Supporting Information

Enantioselective [2 + 2 + 2] Cycloaddition of Ketenes and Carbon Disulfide Catalyzed by N-Heterocyclic Carbenes

Xiao-Na Wang, Li-Tao Shen and Song Ye*

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Molecular Recognition and Function, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China

songye@iccas.ac.cn

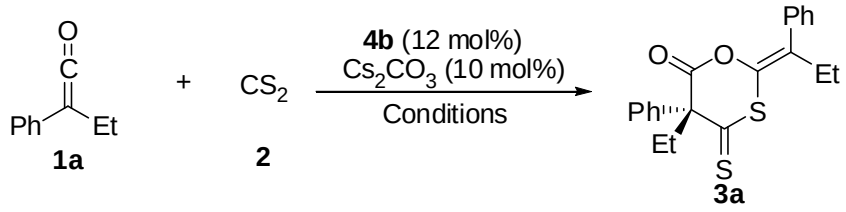
Table of Contents

Part I Experimental Part

General Information

Unless otherwise indicated, all starting materials were obtained from commercial supplies and used as received. Anhydrous toluene、ether and THF were distilled from sodium and benzophenone. Anhydrous CH_2Cl_2 was distilled from CaH_2. Chiral triazolium (4a)[1a], 4b[1b], 4c[1c], 4d[1d] and (4e, 4f, 4g, 4h)[1e] were synthesized according to our previous reports, and 5[1f] was synthesized according to literature. Ketenes were prepared according to the literatures [1g,2]. All reactions utilizing air or moisture sensitive reagents were performed in oven-dried glasswares with magnetic stirring under nitrogen atmosphere. Column chromatograph was performed with silica gel 200~300 mesh. All ^{1}H NMR (300 MHz), ^{13}C NMR (75 MHz) spectra were recorded on a Bruker-DMX 300 spectrometer in $CDCl_3$, with tetramethylsilane as an internal standard and reported in parts per million (ppm, δ). ^{1}H NMR spectroscopy splitting patterns were designated as singlet (s), doublet (d), triplet (t). Splitting patterns that could not be interpreted or easily visualized were designated as multiplet (m) or broad (br). ^{13}C NMR (75 MHz) spectra were reported in ppm with the internal chloroform signal at 77.0 ppm as a standard. Infrared spectra were recorded on a JASCO FT/IR-480 spectrophotometer and reported as wave number (cm^{-1}). Optical rotations were measured on Perkin Elmer/Model-343 digital polarimeter operating at the sodium D line with a 100 mm path cell, and reported as follows: $[\alpha]_D^T$ (concentration (g/100ml), solvent).

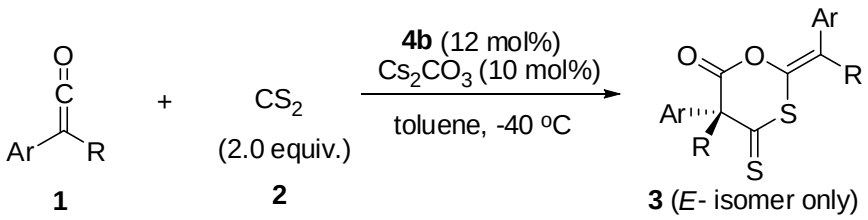
1. Optimization of Reaction Conditions (Table S1)



entry	**1a**:**2**	solvent	T (^{o}C)	yield (%)[b]	ee (%)[c]
1	1:2	toluene	rt	69	95
2	1.5:1	toluene	rt	85	91
3	1:5	toluene	rt	72	95
4	1:2	THF	rt	40	89
5	1:2	Ether	rt	67	96
6	1:2	CH_2Cl_2	rt	51	90
7	1:2	toluene	-40	99	96
8	1:2	toluene	-78	26	99

[a] NHC **4b'** was generated from the corresponding triazolium salt **4b** in the presence of Cs_2CO_3 at room temperature for 1.0 h and used immediately. [b] Isolated yield. [c] Determined by chiral HPLC.

2. Enantioselective NHC-catalyzed [2 + 2 + 2] cycloaddition reaction of ketenes with carbon disulfide (Table 2)

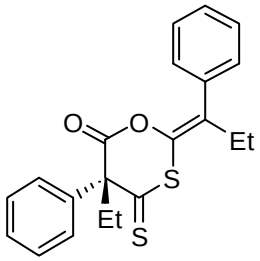


General Procedure. To an oven-dried 50 mL reaction tube containing a stir bar was added NHC precursor **4b** (73.4 mg, 0.12 mmol), Cs_2CO_3 (32.6mg, 0.10 mmol) and toluene (5 mL). The reaction mixture was stirred under N_2 for 1.0 h at room

temperature, and then cooled to -40 °C. Carbon disulfide **2** (152.8 mg, 2.0 mmol) and ketene **1** (1.0 mmol) were added via syringes at -40 °C. After stirring for the specific time (see below), the reaction mixture was quenched by the addition of silica gel and further stirred for five minutes. The reaction mixture was diluted with ethyl acetate, filtered through a pad of silica gel and washed with ethyl acetate. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel to give the desired product.

Racemic samples of **3** for the standard of chiral HPLC spectra were prepared using 10 mol % DMAP as catalyst at -40 °C with same procedure as above except that ketene **1** (1.0 mmol) was added via a syringe pump over 2.0 h after addition of carbon disulfide **2** (382.0 mmg, 5.0 mmol)**.**

(*R,E*)-5-ethyl-5-phenyl-2-(1-phenylpropylidene)-4-thioxo-1,3-oxathian-6-one (3a)

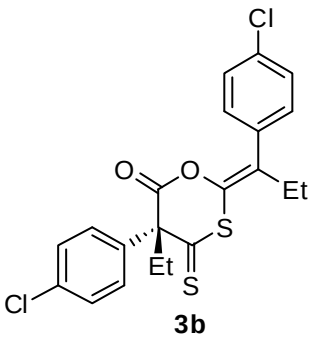


3a

Lactone **3a** (Table 2, entry 1). Reaction time: 9.0 h. R_f = 0.13 (petroleum ether/Et_2O = 90:1). Yield: 184.0 mg, 99%; dark red oil; $[\alpha]_D^{20}$ -507.0 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.25-7.18 (m, 6H), 7.08-7.05 (m, 2H), 6.92-6.90 (m, 2H), 2.28 (q, *J* = 7.2 Hz, 2H), 2.07-1.91 (m, 2H), 0.70 (t, *J* = 7.2 Hz, 3H), 0.49 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 228.0, 165.9, 135.7, 135.4, 133.3, 131.6, 128.7, 128.2, 128.1, 128.0, 127.9, 126.5, 74.8, 31.9, 27.1, 12.2, 9.8; IR (KBr) ν 2970, 2933, 1768, 1492, 1446, 1190, 1132, 1073, 926, 759, 697 cm^{-1}; MS (EI): m/z 368 (M^+, 5.4), 146 ($Ph(C_2H_5)C{=}C{=}O^+$, 100); HRMS (EI) calcd for $C_{21}H_{20}O_2S_2$ $[M]^+$ 368.0905, found

368.0910; HPLC analysis: 96% ee [Daicel CHIRALPAK AD-H column; 20 °C; 0.5 mL/min; solvent system: 2-propanol/hexane = 0.5:99.5; retention times: 13.4 min (minor), 19.6 min (major)].

(*R,E*)-5-(4-chlorophenyl)-2-(1-(4-chlorophenyl)propylidene)-5-ethyl-4-thioxo-1,3-oxathian-6-one (3b)

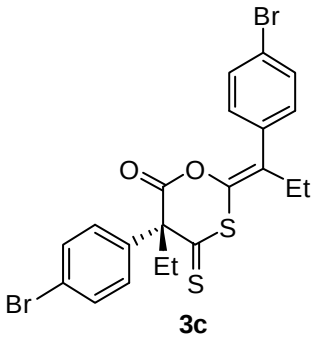


3b

Lactone **3b** (Table 2, entry 2). Reaction time: 8.5 h. R_f = 0.18 (petroleum ether/Et_2O = 90:1). Yield: 190.1 mg, 87%; dark red oil; $[\alpha]_D^{20}$ -214.4 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.4 Hz, 2H), 2.25 (q, *J* = 7.2 Hz, 2H), 2.11-1.96 (m, 2H), 0.70 (t, *J* = 7.2 Hz**,** 3H), 0.58 (t, *J* = 7.5 Hz**,** 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 226.7, 165.3, 134.3, 134.2, 134.1, 133.9, 133.6, 130.7, 129.4, 128.9, 128.5, 127.8, 74.2, 31.7, 27.0, 12.3, 9.7; IR (KBr) ν 2971, 2935, 1770, 1706, 1492, 1461, 1190, 1094, 1014, 822, 760 cm^{-1}; MS (EI): m/z 436 (M^+, 5.1), 180 (*p*-ClPh(C_2H_5)C=C=O^+, 100); HRMS (EI) calcd for $C_{21}H_{18}O_2S_2Cl_2$ $[M]^+$ 436.0125, found 436.0131; HPLC analysis: 97% ee [Daicel CHIRALPAK AD-H column; 20 °C; 0.5 mL/min; solvent system: 2-propanol/hexane = 1:99; retention times: 16.7 min (minor), 21.2 min (major)]

(*R,E*)-5-(4-bromophenyl)-2-(1-(4-bromophenyl)propylidene)-5-ethyl-4-thioxo-1,3-oxathian-6-one (3c)

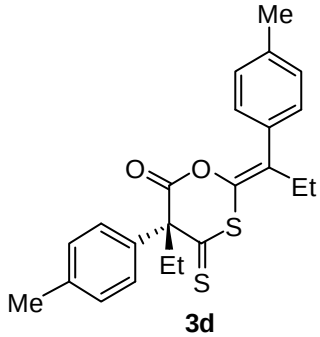
Lactone **3c** (Table 2, entry 3). Reaction time: 5.5 h. R_f = 0.18 (petroleum ether/Et_2O =



3c

90:1). Yield: 207.1 mg, 79%; dark red oil; $[\alpha]_D^{20}$ -234.6 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.7 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 2H), 2.33 (q, *J* = 7.2 Hz, 2H), 2.22-1.98 (m, 2H), 0.78 (t, *J* = 7.4 Hz**,** 3H), 0.66 (t, *J* = 7.5 Hz**,** 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 226.5, 165.2, 134.7, 134.1, 133.9, 131.8, 131.5, 130.8, 129.7, 128.1, 122.4, 122.3, 74.2, 31.6, 27.0, 12.3, 9.7; IR (KBr) ν 2970, 2934, 1769, 1692, 1487, 1461, 1188, 1074, 1010, 923, 819, 759 cm^{-1}; MS (EI): m/z 528 (M^+, 3.0), m/z 526 (M^+, 5.4), m/z 524 (M^+, 2.4), 226 (*p*-$^{81}BrPh(C_2H_5)C{=}C{=}O^+$, 98.5), 224 (*p*-$^{79}BrPh(C_2H_5)C{=}C{=}O^+$, 100); HRMS (EI) calcd for $C_{21}H_{18}O_2S_2{}^{79}Br_2$ $[M]^+$ 523.9115, found 523.9120, calcd for $C_{21}H_{18}O_2S_2{}^{79}Br\,{}^{81}Br$ $[M]^+$ 525.9094, found 525.9100, calcd for $C_{21}H_{18}O_2S_2{}^{81}Br_2$ $[M]^+$ 527.9074, found 527.9071; HPLC analysis: 96% ee [Daicel CHIRALPAK AD-H column; 20 °C; 0.5 mL/min; solvent system: 2-propanol/hexane = 0.5:99.5; retention times: 17.9 min (minor), 24.4 min (major)]

(*R*,*E*)-5-ethyl-4-thioxo-5-*p*-tolyl-2-(1-p-tolylpropylidene)-1,3-oxathian-6-one (3d)

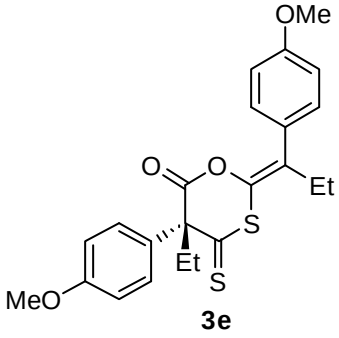


3d

Lactone **3d** (Table 2, entry 4). Reaction time: 24.0 h. R_f = 0.19 (petroleum ether/Et_2O = 90:1). Yield: 142.7 mg, 72%; dark red oil; $[\alpha]_D^{20}$ -284.2 (*c* 1.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.06-6.94 (m, 6H), 6.85 (d, *J* = 8.1 Hz**,** 2H), 2.26 (s, 3H), 2.25 (s, 3H), 2.30-2.20 (m, 2H), 2.09-1.92 (m, 2H), 0.71 (t, *J* = 7.2 Hz**,** 3H), 0.50 (t, *J* = 7.5 Hz**,** 3H); ^{13}C NMR (75

MHz, $CDCl_3$) δ 228.6, 166.2, 138.1, 137.8, 133.2, 132.8, 132.5, 131.3, 129.3, 128.8, 128.0, 126.5, 74.6, 31.9, 27.0, 21.2, 21.0, 12.2, 9.8; IR (KBr) ν 2970, 2934, 1769, 1706, 1511, 1455, 1183, 1131, 1063, 814, 757 cm^{-1}; MS (EI): m/z 396 (M^+, 4.2), 160 (*p*-MePh(C_2H_5)C=C=O^+, 100); HRMS (EI) calcd for $C_{23}H_{24}O_2S_2$ $[M]^+$ 396.1218, found 396.1221; HPLC analysis: 92% ee [Daicel CHIRALPAK AD-H column; 20 °C; 0.7 mL/min; solvent system: 2-propanol/hexane = 1:99; retention times: 11.7 min (minor), 15.8 min (major)]

(*R,E*)-5-ethyl-5-(4-methoxyphenyl)-2-(1-(4-methoxyphenyl)propylidene)-4-thioxo -1,3-oxathian-6-one (3e)

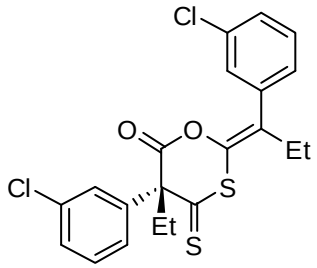


3e

Lactone **3e** (Table 2, entry 5). Reaction time: 7.5 h. R_f = 0.30 (petroleum ether/ ethyl acetate = 9:1). Yield: 69.4 mg, 32%; dark red oil; $[\alpha]_D^{20}$ -458.4 (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.07-7.03 (m, 4H), 6.88-6.85 (m, 2H), 6.81-6.78 (m, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 2.34 (q, *J* = 7.2 Hz**,** 2H), 2.17-2.05 (m, 2H), 0.80 (t, *J* = 7.2 Hz**,** 3H), 0.63 (t, *J* = 7.5 Hz**,** 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 228.7, 166.2, 159.4, 159.2, 132.9, 130.9, 129.6, 127.9, 127.7, 127.5, 114.0, 113.5, 74.2, 55.3, 55.2, 31.9, 26.9, 12.4, 9.8; IR (KBr) ν 2968, 2933, 1768, 1607, 1511, 1462, 1254, 1178, 1033, 828 cm^{-1}; MS (EI): m/z 428 (M^+, 8.9), 176 (*p*-MeOPh(C_2H_5)C=C=O^+, 100); HRMS (EI) calcd for $C_{23}H_{24}O_4S_2$ $[M]^+$ 428.1116, found 428.1122; HPLC analysis: 93% ee [Daicel CHIRALPAK AD-H column; 20 °C; 1.0 mL/min; solvent system: 2-propanol/hexane

= 10:90; retention times: 5.41 min (minor), 7.87 min (major)]

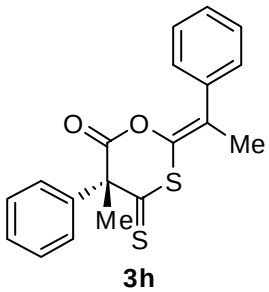
(*R,E*)-5-(3-chlorophenyl)-2-(1-(3-chlorophenyl)propylidene)-5-ethyl-4-thioxo-1,3-oxathian-6-one (3f)



3f

Lactone **3f** (Table 2, entry 6). Reaction time: 91.0 h. R_f = 0.20 (petroleum ether/Et_2O = 90:1). Yield: 155.6 mg, 94%; dark red oil; $[\alpha]_D^{20}$ -253.1 (*c* 1.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.28-7.18 (m, 4H), 7.08-7.07 (m, 1H), 7.01-6.97 (m, 1H), 6.84-6.82 (m, 2H), 2.28 (q, *J* = 7.2 Hz, 2H), 2.09-1.96 (m, 2H), 0.73 (t, *J* = 7.2 Hz, 3H), 0.57 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 226.2, 165.2, 137.6, 137.0, 135.0, 134.2, 134.1, 130.8, 130.1, 129.6, 128.7, 128.3, 128.0, 126.6, 126.4, 124.8, 74.3, 31.8, 27.2, 12.2, 9.8; IR (KBr) ν 2970, 2934, 1770, 1592, 1570, 1476, 1416, 1186, 1134, 1079, 787, 693 cm^{-1}; MS (EI): m/z 436 (M^+, 1.8), 180 (*m*-ClPh(C_2H_5)C=C=O^+, 100); HRMS (EI) calcd for $C_{21}H_{18}O_2S_2Cl_2$ $[M]^+$ 436.0125, found 436.0130; HPLC analysis: 96% ee [Daicel CHIRALPAK AD-H column; 20 °C; 0.7 mL/min; solvent system: 2-propanol/hexane = 1:99; retention times: 12.4 min (minor), 16.5 min (major)]

(*R,E*)-5-methyl-5-phenyl-2-(1-phenylethylidene)-4-thioxo-1,3-oxathian-6-one (3h)

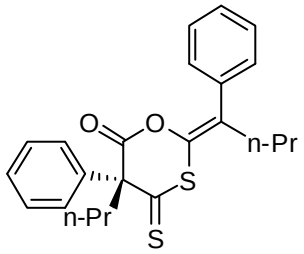


3h

Lactone **3h** (Table 2, entry 8). Reaction time: 6.0 h. R_f = 0.13 (petroleum ether/Et_2O = 90:1). Yield: 117.3 mg, 69%; dark red oil; $[\alpha]_D^{20}$ -342.3 (*c* 1.1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.31-7.17 (m, 6H), 7.11-7.08 (m, 2H), 6.93-6.90 (m, 2H),

1.74 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 228.3, 167.0, 138.5, 136.5, 133.7, 129.1, 128.3, 128.2, 128.1, 127.9, 126.7, 125.1, 71.7, 27.6, 20.0; IR (KBr) ν 1881, 1770, 1695, 1494, 1444, 1202, 1135, 1051, 931, 762, 696 cm^{-1}; MS (EI): m/z 340 (M^+, 1.2), 132 ($Ph(CH_3)C{=}C{=}O^+$, 100); HRMS (EI) calcd for $C_{19}H_{16}O_2S_2$ $[M]^+$ 340.0592, found 340.0595; HPLC analysis: 96% ee [Daicel CHIRALPAK AD-H column; 20 °C; 0.5 mL/min; solvent system: 2-propanol/hexane = 1:99; retention times: 20.0 min (minor), 30.3 min (major)]

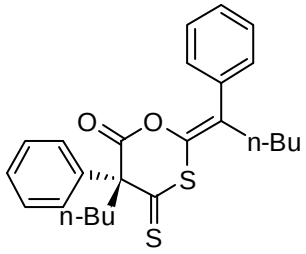
(*R,E*)-5-phenyl-2-(1-phenylbutylidene)-5-propyl-4-thioxo-1,3-oxathian-6-one (3i)



3i

Lactone **3i** (Table 2, entry 9). Reaction time: 9.5 h. R_f = 0.15 (petroleum ether/Et_2O = 90:1). Yield: 185.9 mg, 94%; dark red oil; $[\alpha]_D^{20}$ -364.2 (*c* 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22-7.17 (m, 6H), 7.07-7.04 (m, 2H), 6.91-6.89 (m, 2H), 2.24-2.14 (m, 2H), 2.11-1.86 (m, 2H), 1.22-1.10 (m, 1H), 0.99-0.87 (m, 3H), 0.71 (t, *J* = 7.4 Hz**,** 3H), 0.54 (t, *J* = 7.4 Hz**,** 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 228.2, 165.9, 136.0, 135.5, 133.9, 130.4, 128.7, 128.1, 128.0, 127.8, 126.3, 74.6, 40.8, 35.6, 20.7, 18.3, 14.2, 13.3; IR (KBr) ν 2962, 2931, 1769, 1695, 1494, 1447, 1189, 1132, 967, 755, 697 cm^{-1}; MS (EI): m/z 396 (M^+, 1.5), 160 ($Ph(C_3H_7)C{=}C{=}O^+$, 100); HRMS (EI) calcd for $C_{23}H_{24}O_2S_2$ $[M]^+$ 396.1218, found 396.1223; HPLC analysis: 92% ee [Daicel CHIRALPAK AD-H column; 20 °C; 0.5 mL/min; solvent system: 2-propanol/hexane = 1:99; retention times: 15.1 min (minor), 17.5 min (major)]

(*R*,*E*)-5-butyl-5-phenyl-2-(1-phenylpentylidene)-4-thioxo-1,3-oxathian-6-one (3j)

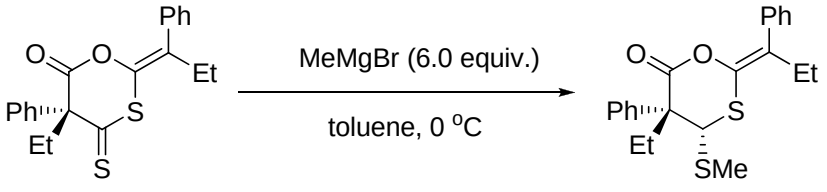


3j

Lactone **3j** (Table 2, entry 10). Reaction time: 10.0 h. R_f = 0.39 (petroleum ether/ ethyl acetate = 9:1). Yield: 203.4 mg, 96%; dark red oil; $[\alpha]_D^{20}$ -372.1 (*c* 1.0, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.25-7.17 (m, 6H), 7.08-7.06 (m, 2H), 6.91 (d, *J* = 6.3 Hz, 2H), 2.22-2.19 (m, 2H), 2.08-1.90 (m, 2H), 1.16-1.09 (m, 3H), 0.94-0.82 (m, 5H), 0.70-0.60 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 228.2, 166.0, 136.1, 135.6, 133.7, 130.5, 128.8, 128.14, 128.06, 127.9, 126.4, 74.6, 38.6, 33.5, 29.6, 27.1, 22.9, 22.0, 13.8, 13.7; IR (KBr) ν 2957, 2930, 2871, 1769, 1693, 1494, 1446, 1189, 1133, 972, 761, 697 cm^{-1}; MS (EI): m/z 424 (M^+, 1.5), 174 ($Ph(C_4H_9)C{=}C{=}O^+$, 100); HRMS (EI) calcd for $C_{25}H_{28}O_2S_2$ $[M]^+$ 424.1531, found 424.1537; HPLC analysis: 96% ee [Daicel CHIRALPAK AD-H column; 20 °C; 0.5 mL/min; solvent system: 2-propanol/hexane = 1:99; retention times: 15.0 min (minor), 17.5 min (major)]

3. Chemical Transformations of Cycloadduct 3a

(4*S*,5*R*,*E*)-5-ethyl-4-(methylthio)-5-phenyl-2-(1-phenylpropylidene)-1,3-oxathian-6-one (*cis*-6)



3a **6**

99% (*cis*:*trans*= 4:1), 96% *ee* (*cis*)

