

## Supporting Information

# Evolution of Two Routes for Asymmetric Total Synthesis of Tetrahydroprotoberberine Alkaloids

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## Table of Contents

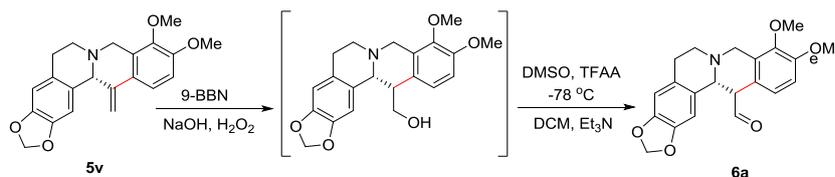
1. General Information	S-2
2. Asymmetric synthesis to Tetrahydroprotoberberines with Redox-A <sup>3</sup> Reaction	S-3
3. Asymmetric synthesis to Tetrahydroprotoberberines via Noyori Transfer Hydrogenation	S-5
• M1: Preparation and Noyori Reduction of Dihydroberberines	S-5
• M2: Noyori Reduction of Quaternary Salts	S-5
4. Copies of NMR Spectra and HPLC Spectra	S-9

## 1. General Information

Reactions were carried out in oven or flame-dried glassware under a nitrogen atmosphere, unless otherwise noted. Tetrahydrofuran (THF) was freshly distilled before use from sodium using benzophenone as indicator. Dichloromethane was freshly distilled before use from calcium hydride (CaH<sub>2</sub>). All other solvents were dried over 3Å or 4Å molecular sieves. Solvents used in workup, extraction and column chromatography were used as received from commercial suppliers without prior purification. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC, 0.25 mm) on Merck pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm) supplied by Grace. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV-400 spectrometer (400 MHz for <sup>1</sup>H, 100 MHz for <sup>13</sup>C). Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform (7.26 ppm for <sup>1</sup>H and 77.0 ppm for <sup>13</sup>C). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Optical rotations were measured on a JASCO Perkin-Elmer model P-2000 polarimeter. Enantiomeric ratios were determined by chiral HPLC with Agilent 1290 Infinity UPLC.

## 2. Asymmetric Synthesis of Tetrahydroprotoberberines with Redox-A<sup>3</sup> Reaction

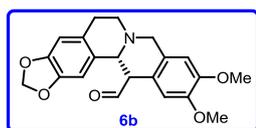
### General Procedure for Hydroboration Oxidation Reaction with 5-v:



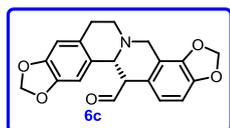
To a round-bottom flask were added **5v** (45 mg, 0.13 mmol) and then 9-BBN (0.5 mol/L, 2.6 mL, 13 mmol) under nitrogen atmosphere, and the mixture was heated to 60 °C and stirred for 12 h. The mixture was then cooled to 0 °C followed by addition of 3 N NaOH (0.4 ml) and 30% H<sub>2</sub>O<sub>2</sub> (0.4 mL) sequentially, and the resulting mixture was stirred for 2h at ambient temperature. The biphasic mixture was separated, and the aqueous layer was extracted with EA (3 × 4 mL). The combined organic layers were washed with saturated aqueous Na<sub>2</sub>SO<sub>3</sub> solution and brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The crude product was subjected to Swern oxidation without further purification.

### General Procedure for Swern Oxidation:

To a solution of dimethyl sulfoxide (58 μL, 1.6 mmol) in dry dichloromethane (3 mL) under a nitrogen atmosphere was added dropwise trifluoroacetic anhydride (57 μL, 0.81 mmol) at -78 °C for 30 min. Then a solution of **5aa** (30 mg, 0.08 mmol) in dry dichloromethane (1 mL) was added dropwise. After stirring for 1 h, triethylamine (342 μL, 2.5 mmol) was added slowly. The reaction mixture was warmed to room temperature after 10 mins, and quenched with saturated aqueous sodium bicarbonate and extracted with DCM (3 × 5 mL), the combined organic layers were washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (Hexane/EA: 4/1) to give **6a** (12 mg, 0.03 mmol, 41%) as a colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.52 (d, *J* = 3.3 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 6.89–6.82 (m, 1H), 6.69 (s, 1H), 6.58 (d, *J* = 2.7 Hz, 1H), 5.97–5.89 (m, 2H), 4.25 (d, *J* = 15.9 Hz, 1H), 3.88 (s, 1H), 3.86 (dd, *J* = 3.0, 1.2 Hz, 6H), 3.85–3.81 (m, 2H), 3.54 (d, *J* = 16.1 Hz, 1H), 3.19 (d, *J* = 9.6 Hz, 1H), 2.74–2.61 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.05, 151.40, 146.63, 146.40, 144.98, 129.23, 126.91, 125.23, 123.26, 111.18, 108.56, 106.06, 100.94, 60.65, 60.21, 55.96, 55.80, 53.72, 51.20, 29.66. [α]<sub>D</sub><sup>25</sup> = +165 (*c* = 1, CHCl<sub>3</sub>); **IR** (film, KBr) *v*<sub>max</sub>: 2920, 2852, 1659, 1577, 1266, 878, 778, 669 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (*m/z*) calcd. for C<sub>21</sub>H<sub>21</sub>NO<sub>5</sub> [M + H]<sup>+</sup> 368.1498; found 368.1509.

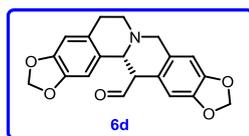


**6b** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.56 (d, *J* = 3.7 Hz, 1H), 6.73 (d, *J* = 14.3 Hz, 2H), 6.62 (d, *J* = 12.6 Hz, 2H), 5.94 (s, 2H), 4.03 (d, *J* = 14.6 Hz, 1H), 3.95 – 3.91 (m, 1H), 3.89 (d, *J* = 1.9 Hz, 6H), 3.84 (dd, *J* = 6.6, 2.9 Hz, 1H), 3.70 (d, *J* = 14.6 Hz, 1H), 3.16 (m, 2H), 2.72 – 2.62 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 202.11, 148.64, 148.04, 146.68, 146.44, 129.22, 127.36, 126.88, 121.74, 111.88, 108.82, 108.59, 106.08, 100.97, 60.93, 57.76, 56.18, 56.00, 55.97, 55.94, 51.16, 29.62. [α]<sub>D</sub><sup>25</sup> = +177 (*c* = 1, CHCl<sub>3</sub>); **IR** (film, KBr) *v*<sub>max</sub>: 2922, 2854, 1658, 1577, 1516, 1200, 1044, 878, 752, 603 cm<sup>-1</sup>; HRMS (CI<sup>+</sup>) (*m/z*) calcd. for C<sub>21</sub>H<sub>21</sub>NO<sub>5</sub> [M + H]<sup>+</sup> 368.1498; found 368.1504.

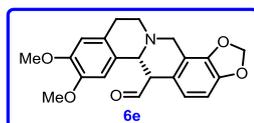


**6c** <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.51 (d, *J* = 3.2 Hz, 1H), 6.74 (s, 2H), 6.70 (s, 1H), 6.58 (s, 1H), 6.00 (d, *J* = 1.4 Hz, 1H), 5.96 (d, *J* = 1.5 Hz, 1H), 5.95 – 5.88 (m, 2H), 4.12 (d, *J* = 15.4 Hz, 1H), 3.93 (s, 1H), 3.85 (t, *J* = 3.1 Hz, 1H), 3.55 (dd, *J* = 15.4, 1.1 Hz, 1H), 3.22 – 3.12 (m, 1H), 3.07 (d, *J* = 13.3 Hz, 1H), 2.78 – 2.55 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 201.69, 146.68, 146.46,

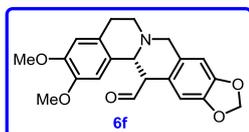
146.30, 143.43, 129.16, 126.78, 124.23, 122.78, 117.13, 108.57, 107.25, 106.04, 101.39, 100.97, 60.89, 56.10, 52.67, 51.11, 29.64.  $[\alpha]_D^{25} = +184$  ( $c = 1$ ,  $\text{CHCl}_3$ ); **IR** (film, KBr)  $\nu_{\text{max}}$ : 2956, 2918, 2852, 1715, 1645, 1475, 1036, 871, 799, 615  $\text{cm}^{-1}$ ; HRMS ( $\text{CI}^+$ ) ( $m/z$ ) calcd. for  $\text{C}_{20}\text{H}_{17}\text{NO}_5$   $[\text{M}]^+$  351.1107; found 351.1105.



**6d**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.50 (d,  $J = 3.3$  Hz, 1H), 6.76 – 6.65 (m, 2H), 6.58 (s, 2H), 5.99 – 5.86 (m, 4H), 3.97 (d,  $J = 14.8$  Hz, 1H), 3.88 (s, 1H), 3.80 – 3.72 (m, 1H), 3.63 (dt,  $J = 14.7, 1.1$  Hz, 1H), 3.12 (ddd,  $J = 10.0, 6.8, 3.2$  Hz, 2H), 2.70 – 2.54 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.78, 147.23, 146.69, 146.57, 146.46, 129.21, 128.42, 126.78, 122.93, 109.31, 108.59, 106.03, 106.01, 101.02, 100.97, 60.77, 58.06, 56.28, 51.06, 29.59.  $[\alpha]_D^{25} = +199$  ( $c = 1$ ,  $\text{CHCl}_3$ ); **IR** (film, KBr)  $\nu_{\text{max}}$ : 2957, 2919, 2852, 1716, 1629, 1577, 1037, 872, 753, 616  $\text{cm}^{-1}$ ; HRMS ( $\text{CI}^+$ ) ( $m/z$ ) calcd. for  $\text{C}_{20}\text{H}_{17}\text{NO}_5$   $[\text{M}]^+$  351.1107; found 351.1119.

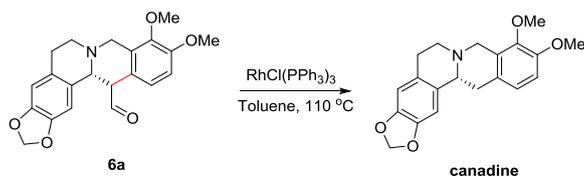


**6e**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.48 (d,  $J = 3.2$  Hz, 1H), 6.75 (s, 2H), 6.69 (s, 1H), 6.61 (d,  $J = 2.0$  Hz, 1H), 5.98 (dd,  $J = 17.1, 1.5$  Hz, 2H), 3.95 (d,  $J = 2.7$  Hz, 1H), 3.91 (t,  $J = 3.3$  Hz, 1H), 3.86 (d,  $J = 1.6$  Hz, 6H), 3.83 (d,  $J = 17.1$  Hz, 1H), 3.55 (dd,  $J = 15.5, 1.0$  Hz, 1H), 3.25 – 3.02 (m, 2H), 2.74 – 2.62 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.68, 147.91, 147.86, 146.28, 143.44, 128.06, 125.62, 124.20, 122.74, 117.20, 111.43, 108.99, 107.24, 101.38, 60.38, 56.11, 55.90, 55.83, 52.71, 51.25, 29.13.  $[\alpha]_D^{25} = +185$  ( $c = 1$ ,  $\text{CHCl}_3$ ); **IR** (film, KBr)  $\nu_{\text{max}}$ : 2920, 2852, 1658, 1577, 1463, 1266, 877, 780, 611  $\text{cm}^{-1}$ ; HRMS ( $\text{CI}^+$ ) ( $m/z$ ) calcd. for  $\text{C}_{21}\text{H}_{21}\text{NO}_5$   $[\text{M}]^+$  367.1420; found 367.1433.



**6f**  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.47 (d,  $J = 3.4$  Hz, 1H), 6.72 (s, 1H), 6.67 (s, 1H), 6.59 (d,  $J = 9.5$  Hz, 2H), 5.92 (dd,  $J = 10.6, 1.5$  Hz, 2H), 3.97 (d,  $J = 14.8$  Hz, 1H), 3.90 – 3.88 (m, 1H), 3.86 (s, 6H), 3.83 (d,  $J = 3.2$  Hz, 1H), 3.66 – 3.60 (m, 1H), 3.19 – 3.07 (m, 2H), 2.74 – 2.57 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  201.76, 147.91, 147.85, 147.18, 146.53, 128.49, 128.11, 125.63, 122.87, 111.49, 109.24, 109.01, 106.02, 100.99, 60.35, 58.11, 56.09, 55.83, 51.18, 43.36, 29.06.  $[\alpha]_D^{25} = +172$  ( $c = 1$ ,  $\text{CHCl}_3$ ); **IR** (film, KBr)  $\nu_{\text{max}}$ : 2919, 2851, 1658, 1578, 1463, 1265, 1042, 878, 781, 665, 615  $\text{cm}^{-1}$ ; HRMS ( $\text{CI}^+$ ) ( $m/z$ ) calcd. for  $\text{C}_{21}\text{H}_{21}\text{NO}_5$   $[\text{M} + \text{H}]^+$  368.1498; found 368.1485.

#### General Procedure for Decarbonylation Reaction of **6a**:



To a solution of **6a** (12 mg, 0.03 mmol) in toluene (2 mL) was added Wilkinson's catalyst  $\text{RhCl}(\text{PPh}_3)_3$  (27.8 mg, 0.03 mmol), and the mixture was heated to 110 °C and stirred for 2h. The reaction mixture was then cooled to room temperature and concentrated to afford a residue which was subjected to flash chromatography on silica gel (Hexane/EA: 1/8 ~ 1/4) to give **canadine** (**7a**, 3.0 mg, 0.009 mmol, 29.5%) as a colorless oil. 97% *ee* (HPLC conditions: Chiralcel AD-H column, hexane/*i*-

PrOH = 80/20, 1.0 mL/min,  $\lambda = 210$  nm,  $t_R(\text{major}) = 11.0$  min,  $t_R(\text{minor}) = 6.7$  min);  $[\alpha]_D^{25} = +30$  ( $c = 0.1$ ,  $\text{CHCl}_3$ )

**Isocanadine (7b)**, 1.1 mg, 18.3%) as a pale-yellow oil. 99% *ee* (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 210$  nm,  $t_R(\text{major}) = 8.9$  min,  $t_R(\text{minor}) = 9.7$  min);  $[\alpha]_D^{25} = +36$  ( $c = 0.1$ ,  $\text{CHCl}_3$ )

**Stylopine (7c)**, 1.0 mg, 18.5%) as a pale-yellow oil. 93% *ee* (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 210$  nm,  $t_R(\text{major}) = 7.5$  min,  $t_R(\text{minor}) = 9.7$  min);  $[\alpha]_D^{25} = +68$  ( $c = 0.1$ ,  $\text{CHCl}_3$ )

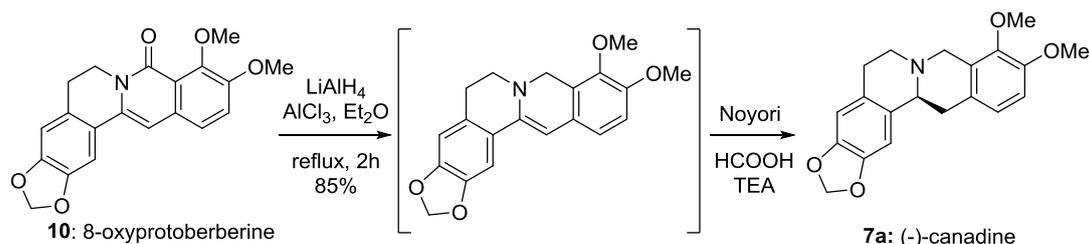
**Tetrahydropseudocoptisine (7d)**, 1.6 mg, 20.0%) as a pale-yellow oil. 93% *ee* (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 210$  nm,  $t_R(\text{major}) = 7.1$  min,  $t_R(\text{minor}) = 11.5$  min);  $[\alpha]_D^{25} = +49$  ( $c = 0.1$ ,  $\text{CHCl}_3$ )

**Sinactine (7e)**, 1.5 mg, 12.0%) as a pale-yellow oil. 88% *ee* (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 210$  nm,  $t_R(\text{major}) = 19.2$  min,  $t_R(\text{minor}) = 14.0$  min);  $[\alpha]_D^{25} = +69$  ( $c = 0.1$ ,  $\text{CHCl}_3$ )

**Isosinactine (7f)**, 1.2 mg, 21.8%) as a pale-yellow oil. 88% *ee* (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 210$  nm,  $t_R(\text{major}) = 8.9$  min,  $t_R(\text{minor}) = 19.7$  min);  $[\alpha]_D^{25} = +31$  ( $c = 0.1$ ,  $\text{CHCl}_3$ )

### 3. Asymmetric synthesis of tetrahydroprotoberberines via Noyori Reduction

#### M1: Preparation and Noyori Reduction of Dihydroberberines:



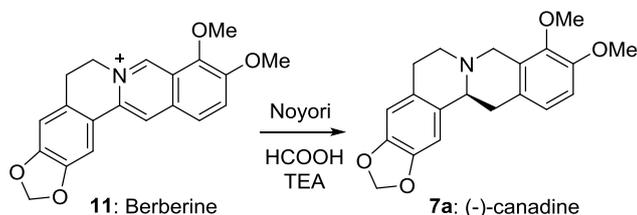
To a suspension of  $\text{LiAlH}_4$  (142 mg, 4 mmol) in  $\text{Et}_2\text{O}$  (15 mL) at 0 °C was added  $\text{AlCl}_3$  (133 mg, 1 mmol). The reaction mixture was warmed to room temperature with vigorous stirring for 0.5 h. 8-Oxyprotoberberine<sup>1</sup> (**9**, 27 mg, 0.077 mmol) was added to ethereal  $\text{AlH}_3$  mixture and the reaction mixture was heated to reflux for 2 h. The reaction was quenched by slow, careful sequential addition of  $\text{H}_2\text{O}$  (0.1 mL), 15%  $\text{NaOH}$  (0.1 mL), and  $\text{H}_2\text{O}$  (0.3 mL). The aluminates were removed by filtration and washed with  $\text{EtOAc}$  (3 x 5 mL). The combined filtrates were dried over  $\text{Na}_2\text{SO}_4$  and evaporated to give the crude product lambertine (**10**, 21 mg, 81%) as yellow solid, which gradually turned brown in air. The crude product was used for Noyori reduction without further purification.

To a stirred solution of **10** (21 mg, 0.063 mmol) in dichloromethane (2 mL) was added formic acid (29 mg, 0.63 mmol), triethylamine (25 mg, 0.252 mmol) and  $\text{RuCl}[(\text{S,S})\text{-TsDPEN}](\text{mesitylene})$  (0.006 mmol, 3.7 mg). The reaction mixture was stirred at room temperature for 40 h. Then the reaction was quenched by addition of  $\text{NaHCO}_3$  and washed with  $\text{CH}_2\text{Cl}_2$  (4 mL). The combined organic fractions were washed with brine, dried over  $\text{Na}_2\text{SO}_4$  and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using eluents ( $\text{EtOAc}/\text{hexane} = 1/1$ ) to afford the product canadine<sup>2</sup> (**7a**, 6.0 mg, 74%) as a pale yellow solid.

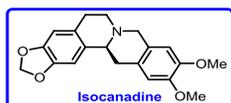
#### M2: Noyori Reduction of Quaternary Salts:

<sup>1</sup> Zhou, S., Tong, R. *Chem. Eur. J.* **2016**, *22*, 7084-7089.

<sup>2</sup> Mastranzo, V. M., Romero, J. L. O., Yuste, F., Ortiz, B., Sánchez-Obregón, R. & Ruano, J. L. G. *Tetrahedron*, **2012**, *68*, 1266-1271.



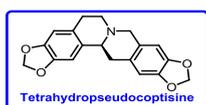
Quaternary salts were prepared according our previous report<sup>1</sup>. To a stirred solution of **11** (8 mg, 0.025 mmol) in dichloromethane (1 mL) was added formic acid (11.5 mg, 0.25 mmol), triethylamine (10 mg, 0.1 mmol) and RuCl[(S,S)-TsDPEN] (mesitylene) (1.5 mg, 0.002 mmol). The reaction mixture was stirred at room temperature for 40 h. Then the reaction was quenched by addition of NaHCO<sub>3</sub> and washed with CH<sub>2</sub>Cl<sub>2</sub> (2 mL). The combined organic fractions were washed brine, dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using eluents (EtOAc/hexane = 1/1) to afford the product **(-)-canadine (7a)**, 7.4 mg, 88% as a pale-yellow solid. 77% *ee* (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda$  = 210 nm,  $t_R$ (major) = 6.7 min,  $t_R$ (minor) = 11.0 min);  $[\alpha]_D^{25} = -52$  ( $c = 0.17$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.86 (d,  $J = 8.4$  Hz, 1H), 6.80 (d,  $J = 8.4$  Hz, 1H), 6.73 (s, 1H), 6.59 (s, 1H), 5.91 (s, 2H), 4.23 (d,  $J = 15.8$  Hz, 1H), 3.84 (s, 6H), 3.53 (d,  $J = 15.4$  Hz, 2H), 3.24–3.07 (m, 3H), 2.81 (dd,  $J = 15.4$  11.7Hz, 1H), 2.67–2.59 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 150.3, 146.1, 145.9, 145.0, 130.8, 128.6, 127.8, 127.6, 123.9, 110.9, 108.4, 105.5, 100.7, 60.1, 59.6, 55.9, 53.9, 51.4, 36.4, 29.6.



**Isocanadine<sup>3</sup> (7b)**, 5.1 mg, 58% yield over 2 steps) as a pale-yellow solid. 99% *ee* (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda$  = 210 nm,  $t_R$ (major) = 9.7 min,  $t_R$ (minor) = 8.9 min);  $[\alpha]_D^{25} = -72$  ( $c = 0.18$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.73 (s, 1H), 6.64 (s, 1H), 6.59 (s, 1H), 6.56 (s, 1H), 5.92 (s, 2H), 3.93 (d,  $J = 14.6$  Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.67 (d,  $J = 14.4$  Hz, 1H), 3.57 (m, 1H), 3.20 (dd,  $J = 15.9$ , 3.8 Hz, 1H), 3.15–3.08 (m, 2H), 2.85–2.78 (m, 1H), 2.67–2.57 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 147.6, 147.4, 146.1, 145.9, 130.9, 127.7, 126.2, 111.4, 109.0, 108.4, 105.5, 100.7, 59.9, 58.2, 56.0, 55.9, 51.2, 36.5, 29.5.



**Stylopine<sup>4</sup> (7c)**, 5.2 mg, 70% yield over 2 steps) as a pale-yellow solid. 86% *ee* (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda$  = 210 nm,  $t_R$ (major) = 9.7 min,  $t_R$ (minor) = 7.5 min);  $[\alpha]_D^{25} = -100$  ( $c = 0.15$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.72 (s, 1H), 6.69 (d,  $J = 7.9$  Hz, 1H), 6.63 (d,  $J = 7.9$  Hz, 1H), 6.59 (s, 1H), 5.94 (d,  $J = 15.4$  Hz, 2H), 5.92 (s, 2H), 4.08 (d,  $J = 15.4$  Hz, 1H), 3.56 (t,  $J = 12.4$  Hz, 2H), 3.23 (dd,  $J = 15.8$ , 3.7 Hz, 1H), 3.20–3.05 (m, 3H), 2.80 (dd,  $J = 15.8$ , 11.4 Hz, 1H), 2.69–2.59 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 146.2, 146.0, 145.0, 143.3, 130.7, 128.6, 127.8, 121.0, 116.9, 108.4, 106.8, 105.5, 101.0, 100.8, 59.8, 52.9, 51.2, 36.5, 29.6.



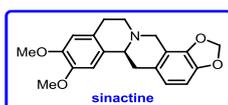
**Tetrahydropseudocoptisine<sup>5</sup> (7d)**, 5.5 mg, 65% yield over 2 steps) as a pale-yellow solid. 86% *ee* (HPLC conditions: Chiralcel AD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda$  = 210 nm,  $t_R$ (major) = 11.5 min,  $t_R$ (minor) = 7.1 min);  $[\alpha]_D^{25} = -85$  ( $c = 0.19$ , CHCl<sub>3</sub>); <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) 6.72 (s, 1H), 6.60 (s, 1H), 6.59 (s, 1H), 6.54 (s, 1H), 5.92 (s, 2H), 5.90 (s, 2H), 3.90

<sup>3</sup> Orito, K., Satoh, Y., Nishizawa, H., Harada, R., Tokuda, M. *Org. Lett.* **2000**, *2*, 2535–2537.

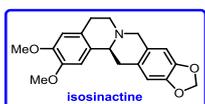
<sup>4</sup> Kim, J. H., Ryu, Y. B., Lee, W. S., Kim, Y. H. *Bioorg. Med. Chem.* **2014**, *22*, 6047–6052.

<sup>5</sup> Gatland, A. E., Pilgrim, B. S., Procopiou, P. A., Donohoe, T. J. *Angew. Chem. Int. Ed.* **2014**, *126*, 14783–14786.

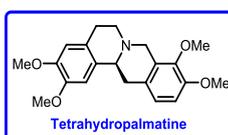
(d,  $J = 14.6$  Hz, 1H), 3.62 (d,  $J = 14.7$  Hz, 1H), 3.54 (dd,  $J = 11.2, 3.5$  Hz, 1H), 3.19–3.06 (m, 3H), 2.78 (dd,  $J = 15.5, 11.6$  Hz, 1H), 2.60 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 146.1, 145.9, 145.9, 145.8, 130.7, 127.7, 127.2, 108.4, 108.4, 106.0, 105.4, 100.8, 100.6, 100.0, 59.8, 58.5, 51.2, 36.9, 29.4.



