

Supporting Information

Phase-transfer catalysed asymmetric synthesis of α -chiral tetrasubstituted α -aminothioesters

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Table of Contents

1. General information	S-1
2. Synthesis of catalysts	S-2
3. Synthesis of substrates	S-2
4. General procedure for the catalytic Michael addition reaction of aldimino thioester	S-8
5. Derivatisation of the product	S-14
6. ^1H-, ^{13}C-, and ^{19}F-NMR spectra and HPLC charts	S-16

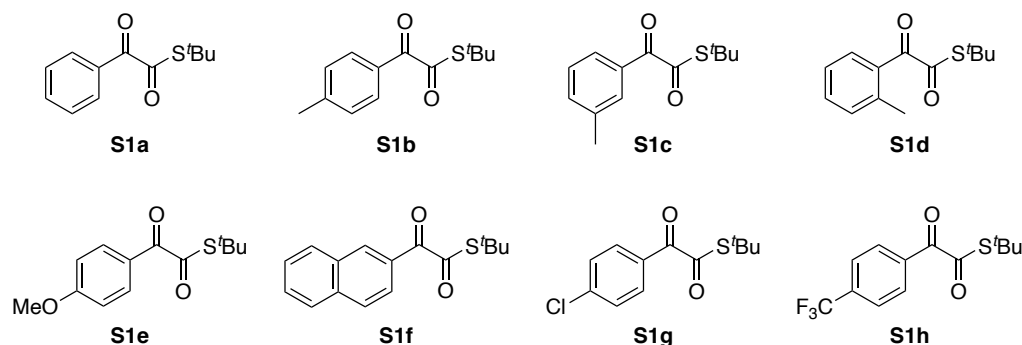
1. General Information

^1H -, ^{13}C -NMR spectra were recorded with Bruker AVANCE III-400M (^1H -NMR 400 MHz, ^{13}C -NMR 100 MHz, ^{19}F -NMR 376 MHz). ^1H -NMR spectra are reported as follows: chemical shift in ppm (δ) relative to the chemical shift of CHCl_3 at 7.26 ppm or tetramethylsilane at 0 ppm, integration, multiplicities (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), and coupling constants (Hz). ^{13}C -NMR spectra reported in ppm (δ) relative to the central line of triplet for CDCl_3 at 77 ppm. $\text{CF}_3\text{CO}_2\text{H}$ used as external standards for ^{19}F . ESI-MS spectra were obtained with Thermo Fisher, Exactive. FT-IR spectra were recorded on a JASCO FT-IR system (FT/IR-460 Plus). Mp was measured with AS ONE ATM-02. Column chromatography on SiO_2 and neutral SiO_2 was performed with Kanto Silica Gel 60 (40-50 μm). All reactions were carried out under Ar atmosphere unless otherwise noted. Commercially available organic and inorganic compounds were used without further purification. All dehydrated solvents were purchased from Wako Pure Chemical Industries, Ltd. or Nacalai Tesque, Inc., and were used without further purification.

1. Synthesis of catalysts

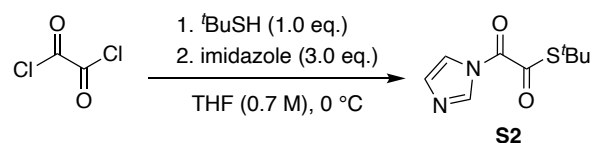
3a,¹ **3b**,² and **3c**³ were synthesized according to the reported procedure. **3d** was purchased from TCI.

2. Synthesis of substrates

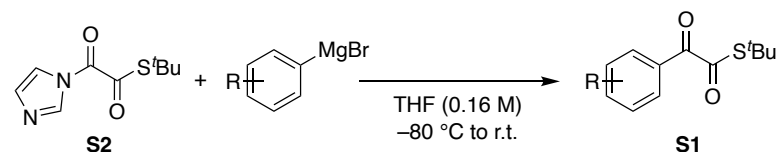


α -Ketothioester **S1a** was synthesized according to the reported procedure.⁴

α -Ketothioester **S1b-h** were prepared as follows, and NMR data for known compound **S1b** was matched with the literature value.⁴

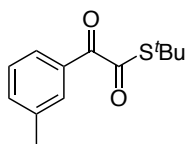


A solution of oxalyl chloride (1.0 eq.) in THF (0.7 M) was cooled to 0 °C, and *tert*-BuSH (1.0 eq.) was added slowly. The reaction was stirred for 1 hour, and the imidazole (3.5 M in THF, 3.0 eq.) was added. The reaction was stirred for 1 hour at the same temperature, which was quenched by the addition of excess amount of precooled (0 °C) diethyl ether. The solution was filtered by Celite (diethyl ether), solvent was evaporated to form crude **S2**, which was used to the next step without further purification.



The solution of **S2** (1.0 eq.) in dry THF (0.16 M) was cooled to -80 °C and added corresponding Grignard reagent solution (1.3 eq. in THF) slowly. The solution was stirred for 10 min. at the same temperature, and warmed up to room temperature gradually (about 30 minutes). The reaction was continued for 2 hours before quenching by the addition of saturated NH_4Cl aq., extracted by EtOAc, dried over Na_2SO_4 , evaporation of solvents provided the crude product. The crude product was purified by column chromatography (Silica-gel, ethyl acetate/hexane) to give the corresponding **S1**.

***S*-(*tert*-butyl) 2-oxo-2-(*m*-tolyl)ethanethioate (S1c)**



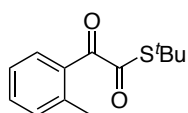
Yellow oil, 659.6 mg, 2.8 mmol, 20% yield.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM- D) δ 7.87-7.84 (m, 2H), 7.46-7.43 (m, 1H), 7.40-7.35 (m, 1H), 2.41 (s, 3H), 1.60 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM- D) δ 193.7, 187.3, 138.6, 135.5, 131.5, 130.8, 128.6, 127.9, 49.0, 29.6, 21.3.

IR (NaCl) ν 2965, 1675, 1364, 1272, 900 cm^{-1} .

HRMS (APCI $^+$ in MeCN) calcd for $\text{C}_{13}\text{H}_{17}\text{O}_2\text{S}$ (M+H) 237.0944 found 237.0943.

***S*-(*tert*-butyl) 2-oxo-2-(*o*-tolyl)ethanethioate (S1d)**



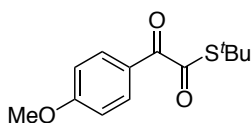
Yellow oil, 671.8 mg, 2.8 mmol, 20% yield.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM- D) δ 7.71 (dd, $J = 8.1, 1.3$ Hz, 1H), 7.49-7.45 (m, 1H), 7.32-7.28 (m, 2H), 2.54 (s, 3H), 1.59 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM- D) δ 194.0, 190.1, 140.9, 133.2, 132.1, 132.0, 131.2, 125.6, 49.0, 29.7, 21.3.

IR (NaCl) ν 2965, 1677, 1661, 1455, 841 cm^{-1} .

HRMS (ESI $^+$ in MeCN) calcd for $\text{C}_{13}\text{H}_{16}\text{O}_2\text{NaS}$ (M+Na) 259.0763 found 259.0760.

***S*-(*tert*-butyl) 2-(4-methoxyphenyl)-2-oxoethanethioate (S1e)**



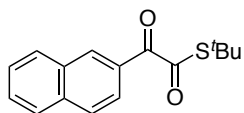
Yellow oil, 406.2 mg, 1.6 mmol, 23% yield.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM- D) δ 8.10-8.06 (m, 2H), 6.98-6.95 (m, 2H), 3.89 (s, 3H), 1.59 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM- D) δ 194.1, 185.6, 164.8, 133.2, 124.4, 114.1, 55.6, 48.8, 29.6.

IR (NaCl) ν 2961, 1667, 1264, 1173, 749 cm^{-1} .

HRMS (ESI $^+$ in MeCN) calcd for $\text{C}_{13}\text{H}_{17}\text{O}_3\text{S}$ (M+H) 253.0893 found 253.0888.

S-(tert-butyl) 2-(naphthalen-2-yl)-2-oxoethanethioate (S1f)



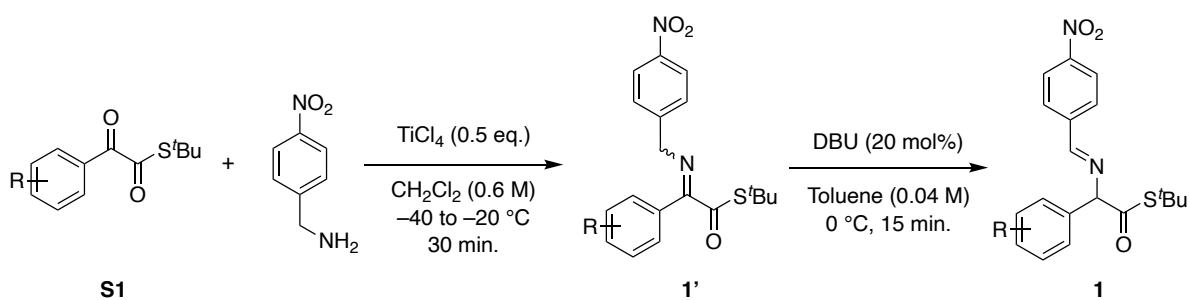
Yellow oil, 866.4 mg, 3.2 mmol, 46% yield.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.68 (s, 1H), 8.05 (dd, *J* = 8.1, 1.6 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.91-7.85 (m, 2H), 7.63 (dd, *J* = 8.0, 7.0 Hz, 1H), 7.56 (dd, *J* = 8.0, 7.0 Hz, 1H), 1.63 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 193.7, 186.9, 136.1, 133.9, 132.2, 130.1, 129.4, 128.78, 128.76, 127.8, 127.0, 124.7, 49.0, 29.6.

IR (NaCl) ν 2963, 1670, 1458, 1362, 1280, 1051, 753 cm⁻¹.

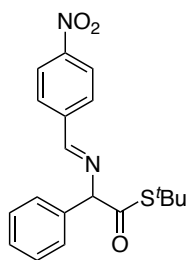
HRMS (APCI⁺ in MeCN) calcd for C₁₆H₁₇O₂S (M+H) 273.0944 found 273.0943.

S1g and **S1h** could not be isolated with *S,S*-di-*tert*-butyl ethanebis(thioate) and used in the next step without further purification.



To a solution of 4-Nitrobenzylamine (3.0 eq.) in CH₂Cl₂ (0.6 M) at -40 °C, α-ketothioester (1.0 eq. in CH₂Cl₂) was added and stirred for 5 minutes. TiCl₄ (1.0 M in CH₂Cl₂, 0.5 eq.) was slowly added and stirred for 30 minutes before increasing the reaction temperature slowly (around 30 minutes) to -20 °C. The reaction was quenched by the adding into pre-cooled (-20 °C) diethyl ether (20 times larger volume to the reaction solvent), and stirred for 20 minutes at -20 °C. The reaction solution was filtered through Celite (diethyl ether) and the solvent was removed by evaporation to give the crude **1'**. The crude **1'** was dissolved in toluene (0.04 M) and cool to 0 °C. DBU (20 mol%) was added to the reaction and the obtained blue solution was stirred for 15 minutes at the same temperature. The reaction was quenched by the addition of saturated NH₄Cl aq., extracted with diethyl ether, dried over Na₂SO₄, filtered and solvents were removed under vacuum to give crude material. The crude product was purified by column chromatography (neutral Silica-gel, ethyl acetate/hexane) to give the corresponding aldiminothioester **1**.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-2-phenylethanethioate (1a)**



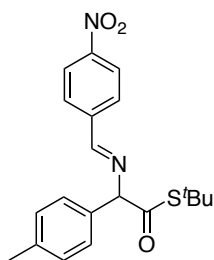
Orange oil, 707.2 mg, 2.0 mmol, 32% yield.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.39 (s, 1H), 8.31-8.28 (m, 2H), 8.04-8.00 (m, 2H), 7.52-7.49 (m, 2H), 7.41-7.31 (m, 3H), 5.14 (s, 1H), 1.45 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 199.3, 161.1, 149.3, 141.0, 137.9, 129.4, 128.8, 128.3, 127.8, 123.9, 84.0, 48.1, 29.7.

IR (NaCl) ν 2963, 1675, 1518, 1347, 1166, 747 cm⁻¹.

HRMS (ESI⁺ in MeCN) calcd for C₁₉H₂₁O₃N₂S (M+H) 357.1267 found 357.1264.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-2-(*p*-tolyl)ethanethioate (1b)**



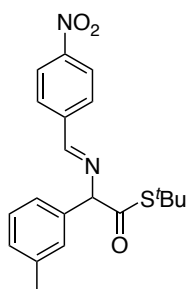
Yellow oil, 144.1 mg, 0.4 mmol, 18% yield.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.37 (s, 1H), 8.30-8.27 (m, 2H), 8.03-7.99 (m, 2H), 7.40-7.37 (m, 2H), 7.21-7.18 (m, 2H), 5.11 (s, 1H), 2.35 (s, 3H), 1.45 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 199.5, 160.9, 149.3, 141.1, 138.2, 135.0, 129.5, 129.4, 127.7, 123.8, 83.7, 48.0, 29.7, 21.2.

IR (NaCl) ν 2966, 2849, 1675, 1519, 1349, 1060, 863 cm⁻¹.

HRMS (ESI⁺ in MeCN) calcd for C₂₀H₂₃O₃N₂S (M+H) 371.1424 found 371.1418.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-2-(*m*-tolyl)ethanethioate (1c)**



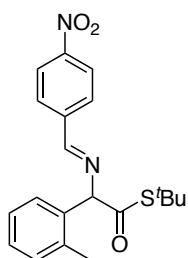
Orange oil, 272.2 mg, 0.7 mmol, 35% yield.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM-D) δ 8.34 (s, 1H), 8.29-8.26 (m, 2H), 8.01-7.98 (m, 2H), 7.57-7.53 (m, 1H), 7.26-7.20 (m, 3H), 5.40 (s, 1H), 2.45 (s, 3H), 1.46 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM-D) δ 199.5, 161.0, 149.2, 141.1, 136.4, 136.2, 130.9, 129.3, 128.9, 128.3, 126.3, 123.8, 80.8, 48.1, 29.7, 20.0.

IR (NaCl) ν 2966, 2859, 1675, 1520, 1347, 1050, 854 cm^{-1} .

HRMS (ESI⁺ in MeCN) calcd for $\text{C}_{20}\text{H}_{23}\text{O}_3\text{N}_2\text{S}$ (M+H) 371.1424 found 371.1419.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-2-(*o*-tolyl)ethanethioate (1d)**



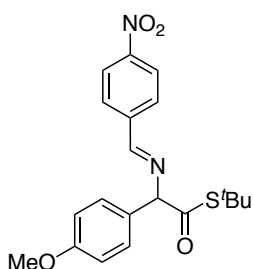
Colorless oil, 215.9 mg, 0.6 mmol, 28% yield.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM-D) δ 8.37 (s, 1H), 8.30-8.27 (m, 2H), 8.03-8.00 (m, 2H), 7.32-7.25 (m, 3H), 7.16-7.13 (m, 1H), 5.11 (s, 1H), 2.37 (s, 3H), 1.45 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM-D) δ 199.4, 161.0, 149.2, 141.0, 138.5, 137.8, 129.4, 129.1, 128.6, 128.4, 124.8, 123.8, 83.9, 48.0, 29.7, 21.4.

IR (NaCl) ν 3103, 3022, 2962, 2887, 1669, 1600, 1521, 1345, 1070, 857 cm^{-1} .

HRMS (ESI⁺ in MeCN) calcd for $\text{C}_{20}\text{H}_{23}\text{O}_3\text{N}_2\text{S}$ (M+H) 371.1424 found 371.1416.

***S*-(*tert*-butyl)(*E*)-2-(4-methoxyphenyl)-2-((4-nitrobenzylidene)amino)ethanethioate (1e)**



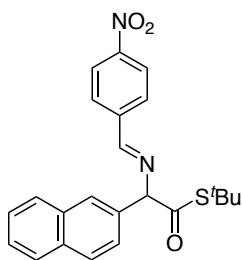
Colorless oil, 129.7mg, 0.3 mmol, 26% yield.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM-D) δ 8.37 (s, 1H), 8.31-8.28 (m, 2H), 8.03-8.00 (m, 2H), 7.44-7.40 (m, 2H), 6.94-6.90 (m, 2H), 5.10 (s, 1H), 3.81 (s, 3H), 1.45 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM-D) δ 199.6, 160.8, 159.6, 149.3, 141.1, 130.0, 129.4, 129.0, 123.9, 114.2, 83.3, 55.3, 48.0, 29.7.

IR (NaCl) ν 2962, 2858, 1675, 1517, 1347, 1257, 1174, 1027, 847 cm^{-1} .

HRMS (ESI⁺ in MeCN) calcd for $\text{C}_{20}\text{H}_{23}\text{O}_4\text{N}_2\text{S}$ (M+H) 387.1373 found 387.1368.

***S*-(*tert*-butyl) (*E*)-2-(naphthalen-2-yl)-2-((4-nitrobenzylidene)amino)ethanethioate (1f)**



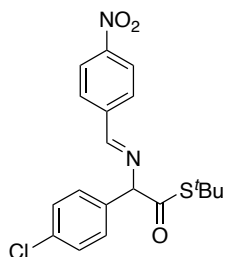
Brown oil, 70.8 mg, 0.1 mmol, 6% yield.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.44 (s, 1H), 8.32-8.29 (m, 2H), 8.06-8.03 (m, 2H), 7.93 (brs, 1H), 7.88-7.82 (m, 3H), 7.65 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.52-7.48 (m, 2H), 5.31 (s, 1H), 1.45 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 199.3, 161.3, 149.3, 141.0, 135.3, 133.2, 133.1, 129.4, 128.6, 128.1, 127.7, 127.1, 126.34, 126.31, 125.2, 123.9, 84.0, 48.2, 29.7.

IR (NaCl) ν 2958, 1679, 1522, 1345, 1056, 854, 755 cm⁻¹.

HRMS (ESI⁺ in MeCN) calcd for C₂₃H₂₃O₃N₂S (M+H) 407.1424 found 407.1415.

***S*-(*tert*-butyl) (*E*)-2-(4-chlorophenyl)-2-((4-nitrobenzylidene)amino)ethanethioate (1g)**



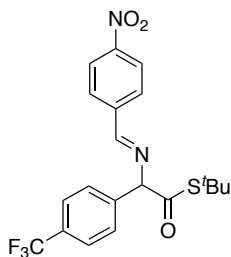
Orange oil, 79.4 mg, 0.20 mmol, 10% yield from **S2**.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.40 (s, 1H), 8.32-8.28 (m, 2H), 8.05-8.01 (m, 2H), 7.49-7.45 (m, 2H), 7.37-7.34 (m, 2H), 5.10 (s, 1H), 1.44 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 198.9, 161.5, 149.3, 140.8, 136.4, 134.2, 129.4, 129.0, 128.9, 123.9, 83.2, 48.2, 29.6.

IR (NaCl) ν 2966, 2865, 1675, 1602, 1524, 1345, 857 cm⁻¹.

HRMS (ESI⁺ in MeCN) calcd for C₁₉H₁₉ClN₂O₃S (M+H) 391.0878 found 391.0877.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-2-(4-(trifluoromethyl)phenyl)ethanethioate (1h)**



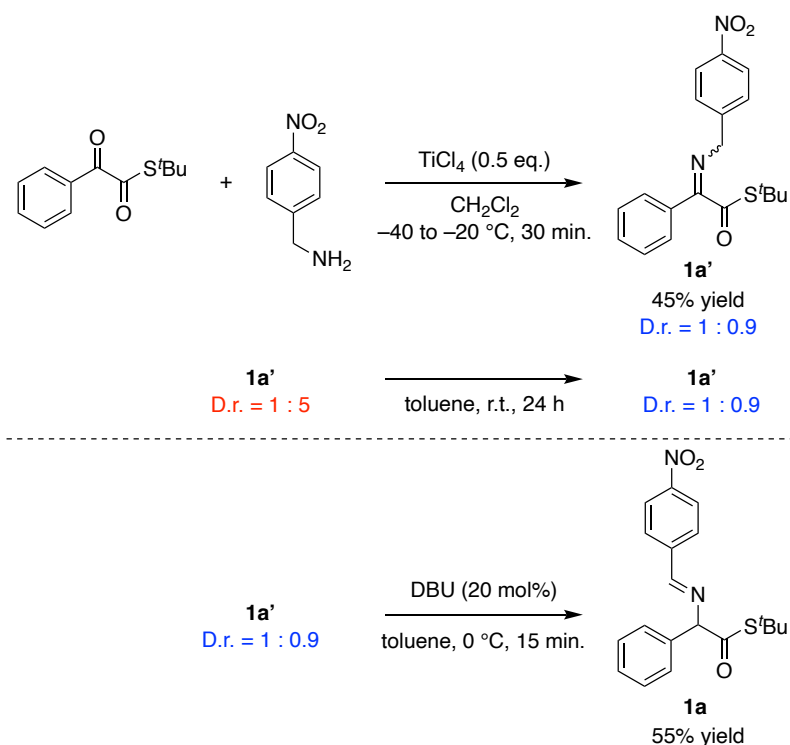
Orange oil, 127.2 mg, 0.30 mmol, 14% yield from **S2**.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM-D) δ 8.45 (s, 1H), 8.32-7.29 (m, 2H), 8.07-8.03 (m, 2H), 7.70-7.66 (m, 2H), 7.66-7.62 (m, 2H), 5.19 (s, 1H), 1.45 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM-D) δ 198.4, 161.9, 149.4, 141.7, 140.7, 130.4 (q, $J = 32.1$ Hz), 129.5, 128.0, 125.6 (q, $J = 3.7$ Hz), 123.89, 123.94 (q, $J = 270.2$ Hz), 83.5, 48.4, 29.6; $^{19}\text{F-NMR}$ (377 MHz, CHLOROFORM-D) δ -62.5.

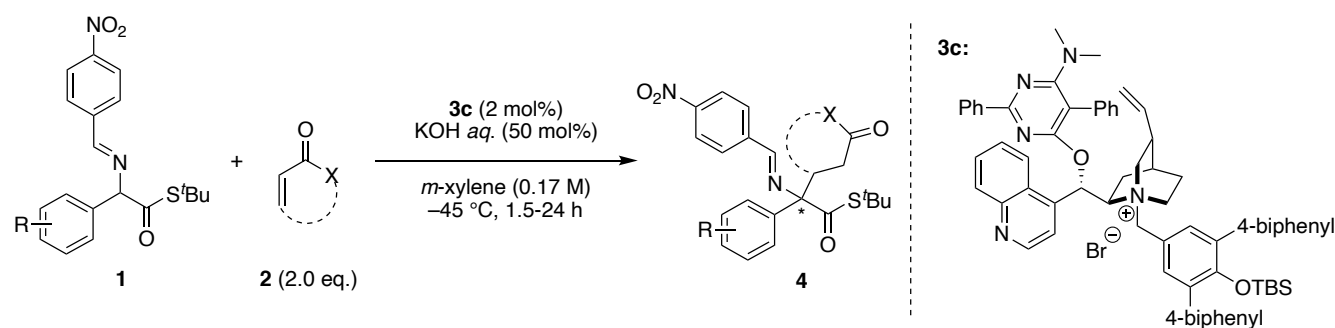
IR (NaCl) ν 2968, 2865, 1677, 1602, 1526, 1325, 857 cm^{-1} .

HRMS (ESI $^+$ in MeCN) calcd for $\text{C}_{20}\text{H}_{20}\text{F}_3\text{N}_2\text{O}_3\text{S}$ (M+H) 425.1141 found 425.1132.

The isolation of the ketimine **1a'** for the substrate of umpolung reaction was failed due to the instability of C–N double bond (Please see the following schemes).



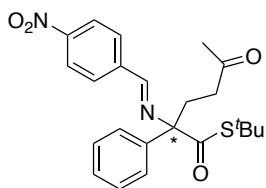
3. General procedure for the catalytic Michael addition reaction of aldimino thioester **1**



A solution of aldimino thioester **1** (1.0 eq.) and **3c** (2 mol%) in *m*-xylene (0.17 M) at -45 $^\circ\text{C}$ was added enone (2.0 eq.) and followed by aqueous potassium hydroxide solution (50 wt%, 50 mol%). The reaction was stirred at the same temperature until the consumption of the substrate observed. The reaction was quenched by passing the short column (neutral Silica-gel, ethyl acetate) to give the crude product, which was purified by column chromatography (Silica-gel, hexane/ethyl acetate) to

give 4.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-5-oxo-2-phenylhexanethioate (4a)**



Orange oil, 18.5 mg, 0.043 mmol, 77%, 81% ee.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM- D) δ 8.31-8.27 (m, 2H), 8.00 (s, 1H), 7.95-7.92 (m, 2H), 7.40-7.32 (m, 5H), 2.75-2.46 (m, 4H), 2.12 (s, 3H), 1.49 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM- D) δ 207.6, 204.2, 159.6, 149.4, 141.2, 140.1, 129.3, 128.8, 128.2, 127.5, 123.9, 79.6, 47.6, 38.0, 32.3, 30.2, 29.6.

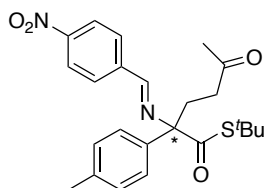
IR (NaCl) ν 2962, 2922, 1717, 1676, 1524, 1346, 1166 cm^{-1} .

HRMS (ESI $^+$ in MeCN) calcd for $\text{C}_{23}\text{H}_{27}\text{O}_4\text{N}_2\text{S}$ (M+H) 427.1686 found 427.1683.

$[\alpha]_{\text{D}}^{20} = +71.94$ ($c = 0.416$, CHCl_3).

Enantiomeric excess was determined by HPLC (CHIRALPAK AD-H, hexane/2-propanol = 80/20, flow rate 0.7 mL/min, 25 $^{\circ}\text{C}$, 254 nm) first peak: $t_{\text{R}} = 11.0$ min, second peak: $t_{\text{R}} = 13.4$ min.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-5-oxo-2-(*p*-tolyl)hexanethioate (4b)**



White oil, 55.7 mg, 0.13 mmol, 93%, 65% ee.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM- D) δ 8.31-8.27 (m, 2H), 7.98 (s, 1H), 7.95-7.92 (m, 2H), 7.28-7.25 (m, 2H), 7.20-7.18 (m, 2H), 2.74-2.39 (m, 4H), 2.36 (s, 3H), 2.13 (s, 3H), 1.49 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM- D) δ 207.8, 204.5, 159.5, 149.2, 141.3, 138.0, 137.0, 129.4, 129.3, 127.3, 123.9, 79.3, 47.5, 37.9, 32.3, 30.2, 29.6, 21.1.

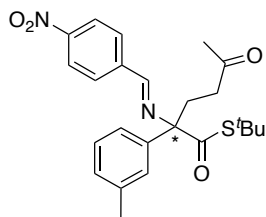
IR (NaCl) ν 2961, 2292, 1718, 1674, 1522, 1346, 1165 cm^{-1} .

HRMS (ESI $^+$ in MeCN) calcd for $\text{C}_{24}\text{H}_{29}\text{O}_4\text{N}_2\text{S}$ (M+H) 441.1843 found 441.1838.

$[\alpha]_{\text{D}}^{20} = +60.74$ ($c = 0.410$, CHCl_3).

Enantiomeric excess was determined by HPLC (CHIRALPAK AD-H, hexane/2-propanol = 80/20, flow rate 0.7 mL/min, 25 $^{\circ}\text{C}$, 254 nm) first peak: $t_{\text{R}} = 12.8$ min, second peak: $t_{\text{R}} = 25.9$ min.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-5-oxo-2-(*m*-tolyl)hexanethioate (4c)**



Orange oil, 58.2 mg, 0.13 mmol, 97%, 78% ee.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM-D) δ 8.31-8.27 (m, 2H), 7.97 (s, 1H), 7.94-7.93 (m, 2H), 7.29-7.25 (m, 1H), 7.20-7.14 (m, 3H), 2.75-2.39 (m, 4H), 2.36 (s, 3H), 2.13 (s, 3H), 1.50 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM-D) δ 207.8, 204.5, 159.6, 149.2, 141.3, 140.0, 138.4, 129.3, 128.9, 128.6, 128.0, 124.5, 123.9, 79.4, 47.5, 37.9, 32.2, 30.2, 29.5, 21.6.

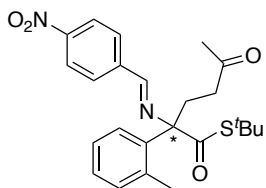
IR (NaCl) ν 2962, 2924, 1715, 1674, 1524, 1345, 1168 cm^{-1} .

HRMS (ESI⁺ in MeCN) calcd for C₂₄H₂₉O₄N₂S (M+H) 441.1843 found 441.1838.

$[\alpha]_{\text{D}}^{20} = +64.40$ ($c = 0.470$, CHCl₃).

Enantiomeric excess was determined by HPLC (CHIRALPAK IA-3, hexane/ethanol = 98/2, flow rate 0.6 mL/min, 25 °C, 254 nm) first peak: $t_{\text{R}} = 21.3$ min, second peak: $t_{\text{R}} = 22.6$ min.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-5-oxo-2-(*o*-tolyl)hexanethioate (4d)**



White oil, 50.9 mg, 0.12 mmol, 85%, 47% ee.

$^1\text{H-NMR}$ (400 MHz, CHLOROFORM-D) δ 8.29-8.26 (m, 2H), 7.94-7.91 (m, 2H), 7.83 (s, 1H), 7.56-7.52 (m, 1H), 7.34-7.28 (m, 2H), 7.20-7.16 (m, 1H), 2.71-2.35 (m, 4H), 2.14 (s, 3H), 2.11 (s, 3H), 1.52 (s, 9H); $^{13}\text{C-NMR}$ (101 MHz, CHLOROFORM-D) δ 207.4, 204.8, 157.4, 149.2, 141.3, 138.0, 137.3, 132.3, 129.1, 128.5, 128.3, 125.7, 123.9, 80.0, 47.3, 38.3, 33.7, 30.3, 29.6, 22.0.

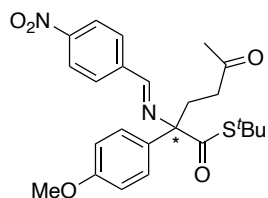
IR (NaCl) ν 2962, 1719, 1676, 1523, 1167, 851 cm^{-1} .

HRMS (ESI⁺ in MeCN) calcd for C₂₄H₂₉O₄N₂S (M+H) 441.1843 found 441.1837.

$[\alpha]_{\text{D}}^{20} = +29.97$ ($c = 0.757$, CHCl₃).

Enantiomeric excess was determined by HPLC (CHIRALPAK IA-3, hexane/ethanol = 98/2, flow rate 0.6 mL/min, 25 °C, 254 nm) first peak: $t_{\text{R}} = 22.4$ min, second peak: $t_{\text{R}} = 27.1$ min.

***S*-(*tert*-butyl) (*E*)-2-(4-methoxyphenyl)-2-((4-nitrobenzylidene)amino)ethanethioate (4e)**



White oil, 18.4 mg, 0.040 mmol, 31%, 50% ee.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.30-8.27 (m, 2H), 7.98 (s, 1H), 7.95-7.92 (m, 2H), 7.32-7.29 (m, 2H), 6.93-6.89 (m, 2H), 3.82 (s, 3H), 2.73-2.40 (m, 4H), 2.13 (s, 3H), 1.49 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 207.8, 204.5, 159.4, 159.2, 149.2, 141.3, 132.0, 129.3, 128.7, 123.9, 114.0, 79.1, 55.2, 47.5, 38.0, 32.4, 30.3, 29.6.

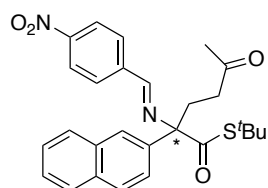
IR (NaCl) ν 2960, 2924, 1717, 1673, 1522, 1346, 1253 cm⁻¹.

HRMS (ESI⁺ in MeCN) calcd for C₂₄H₂₉O₅N₂S (M+H) 457.1792 found 457.1785.

$[\alpha]_D^{20} = +46.78$ ($c = 0.572$, CHCl₃).

Enantiomeric excess was determined by HPLC (CHIRALPAK IA, hexane/ethanol = 90/10, flow rate 0.7 mL/min, 25 °C, 254 nm) first peak: $t_R = 16.6$ min, second peak: $t_R = 18.8$ min.

***S*-(*tert*-butyl) (*E*)-2-(naphthalen-2-yl)-2-((4-nitrobenzylidene)amino)ethanethioate (4f)**



Yellow oil, 39.5 mg, 0.082 mmol, 93%, 65% ee.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.30-8.27 (m, 2H), 8.00 (s, 1H), 7.98 (d, $J = 1.9$ Hz, 1H), 7.95-7.92 (m, 2H), 7.90-7.82 (m, 3H), 7.56-7.50 (m, 2H), 7.38 (dd, $J = 8.7, 1.9$ Hz, 1H), 2.91-2.54 (m, 4H), 2.14 (s, 3H), 1.51 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 207.7, 204.3, 160.0, 149.3, 141.2, 137.4, 133.0, 132.8, 129.3, 128.7, 128.4, 127.5, 126.8, 126.7, 126.5, 125.1, 123.9, 79.6, 47.7, 37.9, 32.4, 30.3, 29.6.

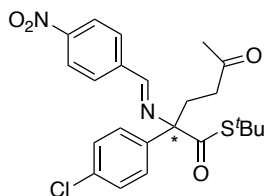
IR (NaCl) ν 2959, 2922, 1718, 1674, 1522, 1345, 1165 cm⁻¹.

HRMS (ESI⁺ in MeCN) calcd for C₂₇H₂₉N₂O₄S (M+H) 477.1843 found 477.1834.

$[\alpha]_D^{20} = +73.72$ ($c = 0.436$, CHCl₃).

Enantiomeric excess was determined by HPLC (CHIRALPAK IA, hexane/ethanol = 98/2, flow rate 0.7 mL/min, 25 °C, 254 nm) first peak: $t_R = 28.6$ min, second peak: $t_R = 31.4$ min.

***S*-(*tert*-butyl) (*E*)-2-(4-chlorophenyl)-2-((4-nitrobenzylidene)amino)-5-oxohexanethioate (4g)**



Yellow oil, 46.3 mg, 0.10 mmol, 80%, 69% ee.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.32-8.28 (m, 2H), 8.02 (s, 1H), 7.97-7.94 (m, 2H), 2.73-2.42 (m, 4H), 2.12 (s, 3H), 1.48 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 207.4, 203.7, 159.8, 149.4, 141.0, 138.8, 134.1, 129.3, 128.9, 128.9, 123.9, 79.0, 47.8, 37.7, 32.1, 30.2, 29.5.

