# Thioether-Directed Rh(III)-Catalyzed *Peri*-Selective Acyloxylation of Arenes

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# *Supporting Information*

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# 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-ESI (Quadrupole) 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

The substrates of methyl(naphthalen-1-yl)sulfane **1** were prepared accroding to the previous procedure.[1]

# 3. General procedure and characterization of products

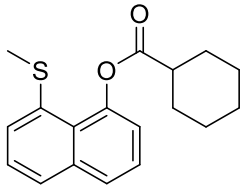
## General procedure A

In an oven-dried Schlenk tube under air, a mixture of the substrates **1** (0.2 mmol, 1.0 equiv), aliphatic carboxylic acid **2** (0.3 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (3.6 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.8 mg, 0.02mmol, 10.0 mmol%), $Ag_2O$ (69.5 mg, 0.3 mmol, 1.5 equiv), $H_3BO_3$ (12.4 mg, 0.2 mmol, 1.0 equiv), and HFIP (1.0 mL) was stirred at 100 °C for 5h-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 **3**.

## General procedure B

In an oven-dried Schlenk tube under air, a mixture of the substrates **1** (0.2 mmol, 1.0 equiv), aryl carboxylic acids **2** (0.4 mmol, 2.0 equiv), $[Cp^*RhCl_2]_2$ (3.6 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.8 mg, 0.02mmol, 10.0 mmol%), $Ag_2CO_3$ (110.3 mg, 0.4 mmol, 2.0 equiv), and HFIP (1.0 mL) was stirred at 100 °C for 5h-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 **3**.

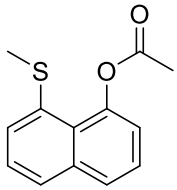
**8-(methylthio)naphthalen-1-yl cyclohexanecarboxylate (3a)**




Following the general procedure A, the product **3a** was obtained in 86% yield (51.7 mg, 0.2 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.22. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.41 (dt, *J* = 21.8, 7.9 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 2.80 (tt, *J* = 11.2, 3.6 Hz, 1H), 2.52 (s, 3H), 2.22 (dd, *J* = 13.0, 2.7 Hz, 2H), 1.91 – 1.83 (m, 2H), 1.69 (ddd, *J* = 24.8, 11.9, 4.7 Hz, 3H), 1.49 – 1.30 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 175.28, 147.43, 136.27, 134.63, 127.09, 125.98, 125.84, 125.26, 125.23, 122.34, 120.31, 43.96,

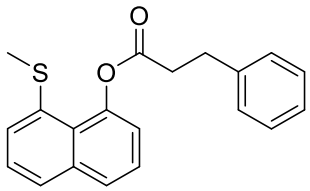
28.94, 25.96, 25.58, 16.72. **HRMS (ESI)** *m/z* calcd. for $C_{18}H_{20}O_2S$ $[M+Na]^+$ 323.1076; Found 323.1071.

**8-(methylthio)naphthalen-1-yl acetate (3b)**



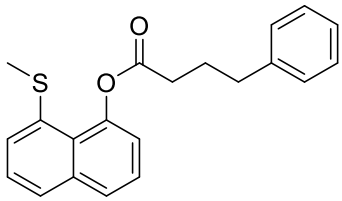
Following the general procedure A, the product **3b** was obtained in 40% yield (18.4 mg, 0.2 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.21. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 2.53 (s, 3H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 170.21, 146.94, 136.34, 134.46, 127.36, 126.07, 125.86, 125.41, 125.07, 122.67, 120.55, 22.44, 16.85. **HRMS (ESI)** *m/z* calcd. for $C_{13}H_{13}O_2S$ $[M+H]^+$ 233.0558; Found 233.0556.

**8-(methylthio)naphthalen-1-yl 3-phenylpropanoate (3c)**



Following the general procedure A, the product **3c** was obtained in 67% yield (43.4 mg, 0.2 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.21. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.45 – 7.34 (m, 2H), 7.33 (d, *J* = 6.1 Hz, 4H), 7.24 (d, *J* = 0.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 3.19 – 3.07 (m, 4H), 2.46 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.09, 146.92, 140.56, 136.29, 134.47, 128.67, 128.65, 127.29, 126.47, 126.04, 125.84, 125.34, 125.00, 122.53, 120.45, 77.48, 76.84, 37.01, 30.75, 16.76. **HRMS (ESI)** *m/z* calcd. for $C_{20}H_{18}O_2S$ $[M+H]^+$ 323.1101; Found 323.1101.

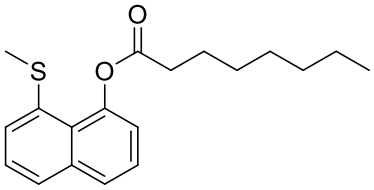
**8-(methylthio)naphthalen-1-yl 4-phenylbutanoate (3d)**



Following the general procedure A, the product **3d** was obtained in 61% yield (41.0 mg, 0.2 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.24. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.41 (dt, *J* = 22.3, 7.8 Hz, 2H), 7.32 (t,

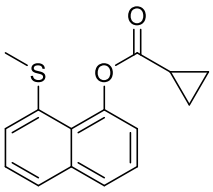
*J* = 7.4 Hz, 2H), 7.27 – 7.18 (m, 4H), 7.08 (d, *J* = 7.5 Hz, 1H), 2.80 (t, *J* = 7.5 Hz, 4H), 2.48 (s, 3H), 2.16 (p, *J* = 7.5 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.65, 146.99, 141.58, 136.32, 134.48, 128.71, 128.56, 127.27, 126.15, 126.04, 125.85, 125.36, 125.07, 122.53, 120.49, 35.24, 34.67, 26.26, 16.74. **HRMS (ESI)** *m/z* calcd. for $C_{21}H_{20}O_2SNa$ $[M+Na]^+$ 359.1076; Found 359.1080.

**8-(methylthio)naphthalen-1-yl octanoate (3e)**



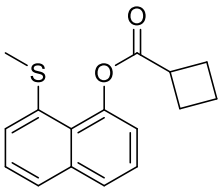
Following the general procedure A, the product **3e** was obtained in 49% yield (31.2 mg, 0.2 mmol) as a white solid after column chromatography (eluent = Petroleum ether). RF (Petroleum ether): 0.22. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.7 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.42 (dt, *J* = 22.7, 7.8 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.10 (dd, *J* = 7.5, 0.8 Hz, 1H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.52 (s, 3H), 1.87 – 1.78 (m, 2H), 1.47 (dt, *J* = 14.1, 6.0 Hz, 2H), 1.41 – 1.29 (m, 6H), 0.91 (t, *J* = 6.8 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.00, 147.08, 136.31, 134.56, 127.19, 126.01, 125.85, 125.32, 125.11, 122.42, 120.49, 35.44, 31.84, 29.29, 29.14, 24.72, 22.78, 16.75, 14.25. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{24}O_2S$ $[M+H]^+$ 317.1570; Found 317.1565.

**8-(methylthio)naphthalen-1-yl cyclopropanecarboxylate (3f)**



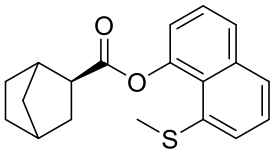
Following the general procedure A, the product **3f** was obtained in 51% yield (26.1 mg, 0.2 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether). RF (Petroleum ether): 0.21. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.6 Hz, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.41 (dt, *J* = 20.2, 7.9 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.12 (dd, *J* = 7.5, 1.0 Hz, 1H), 2.53 (s, 3H), 2.11 – 2.01 (m, 1H), 1.29 – 1.23 (m, 2H), 1.12 – 1.05 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.28, 147.25, 136.30, 134.89, 127.18, 126.02, 125.84, 125.25, 125.21, 122.38, 120.45, 16.82, 14.08, 9.52. **HRMS (ESI)** *m/z* calcd. for $C_{15}H_{14}O_2S$ $[M+H]^+$ 259.0788; Found 259.0784.

**8-(methylthio)naphthalen-1-yl cyclobutanecarboxylate (3g)**



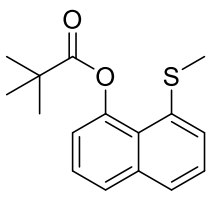
Following the general procedure A, the product **3g** was obtained in 91% yield (49.4 mg, 0.2 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether). RF (Petroleum ether): 0.21. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.42 (dt, *J* = 24.7, 7.8 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 1H), 3.62 (p, *J* = 8.6 Hz, 1H), 2.58 (ddd, *J* = 18.6, 9.1, 2.1 Hz, 2H), 2.50 (s, 3H), 2.15 – 1.95 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.63, 147.29, 136.31, 134.69, 127.16, 126.01, 125.85, 125.30, 125.19, 122.45, 120.36, 39.04, 25.49, 18.64, 16.76. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{16}O_2S$ $[M+H]^+$ 273.0944; Found 273.0944.

**8-(methylthio)naphthalen-1-yl (2S)-bicyclo[2.2.1]heptane-2-carboxylate (3h)**



Following the general procedure A, the product **3h** was obtained in 49% yield (30.8 mg, 0.2 mmol) as a colorless oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.21. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.08 (dd, *J* = 11.2, 7.5 Hz, 1H), 3.33 – 3.25 (m, 1H), 2.85 (dd, *J* = 16.9, 12.6 Hz, 1H), 2.51 (d, *J* = 2.5 Hz, 3H), 2.36 (t, *J* = 11.9 Hz, 1H), 1.87 – 1.81 (m, 1H), 1.62 (tdd, *J* = 14.6, 11.4, 6.2 Hz, 5H), 1.49 – 1.36 (m, 2H), 1.29 (t, *J* = 9.6 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 175.37, 174.37, 147.43, 147.36, 136.29, 134.69, 134.66, 127.06, 127.02, 125.97, 125.84, 125.82, 125.25, 125.23, 125.17, 122.30, 122.18, 120.44, 120.24, 47.59, 47.32, 41.05, 40.67, 40.48, 37.29, 36.76, 36.26, 34.39, 32.29, 29.68, 29.31, 28.82, 25.43, 16.74, 16.69. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{20}O_2S$ $[M+H]^+$ 313.1257; Found 313.1267.

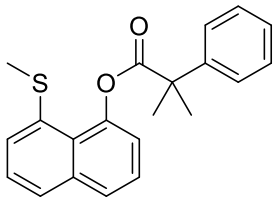
**8-(methylthio)naphthalen-1-yl pivalate (3i)**



Following the general procedure A, the product **3i** was obtained in 78% yield (43.0 mg, 0.2 mmol) as a yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.22. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 14.3, 8.1 Hz, 1H), 7.62 (dd, *J* = 14.6, 8.2 Hz, 1H), 7.48 – 7.33 (m, 2H), 7.21 (dd, *J* = 14.6, 7.4 Hz, 1H), 6.99 (dd, *J* = 14.2, 7.4 Hz,

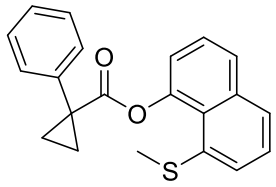
1H), 2.50 (d, *J* = 15.3 Hz, 3H), 1.49 (d, *J* = 15.2 Hz, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.14, 148.32, 136.26, 134.60, 127.18, 125.96, 125.86, 125.47, 125.33, 122.48, 120.05, 39.49, 27.48, 16.67. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{18}O_2SNa$ $[M+Na]^+$ 297.0920; Found 297.0926.

**8-(methylthio)naphthalen-1-yl 2-methyl-2-phenylpropanoate (3j)**



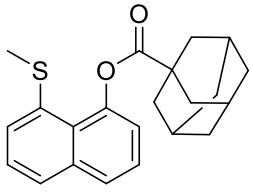
Following the general procedure A, the product **3j** was obtained in 58% yield (38.9 mg, 0.2 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.23. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.8 Hz, 1H), 7.61 (dd, *J* = 12.7, 7.8 Hz, 3H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.35 (ddd, *J* = 17.6, 11.5, 4.8 Hz, 3H), 7.17 (d, *J* = 7.5 Hz, 1H), 6.77 (dd, *J* = 7.5, 0.8 Hz, 1H), 2.40 (s, 3H), 1.89 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 175.85, 148.44, 143.78, 136.24, 134.81, 128.55, 127.25, 127.12, 126.55, 125.98, 125.85, 125.38, 125.28, 122.52, 119.62, 46.90, 26.37, 16.65. **HRMS (ESI)** *m/z* calcd. for $C_{21}H_{20}O_2S$ $[M+H]^+$ 337.1257; Found 337.1256.

**8-(methylthio)naphthalen-1-yl 1-phenylcyclopropane-1-carboxylate (3k)**



Following the general procedure A, the product **3k** was obtained in 56% yield (37.1 mg, 0.2 mmol) as a pale yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.21. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.58 (dd, *J* = 7.8, 2.7 Hz, 3H), 7.42 – 7.32 (m, 4H), 7.27 (dd, *J* = 13.4, 6.1 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 7.4 Hz, 1H), 2.48 (s, 3H), 1.93 (q, *J* = 4.0 Hz, 2H), 1.42 (q, *J* = 4.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.09, 147.80, 139.34, 136.22, 134.62, 131.24, 128.26, 127.48, 127.33, 125.95, 125.77, 125.44, 125.41, 123.05, 120.24, 30.20, 17.48, 17.01. **HRMS (ESI)** *m/z* calcd. for $C_{21}H_{18}O_2S$ $[M+Na]^+$ 335.0920; Found 335.0920.

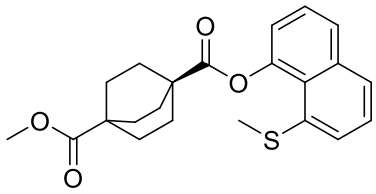
**8-(methylthio)naphthalen-1-yl adamantane-1-carboxylate (3l)**



Following the general procedure A, the product **3l** was obtained in 61% yield (43.2 mg, 0.2 mmol) as a pale yellow solid after column

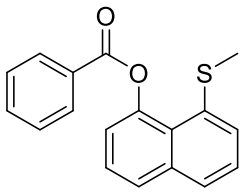
chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.23. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.41 (dt, *J* = 17.9, 7.8 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 2.51 (s, 3H), 2.23 (d, *J* = 2.4 Hz, 6H), 2.14 (s, 3H), 1.82 (s, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 177.29, 148.41, 136.25, 134.74, 127.09, 125.95, 125.89, 125.54, 125.28, 122.34, 120.17, 41.40, 38.96, 36.65, 28.10, 16.68. **HRMS (ESI)** *m/z* calcd. for $C_{22}H_{24}O_2S$ $[M+H]^+$ 353.1570; Found 353.1571.

**1-methyl 4-(8-(methylthio)naphthalen-1-yl) bicyclo[2.2.2]octane-1,4-dicarboxylate (3m)**



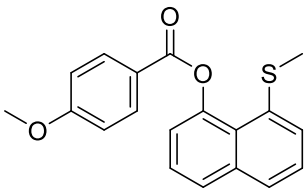
Following the general procedure A, the product **3m** was obtained in 37% yield (28.6 mg, 0.2 mmol) as a pale yellow oil after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.22. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.40 (dt, *J* = 13.7, 7.9 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 3.68 (s, 3H), 2.51 (s, 3H), 2.14 (dd, *J* = 9.9, 6.0 Hz, 6H), 1.92 (dd, *J* = 9.9, 6.0 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 178.01, 177.09, 148.07, 136.29, 134.49, 127.32, 126.04, 125.89, 125.41, 122.55, 120.16, 51.96, 39.51, 39.01, 28.01, 27.95, 16.76. **HRMS (ESI)** *m/z* calcd. for $C_{22}H_{24}O_4S$ $[M+H]^+$ 385.1468; Found 385.1468.

**8-(methylthio)naphthalen-1-yl benzoate (3n)**



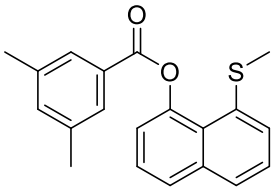
Following the general procedure B, the product **3n** was obtained in 65% yield (38.1 mg, 0.2 mmol) as a pale yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.20. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 7.5 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.69 – 7.63 (m, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.21 (dd, *J* = 6.8, 5.0 Hz, 1H), 2.40 (s, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.89, 147.36, 136.38, 134.94, 133.62, 130.94, 130.31, 128.65, 127.43, 126.09, 125.93, 125.33, 125.24, 122.30, 120.61, 16.68. **HRMS (ESI)** *m/z* calcd. for $C_{18}H_{14}O_2SNa$ $[M+Na]^+$ 317.0607; Found 317.0605.

**8-(methylthio)naphthalen-1-yl 4-methoxybenzoate (3o)**



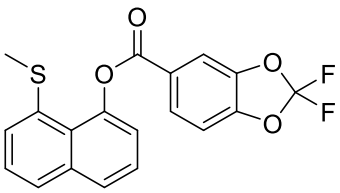
Following the general procedure B, the product **3o** was obtained in 36% yield (23.2 mg, 0.2 mmol) as a yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.20. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.7 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 7.65 (d, *J* = 8.2 Hz, 1H), 7.45 (dt, *J* = 36.1, 7.8 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 2H), 2.40 (s, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 165.55, 163.94, 147.44, 136.35, 135.04, 133.06, 127.23, 126.02, 125.91, 125.42, 125.13, 122.67, 122.03, 120.65, 113.92, 55.63, 16.62. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{16}O_3S$ $[M+Na]^+$ 347.0712; Found 347.0719.

**8-(methylthio)naphthalen-1-yl 3,5-dimethylbenzoate (3p)**



Following the general procedure B, the product **3p** was obtained in 61% yield (39.2 mg, 0.2 mmol) as a whiye solid after column chromatography (eluent = Petroleum ether/EtOAc 30:1 v/v). RF (Petroleum ether/EtOAc 30:1): 0.21. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.45 (dt, *J* = 34.3, 7.8 Hz, 1H), 7.30 (s, 1H), 7.23 – 7.17 (m, 1H), 2.44 (s, 3H), 2.41 (s, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.23, 147.50, 138.31, 136.37, 135.37, 135.00, 130.17, 128.63, 127.35, 126.06, 125.94, 125.44, 125.21, 122.26, 120.57, 21.40, 16.74. **HRMS (ESI)** *m/z* calcd. for $C_{20}H_{18}O_2S$ $[M+H]^+$ 323.1101; Found 323.1106.

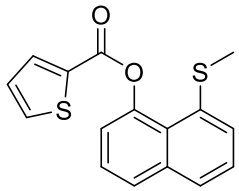
**8-(methylthio)naphthalen-1-yl 2,2-difluorobenzo[d][1,3]dioxole-5-carboxylate (3q)**



Following the general procedure B, the product **3q** was obtained in 36% yield (26.8 mg, 0.2 mmol) as a pale yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.24. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 8.4, 1.5 Hz, 1H), 8.04 (d, *J* = 1.4 Hz, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.46 (dt, *J* = 30.9, 7.9 Hz, 2H), 7.24 – 7.18 (m, 3H), 2.42 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 164.40, 147.59, 147.03, 143.95, 136.41, 134.63, 131.90 (t, *J* = 257.3 Hz), 128.08,

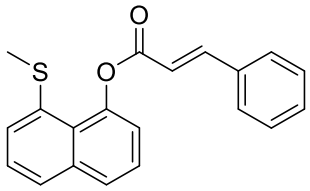
127.71, 126.55, 126.20, 125.92, 125.34, 125.13, 122.41, 120.53, 112.03, 109.49, 16.66. $^{19}$F NMR (376 MHz, CDCl3) δ -49.57. **HRMS (ESI)** *m/z* calcd. for $C_{19}H_{12}F_2O_4S$ $[M+H]^+$ 374.0497; Found 372.0501.

**8-(methylthio)naphthalen-1-yl thiophene-2-carboxylate (3r)**



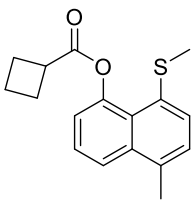
Following the general procedure B, the product **3r** was obtained in 35% yield (21.0 mg, 0.2 mmol) as a pale yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 30:1 v/v). RF (Petroleum ether/EtOAc 30:1): 0.20. $^1$H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 3.7 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 4.9 Hz, 1H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.23 (t, *J* = 7.0 Hz, 3H), 2.44 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 161.25, 146.88, 136.38, 135.36, 134.96, 133.89, 133.82, 128.10, 127.57, 126.13, 125.87, 125.28, 125.25, 122.52, 120.69, 16.83. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{12}O_2S_2$ $[M+Na]^+$ 323.0171; Found 323.0179.

**8-(methylthio)naphthalen-1-yl cinnamate (3s)**



Following the general procedure B, the product **3s** was obtained in 36% yield (23.1 mg, 0.2 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.20. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 16.0 Hz, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.65 (dd, *J* = 10.0, 5.9 Hz, 3H), 7.45 (tt, *J* = 20.7, 7.8 Hz, 5H), 7.21 (dd, *J* = 7.4, 2.8 Hz, 2H), 6.83 (d, *J* = 16.0 Hz, 1H), 2.49 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 166.01, 147.08, 146.99, 136.35, 134.93, 134.49, 130.81, 129.12, 128.58, 127.30, 126.08, 125.91, 125.23, 125.21, 122.20, 120.50, 118.24, 16.72. **HRMS (ESI)** *m/z* calcd. for $C_{20}H_{16}O_2S$ $[M+H]^+$ 321.0944; Found 321.0953.

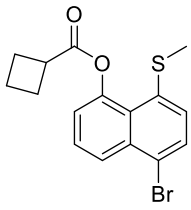
**5-methyl-8-(methylthio)naphthalen-1-yl cyclobutanecarboxylate (3t)**



Following the general procedure A, the product **3t** was obtained in 26% yield (15.0 mg, 0.2 mmol) as a colorless liquid after column chromatography

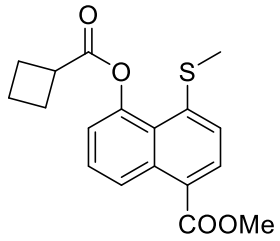
(eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.23.$^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 1H), 7.50 (t, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 9.0 Hz, 1H), 7.11 (d, *J* = 7.0 Hz, 2H), 3.62 (p, *J* = 8.6 Hz, 1H), 2.63 (s, 3H), 2.60 – 2.52 (m, 2H), 2.47 (s, 3H), 2.38 (td, *J* = 12.3, 3.6 Hz, 2H), 2.13 – 1.99 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.69, 147.71, 135.49, 132.25, 131.18, 127.09, 125.68, 125.35, 123.18, 122.61, 120.18, 53.58, 39.07, 25.50, 20.11, 18.63, 16.99. **HRMS (ESI)** *m/z* calcd. for $C_{17}H_{19}O_2S$ $[M+H]^+$ 287.1101; Found 287.1107.

**5-bromo-8-(methylthio)naphthalen-1-yl cyclobutanecarboxylate (3u)**



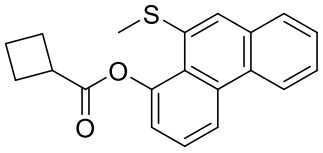

Following the general procedure A, the product **3u** was obtained in 45% yield (31.4 mg, 0.2 mmol) as a pale yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.21. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.5 Hz, 1H), 7.69 (d, *J* = 8.1 Hz, 1H), 7.57 (t, *J* = 8.0 Hz, 1H), 7.17 (d, *J* = 7.5 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 3.61 (p, *J* = 8.6 Hz, 1H), 2.61 – 2.51 (m, 2H), 2.48 (s, 3H), 2.43 – 2.35 (m, 2H), 2.11 (dt, *J* = 19.5, 8.9 Hz, 1H), 2.01 (dd, *J* = 9.6, 5.0 Hz, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.43, 147.47, 135.45, 134.08, 130.16, 127.13, 126.46, 126.30, 122.31, 121.26, 119.40, 38.99, 25.49, 18.63, 16.85. **HRMS (ESI)** *m/z* calcd. for $C_{16}H_{15}BrO_2SNa$ $[M+Na]^+$ 372.9868; Found 372.9869.

**methyl 5-((cyclobutanecarbonyl)oxy)-4-(methylthio)-1-naphthoate (3v)**



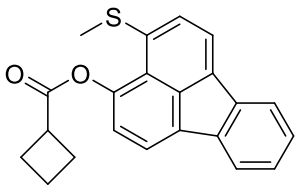

Following the general procedure A, the product **3v** was obtained in 50% yield (32.8 mg, 0.2 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.25. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, *J* = 8.7 Hz, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 7.58 (t, *J* = 8.1 Hz, 1H), 7.16 (dd, *J* = 7.7, 4.8 Hz, 2H), 3.97 (s, 3H), 3.61 (p, *J* = 8.6 Hz, 1H), 2.62 – 2.48 (m, 6H), 2.15 – 1.94 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.45, 167.99, 147.51, 142.20, 133.84, 130.13, 127.54, 125.43, 124.66, 123.36, 120.69, 119.92, 52.34, 39.03, 29.85, 25.49, 18.63, 16.65. **HRMS (ESI)** *m/z* calcd. for $C_{18}H_{18}O_4S$ $[M+H]^+$ 331.1000; Found 331.1002.

**10-(methylthio)phenanthren-1-yl cyclobutanecarboxylate (3w)**



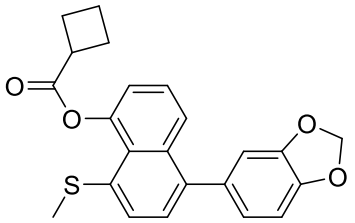
Following the general procedure A, the product **3w** was obtained in 40% yield (25.8 mg, 0.2 mmol) as a white solid after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.23. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.3 Hz, 1H), 8.57 (dd, *J* = 6.0, 3.4 Hz, 1H), 7.75 (dt, *J* = 6.9, 3.5 Hz, 1H), 7.64 (t, *J* = 8.0 Hz, 1H), 7.56 (dq, *J* = 6.9, 3.6 Hz, 2H), 7.40 (s, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 3.64 (p, *J* = 8.6 Hz, 1H), 2.65 – 2.52 (m, 5H), 2.46 – 2.34 (m, 2H), 2.18 – 2.05 (m, 1H), 2.06 – 1.97 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.65, 147.97, 133.21, 132.81, 131.87, 128.15, 127.54, 127.41, 126.78, 126.28, 124.05, 123.07, 122.55, 121.73, 121.36, 39.08, 29.85, 25.51, 18.65, 16.93. **HRMS (ESI)** *m/z* calcd. for $C_{20}H_{18}O_2S$ $[M+H]^+$ 323.1101; Found 323.1100.

**4-(methylthio)fluoranthen-3-yl cyclobutanecarboxylate (3x)**



Following the general procedure A, the product **3x** was obtained in 48% yield (33.2 mg, 0.2 mmol) as a pale yellow solid after column chromatography (eluent = Petroleum ether/EtOAc 64:1 v/v). RF (Petroleum ether/EtOAc 64:1): 0.21. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.5 Hz, 1H), 7.87 (t, *J* = 7.0 Hz, 3H), 7.41 – 7.35 (m, 2H), 7.29 (dd, *J* = 6.4, 3.9 Hz, 2H), 3.66 (p, *J* = 8.6 Hz, 1H), 2.69 – 2.56 (m, 5H), 2.50 – 2.39 (m, 2H), 2.24 – 2.09 (m, 1H), 2.09 – 2.02 (m, 1H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.61, 147.53, 139.07, 138.45, 136.17, 135.45, 134.56, 133.70, 127.46, 127.43, 123.27, 122.62, 121.66, 121.30, 121.21, 120.83, 120.63, 38.97, 29.85, 25.52, 18.66, 16.34. **HRMS (ESI)** *m/z* calcd. for $C_{22}H_{18}O_2S$ $[M+H]^+$ 347.1101; Found 347.1102.

