Supporting Information for

A New Organocatalyzed Michael-Michael Cascade Reaction Generates Highly Substituted Fused Carbocycles

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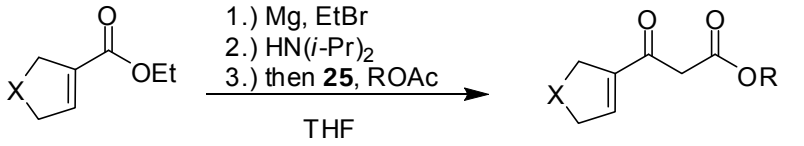
General Information

All chemicals and solvents were purchased from Sigma-Aldrich or Fisher Scientific. ^{1}H and ^{13}C NMR spectra were collected using a Bruker 400 MHz Biospin. The NMR data herein uses the following abbreviations: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet, dd=doublet of doublets, td=triplet of doublets, dt=doublet of triplets. Enantiomeric excesses were determined using a Perkin Elmer Series 200 HPLC with Daicel Chemical Industries, LTD. Chiralpak AD-H (0.46 x 25 cm), Chiralpak OD-H (0.46 x 25 cm), and Chiralpak AS-H (0.46 x 25 cm) columns. Optical rotations were determined using a Jasco P-1020 polarimeter. IR spectra were collected using a Nicolet 6700 FT-IR. High resolution mass spectra were collected using an Agilent 6520 Q-TOF. Flash chromatography was carried out with Merck, grade 9385, 230-400 mesh, 600 Å silica gel and with Merck, silica 60F-254 on glass, 250 µm layer TLC plates with fluorescent indicator. Solvents were dried and kept air free in a solvent purification unit. Solvents were evaporated using a standard rotovapor and a high vacuum. All reactions were carried out in oven dried glassware and conducted under an argon atmosphere.

Preparation of catalysts (1a-e) and starting enals (3b, 3c, 3e)

Catalysts **1a-e**[1,2] were prepared from the corresponding diarylprolinols[3] using known procedures. Noncommercially available enals **3b**, **3c**, and **3e,** were prepared according to a known procedure.[4]

Preparation of β-ketoesters (9a-c) and characterization (9b-c)



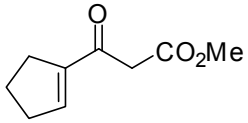
25a, X=CH_2
25b, X=S

9a, X=CH_2, R=Et
9b, X=CH_2, R=Me
9c, X=S, R=Et

The β-ketoester **9a** was prepared using an adapted procedure.[5] To a two-neck, round-bottom flask equipped with an internal thermometer was added magnesium metal (2.5 g, 103 mmol) and THF (21 mL). Bromoethane (7.5 mL, 100 mmol) was slowly added to this solution while maintaining the internal temperature below 25 ºC. The mixture was allowed to stir at room temperature until all the metal had reacted (~1h). The flask was equipped with an outlet and a solution of diisopropylamine (14.2 ml, 100 mmol) in THF (21 mL) was slowly added while maintaining the internal temperature below 25 ºC. The mixture was allowed to stir at room temperature for 3h. The temperature of the mixture was lowered to 10 ºC and a solution of **25a**[6] (7.0 g, 50 mmol), ethyl acetate (4.90 mL, 50 mmol), and THF (35 mL) was added while maintaining the internal temperature between 10-15 ºC. The reaction was allowed to stir at room temperature for 3h and the reaction was poured into 4M H_2SO_4 (*aq*) with ice. The mixture was extracted three times with Et_2O. The ether extracts were combined, dried over $MgSO_4$, filtered and concentrated. The mixture was purified via flash chromatography (97/3, petroleum ether/Et_2O) and β-ketoester **9a** was isolated in 70% yield. Characterization of **9a** was in agreement with experimental data.[5]

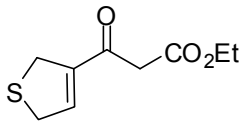
β-ketoesters **9b** and **9c** were prepared from **25a**[6] and **25b**[7], respectively, using the same procedure and were obtained in similar yields.

9b: *methyl 3-cyclopentenyl-3-oxopropanoate*



pale yellow oil. IR (thin film, KBr): 2954, 2843, 1747, 1656, 1588, 1445, 1363, 1263, 1209, 1063, 1004, 954, 800, 729 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$), keto form: δ 6.79 (m, 1H), 3.73 (s, 3H), 3.71 (s, 2H), 2.59 (m, 4H), 1.95 (quintet, *J* = 7.6 Hz, 2H) ppm, enol form: δ 11.75 (s, 1H), 6.61 (m, 1H), 5.06 (s, 1H), 3.75 (s, 3H), 2.52-2.46 (m, 4H), 1.97 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$), keto and enol form: δ 190.3, 173.5, 168.5, 168.1, 146.1, 145.5, 138.2, 137.6, 88.5, 52.4, 51.3, 46.1, 31.2, 33.6, 31.0, 30.7, 23.2, 22.9 ppm. HRMS (ESI) : $[M^+]$ calcd for $[C_9H_{12}O_3]$: 168.0786, found: 168.0790.

9c: *ethyl 3-(2,5-dihydrothiophen-3-yl)-3-oxopropanoate*



pale yellow oil. IR (thin film, KBr): 2982, 1740, 1675, 1599, 1422, 1252, 1222, 1182, 1034, 797 cm^{-1}; ^1H NMR (400 MHz, CD_3OD), keto form: δ 7.06 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.00 (m, 2H), 3.87 (m, 2H), 3.84 (s, 2H), 1.26 (t, *J* = 7.2 Hz, 3H) ppm, enol form: δ 6.73 (m, 1H), 5.15 (s, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.88-3.82 (m, 4H), 1.28 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$), keto and enol form: δ 189.3, 172.7, 167.0, 166.7, 144.0, 142.2, 136.8, 134.3, 90.0, 61.6, 60.5, 46.9, 39.7, 39.2, 37.0, 36.5, 14.3, 14.2 ppm. HRMS (ESI) : $[M^+]$ calcd for $[C_9H_{12}O_3S]$: 200.0507, found: 200.0512.

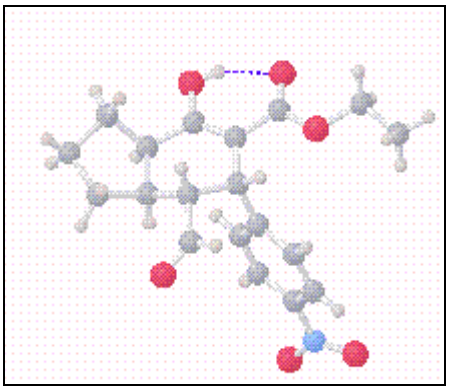
General Procedure for synthesis of carbocycles (10-11, 17-24)

To an oven dried flask was added catalyst **1a** (32.6 mg, 0.1 mmol), solvent (3.33 mL), β-ketoester **9a** (182.2 mg, 1.0 mmol), and enal **3a** (177.2 mg, 1.0 mmol). The reaction was allowed to stir for the indicated time at room temperature. The reaction mixture was filtered through a plug of silica and concentrated. The percent conversion of the crude reaction mixture could be determined using an internal standard. The diastereomeric mixture of **10a**, **10b** and **11** was then purified via column chromatography (85/15, petroleum ether/Et_2O) and an isolated yield was determined. The diastereomeric ratio of the isolated product was determined through comparison of the relative integrations of the aldehyde and/or enol peaks in the ^1H NMR spectrum. Samples of the pure diastereomers **10a**, **10b** and **11** were obtained through further flash chromatography. Carbocycles **17-24** were prepared and purified using the same procedure.

Racemic samples of the Michael-Michael products **10-11** and **17-24** were prepared in a similar manner using racemic catalyst **1a**.

Determination of absolute configurations

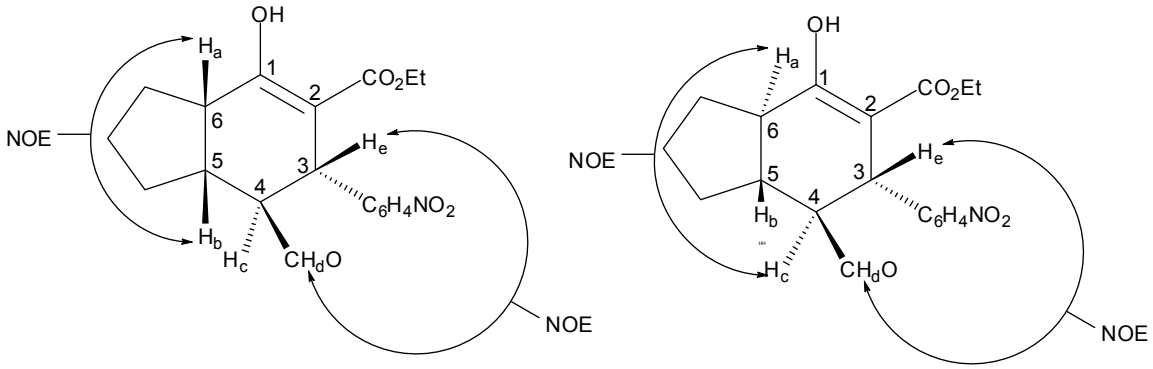
The stereochemistry of **10a** at *C3* was assigned by analogy to other **1a**-catalyzed conjugate additions. The relative configuration of Michael-Michael product **10a** was determined via X-ray crystallography.



10a

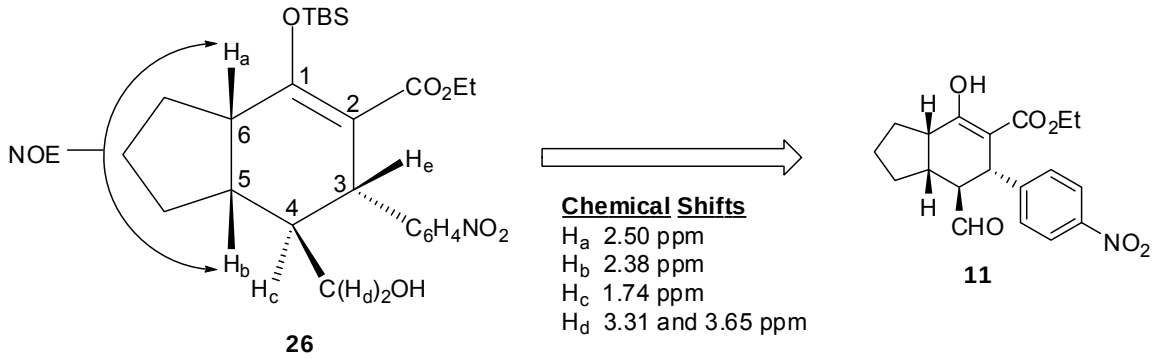
It was established that **10b** was the *C4* epimer of **10a** by subjecting pure **10a** to **1a** (20 mol %) and benzoic acid (20 mol %) in EtOH (0.3 M), which produced a mixture of **10a** and **10b**. The configurations of Michael-Michael products **17-24a** and **17-24b** were assigned by analogy.

The configuration of **11** was assigned as one of the two structures shown below, using NOE.

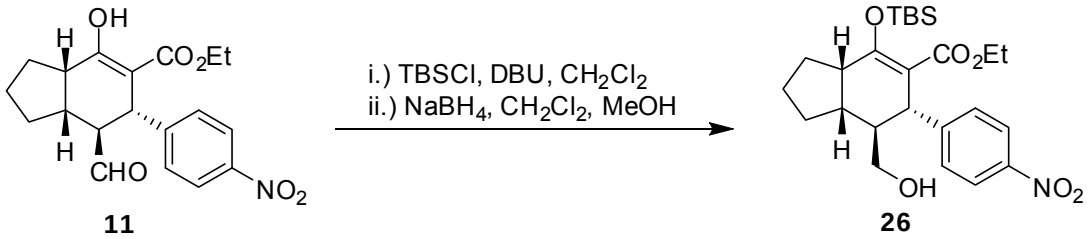


An NOE interaction between H_e and H_d was observed indicating that the aldehyde functionality at the *C4* position was *cis* to H_e. The signals for H_b and H_c overlapped completely, complicating further analysis of NOE interactions. However, another NOE interaction was observed between H_a and the overlapping ^1H signals for H_b and H_c. This indicated that the H_a proton was *cis* to either H_b or H_c. Due to the overlapping of the ^1H signals for H_b and H_c, the stereochemistry at *C6* could not be determined from the NOE spectrum of **11**.

Aldehyde **11** was silylated and reduced to alcohol **26** (see below). The nature of the ring junction in **26** was determined using NOE. An NOE interaction between H_a and H_b was observed indicating that the ring junction in **26** was *cis*. Thus, it was determined that the ring junction in **11** was *cis*, having the configuration shown below.



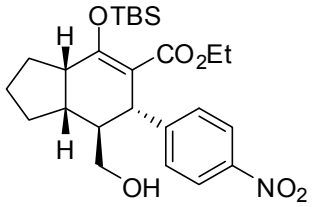
Formation and Characterization of Alcohol 26



To an oven dried flask was added (±)-**11** (13.0 mg, 36 µmol), CH_2Cl_2 (1.4 mL), and TBSCl (11.3 mg, 75 µmol). DBU (11.2 µL, 75 µmol) was added dropwise to the stirring solution of (±)-**11**. The reaction was monitored by TLC and was quenched when (±)-**11** was completely consumed (~1.5 h). The reaction was diluted with CH_2Cl_2 (15 mL) and washed with saturated NH_4Cl (*aq*) (15 mL). The aqueous layer was washed with CH_2Cl_2 (2 x 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. The silylated intermediate was purified via column chromatography (90/10, petroleum ether/Et_2O) and used in step ii.).

To an oven dried flask was added, the silylated intermediate from step i.) (17.1 mg, 36 µmol) and a 1/1 mixture of MeOH/CH_2Cl_2 (1 mL). The stirring solution was cooled in an ice bath and $NaBH_4$ (9.5 mg, 252 µmol) was added. The reaction was stirred at 0º C and was monitored by TLC. The reaction was quenched after the silylated intermediate was completely consumed (~30 min). The reaction was diluted with CH_2Cl_2 (15 mL) and washed with saturated NH_4Cl (*aq*) (15 mL). The aqueous layer was washed with CH_2Cl_2 (2 x 15 mL). The organic layers were combined, dried over Na_2SO_4, filtered and concentrated. Alcohol (±)-**26** was purified via column chromatography (80/20, petroleum ether/EtOAc).

26: *(3aS,6S,7S,7aS)-ethyl 4-(tert-butyldimethylsilyloxy)-7-(hydroxymethyl)-6-(4-nitrophenyl)-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*

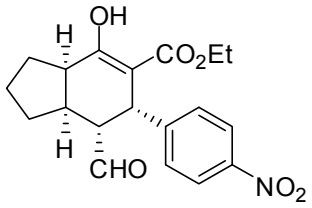


colorless crystals. m.p.: 135-137 °C. IR (thin film, KBr): 3444, 2956, 2931, 2859, 1704, 1519, 1347, 1255, 1201, 1062, 781, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.42 (d, *J* = 8.6 Hz, 2H), 4.15 (d, *J* = 9.0 Hz, 1H), 3.87 (m, 1H), 3.72 (m, 1H), 3.65 (dd, *J* = 3.4, 11.1 Hz, 1H), 3.31 (dd, *J* = 2.6, 11.1 Hz, 1H), 2.50 (q, *J* = 8.1 Hz, 1H), 2.38 (m, 1H), 2.14 (m, 1H), 1.74 (m, 3H), 1.51-1.60 (m, 3H), 0.94 (s, 9H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.17 (s, 3H), 0.15 (s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 158.8, 152.9, 146.7, 129.4, 123.5, 112.1, 61.2,

59.9, 45.0, 44.9, 44.6, 38.2, 31.3, 29.9, 25.9, 24.1, 18.5, 14.0, -3.8, -3.8 ppm; HRMS (ESI) : [M^+] calcd for [$C_{25}H_{37}NO_6Si$]: 475.2390, found: 475.2390.

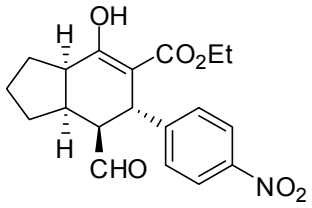
Characterization of carbocycles (10-11, 17-24)

10a: *(3aR,6S,7R,7aS)-ethyl 7-formyl-4-hydroxy-6-(4-nitrophenyl)-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



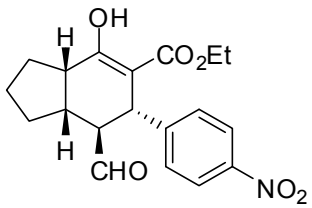
colorless crystals. m.p.: 84-86 °C. $[\alpha]_D^{23}$ = +177.8 (*c* 1.00, CH_2Cl_2, 99% ee); IR (thin film, KBr): 2962, 2870, 1721, 1650, 1615, 1519, 1348, 1280, 1243, 1213, 855, 826, 706 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 9.38 (d, *J* = 1.7 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 2H), 7.26 (d, *J* = 8.7 Hz, 2H), 4.45 (d, *J* = 3.9 Hz, 1H), 4.05 (m, 2H), 2.98 (q, *J* = 8.2 Hz, 1H), 2.59 (m, 2H), 2.32 (m, 1H), 2.06 (m, 1H), 1.80 (m, 1H), 1.59 (m, 2H), 1.33 (m, 1H), 1.07 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 176.0, 171.2, 147.8, 147.3, 129.9, 123.6, 99.1, 60.9, 54.5, 43.2, 41.5, 32.5, 31.7, 31.3, 25.0, 14.1 ppm; the enantiomeric excess was determined by HPLC with an AS-H column (*n*-hexane: *i*-PrOH = 99:1), 1.0 mL/min; major enantiomer t_R = 20.7 min, minor enantiomer t_R = 24.8 min. HRMS (ESI) : [M^-] calcd for [$C_{19}H_{21}NO_6$]: 359.1369, found: 359.1377.

10b: *(3aR,6S,7S,7aS)-ethyl 7-formyl-4-hydroxy-6-(4-nitrophenyl)-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



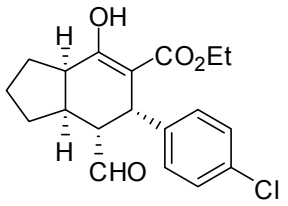
colorless amorphous solid. $[\alpha]_D^{23}$ = +65.9 (*c* 0.500, CH_2Cl_2, 99% ee); IR (thin film, KBr): 2958, 1721, 1647, 1608, 1519, 1347, 1235, 1109, 853 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.65 (s, 1H), 9.66 (d, *J* = 1.5 Hz, 1H), 8.13 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.8 Hz, 2H), 4.34 (d, *J* = 7.8 Hz, 1H), 3.93 (m, 2H), 3.00 (q, *J* = 6.3 Hz, 1H), 2.79 (m, 1H), 2.57 (m, 1H), 2.07 (m, 1H), 1.98 (m, 1H), 1.71 (m, 3H), 1.55 (m, 1H), 0.87 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 174.8, 171.7, 153.1, 146.8, 129.0, 123.7, 98.3, 60.8, 56.3, 43.5, 37.7, 36.9, 29.6. 26.1. 23.9. 13.8 ppm; the enantiomeric excess was determined by HPLC with an AS-H column (*n*-hexane: *i*-PrOH = 99:1), 1.0 mL/min; minor enantiomer t_R = 27.4 min, major enantiomer t_R = 32.3 min. HRMS (ESI) : [M^-] calcd for [$C_{19}H_{21}NO_6$]: 359.1369, found: 359.1370.

11: *(6S,7S,7aR)-ethyl 7-formyl-4-hydroxy-6-(4-nitrophenyl)-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



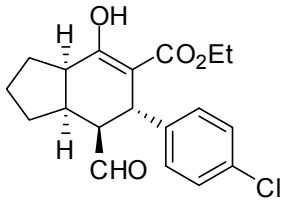
colorless crystals. m.p.: 95-97 °C. $[\alpha]_D^{25}$ = +20.1 (*c* 0.500, CH_2Cl_2, 37% ee); IR (thin film, KBr): 2963, 2874, 1725, 1650, 1613, 1519, 1348, 1286, 1228, 855 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.59 (s, 1H), 9.66 (d, *J* = 1.2 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 2H), 7.31 (d, *J* = 8.7 Hz, 2H), 4.35 (d, *J* = 5.9 Hz, 1H), 3.95 (m, 2H), 2.80 (q, *J* = 7.6 Hz, 1H), 2.58 (m, 2H), 2.29 (m, 1H), 1.52-1.78 (m, 4H), 1.28 (m, 1H), 0.86 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 176.1, 171.6, 152.9, 146.7, 128.3, 123.9, 97.1, 60.8, 56.5, 42.0, 39.9, 37.4, 31.0, 29.9, 24.2, 13.9 ppm; the enantiomeric excess was determined by HPLC with an AS-H column (*n*-hexane: *i*-PrOH = 95:5), 1.0 mL/min; major enantiomer t_R = 22.5 min, minor enantiomer t_R = 66.5 min. HRMS (ESI) : [M^-] calcd for [$C_{19}H_{21}NO_6$]: 359.1369, found: 359.1370.

17a: *(3aR,6S,7R,7aS)-ethyl 6-(4-chlorophenyl)-7-formyl-4-hydroxy-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



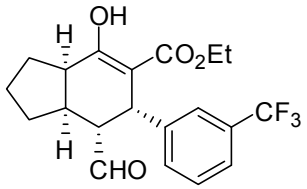
colorless amorphous solid. $[\alpha]_D^{24}$ = +120.7 (*c* 1.00, CH_2Cl_2, 99% ee); IR (thin film, KBr): 2961, 2871, 1723, 1650, 1616, 1279, 1242, 1213, 1093, 832 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.51 (s, 1H), 9.32 (d, *J* = 2.8 Hz, 1H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 4.31 (d, *J* = 4.9 Hz, 1H), 4.05 (m, 2H), 2.88 (q, *J* = 8.6 Hz, 1H), 2.60 (m, 1H), 2.48 (m, 1H), 2.29 (m, 1H), 2.02 (m, 1H), 1.78 (m, 1H), 1.61 (m, 2H), 1.29 (m, 1H), 1.08 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.2, 175.4, 171.5, 138.4, 133.0, 130.2, 128.6, 99.7, 60.8, 54.6, 43.2, 41.0, 32.4, 31.6, 31.3, 25.0, 14.1 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 99:1), 0.5 mL/min; major enantiomer t_R = 14.3 min, minor enantiomer t_R = 18.7 min. HRMS (ESI) : [M^+] calcd for [$C_{19}H_{21}ClO_4$]: 348.1128, found: 348.1129.

17b: *(3aR,6S,7S,7aS)-ethyl 6-(4-chlorophenyl)-7-formyl-4-hydroxy-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



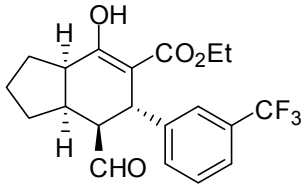
colorless oil. $[\alpha]_D^{24}$ = +31.3 (*c* 0.500, CH_2Cl_2, 98% ee); IR (thin film, KBr): 2958, 2874, 1723, 1647, 1613, 1490, 1308, 1235, 1091, 1014, 841 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.59 (s, 1H), 9.68 (d, *J* = 1.7 Hz, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 4.19 (d, *J* = 7.0 Hz, 1H), 3.96 (m, 2H), 2.94 (q, *J* = 7.3 Hz, 1H), 2.70 (m, 1H), 2.52 (m, 1H), 2.08 (m, 1H), 1.88 (m, 1H), 1.78-1.87 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.5, 174.4, 172.0, 143.3, 132.2, 129.4, 128.6, 98.7, 60.6, 56.5, 43.4, 37.6, 36.7, 29.8, 26.4, 24.1, 13.8 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 99:1), 0.3 mL/min; major enantiomer t_R = 24.3 min, minor enantiomer t_R = 31.6 min. HRMS (ESI) : [M^+] calcd for [$C_{19}H_{21}ClO_4$]: 348.1128, found: 348.1131.

18a: *(3aR,6S,7R,7aS)-ethyl 7-formyl-4-hydroxy-6-(3-(trifluoromethyl)phenyl)-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



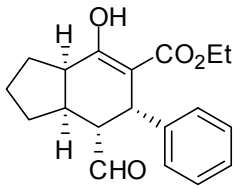
colorless oil. $[\alpha]_D^{24}$ = +126.1 (*c* 1.00, CH_2Cl_2, 99% ee); IR (thin film, KBr): 2964, 2872, 1724, 1651, 1618, 1328, 1244, 1165, 1126, 1033, 831, 806, 708 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.52 (s, 1H), 9.34 (d, *J* = 2.6 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 1H), 7.38 (t, *J* = 7.7 Hz, 1H), 7.32 (s, 1H), 7.28 (d, *J* = 8.5 Hz, 1H), 4.39 (d, *J* = 4.9 Hz, 1H), 4.04 (m, 2H), 2.98 (q, *J* = 8.5 Hz, 1H), 2.62 (m, 1H), 2.53 (m, 1H), 2.31 (m, 1H), 2.05 (m, 1H), 1.79 (m, 1H), 1.63 (m, 2H), 1.07 (m, 1H), 1.05 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.8, 175.7, 171.4, 141.2, 132.3, 131.0, 130.7, 128.9, 125.6, 124.1, 99.5, 60.8, 54.6, 43.2, 41.5, 32.5, 31.7, 31.4, 25.0, 14.0 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 99:1), 0.2 mL/min; major enantiomer t_R = 38.4 min, minor enantiomer t_R = 43.8 min. HRMS (ESI) : $[M^-]$ calcd for $[C_{20}H_{21}F_3O_4]$: 382.1392, found: 382.1395.

18b: *(3aR,6S,7S,7aS)-ethyl 7-formyl-4-hydroxy-6-(3-(trifluoromethyl)phenyl)-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



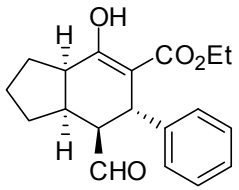
colorless oil. $[\alpha]_D^{23}$ = +18.7 (*c* 1.00, CH_2Cl_2, 99% ee); IR (thin film, KBr): 2962, 2877, 1724, 1648, 1613, 1329, 1236, 1163, 1125, 836, 802, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.63 (s, 1H), 9.68 (d, *J* = 1.8 Hz, 1H), 7.45 (m, 2H), 7.38 (m, 2H), 4.28 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.93 (m, 2H), 2.99 (q, *J* = 6.5 Hz, 1H), 2.78 (m, 1H), 2.55 (m, 1H), 2.07 (m, 1H), 1.95 (m, 1H), 1.57-1.79 (m, 4H), 0.84 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 174.6, 171.9, 146.1, 131.4, 131.0, 130.7, 128.9, 125.0, 123.3, 98.6, 60.6, 56.4, 43.4, 37.8, 36.8, 29.6, 26.2, 24.0, 13.6 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 99:1), 0.3 mL/min; minor enantiomer t_R = 25.3 min, major enantiomer t_R = 30.3 min. HRMS (ESI) : $[M^-]$ calcd for $[C_{20}H_{21}F_3O_4]$: 382.1392, found: 382.1395.

19a: *(3aR,6S,7R,7aS)-ethyl 7-formyl-4-hydroxy-6-phenyl-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



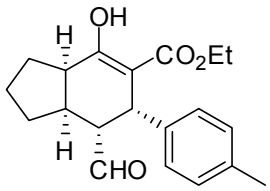
colorless oil. $[\alpha]_D^{23}$ = +117.4 (*c* 1.00, CH_2Cl_2, 99% ee); IR (thin film, KBr): 2962, 1722, 1648, 1617, 1280, 1243, 1212, 1084, 832, 704 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 9.32 (d, *J* = 3.0 Hz, 1H), 7.26 (m, 3H), 7.09 (d, *J* = 7.2 Hz, 2H), 4.35 (d, *J* = 4.9 Hz, 1H), 4.07 (m, 2H), 2.97 (q, *J* = 9.4 Hz, 1H), 2.59 (m, 1H), 2.49 (m, 1H), 2.31 (m, 1H), 2.01 (m, 1H), 1.80 (m, 1H), 1.63 (m, 2H), 1.30 (m, 1H), 1.09 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.7, 175.3, 171.7, 139.7, 128.9, 128.4, 127.1, 99.9, 60.7, 54.8, 43.2, 41.7, 32.5, 31.6, 31.4, 25.0, 14.1 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 99:1), 1.0 mL/min; minor enantiomer t_R = 7.0 min, major enantiomer t_R = 8.9 min. HRMS (ESI) : $[M^+]$ calcd for $[C_{19}H_{22}O_4]$: 314.1518, found: 314.1520.

19b: *(3aR,6S,7S,7aS)-ethyl 7-formyl-4-hydroxy-6-phenyl-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



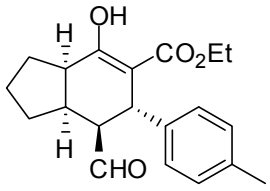
colorless oil. $[\alpha]_D^{21}$ = +23.6 (*c* 0.500, CH_2Cl_2, 98% ee); IR (thin film, KBr): 2958, 2874, 1720, 1646, 1614, 1234, 1096, 1029, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.59 (s, 1H), 9.71 (d, *J* = 2.0 Hz, 1H), 7.26 (m, 2H), 7.18 (m, 3H), 4.20 (d, *J* = 6.8 Hz, 1H), 3.95 (m, 2H), 2.93 (q, *J* = 7.7 Hz, 1H), 2.72 (m, 1H), 2.52 (m, 1H), 2.09 (m, 1H), 1.58-1.89 (m, 5H), 0.88 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 174.3, 172.2, 144.4, 128.5, 128.0, 126.4, 99.0, 60.5, 56.6, 43.4, 38.4, 36.7, 29.9, 26.5, 24.2, 13.8 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 99:1), 0.3 mL/min; minor enantiomer t_R = 24.0 min, major enantiomer t_R = 41.4 min. HRMS (ESI) : [M^+] calcd for [$C_{19}H_{22}O_4$]: 314.1518, found: 314.1521.

20a: *(3aR,6S,7R,7aS)-ethyl 7-formyl-4-hydroxy-6-p-tolyl-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



colorless oil. $[\alpha]_D^{26}$ = +109.4 (*c* 1.00, CH_2Cl_2, 99% ee); IR (thin film, KBr): 2962, 2870, 1722, 1648, 1401, 1379, 1242, 1212, 1083, 1034, 821 cm^{-1}; NMR (400 MHz, $CDCl_3$) δ 12.51 (s, 1H), 9.31 (d, *J* = 3.0 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 2H), 6.95 (d, *J* = 7.8 Hz, 2H), 4.30 (d, *J* = 4.8 Hz, 1H), 4.10 (m, 1H), 3.99 (m, 1H), 2.94 (q, *J* = 8.6 Hz, 1H), 2.65 (m, 1H), 2.44 (m, 1H), 2.29 (s, 3H), 2.29 (m, 1H), 1.99 (m, 1H), 1.77 (m, 1H), 1.60 (m, 2H), 1.27 (m, 1H), 1.09 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 175.2, 171.8, 136.7, 136.6, 129.1, 128.8, 100.1, 60.7, 54.9, 43.2, 41.2, 32.5, 31.6, 31.4, 25.1, 21.1, 14.1 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 99:1), 0.5 mL/min; major enantiomer t_R = 13.0 min, minor enantiomer t_R = 15.1 min. HRMS (ESI) : [M^-] calcd for [$C_{20}H_{24}O_4$]: 328.1675, found: 328.1676.

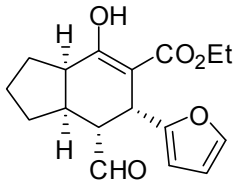
20b: *(3aR,6S,7S,7aS)-ethyl 7-formyl-4-hydroxy-6-p-tolyl-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



colorless oil. $[\alpha]_D^{24}$ = +26.3 (*c* 0.800, CH_2Cl_2, 99% ee); IR (thin film, KBr): 2958, 2875, 1721, 1646, 1613, 1307, 1272, 1233, 812 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 12.58 (s, 1H), 9.71 (d, *J* = 2.2 Hz, 1H), 7.06 (m, 4H), 4.17 (d, *J* = 6.2 Hz, 1H), 3.97 (m, 2H), 2.91 (q, *J* = 7.3 Hz, 1H), 2.68 (m, 1H), 2.51 (m, 1H), 2.30 (s, 3H), 2.10 (m, 1H), 1.58-1.85 (m, 5H), 0.93 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.9, 175.2, 171.8, 136.7, 136.6, 129.1, 128.8, 100.1, 60.7, 54.9, 43.2, 41.2, 32.5, 31.6, 31.4, 25.1, 21.1, 14.1 ppm; the enantiomeric excess was determined by

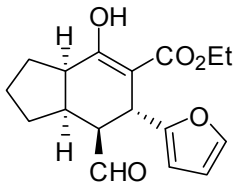
HPLC with an AS-H column (*n*-hexane: *i*-PrOH = 99:1), 0.5 mL/min; major enantiomer t_R = 15.7 min, minor enantiomer t_R = 16.9 min. HRMS (ESI) : [M$^-$] calcd for [$C_{20}H_{24}O_4$]: 328.1675, found: 328.1681.

21a: *(3aR,6R,7R,7aS)-ethyl 7-formyl-6-(furan-2-yl)-4-hydroxy-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



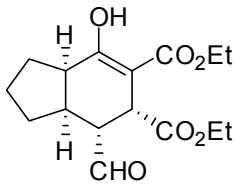
colorless oil. $[\alpha]_D^{23}$ = +58.9 (*c* 1.00, CH_2Cl_2, 98% ee); IR (thin film, KBr): 2963, 2870, 1724, 1648, 1288, 1242, 1081, 834, 741, 599 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 9.58 (d, *J* = 2.4 Hz, 1H), 7.27 (dd, *J* = 1.8, 0.8 Hz, 1H), 6.24 (dd, *J* = 3.2, 1.9 Hz, 1H), 5.95 (dd, *J* = 2.5, 0.7 Hz, 1H), 4.41 (d, *J* = 4.3 Hz, 1H), 4.16 (m, 2H), 2.86 (q, *J* = 8.9 Hz, 1H), 2.61 (m, 1H), 2.39 (m, 1H), 2.23 (m, 1H), 2.06 (m, 1H), 1.75 (m, 1H), 1.57 (m, 2H), 1.33 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.3, 176.2, 171.6, 154.3, 141.9, 110.3, 107.7, 97.8, 60.8, 54.9, 42.8, 34.8, 33.5, 31.8, 31.0, 25.3, 14.2 ppm; the enantiomeric excess was determined by HPLC with an AS-H column (*n*-hexane: *i*-PrOH = 99:1), 0.5 mL/min; major enantiomer t_R = 23.6 min, minor enantiomer t_R = 27.2 min. HRMS (ESI) : [M$^-$] calcd for [$C_{17}H_{20}O_5$]: 304.1311, found: 304.1316.

21b: *(3aR,6R,7S,7aS)-ethyl 7-formyl-6-(furan-2-yl)-4-hydroxy-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



colorless oil. $[\alpha]_D^{22}$ = -12.3 (*c* 1.00, CH_2Cl_2, 98% ee); IR (thin film, KBr): 2961, 2876, 1720, 1647, 1276, 1222, 1086, 1011, 837, 736, 599 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.61 (s, 1H), 9.75 (d, *J* = 1.8 Hz, 1H), 7.29 (d, *J* = 1.0 Hz, 1H), 6.26 (dd, *J* = 3.1, 1.8 Hz, 1H), 5.97 (d, *J* = 3.2 Hz, 1H), 4.32 (d, *J* = 5.4 Hz, 1H), 4.11 (m, 2H), 2.88 (td, *J* = 5.4, 2.1 Hz, 1H), 2.83 (q, *J* = 8.0 Hz, 1H), 2.57 (m, 1H), 2.12 (m, 1H), 1.86 (m, 1H), 1.59-1.77 (m, 4H), 1.12 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.0, 175.0, 172.1, 156.4, 141.3, 110.4, 106.5, 96.6, 60.7, 53.4, 43.1, 36.7, 32.9, 30.2, 27.1, 24.5, 14.1 ppm; the enantiomeric excess was determined by HPLC with an AS-H column (*n*-hexane: *i*-PrOH = 99:1), 0.5 mL/min; major enantiomer t_R = 21.5 min, minor enantiomer t_R = 27.6 min. HRMS (ESI) : [M$^-$] calcd for [$C_{17}H_{20}O_5$]: 304.1311, found: 304.1316.

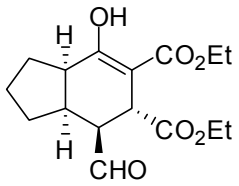
22a: *(3aS,4R,5R,7aR)-diethyl 4-formyl-7-hydroxy-2,3,3a,4,5,7a-hexahydro-1H-indene-5,6-dicarboxylate*



colorless oil. $[\alpha]_D^{24}$ = +30.2 (*c* 1.00, CH_2Cl_2, 98% ee); IR (thin film, KBr): 2979, 2872, 1728, 1652, 1618, 1243, 1189, 1095, 1035, 835 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.47 (s, 1H), 9.78 (d, *J* = 1.5 Hz, 1H), 4.23 (m, 2H), 4.10 (m, 2H), 4.04 (d, *J* = 4.6 Hz, 1H), 2.83 (q, *J* = 9.4 Hz, 1H), 2.68 (m, 1H), 2.36 (m, 1H), 2.18 (m, 2H), 1.75 (m, 1H), 1.58 (m, 2H), 1.37 (m, 1H), 1.29 (t, *J* = 7.1 Hz,

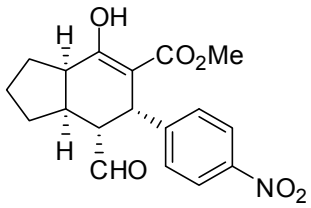
3H), 1.21 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 176.6, 172.0, 171.4, 96.0, 61.3, 60.9, 52.7, 42.8, 41.3, 34.1, 32.4, 30.8, 25.3, 14.4, 14.3 ppm; the enantiomeric excess was determined by HPLC with an AS-H column (*n*-hexane: *i*-PrOH = 99:1), 1.0 mL/min; major enantiomer t_R = 15.1 min, minor enantiomer t_R = 26.4 min. HRMS (ESI) : [M^+] calcd for [$C_{16}H_{22}O_6$]: 310.1416, found: 310.1416.

22b: *(3aS,4S,5R,7aR)-diethyl 4-formyl-7-hydroxy-2,3,3a,4,5,7a-hexahydro-1H-indene-5,6-dicarboxylate*



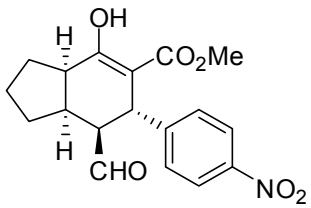
colorless oil. $[\alpha]_D^{24}$ = -18.8 (*c* 1.00, CH_2Cl_2, 98% ee); IR (thin film, KBr): 2979, 1728, 1654, 1616, 1234, 1183, 1033 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.55 (s, 1H), 9.76 (d, *J* = 2.2 Hz, 1H), 4.10-4.27 (m, 4H), 3.82 (dd, *J* = 8.9, 1.5 Hz, 1H), 2.87 (m, 2H), 2.56 (m, 1H), 1.98 (m, 1H), 1.86 (m, 1H), 1.79 (m, 1H), 1.65 (m, 2H), 1.49 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 174.8, 174.1, 171.7, 95.2, 61.2, 61.0, 51.1, 43.1, 38.8, 38.0, 29.1, 25.7, 24.0, 14.3, 14.2 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 99:1), 1.0 mL/min; minor enantiomer t_R = 29.2 min, major enantiomer t_R = 39.5 min. HRMS (ESI) : [M^+] calcd for [$C_{16}H_{22}O_6$]: 310.1416, found: 310.1422.

