Electronic Supplementary Information (ESI)

Highly Efficient Asymmetric Aldol Reaction in Brine Using Fluorous Sulfonamide Organocatalyst

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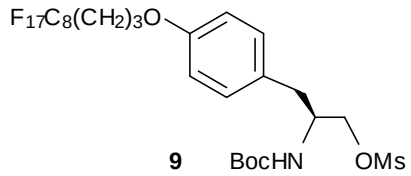
1. General Information.

^{1}H NMR and ^{13}C NMR spectra were measured with a JEOL AL 400 spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR), or JEOL ECA-500 spectrometer (500 MHz for ^{1}H NMR and 125 MHz for ^{13}C NMR). The chemical shifts are expressed in ppm downfield from tetramethylsilane (δ = 0.00) as an internal standard. For thin layer chromatographic (TLC) analyses, Merck precoated TLC plates (silica gel 60 F_{254}, Art 5715) were used. The products were isolated by flash column chromatography on silica gel (Kanto Chemical, silica gel 60N, spherical, neutral, 40-50 μm).

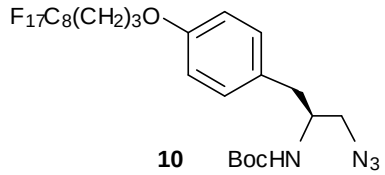
2. Preparation of fluorous organocatalyst 4

2-1. Compound 9



To a solution of compound **8**[1] (1.85 g, 2.54 mmol) in dry THF (18 mL) were added triethylamine (0.71 mL, 5.09 mmol) and methanesulfonyl chloride (236 μL, 3.05 mmol) at room temperature. After stirring for 2.5 h at room temperature, the reaction mixture was added to water and extracted three times with AcOEt. The AcOEt layers were combined, washed with brine, dried over anhydrous $MgSO_4$, and evaporated. Hexane was added to the residue, and the precipitate was collected over grass filter. The precipitate was washed with hexane to give compound **9** (2.01 g, 98%) as a white powder. Mp 108-110 ^{o}C; $[\alpha]^{19}_D$ = -7.3^o (c 0.50, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.42 (s, 9H), 2.08-2.12 (m, 2H), 2.26-2.36 (m, 2H), 2.79 (dd, *J* = 8.1, 13.7 Hz, 1H), 2.85-2.89 (m, 1H), 3.02 (s, 3H), 4.02 (t, *J* = 6.3 Hz, 2H), 4.05 (brs, 1H), 4.11 (dd, *J* = 4.0, 10.3 Hz, 1H), 4.23 (brs, 1H), 4.72 (brs, 1H), 6.85 (d, *J* = 8.5 Hz, 2H), 7.13 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.7, 27.9 (t, $^2J_{C\text{-}F}$ = 21.5 Hz), 28.3, 36.2, 37.2, 50.9, 66.3, 69.7, 80.0, 114.7, 128.9, 130.3, 155.1, 157.6; Anal. Calcd for $C_{26}H_{28}F_{17}NO_6S$: C, 38.77; H, 3.50; N, 1.74. Found: C, 38.52; H, 3.34; N, 1.75.

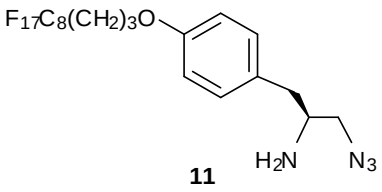
2-2. Compound 10



To a solution of compound **9** (1.99 g, 2.47 mmol) in dry DMF (15 mL) was added NaN_3 (241 mg, 3.71 mmol) at room temperature. After stirring for 3 days at 80 ^{o}C, the reaction mixture was added to water and extracted with AcOEt. The AcOEt layers were washed with water and brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by flash column chromatography on silica gel with a 9:1 mixture of hexane and AcOEt to give the pure **10** (1.58 g, 85%) as a white powder. Mp 74-76 ^{o}C; $[\alpha]^{18}_D$ = -1.9^o (c 0.50, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.43 (s, 9H), 2.07-2.12 (m, 2H), 2.26-2.36 (m, 2H), 2.72 (dd, *J* = 8.0, 13.8 Hz, 1H), 2.80-2.84 (m, 1H), 3.29 (dd, *J* = 4.0, 12.0 Hz, 1H), 3.40-3.43 (m, 1H), 3.92 (brs, 1H), 4.02 (t, *J* = 5.7 Hz, 2H), 4.63 (brs, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 7.11 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.6, 27.9 (t, $^2J_{C\text{-}F}$ = 21.0 Hz), 28.3, 37.2, 51.4, 53.0, 66.3, 79.8,

114.6, 129.5, 130.3, 155.1, 157.4; Anal. Calcd for $C_{25}H_{25}F_{17}N_4O_3$: C, 39.00; H, 3.35; N, 7.45. Found: C, 39.78; H, 3.18; N, 7.22.

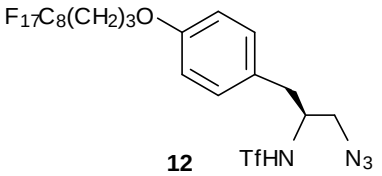
2-3. Compound 11



11

To a solution of compound **10** (1.03 g, 1.36 mmol) in AcOEt (7 mL) was added 2.5 mL of a 4M solution of hydrochloric acid in AcOEt at 0 °C. After stirring for 3 h at room temperature, the reaction mixture was evaporated. The residue was added to saturated aqueous $NaHCO_3$ and extracted three times with AcOEt. The AcOEt layers were combined, washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by flash column chromatography on silica gel with a 50:1 mixture of $CHCl_3$ and MeOH to give the pure **11** (879 mg, 99%) as a white powder. Mp 40-41 °C; $[\alpha]^{20}_D$ = +4.6° (c 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.55 (brs, 2H), 2.07-2.13 (m, 2H), 2.25-2.39 (m, 2H), 2.54 (dd, *J* = 7.7, 13.5 Hz, 1H), 2.73 (dd, *J* = 5.3, 13.5 Hz, 1H), 3.11-3.17 (m, 1H), 3.20 (dd, *J* = 6.8, 11.6 Hz, 1H); 3.38 (dd, *J* = 3.9, 11.6 Hz, 1H); 4.03 (t, *J* = 5.8 Hz, 2H), 6.85 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.6, 27.9 (t, $^2J_{C\text{-}F}$ = 21.0 Hz), 40.5, 52.5, 57.4, 66.3, 114.6, 130.2, 130.5, 157.3; Anal. Calcd for $C_{20}H_{17}F_{17}N_4O$: C, 36.82; H, 2.63; N, 8.59. Found: C, 36.64; H, 2.53; N, 8.34.

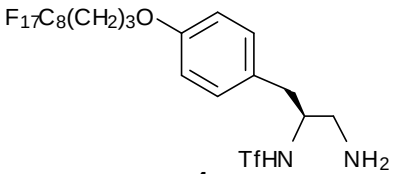
2-4. Compound 12



12

To a solution of **11** (820 mg, 1.26 mmol) in dry CH_2Cl_2 (13 mL) was added triethylamine (700 μL, 5.03 mmol) at room temperature under an argon atmosphere. After stirring for 5 min, trifluoromethanesulfonic anhydride (317 μL, 1.89 mmol) was added to the reaction mixture at 0 °C. After stirring for 1 h at 0 °C, the reaction mixture was additionally stirred for 7 h at room temperature. The reaction mixture was added to water and extracted three times with AcOEt. The AcOEt layers were combined, washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by flash column chromatography on silica gel with $CHCl_3$ to give pure **12** (961 mg, 97%) as a white powder. Mp 61-62 °C; $[\alpha]^{16}_D$ = +2.0° (c 1.00, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.08-2.13 (m, 2H), 2.26-2.37 (m, 2H), 2.86 (dd, *J* = 8.6, 13.8 Hz, 1H), 2.94 (dd, *J* = 5.7, 13.8 Hz, 1H), 3.41 (dd, *J* = 3.4, 12.6 Hz, 1H), 3.50 (dd, *J* = 4.6, 12.6 Hz, 1H), 3.85 (brs, 1H), 4.03 (t, *J* = 5.7 Hz, 2H), 4.98 (brs, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 7.10 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.5, 27.9 (t, $^2J_{C\text{-}F}$ = 21.0 Hz), 38.1, 53.2, 55.9, 66.3, 115.0, 127.5, 130.5, 158.0; Anal. Calcd for $C_{21}H_{16}F_{20}N_4O_3S$: C, 32.15; H, 2.06; N, 7.14. Found: C, 32.11; H, 2.10; N, 7.07.

2-5. Organocatalyst 4



4

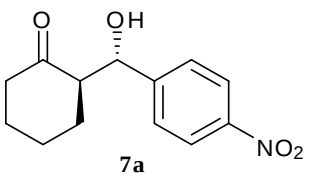
To a solution of **12** (402 mg, 0.513 mmol) in THF (30 mL)-H_2O (10 mL) was added triphenylphosphine (161 mg, 0.615 mmol) at room temperature. After stirring for 22 h at 70 ^oC, the reaction mixture was evaporated. The residue was added to water and extracted three times with AcOEt. The AcOEt layers were combined, washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by flash column chromatography on silica gel with a 9:1:0.08 mixture of $CHCl_3$, MeOH, and H_2O to give the pure **4** (265 mg, 68%). White powder; mp 188-190 ^oC; $[\alpha]^{20}_D$ = -8.3^o (c 0.50, MeOH); ^1H NMR (400 MHz, CD_3OD): δ = 2.01-2.09 (m, 2H), 2.31-2.44 (m, 2H), 2.54-2.60 (m, 2H), 2.79 (dd, *J* = 3.4, 12.6 Hz, 1H), 2.89 (dd, *J* = 5.3, 14.0 Hz, 1H), 3.50-3.62 (m, 1H), 4.05 (t, *J* = 6.3 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 7.12 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (125 MHz, CD_3OD): δ = 21.7, 28.7 (t, $^2J_{C\text{-}F}$ = 21.5 Hz), 42.2, 45.7, 57.4, 67.4, 115.7, 131.5, 131.7, 158.9; Anal. Calcd for $C_{21}H_{18}F_{20}N_2O_3S$: C, 33.26; H, 2.39; N, 3.69. Found: C, 33.42; H, 2.45; N, 3.54.

3. Procedure for recycling and reusing fluorous organocatalyst 4 (Table 3):

A typical procedure of the aldol condensation using **4** and **5a** is as follows: To a colorless suspension of **5a** (90.7 mg, 0.60 mmol) and the organocatalyst **4** (22.7 mg, 0.030 mmol) in 1.2 mL of brine was added cyclohexanone (311 μL, 3.00 mmol) at room temperature. The reaction mixture was stirred at room temperature for 48h. The reaction mixture was chromatographed on fluorous silica gel with 70% methanol (MeOH-H_2O = 7:3). Next, the fluorous silica gel was eluted with methanol, and the methanol fraction was evaporated to recover the fluorous organocatalyst **4** (22.7 mg, 100%). The 70% methanol fractions were evaporated to a one-third to original volume. The residue was extracted three times with AcOEt. The AcOEt layers were combined, washed with brine, dried over anhydrous $MgSO_4$, and evaporated. The residue was purified by flash column chromatography on silica gel with a 2:1 mixture of hexane and AcOEt to afford the pure **7a** (122 mg, 82%) as a colorless powder.

All the aldol products in the paper are known compounds that exhibited spectroscopic data identical to those reported in the literature.[2-5]

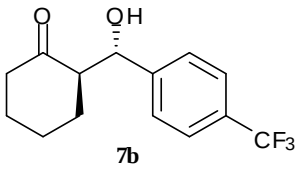
(*2R,1'S*)-2-[Hydroxy(4-nitrophenyl)methyl]cyclohexan-1-one (7a)[2,3,5]:



7a

Enantiomeric excess was determined by HPLC with Chiralpak AS-H column (hexane/2-propanol = 80:20), flow rate = 1.0 mL/min; λ = 254nm; t_{minor} = 16.9 min, t_{major} = 19.1 min.

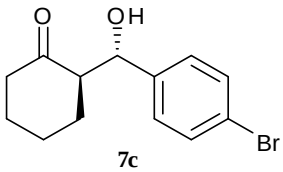
(*2R,1'S*)-2-[Hydroxy(4-trifluoromethylphenyl)methyl]cyclohexan-1-one (7b)[3]:



7b

$[\alpha]^{20}_{D}$ = -19.2° (c 1.00, $CHCl_3$); 94% ee; Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 80:20), flow rate = 0.5 mL/min; λ = 216 nm; t_{major} = 10.0 min, t_{minor} = 11.2 min.

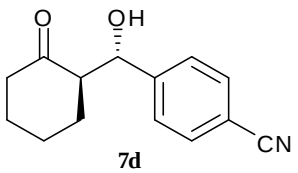
(*2R,1'S*)-2-[Hydroxy(4-bromophenyl)methyl]cyclohexan-1-one (7c)[2,3]:



7c

$[\alpha]^{24}_{D}$ = -19.9° (c 0.96, $CHCl_3$); 95% ee; Enantiomeric excess was determined by HPLC with Chiralpak AS-H column (hexane/2-propanol = 90:10), flow rate = 0.5 mL/min; λ = 217 nm; t_{minor} = 28.0 min, t_{major} = 29.3 min.

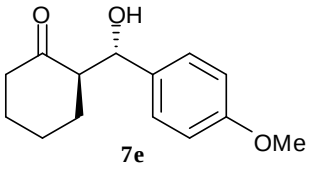
4-((*S*)-Hydroxy((*R*)-2-oxocyclohexyl)methyl)benzonitrile (7d)[2]:



7d

Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 70:30), flow rate = 0.5 mL/min; λ = 234 nm; t_{major} = 12.9 min, t_{minor} = 16.2 min.

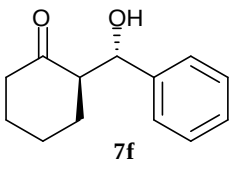
(*2R,1'S*)-2-[Hydroxy(4-methoxyphenyl)methyl]cyclohexan-1-one (7e)[2,3,5]**:**



7e

Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 90:10), flow rate = 0.5 mL/min; λ = 225 nm; t_{minor} = 20.8 min, t_{major} = 27.8 min.

(*2R,1'S*)-2-(Hydroxyphenylmethyl)cyclohexan-1-one (7f)[2,3,5]:

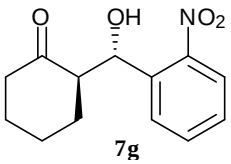


7f

$[\alpha]^{20}_{D}$ = -20.8° (c 1.00, $CHCl_3$); 94% ee; Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 95:5), flow rate = 1.0 mL/min; λ = 210 nm; t_{minor} = 11.5 min, t_{major} =

16.4 min.

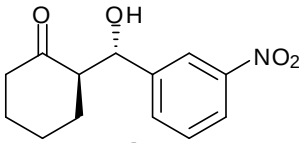
(*2R,1'S*)-2-[Hydroxy(2-nitrophenyl)methyl]cyclohexan-1-one (7g)[2,5]:



7g

$[\alpha]^{17}_{D}$ = -14.9^{o} (c 1.00, $CHCl_3$); 96% ee; Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 80:20), flow rate = 0.5 mL/min; λ = 250 nm; t_{minor} = 13.9 min, t_{major} = 15.4 min.

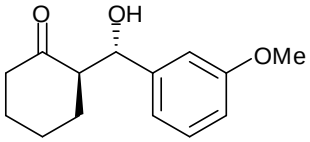
(*2R,1'S*)-2-[Hydroxy(3-nitrophenyl)methyl]cyclohexan-1-one (7h)[2]:



7h

$[\alpha]^{24}_{D}$ = -24.2^{o} (c 1.07, $CHCl_3$); 91% ee; Enantiomeric excess was determined by HPLC with Chiralcel OD-H column (hexane/2-propanol = 80:20), flow rate = 0.5 mL/min; λ = 254 nm; t_{minor} = 14.9 min, t_{major} = 18.4 min.

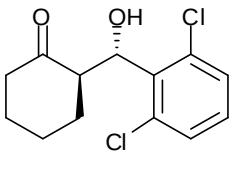
(*2R,1'S*)-2-[Hydroxy(3-methoxyphenyl)methyl]cyclohexan-1-one (7i)[4]:



7i

$[\alpha]^{22}_{D}$ = -6.6^{o} (c 1.00, $CHCl_3$); 94% ee; Enantiomeric excess was determined by HPLC with Chiralpak AS column (hexane/2-propanol = 90:10), flow rate = 1.0 mL/min; λ = 220 nm; t_{minor} = 13.7 min, t_{major} = 17.2 min.

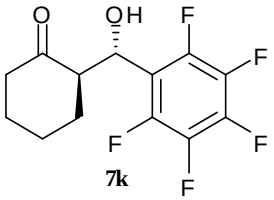
(*2R,1'S*)-2-[Hydroxy(2,6-dichlorophenyl)methyl]cyclohexan-1-one (7j)[5]:



7j

$[\alpha]^{24}_{D}$ = +32.9^{o} (c 0.99, $CHCl_3$); 94% ee; Enantiomeric excess was determined by HPLC with Chiralcel OJ-H column (hexane/2-propanol = 95:5), flow rate = 1.0 mL/min; λ = 210 nm; t_{major} = 9.5 min, t_{minor} = 11.0 min.

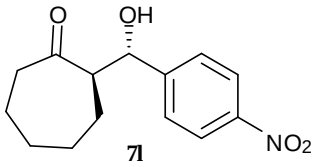
(*2R,1'S*)-2-[Hydroxy(2,3,4,5,6-pentafluorophenyl)methyl]cyclohexan-1-one (7k)[5]:



7k

$[\alpha]^{18}_{D}$ = +7.2° (c 1.00, $CHCl_3$); 84% ee; Enantiomeric excess was determined by HPLC with Chiralpak AS-H column (hexane/2-propanol = 90:10), flow rate = 0.5 mL/min; λ = 210 nm; t_{minor} = 14.4 min, t_{major} = 18.2 min.

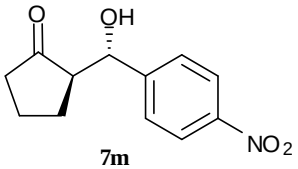
(*2R,1'S*)-2-[Hydroxy(4-nitrophenyl)methyl]cycloheptan-1-one (7m)[2,5]:



7l

$[\alpha]^{26}_{D}$ = +10.7° (c 1.08, $CHCl_3$); 73% ee; Enantiomeric excess was determined by HPLC with Chiralpak AD-H column (hexane/2-propanol = 90:10), flow rate = 1.0 mL/min; λ = 254 nm; t_{major} = 20.0 min, t_{minor} = 47.9 min.

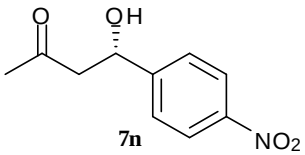
(*2R,1'S*)-2-[Hydroxy(4-nitrophenyl)methyl]cyclopentan-1-one (7m)[2,5]:



7m

Enantiomeric excess was determined by HPLC with Chiralpak AD-H column (hexane/2-propanol = 95:5), flow rate = 1.0 mL/min; λ = 265 nm; t_{major} = 45.8 min, t_{minor} = 48.5 min.

(*4S*)-4-Hydroxy-*p*-nitrophenylbutan-2-one (7n)[2,3,5]:



7n

$[\alpha]^{26}_{D}$ = -42.62° (c 1.00, $CHCl_3$); 70% ee; Enantiomeric excess was determined by HPLC with Chiralcel OJ column (hexane/2-propanol = 90:10), flow rate = 1.0 mL/min; λ = 266 nm; t_{minor} = 32.0 min, t_{major} = 36.0 min.

4. References

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2) N. Mase, Y. Nakai, N. Ohara, H. Yoda, K. Takabe, F. Tanaka and C. F. Barbas, *J. Am. Chem. Soc.*, 2006, **128**, 734.

3) D. Font, C. Jimeno and M. A. Pericàs, *Org. Lett.*, 2006, **8**, 4653.