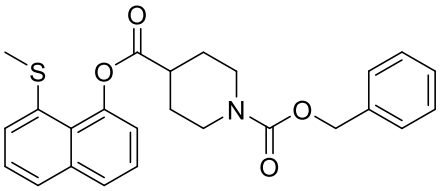
**5-(benzo[d][1,3]dioxol-5-yl)-8-(methylthio)naphthalen-1-yl cyclobutanecarboxylate (3y)**



Following the general procedure A, the product **3y** was obtained in 22% yield (17.6 mg, 0.2 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 32:1 v/v). RF (Petroleum ether/EtOAc 32:1): 0.25. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.4 Hz, 1H), 7.39 (t, *J* = 8.0 Hz, 1H), 7.30 (d, *J* = 7.7 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 1H), 7.10 (d, *J* = 7.4 Hz, 1H), 6.90 (q, *J* = 8.0 Hz, 3H), 3.63 (p, *J* = 8.6 Hz, 1H), 2.58 (dd, *J* = 21.1, 9.2

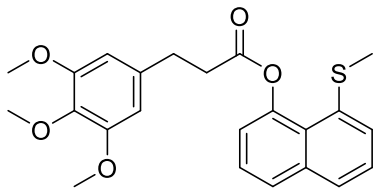
Hz, 2H), 2.52 (s, 3H), 2.45 – 2.35 (m, 2H), 2.15 – 1.97 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 174.73, 147.62, 147.48, 147.04, 136.82, 134.81, 134.63, 134.07, 127.18, 125.77, 125.33, 123.61, 121.86, 120.31, 110.80, 108.40, 101.29, 39.07, 29.85, 25.52, 18.65, 16.88. **HRMS (ESI)** *m/z* calcd. for $C_{23}H_{21}O_4S$ $[M+H]^+$ 393.1155; Found 393.1157.

**1-benzyl 4-(8-(methylthio)naphthalen-1-yl) piperidine-1,4-dicarboxylate (3z)**



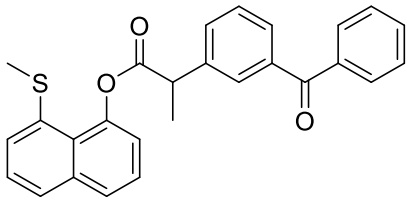
Following the general procedure A, the product **3z** was obtained in 50% yield (43.6 mg, 0.2 mmol) as a pale red liquid after column chromatography (eluent = Petroleum ether/EtOAc 10:1 v/v). RF (Petroleum ether/EtOAc 10:1): 0.20. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 1H), 7.63 (d, *J* = 8.2 Hz, 1H), 7.48 – 7.39 (m, 2H), 7.39 – 7.31 (m, 5H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 5.16 (s, 2H), 4.20 (s, 2H), 3.08 (t, *J* = 10.9 Hz, 2H), 3.01 – 2.92 (m, 1H), 2.51 (s, 3H), 2.19 (s, 2H), 1.90 (d, *J* = 9.5 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 173.60, 155.36, 147.08, 136.85, 136.31, 134.26, 128.64, 128.16, 128.03, 127.44, 126.10, 125.85, 125.45, 125.04, 122.64, 120.28, 67.31, 43.42, 41.87, 27.91, 16.75. **HRMS (ESI)** *m/z* calcd. for $C_{25}H_{25}O_4S$ $[M+H]^+$ 435.1577; Found 435.1585.

**8-(methylthio)naphthalen-1-yl 3-(3,4,5-trimethoxyphenyl)propanoate (3aa)**



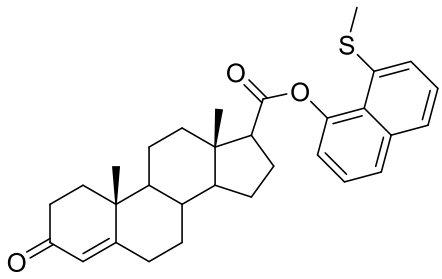
Following the general procedure A, the product **3aa** was obtained in 30% yield (25.0 mg, 0.2 mmol) as a pale yellow liquid after column chromatography (eluent = Petroleum ether/EtOAc 8:1 v/v). RF (Petroleum ether/EtOAc 8:1): 0.26. $^1$H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.1 Hz, 1H), 7.63 (d, *J* = 8.1 Hz, 1H), 7.42 (dt, *J* = 15.3, 7.9 Hz, 2H), 7.21 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.54 (s, 2H), 3.86 (d, *J* = 7.4 Hz, 10H), 3.10 (s, 4H), 2.48 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 172.07, 153.35, 146.94, 136.54, 136.41, 136.34, 134.43, 127.39, 126.10, 125.85, 125.40, 125.01, 122.56, 120.41, 105.54, 61.04, 56.24, 37.12, 31.14, 16.77. **HRMS (ESI)** *m/z* calcd. for $C_{23}H_{24}O_5S$ $[M+H]^+$ 413.1417; Found 413.1421.

**8-(methylthio)naphthalen-1-yl 2-(3-benzoylphenyl)propanoate (3ab)**



Following the general procedure A, the product **3ab** was obtained in 42% yield (34.8 mg, 0.2 mmol) as a colorless liquid after column chromatography (eluent = Petroleum ether/EtOAc 50:1 v/v). RF (Petroleum ether/EtOAc 50:1): 0.22. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.94 (s, 1H), 7.84 (d, *J* = 7.3 Hz, 2H), 7.74 (t, *J* = 8.1 Hz, 2H), 7.70 (d, *J* = 8.2 Hz, 1H), 7.63 – 7.57 (m, 2H), 7.50 (dt, *J* = 20.3, 7.6 Hz, 3H), 7.39 (dd, *J* = 14.6, 7.6 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.4 Hz, 1H), 4.31 (q, *J* = 7.2 Hz, 1H), 2.46 (s, 3H), 1.74 (d, *J* = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 196.66, 173.30, 147.12, 140.46, 138.14, 137.59, 136.27, 134.44, 132.66, 132.06, 130.24, 129.87, 129.27, 128.85, 128.46, 127.39, 126.07, 125.78, 125.37, 124.99, 122.68, 120.05, 46.36, 18.68, 16.75. **HRMS (ESI)** *m/z* calcd. for $C_{27}H_{22}O_3S$ $[M+H]^+$ 427.1363; Found 427.1365.

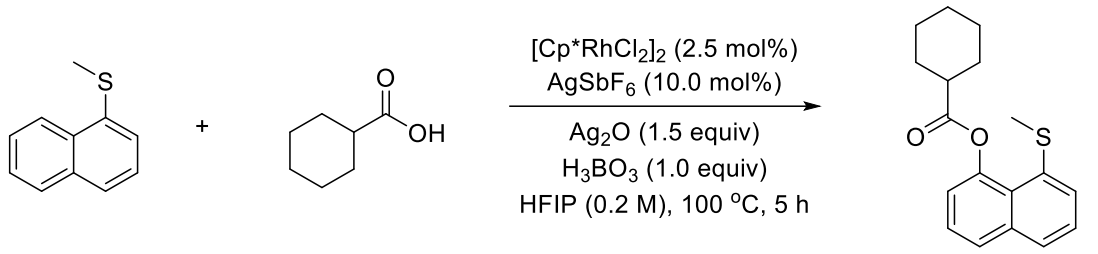
**8-(methylthio)naphthalen-1-yl (10R,13S)-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthrene-17-carboxylate (3ac)**



Following the general procedure A, the product **3ac** was obtained in 35% yield (34.4 mg, 0.2 mmol) as a pale red oil after column chromatography (eluent = Petroleum ether/EtOAc 10:1 v/v). RF (Petroleum ether/EtOAc 10:1): 0.20. $^{1}$H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 1H), 7.44 (t, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.4 Hz, 1H), 5.75 (s, 1H), 2.91 (t, *J* = 9.5 Hz, 1H), 2.50 (s, 3H), 2.47 (s, 1H), 2.44 – 2.41 (m, 1H), 2.40 – 2.34 (m, 2H), 2.30 (d, *J* = 11.4 Hz, 3H), 2.11 – 1.98 (m, 2H), 1.94 – 1.86 (m, 1H), 1.81 (ddd, *J* = 11.7, 9.3, 4.7 Hz, 1H), 1.75 – 1.67 (m, 1H), 1.68 – 1.62 (m, 3H), 1.62 – 1.55 (m, 1H), 1.50 (dd, *J* = 17.4, 8.1 Hz, 2H), 1.43 – 1.33 (m, 1H), 1.27 (dd, *J* = 10.6, 5.0 Hz, 1H), 1.21 (s, 3H), 1.14 – 1.04 (m, 1H), 1.03 – 0.99 (m, 1H), 0.97 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 199.65, 173.04, 171.16, 146.98, 136.24, 134.47, 127.04, 125.95, 125.65, 125.22, 125.07, 123.96, 122.31, 120.21, 56.17, 55.52, 53.78, 44.36, 38.64, 38.31, 35.75, 35.72, 33.98, 32.84, 31.95, 24.48, 23.76, 20.95, 17.41, 16.71, 14.10. **HRMS (ESI)** *m/z* calcd. for $C_{31}H_{36}O_3S$ $[M+H]^+$ 489.2458; Found 489.2452.

# 4. Synthetic application of the product

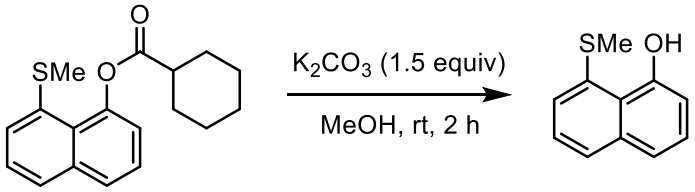
## 4.1 Gram- Scale Synthesis




**1a**, 2.0 mmol **2a**, 1.5 equiv **3a**, 310.4 mg, 52%

In an oven-dried Schlenk tube under air, a mixture of methyl(naphthalen-1-yl)sulfane**.1a** (2.0 mmol, 1.0 equiv), cyclohexanecarboxylic acid **2a** (3.0 mmol, 1.5 equiv), $[Cp^*RhCl_2]_2$ (36.0 mg, 0.05 mmol, 2.5 mmol%), $AgSbF_6$ (68.0 mg, 0.2 mmol, 10.0 mmol%), $Ag_2O$ (695.0 mg, 3.0 mmol, 1.5 equiv), $H_3BO_3$ (124.0 mg, 2.0 mmol, 1.0 equiv), and HFIP (10.0 mL) was stirred at 100 °C for 5h. The reaction mixture was then diluted with DCM (50.0 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 **3a** (310.4 mg, 52%).

## 4.2 Synthetic application of the product

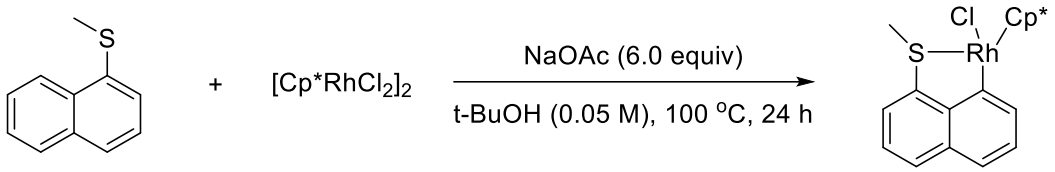



**3a**, 0.2 mmol **4**, 98%

Under a $N_2$ atmosphere, a mixture of **3a** (60.1 mg, 0.2 mmol), $K_2CO_3$ (41.5 mg, 0.3 mmol) in MeOH (1 mL) were stirred at room temperature until disappearance of starting material (monitored by TLC). The reaction mixture was quenched with $H_2O$ and extracted with ethyl acetate (3 x 10 mL). The combined organic layers were collected, dried over sodium sulfate, and evaporated under vacuum. Then, the crude product **4** was purified by flash chromatography (petroleum ether/ethyl acetate 100:1) to give a yellow liquid in 98% yield (37.2 mg). $^1H$ NMR (400 MHz, $CDCl_3$) δ 10.77 (s, 1H), 7.83 (d, *J* = 8.2 Hz, 1H), 7.67 (d, *J* = 7.1 Hz, 1H), 7.41 (d, *J* =

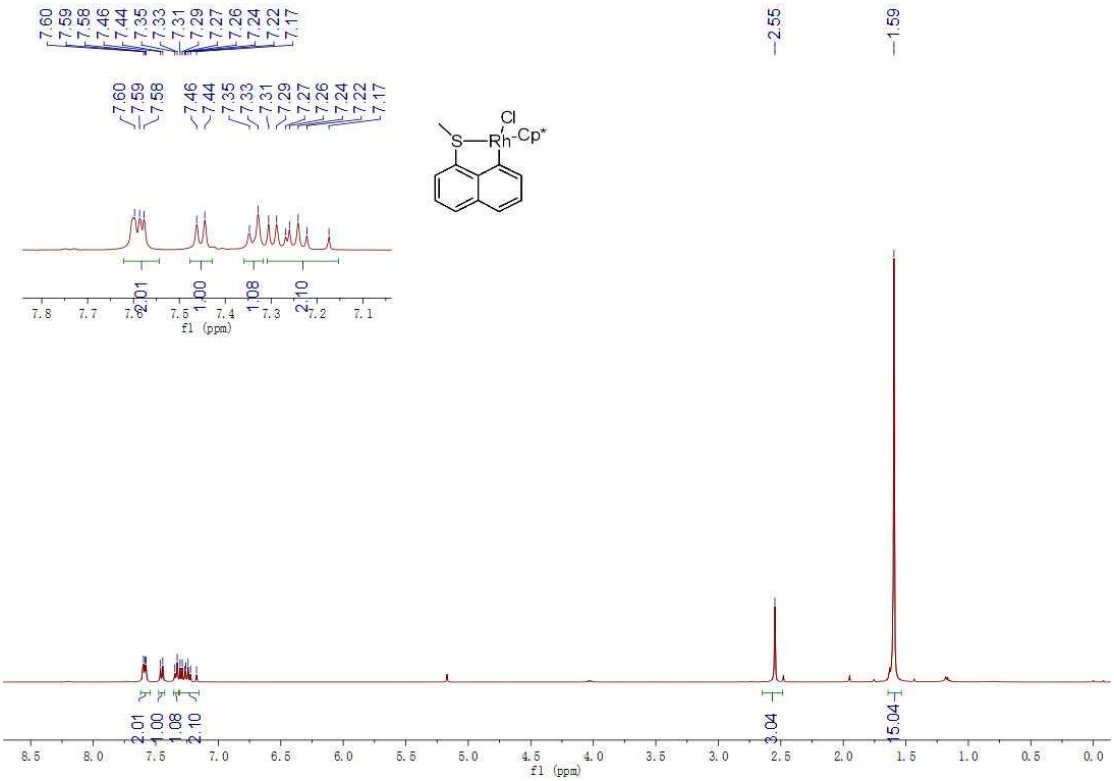
4.4 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 4.4 Hz, 1H), 2.52 (s, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) δ 154.71, 136.54, 135.90, 131.07, 128.70, 127.41, 125.55, 122.81, 120.72, 112.69, 23.07. **HRMS (ESI)** *m/z* calcd. for $C_{11}H_{11}OS$ $[M+H]^+$ 191.0452; Found 191.0453.

# 5. Mechanistic Studies




**1a** **5**

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 **5** as a red orange solid (86.3 mg, 47% yield). $^1$H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.54 (m, 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]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7.59
7.58
7.46
7.44
7.35
7.33
7.31
7.29
7.27
7.26
7.24
7.22
7.17
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Rh
Cp*
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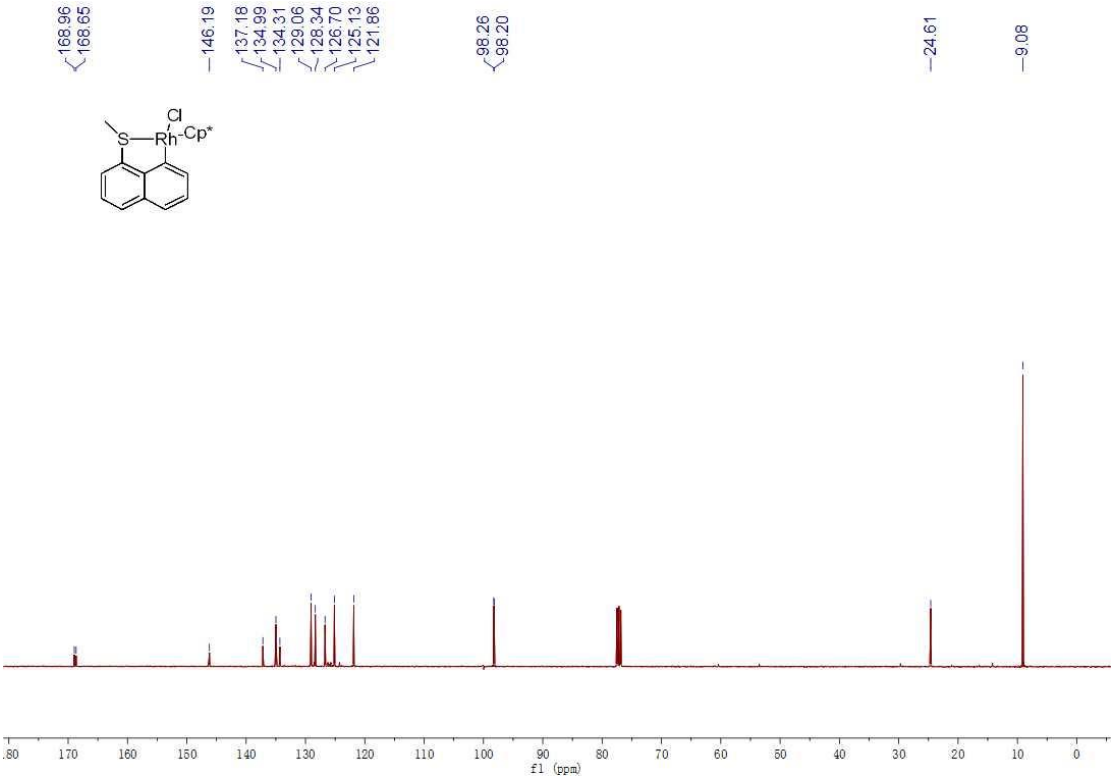
1.00
1.08
2.10
3.04
15.04
f1 (ppm)


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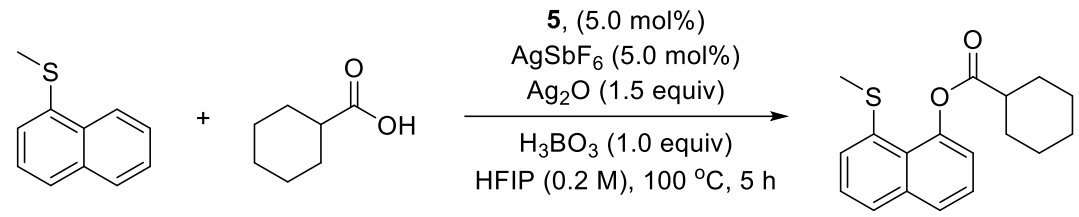
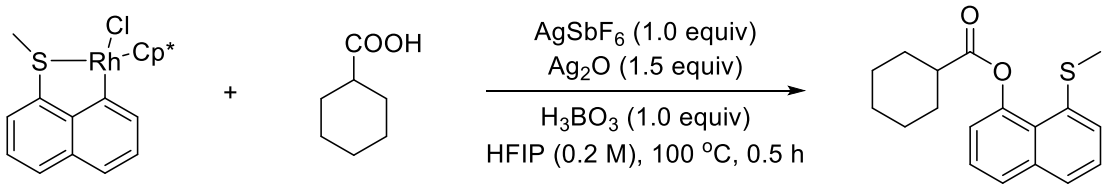
9.08
Cl
S
Rh
Cp*
f1 (ppm)



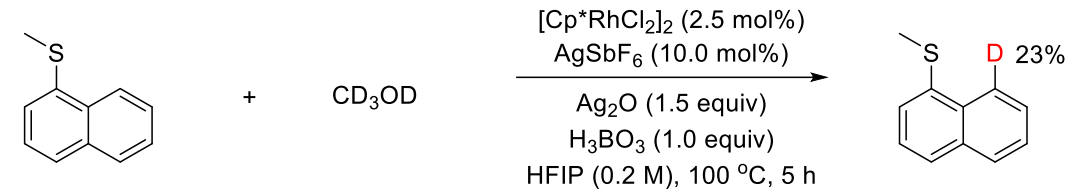

**1a**, 0.2 mmol **2a**, 1.5 equiv **3a**, 30 mg, 50%

In an oven-dried Schlenk tube under air, a mixture of methyl(naphthalen-1-yl)sulfane **1a** (0.2 mmol, 1.0 equiv), cyclohexanecarboxylic acid **2a** (0.3 mmol, 1.5 equiv), **5** (4.6 mg, 0.01 mmol, 5.0 mmol%), $AgSbF_6$ (3.4 mg, 0.01 mmol, 5.0 mmol%), $Ag_2O$ (69.5 mg, 0.3 mmol, 1.5 equiv), $H_3BO_3$ (12.4 mg, 0.2 mmol, 1.0 equiv), and HFIP (1.0 mL) was stirred at 100 °C for 5h. 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 **3a** (30 mg, 50%).



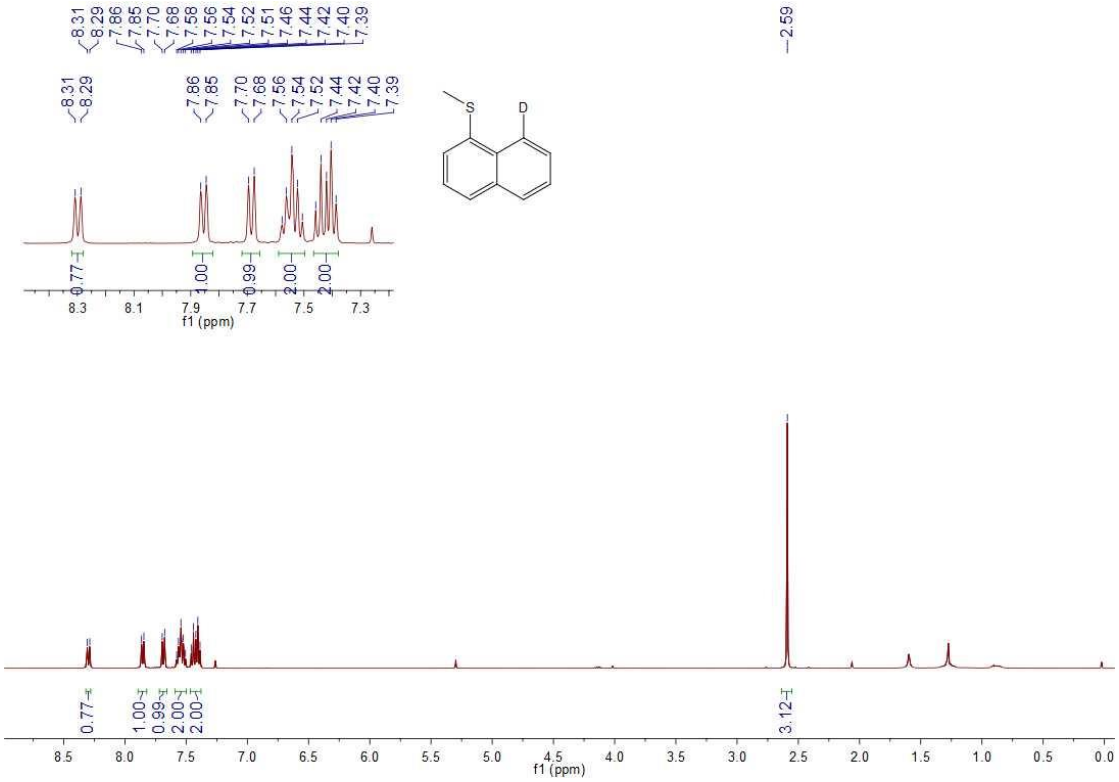

**5**, 0.1 mmol **2a**, 1.5 equiv **3a**, 61%

In an oven-dried Schlenk tube under air, a mixture of **5** (0.1 mmol, 1.0 equiv), cyclohexanecarboxylic acid **2a** (0.15 mmol, 1.5 equiv), $AgSbF_6$ (34.3 mg, 1.0 equiv), $Ag_2O$ (34.8 mg, 0.15 mmol, 1.5 equiv), $H_3BO_3$ (6.2 mg, 0.1 mmol, 1.0 equiv), and HFIP (0.5 mL) was stirred at 100 °C for 0.5 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 **3a** (18.2 mg, 61%).