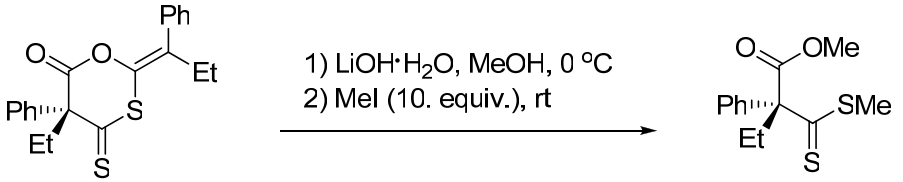
To a solution of **3a** (41.0 mg, 0.11 mmol) in toluene (1.0 mL) was added MeMgBr

(3M in ether, 0.22 mL, 0.66 mmol, 6.0 eq.) at 0 ^{o}C. The reaction mixture was stirred under N_2 for 0.5 h until TLC indicated complete consumption of the **3a**.[3] The reaction was quenched by the addition of saturated NH_4Cl (aq) (1 mL), and then diluted with CH_2Cl_2, dried over Na_2SO_4, and then passed through a short silica pad. The solution was concentrated under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether /ethyl acetate = 15:1) to give the desired product **6**. Yield: 42.0 mg, 99%. *cis*-**6**: R_f = 0.46 (*cis*), (petroleum ether/ ethyl acetate = 9:1). white solid, mp: 93-94 ^{o}C. $[\alpha]_D^{20}$ +176.4 (*c* 1.4, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51-7.48 (m, 2H), 7.35-7.22 (m, 6H), 7.10-7.07 (m, 2H), 4.55 (s, 1H), 2.40-2.32 (m, 4H), 2.30 (s, 3H), 1.04 (t, *J* = 7.4 Hz**,** 3H), 0.80 (t, *J* = 7.4 Hz**,** 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 137.5, 136.9, 136.0, 128.4, 128.1, 128.0, 127.8, 127.6, 127.1, 59.5, 54.8, 31.4, 26.9, 17.4, 12.5, 9.7; IR (KBr) ν 2968, 2930, 1758, 1494, 1444, 1188, 1118, 1077, 760, 697 cm^{-1}; MS (EI): m/z 384 (M^+, 1.8), 146 ($Ph(C_2H_5)C{=}C{=}O^+$, 100); HRMS (EI) calcd for $C_{22}H_{24}O_2S_2$ $[M]^+$ 384.1218, found 384.1221; HPLC analysis: 96% ee [Daicel CHIRALPAK AD-H column; 20 ^{o}C; 1.0 mL/min; solvent system: 2-propanol/hexane = 10:90; retention times: 10.6 min (major), 13.1 min (minor)].

trans-**6:** R_f = 0.44 (*trans*) (petroleum ether/ ethyl acetate = 9:1). colorless oil; $[\alpha]_D^{20}$ -24.8 (*c* 0.7, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.30 (m, 3H), 7.27-7.18 (m, 5H), 6.87 (d, *J* = 7.2 Hz**,** 2H), 5.08 (s, 1H), 2.40-2.27 (m, 1H), 2.34 (s, 3H), 2.16-2.03 (m, 2H), 2.10-1.91 (m, 1H), 0.64 (t, *J* = 7.5 Hz**,** 3H), 0.57 (t, *J* = 7.5 Hz**,** 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.8, 136.8, 136.5, 135.1, 128.4, 128.24, 128.16, 127.8,

127.6, 126.9, 126.6, 58.2, 52.3, 31.4, 26.9, 13.8, 12.1, 7.3; IR (KBr) ν 2969, 2932, 1760, 1494, 1445, 1250, 1117, 1075, 763, 697 cm^{-1}; MS (EI): m/z 384 (M^+, 2.1), 146 ($Ph(C_2H_5)C{=}C{=}O^+$, 100), 91 ($PhCH_2^+$, 85.7); HRMS (EI) calcd for $C_{22}H_{24}O_2S_2$ $[M]^+$ 384.1218, found 384.1222; HPLC analysis: 96% ee [Daicel CHIRALPAK AD-H column; 20 °C; 0.8 mL/min; solvent system: 2-propanol/hexane = 10:90; retention times: 9.2 min (major), 9.9 min (minor)].

(*R*)-methyl 2-(methylthiocarbonothioyl)-2-phenylbutanoate (7)

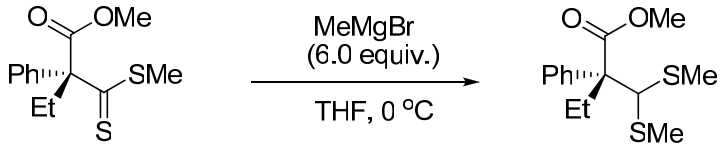


3a **7** 81%, 96% *ee*

To a solution of **3a** (87.3 mg, 0.24 mmol) in MeOH (3.8 mL) was added $LiOH{\cdot}H_2O$ (258.8 mg, 6.17 mmol) at 0 °C. After stirring at 0 °C for 25.0 min, the reaction mixture was allowed to warm to room temperature. MeI (0.15 mL, 2.37 mmol) was then added and stirred at room temperature for 1.0 h. The mixture was filtered through a short plug of silica gel and washed with ethyl acetate. The solvent was removed under reduced pressure and the residue was purified by flash chromatography on silica gel (petroleum ether) to give desired product **7.** Yield: 52.1 mg, 81%; R_f = 0.55 (petroleum ether/ ethyl acetate = 9:1). colorless oil; $[\alpha]_D^{20}$ +32.4 (*c* 1.2, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.56-7.52 (m, 2H), 7.36-7.29 (m, 3H), 3.73 (s, 3H), 2.75-2.61 (m, 2H), 2.56 (m, 3H), 0.92 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 238.9, 171.6, 138.7, 129.0, 127.8, 127.7, 74.3, 52.5, 32.2, 20.6, 10.0; IR (KBr) ν

2968, 2948, 1738, 1446, 1226, 1073, 985, 699 cm^{-1}; MS (EI): m/z 268 (M^+, 18.2), 121 ($PhC_3H_7^+$, 100), 91 ($PhCH_2^+$, 75.0); HRMS (EI) calcd for $C_{13}H_{16}O_2S_2$ $[M]^+$ 268.0592, found 268.0595; HPLC analysis: 96% ee [Daicel CHIRALPAK OD-H column; 20 °C; 1.0 mL/min; solvent system: 2-propanol/hexane = 2:98; retention times: 8.2 min (minor), 9.4 min (major)]**.**

(*R*)-methyl 2-(bis(methylthio)methyl)-2-phenylbutanoate (8)

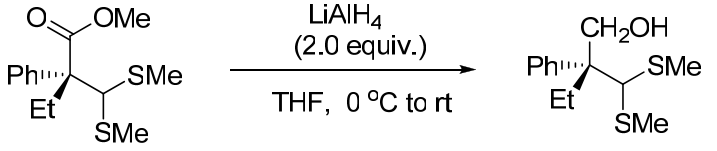


7 81%, 96% *ee* **8** 73%, 96% *ee*

To a solution of **7** (89.1 mg, 0.33 mmol) in THF (3.3 mL) was added MeMgBr (3M in ether) (0.66 mL, 1.98 mmol, 6.0 eq.) at 0 °C. The reaction mixture was stirred at 0 °C for 15.0 min until TLC indicated complete consumption of **7**. The reaction was quenched by the addition of saturated NH_4Cl (aq) (3.3 mL), and then diluted with ethyl acetate, dried over Na_2SO_4, and then passed through a short silica pad. The solution was concentrated under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether/Et_2O = 90:1) to give the desired product **8**. Yield: 68.5 mg (73%); R_f = 0.52 (petroleum ether/ ethyl acetate = 9:1). Colorless oil; $[\alpha]_D^{20}$ +8.18 (*c* 0.6, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.39-7.36 (m, 2H), 7.24-7.20 (m, 3H), 4.20 (s, 1H), 3.70 (s, 3H), 2.46-2.36 (m, 1H), 2.31-2.17 (m, 1H), 1.79 (s, 3H), 1.77 (s, 3H), 0.83 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 174.0, 136.9, 129.2, 127.4, 127.3, 62.7, 62.0, 52.0, 29.6, 15.3, 14.7, 9.5; IR (KBr) ν 2963, 2918, 2853, 1734, 1435, 1260, 1222, 1123, 1011, 798, 700 cm^{-1}; MS

(EI): m/z 284 (M^+, 22.6), 108 ($(CH_3S)_2CH_2^+$, 100), 91 ($PhCH_2^+$, 57.7); HRMS (EI) calcd for $C_{14}H_{20}O_2S_2$ $[M]^+$ 284.0905, found 284.0908; HPLC analysis: 96% ee [Daicel CHIRALPAK OD-H column; 20 °C; 0.5 mL/min; solvent system: 2-propanol/hexane = 2:98; retention times: 10.8 min (minor), 11.2 min (major)].

(*R*)-2-(bis(methylthio)methyl)-2-phenylbutan-1-ol (9)

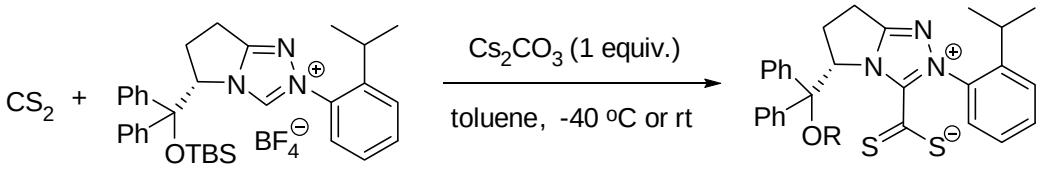


8 73%, 96% *ee* **9** 92%, 96% *ee*

To a solution of **8** (40.0 mg, 0.14 mmol) in THF (1.4 mL) was added $LiAlH_4$ (10.7 mg, 0.28 mmol) at 0 °C.[4] After addition, the reaction mixture was allowed to warm to room temperature, and stirred for 1.0 h until TLC indicated complete consumption of **8**. The reaction was quenched by the addition of saturated NH_4Cl (aq) (1.4 mL), then diluted with ethyl acetate, dried over Na_2SO_4, and then passed through a short silica pad. The solution was concentrated under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether/ ethyl acetate = 9:1) to give the desired product **9**. Yield: 33.0 mg, 92%; R_f = 0.20 (petroleum ether/ ethyl acetate = 9:1). colorless oil; $[\alpha]_D^{20}$ +21.5 (*c* 0.6, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.26-7.21 (m, 1H), 4.40-4.34 (m, 1H), 4.07-4.01 (m, 1H), 3.90 (s, 1H), 2.33-2.24 (m, 2H), 2.07-1.97 (m, 1H), 2.02 (s, 3H), 1.82 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 141.3, 128.0, 127.8, 126.7, 66.5, 66.0, 51.6, 25.9, 16.3, 16.2, 8.6; IR (KBr) ν 3861, 2967, 2917, 1499, 1444, 1419, 1044, 761, 699, 604 cm^{-1}; MS (EI): m/z 256 (M^+, 2.4), 178 (M^+−

C_6H_6, 100); HRMS (EI) calcd for $C_{13}H_{20}OS_2$ $[M]^+$ 256.0956, found 256.0953; HPLC analysis: 96% ee [Daicel CHIRALPAK AS-H column; 20 °C; 1.0 mL/min; solvent system: 2-propanol/hexane = 2:98; retention times: 19.6 min (minor), 21.1 min (major)].

4. Control Experiments of Mechanism Investigation



4b **10**

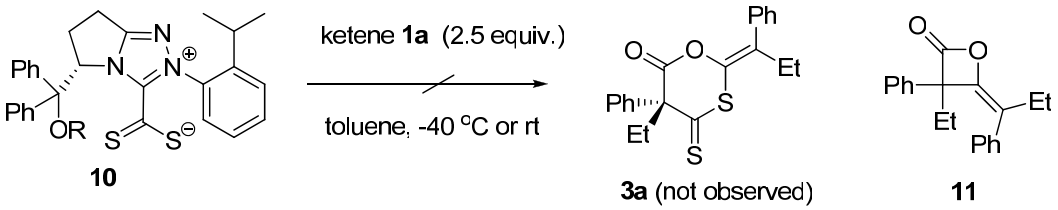
No reaction at -40 °C
33% of **10** at rt

To an oven-dried 50 mL reaction tube containing a stir bar was added NHC precursor **4b** (1223.2 mg, 2.0 mmol) and Cs_2CO_3 (651.6 mg, 2.0 mmol) and toluene (40 mL). The reaction mixture was stirred under N_2 for 1.0 h at room temperature, and then cooled to -40 °C (or kept at room temperature). Carbon disulfide **2** (152.8 mg, 2.0 mmol) was then added via a syringe at -40 °C (or room temperature).

For the reaction at -40 °C: TLC analysis revealed that no reaction occurred after the reaction mixture was stirred at -40 °C for 45 h.

For the reaction at room temperature: After stirring for 1.0 h, the reaction mixture could turn red. The reaction mixture was further stirred for 37.0 h, then diluted with CH_2Cl_2, filtered through a pad of silica gel and washed with CH_2Cl_2. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether/ ethyl acetate = 10:1) to give adduct **10.** R_f = 0.49

(petroleum ether/EtOH = 10:1). Yield: 398.1 mg, 33%; red solid; $[\alpha]_D^{20}$ -1238.0 (*c* 0.15, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$) δ 7.47-7.45 (m, 4H), 7.33-7.15 (m, 9H), 7.04-7.02 (m, 1H), 5.82 (d, *J* = 8.5 Hz, 1H), 3.20-3.13 (m, 1H), 2.90-2.83 (m, 1H), 2.71-2.67 (m, 1H), 2.36-2.27 (m, 1H), 1.18-1.10 (m, 7H), 0.90 (s, 9H), -0.50 (s, 3H), -0.57 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 217.9, 158.9, 151.2, 145.4, 139.1, 138.4, 133.2, 131.1, 129.3, 129.2, 128.3, 128.1, 128.0, 127.4, 126.5, 126.0, 81.4, 64.5, 30.0, 28.2, 26.0, 23.9, 22.7, 19.9, 18.6, -3.7, -3.9; IR (KBr) ν 2959, 2928, 2856, 1598, 1473, 1454, 1426, 1259, 1067, 1028, 887, 836, 764, 750, 698 cm^{-1}; MS (ESI): m/z 600 ($[M+H]^+$, 100); HRMS (P-SIMS) calcd for $C_{34}H_{41}N_3OS_2Si$ $[M+H]^+$ 600.2523, found 600.2523.



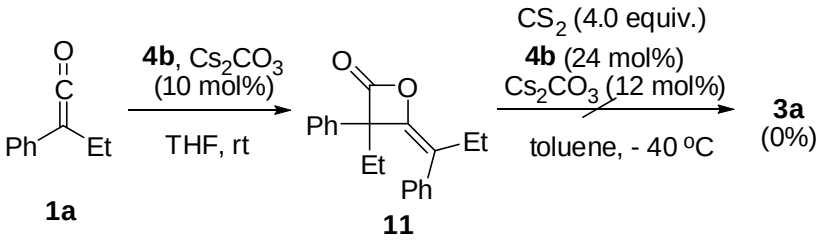
No reaction at -40 °C
74% recover of **10**, puls 48% of ketene dimer **11** at rt

To an oven-dried 50 mL reaction tube containing NHC-CS_2 adduct **10** (119.8 mg, 0.2 mmol) and toluene (2.5 mL) was added ketene **1a** (73.0 mg, 0.5 mmol) at -40 °C or room temperature.

For reaction at -40 °C: TLC analysis revealed that no reaction occurred after the reaction mixture was stirred at -40 °C for 13.5 h.

For reaction at room temperature: The reaction mixture was stirred at room temperature for 24.0 h, it was diluted with CH_2Cl_2, then filtered through a pad of silica gel and washed with CH_2Cl_2. The solvent was removed under reduced pressure

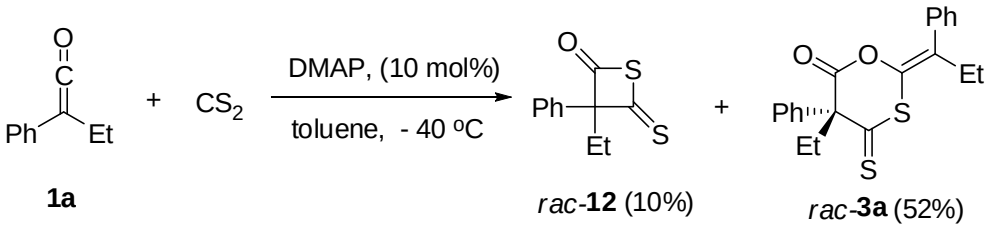
and the residue was purified by chromatography on silica gel to give 34.8 mg (47.6%) of the ketene dimer **11**[1g] and 88.1 mg (74%) of recovered adduct **10**.



To the solution of NHC **4b'**, which was freshly prepared from NHC **4b** precursor (122.3 mg, 0.20 mmol), Cs_2CO_3 (65.2mg, 0.20 mmol) and THF (8 mL) at rt for 1.0 h, was added ketene **1a** (292.0 mg, 2.0 mmol) and the reaction mixture was stirred at room temperature for 3.5 h. Then it was quenched by the addition of silica gel, the mixture was further stirred for five minutes. The reaction mixture was diluted with ethyl acetate, then filtered through a pad of silica gel and washed with ethyl acetate. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether/Et_2O = 100:1) to give 172.7 mg (59.14%) of the ketene dimer **11.**[1g]

To an oven-dried 50 mL reaction tube containing a stir bar was added NHC precursor **4b** (41.5 mg, 0.07 mmol), Cs_2CO_3 (18.4 mg, 0.06 mmol) and toluene (5 mL). The reaction mixture was stirred under N_2 for 1.0 h at room temperature, and then cooled to -40 ^oC directly. Carbon disulfide **2** (86.3 mg, 1.13 mmol) and ketene dimer **11** (81.8 mg, 0.28 mmol) were added. After stirring at -40 ^oC for 9.5 h, the reaction mixture was quenched by the addition of silica gel, diluted with ethyl acetate, then filtered through a pad of silica gel. The solvent was removed under reduced

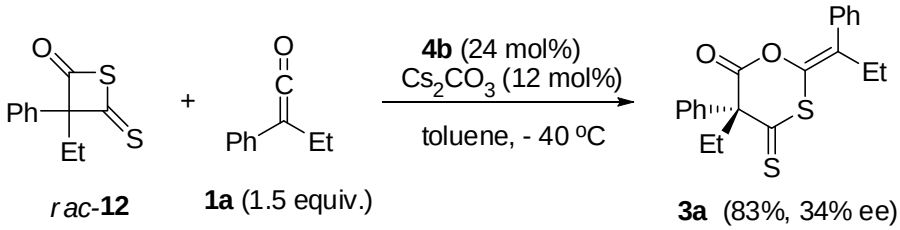
pressure to give oil. TLC and ^{1}H NMR analysis revealed that no reaction occurred but the ketene dimmer **11** was recovered.



1a *rac*-**12** (10%) *rac*-**3a** (52%)

To an oven-dried 50 mL reaction tube containing a stir bar was added DMAP (3.67 mg, 0.30 mmol) and toluene (4.5 mL). The reaction mixture was then cooled to -40 °C directly and carbon disulfide **2** (2.29 g, 30.0 mmol) was then added. Ketene **1a** (438.0 mg, 3.0 mmol) was added via a syringe pump over 3.0 h**.** After stirring room temperature for 0.5 h, the reaction was quenched by the addition of silica gel, diluted with ethyl acetate, filtered through a pad of silica gel and washed with ethyl acetate. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel (petroleum ether/Et_2O = 150:1) to give 65.2 mg (10%) of [2 + 2] cycloadduct **12** and 287.9 mg (52 %) of [2 + 2 + 2] cycloadduct **3a**.

3-ethyl-3-phenyl-4-thioxothietan-2-one (12). R_f = 0.29 (petroleum ether/Et_2O = 90:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.59-7.55 (m, 2H), 7.40-7.31 (m, 3H), 2.38-2.17 (m, 2H), 1.11 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 228.2, 188.2, 135.0, 128.9, 128.6, 125.3, 102.1, 31.8, 9.2; IR (KBr) ν 1793, 1541, 1507, 1457, 1221, 756, 694 cm^{-1}; MS (EI): m/z 222 (M^+, 1.2), 146 ($Ph(C_2H_5)C{=}C{=}O^+$, 100); HRMS (EI) calcd for $C_{11}H_{10}OS_2$ $[M]^+$ 222.0173, found 222.0169.



To an oven-dried 50 mL reaction tube containing a stir bar was added NHC precursor **4b** (14.7 mg, 0.024 mmol) and Cs_2CO_3 (6.5 mg, 0.02 mmol) and toluene (1.5 mL). The reaction mixture was stirred under N_2 for 1.0 h at room temperature. The reaction mixture was cooled to -40 ^oC and then added cycloadduct **12** (22.1 mg, 0.1 mmol) and ketene **1a** (21.9 mg, 0.15 mol). After stirring at -40 ^oC for 9.0 h, the reaction mixture was quenched by silica gel, diluted with ethyl acetate, and then filtered through a pad of silica gel. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel to give 30.2 mg (82.5%, 34% ee) of the cycloadduct **3a.**

5 Determination of the relative and absolute configurations

(1) X-Ray Crystal Structure of Racemic Sample of 4-thioxo-1,3-oxathian-6-one 3h

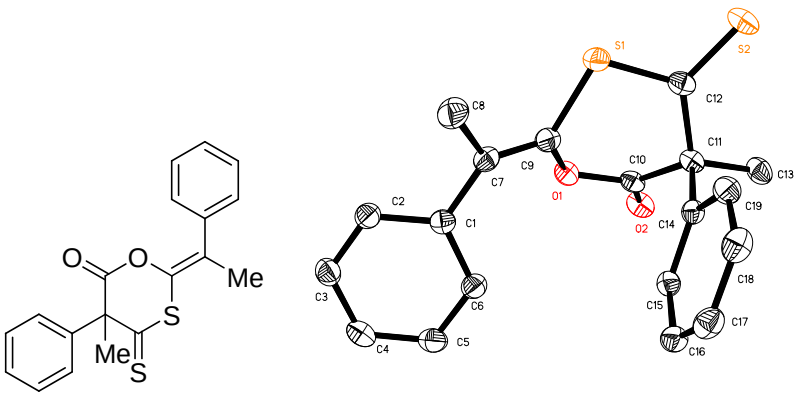
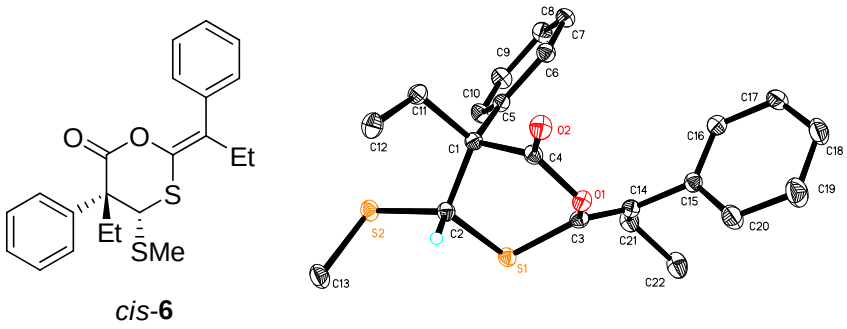


Figure S1. X-ray crystal structure of *rac*-**3h**

The crystal of *rac*-**3h** was obtained by slow evaporation of the solution of racemic sample of **3h** in petroleum ether/Et_2O (120:1) at room temperature. It is necessary to note that the preparation of the suitable crystal of (-)-**3h** for X-ray failed by the same way as *rac*-3h.

A dark red crystal of approximate dimensions 0.50 x 0.44 x 0.40 mm was mounted on a glass fiber and *trans*ferred to a Rigaku Raxis Rapid-IP diffractometer. The Rigaku data-collection program was used to determine the unit cell parameters. The data were collected at room temperature. The raw frame data were processed using Rigaku data-processing program. The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques.

