

Supplementary Information

Lithium acetylides as alkynylating reagents for the enantioselective alkynylation of ketones catalyzed by lithium binaphtholate

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General Methods

¹H and ¹³C NMR spectra were measured in CDCl₃ with JEOL JNM-ECX400 spectrometer. Tetramethylsilane (TMS) (δ = 0 ppm) and CDCl₃ (δ = 77.0 ppm) served as internal standards for ¹H and ¹³C NMR, respectively. Infrared spectra were recorded on JEOL JIR 6500-W. Mass spectra were measured with JEOL JMS-DX303HF mass spectrometer. Optical rotations were recorded on JASCO P-1010 polarimeter. High-pressure liquid chromatography (HPLC) was performed on JASCO P-980 and UV-1575. Dry THF was purchased from Kanto Chemical. (*S*)-3,3'-diphenylbinaphthol was prepared by Suzuki coupling according to the literature method.¹ All other chemicals were purified based on standard procedures.

Representative procedure for the enantioselective alkynylation

Under Ar atmosphere, *n*-BuLi (1.65 M in hexane, 0.57 mL, 0.941 mmol) was added to the solution of (*R*)-3,3'-diphenyl-1,1'-binaphthalene-2,2'-diol (**1**) (21 mg, 0.047 mmol) and phenylacetylene (**3a**) (0.10 mL, 0.94 mmol) in THF (3 mL) at -78 °C. To the mixture, acetophenone (**2b**) (56 mg, 0.47 mmol) in THF (0.5 mL) was added dropwise at the same temperature and the solution was stirred for 12 h. The reaction was quenched with NH₄Cl sat. aq. and the mixture was extracted with AcOEt. The organic layer was washed with NaHCO₃ and brine. After drying over Na₂SO₄, the solvent was removed and the residue was purified by silica gel column chromatography (hexane/CH₂Cl₂=1:1), affording **4ba** (100 mg, 96%) as an oil. The ee was determined by chiral HPLC (Daicel OD-H) to be 93% ee.

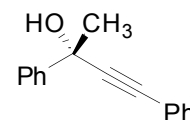
2,4-Diphenyl-but-3-yn-2-ol (**4ba**)²

[α]_D¹⁷ -7.0 (*c* 1.16, CHCl₃, 93% ee) [lit.: [α]_D¹⁶ -6.6 (*c* 1.00, CHCl₃), 81% ee, *S*].

HPLC (Daicel chiralcel OD-H, hexane/IPA = 19/1, 1.0 mL/min):

*t*_R(min) 8.8 (minor), 11.5 (major).

¹H NMR (CDCl₃, 400 MHz): δ 1.87 (s, 3H, CH₃), 2.46 (s, 1H, OH), 7.30-7.50 (m, 8H, Ar-*H*), 7.73-7.75 (m, 2H, Ar-*H*).



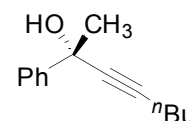
2-Phenyl-3-octyn-2-ol (**4bb**)³

[α]_D²⁴ -0.7 (*c* 0.67, CHCl₃, 87% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 200/1, 1.0 mL/min):

*t*_R(min) 19.6 (minor), 21.5 (major).

¹H NMR (CDCl₃, 400 MHz): δ 0.93 (t, 3H, *J* = 7.3 Hz, CH₃), 1.39-1.48 (m, 2H), 1.50-1.58 (m, 2H), 1.75 (s,



3H, CH_3), 2.28 (t, 2H, $J=7.3$ Hz), 2.31 (brs, 1H, OH), 7.26-7.30 (m, 1H), 7.34-7.37 (m, 2H), 7.65-7.67 (m, 2H).

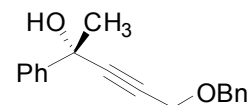
1-Benzyloxy-4-phenyl-2-pentyn-4-ol (4bc)⁴

$[\alpha]_D^{24}$ -4.0 (c 1.15, $CHCl_3$, 86% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 19/1, 1.0 mL/min):

t_R (min) 14.8 (minor), 17.2 (major).

1H NMR ($CDCl_3$, 400 MHz): δ 1.76 (s, 3H), 2.93 (s, 1H, OH), 4.22 (s, 2H), 4.58 (s, 2H), 7.24-7.36 (m, 8H), 7.63 (d, 2H, $J=7.3$ Hz).



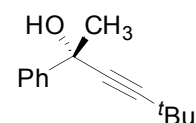
5,5-Dimethyl-2-phenyl-3-hexyn-2-ol (4bd)⁵

$[\alpha]_D^{23}$ +3.4 (c 0.41, $CHCl_3$, 55% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 39/1, 1.0 mL/min):

t_R (min) 9.5 (major), 10.3 (minor).

1H NMR ($CDCl_3$, 400 MHz): δ 1.27 (s, 9H, $(CH_3)_3$), 1.73 (s, 3H, CH_3), 2.26 (s, 1H, OH), 7.26-7.30 (m, 1H), 7.34-7.36 (m, 2H), 7.65-7.67 (m, 2H).