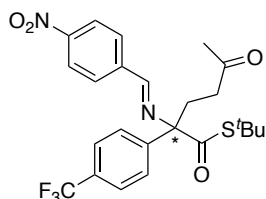
IR (NaCl) ν 2961, 2900, 2361, 2339, 1717, 1522, 1345, 852 cm⁻¹.

[α]_D²⁰ = +74.14 (c = 1.0, CHCl₃).

HRMS (ESI⁺ in MeCN) calcd for C₂₃H₂₆O₄N₂ClS (M+H) 461.1296 found 461.1290.

Enantiomeric excess was determined by HPLC (CHIRALPAK IA, hexane/ethanol = 98/2, flow rate 0.7 mL/min, 25 °C, 254 nm) first peak: t_R = 25.7 min, second peak: t_R = 33.2 min.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-5-oxo-2-(4-(trifluoromethyl)phenyl)hexanethioate (4h)**



Yellow oil, 57.3 mg, 0.12 mmol, 86%, 40% ee.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.31-8.29 (m, 2H), 8.06 (s, 1H), 7.99-7.96 (m, 2H), 7.68-7.63 (m, 2H), 7.60-7.54 (m, 2H), 2.78-2.67 (m, 1H), 2.65-2.48 (m, 3H), 2.12 (s, 3H), 1.49 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 207.2, 203.4, 160.1, 149.4, 144.3, 140.9, 130.2 (q, J = 32.2 Hz), 129.3, 127.9, 125.6 (q, J = 3.8 Hz), 123.9, 123.8 (q, J = 270.2 Hz), 79.1, 47.9, 37.6, 32.0, 30.1, 29.5; ¹⁹F-NMR (377 MHz, CHLOROFORM-D) δ -62.6.

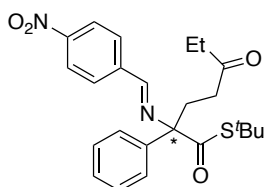
IR (NaCl) ν 2964, 2360, 1717, 1674, 1524, 1346, 1326, 1125, 853 cm⁻¹.

HRMS (ESI⁺ in MeCN) calcd for C₂₄H₂₆O₄N₂F₃S (M+H) 495.1560 found 495.1552.

[α]_D²⁰ = +32.61 (c = 1.0, CHCl₃).

Enantiomeric excess was determined by HPLC (CHIRALPAK IA, hexane/ethanol = 98/2, flow rate 0.7 mL/min, 25 °C, 254 nm) first peak: t_R = 23.1 min, second peak: t_R = 31.9 min.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-5-oxo-2-phenylheptanethioate (4i)**



Orange oil, 39.2 mg, 0.089 mmol, 79%, 64% ee.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.30-8.27 (m, 2H), 7.99 (s, 1H), 7.95-7.92 (m, 2H), 7.40-7.32 (m, 5H), 2.77-2.48 (m, 4H), 2.41 (q, $J = 7.3$ Hz, 2H), 1.49 (s, 9H), 0.97 (t, $J = 7.3$ Hz, 3H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 210.4, 204.4, 159.6, 149.2, 141.3, 140.2, 129.3, 128.7, 128.1, 127.5, 123.9, 79.6, 47.5, 36.5, 36.2, 32.2, 29.6, 7.7.

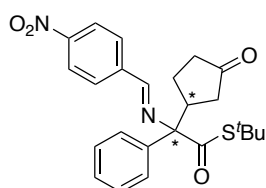
IR (NaCl) ν 2966, 1715, 1675, 1524, 1346, 1111, 853 cm^{-1} .

HRMS (ESI⁺ in MeCN) calcd for C₂₄H₂₉O₄N₂S (M+H) 441.1843 found 441.1838.

$[\alpha]_{\text{D}}^{20} = +50.90$ ($c = 0.456$, CHCl₃).

Enantiomeric excess was determined by HPLC (CHIRALPAK IA, hexane/ethanol = 98/2, flow rate 0.6 mL/min, 25 °C, 254 nm) first peak: $t_{\text{R}} = 22.9$ min, second peak: $t_{\text{R}} = 24.4$ min.

***S*-(*tert*-butyl) (*E*)-2-((4-nitrobenzylidene)amino)-2-(3-oxocyclopentyl)-2-phenylethanethioate (4j)**



Yellow oil, 25.5 mg, 0.058 mmol, 58%, dr = 5 : 1, 11% ee for major diastereomer.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.33-8.28 (m, 2.38H), 8.11 (s, 0.16H), 8.03 (s, 1H), 7.98-7.92 (m, 2.44H), 7.45-7.31 (m, 6.44H), 3.54-3.46 (m, 1.03H), 3.44-3.36 (m, 0.18H), 2.62 (dd, $J = 18.8, 9.2$ Hz, 0.16H), 2.53-2.44 (m, 1.15H), 2.31-2.13 (m, 4.56H), 2.03 (dd, $J = 18.8, 9.2$ Hz, 1.02H), 1.48 (s, 9H), 1.46 (s, 1.43H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 217.6, 203.8, 160.6, 149.4, 140.9, 138.5, 129.4, 128.8, 128.3, 128.2, 124.0, 82.7, 47.9, 43.2, 40.7, 37.8, 29.6, 24.7 (Assigned only for major diastereomer).

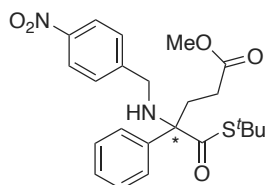
IR (NaCl) ν 2963, 2925, 1741, 1673, 1523, 1346, 842, 752 cm^{-1} .

HRMS (ESI⁺ in MeCN) calcd for C₂₄H₂₇O₄N₂S (M+H) 439.1686 found 439.1683.

$[\alpha]_{\text{D}}^{20} = +6.76$ ($c = 0.3$, CHCl₃).

Enantiomeric excess was determined by HPLC (CHIRALPAK IA, hexane/ethanol = 98/2, flow rate 0.7 mL/min, 25 °C, 254 nm) first peak: $t_{\text{R}} = 33.7$ min, second peak: $t_{\text{R}} = 52.5$ min.

methyl 5-(*tert*-butylthio)-4-((4-nitrobenzyl)amino)-5-oxo-4-phenylpentanoate (4k)



Yellow oil, 2.6 mg, 0.0058 mmol, 15%, Rac.

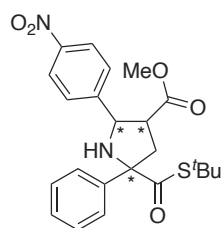
¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.26-8.21 (m, 2H), 7.62-7.56 (m, 2H), 7.46-7.43 (m, 2H), 7.39-7.35 (m, 2H), 7.33-7.29 (m, 1H), 3.77-3.64 (m, 2H), 3.59 (s, 3H), 2.63-2.55 (m, 1H), 2.46-2.39 (m, 1H), 2.33-2.25 (m, 2H), 2.17-2.09 (m, 1H), 1.45 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 204.0, 173.7, 147.6, 147.2, 140.0, 128.8, 128.6, 128.0, 126.3, 123.7, 73.2, 51.7, 48.2, 46.4, 29.8, 29.3, 28.3.

IR (NaCl) ν 3343, 2959, 1736, 1673, 1605, 1521, 1345, 1169, 853 cm^{-1} .

HRMS (ESI⁺ in MeCN) calcd for C₂₃H₂₉O₅N₂S (M+H) 445.1792 found 445.1786.

Enantiomeric excess was determined by HPLC (CHIRALPAK IA, hexane/ethanol = 98/2, flow rate 1.0 mL/min, 25 °C, 254 nm) first peak: t_R = 11.3 min, second peak: t_R = 12.3 min.

methyl 5-((*tert*-butylthio)carbonyl)-2-(4-nitrophenyl)-5-phenylpyrrolidine-3-carboxylate (4k')



Yellow oil, 3.1 mg, 0.0070 mmol, 18%, Rac.

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.23-8.18 (m, 2H), 7.66-7.63 (m, 2H), 7.55-7.51 (m, 2H), 7.43-7.39 (m, 2H), 7.36-7.32 (m, 1H), 4.77 (dd, J = 8.3, 6.7 Hz, 1H), 3.37-3.31 (m, 1H), 3.24 (s, 3H), 3.10 (d, J = 6.7 Hz, 1H), 3.01 (dd, J = 13.3, 8.3 Hz, 1H), 2.67 (dd, J = 13.3, 8.3 Hz, 1H), 1.46 (s, 9H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 203.3, 171.6, 148.1, 147.3, 141.6, 128.7, 128.4, 127.9, 125.7, 123.3, 77.3, 62.5, 51.5, 48.9, 47.5, 38.8, 29.7.

IR (NaCl) ν 3373, 2958, 2924, 2857, 1734, 1674, 1521, 1345, 852 cm^{-1} .

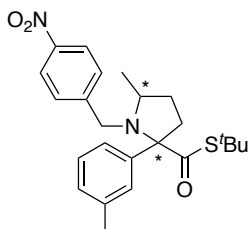
HRMS (ESI⁺ in MeCN) calcd for C₂₃H₂₇O₅N₂S (M+H) 443.1635 found 443.1631.

Enantiomeric excess was determined by HPLC (CHIRALPAK IB, hexane/ethanol = 9/1, flow rate 1.0 mL/min, 25 °C, 254 nm) first peak: t_R = 10.1 min, second peak: t_R = 13.3 min.

4. Derivatisation of the product 4c

To a solution of **4c** (1.0 eq.) in EtOH (0.1 M) at 0 °C, NaBH₃CN (2.0 eq) and followed by AcOH (5.0 eq.) were added. The reaction was stirred for 1 hour at the same temperature, which was quenched by the addition of saturated NaHCO₃ aq., extracted with CH₂Cl₂, dried over Na₂SO₄ and filtered to give the crude **5**. The crude **5** was purified by column chromatography (Silica-gel, hexane/ethyl acetate) to give pure **5**.

S-(*tert*-butyl) 5-methyl-1-(4-nitrobenzyl)-2-(*m*-tolyl)pyrrolidine-2-carbothioate (**5**)



Yellow oil, 44.5 mg, 0.10 mmol, Quant., dr = 1.4 : 1

¹H-NMR (400 MHz, CHLOROFORM-D) δ 8.10-8.05 (m, 4.8H), 7.50-7.46 (m, 2.8H), 7.45-7.41 (m, 2H), 7.24-7.05 (m, 9.6H), 4.12 (d, *J* = 16.6 Hz, 1H), 4.05 (d, *J* = 15.8 Hz, 1.4H), 3.90 (d, *J* = 16.6 Hz, 1H), 3.43 (d, *J* = 15.8 Hz, 1.4H), 3.37-3.33 (m, 1H), 3.28-3.18 (m, 1.4H), 2.63-2.57 (m, 2.4H), 2.47-2.34 (m, 2.4H), 2.322 (s, 4.2H), 2.317 (s, 3H), 2.22-2.09 (m, 2.4H), 1.69-1.55 (m, 2.4H), 1.53 (s, 9H), 1.52 (s, 12.6H), 0.93 (d, *J* = 6.2 Hz, 4.2H), 0.86 (d, *J* = 6.3 Hz, 3H); ¹³C-NMR (101 MHz, CHLOROFORM-D) δ 207.9, 206.4, 150.2, 149.1, 146.6, 146.5, 140.6, 140.2, 137.62, 137.61, 129.1, 128.9, 128.7, 128.34, 128.33, 128.26, 128.02, 128.00, 125.3, 125.1, 123.04, 122.97, 82.4, 81.8, 60.0, 58.3, 53.7, 52.2, 48.2, 47.2, 37.8, 37.5, 32.2, 31.1, 29.8, 29.6, 21.7, 21.6, 21.2, 20.9.

IR (NaCl) ν 2961, 2926, 2367, 1670, 1604, 1519, 1344, 758 cm⁻¹.

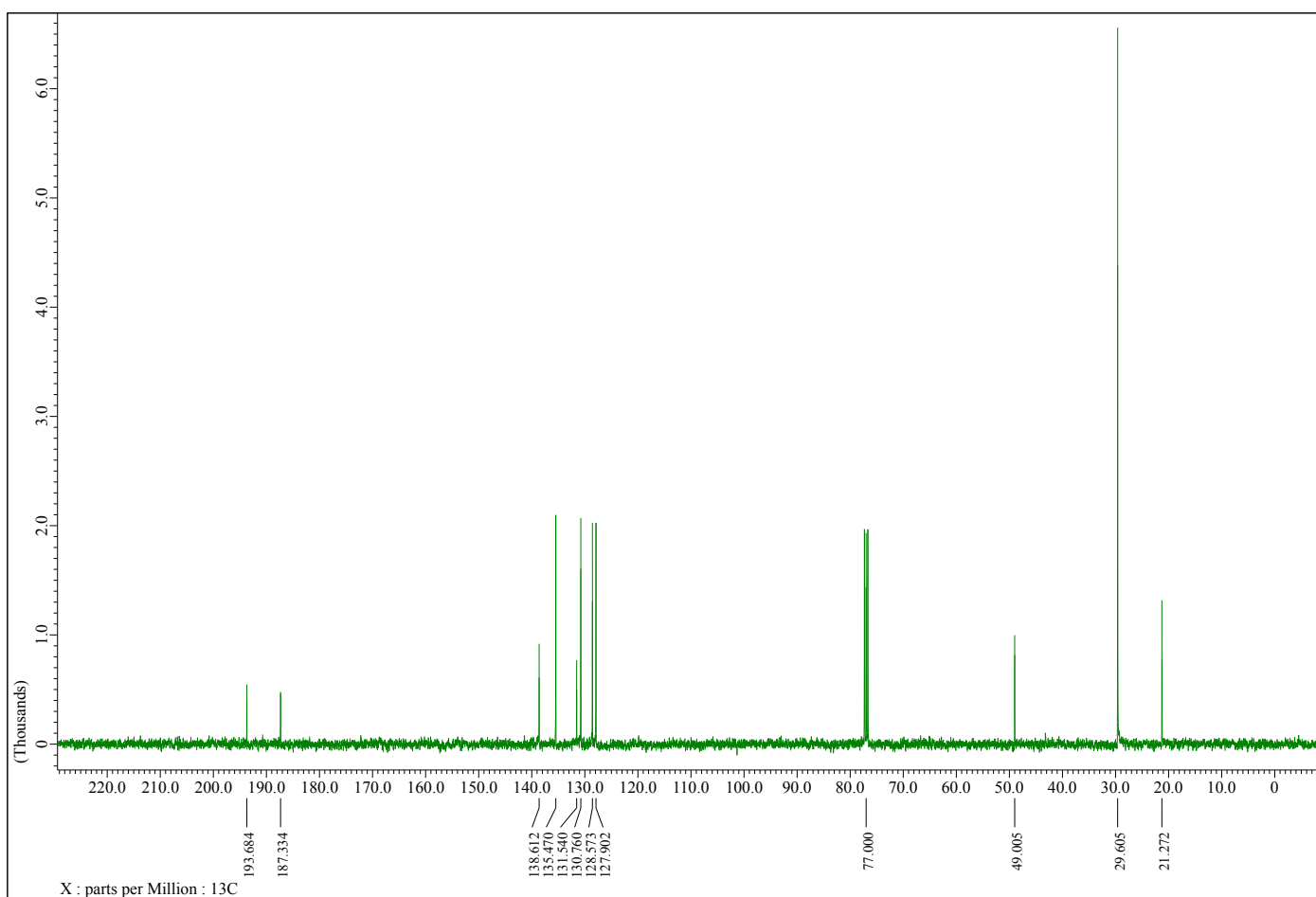
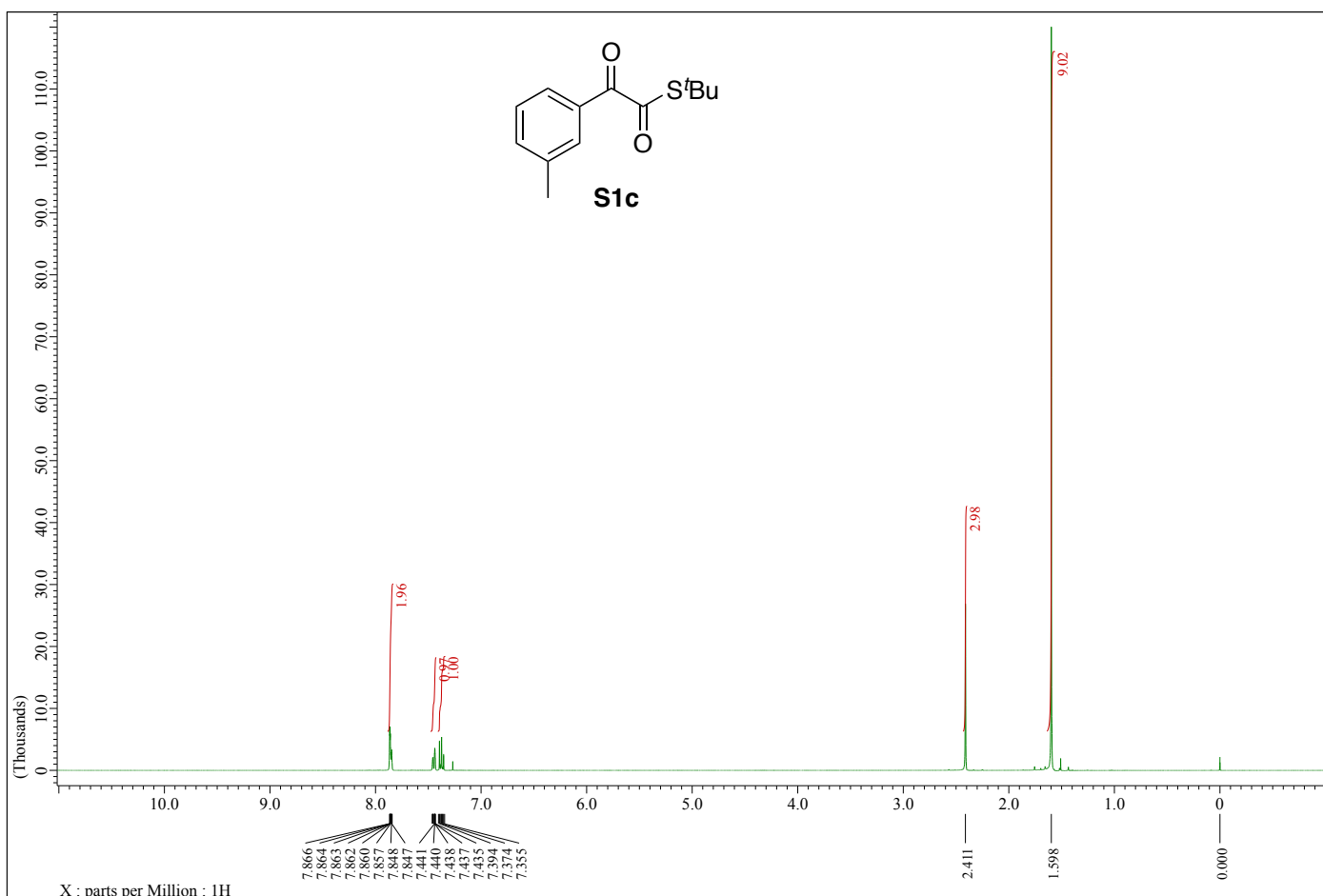
HRMS (ESI⁺ in MeCN) calcd for C₂₄H₃₁O₃N₂S (M+H) 427.2050 found 427.2038.

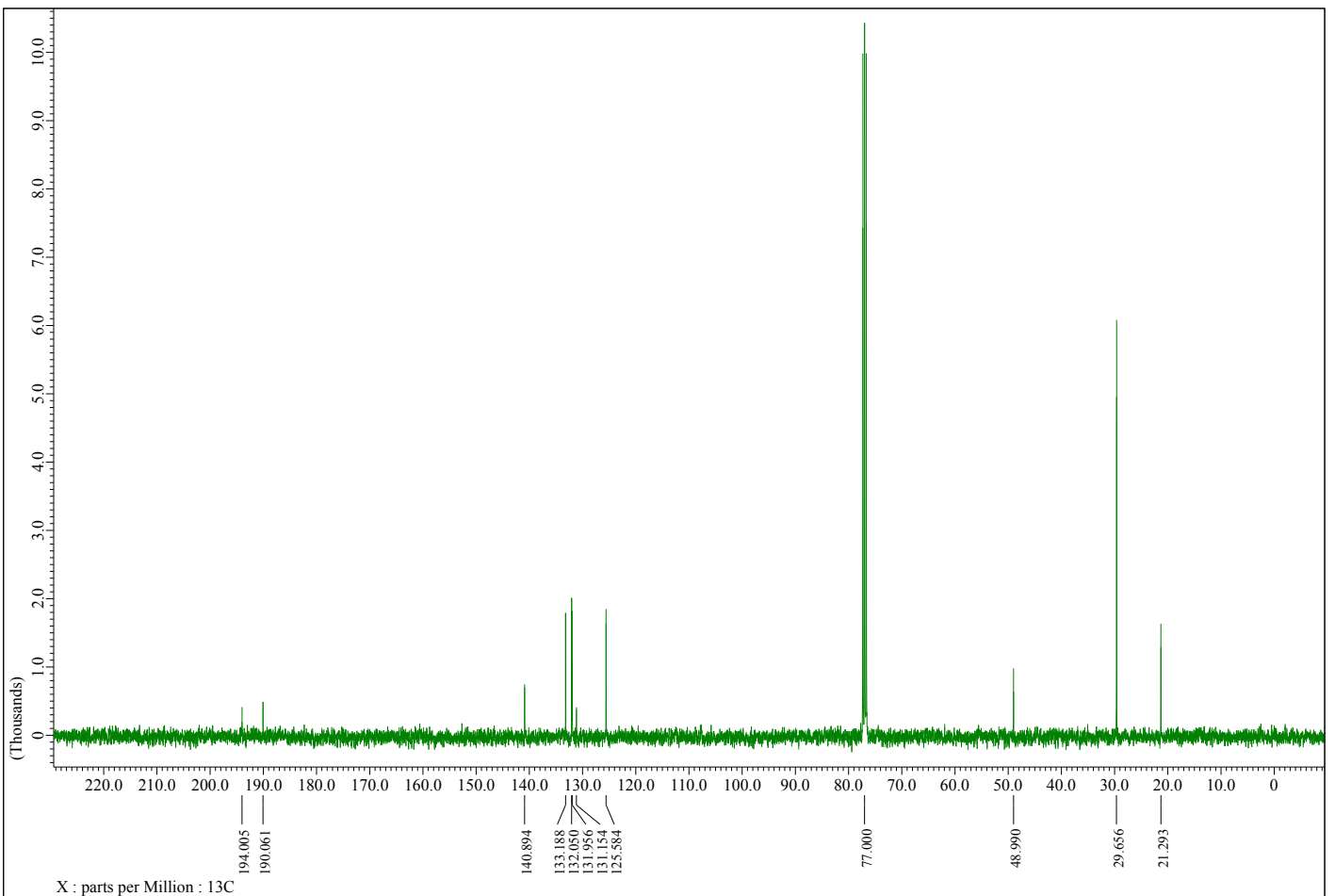
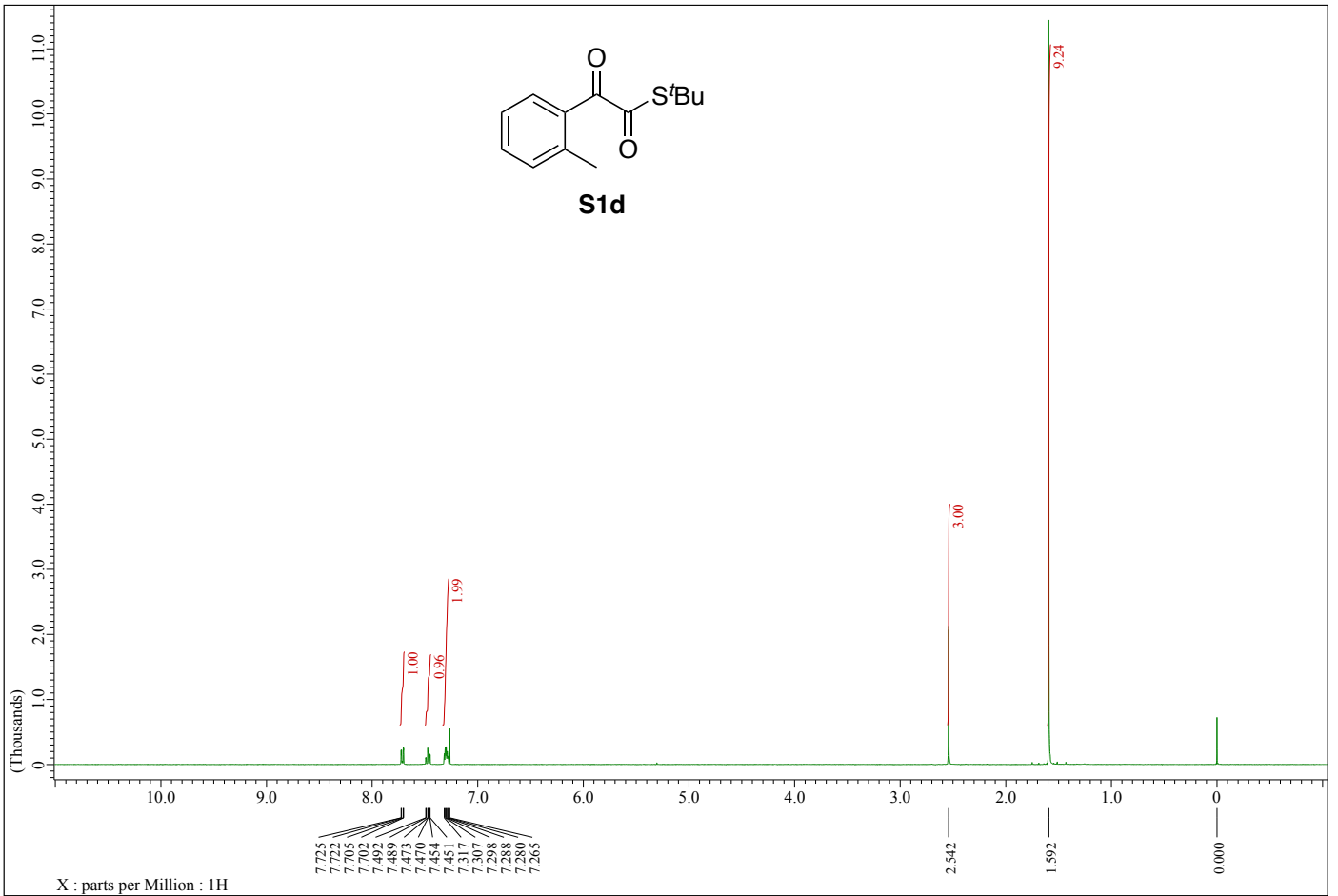
[α]_D²⁰ = -48.32 (*c* = 0.9, CHCl₃).

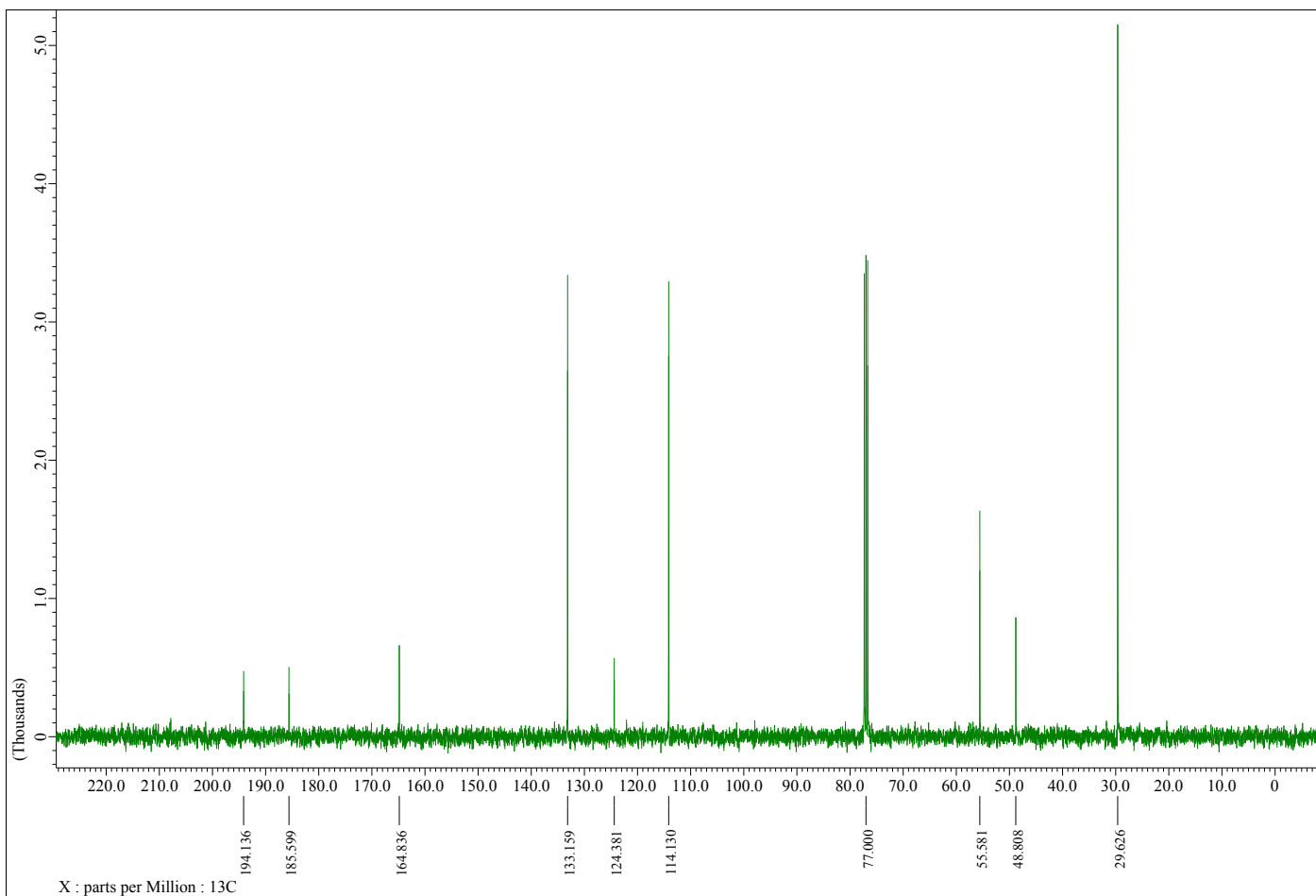
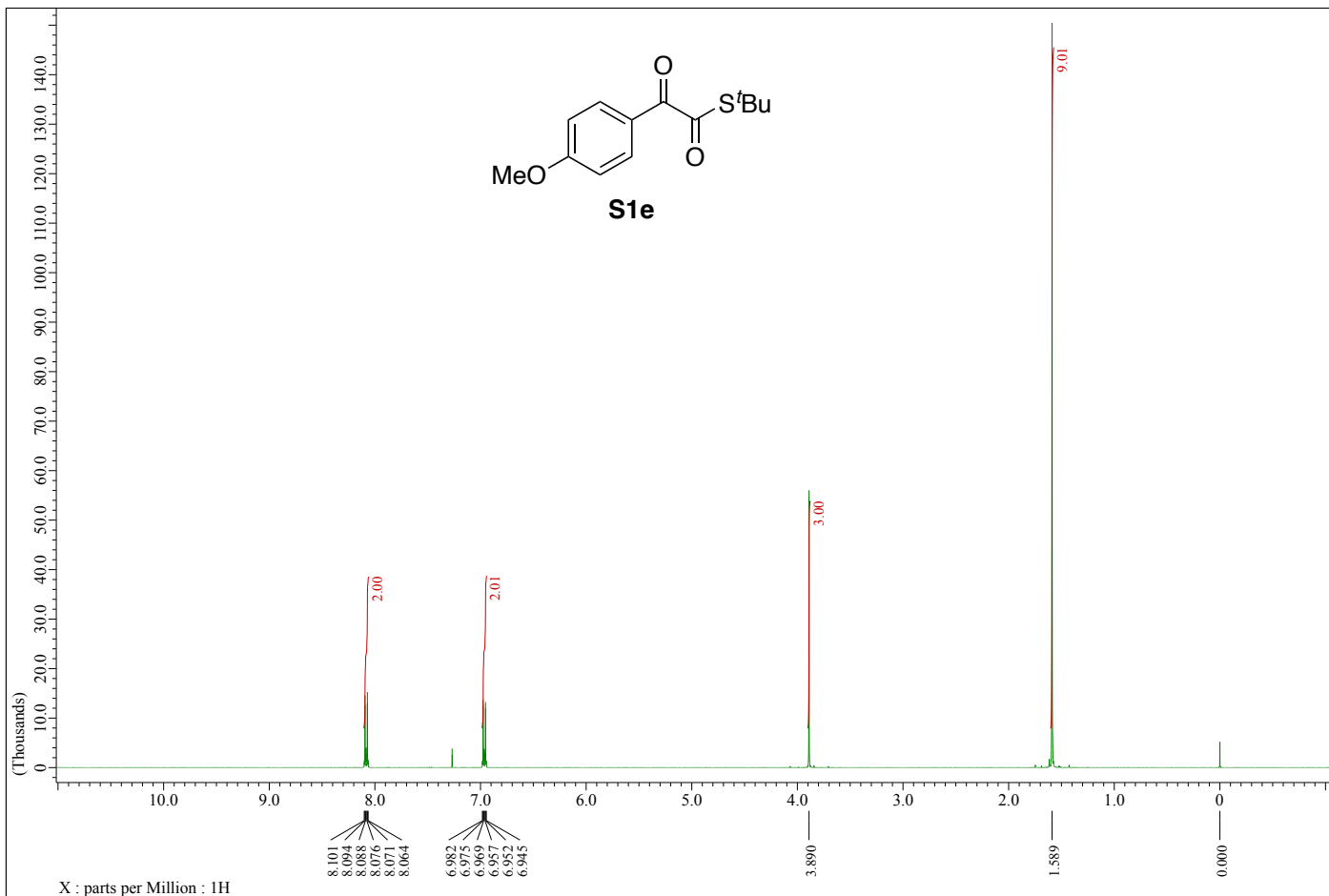
References

