

**Chiral Sc-catalyzed Asymmetric Michael Reactions of Thiols with
Enones in Water**

Masaharu Ueno, Taku Kitanosono, Masaru Sakai, and Shū Kobayashi*

Department of Chemistry, School of Science and Graduate School of Pharmaceutical
Sciences, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Electronic Supplementary Information

General

Nuclear magnetic Resonance (NMR) spectra were recorded on a JEOL ECX-600 or ECX-500 spectrometer, operating at 600 MHz or 500 MHz for ^1H and 150 MHz or 125 MHz for ^{13}C NMR in CDCl_3 unless otherwise noted. Tetramethylsilane (TMS) served as the internal standard ($\delta = 0$) for ^1H NMR and CDCl_3 was used as the internal standard ($\delta = 77.0$) for ^{13}C NMR. Infrared (IR) spectra were obtained using a JASCO FT/IR-4200 spectrometer. Data are represented as frequency of absorption (cm^{-1}). All melting points were determined on a YAZAWA micro melting point BY-1 apparatus and are uncorrected. High-performance liquid chromatography was carried out using following apparatuses; SHIMADZU LC-10ATvp (liquid chromatograph), SHIMADZU SPD-10A (UV detector) and SHIMADZU C-R8A (Chromatopac) using Daicel chiralpak[®] or chiralcel[®] columns. Preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F from Wako Pure Chemical Industries, Ltd. Preparative thin-layer chromatography was carried out using Wakogel B-5F. Deionized water from a MILLIPORE MilliQ machine (Gradient A 10) was used as solvent without further treatment. All organic solvents used were commercially available dry solvents, which were distilled appropriately under an argon atmosphere or were stored over molecular sieves prior to use. All α,β -unsaturated ketones **2** in this study were commercially available and were distilled –or recrystallized prior to use. Thiols **3** were commercially available and were used without any purification prior to use. Chiral bipyridine ligand **1**¹, $\text{Sc}(\text{OTf})_3$ ² and $\text{Sc}(\text{OSO}_3\text{C}_{12}\text{H}_{25})_3$ ³ were prepared by known method.

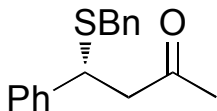
Typical Experimental Procedure for allylation reaction in aqueous media (Table 3, entry 1):

800 μ L of 0.005 M aqueous Sc(OTf)₃ solution (0.004 mmol) was added to chiral bipyridine ligand **1** (1.6 mg, 0.0048 mmol) and the mixture was stirred for 1 h at room temperature. After addition of pyridine (3.2 μ L, 0.04 mmol), benzalacetone **2a** (58.5 mg, 0.4 mmol) and benzylthiol **3a** (56.3 μ L, 0.48 mmol) successively, the reaction mixture was vigorously stirred for 24 h at room temperature. The resulting mixture was quenched with sat. NaHCO₃ aq. and brine. The aqueous layer was extracted with dichloromethane (three times), and the combined organic layers were washed with brine, and dried over Na₂SO₄. After filtration, the solvent was removed under reduced pressure. The residue was purified by preparative TLC (elution: chloroform/ethyl acetate = 200/1) to give the corresponding thio ethers **4a** (99.8 mg, 92% yield). The enantiomeric excess was determined by chiral HPLC analysis.

Analytical data for Michael reactions of thiols 4a-n

Michael reactions of thiols **4a**⁴, **4b**⁴, **4c**⁴, **4d**⁴, **4e**⁵, **4f**⁴, **4g**⁴, **4h**⁶, **4i**⁶, **4j**⁶, **4k**⁶, **4l**⁶, **4m**⁷ are literature-known; obtained analytical data for these compounds is in full agreement with reported data. The absolute configuration of the optically active compounds was determined by comparison of the measured HPLC data with the value reported in the literature.⁴⁻⁷

4a: (*R*)-4-(benzylthio)-4-phenylbutan-2-one⁴



colorless oil

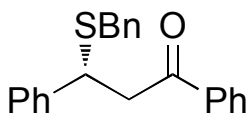
IR (KBr): $\nu = 3060, 3027, 2917, 1716, 1600, 1492, 1452, 1416, 1358, 1329, 1240, 1154, 1074, 1024, 761, 699 \text{ cm}^{-1}$.

¹H NMR (500 MHz, CDCl₃): $\delta = 1.99$ (s, 3H), 2.91 (m, 2H), 3.47 (dd, 2H, $J = 13.3, 19.1$ Hz), 4.19 (t, 1H, $J = 7.4$ Hz), 7.18-7.34 (m, 10H).

¹³C NMR (125 MHz, CDCl₃): $\delta = 30.4, 35.6, 43.8, 49.9, 126.9, 127.3, 127.9, 128.4, 128.5, 128.8, 137.7, 141.4, 205.2$.

HPLC: Daicel Chiralcel OD-H, hexane/*i*PrOH = 9/1, flow rate = 1.0 ml/min.: $t_R = 8.3$ min (*R*), $t_R = 9.7$ min (*S*).

4b: (*R*)-3-(benzylthio)-1,3-diphenylpropan-1-one⁴



colorless solid; Mp 60 – 62 °C

IR (KBr): $\nu = 3058, 3023, 2894, 1679, 1595, 1448, 1341, 1224, 981, 921, 727, 693 \text{ cm}^{-1}$.

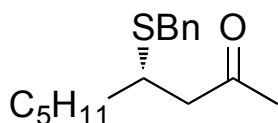
¹H NMR (600 MHz, CDCl₃): $\delta = 3.37$ -3.50 (m, 4H), 4.38 (d, 1H, $J = 5.1$ Hz), 7.12-7.25 (m, 8H), 7.30-7.34 (m, 4H), 7.45 (t, 1H, $J = 7.2$ Hz), 7.77 (d, 2H, $J = 6.9$ Hz).

¹³C NMR (150 MHz, CDCl₃): $\delta = 35.8, 44.1, 45.2, 127.0, 127.3, 128.0, 128.5, 128.5,$

128.9, 133.1, 136.6, 137.8, 141.7, 196.7.

HPLC: Daicel Chiralcel OJ-H, hexane/*i*PrOH = 4/1, flow rate = 1.0 ml/min.: t_R = 22.6 min (*S*), t_R = 33.1 min (*R*).

4c: (*S*)-4-(benzylthio)nonan-2-one⁴



colorless oil

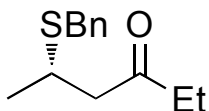
IR (KBr): ν = 2954, 2927, 2856, 1715, 1455, 1419, 1359, 1157, 701 cm^{-1} .

¹H NMR (600 MHz, CDCl₃): δ = 0.86 (t, 3H, J = 7.2 Hz), 1.16-1.37 (m, 6H), 1.46-1.50 (m, 2H), 2.08 (s, 3H), 2.63 (ddd, 2H, J = 6.7, 16.7, 20.2 Hz), 3.03 (t, 1H, J = 6.9 Hz), 3.73 (dd, 2H, J = 13.1, 8.3 Hz), 7.21-7.33 (m, 5H).

¹³C NMR (150 MHz, CDCl₃): δ = 14.0, 22.5, 26.2, 30.5, 31.5, 35.0, 40.3, 49.6, 126.9, 128.4, 128.9, 138.5, 207.0.

HPLC: Daicel Chiralcel OD-H, hexane/*i*PrOH = 100/1, flow rate = 1.0 ml/min.: t_R = 8.0 min (*S*), t_R = 8.7 min (*R*).

4d: (*S*)-5-(benzylthio)hexan-3-one⁴



colorless oil

IR (KBr): ν = 3061, 3028, 2973, 2934, 1712, 1494, 1454, 1410, 1361, 1239, 1199, 1115,

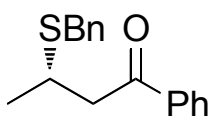
1070, 1027, 986, 769, 701 cm^{-1} .

^1H NMR (600 MHz, CDCl_3): δ = 1.02 (t, 3H, J = 7.2 Hz), 1.26 (d, 3H, J = 6.9 Hz), 2.34-2.37 (m, 2H), 2.50 (dd, 1H, J = 8.2, 16.7 Hz), 2.66 (dd, 1H, J = 7.6, 16.7 Hz), 3.15-3.21 (m, 1H), 3.75 (dd, 2H, J = 13.1, 7.9 Hz), 7.21-7.32 (m, 5H).

^{13}C NMR (150 MHz, CDCl_3): δ = 7.6, 21.5, 35.0, 35.5, 36.5, 49.5, 127.0, 128.5, 128.8, 138.3, 209.2.

HPLC: Daicel Chiralcel OD-H, hexane/*i*PrOH = 100/1, flow rate = 0.8 ml/min.: t_{R} = 13.2 min (*R*), t_{R} = 14.1 min (*S*).

4e: (*S*)-3-(benzylthio)-1-phenylbutan-1-one ⁵



colorless oil

IR (KBr): ν = 3584, 3060, 3027, 2964, 2921, 1683, 1597, 1580, 1493, 1449, 1353, 1221, 1180, 1071, 986, 753, 690, 641 cm^{-1} .

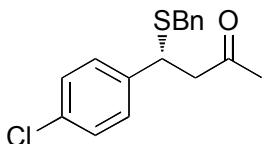
^1H NMR (500 MHz, CDCl_3): δ = 1.33 (d, 3H, J = 6.8 Hz), 3.05 (dd, 1H, J = 9.1, 17.0 Hz), 3.29 (dd, 1H, J = 5.1, 17.0 Hz), 3.34-3.41 (m, 1H), 1.53-1.58 (m, 1H), 3.80 (dd, 2H, J = 13.6, 17.6 Hz), 7.21-7.26 (m, 1H), 7.28-7.36 (m, 4H, J = 9.5), 7.40-7.48 (m, 2H), 7.53-7.56 (m, 1H), 7.83-7.92 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3): δ = 21.4, 35.3, 35.6, 46.0, 126.9, 128.0, 128.5, 128.6, 128.8, 133.1, 136.8, 138.3, 198.0.

HPLC: Daicel Chiralcel OD-H, hexane/*i*PrOH = 9/1, flow rate = 1.0 ml/min.: t_{R} = 7.1

min (*S*), $t_R = 7.8$ min (*R*).

4f: (*R*)-4-(benzylthio)-4-(4-chlorophenyl)butan-2-one ⁴



colorless oil

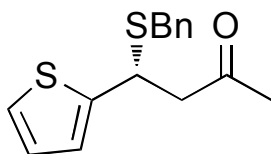
IR (KBr): $\nu = 3437, 2922, 1716, 1596, 1453, 1417, 1367, 1201, 1099, 953, 699$ cm^{-1} .

¹H NMR (600 MHz, CDCl₃): $\delta = 2.02$ (s, 3H), 2.89 (d, 2H, $J = 7.6$ Hz), 3.42 (d, 1H, $J = 13.7$ Hz), 3.52 (d, 1H, $J = 13.7$ Hz), 4.16 (t, 3H, $J = 7.5$ Hz), 7.18-7.29 (m, 9H).

¹³C NMR (150 MHz, CDCl₃): $\delta = 30.5, 35.7, 43.0, 49.8, 127.1, 128.5, 128.7, 128.9, 129.3, 132.9, 137.5, 140.1, 204.9$.

HPLC: Daicel Chiralpak AS-H, hexane/*i*PrOH = 9/1, flow rate = 0.5 ml/min.: $t_R = 19.8$ min (*R*), $t_R = 20.9$ min (*S*).

4g: (*R*)-4-(benzylthio)-4-(thiophen-2-yl)butan-2-one ⁴



colorless oil

IR (KBr): $\nu = 3583, 3063, 3028, 2918, 1713, 1493, 1450, 1417, 1360, 1242, 1154, 1043, 701, 661$ cm^{-1} .

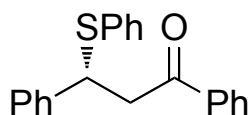
¹H NMR (600 MHz, CDCl₃): $\delta = 2.05$ (s, 3H), 2.97(ddd, 2H, $J = 7.2, 16.8, 21.3$ Hz),

3.61(dd, 2H, $J = 13.7, 18.5$ Hz), 4.51(t, 1H, $J = 7.2$ Hz), 6.91(m, 2H), 7.22-7.26 (m, 4H), 7.28-7.31 (m, 2H).

^{13}C NMR (150 MHz, CDCl_3): $\delta = 30.5, 35.9, 39.1, 50.8, 124.8, 125.8, 126.4, 127.1, 128.5, 128.9, 137.6, 146.3, 204.9$.

HPLC: Daicel Chiralpak AD-H, hexane/*i*PrOH = 9/1, flow rate = 0.5 ml/min.: $t_R = 13.1$ min (*S*), $t_R = 15.0$ min (*R*).

4h: (*R*)-1,3-diphenyl-3-(phenylthio)propan-1-one ⁶



colorless solid; Mp 115 – 118 °C

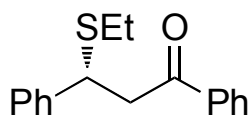
IR (KBr): $\nu = 3062, 2901, 1675, 1587, 1450, 1335, 1229, 1079, 981, 743, 734, 691$ cm^{-1} .

^1H NMR (600 MHz, CDCl_3): $\delta = 3.62$ (ddd, 2H, $J = 7.2, 17.2, 27.0$ Hz), 4.96 (dd, 1H, $J = 5.5, 8.3$ Hz), 7.17-7.34 (m, 10H), 7.42-7.45 (m, 2H), 7.53-7.56 (m, 1H), 7.87-7.89 (m, 2H).

^{13}C NMR (150 MHz, CDCl_3): $\delta = 14.0, 22.5, 26.3, 30.6, 31.5, 35.1, 35.7, 40.4, 44.6, 48.2, 49.6, 127.0, 127.4, 127.5, 127.8, 128.1, 128.4, 128.5, 128.6, 128.8, 132.7, 133.3, 134.2, 136.7, 138.5, 141.1, 197.0, 207.0$.

HPLC: Daicel Chiralcel OJ-H, hexane/*i*PrOH = 4/1, flow rate = 1.0 ml/min.: $t_R = 26.8$ min (*S*), $t_R = 60.3$ min (*R*).

4i: (*R*)-3-(ethylthio)-1,3-diphenylpropan-1-one ⁶



colorless solid; Mp 57 – 60 °C

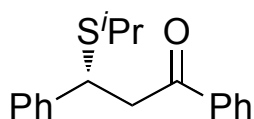
IR (KBr): $\nu = 2968, 2923, 1683, 1594, 1448, 1409, 1365, 1338, 1222, 979, 752, 713, 695 \text{ cm}^{-1}$.

¹H NMR (600 MHz, CDCl₃): $\delta = 1.17$ (t, 3H, $J = 7.2$ Hz), 2.36 (q, 2H, $J = 7.6$ Hz), 3.54 (dd, 2H, $J = 3.7, 7.2$ Hz), 4.59 (t, 1H), 7.26-7.55 (m, 8H), 7.92 (d, 2H, $J = 8.3$ Hz).

¹³C NMR (150 MHz, CDCl₃): $\delta = 14.3, 25.4, 43.9, 45.3, 127.2, 127.8, 128.1, 128.5, 128.6, 133.2, 136.7, 142.2, 197.0$.

HPLC: Daicel Chiralpak AS-H, hexane/*i*PrOH = 9/1, flow rate = 0.5 ml/min.: $t_R = 12.4$ min (*R*), $t_R = 15.7$ min (*S*).

4j: (*R*)-3-(isopropylthio)-1,3-diphenylpropan-1-one ⁶



colorless solid; Mp 77 – 80 °C

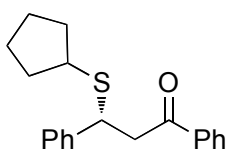
IR (KBr): $\nu = 3061, 2965, 2924, 2866, 1638, 1589, 1449, 1364, 1334, 1222, 979, 750, 710, 694 \text{ cm}^{-1}$.

¹H NMR (600 MHz, CDCl₃): $\delta = 1.06$ (d, 3H, $J = 6.9$ Hz), 1.20 (d, 3H, $J = 6.9$ Hz), 2.56 (sep, 1H, $J = 6.7$ Hz), 3.45 (m, 2H), 4.56 (t, 1H, $J = 1.7$ Hz), 7.12-7.15 (m, 1H), 7.21-7.24 (m, 2H), 7.35-7.38 (m, 4H), 7.46-7.49 (m, 1H), 7.84 (d, 2H, $J = 7.5$ Hz).

^{13}C NMR (150 MHz, CDCl_3): $\delta = 22.9, 23.4, 34.6, 43.3, 45.7, 127.1, 127.8, 128.1, 128.5, 128.6, 133.2, 136.8, 142.6, 197.0$.

HPLC: Daicel Chiralpak AS-H, hexane/*i*PrOH = 9/1, flow rate = 0.5 ml/min.: $t_{\text{R}} = 10.8$ min (*R*), $t_{\text{R}} = 12.2$ min (*S*).

4k: (*R*)-3-(cyclopentylthio)-1,3-diphenylpropan-1-one ⁶



colorless solid; Mp 67 – 69 °C

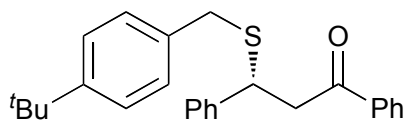
IR (KBr): $\nu = 2953, 2861, 1714, 1682, 1595, 1493, 1449, 1410, 1361, 1337, 1229, 1075, 1050, 980, 749, 725, 700, 687 \text{ cm}^{-1}$.

