Supporting Information

A concise synthesis of thioaurones via NBS-induced cyclization of MOM-protected 2′-mercaptochalcone

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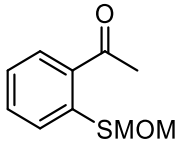
Experimental Procedures and Data

All chemicals were obtained from Sigma Aldrich, TCI, Nakalai Chemical or Fujifilm Wako chemical as reagent grade and were used as received. TLC were performed on Merck Silica gel F_{254} plates (0.25 mm). ^{1}H and ^{13}C NMR spectra were recorded on the JEOL JMN-400 or Bruker AVANCE III 600 spectrometers in $CDCl_3$ or DMSO-d_6. Chemical shifts are expressed in ppm (δ) and coupling constants (*J*) are in hertz (Hz). Standard abbreviations were us ed for defining signal multiplicities. High-resolution mass spectra were measured by SHIMAZU IRAffinity-1 instrument (FABMS) or Exactive Plus mass spectrometer (Thermo Fisher Scientific Inc.) (ESIMS).

1-(2-((Methoxymethyl)thio)phenyl)ethan-1-one (7)[1)]



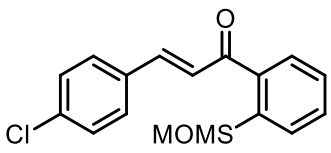
To a solution of thiosalicylic acid (1.50 g, 9.60 mmol) in anhydrous THF (48 mL) was added NaH (60% in mineral oil, 999 mg, 25.0 mmol) at 0 °C under argon atmosphere. The resulting slurry was refluxed for 30 min. After cooling to 0 °C, MeLi (3.1 M solution in Et_2O, 4.6 mL, 14.4 mmol) was added dropwise, and the resulting dark mixture was stirred at room temperature for 30 min. The reaction was quenched with H_2O, acidified with 3% HCl aq., and then extracted with AcOEt. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in vacuo. The crude 1-(2-mercaptophenyl)-ethan-1-one was dissolved in CH_2Cl_2 (50 mL), and then Et_3N (3.0 mL, 21.5 mmol) and MOMCl (0.92 mL, 11.5 mmol) were added dropwise. After stirring for 1 h, the reaction was quenched with MeOH and H_2O. The mixture was extracted with AcOEt and the combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/AcOEt = 4/1) to afford desired acetophenone **7** (1.69 g, 89%) as light brown solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.61 (s, 3H), 3.45 (s, 3H), 4.97 (s, 2H), 7.25 (td, *J* = 0.8, 7.6 Hz, 1H), 7.45 (td, *J* = 1.6, 7.6 Hz, 1H), 7.75 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.78 (dd, *J* = 0.8, 8.4 Hz, 1H).

General procedure for synthesis of chalcone (1a-p)

To a solution of acetophenone **7** (1 equiv.) and aldehyde (1.0-1.6 equiv.) in EtOH was added NaOH or LiOH・H_2O (1.5-3 equiv.) dissolved in small amount of water at 0 °C or room temperature. After completion of the reaction as indicated by TLC monitoring, water was added and the mixture was extracted with AcOEt. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in vacuo. The residue was purified by silica gel column chromatography or filtration to afford chalcone **1**.

(*E*)-3-(4-Chlorophenyl)-1-(2-((methoxymethyl)thio)phenyl)prop-2-en-1-one (1a)

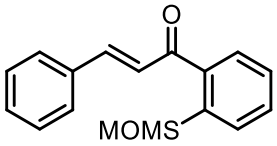


According to the general procedure, the reaction of acetophenone **7** (199 mg, 1.02 mmol) and 4-chlorobenzaldehyde (164 mg, 1.17 mmol) with NaOH (93 mg, 2.33 mmol) in EtOH (2.0 mL) gave **1a** (174 mg, 54%) as yellow oil. Reaction time: 2 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 8/1.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 3.41 (s, 3H), 4.94 (s, 2H), 7.19 (d, *J* = 16.0 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.44-7.52 (m, 4H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 56.3,

77.6, 126.1, 126.2, 128.8, 129.3, 129.7, 130.4, 131.5, 133.2, 136.6, 136.7, 139.8, 144.0, 193.7; HRESIMS : calcd for $C_{17}H_{15}O_2SClNa$ $[M+Na]^+$ 341.0379, found 341.0369.

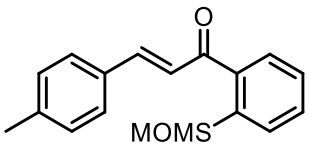
(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-phenylprop-2-en-1-one (1b)



According to the general procedure, the reaction of acetophenone **7** (106 mg, 0.510 mmol) and benzaldehyde (78 µL, 0.764 mmol) with NaOH (61 mg, 1.53 mmol) in EtOH (1.0 mL) gave **1b** (122 mg, 79%) as yellow oil. Reaction time: 15 min. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 8/1.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 3.42 (s, 3H), 4.95 (s, 2H), 7.22 (d, *J* = 16.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 1H), 7.40-7.41 (m, 3H), 7.46 (t, *J* = 8.0 Hz, 1H), 7.52-7.59 (m, 4H), 7.78 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 56.3, 77.7, 126.0, 126.2, 128.6, 128.8, 129.1, 130.7, 130.8, 131.4, 134.8, 136.6, 140.3, 145.9, 194.4; HRESIMS : calcd for $C_{17}H_{16}O_2SNa$ $[M+Na]^+$ 307.0769, found 307.0757.

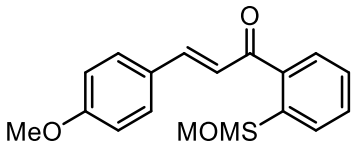
(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-(*p*-tolyl)prop-2-en-1-one (1c)



According to the general procedure, the reaction of acetophenone **7** (200 mg, 1.02 mmol) and *p*-tolualdehyde (226 mg, 1.50 mmol) with NaOH (120 mg, 3.00 mmol) in EtOH (2.0 mL) gave **1c** (240 mg, 80%) as yellow oil. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 5/1.

^{1}H NMR (600 MHz, $CDCl_3$) δ : 2.38 (s, 3H), 3.41 (s, 3H), 4.94 (s, 2H), 7.16 (d, *J* = 15.6 Hz, 1H), 7.21 (d, *J* = 7.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.43-7.51 (m, 4H), 7.56 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 21.6, 56.3, 77.7, 125.0, 126.1, 128.6, 128.7, 129.8, 130.6, 131.2, 132.0, 136.4, 140.4, 141.4, 146.1, 194.5; HRESIMS : calcd for $C_{18}H_{18}O_2SNa$ $[M+Na]^+$ 321.0925, found 321.0913.

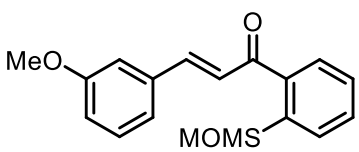
(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-(4-methoxyphenyl)prop-2-en-1-one (1d)



According to the general procedure, the reaction of acetophenone **7** (394 mg, 2.01 mmol) and *p*-anisaldehyde (0.36 mL, 3.02 mmol) with NaOH (240 mg, 6.00 mmol) in EtOH (4.0 mL) gave **1d** (602 mg, 96%) as yellow oil. Reaction time: 3 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 3.41 (s, 3H), 3.85 (s, 3H), 3.94 (s, 2H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 15.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.42-7.55 (m, 5H), 7.76 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 55.5, 56.3, 77.8, 114.6, 124.0, 126.3, 127.6, 128.7, 130.5, 130.8, 131.2, 136.3, 140.8, 146.0, 162.1, 194.7; HRESIMS : calcd for $C_{18}H_{18}O_3SNa$ $[M+Na]^+$ 337.0869, found 337.0859.

(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-(3-methoxyphenyl)prop-2-en-1-one (1e)

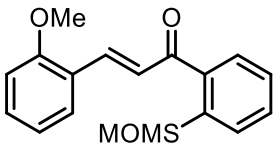


According to the general procedure, the reaction of acetophenone **7** (196 mg, 1.00 mmol) and 3-methoxybenzaldehyde (204 mg, 1.50 mmol) with NaOH (120 mg, 3.00 mmol) in EtOH (2.0 mL) gave **1e** (289 mg, 92%) as yellow oil. Reaction time: 2 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 3.41 (s, 3H), 3.84 (s, 3H), 4.94 (s, 2H), 6.96 (dd, *J* = 2.4, 8.0 Hz, 1H), 7.09 (s, 1H), 7.16-7.21 (m, 2H), 7.29-7.33 (m, 2H), 7.44-7.51 (m, 2H), 7.57 (dd, *J* = 1.6, 7.6 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H); ^{13}C NMR

(151 MHz, $CDCl_3$) δ : 55.3, 56.2, 77.6, 113.4, 116.7, 121.3, 126.17, 126.24, 128.8, 130.1, 130.6, 131.4, 136.2, 136.6, 140.2, 145.7, 160.1, 194.4; HRESIMS : calcd for $C_{18}H_{18}O_3SNa$ $[M+Na]^+$ 337.0869, found 337.0863.

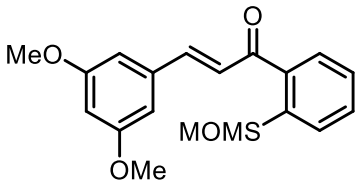
(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-(2-methoxyphenyl)prop-2-en-1-one (1f)



According to the general procedure, the reaction of acetophenone **7** (62.7 mg, 0.320 mmol) and 2-methoxybenzaldehyde (45.7 mg, 0.335 mmol) with $LiOH \cdot H_2O$ (40.2 mg, 0.959 mmol) in EtOH (1.6 mL) gave **1f** (85.7 mg, 85%) as colorless oil. Reaction time:2 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.42 (s, 3H), 3.87 (s, 3H), 4.94 (s, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.98 (t, *J* = 8.4 Hz, 1H), 7.29-7.32 (m, 2H), 7.37 (t, *J* = 8.4 Hz, 1H), 7.44 (t, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 7.8 Hz, 1H), 7.86 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ; 55.6, 56.3, 77.7, 111.3, 120.9, 123.8, 126.1, 126.5, 128.8, 129.3, 130.5, 131.1, 132.0, 136.5, 140.5, 141.4, 158.8, 194.9. HRESIMS : calcd for $C_{18}H_{18}O_3SNa$ $[M+Na]^+$ 337.0869, found 337.0867.

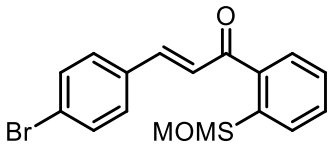
(*E*)-3-(3,5-Dimethoxyphenyl)-1-(2-((methoxymethyl)thio)phenyl)prop-2-en-1-one (1g)



According to the general procedure, the reaction of acetophenone **7** (100 mg, 0.509 mmol) and 3,5-dimethoxybenzaldehyde (128 mg, 0.771 mmol) with NaOH (61.0 mg, 1.53 mmol) in EtOH (1.0 mL) gave **1g** (149 mg, 85%) as yellow oil. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 3.41 (s, 3H), 3.81 (s, 6H), 4.94 (s, 2H), 6.51 (t, *J* = 2.4 Hz, 1H), 6.71 (d, *J* = 2.4 Hz, 2H), 7.17 (d, *J* = 16.0 Hz, 1H), 7.32 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.42-7.48 (m, 2H), 7.57 (dd, *J* = 1.6, 7.2 Hz, 1H), 7.77 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 55.4, 56.1, 77.5, 103.0, 106.4, 126.1, 126.4, 128.8, 130.6, 131.3, 136.5, 136.6, 140.1, 145.9, 161.2, 194.5; HRESIMS : calcd for $C_{19}H_{20}O_4SNa$ $[M+Na]^+$ 367.0975, found 367.0970.

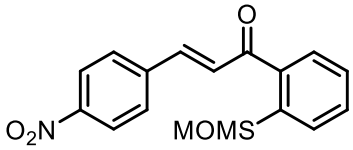
(*E*)-3-(4-Bromophenyl)-1-(2-((methoxymethyl)thio)phenyl)prop-2-en-1-one (1h)



According to the general procedure, the reaction of acetophenone **7** (100 mg, 0.510 mmol) and *p*-bromobenzaldehyde (99.0 mg, 0.535 mmol) with $LiOH \cdot H_2O$ (64.1 mg, 1.53 mmol) in EtOH (2.5 mL) gave **1h** (148 mg, 80%) as yellow oil. Reaction time:2 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.41 (s, 3H), 4.94 (s, 2H), 7.21 (d, *J* = 15.6 Hz, 1H), 7.31 (t, *J* = 8.4 Hz, 1H), 7.43-7.48 (m, 4H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.8 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ ; 56.4, 77.7, 125.1, 126.2, 126.4, 128.9, 130.0, 130.6, 131.6, 132.4, 133.7, 136.8, 140.0, 144.2, 193.9; HRESIMS : calcd for $C_{17}H_{15}O_2SBrNa$ $[M+Na]^+$ 384.9868, found 384.9868.

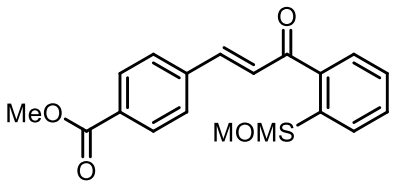
(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-(4-nitrophenyl)prop-2-en-1-one (1i)



According to the general procedure, the reaction of acetophenone **7** (98.5 mg, 0.502 mmol) and *p*-nitrobenzaldehyde (114 mg, 0.752 mmol) with NaOH (60.2 mg, 1.51 mmol) in EtOH (1.0 mL) gave **1i** (122 mg, 74%) as a yellow solid. Reaction time: 15 min. The product was collected by filtration and washed with water and Et_2O.

mp 150-151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.42 (s, 3H), 4.96 (s, 2H), 7.33-7.37 (m, 2H), 7.49 (t, *J* = 7.8 Hz, 1H), 7.58-7.63 (m, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.80 (d, *J* = 7.8 Hz, 1H), 8.26 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (151 MHz, DMSO-d_6) δ 55.8, 75.9, 123.9, 125.8, 129.0, 129.2, 129.5, 129.8, 131.9, 137.0, 138.3, 140.9, 141.5, 148.1, 192.2; HRESIMS : calcd for $C_{17}H_{15}NO_4SNa$ $[M+Na]^+$ 352.0619, found 352.0610.

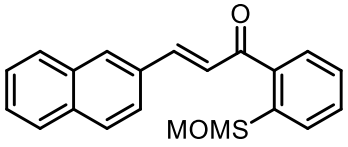
(*E*)-Methyl-4-(3-(2-((methoxymethyl)thio)phenyl)-3-oxoprop-1-en-1-yl)benzoate (1j)



According to the general procedure, the reaction of acetophenone **7** (100 mg, 0.510 mmol) and methyl 4-formylbenzoate (87.8 mg, 0.535 mmol) with LiOH・H_2O (64.1 mg, 1.53 mmol) in EtOH (2.5 mL) gave **1j** (143 mg, 82%) as a yellow solid. Reaction time: 3 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 5/1.

mp 80-81 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.41 (s, 3H), 3.93 (s, 3H), 4.95 (s, 2H), 7.29-7.34 (m, 2H), 7.47 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 16.2 Hz, 1H), 7.60 (d, *J* = 7.2 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 52.5, 56.4, 77.7, 126.2, 127.8, 128.4, 129.0, 130.3, 130.6, 131.70, 131.74, 137.0, 139.1, 139.8, 143.9, 166.6, 193.7; HRESIMS : calcd for $C_{19}H_{18}O_4SNa$ $[M+Na]^+$ 365.0818, found 365.0821.

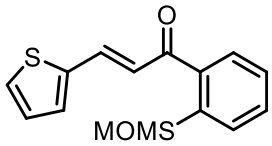
(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-(naphthalen-2-yl)prop-2-en-1-one (1k)



According to the general procedure, the reaction of acetophenone **7** (52.5 mg, 0.268 mmol) and 2-naphthaldehyde (50.1 mg, 0.321 mmol) with NaOH (32.1 mg, 0.803 mmol) in EtOH (1.3 mL) gave **1k** (54.9 mg, 79%) as a yellow solid. Reaction time: 2 h. The product was collected by filtration and washed with water and Et_2O.

mp 81-82 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 3.42 (s, 3H), 4.96 (s, 2H), 7.30-7.36 (m, 2H), 7.45-7.49 (m, 3H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.69 (s, *J* = 16.0 Hz, 1H), 7.28-7.87 (m, 5H), 7.96 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 56.3, 77.8, 123.9, 126.25, 126.30, 127.0, 127.6, 128.0, 128.8, 128.9, 129.0, 130.8, 130.9, 131.4, 132.4, 133.5, 134.6, 136.6, 140.5, 146.0, 194.5; HRESIMS : calcd for $C_{21}H_{18}O_2SNa$ $[M+Na]^+$ 357.0920, found 357.0914.

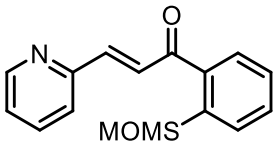
(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-(thiophen-2-yl)prop-2-en-1-one (1l)



According to the general procedure, the reaction of acetophenone **7** (72.0 mg, 0.367 mmol) and 2-thiophenecarboxaldehyde (49.2 mg, 0.440 mmol) with NaOH (46.2 mg, 1.15 mmol) in EtOH (0.7 mL) gave **1l** (94.0 mg, 76%) as maroon oil. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 5/1.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 3.35 (s, 3H), 4.88 (s, 2H), 6.95 (d, *J* = 15.6 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 7.20-7.24 (m, 2H), 7.35-7.40 (m, 2H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.60 (d, *J* = 15.6 Hz, 1H), 7.70 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 56.3, 77.7, 124.8, 126.2, 128.6, 128.8, 129.4, 130.6, 131.4, 132.2, 136.7, 138.1, 140.2, 140.3, 193.8; HRESIMS : calcd for $C_{15}H_{14}O_2S_2Na$ $[M+Na]^+$ 313.0327, found 313.0321.

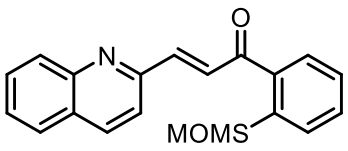
(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-(pyridin-2-yl)prop-2-en-1-one (1m)



According to the general procedure, the reaction of acetophenone **7** (108 mg, 0.546 mmol) and 2-pyridinecarboxaldehyde (78 μL, 0.819 mmol) with NaOH (65.5 mg, 1.64 mmol) in EtOH (1.0 mL) gave **1m** (109 mg, 70%) as yellow oil. Reaction time: 15 min. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 3.42 (s, 3H), 4.95 (s, 2H), 7.27-7.32 (m, 2H), 7.43-7.48 (m, 2H), 7.56 (d, *J* = 15.6 Hz, 1H), 7.68-7.79 (m, 4H), 8.66 (d, *J* = 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 56.3, 77.5, 124.6, 125.0, 126.1, 129.1, 129.4, 130.3, 131.8, 137.0, 137.5, 139.5, 143.9, 150.5, 153.5, 194.0; HRESIMS : calcd for $C_{16}H_{15}NO_2SNa$ $[M+Na]^+$ 308.0716, found 308.0709.

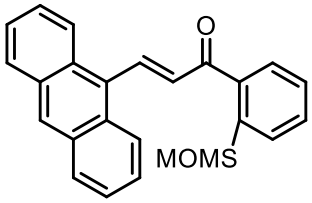
(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-(quinolin-2-yl)prop-2-en-1-one (1n)



According to the general procedure, the reaction of acetophenone **7** (50.0 mg, 0.255 mmol) and 2-quinolinecarboxaldehyde (40.0 mg, 0.255 mmol) with NaOH (16.0 mg, 0.382 mmol) in EtOH (0.5 mL) gave **1n** (60.5 mg, 71%) as a brown solid. Reaction time: 1.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 91-92 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 3.42 (s, 3H), 4.95 (s, 2H), 7.33 (dt, *J* = 1.2, 7.6 Hz, 1H), 7.47 (dt, *J* = 1.6, 8.4 Hz, 1H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.66-7.83 (m, 7H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.19 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 56.3, 77.6, 120.9, 126.2, 127.6, 127.7, 128.3, 129.2, 130.0, 130.3, 130.6, 130.7, 131.7, 137.0, 137.1, 139.7, 144.9, 148.5, 153.7, 194.5; HRESIMS : calcd for $C_{20}H_{17}NO_2SNa$ $[M+Na]^+$ 358.0878, found 358.0866.

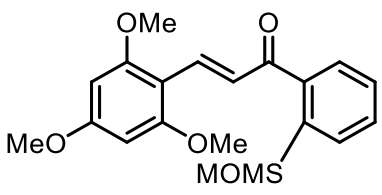
(*E*)-3-(Anthracen-9-yl)-1-(2-((methoxymethyl)thio)phenyl)prop-2-en-1-one (1o)



According to the general procedure, the reaction of acetophenone **7** (50.0 mg, 0.255 mmol) and 9-anthracenecarboxaldehyde (78.9 mg, 0.383 mmol) with NaOH (30.6 mg, 0.764 mmol) in EtOH (1.3 mL) gave **1o** (79.4 mg, 79%) as a yellow solid. Reaction time: 3 h. Eluent of SiO_2 column chromatography: $CHCl_3$.

mp 110-111 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.29 (s, 3H), 4.51 (s, 2H), 6.40 (t, *J* = 7.8 Hz, 1H), 6.80 (dt, *J* = 1.2, 7.8 Hz, 1H), 6.94 (dd, *J* = 1.2, 7.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 12.0 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 12.0 Hz, 1H) 8.08 (d, *J* = 8.4 Hz, 2H), 8.19 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 56.0, 77.9, 124.5, 125.1, 125.9, 126.0, 127.2, 128.6, 128.9, 129.0, 129.1, 130.3, 130.7, 131.0, 134.1, 136.9, 138.7, 138.8, 195.6; HRESIMS : calcd for $C_{25}H_{20}O_2SNa$ $[M+Na]^+$ 407.1082, found 407.1065.

(*E*)-1-(2-((Methoxymethyl)thio)phenyl)-3-(2,4,6-trimethoxyphenyl)prop-2-en-1-one (1p)

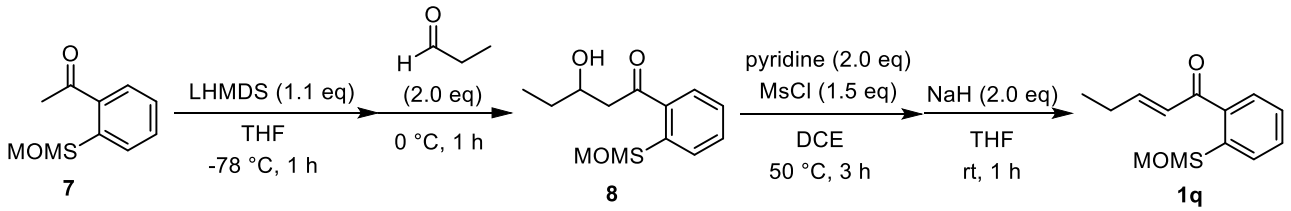


According to the general procedure, the reaction of acetophenone **7** (101 mg, 0.514 mmol) and 2,4,6-trimethoxybenzaldehyde (121 mg, 0.617 mmol) with $LiOH \cdot H_2O$ (64.7 mg, 1.54 mmol) in EtOH (2.6 mL) gave **1p** (171 mg, 89%) as a yellow solid. Reaction time: 10 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 1/1.

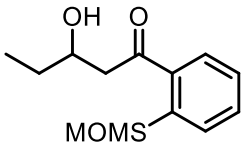
mp 114-115 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.42 (s, 3H), 3.85 (s, 9H), 4.93 (s, 2H), 6.11 (s, 2H), 7.28 (t, *J* = 7.8 Hz,

1H), 7.40 (dt, *J* = 1.2, 7.8 Hz, 1H), 7.54-7.56 (m, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 8.00 (d, *J* = 16.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 55.5, 55.9, 56.2, 77.7, 90.6, 106.5, 125.8, 125.9, 128.7, 130.4, 130.6, 136.2, 137.6, 141.4, 161.8, 163.5, 196.2; HRESIMS : calcd for $C_{20}H_{22}O_5SNa$ $[M+Na]^+$ 397.1080, found 397.1057.

Chalcone **1q** was synthesized by the following scheme.



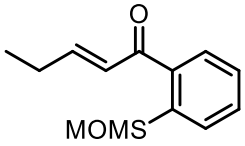
3-Hydroxy-1-(2-((methoxymethyl)thio)phenyl)pentan-1-one (8)



To a solution of acetophenone **7** (100 mg, 0.510 mmol) in THF (5.1 mL) was cool to -78 °C under argon, and then LHMDS (0.56 mL of 1.0 M solution in THF, 0.56 mmol) was added dropwise over 1 min. After stirring for 1 h at -78 °C, propionaldehyde (73 µL, 1.02 mmol) was added dropwise to the solution and the temperature was raised to 0 °C over 1 h. The reaction mixture was quenched with sat. NH_4Cl aq and then extracted with AcOEt. The organic layer was dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel chromatography (hexane/AcOEt = 2:1) to give **8** (74.0 mg, 57%) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ : 1.00 (t, *J* = 7.2 Hz, 3H) , 1.52-1.66 (m, 2H), 3.03 (dd, *J* = 9.0, 17.4 Hz, 1H), 3.13-3.16 (m, 2H), 3.45 (s, 3H), 4.13-4.19 (m, 1H), 4.97 (d, *J* = 2.4 Hz, 1H), 7.26 (t, *J* = 8.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 10.0, 29.5, 46.9, 56.4, 69.4, 76.4, 125.3, 128.7, 129.7, 132.6, 136.7, 139.2, 203.0; HRESIMS : calcd for $C_{13}H_{18}O_3SNa$ $[M+Na]^+$ 277.0869, found277.0866.

(*E*)-1-(2-((Methoxymethyl)thio)phenyl)pent-2-en-1-one (1q)



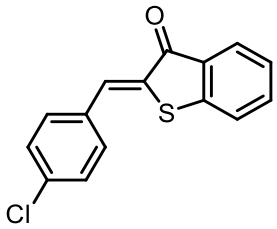
To a solution of **8** (17.6 mg, 0.0691 mmol) and pyridine (27 µL, 0.346 mmol) in DCE (1.2 mL) was added MsCl (24 µL, 0.208 mmol). After stirring for 7 h at 80 °C, the reaction mixture was quenched with sat. NH_4Cl and then extracted with AcOEt. The organic layer was dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel chromatography ($CHCl_3$) to give **1q** (7.6 mg, 46%) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ : 1.10 (t, *J* = 7.2 Hz, 3H), 2.31 (quin, *J* = 7.2 Hz, 2H), 3.42 (s, 3H), 4.92 (s, 2H), 6.55 (d, *J* = 15.6 Hz, 1H), 6.83 (1H, dt, *J* = 6.6, 15.6 Hz), 7.25-7.28 (m, 1H), 7.41 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 7.8 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 12.3, 26.0, 56.3, 77.7, 126.0, 128.7, 129.0, 130.5, 131.1, 136.4, 140.1, 153.1, 194.9; HRESIMS : calcd for $C_{13}H_{16}O_2SNa$ $[M+Na]^+$ 259.0763, found259.0748.

General procedure for synthesis of thioaurones (2a-q)

To a solution of chalcone **1** (1 equiv.) and pyridine (1.5 equiv.) in DCE (0.1 M) were added NBS (1.5 equiv.) at room temperature. After completion of the reaction as indicated by TLC monitoring, the reaction was quenched with H_2O and the mixture was extracted with AcOEt. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in vacuo. The residue was purified by silica gel column chromatography to afford thioaurones **2**.

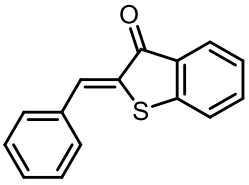
(*Z*)-2-(4-Chlorobenzylidene)benzo[*b*]thiophen-3(2*H*)-one (2a)[2)]



According to the general procedure, the reaction of chalcone **1a** (18.4 mg, 0.058 mmol) with pyridine (8 µL, 0.087 mmol) and NBS (15.5 mg, 0.087 mmol) in DCE (0.6 mL) gave **2a** (15.8 mg, 99%) as yellow solid. Reaction time: 1.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 173-174 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 7.32 (t, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 7.8 Hz, 1H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.90 (s, 1H), 7.92 (d, *J* = 7.8 Hz, 1H).

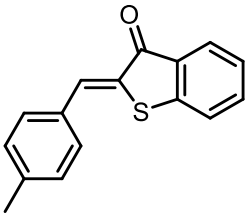
(*Z*)-2-Benzylidenebenzo[*b*]thiophen-3(2*H*)-one (2b)[2)]



According to the general procedure, the reaction of chalcone **1b** (11.0 mg, 0.039 mmol) with pyridine (5 µL, 0.058 mmol) and NBS (10.3 mg, 0.058 mmol) in DCE (0.4 mL) gave **2b** (8.6 mg, 93%) as yellow solid. Reaction time: 30 min. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 125-126 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 7.31 (t, *J* = 7.8 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.48-7.52 (m, 3H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 2H), 7.95 (d, *J* = 7.8 Hz, 1H), 7.98 (s, 1H).

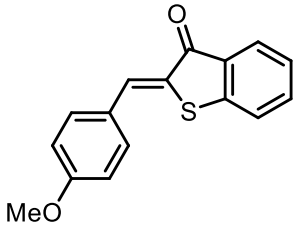
(*Z*)-2-(4-Methylbenzylidene)benzo[*b*]thiophen-3(2*H*)-one (2c) [3)]



According to the general procedure, the reaction of chalcone **1c** (237.6 mg, 0.796 mmol) with pyridine (96 µL, 1.194 mmol) and NBS (212.5 mg, 1.194 mmol) in DCE (8.0 mL) gave **2c** (188.6 mg, 94%) as yellow solid. Reaction time: 1.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 164-165 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 2.42 (s, 3H), 7.29-7.32 (m, 3H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.94-7.96 (m, 2H).

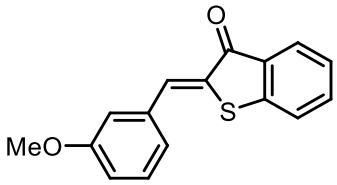
(*Z*)-2-(4-Methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one (2d)[3)]



According to the general procedure, the reaction of chalcone **1d** (22.0 mg, 0.070 mmol) with pyridine (9 µL, 0.105 mmol) and NBS (12.5 mg, 0.070 mmol) in DCE (0.7 mL) gave **2d** (16.1 mg, 86%) as yellow solid. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 3.88 (s, 3H), 7.02 (d, *J* = 8.8 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.51 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.2 Hz, 1H), 7.69 (d, *J* = 8.8 Hz, 2H), 7,94-7.95 (m, 2H).

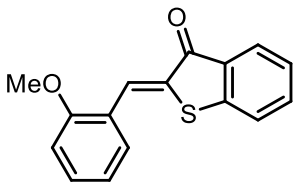
(*Z*)-2-(3-Methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one (2e)



According to the general procedure, the reaction of chalcone **1e** (20.0 mg, 0.064 mmol) with pyridine (8 μL, 0.095 mmol) and NBS (11.3 mg, 0.095 mmol) in DCE (0.6 mL) gave **2e** (15.9 mg, 93%) as yellow solid. Reaction time: 30 min. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 95-96 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.89 (s, 3H), 6.98 (dd, *J* = 2.4 Hz, 7.8 Hz, 1H), 7.25 (s, 1H), 7.30-7.32 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.94-7.95 (m, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 55.5, 115.7, 116.6, 123.9, 124.1, 125.9, 127.3, 130.2, 130.7, 130.8, 133.7, 135.5, 135.8, 146.3, 160.2, 188.9; HRESIMS : calcd for $C_{16}H_{12}O_2SNa$ $[M+Na]^+$ 291.0456, found 291.0448.

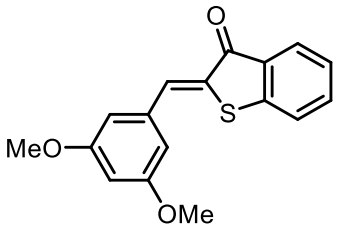
(*Z*)-2-(2-Methoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one (2f)



According to the general procedure, the reaction of chalcone **1f** (15.8 mg, 0.050 mmol) with pyridine (6 μL, 0.075 mmol) and NBS (9.0 mg, 0.050 mmol) in DCE (1.0 mL) gave **2f** (12.3 mg, 91%) as a yellow solid. Reaction time: 1.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 178-179 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.92 (s, 3H), 6.95 (d, *J* = 8.4 Hz, 1H), 7.07 (t, *J* = 7.8 Hz, 1H), 7.29 (t, *J* = 8.4 Hz, 1H), 7.40 (dt, *J* = 1.2, 8.4 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.57 (dt, *J* = 1.8, 8.4 Hz, 1H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 7.8 Hz, 1H), 8.44 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 55.8, 111.1, 120.9, 123.7, 124.0, 125.6, 127.2, 128.7, 130.0, 130.3, 131.0, 132.0, 135.2, 146.4, 159.3, 188.7; HRESIMS : calcd for $C_{16}H_{12}O_2SNa$ $[M+Na]^+$ 291.0450, found 291.0449.

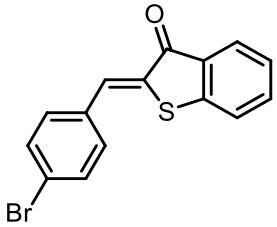
(*Z*)-2-(3,5-Dimethoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one (2g)[4)]



According to the general procedure, the reaction of chalcone **1g** (15.8 mg, 0.046 mmol) with pyridine (6 μL, 0.069 mmol) and NBS (8.2 mg, 0.069 mmol) in DCE (0.5 mL) gave **2g** (12.4 mg, 91%) as a yellow solid. Reaction time: 30 min. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 180-181 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.87 (s, 6H), 6.54 (s, 1H), 6.87 (2H, d, *J* = 1.8 Hz, 2H), 7.31 (t, *J* = 7.2 Hz, 1H), 7.50 (d, *J* = 7.8 Hz, 1H), 7.59 (t, *J* = 7.8 Hz, 1H), 7.89 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H).

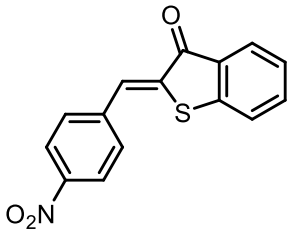
(*Z*)-2-(4-Bromobenzylidene)benzo[*b*]thiophen-3(2*H*)-one (2h)[4)]



According to the general procedure, the reaction of chalcone **1h** (18.9 mg, 0.0503 mmol) with pyridine (7 μL, 0.0800 mmol) and NBS (14.2 mg, 0.08 mmol) in DCE (1.0 mL) gave **2h** (14.3 mg, 90.0%) as a yellow solid. Reaction time: 2 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 155-156 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 7.32 (t, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.56-7.63 (m, 5H), 7.88 (s, 1H), 7.95 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 124.1, 124.7, 126.0, 127.3, 130.4, 131.1, 132.2, 132.4, 132.5, 133.4, 135.6, 145.9, 188.7; HRESIMS : calcd for $C_{15}H_{10}OSBr$ $[M+H]^+$ 316.9630, found 316.9610.

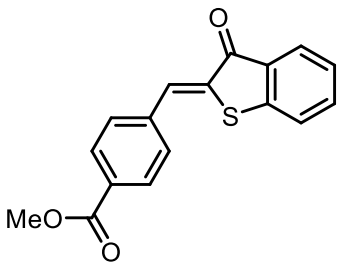
(*EZ*)-2-(4-Nitrobenzylidene)benzo[*b*]thiophen-3(2*H*)-one (2i)[2)]



According to the general procedure, the reaction of chalcone **1i** (19.2 mg, 0.058 mmol) with pyridine (7 μL, 0.087 mmol) and NBS (15.6 mg, 0.087 mmol) in DCE (1.2 mL) gave **2i** (12.8 mg, 78%) as red solid. Reaction time: 24 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1. The pure *Z* isomer was obtained by recrystallization from Hexane/AcOEt.

mp decomposed; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 7.35 (t, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.8 Hz, 1H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.94 (s, 1H), 7.96 (d, *J* = 7.8 Hz, 1H), 8.33 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 124.3, 124.4, 126.4, 127.6, 129.9, 130.0, 131.4, 134.5, 136.1, 140.7, 145.6, 147.8, 188.5.

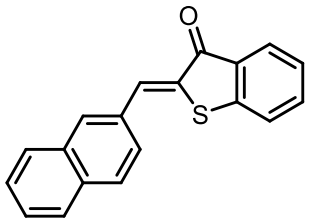
(*EZ*)-Methyl-4-((3-oxobenzo[*b*]thiophen-2(3*H*)-ylidene)methyl)benzoate (2j)



According to the general procedure, the reaction of chalcone **1j** (34.2 mg, 0.100 mmol) with pyridine (12 μL, 0.150 mmol) and NBS (26.7 mg, 0.150 mmol) in DCE (1.0 mL) gave **2j** (29.4 mg, 99%, *E*/*Z* = 17:83) as yellow solid. Reaction time: 6 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1. he pure *Z* isomer was obtained by recrystallization from Hexane/AcOEt.

mp 84-85 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.95 (s, 3H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.94-7.96 (m, 2H), 8.13 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 52.5, 124.1, 126.1, 127.4, 130.27, 130.28, 130.8, 131.0, 131.9, 132.7, 135.8, 138.7, 146.0, 166.5, 188.7; HRESIMS : calcd for $C_{17}H_{12}O_3SNa$ $[M+Na]^+$ 319.0399, found 319.0373.

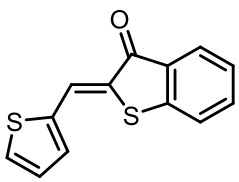
(*Z*)-2-(Naphthalen-2-ylmethylene)benzo[*b*]thiophen-3(2*H*)-one (2k)[2)]



According to the general procedure, the reaction of chalcone **1k** (20.8 mg, 0.0622 mmol) with NBS (13.3 mg, 0.0746 mmol) in DCE (0.6 mL) gave **2k** (18.3 mg, 99%, *E*/*Z* = 27:73) as red solid. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 202-203 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.33 (t, *J* = 7.6 Hz, 1H), 7.54-7.63 (m, 4H), 7.80-7.99 (m, 5H), 8.14 (s, 1H), 8.22 (s, 1H).

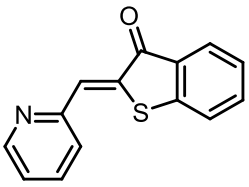
(*Z*)-2-(Thiophen-2-ylmethylene)benzo[*b*]thiophen-3(2*H*)-one (2l)[2)]



According to the general procedure, the reaction of chalcone **1l** (20.5 mg, 0.071 mmol) with pyridine (9 μL, 0.106 mmol) and NBS (18.8 mg, 0.106 mmol) in DCE (0.7 mL) gave **2l** (17.1 mg, 98%) as a yellow solid. Reaction time: 1.5 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 130-131 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 7.20 (t, *J* = 4.2 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.51-7.53 (m, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.66 (d, *J* = 4.8 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 1H), 8.15 (s, 1H).

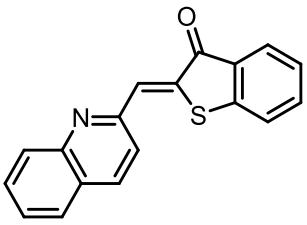
(*Z*)-2-(Pyridin-2-ylmethylene)benzo[*b*]thiophen-3(2*H*)-one (2m)[4)]



According to the general procedure, the reaction of chalcone **1m** (23.7 mg, 0.083 mmol) with pyridine (10 μL, 0.125 mmol) and NBS (22.2 mg, 0.125 mmol) in DCE (0.8 mL) gave **2m** (15.9 mg, 80%) as yellow solid. Reaction time: 2 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.24-7.28 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.54-7.58 (m, 2H), 7.75 (dt, *J* = 2.0, 8.0 Hz, 1H), 7.87 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 8.79 (d, *J* = 4.4 Hz, 1H).

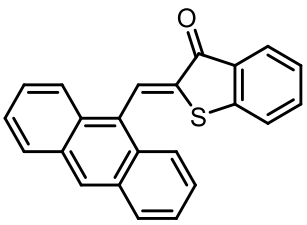
(*Z*)-2-(Quinolin-2-ylmethylene)benzo[*b*]thiophen-3(2*H*)-one (2n)



According to the general procedure, the reaction of chalcone **1n** (22.8 mg, 0.0680 mmol) with NBS (12.2 mg, 0.0685 mmol) in DCE (0.7 mL) gave **2n** (19.6 mg, 99%) as a yellowish brown solid. Reaction time: 2 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 199-200 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ : 7.27 (t, *J* = 7.2 Hz, 1H), 7.54-7.62 (m, 4H), 7.75-7.82 (m, 2H), 7.93 (d, *J* = 7.2 Hz, 1H), 7.99 (s, 1H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ : 124.3, 124.5, 125.7, 127.0, 127.5, 127.7, 127.8, 129.1, 129.7, 130.3, 130.6, 135.7, 136.7, 136.8, 148.4, 150.4, 153.2, 189.9; HRESIMS : calcd for $C_{18}H_{12}NOS$ $[M+H]^+$ 290.0634, found 290.0627.

