

Supporting Information

Phosphine-Catalyzed Asymmetric (3+2) Annulations of δ -Acetoxy Allenates with 2-Naphthols

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1. General Information

Unless otherwise noted, all reagents were obtained commercially and used without further purification.

NMR spectrum: ^1H and ^{13}C spectra are recorded on the Bruker AVANCE spectrometer, operating at 400 MHz (300 MHz or 500 MHz) for ^1H NMR and 100 MHz (75 MHz or 125 MHz) for ^{13}C NMR. Chemical shifts are reported in parts per million (ppm). Chemical shifts are reported downfield from CDCl_3 (δ : 7.28 ppm) for ^1H NMR. Chemical shifts of ^{13}C NMR are reported in the scale relative to the solvent of CDCl_3 (δ : 77.0 ppm) used as an internal reference. Multiplicities are recorded as follows: s (singlet), d (doublet), t (triplet), dd (doublet of doublet), dt (doublet of triplet), m (multiplet), brs (broad singlet), qd (quartet of double). Coupling constants are reported in Hertz (Hz).

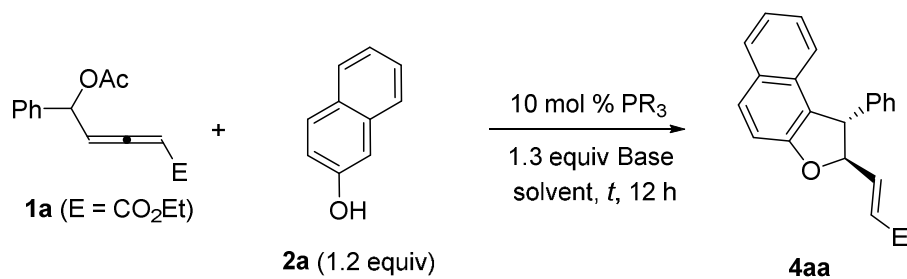
Mass spectroscopy: Mass spectra were in general recorded on an AMD 402/3 or a HP 5989A mass selective detector.

High Performance Liquid Chromatography: HPLC analysis was performed on Waters equipment using Daicel Chiralpak AD-H and OD-H column.

Spectropolarimeter: Optical rotations were measured on a Autopol IV-T polarimeter.

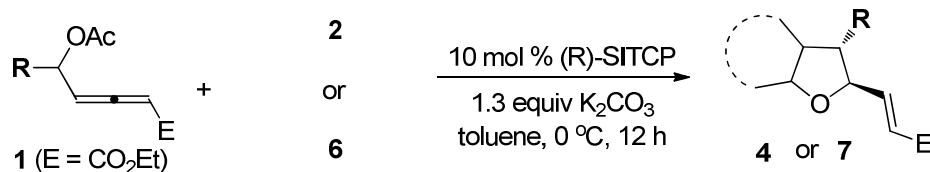
Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

2. Optimization of Reaction Conditions^a

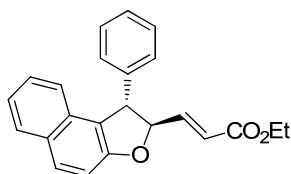


entry	Cat.	Solvent	Base	T (°C)	yield (%)	ee (%)
1	PPh ₃	toluene	K ₂ CO ₃	rt	67	--
2	PBu ₃	toluene	K ₂ CO ₃	rt	43	--
3	PPh ₂ Me	toluene	K ₂ CO ₃	rt	81	--
4	PPhMe ₂	toluene	K ₂ CO ₃	rt	95	--
5	PPhMe ₂	DCM	K ₂ CO ₃	rt	68	--
6	PPh ₂ Me	EtOAc	K ₂ CO ₃	rt	57	--
7	PPh ₂ Me	THF	K ₂ CO ₃	rt	61	--
8	PPh ₂ Me	CHCl ₃	K ₂ CO ₃	rt	34	-
9	PPh ₂ Me	CH ₃ CN	K ₂ CO ₃	rt	< 5	--
10	PPhMe ₂	toluene	Na ₂ CO ₃	rt	90	--
11	PPhMe ₂	toluene	Cs ₂ CO ₃	rt	76	--
12	PPhMe ₂	toluene	Et ₃ N	rt	83	--
13	PPhMe ₂	toluene	DBU	rt	<5	--
14	(R)-SITCP	toluene	K ₂ CO ₃	rt	95	88
15	(R)-SITCP	toluene	K ₂ CO ₃	0	94	92
16	(R)-SITCP	toluene	K ₂ CO ₃	-20	51	91
17	(R)-SITCP	toluene	K ₂ CO ₃	-40	trace	--

3. Synthesis of products 4 and 7



General Procedure: To a 25 mL flask was added catalysts (R)-SITCP (0.02 mmol, 7.1 mg), K_2CO_3 (0.26 mmol, 35.9 mg), **2** or **6** (0.24 mmol), and toluene (1.5 mL). After the mixture was stirred at 0°C for five minutes, a solution of **1** (0.20 mmol) in toluene (1.5 mL) was slowly added. After 12 h, the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product.



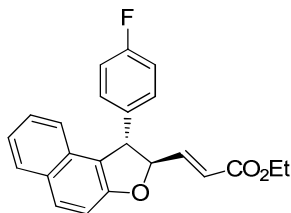
4aa, Yield = 94%, 64.6 mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.86-7.82(m, 2H), 7.38-7.26 (m, 9H), 7.20 (dd, $J = 5.2$ Hz, $J = 15.6$ Hz, 1H), 6.20 (d, $J = 15.6$ Hz, 1H), 5.33 (t, $J = 5.6$ Hz, 1H), 4.83 (d, $J = 6.0$ Hz, 1H), 4.25 (q, $J = 7.2$ Hz, 2H), 1.33 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 166.14, 157.26, 144.81, 142.05, 130.60, 129.17, 128.90, 127.50, 126.95, 123.24, 122.85, 121.56, 119.67, 112.17, 90.30, 60.72, 54.54, 14.29.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{20}\text{O}_3$ ($\text{M}+\text{Na}^+$) 367.1305, found 367.1307.

$[\alpha]_D^{25} = +181.6$ ($c = 0.5$ in CH_2Cl_2); 92% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_R = 5.1$ min and 7.5 min].



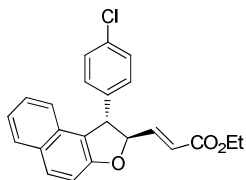
4ba, Yield = 80 %, 60.2mg, light yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.85-7.81(m, 2H), 7.32-7.20 (m, 6H), 7.15 (dd, $J = 5.6$ Hz, $J = 15.6$ Hz, 1H), 7.06-7.00(m, 2H), 6.16 (dd, $J = 1.6$ Hz, $J = 15.6$ Hz, 1H), 5.27-5.22(m, 1H), 4.79 (d, $J = 6.0$ Hz, 1H), 4.23 (q, $J = 7.2$ Hz, 2H), 1.31 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.06, 157.18, 144.49, 130.74, 130.42, 130.05, 129.33, 129.22, 128.95, 127.00, 123.30, 122.64, 121.72, 119.37, 116.18, 115.89, 112.16, 90.21, 60.74, 53.74, 14.24.

HRMS (ESI) Calcd for C₂₃H₁₉FO₃ (M+Na⁺) 385.1210, found 385.1214.

[α]_D²⁵ = +412.0 (c = 0.75 in CH₂Cl₂); 93% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, $\lambda_{\max}$ 254 nm, t_R = 5.2 min and 7.0 min].



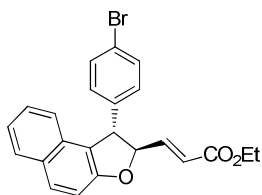
4ca, Yield = 69 %, 52.3mg, light yellow liquid.

¹H NMR (400 MHz, CDCl₃): δ 7.85-7.81(m, 2H), 7.33-7.11 (m, 9H), 6.16 (dd, J =1.2 Hz, J = 15.6 Hz, 1H), 5.26-5.22(m, 1H), 4.78 (d, J = 6.0 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 166.02, 157.26, 144.38, 140.47, 133.32, 130.83, 130.38, 130.04, 129.33, 129.09, 128.97, 127.08, 123.35, 122.61, 119.11, 112.18, 90.09, 60.76, 53.88, 14.24.

HRMS (ESI) Calcd for C₂₃H₁₉ClO₃ (M+H⁺) 379.1095, found 379.1096.

[α]_D²⁵ = +324.4 (c = 1.3 in CH₂Cl₂); 92% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, $\lambda_{\max}$ 254 nm, t_R = 5.4 min and 7.2 min].



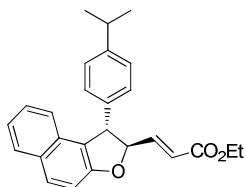
4da, Yield = 78%, 66.3 mg, yellow liquid.

¹H NMR (400 MHz, CDCl₃): δ 7.85-7.81(m, 2H), 7.48-7.44(m, 2H), 7.33-7.11 (m, 7H), 6.16 (dd, J =1.6 Hz, J = 15.6 Hz, 1H), 5.26-5.22(m, 1H), 4.76 (d, J = 7.0 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 166.02, 157.28, 144.36, 140.99, 132.28, 130.84, 130.37, 130.04, 129.45, 128.97, 127.09, 123.36, 122.60, 121.83, 121.42, 119.03, 112.16, 90.02, 60.76, 53.95, 14.24.

HRMS (ESI) Calcd for C₂₃H₁₉BrO₃ (M+Na⁺) 445.0410, found 445.0413.

[α]_D²⁵ = +166.4 (c = 0.5 in CH₂Cl₂); 89% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, $\lambda_{\max}$ 254 nm, t_R = 5.7 min and 7.8 min].



4ea, Yield = 96%, 74.2 mg, yellow liquid.

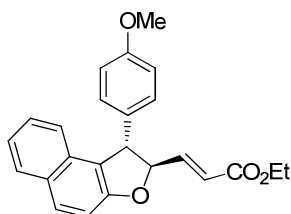
¹H NMR (300 MHz, CDCl₃): δ 7.74-7.68(m, 2H), 7.21-7.14 (m, 4H), 7.10-7.02 (m,

5H), 6.06 (dd, $J=1.5$ Hz, $J=15.6$ Hz, 1H), 5.19(m, 1H), 4.66 (d, $J=5.7$ Hz, 1H), 4.12 (q, $J=7.2$ Hz, 2H), 2.84-2.74 (m, 1H), 1.20 (t, $J=7.2$ Hz, 3H), 1.15 (d, $J=2.1$ Hz, 3H), 1.13 (d, $J=2.1$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.19, 157.12, 147.99, 144.99, 139.35, 130.64, 130.44, 129.99, 128.83, 127.14, 126.84, 123.15, 122.93, 121.36, 119.87, 112.16, 90.28, 60.67, 54.07, 33.75, 23.96, 14.25.

HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_3$ ($\text{M}+\text{H}^+$) 387.1955, found 387.1956.

$[\alpha]_D^{25} = +405.2$ ($c = 1.8$ in CH_2Cl_2); 93% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_R = 4.4$ min and 5.3 min].



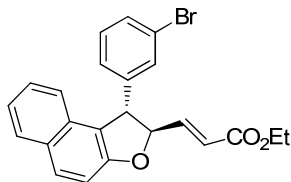
4fa, Yield = 99%, 74.1 mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.87-7.79(m, 2H), 7.29-7.26 (m, 4H), 7.19-7.13(m, 3H), 6.87 (d, $J=8.8$ Hz, 2H), 6.16 (dd, $J=1.2$ Hz, $J=15.6$ Hz, 1H), 5.27-5.23(m, 1H), 4.76 (d, $J=6.4$ Hz, 1H), 4.23 (q, $J=7.2$ Hz, 2H), 3.80(s, 3H), 1.30 (t, $J=7.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.17, 158.88, 157.09, 144.85, 134.07, 130.58, 130.46, 130.02, 128.85, 128.80, 126.85, 123.17, 122.82, 121.45, 119.83, 114.46, 112.13, 90.43, 60.69, 55.28, 53.79, 14.24.

HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_4$ ($\text{M}+\text{Na}^+$) 397.1410, found 397.1412.

$[\alpha]_D^{25} = +339.6$ ($c = 2.2$ in CH_2Cl_2); 91% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_R = 6.4$ min and 8.1 min].



4ga, Yield = 85%, 71.6mg, yellow liquid

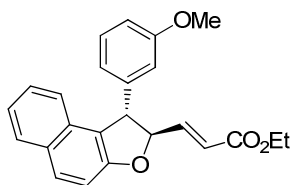
^1H NMR (400 MHz, CDCl_3): δ 7.85-7.82(m, 2H), 7.44-7.42 (m, 2H), 7.33-7.11 (m, 7H), 6.17 (d, $J=15.6$ Hz, 1H), 5.28(t, $J=5.2$ Hz, 1H), 4.75 (d, $J=6.0$ Hz, 1H), 4.203(q, $J=7.2$ Hz, 2H), 1.31 (t, $J=7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 166.02, 157.30, 144.41, 144.34, 130.95, 130.75, 130.68, 130.38, 130.06, 128.99, 127.17, 126.42, 123.41, 123.25, 122.61, 121.85, 118.92, 112.20, 89.96, 60.78, 54.09, 14.27.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{19}\text{BrO}_3$ ($\text{M}+\text{Na}^+$) 445.0410, found 445.0411.

$[\alpha]_D^{25} = +197.8$ ($c = 0.5$ in CH_2Cl_2); 85% ee [Chiralcel OD-H column, hexane /

i-PrOH = 90:10, 1.0 mL/min, $\lambda_{\max}$ 254 nm, t_R = 5.6 min and 7.9 min].



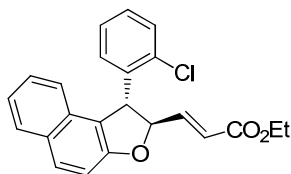
4ha, Yield = 90%, 67.4 mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.80-7.76(m, 2H), 7.27-7.20 (m, 4H), 7.12 (dd, J =5.6 Hz, J = 15.6 Hz, 1H), 6.83-6.75(m, 3H), 6.13 (dd, J = 1.6 Hz, J = 15.6 Hz, 1H), 5.29-5.25(m, 1H), 4.73 (d, J = 6.0 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 3.73(s, 3H), 1.27 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.14, 160.13, 157.20, 144.82, 143.66, 130.58, 130.16, 129.99, 128.84, 126.93, 123.22, 122.82, 121.51, 120.09, 119.50, 113.65, 112.47, 112.12, 90.14, 60.71, 55.23, 54.52, 23.87, 14.25.

HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_4$ ($\text{M}+\text{Na}^+$) 397.1410, found 397.1413.

$[\alpha]^{25}_{\text{D}} = +169.8$ (c = 0.5 in CH_2Cl_2); 91% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, $\lambda_{\max}$ 254 nm, t_R = 6.2 min and 8.8 min].



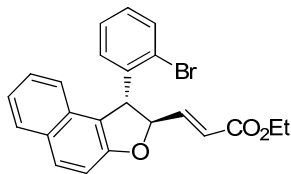
4ia, Yield = 45%, 34.1mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.86-7.83(m, 2H), 7.49 (d, J = 8.0 Hz, 1H), 7.36-7.17(m, 6H), 7.06 (t, J = 8.2 Hz, 1H), 6.72-6.70 (m, 1H), 6.20-6.16(m, 1H), 5.36-5.27(m, 2H), 4.20 (q, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 166.15, 157.66, 145.02, 133.27, 130.79, 130.57, 129.95, 129.71, 128.89, 128.62, 127.50, 127.21, 123.41, 122.85, 121.54, 118.48, 112.24, 89.18, 60.65, 29.72, 14.22.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{19}\text{ClO}_3$ ($\text{M}+\text{Na}^+$) 401.0915, found 401.0912.

$[\alpha]^{25}_{\text{D}} = +49.2$ (c = 0.5 in CH_2Cl_2); 91% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, $\lambda_{\max}$ 254 nm, t_R = 5.1 min and 6.0 min].



4ja, Yield = 40%, 33.9 mg, yellow liquid.

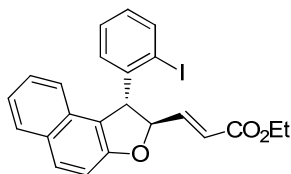
^1H NMR (300 MHz, CDCl_3): δ 7.86-7.83(m, 2H), 7.67-7.66(m, 1H), 7.35-7.23(m, 6H), 7.13-7.09(m, 1H), 6.70-6.68 (m, 1H), 6.18 (dd, J = 1.5 Hz, J = 15.6 Hz,

1H), 5.30-5.25(m, 2H), 4.20 (q, $J = 7.2$ Hz, 2H), 1.28 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 166.14, 157.65, 145.02, 132.99, 130.82, 129.96, 129.52, 128.93, 128.16, 127.23, 123.82, 123.43, 122.92, 121.63, 118.88, 112.23, 89.32, 60.65, 52.23, 29.34, 14.22.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{19}\text{BrO}_3$ ($\text{M}+\text{Na}^+$) 445.0410, found 445.0411.

$[\alpha]^{25}_{\text{D}} = +73.4$ ($c = 0.5$ in CH_2Cl_2); 92% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_{\text{R}} = 5.1$ min and 6.0min].



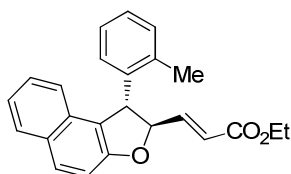
4ka, Yield = 34%, 32.1mg, yellow liquid.

^1H NMR (300 MHz, CDCl_3): δ 7.98(d, $J = 7.8$ Hz, 1H), 7.86(d, $J = 8.4$ Hz, 2H), 7.39-7.23(m, 5H), 7.15 (t, $J = 7.5$ Hz 1H), 6.97 (t, $J = 7.2$ Hz 1H), 6.71 (d, $J = 7.5$ Hz 1H), 6.24 (d, $J = 15.3$ Hz 1H), 5.24(s, 2H), 4.23(q, $J = 7.2$ Hz, 2H), 1.31(t, $J = 7.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.10, 157.60, 145.10, 144.19, 139.74, 130.85, 130.43, 130.06, 129.24, 129.14, 128.90, 127.28, 123.47, 123.07, 121.82, 119.74, 110.12, 89.64, 60.65, 57.26, 14.28.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{19}\text{IO}_3$ ($\text{M}+\text{Na}^+$) 493.0271, found 493.0272.

$[\alpha]^{25}_{\text{D}} = +78.6$ ($c = 0.5$ in CH_2Cl_2); 90% ee [Chiralcel AD-H column, hexane / i-PrOH = 95:5, 1.0 mL/min, λ_{max} 254 nm, $t_{\text{R}} = 11.5$ min and 13.7 min].



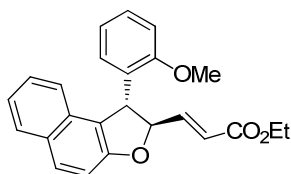
4la, Yield = 93%, 66.6 mg, yellow liquid.

^1H NMR (300 MHz, CDCl_3): δ 7.75-7.69(m, 2H), 7.19-7.15 (m, 4H), 7.11-7.04(m, 3H), 6.97-6.93(m, 1H), 6.83-6.59(m, 1H), 6.07 (dd, $J = 1.5$ Hz, $J = 15.6$ Hz, 1H), 5.15 (s, 1H), 4.95 (d, $J = 5.4$ Hz, 1H), 4.12 (q, $J = 7.2$ Hz, 2H), 2.46 (s, 3H), 1.20 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.13, 157.42, 144.96, 135.27, 130.84, 130.77, 130.72, 130.69, 130.00, 128.88, 128.80, 127.24, 127.00, 126.92, 123.26, 122.77, 121.71, 119.84, 112.13, 60.72, 20.28, 14.29.

HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_3$ ($\text{M}+\text{H}^+$) 359.1642, found 359.1645.

$[\alpha]^{25}_{\text{D}} = +293.2$ ($c = 1.0$ in CH_2Cl_2); 88% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_{\text{R}} = 4.9$ min and 6.4 min].



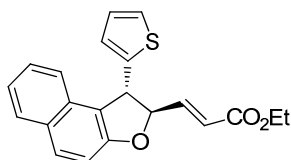
4ma, Yield = 85%, 63.6 mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.87-7.81(m, 2H), 7.34-7.24 (m, 7H), 6.99 (d, J = 8.0Hz, 1H), 6.77 (t, J = 7.2 Hz, 1H), 6.69 (d, J = 7.2 Hz, 1H), 6.18 (d, J = 15.6 Hz, 1H), 5.27 (t, J = 4.0 Hz, 1H), 5.18 (d, J = 4.0 Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 4.00(s, 3H), 1.30 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.48, 157.63, 156.67, 148.37, 131.02, 130.27, 129.91, 129.81, 128.82, 128.43, 128.33, 126.88, 123.19, 123.14, 120.80, 120.54, 118.58, 112.26, 110.33, 89.45, 60.55, 55.477, 46.86, 14.26.

HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{22}\text{O}_4$ ($\text{M}+\text{H}^+$) 375.1591, found 375.1593.

$[\alpha]_D^{25} = +254.7$ (c = 1.6 in CH_2Cl_2); 85% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, t_R = 5.4 min and 6.3 min].



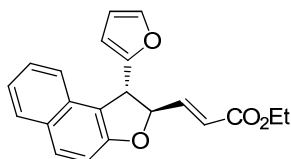
4na, Yield = 67%, 46.9 mg, brown liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.84-7.80(m, 2H), 7.43-7.40 (m, 1H), 7.37-7.29 (m, 2H), 7.25-7.22 (m, 2H), 7.15 (dd, J = 5.2 Hz, J = 15.6 Hz, 1H), 6.18 (dd, J = 1.6 Hz, J = 15.6 Hz, 1H), 5.37-5.33(m, 1H), 5.09 (d, J = 6.0Hz, 1H), 4.22 (q, J = 7.2 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.02, 156.86, 145.34, 144.23, 130.95, 130.55, 130.00, 128.90, 127.13, 127.06, 125.25, 125.14, 123.34, 122.56, 121.95, 119.07, 112.18, 90.17, 60.74, 49.30, 14.23.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_3\text{S}$ ($\text{M}+\text{Na}^+$) 373.0869, found 373.0866.

$[\alpha]_D^{25} = +141.2$ (c = 1.0 in CH_2Cl_2); 91% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, t_R = 5.9 min and 7.3 min].



4oa, Yield = 50%, 33.4 mg, yellow liquid.

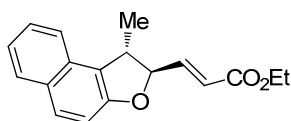
^1H NMR (400 MHz, CDCl_3): δ 7.84-7.78(m, 2H), 7.47 (d, J = 8.4Hz, 1H), 7.40-7.36 (m, 2H), 7.33-7.28 (m, 1H), 7.22 (d, J = 8.8Hz, 1H), 7.14 (dd, J = 4.8 Hz, J = 15.6 Hz, 1H), 6.33-6.31 (m, 1H), 6.19 (dd, J = 1.6 Hz, J = 15.6 Hz, 1H), 6.09 (d, J = 3.2Hz, 1H),

5.50-5.46(m, 1H), 4.90 (d, $J = 5.6$ Hz, 1H), 4.21 (q, $J = 7.2$ Hz, 2H), 1.29 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 166.02, 157.03, 153.64, 144.60, 142.46, 130.78, 130.68, 129.86, 128.85, 127.07, 123.30, 122.39, 121.88, 116.92, 112.22, 110.52, 107.31, 86.71, 60.70, 47.50, 14.22.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_4$ ($\text{M}+\text{Na}^+$) 357.1097, found 357.1095.

$[\alpha]_D^{25} = +29.6$ ($c = 0.5$ in CH_2Cl_2); 88% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_R = 5.1$ min and 6.1 min].



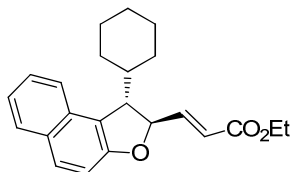
4pa, Yield = 75%, 42.3 mg, white liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.84(d, $J = 8.4$ Hz, 1H), 7.75-7.69 (m, 2H), 7.49 (t, $J = 7.2$ Hz, 1H), 7.33 (t, $J = 7.2$ Hz, 1H), 7.18(d, $J = 8.8$ Hz, 1H), 7.05 (dd, $J = 5.2$ Hz, $J = 15.6$ Hz, 1H), 6.13 (d, $J = 15.6$ Hz, 1H), 5.05 (t, $J = 3.6$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 3.74 (t, $J = 6.4$ Hz, 1H), 1.57 (d, $J = 6.8$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 166.19, 156.05, 145.35, 130.52, 129.86, 129.79, 129.12, 126.85, 123.08, 122.19, 121.88, 121.08, 112.25, 88.77, 60.62, 42.43, 20.48, 14.25.

HRMS (ESI) Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_3$ ($\text{M}+\text{H}^+$) 283.1329, found 283.1328.

$[\alpha]_D^{25} = +435.2$ ($c = 1.3$ in CH_2Cl_2); 87% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0mL/min, λ_{max} 254 nm, $t_R = 5.2$ min and 5.5 min].



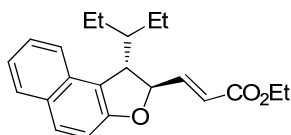
4qa, Yield = 65%, 45.6 mg, light yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.83(d, $J = 8.0$ Hz, 1H), 7.73(d, $J = 8.8$ Hz, 1H), 7.69(d, $J = 8.4$ Hz, 1H), 7.50-7.44 (m, 1H), 7.34-7.29 (m, 1H), 7.16 (d, $J = 8.8$ Hz 1H), 6.93 (dd, $J = 4.8$ Hz, $J = 15.6$ Hz, 1H), 6.04 (dd, $J = 1.6$ Hz, $J = 15.6$ Hz, 1H), 5.35-5.32 (m, 1H), 4.16 (q, $J = 7.2$ Hz, 2H), 3.60 (t, $J = 3.2$ Hz, 1H), 2.12-2.08 (m, 1H), 1.82 (d, $J = 6.4$ Hz, 2H), 1.69-1.61 (m, 1H), 1.35-1.20 (m, 7H), 1.16-1.04 (m, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.29, 156.52, 146.87, 129.80, 129.06, 126.65, 122.92, 122.71, 120.33, 118.82, 111.99, 82.67, 60.55, 53.53, 40.87, 31.57, 27.10, 26.57, 26.11, 14.21.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{26}\text{O}_3$ ($\text{M}+\text{H}^+$) 351.1955, found 351.1956.

$[\alpha]_D^{25} = +114.3$ ($c = 0.9$ in CH_2Cl_2); 96% ee [Chiralcel OD-H column, hexane / i-PrOH = 96:4, 0.5 mL/min, λ_{max} 254 nm, $t_R = 11.5$ min and 12.7 min].



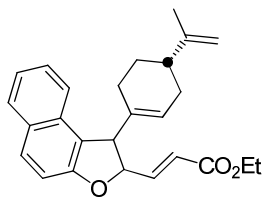
4ra, Yield = 35%, 23.7 mg, light yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.83(d, J = 8.4 Hz, 1H), 7.73(d, J = 8.8 Hz, 1H), 7.65(d, J = 8.0 Hz, 1H), 7.48-7.43(m, 1H), 7.34-7.29(m, 1H), 7.15(d, J = 8.8 Hz, 1H), 6.92(dd, J = 5.2 Hz, J = 15.6 Hz, 1H), 6.04(dd, J = 1.6 Hz, J = 15.6 Hz, 1H), 5.29-5.26(m, 1H), 4.16(q, J = 7.2 Hz, 2H), 3.89(t, J = 3.2 Hz, 1H), 2.12-2.08(m, 1H), 1.82(d, J = 6.4 Hz, 2H), 1.69-1.61(m, 1H), 1.35-1.20(m, 7H), 1.96-1.89(m, 1H), 1.78-1.70(m, 1H), 1.30-1.23(m, 4H), 1.18-1.11(m, 4H), 0.68(t, J = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 166.28, 156.66, 146.71, 130.66, 129.88, 129.82, 129.09, 126.69, 122.96, 122.35, 120.38, 119.39, 112.00, 82.20, 60.57, 49.97, 44.44, 24.46, 21.85, 14.20, 12.40, 12.34.

HRMS (ESI) Calcd for $\text{C}_{22}\text{H}_{26}\text{O}_3$ ($\text{M}+\text{Na}^+$) 361.1774, found 361.1776.

$[\alpha]_D^{25} = +75.2$ (c = 0.5 in CH_2Cl_2); 96% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, t_R = 5.8 min and 8.0 min].

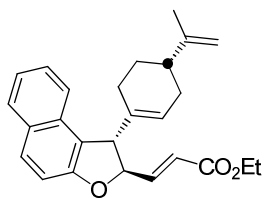


4sa (rac) Yield = 62%, 48.1 mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.81(d, J = 8.8 Hz, 3H), 7.74(d, J = 8.8 Hz, 3H), 7.70-7.64(m, 3H), 7.46-7.40(m, 3H), 7.34-7.29(m, 3H), 7.16(d, J = 8.8 Hz, 3H), 7.11-7.08(m, 1.5H), 7.07-7.04(m, 1.5H), 6.15(dd, J = 1.6 Hz, J = 15.6 Hz, 2H), 6.14(dd, J = 1.6 Hz, J = 15.6 Hz, 1H), 5.80(m, 1H), 5.20-5.12(m, 3H), 4.73-4.70(m, 6H), 4.27(t, J = 6.4 Hz, 3H), 4.20(q, J = 7.2 Hz, 6H), 2.27-2.16(m, 6H), 2.13-2.03(m, 6H), 1.80-1.74(m, 6H), 1.73(s, 6H), 1.51-1.38(m, 3H), 1.29(t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.24, 157.04, 155.86, 149.45, 145.68, 136.45, 131.21, 130.10, 128.79, 126.88, 126.83, 125.12, 123.14, 122.25, 120.94, 112.04, 108.85, 86.08, 60.63, 56.47, 41.02, 30.81, 27.48, 25.16, 20.86, 20.81, 14.24.

HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{28}\text{O}_3$ ($\text{M}+\text{H}^+$) 389.2111, found 389.2113.



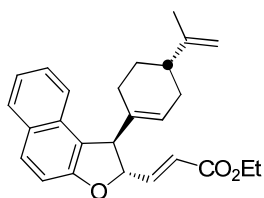
4sa Yield = 51%, 39.6 mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.81(d, J = 8.0 Hz, 1H), 7.74(d, J = 8.8 Hz, 1H), 7.69(d, J = 8.4 Hz, 1H), 7.46-7.42(m, 1H), 7.34-7.29(m, 1H), 7.15(d, J = 8.8 Hz, 1H), 7.07(dd, J = 5.2 Hz, J = 15.6 Hz, 1H), 6.14(dd, J = 1.6 Hz, J = 15.6 Hz, 1H), 5.80-5.79(m,

1H), 5.16-5.12 (m, 1H), 4.72 (m, $J = 11.2$ Hz, 2H), 4.278 (m, $J = 7.0$ Hz, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 2.27-2.01 (m, 4H), 1.77-1.72 (m, 5H), 1.55-1.44 (m, 1H), 1.29 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.24, 157.17, 149.48, 145.73, 136.62, 131.22, 130.11, 128.83, 126.69, 124.71, 123.14, 122.18, 120.90, 117.85, 112.04, 106.83, 86.45, 60.03, 56.28, 40.77, 30.74, 27.53, 25.40, 20.81, 14.25.

HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{28}\text{O}_3$ ($\text{M}+\text{H}^+$) 389.2111, found 389.2114.

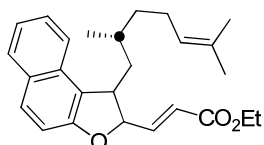


ent-4sa Yield = 50%, 39 mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.81 (d, $J = 8.4$ Hz, 1H), 7.74 (d, $J = 8.8$ Hz, 1H), 7.66 (d, $J = 8.8$ Hz, 1H), 7.45-7.40 (m, 1H), 7.34-7.29 (m, 1H), 7.15 (d, $J = 8.8$ Hz, 1H), 7.08 (dd, $J = 4.8$ Hz, $J = 15.6$ Hz, 1H), 6.15 (dd, $J = 1.6$ Hz, $J = 15.6$ Hz, 1H), 5.80-5.79 (m, 1H), 5.20-5.16 (m, 1H), 4.73-4.72 (m, 2H), 4.27-4.25 (m, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 2.25-2.03 (m, 4H), 1.80-1.75 (m, 2H), 1.73 (s, 3H), 1.44-1.39 (m, 1H), 1.29 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): 166.23, 157.16, 149.48, 145.72, 136.61, 131.21, 130.10, 129.61, 128.82, 126.88, 124.70, 123.13, 122.17, 120.88, 117.84, 112.04, 108.83, 86.43, 60.62, 56.27, 40.77, 30.73, 27.52, 25.39, 20.81, 14.24.

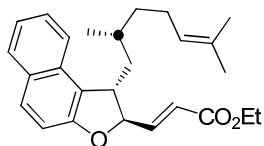
HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{28}\text{O}_3$ ($\text{M}+\text{H}^+$) 389.2111, found 389.2110.



4ta (rac), Yield = 78%, 61.2mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.72 (dd, $J = 2.0$ Hz, $J = 8.8$ Hz, 2H), 7.61 (dd, $J = 2.4$ Hz, $J = 8.4$ Hz, 2H), 7.50-7.44 (m, 2H), 7.34-7.29 (m, 2H), 7.17 (dd, $J = 2.4$ Hz, $J = 8.8$ Hz, 2H), 6.99-6.92 (m, 2H), 6.07 (dd, $J = 1.6$ Hz, $J = 15.6$ Hz, 2H), 5.22-5.08 (m, 4H), 4.20-4.14 (m, 4H), 3.73-3.66 (m, 2H), 2.17-1.88 (m, 6H), 1.74-1.60 (m, 20H), 1.28-1.24 (m, 6H), 1.15 (d, $J = 6.4$ Hz, 3H), 1.00 (d, $J = 6.4$ Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 166.25, 166.20, 155.87, 146.06, 145.83, 131.89, 131.66, 130.37, 130.31, 129.86, 129.71, 126.83, 124.38, 124.35, 123.02, 122.23, 122.16, 121.15, 120.82, 120.73, 112.19, 86.63, 86.33, 60.59, 45.67, 45.51, 42.27, 41.63, 37.92, 35.73, 30.71, 30.76, 25.77, 25.44, 25.32, 20.66, 19.24, 17.75, 14.21.

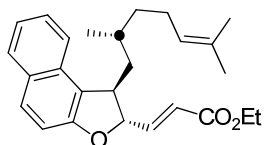


4ta, Yield = 70%, 54.9mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, J = 8.4Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 8.4 Hz, 1H), 7.50-7.45(m, 1H), 7.35-7.30 (m, 1H), 7.18 (d, J = 8.8 Hz, 1H), 6.97 (dd, J = 5.2 Hz, J = 15.6 Hz, 1H), 6.08 (dd, J = 1.6 Hz, J = 15.6 Hz, 1H), 5.23-5.16(m, 2H), 4.18 (q, J = 7.2 Hz, 2H), 3.72-3.68(m, 1H), 2.18-2.14 (m, 1H), 2.08-2.03 (m, 1H), 1.96-1.89(m, 1H), 1.75-1.66 (m, 10H), 1.27 (t, J = 7.2 Hz, 3H), 1.00 (d, J = 6.8 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.20, 155.67, 145.83, 131.90, 130.37, 129.86, 129.72, 129.10, 126.83, 123.02, 122.24, 121.26, 120.82, 112.19, 86.62, 60.59, 45.67, 42.28, 35.72, 30.71, 25.79, 25.33, 20.67, 17.77, 14.22.

HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{32}\text{O}_3$ ($\text{M}+\text{Na}^+$) 415.2244, found 415.2247.

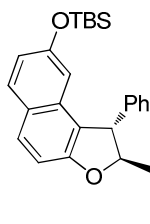


ent-4ta, Yield = 65%, 51.0mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.83 (d, J = 8.0Hz, 1H), 7.72 (d, J = 8.8 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.50-7.45(m, 1H), 7.34-7.30 (m, 1H), 7.17 (d, J = 8.4 Hz, 1H), 6.96 (dd, J = 4.8 Hz, J = 15.6 Hz, 1H), 6.07 (dd, J = 1.6 Hz, J = 15.6 Hz, 1H), 5.19-5.16(m, 1H), 5.11-5.06(m, 1H), 4.17 (q, J = 7.2 Hz, 2H), 3.73-3.68(m, 1H), 2.04-2.01 (m, 2H), 1.70 (s, 4H), 1.61(s, 4H), 1.35-1.29 (m, 3H), 1.26 (t, J = 7.2 Hz, 3H), 1.15 (d, J = 6.4 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.25, 155.87, 146.06, 131.66, 130.31, 129.85, 129.70, 129.10, 126.83, 124.33, 122.16, 121.15, 120.73, 112.21, 86.33, 60.61, 45.51, 41.63, 37.92, 30.47, 25.77, 25.44, 19.24, 17.74, 14.21.

HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{32}\text{O}_3$ ($\text{M}+\text{Na}^+$) 415.2244, found 415.2242.



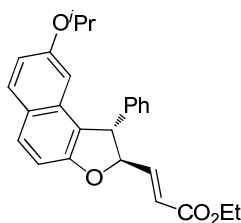
4ab, Yield = 90%, 85.4 mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.70(t, J = 9.2Hz, 2H), 7.37-7.32 (m, 2H), 7.31-7.25 (m, 3H), 7.17 (dd, J = 5.2 Hz, J = 15.6Hz, 1H), 7.10(d, J = 8.8 Hz, 1H), 6.85 (dd, J = 2.4 Hz, J = 15.6 Hz, 1H), 5.31-5.26 (m, 1H), 4.71 (d, J = 7.6 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.30 (t, J = 7.2 Hz, 3H), 0.88(s, 9H), 0.00(s, 3H), -0.07(s, 3H).

^{13}C NMR (100 MHz, CDCl_3): δ 166.18, 157.56, 154.40, 144.76, 144.75, 131.75, 130.36, 130.16, 129.19, 127.91, 127.50, 125.68, 121.51, 119.48, 118.49, 110.00, 109.69, 90.28, 60.69, 54.79, 25.66, 18.21, 14.25, -4.55, -4.84.

HRMS (ESI) Calcd for $\text{C}_{29}\text{H}_{34}\text{O}_4\text{Si}$ ($\text{M}+\text{Na}^+$) 497.2119, found 497.2117.

$[\alpha]_D^{25} = +92.4$ ($c = 0.5$ in CH_2Cl_2); 87% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_R = 3.9$ min and 4.7 min].



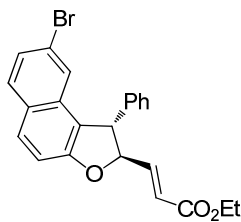
4ac, Yield = 95%, 76.5 mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.70 (d, $J = 2.4\text{Hz}$, 1H), 7.68 (d, $J = 2.4\text{Hz}$, 1H), 7.37-7.33 (m, 2H), 7.31-7.27 (m, 3H), 7.19 (dd, $J = 5.6\text{ Hz}$, $J = 15.6\text{ Hz}$, 1H), 7.08 (d, $J = 8.8\text{Hz}$, 1H), 6.88 (dd, $J = 2.4\text{Hz}$, $J = 8.8\text{ Hz}$, 1H), 6.46 (d, $J = 2.4\text{Hz}$, 1H), 6.18 (dd, $J = 1.2\text{Hz}$, $J = 15.6\text{ Hz}$, 1H), 6.32 (m, 1H), 4.73 (d, $J = 6.8\text{ Hz}$, 1H), 4.25-4.21 (m, 2H), 1.34-1.29 (m, 6H), 1.01 (d, $J = 7.0\text{Hz}$, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.19, 157.65, 156.38, 144.78, 141.76, 131.78, 130.36, 130.36, 130.11, 129.14, 127.92, 127.48, 125.13, 121.56, 118.69, 116.94, 109.28, 103.40, 90.21, 69.50, 60.70, 54.78, 22.19, 21.06, 14.26.

HRMS (ESI) Calcd for $\text{C}_{26}\text{H}_{26}\text{O}_4$ ($\text{M}+\text{H}^+$) 403.1904, found 403.1906.

$[\alpha]_D^{25} = +417.2$ ($c = 1.35$ in CH_2Cl_2); 92% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_R = 4.7$ min and 5.4 min].