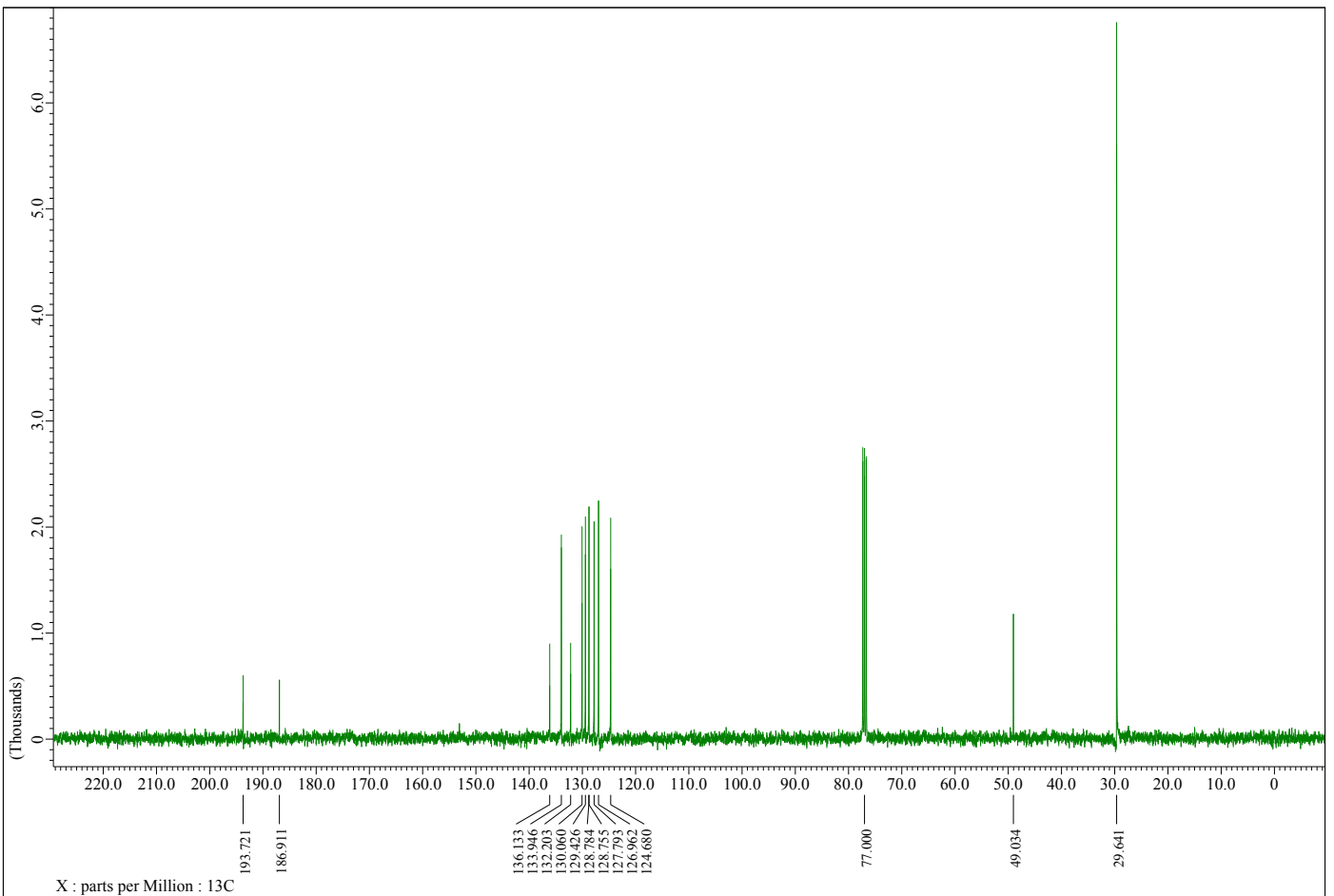
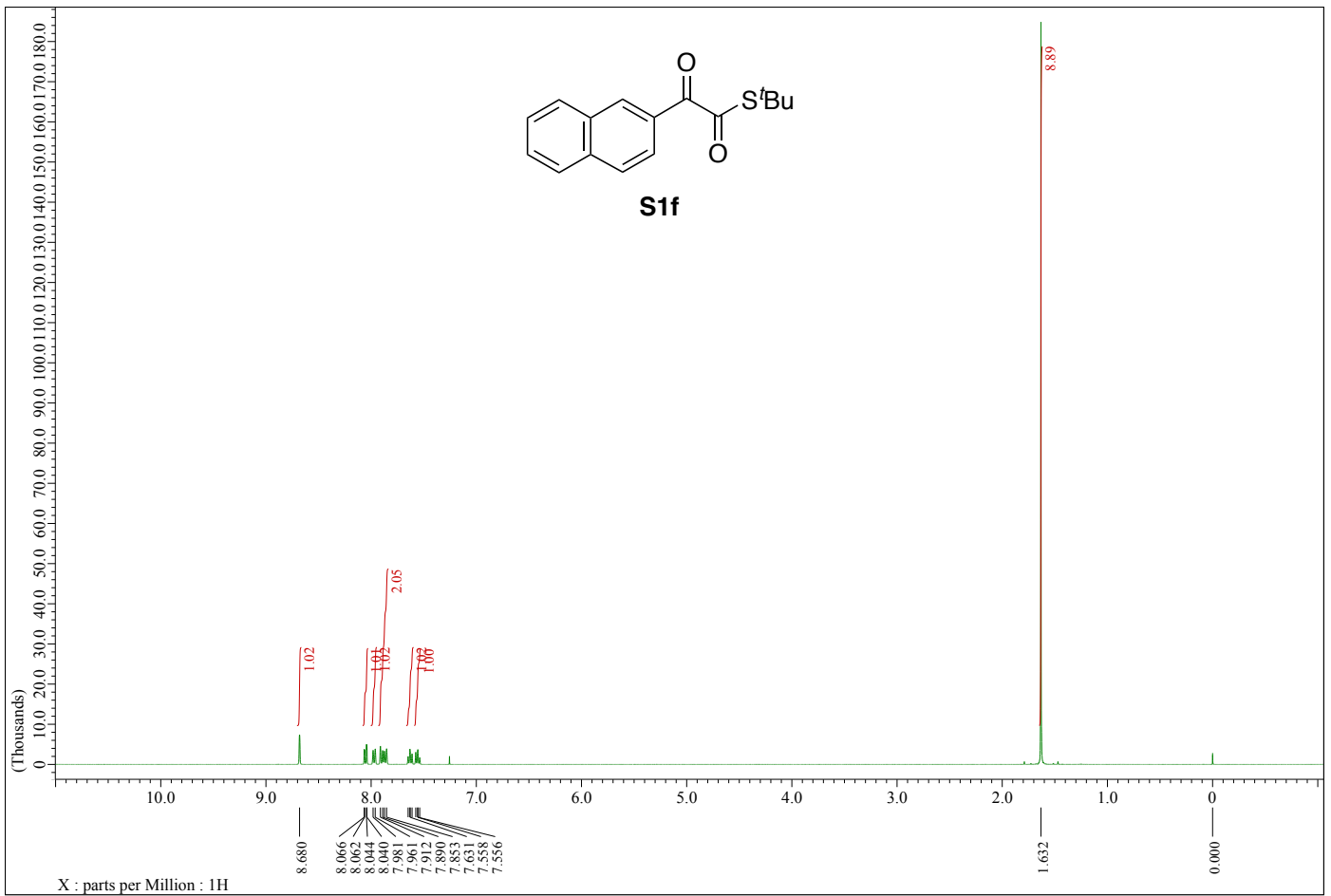
1. L. Deng *et al.* *Nature* **2015**, 523, 445.
2. Y. Yoshida *et al.* *Chem. Eur. J.* **2017**, 23, 12749.
3. Y. Yoshida *et al.* *Adv. Synth. Catal.* **2018**, 360, 4142.
4. C. T. Chen *et al.* *J. Org. Chem.* **2007**, 72, 8175.

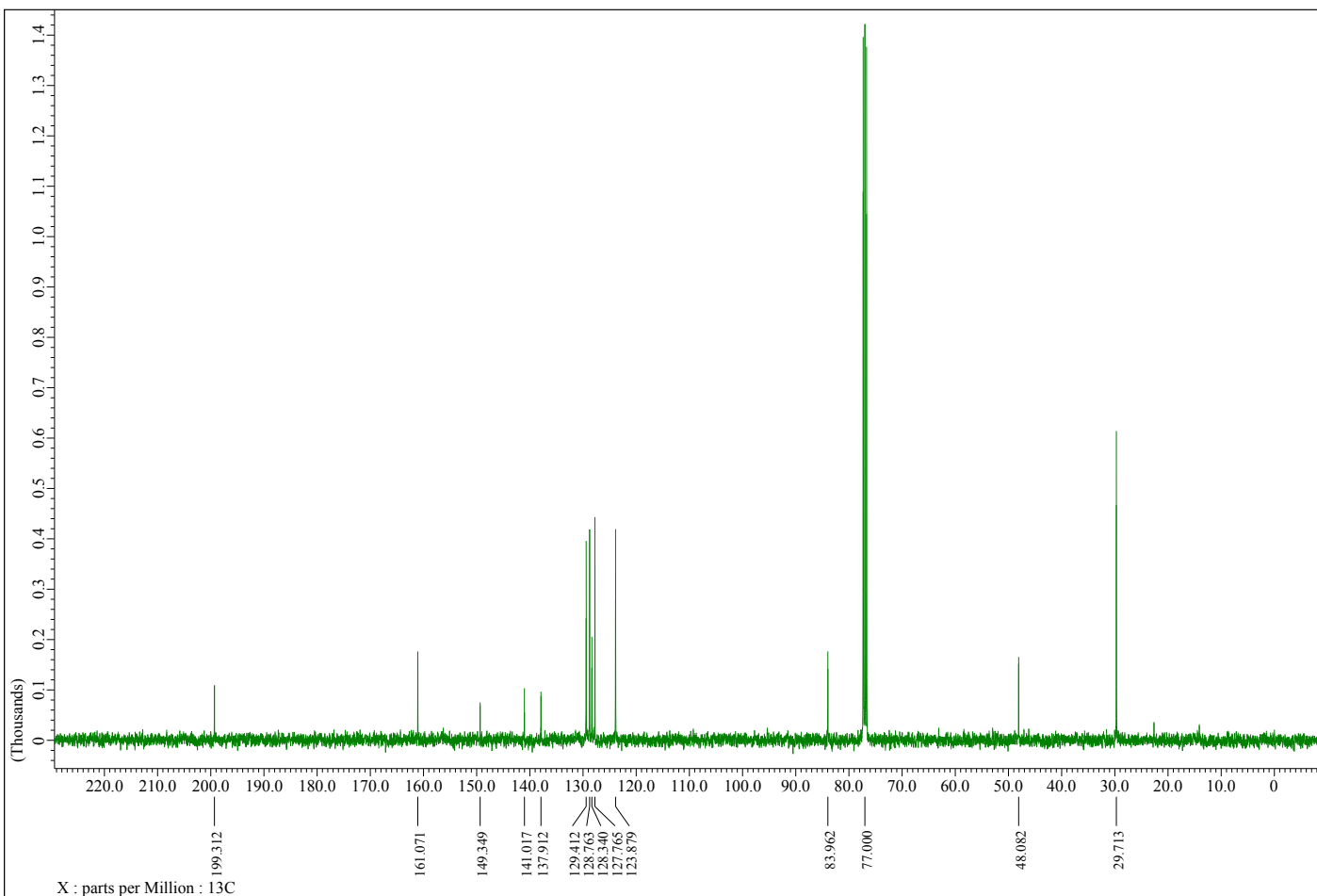
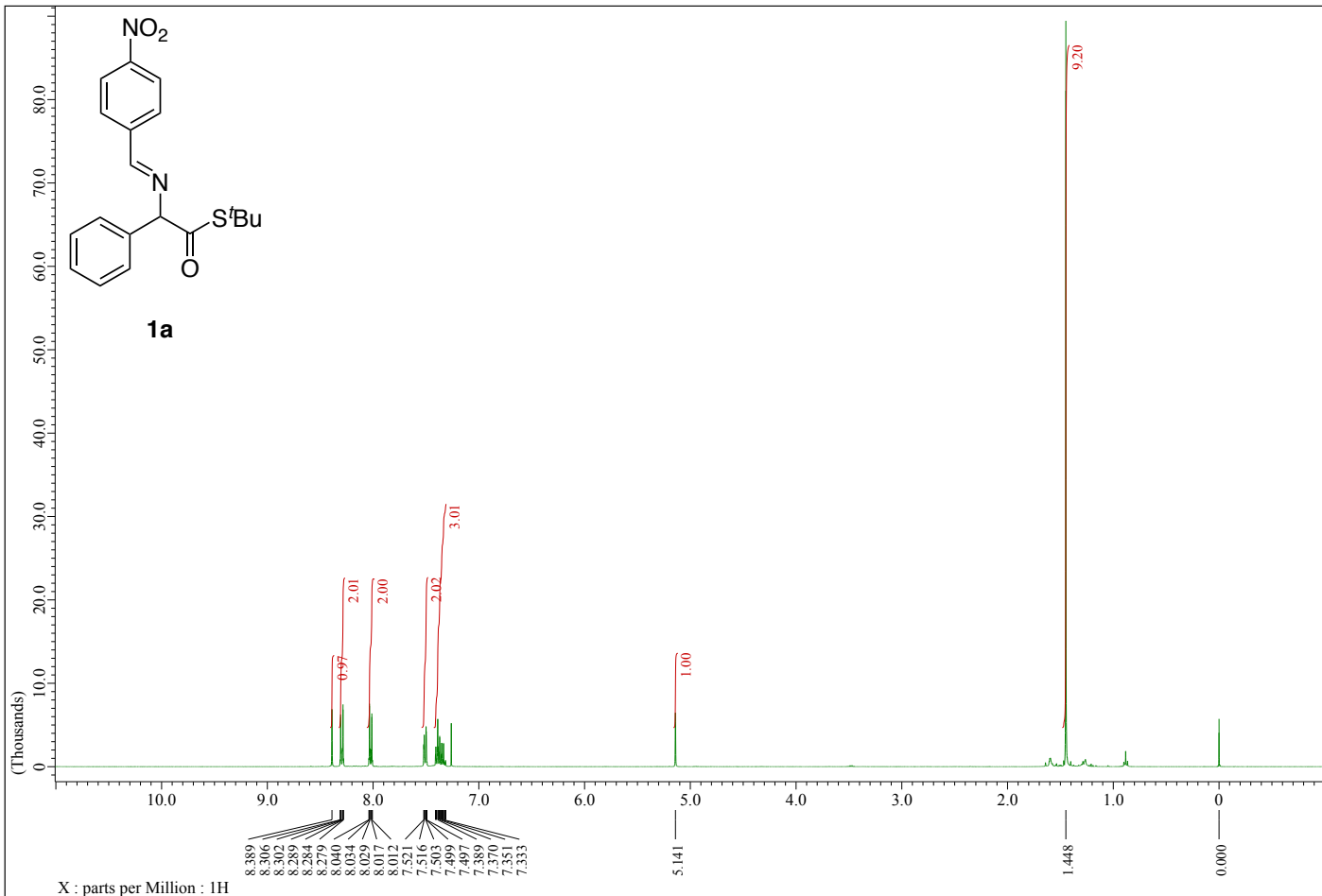
5. ¹H-, ¹³C-, and ¹⁹F-NMR spectra and HPLC charts.

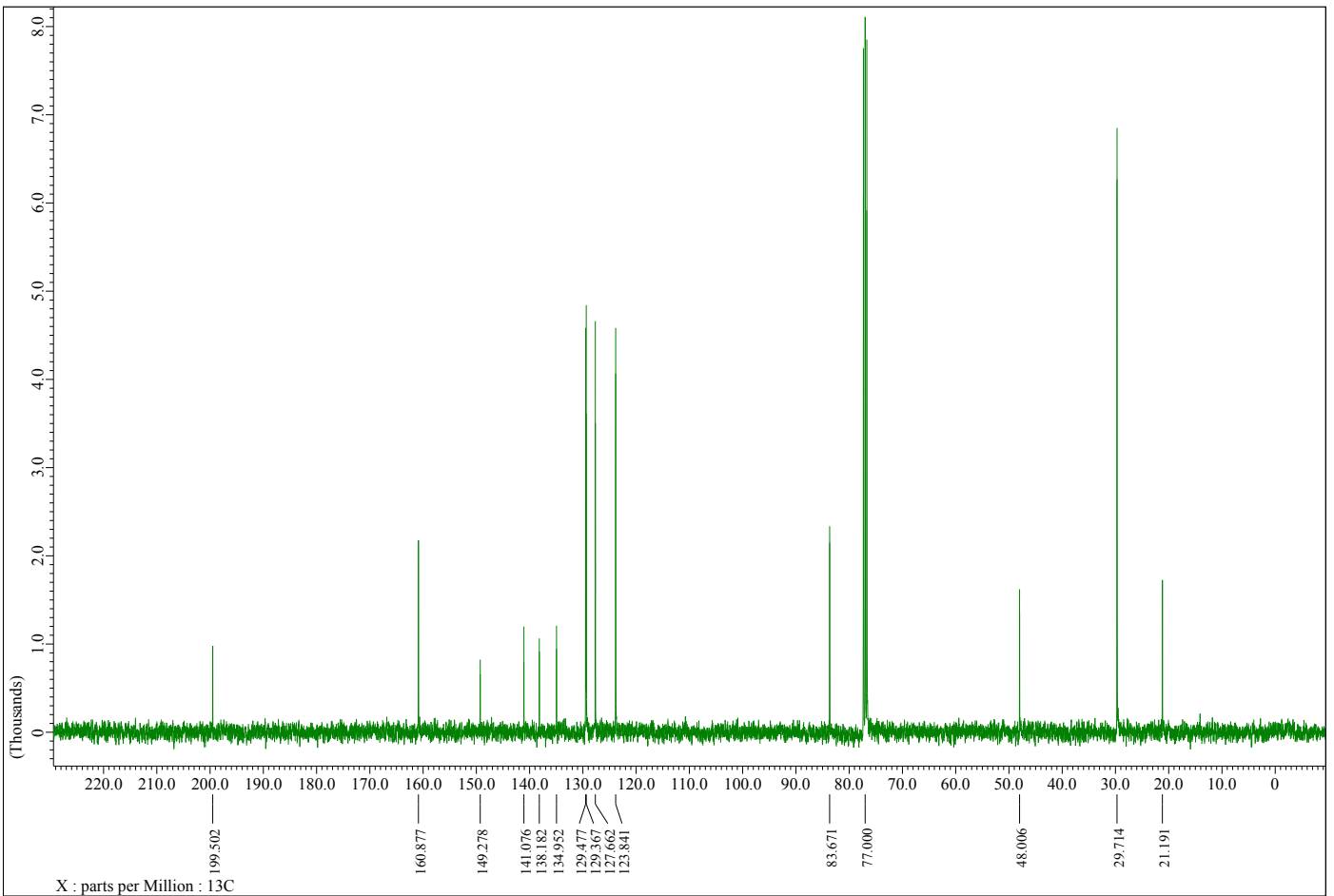
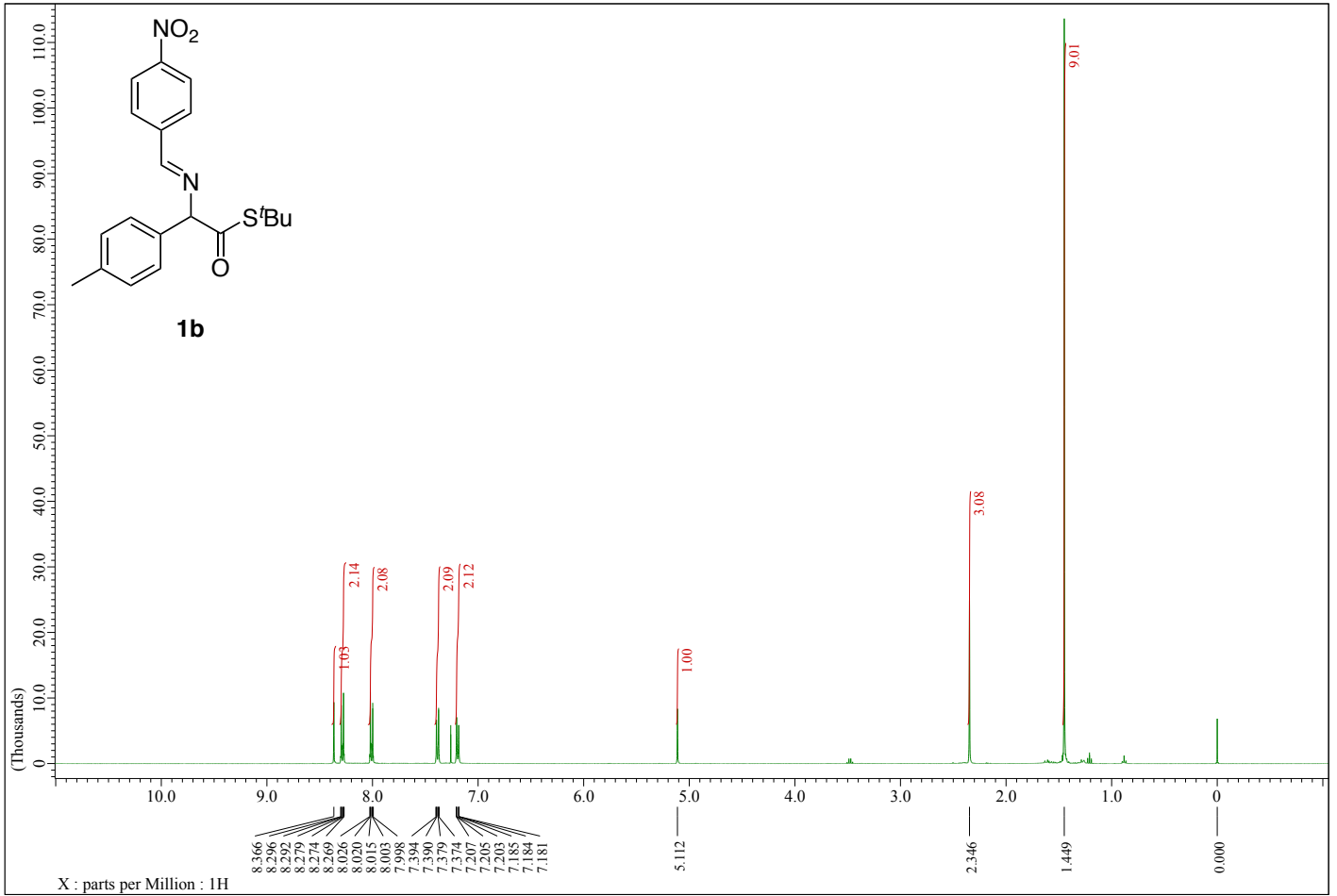


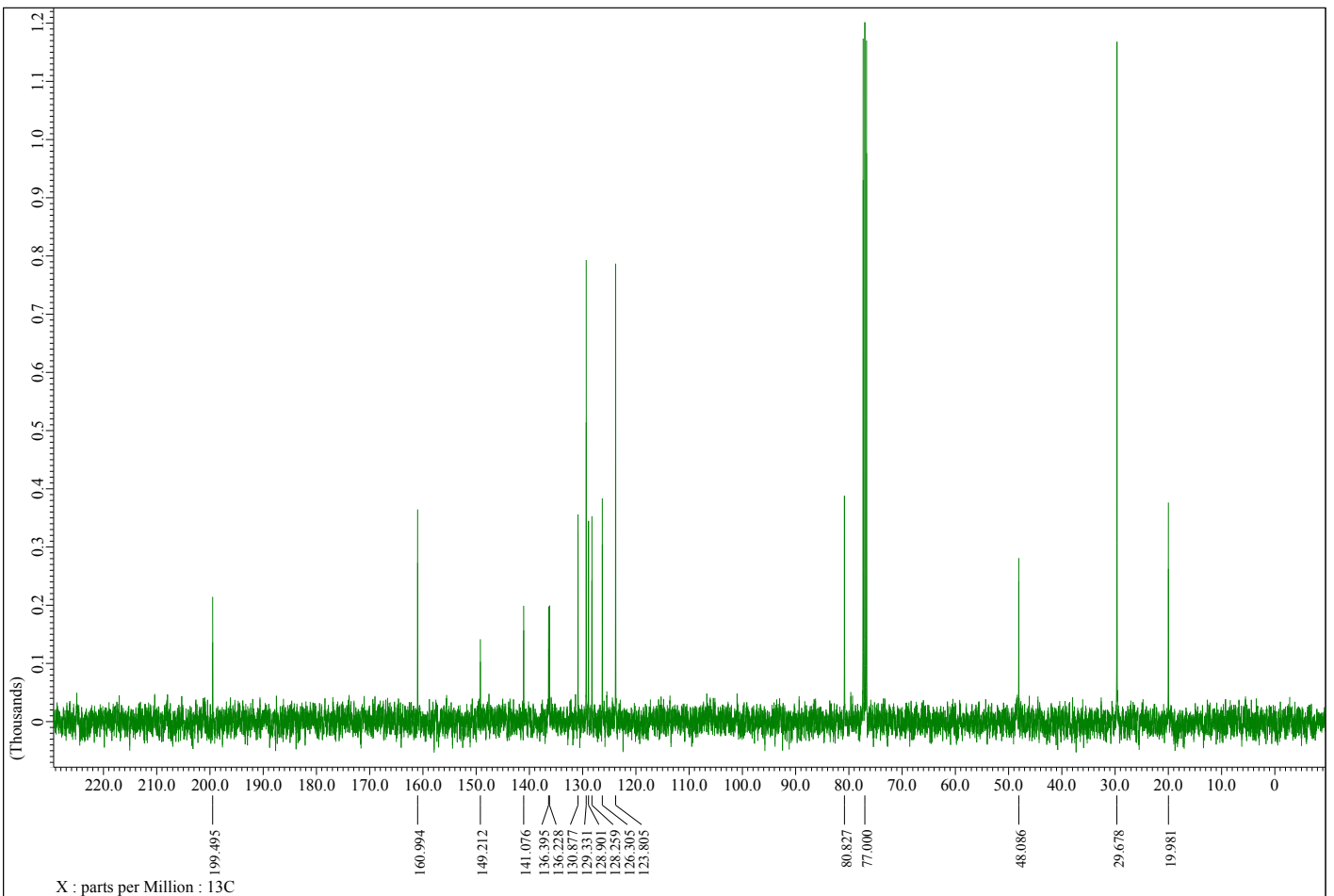
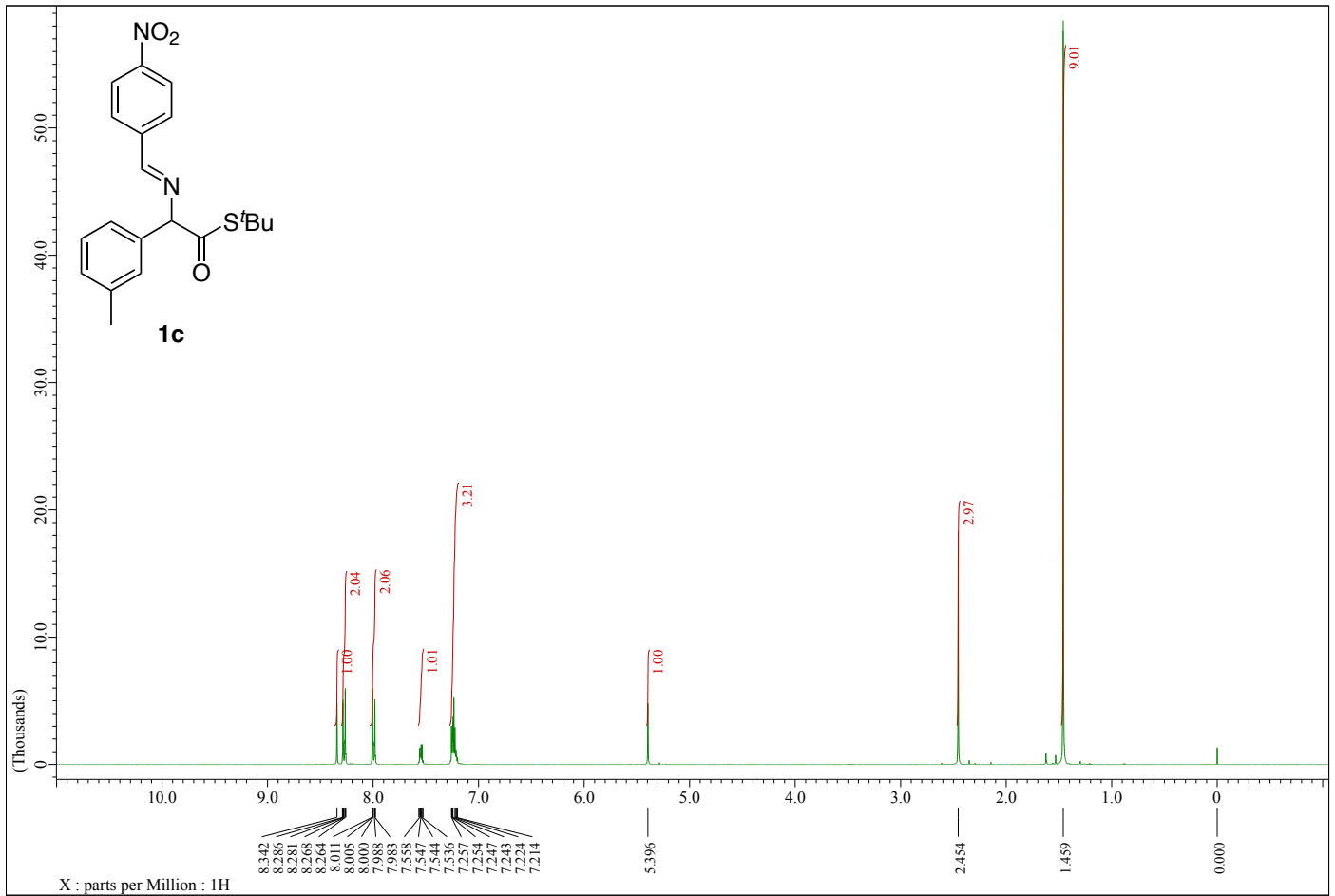


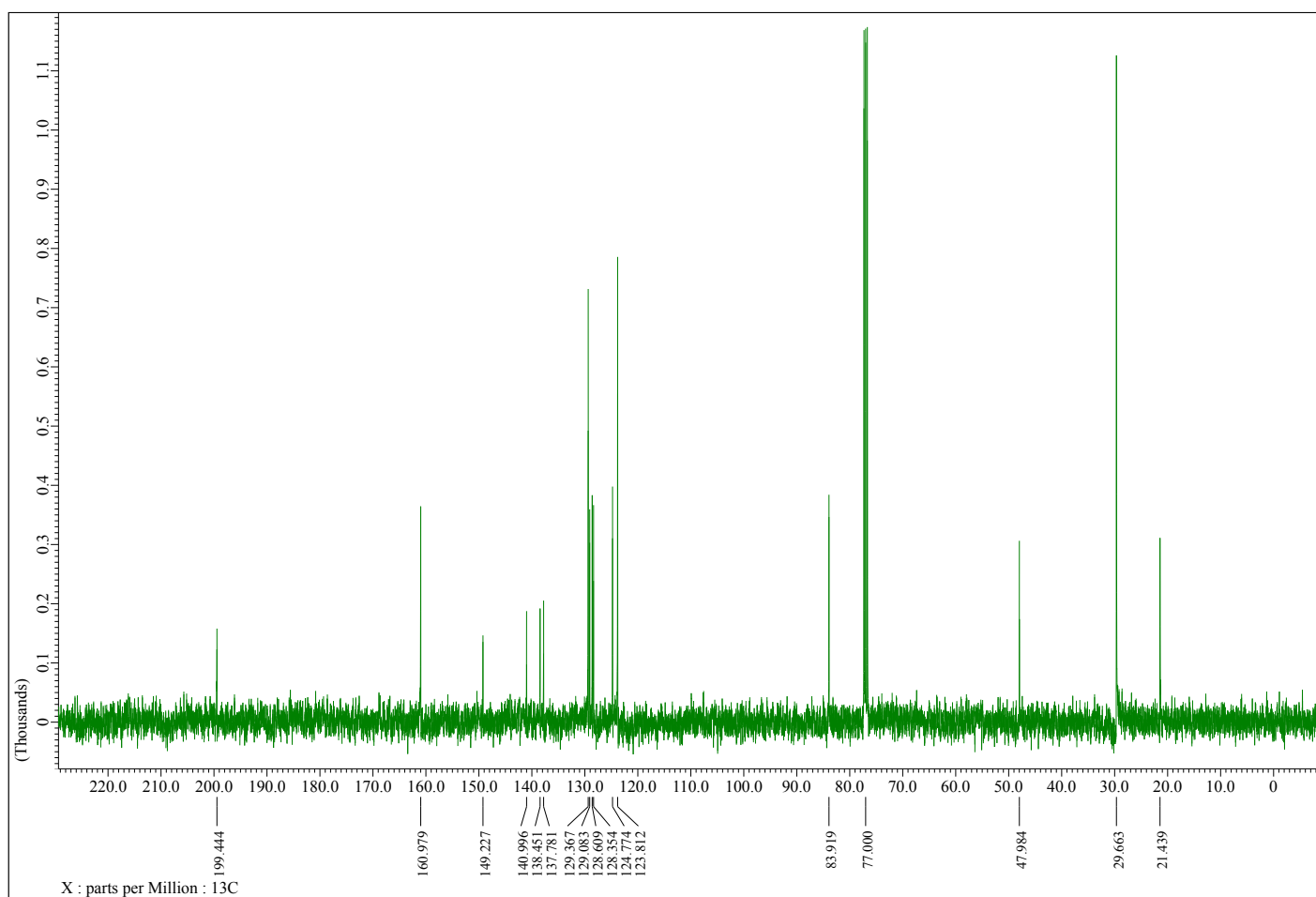
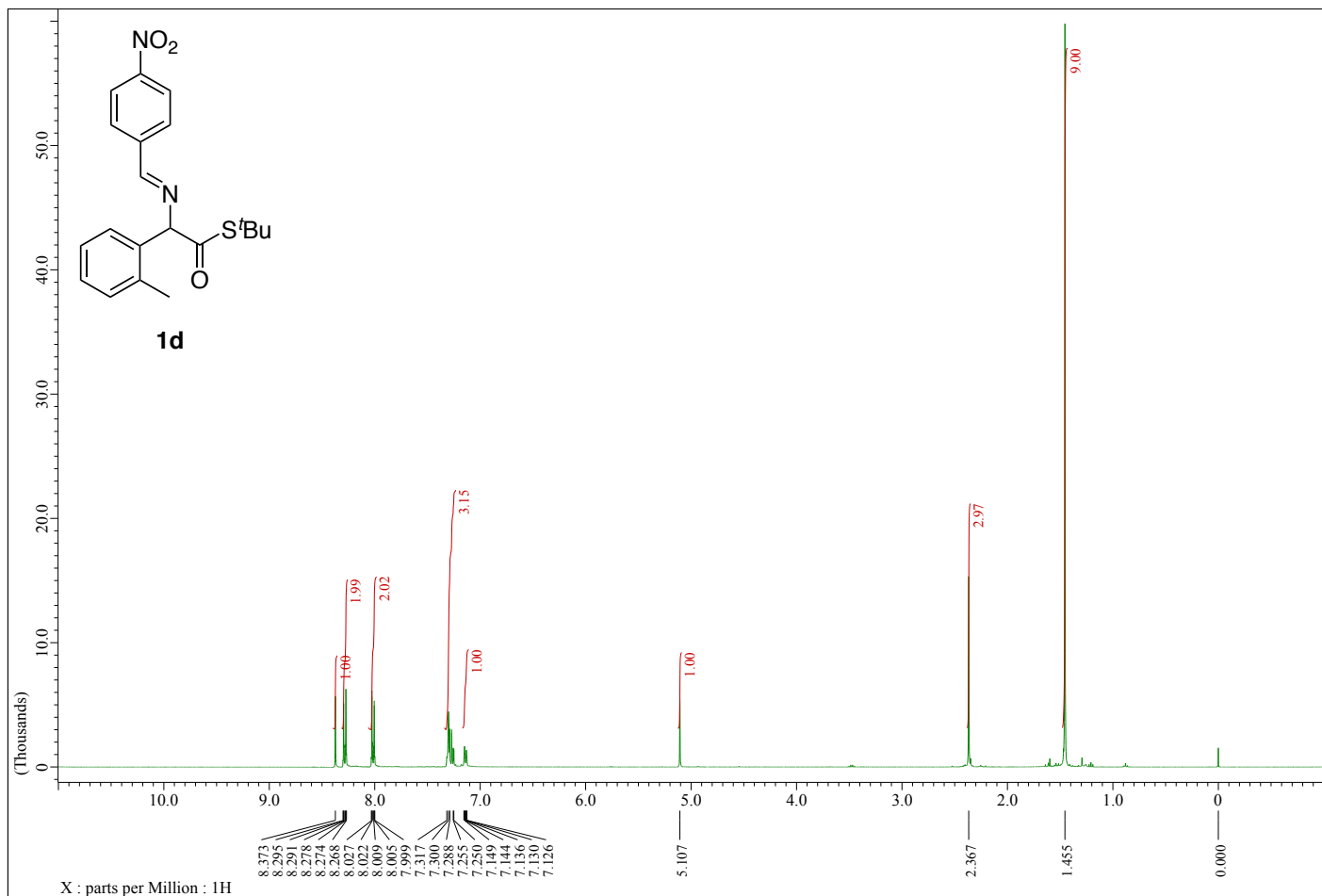