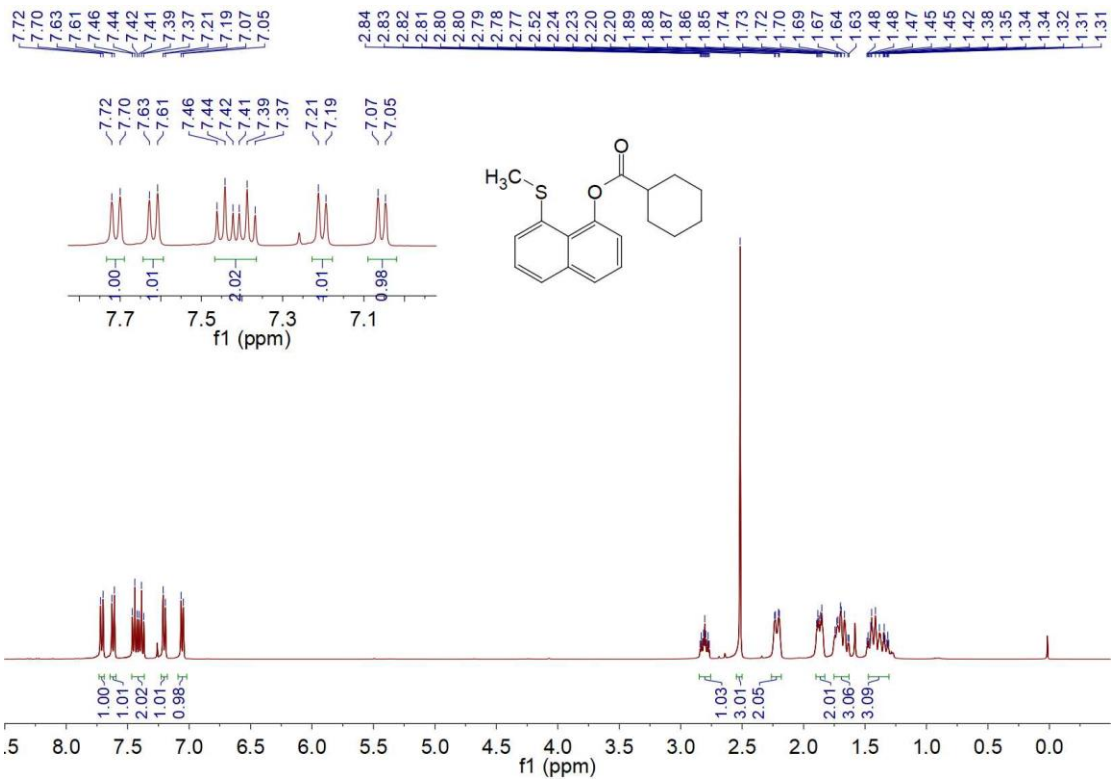


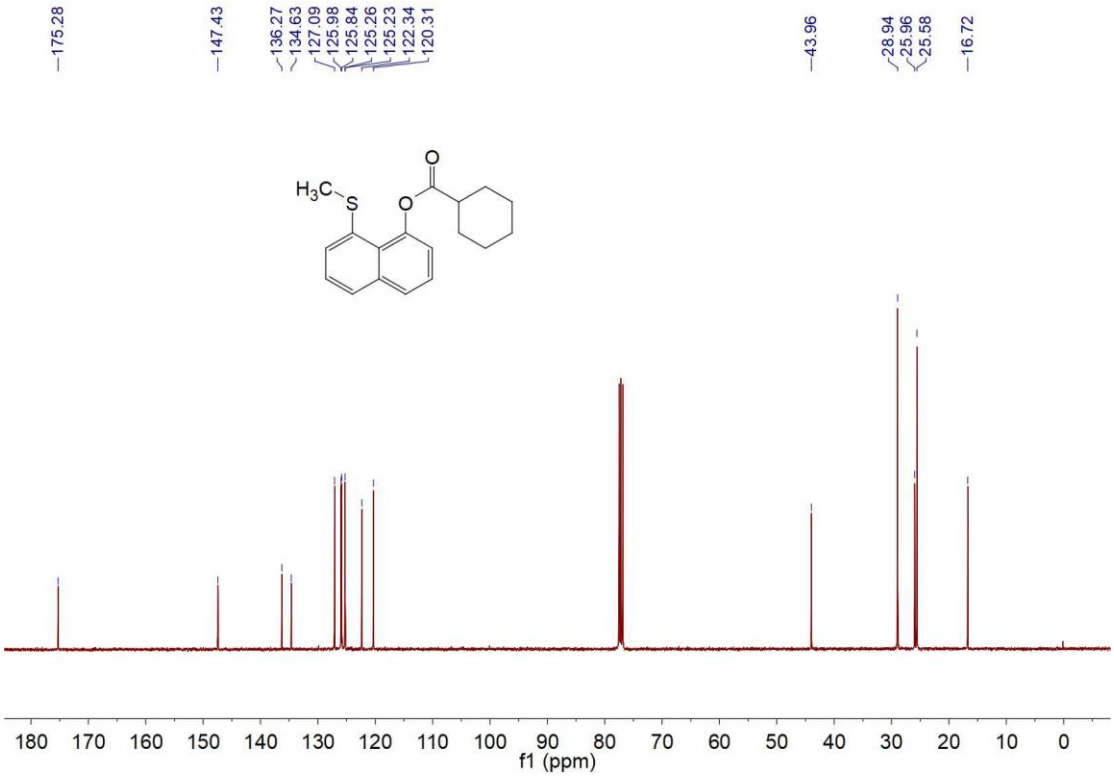

**1a**, (0.2 mmol) 20.0 equiv **D-3a**, 67%

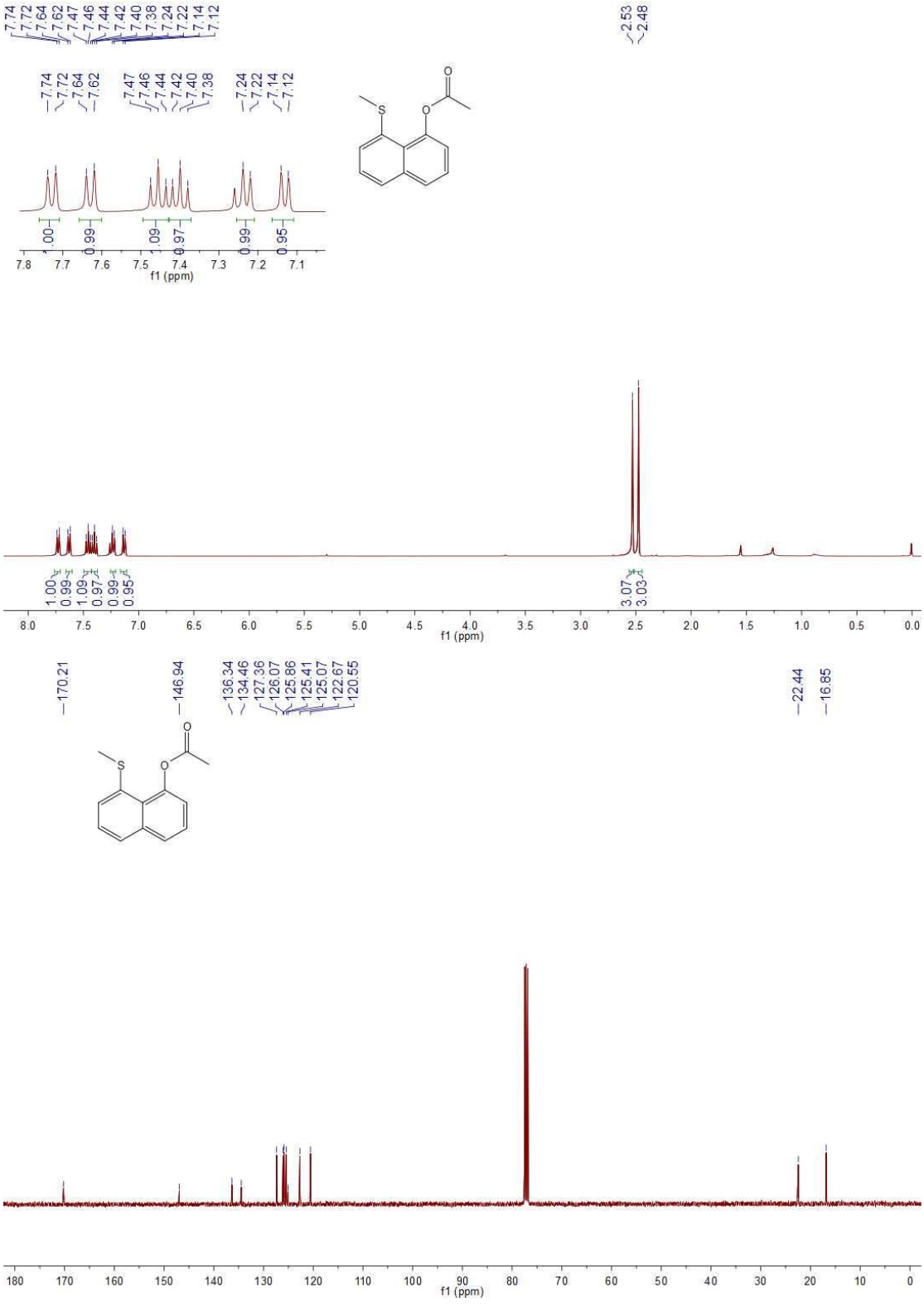
In an oven-dried Schlenk tube under air, a mixture of the substrates **1a** (0.2 mmol, 1.0 equiv), $CD_3OD$ (4 mmol, 20.0 equiv), $[Cp^*RhCl_2]_2$ (3.6 mg, 0.005 mmol, 2.5 mmol%), $AgSbF_6$ (6.8 mg, 0.02mmol, 10.0 mmol%), $Ag_2O$ (69.5 mg, 0.3 mmol, 1.5 equiv), $H_3BO_3$ (12.4 mg, 0.2 mmol, 1.0 equiv), and HFIP (1.0 mL) was stirred at 100 °C for 5h. 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 **D-3a** (23.5 mg, 67%).



# 6. NMR Spectra for New Compounds

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7.64
7.62
7.47
7.46
7.44
7.42
7.40
7.38
7.24
7.22
7.14
7.12
2.53
2.48
1.00
0.99
1.09
0.97
0.99
0.95
3.07
3.03
f1 (ppm)
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146.94
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126.07
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125.41
125.07
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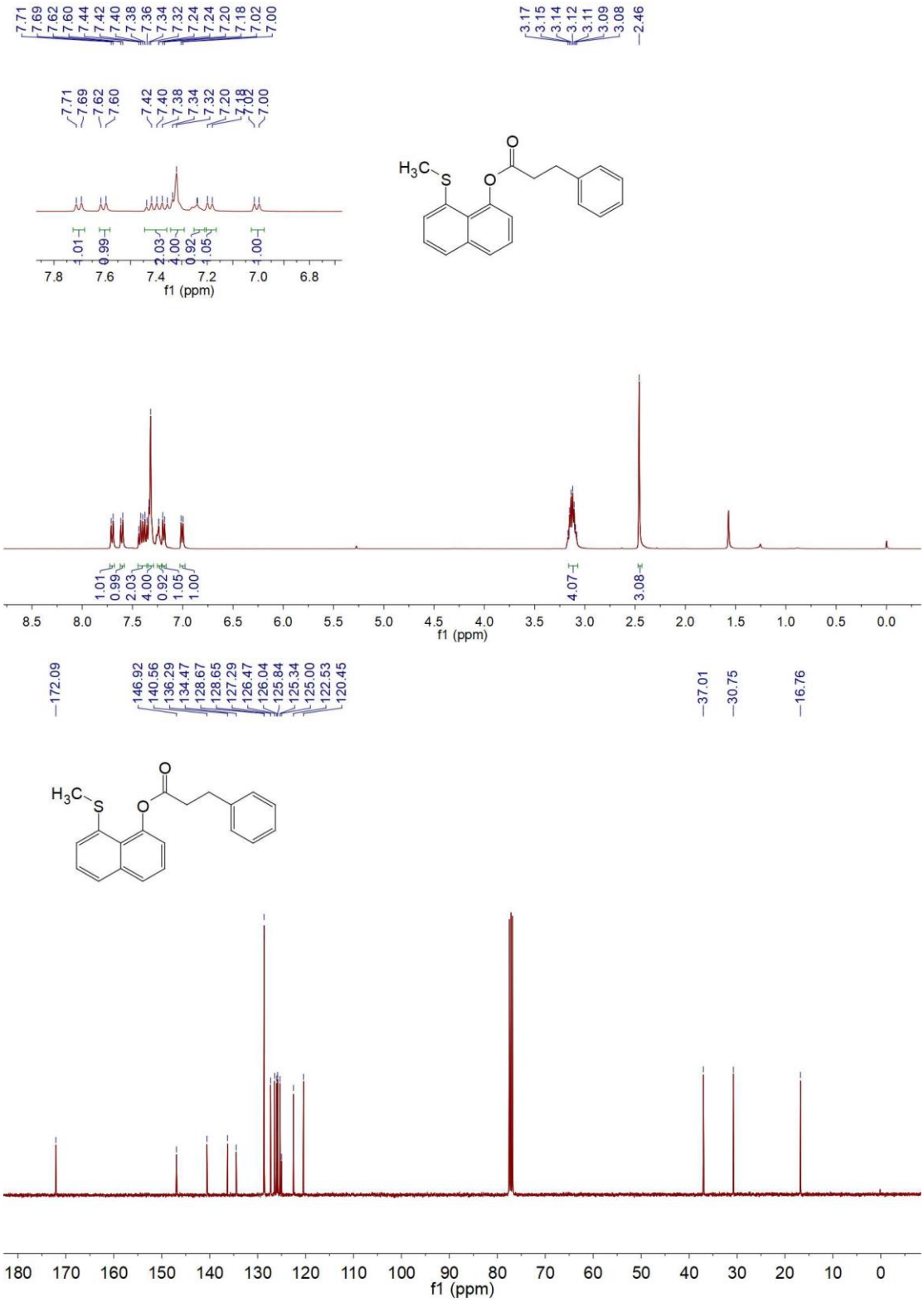
22.44
16.85
f1 (ppm)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7.60
7.44
7.42
7.40
7.38
7.36
7.34
7.32
7.24
7.24
7.20
7.18
7.02
7.00
3.17
3.15
3.14
3.12
3.11
3.09
3.08
2.46
1.01
0.99
2.03
4.00
0.92
1.05
1.00
4.07
3.08
f1 (ppm)
H3C
S
O
O
172.09
146.92
140.56
136.29
134.47
128.67
128.65
127.29
126.47
126.04
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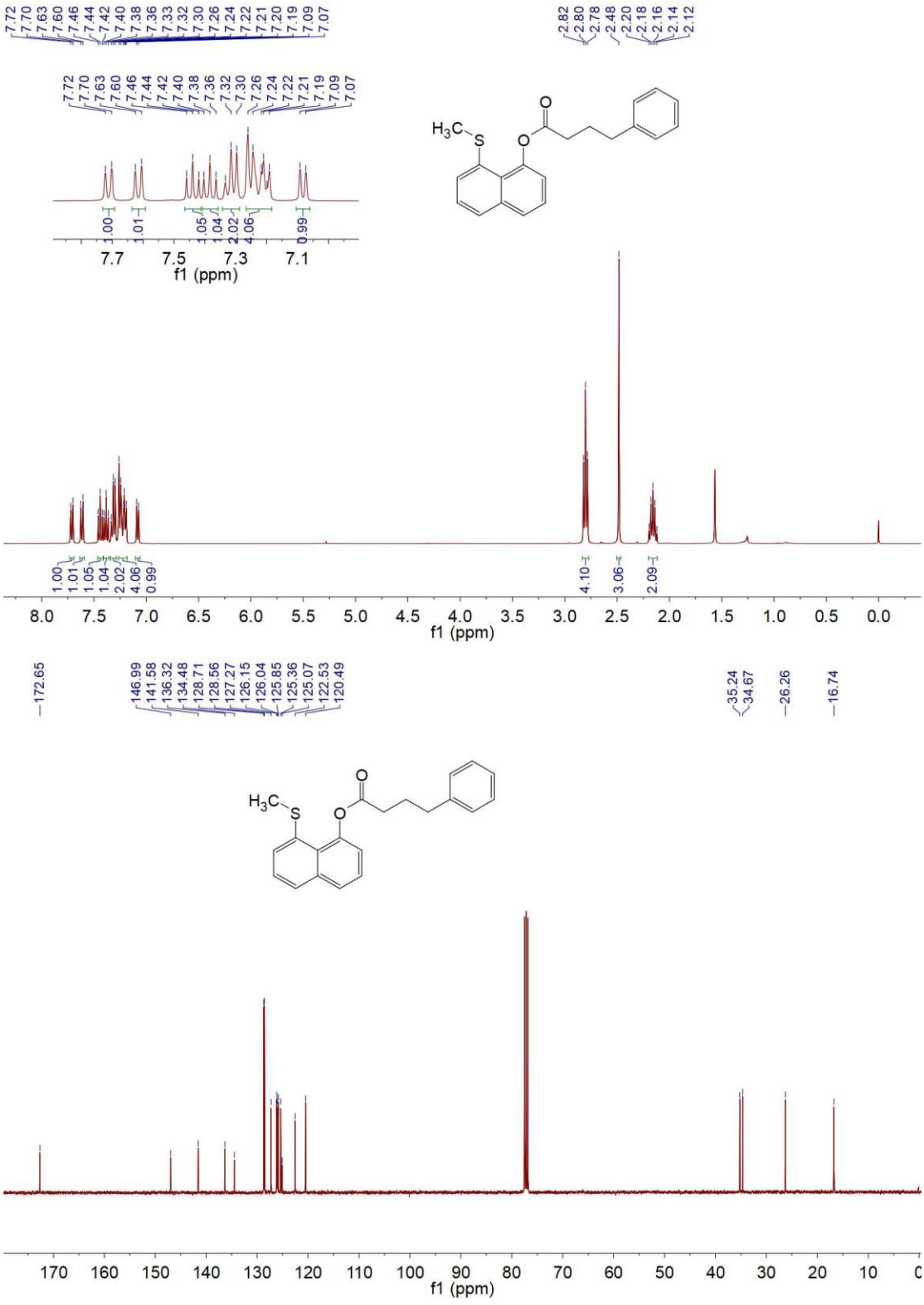
125.34
125.00
122.53
120.45
37.01
30.75
16.76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7.44
7.42
7.40
7.38
7.36
7.33
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7.30
7.26
7.24
7.22
7.21
7.20
7.19
7.09
7.07
2.82
2.80
2.78
2.48
2.20
2.18
2.16
2.14
2.12
H3C
S
O
O
1.00
1.01
1.05
1.04
2.02
4.06
0.99
4.10
3.06
2.09
f1 (ppm)
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146.99
141.58
136.32
134.48
128.71
128.56
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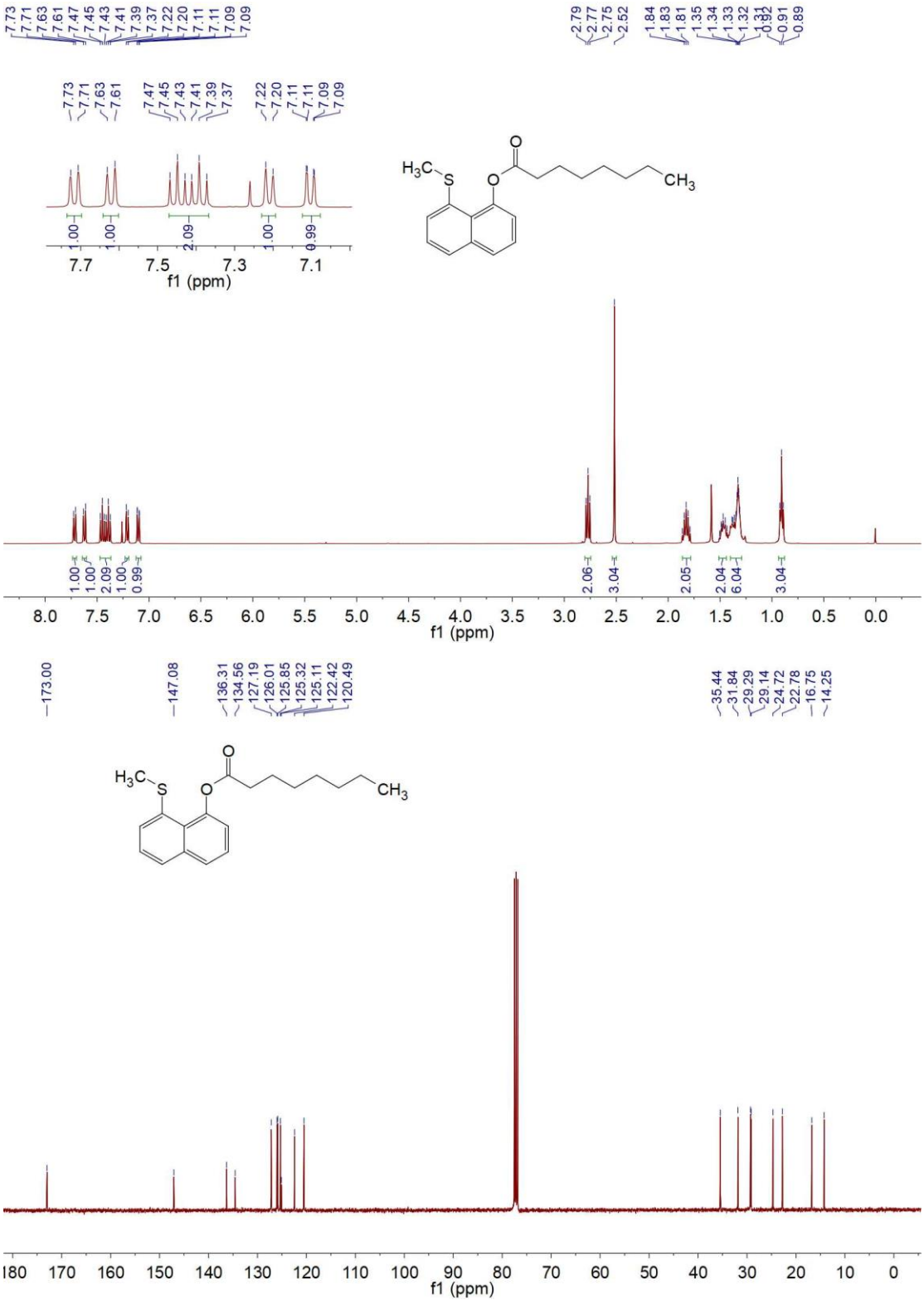
122.53
120.49
35.24
34.67
26.26
16.74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7.45
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7.22
7.20
7.11
7.11
7.09
7.09
2.79
2.77
2.75
2.52
1.84
1.83
1.81
1.35
1.34
1.33
1.32
0.91
0.89
1.00
1.00
2.09
1.00
0.99
2.06
3.04
2.05
2.04
6.04
3.04
f1 (ppm)
H3C
S
O
O
CH3
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134.56
127.19
126.01
125.85
125.32
125.11
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35.44
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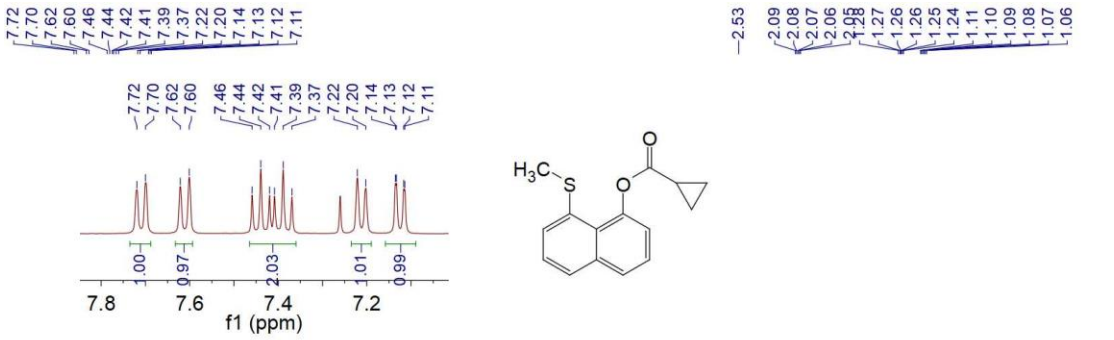
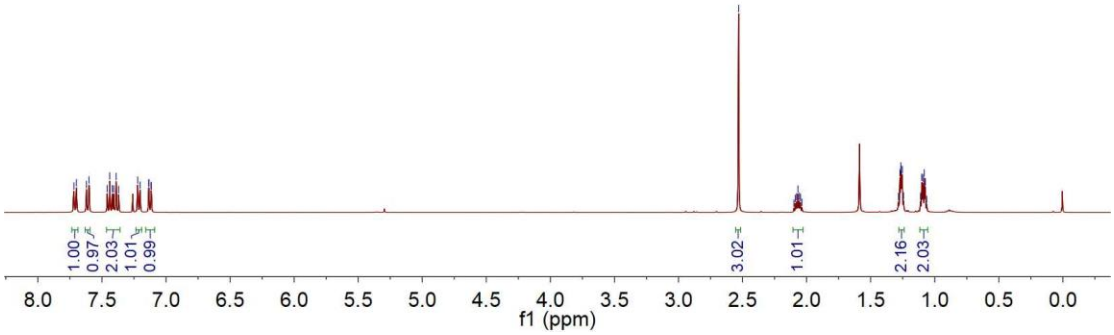
29.29
29.14
24.72
22.78
16.75
14.25
f1 (ppm)


7.72
7.70
7.62
7.60
7.46
7.44
7.42
7.41
7.39
7.37
7.22
7.20
7.14
7.13
7.12
7.11
2.53
2.09
2.08
2.07
2.06
1.27
1.26
1.25
1.24
1.11
1.10
1.09
1.08
1.07
1.06
1.00
0.97
2.03
1.01
0.99
7.8
7.6
7.4
7.2
f1 (ppm)
H3C
S
O
O