4ad, Yield = 50%, 42.3 mg, yellow liquid.

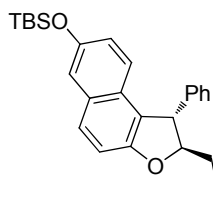
^1H NMR (300 MHz, CDCl_3): δ 7.68 (d, $J = 9.0\text{Hz}$, 1H), 7.56 (d, $J = 8.2\text{Hz}$, 1H), 7.32-7.12 (m, 9H), 7.04 (dd, $J = 5.1\text{ Hz}$, $J = 15.6\text{ Hz}$, 1H), 6.05 (dd, $J = 1.8\text{ Hz}$, $J = 15.6\text{ Hz}$, 1H), 5.21 (m, 1H), 4.64 (d, $J = 5.7\text{ Hz}$, 1H), 4.13 (q, $J = 7.2\text{ Hz}$, 2H), 1.21 (t, $J = 7.2\text{ Hz}$, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.00, 157.97, 144.41, 141.43, 131.77, 130.60, 130.47, 129.28, 128.37, 127.71, 127.60, 126.66, 124.95, 121.68, 121.41, 119.07, 112.57, 90.42, 60.74, 54.19, 14.23.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{19}\text{BrO}_3$ ($\text{M}+\text{Na}^+$) 445.0410, found 445.0413.

$[\alpha]_D^{25} = +116.8$ ($c = 0.75$ in CH_2Cl_2); 83% ee [Chiralcel OD-H column, hexane /

i-PrOH = 90:10, 1.0 mL/min, $\lambda_{\max}$ 254 nm, t_R = 5.3 min and 7.3 min].



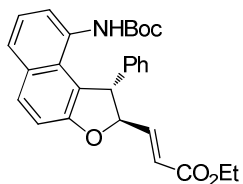
4ae, Yield = 91%, 86.4 mg, colorless liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.66 (d, J = 8.8 Hz, 1H), 7.33-7.13 (m, 9H), 6.90 (dd, J = 2.4 Hz, J = 9.2 Hz, 1H), 6.16 (dd, J = 1.2 Hz, J = 15.6 Hz, 1H), 5.28-5.24 (m, 1H), 4.76 (d, J = 6.4 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H), 1.01 (s, 9H), 0.22 (s, 9H).

^{13}C NMR (100 MHz, CDCl_3): δ 166.17, 155.78, 151.37, 144.91, 142.06, 131.14, 129.11, 129.04, 127.79, 127.44, 126.15, 124.07, 122.96, 121.47, 119.71, 116.08, 112.39, 90.05, 60.68, 54.71, 25.72, 18.22, 14.25, -4.34.

HRMS (ESI) Calcd for $\text{C}_{29}\text{H}_{34}\text{O}_4\text{Si}$ ($\text{M}+\text{Na}^+$) 497.2119, found 497.2122.

$[\alpha]_D^{25} = +70.8$ (c = 0.5 in CH_2Cl_2); 88% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, $\lambda_{\max}$ 254 nm, t_R = 3.8 min and 4.3 min].



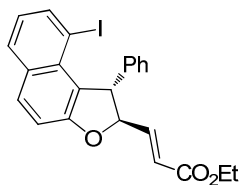
4af, Yield = 30%, 27.6 mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, J = 8.8 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.55 (m, 1H), 7.38-7.26 (m, 6H), 7.15-7.12 (m, 2H), 7.08 (dd, J = 5.2 Hz, J = 15.6 Hz, 1H), 6.32-6.24 (m, 1H), 6.11 (dd, J = 1.6 Hz, J = 15.6 Hz, 1H), 5.18 (m, 1H), 4.94 (d, J = 3.2 Hz, 1H), 4.21 (q, J = 7.2 Hz, 2H), 1.52 (s, 9H), 1.29 (t, J = 7.2 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.11, 158.60, 153.97, 145.07, 143.04, 131.89, 131.82, 131.11, 129.77, 128.74, 127.42, 127.03, 123.39, 121.73, 116.44, 112.65, 89.03, 80.39, 60.81, 55.30, 29.81, 28.53, 14.30.

HRMS (ESI) Calcd for $\text{C}_{28}\text{H}_{29}\text{NO}_5$ ($\text{M}+\text{Na}^+$) 482.1938, found 482.1935.

$[\alpha]_D^{25} = +9.6$ (c = 0.5 in CH_2Cl_2); 89% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, $\lambda_{\max}$ 254 nm, t_R = 5.6 min and 6.3 min].



4ag, Yield = 27%, 25.4 mg, yellow liquid.

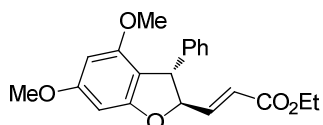
^1H NMR (400 MHz, CDCl_3): δ 8.05 (d, J = 7.6 Hz, 1H), 7.86 (d, J = 4.0 Hz, 1H), 7.84

(d, $J = 3.2$ Hz, 1H), 7.34 (d, $J = 14$ Hz, 1H), 7.28-7.22 (m, 4H), 7.17 (dd, $J = 4.8$ Hz, $J = 15.6$ Hz, 1H), 6.98-6.90 (m, 2H), 6.16 (dd, $J = 1.6$ Hz, $J = 15.6$ Hz, 1H), 5.85 (d, $J = 1.6$ Hz, 1H), 5.21 (m, 1H), 4.22 (q, $J = 7.2$ Hz, 2H), 1.30 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.23, 159.63, 145.50, 144.31, 141.80, 132.85, 132.70, 131.86, 130.41, 128.98, 127.58, 127.07, 124.49, 121.73, 119.01, 113.26, 89.66, 88.98, 60.84, 53.84, 14.33.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{19}\text{IO}_3$ ($\text{M}+\text{Na}^+$) 493.0271, found 493.0270.

$[\alpha]_D^{25} = +49.2$ ($c = 0.35$ in CH_2Cl_2); 85% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_R = 5.3$ min and 6.2 min].



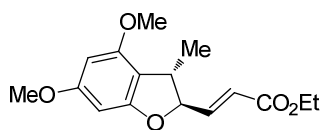
7a, Yield = 47%, 33.3 mg, Yellow-green liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.33-7.24 (m, 3H), 7.18-7.15 (m, 2H), 7.05 (dd, $J = 5.2$ Hz, $J = 15.6$ Hz, 1H), 6.19 (d, $J = 2.0$ Hz, 1H), 6.08 (dd, $J = 1.6$ Hz, $J = 15.6$ Hz, 1H), 6.03 (d, $J = 2.0$ Hz, 1H), 5.16-5.12 (m, 1H), 4.37 (d, $J = 4.8$ Hz, 1H), 4.21 (q, $J = 7.2$ Hz, 2H), 3.81 (s, 3H), 3.61 (s, 3H), 1.30 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.17, 162.45, 161.21, 157.30, 145.09, 142.34, 128.67, 127.21, 126.98, 121.17, 107.85, 92.10, 90.11, 86.34, 60.64, 55.61, 55.38, 52.04, 14.24.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{22}\text{O}_5$ ($\text{M}+\text{Na}^+$) 377.1359, found 377.1360.

$[\alpha]_D^{25} = +67.6$ ($c = 0.5$ in CH_2Cl_2); 96% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_R = 5.4$ min and 9.3 min].



7b, Yield = 50%, 29.2 mg, white liquid.

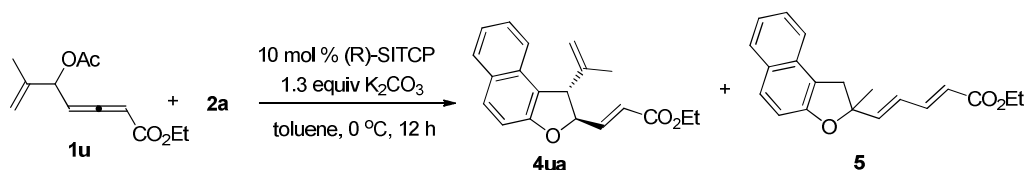
^1H NMR (300 MHz, CDCl_3): δ 6.98 (dd, $J = 2.4$ Hz, $J = 15.6$ Hz, 1H), 6.08 (dd, $J = 1.8$ Hz, $J = 15.6$ Hz, 1H), 6.08 (d, $J = 1.8$ Hz, 1H), 6.03 (d, $J = 1.8$ Hz, 1H), 4.86-4.81 (m, 1H), 4.20 (q, $J = 7.2$ Hz, 2H), 3.78 (d, $J = 0.9$ Hz, 1H), 3.55-3.26 (m, 1H), 1.33 (d, $J = 6.4$ Hz, 3H), 1.29 (t, $J = 7.2$ Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3): δ 166.23, 161.86, 160.54, 157.23, 145.31, 120.95, 109.56, 91.68, 89.22, 86.40, 60.57, 55.59, 55.26, 41.26, 18.93, 14.23.

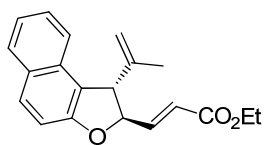
HRMS (ESI) Calcd for $\text{C}_{16}\text{H}_{20}\text{O}_5$ ($\text{M}+\text{H}^+$) 293.1384, found 293.1386.

$[\alpha]_D^{25} = +3.6$ ($c = 0.5$ in CH_2Cl_2); 96% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_R = 5.1$ min and 9.9 min].

4. Synthesis of products 4ua and 5



To a 25 mL flask was added catalysts (R)-SITCP (0.02 mmol, 7.1 mg), K₂CO₃ (0.26 mmol, 35.9 mg), **2a** (0.24 mmol), and toluene (1.5 mL). After the mixture was stirred at 0°C for five minutes, a solution of **1u** (0.20 mmol) in toluene (1.5 mL) was slowly added. After 12 h, the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give products.



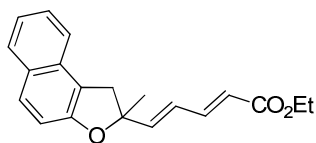
4ua, Yield = 43%, 26.5 mg, yellow liquid.

¹H NMR (400 MHz, CDCl₃): δ 7.82(d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.8 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.32 (t, *J* = 7.2 Hz, 1H), 7.17(d, *J* = 8.8 Hz, 1H), 7.08 (dd, *J* = 5.2 Hz, *J* = 15.6 Hz, 1H), 6.16 (dd, *J* = 1.2 Hz, *J* = 15.6 Hz, 1H), 4.34 (d, *J* = 5.6 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 1.66 (s, 1H), 1.29 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 166.16, 157.10, 145.41, 144.13, 131.14, 130.32, 129.68, 128.83, 126.93, 123.23, 122.18, 121.15, 117.89, 114.18, 112.06, 86.02, 60.65, 56.52, 18.74, 14.24.

HRMS (ESI) Calcd for C₂₀H₂₀O₃ (M+H⁺) 309.1485, found 309.1488.

[α]_D²⁵ = +226.7 (c = 1.25 in CH₂Cl₂); 91% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, t_R = 4.3 min and 5.1 min].



5, Yield = 20%, 12.4 mg, yellow liquid.

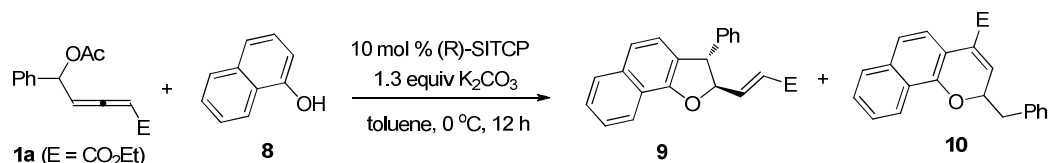
¹H NMR (400 MHz, CDCl₃): δ 7.83(d, *J* = 8.0 Hz, 1H), 7.73(d, *J* = 8.8 Hz, 1H), 7.55(d, *J* = 8.4 Hz, 1H), 7.51-7.46 (m, 1H), 7.34 (d, *J* = 6.4 Hz, 1H), 7.31-7.26 (m, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 6.50 (dd, *J* = 6.8 Hz, *J* = 15.2 Hz, 1H), 6.35 (d, *J* = 15.2 Hz, 1H), 5.92 (d, *J* = 15.2 Hz, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.50 (d, *J* = 15.2 Hz, 1H), 3.41 (d, *J* = 15.2 Hz, 1H), 1.70 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 166.85, 156.03, 145.24, 143.63, 130.90, 129.31, 128.76, 126.78, 125.81, 122.96, 122.58, 122.21, 117.34, 112.20, 87.84, 60.38, 41.40, 26.80, 14.30.

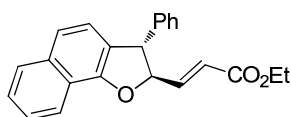
HRMS (ESI) Calcd for $C_{20}H_{20}O_3$ ($M+H^+$) 309.1485, found 309.1484.

$[\alpha]_D^{25} = +4.8$ ($c = 0.5$ in CH_2Cl_2); $<5\%$ ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0 mL/min, λ_{max} 254 nm, $t_R = 8.5$ min and 9.9 min].

5. Synthesis of products 9 and 10



To a 25 mL flask was added catalysts (R)-SITCP (0.02 mmol, 7.1 mg), K₂CO₃ (0.26 mmol, 35.9 mg), **8** (0.24 mmol), and toluene (1.5 mL). After the mixture was stirred at 0°C for five minutes, a solution of **1a** (0.20 mmol) in toluene (1.5 mL) was slowly added. After 12 h, the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product.



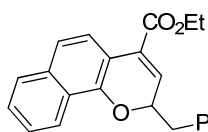
9, Yield = 43%, 29.6mg, yellow liquid.

¹H NMR (300 MHz, CDCl₃): δ 8.00-7.96 (m, 1H), 7.76-7.72 (m, 1H), 7.43-7.38 (m, 2H), 7.34-7.28 (m, 1H), 7.26-7.20 (m, 1H), 7.17-7.12 (m, 2H), 7.11-7.05 (m, 1H), 7.01 (d, *J* = 2.0 Hz, 1H), 6.10 (dd, *J* = 1.5 Hz, *J* = 15.6 Hz, 1H), 5.30-5.24 (m, 1H), 4.53 (d, *J* = 7.5 Hz, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 1.20 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (75 MHz, CDCl₃): δ 166.18, 154.70, 144.74, 141.82, 134.42, 129.06, 128.04, 128.01, 127.57, 126.28, 125.76, 122.71, 122.23, 121.68, 121.59, 121.40, 120.57, 90.19, 60.72, 55.67, 14.25.

HRMS (ESI) Calcd for C₂₃H₂₀O₃ (M+Na⁺) 367.1305, found 367.1307.

[α]_D²⁵ = +116.4 (c = 0.5 in CH₂Cl₂); 92% ee [Chiralcel OD-H column, hexane / i-PrOH = 90:10, 1.0mL/min, λ_{max} 254 nm, t_R = 5.6 min and 6.7 min].



10, Yield = 32%, 22.1 mg, rufous liquid.

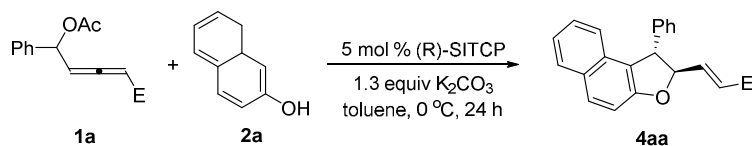
¹H NMR (400 MHz, CDCl₃): δ 8.04 (d, *J* = 8.8 Hz, 1H), 8.03 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.51-7.41 (m, 3H), 7.37-7.29 (m, 3H), 7.26-7.23 (m, 2H), 6.77 (d, *J* = 4.4 Hz, 1H), 5.28-5.25 (m, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 3.25 (dd, *J* = 4.4 Hz, *J* = 14.0 Hz, 1H), 3.06 (dd, *J* = 5.6 Hz, *J* = 14.0 Hz, 1H), 1.41 (t, *J* = 7.2 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃): δ 165.33, 148.79, 136.55, 134.55, 132.42, 129.71, 128.84, 128.47, 127.82, 127.46, 126.89, 126.75, 125.45, 124.74, 123.58, 123.43, 122.48, 120.49, 114.01, 75.74, 61.13, 39.81, 14.29.

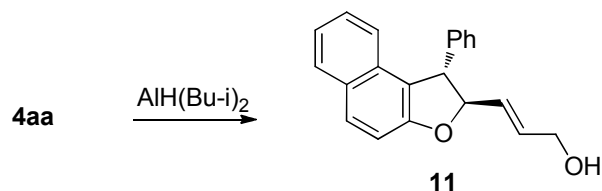
HRMS (ESI) Calcd for C₂₃H₂₀O₃ (M+Na⁺) 367.1305, found 367.1302.

[α]_D²⁵ = +12.8 (c = 0.5 in CH₂Cl₂); 27% ee [Chiralcel AD-H column, hexane / i-PrOH = 90:10, 1.0mL/min, λ_{max} 254 nm, t_R = 6.4 min and 7.5 min].

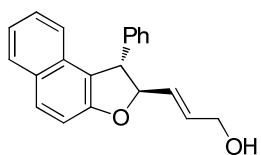
6. Synthetic Applications



To a 25 mL flask was added catalysts (R)-SITCP (0.05 mmol, 17.7 mg), K_2CO_3 (1.3 mmol, 179.5 mg), **2a** (1.2 mmol, 0.175 g), and toluene (5 mL). After the mixture was stirred at 0°C for five minutes, a solution of **1a** (0.20 mmol, 0.26 g) in toluene (2 mL) was slowly added. After 24 h, the solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product **4aa** (0.32g, 92% yield).



To a solution of **4aa** (58 mg, 0.17 mmol) in THF (20 mL) cooled to -78 °C, a solution of DIBAL (0.5 mL, 0.5 mmol) in THF (2 mL) was added dropwise and the pale yellow solution stirred for 2 h. The system quenched with three drop of water. The solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product.



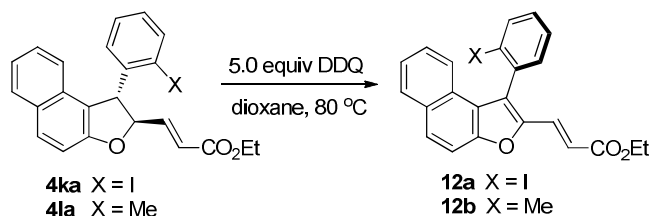
11, Yield = 98%, 59.3 mg, white solid.

^1H NMR (300 MHz, CDCl_3): δ 7.85-7.78(m, 2H), 7.37-7.33(m, 1H), 7.47-7.25(m, 5H), 7.32-7.29 (m, 2H), 7.27-7.23(m, 5H), 6.12-6.04(m, 1H), 6.03-5.94(m, 1H), 5.17 (t, J = 6.3 Hz, 1H), 4.75 (d, J = 6.3 Hz, 1H), 4.23 (q, J = 7.2 Hz, 2H).

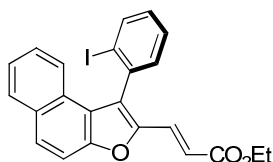
^{13}C NMR (100 MHz, CDCl_3): δ 157.32, 142.47, 132.37, 130.70, 130.30, 129.87, 129.14, 128.98, 128.84, 127.89, 127.19, 126.75, 122.96, 122.87, 120.20, 112.20, 92.24, 62.69, 54.96.

HRMS (ESI) Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_2$ ($\text{M}+\text{Na}^+$) 325.1199, found 325.1202.

$[\alpha]_D^{25} = +151.2$ (c = 0.5 in CH_2Cl_2); 91% ee [Chiralcel OD-H column, hexane / i-PrOH = 85:15, 1.0 mL/min, λ_{max} 254 nm, t_R = 7.5 min and 10.6 min].



To a 25 mL sealed tube was added DDQ (1 mmol, 227 mg), and dioxane (1.5 mL), followed by solution of **4ka** or **4la** (0.20 mmol) in dioxane (1.5 mL) was added. After the mixture was stirred at 80°C for 48h. The solvent was removed and the residue was directly subjected to silica gel column chromatography (petroleum ether/ethyl acetate as eluent) to give product.



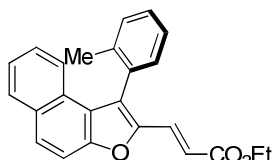
12a, Yield = 47%, 44.3mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.99 (d, J = 7.8 Hz, 1H), 7.83 (d, J = 7.8 Hz, 1H), 7.75 (d, J = 9.0 Hz, 1H), 7.59 (d, J = 9.0 Hz, 1H), 7.47-7.25(m, 5H), 7.23-7.14(m, 2H), 6.55 (d, J = 15.9 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 1.23 (t, J = 7.2 Hz, 3H).

^{13}C NMR (125 MHz, CDCl_3): δ 166.96, 152.87, 148.73, 139.63, 137.50, 131.48, 130.77, 130.49, 129.57, 129.47, 128.71, 128.56, 128.03, 126.98, 125.02, 123.05, 122.30, 118.26, 112.31, 101.26, 60.66, 14.38.

HRMS (ESI) Calcd for $\text{C}_{23}\text{H}_{17}\text{IO}_3$ ($\text{M}+\text{Na}^+$) 491.0115, found 491.0112.

$[\alpha]_D^{25} = +63.7$ (c = 0.5 in CH_2Cl_2); 90% ee [Chiralcel AD-H column, hexane / i-PrOH = 95:5, 0.5 mL/min, λ_{max} 254 nm, t_R = 11.2 min and 13.9 min].



12b, Yield = 63%, 45.2mg, yellow liquid.

^1H NMR (400 MHz, CDCl_3): δ 7.94 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 9.2 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.48-7.42(m, 4H), 7.37-7.27(m, 4H), 6.62 (d, J = 15.6 Hz, 1H), 4.25 (q, J = 7.2 Hz, 2H), 2.14(s, 4H), 1.33 (t, J = 7.2 Hz, 3H).

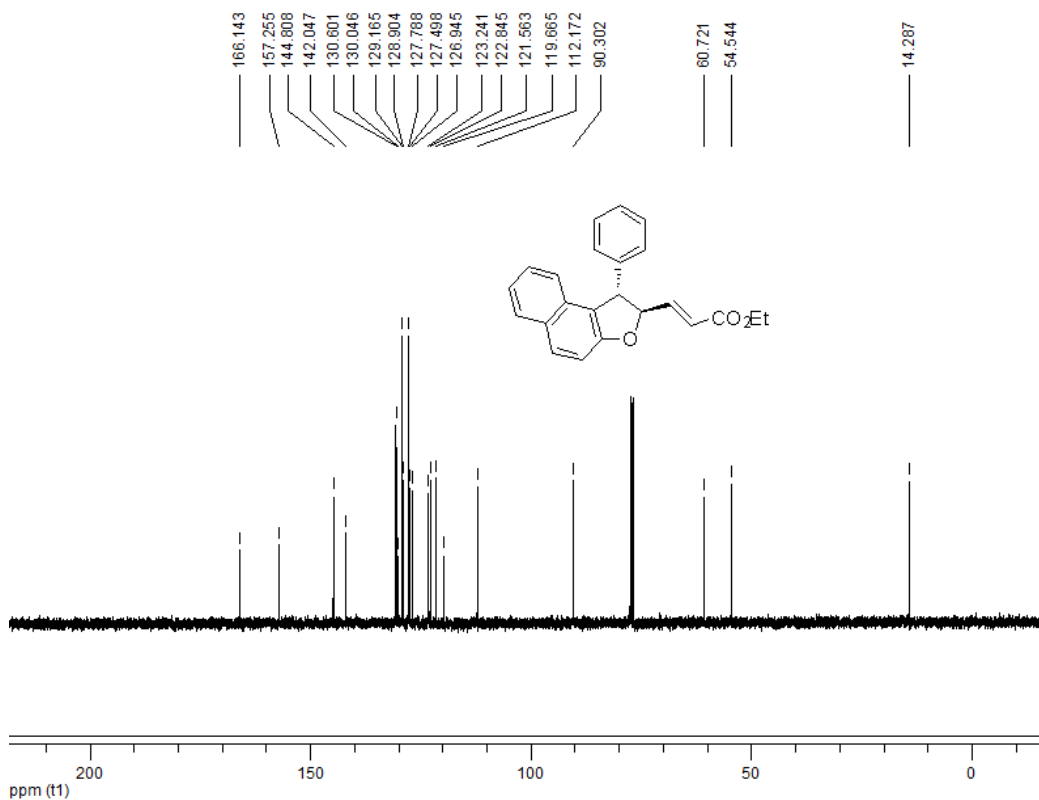
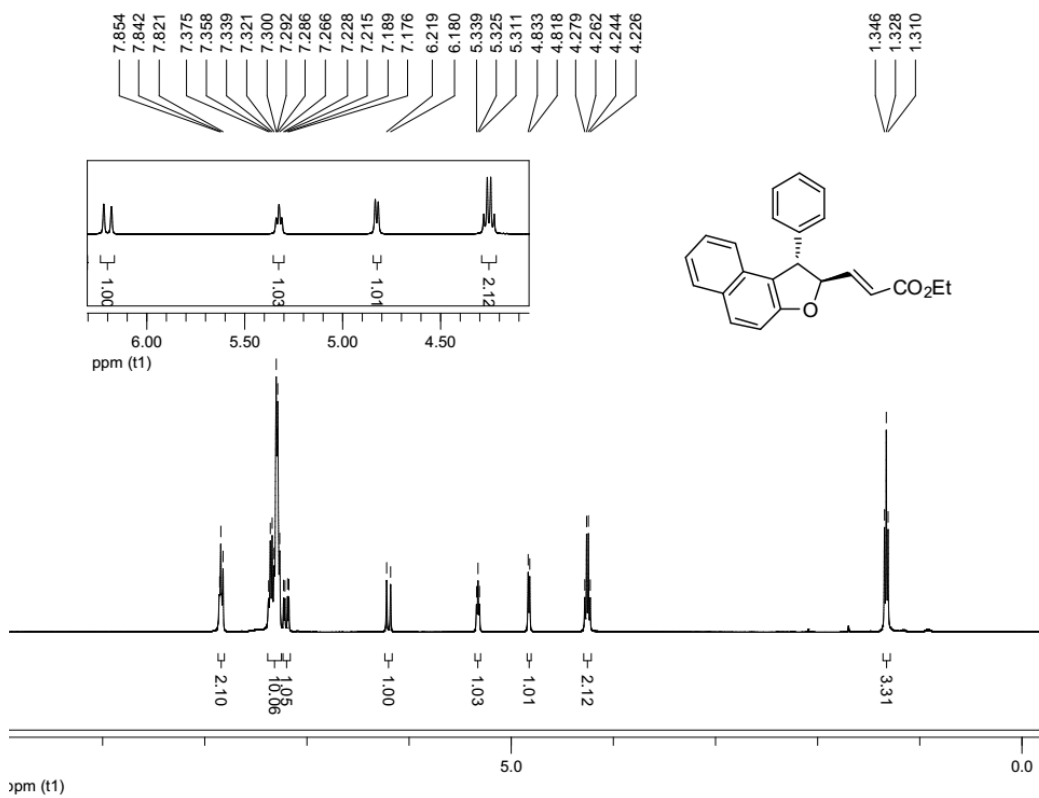
^{13}C NMR (125 MHz, CDCl_3): δ 167.06, 153.05, 148.52, 137.91, 131.55, 130.73, 130.47, 129.86, 129.04, 126.98, 126.81, 126.36, 124.89, 122.79, 122.64, 117.63, 112.31, 60.57, 20.09, 14.36.

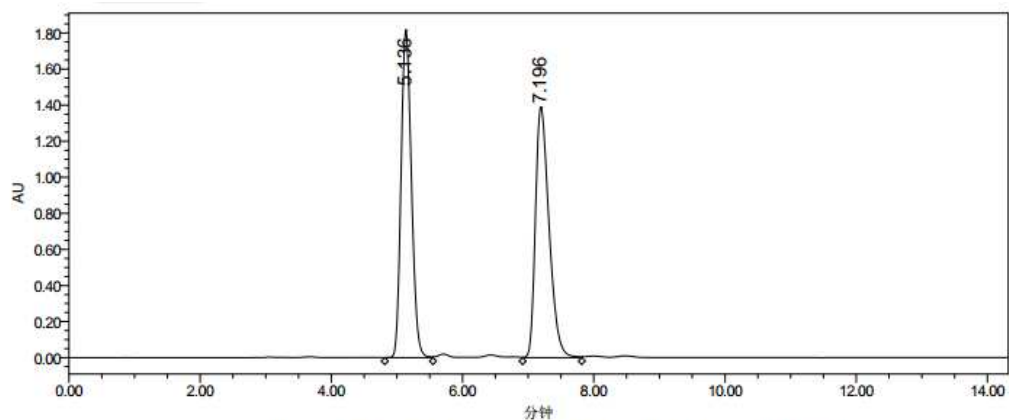
HRMS (ESI) Calcd for $\text{C}_{24}\text{H}_{20}\text{O}_3$ ($\text{M}+\text{Na}^+$) 379.1305, found 379.1307.

$[\alpha]_D^{25} = +54.2$ (c = 0.5 in CH_2Cl_2); 70% ee [Chiralcel AD-H column, hexane / i-PrOH = 95:5, 0.5 mL/min, λ_{max} 254 nm, t_R = 8.8 min and 10.0 min].

7. The Spectra of Products

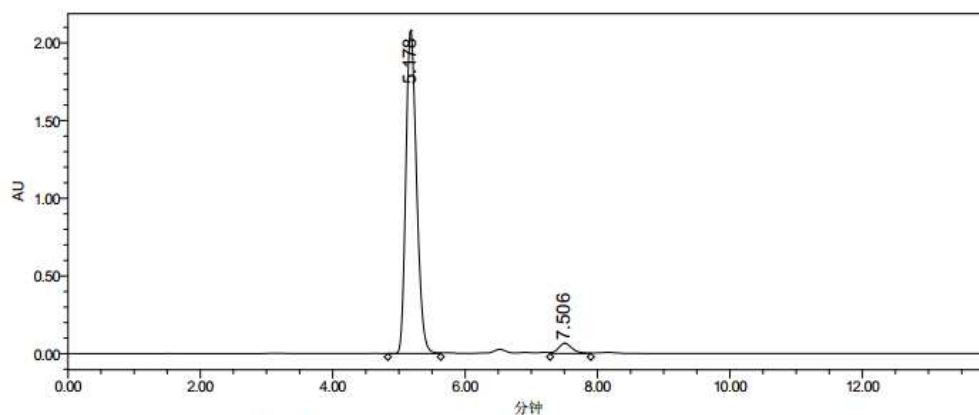
4aa





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: zwpl441

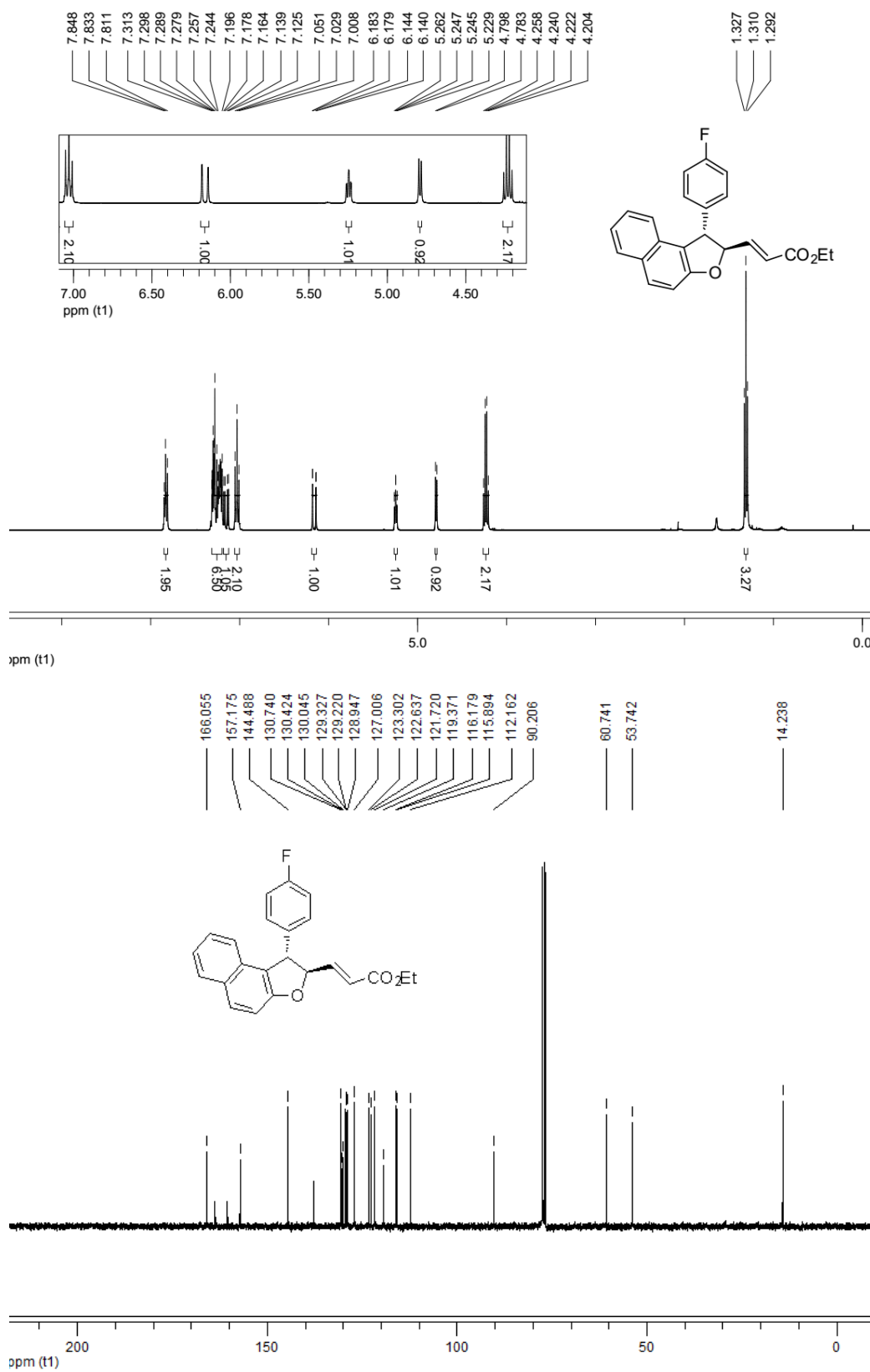
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.136	19876093	49.88	1818755
2	W2489 ChA 254nm	7.196	19968533	50.12	1390021

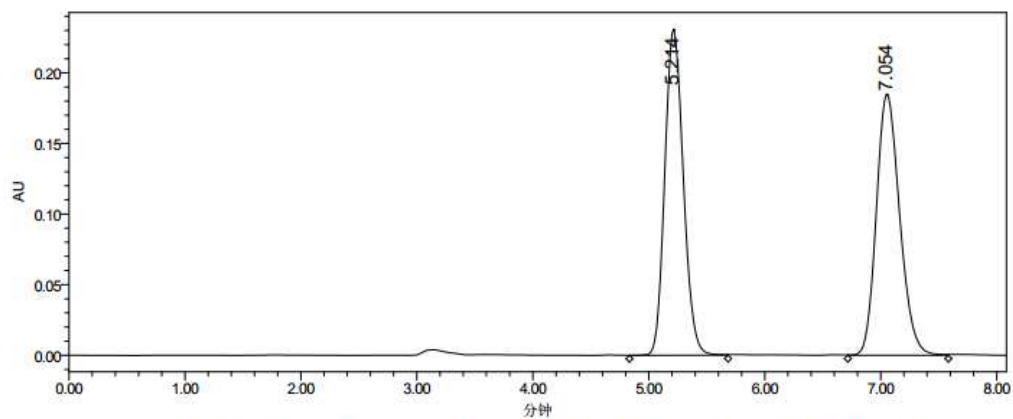


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 1501 0

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.178	23323599	96.01	2087046
2	W2489 ChA 254nm	7.506	970034	3.99	65686

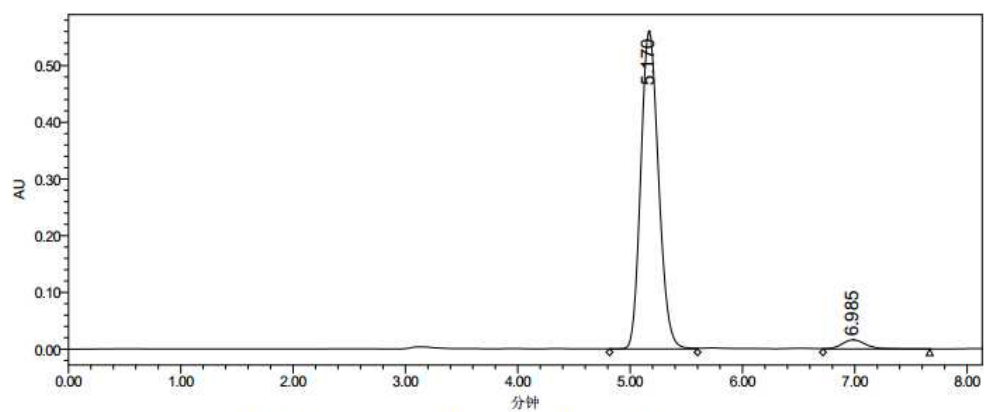
4ba





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

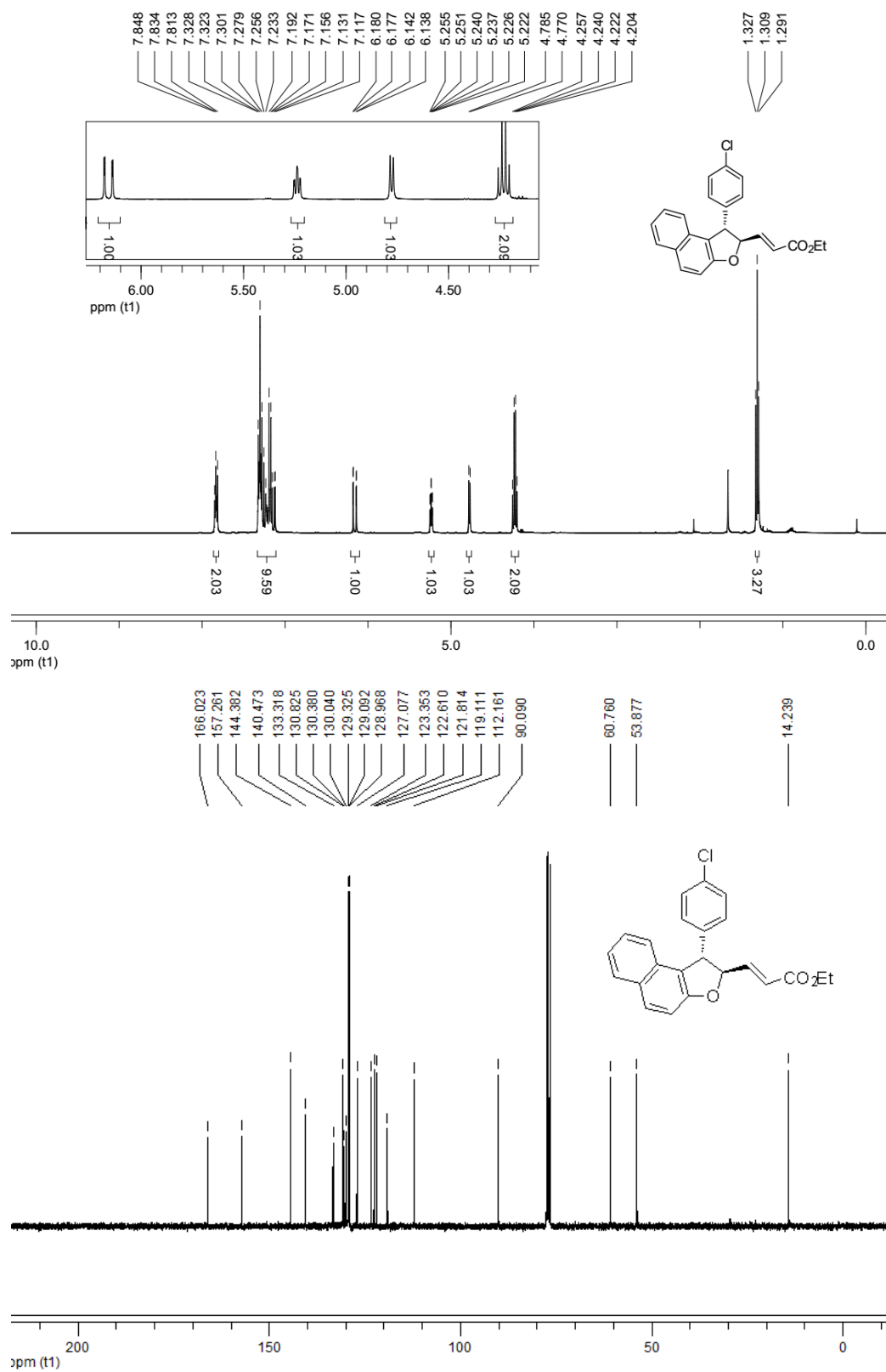
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.214	2564071	49.79	231144
2	W2489 ChA 254nm	7.054	2585337	50.21	185129

