Supplementary Material (ESI) for Chemical Communications

Enantioselective Conjugate Addition of Boronic Acids to Enones Catalyzed by *O*-Monoacyltartaric Acids

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Supplementary Information

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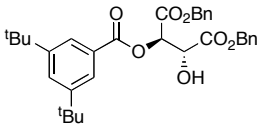
General Methods

Melting points (mp) are uncorrected. ^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ or DMSO-d_6 with JEOL JNM-ECX400 spectrometer. Tetramethylsilane (TMS) (δ = 0 ppm) and $CDCl_3$ (δ = 77.0 ppm) or DMSO-d_6 (δ = 39.52 ppm) served as internal standards for ^{1}H and ^{13}C NMR, respectively. Infrared spectra were recorded on JEOL JIR-6500W. 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. Thin-layer chromatography (TLC) analysis was carried out using Merck silica gel plates. Visualization was accomplished with UV light, phosphomolybdic acid and/or anisaldehyde. Column chromatography was performed using Kanto Chemical Silica Gel 60N (spherical, neutral, 63-210 μm).

Chalcone (**2a**) was purchased from Tokyo Kasei Kogyo (TCI) and used without purification. Benzalacetone (**2b**) was purchased from TCI and used after vacuum distillation. Enone **2c** was prepared *via* addition of phenylmagnesium bromide to crotonaldehyde and subsequent MnO_2-oxidation. Enone **2d** was prepared by TsOH-catalyzed aldol condensation of acetophenone with ethyl glyoxylate (polymer form) according to the literature.[1] Enones **2e** and **2f** were prepared by NaOH-promoted aldol condensation of acetophenone with the corresponding aldehyde.[2] (*E*)-Styrylboronic acid (**3a**) and (*E*)-1-octenylboronic acid (**3b**) were purchased from Sigma-Aldrich and used without purification. 2-Furanboronic acid (**3c**) and 2-benzofuranboronic acid (**3e**) were purchased from Wako Pure Chemical Industries and used without purification. Dichloromethane (dehydrated) and toluene (99%) were purchased from Kanto Chemical and nacalai tesque, respectively and stored over 4Å MS prior to use. All other solvents were purified based on standard procedures.

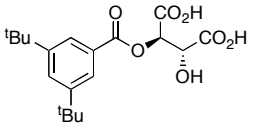
Synthesis of Catalyst 1k



(*R*,*R*)-Dibenzyl tartrate mono-3,5-di(tert-butyl)benzoate

To a solution of (*R*,*R*)-dibenzyl tartrate (495.8 mg, 1.50 mmol), triethylamine (0.33 mL, 2.34 mmol) and DMAP (4.5 mg, 2 mol %) in dry dichloromethane (6 mL) was added dropwise 3,5-di(*tert*-butyl)benzoyl chloride (379 mg, 1.0 equiv) in dry dichloromethane (4 mL) at rt. The reaction was stirred at rt for 19 h and quenched with water (10 mL). The mixture was extracted with dichloromethane (3×). The combined organic layers were dried over anhydrous Na_2SO_4, filtered, evaporated, and purified by silica gel column chromatography (SiO_2 18g, hexane/Et_2O/CH_2Cl_2 = 5/1/3) to give (*R*,*R*)-dibenzyl tartrate mono-3,5-di(*tert*-butyl)benzoate (594.8 mg, 73%).

^{1}H-NMR (400 MHz, $CDCl_3$): δ 1.34 (s, 18H), 3.41 (d, *J* = 7.4 Hz, 1H), 4.92 (dd, *J* = 1.8, 7.4 Hz, 1H), 5.10 (d, *J* = 11.9 Hz, 1H), 5.24 (d, *J* = 11.9 Hz, 1H), 5.26 (s, 2H), 5.67 (d, *J* = 1.8 Hz, 1H), 7.05 - 7.38 (m, 10 H), 7.65 (s, 1H), 7.82 (s, 2H).



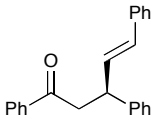
(*R*,*R*)-Tartaric acid mono-3, 5-di(*tert*-butyl)benzoate (1k)

A suspension of (*R*,*R*)-dibenzyl tartrate mono-3, 5-di(*tert*-butyl)benzoate (594.8 mg, 1.09 mmol) and 10% Pd/C (59.4 mg) in ethyl acetate (20 mL) was vigorously stirred under hydrogen atmosphere at rt for 18 h. The mixture was filtered through a Celite pad with ethyl acetate and concentrated under vacuum to give (*R*,*R*)-tartaric acid mono-3,5-di(*tert*-butyl)benzoate (**1k**) (411.5 mg, quant).

mp 178-181 °C; $[\alpha]_D^{27}$ –4.3 (c 1.00, ethanol); IR (KBr, cm^{-1}) 3408, 2964, 1732, 1230, 1120, 1063, 895, 769, 702; ^{1}H-NMR (400 MHz, DMSO-d_6) δ 1.32 (s, 18H), 4.66 (d, *J* = 2.3 Hz, 1H), 5.42 (d, *J* = 2.3 Hz, 1H), 7.71 (s, 1H), 7.84 (s, 2H); ^{13}C-NMR (100 MHz, DMSO-d_6) δ 31.1, 34.6, 70.2, 74.1, 123.5, 127.6, 128.5, 151.0, 165.6, 168.3, 172.0; Anal. Calcd. for $C_{19}H_{26}O_7 \cdot 0.8H_2O$ C, 59.92; H, 7.31; Found: C, 59.79; H, 7.17.

General Procedure for Conjugate Addition of Boronic Acids to Enones Catalyzed by 1k

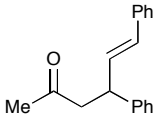
Under an argon atmosphere, a 20-mL screw-top test tube was charged with an enone **2** (0.3 mmol), a boronic acid **3** (0.36 mmol, 1.2 equiv), catalyst **1k** (11.1 mg, 10 mol %), methanol (0.72 mmol) and toluene (1 mL) at rt. Then, the mixture was heated at 50 °C for the indicated time (monitored by TLC analysis). The reaction mixture was cooled to rt and concentrate under vacuum. The residue was purified by silica gel column chromatography (hexane/AcOEt) to give an adduct **4**. The enantiomeric excess of **4** was determined by HPLC analysis using a chiral stationary phase column.



(3*S*,4*E*)-1,3,5-Triphenylpent-4-en-1-one (4a)

According to the general procedure, the reaction of chalcone (**2a**) (62.3 mg) and (*E*)-styrylboronic acid (**3a**) (53.5 mg) at 50 °C for 24 h gave adduct **4a** (86.0 mg, 92%, 87% ee (*S*)). The spectral data were consistent with the literature.[3] The absolute configuration was determined to be *S* in comparison with HPLC data.[3]

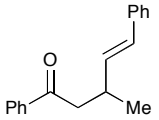
HPLC (Chiralpak AD-H, hexane/2-propanol = 200/1, flow rate = 1.0 mL/min, UV detection at 254 nm) t_R = 50.7 min (*R*, minor), 55.0 min (*S*, major).



(*E*)-4,6-Diphenylhex-5-en-2-one (4b)

According to the general procedure, the reaction of benzalacetone (**2b**) (43.9 mg) and (*E*)-styrylboronic acid (**3a**) (53.3 mg) at 60 °C for 48 h gave adduct **4b** (34.6 mg, 46%, 81% ee). The spectral data were consistent with the literature.[4]

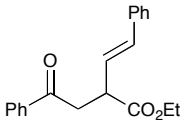
$[\alpha]_D^{28}$ −15.6 (c 2.07, $CHCl_3$ for 81% ee); HPLC (Chiralpak AD-H, hexane/2-propanol = 300/1, flow rate = 1.0 mL/min, UV detection at 254 nm) t_R = 32.1 min (minor), 37.0 min (major).



(*E*)-1,5-Diphenyl-3-methylpent-4-en-1-one (4c)

According to the general procedure, the reaction of (*E*)-1-phenylbut-2-en-1-one (**2c**) (44.2 mg) and (*E*)-styrylboronic acid (**3a**) (53.3 mg) at 50 °C for 24 h gave adduct **4c** (69.3 mg, 92%, 81% ee). The spectral data were consistent with the literature.[5]

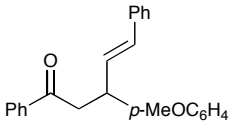
$[\alpha]_D^{29}$ +45.3 (c 1.09, $CHCl_3$ for 81% ee); HPLC (Chiralpak AD-H, hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, UV detection at 254 nm) t_R = 10.2 min (major), 11.7 min (minor).



Ethyl 4-oxo-4-phenyl-2-((*E*)-2-phenylethenyl)butanote (4d)

According to the general procedure, the reaction of (*E*)-ethyl 4-oxo-4-phenylbut-2-enoate (**2d**) (61.4 mg) and (*E*)-styrylboronic acid (**3a**) (53.1 mg) at 50 °C for 48 h gave adduct **4d** (68.4 mg, 74%, 85% ee).

mp 71-73 °C; $[\alpha]_D^{28}$ +86.8 (c 1.01, $CHCl_3$ for 85% ee); IR (KBr, cm^{-1}) 3059, 3028, 2981, 1728, 1687, 1597, 1448, 1215, 1163, 966, 756, 692; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.27 (t, *J* = 7.3 Hz, 3H), 3.25 (dd, *J* = 4.6, 17.9 Hz, 1H), 3.69 (dd, *J* = 9.2, 17.9 Hz, 1H), 3.88 (ddd, *J* = 4.6, 8.2, 9.2 Hz, 1H), 4.19 (m, 2H), 6.28 (dd, *J* = 8.2, 16.0 Hz, 1H), 6.60 (d, *J* = 16.0 Hz, 1H), 7.24 (t, *J* = 7.8 Hz, 1H), 7.31 (t, *J* = 7.8 Hz, 2H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 40.8, 44.2, 61.0, 126.1, 126.3, 127.7, 128.0, 128.5, 128.6, 132.7, 133.2, 136.43, 136.48, 173.2, 197.4; HRMS (FAB) Calcd. for $C_{20}H_{21}O_3$ ($M+H^+$) 309.1491, found 309.1484; HPLC (Chiralpak AD-H, hexane/2-propanol = 19/1, flow rate = 1.0 mL/min, UV detection at 254nm) t_R = 16.1 min (minor), 19.8 min (major).

