

Supporting Information
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Supporting Information for

D-Camphor-derived Triazolium Salts for Enantioselective

Intramolecular Stetter Reactions

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General Methods. Unless stated otherwise, all reactions were carried out in flame-dried glassware under argon atmosphere. All solvents were purified and dried according to standard methods prior to use.

¹H NMR spectra were obtained at 300 MHz or 400 MHz and recorded relative to tetramethylsilane signal (0 ppm) or residual protio-solvent. ¹³C NMR spectra were obtained at 75 MHz or 100 MHz, and chemical shifts were recorded relative to the solvent resonance (CDCl₃, 77.0 ppm). Data for ¹H NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant(s) in Hz, integration). Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm).

The D-Camphor-derived Triazolium Salts¹, starting material **1a-1d**², **1e-1k**³, **1l**⁴, **1m**² were prepared according to the reported procedures.

(1) Li, Y.; Feng, Z.; You, S.-L. *Chem. Commun.* **2008**, 2263.

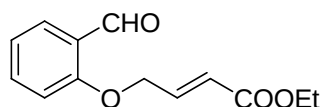
(2) Ciganek, E. *Synthesis* **1995**, 5, 1311.

(3) Han, X.; Ye, L.-W.; Sun, X.-L.; Tang, Y. *J. Org. Chem.* **2009**, 74, 3394.

(4) Nemoto, T.; Fukuda, T.; Hamada, Y. *Tetrahedron Lett.* **2006**, 47, 4365.

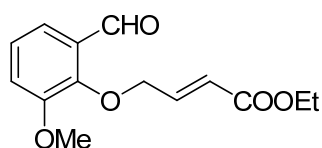
(5) Read de Alaniz, J.; Kerr, M. S.; Moore, J. L.; Rovis, T. *J. Org. Chem.* **2008**, 73, 2033.

(6) Cui, S.-L.; Wang, J.; Lin, X.-F.; Wang, Y.-G. *J. Org. Chem.* **2007**, 72, 7779.



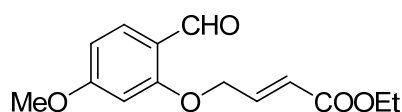
1a⁵

White solid. ¹H NMR (300 MHz, CDCl₃) δ 10.57 (s, 1H), 7.88 (d, *J* = 7.5 Hz, 1H), 7.56 (dd, *J* = 6.9, 8.7 Hz, 1H), 7.15-7.06 (m, 2H), 6.95 (d, *J* = 8.4 Hz, 1H), 6.22 (d, *J* = 15.9 Hz, 1H), 4.84 (dd, *J* = 2.1, 3.9 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).



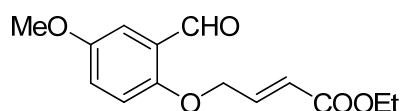
1b⁵

White solid. ¹H NMR (300 MHz, CDCl₃) δ 10.44 (s, 1H), 7.44 (dd, *J* = 4.2, 4.8 Hz, 1H), 7.17 (d, *J* = 4.5 Hz, 2H), 7.09 (dt, *J* = 4.5, 15.9 Hz, 1H), 6.24 (dt, *J* = 1.5, 15.6 Hz, 1H), 4.83 (dd, *J* = 1.5, 4.2 Hz, 2H), 4.23 (q, *J* = 6.9 Hz, 2H), 3.91 (s, 3H), 1.31 (t, *J* = 6.9 Hz, 3H).



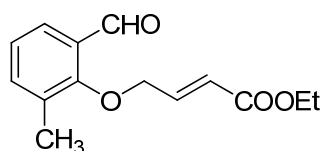
1c⁵

Yellow solid. ¹H NMR (300 MHz, CDCl₃) δ 10.33 (s, 1H), 7.85 (d, *J* = 9.0 Hz, 1H), 6.68 (dd, *J* = 1.5, 8.7 Hz, 1H), 6.57 (d, *J* = 5.7 Hz, 1H), 6.52 (d, *J* = 2.1 Hz, 1H), 5.25 (dd, *J* = 6.3, 12.9 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.87 (s, 3H), 3.31 (d, *J* = 7.2 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H).



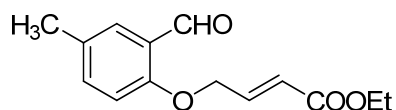
1d⁵

White solid. ¹H NMR (300 MHz, CDCl₃) δ 10.53 (s, 1H), 7.36 (d, *J* = 3.0 Hz, 1H), 7.12-7.06 (m, 2H), 6.90 (d, *J* = 9.3 Hz, 1H), 6.20 (dt, *J* = 2.1, 15.6 Hz, 1H), 4.79 (dd, *J* = 2.1, 3.9 Hz, 2H), 4.23 (q, *J* = 6.9 Hz, 2H), 3.82 (s, 3H), 1.31 (t, *J* = 6.9 Hz, 3H).



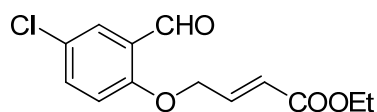
1e⁵

White solid. ¹H NMR (300 MHz, CDCl₃) δ 10.33 (s, 1H), 7.70 (d, *J* = 7.5 Hz, 1H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.09 (dt, *J* = 4.2, 15.6 Hz, 1H), 6.34 (d, *J* = 15.6 Hz, 1H), 4.62 (dd, *J* = 1.8, 3.9 Hz, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H).



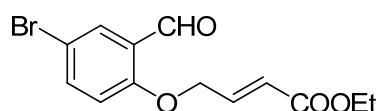
1f⁵

White solid. ¹H NMR (300 MHz, CDCl₃) δ 10.53 (s, 1H), 7.67 (s, 1H), 7.35 (d, *J* = 8.4 Hz, 1H), 7.10 (dt, *J* = 4.2, 15.6 Hz, 1H), 6.84 (d, *J* = 8.7 Hz, 1H), 6.21 (dd, *J* = 2.1, 15.9 Hz, 2H), 4.81 (dd, *J* = 1.8, 3.6 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.33 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H).



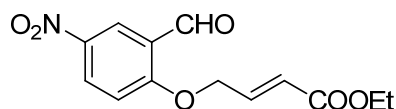
1g⁵

White solid. ¹H NMR (300 MHz, CDCl₃) δ 10.49 (s, 1H), 7.82 (d, *J* = 2.4 Hz, 1H), 7.49 (dd, *J* = 2.4, 9.0 Hz, 1H), 7.08 (dt, *J* = 4.5, 15.9 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.19 (dt, *J* = 1.8, 15.9 Hz, 1H), 4.83 (dd, *J* = 1.8, 3.9 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H).



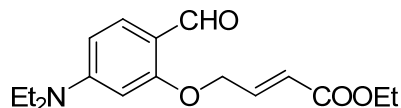
1h⁵

White solid. ¹H NMR (300 MHz, CDCl₃) δ 10.47 (s, 1H), 7.96 (d, *J* = 2.4 Hz, 1H), 7.63 (dd, *J* = 2.4, 8.7 Hz, 1H), 7.09 (dt, *J* = 4.5, 15.3 Hz, 1H), 6.85 (d, *J* = 8.7 Hz, 1H), 6.19 (d, *J* = 15.6 Hz, 1H), 4.83 (dd, *J* = 2.1, 4.2 Hz, 2H), 4.23 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H).



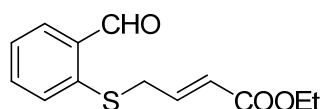
1i

White solid. ^1H NMR (400 MHz, CDCl_3) δ 10.53 (s, 1H), 8.71 (d, $J = 2.8$ Hz, 1H), 8.43 (dd, $J = 3.2, 9.2$ Hz, 1H), 7.13 (t, $J = 4.4$ Hz, 1H), 7.11-7.08 (m, 1H), 6.22 (dt, $J = 2.0, 16.0$ Hz, 1H), 5.00 (dd, $J = 2.0, 4.4$ Hz, 2H), 4.25 (q, $J = 7.2$ Hz, 2H), 1.32 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 186.9, 165.3, 163.7, 142.0, 139.3, 130.5, 124.9, 124.8, 123.5, 113.1, 67.8, 60.9, 14.1. IR (thin film): ν_{max} (cm^{-1}) = 3080, 2966, 2903, 1694, 1588, 1524, 1368, 1342, 1273, 1193, 1025, 945, 749, 676; MS (EI, m/z , rel. intensity) 233 (24), 206 (33), 85 (100); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_6$ (M^+): 279.0743. Found: 279.0747; m.p. 71-73 $^\circ\text{C}$.



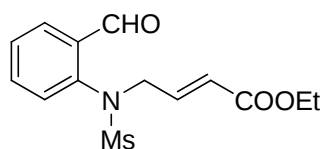
1j⁵

Orange solid. ^1H NMR (300 MHz, CDCl_3) δ 10.22 (s, 1H), 7.73 (d, $J = 9.0$ Hz, 1H), 7.11 (dt, $J = 3.9, 15.9$ Hz, 1H), 6.31 (d, $J = 10.2$ Hz, 1H), 6.25 (d, $J = 15.9$ Hz, 1H), 5.97 (d, $J = 1.8$ Hz, 1H), 4.79 (dd, $J = 2.1, 6.9$ Hz, 2H), 4.22 (q, $J = 7.2$ Hz, 2H), 3.41 (q, $J = 7.2$ Hz, 4H), 1.31 (t, $J = 7.2$ Hz, 3H), 1.21 (t, $J = 7.2$ Hz, 6H).



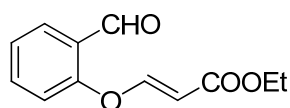
1k

Yellow oil. ^1H NMR (300 MHz, CDCl_3) δ 10.31 (s, 1H), 7.83 (d, $J = 7.5$ Hz, 1H), 7.52 (t, $J = 8.1$ Hz, 1H), 7.39-7.31 (m, 2H), 6.97 (dt, $J = 6.9, 15.6$ Hz, 1H), 5.94 (d, $J = 15.6$ Hz, 1H), 4.15 (q, $J = 7.2$ Hz, 2H), 3.70 (d, $J = 6.6$ Hz, 2H), 1.25 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 191.1, 165.3, 141.4, 139.3, 133.8, 133.7, 132.3, 128.3, 125.7, 123.9, 60.2, 33.9, 13.9. IR (thin film): ν_{max} (cm^{-1}) = 3061, 2981, 2848, 2742, 1716, 1652, 1587, 1461, 1368, 1317, 1267, 1198, 1041, 978, 754, 679; MS (EI, m/z , rel. intensity) 250 (M^+ , 2), 137 (100); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{14}\text{O}_3\text{S}$ (M^+): 250.0664. Found: 250.0663.



1l⁴

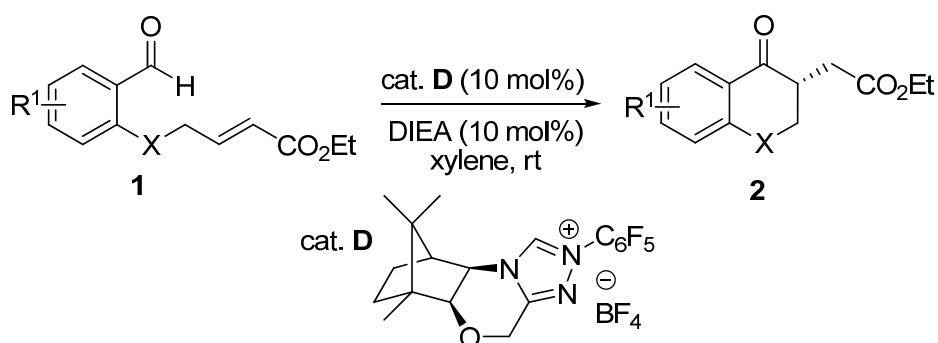
Yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 10.30 (s, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 7.69 (t, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.8 Hz, 1H), 6.86 (dt, *J* = 6.9, 15.6 Hz, 1H), 5.90 (d, *J* = 15.6 Hz, 1H), 4.46 (d, *J* = 6.6 Hz, 2H), 4.16 (q, *J* = 6.9 Hz, 2H), 2.98 (s, 3H), 1.26 (t, *J* = 6.9 Hz, 3H).



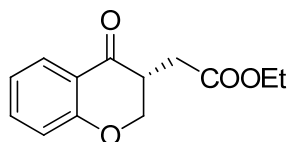
1m⁶

Yellow oil. ¹H NMR (300 MHz, CDCl₃) δ 10.37 (s, 1H), 7.93 (dd, *J* = 1.8, 7.8 Hz, 1H), 7.85 (d, *J* = 12.3 Hz, 1H), 7.69-7.63 (m, 1H), 7.33 (t, *J* = 7.5 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 1H), 5.64 (d, *J* = 12.0 Hz, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 1.30 (t, *J* = 7.2 Hz, 3H).

General Procedure for Enantioselective Intramolecular Stetter Reactions:

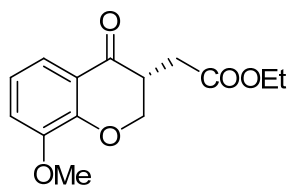


A flame dried Schlenk tube was cooled to room temperature and filled with argon. To this tube were added triazolium salt **D** (4.9 mg, 0.01 mmol, 10 mol%) and xylene (0.3 mL). Then to this solution was added DIEA (2.1 μL, 0.01 mmol, 10 mol%) and xylene (0.2 mL), and the solution was stirred at room temperature for 20 minutes. The substrate **1** (0.1 mmol) and xylene (0.5 mL) were then added. After the reaction was complete (monitored by TLC), the reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford the product **2**.



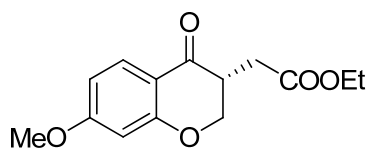
2a⁵

Yellow oil, 94% yield, 96% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 97/3, ν = 0.7 mL · min⁻¹, λ = 254 nm, t (major) = 20.43 min, t (minor) = 29.49 min]; $[\alpha]_D^{20}$ = -15.8 (c = 1.0, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃) δ 7.89 (dd, J = 1.5, 7.8 Hz, 1H), 7.51-7.45 (m, 1H), 7.05-6.96 (m, 2H), 4.60 (dd, J = 5.4, 11.1 Hz, 1H), 4.30 (t, J = 11.7 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.39-3.29 (m, 1H), 2.93 (dd, J = 4.8, 16.8 Hz, 1H), 2.42 (dd, J = 8.1, 17.1 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H).



2b⁵

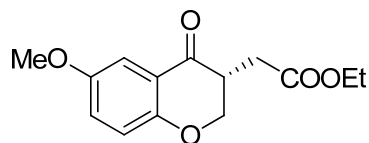
Yellow oil, 95% yield, 96% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 90/10, ν = 1.0 mL · min⁻¹, λ = 254 nm, t (major) = 15.94 min, t (minor) = 21.75 min]; $[\alpha]_D^{20}$ = -40.7 (c = 1.0, CH₂Cl₂). ¹H NMR (300 MHz, CDCl₃) δ 7.49 (dd, J = 1.5, 8.1 Hz, 1H), 7.07 (dd, J = 1.2, 8.1 Hz, 1H), 6.98 (t, J = 8.1 Hz, 1H), 4.71 (dd, J = 5.4, 11.4 Hz, 1H), 4.38 (t, J = 11.7 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.92 (s, 3H), 3.41-3.31 (m, 1H), 2.91 (dd, J = 5.1, 16.8 Hz, 1H), 2.45 (dd, J = 8.1, 17.1 Hz, 1H), 1.28 (t, J = 7.2 Hz, 3H).



2c⁵

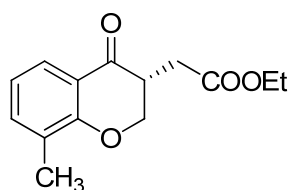
Yellow oil, 89% yield, 97% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 95/5, ν = 1.0 mL · min⁻¹, λ = 254 nm, t (major) = 22.00 min, t (minor) = 28.04 min]; $[\alpha]_D^{20}$ = -10.8 (c = 1.0, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.83 (d, J = 8.7 Hz, 1H), 6.59 (dd, J = 2.4, 8.7 Hz, 1H), 6.41 (d, J = 2.1 Hz, 1H), 4.59 (dd, J = 5.1, 11.1 Hz, 1H), 4.28 (t, J = 11.4 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.84 (s, 3H), 3.33-3.23 (m, 1H),

2.97 (dd, $J = 4.5, 17.1$ Hz, 1H), 2.39 (dd, $J = 8.4, 17.1$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H).



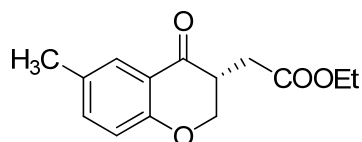
2d⁵

Yellow oil, 97% yield, 96% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 95/5, $\nu = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, t (major) = 16.38 min, t (minor) = 22.83 min]; $[\alpha]_{\text{D}}^{20} = -30.2$ ($c = 1.0$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.31 (d, $J = 3.0$ Hz, 1H), 7.10 (dd, $J = 3.3, 9.0$ Hz, 1H), 6.91 (d, $J = 8.7$ Hz, 1H), 4.56 (dd, $J = 5.1, 11.1$ Hz, 1H), 4.26 (t, $J = 11.1$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 3.80 (s, 3H), 3.36-3.26 (m, 1H), 2.92 (dd, $J = 4.8, 16.8$ Hz, 1H), 2.43 (dd, $J = 8.1, 17.1$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H).



2e⁵

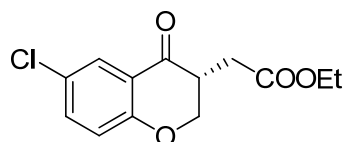
Yellow oil, 95% yield, 95% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 97/3, $\nu = 0.7 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, t (major) = 15.74 min, t (minor) = 20.69 min]; $[\alpha]_{\text{D}}^{20} = -28.0$ ($c = 1.0$, CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3) δ 7.74 (d, $J = 8.1$ Hz, 1H), 7.34 (d, $J = 6.6$ Hz, 1H), 6.92 (t, $J = 7.8$ Hz, 1H), 4.64 (dd, $J = 5.4, 11.1$ Hz, 1H), 4.29 (t, $J = 11.4$ Hz, 1H), 4.19 (q, $J = 6.9$ Hz, 2H), 3.37-3.27 (m, 1H), 2.94 (dd, $J = 4.8, 17.1$ Hz, 1H), 2.40 (dd, $J = 8.4, 16.8$ Hz, 1H), 2.24 (s, 3H), 1.29 (t, $J = 6.9$ Hz, 3H).



2f⁵

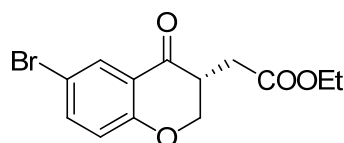
Yellow oil, 95% yield, 97% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 95/5, $\nu = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, t (major) = 11.95 min, t (minor) = 18.10 min]; $[\alpha]_{\text{D}}^{20} = -26.9$ ($c = 1.0$, CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3) δ 7.67 (d, $J = 1.8$ Hz, 1H), 7.29

(dd, $J = 2.1, 8.7$ Hz, 1H), 6.88 (d, $J = 8.4$ Hz, 1H), 4.57 (dd, $J = 5.1, 10.8$ Hz, 1H), 4.26 (t, $J = 11.4$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 3.36-3.26 (m, 1H), 2.92 (dd, $J = 4.8, 17.1$ Hz, 1H), 2.41 (dd, $J = 8.1, 16.8$ Hz, 1H), 2.30 (s, 1H), 1.28 (t, $J = 7.2$ Hz, 1H).



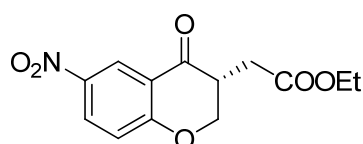
2g⁵

Yellow oil, 94% yield, 93% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 95/5, $\nu = 1.0$ mL $\cdot$ min⁻¹, $\lambda = 254$ nm, t (major) = 12.61 min, t (minor) = 18.19 min]; $[\alpha]_D^{20} = -29.4$ (c = 1.0, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.83 (d, $J = 2.7$ Hz, 1H), 7.42 (dd, $J = 2.4, 8.7$ Hz, 1H), 6.95 (d, $J = 9.0$ Hz, 1H), 4.61 (dd, $J = 5.1, 11.4$ Hz, 1H), 4.30 (t, $J = 12.0$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 3.37-3.27 (m, 1H), 2.92 (dd, $J = 4.8, 17.1$ Hz, 1H), 2.44 (dd, $J = 7.8, 17.1$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H).



2h⁵

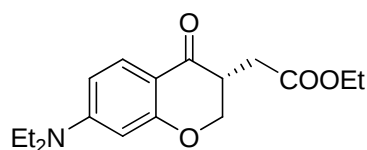
Yellow oil, 94% yield, 94% ee [Daicel Chiralcel OD-H, hexane/2-propanol = 97/3, $\nu = 0.5$ mL $\cdot$ min⁻¹, $\lambda = 254$ nm, t (minor) = 29.32 min, t (major) = 31.02 min]; $[\alpha]_D^{20} = -15.4$ (c = 1.0, CHCl₃). ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, $J = 2.4$ Hz, 1H), 7.55 (dd, $J = 2.8, 9.2$ Hz, 1H), 6.89 (d, $J = 8.4$ Hz, 1H), 4.61 (dd, $J = 5.2, 11.2$ Hz, 1H), 4.30 (dd, $J = 11.2, 12.0$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 3.36-3.28 (m, 1H), 2.92 (dd, $J = 4.8, 16.8$ Hz, 1H), 2.43 (dd, $J = 8.0, 16.8$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H).



2i

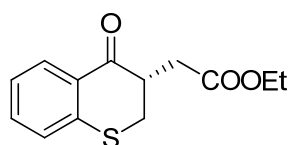
White solid, 86% yield, 68% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 70/30, $\nu = 1.0$ mL $\cdot$ min⁻¹, $\lambda = 254$ nm, t (major) = 13.29 min, t (minor) = 21.61 min]; $[\alpha]_D^{20} = -47.0$ (c = 1.0, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 8.78 (d, $J = 2.7$ Hz, 1H), 8.34

(dd, $J = 2.7, 9.3$ Hz, 1H), 7.13 (d, $J = 9.3$ Hz, 1H), 4.76 (dd, $J = 5.7, 11.7$ Hz, 1H), 4.44 (t, $J = 11.7$ Hz, 1H), 4.20 (q, $J = 6.9$ Hz, 1H), 3.45-3.35 (m, 1H), 2.96 (dd, $J = 4.8, 17.4$ Hz, 1H), 2.51 (dd, $J = 8.1, 17.1$ Hz, 1H), 1.30 (t, $J = 6.9$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3) δ 190.6, 170.8, 165.6, 142.1, 130.3, 123.9, 120.0, 119.2, 70.6, 61.2, 42.1, 29.8, 14.1. IR (thin film): ν_{max} (cm^{-1}) = 2986, 1731, 1692, 1439, 1339, 1012, 856, 750, 622; MS (EI, m/z , rel. intensity) 279 (M^+ , 1), 192 (100); HRMS (EI) calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_6$ (M^+): 279.0743. Found: 279.0745; m.p. 86-88 °C.



2j⁵

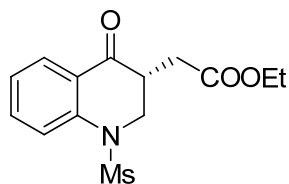
Yellow oil, 90% yield, 97% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 90/10, $\nu = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, t (major) = 20.48 min, t (minor) = 22.47 min]; $[\alpha]_{\text{D}}^{20} = +12.9$ ($c = 1.0$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.74 (d, $J = 9.0$ Hz, 1H), 6.35 (dd, $J = 2.4, 9.3$ Hz, 1H), 6.05 (d, $J = 2.1$ Hz, 1H), 4.53 (dd, $J = 5.1, 11.1$ Hz, 1H), 4.15-4.26 (m, 3H), 3.39 (q, $J = 7.2$ Hz, 4H), 3.25-3.15 (m, 1H), 2.95 (dd, $J = 4.5, 16.5$ Hz, 1H), 2.36 (dd, $J = 8.7, 16.5$ Hz, 1H), 1.28 (t, $J = 6.9$ Hz, 3H), 1.20 (t, $J = 7.2$ Hz, 6H).