1.00
0.97
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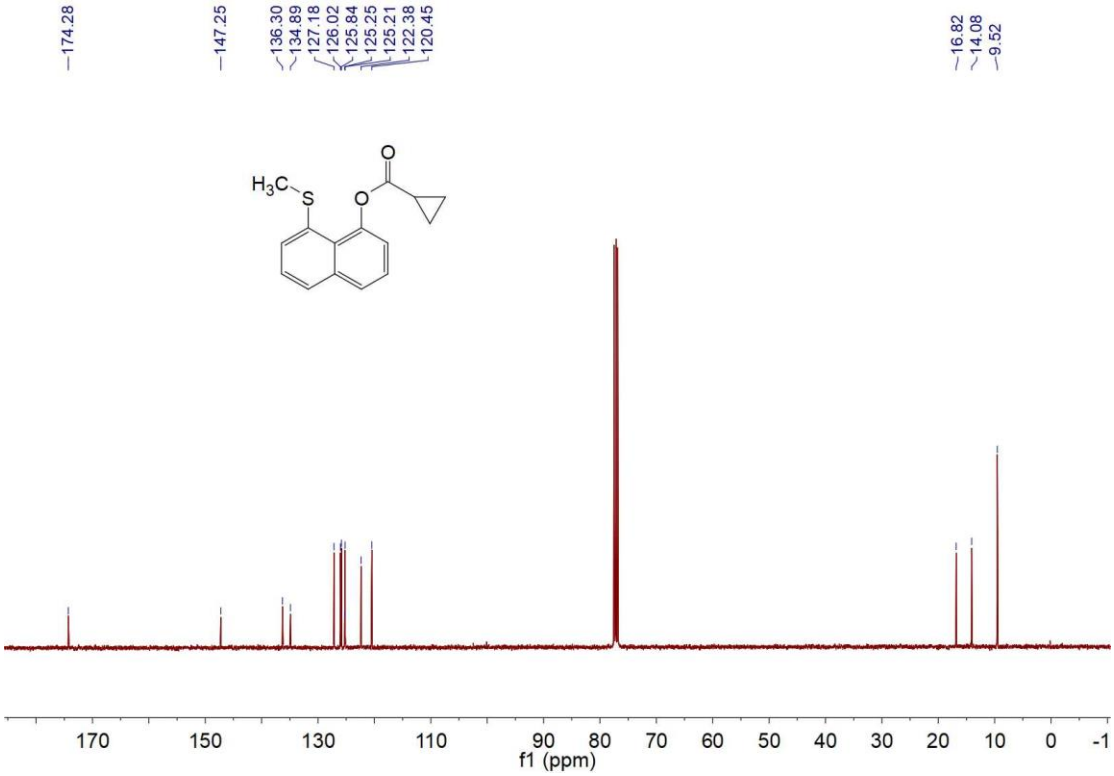
1.01
0.99
3.02
1.01
2.16
2.03
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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127.18
126.02
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125.25
125.21
122.38
120.45
16.82
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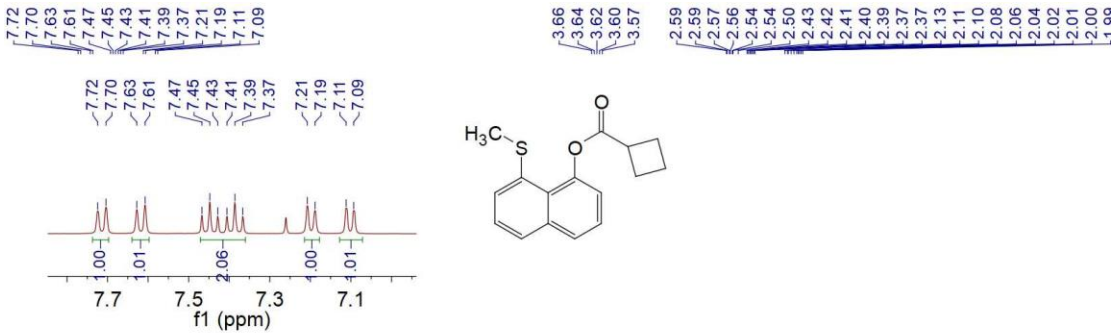
9.52
H3C
S
O
O
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.19
7.11
7.09
3.66
3.64
3.62
3.60
3.57
2.59
2.57
2.56
2.54
2.50
2.43
2.42
2.41
2.40
2.39
2.37
2.13
2.11
2.10
2.08
2.06
2.04
2.02
2.01
2.00
1.00
1.01
2.06
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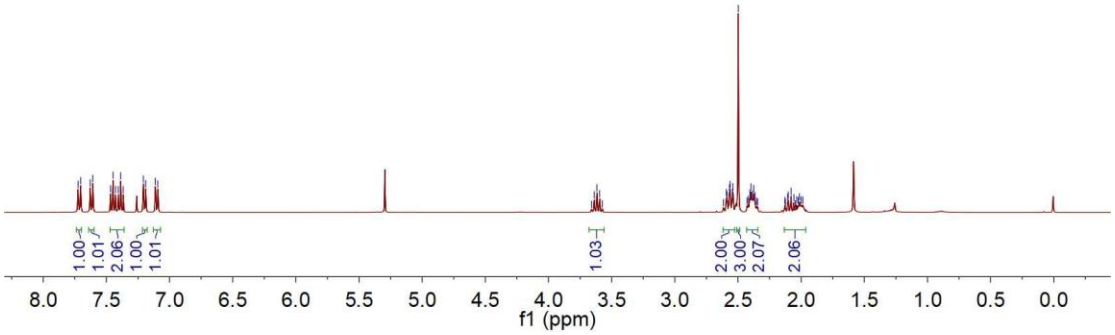
1.01
7.7
7.5
7.3
7.1
f1 (ppm)
H3C
S
O
O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3.00
2.07
2.06
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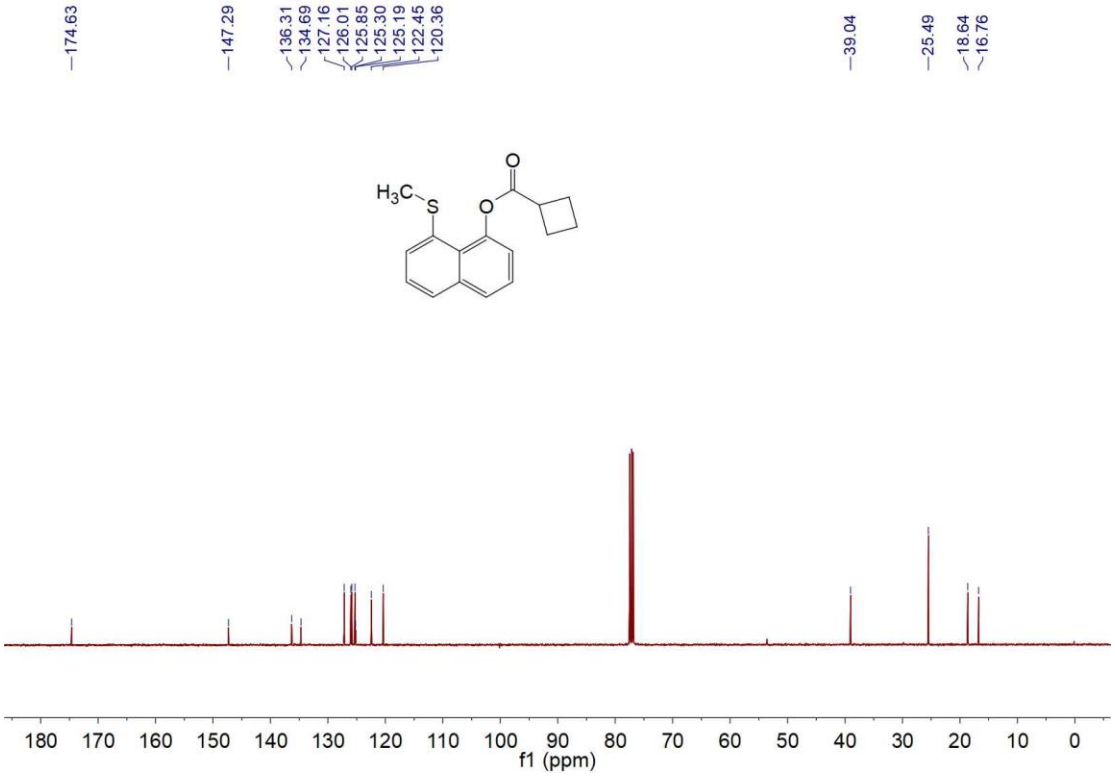
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.69
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125.30
125.19
122.45
120.36
39.04
25.49
18.64
16.76
H3C
S
O
O
180
170
160
150
140
130
120
110
100
90
80
70
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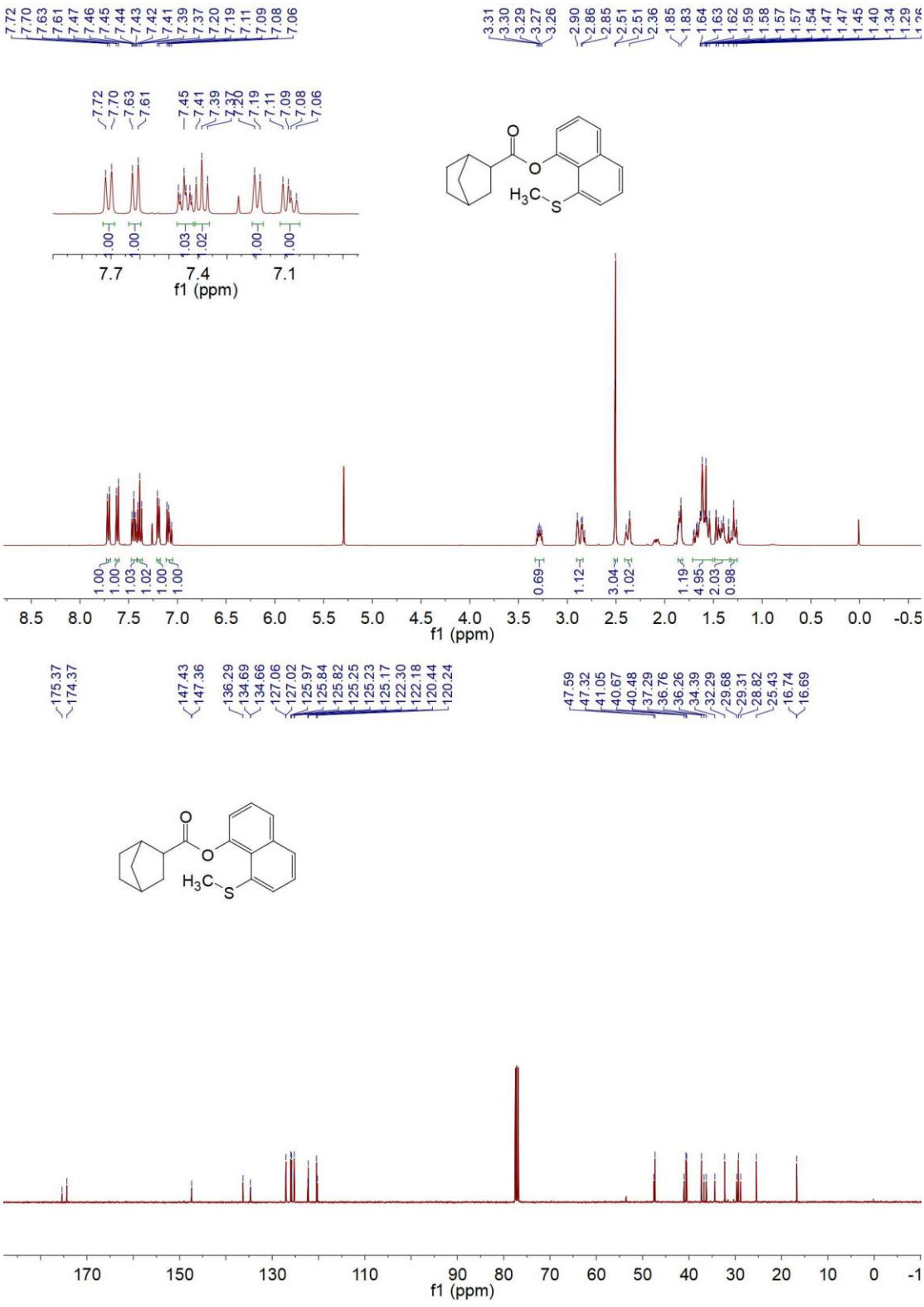
50
40
30
20
10
0
f1 (ppm)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7.37
7.20
7.19
7.11
7.09
7.08
7.06
3.31
3.30
3.29
3.27
3.26
2.90
2.86
2.85
2.51
2.51
2.36
1.85
1.83
1.64
1.63
1.62
1.59
1.58
1.57
1.57
1.54
1.47
1.47
1.45
1.40
1.34
1.29
O
O
H3C
S
1.00
1.00
1.03
1.02
1.00
1.00
0.69
1.12
3.04
1.02
1.19
4.95
2.03
0.98
7.7
7.4
7.1
f1 (ppm)
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)
175.37
174.37
147.43
147.36
136.29
134.69
134.66
127.06
127.02
125.97
125.84
125.82
125.25
125.23
125.17
122.30
122.18
120.44
120.24
47.59
47.32
41.05
40.67
40.48
37.29
36.76
36.26
34.39
32.29
29.68
29.31
28.82
25.43
16.74
16.69
O
O
H3C
S
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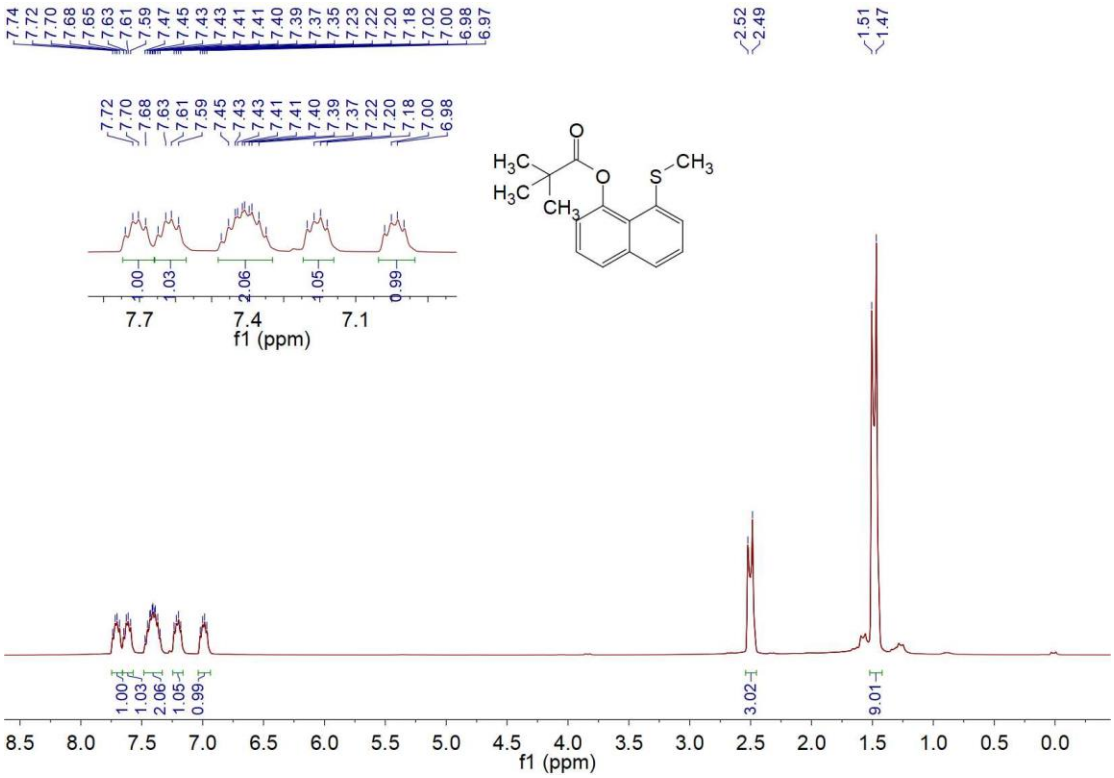
150
130
110
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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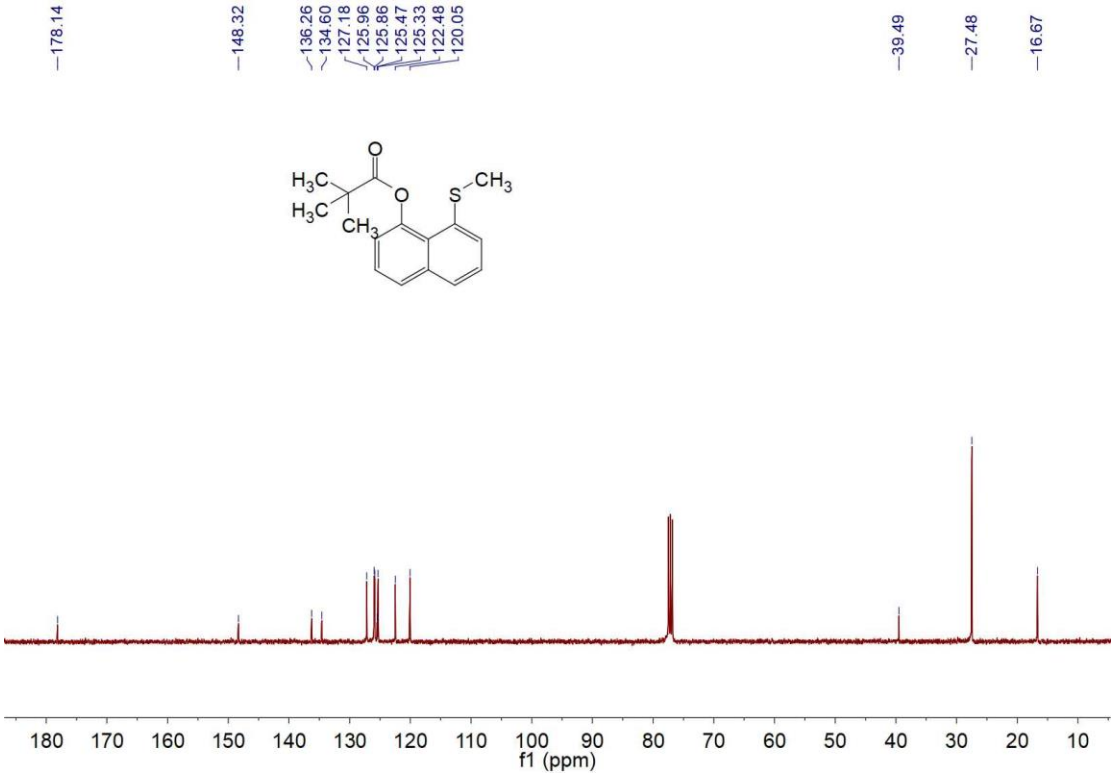
7.43
7.41
7.41
7.40
7.39
7.37
7.35
7.23
7.22
7.20
7.18
7.02
7.00
6.98
6.97
2.52
2.49
1.51
1.47
1.00
1.03
2.06
1.05
0.99
3.02
9.01
f1 (ppm)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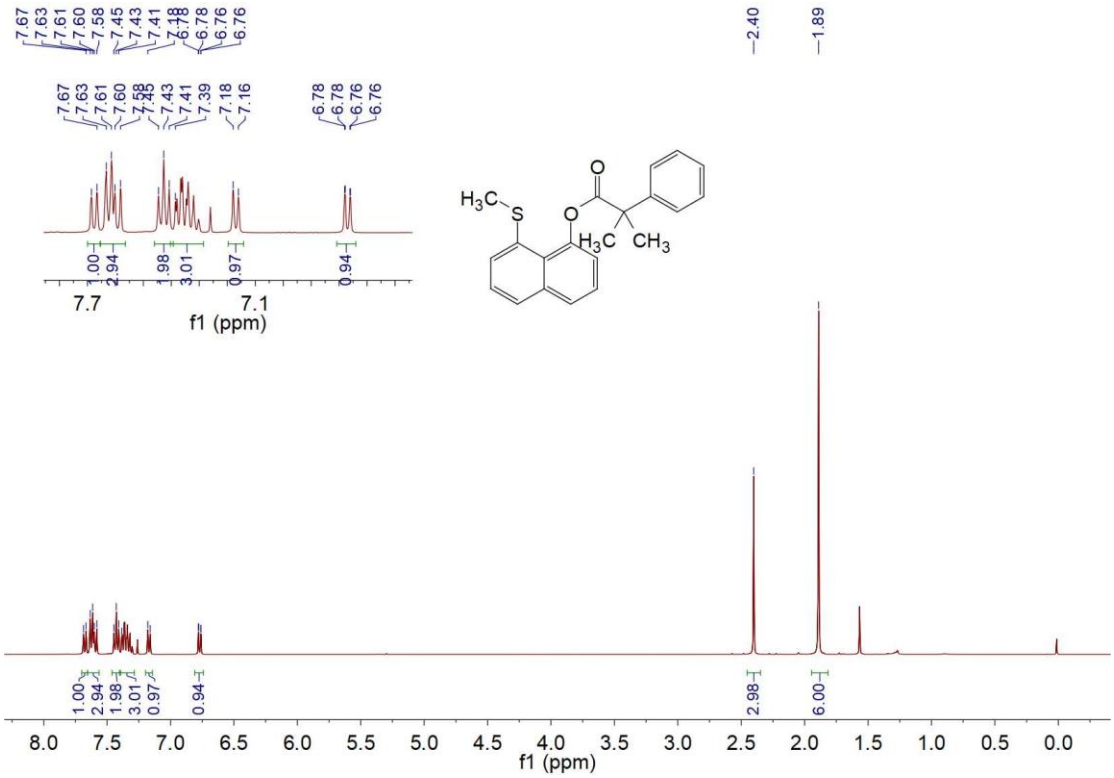
125.47
125.33
122.48
120.05
39.49
27.48
16.67
f1 (ppm)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7.45
7.43
7.41
7.18
7.16
6.78
6.76
6.76
2.40
1.89
1.00
2.94
1.98
3.01
0.97
0.94
2.98
6.00
7.7
7.1
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
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2.0
1.5
1.0
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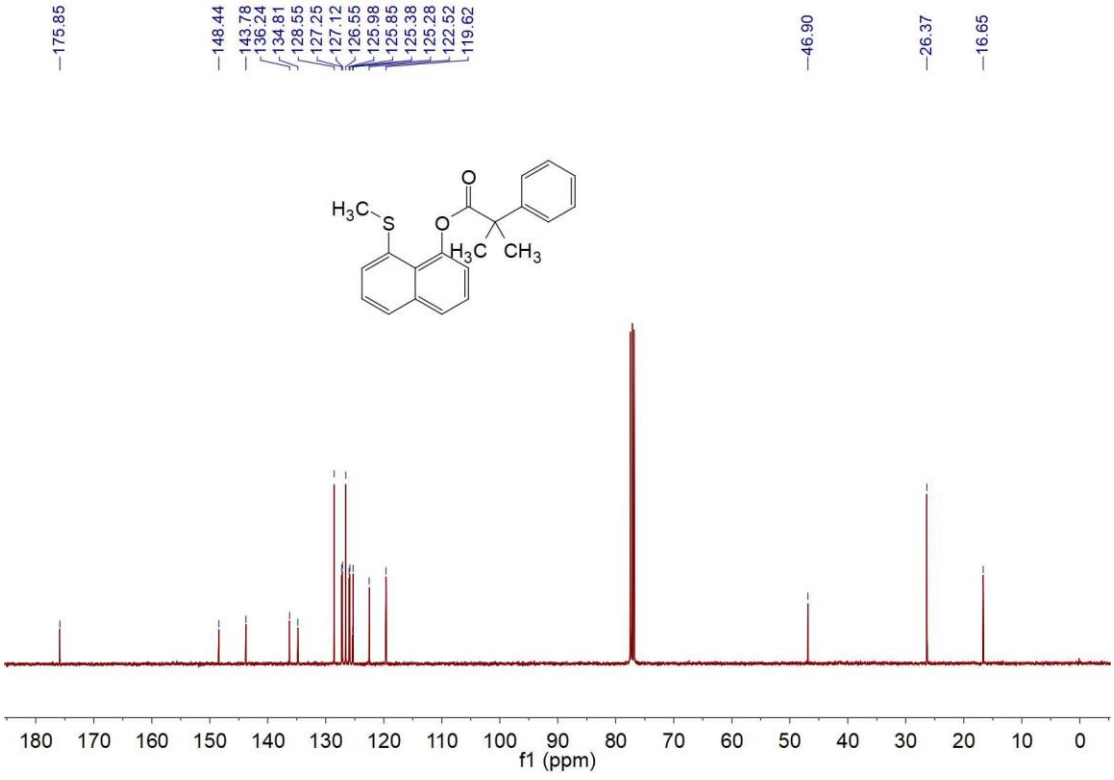
0.0
H3C
S
O
O
H3C
CH3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127.12
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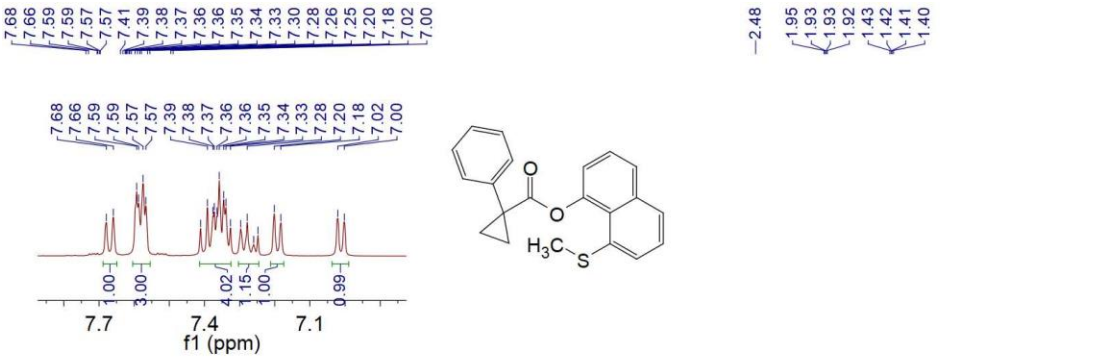
125.98
125.85
125.38
125.28
122.52
119.62
46.90
26.37
16.65
H3C
S
O
O
H3C
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.39
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7.37
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7.35
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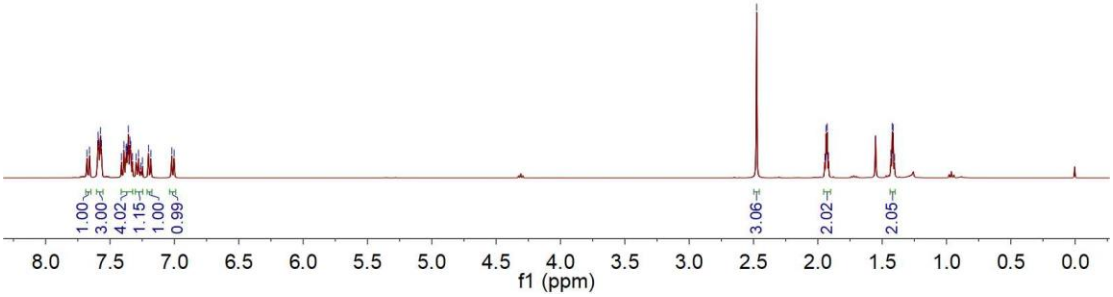
7.30
7.28
7.26
7.25
7.20
7.18
7.02
7.00
2.48
1.95
1.93
1.92
1.43
1.42
1.41
1.40
O
O
H3C
S
1.00
3.00
4.02
1.15
1.00
0.99
7.7
7.4
7.1
f1 (ppm)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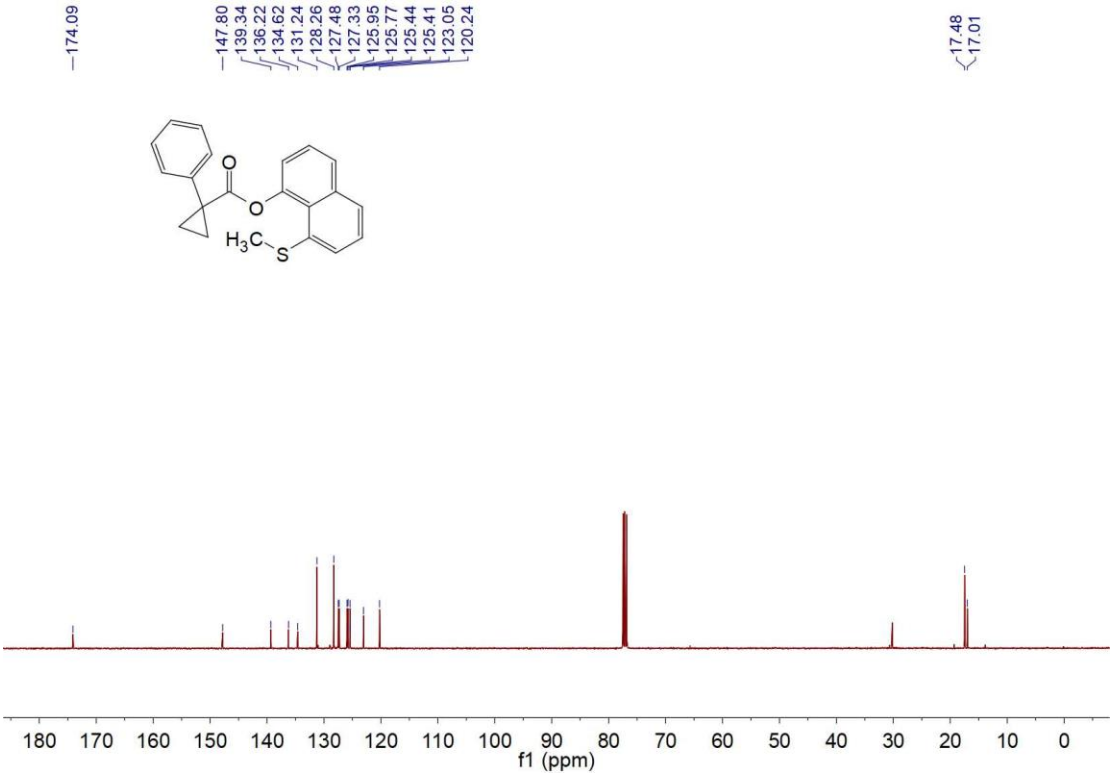
3.00
4.02
1.15
1.00
0.99
3.06
2.02
2.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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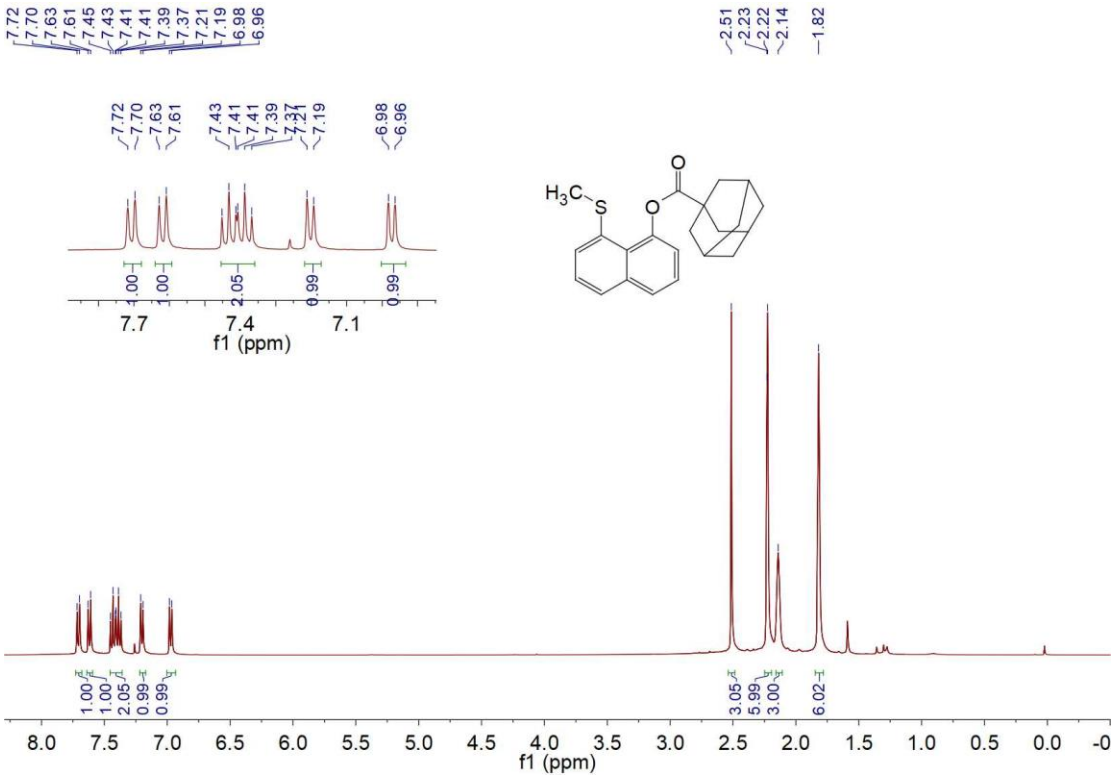