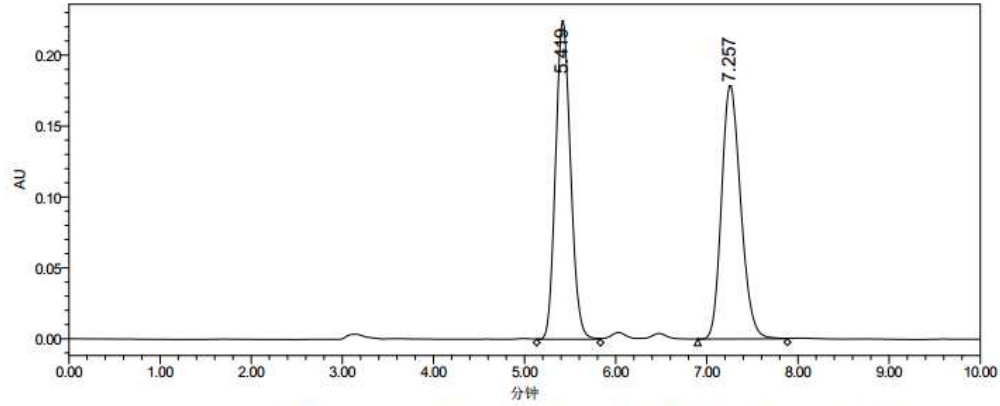


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.170	6145903	96.40	561204
2	W2489 ChA 254nm	6.985	229425	3.60	15951

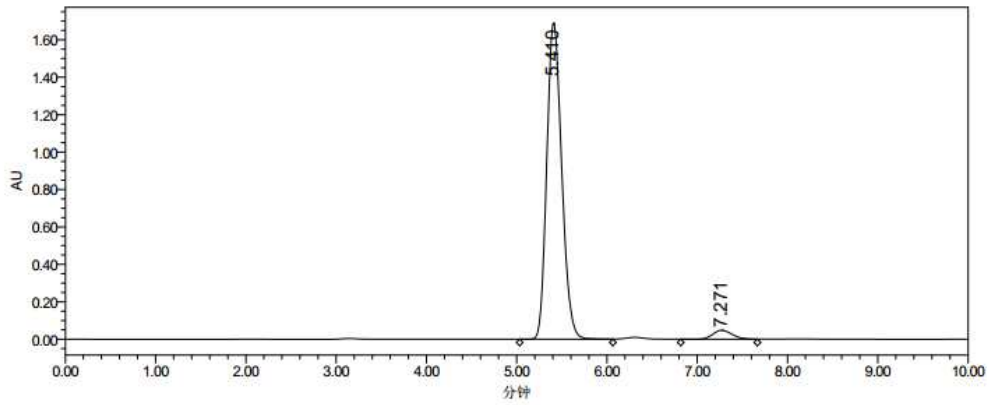
4ca





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

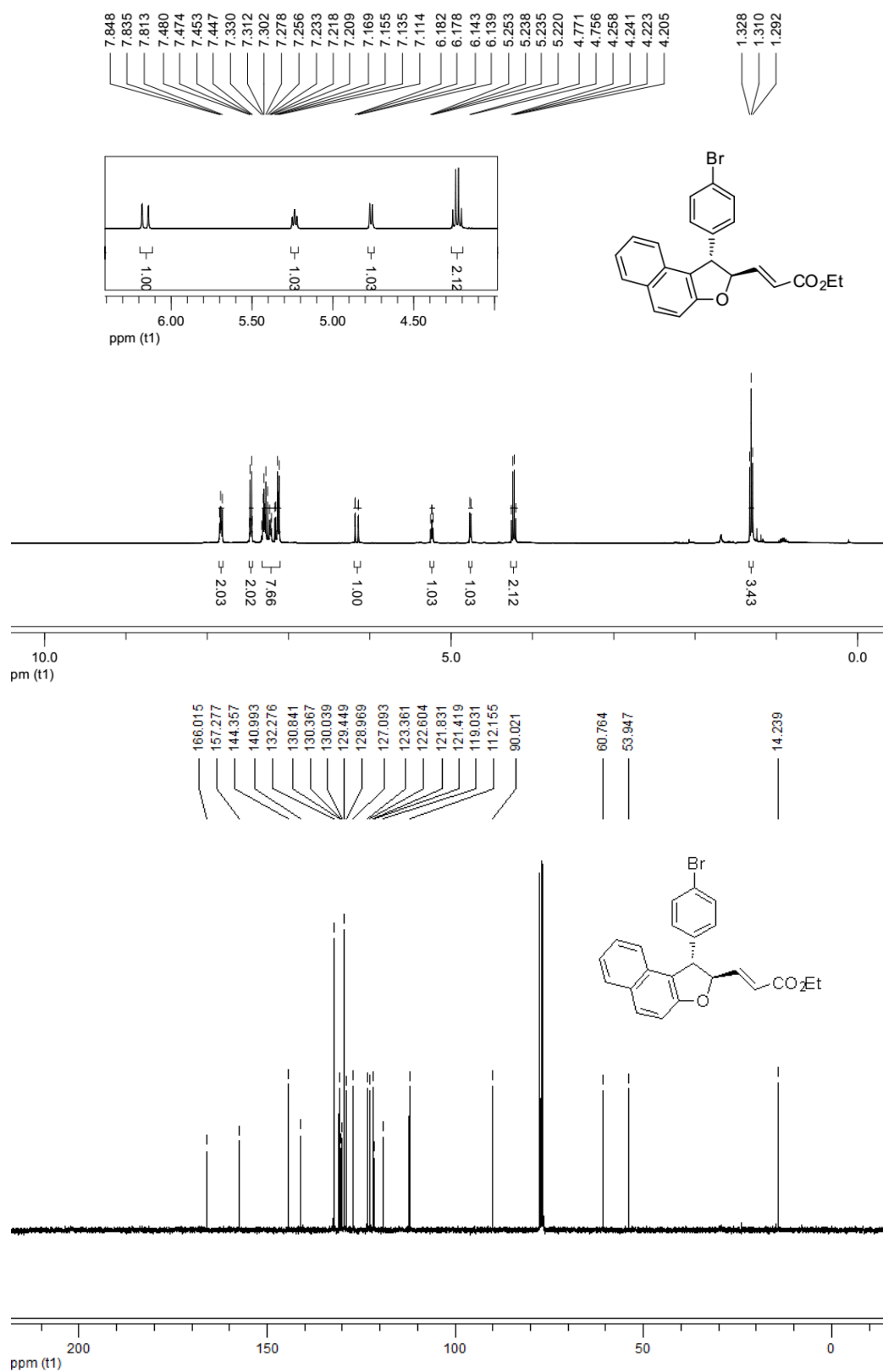
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.419	2574547	49.59	224879
2	W2489 ChA 254nm	7.257	2617154	50.41	179153

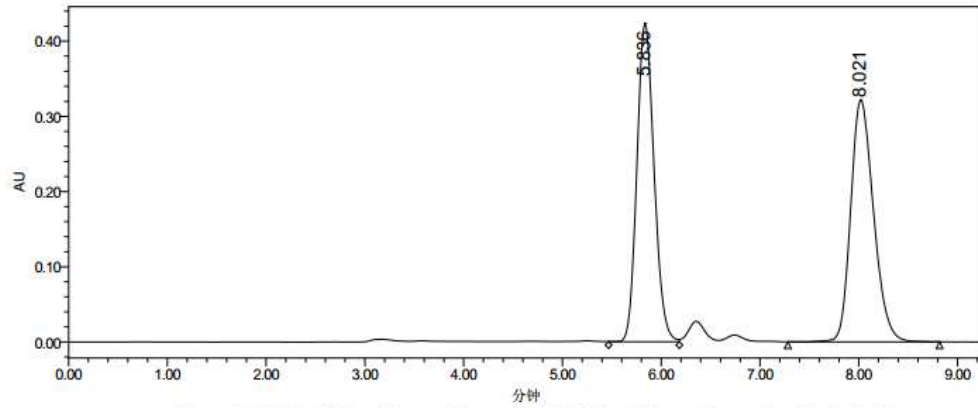


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

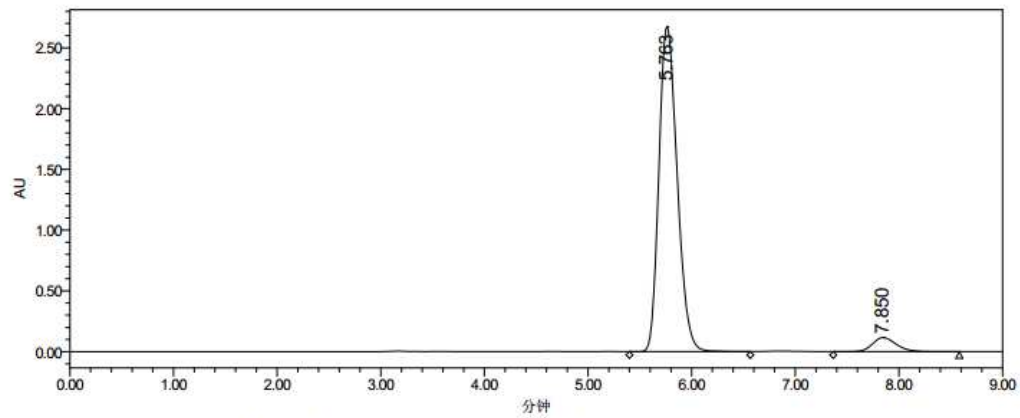
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.410	19465390	96.42	1694838
2	W2489 ChA 254nm	7.271	723398	3.58	48055

4da



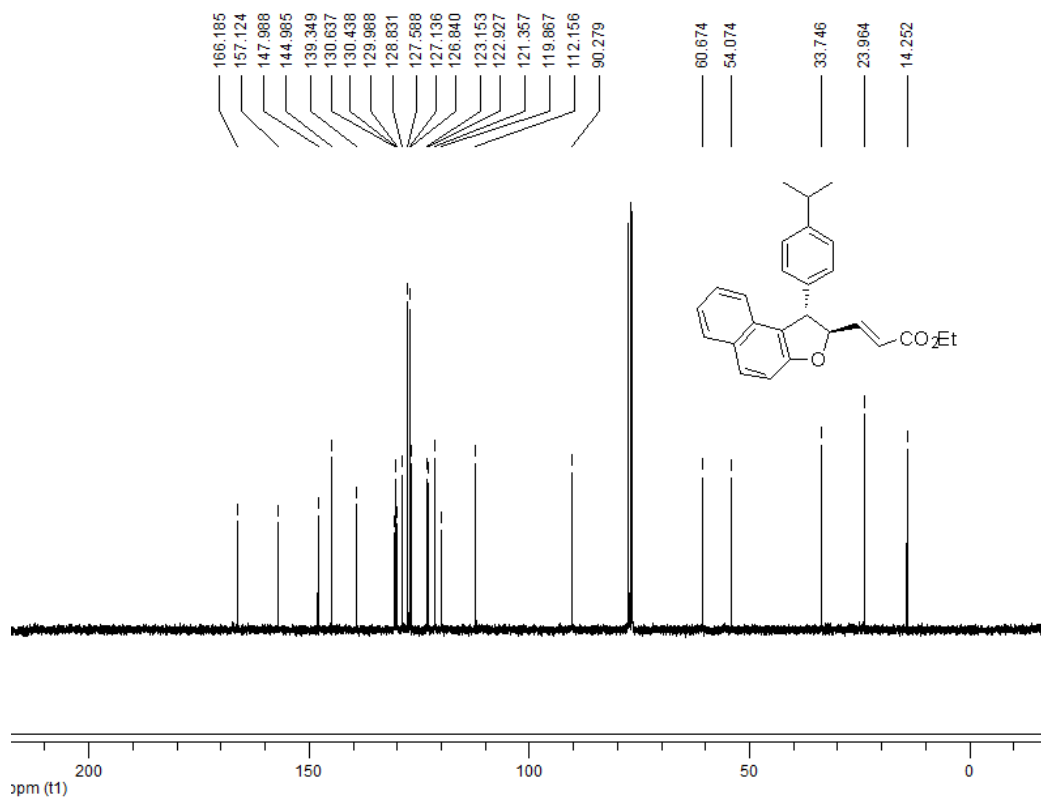
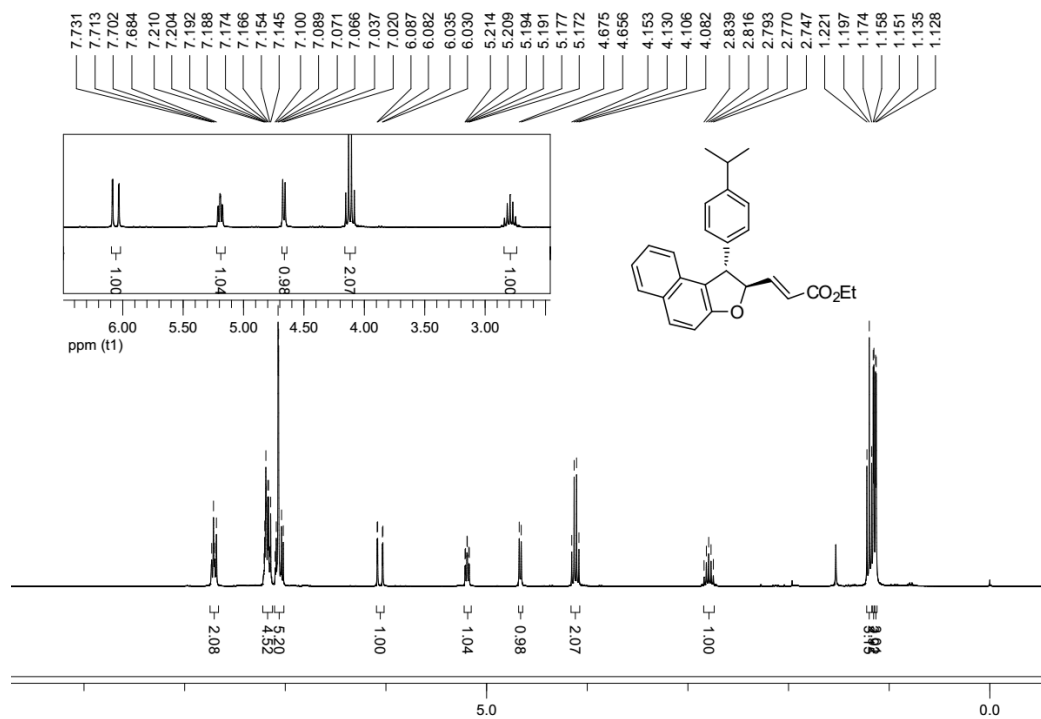


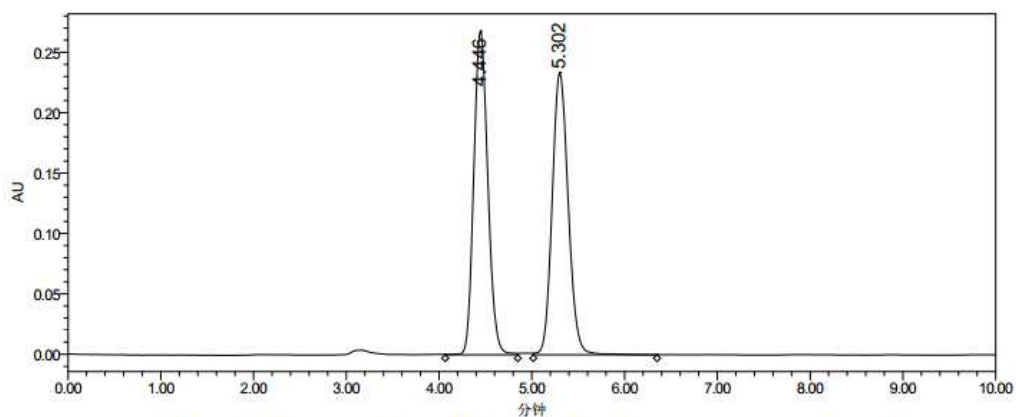
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.836	5116179	49.70	424095
2	W2489 ChA 254nm	8.021	5177550	50.30	322075



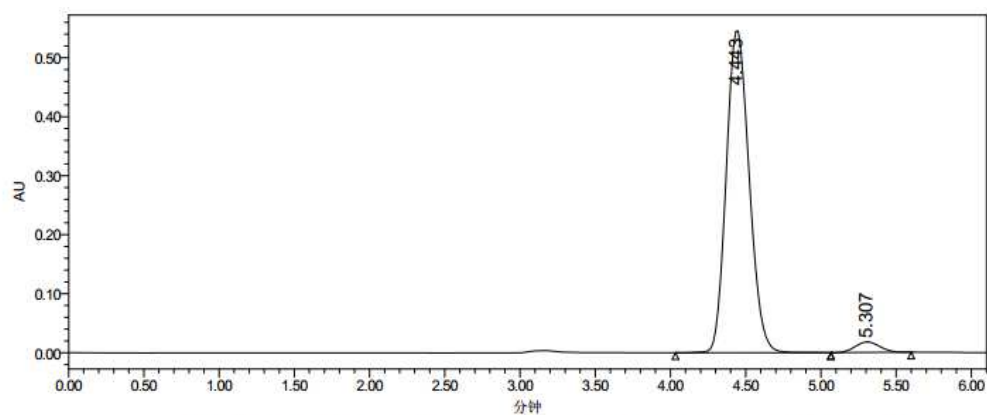
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.763	32744033	94.70	2679688
2	W2489 ChA 254nm	7.850	1831139	5.30	115414

4ea



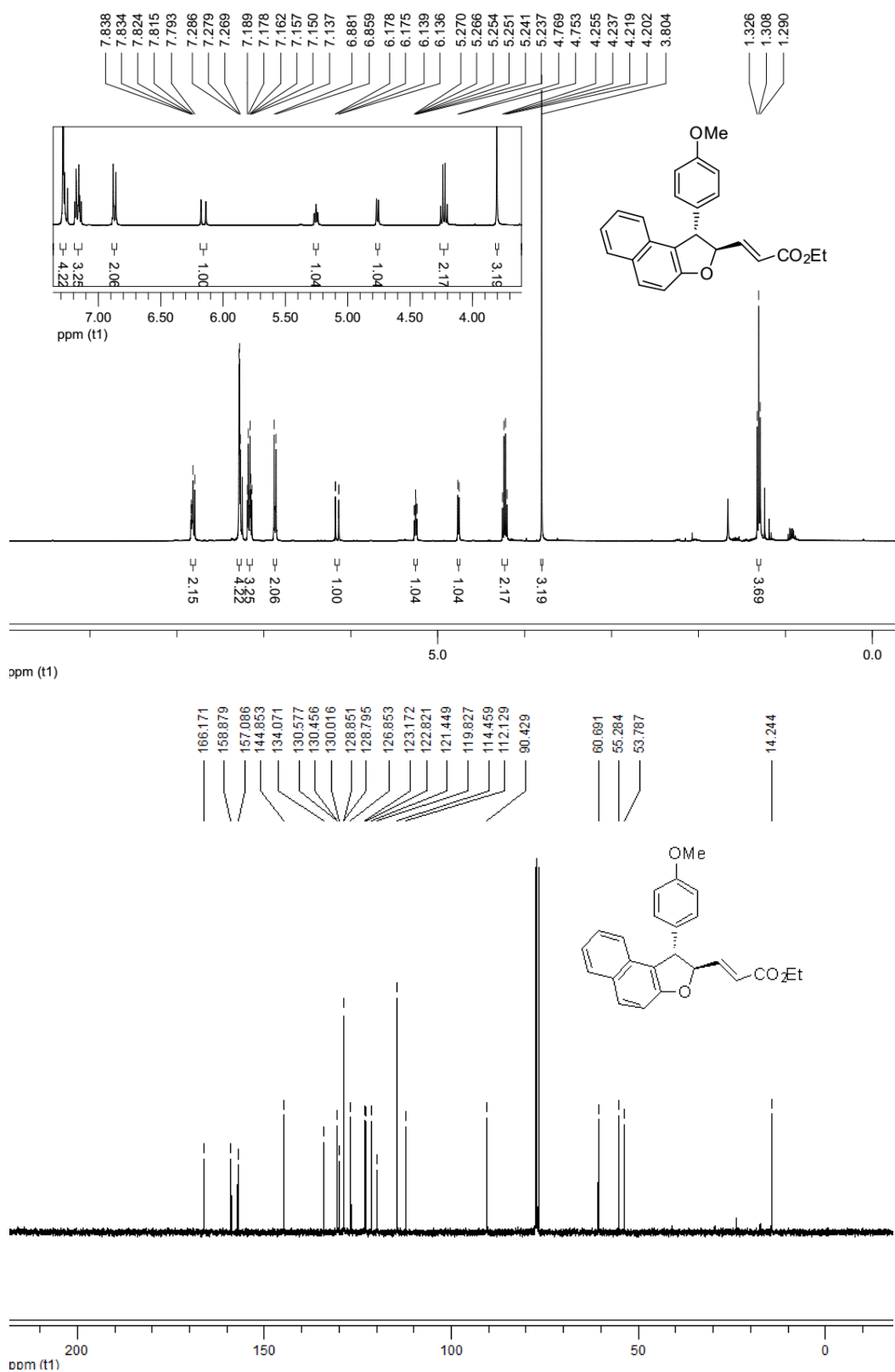


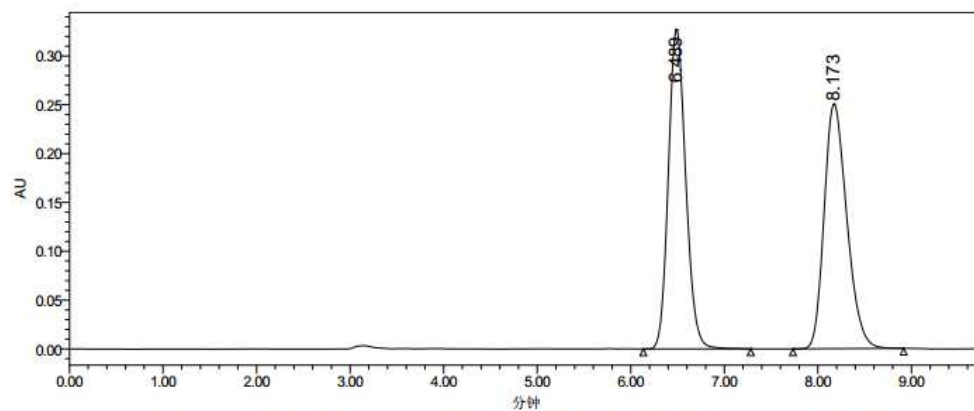
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	4.446	2819418	50.06	268914
2	W2489 ChA 254nm	5.302	2812442	49.94	234200



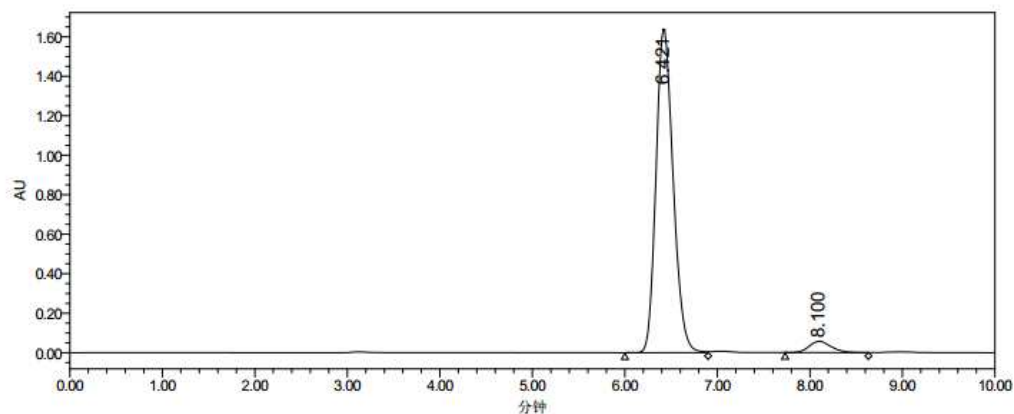
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	4.443	5781393	96.64	547348
2	W2489 ChA 254nm	5.307	201174	3.36	17755

4fa



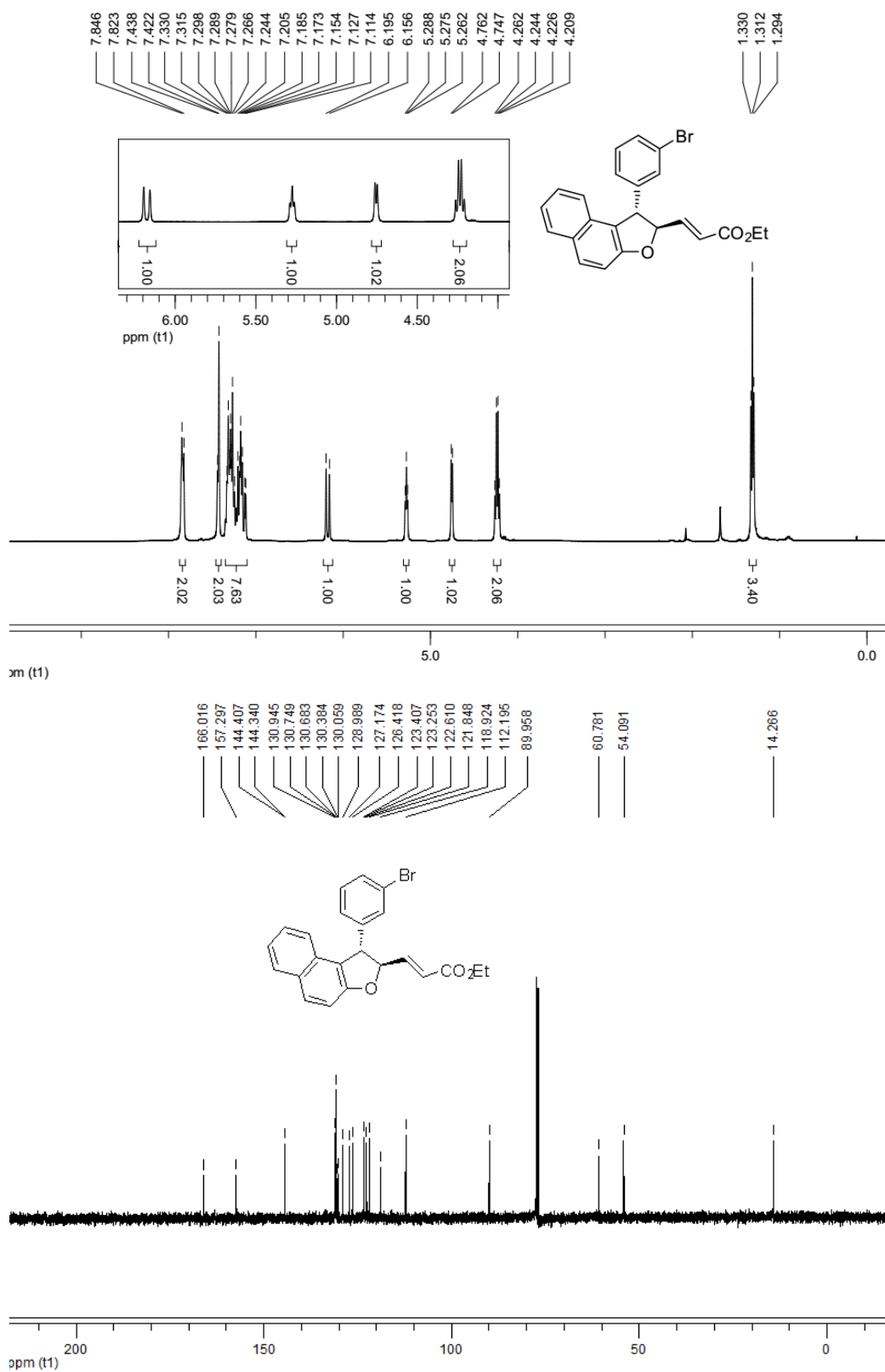


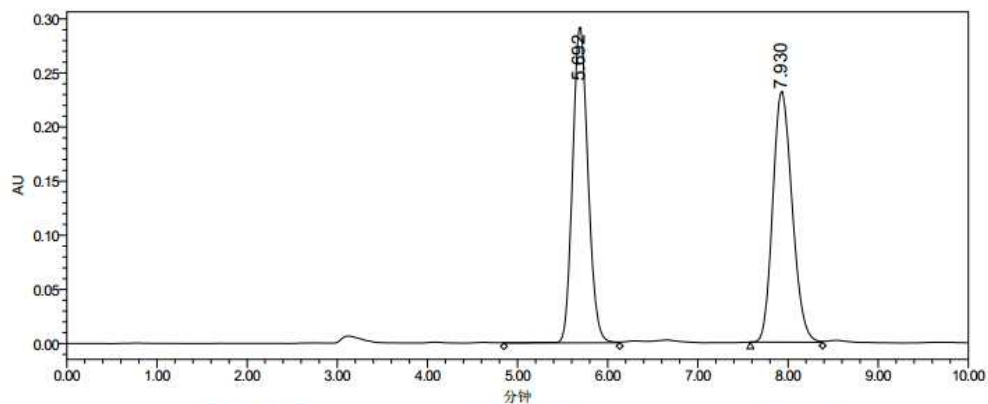
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	6.489	4221138	50.00	328173
2	W2489 ChA 254nm	8.173	4220762	50.00	251128



	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	6.421	21128094	95.74	1641797
2	W2489 ChA 254nm	8.100	940986	4.26	56991

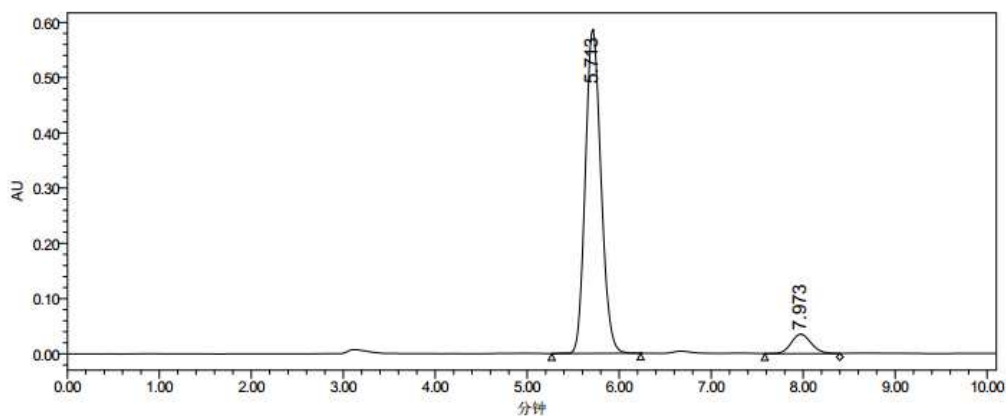
4ga





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: ZWP 1525 A

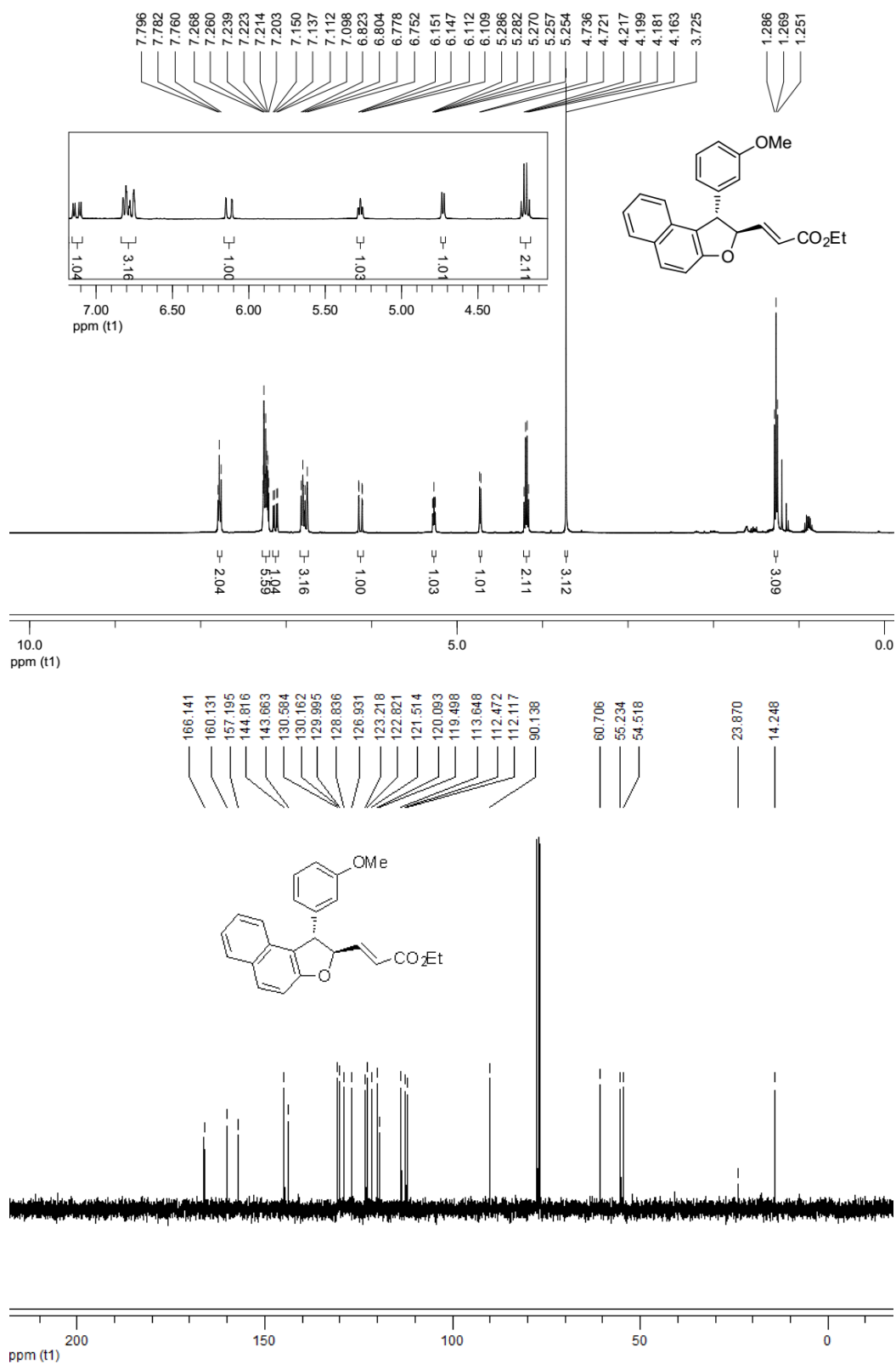
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.692	3475886	50.00	292583
2	W2489 ChA 254nm	7.930	3476433	50.00	231612

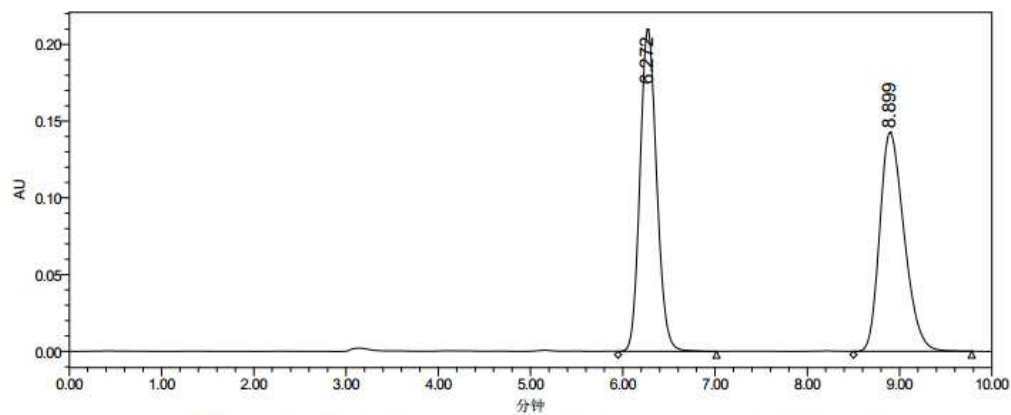


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: ZWP 1525 E

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.713	6960331	92.94	587204
2	W2489 ChA 254nm	7.973	528768	7.06	35077

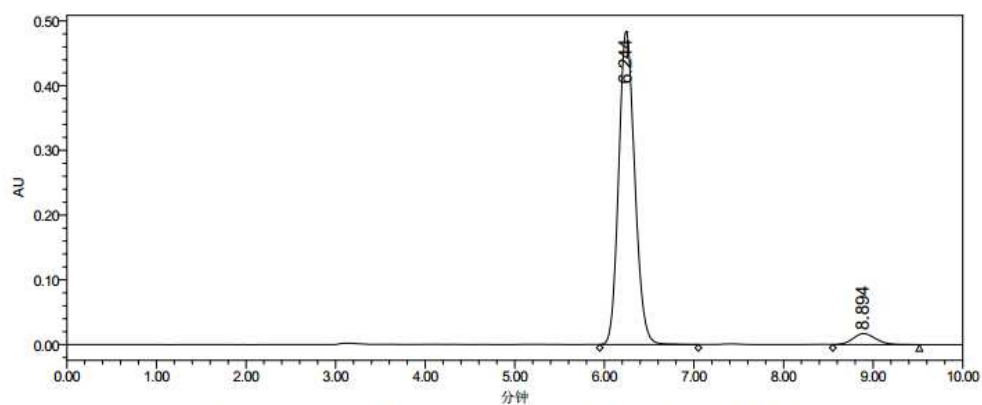
4ha





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

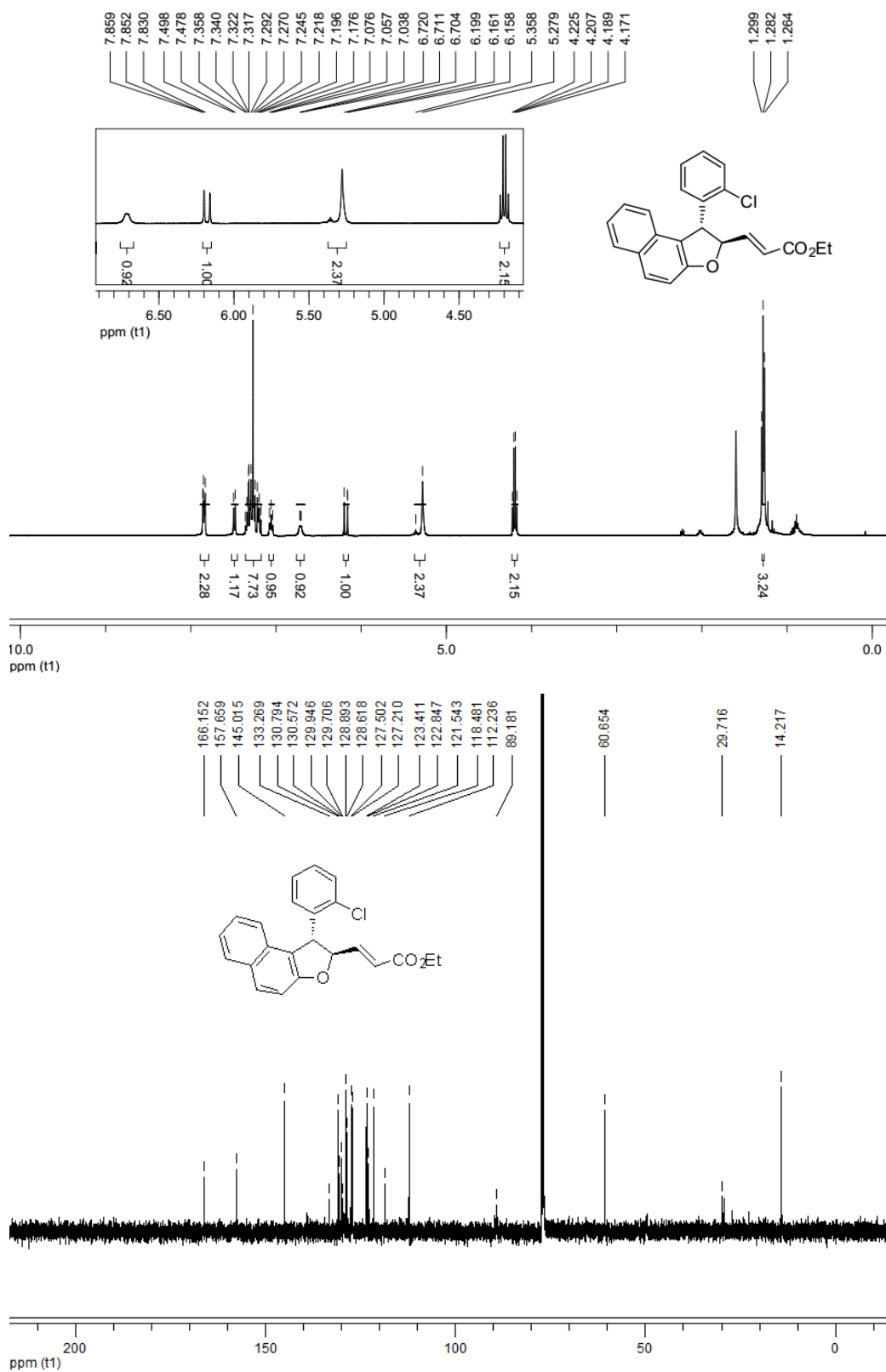
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	6.272	2642631	50.16	210735
2	W2489 ChA 254nm	8.899	2625365	49.84	142845

