Supporting Information for

Asymmetric phase-transfer catalyst catalyzed [4+1] cycloaddition of *ortho*-quinone methides and bromomalonate

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General Information: NMR spectra were recorded on a Brucker-400 MHz spectrometer. Mass spectra were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Bruker Daltonics Inc (EI+). Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. HPLC analysis was performed on Waters-Breeze (2487 Dual Absorbance Detector and 1525 Binary HPLC Pump, UV detection monitored at 254 nm). All chiral columns were purchased from Daicel Chemical Industries, LTD. Optical rotations were measured on Perkin Elmer Model 343 Polarimeter. Toluene, diethyl ether and tetrahydrofuran were dried over Na and distilled prior to use. Dichloromethane and dichloroethane were dried over CaH_2 and distilled prior to use.

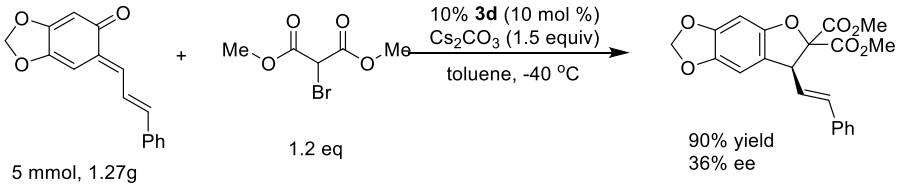
Materials: Analytical grade solvents for the column chromatography were used as received. Dimethyl bromomalonate **2** was purchased from TCI. All commercially available reagents were used directly unless indicated otherwise. Vinyl *ortho*-quinone methides **1** were prepared following the known procedures[1] and PTC **3** were synthesized according to the literatures[2].

General Procedure for Cycloaddition reaction:

The reaction of **1** (0.1 mmol) and **2** (0.12 mmol) was carried out in 2 mL toluene at -40 °C in the presence of catalyst **3a** (10 mol%) and 1.5eq Cs_2CO_3（40mg）for 5-6 days. After completion of reaction the mixture is objected to flash column chromatography washed with PE: EtOAc = 4:1, by evaporation of solvent the product is collected.

Gram-Scale experiment:

A gram-scale experiment was performed at the standard reaction condition. A significant drop of enantioselectivity was observed.



Characterization of the Cycloaddition Products 4:

Dimethyl (S,E)-7-styryl-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4a)

Colorless oil. 37.5 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.20 (m, 6H), 6.60 (dd, *J* = 23.2, 12.0 Hz, 3H), 6.06 (dd, *J* = 15.7, 9.0 Hz, 1H), 5.92 (d, *J* = 2.2 Hz, 2H), 4.93 (d, *J* = 9.0 Hz, 1H), 3.87 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.86, 166.49, 152.16, 148.31, 143.03, 136.25, 134.22, 128.65, 128.06, 126.52, 125.14, 117.94, 104.90, 101.57, 93.73, 93.31, 53.72, 53.02, 51.69. IR (KBr): γ 3437, 1745, 1630, 1552, 1474, 1265, 1089, 1036 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{21}H_{19}O_7]^+$ requires 383.11253, found 383.11368. $[\alpha]_D^{20}$ = +24.1 (c=0.64, $CHCl_3$).

Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 7.690 min (minor), tR = 10.797 min (major).

Dimethyl (S,E)-7-(4-methylstyryl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4b)

Colorless oil. 39.5 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.1 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 6.66 – 6.51 (m, 3H), 6.00 (dd, *J* = 15.7, 9.0 Hz, 1H), 5.91 (dd, *J* = 3.5, 1.2 Hz, 2H), 4.91 (d, *J* = 9.0 Hz, 1H), 3.86 (s, 3H), 3.68 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.90, 166.51, 152.14, 148.26, 143.00, 137.97, 134.09, 133.48, 129.34, 126.43, 124.05, 104.93, 101.55, 93.70, 93.36, 53.69, 52.99, 51.72, 21.23. IR (KBr): γ 3439, 1746, 1631, 1547, 1475, 1265, 1149, 1036 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{22}H_{11}O_7]^+$ requires 397.12818, found 397.12933. $[\alpha]_D^{20}$ = +108.2 (c=0.72, $CHCl_3$). Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 7.512 min (minor), tR = 11.549 min (major).

Dimethyl (S,E)-7-(2-methoxystyryl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4c)

Colorless oil. 40.9 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.25 – 7.19 (m, 1H), 6.95 (d, *J* = 15.8 Hz, 1H), 6.87 (dd, *J* = 13.2, 7.8 Hz, 2H), 6.57 (d, *J* = 17.9 Hz, 2H), 6.06 (dd, *J* = 15.8, 9.3 Hz, 1H), 5.91 (d, *J* = 1.8 Hz, 2H), 4.93 (d, *J* = 9.3 Hz, 1H), 3.86 (s, 3H), 3.84 (s, 3H), 3.70 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.90, 166.56, 156.90, 152.05, 148.19, 142.98, 129.24, 129.06, 127.14, 125.72, 125.26, 120.61, 118.42, 110.84, 105.00, 101.51, 93.67, 93.36, 55.38, 53.66, 52.94, 52.35. IR (KBr): γ 3436, 1748, 1641, 1487, 1456, 1286, 1247, 1147 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{22}H_{21}O_8]^+$ requires 413.12309, found 413.12424. $[\alpha]_D^{20}$ = +126.2 (c=0.99, $CHCl_3$). Enantiomeric excess: 91%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 9.733 min (minor), tR = 16.673 min (major).

Dimethyl (S,E)-7-(4-methoxystyryl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4d)

Colorless oil. 40.5 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.25 (s, 1H), 6.83 (d, *J* = 8.7 Hz, 2H), 6.64 – 6.49 (m, 3H), 5.98 – 5.85 (m, 3H), 4.90 (d, *J* = 9.0 Hz, 1H), 3.86 (s, 3H), 3.80 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.92, 166.54, 159.53, 152.12, 148.23, 142.99, 133.65, 129.03, 127.74, 122.83, 118.19, 114.03, 104.93, 101.54, 93.69, 93.39, 55.31, 53.68, 52.98, 51.75. IR (KBr): γ 3437, 1747, 1607, 1512, 1474, 1456, 1251, 1149, 1036 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{22}H_{21}O_8]^+$ requires 413.12309, found 413.12418. $[\alpha]_D^{20}$ = +91.3 (c=1.04, $CHCl_3$). Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 11.505 min (minor), tR = 21.944 min (major).

Dimethyl(S,E)-7-(4-bromostyryl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4e)

Colorless oil. 45.6 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.5 Hz, 2H), 7.19 (d, *J* = 8.5 Hz, 2H), 6.56 (dd, *J* = 10.1, 5.6 Hz, 3H), 6.07 (dd, *J* = 15.8, 9.0 Hz, 1H), 5.92 (dd, *J* = 3.6, 1.2 Hz, 2H), 4.92 (d, *J* = 8.9 Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.79, 166.44, 152.20, 148.40, 143.08, 135.16, 132.98, 131.80, 128.00, 126.04, 122.88, 117.60, 104.83, 101.61, 93.78,

93.23, 53.76, 53.03, 51.58. IR (KBr): γ 3436, 1746, 1631, 1627, 1474, 1455, 1285, 1150, 1036 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{21}H_{18}O_7Br]^+$ requires 461.02304, found 461.02448. $[\alpha]_D^{20}$ = +75.9 (c=0.90, $CHCl_3$). Enantiomeric excess: 94%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 8.211 min (minor), tR = 13.437 min (major).

Dimethyl (S,E)-7-(4-chlorostyryl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4f)

Colorless oil. 41.3 mg, 98% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.23 (m, 5H), 6.57 (dd, *J* = 10.2, 5.4 Hz, 3H), 6.05 (dd, *J* = 15.7, 9.0 Hz, 1H), 5.92 (d, *J* = 2.4 Hz, 2H), 4.92 (d, *J* = 8.9 Hz, 1H), 3.87 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.80, 166.45, 152.19, 148.39, 143.07, 134.72, 133.75, 132.93, 128.85, 127.69, 125.90, 117.65, 104.84, 101.60, 93.78, 93.26, 53.75, 53.03, 51.58. IR (KBr): γ 3433, 1747, 1630, 1474, 1456, 1287, 1150, 1094, 1036 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{21}H_{18}O_7Cl]^+$ requires 417.07356, found 417.07471. $[\alpha]_D^{20}$ = +33.3 (c=0.91, $CHCl_3$). Enantiomeric excess: 97%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 7.846 min (minor), tR = 12.724 min (major).

Dimethyl (S,E)-7-(4-fluorostyryl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4g)

Colorless oil. 39.7 mg, 98% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.27 (m, 2H), 6.99 (dd, *J* = 12.0, 5.3 Hz, 2H), 6.58 (dd, *J* = 11.2, 6.9 Hz, 3H), 5.98 (dd, *J* = 15.7, 9.0 Hz, 1H), 5.92 (dd, *J* = 3.5, 1.1 Hz, 2H), 4.91 (d, *J* = 9.0 Hz, 1H), 3.87 (s, 3H), 3.69 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.83, 166.48, 163.78, 161.32, 152.16, 148.35, 143.05, 132.42 (d, *J* = 3.3 Hz), 128.06 (d, *J* = 8.1 Hz), 124.93 (d, *J* = 2.3 Hz), 117.81, 115.61 (d, *J* = 21.7 Hz), 104.85, 101.59, 93.76, 93.29, 53.73, 53.01, 51.61. IR (KBr): γ 3434, 1747, 1631, 1508, 1474, 1226, 1149, 1036 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{21}H_{18}O_7F]^+$ requires 401.10311, found 401.10408. $[\alpha]_D^{20}$ = +76.3 (c=0.88, $CHCl_3$). Enantiomeric excess: 95%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 7.609 min (minor), tR = 12.803 min (major).

Dimethyl (S,E)-7-(2-(naphthalen-1-yl)vinyl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4h)

Colorless oil. 42.9 mg, 98% yield. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 1H), 7.84 (d, *J* = 7.6 Hz, 1H), 7.78 (d, *J* = 8.1 Hz, 1H), 7.60 – 7.46 (m, 3H), 7.40 (dd, *J* = 15.4, 7.7 Hz, 2H), 6.67 (s, 1H), 6.59 (s, 1H), 6.11 (dd, *J* = 15.5, 8.9 Hz, 1H), 5.93 (d, *J* = 1.2 Hz, 2H), 5.07 (d, *J* = 8.9 Hz, 1H), 3.89 (s, 3H), 3.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.91, 166.59, 152.27, 148.37, 143.11, 134.09, 133.55, 131.84, 131.08, 128.57, 128.48, 128.40, 126.27, 125.93, 125.59, 124.10, 123.70, 117.99, 104.88, 101.61, 93.82, 93.42, 53.76, 53.10, 51.93. IR (KBr): γ 3435, 1746, 1632, 1474, 1455, 1286, 1149, 1036 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{25}H_{21}O_7]^+$ requires 433.12818, found 433.12924. $[\alpha]_D^{20}$ = +73.3 (c=0.94, $CHCl_3$). Enantiomeric excess: 92%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 8.437 min (minor), tR = 13.695 min (major).

Dimethyl (S,E)-7-(2-(thiophen-2-yl)vinyl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate(4i)

Colorless oil. 38.5 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 1H), 6.94 (d, *J* = 3.3 Hz, 2H), 6.73 (d, *J* = 15.6 Hz, 1H), 6.58 (s, 1H), 6.55 (s, 1H), 5.97 – 5.83 (m, 3H), 4.90 (d, *J* = 8.8 Hz, 1H), 3.86 (s, 3H), 3.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.78, 166.46, 152.23, 148.37, 143.04, 141.25, 127.46, 127.40, 126.53, 124.80, 124.55, 117.59, 104.89, 101.59, 93.72, 93.26, 53.73, 53.07, 51.52. IR (KBr): γ 3435, 1746, 1632, 1474, 1455, 1286, 1150, 1035 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{19}H_{17}O_7S]^+$ requires 389.06895, found 389.07001. $[\alpha]_D^{20}$ = +81.2 (c=0.68, $CHCl_3$). Enantiomeric excess: 93%, determined by HPLC (Daicel Chirapak OD-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 10.710 min (minor), tR = 11.783 min (major).

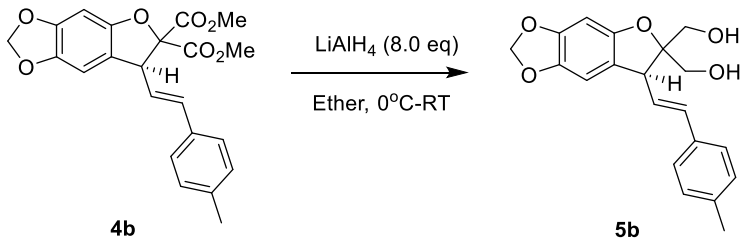
Dimethyl (S)-7-(4-methoxyphenyl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4j)

Colorless oil. 38.3 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.6 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.60 (s, 1H), 6.45 (s, 1H), 5.92 (dd, *J* = 7.1, 1.1 Hz, 2H), 5.39 (s, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 3.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.09, 166.24, 159.23, 152.50, 148.22, 143.13, 130.39, 129.80, 119.12, 113.63, 104.93, 101.55, 94.31, 93.50, 55.24, 53.71, 53.56, 52.50. IR (KBr): γ 3435, 1746, 1612, 1512, 1249, 1177, 1147, 1036 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{20}H_{19}O_8]^+$ requires 387.10744, found 387.10837. $[\alpha]_D^{20}$ = +58.7 (c=0.72, $CHCl_3$). Enantiomeric excess: 73%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 9.877 min (minor), tR = 14.521 min (major).

Dimethyl (S,E)-7-(2-methylprop-1-en-1-yl)-[1,3]dioxolo[4,5-f]benzofuran-6,6(7H)-dicarboxylate (4k)

Colorless oil. 33.1 mg, 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (d, *J* = 4.9 Hz, 2H), 5.90 (s, 2H), 5.05 (d, *J* = 10.2 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 3.84 (s, 3H), 3.74 (s, 3H), 1.83 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.12, 166.79, 151.75, 147.84, 142.88, 137.69, 120.91, 119.64, 104.51, 101.43, 93.53, 93.41, 53.57, 52.63, 47.41, 25.89, 18.24. IR (KBr): γ 3435, 1747, 1632, 1474, 1284, 1182, 1150, 1036 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{17}H_{19}O_7]^+$ requires 335.11253, found 335.11365. $[\alpha]_D^{20}$ = +61.5 (c=0.75, $CHCl_3$). Enantiomeric excess: 44%, determined by HPLC (Daicel Chirapak IC-H, hexane/ isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C, 254 nm): tR = 7.029 min (minor), tR = 10.489 min (major).

Synthesis of 5b for X-ray analysis:

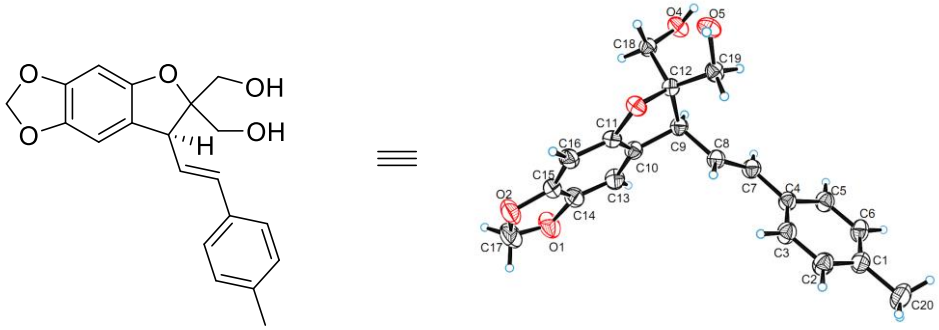


4b **5b**

A solution of lithium aluminium tetrahydride in ether (2 mL, 0.4 mmol) was added dropwise to a solution of **4b** (23mg, 0.06 mmol) in ether (1 mL) at 0 °C under nitrogen. The reaction was allowed to warm to ambient temperature and was stirred for 16 h. The reaction mixture was quenched with water

(5 mL), and extracted with DCM (3 x 5 mL). The organic phases were combined and evaporated to dryness. The residue was purified by flash silica gel chromatography to afford **5b** as a colourless oil(95%, 19mg).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 7.7 Hz, 2H), 6.57 (d, *J* = 14.0 Hz, 2H), 6.41 (s, 1H), 6.21 (dd, *J* = 15.7, 9.3 Hz, 1H), 5.90 (d, *J* = 3.2 Hz, 2H), 4.12 (d, *J* = 9.2 Hz, 1H), 3.90 (t, *J* = 11.4 Hz, 2H), 3.79 (s, 2H), 2.34 (s, 3H), 2.23 (s, 1H), 2.06 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.48, 147.88, 142.07, 133.78, 133.62, 129.38, 126.38, 124.74, 120.55, 105.41, 101.32, 93.34, 93.11, 64.95, 63.10, 50.09, 21.24. HRMS (ESI): m/z $[M + H]^+$ calcd for $[C_{20}H_{21}O_5]^+$ requires 341.1384, found 341.1387.

