Supplementary Information

Efficient asymmetric syntheses of α-quaternary lactones and esters through chiral bifunctional sulfide-catalyzed desymmetrizing bromolactonization of α,α-diallyl carboxylic acids

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Table of Contents

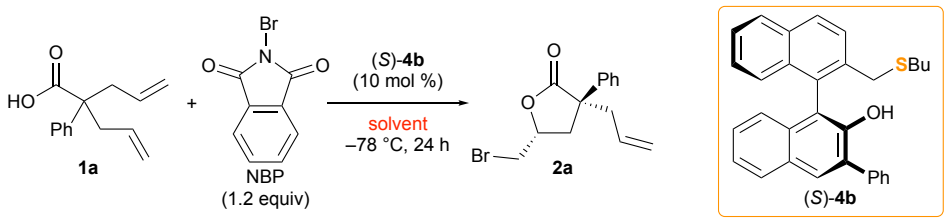
General Information

^{1}H and ^{13}C NMR spectra were measured on JEOL JNM-AL 400 and JEOL JNM-ECZ 400R NMR instruments (400 MHz for ^{1}H NMR, 100 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^{1}H NMR, and $CDCl_3$ served as the internal standard (77.0 ppm) for ^{13}C NMR. The following abbreviations were used to express the multiplicities: s = singlet; d = doublet; t = triplet; m = multiplet; br = broad. High-resolution mass spectra (HRMS) were measured on a JEOL JMS-700N. Infrared spectra (IR) were measured on a JASCO FT/IR-4200 spectrometer. Optical rotations were measured on a JASCO P-2100 polarimeter. High performance liquid chromatography (HPLC) was performed on Shimadzu LC-20AT and SPD-20A instruments using Daicel Chiralpak IA-3, IB-3, IC-3, ID-3, IF-3, IG-3, or Chiralcel OD-3 columns (4.6 mm × 250 mm). All reactions were monitored by thin-layer chromatography using Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), with visualization by the use of UV lamp (254 nm) or dyes. The products were purified by flash column chromatography on silica gel. Dehydrated solvents were purchased from Kanto Chemical.

Acknowledgements

This work was supported by JSPS KAKENHI Grant Numbers JP19K05480 (for S. S.) and JP21J20978 (for R. N.), by the Cooperative Research Program of "Network Joint Research Center for Materials and Devices" (20211315 for S. S.), and by the Takahashi Industrial and Economic Research Foundation (for S. S.). R. N. thanks JSPS for a research fellowship. A. A. N. thanks the Embassy of the Arab Republic of Egypt for a research fellowship.

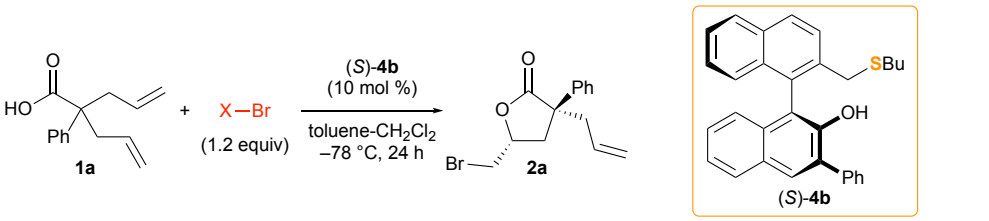
Table S1 Optimization of reaction solvents[a]

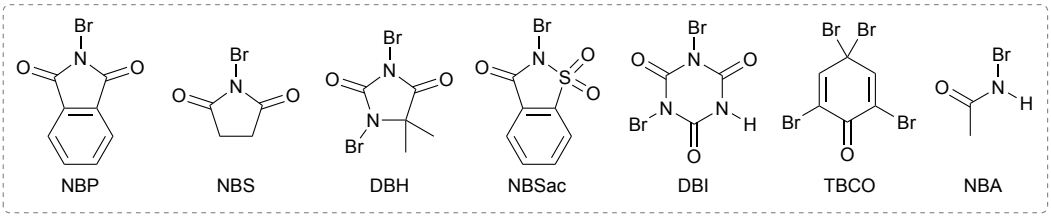


Entry	Solvent	Yield[b] (%)	dr[c]	er[d]
1	CH_2Cl_2 (2.0 mL)	99	>20: 1	88:12
2	toluene (2.0 mL)	60	14: 1	82:18
3	toluene (1.0 mL)-CH_2Cl_2 (1.0 mL)	98	>20: 1	93: 7
4	hexane (1.0 mL)-CH_2Cl_2 (1.0 mL)	99	>20: 1	91: 9
5	toluene (1.5 mL)-CH_2Cl_2 (0.5 mL)	99	>20: 1	94: 6

[a] Reaction conditions: **1a** (0.10 mmol), NBP (0.12 mmol), (*S*)-**4b** (10 mol %, 0.010 mmol), solvent (2.0 mL), –78 °C, 24 h. [b] Yield of isolated product **2a**. [c] The diastereomeric ratio (dr) was determined via ^{1}H NMR analysis. [d] The enantiomeric ratio (er) was determined via HPLC analysis on a chiral stationary phase.

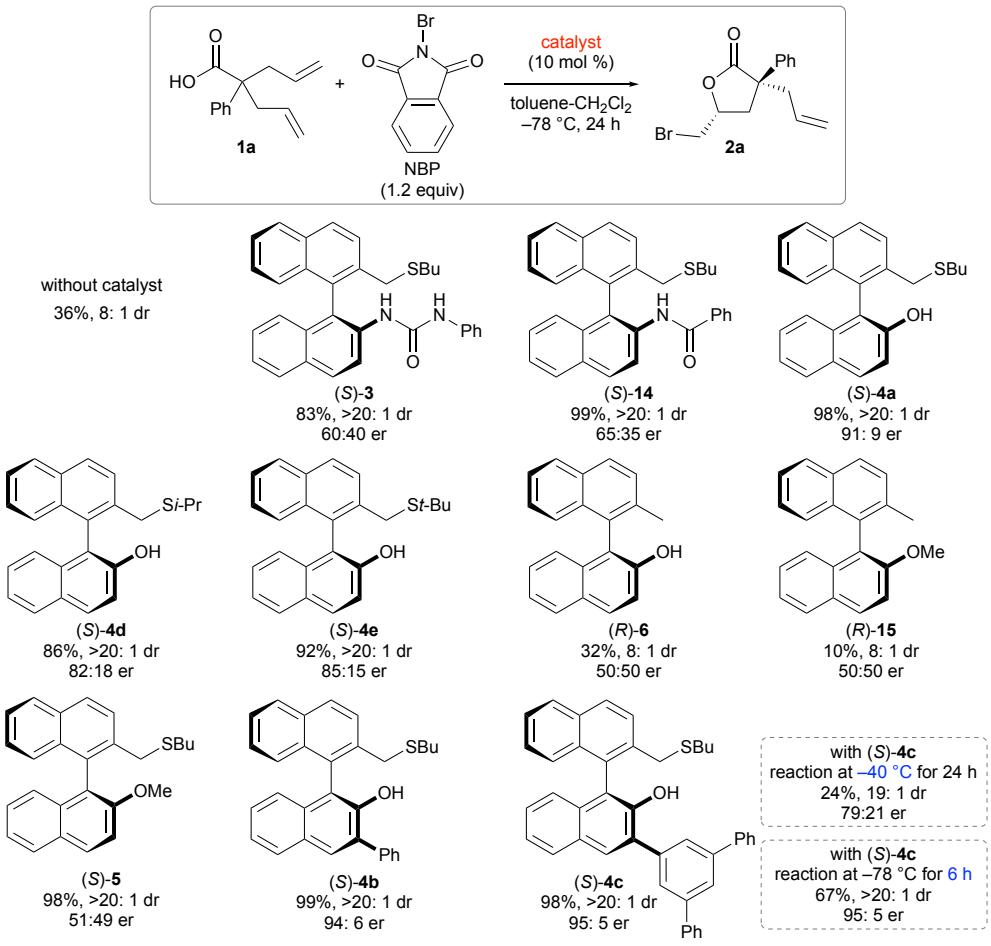
Table S2 Effect of brominating reagents[a]



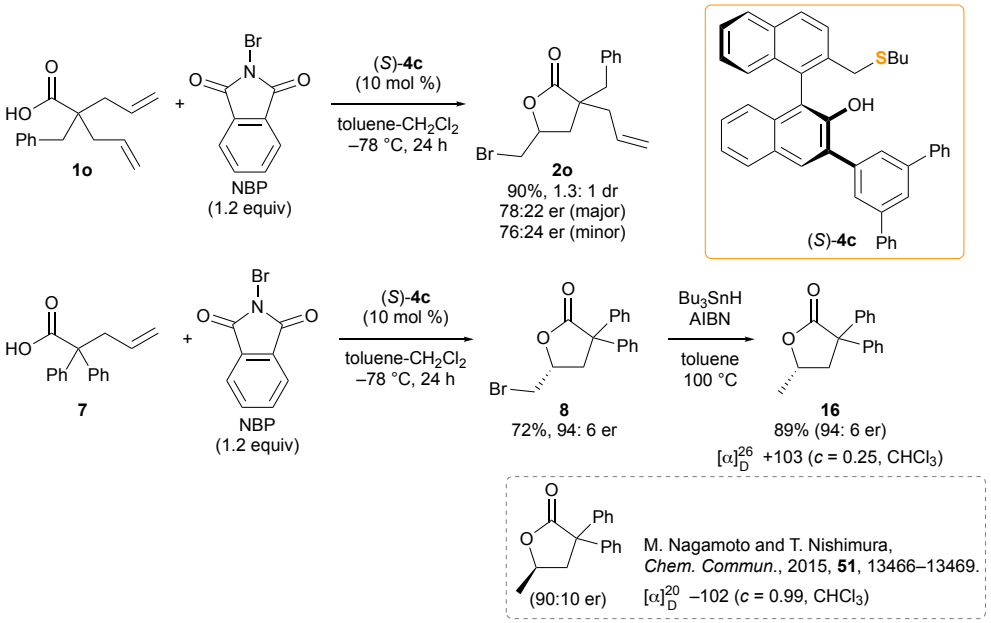


Entry	Brominating reagent	Yield[b] (%)	dr[c]	er[d]
1	NBP	99	>20: 1	94: 6
2	NBS	96	>20: 1	91: 9
3	DBH	98	>20: 1	94: 6
4	NBSac	94	>20: 1	93: 7
5	DBI	64	9: 1	70:30
6	TBCO	89	>20: 1	92: 8
7	NBA	93	>20: 1	92: 8
8	Br_2	89	12: 1	53:47

[a] Reaction conditions: **1a** (0.10 mmol), brominating reagent (0.12 mmol), (*S*)-**4b** (10 mol %, 0.010 mmol), toluene (1.5 mL)-CH_2Cl_2 (0.5 mL), –78 °C, 24 h. [b] Yield of isolated product **2a**. [c] The diastereomeric ratio (dr) was determined via ^{1}H NMR analysis. [d] The enantiomeric ratio (er) was determined via HPLC analysis on a chiral stationary phase.

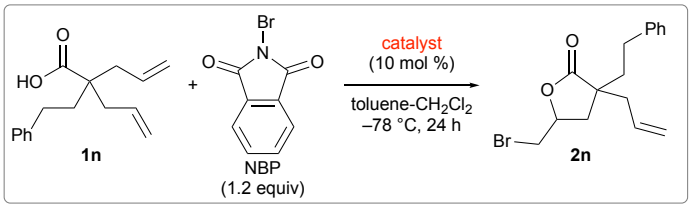


Scheme S1 Effect of chiral catalysts.

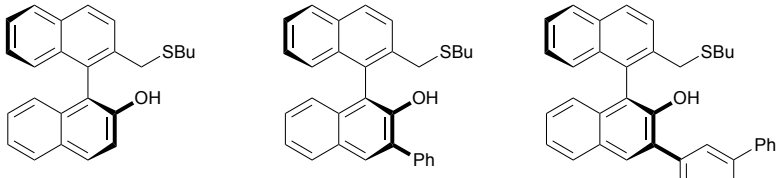


Scheme S2 Additional substrate scope.

When a reaction of **1n** was performed in the absence of a catalyst, product **2n** was obtained in a low yield with poor diastereoselectivity (1.1: 1 dr). Unfortunately, the reactions using chiral bifunctional sulfide catalysts did not improve the low diastereoselectivity of **2n**, although moderate levels of enantioselectivity were observed.



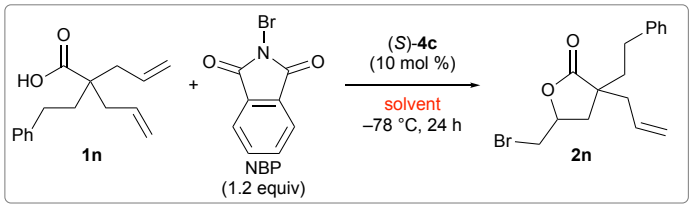
without catalyst
20%, 1.1: 1 dr



(*S*)-**4a**
76%, 1.2: 1 dr
81:19 er (major)
81:19 er (minor)

(*S*)-**4b**
77%, 1.2: 1 dr
84:16 er (major)
84:16 er (minor)

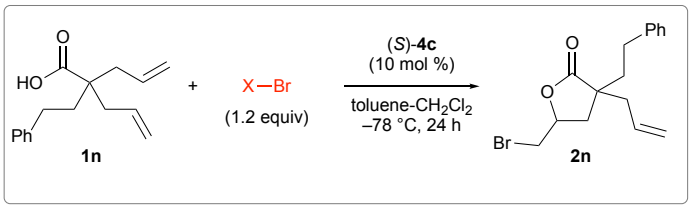
(*S*)-**4c**
76%, 1.3: 1 dr
85:15 er (major)
86:14 er (minor)

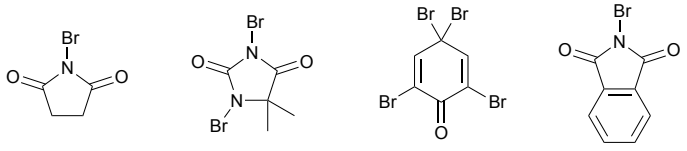


in CH_2Cl_2 (2 mL)
89%, 1.2: 1 dr
80:20 er (major)
79:21 er (minor)

in toluene (2 mL)
31%, 1.3: 1 dr
76:24 er (major)
76:24 er (minor)

in toluene (1.5 mL)-CH_2Cl_2 (0.5 mL)
76%, 1.3: 1 dr
85:15 er (major)
86:14 er (minor)





NBS
62%, 1.2: 1 dr
81:19 er (major)
81:19 er (minor)

DBH
98%, 1.2: 1 dr
61:39 er (major)
62:38 er (minor)

TBCO
61%, 1.2: 1 dr
81:19 er (major)
81:19 er (minor)

NBP
76%, 1.3: 1 dr
85:15 er (major)
86:14 er (minor)

Scheme S3 Optimization of reaction conditions for substrate **1n**.

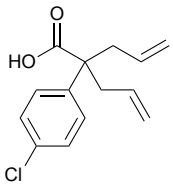
Experimental Section

1. Synthesis of catalysts

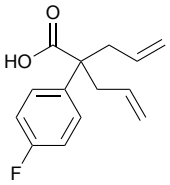
Chiral sulfide catalysts (*S*)-**3**, (*S*)-**4a**–**4e**, (*S*)-**5**, and (*S*)-**14** were prepared according to the literature.[1]

2. Synthesis of substrates

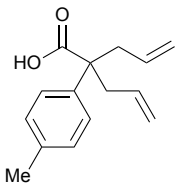
Substrates **1** were prepared according to the literature method.[2] Substrate **7** was also prepared according to the literature method.[3]



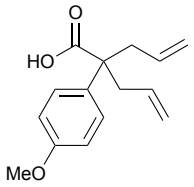
1b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.8 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 5.59–5.48 (m, 2H), 5.11–5.07 (m, 4H), 2.80 (dd, *J* = 7.6, 14.0 Hz, 2H), 2.73 (dd, *J* = 6.8, 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 139.4, 133.1, 132.6, 128.6, 128.0, 119.2, 53.1, 38.5; IR (neat): 3078, 3007, 2980, 2921, 1700, 1494, 1282, 1234, 1096, 1013, 995, 918, 826, 754, 725 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{15}ClO_2$: 250.0761 ([M]$^+$), found 250.0761.



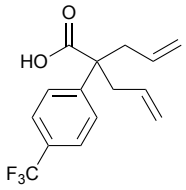
1c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 5.4, 9.0 Hz, 2H), 7.04 (dd, *J* = 8.8, 8.8 Hz, 2H), 5.59–5.49 (m, 2H), 5.11–5.07 (m, 4H), 2.81 (dd, *J* = 7.8, 13.8 Hz, 2H), 2.73 (dd, *J* = 6.8, 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.2, 161.7 (d, *J* = 245 Hz), 136.6 (d, *J* = 3.3 Hz), 132.7, 128.3 (d, *J* = 8.3 Hz), 119.1, 115.3 (d, *J* = 21.4 Hz), 52.9, 38.7; IR (neat): 3079, 2981, 2922, 1699, 1509, 1282, 1234, 1165, 995, 917, 832, 815, 734, 679, 650 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{15}FO_2$: 234.1056 ([M]$^+$), found 234.1056.



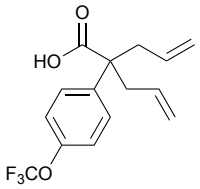
1d: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 8.8 Hz, 2H), 5.61–5.50 (m, 2H), 5.11–5.05 (m, 4H), 2.81 (dd, *J* = 7.6, 13.6 Hz, 2H), 2.75 (dd, *J* = 6.8, 14.0 Hz, 2H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.1, 137.9, 136.8, 133.2, 129.2, 126.4, 118.8, 52.9, 38.5, 21.0; IR (neat): 3077, 3007, 2980, 2947, 2923, 1698, 1515, 1282, 1234, 1132, 995, 915, 819, 730 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{18}O_2$: 230.1307 ([M]$^+$), found 230.1307.



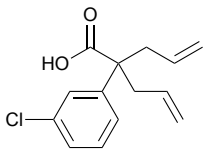
1e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 5.60–5.50 (m, 2H), 5.11–5.05 (m, 4H), 3.80 (s, 3H), 2.81 (dd, *J* = 7.6, 14.0 Hz, 2H), 2.73 (dd, *J* = 6.8, 14.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9, 158.5, 133.2, 132.9, 127.6, 118.8, 113.8, 55.2, 52.5, 38.5; IR (neat): 3077, 3004, 2979, 2954, 2936, 1699, 1514, 1292, 1252, 1185, 1035, 918, 830 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{18}O_3$: 246.1256 ([M]$^+$), found 246.1256.



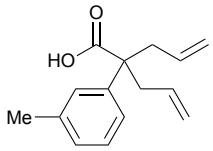
1f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 5.58–5.48 (m, 2H), 5.12–5.08 (m, 4H), 2.84 (dd, *J* = 8.0, 14.0 Hz, 2H), 2.77 (dd, *J* = 6.8, 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 144.9, 132.3, 129.5 (q, *J* = 32.1 Hz), 127.1, 125.4 (q, *J* = 3.3 Hz), 124.0 (q, *J* = 271 Hz), 119.5, 53.7, 38.7; IR (neat): 3081, 2983, 1703, 1326, 1167, 1122, 1071, 1017, 920, 838 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{15}F_3O_2$: 284.1024 ([M]$^+$), found 284.1024.



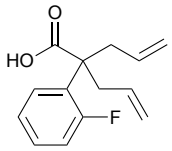
1g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 2H), 5.59–5.48 (m, 2H), 5.12–5.07 (m, 4H), 2.82 (dd, *J* = 8.0, 14.0 Hz, 2H), 2.74 (dd, *J* = 6.8, 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 148.2 (q, *J* = 1.7 Hz), 139.5, 132.5, 128.1, 120.7, 120.4 (q, *J* = 256 Hz), 119.3, 53.1, 38.7; IR (neat): 3080, 2983, 2925, 1703, 1510, 1254, 1212, 1162, 1116, 1019, 995, 920, 849, 686 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{15}F_3O_3$: 300.0973 ([M]$^+$), found 300.0974.



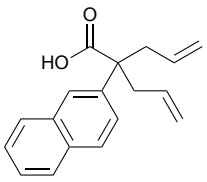
1h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.25 (m, 3H), 7.20 (td, *J* = 2.0, 7.2 Hz, 1H), 5.59–5.49 (m, 2H), 5.13–5.08 (m, 4H), 2.81 (dd, *J* = 7.6, 14.0 Hz, 2H), 2.74 (dd, *J* = 6.8, 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.7, 143.0, 134.5, 132.5, 129.7, 127.4, 126.9, 124.9, 119.4, 53.4, 38.5; IR (neat): 3078, 2980, 1699, 1594, 1573, 1282, 1234, 996, 918, 848, 771, 712, 687, 649 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{16}ClO_2$: 251.0839 ([M+H]$^+$), found 251.0839.



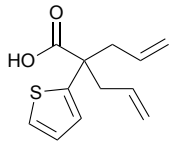
1i: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 1H), 7.12–7.08 (m, 3H), 5.60–5.50 (m, 2H), 5.12–5.06 (m, 4H), 2.82 (dd, *J* = 7.6, 13.6 Hz, 2H), 2.75 (dd, *J* = 6.8, 14.0 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.3, 140.8, 138.0, 133.2, 128.3, 127.9, 127.2, 123.5, 118.8, 53.2, 38.5, 21.6; IR (neat): 3077, 3007, 2979, 2947, 2923, 1698, 1640, 1606, 1442, 1284, 1234, 995, 915, 776, 721, 705, 650 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{19}O_2$: 231.1385 ($[M+H]^+$), found 231.1377.



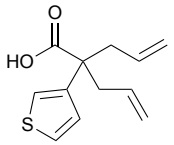
1j: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.23 (m, 2H), 7.14 (dd, *J* = 6.8, 7.6 Hz, 1H), 7.05 (dd, *J* = 8.4, 10.8 Hz, 1H), 5.61–5.51 (m, 2H), 5.10–5.06 (m, 4H), 2.81 (dd, *J* = 6.8, 14.0 Hz, 2H), 2.73 (dd, *J* = 8.0, 14.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.5, 160.5 (d, *J* = 245 Hz), 132.6, 129.0 (d, *J* = 13.2 Hz), 128.9 (d, *J* = 9.1 Hz), 127.8 (d, *J* = 4.1 Hz), 123.8 (d, *J* = 3.3 Hz), 119.1, 115.7 (d, *J* = 22.2 Hz), 50.9, 38.1; IR (neat): 3082, 3009, 2982, 2926, 2876, 1698, 1488, 1446, 1300, 1286, 1241, 1217, 996, 920, 811, 755, 745, 686 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{15}FO_2$: 234.1056 ($[M]^+$), found 234.1056.



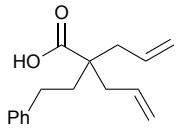
1k: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.75 (m, 4H), 7.51–7.42 (m, 3H), 5.63–5.52 (m, 2H), 5.14–5.06 (m, 4H), 2.94 (dd, *J* = 7.6, 14.0 Hz, 2H), 2.89 (dd, *J* = 6.8, 13.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.6, 138.3, 133.1, 133.0, 132.4, 128.21, 128.15, 127.5, 126.2, 126.1, 125.4, 124.8, 119.0, 53.5, 38.5; IR (neat): 3075, 3061, 3007, 2979, 2923, 1698, 1639, 1282, 1233, 1136, 995, 917, 855, 817, 747 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{18}O_2$: 266.1307 ($[M]^+$), found 266.1306.



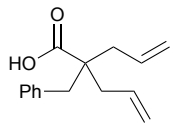
1l:[4] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, *J* = 0.8, 4.8 Hz, 1H), 7.01–6.97 (m, 2H), 5.69–5.59 (m, 2H), 5.15–5.09 (m, 4H), 2.89 (dd, *J* = 7.2, 13.6 Hz, 2H), 2.80 (dd, *J* = 7.2, 14.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.0, 145.0, 132.6, 126.6, 125.1, 124.6, 119.2, 51.7, 40.2; IR (neat): 3074, 3010, 2979, 2964, 2911, 1697, 1641, 1447, 1405, 1294, 1280, 1243, 1230, 996, 926, 889, 852, 703 cm^{-1}.



1m:[5] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 2.8, 4.8 Hz, 1H), 7.16 (dd, *J* = 1.2, 2.8 Hz, 1H), 7.06 (dd, *J* = 1.2, 4.8 Hz, 1H), 5.64‑5.54 (m, 2H), 5.13–5.07 (m, 4H), 2.82 (dd, *J* = 7.6, 14.0 Hz, 2H), 2.75 (dd, *J* = 7.2, 14.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.9, 141.7, 132.9, 126.6, 125.6, 121.6, 118.9, 51.3, 39.0; IR (neat): 3080, 2981, 2954, 2925, 1699, 1281, 1235, 904, 863, 771, 727, 693, 649, 623 cm^{-1}.



1n: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.4 Hz, 2H), 7.20–7.16 (m, 3H), 5.84–5.74 (m, 2H), 5.20–5.13 (m, 4H), 2.61–2.57 (m, 2H), 2.44 (d, *J* = 7.2 Hz, 4H), 1.90–1.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 141.9, 133.1, 128.4, 128.3, 125.9, 118.7, 49.2, 38.6, 37.1, 30.5; IR (neat): 3078, 3027, 2979, 2929, 1697, 1455, 1231, 994, 907, 730, 698 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{20}O_2$: 244.1463 ($[M]^+$), found 244.1462.

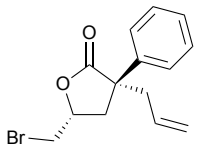


1o: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.18 (m, 5H), 5.90–5.80 (m, 2H), 5.19–5.14 (m, 4H), 2.94 (s, 2H), 2.42 (dd, *J* = 7.2, 14.4 Hz, 2H), 2.31 (dd, *J* = 7.6, 14.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 182.0, 137.0, 133.3, 130.1, 128.2, 126.7, 118.9, 50.7, 41.1, 38.1; IR (neat): 3077, 3031, 2979, 2924, 1698, 1639, 1454, 1446, 1282, 1248, 1232, 992, 916, 737, 701 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{18}O_2$: 230.1307 ($[M]^+$), found 230.1305.

