Electronic Supplementary Material (ESI) for ChemComm.

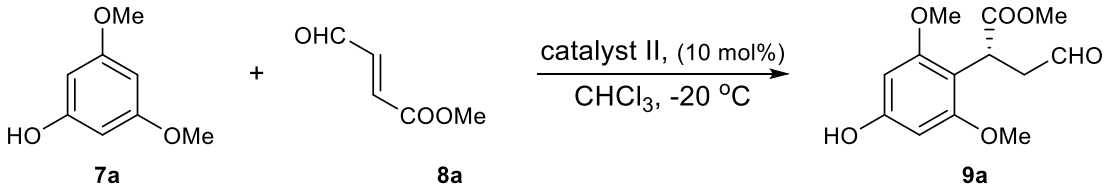
Organocatalytic Enantioselective Direct Alkylation of Phloroglucinol Derivatives: Asymmetric Total Synthesis of (+)-Aflatoxin B_2

Supporting Information – Table of Contents

General Information

Unless stated otherwise, reactions were conducted in dry glassware using anhydrous solvents (passed through activated alumina columns). All commercially available reagents were used as received unless otherwise specified. Reaction temperatures were controlled using an IKAmag temperature modulator, and unless stated otherwise, reactions were performed at room temperature (RT, approximately 23 °C). All reactions under microwave irradiation were performed in a CEM Discover 1-300W system. Thin-layer chromatography (TLC) was conducted on plates (GF254) supplied by Yantai Chemicals (China) and visualized using a combination of UV, anisaldehyde, iodine, and potassium permanganate staining. Silica gel (200-300 mesh) supplied by Tsingtao Haiyang Chemicals (China) was used for flash column chromatography. ^{1}H NMR spectra were recorded on Bruker spectrometers (at 400 MHz) and are reported relative to deuterated solvent signals. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. ^{13}C NMR spectra are reported in terms of chemical shift. High resolution mass spectra were obtained from the Tsinghua University Mass Spectrometry Facility.

General procedure for catalytic enantioselective direct alkylation



7a **8a** **9a**

To a stirred solution of 3,5-dimethoxyphenol **7a** (18.5 mg, 0.12 mmol) and the catalyst **II** (4.5 mg, 0.01 mmol) in $CHCl_3$ (0.7 mL) at -20 °C under N_2 atmosphere was slowly added a solution of fumaraldehydic acid methylester (11.4 mg, 0.10 mmol) in $CHCl_3$ (0.3 mL). The resulting solution was stirred at -20 °C for 12 h until the completion of the reaction, as monitored by TLC. The solvent was removed under reduced pressure to afford the crude residue, which was purified by silica gel chromatography eluting with petroleum ether / ethyl acetate (2:1) to afford the desired product **9a** as a colorless oil (25.5mg, 95%).

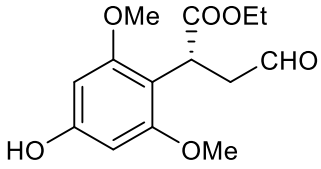
R_f 0.31 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.76 (t, *J* = 1.6 Hz, 1H), 6.01 (s, 2H), 5.82 (s, 1H), 4.66 (dd, *J* = 5.6, 8.0 Hz, 1H), 3.71 (s, 6H), 3.65 (s, 3H), 3.26-3.15 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.4, 174.8, 158.4, 157.1, 107.3, 92.3, 55.8, 52.4, 44.7, 34.6.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{13}H_{17}O_6$, 269.1025; found, 269.1023.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 11.722 min, t_2 = 14.555 min, 97% *ee*.



9b

Prepared by the general procedure, 12 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9b** (28.1 mg, 99%) as a white solid.

R_f 0.31 (petroleum ether / ethyl acetate = 2:1).

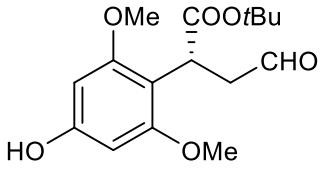
mp 133-135 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.74 (t, *J* = 2.0 Hz, 1H), 5.98 (s, 2H), 4.63 (dd, *J* = 6.0, 8.0 Hz, 1H), 4.25-4.05 (m, 2H), 3.67 (s, 6H), 3.26-3.15 (m, 1H), 2.58-2.45 (m, 1H), 1.17 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.8, 174.6, 158.3, 157.4, 107.0, 92.2, 61.2, 55.6, 44.7, 34.9, 14.2.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{14}H_{19}O_6$, 283.1182; found, 283.1179.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 10.247 min, t_2 = 13.095 min, 98% *ee.*



9c

Prepared by the general procedure, 12 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9c** (29.6 mg, 95%) as a colorless oil. *t*-butyl 4-oxo-2-butenoate was synthesized by following a reported procedure.[1]

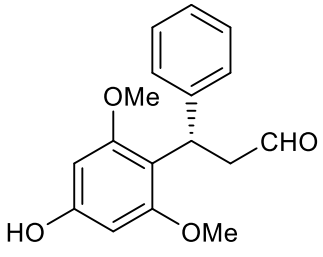
R_f 0.32 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.73 (s, 1H), 5.93 (s, 2H), 4.59 (dd, *J* = 6.0, 8.0 Hz, 1H), 3.68 (s, 6H), 3.20-3.05 (m, 1H), 2.53-2.40 (m, 1H), 1.40 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.9, 173.6, 158.2, 157.2, 107.5, 92.2, 81.2, 55.5, 44.8, 35.9, 28.1.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{16}H_{23}O_6$, 311.1495; found, 311.1482.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 7.282 min, t_2 = 9.290 min, 96% *ee*.



9d

Prepared by the general procedure, 48 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9d** (24.0 mg, 84%) as a pale yellow oil.

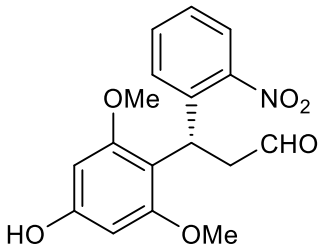
R_f 0.33 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.71 (t, *J* = 2.0 Hz, 1H), 7.61 (t, *J* = 8.4 Hz, 2H), 7.43 (t, J = 7.6 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 5.98 (s, 2H), 5.49 (dd, *J* = 6.8, 9.6 Hz, 1H), 3.67 (s, 6H), 3.48-3.35 (m, 1H), 3.18-3.07 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.6, 159.1, 156.7, 149.9, 138.5, 132.2, 130.5, 126.9, 123.6, 109.6, 92.5, 55.6, 47.3, 31.0.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{17}H_{19}O_4$, 287.1283; found, 287.1276.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AS-H column (90:10 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 14.815 min, t_2 = 15.964 min, 83% *ee*.



9e

Prepared by the general procedure, 48 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9e** (22.2 mg, 67%) as a pale yellow oil.

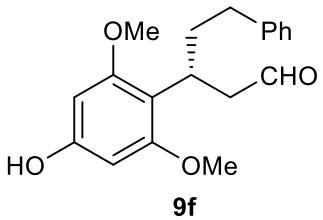
R_f 0.23 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.67 (t, *J* = 2.0 Hz, 1H), 7.30-7.10 (m, 5H), 5.99 (s, 2H), 5.20 (t, *J* = 7.6 Hz, 1H), 3.66 (s, 6H), 3.35-3.15 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 204.3, 159.1, 156.3, 143.8, 128.1, 127.6, 125.8, 111.4, 92.6, 55.7, 46.6, 33.8.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{17}H_{18}NO_6$, 332.1134; found, 332.113.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column(80:20 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 14.709 min, t_2 = 20.707 min, 91% *ee*.



9f

Prepared by the general procedure, 24 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9f** (23.5 mg, 75%) as a colorless oil. 5-phenylpent-2-enal was synthesized by following a reported procedure.[2]

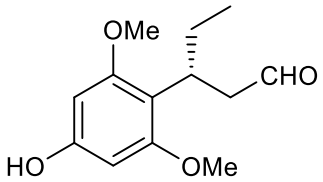
R_f 0.23 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.58 (t, *J* = 2.4 Hz, 1H), 7.35-7.20 (m, 2H), 7.15-7.05 (m, 3H), 6.04 (s, 2H), 3.95-3.80 (m, 1H), 3.71 (s, 6H), 2.95-2.85 (m, 1H), 2.75-2.65 (m, 1H), 2.50-2.40 (m, 2H), 2.30-2.15 (m, 1H), 1.95-1.85 (m, 1H);

^{13}C NMR (100 MHz, $CDCl_3$) δ: 205.1, 159.5, 156.2, 142.8, 128.5, 128.3, 125.6, 110.3, 92.3, 55.6, 48.2, 35.4, 34.3, 29.4.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{19}H_{23}O_4$, 315.1385; found, 315.1374.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® OD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 7.652 min, t_2 = 9.362 min, 90% *ee*.



9g

Prepared by the general procedure, 24 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9g** (19.4 mg, 82%) as a colorless oil.

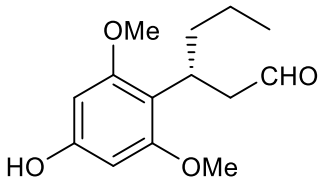
R_f 0.64 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.87 (t, *J* = 2.4 Hz, 1H), 6.02 (s, 2H), 3.73 (s, 6H), 3.75-3.60 (m, 1H), 2.80-2.60 (m, 2H), 1.85-1.60 (m, 2H), 1.60 (t, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 205.2, 159.6, 155.9, 111.0, 92.4, 55.6, 47.9, 31.2, 26.6, 12.5.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{13}H_{19}O_4$, 239.1283; found, 239.1285.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AS-H column (92.5:7.5 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 16.720 min, t_2 = 19.382 min, 96% *ee*.



9h

Prepared by the general procedure, 24 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9h** (22.0 mg, 87%) as a colorless oil.

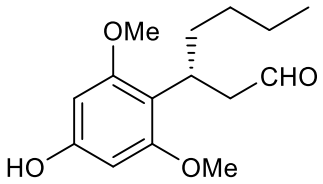
R_f 0.62 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.58 (t, *J* = 2.8 Hz, 1H), 6.01 (s, 2H), 5.48 (s, 1H), 3.85-3.70 (m, 1H), 3.71 (s, 6H), 2.90-2.80 (m, 1H), 2.70-2.60 (m, 1H), 1.85-1.70 (m, 1H), 1.60-1.50 (m, 1H), 1.25-1.05 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 205.3, 159.5, 155.8, 111.2, 92.3, 55.6, 47.1, 35.9, 29.2, 21.1, 14.2.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{14}H_{21}O_4$, 253.1440; found, 253.1446.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AS-H column (92.5:7.5 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 13.947 min, t_2 = 15.917 min, 93% *ee*.



9i

Prepared by the general procedure, 24 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9i** (21.6 mg, 81%) as a colorless oil.

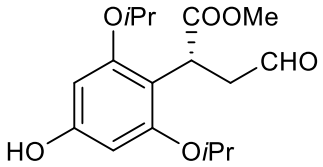
R_f 0.56 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.58 (t, *J* = 2.8 Hz, 1H), 6.01 (s, 2H), 5.22 (s, 1H), 3.85-3.70 (m, 1H), 3.71 (s, 6H), 2.90-2.80 (m, 1H), 2.70-2.60 (m, 1H), 1.90-1.70 (m, 1H), 1.65-1.50 (m, 1H), 1.35-1.00 (m, 4H), 0.82 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 205.4, 159.5, 155.8, 111.2, 92.4, 55.6, 48.1, 33.3, 30.2, 29.5, 22.8, 14.2.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{15}H_{23}O_4$, 267.1596; found, 267.1599.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AS-H column (95:5 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 20.727 min, t_2 = 24.362 min, 91% *ee*.



9j

Prepared by the general procedure, 12 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9j** (26.6 mg, 82%) as a colorless oil. 3,5-diisopropoxyphenol was synthesized by following a reported procedure.[3]

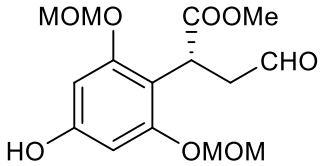
R_f 0.46 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.76 (t, *J* = 2.0 Hz, 1H), 5.98 (s, 2H), 4.66 (dd, *J* = 6.4, 7.6 Hz, 1H), 4.50-4.40 (m, 1H), 3.63 (s, 3H), 3.26-3.15 (m, 1H), 2.55-2.40 (m, 1H), 1.31 (d, *J* = 6.0 Hz, 6H), 1.25 (d, *J* = 6.0 Hz, 6H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.3, 174.7, 156.7, 156.6, 109.1, 93.4, 70.3, 52.1, 44.8, 34.8, 22.1, 22.0.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{17}H_{25}O_6$, 325.1651; found, 325.1656.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 5.847 min, t_2 = 7.021 min, 93% *ee*.



9k

Prepared by the general procedure, 12 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9k** (28.5 mg, 87%) as a colorless oil.

3,5-bis(methoxymethyl)phloroglucinol was synthesized by following a reported procedure.[4]

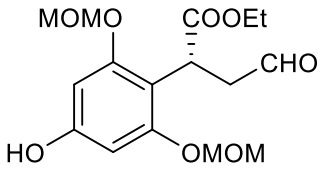
R_f 0.33 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.80 (t, *J* = 1.6 Hz, 1H), 6.31 (s, 2H), 5.86 (s, 1H), 5.10 (s, 4H), 4.73 (dd, *J* = 5.2, 8.4 Hz, 1H), 3.64 (s, 3H), 3.43 (s, 6H), 3.40-3.26 (m, 1H), 2.60-2.48 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.6, 174.4, 156.9, 156.1, 108.8, 96.1, 94.6, 56.3, 52.3, 44.8, 34.7.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{15}H_{21}O_8$, 329.1236; found, 329.1238.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 9.975 min, t_2 = 12.454 min, 91% *ee.*



9l

Prepared by the general procedure, 12 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9l** (31.0 mg, 91%) as a colorless oil.

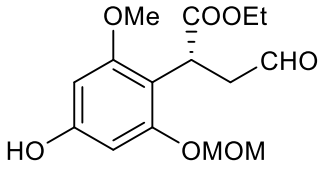
R_f 0.33 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.78 (t, *J* = 2.4 Hz, 1H), 6.55 (s, 1H), 6.28 (s, 2H), 5.10 (dd, *J* = 6.8, 9.2 Hz, 4H), 4.71 (dd, *J* = 5.6, 8.4 Hz, 1H), 4.20-4.10 (m, 2H), 3.41 (s, 6H), 3.40-3.25 (m, 1H), 2.60-2.45 (m, 1H), 1.16 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.0, 174.1, 157.1, 156.1, 108.8, 96.1, 94.5, 61.2, 56.2, 44.7, 35.0, 14.2.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{16}H_{23}O_8$, 343.1393; found, 343.1389.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 8.828 min, t_2 = 11.447 min, 94% *ee.*



9m

Prepared by the general procedure, 12 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9m** (25.2 mg, 81%) as a colorless oil.

R_f 0.31 (petroleum ether / ethyl acetate = 2:1).

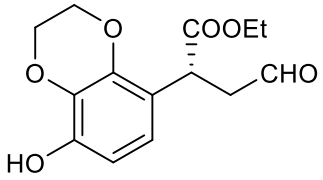
^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.78 (t, *J* = 1.6 Hz, 1H), 6.25 (d, *J* = 2.0 Hz, 1H), 6.08 (d, *J* = 2.4 Hz, 1H), 5.09 (d, *J* = 1.6 Hz, 2H), 4.67 (dd, *J* = 5.6, 8.0 Hz, 1H), 4.20-4.05 (m, 2H), 3.72 (s, 3H), 3.44 (s,

3H), 3.23-3.10 (m, 1H), 2.58-2.45 (m, 1H), 1.17 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.0, 174.0, 158.5, 156.9, 156.1, 108.4, 95.0, 94.6, 93.3, 61.1, 56.3, 55.7, 44.7, 34.9, 14.3.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{15}H_{21}O_7$, 313.1287; found, 313.1281.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 9.895 min, t_2 = 13.255 min, 91% *ee*.



9n

Prepared by the general procedure, 24 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9n** (14.9 mg, 53%) as a colorless oil.

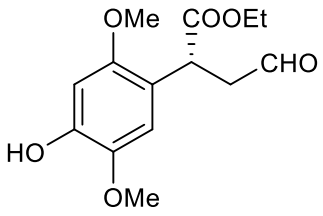
R_f 0.46 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.77 (s, 1H), 6.61 (d, *J* = 8.4 Hz, 1H), 6.48 (d, *J* = 8.4 Hz, 1H), 5.38 (s, 1H), 4.40-4.20 (m, 5H), 4.20-4.10 (m, 2H), 3.30-3.20 (m, 1H), 2.69 (dd, *J* = 5.2, 18.0 Hz, 1H), 1.20 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.5, 173.2, 144.8, 141.3, 131.4, 120.0, 118.3, 107.5, 64.5, 64.5, 61.3, 46.3, 38.8, 14.3.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{14}H_{17}O_6$, 281.1025; found, 281.1018.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® IE column (87:13 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 19.212 min, t_2 = 21.352 min, 87% *ee*.



9o

Prepared by the general procedure, 12 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9o** (24.6 mg, 88%) as a colorless oil. 2,5-dimethoxyphenol was

synthesized by following a reported procedure.[5]

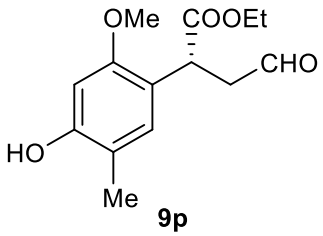
R_f 0.47 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 6.69 (s, 1H), 6.54 (s, 1H), 5.73 (s, 1H), 4.37 (dd, *J* = 5.2, 8.8 Hz, 1H), 4.15 (q, *J* = 7.2, 1H), 3.80 (s, 3H), 3.73 (s, 3H), 3.30-3.20 (m, 1H), 2.68 (dd, *J* = 5.2, 18.0 Hz, 1H), 1.19 (t, *J* = 7.8 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.6, 173.5, 151.4, 145.8, 140.5, 117.4, 111.9, 99.8, 61.1, 56.7, 56.1, 46.5, 39.4, 14.2.

HRMS-ESI (*m*/*z*) $[M-H]^+$ calcd for $C_{14}H_{17}O_6$, 281.1025; found, 281.1032.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 10.226 min, t_2 = 11.355 min, 93.6% *ee*.



9p

Prepared by the general procedure, 12 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9p** (20.2 mg, 76%) as a colorless oil.

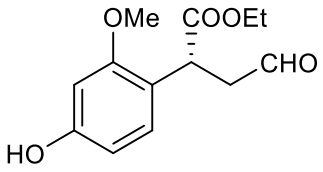
R_f 0.45 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.75 (s, 1H), 6.84 (s, 1H), 6.33 (s, 1H), 5.71 (s, 1H), 4.34 (dd, *J* = 5.2, 8.8 Hz, 1H), 4.20-4.10 (m, 2H), 3.69 (s, 3H), 3.30-3.16 (m, 1H), 2.73-2.63 (m, 1H), 2.12 (s, 3H), 1.20 (d, *J* = 7.2, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.3, 173.9, 155.8, 154.3, 130.8, 118.2, 115.5, 99.3, 61.3, 55.6, 46.3, 39.4, 15.0, 14.2.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{14}H_{19}O_5$, 267.1232; found, 267.1236.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (90:10 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 12.528 min, t_2 = 15.199 min, 93% *ee*.



9q

Prepared by the general procedure, 24 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (2:1) to give product **9q** (18.9 mg, 75%) as a pale yellow oil.

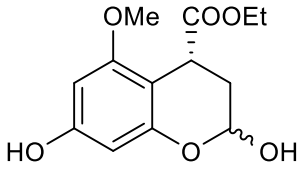
R_f 0.42 (petroleum ether / ethyl acetate =2:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.76 (s, 1H), 6.96 (d, *J* = 8.4, 1H), 6.39 (d, *J* = 2.4, 1H), 6.33 (dd, *J* = 2.4, 8.4 Hz, 1H), 5.55 (s, 1H), 6.33 (dd, *J* = 5.2, 8.8 Hz, 1H), 5.55 (s, 1H), 4.36 (dd, *J* = 5.2, 8.8 Hz, 1H), 4.15 (q, *J* = 7.6 Hz, 2H), 3.75 (s, 3H), 3.24 (q, *J* = 9.2 Hz, 1H), 2.70(dd, *J* = 5.2, 18.0 Hz, 1H), 1.20 (d, *J* = 7.2, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.0, 173.8, 157.9, 156.6, 129.5, 118.9, 107.3, 61.3, 55.5, 46.2, 39.5, 14.2.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{13}H_{17}O_5$, 253.1076; found, 253.1082.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® IE column (90:10 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 12.110 min, t_2 = 14.711 min, 90% *ee*.



9r

Prepared by the general procedure (with 5.0 vol% MeOH added for solubility reasons), 12 h; purified by silica gel column chromatography petroleum ether / ethyl acetate (1:1) to give product **9r** (25.2 mg, 94%) as a colorless oil. 5-methoxyresorcinol was synthesized by following a reported procedure.[6]

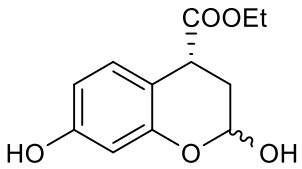
R_f 0.38 (petroleum ether / ethyl acetate = 1:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.19 (s, 1H), 6.05-5.85 (m, 2H), 5.55-5.25 (m, 1.5H), 4.30-4.10 (m, 2H), 3.90-3.75 (m, 1.5H), 3.75-3.65 (m, 3H), 2.40-2.05 (m, 2H), 1.35-1.25 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.1, 176.1, 158.8, 158.5, 157.3, 157.1, 153.6, 152.6, 100.8, 100.0, 97.3, 96.8, 91.4, 91.1, 61.8, 61.2, 55.6, 55.6, 35.2, 33.4, 31.3, 29.5, 14.3, 14.2.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{13}H_{17}O_6$, 269.1025; found, 269.1023.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 21.937 min, t_2 = 31.267 min, 98% *ee.*



9s

Prepared by the general procedure (with 5.0 vol% MeOH added for solubility reasons), 12 h; purified by silica gel column chromatography DCM / MeOH (20:1) to give product **9s** (20.5 mg, 86%) as a colorless oil.

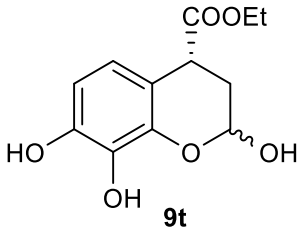
R_f 0.62 (DCM / MeOH = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.05 (d, J = 8.4 Hz, 0.5H), 7.00 (d, *J* = 8.4 Hz, 0.5H), 6.91 (s, 0.5H), 6.80 (s, 0.5H), 6.73 (dd, *J* = 2.8, 7.6 Hz, 0.5H), 6.45-6.20 (m, 2H), 5.65-5.55 (m, 1H), 4.67 (d, *J* = 4.0 Hz, 0.5H), 4.25-4.10 (m, 2H), 3.90-3.75 (m, 1H), 2.50-2.20 (m, 1.5H), 2.15-2.00 (m, 0.5H), 1.30-1.20 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.9, 174.6, 156.9, 156.3, 152.8, 155.0, 130.4, 129.6, 110.4, 109.66, 109.3, 108.7, 105.1, 104.2, 91.4, 95.410, 90.3, 62.6, 61.7, 37.8, 37.5, 30.5, 28.7, 14.2, 14.1.

HRMS-ESI (*m*/*z*) $[M-H]^-$ calcd for $C_{12}H_{13}O_5$, 237.0763; found, 237.0759.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (85:15 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 17.437 min, t_2 = 21.459 min, 90% *ee.*



9t

Prepared by the general procedure (with 7.5 vol% MeOH added for solubility reasons), 24 h; purified by silica gel column chromatography DCM / MeOH (20:1) to give product **9t** (21.2 mg, 83%) as a pale yellow oil.

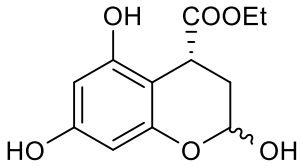
R_f 0.48 (DCM / MeOH = 10:1).

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.67 (d, *J* = 8.8 Hz, 0.5H), 6.61 (d, *J* = 8.8 Hz, 0.5H), 6.51 (d, J = 8.8 Hz, 0.5H), 5.62 (d, *J* = 11.2 Hz, 1H), 4.25-4.10 (m, 2H), 3.90-3.75 (m, 1H), 2.45-2.20 (m, 1.5H), 2.10-2.00 (m, 0.5H), 1.35-1.20 (m, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 176.8, 174.1, 144.2, 143.9, 140.4, 139.5, 132.5, 132.1, 119.9, 119.2, 111.0, 109.2, 108.9, 108.7, 91.8, 90.6, 62.6, 61.5, 37.8, 37.6, 30.4, 28.8, 14.2, 14.1.

HRMS-ESI (*m*/*z*) $[M-H]^-$ calcd for $C_{12}H_{13}O_6$, 253.0712; found, 253.0710.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® AD-H column (87.5:12.5 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 25.604 min, t_2 = 27.403 min, 90% *ee.*



9u

Prepared by the general procedure (with 7.5 % volMeOH added for solubility reasons), 24 h; purified by silica gel column chromatography DCM / MeOH (20:1) to give product **9u** (17.2 mg, 68%) as a pale yellow oil.

R_f 0.40 (DCM / MeOH = 10:1).

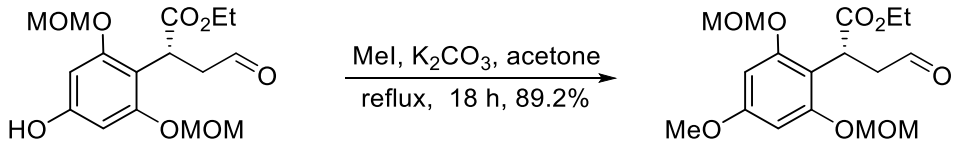
^{1}H NMR (400 MHz, CD_3OD) δ: 5.95-5.80 (m, 1.5H), 5.30-5.45 (m, 1H), 4.20-4.10 (m, 2H), 3.80-3.65 (m, 1H), 2.25-2.00 (m, 2H), 1.30-1.20 (m, 3H).

^{13}C NMR (100 MHz, CD_3OD) δ: 177.7, 176.9, 159.0, 158.9, 157.9, 157.6, 155.7, 155.4, 100.5, 100.4, 96.3, 96.2, 96.0, 96.0, 93.0, 92.2, 79.5, 62.0 61.8, 36.7, 36.2, 32.9, 32.7, 14.4, 14.3.

HRMS-ESI (*m*/*z*) $[M-H]^-$ calcd for $C_{12}H_{13}O_6$, 253.0712; found, 253.0710.

Enantiomeric excess was determined by HPLC using a Daicel Chiralcel® IE column (80:20 Hexane : *i*-PrOH, 1 mL/min, λ = 190 nm): t_1 = 10.335 min, t_2 = 21.771 min, 95% *ee.*

Asymmetric total synthesis of Aflatoxin B_2



9l **12**

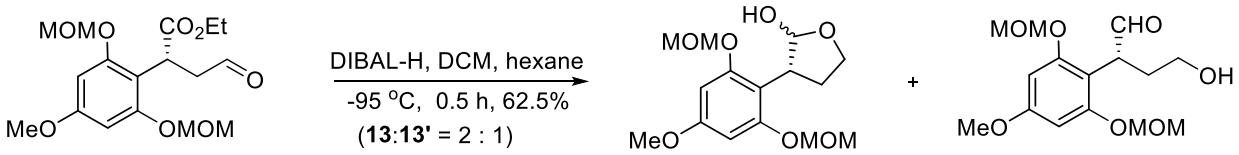
Compound **12**: To a solution of **9l** (180.0 mg, 0.526 mmol) in acetone (2.5 mL) was added potassium carbonate (109 mg, 0.789 mmol, 1.5 equiv), and the solution was stirred for 10 min. To this mixture was added a solution of iodomethane (50.0 μL, 0.789 mmol, 1.5 equiv), and the solution was stirred at reflux for 18 h under nitrogen. The reaction mixture was cooled to room temperature and the acetone removed *in vacuo*. The residue was diluted with water (10 mL) and ethyl acetate (10 mL) and the layers separated. The aqueous phase was extracted with ethyl acetate (3 x 10 mL) and the combined organic solution was washed with water and brine, dried over Na_2SO_4, and concentrated *in vacuo* to give the residue. The crude product was purified by silica gel column chromatography (petroleum ether / ethyl acetate = 2:1) to afford the product **12** (166.8 mg, 89.2 % yield) as a pale yellow oil.