127.48
127.33
125.95
125.77
125.44
125.41
123.05
120.24
17.48
17.01
O
O
H3C
S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.41
7.39
7.37
7.21
7.19
6.98
6.96
2.51
2.23
2.22
2.14
1.82
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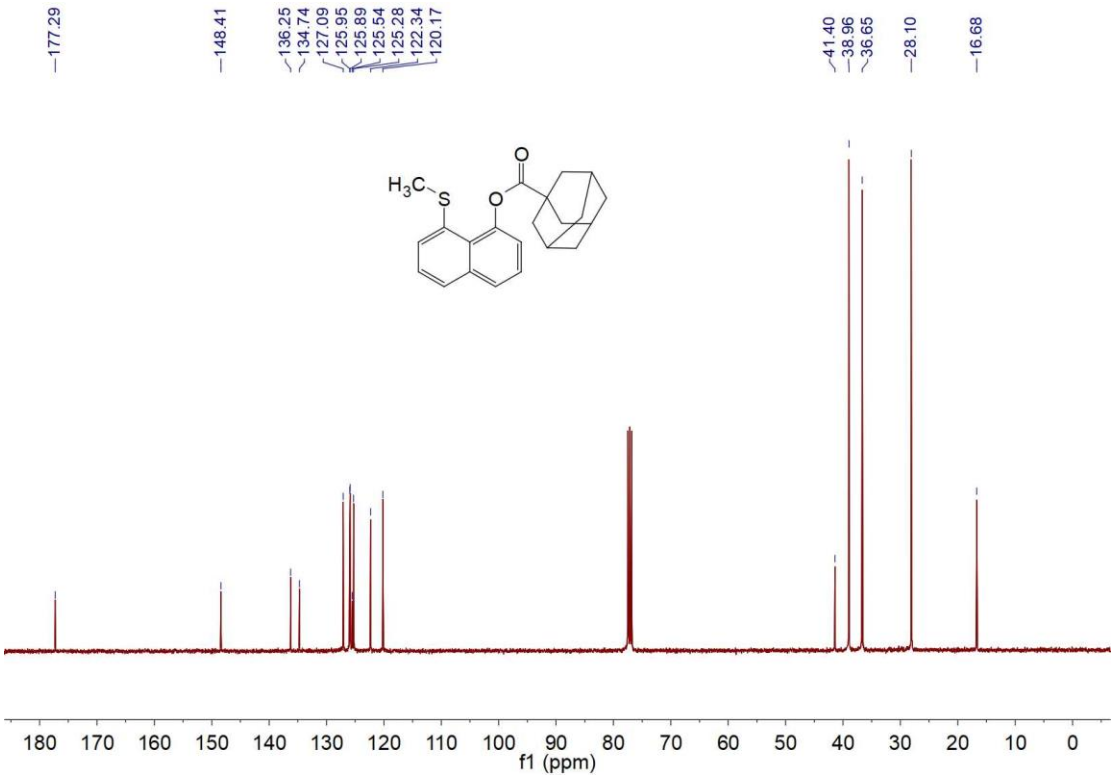
1.00
2.05
0.99
0.99
3.05
5.99
3.00
6.02
f1 (ppm)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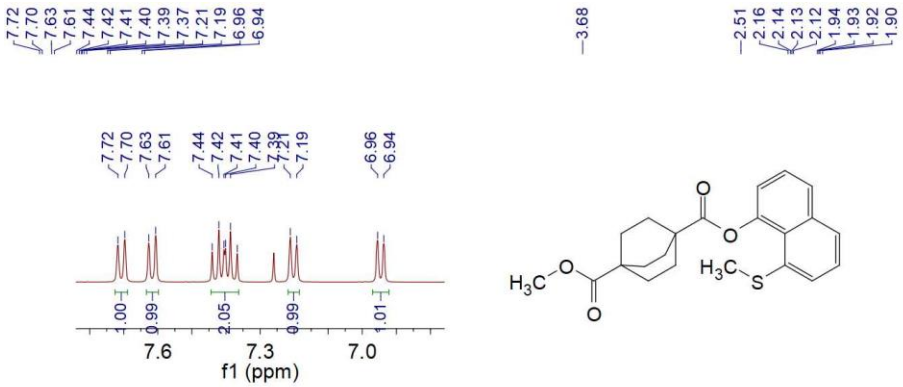
125.54
125.28
122.34
120.17
41.40
38.96
36.65
28.10
16.68
f1 (ppm)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7.61
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7.42
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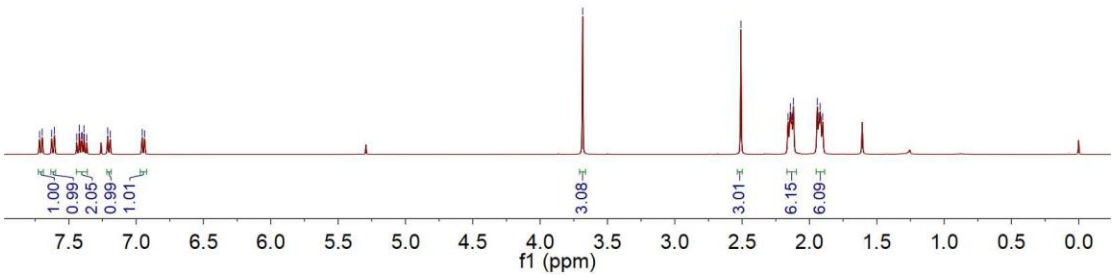
7.40
7.39
7.37
7.21
7.19
6.96
6.94
3.68
2.51
2.16
2.14
2.13
2.12
1.94
1.93
1.92
1.90
1.00
0.99
2.05
0.99
1.01
7.6
7.3
7.0
f1 (ppm)
O
O
O
H3C
O
H3C
S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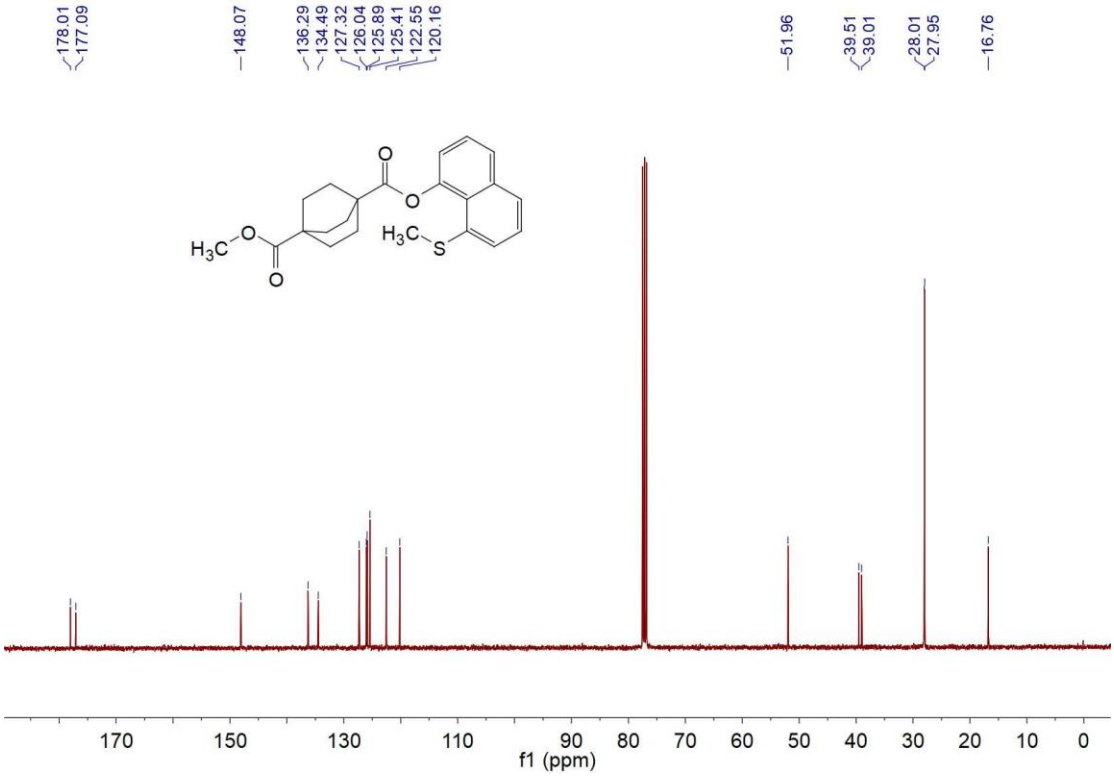
0.99
2.05
0.99
1.01
3.08
3.01
6.15
6.09
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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177.09
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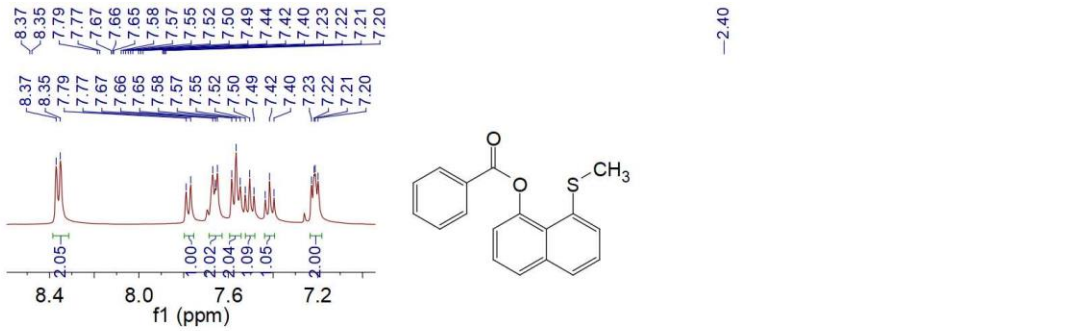
127.32
126.04
125.89
125.41
122.55
120.16
51.96
39.51
39.01
28.01
27.95
16.76
O
O
O
H3C
O
H3C
S
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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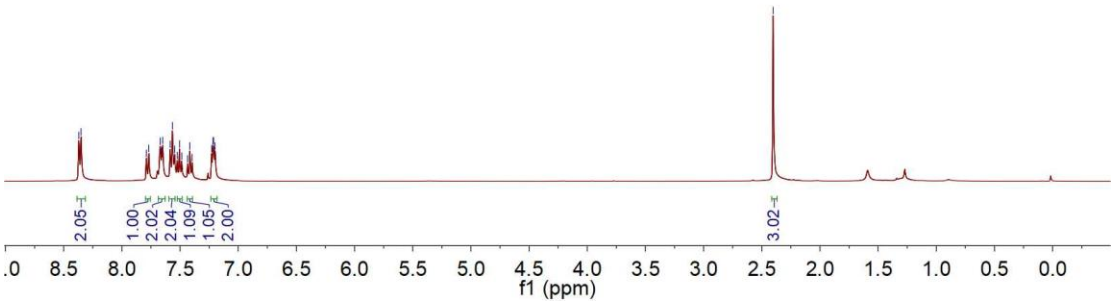
7.58
7.57
7.55
7.52
7.50
7.49
7.44
7.42
7.40
7.23
7.22
7.21
7.20
2.40
2.05
1.00
2.02
2.04
1.09
1.05
2.00
8.4
8.0
7.6
7.2
f1 (ppm)
O
O
S
CH3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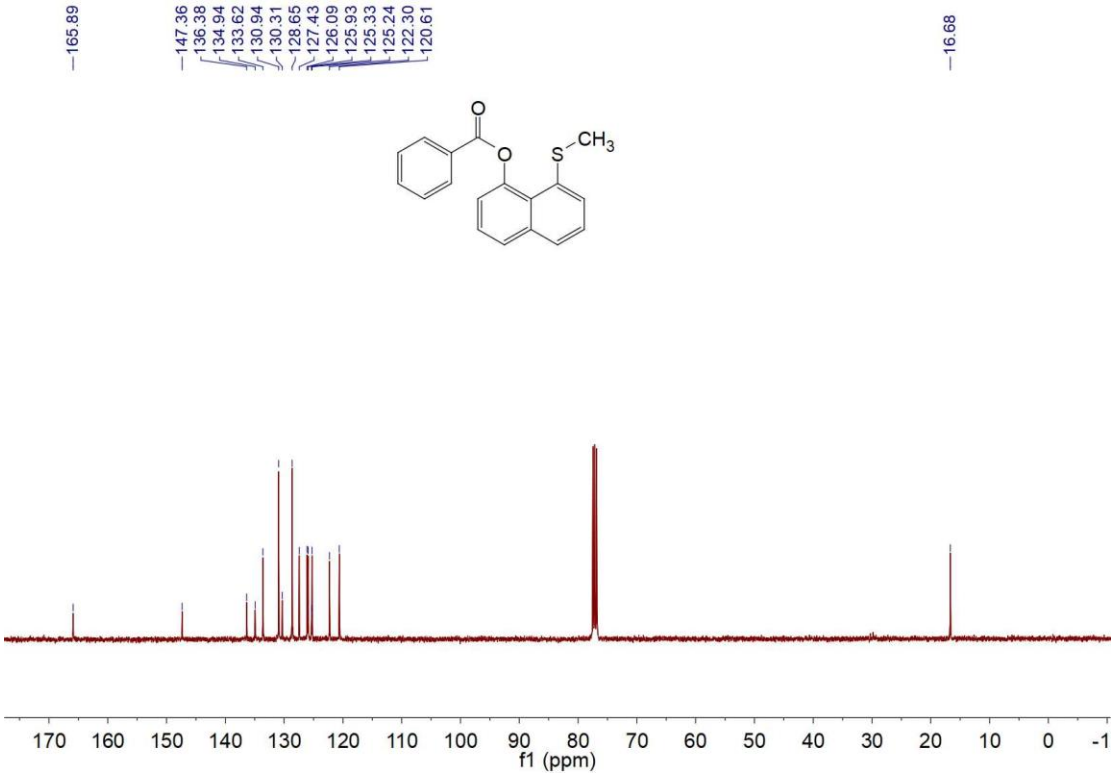
2.02
2.04
1.09
1.05
2.00
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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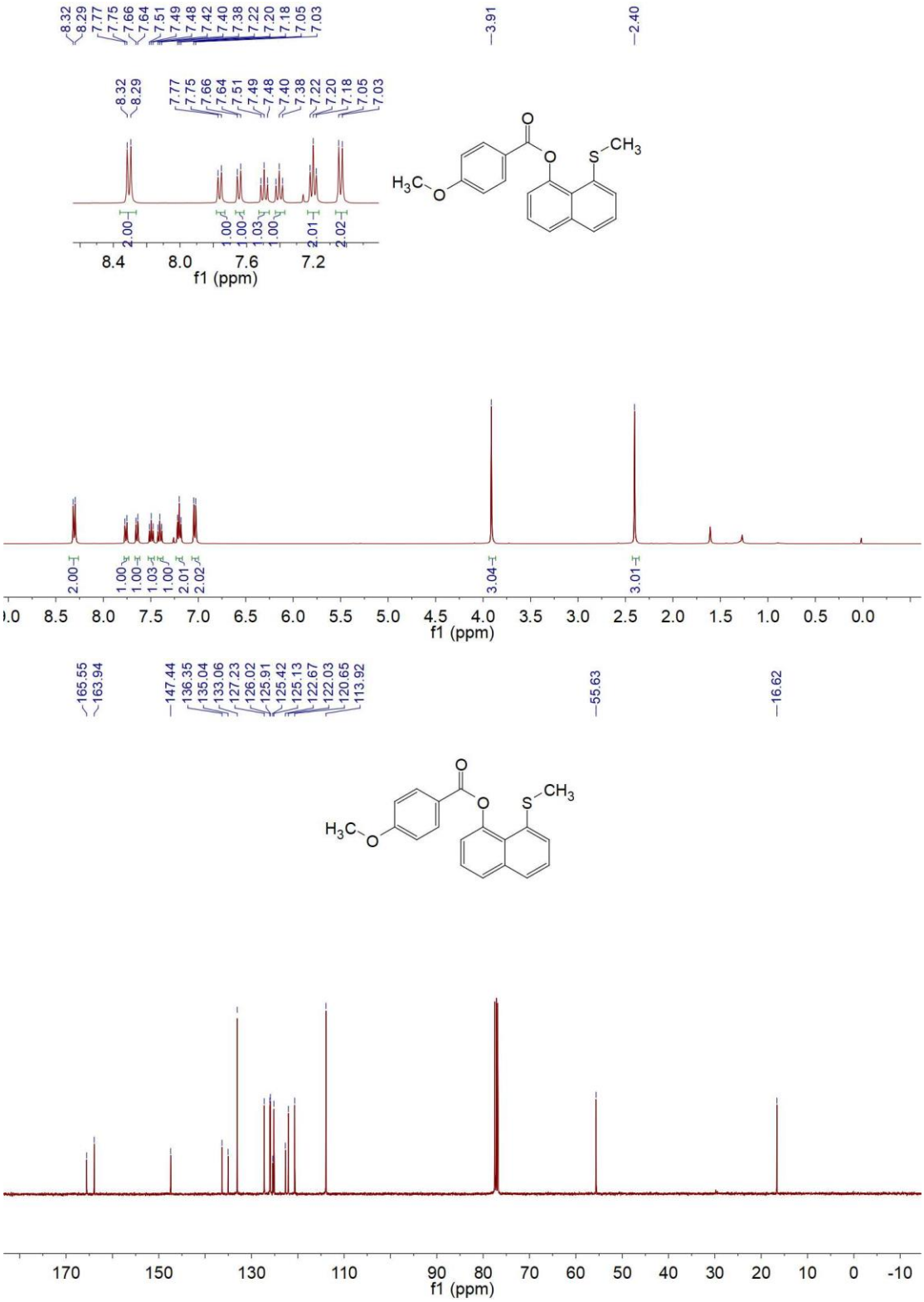
130.94
130.31
128.65
127.43
126.09
125.93
125.33
125.24
122.30
120.61
16.68
O
O
S
CH3
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-1
f1 (ppm)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7.66
7.64
7.51
7.49
7.48
7.42
7.40
7.38
7.22
7.20
7.18
7.05
7.03
3.91
2.40
2.00
1.00
1.00
1.03
1.00
2.01
2.02
8.4
8.0
7.6
7.2
f1 (ppm)
O
O
S
CH3
H3C
O
2.00
1.00
1.00
1.03
1.00
2.01
2.02
3.04
3.01
f1 (ppm)
165.55
163.94
147.44
136.35
135.04
133.06
127.23
126.02
125.91
125.42
125.13
122.67
122.03
120.65
113.92
55.63
16.62
O
O
S
CH3
H3C
O
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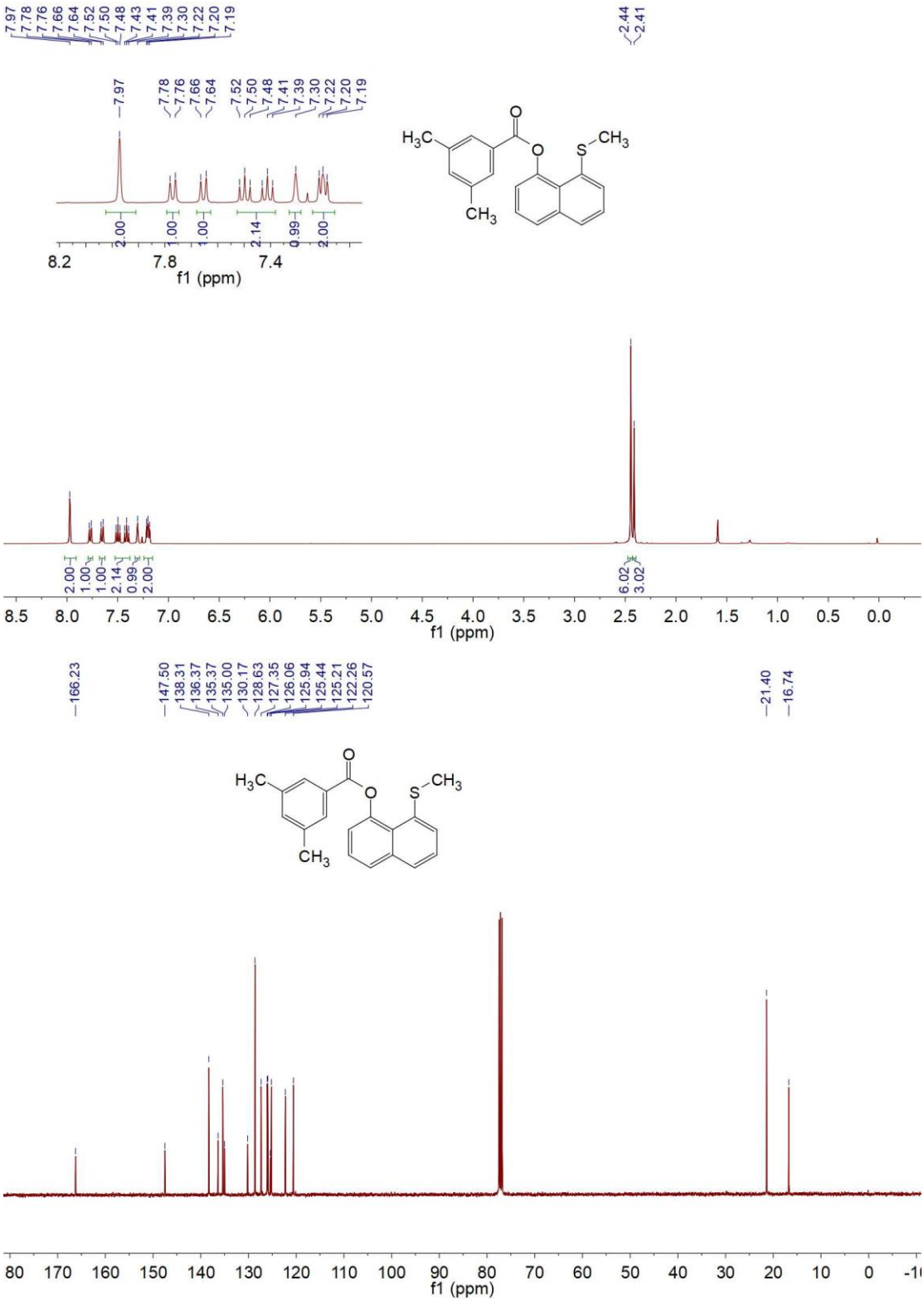
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)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7.48
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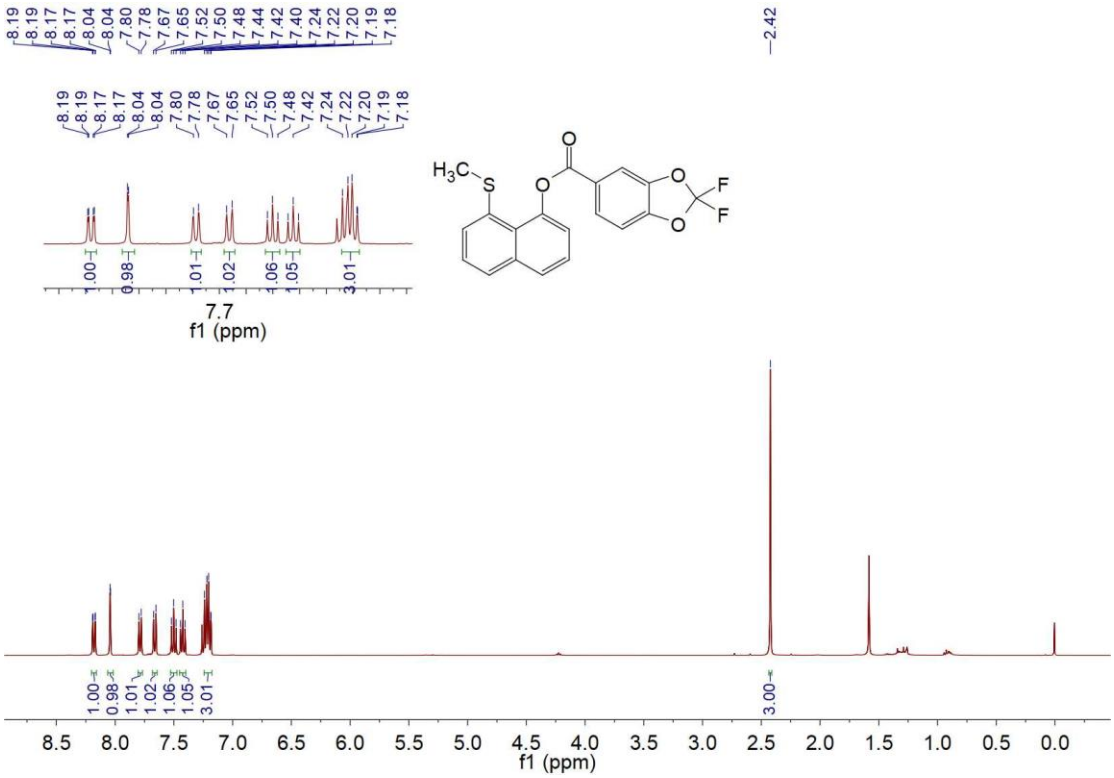
7.41
7.39
7.30
7.22
7.20
7.19
2.44
2.41
2.00
1.00
1.00
2.14
0.99
2.00
6.02
3.02
f1 (ppm)
166.23
147.50
138.31
136.37
135.37
135.00
130.17
128.63
127.35
126.06
125.94
125.44
125.21
122.26
120.57
21.40
16.74
H3C
CH3
O
S
CH3
f1 (ppm)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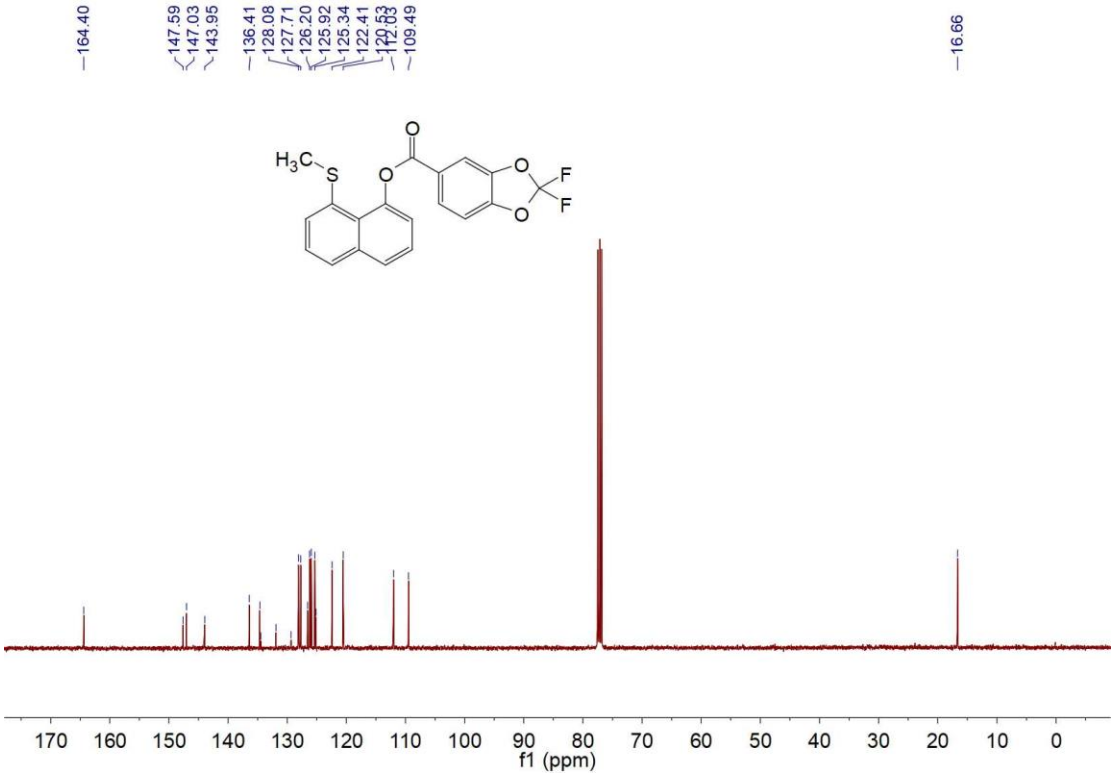
8.19
8.17
8.17
8.04
8.04
7.80
7.78
7.67
7.65
7.52
7.50
7.48
7.44
7.42
7.40
7.24
7.22
7.20
7.19
7.18
2.42
1.00
0.98
1.01
1.02
1.06
1.05
3.01
3.00
7.7
f1 (ppm)
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
H3C
S
O
O
O
F
F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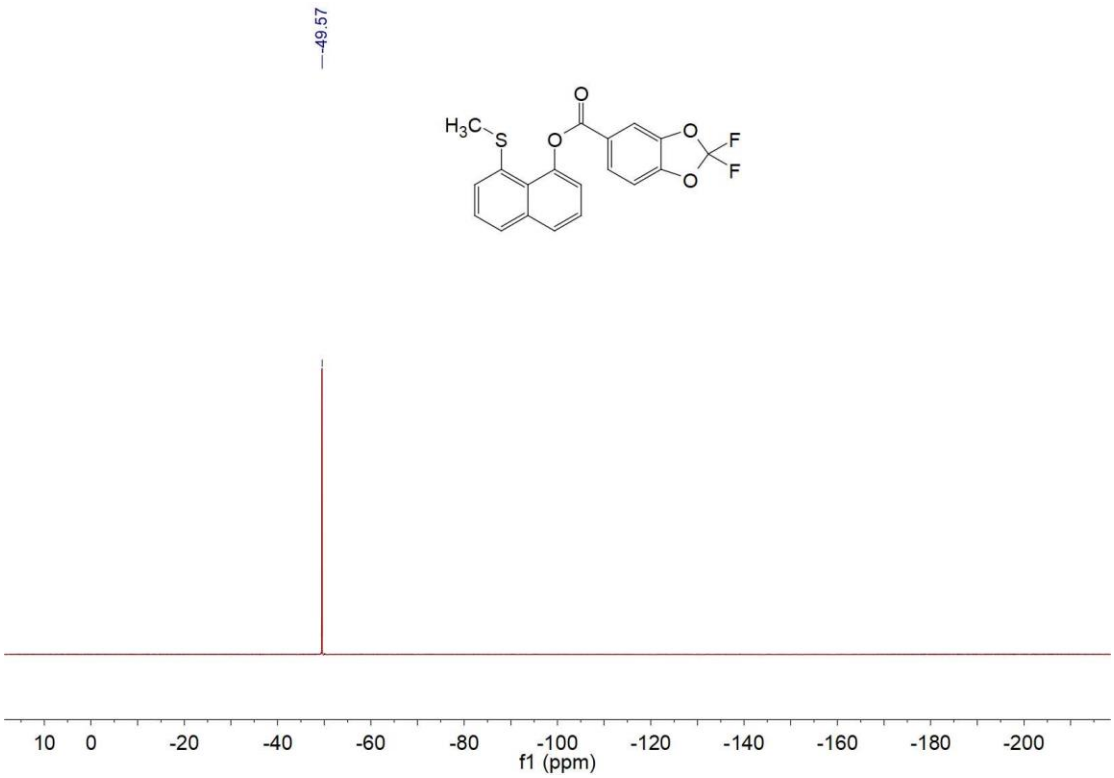
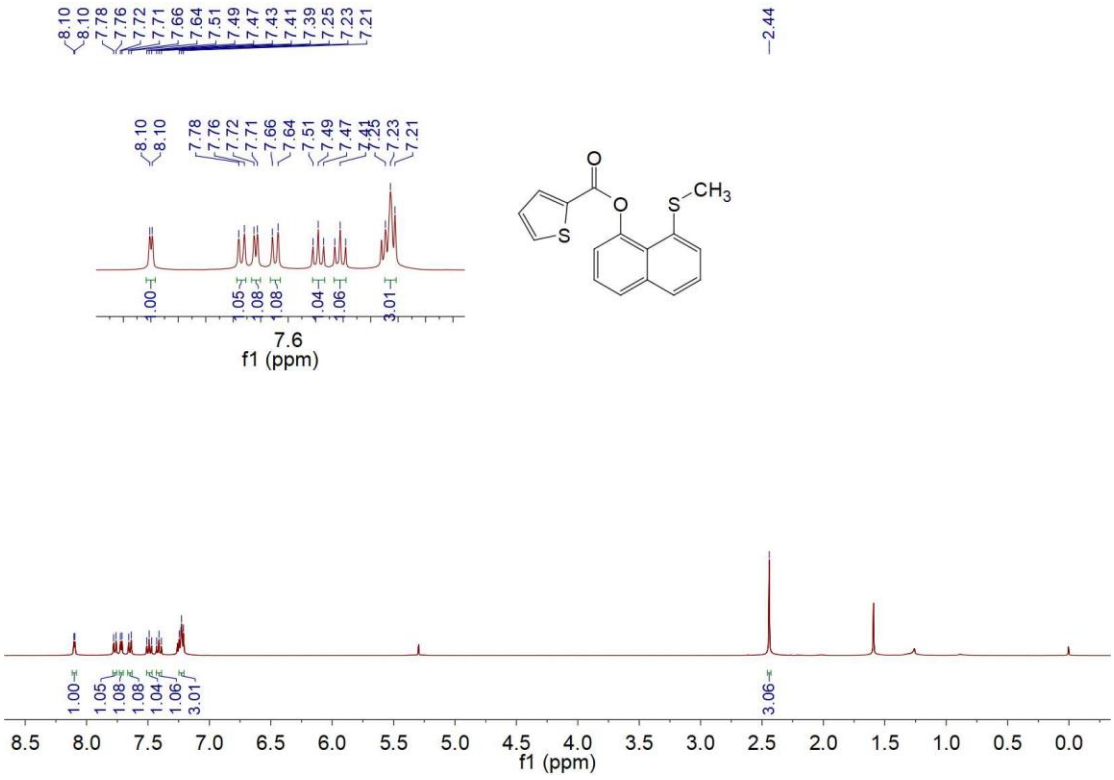
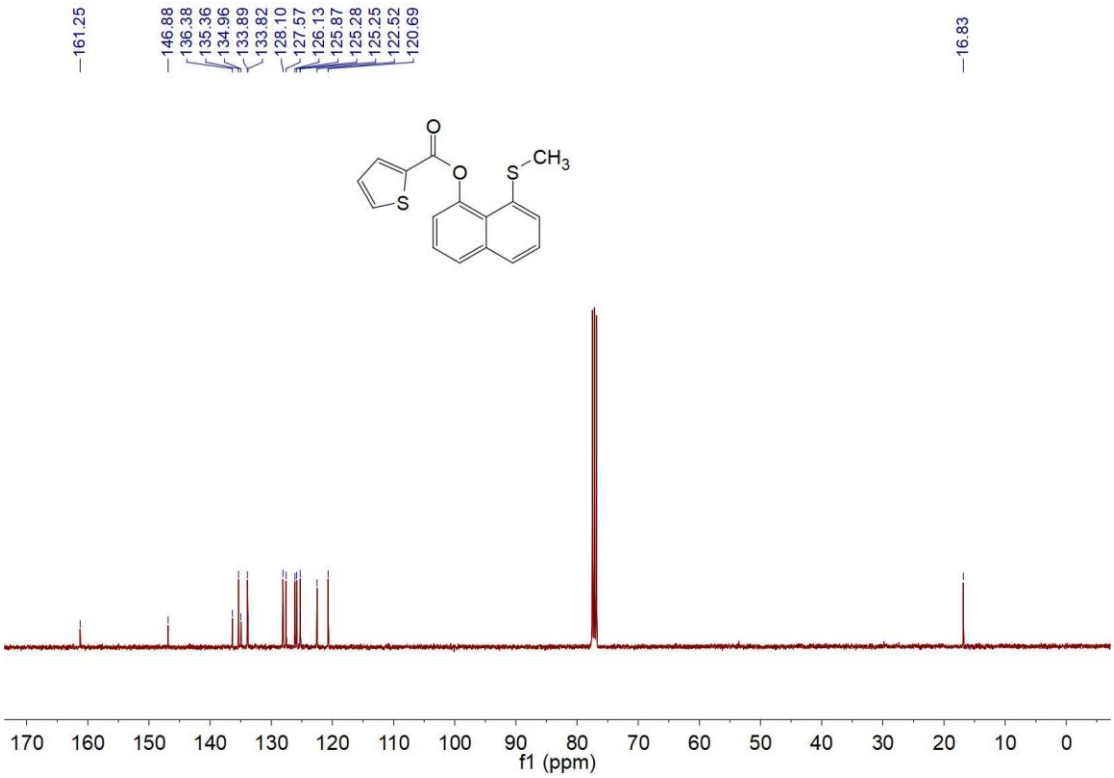
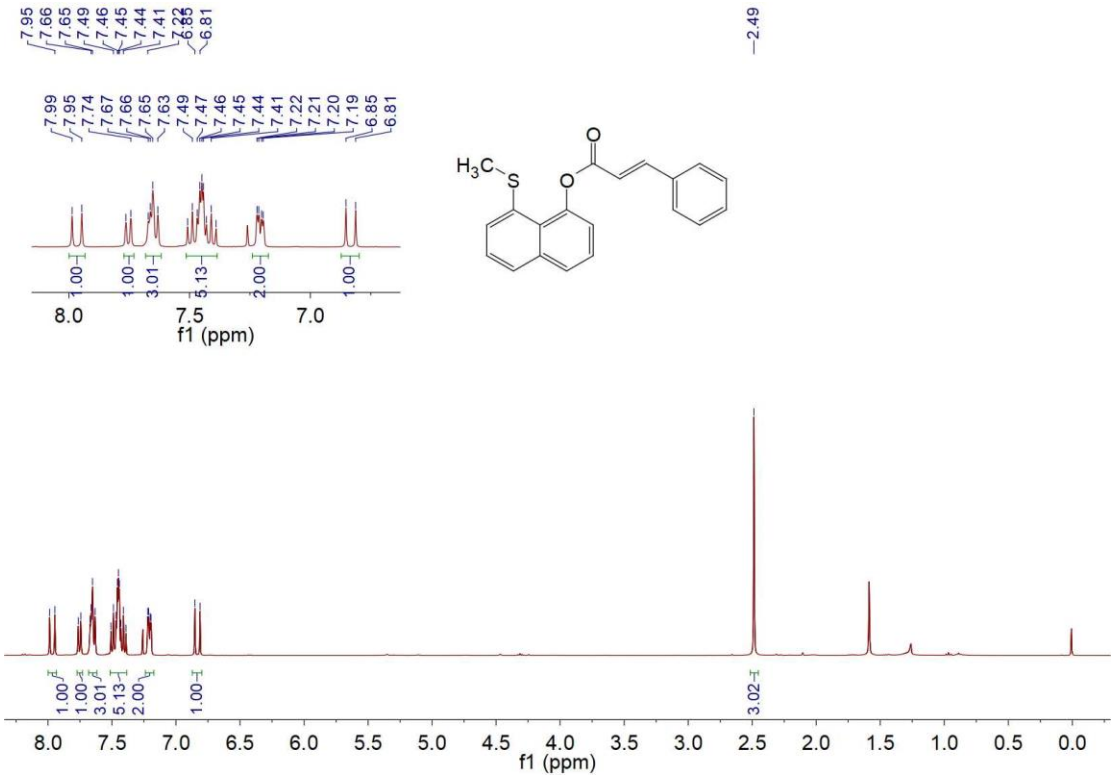
136.41
128.08
127.71
126.20
125.92
125.34
122.41
120.53
112.03
109.49
16.66
H3C
S
O
O
O
F
F
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-49.57
O
H3C
S
O
O
O
F
F
10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200
f1 (ppm)