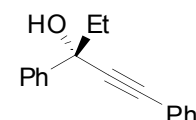
1,3-Diphenyl-pent-1-yn-3-ol (4ca)⁶

$[\alpha]_D^{15}$ -9.0 (c 1.00, $CHCl_3$, 73% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 29/1, 1.0 mL/min):

t_R (min) 10.3 (minor), 11.5 (major).

1H NMR ($CDCl_3$, 400 MHz): δ 1.03 (t, 3H, $J=7.3$ Hz, $-CH_2CH_3$), 1.95-2.11 (m, 2H, $-CH_2CH_3$), 2.45 (s, 1H, OH), 7.30-7.40 (m, 6H Ar-H), 7.48-7.51 (m, 2H, Ar-H), 7.68-7.77 (m, 2H, Ar-H).



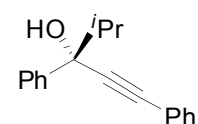
4-Methyl-1,3-diphenyl-pent-1-yn-3-ol (4da)⁷

$[\alpha]_D^{20}$ -1.4 (c 1.30, $CHCl_3$, 7% ee)

HPLC (Daicel chiralcel AD-H, hexane/IPA = 19/1, 1.0 mL/min):

t_R (min) 11.1 (major), 17.1 (minor).

1H NMR ($CDCl_3$, 400 MHz): δ 0.89 (d, 3H, $J=6.8$ Hz), 1.14 (d, 3H, $J=6.8$ Hz), 2.14-2.23 (m, 1H), 2.41 (s, 1H, OH), 7.28-7.39 (m, 6H, Ar-H), 7.49-7.51 (m, 2H, Ar-H), 7.67-7.69 (m, 2H, Ar-H).



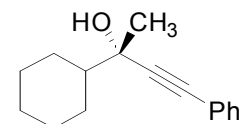
2-Cyclohexyl-4-phenyl-but-3-yn-2-ol (4ea)⁸

$[\alpha]_D^{26}$ +3.8 (c 1.40, $CHCl_3$, 57% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 19/1, 1.0 mL/min):

t_R (min) 6.1 (minor), 8.7 (major).

1H NMR ($CDCl_3$, 400 MHz): δ 1.14-1.30 (m, 5H), 1.51-1.52 (m, 1H), 1.54 (s, 3H, CH_3), 1.68-1.71 (m, 1H), 1.82-1.84 (m, 2H), 1.91-1.95 (m, 1H), 2.02-2.05 (m, 1H), 7.30-7.31 (m, 3H, Ar-H), 7.41-7.44 (m, 2H, Ar-H).



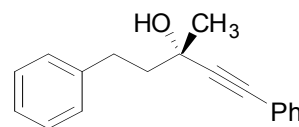
3-Methyl-1,5-diphenyl-pent-1-yn-3-ol (4fa)⁹

$[\alpha]_D^{24} +6.3$ (*c* 1.48, CHCl₃, 39% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 19/1, 1.0 mL/min):

t_R(min) 10.5 (minor), 14.8 (major).

¹H NMR (CDCl₃, 400 MHz) : δ 1.63 (s, 3H, CH₃), 2.01-2.10 (m, 2H), 2.91-2.95 (m, 2H), 7.18-7.22 (m, 8H, Ar-H), 7.43-7.46 (m, 2H, Ar-H).



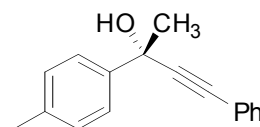
4-Phenyl-2-p-tolyl-but-3-yn-2-ol (4ga)¹⁰

$[\alpha]_D^{27} -4.8$ (*c* 1.16, CHCl₃, 88% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 19/1, 1.0 mL/min):

t_R(min) 8.5 (minor), 11.6 (major).

¹H NMR (CDCl₃, 400 MHz) : δ 1.86 (s, 3H, CH₃), 2.37 (s, 3H, Ar-CH₃), 2.41 (s, 1H, OH), 7.19 (d, 2H, *J* = 8.2 Hz), 7.32-7.33 (m, 3H, Ar-H), 7.47-7.49 (m, 2H, Ar-H), 7.62 (d, 2H, *J* = 8.2 Hz, Ar-H).



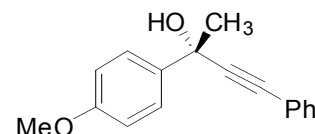
2-(4-Methoxyphenyl)-4-phenyl-but-3-yn-2-ol (4ha)¹¹

$[\alpha]_D^{29} -7.1$ (*c* 0.60, CHCl₃, 92% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 19/1, 1.0 mL/min):

t_R(min) 11.2 (minor), 18.3 (major).