23a: *(3aR,6S,7R,7aS)-methyl 7-formyl-4-hydroxy-6-(4-nitrophenyl)-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



white powder. m.p.: 104-107 °C. $[\alpha]_D^{23}$ = +194.4 (*c* 1.00, CH_2Cl_2, 97% ee); IR (thin film, KBr): 2955, 2870, 1722, 1653, 1614, 1520, 1442, 1349, 1246, 856, 824, 736, 707 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.50 (s, 1H), 9.39 (d, *J* = 1.3 Hz, 1H), 8.13 (d, *J* = 8.6 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 4.45 (d, *J* = 3.8 Hz, 1H), 3.60 (s, 3H), 2.98 (m, 1H), 2.57 (m, 2H), 2.33 (m, 1H), 2.05 (m, 1H), 1.80 (m, 1H), 1.63 (m, 2H), 1.32 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.1, 176.3, 171.7, 147.5, 147.3, 129.8, 123.7, 99.0, 54.7, 52.0, 43.2, 41.3, 32.4, 31.7, 31.3, 25.1 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 95:5), 1.0 mL/min; major enantiomer t_R = 18.4 min, minor enantiomer t_R = 27.4 min. HRMS (ESI) : [M^+] calcd for [$C_{18}H_{19}NO_6$]: 345.1212, found: 345.1218.

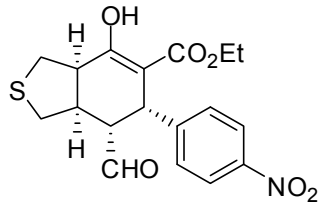
23b: *(3aR,6S,7S,7aS)-methyl 7-formyl-4-hydroxy-6-(4-nitrophenyl)-2,3,3a,6,7,7a-hexahydro-1H-indene-5-carboxylate*



colorless amorphous solid. $[\alpha]_D^{24}$ = +73.8 (*c* 0.500, CH_2Cl_2, 98% ee); IR (thin film, KBr): 2955, 1721, 1652, 1519, 1441, 1348, 1237, 1109, 832 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.58 (s, 1H),

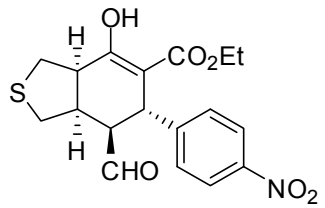
9.68 (d, *J* = 1.6 Hz, 1H), 8.14 (d, *J* = 8.8 Hz, 2H), 7.36 (d, *J* = 8.8 Hz, 2H), 4.36 (d, *J* = 6.6 Hz, 1H), 3.49 (s, 3H), 2.97 (q, *J* = 7.4 Hz, 1H), 2.74 (m, 1H), 2.54 (m, 1H), 2.12 (m, 1H), 1.87 (m, 1H), 1.58-1.76 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 175.1, 172.1, 152.5, 146.8, 128.8, 123.8, 97.9, 56.4, 51.7, 43.4, 37.9, 36.5, 29.8, 26.5, 24.0 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 99:1), 1.0 mL/min; major enantiomer t_R = 46.6 min, minor enantiomer t_R = 52.3 min. HRMS (ESI) : [M^+] calcd for [$C_{18}H_{19}NO_6$]: 345.1212, found: 345.1216.

24a: *(3aR,6S,7S,7aR)-ethyl 7-formyl-4-hydroxy-6-(4-nitrophenyl)-1,3,3a,6,7,7a-hexahydrobenzo[c]thiophene-5-carboxylate*



yellow crystals. m.p.: 180-183 °C. $[\alpha]_D^{22}$ = +86.7 (*c* 1.00, CH_2Cl_2, 98% ee); IR (thin film, KBr): 2927, 1654, 1519, 1350, 1248, 1225, 857, 707 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.54 (s, 1H), 9.48 (d, *J* = 0.8 Hz, 1H), 8.15 (d, *J* = 8.4 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 4.53 (m, 1H), 4.04 (m, 2H), 3.45 (dd, *J* = 11.3, 8.6 Hz, 1H), 3.24 (m, 2H), 3.00 (d, *J* = 1.5 Hz, 2H), 2.91 (dd, *J* = 11.3, 9.7 Hz, 1H), 2.71 (d, *J* = 12.1 Hz, 1H), 1.03 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.5, 173.0, 171.0, 147.4, 147.2, 129.8, 123.8, 98.8, 61.2, 50.8, 46.4, 40.9, 36.7, 36.2, 35.6, 14.0 ppm; the enantiomeric excess was determined by HPLC with an AS-H column (*n*-hexane: *i*-PrOH = 90:10), 1.0 mL/min; major enantiomer t_R = 22.7 min, minor enantiomer t_R = 35.7 min. HRMS (ESI) : [M^-] calcd for [$C_{18}H_{19}NO_6S$]: 377.0933, found: 377.0938.

24b: *(3aR,6S,7R,7aR)-ethyl 7-formyl-4-hydroxy-6-(4-nitrophenyl)-1,3,3a,6,7,7a-hexahydrobenzo[c]thiophene-5-carboxylate*



colorless crystals. m.p.: 101-104 °C. $[\alpha]_D^{23}$ = +46.8 (*c* 1.00, CH_2Cl_2, 96% ee); IR (thin film, KBr): 2937, 1721, 1651, 1518, 1348, 1237, 848, 736 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.76 (s, 1H), 9.79 (d, *J* = 0.9 Hz, 1H), 8.14 (d, *J* = 8.6 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 4.45 (d, *J* = 7.0 Hz, 1H), 3.97 (m, 2H), 3.40 (q, *J* = 4.5 Hz, 1H), 3.21 (d, *J* = 5.9 Hz, 2H), 2.99 (m, 2H), 2.82-2.90 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.7, 171.4, 171.0, 152.5, 146.9, 128.8, 123.9, 98.8, 61.1, 55.9, 47.1, 40.4, 37.4, 32.9, 31.6, 13.8 ppm; the enantiomeric excess was determined by HPLC with an AD-H column (*n*-hexane: *i*-PrOH = 90:10), 1.0 mL/min; major enantiomer t_R = 20.2 min, minor enantiomer t_R = 25.2 min. HRMS (ESI) : [M^-] calcd for [$C_{18}H_{19}NO_6S$]: 377.0933, found: 377.0940.

References

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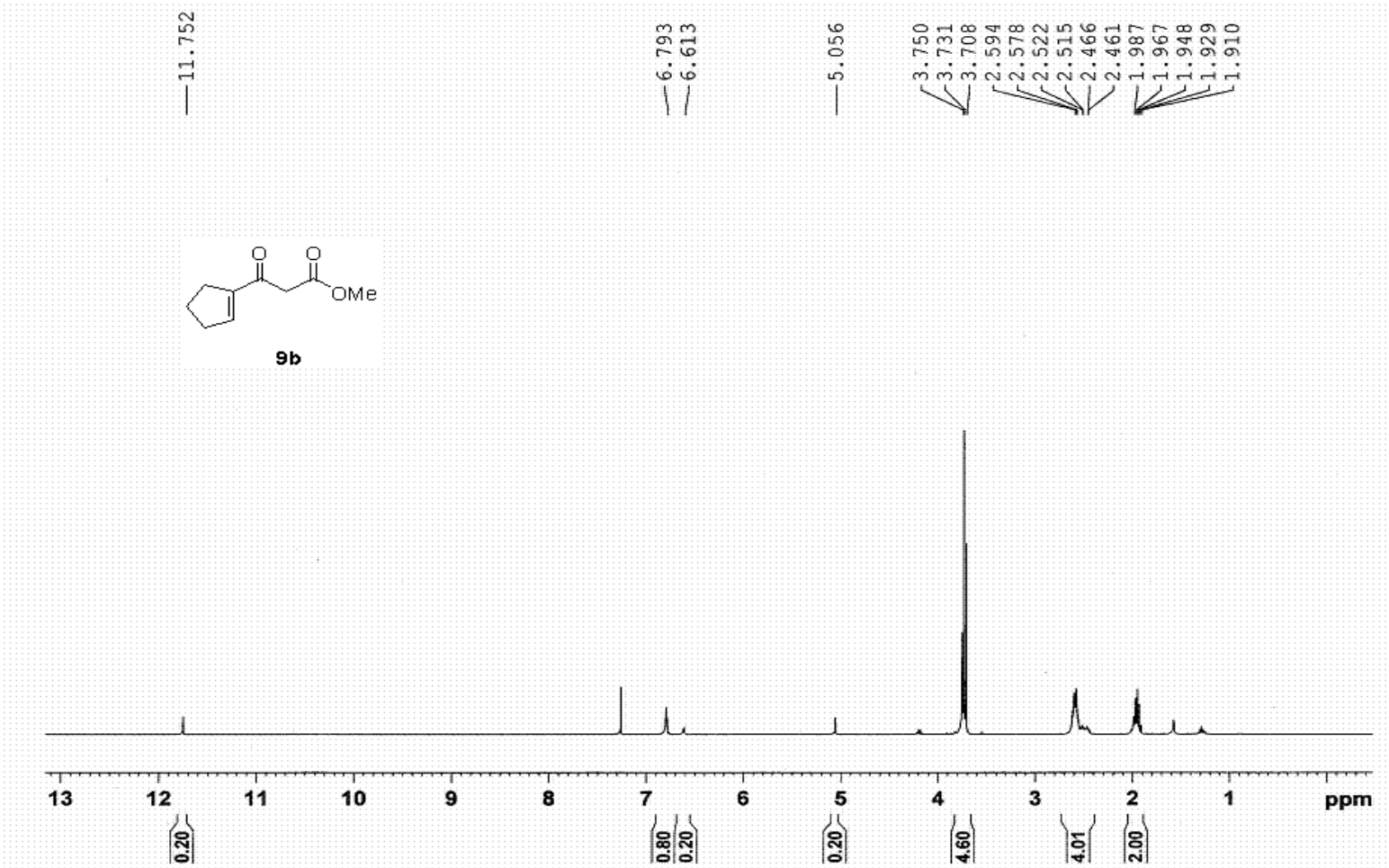
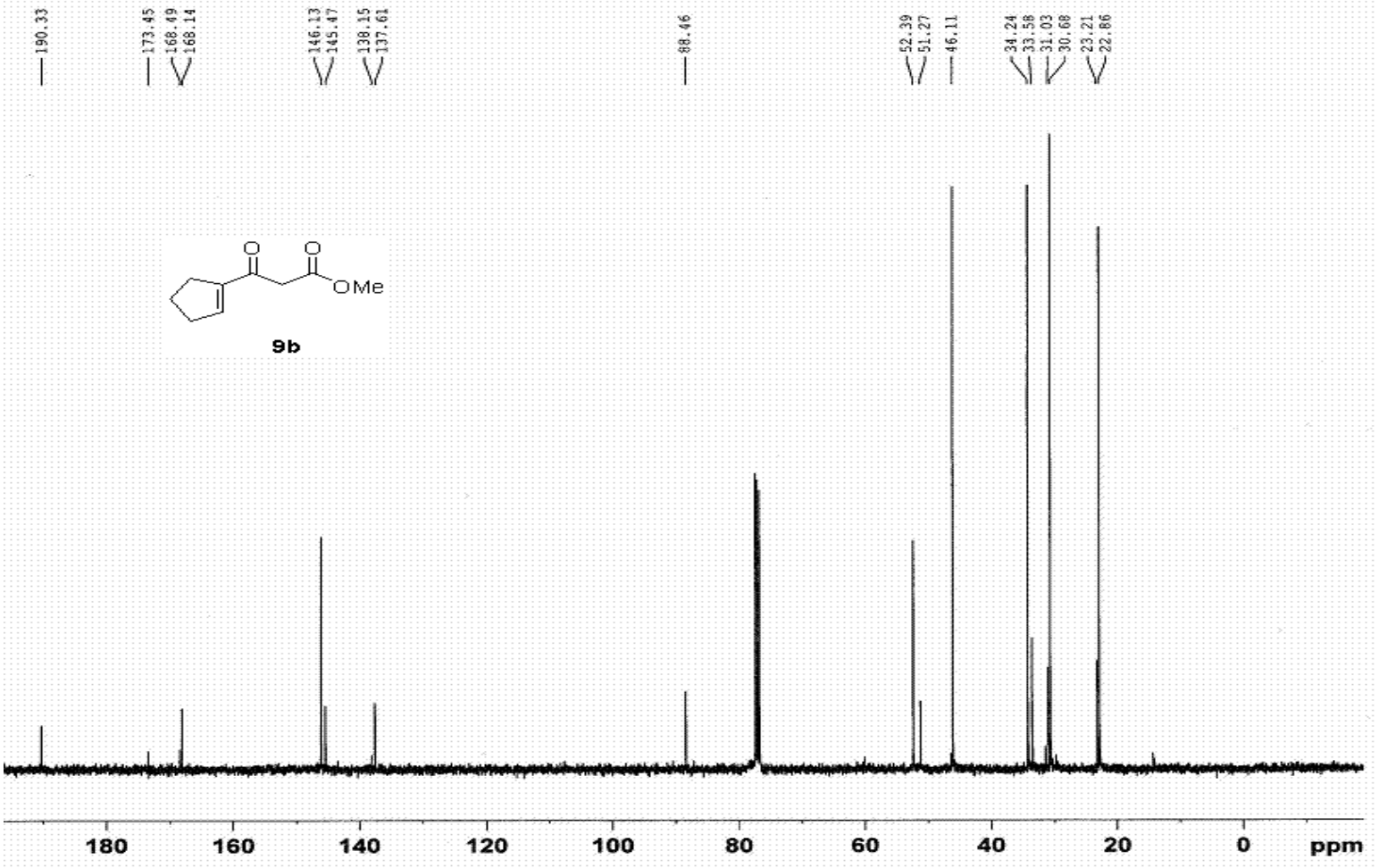
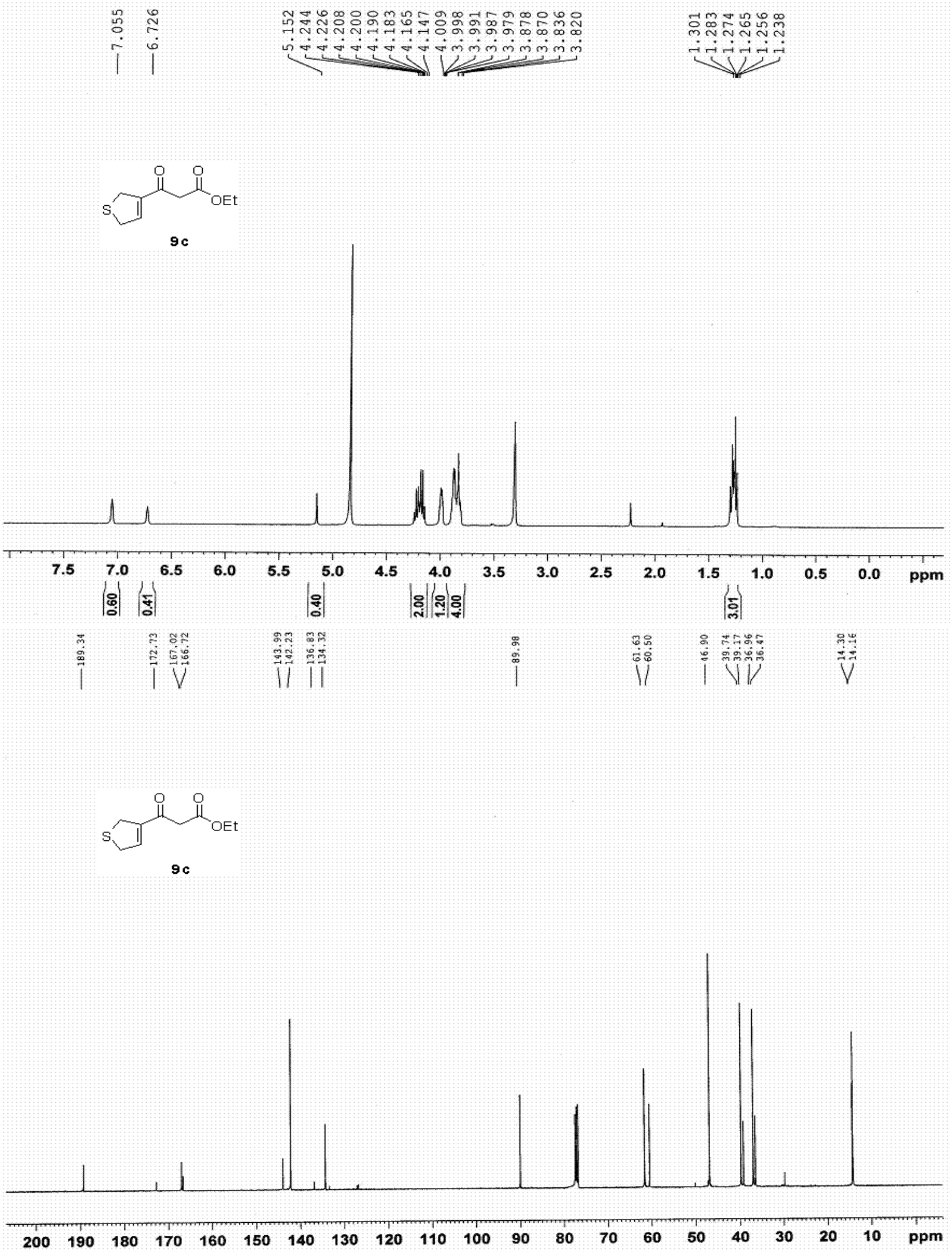
^{1}H, ^{13}C NMR spectra and HPLC chromatograms



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3.991
3.987
3.979
3.878
3.870
3.836
3.820
1.301
1.283
1.274
1.265
1.256
1.238
O
O
OEt
S
9c
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm
0.60
0.41
0.40
2.00
1.20
4.00
3.01
189.34
172.73
167.02
166.72
143.99
142.23
136.83
134.32
89.98
61.63
60.50
46.90
39.74
39.17
36.96
36.47
14.30
14.16
O
O
OEt
S
9c
200
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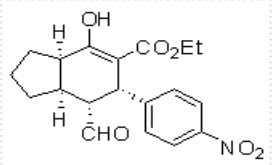
20
10
ppm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CO2Et
H
CHO
NO2

10a

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2.971
2.951
2.329
2.071
2.051
1.802
1.636
1.547
1.348
1.328
1.318
1.084
1.066
1.049
14
13
12
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4
3
2
1
ppm
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1.00
2.00
1.00
2.00
1.00
2.00
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3.00

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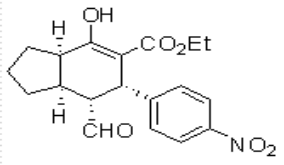
123.60
99.13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CHO
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10a

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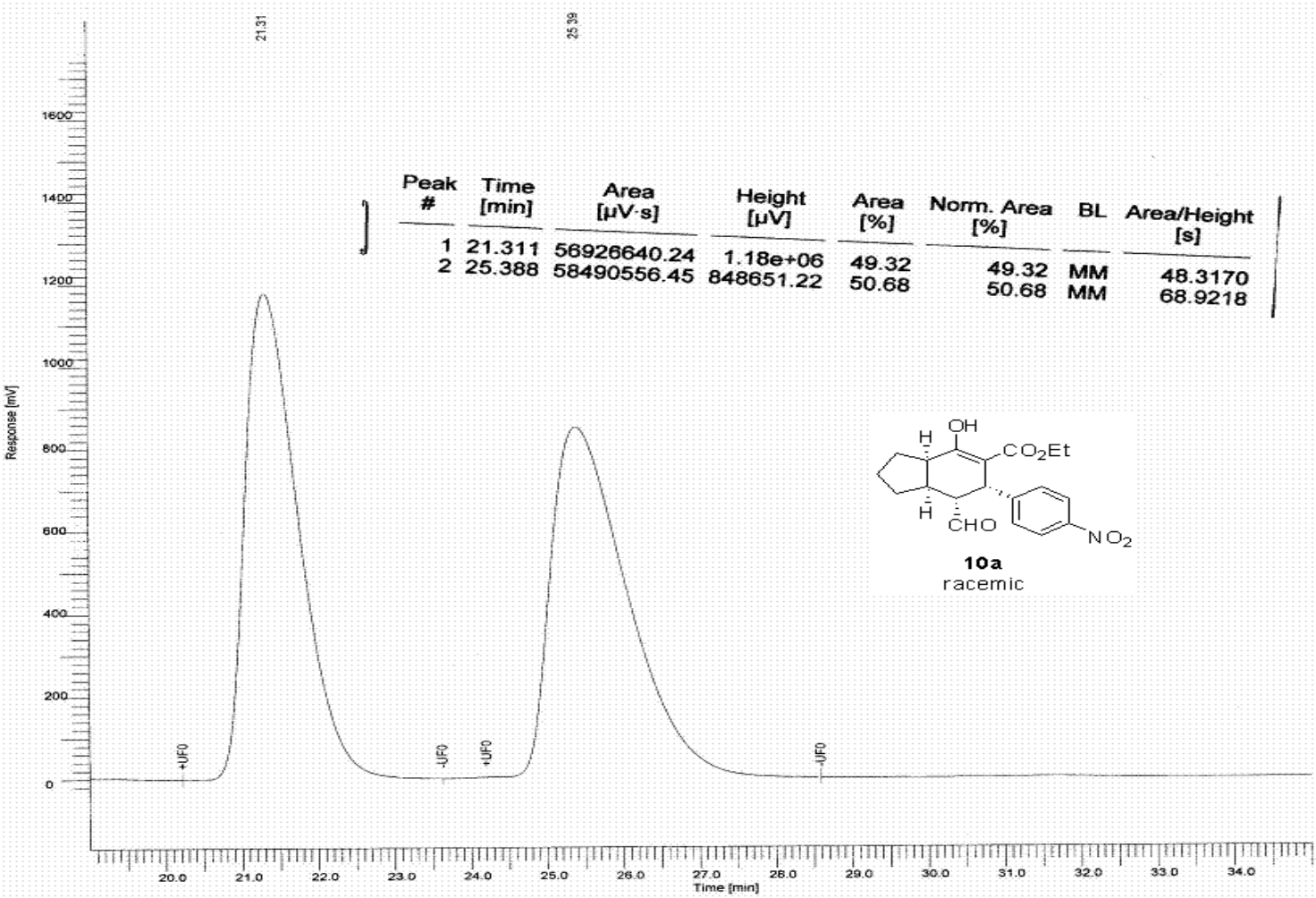
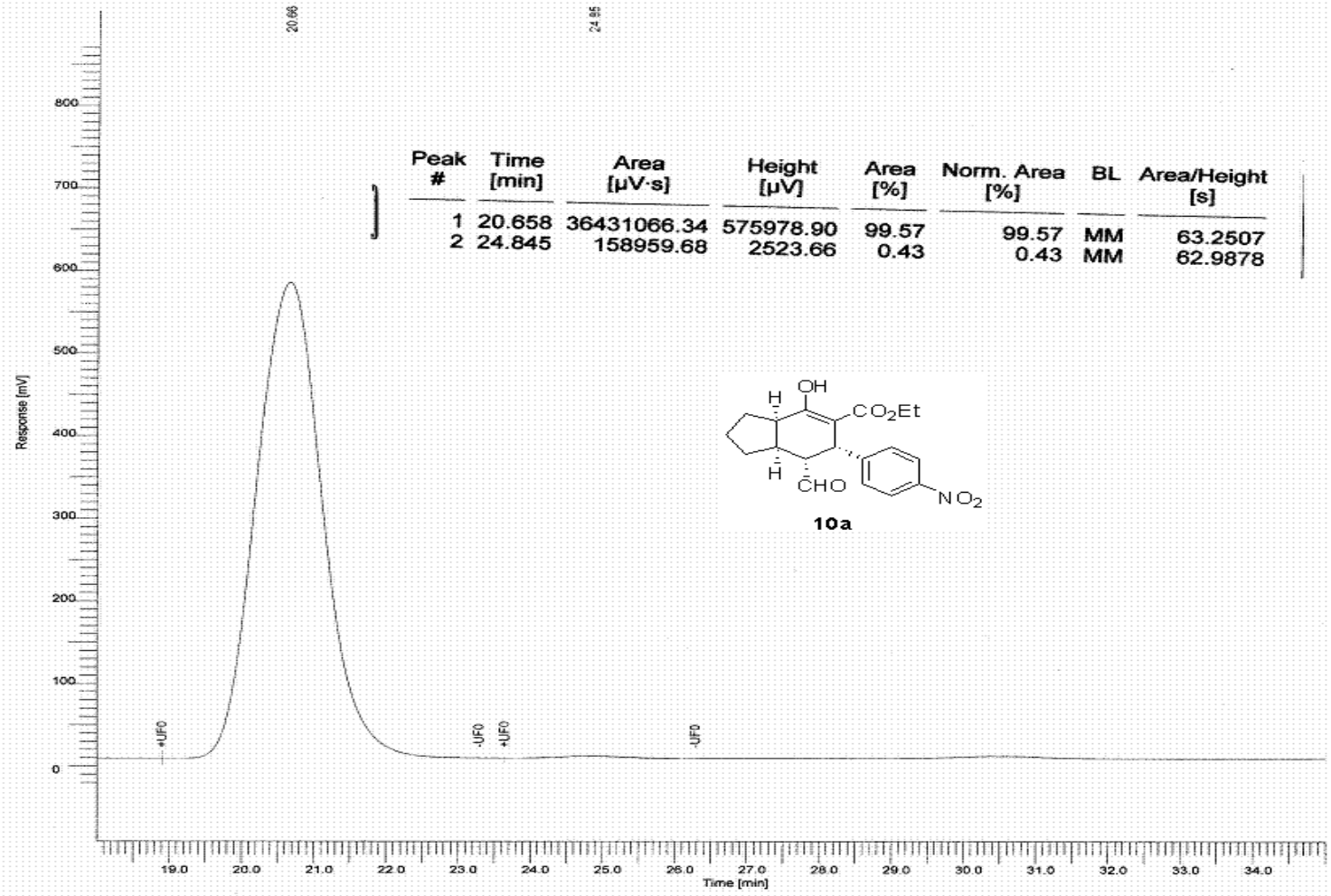
ppm



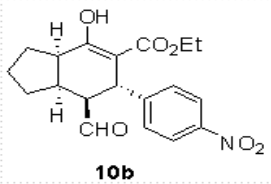
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	21.311	56926640.24	1.18e+06	49.32	49.32	MM	48.3170
2	25.388	58490556.45	848651.22	50.68	50.68	MM	68.9218

10a
racemic



Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	20.658	36431066.34	575978.90	99.57	99.57	MM	63.2507
2	24.845	158959.68	2523.66	0.43	0.43	MM	62.9878

10a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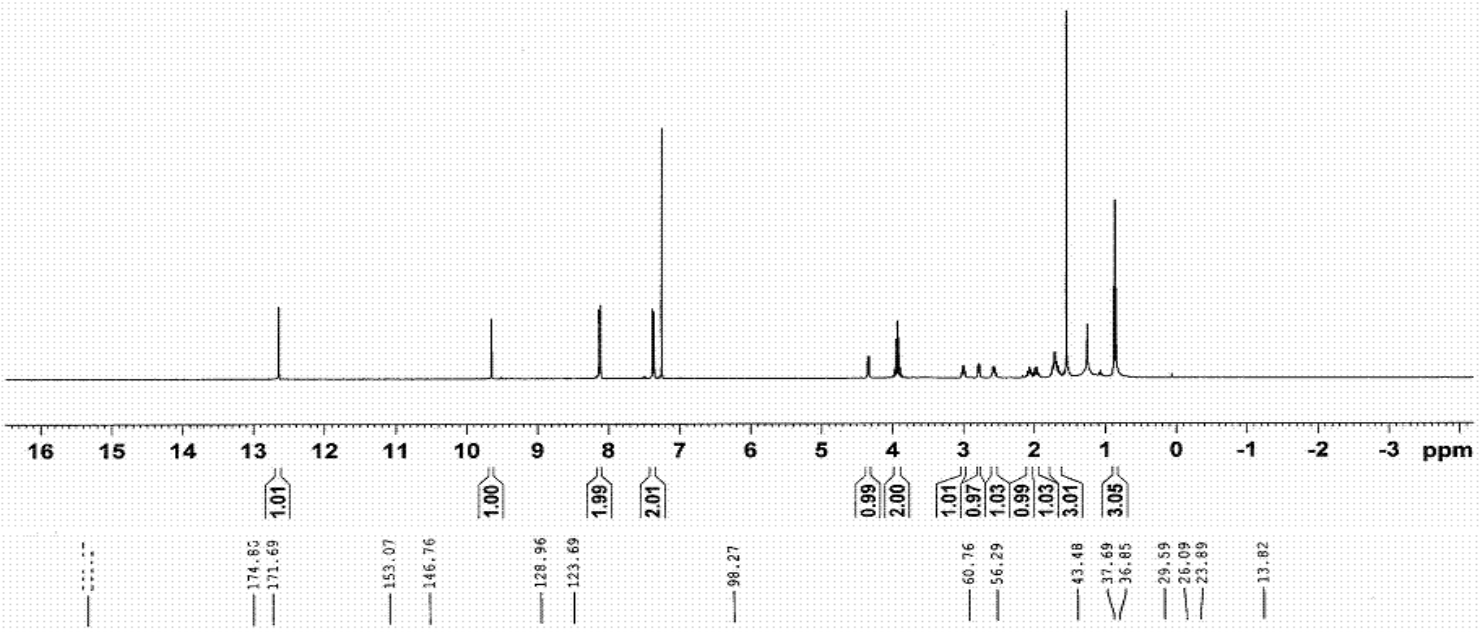
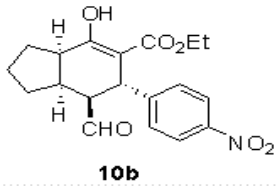
H
CHO
NO2

10b


16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
1.01 1.00 1.99 2.01 0.99 2.00 1.01 0.97 1.03 0.99 1.03 3.01 3.05

174.80
171.69
153.07
146.76
128.96
123.69
98.27
60.76
56.29
43.48
37.69
36.85
29.59
26.09
23.89
13.82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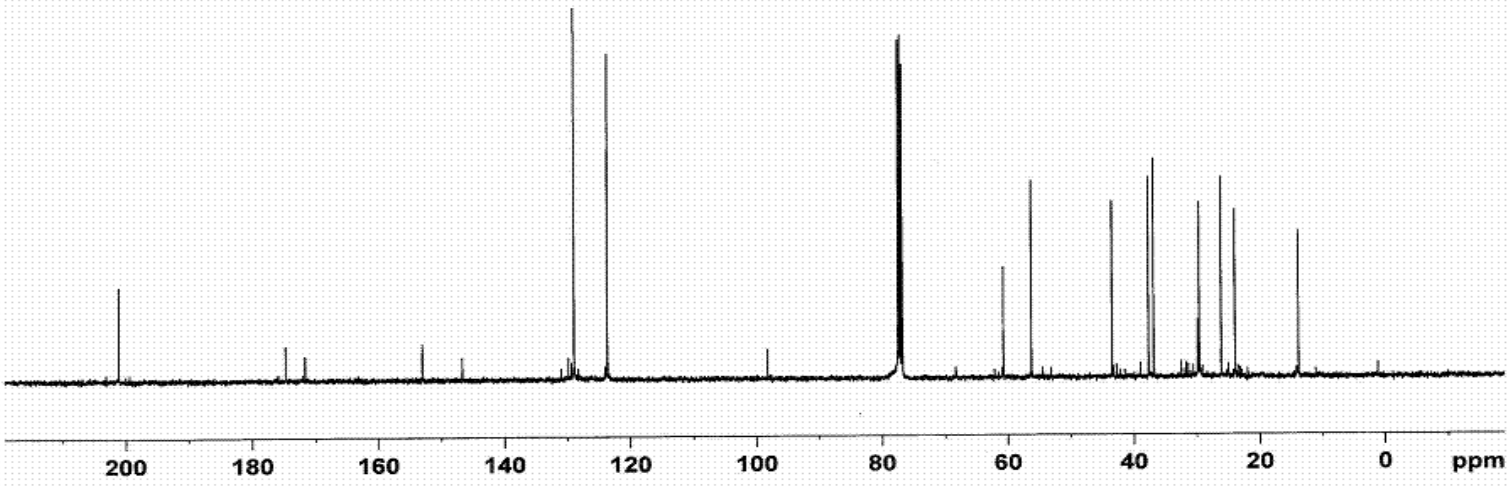
CHO
NO2

10b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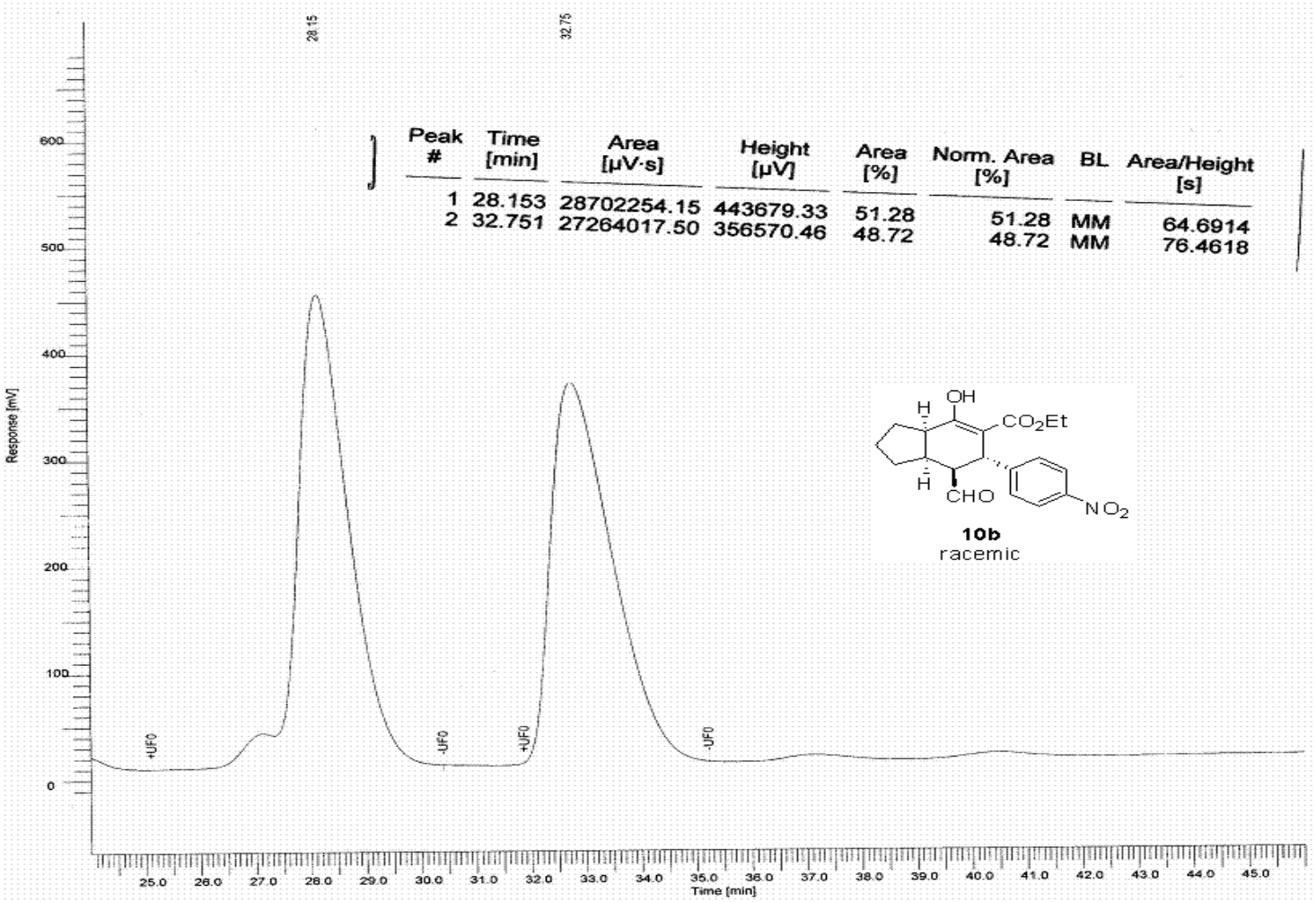
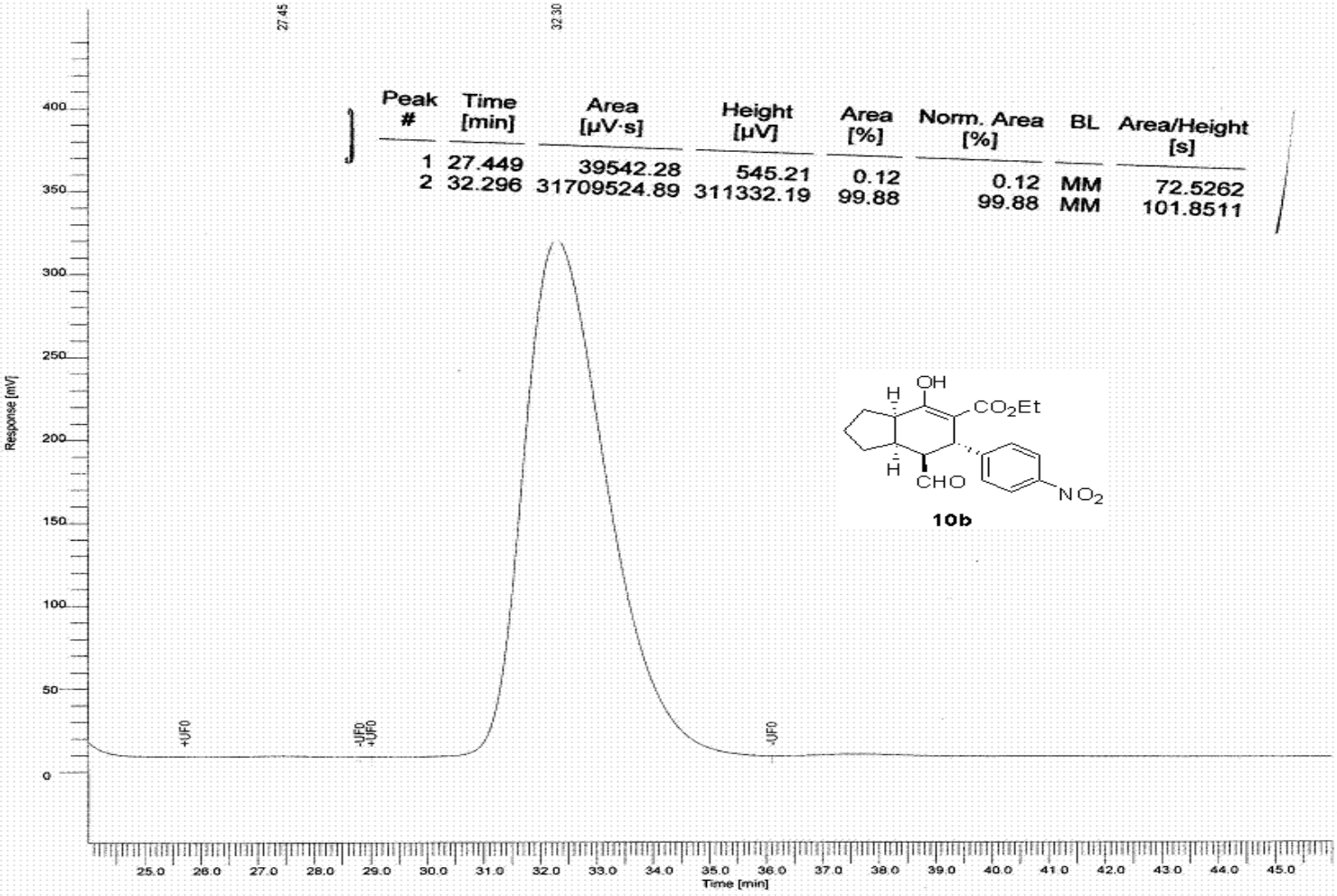