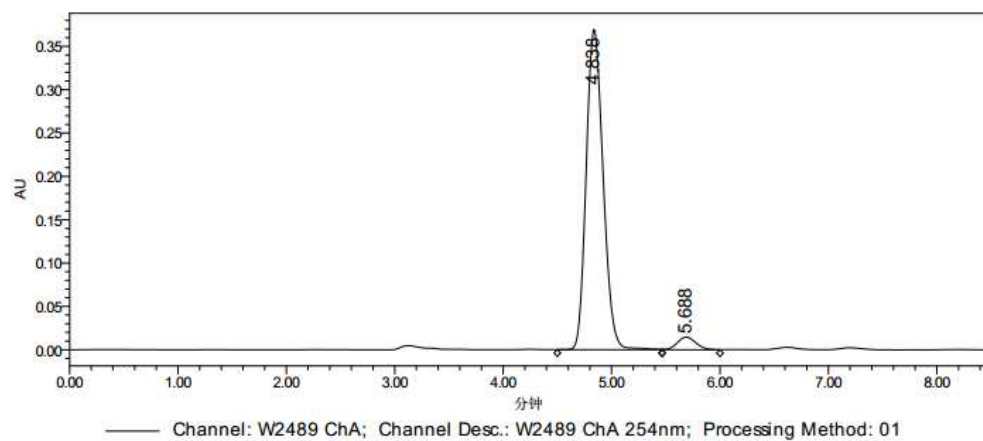
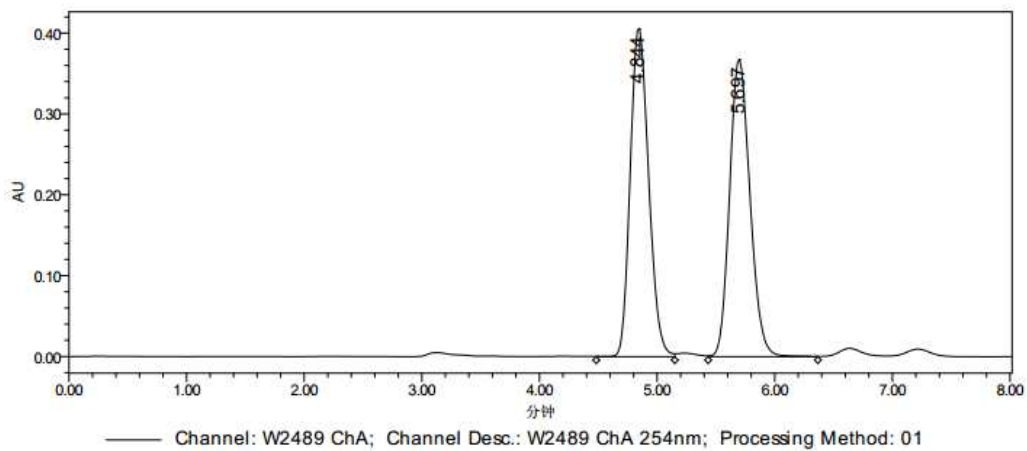


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

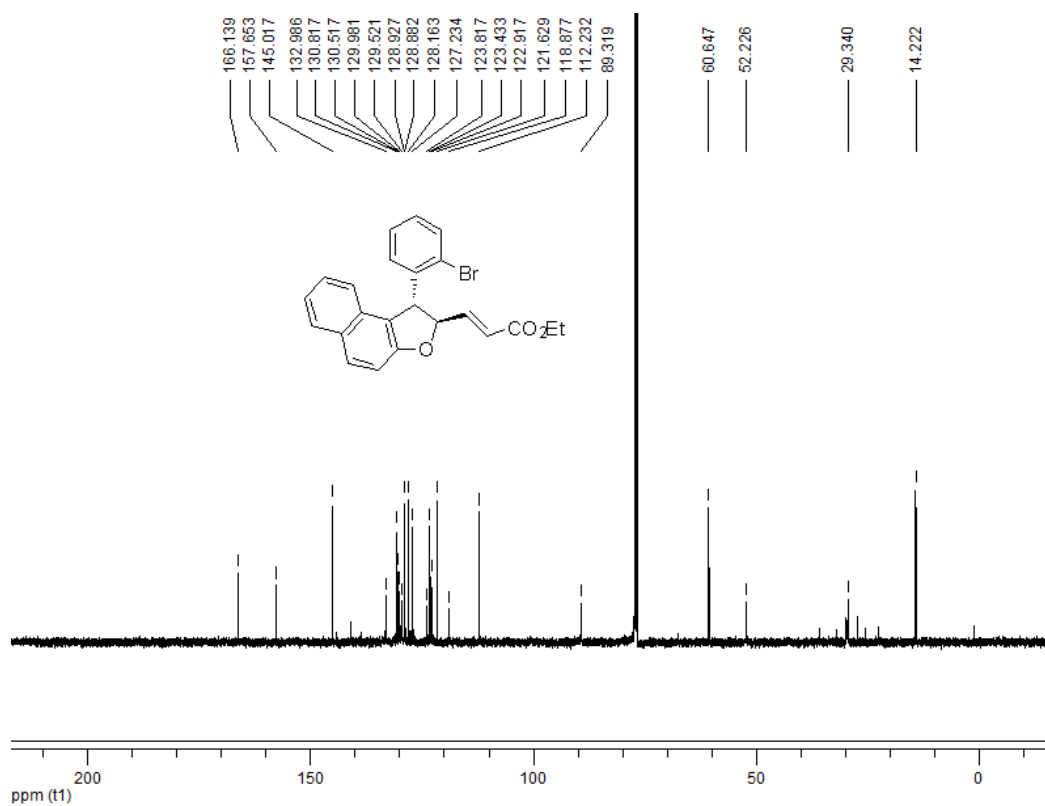
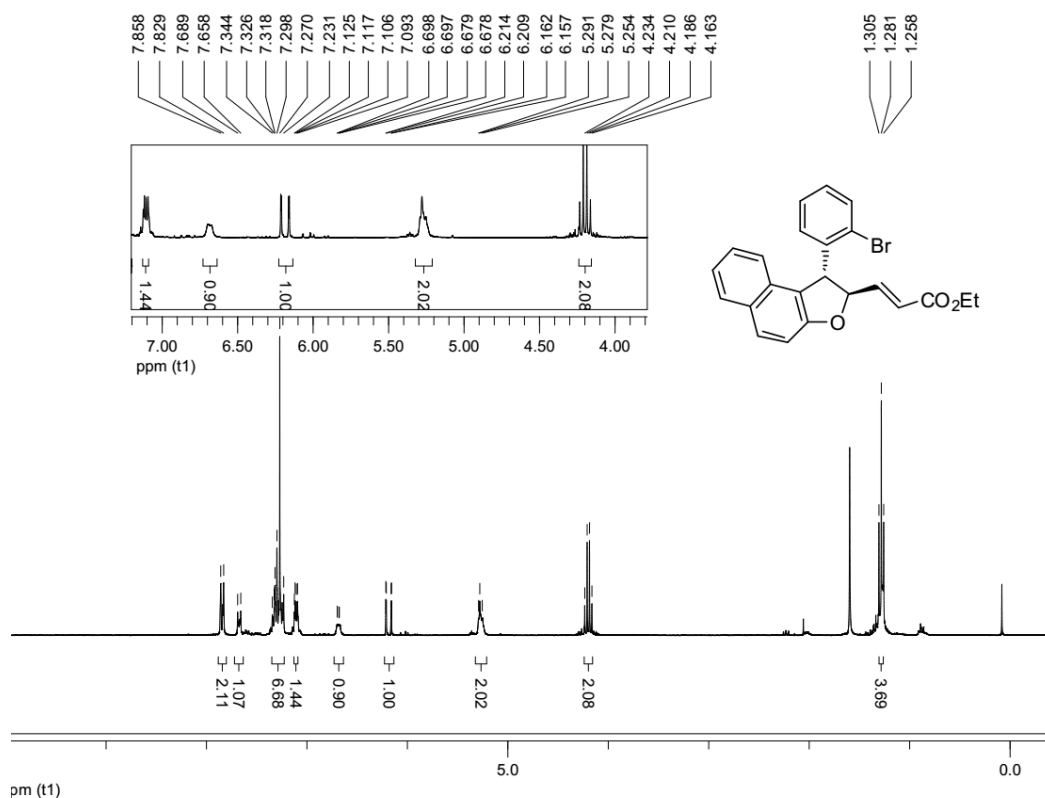
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	6.244	6047810	95.26	485003
2	W2489 ChA 254nm	8.894	300913	4.74	16927

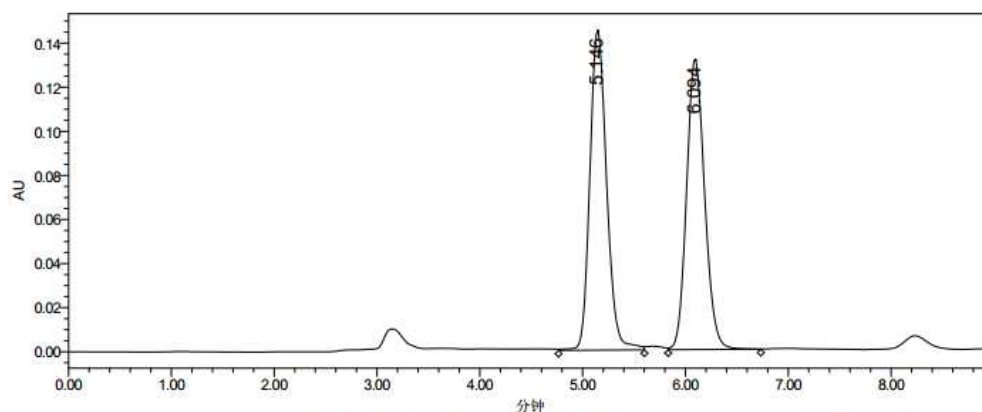
4ia





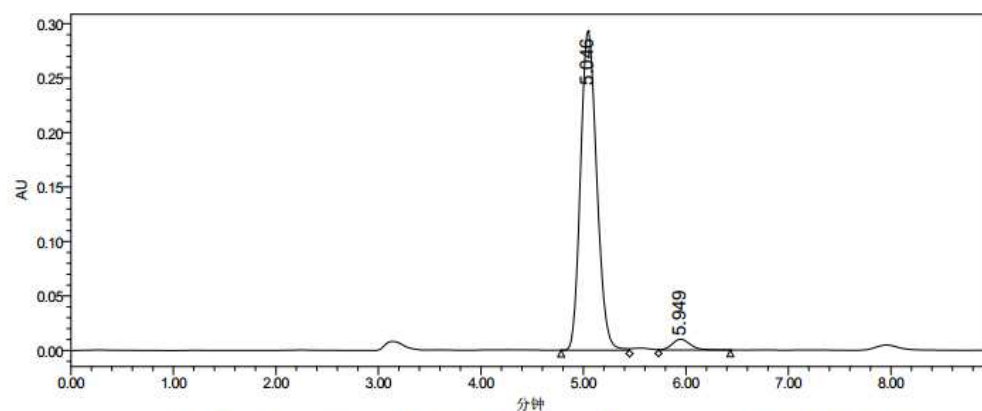
4ja





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

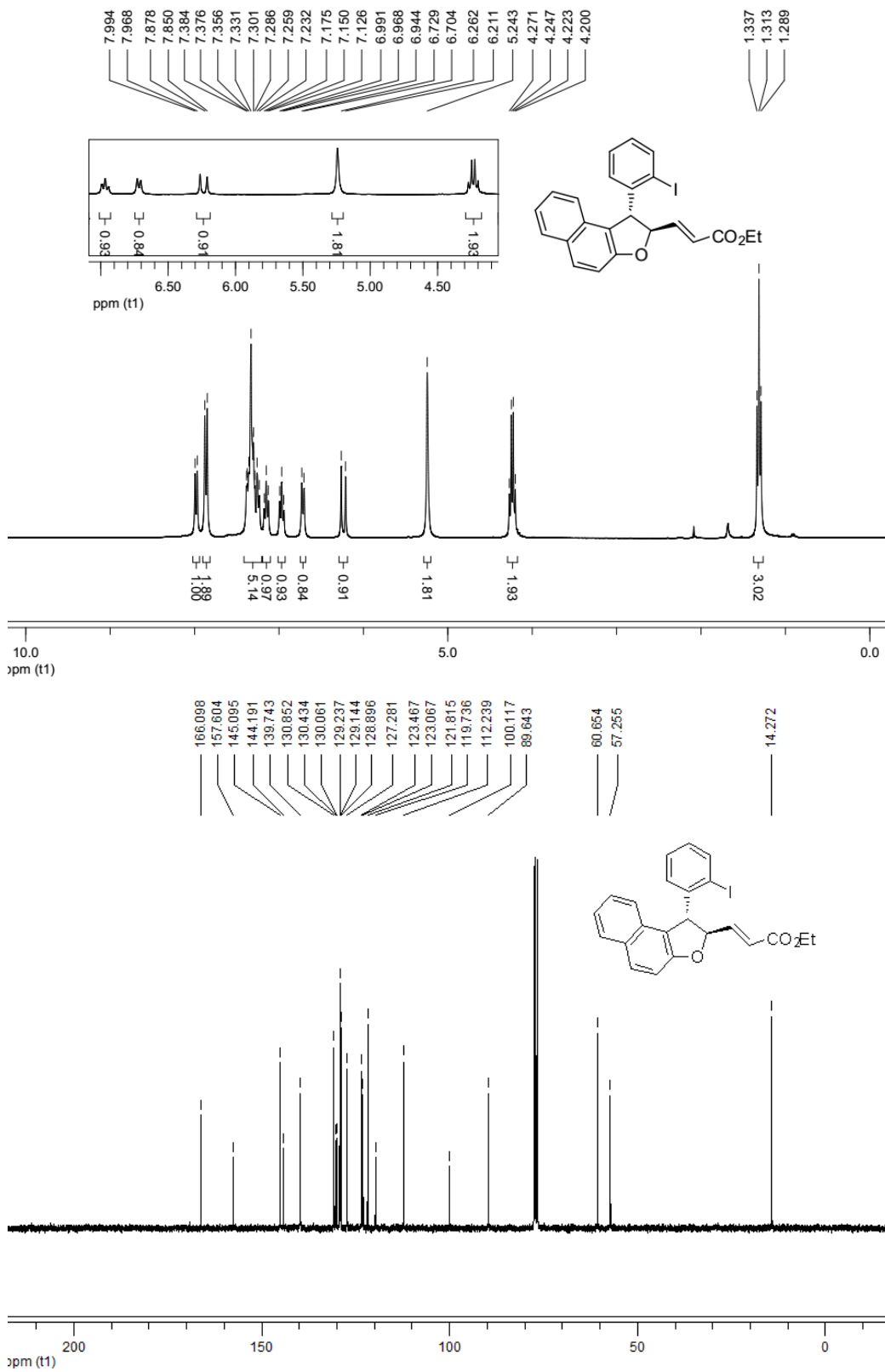
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.146	1643980	50.58	145295
2	W2489 ChA 254nm	6.094	1606230	49.42	131890

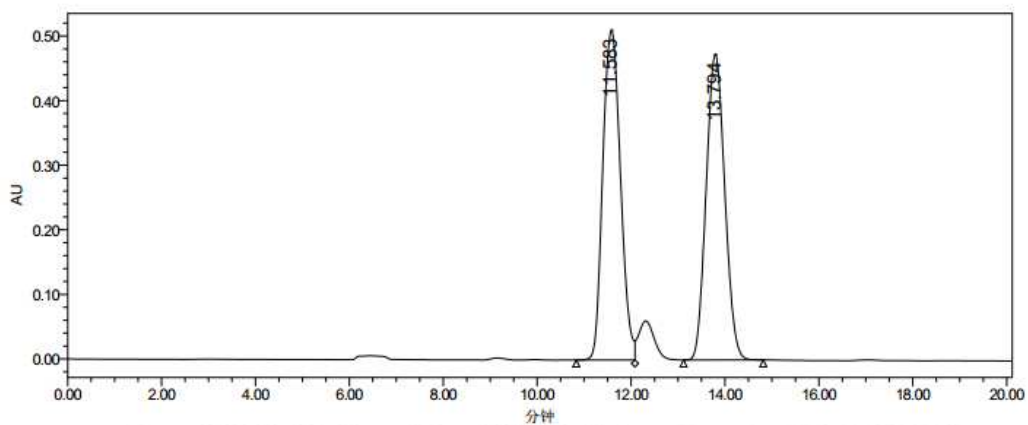


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.046	3223431	96.29	293833
2	W2489 ChA 254nm	5.949	124126	3.71	10021

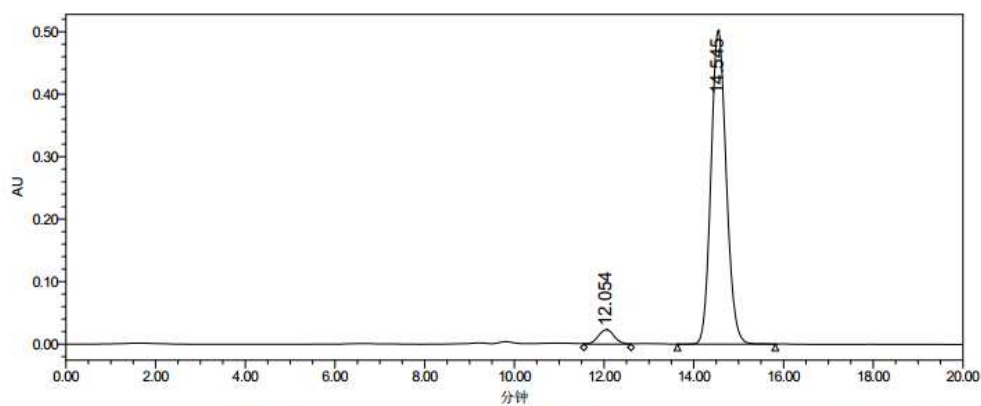
4ka





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: ZWP 1510 A

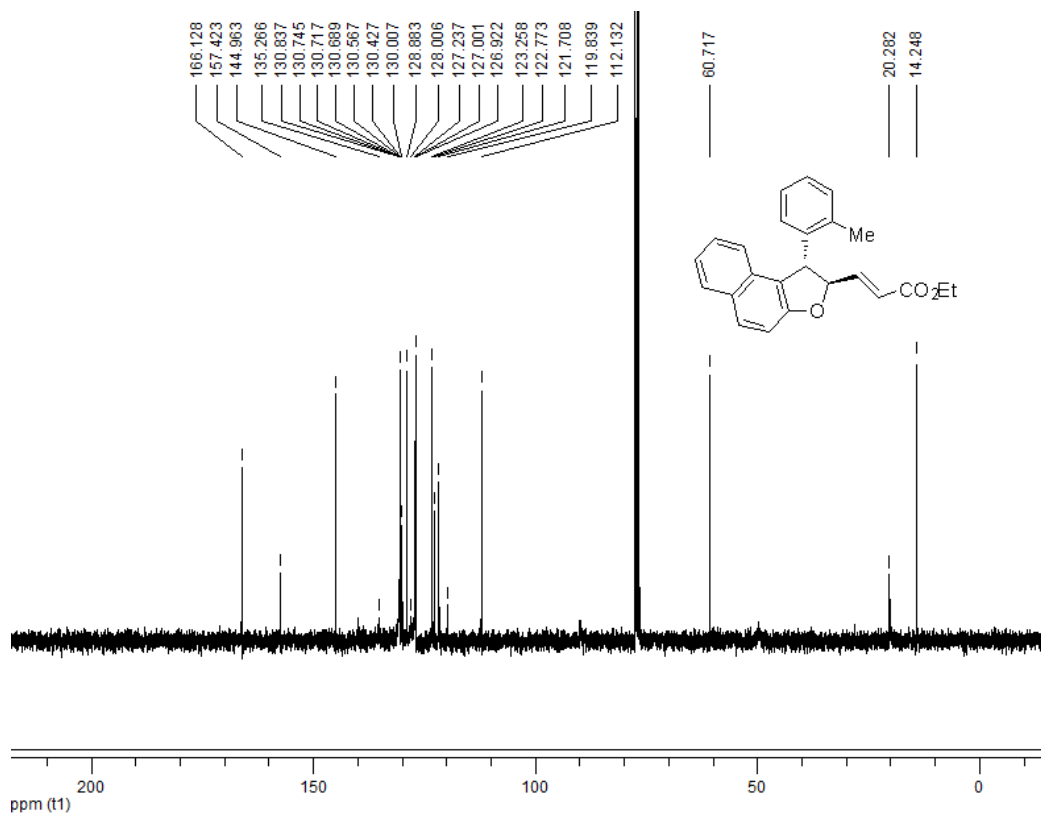
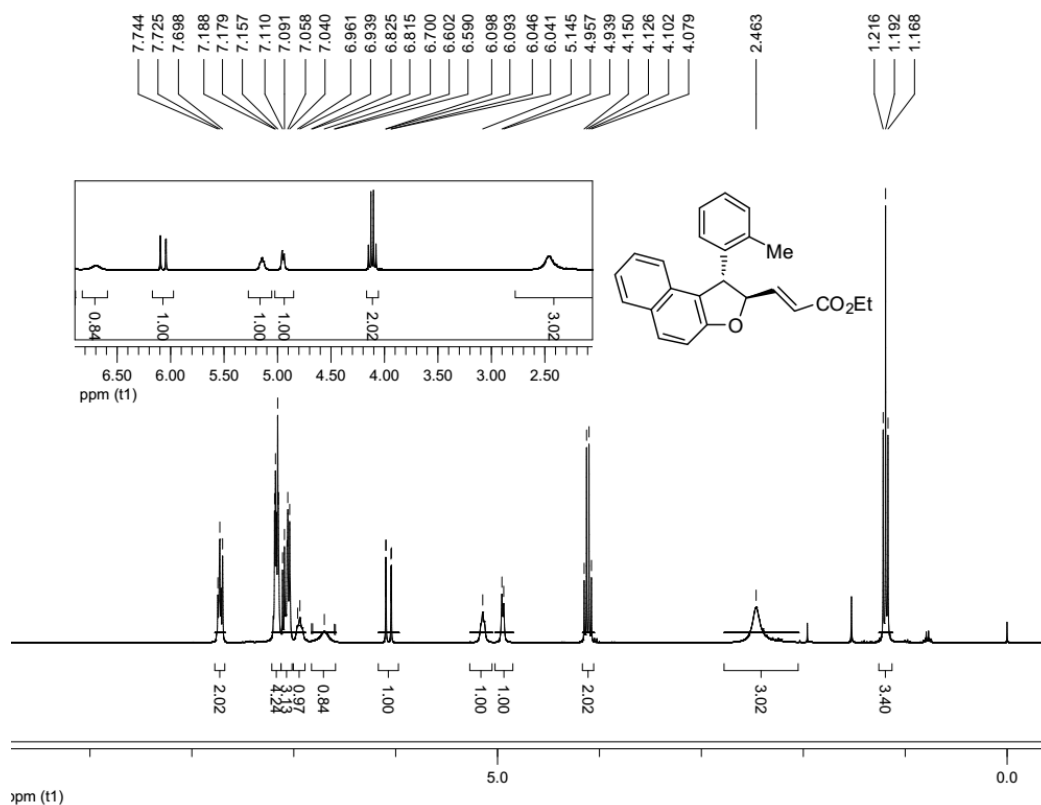
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	11.583	13345181	50.62	510681
2	W2489 ChA 254nm	13.794	13016263	49.38	473699

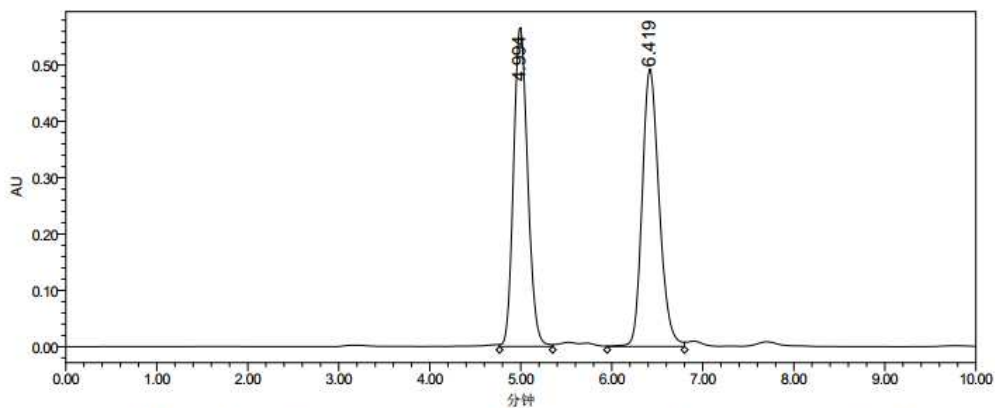


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: ZWP 1510 E 0

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	12.054	569405	4.57	23091
2	W2489 ChA 254nm	14.545	11886105	95.43	502645

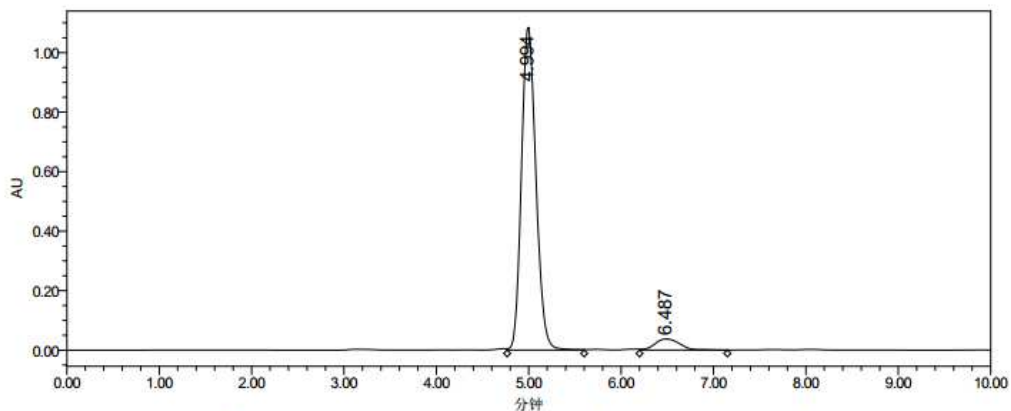
4la





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 1539 A

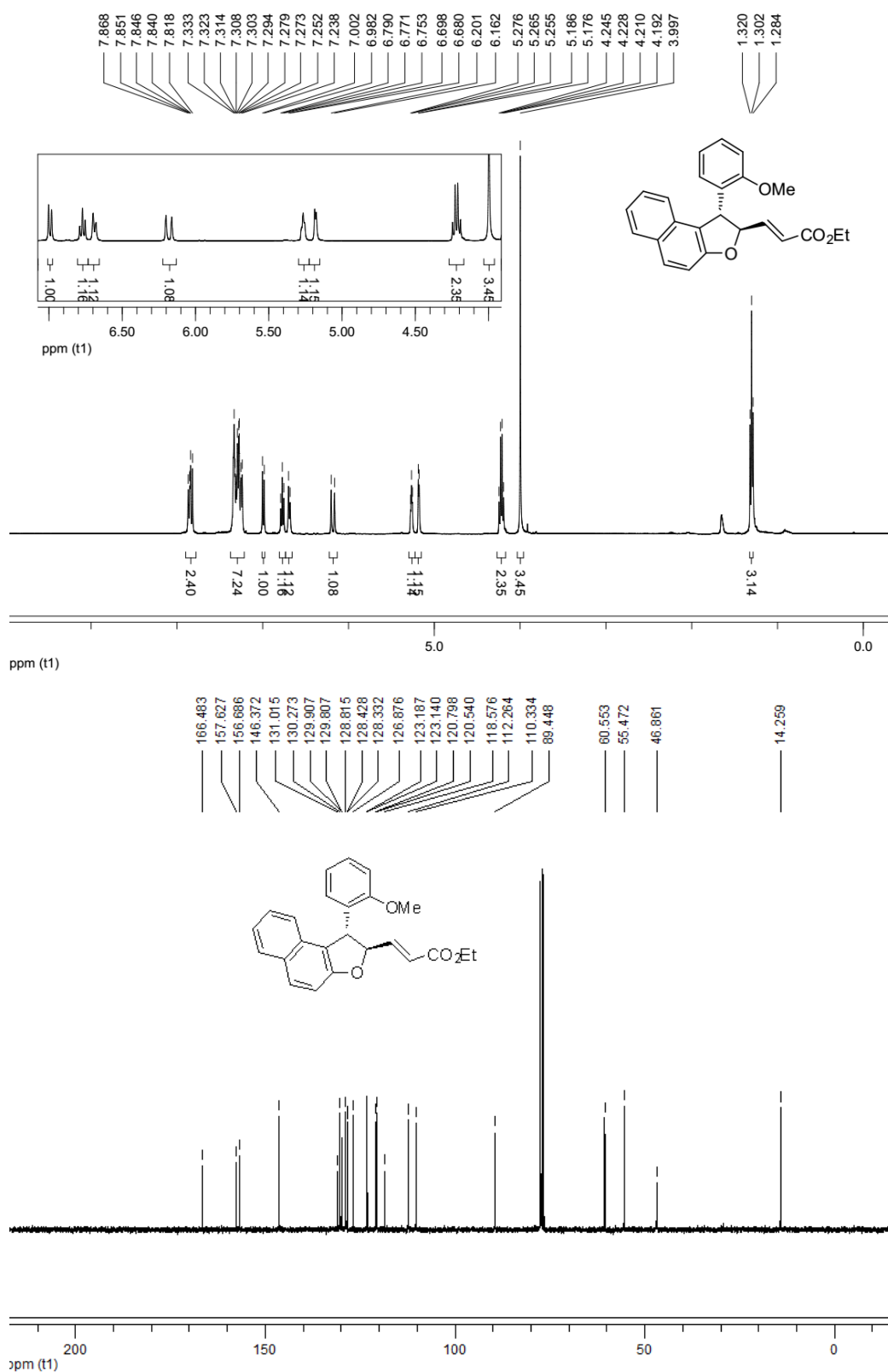
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	4.994	6145236	49.09	567748
2	W2489 ChA 254nm	6.419	6373863	50.91	492619

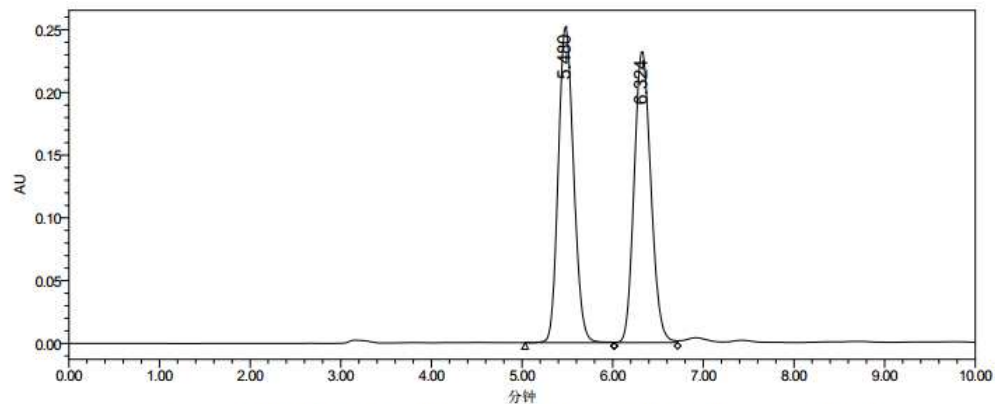


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 1539 E

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	4.994	11851638	94.43	1087079
2	W2489 ChA 254nm	6.487	699111	5.57	37067

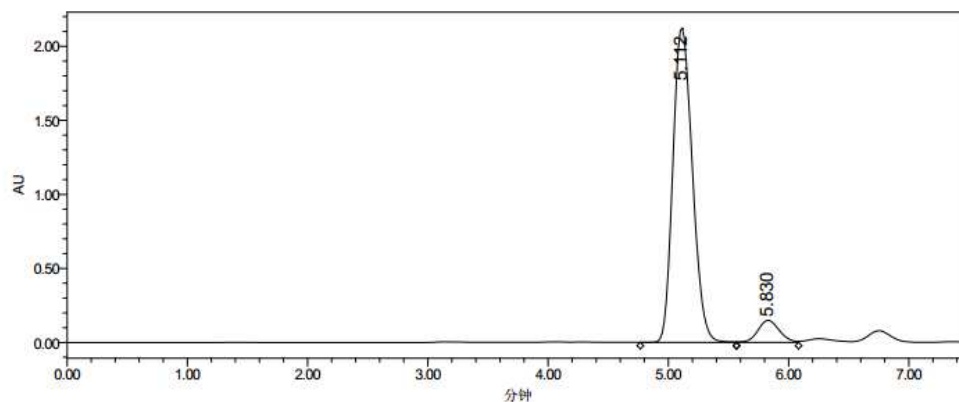
4ma





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

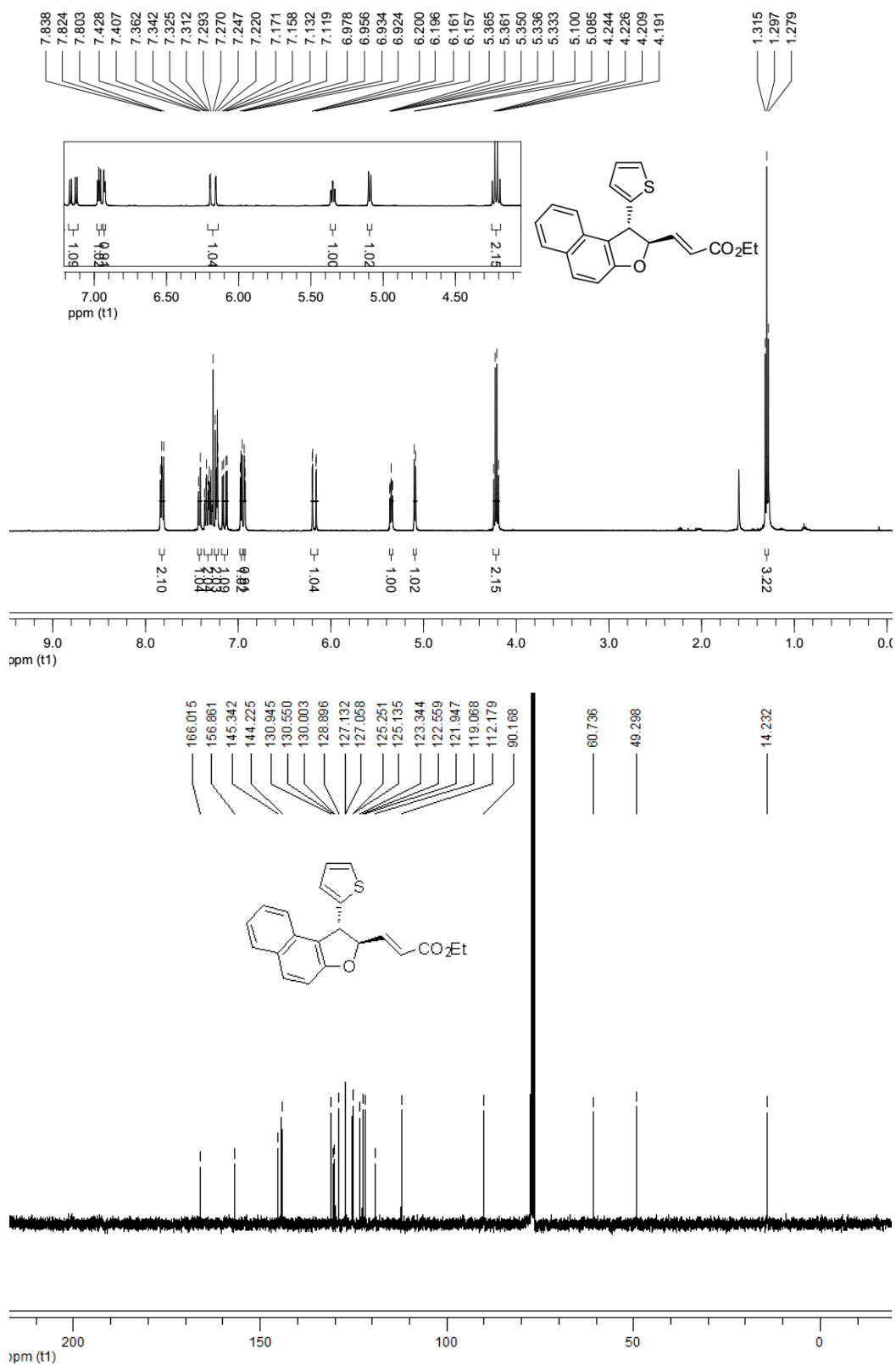
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.480	2971880	50.01	252222
2	W2489 ChA 254nm	6.324	2971045	49.99	232677

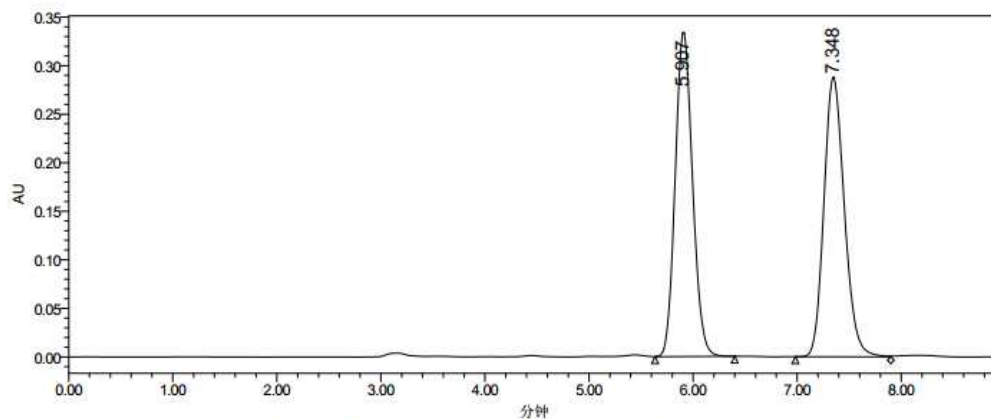


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

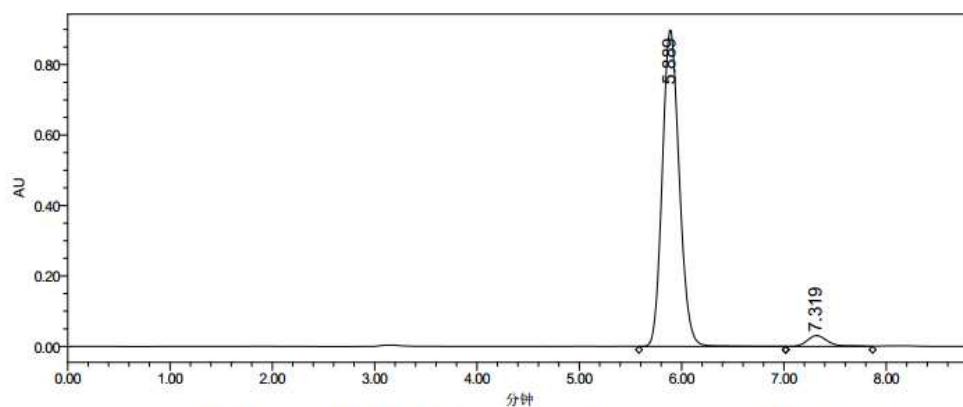
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.112	23929728	92.87	2125860
2	W2489 ChA 254nm	5.830	1836613	7.13	148938