(2) X-Ray Crystal Structure of 1,3-oxathian-6-one (+)-*cis*-6



cis-**6**

Figure S2. X-ray crystal structure of (+)-*cis*-**6**

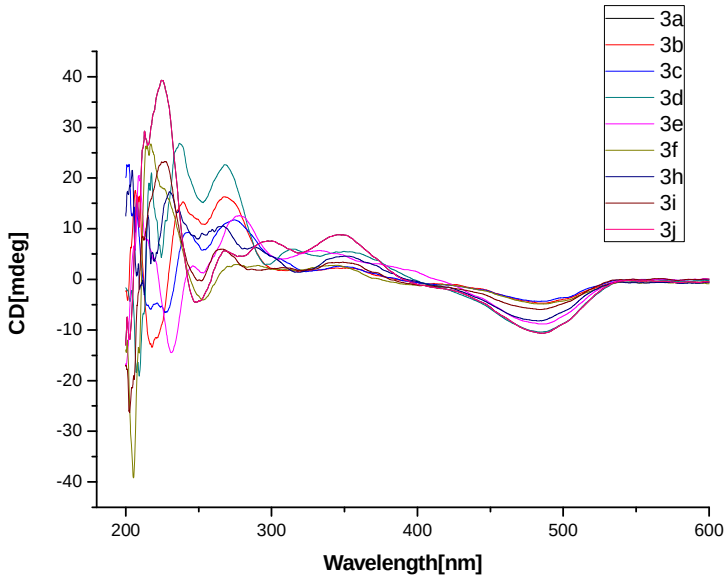
The absolute configuration of the *4S,5R*-(+)-*cis*-**6** was determined by X-ray. The crystal was obtained by slow evaporation of the solution of *cis*-**6** in petroleum ether/ CH_2Cl_2 (5:1) at room temperature.

A colorless crystal of approximate dimensions 0.40 x 0.35 x 0.25 mm was mounted on a glass fiber and *trans*ferred to a Rigaku Raxis Rapid-IP diffractometer. The

Rigaku data-collection program was used to determine the unit cell parameters. The data were collected at room temperature. The raw frame data were processed using Rigaku data-processing program. The structure was solved by direct methods and refined on F2 by full-matrix least-squares techniques. The absolute structure was determined from the Flack parameter, which is 0.02(5).

(3) CD Spectra of 4-thioxo-1,3-oxathian-6-ones 3a-3j

The CD spectra of **3a-3j** were recorded, which showed **3a-3j** have the same absolute configuration (Figure S3).



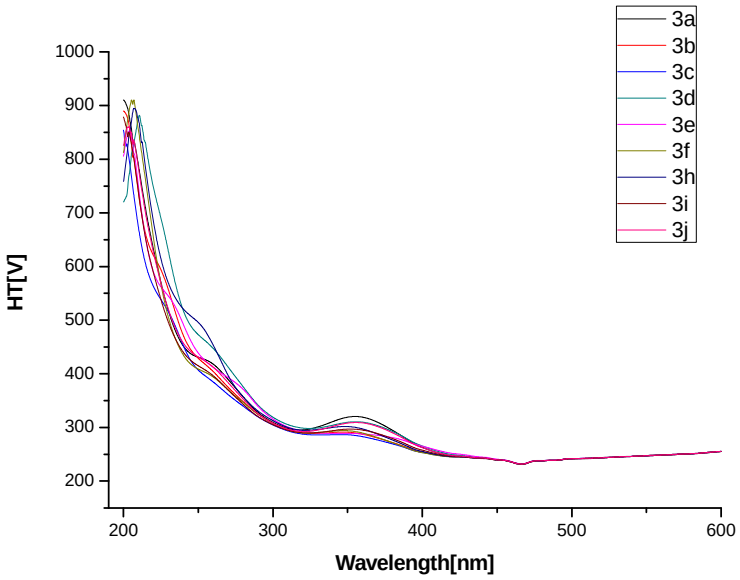


Figure S3. CD Spectra of 3a-3j

References and notes:

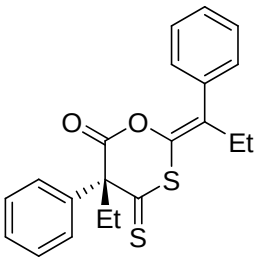
(1) (a) Y.-R. Zhang, L. He, X. Wu, P.-L. Shao and S. Ye, *Org. Lett.* 2008, **10**, 277-280; (b) X.-N. Wang, H. Lv and S. Ye, *Org. Lett.* 2009, **11**, 4029-4031; (c) P.-L. Shao, X.-Y. Chen and S. Ye, *Angew. Chem. Int. Ed.* 2010, **49**, 8412-8416; (d) L.-T. Shen, P.-L. Shao and S. Ye, *Adv. Synth. Catal. doi:* 10.1002/adsc.201100178; (e) L. He, Y.-R. Zhang, X.-L. Huang and S. Ye, *Synthesis.* 2008, 2825-2829; (f) M. S. Kerr and R. D. Alaniz, *J. Org. Chem.* 2005, **70**, 5725-5728; (g) H. Lv, Y.-R. Zhang, X.-L. Huang and S. Ye, *Adv. Synth. Catal.* 2008, **350**, 2715-2718.

(2) (a) L. M. Baigrie, H. R. Seiklay and T. T. Tidwelll, *J. Am. Chem. Soc.* 1985, **107**, 5391-5396; (b) A. D. Allen, L. M. Baigrie, L. Gong and T. T. Tidwelll, *Can. J. Chem.* 1991, **69**, 138-145.

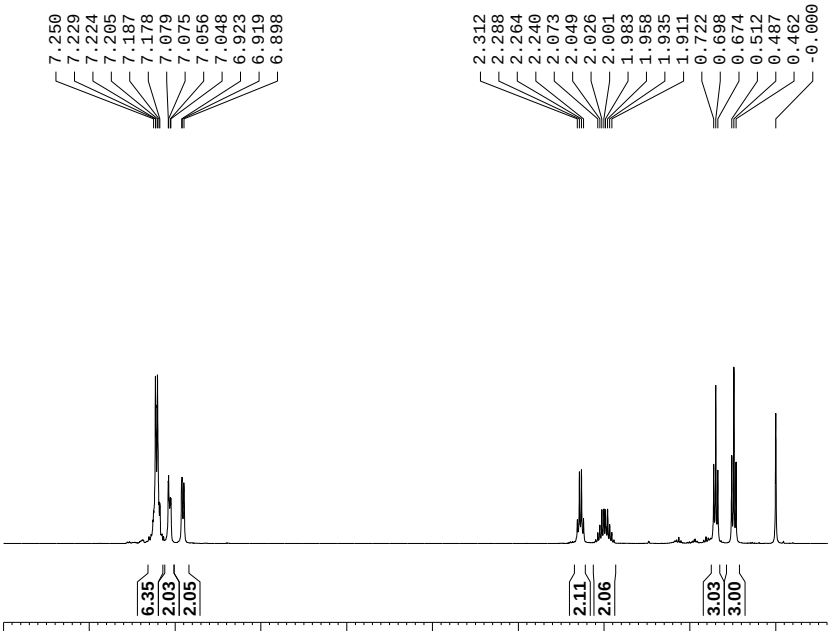
(3) This procedure is based on a literature synthesis of a related compound：C. Schaefer and G.. C. Fu, *Angew. Chem., Int. Ed*. 2005, **44**, 4606-4608.

(4) This procedure is based on a reported synthesis of a related compound：J. C. Wilson and G. C. Fu, *Angew. Chem., Int. Ed.* 2004, **43**, 6358-6360.

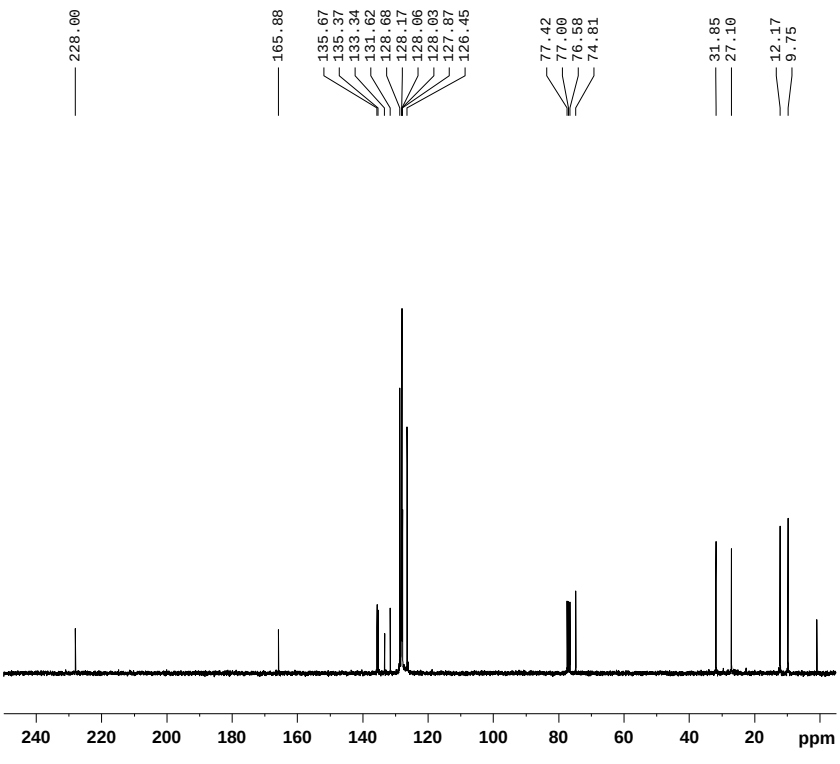
Part II ^{1}H NMR and ^{13}C NMR Spectra



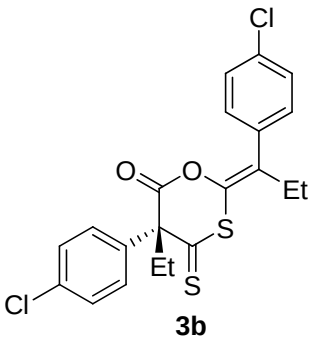
3a



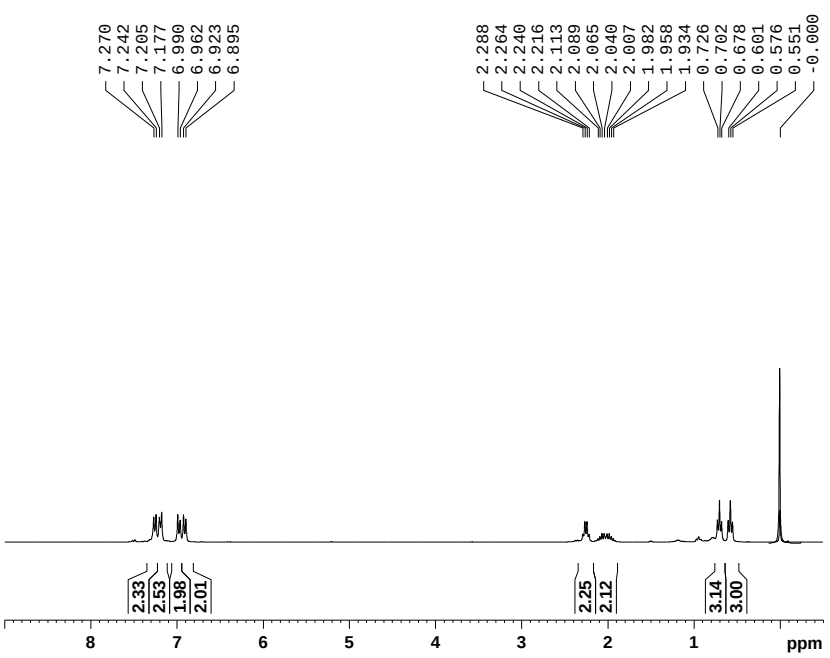

```
Current Data Parameters
NAME          wxn372-b-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100320
Time               16.45
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ            3.6438515 sec
RG                  35.9
DW                55.600 usec
DE                 8.00 usec
TE                295.4 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300435 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



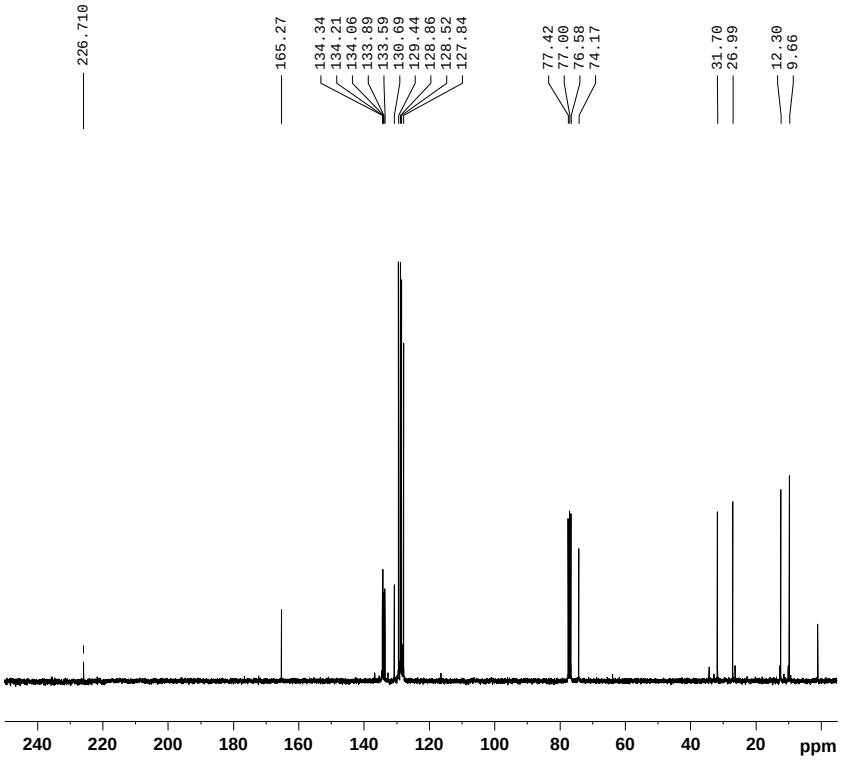

```
Current Data Parameters
NAME          wxn430-a-1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110411
Time               8.35
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   135
DS                     4
SWH            30120.482 Hz
FIDRES          0.459602 Hz
AQ            1.0879476 sec
RG                2580.3
DW                16.600 usec
DE                 6.50 usec
TE                297.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4768051 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677610 MHz
WDW                   EM
```



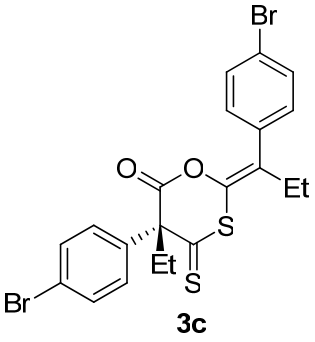
3b



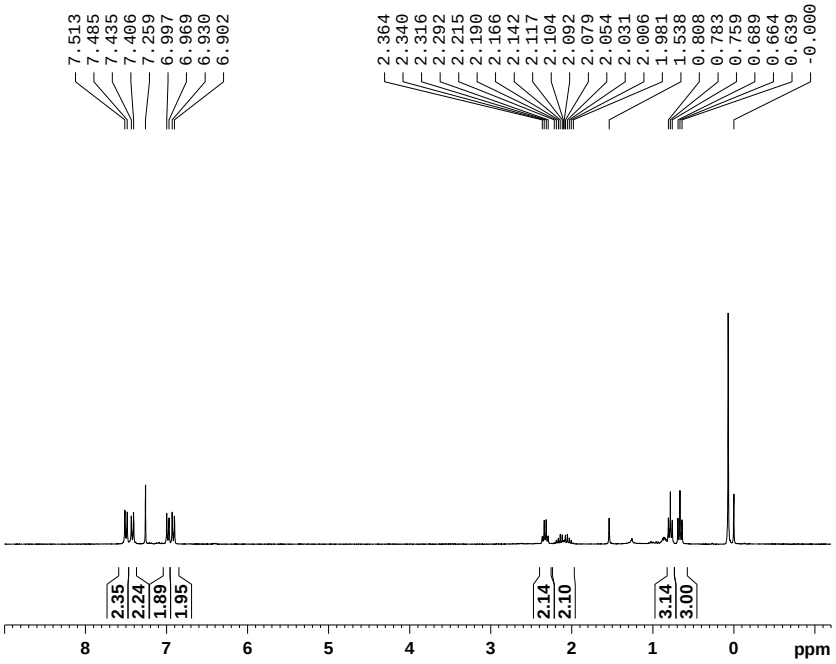

```
Current Data Parameters
NAME         wxn390-1(1)
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100410
Time               17.20
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ            3.6438515 sec
RG                    64
DW               55.600 usec
DE                8.00 usec
TE                298.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300310 MHz
WDW                   EM
SSB                    0
LB                0.30 Hz
GB                     0
PC                1.00
```



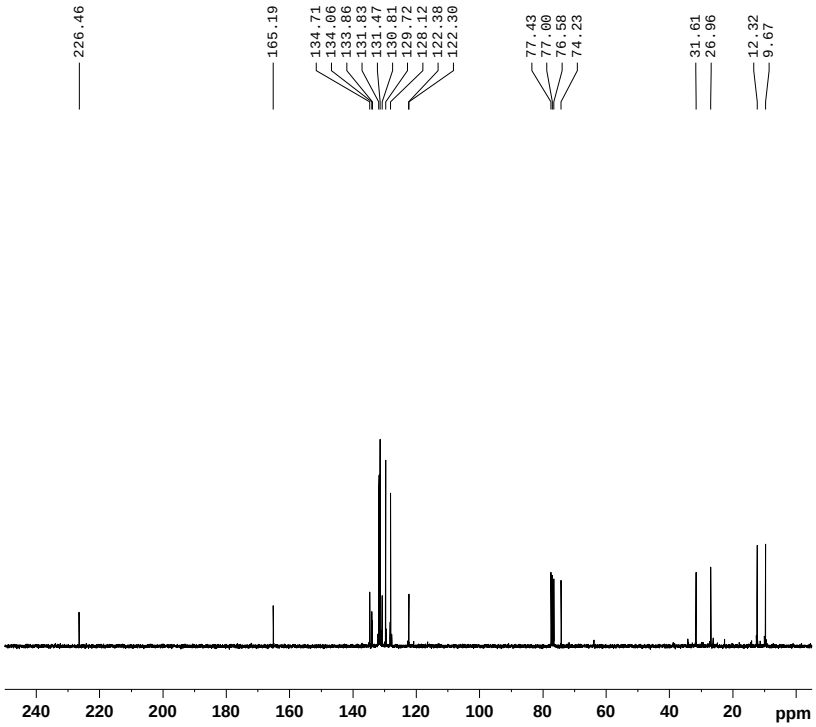

```
Current Data Parameters
NAME         wxn390-1(1)
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100410
Time               17.24
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   304
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                5792.6
DW               27.800 usec
DE                8.00 usec
TE                298.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677556 MHz
WDW                   EM
```



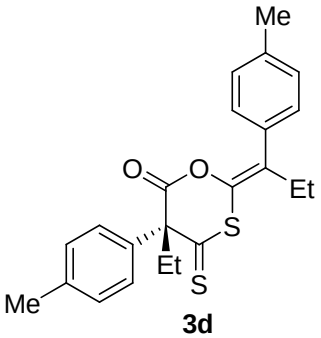
3c



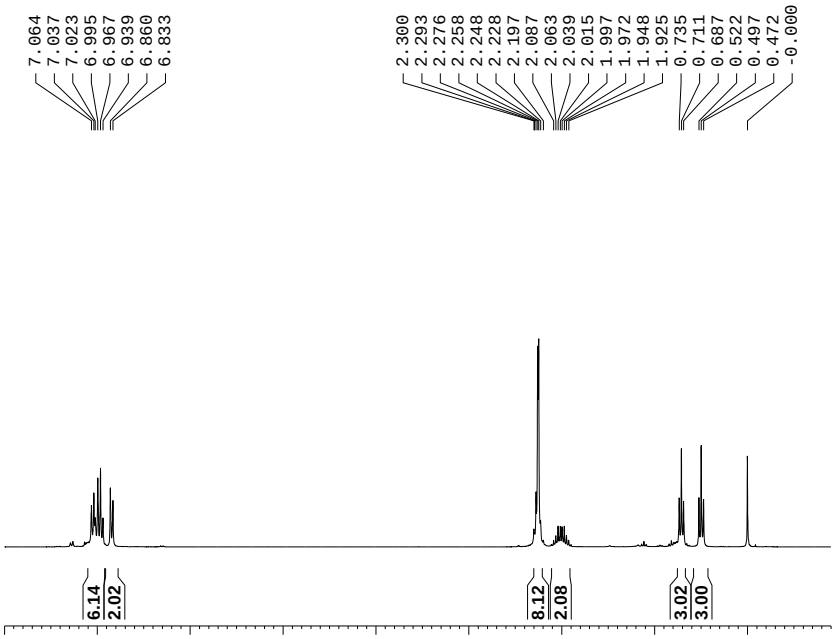

```
Current Data Parameters
NAME            wxn391-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100410
Time               16.36
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                 574.7
DW                55.600 usec
DE                 8.00 usec
TE                298.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300061 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



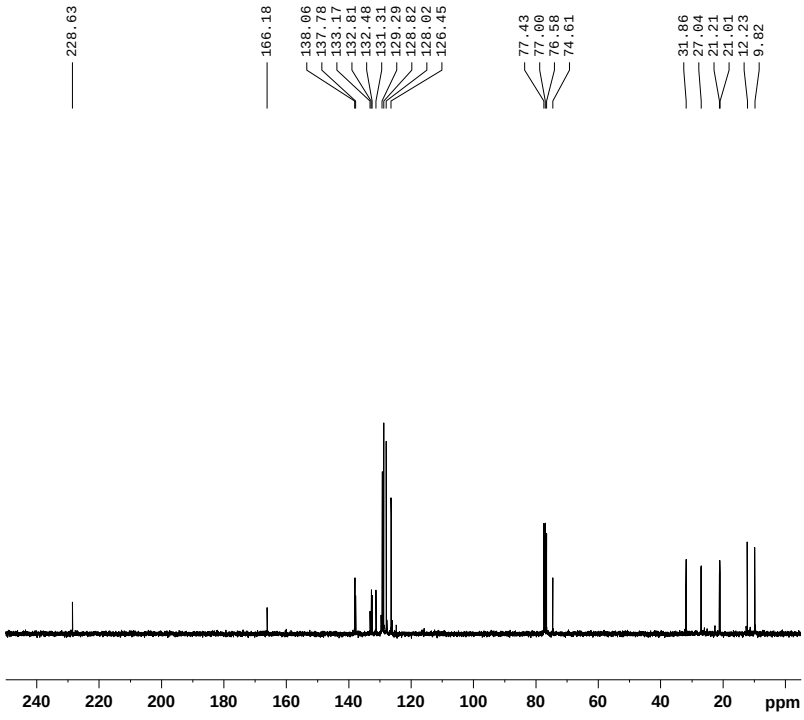

```
Current Data Parameters
NAME      wxn391-1 391-2
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameter
Date_           20110411
Time               8.56
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   102
DS                     4
SWH            30120.482 H
FIDRES          0.459602 H
AQ              1.0879476 s
RG                 456.1
DW                16.600 u
DE                 6.50 u
TE                297.8 K
D1           2.00000000 s
D11          0.03000000 s
TD0                    1

======== CHANNEL f1 =====
NUC1                 13C
P1                12.50 u
PL1                2.00 d
SFO1         75.4768051 M

======== CHANNEL f2 =====
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 u
PL2                3.00 d
PL12              22.33 d
PL13              23.00 d
SFO2         300.1312005 M

F2 - Processing parameter
SI                 32768
SF           75.4677563 M
WDW                   EM
```