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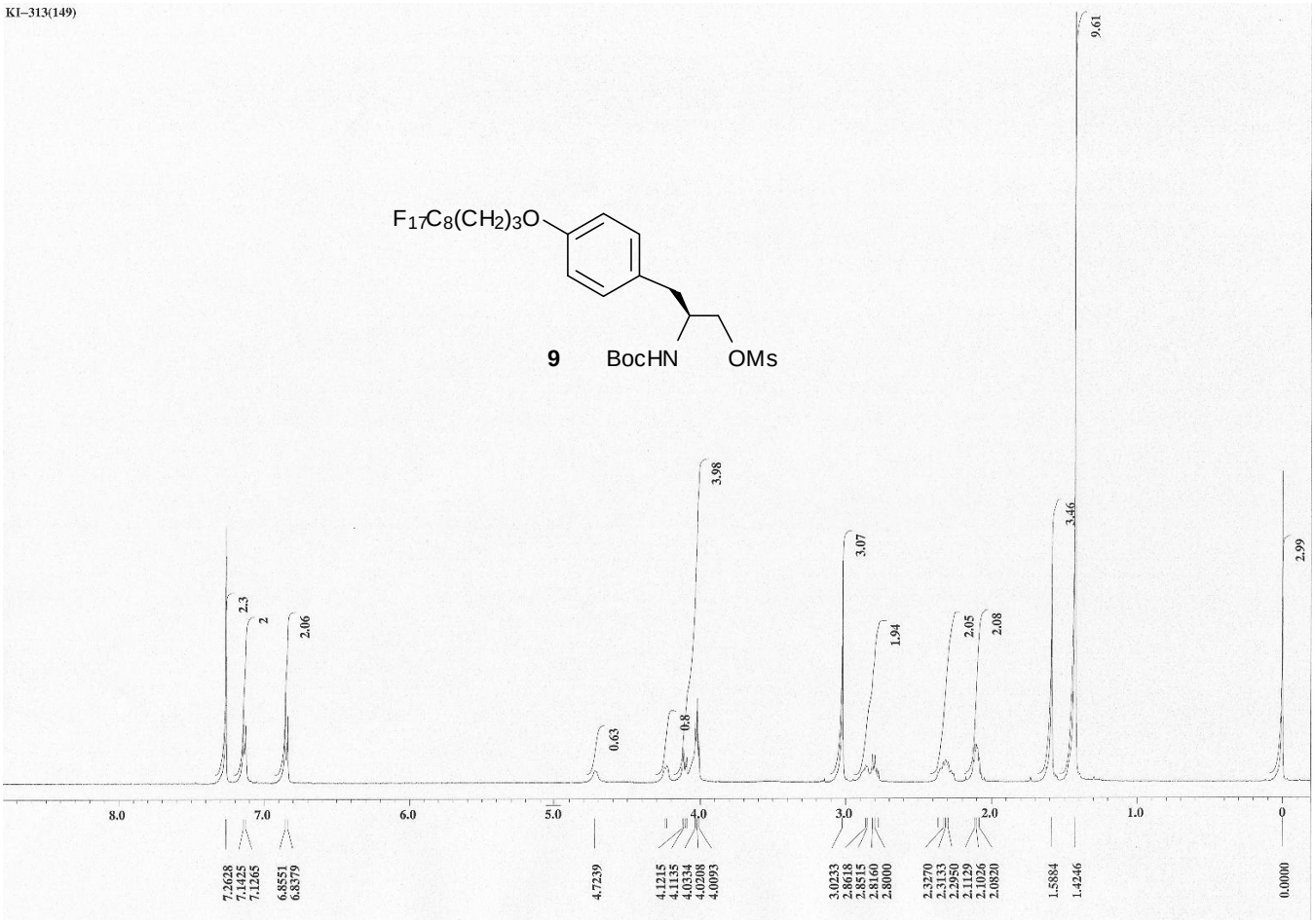
5) H. Tang and R. G. Carter, *Org. Lett.*, 2008, **10**, 4649.

5. NMR data


KI–313(149)
$F_{17}C_8(CH_2)_3O$
9
BocHN
OMs
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3.98
3.46
3.07
2.99
2.3
2
2.06
1.94
2.05
2.08
0.63
0.8
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.2628
7.1425
7.1265
6.8551
6.8579
4.7239
4.1215
4.1135
4.0334
4.0208
4.0093
3.0233
2.8618
2.8515
2.8160
2.8000
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2.3133
2.2950
2.1129
2.1026
2.0820
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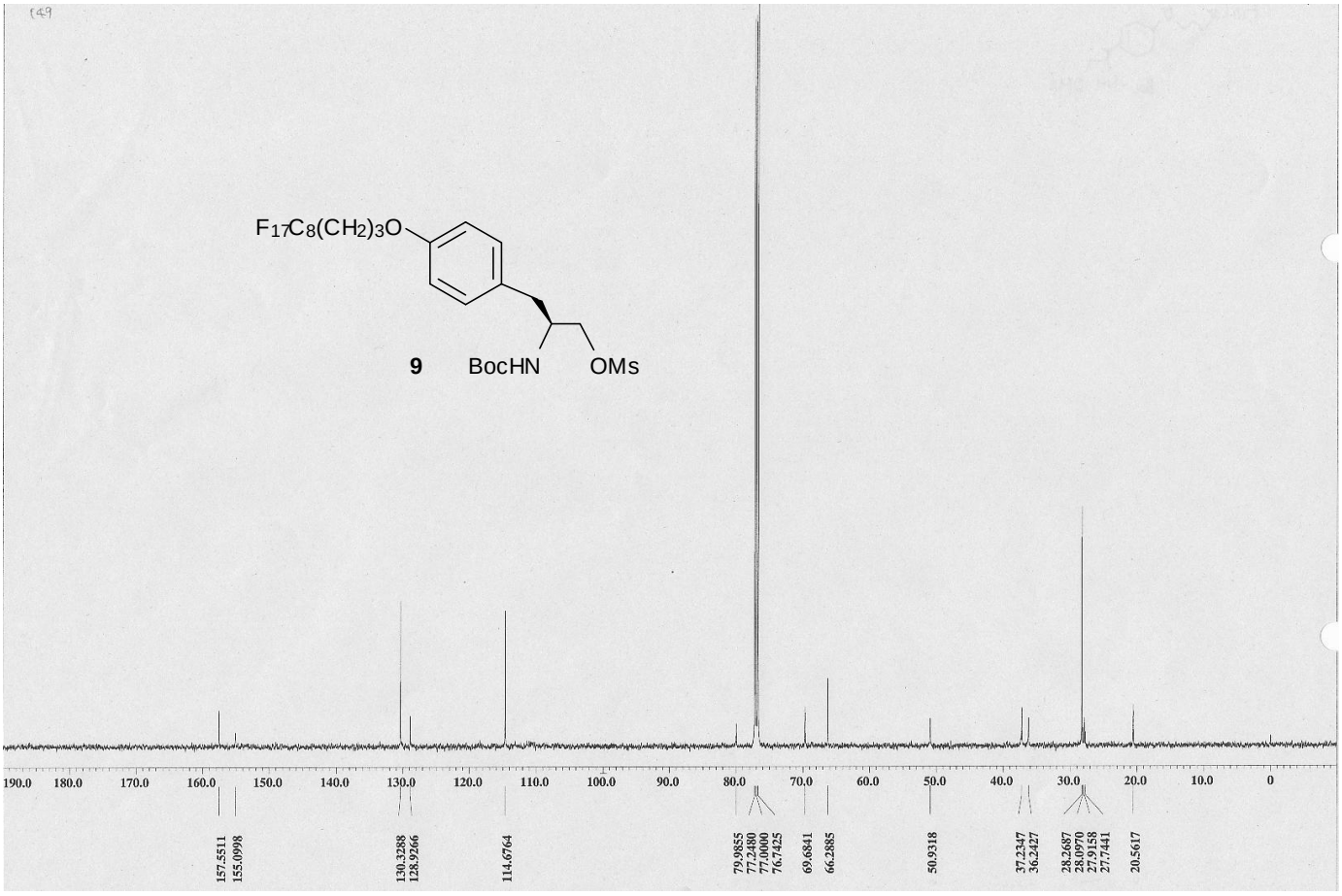
1.4246
0.0000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130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
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155.0998
130.3288
128.9266
114.6764
79.9855
77.2480
77.0000
76.7425
69.6841
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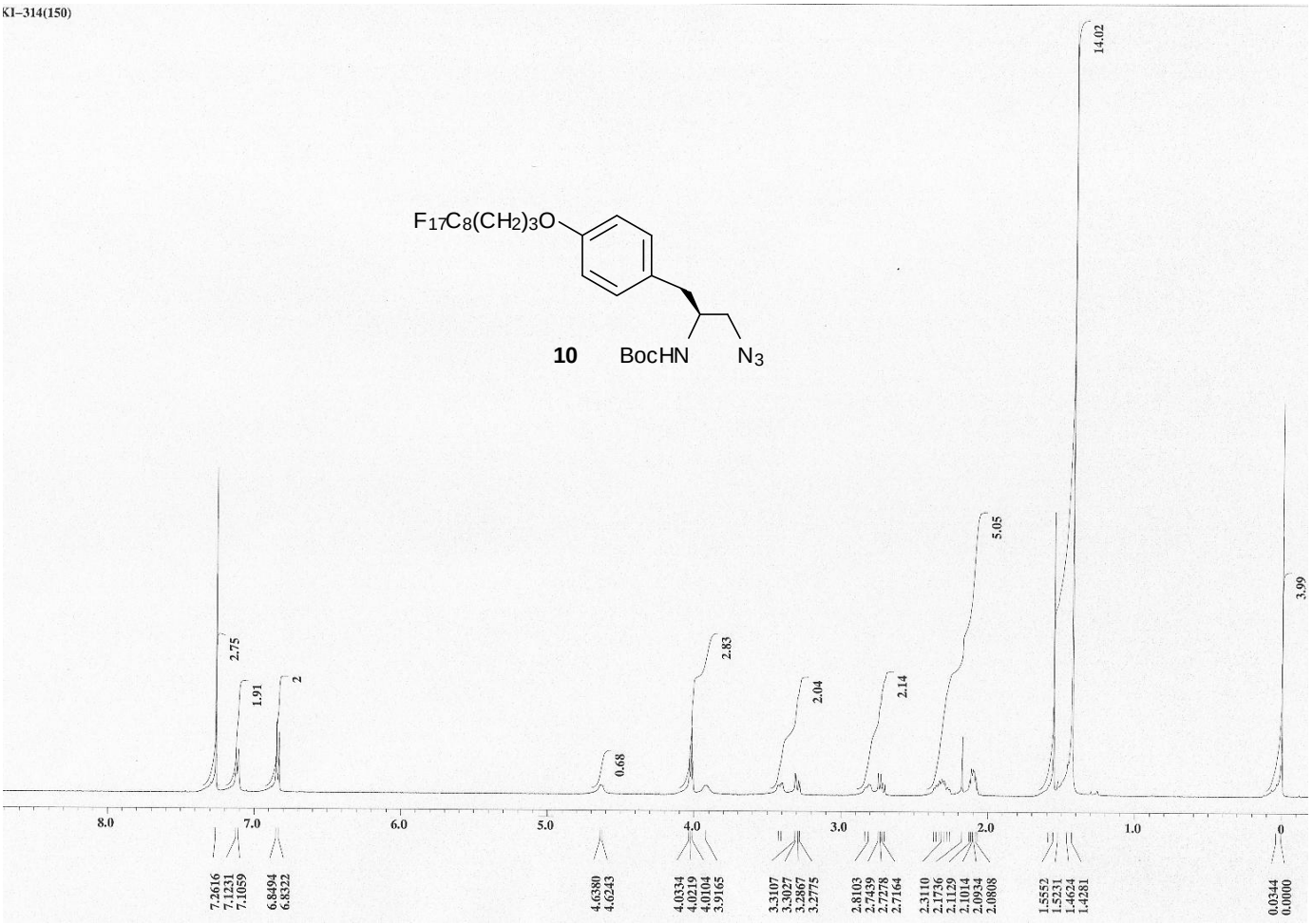
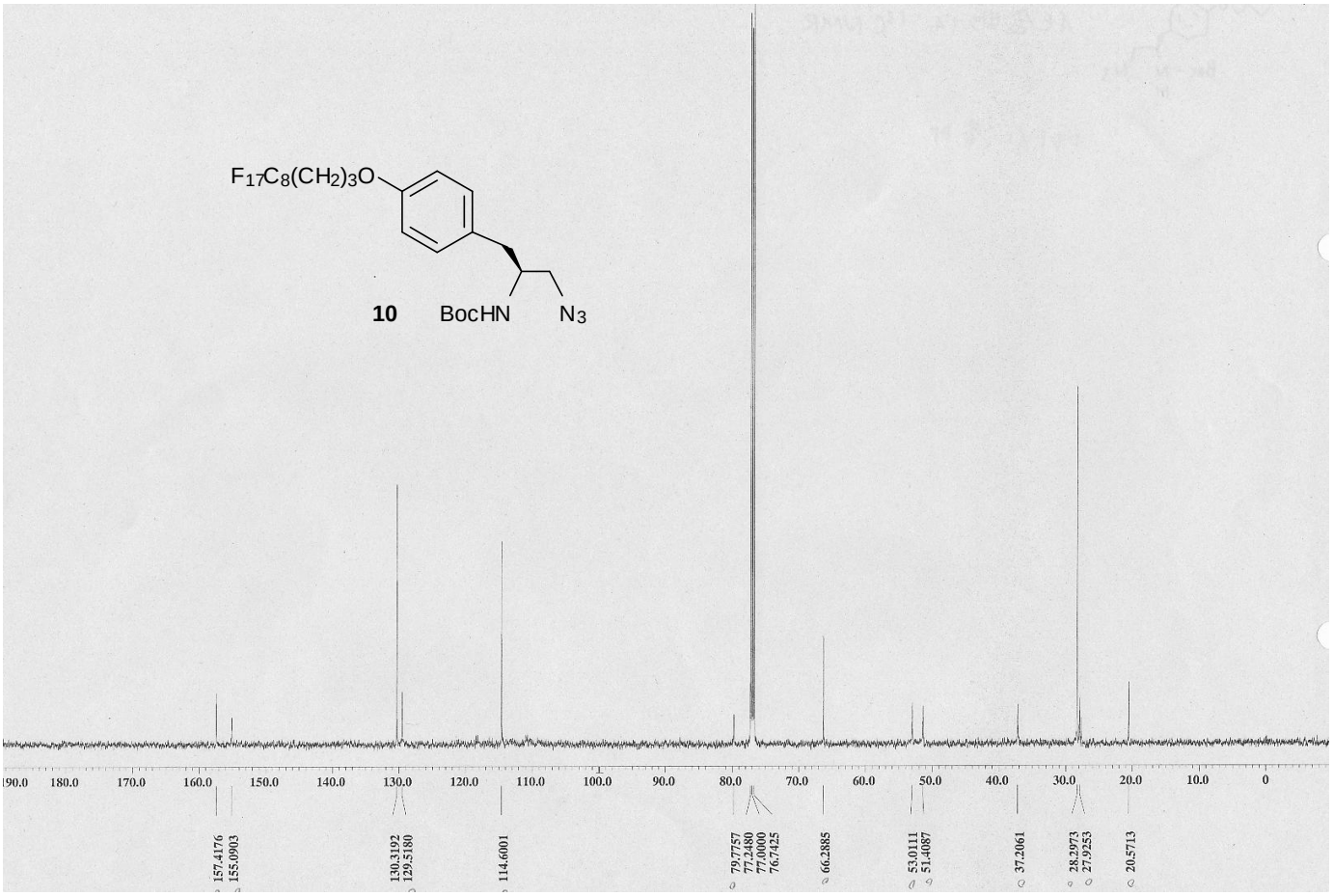
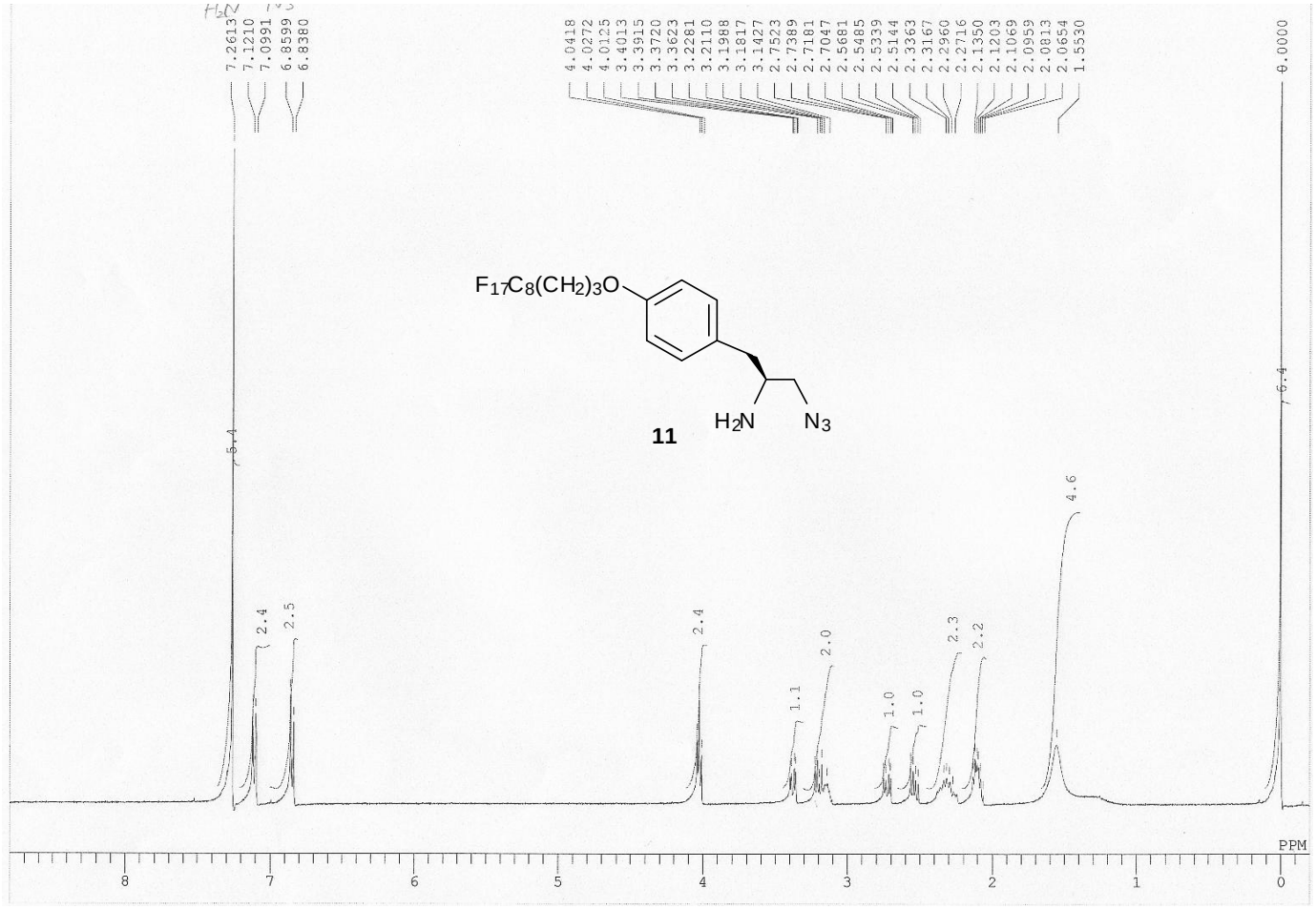
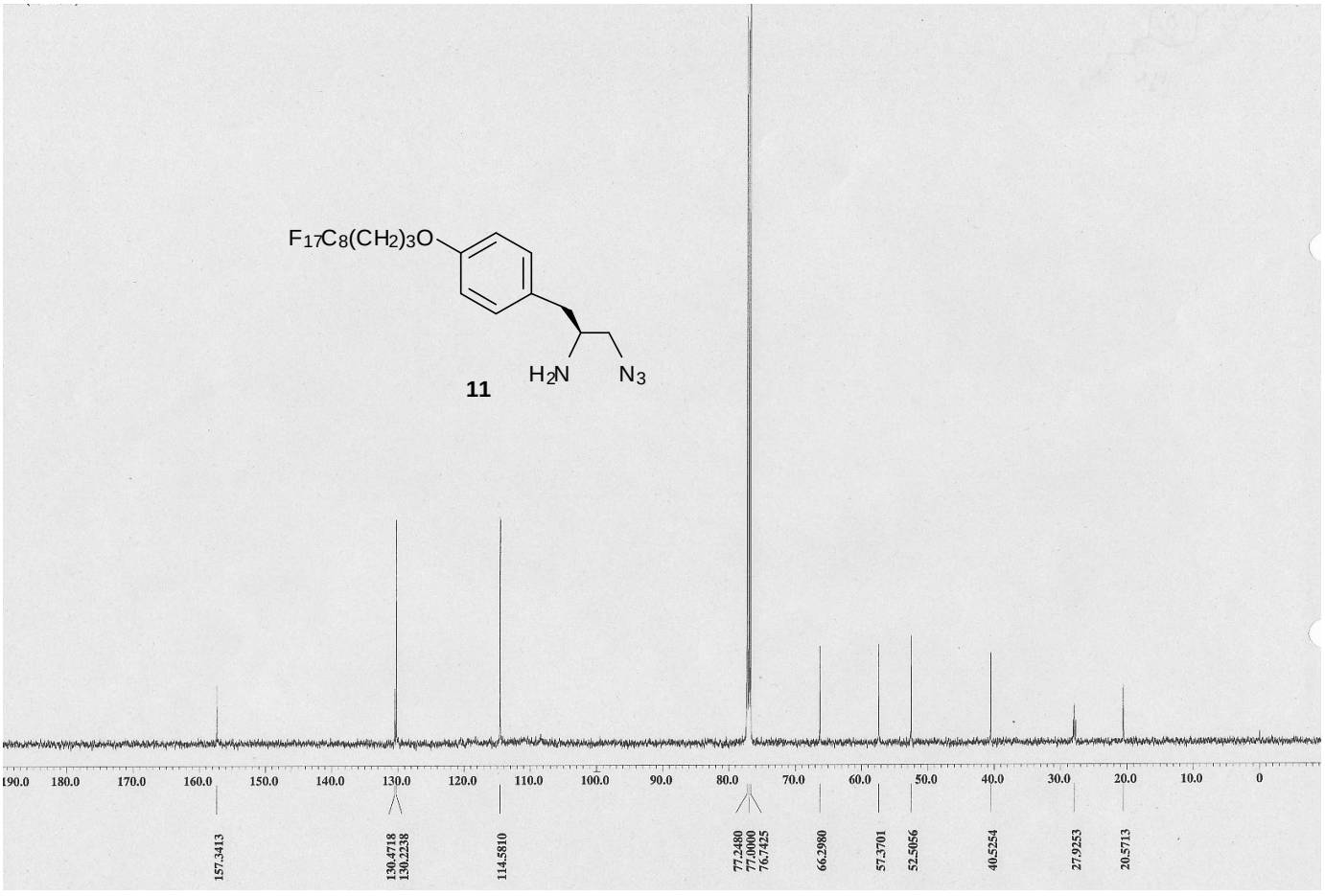
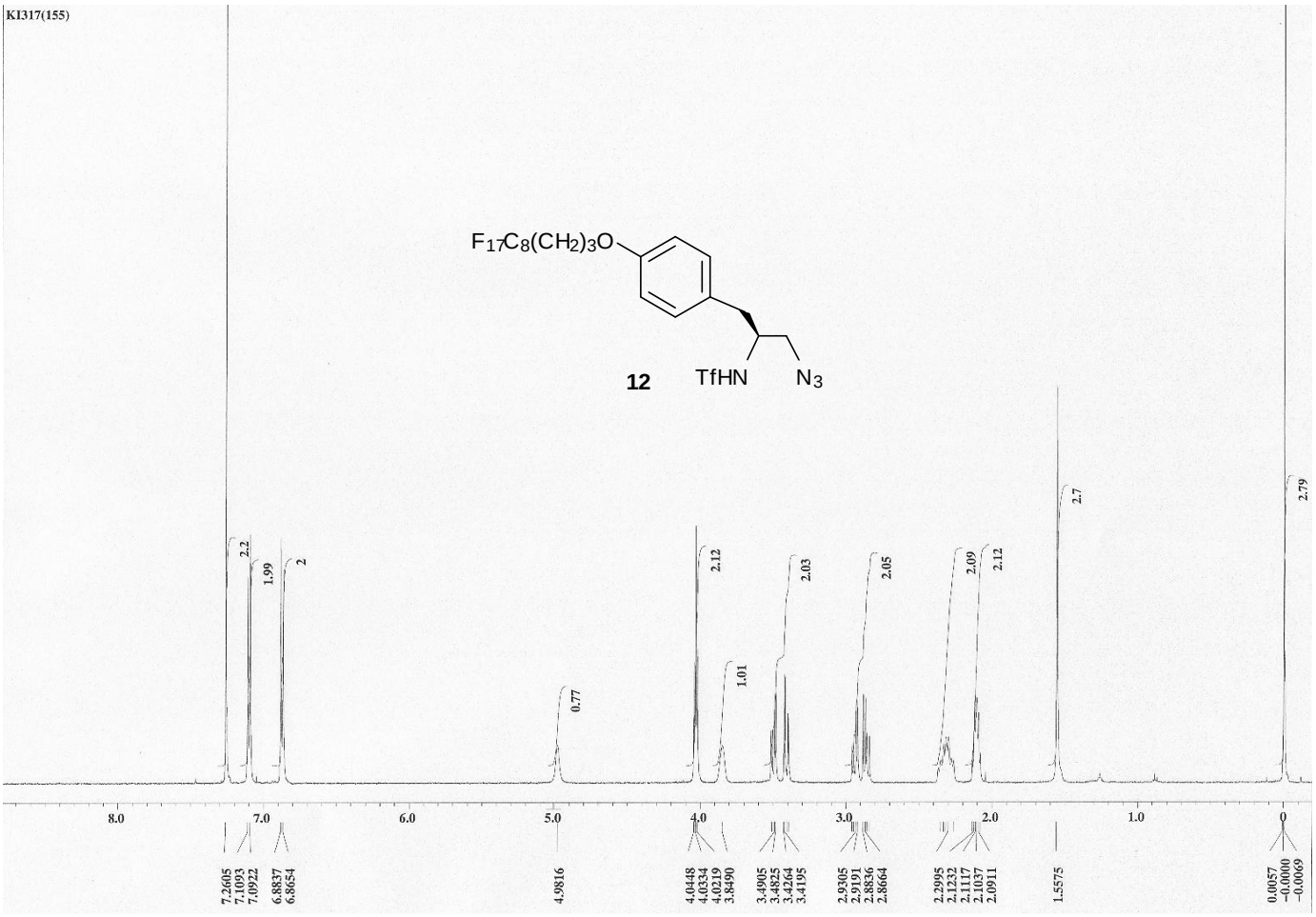
28.0970
27.9158
27.7441
20.5617