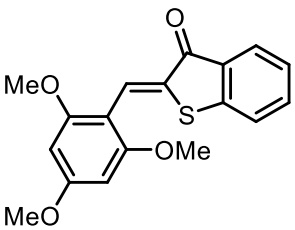
(*Z*)-2-(Anthracen-9-ylmethylene)benzo[*b*]thiophen-3(2*H*)-one (2o)[2)]



According to the general procedure, the reaction of chalcone **1o** (16.4 mg, 0.042 mmol) with pyridine (5 μL, 0.0624 mmol) and NBS (11.1 mg, 0.0624 mmol) in DCE (0.4 mL) gave **2o** (11.8 mg, 84%) as a red solid. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1.

mp 180-181 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 7.30 (t, *J* = 8.4 Hz, 1H), 7.52-7.53 (m, 5H), 8.01 (d, *J* = 8.4 Hz, 1H), 8.06-8.09 (m, 5H), 8.54 (s, 1H), 8.87 (s, 1H).

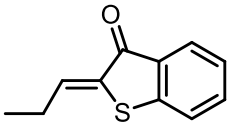
(*Z*)-2-(2,4,6-Trimethoxybenzylidene)benzo[*b*]thiophen-3(2*H*)-one (2p)[2)]



According to the general procedure, the reaction of chalcone **1p** (31.1 mg, 0.083 mmol) with pyridine (10 μL, 0.125 mmol) and NBS (22.2 mg, 0.125 mmol) in DCE (1.7 mL) at 80 °C for 24 h gave **2p** (13.7 mg, 50%) as brown solid. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 2/1.

mp 80-81 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.87 (s, 3H), 3.91 (s, 6H), 6.14 (s, 2H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.2 Hz, 1H), 8.30 (s, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 55.59, 55.62, 90.5, 105.9, 123.3, 124.7, 126.6, 128.1, 130.7, 131.6, 134.7, 147.0, 160.4, 164.1, 189.2; HRESIMS : calcd for $C_{18}H_{16}O_4SNa$ $[M+Na]^+$ 351.0662, found 351.0663.

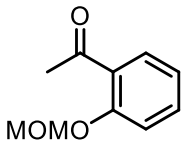
(*Z*)-2-Propylidenebenzo[*b*]thiophen-3(2*H*)-one (2q)



According to the general procedure, the reaction of **1q** (16.3 mg, 0.069 mmol) with pyridine (8 µL, 0.103 mmol) and NBS (18.3 mg, 0.103 mmol) in DCE (1.4 mL) gave **2q** (11.6 mg, 88%) as colorless oil. Reaction time: 24 h. Eluent of SiO_2 column chromatography: $CHCl_3$.

^{1}H NMR (600 MHz, $CDCl_3$) δ : 1.20 (t, *J* = 7.8 Hz, 3H), 2.40 (quin, *J* = 7.8 Hz, 2H), 7.15 (t, *J* = 7.8 Hz ,1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.8 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 12.8, 25.4, 124.2, 125.3, 127.1, 131.9, 133.7, 135.4, 139.9, 146.3, 187.8; HRESIMS : calcd for $C_{11}H_{11}OS$ $[M+H]^+$ 191.0525, found 191.0516.

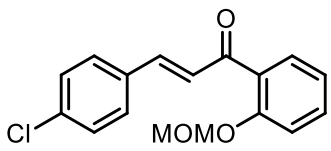
1-(2-(Methoxymethoxy)phenyl)ethan-1-one (9)[5)]



To a solution of 1-(2-hydroxyphenyl)ethan-1-one (0.36 mL, 3.0 mmol) in DCE (10 mL) was added *N*-ethyl-*N*-isopropylpropan-2-amine (1.1 mL, 6.0 mmol) chloromethyl methyl ether (0.29 mL, 3.9 mmol) was added dropwise at 0 °C to room temperature. After stirring for 5 h at room temperature, the reaction mixture was quenched with methanol and extracted with AcOEt. The organic layer was dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/AcOEt = 10/1) to afford desired acetophenone **9** (407 mg, 75%) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ : 2.64 (s, 3H), 3.52 (s, 3H), 5.28 (s, 2H), 7.05 (t, *J* = 8.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.43 (dt, *J* = 1.8, 8.4 Hz, 1H), 7.71 (dd, *J* = 1.8, 7.2 Hz, 1H).

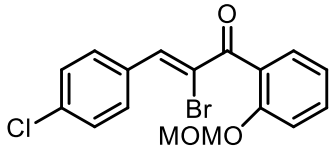
(*E*)-3-(4-Chlorophenyl)-1-(2-(methoxymethoxy)phenyl)prop-2-en-1-one (3)



To a solution of 4-chlorobenzaldehyde (94.2mg, 0.67mmol) and acetophenone **9** (100 mg, 0.56 mmol) in EtOH (2.8 mL) was added NaOH (66.6 mg, 1.67 mmol) at room temperature. After stirring for 4 h, the reaction was quenched with H_2O and the mixture was extracted with AcOEt. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/AcOEt = 4/1) to afford **3** (149 mg, 88%) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.47 (s, 3H), 5.24 (s, 2H), 7.10 (t, *J* = 8.4 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.33 (t, *J* = 16.2 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.46 (dt, *J* = 1.8, 8.4 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 16.2 Hz, 1H), 7.59 (dd, *J* = 1.8, 7.2 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 56.6, 95.0, 115.4, 122.2, 127.6, 129.4, 129.6, 130.2, 130.3, 132.9, 133.7, 136.3, 142.1, 155.7, 193.0; HRESIMS : calcd for $C_{17}H_{16}O_3Cl$ $[M+H]^+$ 303.0782, found 303.0764.

(*Z*)-2-Bromo-3-(4-chlorophenyl)-1-(2-(methoxymethoxy)phenyl)prop-2-en-1-one (4)

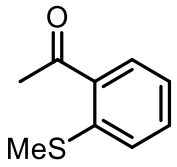


According to the general procedure, the reaction of chalcone **3** (25.8 mg, 0.085 mmol) with pyridine (10 µL, 0.128 mmol) and NBS (22.7 mg, 0.128 mmol) in DCE (0.9 mL) for 24 h gave **4** (18.9 mg, 72%) as a brown solid. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 150-151 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 3.39 (s, 3H), 5.16 (s, 2H), 7.10 (t, *J* = 7.2 Hz, 1H), 7.21 (d, *J* = 8.4 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.69 (s, 1H), 7.79 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR

(151 MHz, $CDCl_3$) δ : 56.5, 94.9, 115.3, 122.0, 125.6, 128.6, 128.9, 129.3, 131.8, 132.31, 132.34, 136.7, 142.4, 154.7, 191.1; HRESIMS : calcd for $C_{17}H_{14}O_3BrClNa$ $[M+Na]^+$ 402.9707, found 402.9703.

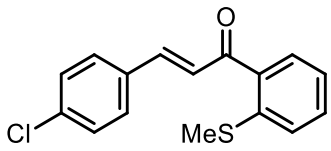
1-(2-(Methylthio)phenyl)ethan-1-one (10)[6)]



To a solution of thiosalicylic acid (708 mg, 4.55 mmol) and K_2CO_3 (1.92 g, 13.6 mmol) in acetone (23 mL) was added MeI (0.31 mL, 5.0 mmol). The mixture was stirred at room temperature for 4.5 h and then concentrated in vacuo. The residue was dissolved in H_2O and acidified by addition of aq. HCl at 0 °C. The precipitate was collected by filtration and washed with H_2O and EtOH. The residue was dissolved in AcOEt and washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in vacuo to give 2-(methylthio)benzoic acid (714 mg, 93%) as a white solid. To the solution of 2-(methylthio)benzoic acid in dry THF (20 mL) was added MeLi (2.5 mL of 3.1 M solution in Et_2O, 7.75 mmol) dropwise at 0 °C. After stirring for 0.5 h, the reaction was quenched with aq. NH_4Cl and the mixture was extracted with AcOEt. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in vacuo to afford acetophenone **10** (531 mg, 86%) as colorless solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ : 2.43 (s, 3H), 2.62 (s, 3H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.48 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.83 (dd, *J* = 1.6, 7.6 Hz, 1H).

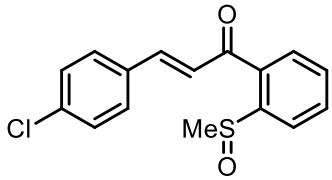
***(E)*-3-(4-Chlorophenyl)-1-(2-(methylthio)phenyl)prop-2-en-1-one (5)[7)]**



To a solution of 4-chlorobenzaldehyde (42.7, 0.30 mmol) and acetophenone **10** (48.1 mg, 0.28 mmol) in EtOH (1.4 mL) was added $LiOH\cdot H_2O$ (36.4 mg, 0.87 mmol) at room temperature. After stirring for 5 h, the reaction was quenched with H_2O and the mixture was extracted with AcOEt. The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4 and then concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/AcOEt = 4/1) to afford chalcone **5** (36.8 mg, 44%) as yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ : 2.47 (s, 3H), 7.24 (t, *J* = 8.4 Hz, 1H), 7.29 (d, *J* = 16.2 Hz, 2H), 7.37-7.39 (m, 3H), 7.48 (dt, *J* = 1.2 Hz, 8.4 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 2H), 7.58 (d, *J* = 16.2 Hz, 1H), 7.69 (dd, *J* = 1.8 Hz, 7.8 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 16.6, 124.3, 125.3, 126.4, 129.4, 129.6, 129.7, 131.8, 133.5, 136.6, 137.2, 140.8, 143.7, 192.7.

(*E*)-3-(4-Chlorophenyl)-1-(2-(methylsulfinyl)phenyl)prop-2-en-1-one (6)



According to the general procedure, the reaction of chalcone **5** (15.4 mg, 0.053 mmol) with pyridine (7 μL, 0.080 mmol) and NBS (14.2 mg, 0.080 mmol) in DCE (0.5 mL) gave **6** (12.9 mg, 79%) as a yellow solid. Reaction time: 1 h. Eluent of SiO_2 column chromatography: Hexane/AcOEt = 4/1.

mp 142-143 °C; ^{1}H NMR (600 MHz, $CDCl_3$) δ : 2.93 (s, 3H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 15.6 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.66 (t, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 15.6 Hz, 1H), 7.87 (t, *J* = 7.8 Hz, 1H), 8.03 (d, *J* = 7.8 Hz, 1H), 8.44 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) δ : 44.9, 121.9, 125.0, 129.4, 129.6, 129.9, 130.3, 133.0, 134.0, 134.8, 137.3, 145.3, 150.9, 189.7; HRESIMS : calcd for $C_{16}H_{13}O_2SClNa$ $[M+Na]^+$ 327.0217, found 327.0214.

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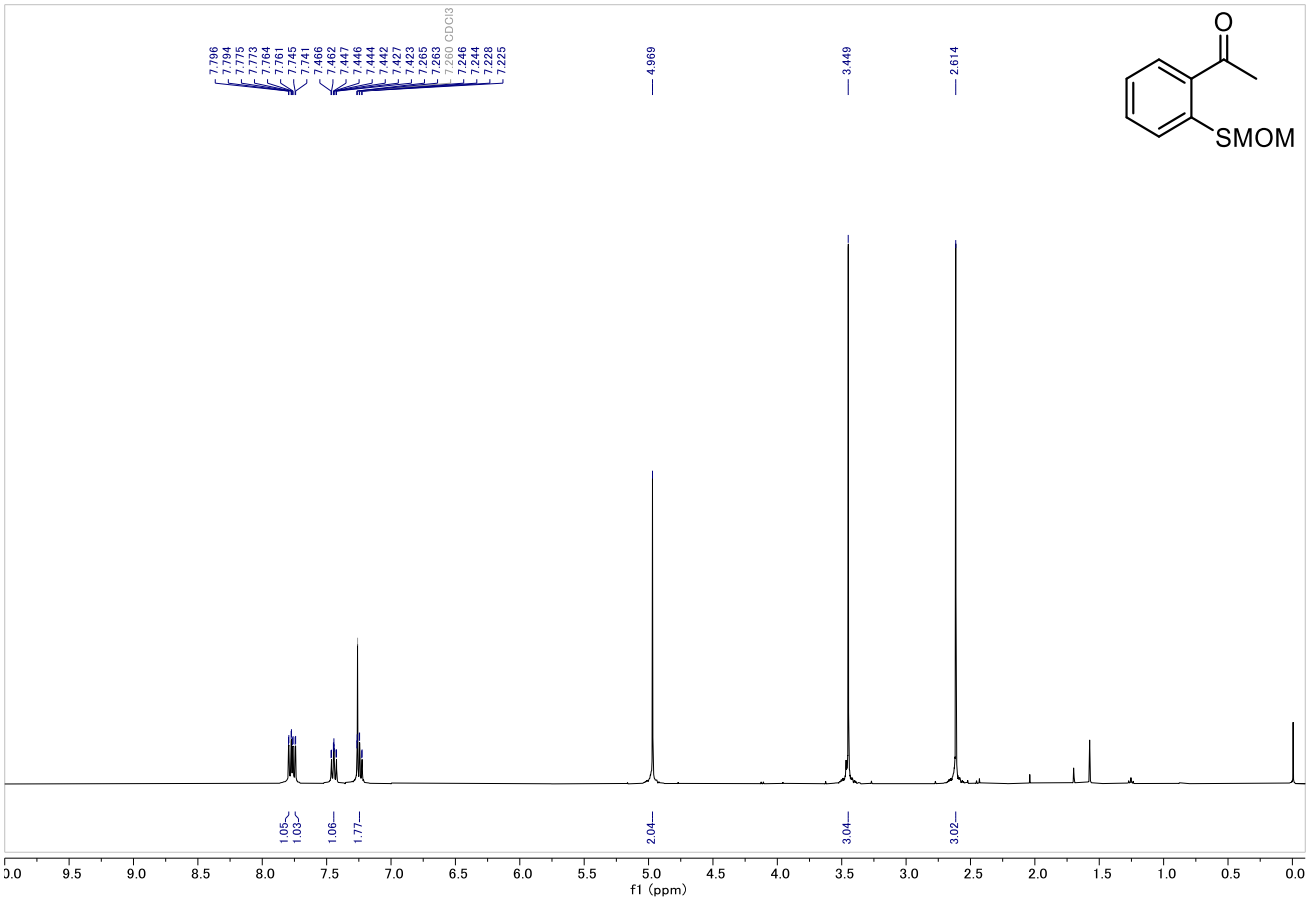
^{1}H NMR **7**


7.796
7.794
7.775
7.773
7.764
7.761
7.745
7.741
7.466
7.462
7.447
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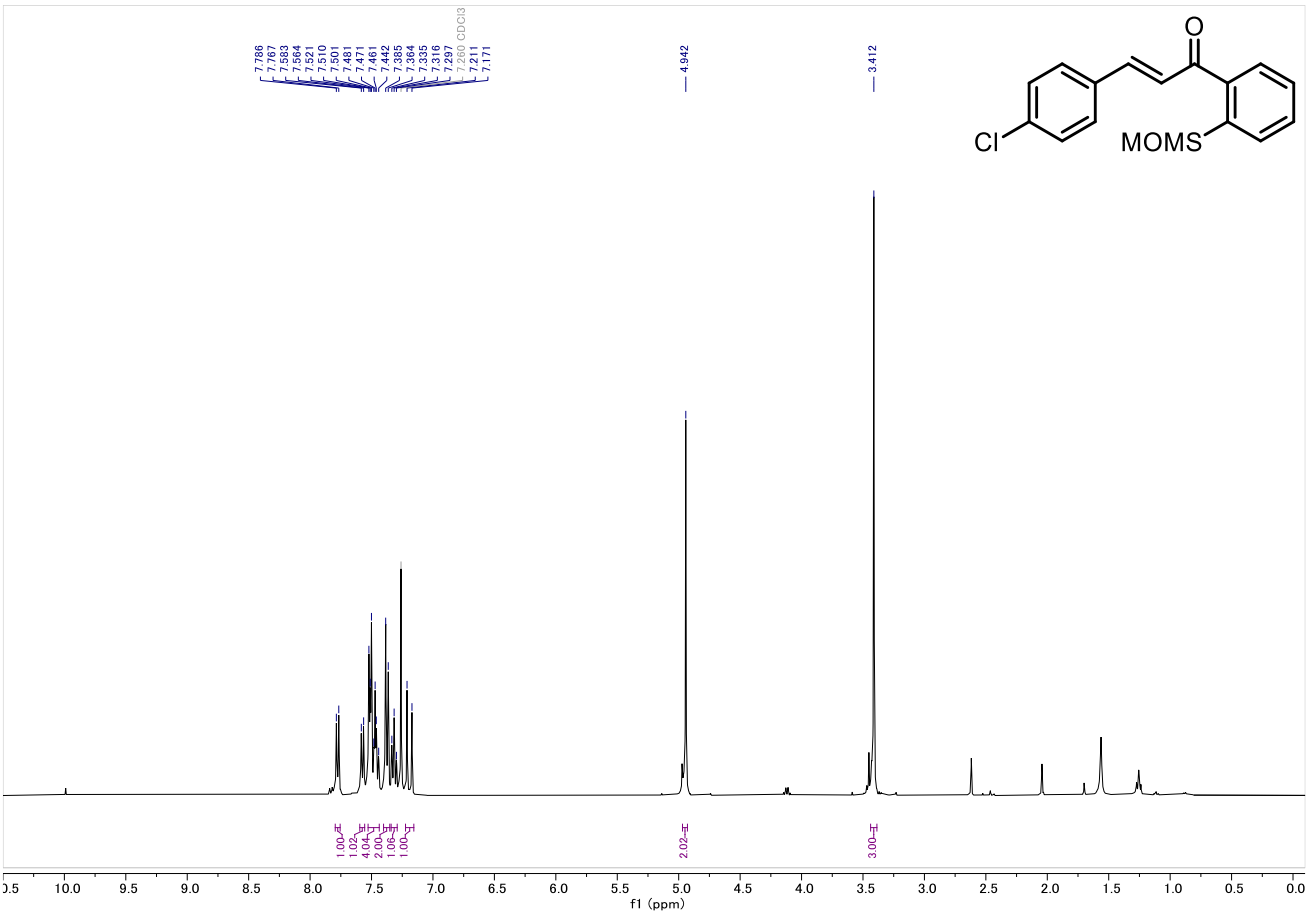
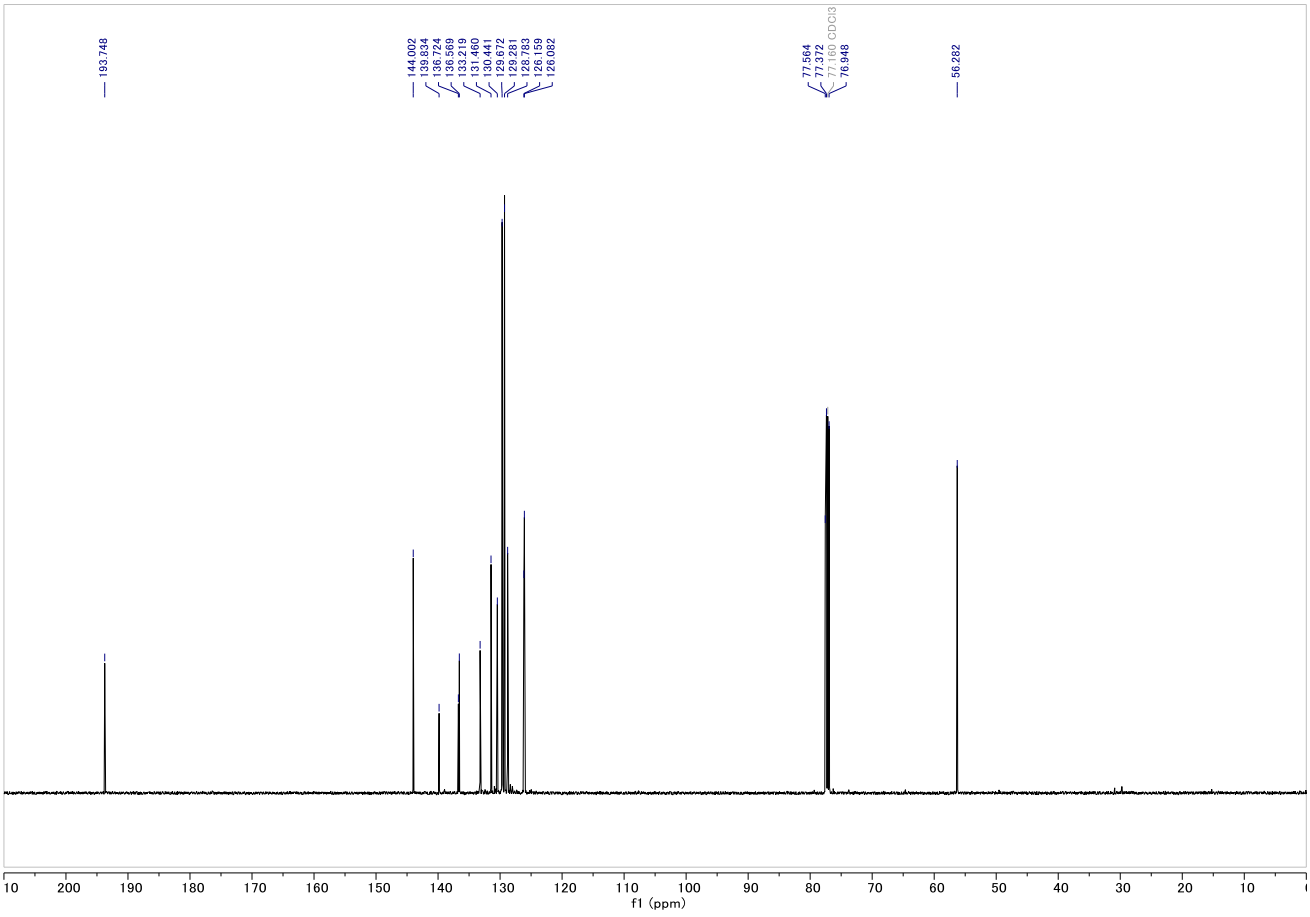
7.444
7.442
7.427
7.423
7.265
CDCl3
7.246
7.244
7.228
7.225
4.969
3.449
2.614
O
SMOM
1.05
1.03
1.06
1.77
2.04
3.04
3.02
f1 (ppm)