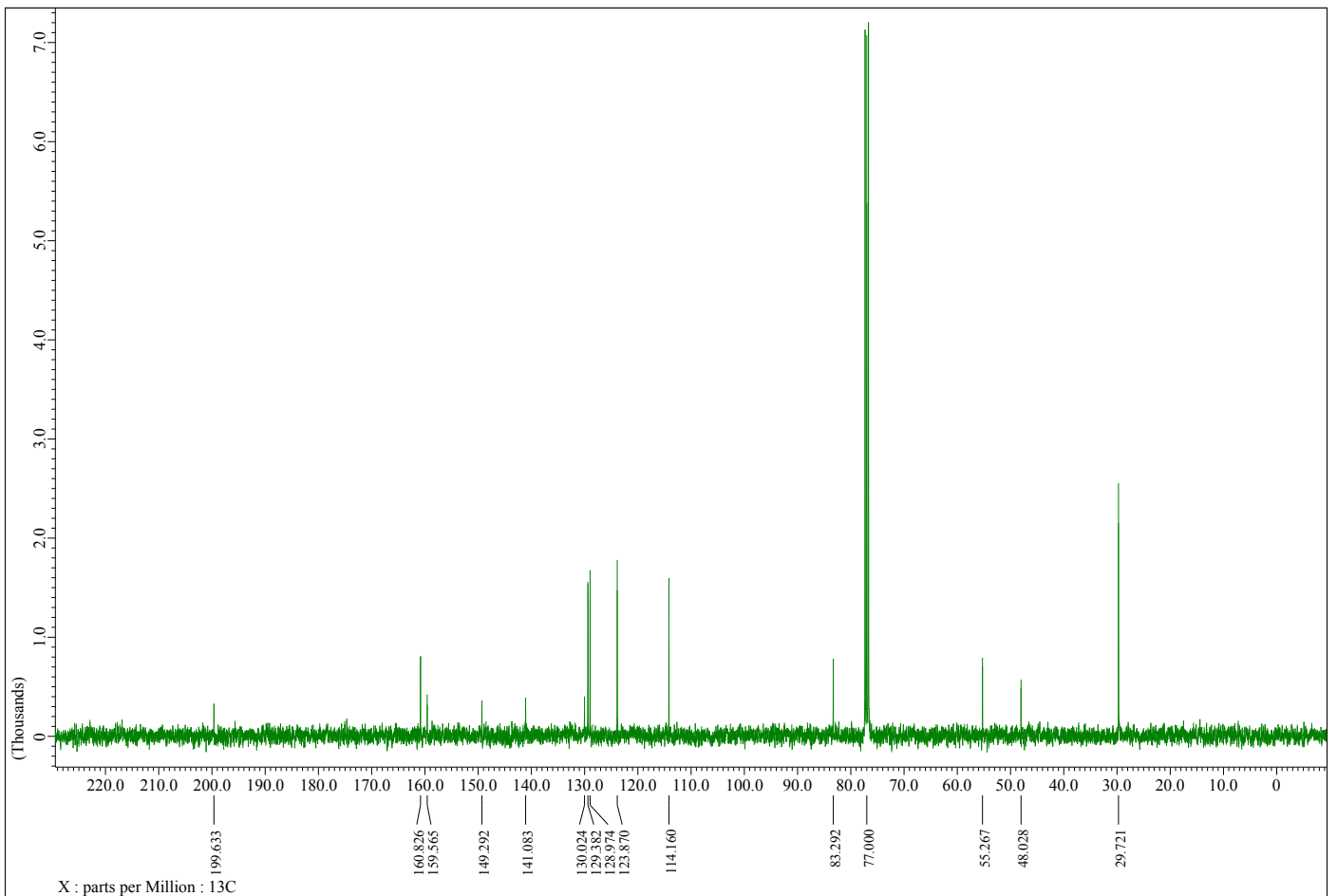
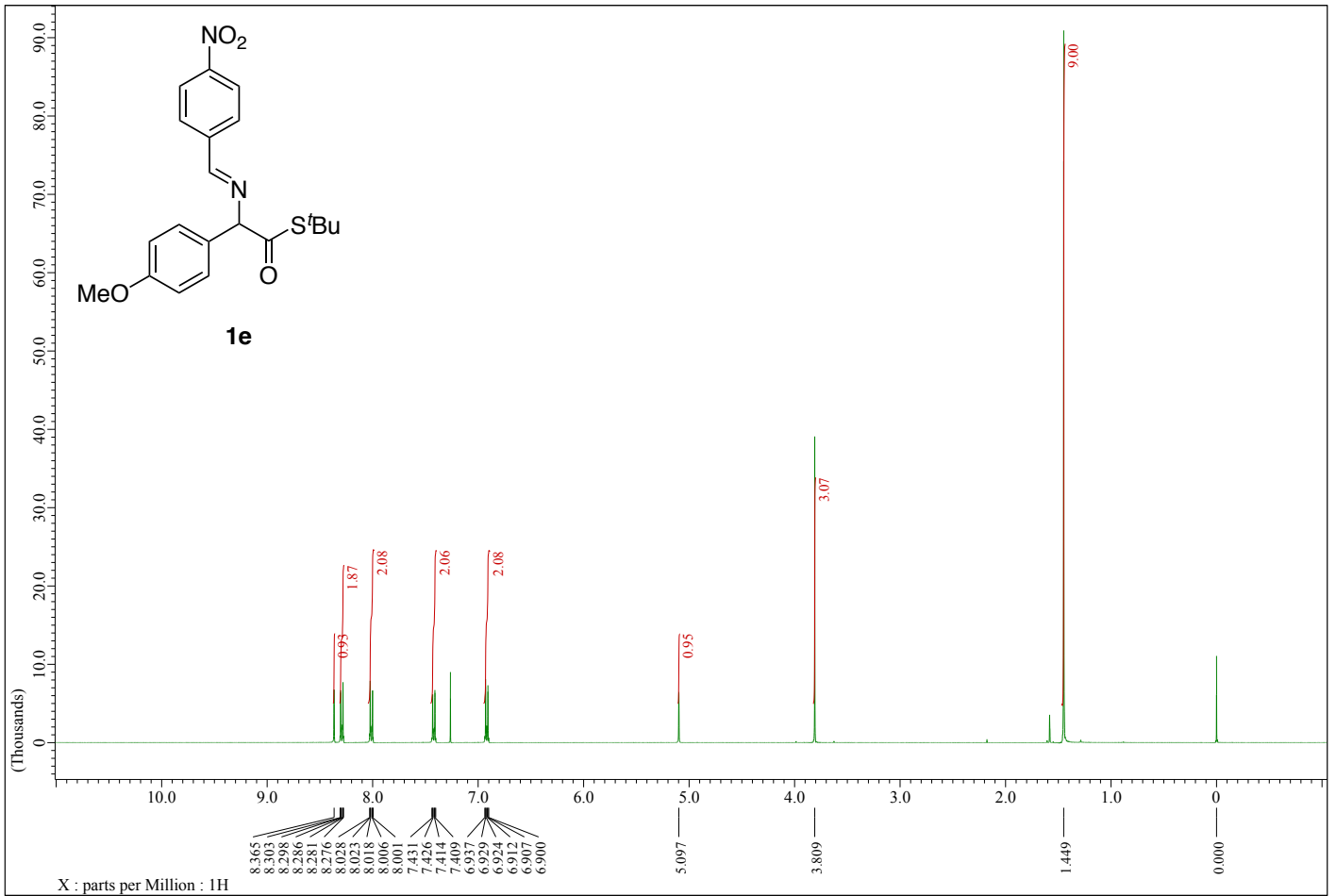


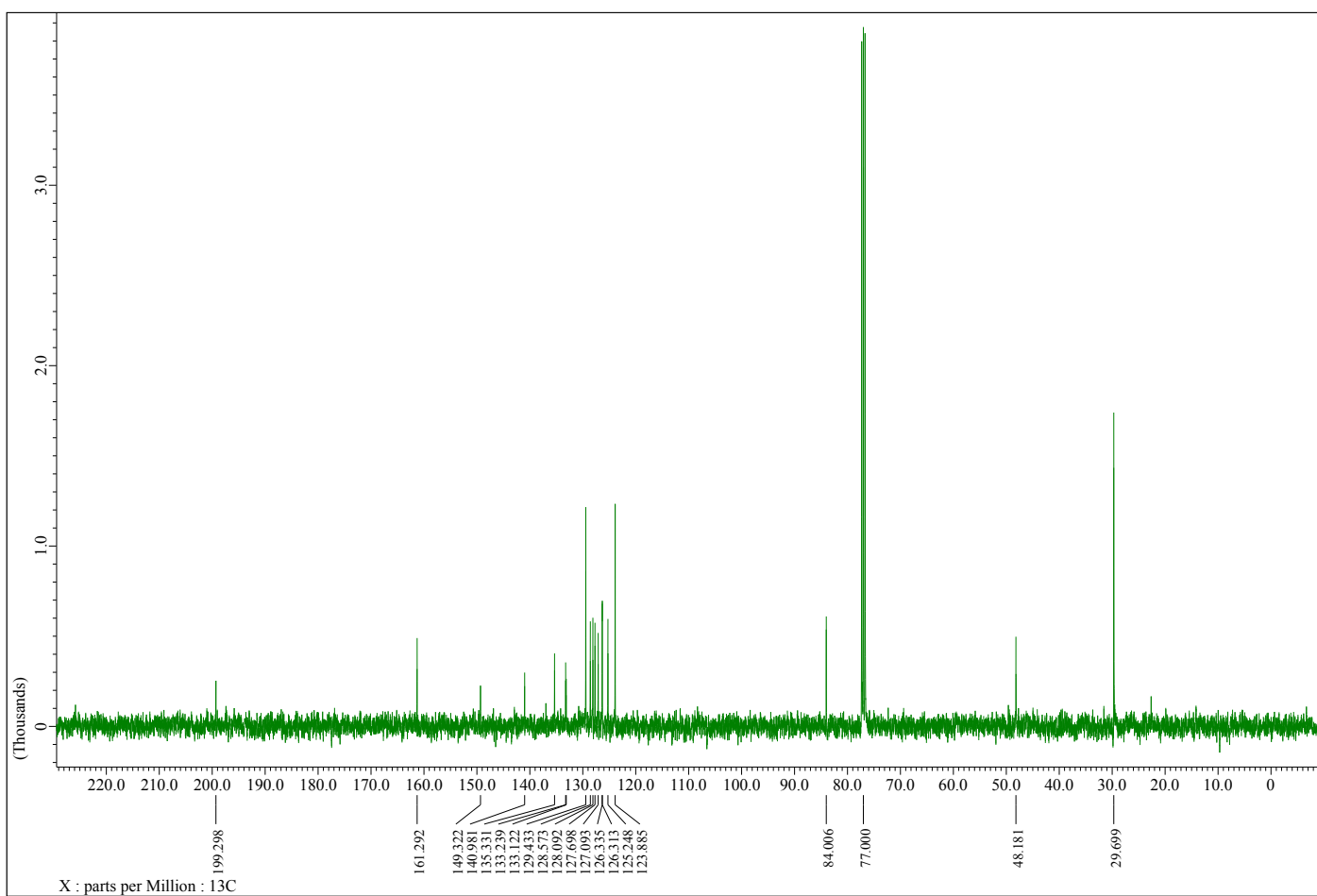
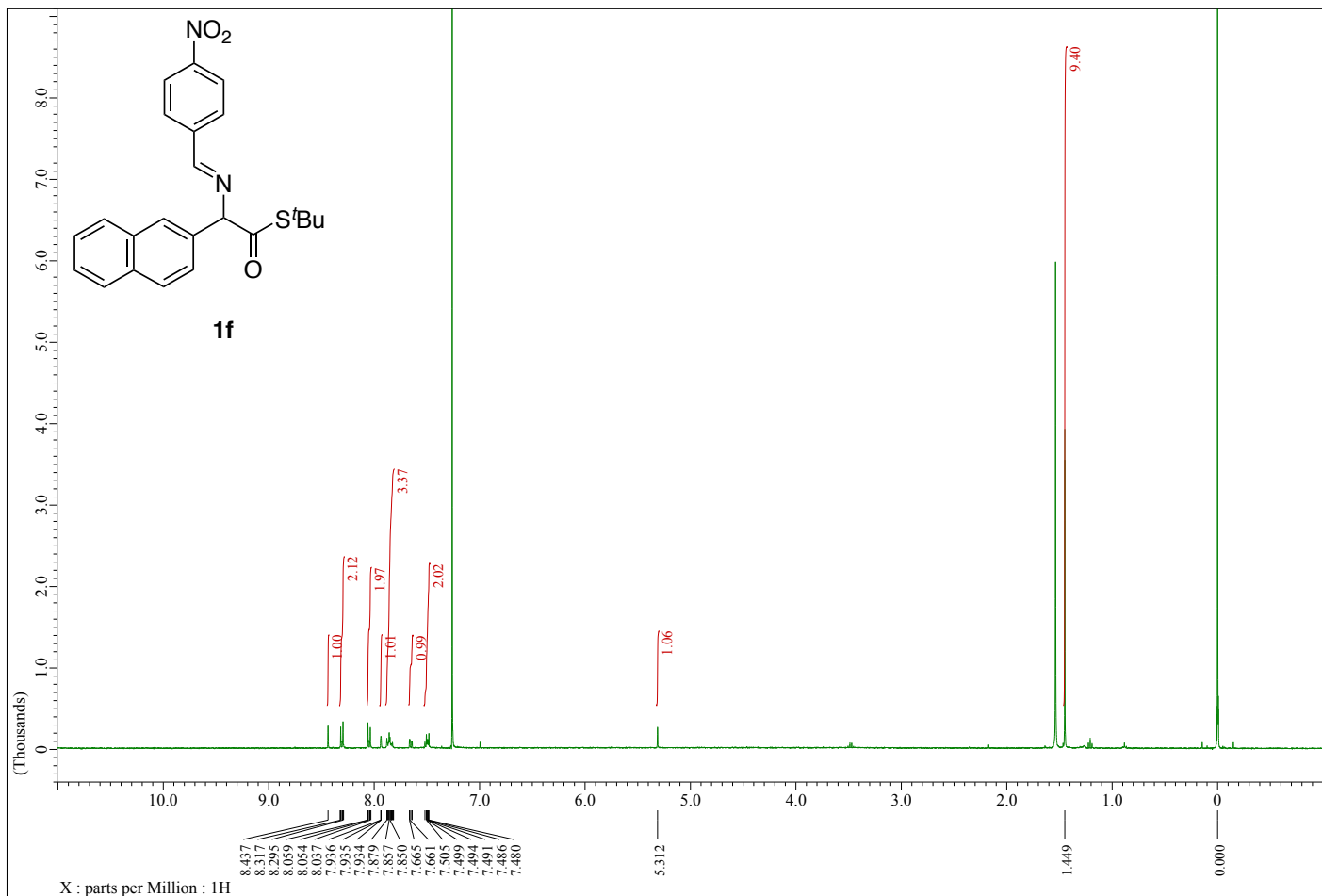


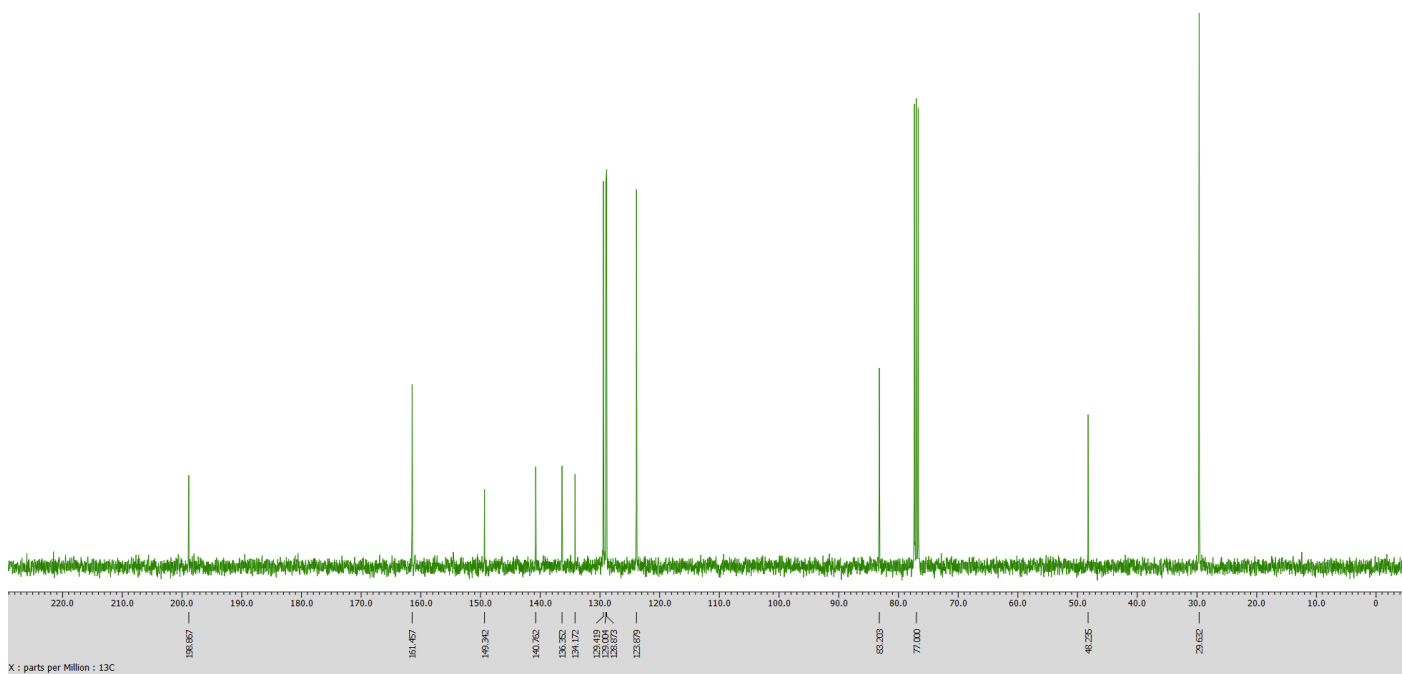
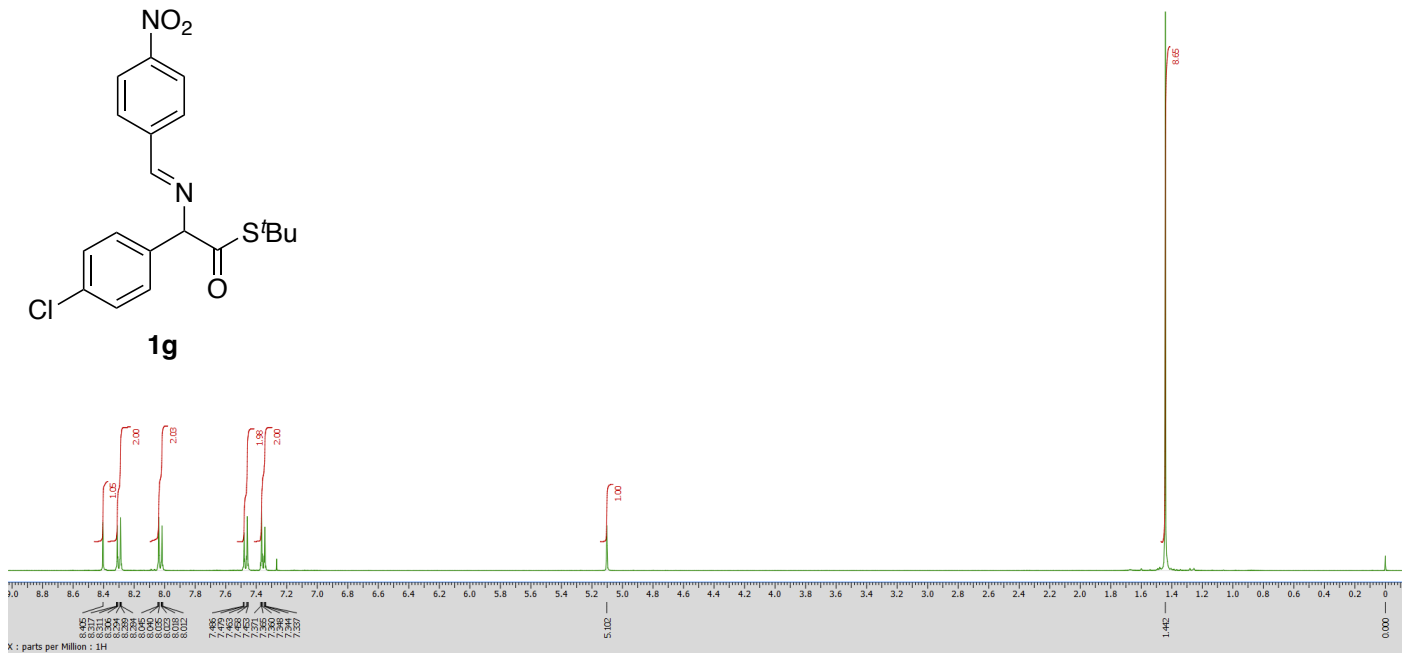
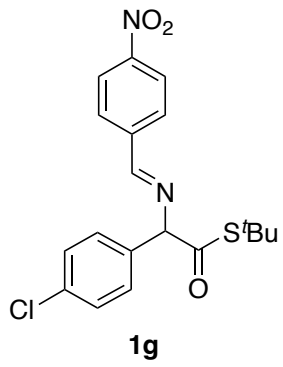


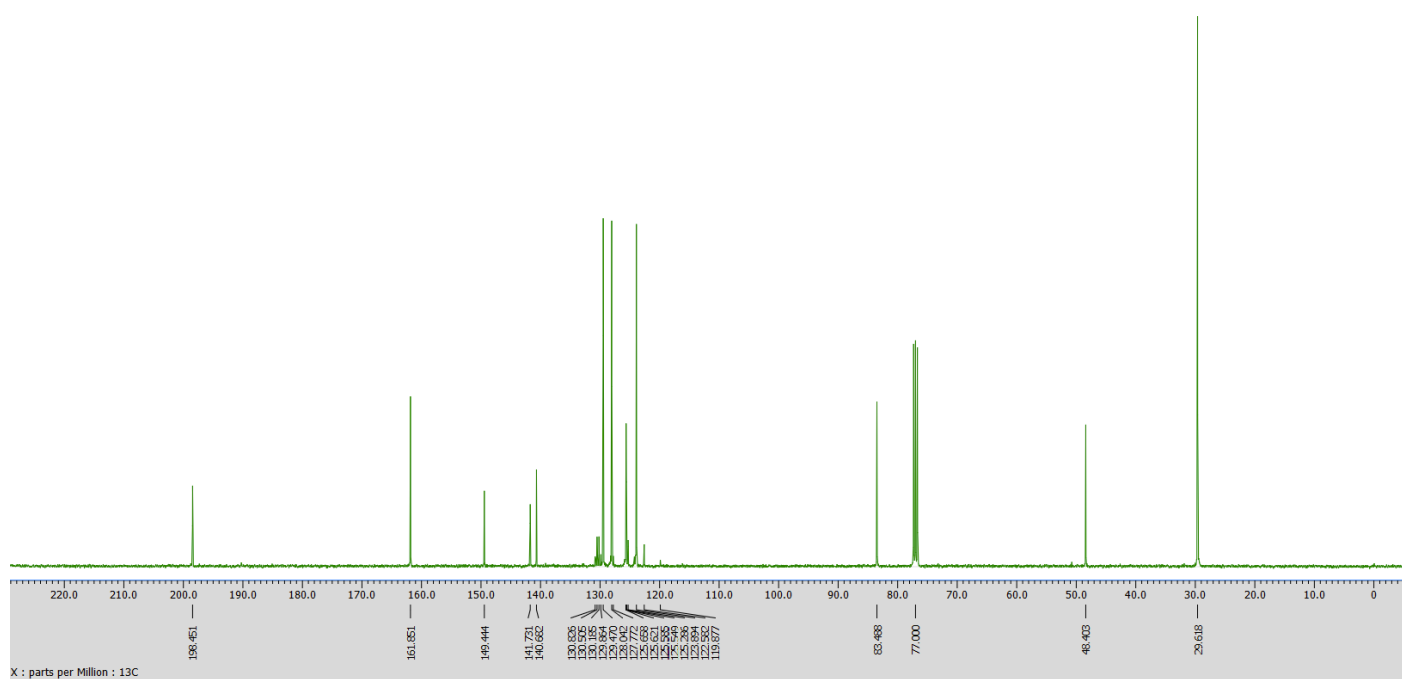
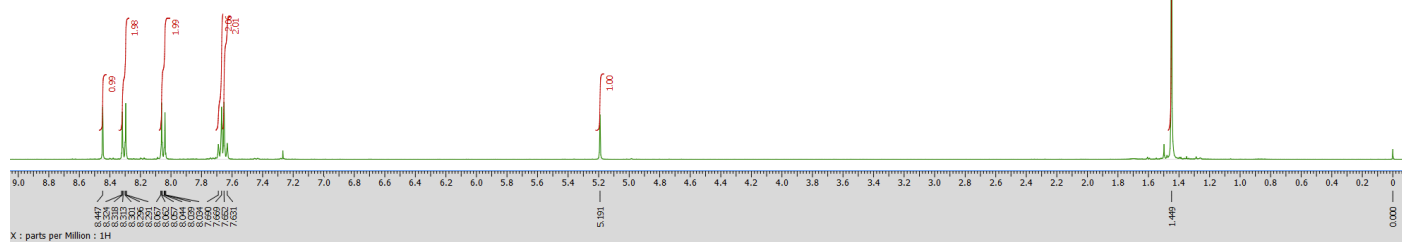
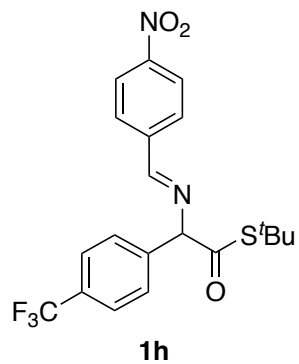