8.10
8.10
7.78
7.76
7.72
7.71
7.66
7.64
7.51
7.49
7.47
7.43
7.41
7.39
7.25
7.23
7.21
2.44
1.00
1.05
1.08
1.08
1.04
1.06
3.01
7.6
f1 (ppm)
O
O
S
S
CH3
3.06
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)


161.25
146.88
136.38
135.36
134.96
133.89
133.82
128.10
127.57
126.13
125.87
125.28
125.25
122.52
120.69
16.83
O
O
S
S
CH3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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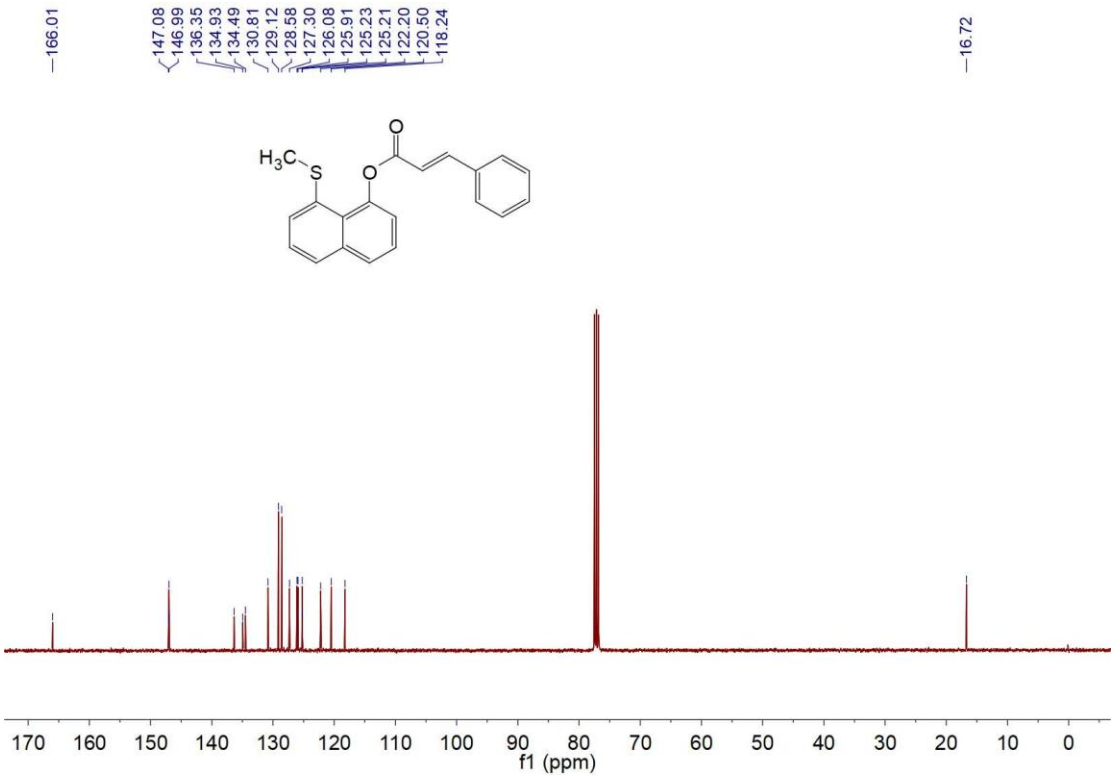
7.45
7.44
7.41
6.81
2.49
7.99
7.95
7.74
7.67
7.66
7.65
7.63
7.49
7.47
7.46
7.45
7.44
7.41
7.22
7.21
7.20
7.19
6.85
6.81
1.00
1.00
3.01
5.13
2.00
1.00
8.0
7.5
7.0
f1 (ppm)
H3C
S
O
O
1.00
1.00
3.01
5.13
2.00
1.00
3.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.01
147.08
146.99
136.35
134.93
134.49
130.81
129.12
128.58
127.30
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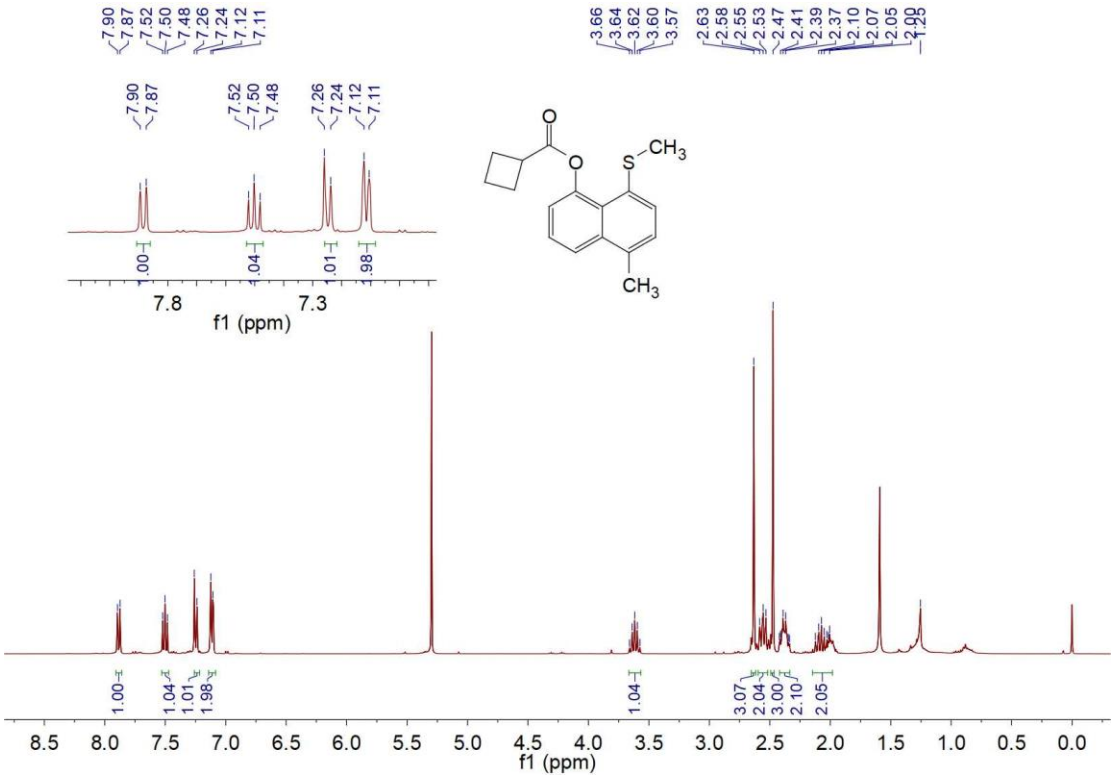
125.91
125.23
125.21
122.20
120.50
118.24
16.72
H3C
S
O
O
f1 (ppm)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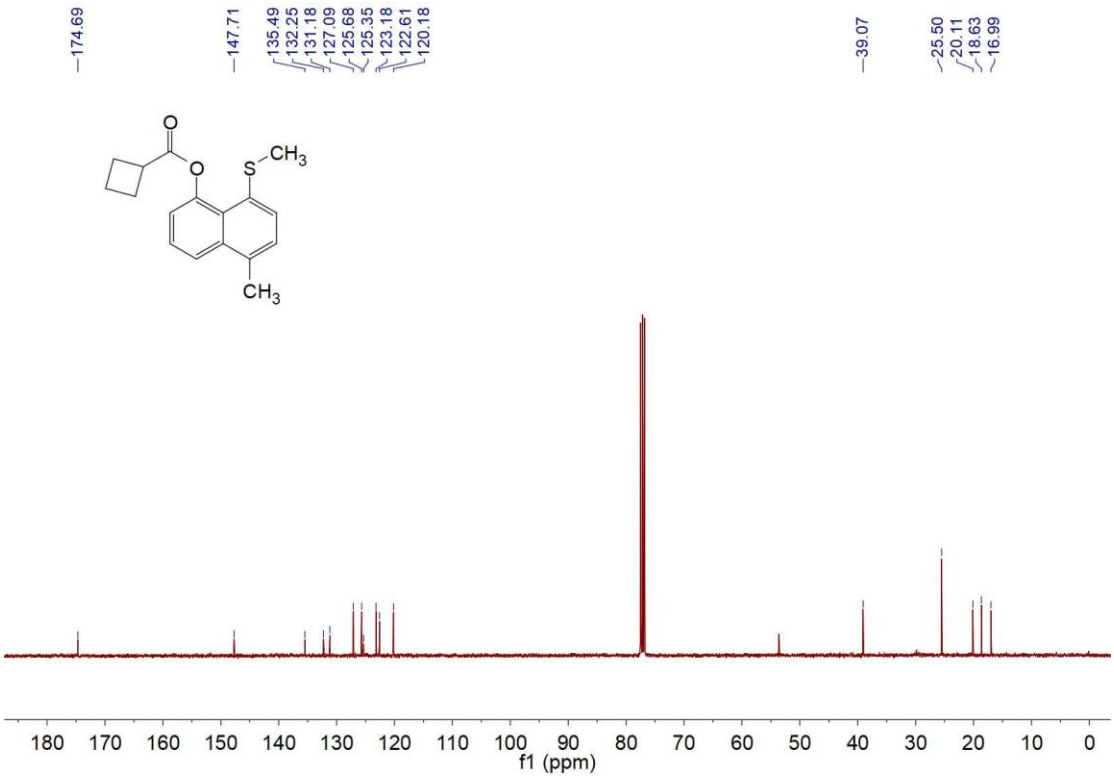
7.87
7.52
7.50
7.48
7.26
7.24
7.12
7.11
3.66
3.64
3.62
3.60
3.57
2.63
2.58
2.55
2.53
2.47
2.41
2.39
2.37
2.10
2.07
2.05
2.00
1.25
1.00
1.04
1.01
1.98
3.07
2.04
3.00
2.10
2.05
CH3
CH3
f1 (ppm)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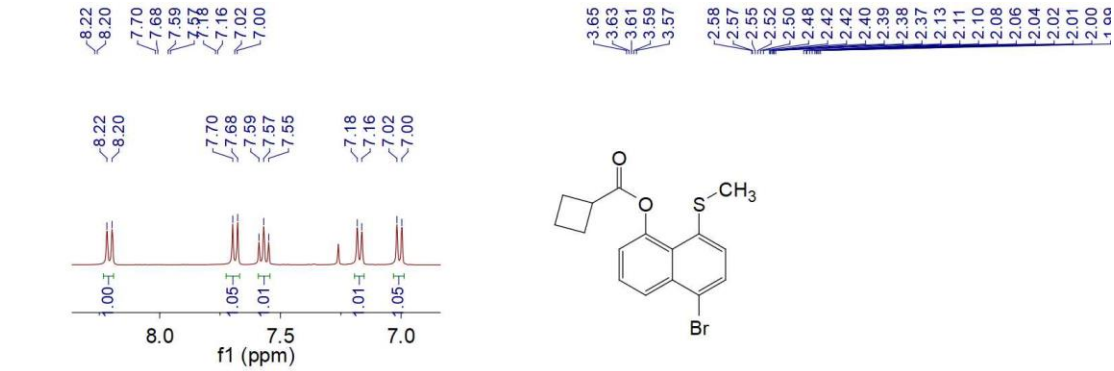
147.71
135.49
132.25
131.18
127.09
125.68
125.35
123.18
122.61
120.18
39.07
25.50
20.11
18.63
16.99
O
O
S
CH3
CH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.20
7.70
7.68
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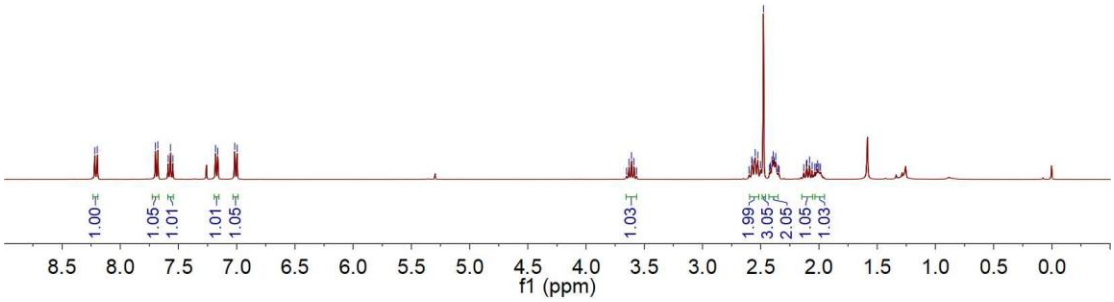
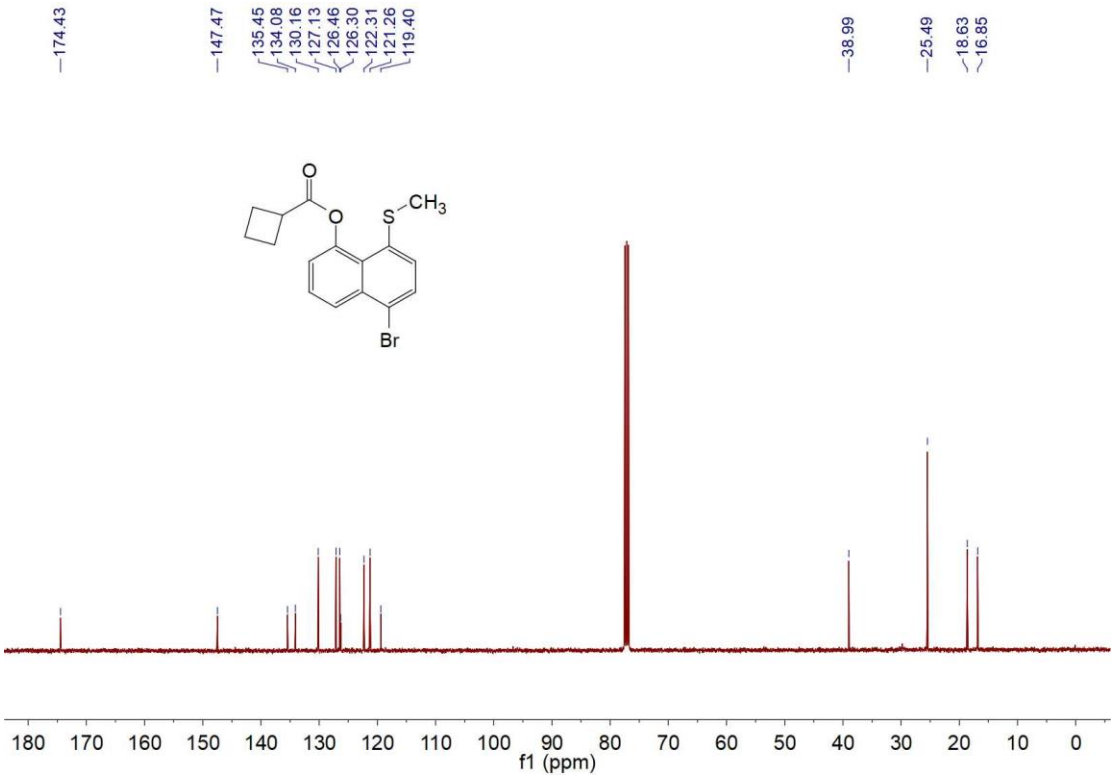
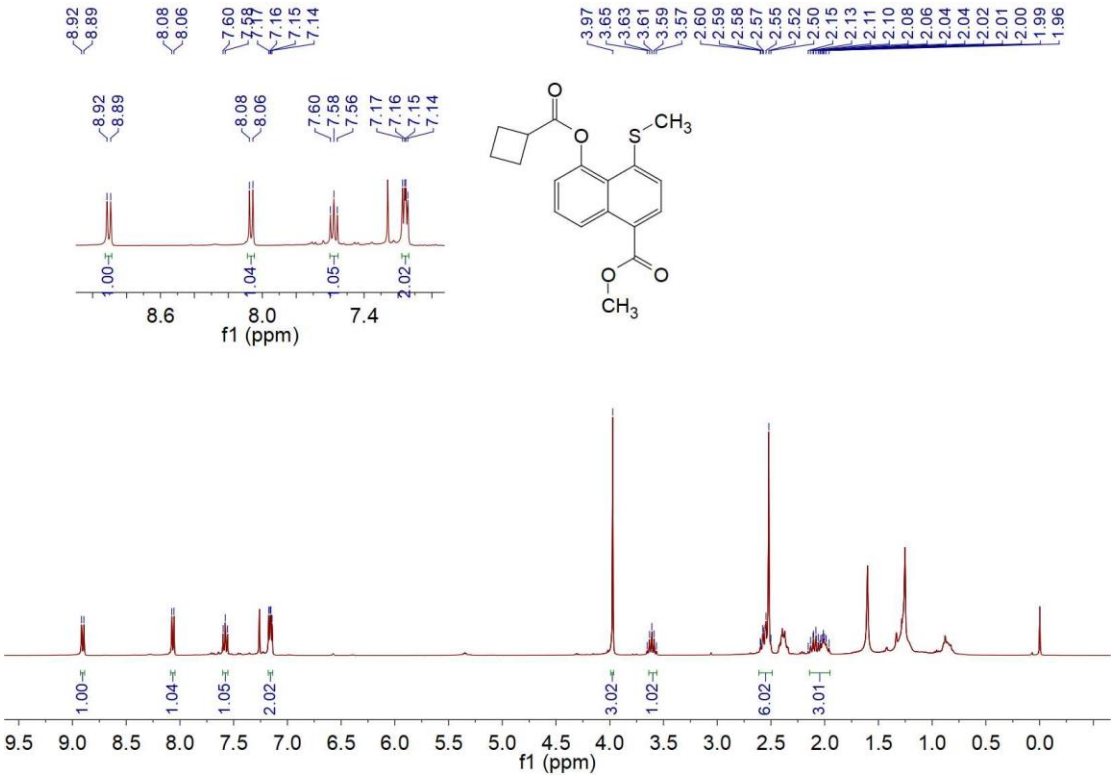
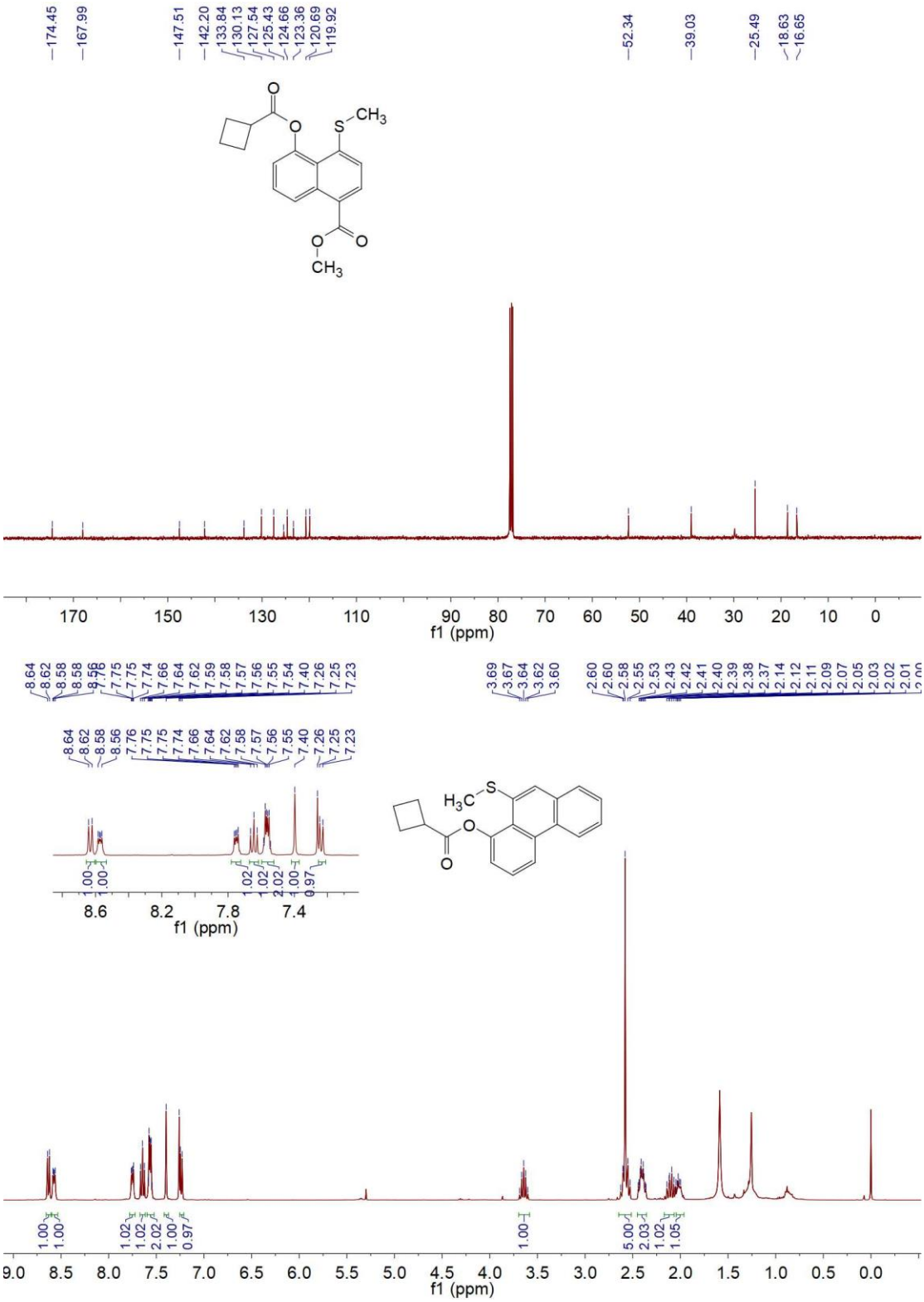
7.57
7.55
7.18
7.16
7.02
7.00
3.65
3.63
3.61
3.59
3.57
2.58
2.57
2.55
2.52
2.50
2.48
2.42
2.40
2.39
2.38
2.37
2.13
2.11
2.10
2.08
2.06
2.04
2.02
2.01
2.00
1.00
1.05
1.01
1.01
1.05
8.0
7.5
7.0
f1 (ppm)