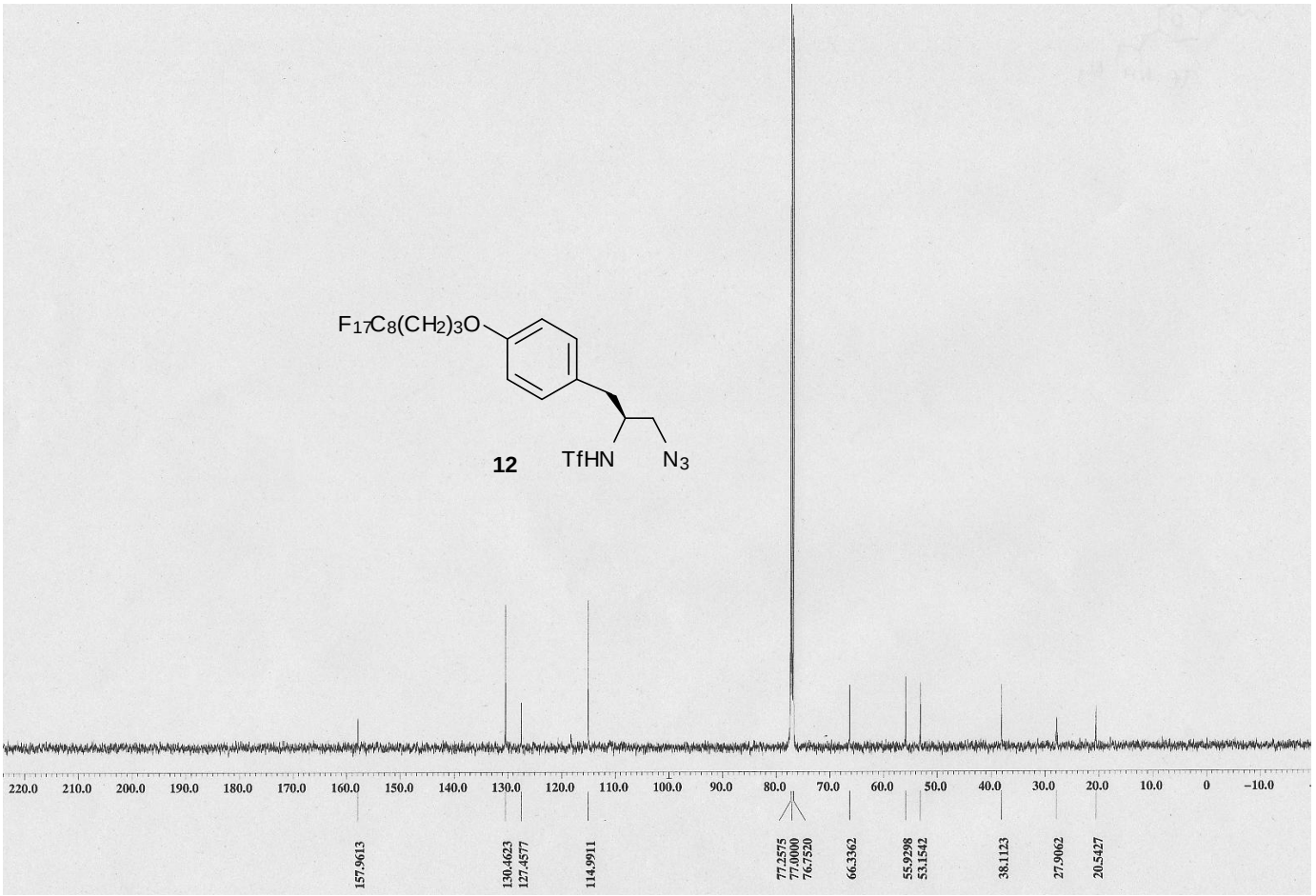


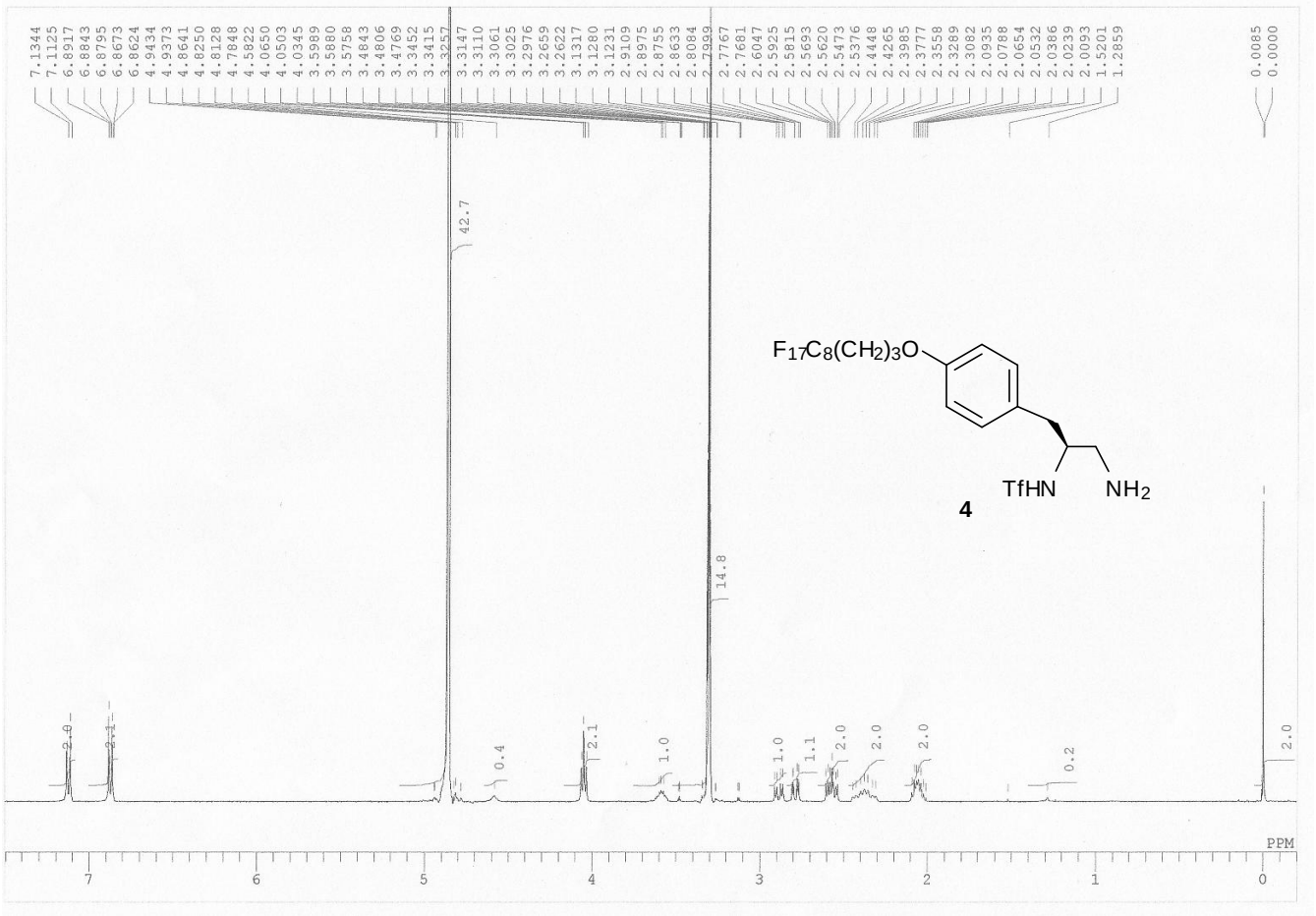


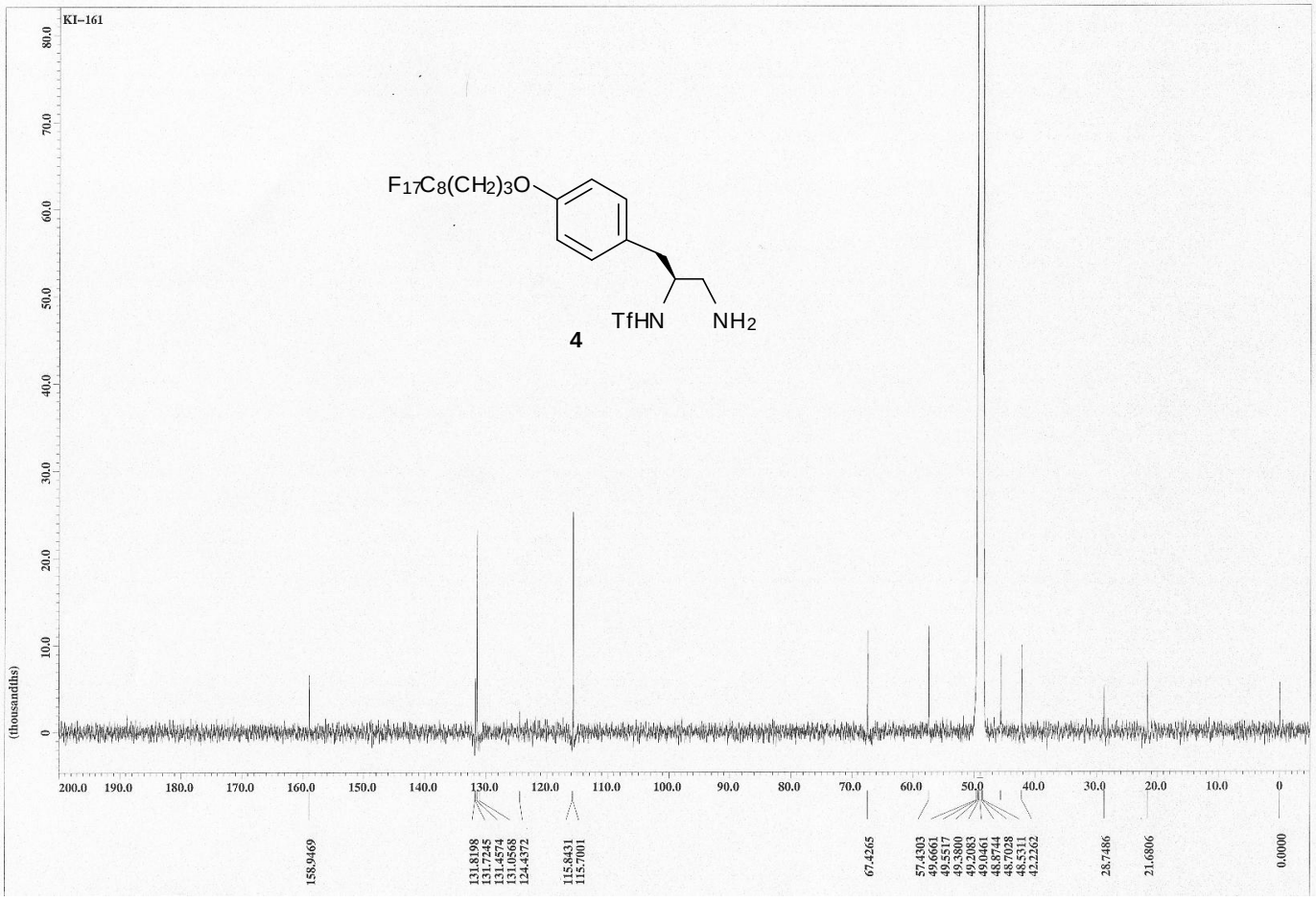


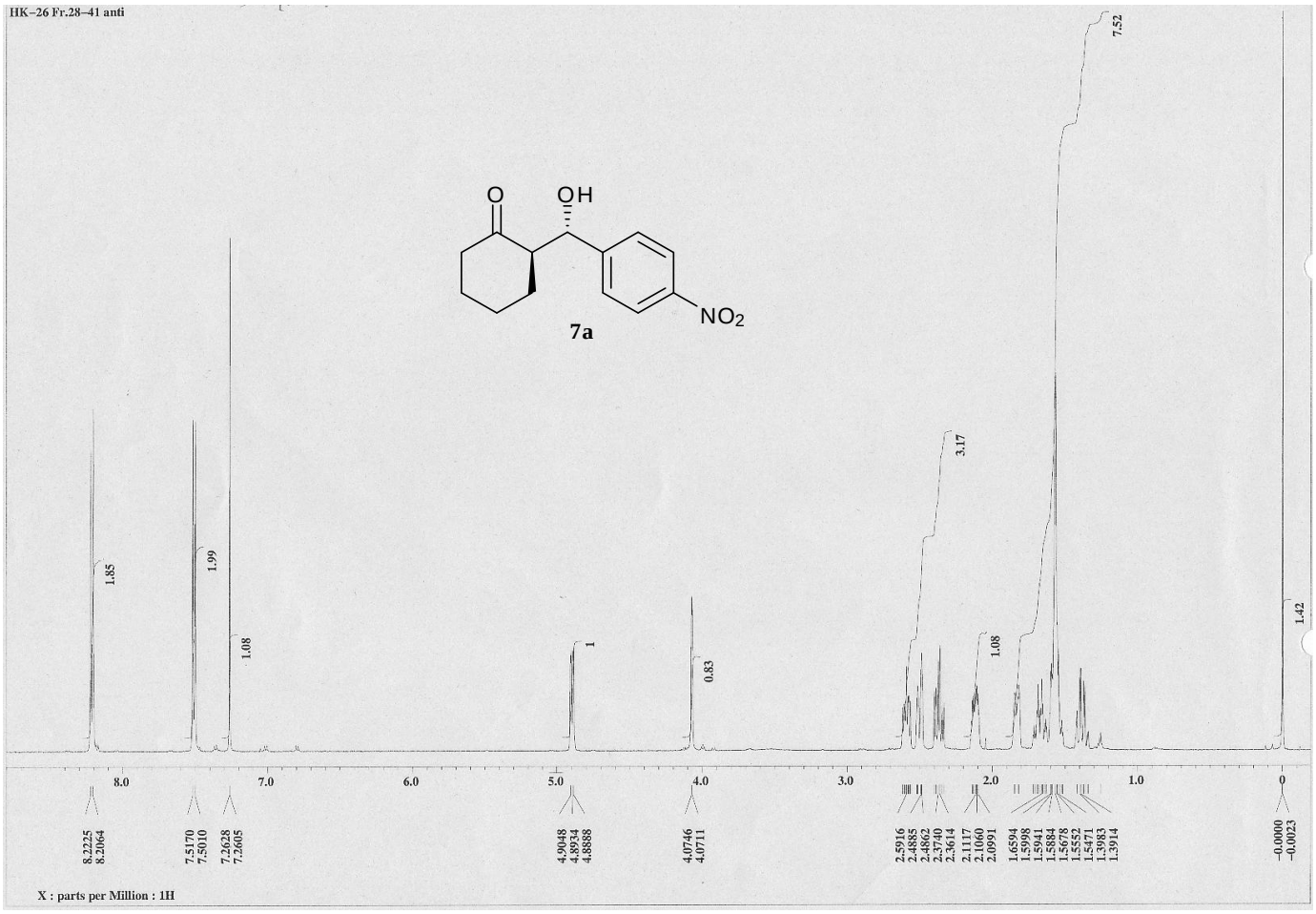


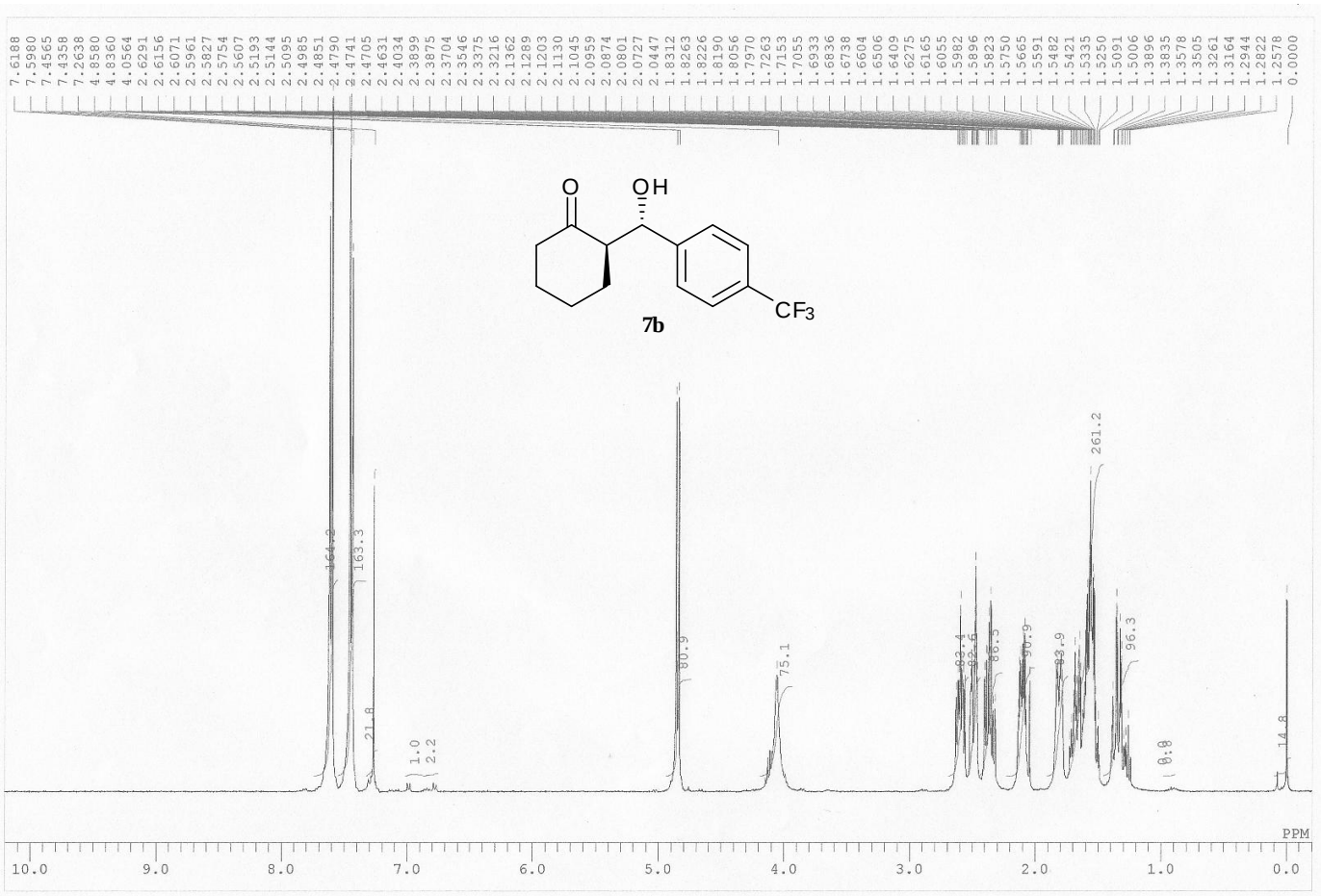


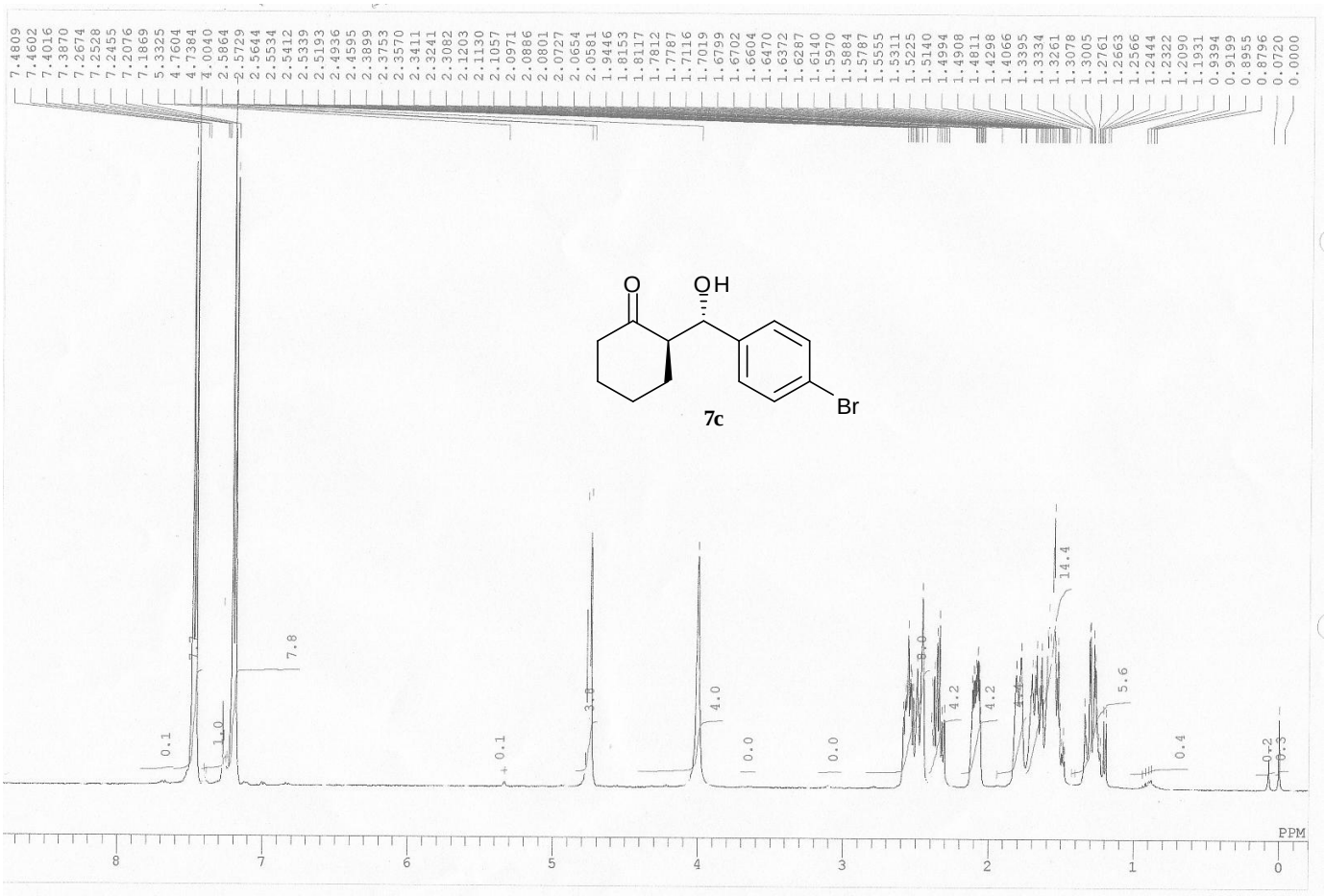




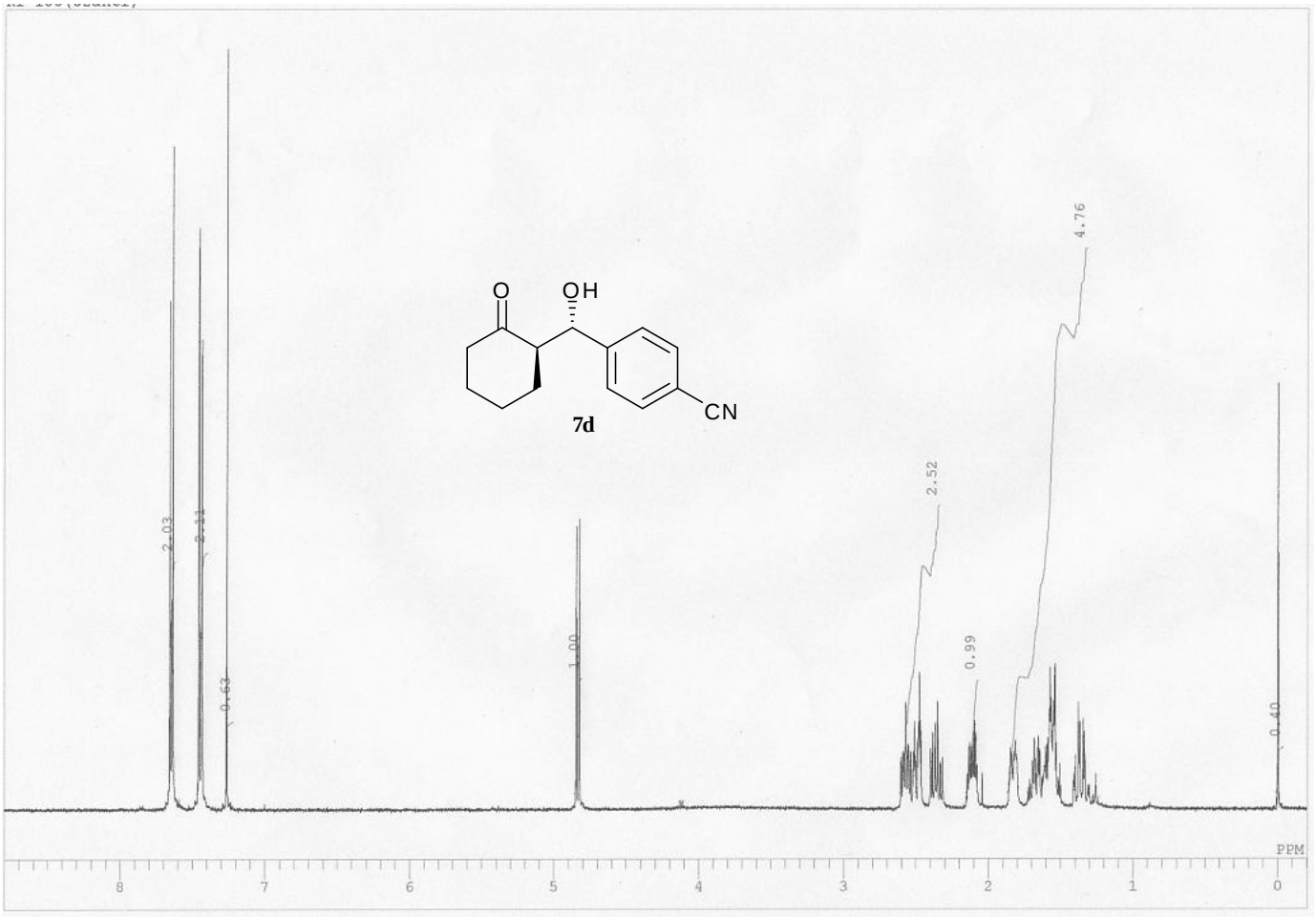




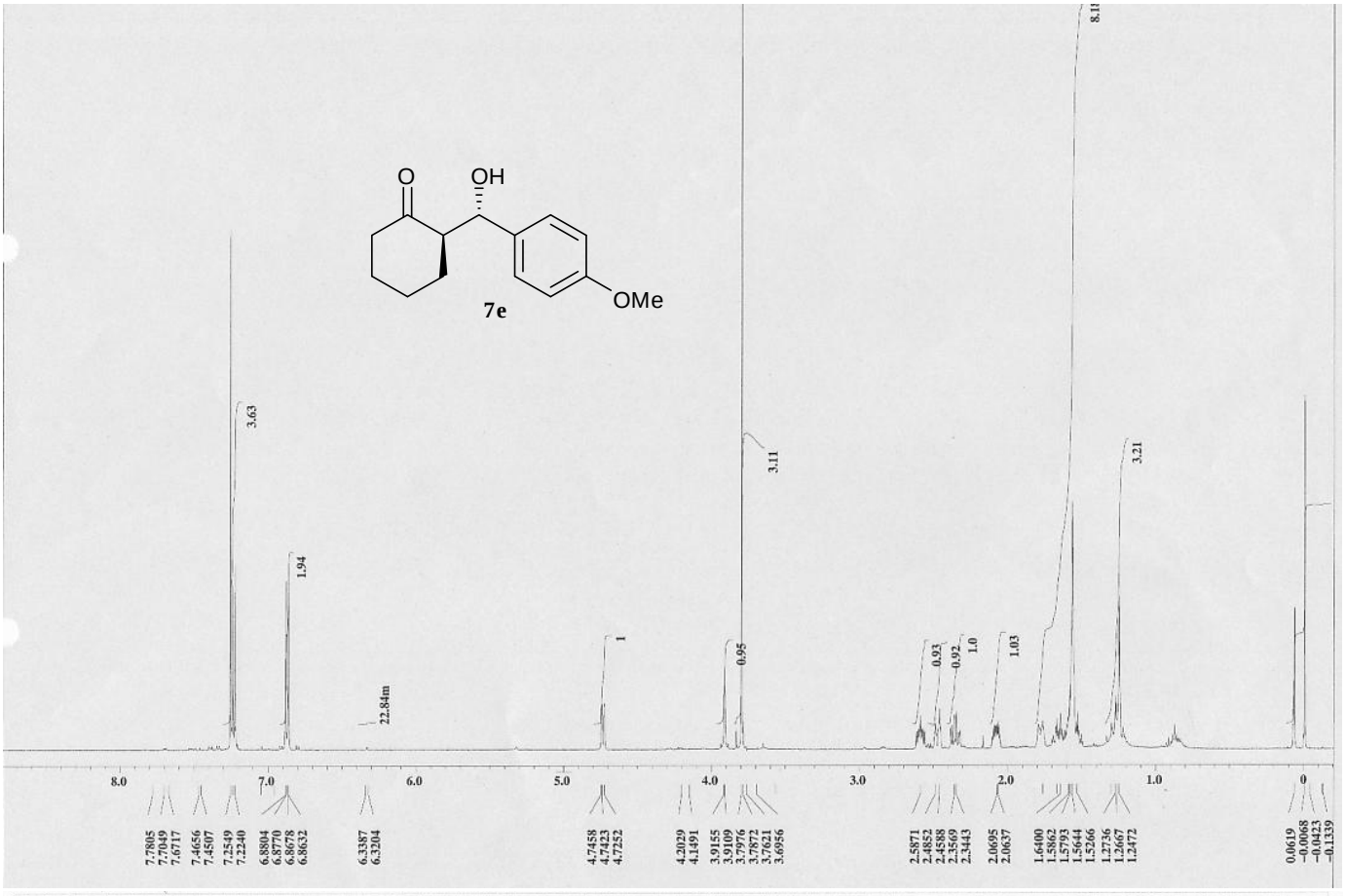


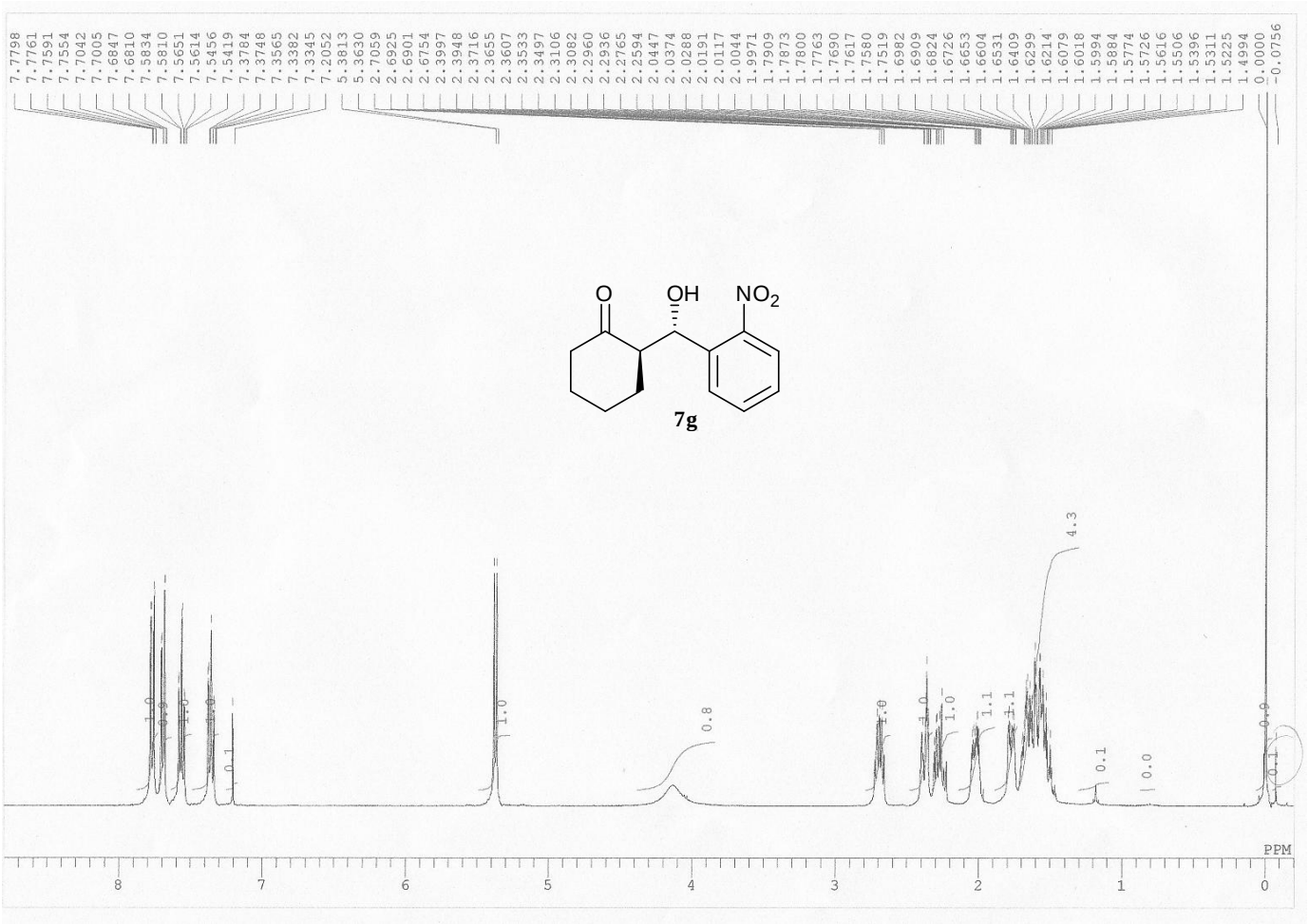


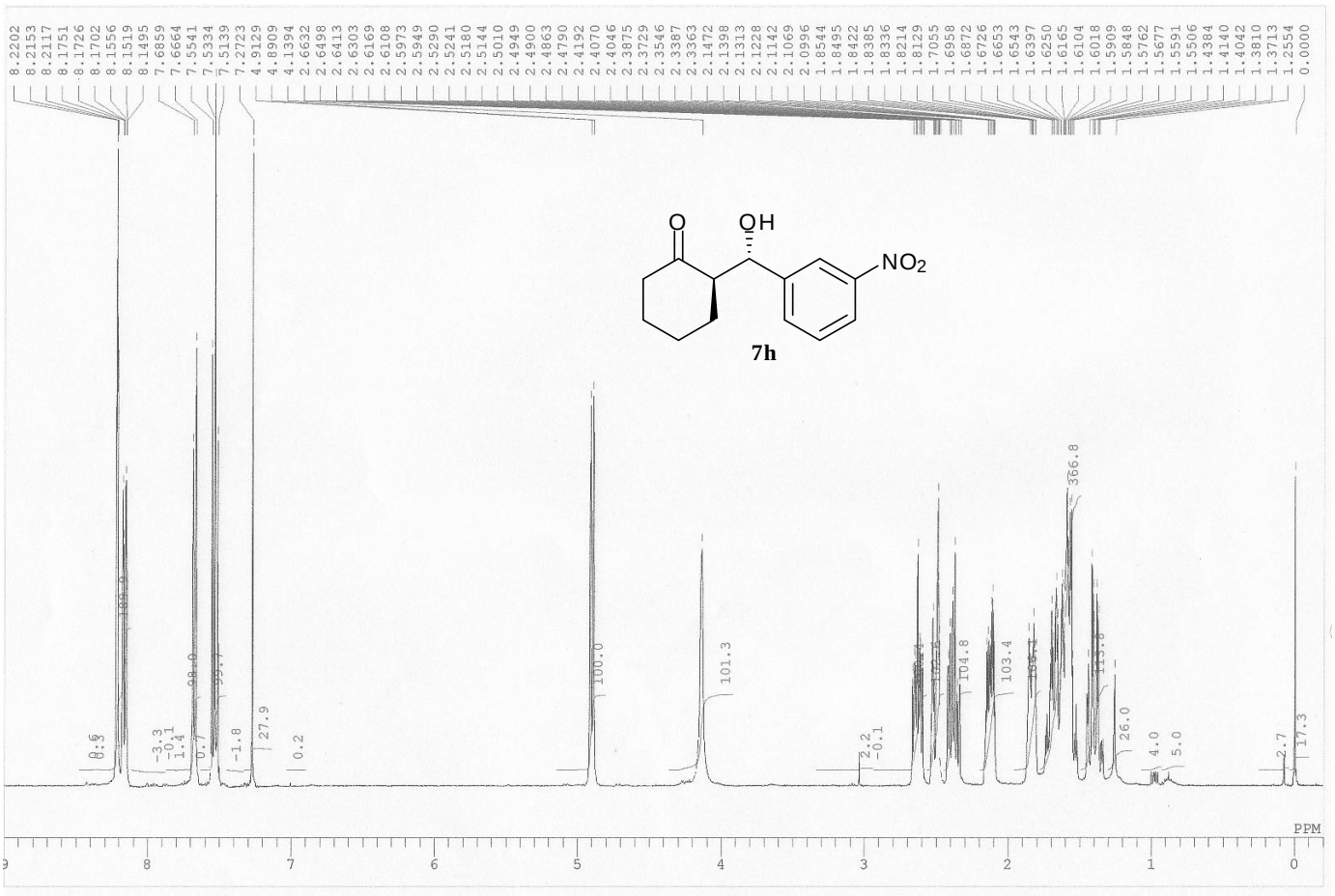
7c

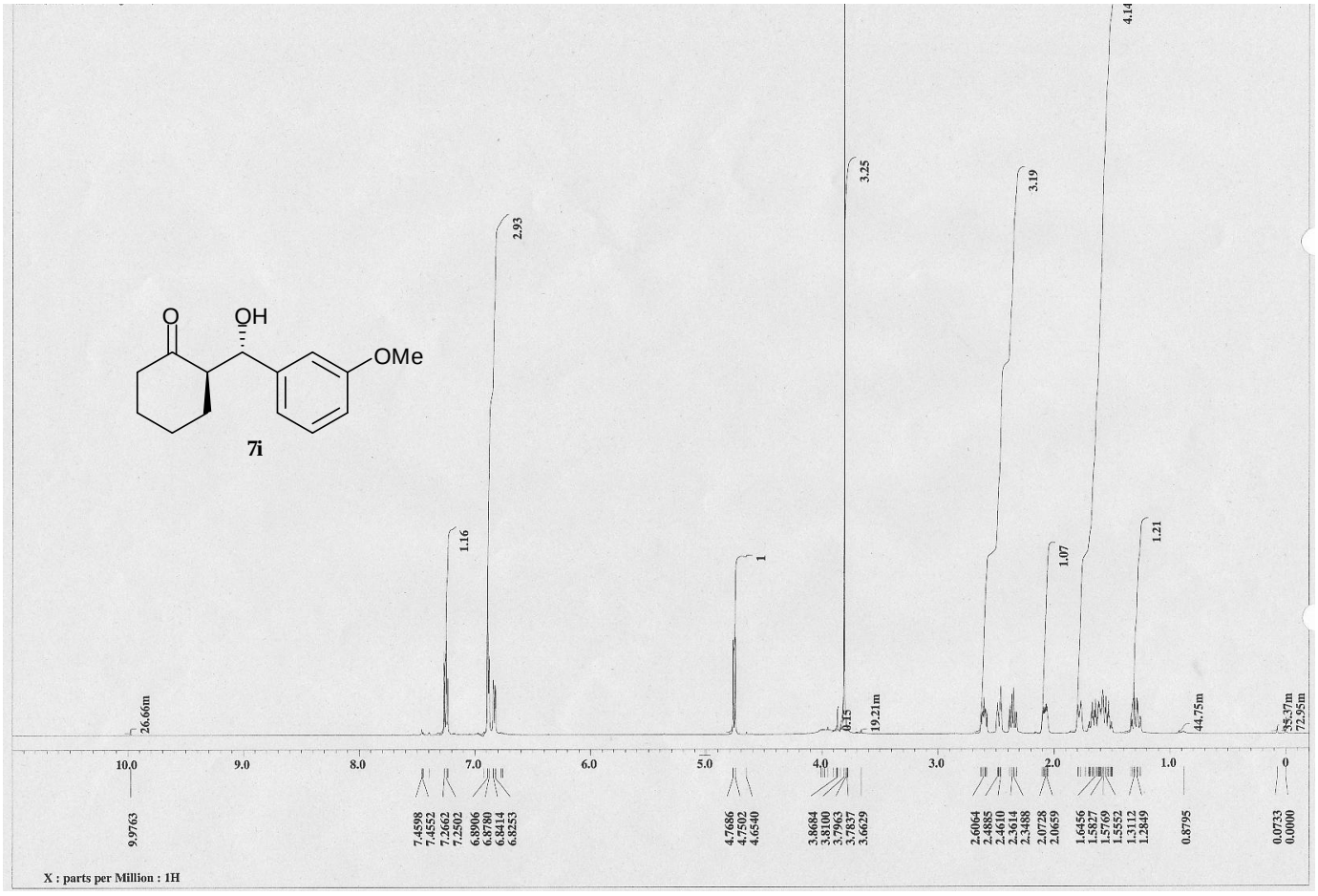


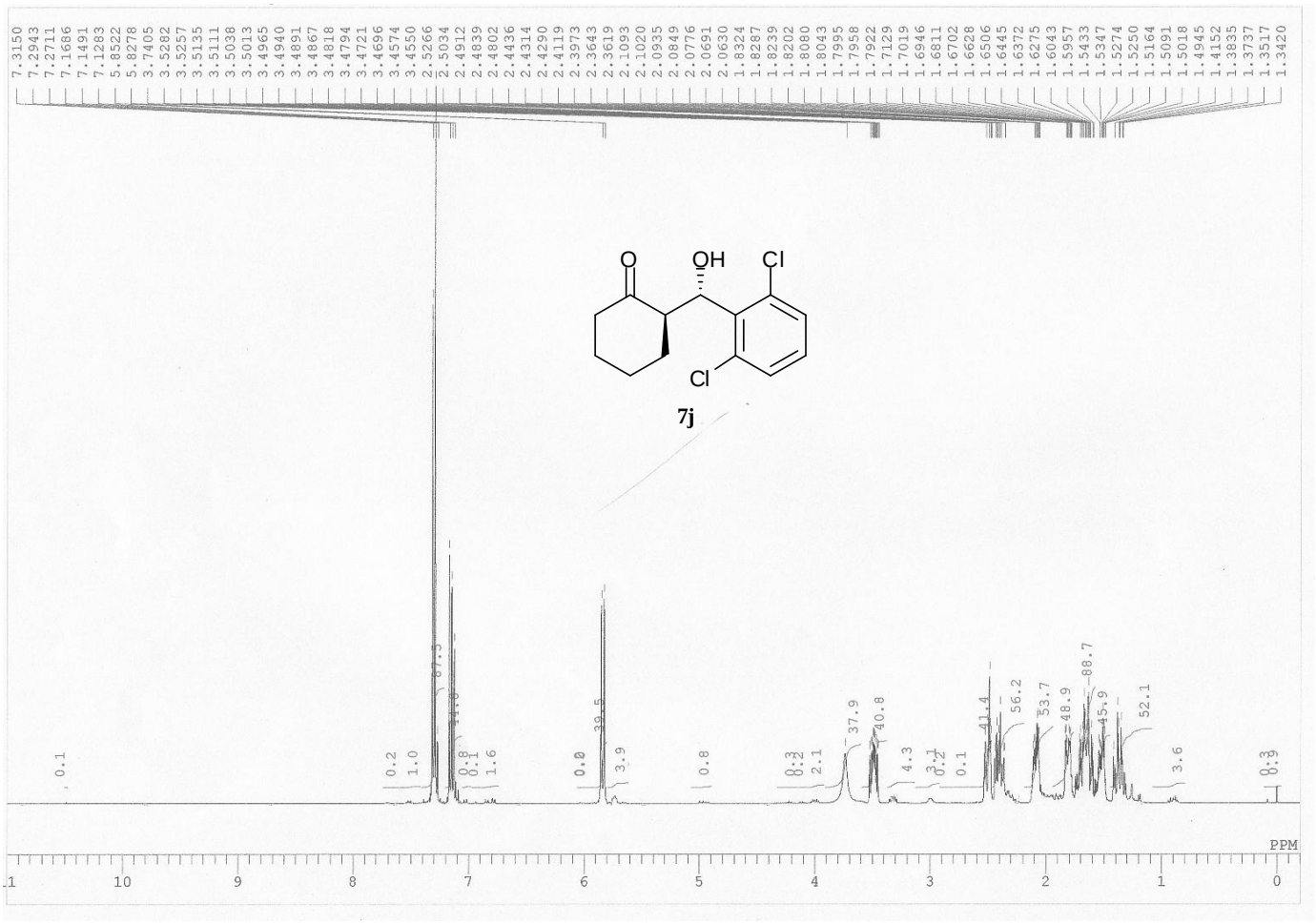
7d

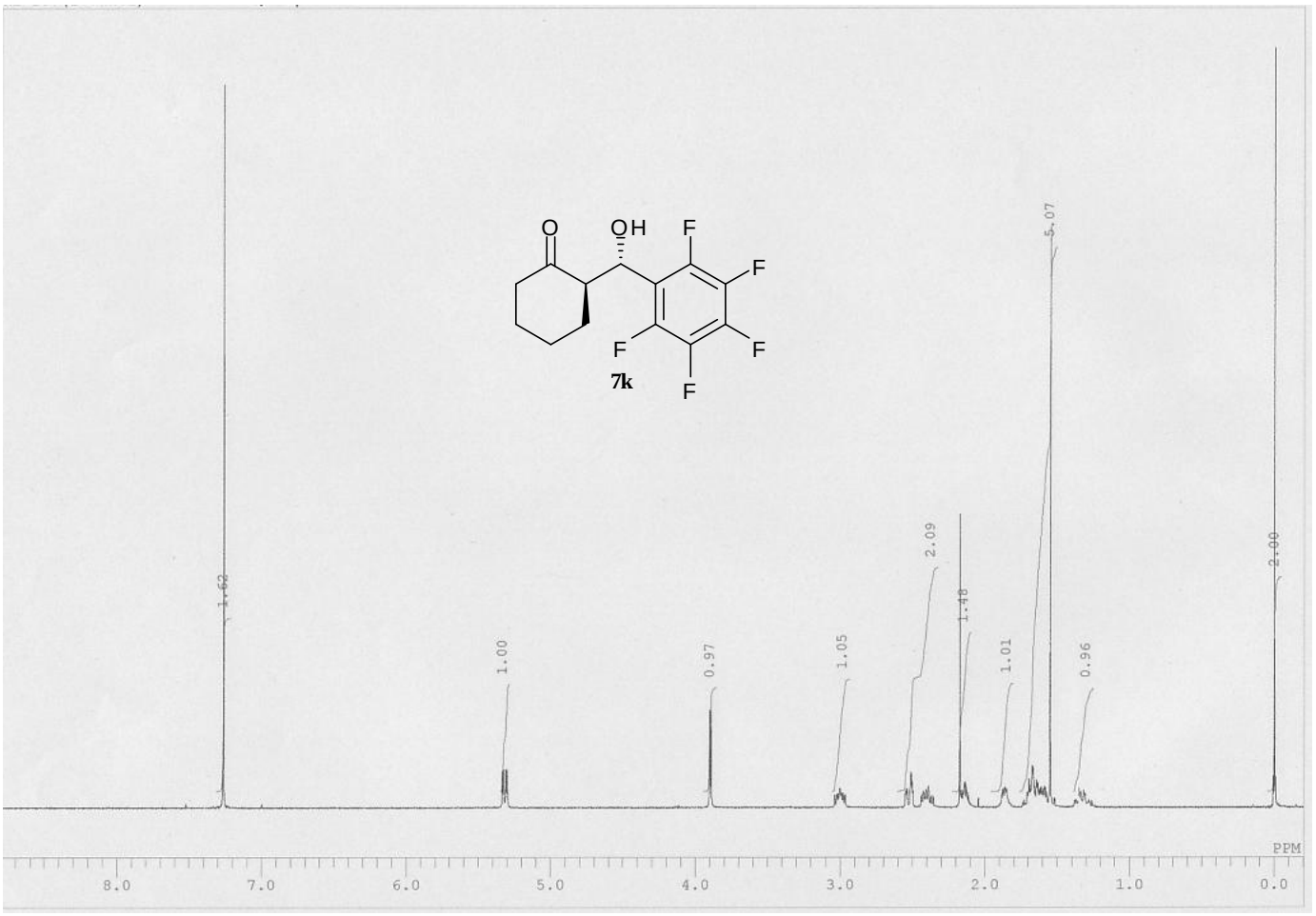


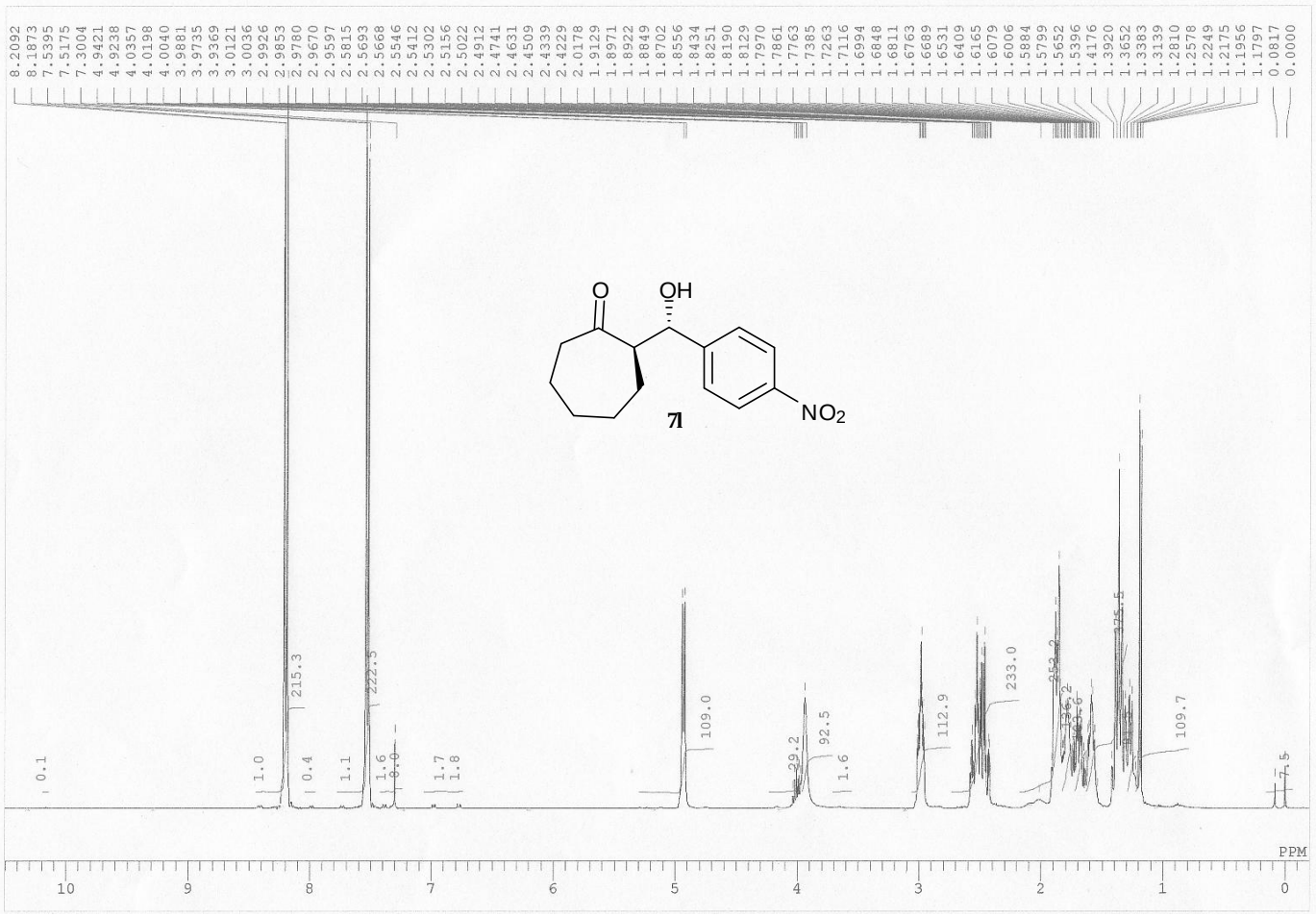


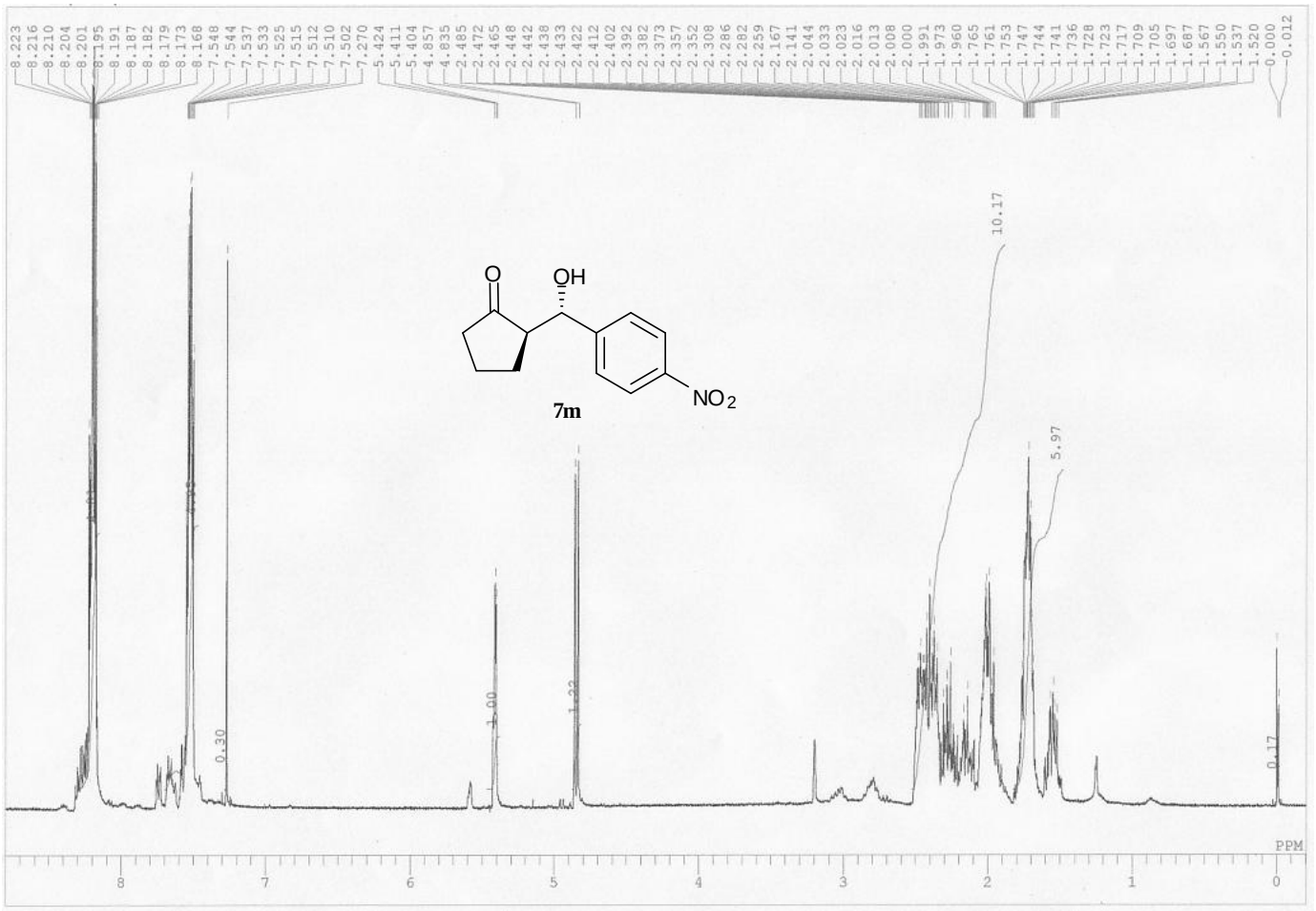




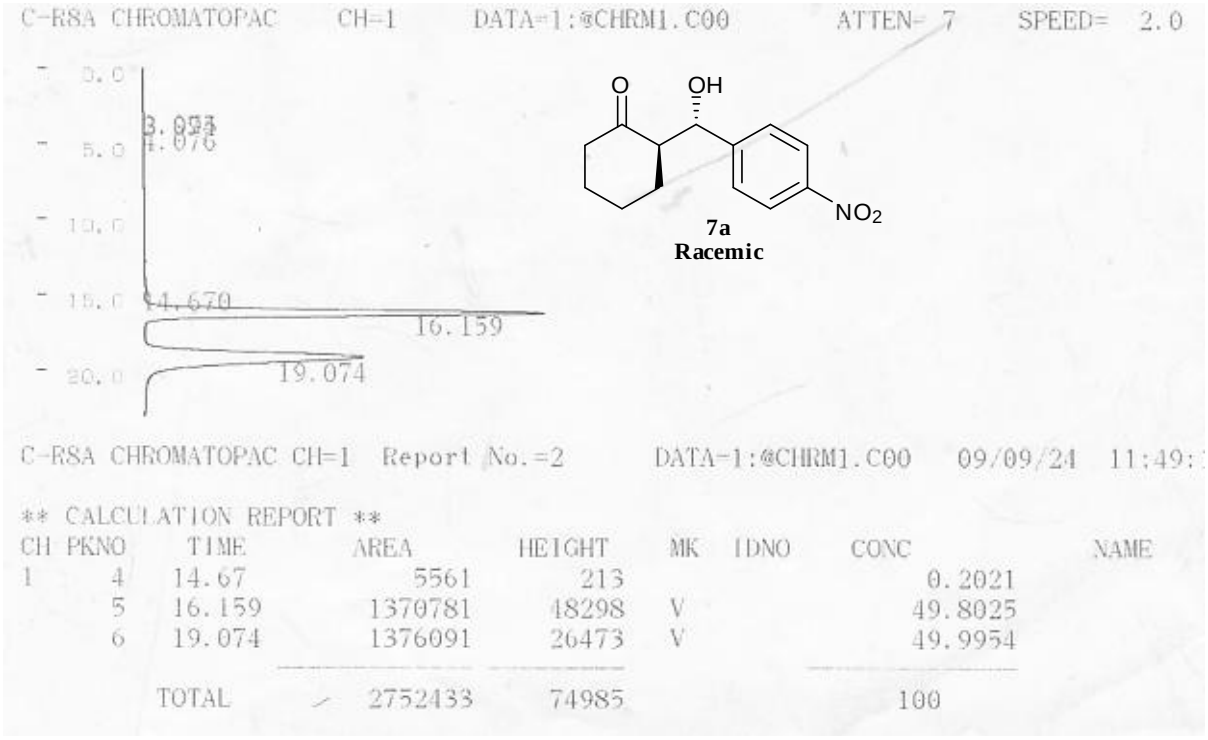


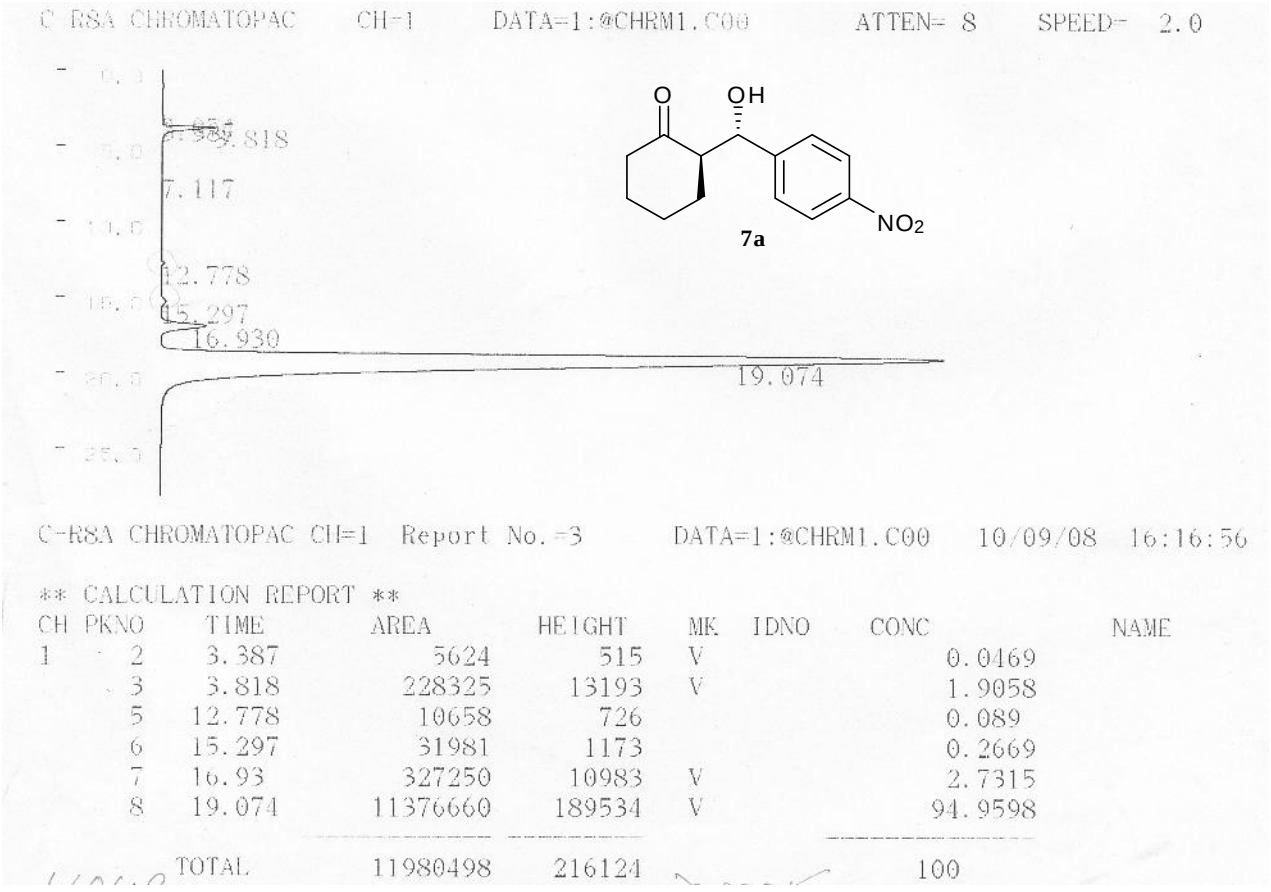






6. HPLC data


C-RSA CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 7 SPEED= 2.0
14.670
16.159
19.074
O
OH
NO2
7a
Racemic
C-RSA CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 09/09/24 11:49:
** CALCULATION REPORT **
CH PKNO TIME AREA HEIGHT MK IDNO CONC NAME
1 4 14.67 5561 213 0.2021
5 16.159 1370781 48298 V 49.8025
6 19.074 1376091 26473 V 49.9954
TOTAL 2752433 74985 100


C-RSA CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 8 SPEED= 2.0
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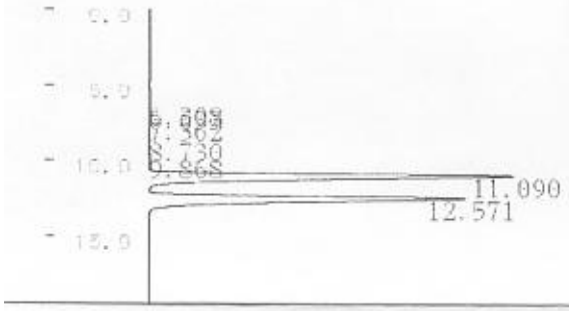