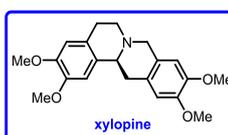
**Sinactine**<sup>6</sup> (**7e**, 5.7 mg, 70% yield over 2 steps) as a pale-yellow solid. 88% *ee* (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 210$  nm,  $t_{\text{R}}$ (major) = 14.0 min,  $t_{\text{R}}$ (minor) = 19.2 min);  $[\alpha]_{\text{D}}^{25} = -136$  ( $c = 0.18$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 6.73 (s, 1H), 6.69 (d,  $J = 7.8$  Hz, 1H), 6.66 (d,  $J = 7.8$  Hz, 1H), 6.62 (s, 1H), 5.97 (s, 1H), 5.93 (s, 1H), 4.10 (t,  $J = 15.1$  Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.61–3.53 (m, 2H), 3.28 (dd,  $J = 15.3, 3.2$  Hz, 1H), 3.26–3.09 (m, 2H), 2.81–2.62 (m, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 147.5, 147.4, 145.0, 143.3, 129.6, 128.6, 126.7, 121.0, 116.9, 111.3, 108.6, 106.7, 101.0, 59.4, 56.1, 55.8, 53.0, 51.3, 36.4, 29.1.



**Isosinactine**<sup>7</sup> (**7f**, 5.7 mg, 58% yield over 2 steps) as a pale-yellow solid. 99% *ee* (HPLC conditions: Chiralcel OD-H column, hexane/*i*-PrOH = 80/20, 1.0 mL/min,  $\lambda = 210$  nm,  $t_{\text{R}}$ (major) = 19.7 min,  $t_{\text{R}}$ (minor) = 8.9 min);  $[\alpha]_{\text{D}}^{25} = -30$  ( $c = 0.21$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 6.72 (s, 1H), 6.63 (s, 1H), 6.62 (s, 1H), 6.54 (s, 1H), 5.91 (s, 2H), 3.93 (d,  $J = 16.2$  Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.67 (d,  $J = 14.3$  Hz, 1H), 3.58 (d,  $J = 8.4$  Hz, 1H), 3.23 (dd,  $J = 16.2, 3.4$  Hz, 1H), 3.19–3.12 (m, 2H), 2.87–2.79 (m, 1H), 2.69–2.59 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 147.6, 147.5, 146.2, 145.9, 129.5, 127.2, 126.6, 111.4, 108.5, 108.4, 106.0, 100.7, 59.5, 58.5, 56.1, 55.9, 51.2, 36.7, 29.70, 28.9.



**Tetrahydropalmatine**<sup>8</sup> (**7g**, 5.5 mg, 80% yield over 2 steps) as a pale-yellow solid. 99% *ee* (HPLC conditions: Chiralcel AD-H column, hexane/EtOH = 80/20, 1.0 mL/min,  $\lambda = 210$  nm,  $t_{\text{R}}$ (major) = 12.7 min,  $t_{\text{R}}$ (minor) = 8.0 min);  $[\alpha]_{\text{D}}^{25} = -48$  ( $c = 0.2$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 6.86 (d,  $J = 8.2$  Hz, 1H), 6.77 (d,  $J = 8.4$  Hz, 1H), 6.73 (s, 1H), 6.61 (s, 1H), 4.23 (d,  $J = 15.3$  Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.55–3.50 (m, 2H), 3.28–3.09 (m, 3H), 2.82 (dd,  $J = 15.3, 11.1$  Hz, 1H), 2.85–2.60 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 150.2, 147.5, 147.4, 145.0, 129.7, 128.7, 127.6, 126.8, 123.8, 111.2, 110.9, 108.6, 60.1, 59.3, 56.0, 55.8, 55.7, 53.9, 51.5, 36.2, 29.0.



**Xylopinine**<sup>9</sup> (**7h**, 6.0 mg, 72% yield over 2 steps) as a pale-yellow solid. 90% *ee* (HPLC conditions: Chiralcel AD-H column, hexane/EtOH = 80/20, 1.0 mL/min,  $\lambda = 210$  nm,  $t_{\text{R}}$ (major) = 12.7 min,  $t_{\text{R}}$ (minor) = 8.0 min);  $[\alpha]_{\text{D}}^{25} = -40$  ( $c = 0.18$ ,  $\text{CHCl}_3$ );  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 6.74 (s, 1H), 6.67 (s, 1H), 6.62 (s, 1H), 6.58 (s, 1H), 3.94 (d,  $J = 14.8$  Hz, 1H), 3.89 (s, 3H), 3.87 (s, 3H), 3.86 (s, 3H), 3.85 (s, 3H), 3.69 (d,  $J = 14.2$  Hz, 1H), 3.62 (dd,  $J = 11.3, 3.4$  Hz, 1H), 3.22 (dd,  $J = 15.8, 3.5$  Hz, 1H), 3.18–3.10

<sup>6</sup> Seger, C., Sturm, S., Strasser, E. M., Ellmerer, E., Stuppner, H. *Magn. Reson. Chem.* **2004**, *42*, 882–886.

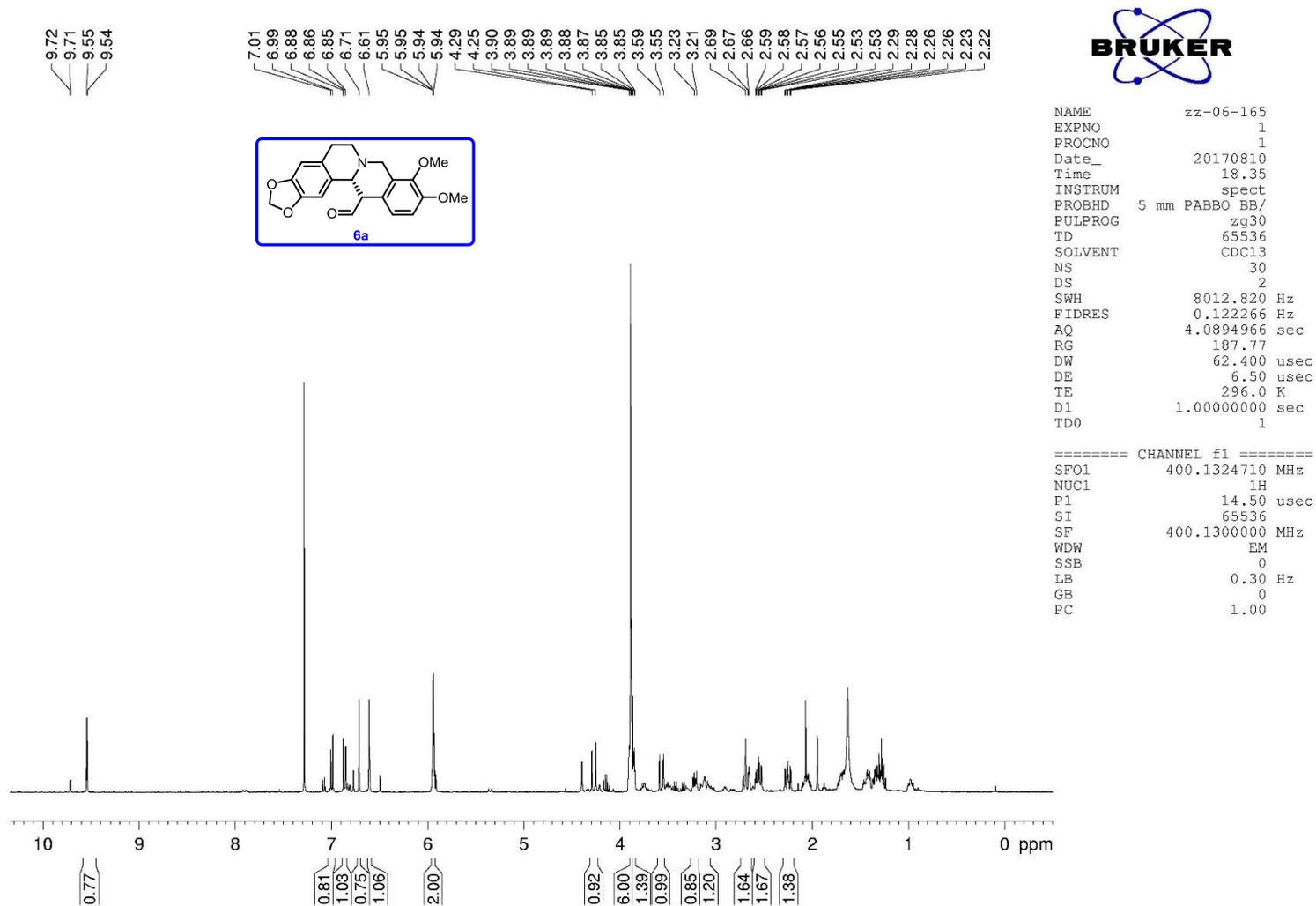
<sup>7</sup> Orito, K., Satoh, Y., Nishizawa, H., Harada, R. & Tokuda, M. *Org. Lett.* **2000**, *2*, 2535–2537.

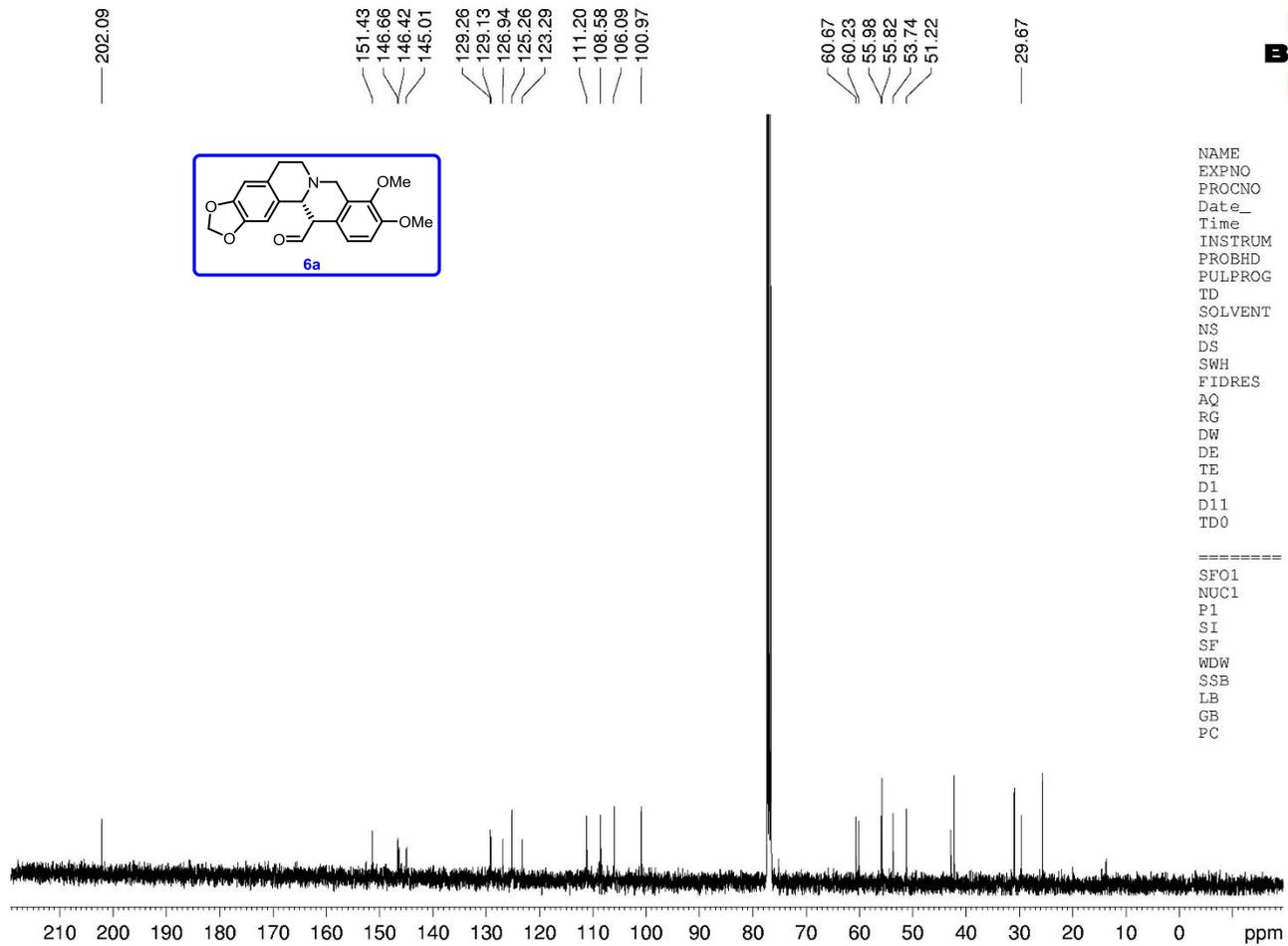
<sup>8</sup> Boudou, M., Enders, D. *J. Org. Chem.* **2005**, *70*, 9486–9494.

<sup>9</sup> Mastranzo, V. M., Yuste, F., Ortiz, B., Sánchez-Obregón, R., Toscano, R. A., García Ruano, J. L. *J. Org. Chem.* **2011**, *76*, 5036–5041.

(m, 2H), 2.85 (dd,  $J = 15.6, 11.4$  Hz, 1H), 2.69–2.59 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm) 147.6, 147.5, 147.4, 147.4, 129.8, 126.7, 126.3, 126.3, 111.3, 109.0, 108.5, 59.6, 58.2, 56.0, 56.0, 55.9, 55.8, 51.3, 36.4, 29.0.

## 5. Copies of NMR Spectra and HPLC Spectra



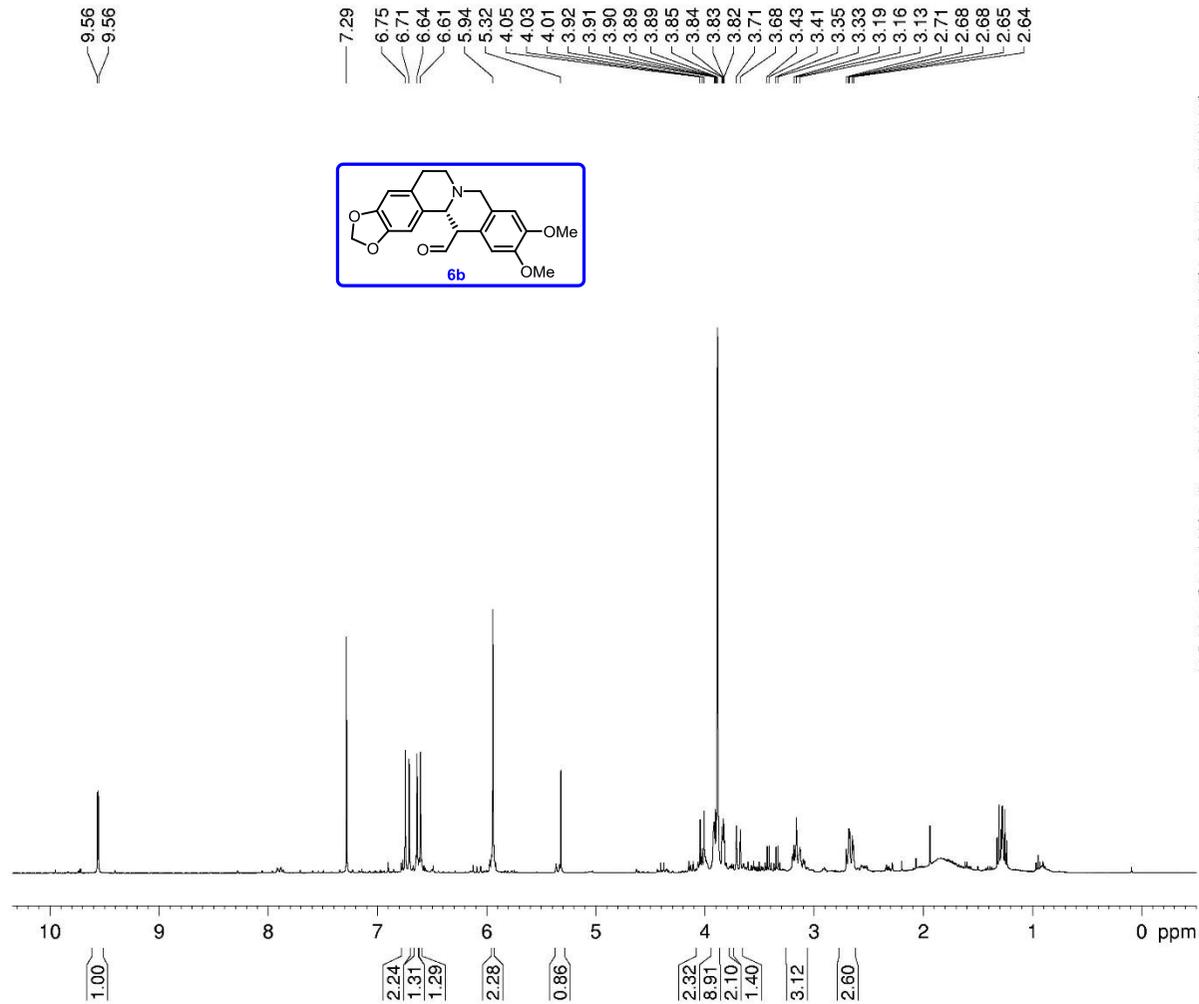


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DS            2
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FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG            196.92
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DE            6.50 usec
TE            296.7 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0           1
  
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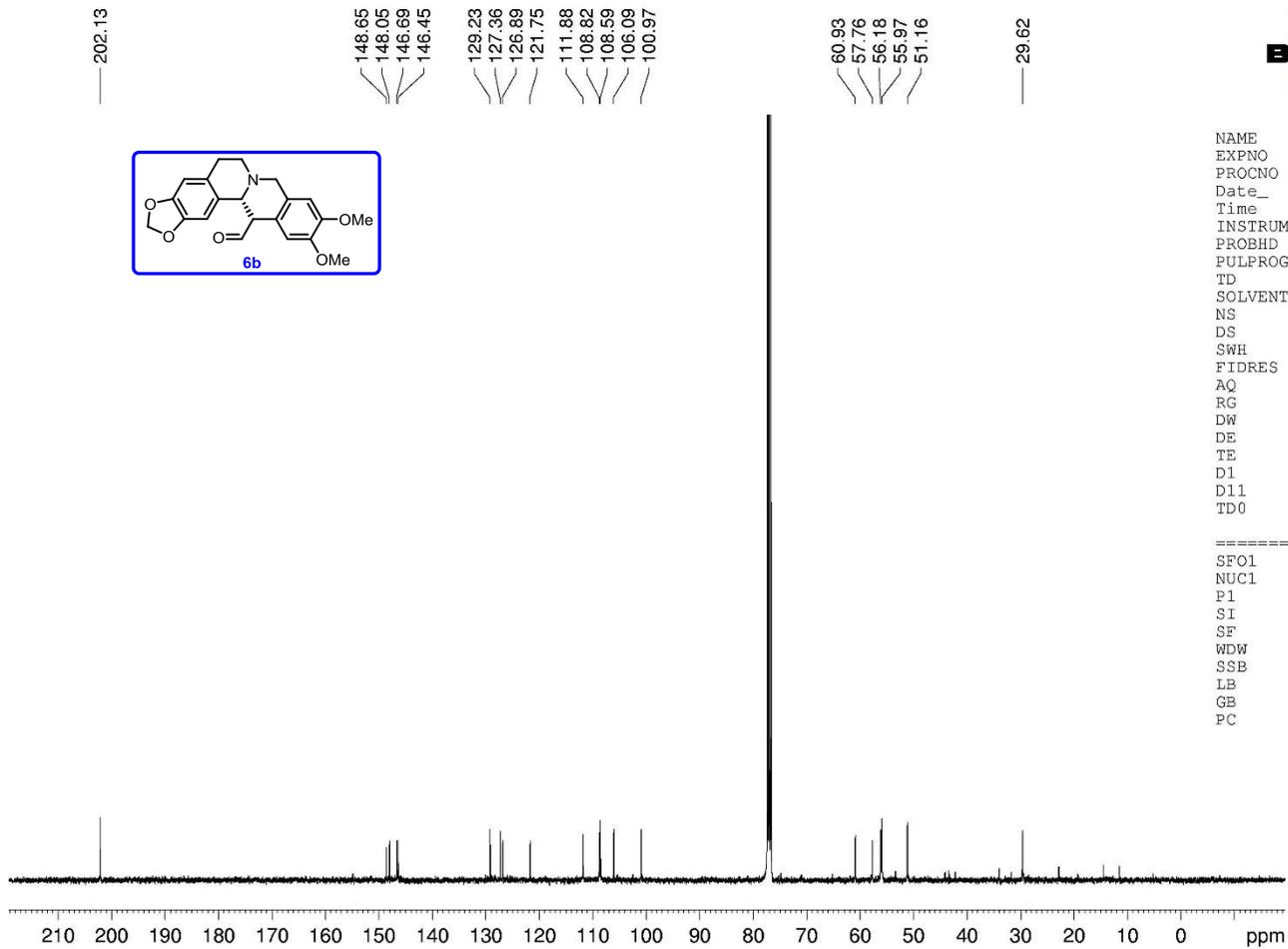
**BRUKER**

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PROCNO        1
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PULPROG       zg30
TD            65536
SOLVENT       CDC13
NS            74
DS            2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
AQ            4.0894966 sec
RG            196.92
DW            62.400 usec
DE            6.50 usec
TE            298.8 K
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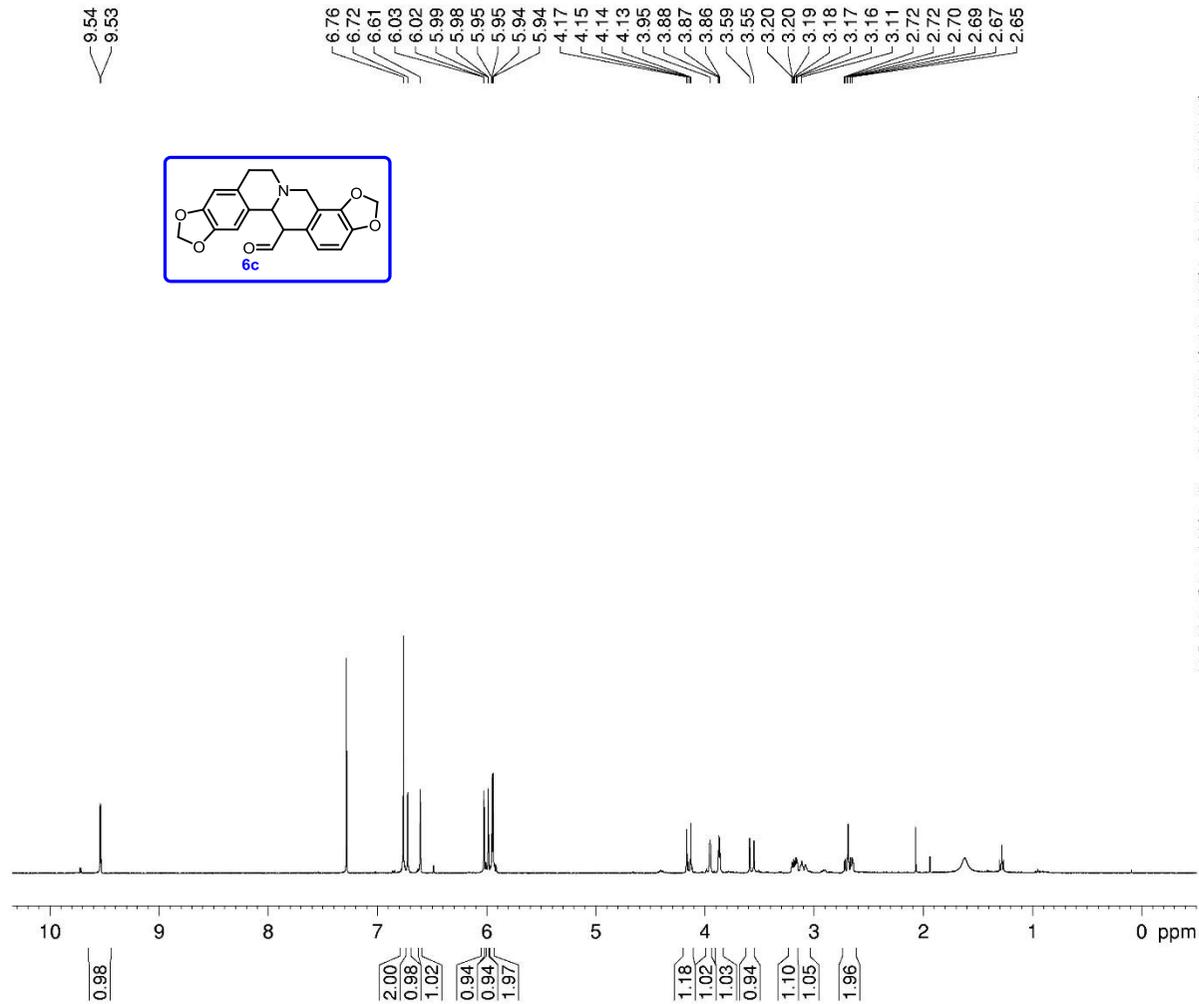


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PULPROG   zgpg30
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SOLVENT   CDCl3
NS         7977
DS         2
SWH       24038.461 Hz
FIDRES    0.366798 Hz
AQ         1.3631988 sec
RG         196.92
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TE         298.9 K
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TD0        1
  