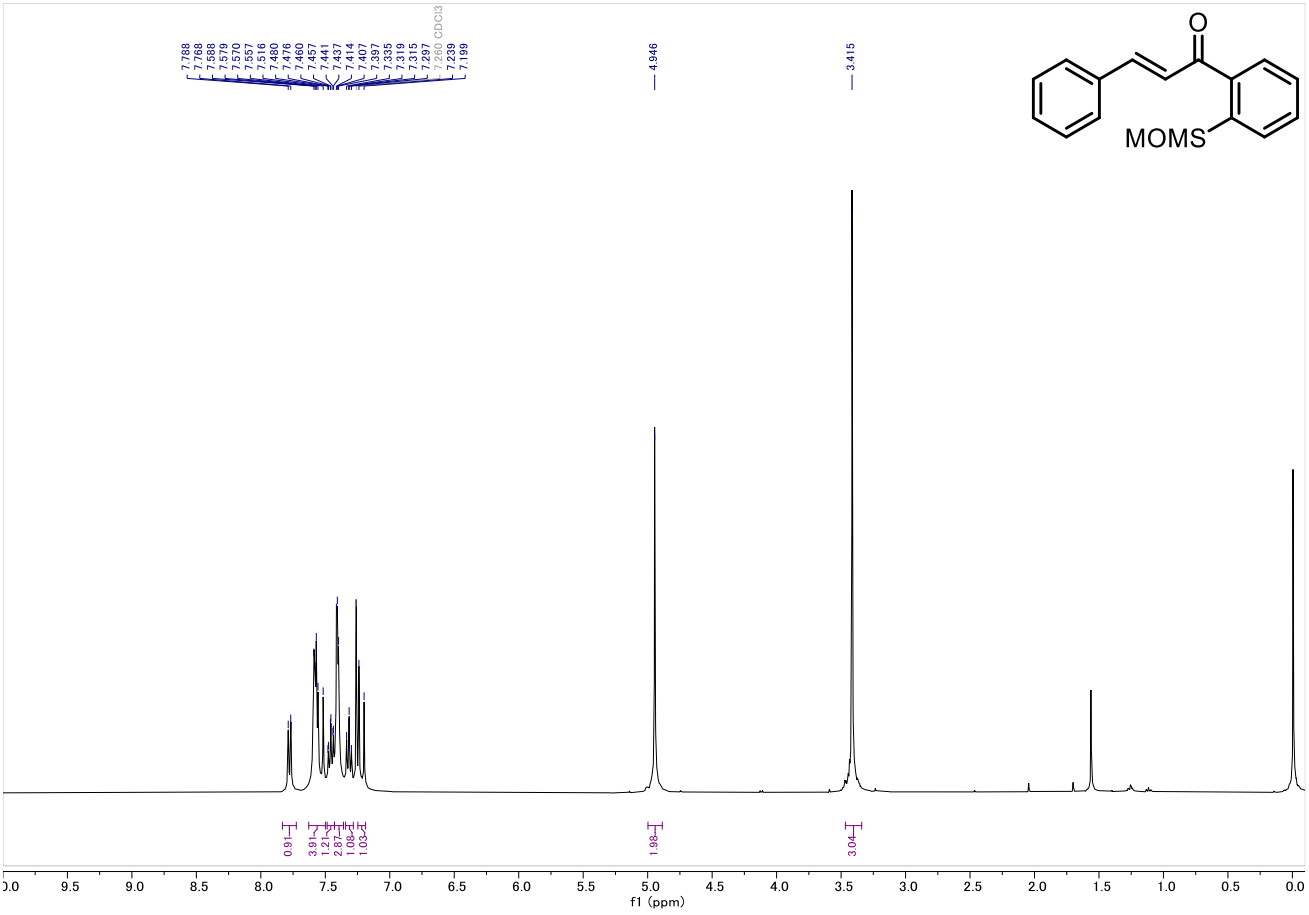
^{1}H NMR **1a**



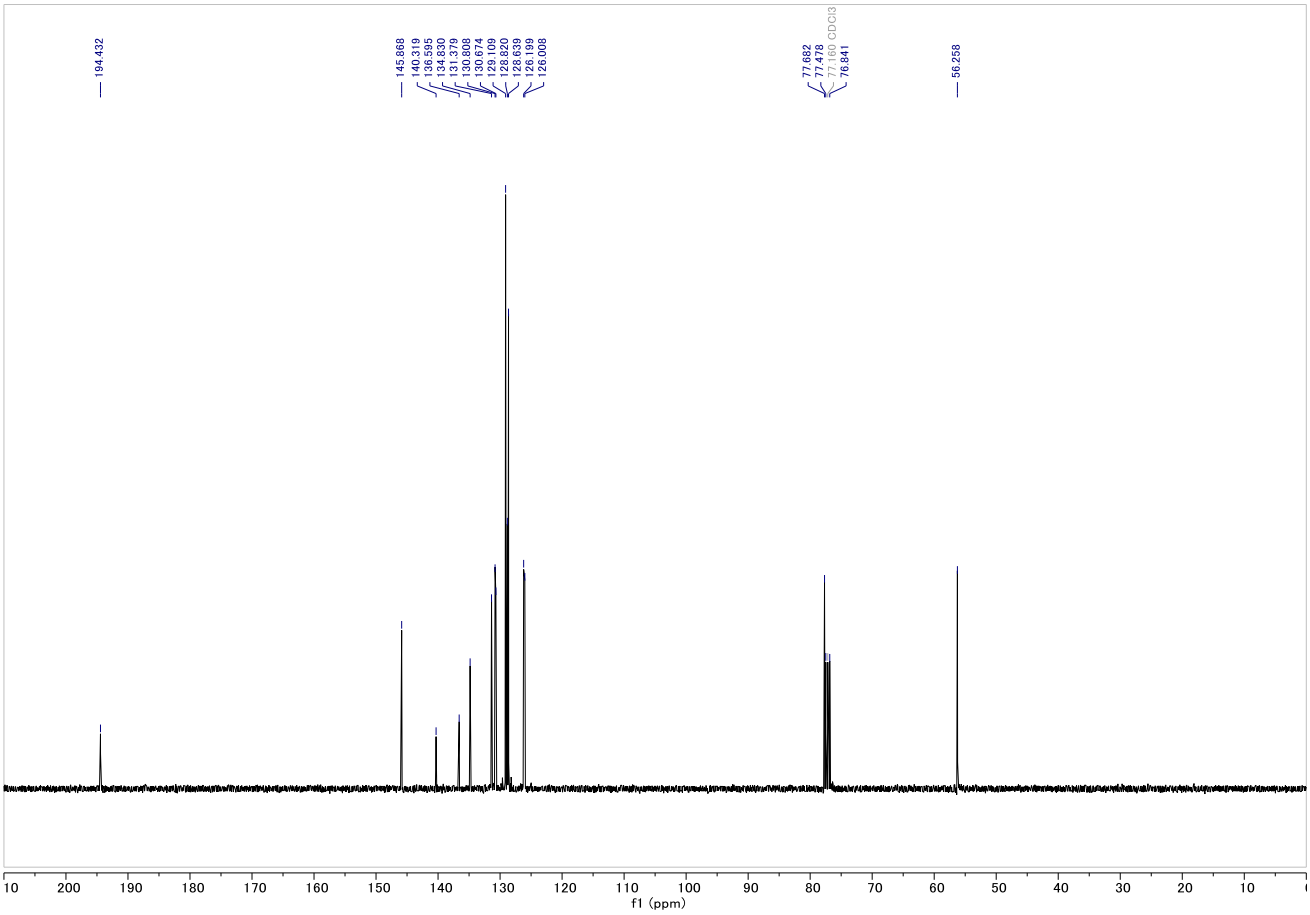
^{13}C NMR **1a**



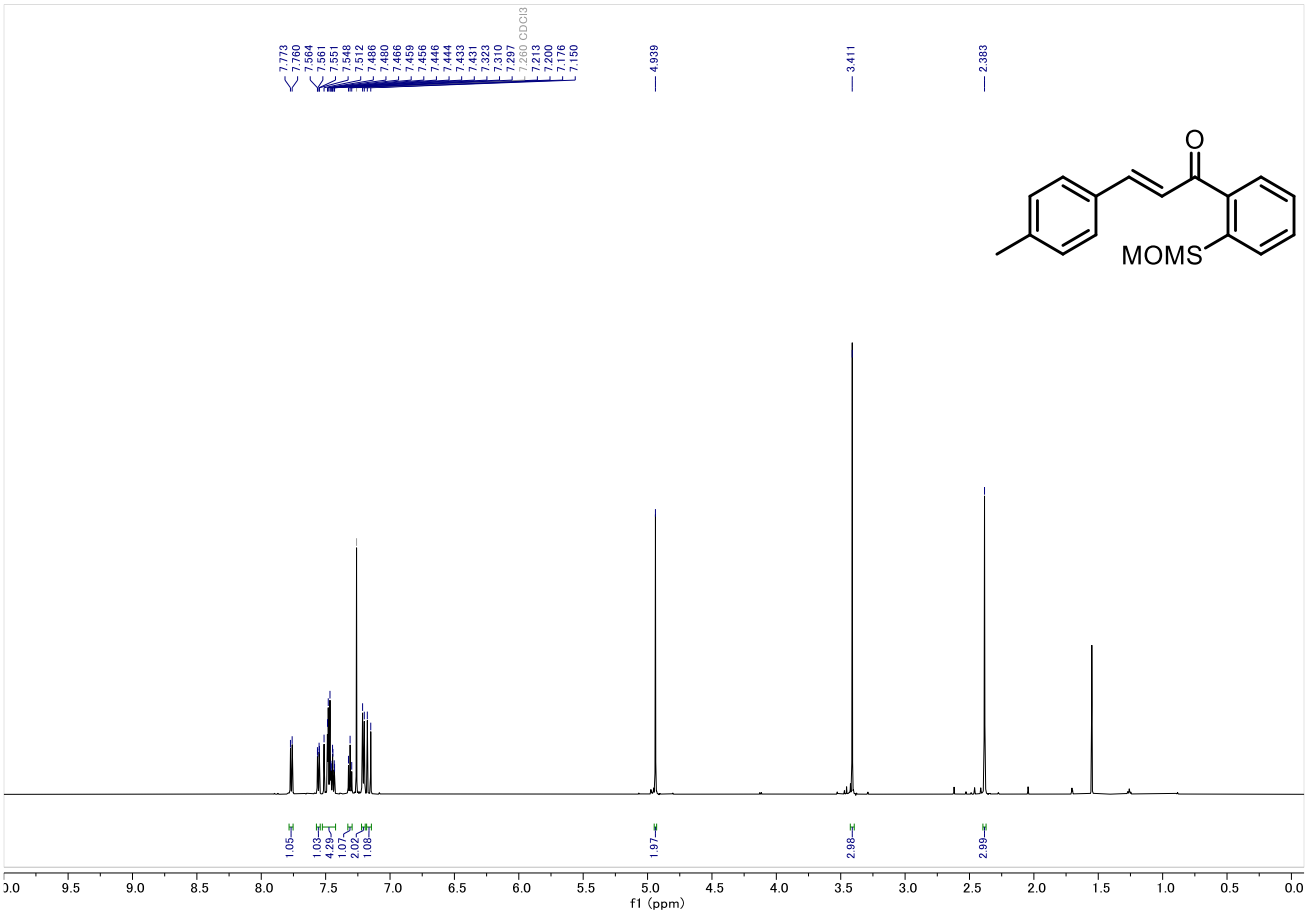
^{1}H NMR **1b**



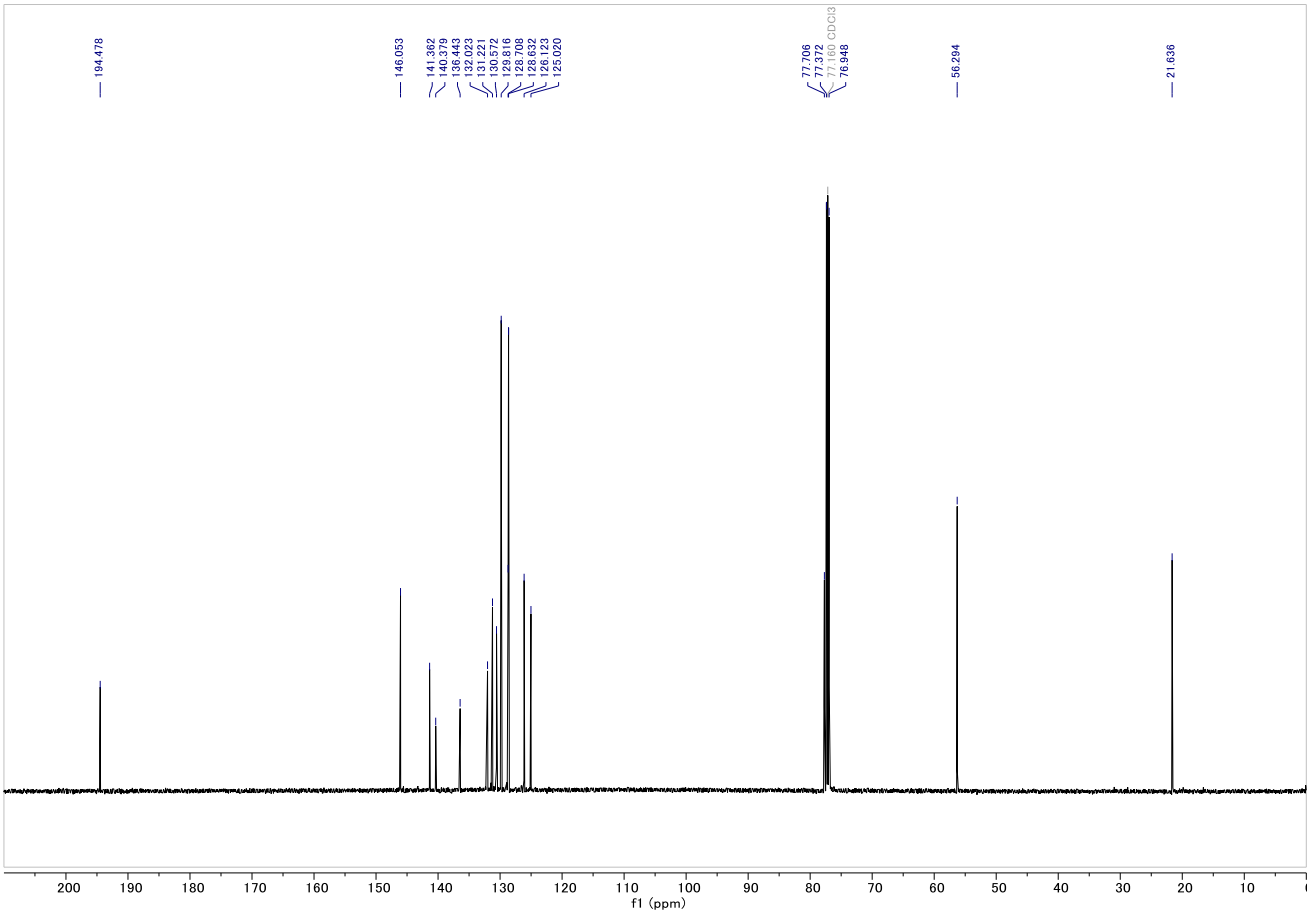
^{13}C NMR **1b**



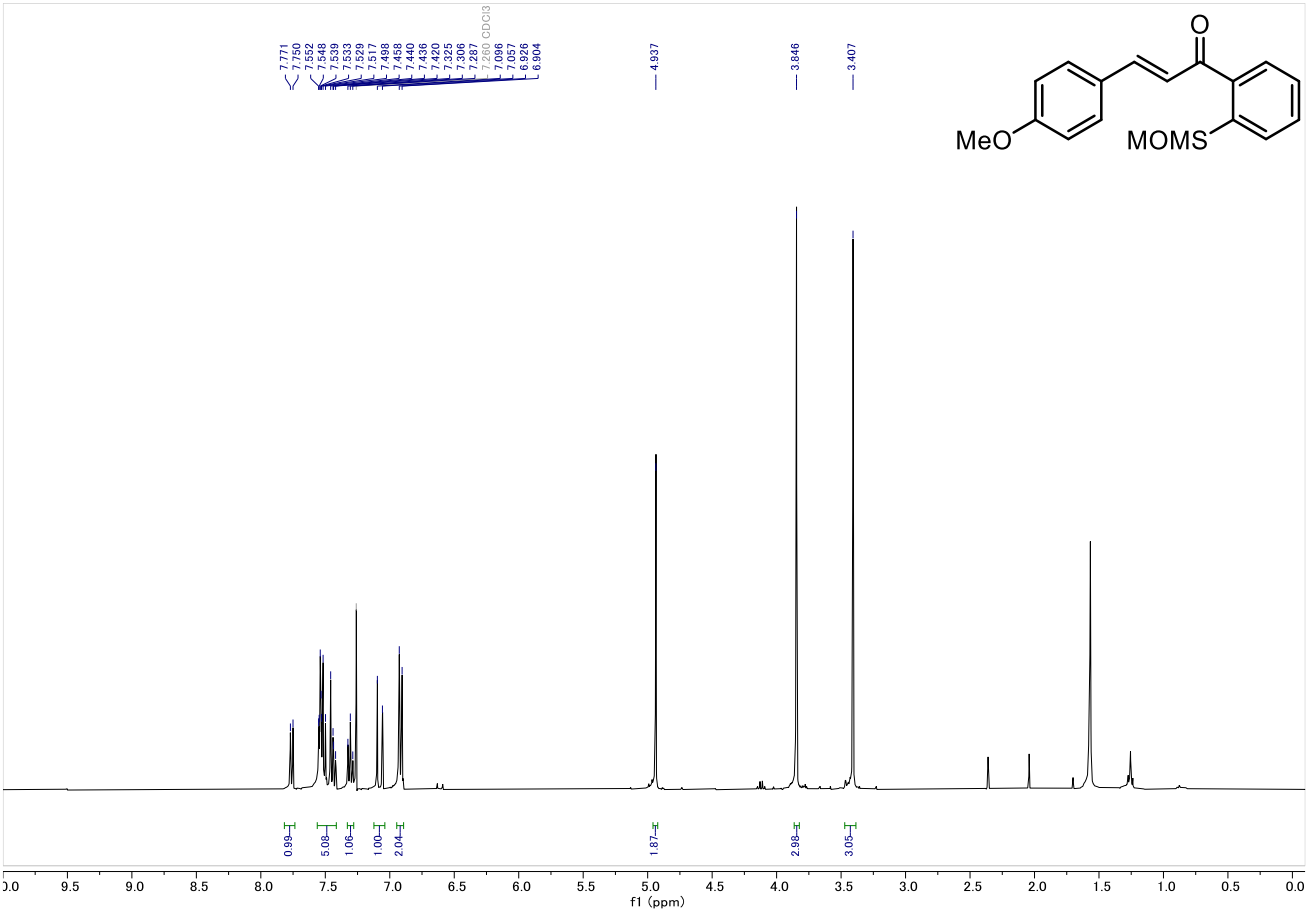
^{1}H NMR **1c**



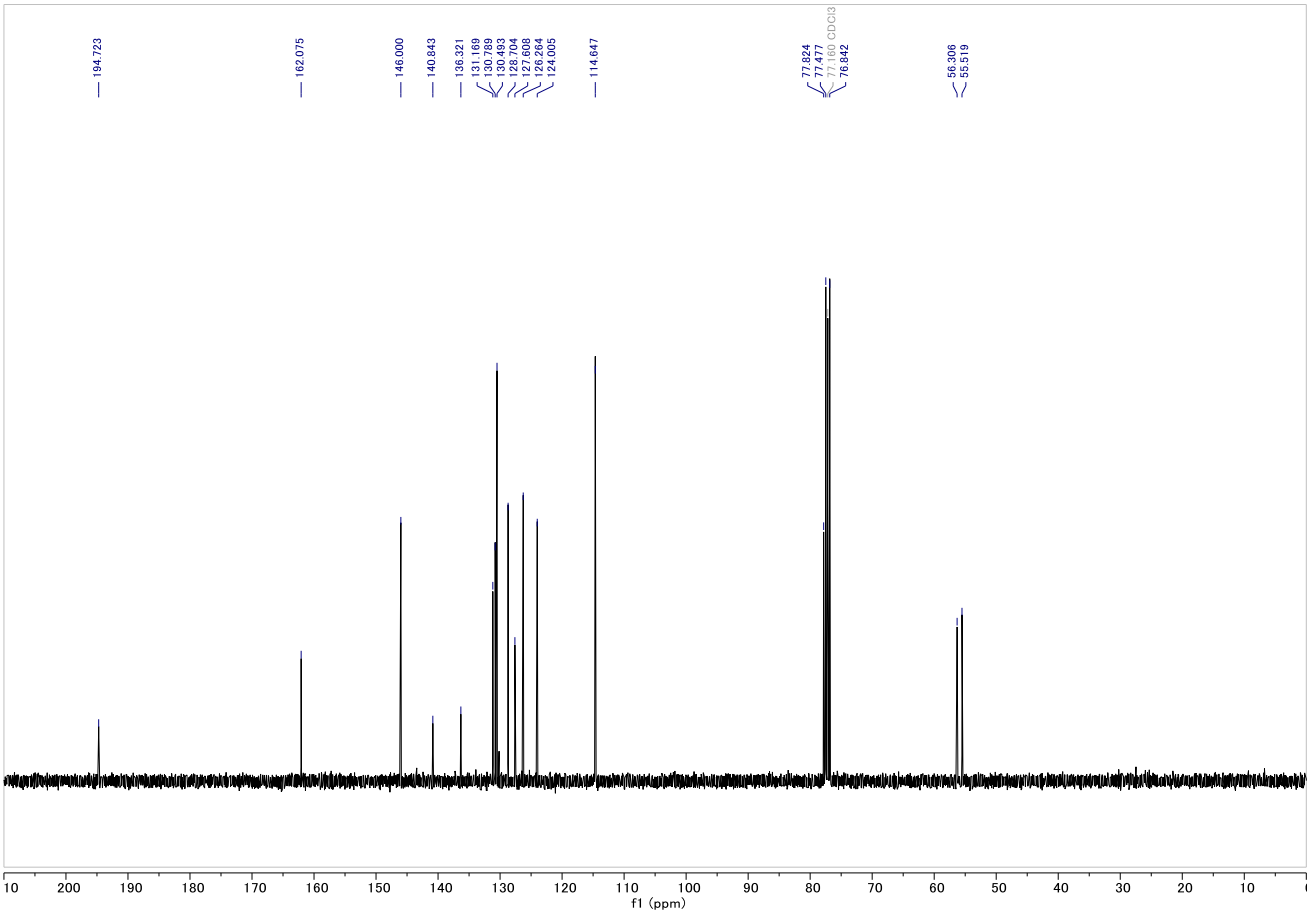
^{13}C NMR **1c**



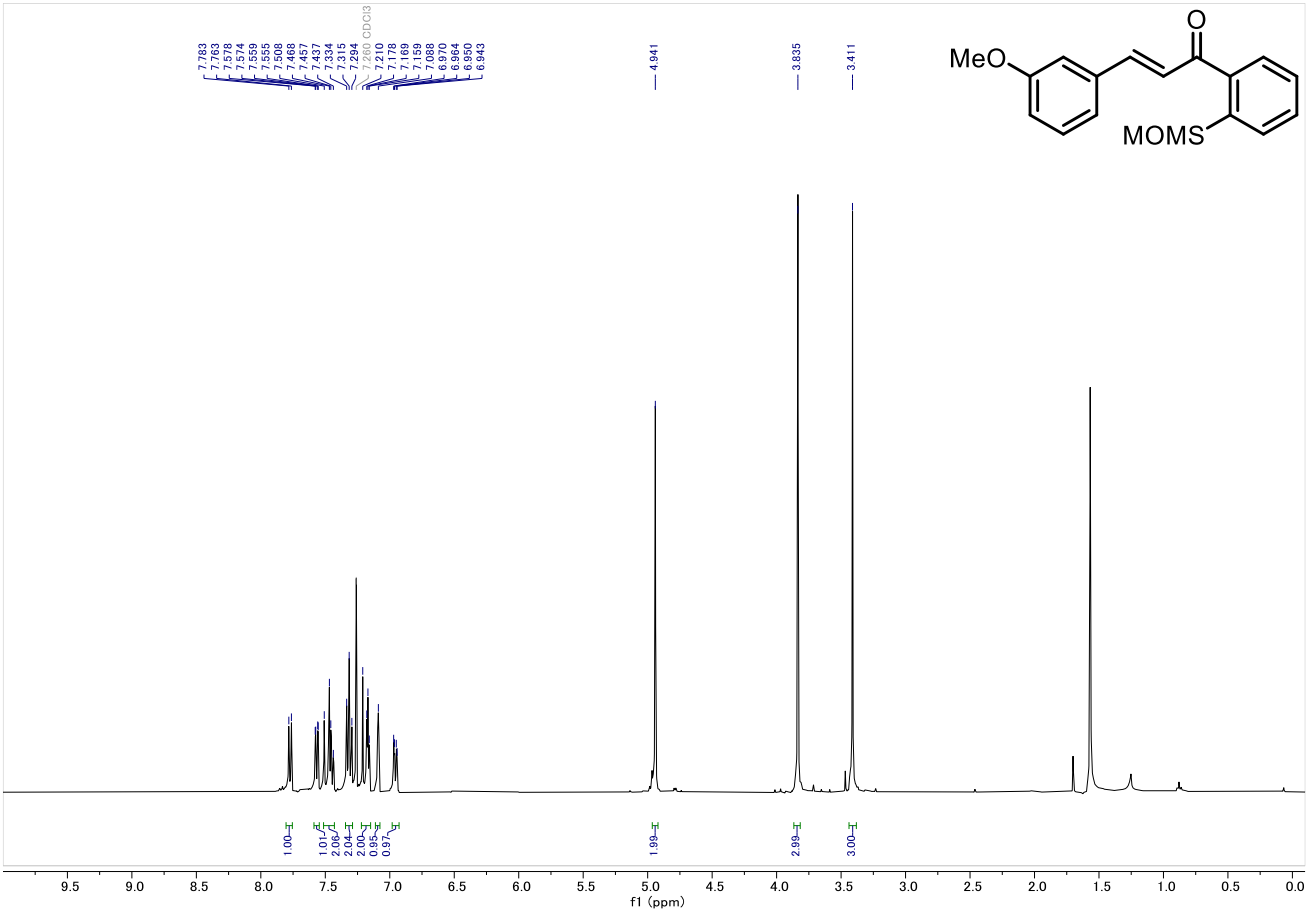
^{1}H NMR **1d**



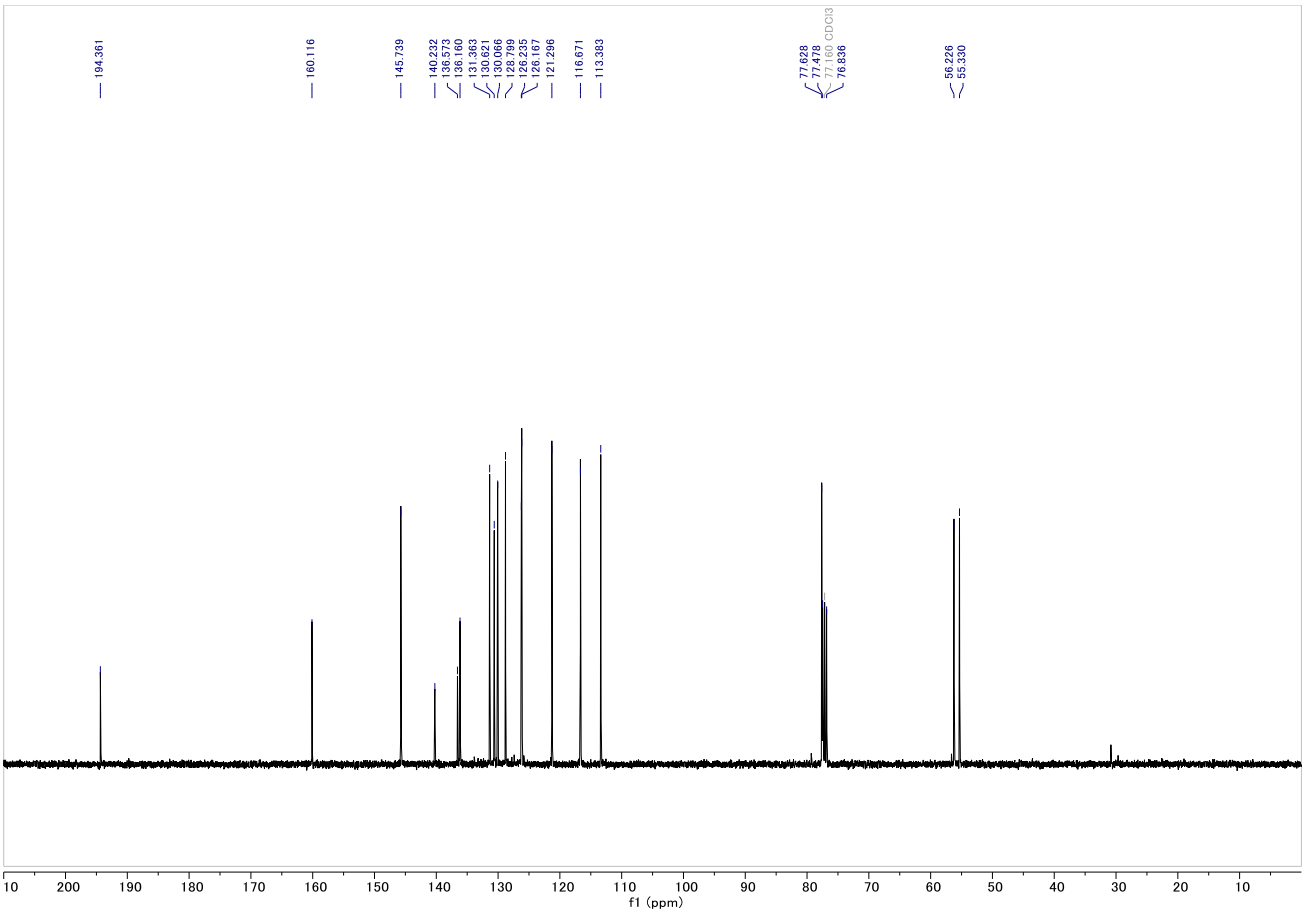
^{13}C NMR **1d**



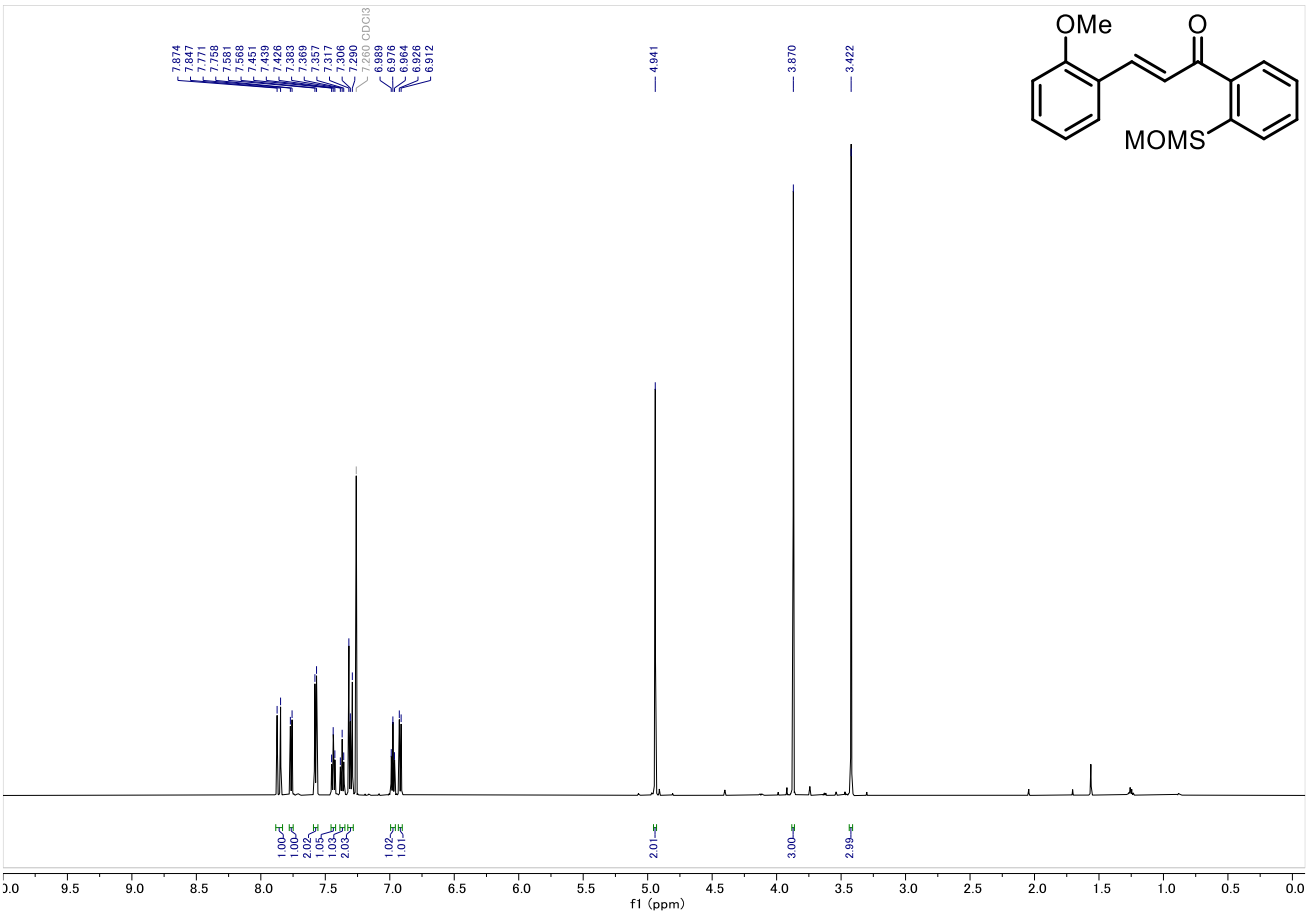
^{1}H NMR **1e**



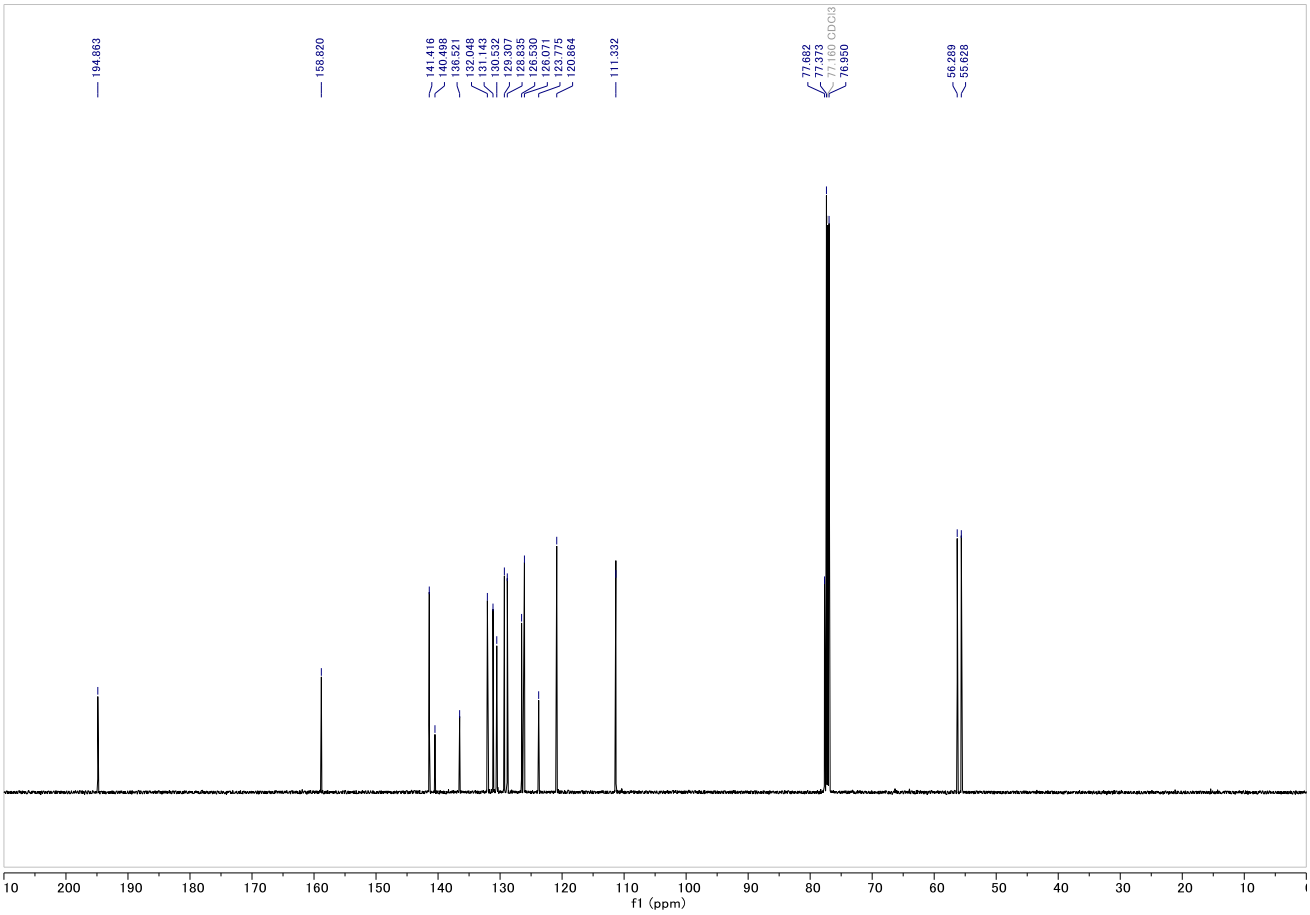
^{13}C NMR **1e**



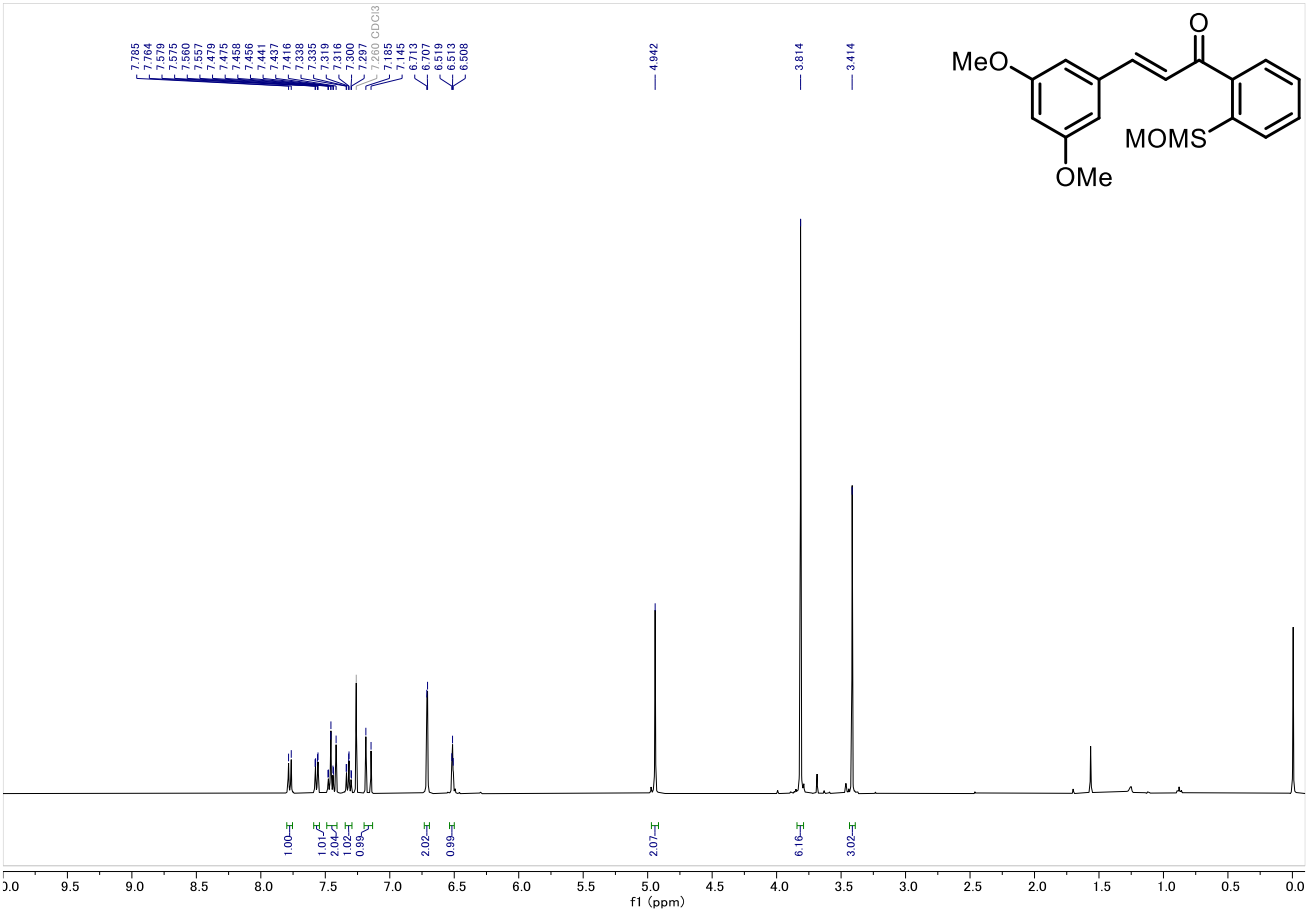
^{1}H NMR **1f**



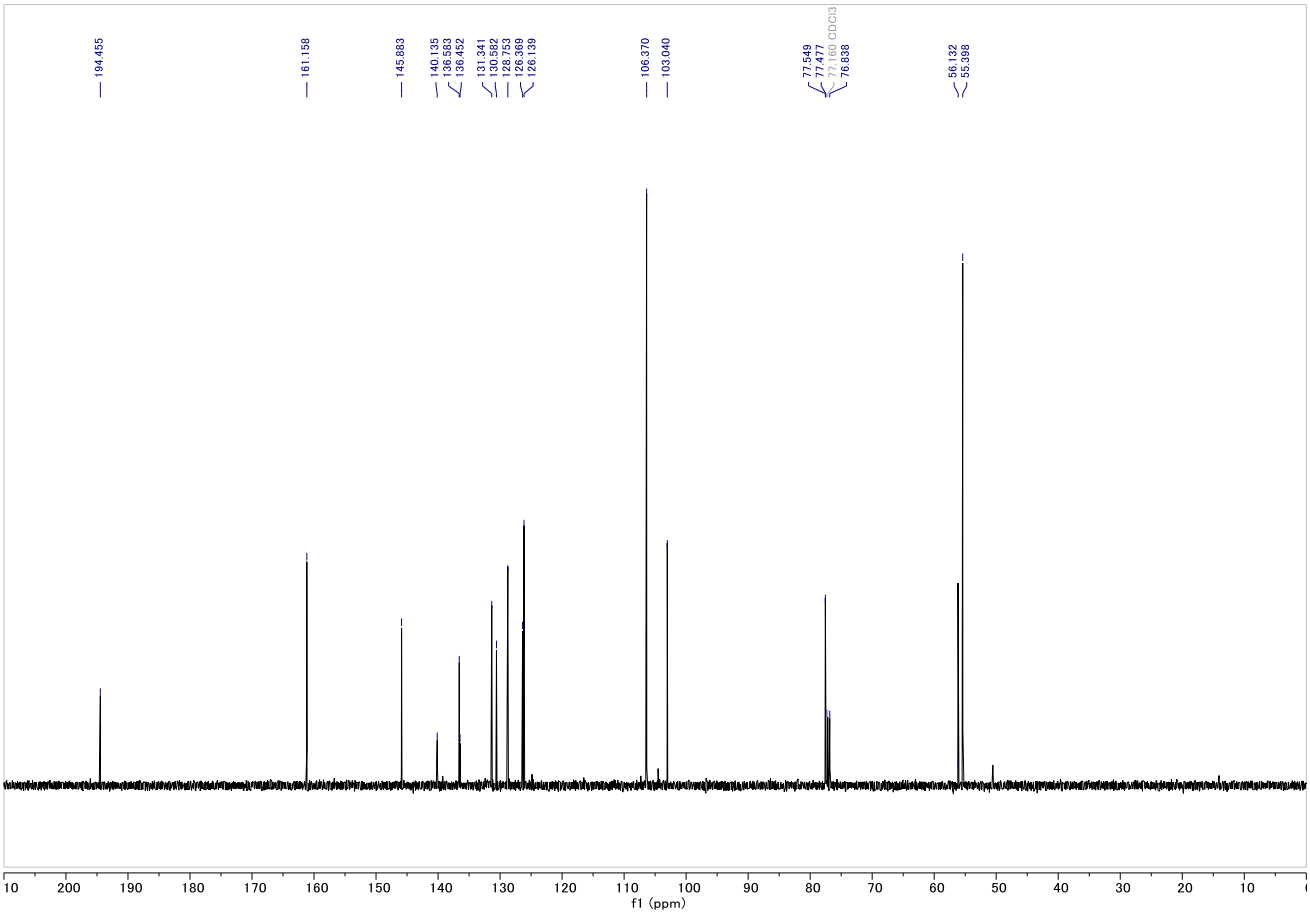
^{13}C NMR **1f**



^{1}H NMR **1g**



^{13}C NMR **1g**



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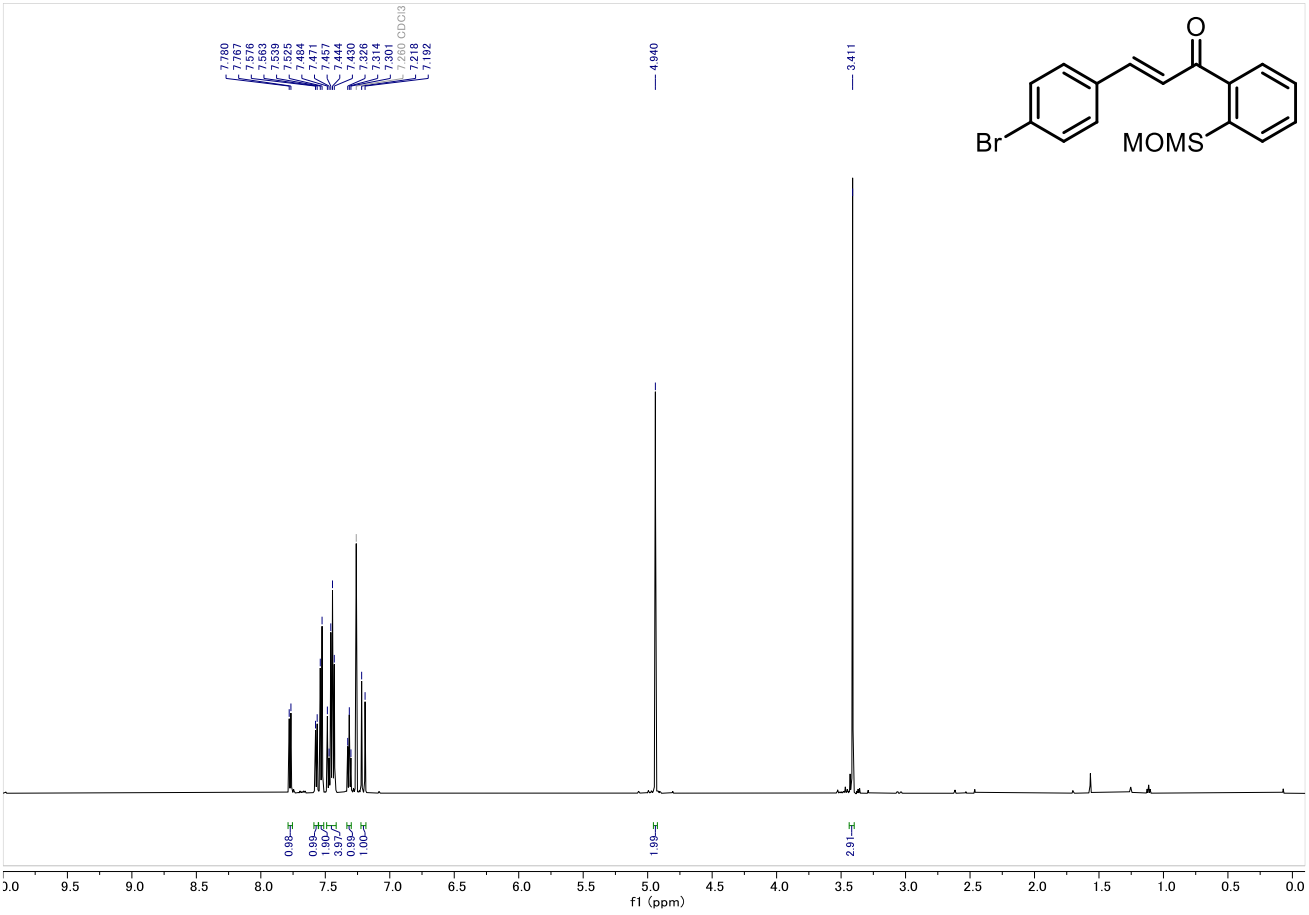
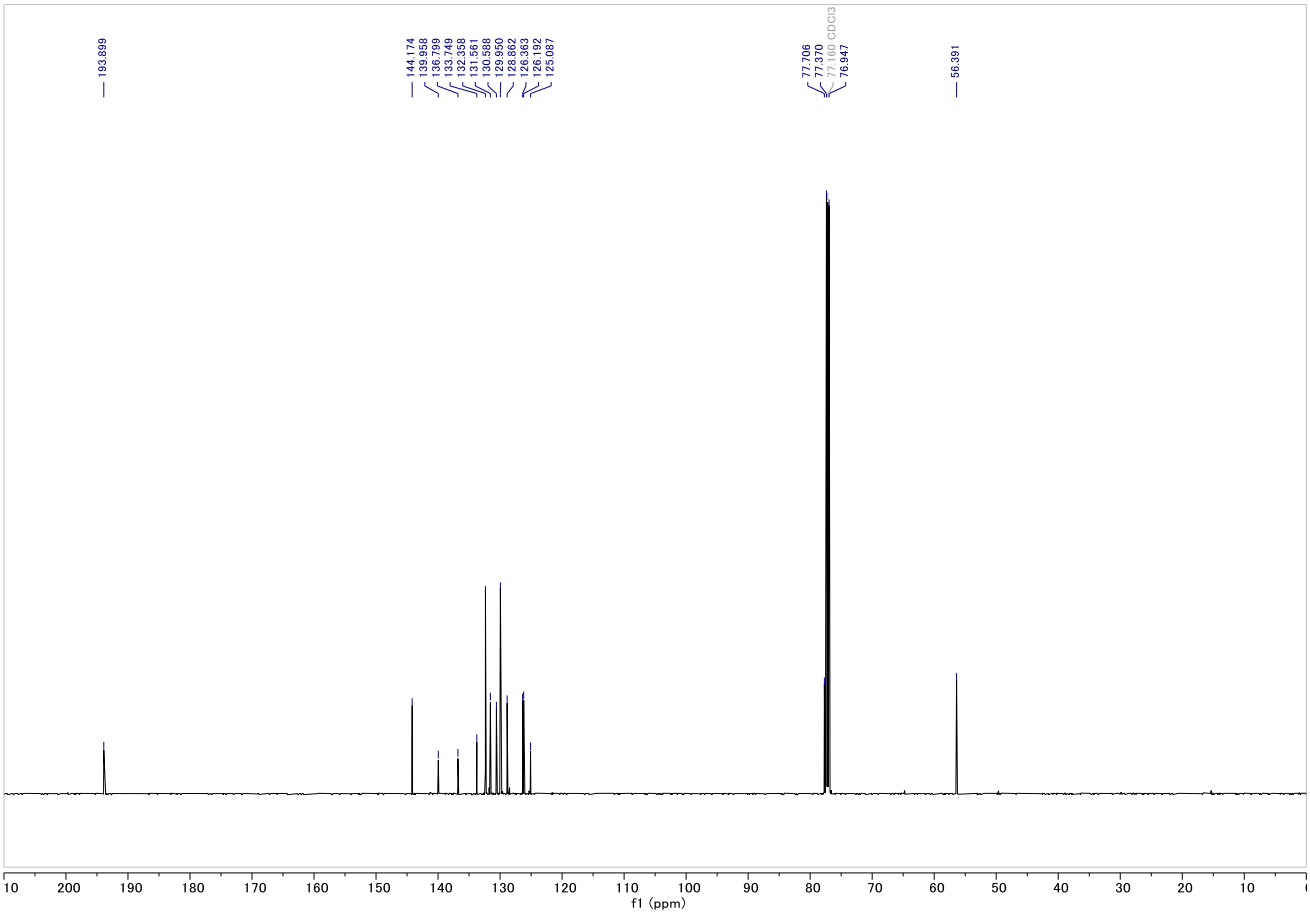
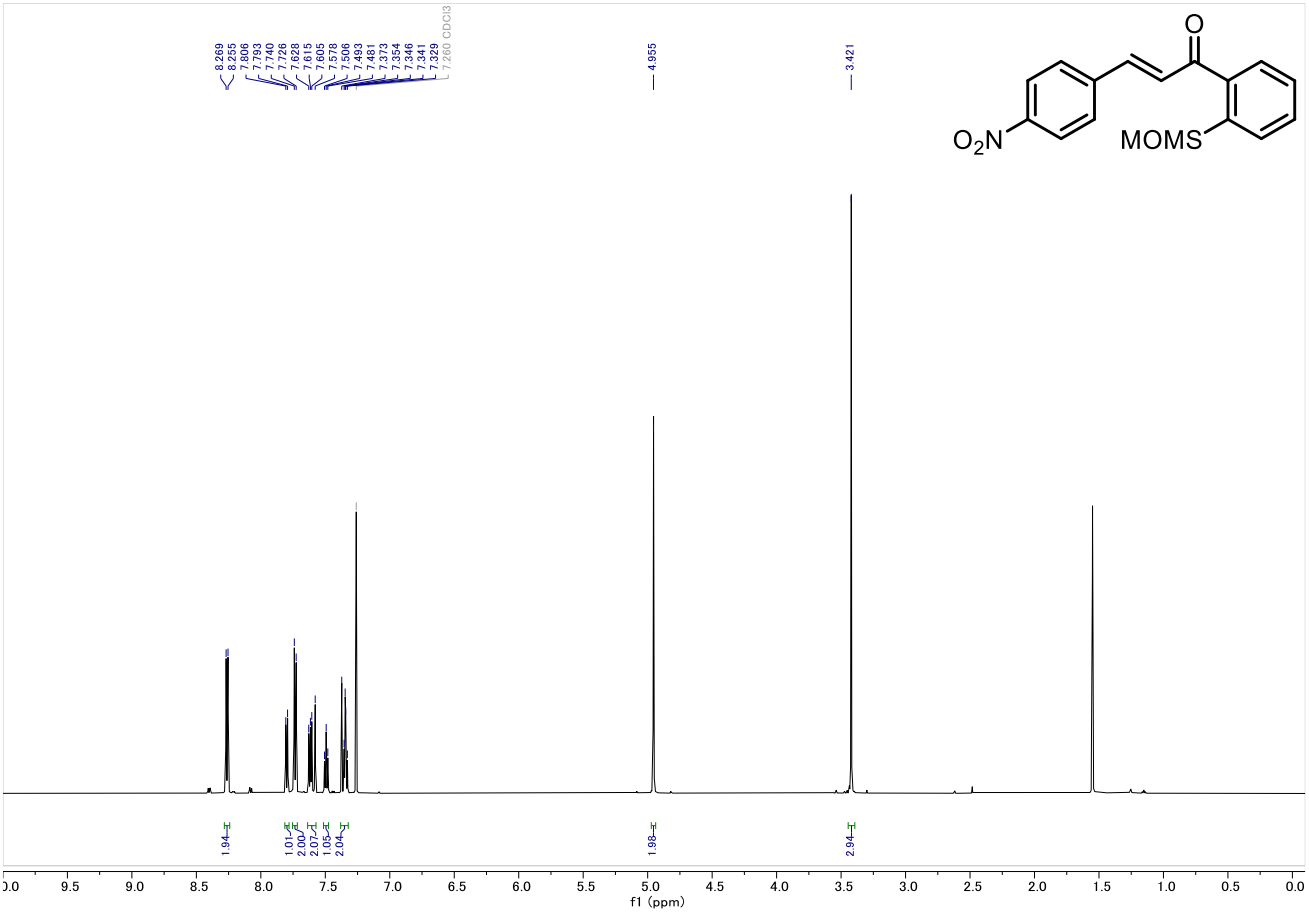