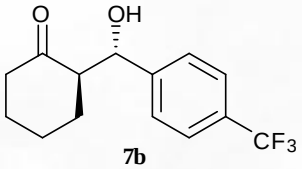
7.117
12.778
15.297
16.930
19.074
O
OH
NO2
7a
C-RSA CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 10/09/08 16:16:56
** CALCULATION REPORT **
CH PKNO TIME AREA HEIGHT MK IDNO CONC NAME
1 2 3.387 5624 515 V 0.0469
3 3.818 228325 13193 V 1.9058
5 12.778 10658 726 0.089
6 15.297 31981 1173 0.2669
7 16.93 327250 10983 V 2.7315
8 19.074 11376660 189534 V 94.9598
TOTAL 11980498 216124 100

C-RSA CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 8 SPEED= 2.0





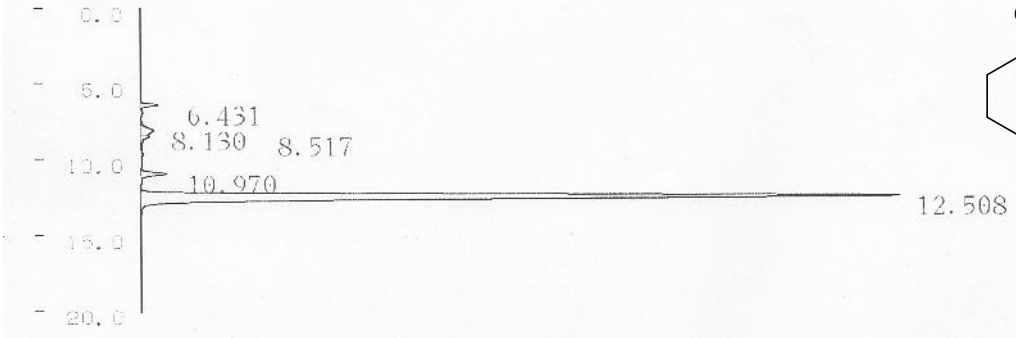
7b
Racemic

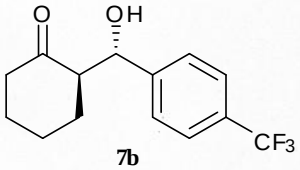
C-RSA CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 09/09/04 11:25:44

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	6	11.09	2060140	89006			49.9519	
	7	12.571	2064105	77169	V		50.0481	
		TOTAL	4124246	166175			100	

C-RSA CHROMATOPAC CH=1 Report No.=5 DATA=1:@CHRM1.C00 11/04/21 19:29:36



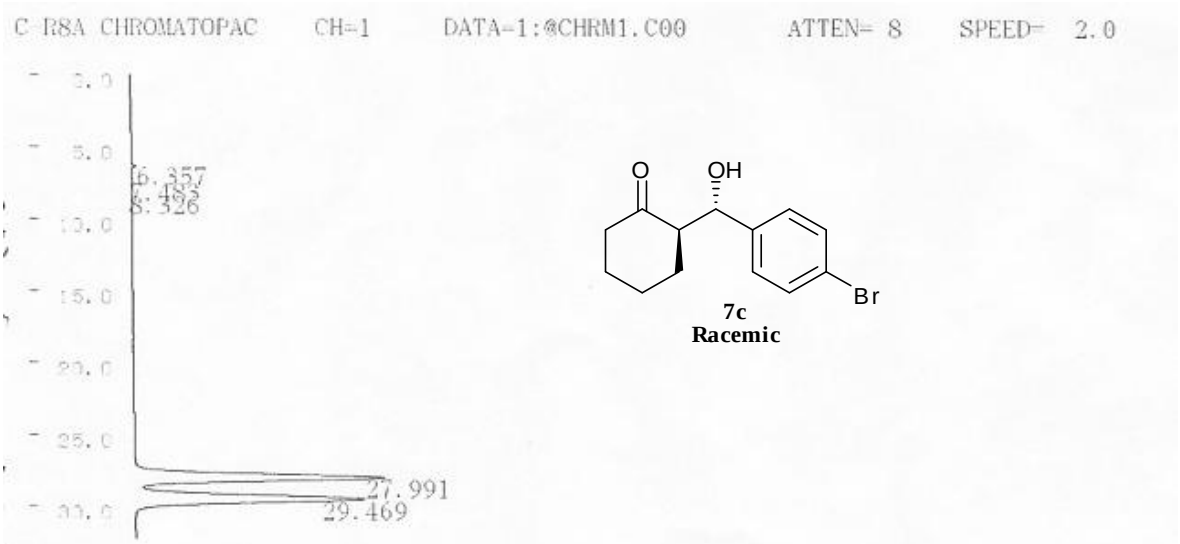


7b

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	6.431	53991	4342	V		1.3465	
	4	8.13	90456	2976	V		2.2558	
	5	8.517	39534	2068	V		0.9859	
	8	10.97	106127	6186	V		2.6467	
	9	12.508	3719740	183020			92.7651	
		TOTAL	4009847	198592			100	

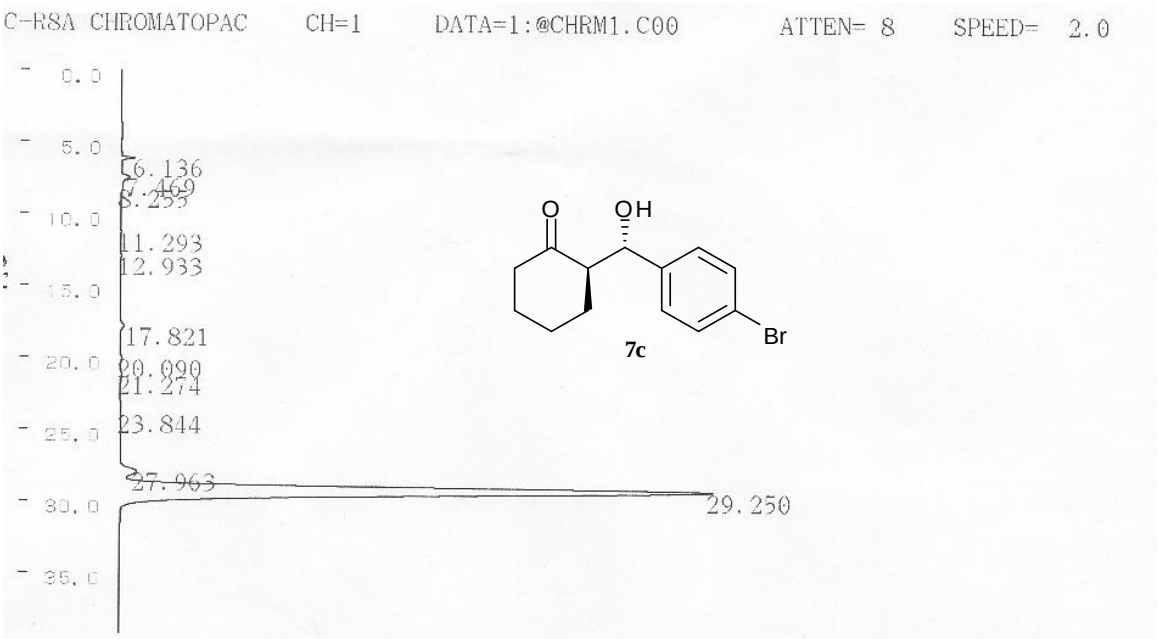
94.45% ee



C R8A CHROMATOPAC CH=1 Report No.=10 DATA=1:@CHRM1.C00 09/09/03 17:50:52