^1H NMR (500 MHz, CDCl_3): $\delta = 1.31\text{-}1.38$ (m, 1H), 1.41-1.54 (m, 2H), 1.57-1.81 (m, 4H), 1.93-2.00 (m, 1H), 2.80 (ddd, 1H, $J = 7.4, 7.2, 14.3$ Hz), 3.53 (q, 2H, $J = 7.1$ Hz), 4.59 (t, 1H, $J = 7.1$ Hz), 7.19-7.22 (m, 1H), 7.26-7.31 (m, 2H), 7.41-7.45 (m, 4H), 7.52-7.55 (m, 1H), 7.90-7.91 (m, 2H).

^{13}C NMR (125 MHz, CDCl_3): $\delta = 24.7, 24.9, 33.1, 34.0, 43.1, 44.4, 45.5, 127.1, 127.7, 128.1, 128.1, 128.4, 128.6, 133.1, 136.8, 197.0$.

HPLC: Daicel Chiralpak AS-H, hexane/*i*PrOH = 9/1, flow rate = 0.5 ml/min.: $t_{\text{R}} = 12.4$ min (*R*), $t_{\text{R}} = 13.6$ min (*S*).

4l: (*R*)-3-((4-(*tert*-butyl)benzyl)thio)-1,3-diphenylpropan-1-one ⁶



colorless solid; Mp 82 – 84 °C

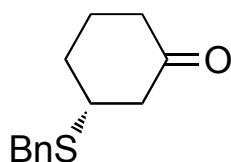
IR (KBr): $\nu = 3429, 2960, 1682, 1450, 1363, 1342, 1230, 754, 705, 696 \text{ cm}^{-1}$.

^1H NMR (500 MHz, CDCl_3): $\delta = 1.29$ (s, 9H), 3.43-3.56 (m, 4H), 4.48 (dd, 1H, $J = 6.2, 7.9$ Hz), 7.14 (d, 2H, $J = 7.9$ Hz), 7.19-7.22 (m, 1H), 7.27-7.31 (m, 4H), 7.35-7.39 (m, 4H), 7.40-7.51 (m, 1H), 7.83 (d, 2H, $J = 7.9$ Hz).

^{13}C NMR (125 MHz, CDCl_3): $\delta = 31.3, 34.4, 35.3, 44.1, 45.2, 125.3, 127.2, 128.0, 128.4, 128.5, 128.5, 133.1, 134.7, 136.6, 141.7, 149.7, 196.7$.

HPLC: Daicel Chiralcel OJ-H, hexane/*i*PrOH = 7/3, flow rate = 0.5 ml/min.: $t_R = 23.7$ min (*R*), $t_R = 30.3$ min (*S*).

4m: (*R*)-3-(benzylthio)cyclohexanone ⁷



colorless oil

IR (KBr): $\nu = 3060, 3027, 2940, 2867, 1712, 1601, 1493, 1451, 1421, 1314, 1222, 1094, 1069, 1030, 971, 766, 703 \text{ cm}^{-1}$.

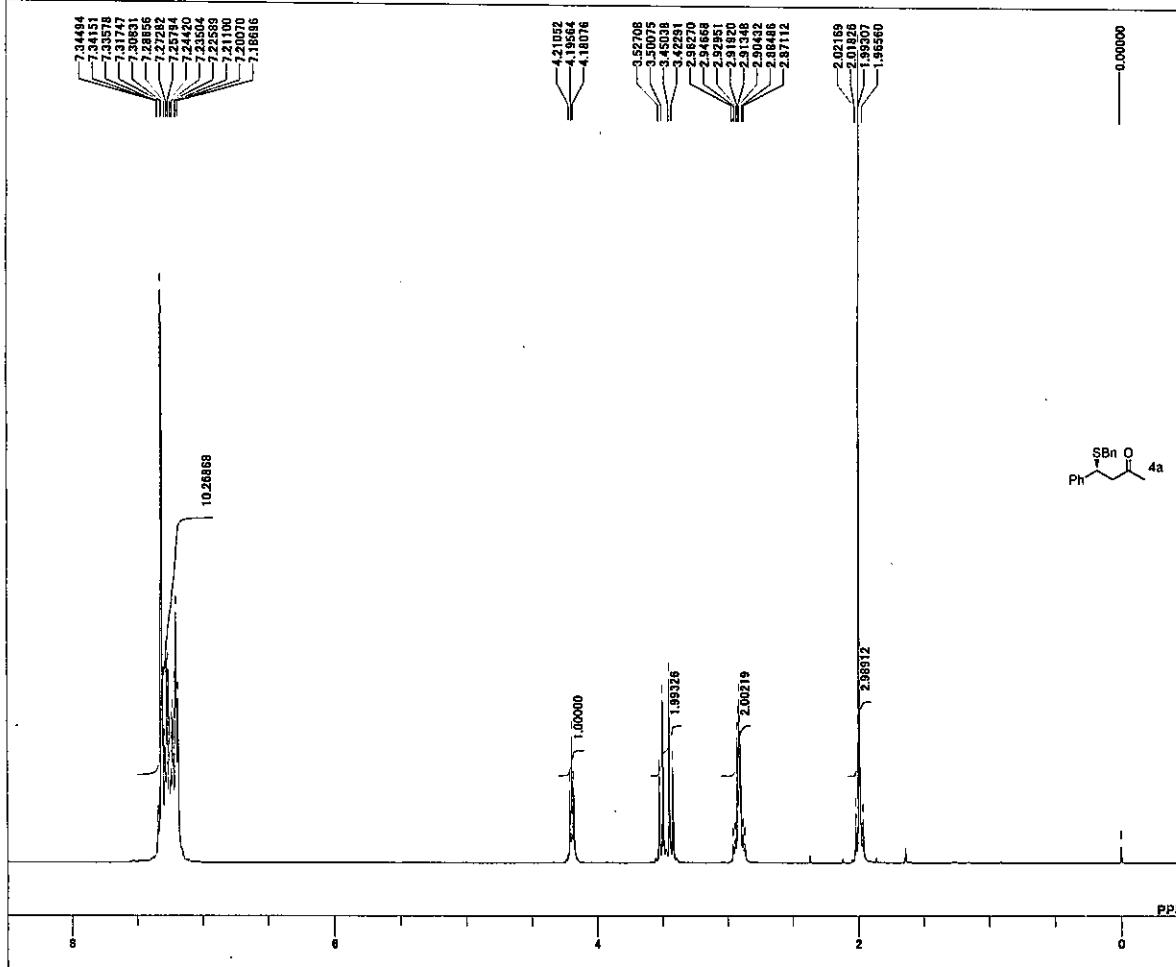
^1H NMR (600 MHz, CDCl_3): $\delta = 1.61$ -1.75 (m, 2H), 2.05-2.12 (m, 2H), 2.26-2.40 (m, 3H), 2.66 (dd, 1H, $J = 4.5$ Hz), 2.89-2.95 (m, 1H), 3.75 (dd, $J = 13.6, 16.4$ Hz), 7.22-7.34 (m, 5H)

^{13}C NMR (150 MHz, CDCl_3): δ = 24.0, 31.2, 34.8, 40.9, 41.8, 47.7, 127.0, 128.5, 128.6, 137.8, 208.7.

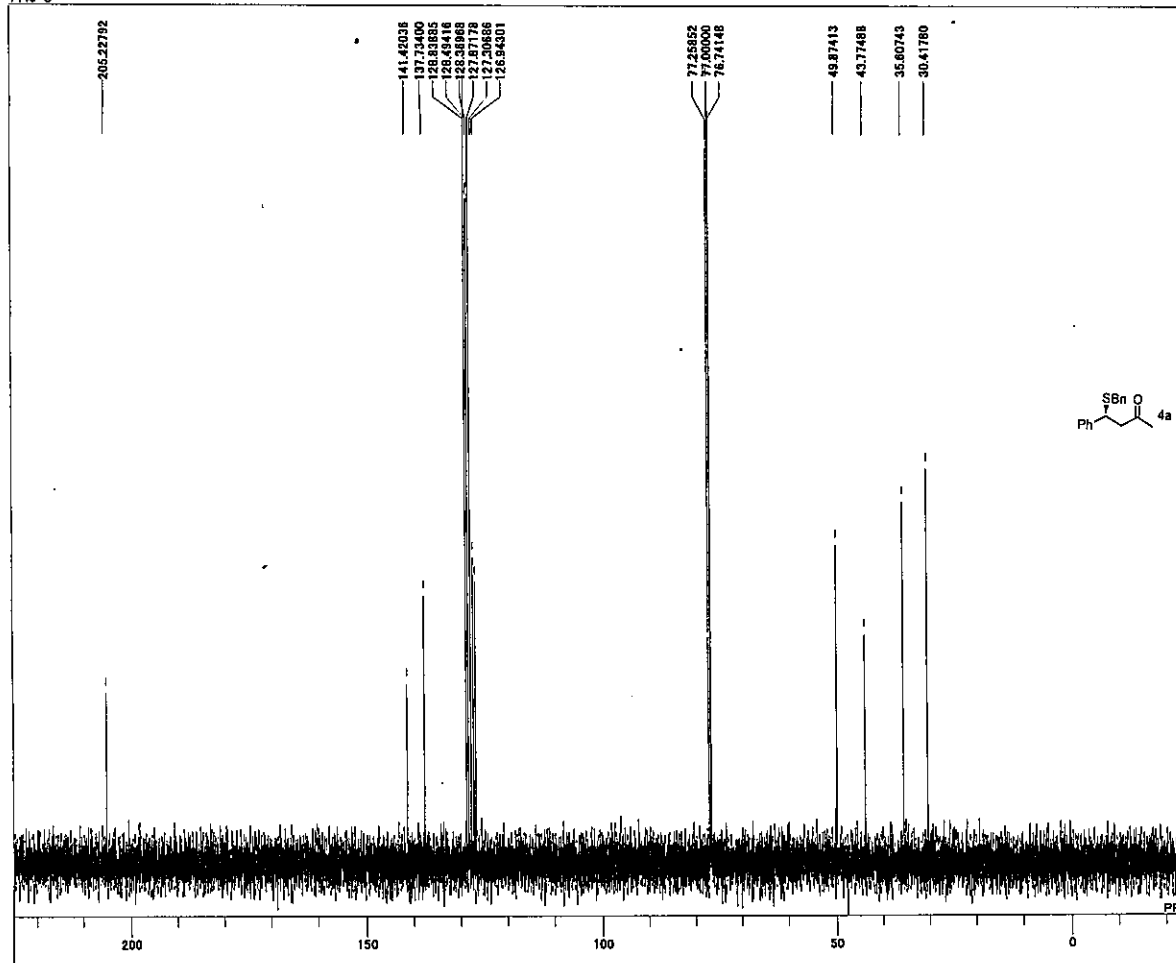
HPLC: Daicel Chiralpak AD-H, hexane/*i*PrOH = 9/1, flow rate = 0.5 ml/min.: t_{R} = 14.6 min (*R*), t_{R} = 16.0 min (*S*).

References

1. Ishikawa, S.; Hamada, T.; Manabe, K.; Kobayashi, S. *Synthesis*, **2005**, 2176.
2. (a) Thom, K. F., **1971**, US Patent 3615169. See, also: (b) Kobayashi, S. *Synlett*, **1994**, 689.
3. Kobayashi, S.; Wakabayashi, T. *Tetrahedron Lett.*, **1998**, 39, 5389.
4. Ricci, P.; Carlone, A.; Bartoli, G.; Bosco, M.; Sambri, L.; Melchiorre, P. *Adv. Synth. Catal.*, **2008**, 350, 49.
5. Yin, Y.; Jiang, H.; Ma, J.; Zhang, H.; Yin, C.; Li, S. *Huaxue Yanjiu Yu Yingyong*, **2010**, 22, 492.
6. Dai, L.; Wang, S-X.; Chen, F-E. *Adv. Synth. Catal.*, **2010**, 352, 2137.
7. Saito, M.; Nakajima, M.; Hashimoto, S. *Tetrahedron*, **2000**, 56, 9589.

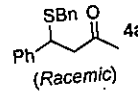
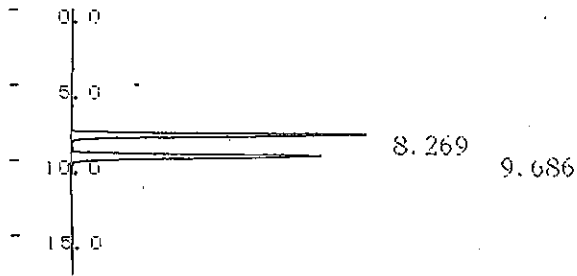


DFILE C:\Documents and Settings\VALICE2\Desktop\1445-H
COMNT 17-01-2011 18:02:42
DATIM 1445-H
OBNUC 1H
EXMOD 1H NMR.ex2
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 3.84 Hz
POINT 16384
FREQU 9286.78 Hz
SCANS 8
ACQTM 1.7842 sec
PD 5.0000 sec
PWI 5.80 usec
IRNUC 1H
CTEMP 19.1 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 32



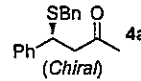
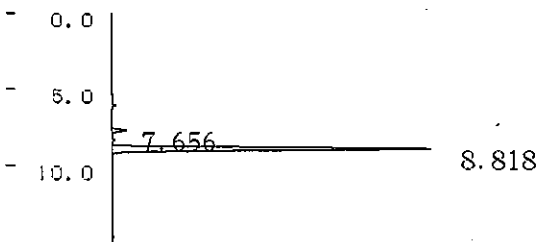
DFILE C:\Documents and Settings\VALICE2\Desktop\1445-C
COMNT 17-01-2011 18:09:50
DATIM 1445-C
OBNUC 13C
EXMOD 13C NMR.ex2
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 32768
FREQU 39082.50 Hz
SCANS 115
ACQTM 6.8389 sec
PD 2.0000 sec
PWI 3.67 usec
IRNUC 1H
CTEMP 19.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

Analysis FILE : 9:@FIL15.FIL



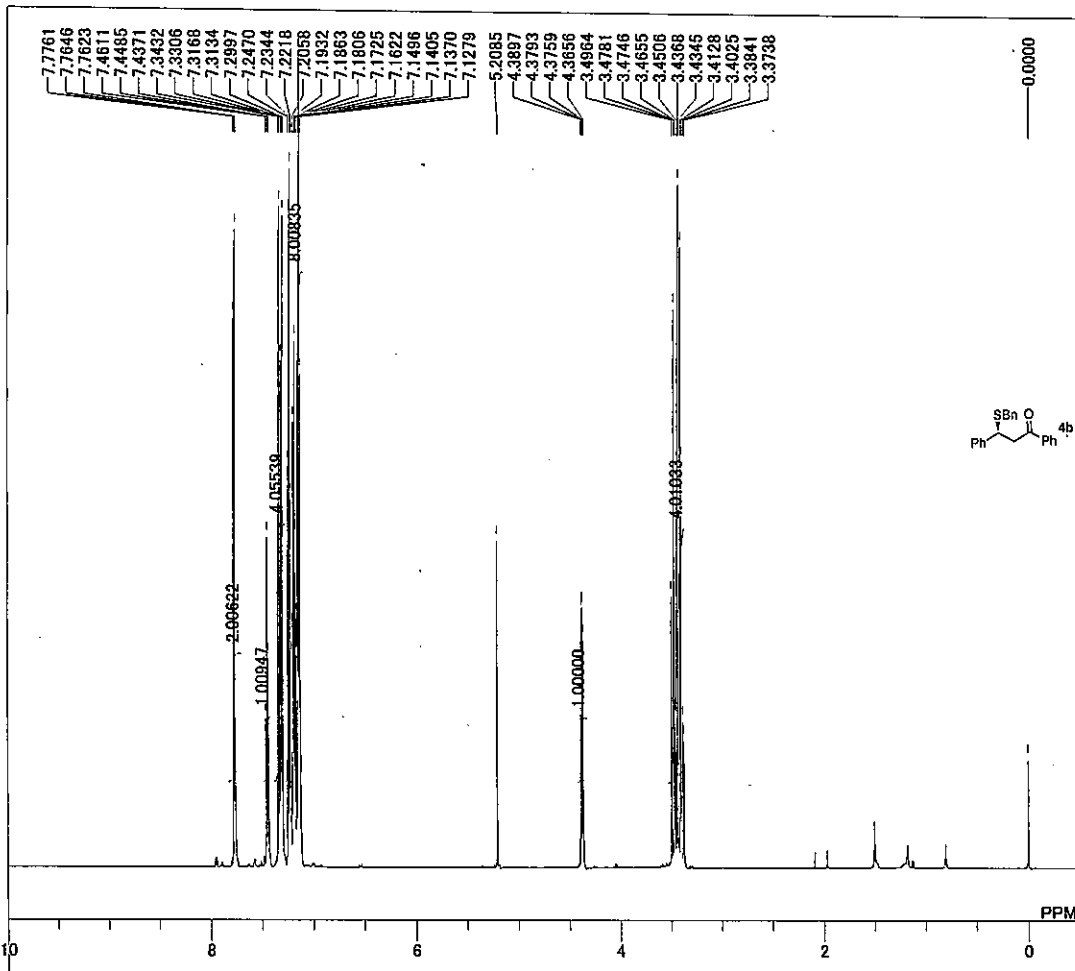
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	12	8.269	275868	17746	V		50.2205	
	14	9.686	273445	15029	V		49.7795	
TOTAL			549313	32775			100	