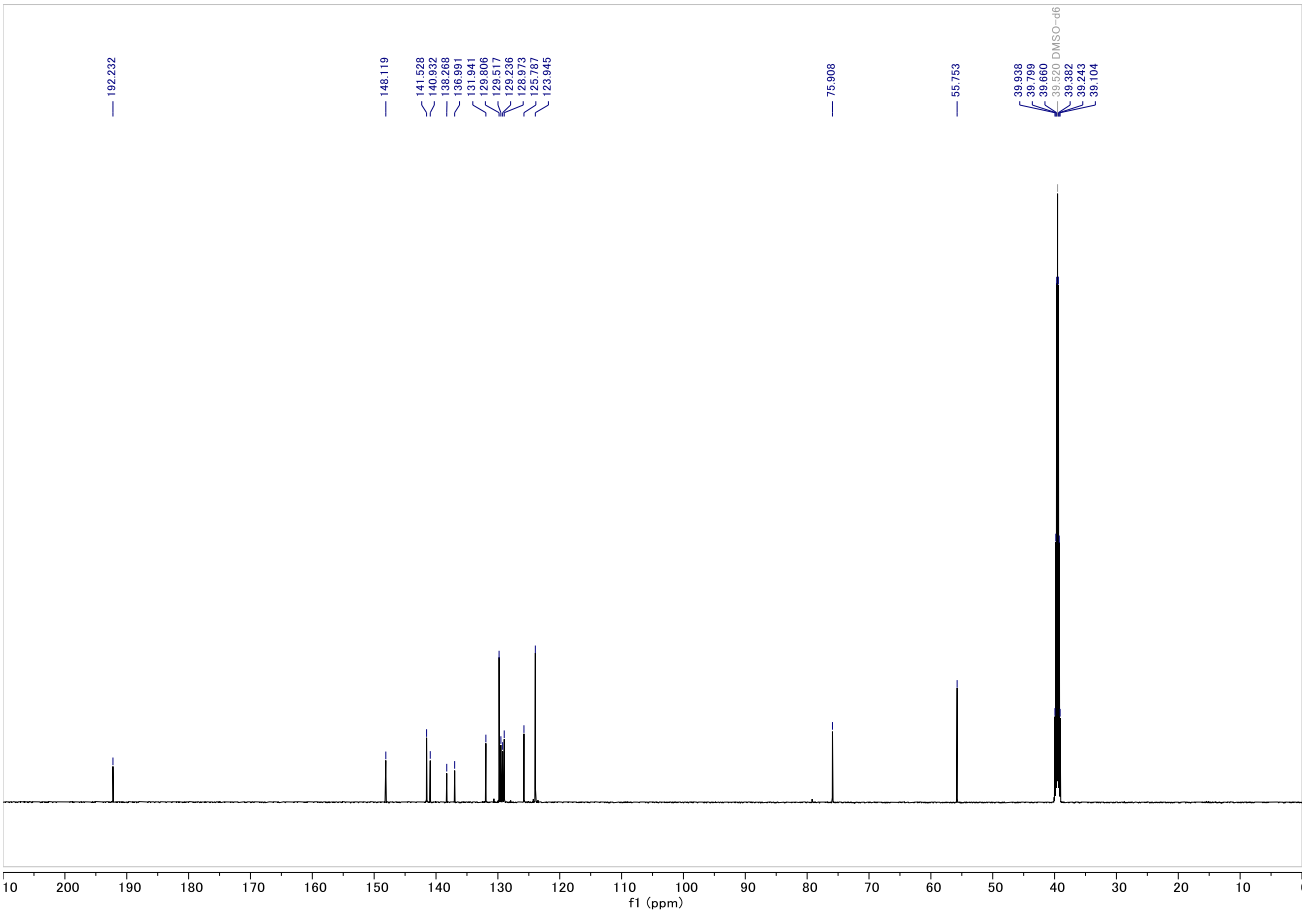
^{13}C NMR **1h**



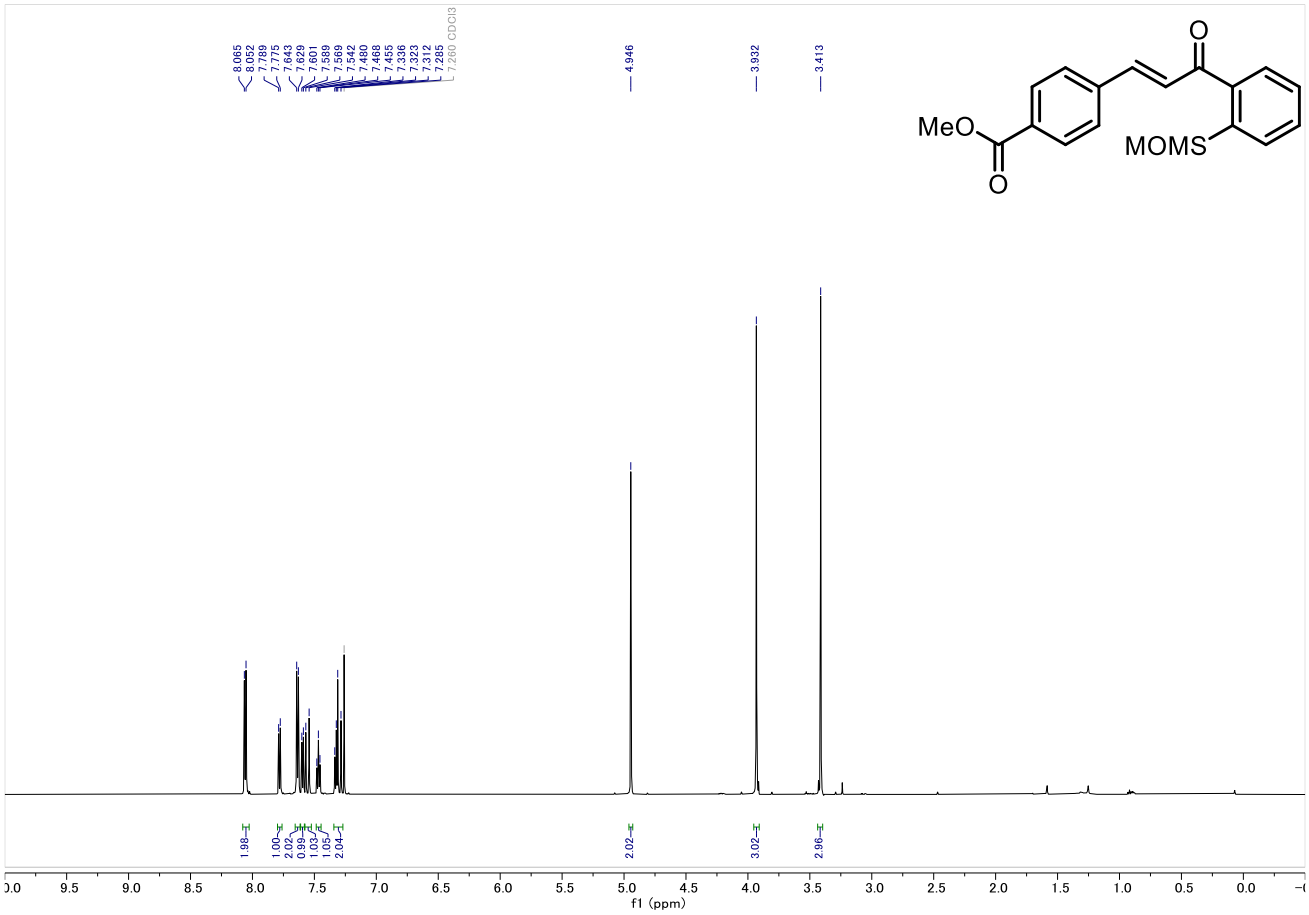
^{1}H NMR **1i**



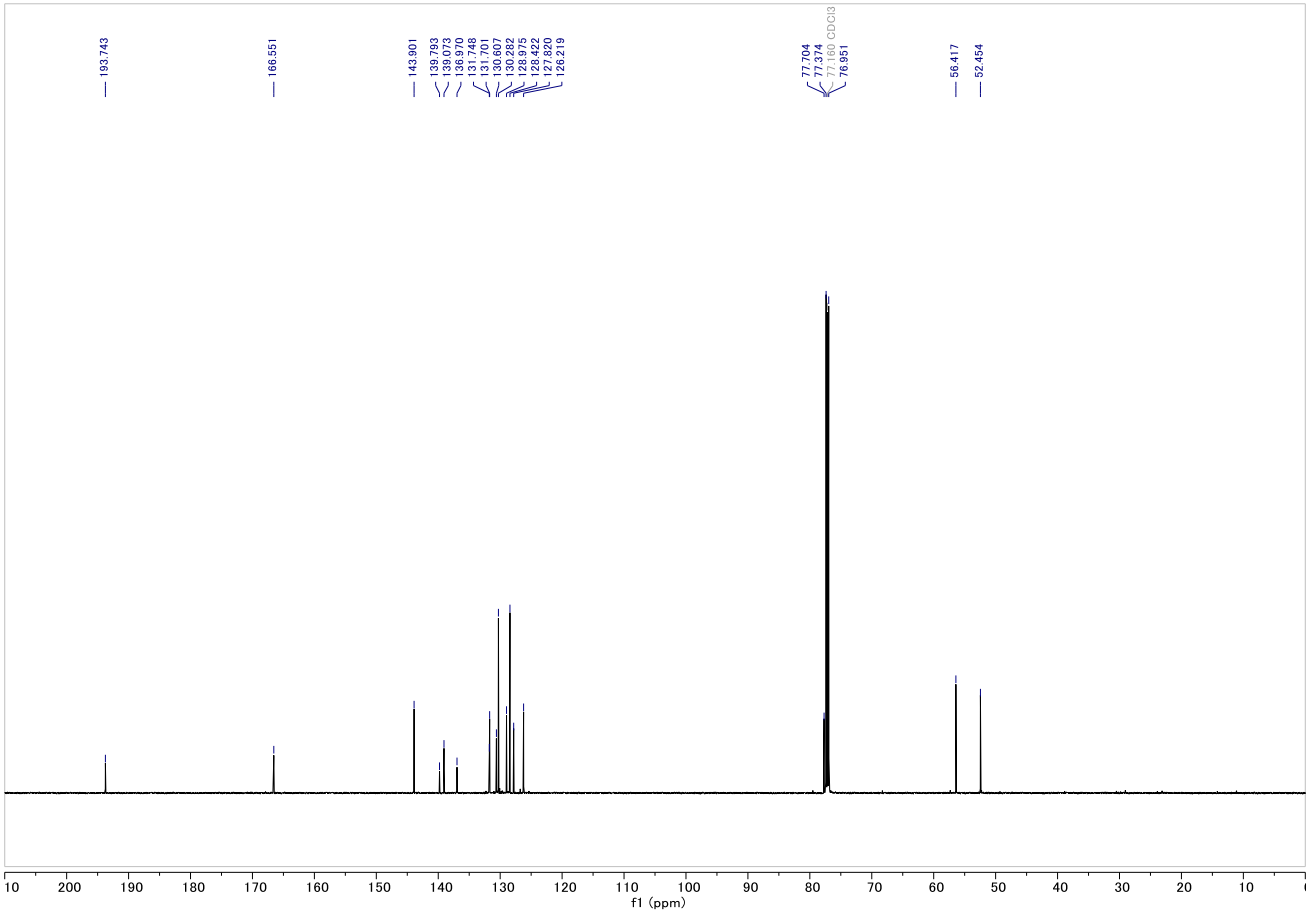
^{13}C NMR **1i**



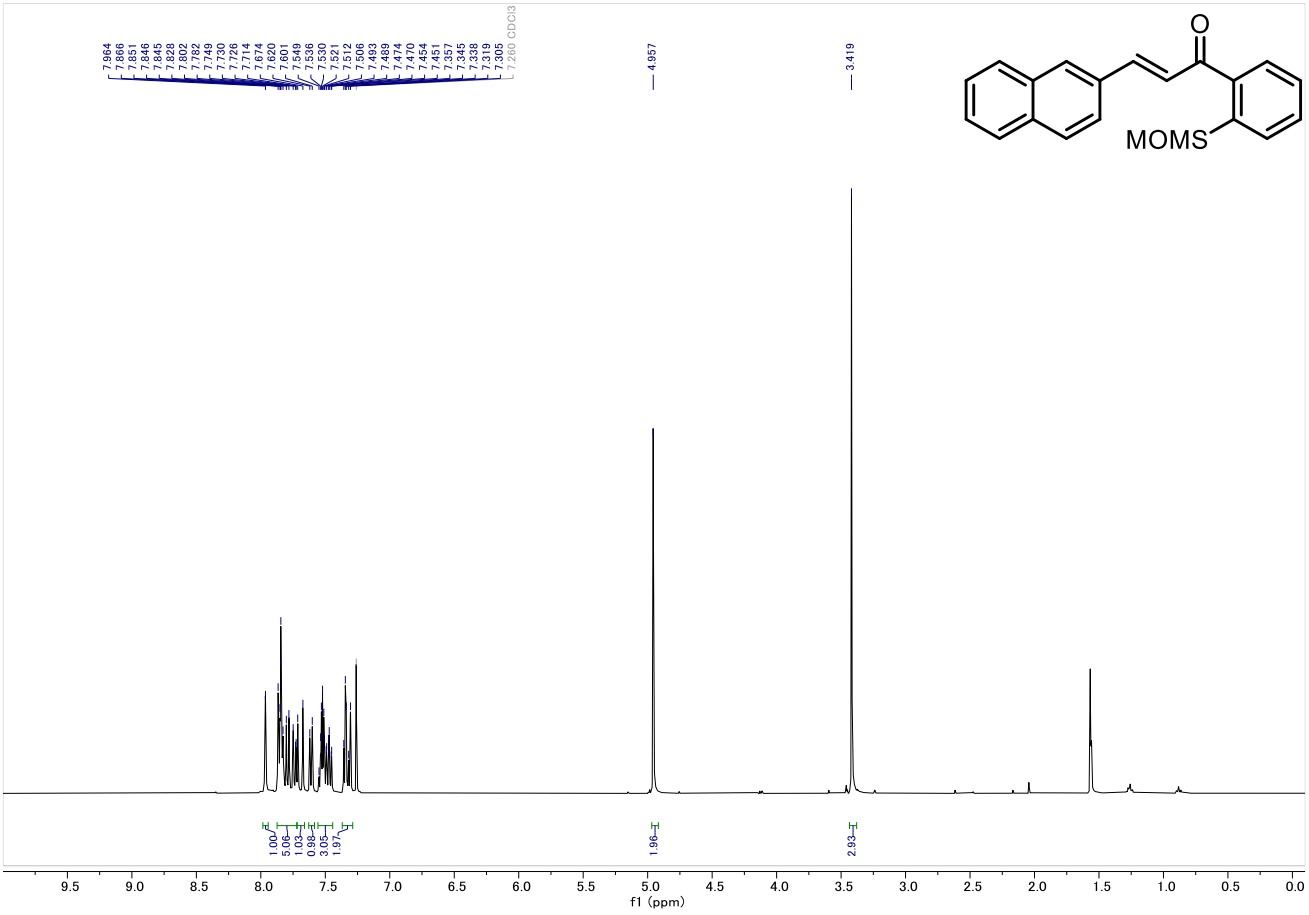
^{1}H NMR **1j**



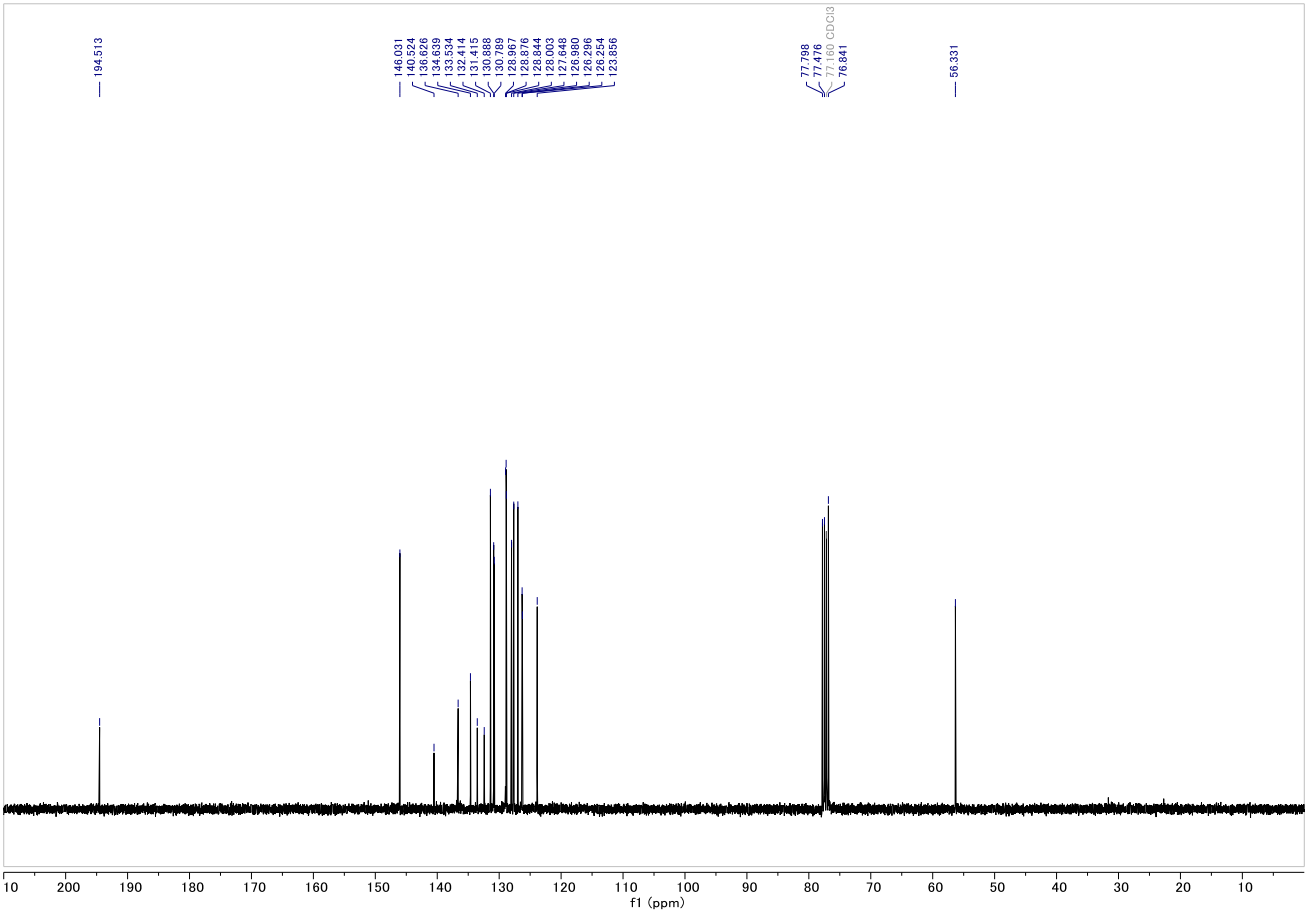
^{13}C NMR **1j**



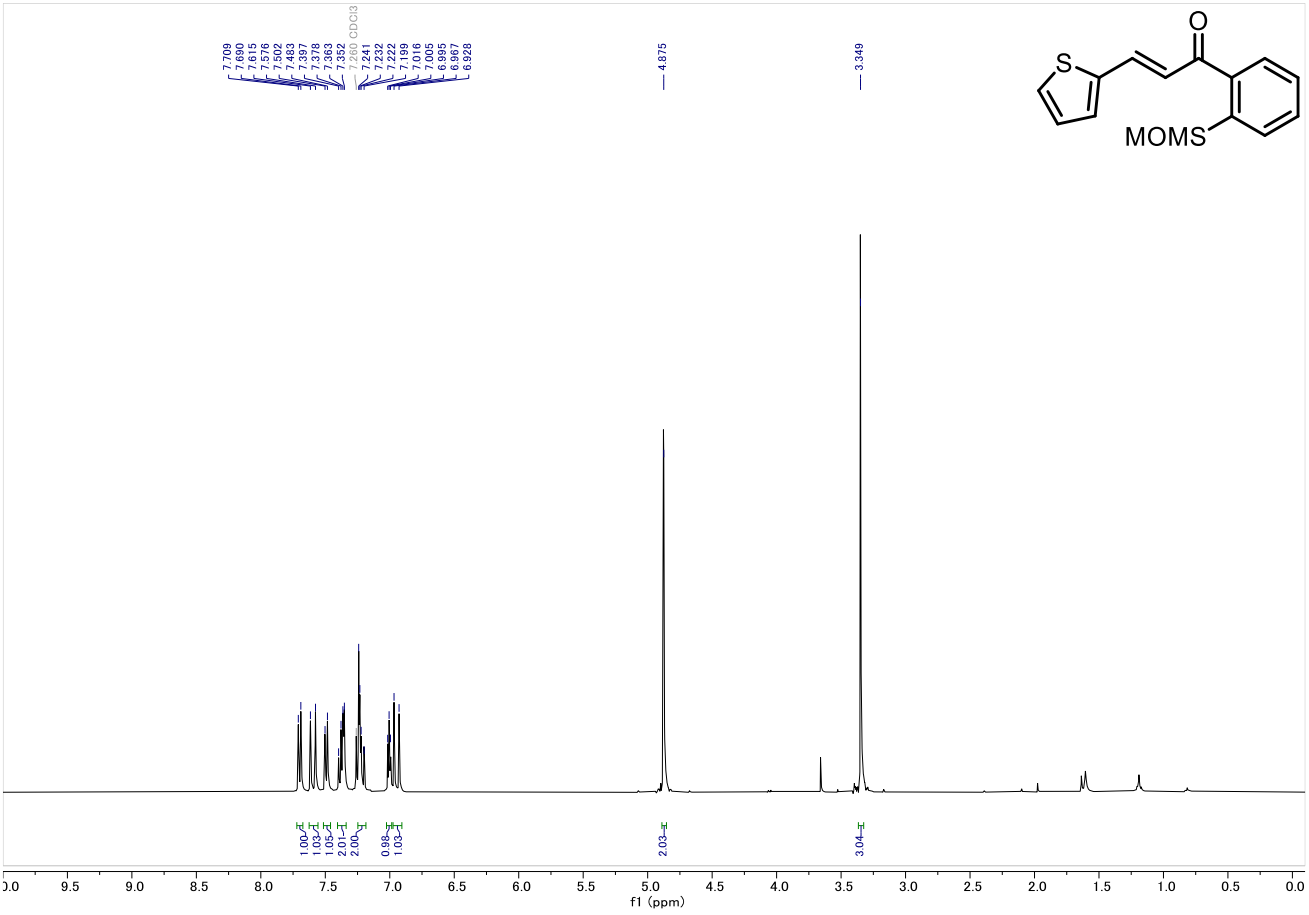
^{1}H NMR **1k**



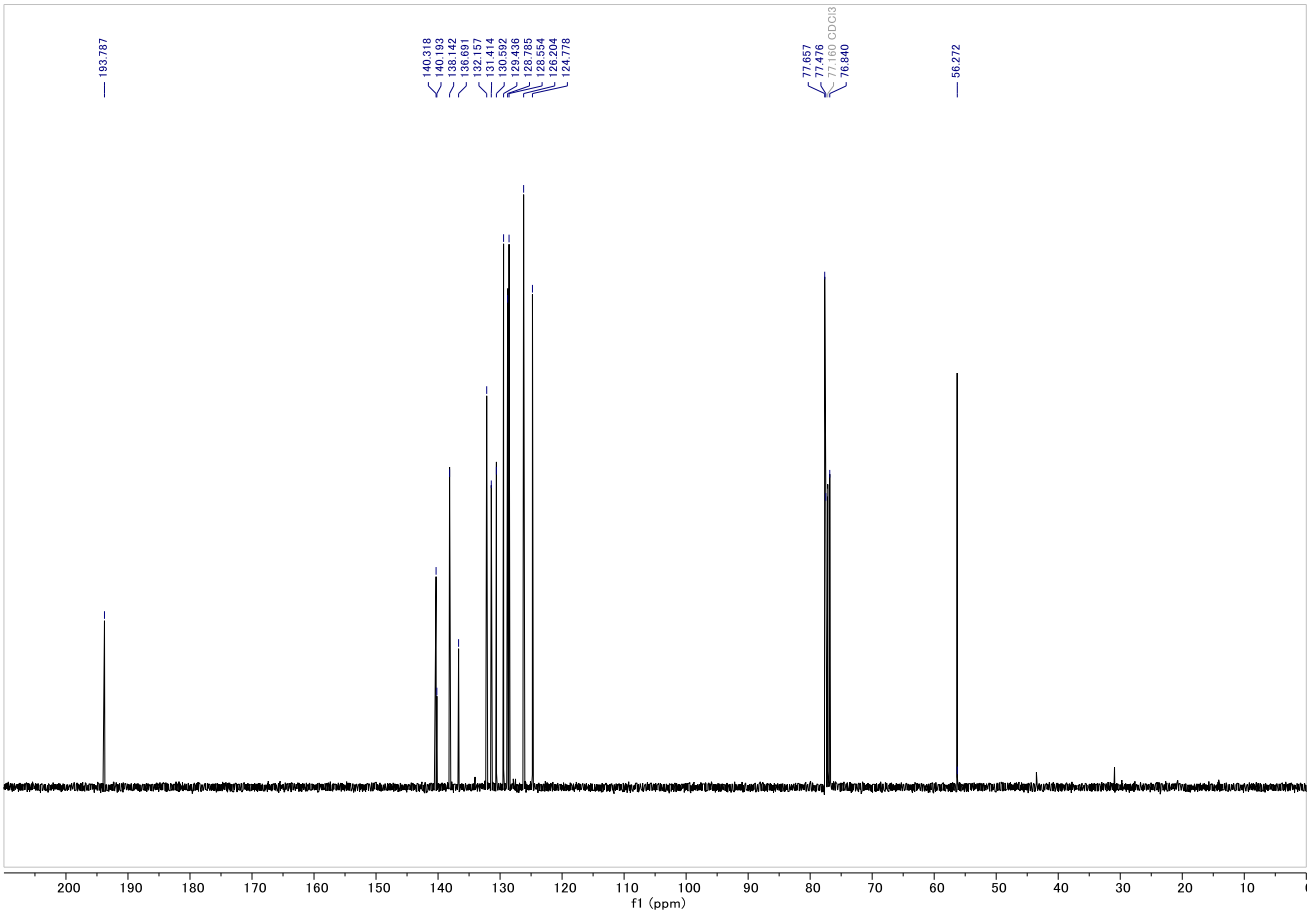
^{13}C NMR **1k**



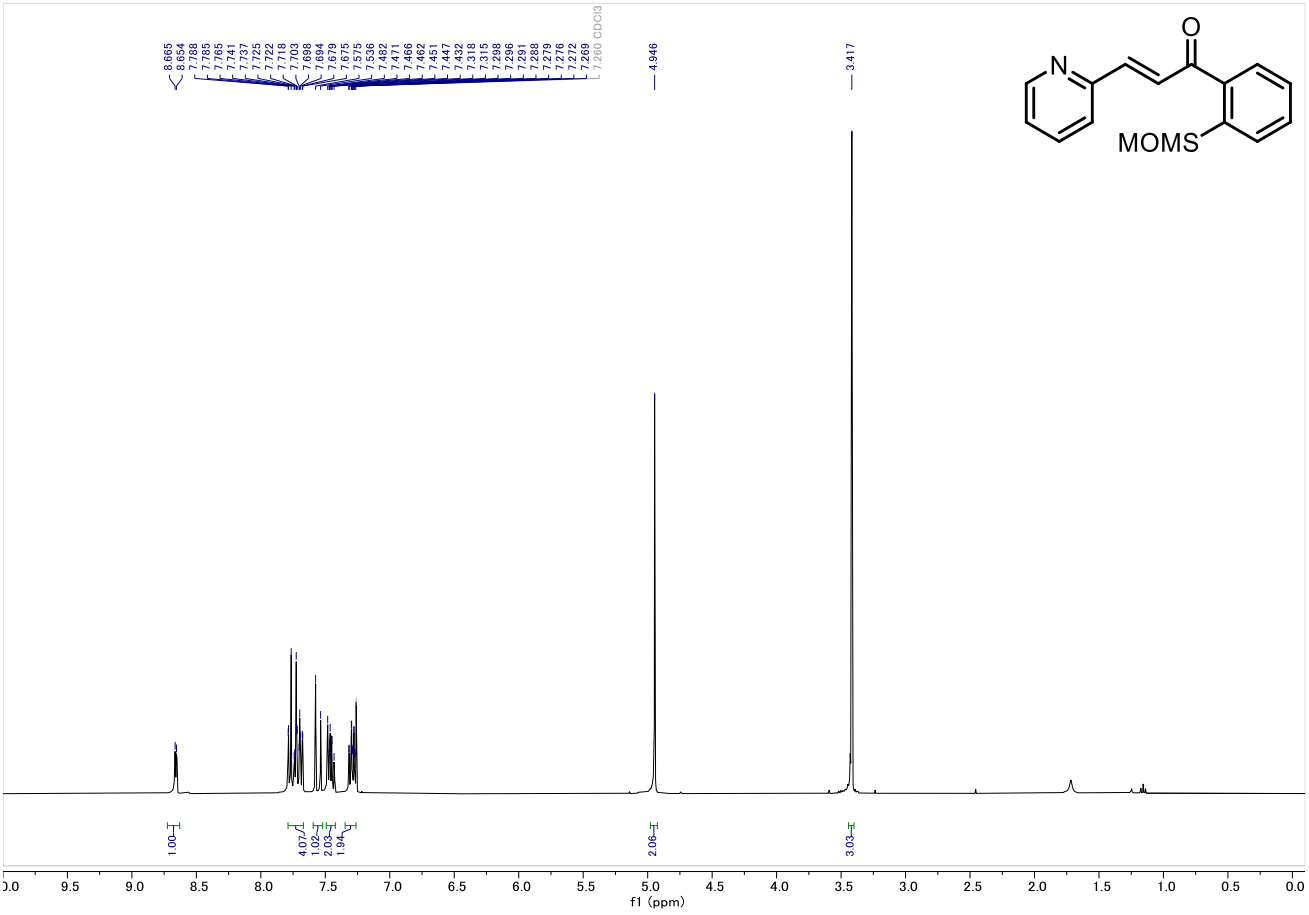
^{1}H NMR **1l**



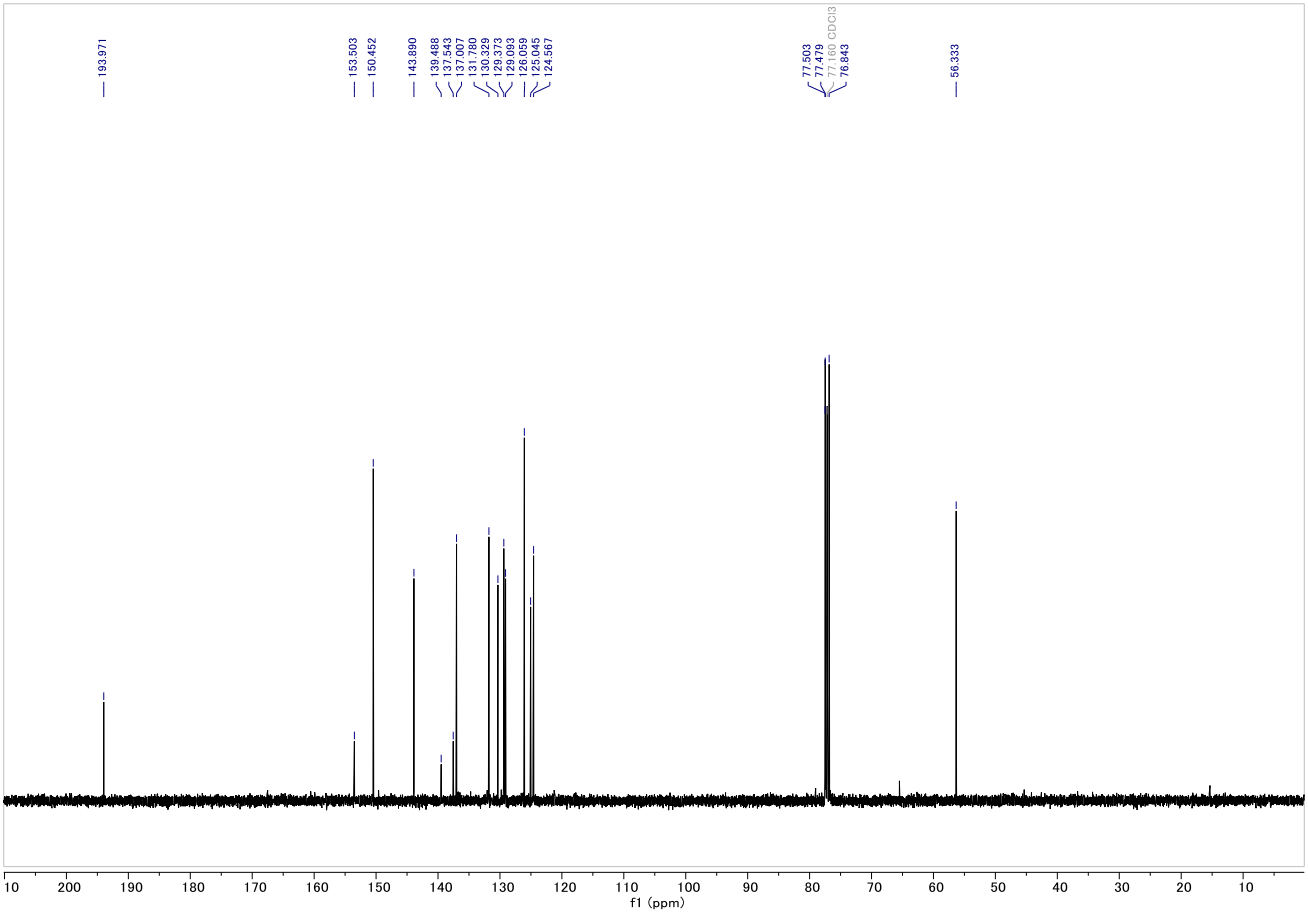
^{13}C NMR **1l**



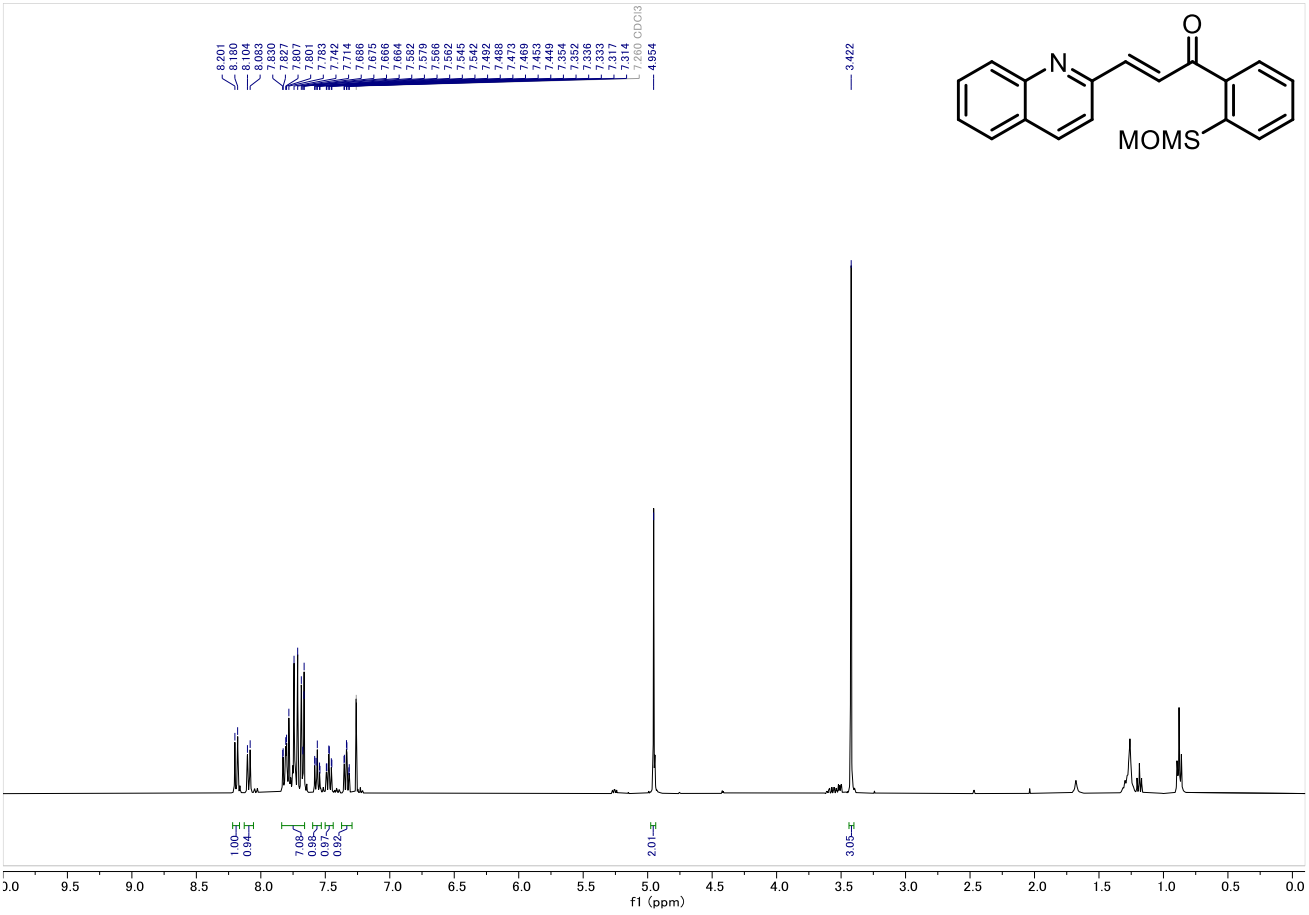
^{1}H NMR **1m**



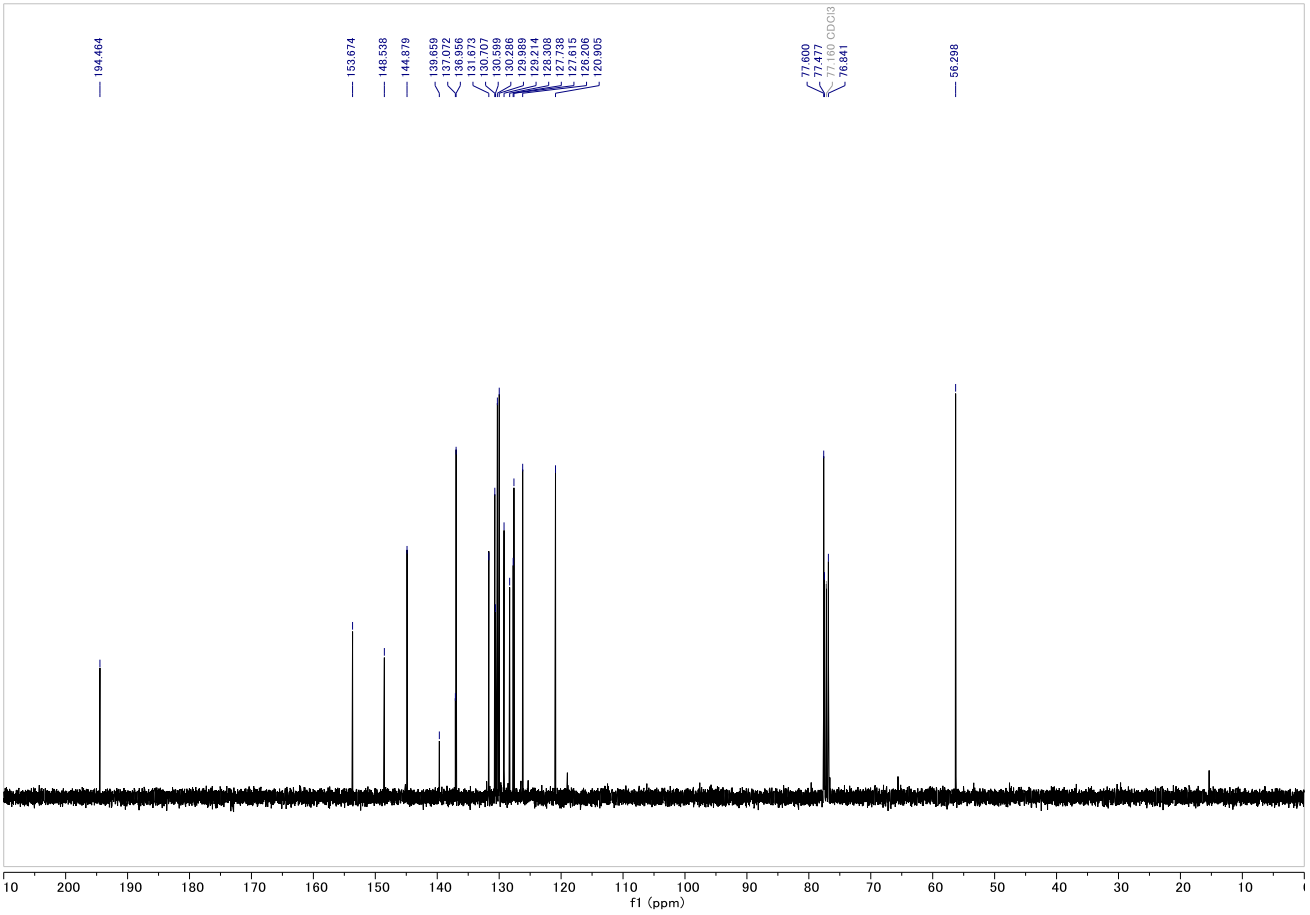
^{13}C NMR **1m**



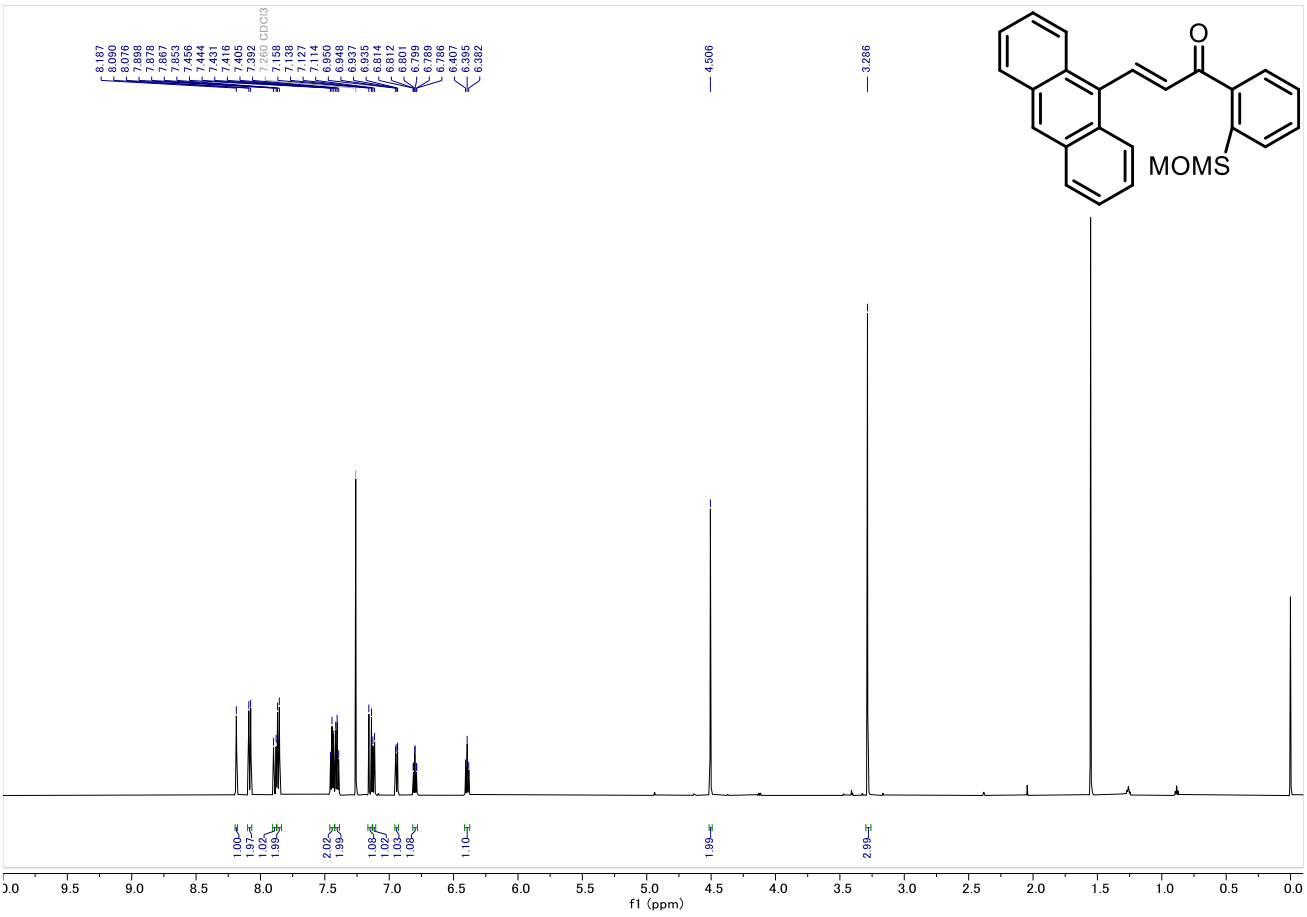
^{1}H NMR **1n**