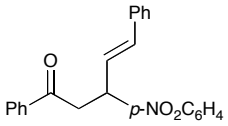


(*E*)-3-(*p*-Methoxyphenyl)-1,5-diphenylpent-4-en-1-one (4e)

According to the general procedure, the reaction of (*E*)-3-(*p*-methoxylphenyl)-1-phenylprop-2-en-1-one (**2e**) (71.5 mg) and (*E*)-styrylboronic acid (**3a**) (53.3 mg) at 50 °C for 24 h gave adduct **4e** (71.5 mg, 84%, 87% ee).

mp 64-66 °C; $[\alpha]_D^{28}$ –7.7 (c 0.97, $CHCl_3$ for 87% ee); IR (KBr, cm^{-1}) 3352, 3059, 2933, 2835, 1693, 1597, 1514, 1446, 1257, 1178, 1034, 966, 829, 750, 692; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.44 (dd, *J* = 6.9, 16.5 Hz, 1H), 3.49 (dd, *J* = 7.4, 16.5 Hz, 1H), 3.78 (s, 3H), 4.25 (ddd, *J* = 5.5, 6.9, 7.4 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 6.40 (dd, *J* = 5.5, 16.0 Hz, 1H), 6.85 (d, *J* =

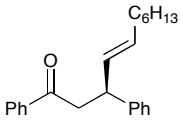
8.7 Hz, 2H), 7.15 - 7.32 (m, 7H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.93 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.0, 44.5, 55.1, 113.9, 126.1, 127.1, 128.0, 128.4, 128.5, 128.6, 129.6, 132.9, 133.0, 135.2, 137.0, 137.1, 158.1, 198.2; HRMS (FAB) : Calcd. for $C_{24}H_{22}O_2Na$ ($M+Na^+$) 365.1517, found 365.1530; HPLC (Chiralpak AS-H, hexane/2-propanol = 19/1, flow rate = 1.0 mL/min, UV detection at 254 nm) t_R = 14.5 min (major), 16.9 min (minor).



(*E*)-3-(*p*-Nitrophenyl)-1,5-diphenylpent-4-en-1-one (4f)

According to the general procedure, the reaction of (*E*)-3-(*p*-nitrophenyl)-1-phenylprop-2-en-1-one (**2f**) (76.2 mg) and (*E*)-styrylboronic acid (**3a**) (53.1 mg) at 50 °C for 24 h gave adduct **4f** (72.7 mg, 68%, 88% ee).

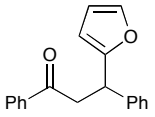
$[\alpha]_D^{29}$ +29.7 (c 1.415, $CHCl_3$ for 87% ee); IR (neat, cm^{-1}) 3059, 2926, 2852, 1687, 1680, 1597, 1514, 1495, 1448, 1344, 1205, 1111, 968, 856, 746, 692; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.54 (dd, *J* = 7.4, 17.0 Hz, 1H), 3.59 (dd, *J* = 6.9, 17.0 Hz, 1H), 4.43 (ddd, *J* = 6.9, 6.9, 7.4 Hz, 1H), 6.37 (dd, *J* = 6.9, 16.0 Hz, 1H), 6.44 (d, *J* = 16.0 Hz, 1H), 7.20-7.35 (m, 5H), 7.40-7.60 (m, 5H), 7.94 (d, *J* = 7.8 Hz, 2H), 8.18 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 43.6, 43.9, 123.9, 126.3, 127.7, 128.0, 128.6, 128.71, 128.73, 130.8, 131.3, 133.4, 136.5, 136.6, 146.7, 150.9, 197.1; HPLC (Chiralpak AS-H, hexane/2-propanol = 9/1, flow rate = 1.0 mL/min, UV detection at 254 nm) t_R = 29.7 min (major), 34.8 min (minor).



(*E*)-1,3-Diphenylundec-4-en-1-one (4g)

According to the general procedure, the reaction of chalcone (**2a**) (62.4 mg) and (*E*)-1-octenylboronic acid (**3b**) (56.0 mg) at 60 °C for 120 h gave adduct **4g** (46.1 mg, 48%, 69% ee (*S*)). The spectral data were consistent with the literature.[3] The absolute configuration was determined to be *S* in comparison with HPLC data.[3]

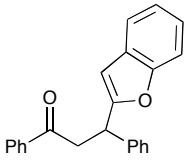
HPLC (Chiralcel OD-H, hexane/2-propanol = 99/1, flow rate = 1.0 mL/min, UV detection at 254nm) t_R = 6.8 min (*R*, minor), 7.6 min (*S*, major).



3-(Furan-2-yl)-1,3-diphenylpropan-1-one (4h)

According to the general procedure, the reaction of chalcone (**2a**) (62.5 mg) and 2-furanboronic acid (**3c**) (40.1 mg) at 50 °C for 24 h gave adduct **4h** (45.6 mg, 55%, 68% ee).

$[\alpha]_D^{28}$ –35.7 (c 0.955, $CHCl_3$ for 68% ee); IR (neat, cm^{-1}) 3061, 3028, 2924, 1684, 1597, 1508, 1448, 1144, 1078, 688; ^1H NMR (400 MHz, $CDCl_3$) δ 3.56 (dd, *J* = 6.9, 17.0 Hz, 1H), 3.82 (dd, *J* = 7.3, 17.0 Hz, 1H), 4.84 (dd, *J* = 6.9, 7.3 Hz, 1H), 6.03 (d, *J* = 3.2 Hz, 1H), 6.26 (dd, *J* = 1.8, 3.2 Hz, 1H), 7.19 - 7.32 (m, 6H), 7.44 (dd, *J* = 7.3, 7.8 Hz, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.93 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 40.2, 43.5, 105.7, 110.1, 126.8, 127.8, 128.0, 128.6, 133.1, 136.8, 141.5, 141.9, 156.7, 197.4 (one carbon is overlapped); HRMS (FAB) Calcd. for $C_{19}H_{16}O_2Na$ ($M+Na^+$) 299.1048, found 299.1038; HPLC (Chiralcel OD-3, hexane/2-propanol = 49/1, flow rate = 1.0 mL/min, UV detection at 254 nm) t_R = 9.8 min (minor), 10.2 min (major).

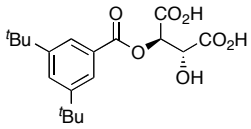


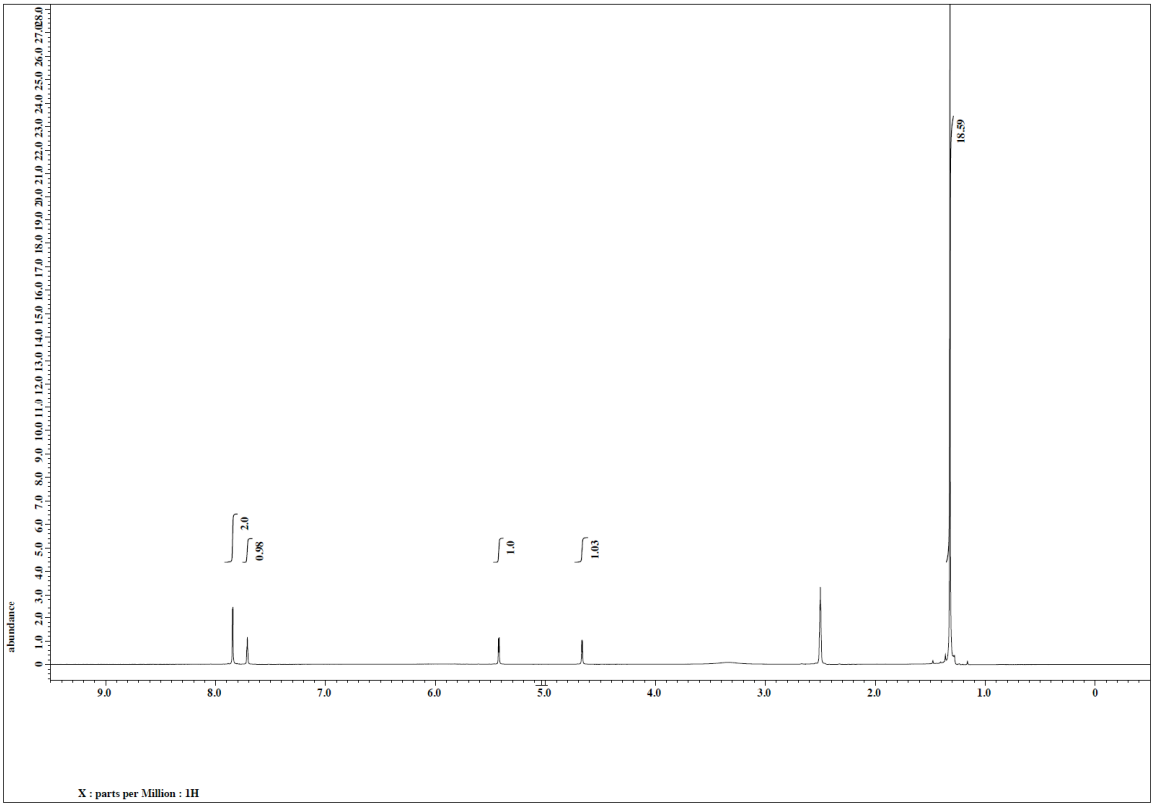
3-(Benzofuran-2-yl)-1,3-diphenylpropan-1-one (4i)