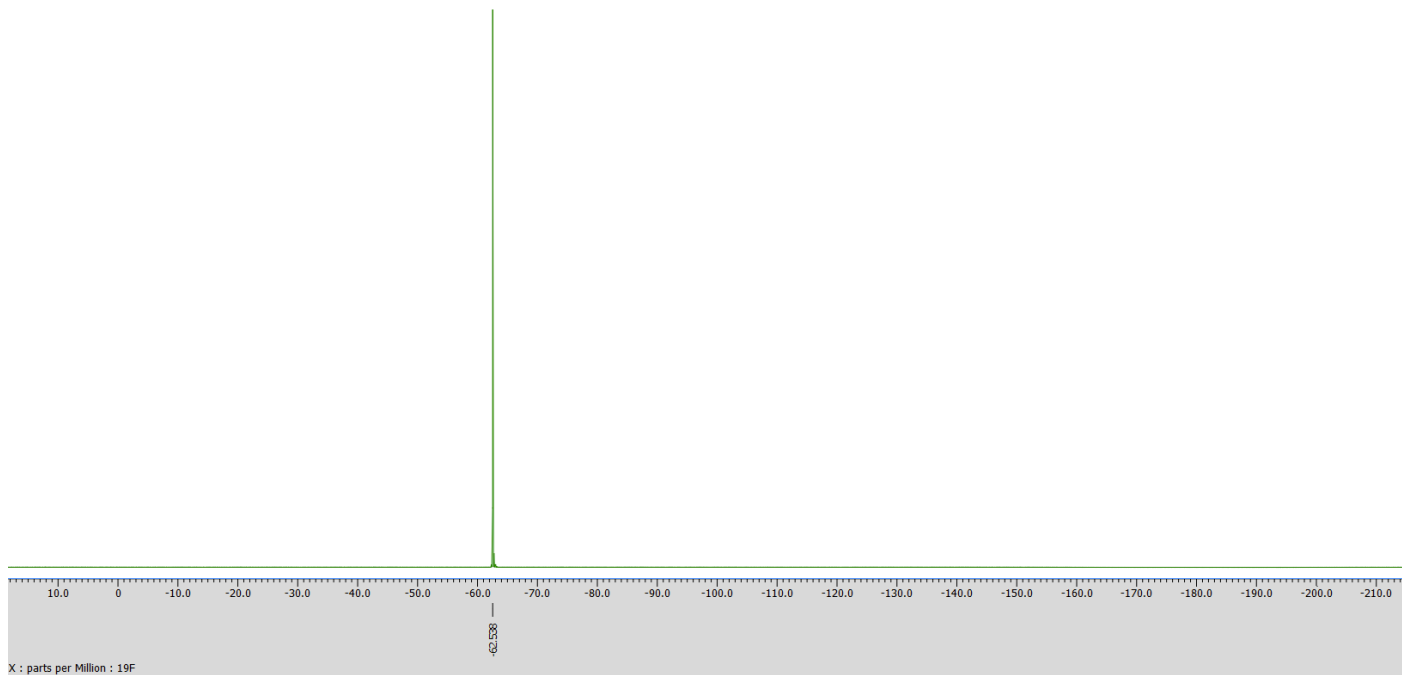


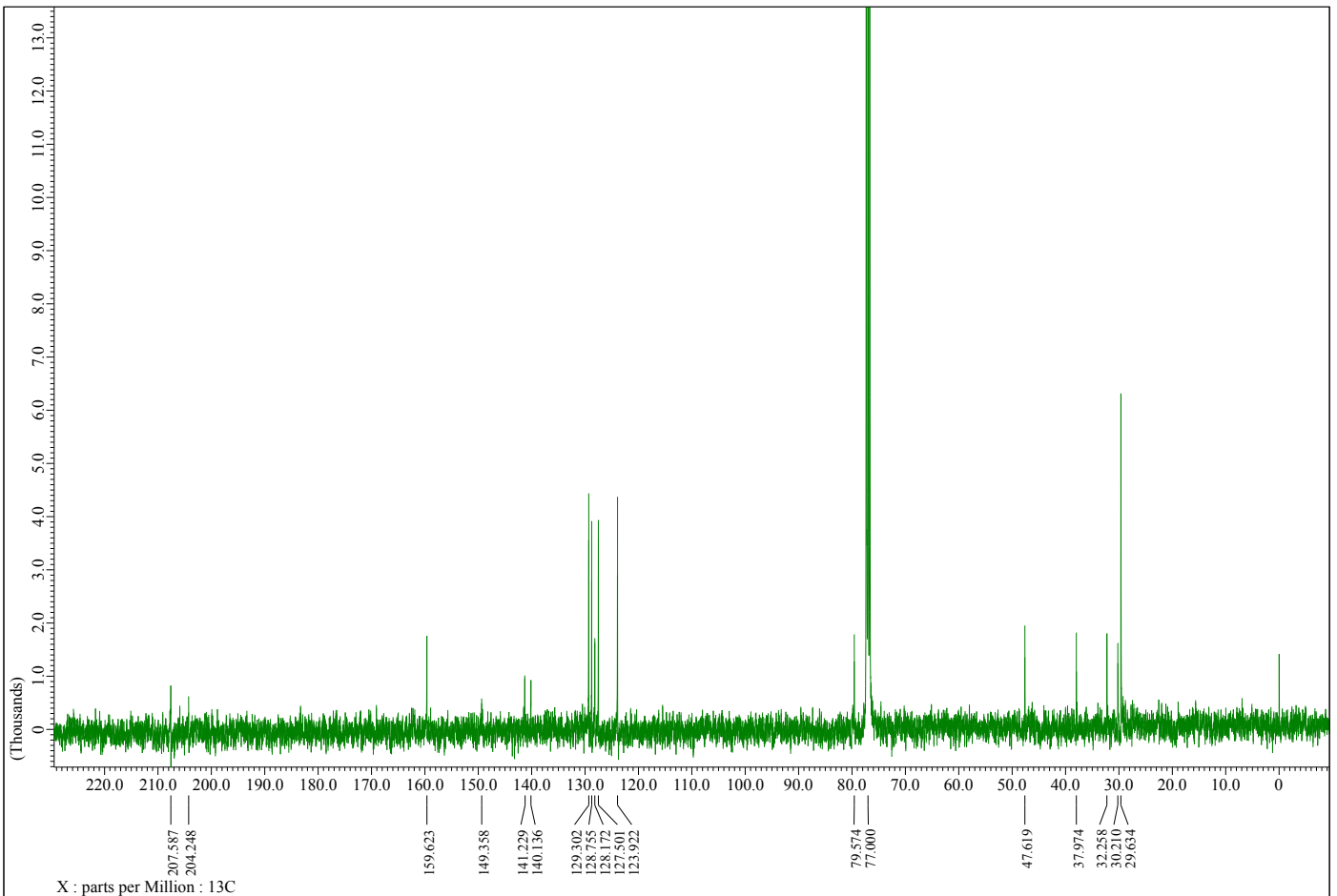
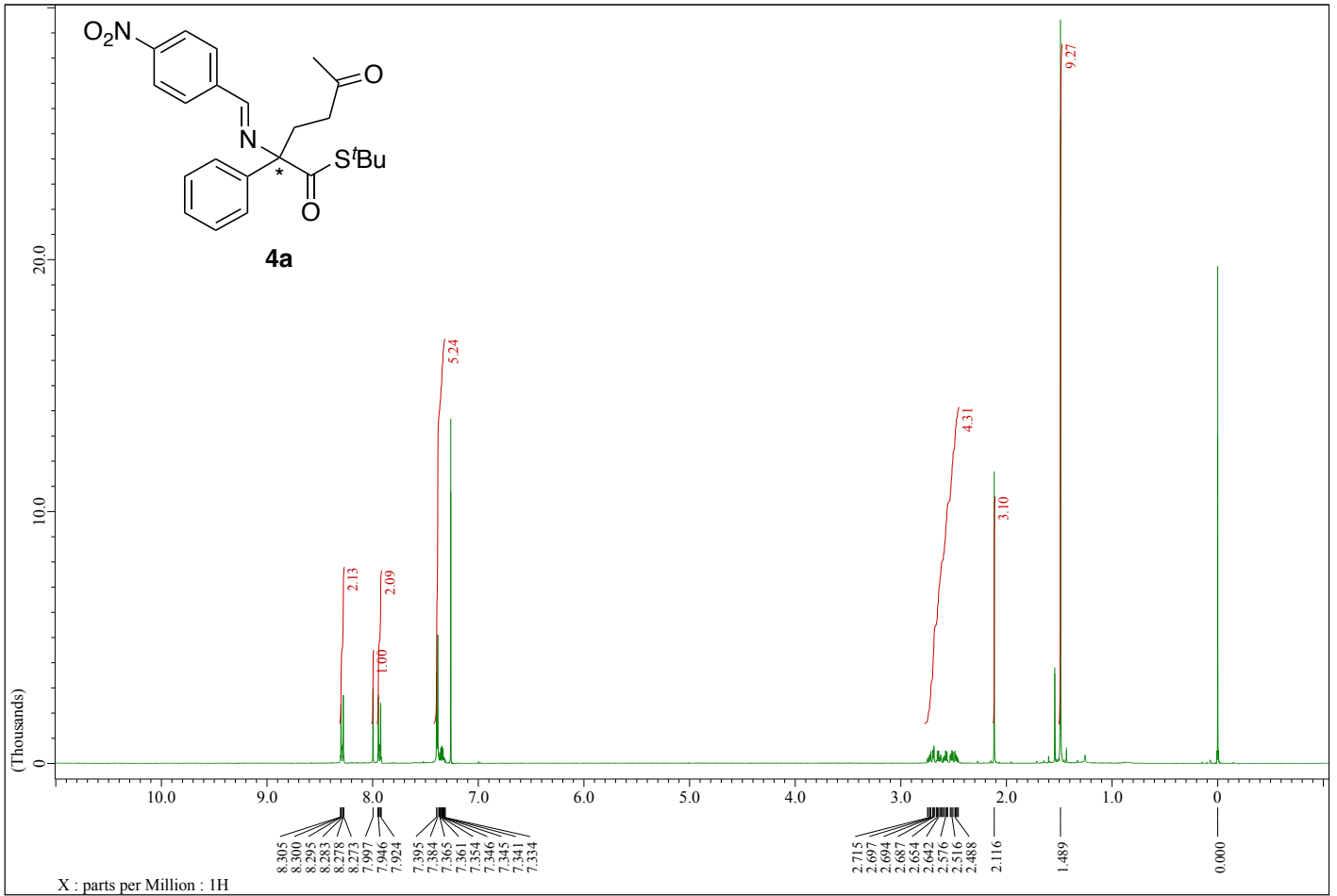




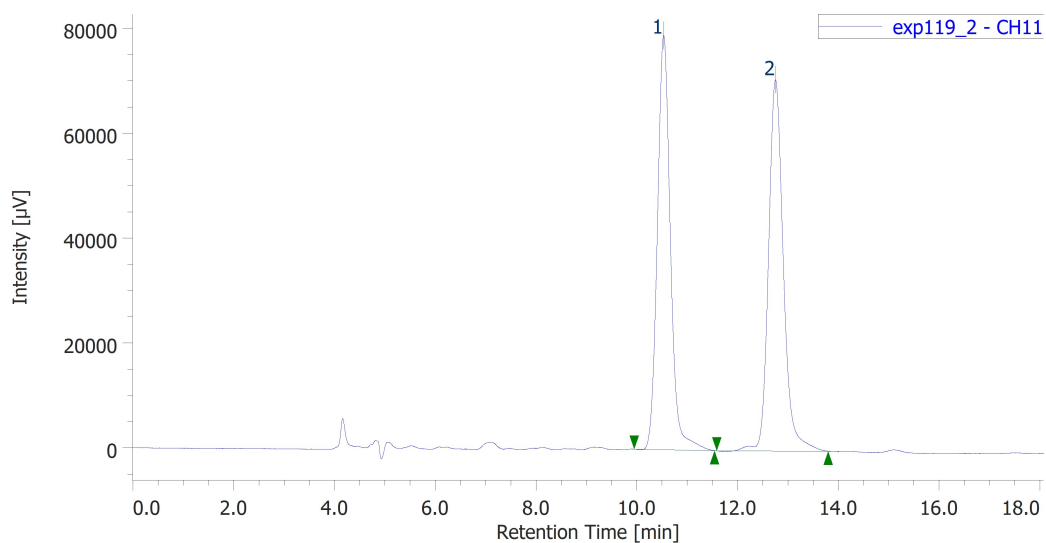






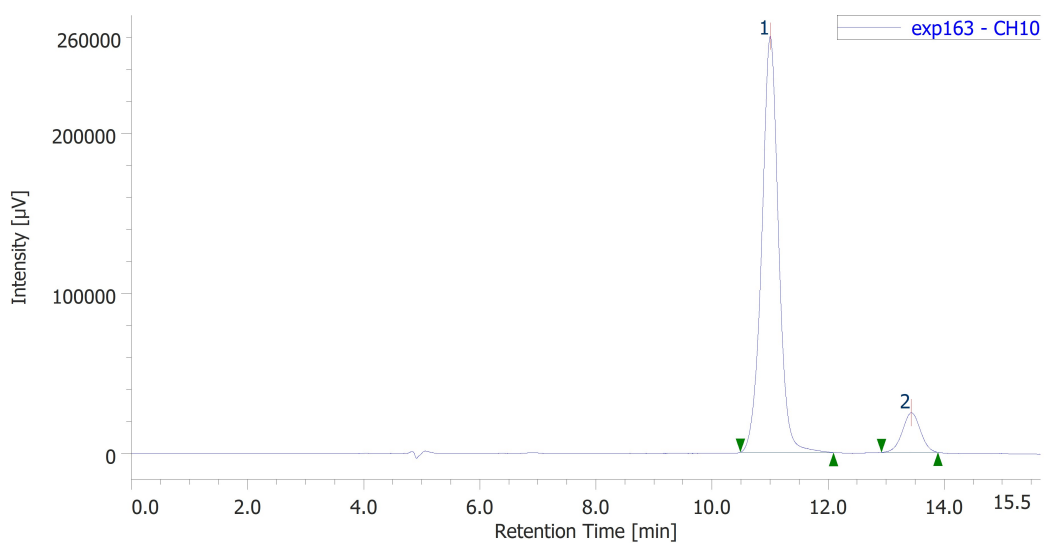


4a (racemate)

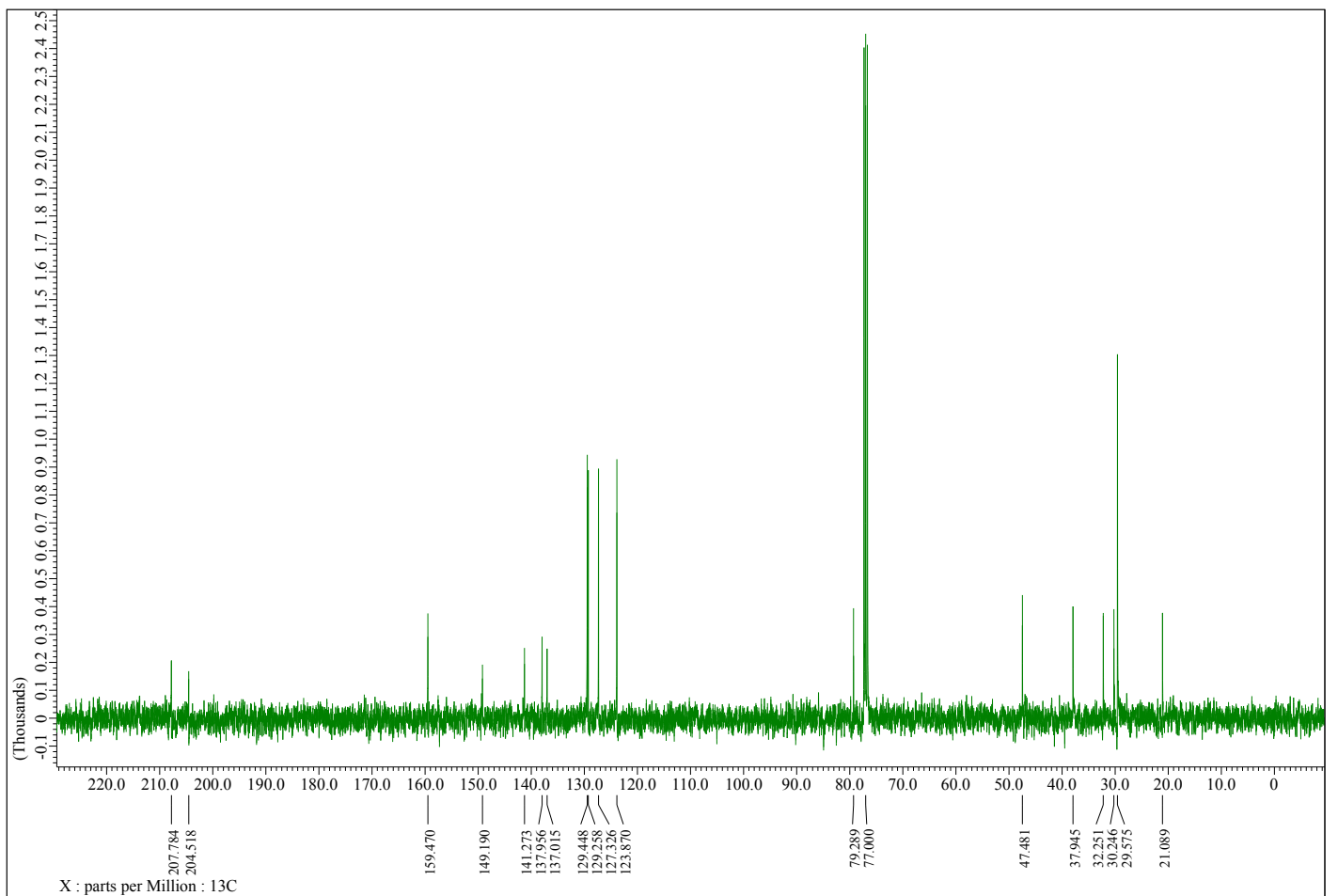
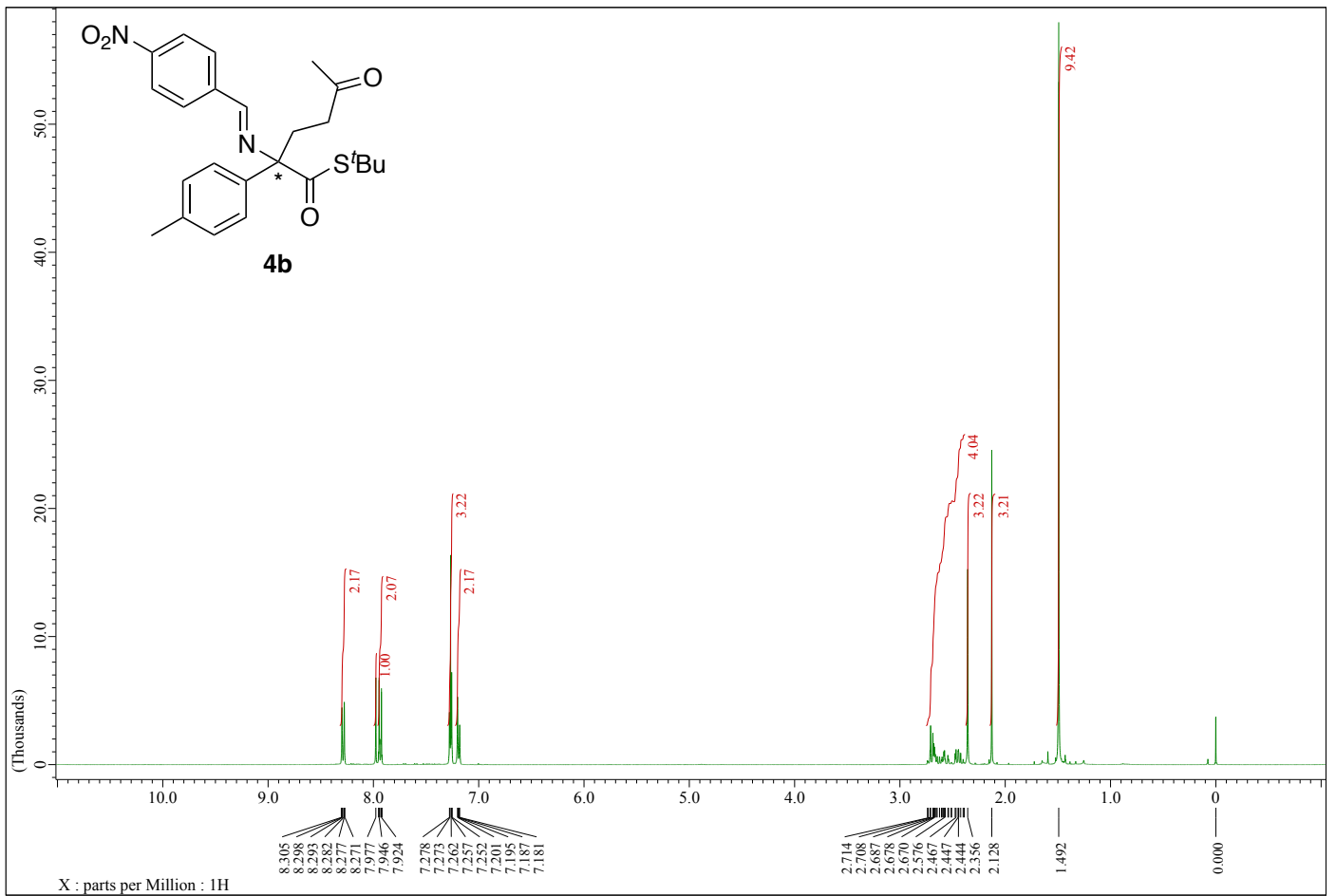


#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	11	10.532	1419796	78988	49.458	52.739	N/A	8642	4.609	1.104	
2	Unknown	11	12.750	1450898	70783	50.542	47.261	N/A	9919	N/A	1.182	

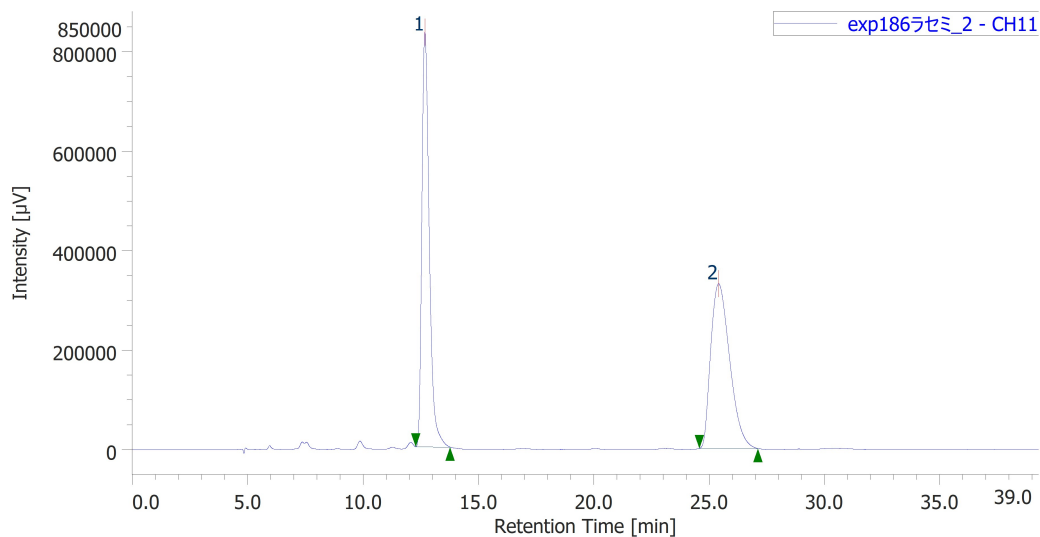
4a



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	10	11.000	5220437	259826	90.716	91.296	N/A	7604	4.552	0.999	
2	Unknown	10	13.430	534263	24772	9.284	8.704	N/A	9009	N/A	1.003	

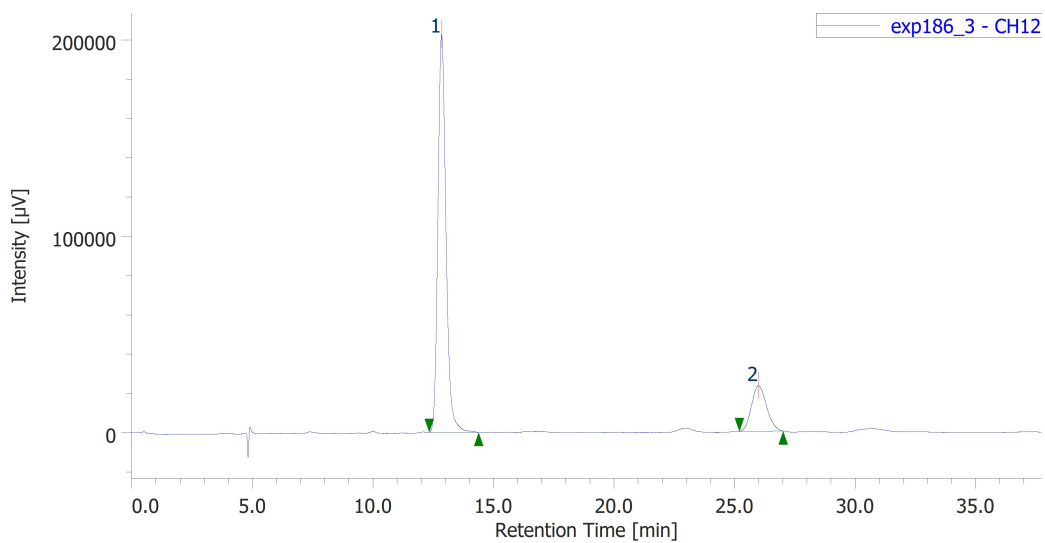


4b (racemate)

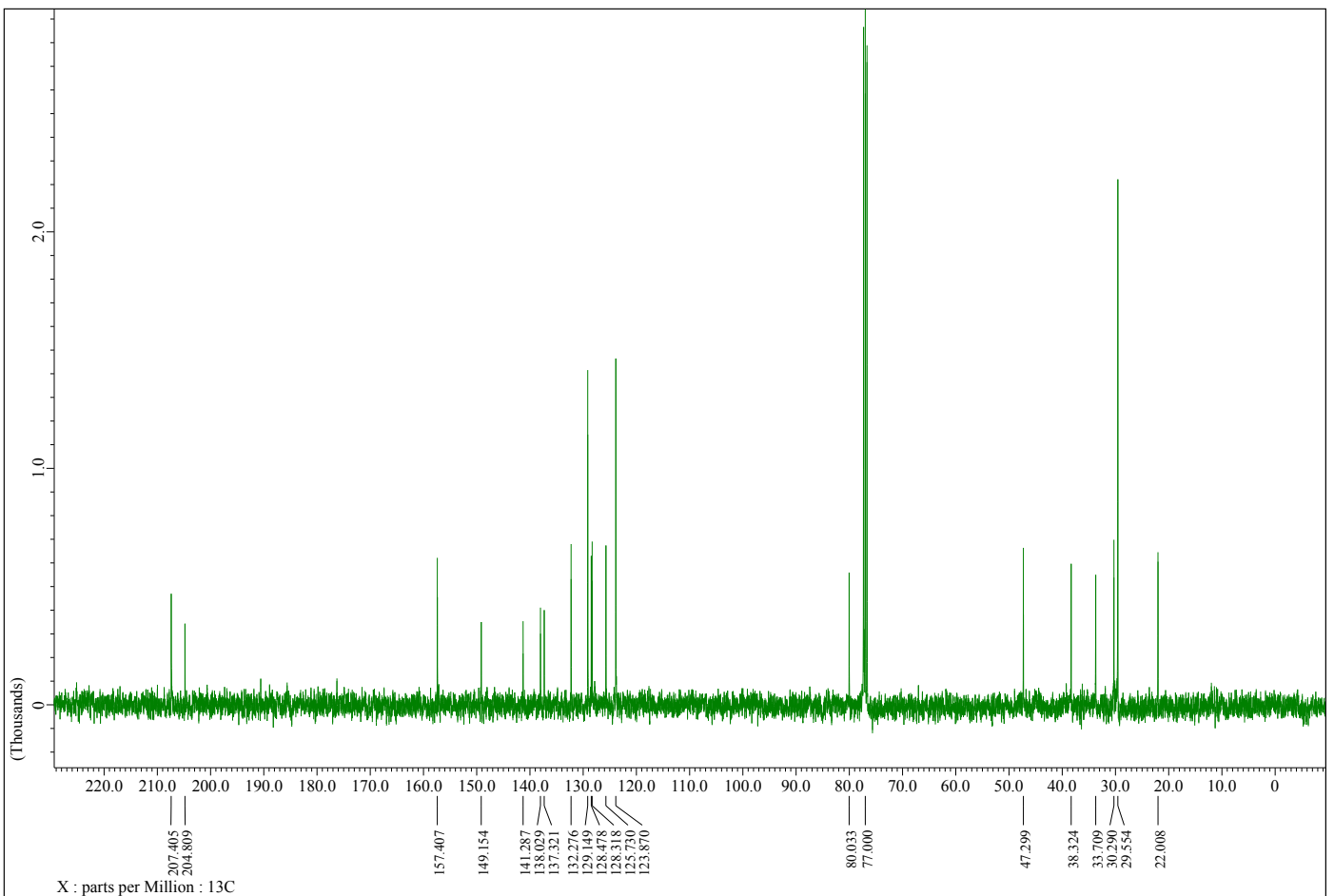
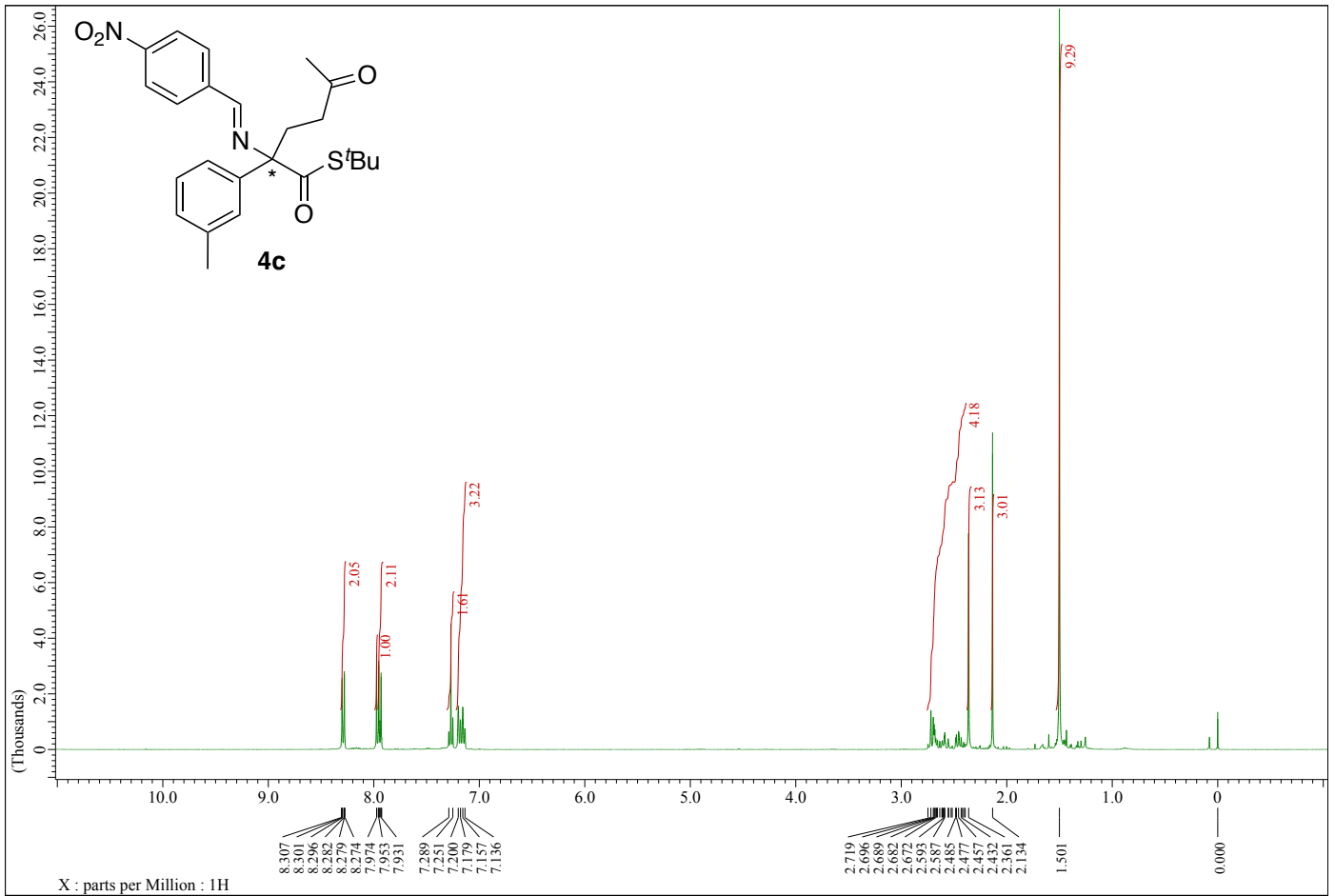


#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	11	12.677	18596724	833561	49.614	71.565	N/A	7905	12.120	1.450	
2	Unknown	11	25.403	18886093	331193	50.386	28.435	N/A	4379	N/A	1.423	

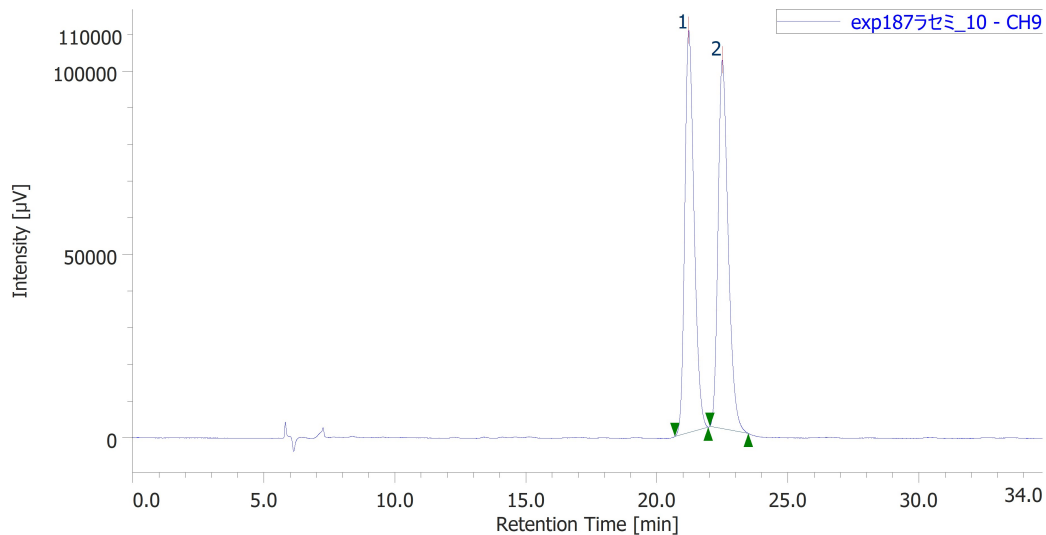
4b



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	12	12.845	4707122	202633	82.334	89.706	N/A	7597	15.119	1.202	
2	Unknown	12	25.987	1009996	23253	17.666	10.294	N/A	8119	N/A	1.144	

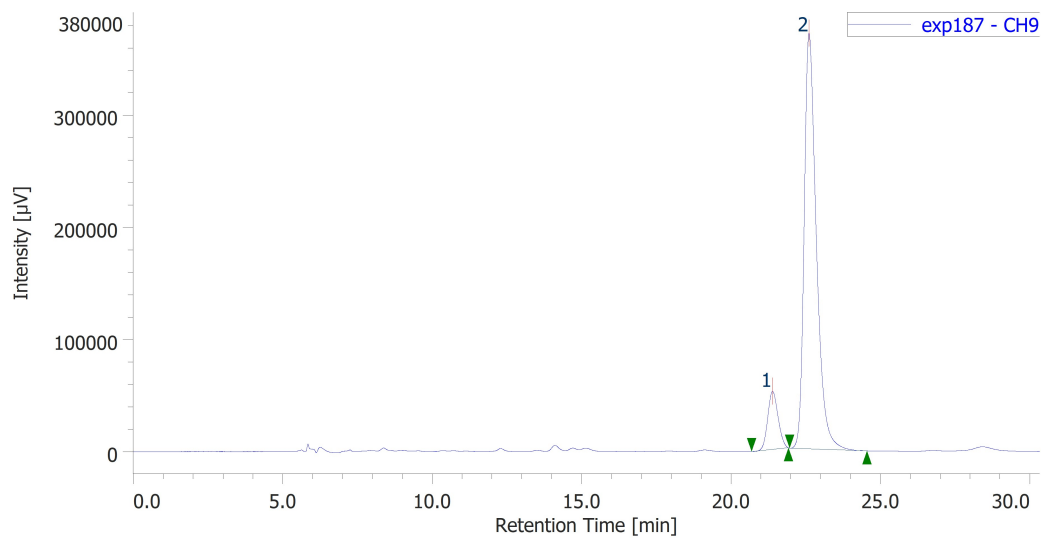


4c (racemate)