X-ray Single Crystal Data for 5b



Empirical formula	$C_{20}H_{20}O_5$
Formula weight	340.36
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Z	8
a/Å	5.6783(2)
b/Å	18.1808(7)
c/Å	34.1983(14)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3530.5(2)
Temperature/K	300 K
ρ, g/cm^3	1.281

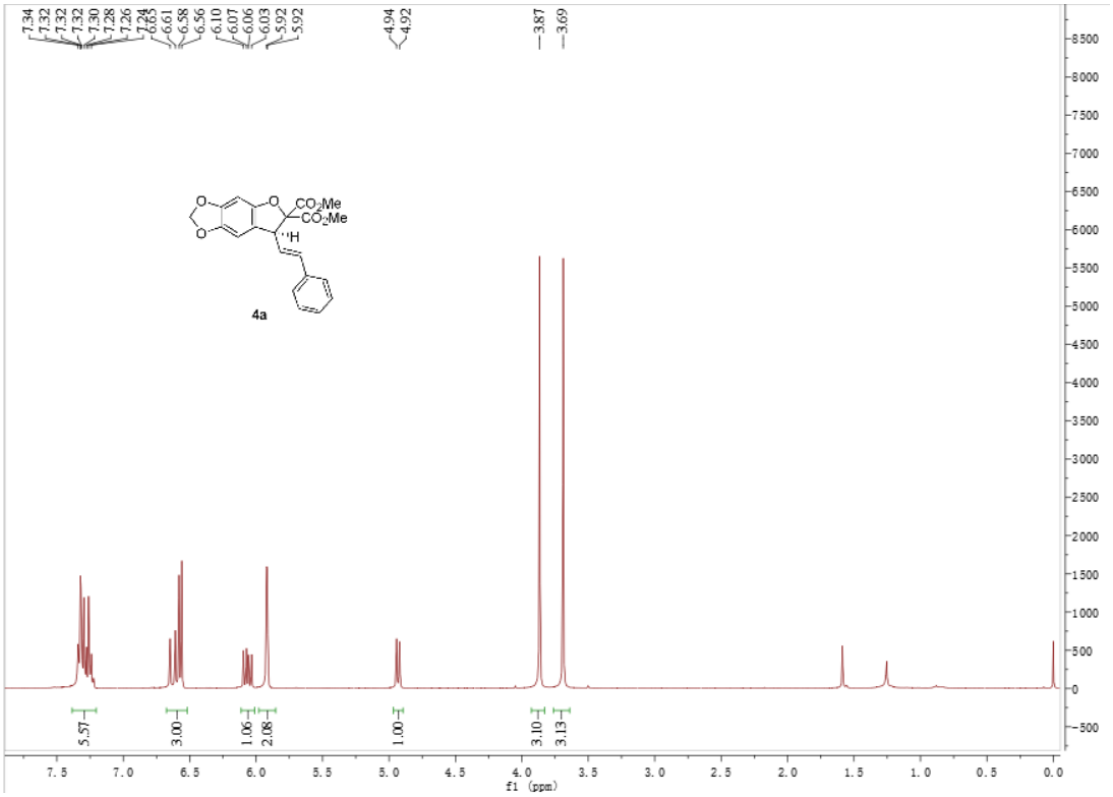
References

[1] Alafate Adili, Zhong-Lin Tao, Dian-Feng Chen and Zhi-Yong Han*, *Org. Bio mol. Chem*., **2015**, *13*, 2247–2250.

[2] Zhong-Lin Tao, Arafate Adili, Xiang Wu, and Prof. Liu-Zhu Gong*, *Chin. J. Chem.*, **2014**, *32*, 969 – 973.

^{1}H- and ^{13}C-NMR Spectra

(4a)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6.10
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6.06
6.03
5.92
5.92
4.94
4.92
3.87
3.69
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CO2Me
H
4a
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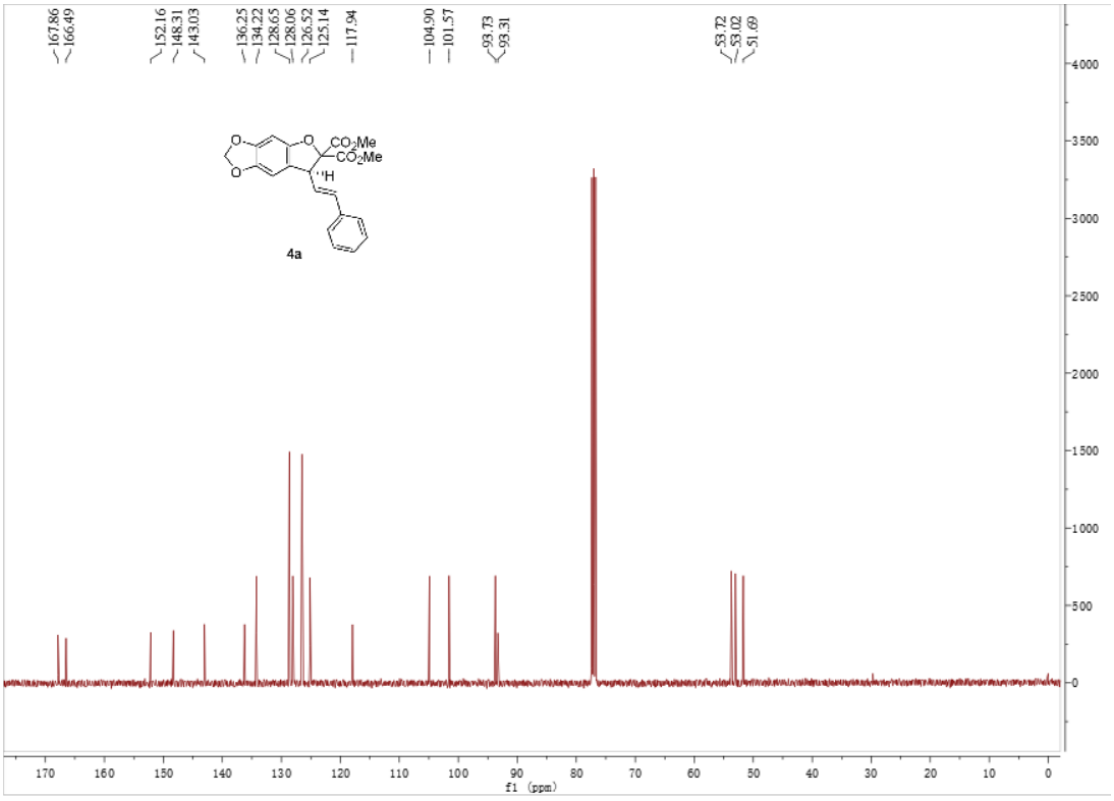
1.06
2.08
1.00
3.10
3.13
f1 (ppm)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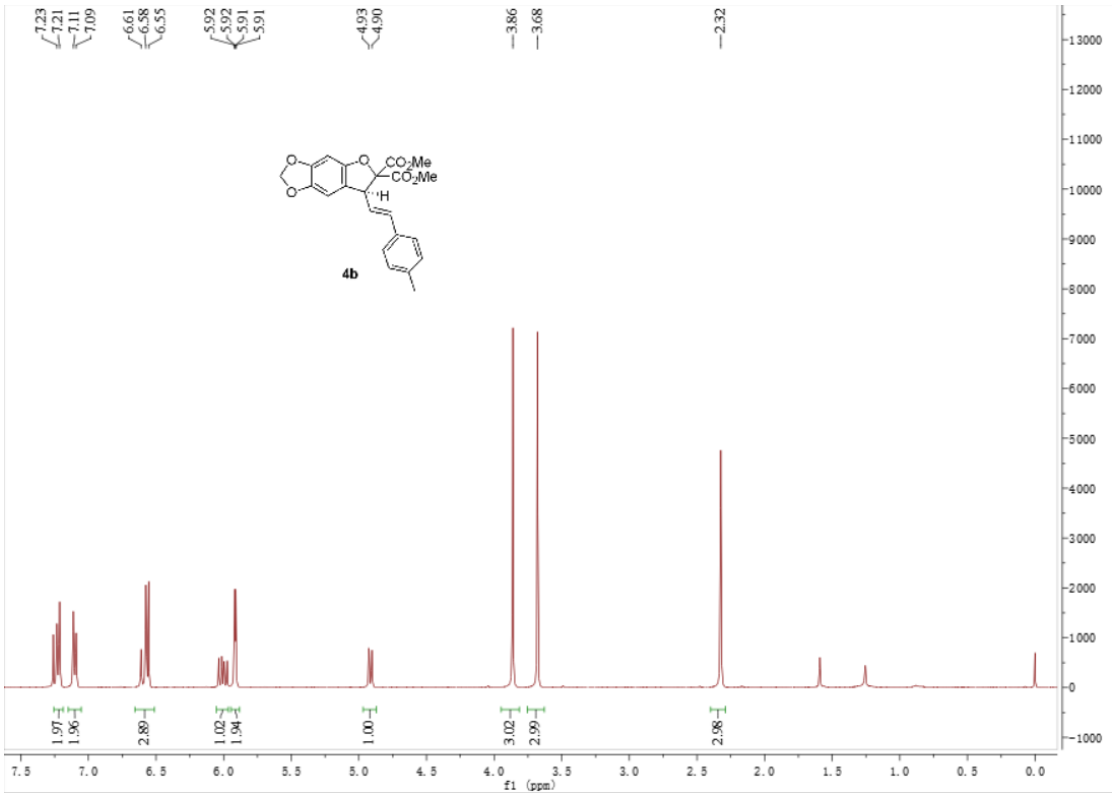
CO2Me
CO2Me
H
4a
f1 (ppm)

(4b)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5.91
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4.90
3.86
3.68
2.32
CO2Me
CO2Me
H
4b
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1.96
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1.94
1.00
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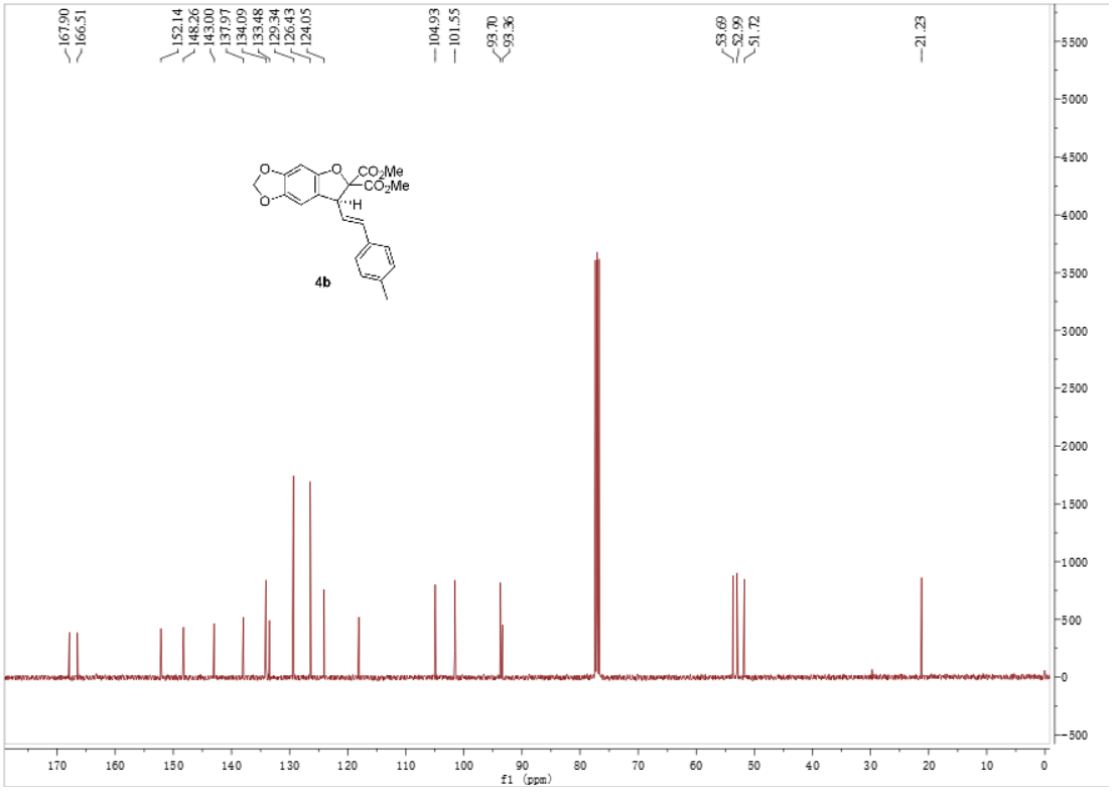
2.99
2.98
f1 (ppm)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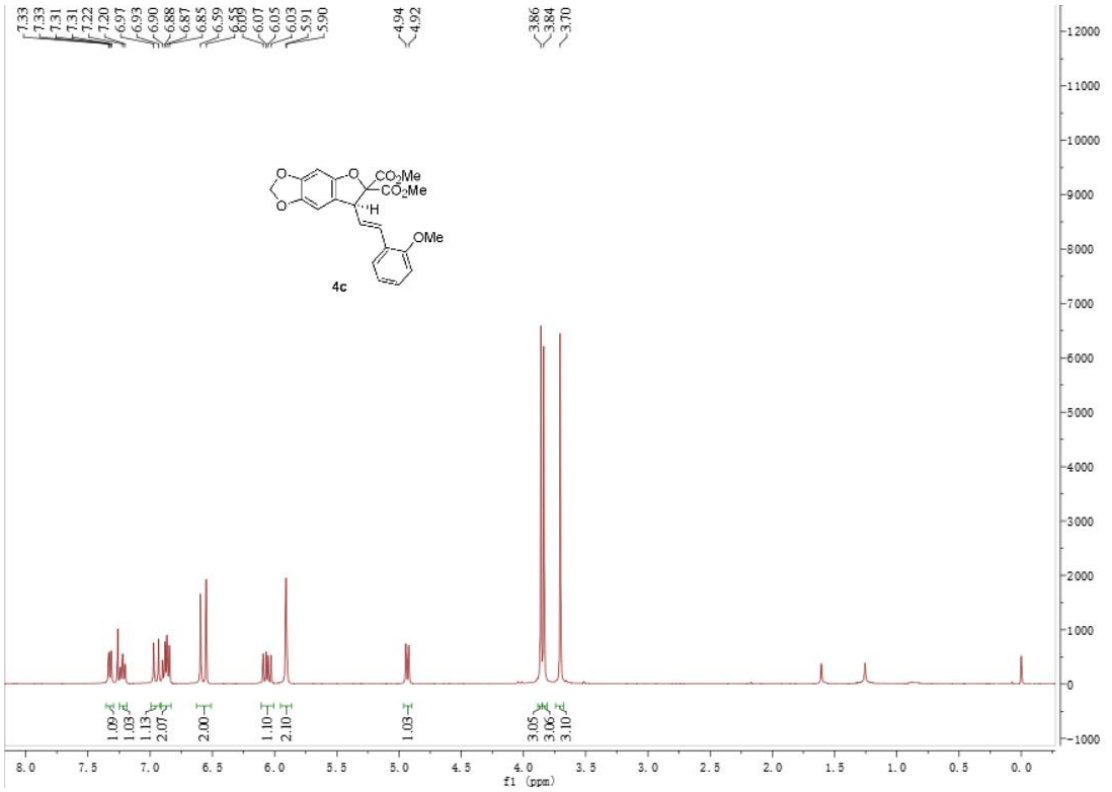
152.14
148.26
143.00
137.97
134.09
133.48
129.34
126.43
124.05
104.93
101.55
93.70
93.36
53.69
52.99
51.72
21.23
CO2Me
CO2Me
H
4b
f1 (ppm)