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	28.153	28702254.15	443679.33	51.28	51.28	MM	64.6914
2	32.751	27264017.50	356570.46	48.72	48.72	MM	76.4618

10b
racemic



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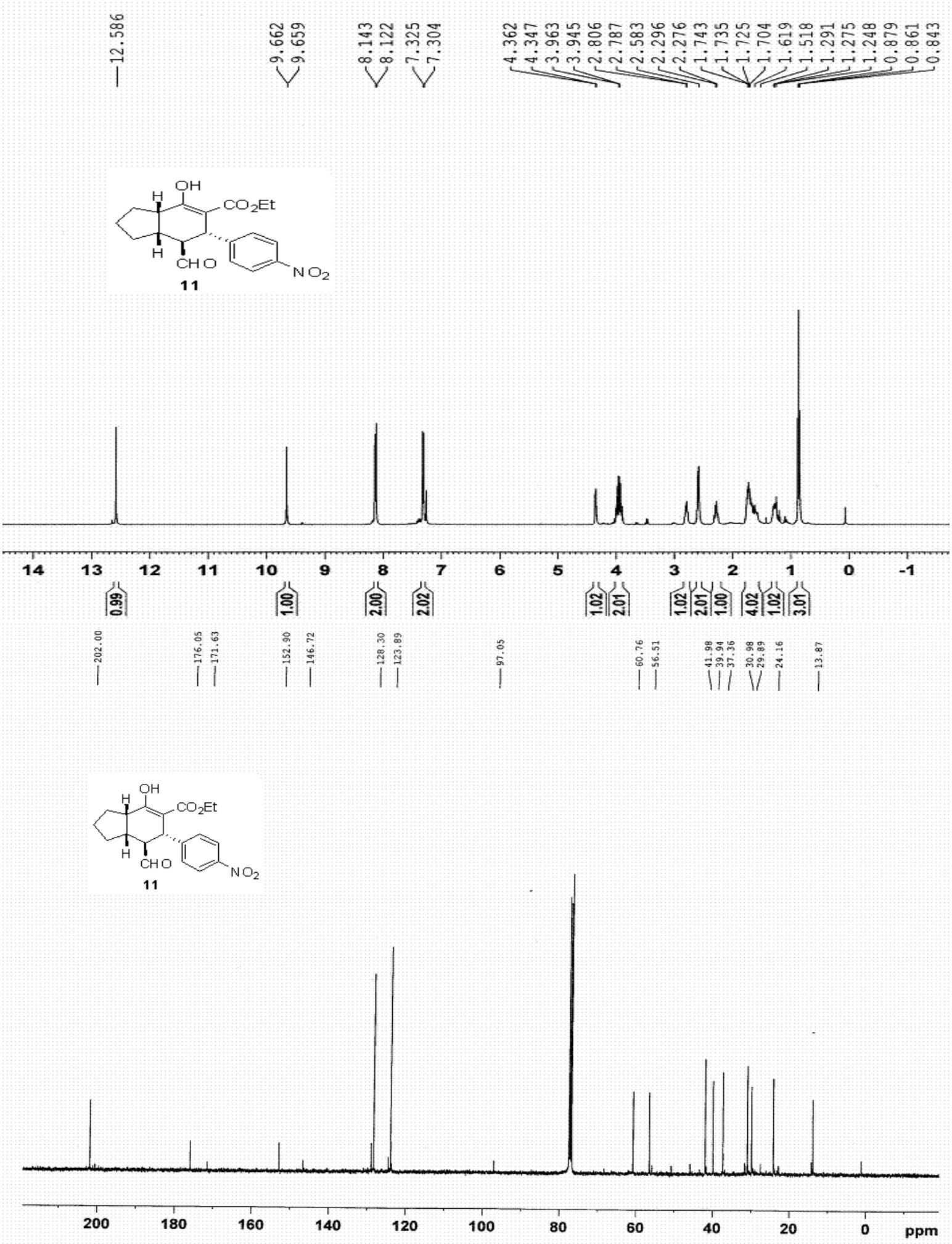
1	27.449	39542.28	545.21	0.12	0.12	MM	72.5262
2	32.296	31709524.89	311332.19	99.88	99.88	MM	101.8511

10b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2.296
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1.725
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1.619
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CO2Et
H
CHO
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12
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8
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CHO
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140
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100
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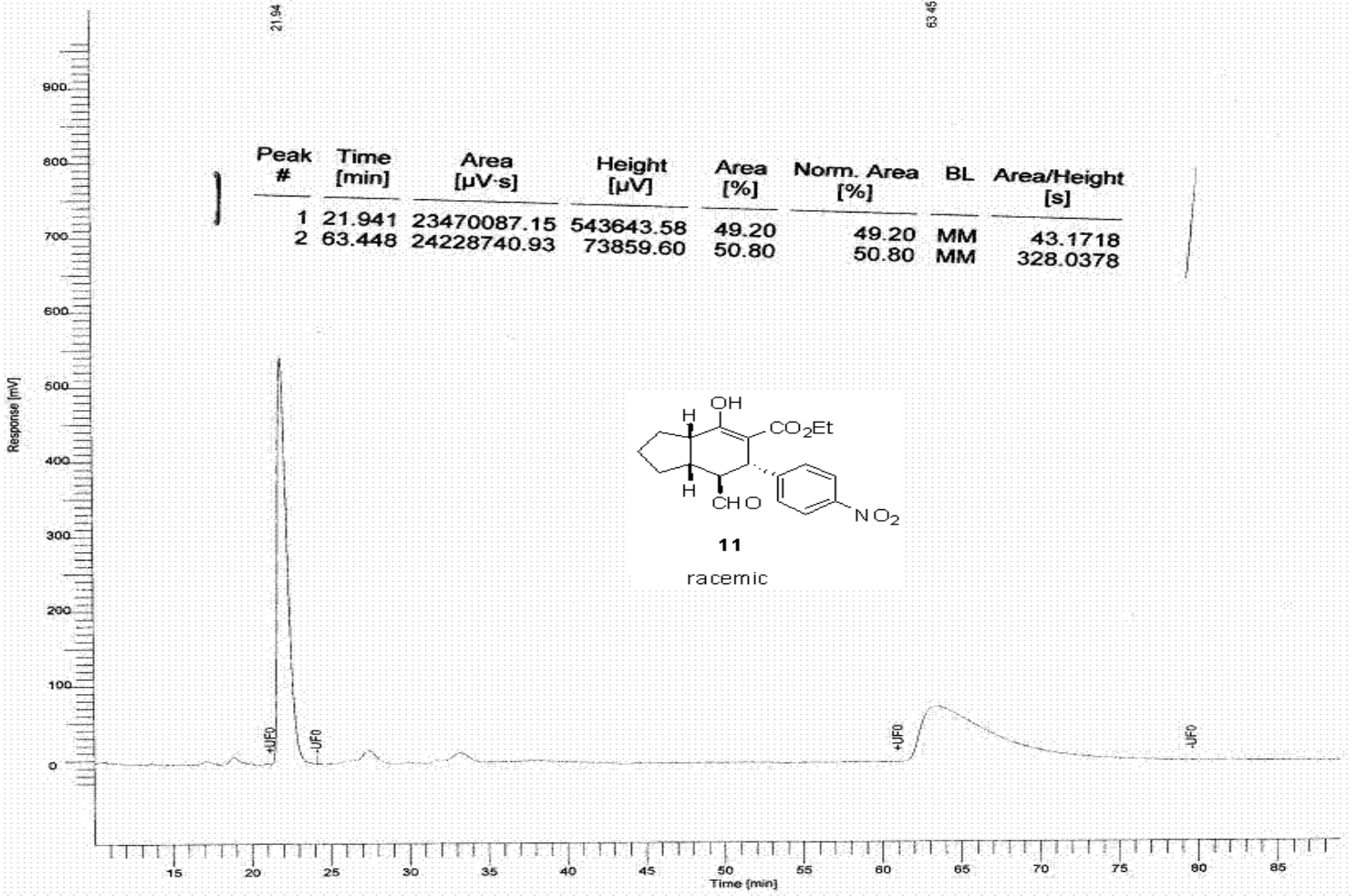
60
40
20
0
ppm

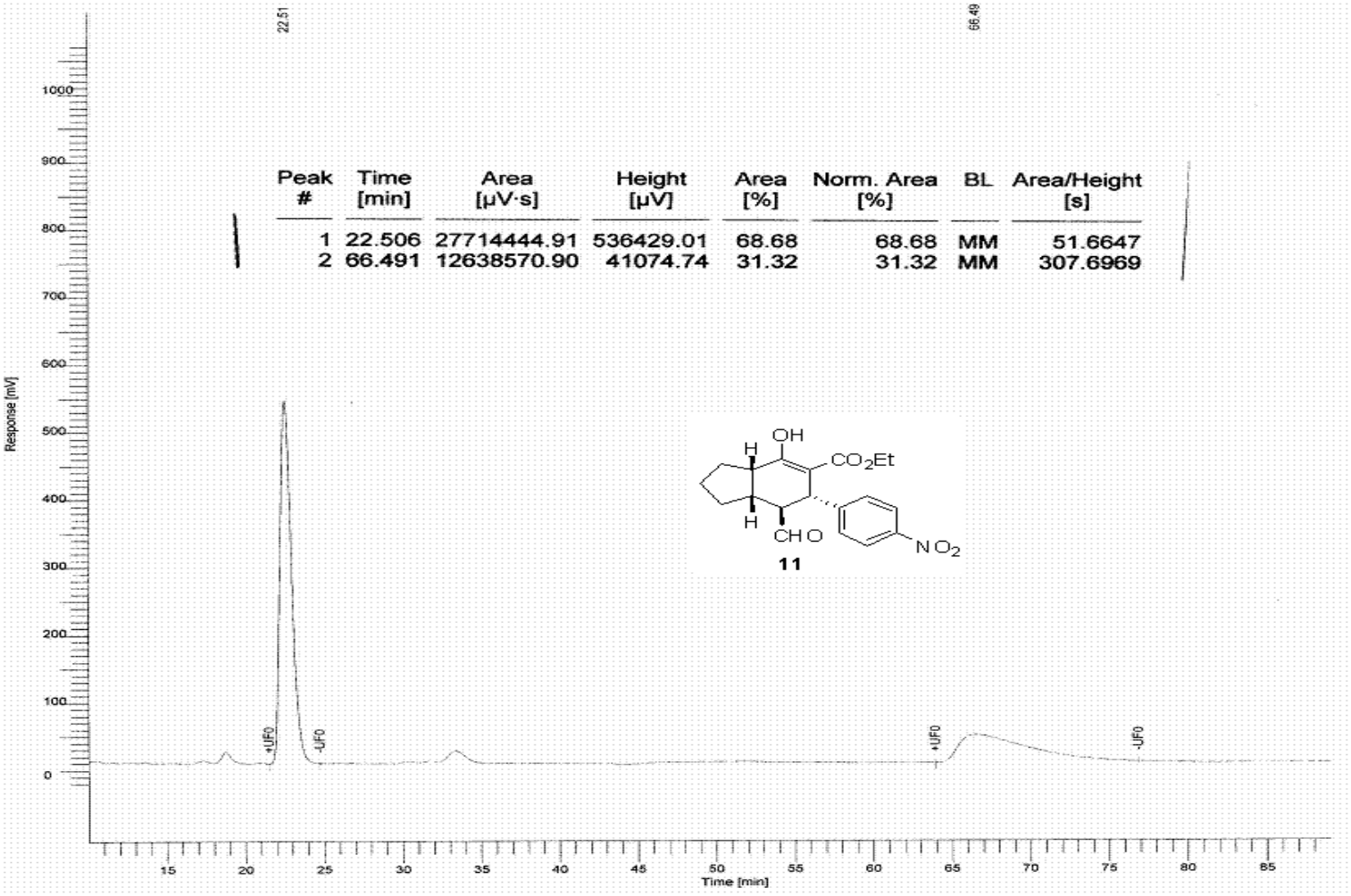
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	21.941	23470087.15	543643.58	49.20	49.20	MM	43.1718
2	63.448	24228740.93	73859.60	50.80	50.80	MM	328.0378



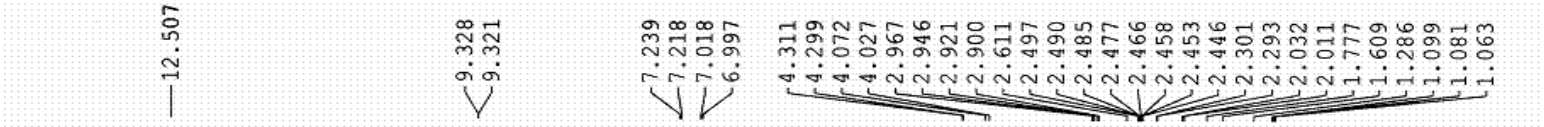
11

racemic

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	22.506	27714444.91	536429.01	68.68	68.68	MM	51.6647
2	66.491	12638570.90	41074.74	31.32	31.32	MM	307.6969



11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2.921
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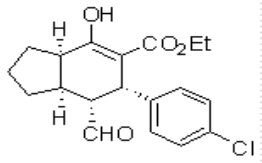
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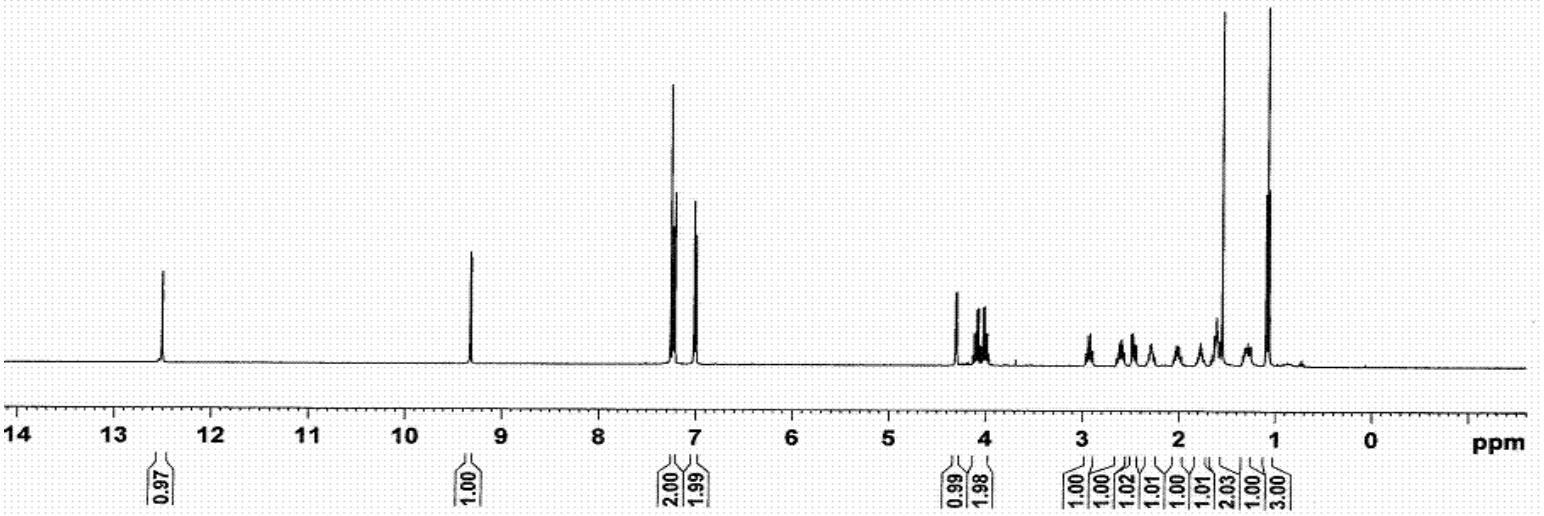
CHO
Cl

17a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3
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ppm
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2.00
1.99
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1.00
1.00
1.02
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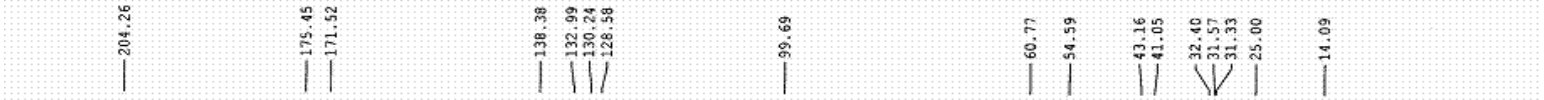
1.00
1.01
2.03
1.00
3.00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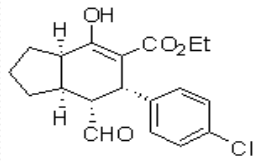
31.33
25.00
14.09


OH
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CO2Et
H
CHO
Cl

17a

200
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140
120
100
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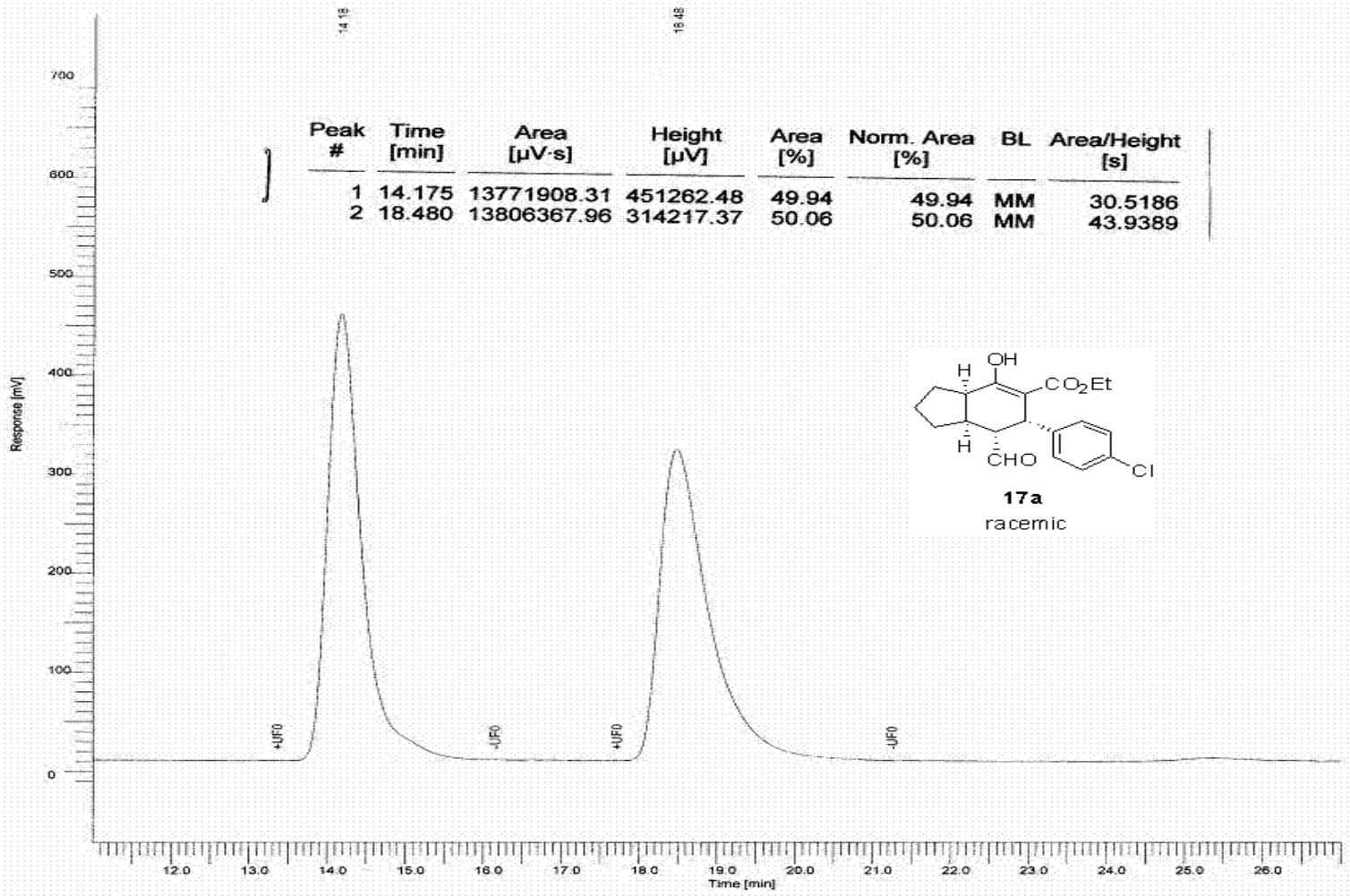
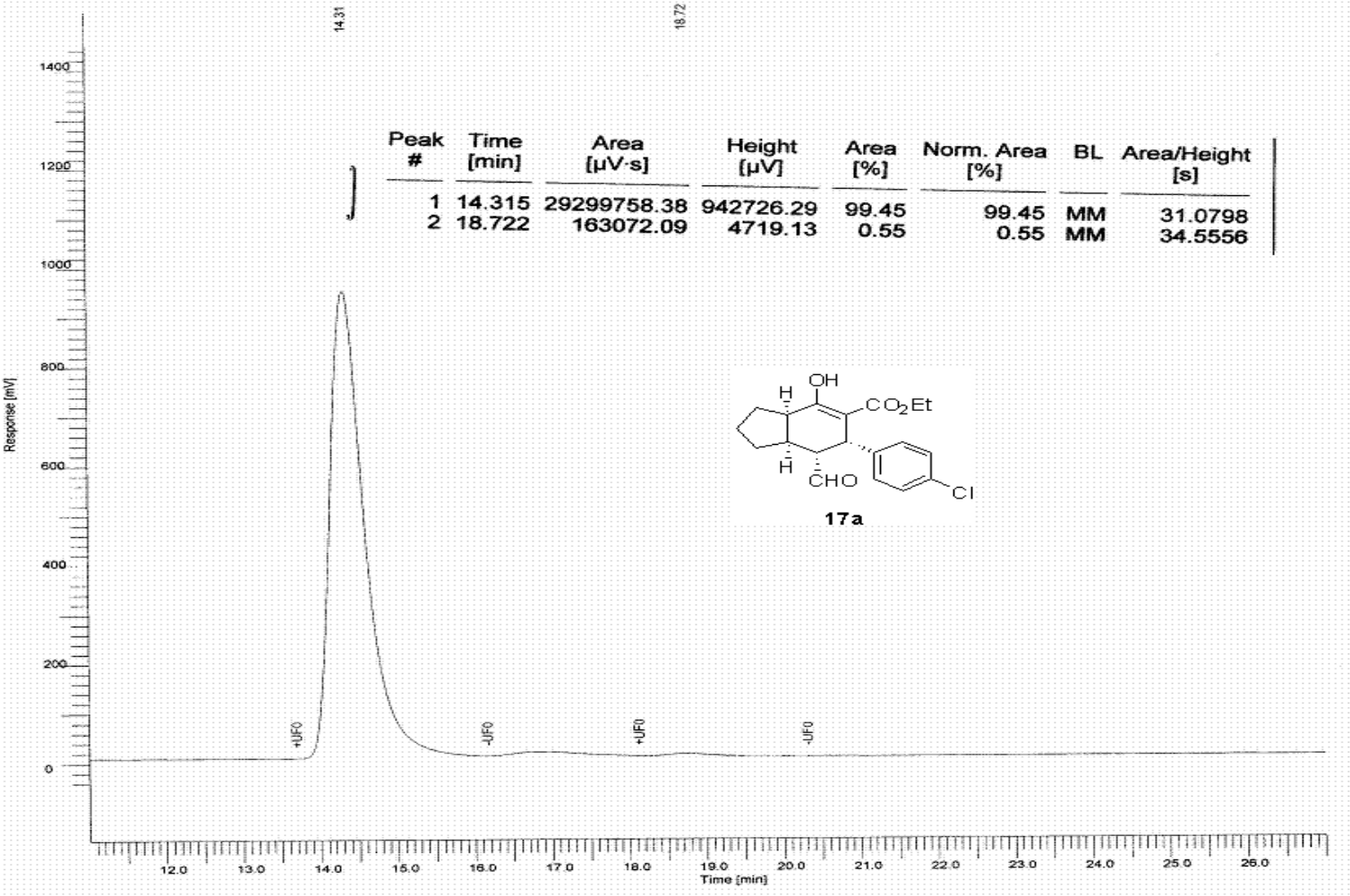
20
0
ppm



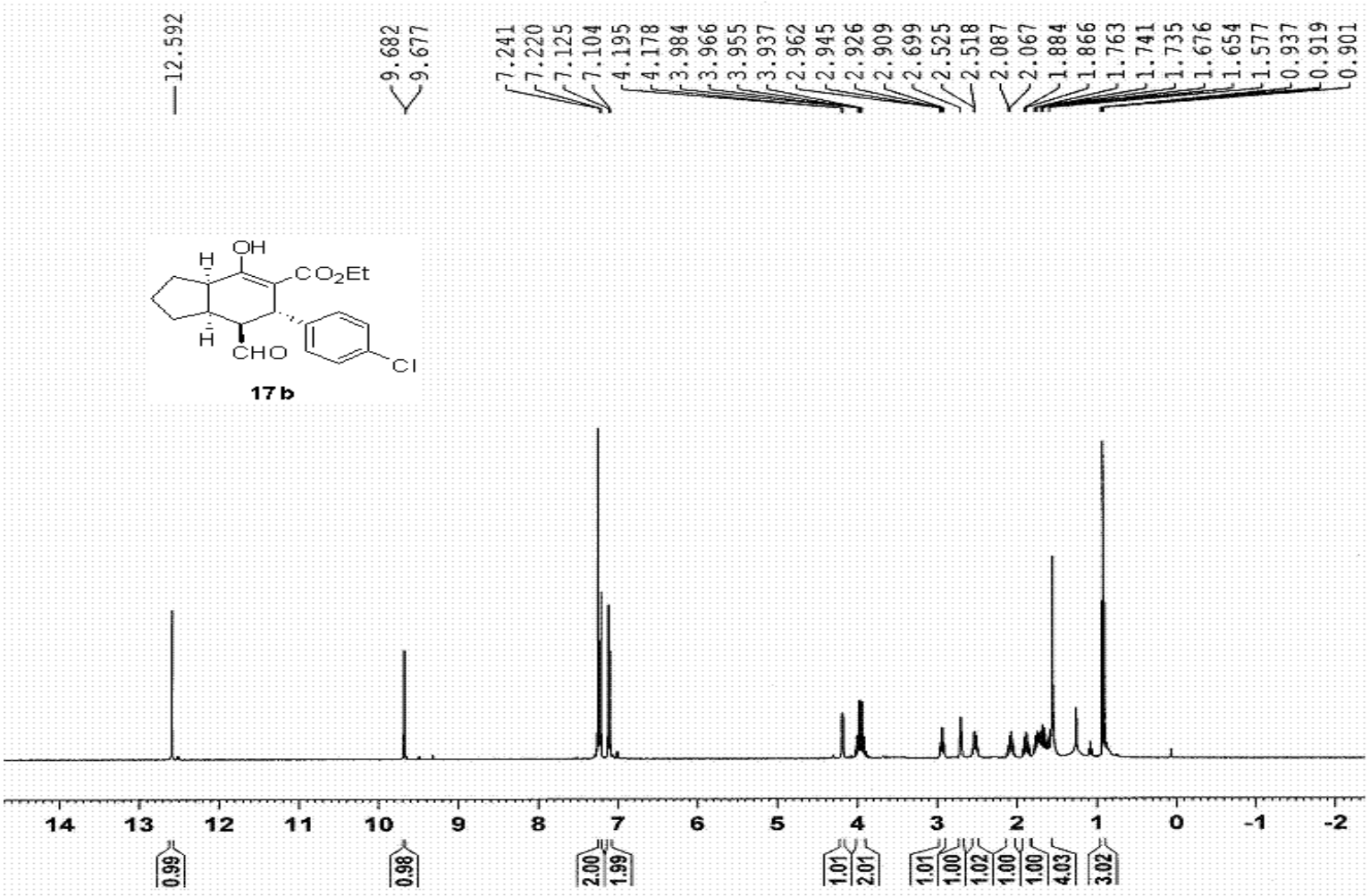
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	14.175	13771908.31	451262.48	49.94	49.94	MM	30.5186
2	18.480	13806367.96	314217.37	50.06	50.06	MM	43.9389

17a
racemic



Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	14.315	29299758.38	942726.29	99.45	99.45	MM	31.0798
2	18.722	163072.09	4719.13	0.55	0.55	MM	34.5556

17a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4.195
4.178
3.984
3.966
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2.926
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2.525
2.518
2.087
2.067
1.884
1.866
1.763
1.741
1.735
1.676
1.654
1.577
0.937
0.919
0.901
OH
CO2Et
H
H
CHO
Cl
17b
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
0.99
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1.02
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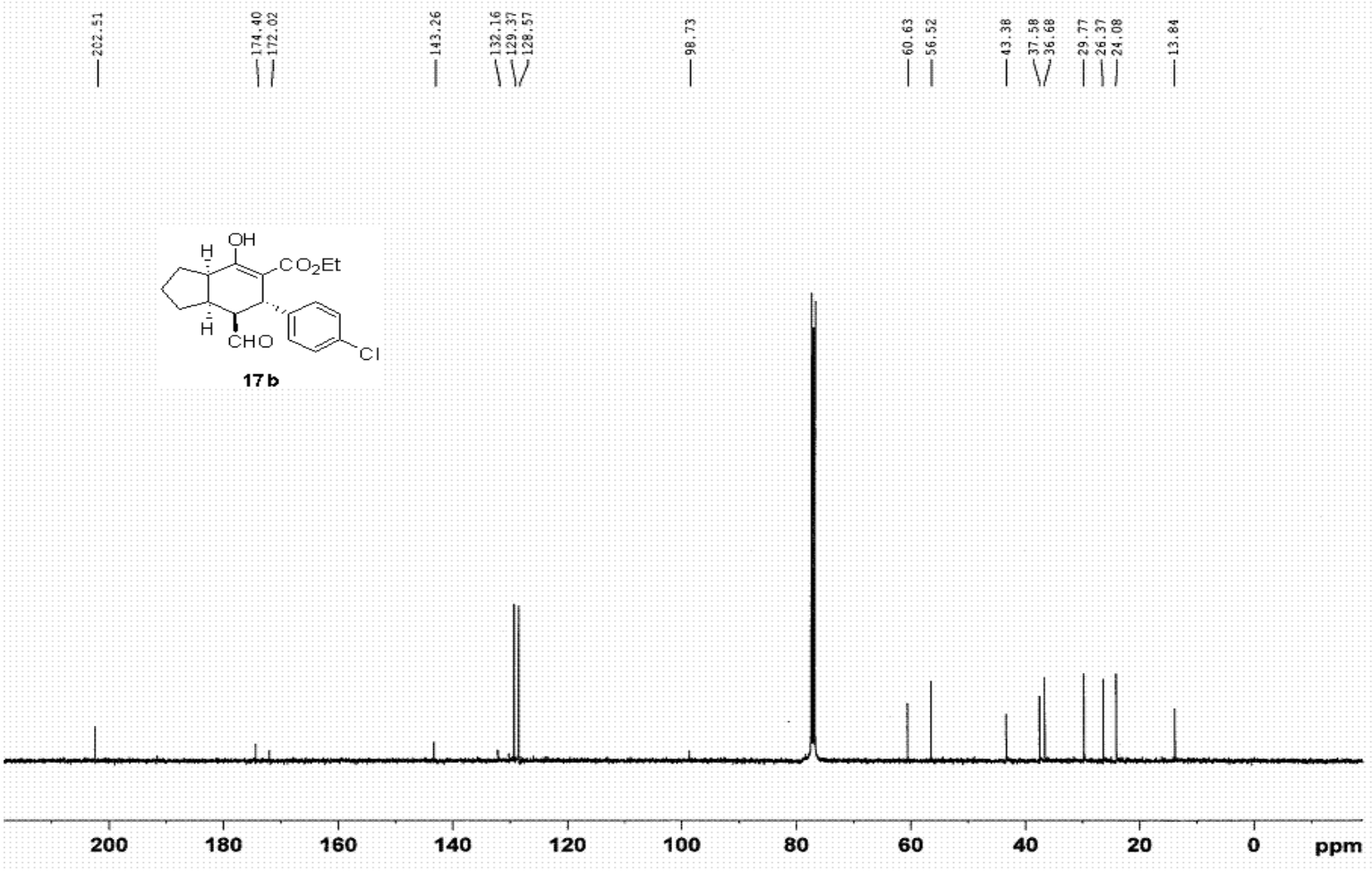
3.02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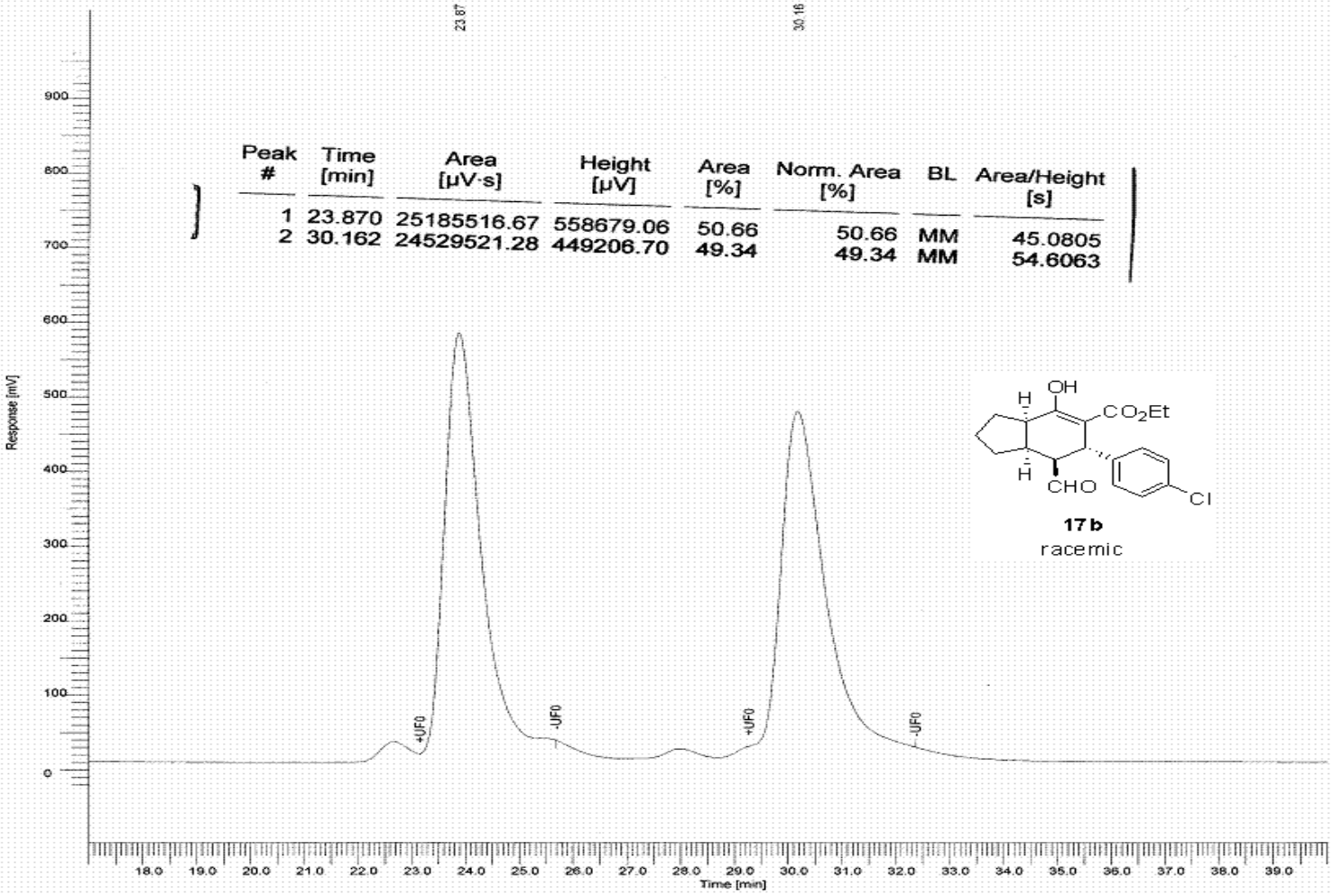
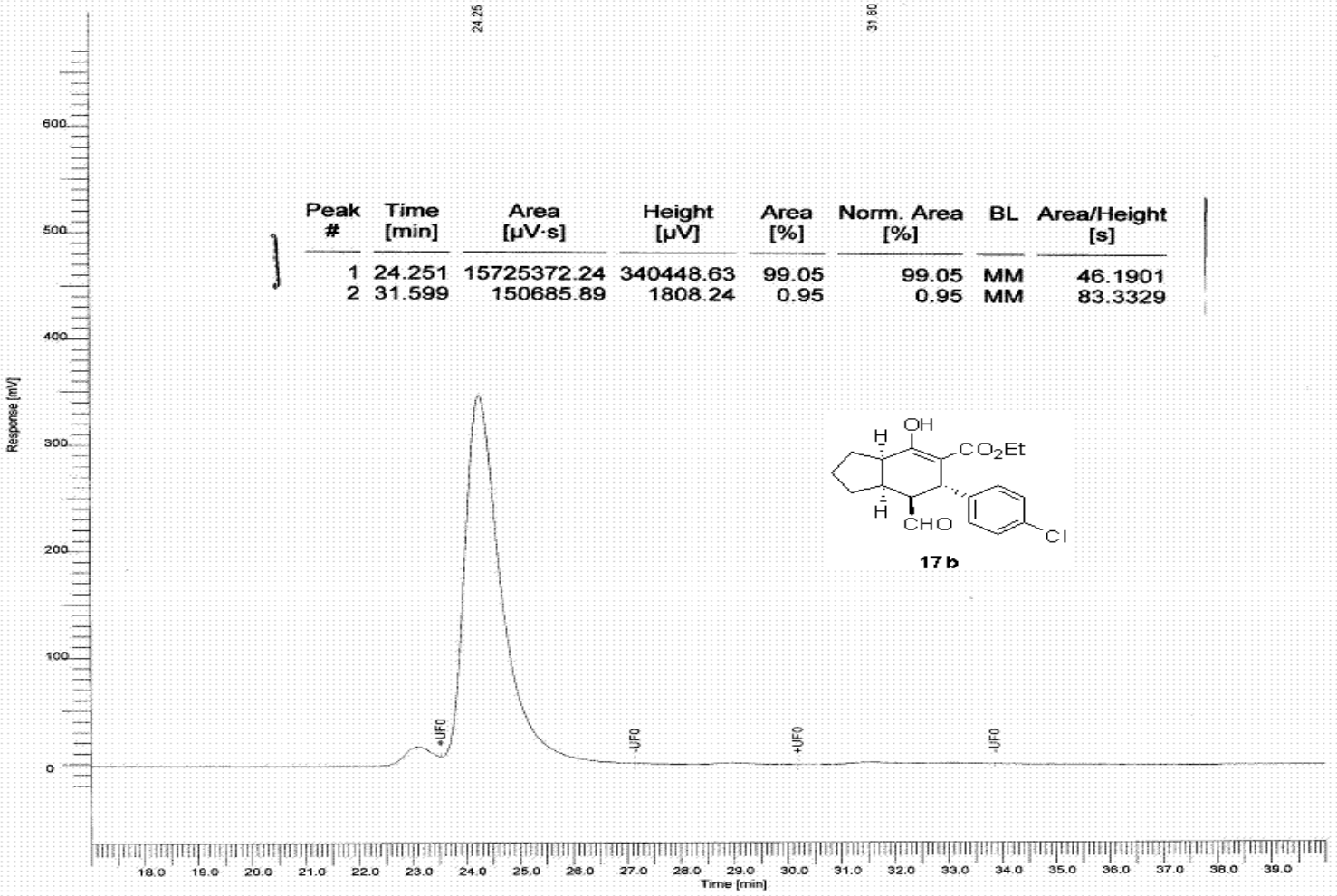
128.57
98.73
60.63
56.52
43.38
37.58
36.68
29.77
26.37
24.08
13.84
OH
CO2Et
H
H
CHO
Cl
17b
200
180
160
140
120
100
80
60
40
20
0
ppm