2k

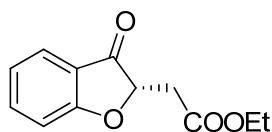
Yellow oil, 26% yield, 88% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 97/3, $\nu = 0.7 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, t (major) = 20.41 min, t (minor) = 24.64 min]; $[\alpha]_{\text{D}}^{20} = -100.1$ ($c = 0.4$, CH_2Cl_2). ^1H NMR (300 MHz, CDCl_3) δ 8.08 (d, $J = 8.1$ Hz, 1H), 7.41-7.36 (m, 1H), 7.26 (d, $J = 7.8$ Hz, 1H), 7.17 (t, $J = 7.5$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 3.43-3.30 (m, 2H), 3.17-3.10 (m, 1H), 2.97 (dd, $J = 4.8, 16.8$ Hz, 1H), 2.58 (dd, $J = 6.9, 16.8$ Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 194.5, 171.6, 141.7, 133.2, 130.3, 129.6, 127.3, 124.9, 60.8, 44.4, 34.3, 30.8, 14.1. IR (thin film): ν_{max} (cm^{-1}) = 2980, 1732, 1681, 1588, 1437, 1177, 1028, 765, 737; MS (EI,

m/z , rel. intensity) 250 (M^+ , 5), 163 (100); HRMS (EI) calcd for $C_{13}H_{14}O_3S$ (M^+): 250.0664. Found: 250.0662.



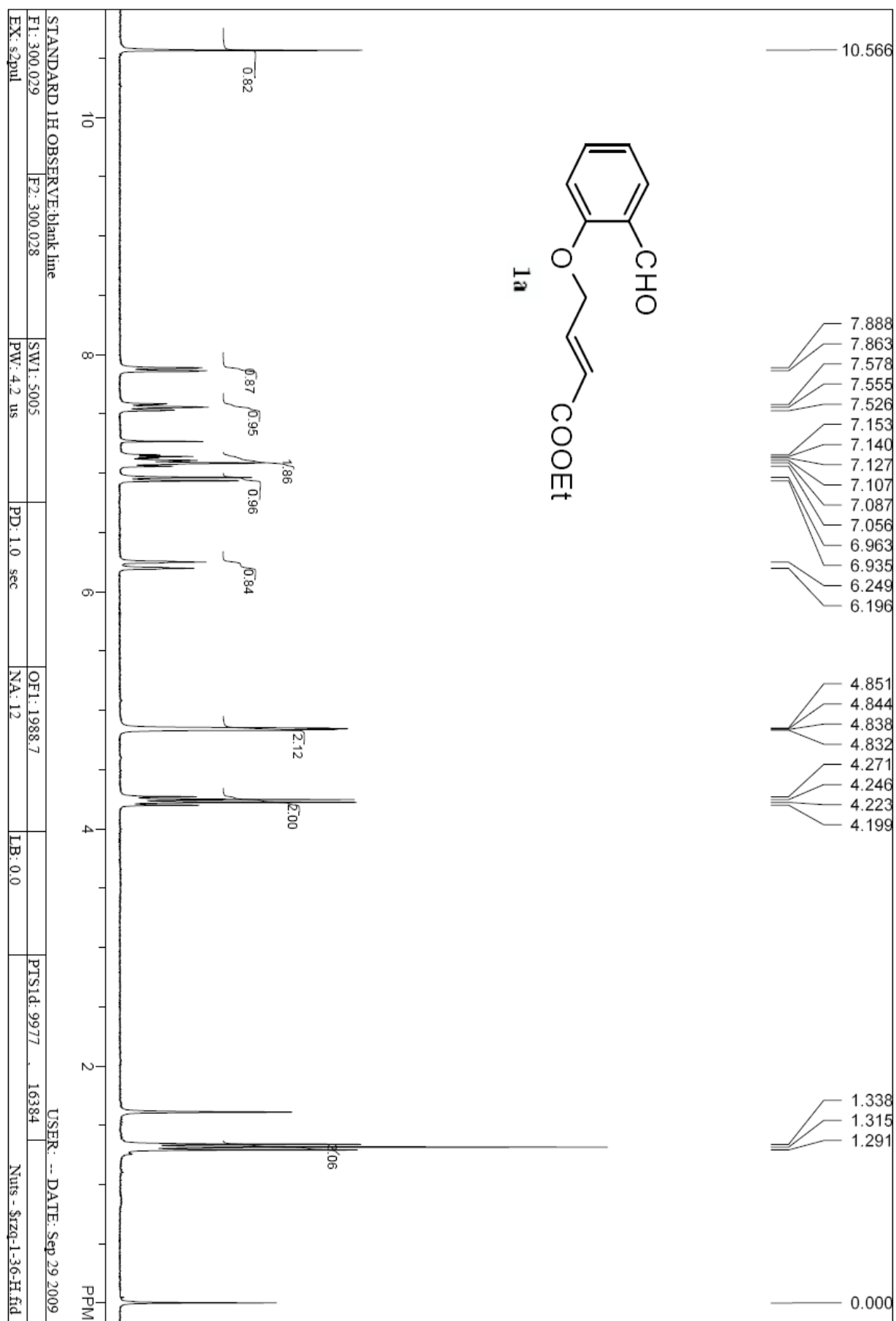
2I⁴

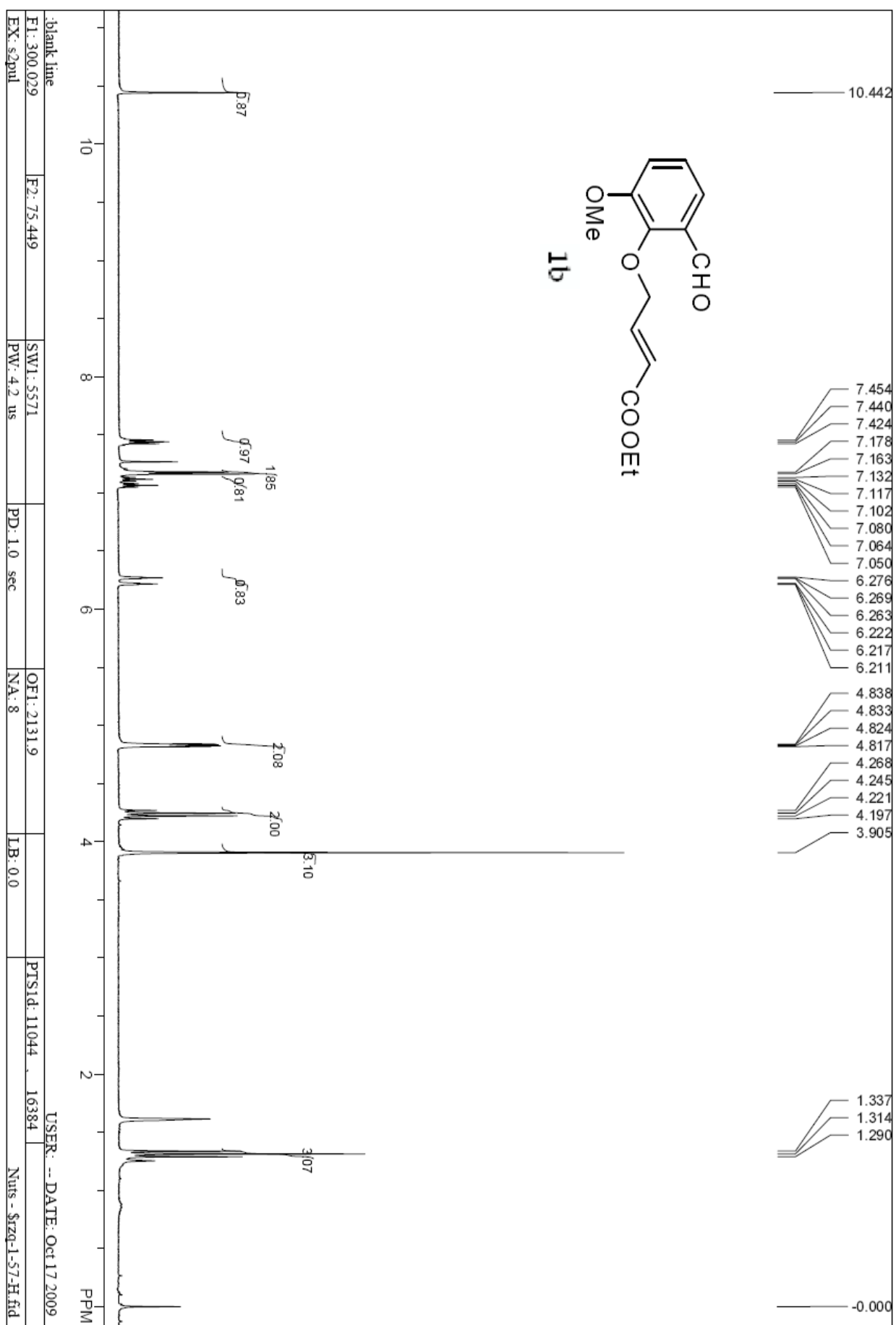
Yellow oil, 77% yield, 56% ee [Daicel Chiralpak AD-H, hexane/2-propanol = 80/20, $\nu = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, t (minor) = 16.42 min, t (major) = 21.87 min]; $[\alpha]_D^{20} = +49.0$ ($c = 1.0$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 8.07 (d, $J = 7.8 \text{ Hz}$, 1H), 7.77 (d, $J = 8.4 \text{ Hz}$, 1H), 7.57 (t, $J = 8.7 \text{ Hz}$, 1H), 7.24 (d, $J = 7.5 \text{ Hz}$, 1H), 4.52 (dd, $J = 5.1$, 13.5 Hz, 1H), 4.20 (q, $J = 7.2 \text{ Hz}$, 2H), 3.82 (t, $J = 13.2 \text{ Hz}$, 1H), 3.36-3.26 (m, 1H), 3.13 (s, 3H), 2.92 (dd, $J = 4.5$, 17.1 Hz, 1H), 2.60 (dd, $J = 7.5$, 17.1 Hz, 1H), 1.29 (t, $J = 7.2 \text{ Hz}$, 3H).

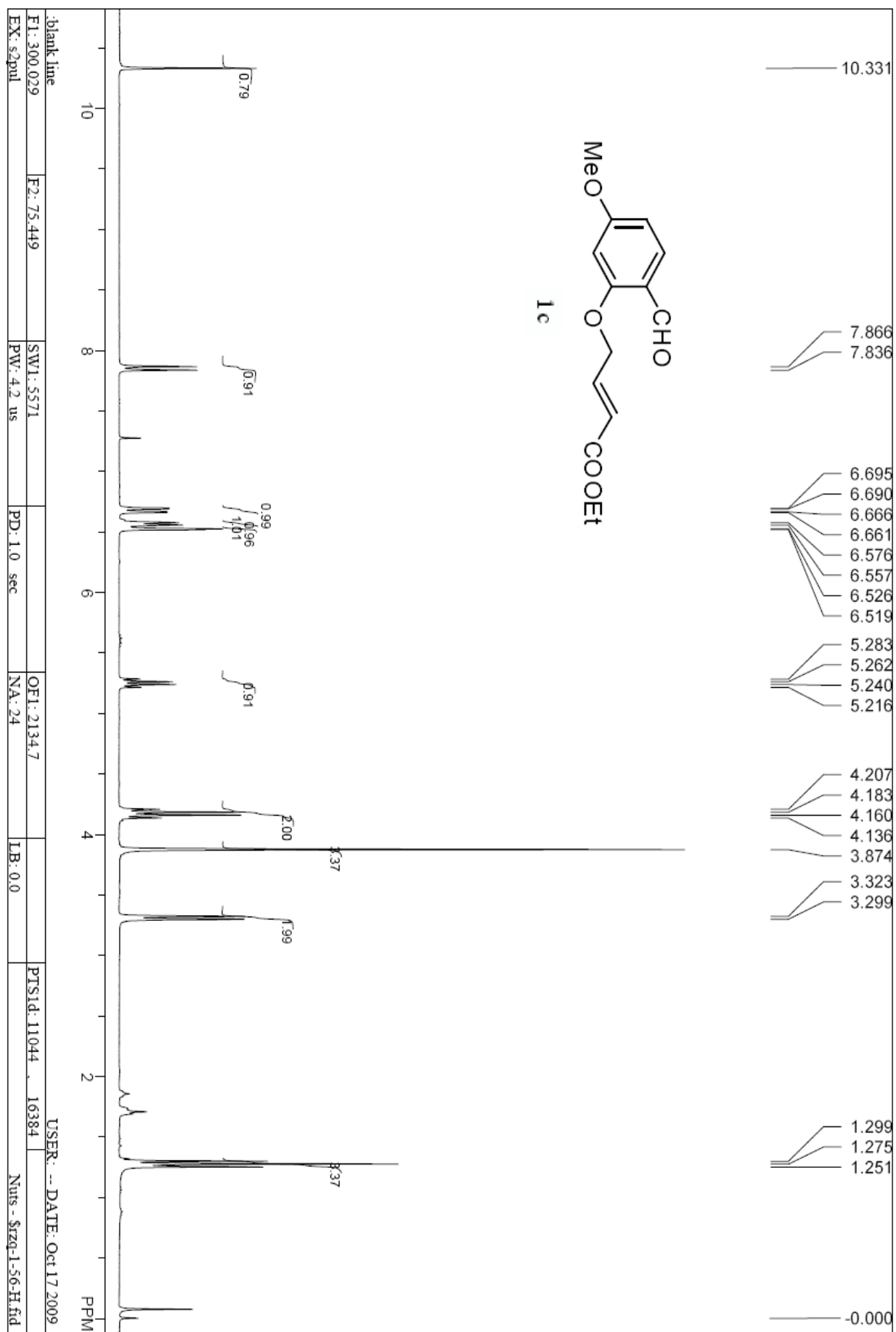


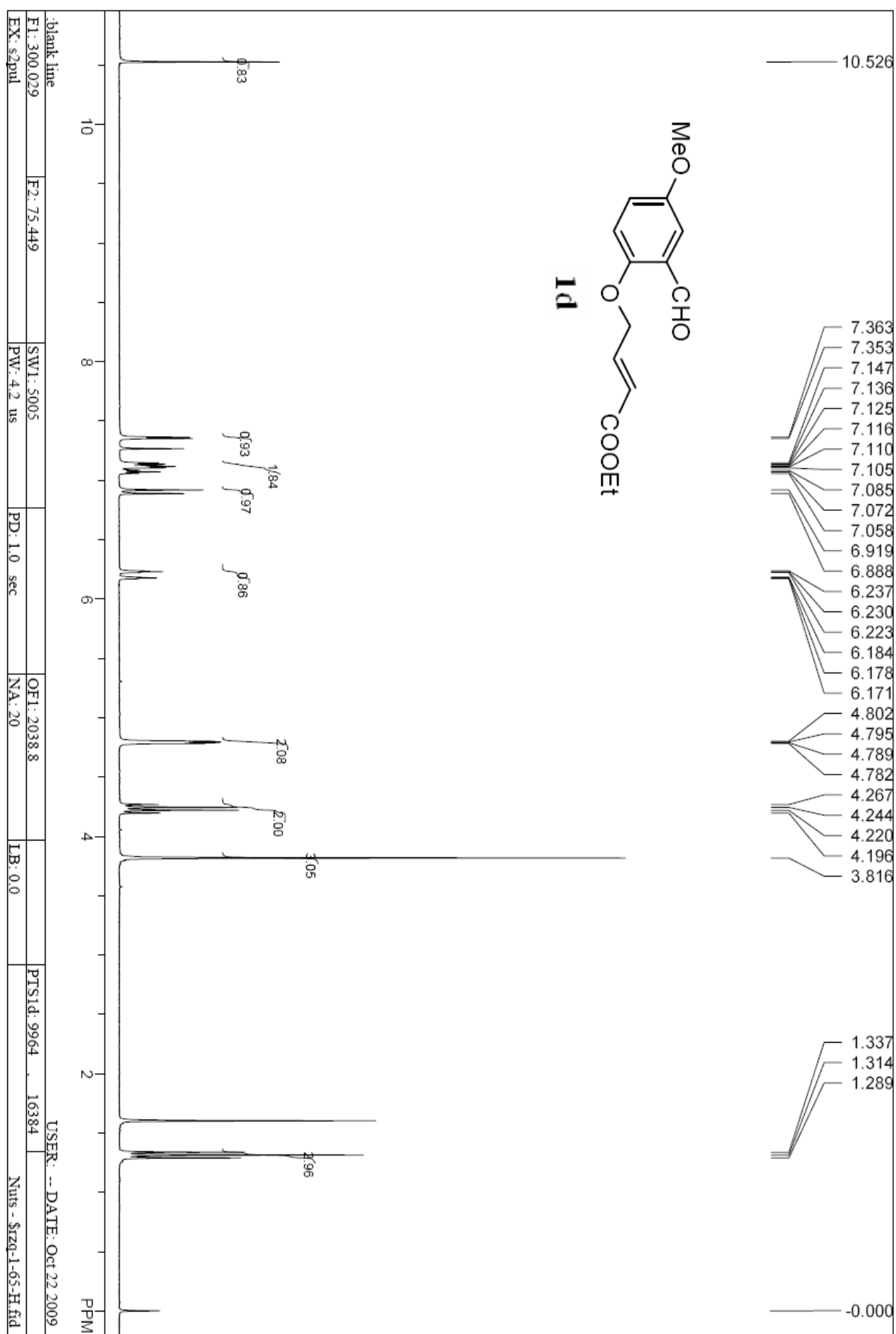
2m

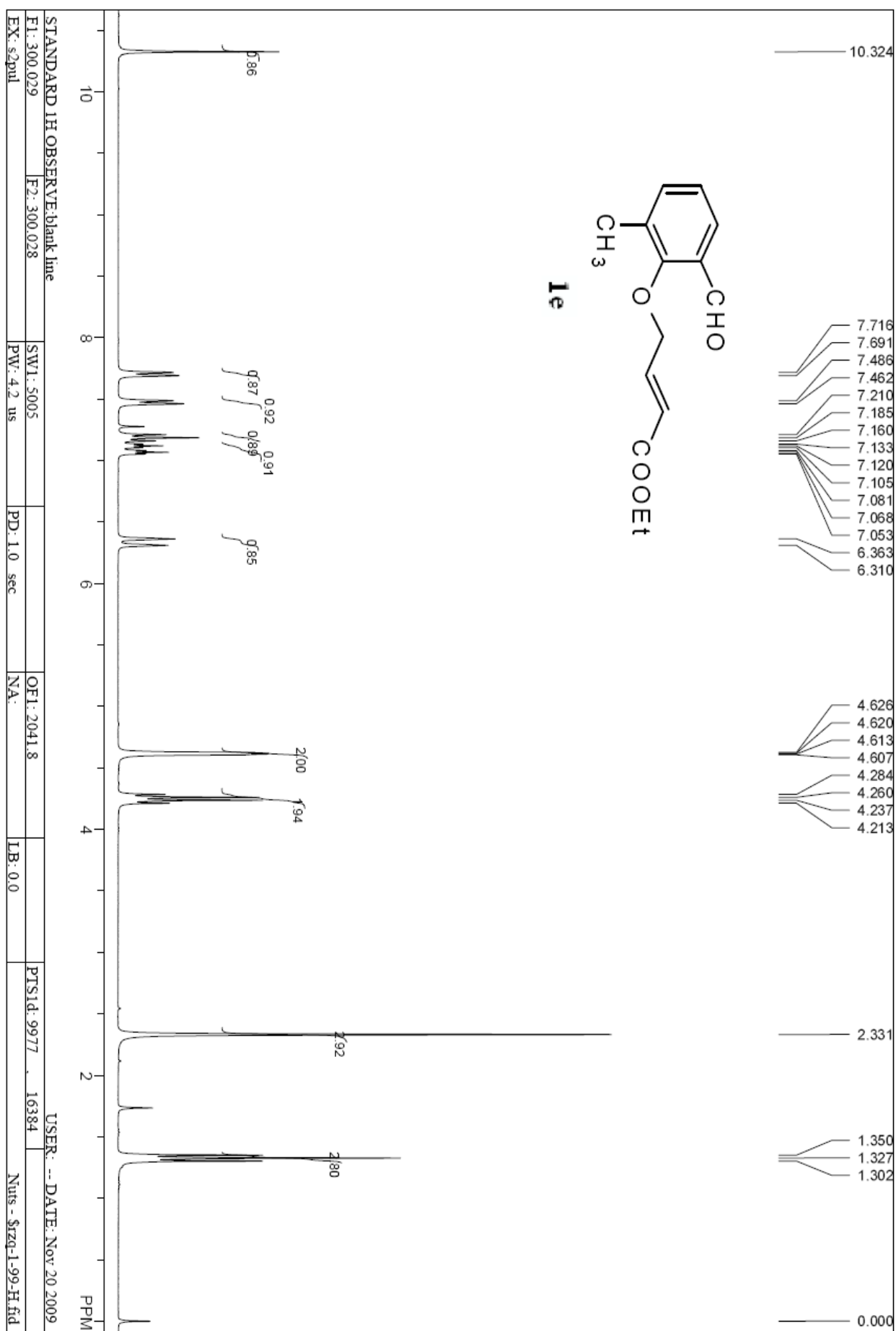
Yellow oil, 82% yield, 30% ee [Daicel Chiralcel OB-H, hexane/2-propanol = 90/10, $\nu = 1.0 \text{ mL} \cdot \text{min}^{-1}$, $\lambda = 254 \text{ nm}$, t (minor) = 20.95 min, t (major) = 38.70 min]; $[\alpha]_D^{20} = +29.9$ ($c = 0.70$, CHCl_3). ^1H NMR (300 MHz, CDCl_3) δ 7.69 (d, $J = 7.8 \text{ Hz}$, 1H), 7.67-7.60 (m, 1H), 7.15-7.09 (m, 2H), 4.89 (dd, $J = 3.6$, 7.2 Hz, 1H), 4.19-4.11 (m, 2H), 3.09 (dd, $J = 3.9$, 17.1 Hz, 1H), 2.83 (dd, $J = 7.8$, 17.4 Hz, 1H), 1.19 (t, $J = 6.9 \text{ Hz}$, 3H). ^{13}C NMR (75 MHz, CDCl_3) δ 200.4, 172.4, 169.3, 138.0, 124.2, 122.1, 120.9, 113.5, 81.0, 61.2, 36.0, 13.9. IR (thin film): ν_{max} (cm^{-1}) = 2983, 2935, 1724, 1615, 1464, 1327, 1191, 1026, 891, 760; MS (EI, m/z , rel. intensity) 220 (M^+ , 28), 147 (100); HRMS (EI) calcd for $C_{12}H_{12}O_4$ (M^+): 220.0736. Found: 220.0739.