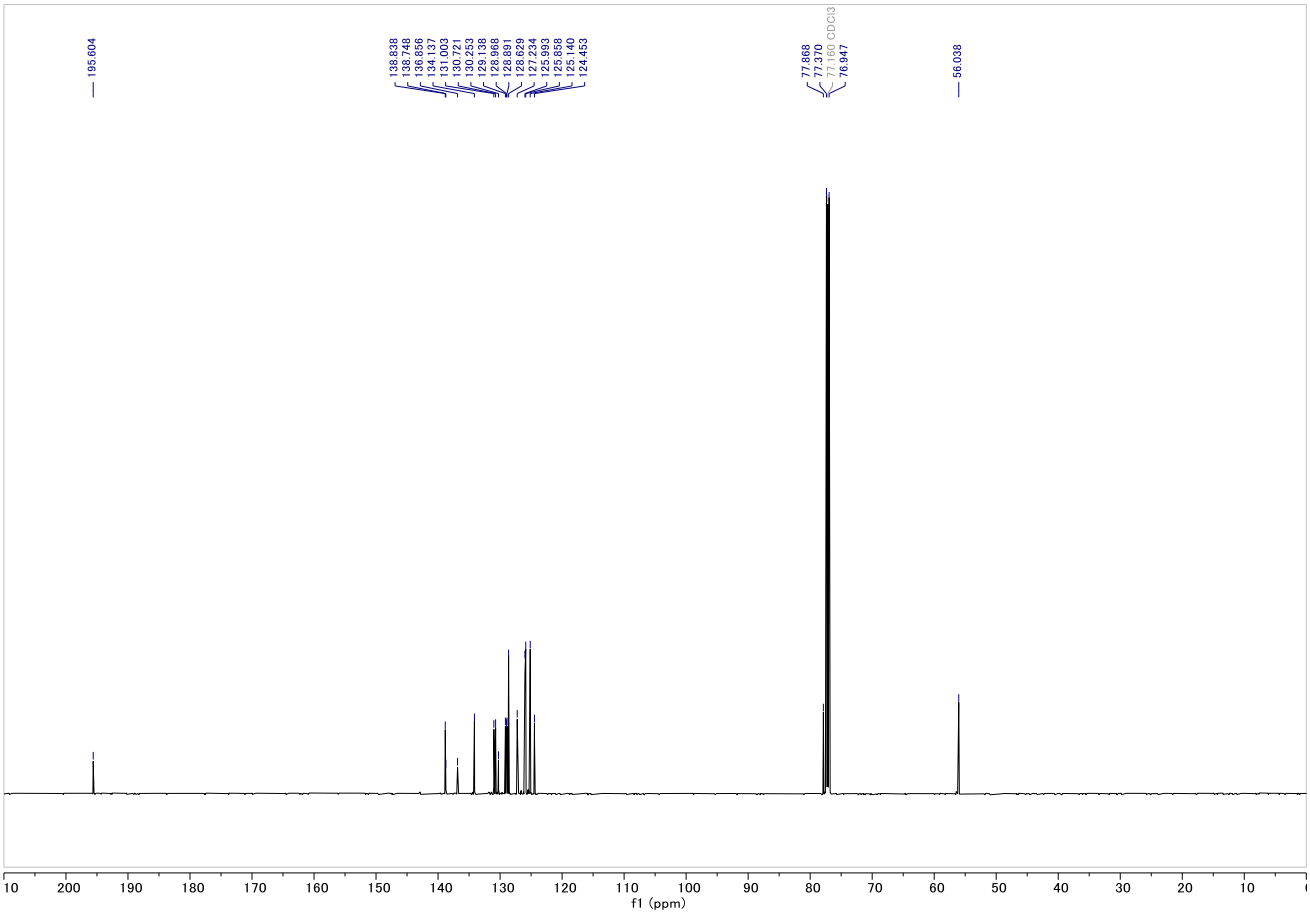
^{13}C NMR **1n**



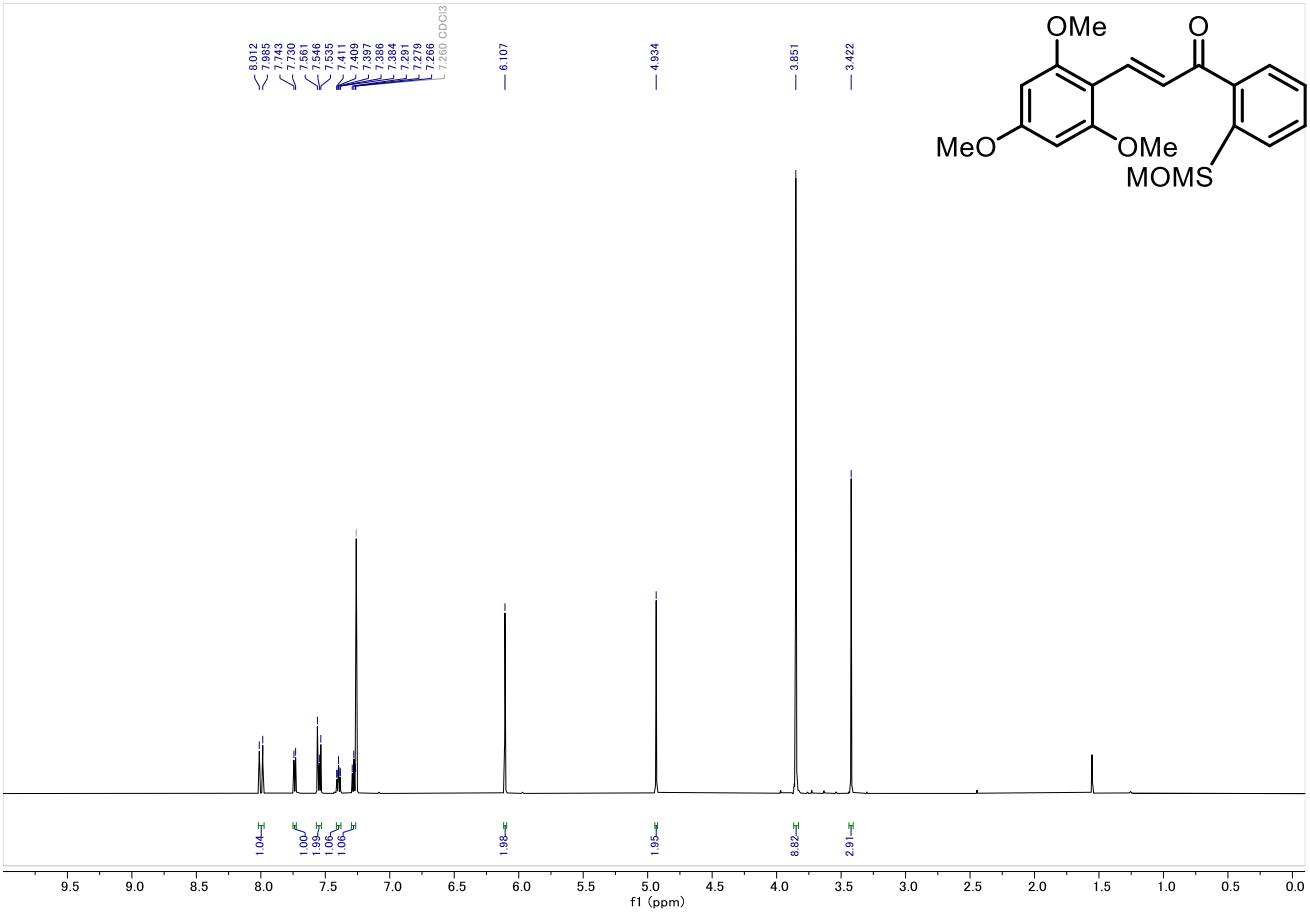
^{1}H NMR **1o**



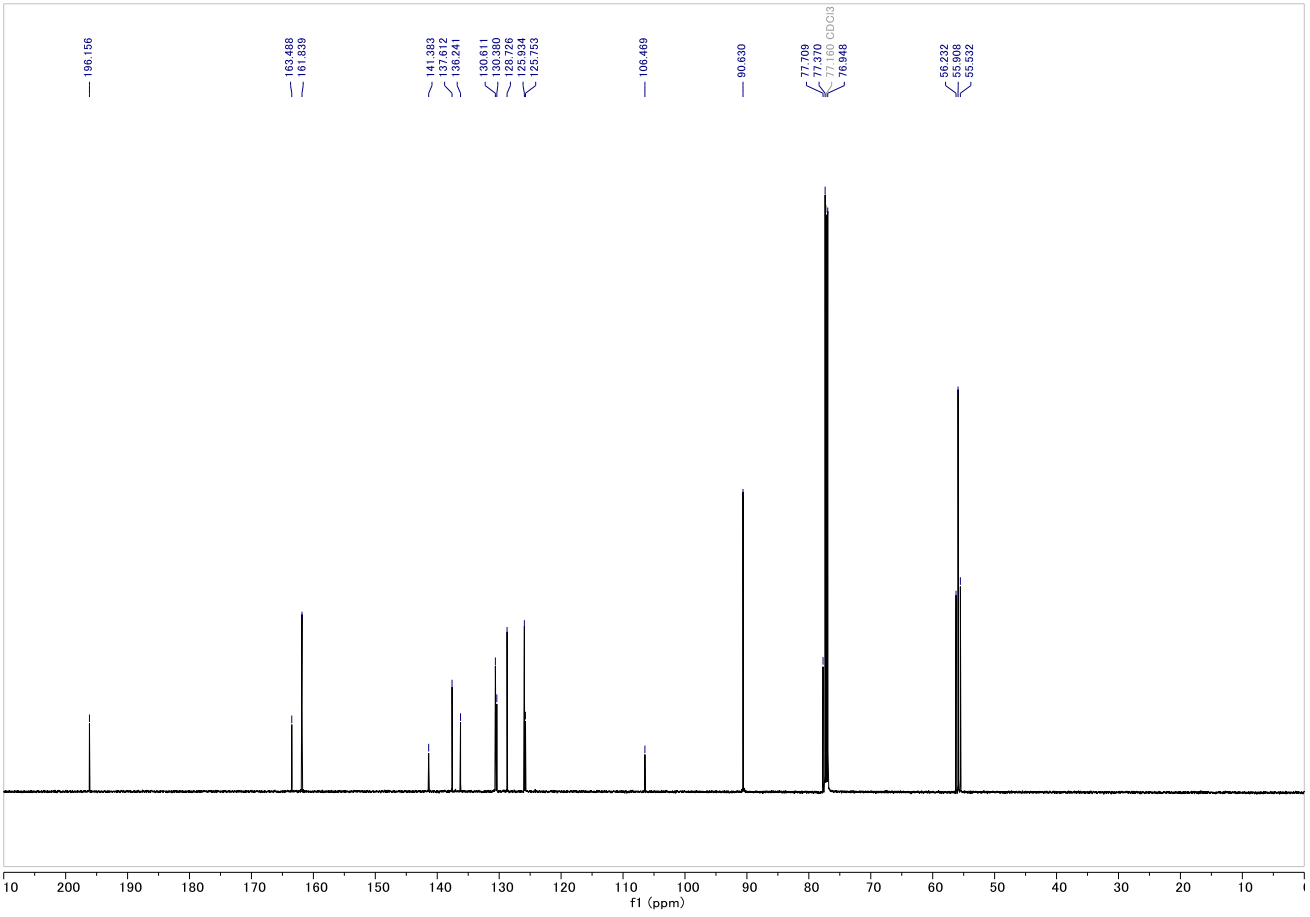
^{13}C NMR **1o**



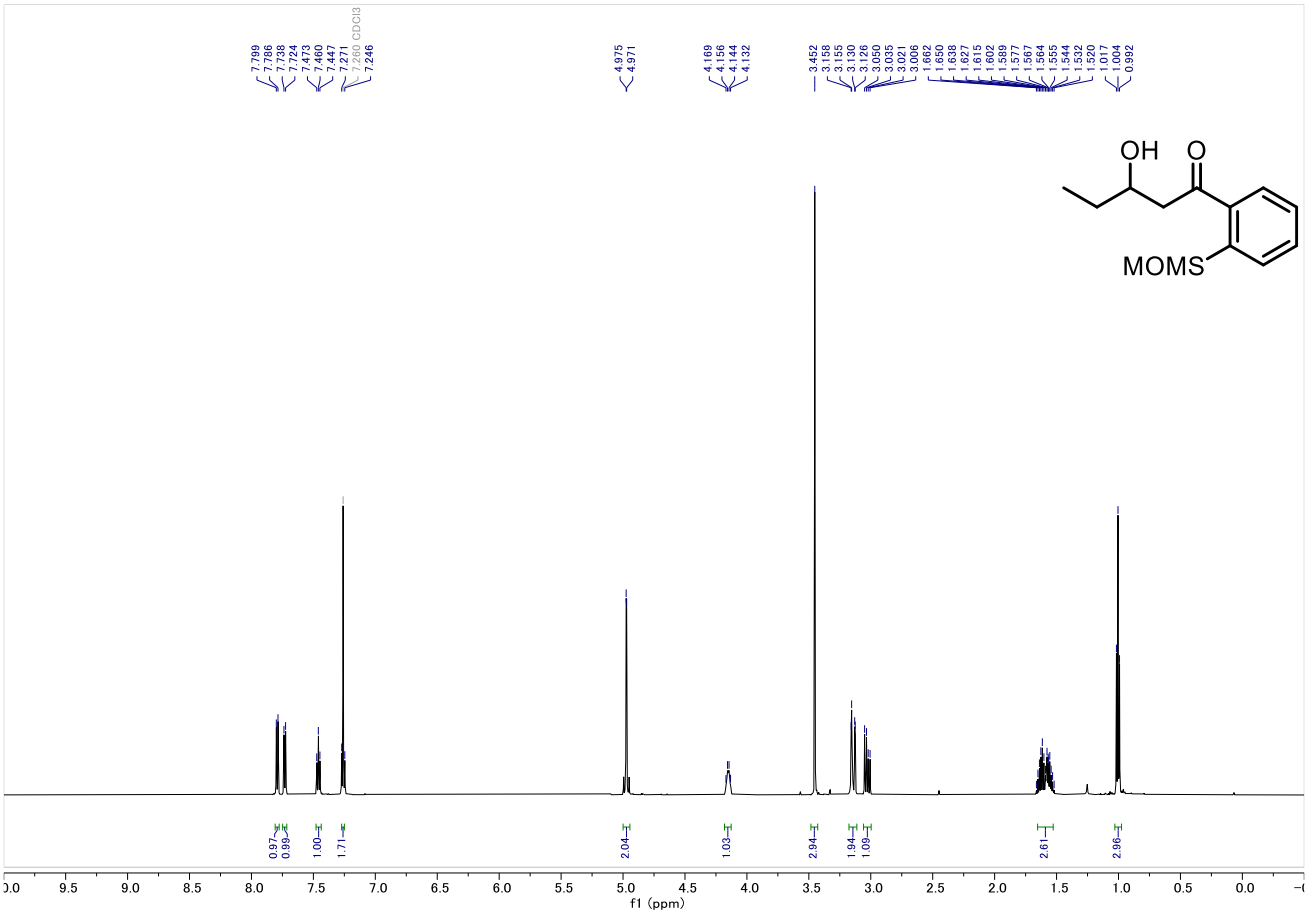
^{1}H NMR **1p**



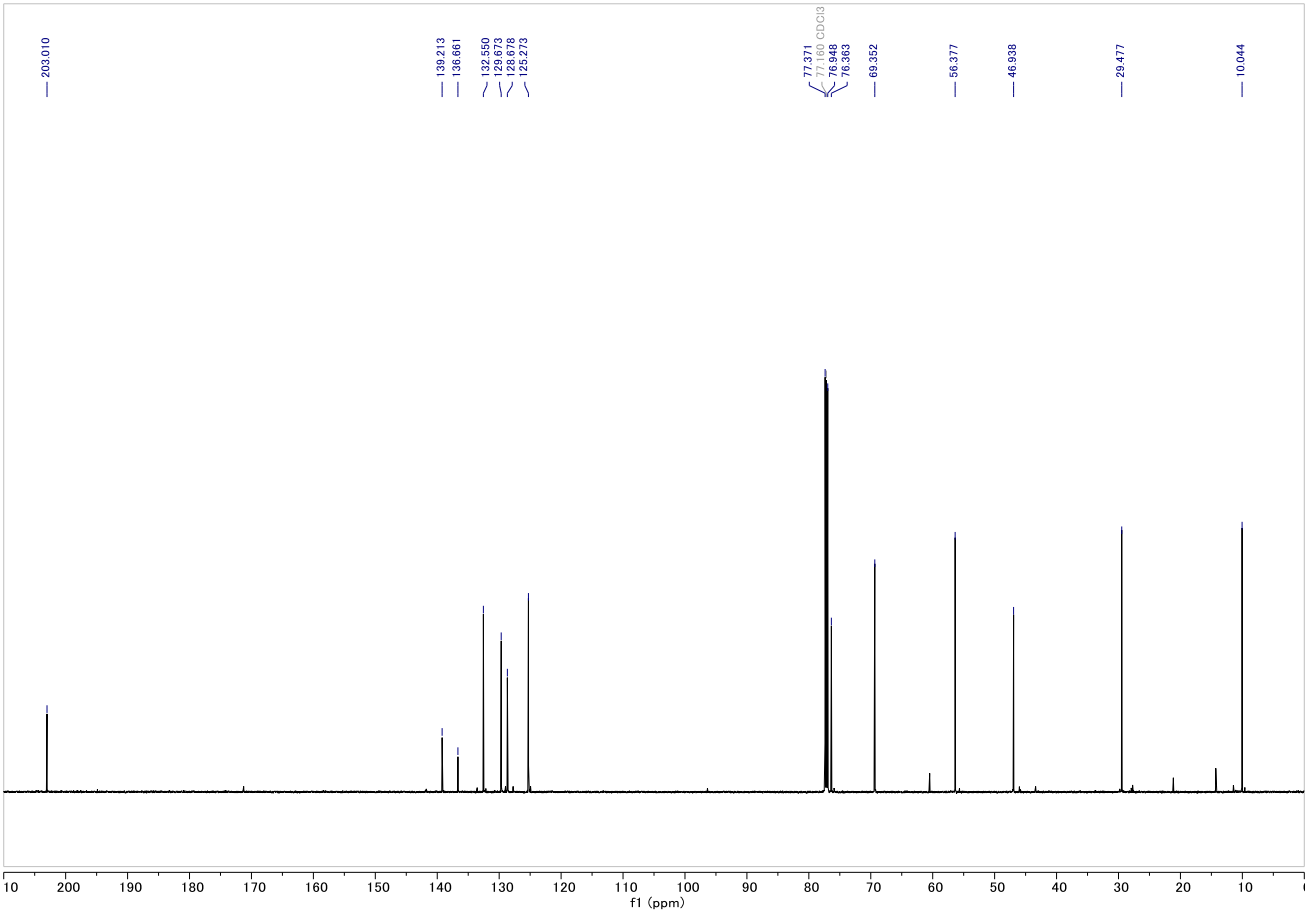
^{13}C NMR **1p**



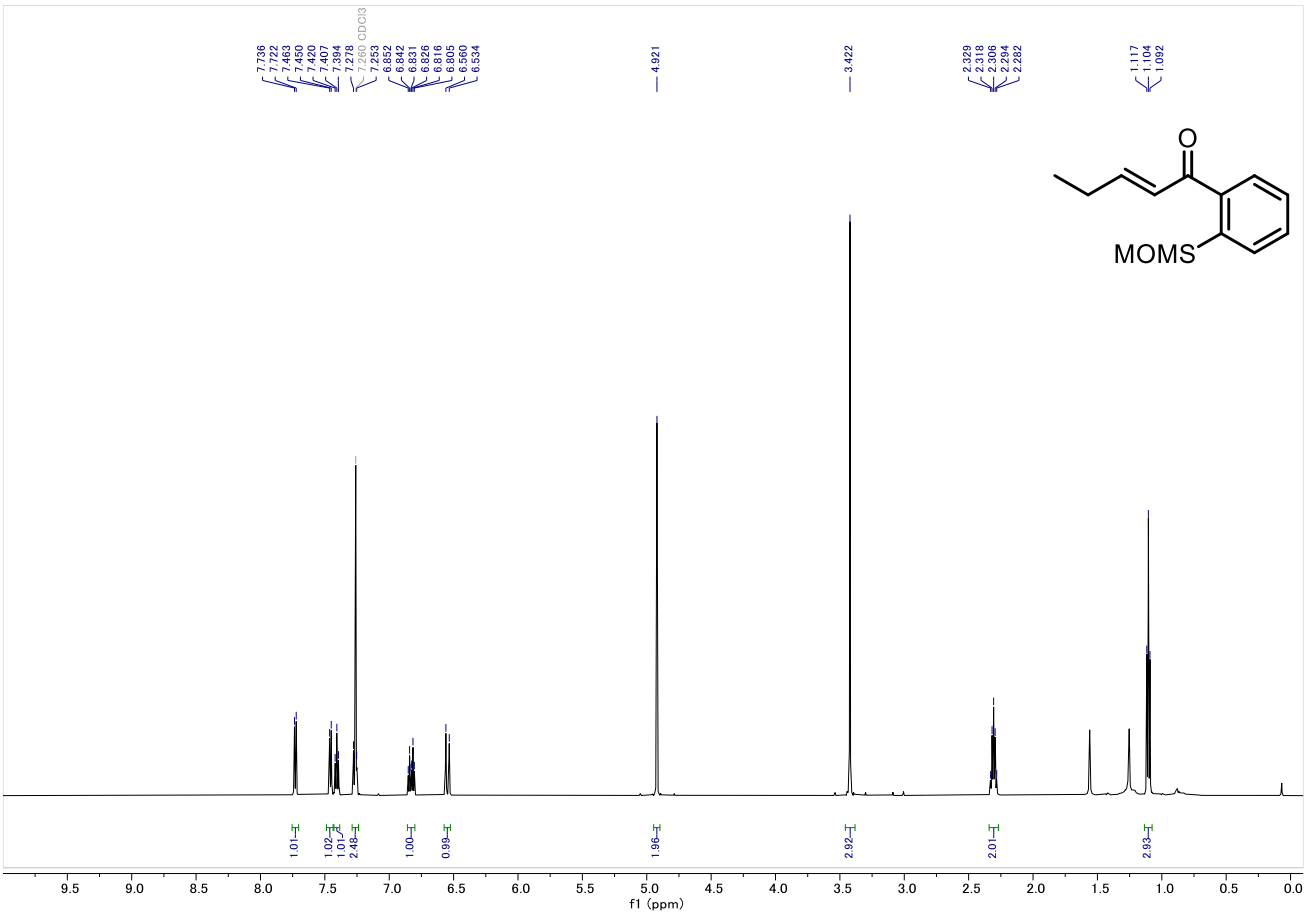
^{1}H NMR **8**



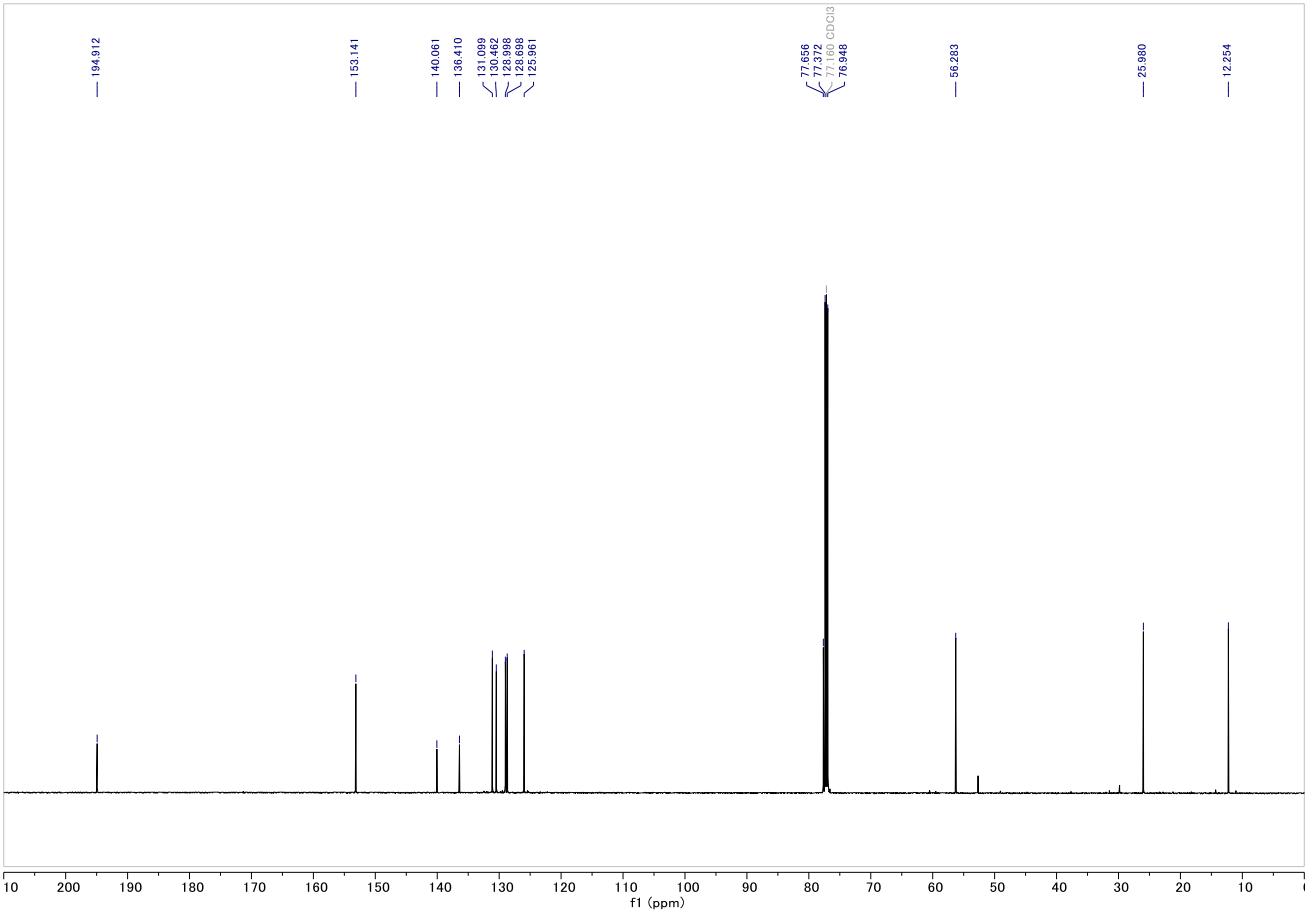
^{13}C NMR **8**



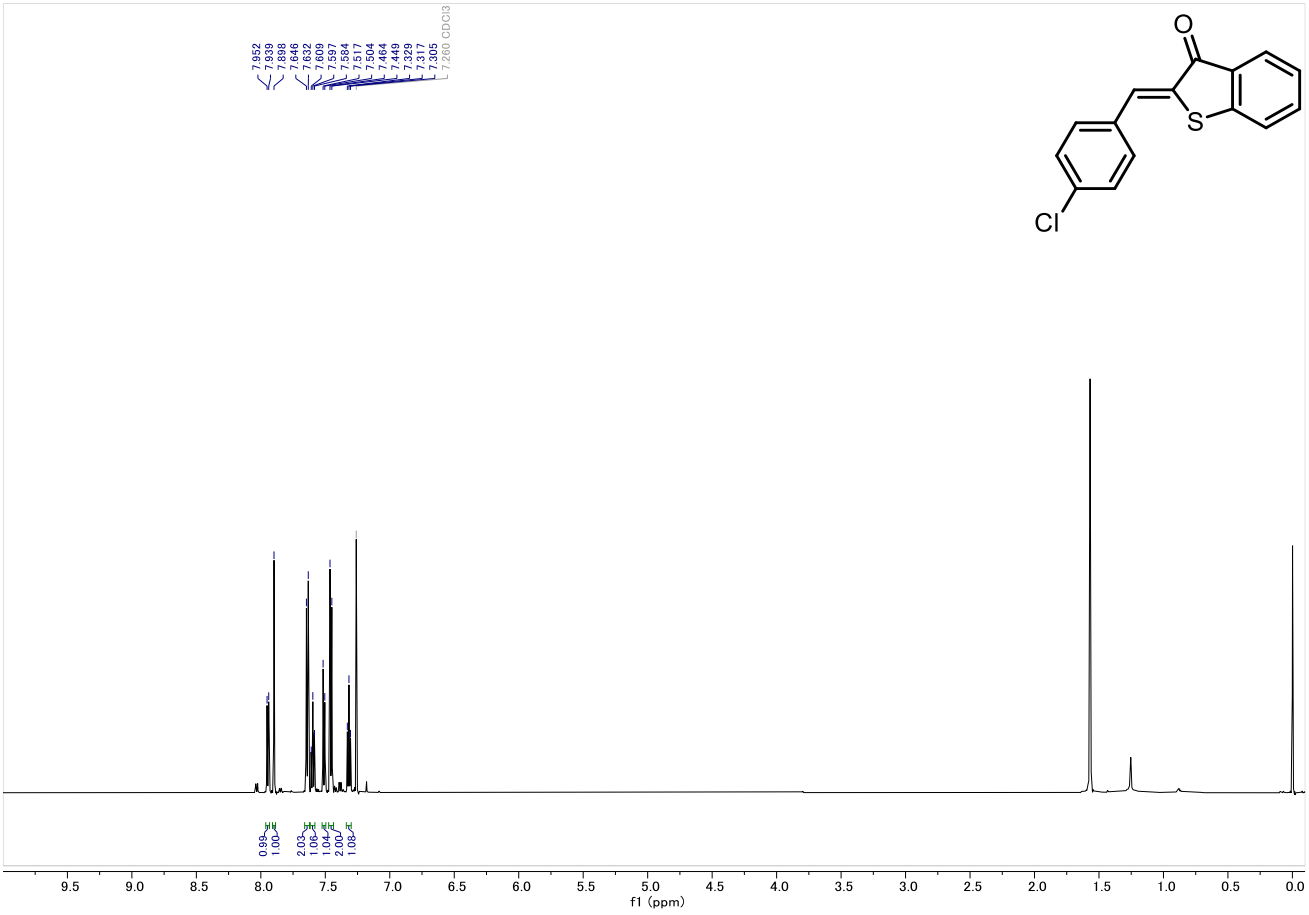
^{1}H NMR **1q**



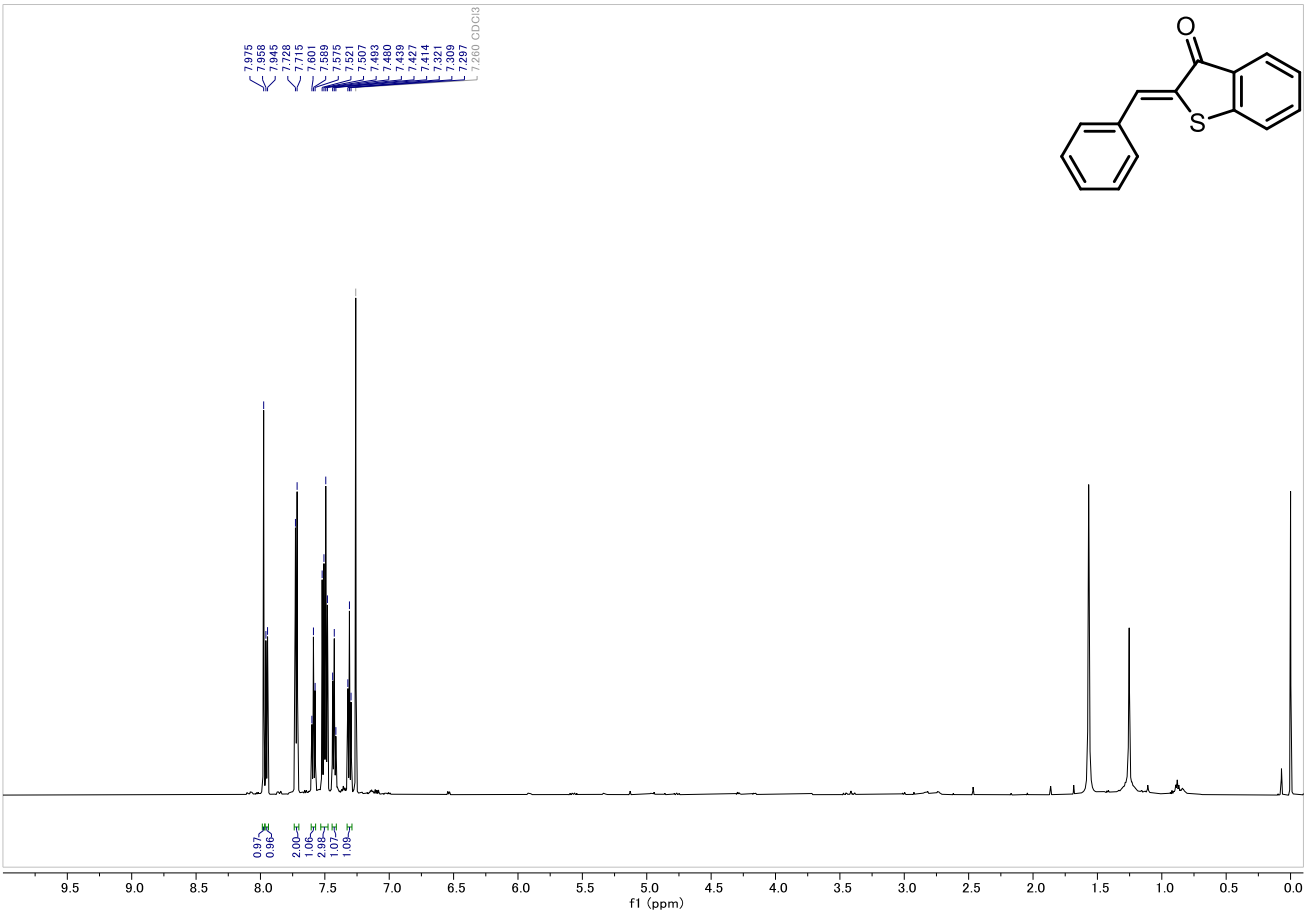
^{13}C NMR **1q**



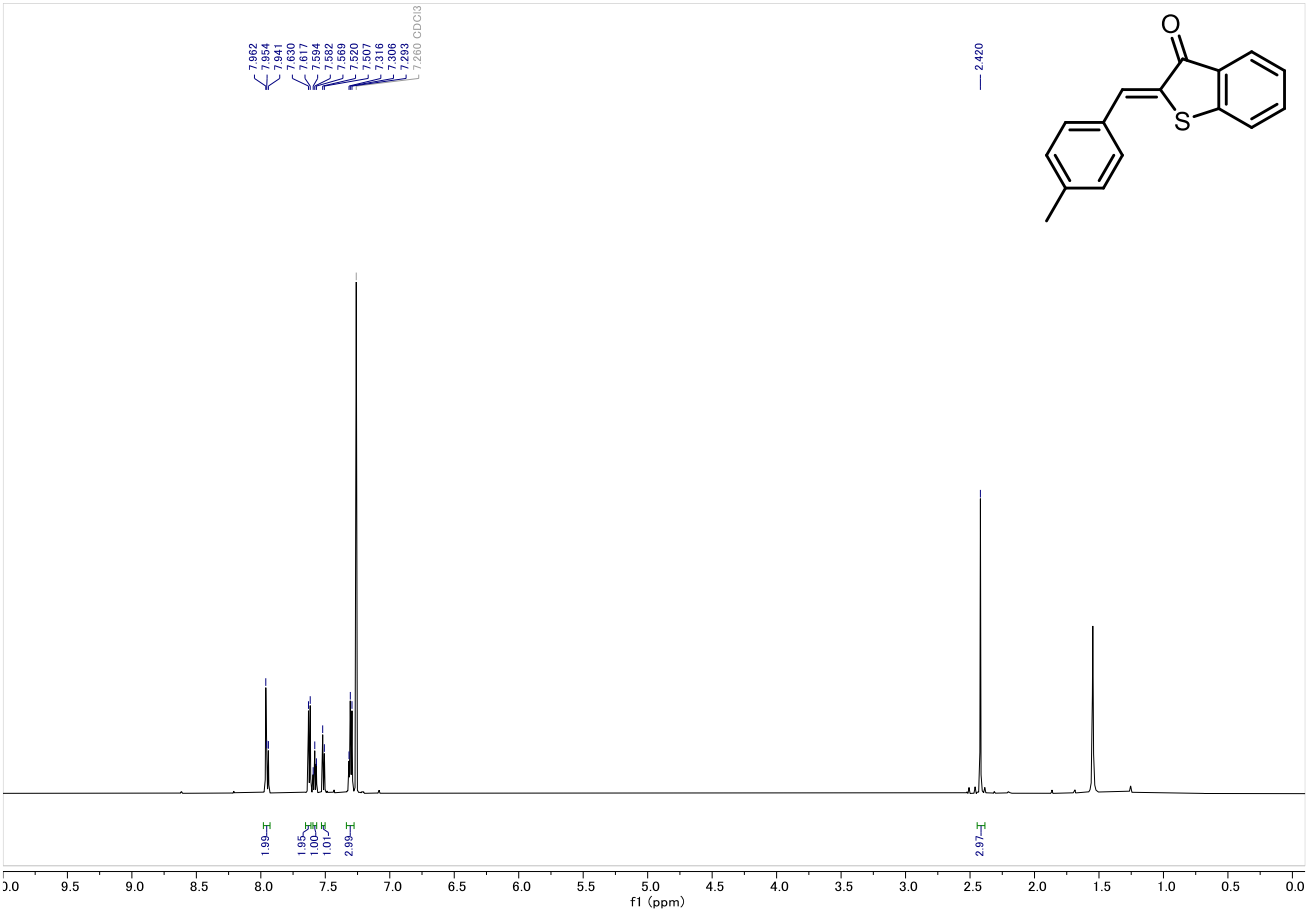
^{1}H NMR **2a**



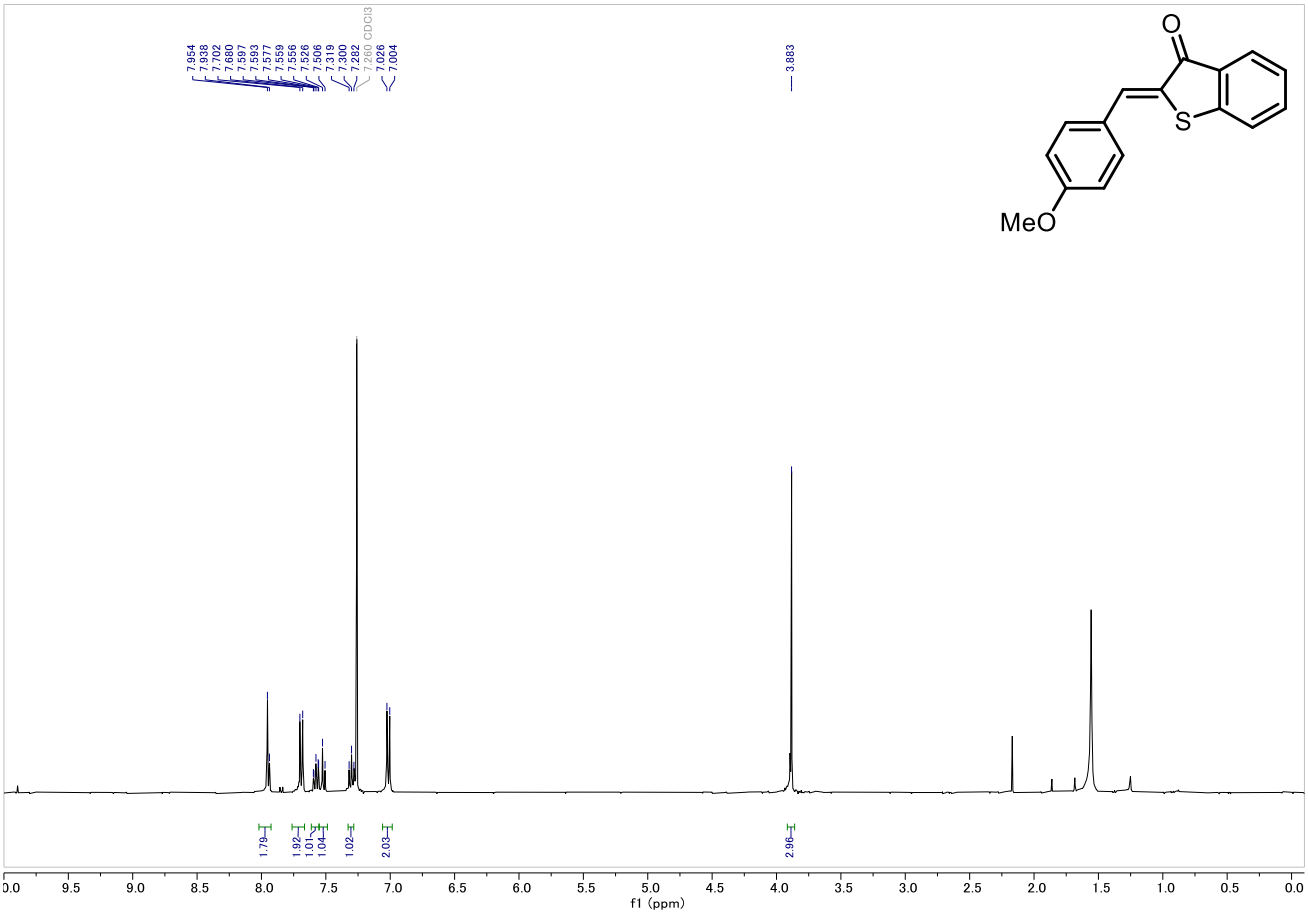
^{1}H NMR **2b**



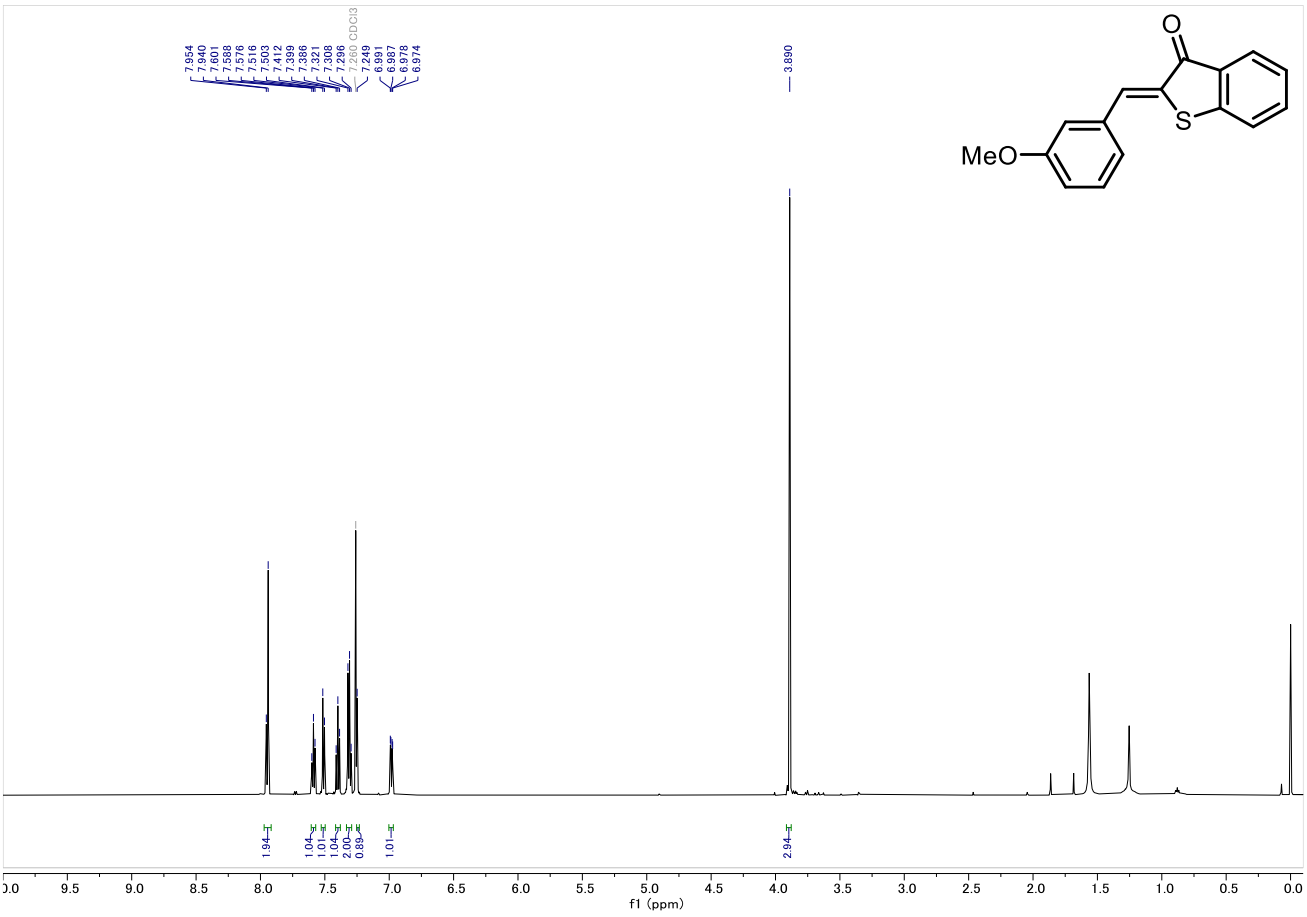
^{1}H NMR **2c**



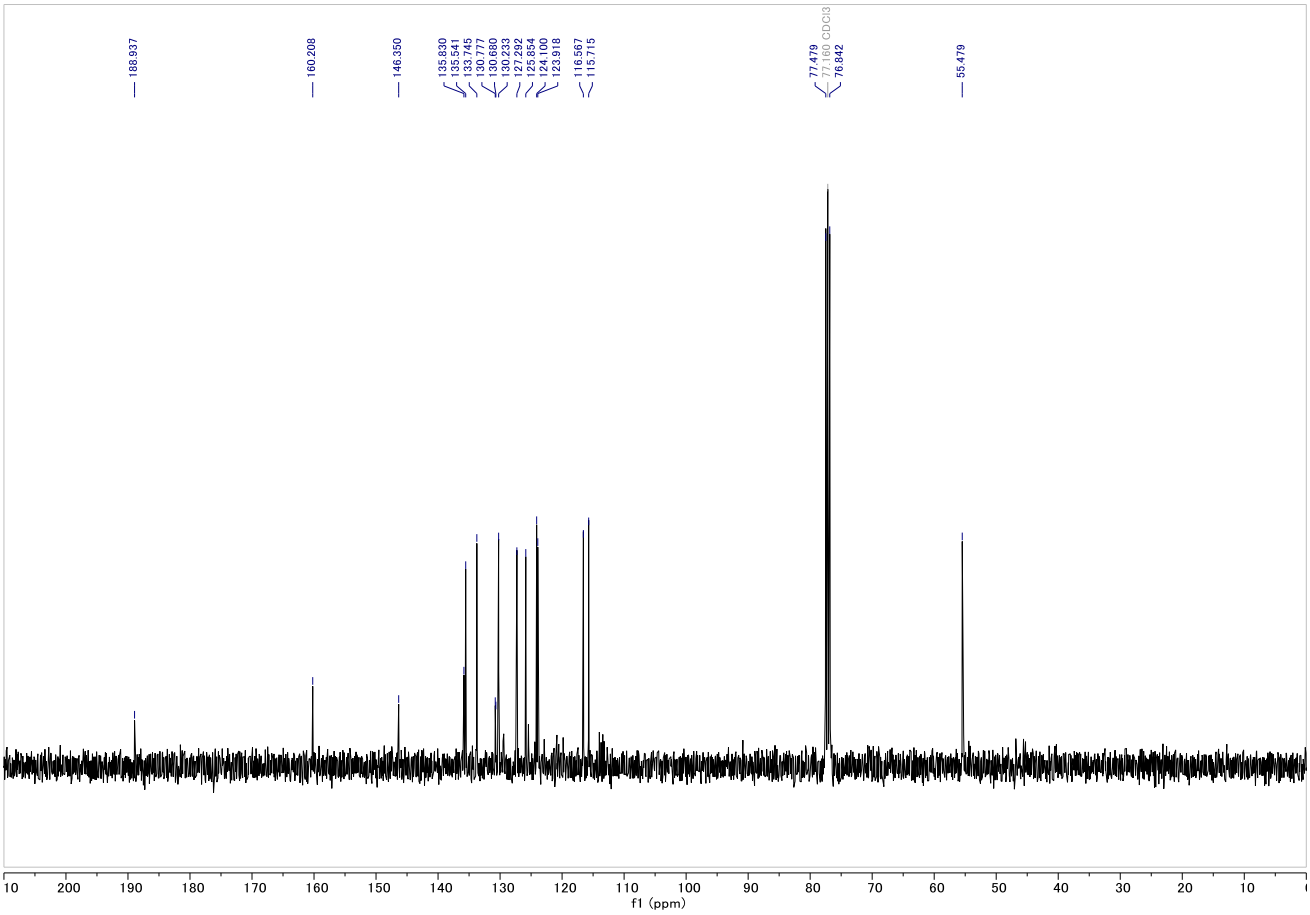