4na



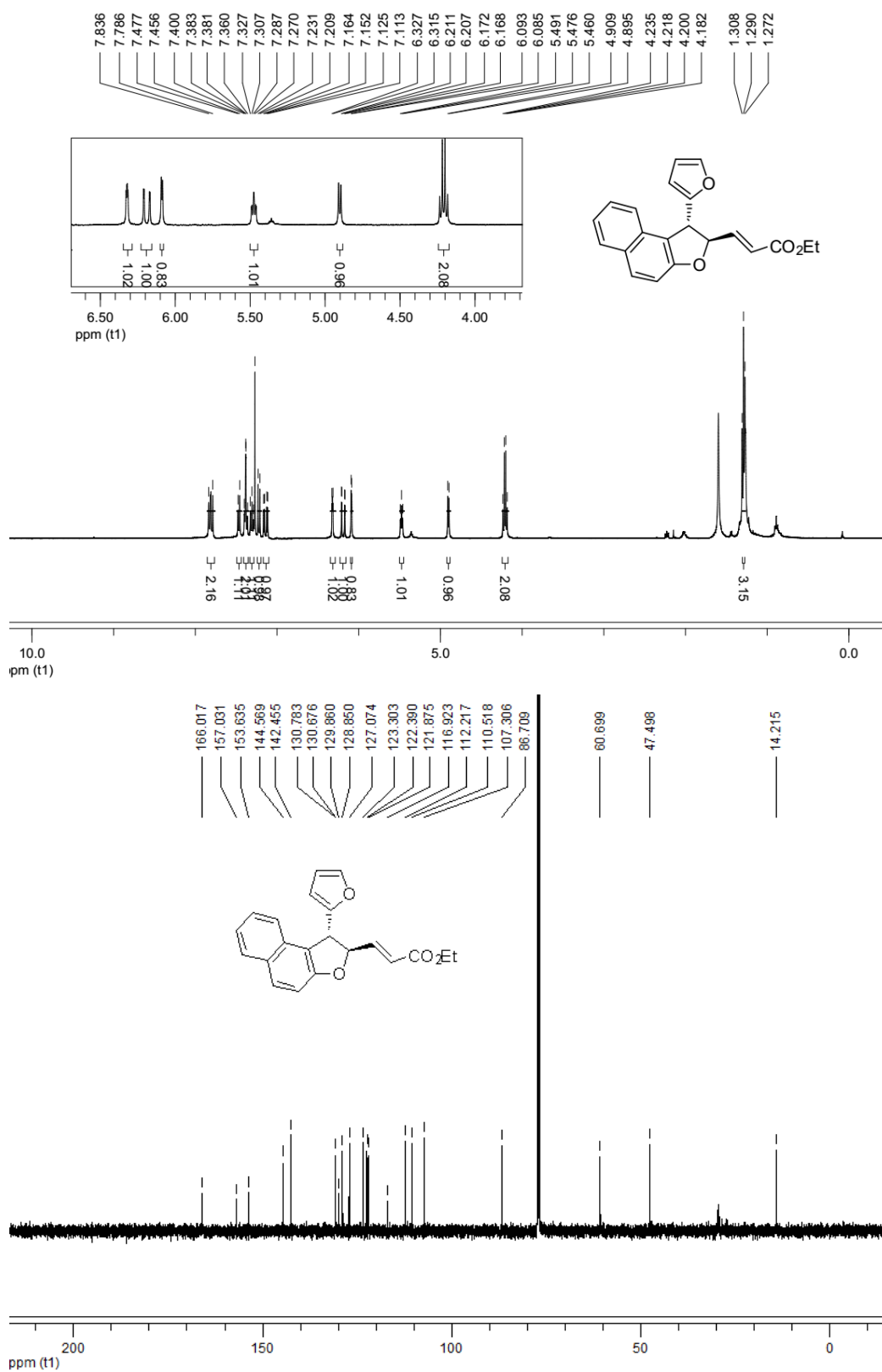


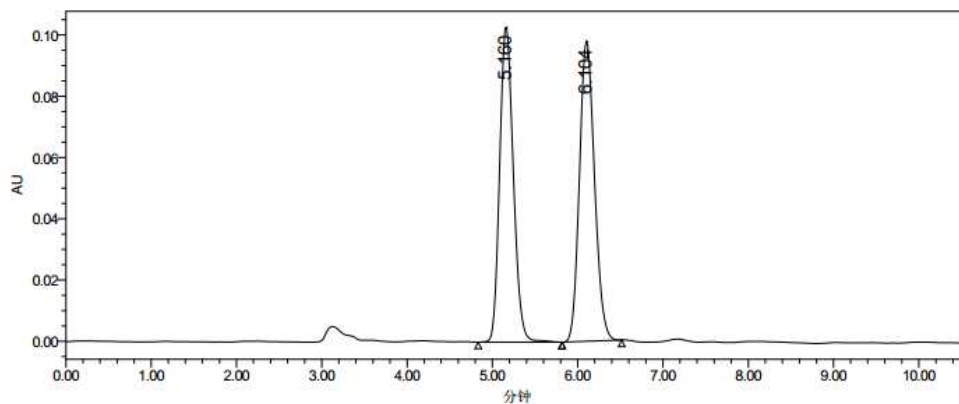
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.907	3868768	49.68	335394
2	W2489 ChA 254nm	7.348	3918283	50.32	288152



	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.889	10327230	95.91	900580
2	W2489 ChA 254nm	7.319	440924	4.09	30753

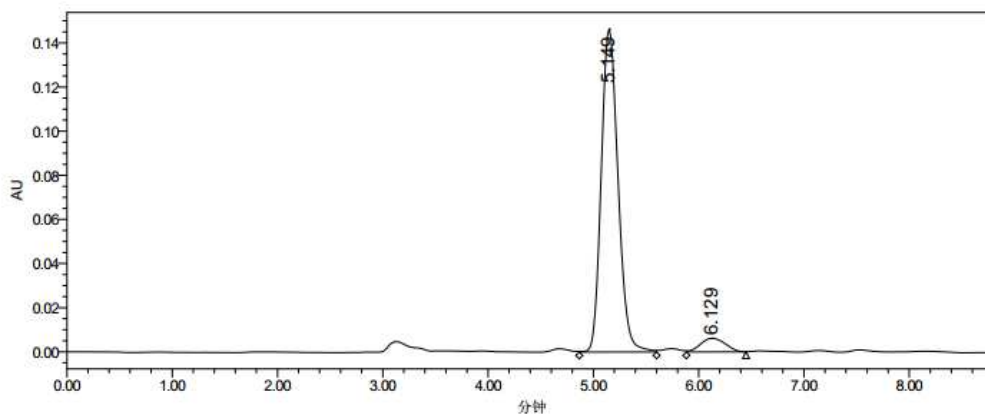
40a





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

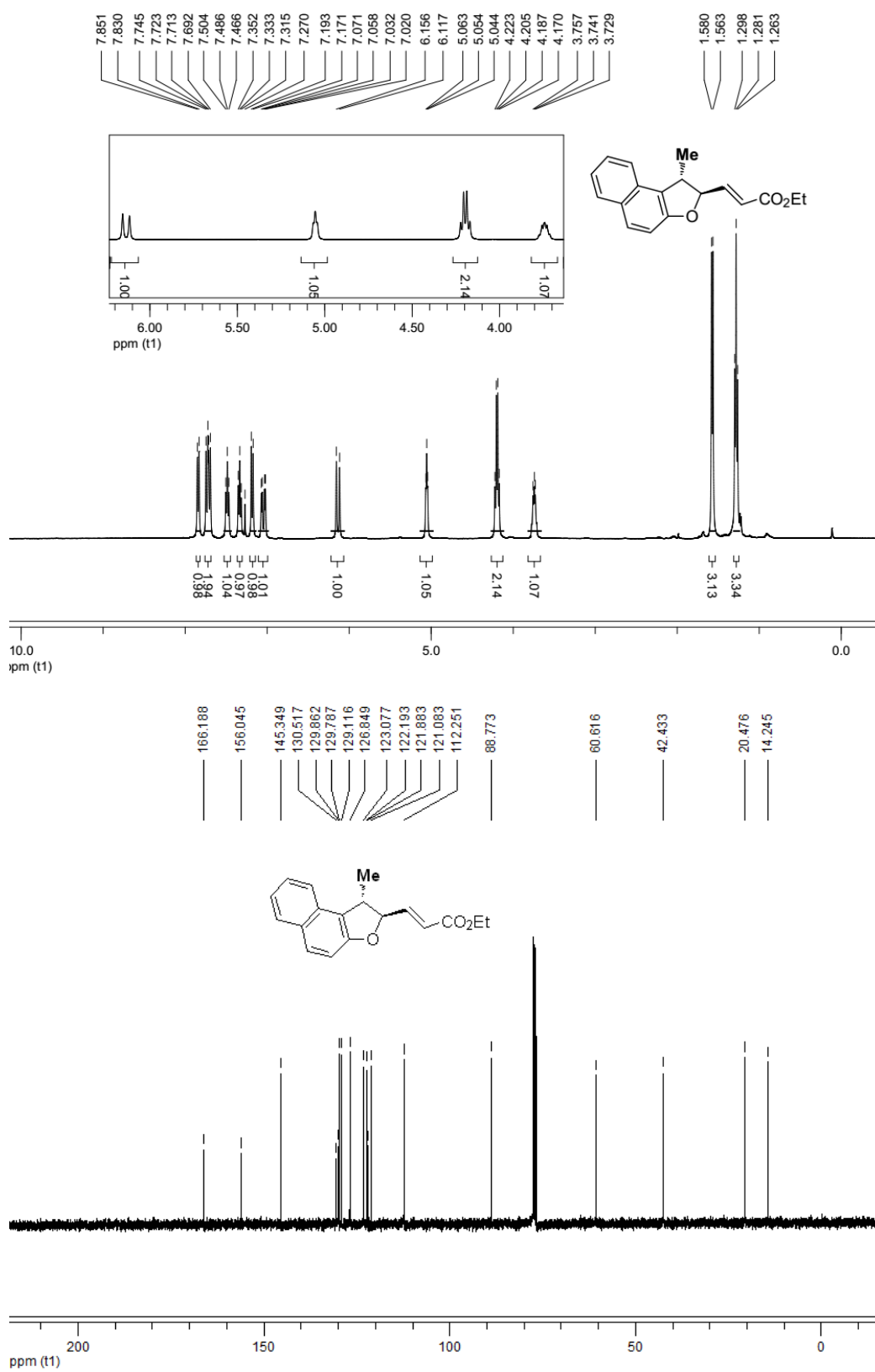
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.160	1149740	48.95	103160
2	W2489 ChA 254nm	6.104	1198853	51.05	98173

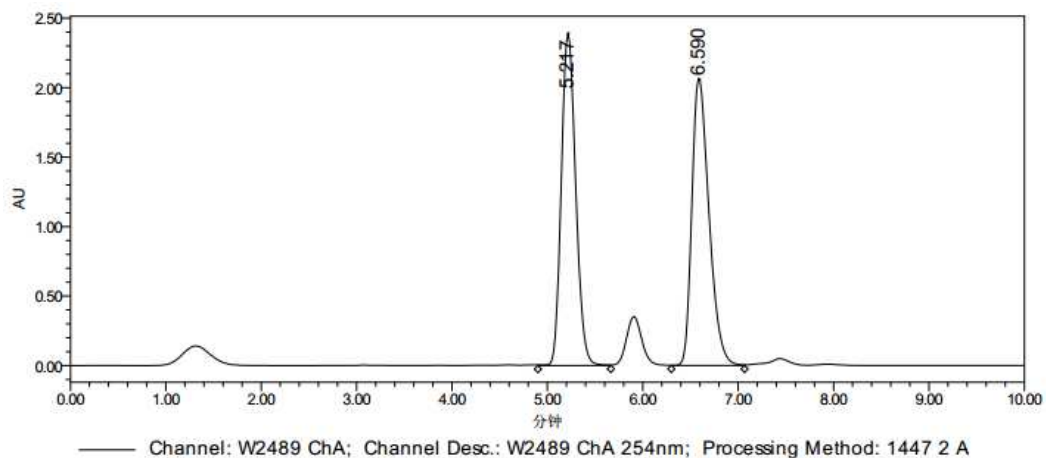


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

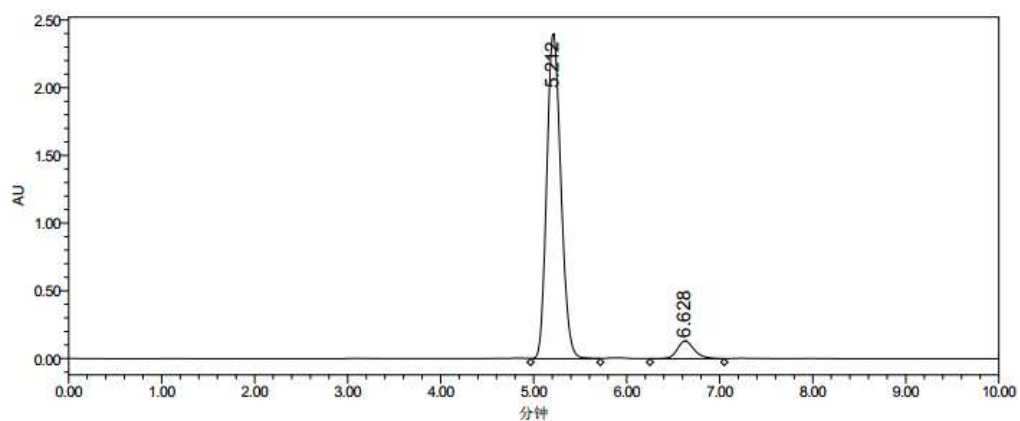
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.149	1627678	94.24	146491
2	W2489 ChA 254nm	6.129	99460	5.76	6123

4pa



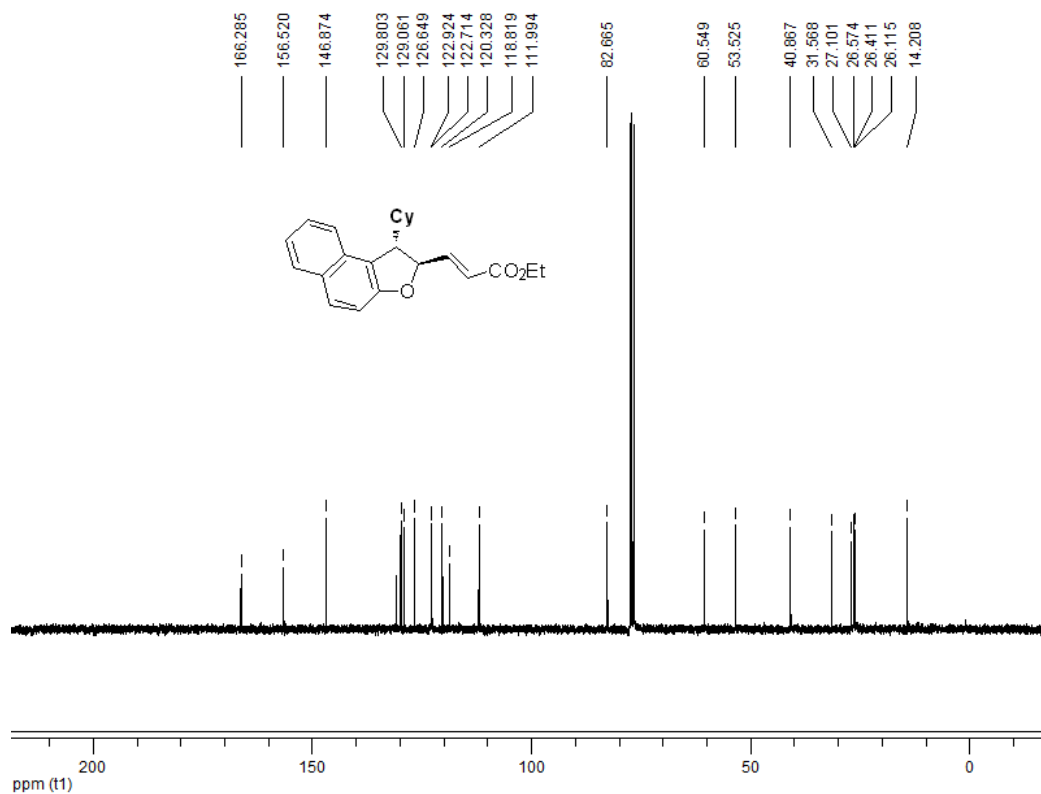
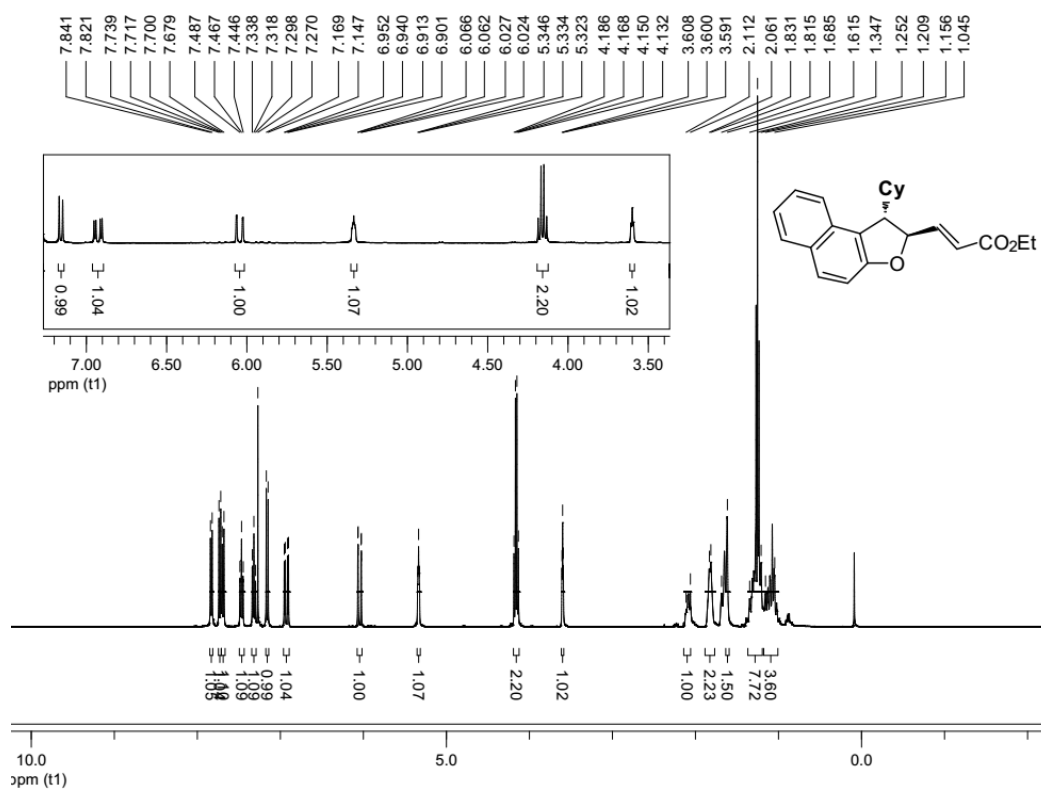


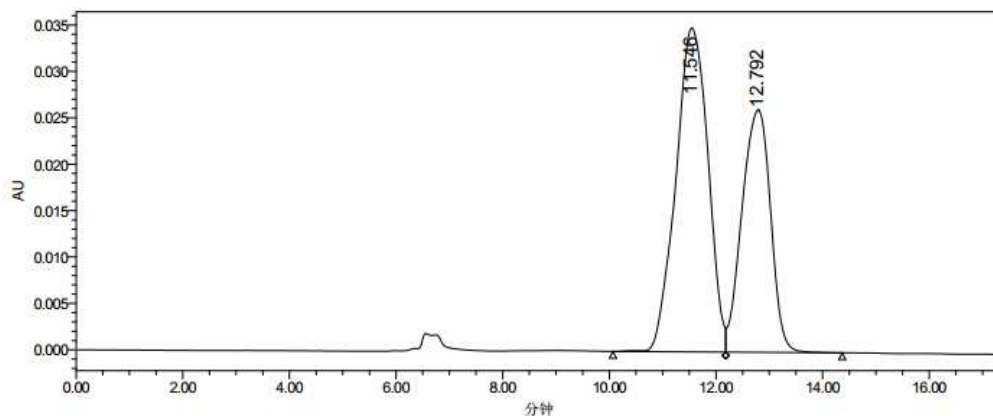
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.217	25092985	49.34	2392353
2	W2489 ChA 254nm	6.590	25761164	50.66	2075090



	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.212	25385039	93.86	2406293
2	W2489 ChA 254nm	6.628	1660336	6.14	131010

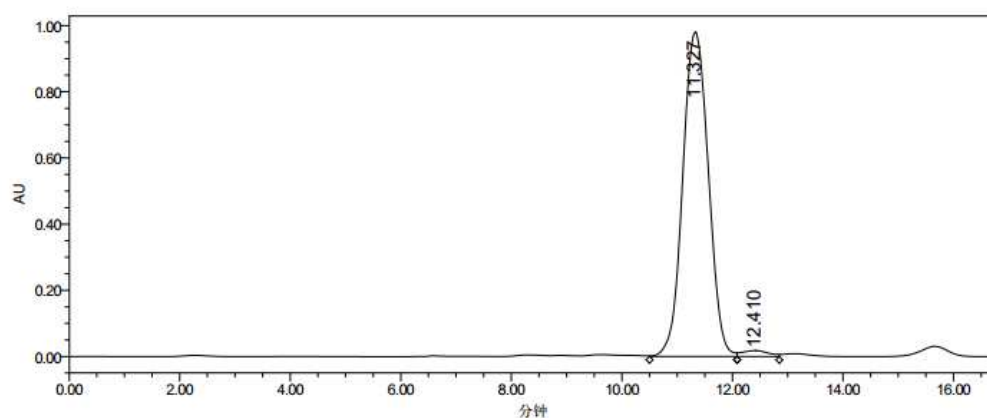
4qa





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

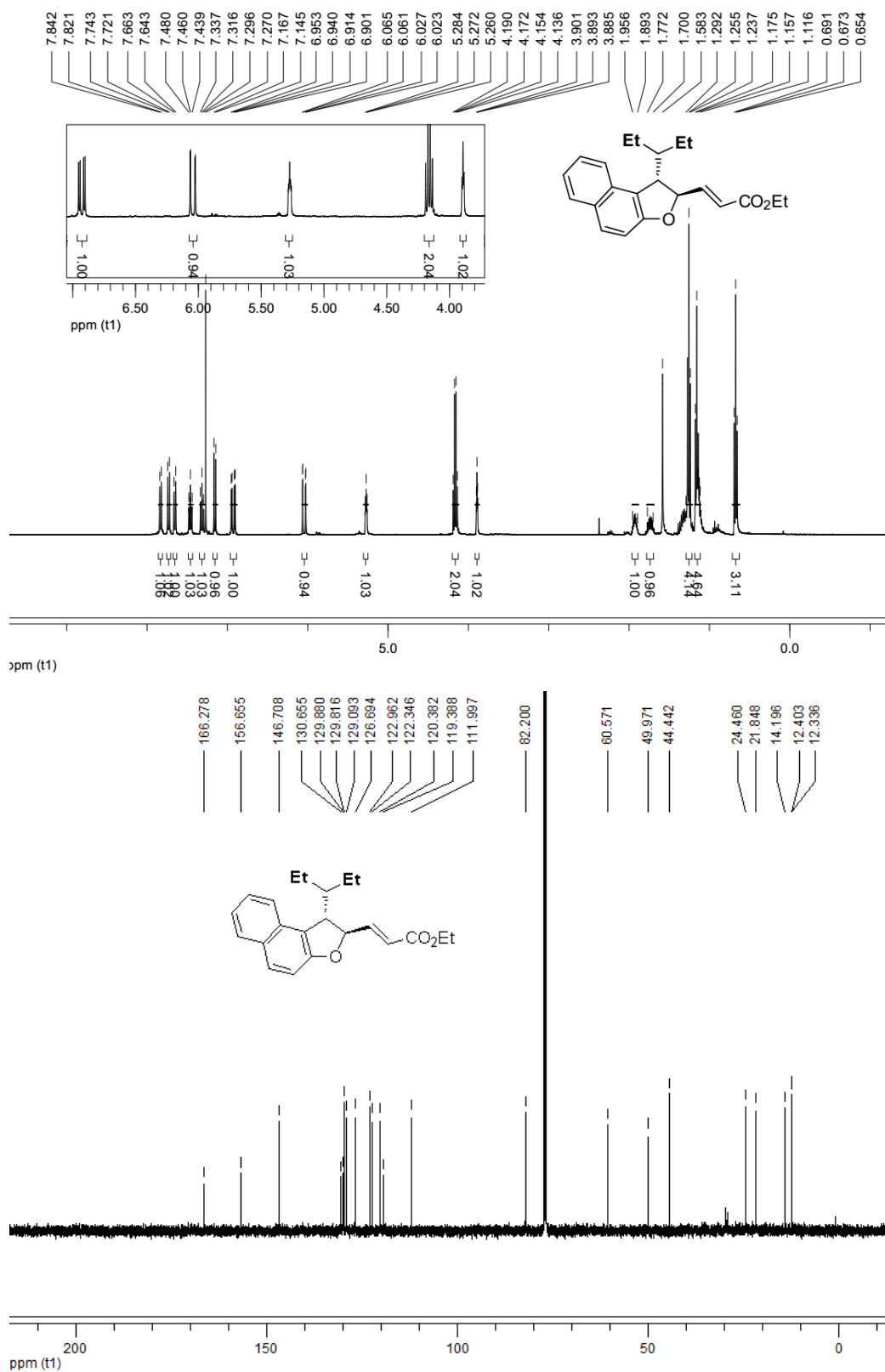
	Channel Description	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	11.546	1463768	60.03	34884
2	W2489 ChA 254nm	12.792	974742	39.97	26128

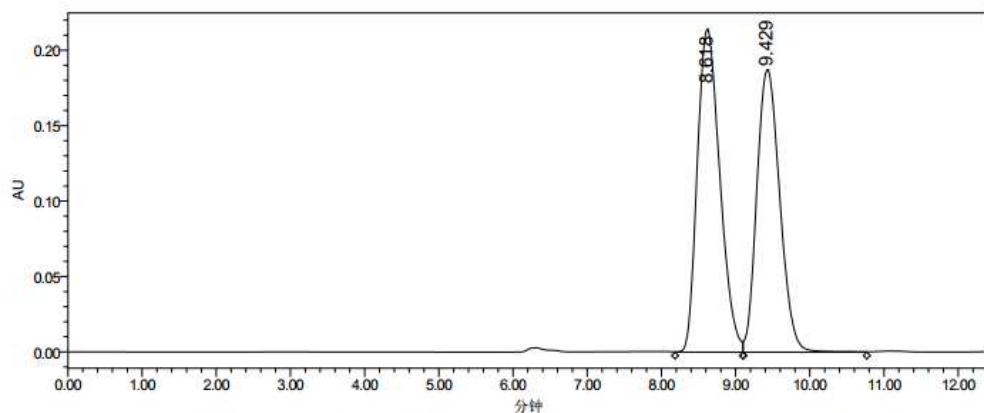


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (磺*sec)	% Area	Height (磺)
1	W2489 ChA 254nm	11.327	31534487	98.15	979901
2	W2489 ChA 254nm	12.410	593404	1.85	17729

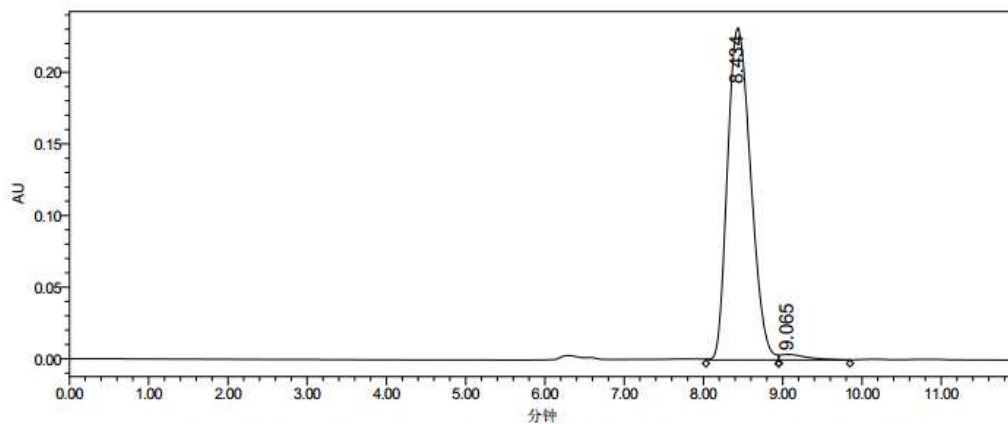
4ra





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

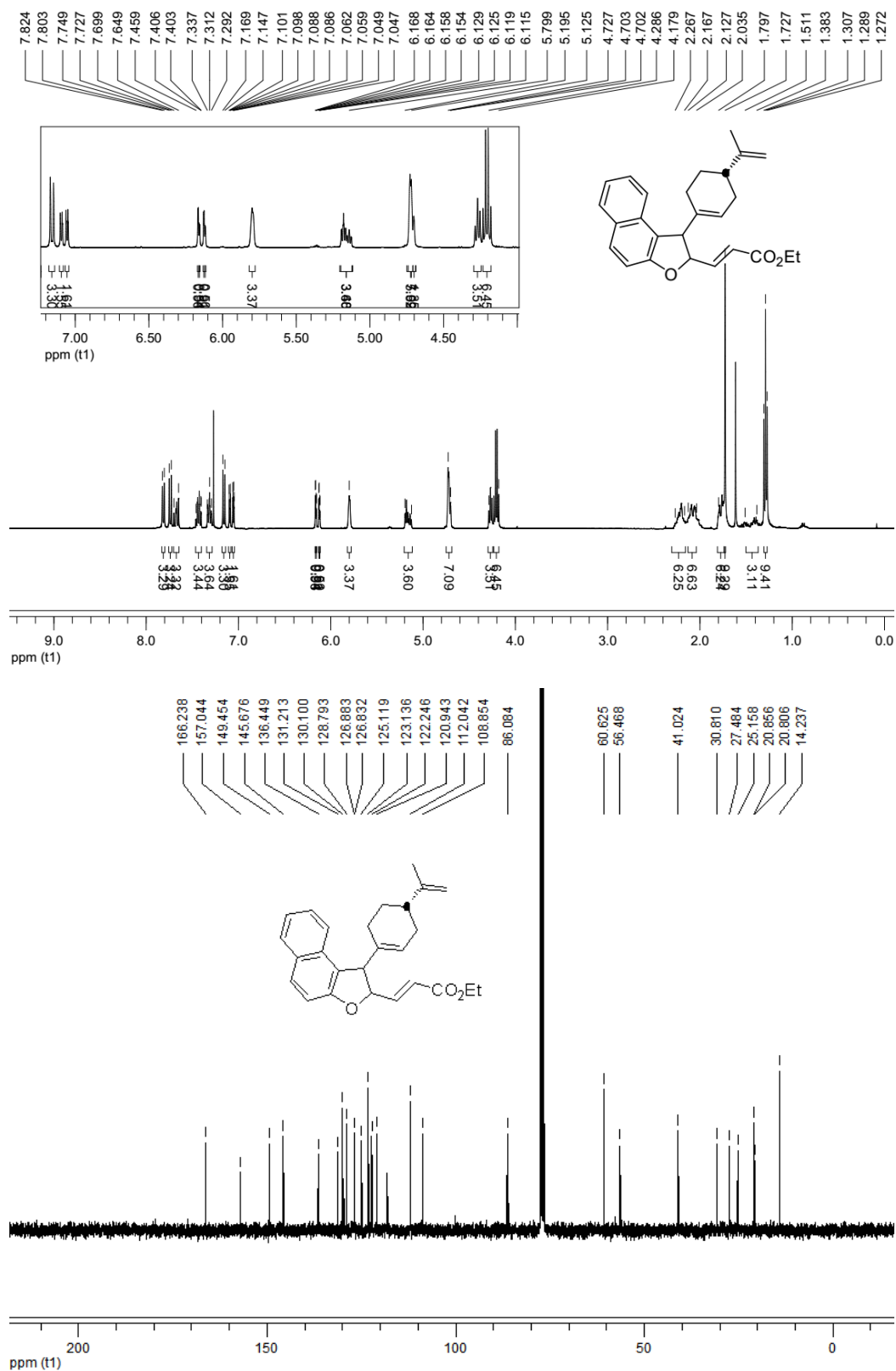
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	8.618	4520439	52.85	214091
2	W2489 ChA 254nm	9.429	4032190	47.15	187414



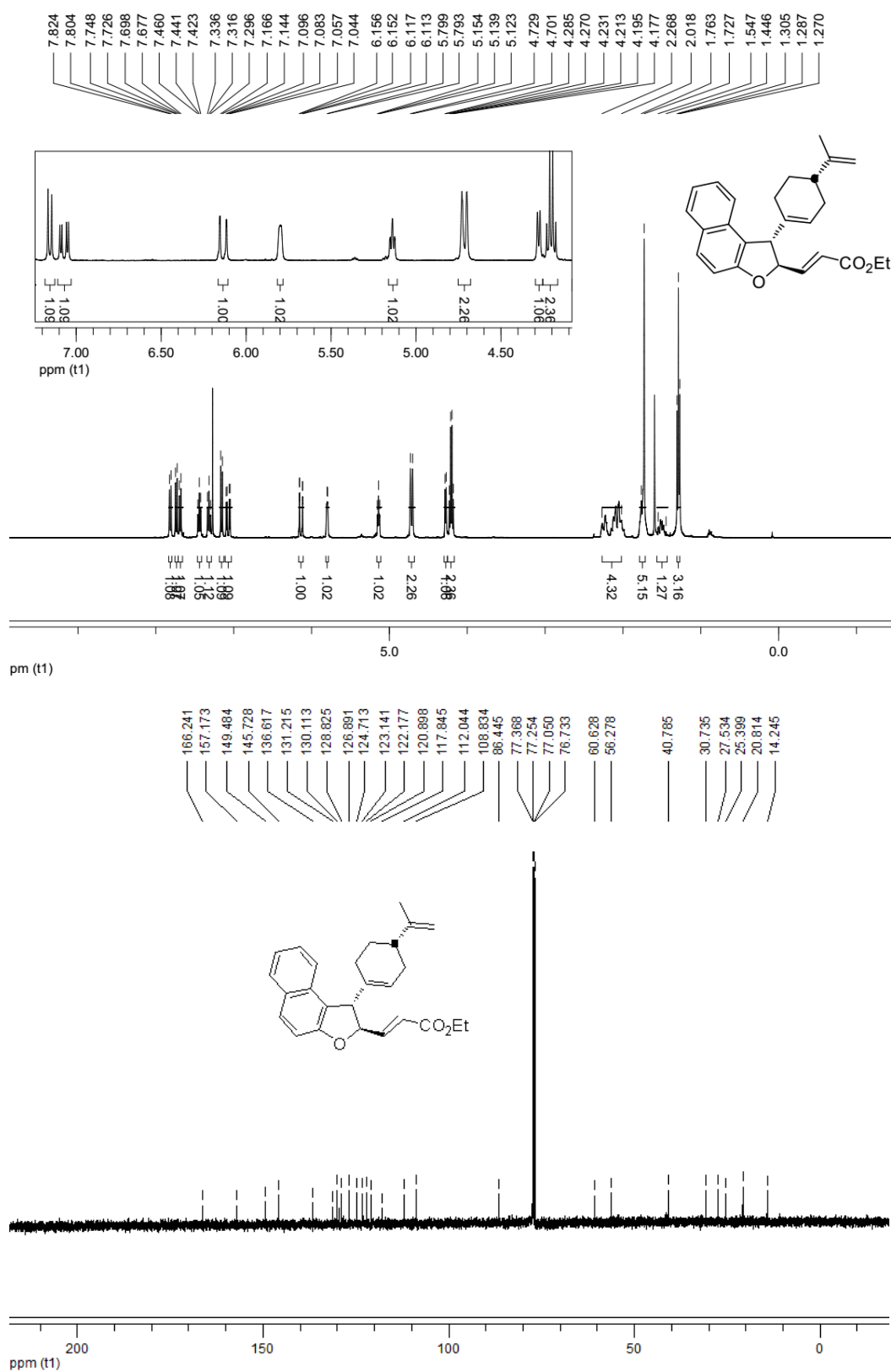
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	8.434	4725322	98.10	231547
2	W2489 ChA 254nm	9.065	91283	1.90	3855

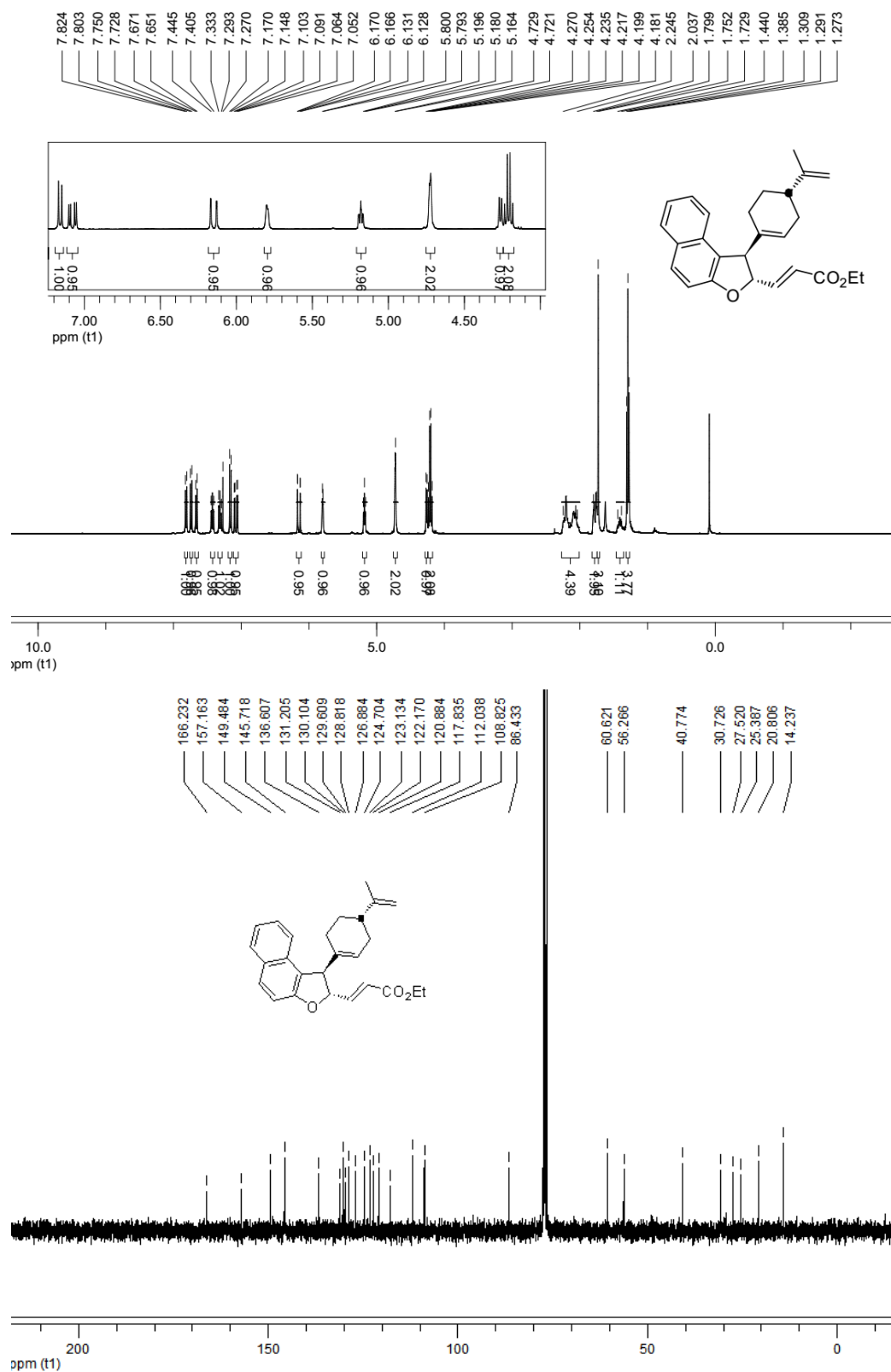
4sa (rac)