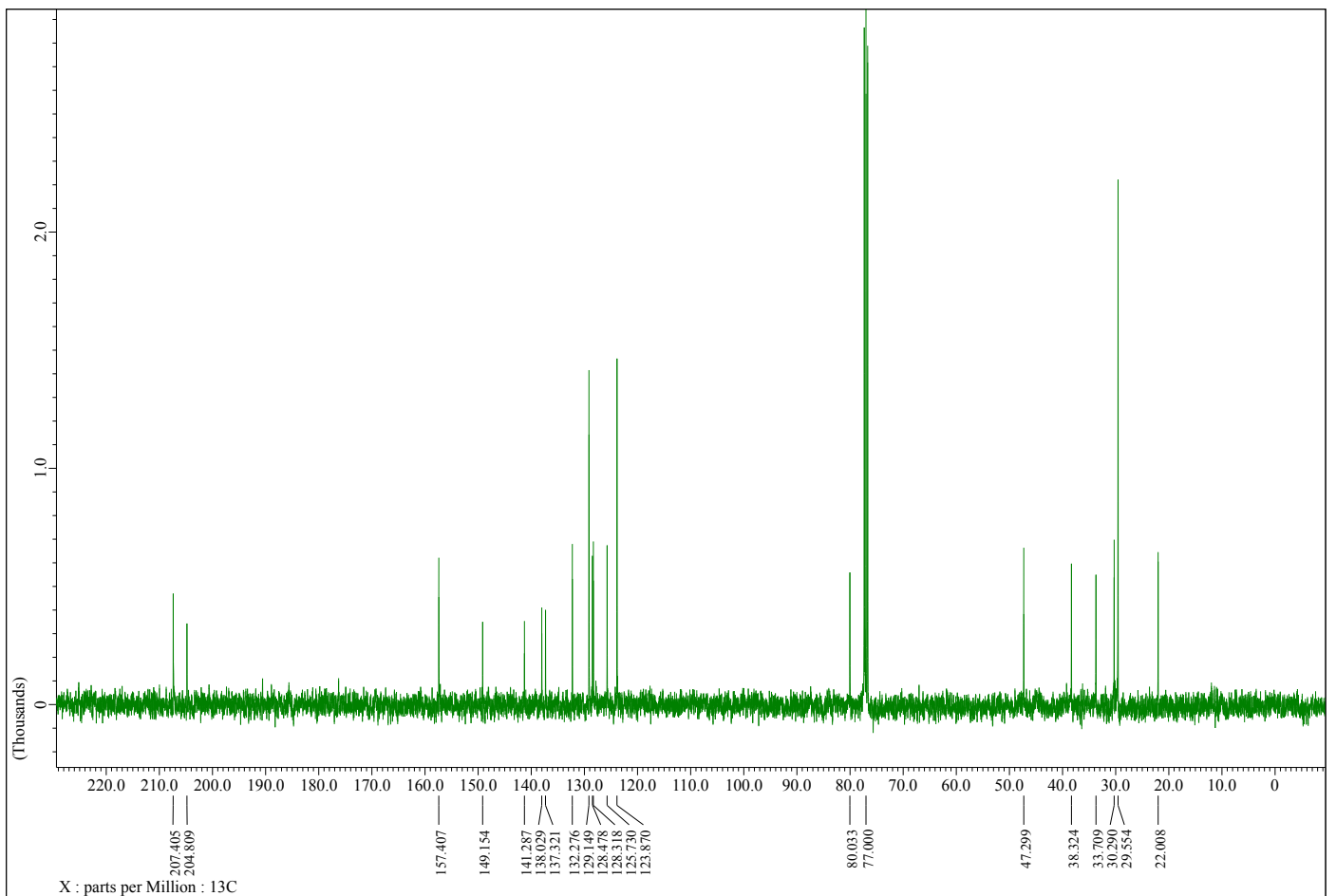
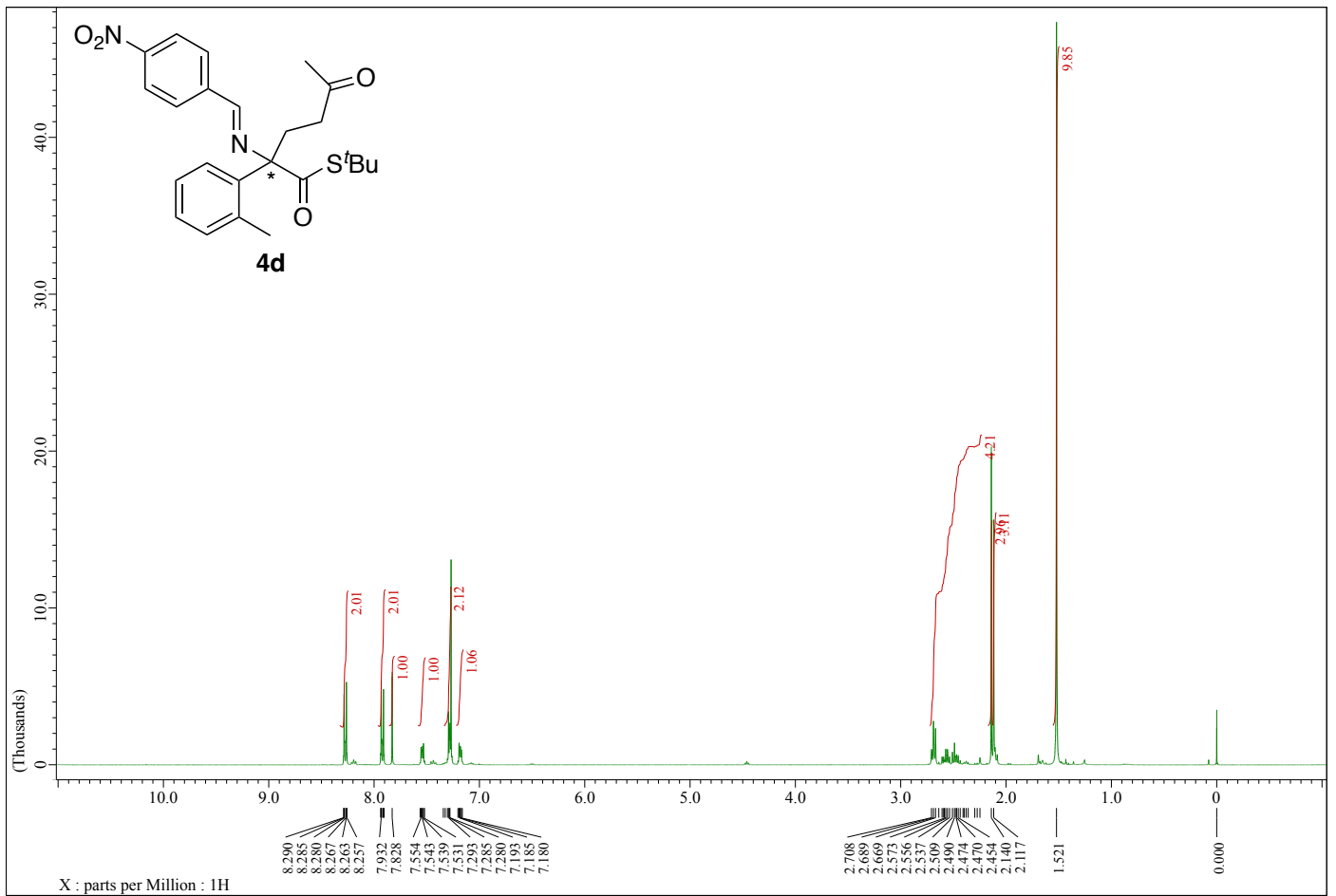


#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	21.210	2706378	109715	50.148	52.193	N/A	17460	1.923	1.265	
2	Unknown	9	22.488	2690428	100494	49.852	47.807	N/A	16946	N/A	1.330	

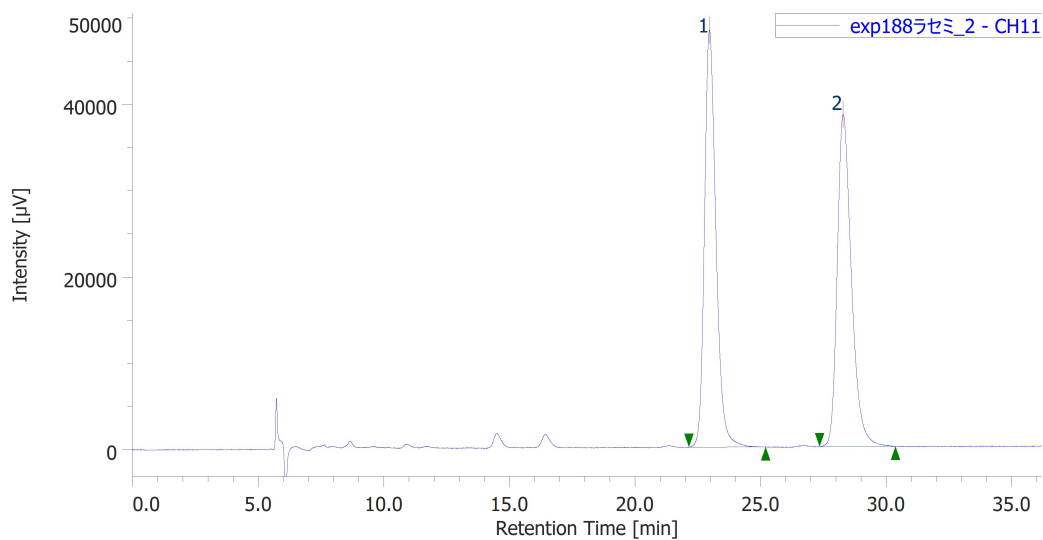
4c



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	21.383	1244705	51836	10.621	12.279	N/A	18070	1.816	1.111	
2	Unknown	9	22.605	10474096	370306	89.379	87.721	N/A	16090	N/A	1.421	

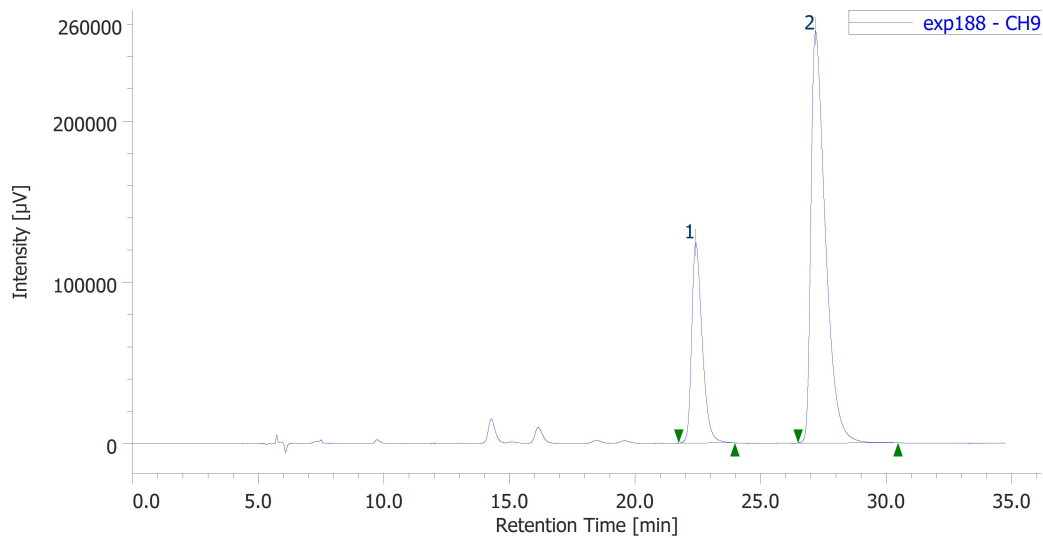


4d (racemate)

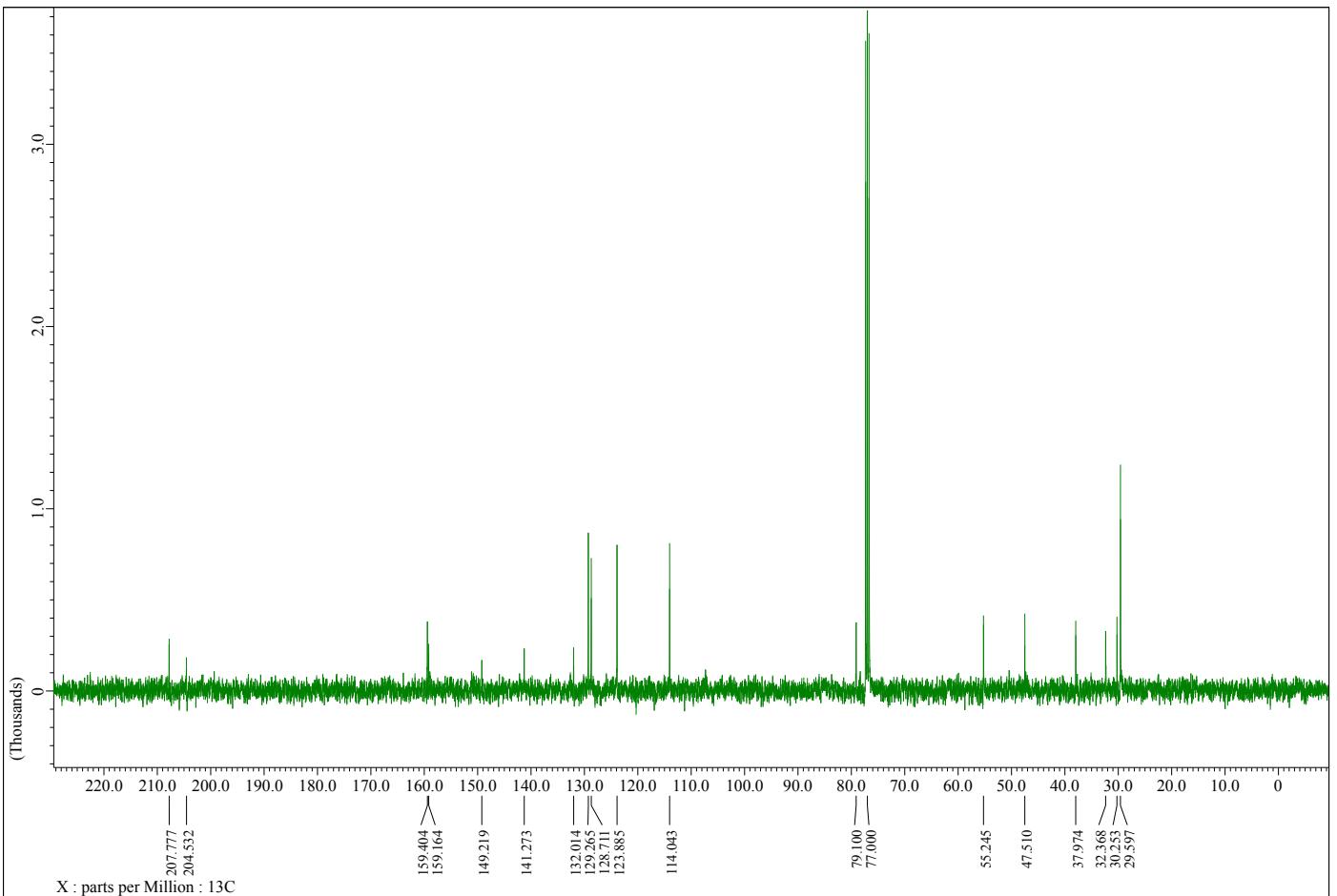
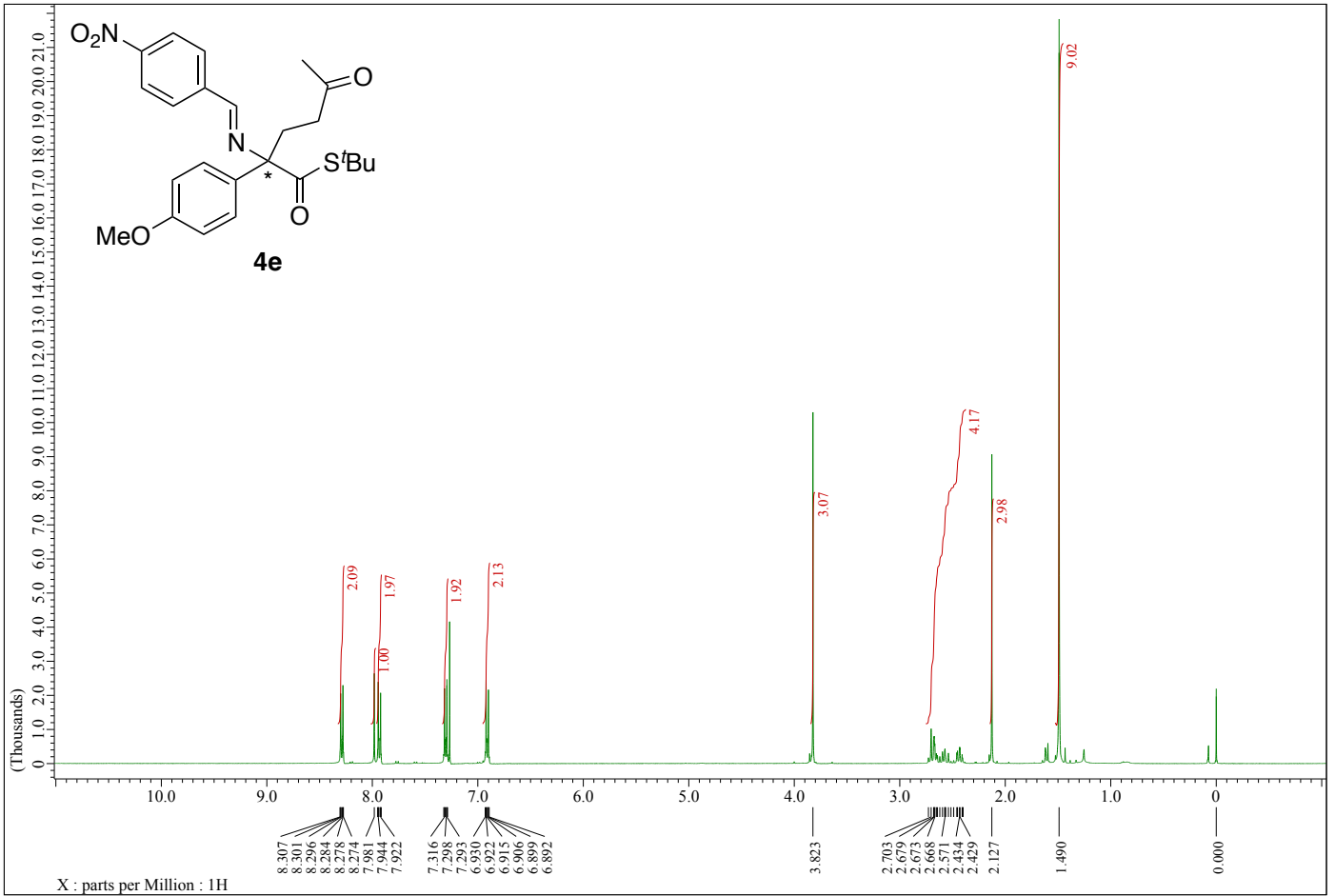


#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	11	22.960	1530264	48261	50.388	55.649	N/A	12982	5.918	1.251	
2	Unknown	11	28.277	1506680	38462	49.612	44.351	N/A	12912	N/A	1.350	

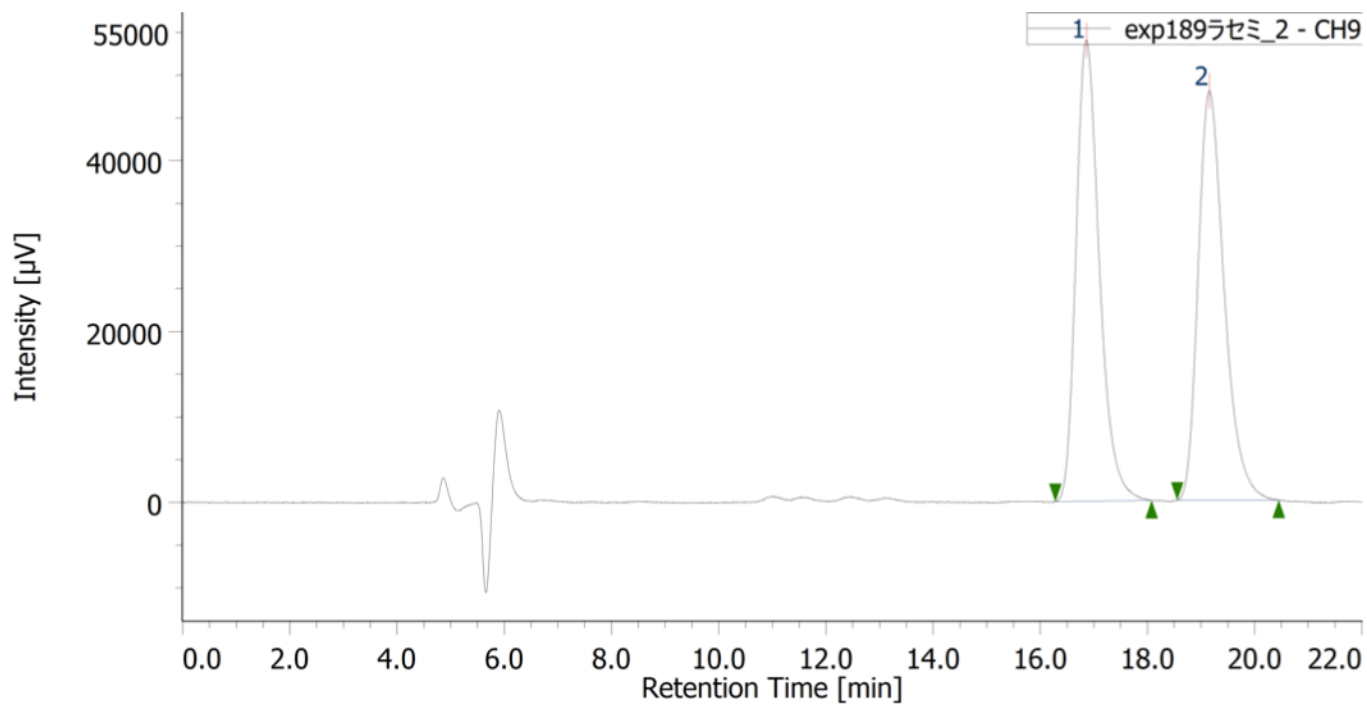
4d



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	22.413	3617428	124229	26.122	32.740	N/A	14619	5.434	1.431	
2	Unknown	9	27.180	10230625	255211	73.878	67.260	N/A	11415	N/A	1.906	

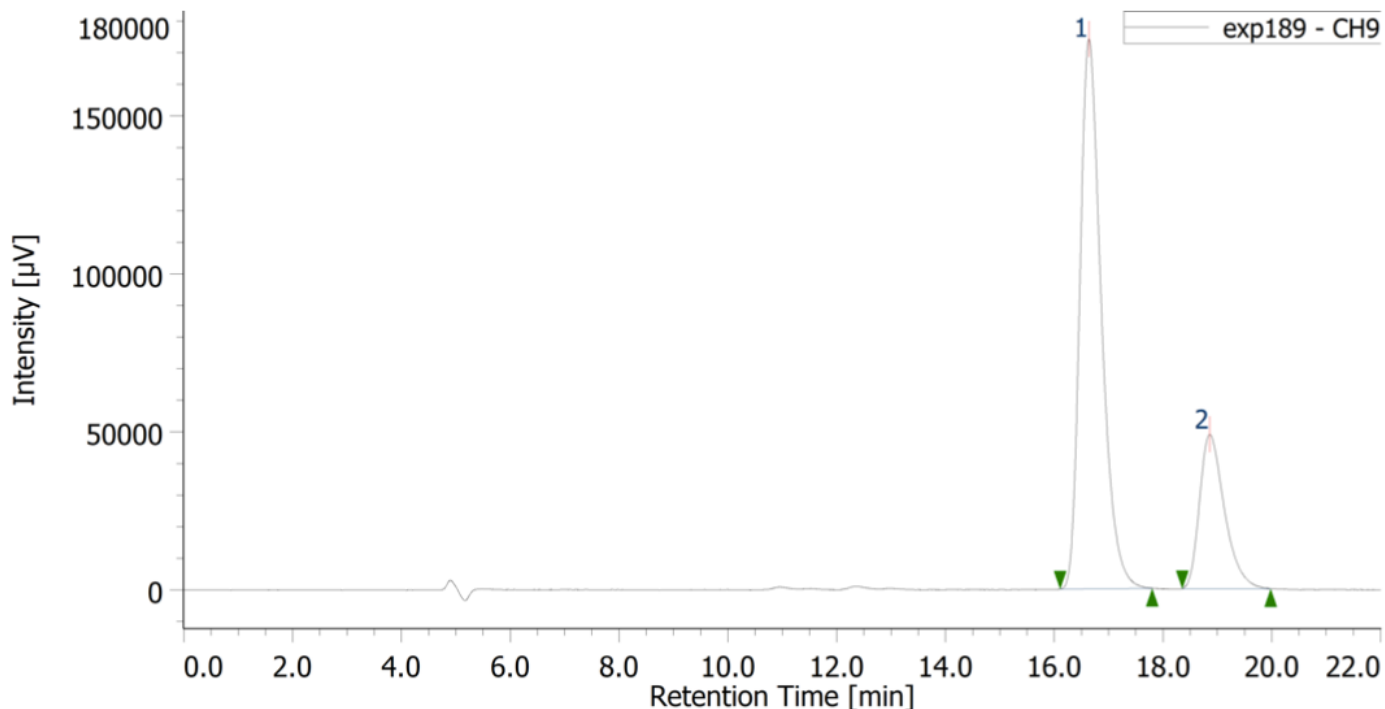


4e (racemate)

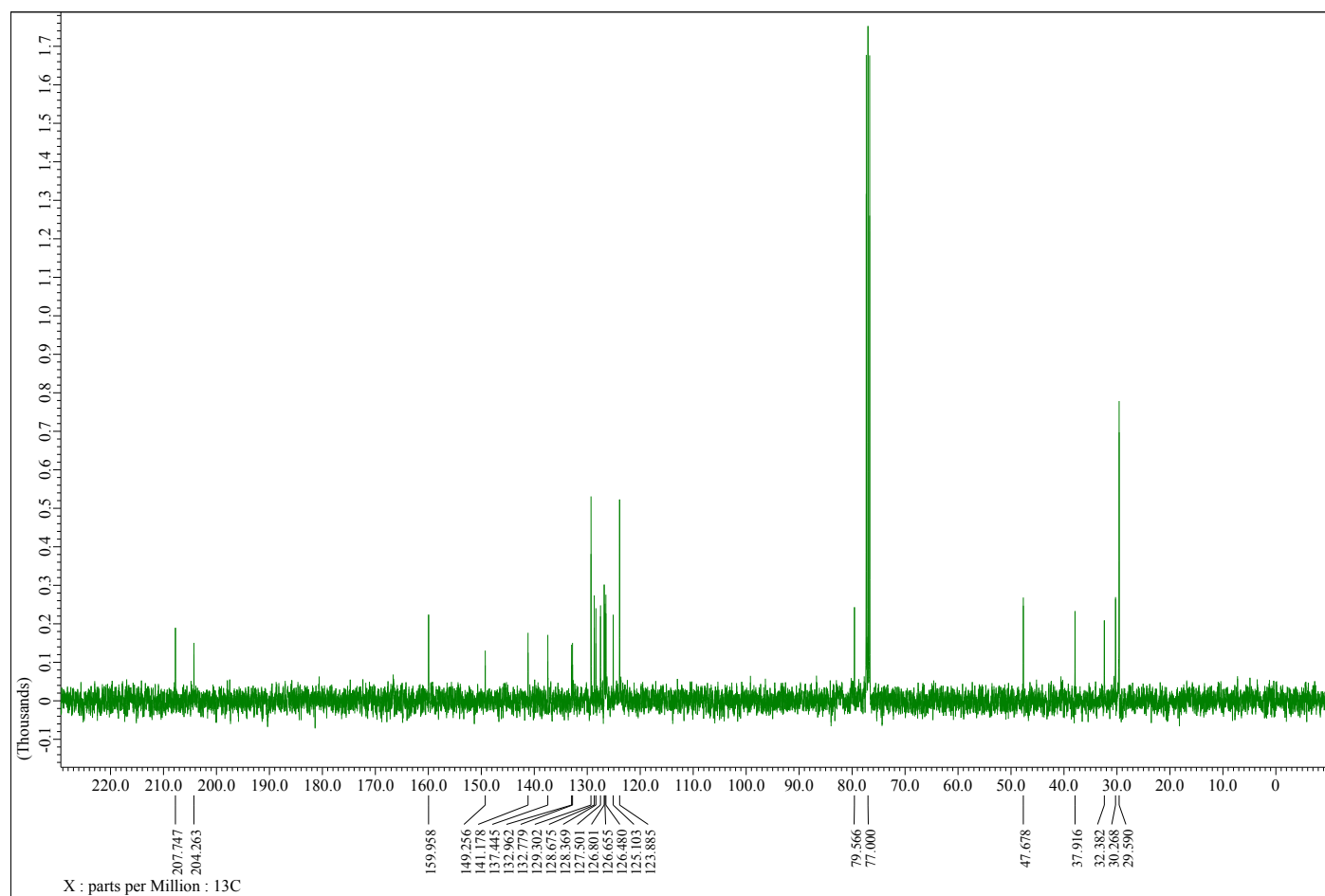
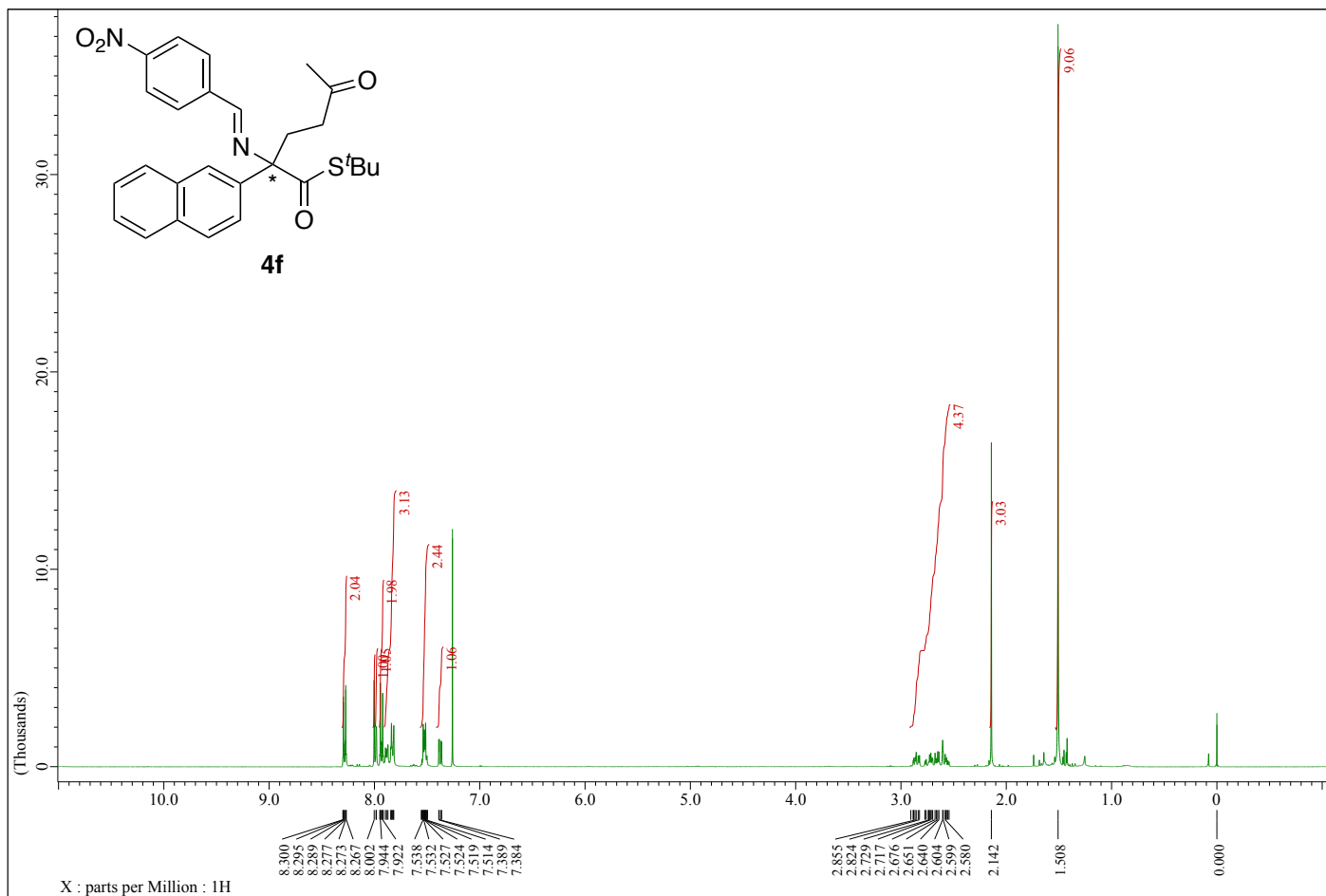


#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	16.857	1633459	53932	50.253	52.971	N/A	7503	2.792	1.299	
2	Unknown	9	19.150	1617042	47882	49.747	47.029	N/A	7770	N/A	1.349	

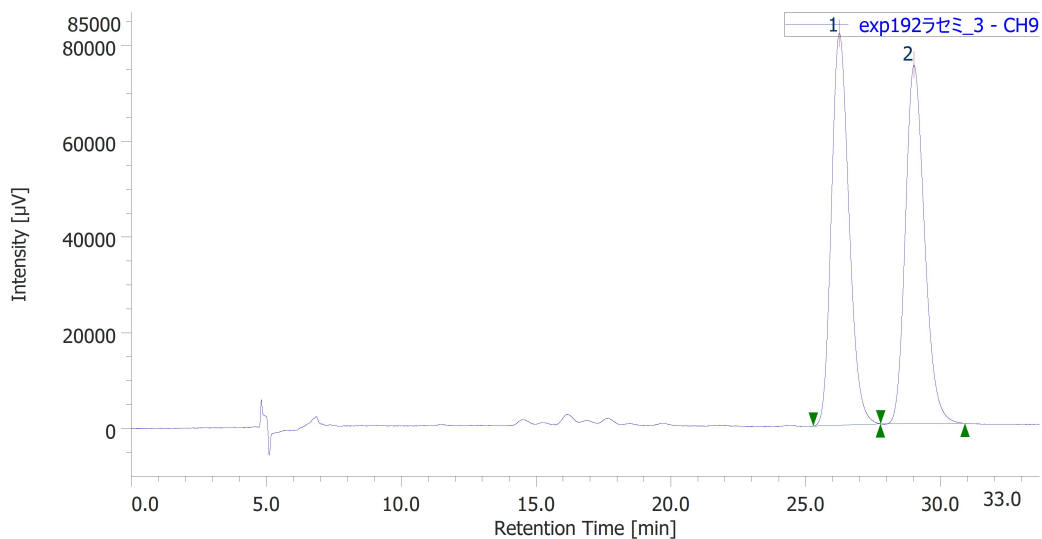
4e



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	16.633	4754024	173903	75.364	78.087	N/A	8972	2.924	1.362	
2	Unknown	9	18.853	1554084	48800	24.636	21.913	N/A	8454	N/A	1.417	

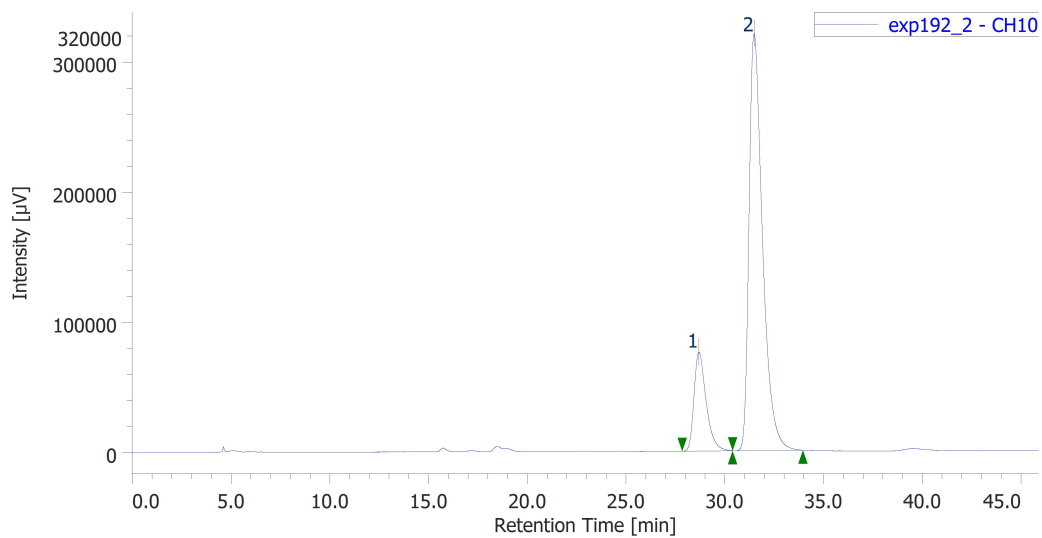


4f (racemate)