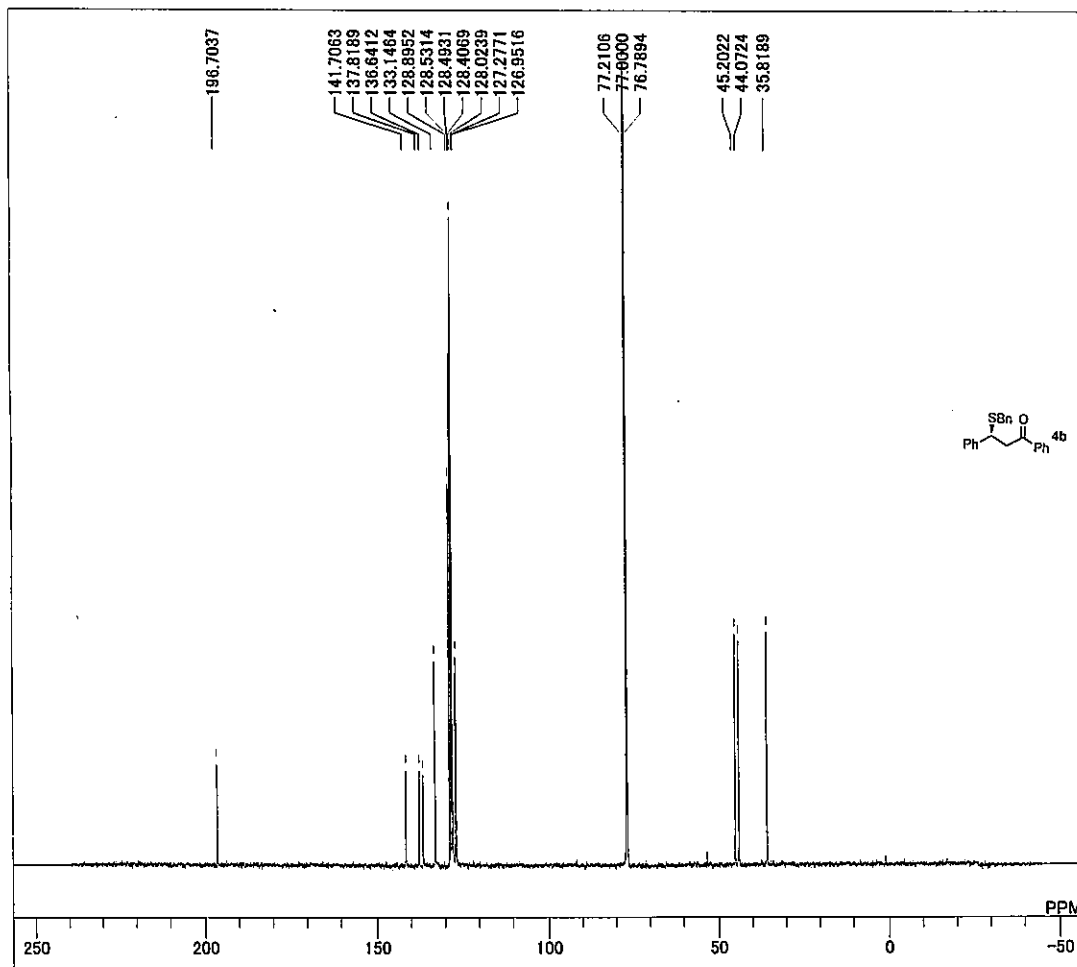


** CALCULATION REPORT **

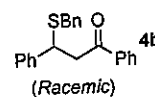
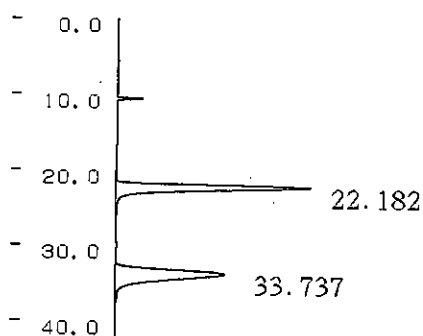
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	18	7.656	152323	13641	V		3.4792	
	20	8.818	4225784	306409	SV		96.5208	
TOTAL			4378107	320051			100	



DFILE 17-02-2011 22:03:54
 COMINT 1H
 DATIM single_pulse.ex2
 OBNUC 600.17 MHz
 EXMOD 5.30 KHz
 OBFRQ 5.47 Hz
 OBSET 16384
 OBFIN 11261.26 Hz
 POINT 16
 FREQU 1.4549 sec
 SCANS 4.0000 sec
 ACQTM 6.50 usec
 PD 1H
 PW1 18.4 c
 IRNUC CDCL3
 CTEMP 0.00 ppm
 SLVNT 0.12 Hz
 EXREF 38
 BF
 RGAIN

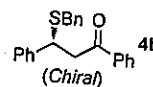


DFILE 17-02-2011 10:17:37
 COMINT 13C
 DATIM single_pulse_dec
 OBNUC 150.92 MHz
 EXMOD 8.52 KHz
 OBFRQ 1.74 Hz
 OBSET 40961
 OBFIN 59186.51 Hz
 POINT 1024
 FREQU 0.8921 sec
 SCANS 2.0000 sec
 ACQTM 2.87 usec
 PD 1H
 PW1 19.9 c
 IRNUC CDCL3
 CTEMP 225.35 ppm
 SLVNT 0.12 Hz
 EXREF 60
 BF
 RGAIN



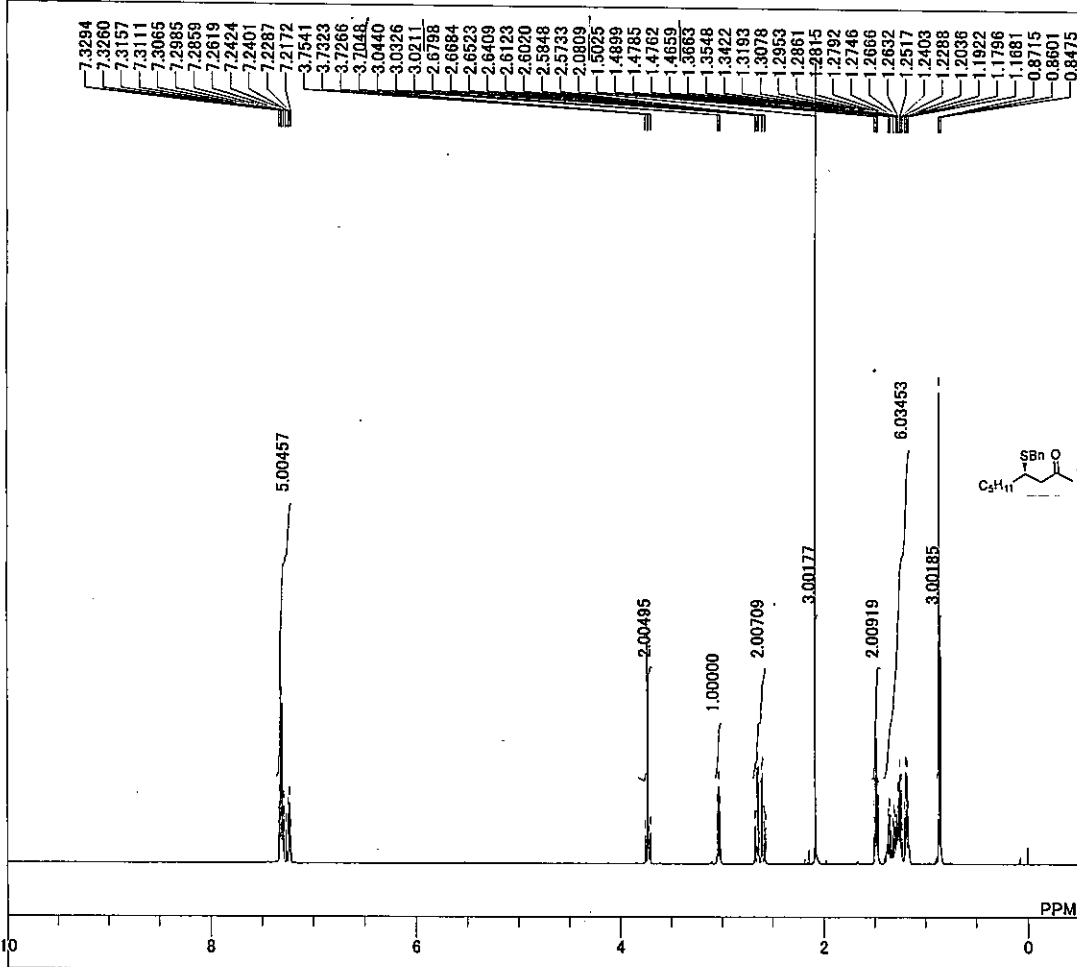
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	18	22.182	9529701	186725			49.874	
	20	33.737	9577868	105408			50.126	
TOTAL			19107568	292133			100	



** CALCULATION REPORT **

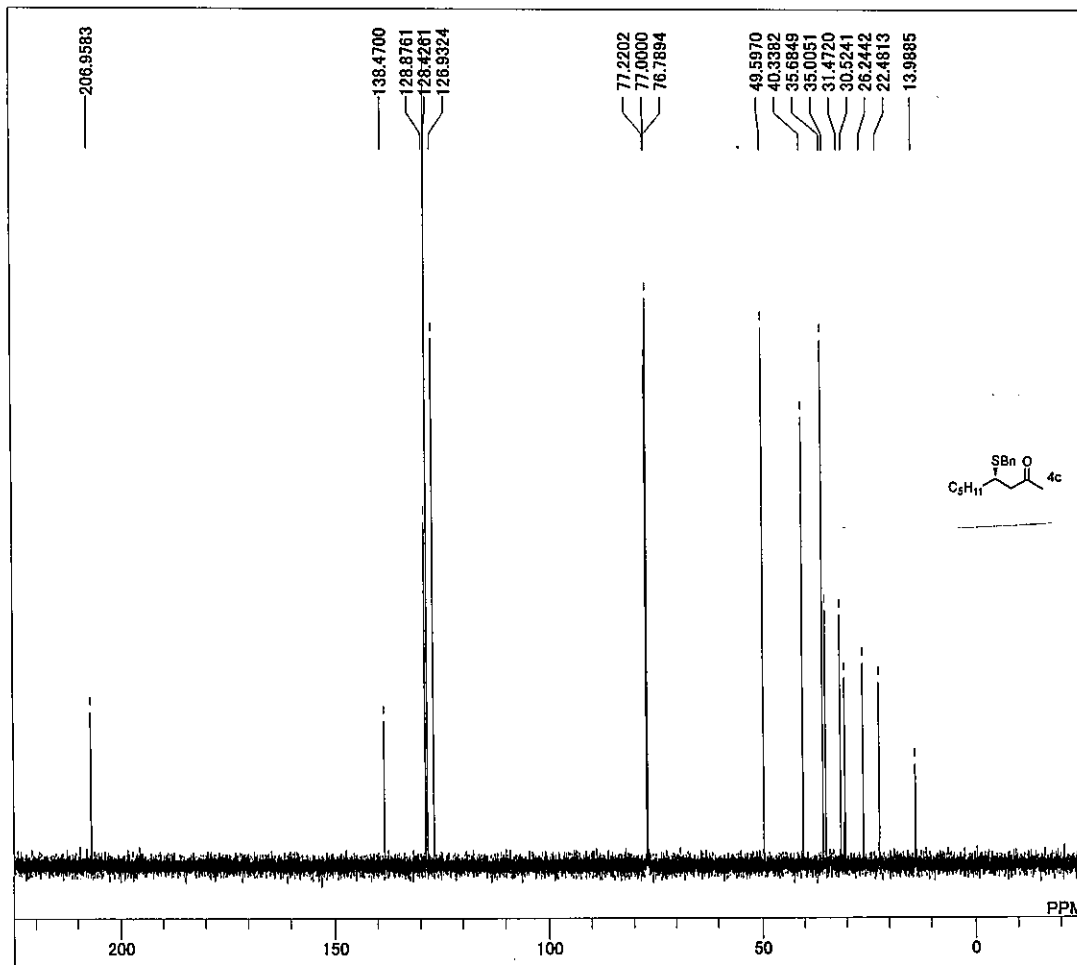
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	51	22.591	66171	1406			13.6724	
	56	33.144	417806	6024			86.3276	
TOTAL			483977	7431			100	



DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFREQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

1H
single_pulse.ex2
600.17 MHz
5.30 KHz
5.47 Hz
16384
11261.26 Hz
8
1.4549 sec
2.0000 sec
6.50 usec

1H
17.9 c
CDCL3
0.00 ppm
0.12 Hz
32



DFILE
COMNT
DATIM
OBNUC
EXMOD
OBFREQ
OBSET
OBFIN
POINT
FREQU
SCANS
ACQTM
PD
PW1
IRNUC
CTEMP
SLVNT
EXREF
BF
RGAIN

13C
18-02-2011 09:58:22
single_pulse_dec
150.92 MHz
8.52 KHz
1.74 Hz
32768
47348.49 Hz
102
0.6921 sec
2.0000 sec
2.87 usec

1H
18.9 c
CDCL3
77.00 ppm
0.12 Hz
60

C-RSA CHROMATOPAC CH=1 Report No.=57

DATA=1:@CHRM1.C00 11/02/18 21:20:08

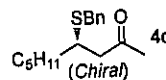
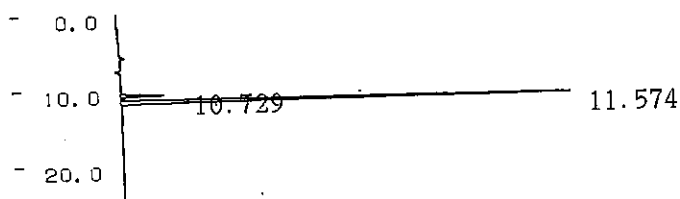


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	30	8.931	842195	68494	V		50.104	
	31	9.645	838698	63154	V		49.8959	
TOTAL			1680893	131648			100	