** CALCULATION REPORT **

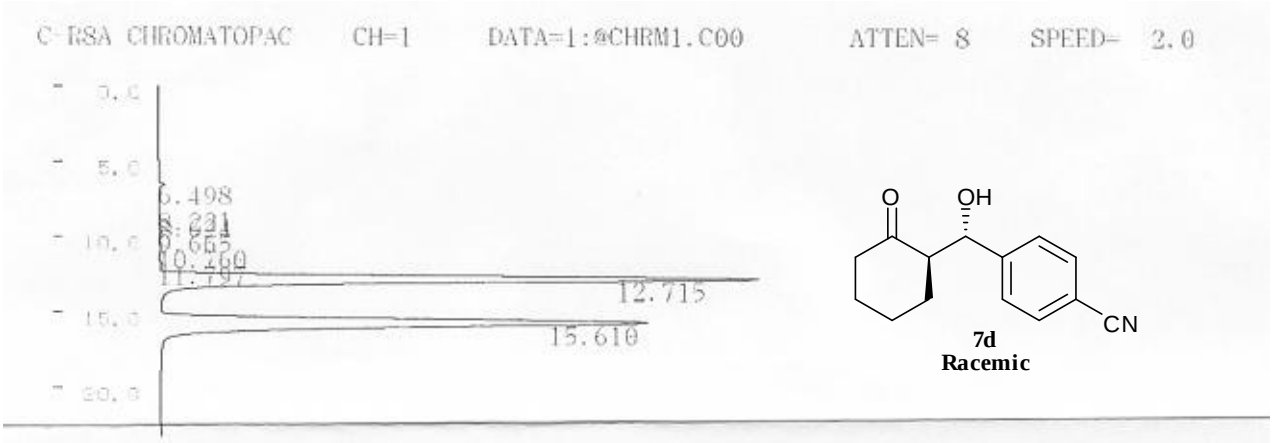
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	4	27.991	2242186	63886			50.144	
	5	29.469	2229312	58744	V		49.856	
		TOTAL	4471498	122629			100	



C-R8A CHROMATOPAC CH=1 Report No.=5 DATA=1:@CHRM1.C00 11/07/07 12:13:36

** CALCULATION REPORT **

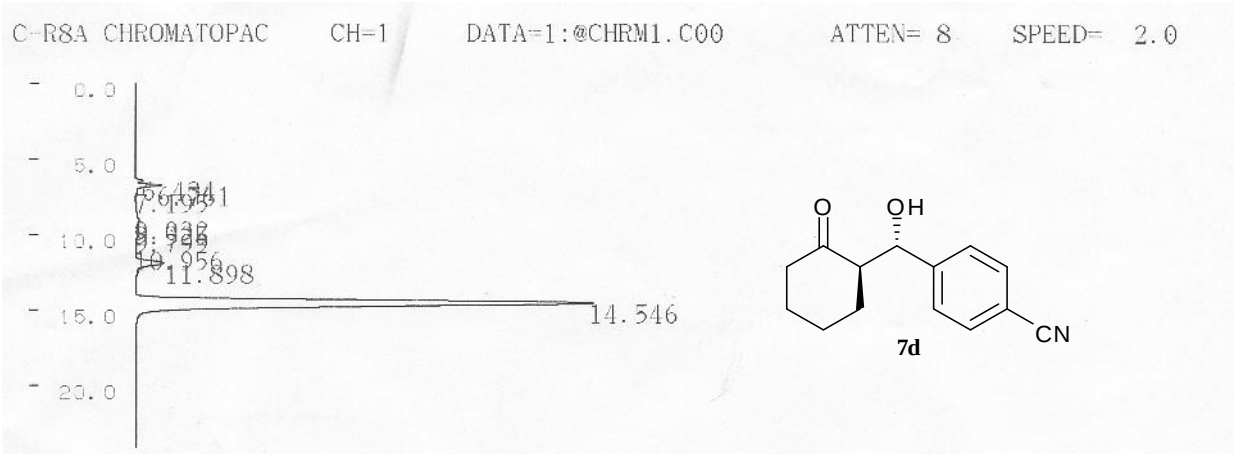
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	6.136	36052	3494			0.5545	
	2	7.469	50847	2280			0.782	
	3	8.255	8534	301	V		0.1312	
	6	17.821	22197	857			0.3414	
	7	20.09	10120	466			0.1557	
	8	21.274	13883	457			0.2135	
	10	27.963	152386	4313			2.3437	
	11	29.25	6207913	151220	V		95.478	
		TOTAL	6501931	163388			100	



C-R8A CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 09/09/03 11:14:58

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	6.498	20839	1324			0.2234	
	4	9.665	15383	710			0.1649	
	7	12.715	4632694	145840	V		49.6575	
	8	15.61	4660375	118596	V		49.9542	
		TOTAL	9329290	266470			100	



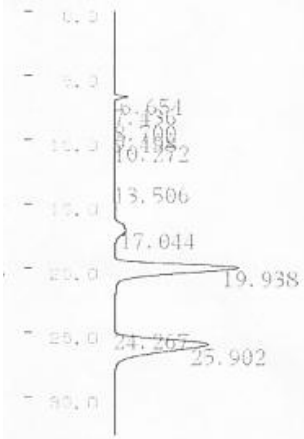
C-R8A CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 11/08/01 16:32:54

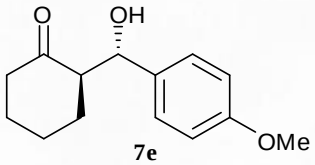
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	6.434	23594	1939			0.6615	
	2	6.761	81351	6398	V		2.2808	
	3	7.195	6708	451	V		0.1881	
	4	9.032	21266	721			0.5962	