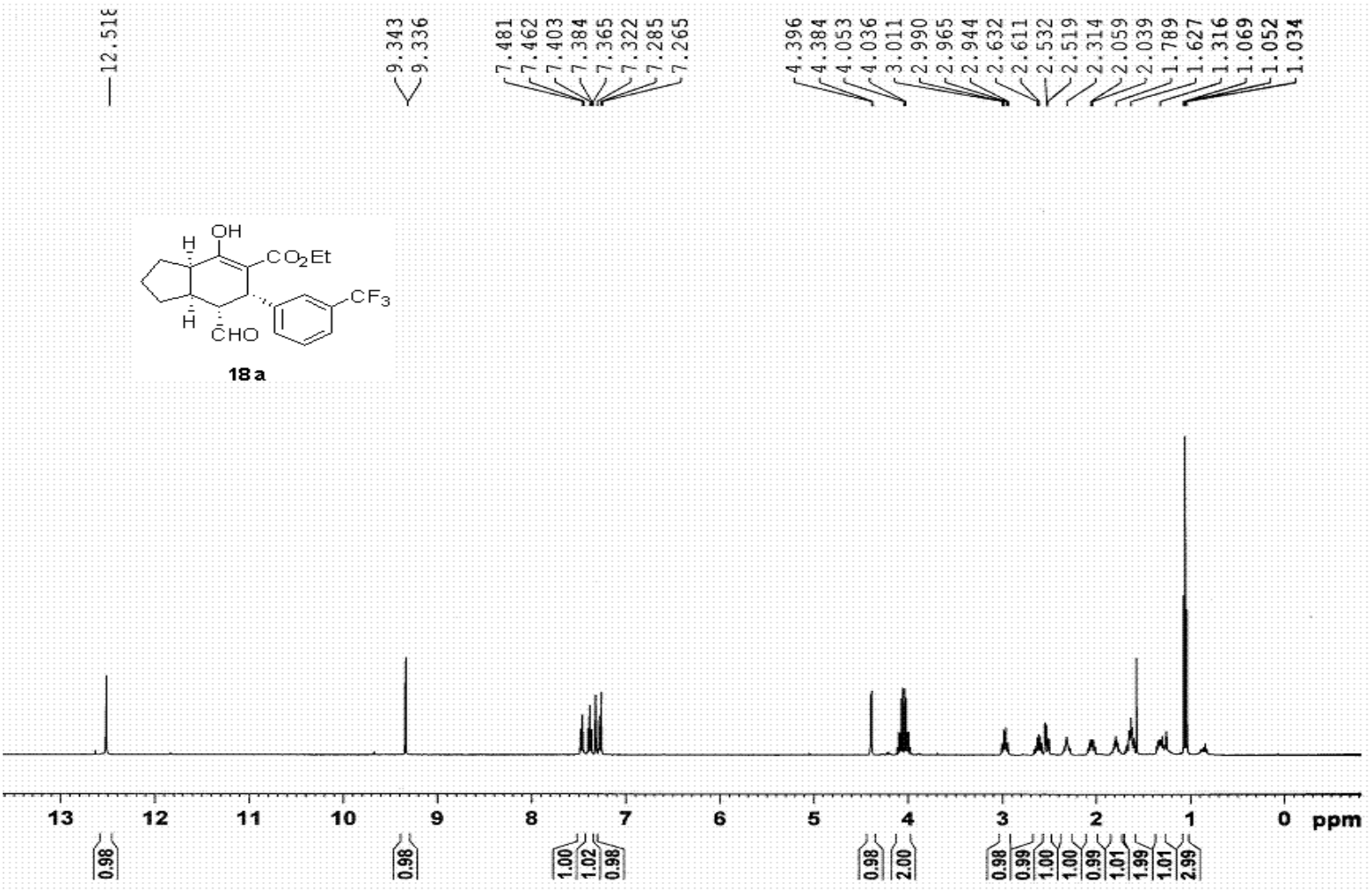
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	23.870	25185516.67	558679.06	50.66	50.66	MM	45.0805
2	30.162	24529521.28	449206.70	49.34	49.34	MM	54.6063

17 b
racemic



Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	24.251	15725372.24	340448.63	99.05	99.05	MM	46.1901
2	31.599	150685.89	1808.24	0.95	0.95	MM	83.3329

17 b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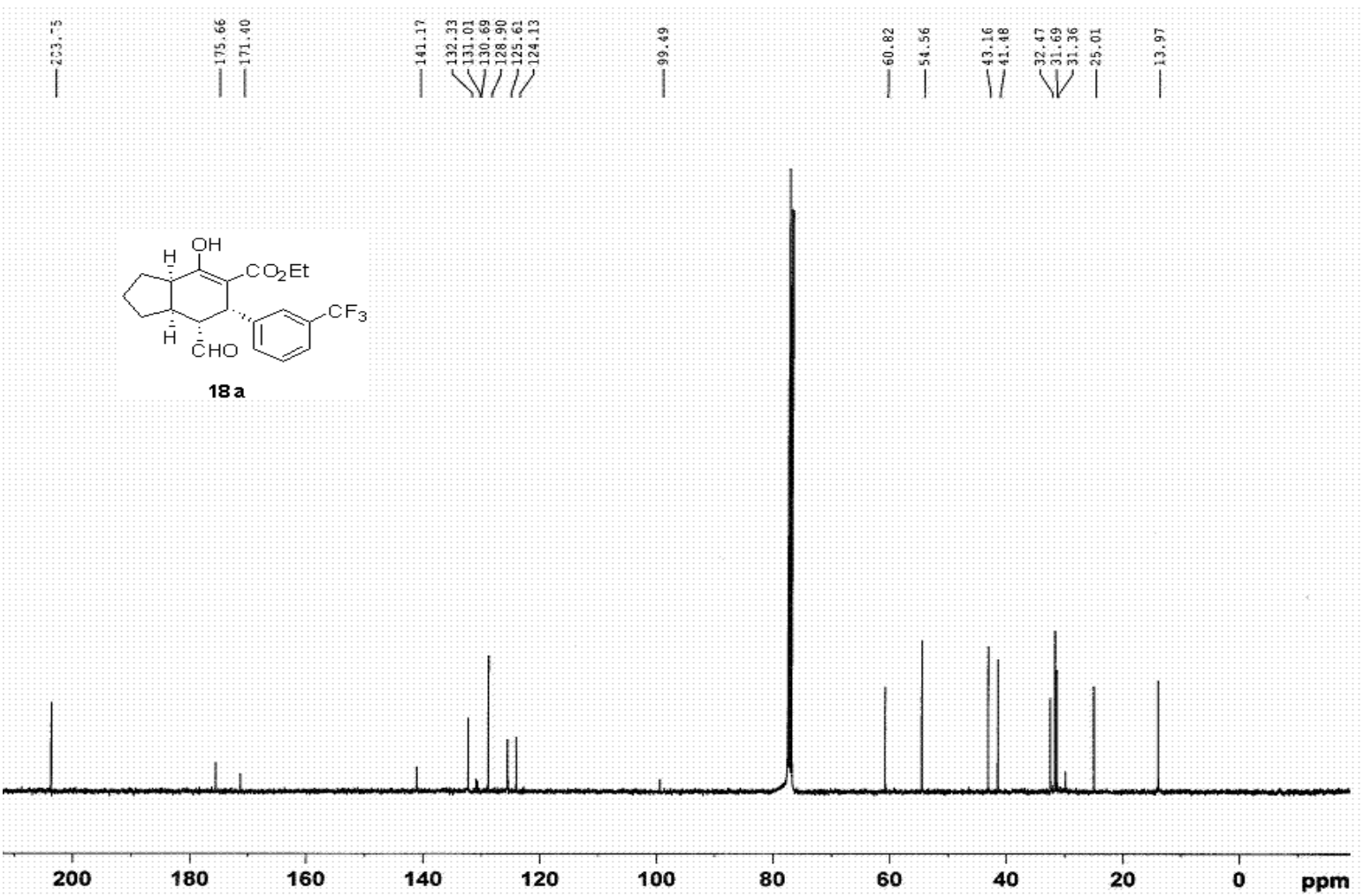
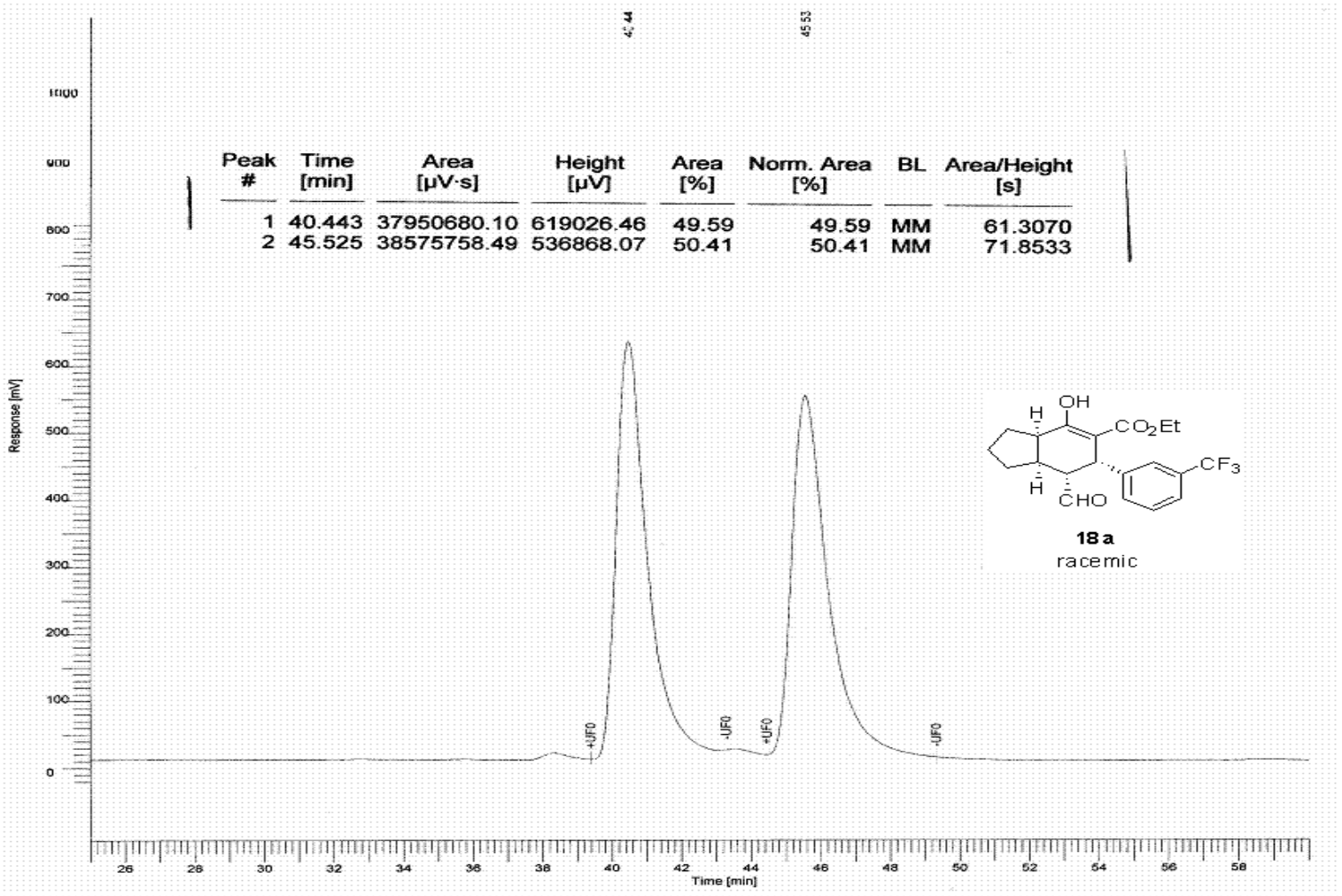
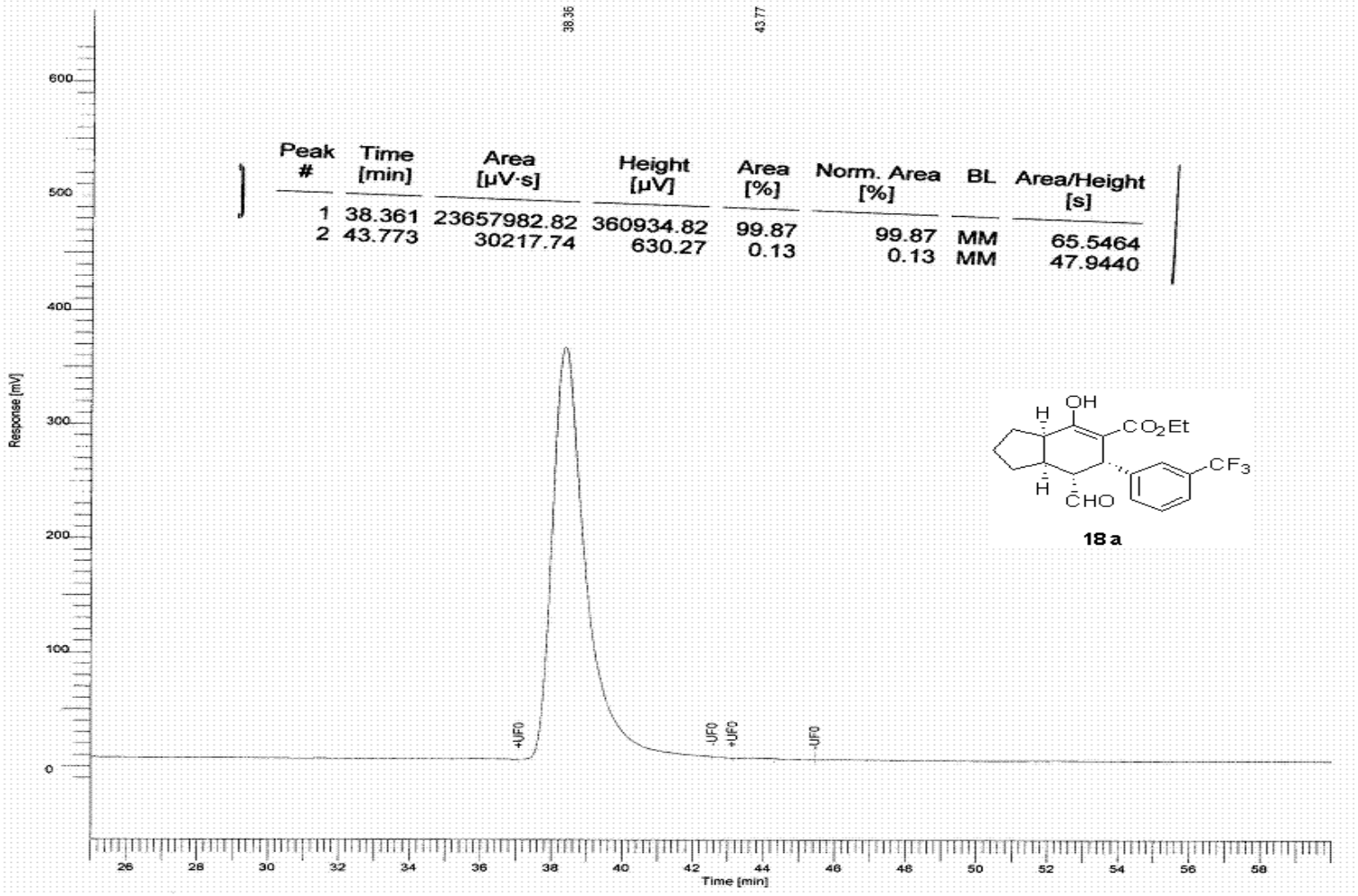
9.343
9.336
7.481
7.462
7.403
7.384
7.365
7.322
7.285
7.265
4.396
4.384
4.053
4.036
3.011
2.990
2.965
2.944
2.632
2.611
2.532
2.519
2.314
2.059
2.039
1.789
1.627
1.316
1.069
1.052
1.034
OH
H
CO2Et
CF3
H
CHO
18a
13 12 11 10 9 8 7 6 5 4 3 2 1 0 ppm
0.98 0.98 1.00 1.02 0.98 0.98 2.00 0.98 0.99 1.00 1.00 0.99 1.01 1.99 1.01 2.99


175.66
171.40
141.17
132.33
131.01
130.69
128.90
125.61
124.13
99.49
60.82
54.56
43.16
41.48
32.47
31.69
31.36
25.01
13.97
OH
H
CO2Et
CF3
H
CHO
18a
200 180 160 140 120 100 80 60 40 20 0 ppm



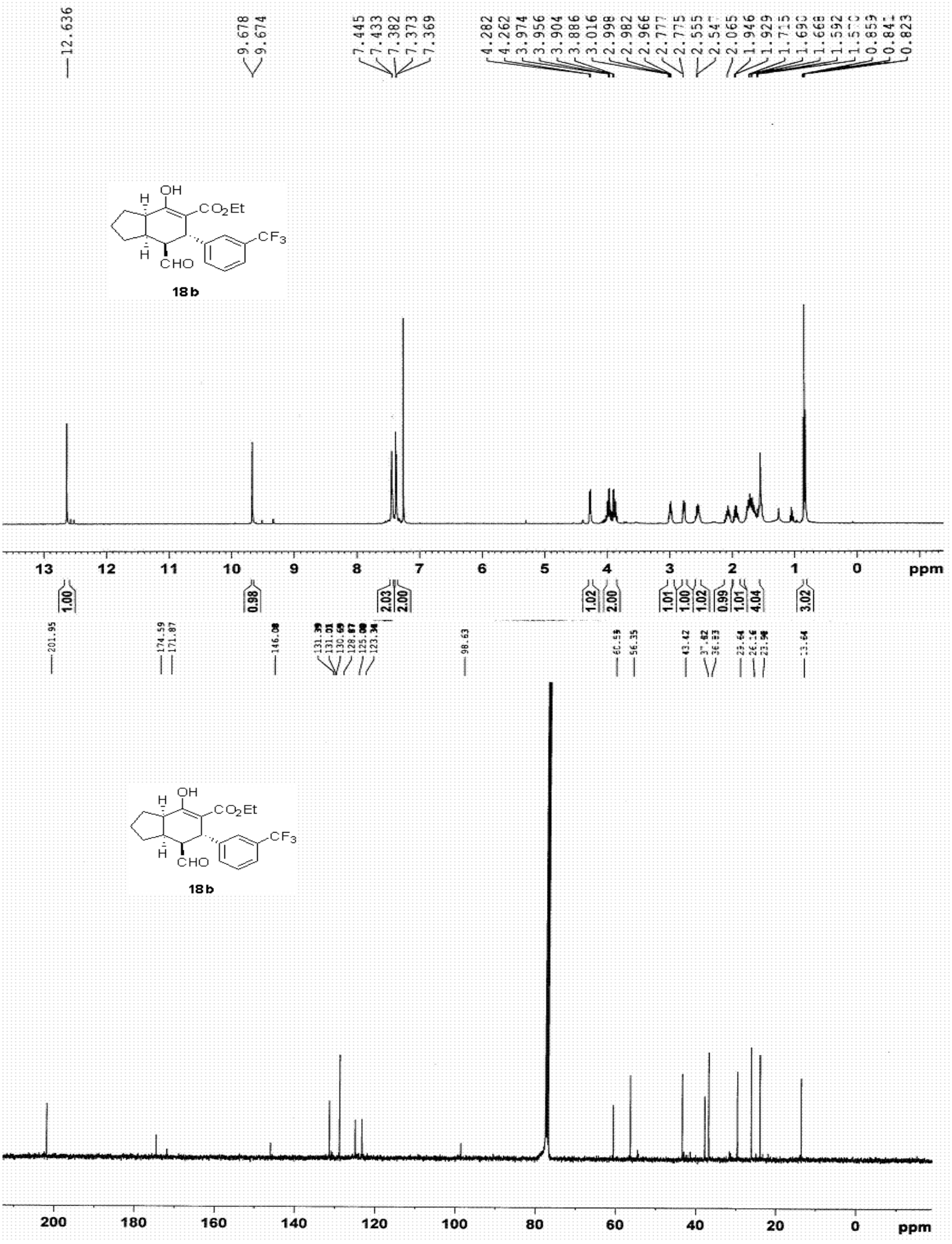
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	40.443	37950680.10	619026.46	49.59	49.59	MM	61.3070
2	45.525	38575758.49	536868.07	50.41	50.41	MM	71.8533

18 a
racemic



Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	38.361	23657982.82	360934.82	99.87	99.87	MM	65.5464
2	43.773	30217.74	630.27	0.13	0.13	MM	47.9440

18 a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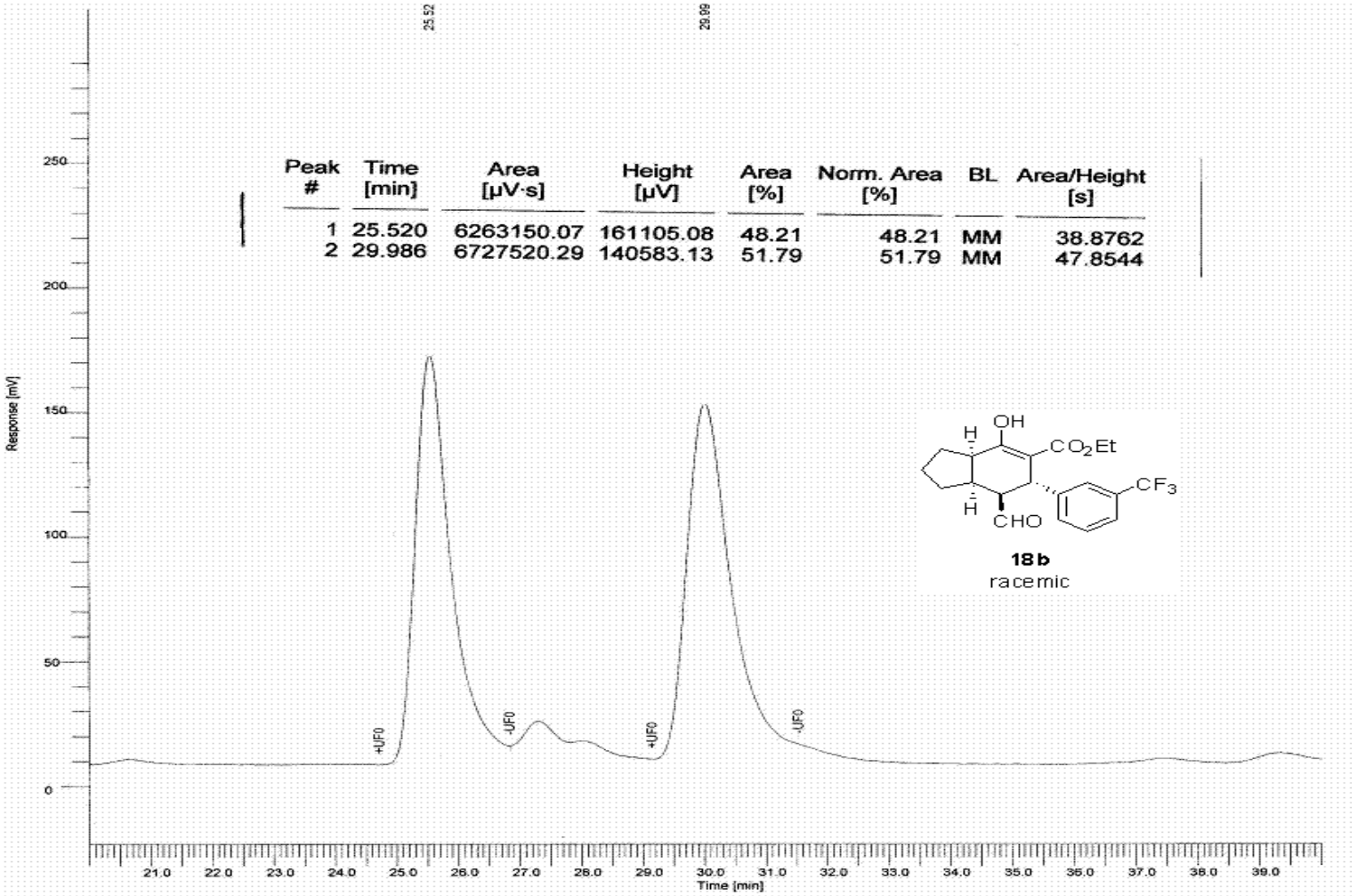
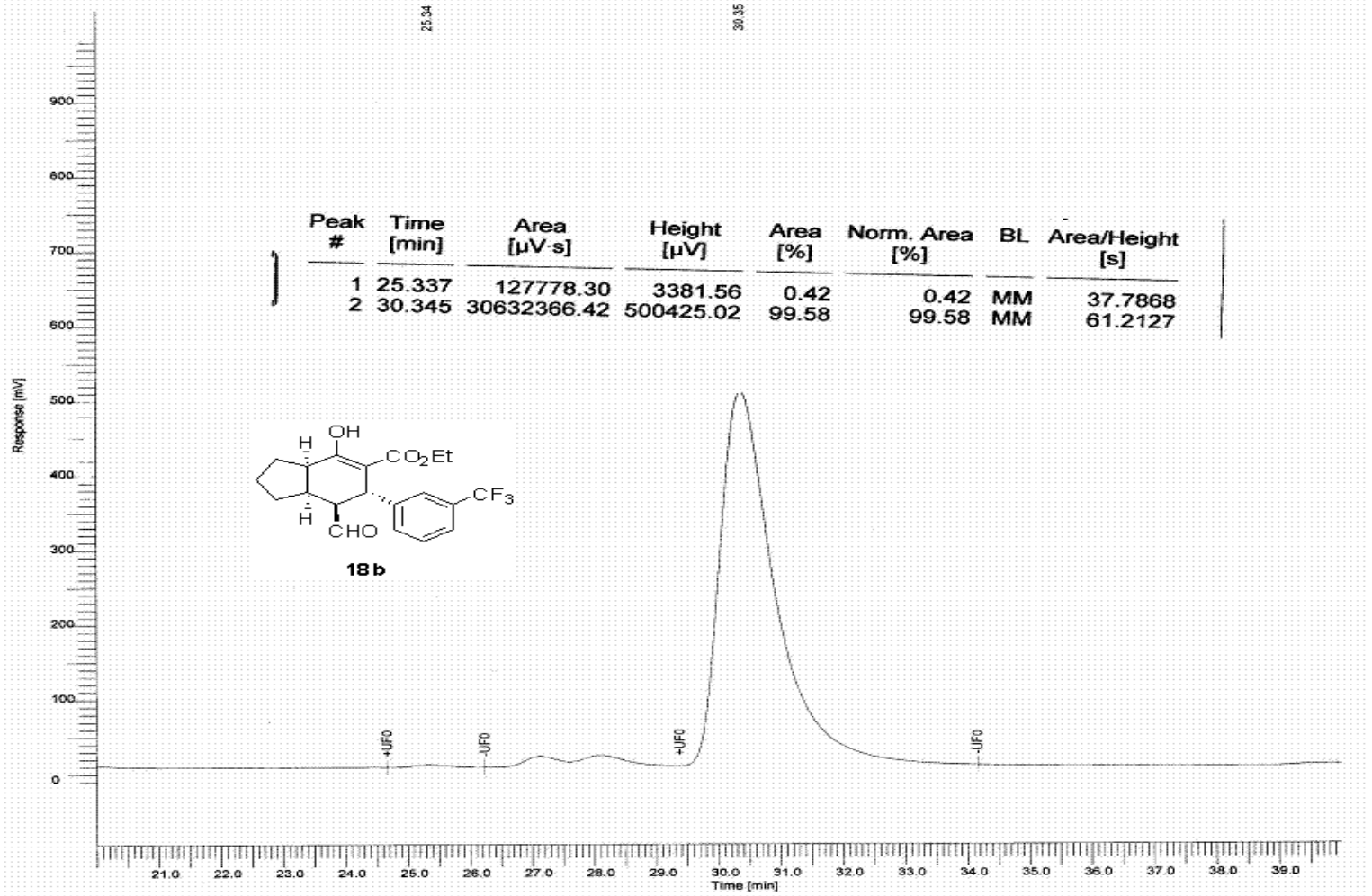
9.674
7.445
7.433
7.382
7.373
7.369
4.282
4.262
3.974
3.956
3.904
3.886
3.016
2.998
2.982
2.966
2.775
2.555
2.065
1.946
1.929
1.668
1.592
0.859
0.823
OH
CO2Et
CF3
CHO
18b
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
0.98
2.03
2.00
1.02
2.00
1.01
1.00
1.02
0.99
1.01
4.04
3.02
201.95
174.59
171.87
146.08
131.39
131.01
130.69
128.87
125.08
123.34
98.63
60.59
56.35
43.42
37.82
36.83
23.64
23.58
13.64
OH
CO2Et
CF3
CHO
18b
200
180
160
140
120
100
80
60
40
20
0
ppm



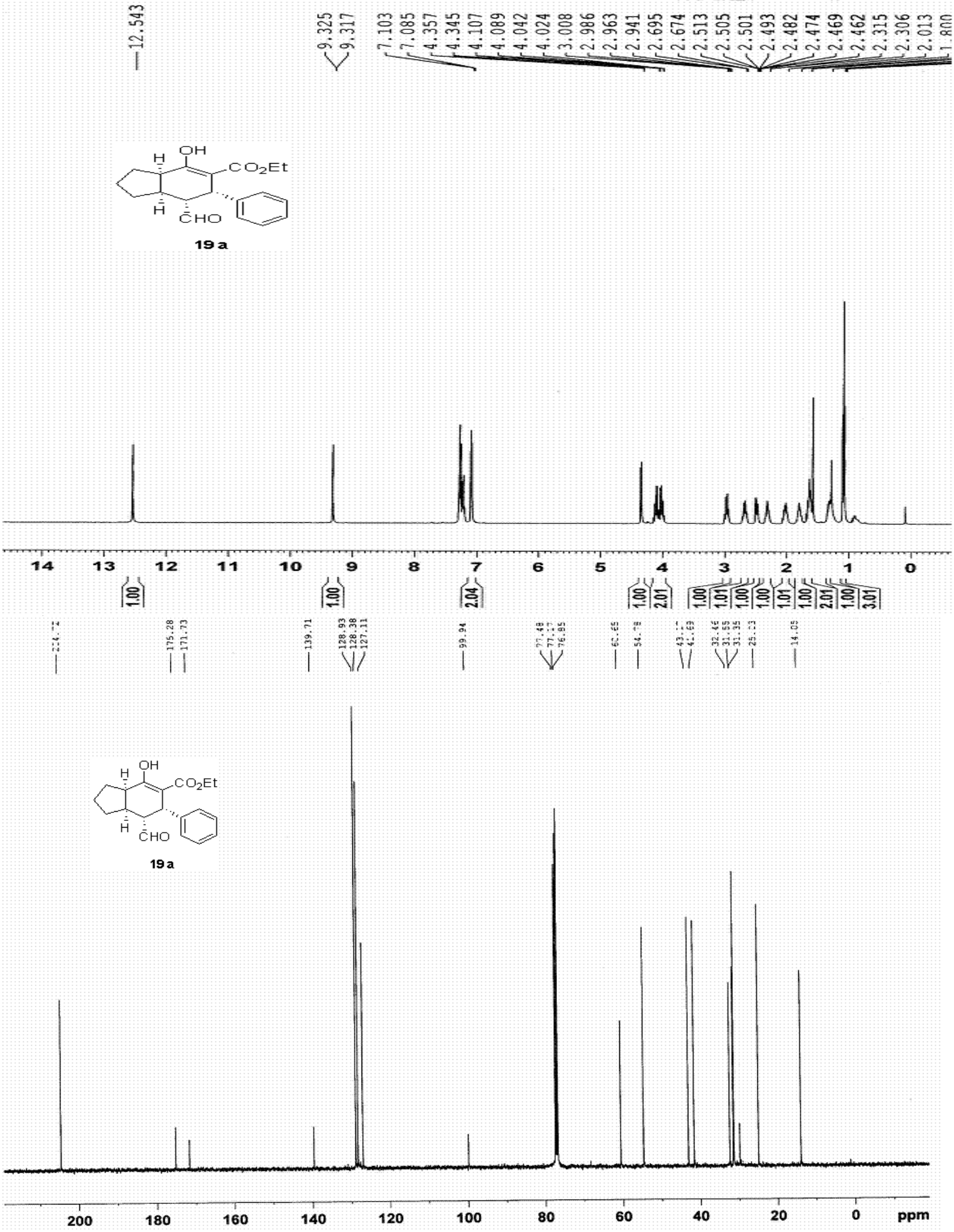
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	25.520	6263150.07	161105.08	48.21	48.21	MM	38.8762
2	29.986	6727520.29	140583.13	51.79	51.79	MM	47.8544

18b
racemic



Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	25.337	127778.30	3381.56	0.42	0.42	MM	37.7868
2	30.345	30632366.42	500425.02	99.58	99.58	MM	61.2127

18b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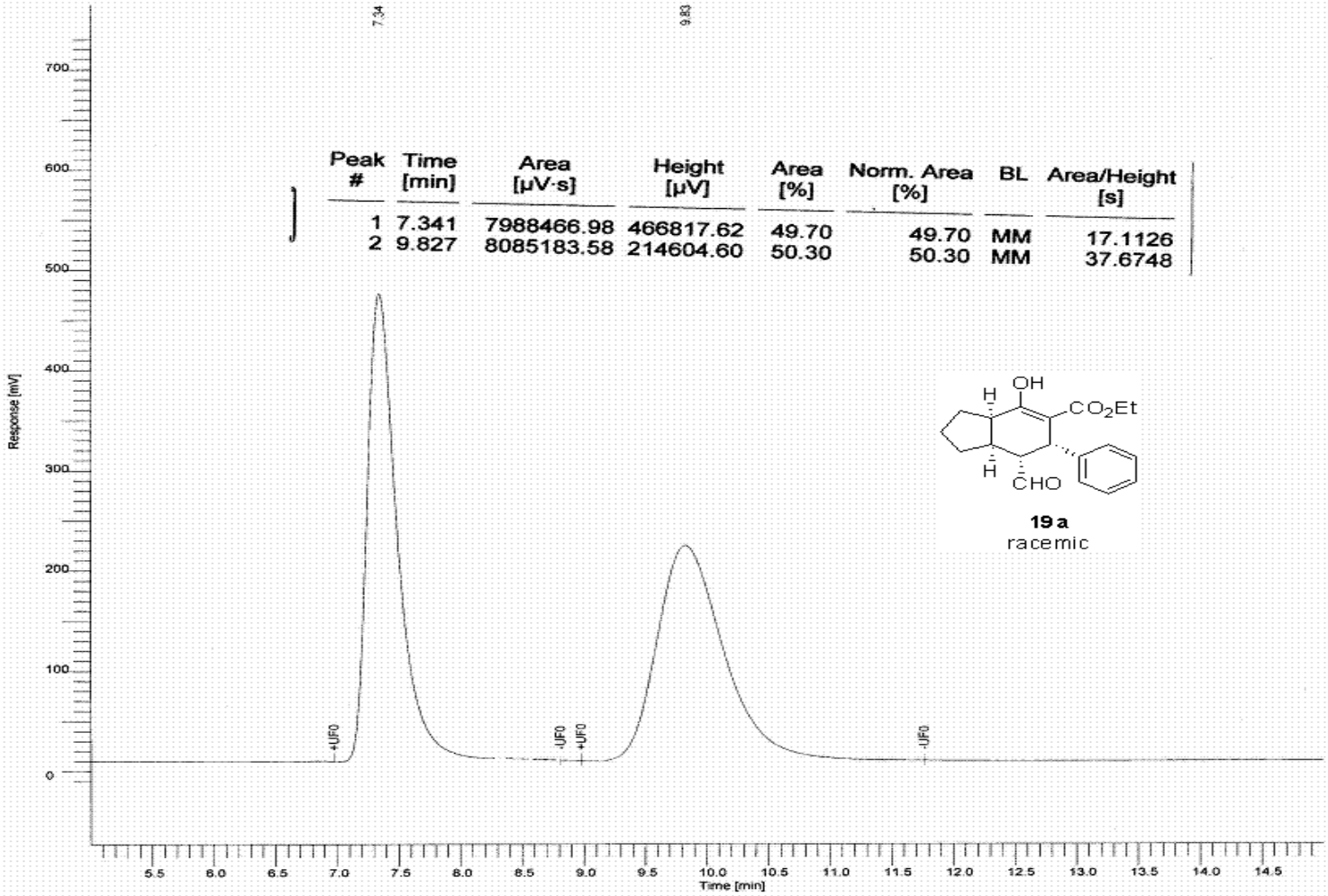
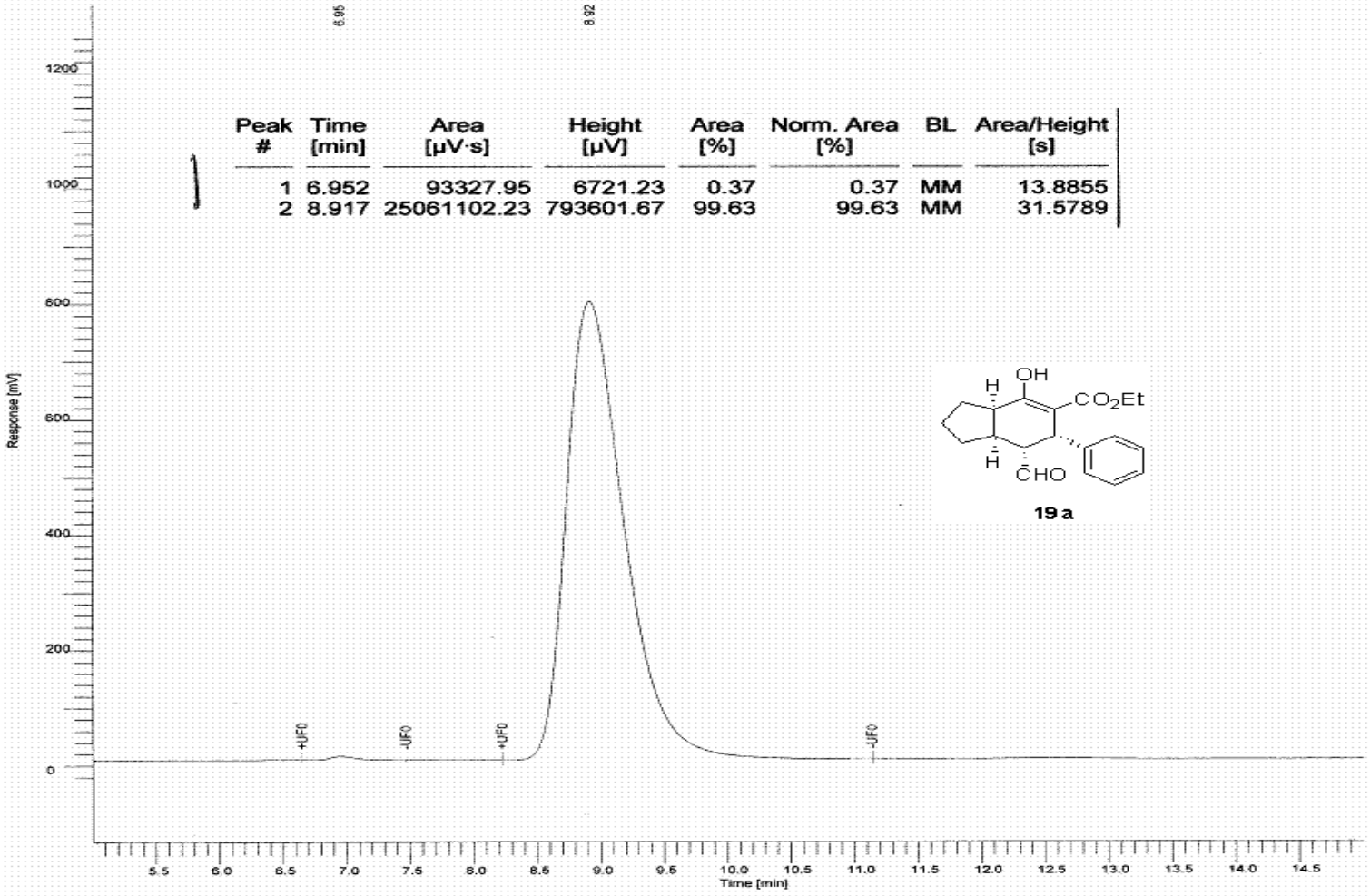
9.317
7.103
7.085
4.357
4.345
4.107
4.089
4.042
4.024
3.008
2.986
2.963
2.941
2.695
2.674
2.513
2.505
2.501
2.493
2.482
2.474
2.469
2.462
2.315
2.306
2.013
OH
H
CO2Et
H
CHO
19 a
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
1.00
1.00
2.04
1.00
2.01
1.00
1.01
1.00
1.00
1.01
1.00
2.01
1.00
3.01
175.28
171.73
139.71
128.93
128.38
127.11
99.94
77.48
77.17
76.85
60.65
54.78
43.17
42.69
32.46
31.55
31.38
25.03
14.05
OH
H
CO2Et
H
CHO
19 a
200
180
160
140
120
100
80
60
40
20
0
ppm