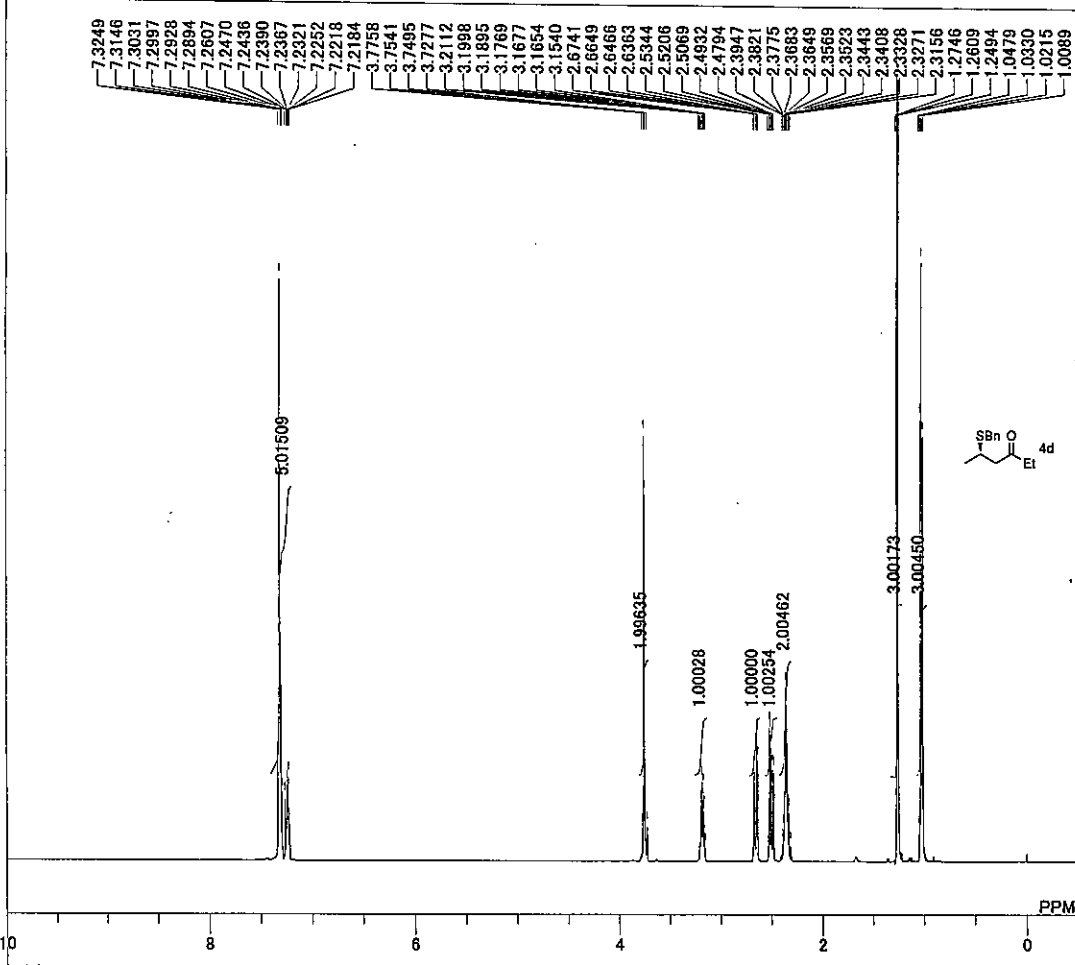
C-RSA CHROMATOPAC CH=1 Report No.=14

DATA=1:@CHRM1.C00 11/02/18 11:13:06

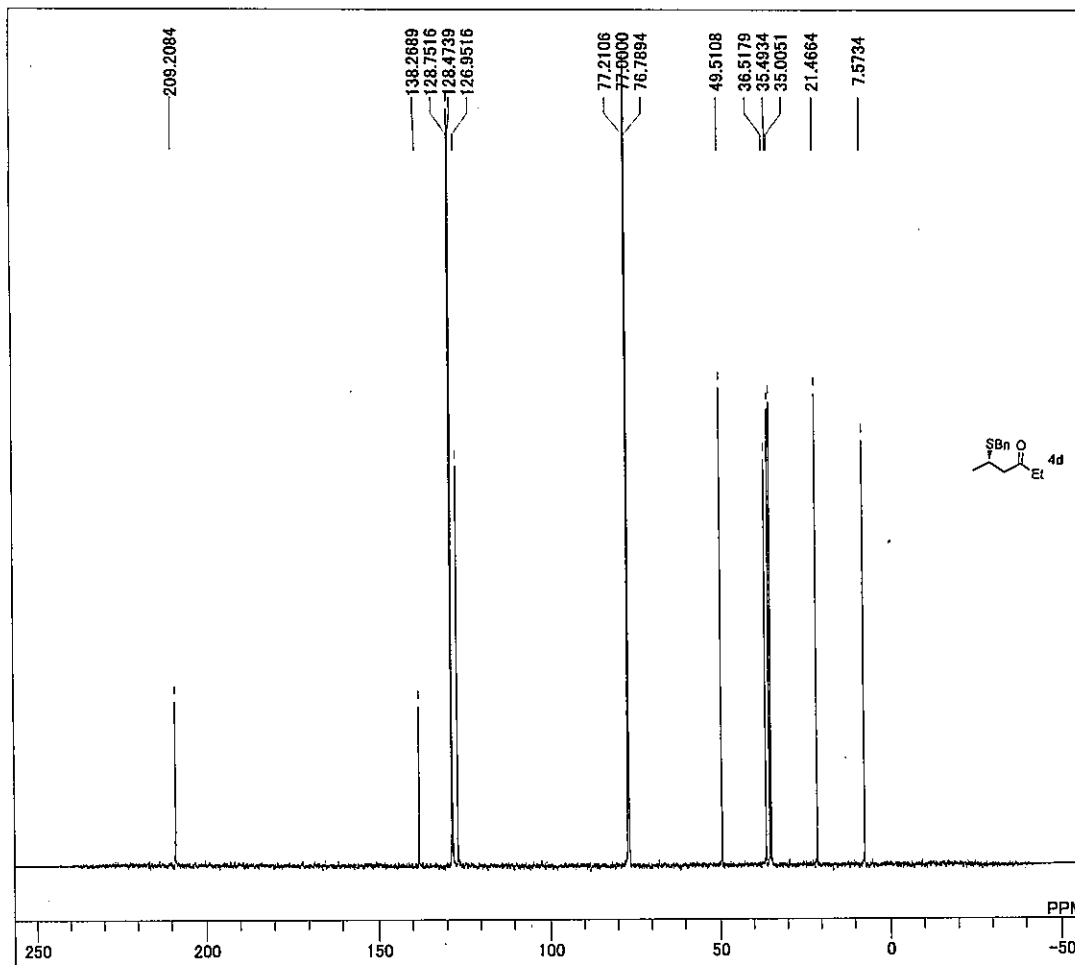


** CALCULATION REPORT **

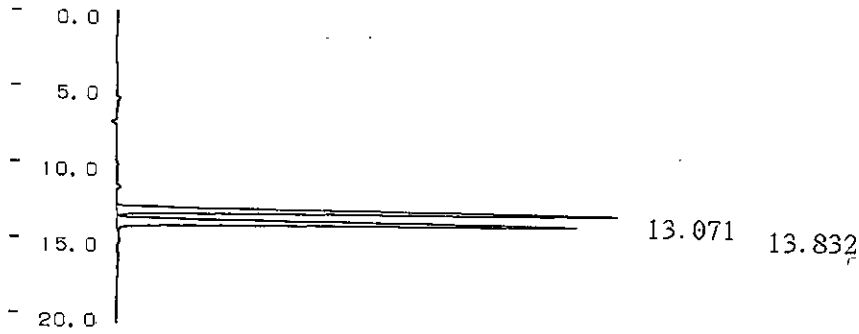
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	4	10.729	146839	10313			8.1848	
	5	11.574	1647210	107556	V		91.8152	
TOTAL			1794049	117869			100	



DFILE
COMNT
DATIM 16-02-2011 02:25:50
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 13107
FREQU 9008.87 Hz
SCANS 8
ACQTM 1.4549 sec
PD 2.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 17.6 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 34

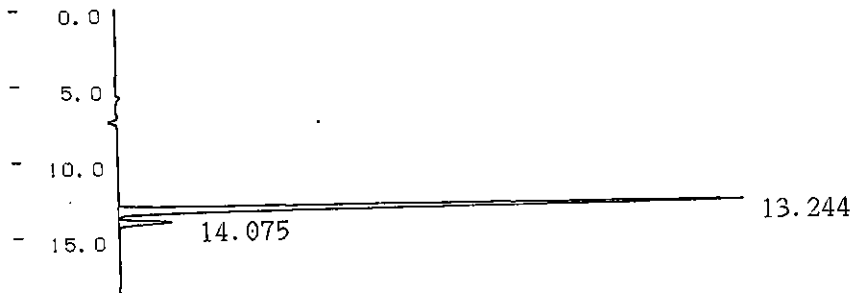
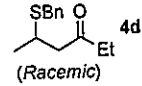


DFILE
COMNT
DATIM 16-02-2011 12:33:59
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 40961
FREQU 59186.51 Hz
SCANS 1024
ACQTM 0.6921 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 19.6 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



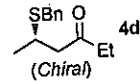
** CALCULATION REPORT **

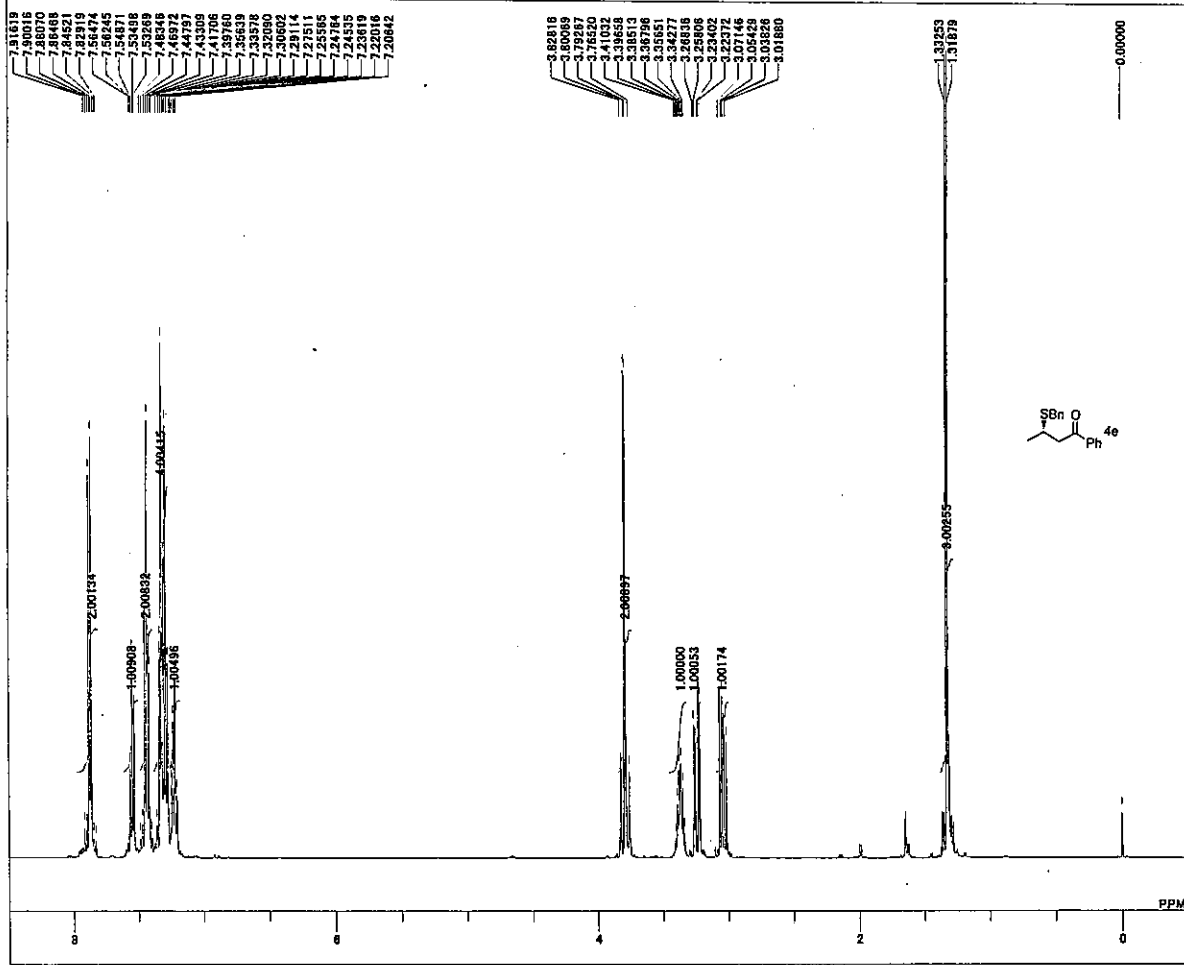
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	7	13.071	919712	60300	V		49.2023	
	8	13.832	949535	55259	V		50.7977	
TOTAL			1869247	115559			100	



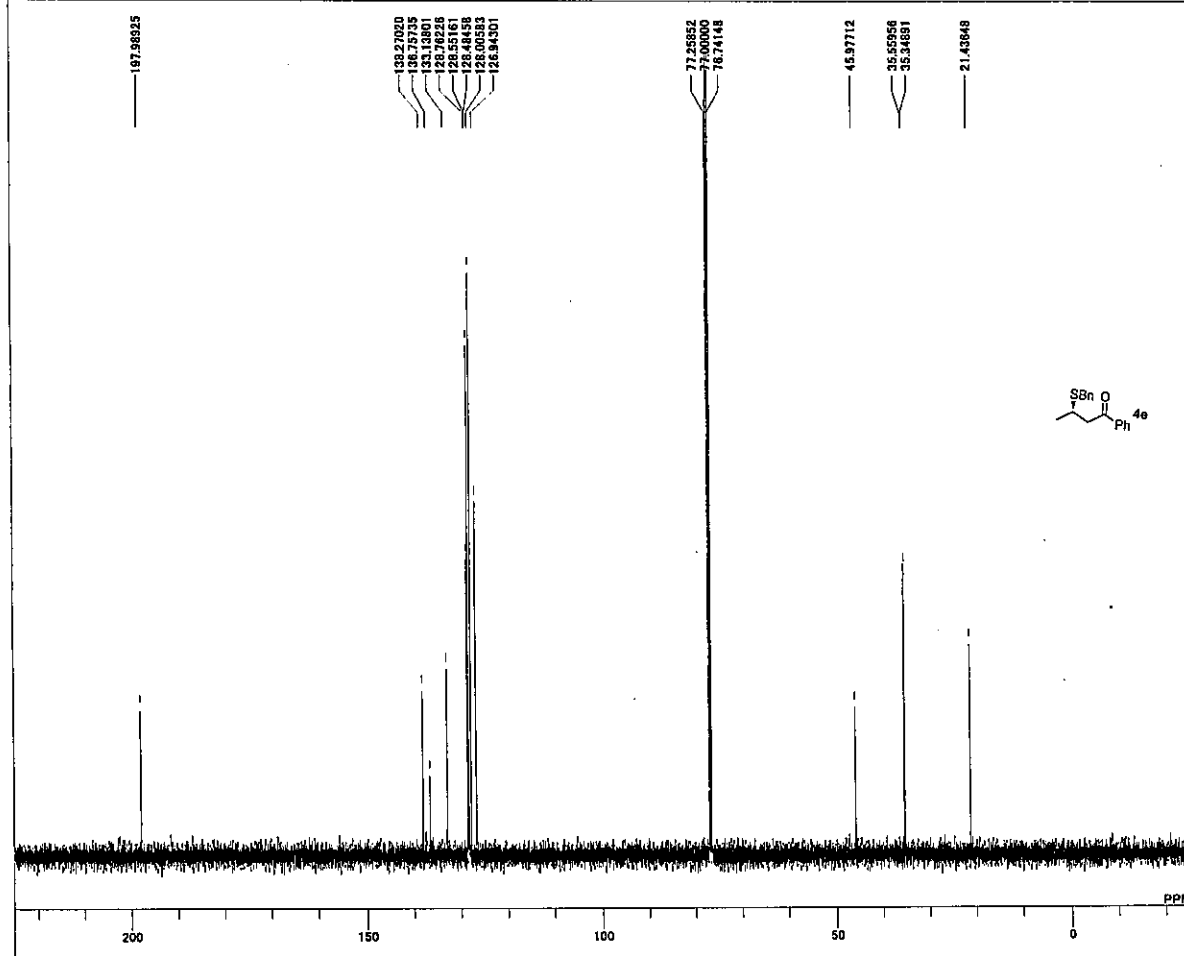
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	7	13.244	1205202	75281	V		91.8344	
	8	14.075	107162	6372	V		8.1656	
TOTAL			1312364	81654			100	





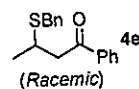
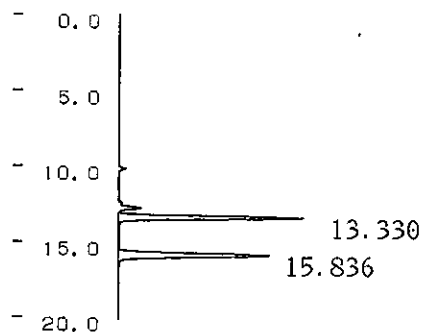
DFILE C:\Documents and Settings\VALICEZY\Desktop\1497-H-1.jdf
COMNT 1497-H
DATM 18-02-2011 13:30:34
IN 1H
INMR 1H NMR.ex2
OBNUC 495.13 MHz
EXMOD 4.38 KHz
OBFRQ 9.84 Hz
OBSET 16384
OBFIN 9286.78 Hz
POINT 8
FREQU 8
SCANS 1.7642 sec
ACQTM 5.0000 sec
PD 5.80 usec
PW1 1H
IRNUC 18.2 °
CTEMP CDCL3
SLVNT 0.00 ppm
EXREF 0.12 Hz
BF 34
RGAIN



DFILE C:\Documents and Settings\VALICEZY\Desktop\1497-C-1.jdf
COMNT 1497-C
DATM 18-02-2011 13:51:06
IN 13C
INMR 13C NMR.ex2
OBNUC 124.51 MHz
EXMOD 3.45 KHz
OBFRQ 6.00 Hz
OBSET 32768
OBFIN 39062.50 Hz
POINT 412
FREQU 0.8389 sec
SCANS 2.0000 sec
ACQTM 3.67 usec
PD 1H
IRNUC 18.9 °
CTEMP CDCL3
SLVNT 77.00 ppm
EXREF 0.12 Hz
BF 80
RGAIN

C-RSA CHROMATOPAC CH=1 Report No.=47

DATA=1:@CHRM1.C00 11/02/18 20:01:04

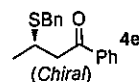
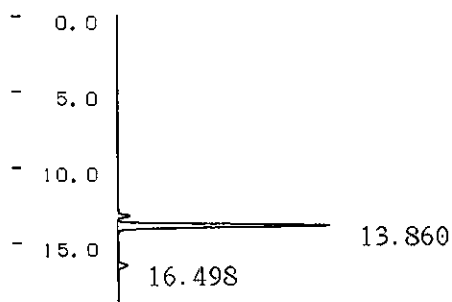


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	32	13.33	5367378	355094	SV		50.2085	
	35	15.836	5322805	288860	V		49.7915	
TOTAL			10690183	643954			100	