O
O
S
CH3
Br


1.00
1.05
1.01
1.01
1.05
1.03
1.99
3.05
2.05
1.05
1.03
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)


174.43
147.47
135.45
134.08
130.16
127.13
126.46
126.30
122.31
121.26
119.40
38.99
25.49
18.63
16.85
O
O
S
CH3
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.92
8.89
8.08
8.06
7.60
7.58
7.56
7.17
7.16
7.15
7.14
3.97
3.65
3.63
3.61
3.59
3.57
2.60
2.59
2.58
2.57
2.55
2.52
2.50
2.15
2.13
2.11
2.10
2.08
2.06
2.04
2.04
2.02
2.01
2.00
1.99
1.96
1.00
1.04
1.05
2.02
8.6
8.0
7.4
f1 (ppm)
O
O
S
CH3
O
O
CH3
3.02
1.02
6.02
3.01
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)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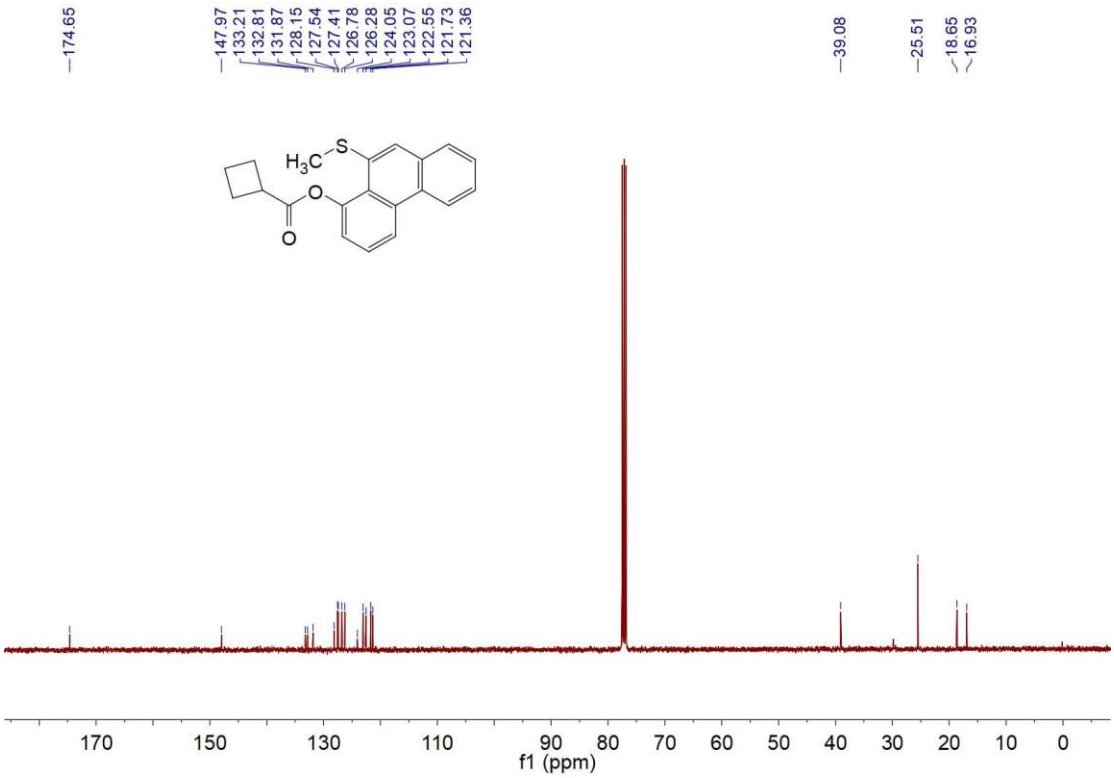
167.99
147.51
142.20
133.84
130.13
127.54
125.43
124.66
123.36
120.69
119.92
52.34
39.03
25.49
18.63
16.65
f1 (ppm)
f1 (ppm)
f1 (ppm)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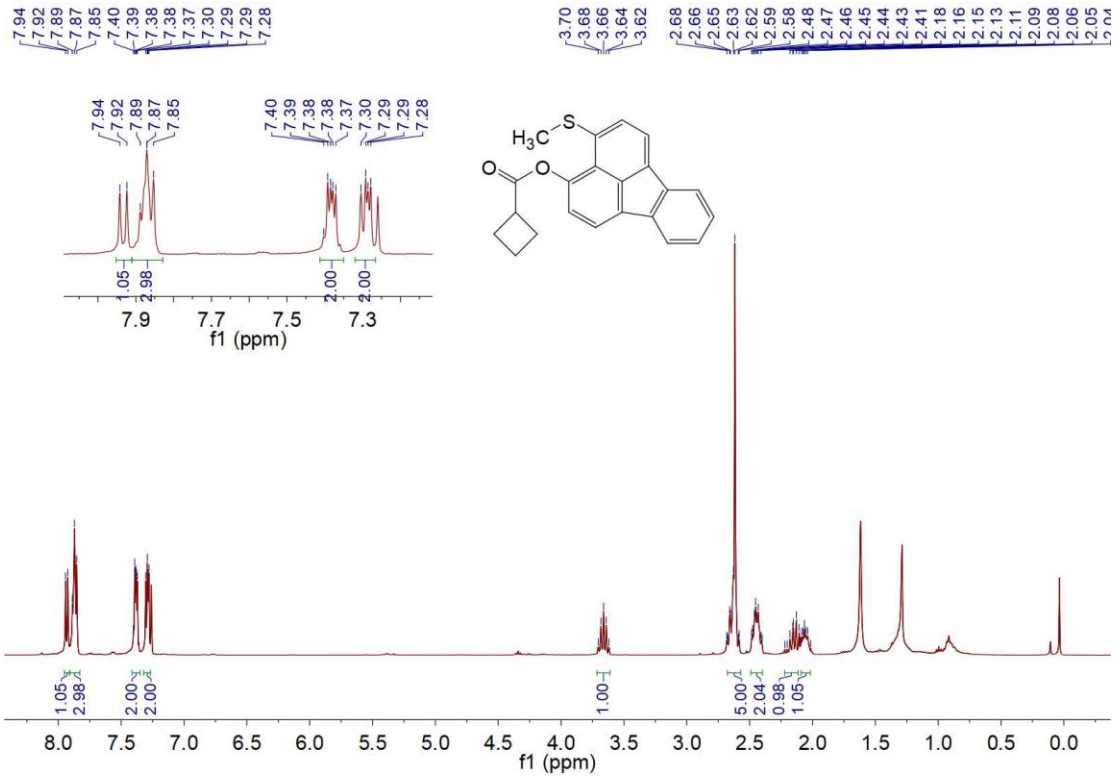
147.97
133.21
132.81
131.87
128.15
127.54
127.41
126.78
126.28
124.05
123.07
122.55
121.73
121.36
39.08
25.51
18.65
16.93
H3C
S
O
O
f1 (ppm)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7.92
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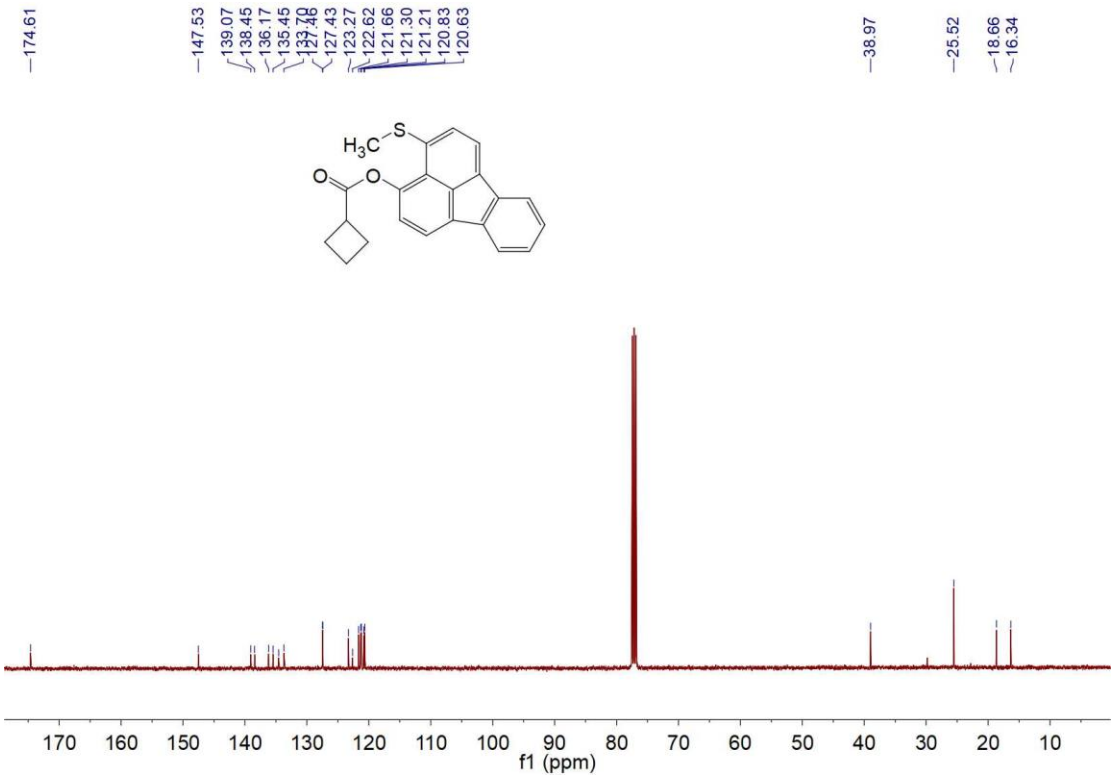
7.87
7.85
7.40
7.39
7.38
7.38
7.37
7.30
7.29
7.28
3.70
3.68
3.66
3.64
3.62
2.68
2.66
2.65
2.63
2.62
2.59
2.58
2.48
2.47
2.46
2.45
2.44
2.43
2.41
2.18
2.16
2.15
2.13
2.11
2.09
2.08
2.06
2.05
1.05
2.98
2.00
2.00
7.9
7.7
7.5
7.3
f1 (ppm)
H3C
S
O
O
1.05
2.98
2.00
2.00
1.00
5.00
2.04
0.98
1.05
8.0
7.5
7.0
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)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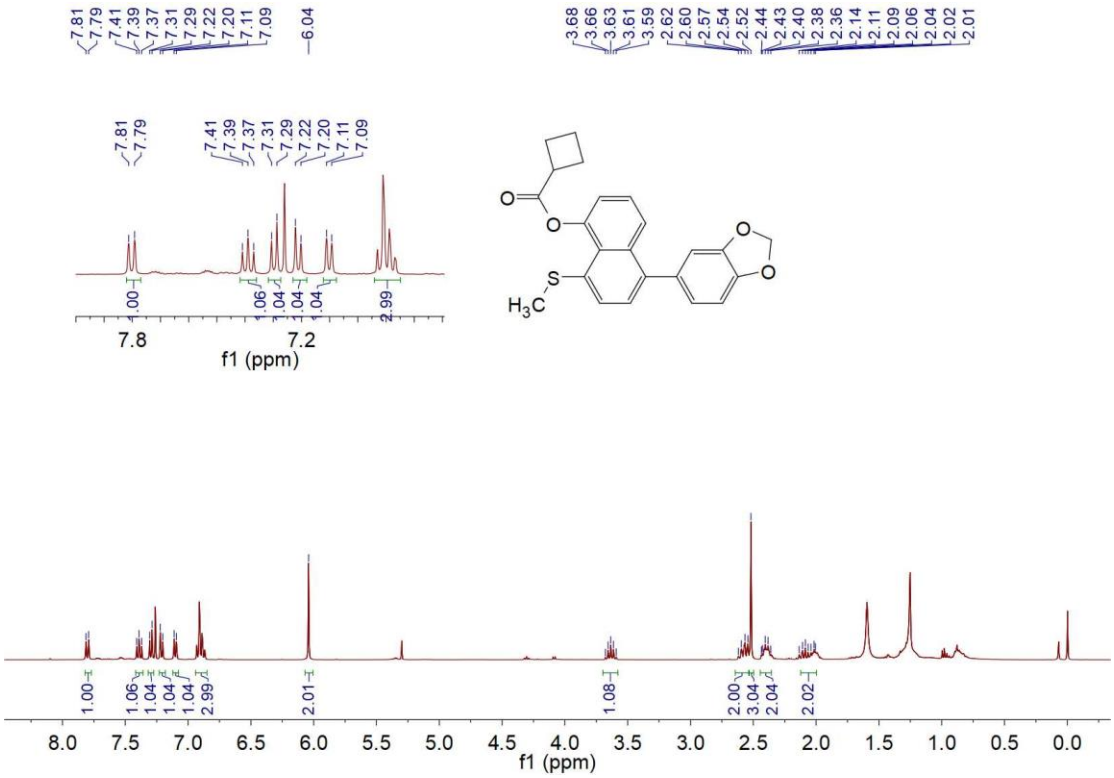
147.53
139.07
138.45
136.17
135.45
127.43
123.27
122.62
121.66
121.30
121.21
120.83
120.63
38.97
25.52
18.66
16.34
H3C
S
O
O
f1 (ppm)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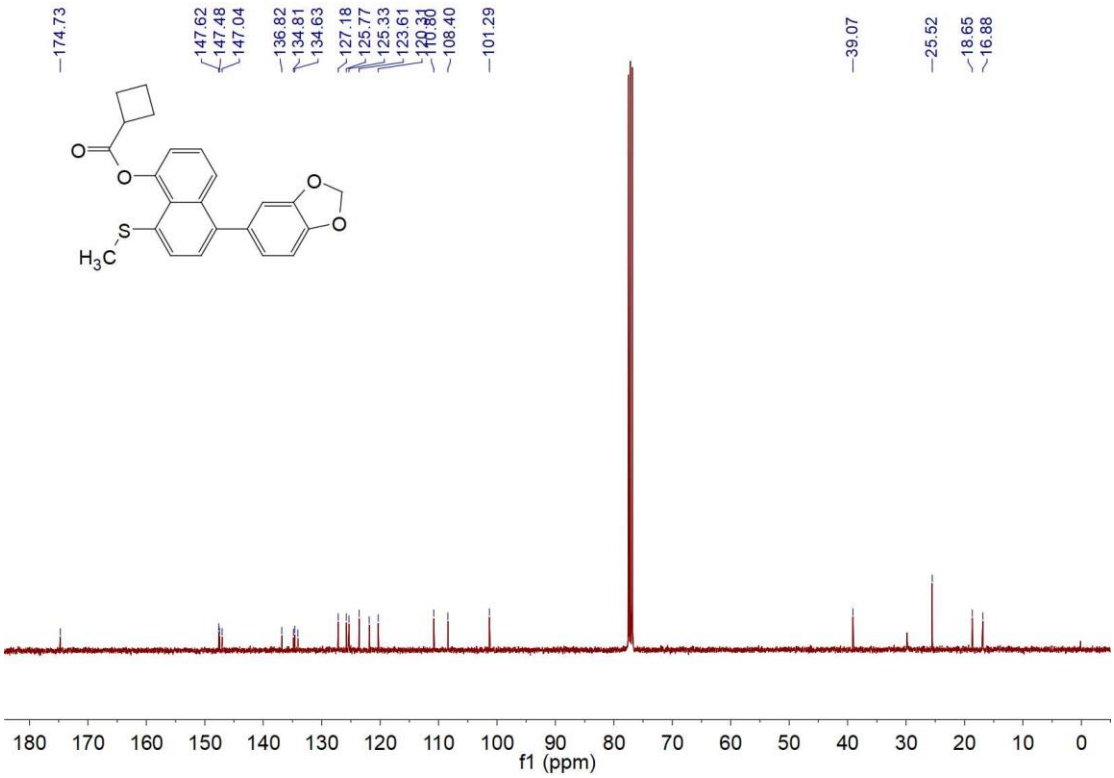
7.79
7.41
7.39
7.37
7.31
7.29
7.22
7.20
7.11
7.09
6.04
3.68
3.66
3.63
3.61
3.59
2.62
2.60
2.57
2.54
2.52
2.44
2.43
2.40
2.38
2.36
2.14
2.11
2.09
2.06
2.04
2.02
2.01
1.00
1.06
1.04
1.04
1.04
2.99
2.01
1.08
2.00
3.04
2.04
2.02
f1 (ppm)