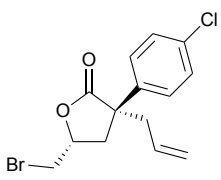
3. General procedure for stereoselective desymmetrizing bromolactonizations of 1

A solution of substrate **1** (0.10 mmol) and catalyst (*S*)-**4c** (10 mol %, 0.010 mmol) in toluene (1.5 mL)-CH_2Cl_2 (0.5 mL) was cooled to –78 °C. After stirring for 10 min at –78 °C, *N*-bromophthalimide (NBP) (0.12 mmol) was added to the cooled reaction solution. The reaction mixture was stirred for 24 h at –78 °C. After 24 h, the reaction mixture was quenched with saturated aqueous Na_2SO_3 (4.0 mL) at –78 °C and stirred for 10 min at –78 °C. The quenched reaction mixture was diluted with CH_2Cl_2 (2 mL) and H_2O (2 mL), and warmed to room temperature. The organic materials were extracted with CH_2Cl_2 for three times (5 mL × 3). The combined extracts were dried over Na_2SO_4 and concentrated. [The ^{1}H NMR analysis of the crude reaction mixture was performed at this stage to confirm diastereoselectivity.] The residue was purified by flash column

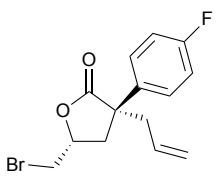
chromatography on silica gel (hexane/ethyl acetate as eluent) to give product **2**. The enantioselectivity of the product **2** was determined by HPLC analysis on a chiral stationary phase.



2a:[2a] $[\alpha]^{21}_{D}$ +52.6 (*c* = 0.84, $CHCl_3$, 95: 5 er); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol = 50:1, flow rate = 0.5 mL/min, 214 nm; retention time: 23.1 min (minor) and 39.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.37 (m, 4H), 7.34–7.29 (m, 1H), 5.71–5.60 (m, 1H), 5.15–5.10 (m, 2H), 4.48–4.41 (m, 1H), 3.59 (dd, *J* = 5.2, 10.8 Hz, 1H), 3.49 (dd, *J* = 6.8, 10.8 Hz, 1H), 2.82 (dd, *J* = 5.2, 13.2 Hz, 1H), 2.75–2.64 (m, 2H), 2.29 (dd, *J* = 10.8, 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 138.3, 132.7, 129.0, 127.9, 126.1, 119.8, 75.1, 53.4, 43.5, 38.2, 32.8; HRMS (FAB) calcd for $C_{14}H_{15}BrO_2$: 294.0255 ($[M]^+$), found 294.0252.

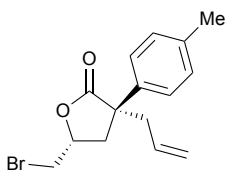


2b: $[\alpha]^{27}_{D}$ +44.8 (*c* = 1.3, $CHCl_3$, 92: 8 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 18.1 min (major) and 20.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.32 (m, 4H), 5.68–5.57 (m, 1H), 5.16–5.09 (m, 2H), 4.46–4.39 (m, 1H), 3.59 (dd, *J* = 5.2, 10.8 Hz, 1H), 3.48 (dd, *J* = 6.8, 10.8 Hz, 1H), 2.78 (dd, *J* = 5.2, 13.6 Hz, 1H), 2.71–2.61 (m, 2H), 2.30 (dd, *J* = 10.8, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 136.8, 134.0, 132.3, 129.2, 127.6, 120.1, 75.1, 53.0, 43.6, 38.1, 32.6; IR (neat): 1768, 1494, 1173, 1012, 926, 827 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{14}BrClO_2$: 327.9866 ($[M]^+$), found 327.9864.

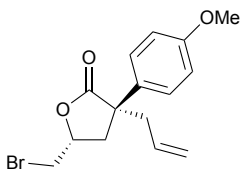


2c: $[\alpha]^{28}_{D}$ +48.1 (*c* = 1.3, $CHCl_3$, 94: 6 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 16.6 min (major) and 18.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 5.2, 8.8 Hz, 2H), 7.08 (dd, *J* = 8.4, 8.8 Hz, 2H), 5.68–5.57 (m, 1H), 5.15–5.09 (m, 2H), 4.47–4.40 (m, 1H), 3.59 (dd, *J* = 5.2, 10.8 Hz, 1H), 3.49 (dd, *J* = 6.4, 10.8 Hz, 1H), 2.79 (dd, *J* = 5.2, 13.6 Hz, 1H), 2.71–2.62 (m, 2H), 2.30 (dd, *J* = 10.8, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 162.2 (d, *J* = 246 Hz), 133.9 (d, *J* = 3.3 Hz), 132.4, 127.9 (d, *J* = 8.2 Hz), 120.0, 115.9 (d,

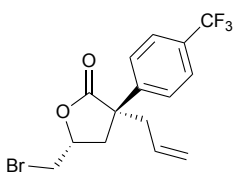
J = 21.4 Hz), 75.1, 52.8, 43.8, 38.2, 32.7; IR (neat): 1769, 1509, 1235, 1174, 1166, 1013, 927, 834 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{15}BrFO_2$: 313.0239 ($[M+H]^+$), found 313.0238.



2d: $[\alpha]^{29}_D$ +37.2 (c = 1.2, $CHCl_3$, 94: 6 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 16.0 min (major) and 18.4 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.0 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 5.70–5.59 (m, 1H), 5.14–5.09 (m, 2H), 4.47–4.40 (m, 1H), 3.58 (dd, J = 4.8, 10.8 Hz, 1H), 3.48 (dd, J = 6.8, 10.8 Hz, 1H), 2.79 (dd, J = 5.6, 13.2 Hz, 1H), 2.72–2.62 (m, 2H), 2.34 (s, 3H), 2.26 (dd, J = 10.8, 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 137.7, 135.2, 132.9, 129.7, 126.0, 119.6, 75.1, 53.0, 43.5, 38.2, 32.8, 20.9; IR (neat): 2922, 1771, 1514, 1233, 1173, 1014, 924, 816 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{17}BrO_2$: 308.0412 ($[M]^+$), found 308.0411.

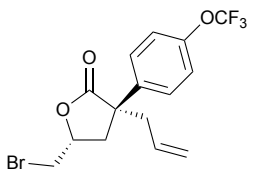


2e: $[\alpha]^{26}_D$ +46.3 (c = 1.0, $CHCl_3$, 94: 6 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 23.1 min (major) and 31.4 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 8.8 Hz, 2H), 6.90 (d, J = 8.8 Hz, 2H), 5.69–5.58 (m, 1H), 5.13–5.08 (m, 2H), 4.48–4.41 (m, 1H), 3.81 (s, 3H), 3.58 (dd, J = 4.8, 10.8 Hz, 1H), 3.48 (dd, J = 6.4, 10.8 Hz, 1H), 2.78 (dd, J = 4.8, 13.2 Hz, 1H), 2.66 (d, J = 8.0 Hz, 2H), 2.25 (dd, J = 10.4, 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.3, 159.1, 132.8, 130.0, 127.3, 119.6, 114.3, 75.1, 55.3, 52.6, 43.7, 38.2, 32.8; IR (neat): 1769, 1512, 1253, 1172, 1031, 1016, 1009, 925, 829 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{18}BrO_3$: 325.0439 ($[M+H]^+$), found 325.0429.

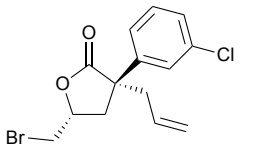


2f: $[\alpha]^{26}_D$ +38.9 (c = 0.78, $CHCl_3$, 91: 9 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 15.6 min (major) and 17.4 min (minor). ^1H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 5.69–5.58 (m, 1H), 5.18–5.11 (m, 2H), 4.46–4.39 (m, 1H), 3.60 (dd, J = 4.8, 10.8 Hz, 1H), 3.50 (dd, J = 6.4, 10.8 Hz, 1H), 2.83 (dd, J = 5.2, 13.2 Hz, 1H), 2.75–2.65

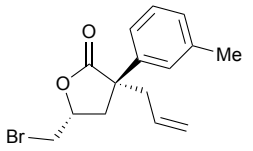
(m, 2H), 2.36 (dd, J = 10.4, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 142.4, 132.0, 130.3 (q, J = 32.1 Hz), 126.7, 126.0 (q, J = 4.1 Hz), 123.8 (q, J = 271 Hz), 120.4, 75.1, 53.4, 43.5, 38.0, 32.5; IR (neat): 1771, 1328, 1170, 1119, 1071, 1015 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{15}BrF_3O_2$: 363.0208 ($[M+H]^+$), found 363.0208.



2g: $[\alpha]^{27}_D$ +39.2 (c = 0.94, $CHCl_3$, 91: 9 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 13.9 min (major) and 15.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 9.2 Hz, 2H), 7.24 (d, J = 8.8 Hz, 2H), 5.68–5.58 (m, 1H), 5.17–5.10 (m, 2H), 4.48–4.41 (m, 1H), 3.60 (dd, J = 4.8, 10.8 Hz, 1H), 3.49 (dd, J = 6.4, 10.8 Hz, 1H), 2.80 (dd, J = 5.2, 13.6 Hz, 1H), 2.73–2.62 (m, 2H), 2.32 (dd, J = 10.8, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.7, 148.8, 136.9, 132.2, 127.8, 121.3, 120.4 (q, J = 257 Hz), 120.2, 75.1, 53.0, 43.7, 38.0, 32.6; IR (neat): 1776, 1509, 1257, 1213, 1169, 1015, 926 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{15}BrF_3O_3$: 379.0157 ($[M+H]^+$), found 379.0156.

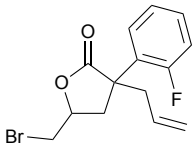


2h: $[\alpha]^{22}_D$ +53.4 (c = 1.3, $CHCl_3$, 96: 4 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 14.5 min (major) and 15.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.35–7.28 (m, 3H), 5.68–5.58 (m, 1H), 5.17–5.11 (m, 2H), 4.48–4.41 (m, 1H), 3.59 (dd, J = 5.2, 10.8 Hz, 1H), 3.50 (dd, J = 6.4, 10.8 Hz, 1H), 2.78 (dd, J = 5.2, 13.6 Hz, 1H), 2.73–2.62 (m, 2H), 2.32 (dd, J = 10.8, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.5, 140.4, 135.0, 132.2, 130.3, 128.2, 126.4, 124.4, 120.2, 75.1, 53.3, 43.5, 38.0, 32.6; IR (neat): 1777, 1173, 1016, 926 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{15}BrClO_2$: 328.9944 ($[M+H]^+$), found 328.9939.

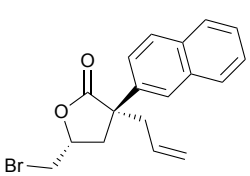


2i: $[\alpha]^{20}_D$ +51.5 (c = 1.1, $CHCl_3$, 93: 7 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 12.1 min (major) and 13.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.11 (m, 4H), 5.71–5.60 (m, 1H), 5.18–5.10 (m, 2H), 4.47–4.40 (m, 1H), 3.58 (dd, J = 5.2, 10.4 Hz, 1H), 3.48 (dd, J = 6.4, 10.4 Hz, 1H), 2.79 (dd, J = 5.6, 13.2 Hz, 1H), 2.73–2.63 (m, 2H), 2.36 (s, 3H), 2.28 (dd, J = 10.4, 13.2 Hz,

1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 138.8, 138.3, 132.9, 128.8, 128.6, 126.8, 123.0, 119.7, 75.1, 53.4, 43.5, 38.2, 32.8, 21.6; IR (neat): 1775, 1171, 1015, 925 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{18}BrO_2$: 309.0490 ($[M+H]^+$), found 309.0491.

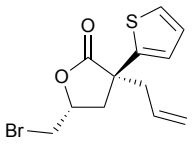


2j: **(Major diastereomer)**: $[\alpha]^{21}_D$ –8.3 (*c* = 1.2, $CHCl_3$, 86:14 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 28.0 min (minor) and 31.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.33–7.28 (m, 1H), 7.17–7.07 (m, 2H), 5.88–5.78 (m, 1H), 5.31–5.23 (m, 2H), 4.73–4.66 (m, 1H), 3.55 (dd, *J* = 5.6, 10.4 Hz, 1H), 3.36 (dd, *J* = 7.6, 10.8 Hz, 1H), 2.86–2.75 (m, 3H), 2.40 (ddd, *J* = 2.0, 8.0, 14.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 160.4 (d, *J* = 245 Hz), 131.7, 129.5 (d, *J* = 9.6 Hz), 128.9 (d, *J* = 11.5 Hz), 127.6 (d, *J* = 3.8 Hz), 124.3 (d, *J* = 2.9 Hz), 120.9, 116.4 (d, *J* = 23.0 Hz), 75.7, 49.6, 41.4, 40.0 (d, *J* = 2.8 Hz), 33.2; IR (neat): 1772, 1489, 1179, 757 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{15}BrFO_2$: 313.0239 ($[M+H]^+$), found 313.0239. **(Minor diastereomer)**: $[\alpha]^{22}_D$ +32.2 (*c* = 0.17, $CHCl_3$, 74:26 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 18.7 min (major) and 19.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.25 (m, 2H), 7.15–7.09 (m, 2H), 5.83–5.72 (m, 1H), 5.22–5.18 (m, 2H), 4.49–4.42 (m, 1H), 3.57 (dd, *J* = 5.2, 10.8 Hz, 1H), 3.48 (dd, *J* = 6.4, 10.8 Hz, 1H), 2.86–2.76 (m, 3H), 2.39 (dd, *J* = 10.4, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.6, 160.7 (d, *J* = 246 Hz), 132.8, 129.8 (d, *J* = 8.6 Hz), 128.2 (d, *J* = 3.8 Hz), 127.1 (d, *J* = 11.5 Hz), 124.6 (d, *J* = 2.8 Hz), 120.4, 116.9 (d, *J* = 23.0 Hz), 75.7, 52.3 (d, *J* = 1.9 Hz), 40.2 (d, *J* = 3.9 Hz), 38.3 (d, *J* = 4.8 Hz), 32.7; IR (neat): 1781, 1491, 1178, 1018, 758 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{15}BrFO_2$: 313.0239 ($[M+H]^+$), found 313.0239.

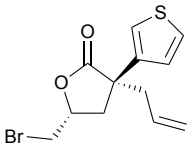


2k: $[\alpha]^{27}_D$ +61.0 (*c* = 1.8, $CHCl_3$, 95: 5 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 22.3 min (major) and 26.8 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.79 (m, 4H), 7.56–7.48 (m, 3H), 5.74–5.64 (m, 1H), 5.16–5.13 (m, 2H), 4.50–4.44 (m, 1H), 3.60 (dd, *J* = 5.2, 10.8 Hz, 1H), 3.51 (dd, *J* = 6.8, 10.8 Hz, 1H), 2.93 (dd, *J* = 5.2, 13.2 Hz, 1H), 2.78 (d, *J* = 6.8 Hz, 2H), 2.38 (dd, *J* = 10.8, 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.1, 135.6, 133.1,

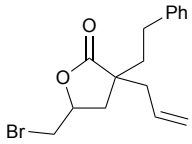
132.7, 132.6, 129.1, 128.1, 127.5, 126.6, 126.5, 125.0, 123.9, 119.8, 75.2, 53.7, 43.4, 38.3, 32.8; IR (neat): 1769, 1173, 1014, 1005, 923, 817, 748 cm^{-1}; HRMS (FAB) calcd for $C_{18}H_{18}BrO_2$: 345.0490 ($[M+H]^+$), found 345.0490.



2l: $[\alpha]^{20}_D$ +27.9 (*c* = 1.3, $CHCl_3$, 95: 5 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 17.7 min (major) and 20.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 1.2, 5.2 Hz, 1H), 7.05 (dd, *J* = 1.2, 3.6 Hz, 1H), 6.99 (dd, *J* = 3.6, 5.2 Hz, 1H), 5.73–5.62 (m, 1H), 5.18–5.13 (m, 2H), 4.70–4.63 (m, 1H), 3.60 (dd, *J* = 4.8, 10.8 Hz, 1H), 3.52 (dd, *J* = 6.4, 10.8 Hz, 1H), 2.80–2.69 (m, 3H), 2.35 (dd, *J* = 10.4, 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 142.5, 132.2, 127.3, 125.2, 125.1, 120.1, 75.5, 50.8, 44.4, 39.5, 32.8; IR (neat): 1768, 1173, 1010, 926, 703 cm^{-1}; HRMS (FAB) calcd for $C_{12}H_{13}BrO_2S$: 299.9820 ($[M]^+$), found 299.9820.

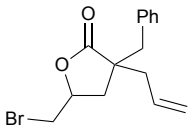


2m: $[\alpha]^{20}_D$ +41.6 (*c* = 0.92, $CHCl_3$, 96: 4 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 20.4 min (major) and 24.1 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 2.8, 5.2 Hz, 1H), 7.21 (dd, *J* = 1.2, 2.8 Hz, 1H), 7.14 (dd, *J* = 1.2, 5.2 Hz, 1H), 5.69–5.59 (m, 1H), 5.15–5.10 (m, 2H), 4.58–4.51 (m, 1H), 3.60 (dd, *J* = 4.8, 10.8 Hz, 1H), 3.50 (dd, *J* = 6.4, 10.4 Hz, 1H), 2.76–2.63 (m, 3H), 2.27 (dd, *J* = 10.4, 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.0, 139.3, 132.5, 127.1, 125.9, 121.5, 119.8, 75.4, 50.8, 43.1, 38.5, 32.9; IR (neat): 1774, 1173, 1016, 927, 789 cm^{-1}; HRMS (FAB) calcd for $C_{12}H_{14}BrO_2S$: 300.9898 ($[M+H]^+$), found 300.9899.

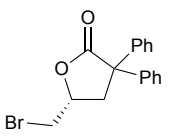


2n: **(Major diastereomer)**: $[\alpha]^{27}_D$ +3.6 (*c* = 0.40, $CHCl_3$, 85:15 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 17.5 min (major) and 18.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (tt, *J* = 1.6, 7.2 Hz, 2H), 7.22–7.18 (m, 3H), 5.85–5.75 (m, 1H), 5.25–5.19 (m, 2H), 4.64–4.57 (m, 1H), 3.57 (dd, *J* = 4.4, 10.8 Hz, 1H), 3.50 (dd, *J* = 6.4, 10.8 Hz, 1H), 2.81–2.73 (m, 1H), 2.59–2.52 (m, 1H), 2.46–2.30 (m, 3H), 2.13 (dd, *J* = 9.2, 13.2 Hz, 1H), 2.00–1.88 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.2, 141.1, 132.0, 128.5, 128.3, 126.2, 120.2, 74.8, 48.3, 41.7, 38.4, 36.2,

34.0, 30.8; IR (neat): 3027, 2925, 1768, 1176, 1020, 925, 700 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{19}BrO_2$: 322.0568 ($[M]^+$), found 322.0568. **(Minor diastereomer)**: $[\alpha]^{27}_D$ –9.2 (*c* = 0.56, $CHCl_3$, 86:14 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 19.2 min (major) and 21.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (tt, *J* = 1.6, 7.4 Hz, 2H), 7.21 (tt, *J* = 1.6, 7.4 Hz, 1H), 7.16 (dd, *J* = 1.2, 8.0 Hz, 2H), 5.80–5.70 (m, 1H), 5.23–5.18 (m, 2H), 4.68–4.61 (m, 1H), 3.57 (dd, *J* = 4.8, 10.8 Hz, 1H), 3.45 (dd, *J* = 6.4, 10.8 Hz, 1H), 2.74–2.61 (m, 2H), 2.51 (tdd, *J* = 1.2, 6.4, 14.0 Hz, 1H), 2.42 (dd, *J* = 8.4, 14.0 Hz, 1H), 2.28 (dd, *J* = 7.2, 13.6 Hz, 1H), 2.14 (dd, *J* = 8.8, 13.6 Hz, 1H), 1.97–1.85 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.0, 140.8, 132.6, 128.6, 128.2, 126.3, 120.1, 75.2, 47.9, 40.4, 39.1, 36.9, 33.8, 30.6; IR (neat): 2922, 1769, 1456, 1165, 1017, 924, 746, 700 cm^{-1}; HRMS (FAB) calcd for $C_{16}H_{19}BrO_2$: 322.0568 ($[M]^+$), found 322.0568.



2o: **(1.3: 1 mixture of diastereomers)**: $[\alpha]^{26}_D$ –9.2 (*c* = 2.3, $CHCl_3$, 78:22 er for major diastereomer, 76:24 er for minor diastereomer); HPLC analysis: Daicel Chiralpak IG-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time for major diastereomer: 24.8 min (major) and 29.6 min (minor); retention time for minor diastereomer: 24.0 min (minor) and 30.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34–7.25 (m, 3H), 7.22–7.18 (m, 2H), 5.86–5.72 (m, 1H), 5.24–5.17 (m, 2H), 4.48–4.41 (m, 0.44H), 3.47–3.40 (m, 0.56H), 3.33 (dd, *J* = 4.4, 10.4 Hz, 0.56H), 3.26 (dd, *J* = 6.4, 10.4 Hz, 0.56H), 3.19 (d, 13.2 Hz, 0.44H), 3.08–3.04 (m, 1H), 2.75–2.69 (m, 1H), 2.63–2.51 (m, 1.44H), 2.39–2.18 (m, 2H), 2.09–2.03 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 179.64, 179.55, 136.5, 136.0, 132.6, 132.1, 130.3, 129.7, 128.74, 128.65, 127.4, 127.2, 120.4, 120.3, 75.1, 74.9, 50.1, 50.0, 43.8, 43.1, 42.5, 42.3, 34.8, 33.8, 33.1; IR (neat): 3030, 2978, 2921, 1769, 1170, 1013, 924, 703 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{17}BrO_2$: 308.0412 ($[M]^+$), found 308.0413.

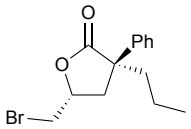


8:[6] $[\alpha]^{27}_D$ +70.2 (*c* = 1.3, $CHCl_3$, 94: 6 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 50:1, flow rate = 0.5 mL/min, 214 nm; retention time: 37.5 min (minor) and 41.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.24 (m, 10H), 4.59–4.53 (m, 1H), 3.62 (dd, *J* = 4.8, 10.8 Hz, 1H), 3.52 (dd, *J* = 6.4, 10.8 Hz, 1H), 3.17 (dd, *J* = 5.2, 13.2 Hz, 1H), 2.83 (dd, *J* = 9.6, 13.2

Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.2, 141.4, 139.3, 129.0, 128.5, 127.9, 127.6, 127.4, 127.2, 74.9, 58.2, 42.2, 32.6; IR (neat): 1778, 1168, 1026, 965, 697 cm^{-1}; HRMS (FAB) calcd for $C_{17}H_{15}BrO_2$: 330.0255 ($[M]^+$), found 330.0255.

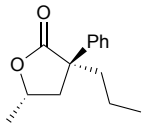
4. Transformations of products 2a and 8

To a solution of **2a** (0.20 mmol) in THF (5 mL) was added 10wt% Pd/C (0.030 mmol). The reaction mixture was warmed to 60 °C and stirred for 4 h under H_2 atmosphere. After 4 h, the reaction mixture was diluted with ethyl acetate and filtered over celite. The filtrate was concentrated and purified by flash column chromatography on silica gel (hexane/ethyl acetate = 50:1–5:1 as eluent) to give product **9**.



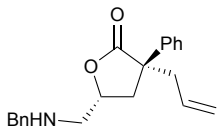
9: $[\alpha]^{21}_D$ +38.5 (*c* = 1.5, $CHCl_3$, 95: 5 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 15.8 min (major) and 18.0 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43–7.28 (m, 5H), 4.46–4.40 (m, 1H), 3.60 (dd, *J* = 4.8, 10.8 Hz, 1H), 3.51 (dd, *J* = 6.4, 10.8 Hz, 1H), 2.91 (dd, *J* = 5.2, 13.2 Hz, 1H), 2.22 (dd, *J* = 10.4, 13.2 Hz, 1H), 2.01 (ddd, *J* = 4.8, 12.4, 14.0 Hz, 1H), 1.83 (ddd, *J* = 4.8, 12.4, 14.0 Hz, 1H), 1.37–1.11 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.7, 138.3, 128.9, 127.7, 126.1, 74.9, 53.5, 41.6, 38.7, 33.0, 18.1, 14.2; IR (neat): 2960, 2933, 2872, 1773, 1178, 1002, 699 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{17}BrO_2$: 296.0412 ($[M]^+$), found 296.0412.

To a solution of **9** (0.16 mmol) in toluene (8 mL) was added 2,2'-azobis(isobutyronitrile) (AIBN) (0.048 mmol) and tributyltin hydride (0.48 mmol). The reaction mixture was warmed to 100 °C and stirred for 22 h. After 22 h, the reaction mixture was cooled to room temperature and quenched with saturated aqueous $NaHCO_3$ (15 mL). The organic materials were extracted with ethyl acetate for three times (5 mL × 3). The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 70:1–10:1 as eluent) to give product **10**.



10:[3] $[\alpha]^{18}_{D}$ +57.8 (*c* = 1.4, $CHCl_3$, 95: 5 er); HPLC analysis: Daicel Chiralpak ID-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 20.7 min (major) and 22.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.6 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 1H), 4.40–4.31 (m, 1H), 2.81 (dd, *J* = 4.8, 13.2 Hz, 1H), 2.02–1.94 (m, 2H), 1.79 (ddd, *J* = 4.8, 12.4, 14.0 Hz, 1H), 1.42 (d, *J* = 6.0 Hz, 3H), 1.36–1.08 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 138.8, 128.8, 127.4, 126.3, 73.7, 53.9, 41.9, 41.8, 20.5, 18.1, 14.2; IR (neat): 2960, 2933, 2872, 1761, 1184 cm^{-1}; HRMS (FAB) calcd for $C_{14}H_{18}O_2$: 218.1307 ($[M]^+$), found 218.1307.