(4c)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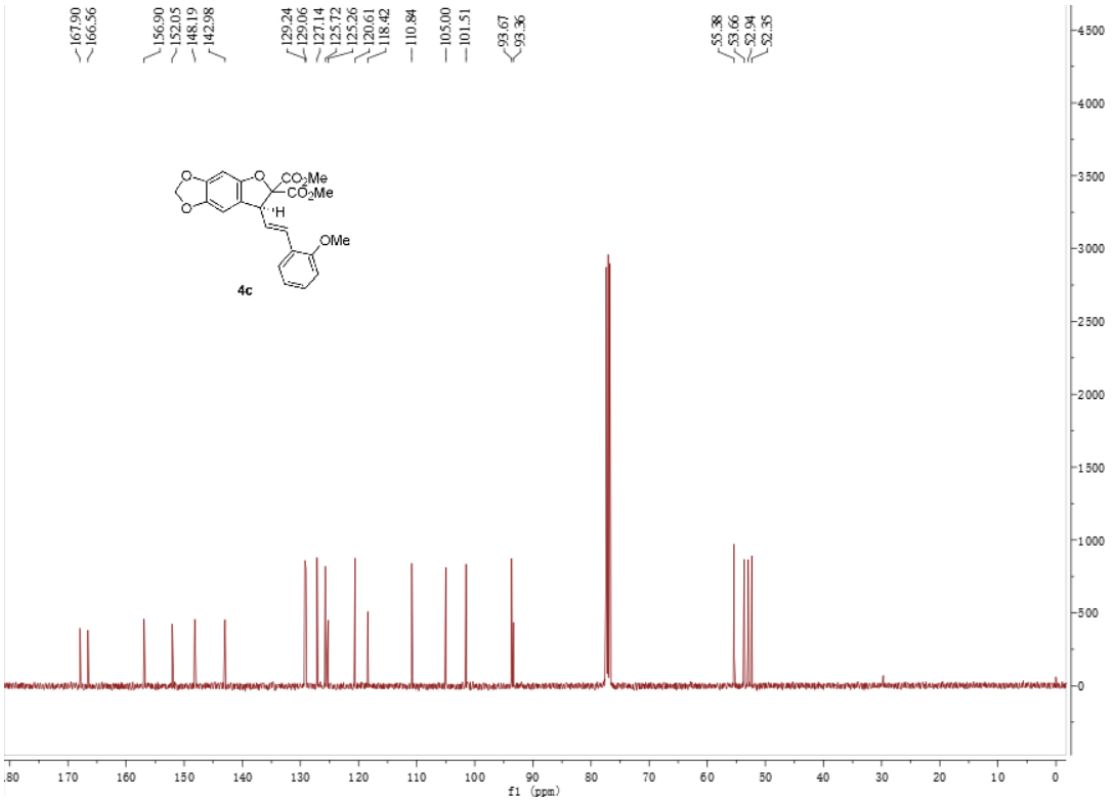
6.93
6.90
6.88
6.87
6.85
6.59
6.55
6.09
6.07
6.05
6.03
5.91
5.90
4.94
4.92
3.86
3.84
3.70
CO2Me
CO2Me
H
OMe
4c
1.09
1.03
1.13
2.07
2.00
1.10
2.10
1.03
3.05
3.06
3.10
f1 (ppm)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142.98
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129.06
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125.72
125.26
120.61
118.42
110.84
105.00
101.51
93.67
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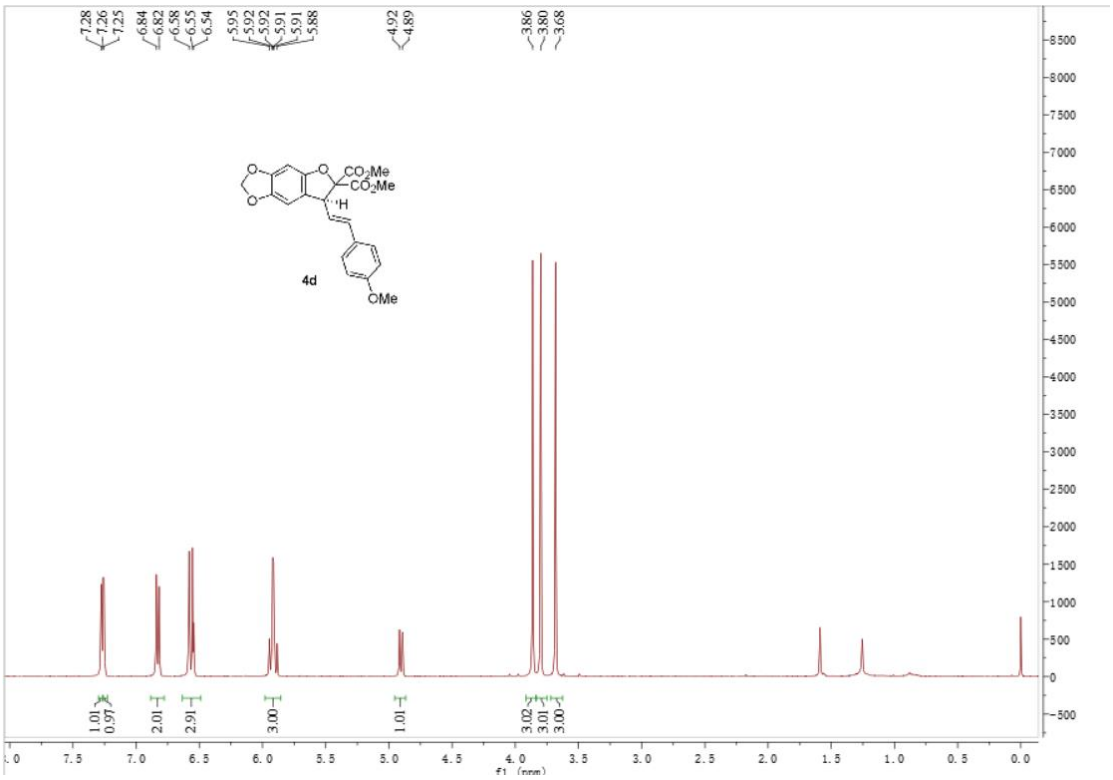
53.66
52.94
52.35
CO2Me
CO2Me
H
OMe
4c
f1 (ppm)

(4d)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5.91
5.91
5.88
4.92
4.89
3.86
3.80
3.68
CO2Me
CO2Me
H
4d
OMe
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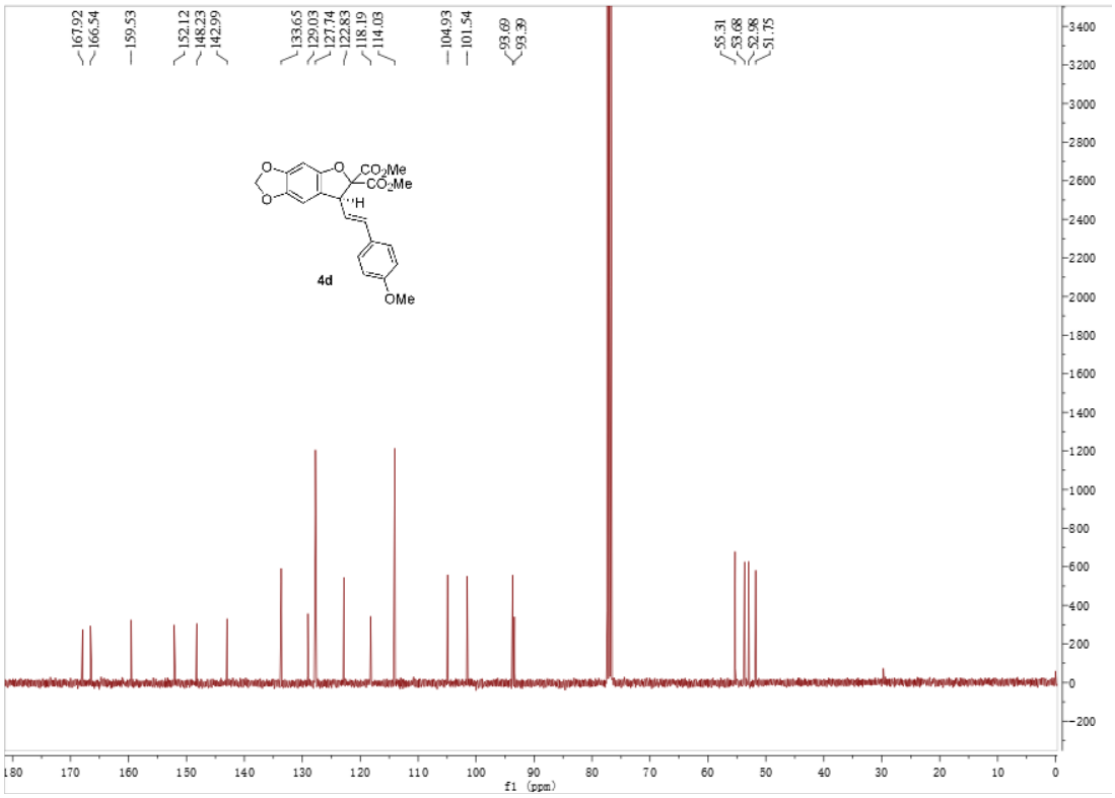
0.97
2.01
2.91
3.00
1.01
3.02
3.01
3.00
f1 (ppm)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104.93
101.54
93.69
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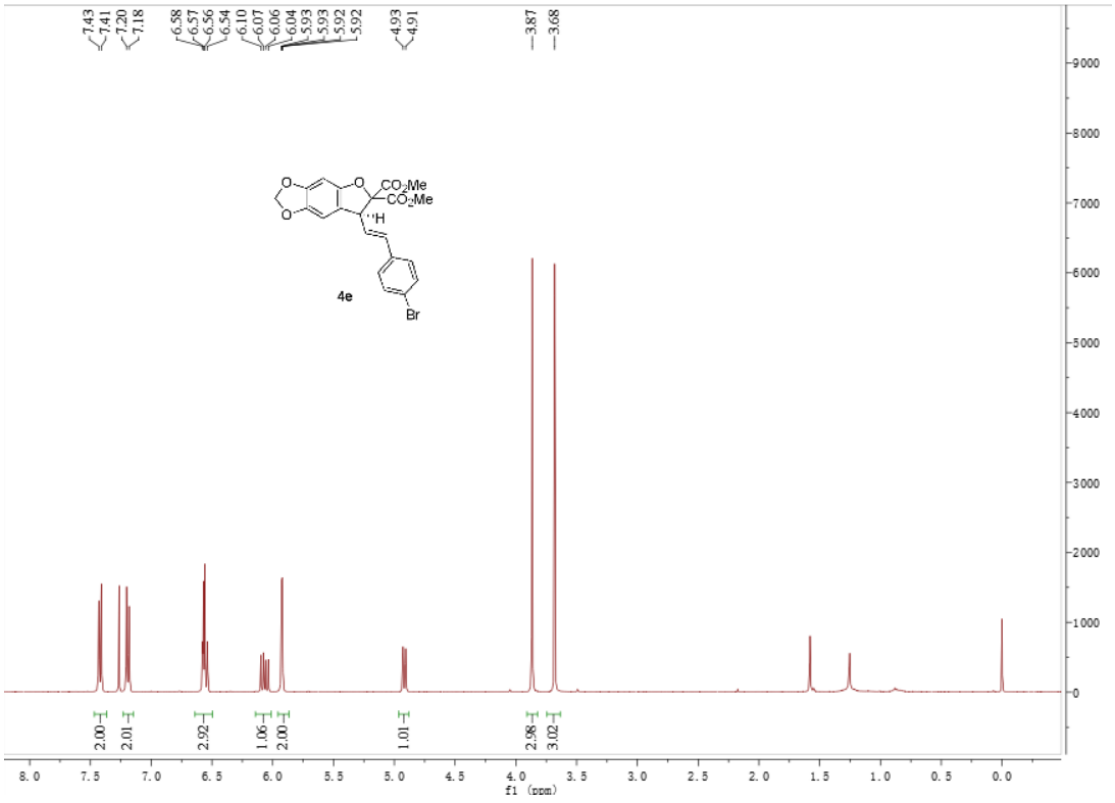
52.98
51.75
CO2Me
CO2Me
H
4d
OMe
f1 (ppm)

(4e)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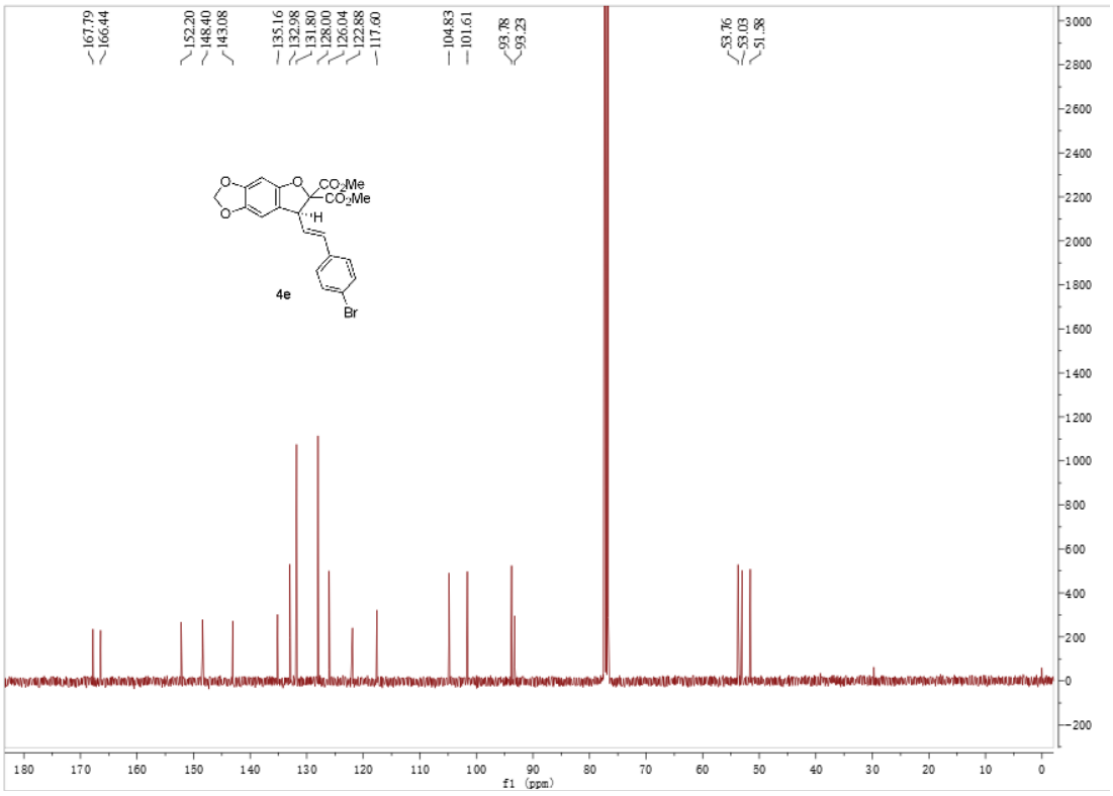
6.07
6.06
6.04
5.93
5.93
5.92
5.92
4.93
4.91
3.87
3.68
CO2Me
CO2Me
H
4e
Br
2.00
2.01
2.92
1.06
2.00
1.01
2.98
3.02
f1 (ppm)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104.83
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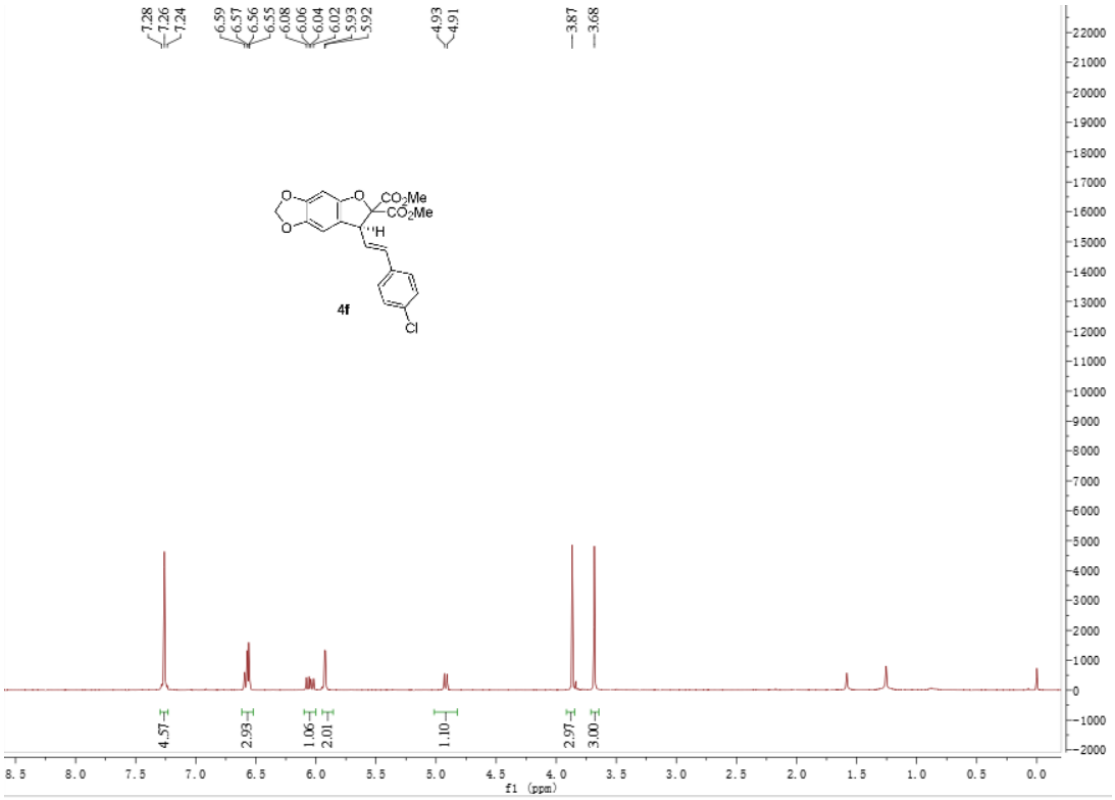
53.03
51.38
CO2Me
CO2Me
H
4e
Br
f1 (ppm)