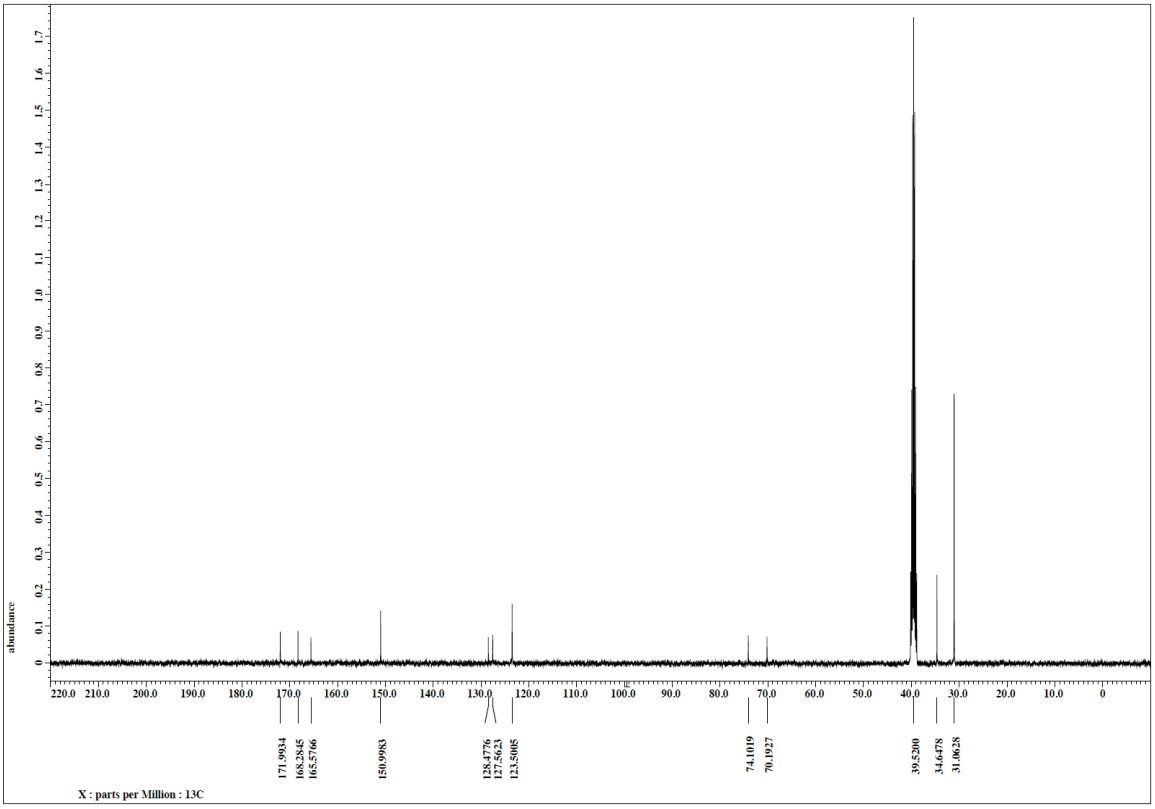
According to the general procedure, the reaction of chalcone (**2a**) (62.3 mg) and 2-benzofuranboronic acid (**3d**) (58.4 mg) at 50 °C for 24 h gave adduct **4i** (77.3 mg, 79%, 81% ee).

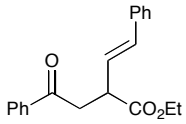
$[\alpha]_D^{28}$ –73.2 (c 0.715, $CHCl_3$ for 81% ee); IR (neat, cm^{-1}) 3032, 2891, 1676, 1599, 1579, 1495, 1454, 1236, 1165, 700; ^1H NMR (400 MHz, $CDCl_3$) δ 3.67 (dd, *J* = 7.3, 17.4 Hz, 1H), 3.94 (dd, *J* = 7.3, 17.4 Hz, 1H), 4.98 (t, *J* = 7.3 Hz, 1H), 6.43 (s, 1H), 7.12 - 7.58 (m, 12H), 7.96 (d, *J* = 7.4 Hz, 2H); ^{13}C NMR (400 MHz, $CDCl_3$) δ 40.5, 43.2, 102.9, 110.9, 120.5, 122.5, 123.5, 127.0, 127.9, 128.0, 128.5, 128.58, 128.65, 133.2, 136.6, 141.2, 154.7, 159.8, 197.1; HRMS (FAB) Calcd. for $C_{23}H_{18}O_2Na$ ($M+Na^+$) 349.1204, found 349.1202; HPLC (Chiralpak AD-H, hexane/2-propanol = 39/1, flow rate = 1.0 mL/min, UV detection at 254 nm) t_R = 19.0 min (major), 25.2 min (minor).

^{1}H and ^{13}C NMR Spectra of New Compounds





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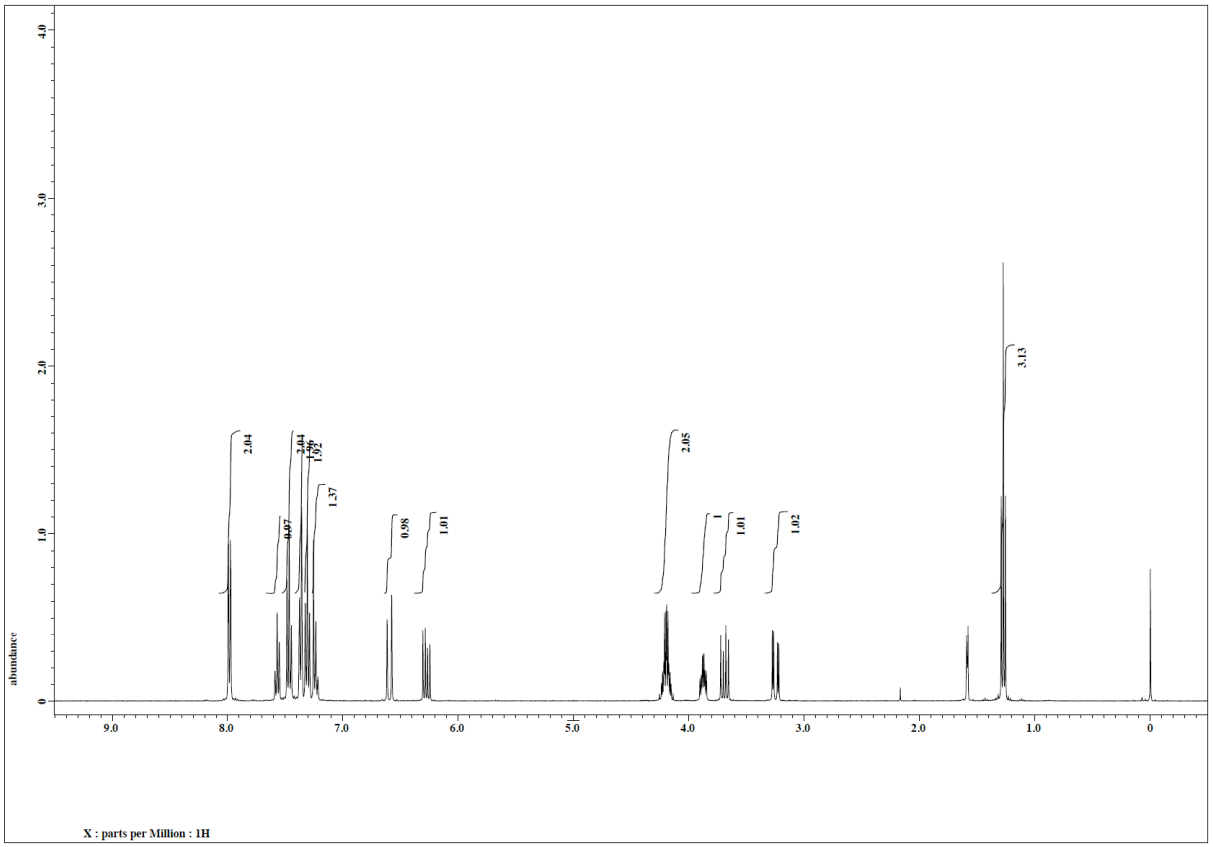
Ph
CO2Et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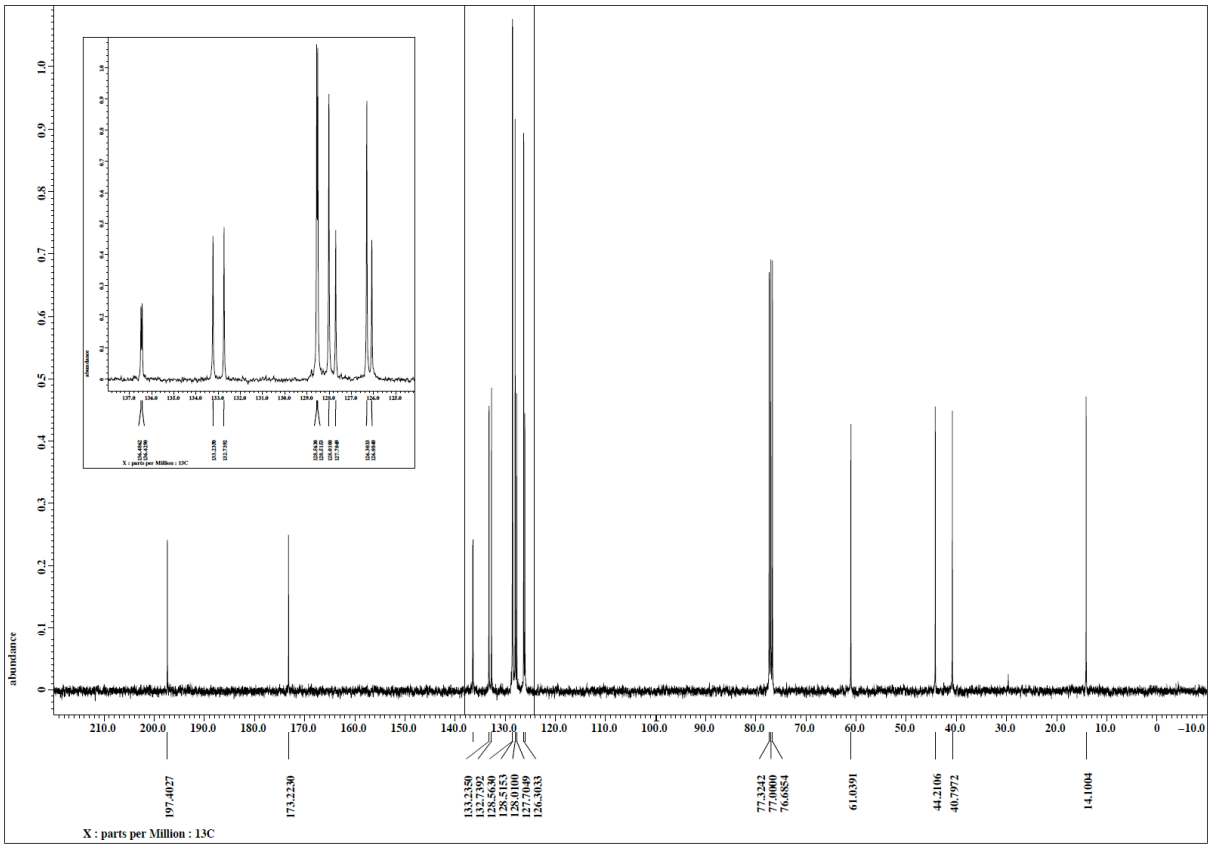
0.97
2.04
1.96
1.92
1.37
0.98
1.01
2.05
1
1.01
1.02
3.13
X : parts per Million : 1H