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```

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PC        1.40
  
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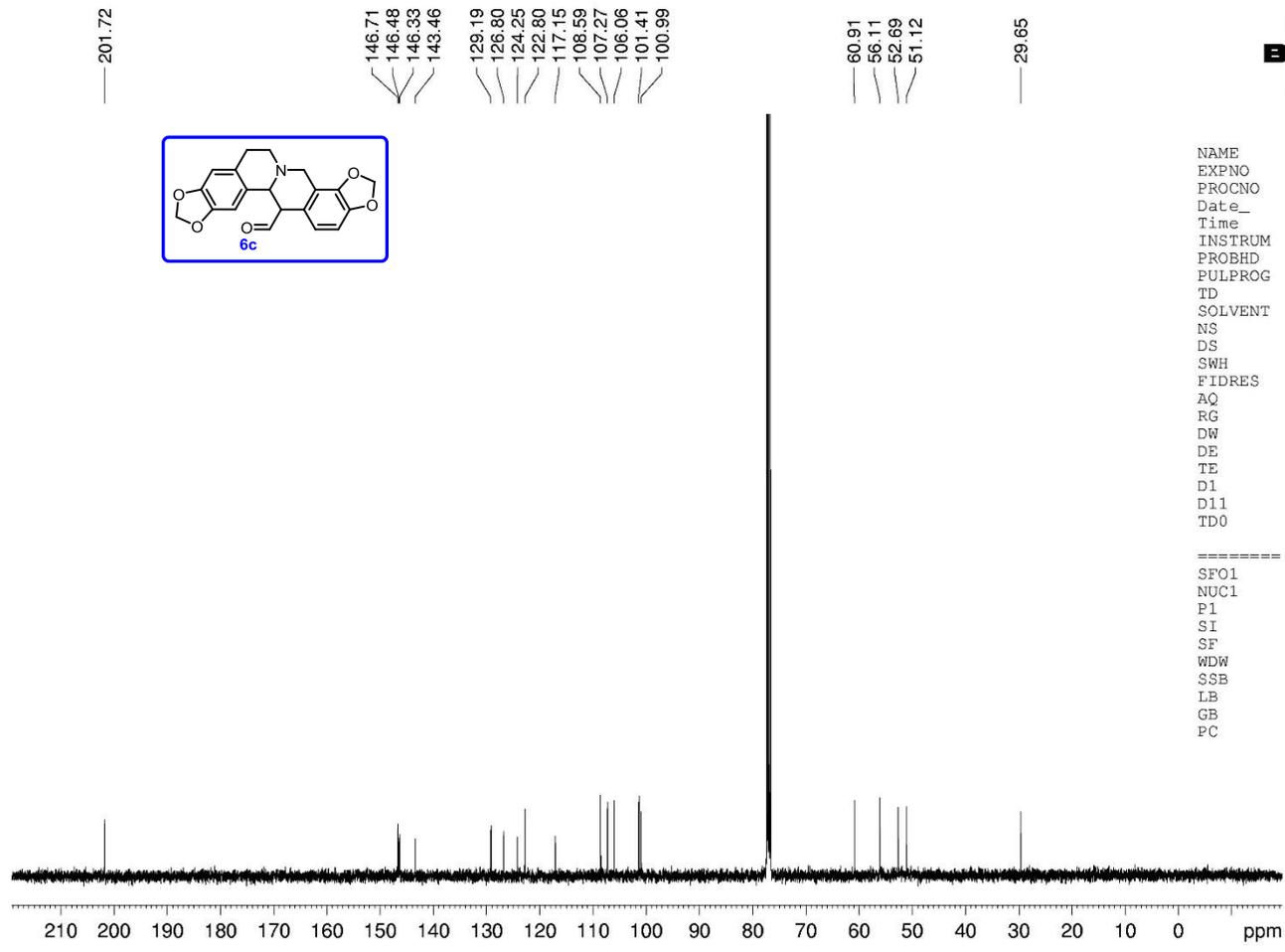


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SOLVENT       CDC13
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DS            2
SWH           8012.820 Hz
FIDRES        0.122266 Hz
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RG            196.92
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DE            6.50 usec
TE            297.0 K
D1            1.00000000 sec
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```

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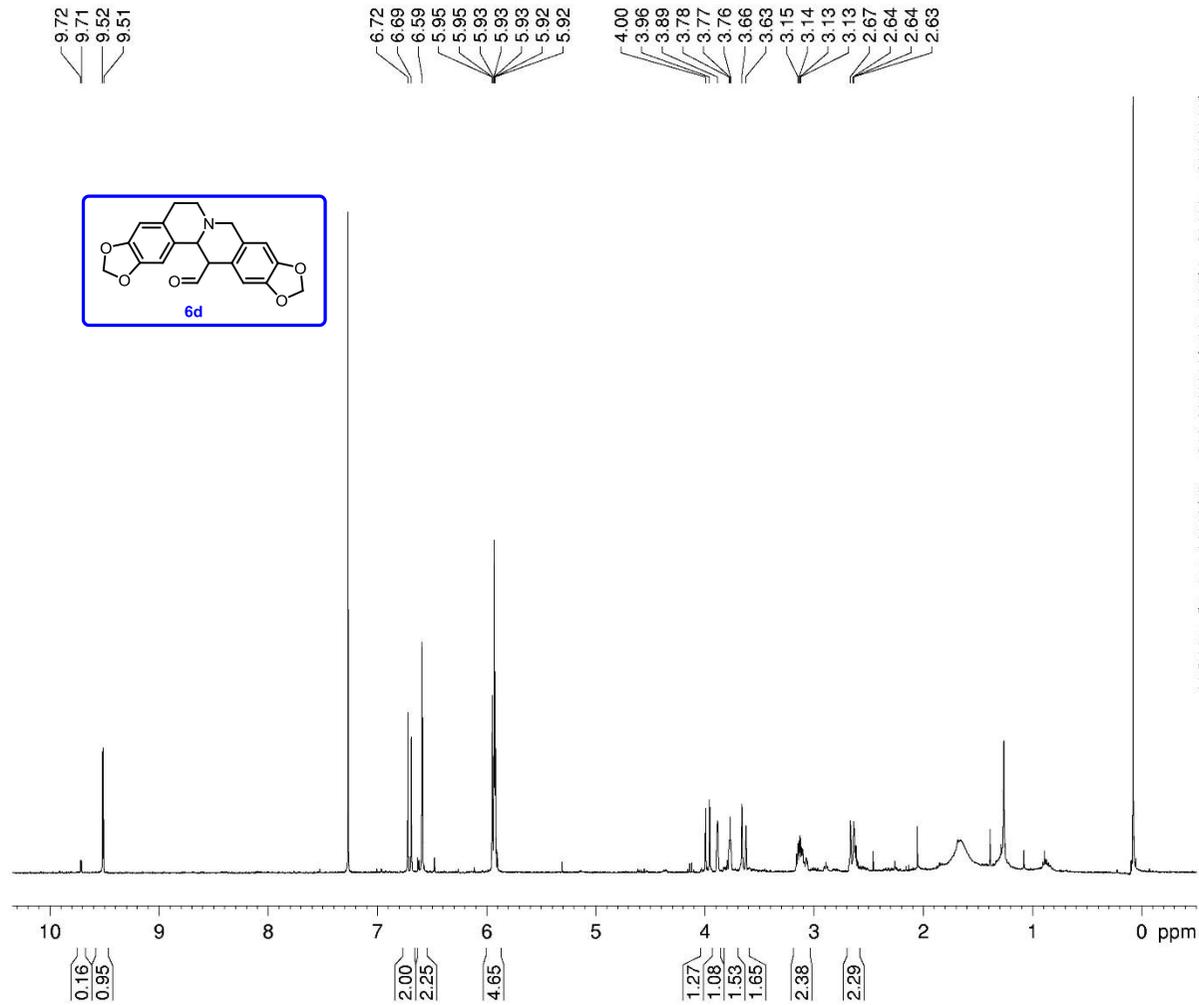


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```

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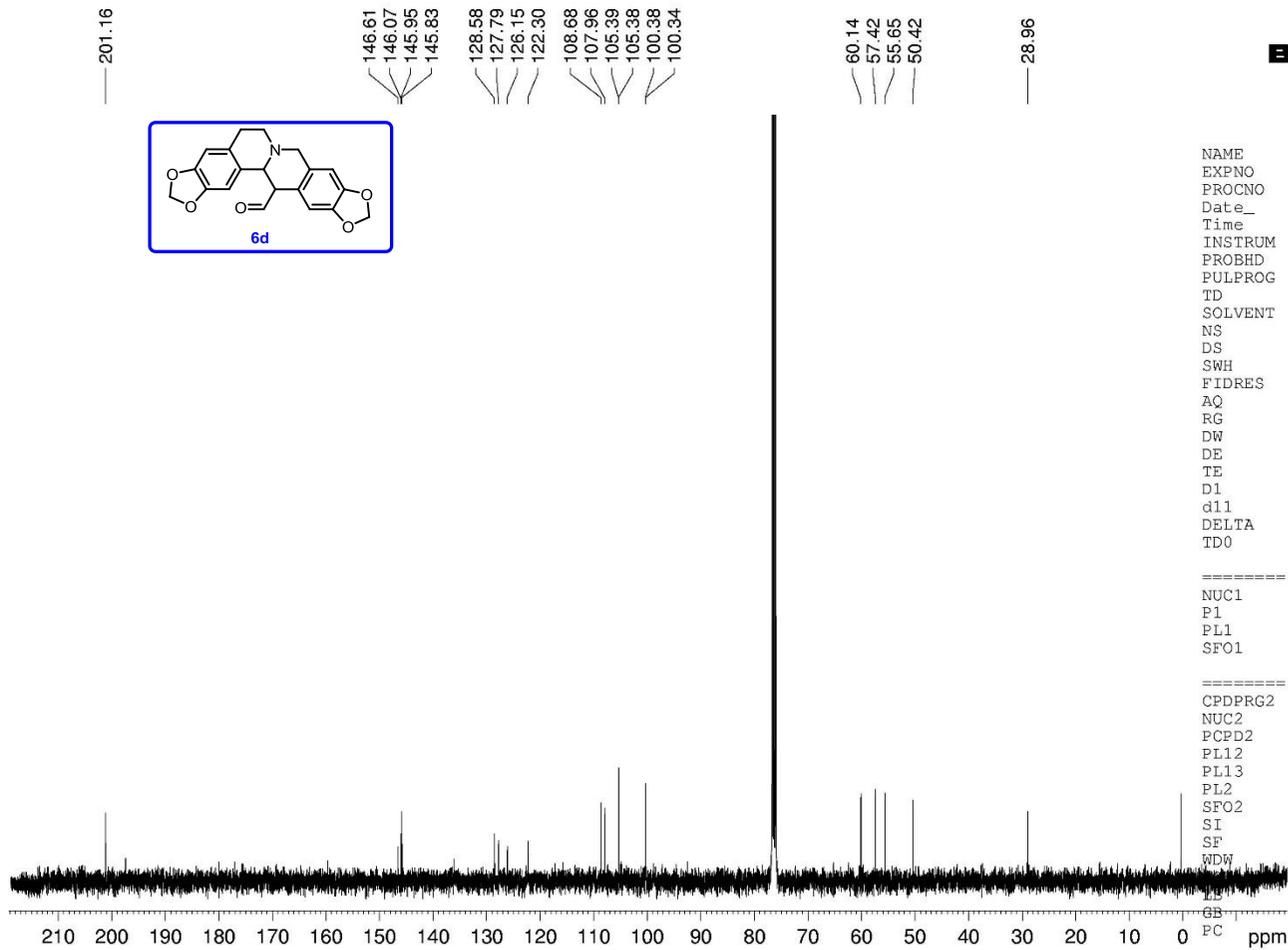


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PROCNO    1
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SOLVENT   CDCl3
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DS         2
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TE         296.6 K
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```

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PC        1.00
  
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PROCNO    1
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Time      23.35
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FIDRES     0.366798 Hz
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DW         20.800 usec
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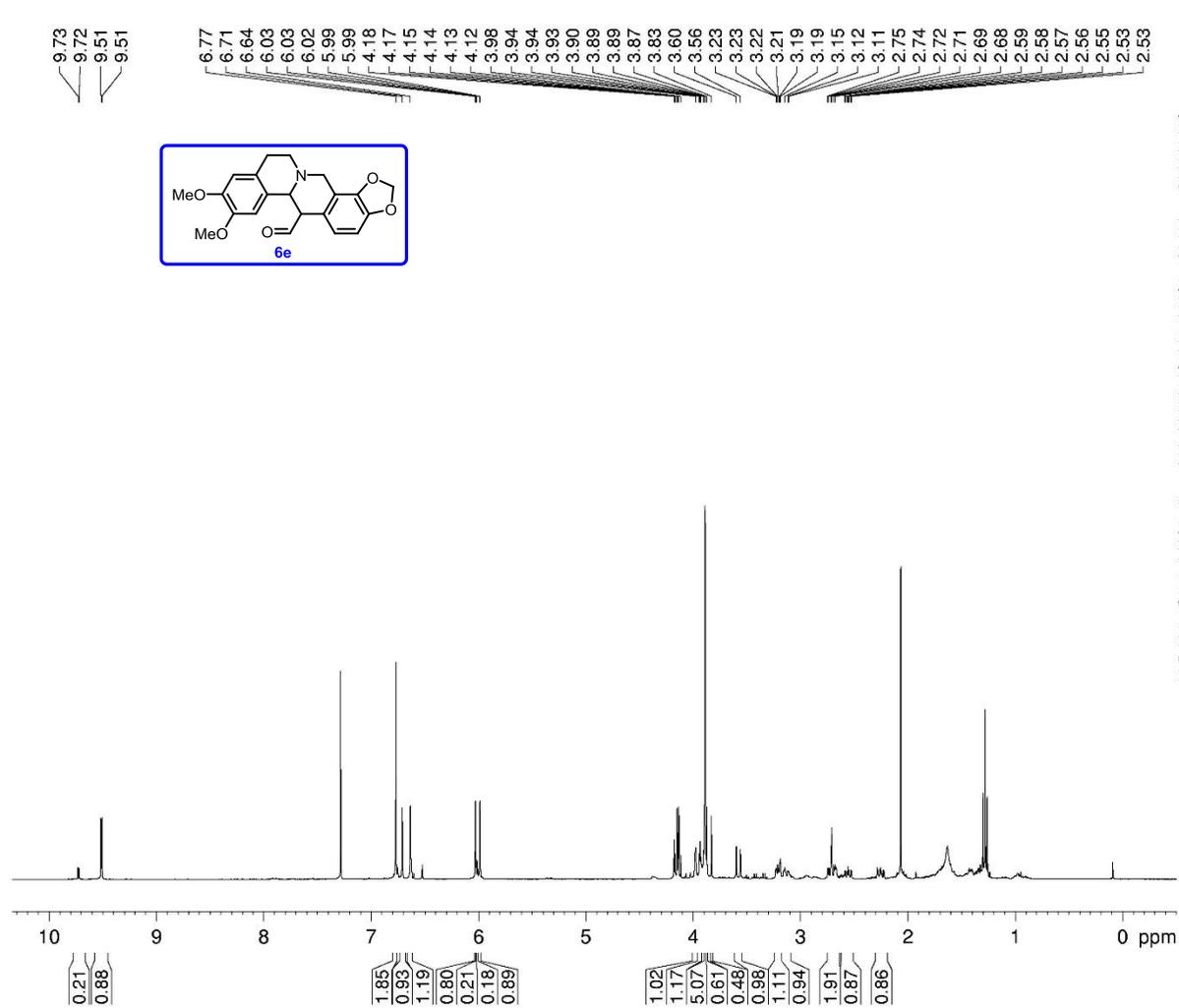
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PL13      18.00 dB
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GB         0
PC         1.40

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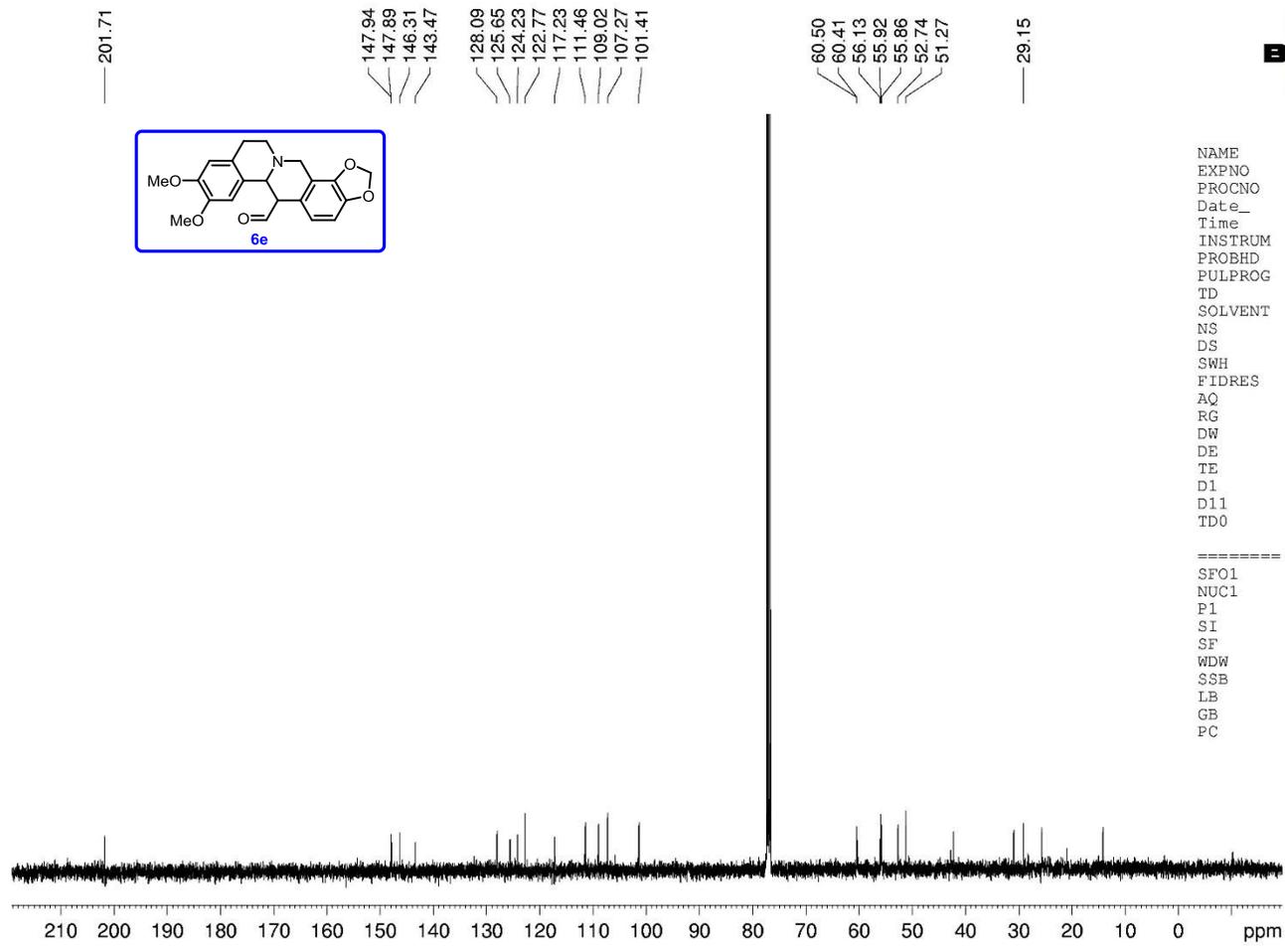


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DE            6.50 usec
TE            296.4 K
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TD0           1
  
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```

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PC            1.00
  
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```

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PROCNO    1
Date_     20170806
Time      16.28
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PULPROG   zgpg30
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SOLVENT   CDC13
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FIDRES    0.366798 Hz
AQ         1.3631988 sec
RG         196.92
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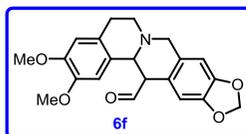
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LB        1.00 Hz
GB        0
PC        1.40

```

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9.54

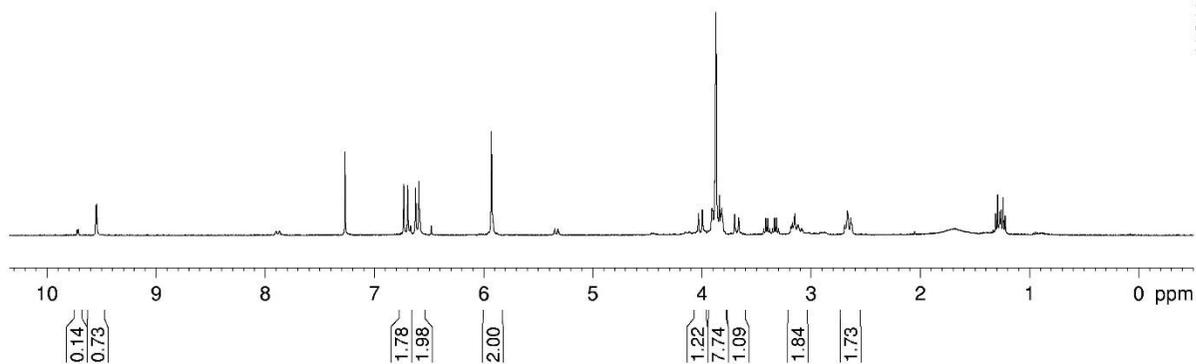
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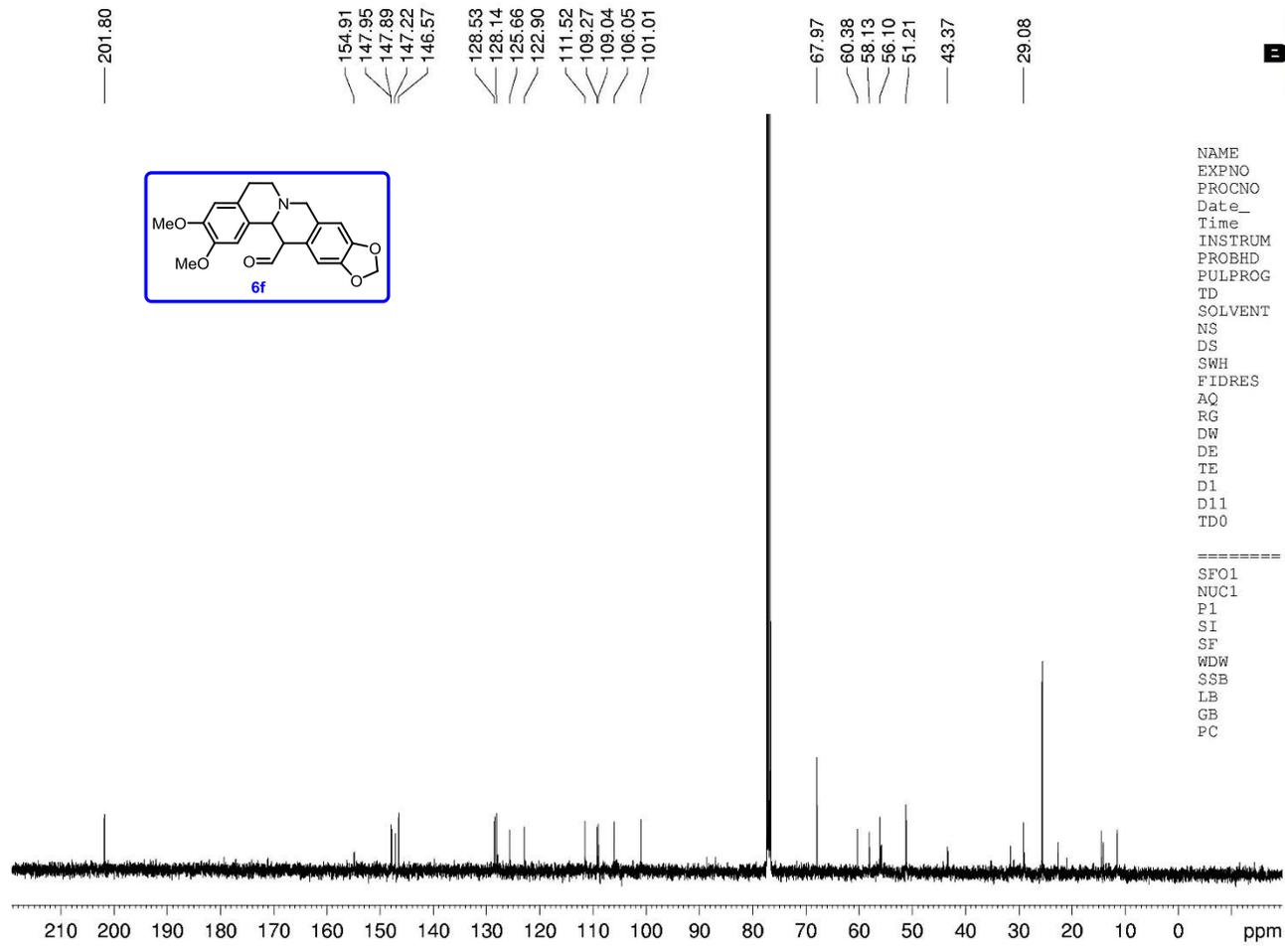
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2.64



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PROCNO        1
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PULPROG       zg30
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SOLVENT       CDCl3
NS            16
DS            2
SWH           8223.685 Hz
FIDRES        0.125483 Hz
AQ            3.9846387 sec
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DE            6.00 usec
TE            297.6 K
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TD0           1
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SI            32768
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SSB           0
LB            0.30 Hz
GB            0
PC            1.00
```