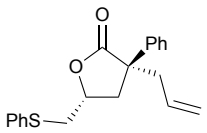
To a solution of **2a** (0.10 mmol) in CH_3CN (1 mL) was added benzylamine (0.50 mmol). The reaction mixture was warmed to 70 °C and stirred for 48 h. After 48 h, the reaction mixture was concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 30:1–1:1 as eluent) to give product **11**.



11: $[\alpha]^{20}_{D}$ +29.1 (*c* = 1.3, $CHCl_3$, 95: 5 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 3:1, flow rate = 0.5 mL/min, 214 nm; retention time: 12.6 min (minor) and 13.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42–7.22 (m, 10H), 5.69–5.58 (m, 1H), 5.11–5.06 (m, 2H), 4.45–4.38 (m, 1H), 3.81 (s, 2H), 2.90 (dd, *J* = 3.6, 12.8 Hz, 1H), 2.82 (dd, *J* = 6.8, 13.2 Hz, 1H), 2.67 (d, *J* = 7.2 Hz, 2H), 2.60 (dd, *J* = 5.2, 13.2 Hz, 1H), 2.28 (dd, *J* = 10.8, 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 139.8, 138.6, 133.1, 128.9, 128.4, 128.1, 127.7, 127.1, 126.2, 119.4, 77.1, 53.8, 53.0, 52.5, 43.5, 36.6; IR (neat): 2920, 2833, 1764, 1181, 1014, 923, 740, 699 cm^{-1}; HRMS (FAB) calcd for $C_{21}H_{23}NO_2$: 321.1729 ($[M]^+$), found 321.1729.

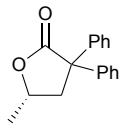
To a solution of **2a** (0.10 mmol) in CH_3CN (1 mL) was added K_2CO_3 (0.30 mmol) and thiophenol (0.50 mmol). The reaction mixture was warmed to 75 °C and stirred for 3 h. After 3 h, the reaction mixture was cooled to room temperature and quenched with saturated aqueous NH_4Cl (5 mL). The organic materials were extracted with ethyl acetate for three times (5 mL × 3). The combined extracts were dried over

Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate = 80:1–5:1 as eluent) to give product **12**.



12: $[\alpha]^{19}_D$ +73.1 (*c* = 1.7, $CHCl_3$, 95: 5 er); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 19.5 min (major) and 21.0 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.20 (m, 10H), 5.67–5.57 (m, 1H), 5.12–5.04 (m, 2H), 4.41–4.34 (m, 1H), 3.37 (dd, *J* = 4.8, 13.2 Hz, 1H), 3.07 (dd, *J* = 7.6, 13.6 Hz, 1H), 2.80 (dd, *J* = 5.2, 13.2 Hz, 1H), 2.71–2.61 (m, 2H), 2.20 (dd, *J* = 10.8, 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.5, 138.4, 134.8, 132.9, 130.2, 129.1, 128.9, 127.7, 127.0, 126.1, 119.6, 75.6, 53.1, 43.7, 38.6, 38.4; IR (neat): 3060, 2929, 1771, 1175, 1005, 921, 740, 698 cm^{-1}; HRMS (FAB) calcd for $C_{20}H_{20}O_2S$: 324.1184 ($[M]^+$), found 324.1183.

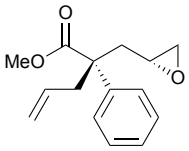
16 was synthesized from **8** in a similar manner for the synthesis of **10**.



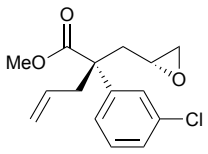
16:[3] $[\alpha]^{26}_D$ +102.9 (*c* = 0.25, $CHCl_3$, 94: 6 er); HPLC analysis: Daicel Chiralcel OD-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 16.7 min (minor) and 17.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39–7.22 (m, 10H), 4.53–4.45 (m, 1H), 3.06 (dd, *J* = 4.8, 12.8 Hz, 1H), 2.60 (dd, *J* = 10.4, 12.8 Hz, 1H), 1.47 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 177.2, 142.0, 139.9, 128.9, 128.3, 127.7, 127.6, 127.3, 127.2, 73.6, 58.6, 45.3, 20.4; IR (neat): 1762, 1180, 699 cm^{-1}; HRMS (FAB) calcd for $C_{17}H_{16}O_2$: 252.1150 ($[M]^+$), found 252.1149.

5. General procedure for the synthesis of α-quaternary esters 13

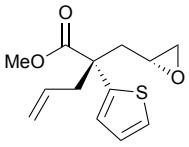
To a solution of **2** (0.10 mmol) in MeOH (1.0 mL) was added K_2CO_3 (0.20 mmol) at room temperature. The reaction mixture was stirred for 48 h at 25 °C. After 48 h, the reaction mixture was quenched with H_2O (10 mL). The organic materials were extracted with ethyl acetate for three times (5 mL × 3). The combined extracts were dried over Na_2SO_4 and concentrated. The residue was purified by flash column chromatography on silica gel (hexane/ethyl acetate as eluent) to give product **13**.



13a: $[\alpha]^{21}_{D}$ +15.5 (*c* = 0.76, $CHCl_3$, 95: 5 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 25.8 min (major) and 38.1 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.32 (m, 2H), 7.29–7.23 (m, 3H), 5.61–5.51 (m, 1H), 5.13–5.06 (m, 2H), 3.69 (s, 3H), 2.97 (dd, *J* = 7.2, 14.0 Hz, 1H), 2.90–2.84 (m, 2H), 2.66 (dd, *J* = 4.4, 4.8 Hz, 1H), 2.40 (dd, *J* = 5.2, 14.4 Hz, 1H), 2.35 (dd, *J* = 2.8, 5.2 Hz, 1H), 2.06 (dd, *J* = 6.0, 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.2, 141.5, 133.1, 128.5, 127.1, 126.2, 119.1, 53.2, 52.2, 49.0, 47.1, 40.3, 38.1; IR (neat): 1731, 1215, 923, 701 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{18}O_3$: 246.1256 ($[M]^+$), found 246.1256.



13h: $[\alpha]^{21}_{D}$ +18.7 (*c* = 2.2, $CHCl_3$, 96: 4 er); HPLC analysis: Daicel Chiralpak IC-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 19.7 min (major) and 29.4 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.23 (m, 3H), 7.13 (td, *J* = 1.6, 7.2 Hz, 1H), 5.58–5.48 (m, 1H), 5.13–5.07 (m, 2H), 3.70 (s, 3H), 2.96 (dd, *J* = 7.6, 14.0 Hz, 1H), 2.87–2.82 (m, 2H), 2.68 (dd, *J* = 4.0, 4.8 Hz, 1H), 2.37 (dd, *J* = 2.4, 5.2 Hz, 1H), 2.32 (dd, *J* = 5.6, 14.4 Hz, 1H), 2.11 (dd, *J* = 6.0, 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 143.5, 134.5, 132.6, 129.7, 127.4, 126.6, 124.6, 119.5, 53.1, 52.4, 48.8, 46.9, 40.1, 37.9; IR (neat): 2952, 2925, 2853, 1731, 1215, 923 cm^{-1}; HRMS (FAB) calcd for $C_{15}H_{17}ClO_3$: 280.0866 ($[M]^+$), found 280.0866.



13l: $[\alpha]^{23}_{D}$ +9.7 (*c* = 2.0, $CHCl_3$, 95: 5 er); HPLC analysis: Daicel Chiralpak IF-3, hexane/2-propanol = 20:1, flow rate = 0.5 mL/min, 214 nm; retention time: 19.1 min (minor) and 21.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (dd, *J* = 1.6, 4.8 Hz, 1H), 6.99–6.95 (m, 2H), 5.68–5.57 (m, 1H), 5.16–5.08 (m, 2H), 3.73 (s, 3H), 3.00 (dd, *J* = 7.2, 14.0 Hz, 1H), 2.93–2.87 (m, 2H), 2.69 (dd, *J* = 4.4, 4.8 Hz, 1H), 2.42 (dd, *J* = 2.8, 4.8 Hz, 1H), 2.38 (dd, *J* = 5.6, 14.4 Hz, 1H), 2.20 (dd, *J* = 6.0, 14.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.9, 145.4, 132.8, 126.6, 124.8, 124.5, 119.3, 52.5, 51.4, 48.9, 47.0, 42.1, 39.7; IR (neat): 2924, 1732, 1216, 700 cm^{-1}; HRMS (FAB) calcd for $C_{13}H_{16}O_3S$: 252.0820 ($[M]^+$), found 252.0820.

6. Determination of the absolute configuration of products

The absolute stereochemistry of products **10** and **16** were confirmed by comparison with reported data.[3]

References

1 (*a*) R. Nishiyori, A. Tsuchihashi, A. Mochizuki, K. Kaneko, M. Yamanaka and S. Shirakawa, *Chem. – Eur. J.*, 2018, **24**, 16747–16752; (*b*) A. Tsuchihashi and S. Shirakawa, *Synlett*, 2019, **30**, 1662–1666; (*c*) M. Okada, K. Kaneko, M. Yamanaka and S. Shirakawa, *Org. Biomol. Chem.,* 2019, **17**, 3747–3751; (*d*) R. Nishiyori, M. Okada, J. R. J. Maynard and S. Shirakawa, *Asian J. Org. Chem.*, 2021, **10**, 1444–1448.

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5 P. De Cointet, P. J. Grossi, C. Pigerol, M. Broll and P. Eymard, *Eur. J. Med. Chem.*, 1980, **15**, 223–227.

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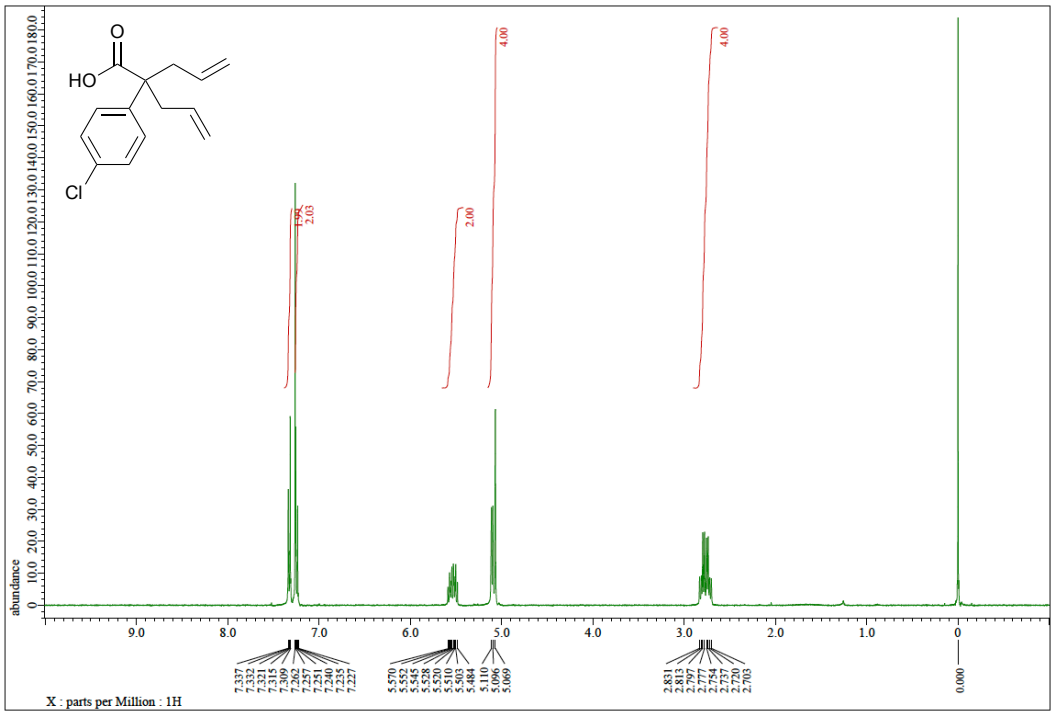
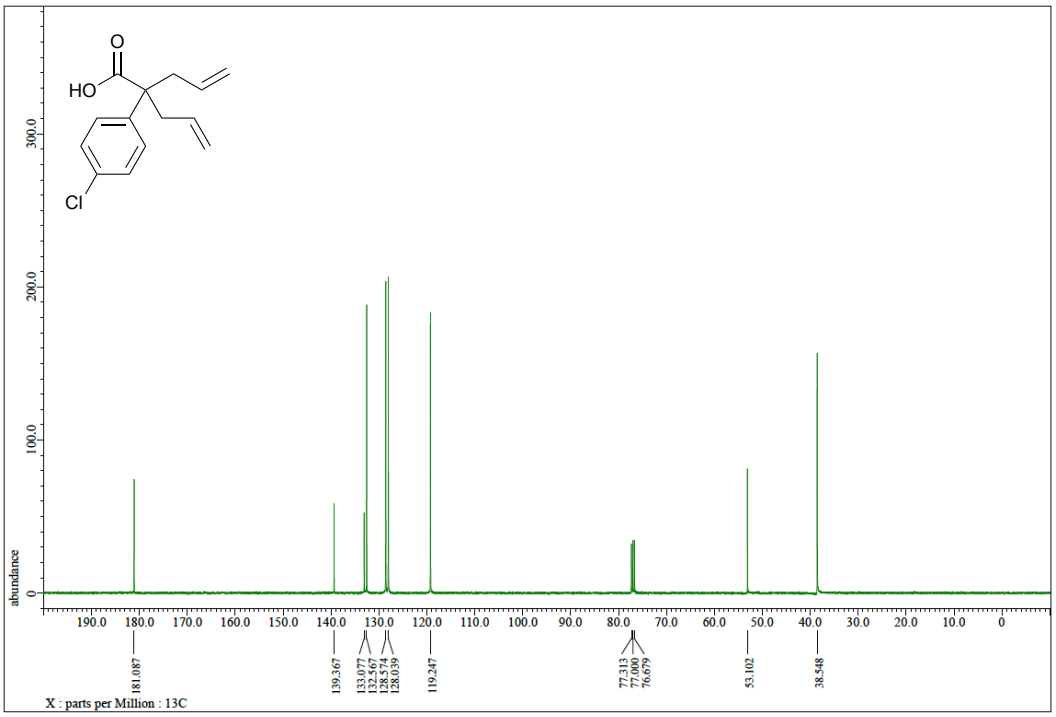
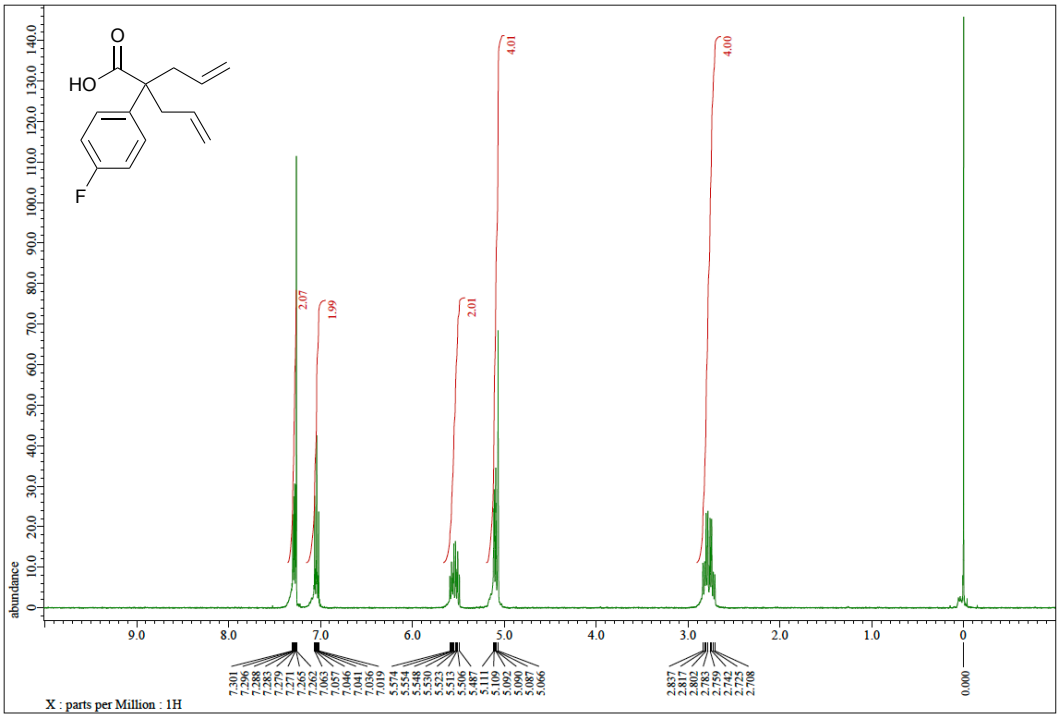
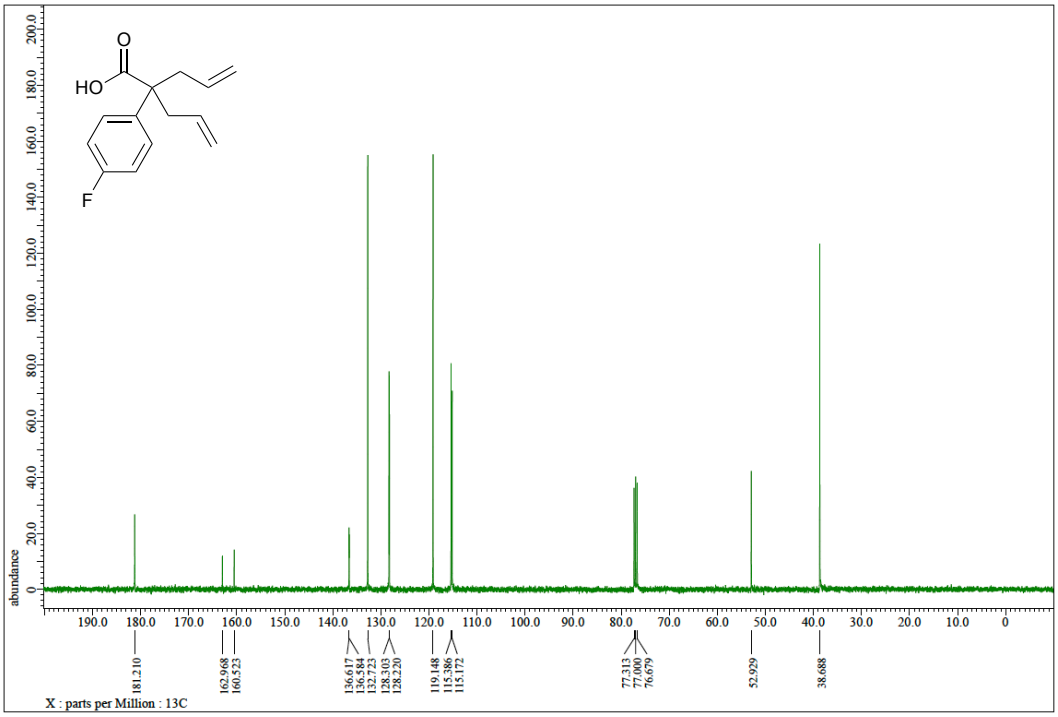
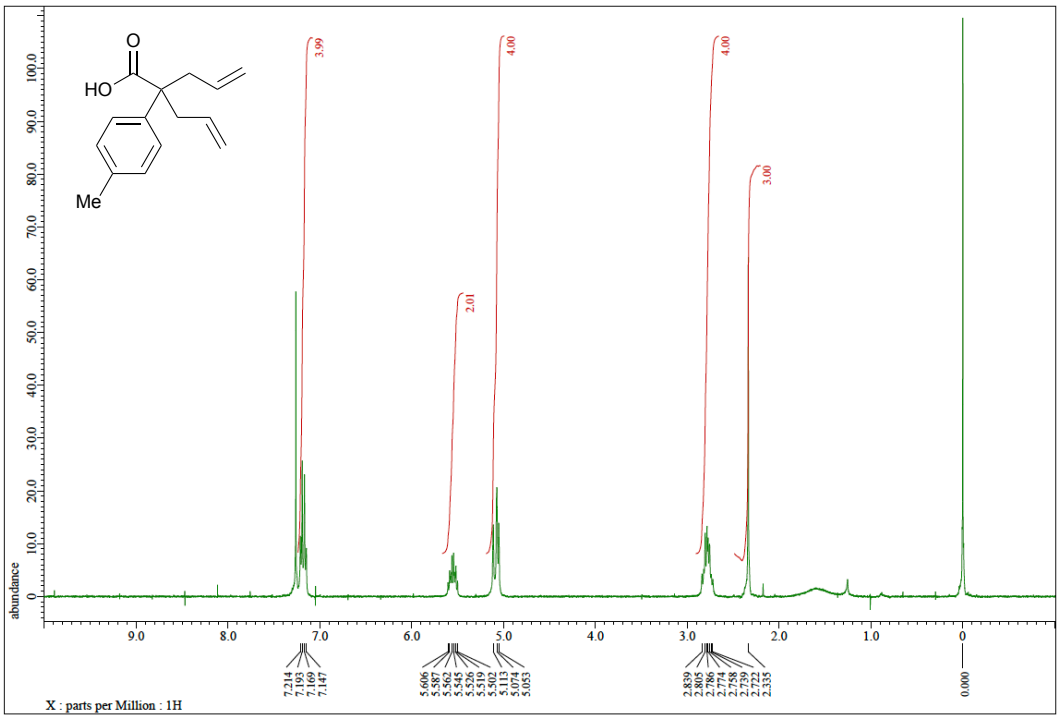
NMR Charts

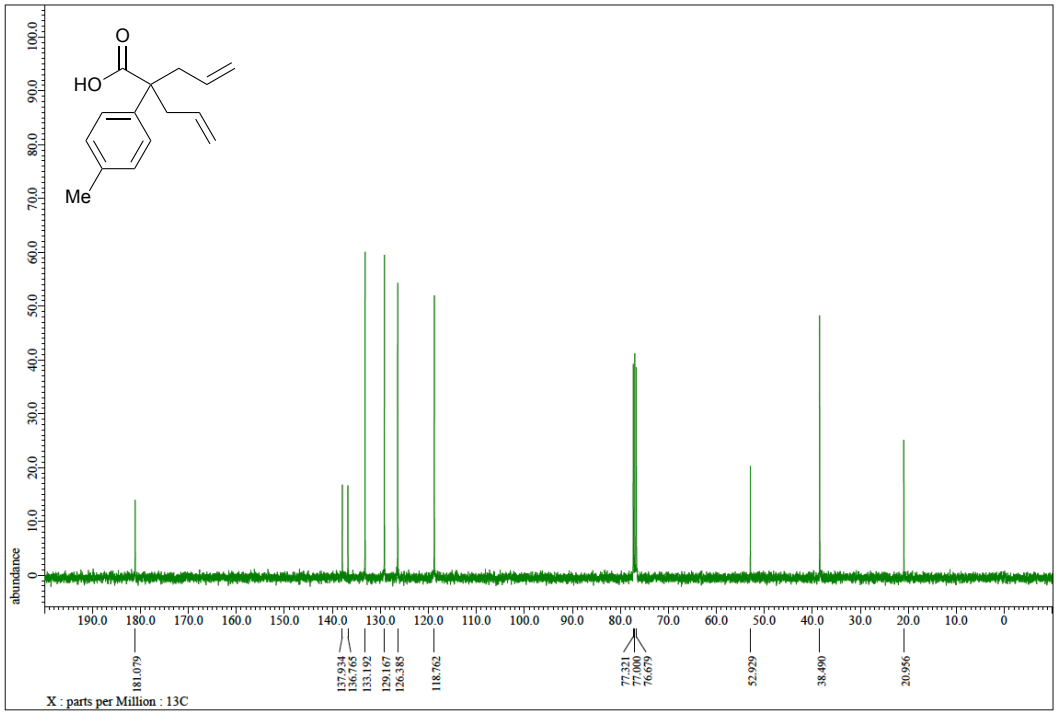

HO
O
Cl
1.95
2.03
2.00
4.00
4.00
abundance
X : parts per Million : 1H

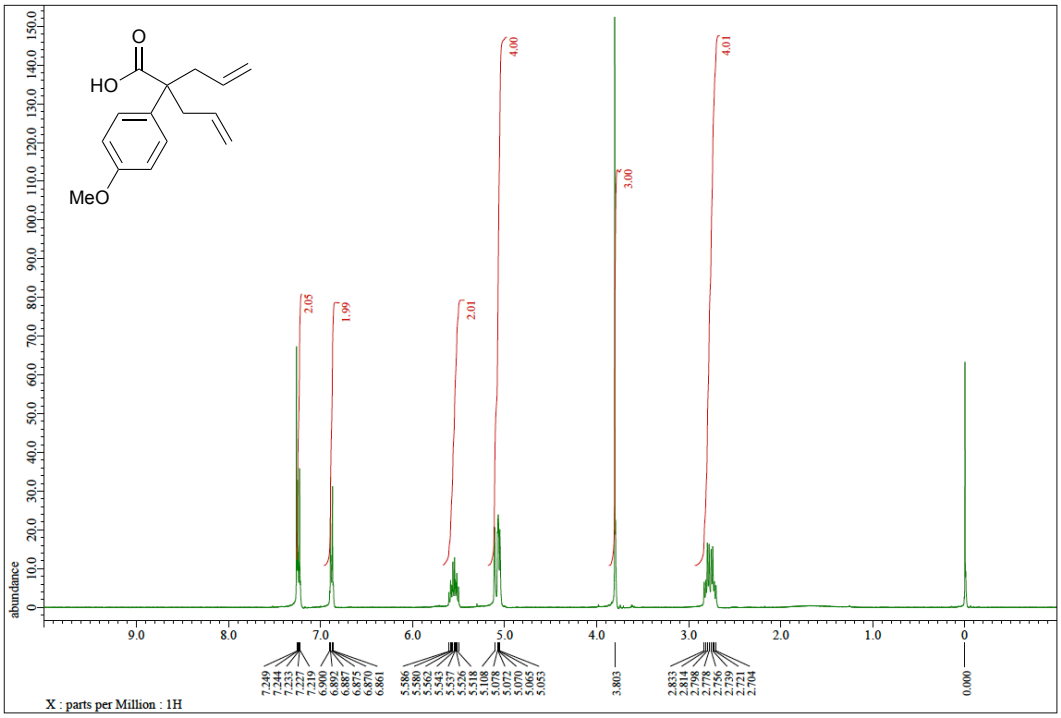

HO
O
Cl
abundance
X : parts per Million : 13C


HO
O
F
2.07
1.99
2.01
4.01
4.00
abundance
X : parts per Million : 1H


HO
O
F
abundance
181.210
162.968
160.523
136.617
136.584
132.723
128.330
128.220
119.148
115.386
115.172
77.313
77.000
76.679
52.929
38.688
X : parts per Million : 13C