abundance
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133.2350
132.7392
128.5630
128.5153
128.0100
127.7049
127.7049
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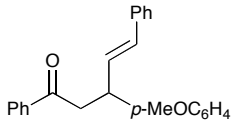
40.7972
14.1004
X : parts per Million : 13C


Ph
O
Ph
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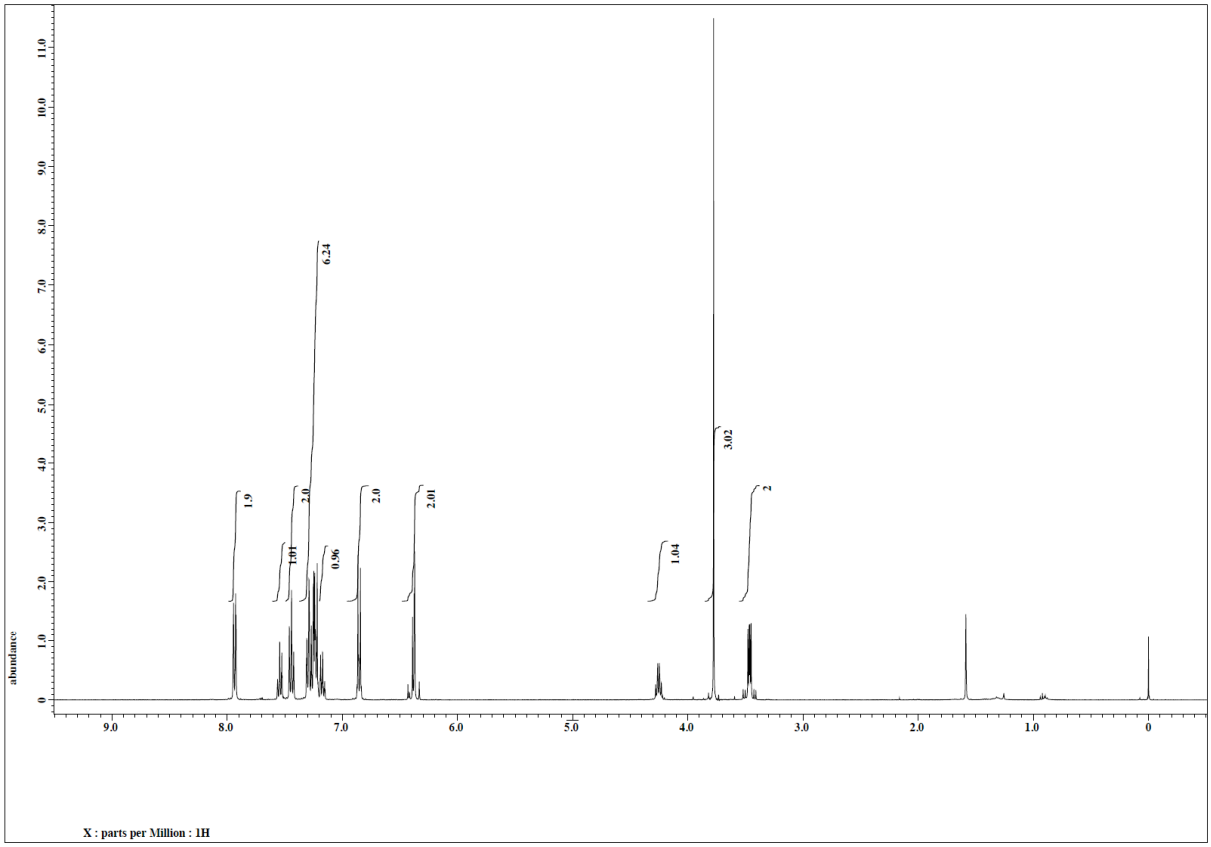
abundance
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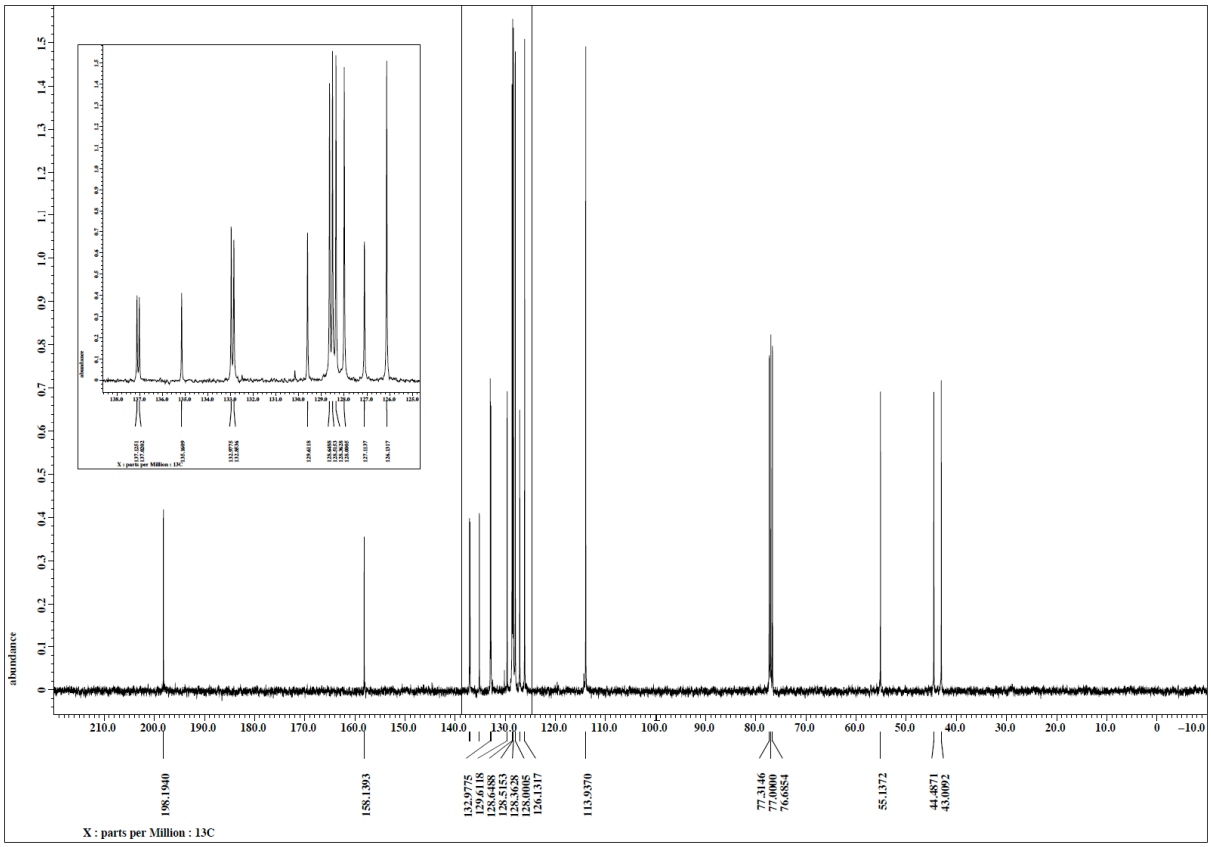
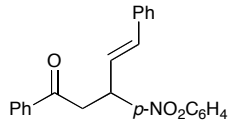
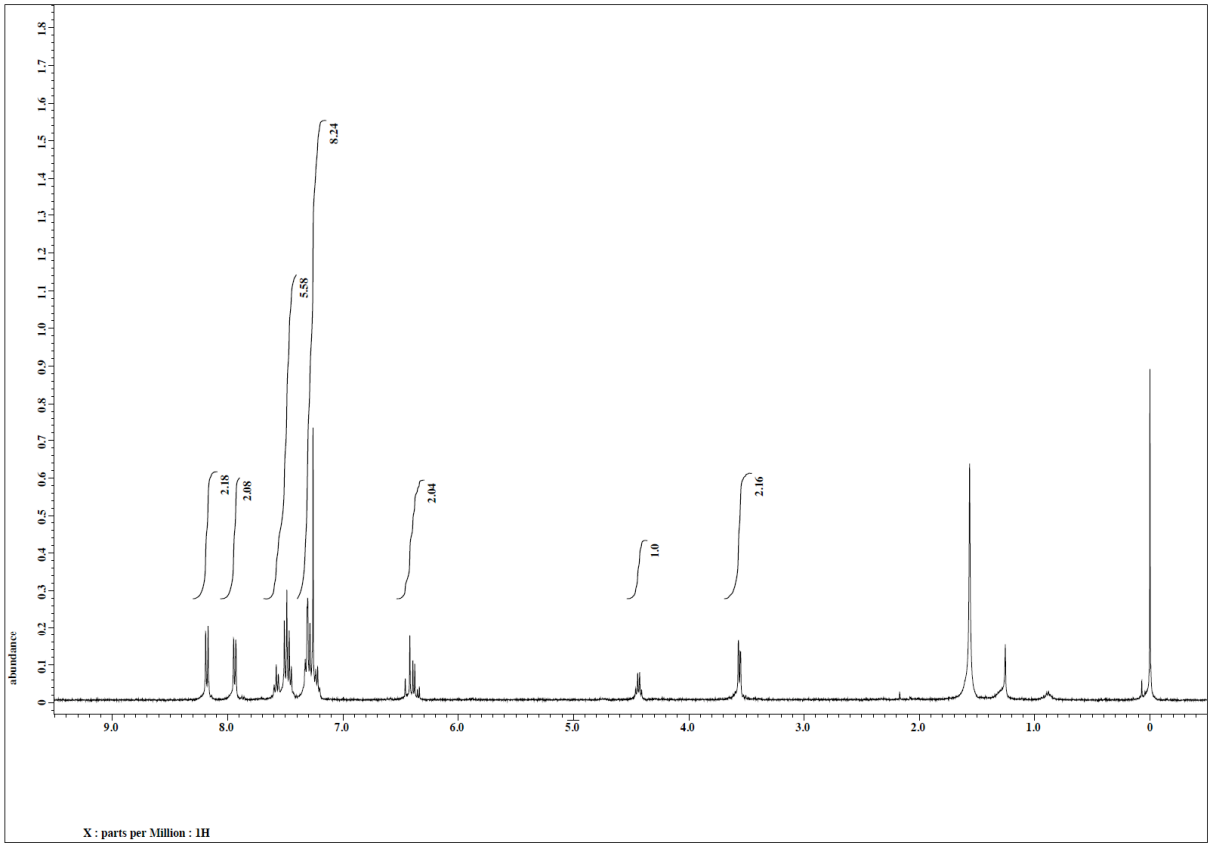
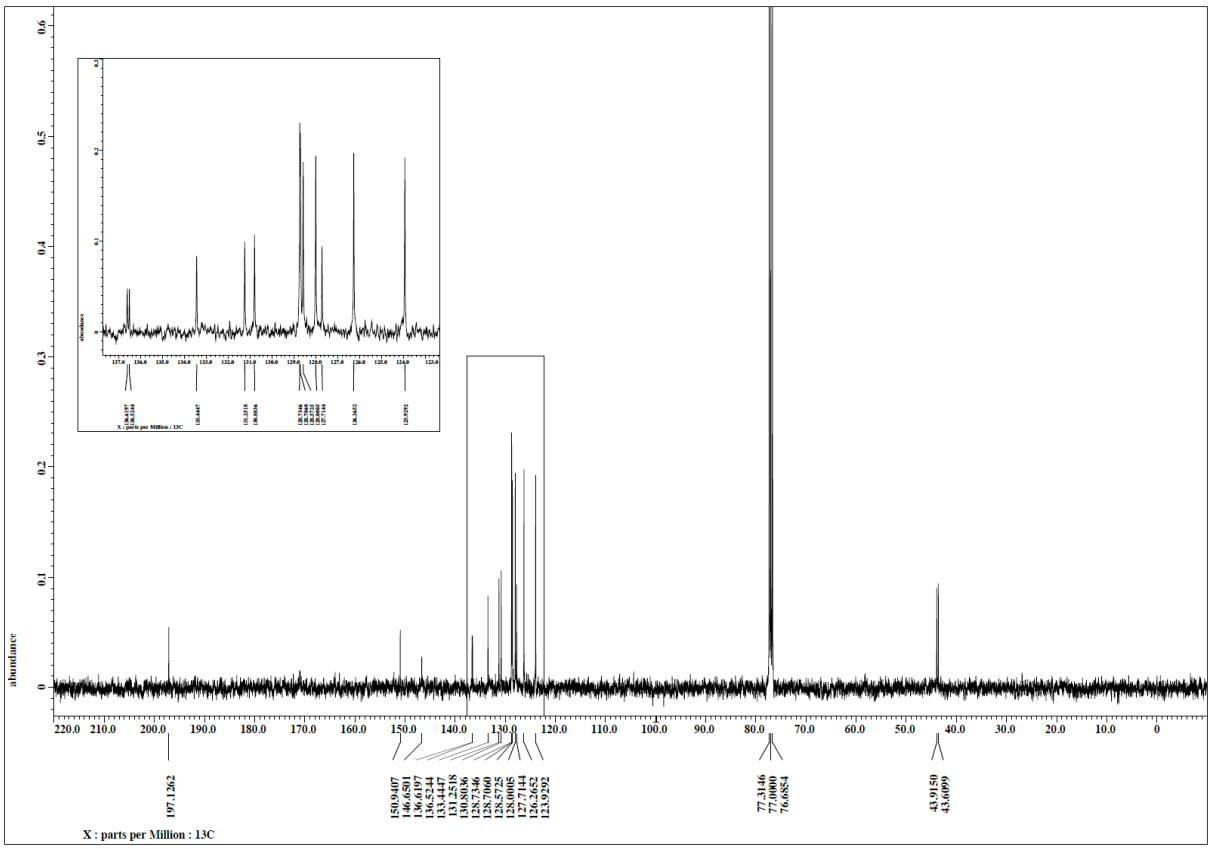
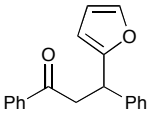
2.0
6.24
0.96
2.0
2.01
1.04
3.02
2
X : parts per Million : 1H