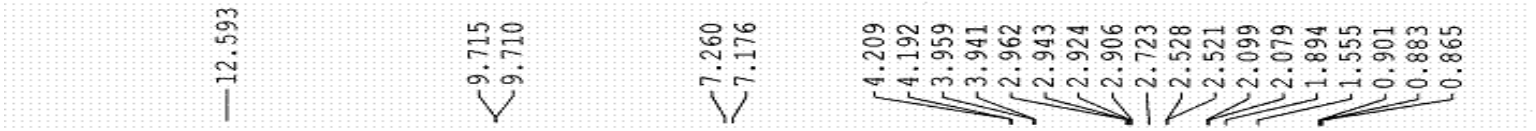
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.341	7988466.98	466817.62	49.70	49.70	MM	17.1126
2	9.827	8085183.58	214604.60	50.30	50.30	MM	37.6748

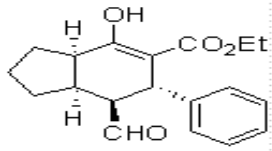
19 a
racemic



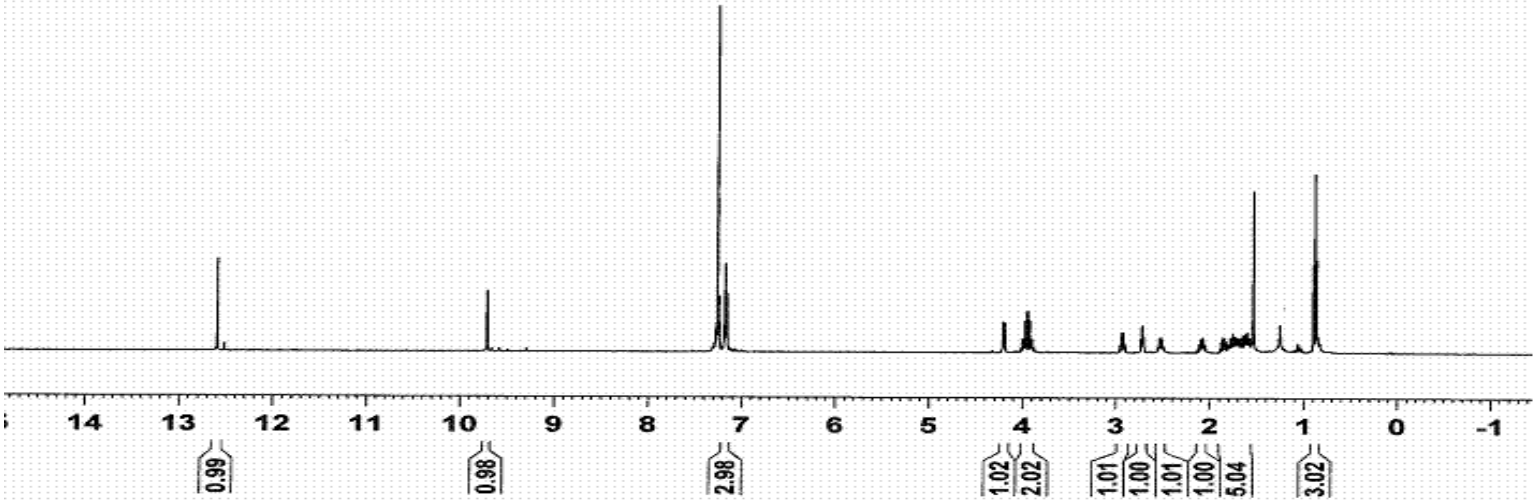
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	6.952	93327.95	6721.23	0.37	0.37	MM	13.8855
2	8.917	25061102.23	793601.67	99.63	99.63	MM	31.5789

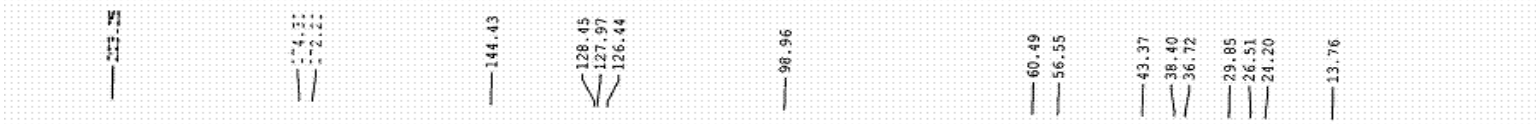
19 a

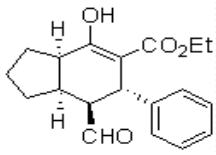

12.593
9.715
9.710
7.260
7.176
4.209
4.192
3.959
3.941
2.962
2.943
2.924
2.906
2.723
2.528
2.521
2.099
2.079
1.894
1.555
0.901
0.883
0.865


OH
H
CO2Et
H
CHO

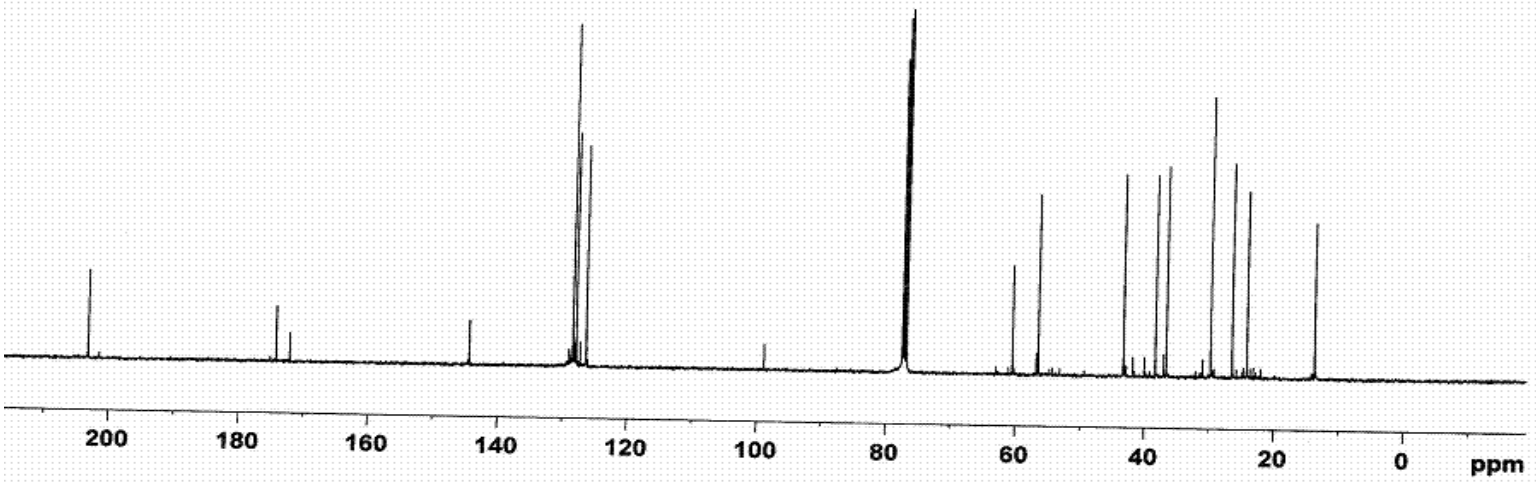
19b

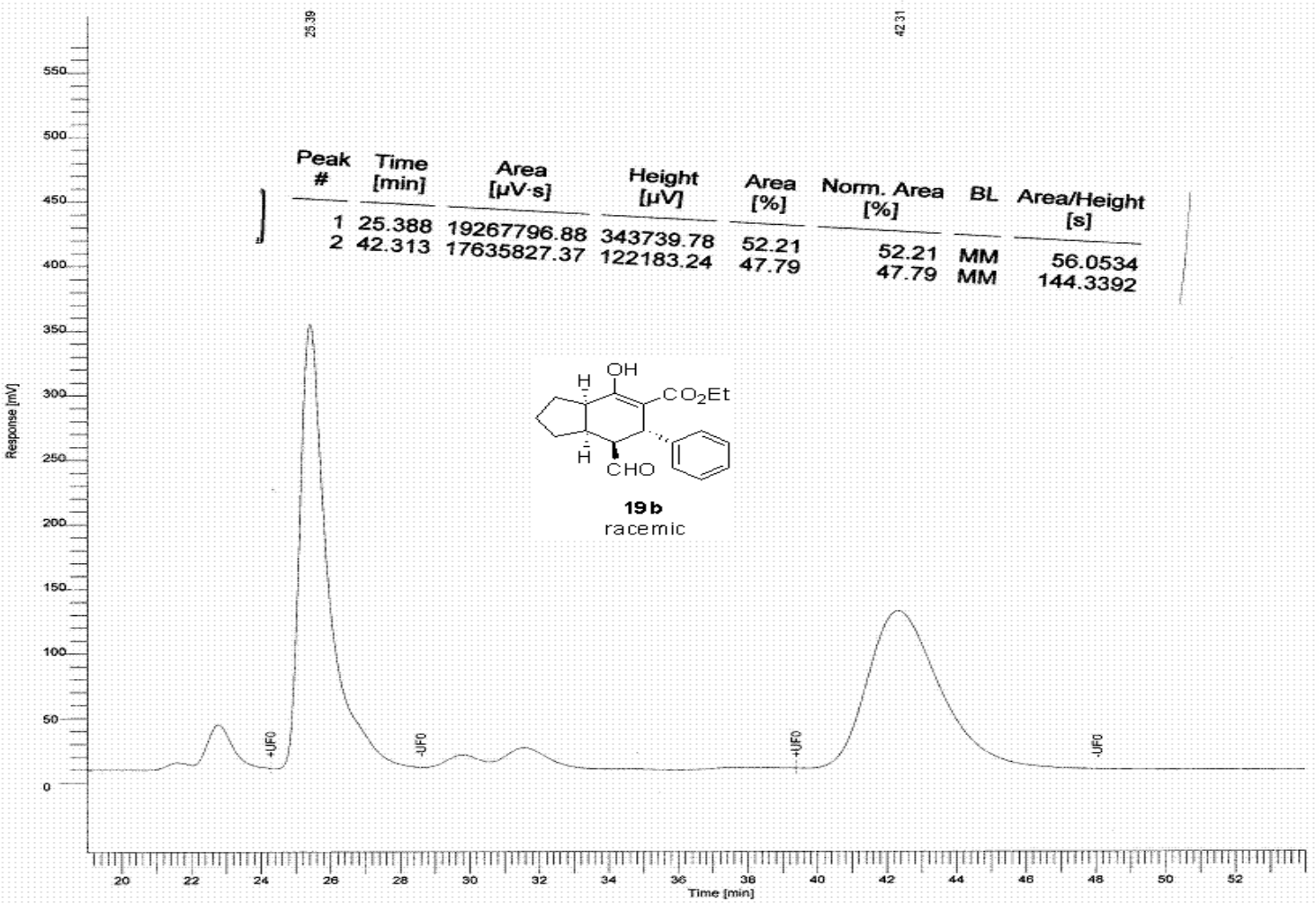

14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
0.99
0.98
2.98
1.02
2.02
1.01
1.00
1.01
1.00
5.04
3.02


144.43
128.45
127.97
126.44
98.96
60.49
56.55
43.37
38.40
36.72
29.85
26.51
24.20
13.76


OH
H
CO2Et
H
CHO

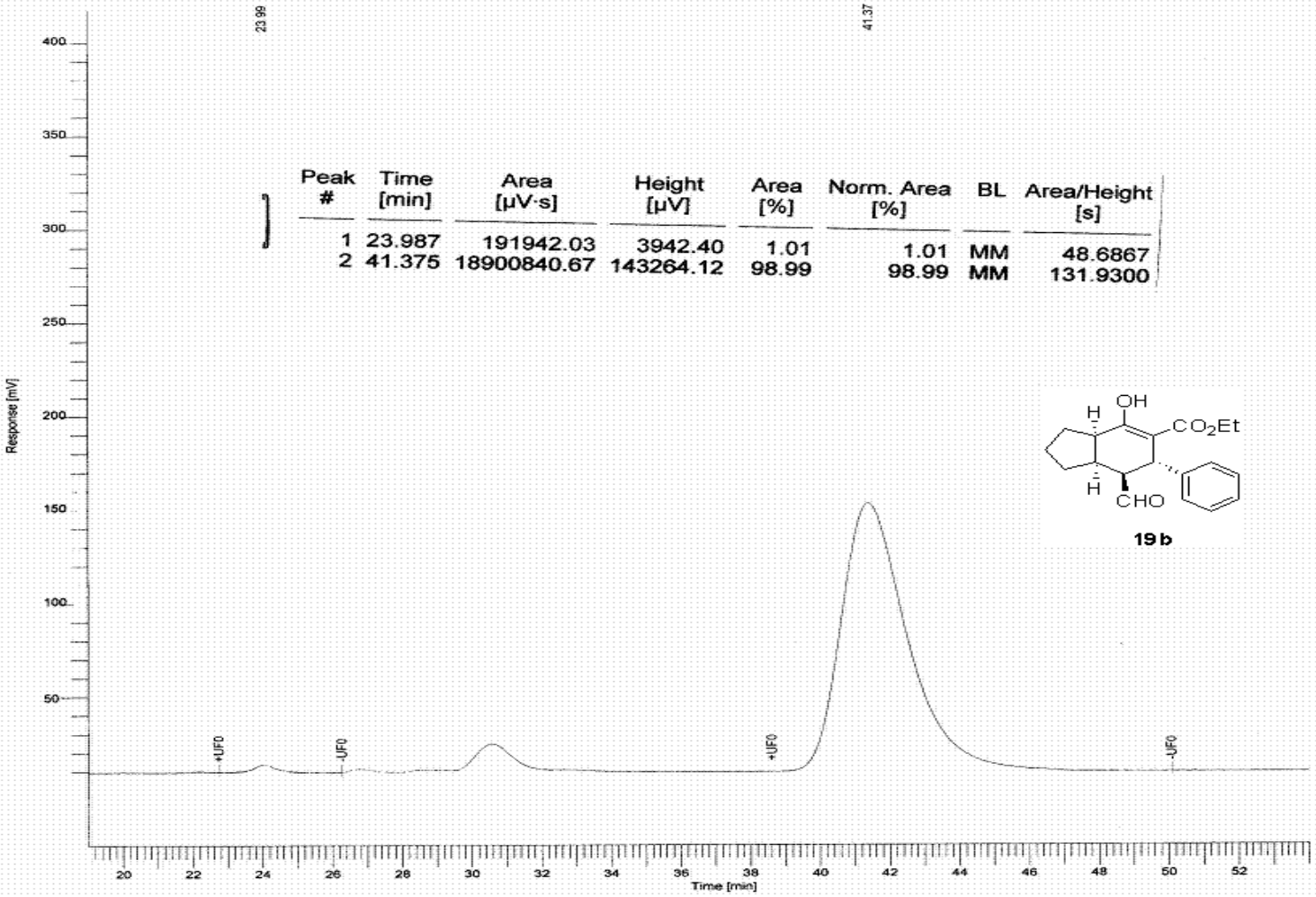
19b


200
180
160
140
120
100
80
60
40
20
0
ppm



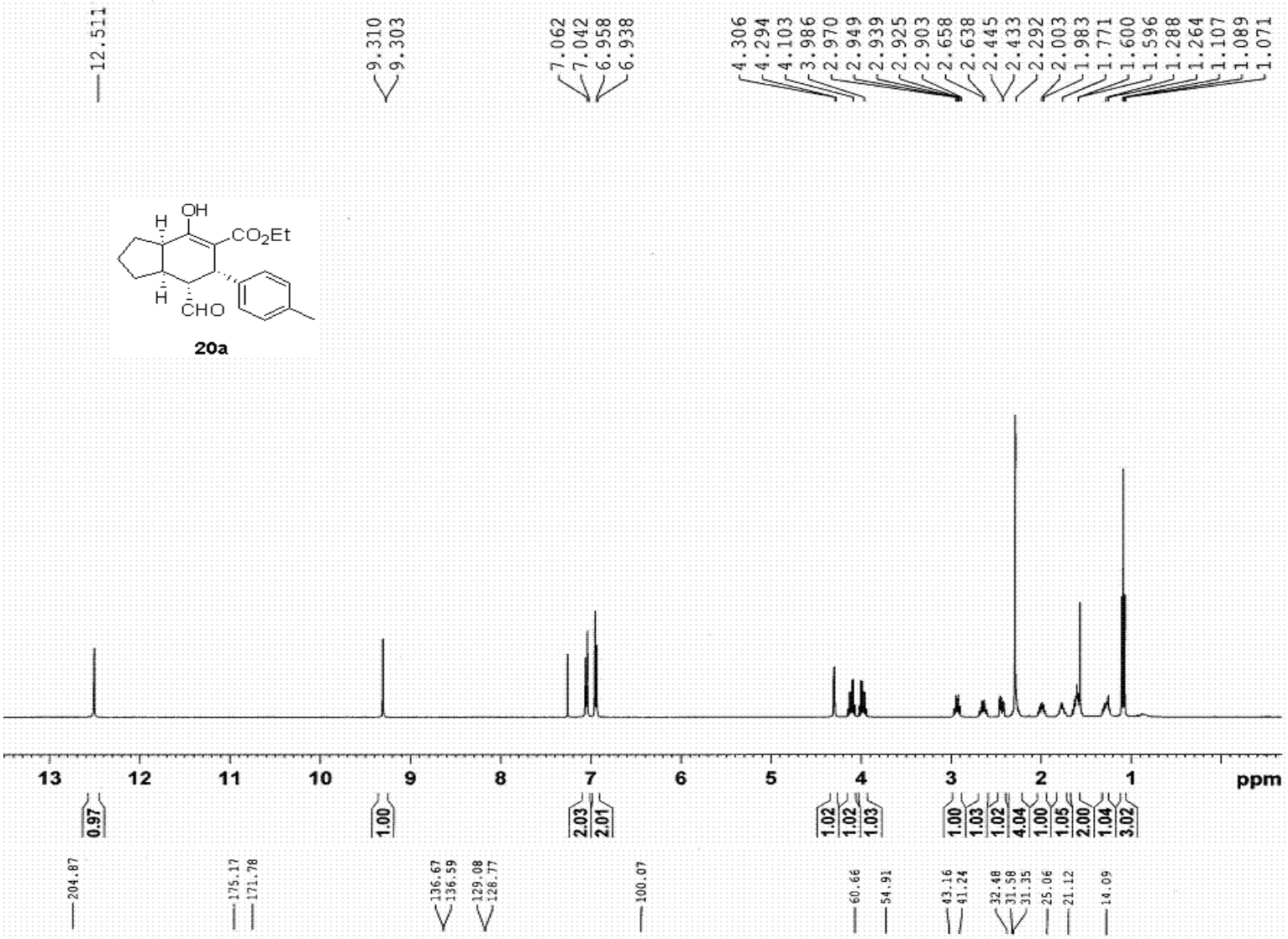
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	25.388	19267796.88	343739.78	52.21	52.21	MM	56.0534
2	42.313	17635827.37	122183.24	47.79	47.79	MM	144.3392

19b
racemic

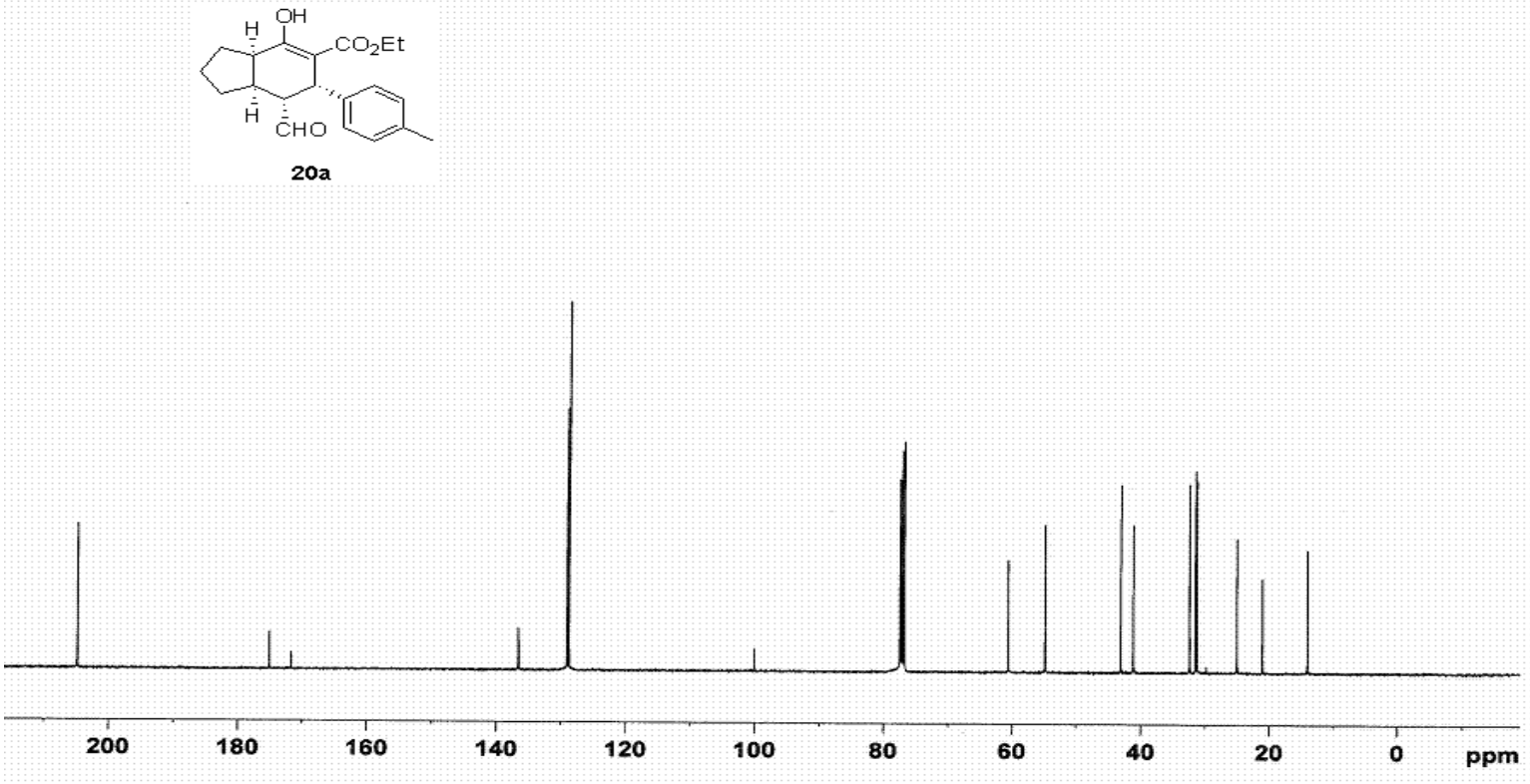


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	23.987	191942.03	3942.40	1.01	1.01	MM	48.6867
2	41.375	18900840.67	143264.12	98.99	98.99	MM	131.9300

19b

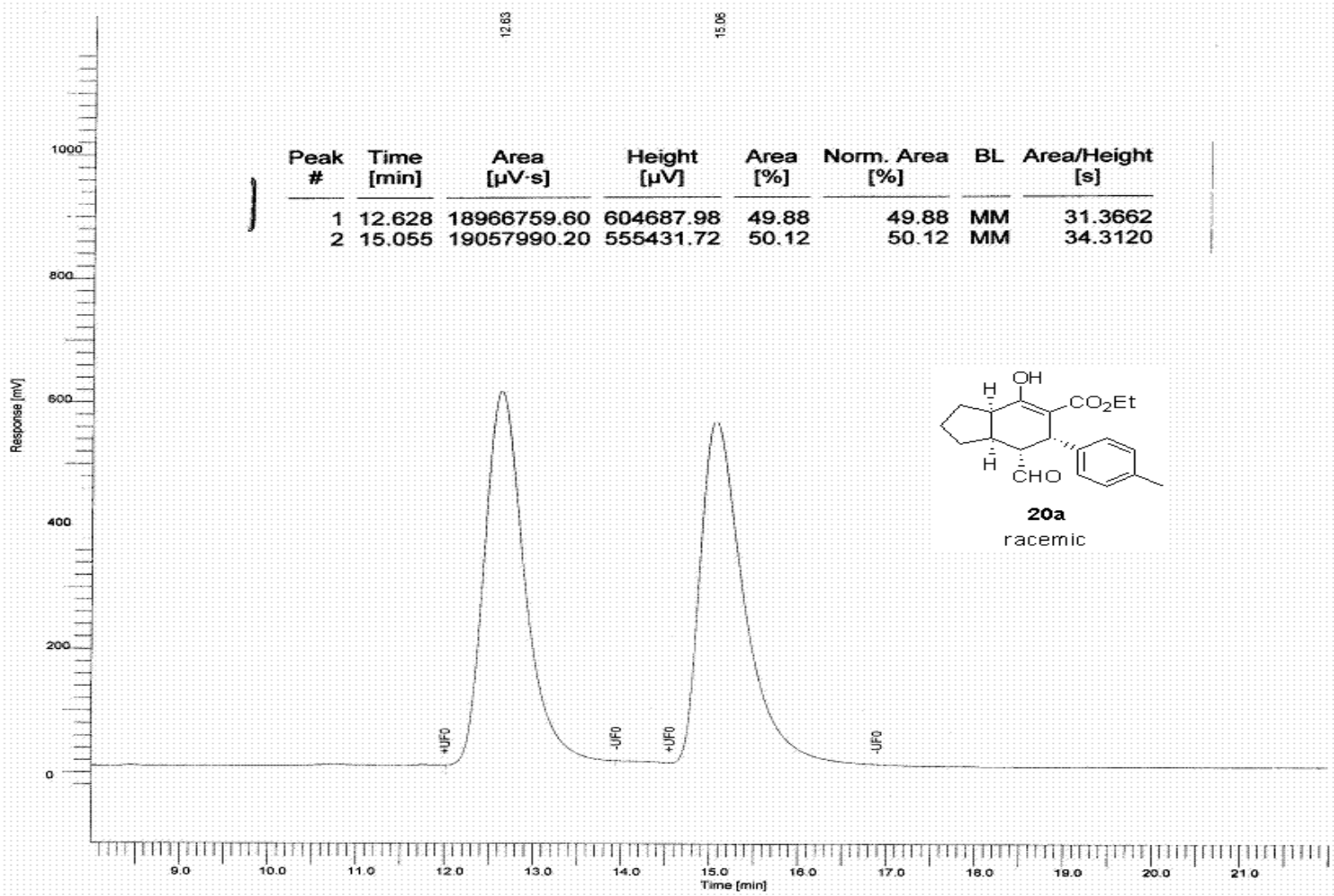

12.511
9.310
9.303
7.062
7.042
6.958
6.938
4.306
4.294
4.103
3.986
2.970
2.949
2.939
2.925
2.903
2.658
2.638
2.445
2.433
2.292
2.003
1.983
1.771
1.600
1.596
1.288
1.264
1.107
1.089
1.071
OH
H
CO2Et
H
CHO
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.97
1.00
2.03
2.01
1.02
1.02
1.03
1.00
1.03
1.02
4.04
1.00
1.05
2.00
1.04
3.02

20a


204.87
175.17
171.78
136.67
136.59
129.08
128.77
100.07
60.66
54.91
43.16
41.24
32.48
31.58
31.35
25.06
21.12
14.09
200
180
160
140
120
100
80
60
40
20
0
ppm

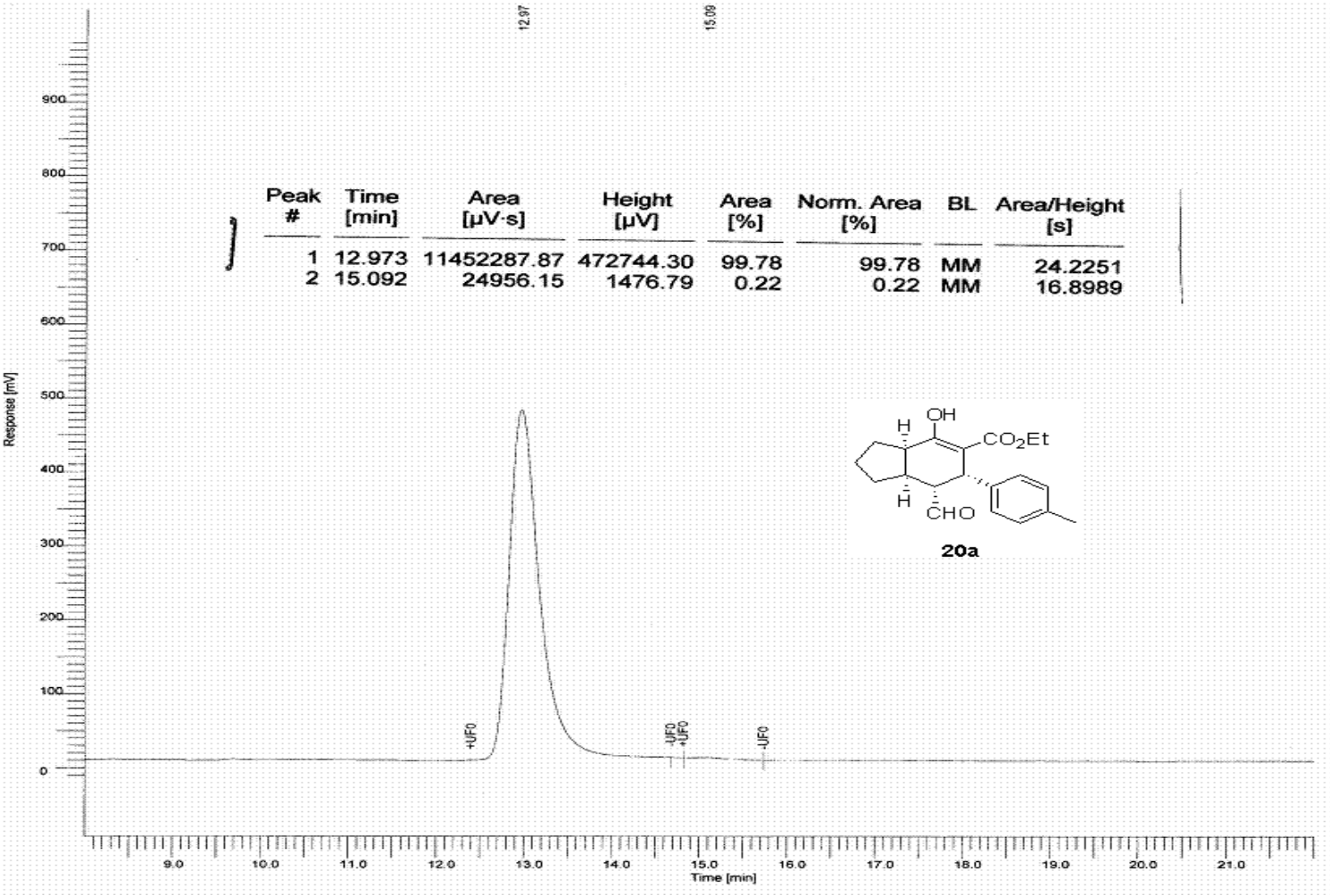
OH
H
CO2Et
H
CHO

20a



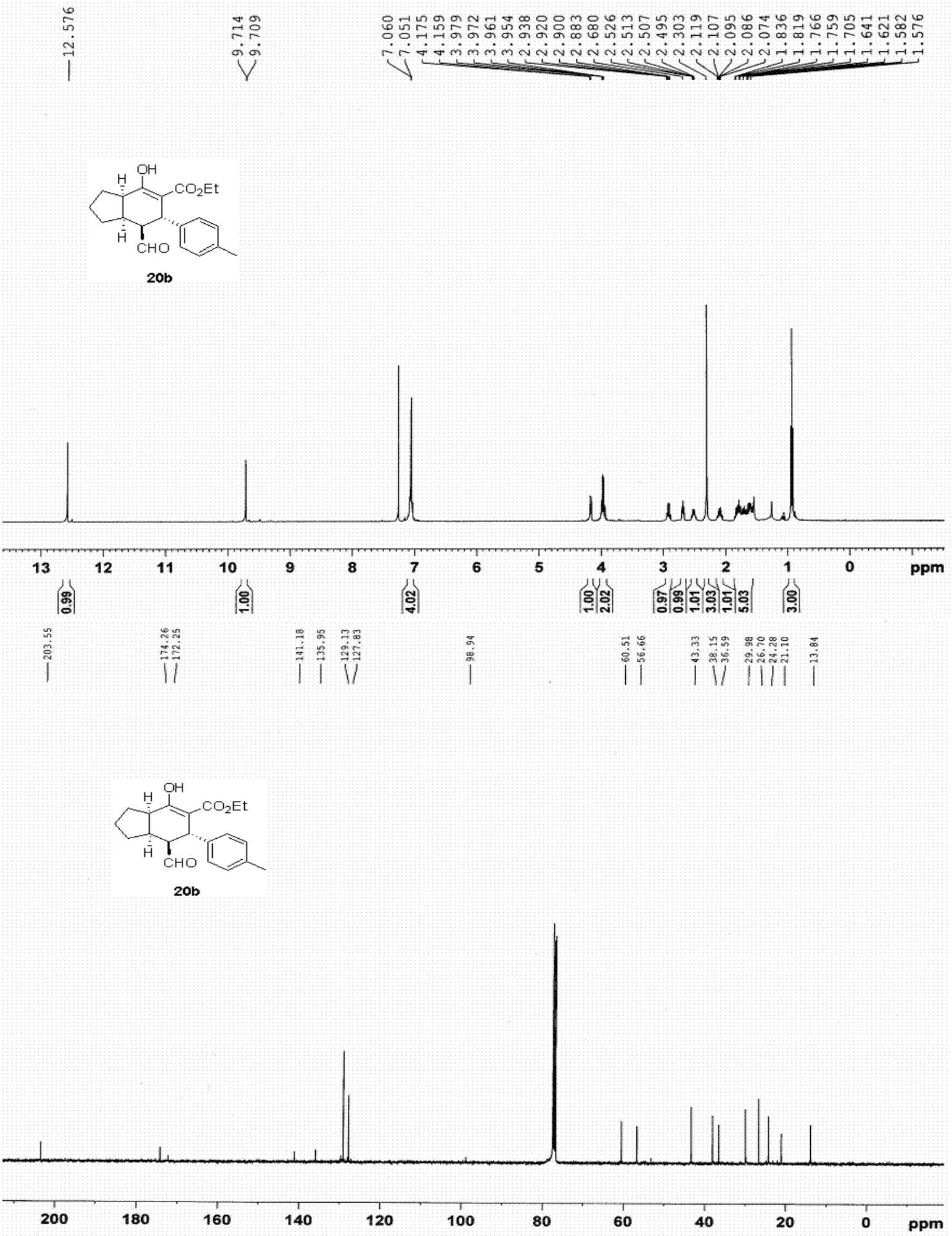
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	12.628	18966759.60	604687.98	49.88	49.88	MM	31.3662
2	15.055	19057990.20	555431.72	50.12	50.12	MM	34.3120

20a
racemic

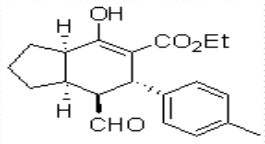


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	12.973	11452287.87	472744.30	99.78	99.78	MM	24.2251
2	15.092	24956.15	1476.79	0.22	0.22	MM	16.8989