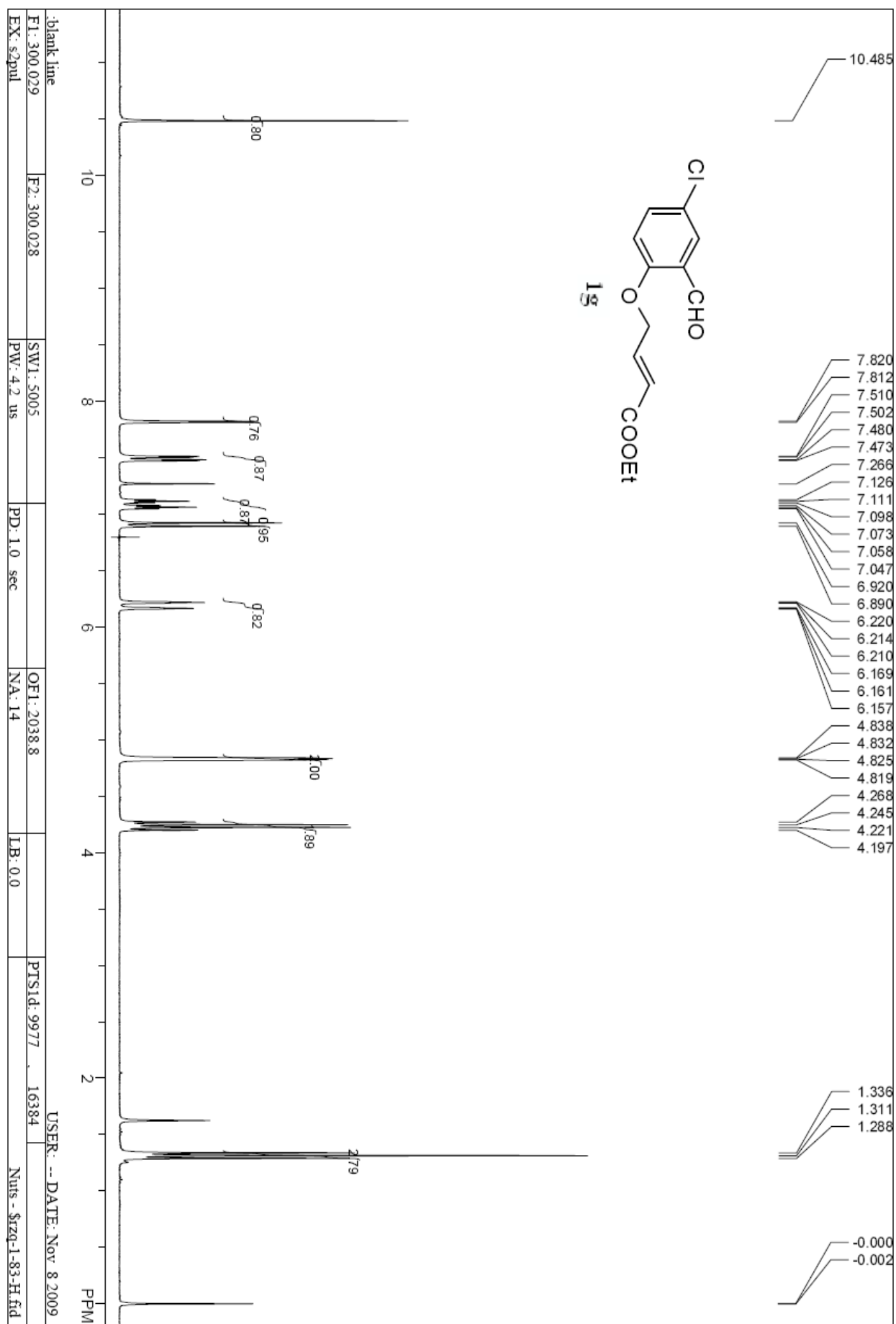


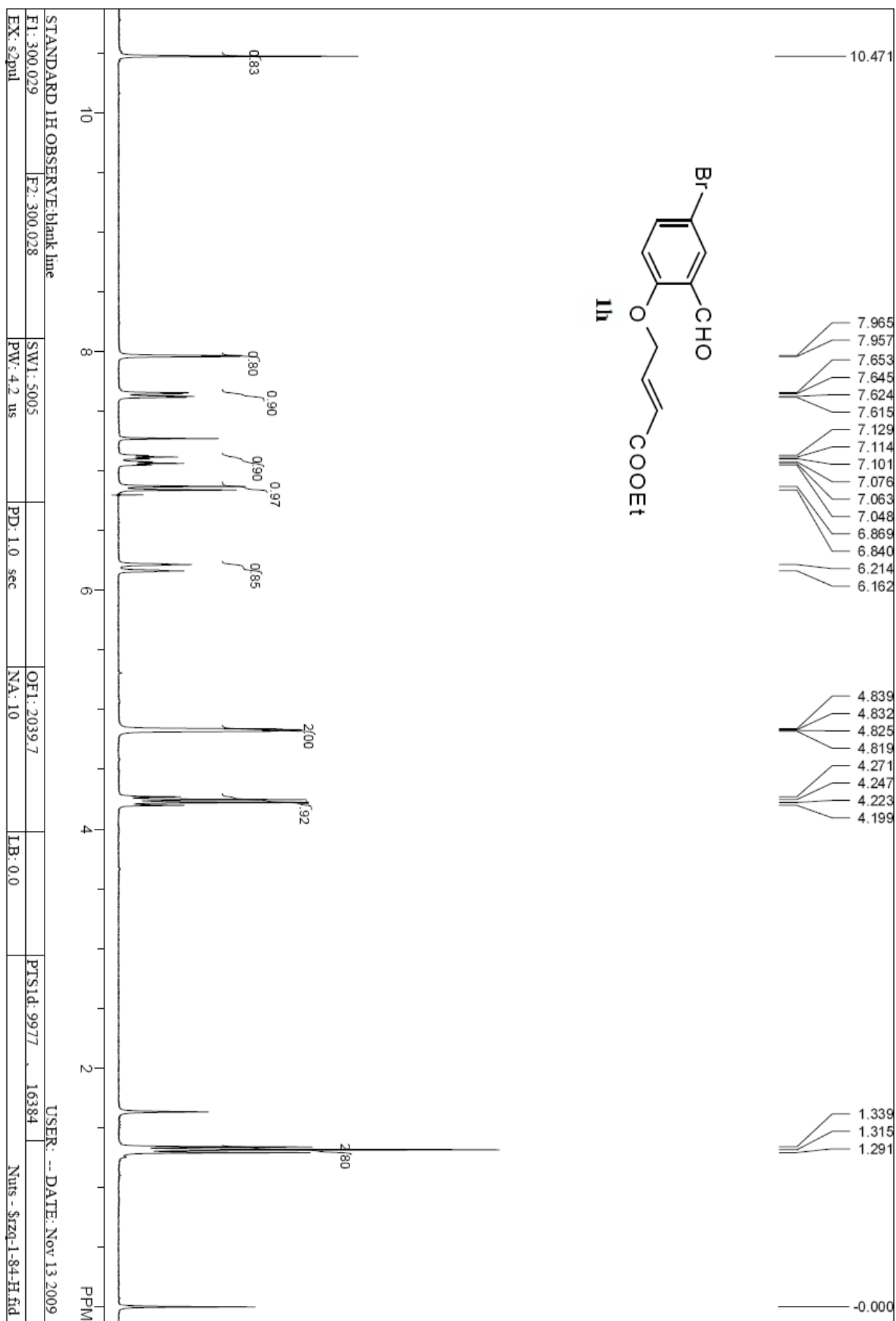


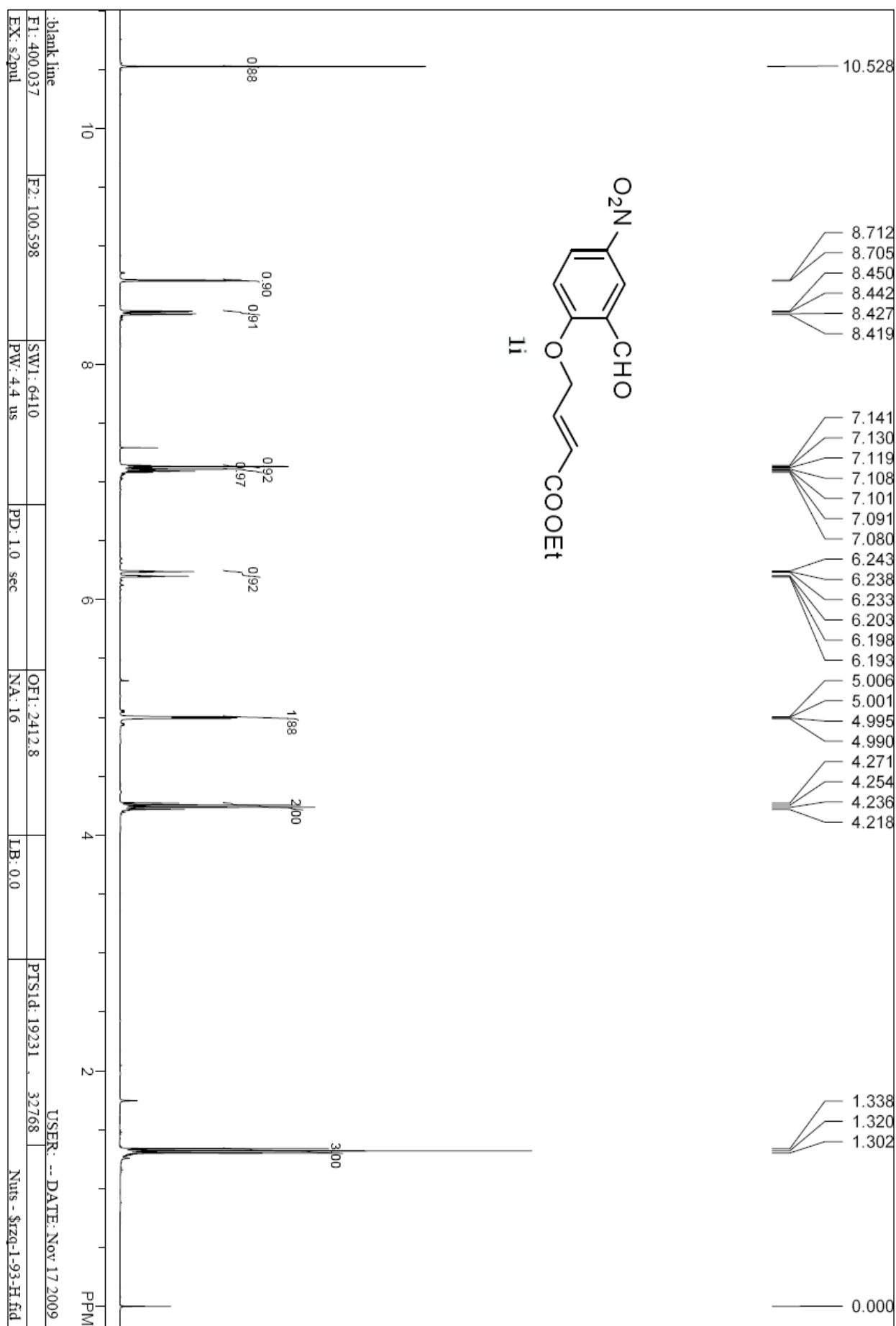


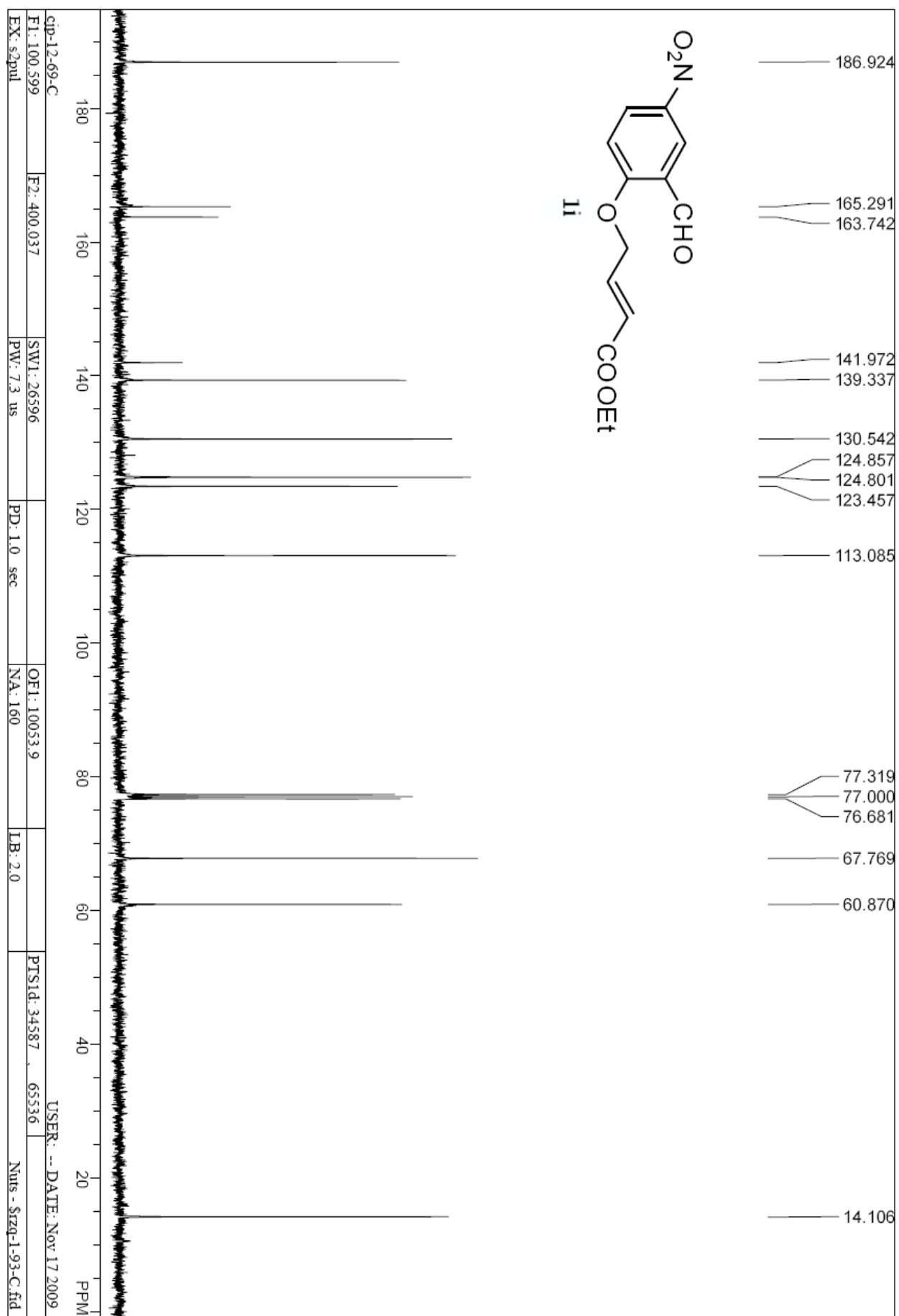


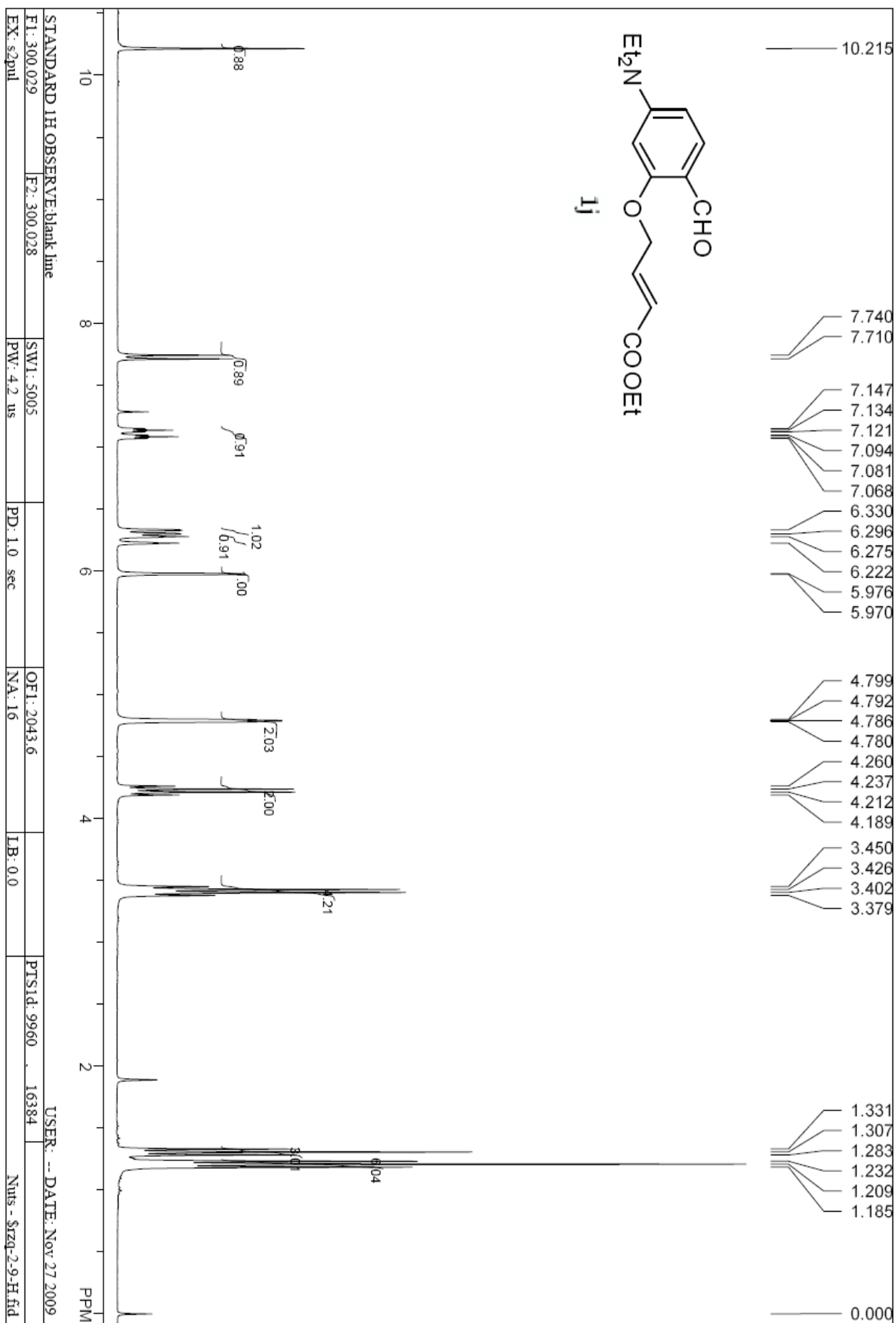


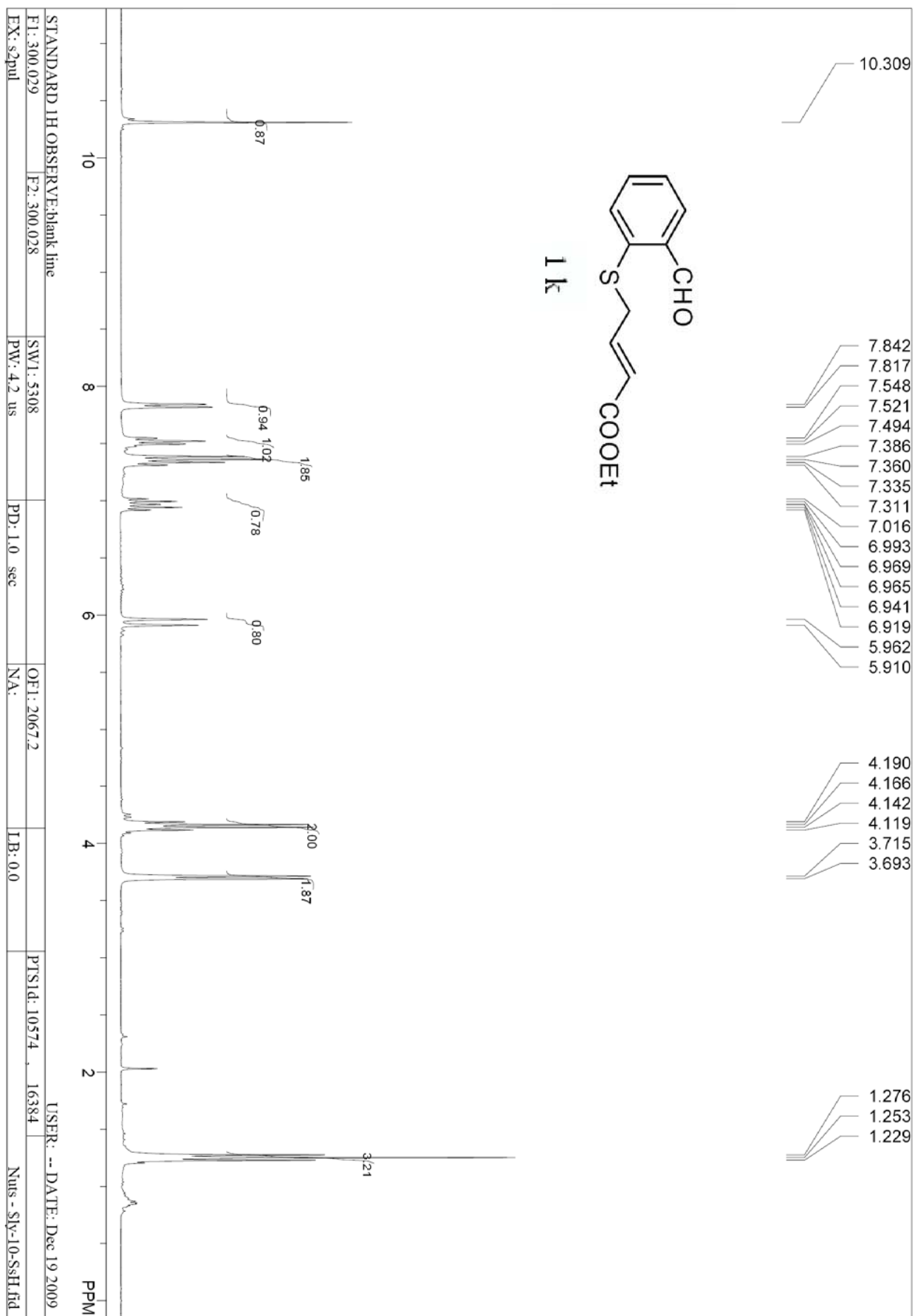


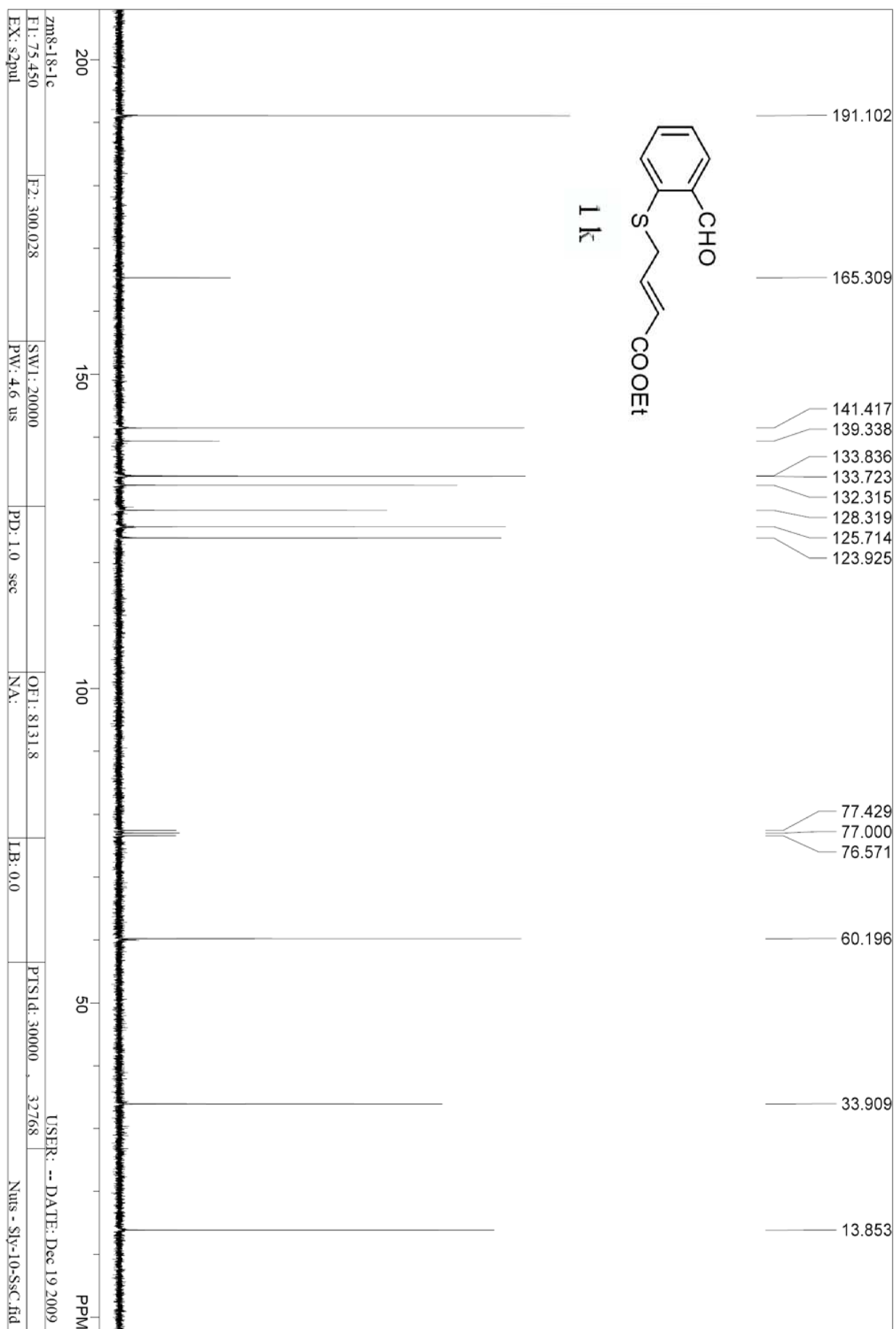


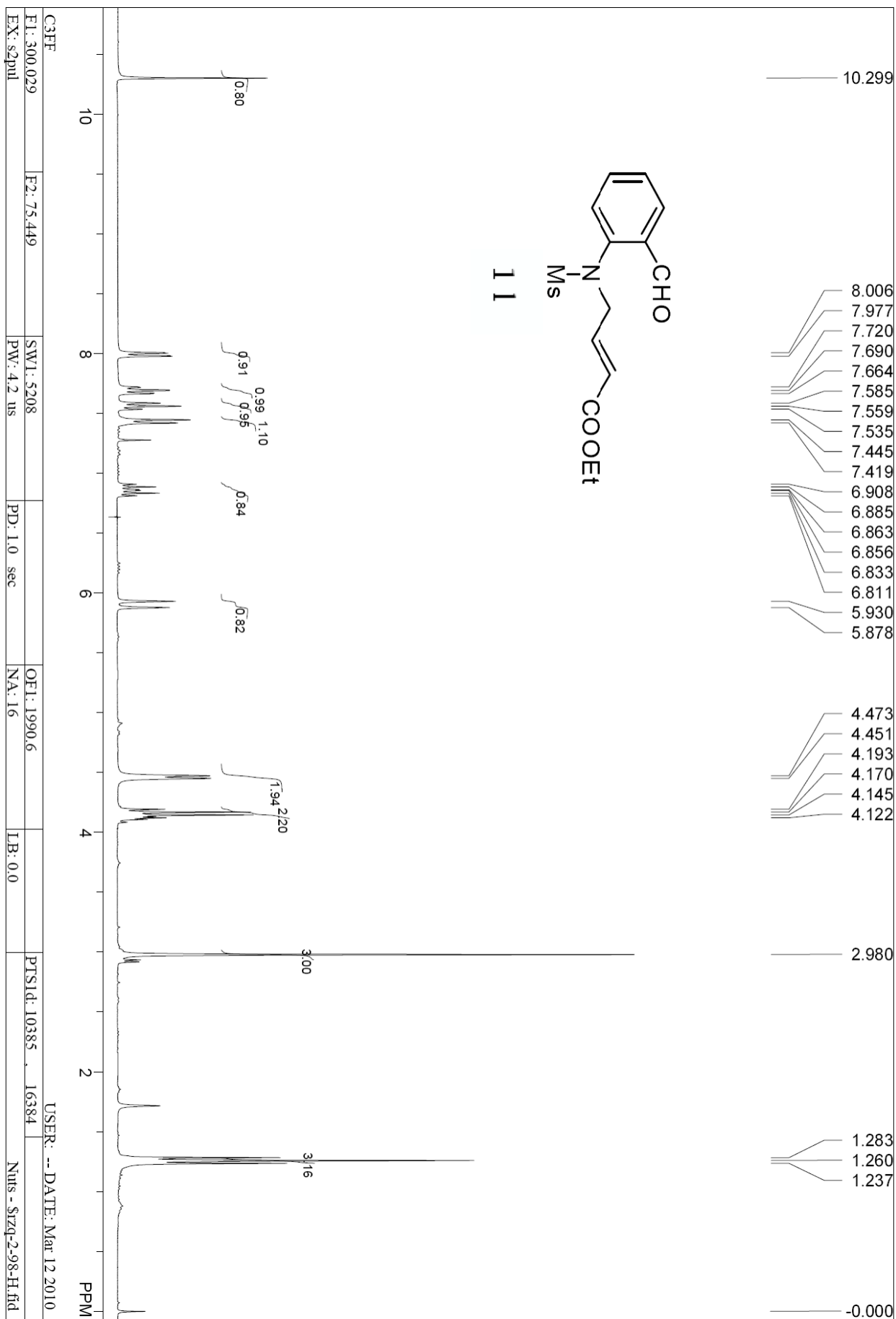


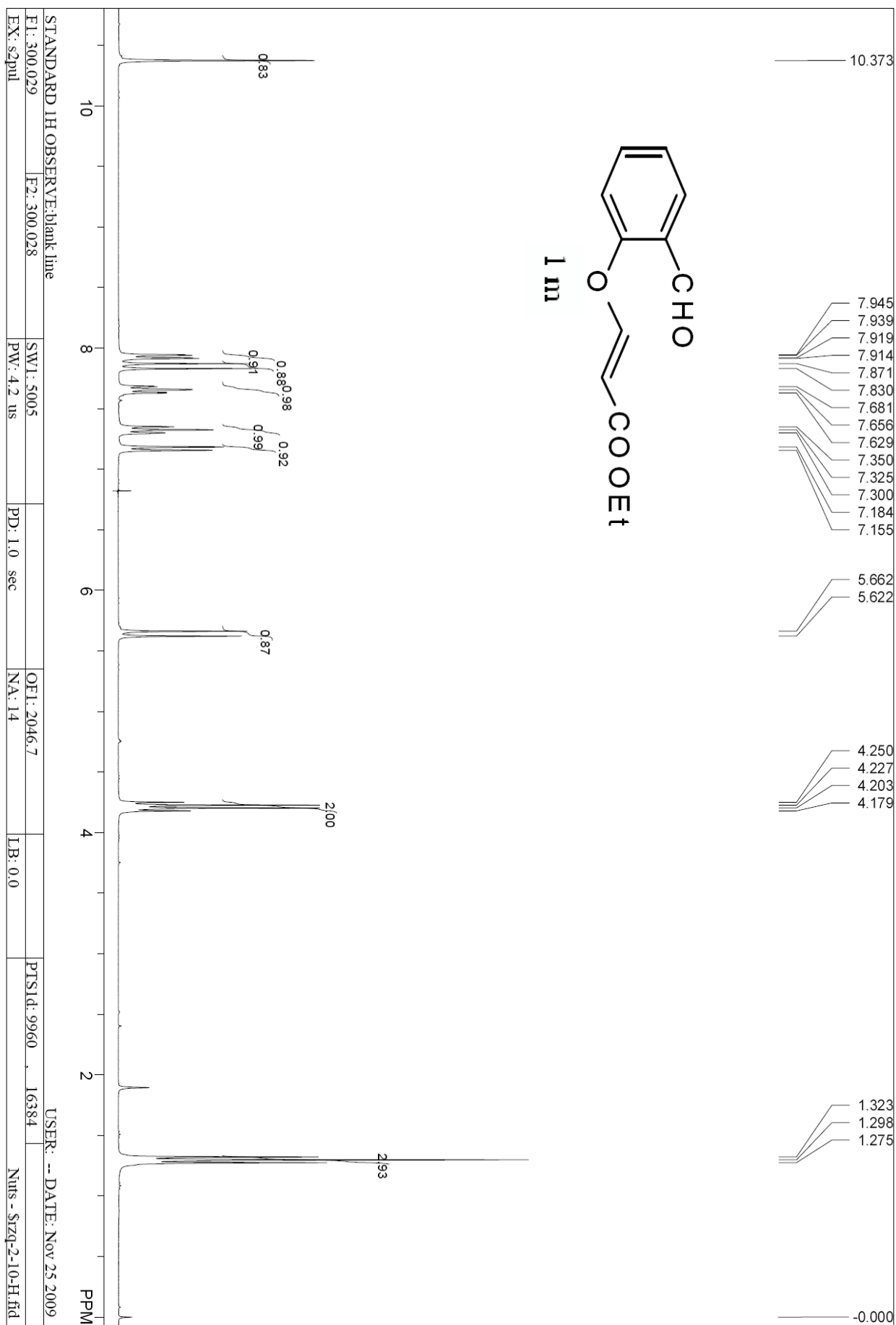


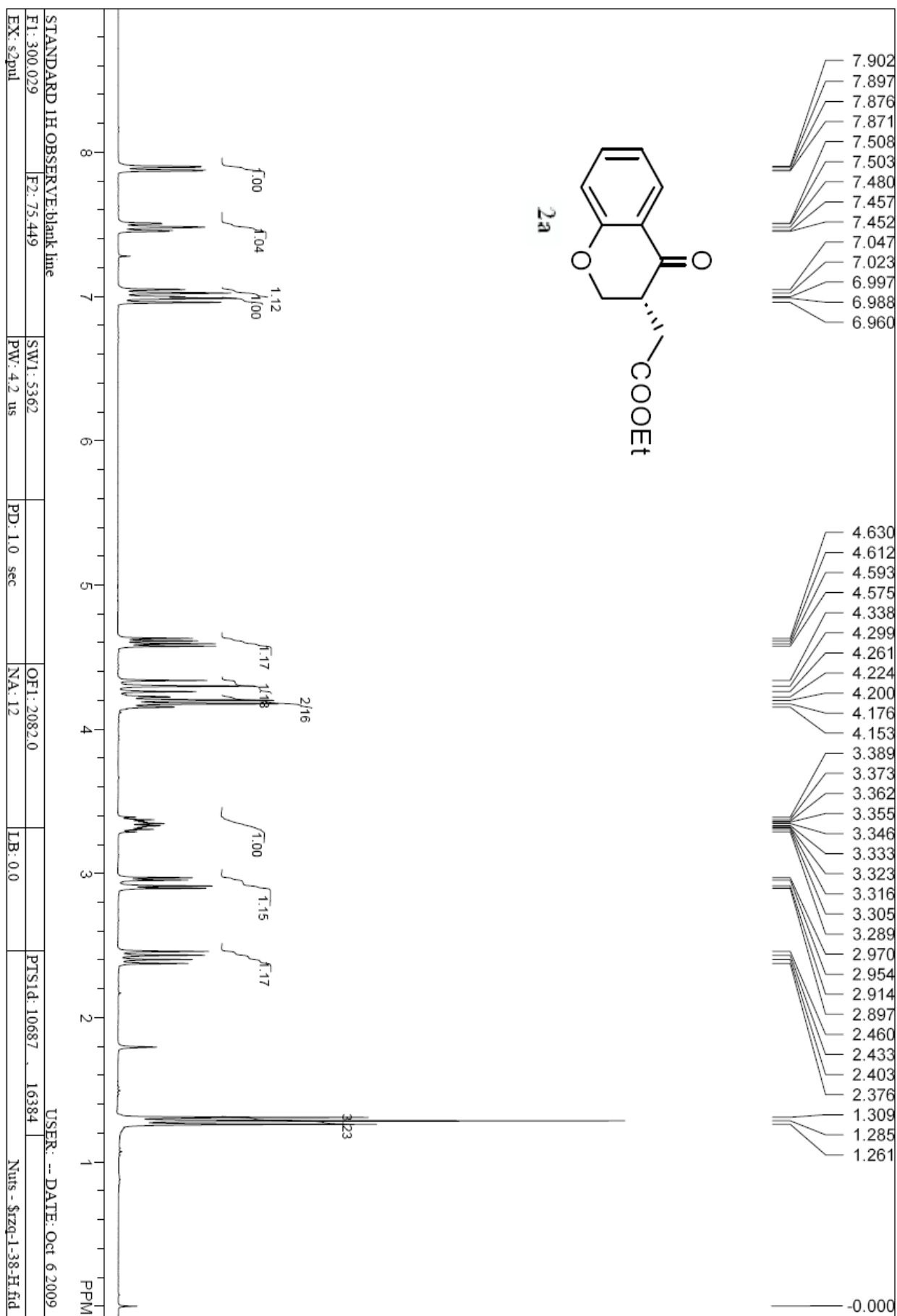


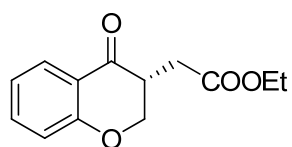




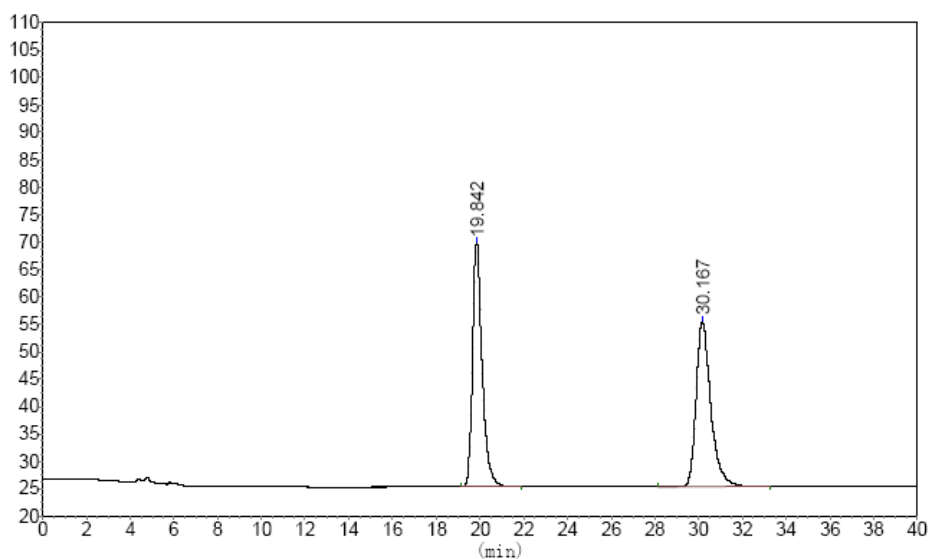