¹H NMR (CDCl₃, 400 MHz) : δ 1.86 (s, 3H, CH₃), 2.42 (s, 1H, OH), 3.82 (s, 3H, OCH₃), 6.90-6.93 (m, 2H, Ar-H), 7.32-7.35 (m, 3H, Ar-H), 7.47-7.49 (m, 2H, Ar-H), 7.64-7.67 (m, 2H, Ar-H).



2-(3,4,5-Trimethoxyphenyl)-4-phenyl-but-3-yn-2-ol (4ia)

$[\alpha]_D^{16} +8.3$ (*c* 0.96, CHCl₃, 92% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 6/1, 1.0 mL/min):

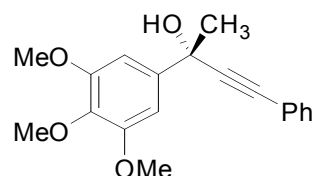
t_R(min) 8.7 (minor), 10.8 (major).

¹H NMR (CDCl₃, 400 MHz) : δ 1.86 (s, 3H, CH₃), 2.81 (s, 1H, OH), 3.85 (s, 3H, Ar-OCH₃), 3.88 (s, 6H, Ar-OCH₃), 6.97 (s, 2H, Ar-H), 7.32-7.34 (m, 3H, Ar-H), 7.45-7.47 (m, 2H, Ar-H).

¹³C NMR (CDCl₃, 100 MHz) : δ 33.3, 56.0, 60.7, 70.3, 84.8, 92.3, 102.1, 122.4, 128.3, 128.5, 131.5, 137.1, 141.4, 152.8.

IR (neat) : ν (cm⁻¹) 3431, 2935, 2835, 1593, 1504, 1454, 1413, 1325, 1236, 1122.

LR-FABMS 335 ((M+Na)⁺, bp), 312, 129, 77. HR-FABMS calcd for C₁₉H₂₀O₄Na ((M+Na)⁺) 335.1259, found 335.1269.



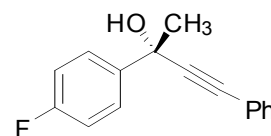
2-(4-Fluorophenyl)-4-phenyl-but-3-yn-2-ol (4ja)¹²

$[\alpha]_D^{27} -9.9$ (*c* 0.83, CHCl₃, 91% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 19/1, 1.0 mL/min):

t_R(min) 8.4 (minor), 10.5 (major).

¹H NMR (CDCl₃, 400 MHz) : δ 1.86 (s, 3H, CH₃), 2.46 (s, 1H, OH), 7.04-7.08 (m, 2H, Ar-H), 7.31-7.35 (m, 3H, Ar-H), 7.47-7.49 (m, 2H, Ar-H), 7.68-7.71 (m, 2H, Ar-H).



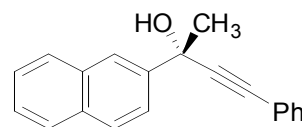
2-(2-Naphthyl)-4-phenyl-but-3-yn-2-ol (**4ka**)¹²

$[\alpha]_D^{24}$ -17.9 (*c* 0.27, CHCl₃, 85% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 9/1, 1.0 mL/min):

t_R(min) 8.3 (minor), 11.0 (major).

¹H NMR (CDCl₃, 400 MHz): δ 1.95 (s, 3H, CH₃), 2.59 (s, 1H, OH), 7.34-7.35 (m, 3H, Ar-*H*), 7.48-7.52 (m, 4H, Ar-*H*), 7.80-7.88 (m, 4H, Ar-*H*), 8.19 (s, 1H, Ar-*H*).



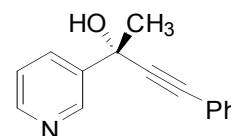
4-Phenyl-2-(pyridin-3-yl)-but-3-yn-2-ol (**4la**)⁶

$[\alpha]_D^{27}$ -1.4 (*c* 0.97, CHCl₃, 87% ee)

HPLC (Daicel chiralcel OD-H, hexane/IPA = 9/1, 1.0 mL/min):

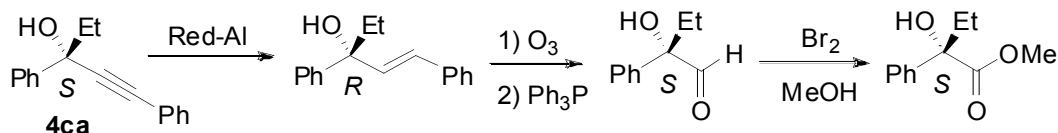
t_R(min) 11.7 (minor), 14.8 (major).

¹H NMR (CDCl₃, 400 MHz): δ 1.89 (s, 3H, CH₃), 7.27-7.35 (m, 4H), 7.46-7.51 (m, 2H, Ar-*H*), 8.01-8.03 (m, 1H, Ar-*H*), 8.54-8.56 (m, 1H, Ar-*H*), 8.99 (s, 1H, Ar-*H*).



Determination of absolute configurations of **4ca**, **4fa**, **4ga**.