R_f 0.56 (petroleum ether / ethyl acetate = 2:1).

^{1}H NMR (400 MHz, $CDCl_3$): 9.80 (s, 1H), 6.39 (s, 2H), 5.13 (dd, *J* = 6.8, 9.2 Hz, 4H), 4.72 (dd, *J* = 5.6, 8.4 Hz, 1H), 4.20-4.10 (m, 2H), 3.75 (s, 3H), 3.44 (s, 6H), 3.40-3.25 (m, 1H), 2.50 (dd, *J* = 5.2, 12.0 Hz, 1H), 1.15 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): 201.4, 173.5, 160.5, 156.2, 109.6, 94.7, 61.0, 56.2, 55.5, 44.7, 35.0, 14.3.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{17}H_{25}O_8$, 357.1549; found, 357.1546.



12 **13** **13'**

Compound **13**: To a solution of **12** (15.6 mg, 0.0438 mmol) in dry dichloromethane (1.0 mL) was added DIBAL-H (1.0 M in hexane, 113.9 μL, 0.114 mmol, 2.6 equiv) under nitrogen at -95°C (MeOH / liquid nitrogen bath). The reaction was stirred at -95 °C for 0.5 hour and then was quenched with ethyl acetate (0.1 mL). The reaction was allowed to warm up to room temperature and then saturated

aqueous sodium potassium tartrate (3.0 mL) was added. The resulting mixture was vigorously stirred until both the aqueous and organic layers were clear. The layers were separated, and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (DCM / MeOH = 20:1) to afford **13** (8.6 mg, 62.5%, **13** : **13'** = 2:1) as a white solid.

R_f 0.22 (petroleum ether / ethyl acetate = 2:1) or **R_f** 0.67 (DCM / MeOH = 10:1).

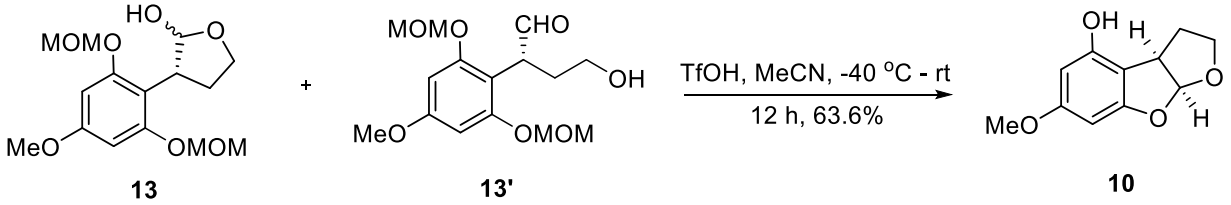
mp 41-43 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.67 (s, 0.42 H), 6.46 (6.45) (6.41) (s, 2 H), 5.66 (t, *J* = 4.4 Hz, 0.46 H), 5.40-5.30 (m, 0.41 H), 5.21(5.18) (5.15) (s, 4 H), 4.15-4.10 (m, 0.93 H), 4.15-4.10 (m, 0.93 H), 3.97 (dd, *J* = 4.8 Hz, 8.8 Hz, 0.53 H), 4.00-3.90 (m, 0.49 H), 3.79 (3.77) (3.77) (s, 3 H), 3.70-3.60 (m, 0.64 H), 3.48(3.45) (s, 6.45 H), 2.61 (d, *J* = 4.4 Hz, 0.44 H), 2.50-2.40 (m, 0.54 H), 2.38-2.30 (m, 0.47 H), 2.25-2.15 (m, 0.63 H), 2.15-2.05 (m, 0.56 H), 2.15-2.05 (m, 0.56 H), 2.08-1.95 (m, 0.30 H), 1.90-1.75 (m, 0.52 H).

^{1}H NMR (400 MHz, Acetone-D6) δ: 9.63 (s, 0.31 H), 6.45 (6.41) (s, 2 H), 5.59 (d, *J* = 5.2 Hz, 0.64 H), 5.20(5.19) (5.19) (s, 4 H), 4.86 (d, *J* = 5.6 Hz, 0.56 H), 4.05-3.90 (m, 1.6 H), 3.85-3.75 (m, 0.8 H), 3.78 (3.75) (3.74) (s, 3 H), 3.55-3.35 (m, 1 H), 3.46 (3.45) (3.42) (s, 6 H), 2.45-2.35 (m, 0.37 H), 2.30-2.20 (m, 0.68 H), 2.14 (d, *J* = 7.6 Hz, 0.41 H), 2.05-1.90 (m, 0.72 H), 1.85-1.75 (m, 0.39 H), 1.57 (d, *J* = 6.0 Hz, 0.48 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 202.7, 161.0, 159.9, 157.0, 156.8, 110.5, 107.8, 102.7, 100.0, 95.7, 95.3, 95.2, 95.0, 94.9, 94.8, 77.5, 77.2, 76.9, 68.0, 66.7, 60.9, 56.6, 56.6, 56.4, 55.6, 55.5, 45.7, 43.7, 39.9, 31.9, 31.2, 27.2.

HRMS-ESI (*m*/*z*) $[M-H_2O+H]^+$ calcd for $C_{15}H_{21}O_6$, 297.1338; found, 297.1344.



Compound **10:**[7] To a stirred solution of **13** and **13'** (15.0 mg, 0.0478 mmol, 1.0 equiv) in acetonitrile (2.0 mL) was added freshly prepared TfOH solution (0.1 M in MeCN, 96 μL, 0.0096 mmol, 0.2 equiv)

under nitrogen at -40 °C. The reaction was stirred at -40 °C for 0.5 hour and then allowed to warm up to room temperature and stirred at room temperature for another 12 hours. Then saturated aqueous $NaHCO_3$ solution, water and ethyl acetate were added. The layers were separated, and the aqueous layer was extracted 3 times with ethyl acetate. The combined organic layers were dried over Na_2SO_4. Evaporation of the solvent under reduced pressure afforded the crude product, which was purified by silica gel column chromatography (etroleum ether / ethyl acetate = 3:2) to afford **10** (6.3 mg, 63.6%) as a white solid.

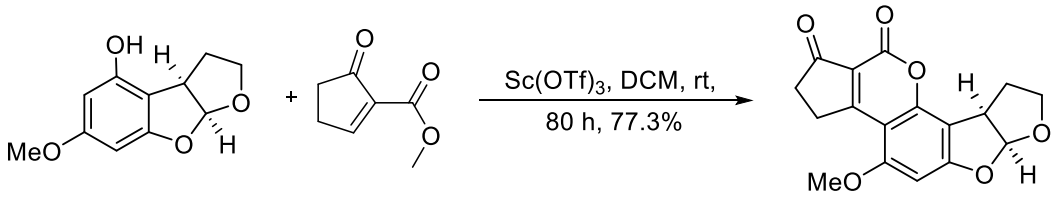
R_f 0.54 (petroleum ether / ethyl acetate =3:2).

mp 153-155 ºC.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.32 (d, *J* = 5.6 Hz, 1 H), 6.04 (d, *J* = 1.2 Hz, 1 H), 5.92 (d, *J* = 2.0 Hz, 1 H), 4.98 (brs, OH), 4.11-4.03 (m, 1 H), 3.98 (t, *J* = 7.2 Hz, 1 H), 3.73 (s, 3 H), 3.72 - 3.58 (m, 1 H), 2.22-2.06 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 162.0, 161.9, 152.7, 112.2, 105.6, 95.0, 88.8, 67.6, 55.7, 44.2, 31.7.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{11}H_{13}O_4$, 209.0814; found, 209.0815.



10 **14** **Aflatoxin B_2**

(+)-Aflatoxin B_2: To a stirred mixture of **14** (2.9 mg, 0.021 mmol, 1.0 equiv) and scandium(III) triflate (10.3 mg, 0.021 mmol, 1.0 equiv) in dry dichloromethane (0.7 mL) was added a solution of **10** (5.2 mg, 0.025 mmol, 1.2 equiv) in dry dichloromethane (0.3 mL) at 0 °C for 5 min and then allowed to warm up to room temperature. The reaction was stirred for another 80 hours at room temperature under air environment until the completion of the reaction, as monitored by TLC. The mixture was filtered through a celite pad, which was washed with dichloromethane and the filtrate was concentrated *in vacuo* afforded the crude product. The crude product was purified by silica gel column chromatography (DCM / MeOH = 20:1) to afford **(+)-Aflatoxin B_2** (5.1 mg, 77.3%) as a white solid. The physical and spectral data were identical to those previously reported by Corey group[8].

$[\alpha]_D^{20}$ +405 (*c* 0.09, $CHCl_3$).

mp 300-302 ºC (decomp).

R_f 0.70 (DCM / MeOH = 10:1).

^{1}H NMR (400MHz, $CDCl_3$) δ: 6.48 (d, *J* = 5.6 Hz, 1 H), 6.34 (s, 1 H), 4.20-4.10 (m, 2 H), 3.95 (s, 3 H), 3.64 (q, *J* = 9.2 Hz, 1 H), 3.45-3.35 (m, 2 H), 2.70-2.60 (m, 2 H), 2.33-2.22 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 201.4, 177.2, 167.3, 161.8, 155.4, 153.6, 117.2, 114.0, 107.0, 104.0, 90.2, 68.1, 56.6, 44.2, 35.2, 31.8, 29.2.

HRMS-ESI (*m*/*z*) $[M+H]^+$ calcd for $C_{17}H_{15}O_6$, 315.0869; found, 315.0868.

Comparison of ^{1}H NMR and ^{13}C NMR Spectra of Aflatoxin B_2

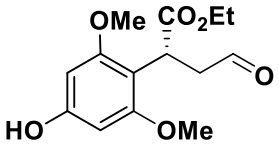
Comparison of ^{1}H NMR Spectral Data

Synthetic (-)-Aflatoxin B_2 by E. J. Corey[8] **(400 MHz, $CDCl_3$)**	**Synthetic (+)-Aflatoxin B_2** by our group **(400 MHz, $CDCl_3$)**
6.48 (d, 1 H, *J* = 6.0 Hz)	6.48 (d, 1 H, *J* = 5.6 Hz)
6.33 (s, 1 H)	6.34 (s, 1 H)
4.15 (m, 2 H)	4.20-4.10 (m, 2 H)
3.94 (s, 3 H)	3.95 (s, 3 H)
3.63 (q, 1 H, *J* = 8.8 Hz)	3.64 (q, 1 H, *J* = 9.2 Hz)
3.40 (m, 2 H)	3.45-3.35 (m, 2 H)
2.63 (m, 2 H)	2.68-2.62 (m, 2 H)
2.27 (m, 2 H)	2.33-2.22 (m, 2 H)

Comparison of ^{13}C NMR Spectral Data

Synthetic (-)-Aflatoxin B_2 by E. J. Corey[8] **(100 MHz, $CDCl_3$)**	**Synthetic (+)-Aflatoxin B_2** by our group **(100 MHz, $CDCl_3$)**
201.6	201.4
177.3	177.2
167.4	167.3
161.9	161.8
155.5	155.4
153.6	153.6
117.2	117.2
114.1	114.0
107.1	107.0
104.0	104.0
90.2	90.2
68.1	68.1
56.7	56.6
44.2	44.2
35.3	35.2
31.8	31.8
29.2	29.2

Crystal Structure of 9b



9b

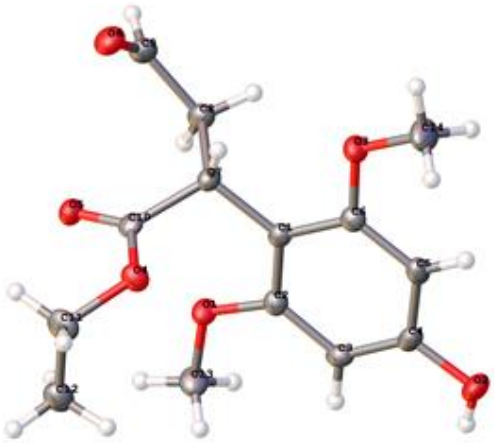


Table 1: Crystal data and structure refinement for exp_5367-9b

Identification code	exp_5367-**9b**
Empirical formula	$C_{14}H_{18}O_6$
Formula weight	282.28
Temperature / K	107.9(5)
Crystal system	orthorhombic
Space group	P212121
a / Å, b / Å, c / Å	7.8498(2), 13.1575(4), 13.3327(4)
α/°, β/°, γ/°	90, 90, 90
Volume / Å^3	1377.05(7)
Z	4
ρ_{calc} / mg mm^{-3}	1.362
μ / mm^{-1}	0.899
F(000)	600
Crystal size / mm^3	0.250 × 0.200 × 0.170
2Θ range for data collection	9.444 to 142.198°
Index ranges	-6 ≤ h ≤ 9, -11 ≤ k ≤ 16, -16 ≤ l ≤ 15
Reflections collected	4410
Independent reflections	2587[R(int) = 0.0227 (inf-0.9Å)]
Data/restraints/parameters	2587/0/185
Goodness-of-fit on F^2	1.039
Final R indexes [I>2σ (I) i.e. F_o>4σ (F_o)]	R_1 = 0.0343, wR_2 = 0.0872
Final R indexes [all data]	R_1 = 0.0358, wR_2 = 0.0885
Largest diff. peak/hole / e Å^{-3}	0.188/-0.172
Flack Parameters	0.03(11)
Completeness	0.9979

References

[1] J. B. Lin, S. M. Xu, J. K. Xie, H. Y. Li, P. F. Xu, *Chem*. *Commun*. **2015**, *51*, 3596.

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[4] H. Yoshida, T. Morishita, J. Ohshita, *Chem*. *Lett*. **2010**, *39*, 508.

[5] A. Kirste, G. Schnakenburg, S. R. Waldvogel, *Org*. *Lett*. **2011**, *13*, 3126.

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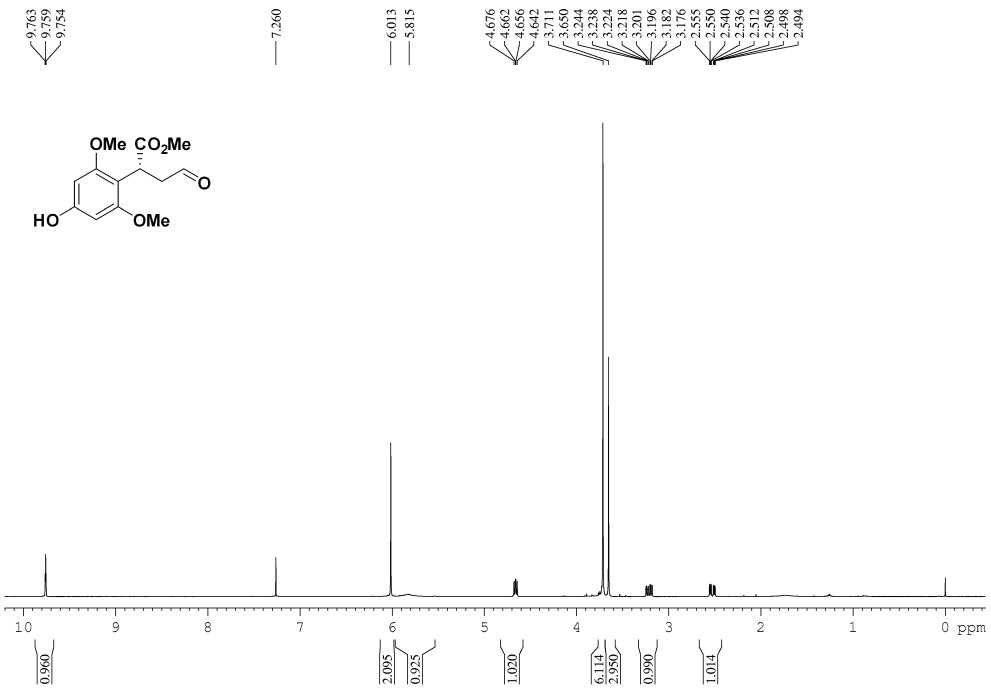
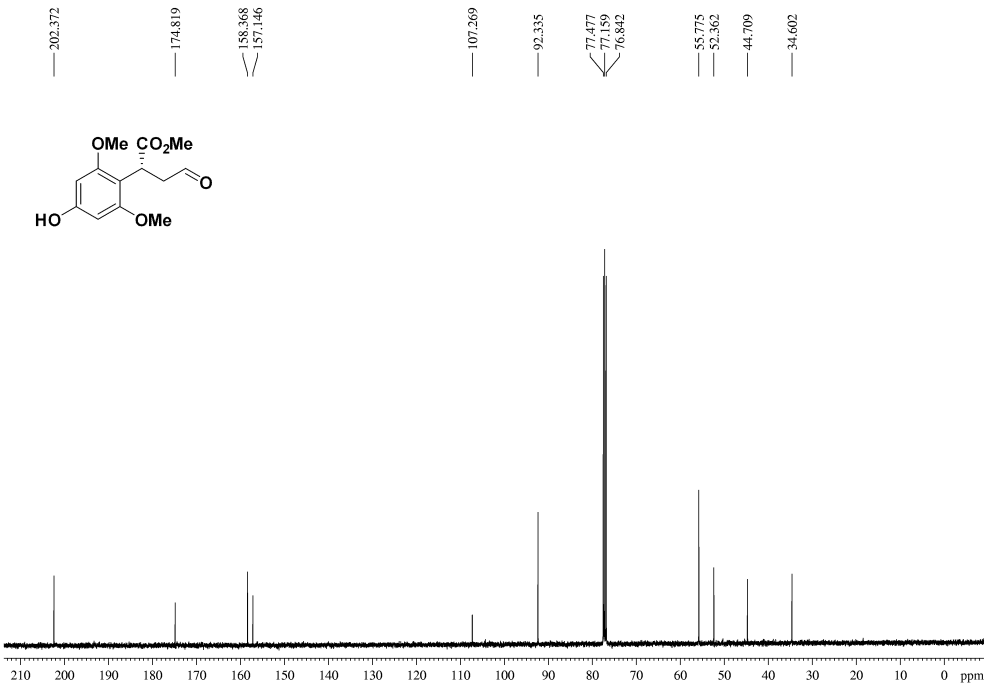
NMR Spectra

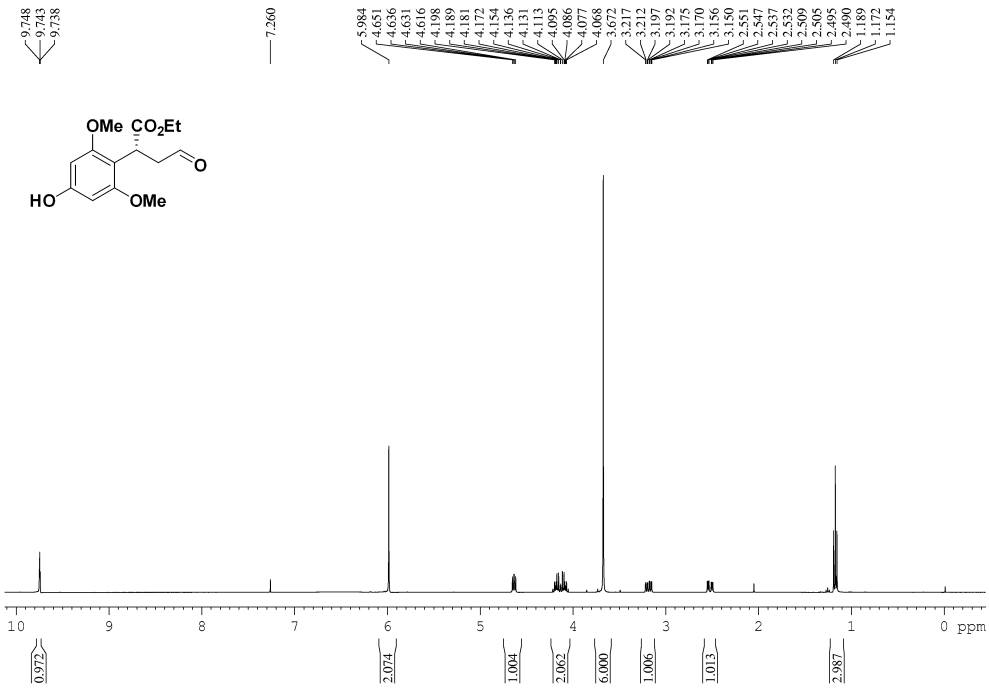
^{1}H NMR of Compound **9a** (400 MHz, $CDCl_3$)



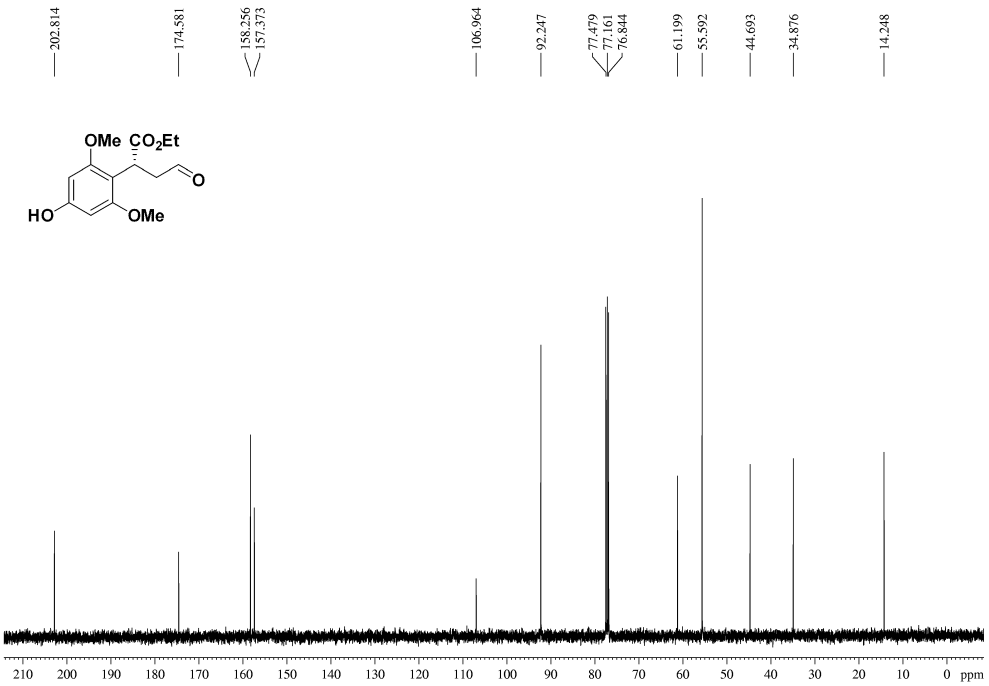
^{13}C NMR of Compound **9a** (100 MHz, $CDCl_3$).



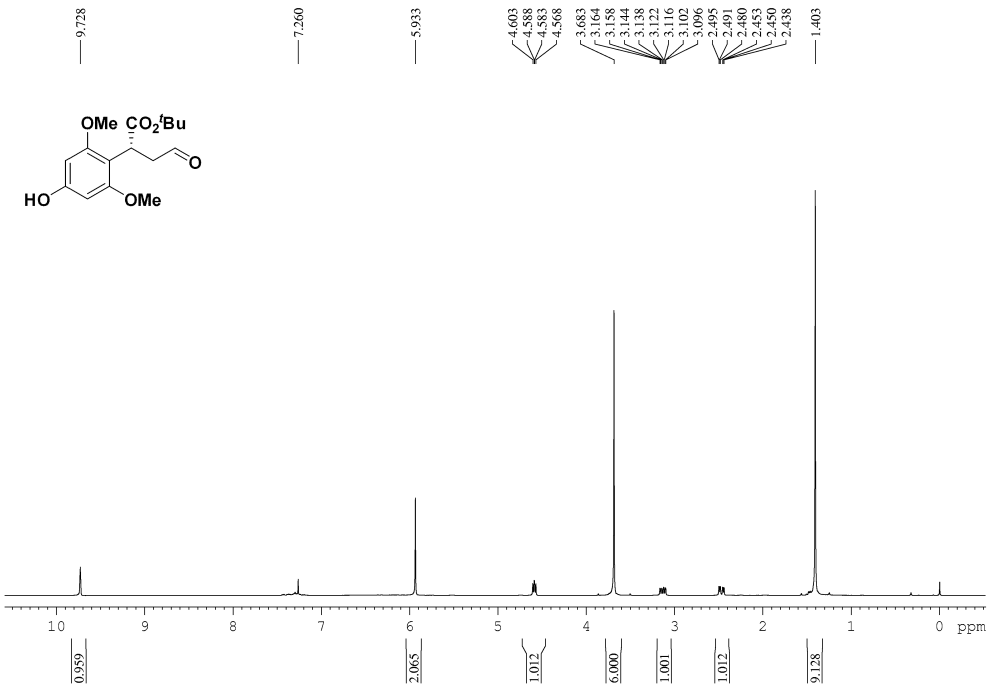
^{1}H NMR of Compound **9b** (400 MHz, $CDCl_3$)



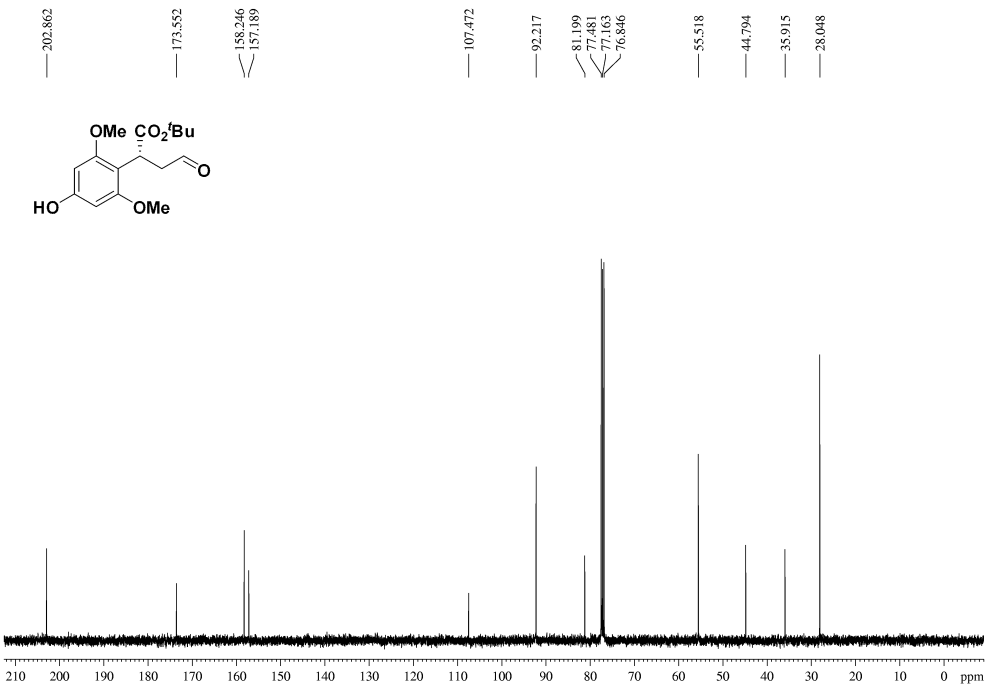
^{13}C NMR of Compound **9b** (100 MHz, $CDCl_3$)