	5	9.325	8729	548	V		0.2447	
	6	9.799	11621	407	V		0.3258	
	8	11.898	148668	6587			4.1682	
	9	14.546	3264747	110769			91.5345	
		TOTAL	3566684	127820			100	

87.3663
95.7029

C-RSA CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 8 SPEED= 2.0





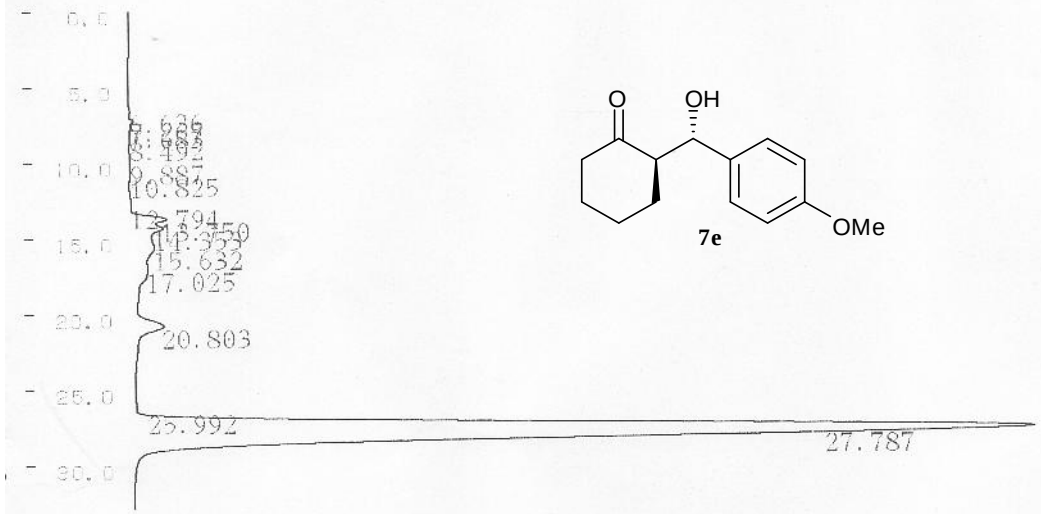
7e
Racemic

C-RSA CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 09/09/07 21:58:20

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	6.654	57386	3825			1.5142	
	7	17.044	195791	3125			5.1661	
	8	19.938	1775398	35320	V		46.8448	
	10	25.902	1761384	26665	V		46.475	
		TOTAL	3789959	68935			100	

C-RSA CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 7 SPEED= 2.0



7e

C-RSA CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 11/03/23 18:19:40

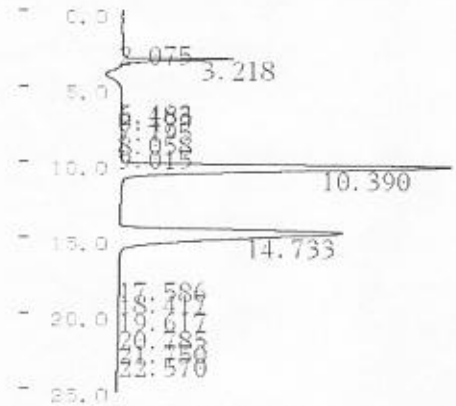
** CALCULATION REPORT **

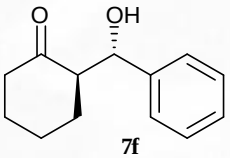
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	6.636	5488	235			0.0642	
	2	7.267	12385	649	V		0.1449	
	3	7.683	6861	316	V		0.0803	
	5	9.887	8048	159			0.0942	
	7	12.794	13577	256			0.1589	
	8	13.75	150808	4482	V		1.7648	
	9	14.353	182632	4028	V		2.1372	
	10	15.632	248676	2968	V		2.9101	
	11	17.025	264564	2087	V		3.096	
	12	20.803	359058	3951	V		4.2018	
	13	25.992	27469	426	V		0.3215	
	14	27.787	7265842	108351	V		85.0263	
		TOTAL	8545408	127910			100	