O
HO
Me
3.99
2.01
4.00
4.00
3.00
abundance
X : parts per Million : 1H


O
HO
Me
abundance
X : parts per Million : 13C


O
HO
MeO
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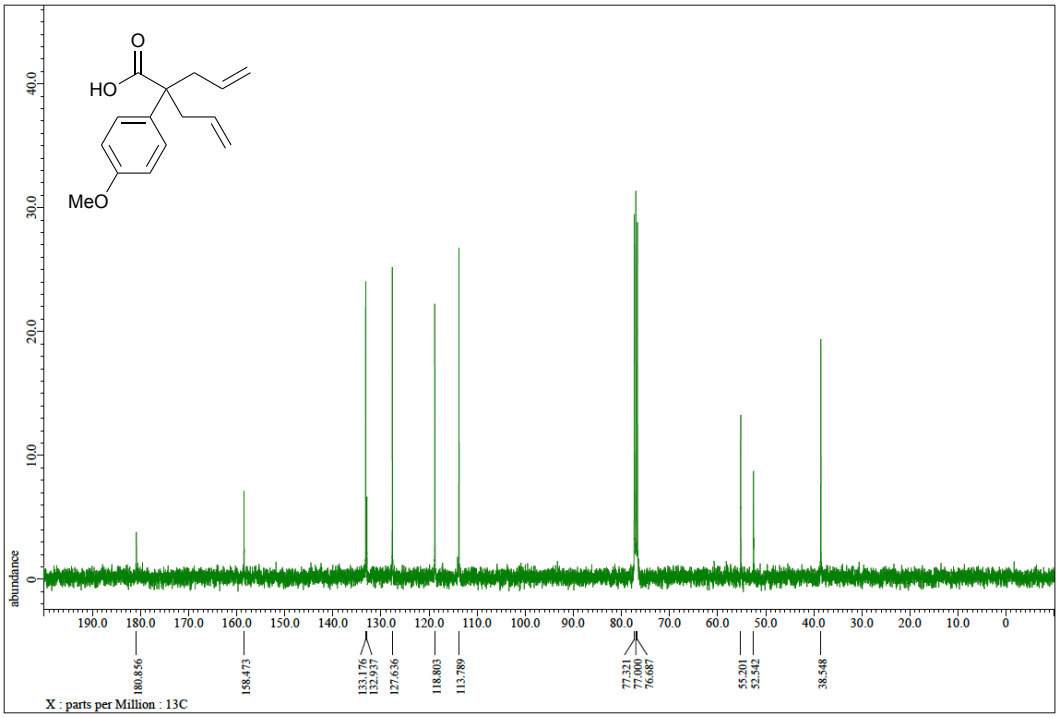
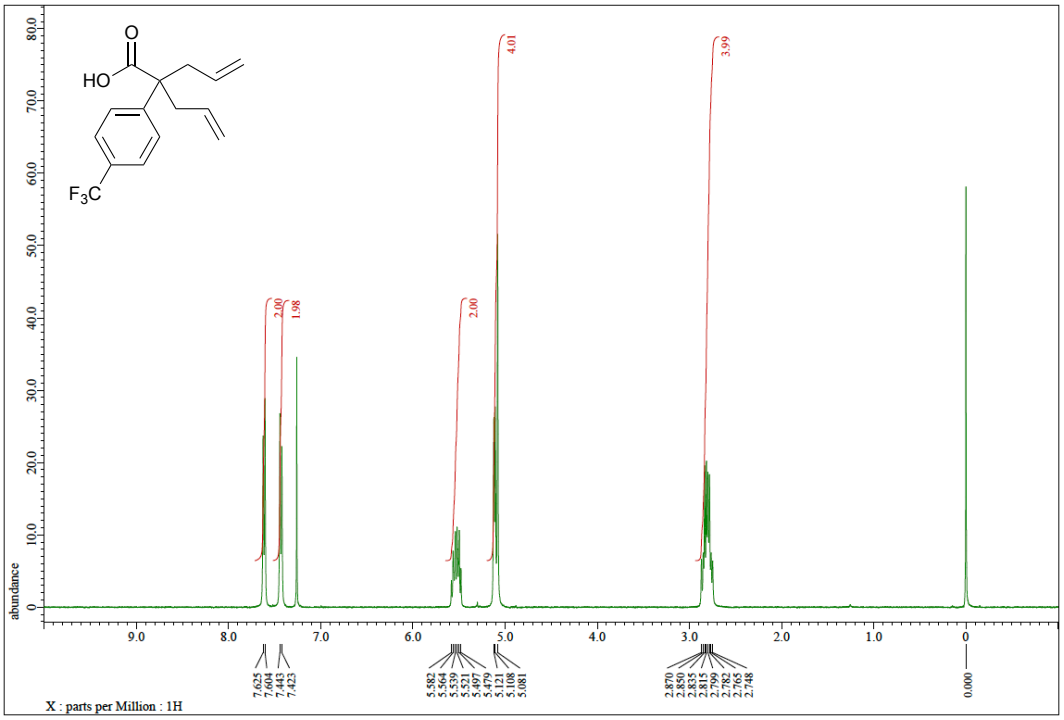
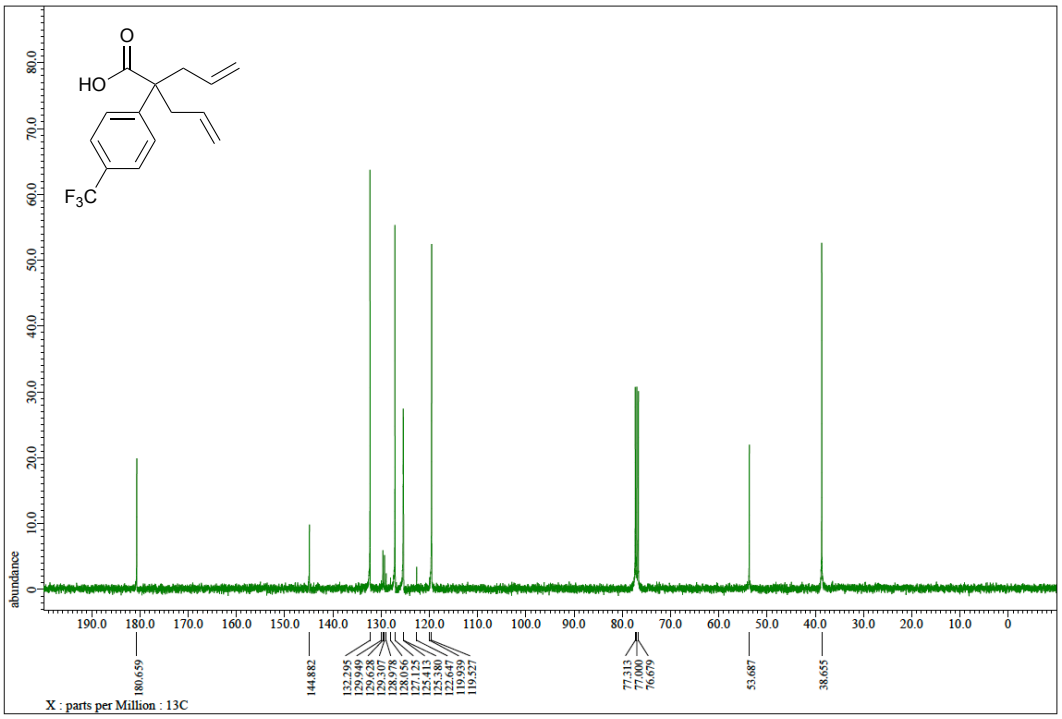
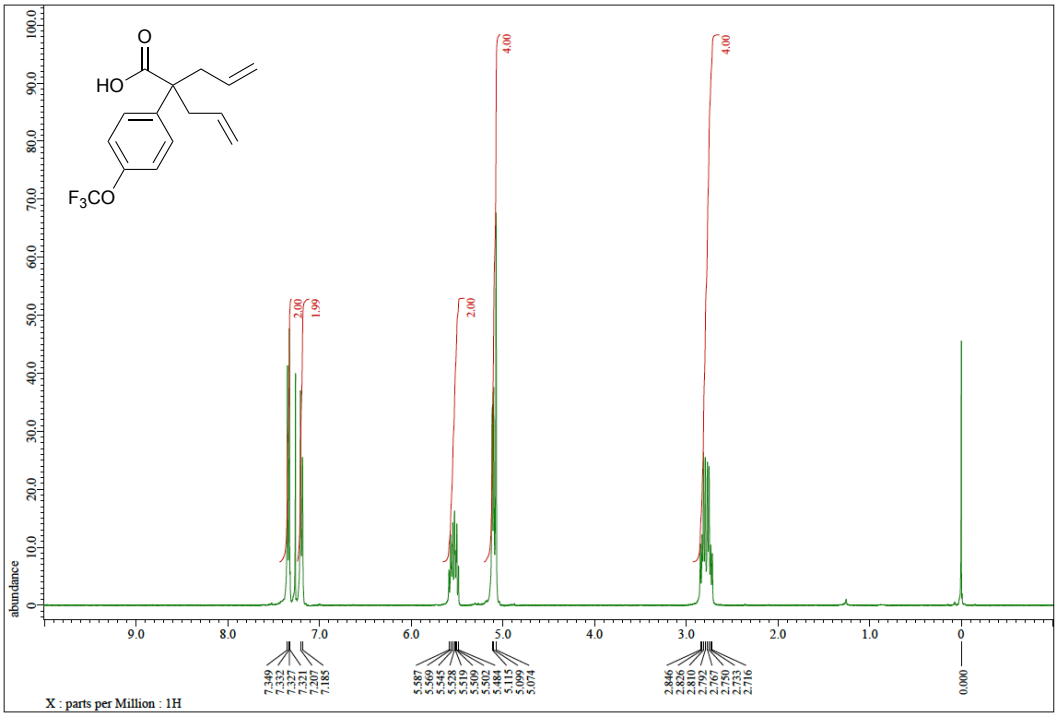
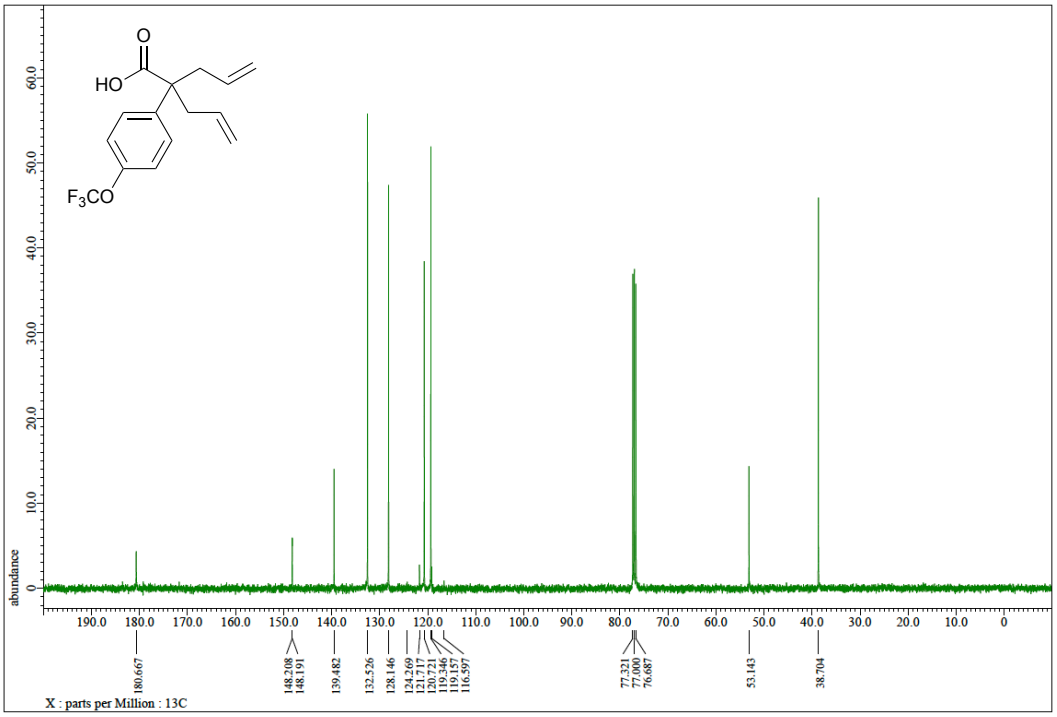
1.99
2.01
4.00
3.00
4.01
abundance
X : parts per Million : 1H

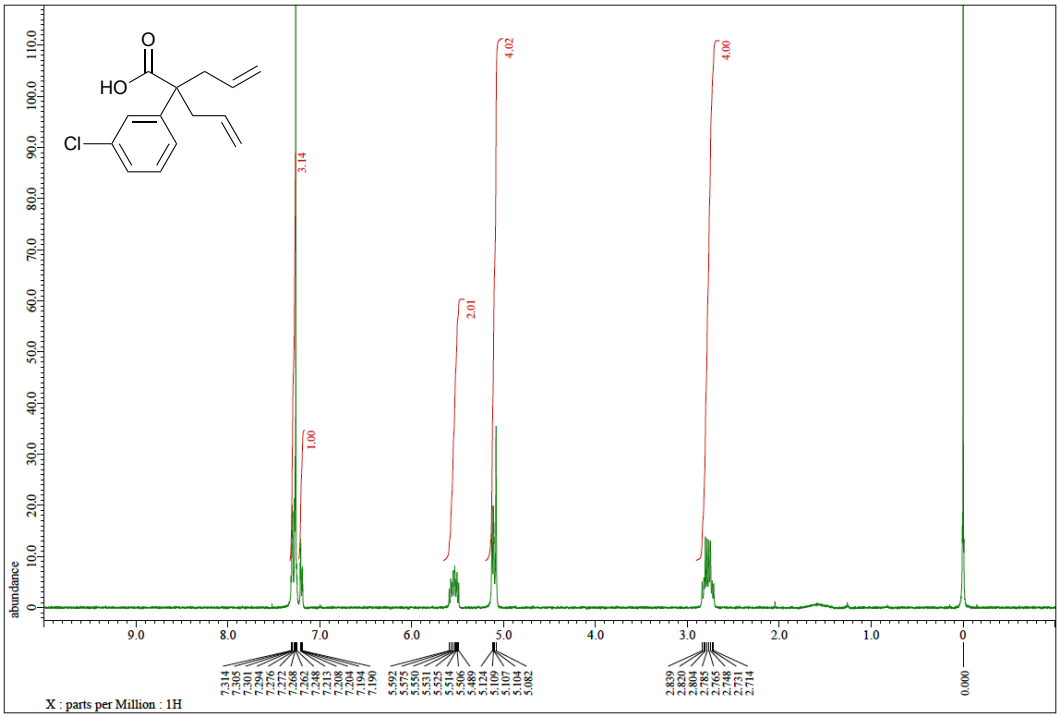

O
HO
MeO
abundance
X : parts per Million : 13C

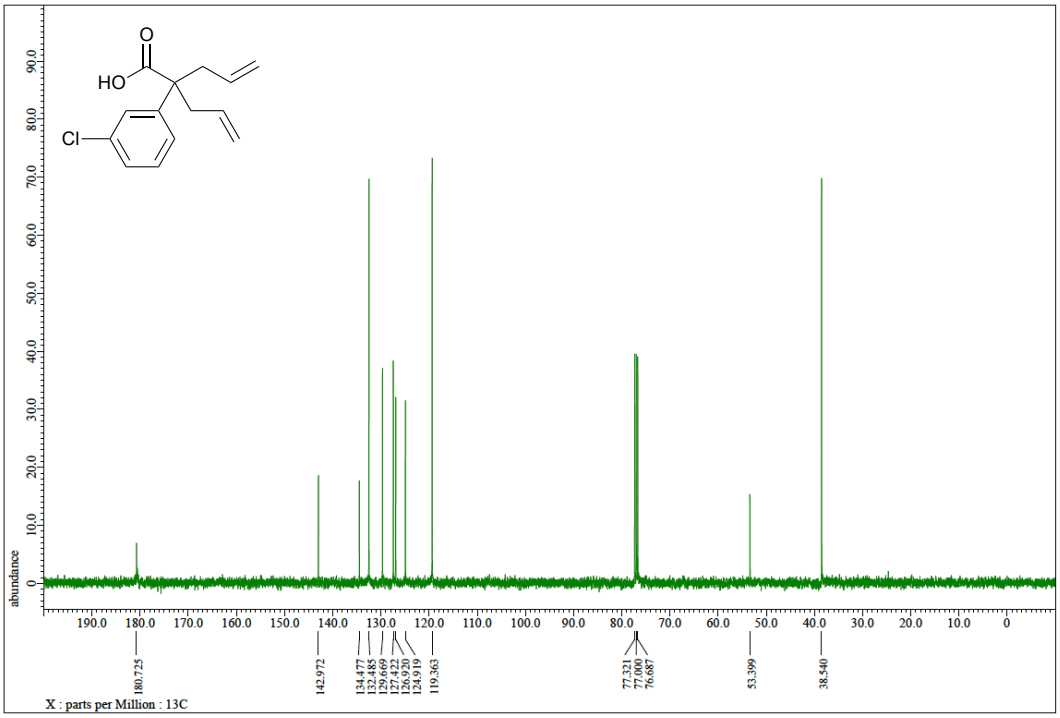

O
HO
F3C
4.01
3.99
2.00
2.00
1.98
abundance
X : parts per Million : 1H


O
HO
F3C
abundance
X : parts per Million : 13C


O
HO
F3CO
abundance
X : parts per Million : 1H


O
HO
F3CO
abundance
X : parts per Million : 13C


O
HO
Cl
3.14
1.00
2.01
4.02
4.00
abundance
X : parts per Million : 1H


O
HO
Cl
abundance
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134.477
132.463
129.468
127.422
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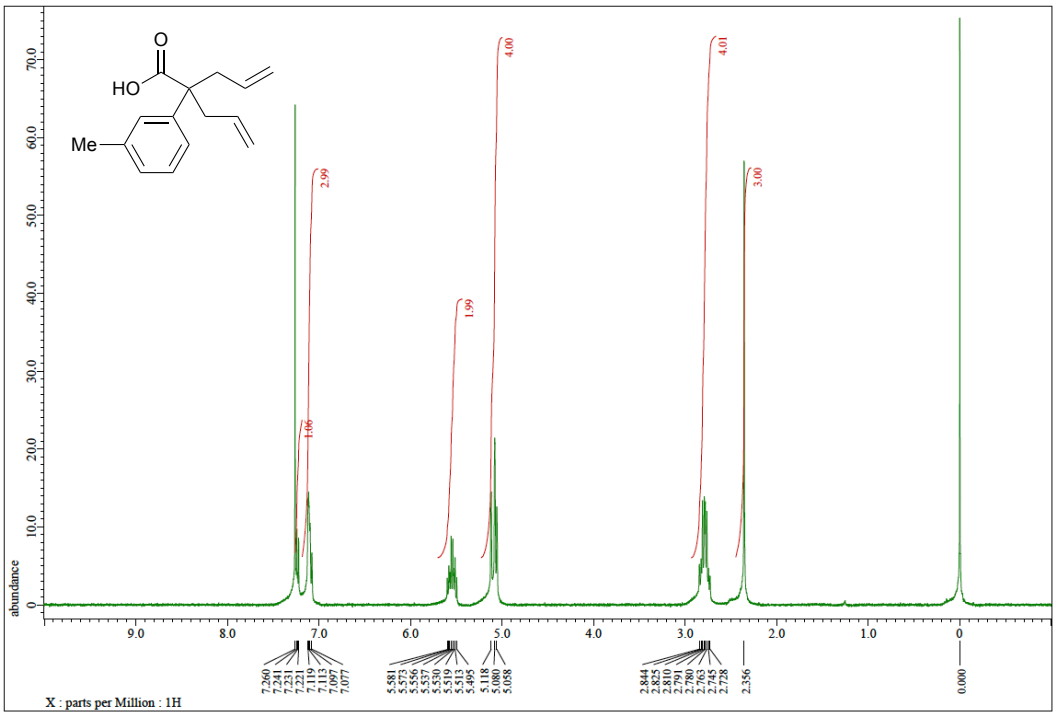
77.321
77.000
76.687
53.399
38.540
X : parts per Million : 13C