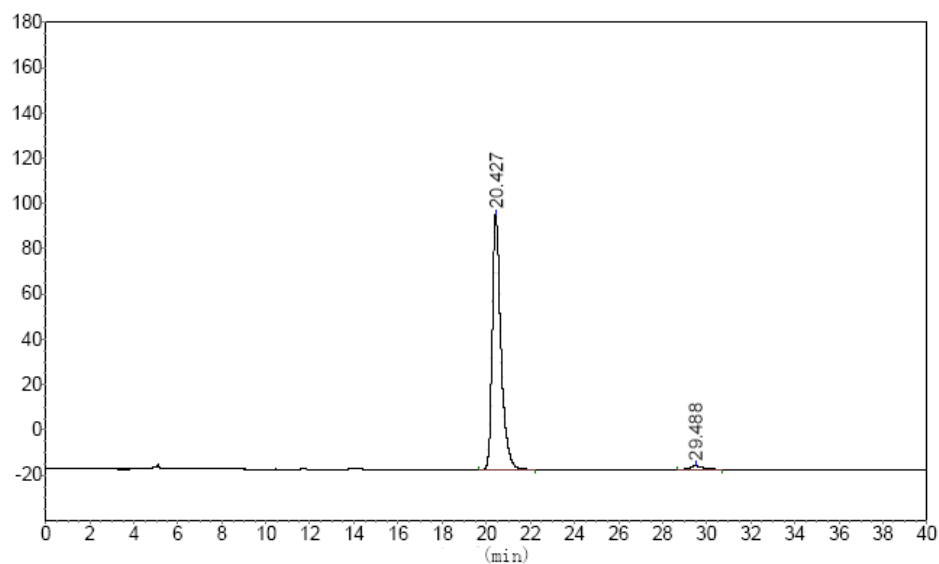




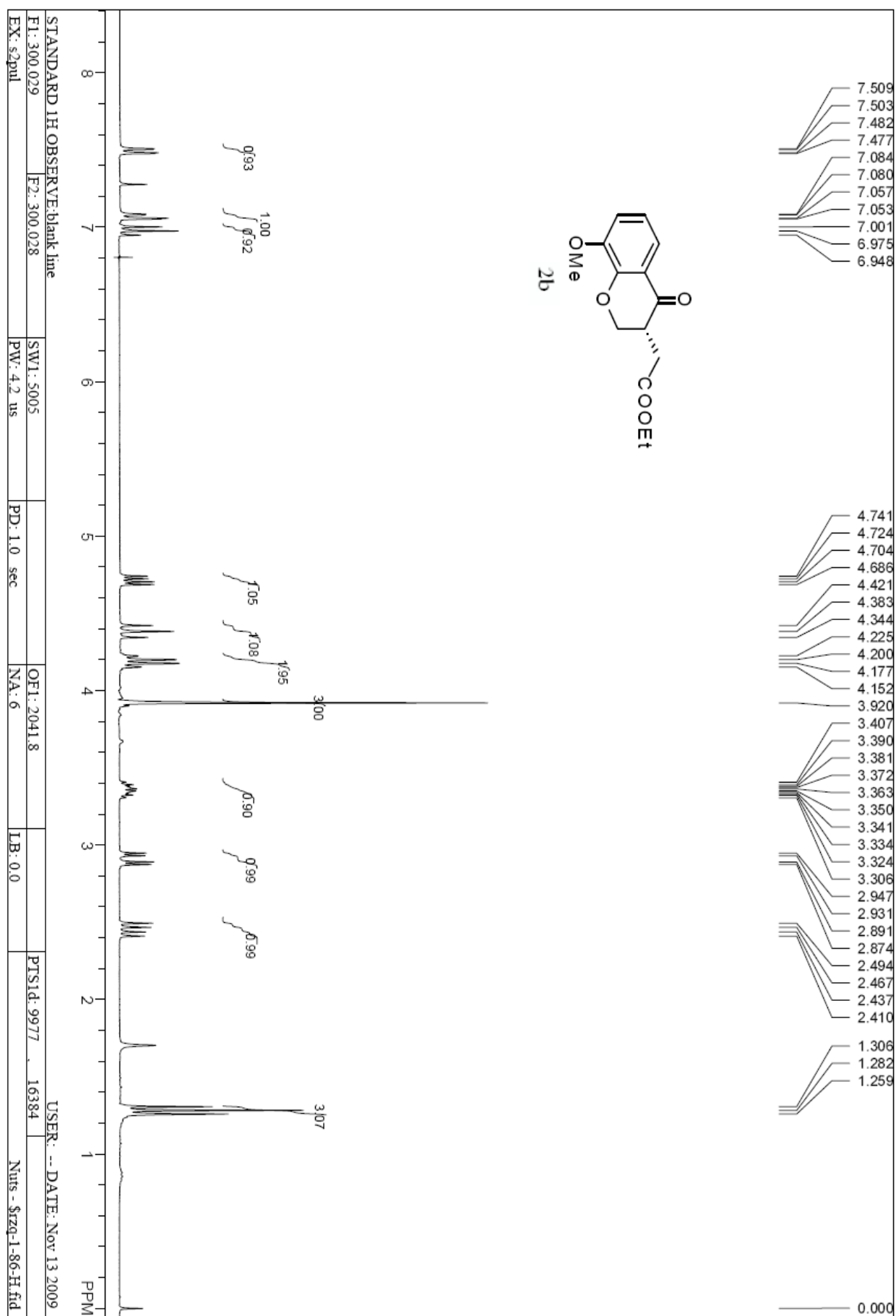
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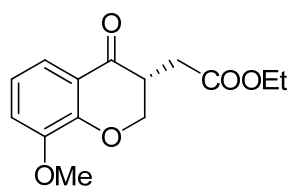


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	19.842	44558.844	1365032.750	49.3874
2	30.167	30209.363	1398897.125	50.6126
Total		74768.207	2763929.875	100.0000

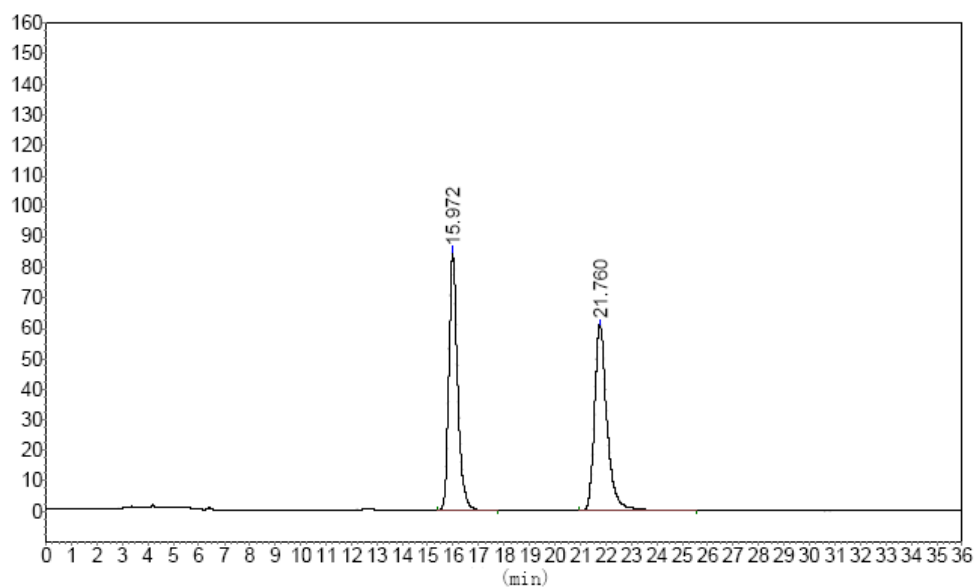


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20.427	112703.258	3084682.500	97.7987
2	29.488	1825.821	69430.047	2.2013
Total		114529.079	3154112.547	100.0000