(4f)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6.55
6.08
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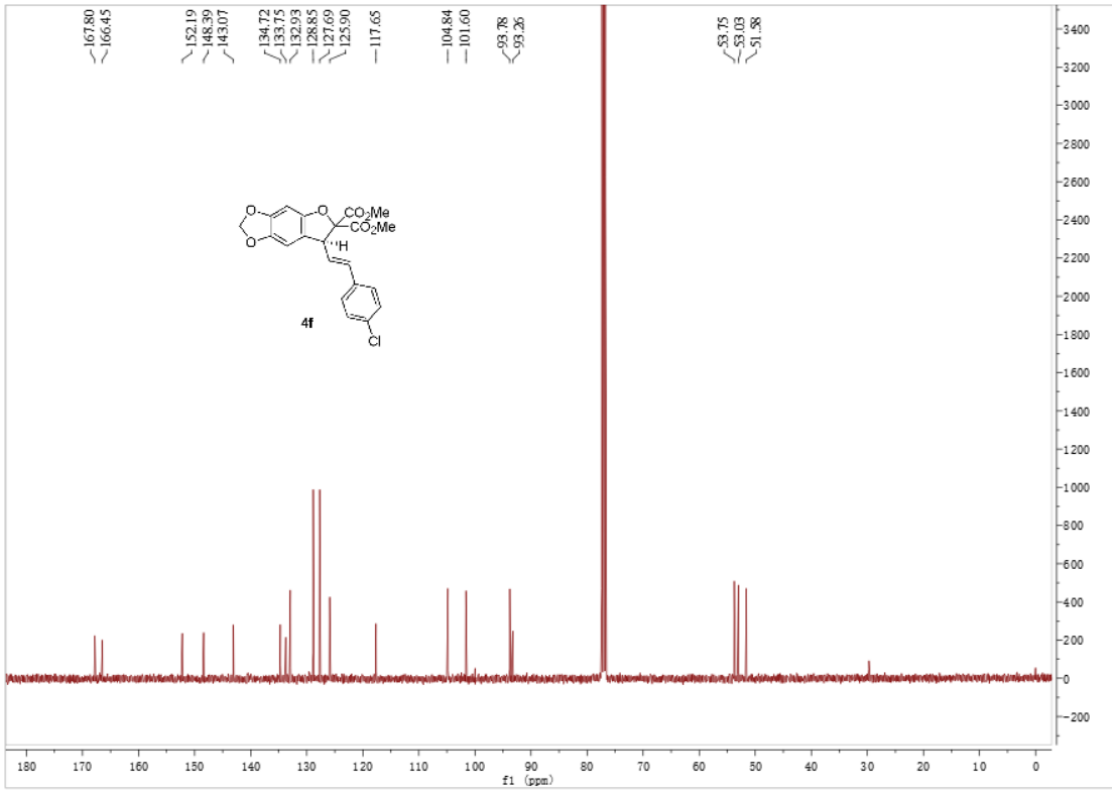
6.04
6.02
5.93
5.92
4.93
4.91
3.87
3.68
CO2Me
CO2Me
H
Cl
4f
4.57
2.93
1.06
2.01
1.10
2.97
3.00
f1 (ppm)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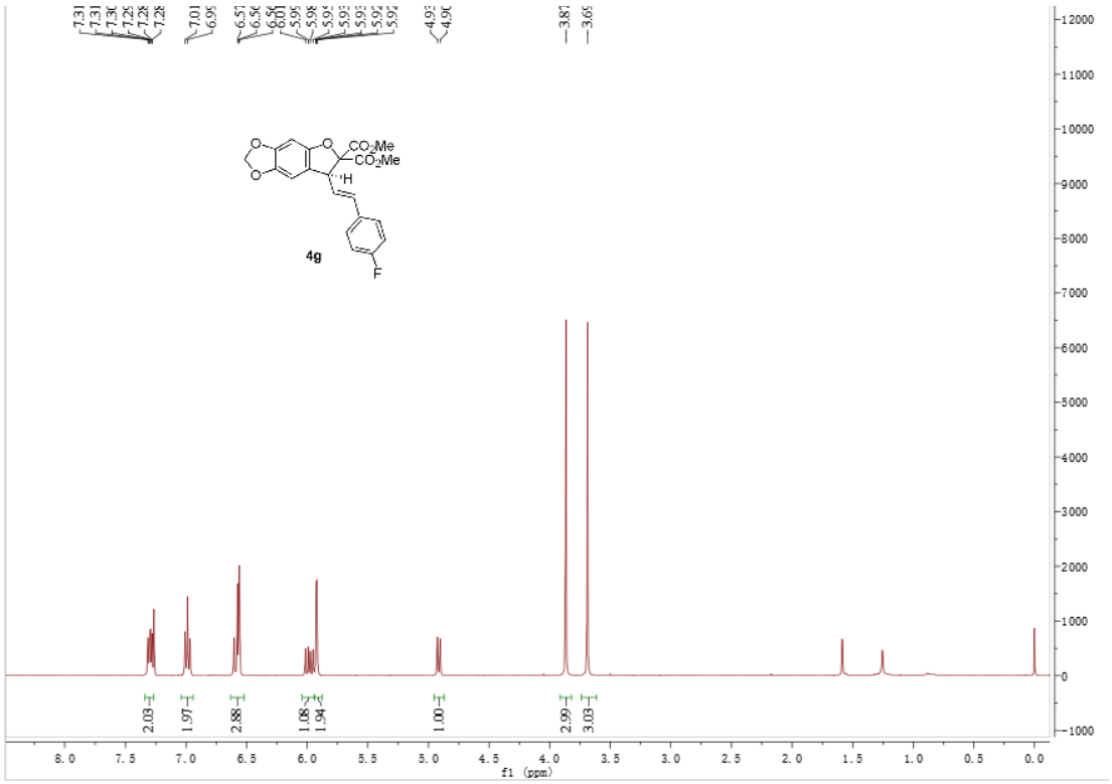
125.90
117.65
104.84
101.60
93.78
93.26
53.75
53.03
51.88
CO2Me
CO2Me
H
Cl
4f
f1 (ppm)

(4g)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7.01
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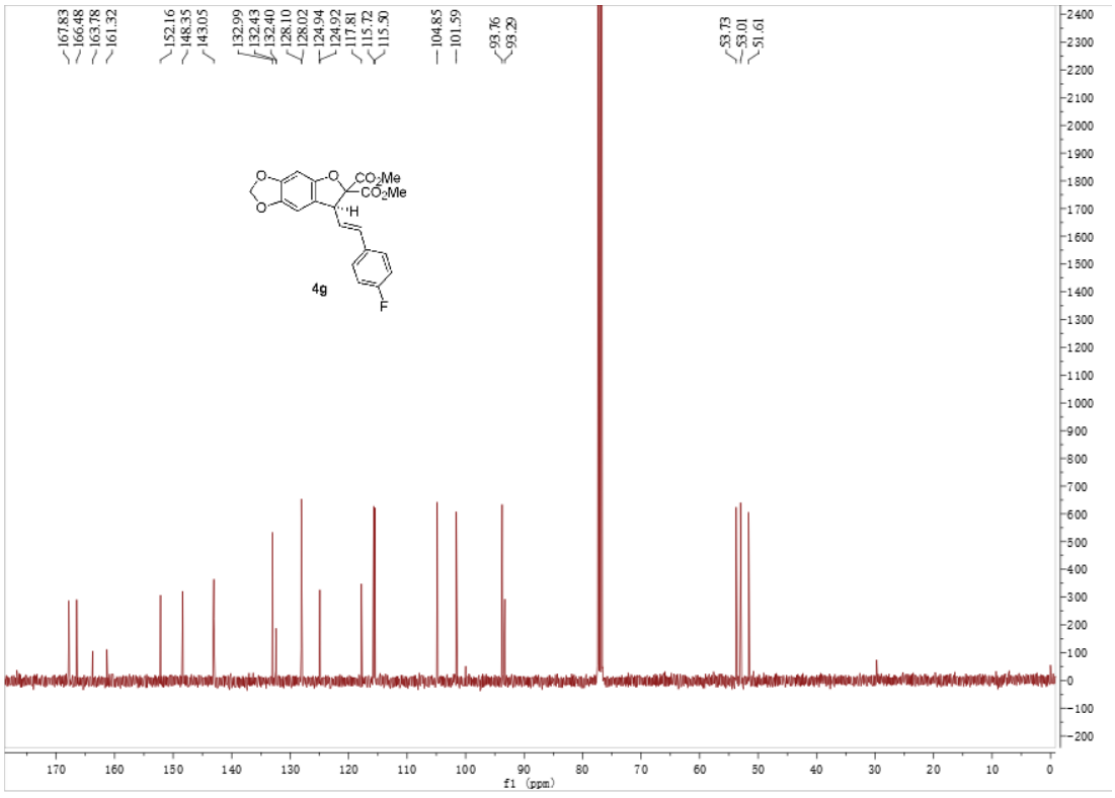
6.50
6.01
5.99
5.98
5.95
5.95
5.92
5.92
4.93
4.90
3.87
3.65
CO2Me
CO2Me
H
4g
F
2.03
1.97
2.88
1.08
1.94
1.00
2.99
3.03
f1 (ppm)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128.10
128.02
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124.92
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115.72
115.50
104.85
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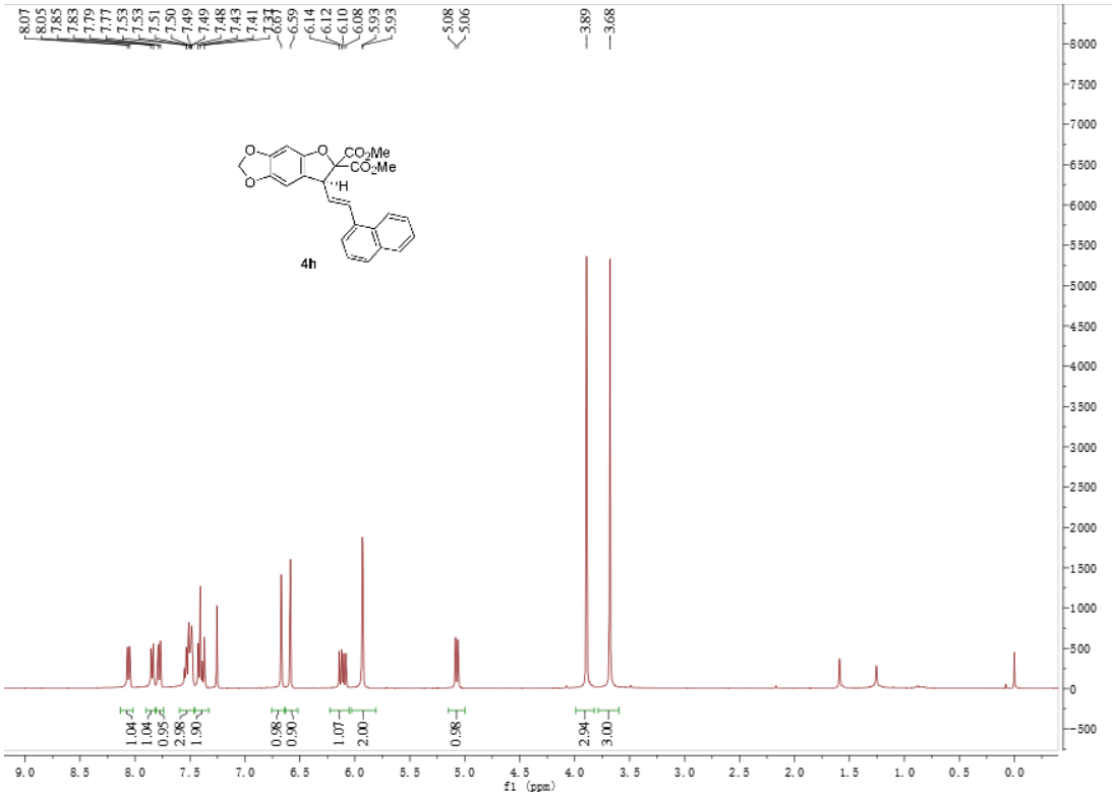
CO2Me
H
4g
F
f1 (ppm)

(4h)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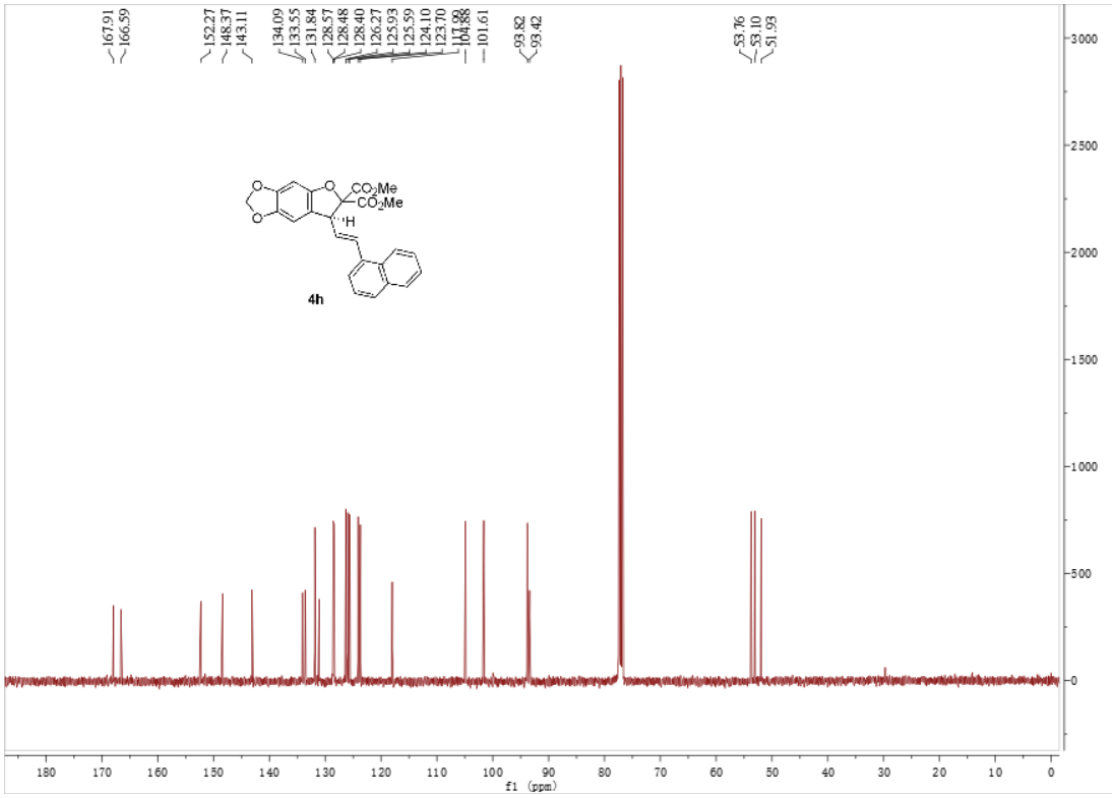
5.08
5.06
3.89
3.68
CO2Me
CO2Me
H
4h
1.04
1.04
0.95
2.98
1.90
0.98
0.90
1.07
2.00
0.98
2.94
3.00
f1 (ppm)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125.93
125.59
124.10
123.70
101.61
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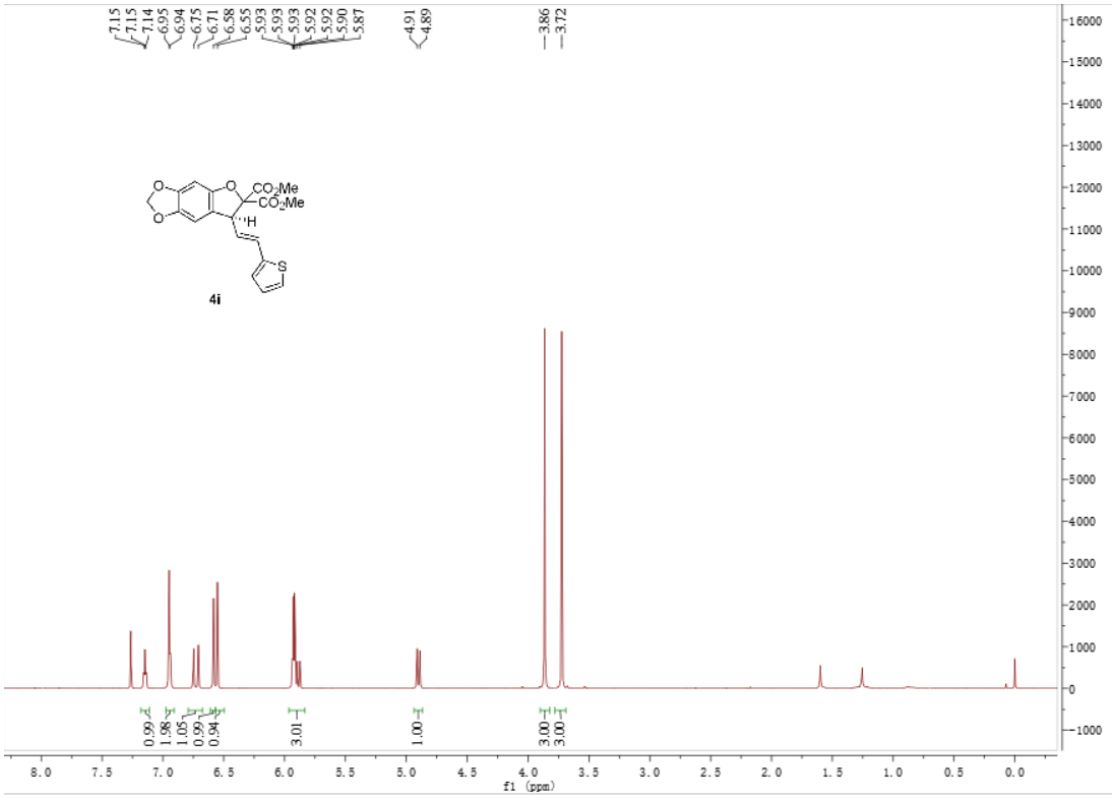
93.42
53.76
53.10
51.93
CO2Me
CO2Me
H
4h
f1 (ppm)