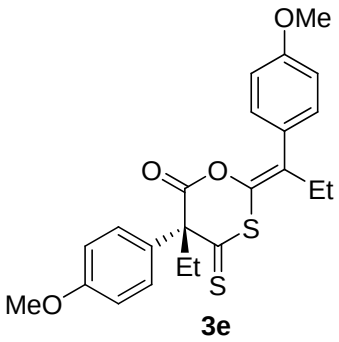
3d



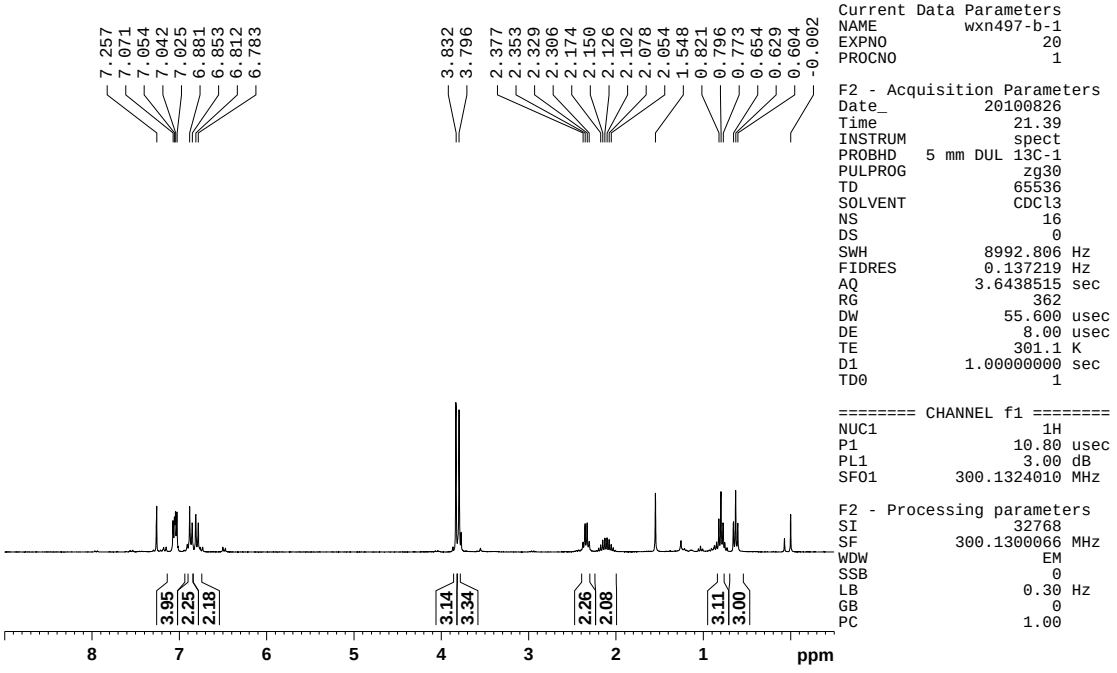

```
Current Data Parameters
NAME          wxn399-a-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100424
Time               18.33
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                  35.9
DW                55.600 usec
DE                 8.00 usec
TE                299.9 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300425 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



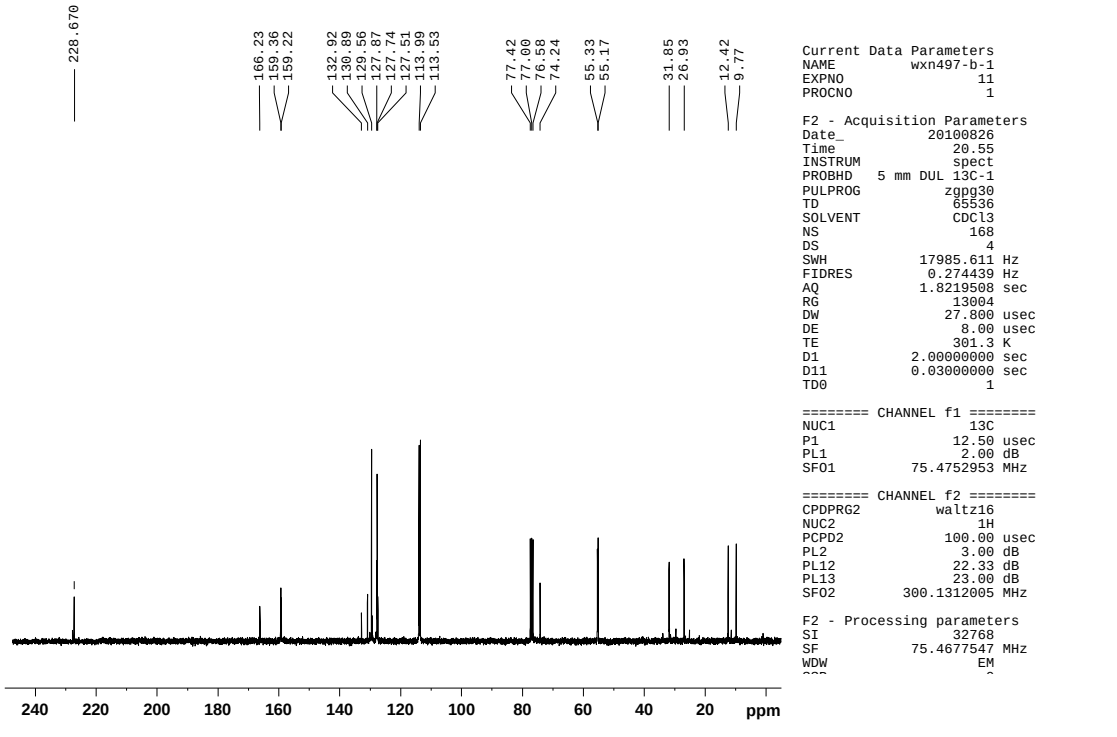

```
Current Data Parameters
NAME          wxn399-a-1
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110411
Time                8.43
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   121
DS                     4
SWH            30120.482 Hz
FIDRES          0.459602 Hz
AQ              1.0879476 sec
RG                 812.7
DW                16.600 usec
DE                 6.50 usec
TE                297.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4768051 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677543 MHz
WDW                   EM
```



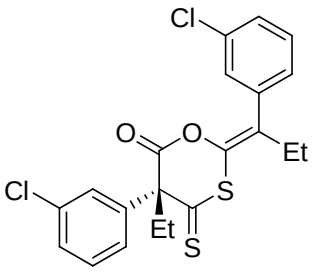
3e



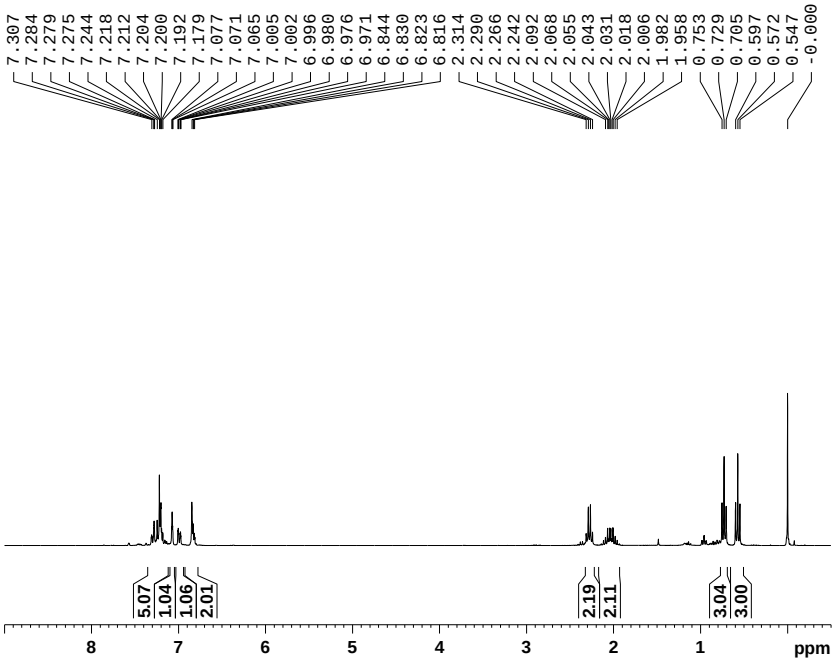

```
Current Data Parameters
NAME          wxn497-b-1
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100826
Time               21.39
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                   362
DW                55.600 usec
DE                 8.00 usec
TE                301.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300066 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



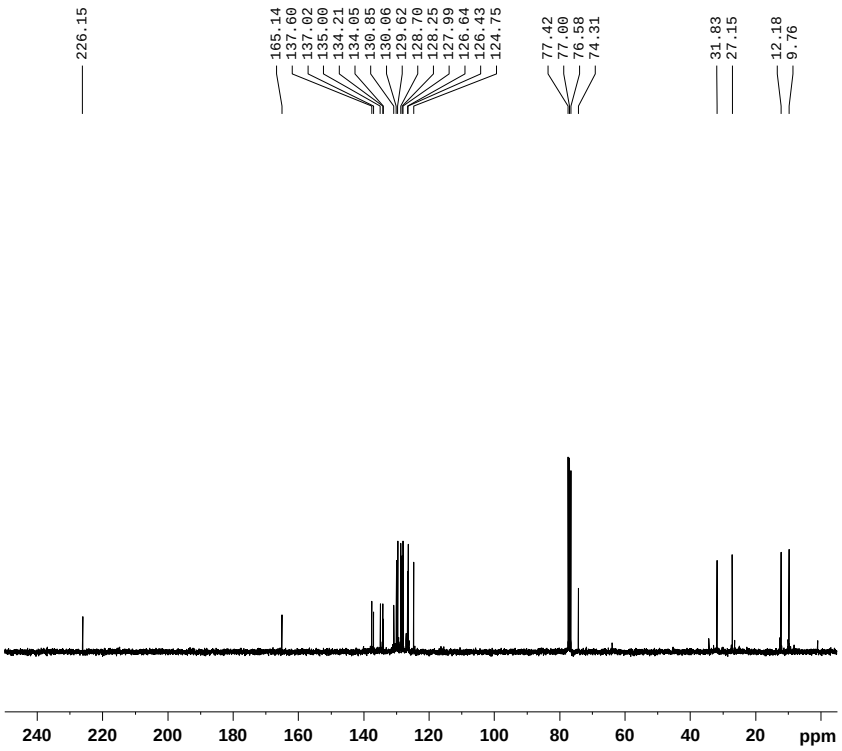

```
Current Data Parameters
NAME          wxn497-b-1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100826
Time               20.55
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   168
DS                     4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                 13004
DW                27.800 usec
DE                 8.00 usec
TE                301.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677547 MHz
WDW                   EM
```



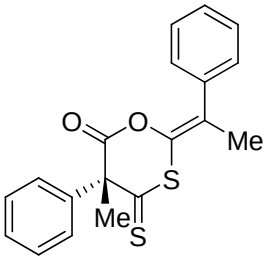
3f



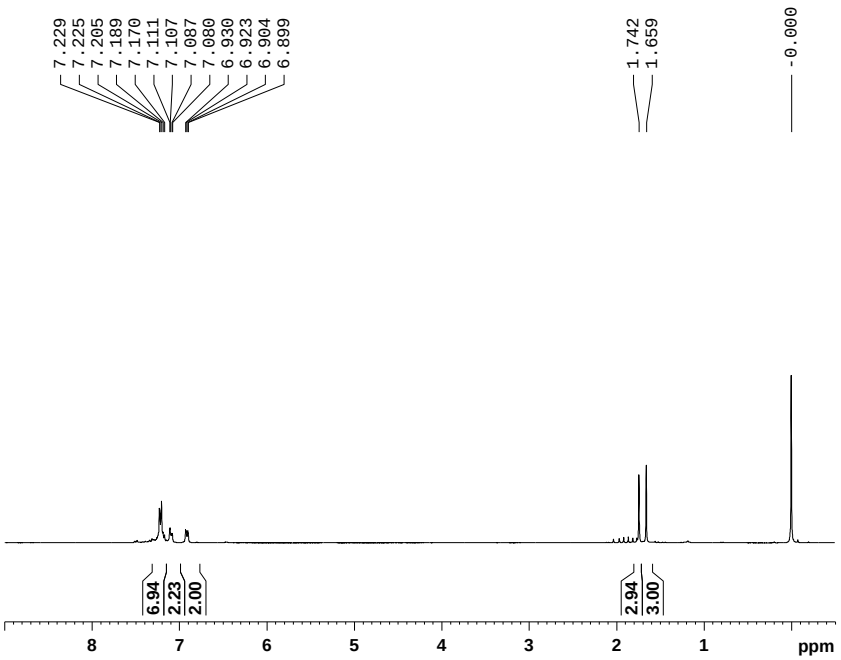

```
Current Data Parameters
NAME          wxn400-b-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100424
Time               19.02
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                299.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300304 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



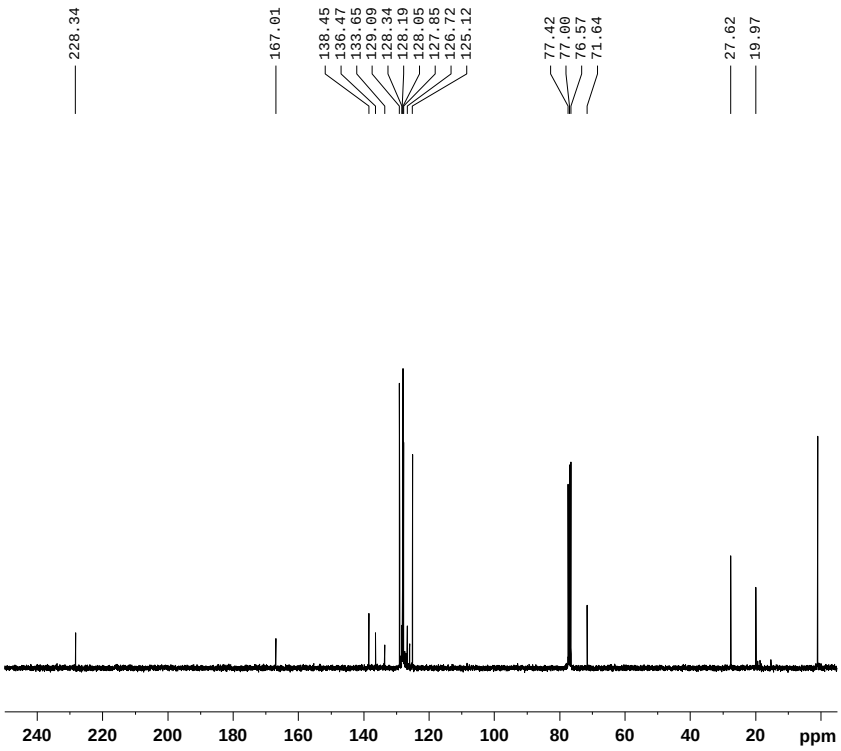

```
Current Data Parameters
NAME          wxn400-b-1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110411
Time               9.06
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   201
DS                     4
SWH            22675.736 Hz
FIDRES          0.346004 Hz
AQ              1.4451188 sec
RG                 456.1
DW                22.050 usec
DE                 6.50 usec
TE                297.5 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4768051 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677531 MHz
WDW                   EM
```



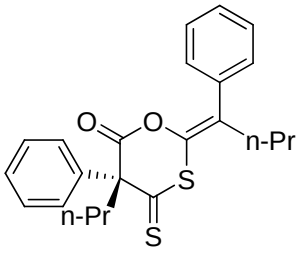
3h



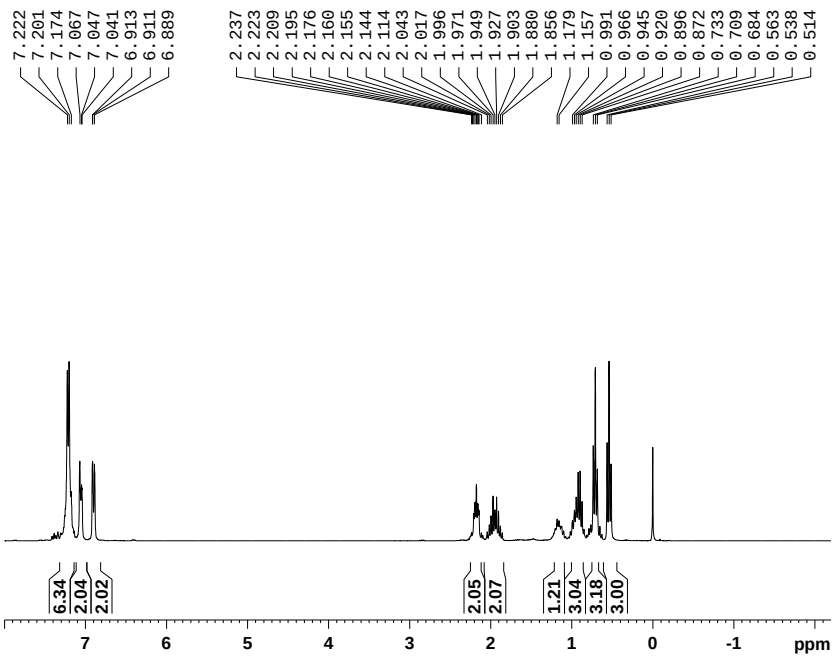

```
Current Data Parameters
NAME          wxn393-b-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110411
Time                7.58
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ            3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                297.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300330 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



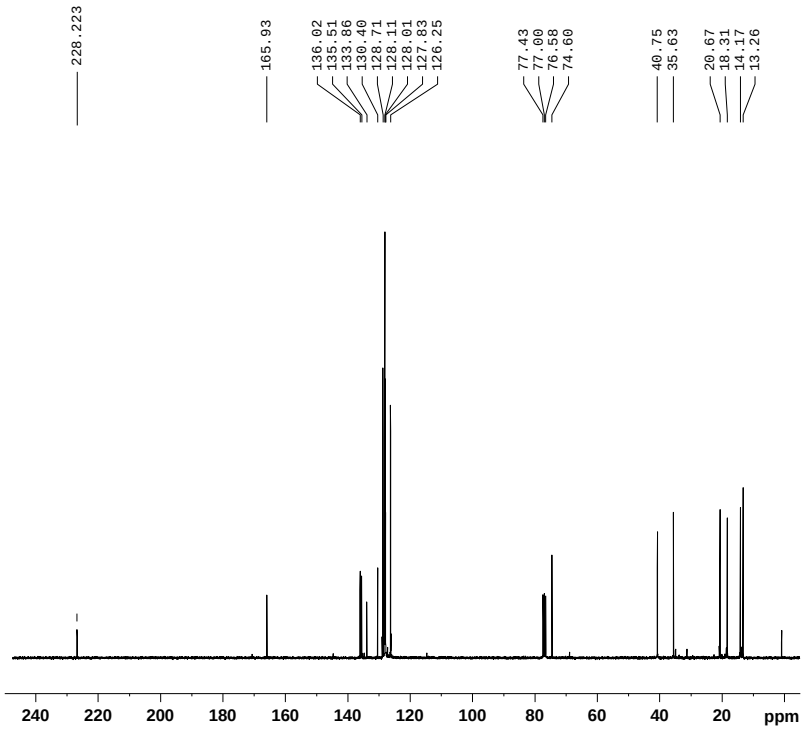

```
Current Data Parameters
NAME          wxn393-b-1
EXPNO                 14
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110411
Time                8.07
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   326
DS                     4
SWH            30120.482 Hz
FIDRES          0.459602 Hz
AQ             1.0879476 sec
RG                   512
DW                16.600 usec
DE                 6.50 usec
TE                297.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4768051 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677534 MHz
WDW                   EM
```



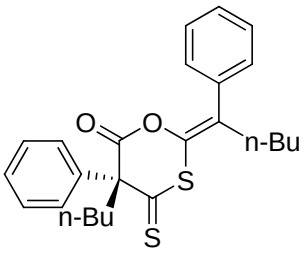
3i



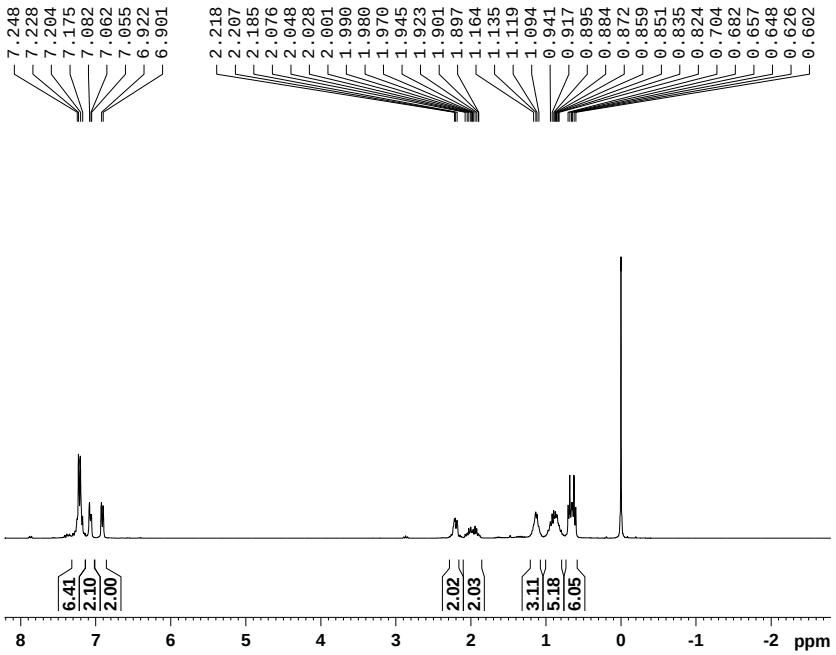

```
Current Data Parameters
NAME          wxn388-a-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100410
Time               16.41
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                    32
DW                55.600 usec
DE                 8.00 usec
TE                298.1 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300433 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



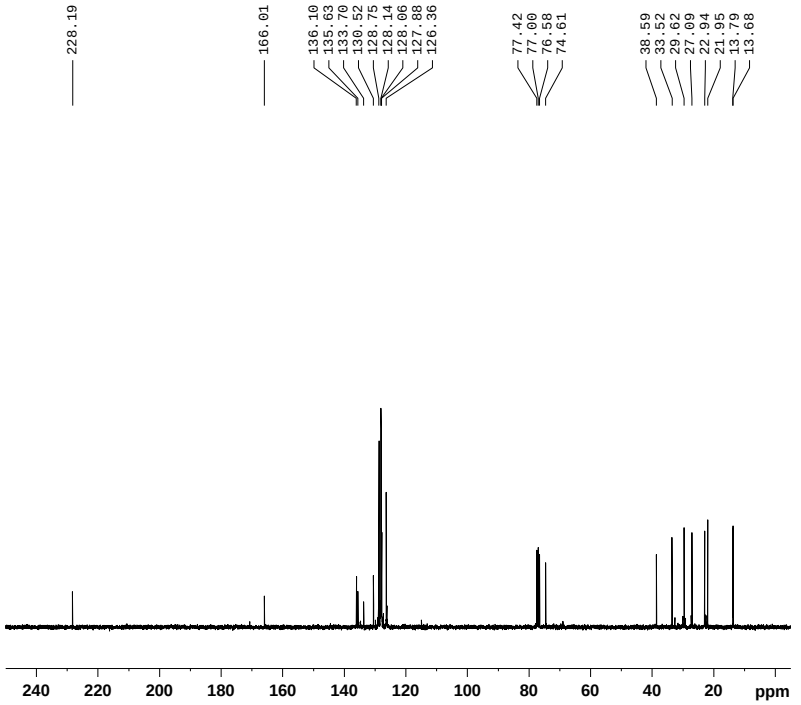