(*S*)-(+)-Methyl 2-hydroxy-2-phenylbutanoate^{13, 14, 15}



A solution of Red-Al in toluene (65%, 0.20 mL) was added to a solution of alcohol **4ca** (46 mg, $[\alpha]_D^{23}$ -6.7 (*c* 1.0, CHCl₃), 61% ee) in ether (10 mL) at 0 °C and the mixture was stirred at room temperature for 4 h. The reaction was quenched by dropwise addition of MeOH (2 mL) at 0 °C. The mixture was diluted with EtOAc and washed with a saturated solution of Rochelle's salt. The organic layer was dried over MgSO₄, filtered, and concentrated under reduced pressure to yield a yellow oil, which was purified by column chromatography (hexane/AcOEt=9:1) to afford alkene (35.0 mg, 75% yield) as an oil.

Ozone was bubbled into a solution of the above alkene (35.0 mg, 0.147 mmol) in dichloromethane (10 mL) at -78 °C until a blue color persists. Oxygen was then passed through the solution and triphenylphosphine (50 mg, 0.19 mmol) was added to the mixture at the same temperature. The resulting mixture was stirred for 1 h at room temperature and concentrated under reduced pressure to yield a colorless oil, which was purified by column chromatography (hexane/AcOEt=9:1) to afford the aldehyde (24.0 mg, 99% yield) as a colorless oil.

Sodium bicarbonate (0.5 g, 6 mmol) was added to a solution of the above aldehyde in MeOH/water (9:1, 0.7 mL). To the mixture was added bromine (0.07 mL, 1.4 mmol) over 30 minutes with vigorous stirring at room temperature. After stirring for 4 h, excess bromine was decomposed with solid Na₂S₂O₃. The mixture was filtered and filtrate was extracted with EtOAc. The organic layer was washed with brine, dried over

Na₂SO₄, filtered, and concentrated in vacuo. The obtained crude product was purified by column chromatography (hexane/AcOEt = 9:1) to give the ester (16 mg, 50% yield) as a colorless oil.

$[\alpha]_{\text{D}}^{24} = +22$ (c 0.50, CHCl₃, 61% ee)

[lit.¹⁵ : $[\alpha]_{\text{D}}^{20} = +34$ (c 0.49, CHCl₃, 81% ee), *S*.]

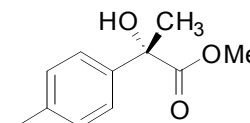
¹H NMR (CDCl₃, 400 MHz) : δ 0.92 (dd, 3H, *J* = 7.3, 7.3 Hz, CH₂CH₃), (dq, 1H, *J* = 7.3, 14.2 Hz, CH₂CH₃), (dq, 1H, *J* = 7.3, 14.2 Hz, CH₂CH₃), 3.75 (s, 1H, OH), 3.78 (s, 3H, OCH₃), 7.25-7.37 (m, 3H, Ar-*H*), 7.57 (m, 2H, Ar-*H*).

(*S*)-(+)-Methyl 2-hydroxy-2-(4-methylphenyl)-propionate¹⁶

According to the above procedure, 4-phenyl-2-p-tolyl-but-3-yn-2-ol ($[\alpha]_{\text{D}}^{18} -5.4$ (c 0.56, CHCl₃), 81% ee) was converted into the corresponding methyl ester.

$[\alpha]_{\text{D}}^{28} = +25$ (c 0.16, CHCl₃, 81% ee) [lit. : $[\alpha]_{\text{D}}^{25} = +54$ (c 1.6, CHCl₃, 85% ee), *S*.]

¹H NMR (CDCl₃, 400 MHz) : δ 1.77 (s, 3H, CH₃), 2.34 (s, 3H, Ar-CH₃), 3.68 (s, 1H, OH), 3.77 (s, 3H, OCH₃), 7.16 (d, 2H, *J* = 7.8 Hz, Ar-*H*), 7.42 (d, 2H, *J* = 8.2 Hz, Ar-*H*).

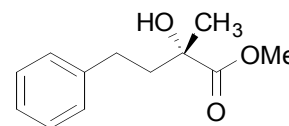


(*S*)-(+)-Methyl 2-hydroxy-2-methyl-4-phenylbutanoate¹⁶

According to the above procedure, 3-methyl-1,5-diphenyl-pent-1-yn-3-ol ($[\alpha]_{\text{D}}^{24} +6.3$ (c 1.48, CHCl₃), 39% ee) was converted into the corresponding methyl ester.

$[\alpha]_{\text{D}}^{25} = +18$ (c 1.50, CHCl₃, 39% ee) [lit. : $[\alpha]_{\text{D}}^{25} = +7.2$ (c 1.5, CHCl₃, 19% ee), *S*.]