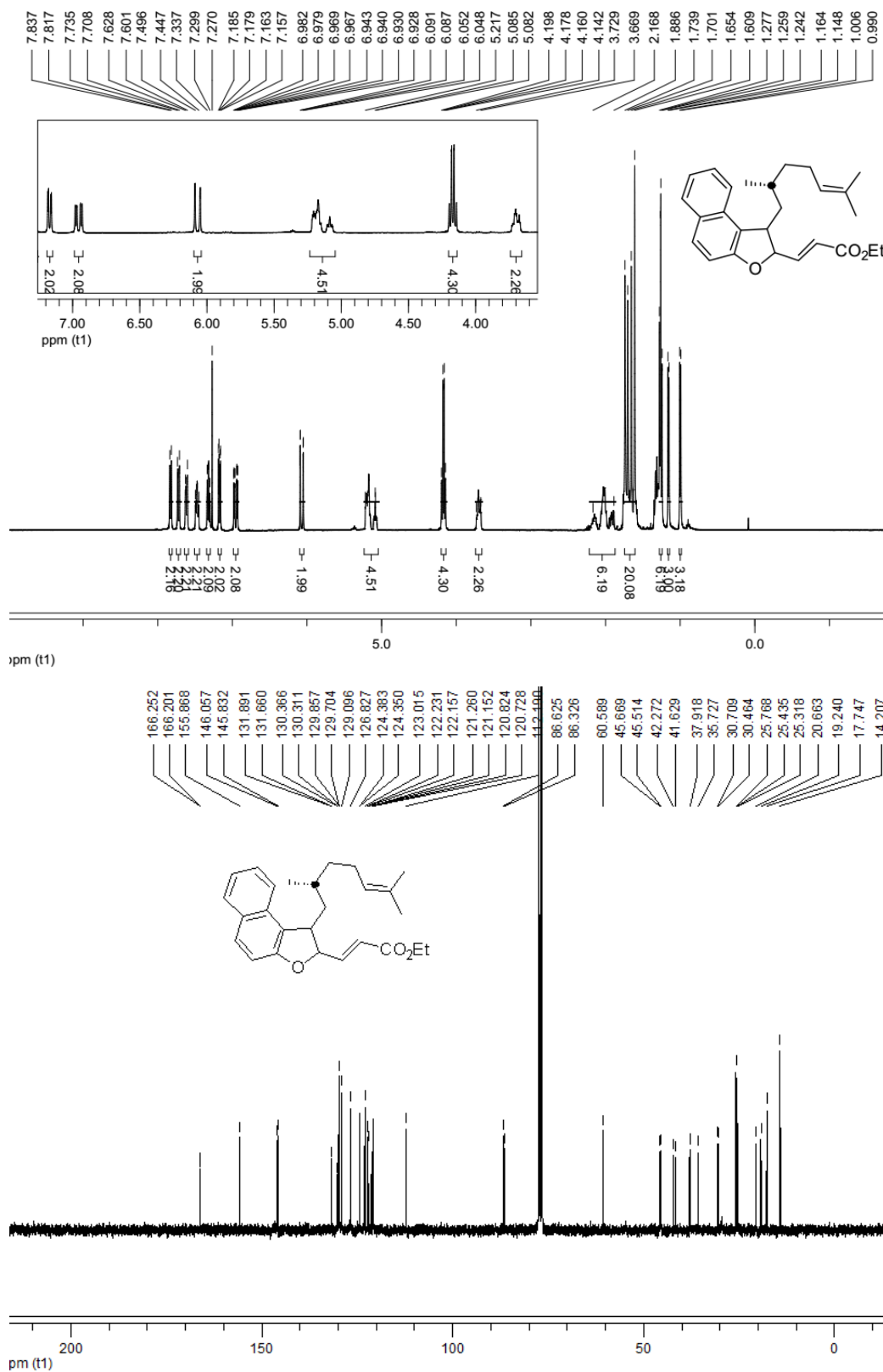
4sa



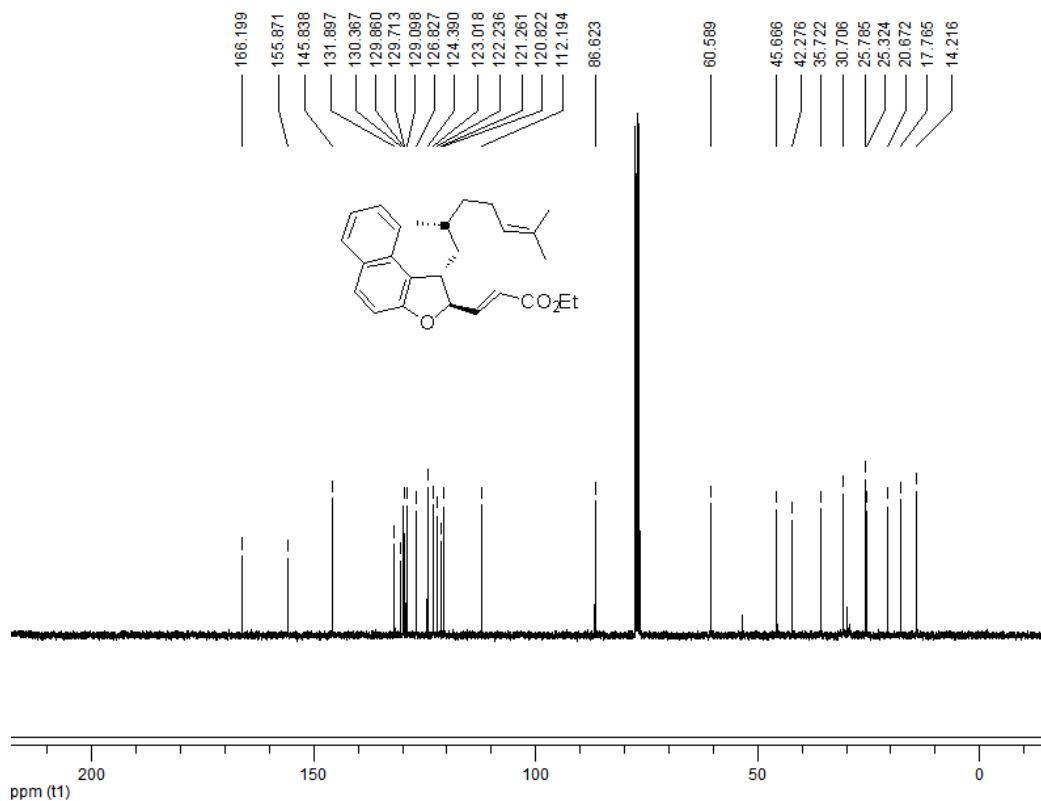
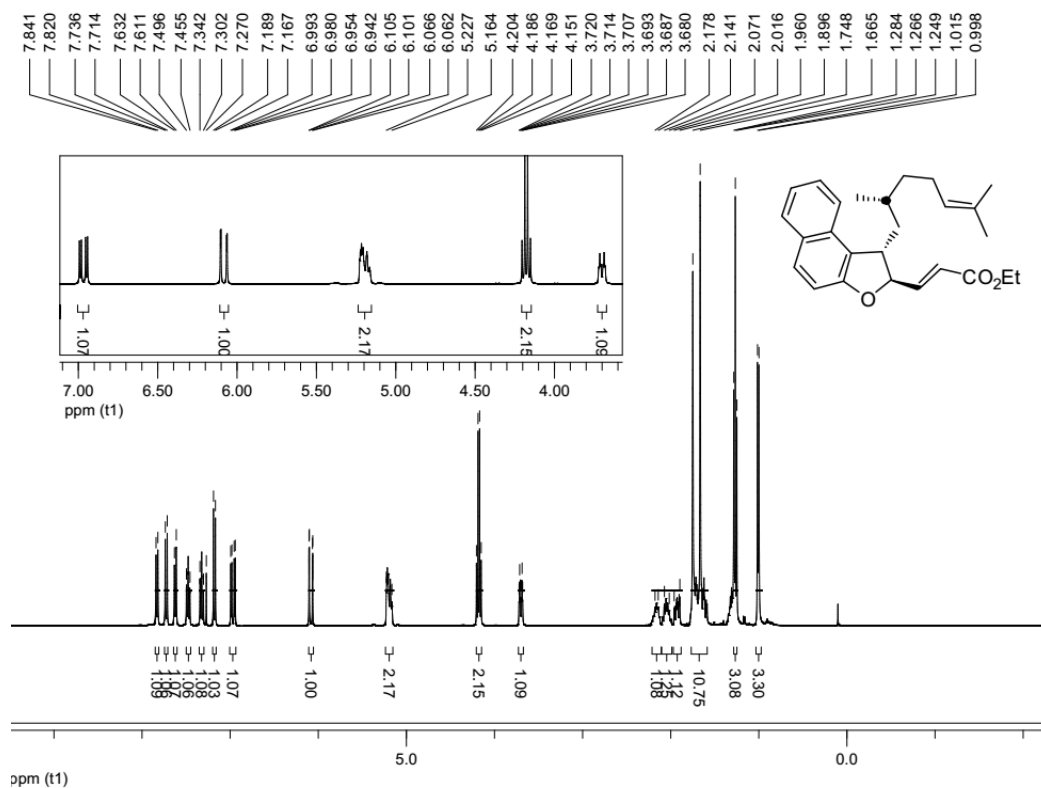
ent-4sa



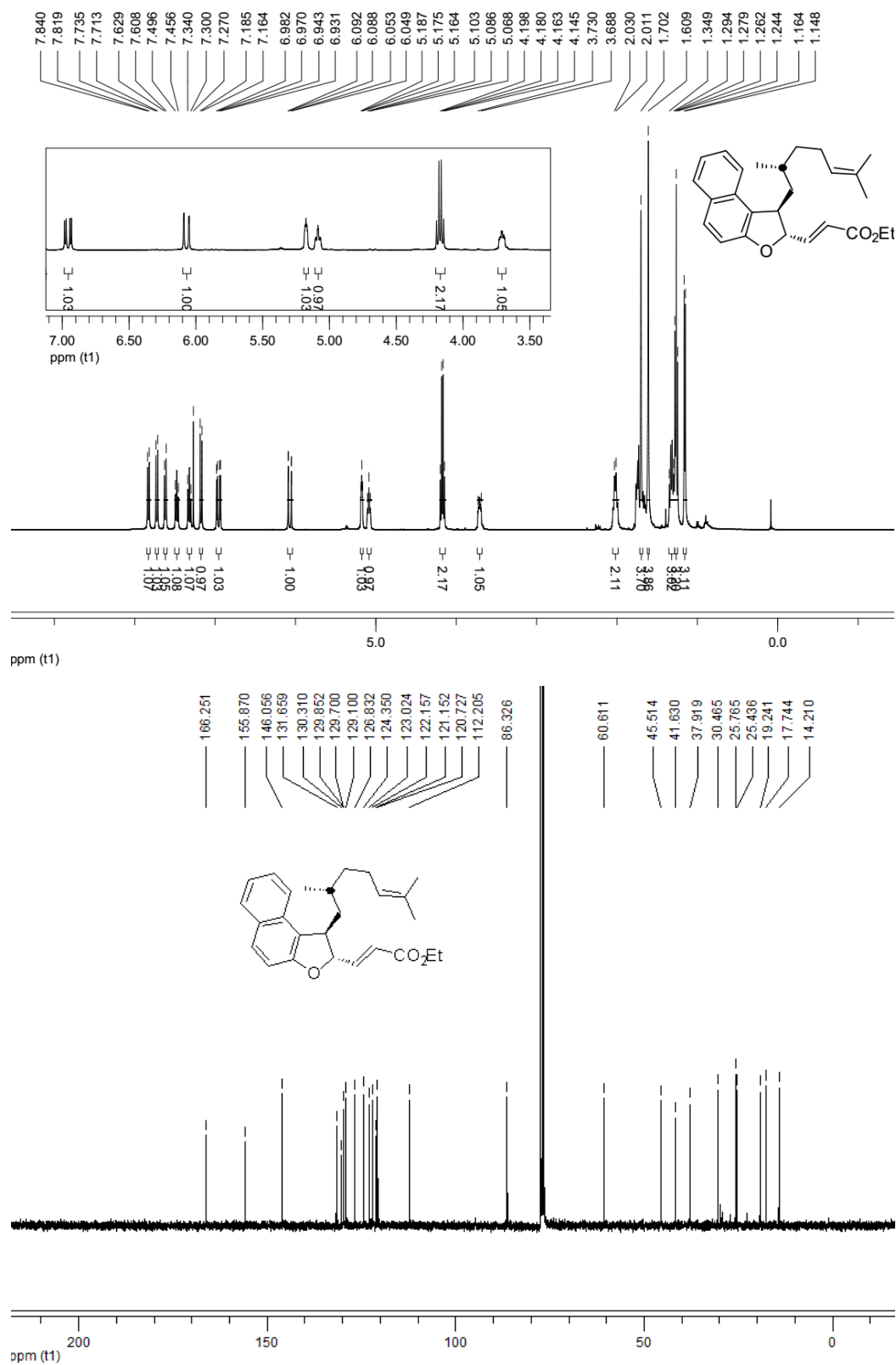
4ta(rac)



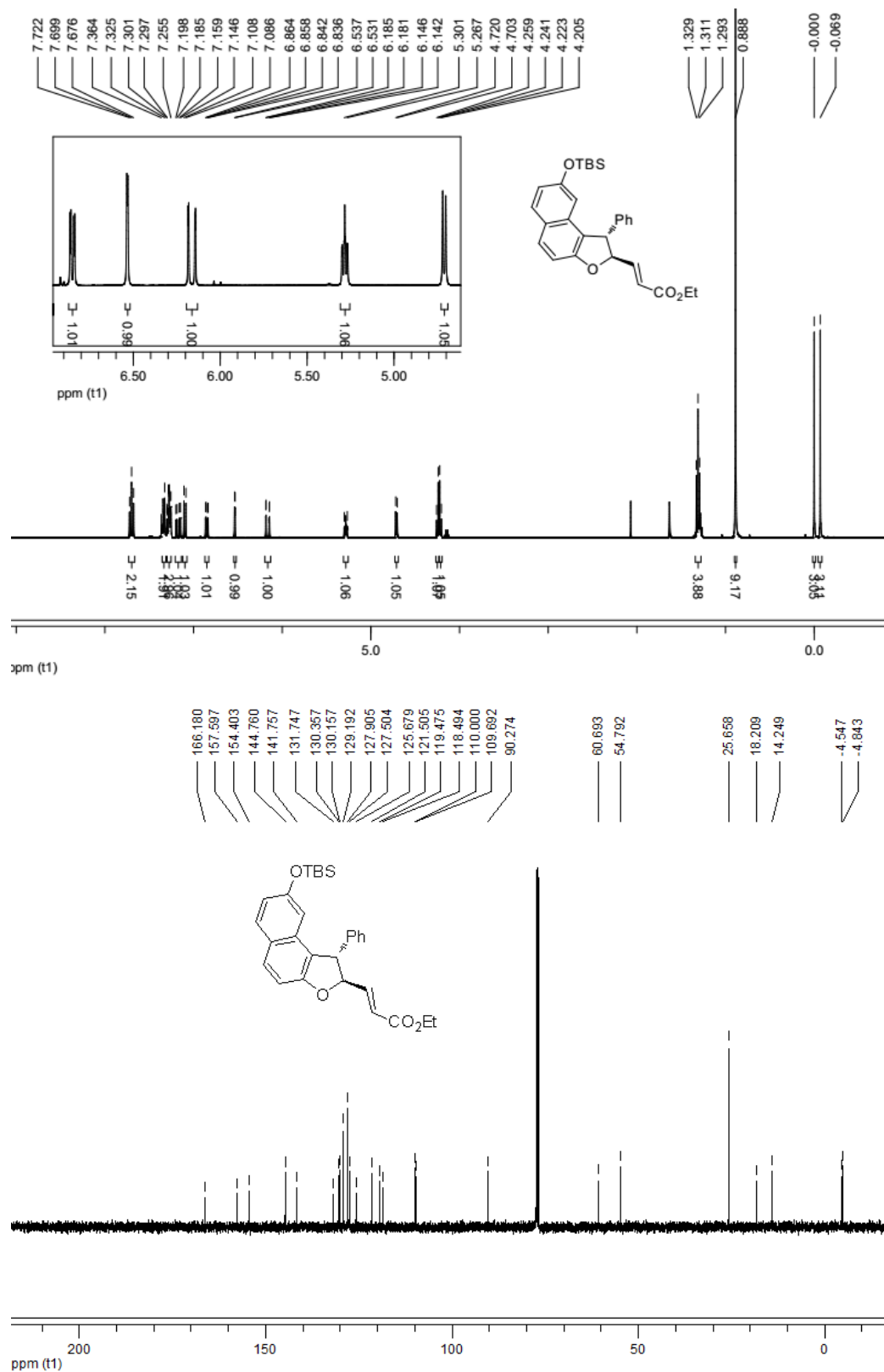
4ta

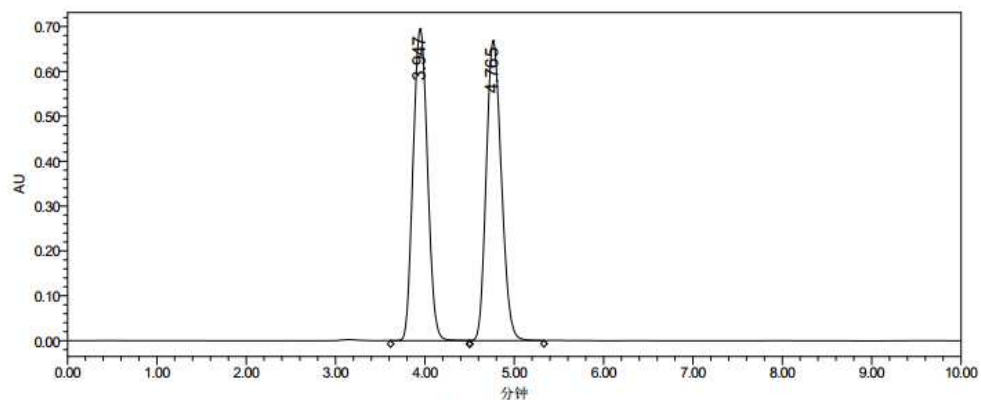


ent-4ta



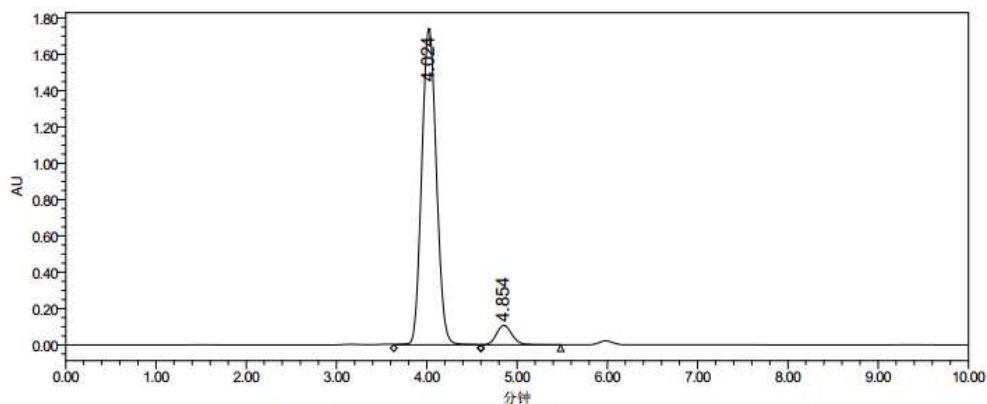
4ab





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

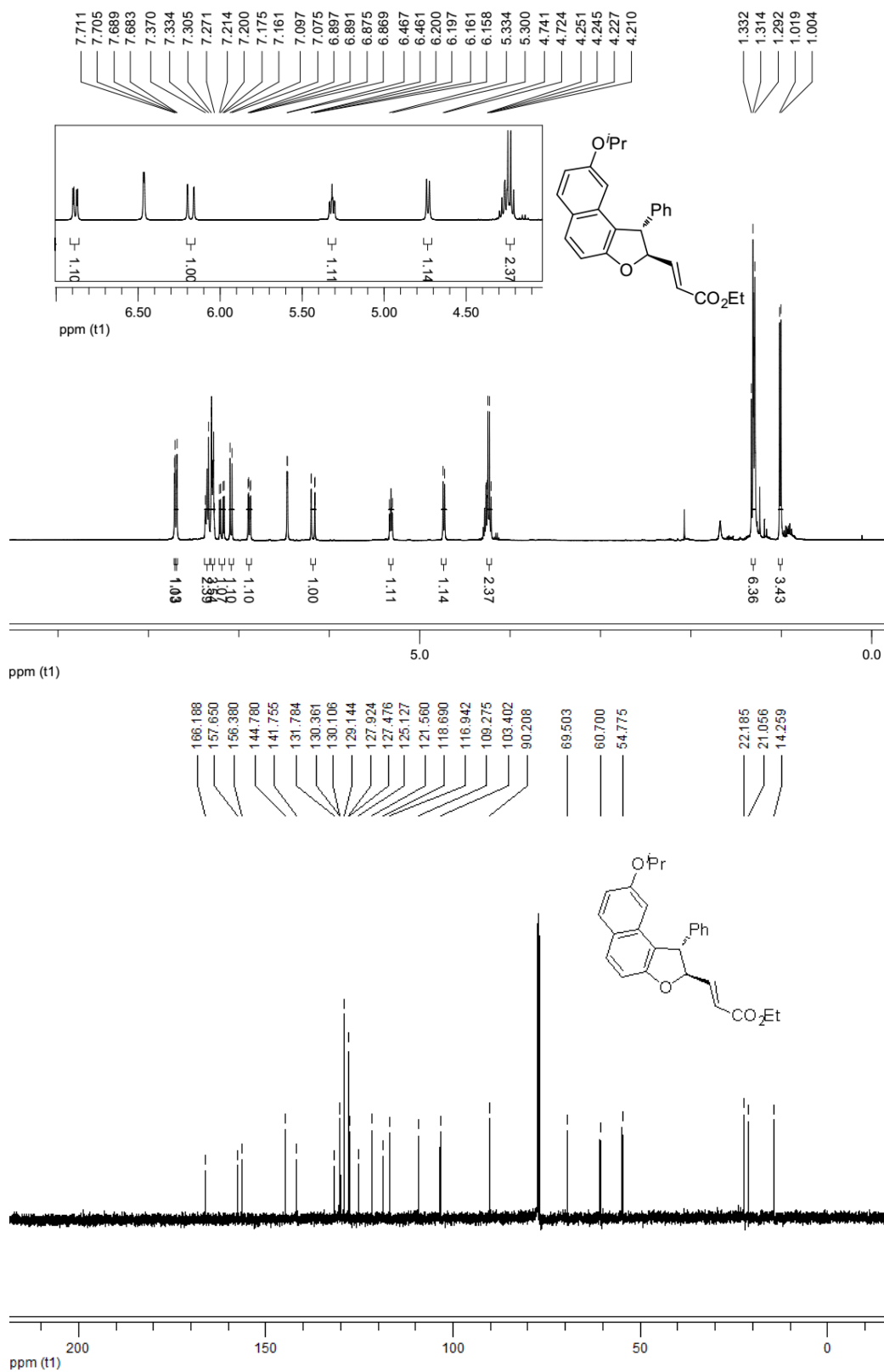
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	3.947	7779326	49.76	696416
2	W2489 ChA 254nm	4.765	7854533	50.24	669009

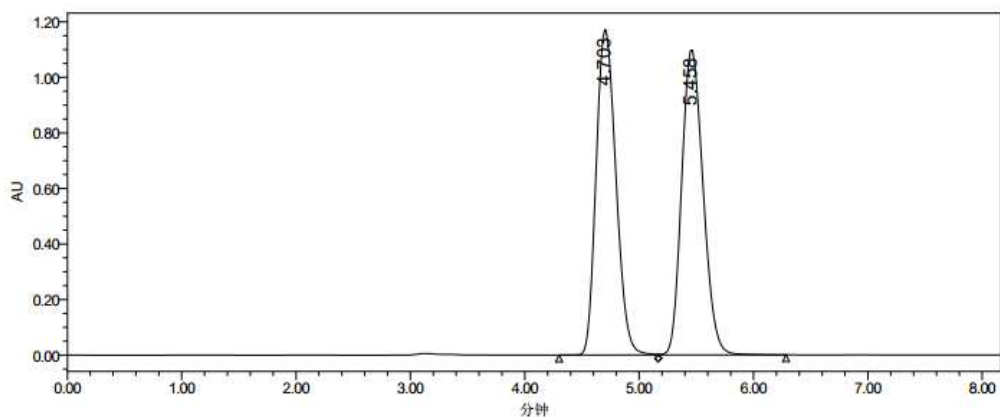


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	4.024	19639647	93.87	1748193
2	W2489 ChA 254nm	4.854	1283206	6.13	106471

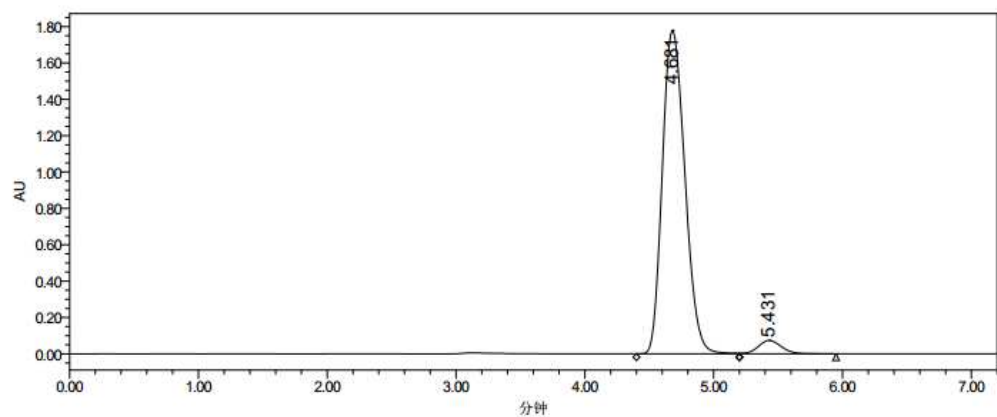
4ac





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

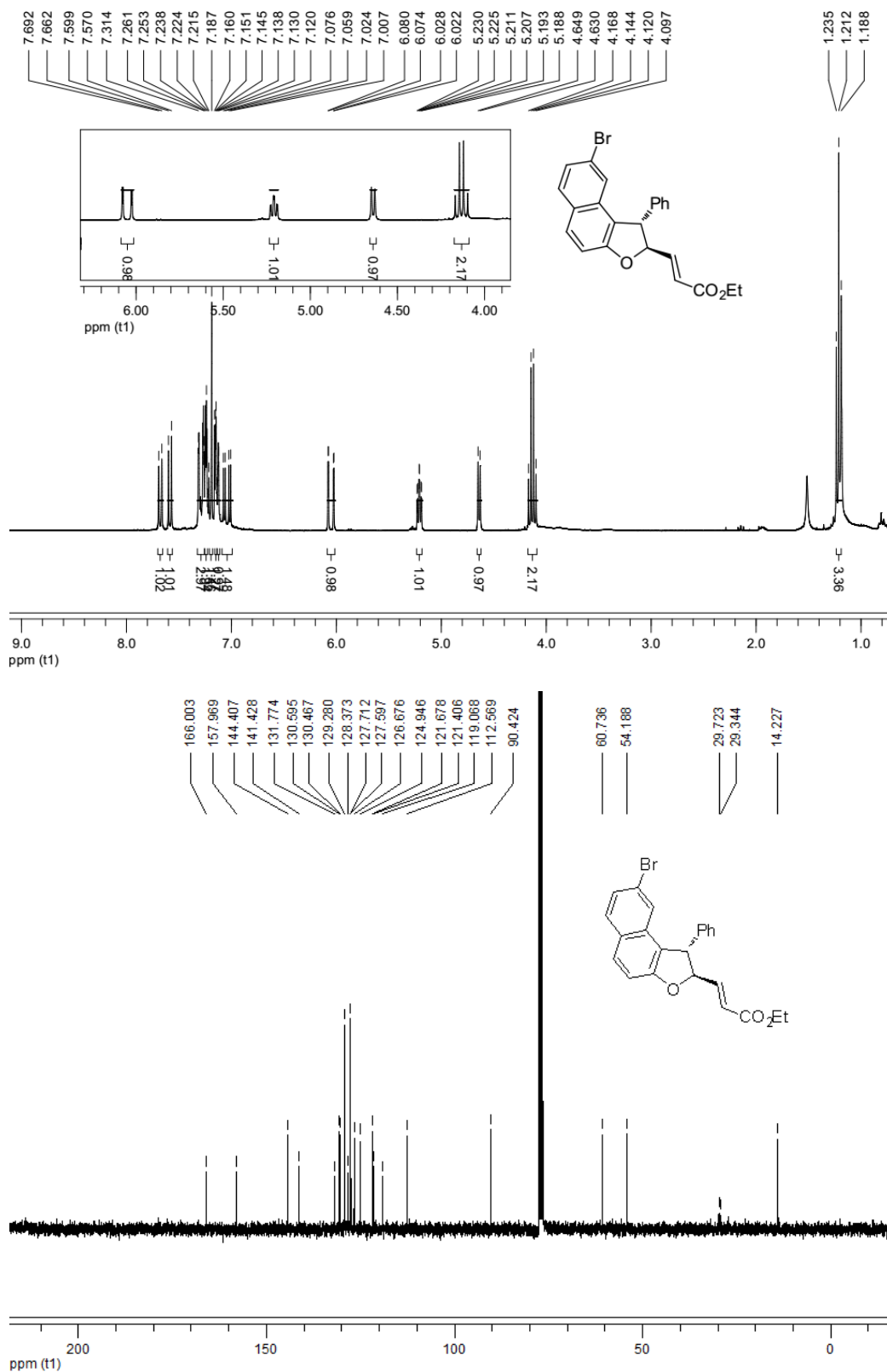
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	4.703	14086083	49.59	1172362
2	W2489 ChA 254nm	5.458	14321071	50.41	1100997

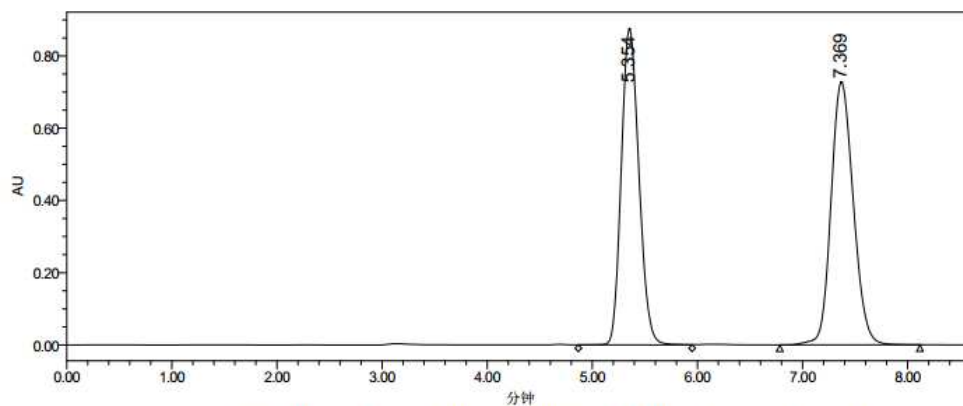


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	4.681	21618737	95.95	1781551
2	W2489 ChA 254nm	5.431	912147	4.05	73692

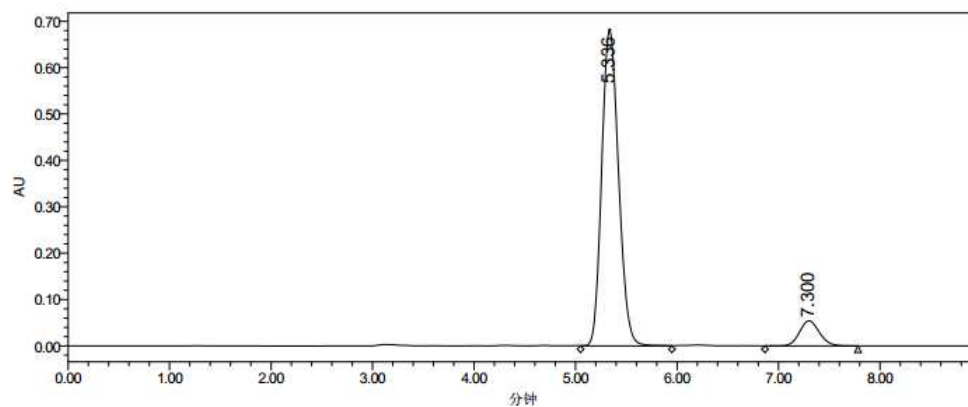
S68





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

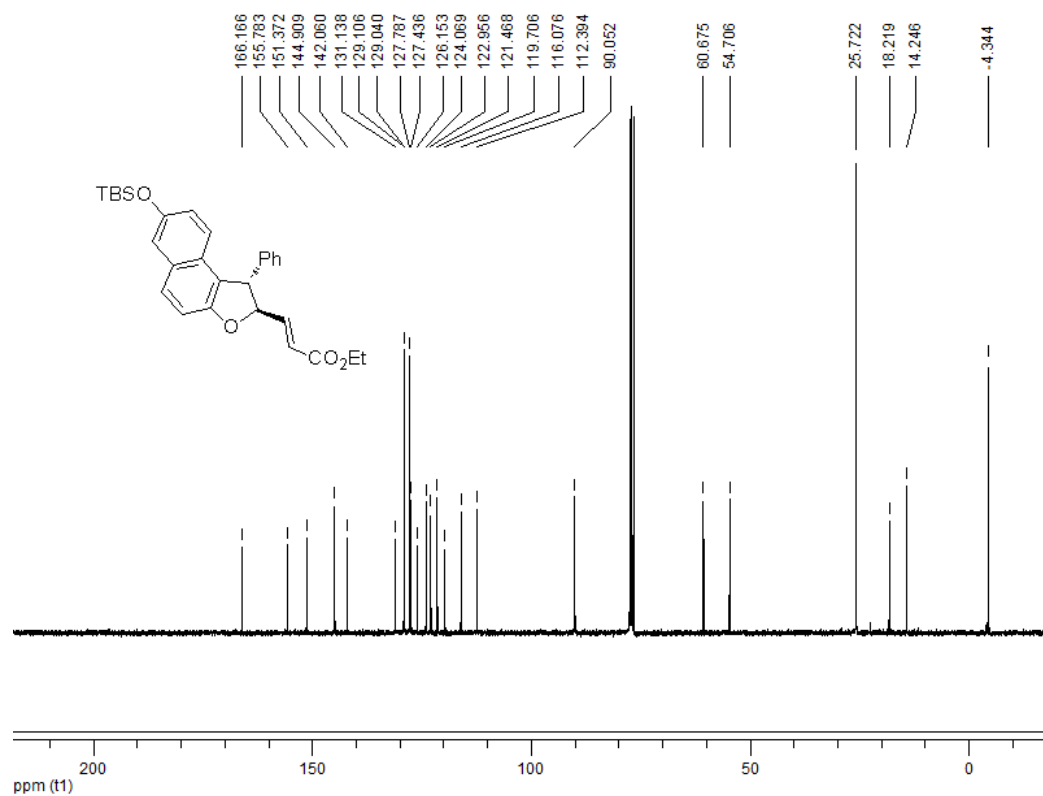
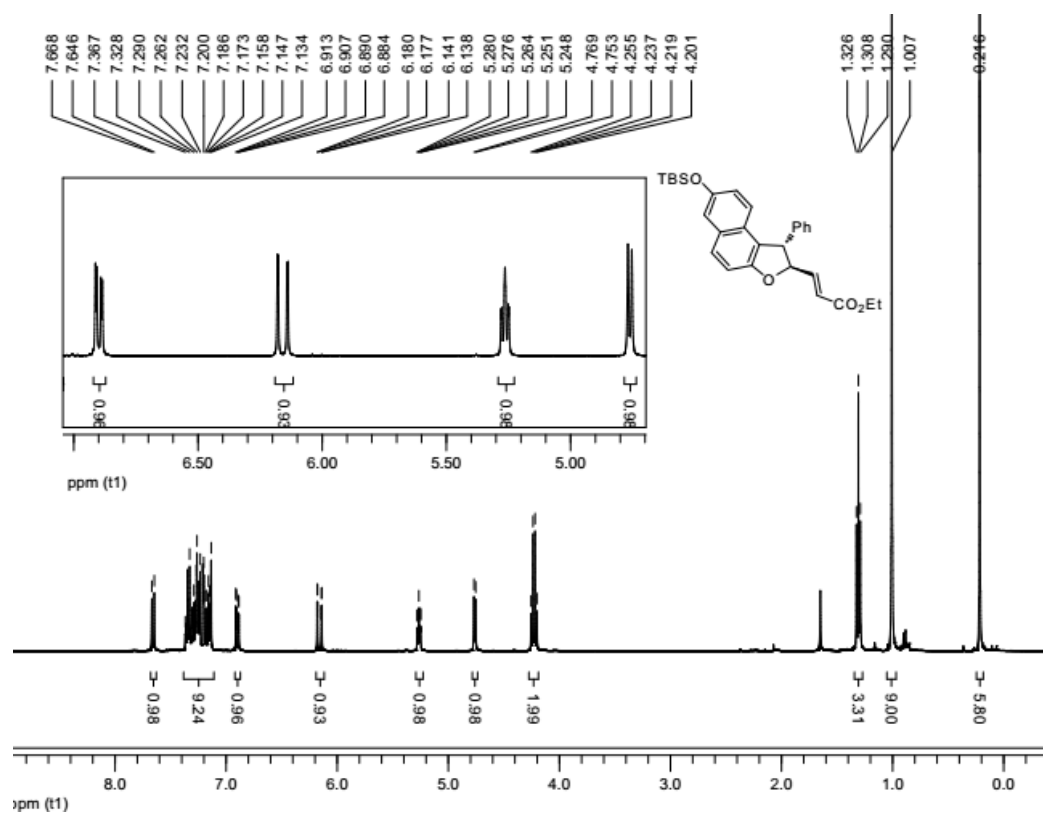
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.354	10195996	48.80	877691
2	W2489 ChA 254nm	7.369	10697737	51.20	728954