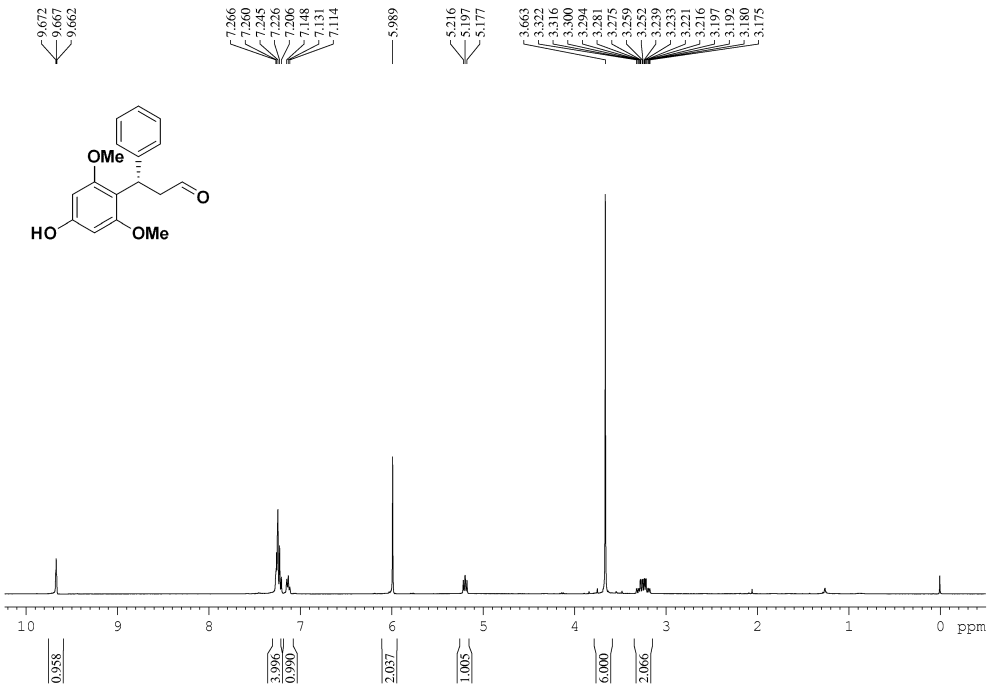
^{1}H NMR of Compound **9c** (400 MHz, $CDCl_3$)



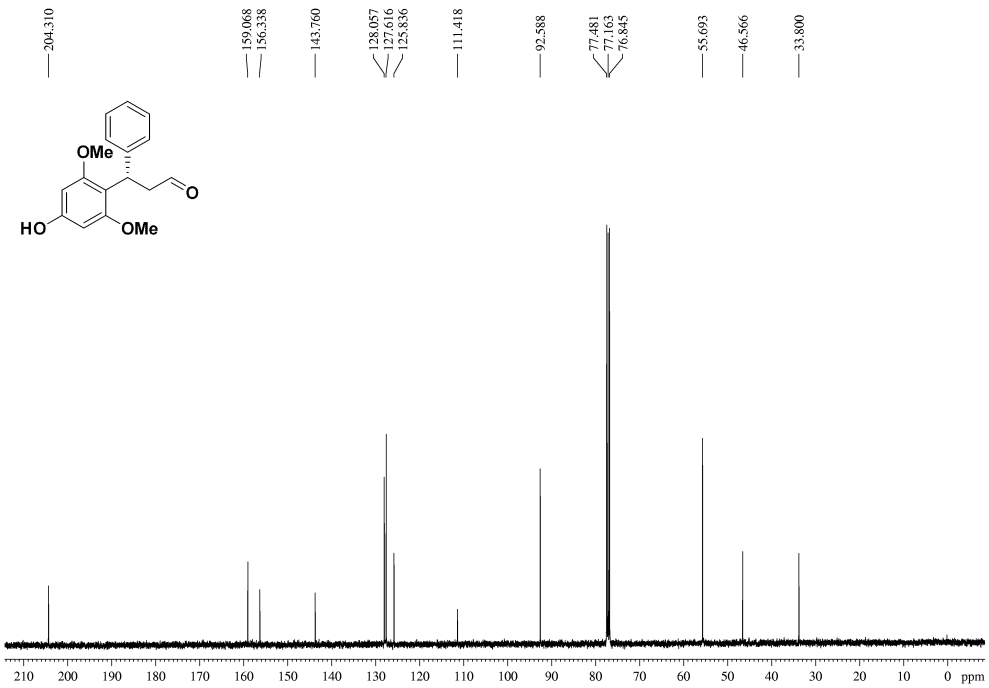
^{13}C NMR of Compound **9c** (100 MHz, $CDCl_3$)



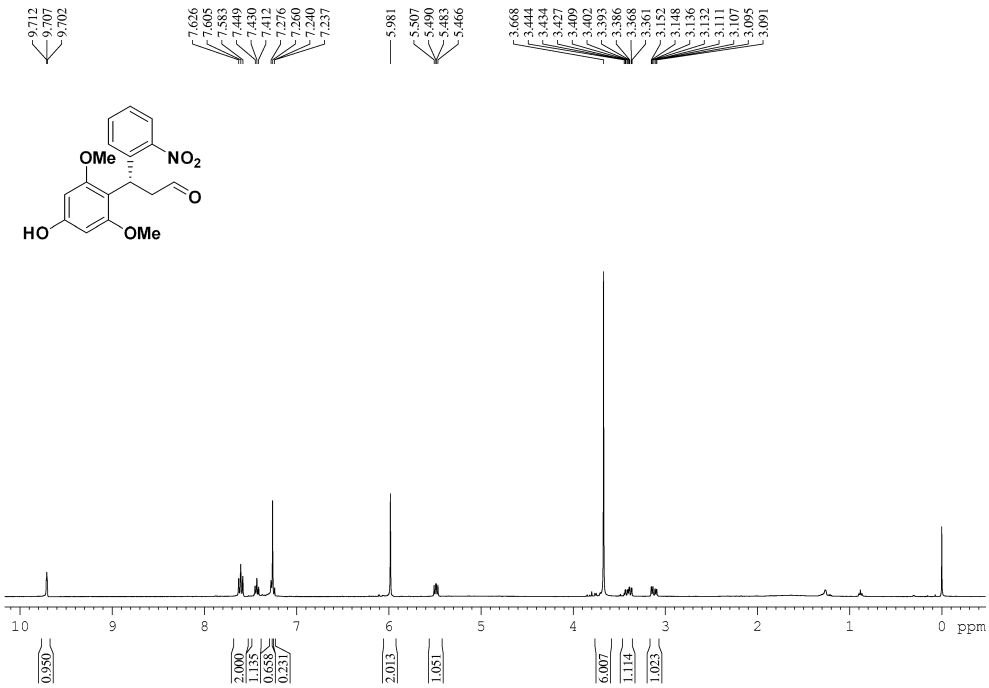
^{1}H NMR of Compound **9d** (400 MHz, $CDCl_3$)



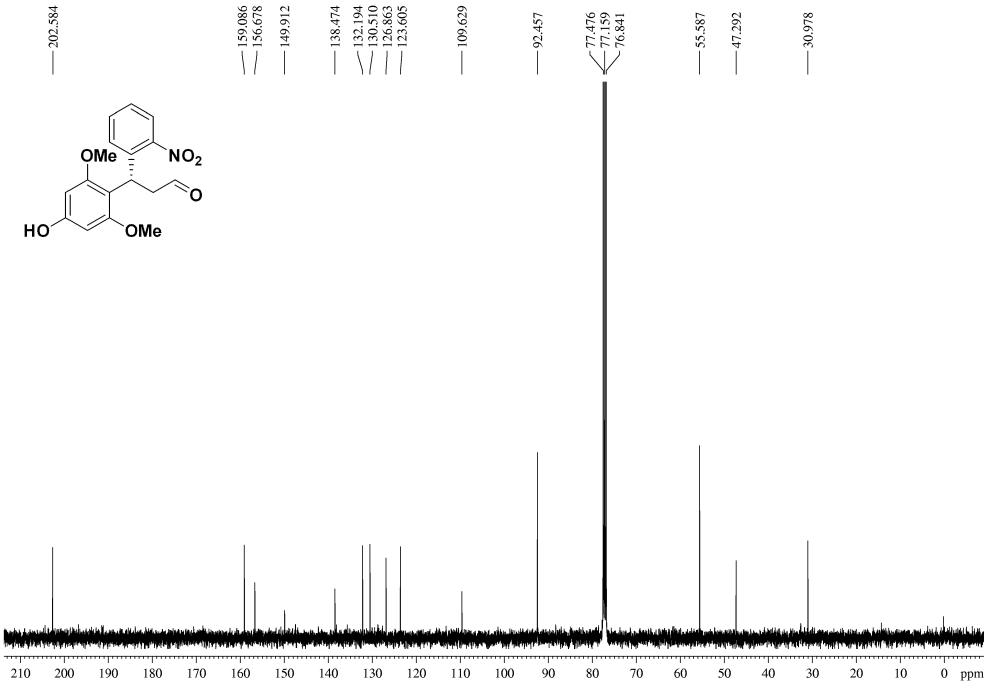
^{13}C NMR of Compound **9d** (100 MHz, $CDCl_3$)



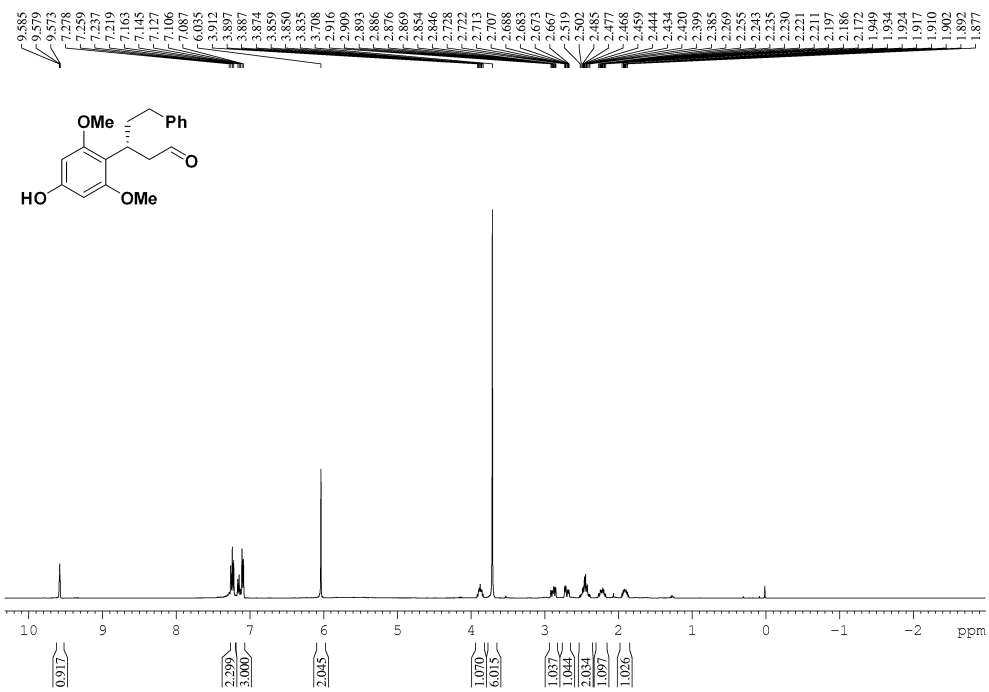
^{1}H NMR of Compound **9e** (400 MHz, $CDCl_3$)



^{13}C NMR of Compound **9e** (100 MHz, $CDCl_3$)



^{1}H NMR of Compound **9f** (400 MHz, $CDCl_3$)



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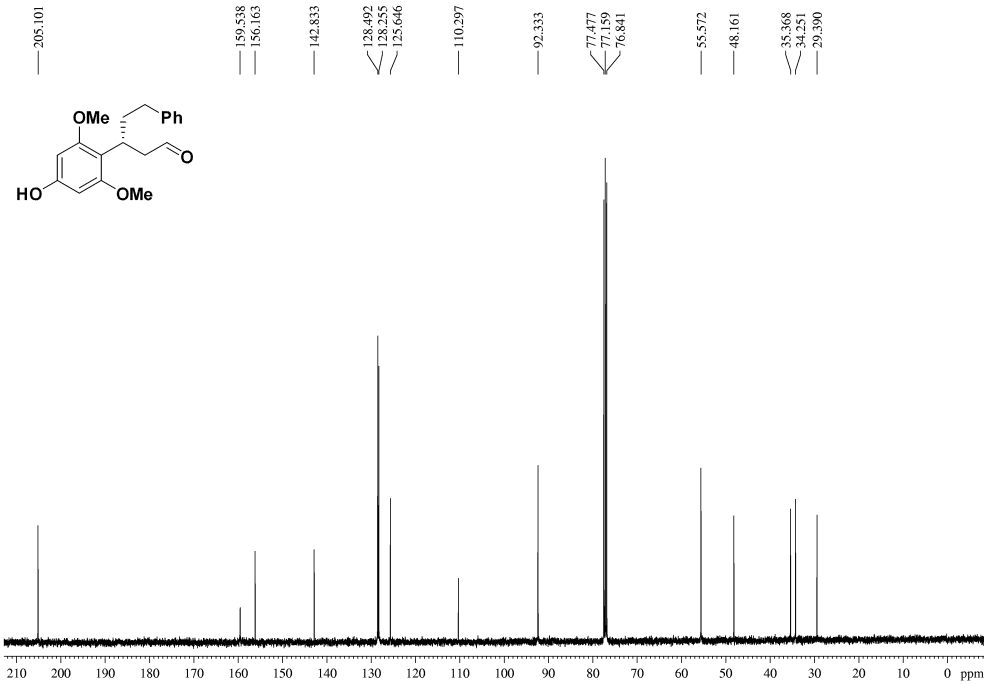
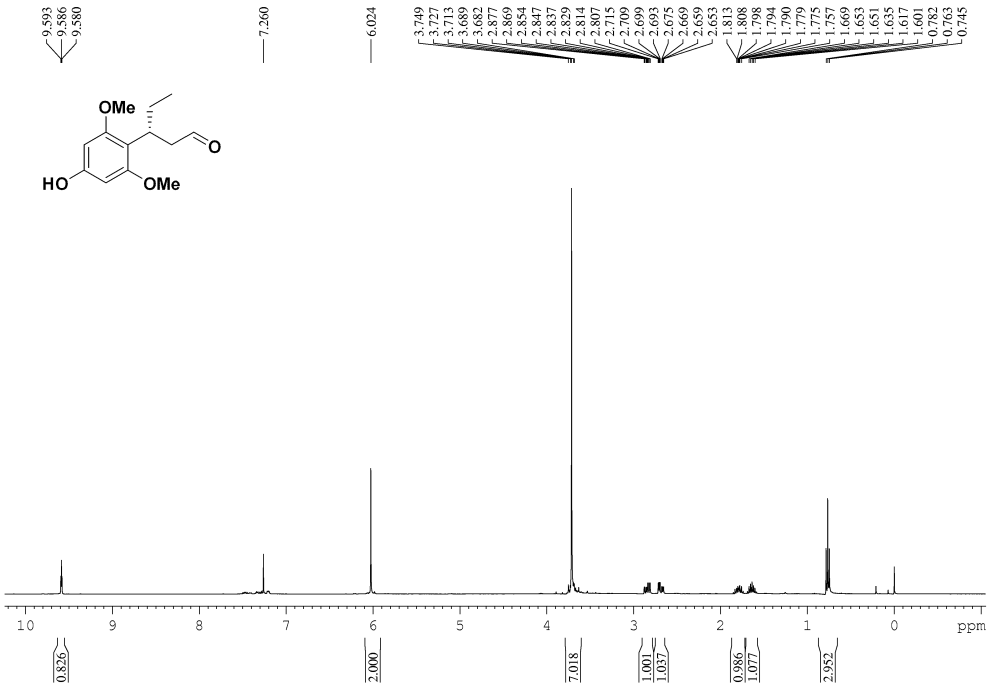
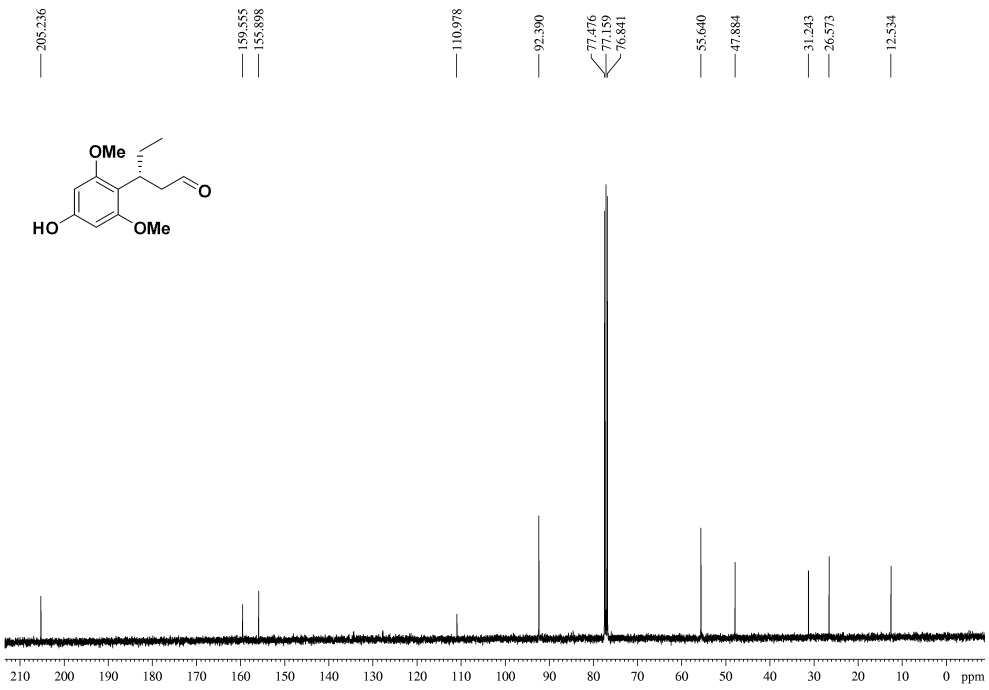


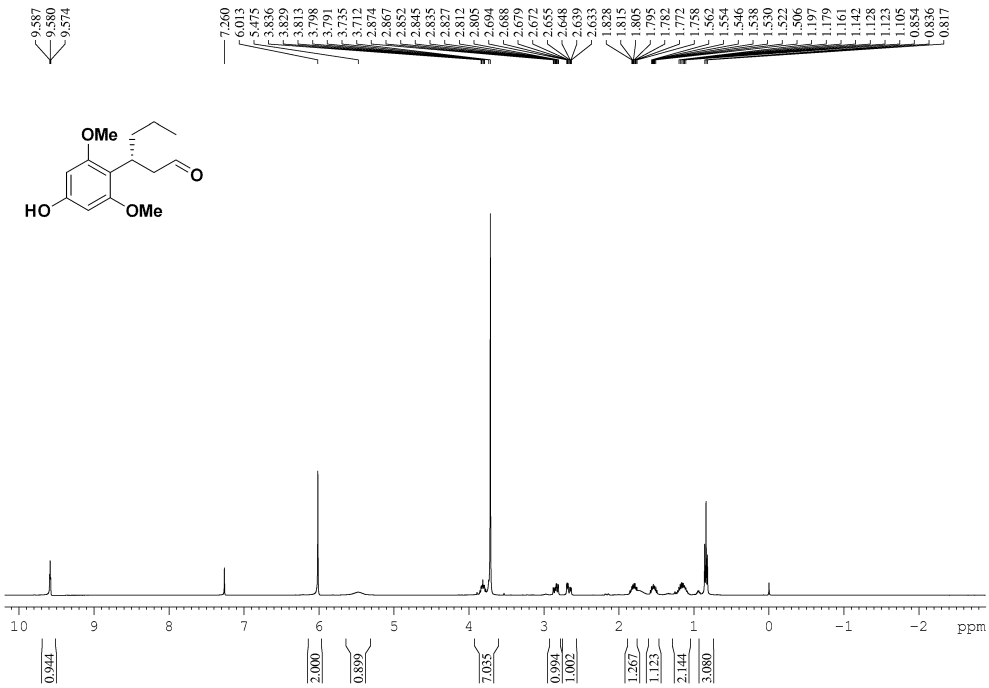
^{1}H NMR of Compound **9g** (400 MHz, $CDCl_3$)



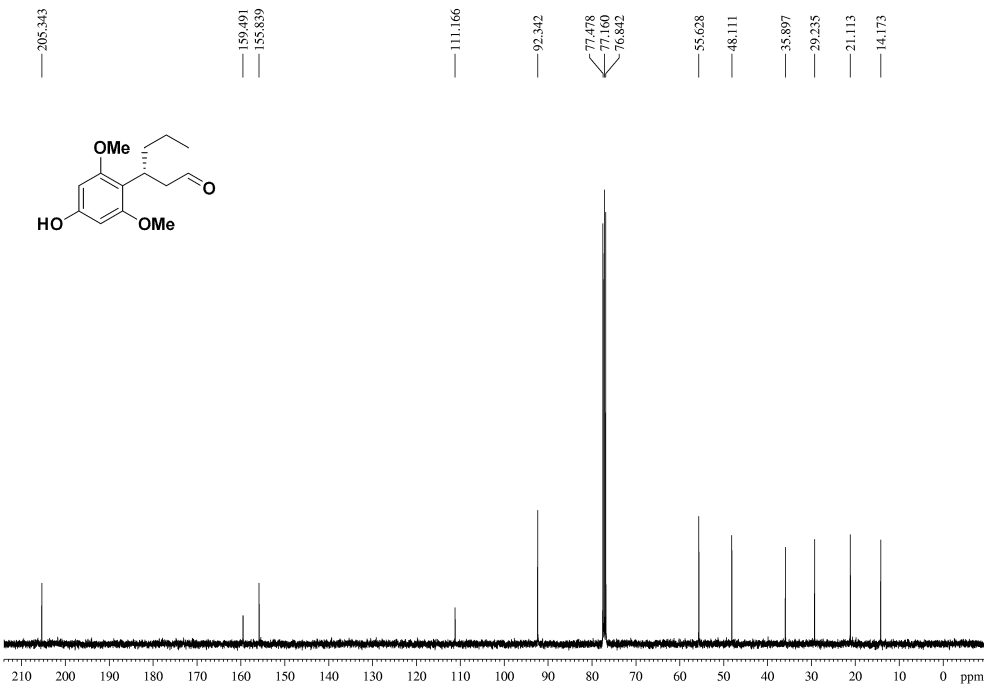
^{13}C NMR of Compound **9g** (100 MHz, $CDCl_3$)



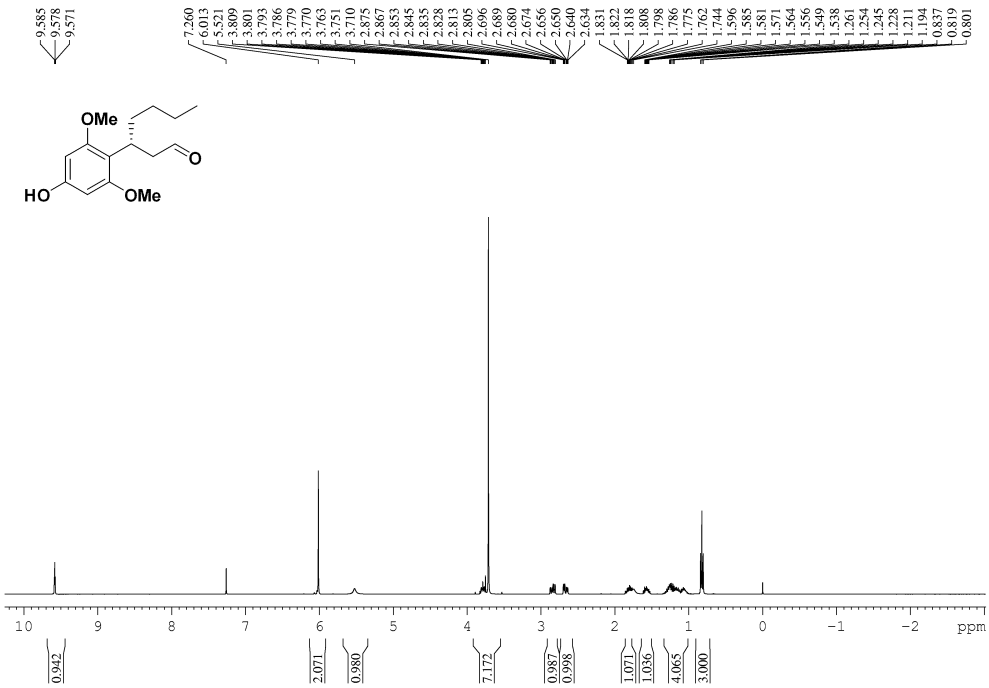
^{1}H NMR of Compound **9h** (400 MHz, $CDCl_3$)



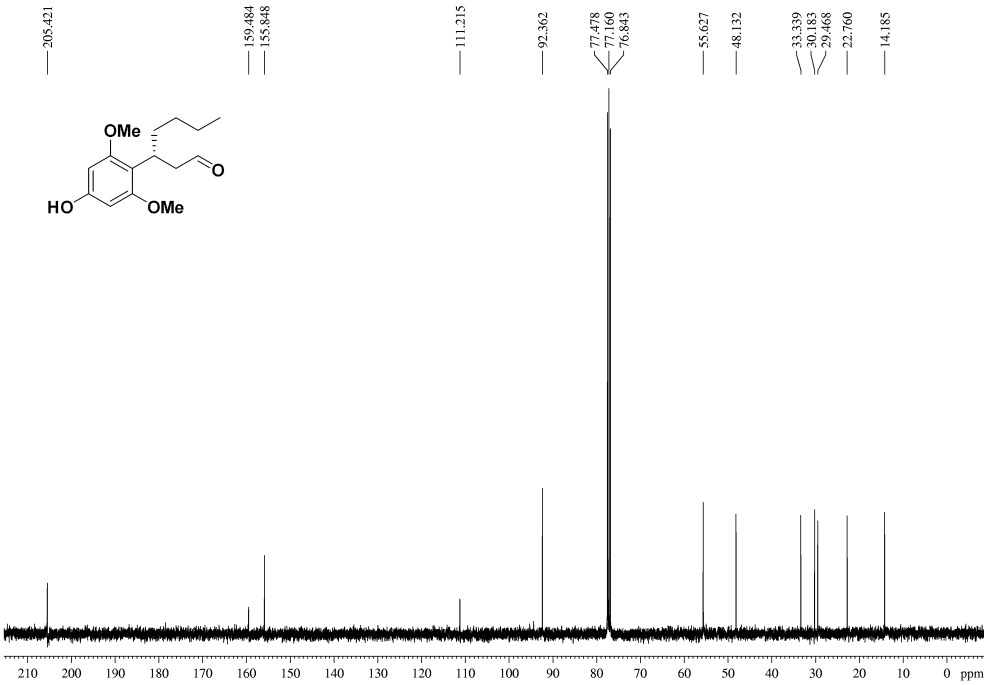
^{13}C NMR of Compound **9h** (100 MHz, $CDCl_3$)