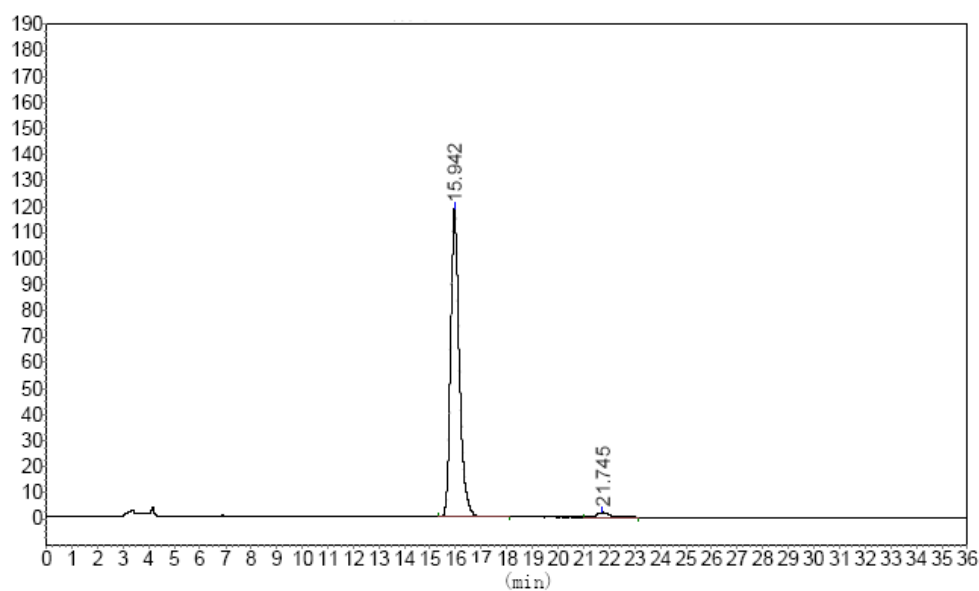




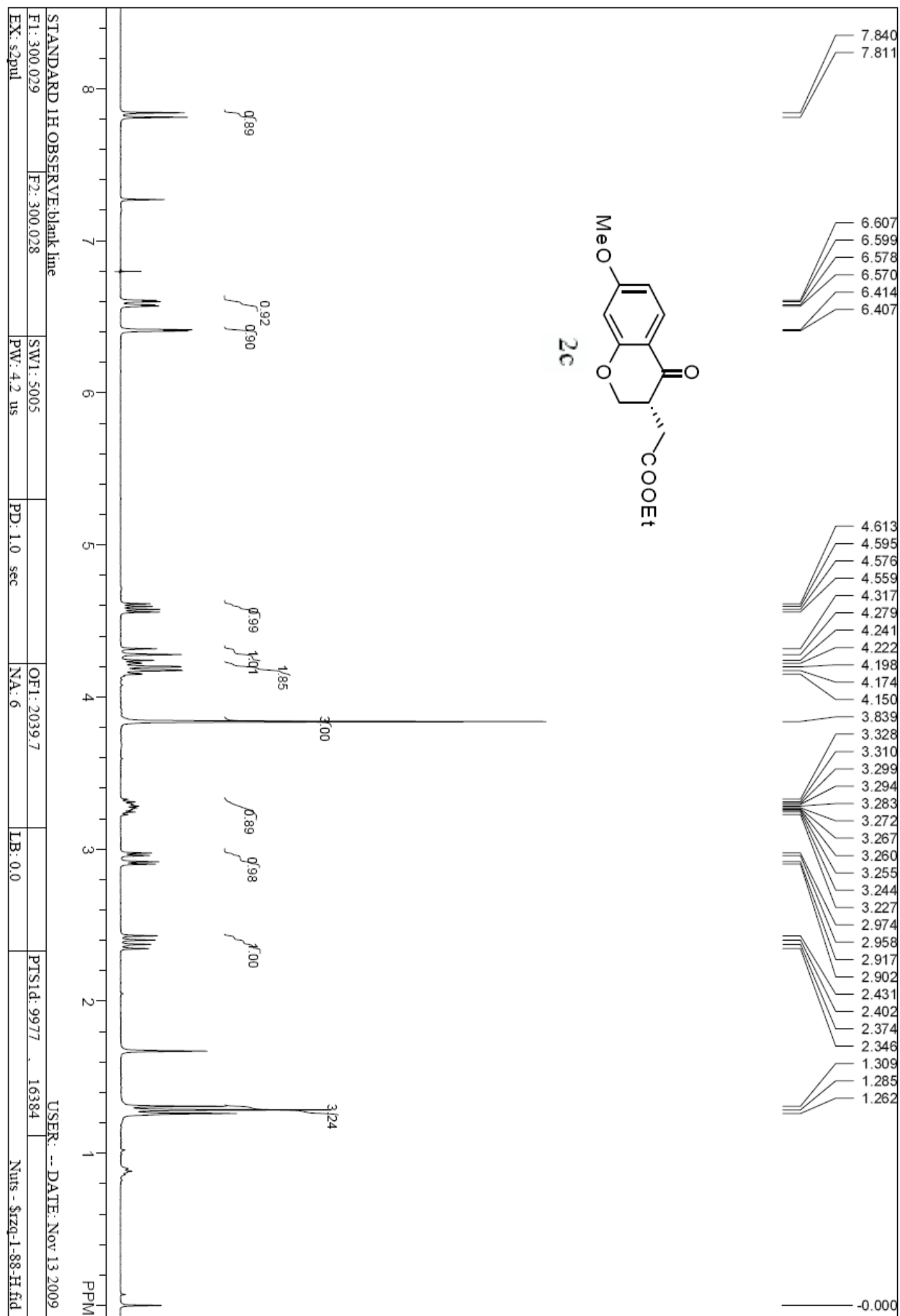
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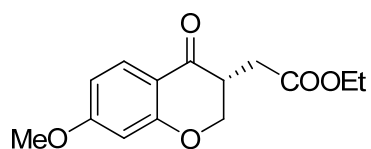


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15.972	84707.875	2026829.250	49.4549
2	21.760	60887.336	2071512.125	50.5451
Total		145595.211	4098341.375	100.0000

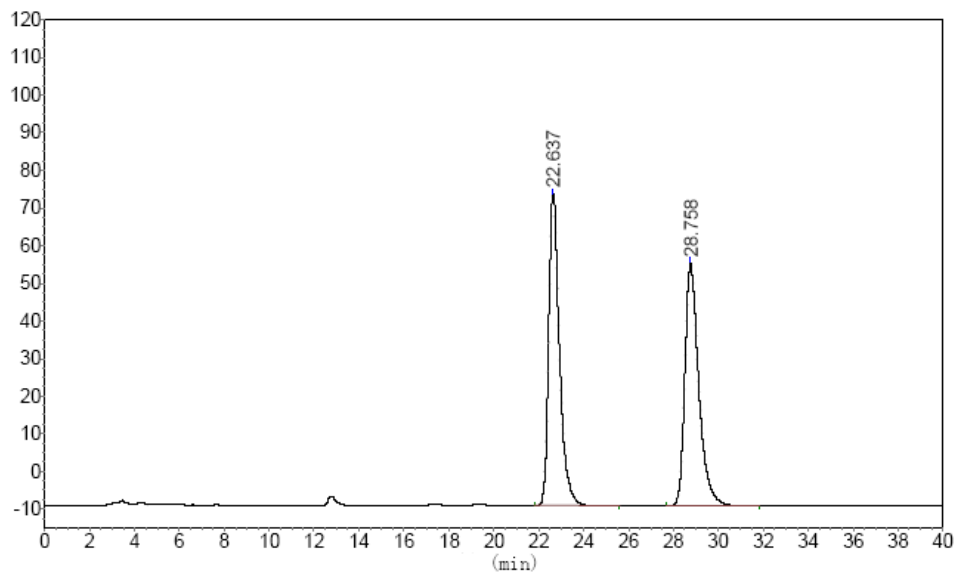


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15.942	118765.781	2842631.250	97.8156
2	21.745	1925.148	63481.352	2.1844
Total		120690.929	2906112.602	100.0000

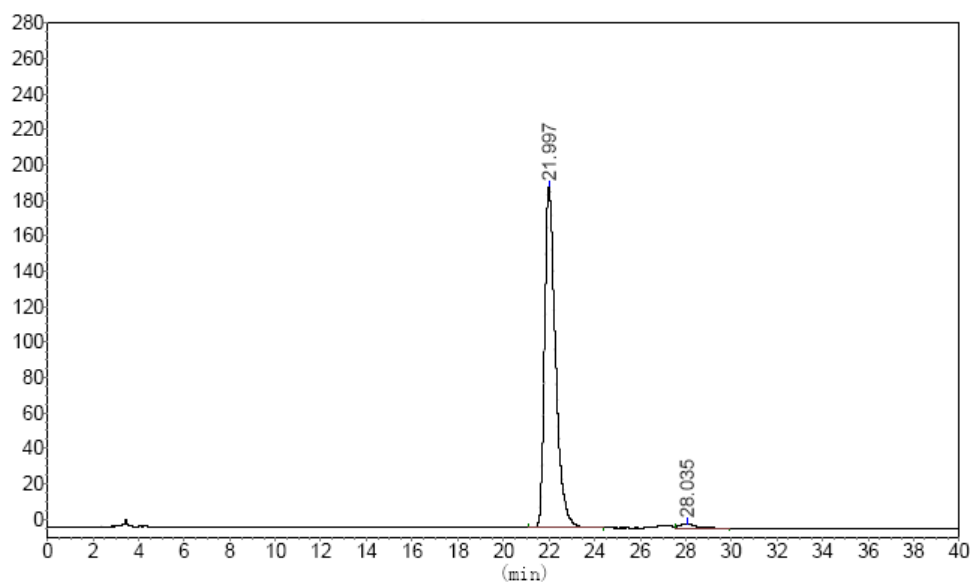




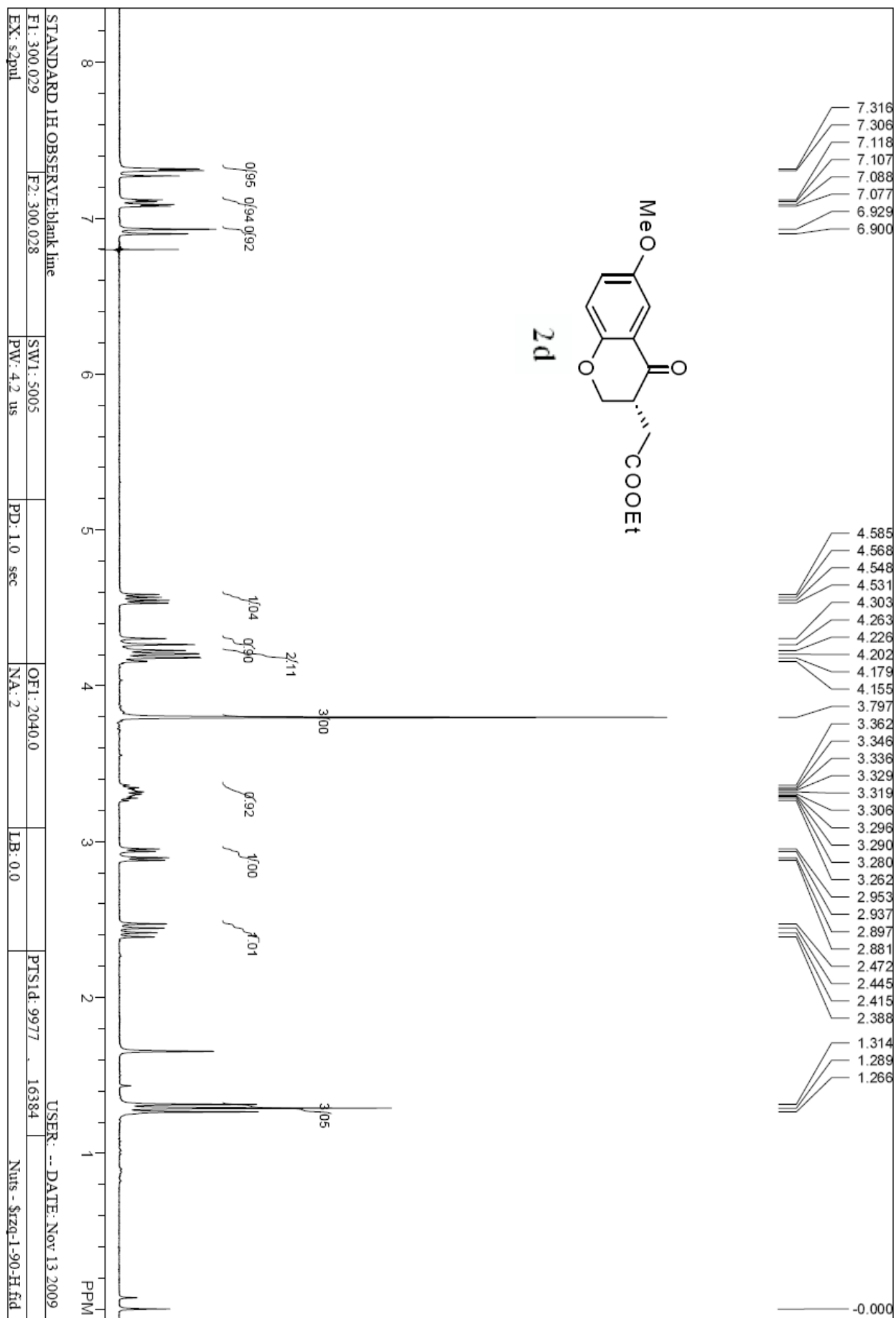
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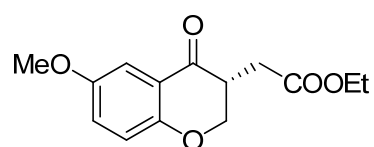


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	22.637	82863.977	2764253.000	49.9860
2	28.758	64568.195	2765807.000	50.0140
Total		147432.172	5530060.000	100.0000

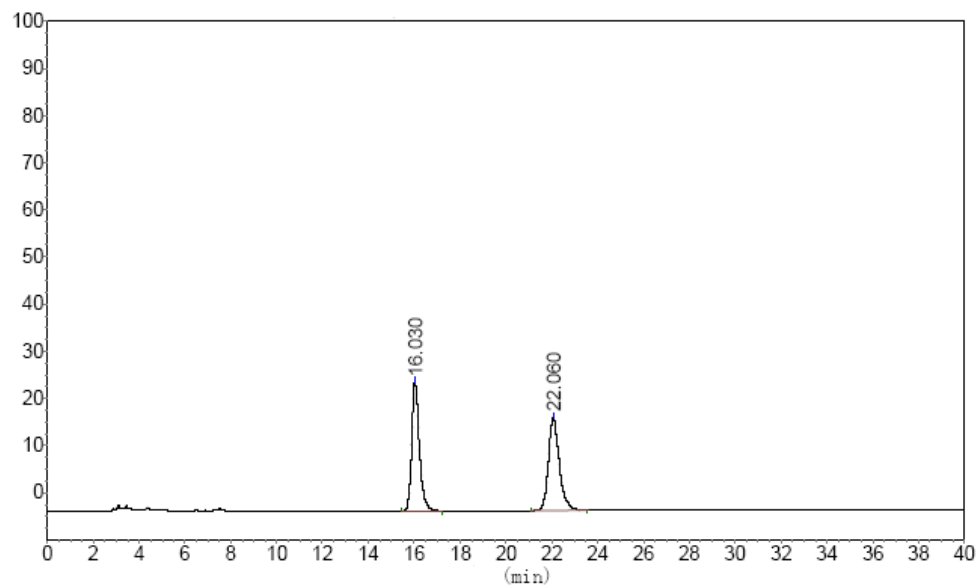


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	21.997	192341.000	6360005.500	98.6538
2	28.035	2064.380	86789.336	1.3462
Total		194405.380	6446794.836	100.0000

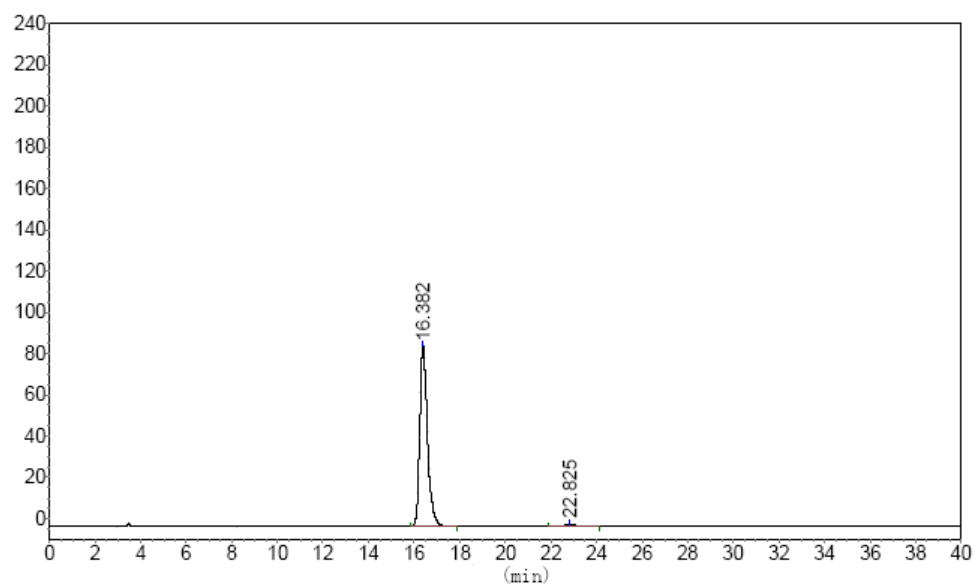




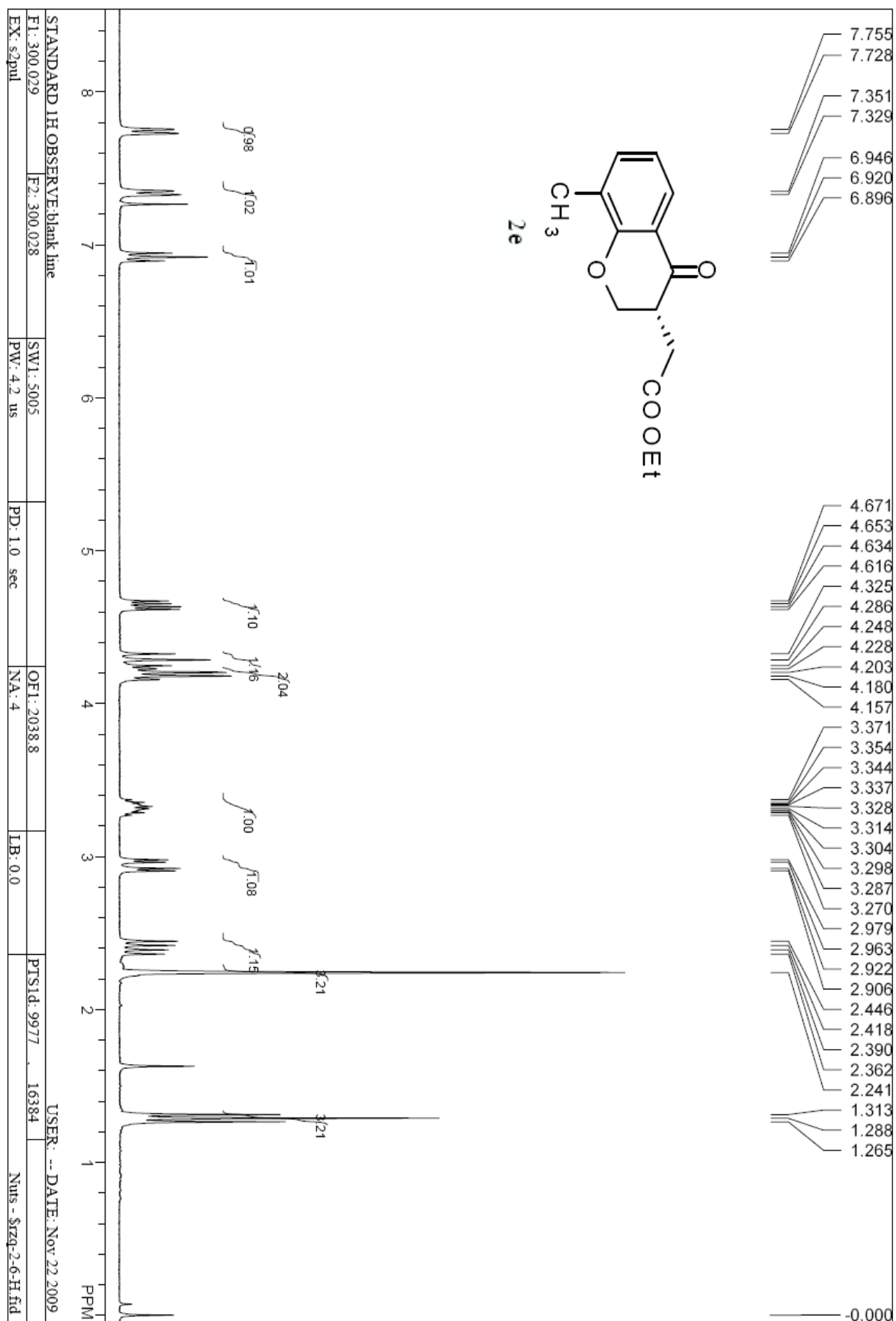
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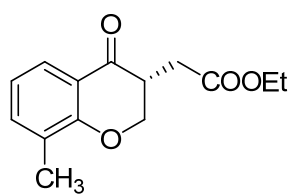


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	16.030	27236.465	621721.000	48.9472
2	22.060	19733.309	648464.938	51.0528
Total		46969.773	1270185.938	100.0000

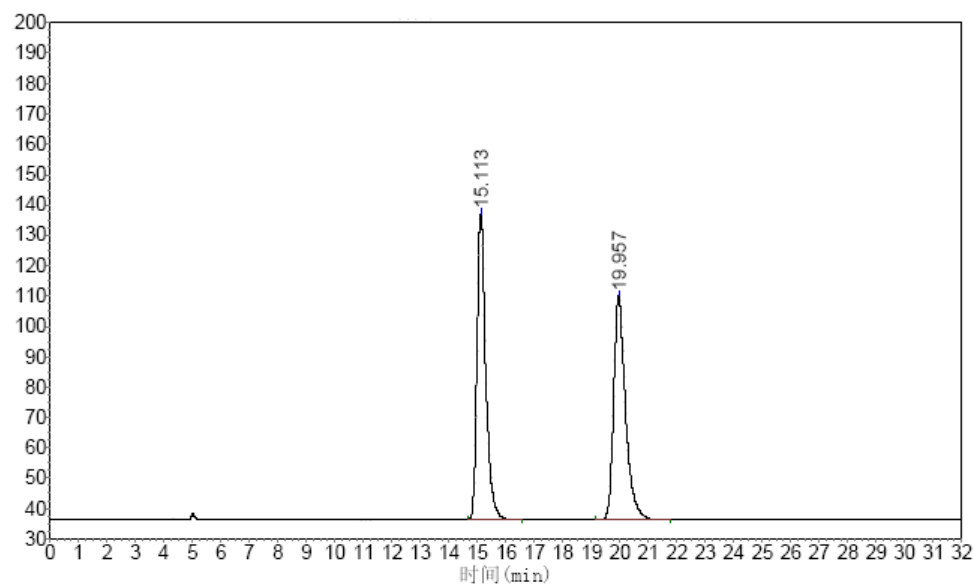


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	16.382	87181.922	2079067.750	98.1809
2	22.825	1064.823	38521.910	1.8191
Total		88246.745	2117589.660	100.0000