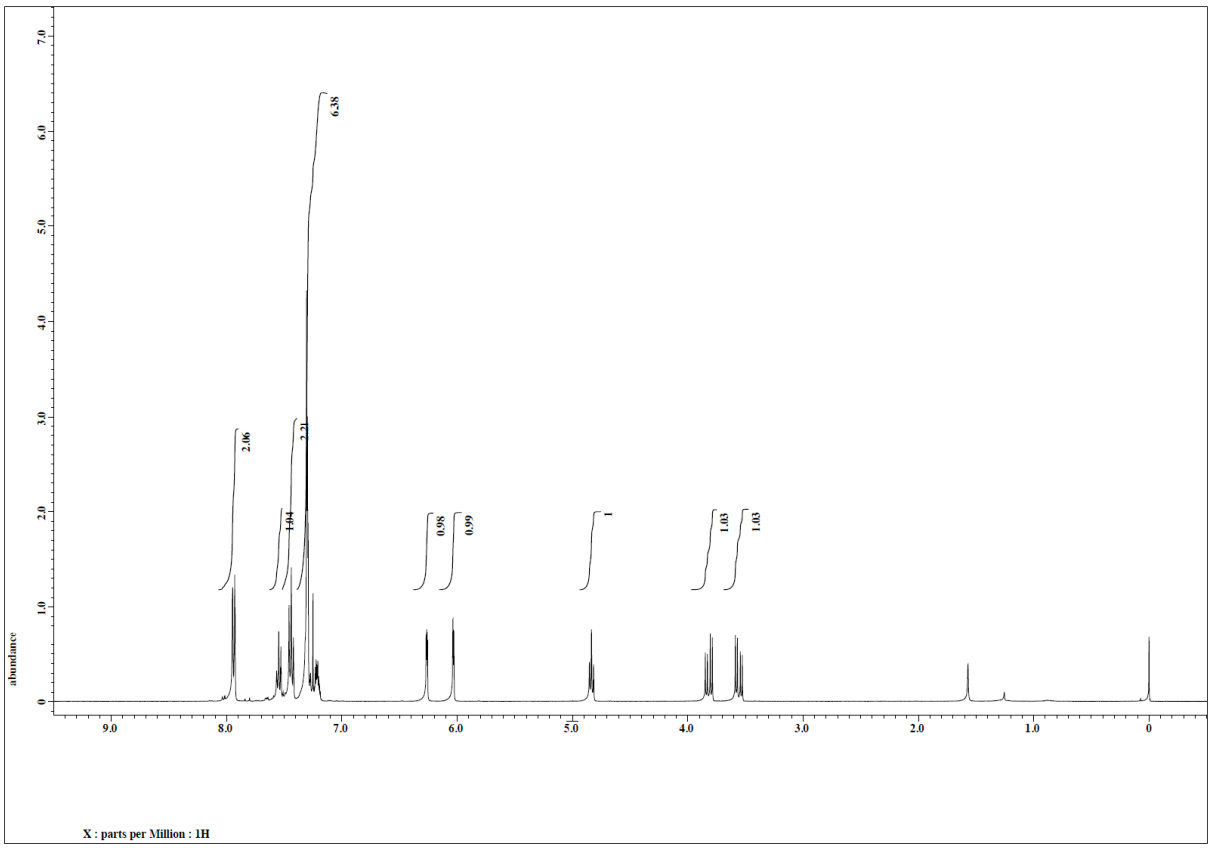

abundance
198.1940
158.1393
132.9775
129.6118
128.6488
128.5153
128.3628
126.1317
113.9370
77.3146
77.0000
76.6854
55.1372
44.4871
43.0092
X : parts per Million : 13C