^{1}H NMR **2d**



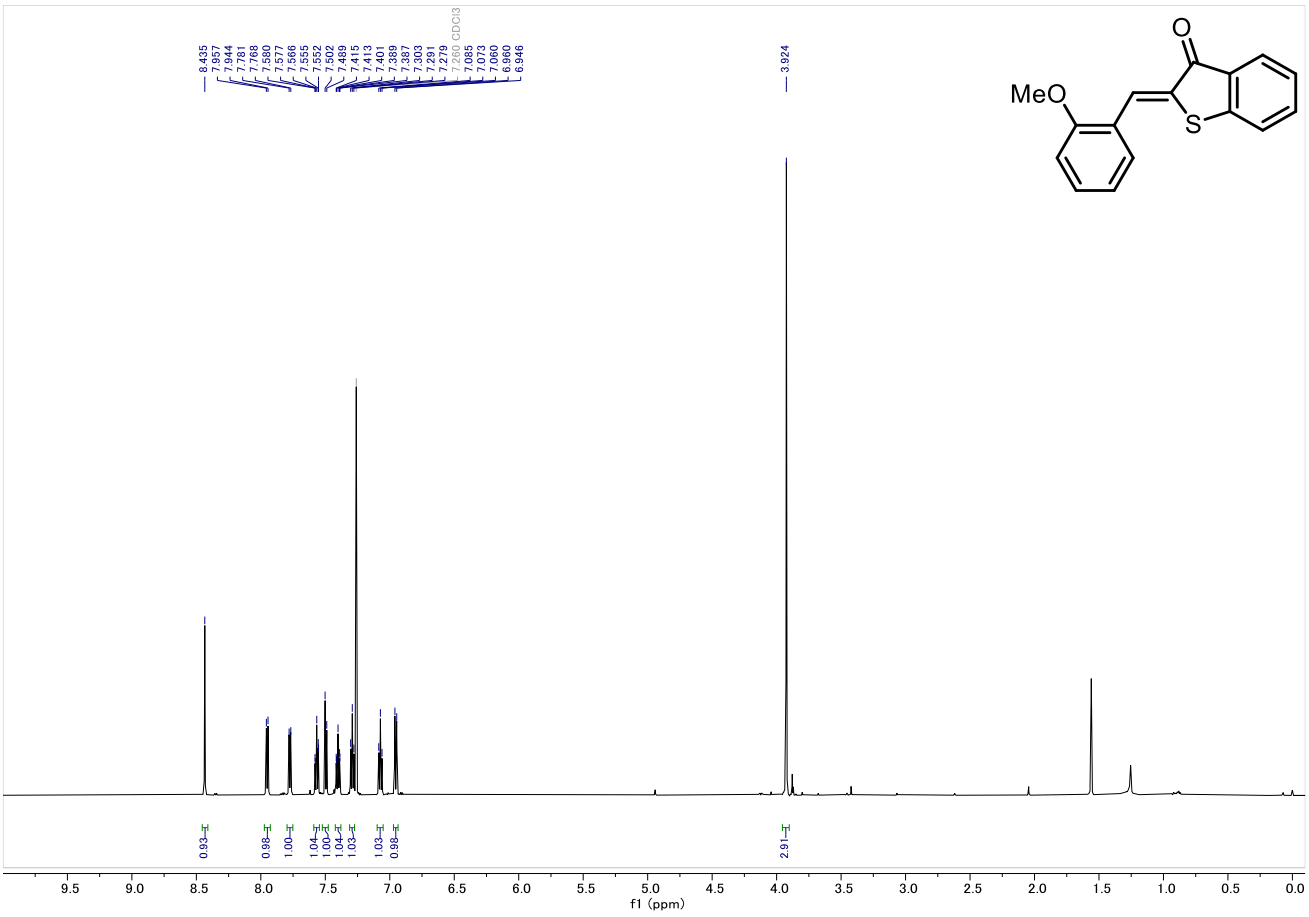
^{1}H NMR **2e**



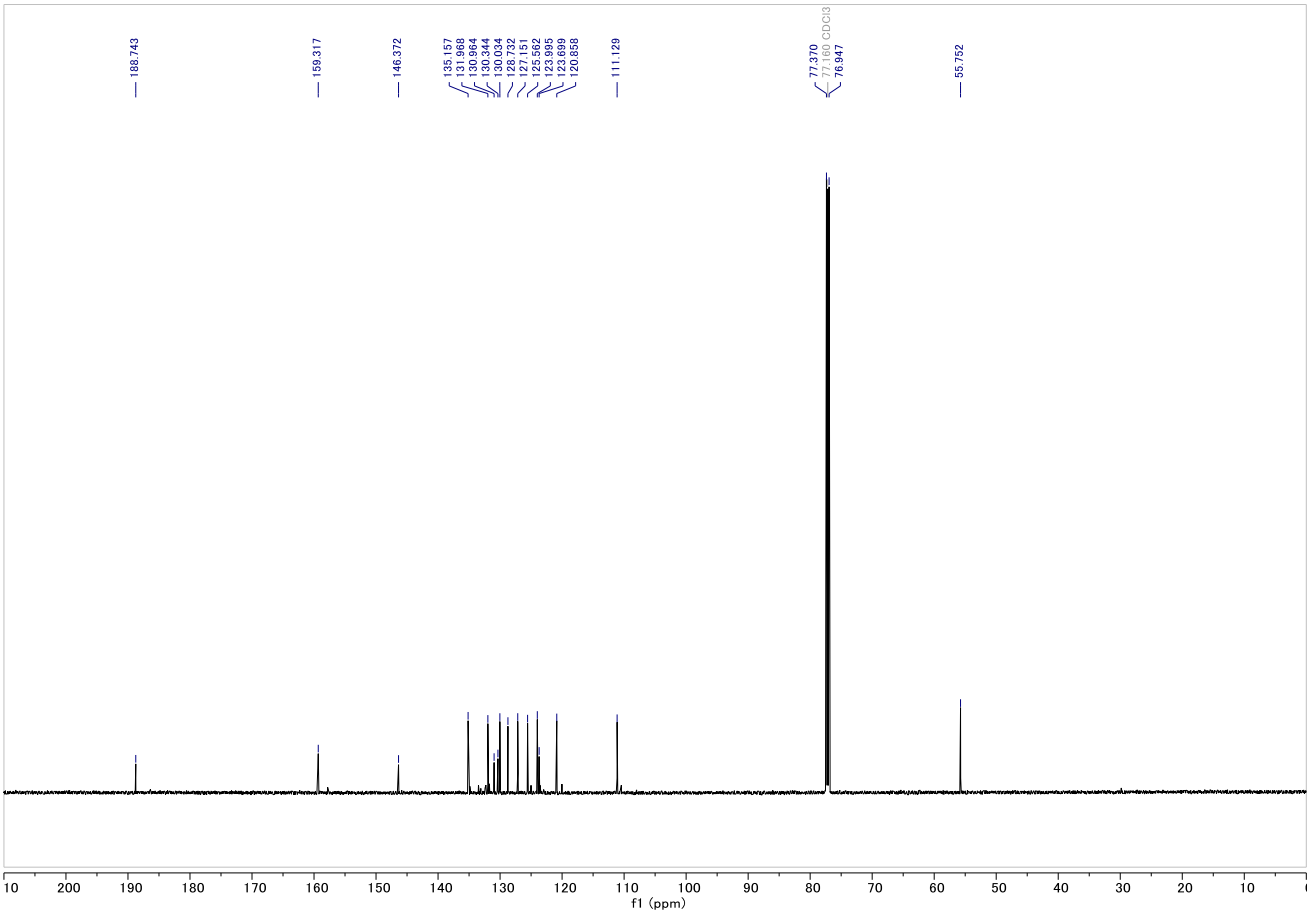
^{13}C NMR **2e**



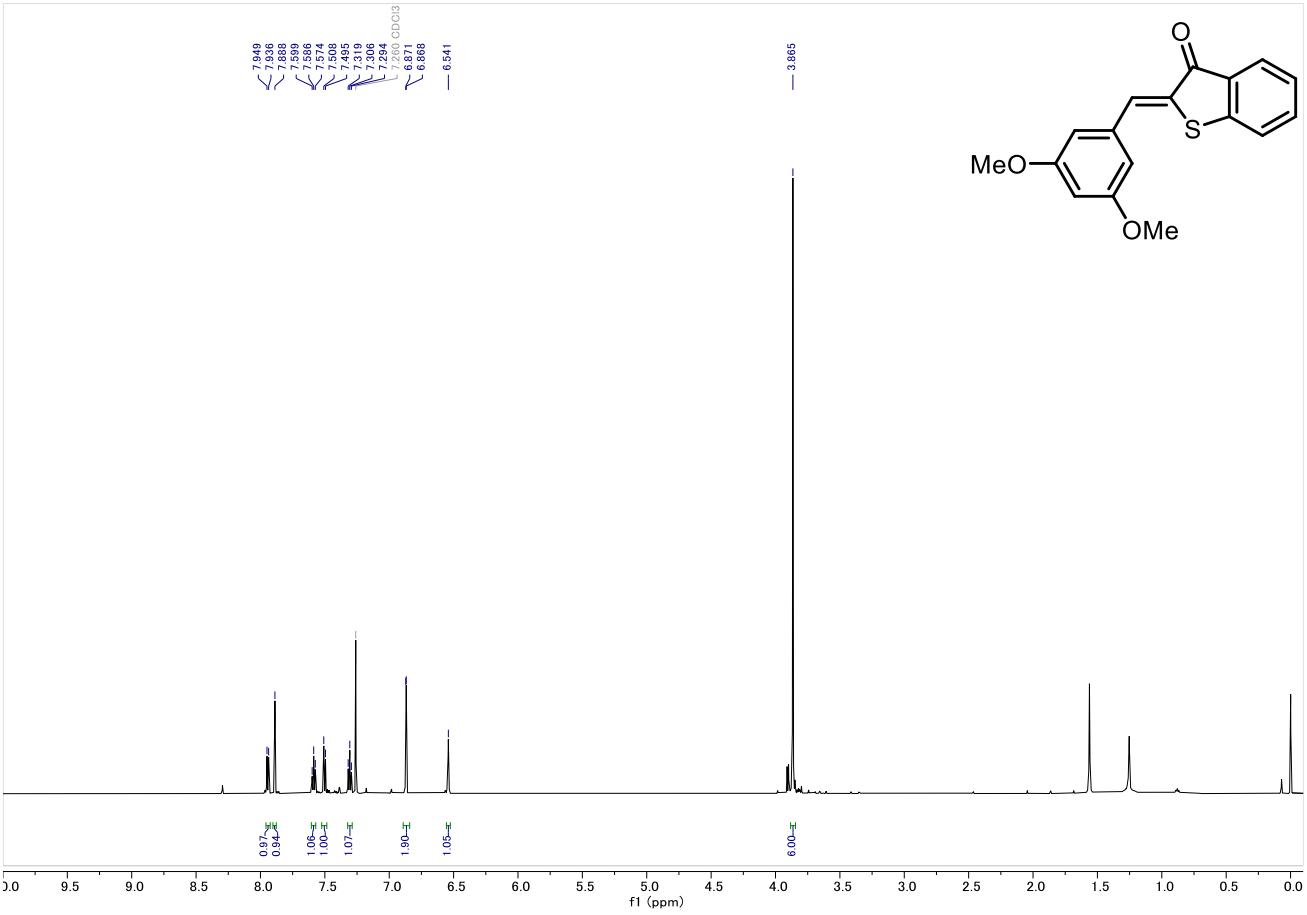
^{1}H NMR **2f**



^{13}C NMR **2f**



^{1}H NMR **2g**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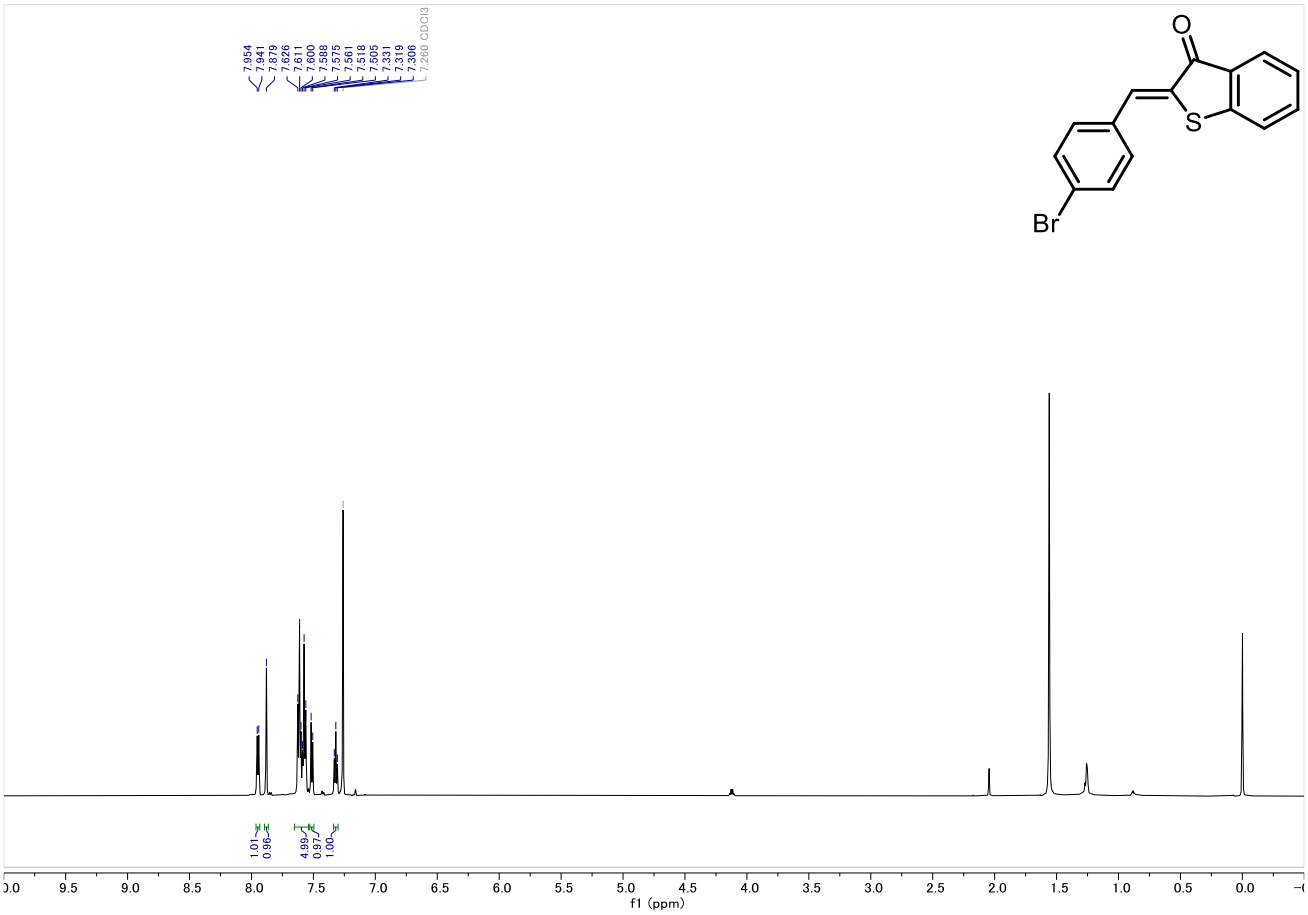
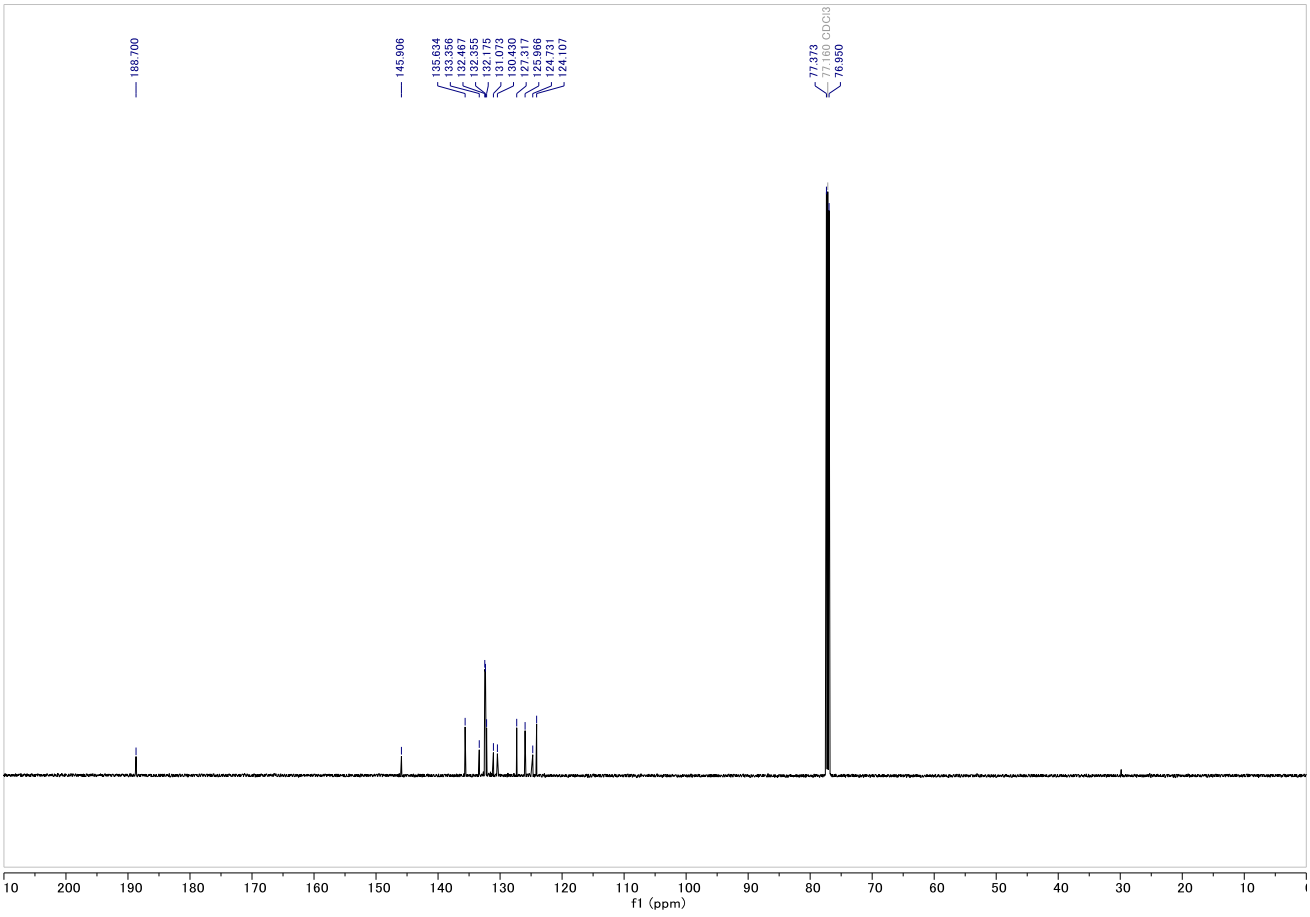
7.936
7.888
7.599
7.596
7.574
7.508
7.495
7.319
7.306
7.294
7.260 CDCl3
6.871
6.868
6.541
3.865
0.97
0.94
1.06
1.00
1.07
1.90
1.05
6.00
f1 (ppm)
O
S
MeO
OMe

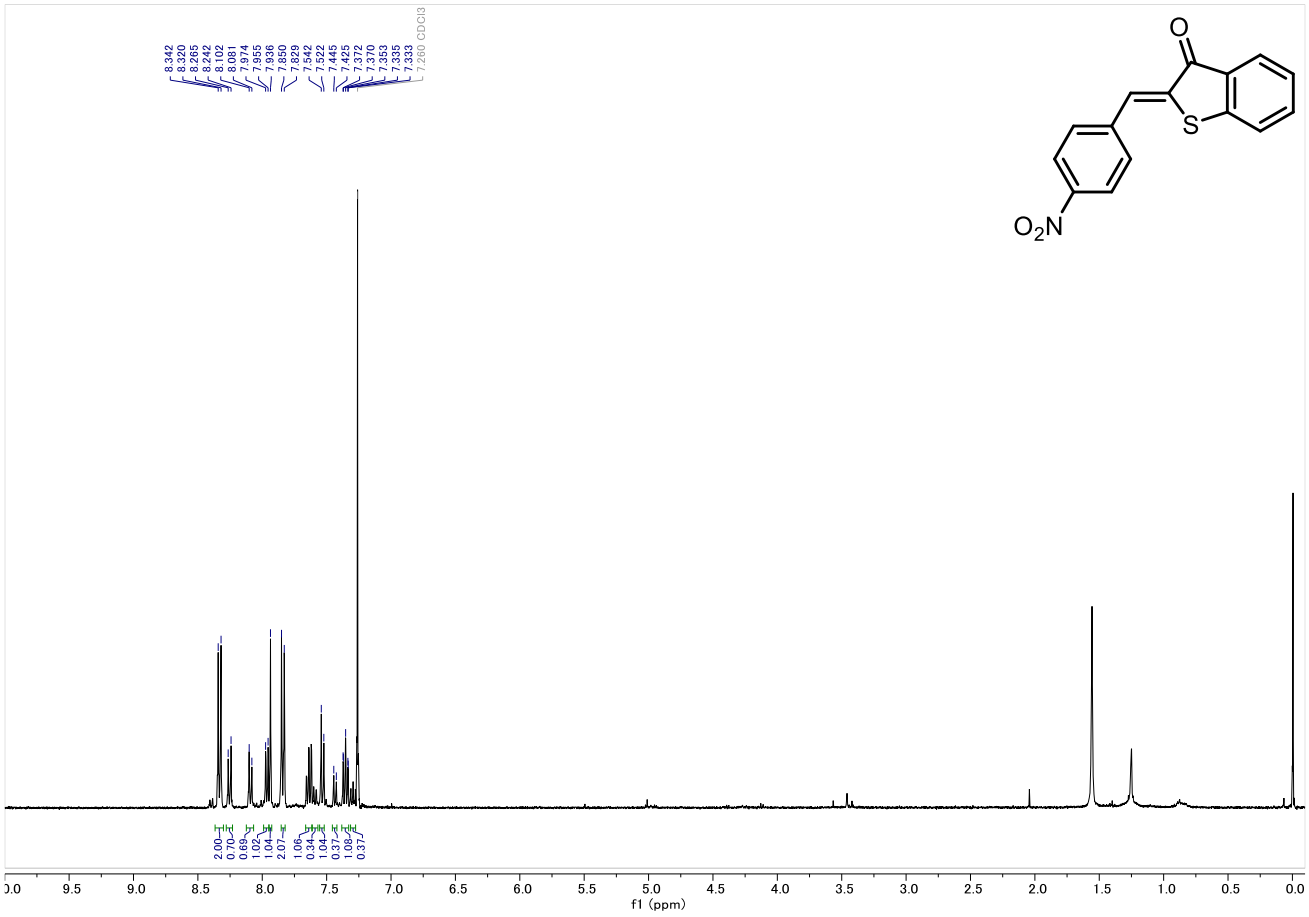
^{1}H NMR **2h**



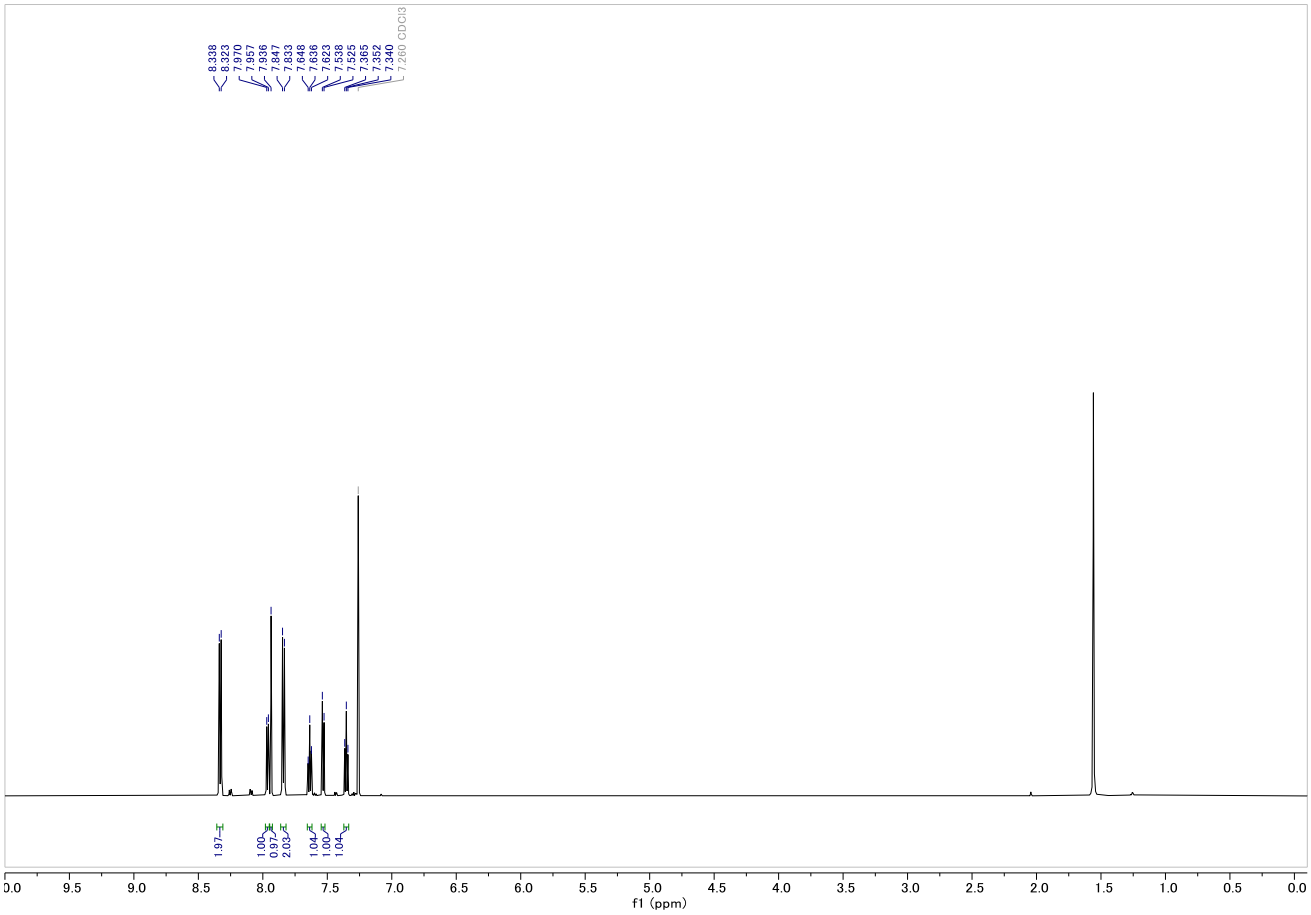
^{13}C NMR **2h**



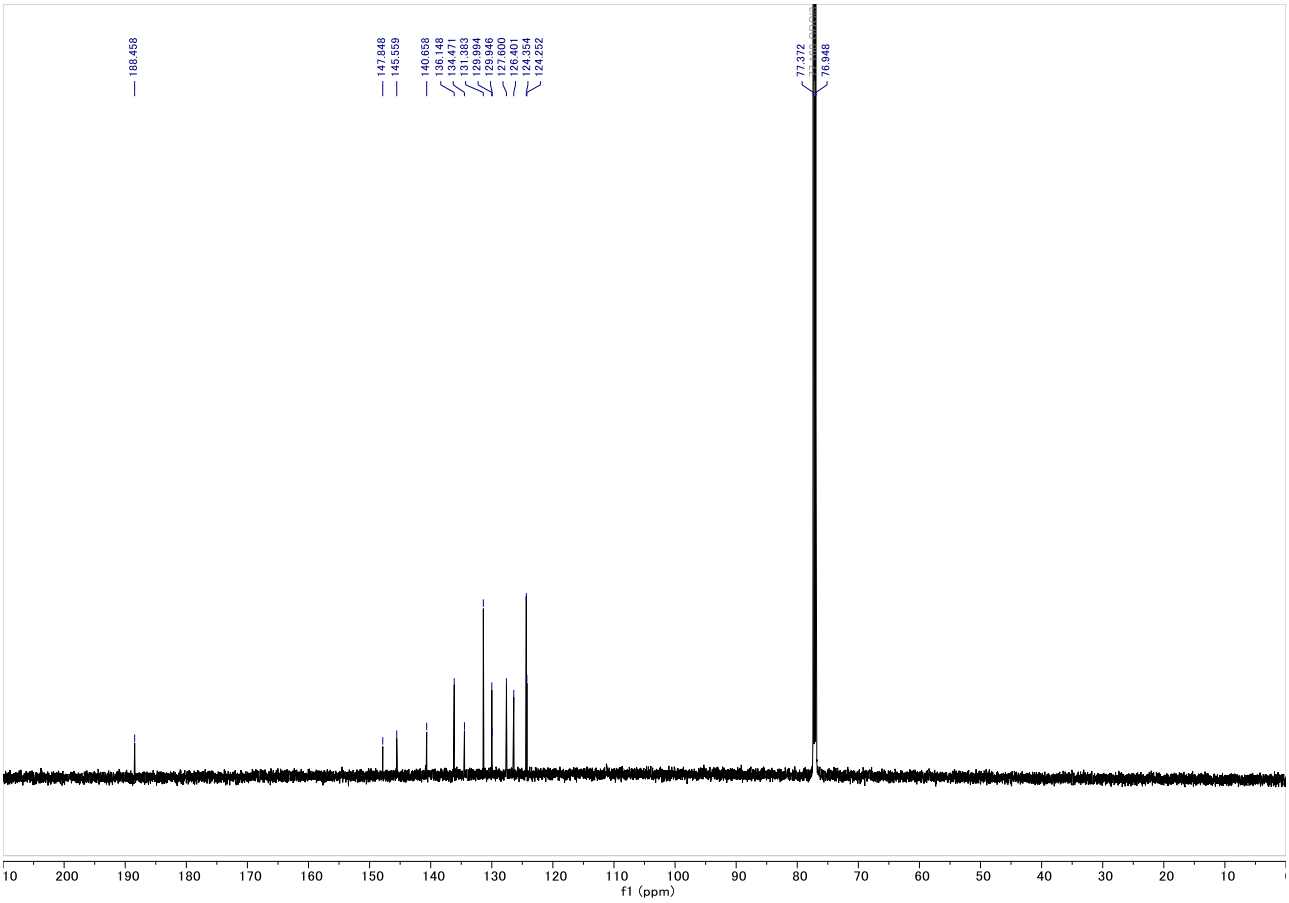
^{1}H NMR **2i** (*EZ* mixture)