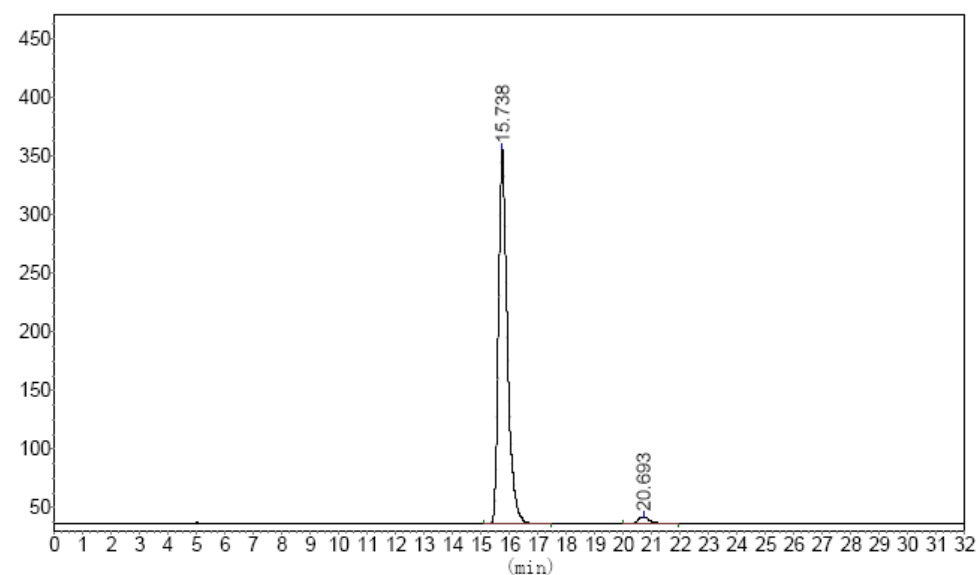




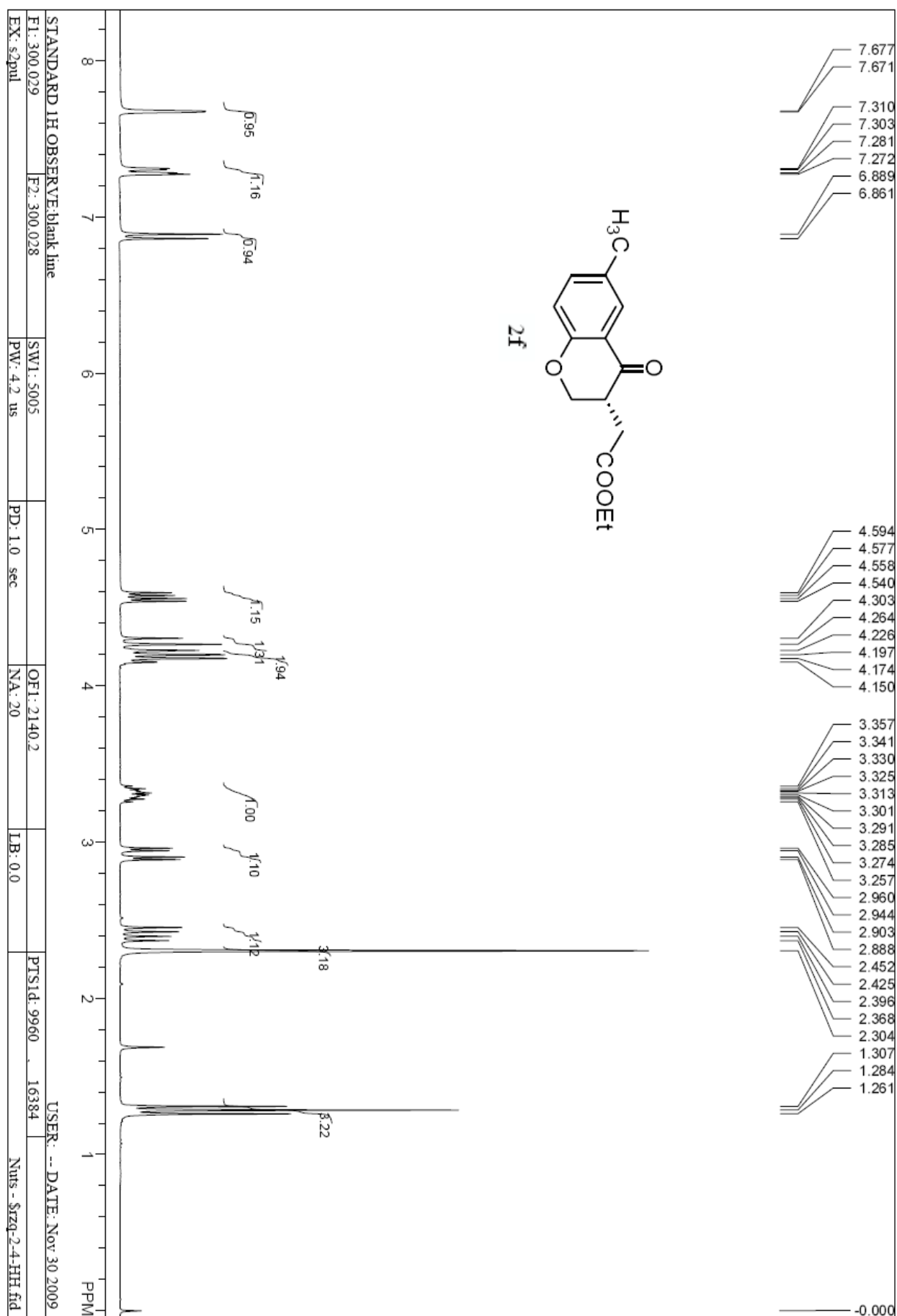
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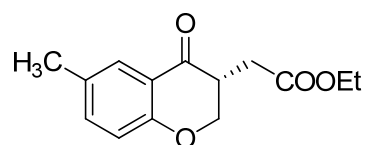


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15.113	100722.195	2131086.750	49.9286
2	19.957	73797.125	2137185.500	50.0714
Total		174519.320	4268272.250	100.0000

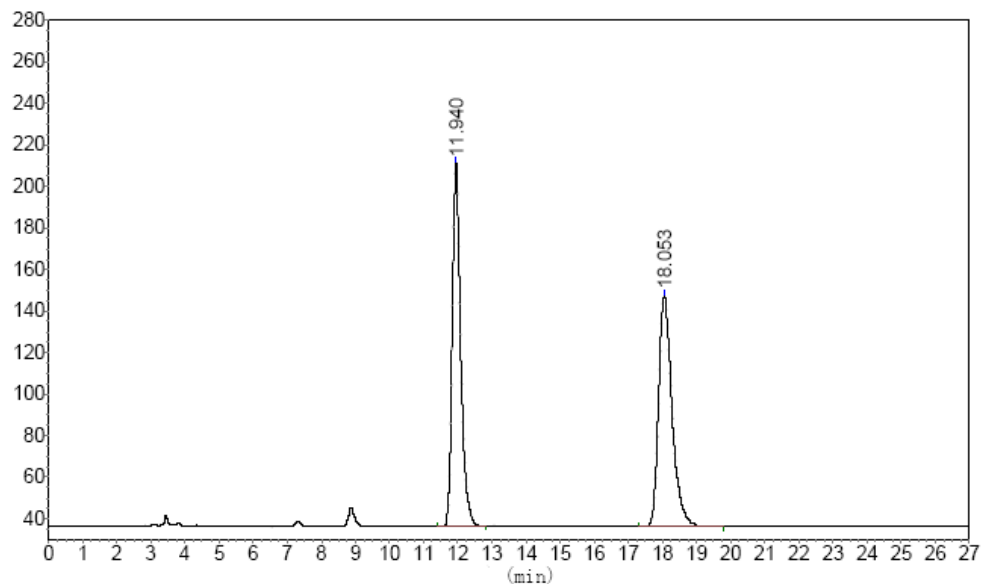


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	15.738	319737.563	6873645.000	97.6806
2	20.693	5801.177	163210.078	2.3194
Total		325538.740	7036855.078	100.0000

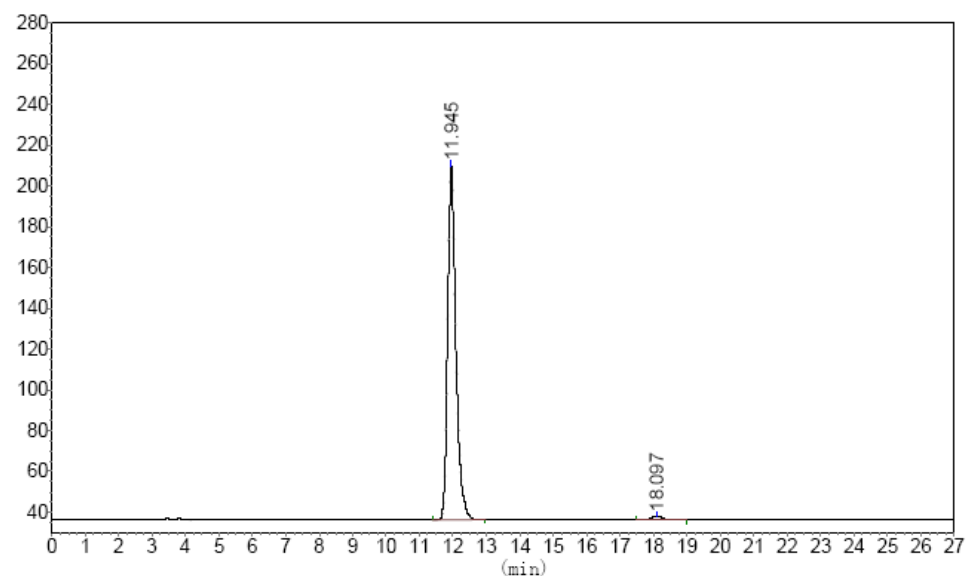




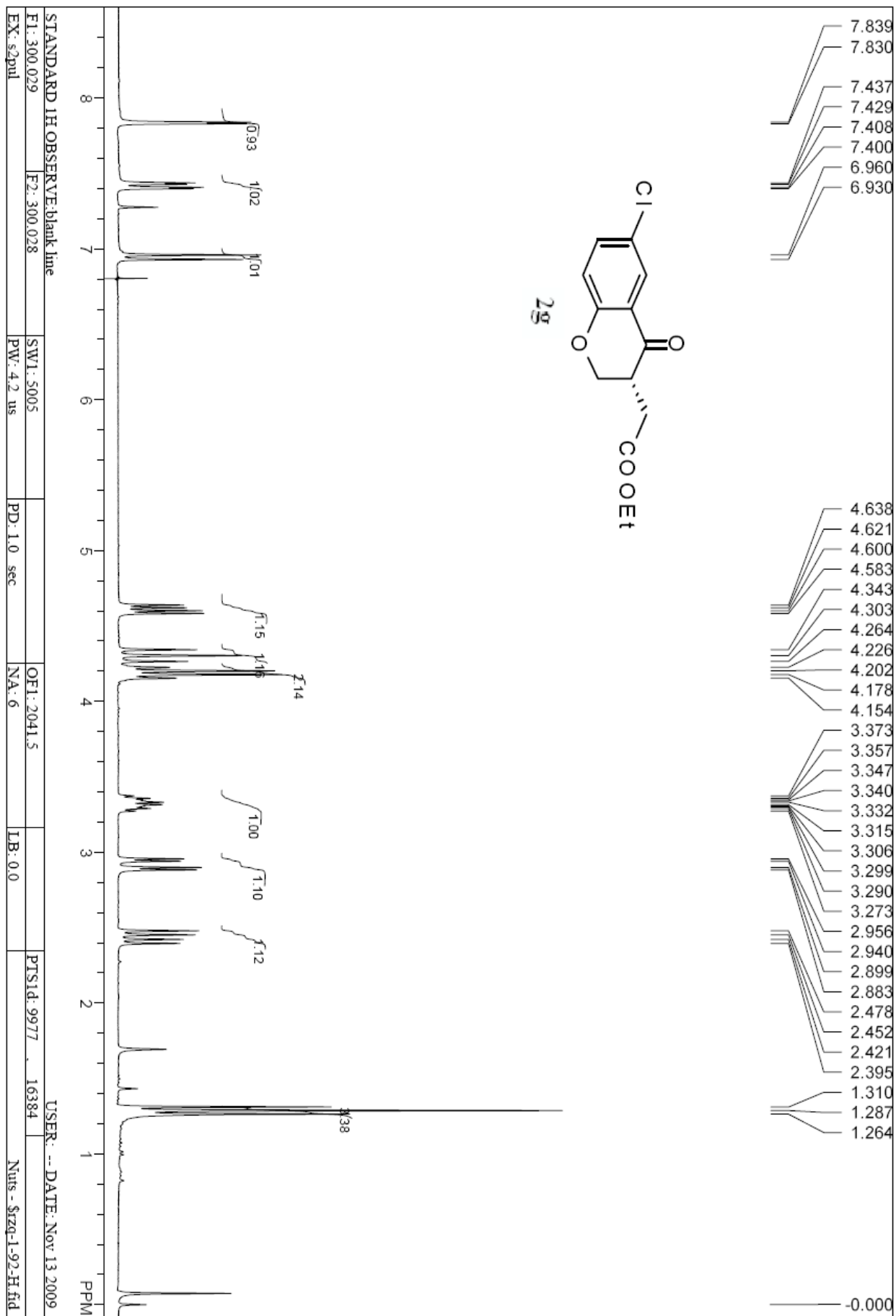
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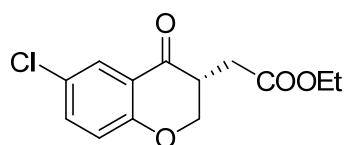


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.940	175482.531	3034205.750	49.9144
2	18.053	111658.234	3044612.750	50.0856
Total		287140.766	6078818.500	100.0000

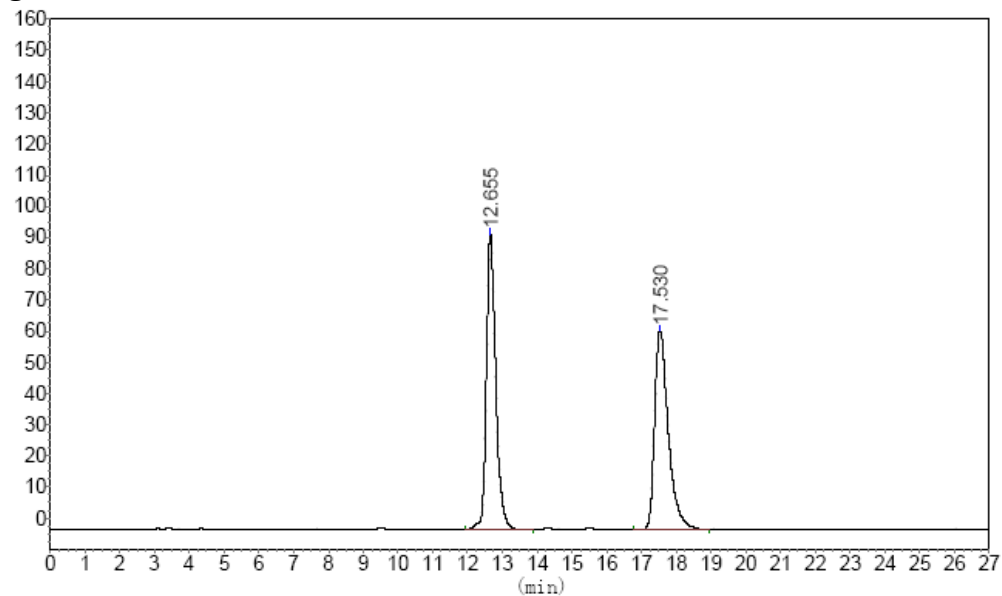


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	11.945	173726.922	2997261.000	98.5814
2	18.097	1629.894	43132.145	1.4186
Total		175356.816	3040393.145	100.0000

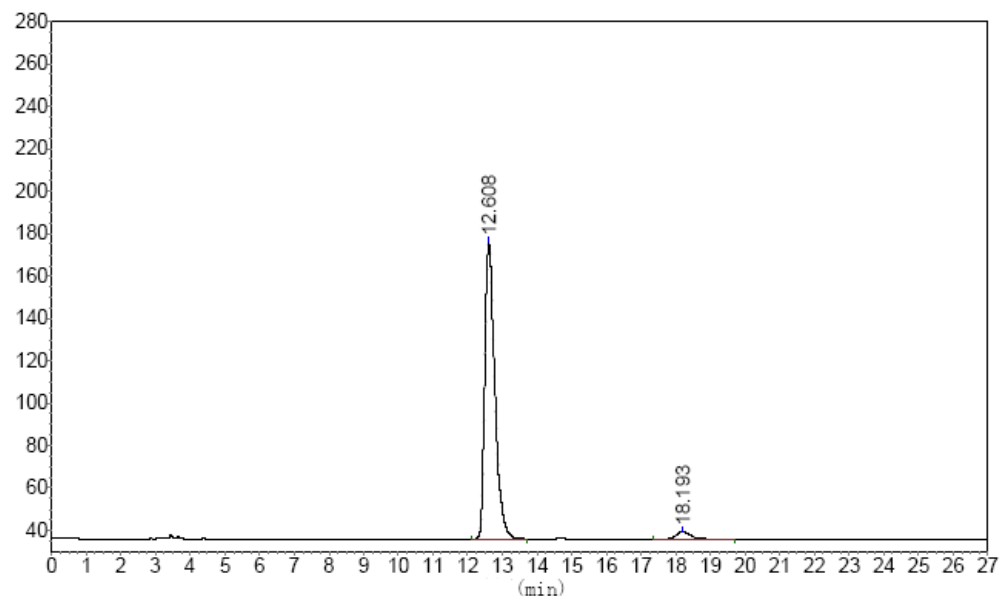




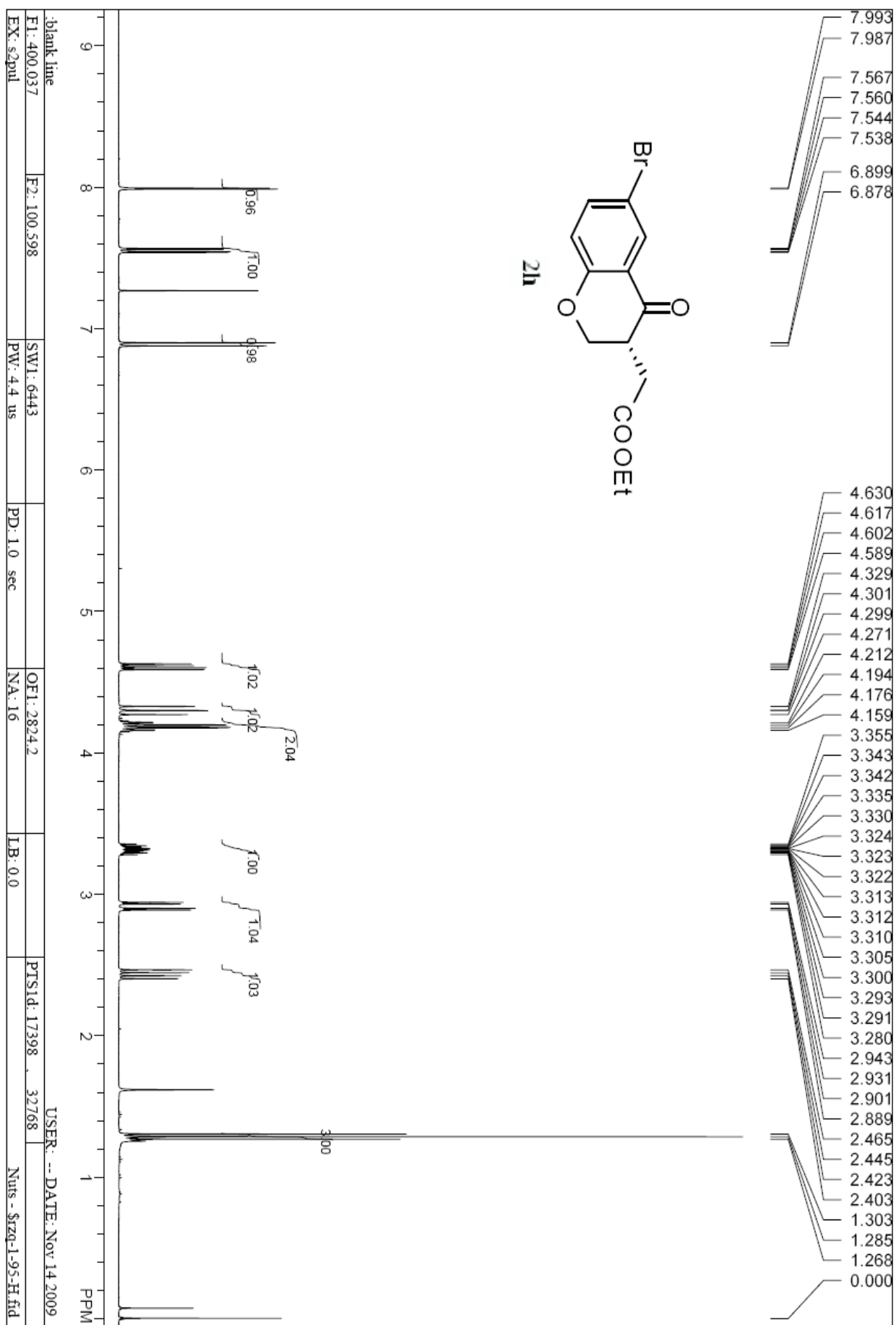
2g

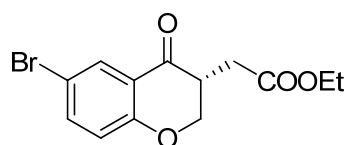


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.655	94711.570	1764997.500	50.4948
2	17.530	63639.520	1730408.375	49.5052
Total		158351.090	3495405.875	100.0000

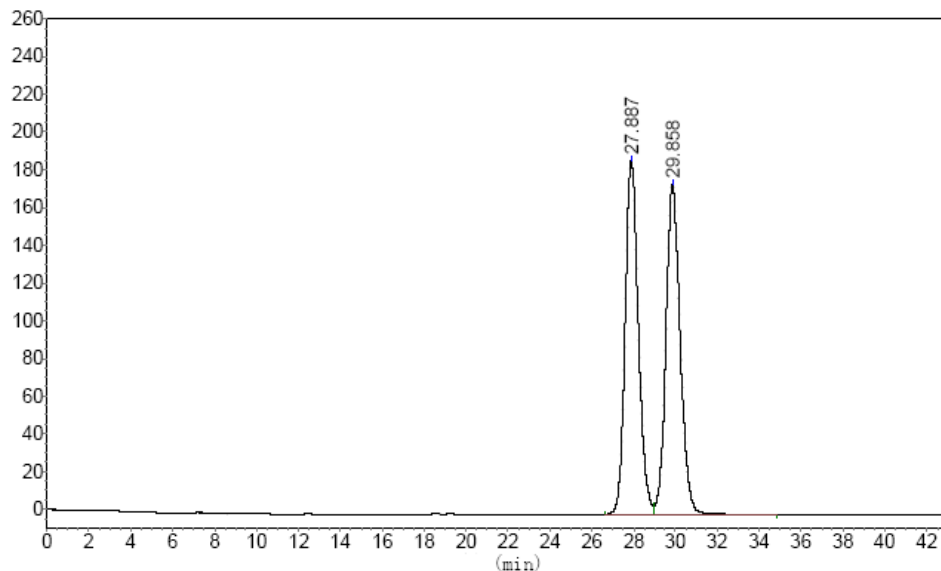


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	12.608	140461.266	2815701.000	96.5413
2	18.193	3531.486	100876.914	3.4587
Total		143992.752	2916577.914	100.0000