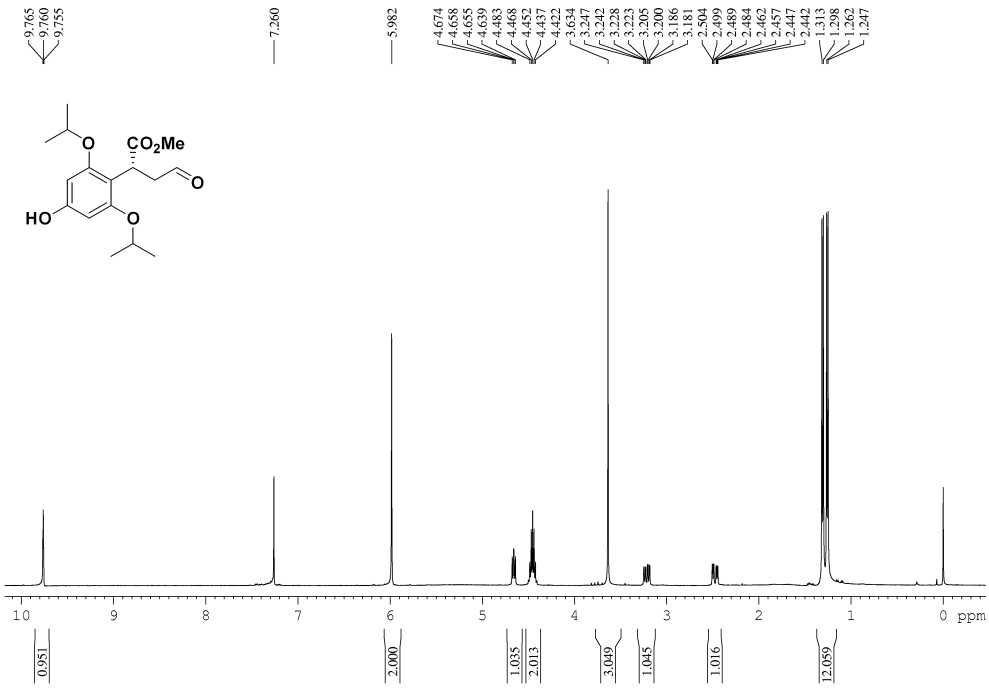
^{1}H NMR of Compound **9i** (400 MHz, $CDCl_3$)



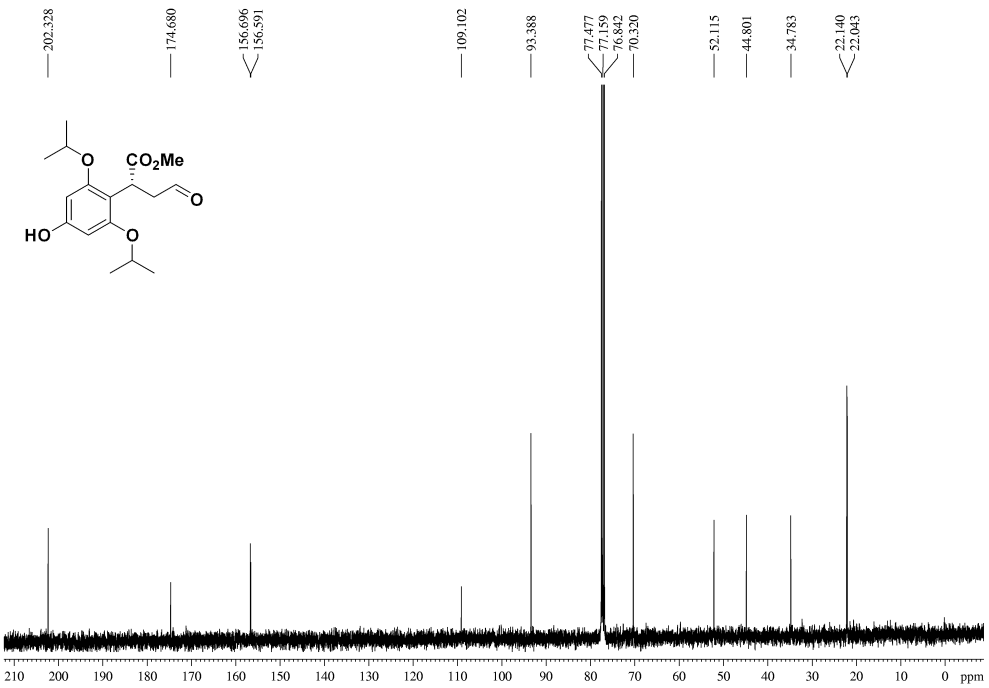
^{13}C NMR of Compound **9i** (100 MHz, $CDCl_3$)



^{1}H NMR of Compound **9j** (400 MHz, $CDCl_3$)



^{13}C NMR of Compound **9j** (100 MHz, $CDCl_3$)



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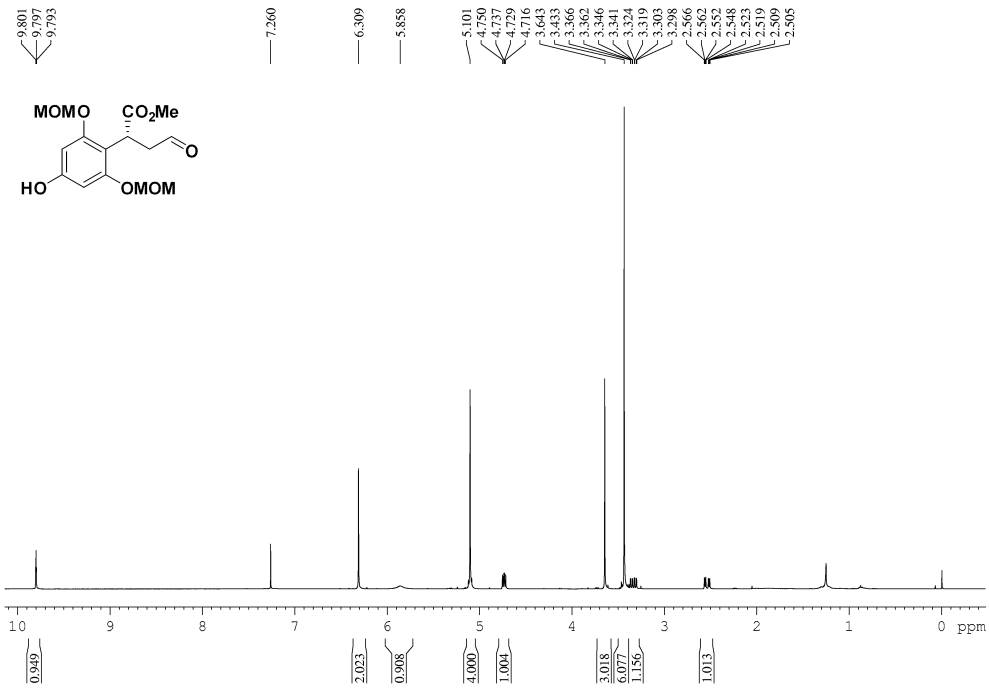

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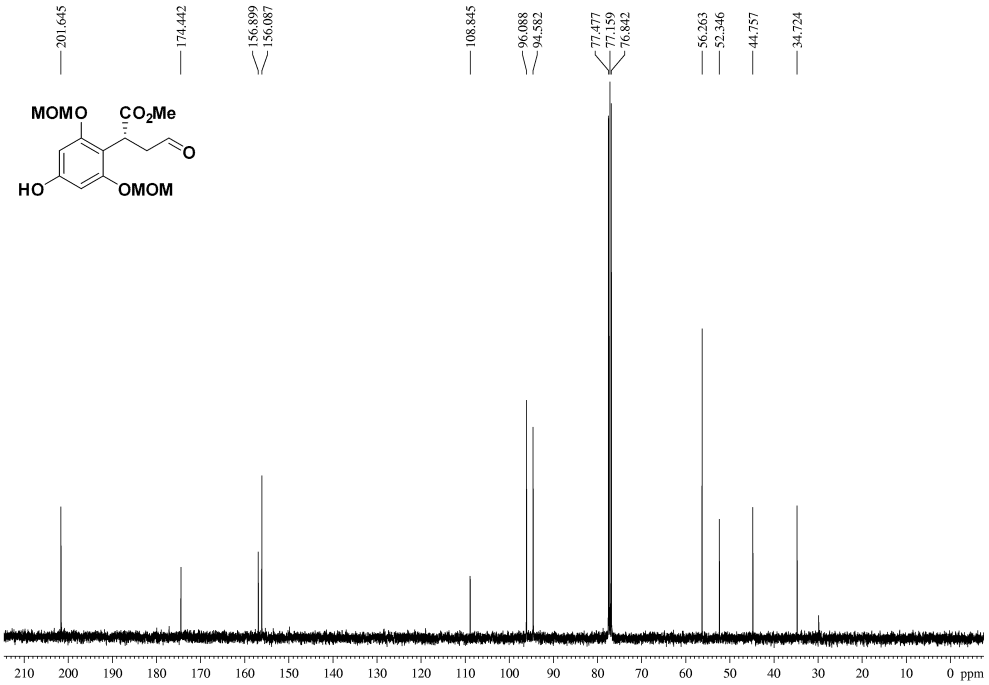
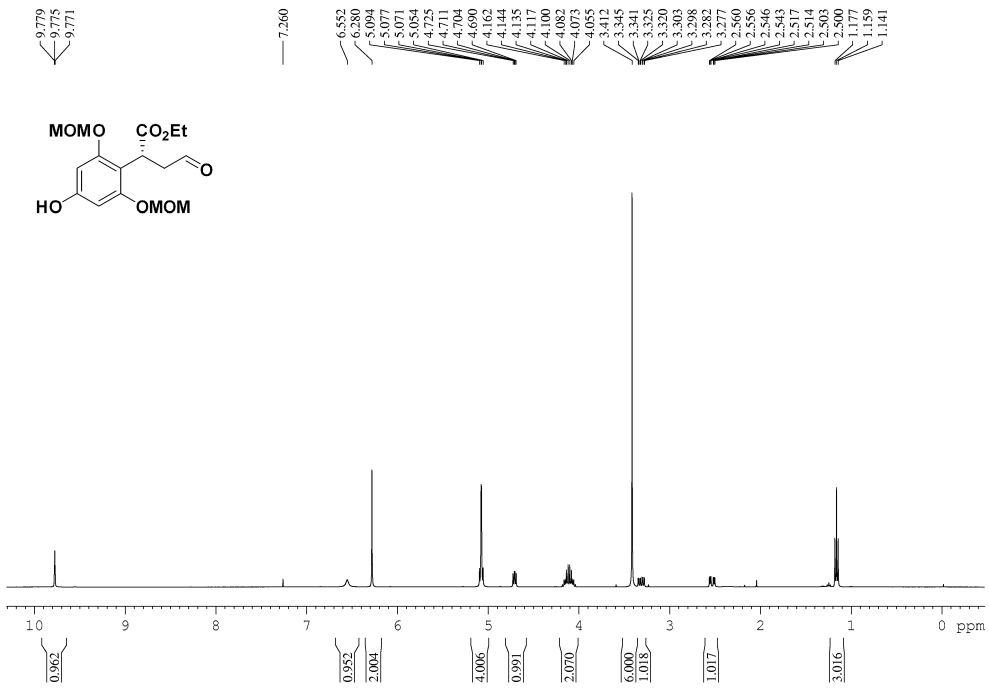
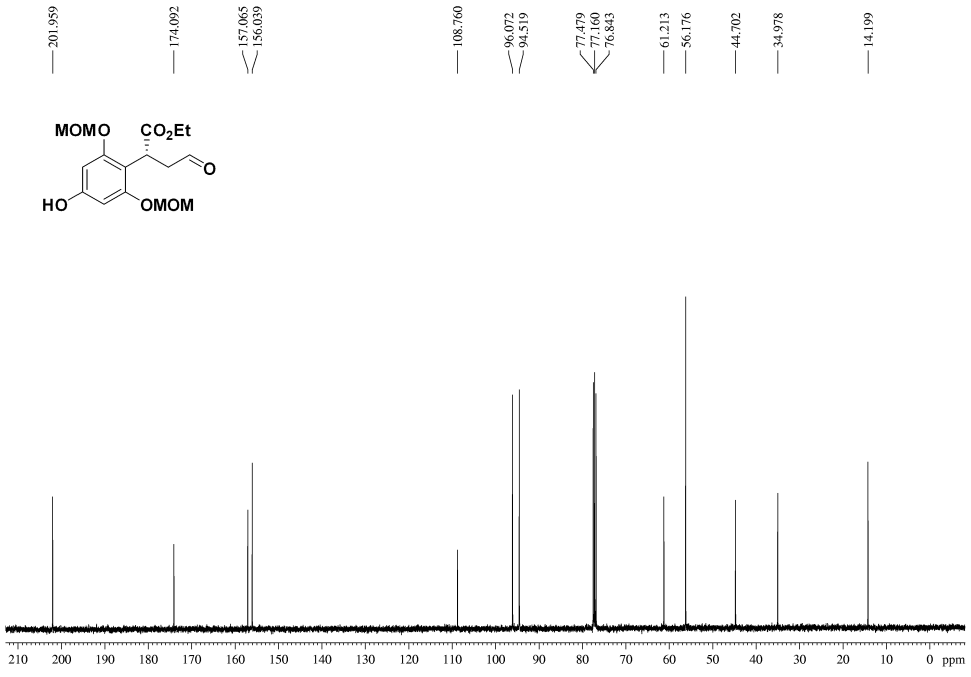


^{1}H NMR of Compound **9l** (400 MHz, $CDCl_3$)



^{13}C NMR of Compound **9l** (100 MHz, $CDCl_3$)



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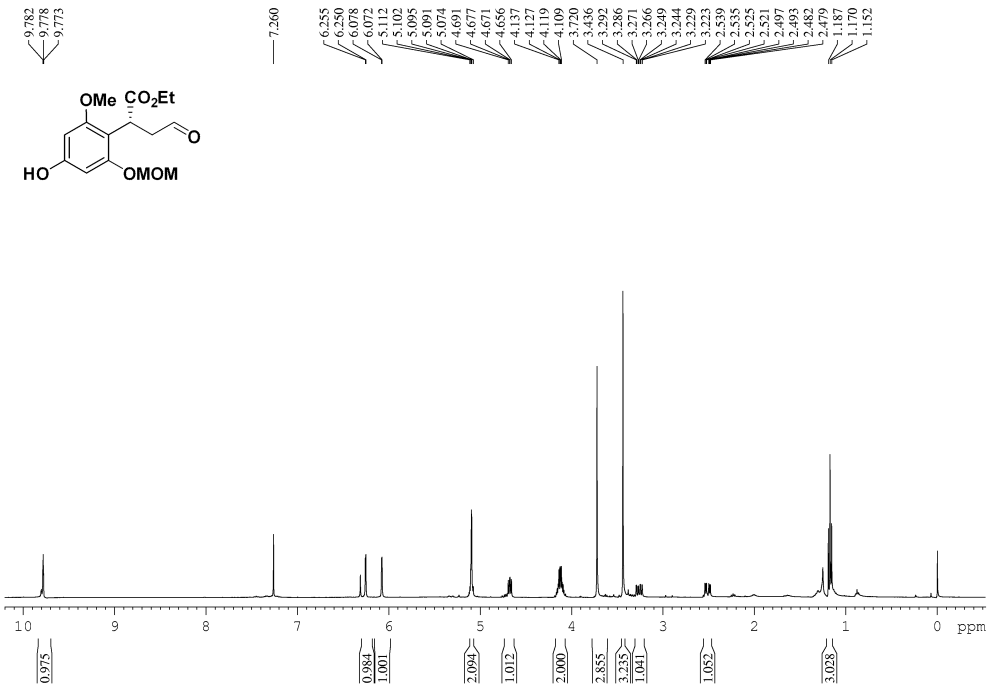
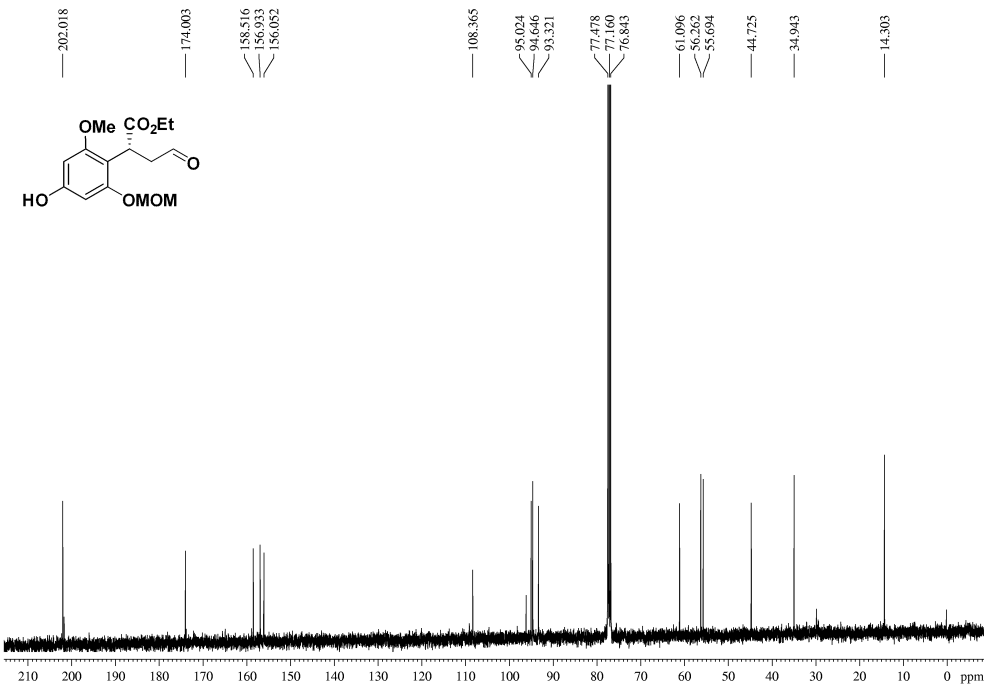


^{13}C NMR of Compound **9m** (100 MHz, $CDCl_3$)



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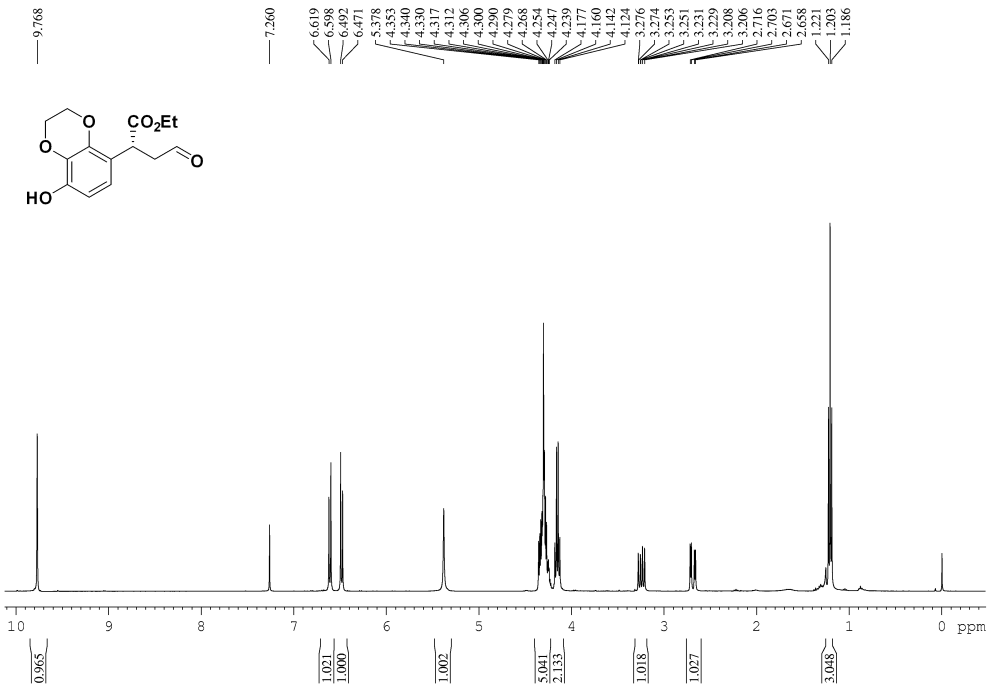
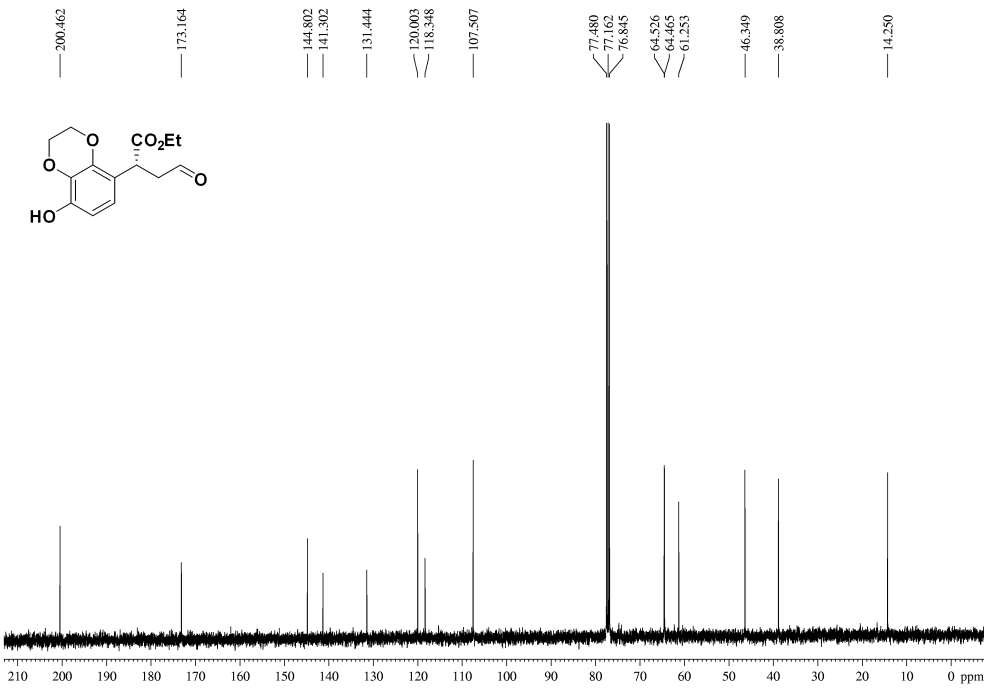
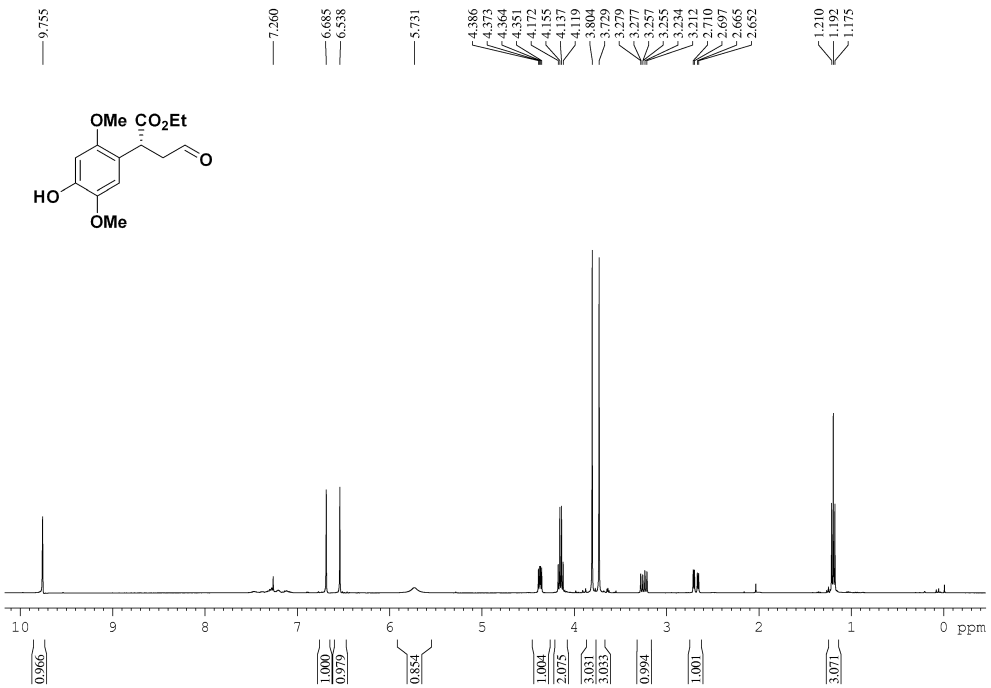


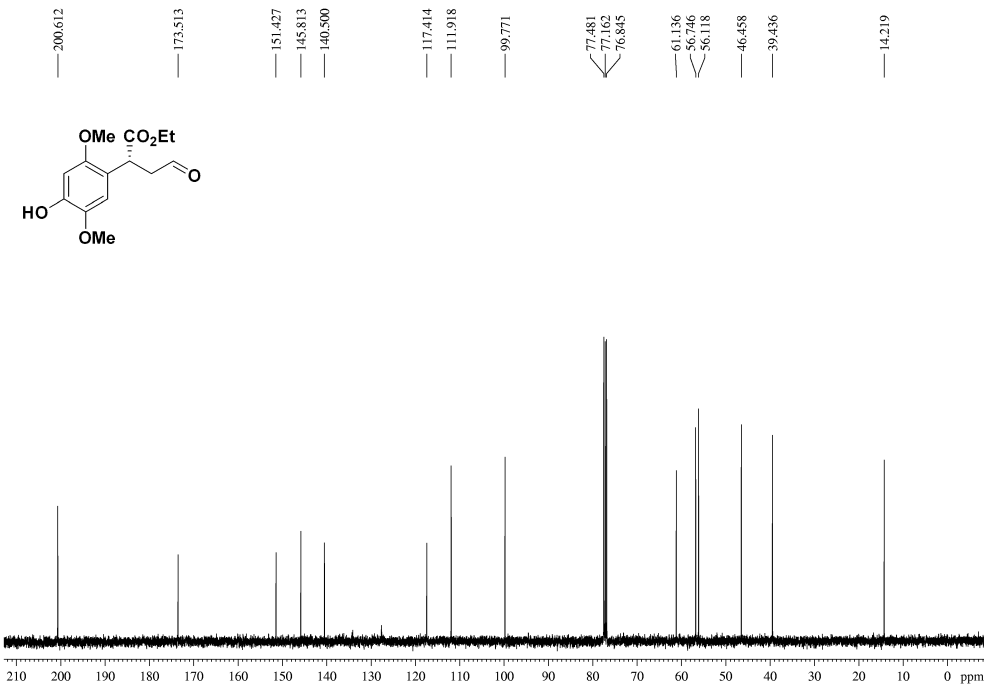
^{13}C NMR of Compound **9n** (100 MHz, $CDCl_3$)



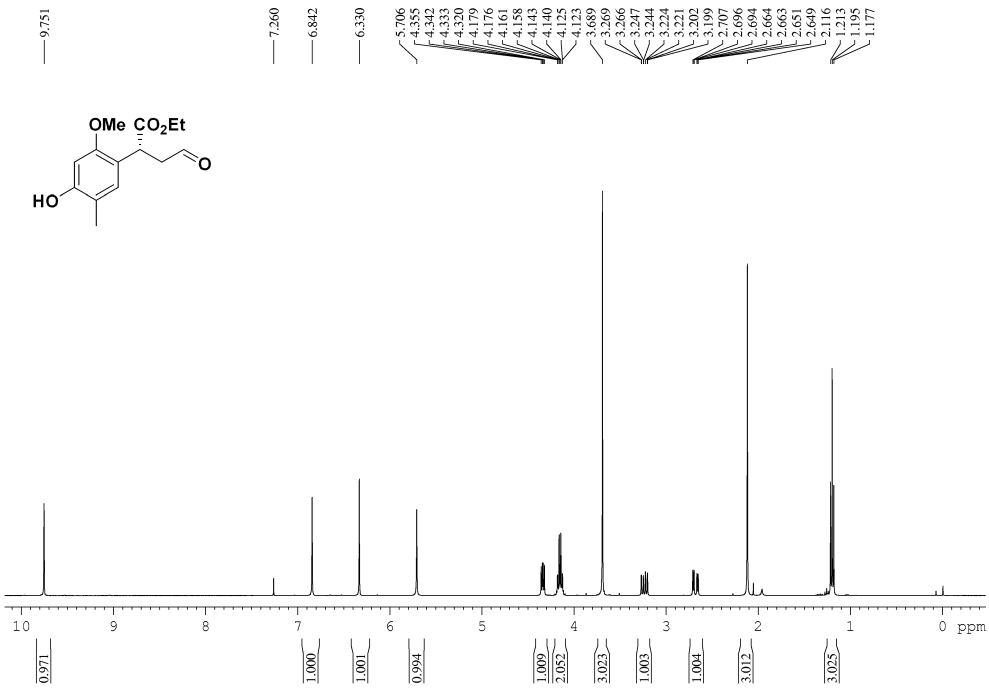
^{1}H NMR of Compound **90** (400 MHz, $CDCl_3$)