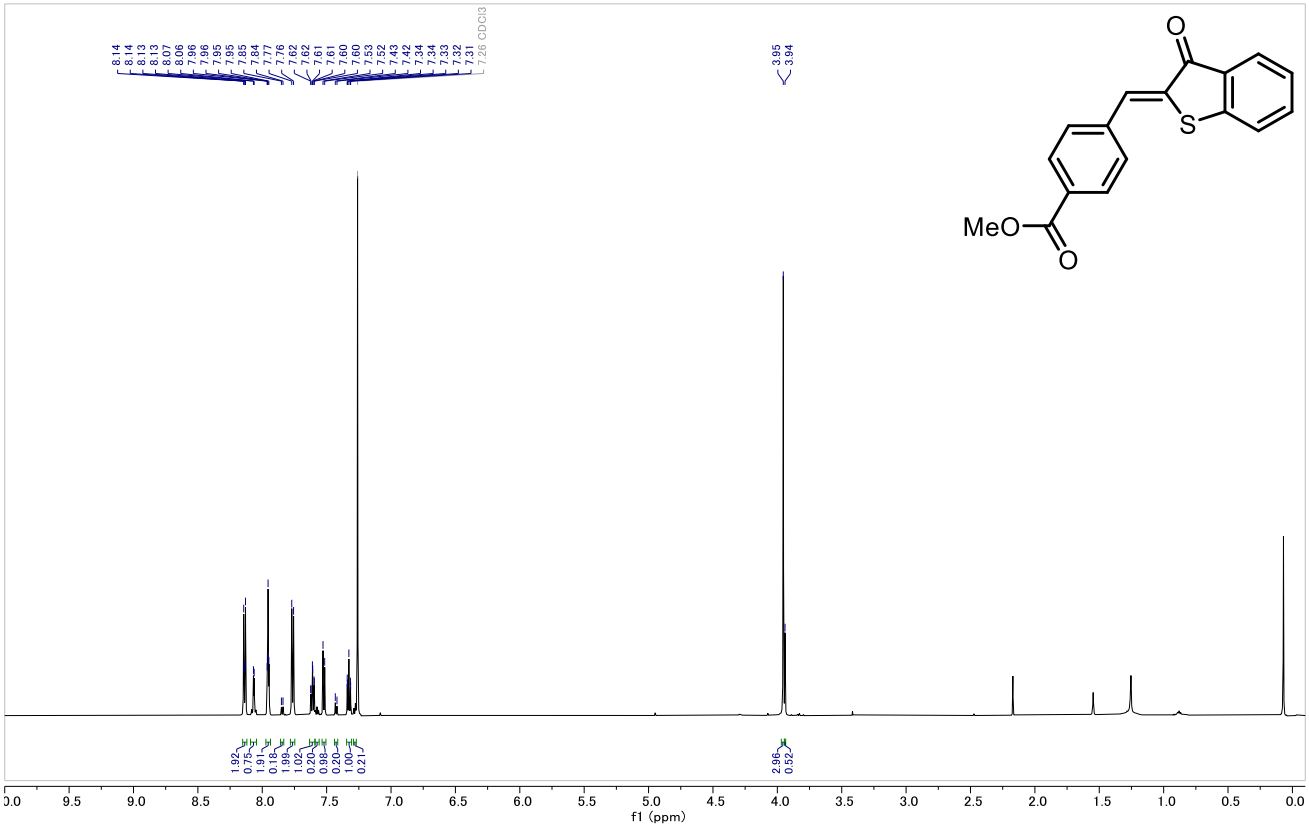
^{1}H NMR **2i (*Z* isomer)**



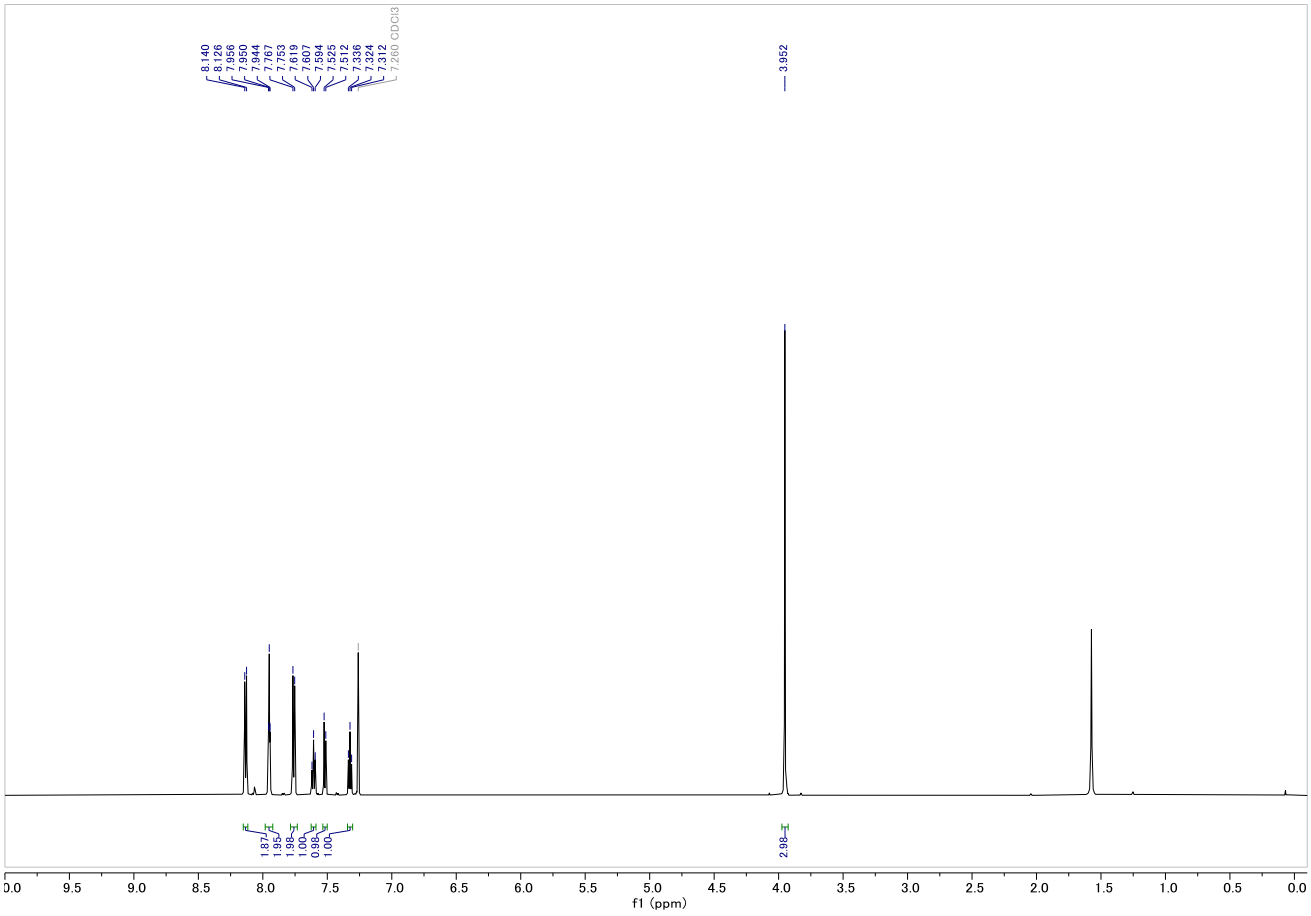
^{13}C NMR **2i (*Z* isomer)**



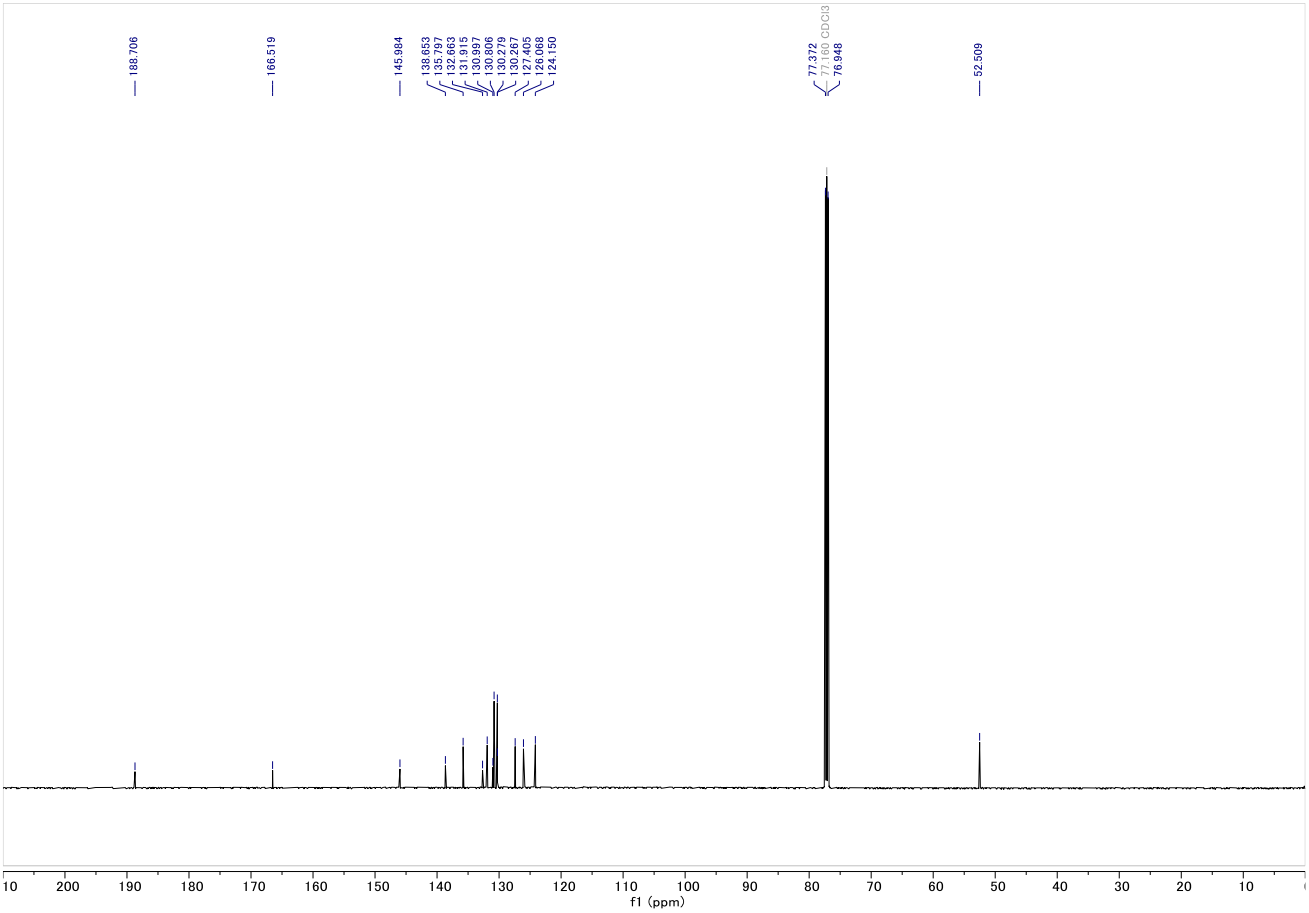
^{1}H NMR **2j** (*EZ* mixture)



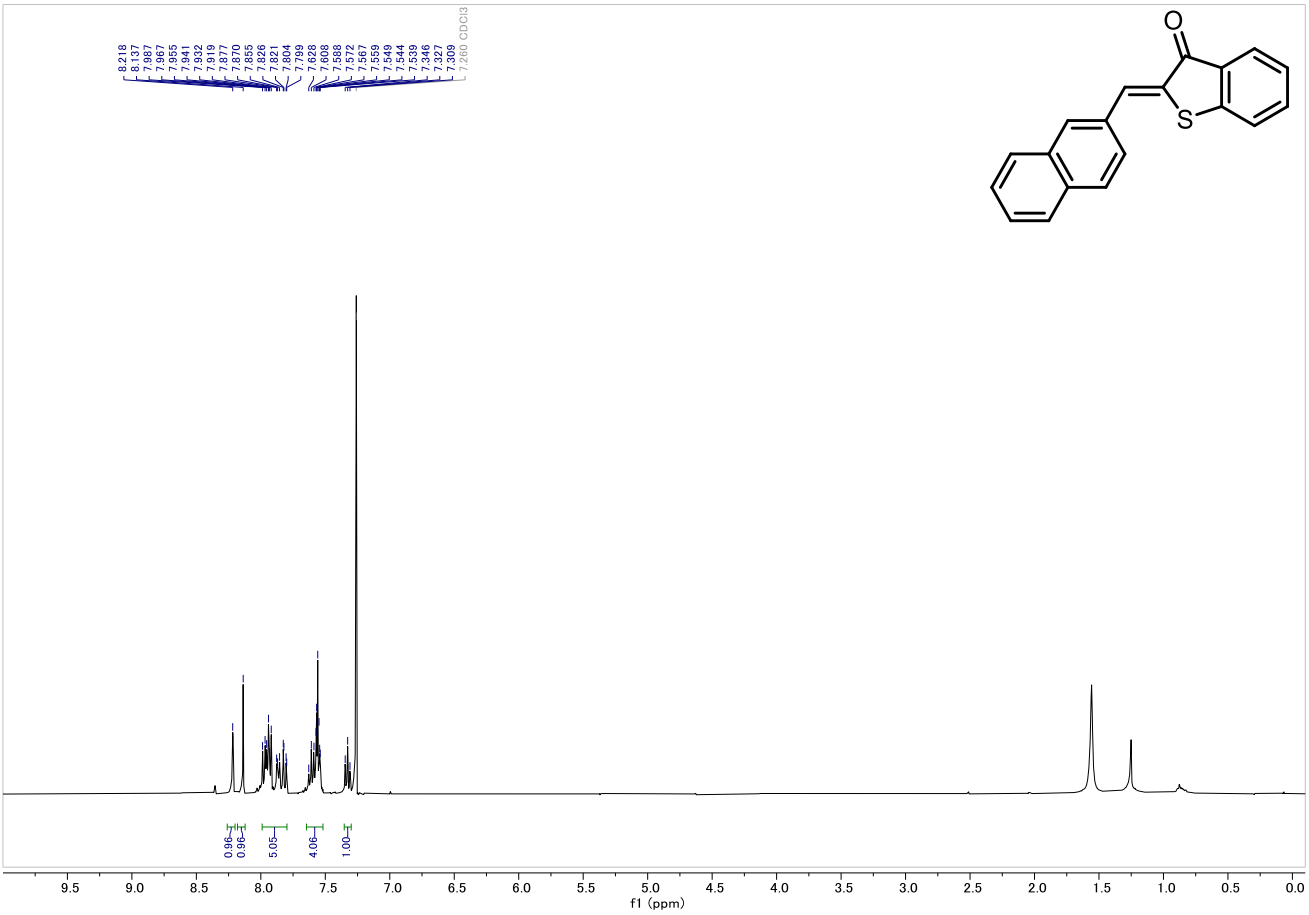
^{1}H NMR **2j (*Z* isomer)**



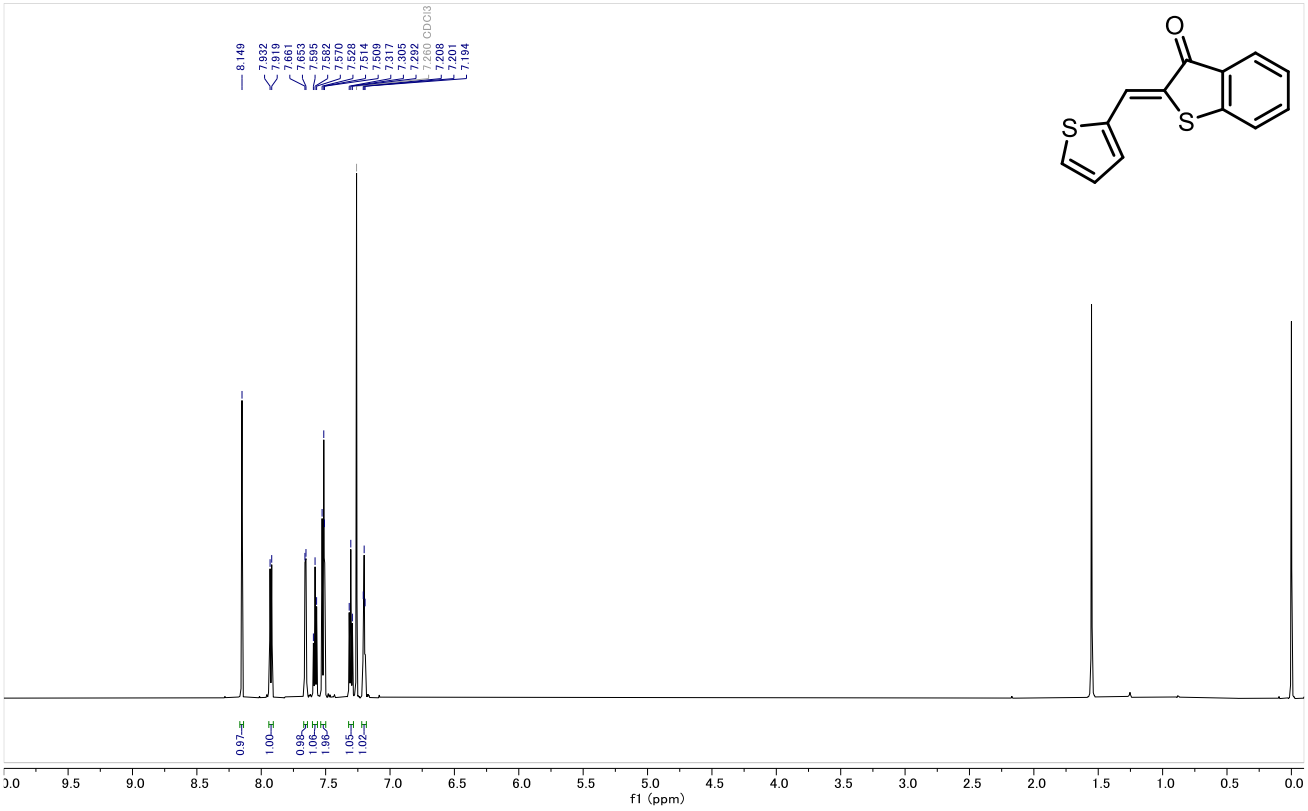
^{13}C NMR **2j (*Z* isomer)**



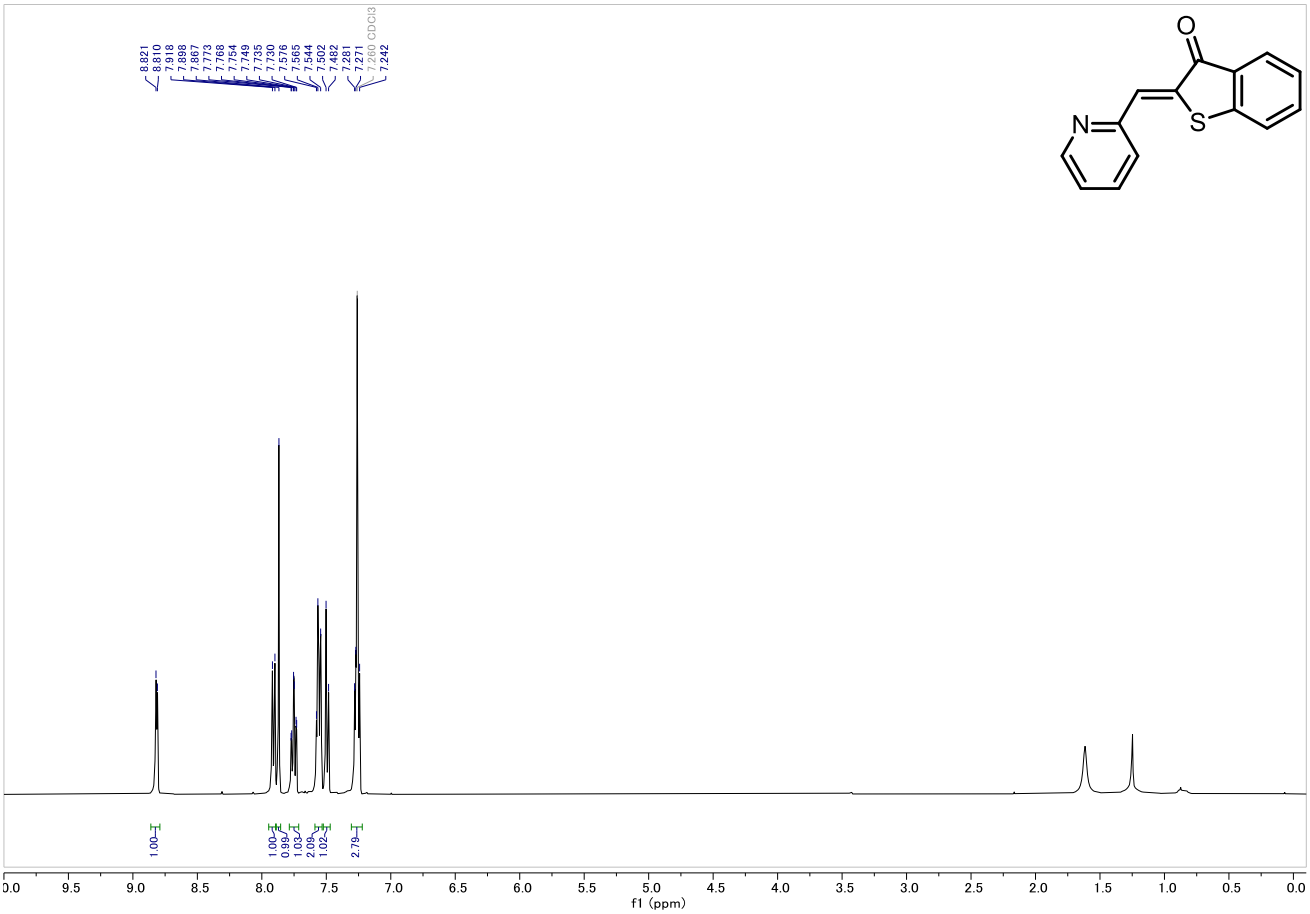
^{1}H NMR **2k**



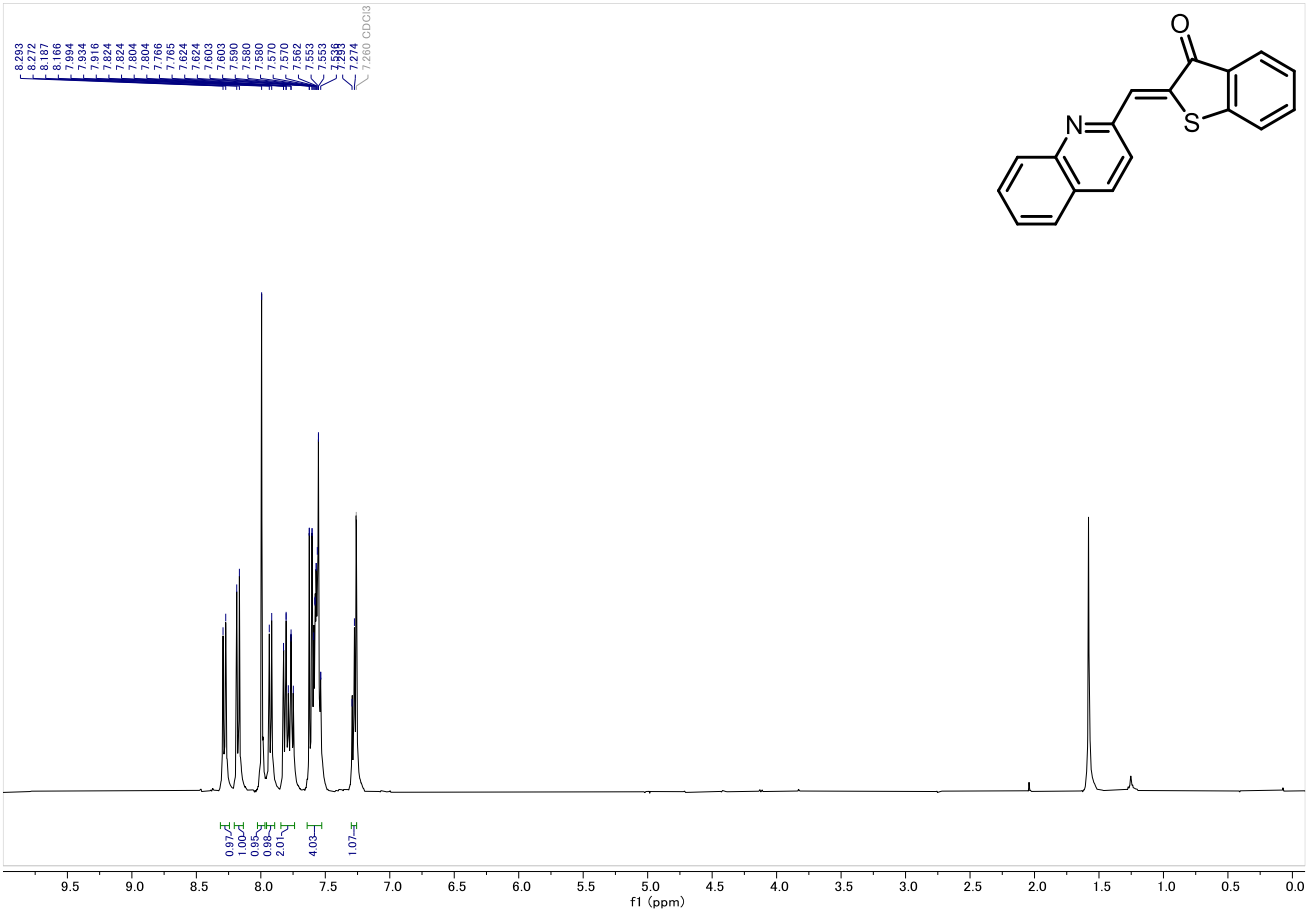
^{1}H NMR **2l**



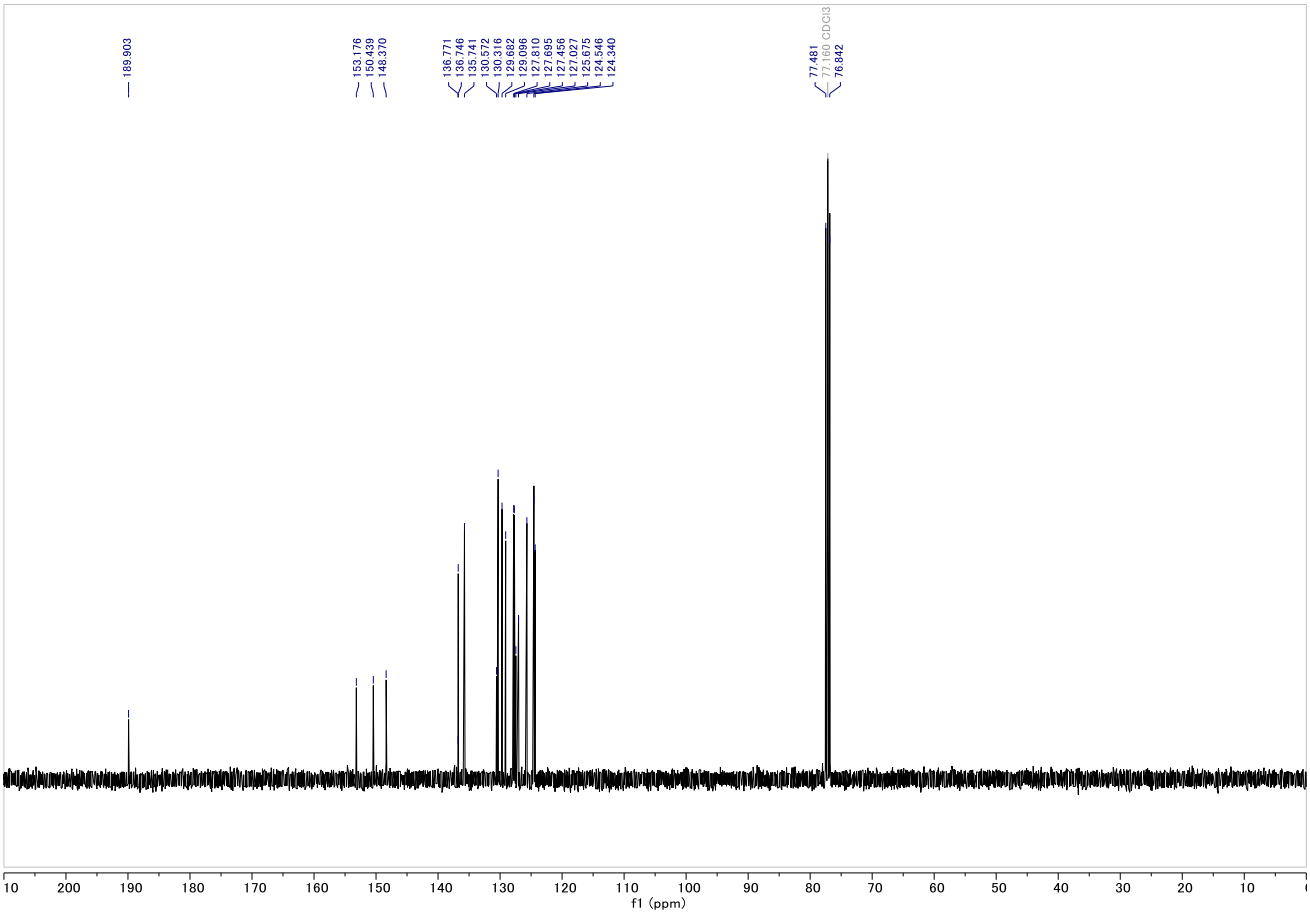
^{1}H NMR **2m**



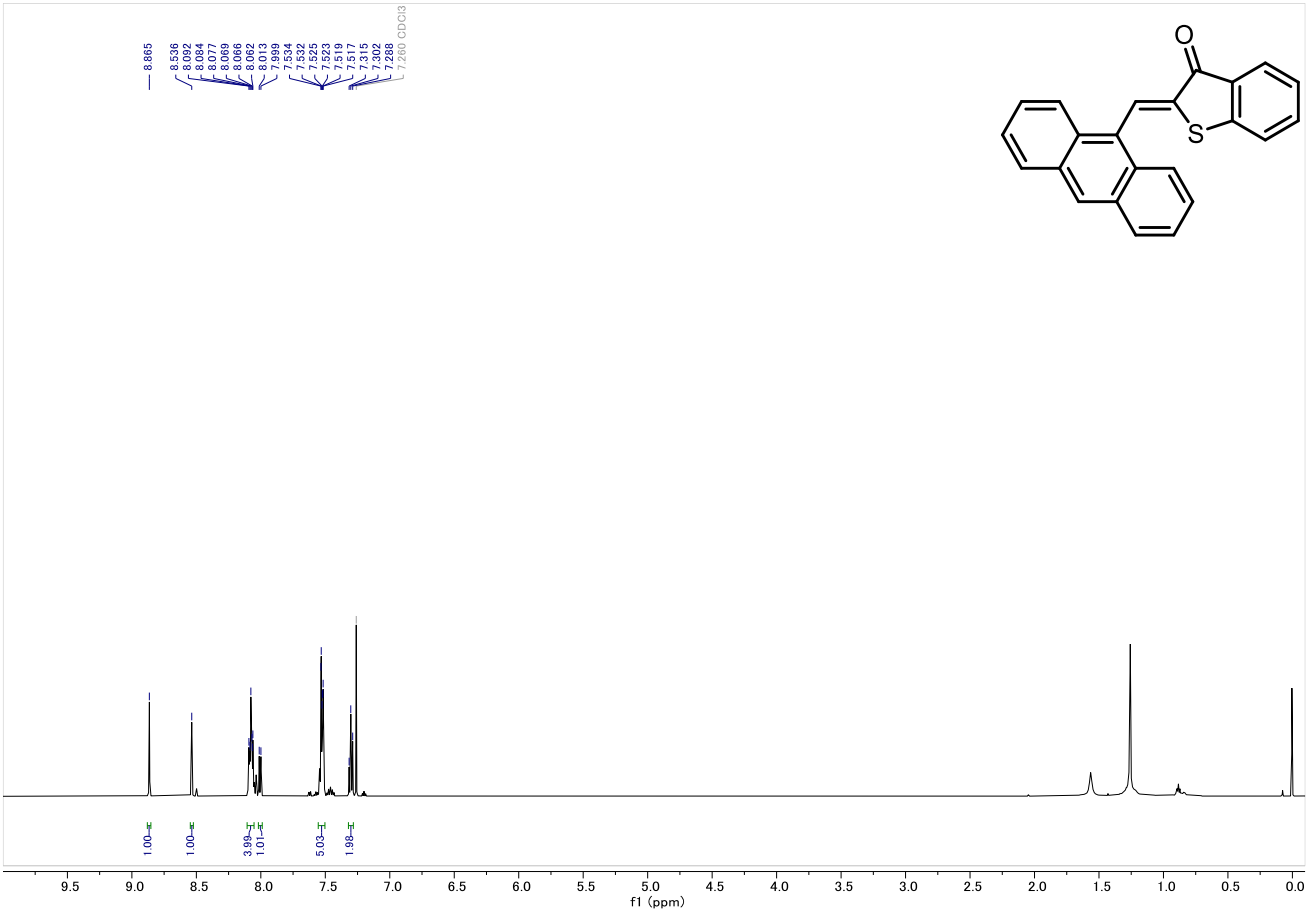
^{1}H NMR **2n**



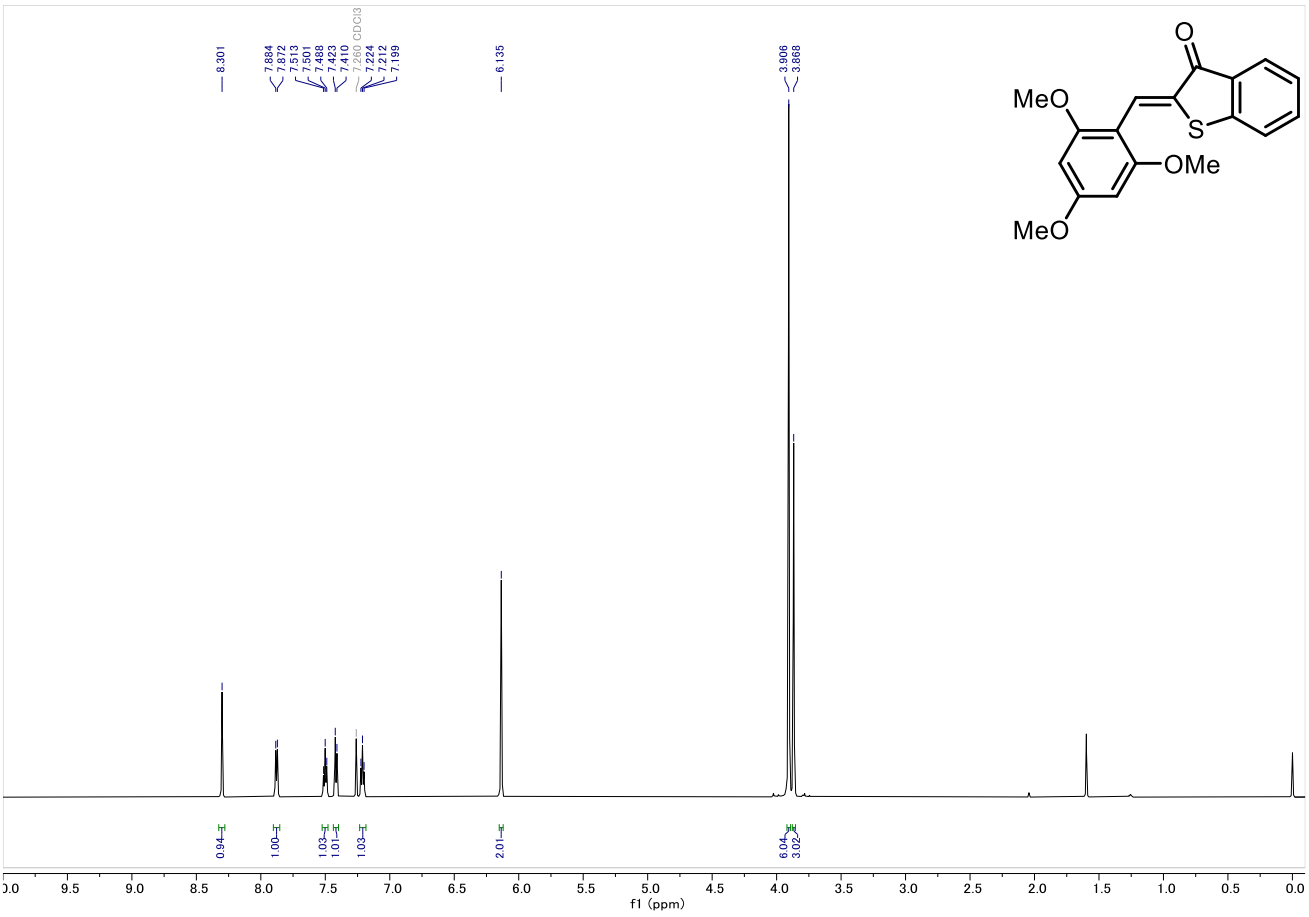
^{13}C NMR **2n**



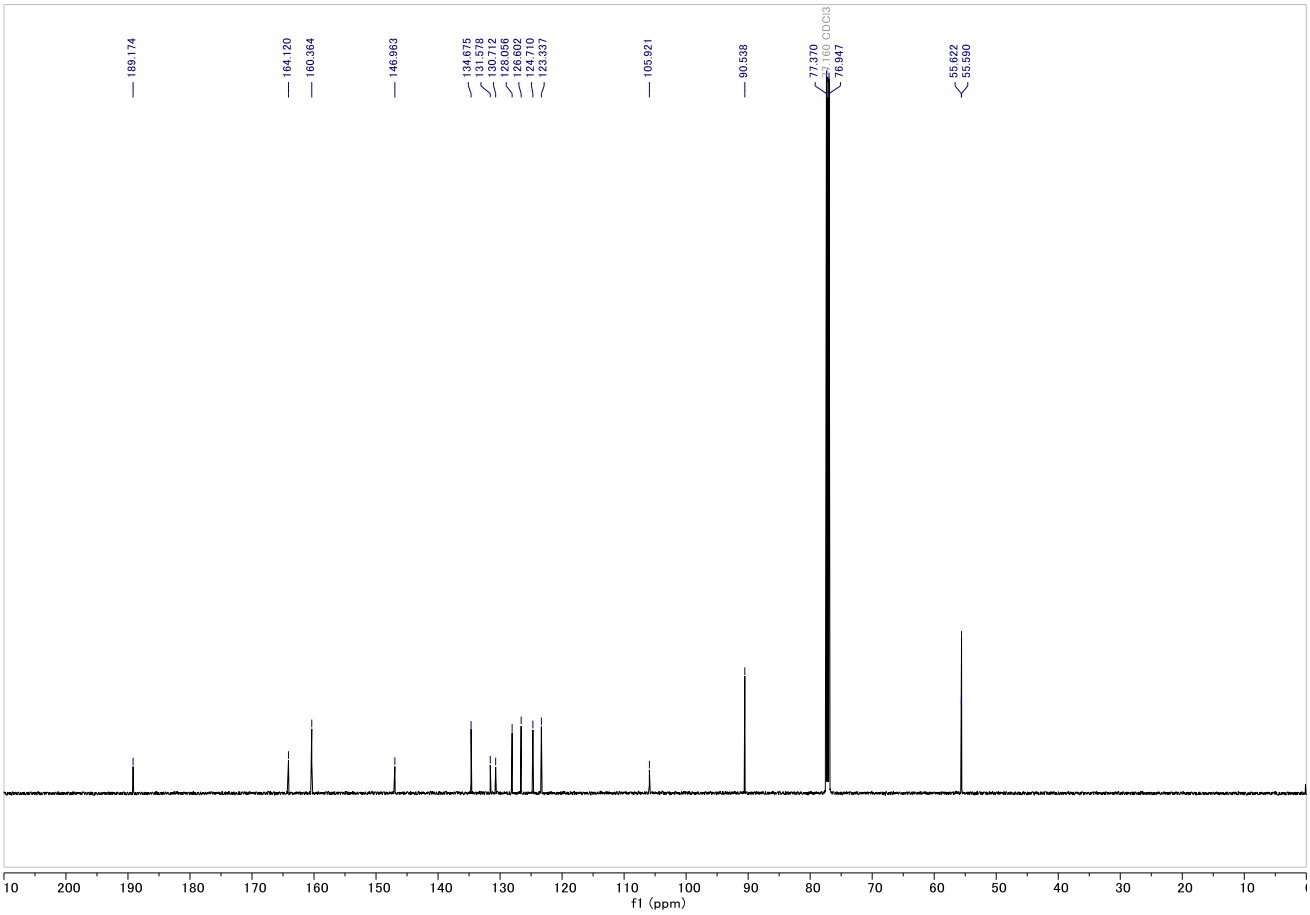
^{1}H NMR **2o**


8.865
8.536
8.092
8.084
8.077
8.069
8.066
8.062
8.013
7.999
7.534
7.532
7.525
7.523
7.519
7.517
7.315
7.302
7.288
7.260 CDCl3
O
S
1.00
1.00
3.99
1.01
5.03
1.98
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)