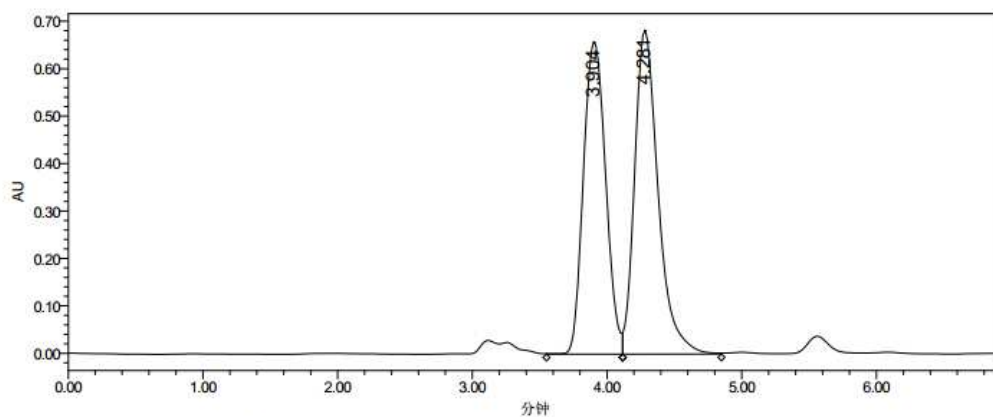


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

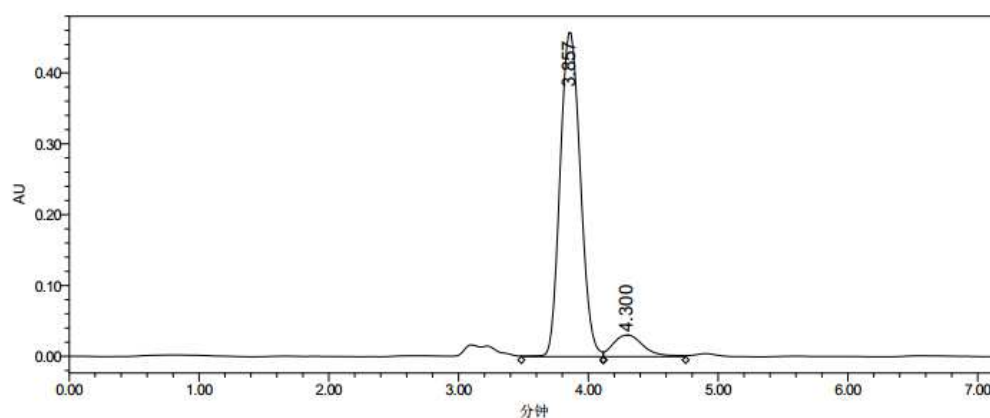
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.336	7861488	91.47	683600
2	W2489 ChA 254nm	7.300	733048	8.53	54003

4ae



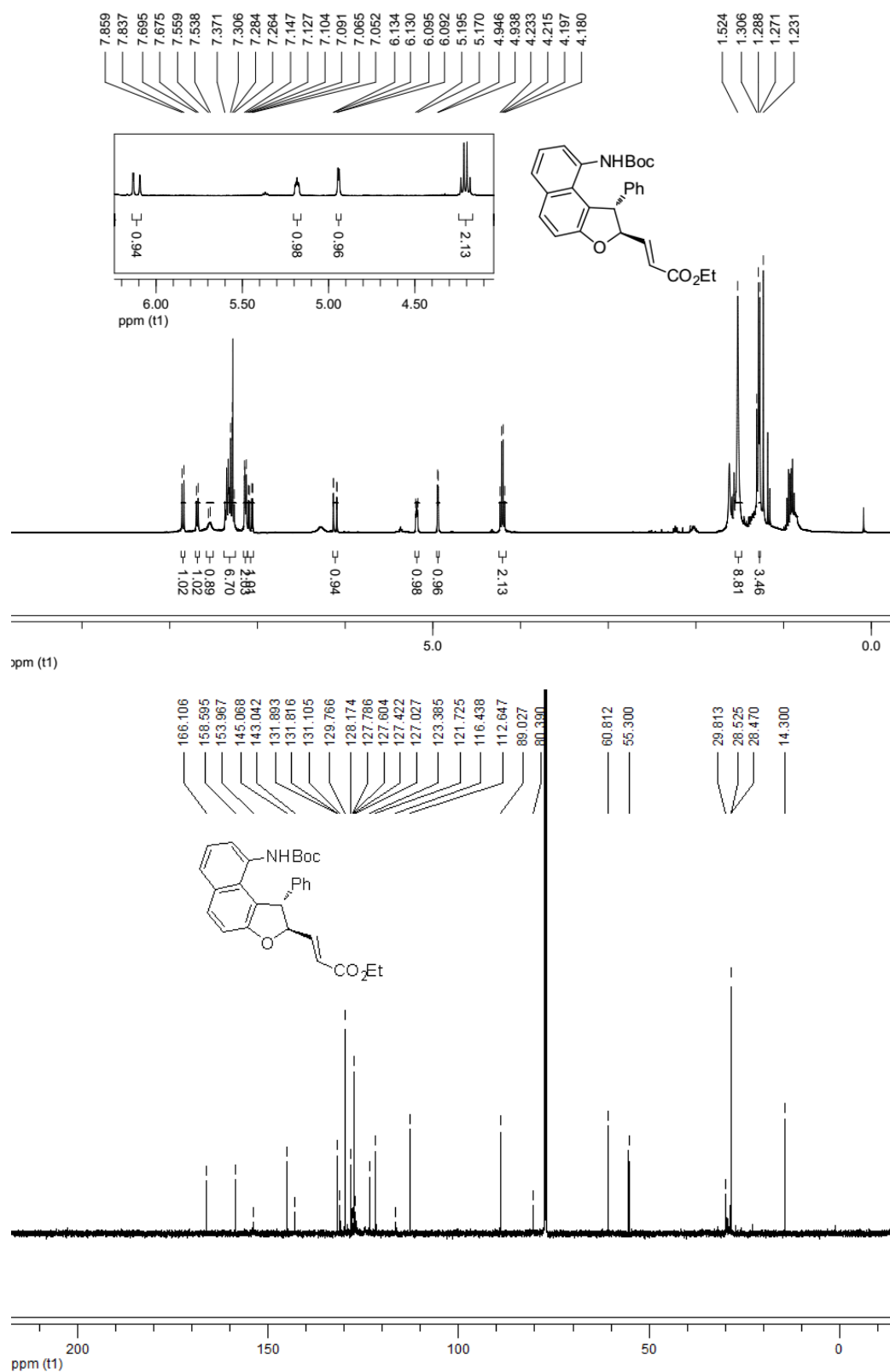


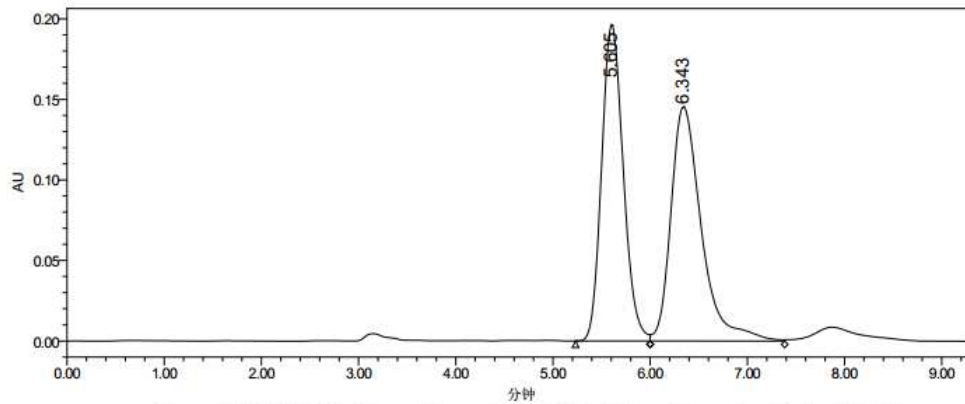
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	3.904	7549859	47.70	659468
2	W2489 ChA 254nm	4.281	8276578	52.30	682981



	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	3.857	4945685	90.96	459187
2	W2489 ChA 254nm	4.300	491572	9.04	30436

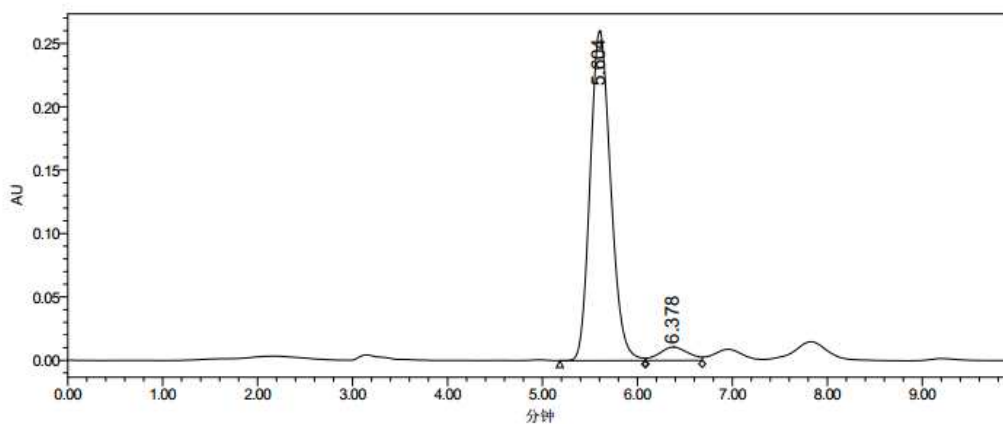
4af





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 0243A

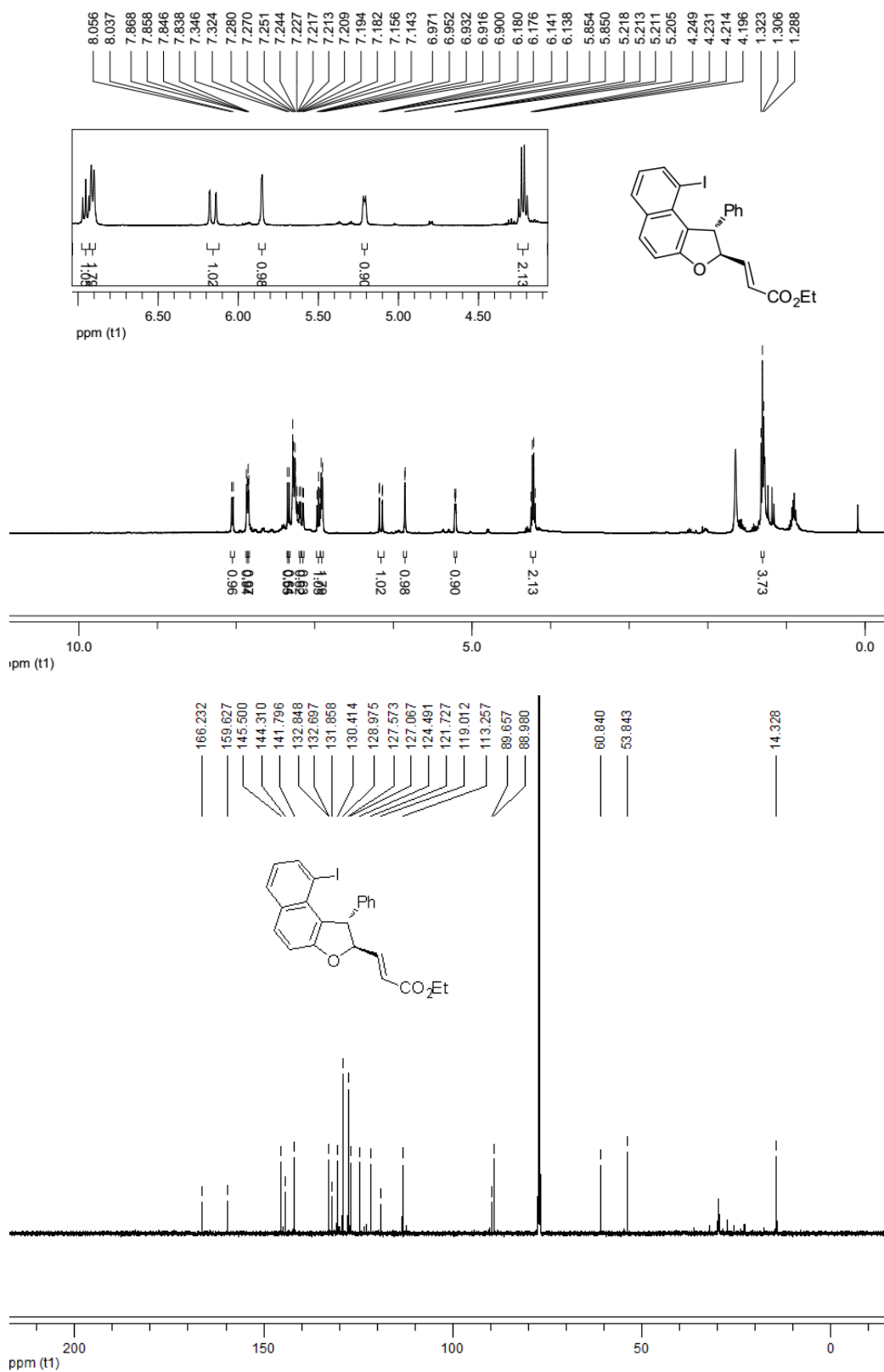
	Channel Description	RT (min)	Area (碱*sec)	% Area	Height (碱)
1	W2489 ChA 254nm	5.605	3038100	48.96	196691
2	W2489 ChA 254nm	6.343	3167455	51.04	145529

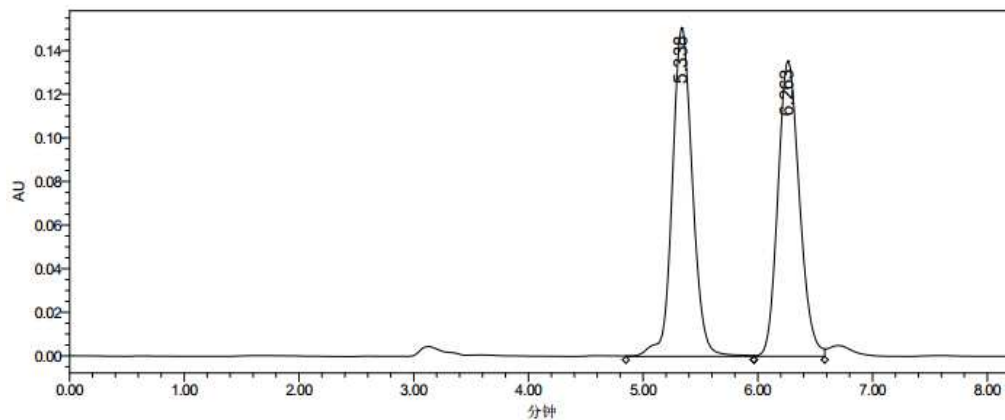


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (碱*sec)	% Area	Height (碱)
1	W2489 ChA 254nm	5.604	3915529	94.65	260487
2	W2489 ChA 254nm	6.378	221191	5.35	10552

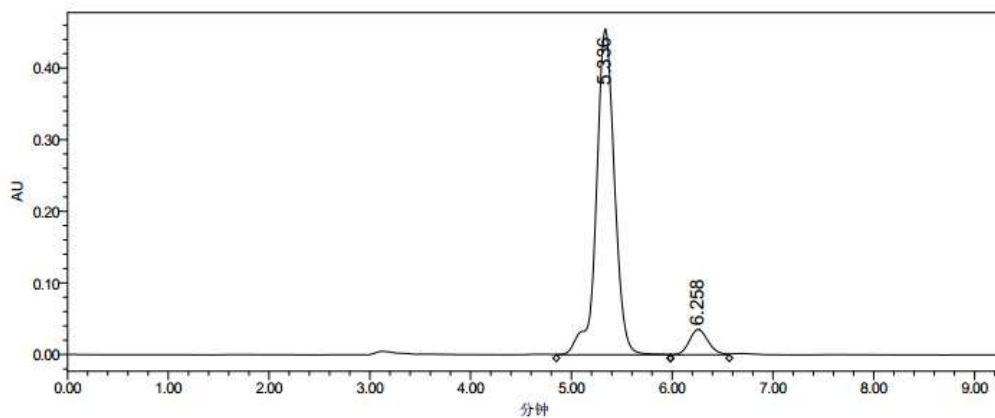
4ag





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

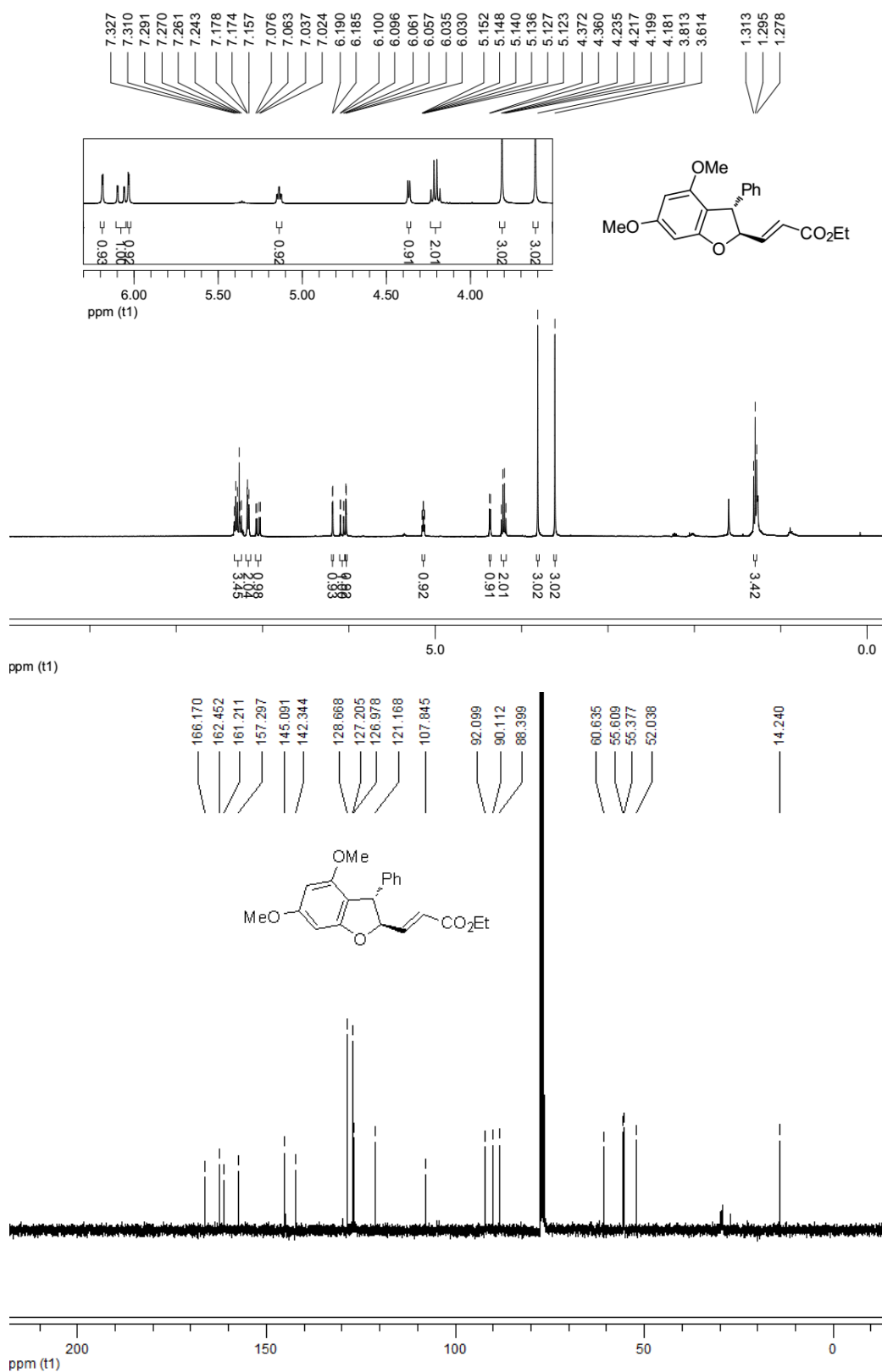
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.338	1846606	51.13	151078
2	W2489 ChA 254nm	6.263	1765318	48.87	135660

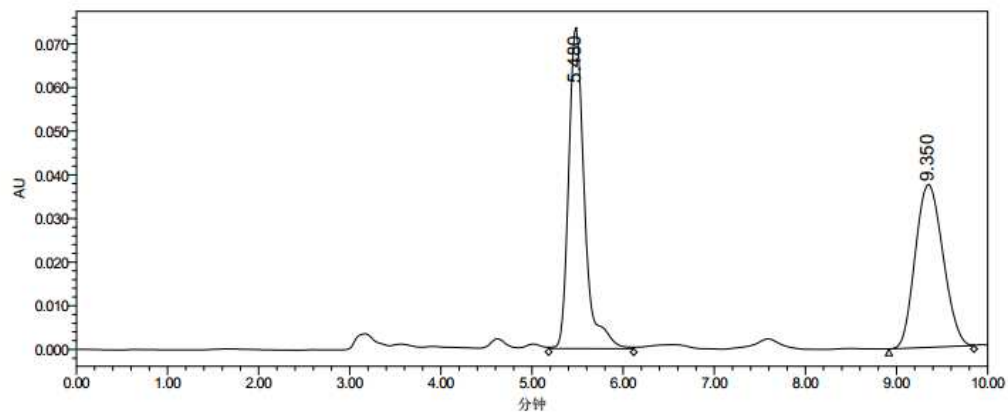


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.336	5708500	92.58	454924
2	W2489 ChA 254nm	6.258	457723	7.42	35250

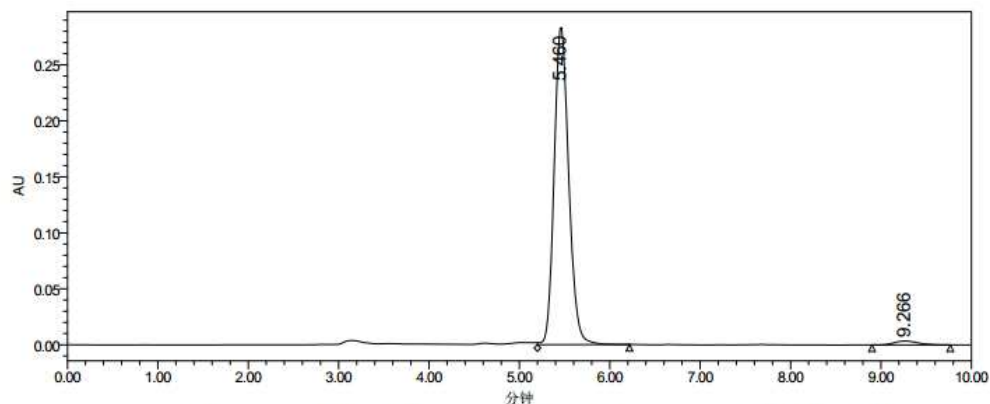
7a





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

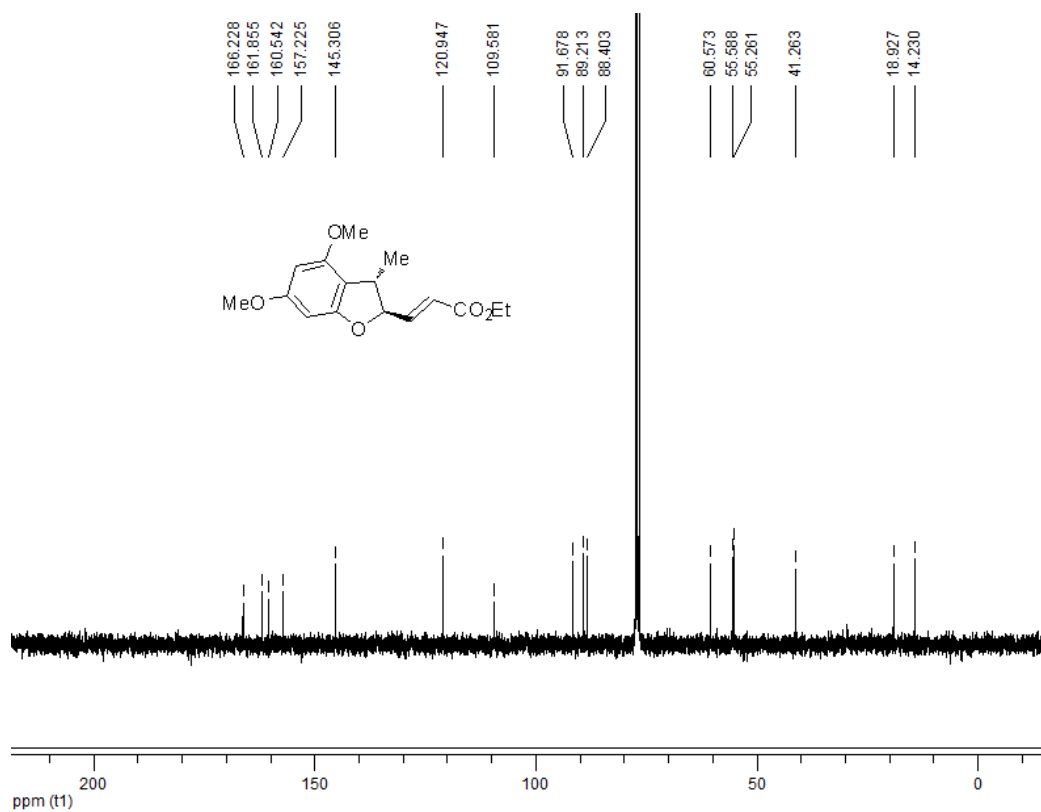
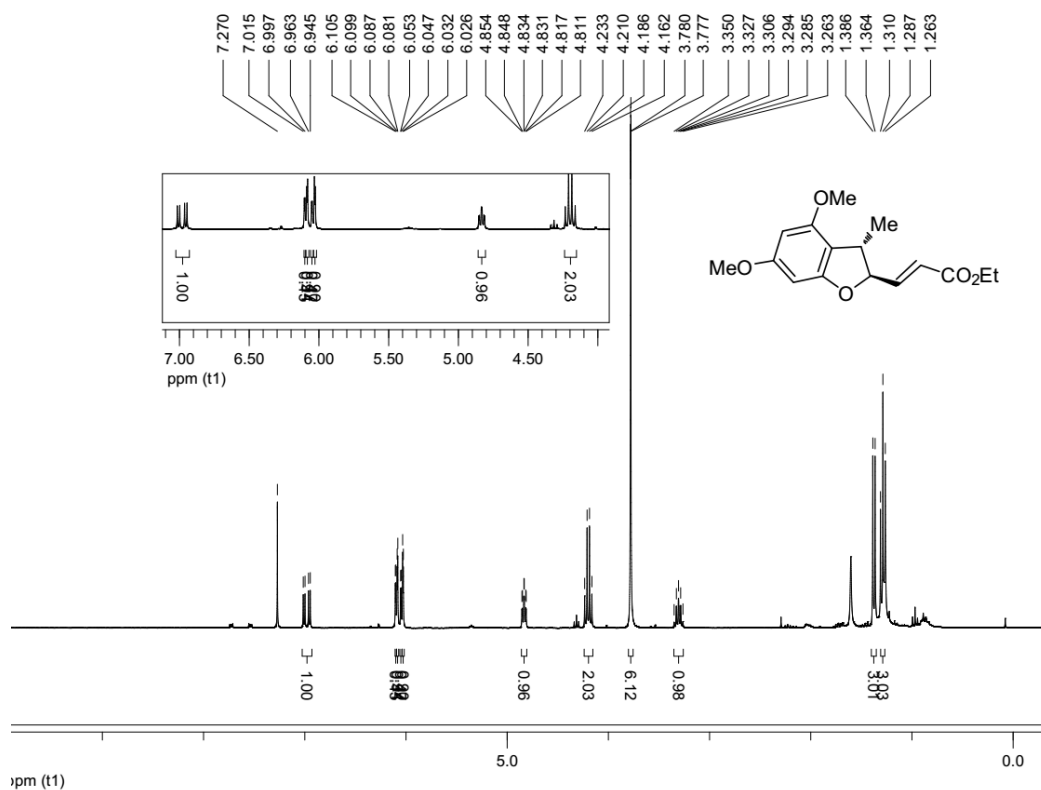
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.480	884894	52.83	73588
2	W2489 ChA 254nm	9.350	790085	47.17	37310

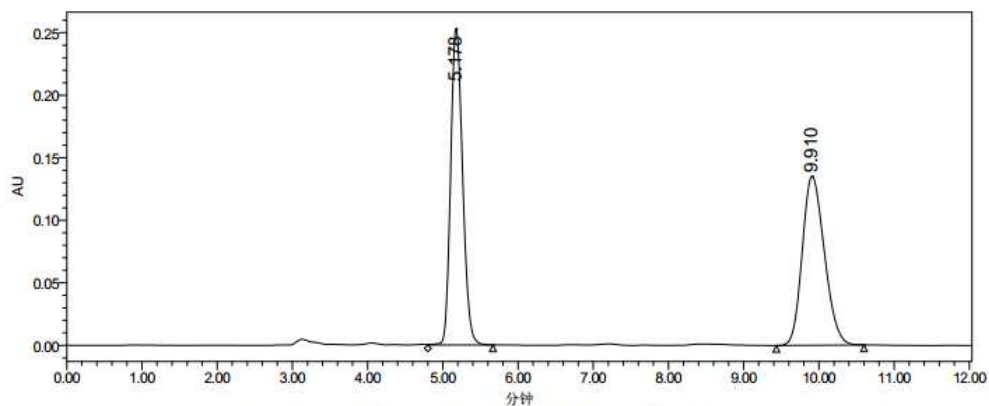


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.460	3185676	98.04	283960
2	W2489 ChA 254nm	9.266	63579	1.96	3503

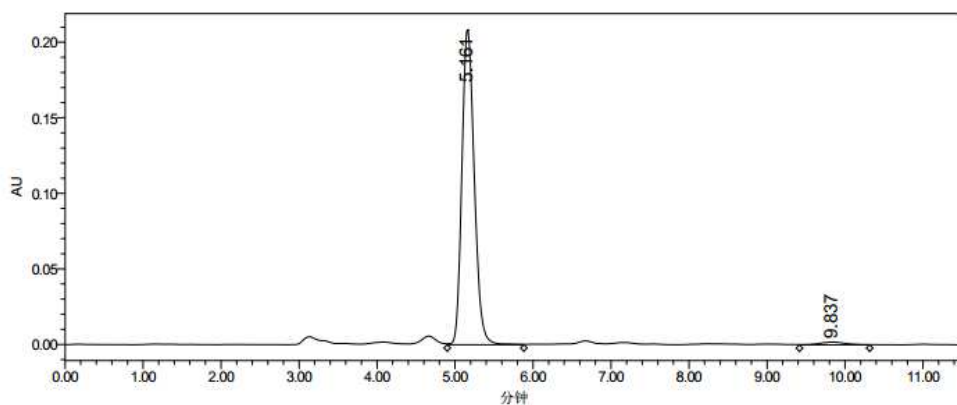
7b





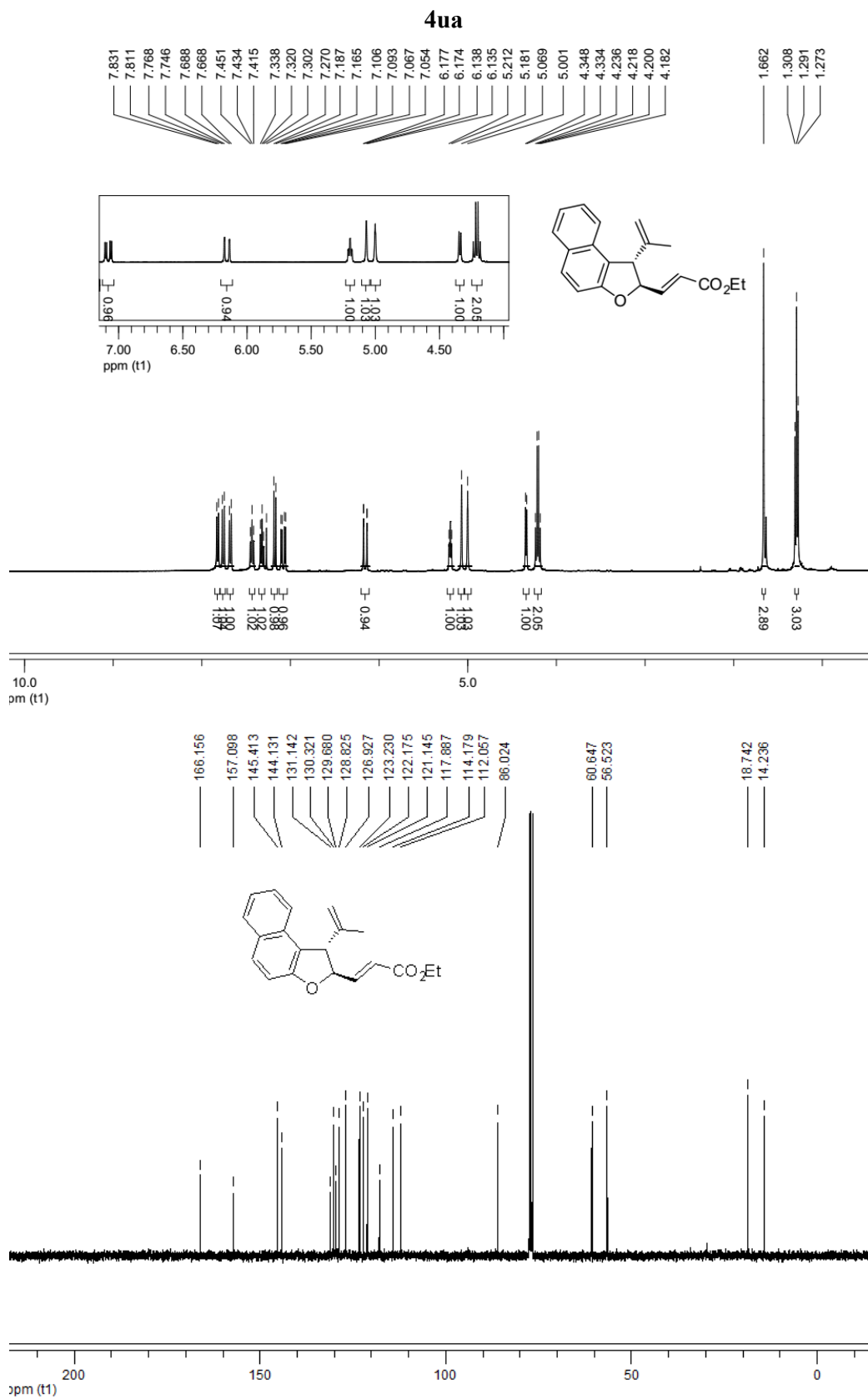
Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

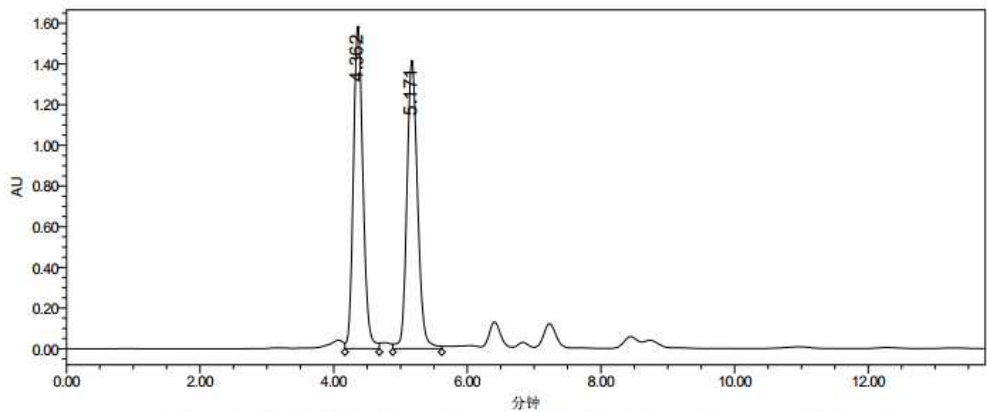
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.178	2795923	50.28	253932
2	W2489 ChA 254nm	9.910	2764471	49.72	135270



Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

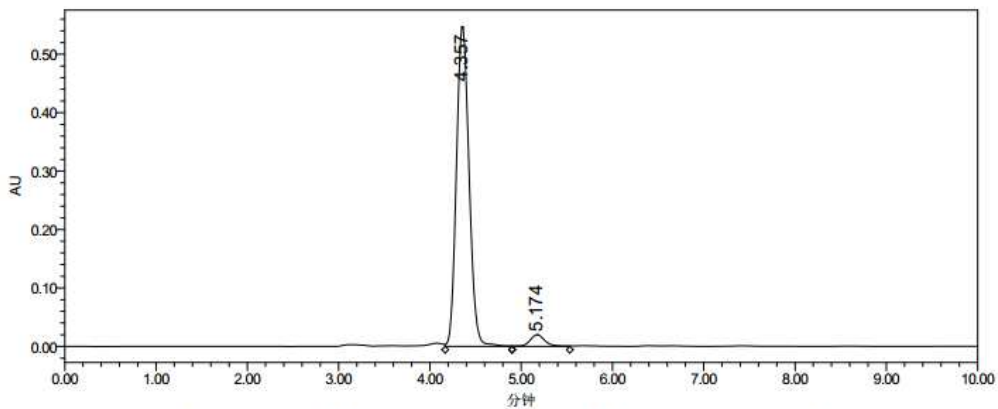
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.161	2305899	98.26	209109
2	W2489 ChA 254nm	9.837	40787	1.74	1750





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

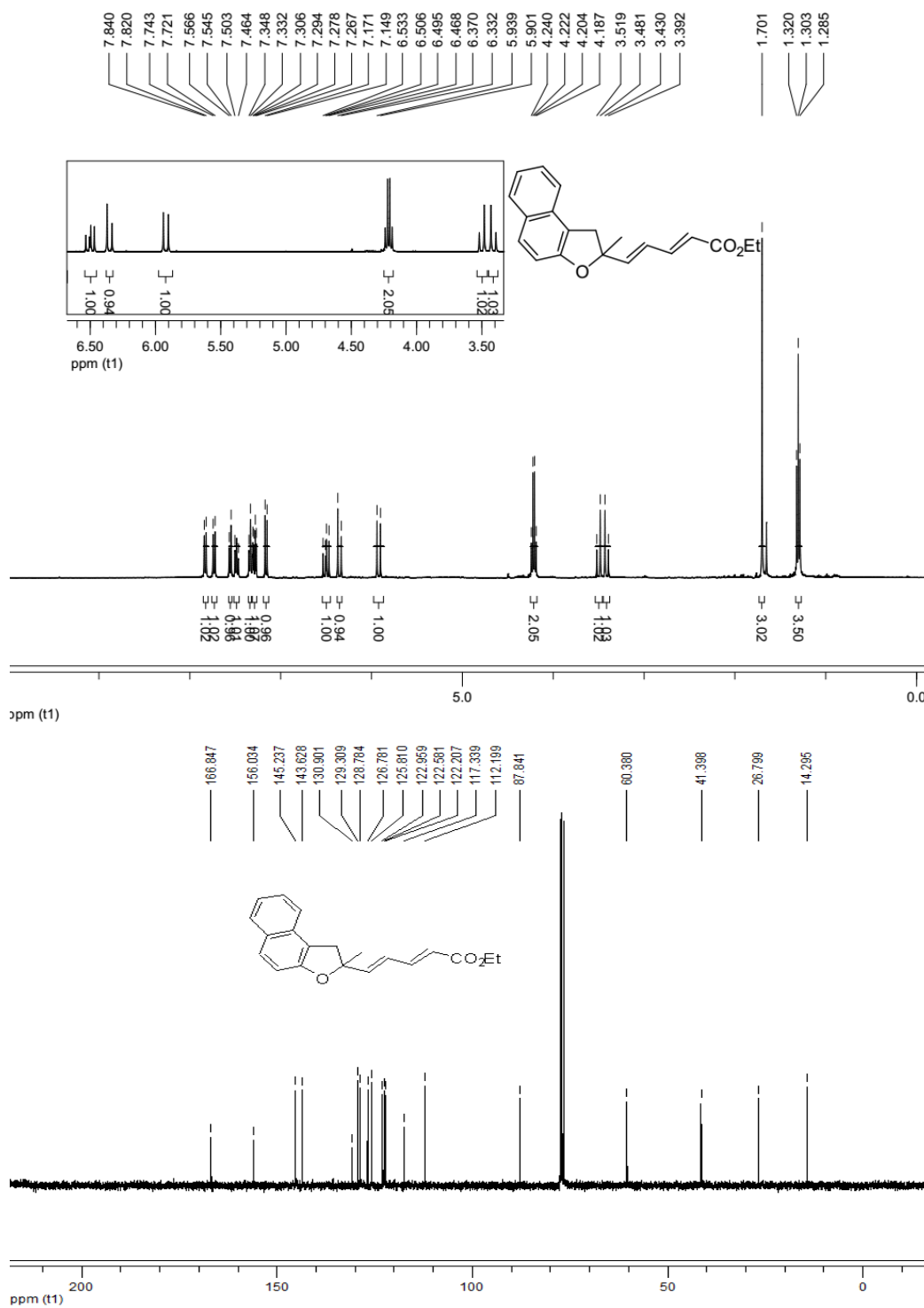
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	4.362	15819161	50.18	1587391
2	W2489 ChA 254nm	5.171	15704733	49.82	1418788