O
HO
Me
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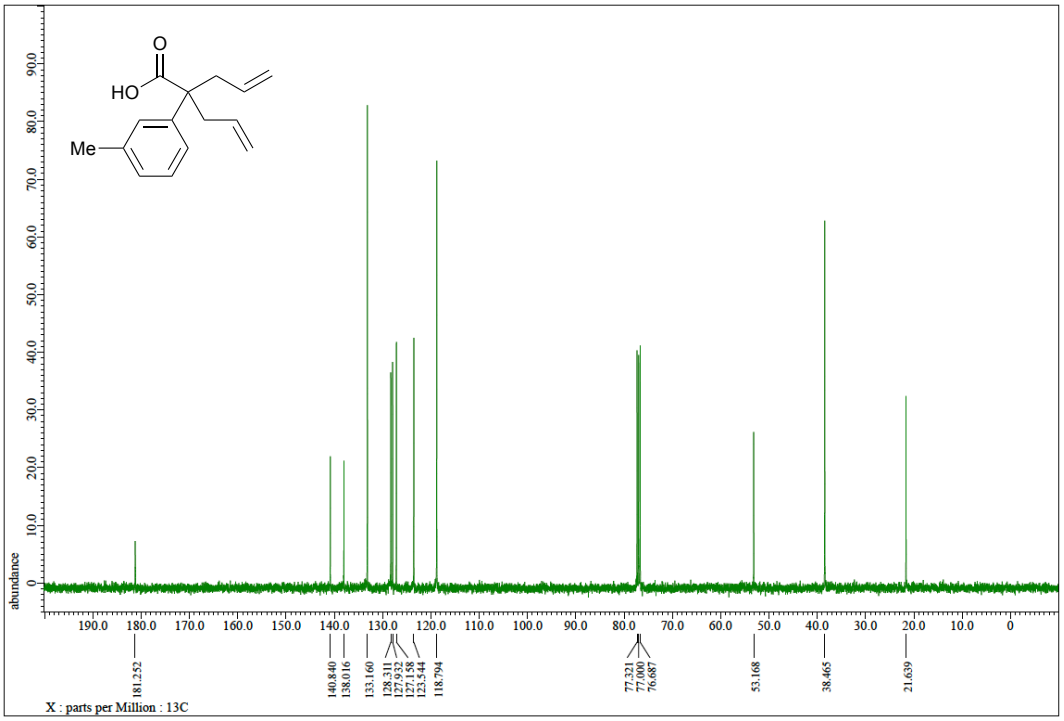
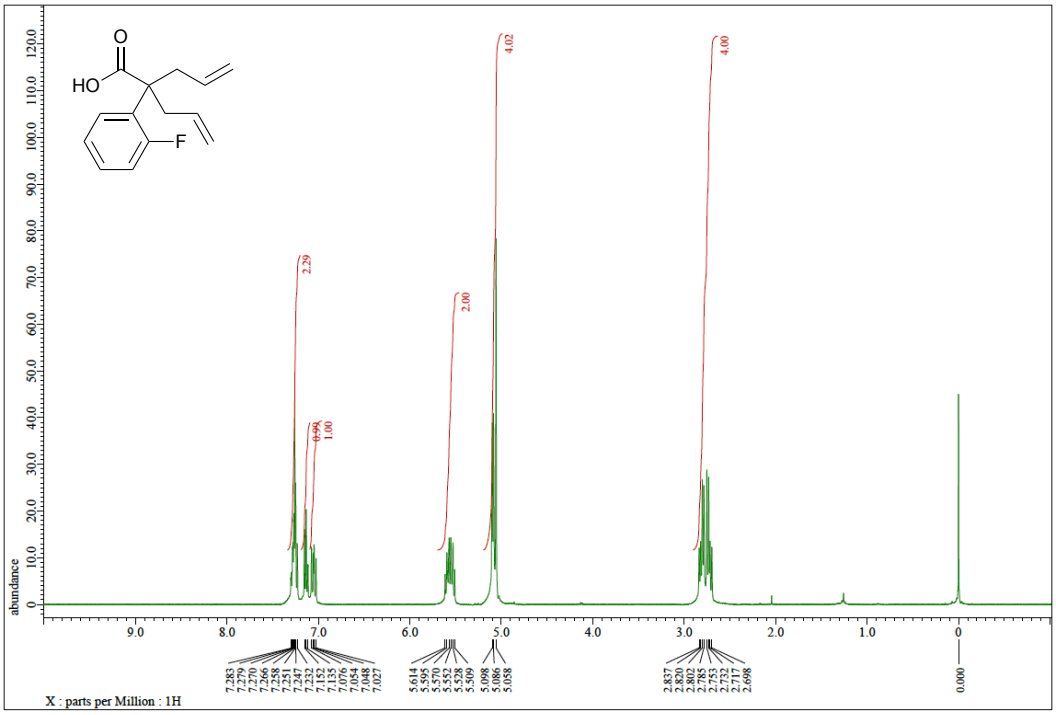
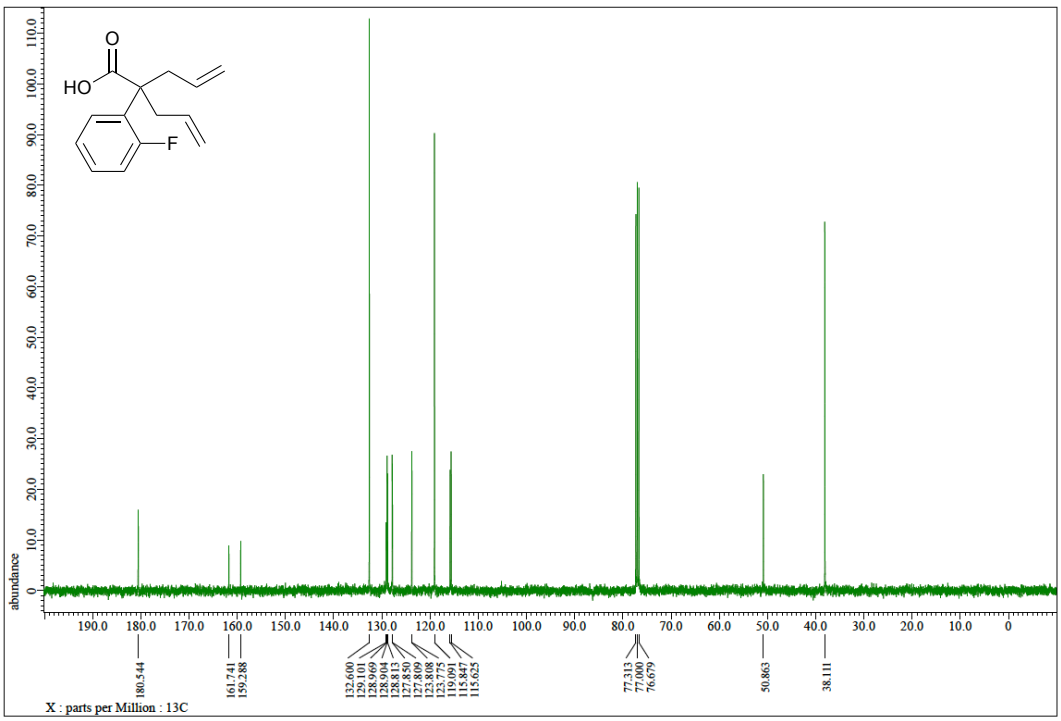
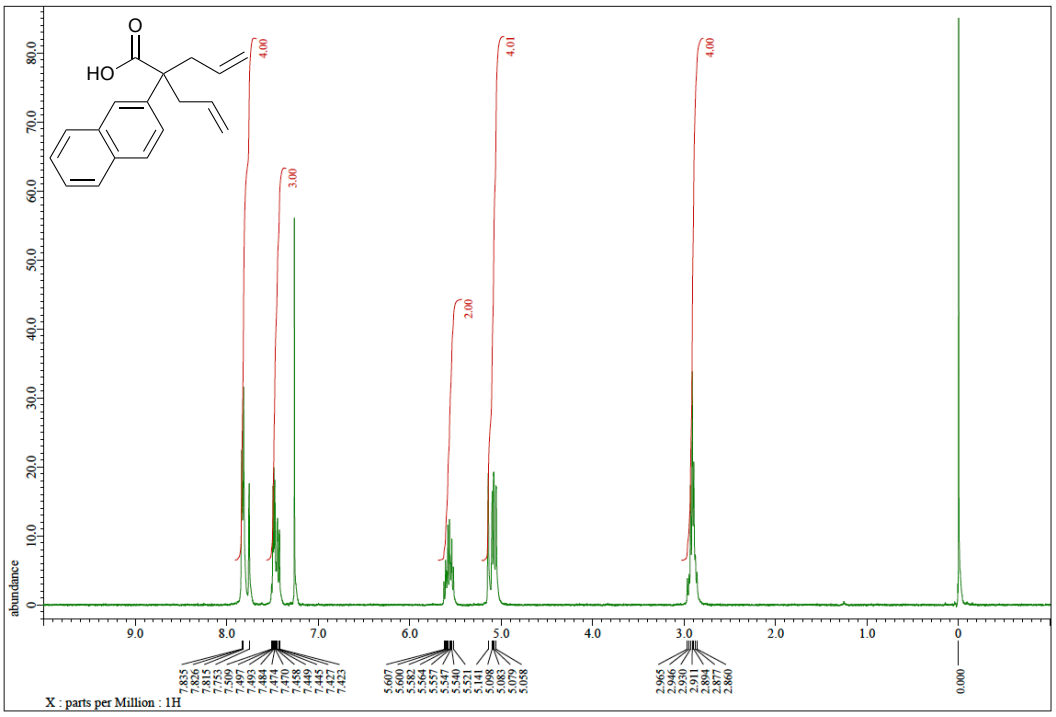
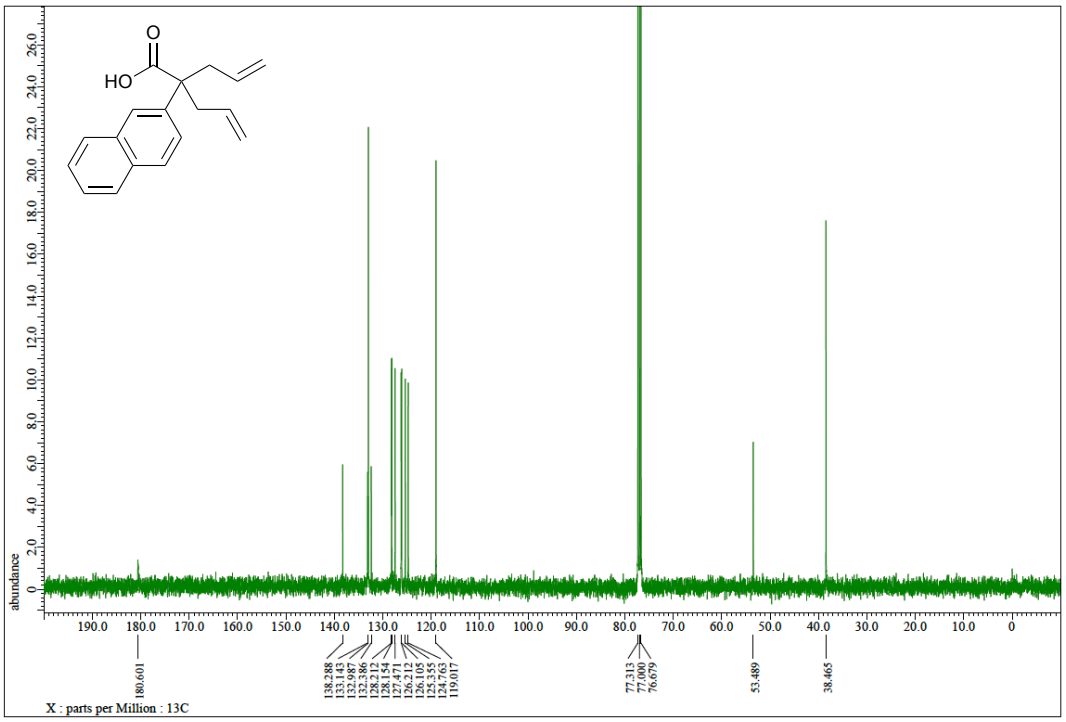
4.00
4.01
3.00
abundance
X : parts per Million : 1H

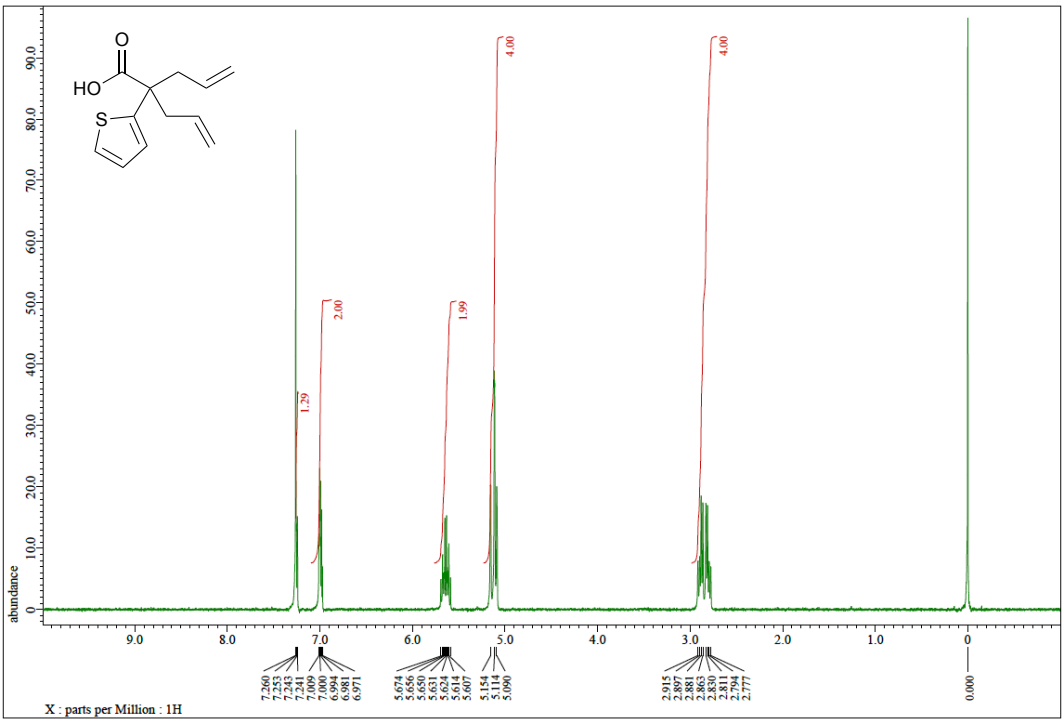

O
HO
Me
abundance
X : parts per Million : 13C


HO
O
F
abundance
X : parts per Million : 1H


HO
O
F
abundance
X : parts per Million : 13C


HO
O
4.00
3.00
2.00
4.01
4.00
abundance
X : parts per Million : 1H


HO
O
abundance
X : parts per Million : 13C


O
HO
S
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4.00
2.00
1.99
1.29
abundance
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7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
7.260
7.253
7.241
7.234
7.009
7.000
6.994
6.981
6.971
5.674
5.656
5.650
5.631
5.624
5.614
5.607
5.154
5.114
5.090
2.915
2.897
2.881
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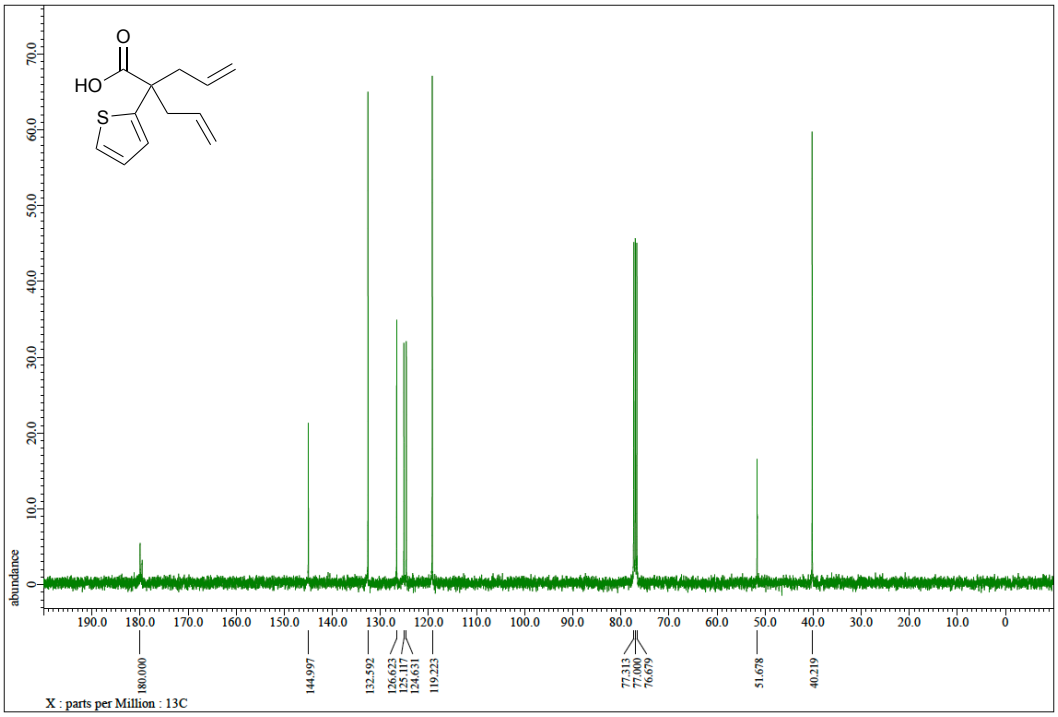
2.830
2.811
2.794
2.777
0.000
X : parts per Million : 1H


O
HO
S
abundance
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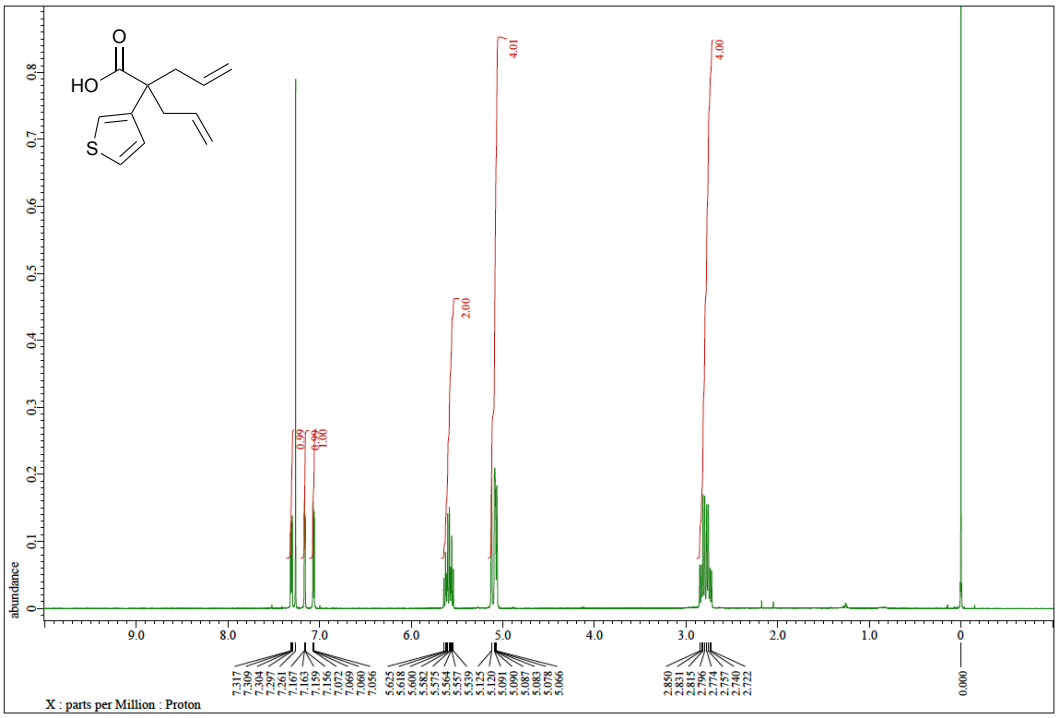
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
180.000
144.997
132.592
126.623
125.117
124.631
119.223
77.313
77.000
76.679
51.678
40.219
X : parts per Million : 13C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O
S
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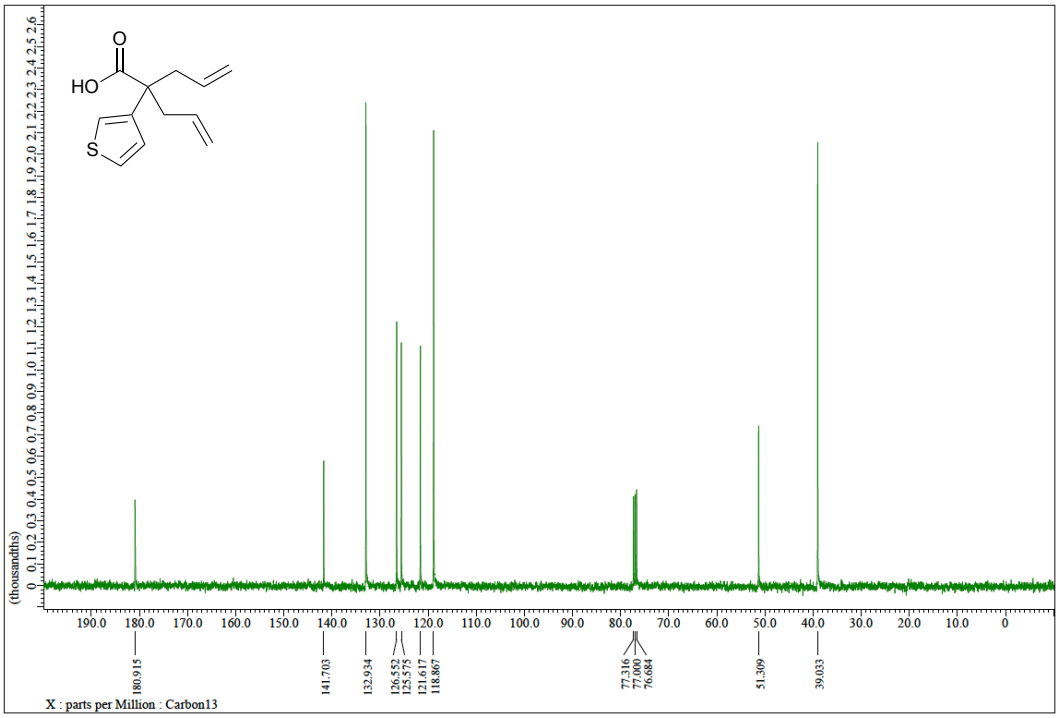
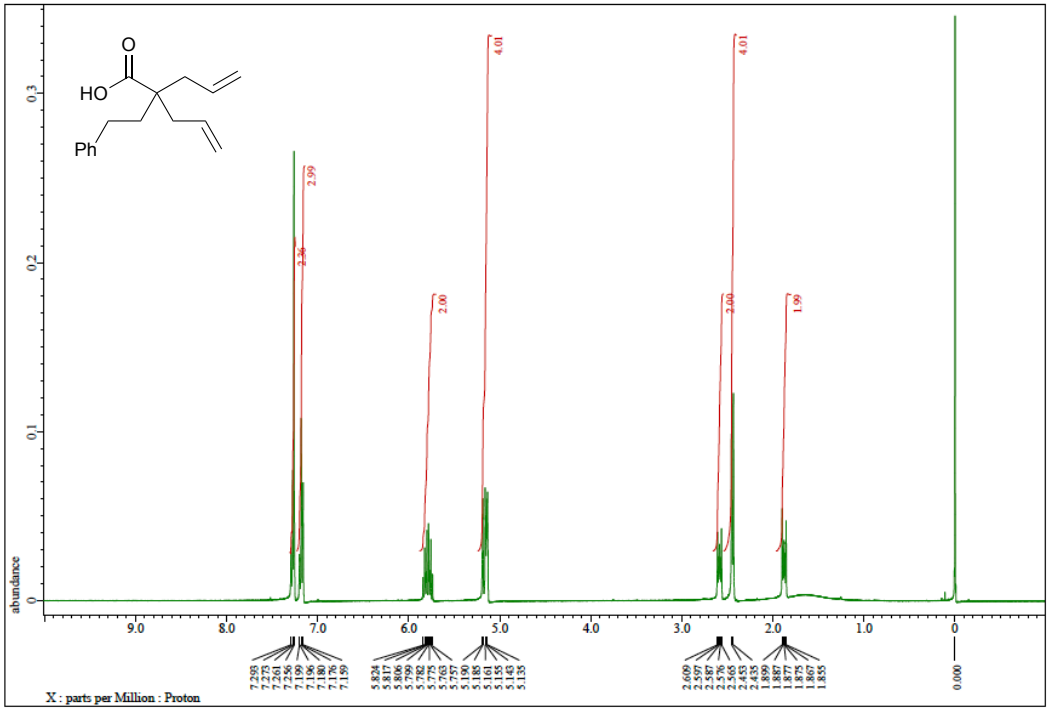
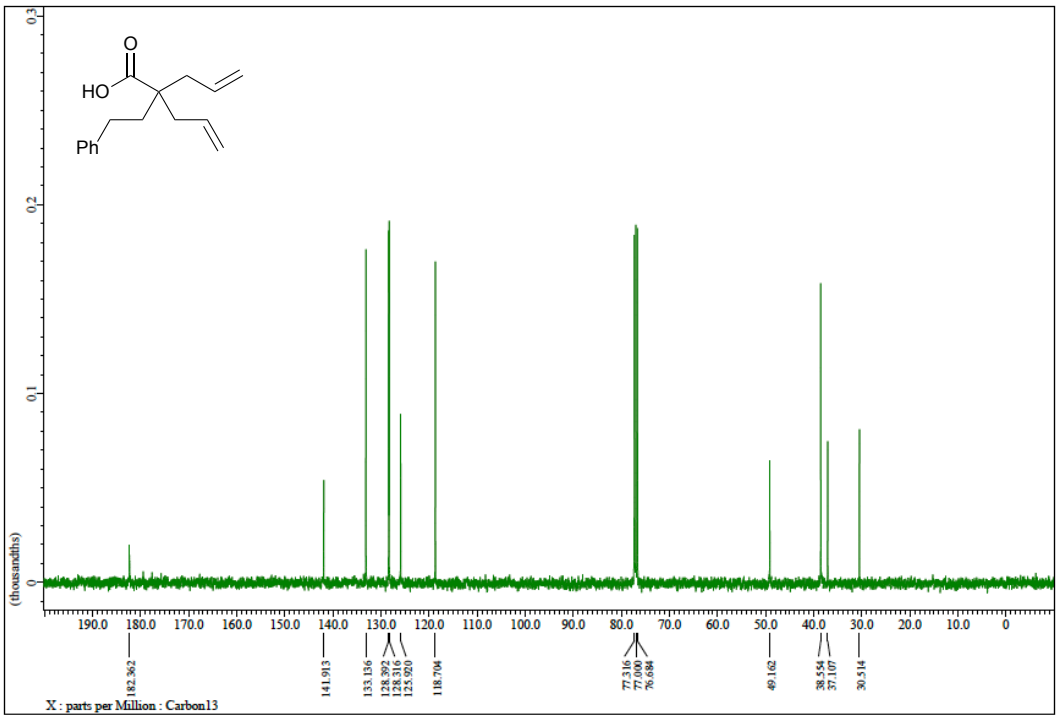
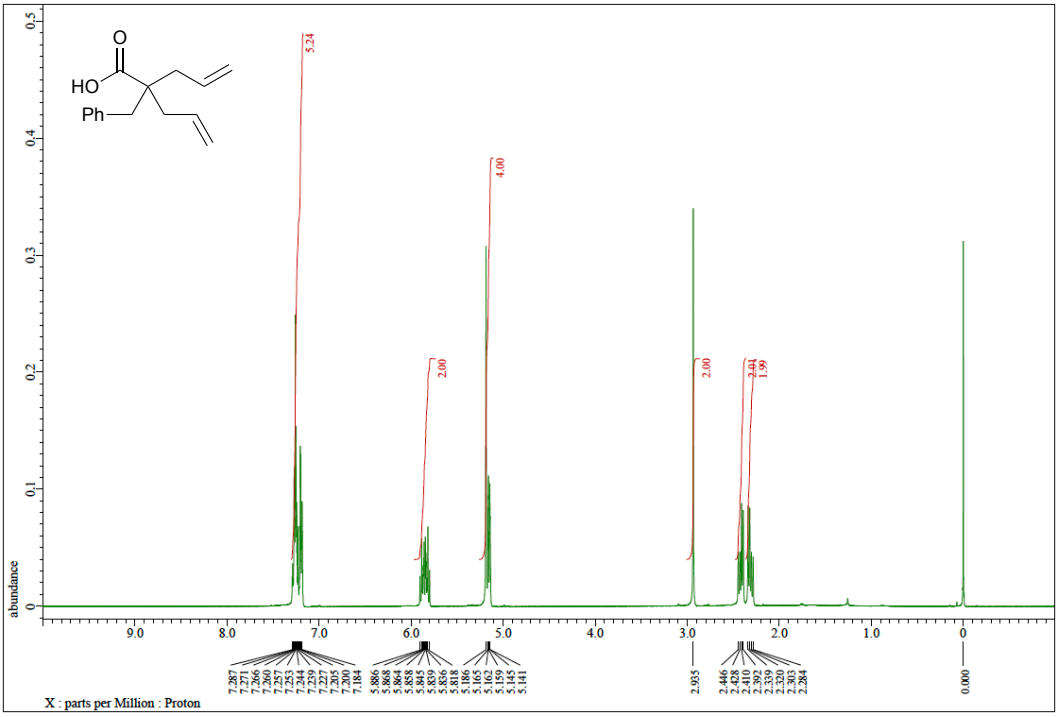
4.00
2.00
0.99
0.93
1.00
abundance
X : parts per Million : Proton


HO
O
S
(thousandths)
180.915
141.703
132.934
126.552
125.575
121.617
118.867
77.316
77.000
76.684
51.309
39.033
X : parts per Million : Carbon13