(4i)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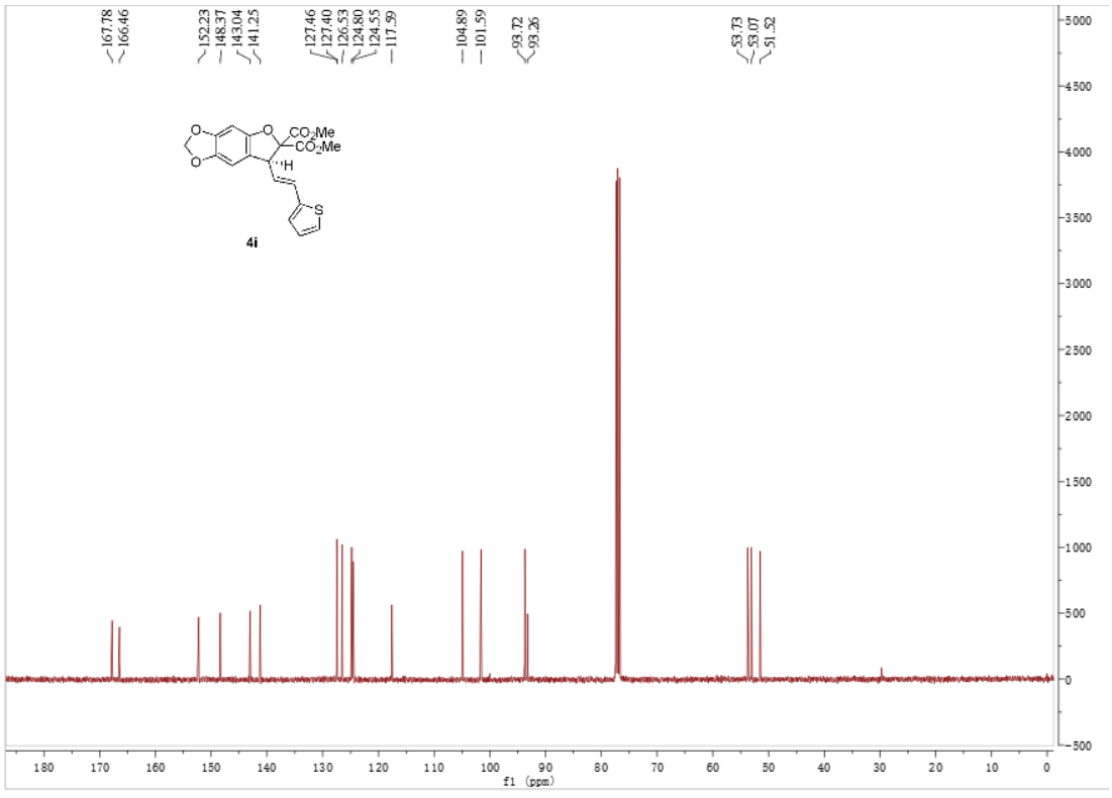
5.93
5.92
5.92
5.90
5.87
4.91
4.89
3.86
3.72
CO2Me
CO2Me
H
S
4i
0.99
1.98
1.05
0.99
0.94
3.01
1.00
3.00
3.00
f1 (ppm)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126.53
124.80
124.55
117.59
104.89
101.59
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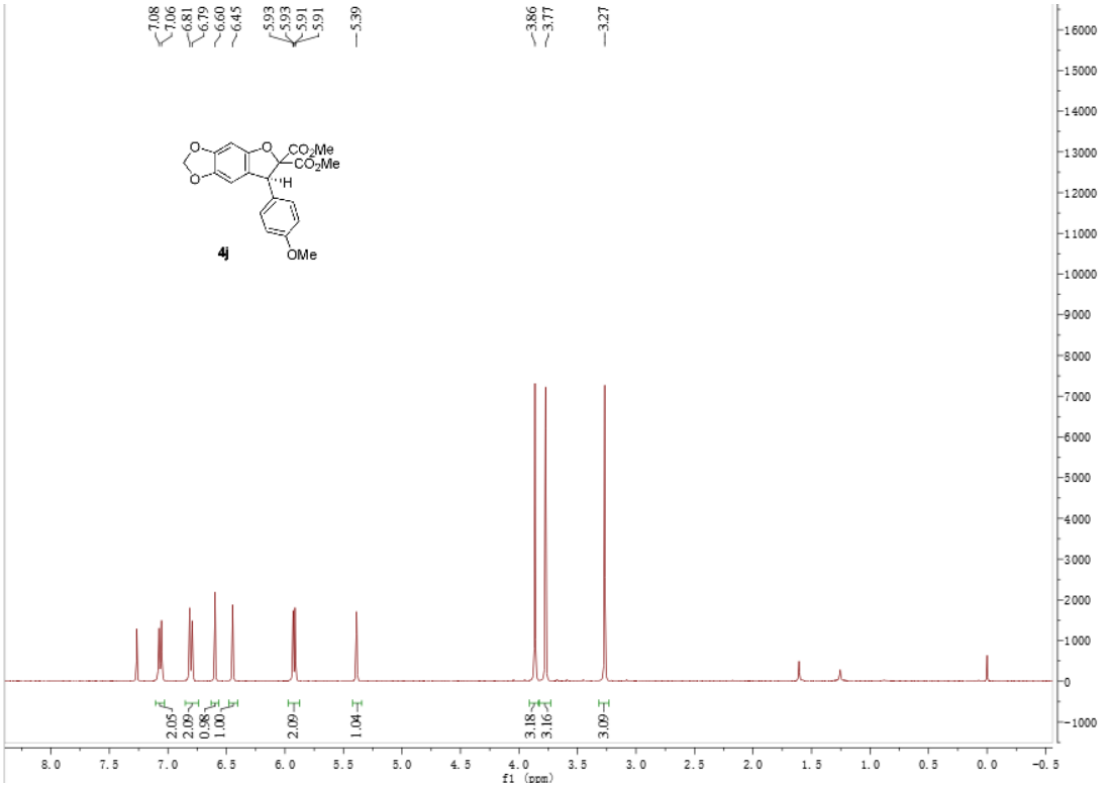
53.73
53.07
51.52
CO2Me
CO2Me
H
S
4i
f1 (ppm)

(4j)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5.39
3.86
3.77
3.27
CO2Me
CO2Me
H
4j
OMe
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2.09
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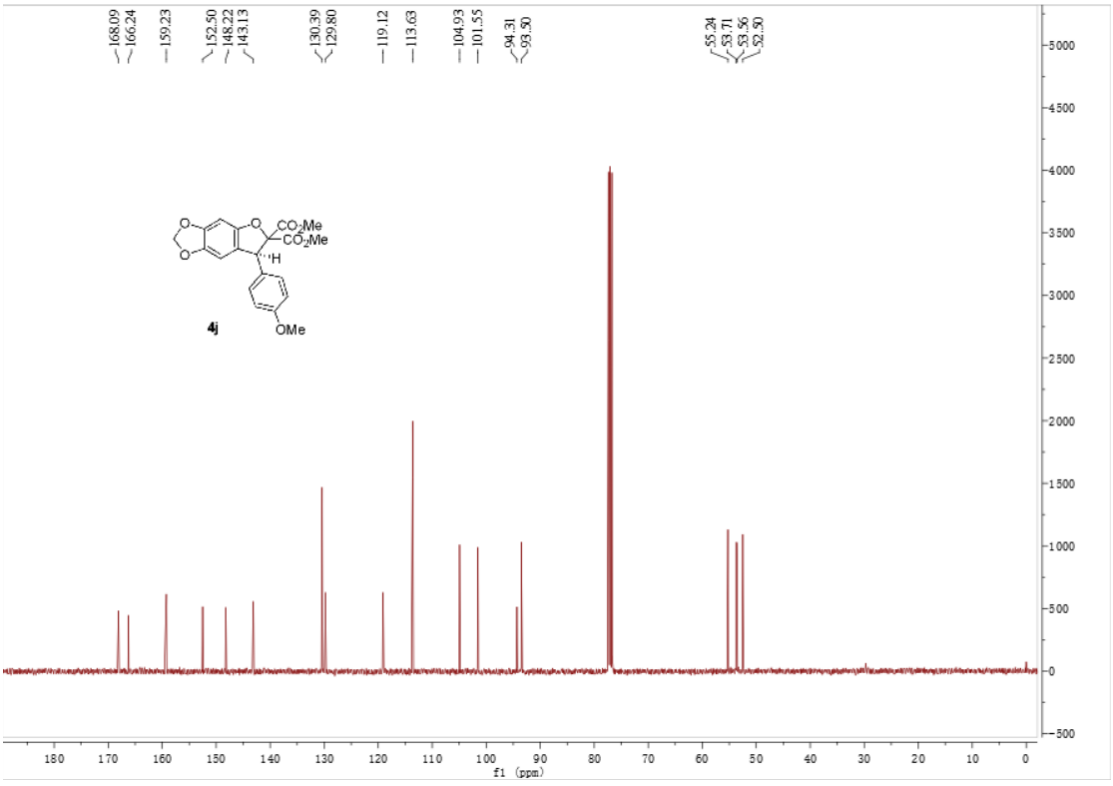
1.00
2.09
1.04
3.18
3.16
3.09
f1 (ppm)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130.39
129.80
119.12
113.63
104.93
101.55
94.31
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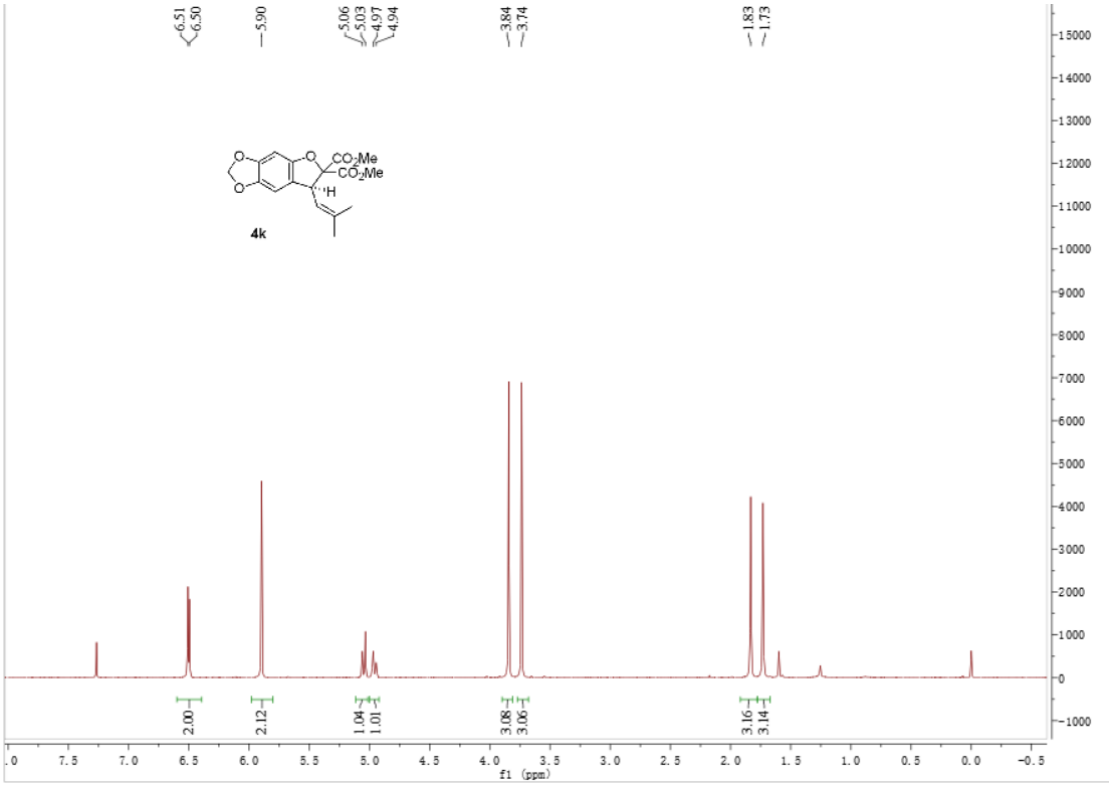
52.50
CO2Me
CO2Me
H
4j
OMe
f1 (ppm)

(4k)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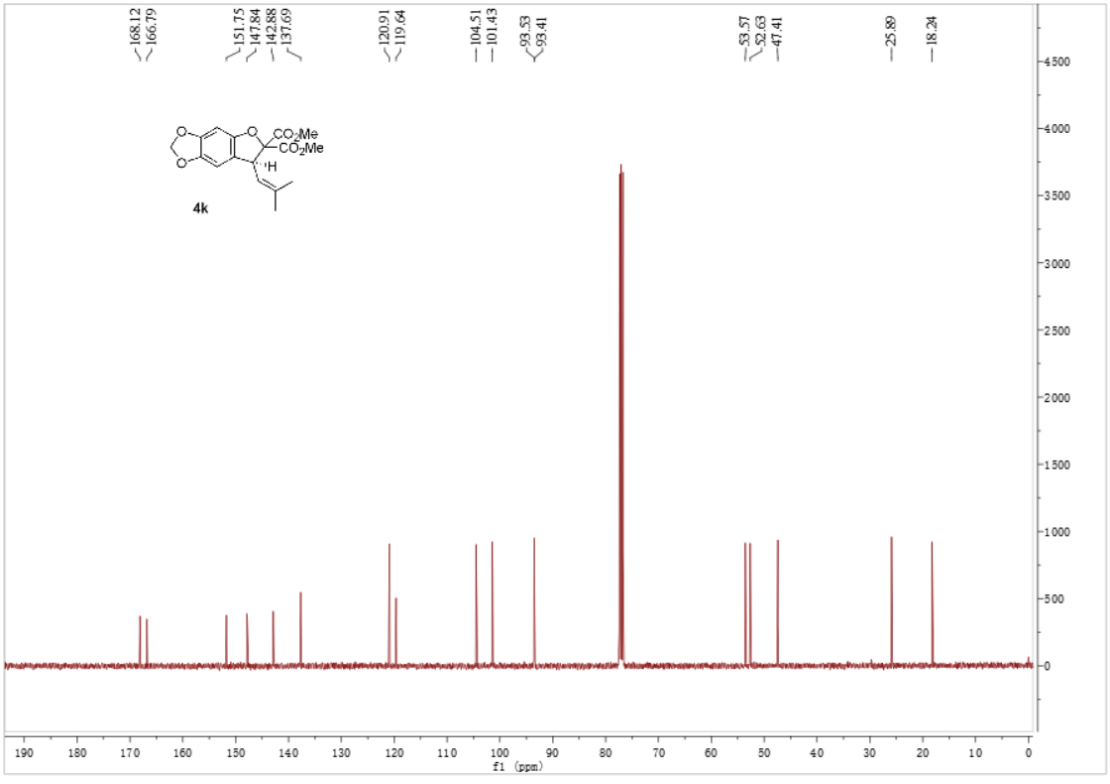
5.03
4.97
4.94
3.84
3.74
1.83
1.73
CO2Me
CO2Me
H
4k
2.00
2.12
1.04
1.01
3.08
3.06
3.16
3.14
f1 (ppm)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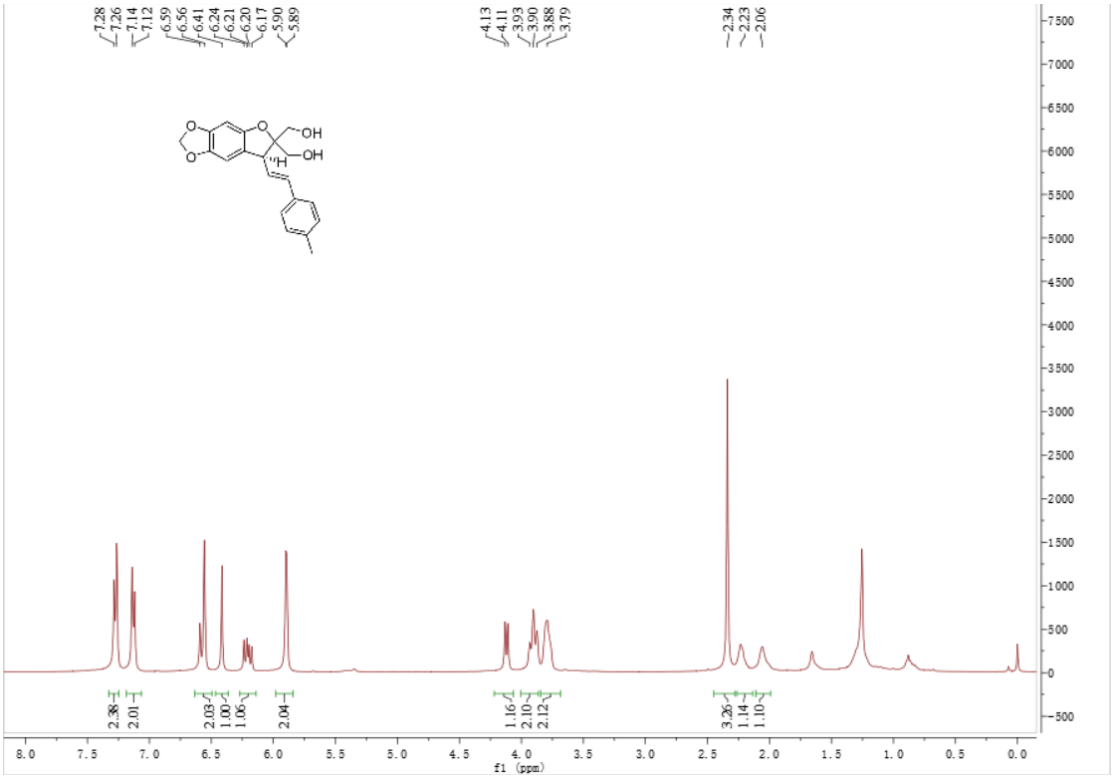
137.69
120.91
119.64
104.51
101.43
93.53
93.41
53.57
52.63
47.41
25.89
18.24
CO2Me
CO2Me
H
4k
f1 (ppm)