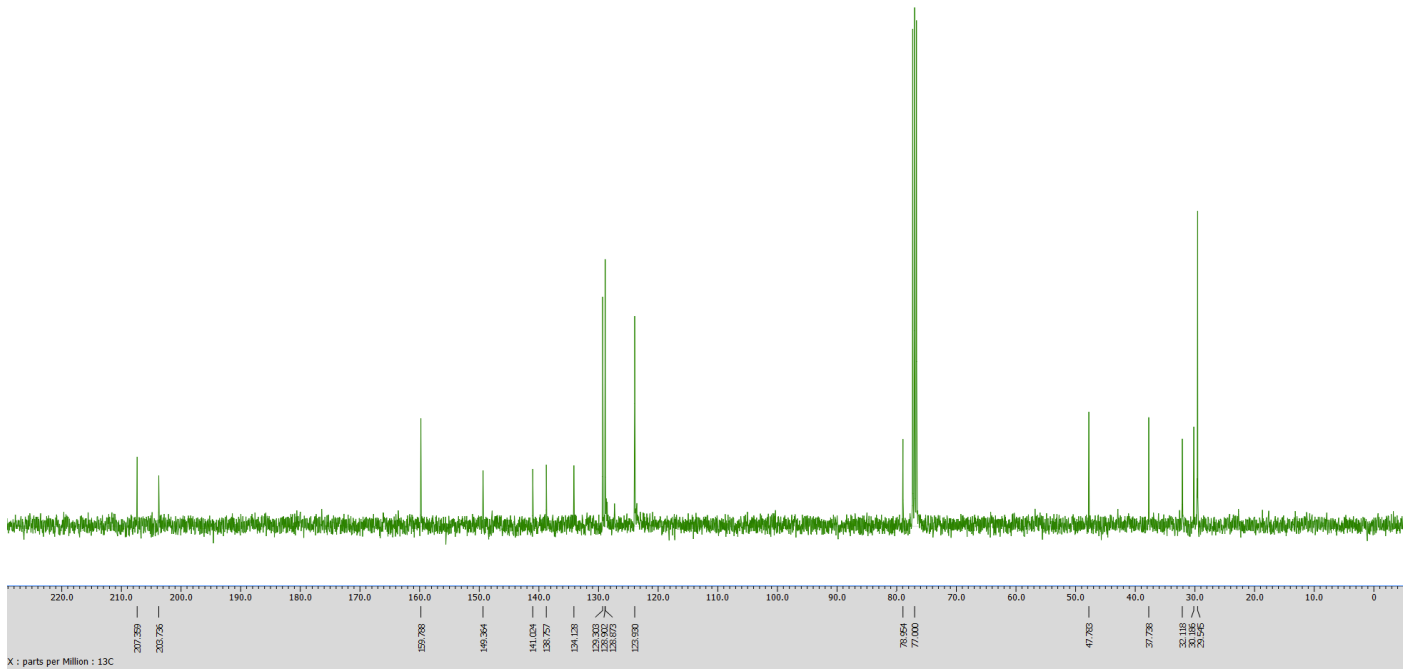
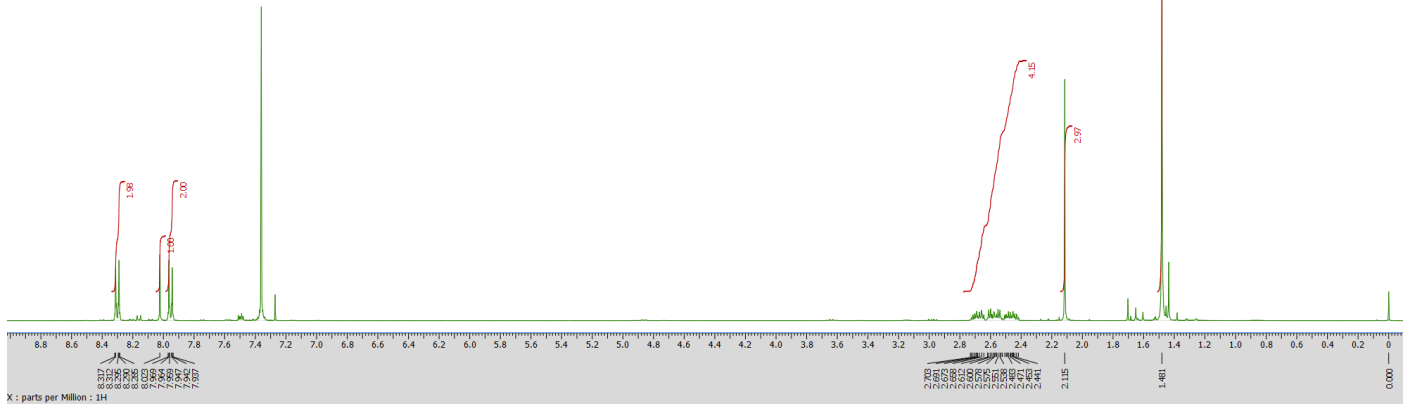
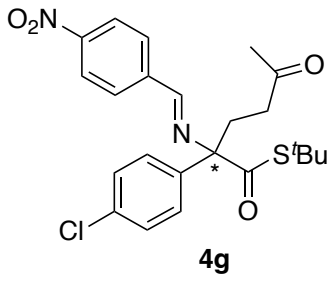


#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	10	28.675	3227290	76040	17.497	19.178	N/A	11330	2.463	1.453	
2	Unknown	10	31.477	15217899	320453	82.503	80.822	N/A	10939	N/A	1.579	

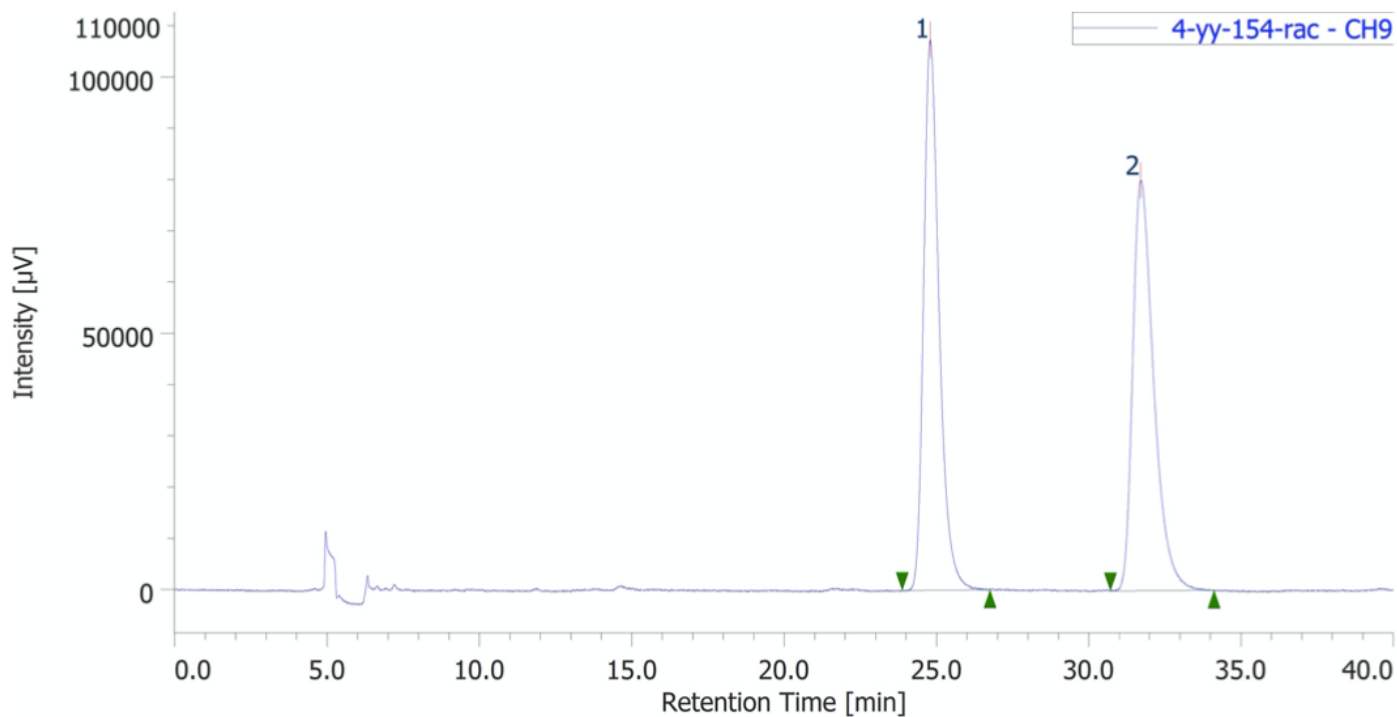
4f



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	26.238	3709244	81822	50.129	52.201	N/A	7804	2.247	1.208	
2	Unknown	9	29.007	3690185	74920	49.871	47.799	N/A	8182	N/A	1.214	

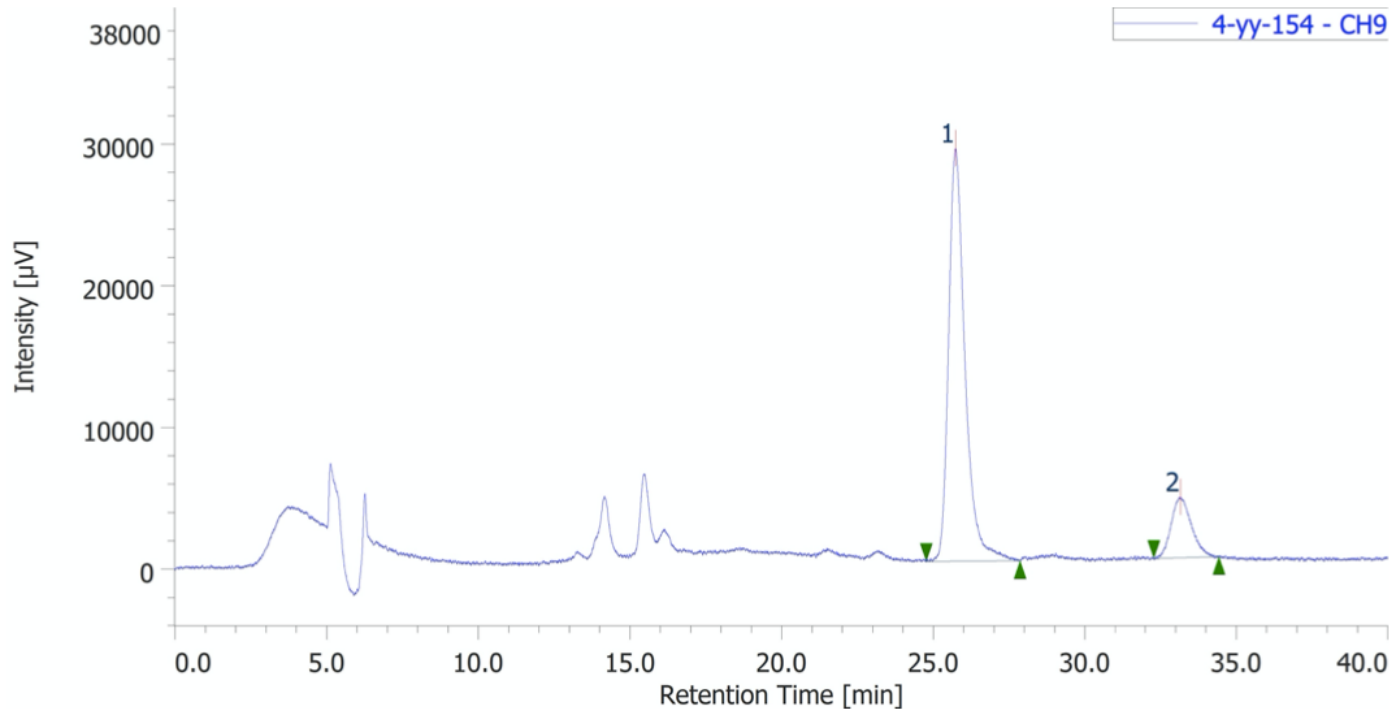


4g (racemate)

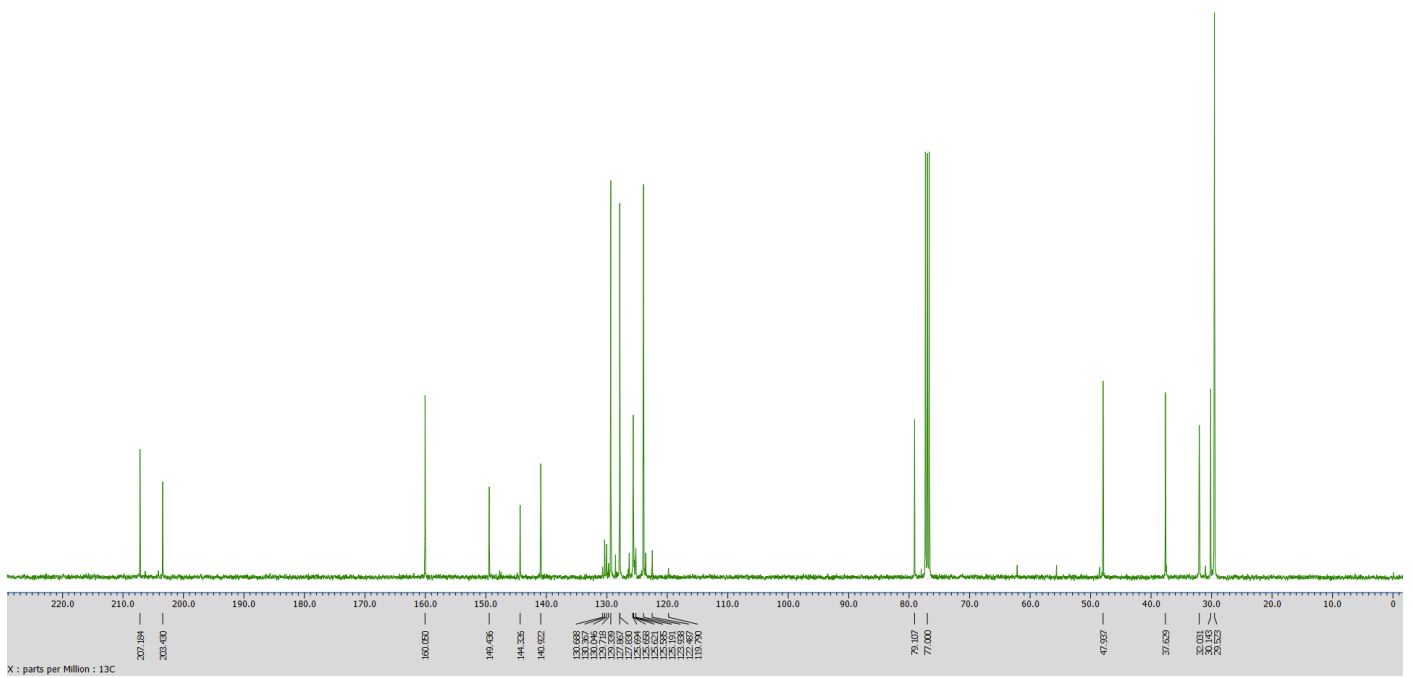
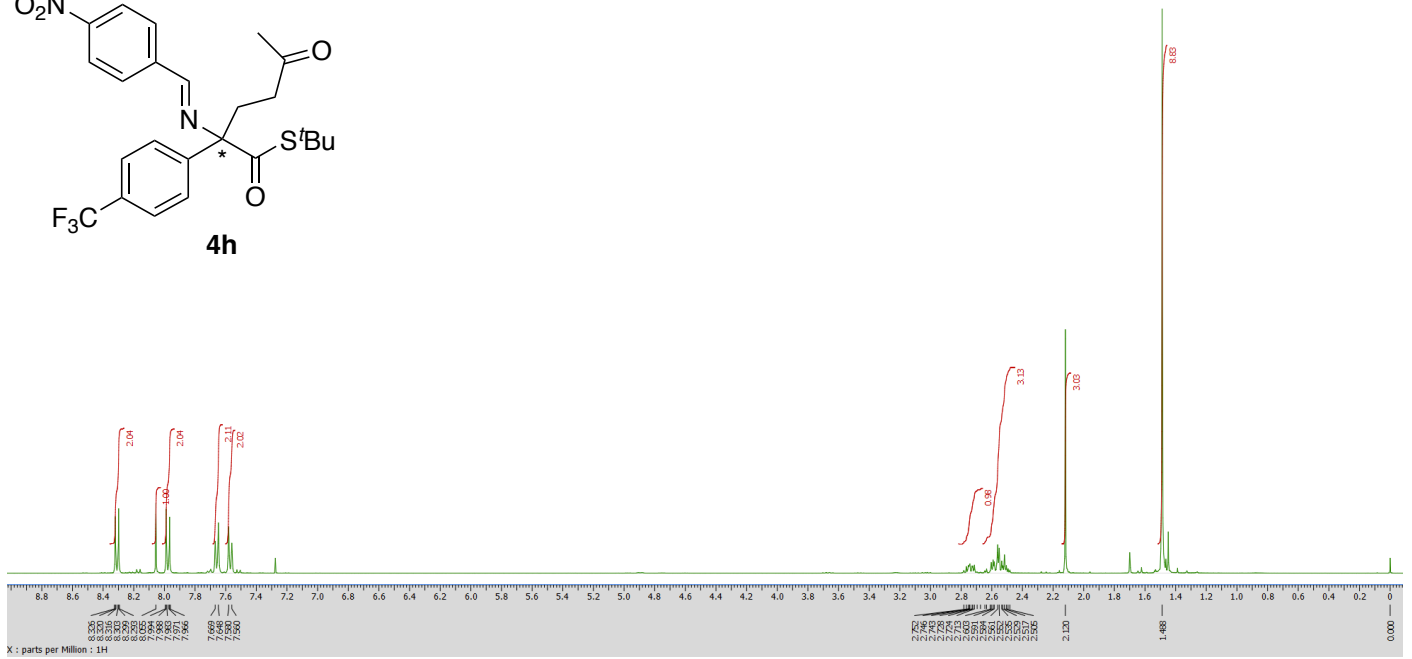
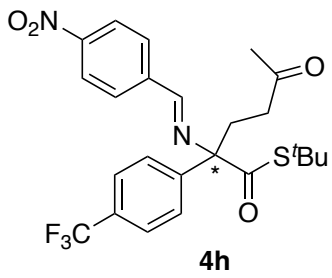


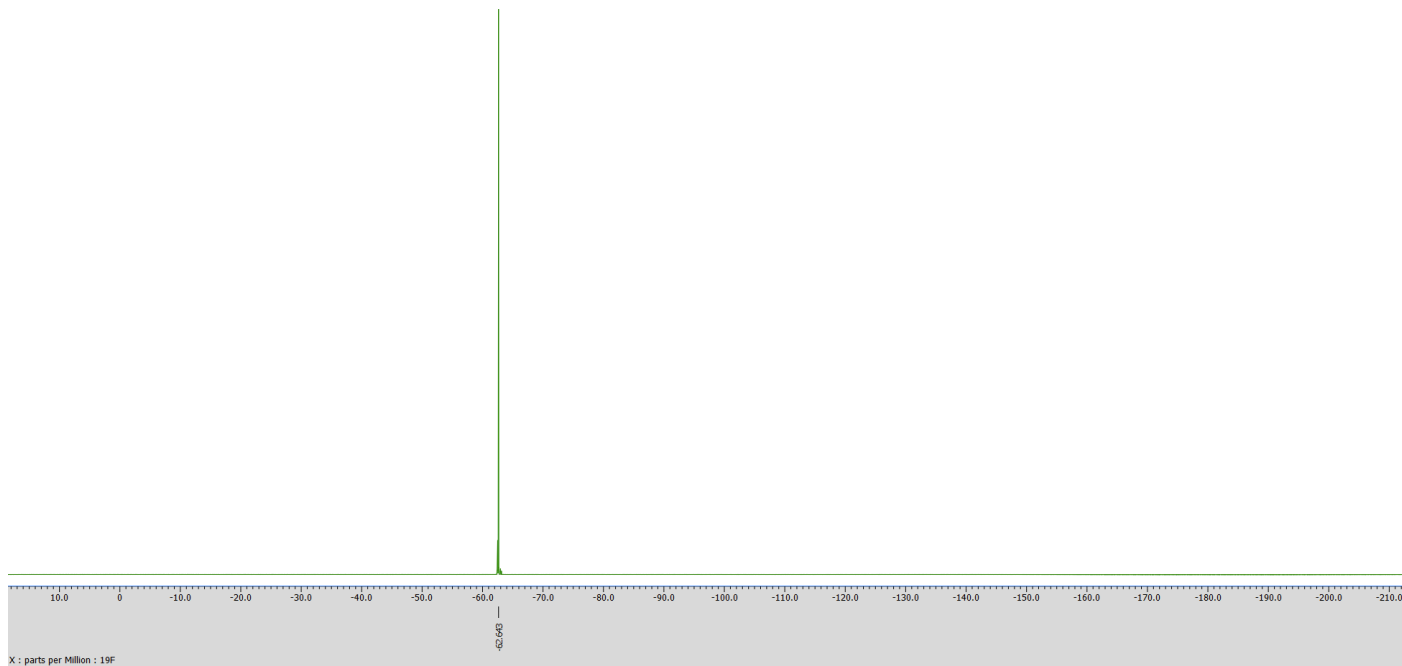
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	24.788	3798049	107318	49.830	57.295	N/A	12246	6.559	1.356	
2	Unknown	9	31.708	3823895	79988	50.170	42.705	N/A	10813	N/A	1.523	

4g

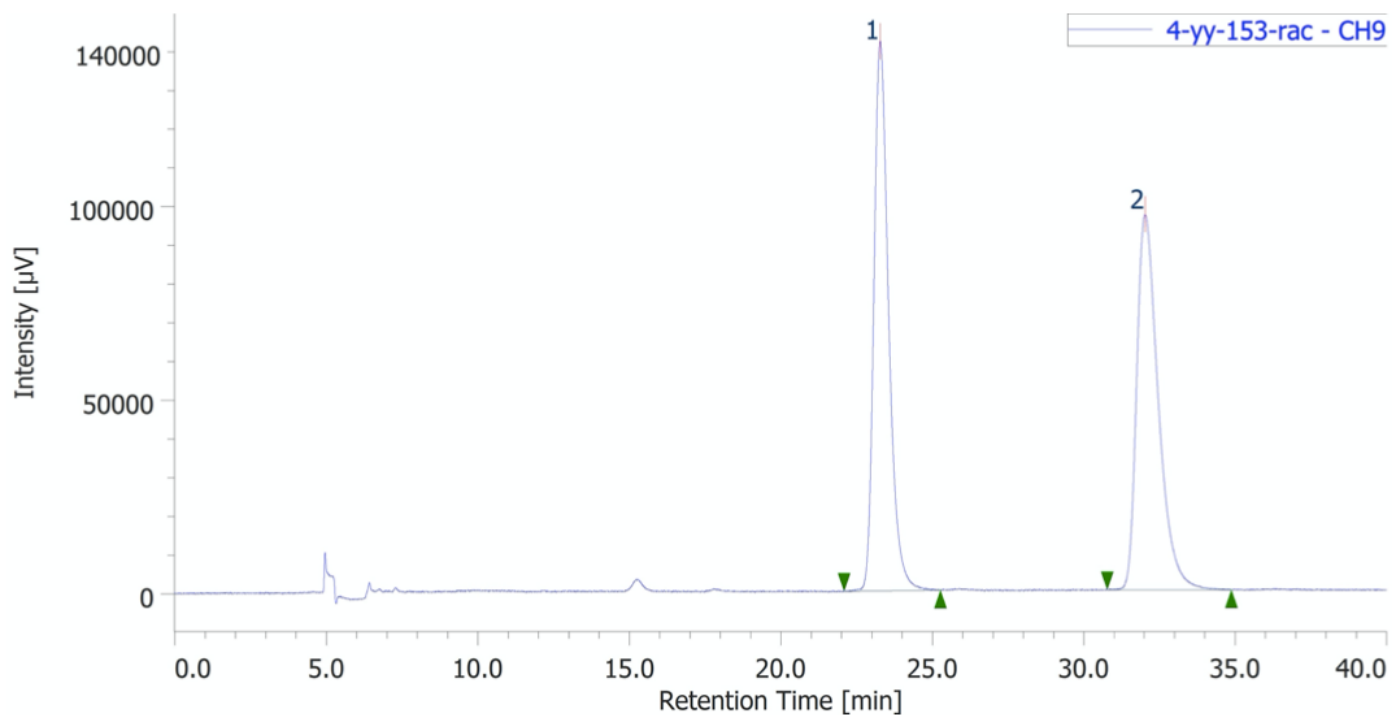


#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	25.727	1092801	29134	84.680	87.194	N/A	12422	7.028	1.390	
2	Unknown	9	33.153	197706	4279	15.320	12.806	N/A	12297	N/A	1.179	



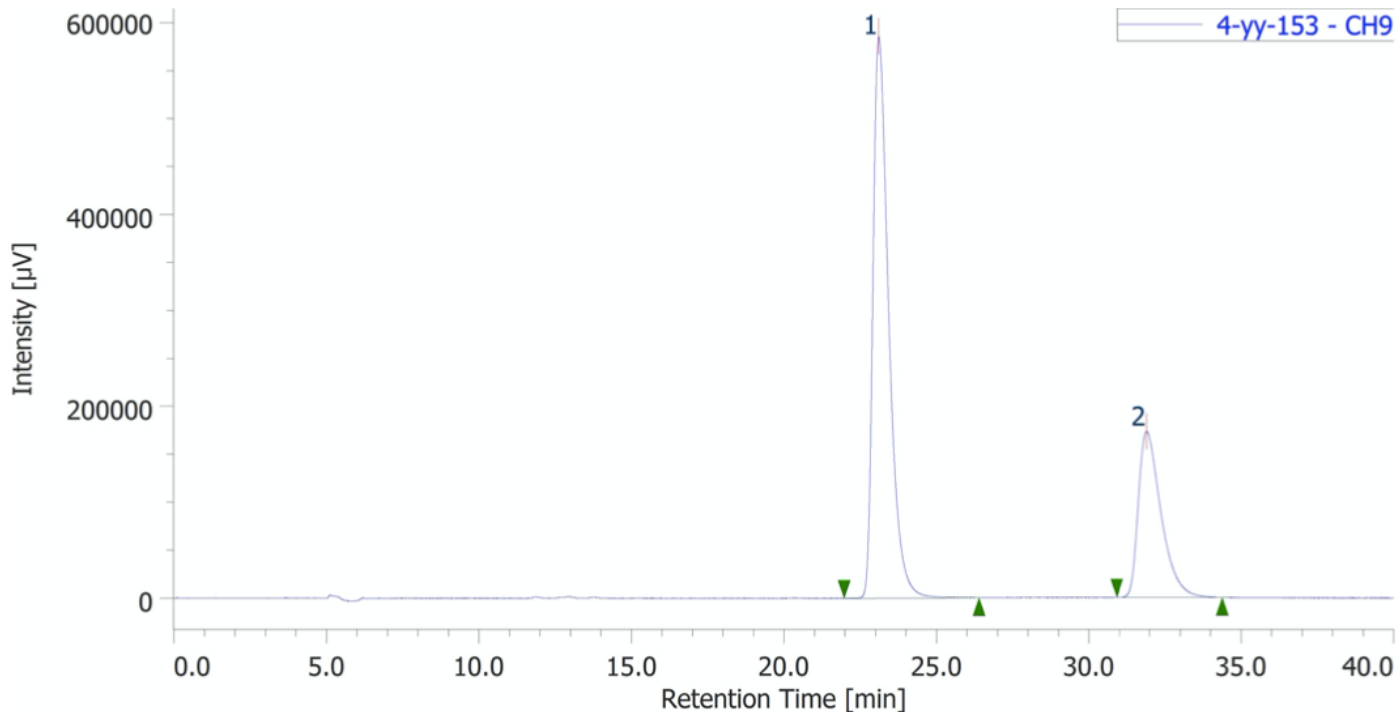


4h (racemate)

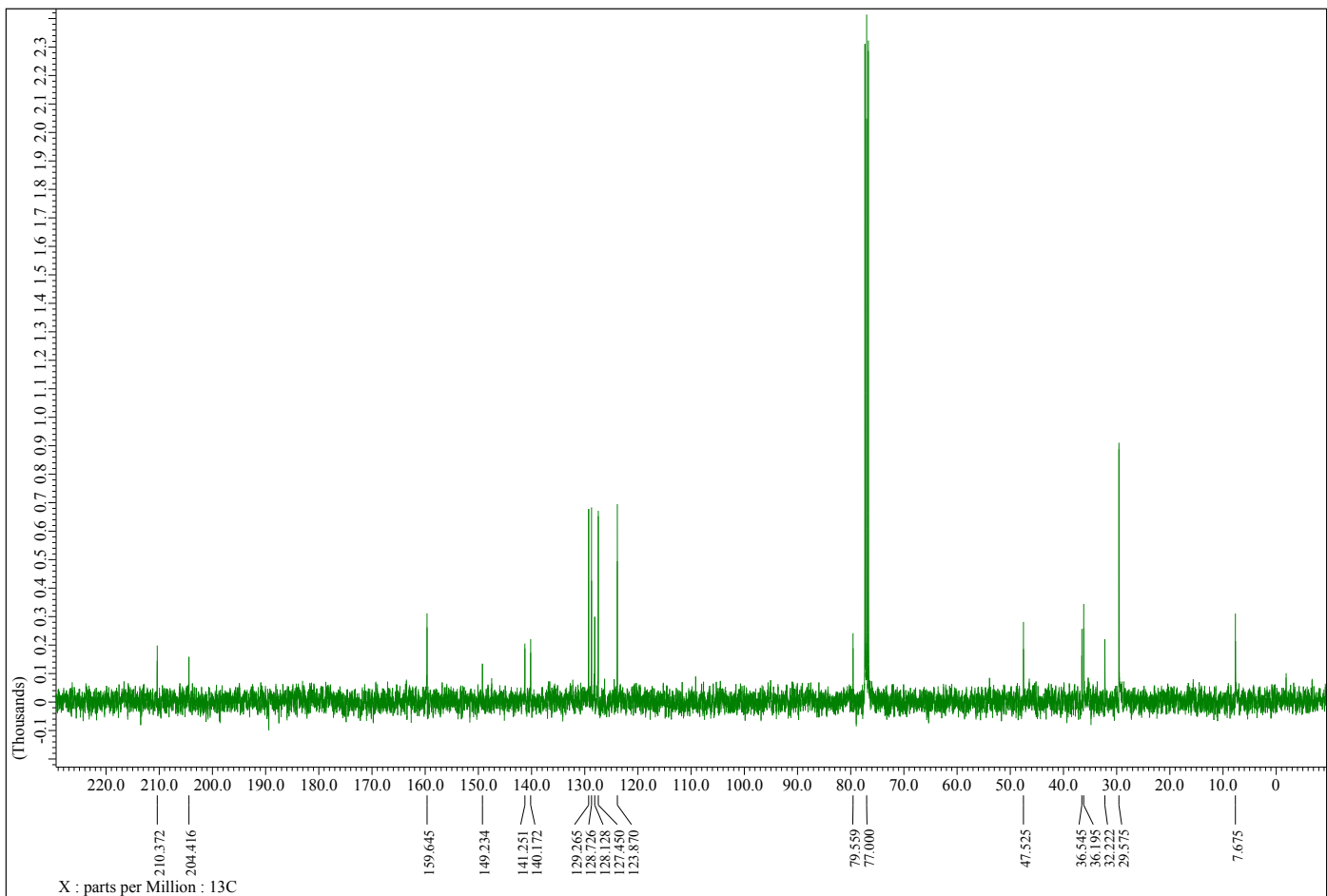
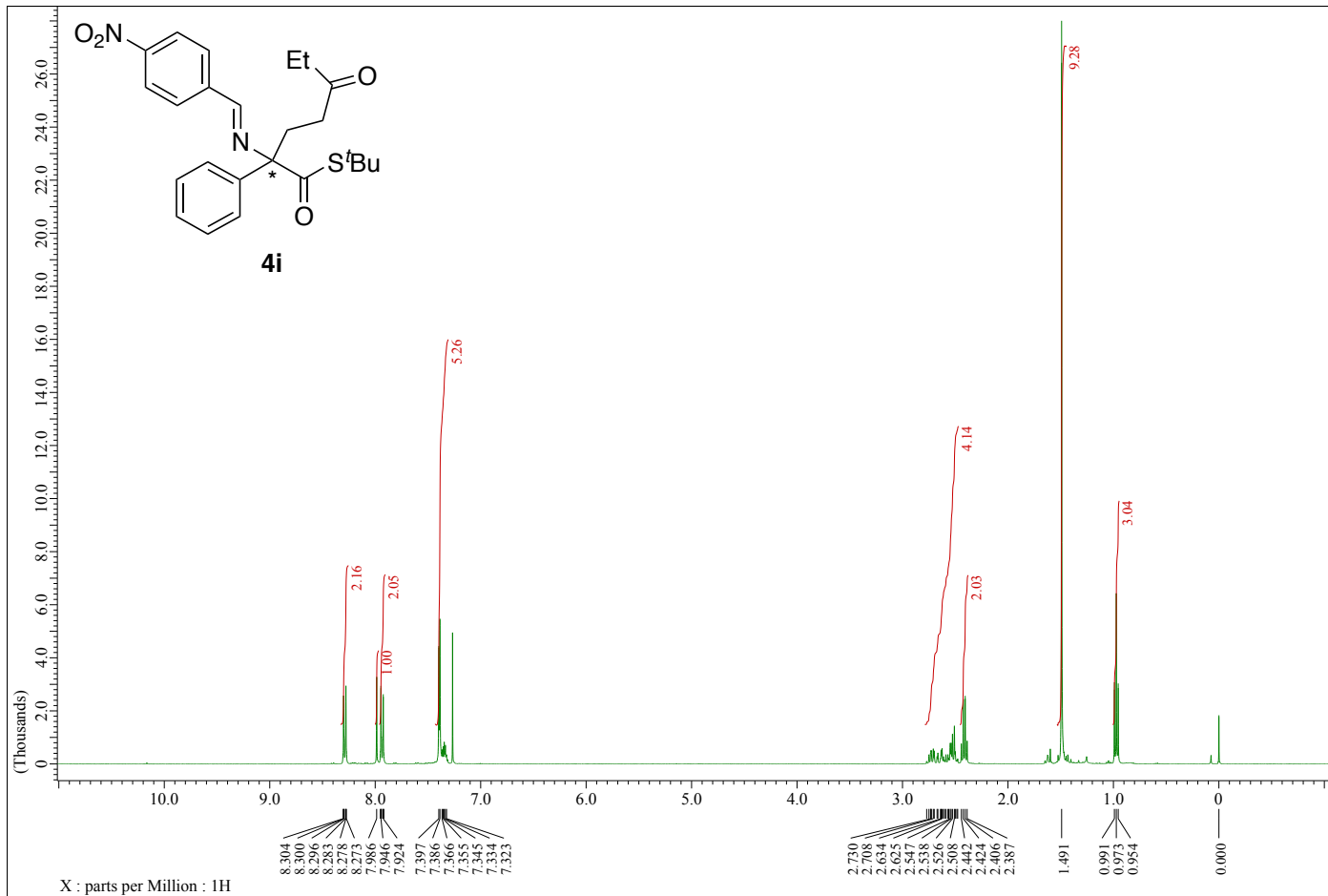