O
HO
Ph
abundance
X : parts per Million : Proton


O
HO
Ph
(thousandths)
X : parts per Million : Carbon13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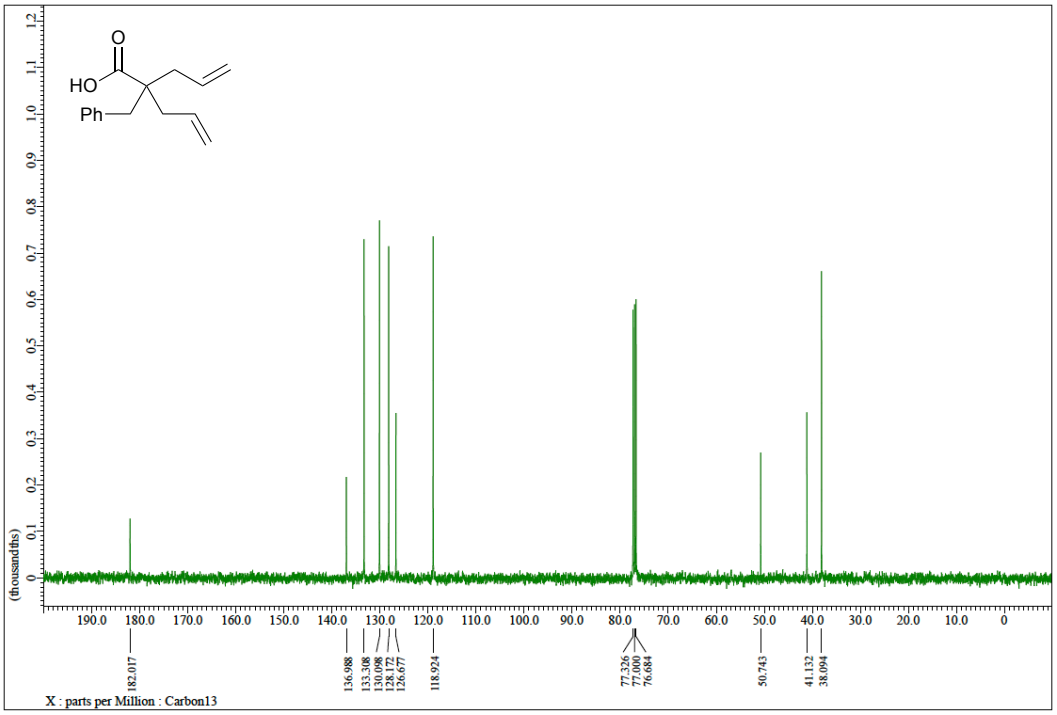
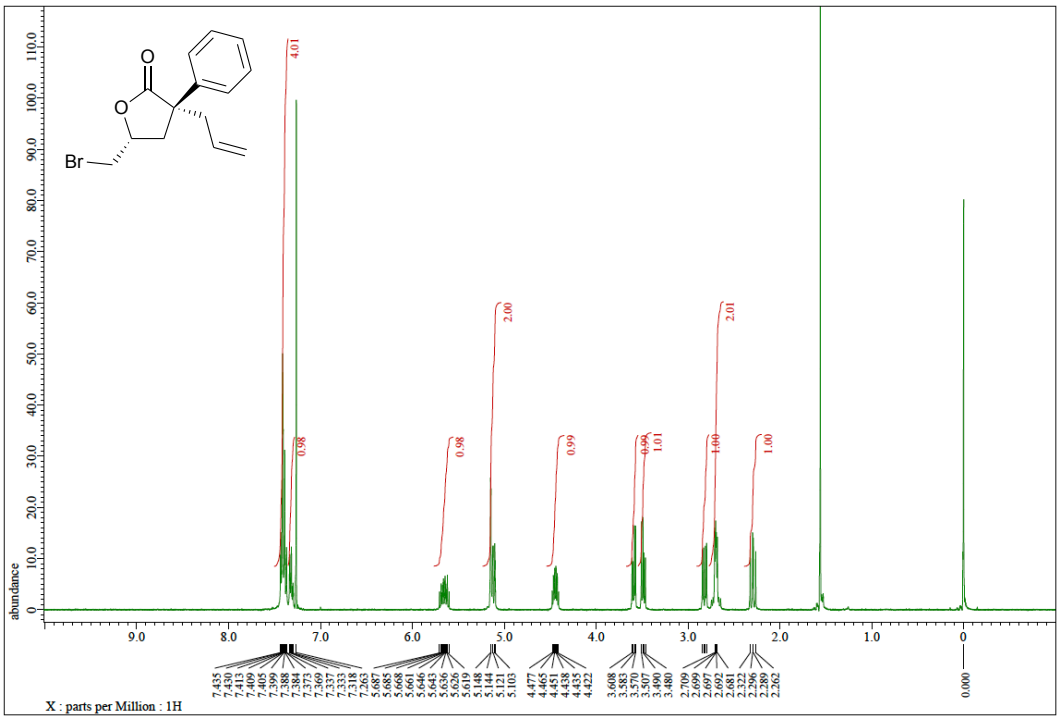
O
Ph
5.24
4.00
2.00
2.00
2.01
1.99
abundance
X : parts per Million : Proton


HO
O
Ph
(thousandths)
X : parts per Million : Carbon13


Br
O
O
4.01
0.98
0.98
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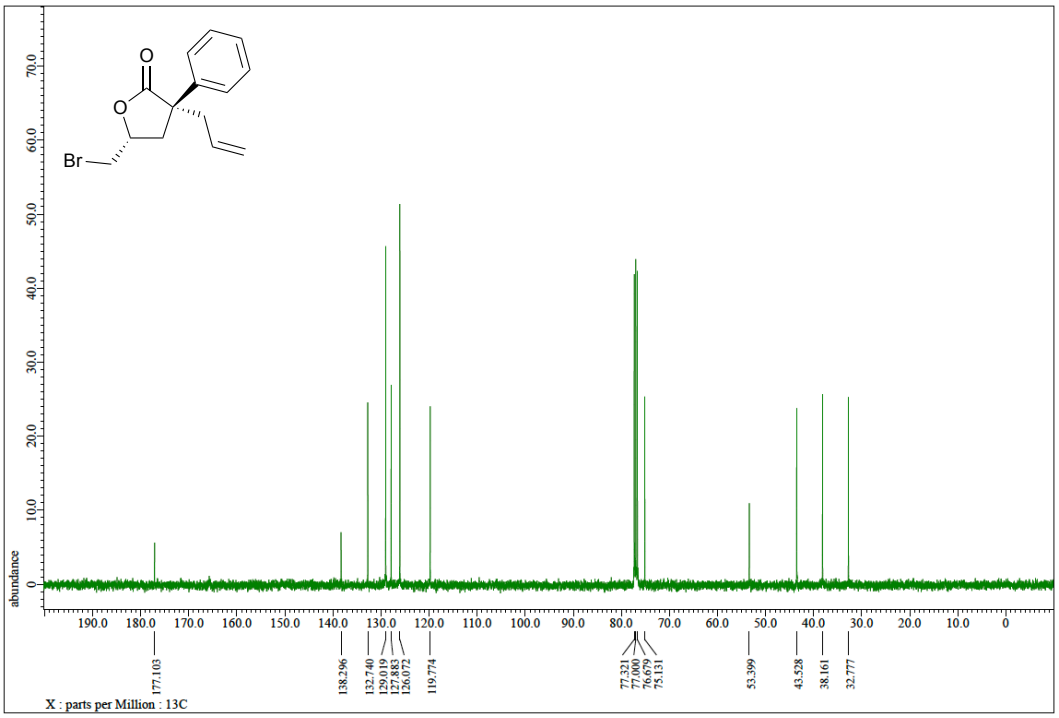
0.99
0.99
1.01
1.00
2.01
1.00
abundance
X : parts per Million : 1H


Br
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O
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77.000
76.679
75.131
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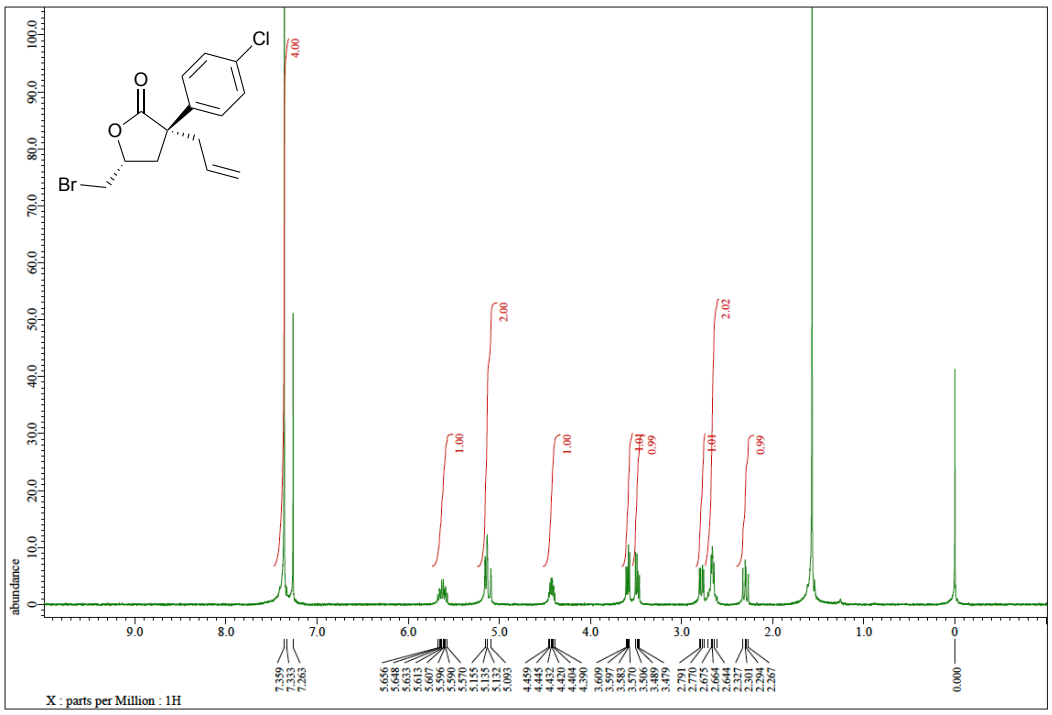
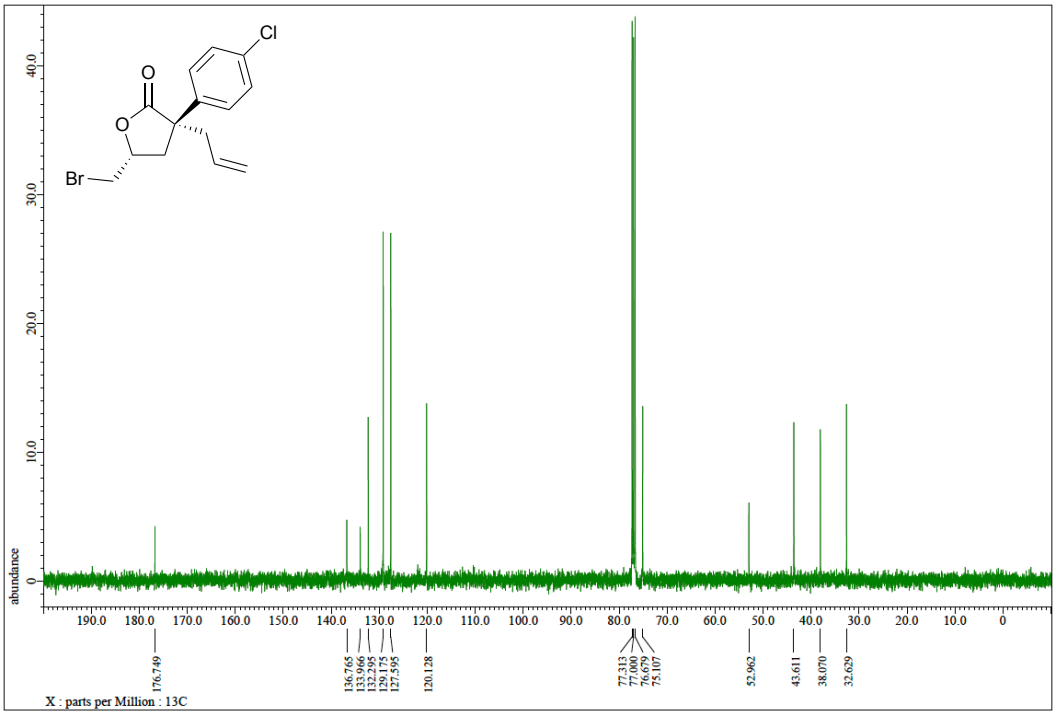
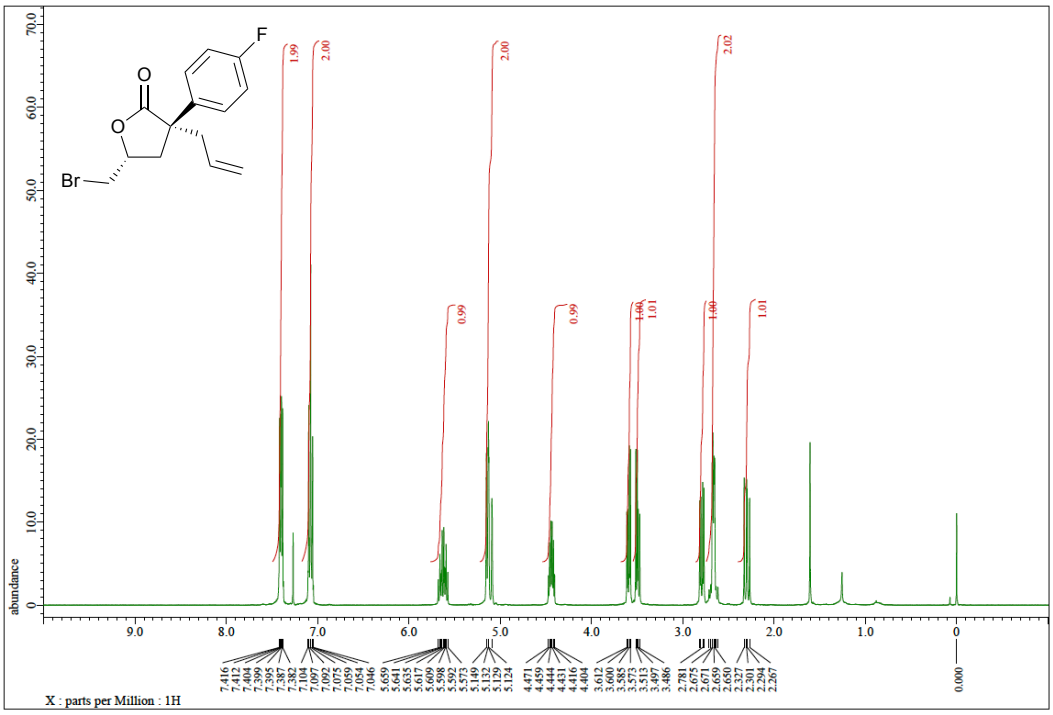
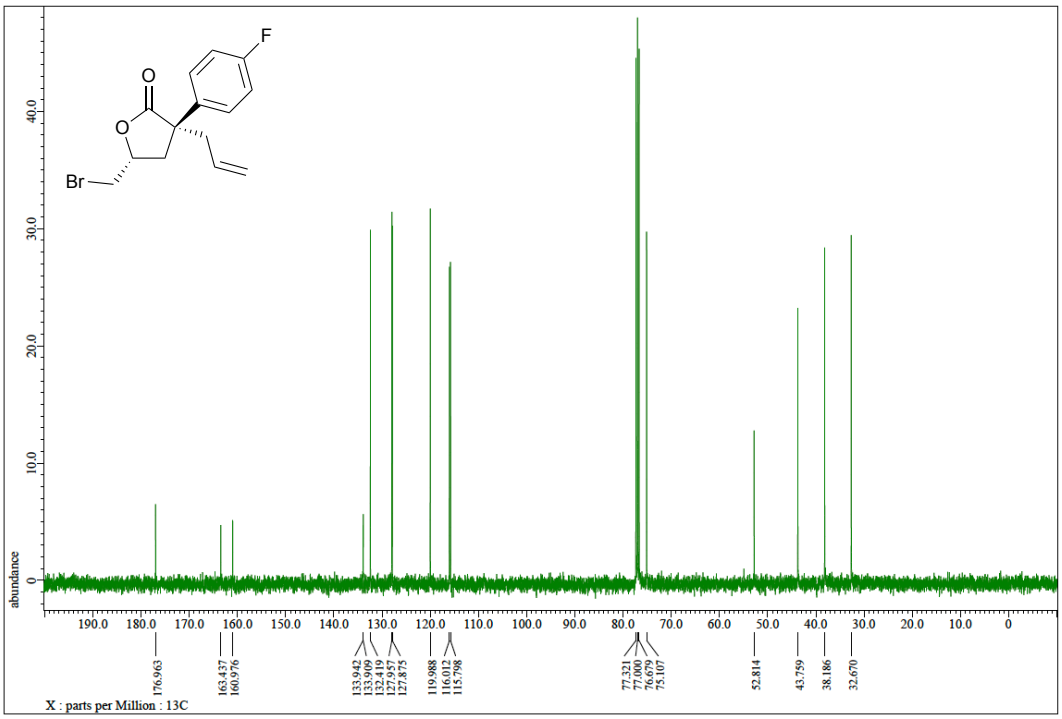
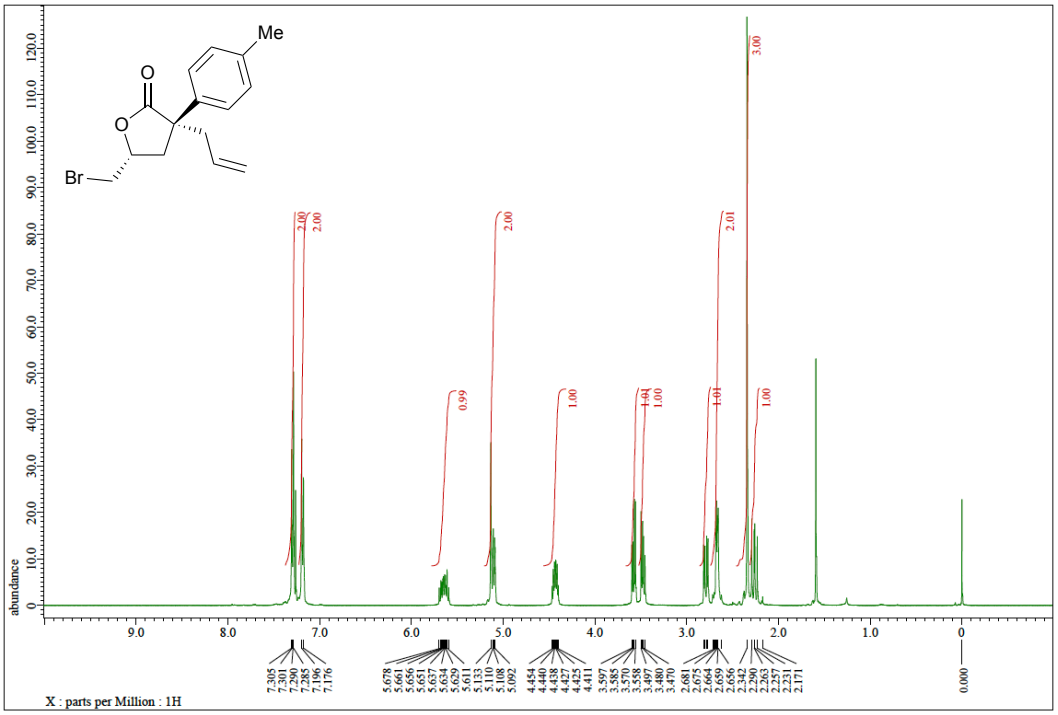
43.528
38.161
32.777
X : parts per Million : 13C