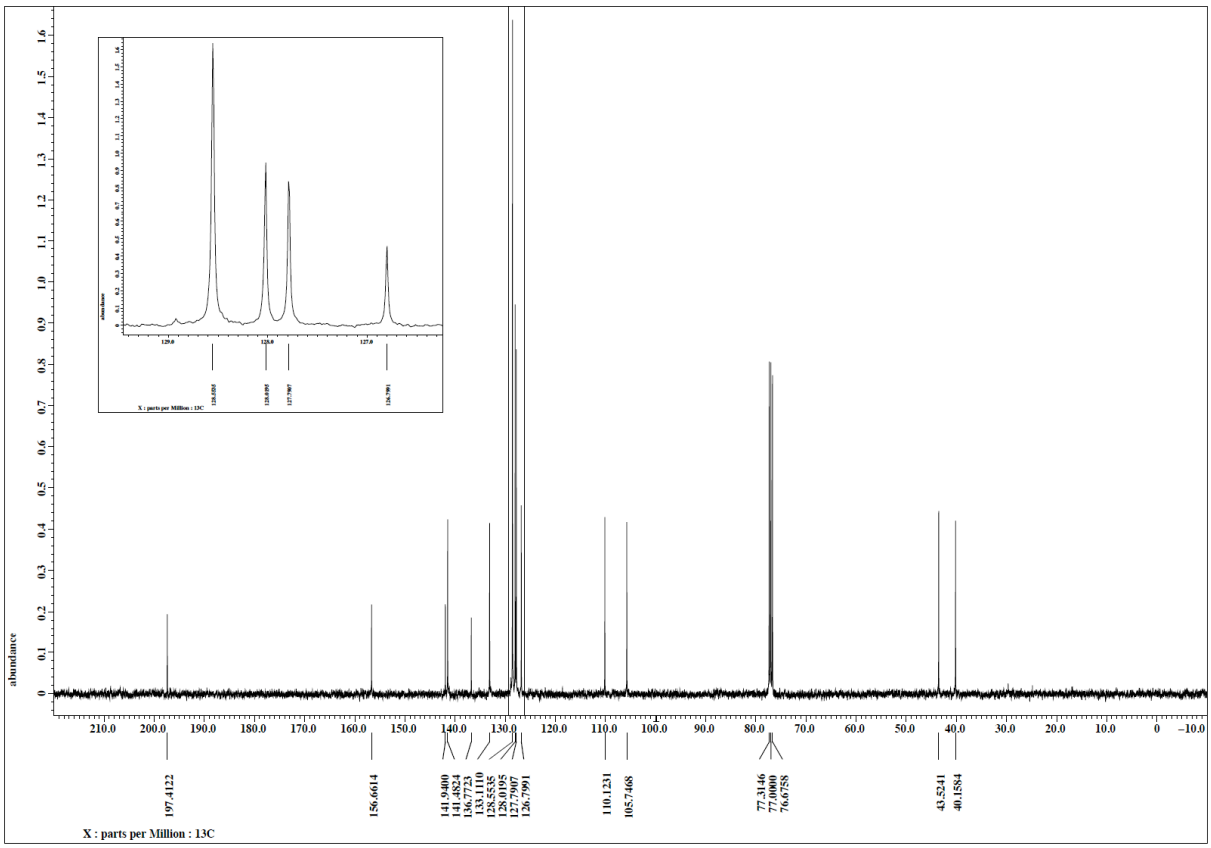

Ph
O
Ph
p-NO2C6H4

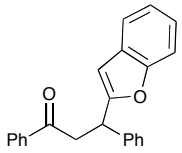

8.24
5.58
2.18
2.08
2.04
1.0
2.16
abundance
X : parts per Million : 1H

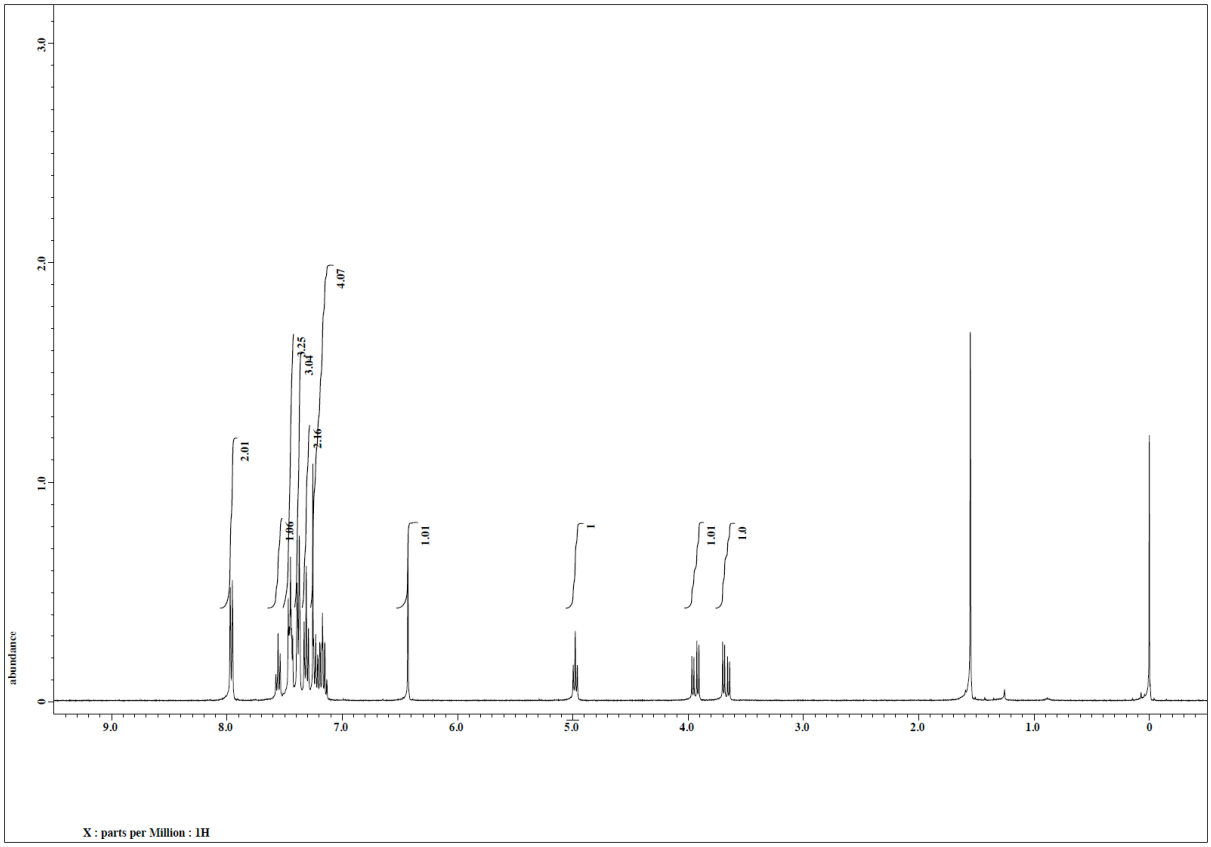

abundance
197.1262
150.9407
146.6501
136.6197
136.5244
131.1457
131.2518
130.8036
128.7346
128.7060
128.5725
128.1005
127.7144
126.2652
123.9292
77.3146
77.0000
76.6854
43.9150
43.6099
X : parts per Million : 13C

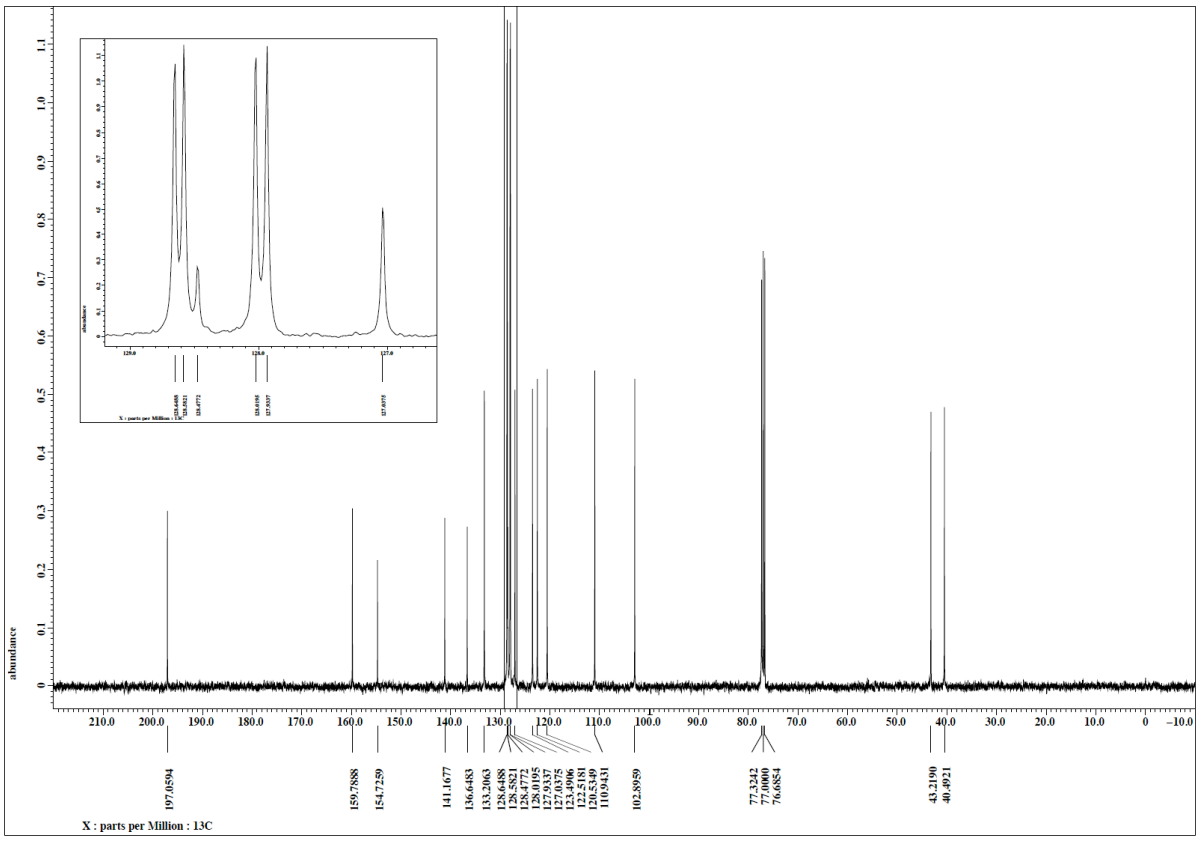

O
O
Ph
Ph


2.06
1.04
2.21
6.38
0.98
0.99
1
1.03
1.03
abundance
X : parts per Million : 1H

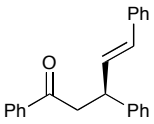

197.4122
156.6614
141.9400
141.5524
136.7721
133.1110
128.5535
128.0195
127.7907
126.7991
110.1231
105.7468
77.3146
77.0000
76.6758
43.5241
40.1584
abundance
X : parts per Million : 13C