O
O
O
O
S
H3C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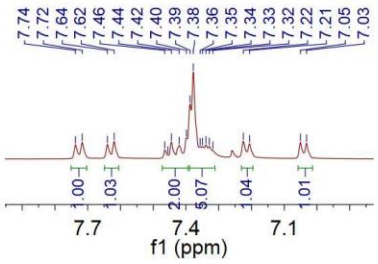
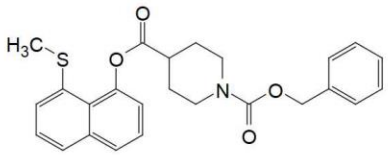
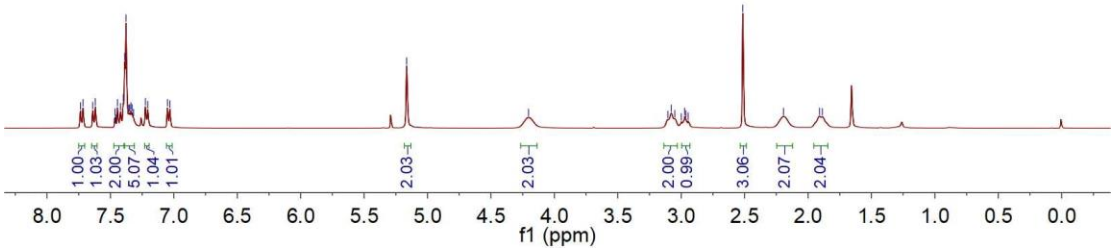
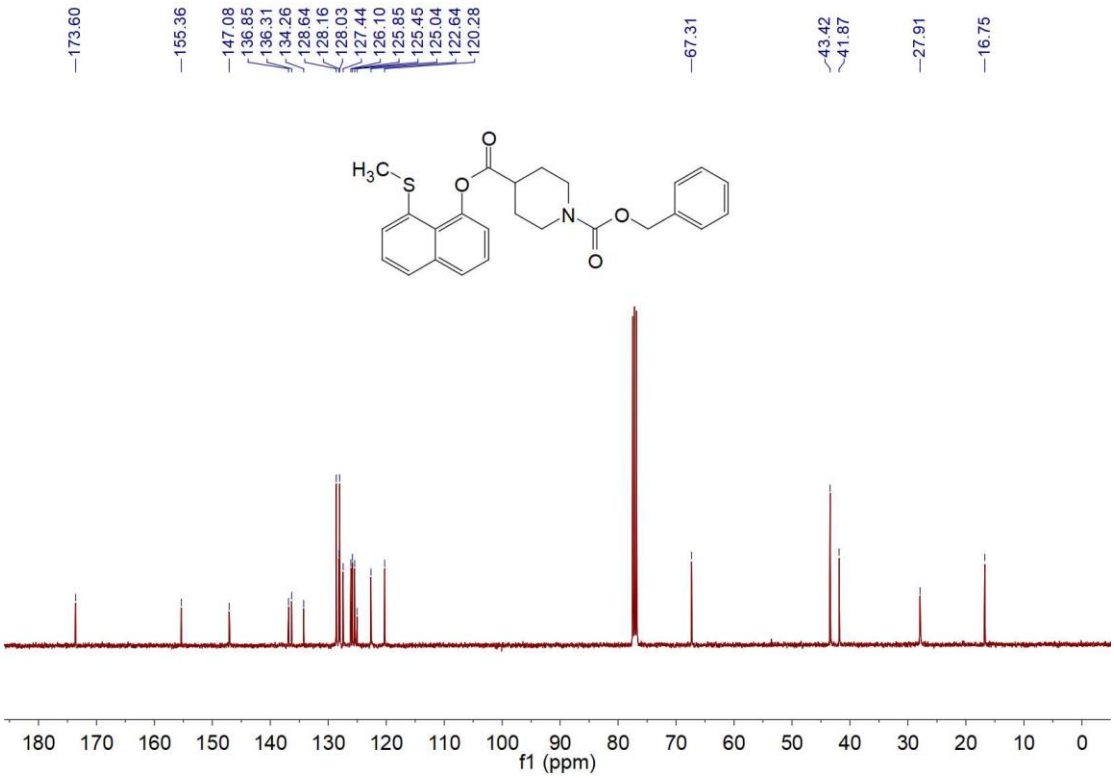
147.62
147.48
147.04
136.82
134.81
134.63
127.18
125.77
125.33
123.61
120.31
120.00
108.40
101.29
39.07
25.52
18.65
16.88
O
O
O
O
S
H3C
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.74
7.72
7.64
7.62
7.46
7.45
7.44
7.42
7.40
7.39
7.38
7.36
7.35
7.34
7.33
7.32
7.22
7.21
7.05
7.03
5.16
4.20
3.10
3.08
3.05
3.00
2.97
2.96
2.95
2.51
2.19
1.91
1.89


1.00
1.03
2.00
5.07
1.04
1.01
7.7
7.4
7.1
f1 (ppm)


H3C
S
O
O
O
N
O
O


1.00
1.03
2.00
5.07
1.04
1.01
2.03
2.03
2.00
0.99
3.06
2.07
2.04
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)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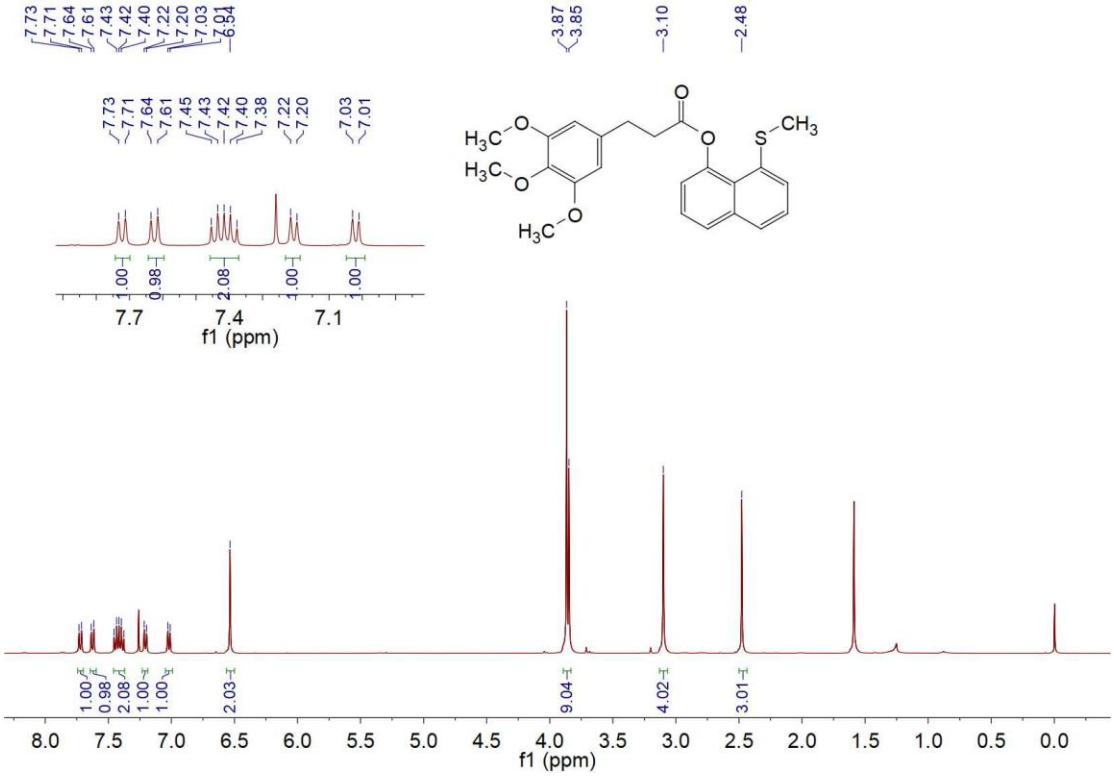
155.36
147.08
136.85
136.31
134.26
128.64
128.16
128.03
127.44
126.10
125.85
125.45
125.04
122.64
120.28
67.31
43.42
41.87
27.91
16.75
f1 (ppm)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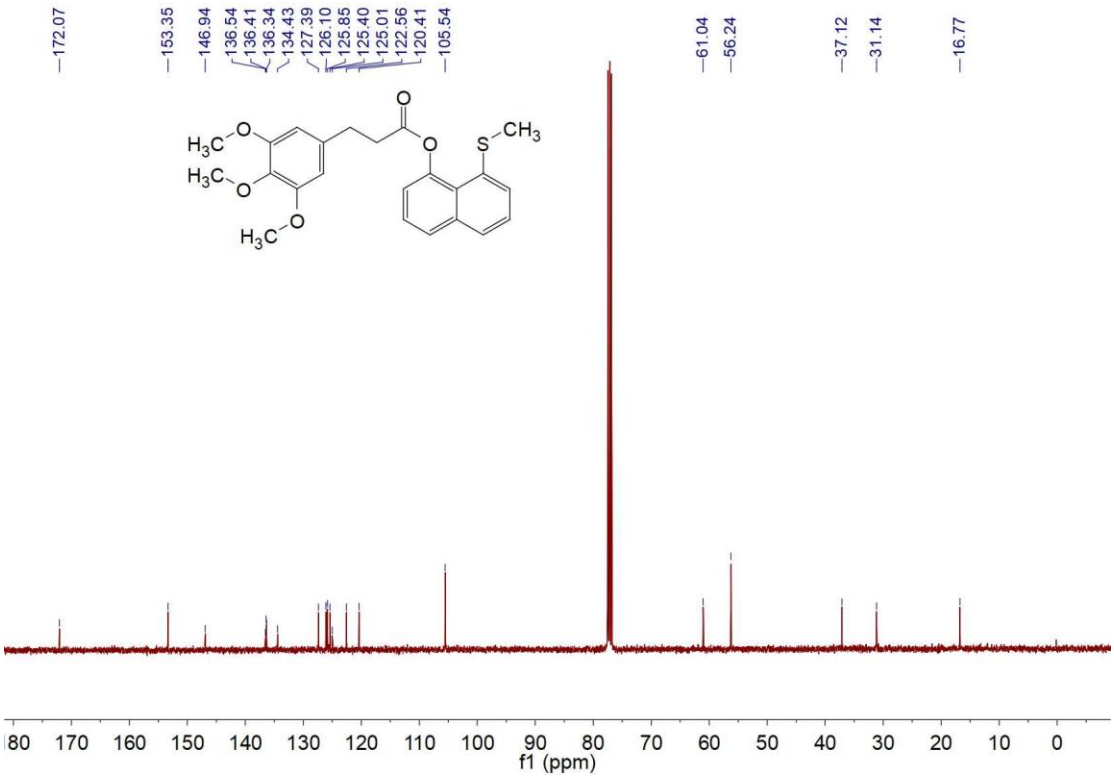
7.71
7.64
7.61
7.43
7.42
7.40
7.22
7.20
7.03
7.01
6.54
3.87
3.85
3.10
2.48
1.00
0.98
2.08
1.00
1.00
2.03
9.04
4.02
3.01
f1 (ppm)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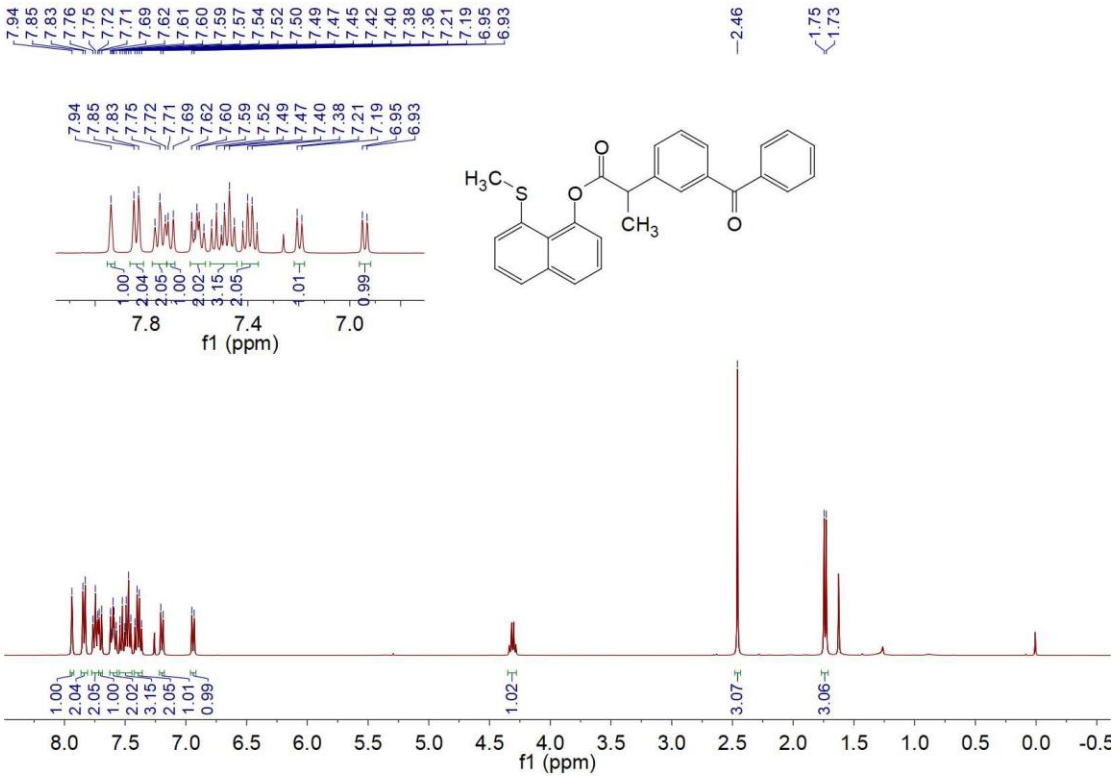
153.35
146.94
136.54
136.41
136.34
134.43
127.39
126.10
125.85
125.40
125.01
122.56
120.41
105.54
61.04
56.24
37.12
31.14
16.77
f1 (ppm)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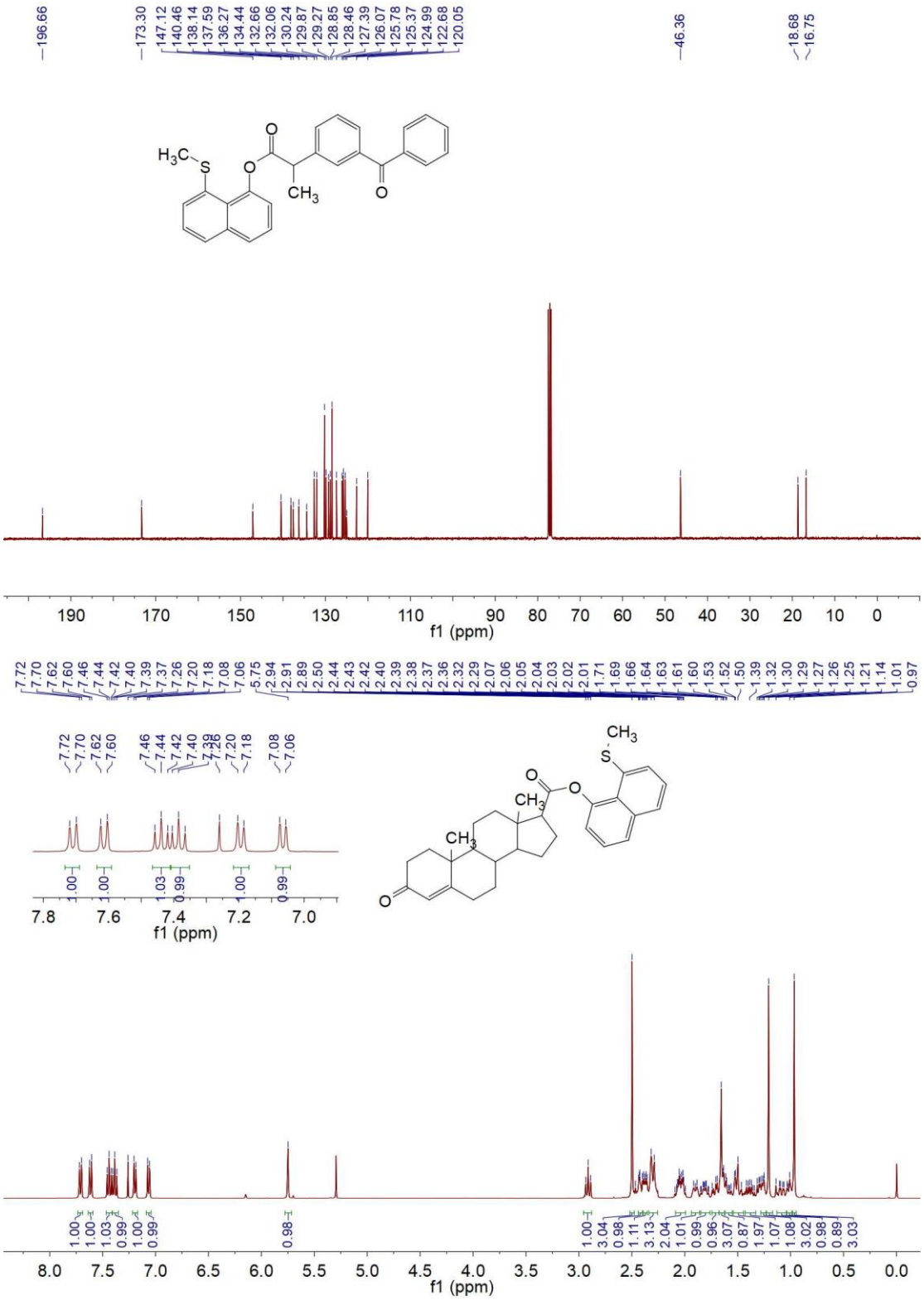
7.85
7.83
7.76
7.75
7.72
7.71
7.69
7.62
7.61
7.60
7.59
7.57
7.54
7.52
7.50
7.49
7.47
7.45
7.42
7.40
7.38
7.36
7.21
7.19
6.95
6.93
2.46
1.75
1.73
f1 (ppm)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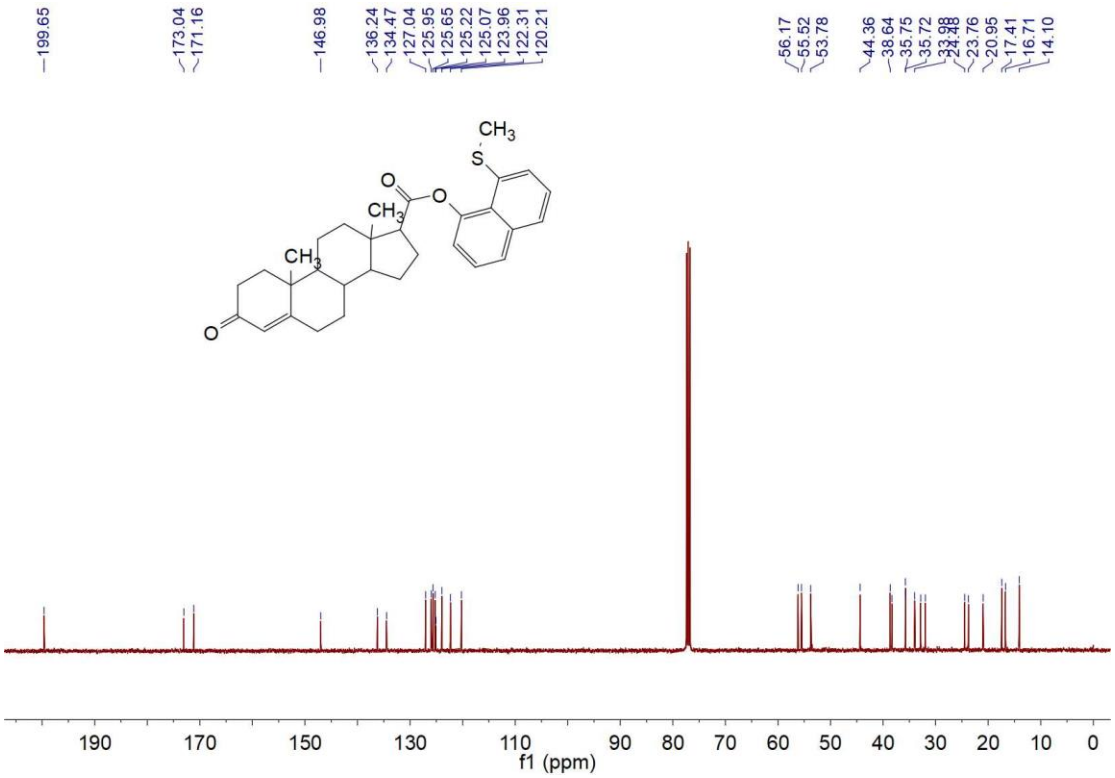
140.46
138.14
137.59
136.27
134.44
132.66
132.06
130.24
129.87
129.27
128.85
128.46
127.39
126.07
125.78
125.37
124.99
122.68
120.05
46.36
18.68
16.75
H3C
S
O
O
CH3
O
f1 (ppm)
7.72
7.70
7.62
7.60
7.46
7.44
7.42
7.40
7.39
7.37
7.26
7.20
7.18
7.08
7.06
5.75
2.94
2.91
2.89
2.50
2.44
2.43
2.42
2.40
2.39
2.38
2.37
2.36
2.32
2.29
2.07
2.06
2.05
2.04
2.03
2.02
2.01
1.71
1.69
1.66
1.64
1.63
1.61
1.60
1.53
1.52
1.50
1.39
1.32
1.30
1.29
1.27
1.26
1.25
1.21
1.14
1.01
0.97
CH3
S
O
O
CH3
CH3
O
1.00
1.00
1.03
0.99
1.00
0.99
0.98
1.00
3.04
0.98
1.11
3.13
2.04
1.01
0.99
0.96
3.07
0.87
1.97
1.07
1.08
3.02
0.98
0.89
3.03
f1 (ppm)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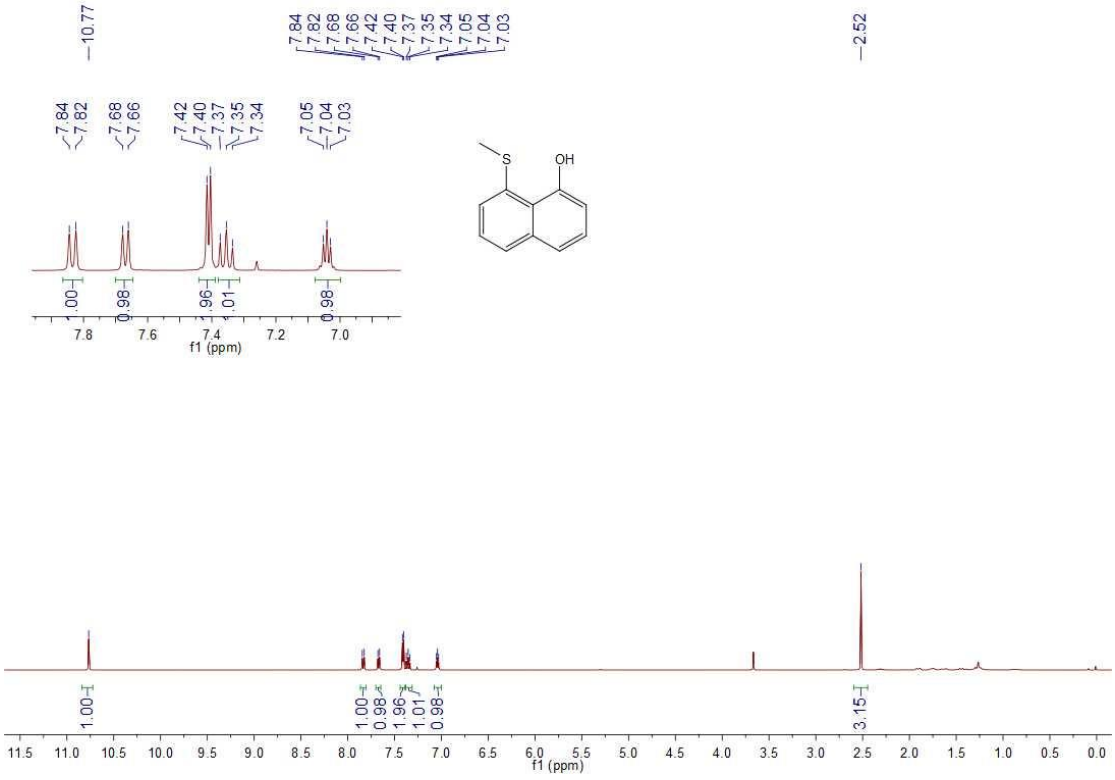
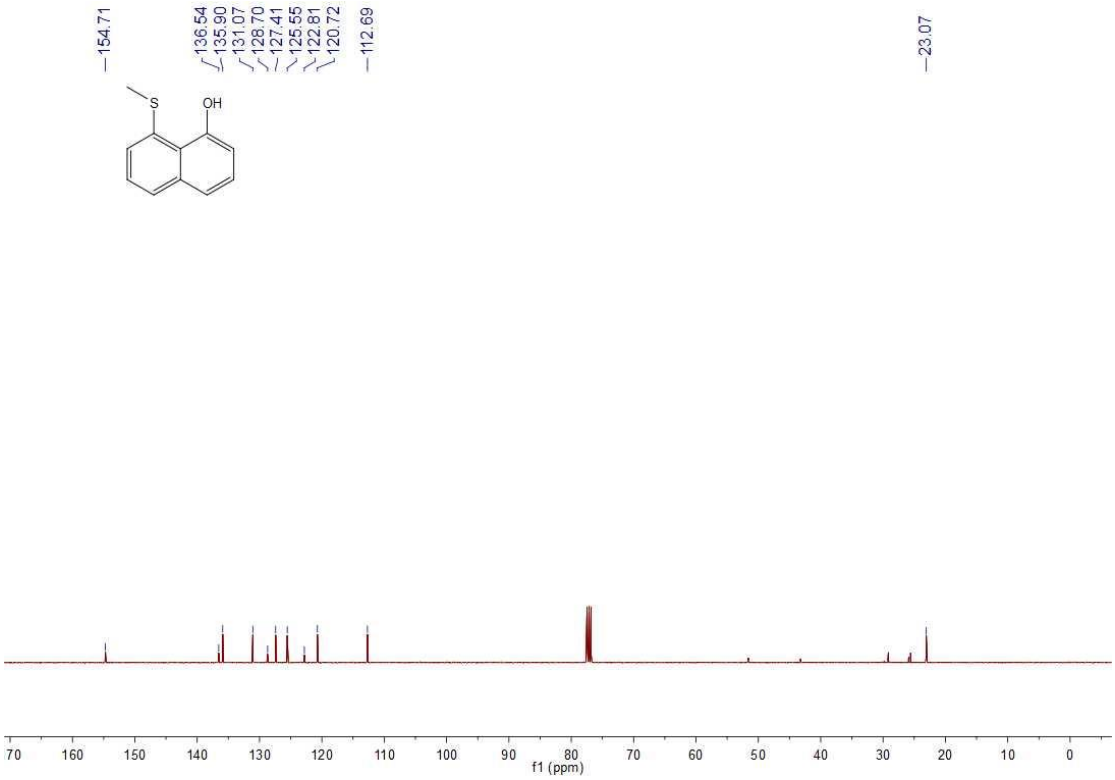
173.04
171.16
146.98
136.24
134.47
127.04
125.95
125.65
125.22
125.07
123.96
122.31
120.21
56.17
55.52
53.78
44.36
38.64
35.75
35.72
33.98
24.48
23.76
20.95
17.41
16.71
14.10
CH3
S
O
O
CH3
CH3
O
f1 (ppm)


10.77
7.84
7.82
7.68
7.66
7.42
7.40
7.37
7.35
7.34
7.05
7.04
7.03
2.52
S
OH
1.00
0.98
1.96
1.01
0.98
3.15
f1 (ppm)


154.71
136.54
135.90
131.07
128.70
127.41
125.55
122.81
120.72
112.69
23.07
S
OH
70
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

# 7. Reference

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