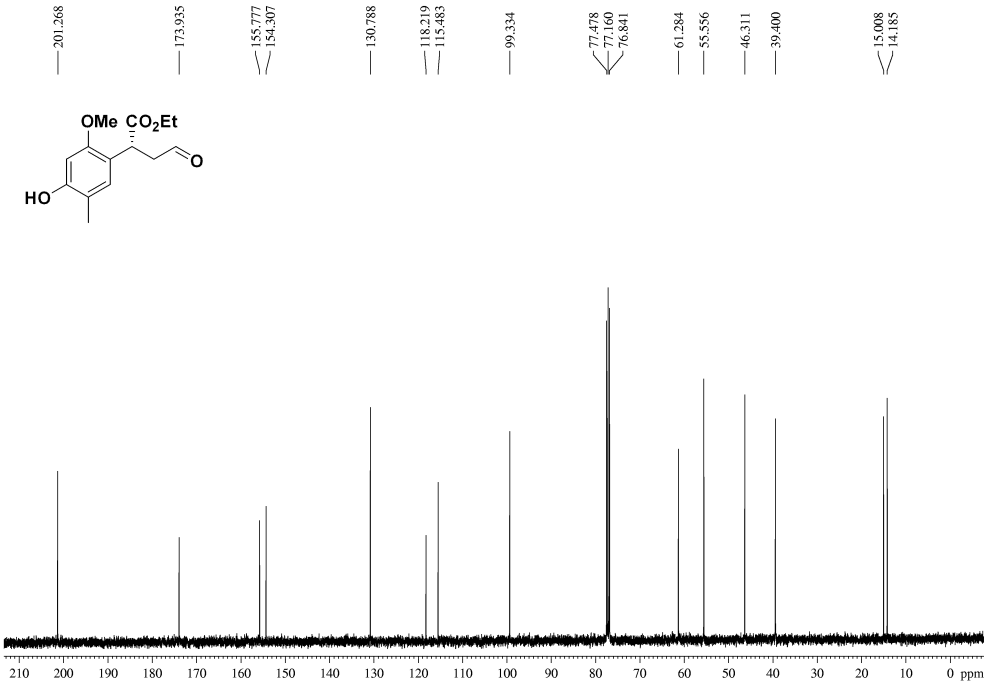
^{13}C NMR of Compound **9o** (100 MHz, $CDCl_3$)



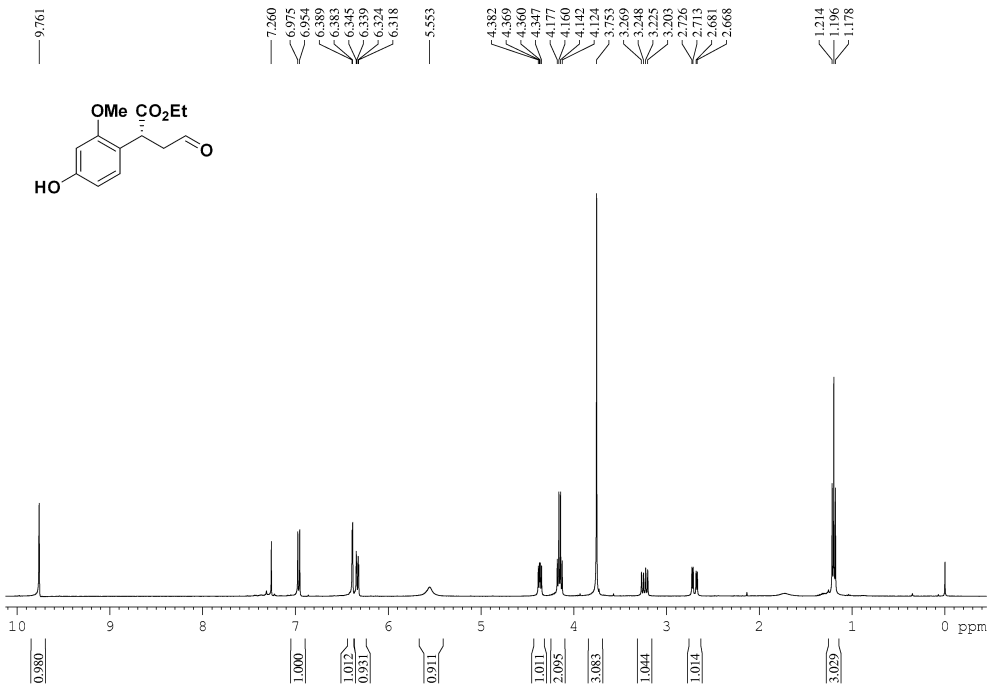
^{1}H NMR of Compound **9p** (400 MHz, $CDCl_3$)



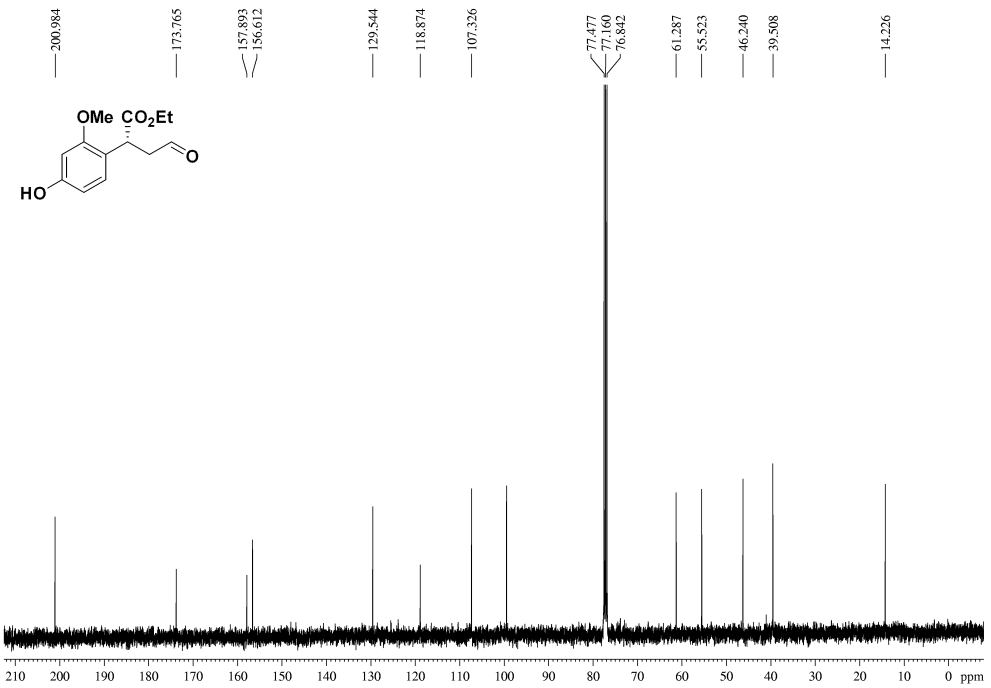
^{13}C NMR of Compound **9p** (100 MHz, $CDCl_3$)



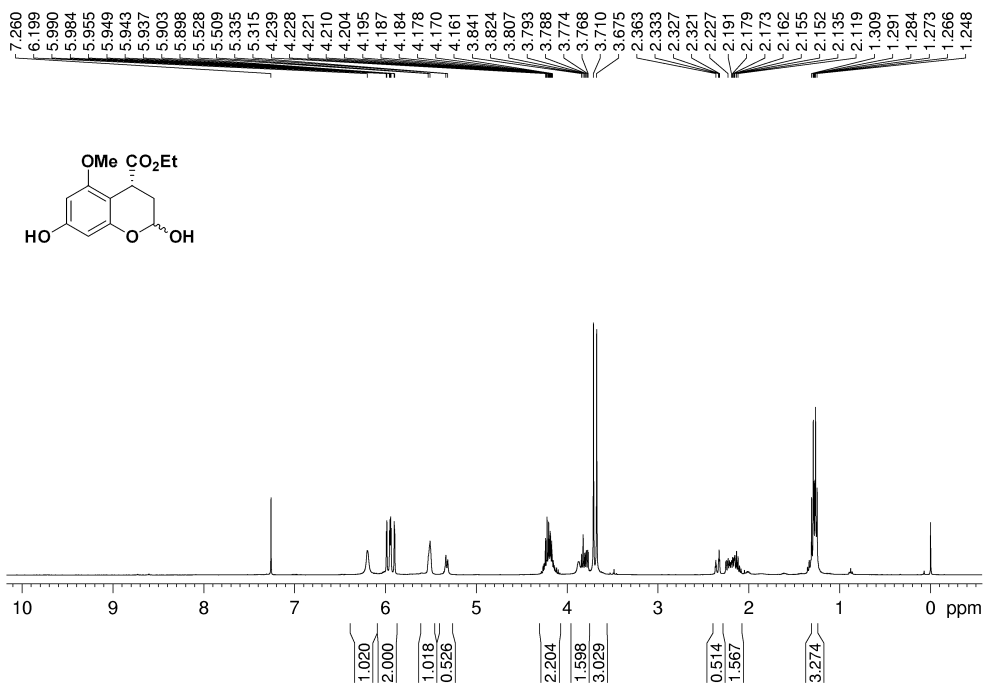
^{1}H NMR of Compound **9q** (400 MHz, $CDCl_3$)



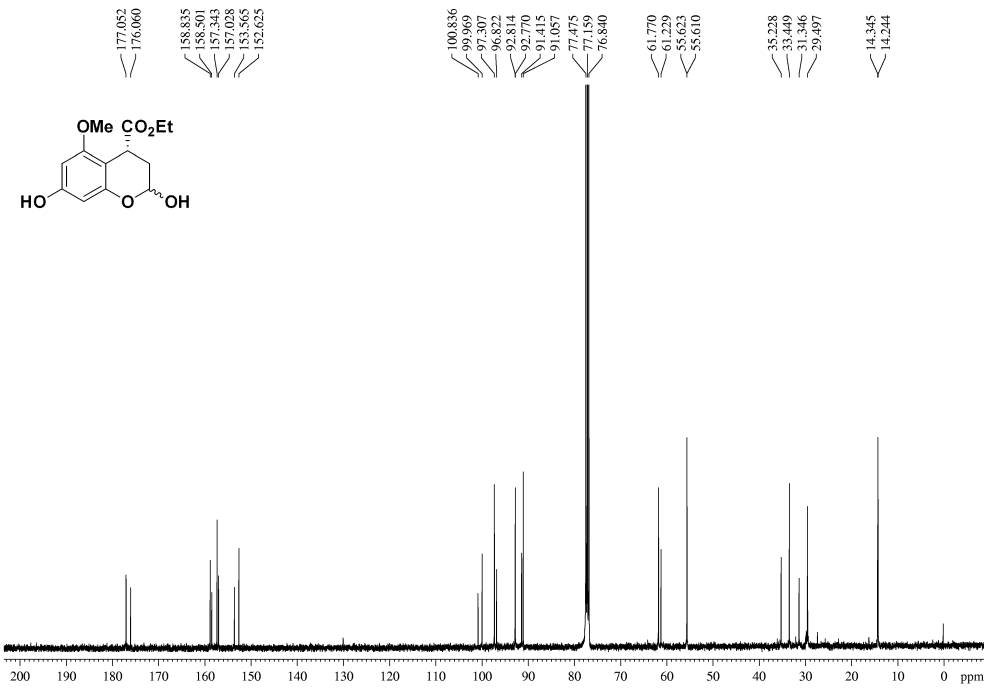
^{13}C NMR of Compound **9q** (100 MHz, $CDCl_3$)



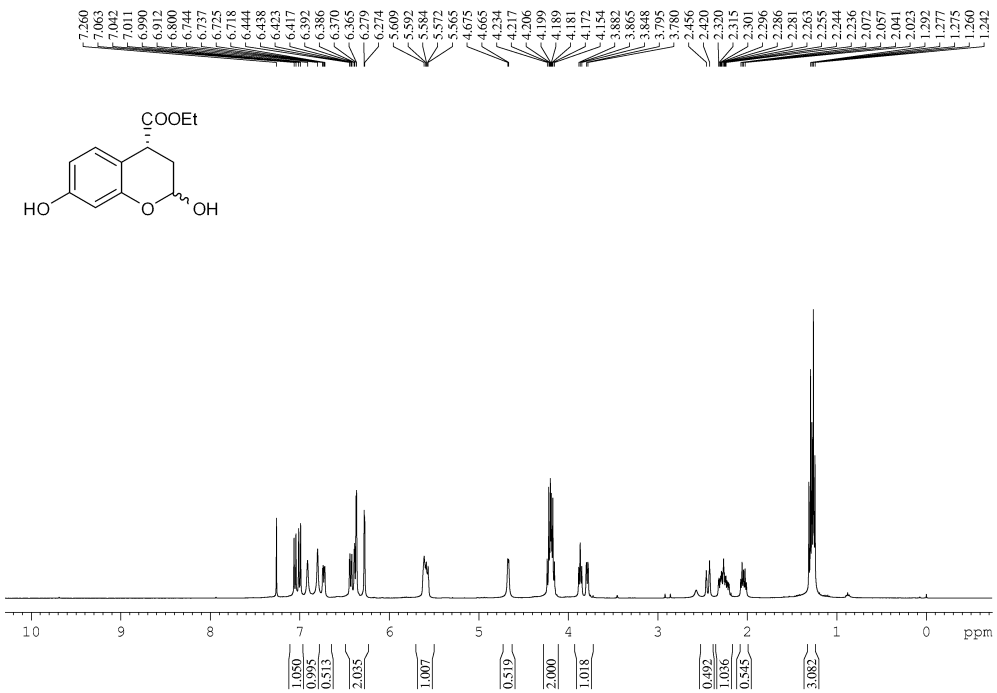
^{1}H NMR of Compound **9r** (400 MHz, $CDCl_3$)



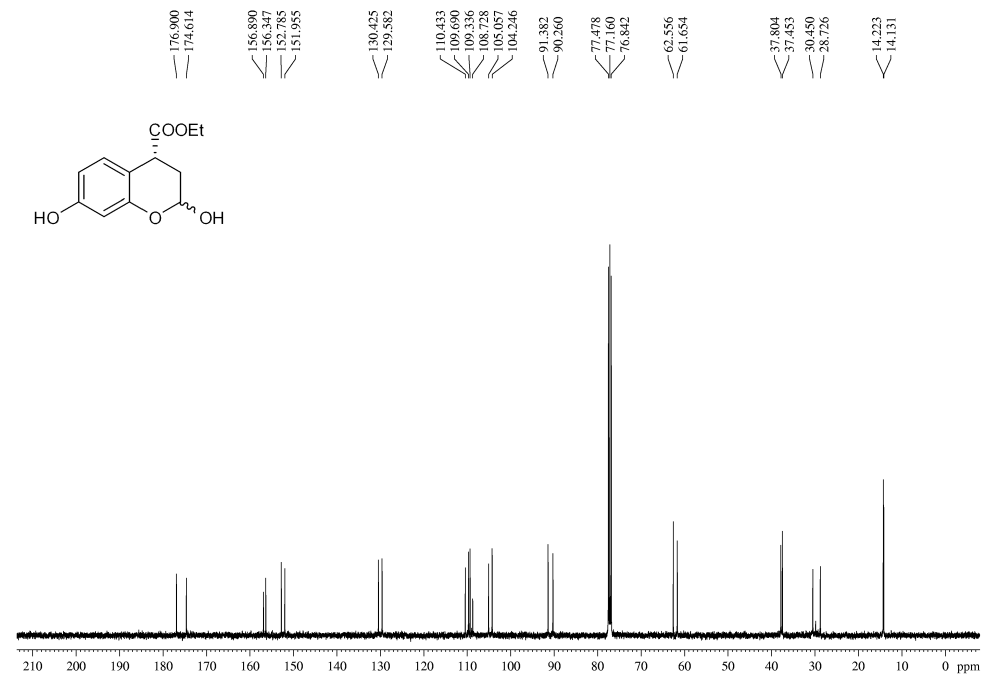
^{13}C NMR of Compound **9r** (100 MHz, $CDCl_3$)



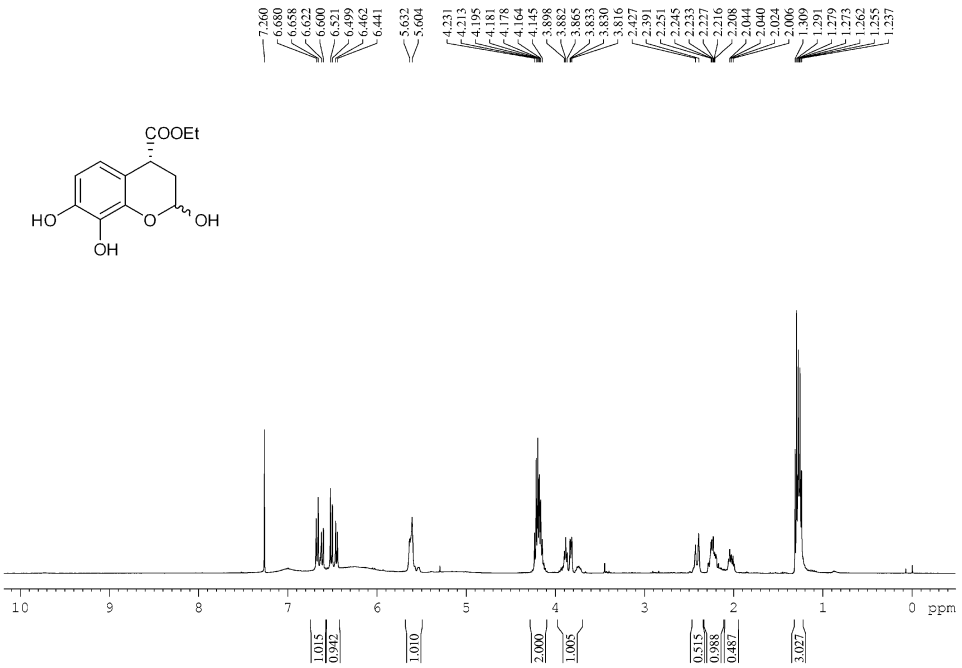
^{1}H NMR of Compound **9s** (400 MHz, $CDCl_3$)



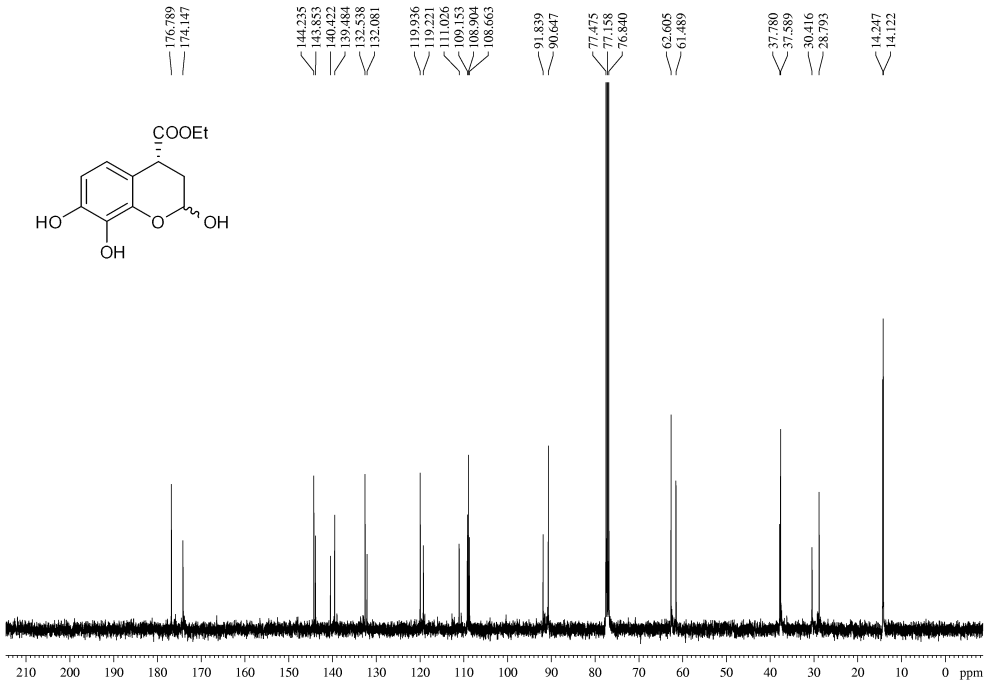
^{13}C NMR of Compound **9s** (100 MHz, $CDCl_3$)



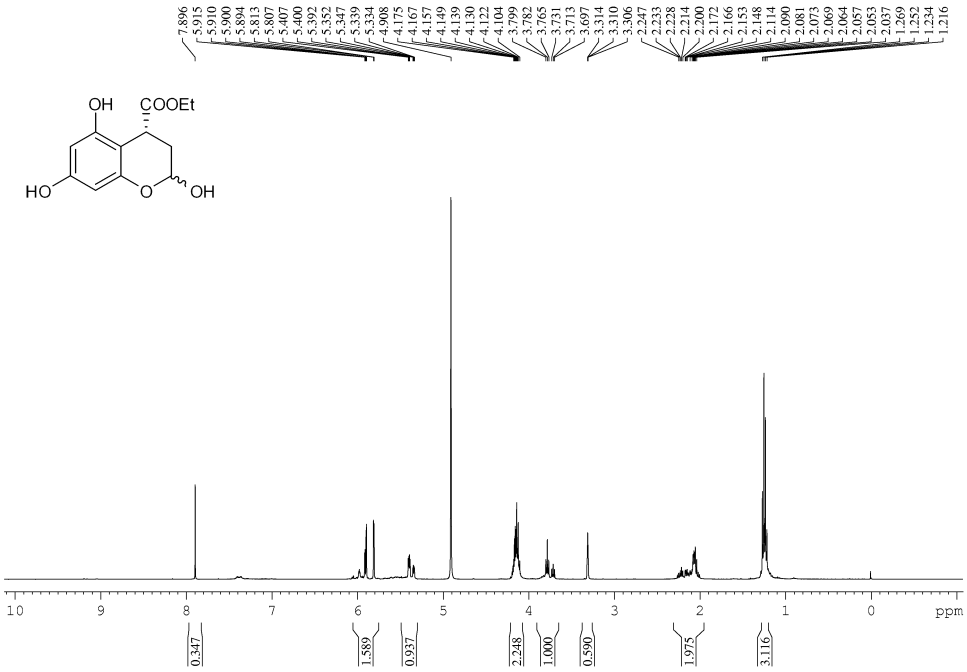
^{1}H NMR of Compound **9t** (400 MHz, $CDCl_3$)



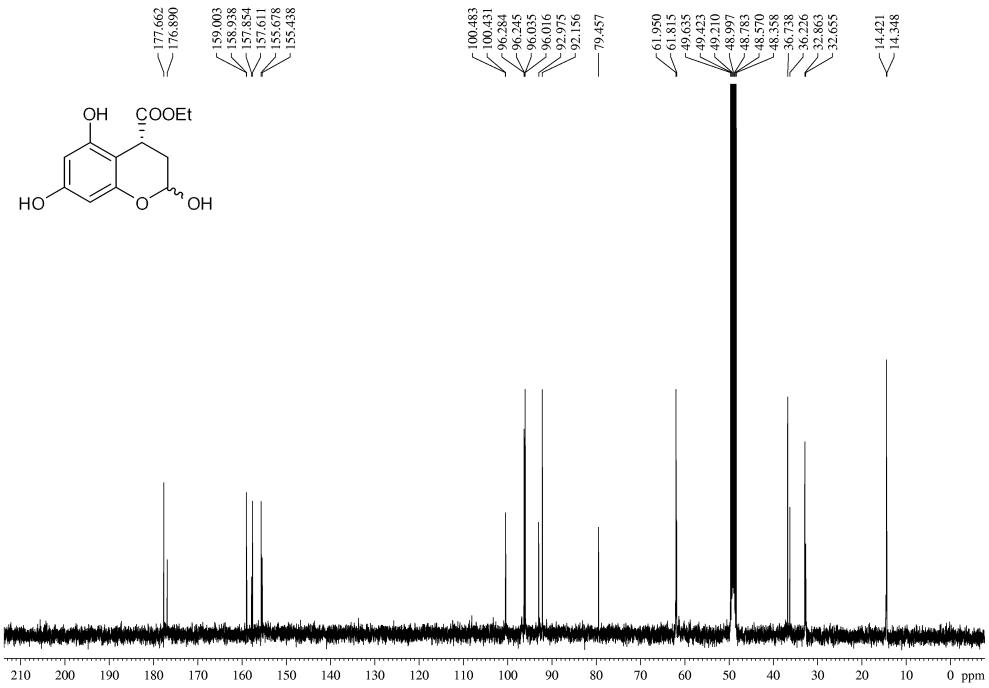
^{13}C NMR of Compound **9t** (100 MHz, $CDCl_3$)



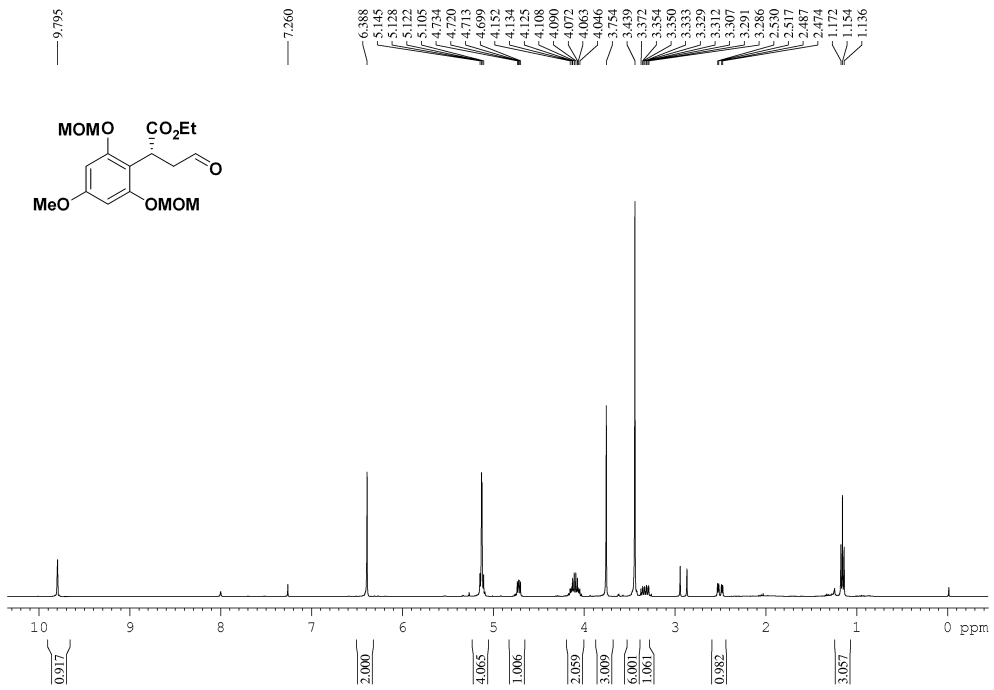
^{1}H NMR of Compound **9u** (400 MHz, CD_3OD)