¹H NMR (CDCl₃, 400 MHz) : δ 1.45 (s, 3H, CH₃), 1.94-2.12 (m, 2H), 2.43-2.50 (m, 1H), 2.76-2.83 (m, 1H), 3.28 (s, 1H, OH), 3.73 (s, 3H, OCH₃), 7.16-7.19 (m, 3H, Ar-*H*), 7.25-7.29 (m, 2H, Ar-*H*).



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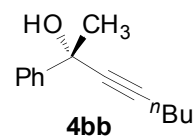
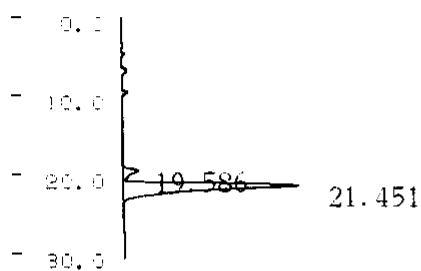
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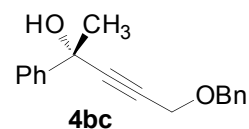
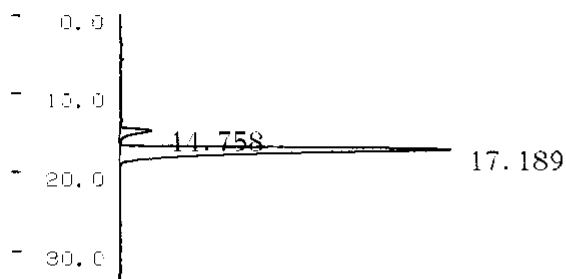


** CALCULATION REPORT **

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	9	21.451	610408	10128	V		93.637	
TOTAL			651888	10991			100	

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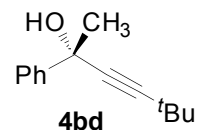
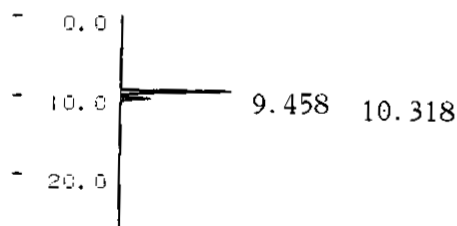


**** CALCULATION REPORT ****

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	10	14.758	155234	3663			7.0346	
	11	17.189	2051491	38573			92.9654	
TOTAL			2206725	42236			100	

C-R8A CHROMATOPAC CH=1 Report No.=2

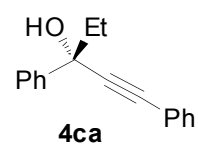
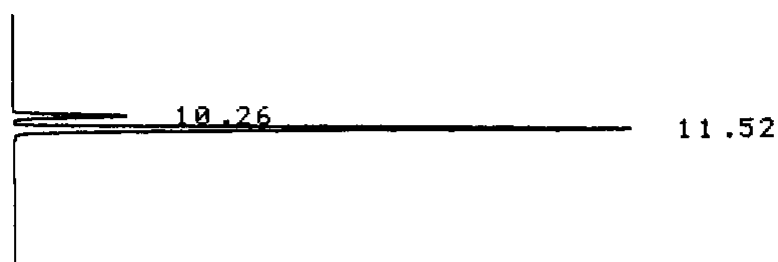
DATA=1:@CHRM1.C00



**** CALCULATION REPORT ****

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	3	9.458	381464	25767			77.5667	
	4	10.318	110324	6899	V		22.4333	
TOTAL			491788	32667			100	

CH. 1 C.S 1.25 ATT 9 OFFS 0



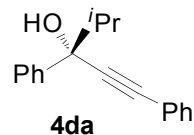
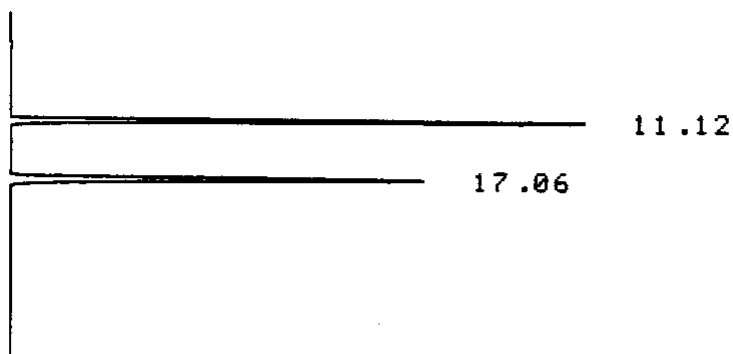
D-2500

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	10.26	900325	13.644	BU
2	11.52	5698409	86.356	UB
TOTAL		6598734	100.000	