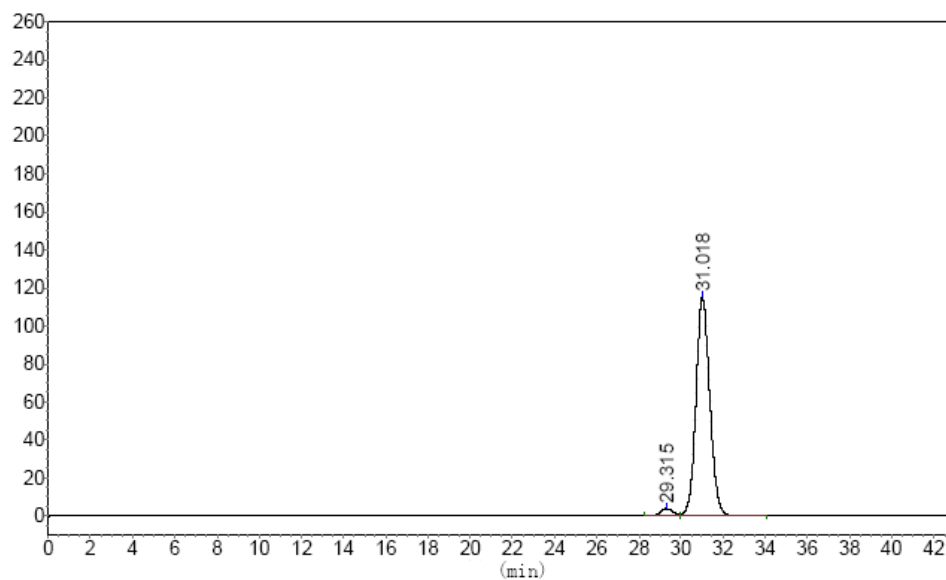




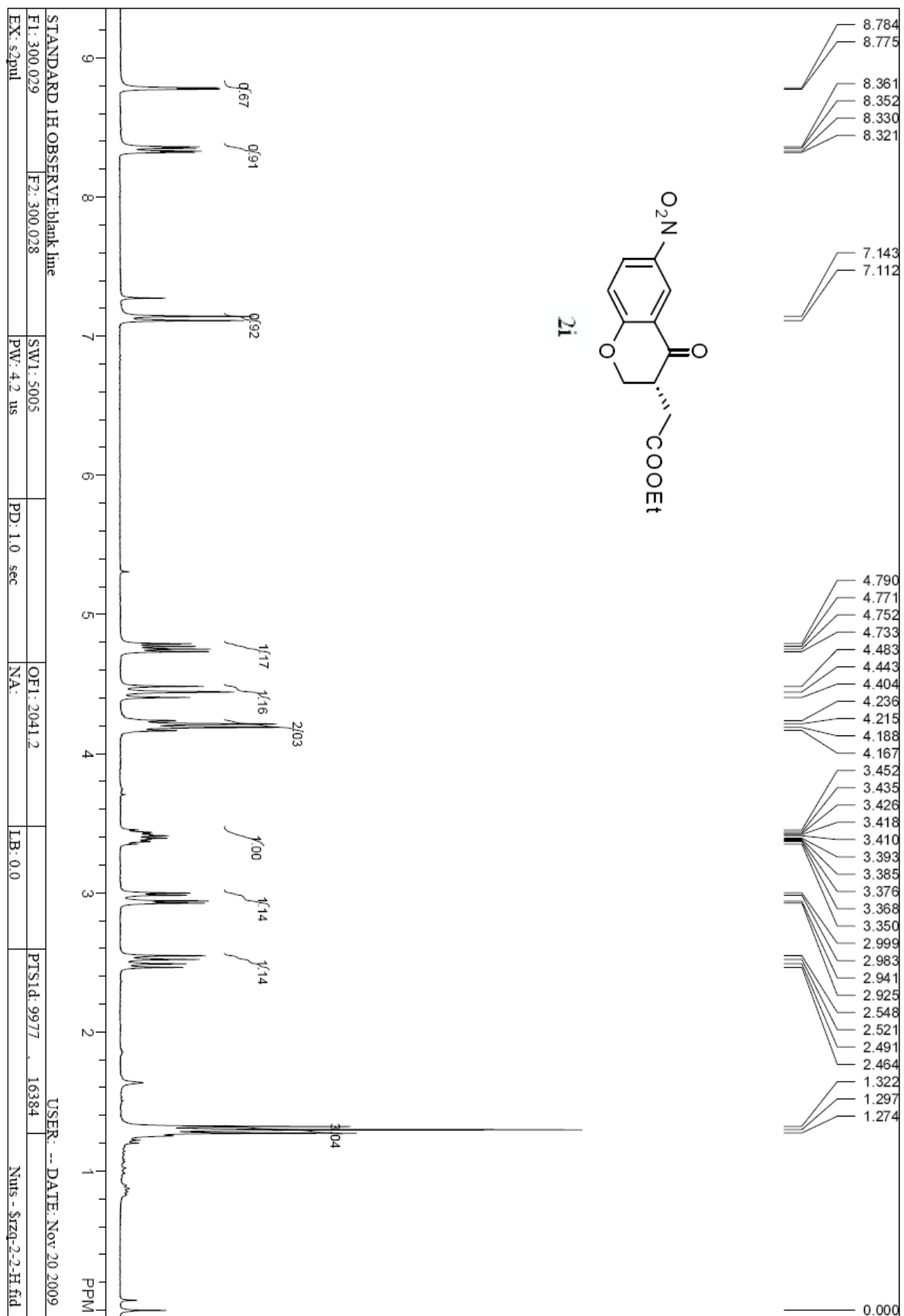
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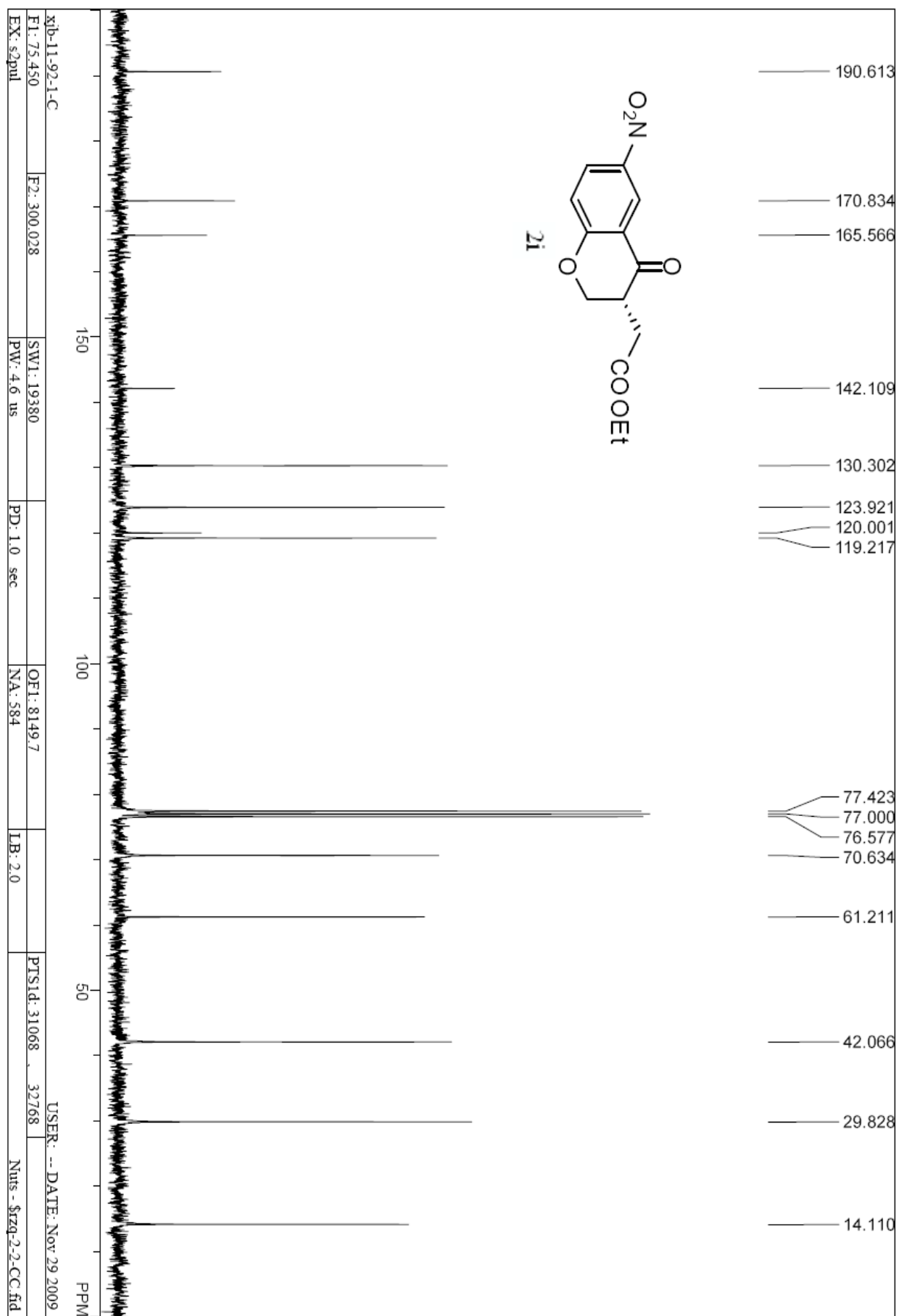


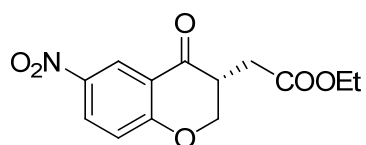
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	27.887	187701.813	8198055.500	49.7439
2	29.858	175099.938	8282472.500	50.2561
Total		362801.750	16480528.000	100.0000



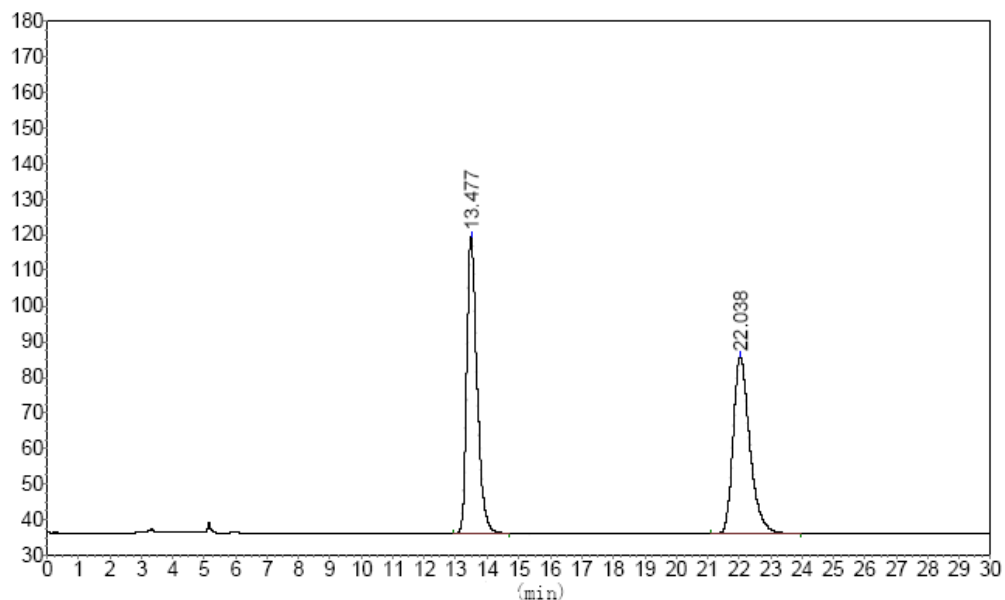
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	29.315	4021.336	167707.969	3.0849
2	31.018	115405.688	5268694.000	96.9151
Total		119427.023	5436401.969	100.0000



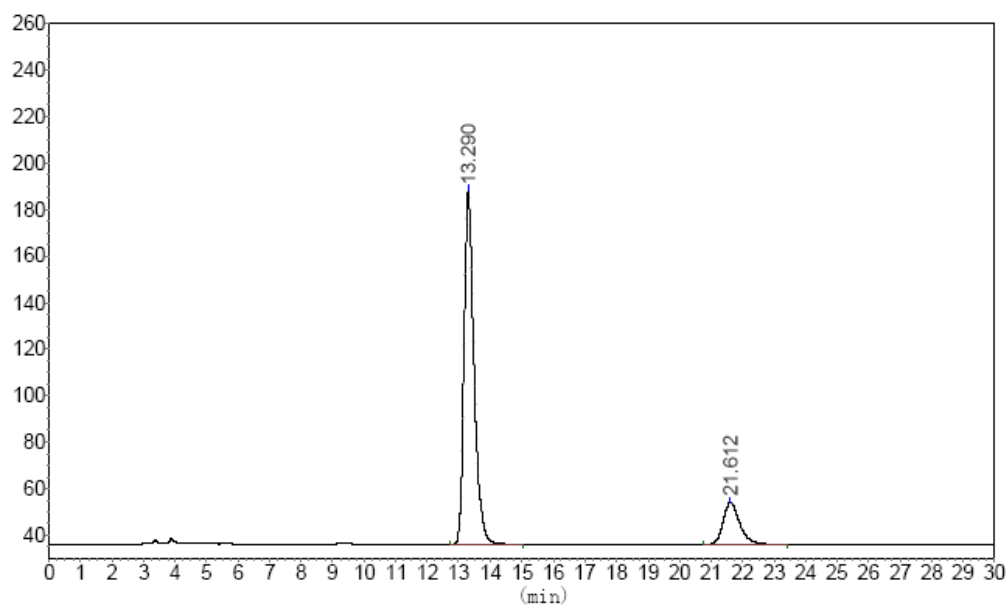




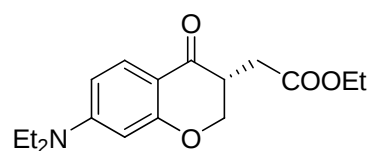
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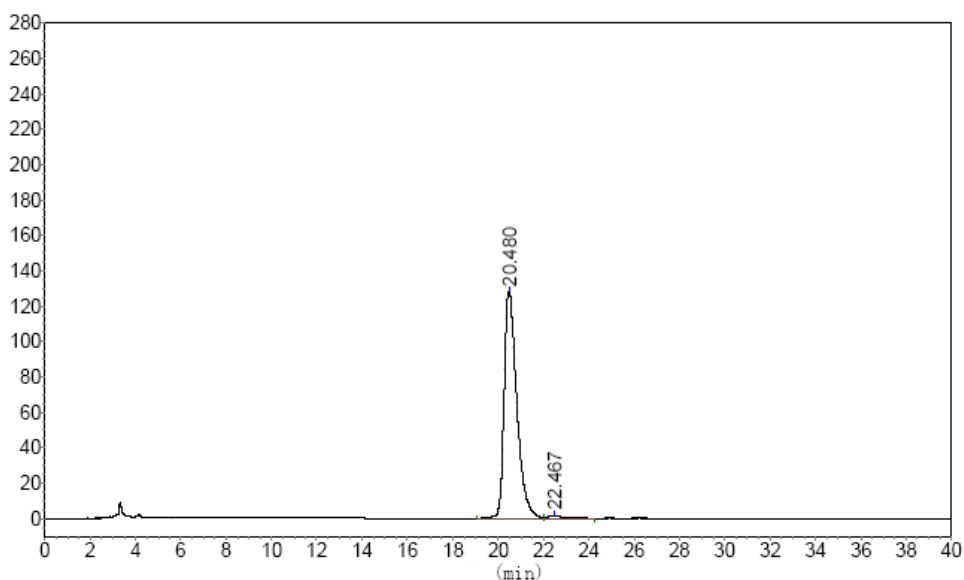
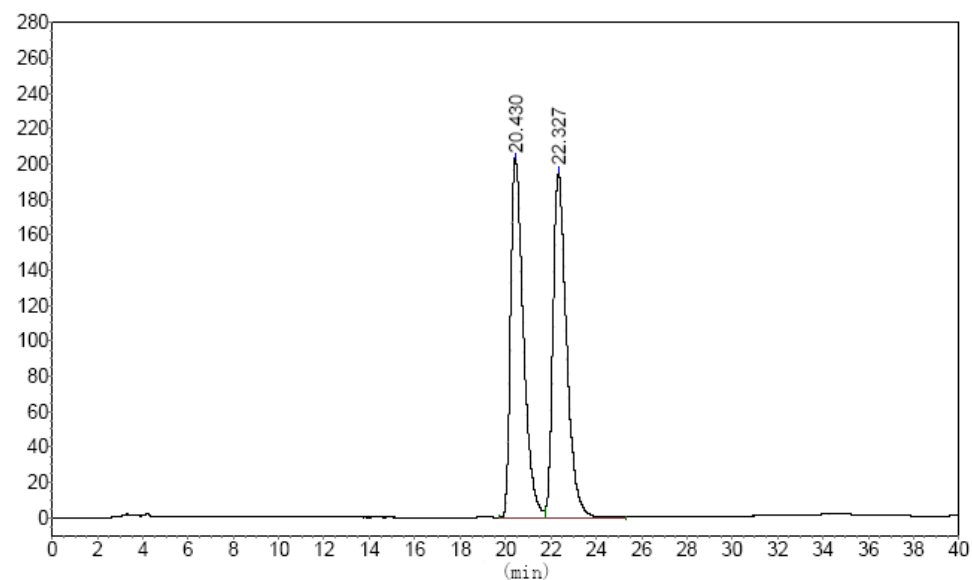
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.477	83393.188	1899135.500	50.9379
2	22.038	49673.727	1829197.750	49.0621
Total		133066.914	3728333.250	100.0000

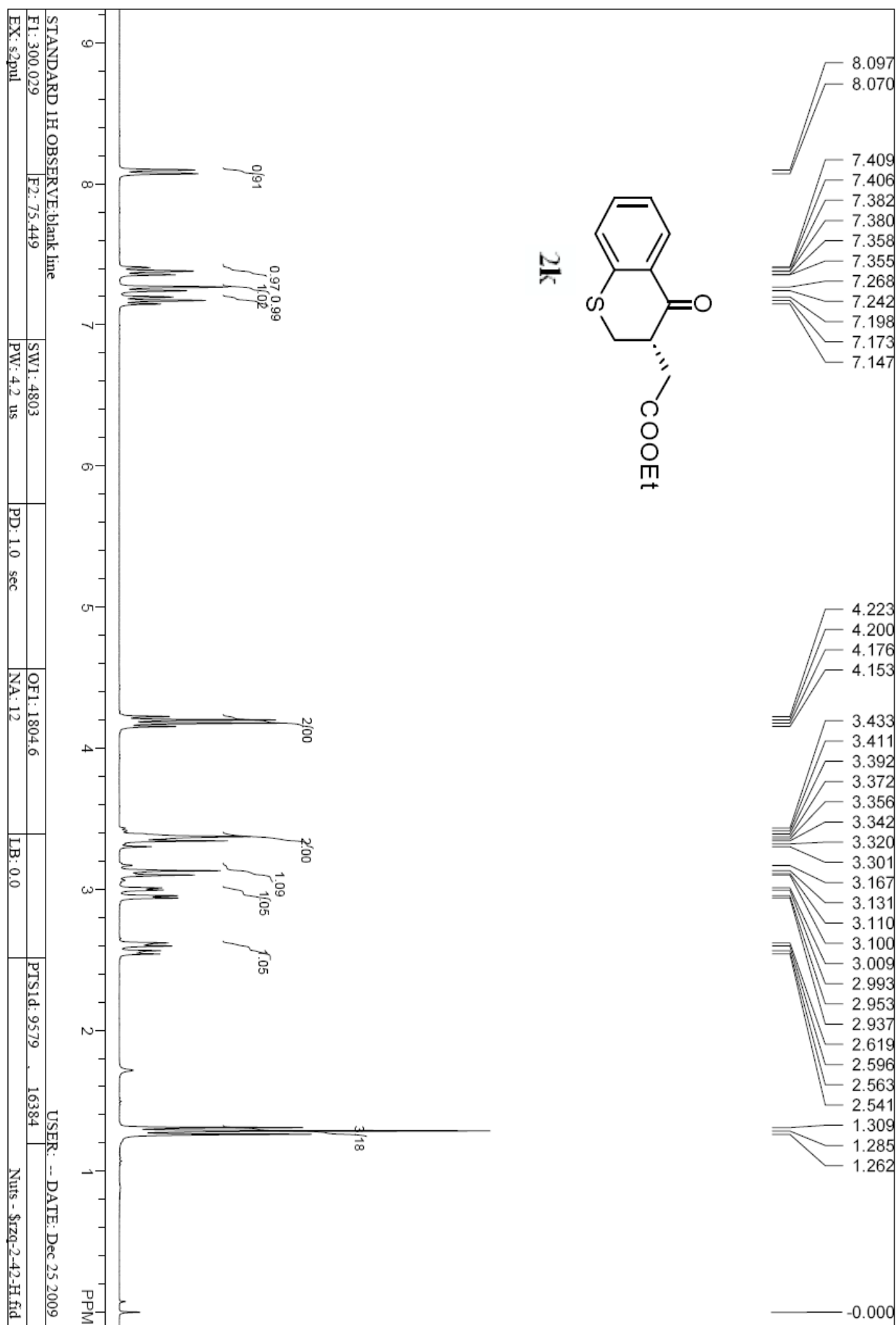


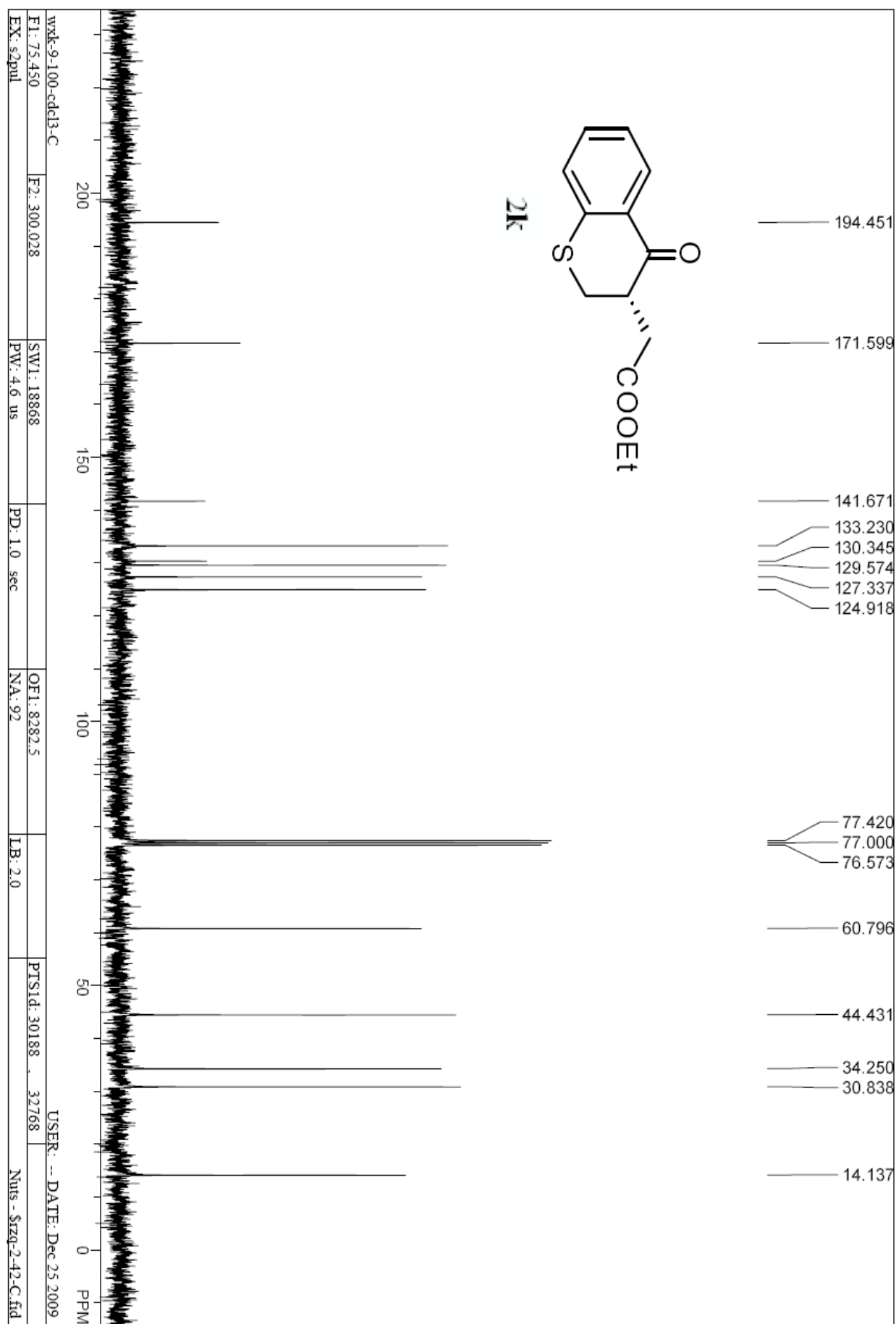
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	13.290	151971.938	3358172.000	83.8386
2	21.612	17961.596	647346.875	16.1614
Total		169933.533	4005518.875	100.0000