90
= 9
89.22

No. 35

C-R8A CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 8 SPEED= 2.0





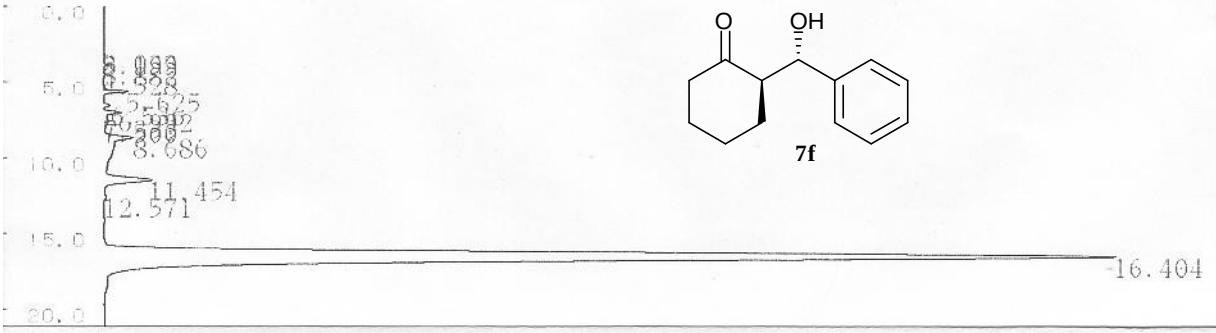
7f
Racemic

C-R8A CHROMATOPAC CH-1 Report No.=8 DATA=1:@CHRM1.C00 09/09/25 18:23

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	3.218	400051	28403			5.4461	
	3	5.483	301310	3558			4.1019	
	4	6.163	62715	3495	V		0.8538	
	5	6.479	116759	3471	V		1.5895	
	6	7.195	190503	3560	V		2.5934	
	7	8.058	154835	3298	V		2.1079	
	8	9.015	130366	3151	V		1.7747	
	9	10.39	3031488	83240	V		41.2695	
	10	14.733	2944585	56322	SV		40.0864	
	12	18.417	7446	119	TV		0.1014	
	14	20.785	5535	95	TV		0.0753	
		TOTAL	7345590	188713			100	

-R8A CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 7 SPEED= 2.0



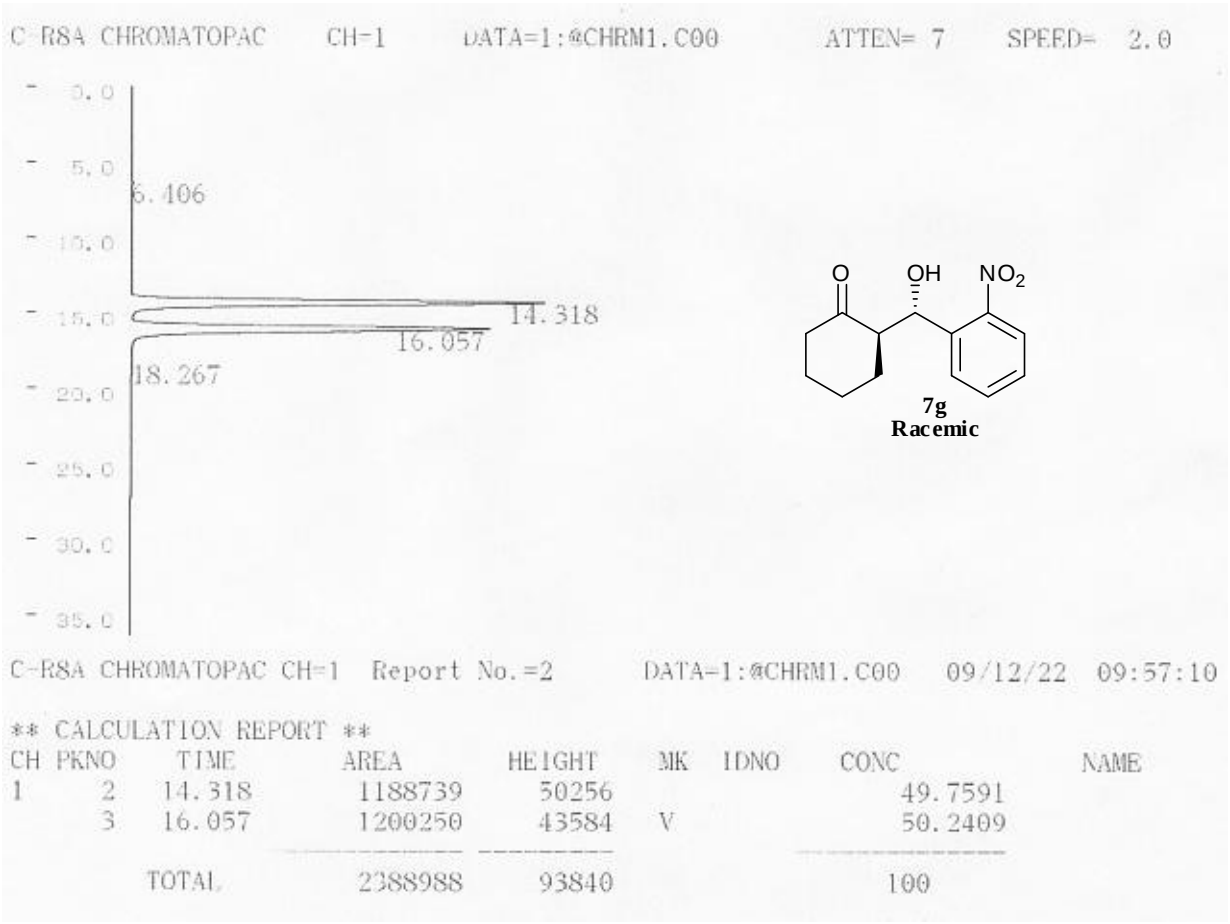
7f

-R8A CHROMATOPAC CH-1 Report No.=3 DATA=1:@CHRM1.C00 11/04/13 21:27:32

CALCULATION REPORT **

PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
2	3.199	1482	212	V		0.03	
3	3.882	4406	566			0.0892	
4	4.528	2331	219			0.0472	
5	5.625	35927	3083			0.727	
6	6.536	10805	807			0.2186	
7	6.992	27585	2055	V		0.5582	
8	7.333	3878	346	V		0.0785	
9	7.56	10118	367	V		0.2047	
10	8.686	49023	2845			0.9919	
11	11.454	132638	5632			2.6839	
12	12.571	4585	215			0.0928	
13	16.404	4659304	121911			94.2781	
	TOTAL	4942082	138257			100	

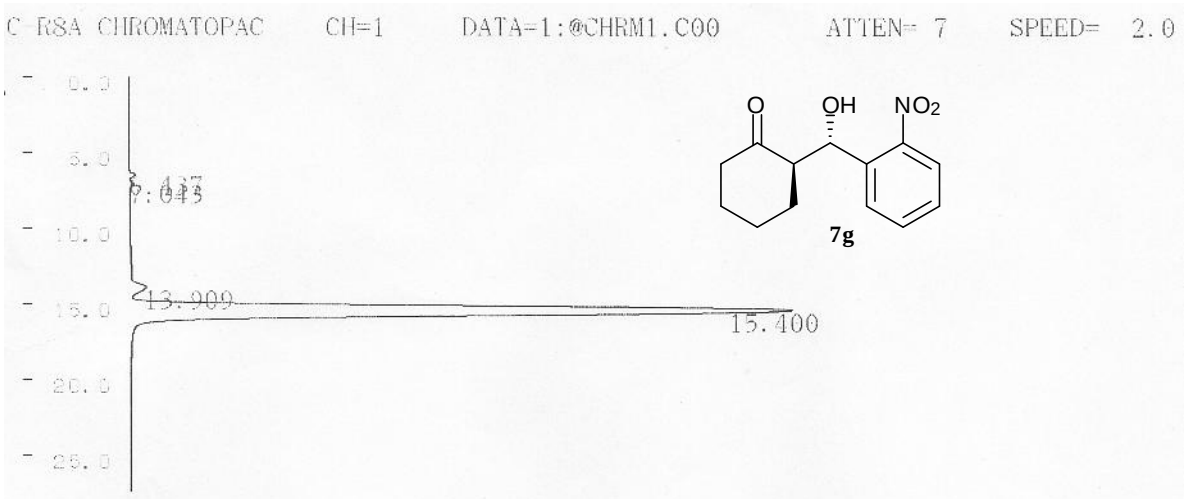
94.46, 96.962



C-R8A CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 09/12/22 09:57:10

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	14.318	1188739	50256			49.7591	
	3	16.057	1200250	43584	V		50.2409	
		TOTAL	2388988	93840			100	

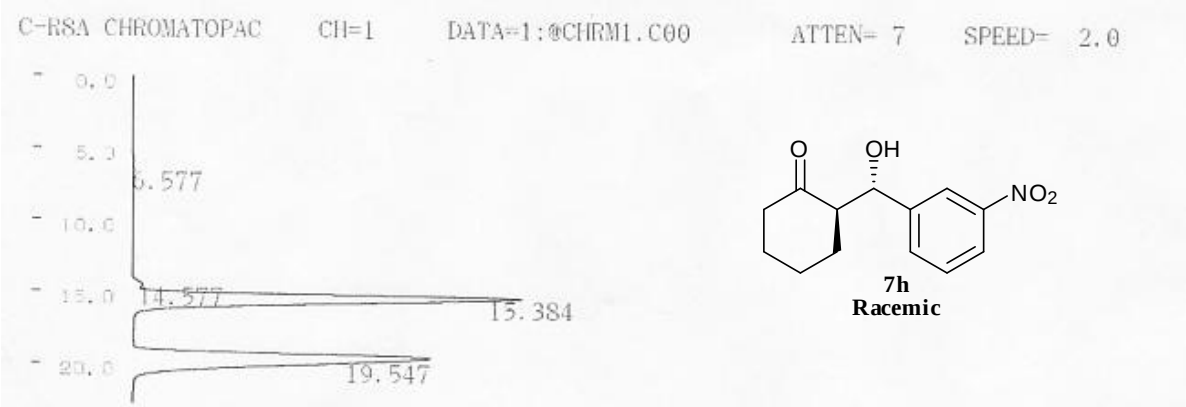


C-R8A CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 11/03/22 22:52:

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	6.437	11765	689			0.3307	
	2	7.043	9289	467	V		0.2611	
	3	13.909	67638	1766			1.9013	95.6
	4	15.4	3468684	79741	V		97.5068	99.4
		TOTAL	3557375	82663			100	

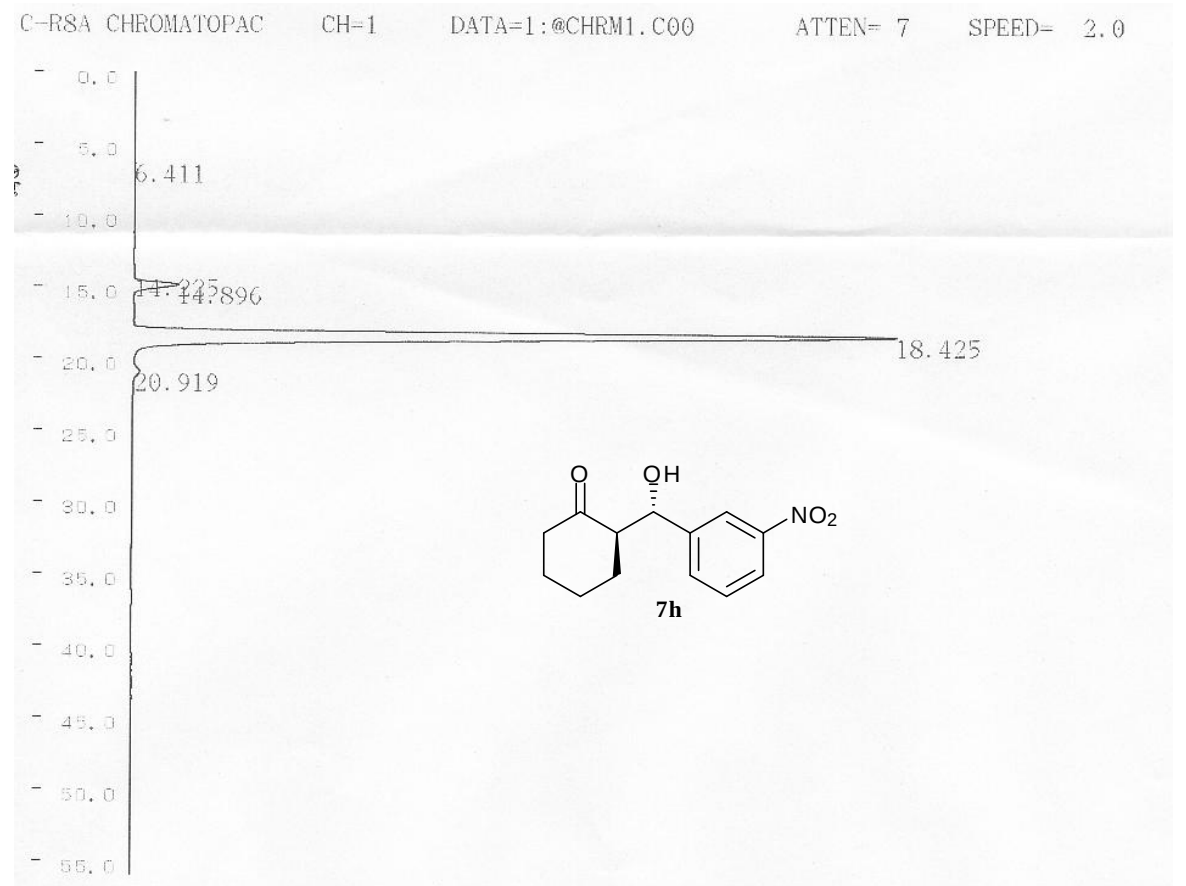
No.2



C-R8A CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 09/10/14 09:48:06

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	14.577	41048	1279			0.9793	
	3	15.384	2083677	49960	V		49.7142	
	4	19.547	2066590	38088	V		49.3065	
		TOTAL	4191314	89327			100	

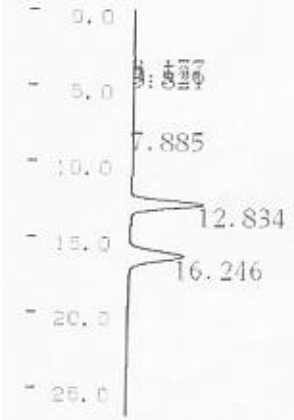


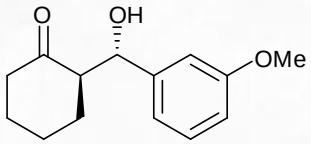
C-R8A CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 11/07/04 14:20:58

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	3	14.896	160995	5706	V		4.2329	90.7698
	4	18.425	3613353	97437			95.0027	99.2356
	5	20.919	29073	738			0.7644	
		TOTAL	3803420	103881			100	

C-R8A CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 8 SPEED= 2.0





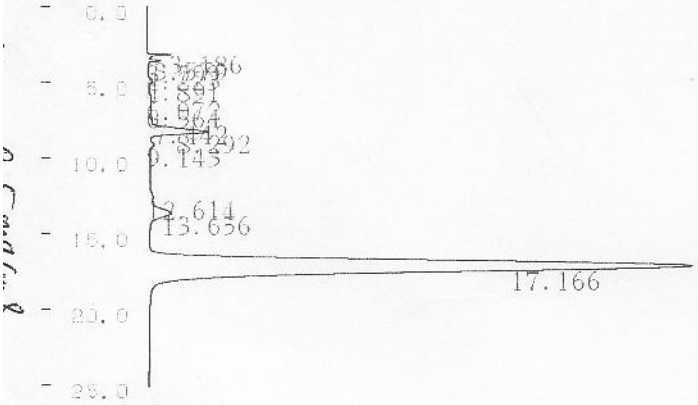
7i
Racemic

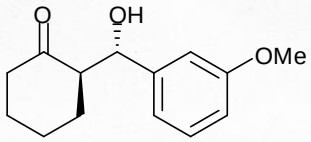
C-R8A CHROMATOPAC CH=1 Report No.=5 DATA=1:@CHRM1.C00 09/10/08 13:05:24

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	5	12.834	623776	17618			49.9004	
	6	16.246	626267	13154			50.0996	
		TOTAL	1250043	30772			100	

C R8A CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 7 SPEED= 2.0





7i

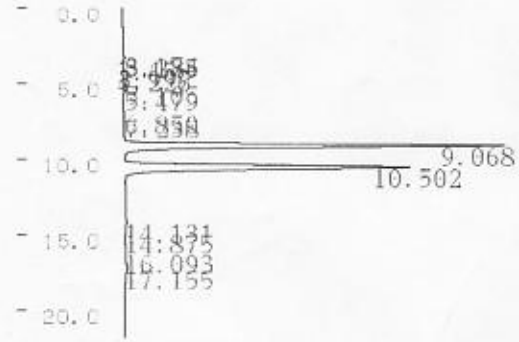
C R8A CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 11/03/14 23:06:06

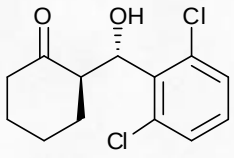
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	3.186	23287	3119			0.5927	
	2	3.579	12880	1705	V		0.3278	
	5	4.891	13562	464	V		0.3452	
	6	6.072	13005	334	V		0.331	
	7	6.564	9813	336	V		0.2498	
	8	7.442	12454	305	V		0.317	
	9	8.292	184178	7200	V		4.6876	
	10	9.143	12266	538	V		0.3122	
	11	12.614	12361	337			0.3146	
	12	13.656	109712	2621	V		2.7923	
	13	17.166	3525534	65359			89.7299	
		TOTAL	3929052	82316			100	

NO.32

C-R8A CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 8 SPEED= 2.0





7j
Racemic

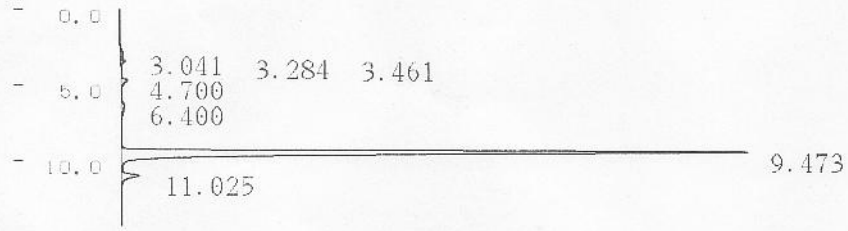
C-R8A CHROMATOPAC CH=1 Report No.=7 DATA=1:@CHRM1.C00 09/10/02 18:07:56

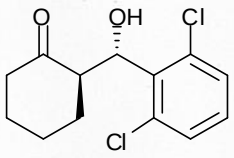
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	10	9.068	1436047	92968			49.2065	
	11	10.502	1432052	69639	V		49.0696	
	12	14.131	8739	258			0.2995	
	14	16.093	9509	198			0.3258	
	15	17.155	32061	740	V		1.0986	
		TOTAL	2918408	163803			100	

OJ-H
220nm
1.0 ml/min
Hexane : i-PrOH
95 : 5

C-R8A CHROMATOPAC CH=1 Report No.=6 DATA=1:@CHRM1.C00 11/06/29 22:07:04





7j

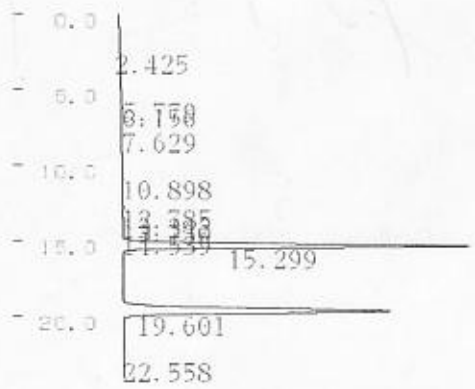
** CALCULATION REPORT **

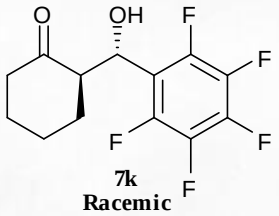
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	3.041	18259	671			0.6511	
	2	3.284	7782	672	V		0.2775	
	3	3.461	15311	1121	V		0.546	
	4	4.7	30341	1496			1.082	
	5	6.4	30937	803			1.1032	
	8	9.473	2620909	151851			93.4618	
	9	11.025	80718	4164	V		2.8784	
		TOTAL	2804258	160780			100	

NO.46

90.5834 / 96.3402 = 94%

C-R8A CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 8 SPEED= 2.0





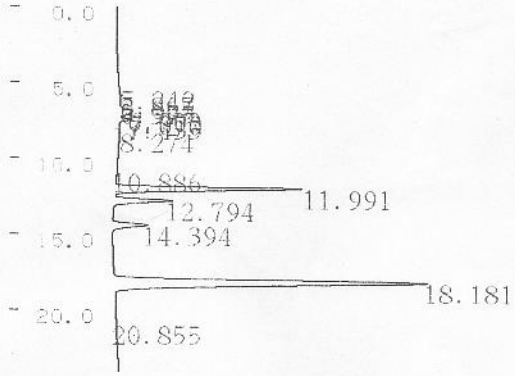
7k
Racemic

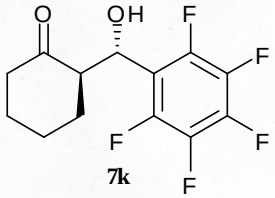
C-R8A CHROMATOPAC CH=1 Report No.=6 DATA=1:@CHRM1.C00 09/10/22 18:30:56