```
Current Data Parameters
NAME      wxn388-a-1(1)
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_           20100410
Time               16.48
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   201
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ             1.8219508 sec
RG                 16384
DW                27.800 usec
DE                 8.00 usec
TE                298.6 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12               22.33 dB
PL13               23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677619 MHz
WDW                   EM
```



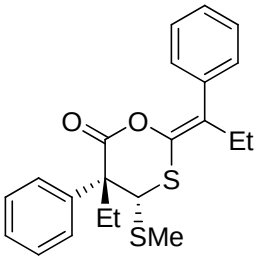
3j



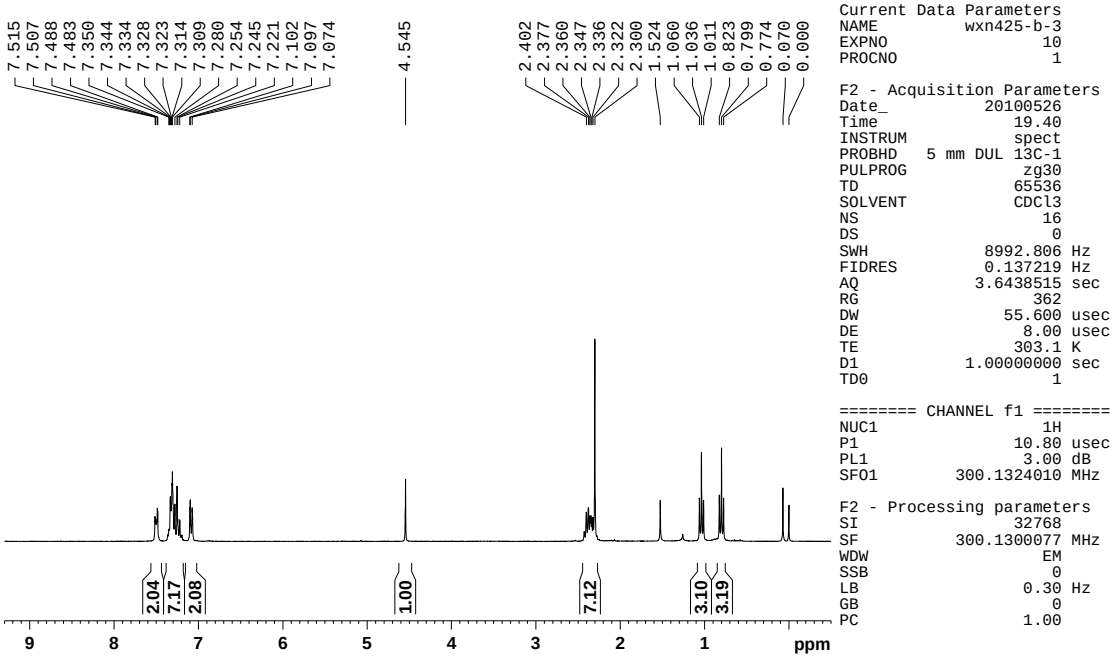

```
Current Data Parameters
NAME            wxn401-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100424
Time               17.37
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                    32
DW                55.600 usec
DE                 8.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300433 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```




```
Current Data Parameters
NAME         wxn396-a-1
EXPNO                11
PROCNO                1

F2 - Acquisition Parameters
Date_          20110411
Time               7.48
INSTRUM           spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                   97
DS                    4
SWH           30120.482 Hz
FIDRES         0.459602 Hz
AQ            1.0879476 sec
RG                812.7
DW               16.600 usec
DE                6.50 usec
TE               297.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 13C
P1               12.50 usec
PL1               2.00 dB
SFO1         75.4768051 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2           100.00 usec
PL2               3.00 dB
PL12             22.33 dB
PL13             23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677562 MHz
WDW                   EM
```



cis-**6**

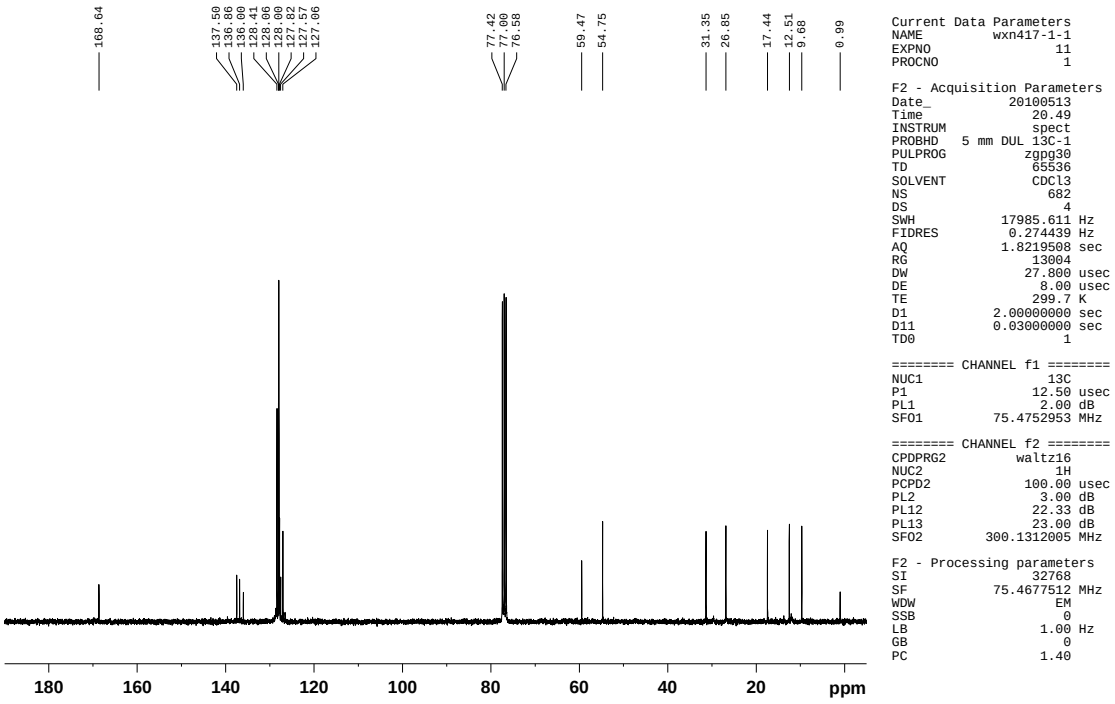


Current Data Parameters
NAME wxn425-b-3
EXPNO 10
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100526
Time 19.40
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 0
SWH 8992.806 Hz
FIDRES 0.137219 Hz
AQ 3.6438515 sec
RG 362
DW 55.600 usec
DE 8.00 usec
TE 303.1 K
D1 1.00000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 1H
P1 10.80 usec
PL1 3.00 dB
SFO1 300.1324010 MHz

F2 - Processing parameters
SI 32768
SF 300.1300077 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



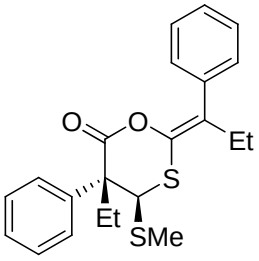
Current Data Parameters
NAME wxn417-1-1
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20100513
Time 20.49
INSTRUM spect
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 682
DS 4
SWH 17985.611 Hz
FIDRES 0.274439 Hz
AQ 1.8219508 sec
RG 13004
DW 27.800 usec
DE 8.00 usec
TE 299.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

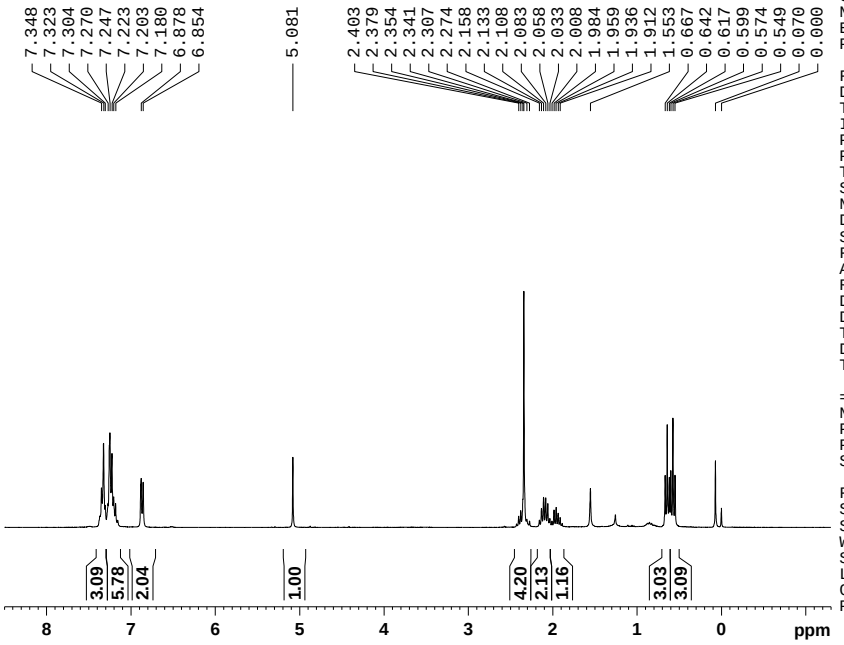
======== CHANNEL f1 ========
NUC1 13C
P1 12.50 usec
PL1 2.00 dB
SFO1 75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 100.00 usec
PL2 3.00 dB
PL12 22.33 dB
PL13 23.00 dB
SFO2 300.1312005 MHz

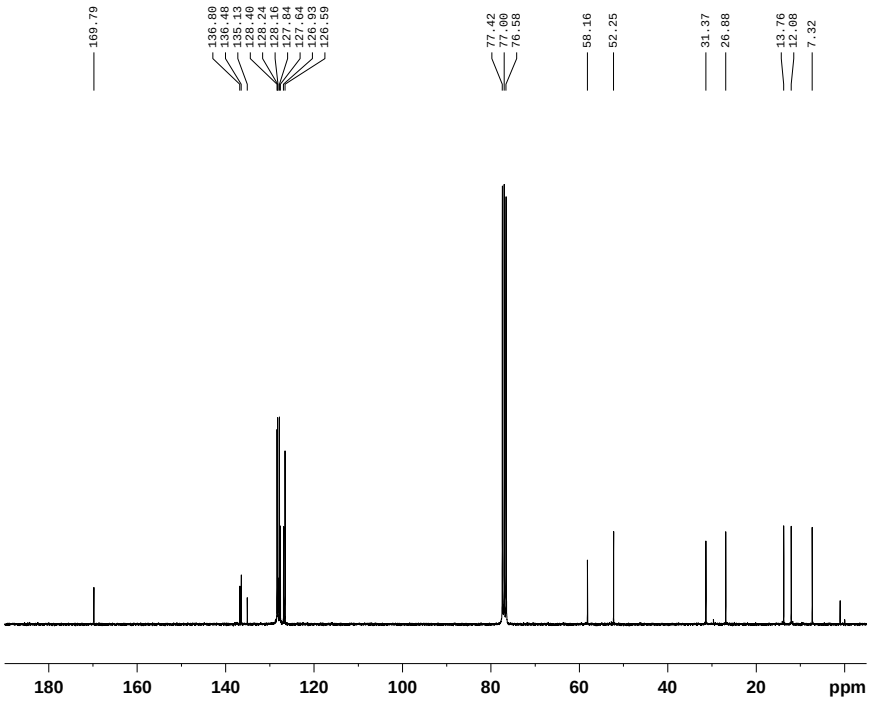
F2 - Processing parameters
SI 32768
SF 75.4677512 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



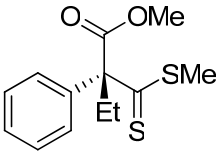
trans-**6**



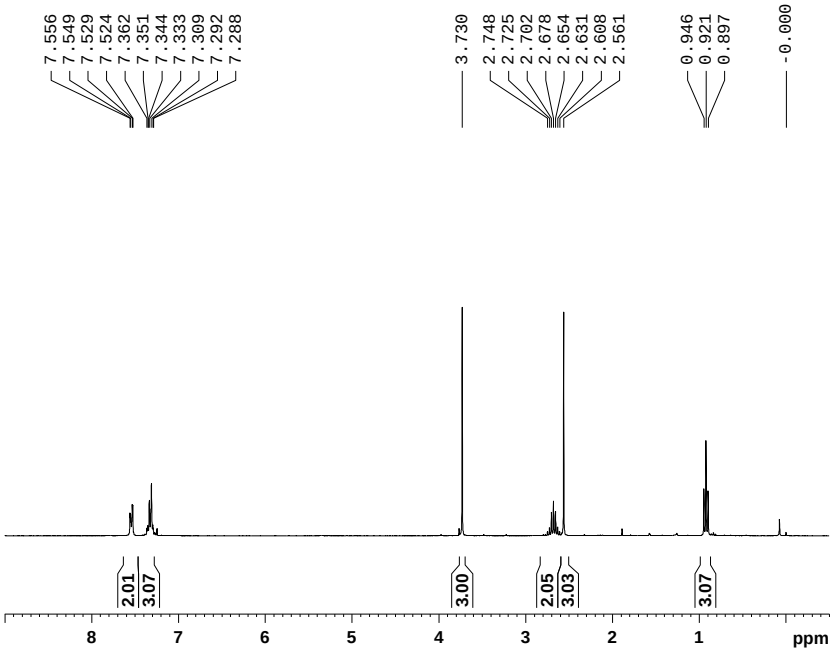

```
Current Data Parameters
NAME          wxn425-a-1
EXPNO                 20
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100526
Time               23.34
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ             3.6438515 sec
RG                   256
DW                55.600 usec
DE                 8.00 usec
TE                299.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300068 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



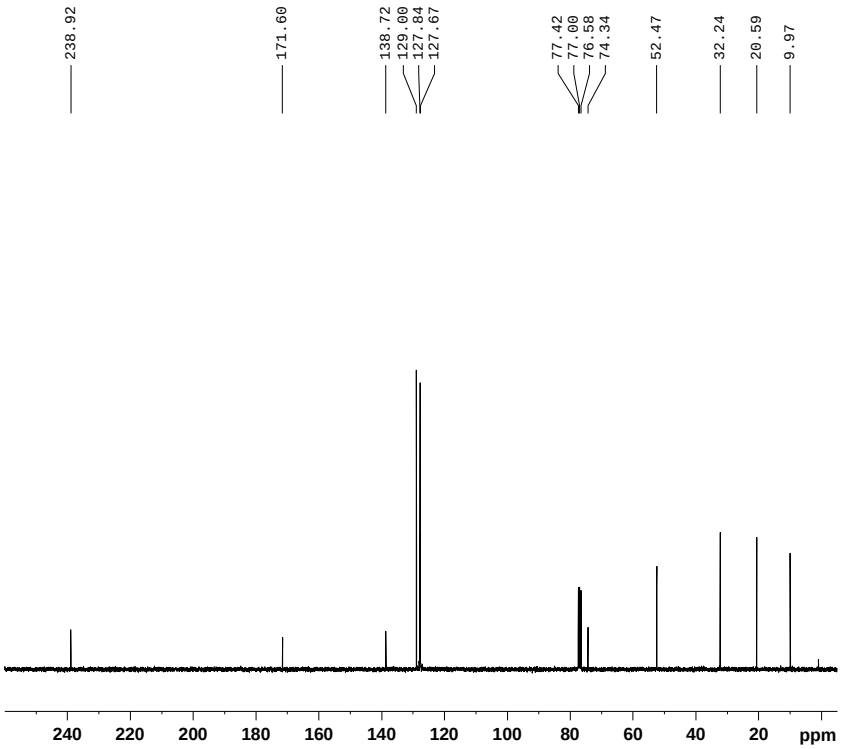

```
Current Data Parameters
NAME          wxn425-a-1
EXPNO                 21
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100526
Time               23.39
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  7421
DS                     4
SWH           17985.611 Hz
FIDRES         0.274439 Hz
AQ             1.8219508 sec
RG                 16384
DW                27.800 usec
DE                 8.00 usec
TE                300.0 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677499 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



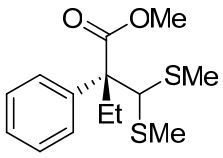
7



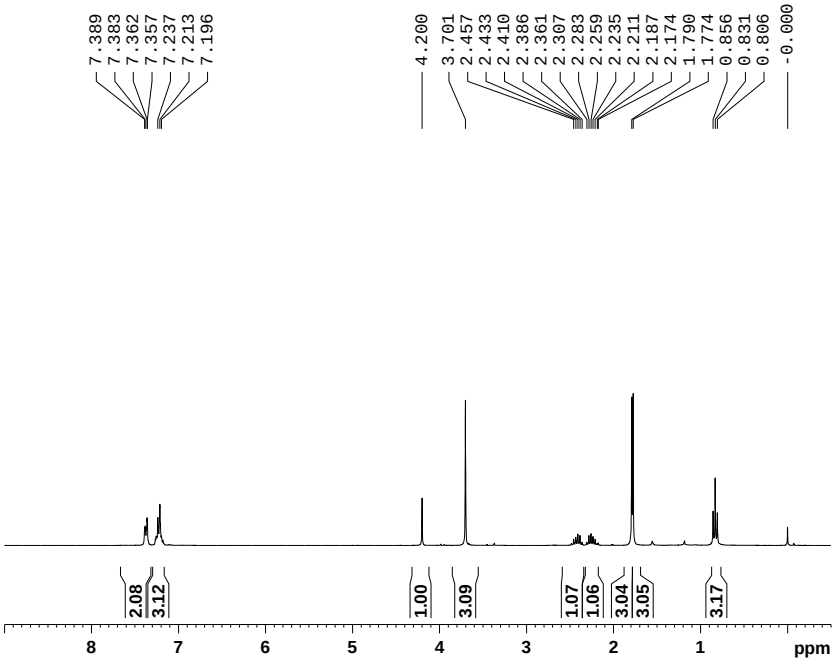

```
Current Data Parameters
NAME          wxn482-2-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110411
Time               22.31
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                     7
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                299.1 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300108 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



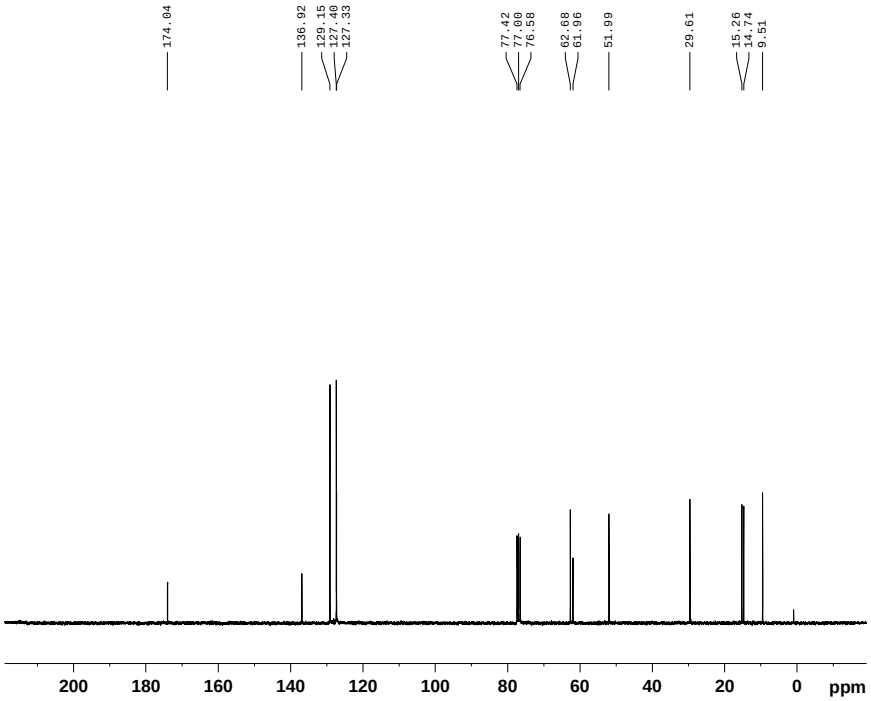

```
Current Data Parameters
NAME          wxn482-2-1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110411
Time               22.35
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   176
DS                     4
SWH            30120.482 Hz
FIDRES          0.459602 Hz
AQ              1.0879476 sec
RG                1290.2
DW                16.600 usec
DE                 6.50 usec
TE                299.5 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4768051 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677544 MHz
WDW                   EM
```



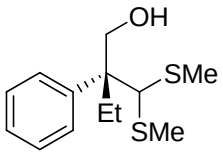
8



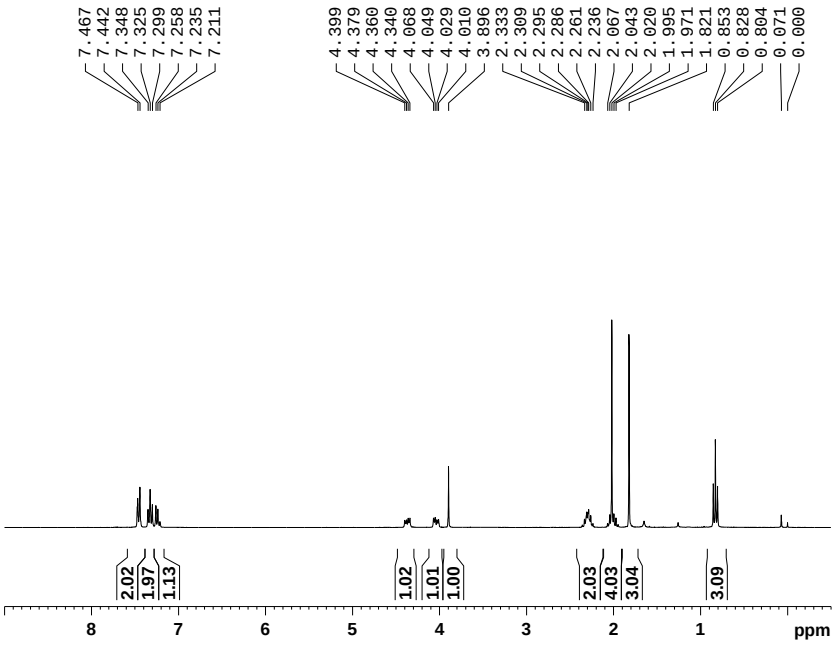

```
Current Data Parameters
NAME            wxn483-2
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100725
Time               20.29
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                    64
DW                55.600 usec
DE                 8.00 usec
TE                299.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300300 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