CH. 1 C.S 1.25 ATT 9 OFFS 0



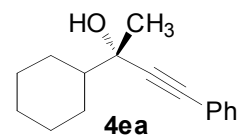
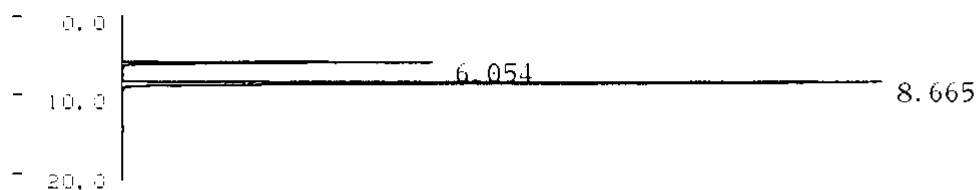
D-2500

METHOD: TAG: 2 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.12	3476607	46.627	BB
2	17.06	3979612	53.373	BB
TOTAL		7456219	100.000	

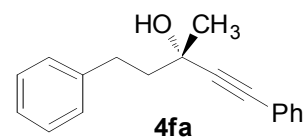
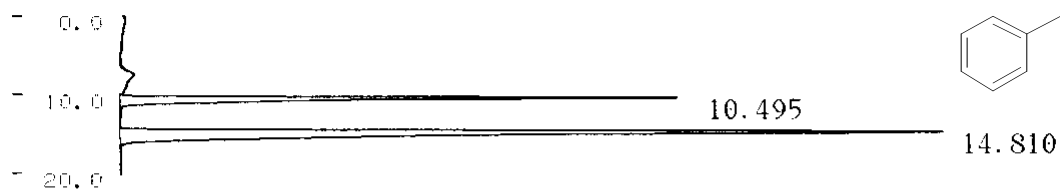
C-RSA CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00



**** CALCULATION REPORT ****

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	6	6.054	738085	72287			21.3246	
	8	8.665	2723112	176412			78.6754	
TOTAL			3461197	248700			100	

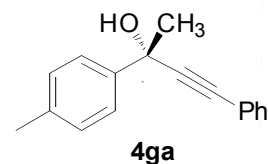
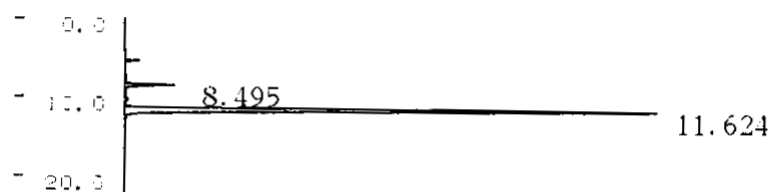
C-R8A CHROMATOPAC CH=1 Report No.=7 DATA=1:@CHRM1.C00



**** CALCULATION REPORT ****

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	10	10.495	14153062	515722	SV		30.439	
	12	14.81	32343446	760972			69.561	
TOTAL			46496508	1276694			100	

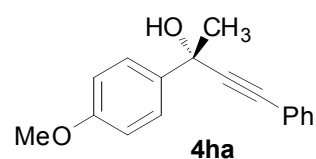
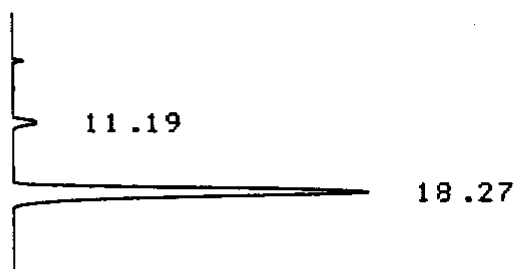
C-R8A CHROMATOPAC CH=1 Report No.=6 DATA=1:@CHRM1.C00



**** CALCULATION REPORT ****

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	8	8.495	91706	5821			6.1642	
	10	11.624	1396015	61841			93.8358	
TOTAL			1487721	67662			100	

CH. 1 C.S 1.25 ATT 8 OFFS 0



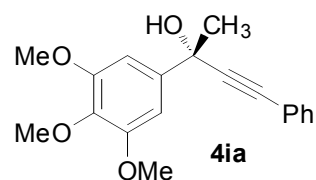
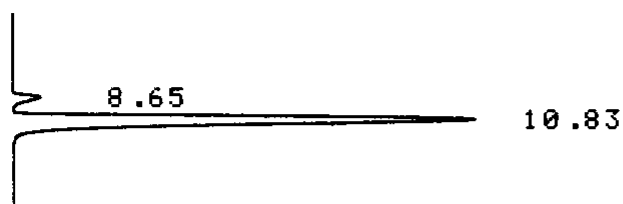
D-2500

METHOD: TAG: 1 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	11.19	181145	4.062	BB
2	18.27	4278812	95.938	BB
TOTAL		4459957	100.000	