(5b)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7.12
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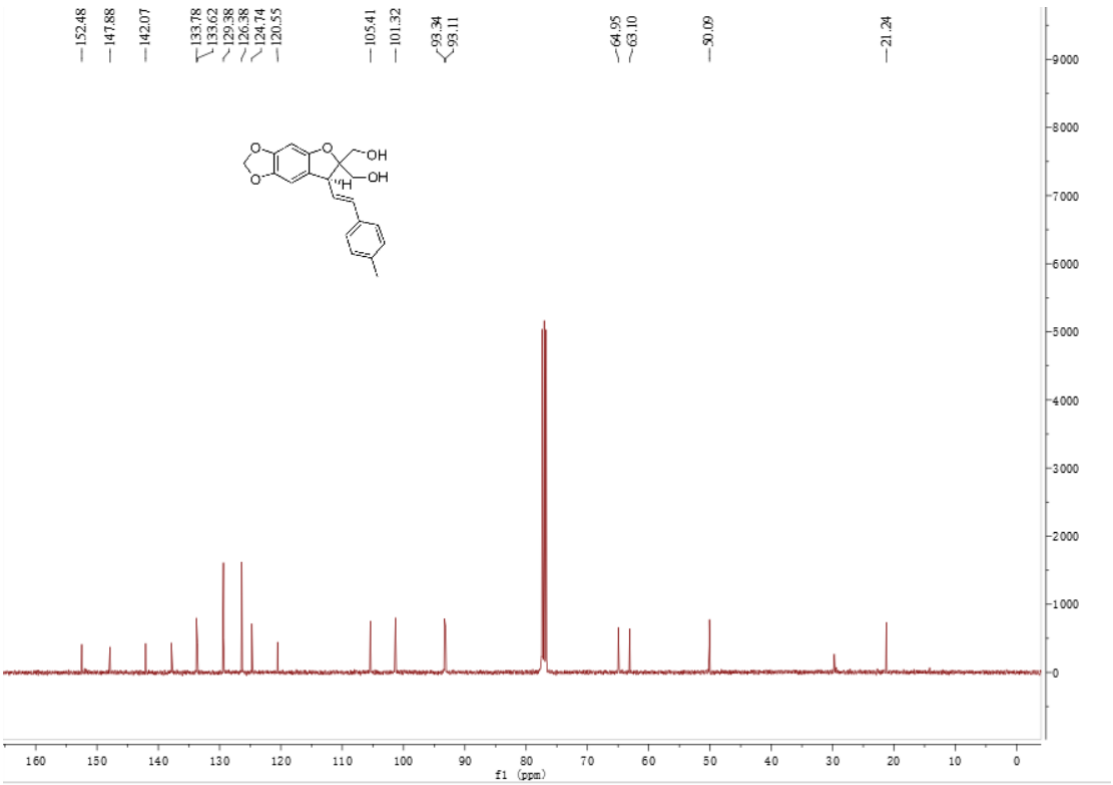
6.56
6.41
6.24
6.21
6.20
6.17
5.90
5.89
4.13
4.11
3.93
3.90
3.88
3.79
2.34
2.23
2.06
OH
OH
H
2.38
2.01
2.03
1.00
1.06
2.04
1.16
2.10
2.12
3.26
1.14
1.10
f1 (ppm)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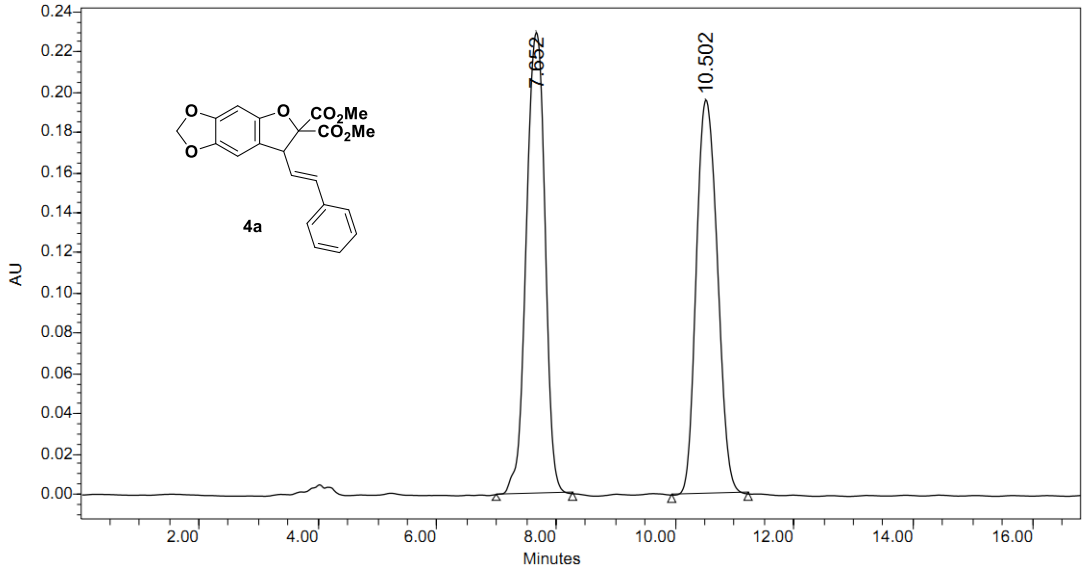
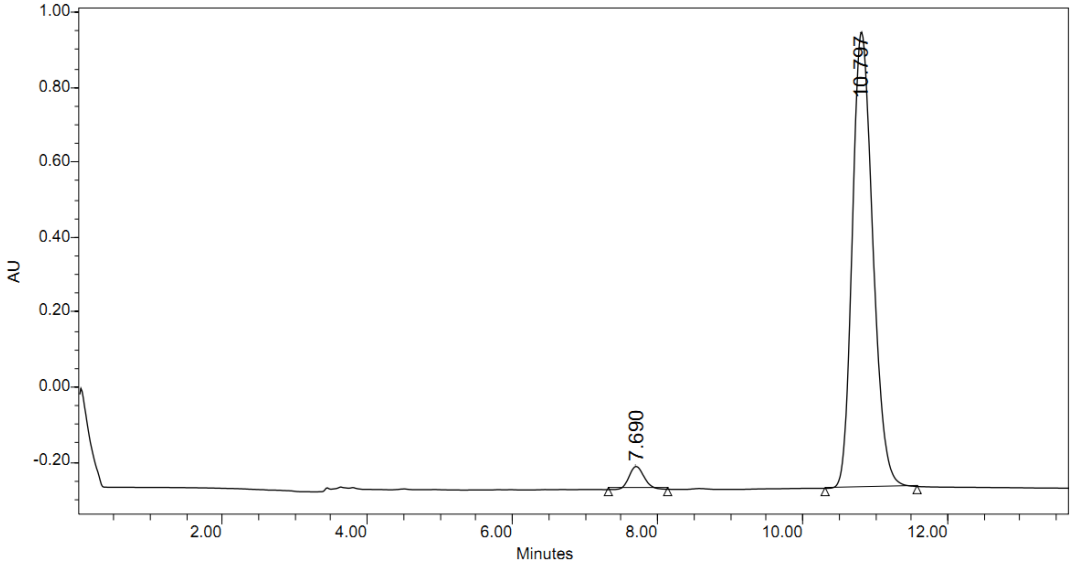
142.07
133.78
133.62
129.38
126.38
124.74
120.55
105.41
101.32
93.34
93.11
64.95
63.10
50.09
21.24
OH
OH
H
f1 (ppm)

HPLC

(4a)

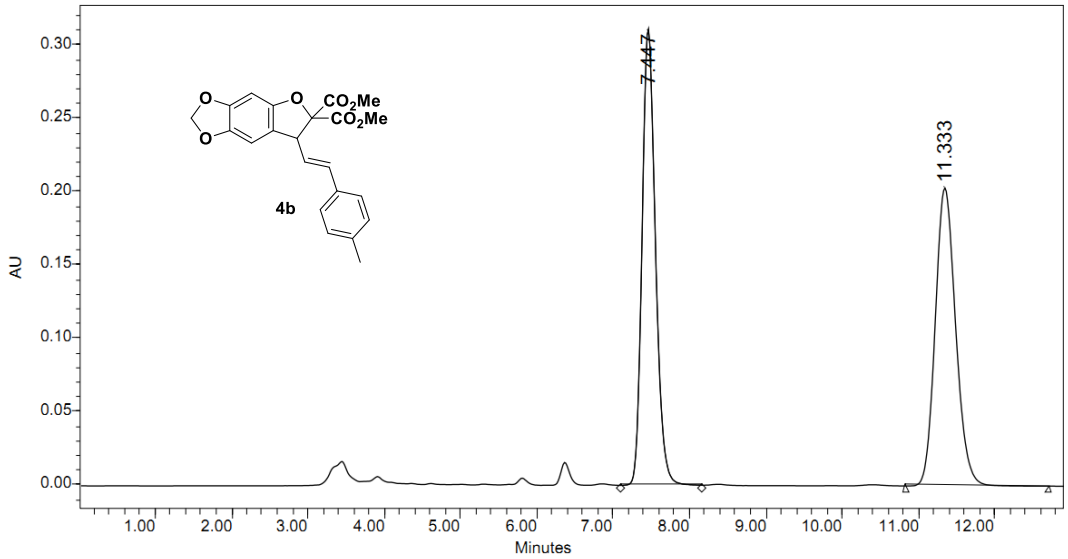


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.652	5054454	50.92	229816	53.90
2	10.502	4871300	49.08	196580	46.10

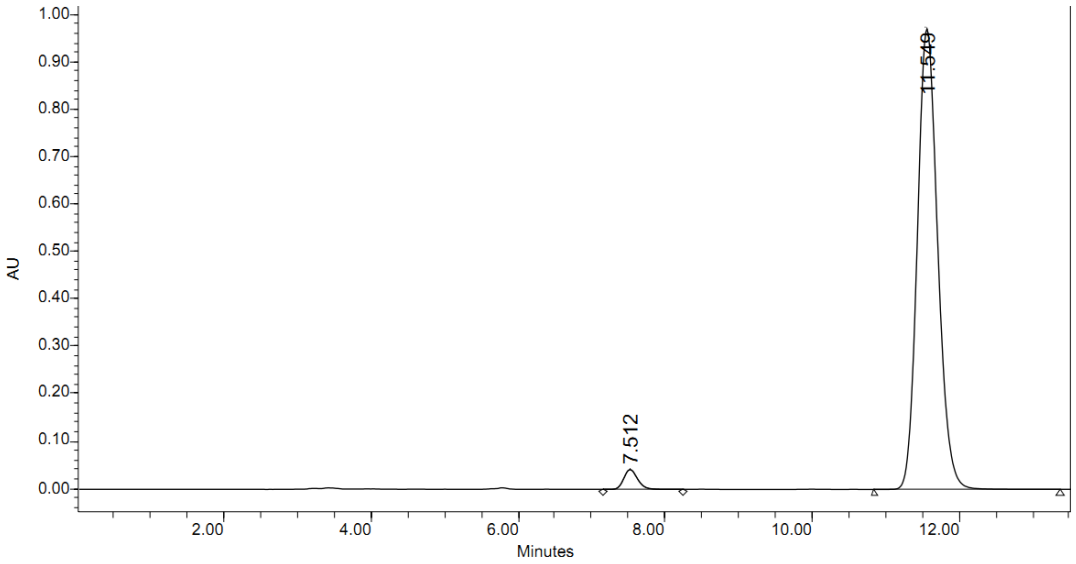


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.690	892111	3.59	61382	4.80
2	10.797	23977483	96.41	1216131	95.20

(4b)

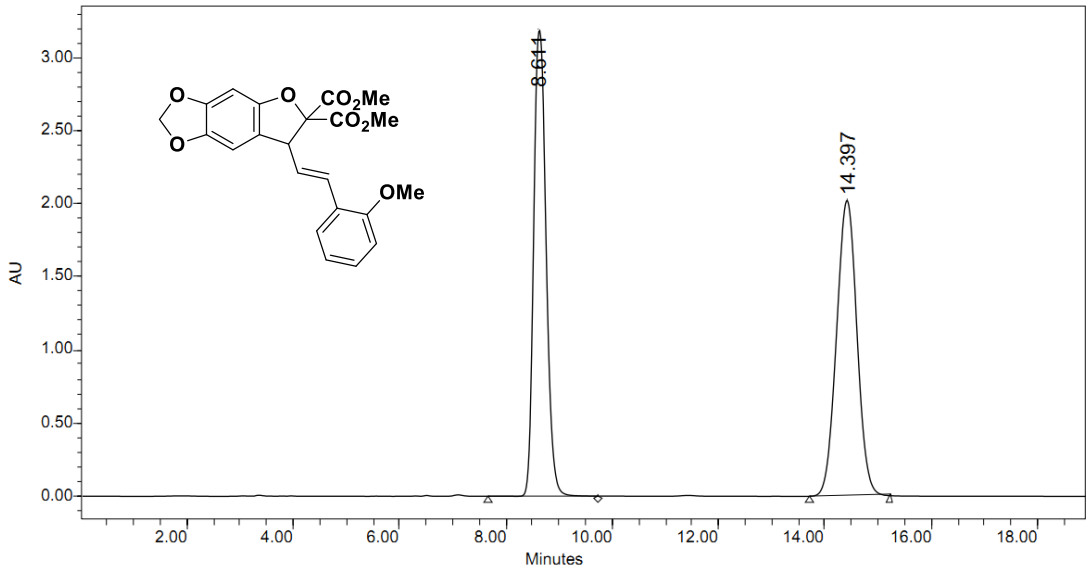


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.447	3803831	50.14	311236	60.51
2	11.333	3783185	49.86	203160	39.49

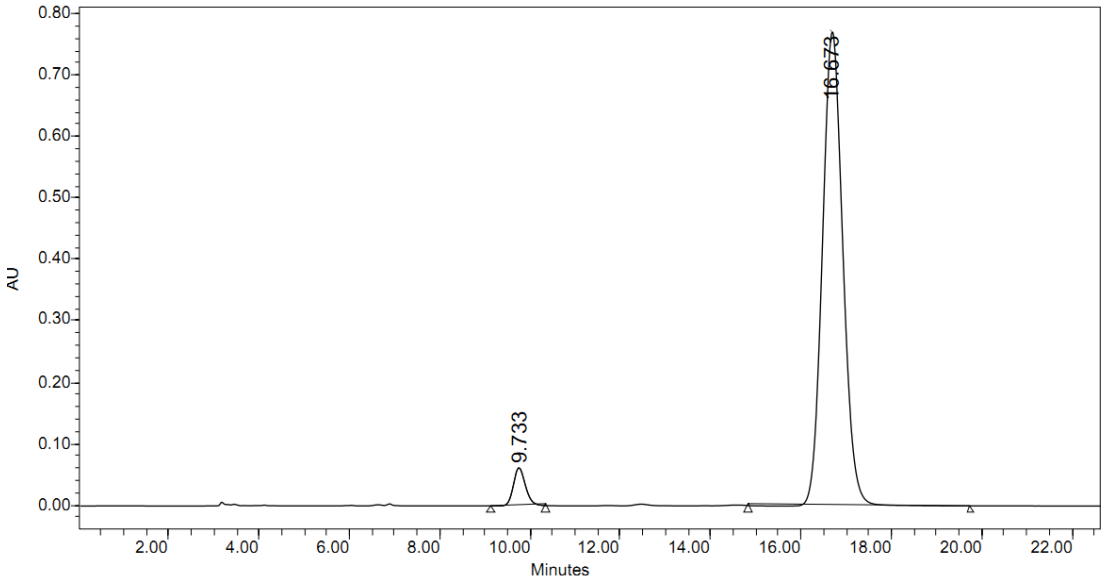


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.512	550419	2.86	41839	4.13
2	11.549	18683095	97.14	971584	95.87