O
O
Ph
Ph


abundance
2.01
1.06
3.25
3.04
2.16
4.07
1.01
1
1.01
1.0
X : parts per Million : 1H

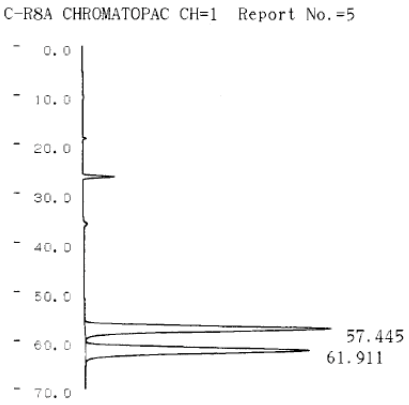

abundance
197.0584
159.7888
154.7259
141.1677
136.6483
133.2063
128.6488
128.5571
128.4772
128.0195
127.9337
127.0375
123.1906
122.5315
120.5349
110.9431
102.8959
77.3342
77.0000
76.6654
43.2190
40.4921
X : parts per Million : 13C

HPLC Traces of Optically Active Compounds



(*S*)-**4a**
CHIRALPAK AD-H
Hexane/^{i}PrOH = 200/1
1.0 mL/min, 254 nm

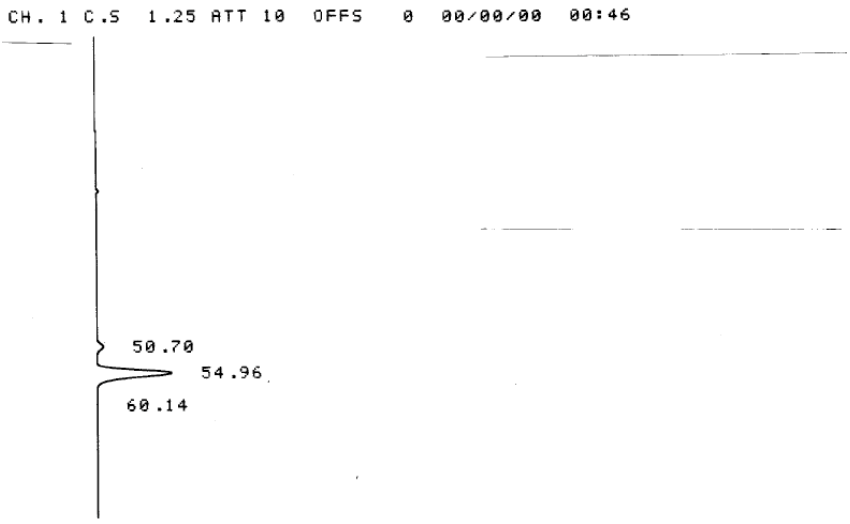
1. Racemic



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	8	57.445	7238330	92439			49.9225	
	9	61.911	7260799	84120			50.0775	
		TOTAL	14499129	176559			100	

2. Optically active (87% ee)



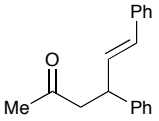
D-2500 00/00/00 00:46

METHOD: TAG: 1 CH: 1

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

NO.	RT	AREA	CONC	BC
1	50.70	579981	6.628	BV
2	54.96	8171121	93.372	VB
TOTAL		8751102	100.000	

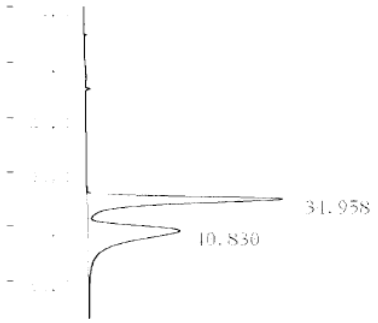
PEAK REJ : 0



4b
CHIRALPAK AD-H
Hexane/^{i}PrOH = 300/1
1.0 mL/min, 254 nm

1. Racemic

C:¥SA CHROMATOPAC CH-1 Report No.=12 DATA-1:¥CHRM1.C00 10-05-19 16:55:18



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	5	34.958	1511650	16212			50.1171	
	6	40.83	1534445	7653	V		49.8829	
		TOTAL	3076095	23865			100	

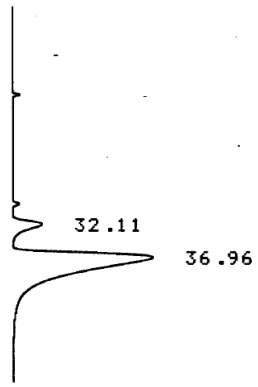
C:¥SA CHROMATOPAC CH-1 Report No.=1 DATA-1:¥CHRM1.C00 10-05-20 09:55:22

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	11.602	511[illegible]	3661			10.2043	
	2	45.909	450367[illegible]	28411	V		89.7957	
		TOTAL	5015443	34071			100	

2. Optically active (81% ee)

CH. 1 C.S 1.25 ATT 8 OFFS 0 00/00/00 00:40

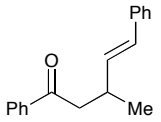


D-2500 00/00/00 00:40

METHOD: TAG: 1 CH: 1

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

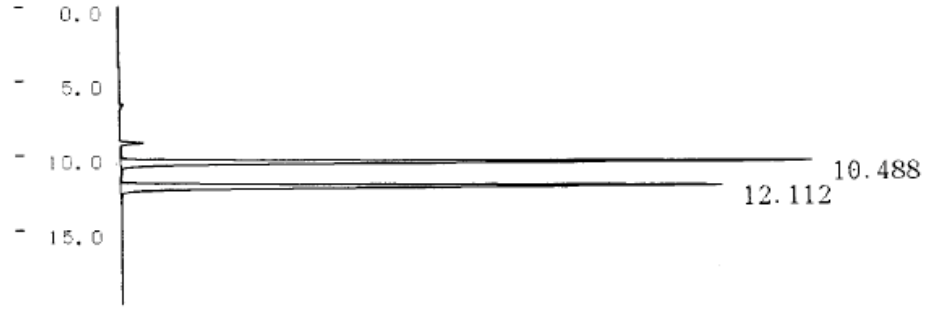
NO.	RT	AREA	CONC	BC
1	32.11	782281	9.298	BB
2	36.96	7631590	90.702	BB
TOTAL		8413871	100.000	
PEAK REJ :		0		



4c
CHIRALPAK AD-H
Hexane/^{i}PrOH = 99/1
1.0 mL/min, 254 nm

1. Racemic

C-R8A CHROMATOPAC CH=1 Report No.=4 DATA=1:@CHRM1.C00 09/09/17 12:50:50

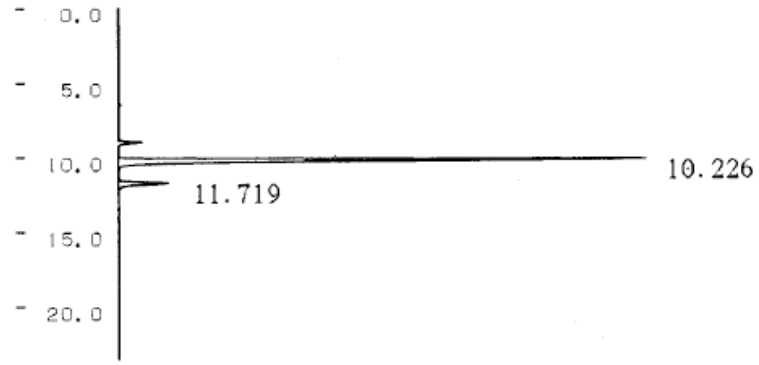


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	6	10.488	2191120	170875			50.1068	
	7	12.112	2181777	148769	S		49.8932	
		TOTAL	4372898	319644			100	

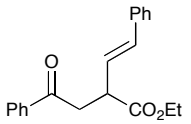
2. Optically active (81% ee)

C-R8A CHROMATOPAC CH=1 Report No.=5 DATA=1:@CHRM1.C00 10/07/13 17:54:14



** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	15	10.226	12170047	1045039	E		90.407	
	16	11.719	1291356	97330	V		9.593	
		TOTAL	13461401	1142370			100	



4d
CHIRALPAK AD-H
Hexane/^{i}PrOH = 19/1
1.0 mL/min, 254 nm

1. Racemic

C-R8A CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 09/09/12 14:58:10

** CALCULATION REPORT **

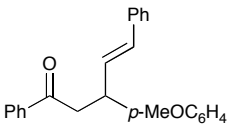
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	9	15.869	5245144	264449			49.4619	
	11	19.182	5359266	217235			50.5381	
		TOTAL	10604410	481683			100	

2. Optically active (85% ee)

C-R8A CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 10/05/14 09:17:26

** CALCULATION REPORT **

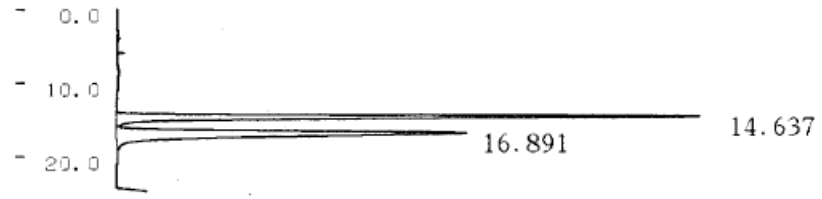
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	5	16.132	296307	14047			7.6861	
	6	19.827	3558801	135279			92.3139	
		TOTAL	3855107	149326			100	