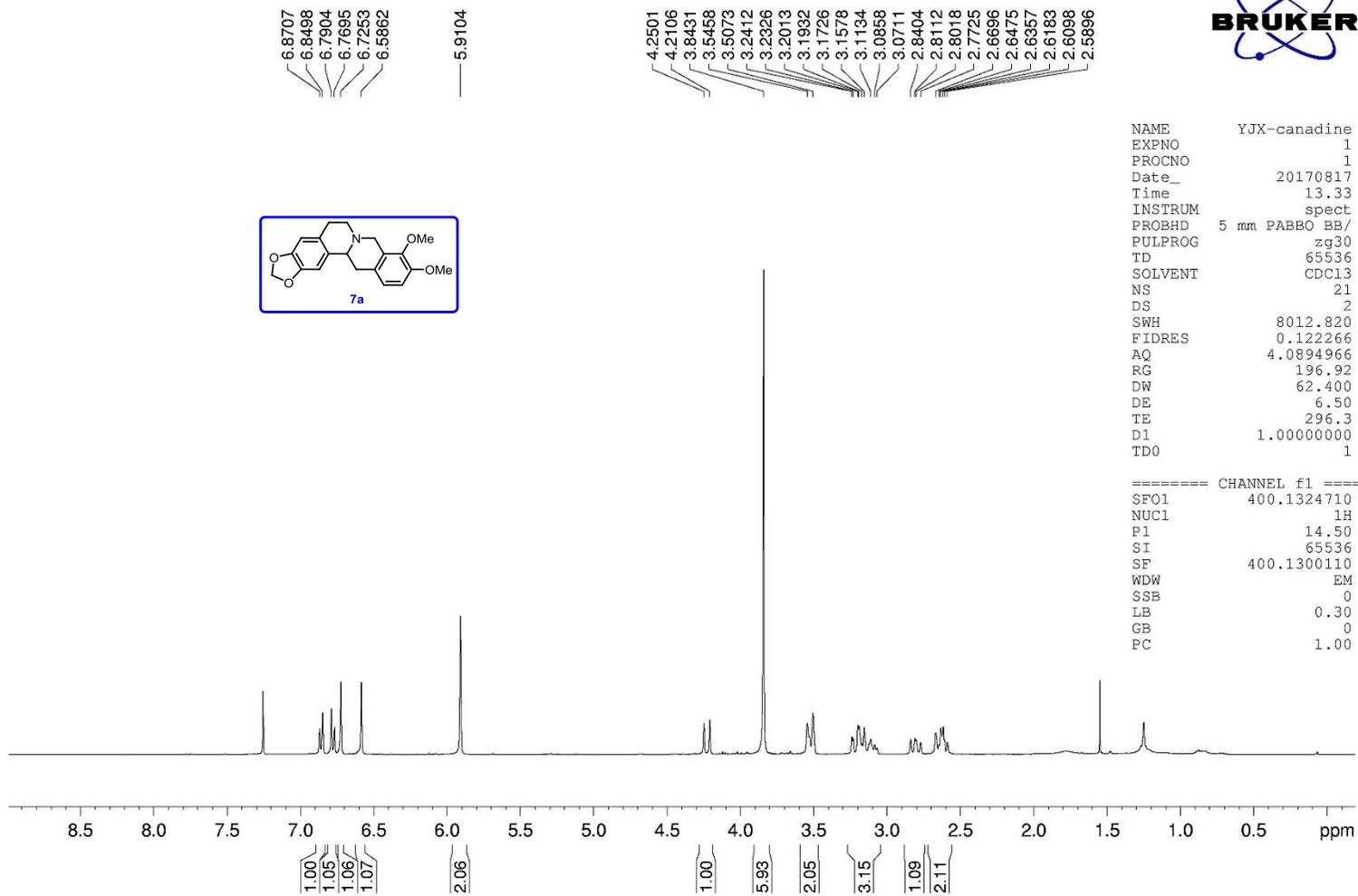
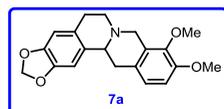


```

NAME          zz-06-176-03
EXPNO         2
PROCNO        1
Date_         20170815
Time          1.32
INSTRUM       spect
PROBHD        5 mm PABBO BB/
PULPROG       zgpg30
TD            65536
SOLVENT       CDC13
NS            497
DS            2
SWH           24038.461 Hz
FIDRES        0.366798 Hz
AQ            1.3631988 sec
RG            196.92
DW            20.800 usec
DE            6.50 usec
TE            299.0 K
D1            2.0000000 sec
D11           0.0300000 sec
TD0           1

===== CHANNEL f1 =====
SFO1          100.6228298 MHz
NUC1          13C
P1            9.70 usec
SI            32768
SF            100.6127690 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40

```

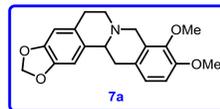




150.25  
146.11  
145.88  
145.04  
130.81  
128.60  
127.78  
127.66  
123.87  
110.93  
108.38  
105.50  
100.73

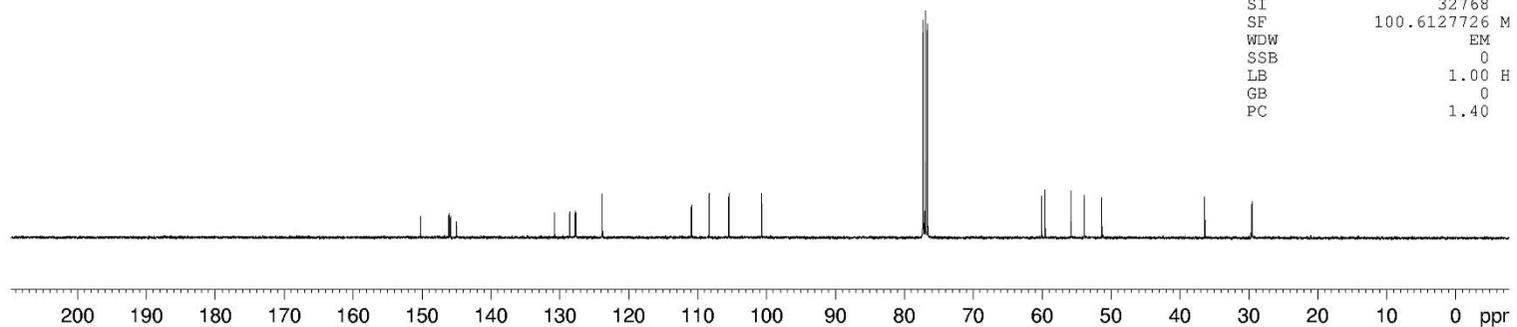
60.14  
59.61  
55.86  
53.91  
51.37

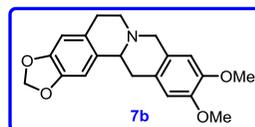
36.43  
29.56



```
NAME      YJX-canadine
EXPNO     6
PROCNO    1
Date_     20170817
Time      13.37
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   CDC13
NS         658
DS         2
SWH        24038.461 H
FIDRES     0.366798 H
AQ         1.3631988 s
RG         196.92
DW         20.800 u
DE         6.50 u
TE         296.8 K
D1         2.0000000 s
D11        0.0300000 s
TD0        1
```

```
===== CHANNEL f1 =====
SFO1      100.6228298 M
NUC1       13C
P1         9.70 u
SI         32768
SF         100.6127726 M
WDW        EM
SSB        0
LB         1.00 H
GB         0
PC         1.40
```



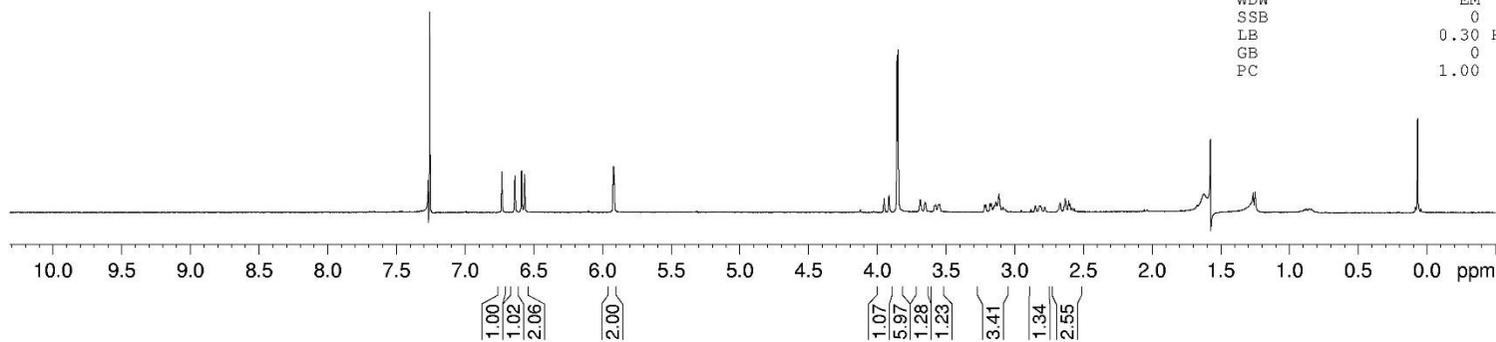


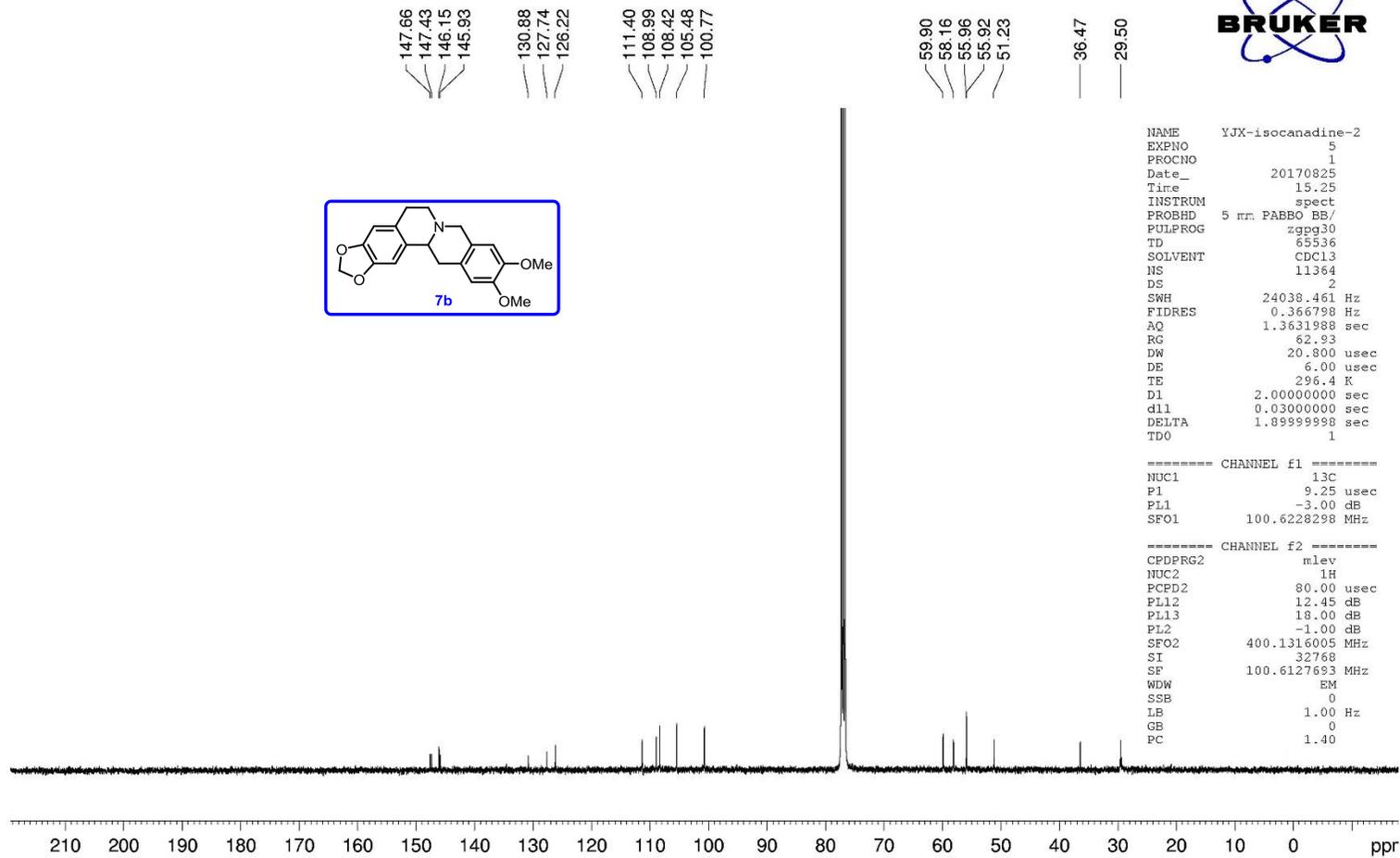
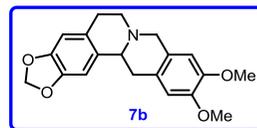
6.7354  
6.6405  
6.5915  
6.5697  
5.9247  
5.9192

3.9529  
3.9164  
3.8585  
3.8515  
3.6894  
3.6534  
3.5772  
3.5572  
3.5497  
3.2210  
3.2115  
3.1812  
3.1715  
3.1494  
3.1375  
3.1162  
3.0877  
2.8510  
2.8227  
2.8120  
2.7832  
2.6713  
2.6341  
2.6086  
2.6001  
2.5839  
2.5686

NAME YJX-isocanadine-2  
EXPNO 3  
PROCNO 1  
Date\_ 20170825  
Time 15.15  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 65536  
SOLVENT CDC13  
NS 25  
DS 2  
SWH 8223.685 Hz  
FIDRES 0.125483 Hz  
AQ 3.9846387 sec  
RG 196.92  
DW 60.800 usec  
DE 6.00 usec  
TE 295.6 K  
D1 1.00000000 sec  
TD0 1

==== CHANNEL f1 =====  
NUC1 1H  
P1 13.60 usec  
PL1 -1.00 dB  
SF01 400.1324710 MHz  
SI 32768  
SF 400.1300053 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00

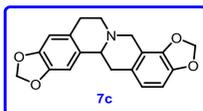






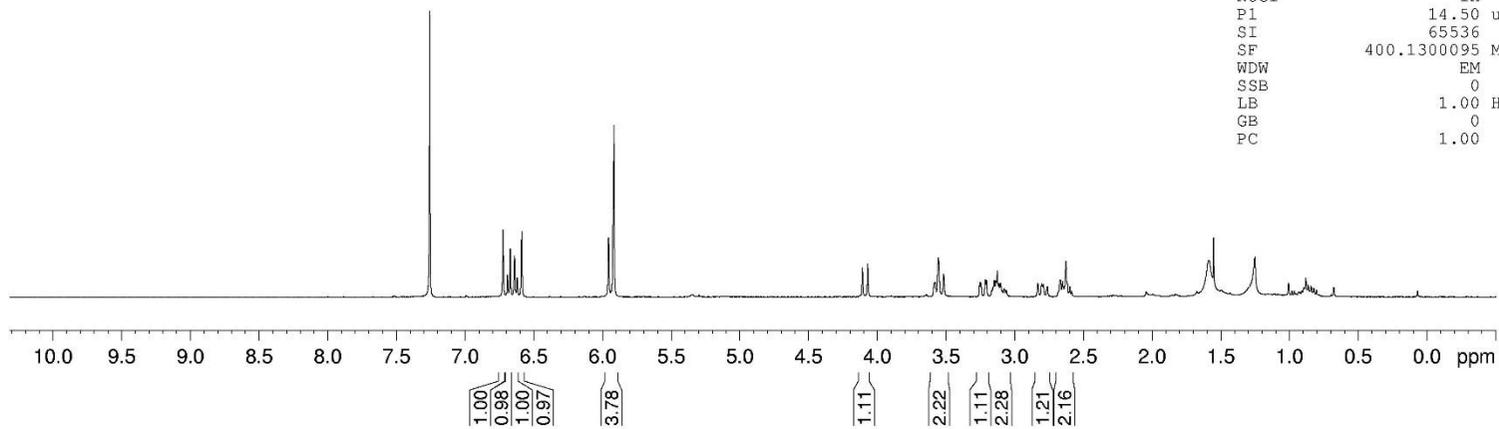
6.7265  
6.6935  
6.6736  
6.6429  
6.6230  
6.5905  
5.9574  
5.9194

4.1099  
4.0716  
3.5809  
3.5572  
3.5189  
3.2561  
3.2473  
3.2162  
3.2074  
3.1690  
3.1620  
3.1492  
3.1393  
3.1282  
3.1179  
3.1051  
3.0782  
3.0627  
2.8334  
2.8047  
2.7938  
2.7655  
2.6844  
2.6703  
2.6528  
2.6282  
2.6193  
2.6009  
2.5876



```
NAME YJX-Stylopine
EXPNO 3
PROCNO 1
Date_ 20170817
Time 12.36
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 17
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 187.77
DW 62.400 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
```

```
===== CHANNEL f1 =====
SFO1 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300095 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.00
```

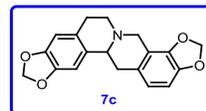




146.17  
145.97  
144.97  
143.27  
130.72  
128.55  
127.77  
121.04  
116.87  
108.42  
106.75  
105.52  
101.03  
100.78

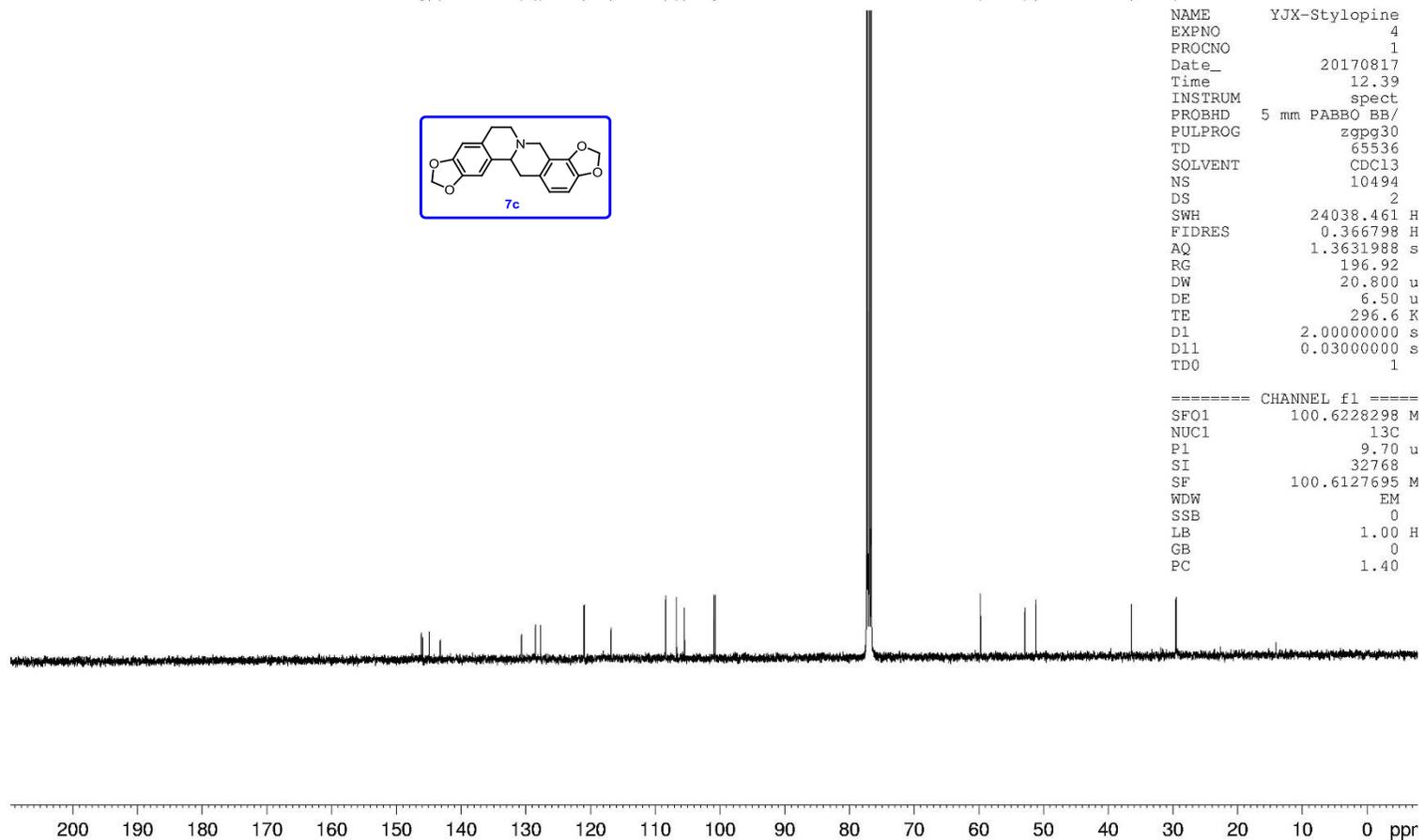
59.76  
52.92  
51.22

36.48  
29.58



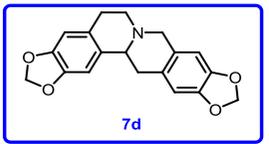
```
NAME      YJX-Stylopine
EXPNO     4
PROCNO    1
Date_     20170817
Time      12.39
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD        65536
SOLVENT   CDC13
NS        10494
DS        2
SWH       24038.461 H
FIDRES    0.366798 H
AQ        1.3631988 s
RG        196.92
DW        20.800 u
DE        6.50 u
TE        296.6 K
D1        2.0000000 s
D11       0.0300000 s
TD0       1
```

```
===== CHANNEL f1 =====
SFO1     100.6228298 M
NUC1     13C
P1       9.70 u
SI       32768
SF       100.6127695 M
WDW      EM
SSB      0
LB       1.00 H
GB       0
PC       1.40
```



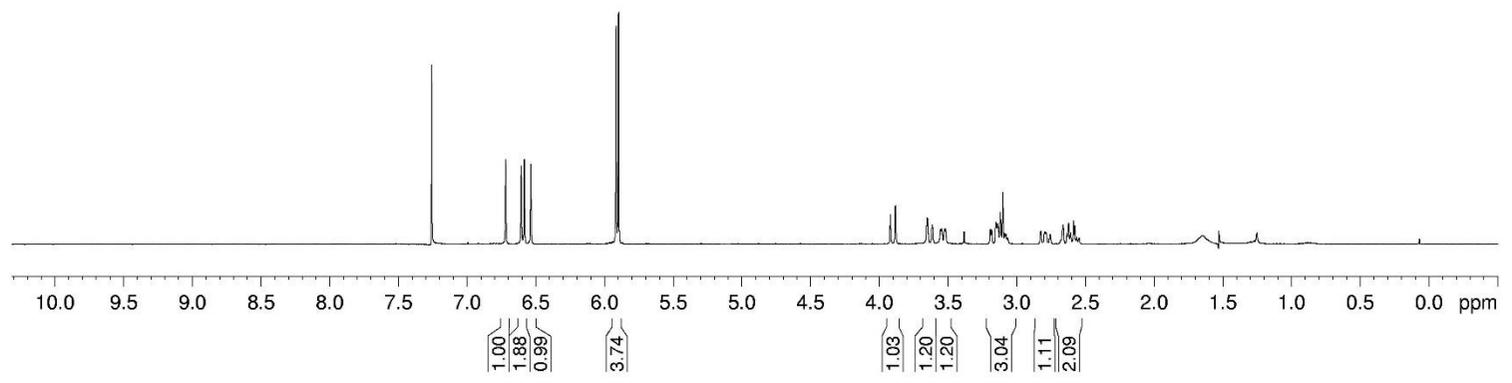


7.2602  
6.7217  
6.6081  
6.5860  
6.5390  
5.9176  
5.9005  
3.9210  
3.8844  
3.6528  
3.6160  
3.5561  
3.5476  
3.5285  
3.5197  
3.1937  
3.1843  
3.1532  
3.1438  
3.1367  
3.1205  
3.1027  
3.0889  
3.0800  
3.0679  
2.8262  
2.7971  
2.7866  
2.7578  
2.6636  
2.6361  
2.6241  
2.6092  
2.5872  
2.5785  
2.5650  
2.5466



```
NAME YXX-Tetrahydroisoquinoline
EXPNO 1
PROCNO 1
DATE_ 20170814
Time 13.03
INSTRUM spect
PROBHD 5 mm PABBO B3/
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 18
DS 2
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 187.77
DW 62.400 usec
DE 6.50 usec
TE 301.1 K
D1 1.0000000 sec
TDC 1

===== CHANNEL f1 =====
SFO 400.1324710 MHz
NUC1 1H
P1 14.50 usec
SI 65536
SF 400.1300081 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
```