(4c)

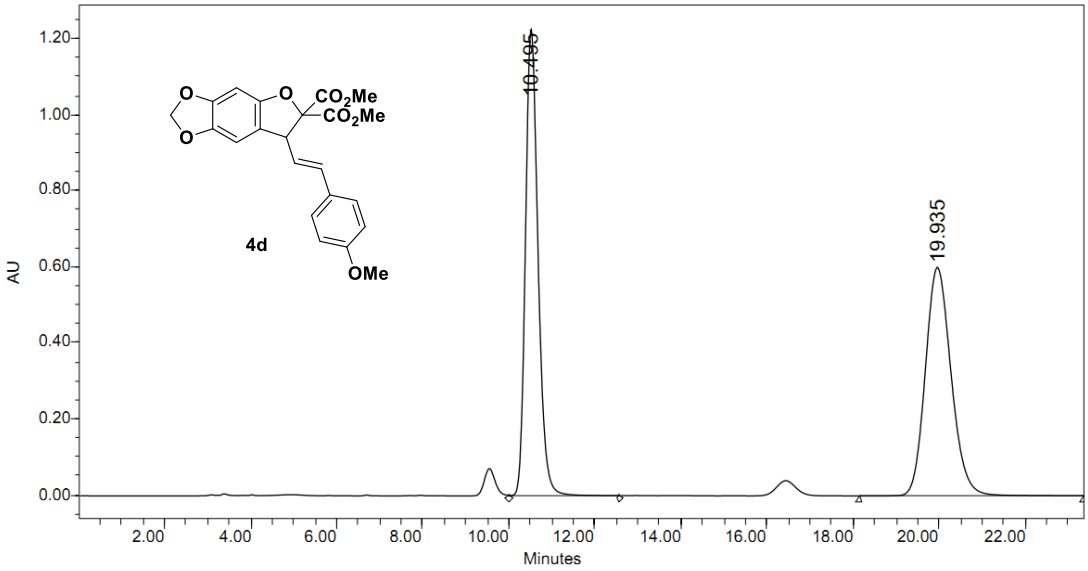


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.611	51927410	48.89	3203271	61.20
2	14.397	54294455	51.11	2030813	38.80

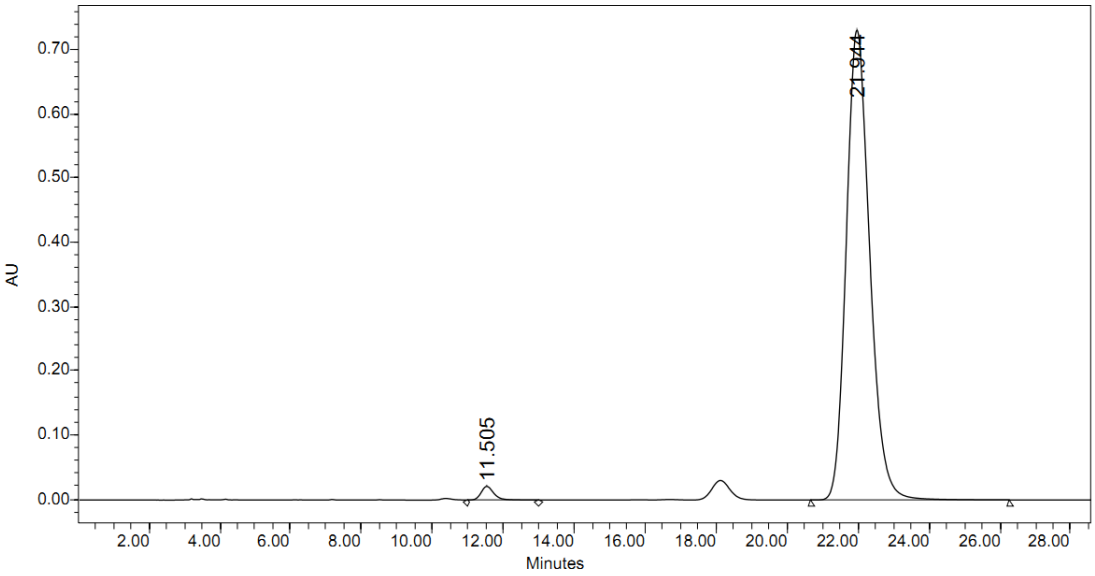


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.733	1146283	4.51	61539	7.38
2	16.673	24275031	95.49	771872	92.62

(4d)

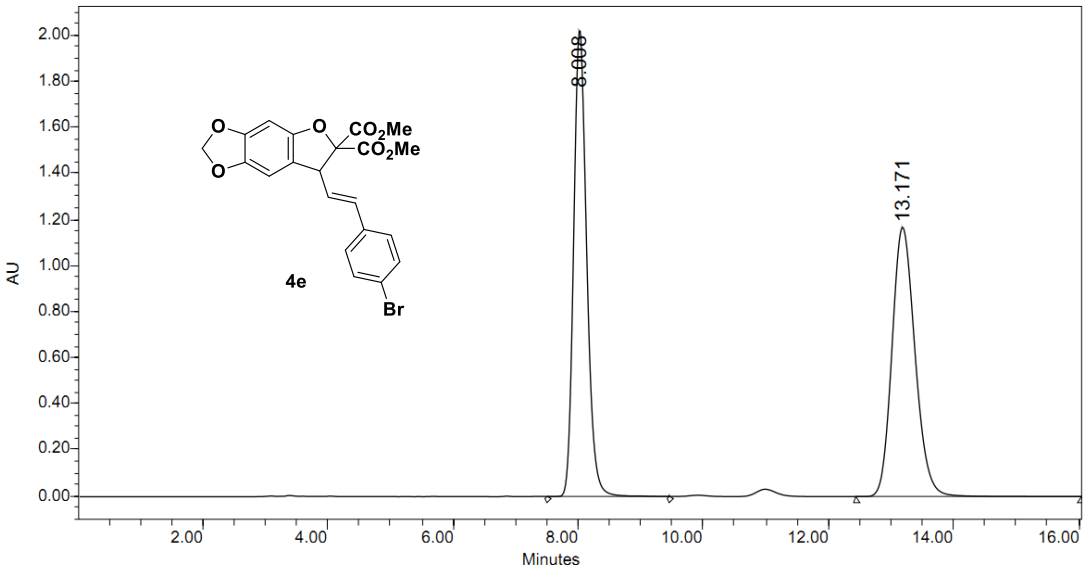


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.495	24964063	50.00	1227355	67.16
2	19.935	24968198	50.00	600250	32.84

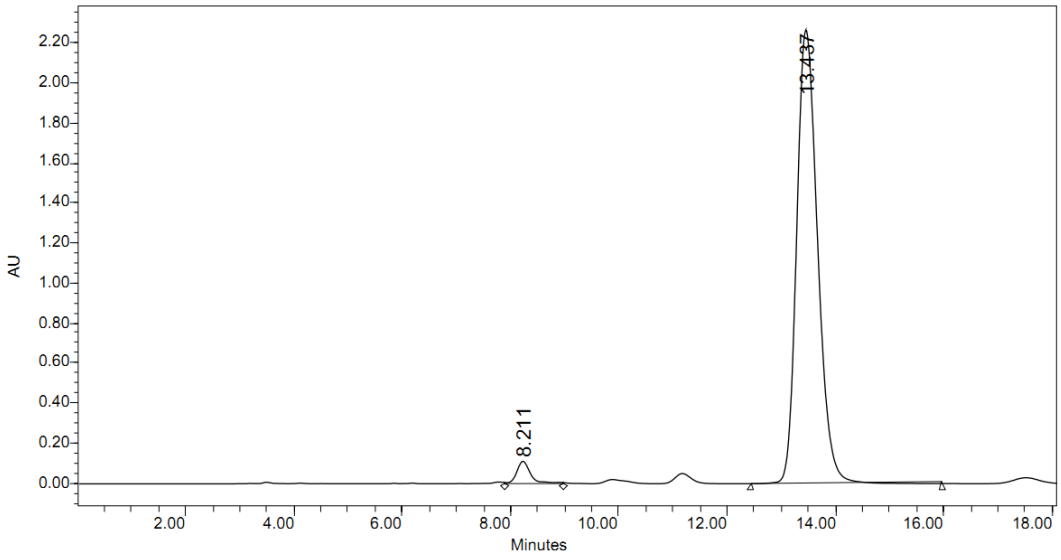


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	11.505	537599	1.57	21244	2.82
2	21.944	33680423	98.43	732648	97.18

(4e)

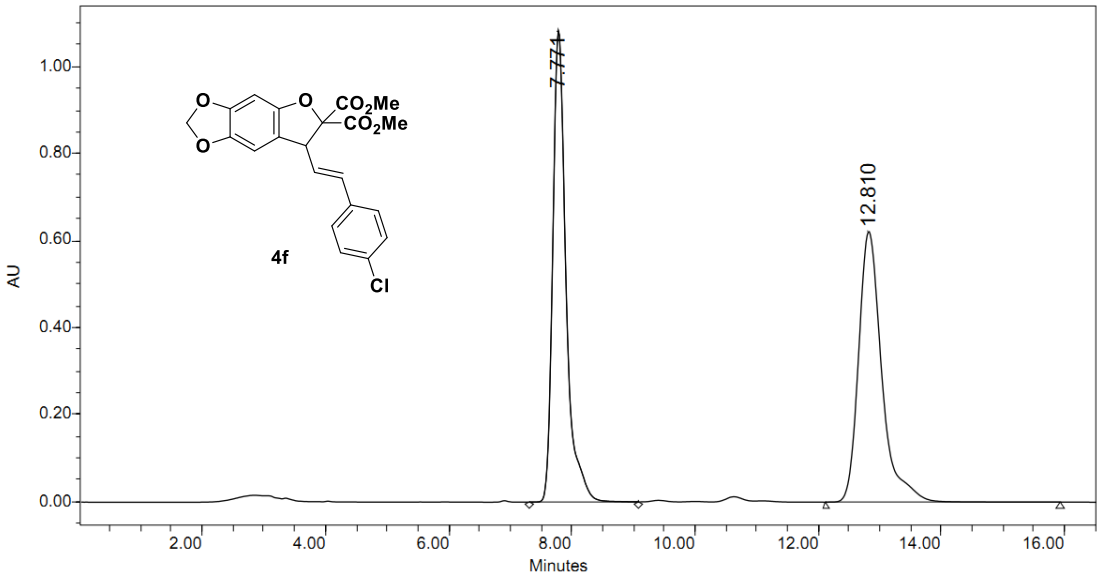


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.008	29728462	49.79	2030473	63.44
2	13.171	29982394	50.21	1170148	36.56

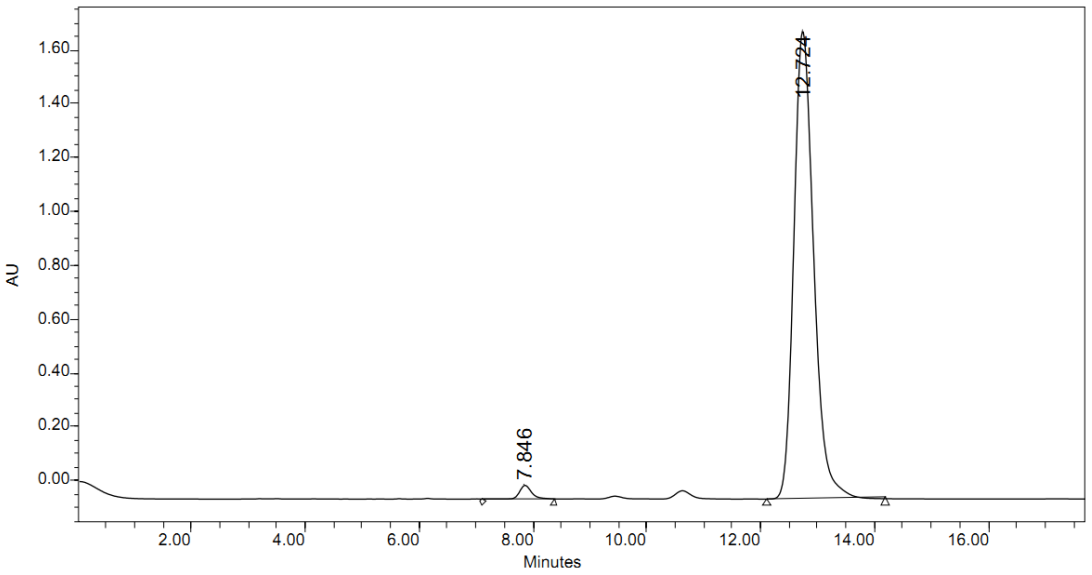


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.211	2041567	3.25	111912	4.70
2	13.437	60841299	96.75	2269637	95.30

(4f)

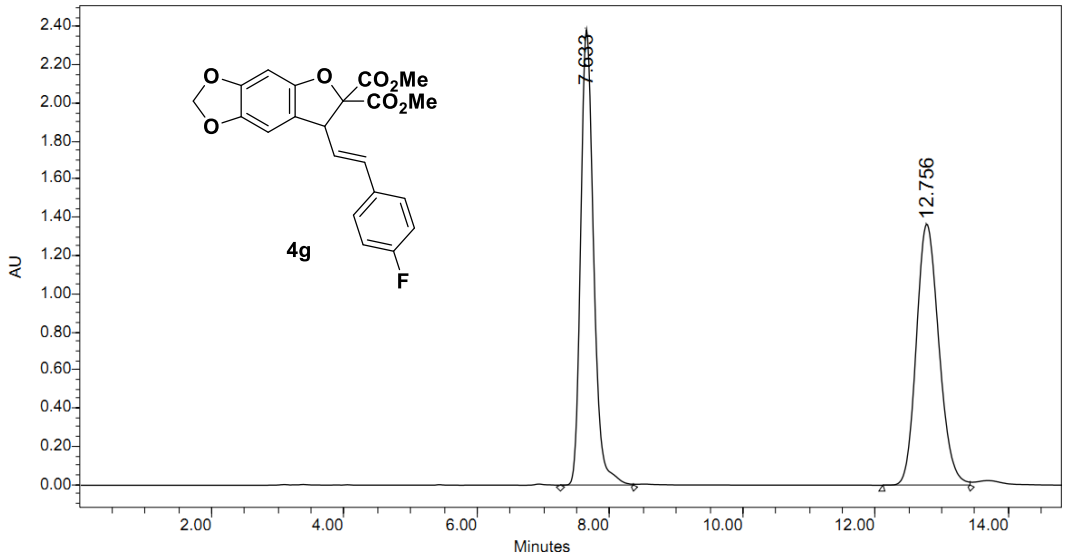


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.771	16342390	50.02	1085508	63.54
2	12.810	16326690	49.98	622773	36.46

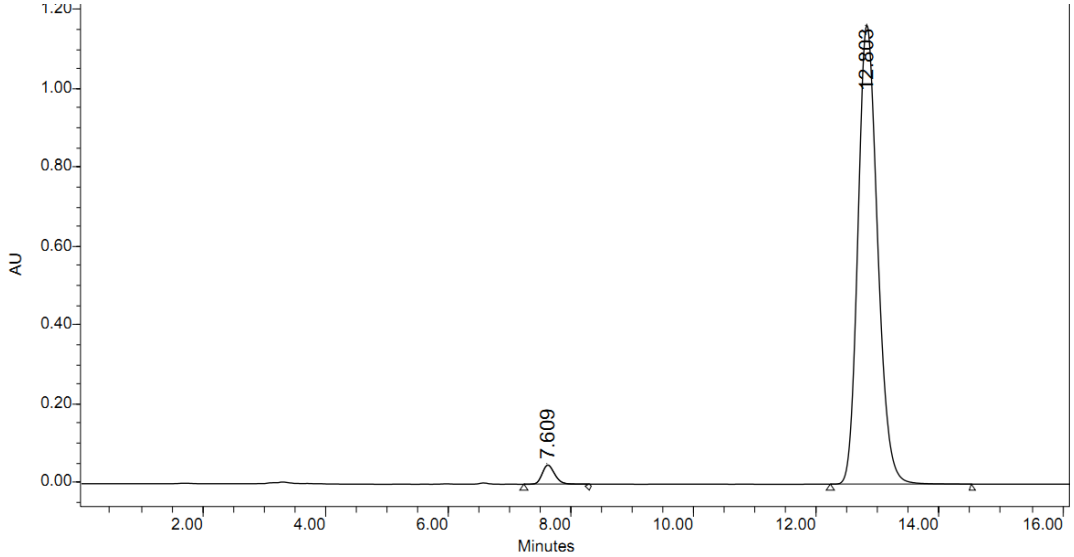


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.846	733209	1.71	50542	2.83
2	12.724	42213352	98.29	1737334	97.17