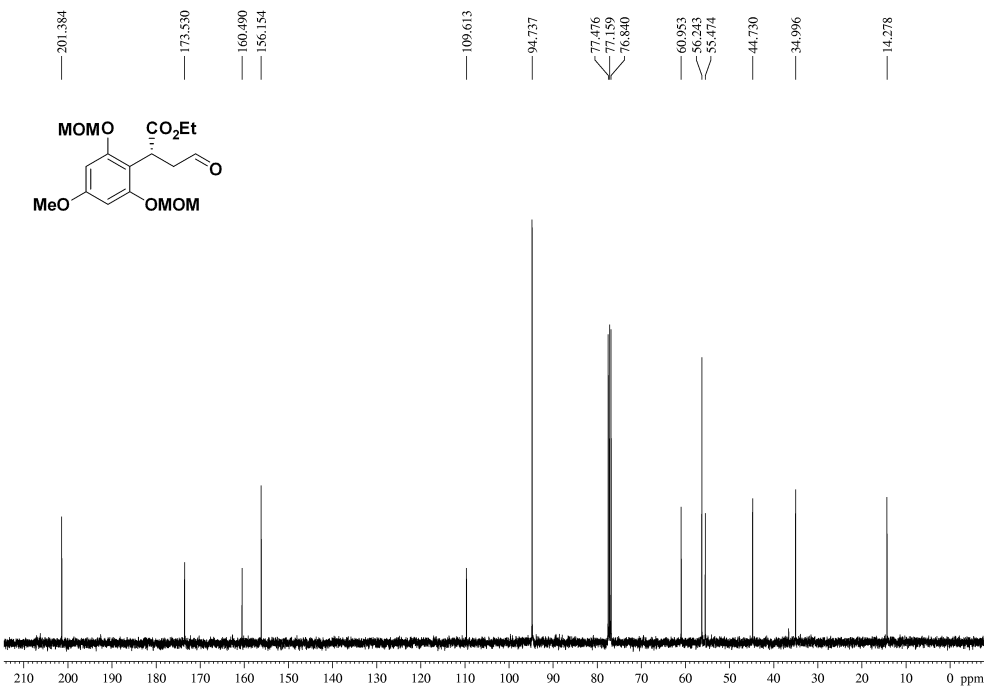
^{13}C NMR of Compound **9u** (100 MHz, CD_3OD)



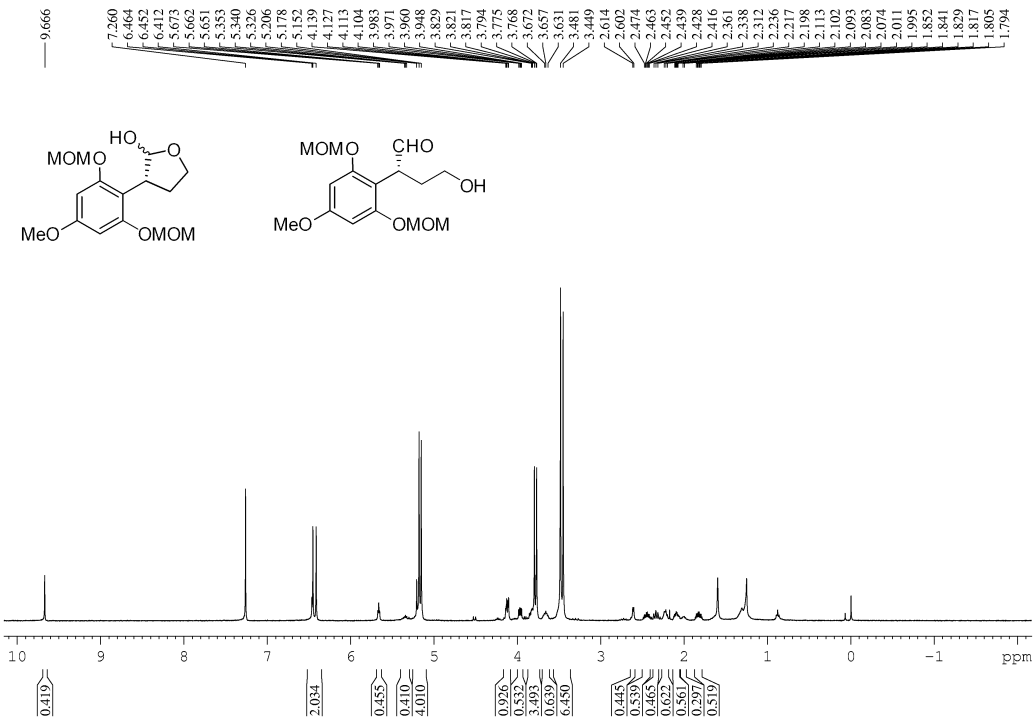
^{1}H NMR of Compound **12** (400 MHz, $CDCl_3$)



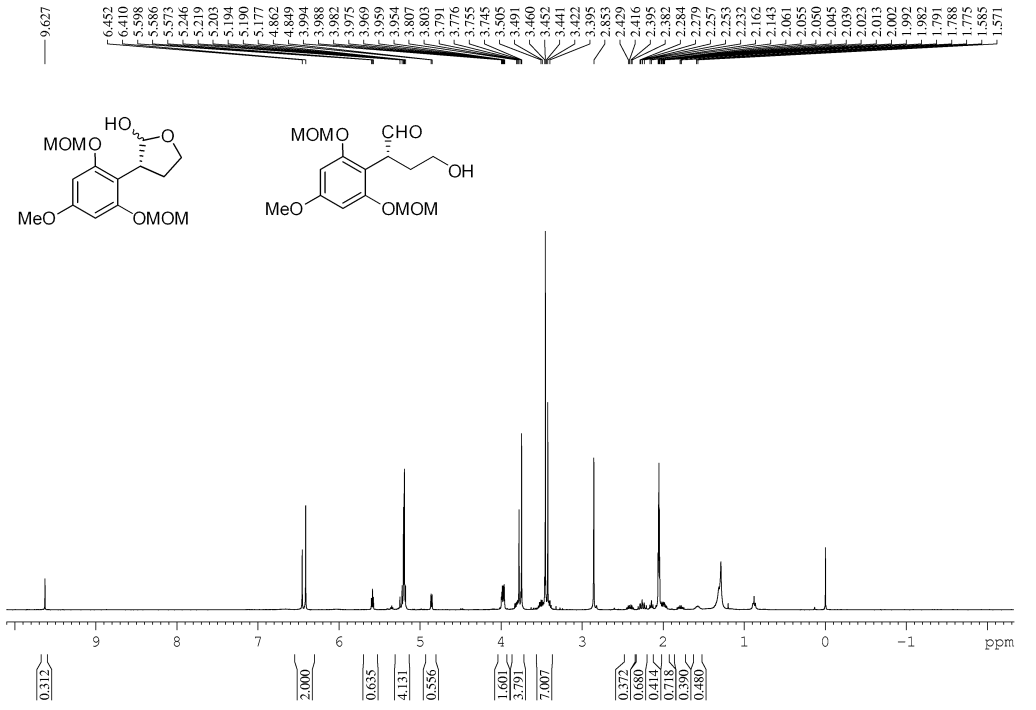
^{13}C NMR of Compound **12** (100 MHz, $CDCl_3$)



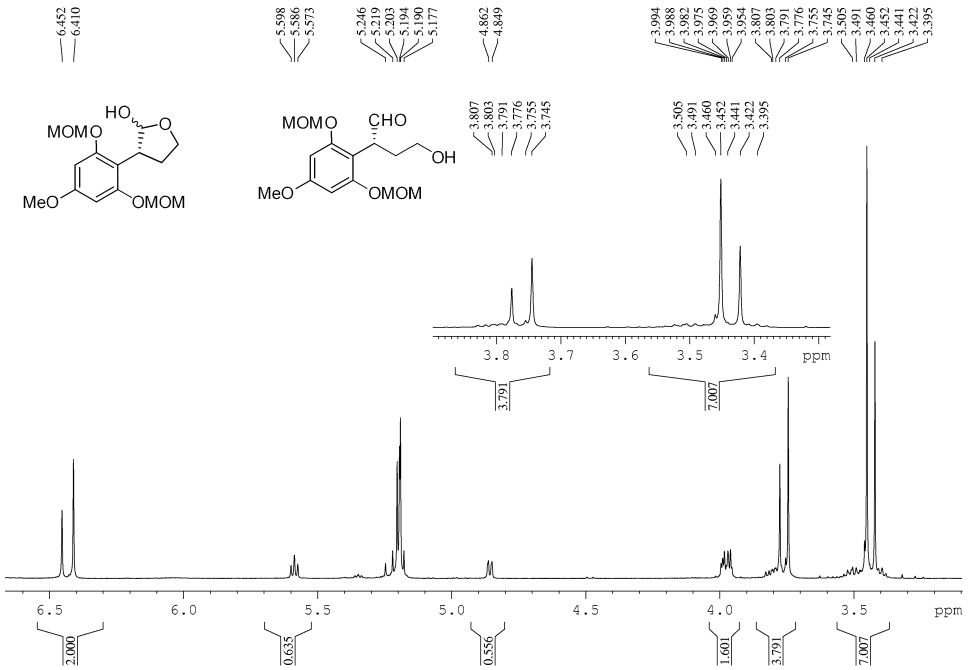
^{1}H NMR of Compound **13** (400 MHz, $CDCl_3$)



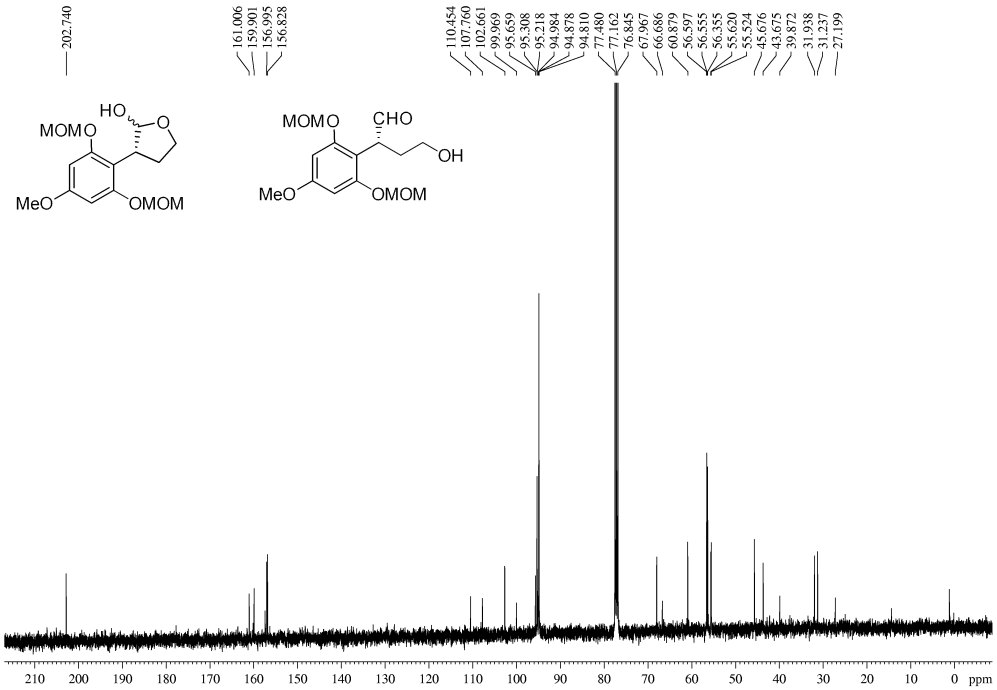
^{1}H NMR of Compound **13** (400 MHz, Acetone-D6)



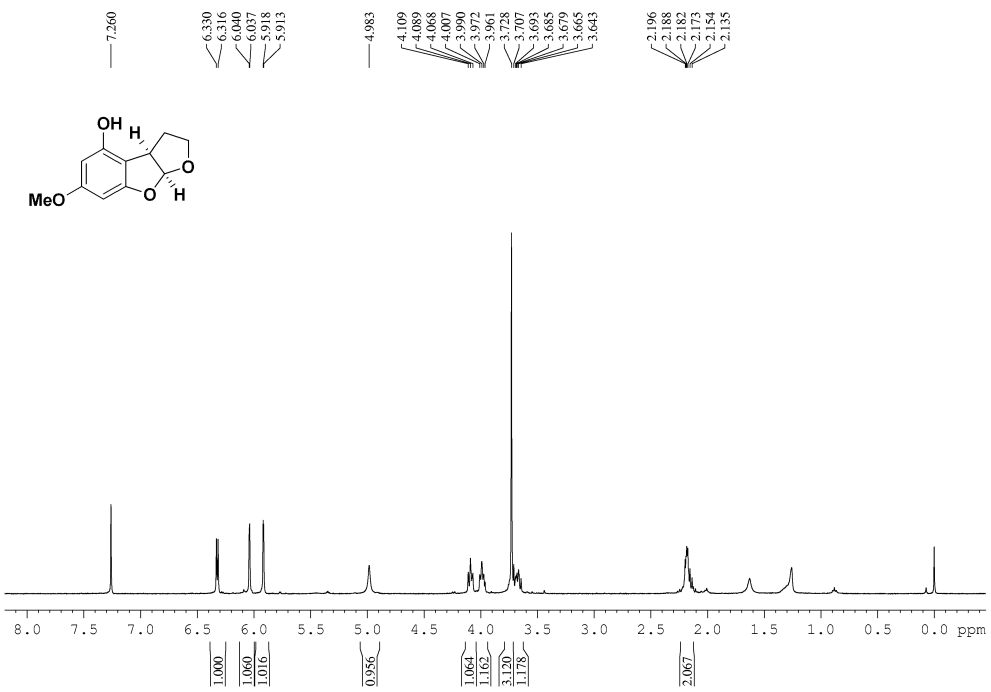
^{1}H NMR of Compound **13** (400 MHz, Acetone-D6)



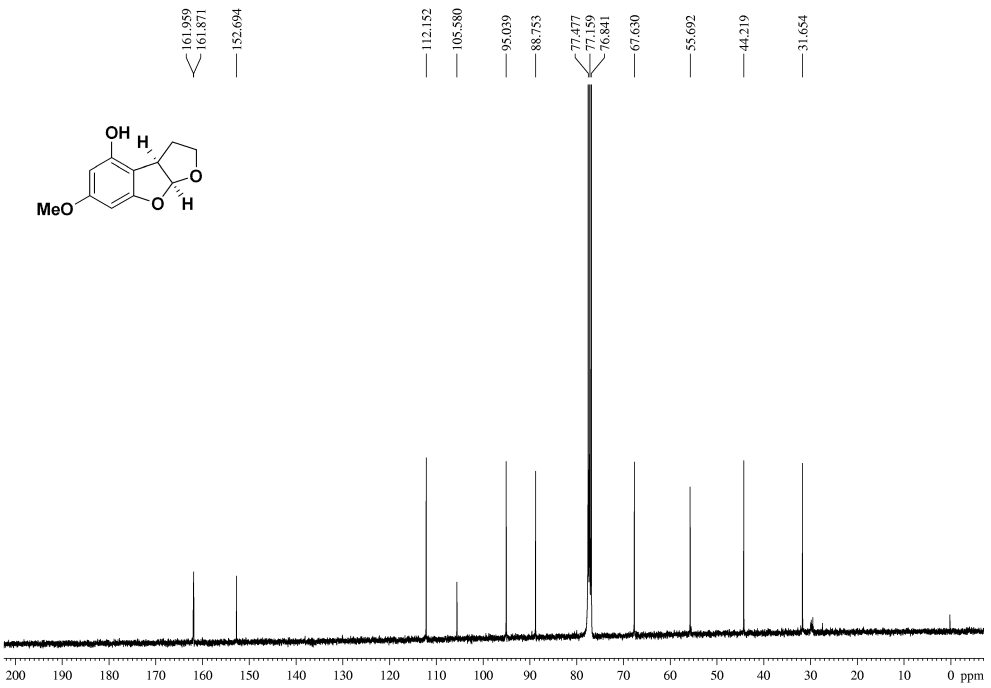
^{13}C NMR of Compound **13** (100 MHz, $CDCl_3$)



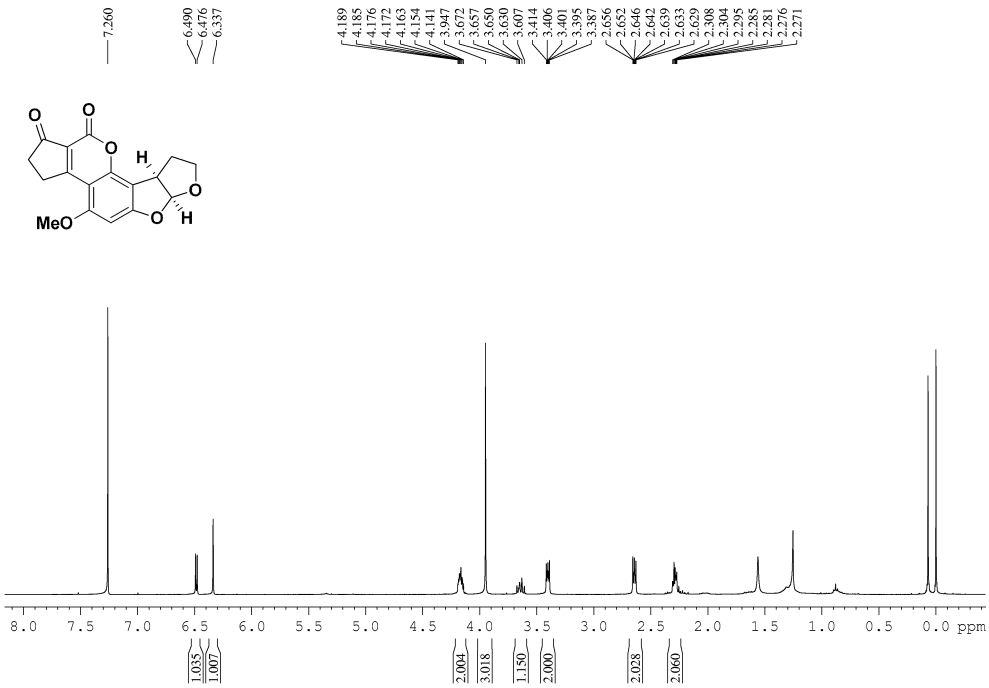
^{1}H NMR of Compound **10** (400 MHz, $CDCl_3$)



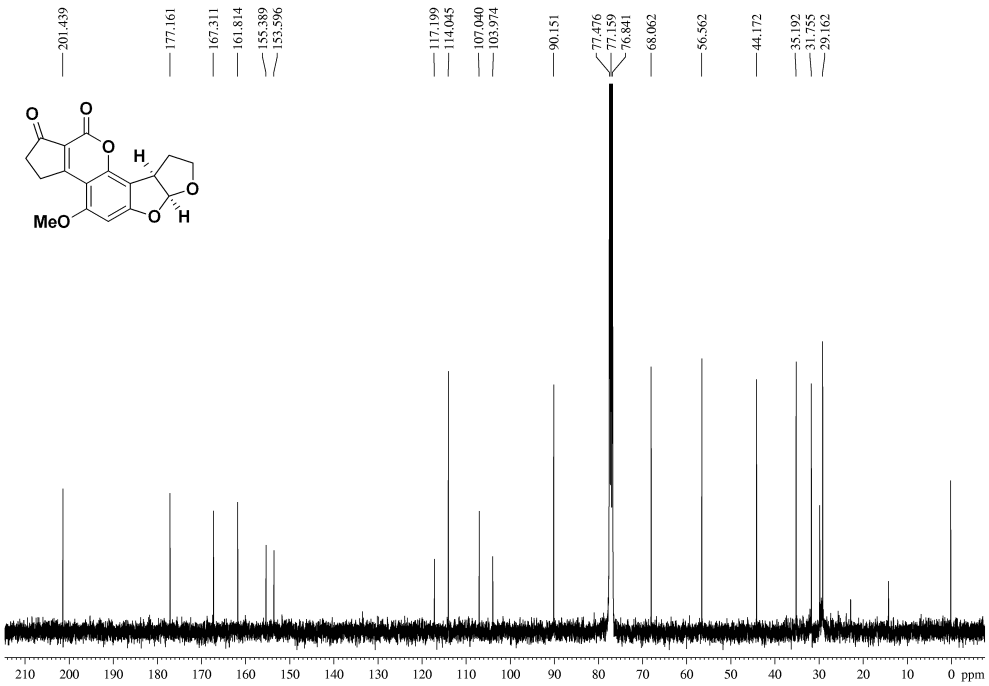
^{13}C NMR of Compound **10** (100 MHz, $CDCl_3$)



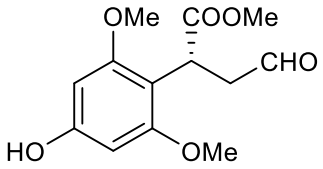
^{1}H NMR of Compound **5** (400 MHz, $CDCl_3$)



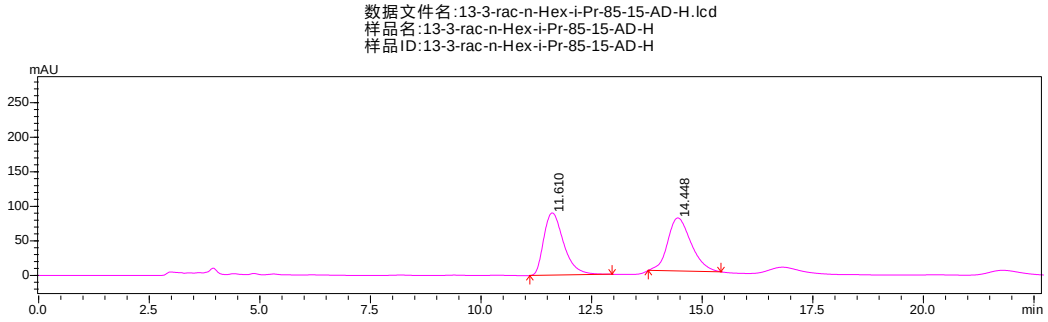
^{13}C NMR of Compound **5** (100 MHz, $CDCl_3$)



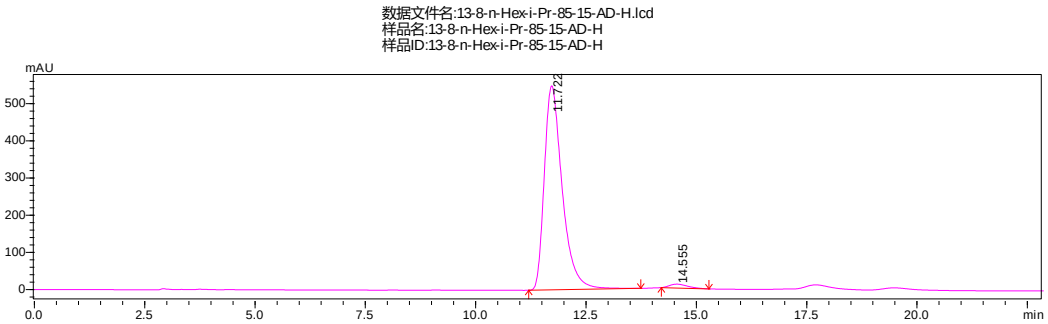
HPLC Spectra



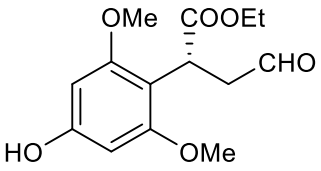
9a



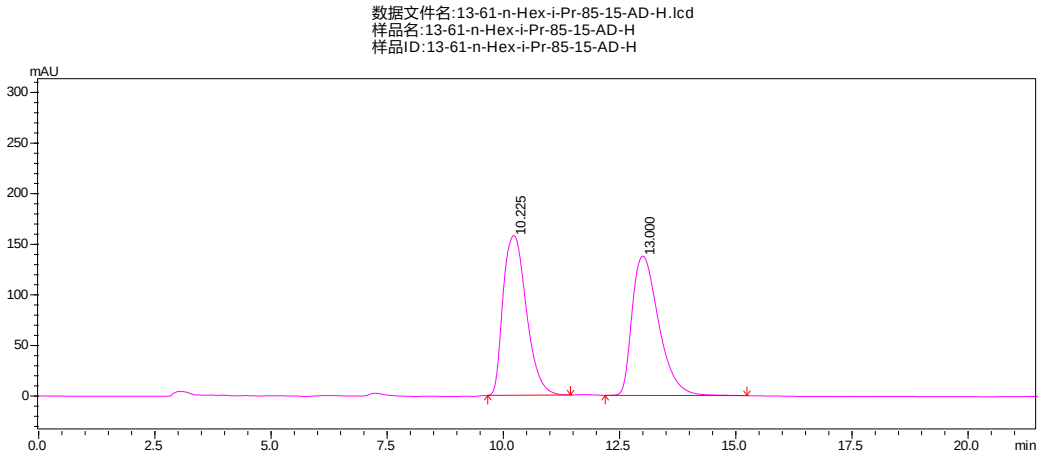
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	11.610	2836784	90171	50.037
2	14.448	2832547	76854	49.963
Total		5669331	167026	100.000



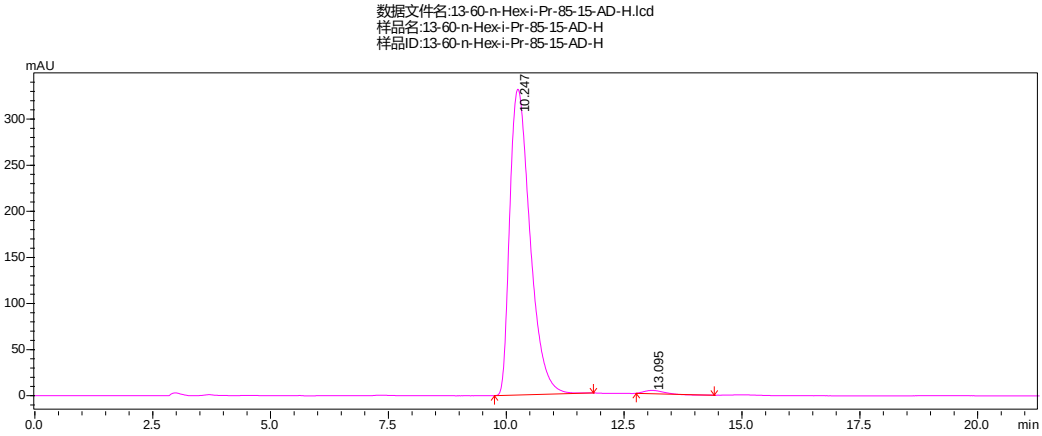
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	11.722	15512866	548496	98.531
2	14.555	231258	10339	1.469
Total		15744124	558835	100.000



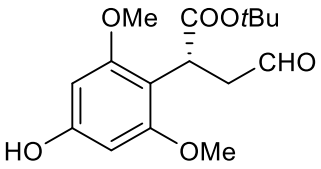
9b



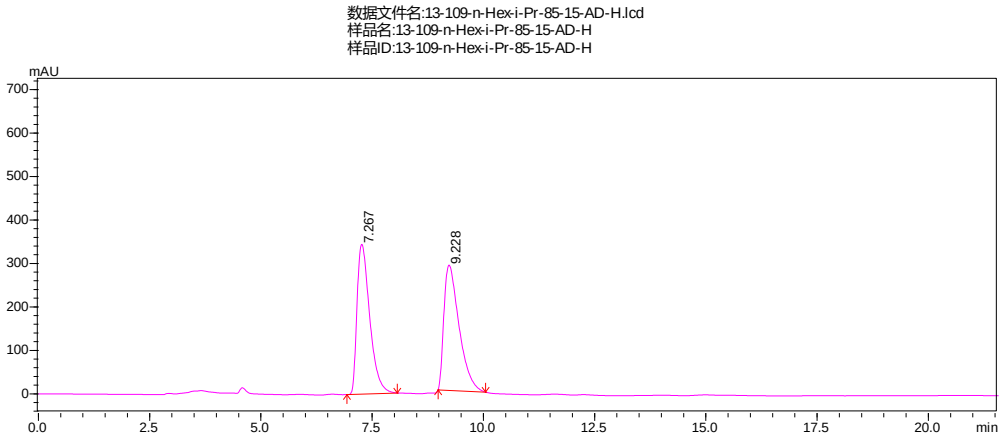
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	10.225	5496730	157796	50.028
2	13.000	5490478	137608	49.972
Total		10987208	295405	100.000