146.14  
145.93  
145.85

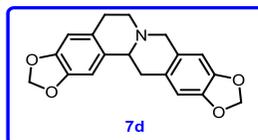
130.72  
127.68  
127.20

108.42  
108.39  
106.00  
105.43  
100.75  
100.62

59.76  
58.48

51.15

36.86  
29.46

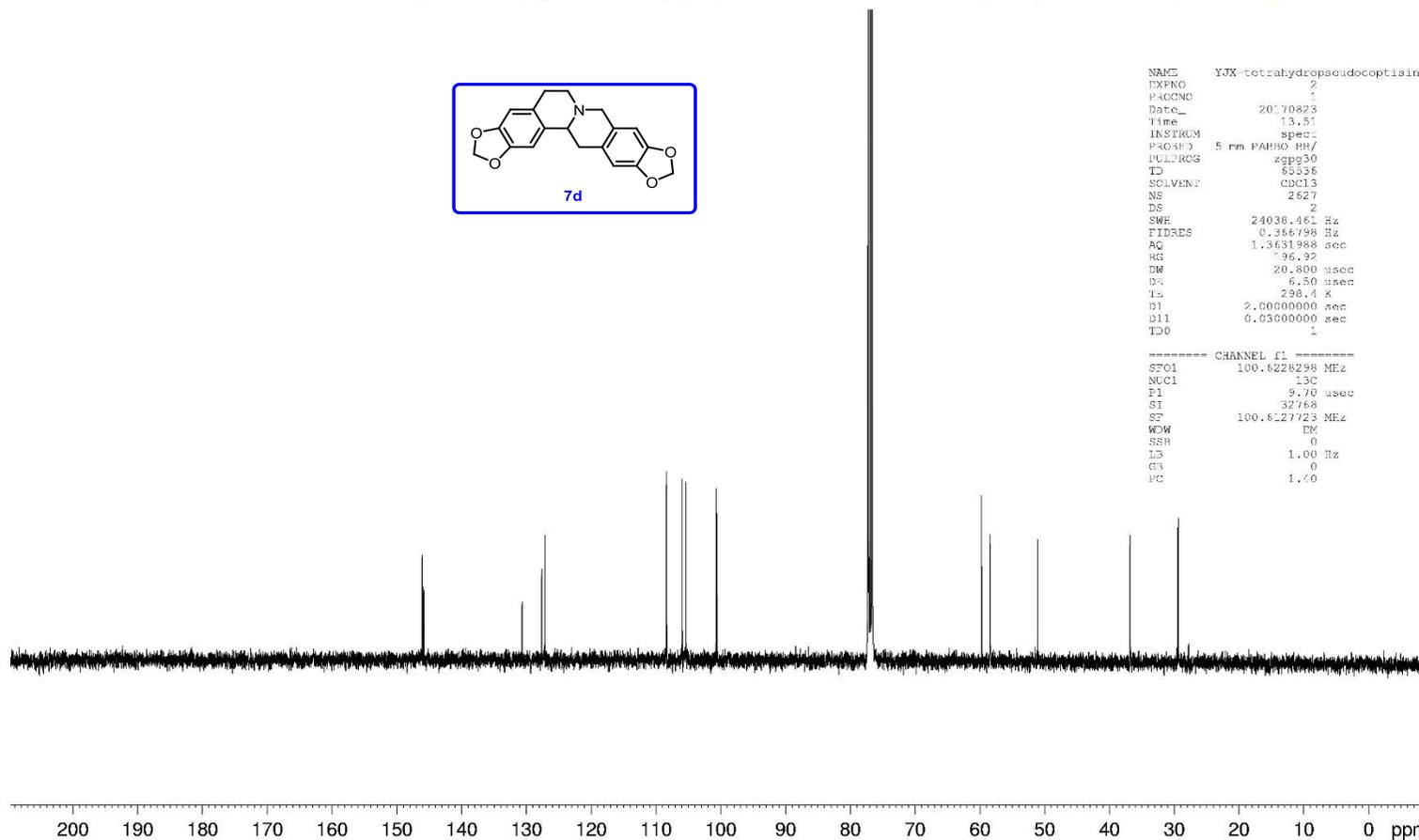


```

NAME      YJX-tetrahydropseudocoptisin
EXPNO     2
PROCNO    1
Date_     20170823
Time      13.51
INSTRUM   spect
PROBHD    5 mm PABBO BH/
PULPROG   zgpg30
TD        65536
SOLVENT   CDCl3
NS        2627
DS        2
SWE       24038.461 Hz
FIDRES    0.366798 Hz
AQ        1.3631988 sec
RG        96.92
DW        20.800 usec
DE        6.50 usec
TE        298.2 K
D1        2.0000000 sec
d11       0.0300000 sec
TD0       1
  
```

```

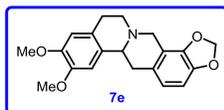
----- CHANNEL f1 -----
SF01     100.6228280 MHz
NUC1     13C
P1       9.70 usec
SI       32768
SF       100.6227723 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.00
  
```





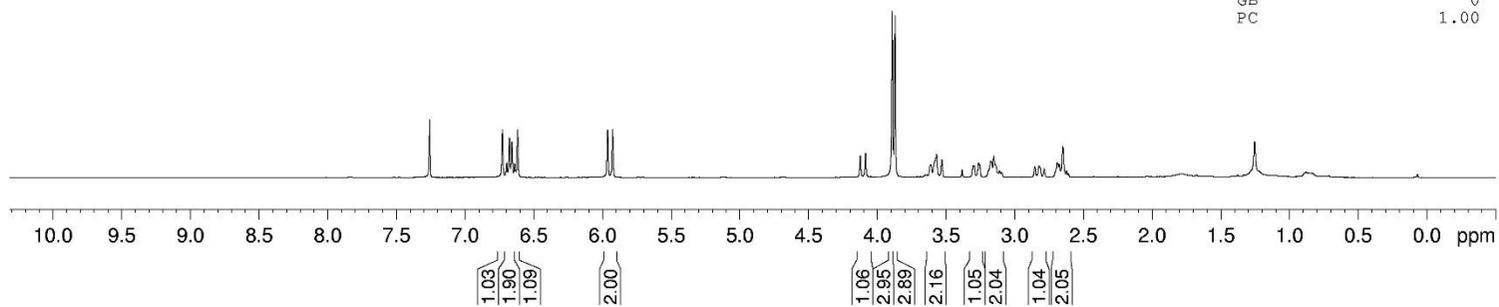
6.7309  
6.6999  
6.6801  
6.6615  
6.6414  
6.6202  
5.9652  
5.9289

4.1253  
4.0870  
3.8929  
3.8723  
3.6116  
3.5707  
3.5322  
3.3041  
3.2966  
3.2645  
3.2570  
3.1780  
3.1541  
3.1389  
3.1115  
3.0970  
2.8546  
2.8254  
2.8159  
2.7868  
2.6922  
2.6764  
2.6513  
2.6235



NAME YJX-sinactine  
EXPNO 5  
PROCNO 1  
Date\_ 20170824  
Time 23.53  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 65536  
SOLVENT CDC13  
NS 18  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 196.92  
DW 62.400 usec  
DE 6.50 usec  
TE 298.6 K  
D1 1.00000000 sec  
TD0 1

==== CHANNEL f1 =====  
SFO1 400.1324710 MHz  
NUC1 1H  
P1 14.50 usec  
SI 65536  
SF 400.1300090 MHz  
WDW EM  
SSB 0  
LB 0.50 Hz  
GB 0  
PC 1.00

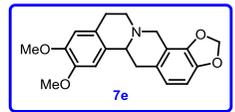




147.50  
147.45  
144.95  
143.27  
129.55  
128.60  
126.73  
120.99  
116.93  
111.33  
108.55  
106.72  
101.02

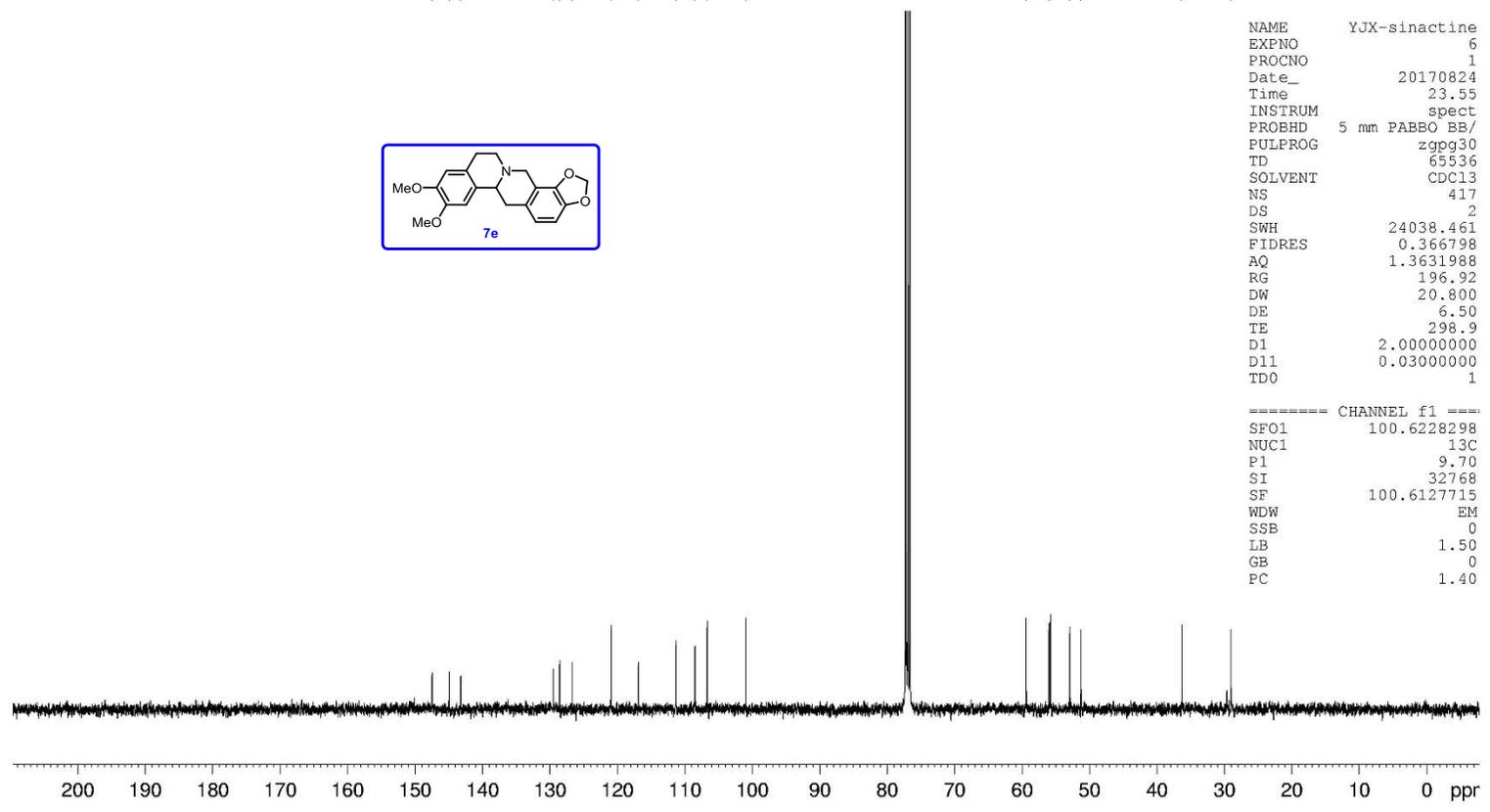
59.44  
56.06  
55.83  
52.98  
51.33

36.38  
29.09



NAME YJX-sinactine  
EXPNO 6  
PROCNO 1  
Date\_ 20170824  
Time 23.55  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgpg30  
TD 65536  
SOLVENT CDCl3  
NS 417  
DS 2  
SWH 24038.461  
FIDRES 0.366798  
AQ 1.3631988  
RG 196.92  
DW 20.800  
DE 6.50  
TE 298.9  
D1 2.0000000  
D11 0.0300000  
TD0 1

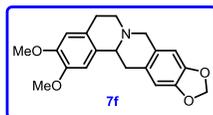
----- CHANNEL f1 -----  
SFO1 100.6228298  
NUC1 13C  
P1 9.70  
SI 32768  
SF 100.6127715  
WDW EM  
SSB 0  
LB 1.50  
GB 0  
PC 1.40





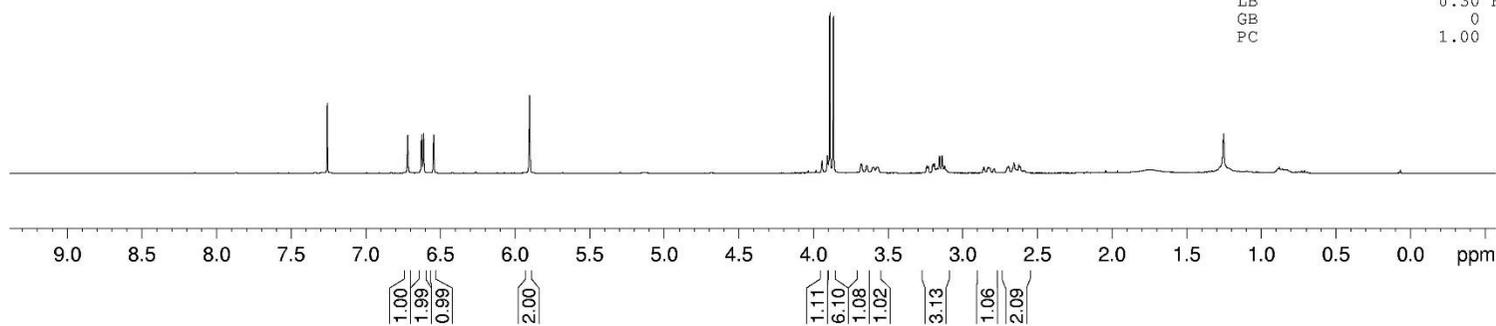
6.7214  
6.6285  
6.6151  
6.5473  
5.9052

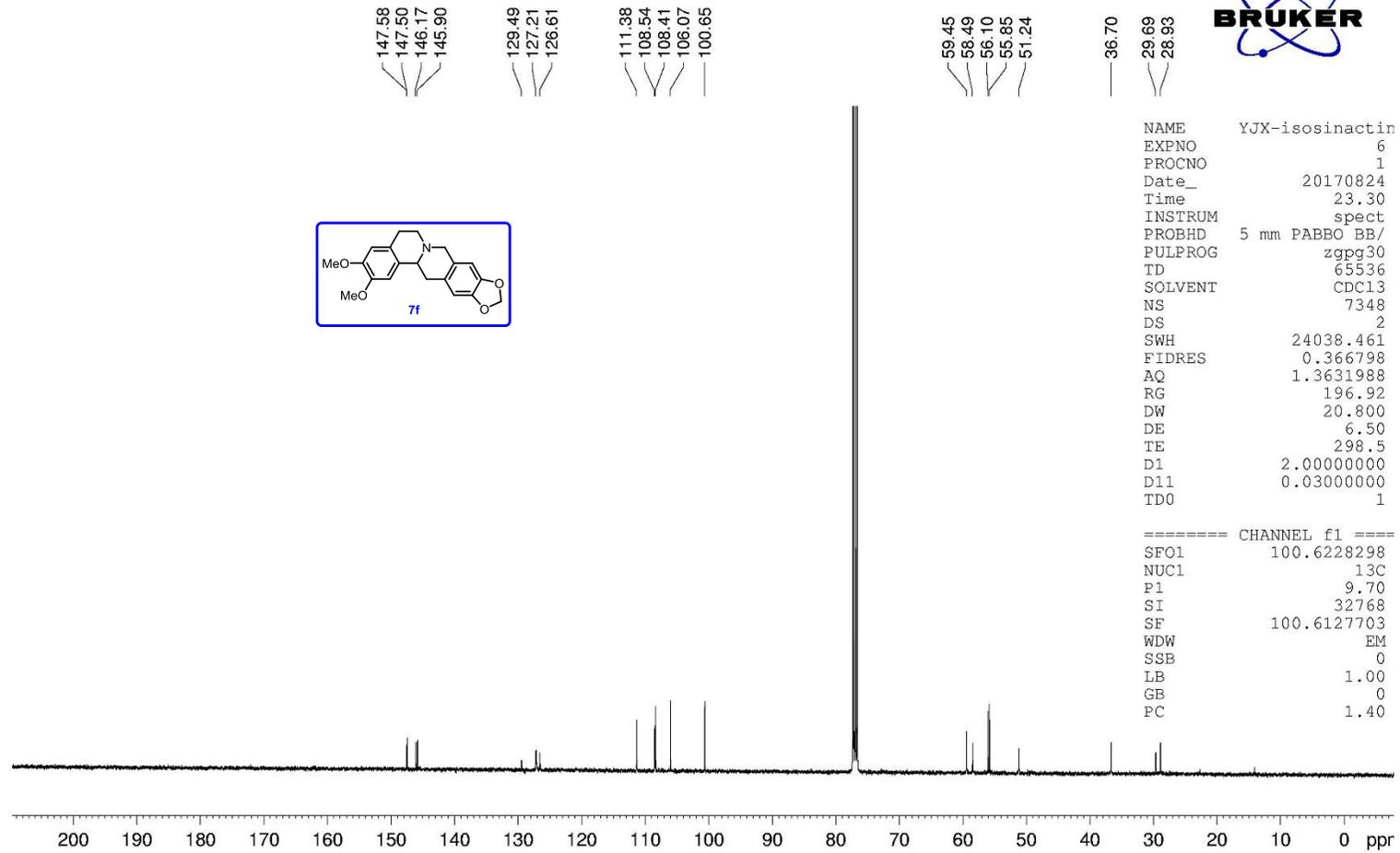
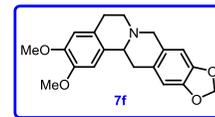
3.9452  
3.9083  
3.8926  
3.8687  
3.6819  
3.6451  
3.5980  
3.5770  
3.2429  
3.2336  
3.2029  
3.1931  
3.1720  
3.1582  
3.1402  
3.1242  
2.8605  
2.8321  
2.8229  
2.7923  
2.6947  
2.6582  
2.6253  
2.6167  
2.5918



NAME YJX-isosinactine  
EXPNO 5  
PROCNO 1  
Date\_ 20170824  
Time 23.27  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zg30  
TD 65536  
SOLVENT CDC13  
NS 18  
DS 2  
SWH 8012.820 Hz  
FIDRES 0.122266 Hz  
AQ 4.0894966 sec  
RG 187.77  
DW 62.400 usec  
DE 6.50 usec  
TE 298.1 K  
D1 1.00000000 sec  
TD0 1

==== CHANNEL f1 =====  
SFO1 400.1324710 MHz  
NUC1 1H  
P1 14.50 usec  
SI 65536  
SF 400.1300094 MHz  
WDW EM  
SSB 0  
LB 0.30 Hz  
GB 0  
PC 1.00





NAME YJX-isosinactin  
EXPNO 6  
PROCNO 1  
Date\_ 20170824  
Time 23.30  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgpg30  
TD 65536  
SOLVENT CDC13  
NS 7348  
DS 2  
SWH 24038.461  
FIDRES 0.366798  
AQ 1.3631988  
RG 196.92  
DW 20.800  
DE 6.50  
TE 298.5  
D1 2.00000000  
D11 0.03000000  
TD0 1

===== CHANNEL f1 =====  
SFO1 100.6228298  
NUC1 13C  
P1 9.70  
SI 32768  
SF 100.6127703  
WDW EM  
SSB 0  
LB 1.00  
GB 0  
PC 1.40



150.27  
147.46  
147.42  
145.06

129.72  
128.70  
127.74  
126.80  
123.88

111.33  
110.92  
108.58



60.17  
59.33  
56.07  
55.86  
55.84  
54.03  
51.54

36.37  
29.13

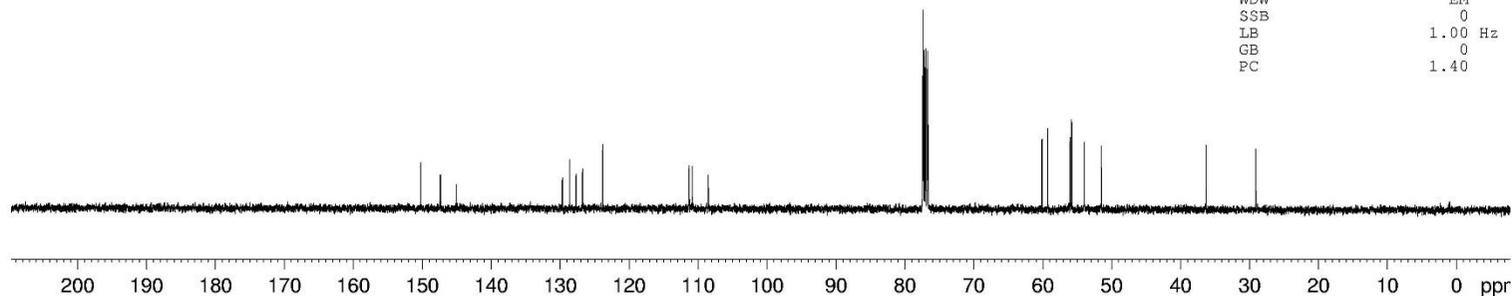


```

NAME      YJX-tetrahydropalm
EXPNO     6
PROCNO    1
Date_     20170824
Time      23.25
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         65536
SOLVENT   CDC13
NS         117
DS         2
SWH        24038.461 Hz
FIDRES     0.366798 Hz
AQ         1.3631988 sec
RG         196.92
DW         20.800 use
DE         6.50 use
TE         298.4 K
D1         2.0000000 sec
D11        0.0300000 sec
TD0        1
  
```

```

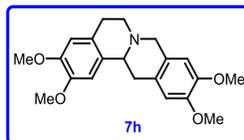
===== CHANNEL f1 =====
SF01     100.6228298 MHz
NUC1      13C
P1         9.70 use
SI         32768
SF         100.6127690 MHz
WDW        EM
SSB         0
LB         1.00 Hz
GB         0
PC         1.40
  
```





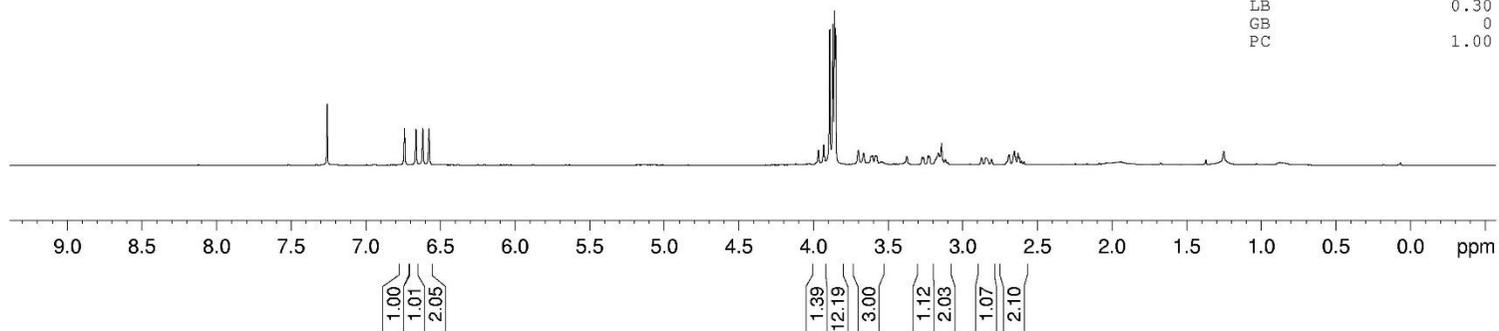
6.7428  
6.6658  
6.6203  
6.5788

3.9697  
3.9333  
3.8927  
3.8718  
3.8602  
3.8537  
3.7024  
3.6665  
3.6165  
3.6077  
3.5882  
3.5797  
3.5488  
3.2734  
3.2642  
3.2337  
3.2245  
3.1764  
3.1666  
3.1565  
3.1443  
3.1188  
3.1027  
2.8761  
2.8469  
2.8371  
2.8083  
2.6914  
2.6561  
2.6310  
2.6223  
2.6075  
2.5910



```
NAME      YJX-xylopine
EXPNO     1
PROCNO    1
Date_     20170824
Time      23.47
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zg30
TD        65536
SOLVENT   CDC13
NS        18
DS        2
SWH       8012.820 Hz
FIDRES    0.122266 Hz
AQ        4.0894966 sec
RG        196.92
DW        62.400 use
DE        6.50 use
TE        298.4 K
D1        1.00000000 sec
TD0       1
```

```
===== CHANNEL f1 =====
SFO1      400.1324710 MHz
NUC1      1H
P1        14.50 use
SI        65536
SF        400.1300089 MHz
WDW       EM
SSB       0
LB        0.30 Hz
GB        0
PC        1.00
```





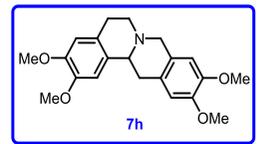
147.62  
147.48  
147.43  
147.39

129.75  
126.73  
126.32  
126.27

111.34  
109.01  
108.53

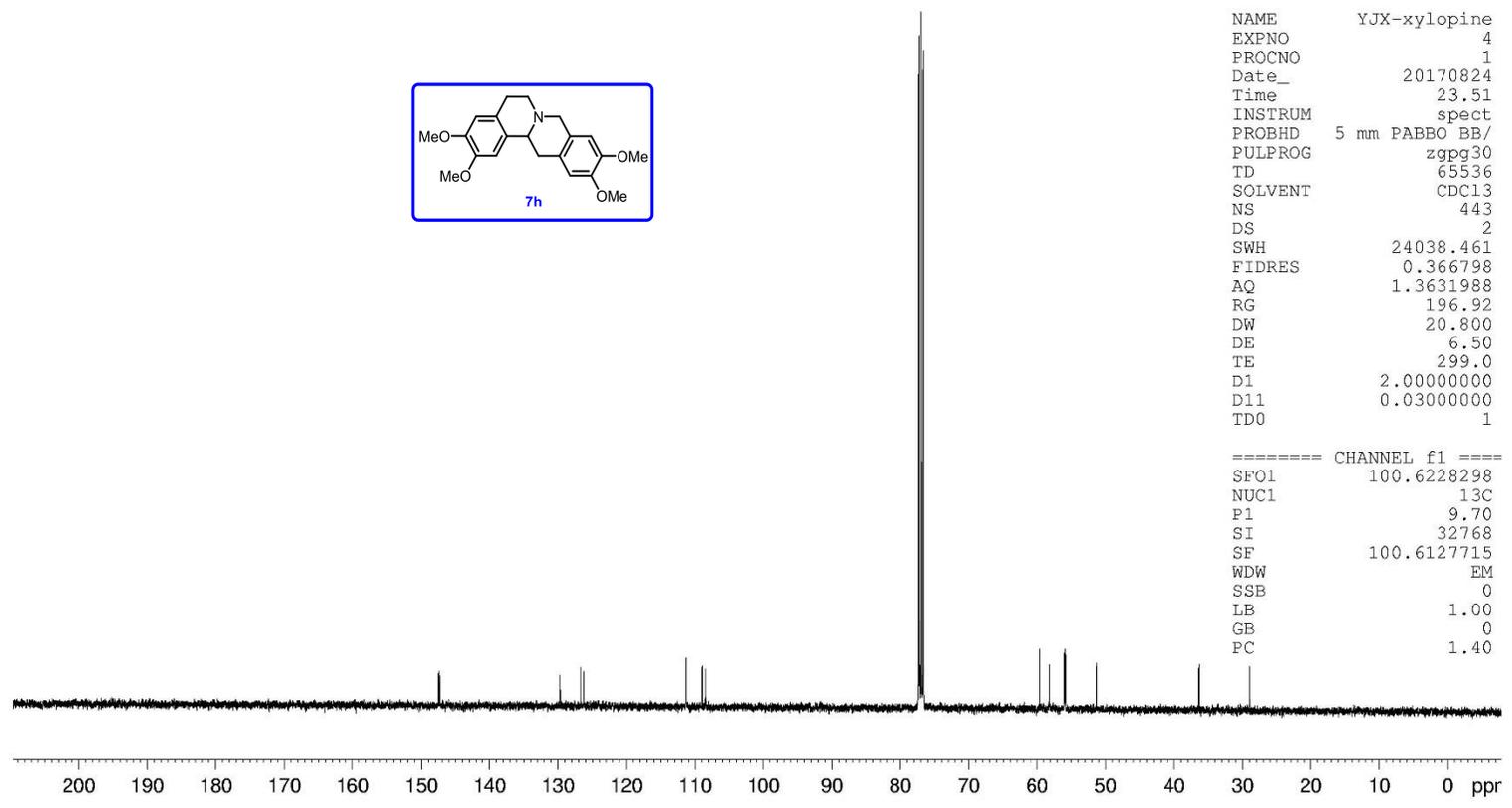
59.58  
58.21  
56.04  
55.94  
55.89  
55.83  
51.34