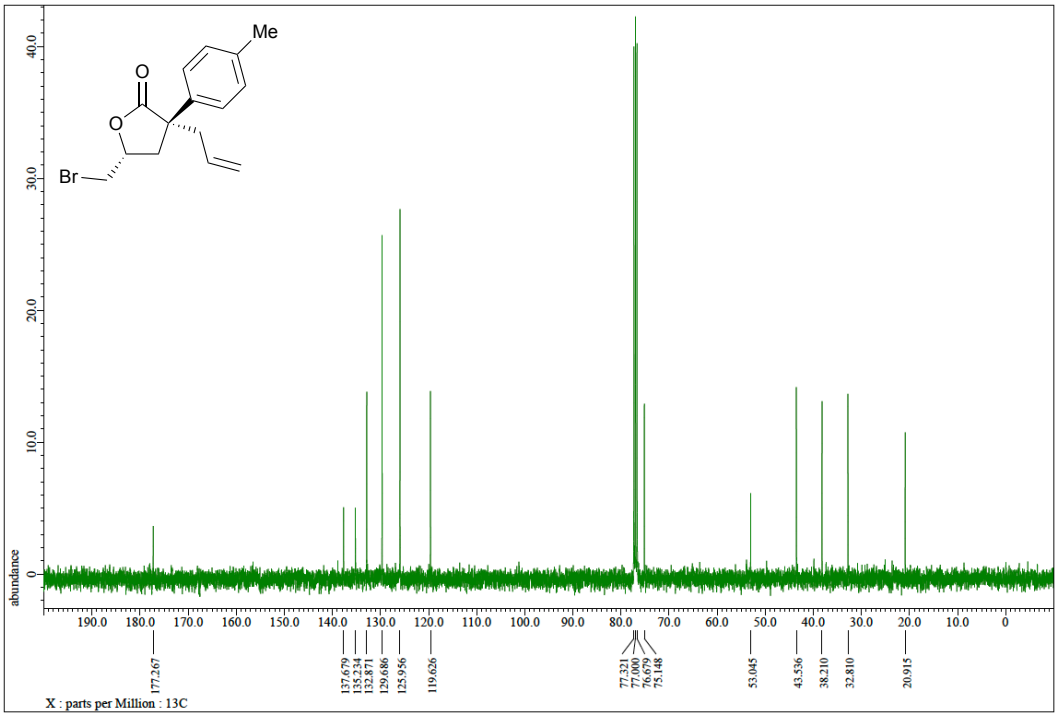

Cl
O
O
Br
abundance
X : parts per Million : 1H

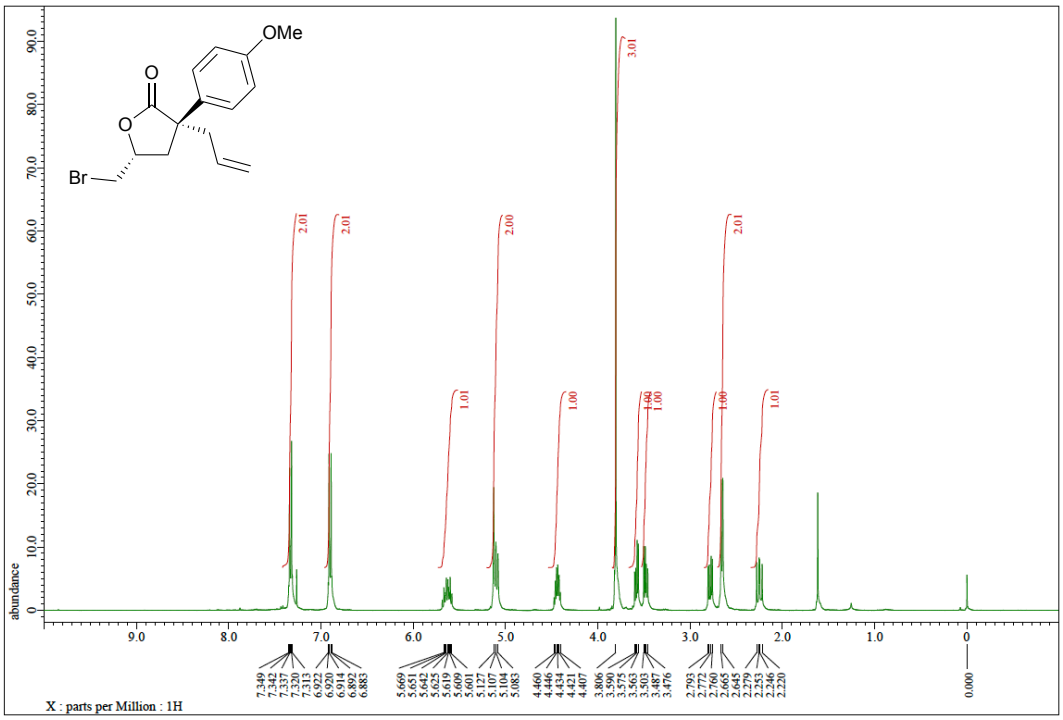

Cl
O
O
Br
abundance
X : parts per Million : 13C

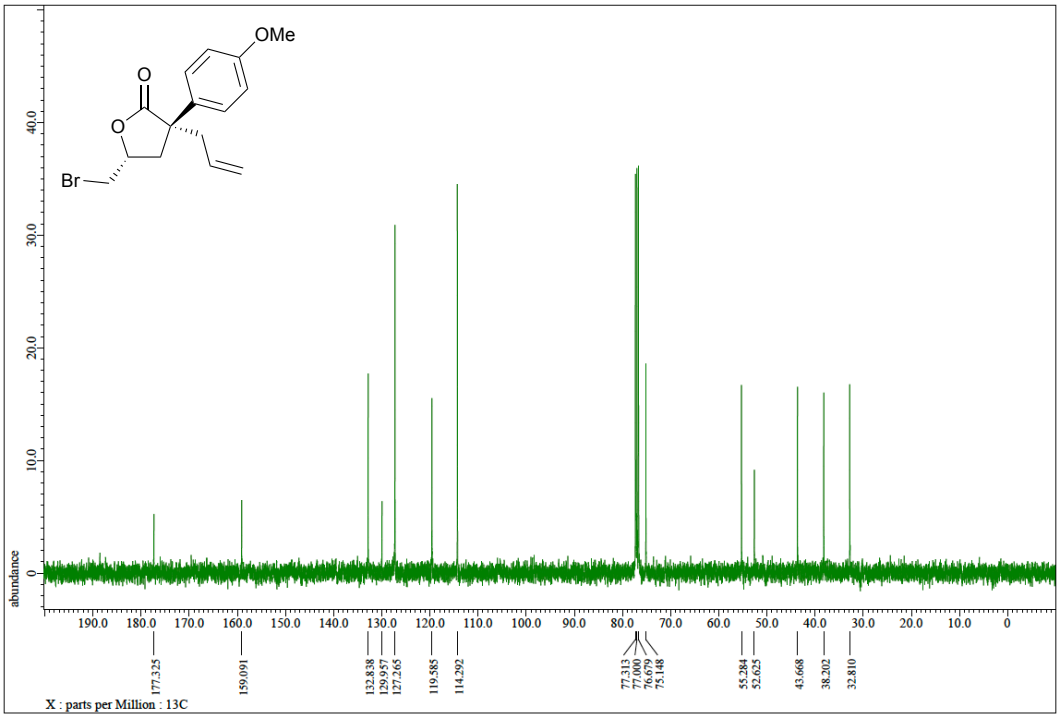

F
O
O
Br
abundance
X : parts per Million : 1H

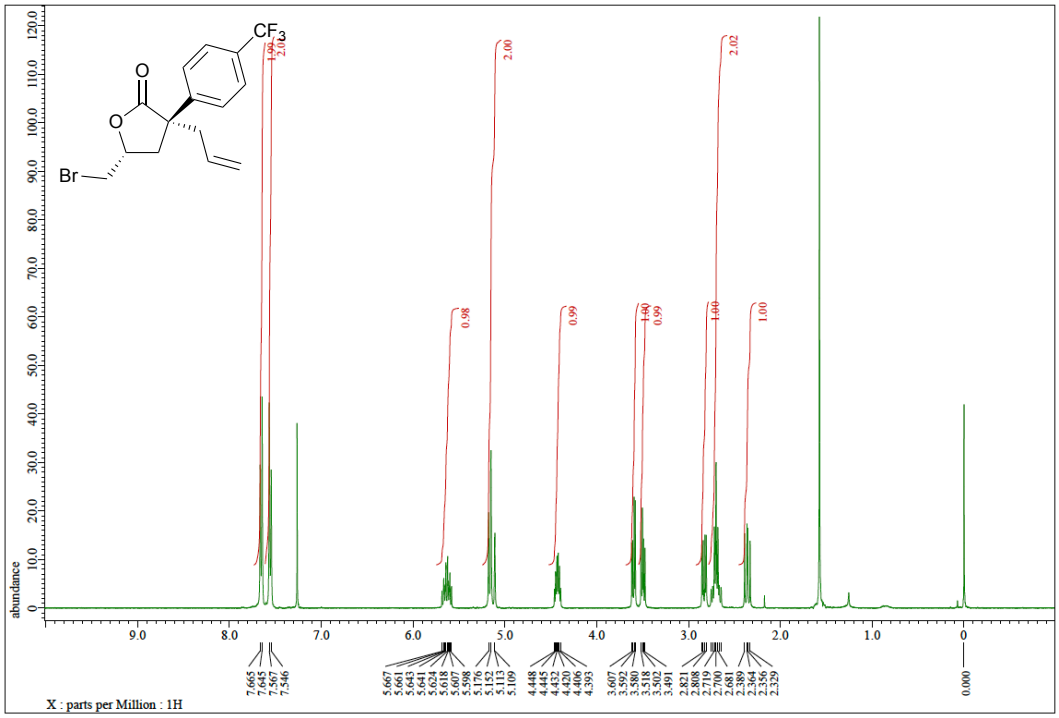

F
O
O
Br
abundance
X : parts per Million : 13C

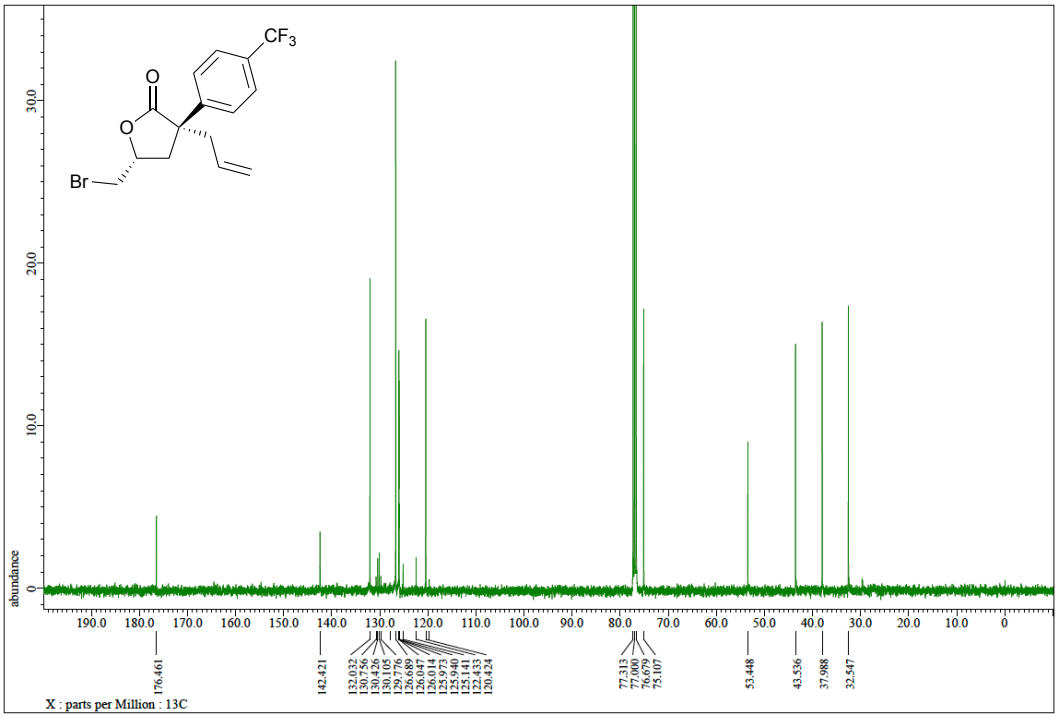

Me
O
O
Br
abundance
X : parts per Million : 1H

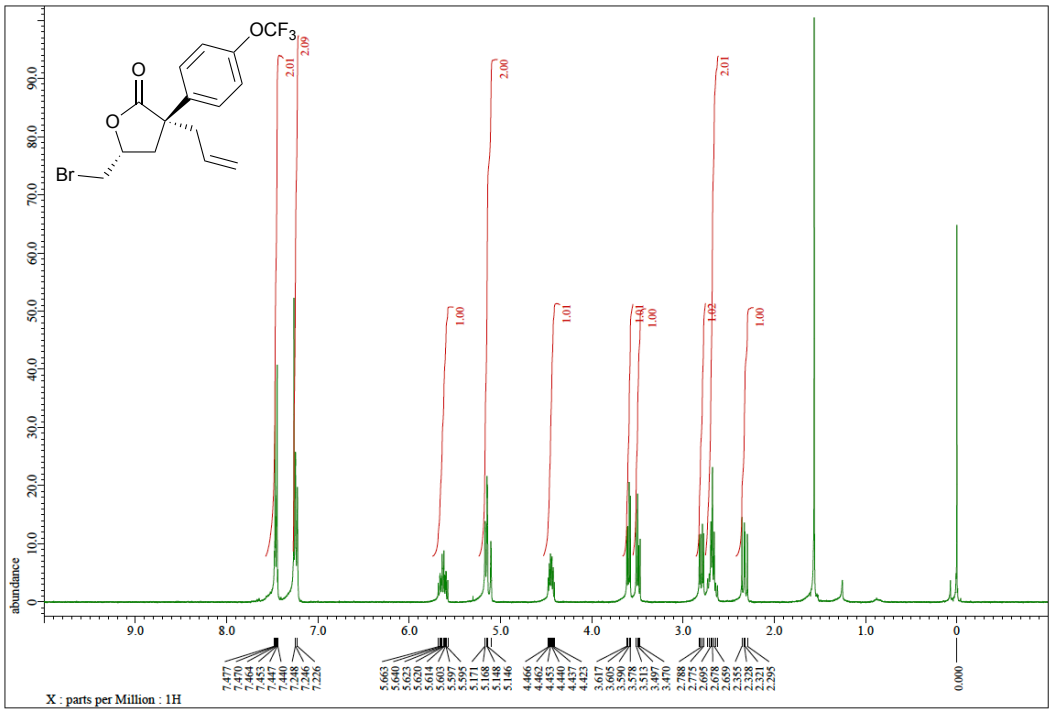

Me
O
O
Br
abundance
X : parts per Million : 13C

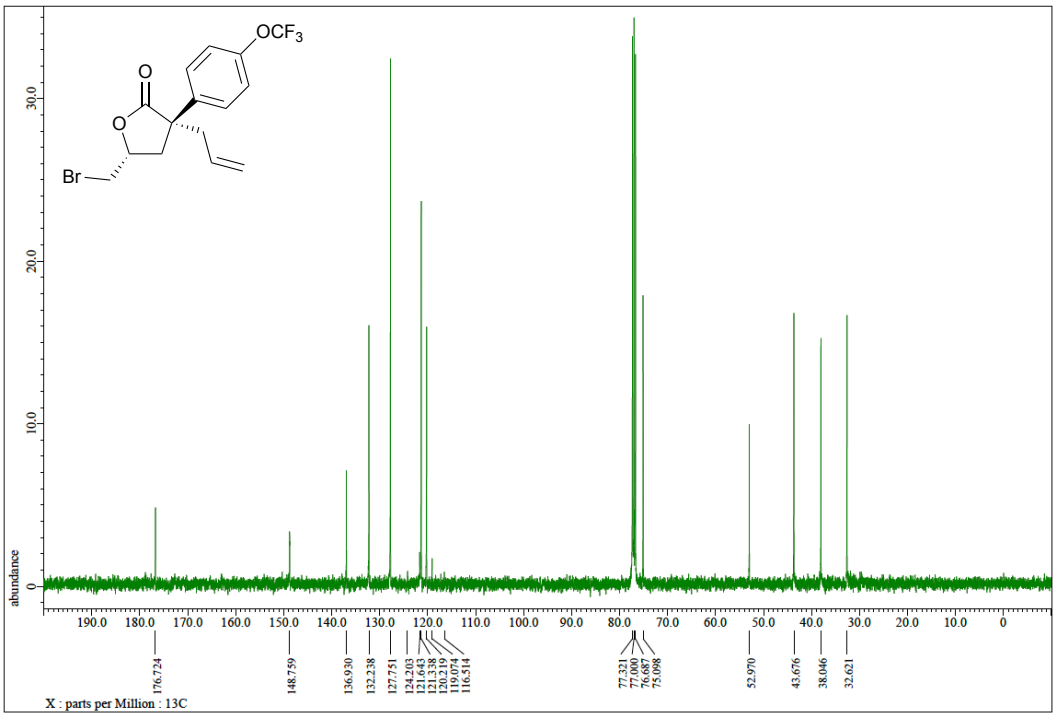

OMe
O
O
Br
abundance
X : parts per Million : 1H

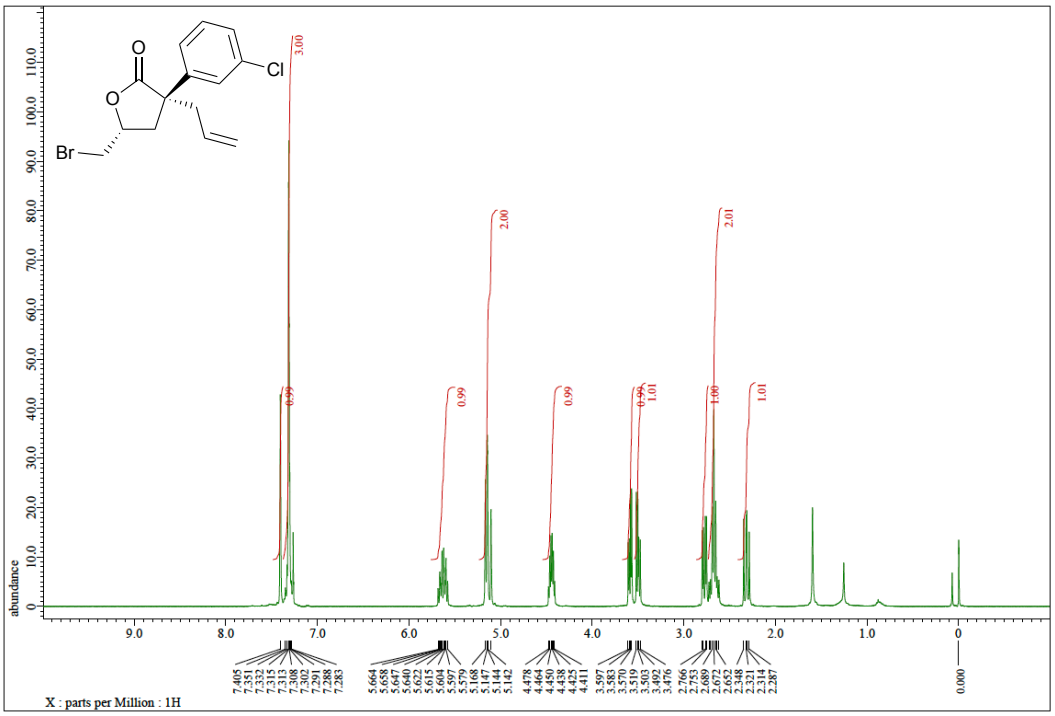

OMe
O
O
Br
abundance
X : parts per Million : 13C

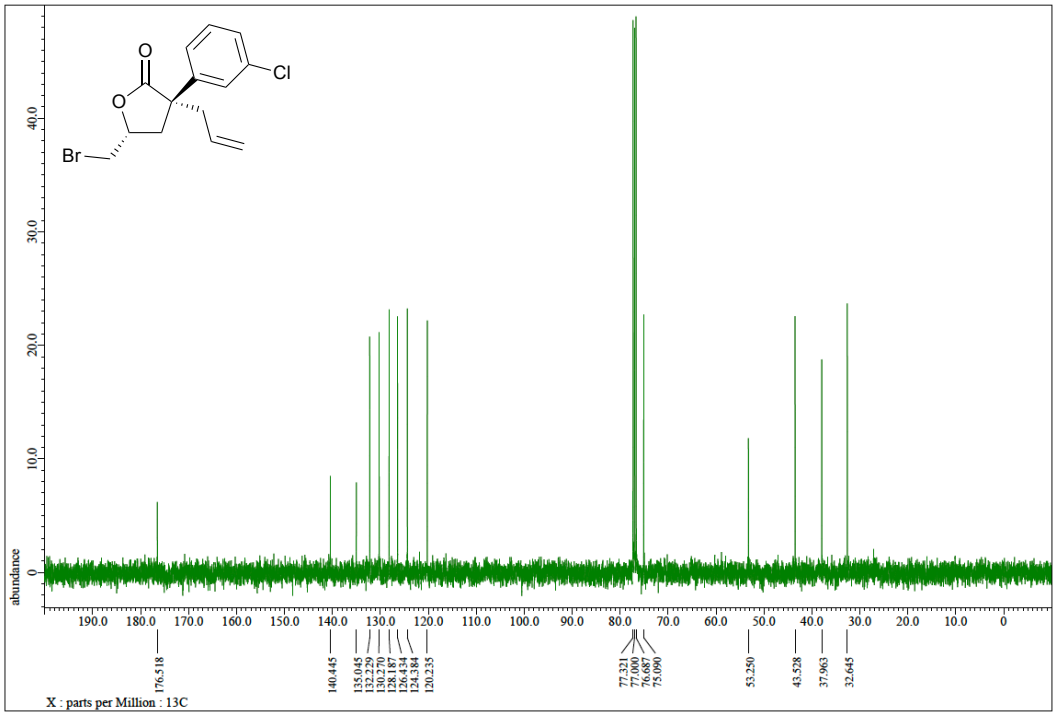

CF3
O
O
Br
abundance
X : parts per Million : 1H

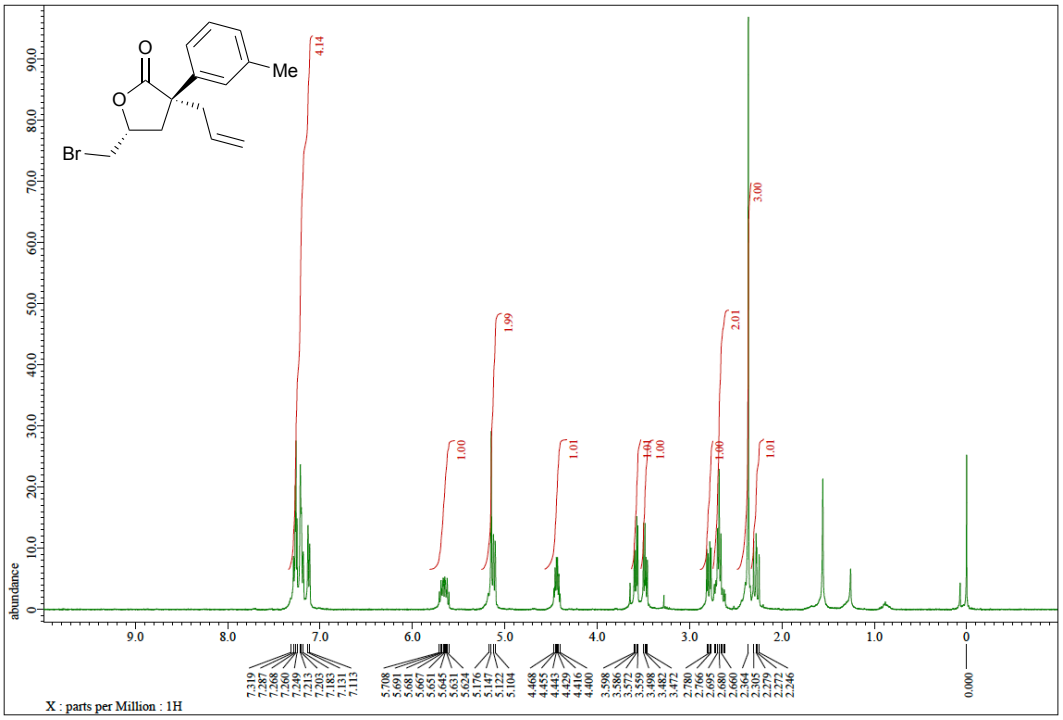

CF3
O
O
Br
abundance
X : parts per Million : 13C

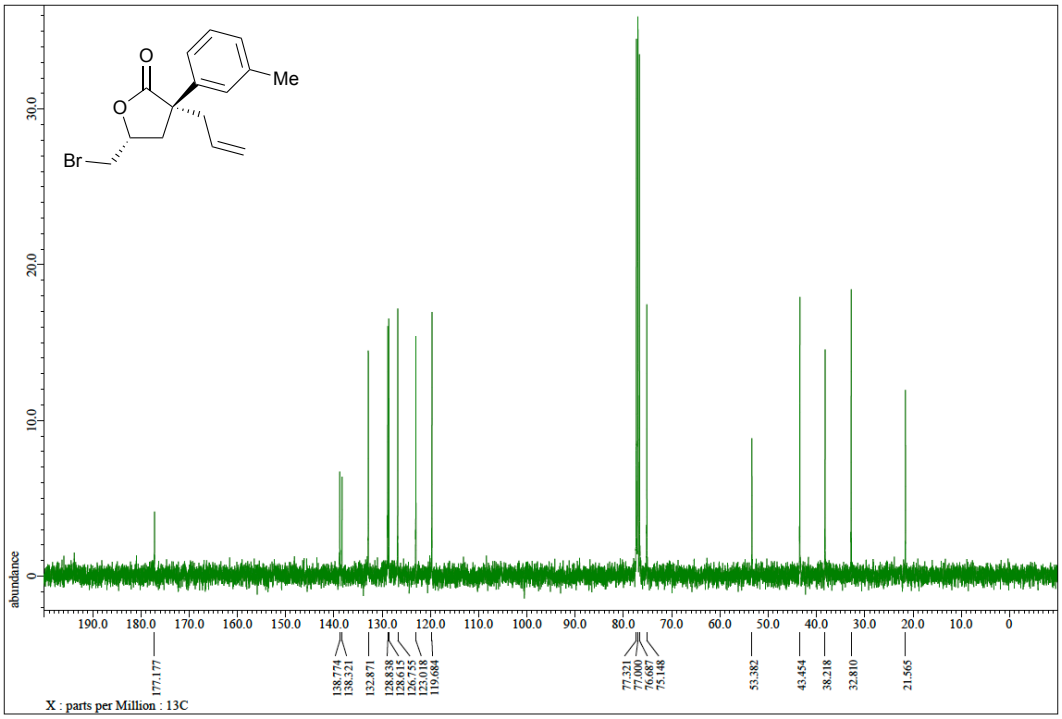

OCF3
O
O
Br
abundance
X : parts per Million : 1H

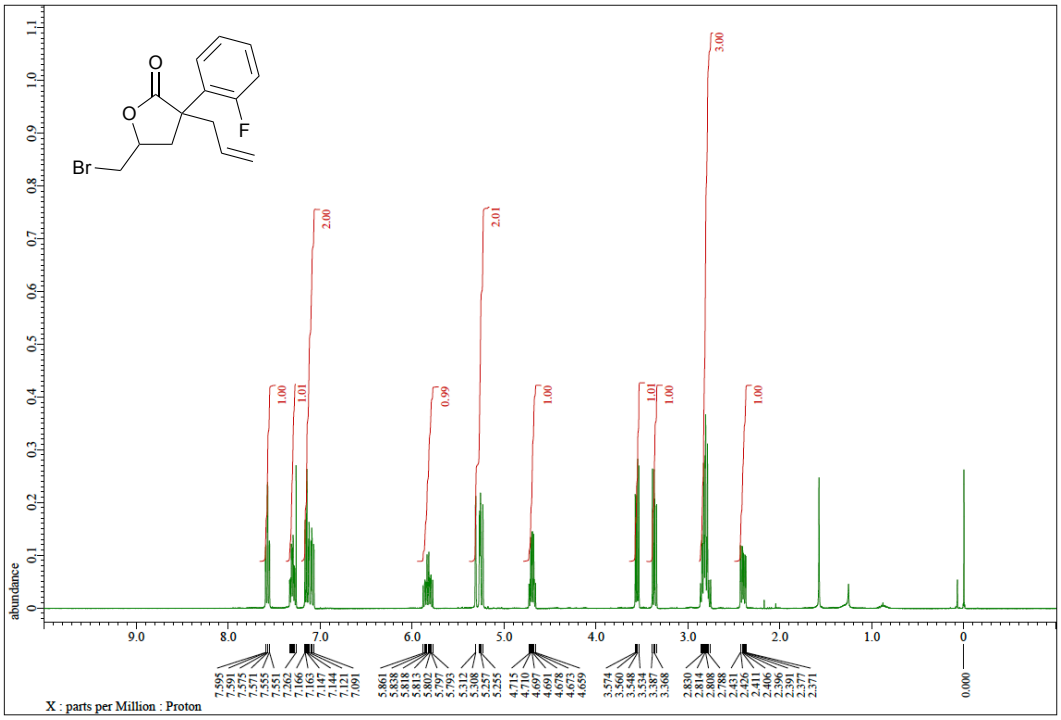

OCF3
O
O
Br
abundance
X : parts per Million : 13C

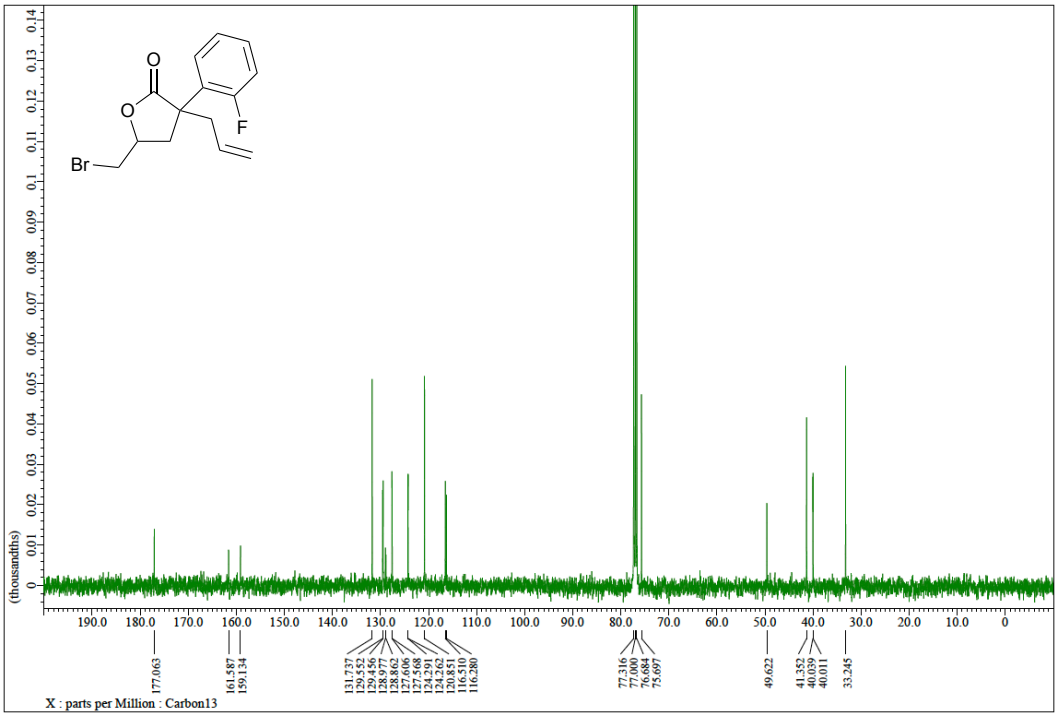

O
O
Cl
Br
3.00
2.00
2.01
0.99
0.99
0.99
1.01
1.00
1.01
abundance
X : parts per Million : 1H