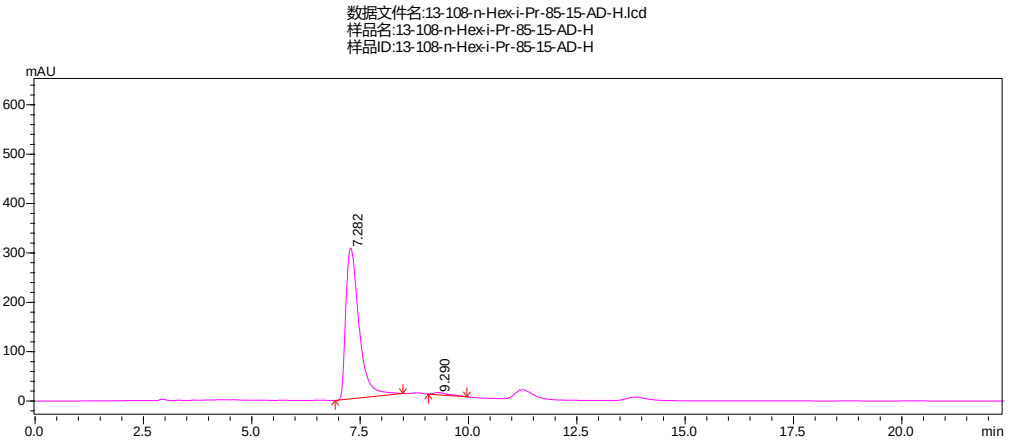
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	10.247	9934448	331585	99.154
2	13.095	84737	3498	0.846
Total		10019184	335083	100.000



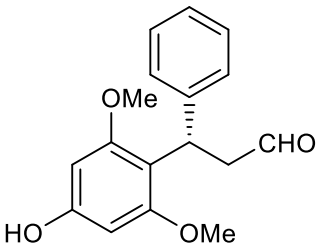
9c



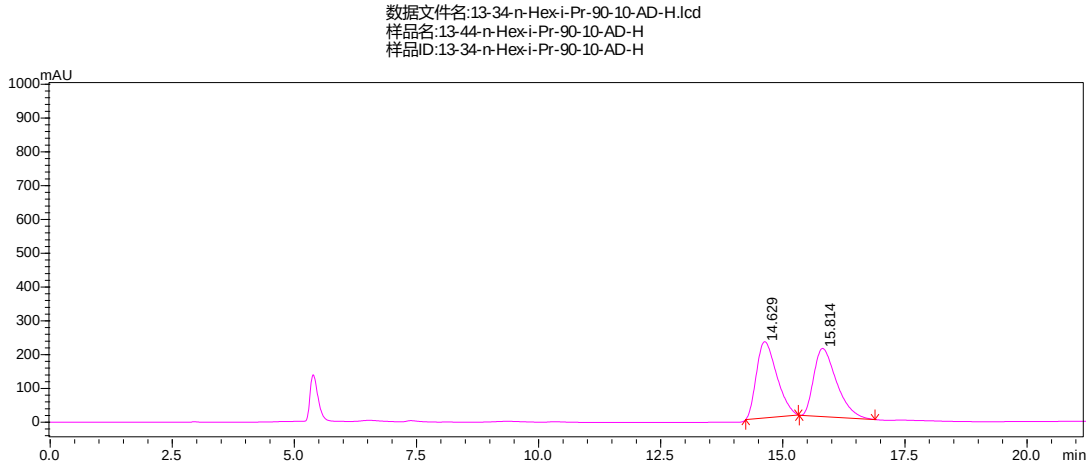
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	7.267	6856773	344898	50.032
2	9.228	6847888	288609	49.968
Total		13704661	633506	100.000



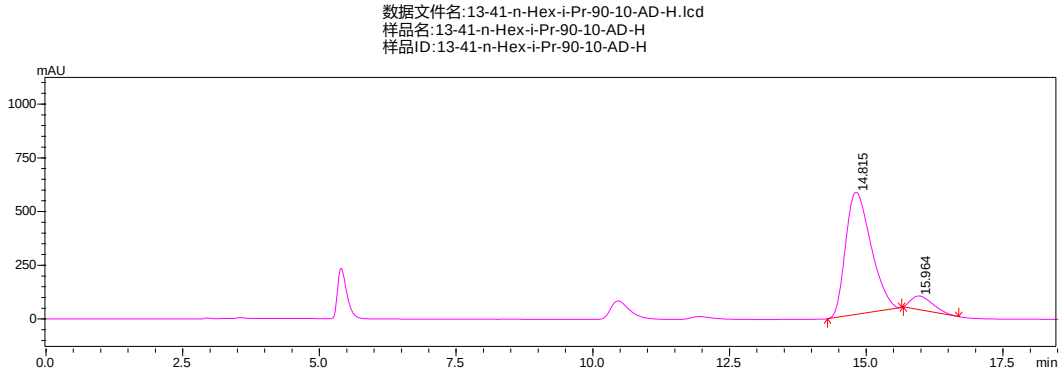
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	7.282	6561079	305764	98.290
2	9.290	114144	4530	1.710
Total		6675223	310293	100.000



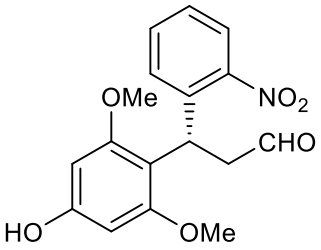
9d



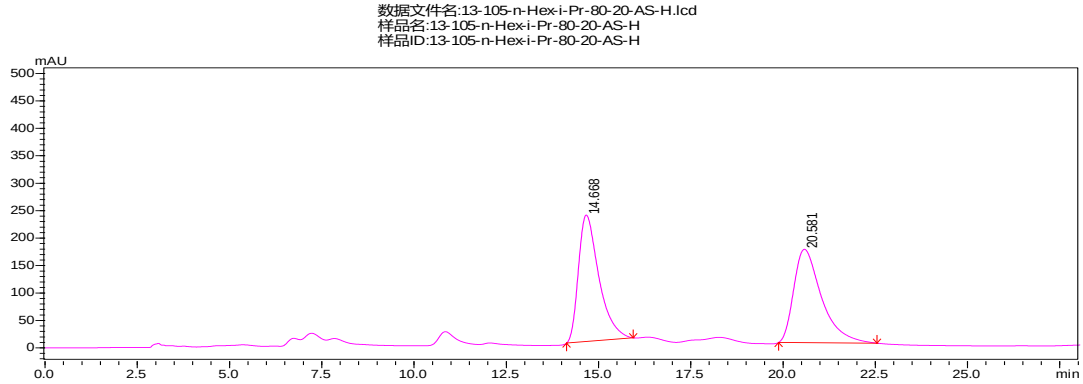
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	14.629	6549435	225609	49.947
2	15.814	6563205	201646	50.053
Total		13112640	427255	100.000



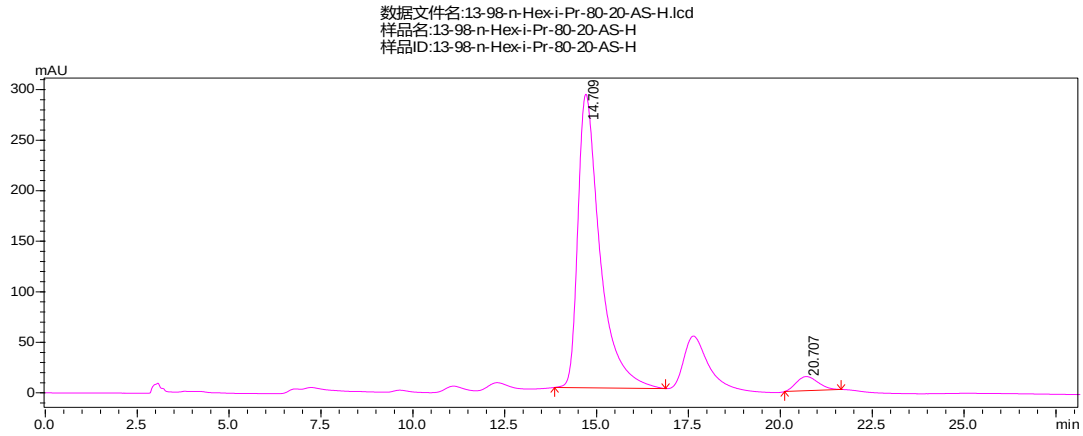
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	14.815	18444592	568933	91.328
2	15.964	1751352	62979	8.672
Total		20195945	631912	100.000



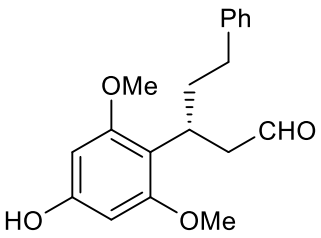
9e



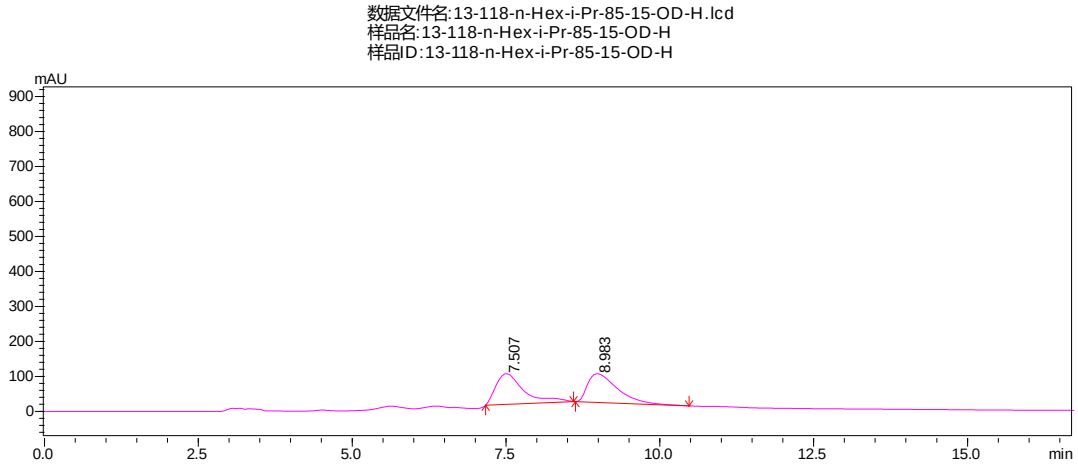
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	14.668	8913202	230539	50.059
2	20.581	8892107	170066	49.941
Total		17805309	400606	100.000



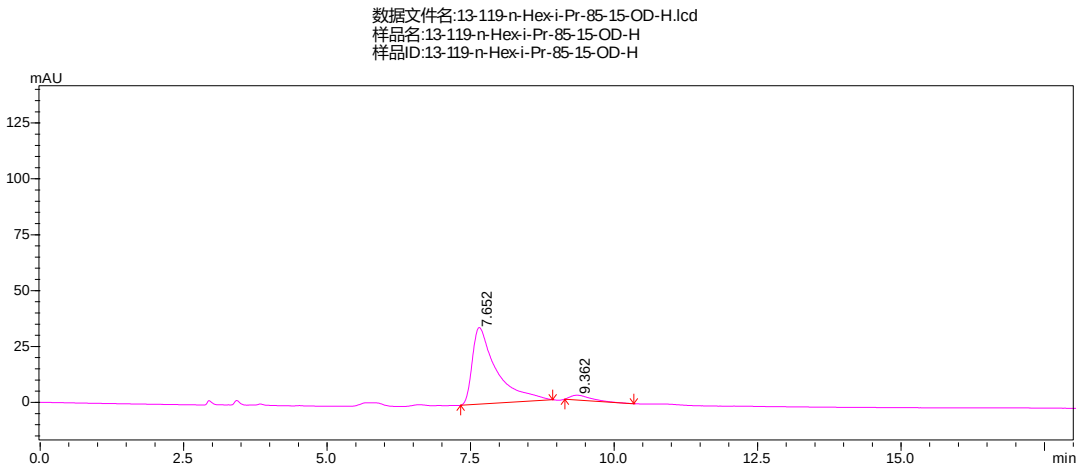
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	14.709	12144993	290438	95.446
2	20.707	579512	14002	4.554
Total		12724506	304440	100.000



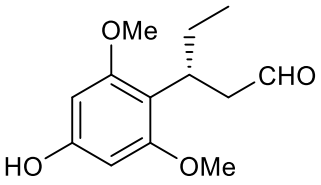
9f



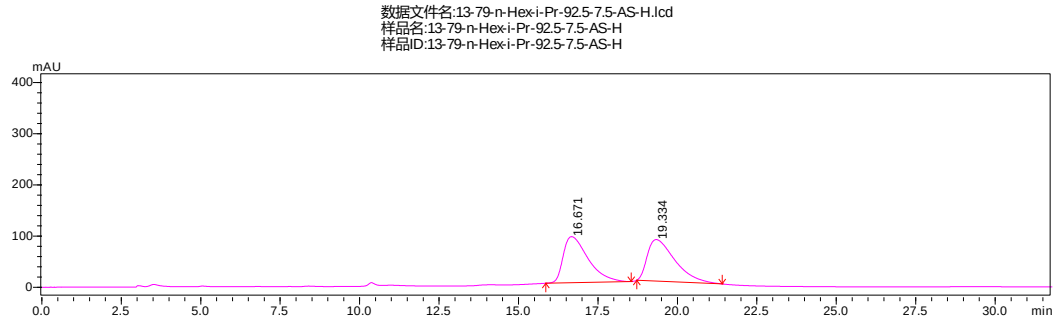
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	7.507	2776149	87505	49.974
2	8.983	2778982	82021	50.026
Total		5555131	169526	100.000



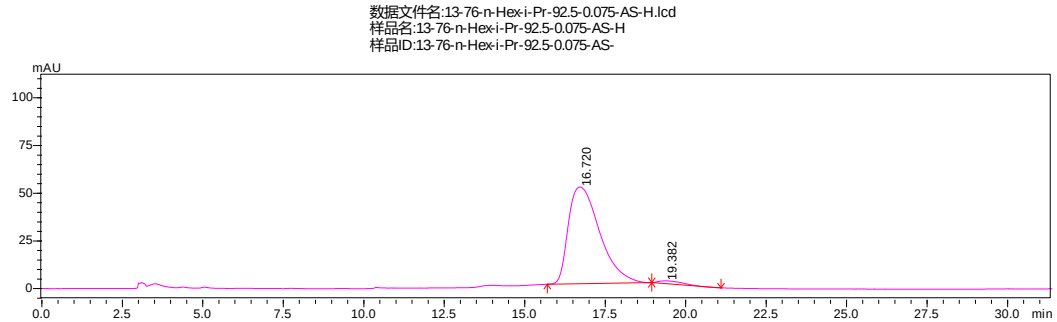
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	7.652	1004494	34242	95.107
2	9.362	51680	2128	4.893
Total		1056174	36370	100.000



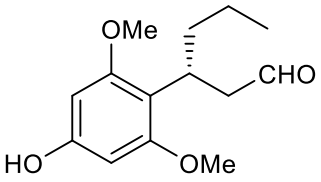
9g



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	16.671	4919808	90162	49.980
2	19.334	4923756	81107	50.020
Total		9843564	171269	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	16.720	3440095	50661	97.850
2	19.382	75584	1491	2.150
Total		3515679	52152	100.000



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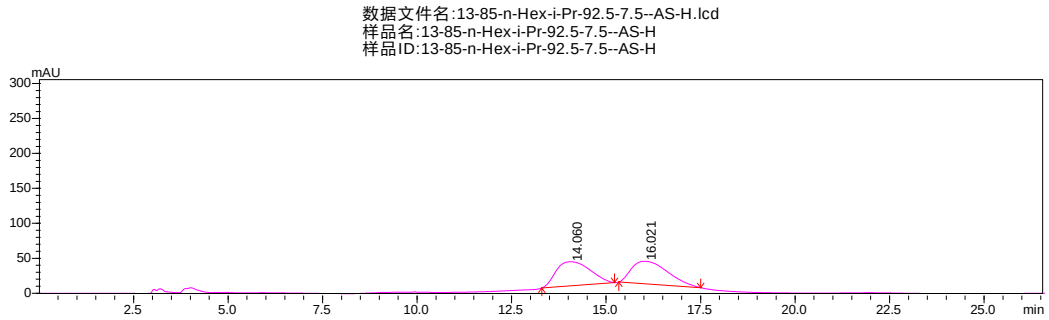
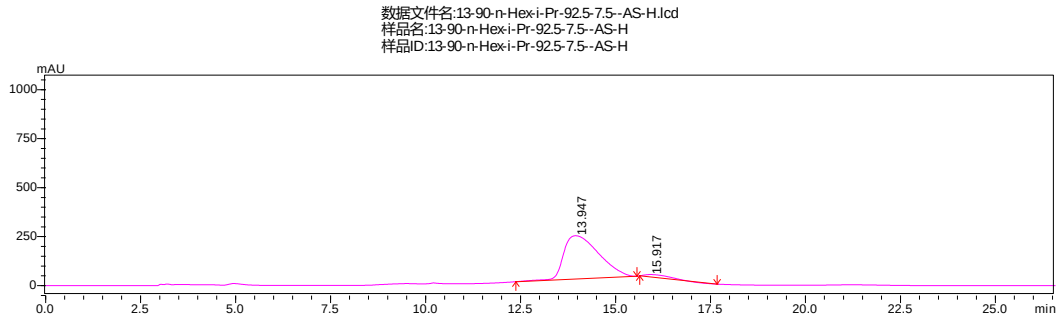
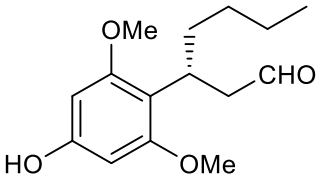


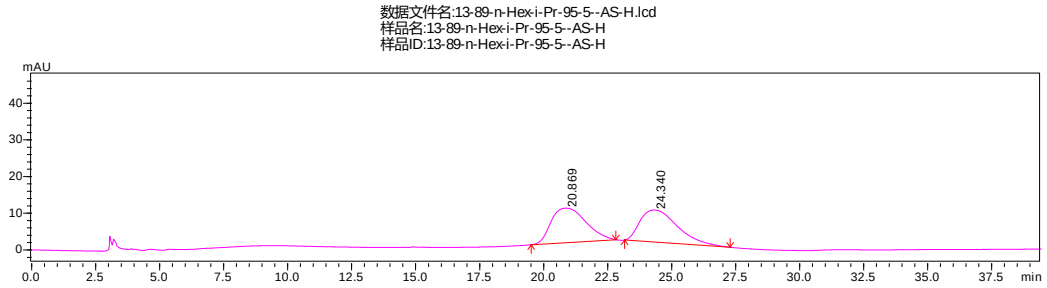
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	14.060	2167944	34501	49.926
2	16.021	2174399	32203	50.074
Total		4342343	66704	100.000



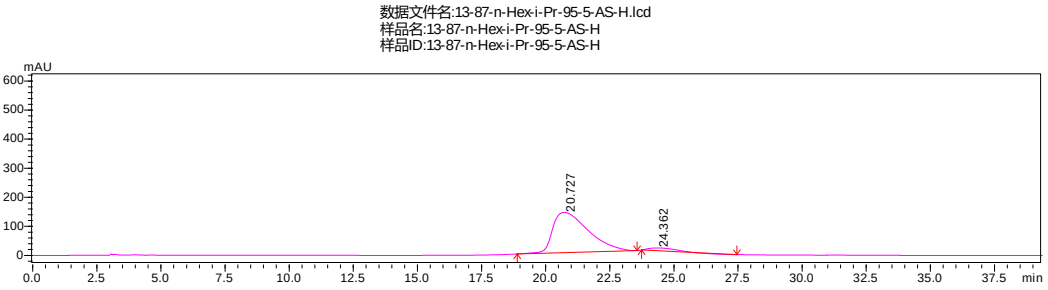
Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	13.947	14135186	220416	96.312
2	15.917	541204	12270	3.688
Total		14676391	232686	100.000



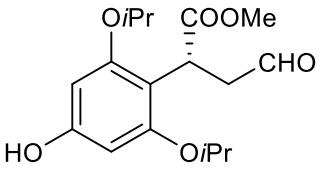
9i



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	20.869	892502	9410	49.958
2	24.340	894011	8741	50.042
Total		1786513	18151	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	20.727	13315797	138334	95.565
2	24.362	617983	9778	4.435
Total		13933780	148112	100.000



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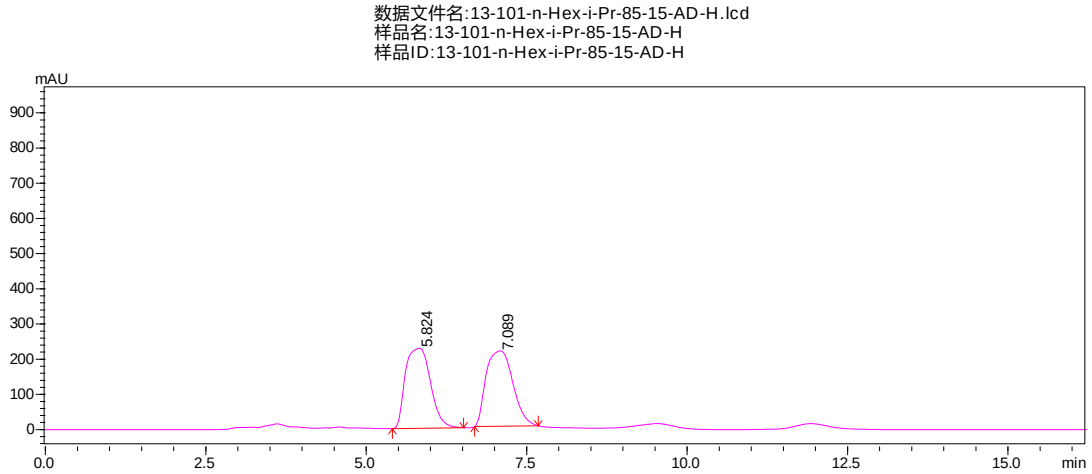
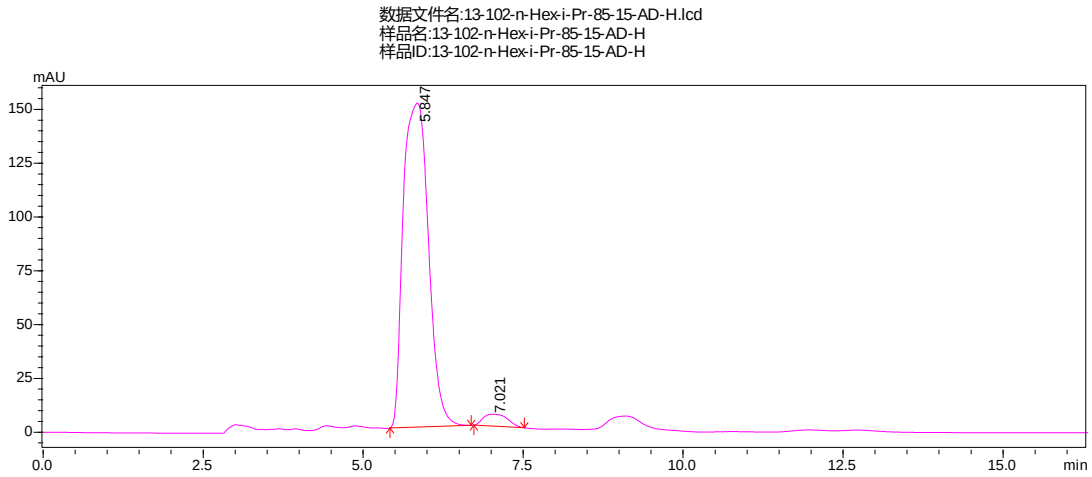
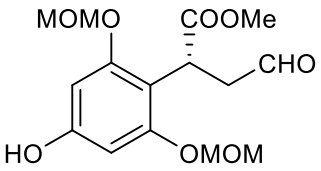


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	5.824	6192013	227341	49.899
2	7.089	6216983	214254	50.101
Total		12408995	441595	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	5.847	4132723	150586	96.555
2	7.021	147473	5506	3.445
Total		4280197	156091	100.000



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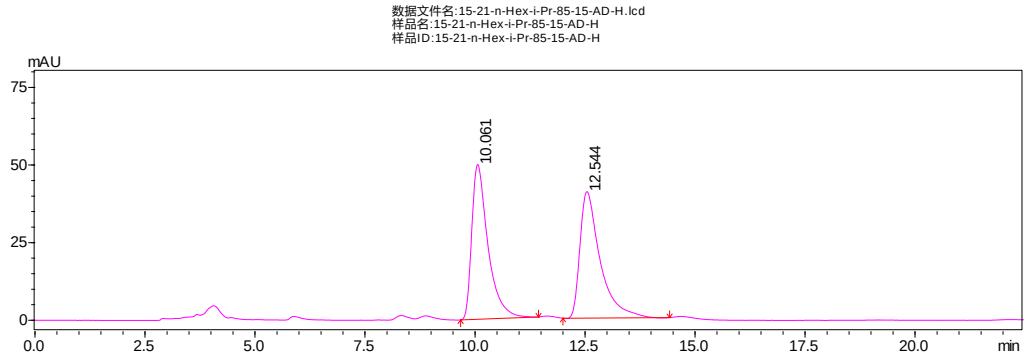
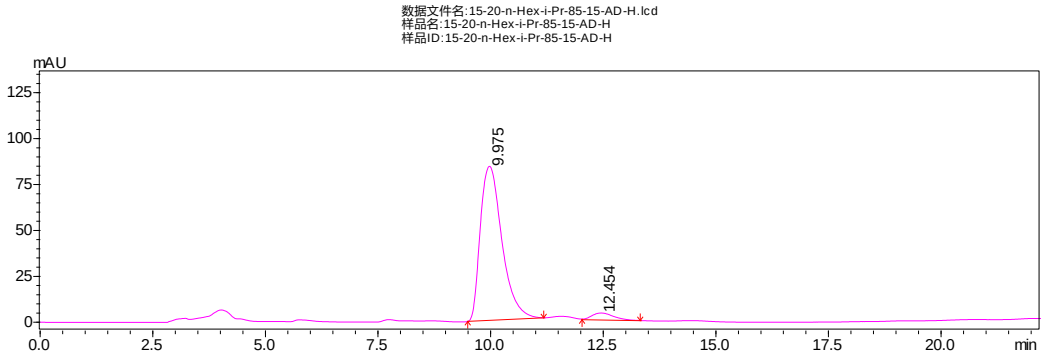
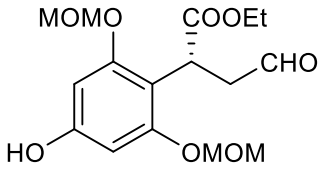


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	10.061	1277097	49834	49.617
2	12.544	1296822	40730	50.383
Total		2573920	90564	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	9.975	2804914	83876	95.537
2	12.454	131031	3806	4.463
Total		2935945	87682	100.000