4e
CHIRALPAK AS-H
Hexane/^{i}PrOH = 19/1
1.0 mL/min, 254 nm

1. Racemic

C-R8A CHROMATOPAC CH=1 Report No.=12 DATA=1:@CHRM1.C00 10/07/16 18:06:00



** CALCULATION REPORT **

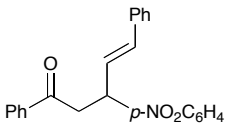
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	17	14.637	4631026	146854			50.5447	
	18	16.891	4531222	87770	V		49.4553	
		TOTAL	9162248	234624			100	

2. Optically active (87% ee)

C-R8A CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 10/07/16 15:29:02

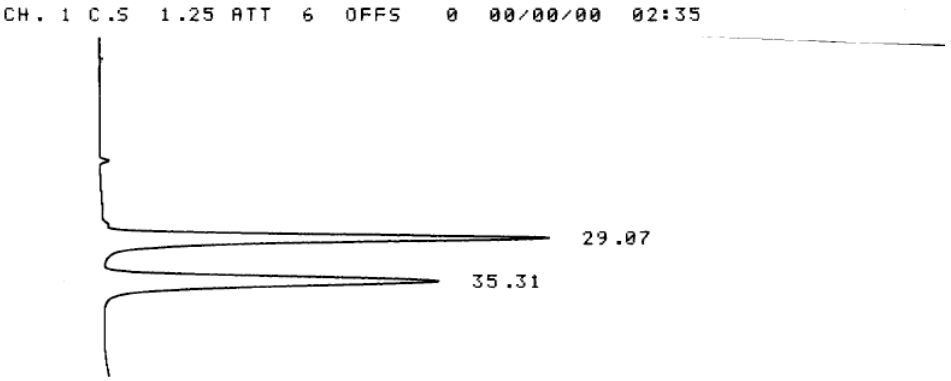
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	23	14.472	28049416	893105			93.3976	
	24	16.937	1982846	37216	SV		6.6024	
		TOTAL	30032262	930320			100	



4f
CHIRALPAK AS-H
Hexane/^{i}PrOH = 9/1
1.0 mL/min, 254 nm

1. Racemic



D-2500 00/00/00 02:35

METHOD: TAG: 2 CH: 1

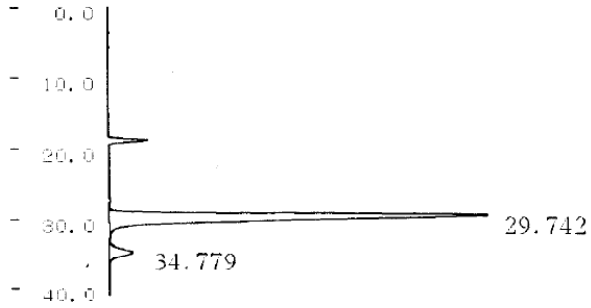
FILE: 0 CALC-METHOD: AREA% TABLE: 0 CONC: AREA

NO.	RT	AREA	CONC	BC
1	29.07	2498870	50.720	BB
2	35.31	2427920	49.280	BB
TOTAL		4926790	100.000	

PEAK REJ : 0

2. Optically active (87% ee)

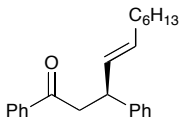
C-R8A CHROMATOPAC CH=1 Report No.=1 DATA=1:@CHRM1.C00 10/07/17 10:40:12



** CALCULATION REPORT **

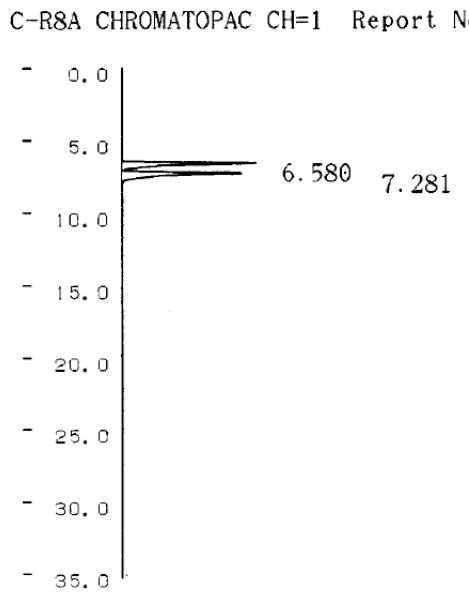
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	10	29.742	12714868	198363			93.3704	
	11	34.779	902790	12080			6.6296	
		TOTAL	13617657	210443			100	

C-R8A CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 10/07/17 10:40:12



(*S*)-**4g**
CHIRALCEL OD-H
Hexane/^{i}PrOH = 99/1
1.0 mL/min, 254 nm

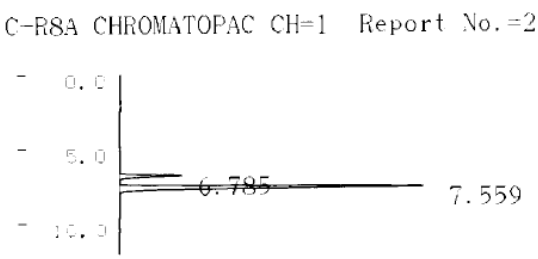
1. Racemic



** CALCULATION REPORT **

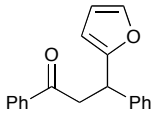
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	3	6.58	902225	69007			49.9261	
	4	7.281	904896	61571	V		50.0739	
		TOTAL	1807120	130578			100	

2. Optically active (69% ee)



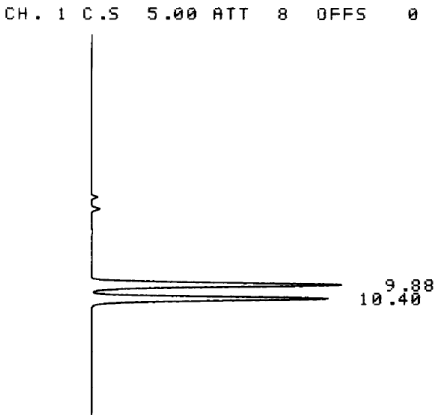
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	3	6.785	168302	15691			15.5901	
	4	7.559	911238	75261	V		84.4099	
		TOTAL	1079540	90952			100	



4h
CHIRALCEL OD-3
Hexane/^{i}PrOH = 49/1
1.0 mL/min, 254 nm

1. Racemic



D-2500 00/00/00 00:35

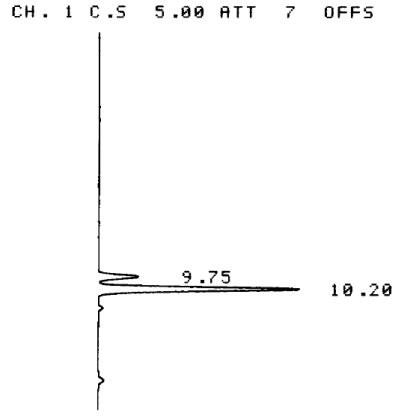
METHOD: TAG: 1 CH: 1

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

NO.	RT	AREA	CONC	BC
1	9.88	837471	49.856	BV
2	10.40	842313	50.144	VB
TOTAL		1679784	100.000	

PEAK REJ : 0

2. Optically active (68% ee)



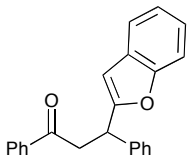
D-2500 00/00/00 01:36

METHOD: TAG: 3 CH: 1

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

NO.	RT	AREA	CONC	BC
1	9.75	65234	15.974	BV
2	10.20	343148	84.026	VB
TOTAL		408382	100.000	

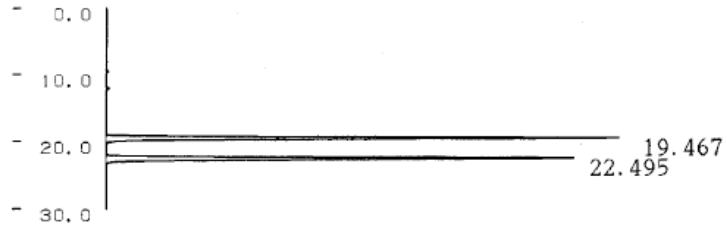
PEAK REJ : 0



4i
CHIRALPAK AD-H
Hexane/^{i}PrOH = 39/1
1.0 mL/min, 254 nm

1. Racemic

C-R8A CHROMATOPAC CH=1 Report No.=5 DATA=1:@CHRM1.C00 09/08/06 16:30:12

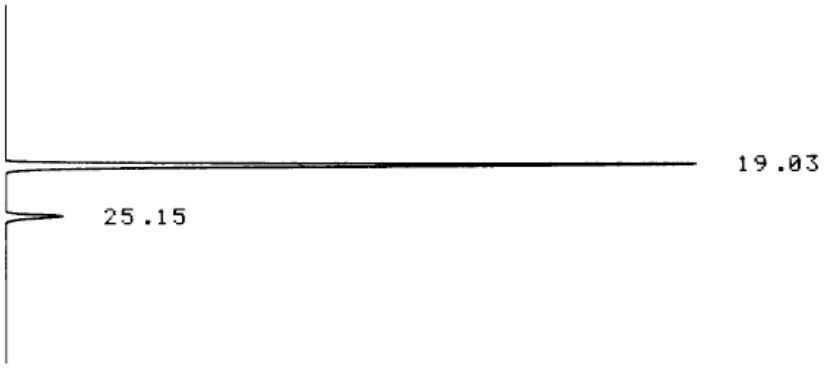


** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	15	19.467	3231387	140497	S		49.9885	
	17	22.495	3232877	128072	S		50.0115	
		TOTAL	6464264	268569			100	

2. Optically active (81% ee)

CH. 1 C.S 1.25 ATT 9 OFFS 0 00/00/00 00:07



D-2500 00/00/00 00:07

METHOD: TAG: 1 CH: 1

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

NO.	RT	AREA	CONC	BC
1	19.03	8102660	90.287	BB
2	25.15	871633	9.713	BB
TOTAL		8974293	100.000	

PEAK REJ : 0

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