(4g)

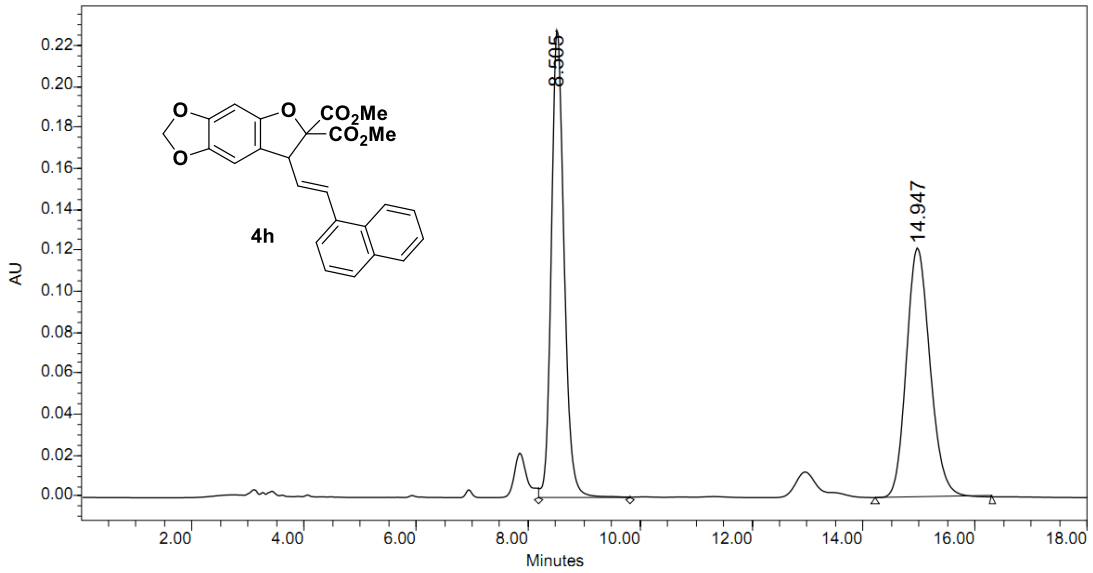


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.633	32475396	50.09	2389075	63.55
2	12.756	32354626	49.91	1370489	36.45

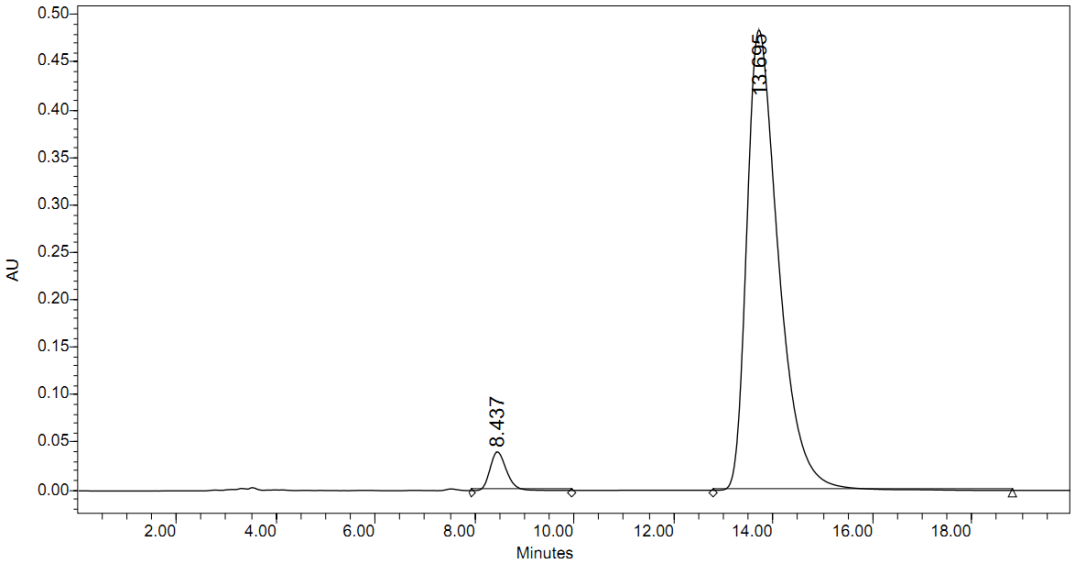


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.609	693722	2.60	48517	4.00
2	12.803	25944459	97.40	1164859	96.00

(4h)

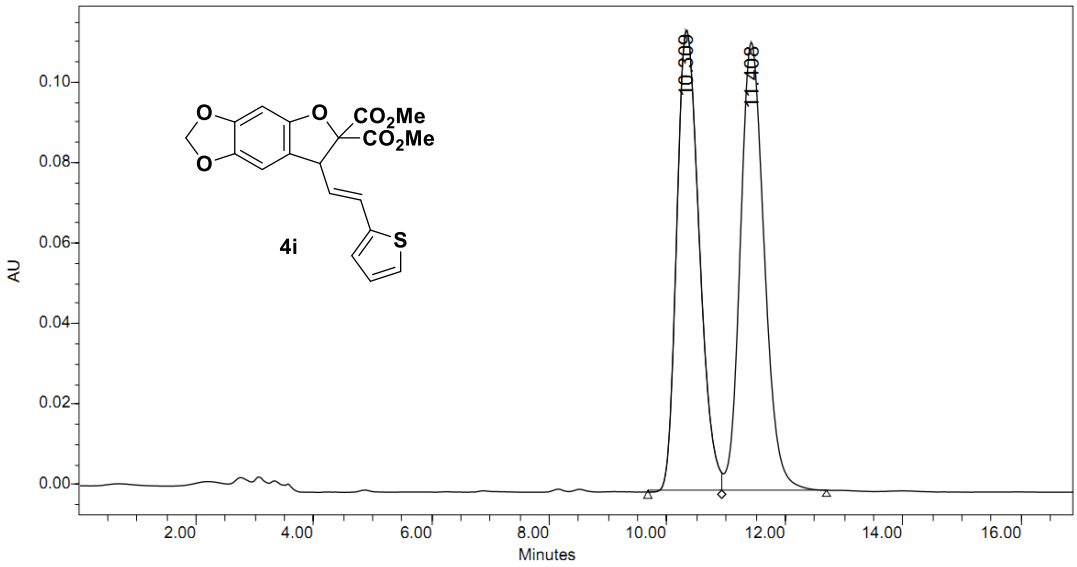


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.505	3629849	50.31	227902	65.25
2	14.947	3585606	49.69	121377	34.75

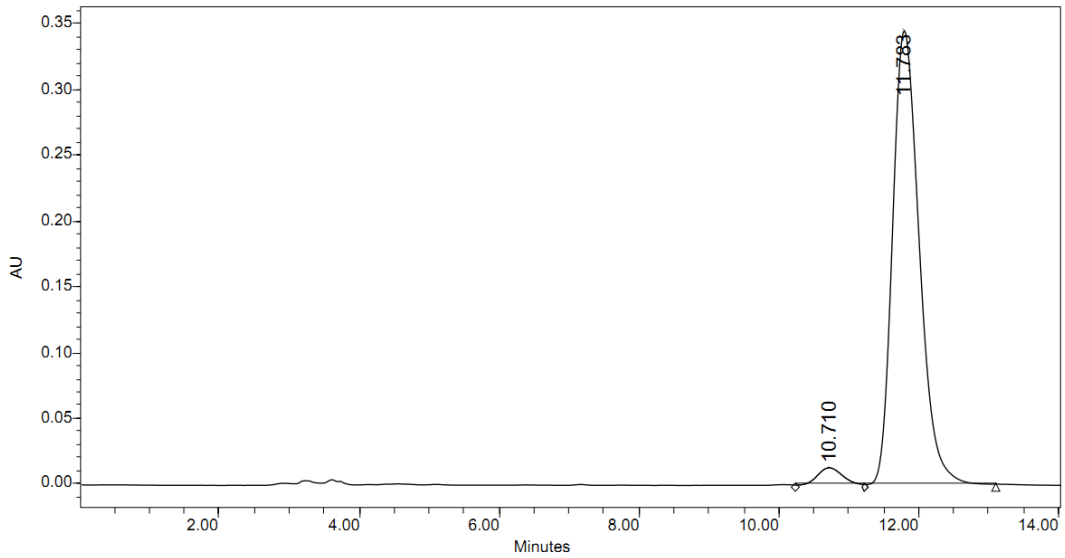


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	8.437	965072	4.27	40790	7.76
2	13.695	21625482	95.73	484724	92.24

(4i)

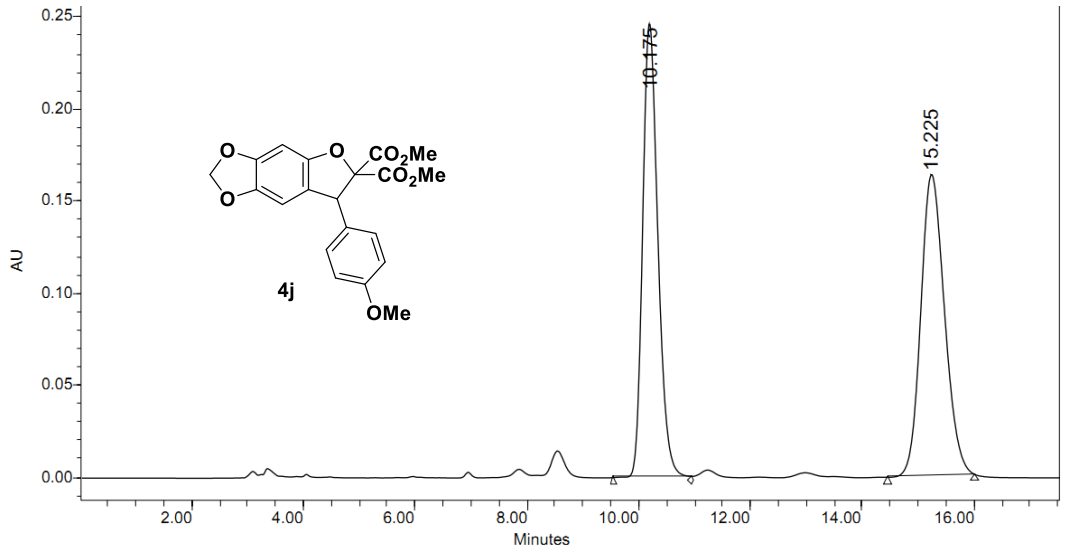


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.309	3058558	49.25	114696	50.71
2	11.408	3151142	50.75	111494	49.29

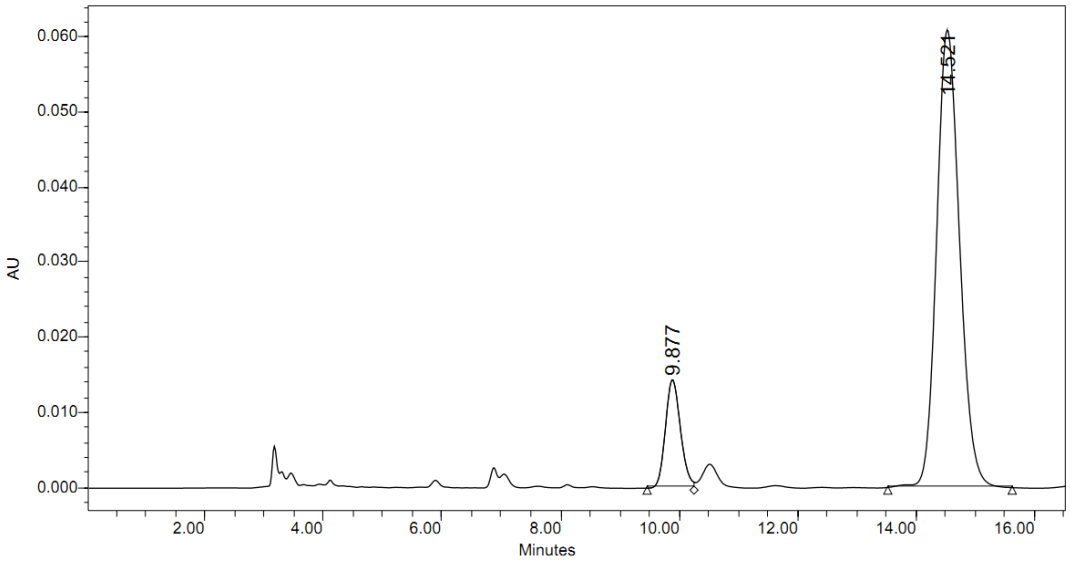


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.710	322931	3.41	13088	3.65
2	11.783	9144967	96.59	345351	96.35

(4j)

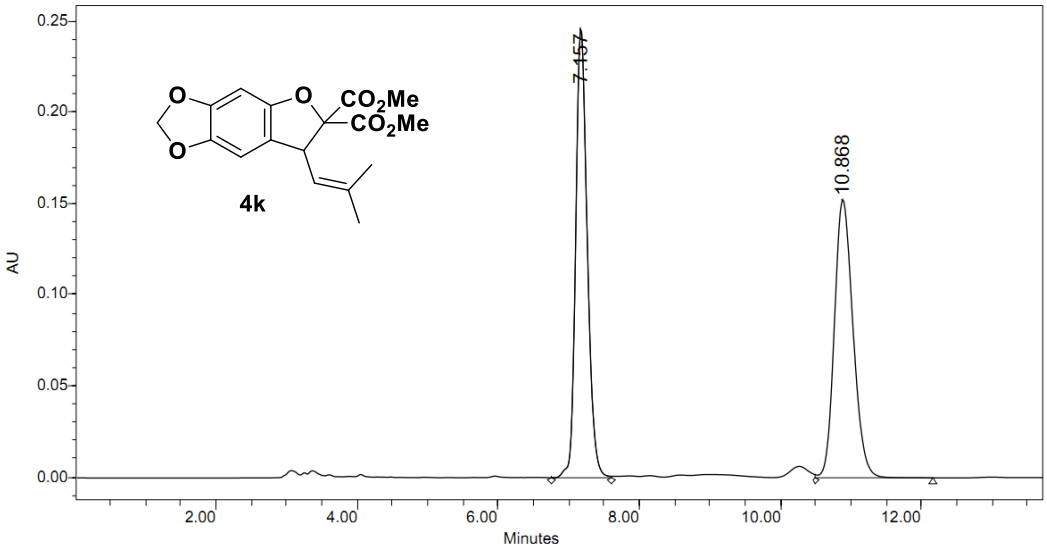


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	10.175	4698058	49.31	247026	60.12
2	15.225	4829420	50.69	163835	39.88

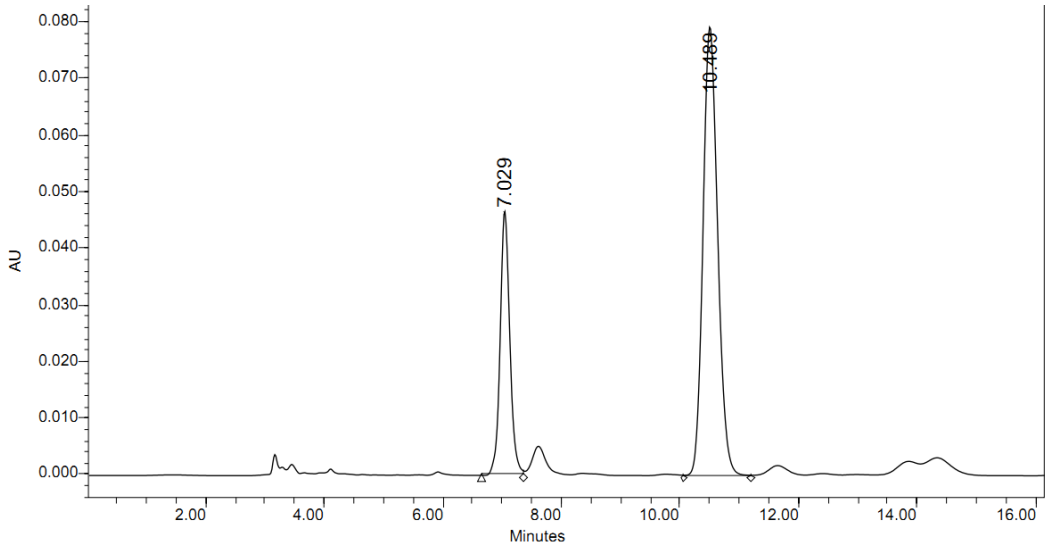


	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	9.877	257133	13.47	14425	19.12
2	14.521	1651438	86.53	61010	80.88

(4k)



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.157	2812431	50.14	246845	61.81
2	10.868	2796817	49.86	152540	38.19



	RT (min)	Area (V*sec)	% Area	Height (V)	% Height
1	7.029	531987	28.12	46614	37.03
2	10.489	1359900	71.88	79256	62.97