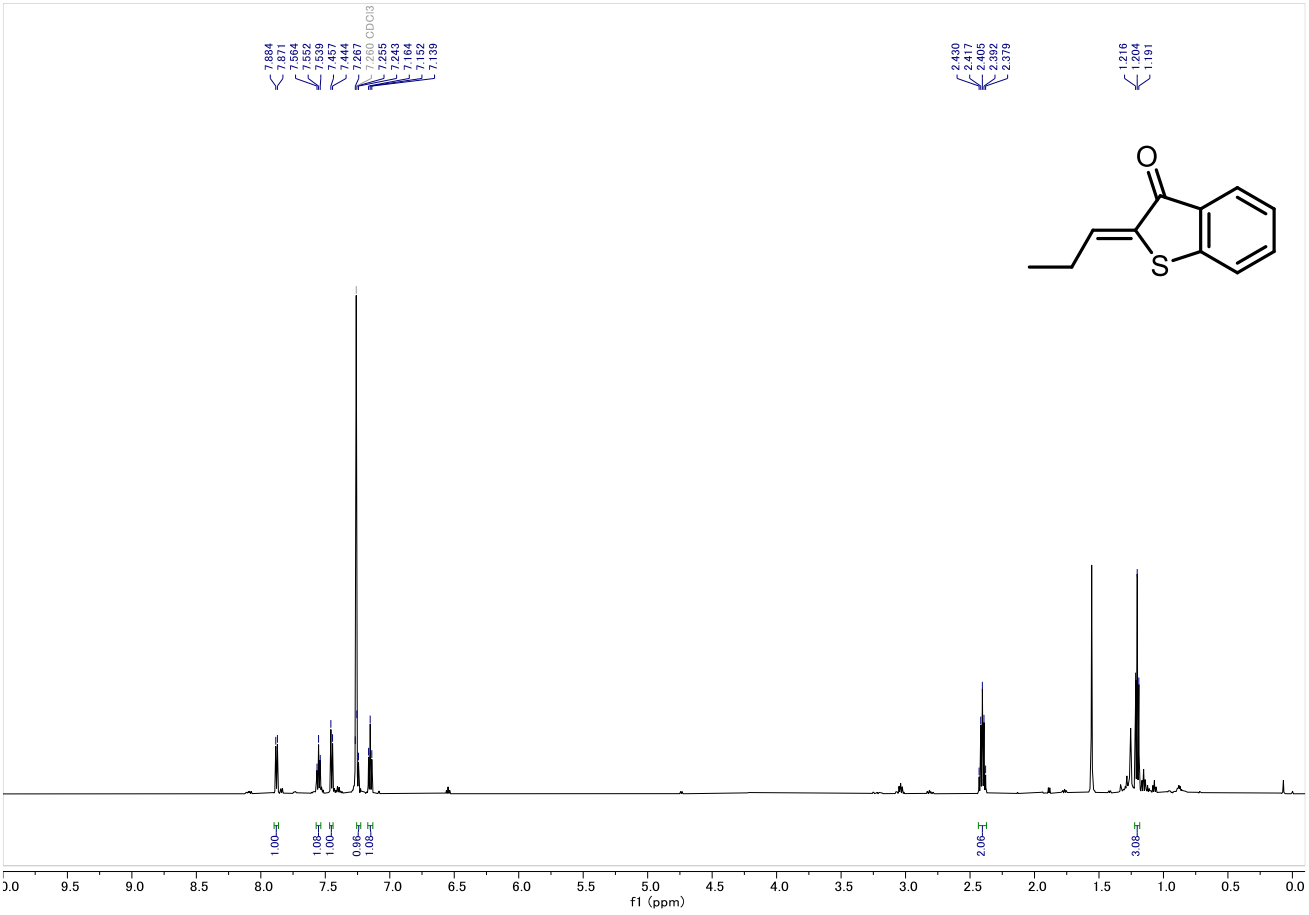
^{1}H NMR **2p**



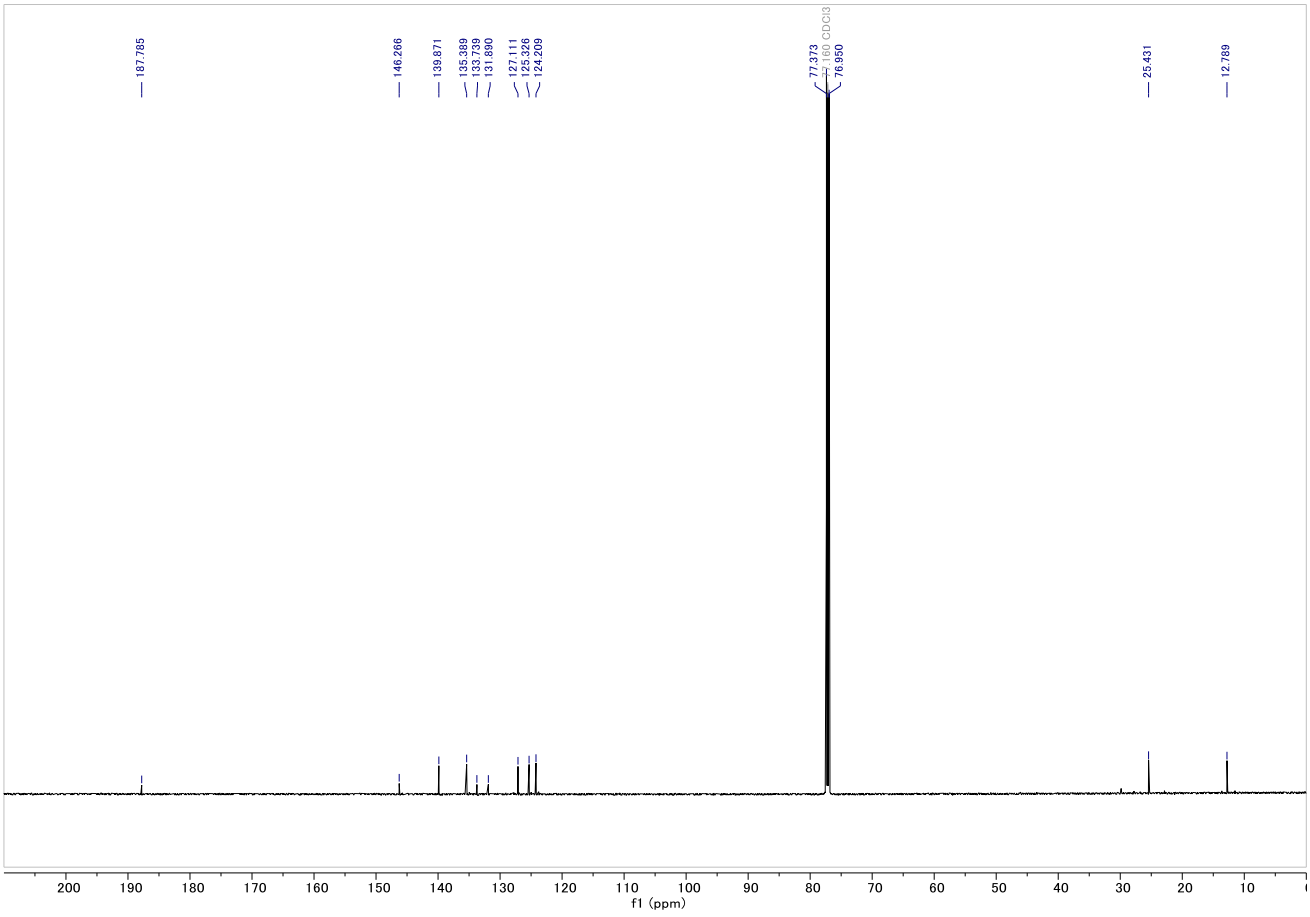
^{13}C NMR **2p**



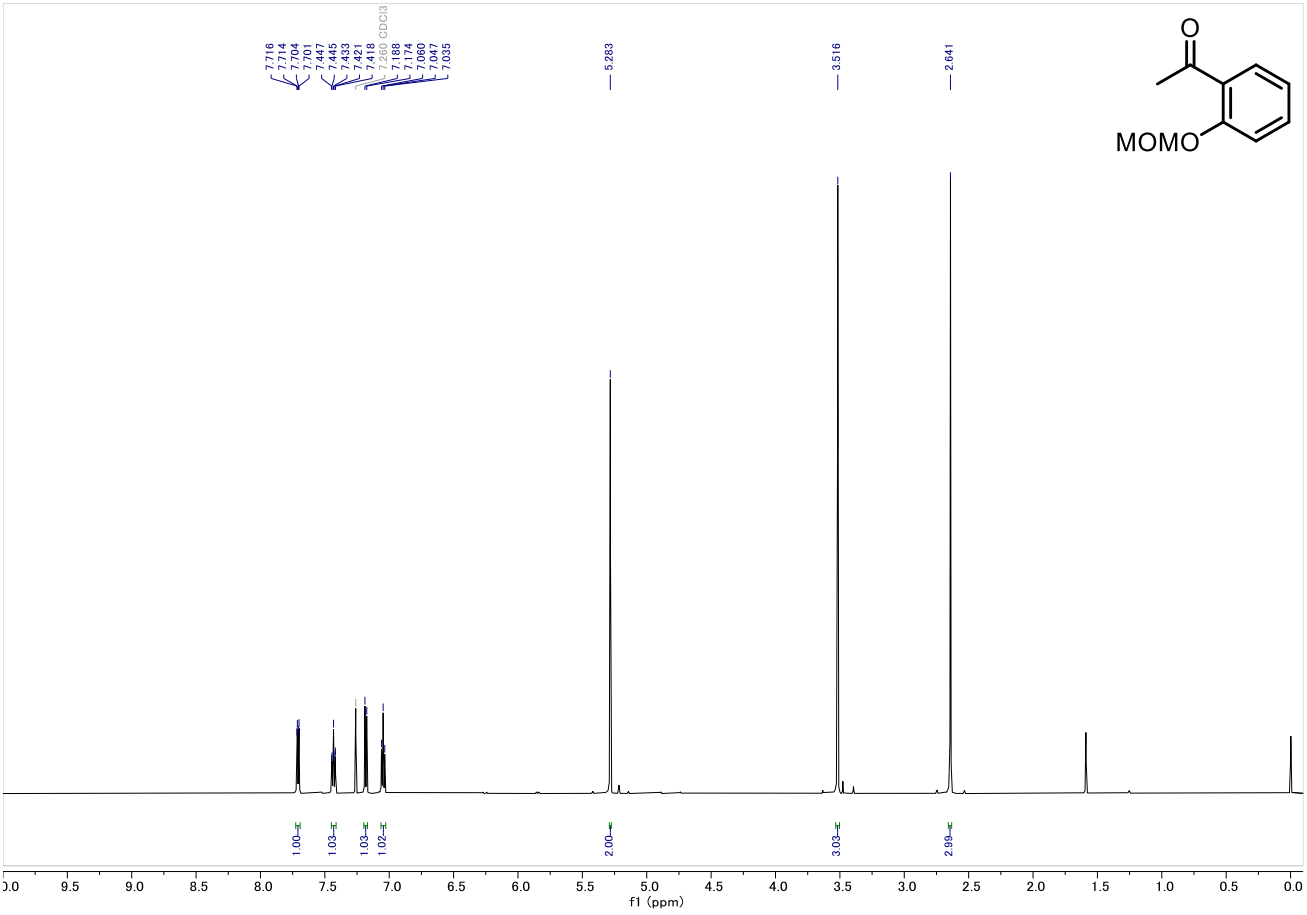
^{1}H NMR **2q**



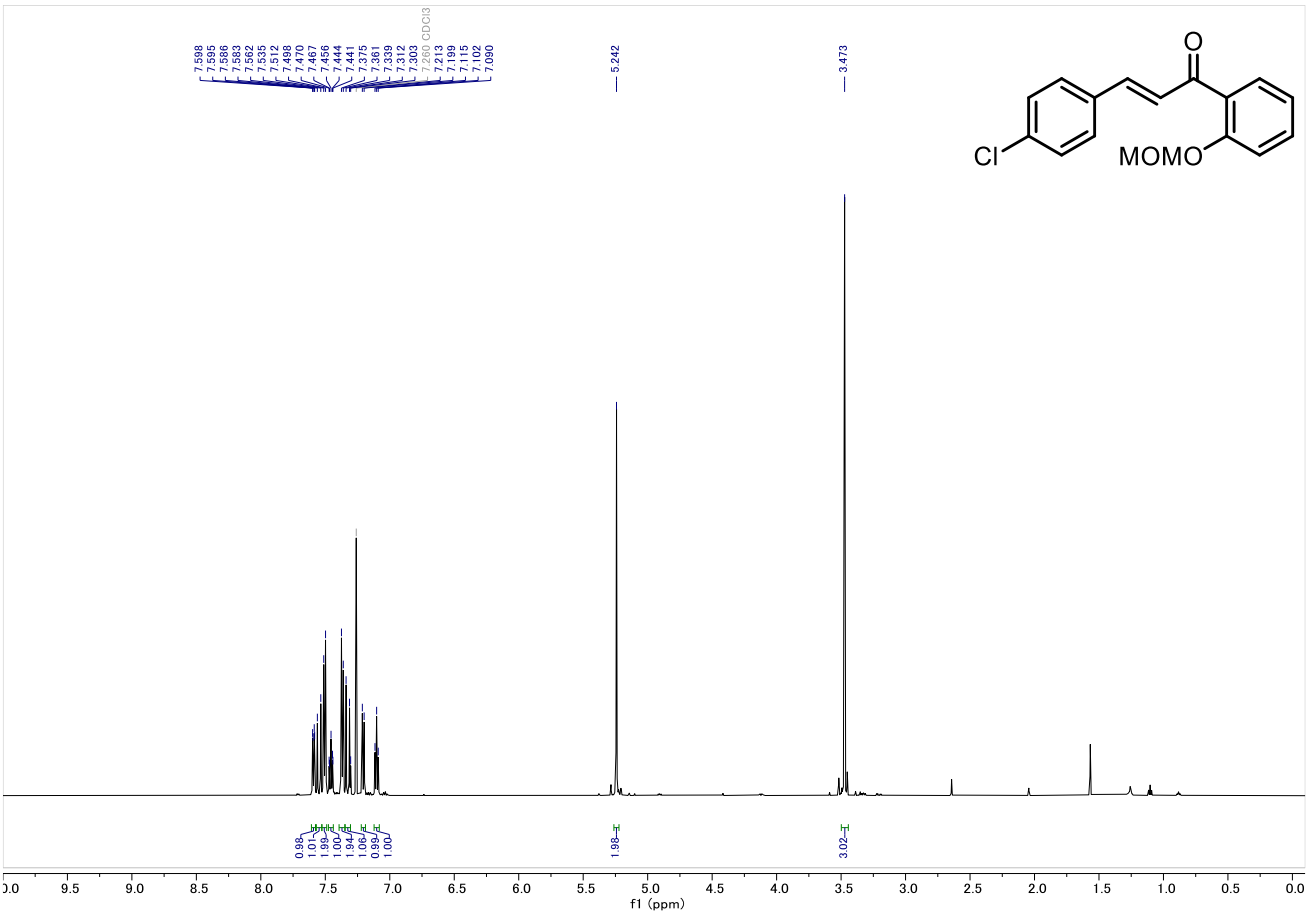
^{13}C NMR **2q**



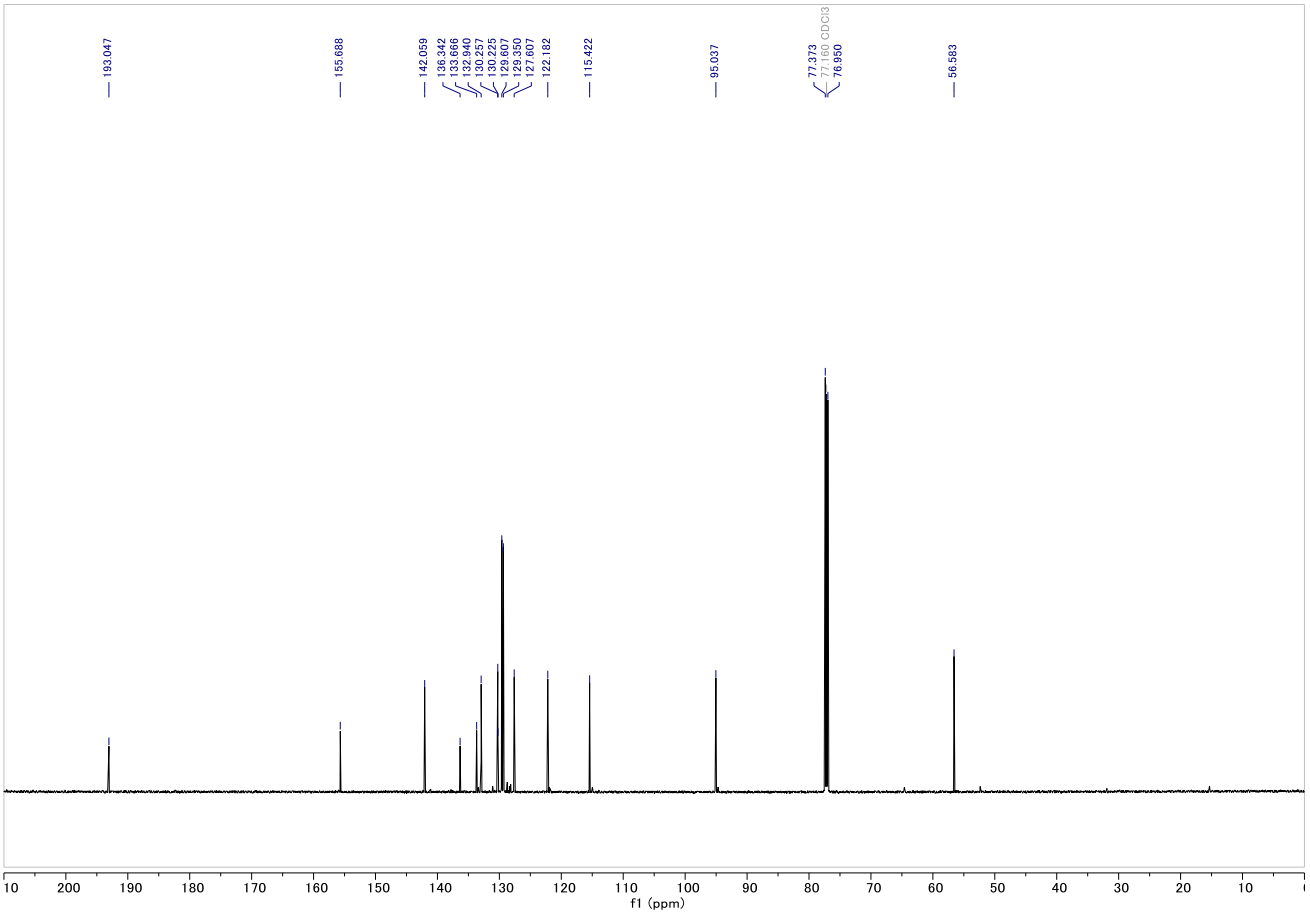
^{1}H NMR **9**


7.716
7.714
7.704
7.701
7.447
7.445
7.433
7.421
7.418
7.260 CDCl3
7.188
7.174
7.060
7.047
7.035
5.283
3.516
2.641
O
MOMO
1.00
1.03
1.03
1.02
2.00
3.03
2.99
f1 (ppm)

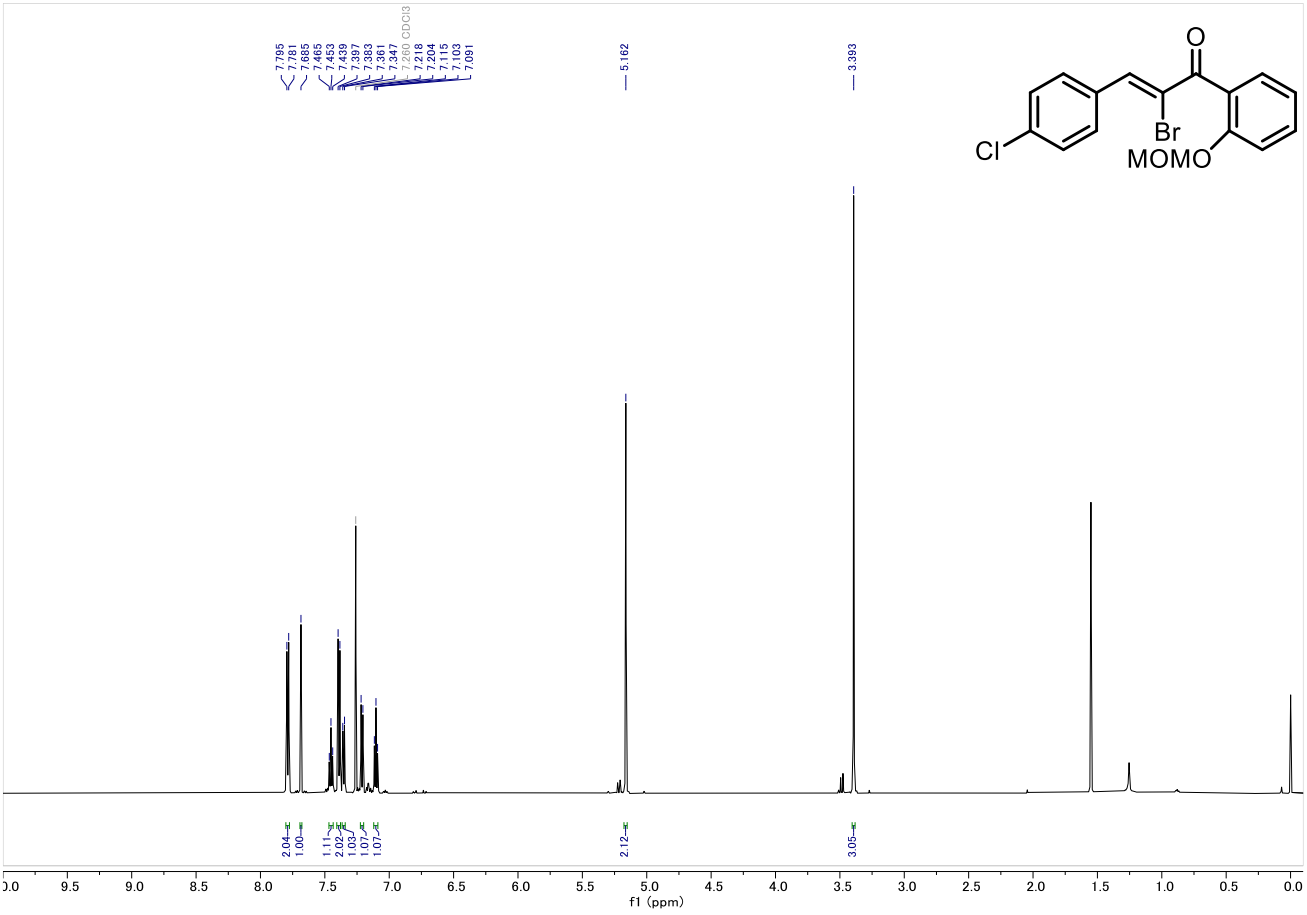
^{1}H NMR **3**



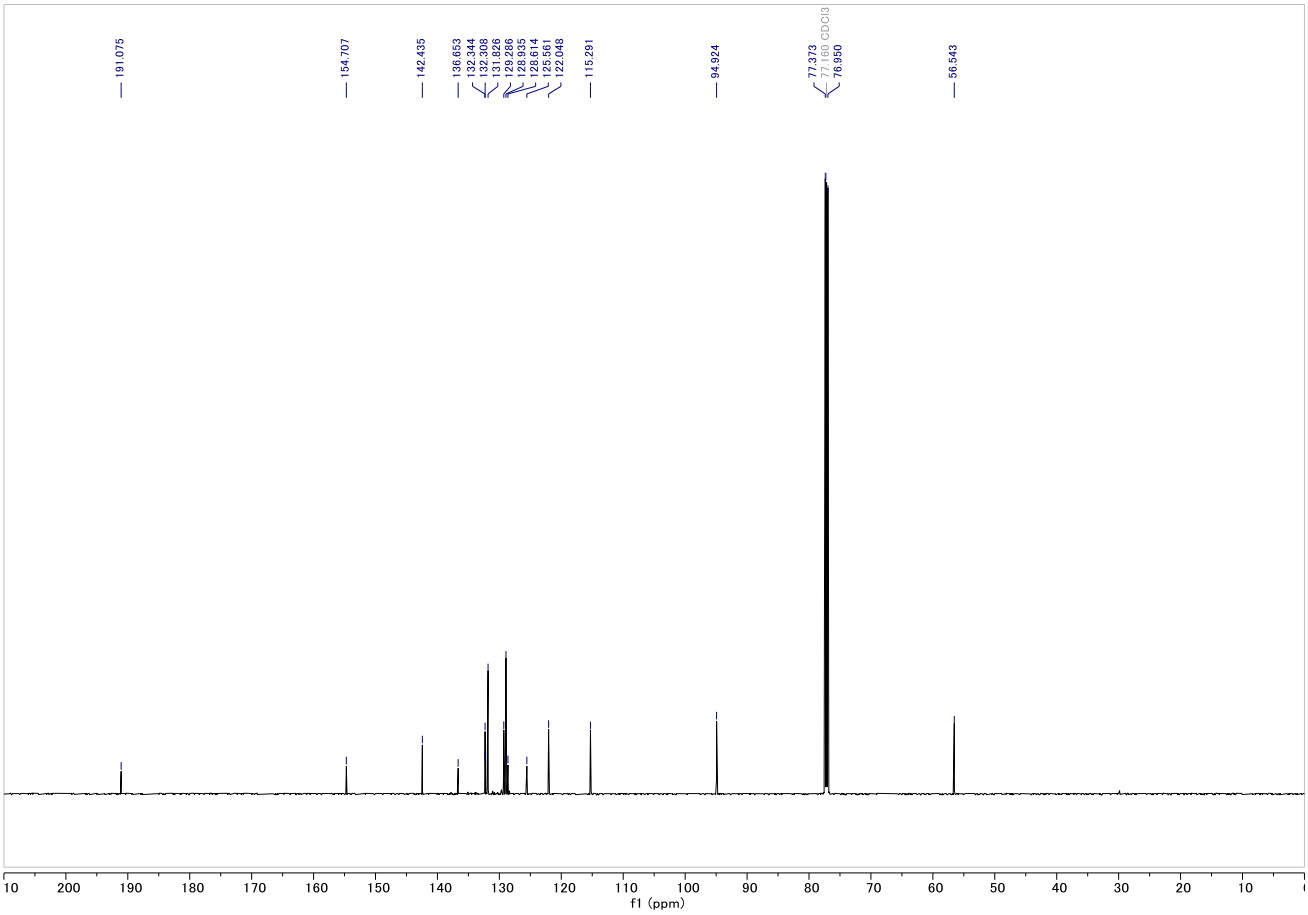
^{13}C NMR **3**



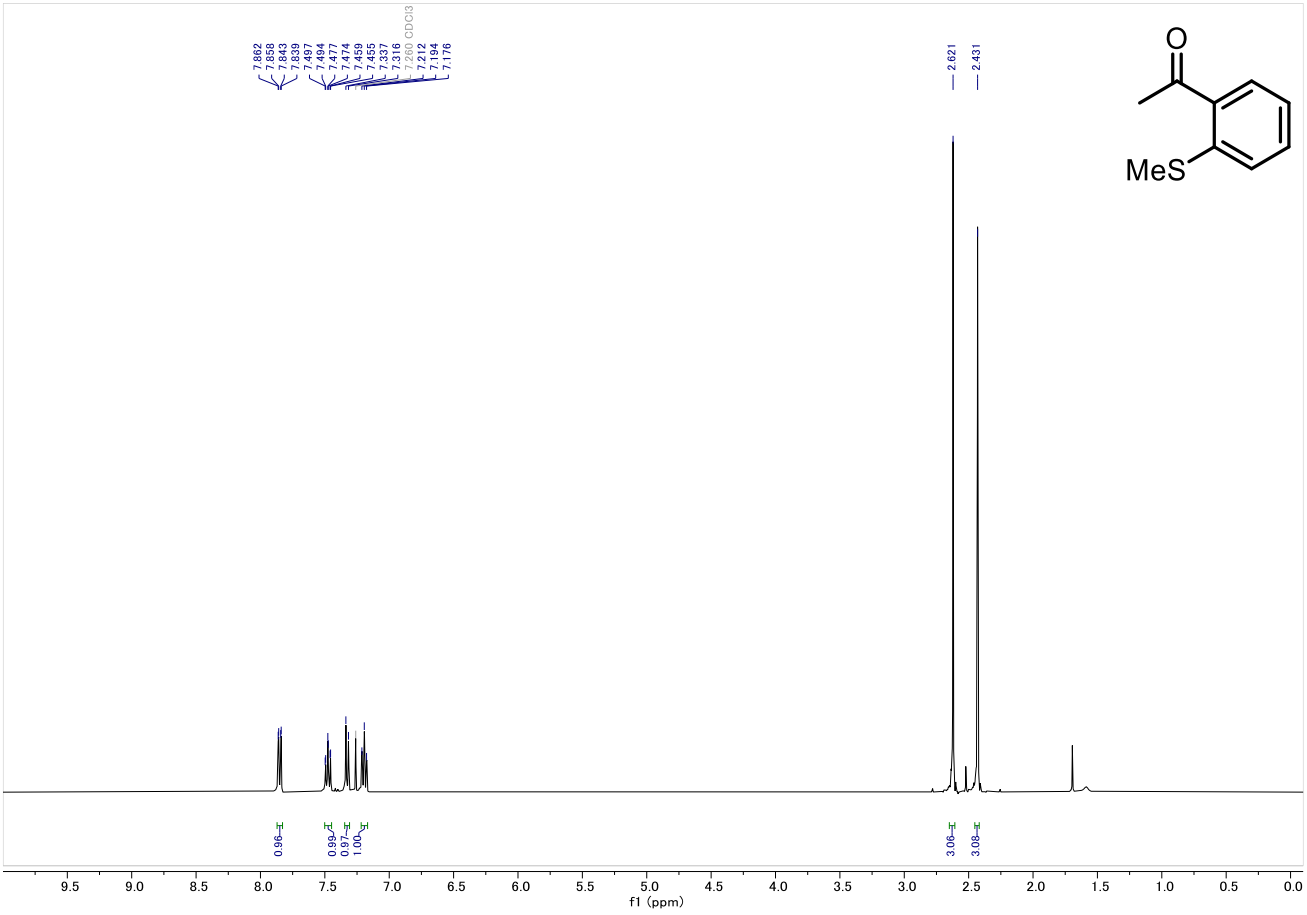
^{1}H NMR **4**



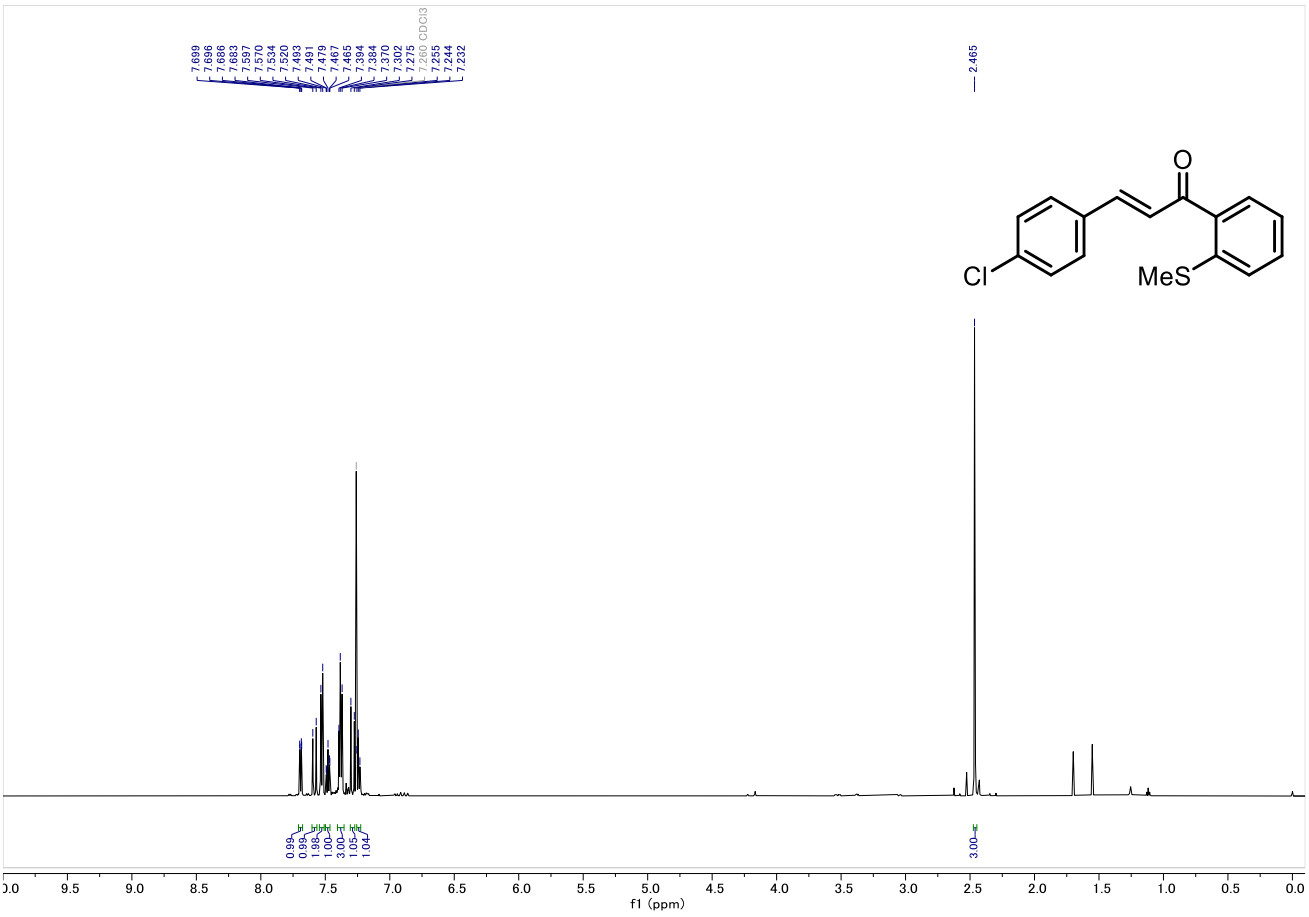
^{13}C NMR **4**



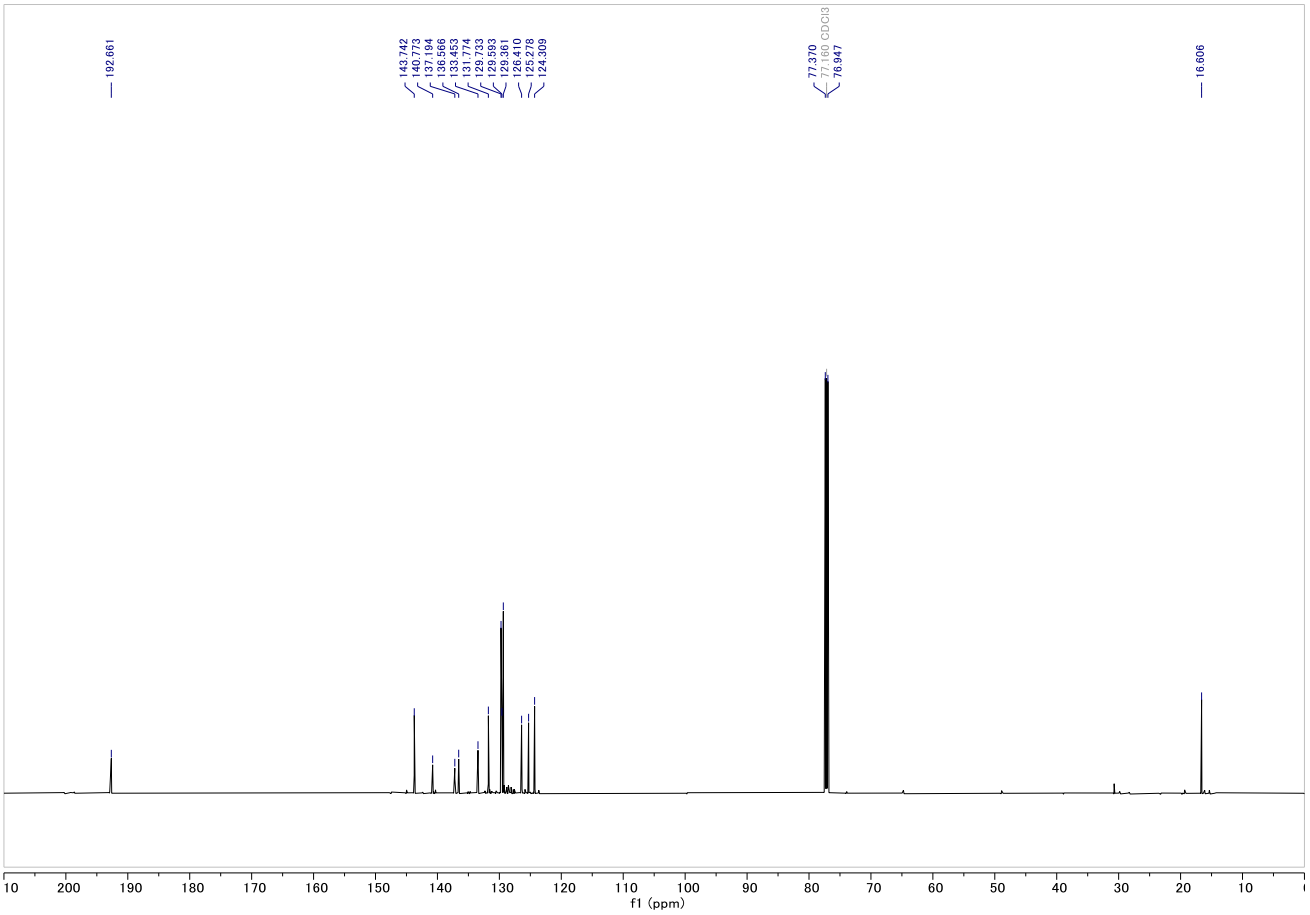
^{1}H NMR **10**


7.862
7.858
7.843
7.839
7.497
7.494
7.477
7.474
7.459
7.455
7.337
7.316
7.260 CDCl3
7.212
7.194
7.176
2.621
2.431
O
MeS
0.96
0.99
0.97
1.00
3.06
3.08
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)

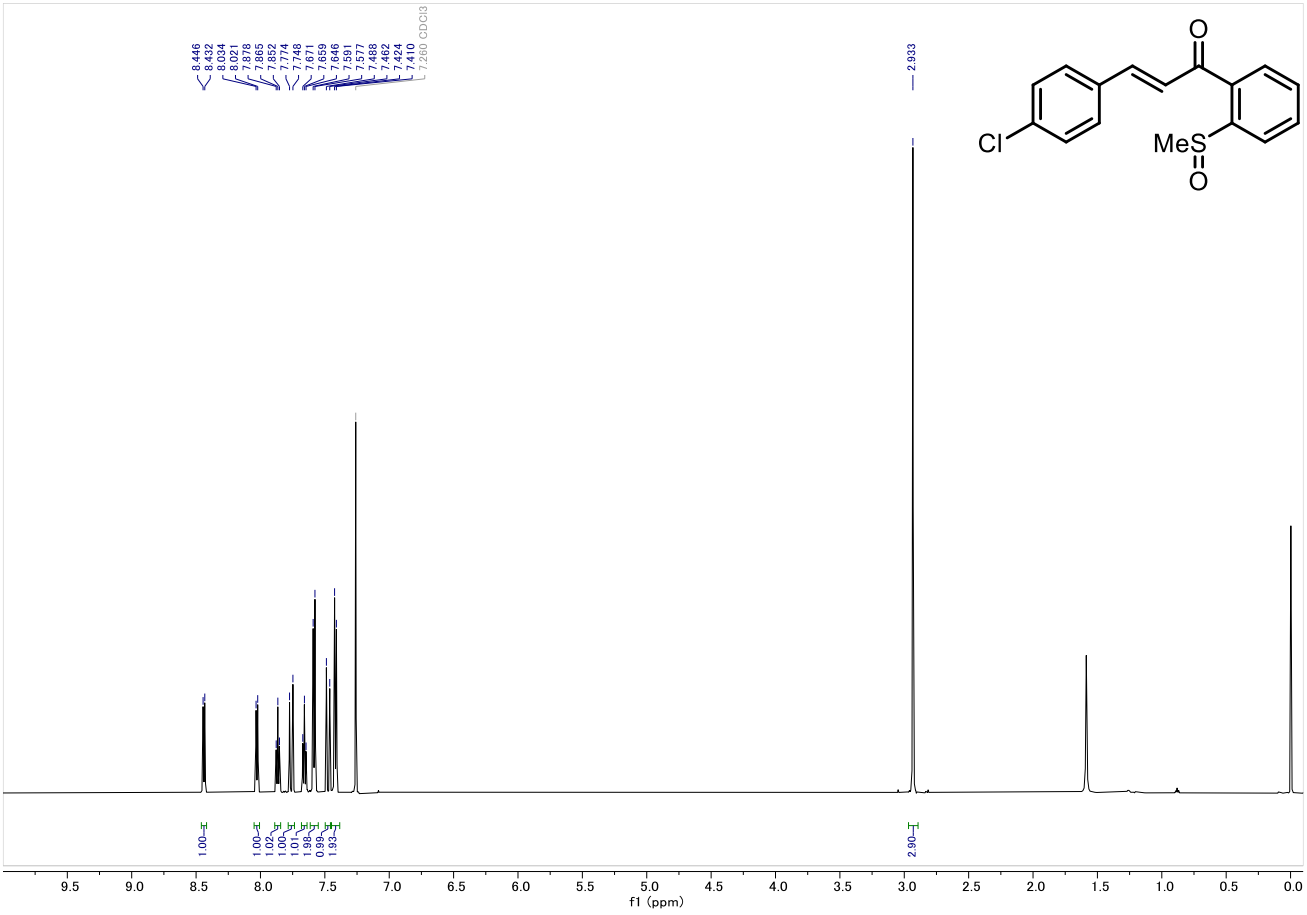
^{1}H NMR **5**



^{13}C NMR **5**



^{1}H NMR **6**



^{13}C NMR **6**