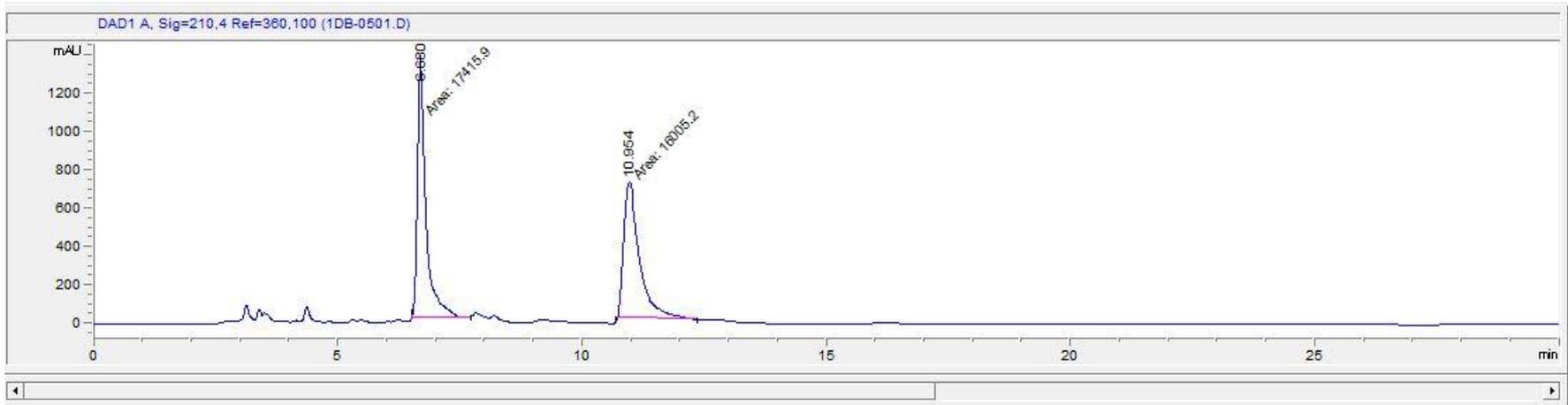
36.38  
29.03



NAME YJX-xylopine  
EXPNO 4  
PROCNO 1  
Date\_ 20170824  
Time 23.51  
INSTRUM spect  
PROBHD 5 mm PABBO BB/  
PULPROG zgpg30  
TD 65536  
SOLVENT CDC13  
NS 443  
DS 2  
SWH 24038.461  
FIDRES 0.366798  
AQ 1.3631988  
RG 196.92  
DW 20.800  
DE 6.50  
TE 299.0  
D1 2.00000000  
D11 0.03000000  
TD0 1

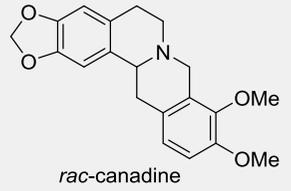
===== CHANNEL f1 =====  
SFO1 100.6228298  
NUC1 13C  
P1 9.70  
SI 32768  
SF 100.6127715  
WDW EM  
SSB 0  
LB 1.00  
GB 0  
PC 1.40

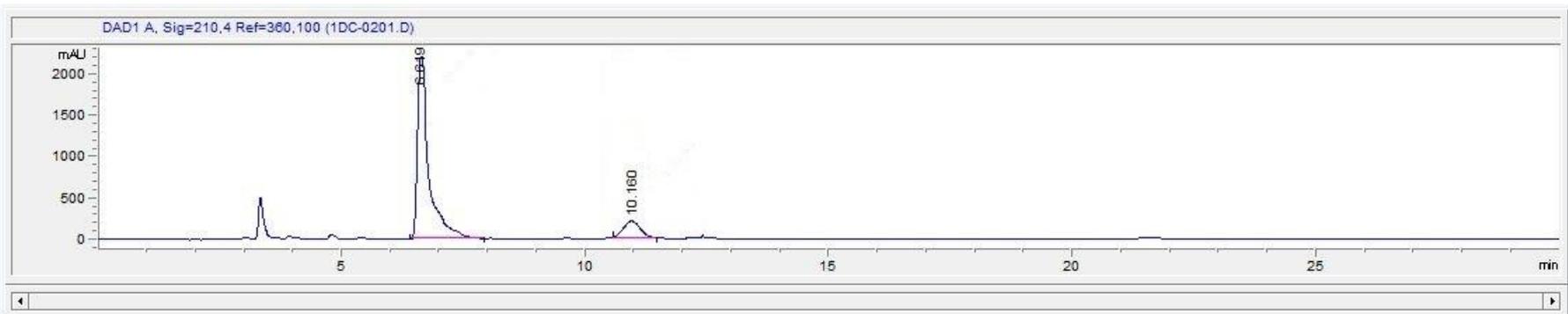




File Information	
LC-File	1DB-0501.D
File Path	C:\CHEM32\1\DATA\
Date	15-Aug-17, 03:42:35
Sample	YJX834-1-1r
Sample Info	
Barcode	
Operator	LLX
Method	AD-20-50.M
Analysis Time	50 min
Sampling Rate	0.0067 min (0.402 sec), 7501 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.68	17415.9	1366.3	0.2124	52.111	0.526
2	10.954	16005.2	710.4	0.3755	47.889	0.489





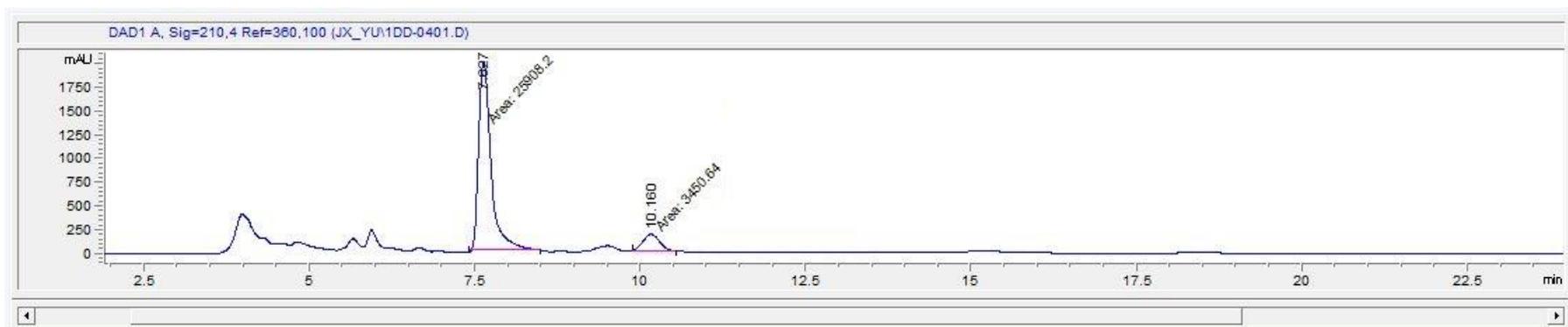
**File Information**

LC-File	1DC-0201.D
File Path	C:\CHEM32\1\DATA\
Date	15-Aug-17, 13:25:44
Sample	YJX834-1-1a
Sample Info	
Barcode	
Operator	LLX
Method	AD-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.619	36325.3	2210	0.274	89.985	0.418
2	10.74	4448.1	727.5	0.1706	11.015	0.468

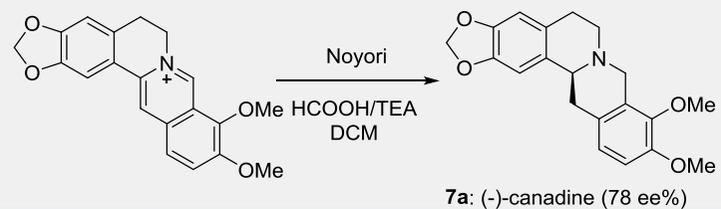
Reaction scheme showing the conversion of a starting material (a benzimidazole derivative with a furfuryl group and a 3,4-dimethoxyphenyl group) to the product **7a: (-)-canadine (77 ee%)**. The reaction is catalyzed by Noyori and uses HCOOH/TEA in DCM.

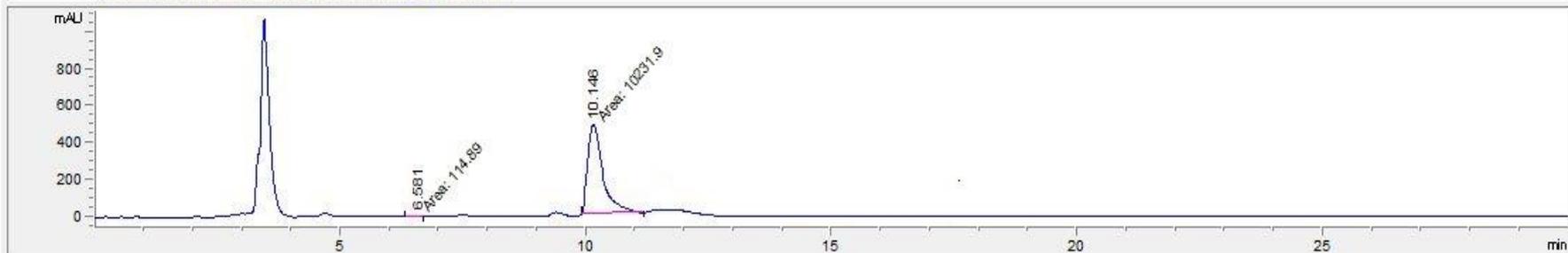


#### File Information

LC-File	1DD-0401.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	25-Aug-17, 15:07:32
Sample	YJX834-1-1sa
Sample Info	
Barcode	
Operator	YJX
Method	AD-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.627	25908.2	1983.8	0.2177	88.247	0.62
2	10.16	3450.6	184.9	0.3111	11.753	0.947

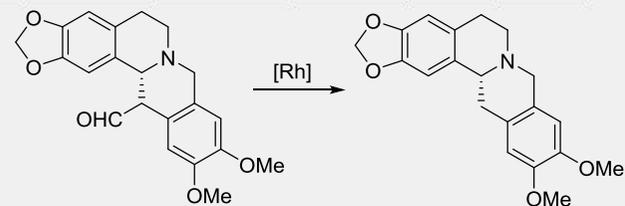




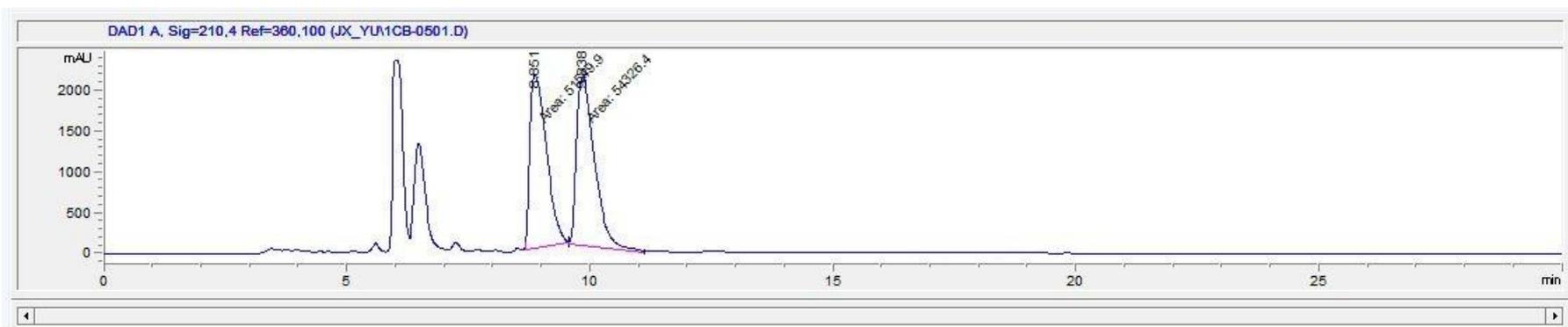
## File Information

LC-File	ZZH0000007.D
File Path	C:\CHEM32\1\DATA\ZHANG ZH\
Date	16-Aug-17, 18:58:18
Sample	zz-168-02
Sample Info	
Barcode	
Operator	ZZH
Method	AD-20-30.M
Analysis Time	30 min
Sampling Rate	0.0067 min (0.402 sec), 4501 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.581	114.9	6	0.3173	1.110	0.254
2	10.146	10231.9	482.1	0.3538	98.890	0.542



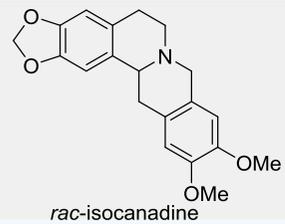
7b: (+)-isocanadine (97 ee%)

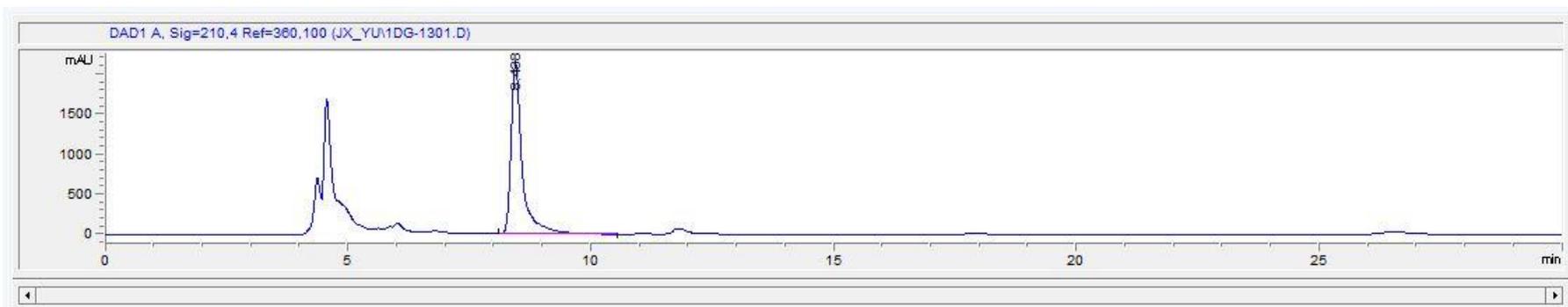


**File Information**

LC-File	1CB-0501.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	19-Aug-17, 15:54:28
Sample	YJX877-1-1r
Sample Info	
Barcode	
Operator	YJX
Method	00-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

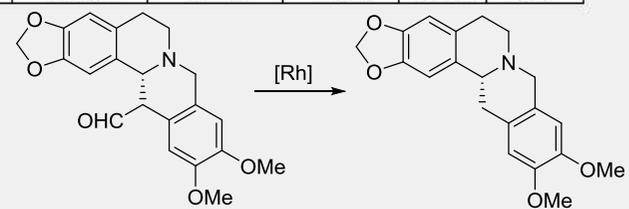
#	Time	Area	Height	Width	Area%	Symmetry
1	8.851	51549.9	2134.9	0.4024	48.689	0.419
2	9.838	54326.4	2064	0.4387	51.311	0.463



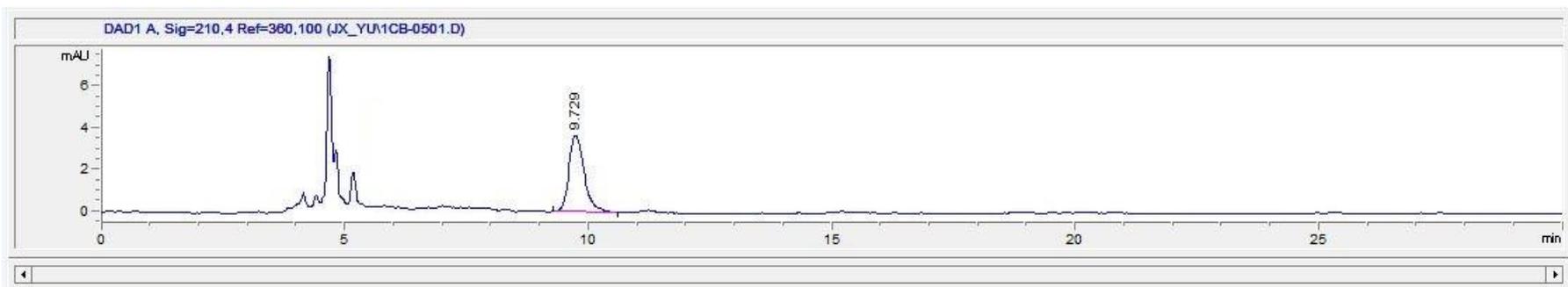


File Information	
LC-File	1DG-1301.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	22-Aug-17, 21:46:53
Sample	ZZ-06-180-01
Sample Info	
Barcode	
Operator	YJX
Method	0D-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.438	35379.9	2153.8	0.2456	100.000	0.587



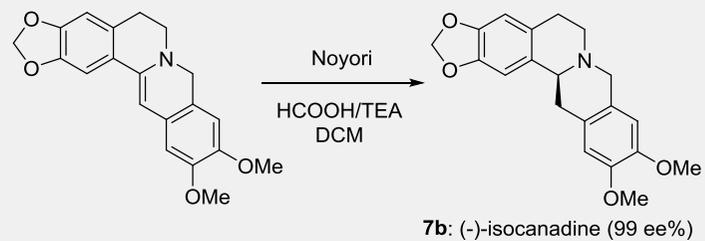
**7b: (+)-isocanadine (99 ee%)**

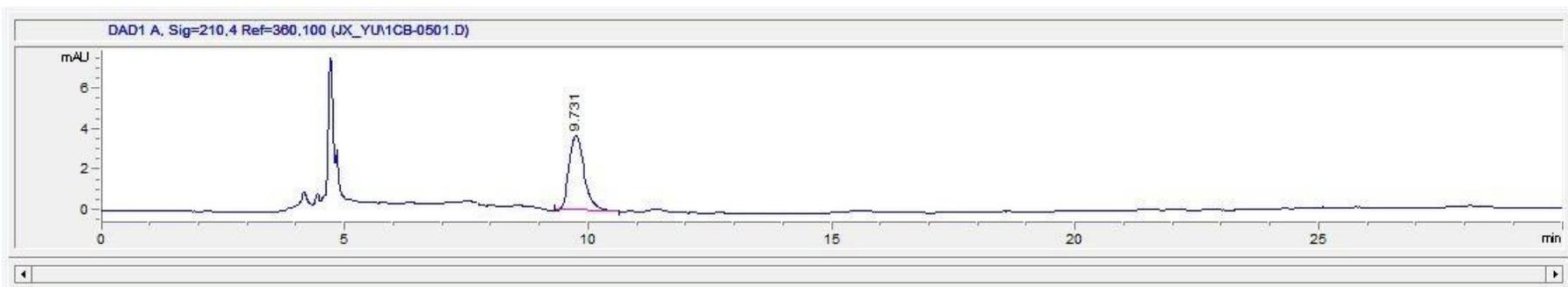


**File Information**

LC-File	1DC-0201.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	26-Aug-17, 14:00:57
Sample	YJX849-1-1
Sample Info	
Barcode	
Operator	YJX
Method	0D-20-30.M
Analysis Time	30 min
Sampling Rate	0.0067 min (0.402 sec), 4501 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.729	79.5	3.7	0.3099	100.000	0.746

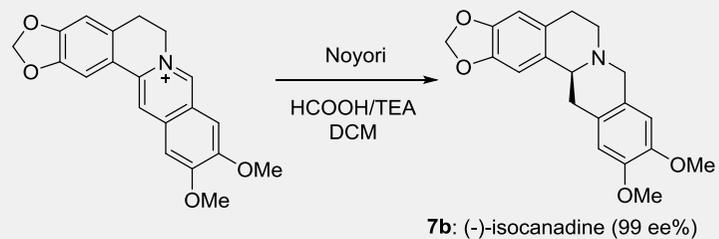


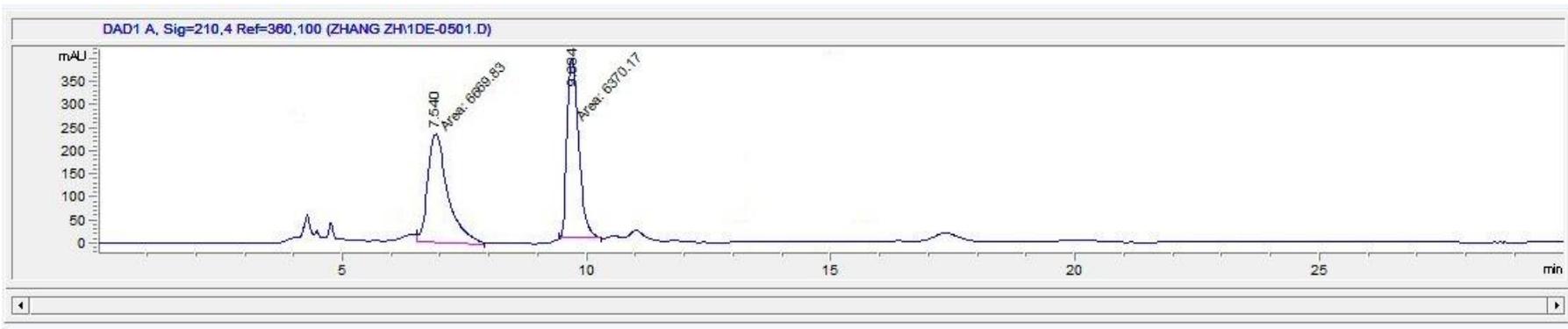


**File Information**

LC-File	1DC-0401.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	26-Aug-17, 15:02:53
Sample	YJX849-1-1sa
Sample Info	
Barcode	
Operator	YJX
Method	0D-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.731	81.6	3.7	0.3301	100.000	0.738

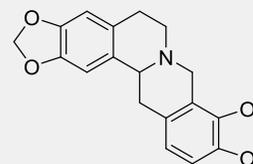




**File Information**

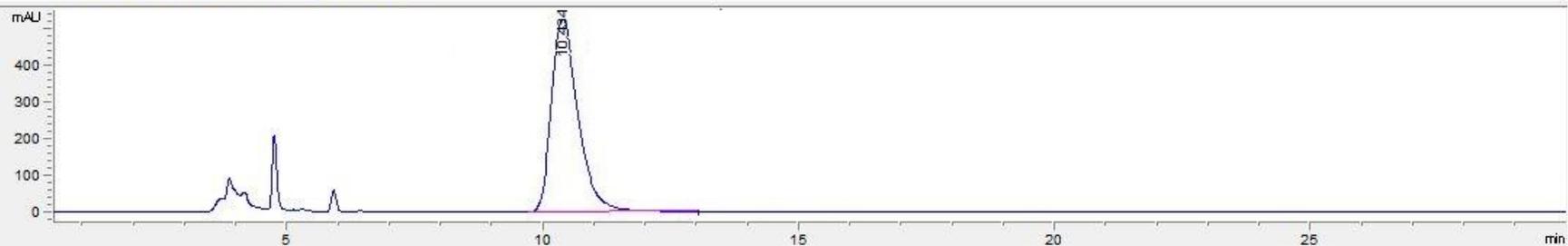
LC-File	1DE-0501.D
File Path	C:\CHEM32\1\DATA\ZHANG ZH\
Date	21-Aug-17, 22:03:41
Sample	ZZ-06-138-R
Sample Info	
Barcode	
Operator	ZZH
Method	0D-20-30.M
Analysis Time	30 min
Sampling Rate	0.0067 min (0.402 sec), 4501 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.540	6669.8	234.4	0.4743	51.149	0.678
2	9.684	6370.2	391.9	0.2709	48.851	0.59



rac-stylopine

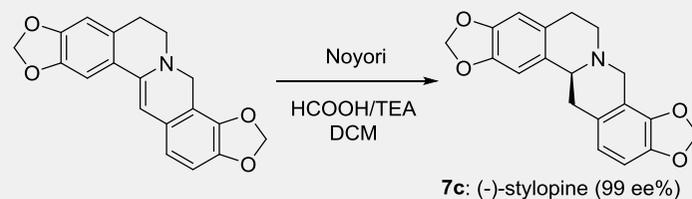
DAD1 A, Sig=210,4 Ref=360,100 (JX\_YU\1DB-0201.D)



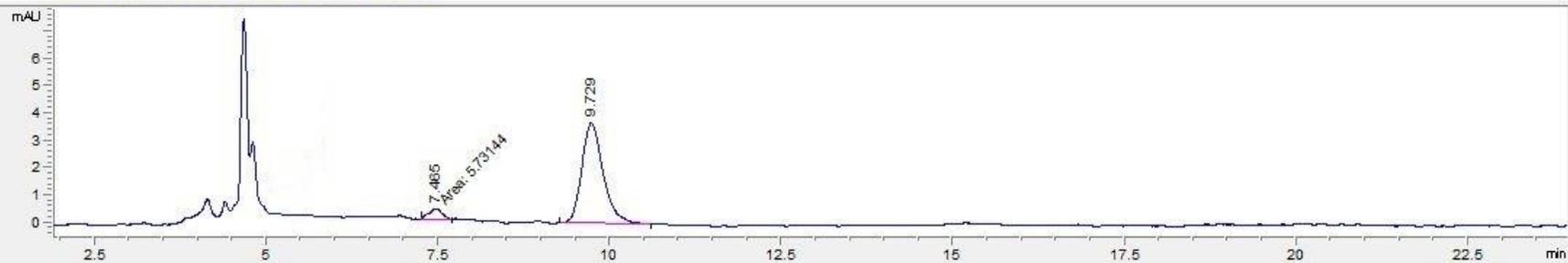
**File Information**

LC-File	1DB-0201.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	26-Aug-17, 22:59:12
Sample	YJX849-1-1a
Sample Info	
Barcode	
Operator	YJX
Method	0D-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	10.434	19234.1	528.8	0.5483	100.000	0.649