20a

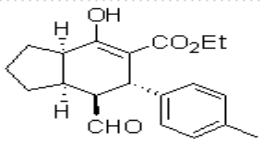

12.576
9.714
9.709
7.060
7.051
4.175
4.159
3.979
3.972
3.961
3.954
2.938
2.920
2.900
2.883
2.680
2.526
2.513
2.507
2.495
2.303
2.119
2.107
2.095
2.086
2.074
1.836
1.819
1.766
1.759
1.705
1.641
1.621
1.582
1.576
OH
H
CO2Et
H
CHO
20b
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.99
1.00
4.02
1.00
2.02
0.97
0.99
1.01
3.03
1.01
5.03
3.00
203.55
174.26
172.25
141.18
135.95
129.13
127.83
98.94
60.51
56.66
43.33
38.15
36.59
29.98
26.70
24.28
21.10
13.84
OH
H
CO2Et
H
CHO
20b
200
180
160
140
120
100
80
60
40
20
0
ppm

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	15.891	2292980.27	96219.99	50.15	50.15	MM	23.8306
2	16.925	2279469.80	93193.33	49.85	49.85	MM	24.4596

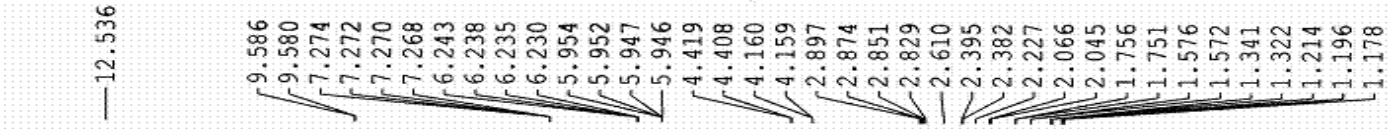


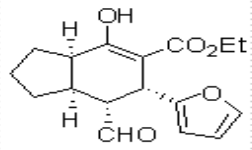
20b
racemic

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	15.723	28213444.61	1.01e+06	99.77	99.77	MM	27.9091
2	16.933	63951.83	3775.20	0.23	0.23	MM	16.9400

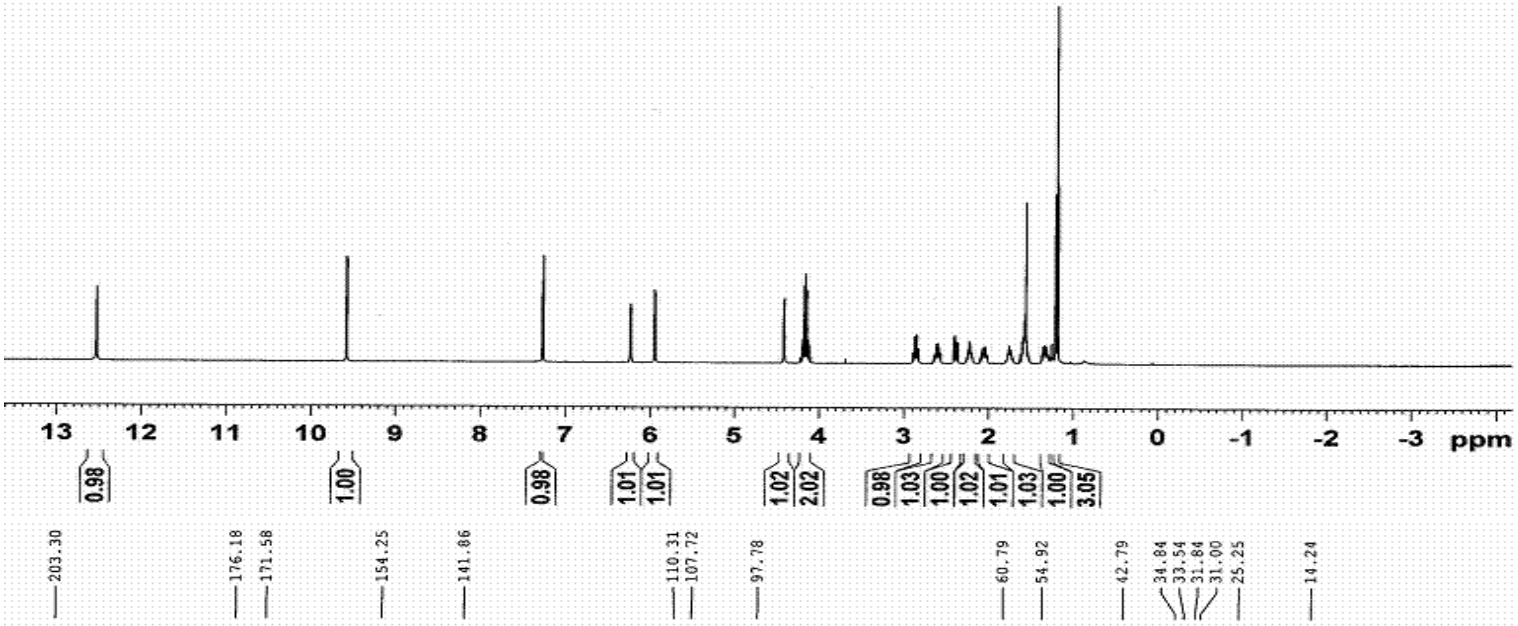


20b

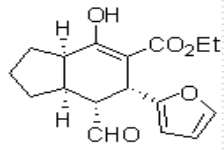

12.536
9.586
9.580
7.274
7.272
7.270
7.268
6.243
6.238
6.235
6.230
5.954
5.952
5.947
5.946
4.419
4.408
4.160
4.159
2.897
2.874
2.851
2.829
2.610
2.395
2.382
2.227
2.066
2.045
1.756
1.751
1.576
1.572
1.341
1.322
1.214
1.196
1.178


OH
CO2Et
H
O
H
CHO

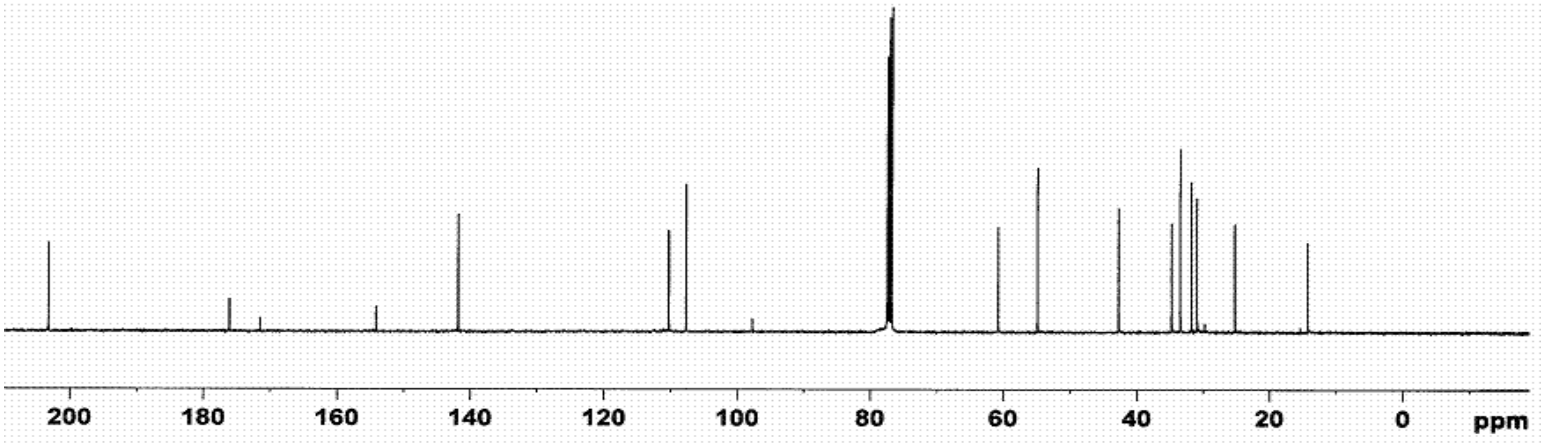
21a

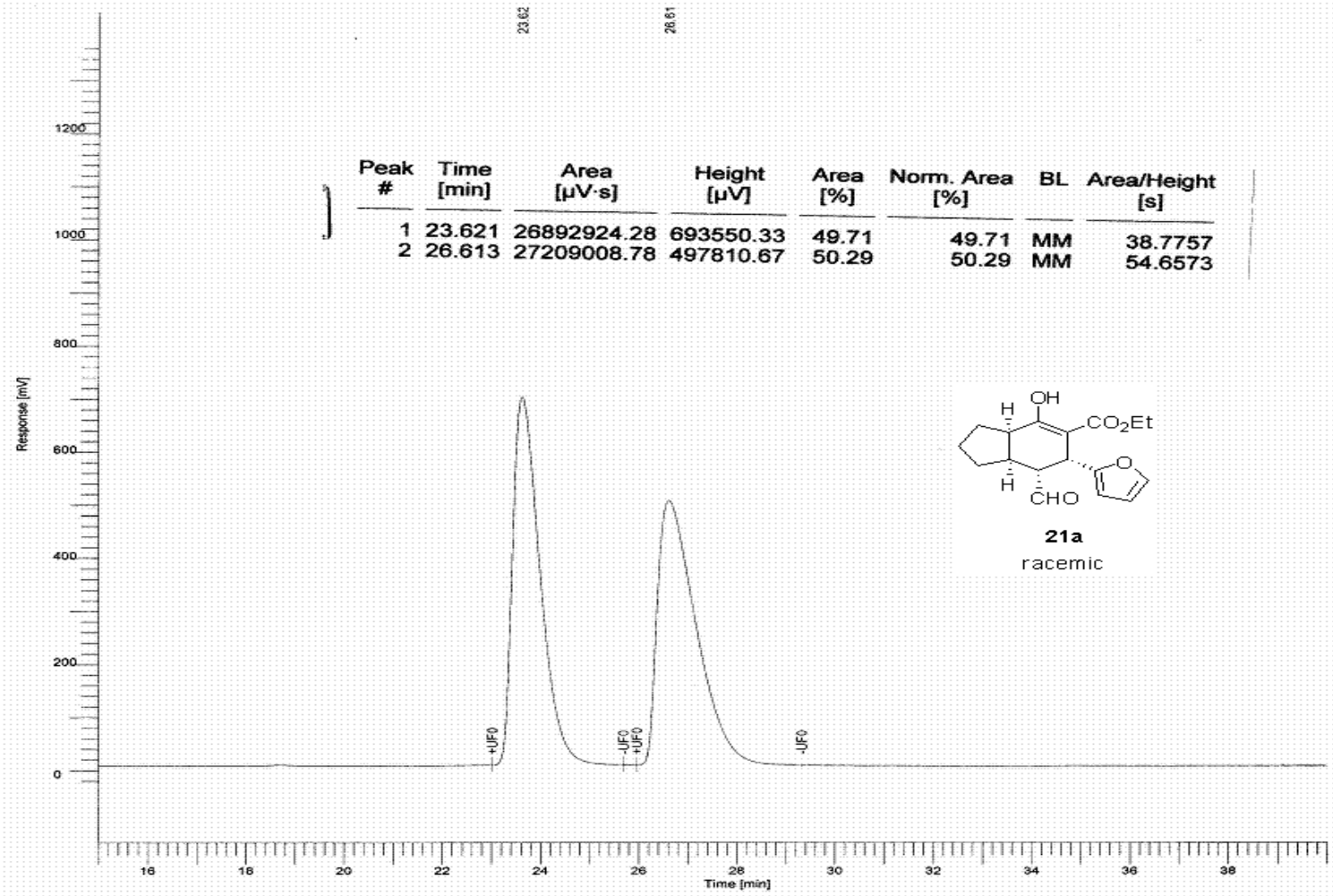

13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
0.98
1.00
0.98
1.01
1.01
1.02
2.02
0.98
1.03
1.00
1.02
1.01
1.03
1.00
3.05

203.30
176.18
171.58
154.25
141.86
110.31
107.72
97.78
60.79
54.92
42.79
34.84
33.54
31.84
31.00
25.25
14.24


H
OH
CO2Et
O
H
CHO

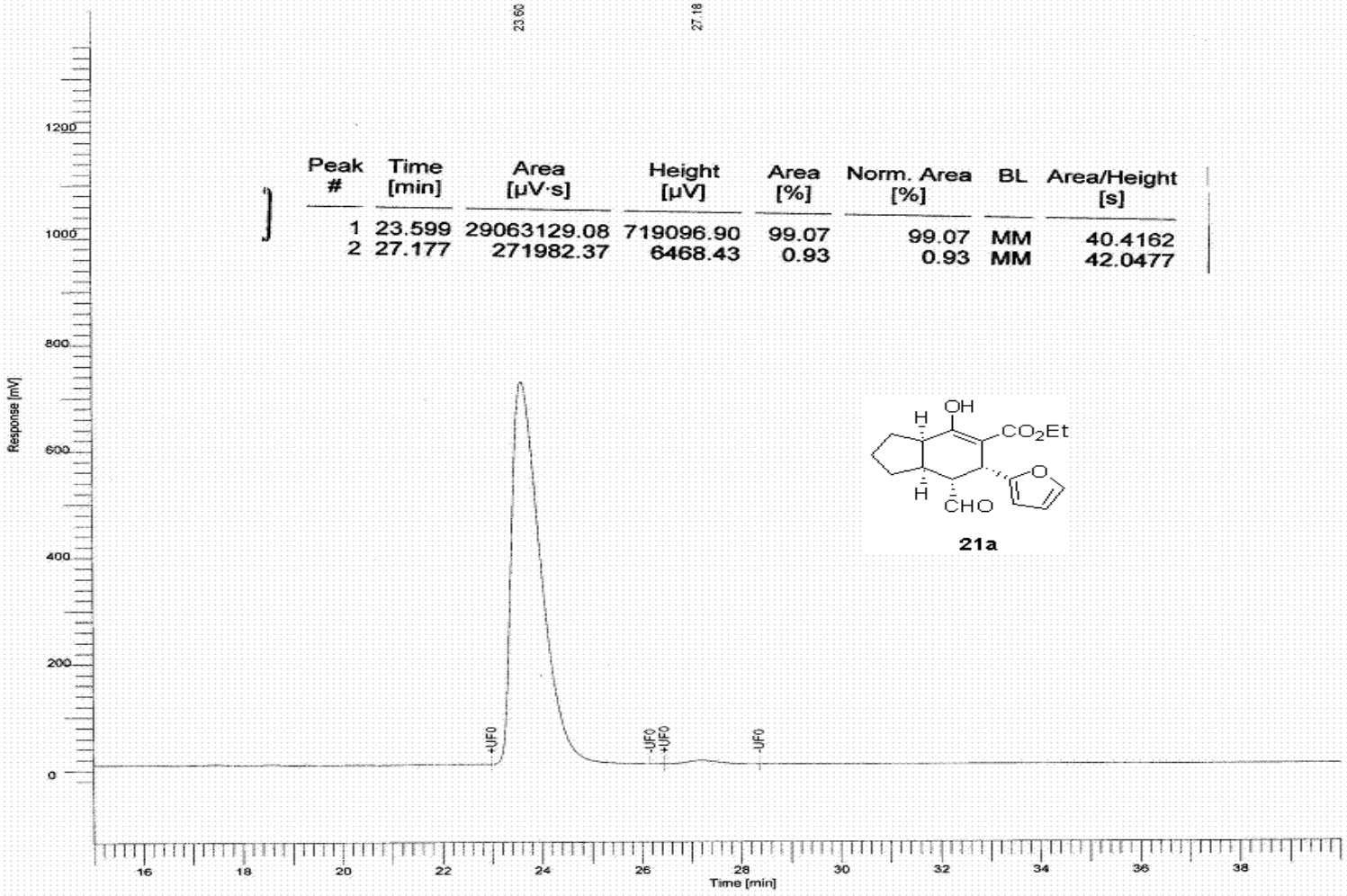
21a


200
180
160
140
120
100
80
60
40
20
0
ppm



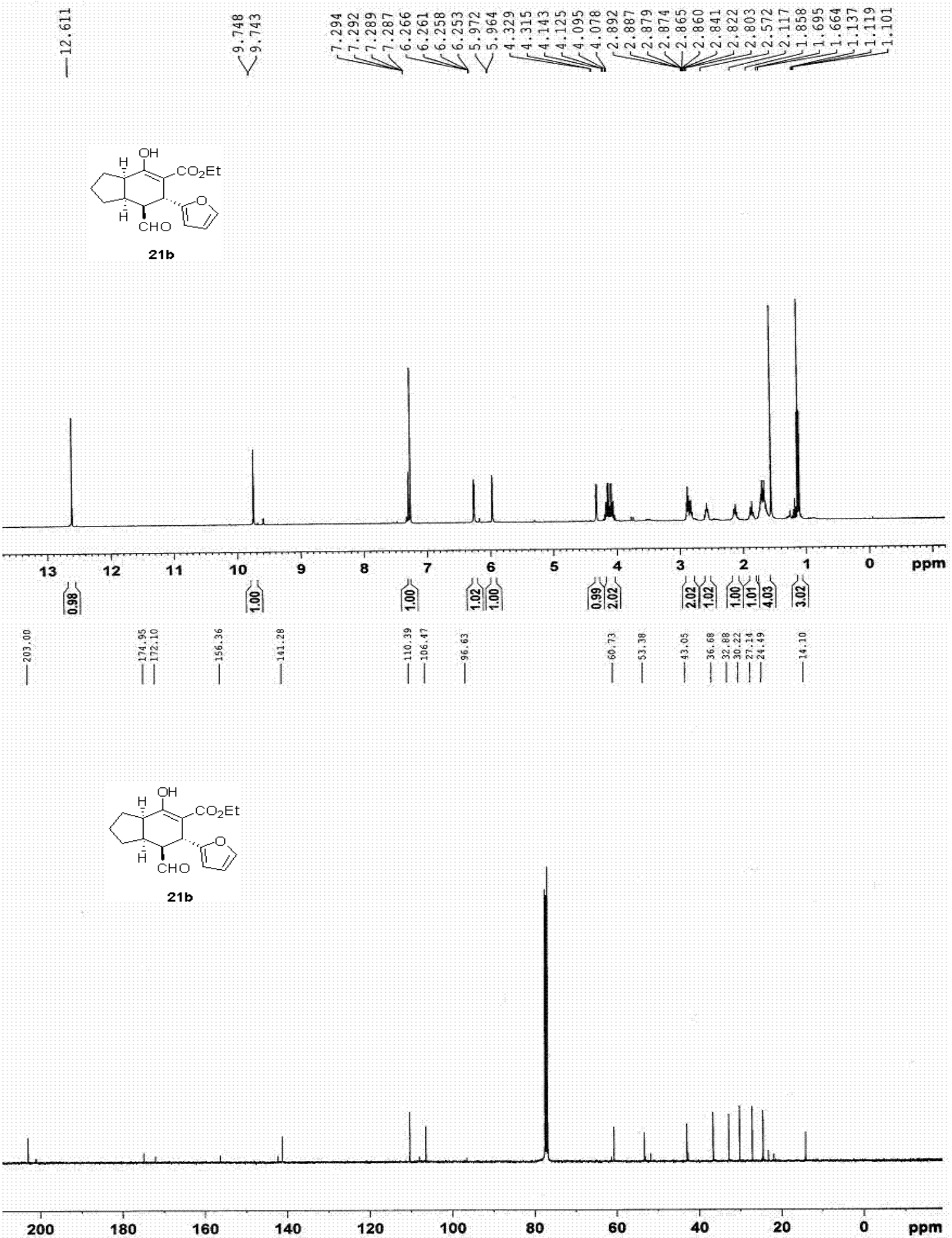
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	23.621	26892924.28	693550.33	49.71	49.71	MM	38.7757
2	26.613	27209008.78	497810.67	50.29	50.29	MM	54.6573

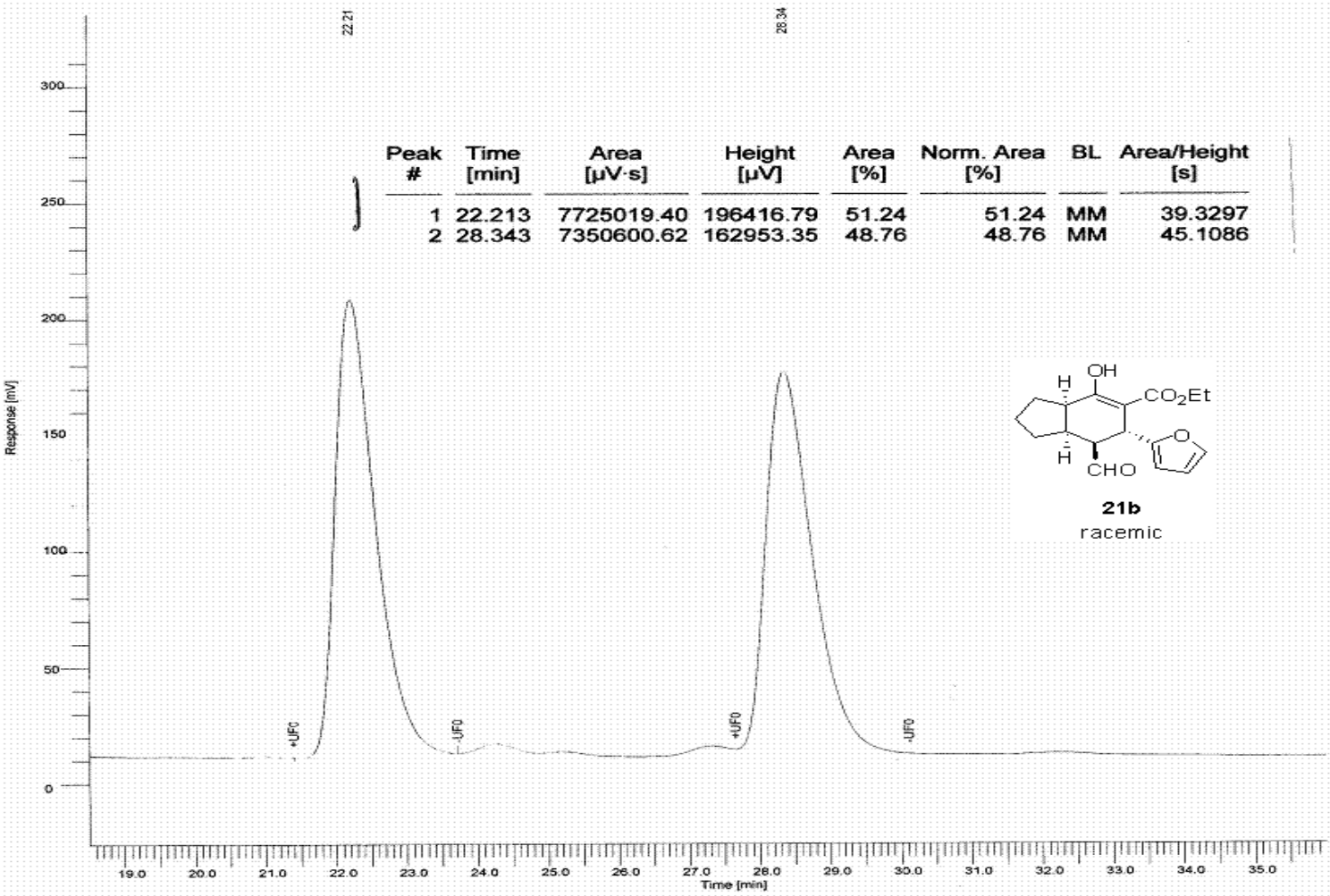
21a
racemic



Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	23.599	29063129.08	719096.90	99.07	99.07	MM	40.4162
2	27.177	271982.37	6468.43	0.93	0.93	MM	42.0477

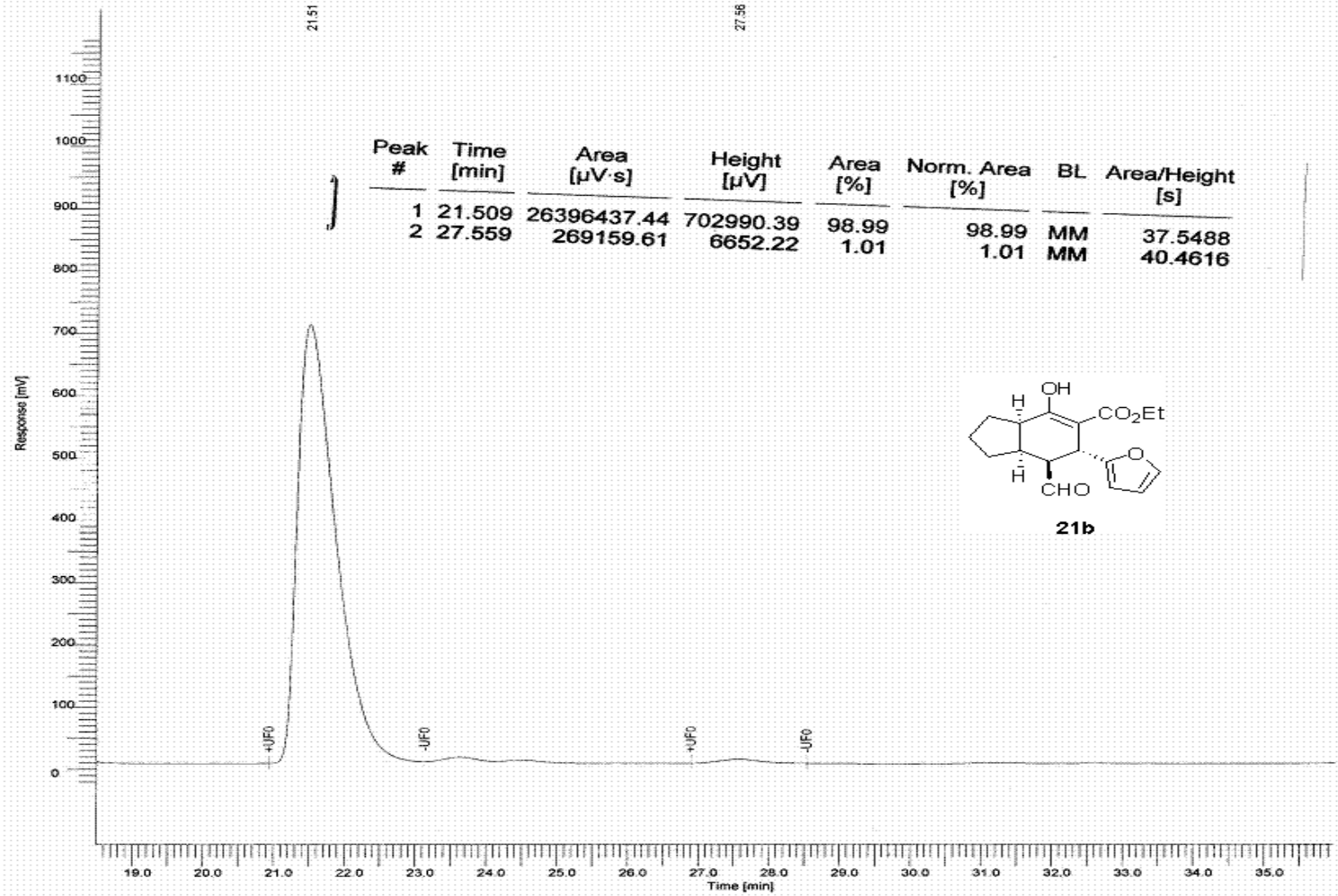
21a


12.611
9.748
9.743
7.294
7.292
7.289
7.287
6.266
6.261
6.258
6.253
5.972
5.964
4.329
4.315
4.143
4.125
4.095
4.078
2.892
2.887
2.879
2.874
2.865
2.860
2.841
2.822
2.803
2.572
2.117
1.858
1.695
1.664
1.137
1.119
1.101
OH
H
CO2Et
O
H
CHO
21b
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
0.98
1.00
1.00
1.02
1.00
0.99
2.02
2.02
1.02
1.00
1.01
4.03
3.02
203.00
174.95
172.10
156.36
141.28
110.39
106.47
96.63
60.73
53.38
43.05
36.68
32.88
30.22
27.14
24.49
14.10
OH
H
CO2Et
O
H
CHO
21b
200
180
160
140
120
100
80
60
40
20
0
ppm



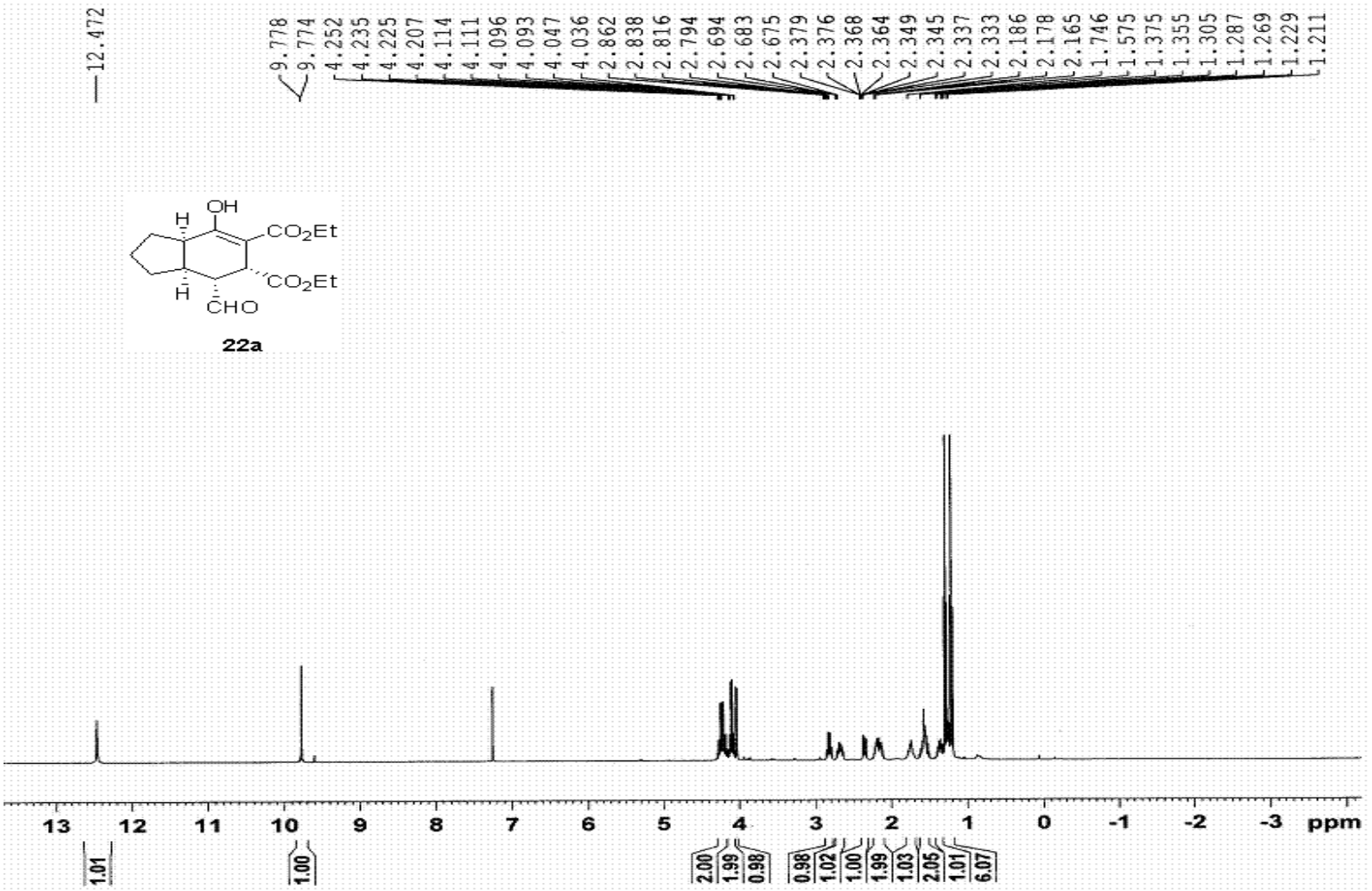
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	22.213	7725019.40	196416.79	51.24	51.24	MM	39.3297
2	28.343	7350600.62	162953.35	48.76	48.76	MM	45.1086

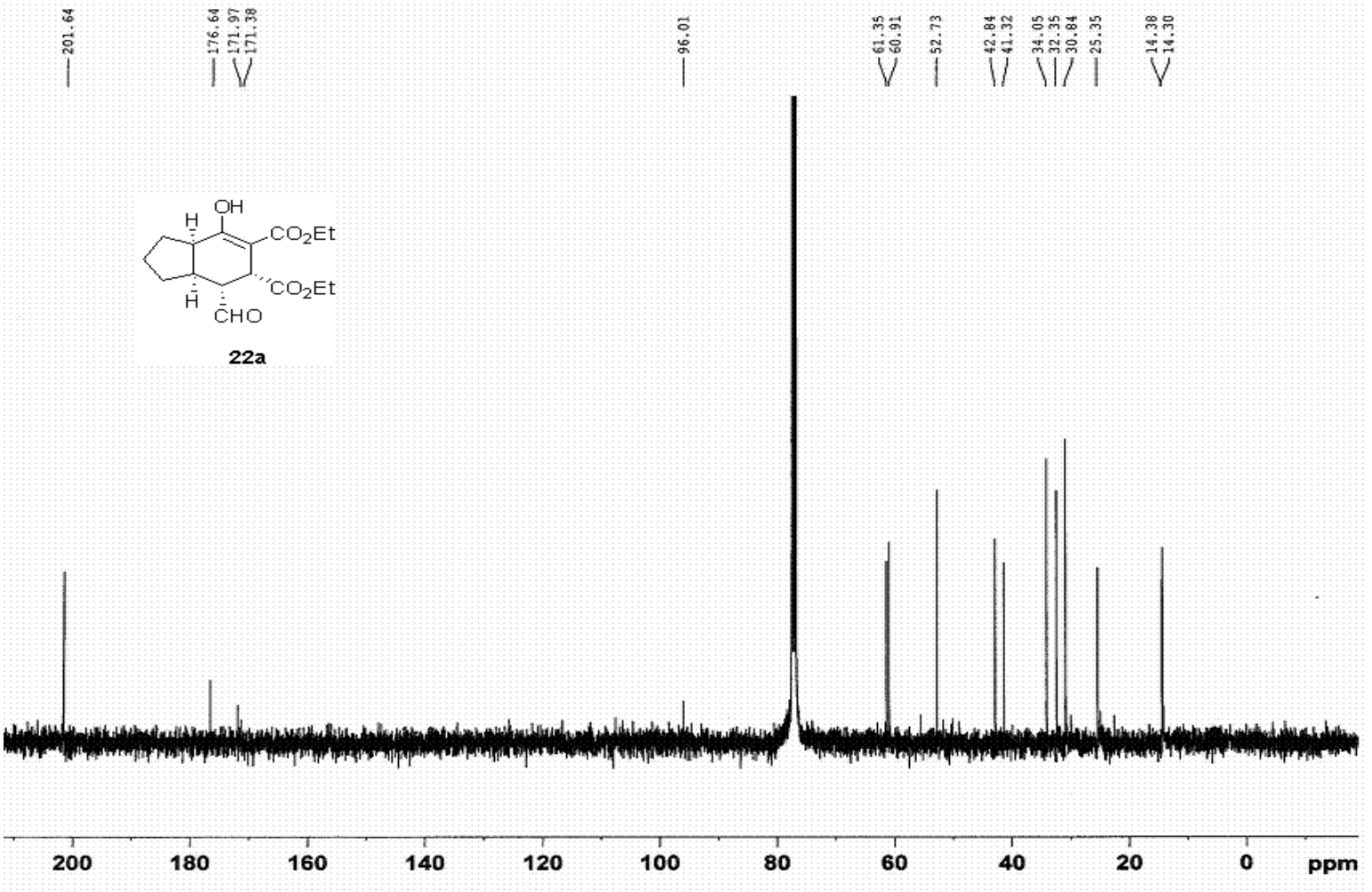
21b
racemic

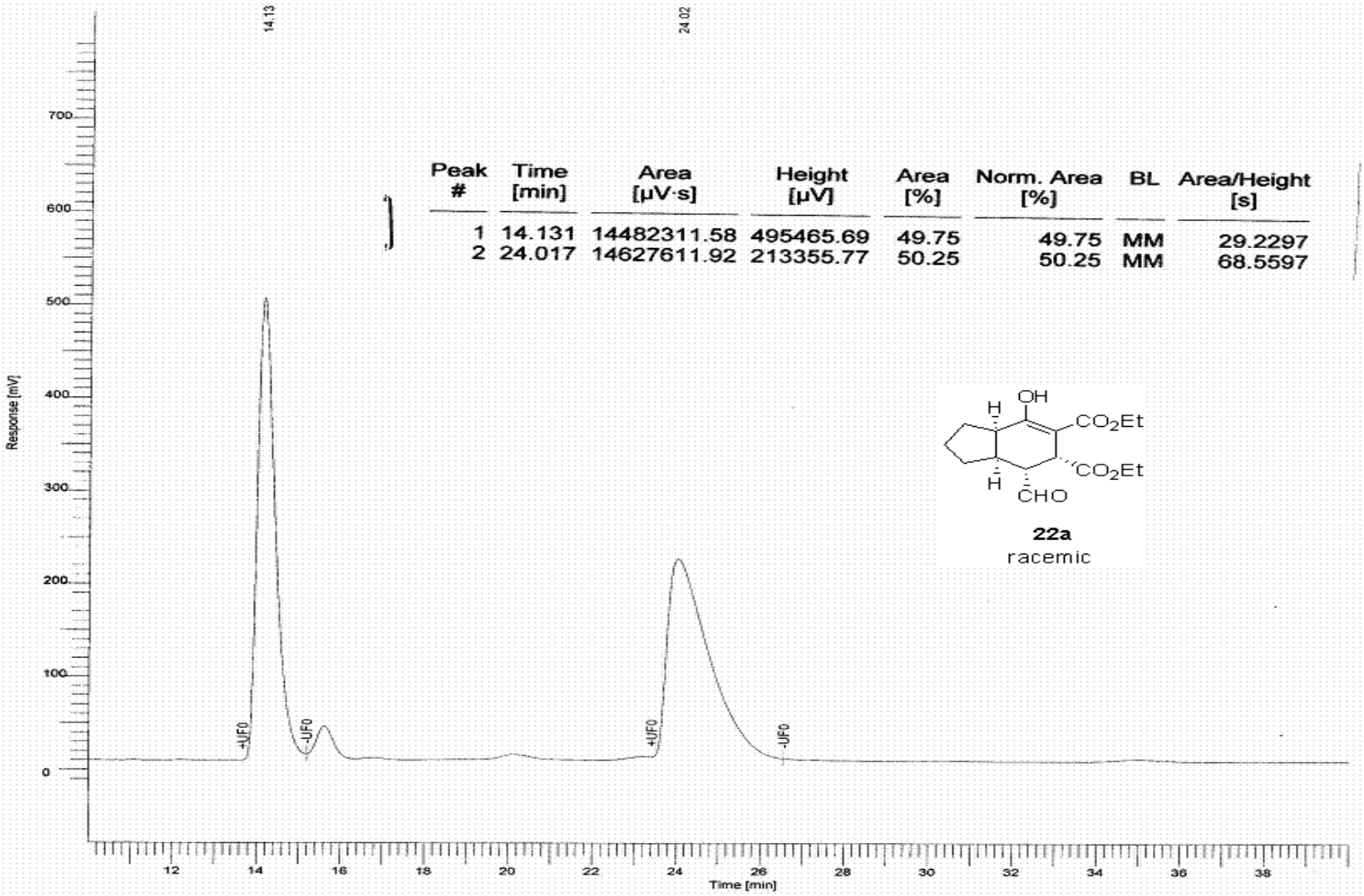


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	21.509	26396437.44	702990.39	98.99	98.99	MM	37.5488
2	27.559	269159.61	6652.22	1.01	1.01	MM	40.4616