#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	23.268	4806819	141900	50.077	59.412	N/A	11743	8.288	1.351	
2	Unknown	9	32.023	4792103	96942	49.923	40.588	N/A	10345	N/A	1.520	

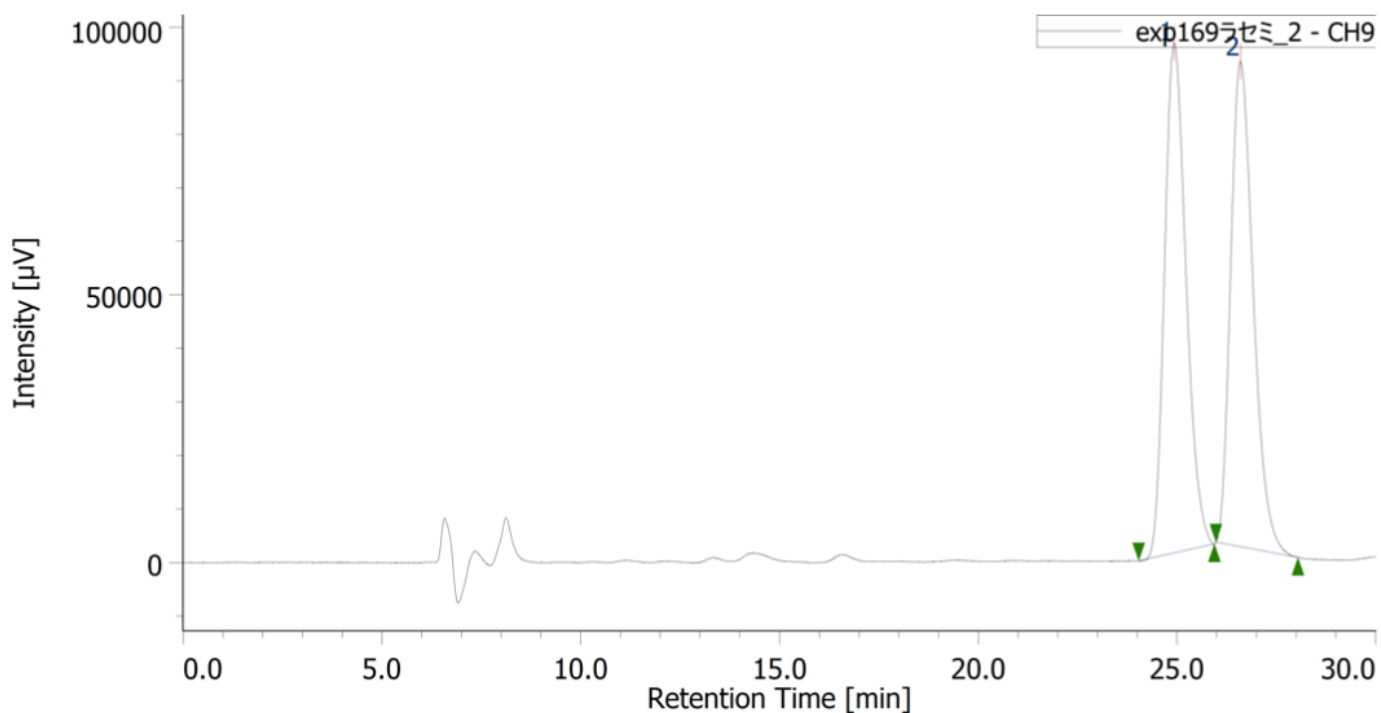
4h



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	23.103	21046361	585702	70.192	77.214	N/A	10236	7.871	1.614	
2	Unknown	9	31.885	8937498	172839	29.808	22.786	N/A	9280	N/A	1.679	

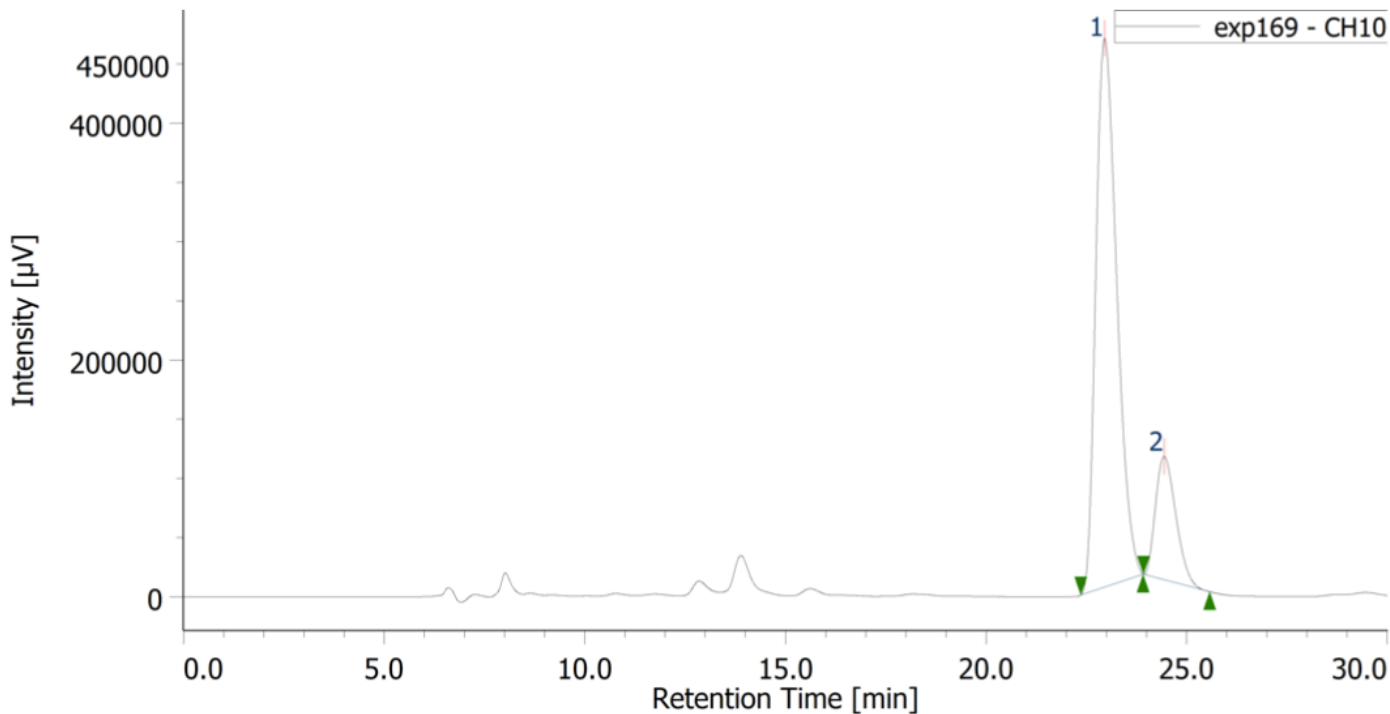


4i (racemate)

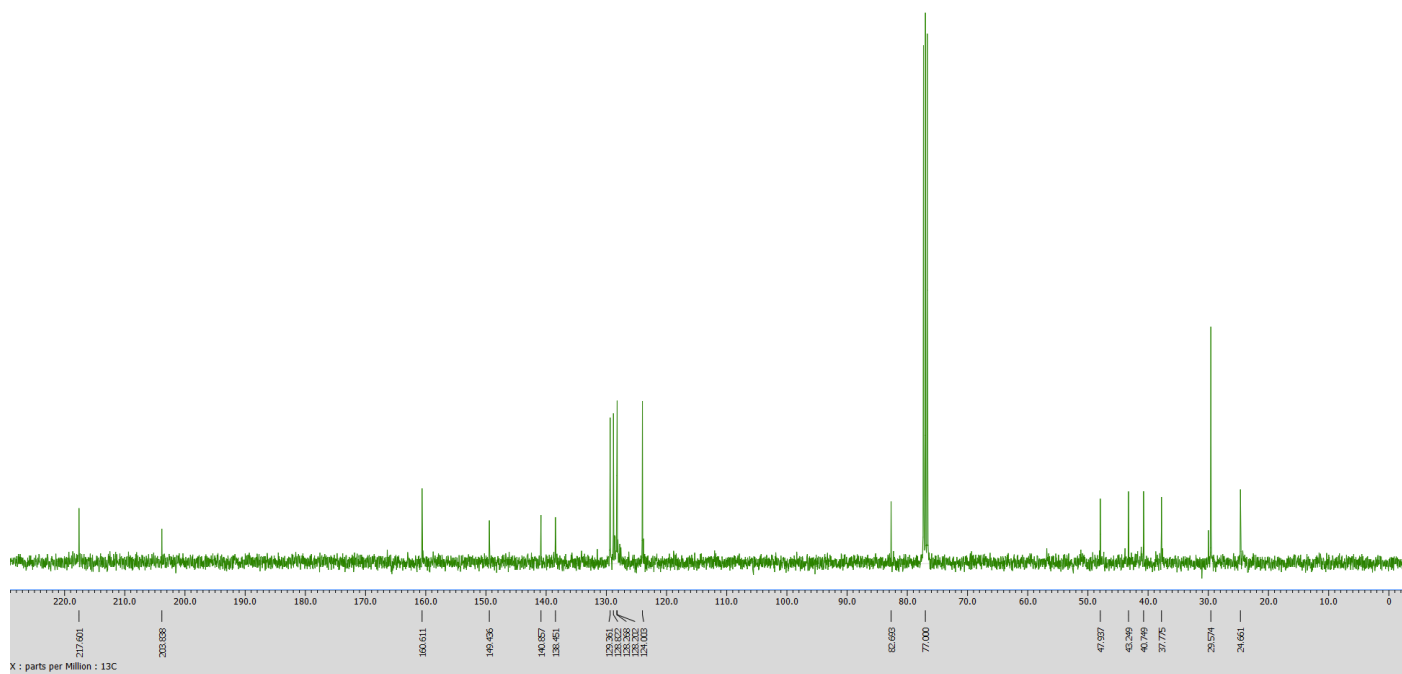
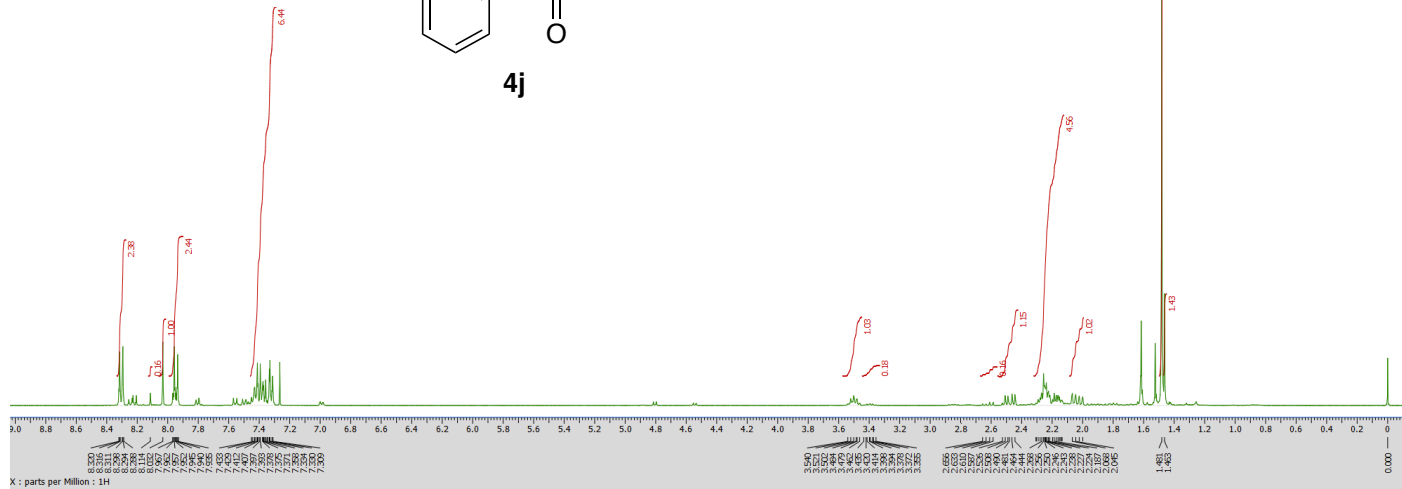
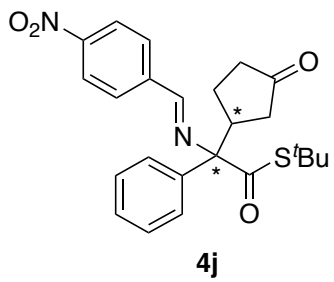


#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	24.923	3584753	95224	50.092	51.241	N/A	10071	1.654	1.239	
2	Unknown	9	26.597	3571540	90611	49.908	48.759	N/A	10548	N/A	1.304	

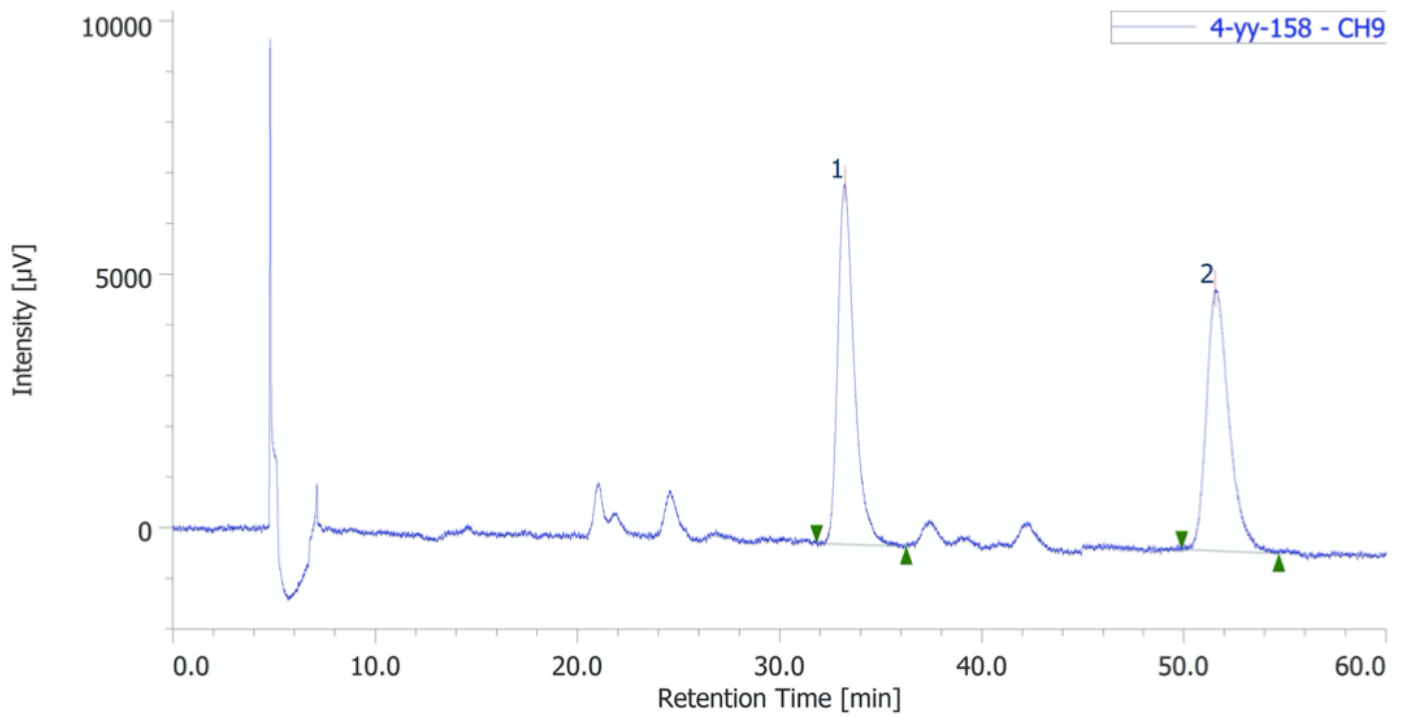
4i



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	10	22.950	16855830	463254	82.137	81.673	N/A	8948	1.550	1.351	
2	Unknown	10	24.433	3665866	103955	17.863	18.327	N/A	10615	N/A	1.332	

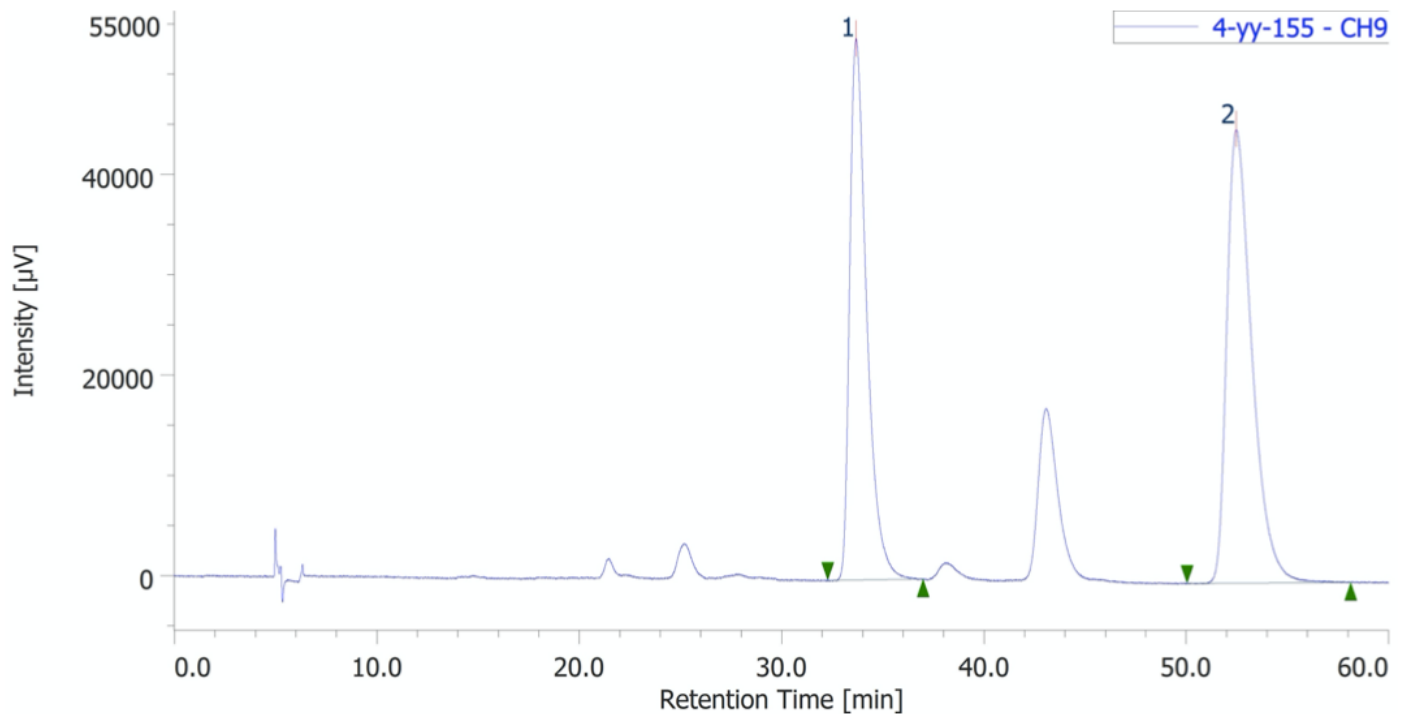


4j (racemate)



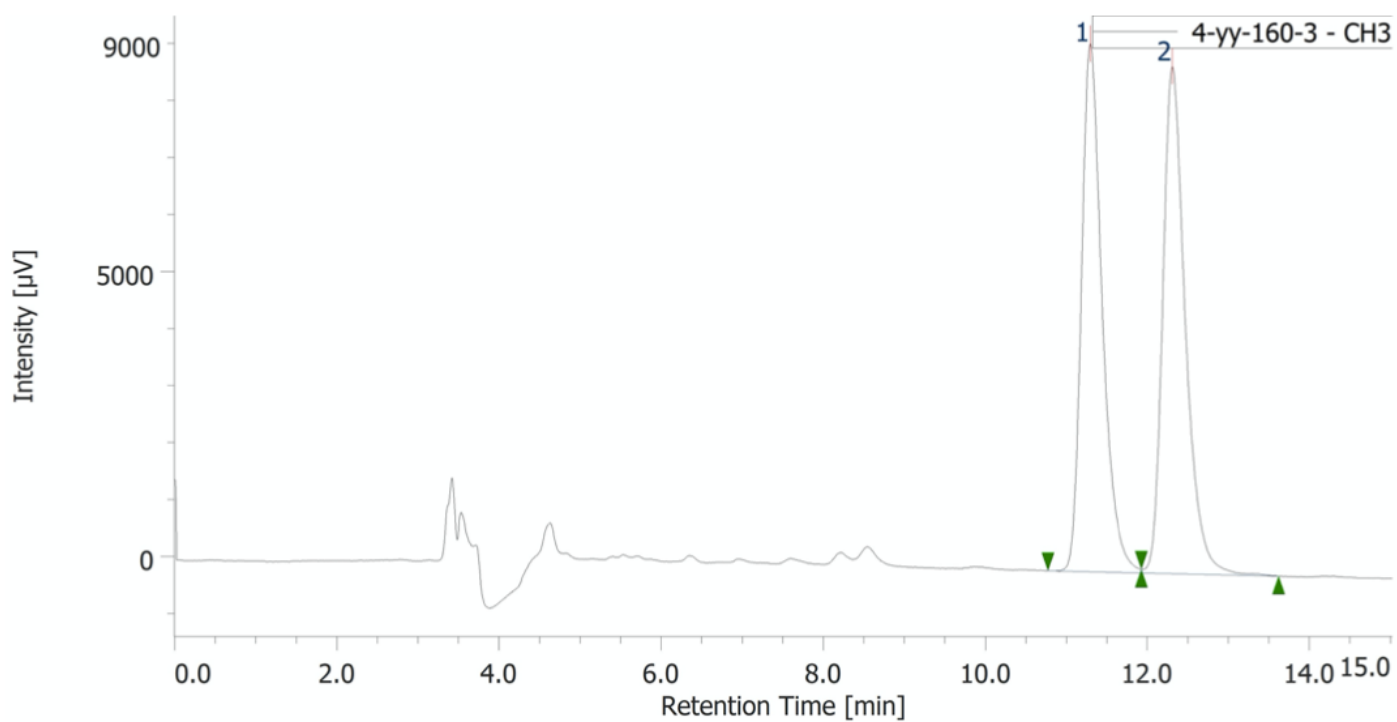
#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	33.225	402531	7105	50.089	57.887	N/A	8826	10.887	1.415	
2	Unknown	9	51.547	401108	5169	49.911	42.113	N/A	11063	N/A	1.484	

4j

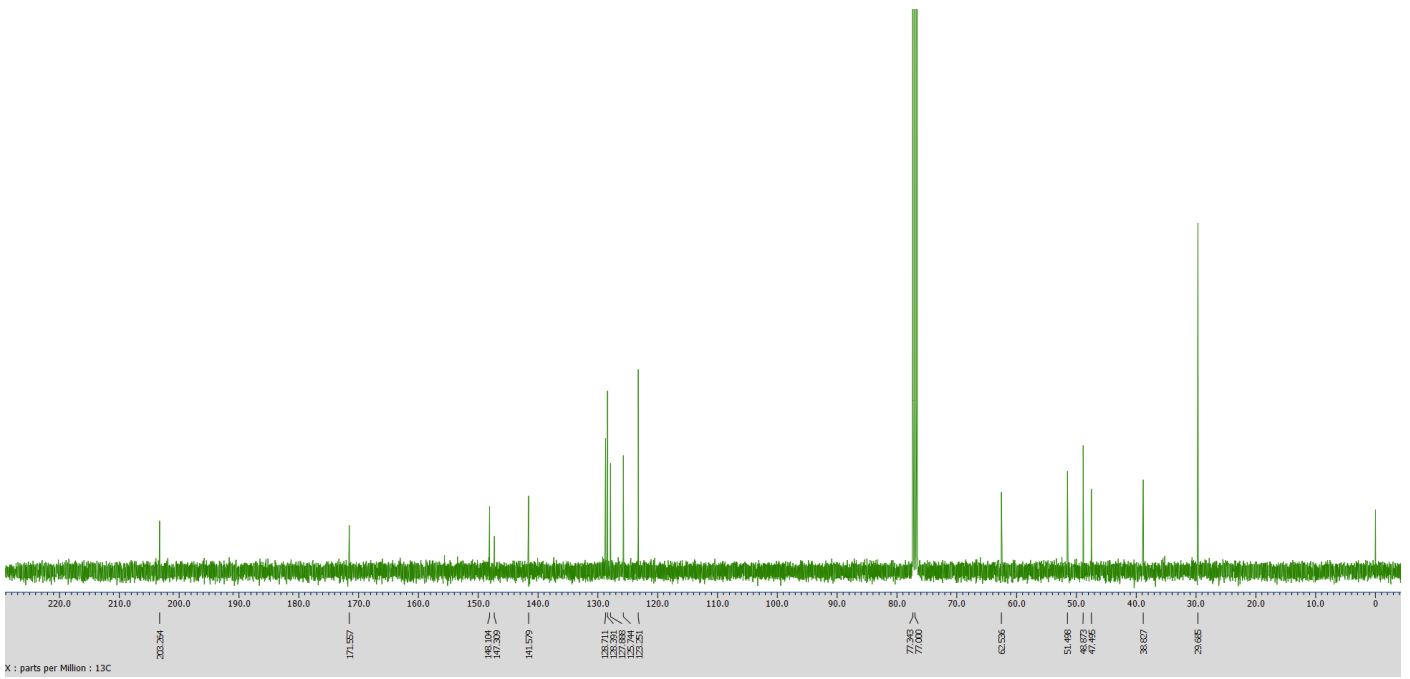
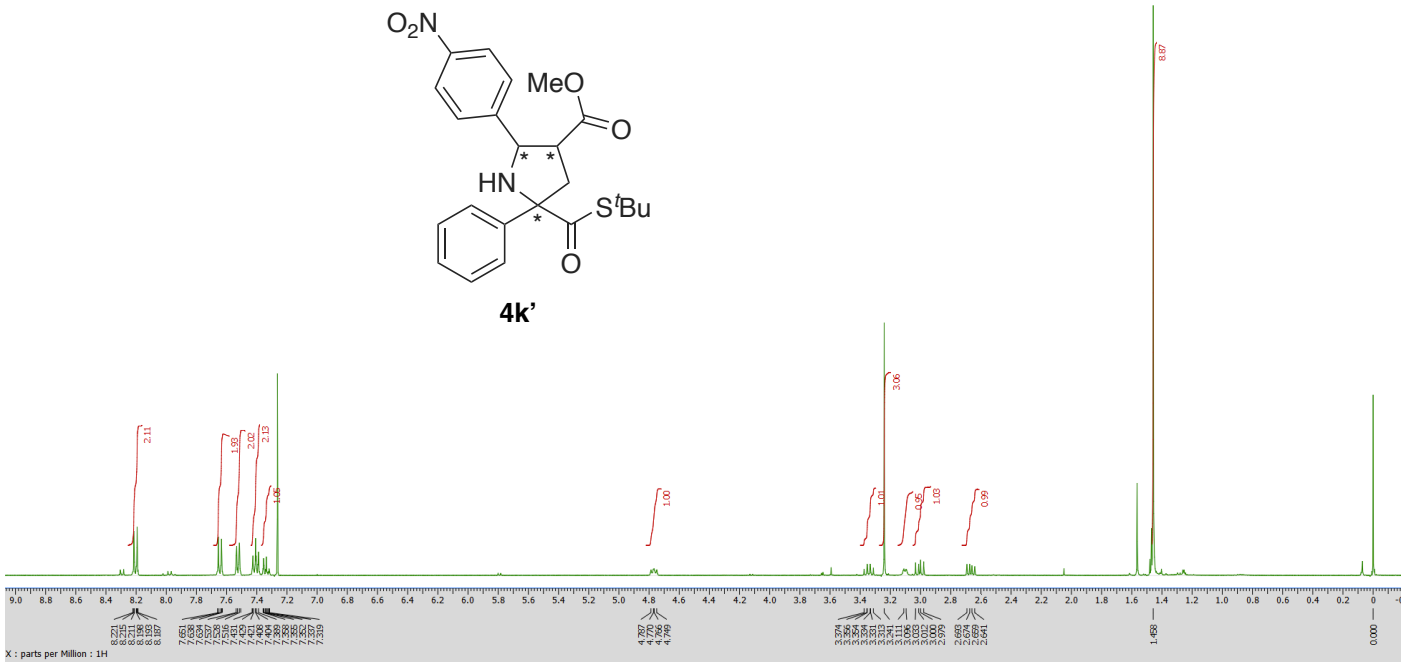
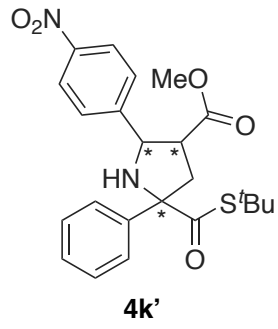


#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	9	33.663	3143090	53956	44.698	54.404	N/A	8355	10.244	1.647	
2	Unknown	9	52.462	3888695	45219	55.302	45.596	N/A	9042	N/A	1.582	

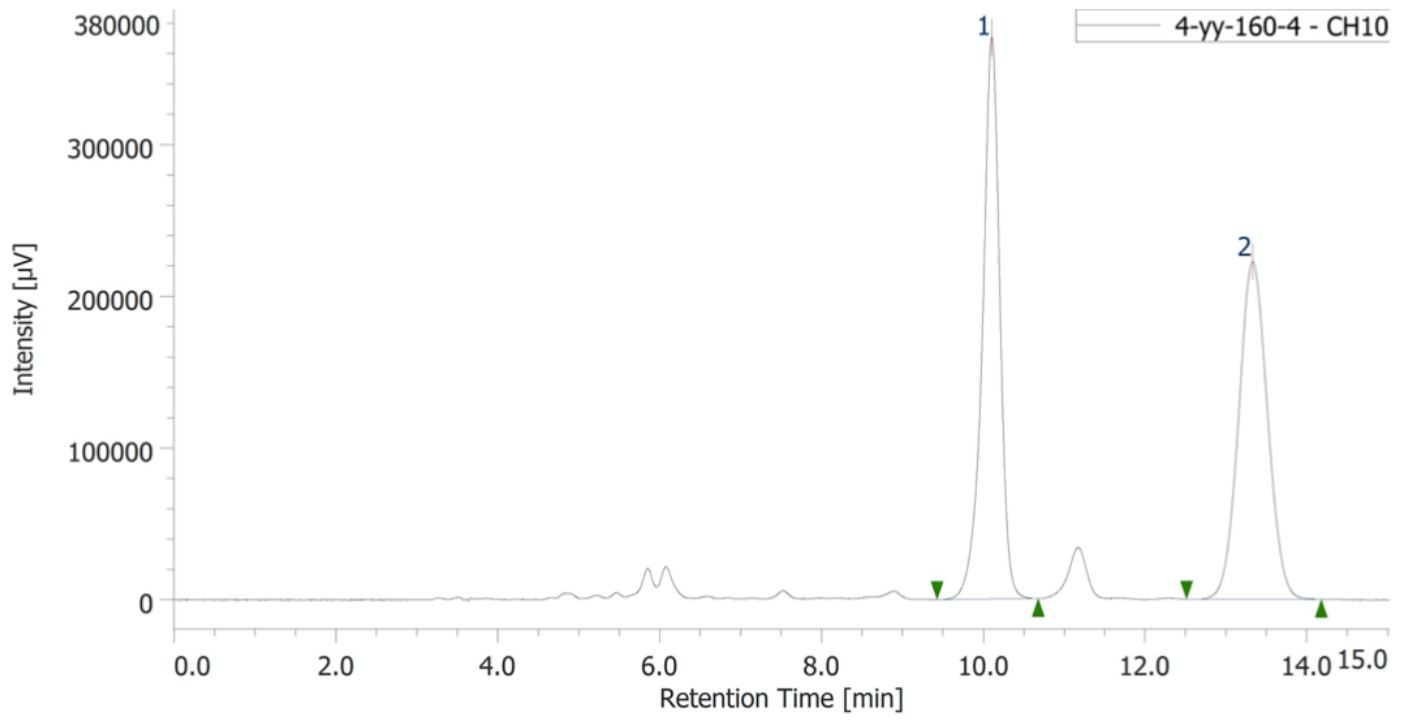
4k



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	3	11.292	165266	9261	49.022	51.012	N/A	10029	2.179	1.352	
2	Unknown	3	12.308	171862	8893	50.978	48.988	N/A	10317	N/A	1.339	



4k'



#	ピーク名	CH	tR [min]	面積 [μV·sec]	高さ [μV]	面積%	高さ%	定量値	NTP	分離度	シンメトリー係数	警告
1	Unknown	10	10.100	5531748	370241	50.078	62.482	N/A	11924	6.327	0.885	
2	Unknown	10	13.328	5514616	222312	49.922	37.518	N/A	6659	N/A	1.044	