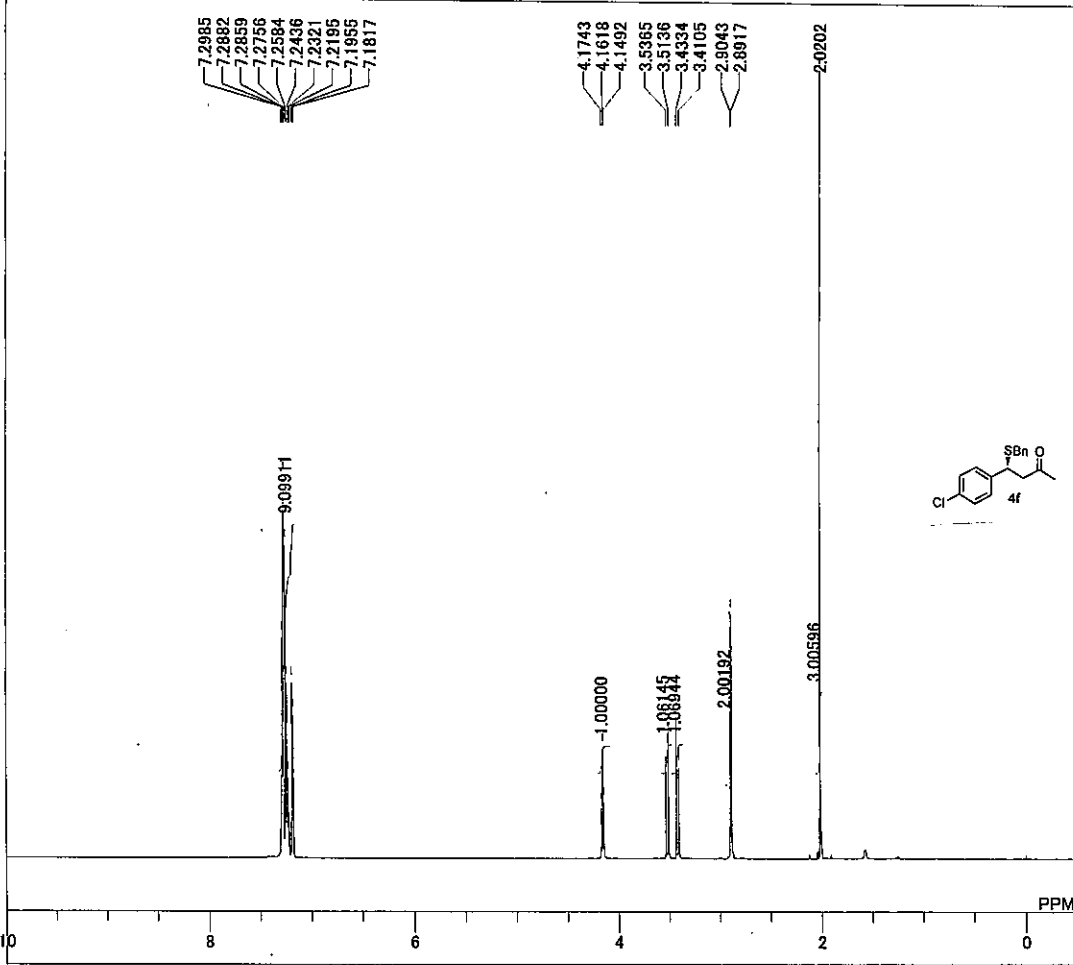
C-RSA CHROMATOPAC CH=1 Report No.=31

DATA=1:@CHRM1.C00 11/02/17 22:03:50

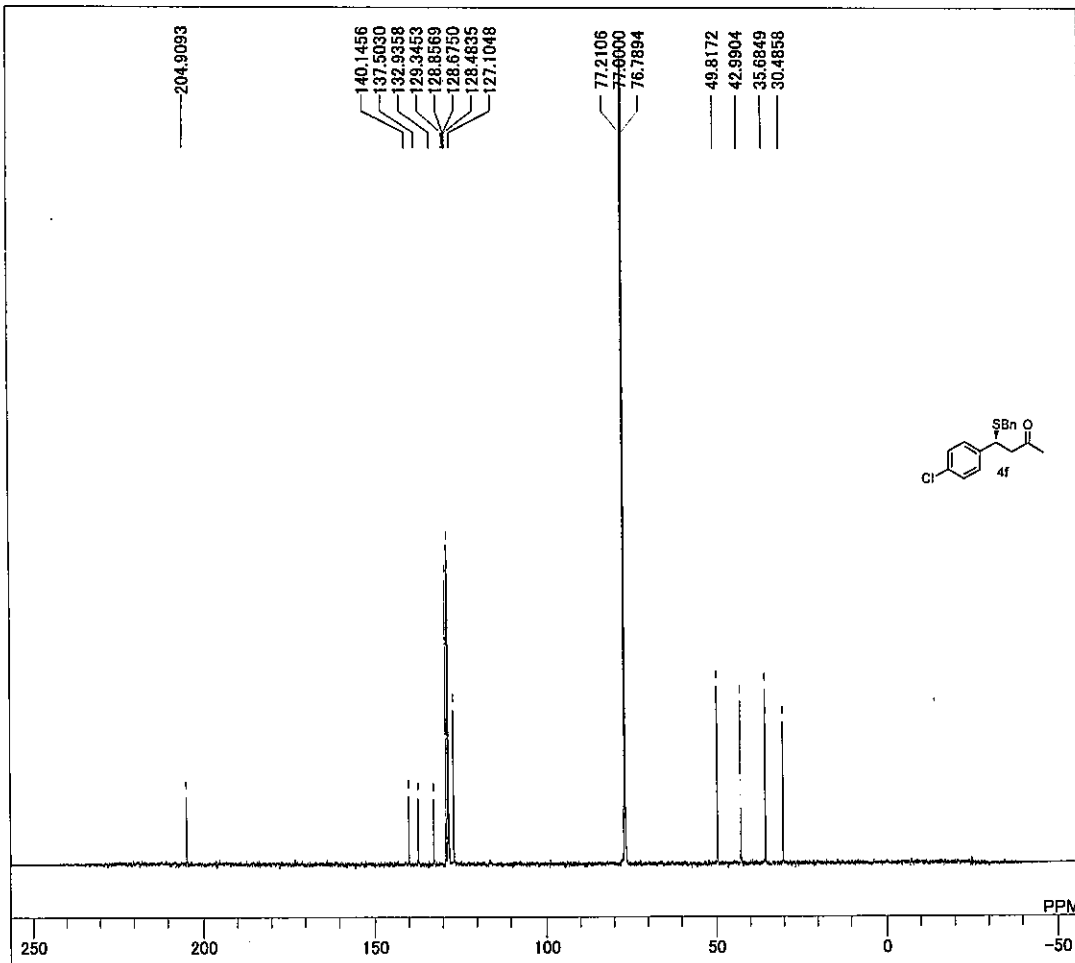


** CALCULATION REPORT **

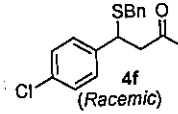
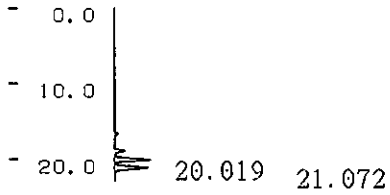
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	26	13.86	6256930	408504	SV		95.0076	
	29	16.498	328787	17682			4.9924	
TOTAL			6585717	426186			100	



DFILE C:\Documents and Settings\delta\My D
COMNT single_pulse
DATIM 15-02-2011 05:24:44
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 13107
FREQU 9008.87 Hz
SCANS 8
ACQTM 1.4549 sec
PD 2.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 18.0 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 40

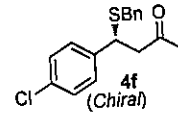


DFILE C:\Documents and Settings\delta\デスク
COMNT 16-02-2011 09:51:12
DATIM
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 40961
FREQU 59186.51 Hz
SCANS 1024
ACQTM 0.6921 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 19.2 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 58



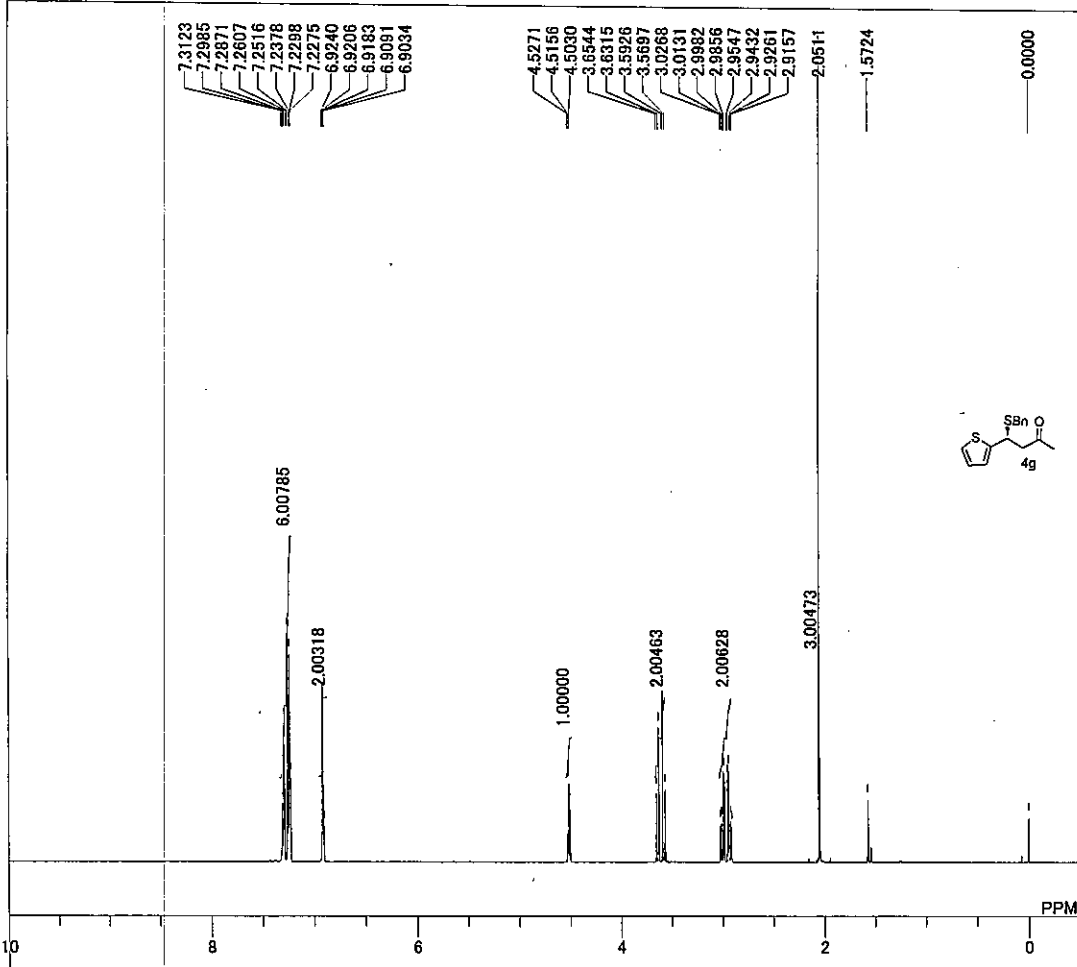
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	51	20.019	422989	16888	V		50.3544	
	52	21.072	417034	15733	V		49.6455	
TOTAL			840023	32621			100	

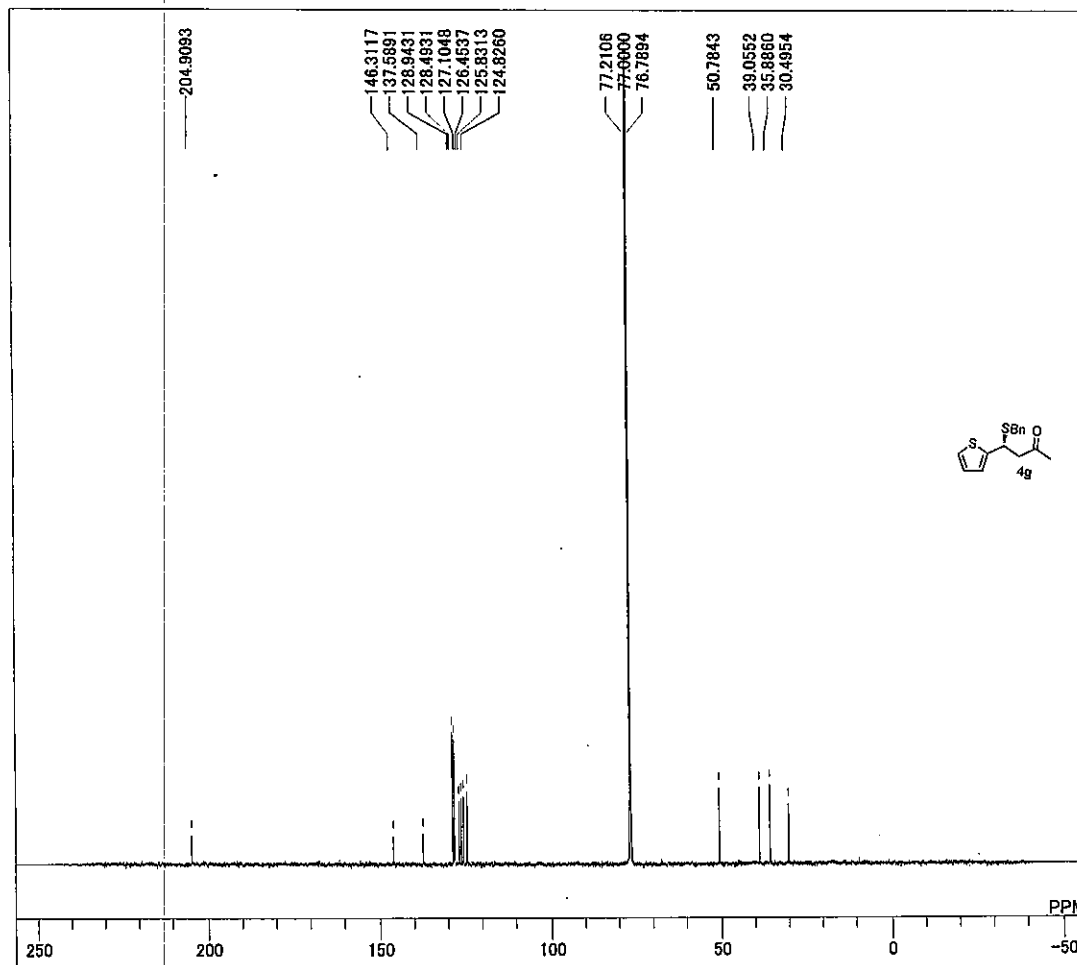
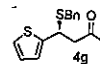


** CALCULATION REPORT **

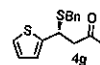
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	37	19.834	6071240	236693	V		96.2743	
	38	20.945	234947	8628	V		3.7257	
TOTAL			6306187	245320			100	



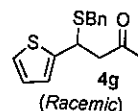
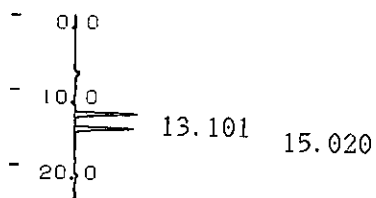
DFILE C:\Documents and Settings\delta\My D
COMNT single_pulse
DATIM 16-02-2011 02:44:54
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 13107
FREQU 9008.87 Hz
SCANS 8
ACQTM 1.4549 sec
PD 2.0000 sec
PWI 6.50 usec
IRNUC 1H
CTEMP 17.8 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42



DFILE C:\Documents and Settings\delta\My D
COMNT single_pulse_dec
DATIM 16-02-2011 13:28:06
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 40961
FREQU 59186.51 Hz
SCANS 1024
ACQTM 0.6921 sec
PD 2.0000 sec
PWI 2.87 usec
IRNUC 1H
CTEMP 19.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



Analysis FILE : 9:@FIL15.FIL



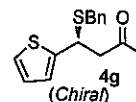
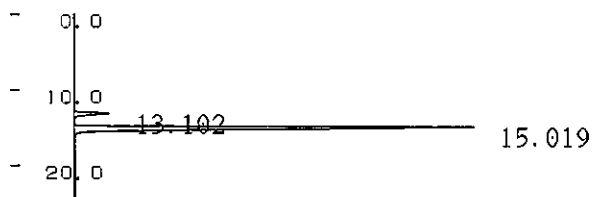
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	7	13.101	83705	3770			50.4681	
	8	15.02	82152	3498			49.5319	
TOTAL			165857	7268			100	