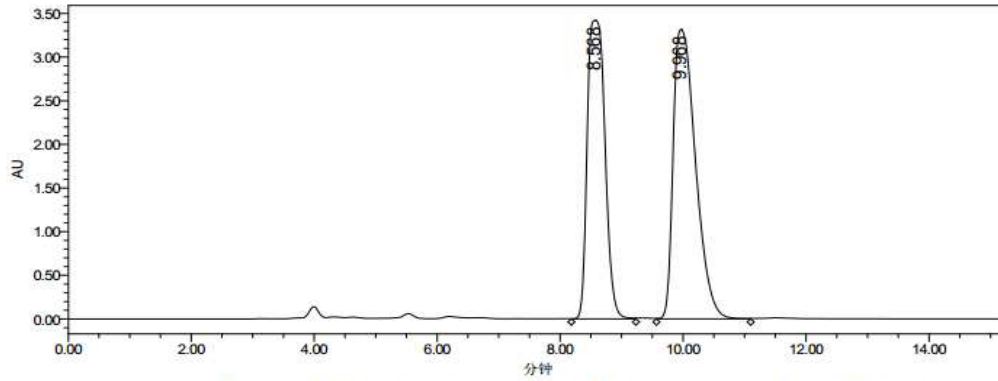


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

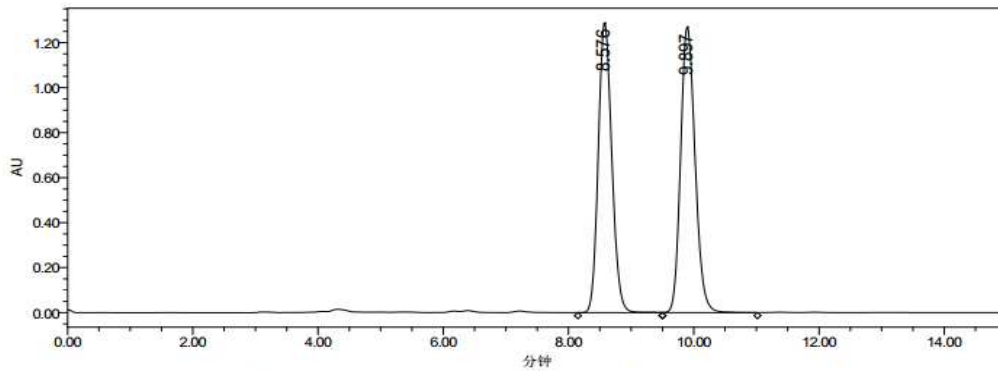
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	4.357	5260209	95.81	550471
2	W2489 ChA 254nm	5.174	230084	4.19	20033

5



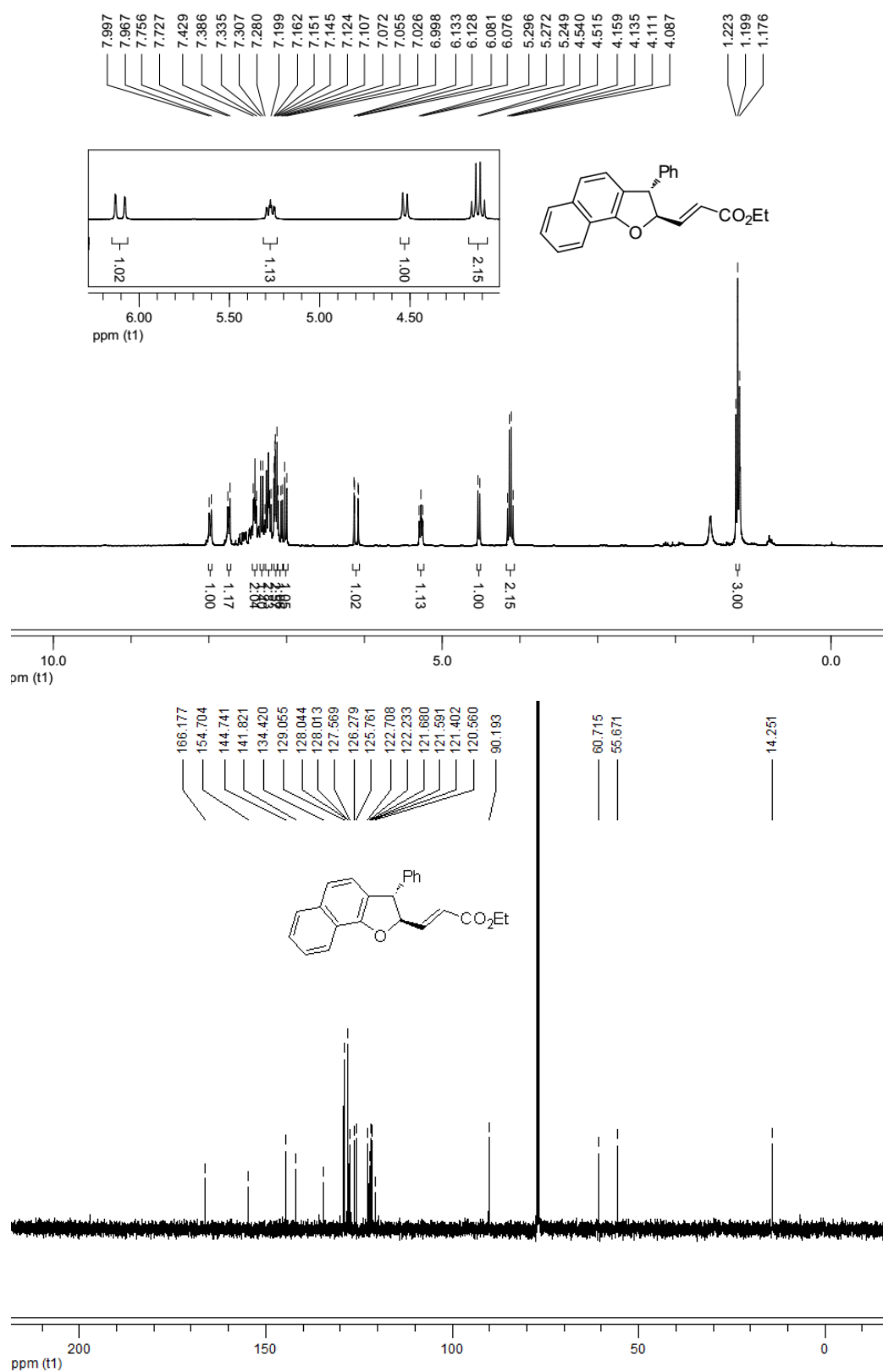


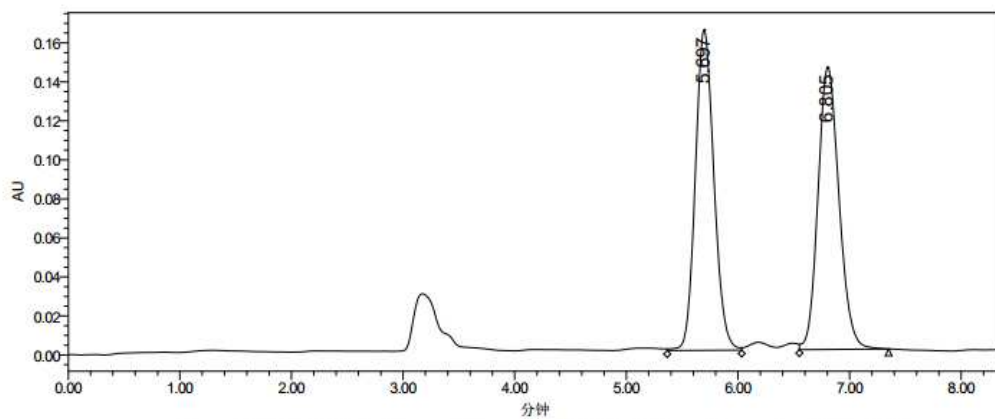
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	8.568	68654820	45.07	3419167
2	W2489 ChA 254nm	9.968	83686818	54.93	3316067



	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	8.576	19359500	48.63	1290961
2	W2489 ChA 254nm	9.897	20453071	51.37	1271368

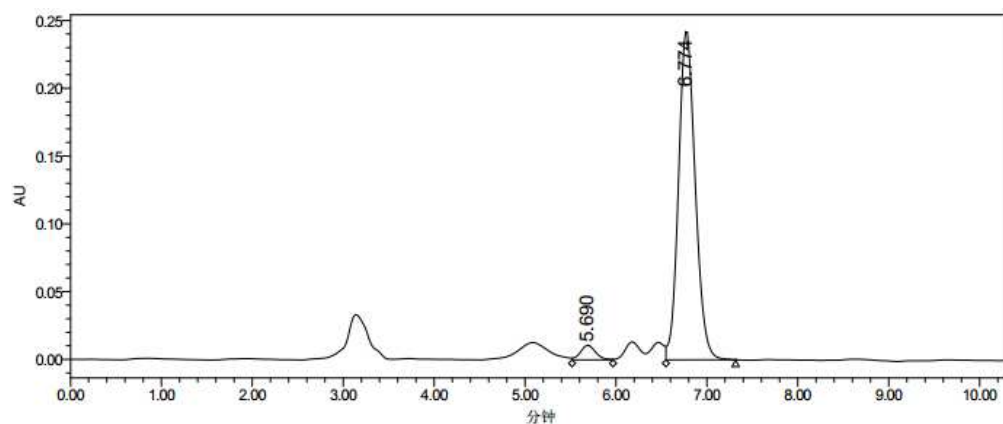
9





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

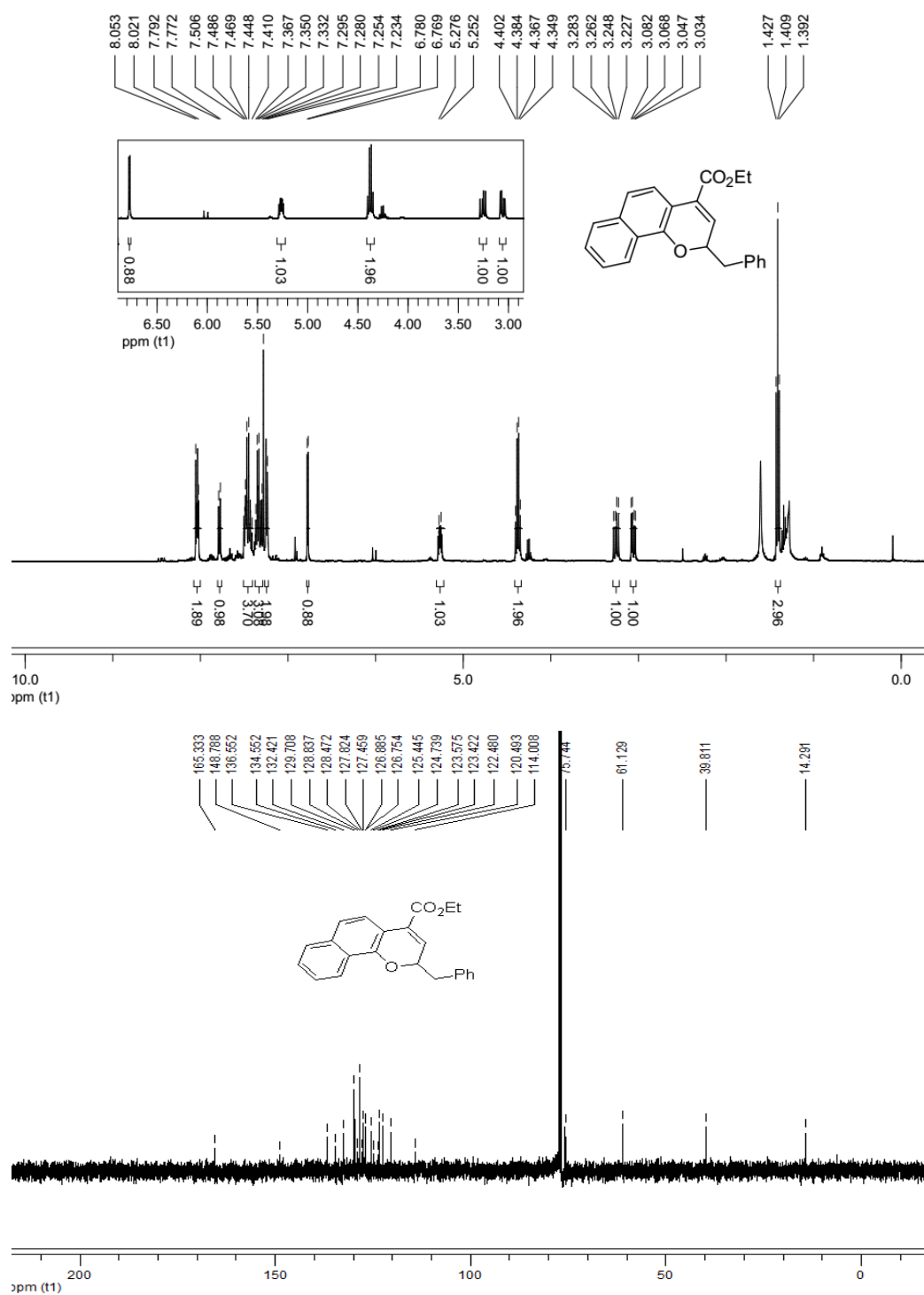
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.697	1905671	50.11	164779
2	W2489 ChA 254nm	6.805	1897048	49.89	145113

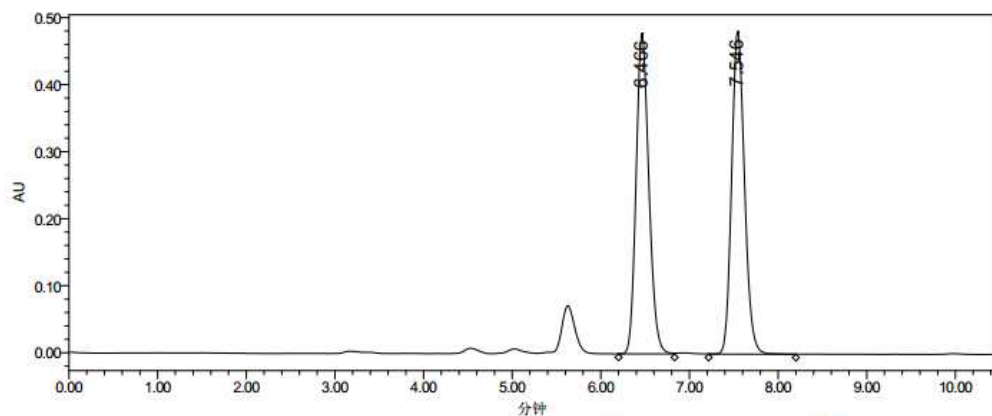


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	5.690	123184	3.81	10676
2	W2489 ChA 254nm	6.774	3106197	96.19	242927

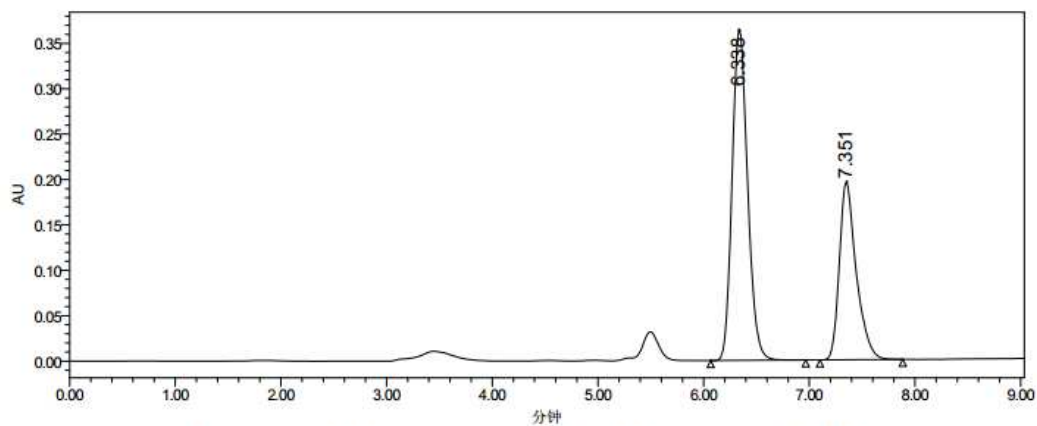
10





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

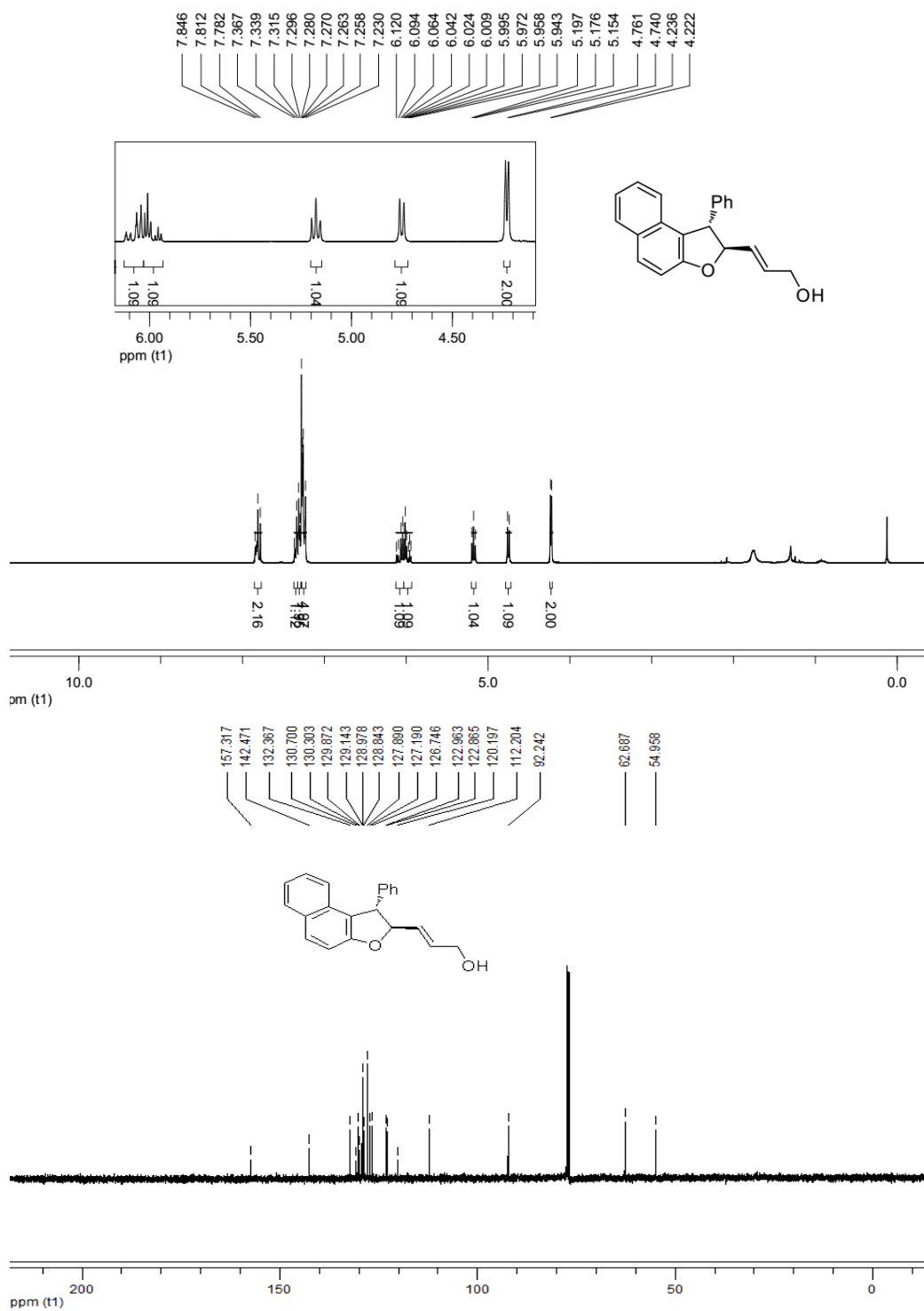
	Channel Description	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	6.466	4814820	49.85	478341
2	W2489 ChA 254nm	7.546	4842912	50.15	482465

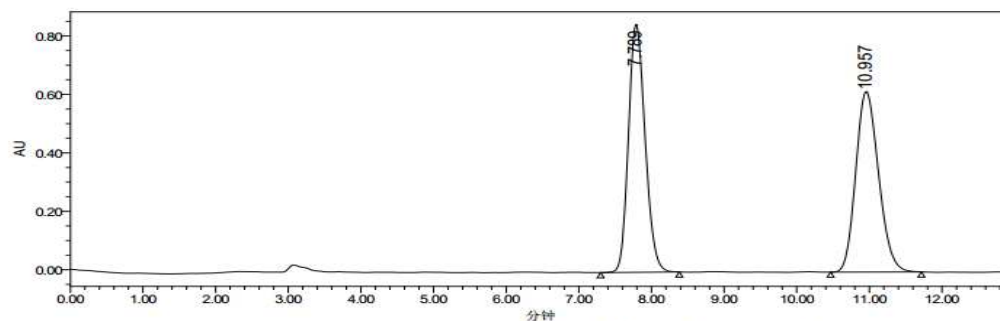


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

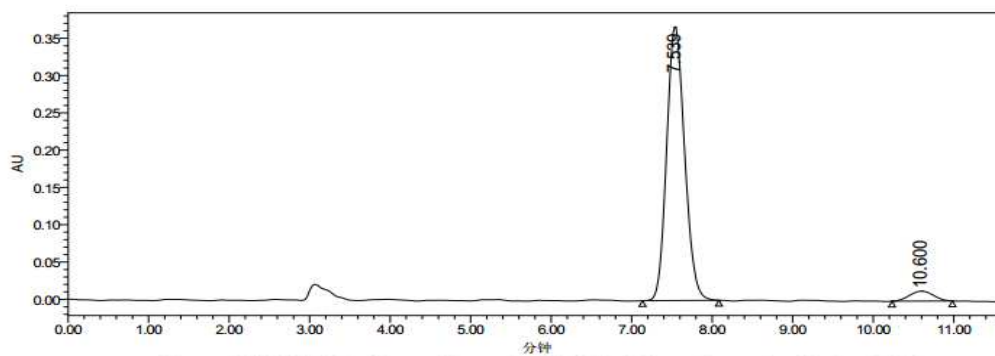
	Channel Description	RT (min)	Area (礦*sec)	% Area	Height (礦)
1	W2489 ChA 254nm	6.338	3706445	63.02	365708
2	W2489 ChA 254nm	7.351	2174476	36.98	196555

11



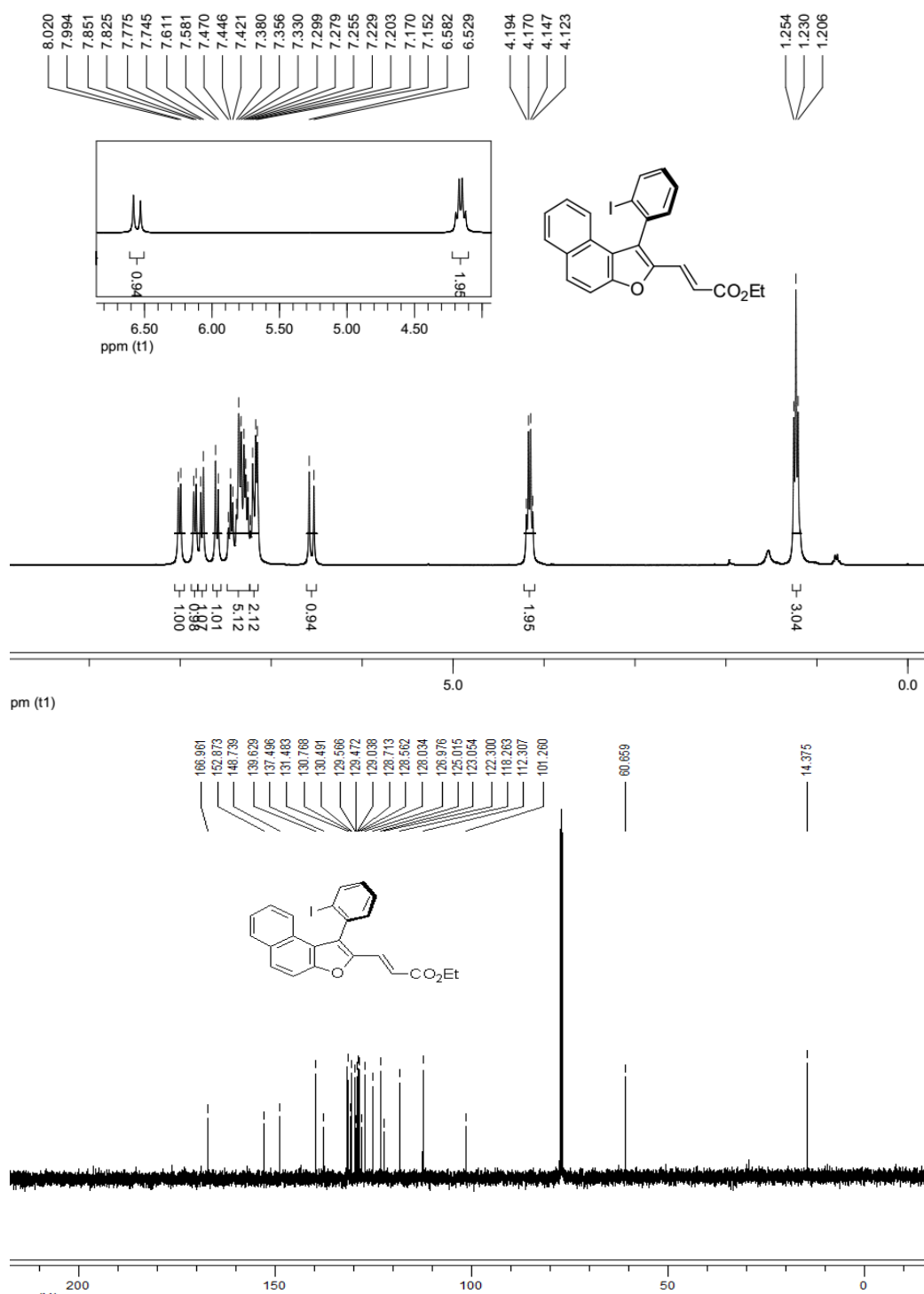


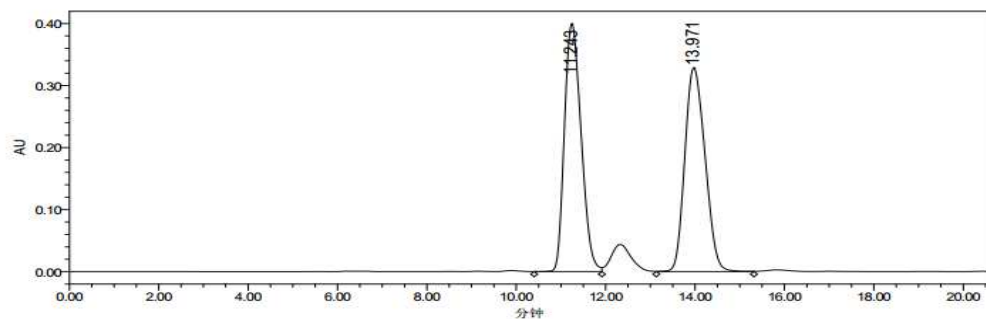
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	7.789	13519373	50.03	849074
2	W2489 ChA 254nm	10.957	13504075	49.97	617647



	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	7.539	5703682	95.43	367603
2	W2489 ChA 254nm	10.600	272957	4.57	13291

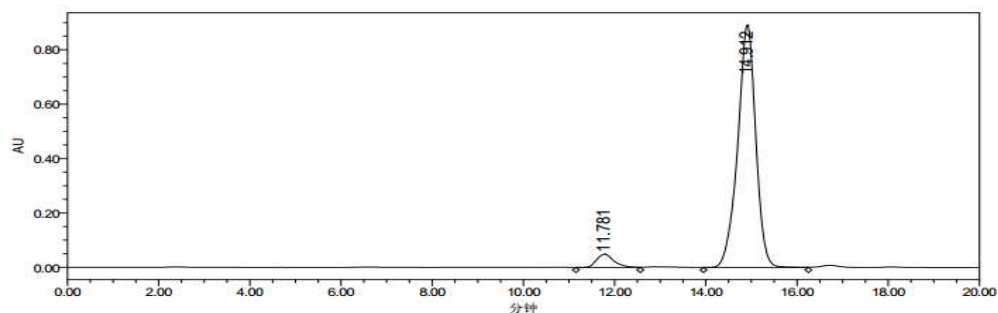
12a





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: ZWP1511 A

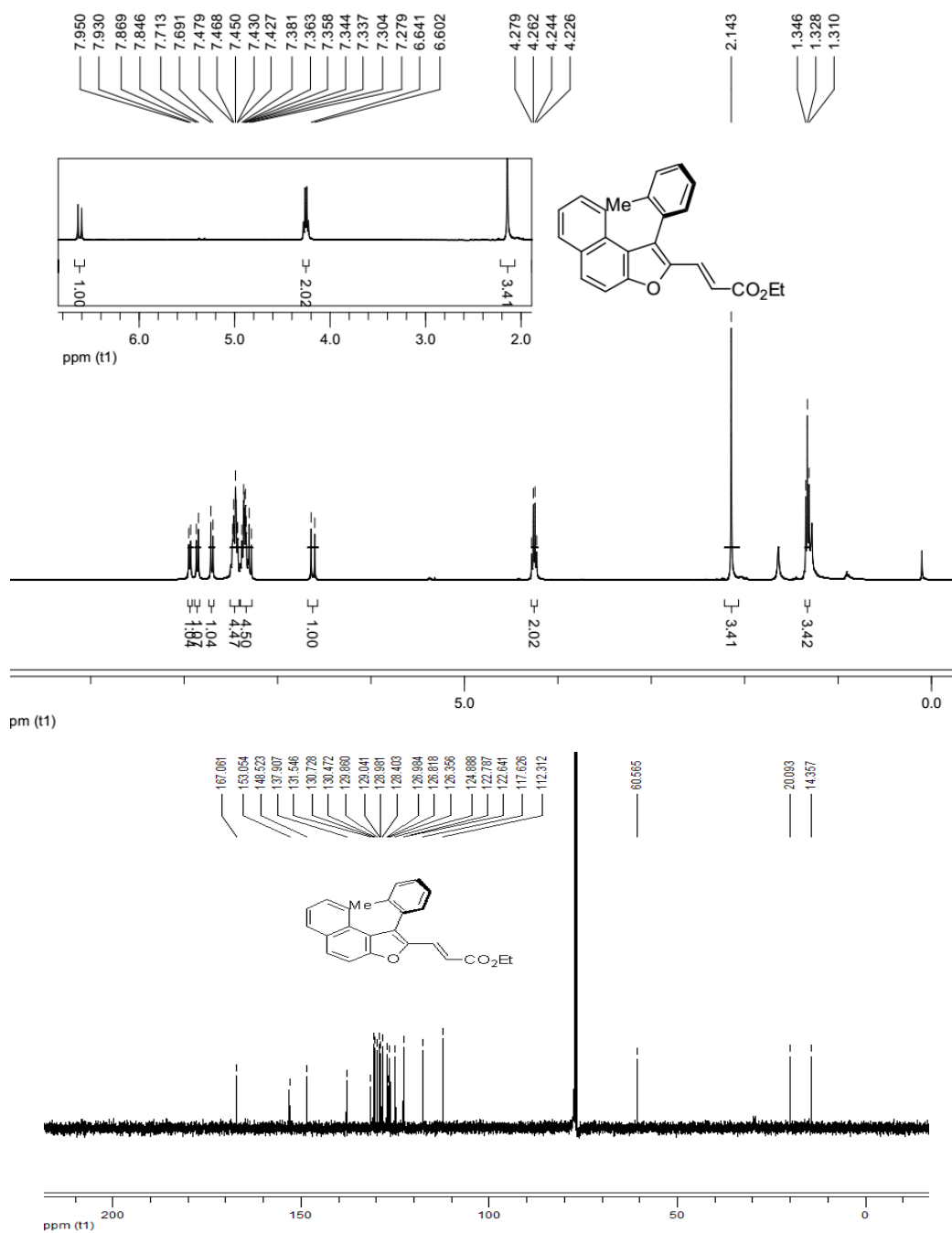
	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	11.243	10401849	50.08	399991
2	W2489 ChA 254nm	13.971	10367448	49.92	328868

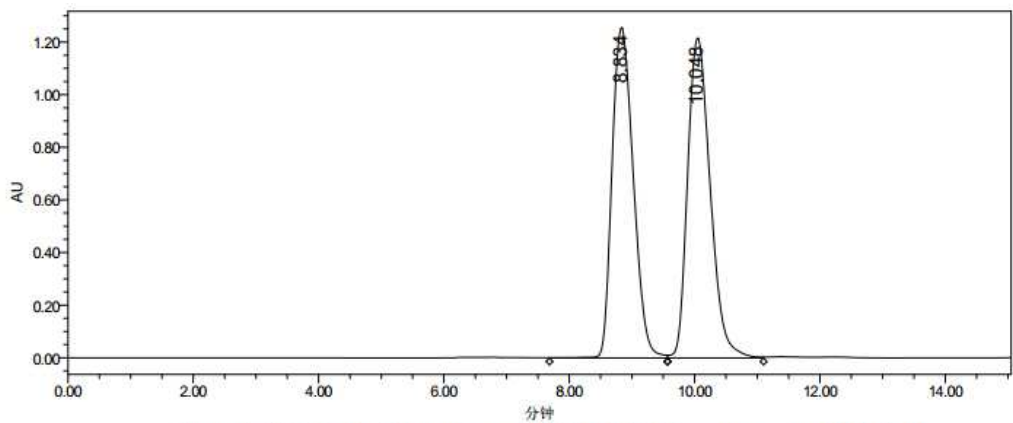


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: ZWP 1511 E 50

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	11.781	1287960	4.98	48707
2	W2489 ChA 254nm	14.912	24558467	95.02	892140

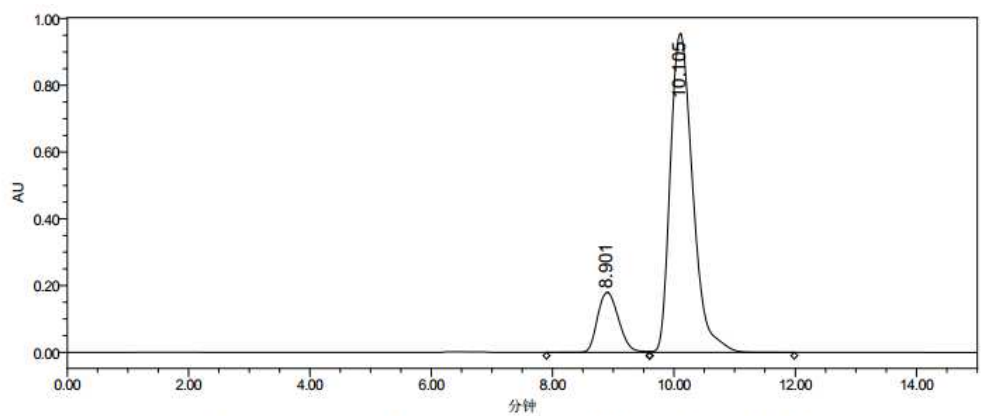
12b





Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	8.834	29508516	49.19	1254407
2	W2489 ChA 254nm	10.048	30486220	50.81	1215583

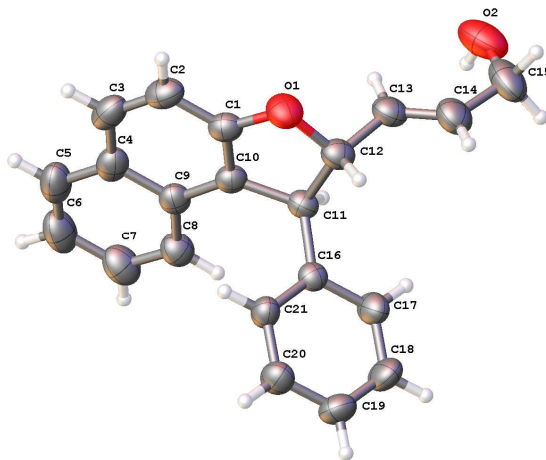


Channel: W2489 ChA; Channel Desc.: W2489 ChA 254nm; Processing Method: 01

	Channel Description	RT (min)	Area (峰*sec)	% Area	Height (峰)
1	W2489 ChA 254nm	8.901	4349298	15.03	180068
2	W2489 ChA 254nm	10.105	24592769	84.97	955536

8. X-ray Analysis

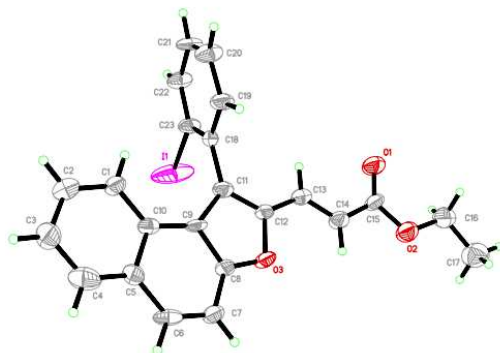
a) Compound 11



Identification code	mjr17057_0m
Empirical formula	C ₂₁ H ₁₈ O ₂
Formula weight	302.35
Temperature	303.99 K
Wavelength	1.34139 Å
Crystal system	Monoclinic
Space group	P 1 21 1
Unit cell dimensions	a = 5.51350(10) Å = 90°. b = 9.1589(2) Å = 92.8320(10)°. c = 15.7434(3) Å = 90°.
Volume	794.03(3) Å ³
Z	2
Density (calculated)	1.265 Mg/m ³
Absorption coefficient	0.406 mm ⁻¹
F(000)	320
Crystal size	0.12 x 0.08 x 0.02 mm ³
Theta range for data collection	6.455 to 60.600°.
Index ranges	-7 ≤ h ≤ 7, -11 ≤ k ≤ 11, -19 ≤ l ≤ 20
Reflections collected	9058
Independent reflections	3577 [R(int) = 0.0338]
Completeness to theta = 53.594°	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7519 and 0.6241
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3577 / 1 / 217
Goodness-of-fit on F ²	1.016
Final R indices [I > 2σ(I)]	R1 = 0.0348, wR2 = 0.0833
R indices (all data)	R1 = 0.0420, wR2 = 0.0882
Absolute structure parameter	-0.11(15)

Extinction coefficient	n/a
Largest diff. peak and hole	0.100 and -0.104 e.Å ⁻³

b) Compound 12a



Identification code	mo_dm17017_0m	
Empirical formula	'C ₂₃ H ₁₇ I O ₃	
Formula weight	468.26	
Temperature	296 K	
Wavelength	0.71073 Å	
Crystal system	monoclinic	
Space group	P 21	
Unit cell dimensions	a = 7.904(3) Å	= 90°.
	b = 24.357(12) Å	= 110.973(9)°.
	c = 11.224(5) Å	= 90°.
Volume	2017.8(16) Å ³	
Z	4	
Density (calculated)	1.541 Mg/m ³	
Absorption coefficient	1.606 mm ⁻¹	
F(000)	928	
Crystal size	0.27 x 0.25 x 0.22 mm ³	
Theta range for data collection	2.564 to 25.009°.	
Index ranges	-9 ≤ h ≤ 9, -24 ≤ k ≤ 28, -12 ≤ l ≤ 13	
Reflections collected	12304	
Independent reflections	4750 [R(int) = 0.0631]	
Completeness to theta = 25.009°	99.3 %	
Absorption correction	none	
Max. and min. transmission	0.671 and 0.719	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6272 / 1 / 489	
Goodness-of-fit on F ²	1.092	
Final R indices [I > 2σ(I)]	R ₁ = 0.0872, wR ₂ = 0.1967	

R indices (all data)	$R1 = 0.0631$, $wR2 = 0.1786$
Extinction coefficient	n/a
Largest diff. peak and hole	1.020 and -1.155 e.Å ⁻³