CH. 1 C.S 1.25 ATT 10 OFFS 0

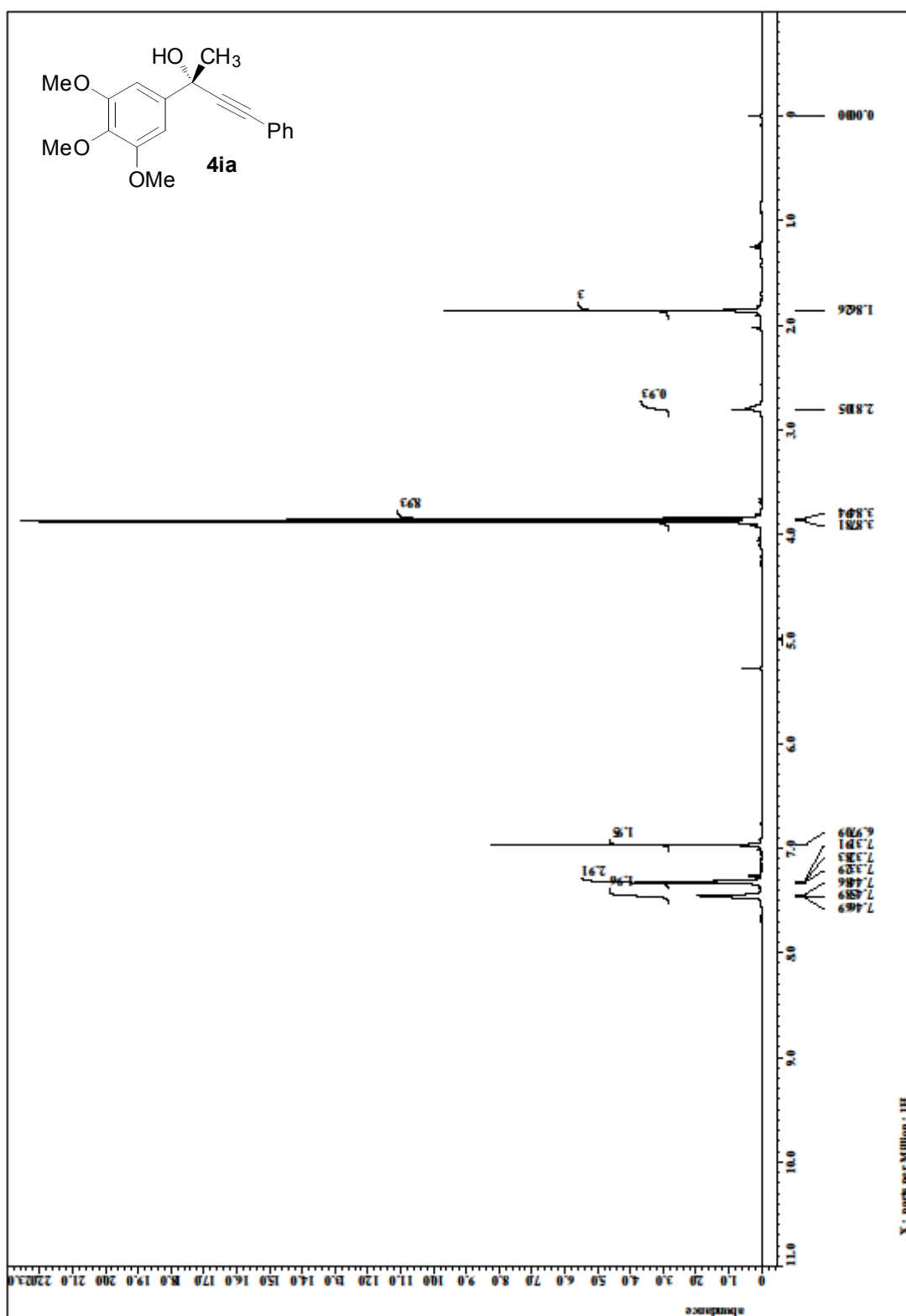


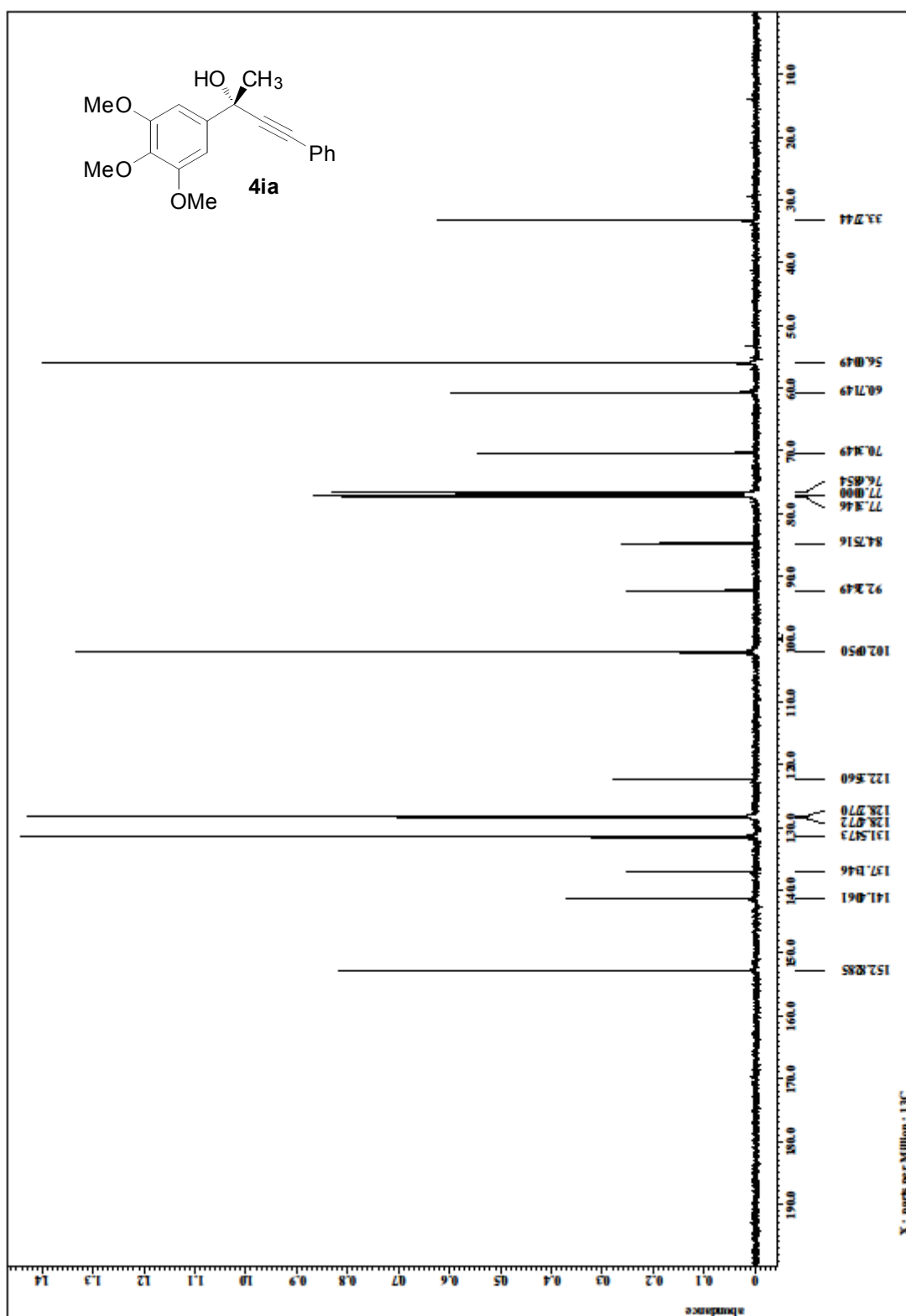
D-2500

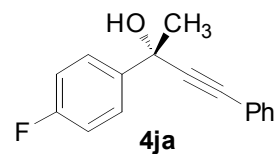
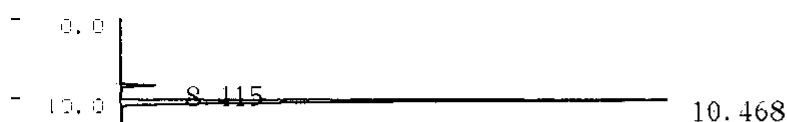
METHOD: TAG: 3 CH: 1

FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	8.65	887096	4.012	BU
2	10.83	21225511	95.988	UB
TOTAL		22112607	100.000	





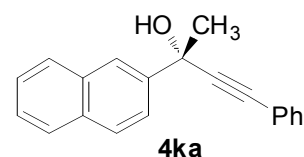


**** CALCULATION REPORT ****

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	8.415	118081	8031			4.651	
	2	10.468	2420739	126901			95.349	
TOTAL			2538820	134933			100	