C-RSA CHROMATOPAC CH=1 Report No.=6

DATA=1:@CHRM1.C00 11/02/17 23:13:42

Analysis FILE : 9:@FIL15.FIL

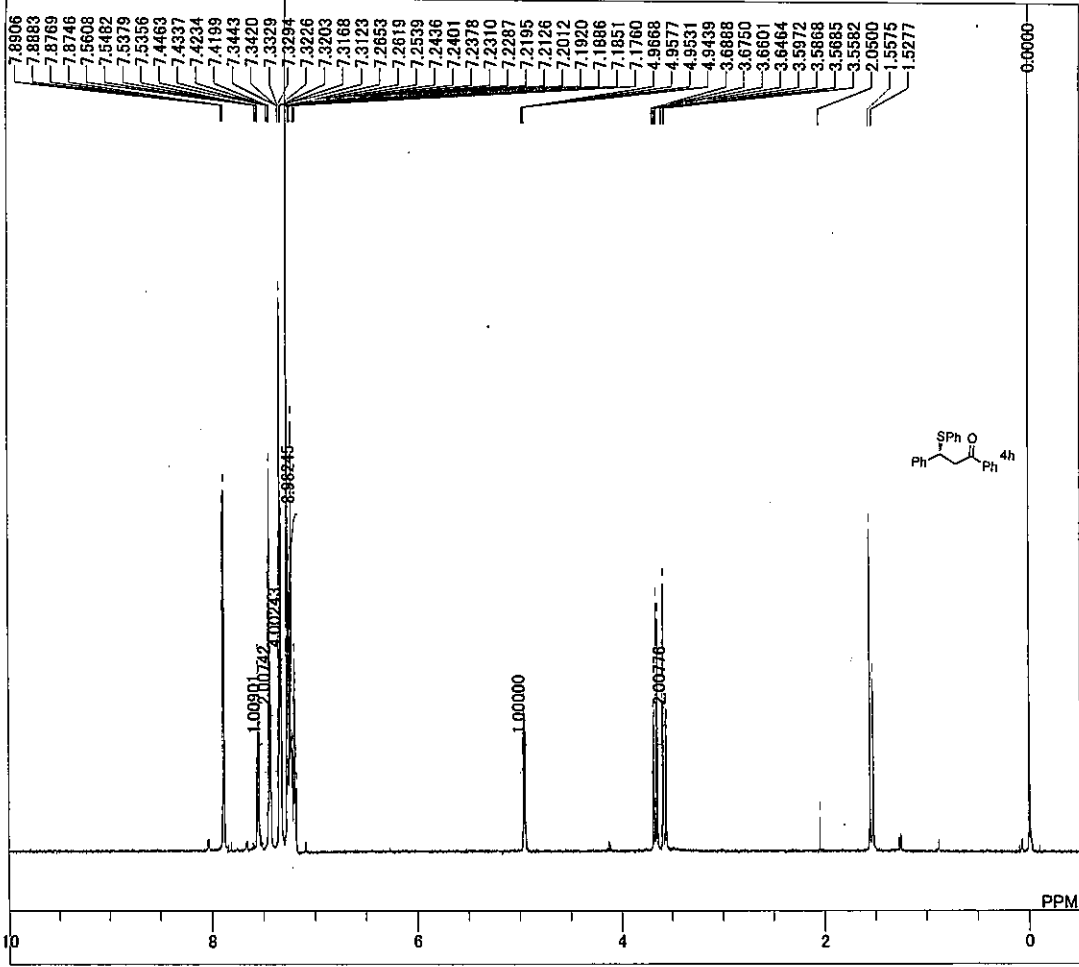


** CALCULATION REPORT **

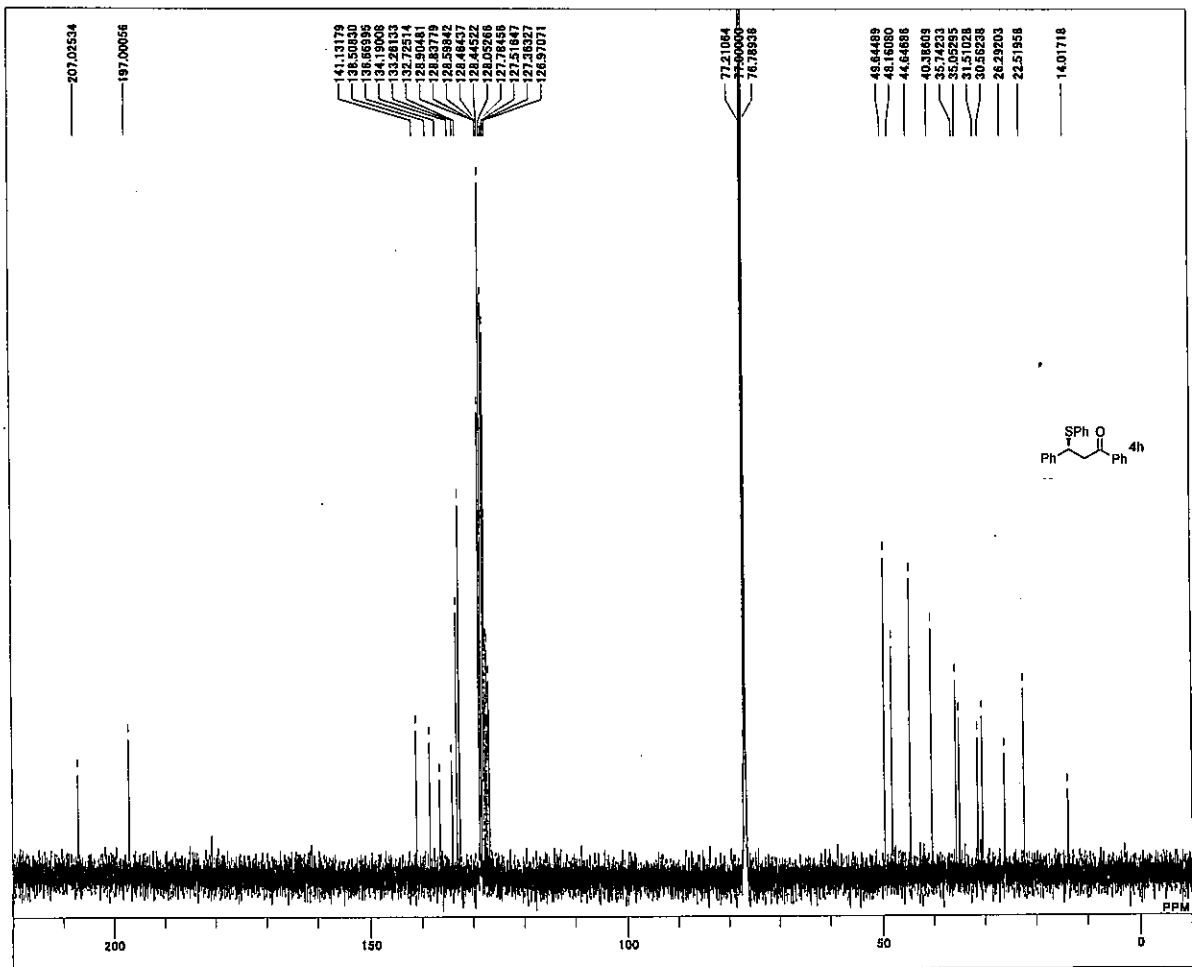
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	7	13.102	91986	4153	V		7.4834	
	8	15.019	1137222	48247	S		92.5166	
TOTAL			1229208	52400			100	

C-RSA CHROMATOPAC CH=1 Report No.=9

DATA=1:@CHRM1.C00 11/02/17 23:40:30

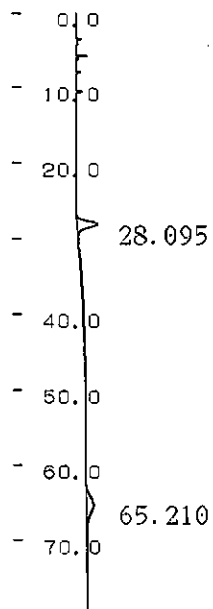


DFILE
COMNT
DATIM 10-02-2011 02:17:38
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 13107
FREQU 9008.87 Hz
SCANS 8
ACQTM 1.4549 sec
PD 2.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 18.3 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 44



DFILE
COMNT
DATIM 18-02-2011 17:36:05
OBNUC 13C
EXMOD single_pulse.dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 32768
FREQU 47348.49 Hz
SCANS 9999
ACQTM -0.8821 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 19.0 o
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 80

Analysis FILE : 9:@FIL15.FIL

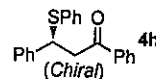
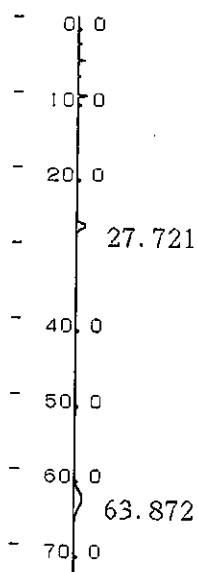


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	18	28.095	147114	2467			50.0568	
	20	65.21	146780	853			49.9432	
TOTAL			293893	3320			100	

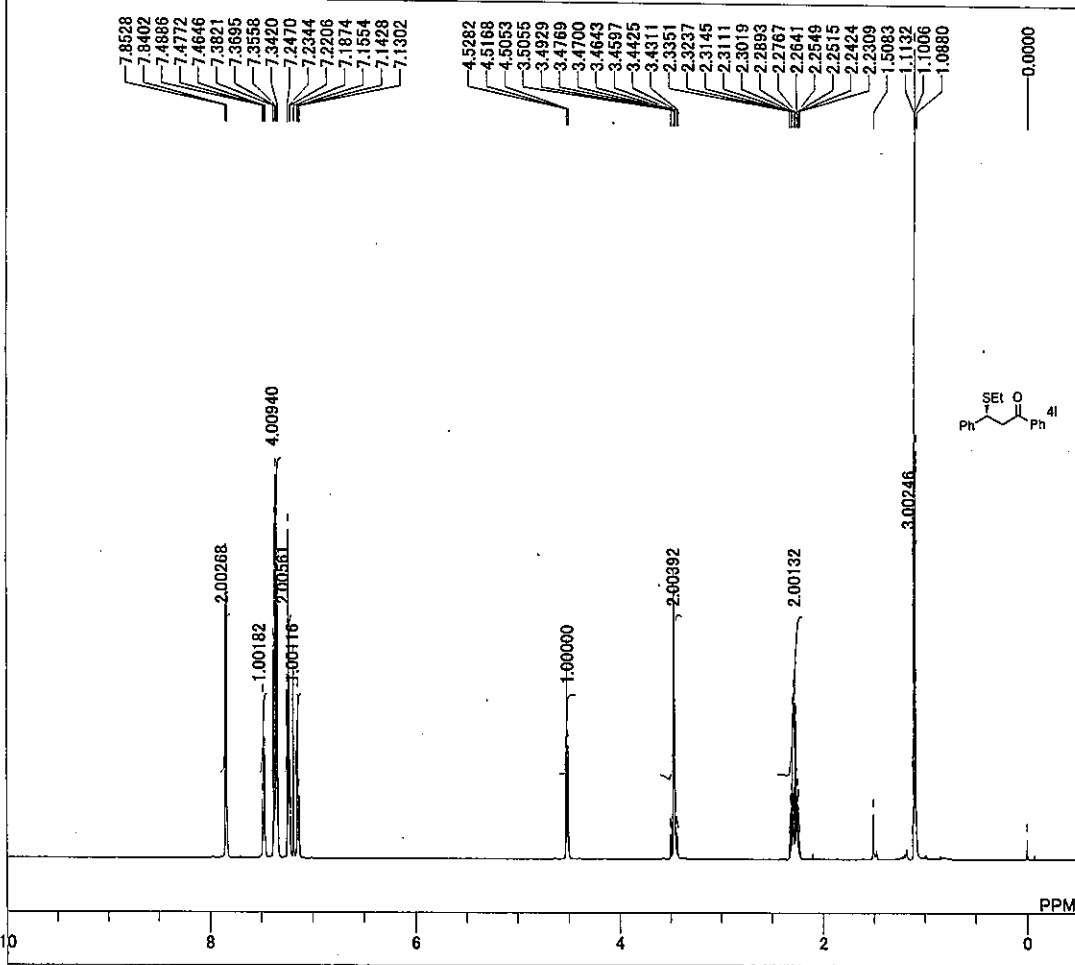
C-RSA CHROMATOPAC CH=1 Report No.=14 DATA=1:@CHRM1.C00 11/02/18 22:05:44

Analysis FILE : 9:@FIL15.FIL

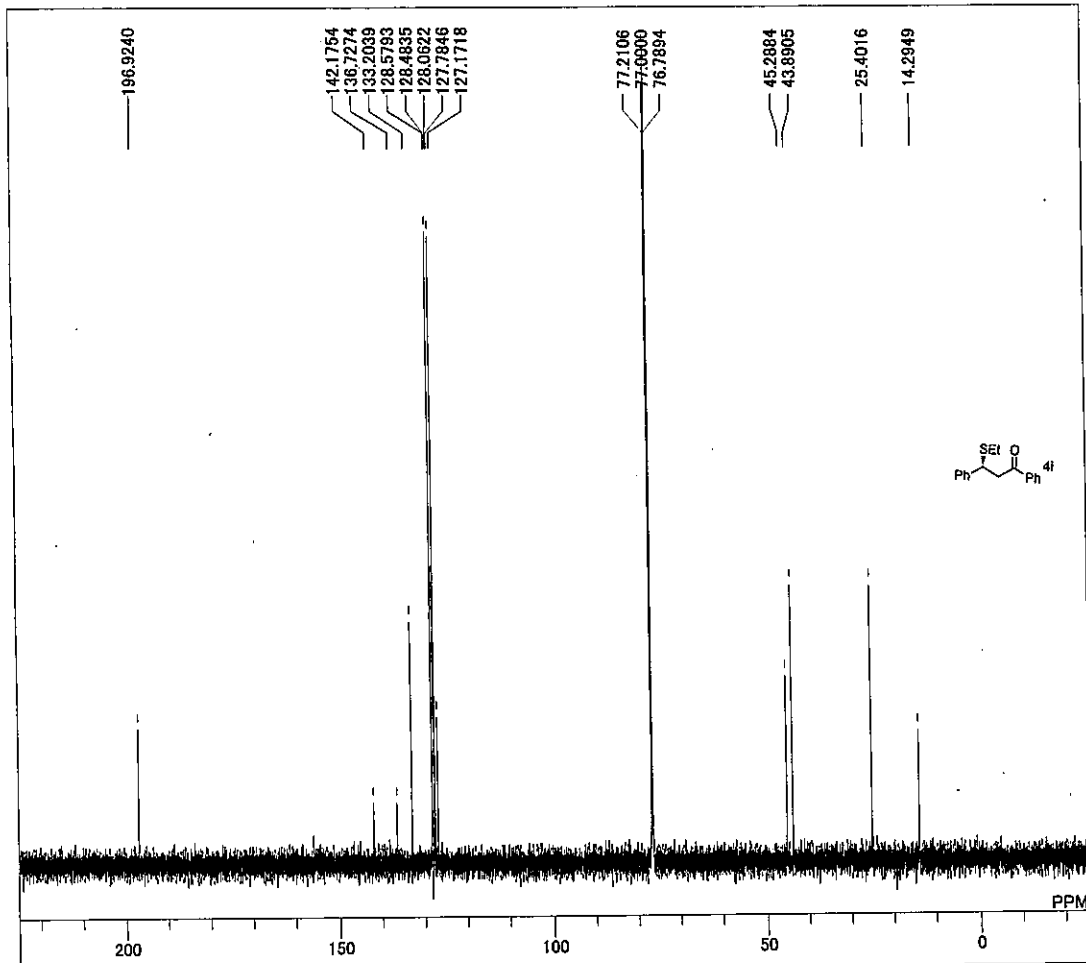


** CALCULATION REPORT **

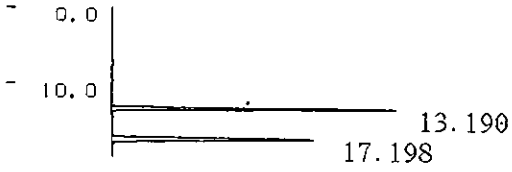
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	17	27.721	140865	2402			29.5719	
	22	63.872	335483	2019			70.4281	
TOTAL			476349	4421			100	



DFILE
COMNT
DATIM 18-02-2011 08:40:50
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 16384
FREQU 11261.26 Hz
SCANS 20
ACQTM 1.4549 sec
PD 2.0000 sec
PW1 6.50 usec
IRNUC 1H
CTEMP 18.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42



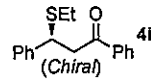
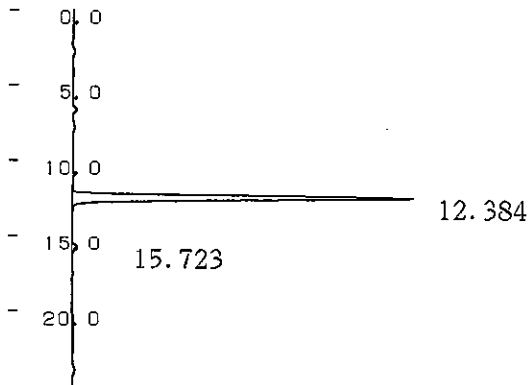
DFILE
COMNT
DATIM 18-02-2011 05:16:43
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 32768
FREQU 47348.49 Hz
SCANS 140
ACQTM 0.6921 sec
PD 2.0000 sec
PW1 2.87 usec
IRNUC 1H
CTEMP 18.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60



** CALCULATION REPORT **

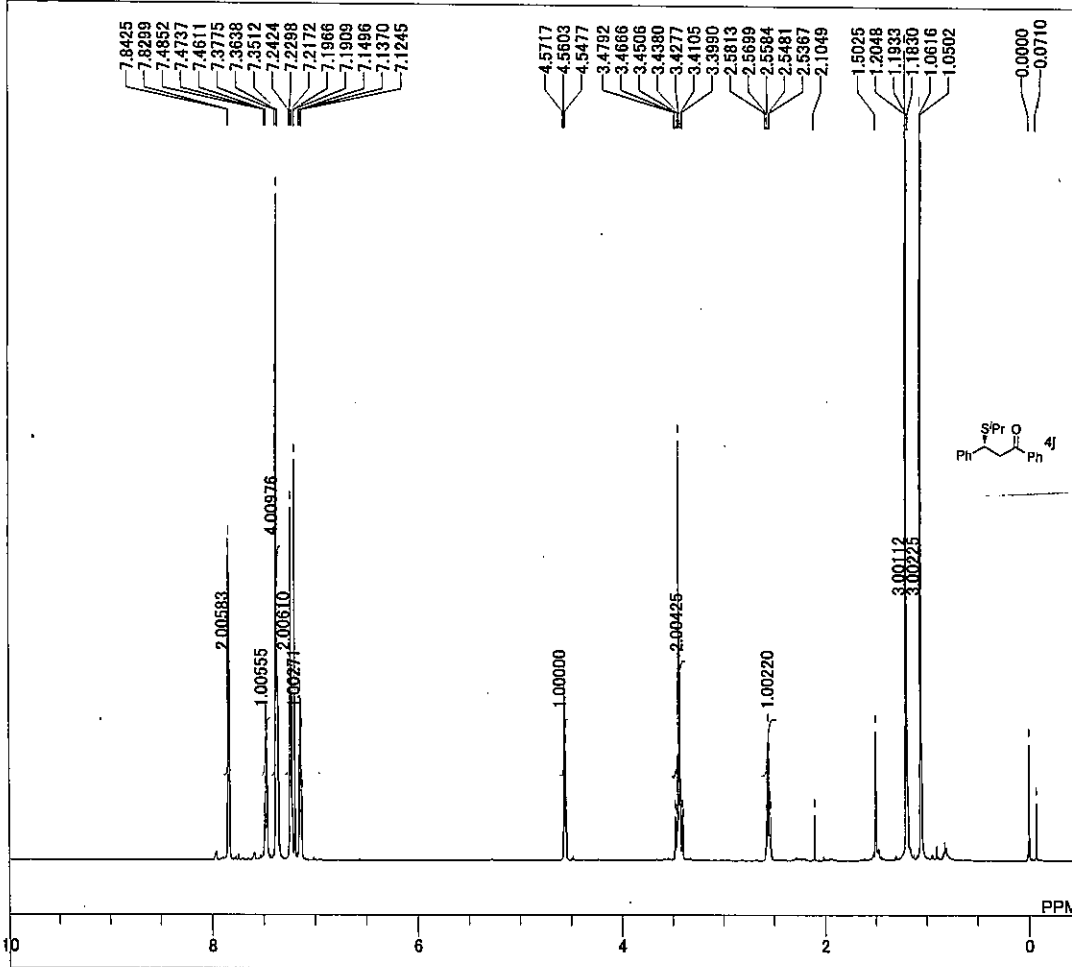
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	21	13.19	2073155	136578	SV		50.0061	
	24	17.198	2072652	94134			49.9939	
TOTAL			4145808	230712			100	