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	10	15.299	1519478	84101	V		49.9599	
	11	19.601	1521917	64088			50.0401	
		TOTAL	3041395	148189			100	

C-R8A CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 8 SPEED= 2.0





7k

C-R8A CHROMATOPAC CH=1 Report No.=6 DATA=1:@CHRM1.C00 11/04/12 22:15:14

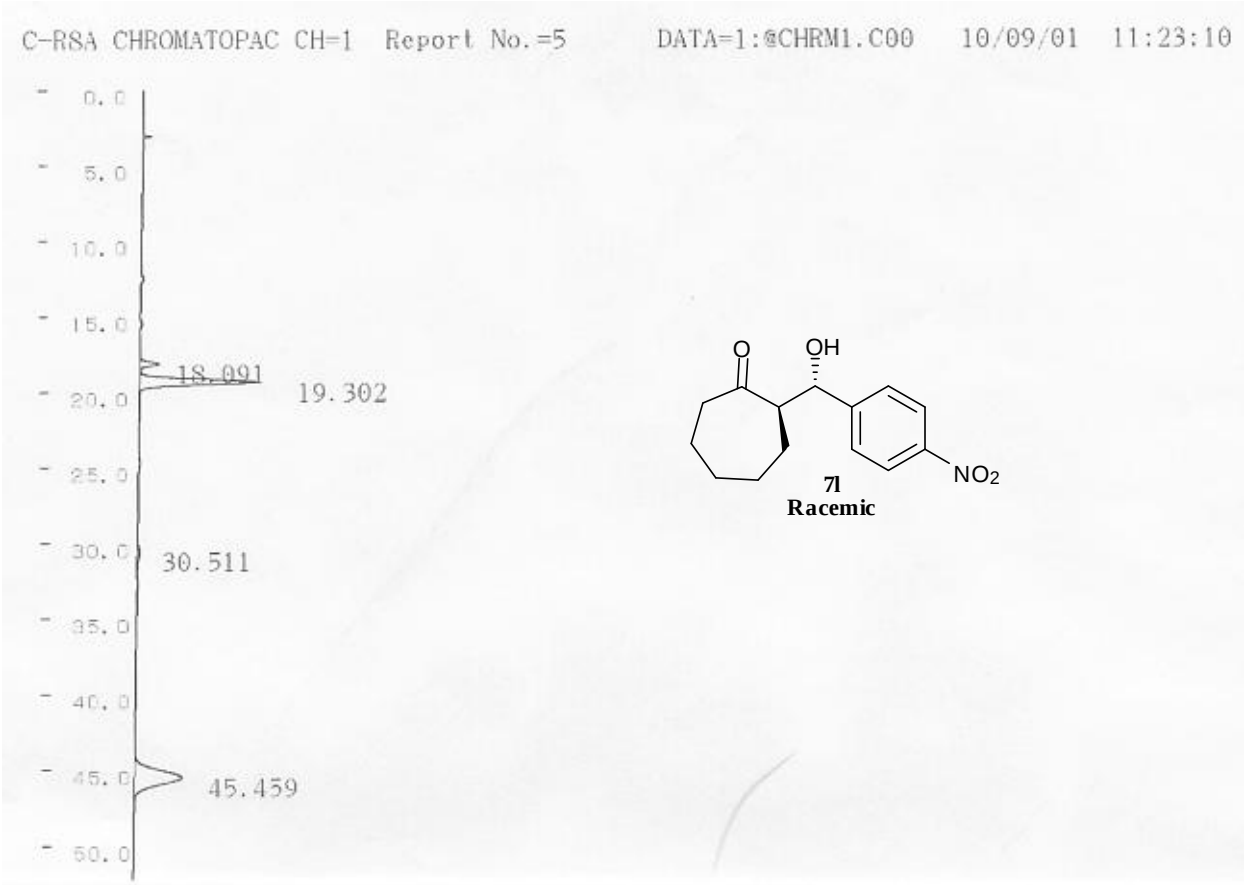
** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	5.242	7172	153			0.2328	
	2	5.867	9567	571	V		0.3105	
	3	6.065	6906	516	V		0.2241	
	4	6.375	5382	420	V		0.1747	
	5	6.903	51874	3352	V		1.6835	
	6	7.07	31718	3015	V		1.0294	
	7	7.435	36670	3240	V		1.1901	
	8	8.274	1561	124			0.0507	
	9	10.886	2701	163			0.0876	
	10	11.991	719228	45109			23.3421	
	11	12.794	232335	14092			7.5403	
	12	14.394	159677	8564			5.1822	
	13	18.181	1813689	75799			58.862	
	14	20.855	2776	116			0.0901	
		TOTAL	3081254	155233			100	

83.8

64.0442

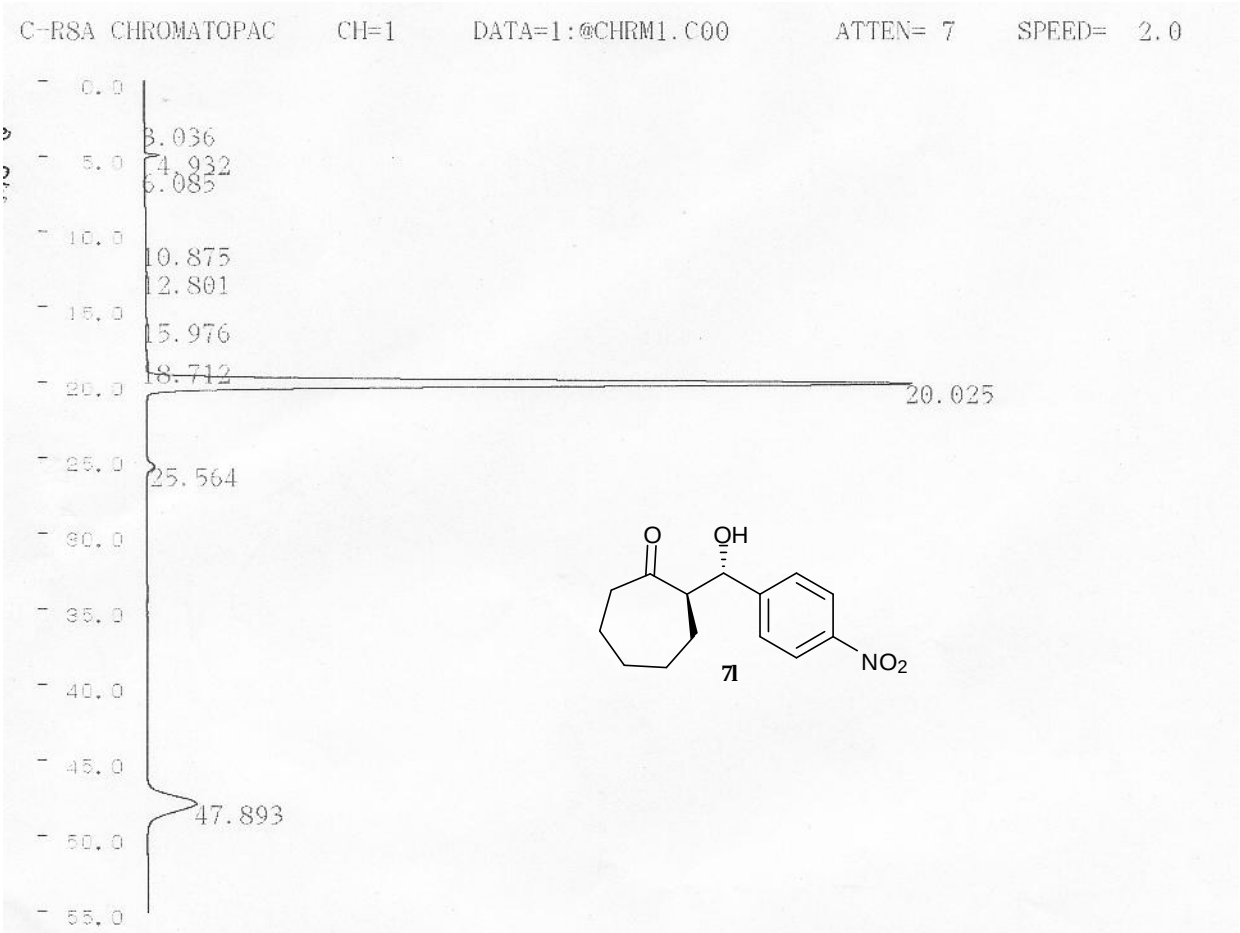
No.36



7l
Racemic

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	5	18.091	23549	1189			5.6733	
	6	19.302	191969	7081			46.2484	
	8	30.511	6725	147			1.6202	
	10	45.459	192840	2896			46.4581	
		TOTAL	415083	11313			100	

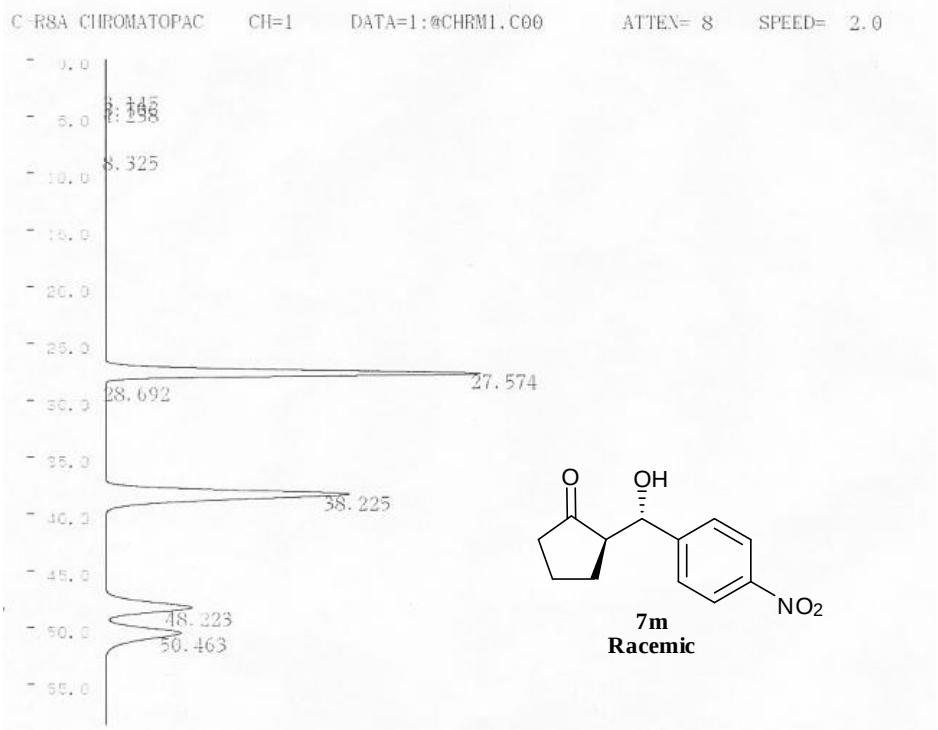


C-R8A CHROMATOPAC CH=1 Report No.=4 DATA=1:@CHRM1.C00 11/06/28 22:57:30

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	4.932	20692	1823			0.6378	
	8	20.025	2760757	92913			85.101	
	9	25.564	32206	922			0.9928	
	10	47.893	430440	5891			13.2684	
		TOTAL	3244095	101549			100	

71.8326 / 98.3694 ?

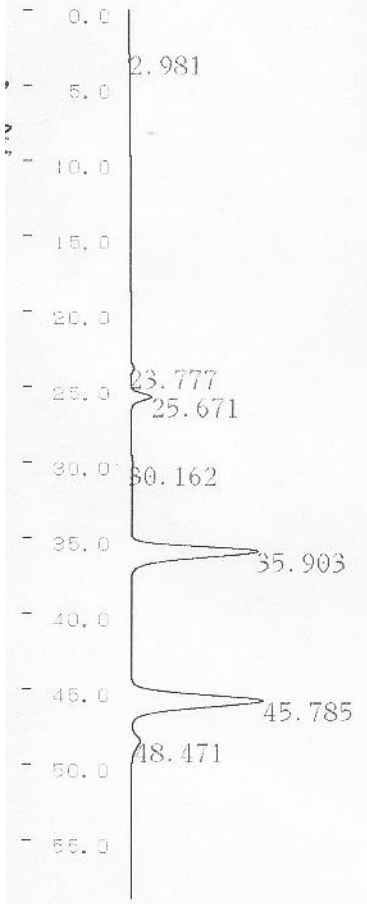


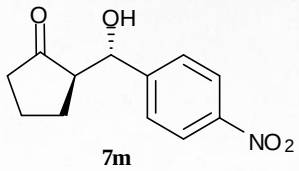
C-R8A CHROMATOPAC CH=1 Report No.=6 DATA=1:@CHRM1.C00 09/09/14 17:21:58

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	5	27.574	4575498	121314	S		36.1065	
	7	38.225	4577506	78870			36.1223	
	8	48.223	1762534	27853			13.9086	
	9	50.463	1756691	24428	V		13.8625	
		TOTAL	12672228	252465			100	

C-RSA CHROMATOPAC CH=1 DATA=1:@CHRM1.C00 ATTEN= 7 SPEED= 2.0



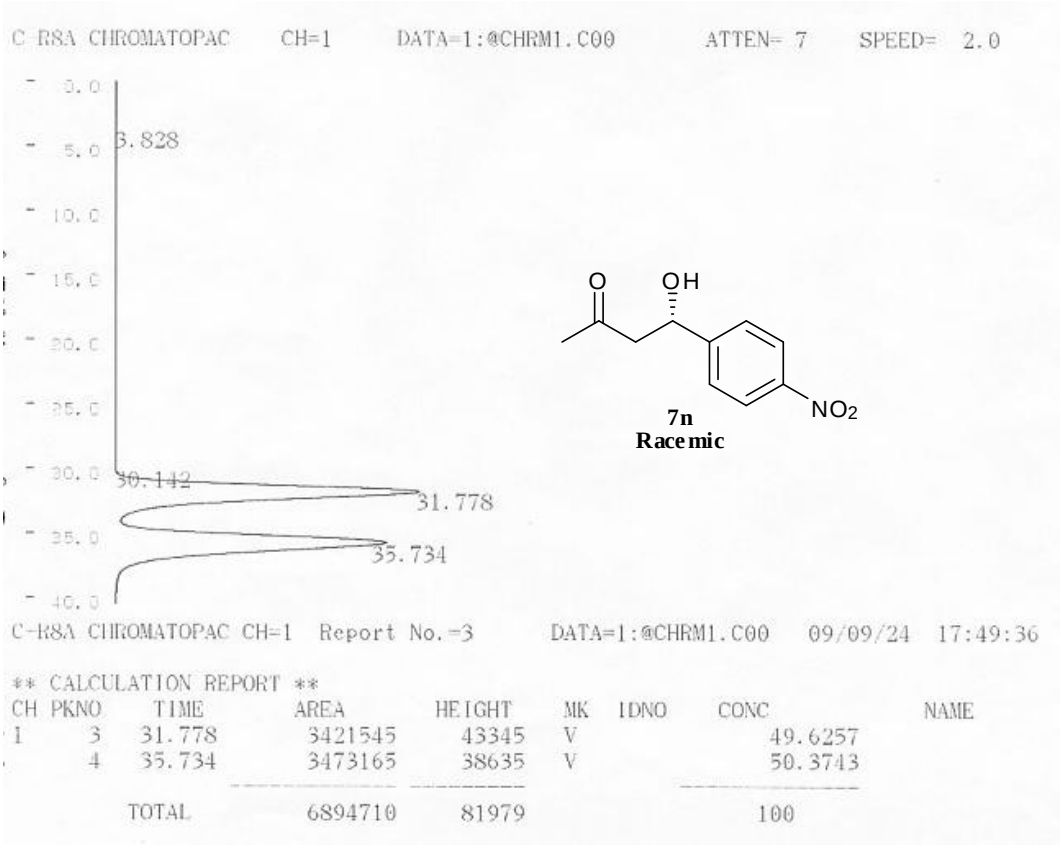


7m

C-RSA CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 11/06/28 09:20:16

** CALCULATION REPORT **

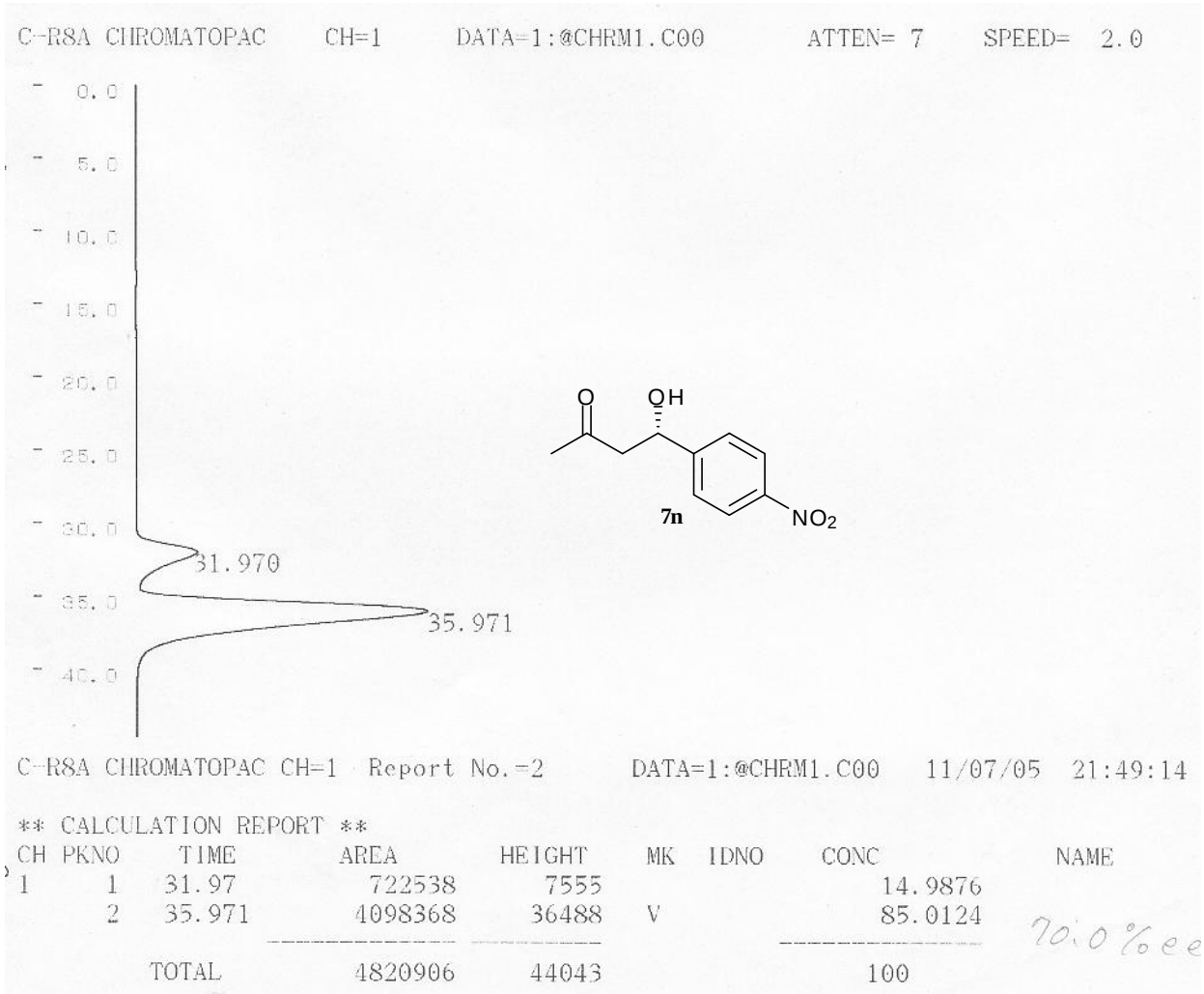
CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	2	23.777	7834	306			0.4026	
	3	25.671	84654	2408			4.3504	
	4	30.162	6493	193			0.3337	
	5	35.903	817319	15369			42.0025	
	6	45.785	968614	15897			49.7776	
	7	48.471	60968	965			3.1332	
		TOTAL	1945882	35139			100	



C-R8A CHROMATOPAC CH=1 Report No.=3 DATA=1:@CHRM1.C00 09/09/24 17:49:36

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	3	31.778	3421545	43345	V		49.6257	
	4	35.734	3473165	38635	V		50.3743	
		TOTAL	6894710	81979			100	



C-R8A CHROMATOPAC CH=1 Report No.=2 DATA=1:@CHRM1.C00 11/07/05 21:49:14

** CALCULATION REPORT **

CH	PKNO	TIME	AREA	HEIGHT	MK	IDNO	CONC	NAME
1	1	31.97	722538	7555			14.9876	
	2	35.971	4098368	36488	V		85.0124	
		TOTAL	4820906	44043			100	

70.0 %ee