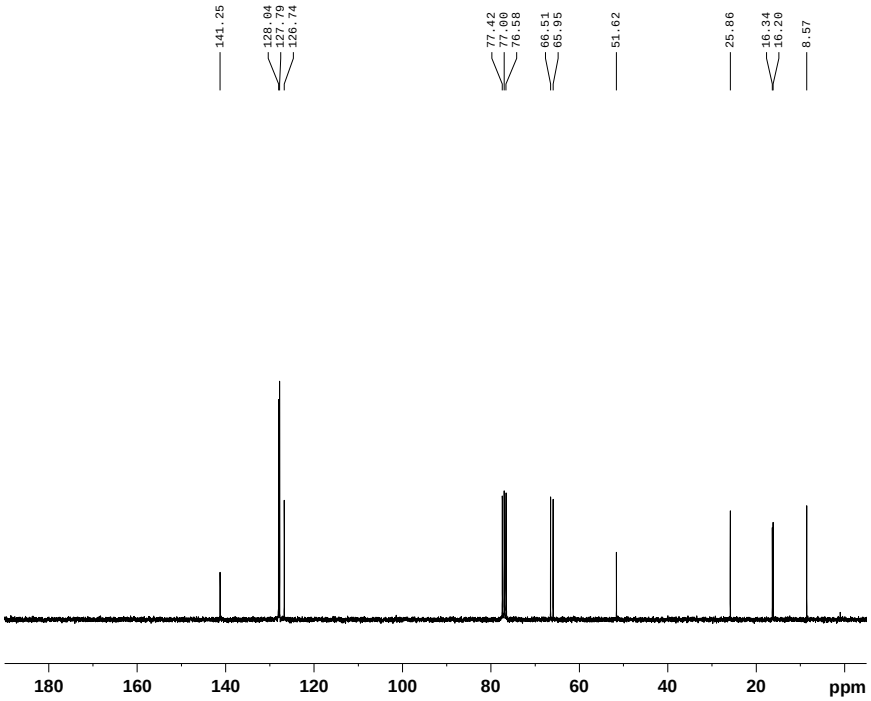

```
Current Data Parameters
NAME            wxn483-2
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100725
Time               20.32
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   204
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                5160.6
DW                27.800 usec
DE                 8.00 usec
TE                300.1 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677556 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



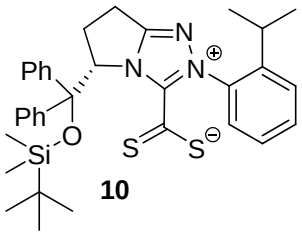
9



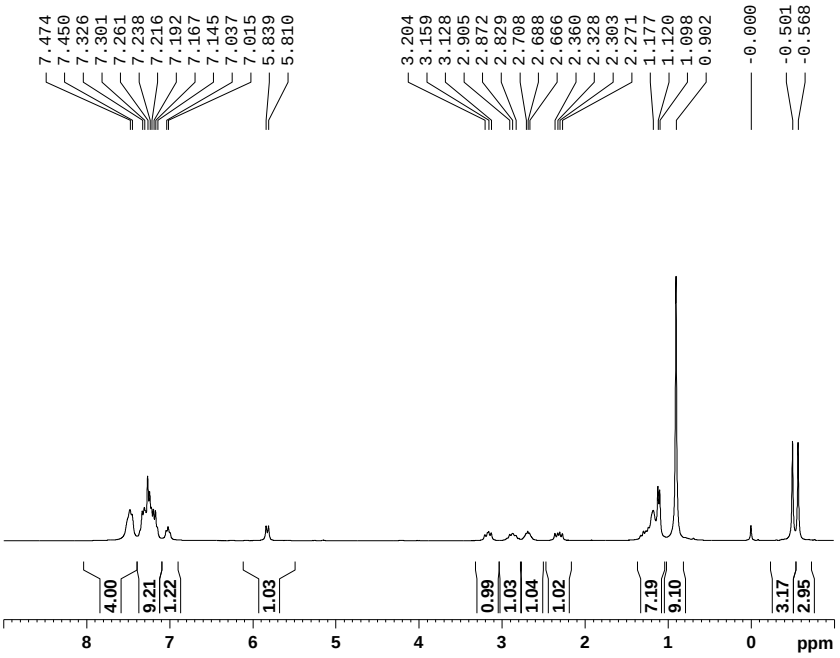

```
Current Data Parameters
NAME            wxn484-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100726
Time               18.23
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                301.8 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300070 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



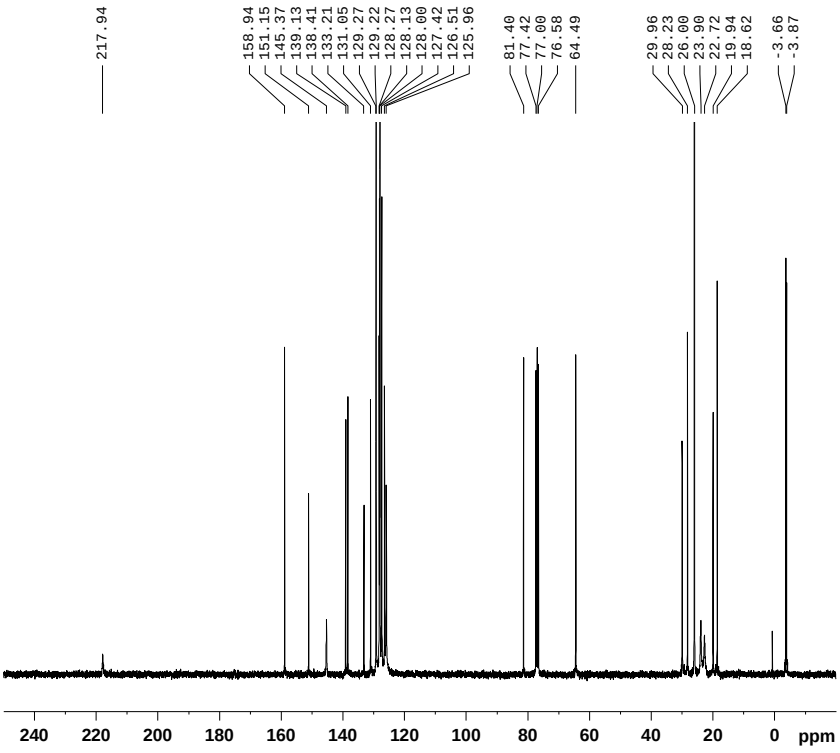

```
Current Data Parameters
NAME            wxn484-1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100726
Time               18.27
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   187
DS                     4
SWH            17985.611 Hz
FIDRES          0.274439 Hz
AQ              1.8219508 sec
RG                 16384
DW                27.800 usec
DE                 8.00 usec
TE                302.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4752953 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677520 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```



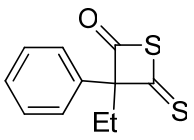
10



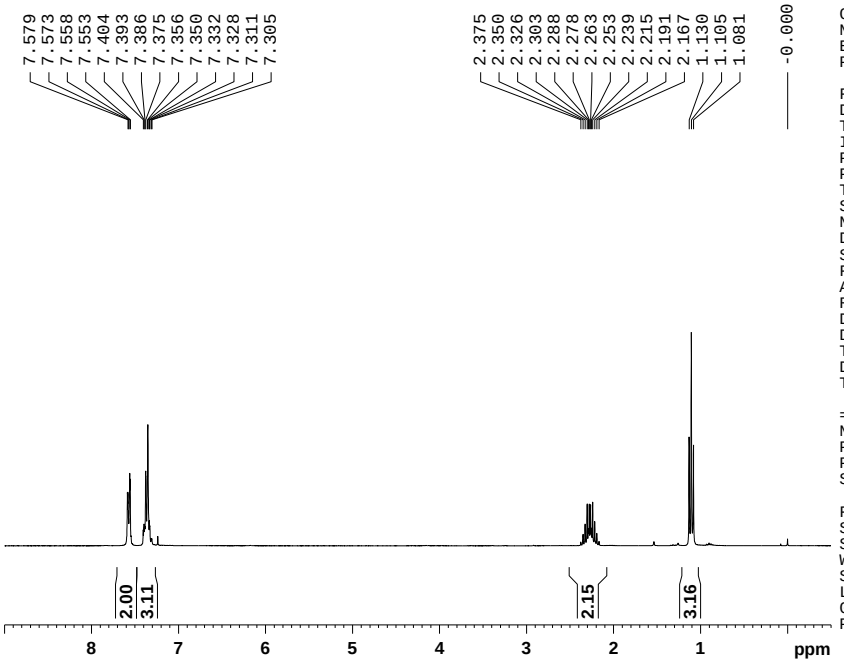

```
Current Data Parameters
NAME            wxn598-2
EXPNO                 30
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110409
Time               20.52
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                  28.5
DW                55.600 usec
DE                 8.00 usec
TE                299.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1        300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF          300.1300273 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                  1.00
```



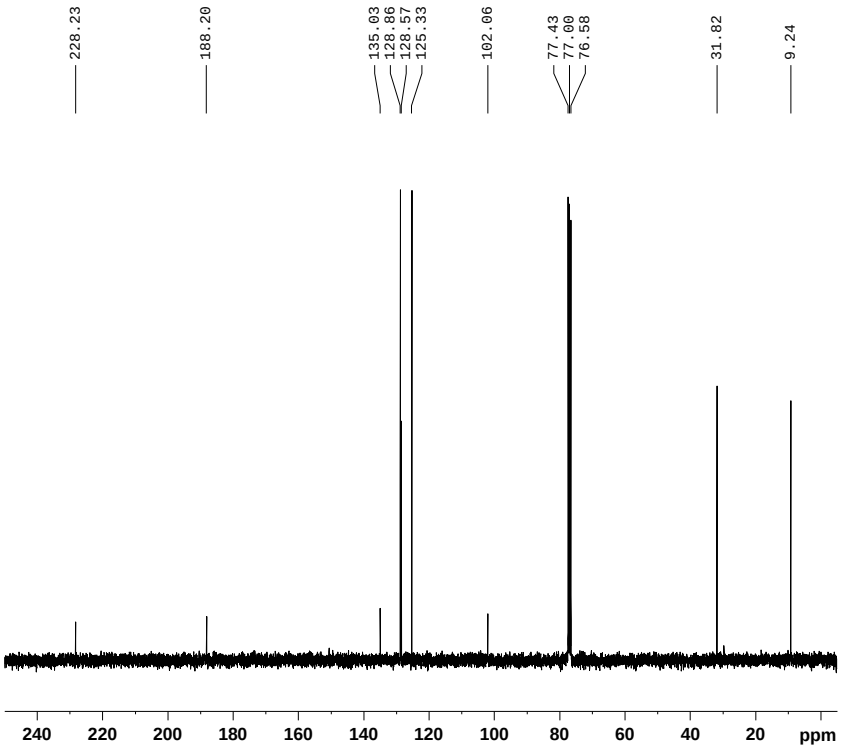

```
Current Data Parameters
NAME            wxn598-2
EXPNO                 31
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110409
Time               20.56
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   652
DS                     4
SWH            30120.482 Hz
FIDRES          0.459602 Hz
AQ              1.0879476 sec
RG                1149.4
DW                16.600 usec
DE                 6.50 usec
TE                299.2 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4768051 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2        300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF          75.4677745 MHz
WDW                   EM
```



12



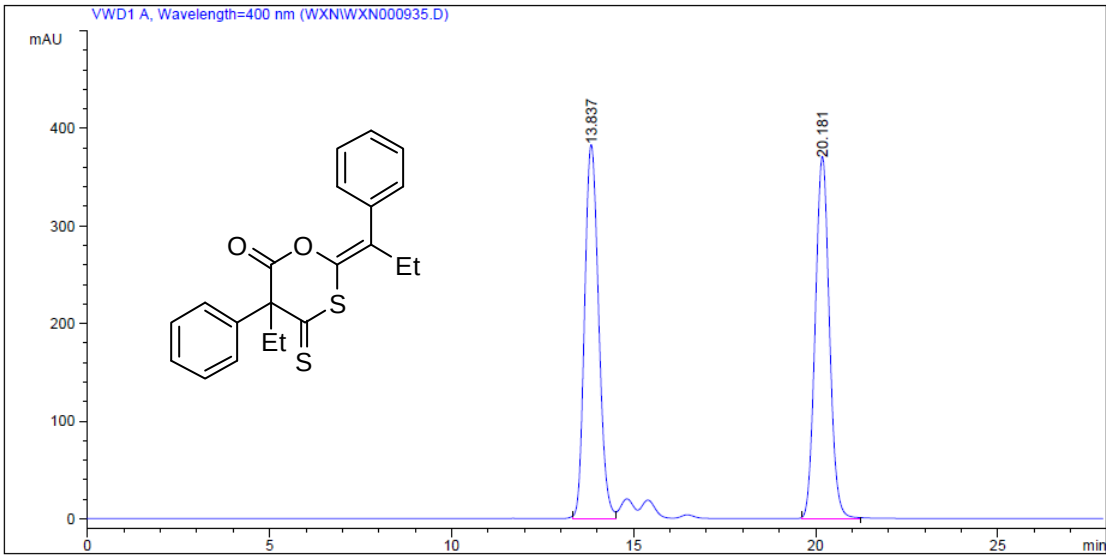

```
Current Data Parameters
NAME            wxn415-1
EXPNO                 11
PROCNO                 1

F2 - Acquisition Parameters
Date_           20100505
Time               22.24
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     0
SWH             8992.806 Hz
FIDRES          0.137219 Hz
AQ              3.6438515 sec
RG                   128
DW                55.600 usec
DE                 8.00 usec
TE                298.4 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                10.80 usec
PL1                3.00 dB
SFO1         300.1324010 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300131 MHz
WDW                   EM
SSB                    0
LB                 0.30 Hz
GB                     0
PC                 1.00
```



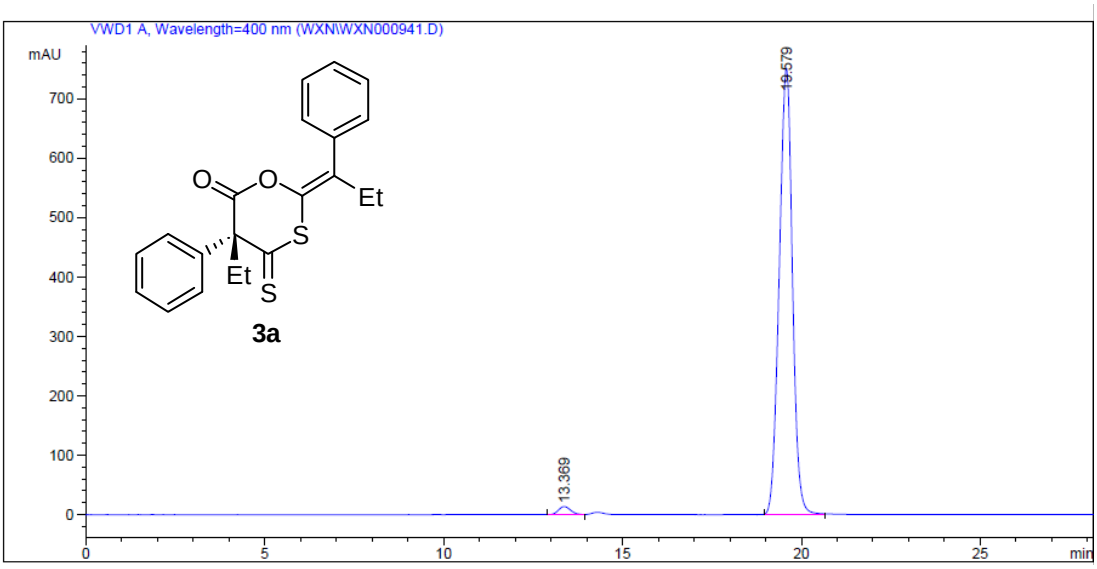

```
Current Data Parameters
NAME            wxn415-1
EXPNO                 10
PROCNO                 1

F2 - Acquisition Parameters
Date_           20110411
Time               18.32
INSTRUM            spect
PROBHD   5 mm DUL 13C-1
PULPROG          zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   411
DS                     4
SWH            30120.482 Hz
FIDRES          0.459602 Hz
AQ              1.0879476 sec
RG                 574.7
DW                16.600 usec
DE                 6.50 usec
TE                300.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                12.50 usec
PL1                2.00 dB
SFO1         75.4768051 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                  1H
PCPD2            100.00 usec
PL2                3.00 dB
PL12              22.33 dB
PL13              23.00 dB
SFO2         300.1312005 MHz