Analysis FILE : 9:@FIL15.FIL

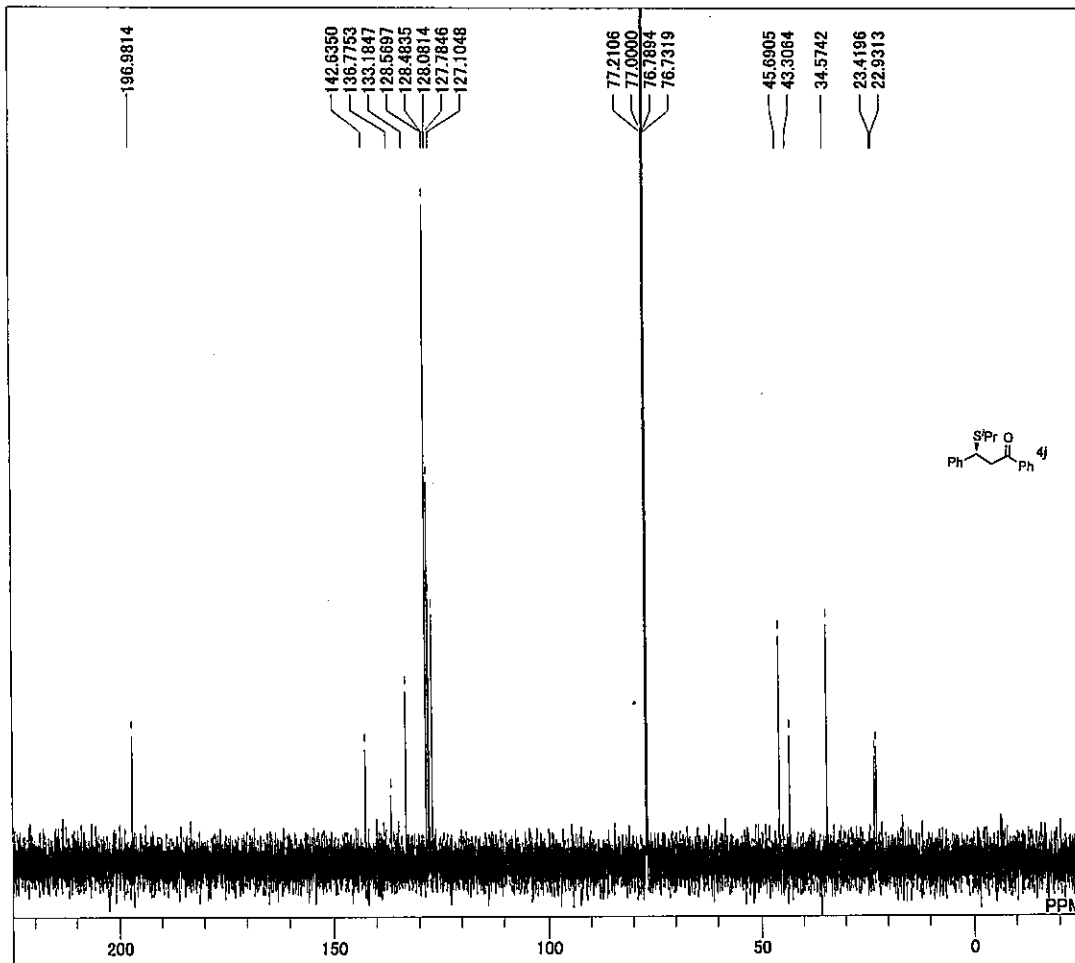


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	10	12.384	415088	20565			98.13	
	12	15.723	7910	324	V		1.87	
TOTAL			422999	20889			100	



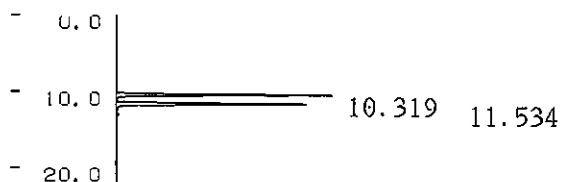
DFILE
COMNT
DATIM 18-02-2011 08:51:22
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 600.17 MHz
OBSET 5.30 KHz
OBFIN 5.47 Hz
POINT 16384
FREQU 11261.26 Hz
SCANS 24
ACQTM 1.4549 sec
PD 2.0000 sec
PWI 6.50 usec
IRNUC 1H
CTEMP 17.9 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 42



DFILE
COMNT
DATIM 18-02-2011 09:02:55
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 150.92 MHz
OBSET 8.52 KHz
OBFIN 1.74 Hz
POINT 32768
FREQU 47348.49 Hz
SCANS 205
ACQTM 0.6921 sec
PD 2.0000 sec
PWI 2.87 usec
IRNUC 1H
CTEMP 19.3 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

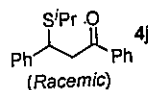
C-RSA CHROMATOPAC CH=1 Report No.=3

DATA=1:@CHRM1.C00 11/02/22 18:54:24



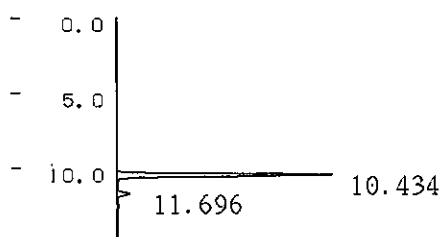
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	7	10.319	5255850	414441	V		49.5586	
	8	11.534	5349472	364825	V		50.4414	
TOTAL			10605321	779266			100	



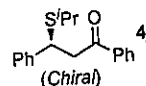
C-RSA CHROMATOPAC CH=1 Report No.=16

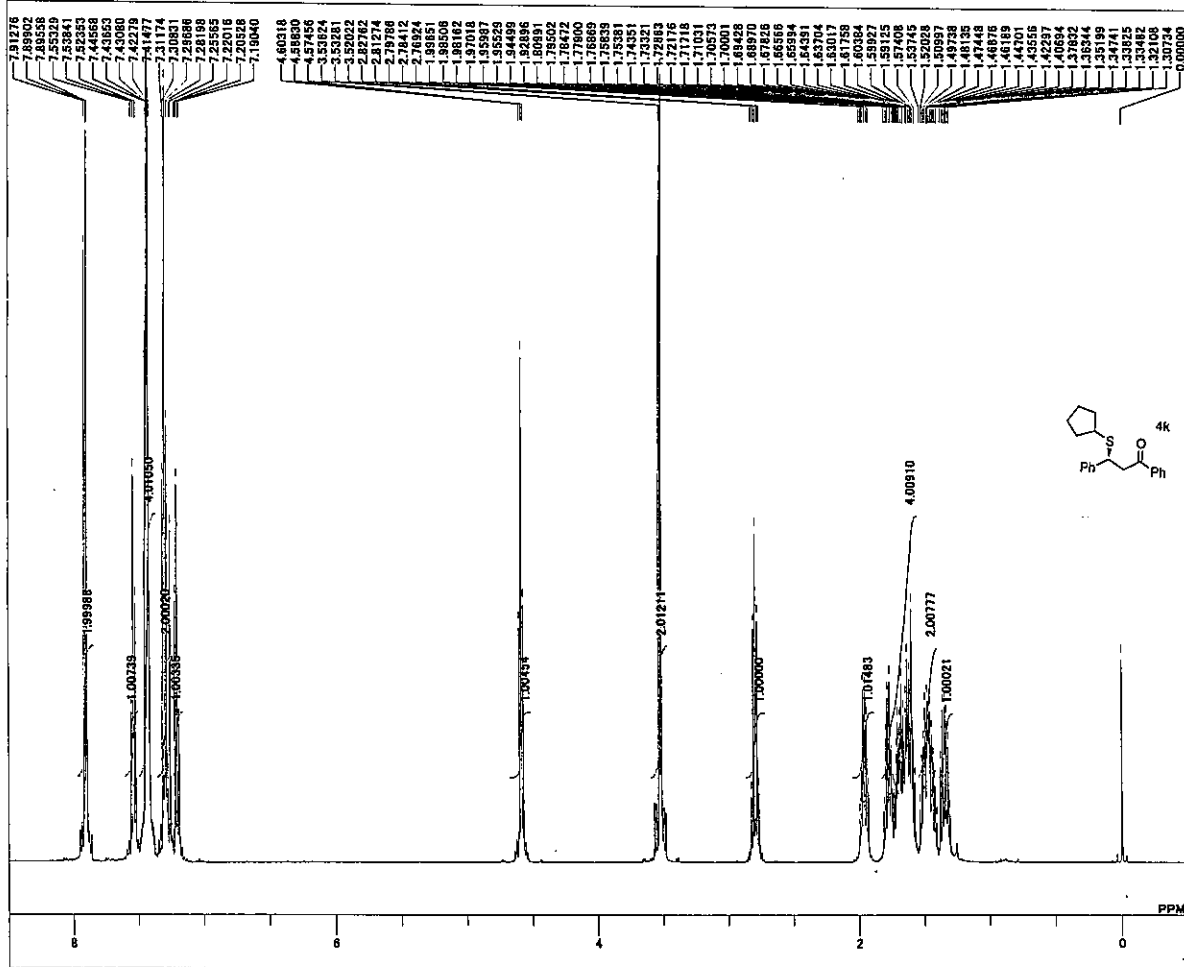
DATA=1:@CHRM1.C00 11/02/20 20:50:18



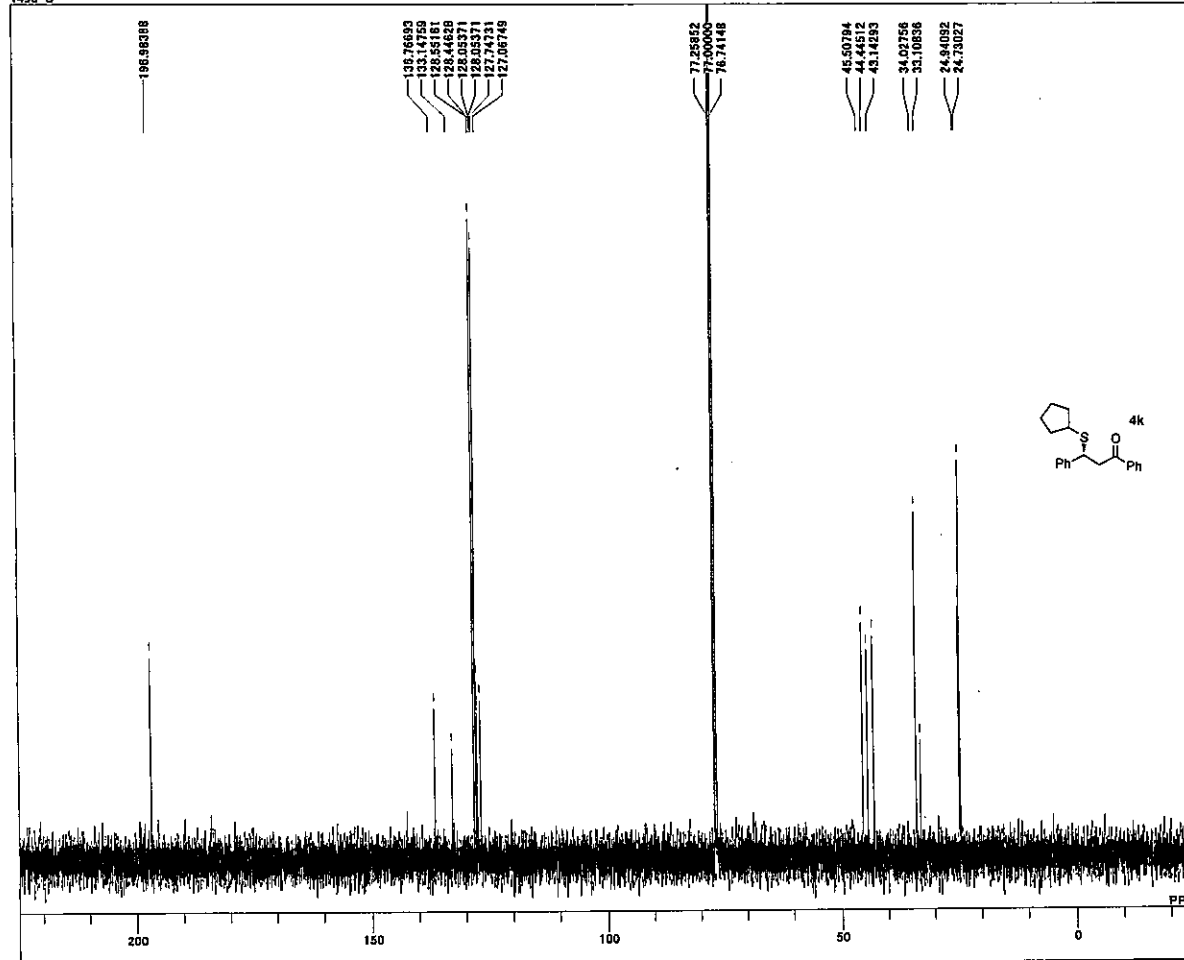
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	28	10.434	10502692	825966			92.9622	
	29	11.696	795121	47475	V		7.0378	
TOTAL			11297812	873441			100	

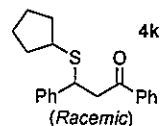
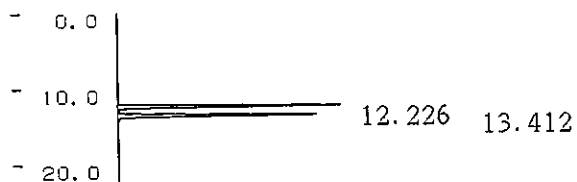




DFILE C:\Documents and Settings\VALICE2\Desktop\1498-H
COMNT 1498-H
DATIM 18-02-2011 13:55:55
OBNUC 1H
EXMOD 1H NMR.ex2
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 9.64 Hz
POINT 18384
FREQU 9286.78 Hz
SCANS 8
ACQTM 1.7842 sec
PD 5.0000 sec
PWI 5.80 usec
IRNUC 1H
CTEMP 18.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 36

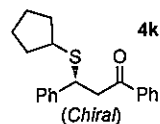


DFILE C:\Documents and Settings\VALICE2\Desktop\1498-C
COMNT 1498-C
DATIM 18-02-2011 14:12:09
OBNUC 13C
EXMOD 13C NMR.ex2
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 32768
FREQU 39082.50 Hz
SCANS 313
ACQTM 0.8389 sec
PD 2.0000 sec
PWI 3.67 usec
IRNUC 1H
CTEMP 18.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 80



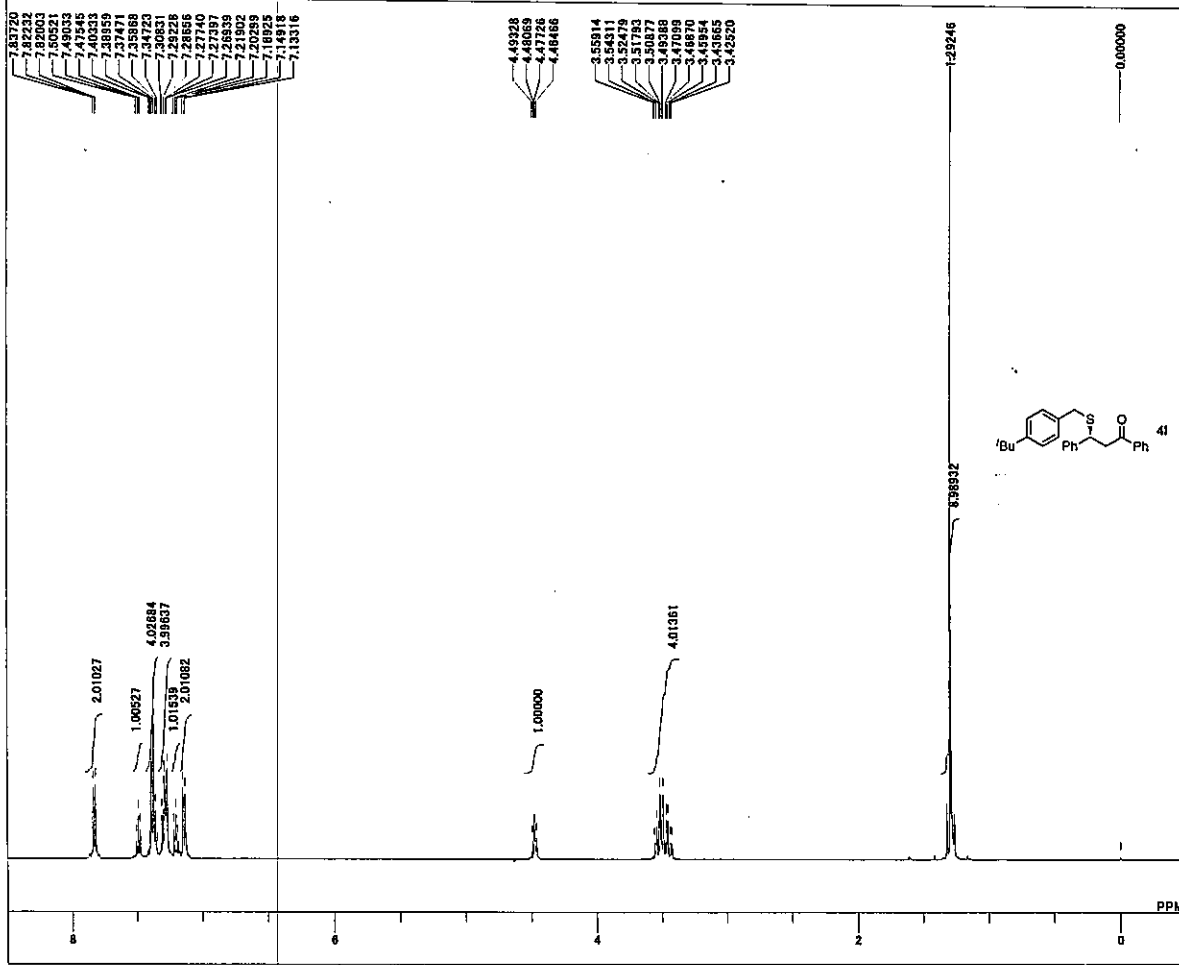
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	25	12.226	6608326	426840			49.8485	
	26	13.412	6648489	378299	SV		50.1515	
TOTAL			13256815	805139			100	