21b

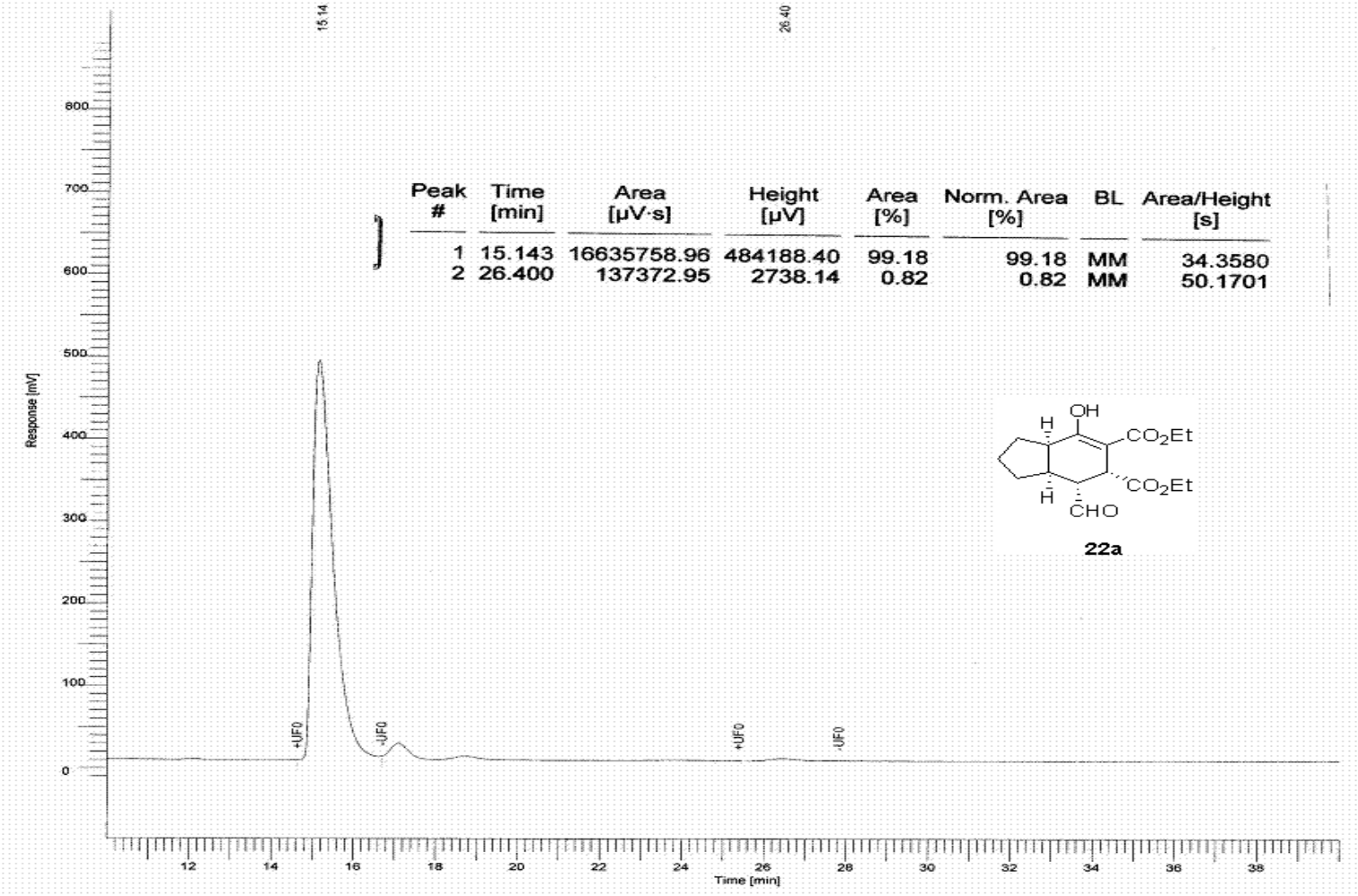

12.472
9.778
9.774
4.252
4.235
4.225
4.207
4.114
4.111
4.096
4.093
4.047
4.036
2.862
2.838
2.816
2.794
2.694
2.683
2.675
2.379
2.376
2.368
2.364
2.349
2.345
2.337
2.333
2.186
2.178
2.165
1.746
1.575
1.375
1.355
1.305
1.287
1.269
1.229
1.211
OH
CO2Et
CO2Et
CHO
22a
13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 ppm
1.01
1.00
2.00
1.99
0.98
0.98
1.02
1.00
1.99
1.03
2.05
1.01
6.07


201.64
176.64
171.97
171.38
96.01
61.35
60.91
52.73
42.84
41.32
34.05
32.35
30.84
25.35
14.38
14.30
OH
CO2Et
CO2Et
CHO
22a
200 180 160 140 120 100 80 60 40 20 0 ppm



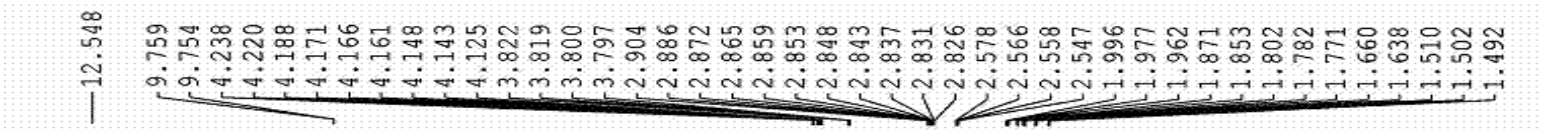
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	14.131	14482311.58	495465.69	49.75	49.75	MM	29.2297
2	24.017	14627611.92	213355.77	50.25	50.25	MM	68.5597

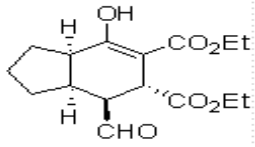
22a
racemic



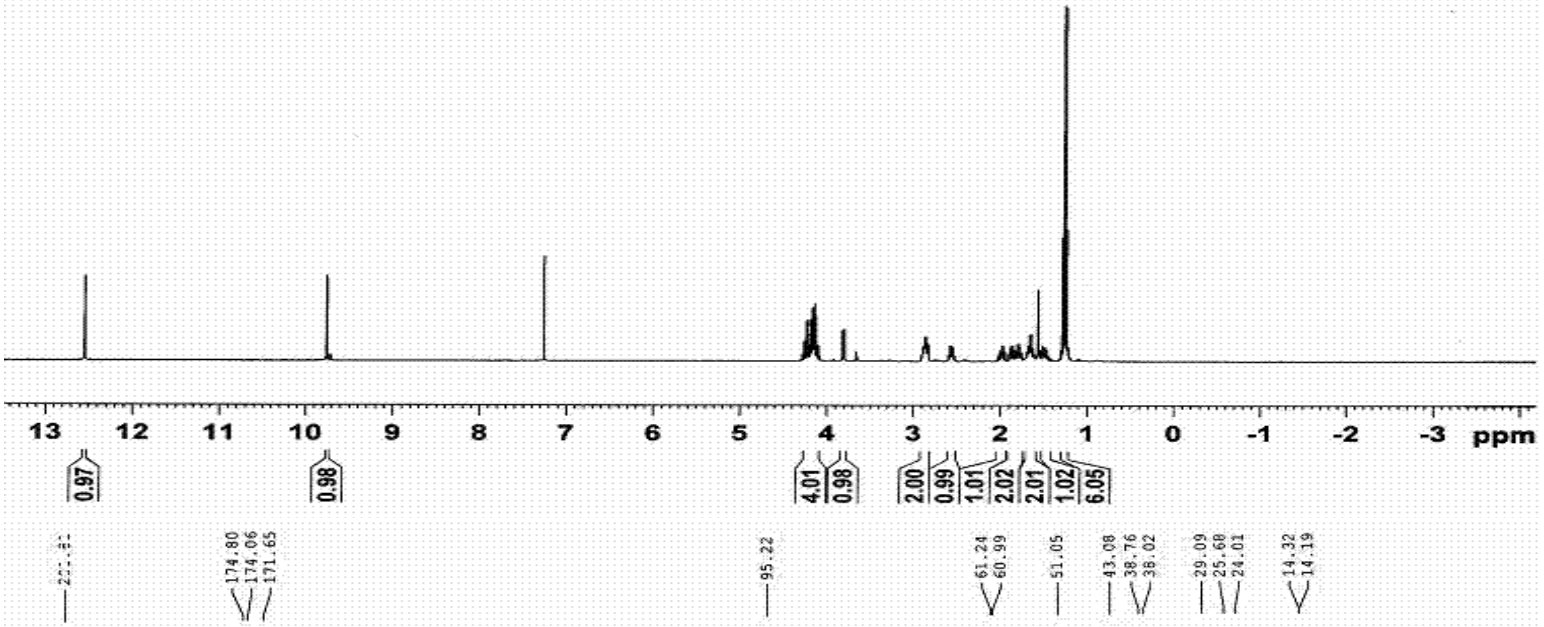
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	15.143	16635758.96	484188.40	99.18	99.18	MM	34.3580
2	26.400	137372.95	2738.14	0.82	0.82	MM	50.1701

22a

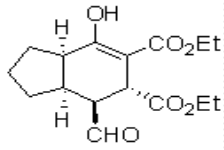

12.548
9.759
9.754
4.238
4.220
4.188
4.171
4.166
4.161
4.148
4.143
4.125
3.822
3.819
3.800
3.797
2.904
2.886
2.872
2.865
2.859
2.853
2.848
2.843
2.837
2.831
2.826
2.578
2.566
2.558
2.547
1.996
1.977
1.962
1.871
1.853
1.802
1.782
1.771
1.660
1.638
1.510
1.502
1.492


OH
H
CO2Et
CO2Et
H
CHO

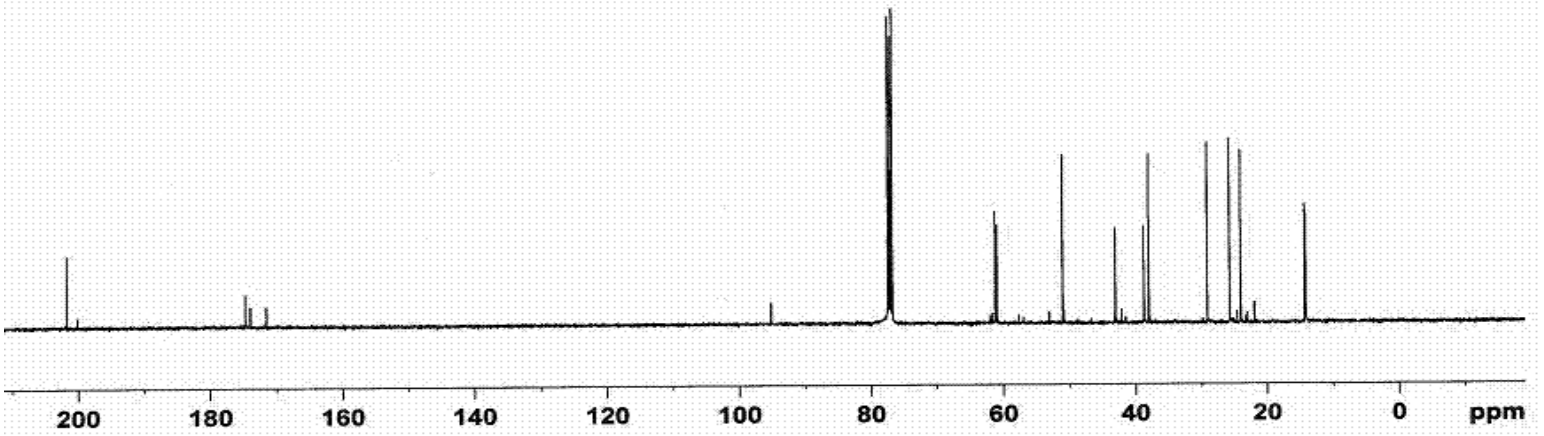
22b

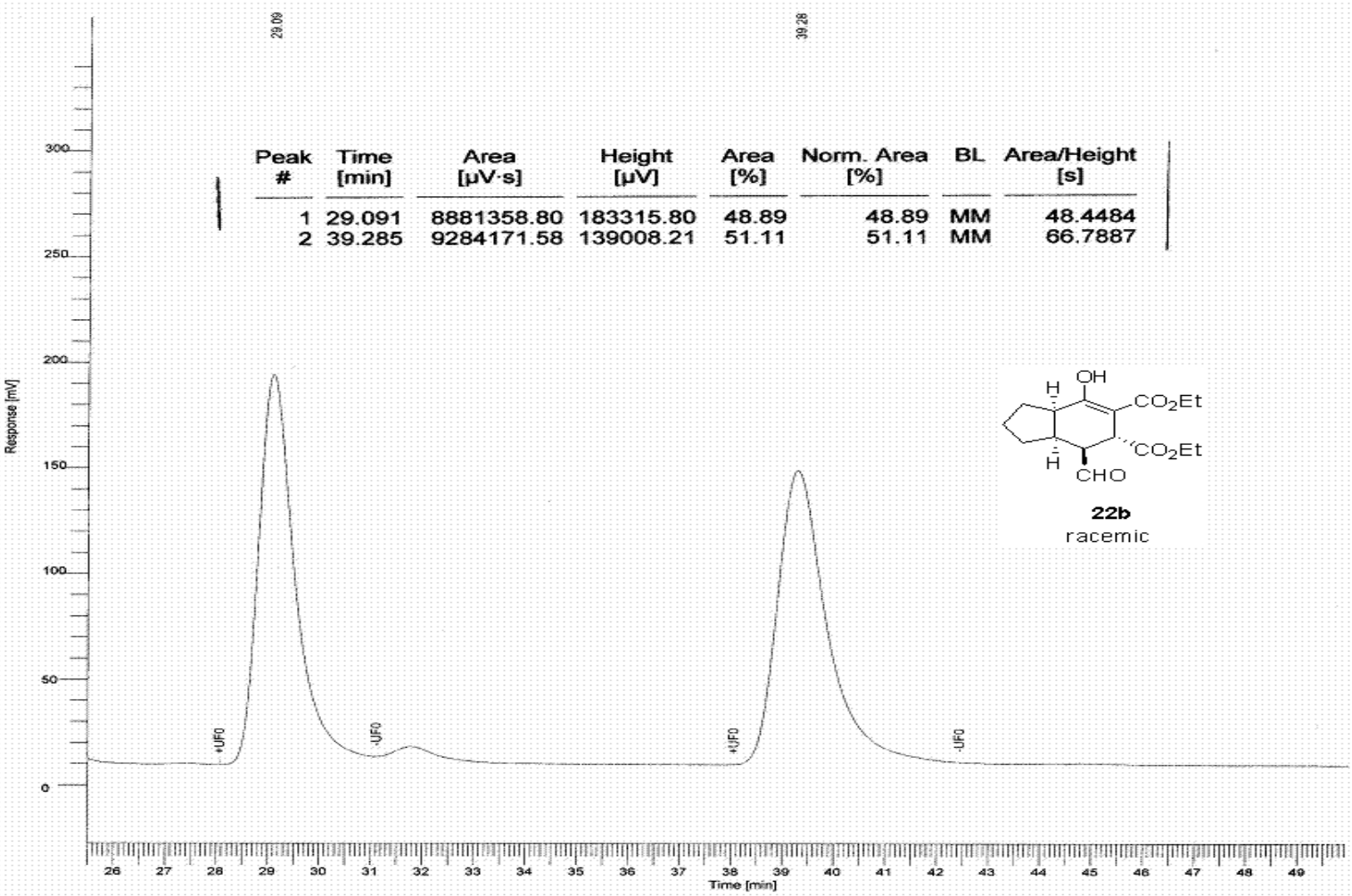

13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
0.97
0.98
4.01
0.98
2.00
0.99
1.01
2.02
2.01
1.02
6.05

174.80
174.06
171.65
95.22
61.24
60.99
51.05
43.08
38.76
38.02
29.09
25.60
24.01
14.32
14.19


OH
H
CO2Et
CO2Et
H
CHO

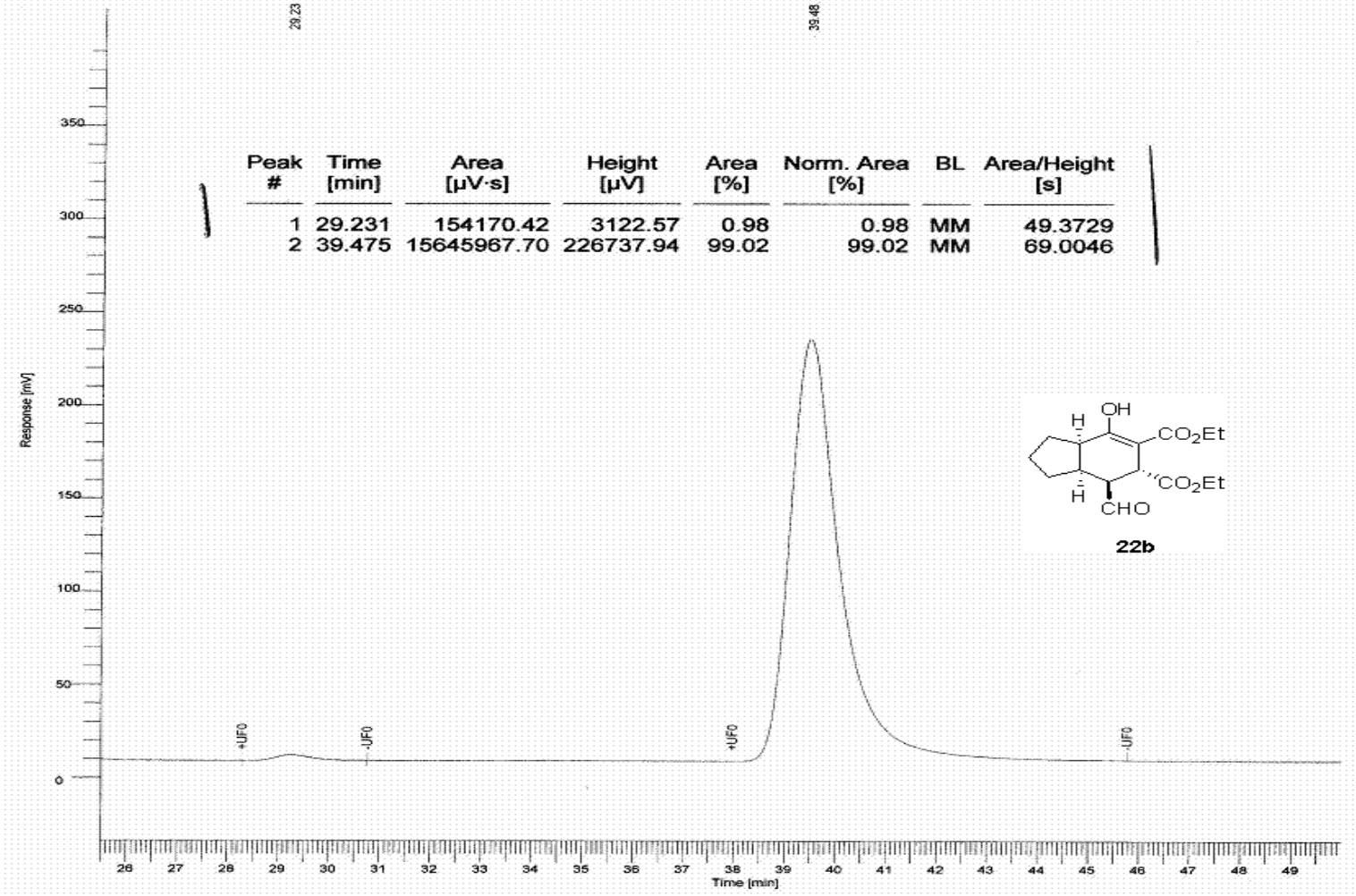
22b


200
180
160
140
120
100
80
60
40
20
0
ppm



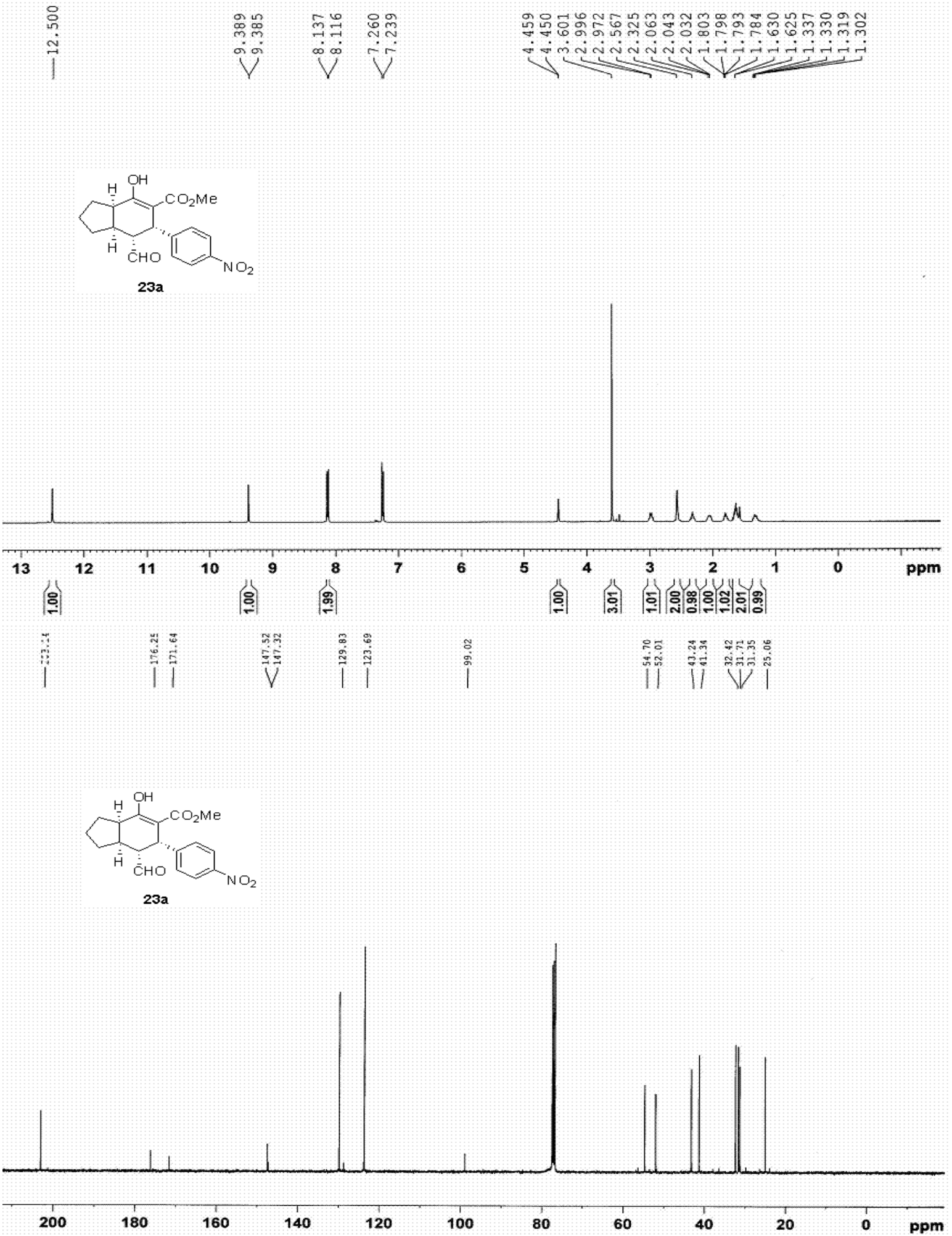
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	29.091	8881358.80	183315.80	48.89	48.89	MM	48.4484
2	39.285	9284171.58	139008.21	51.11	51.11	MM	66.7887

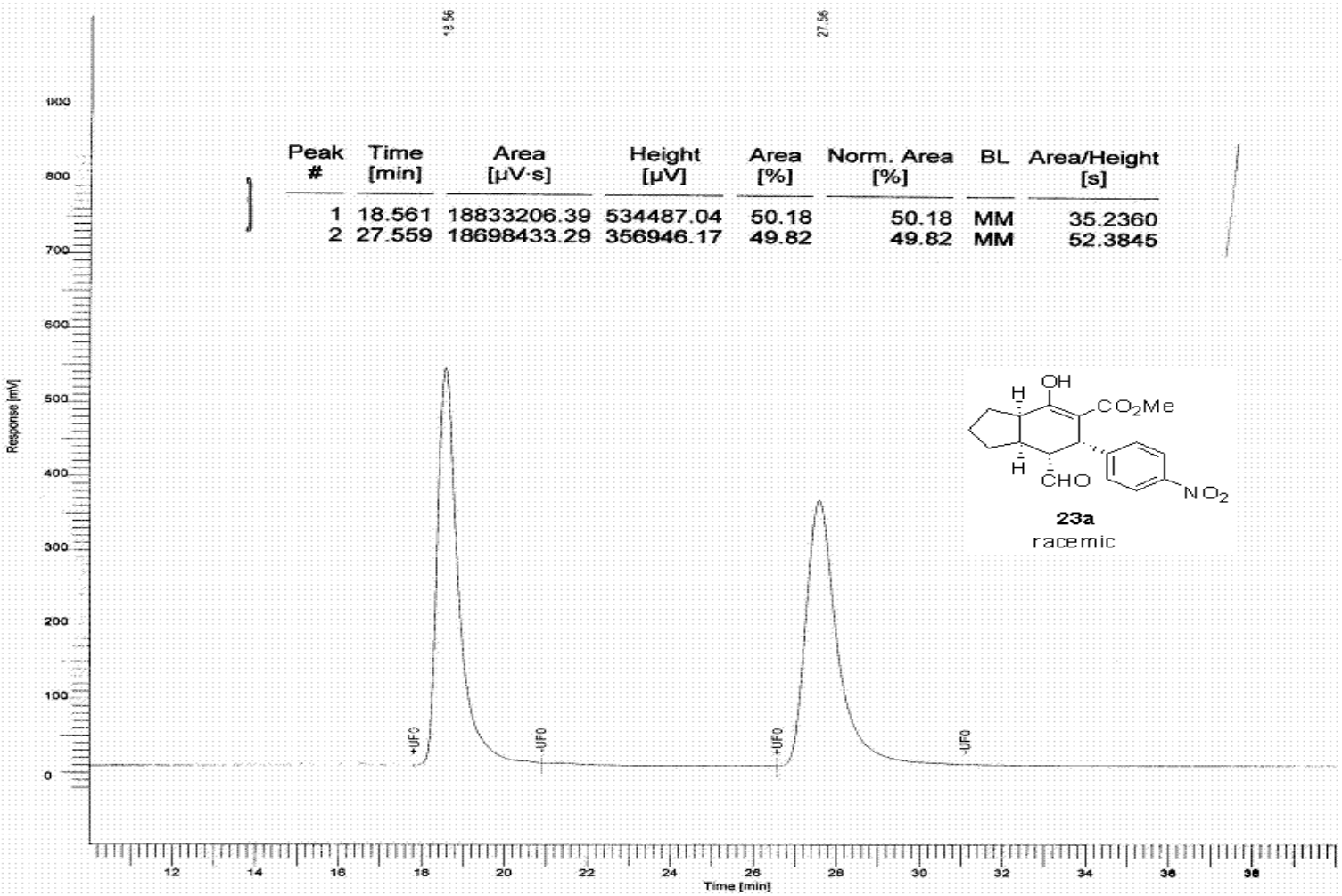
22b
racemic



Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	29.231	154170.42	3122.57	0.98	0.98	MM	49.3729
2	39.475	15645967.70	226737.94	99.02	99.02	MM	69.0046

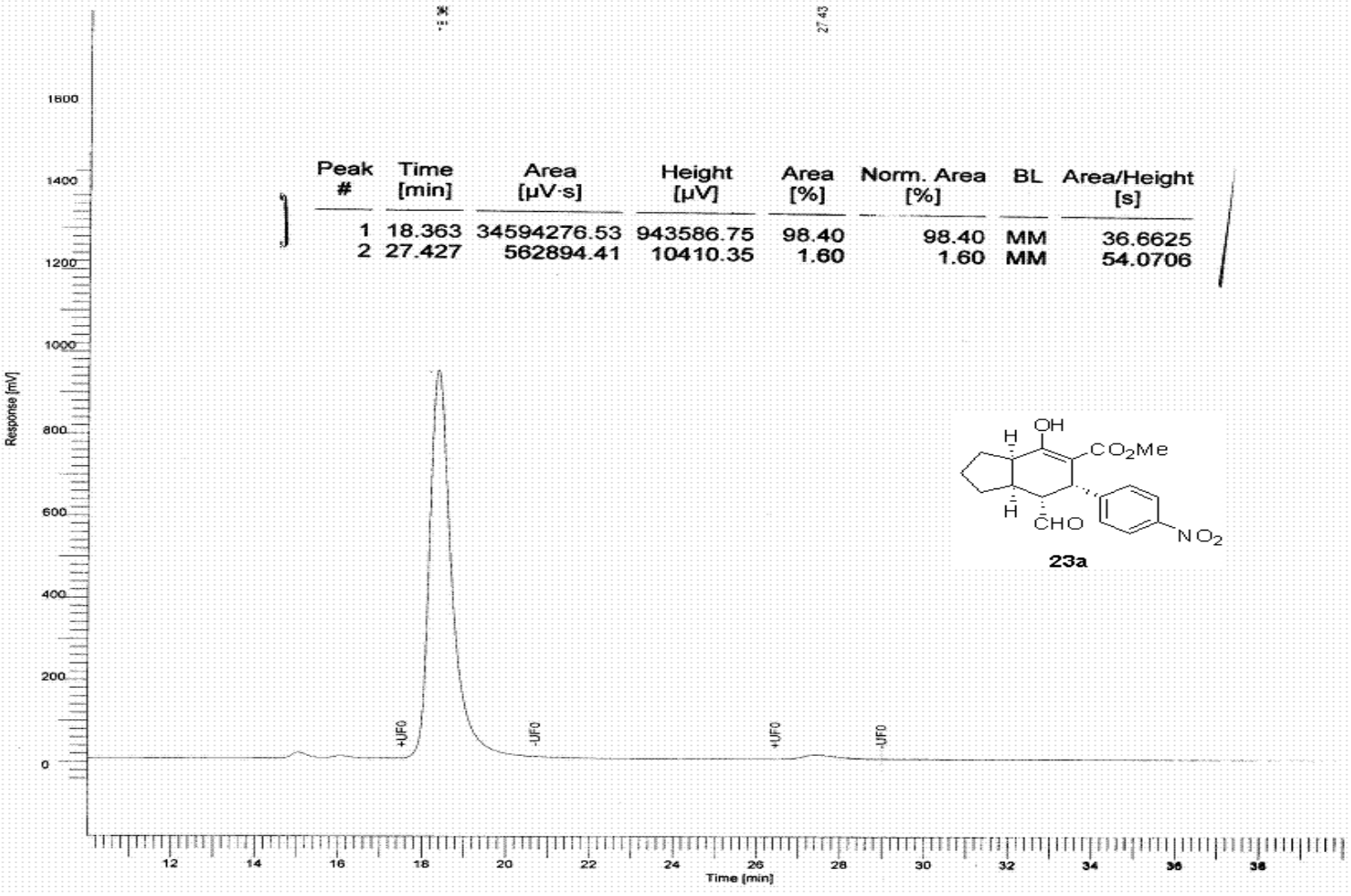
22b


12.500
9.389
9.385
8.137
8.116
7.260
7.239
4.459
4.450
3.601
2.996
2.972
2.567
2.325
2.063
2.043
2.032
1.803
1.798
1.793
1.784
1.630
1.625
1.337
1.330
1.319
1.302
OH
CO2Me
H
H
CHO
NO2
23a
13
12
11
10
9
8
7
6
5
4
3
2
1
0
ppm
1.00
1.00
1.99
1.00
3.01
1.01
2.00
0.98
1.00
1.02
2.01
0.99
176.25
171.64
147.52
147.32
129.83
123.69
99.02
54.70
52.01
43.24
41.34
32.42
31.71
31.35
25.06
OH
CO2Me
H
H
CHO
NO2
23a
200
180
160
140
120
100
80
60
40
20
0
ppm



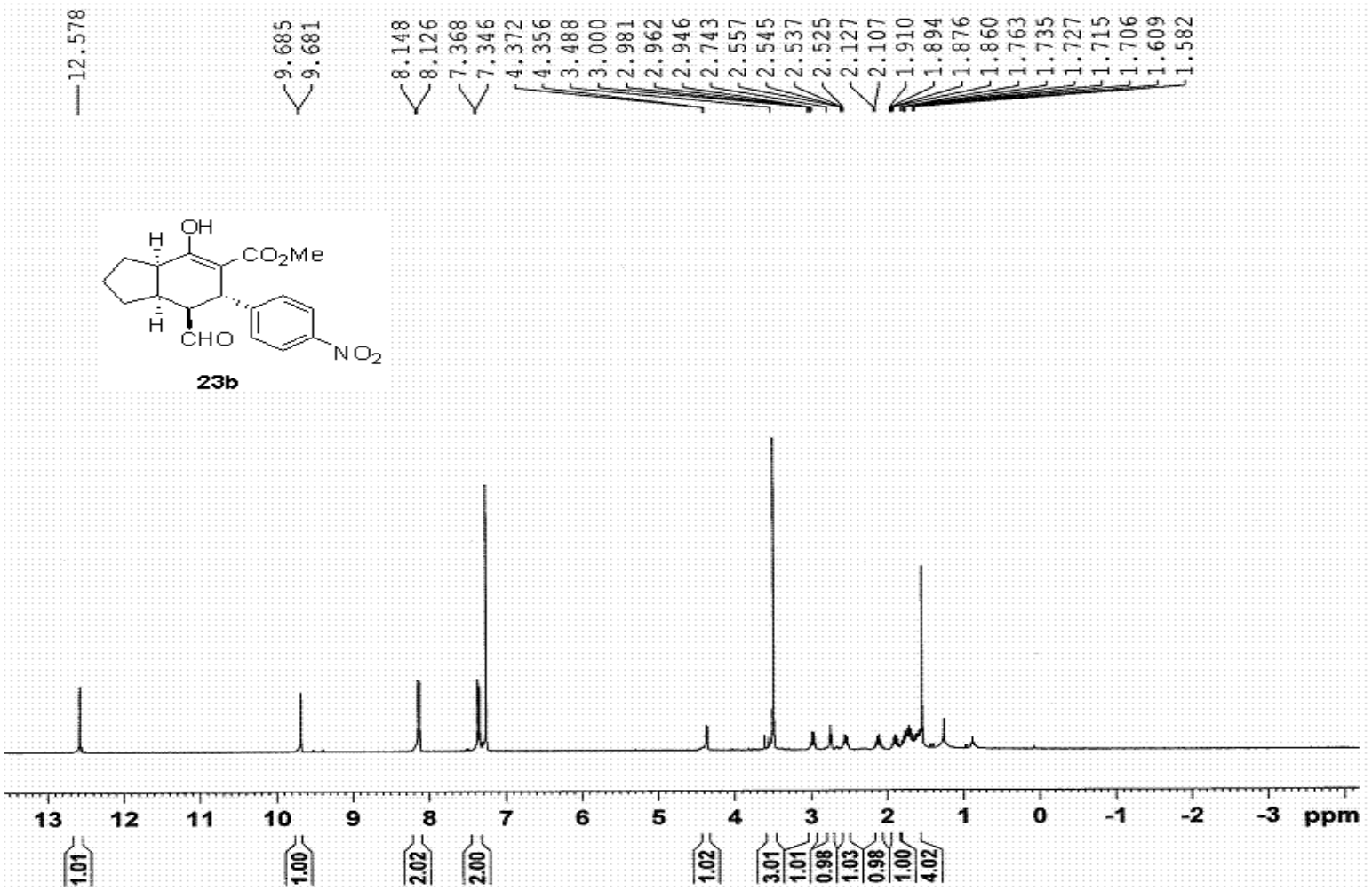
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	18.561	18833206.39	534487.04	50.18	50.18	MM	35.2360
2	27.559	18698433.29	356946.17	49.82	49.82	MM	52.3845

23a
racemic



Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	18.363	34594276.53	943586.75	98.40	98.40	MM	36.6625
2	27.427	562894.41	10410.35	1.60	1.60	MM	54.0706