F2 - Processing parameters
SI                 32768
SF           75.4677498 MHz
WDW                   EM
```

Part III GC and HPLC spectra

Sample Info : Hex:Ipr = 99.5:0.5 AD-H 0.5ml/min

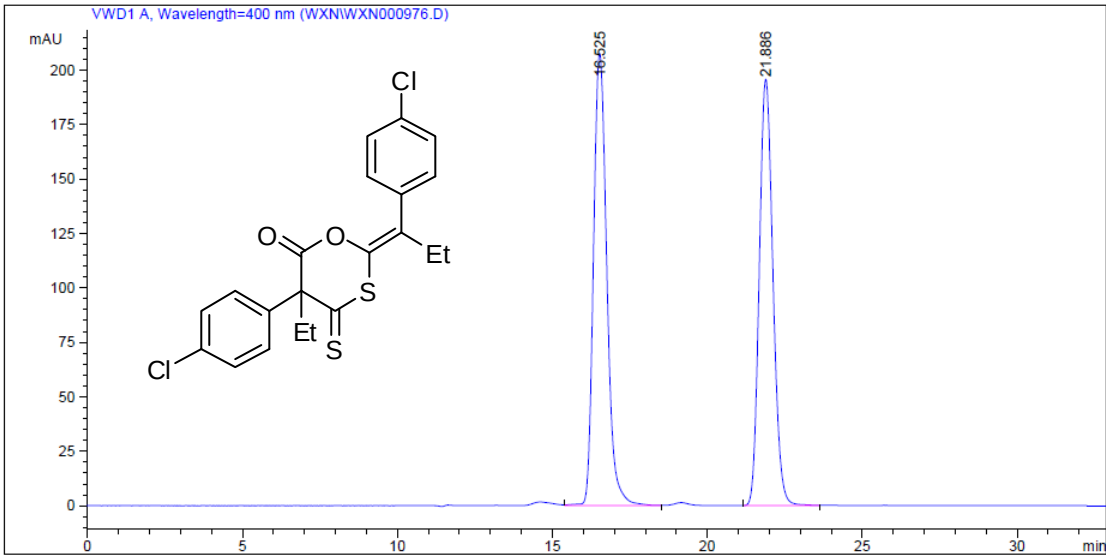


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.837	BV	0.4321	1.02575e4	379.17889	50.5560
2	20.181	BB	0.4358	1.00319e4	366.48383	49.4440

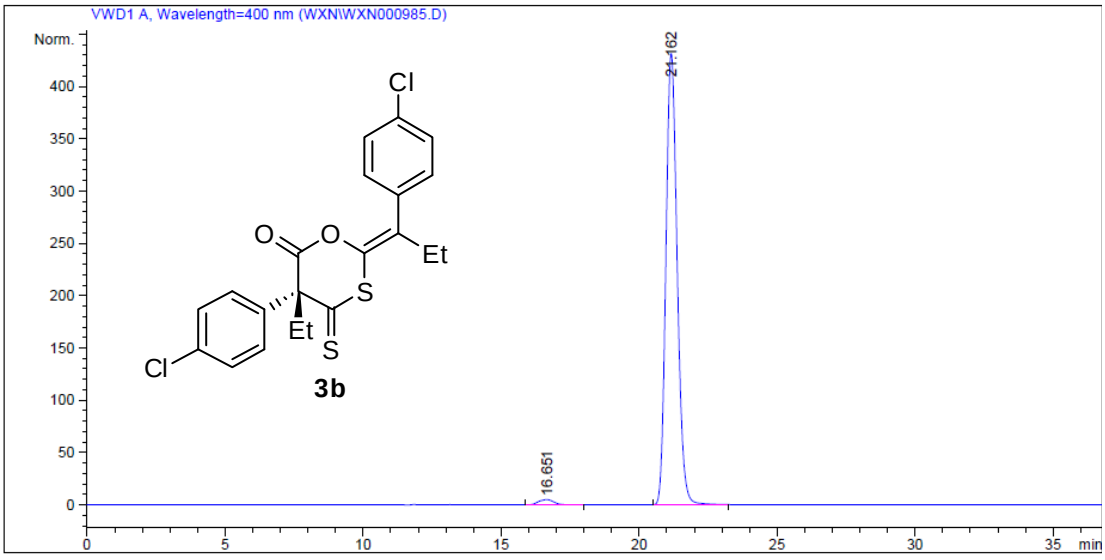


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.369	BV	0.3769	320.43536	13.45475	1.6367
2	19.579	BB	0.3983	1.92577e4	750.77002	98.3633

Sample Info : AD-H Hex:Ipr = 99:1 0.5 ml/min

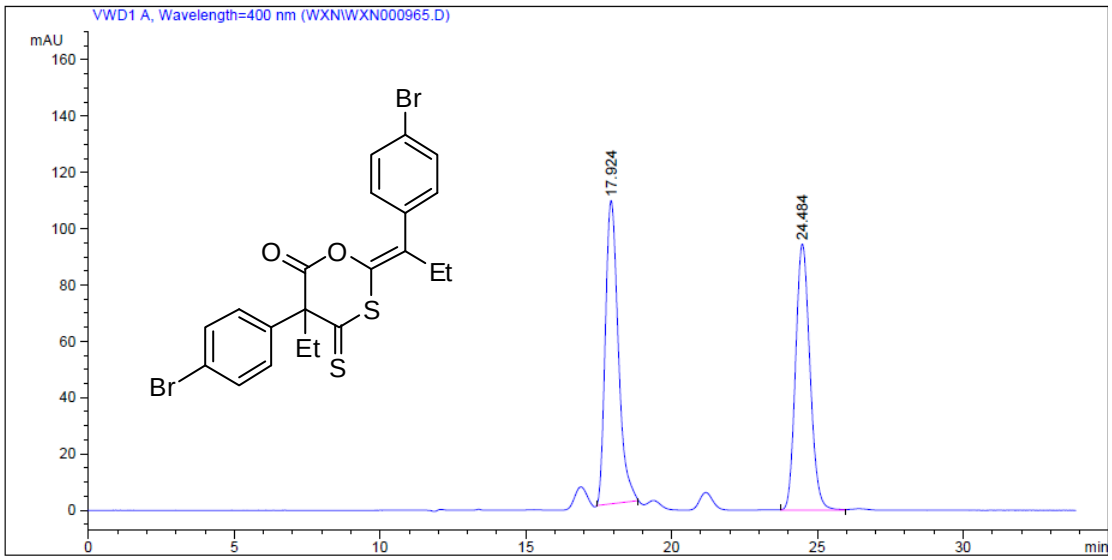


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.525	VV	0.4655	6207.96631	207.52451	50.8059
2	21.886	BB	0.4749	6011.01416	195.68506	49.1941

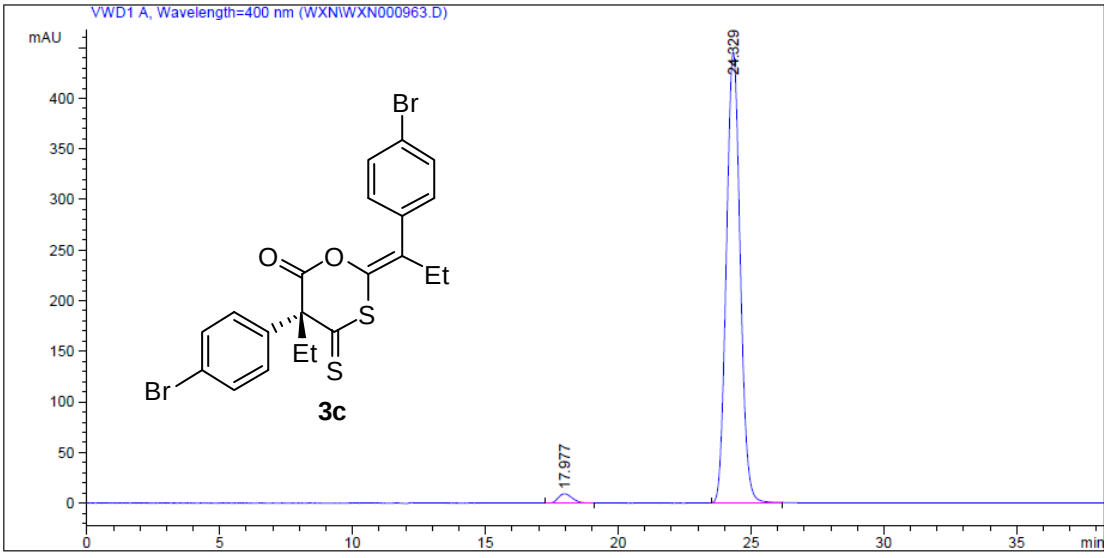


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.651	BB	0.6146	181.85056	4.82295	1.4663
2	21.162	BB	0.4324	1.22197e4	431.37866	98.5337

Sample Info : AD-H Hex:Ipr = 99.5:0.5 0.5 ml/min

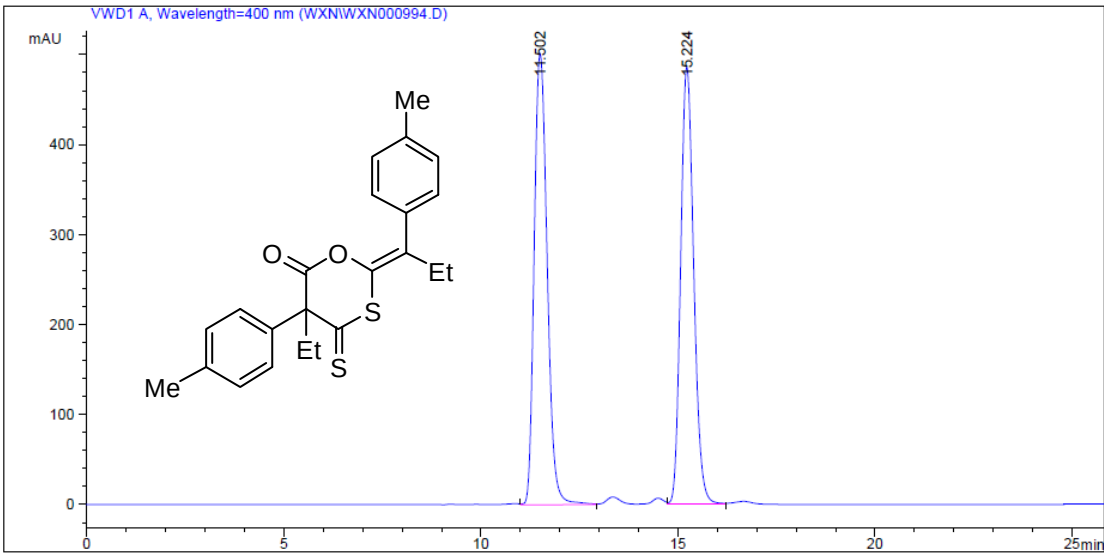


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.924	MM	0.5142	3325.86572	107.79646	50.6185
2	24.484	BB	0.5229	3244.59204	94.50054	49.3815

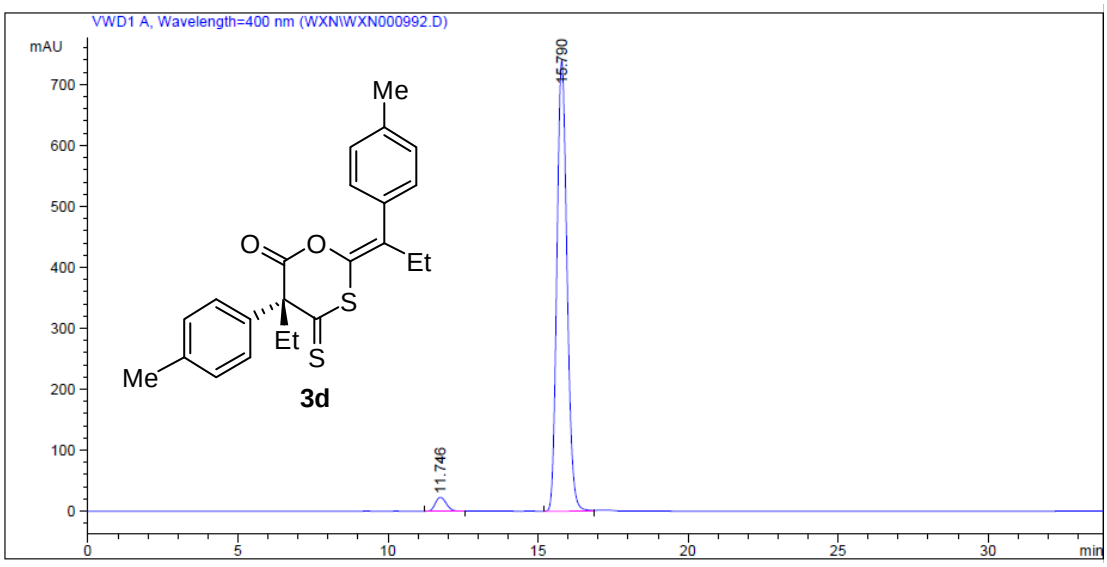


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.977	BB	0.5769	333.56131	9.14620	2.0258
2	24.329	BB	0.5623	1.61318e4	445.40353	97.9742

Sample Info : AD-H Hex:Ipr =99:1 0.7 ml/min

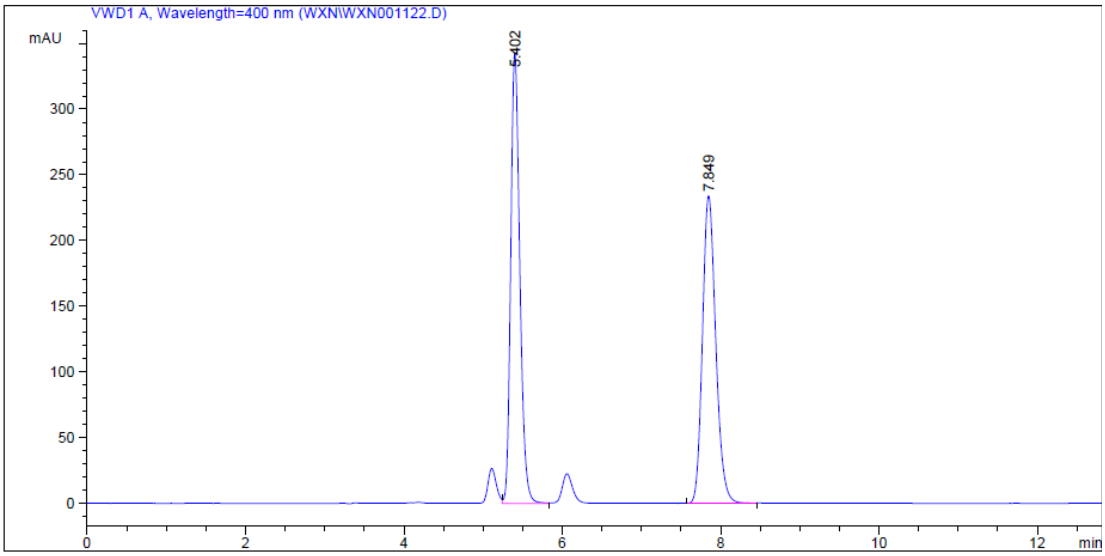


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.502	VV	0.3665	1.14886e4	501.12247	50.5749
2	15.224	VV	0.3629	1.12274e4	485.67645	49.4251

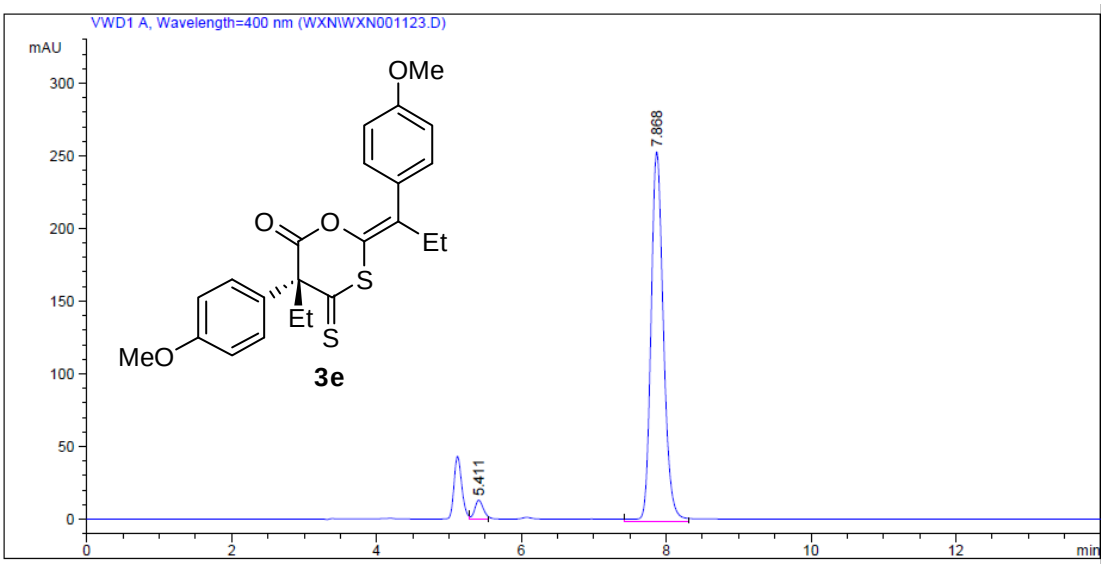


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.746	BV	0.4041	577.11548	22.71974	3.2221
2	15.790	BV	0.3671	1.73338e4	738.21271	96.7779

Sample Info : AD-H Hex:Ipr=90:101.0ml/min

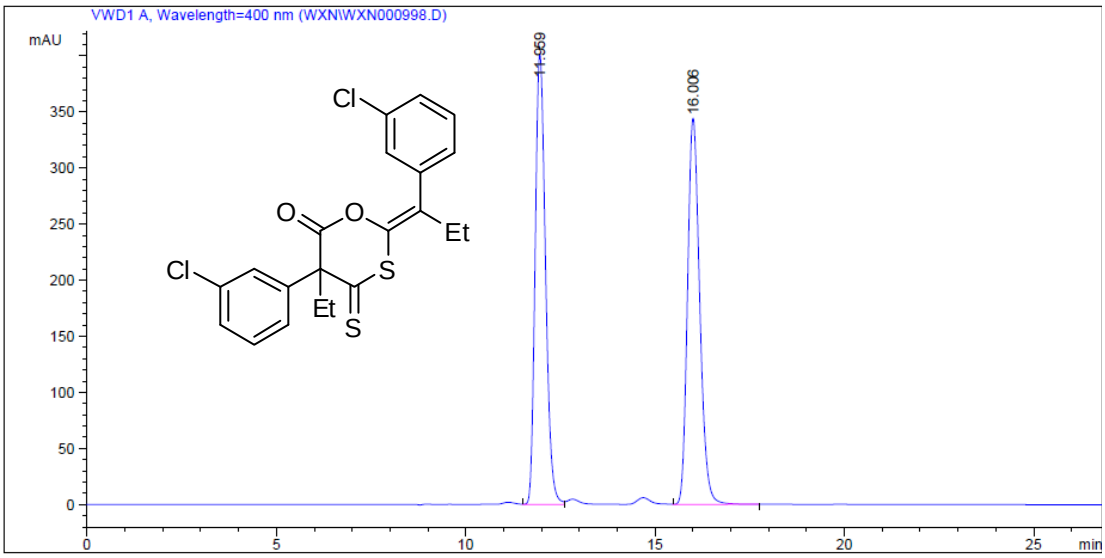


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.402	VV	0.1252	2739.40991	342.96857	50.1032
2	7.849	BB	0.1797	2728.12939	233.98138	49.8968

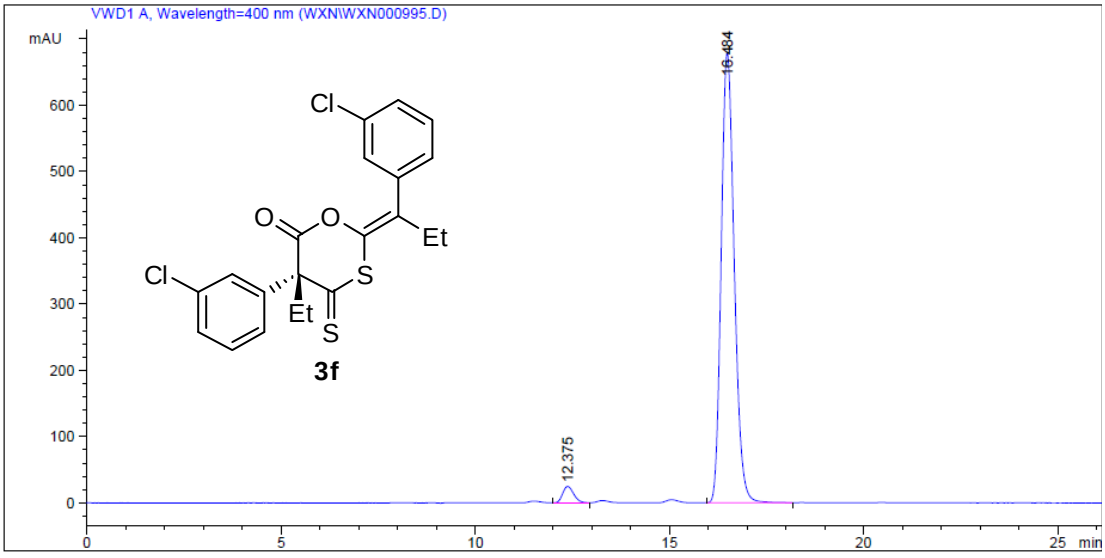


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.411	MM	0.1358	104.73414	12.85556	3.3490
2	7.868	MM	0.1982	3022.60449	254.14679	96.6510

Sample Info : AD-H Hex:Ipr =99:1 0.7 ml/min



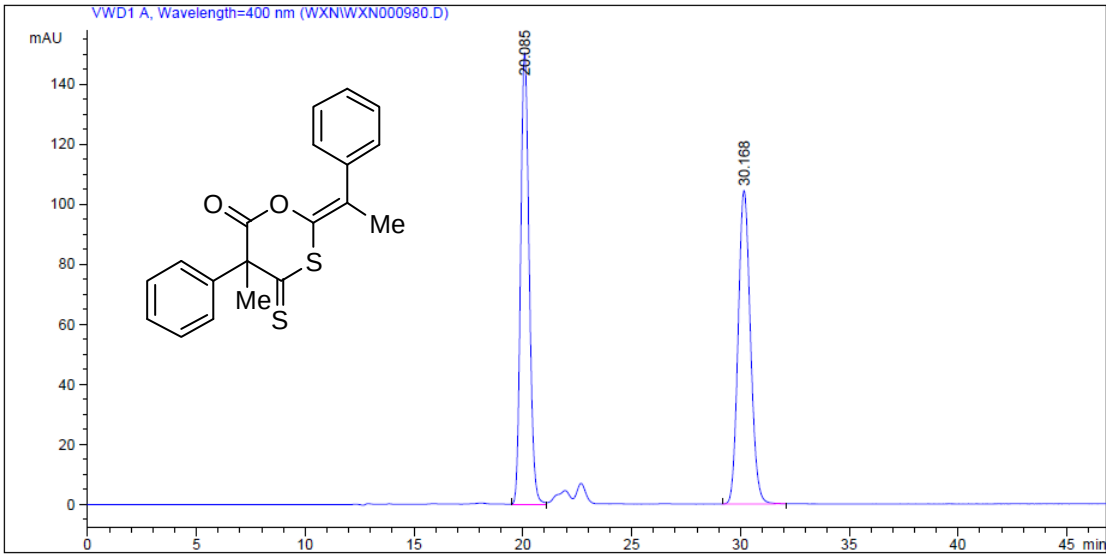
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	11.959	VV	0.2972	7610.93408	400.94656	49.7390
2	16.006	VB	0.3481	7690.80078	344.14713	50.2610



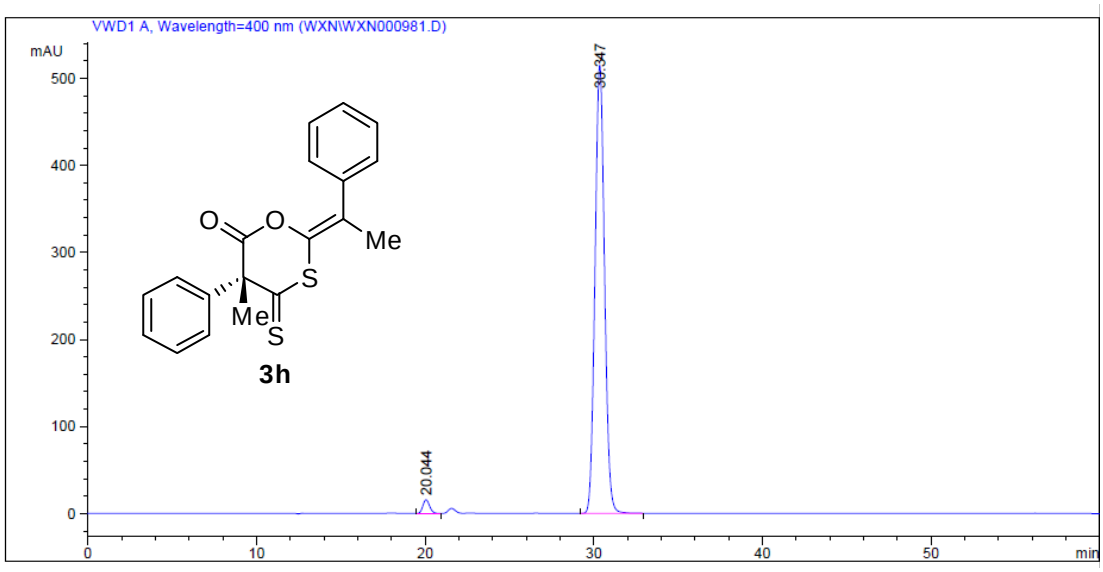
3f

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.375	VV	0.3109	494.66577	24.84583	3.0312
2	16.484	BB	0.3653	1.58243e4	678.53644	96.9688

Sample Info : AD-H Hex:Ipr = 99:1 0.5 ml/min

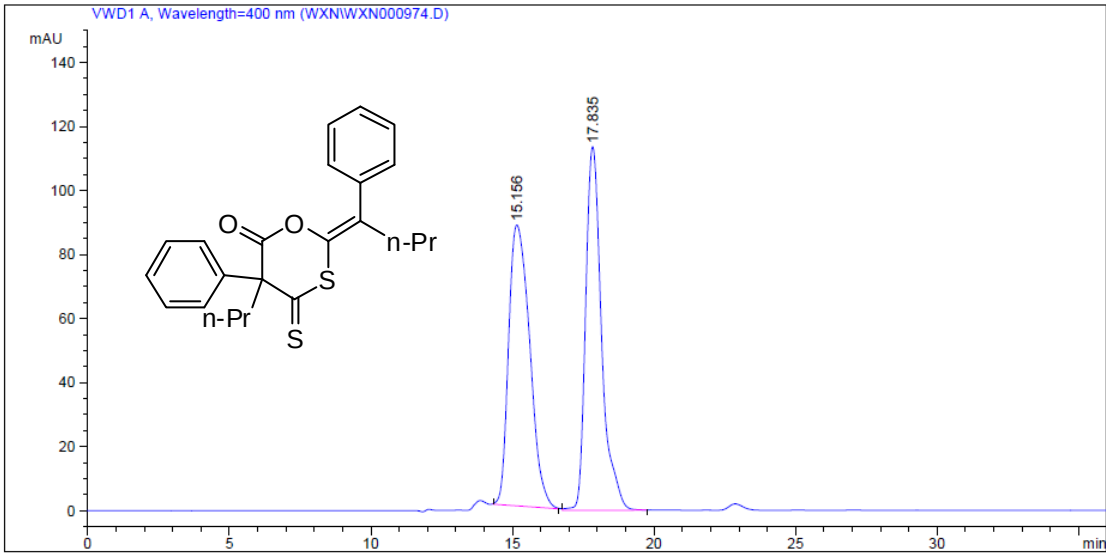


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.085	BV	0.3992	4090.47583	150.23555	49.9881
2	30.168	BB	0.5741	4092.42627	104.33411	50.0119

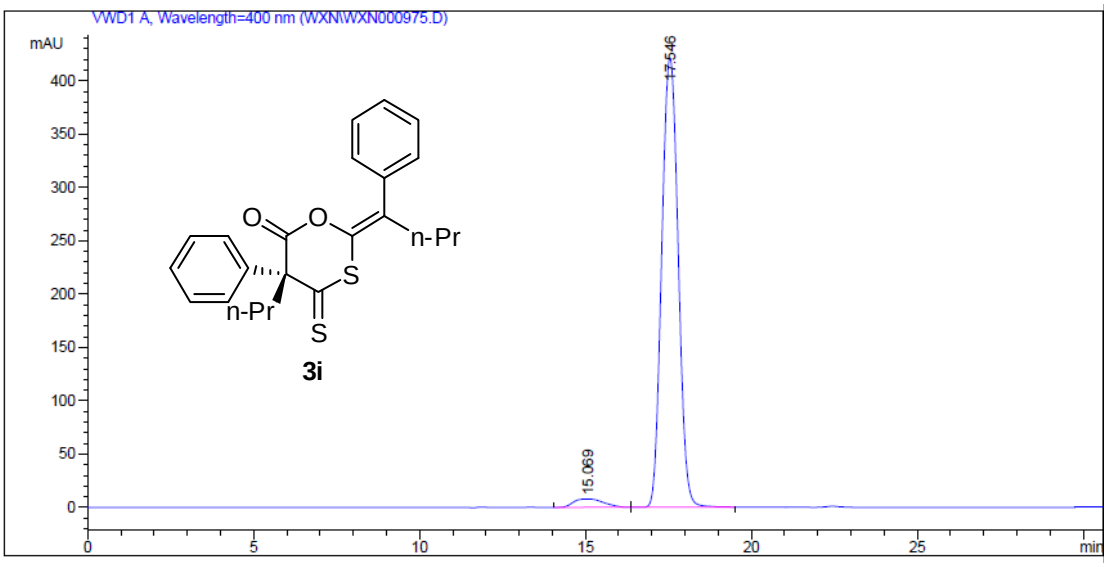