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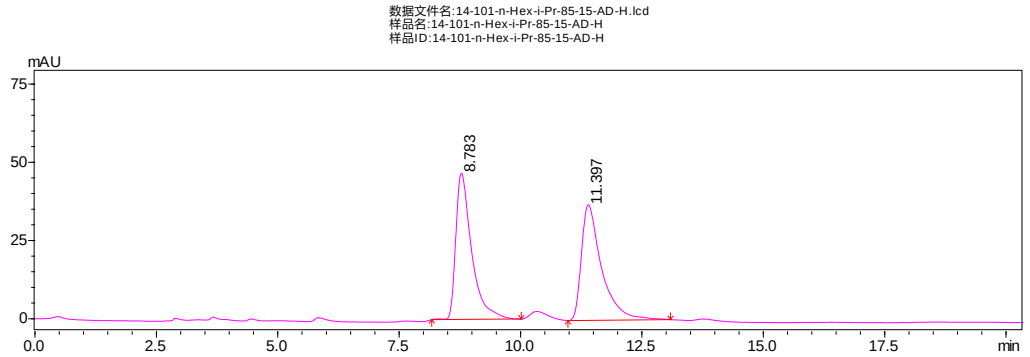
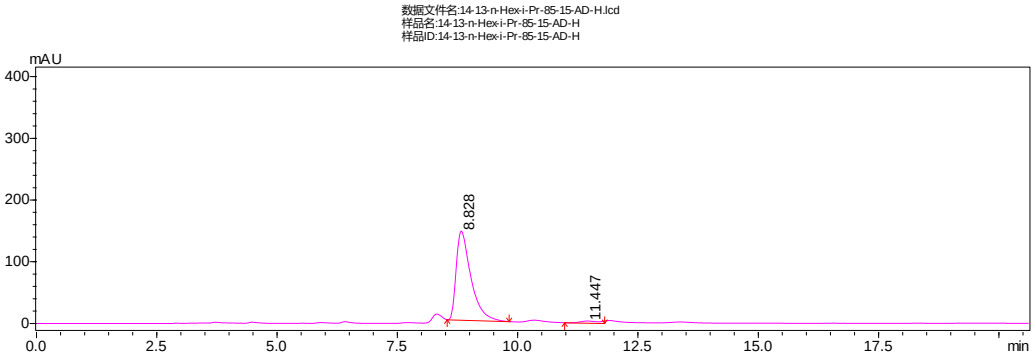
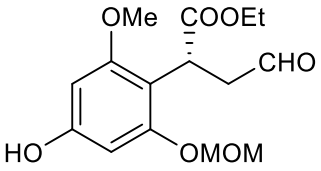


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	8.783	1061903	46762	49.816
2	11.397	1069742	36936	50.184
Total		2131645	83699	100.000

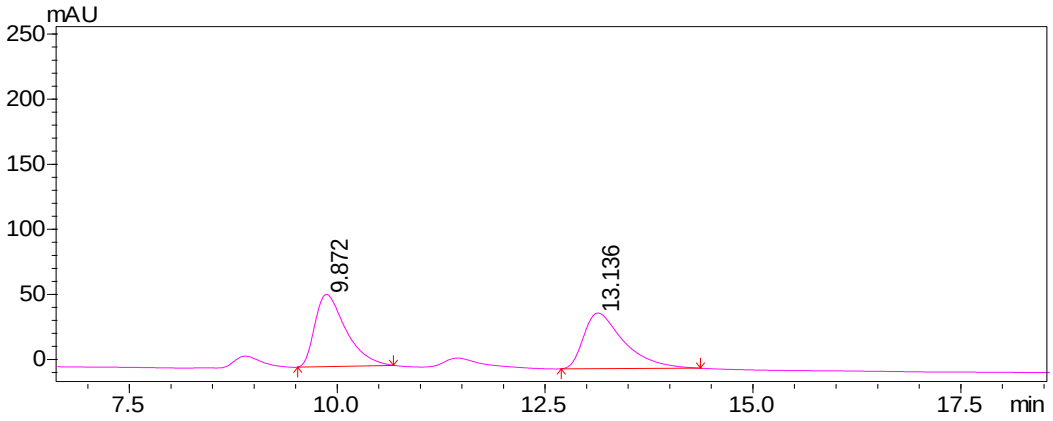


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	8.828	3073111	144381	96.812
2	11.447	101191	3425	3.188
Total		3174302	147807	100.000



9m

数据文件名:wzl-15-102-n-Hex-i-Pr-85-15-AD-H.lcd
样品名:wzl-15-102-n-Hex-i-Pr-85-15-AD-H
样品ID:wzl15-102-n-Hex-i-Pr-85-15-AD-H



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	9.872	1439171	55440	49.996
2	13.136	1439398	42727	50.004
Total		2878570	98167	100.000

数据文件名:wzl-15-103-n-Hex-i-Pr-85-15-AD-H.lcd
样品名:wzl-15-103-n-Hex-i-Pr-85-15-AD-H
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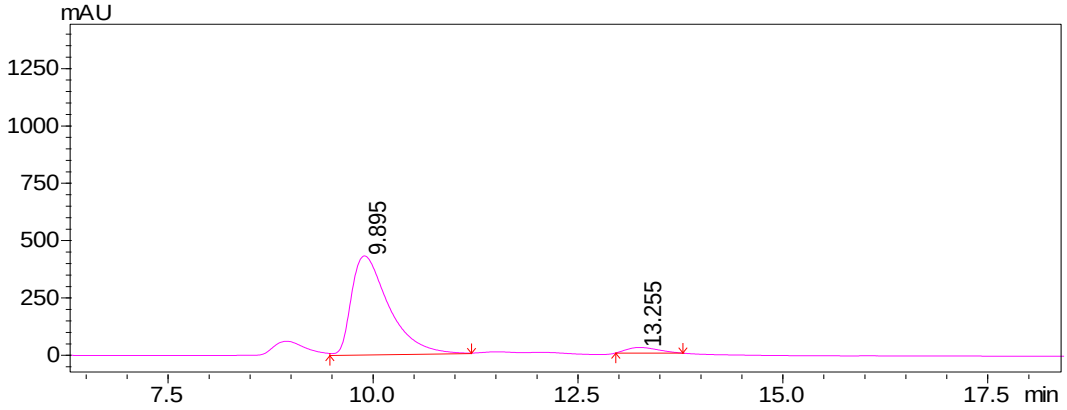
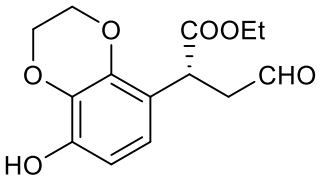


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	9.895	13800396	431979	95.508
2	13.255	649115	24237	4.492
Total		14449511	456217	100.000



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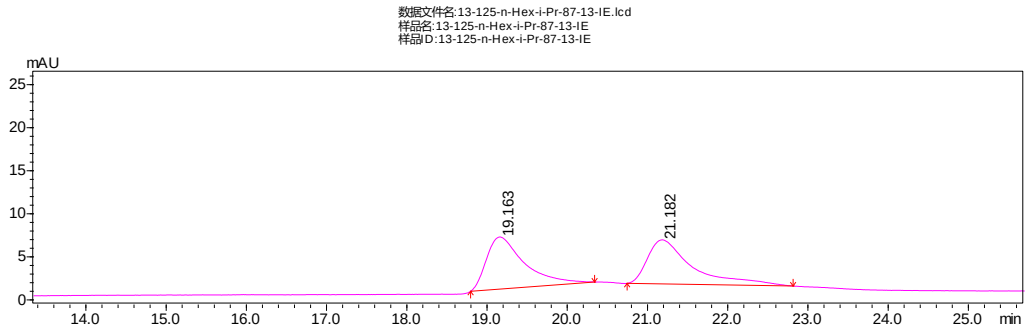
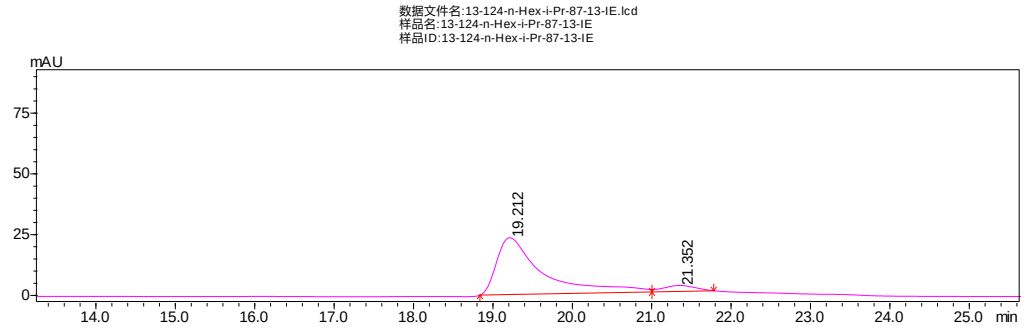
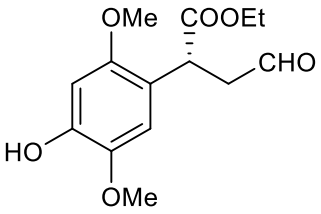


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	19.163	200079	6048	50.176
2	21.182	198677	5119	49.824
Total		398756	11167	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	19.212	933414	23399	93.196
2	21.352	68151	2423	6.804
Total		1001565	25822	100.000



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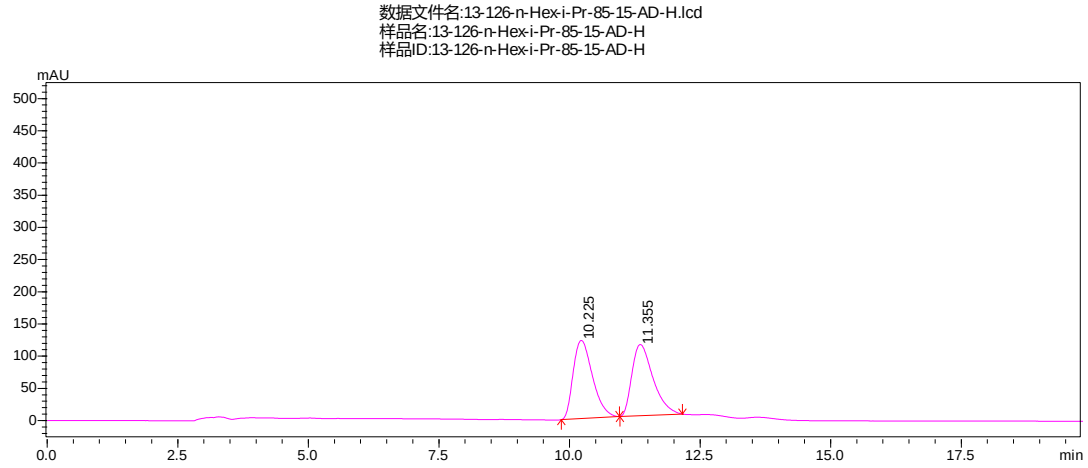
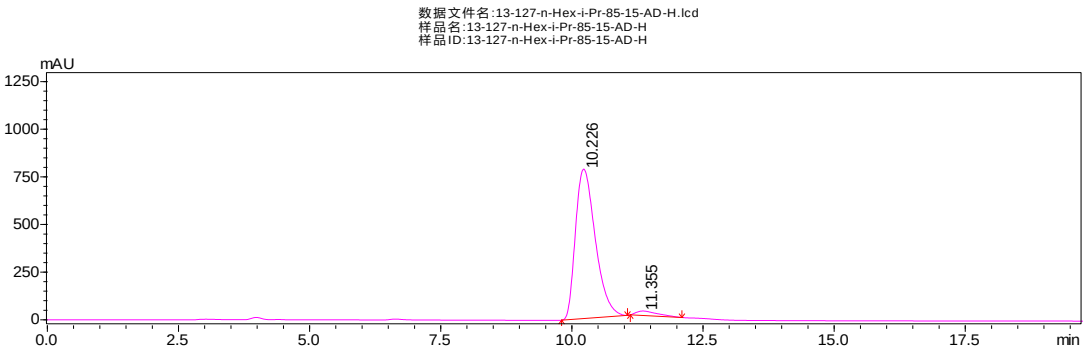
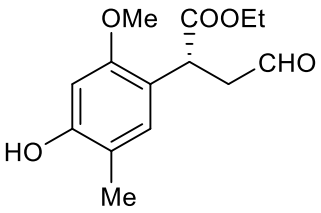


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	10.225	3128234	121419	50.096
2	11.355	3116289	110577	49.904
Total		6244523	231996	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	10.226	20684857	784551	96.800
2	11.355	683766	23458	3.200
Total		21368623	808008	100.000



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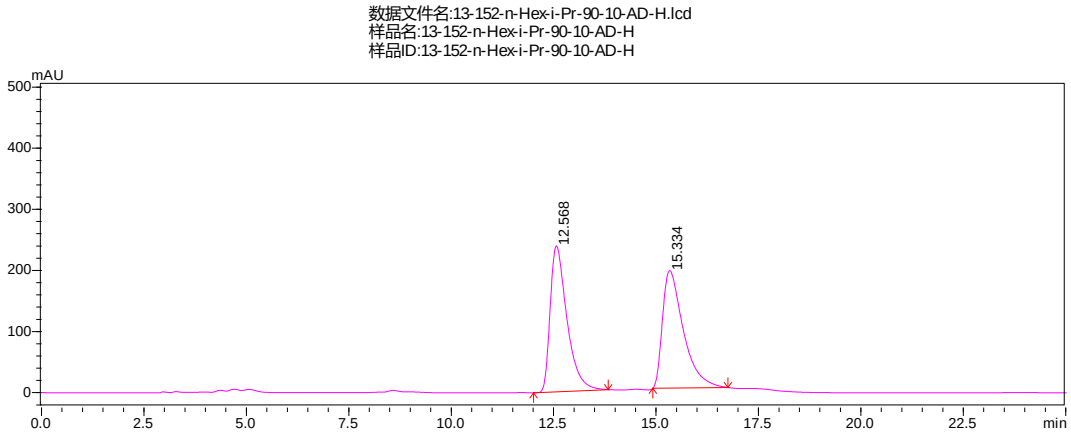
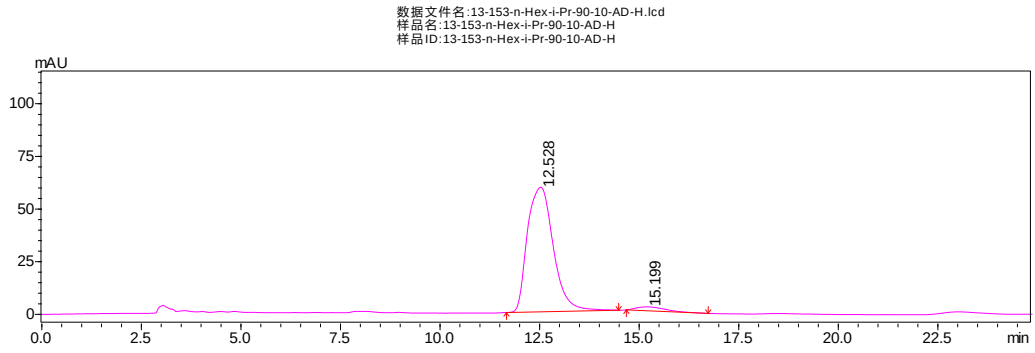
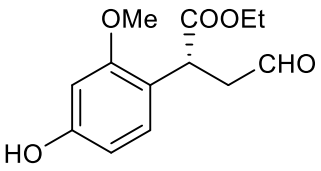


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	12.568	6799652	238559	49.984
2	15.334	6803891	192233	50.016
Total		13603543	430793	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	12.528	2677877	59135	96.632
2	15.199	93324	1851	3.368
Total		2771201	60986	100.000



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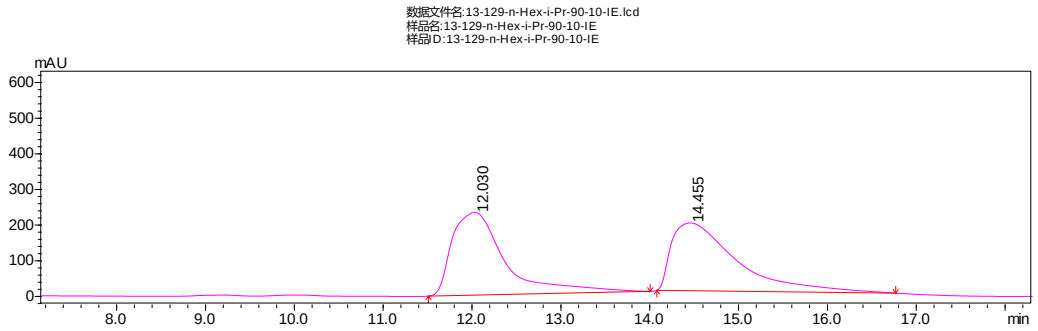
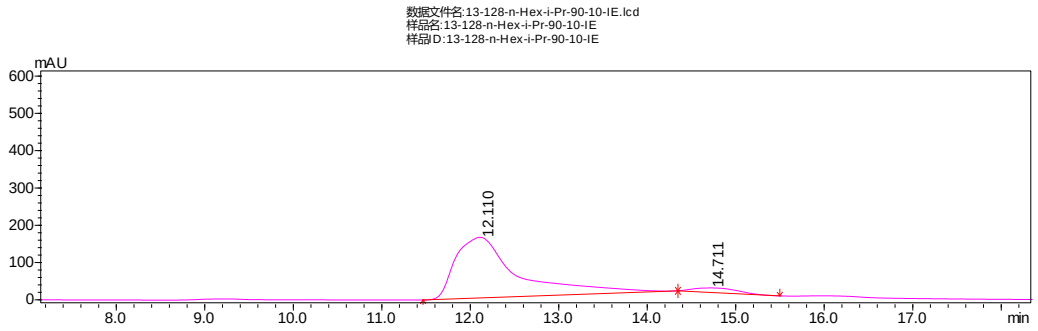
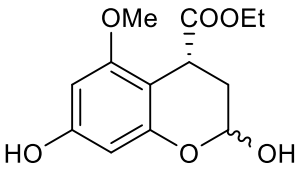


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	12.030	9671976	232171	49.961
2	14.455	9687119	190331	50.039
Total		19359095	422502	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	12.110	7914363	162540	94.992
2	14.711	417220	11938	5.008
Total		8331583	174478	100.000



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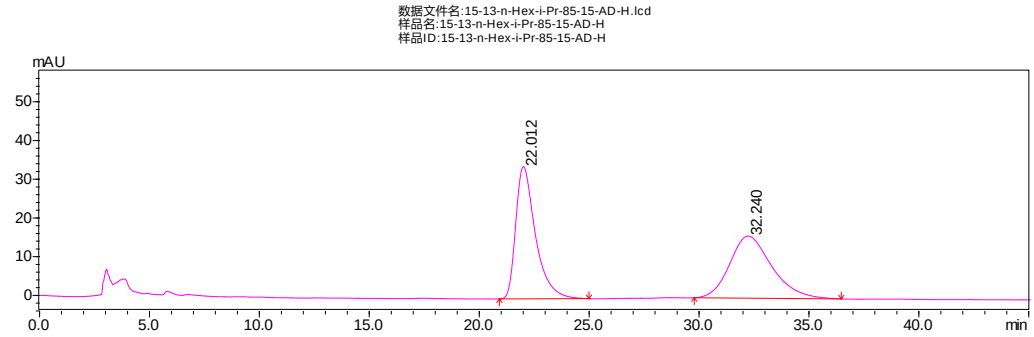
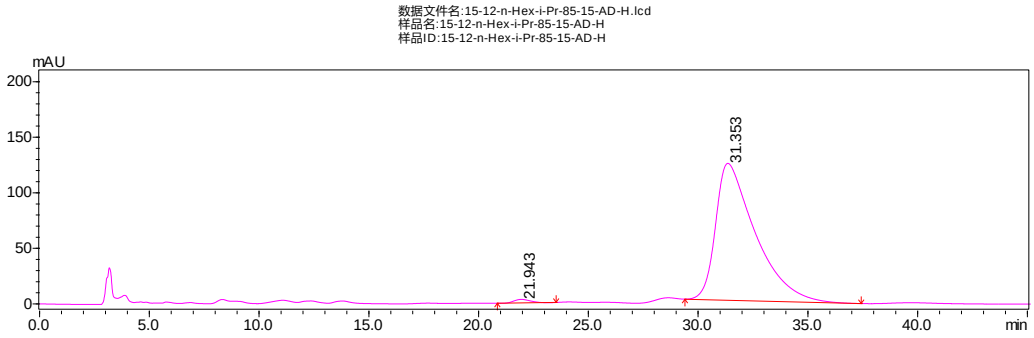
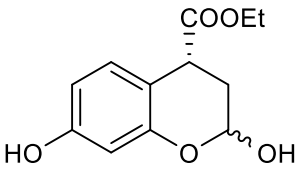


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	22.012	2130052	34146	49.929
2	32.240	2136141	16046	50.071
Total		4266193	50192	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	21.943	156336	3165	1.003
2	31.353	15426326	127655	98.997
Total		15582662	130820	100.000



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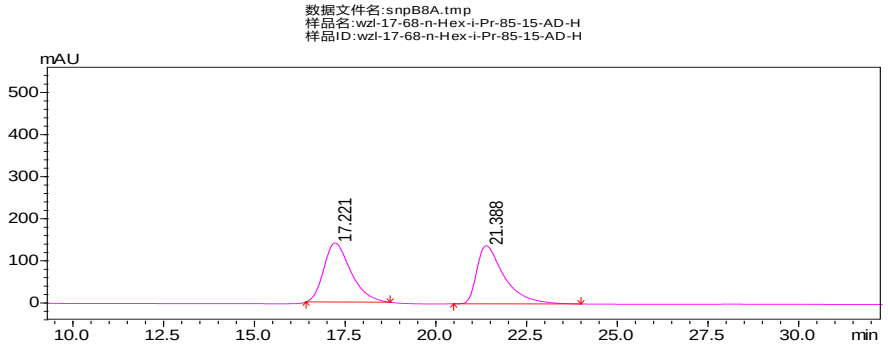
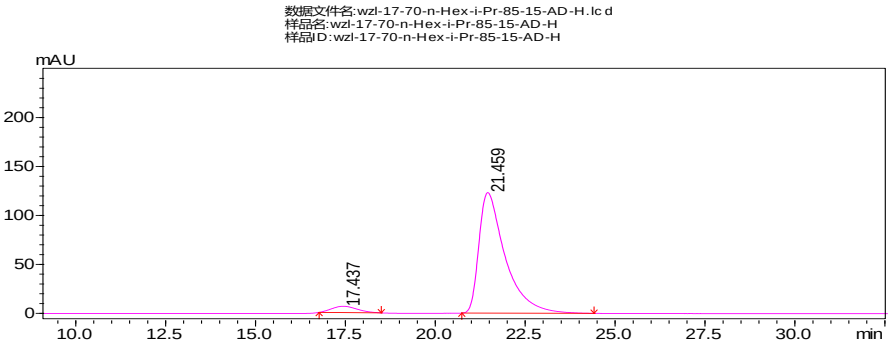
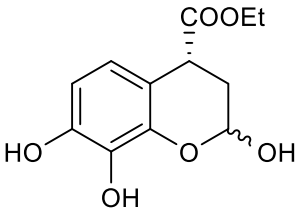


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	17.221	7288956	140191	50.104
2	21.388	7258671	138298	49.896
Total		14547627	278490	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	17.437	316379	6446	4.799
2	21.459	6276407	123158	95.201
Total		6592786	129604	100.000



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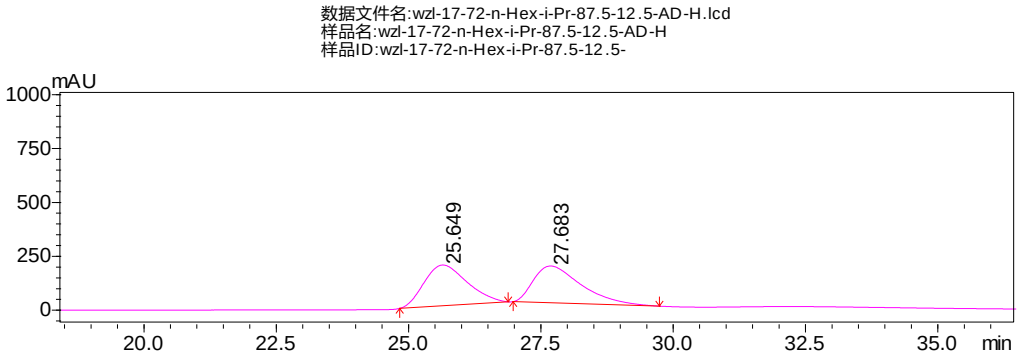
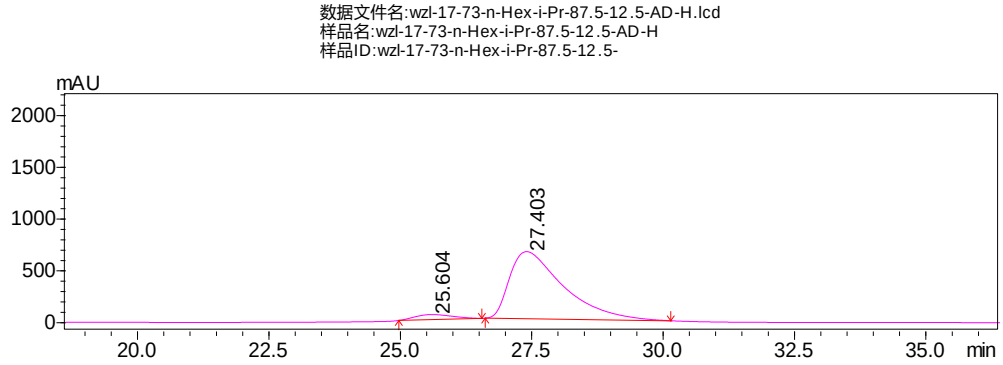
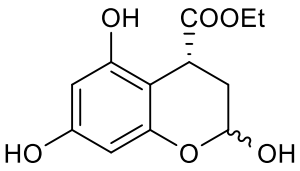


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	25.649	10715263	189293	49.945
2	27.683	10738765	170584	50.055
Total		21454029	359877	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	25.604	2390284	48432	4.912
2	27.403	46268965	648941	95.088
Total		48659249	697373	100.000



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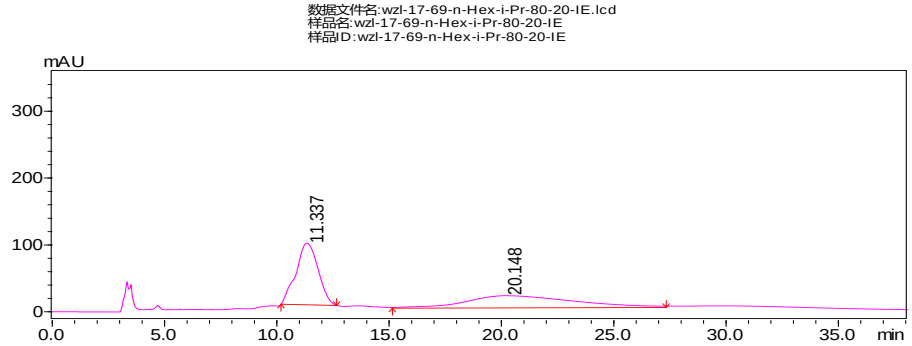
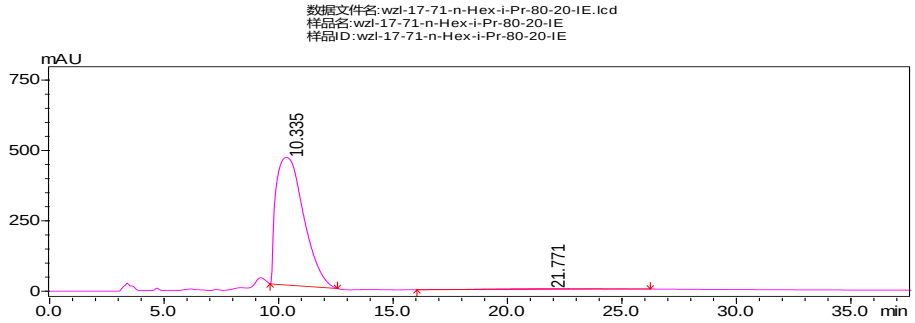


Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	11.337	6310705	92038	50.254
2	20.148	6246819	18273	49.746
Total		12557524	110311	100.000



Peak No.	Ret. Time	Peak Area	Peak height	Percent %
1	10.335	38166656	453213	97.489
2	21.771	983234	2892	2.511
Total		39149889	456105	100.000