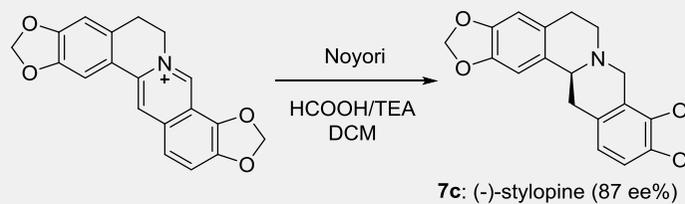
DAD1 A, Sig=210.4 Ref=360.100 (JX\_YU1CB-0501.D)

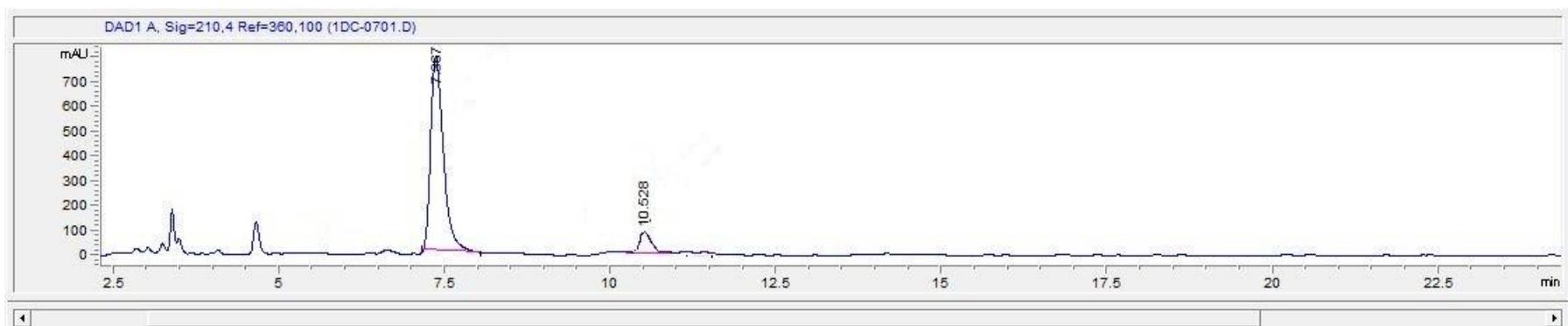


**File Information**

LC-File	1DC-0201.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	26-Aug-17, 14:00:57
Sample	YJX849-1-1
Sample Info	
Barcode	
Operator	YJX
Method	0D-20-30.M
Analysis Time	30 min
Sampling Rate	0.0067 min (0.402 sec), 4501 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.465	5.7	4.2E-1	0.2268	6.725	1.058
2	9.729	79.5	3.7	0.3099	93.275	0.746

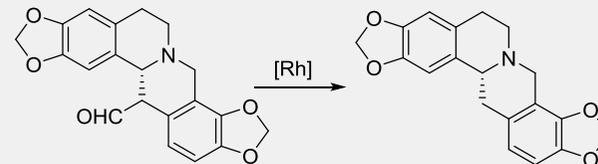




**File Information**

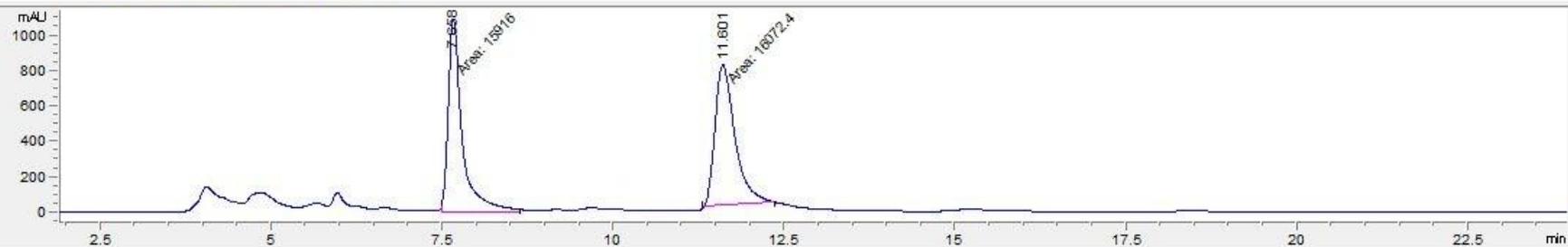
LC-File	1DC-0701.D
File Path	C:\CHEM32\1\DATA\
Date	17-Aug-17, 18:15:43
Sample	ZZ138-2
Sample Info	
Barcode	
Operator	ZZH
Method	00-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.367	10498.5	783.1	0.2235	88.466	0.657
2	10.528	1369	121.2	0.3982	11.534	0.668



**7c: (+)-stylopine (77 ee%)**

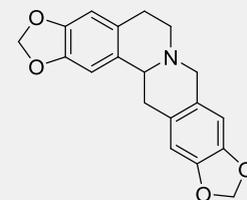
DAD1 A, Sig=210,4 Ref=360,100 (JX\_YU1DD-0201.D)



**File Information**

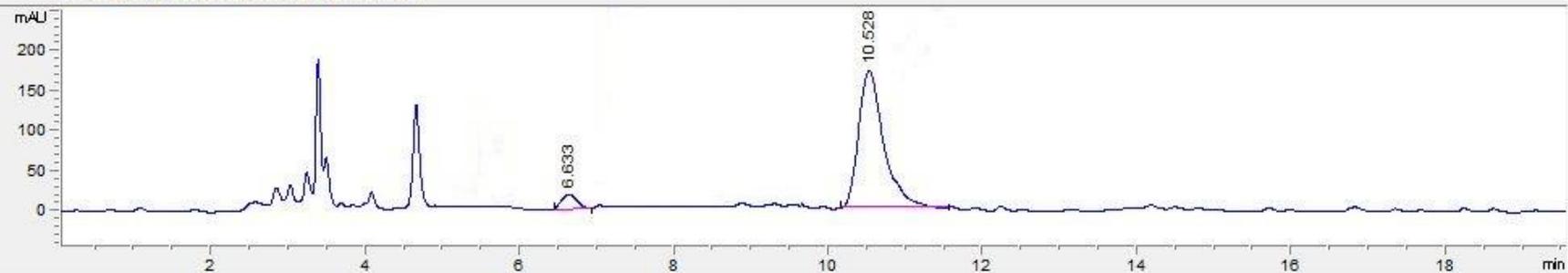
LC-File	1DD-0201.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	25-Aug-17, 14:05:36
Sample	YJX834-1-1a
Sample Info	
Barcode	
Operator	YJX
Method	AD-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.658	15916	1095.9	0.242	49.756	0.525
2	11.601	16072.4	794.2	0.3373	50.244	0.622



*rac*-tetrahydropseudocoptisine

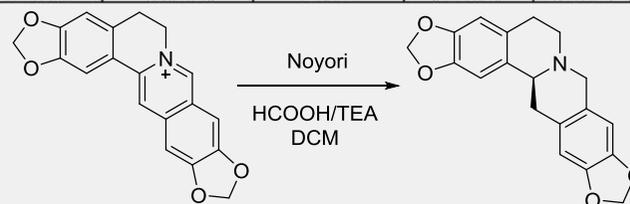
DAD1 A, Sig=210,4 Ref=360,100 (1DC-0701.D)



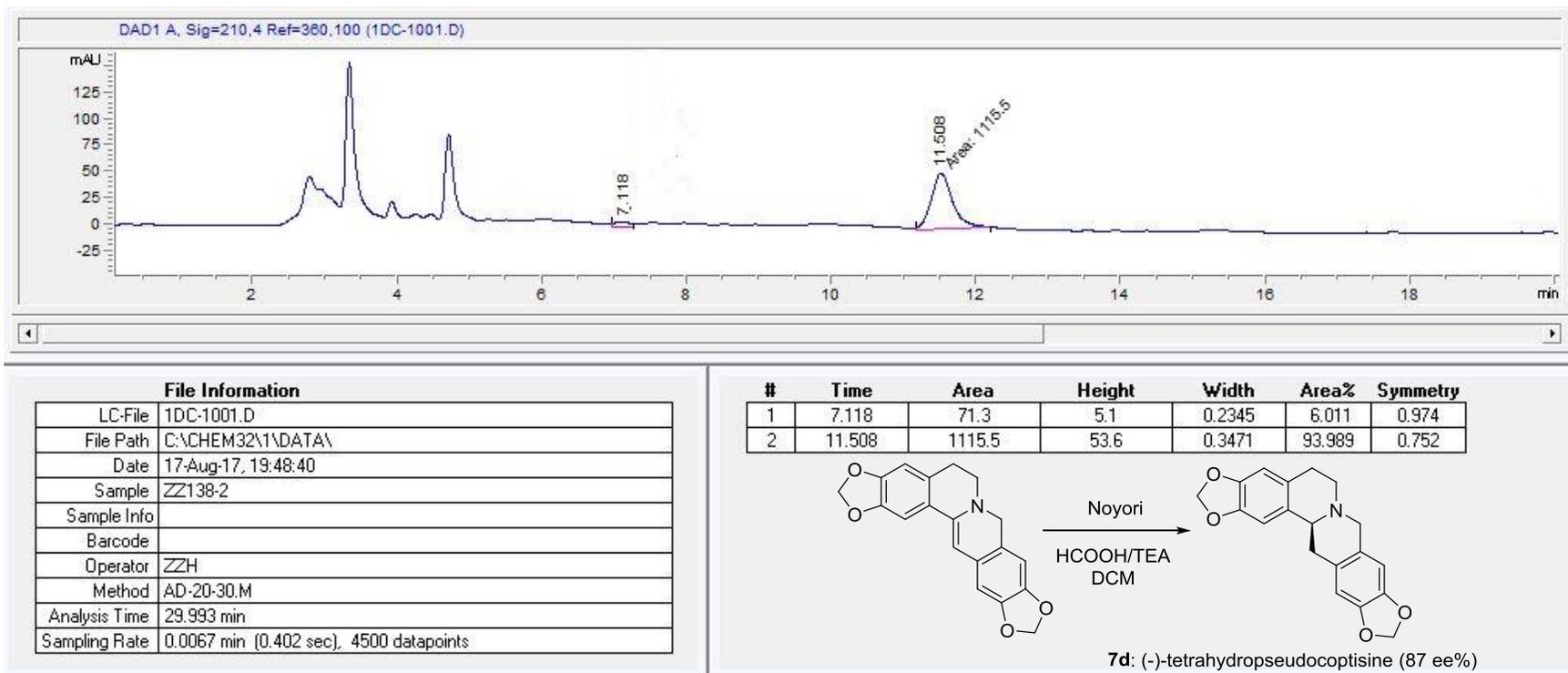
**File Information**

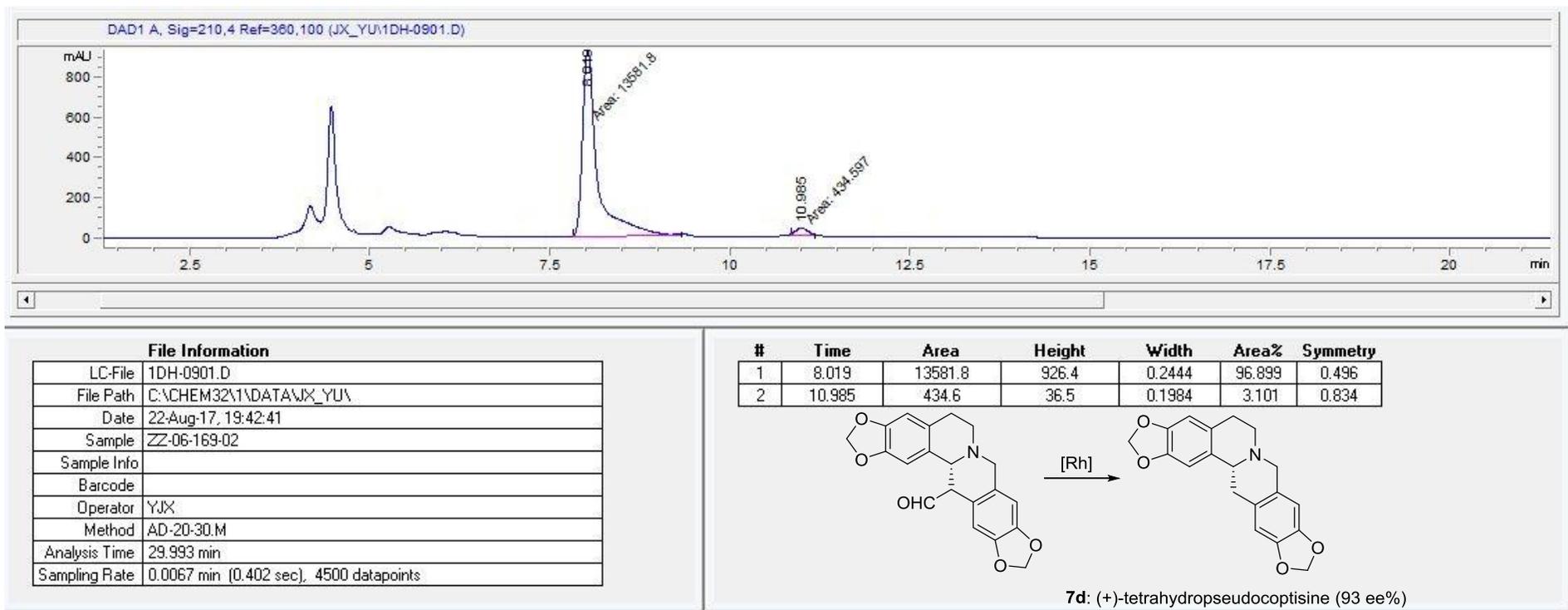
LC-File	1DC-0701.D
File Path	C:\CHEM32\1\DATA\
Date	17-Aug-17, 18:15:43
Sample	ZZ138-2
Sample Info	
Barcode	
Operator	ZZH
Method	0D-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

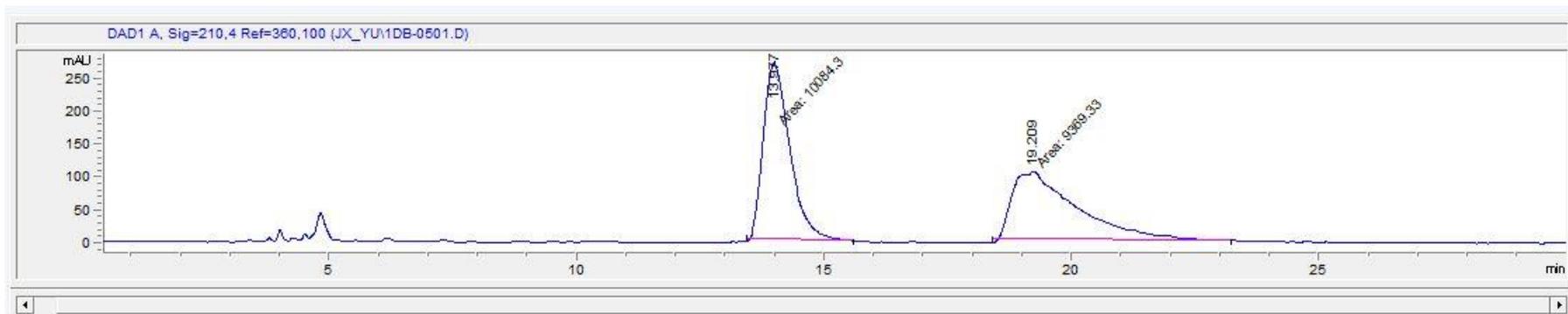
#	Time	Area	Height	Width	Area%	Symmetry
1	6.633	281.7	19.2	0.2451	6.834	0.955
2	10.528	3840.6	171.4	0.3734	93.166	0.726



**7d:** (-)-tetrahydropseudocoptisine (86 ee%)



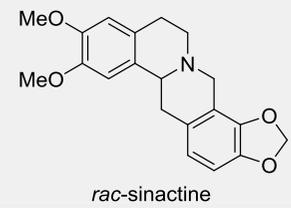


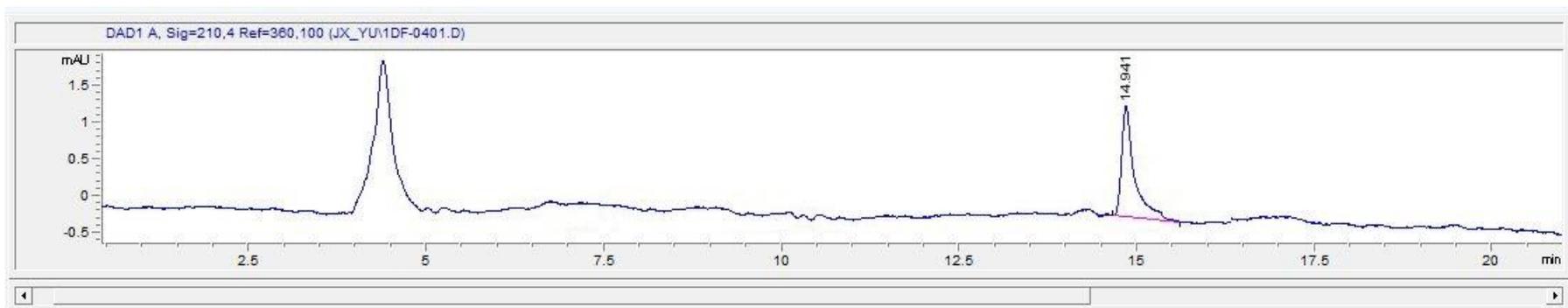


**File Information**

LC-File	1DB-0501.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	21-Aug-17, 15:59:26
Sample	YJX840-1-1r
Sample Info	
Barcode	
Operator	YJX
Method	DD-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	13.977	10084.3	270.7	0.6209	51.838	0.645
2	19.209	9369.3	104.1	1.4993	48.162	0.245

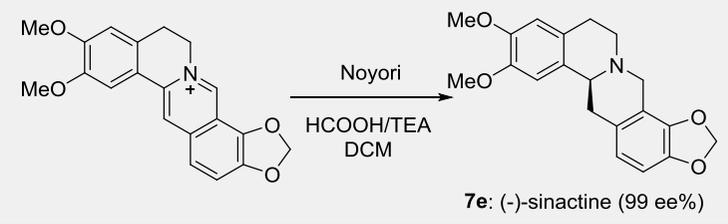


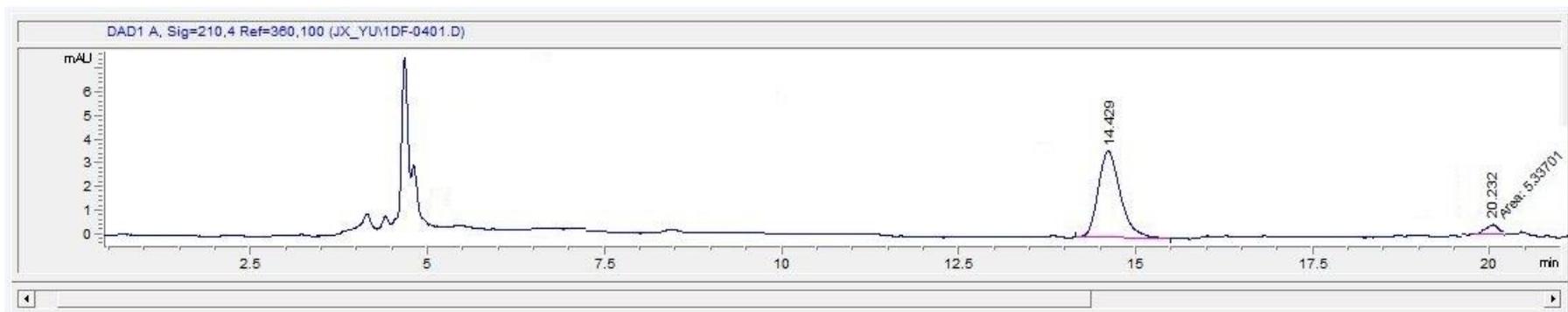


**File Information**

LC-File	1FB-0201.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	24-Aug-17, 10:43:22
Sample	YJX877-1-1a
Sample Info	
Barcode	
Operator	YJX
Method	00-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	6.241	19.4	1.5	0.18	100.000	0.45

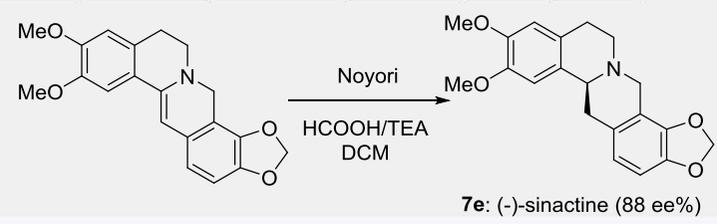


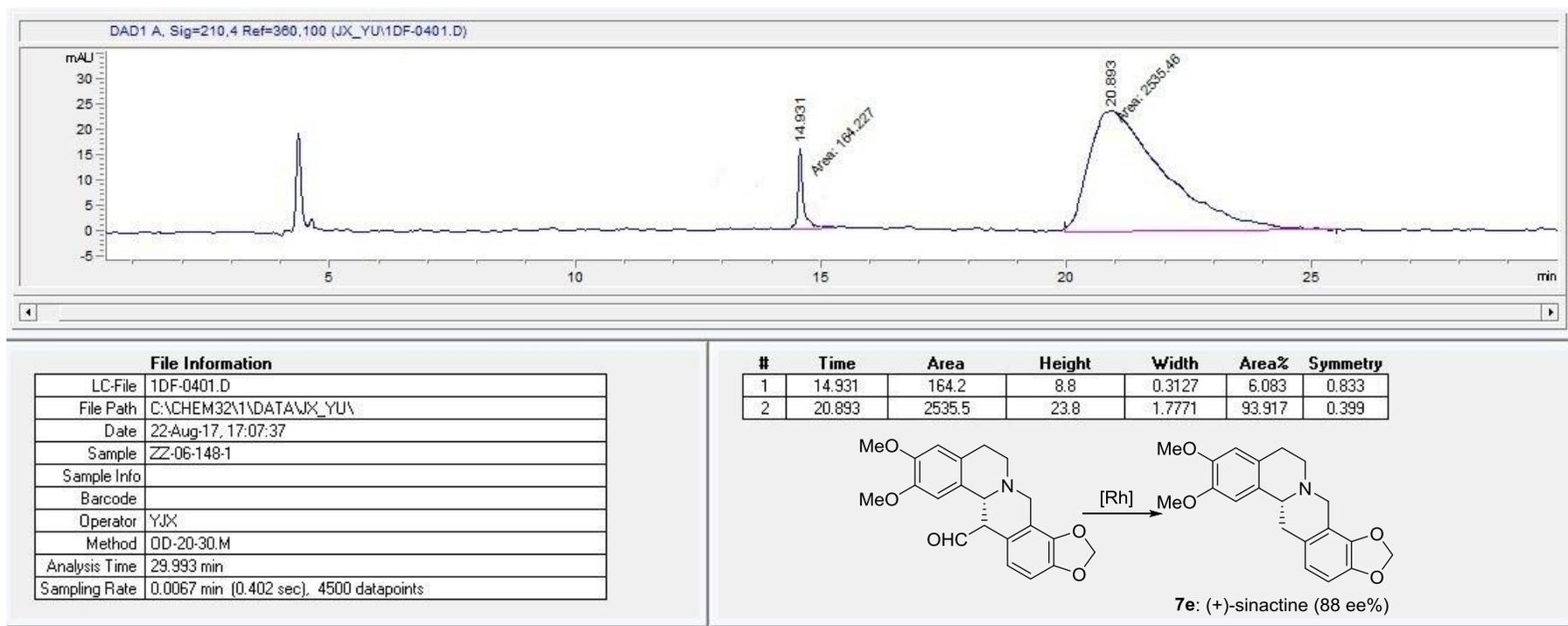


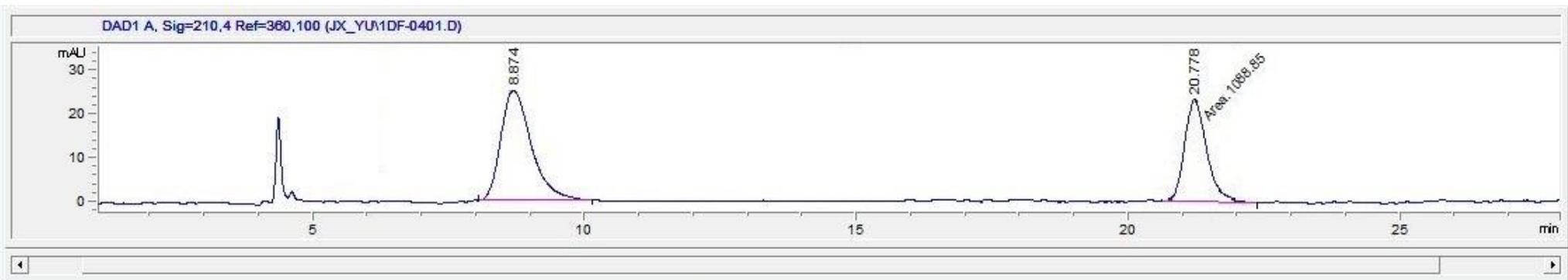
**File Information**

LC-File	1DC-0201.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	26-Aug-17, 14:00:57
Sample	YJX849-1-1
Sample Info	
Barcode	
Operator	YJX
Method	0D-20-30.M
Analysis Time	30 min
Sampling Rate	0.0067 min (0.402 sec), 4501 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	5.732	5.3	1.7	0.0508	6.291	1.387
2	9.729	79.5	3.7	0.3099	93.709	0.746