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.044	BV	0.4081	439.83502	15.71362	2.1256
2	30.347	BB	0.5988	2.02525e4	514.74127	97.8744

Sample Info : AD-H Hex:Ipr = 99:1 0.5 ml/min

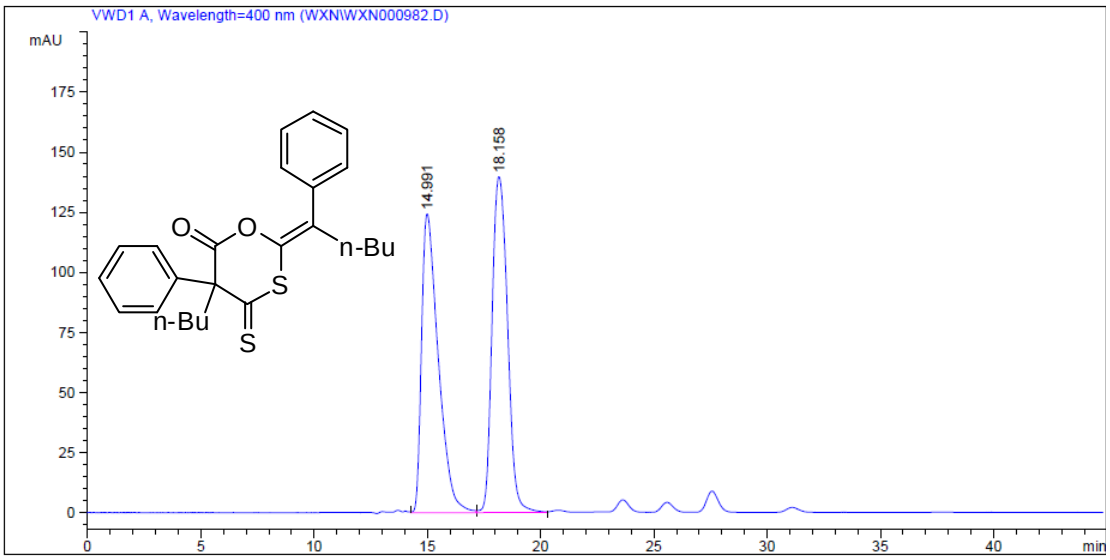


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.156	MM	0.8617	4536.83057	87.74915	50.4605
2	17.835	VB	0.5798	4454.03271	113.57083	49.5395

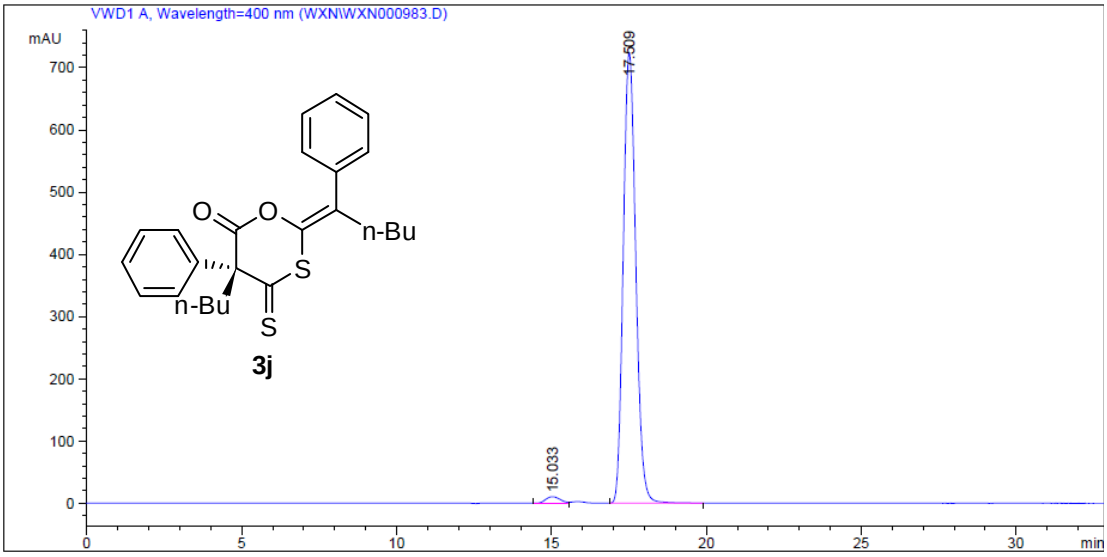


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.069	BV	0.7529	485.39758	7.73044	3.2367
2	17.546	VB	0.5243	1.45111e4	421.17798	96.7633

Sample Info : AD-H Hex:Ipr =99:1 0.5 ml/min

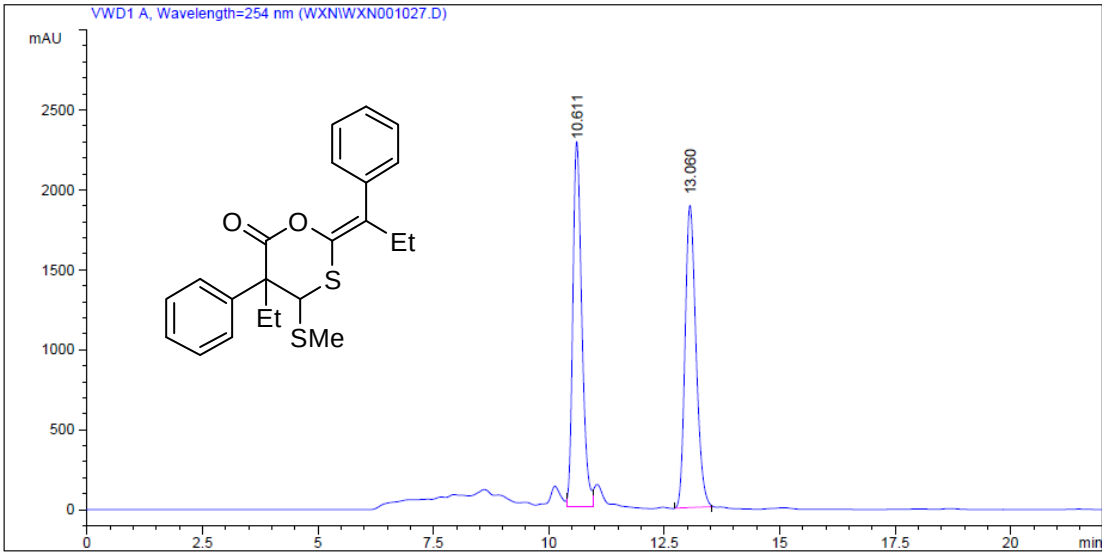


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	14.991	VV	0.7182	6382.09229	124.34306	49.0669
2	18.158	VB	0.6957	6624.82031	139.74948	50.9331

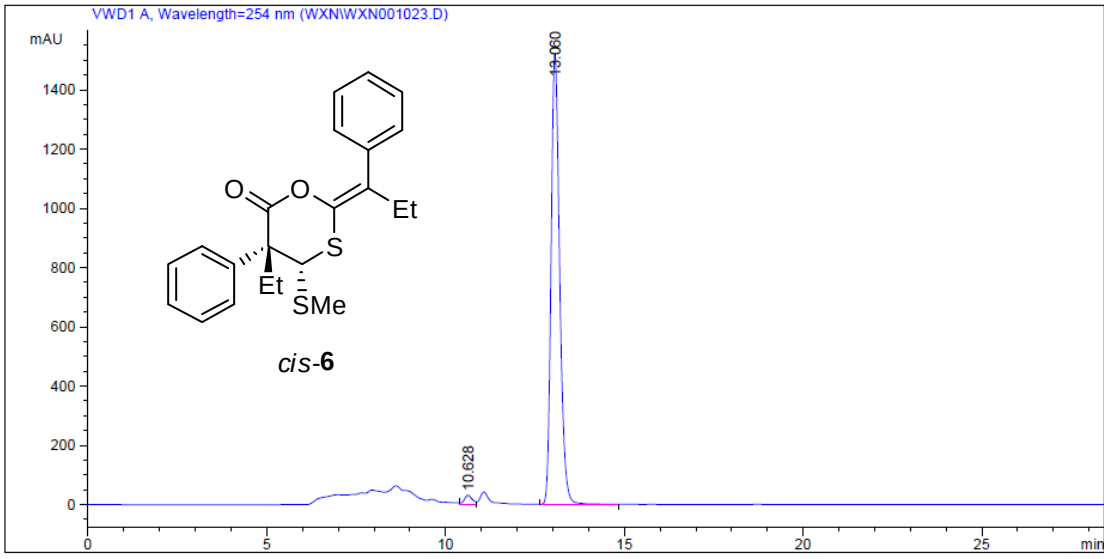


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	15.033	BV	0.5035	347.70541	10.56035	1.6825
2	17.509	BB	0.4265	2.03181e4	723.70740	98.3175

Sample Info : AD-H Hex:Ipr=90:10 1.0ml/min



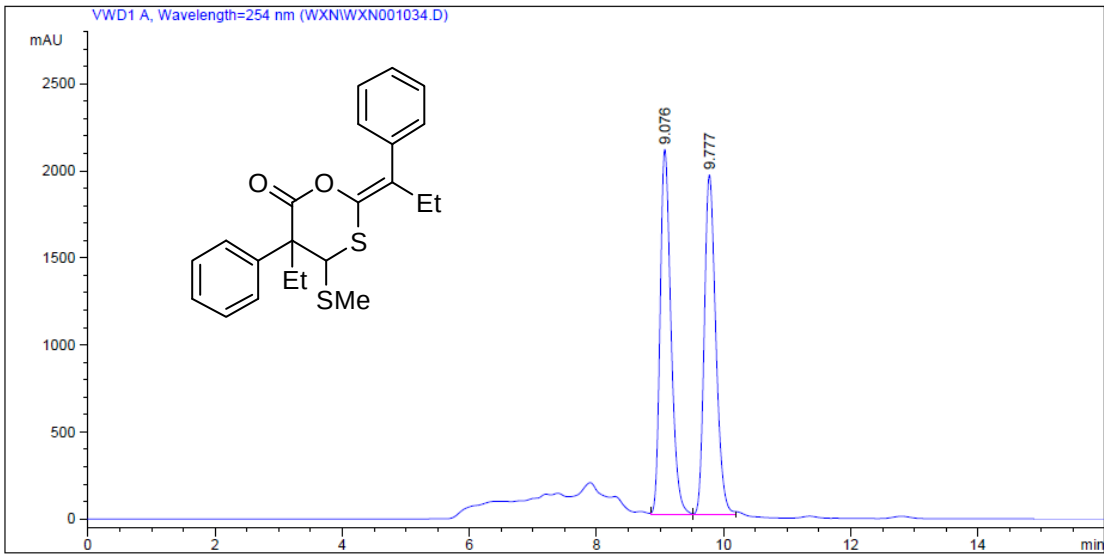
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.611	MM	0.2266	3.09062e4	2272.84888	49.8834
2	13.060	MM	0.2680	3.10507e4	1930.76160	50.1166



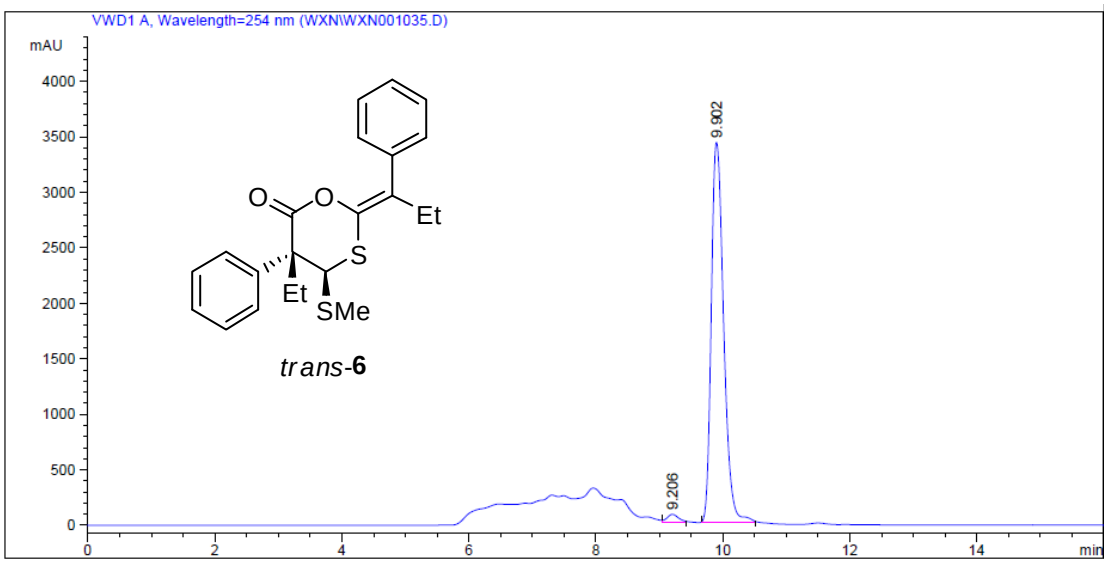
cis-**6**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.628	VV	0.2388	503.67413	31.52330	1.9398
2	13.060	VV	0.2591	2.54620e4	1523.29688	98.0602

Sample Info : AD-H Hex:Ipr=90.10 0.8ml/min



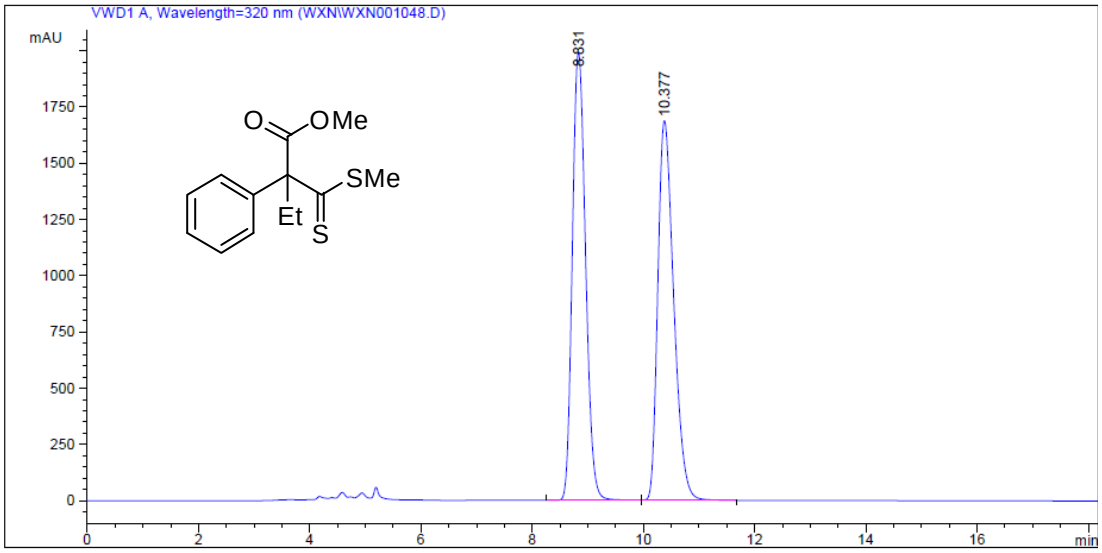
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.076	MM	0.1965	2.47830e4	2101.72119	50.1847
2	9.777	MM	0.2096	2.46006e4	1955.92920	49.8153



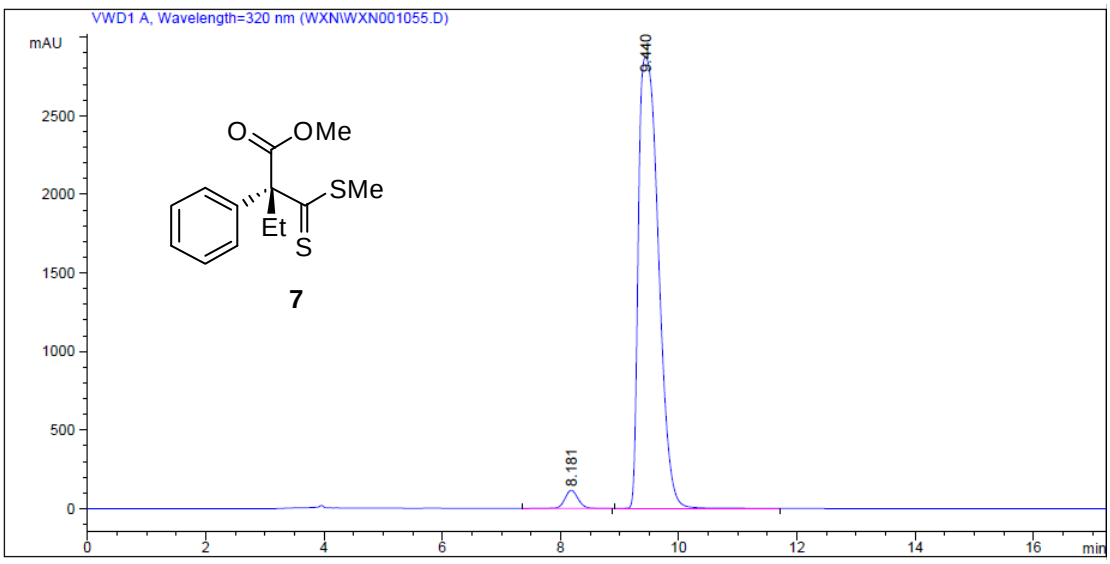
trans-**6**

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.206	MM	0.2053	841.11884	68.29365	1.7888
2	9.902	MM	0.2248	4.61812e4	3424.02417	98.2112

Sample Info : OD-H Hex:Ipr=98:2 1.0ml/min



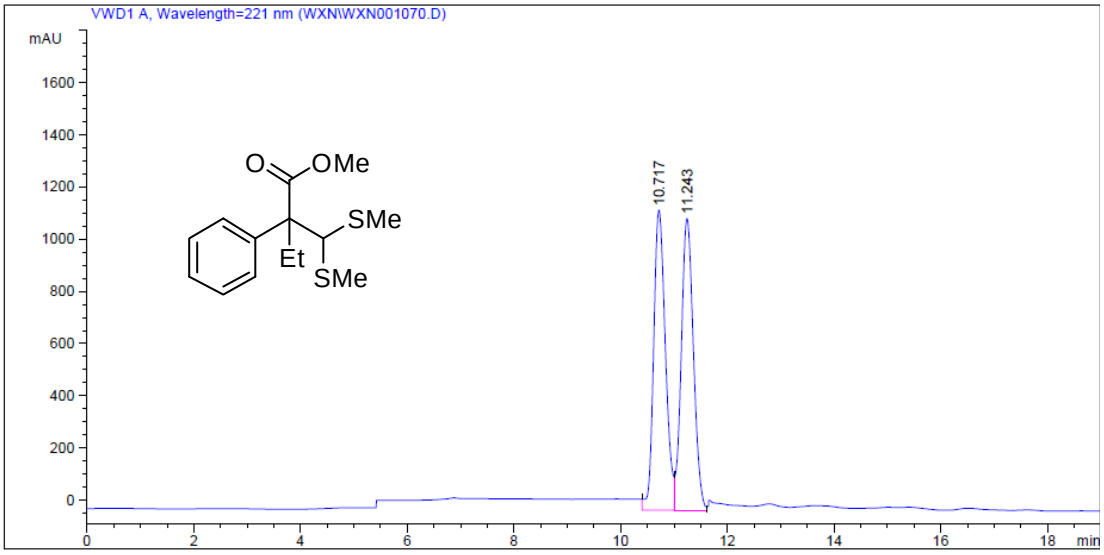
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.831	VB	0.2585	3.29423e4	1991.31628	49.6230
2	10.377	BB	0.3055	3.34428e4	1687.34424	50.3770



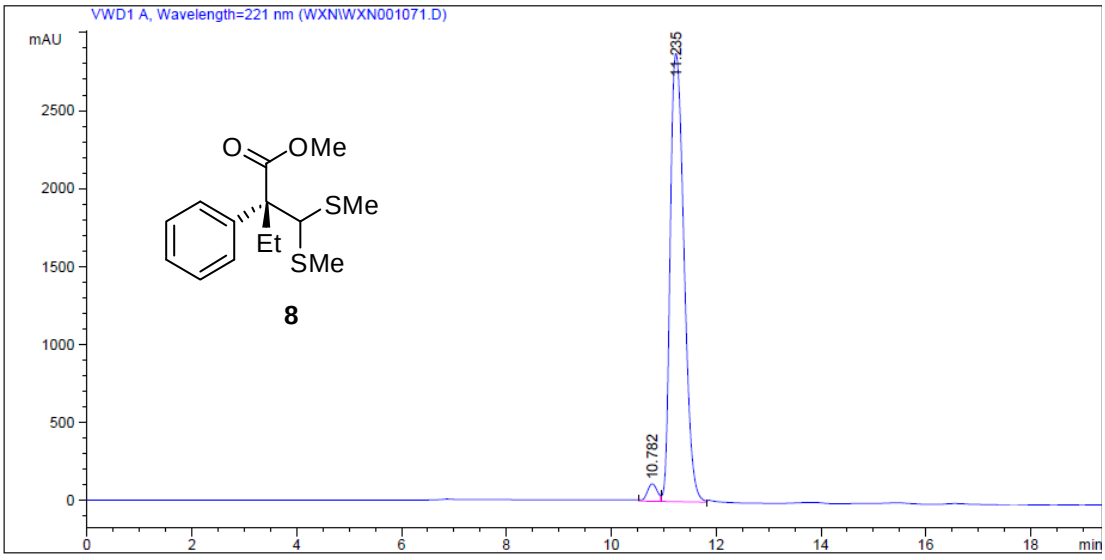
7

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.181	VB	0.2448	1850.97424	115.72986	2.6737
2	9.440	BB	0.3755	6.73780e4	2873.60327	97.3263

Sample Info : OD-H Hex:Ipr=98:2 0.5ml/min



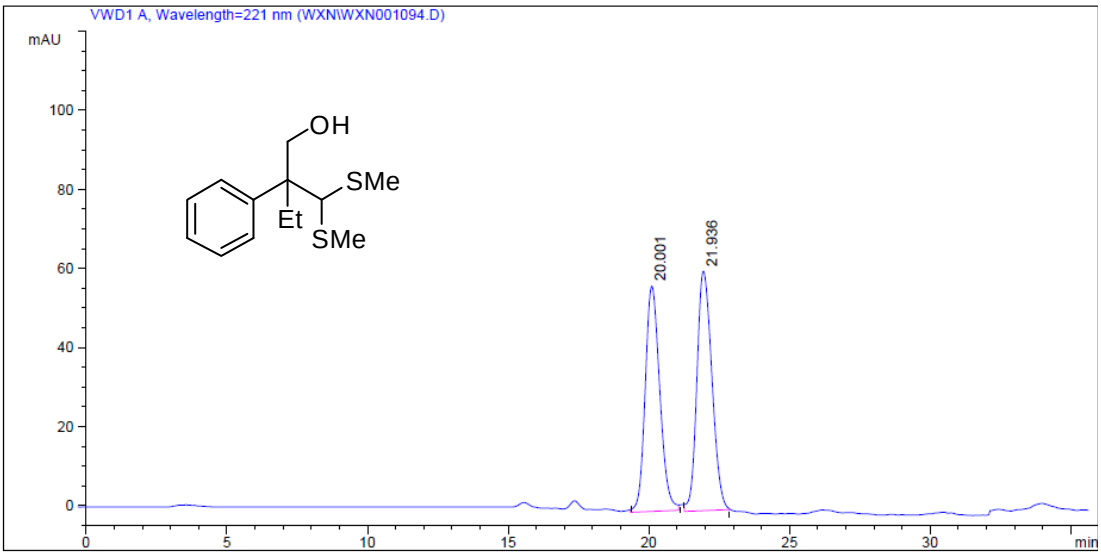
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.717	VV	0.2396	1.75652e4	1148.48584	49.8169
2	11.243	VV	0.2460	1.76944e4	1116.78467	50.1831



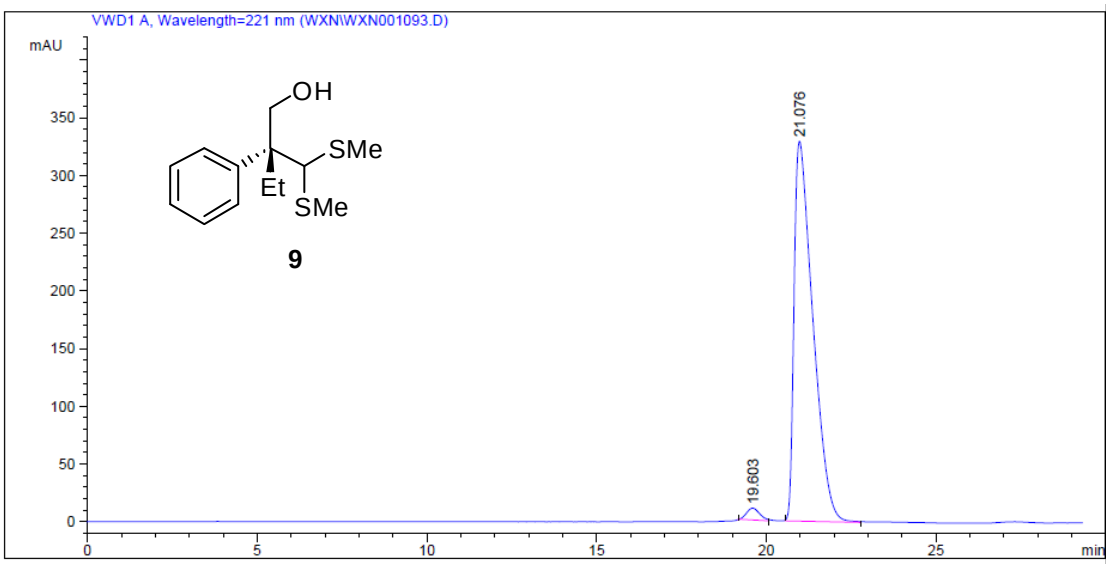
8

Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	10.782	VV	0.2084	1466.63989	111.75159	2.7136
2	11.235	VV	0.2920	5.25821e4	2874.73120	97.2864

Sample Info : AS-H Hex:Ipr=98:2 1.0ml/min



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	20.001	MM	0.5964	2029.11194	56.70001	49.1296
2	21.936	MM	0.6076	2186.82031	59.98262	50.8704



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.603	MM	0.4454	274.22546	10.26105	2.1230
2	21.076	MM	0.6401	1.26429e4	329.17084	97.8770