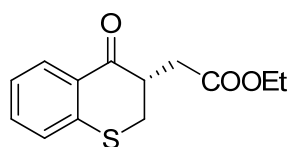


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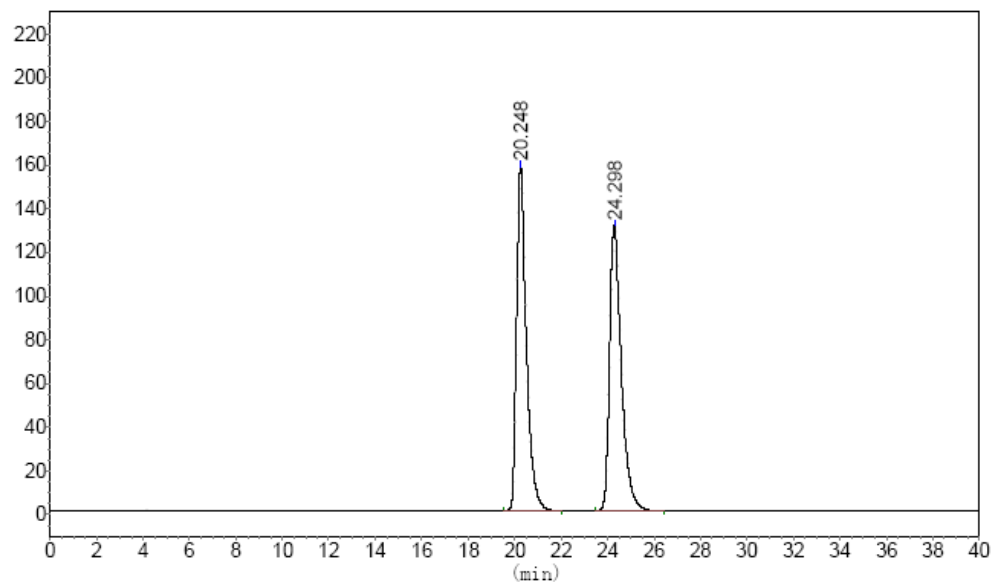




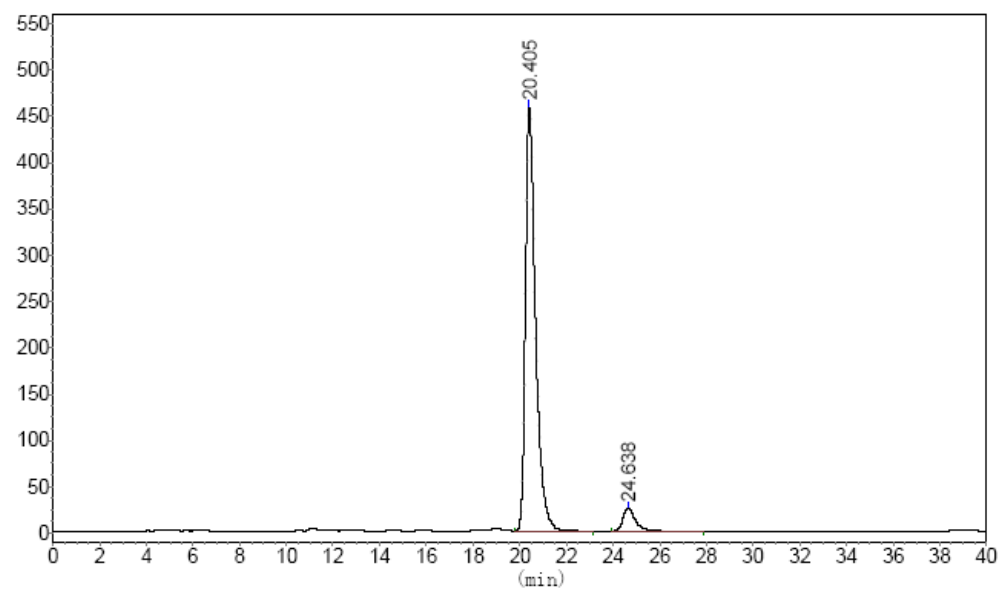




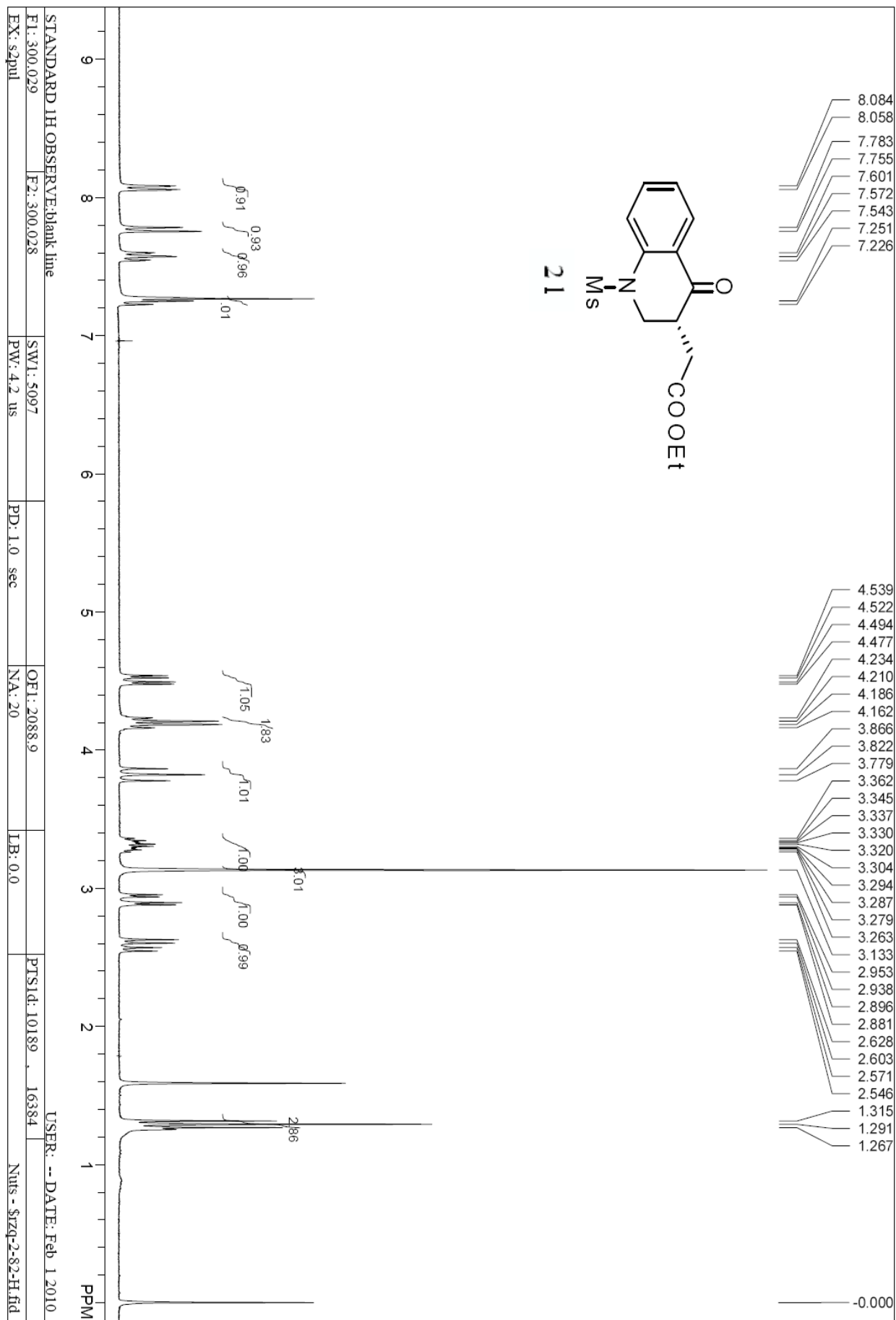
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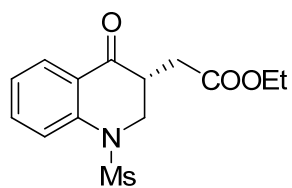


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20.248	157529.031	4598128.000	50.0381
2	24.298	130613.055	4591133.500	49.9619
Total		288142.086	9189261.500	100.0000

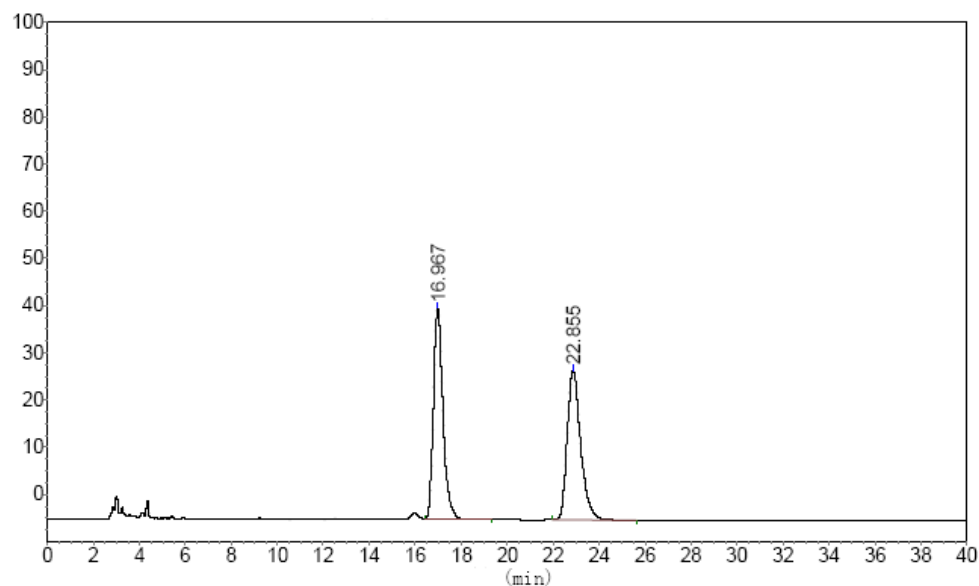


Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20.405	459216.469	13779534.000	93.9723
2	24.638	24825.555	883867.313	6.0277
Total		484042.023	14663401.313	100.0000

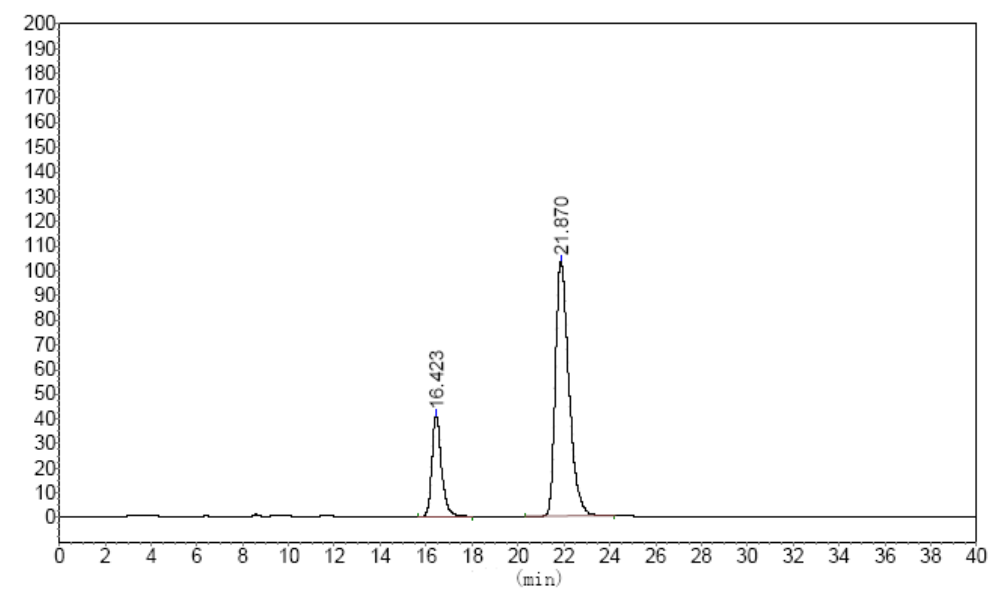




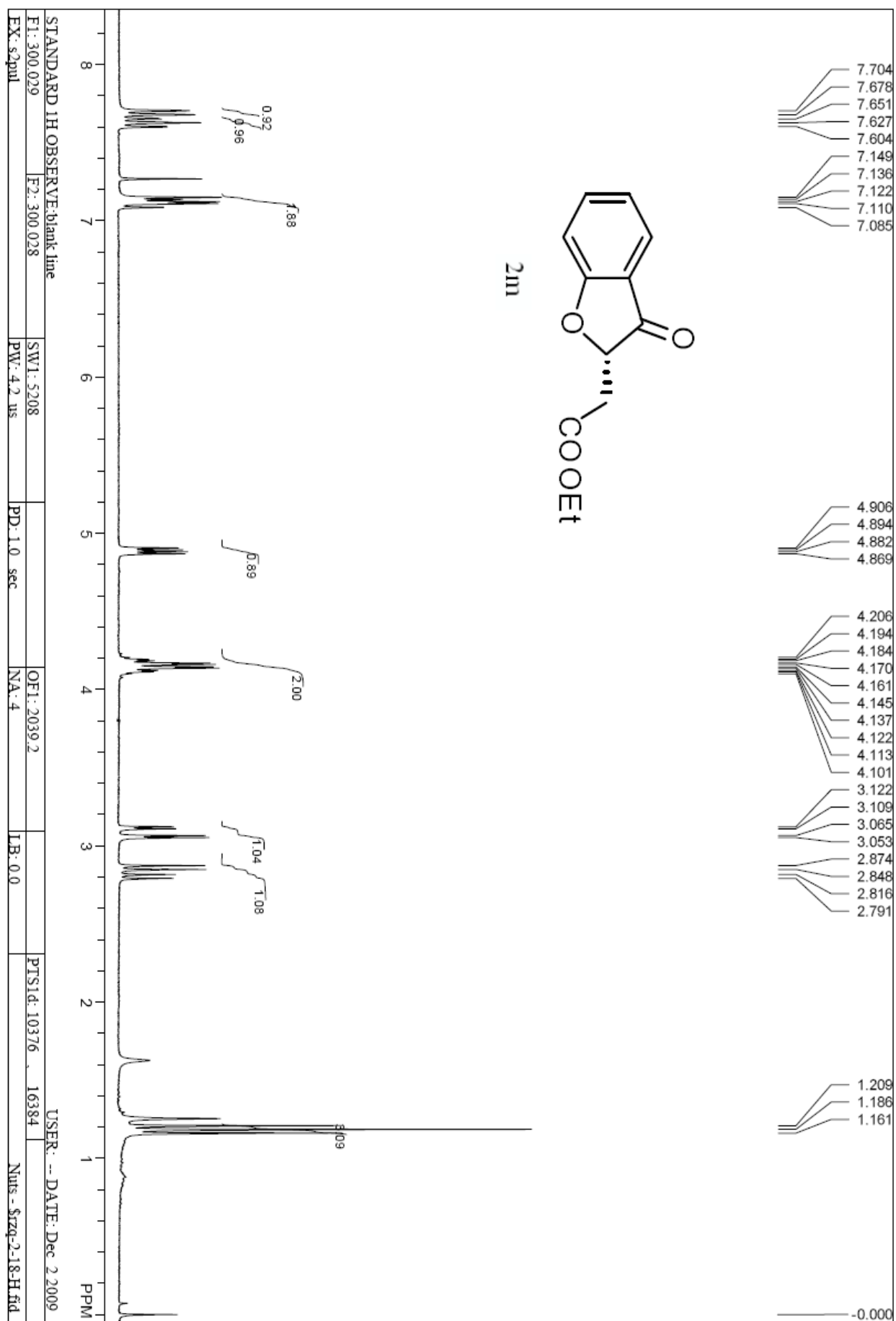
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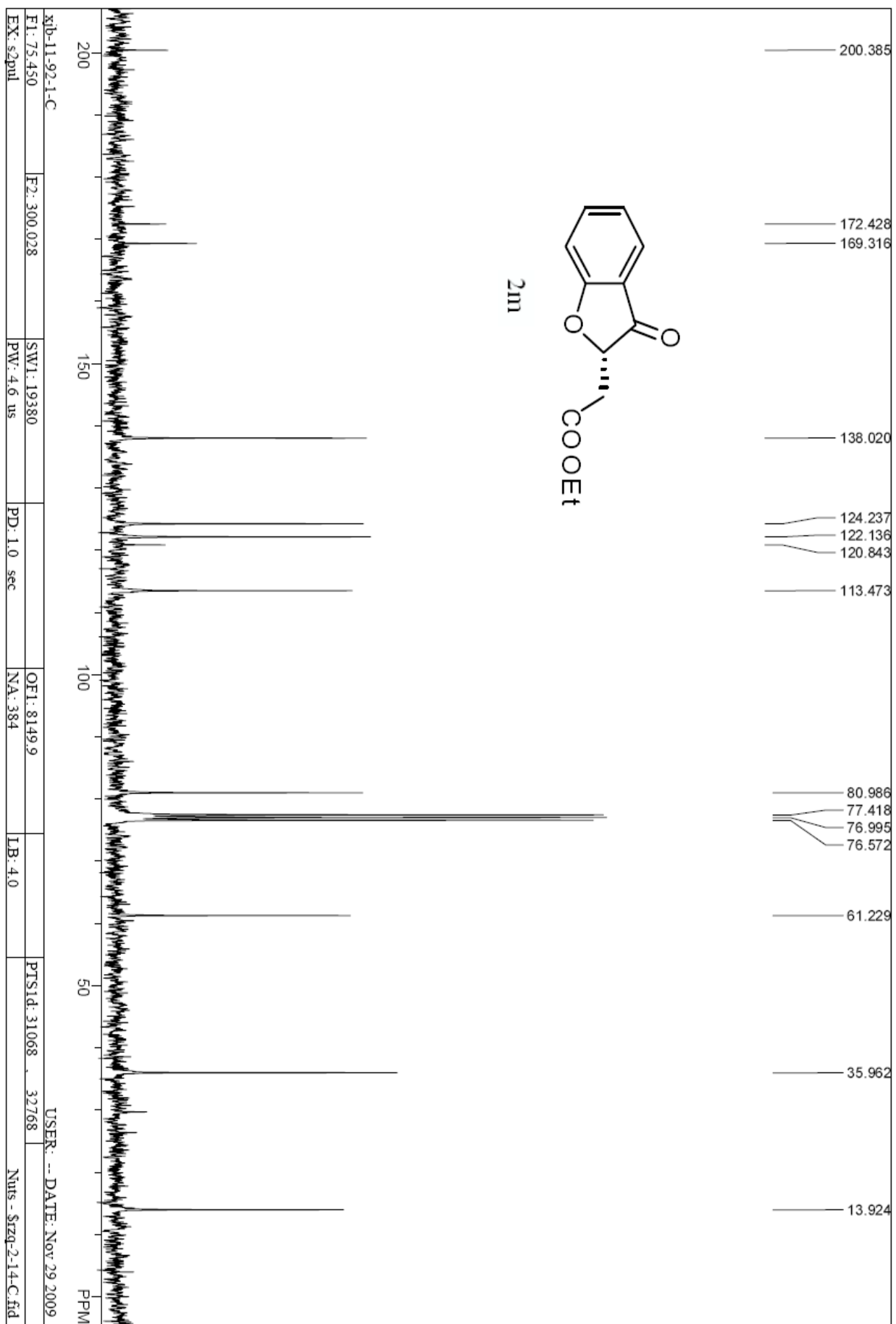


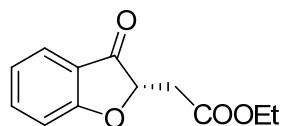
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	16.967	44883.520	1312007.125	50.3181
2	22.855	31734.691	1295417.250	49.6819
Total		76618.211	2607424.375	100.0000



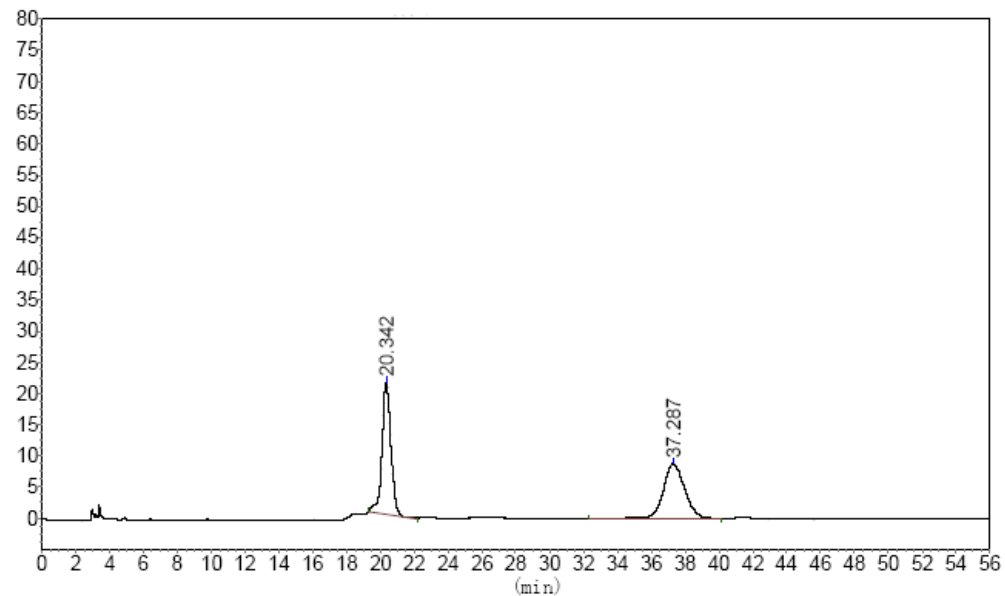
Peak No.	R. Time	Peak Height	Peak Area	Percent
1	16.423	40916.996	1187172.375	21.9969
2	21.870	103373.563	4209817.000	78.0031
Total		144290.559	5396989.375	100.0000



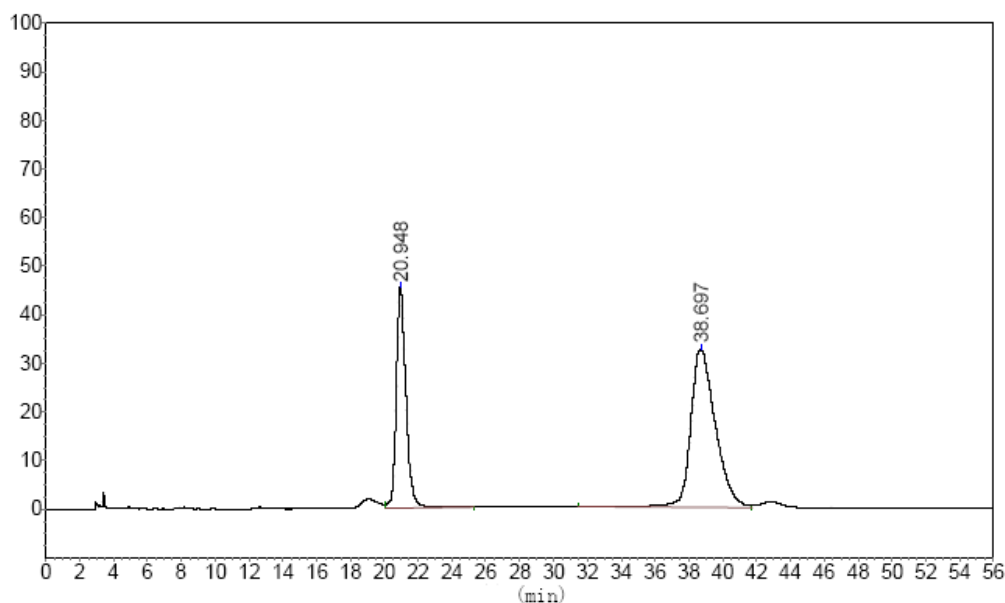




2m



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20.342	21179.414	771577.500	49.9817
2	37.287	8756.937	772141.625	50.0183
Total		29936.351	1543719.125	100.0000



Peak No.	R. Time	Peak Height	Peak Area	Percent
1	20.948	45327.813	1787684.250	35.1421
2	38.697	32604.576	3299338.000	64.8579
Total		77932.389	5087022.250	100.0000