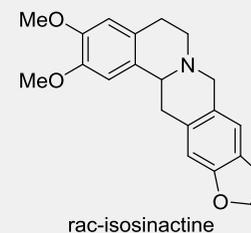


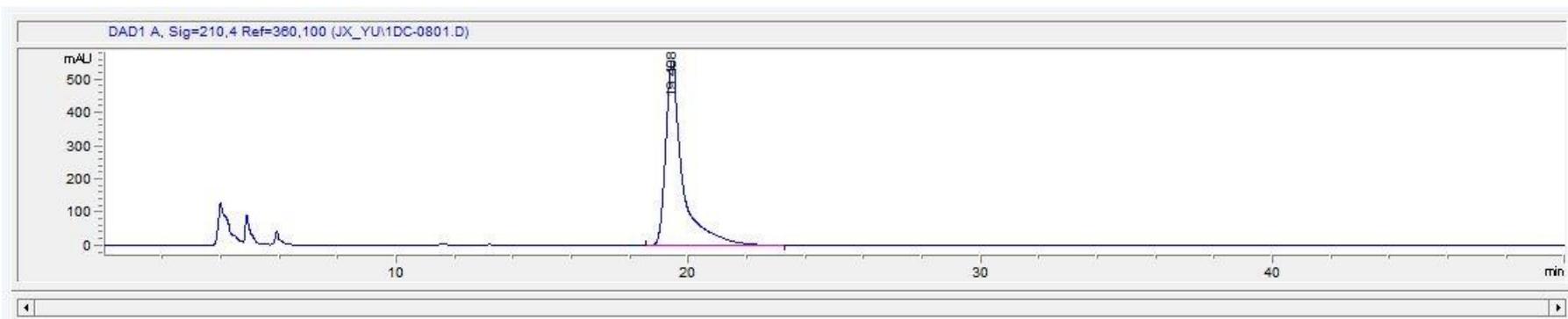


**File Information**

LC-File	1DF-0401.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	22-Aug-17, 17:07:37
Sample	ZZ-06-148-1
Sample Info	
Barcode	
Operator	YJX
Method	0D-20-30.M
Analysis Time	29.993 min
Sampling Rate	0.0067 min (0.402 sec), 4500 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	8.874	982.5	25.1	0.5722	47.432	0.666
2	20.778	1088.8	17.8	1.0181	52.568	0.468

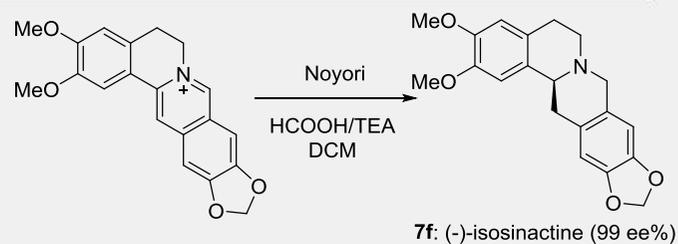


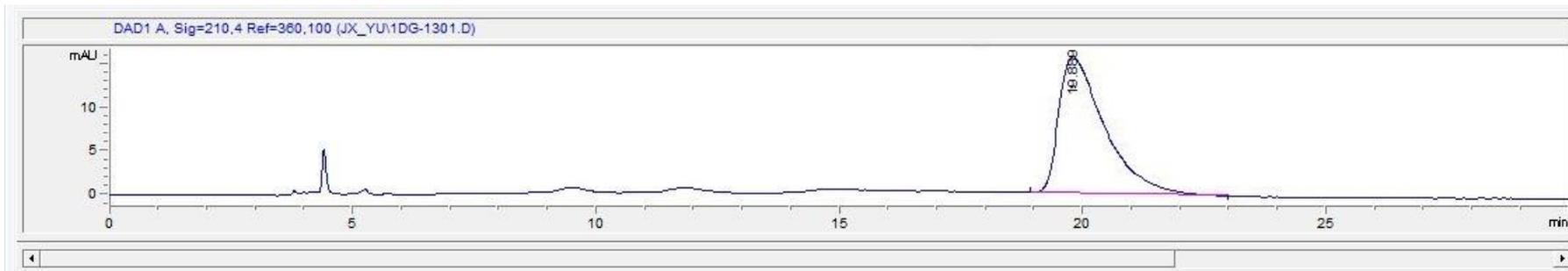


**File Information**

LC-File	1DC-0801.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	24-Aug-17, 03:07:01
Sample	YJX880-1-1a
Sample Info	
Barcode	
Operator	YJX
Method	0D-20-30.M
Analysis Time	50 min
Sampling Rate	0.0067 min (0.402 sec), 7501 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	19.408	23301.8	557.8	0.6094	100.000	0.517

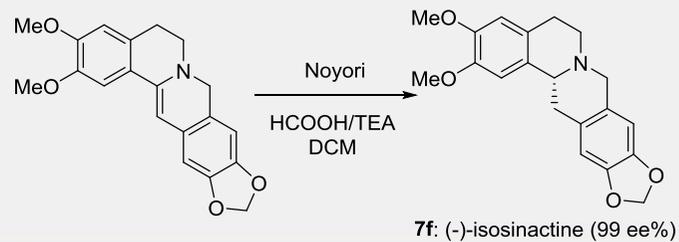


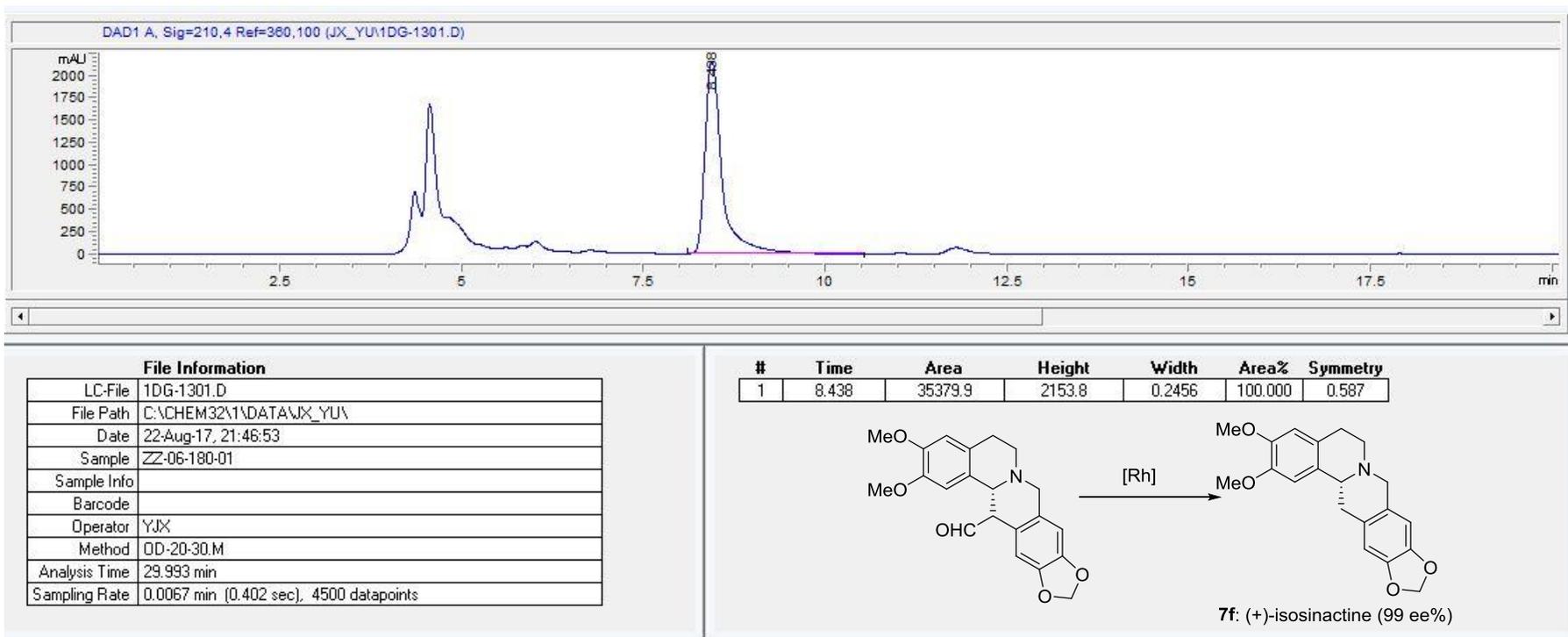


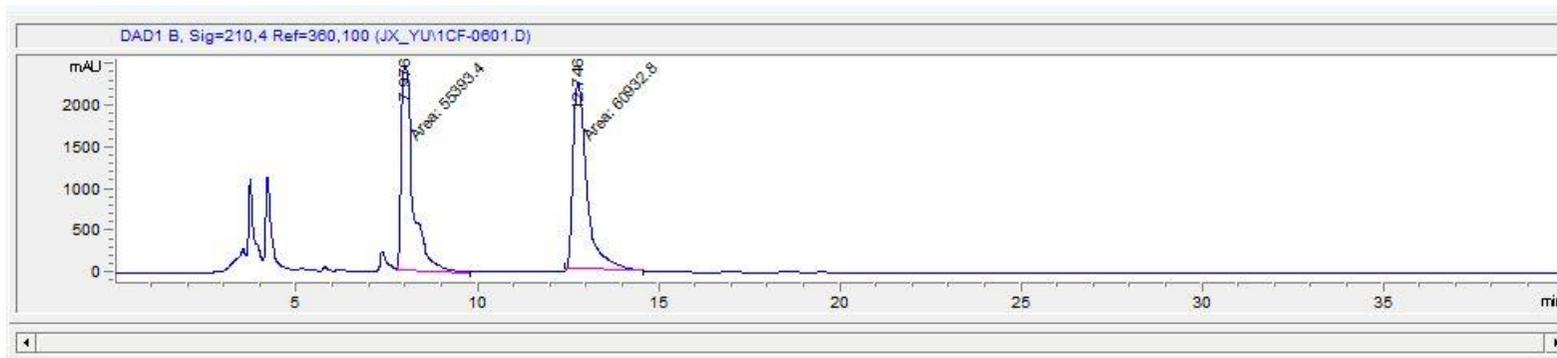
**File Information**

LC-File	1CD-0201.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	28-Aug-17, 14:59:08
Sample	YJX881-1-1r
Sample Info	
Barcode	
Operator	YJX
Method	0D-20-40.M
Analysis Time	39.993 min
Sampling Rate	0.0067 min (0.402 sec), 6000 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	19.889	1022.2	15.7	0.8899	100.000	0.418

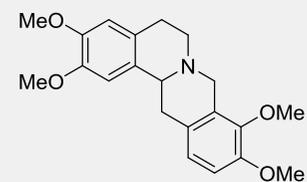




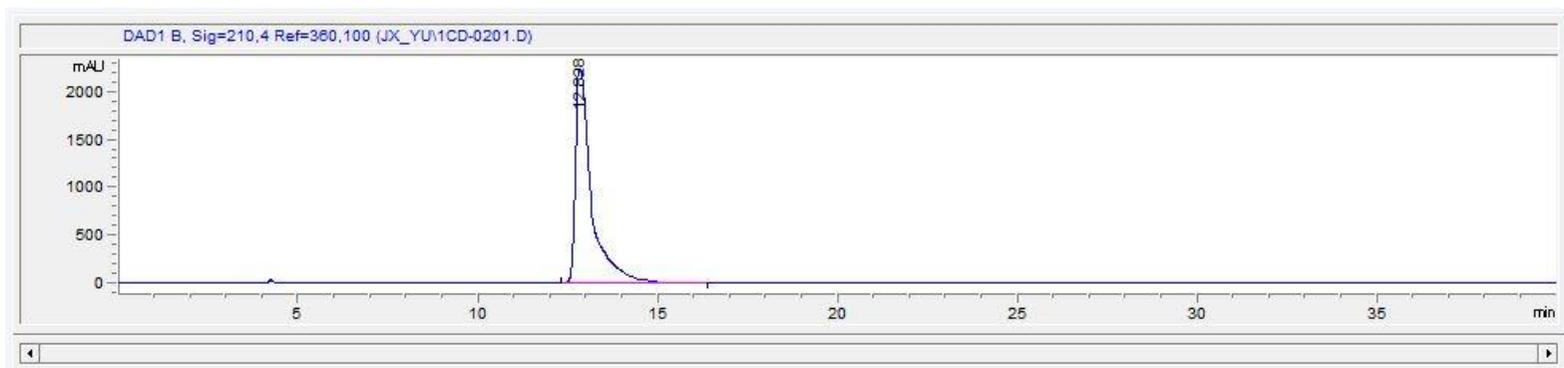


File Information	
LC-File	1CF-0601.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	29-Aug-17, 01:24:36
Sample	YJX881-1-1a
Sample Info	
Barcode	
Operator	YJX
Method	AD-20-40_(A1+B2).M
Analysis Time	39.993 min
Sampling Rate	0.0067 min (0.402 sec), 6000 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	7.976	55393.4	2425.6	0.3806	47.619	0.408
2	12.746	60932.8	2242.8	0.4528	52.381	0.517

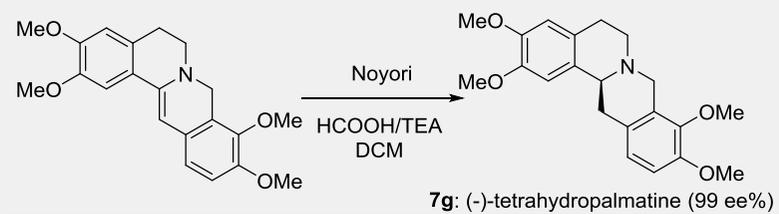


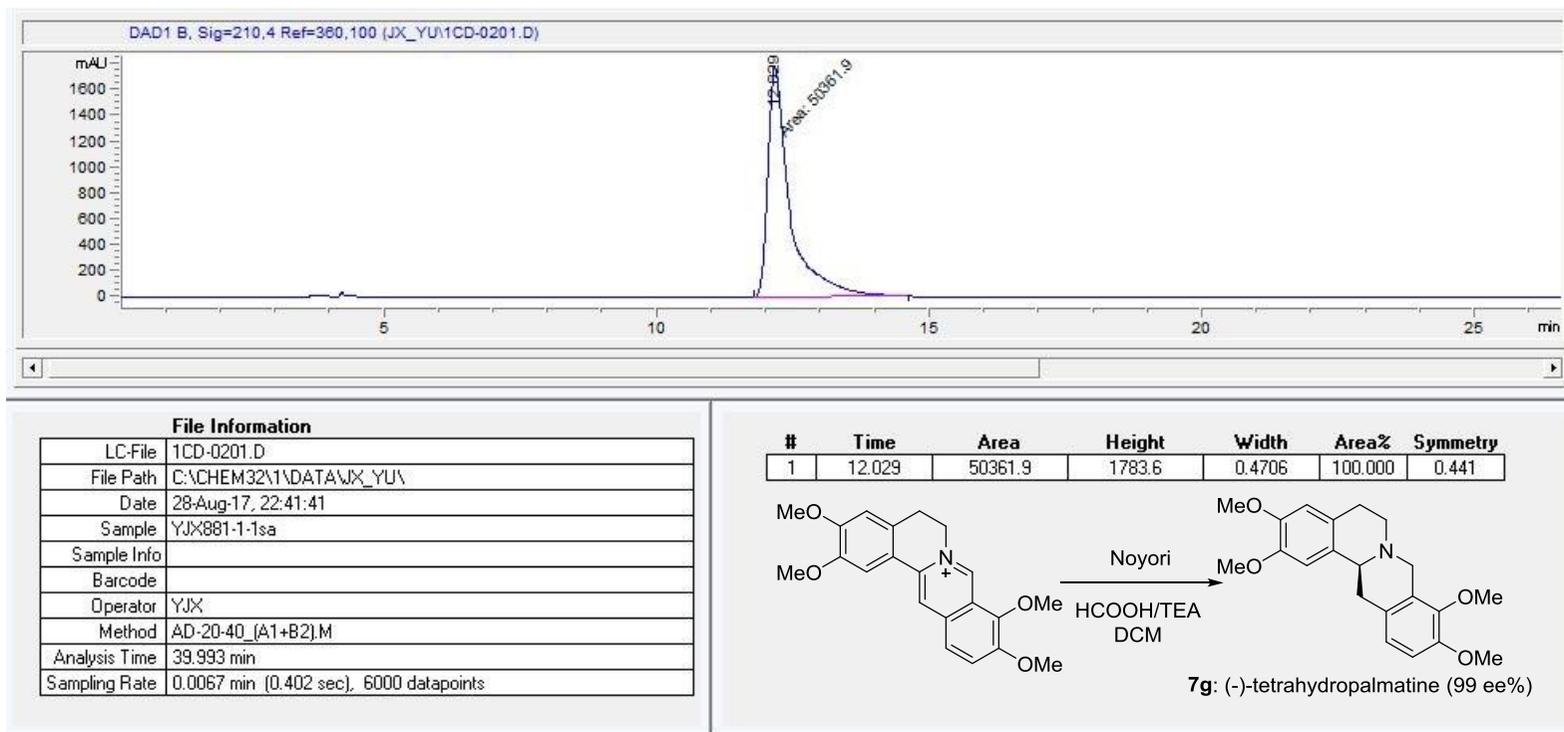
*rac*-tetrahydropalmatine



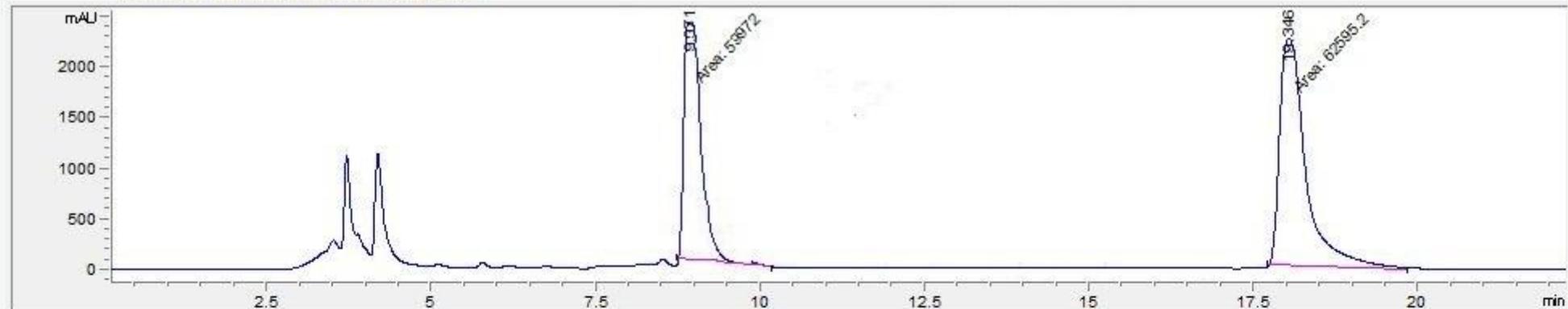
File Information	
LC-File	1CD-0201.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	28-Aug-17, 22:41:41
Sample	YJX881-1-1r
Sample Info	
Barcode	
Operator	YJX
Method	AD-20-40_(A1+B2).M
Analysis Time	39.993 min
Sampling Rate	0.0067 min (0.402 sec), 6000 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	12.828	70961.3	2245.4	0.4647	100.000	0.388





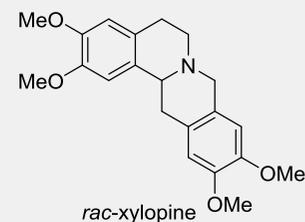
DAD1 B, Sig=210,4 Ref=360,100 (SNAPSHOT.D)

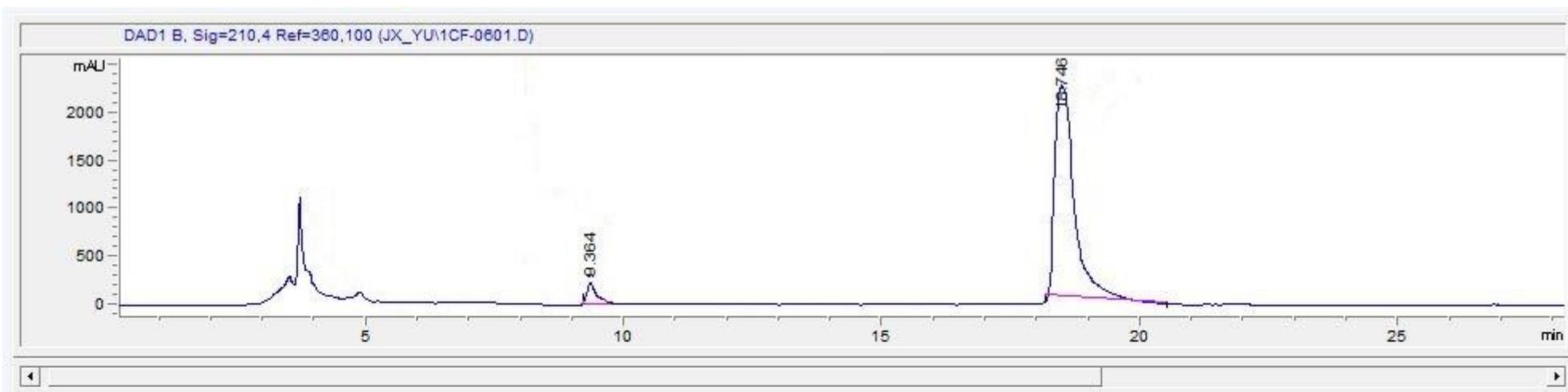


**File Information**

LC-File	SNAPSHOT.D
File Path	C:\CHEM32\1\DATA\
Date	29-Aug-17, 01:24:36
Sample	YJX882-1-1r
Sample Info	
Barcode	
Operator	YJX
Method	AD-20-40_(A1+B2).M
Analysis Time	22.887 min
Sampling Rate	0.0067 min (0.402 sec), 3434 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.071	59972	2357.3	0.3533	48.926	0.439
2	18.346	62595.2	2255.2	0.4626	51.073	0.508

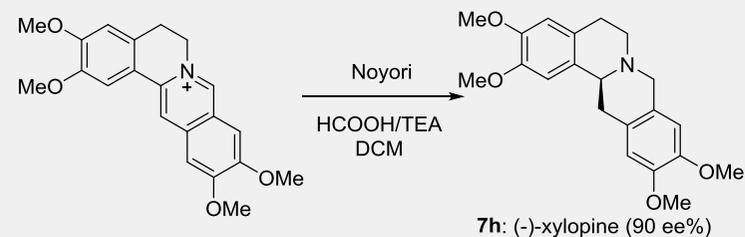


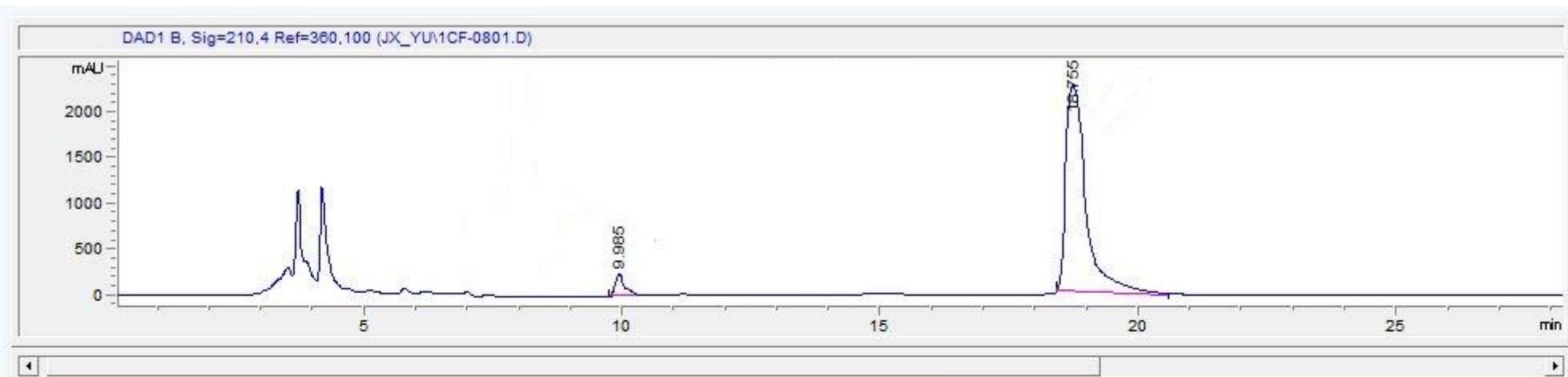


**File Information**

LC-File	1CF-0602.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	29-Aug-17, 02:34:36
Sample	YJX882-1-1a
Sample Info	
Barcode	
Operator	YJX
Method	AD-20-40_(A1+B2).M
Analysis Time	39.993 min
Sampling Rate	0.0067 min (0.402 sec), 6000 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.364	2950.3	228.9	0.2148	4.863	0.505
2	18.746	57719.6	2200.8	0.4371	95.137	0.531





**File Information**

LC-File	1CF-0802.D
File Path	C:\CHEM32\1\DATA\JX_YU\
Date	29-Aug-17, 04:17:02
Sample	YJX882-1-1sa
Sample Info	
Barcode	
Operator	YJX
Method	AD-20-40_(A1+B2).M
Analysis Time	39.993 min
Sampling Rate	0.0067 min (0.402 sec), 6000 datapoints

#	Time	Area	Height	Width	Area%	Symmetry
1	9.985	3222	238.8	0.2249	4.917	0.542
2	18.755	62306.9	2265	0.4585	95.083	0.52