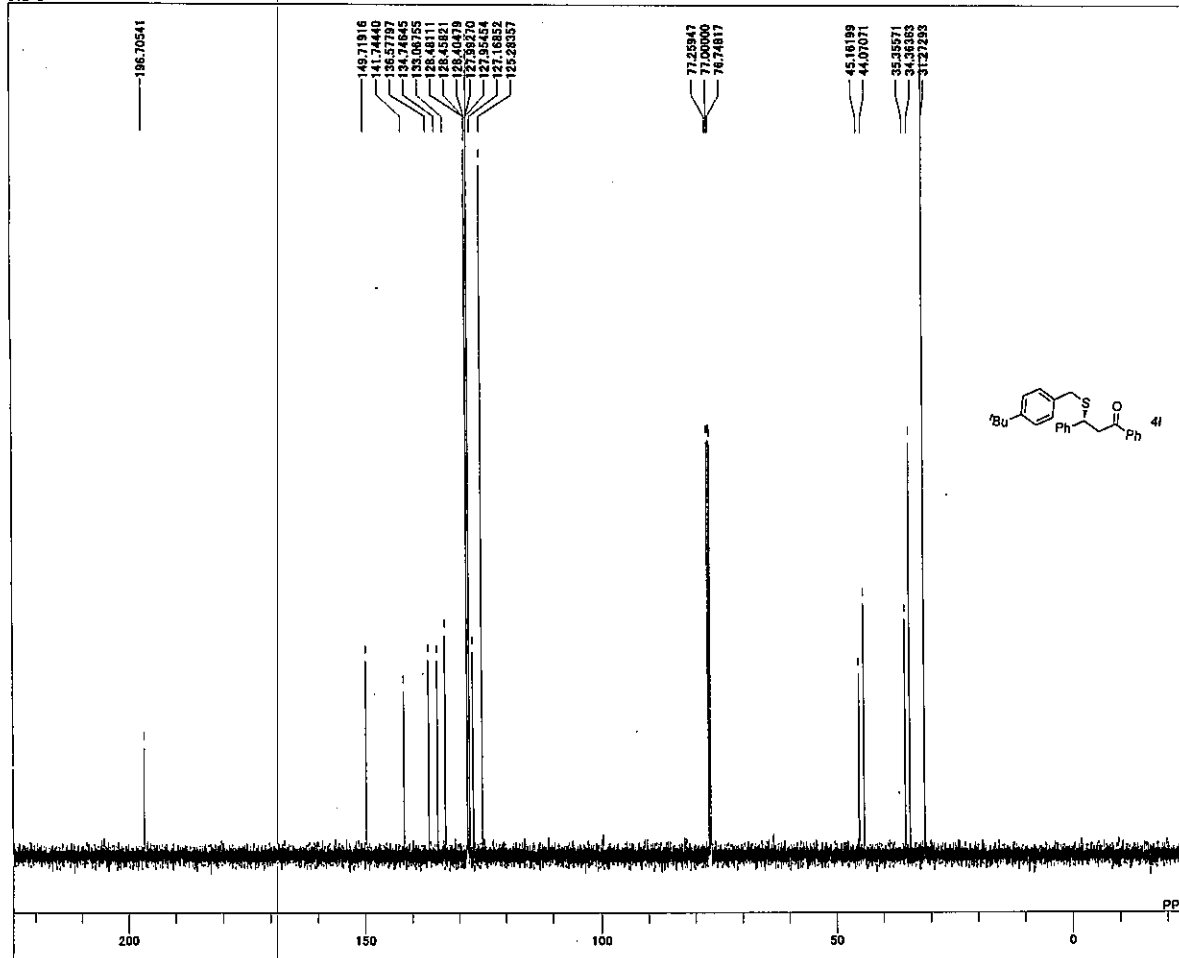


** CALCULATION REPORT **

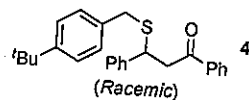
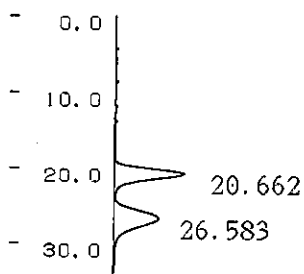
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	32	12.007	12472128	813145			96.3274	
	33	13.135	475520	27400	SV		3.6726	
TOTAL			12947648	840545			100	



DFILE C:\Documents and Settings\VAI Users\Doc
COMNT 312-H
DATIM 18-02-2011 15:25:51
OBNUC 1H
EXMOD 1H NMR.ex2
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 9.64 Hz
POINT 13107
FREQU 7429.31 Hz
SCANS 8
ACQTM 1.7642 sec
PD 5.0000 sec
PWT 5.80 usec
IRNUC 1H
CTEMP 18.4 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 28

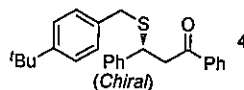
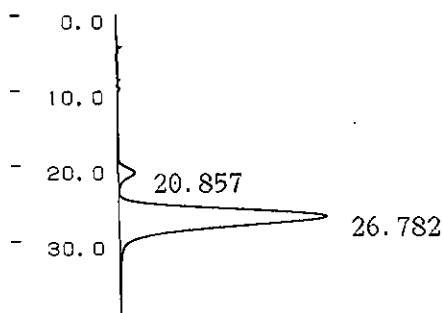


DFILE C:\Documents and Settings\VAI Users\Doc
COMNT 312-C
DATIM 18-02-2011 15:48:17
OBNUC 13C
EXMOD 13C NMR.ex2
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 32768
FREQU 31133.25 Hz
SCANS 421
ACQTM 1.0525 sec
PD 2.0000 sec
PWT 3.87 usec
IRNUC 1H
CTEMP 18.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 76



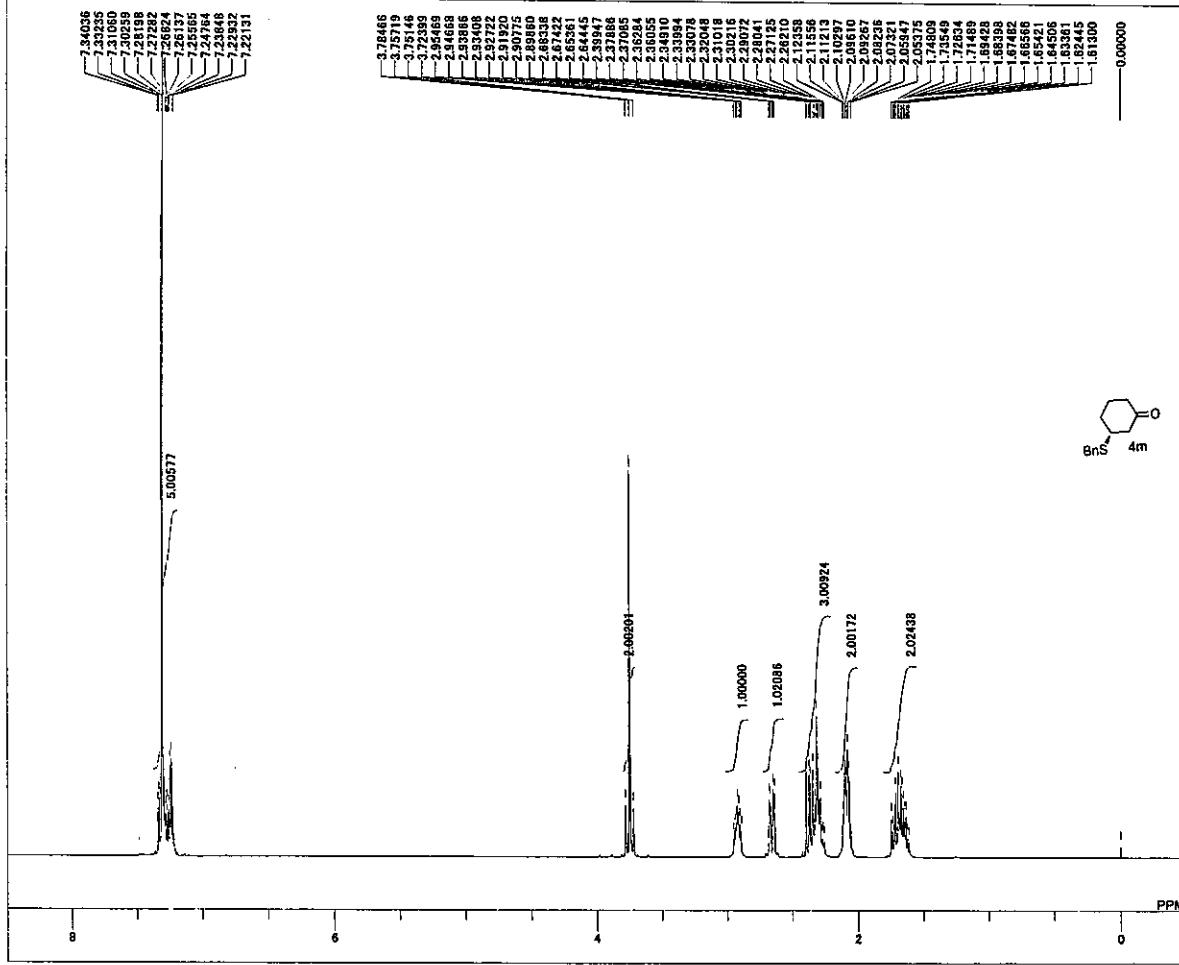
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	31	20.662	1720426	16806	V		49.9637	
	32	26.583	1722927	10783	V		50.0363	
TOTAL			3443353	27589			100	

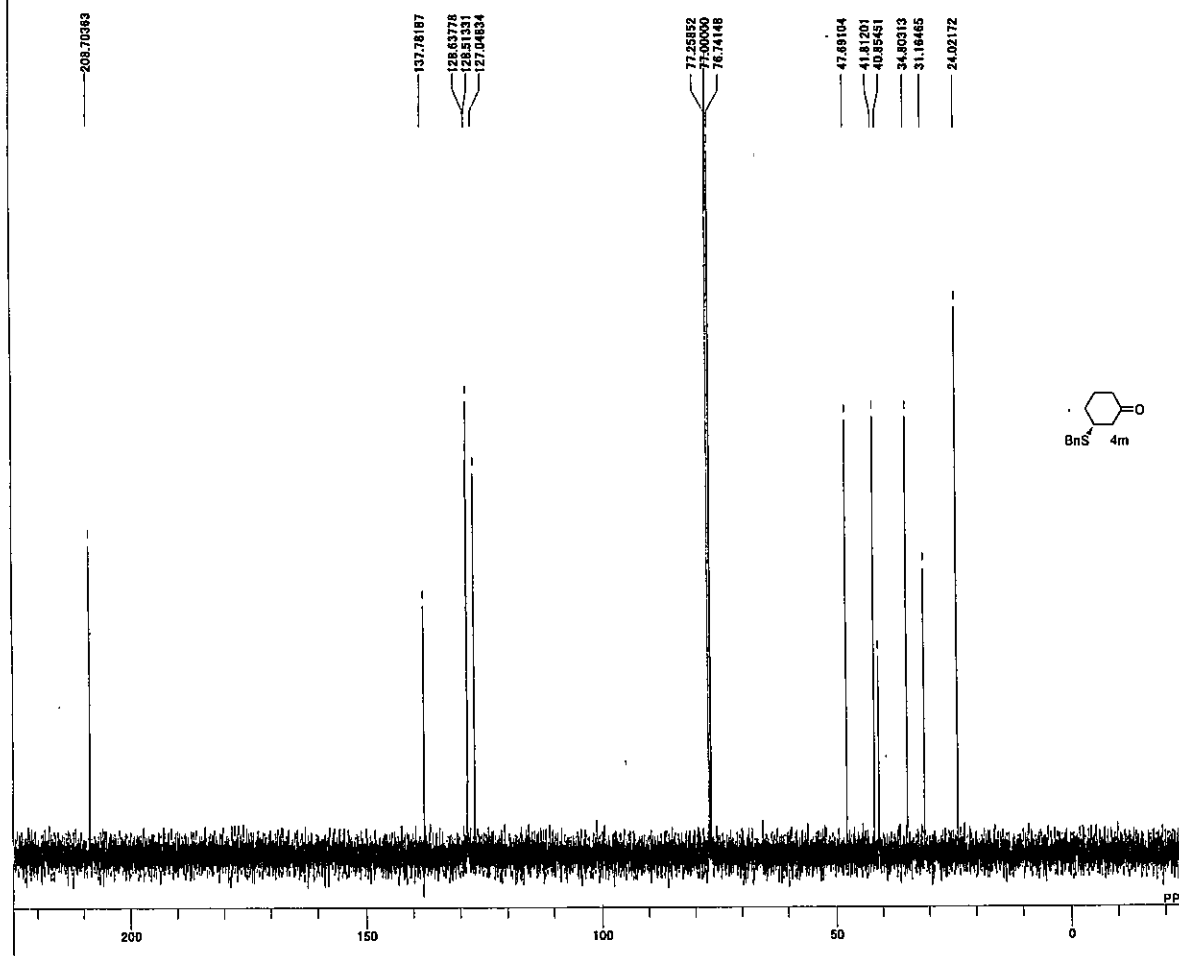


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	26	20.857	827362	7856			4.7947	
	27	26.782	16428209	99764	V		95.2052	
TOTAL			17255568	107620			100	



DFILE C:\Documents and Settings\VALICE2\Desktop\1495-H-1.jdf
COMNT 1495-H
DATIM 17-02-2011 17:34:41
OBNUC 1H
EXMOD 1H NMR.ex2
OBFRQ 495.13 MHz
OBSET 4.38 KHz
OBFIN 9.64 Hz
POINT 18384
FREQU 9286.78 Hz
SCANS 8
ACQTM 1.7642 sec
PD 5.0000 sec
PWI 5.80 usec
IRNUC 1H
CTEMP 18.2 c
SLVNT CDCL3
EXREF 0.00 ppm
BF 0.12 Hz
RGAIN 32

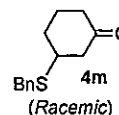
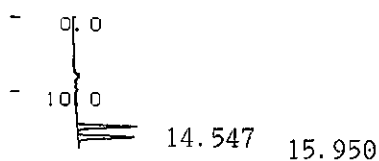


DFILE C:\Documents and Settings\VALICE2\Desktop\1495-C-1.jdf
COMNT 1495-C
DATIM 17-02-2011 17:42:20
OBNUC 13C
EXMOD 13C NMR.ex2
OBFRQ 124.51 MHz
OBSET 3.45 KHz
OBFIN 6.00 Hz
POINT 32788
FREQU 39882.50 Hz
SCANS 145
ACQTM 0.8389 sec
PD 2.0000 sec
PWI 3.67 usec
IRNUC 1H
CTEMP 18.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 0.12 Hz
RGAIN 60

C-RSA CHROMATOPAC CH=1 Report No.=1

DATA=1:@CHRM1.C00 11/02/17 22:31:34

Analysis FILE : 9:@FIL15.FIL



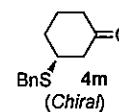
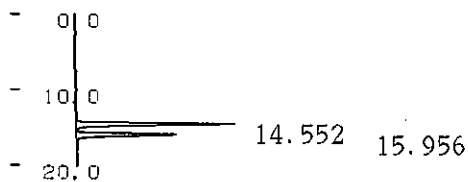
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	9	14.547	39964	1776			49.7715	
	10	15.95	40331	1686			50.2285	
TOTAL			80295	3462			100	

C-RSA CHROMATOPAC CH=1 Report No.=2

DATA=1:@CHRM1.C00 11/02/17 22:31:34

Analysis FILE : 9:@FIL15.FIL



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	10	14.552	216133	9499			59.9071	
	11	15.956	144647	6027	V		40.0929	
TOTAL			360779	15526			100	

C-RSA CHROMATOPAC CH=1 Report No.=4

DATA=1:@CHRM1.C00 11/02/17 22:50:24