23a


12.578
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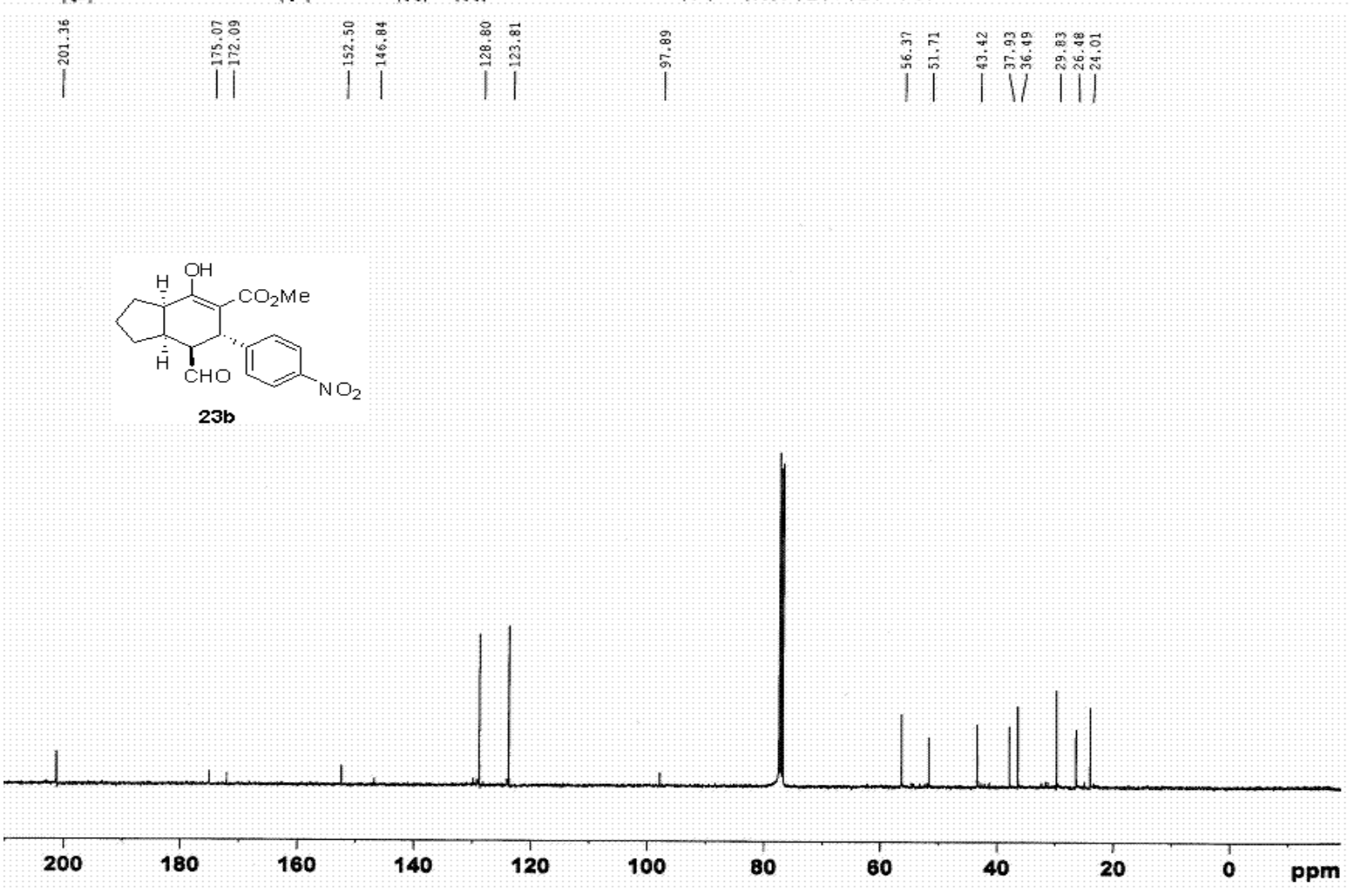
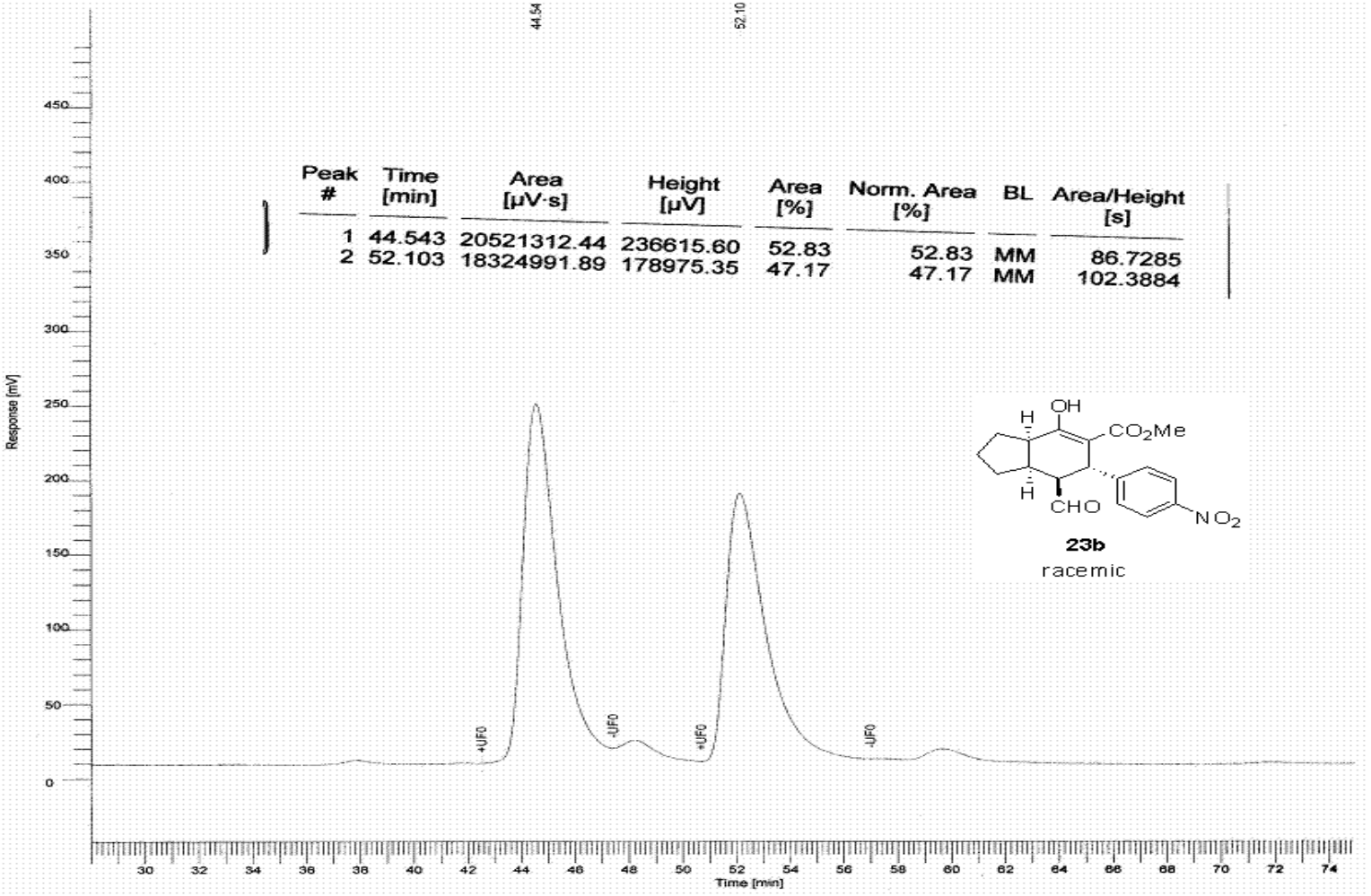
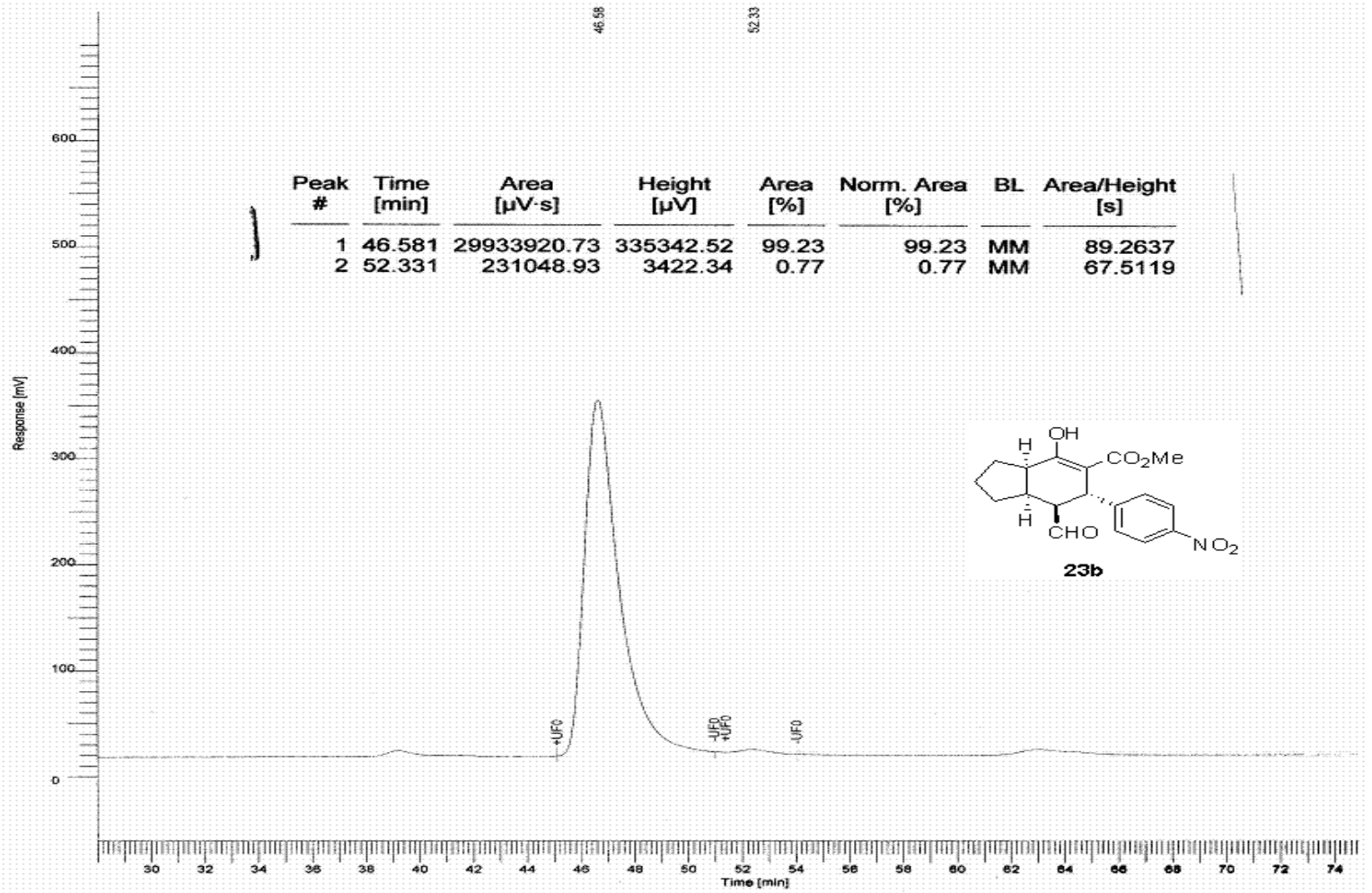
8.148
8.126
7.368
7.346
4.372
4.356
3.488
3.000
2.981
2.962
2.946
2.743
2.557
2.545
2.537
2.525
2.127
2.107
1.910
1.894
1.876
1.860
1.763
1.735
1.727
1.715
1.706
1.609
1.582
OH
H
CO2Me
H
CHO
NO2
23b
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
ppm
1.01
1.00
2.02
2.00
1.02
3.01
1.01
0.98
1.03
0.98
1.00
4.02


201.36
175.07
172.09
152.50
146.84
128.80
123.81
97.89
56.37
51.71
43.42
37.93
36.49
29.83
26.48
24.01
OH
H
CO2Me
H
CHO
NO2
23b
200
180
160
140
120
100
80
60
40
20
0
ppm



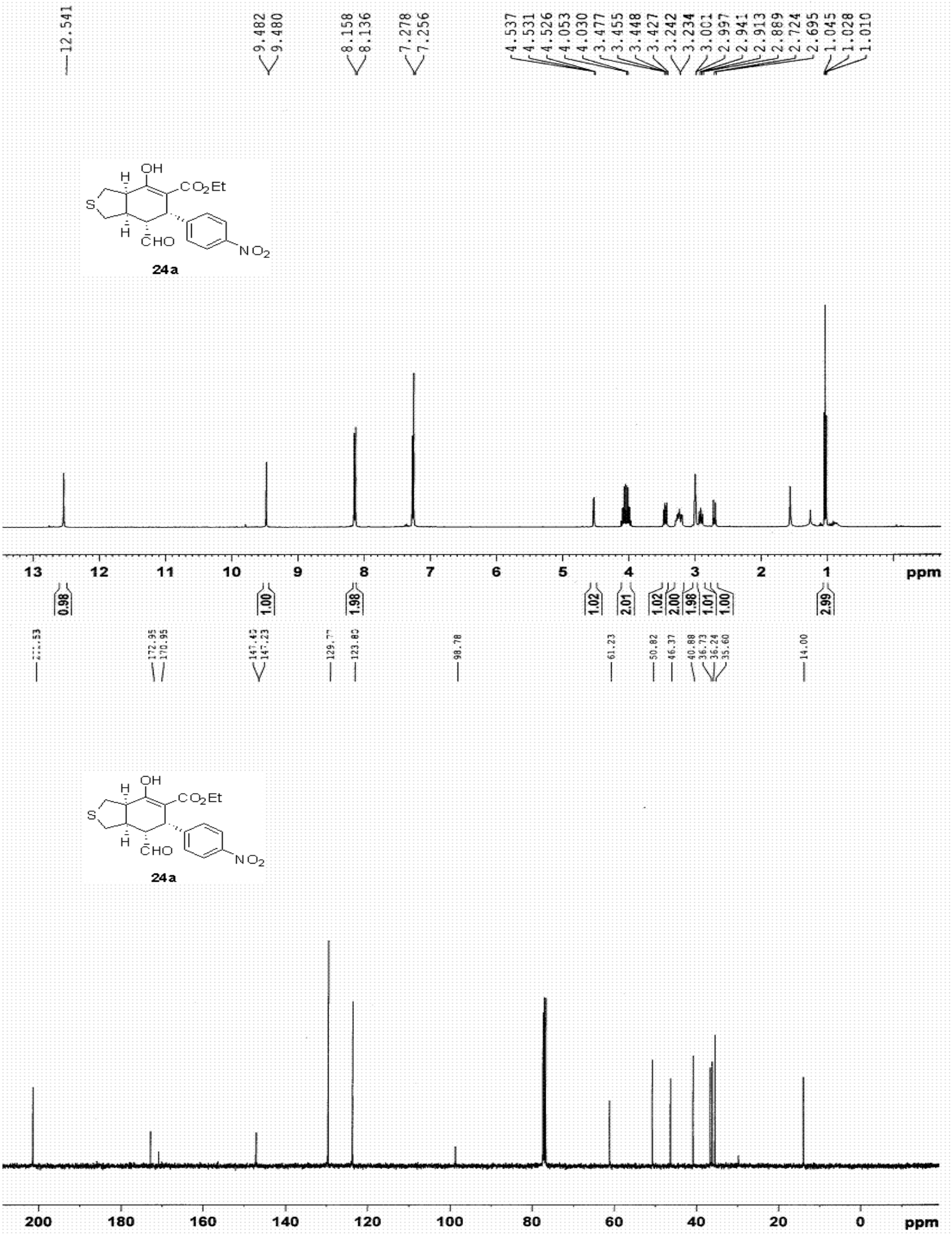
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	44.543	20521312.44	236615.60	52.83	52.83	MM	86.7285
2	52.103	18324991.89	178975.35	47.17	47.17	MM	102.3884

23b
racemic

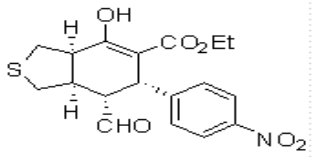


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	46.581	29933920.73	335342.52	99.23	99.23	MM	89.2637
2	52.331	231048.93	3422.34	0.77	0.77	MM	67.5119

23b

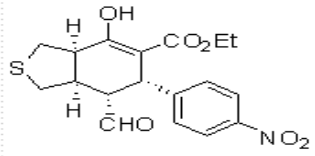

12.541
9.482
9.480
8.158
8.136
7.278
7.256
4.537
4.531
4.526
4.053
4.030
3.477
3.455
3.448
3.427
3.242
3.234
3.001
2.997
2.941
2.913
2.889
2.724
2.695
1.045
1.028
1.010
OH
H
CO2Et
S
H
CHO
NO2
24a
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.98
1.00
1.98
1.02
2.01
1.02
2.00
1.98
1.01
1.00
2.99
172.95
170.95
147.45
147.23
123.80
98.78
61.23
50.82
46.37
40.88
36.73
36.24
35.60
14.00
OH
H
CO2Et
S
H
CHO
NO2
24a
200
180
160
140
120
100
80
60
40
20
0
ppm

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	23.122	17315870.14	281069.72	52.78	52.78	MM	61.6070
2	36.725	15491219.63	149134.50	47.22	47.22	MM	103.8742

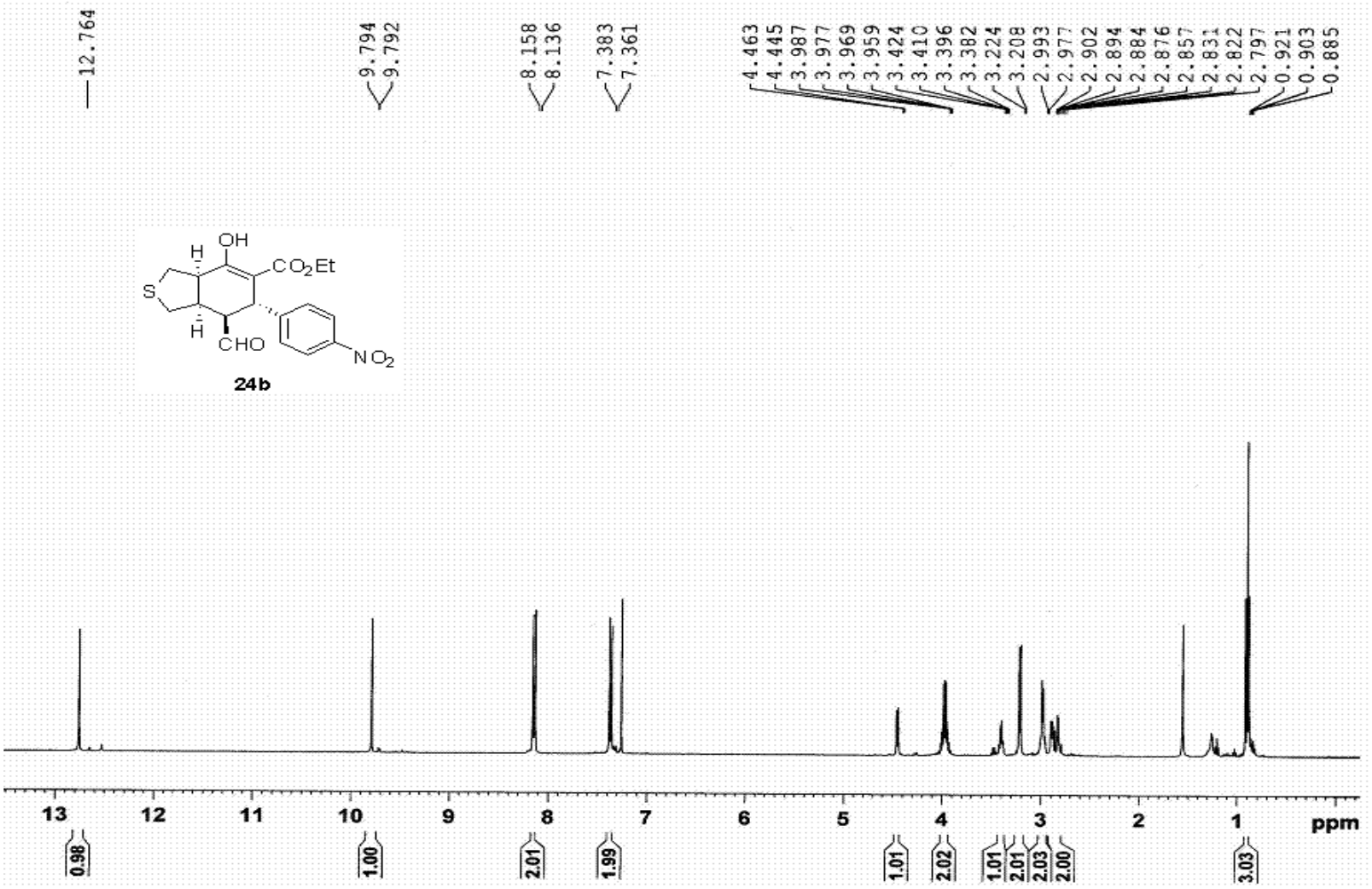


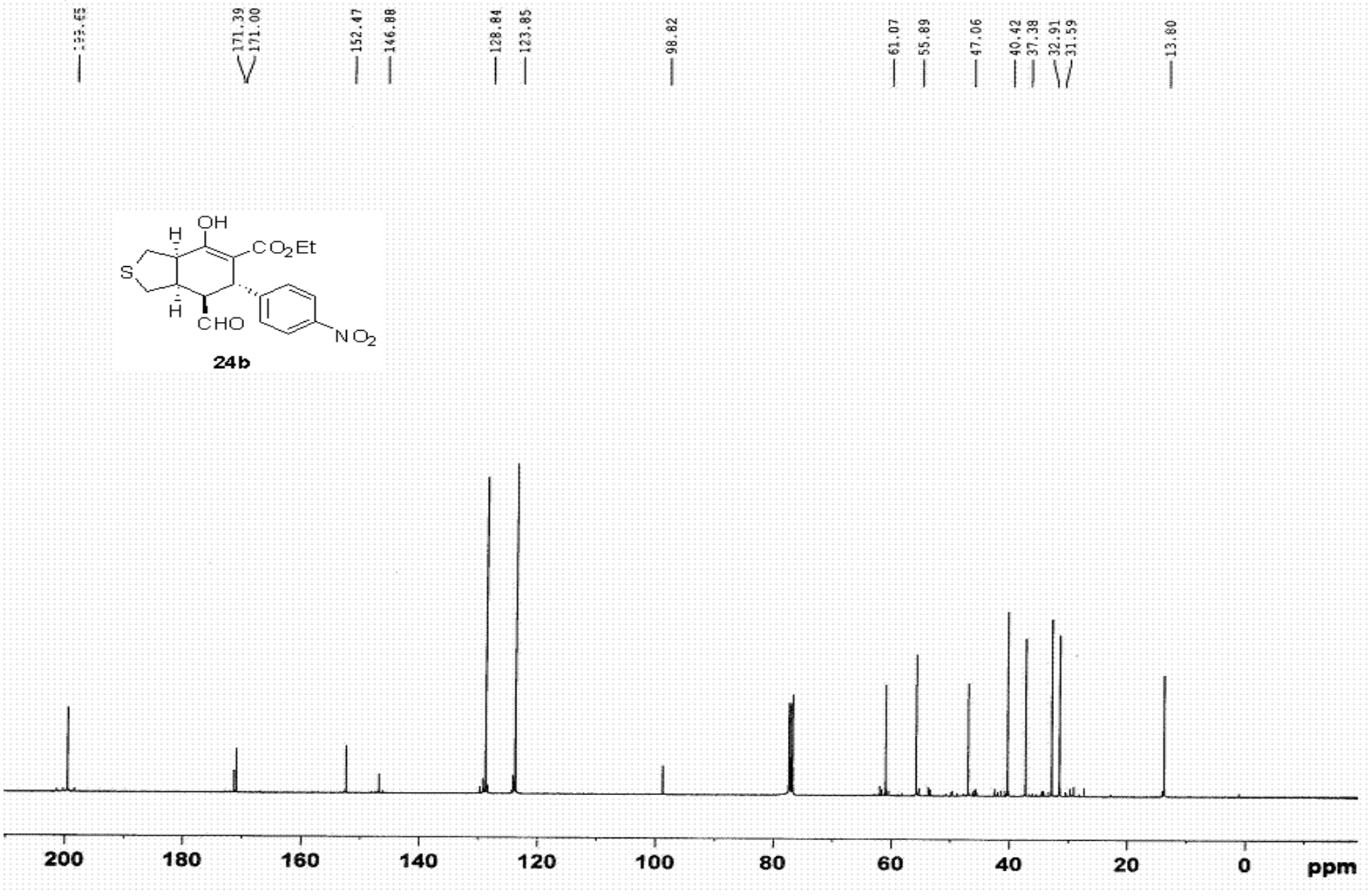
24a
racemic

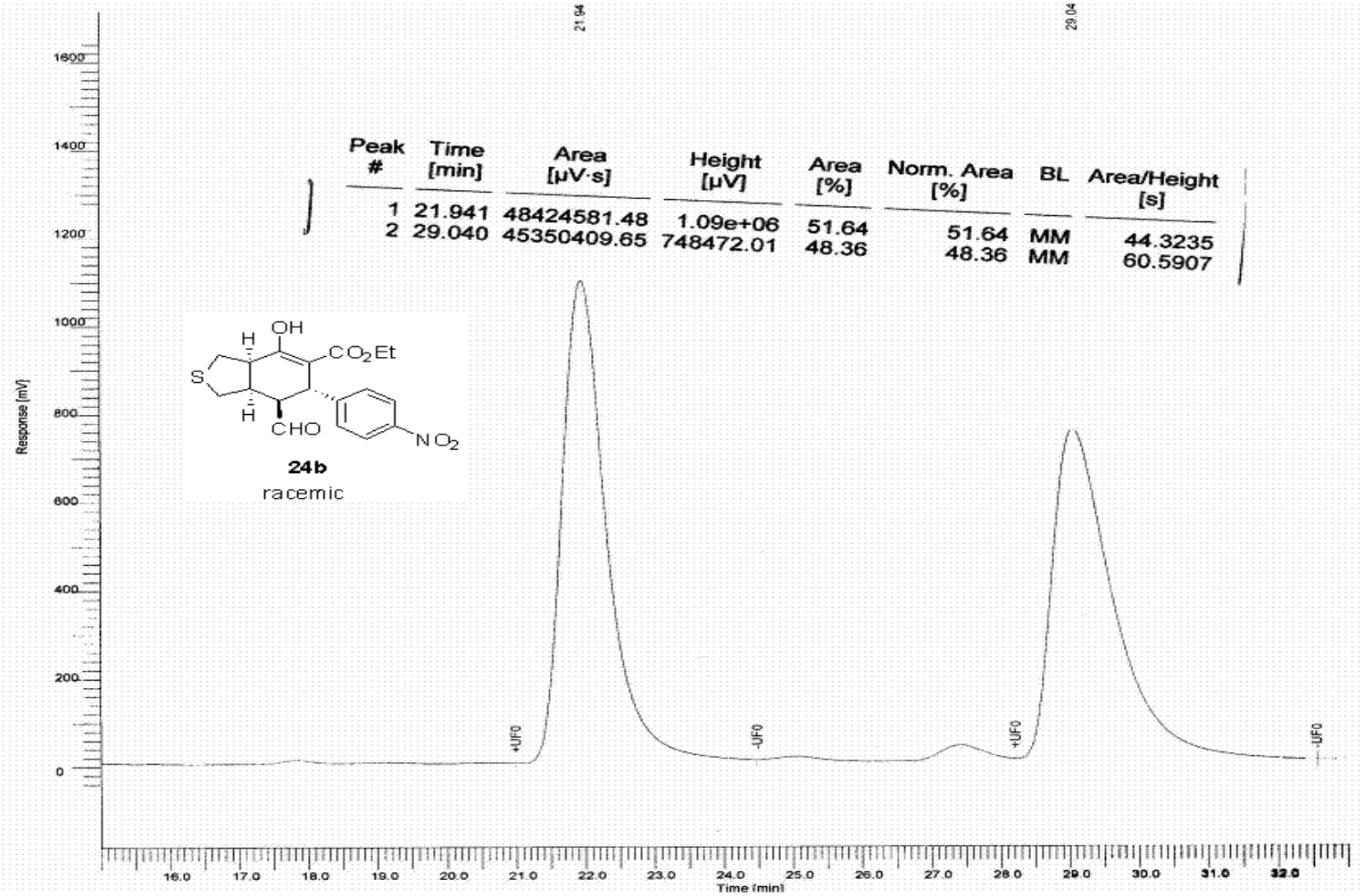
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	22.719	39791282.76	846440.76	99.06	99.06	MM	47.0101
2	35.699	378739.07	5434.19	0.94	0.94	MM	69.6956



24a

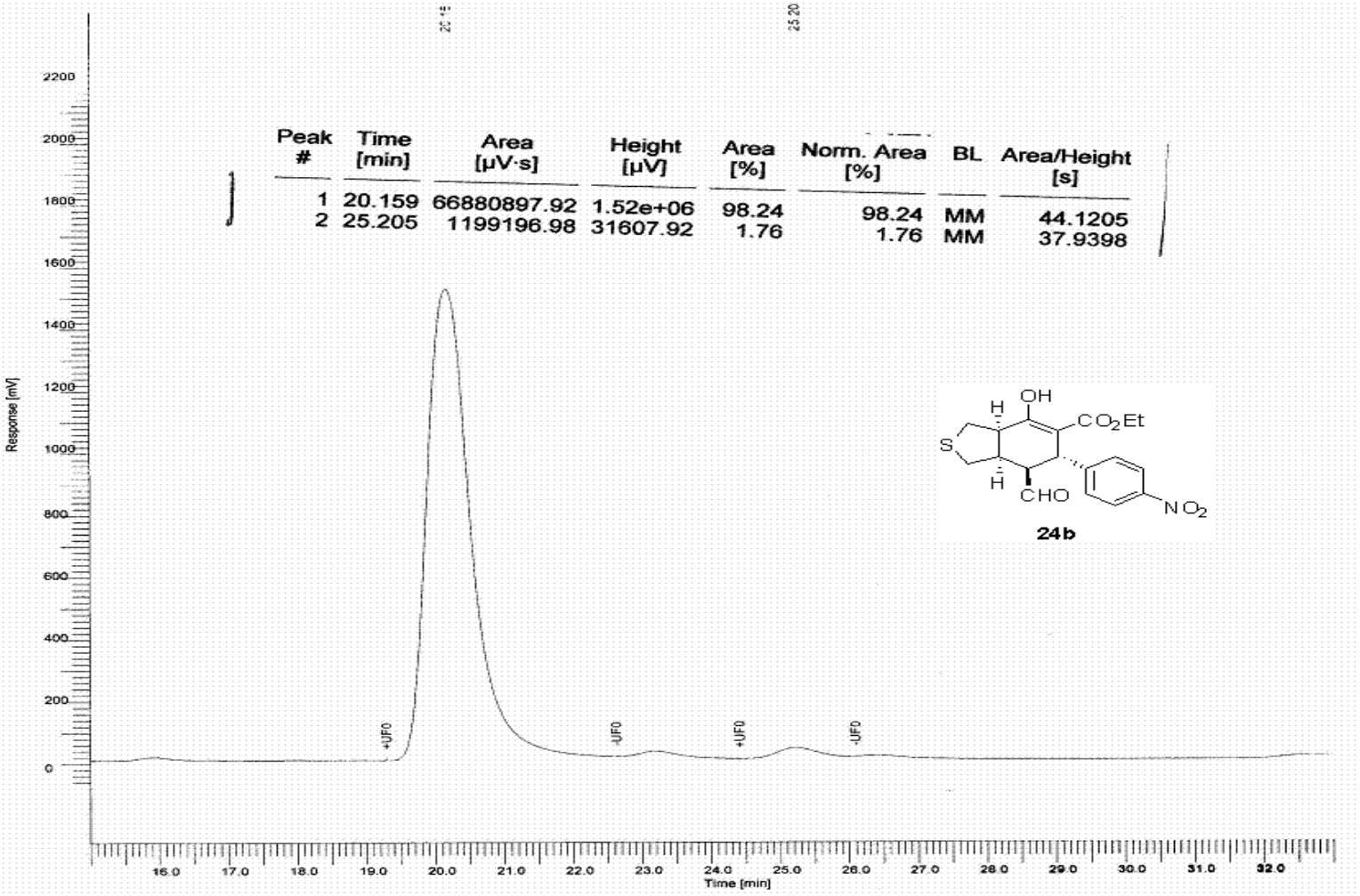

12.764
9.794
9.792
8.158
8.136
7.383
7.361
4.463
4.445
3.987
3.977
3.969
3.959
3.424
3.410
3.396
3.382
3.224
3.208
2.993
2.977
2.902
2.894
2.884
2.876
2.857
2.831
2.822
2.797
0.921
0.903
0.885
OH
H
CO2Et
S
H
CHO
NO2
24b
13
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.98
1.00
2.01
1.99
1.01
2.02
1.01
2.01
2.03
2.00
3.03


171.39
171.00
152.47
146.88
128.84
123.85
98.82
61.07
55.89
47.06
40.42
37.38
32.91
31.59
13.80
OH
H
CO2Et
S
H
CHO
NO2
24b
200
180
160
140
120
100
80
60
40
20
0
ppm



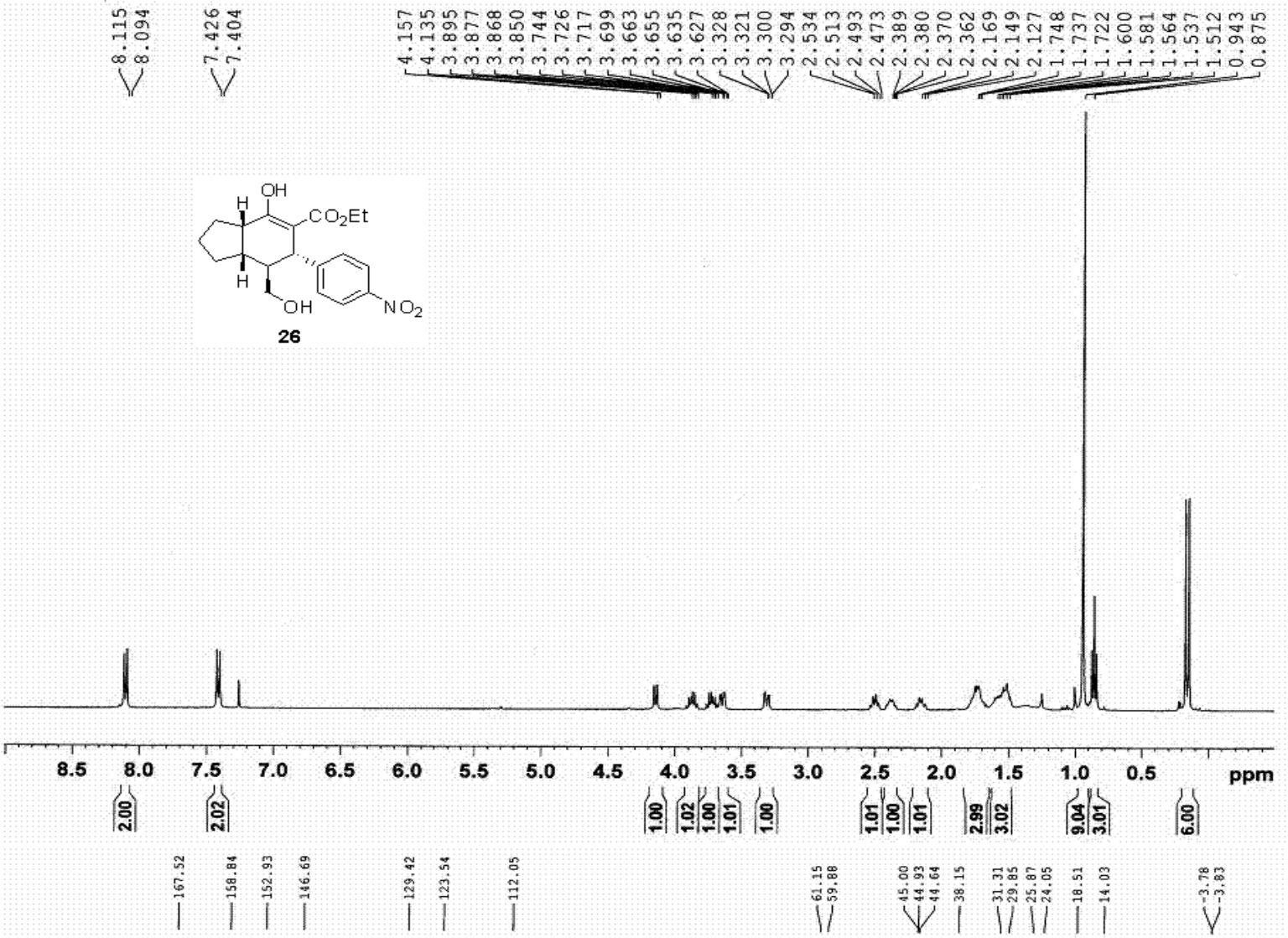
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	21.941	48424581.48	1.09e+06	51.64	51.64	MM	44.3235
2	29.040	45350409.65	748472.01	48.36	48.36	MM	60.5907

24b
racemic

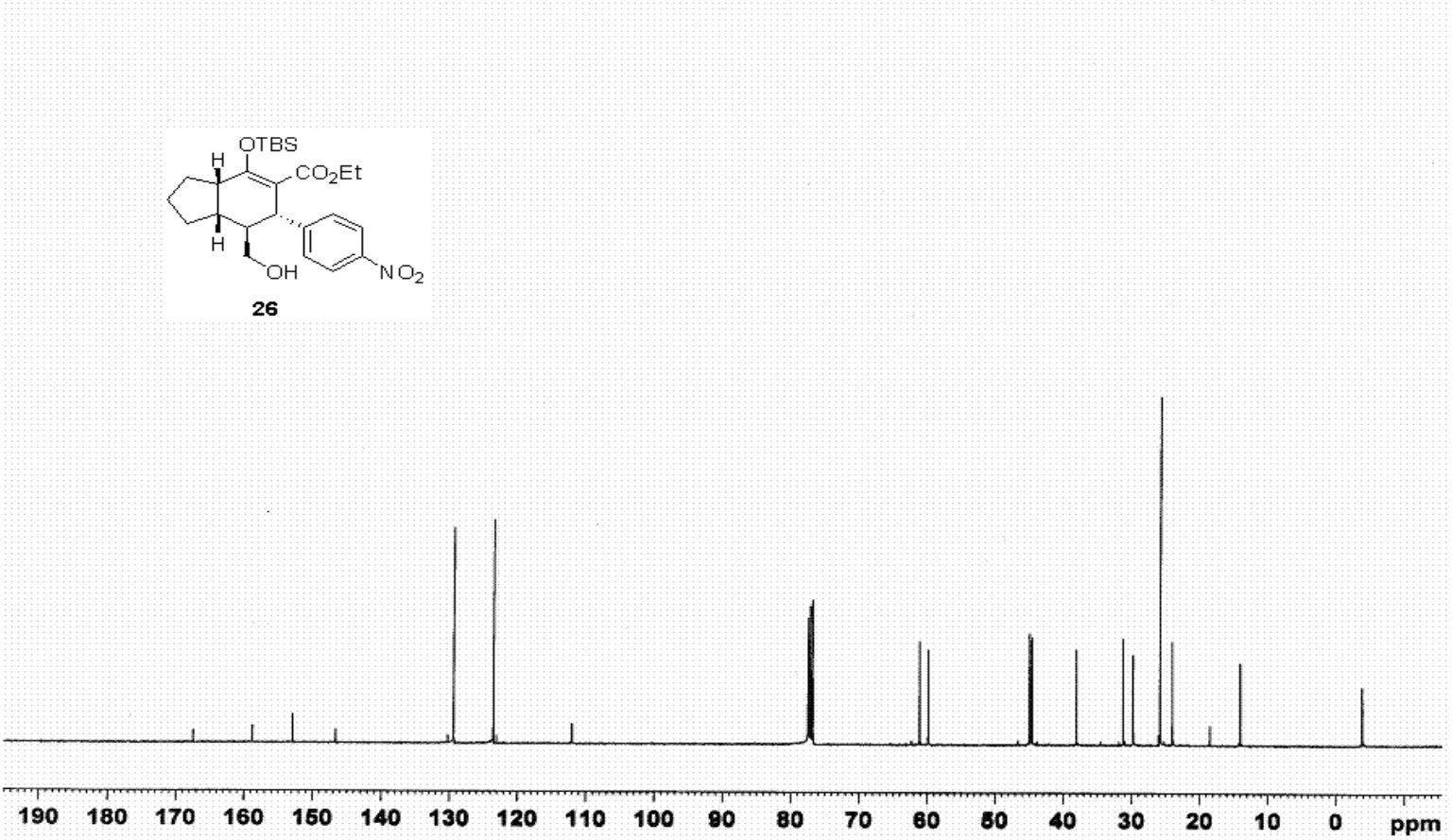


Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	20.159	66880897.92	1.52e+06	98.24	98.24	MM	44.1205
2	25.205	1199196.98	31607.92	1.76	1.76	MM	37.9398

24b



26



OTBS
H
CO2Et
H
OH
NO2

26