C-RSA CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00

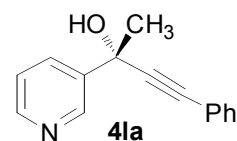
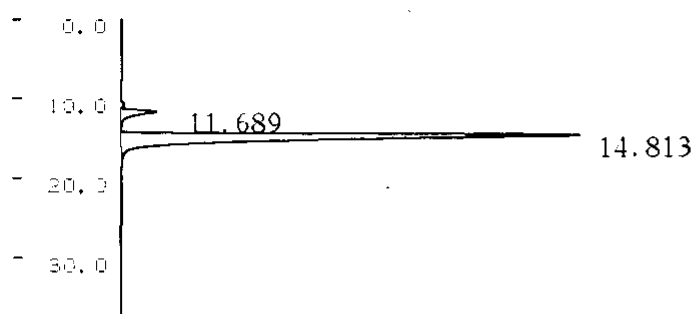
C-RSA CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00



**** CALCULATION REPORT ****

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	7	8.325	241235	10911			7.5882	
	8	10.99	2937861	97128			92.4118	
TOTAL			3179095	108040			100	

C-RSA CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00



**** CALCULATION REPORT ****

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	5	11.689	358967	8371	V		6.3958	
	6	14.813	5253583	106831	S		93.6042	
TOTAL			5612550	115202			100	