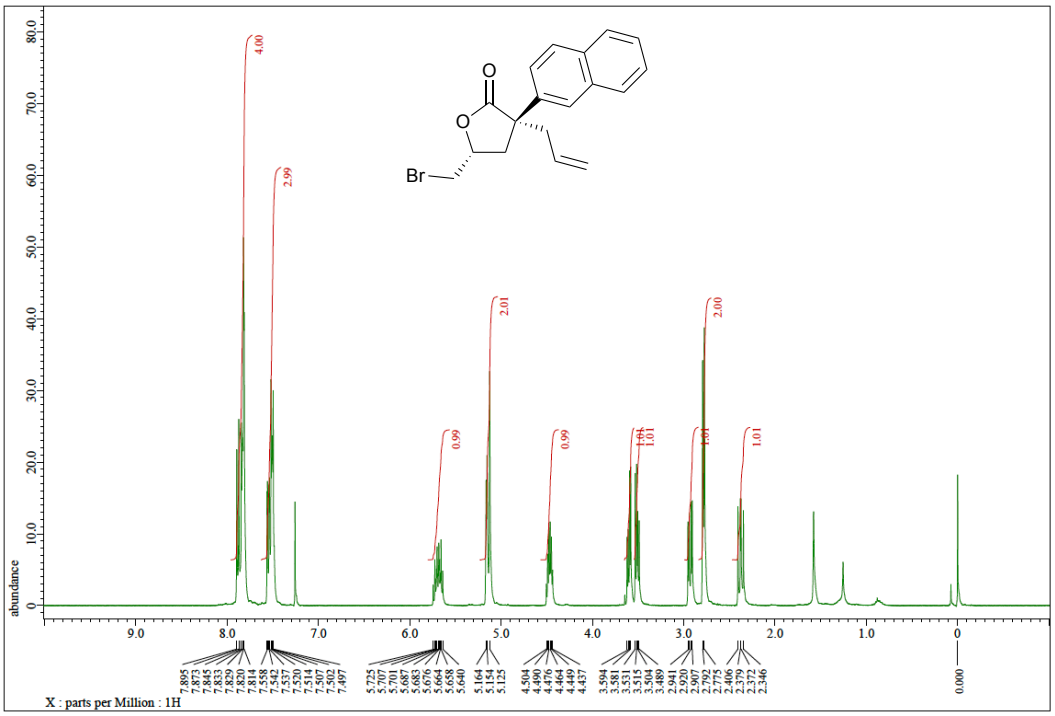

O
O
Cl
Br
abundance
X : parts per Million : 13C

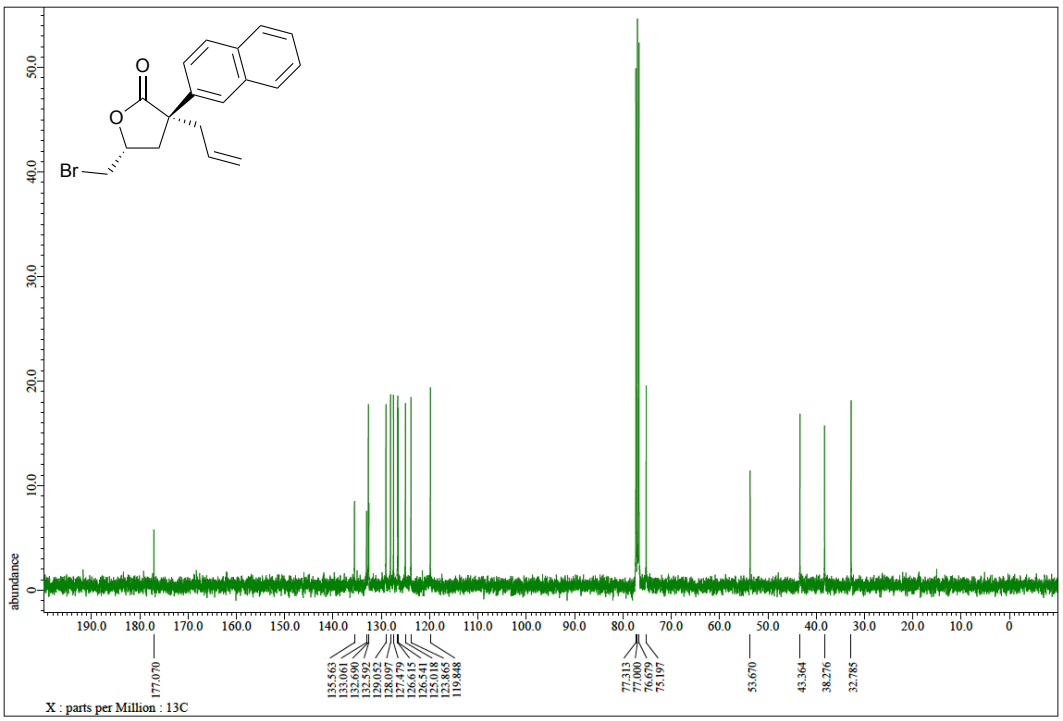

O
O
Me
Br
4.14
1.00
1.99
1.01
1.04
1.00
1.00
2.01
3.00
1.01
abundance
X : parts per Million : 1H

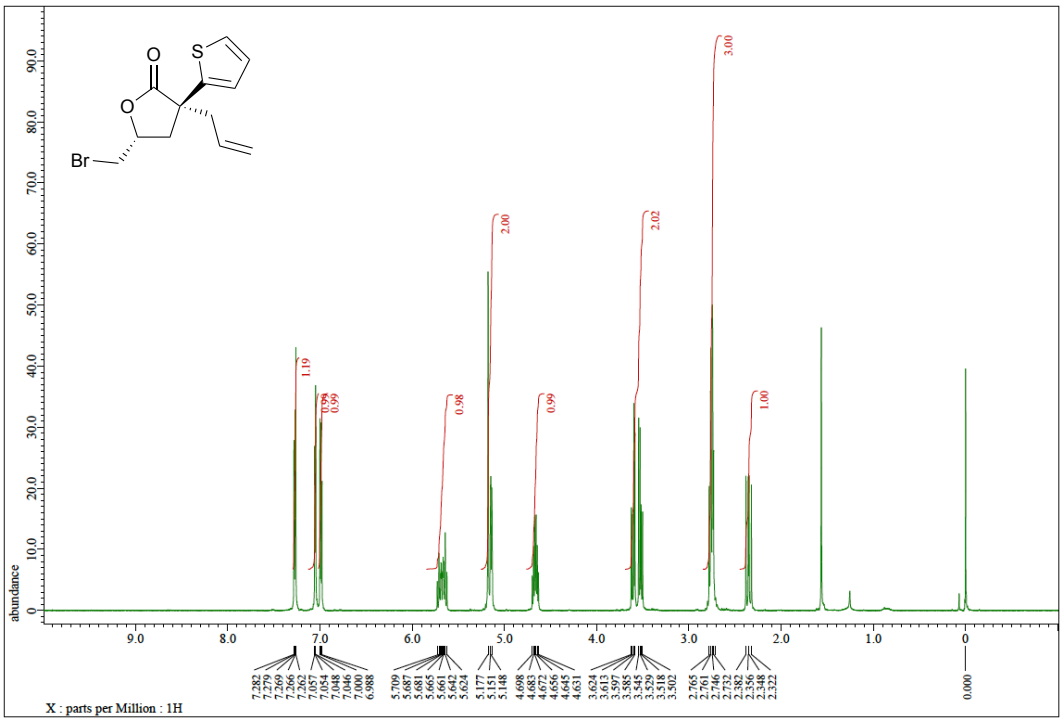

O
O
Me
Br
abundance
X : parts per Million : 13C

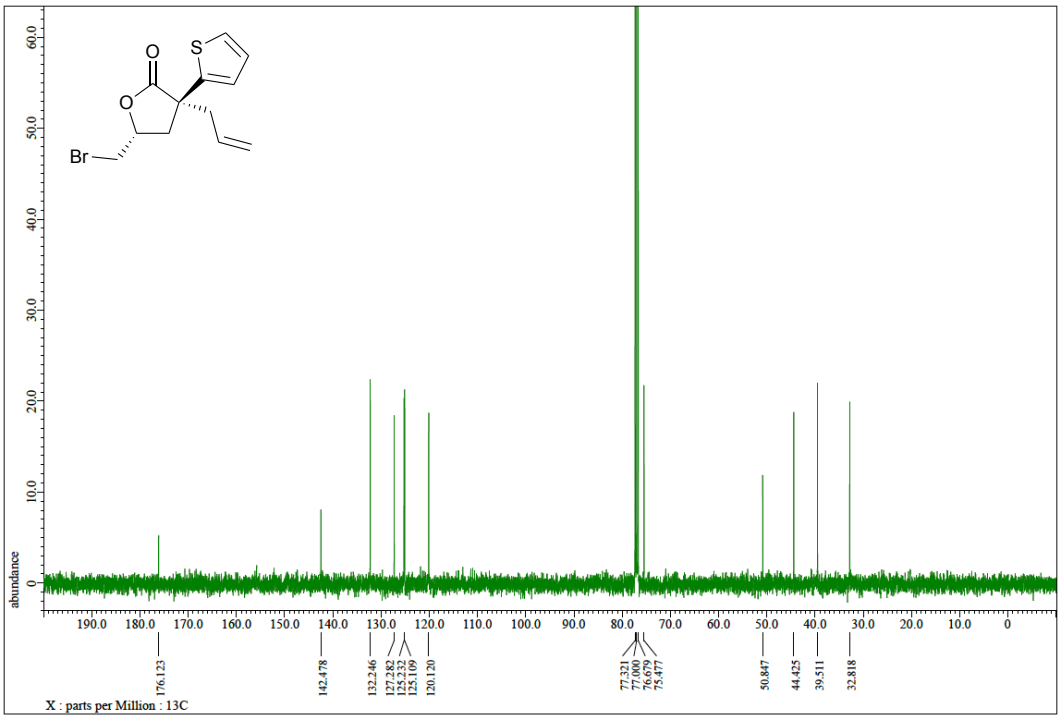

O
O
F
Br
abundance
X : parts per Million : Proton

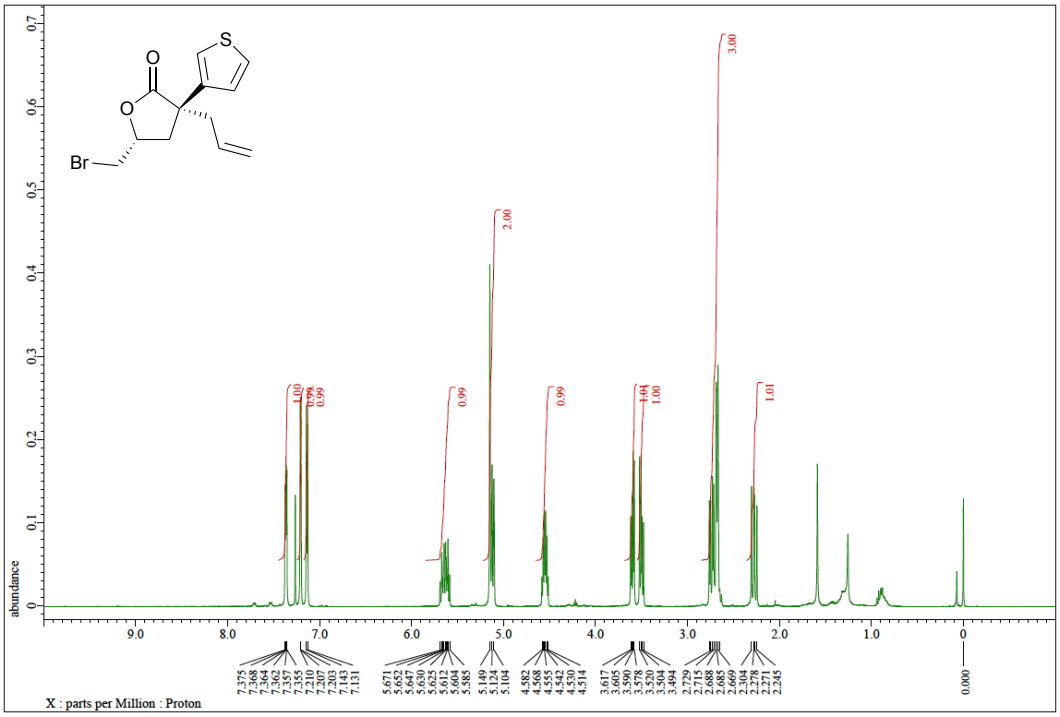

O
O
F
Br
(thousandths)
X : parts per Million : Carbon13

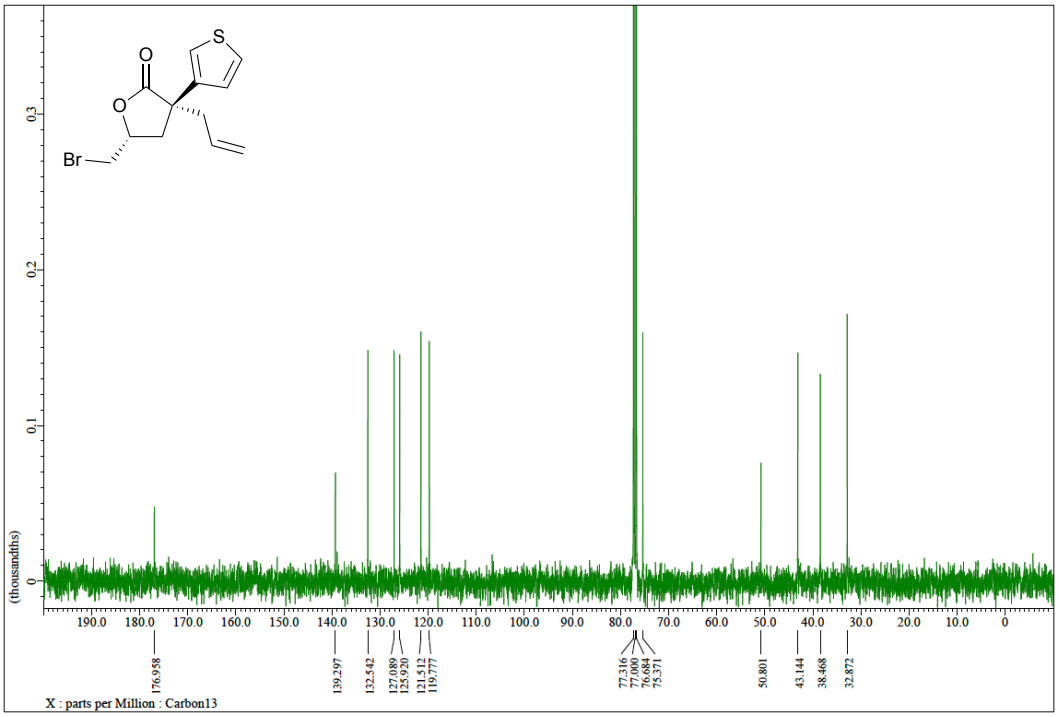

O
O
Br
4.00
2.99
2.01
2.00
0.99
0.99
1.01
1.01
1.00
1.01
abundance
X : parts per Million : 1H

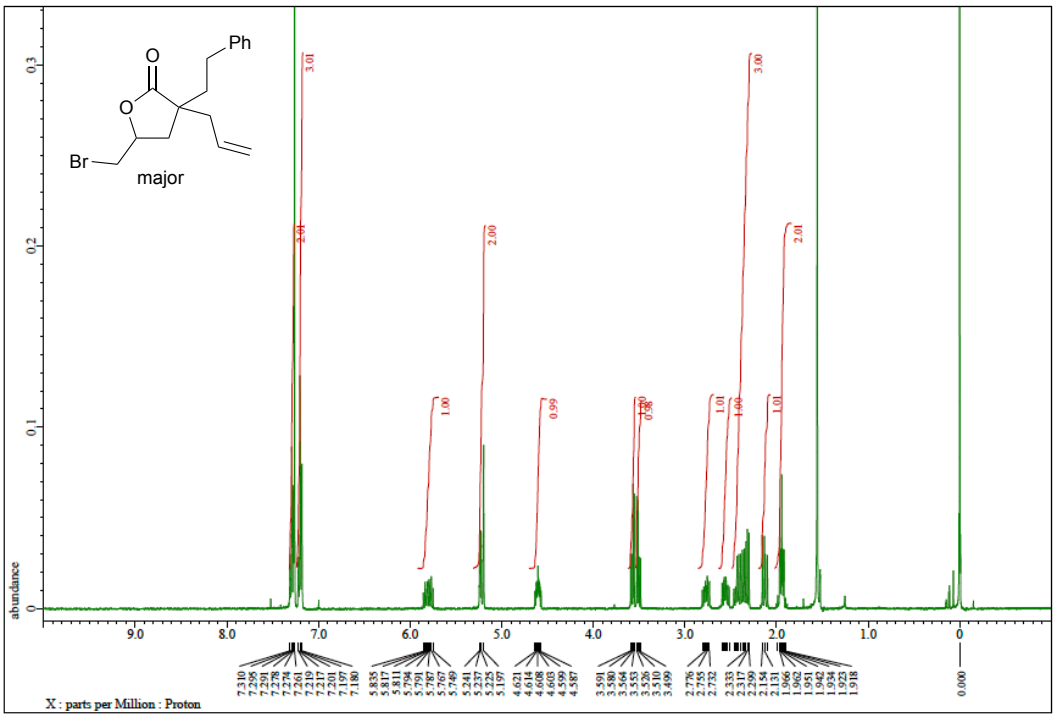

O
O
Br
abundance
177.070
135.563
133.641
132.690
132.592
129.052
128.097
127.479
126.615
126.541
125.018
123.865
119.848
77.313
77.000
76.679
75.197
53.670
43.364
38.276
32.785
X : parts per Million : 13C

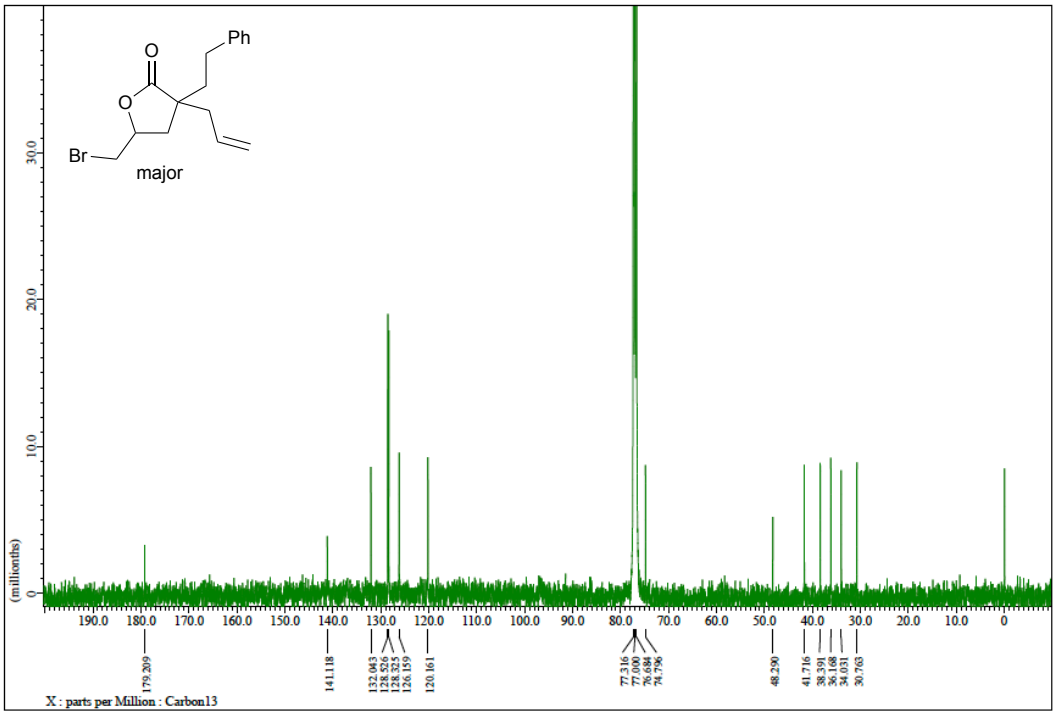

O
S
O
Br
abundance
X : parts per Million : 1H

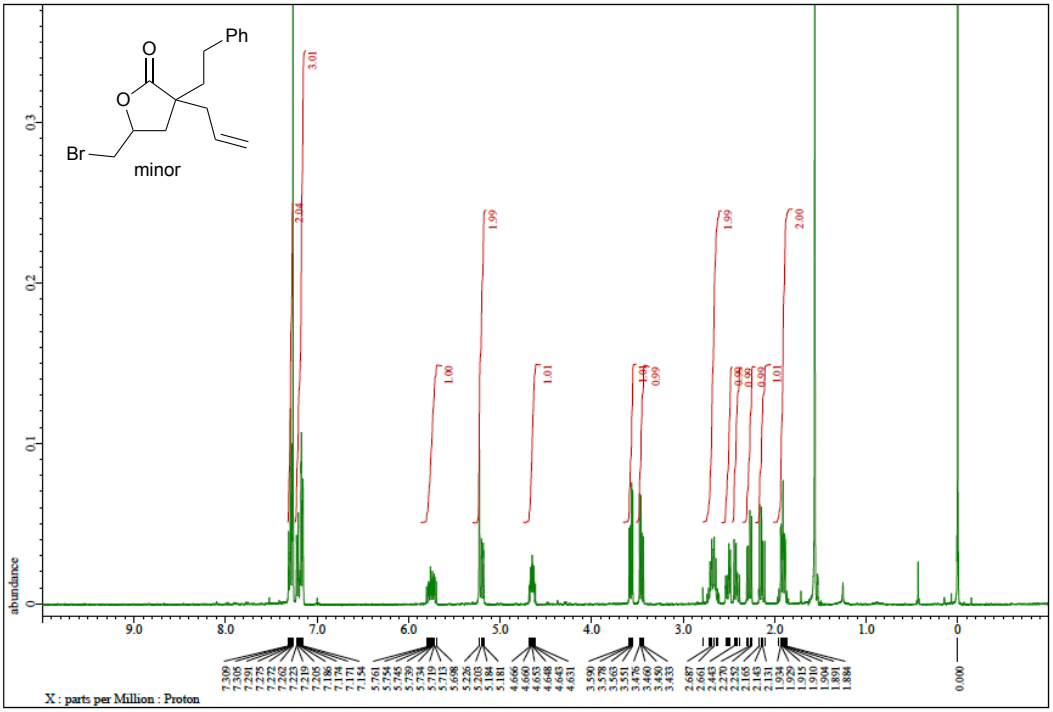

O
S
O
Br
abundance
X : parts per Million : 13C

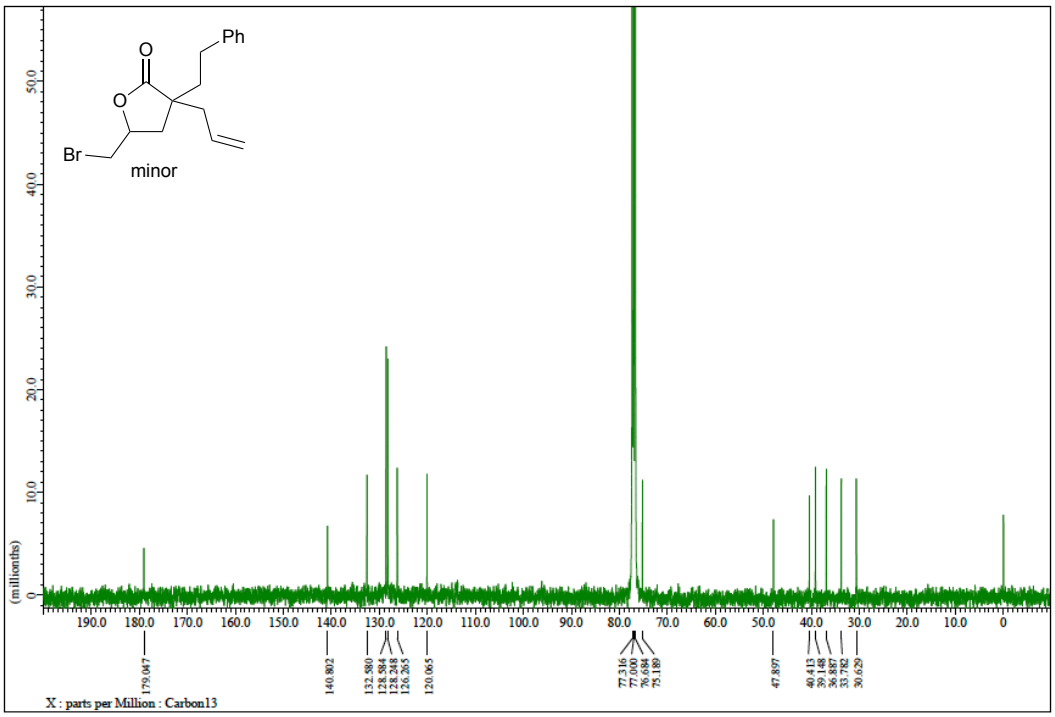

O
S
O
Br
abundance
X : parts per Million : Proton

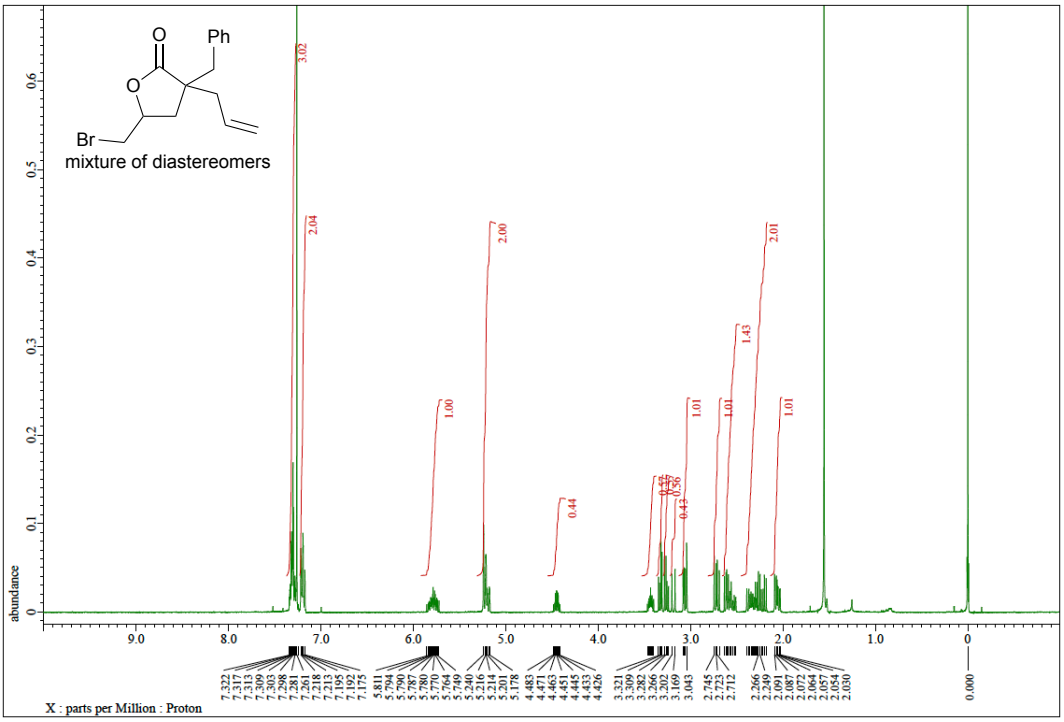

O
S
O
Br
(thousandths)
X : parts per Million : Carbon13

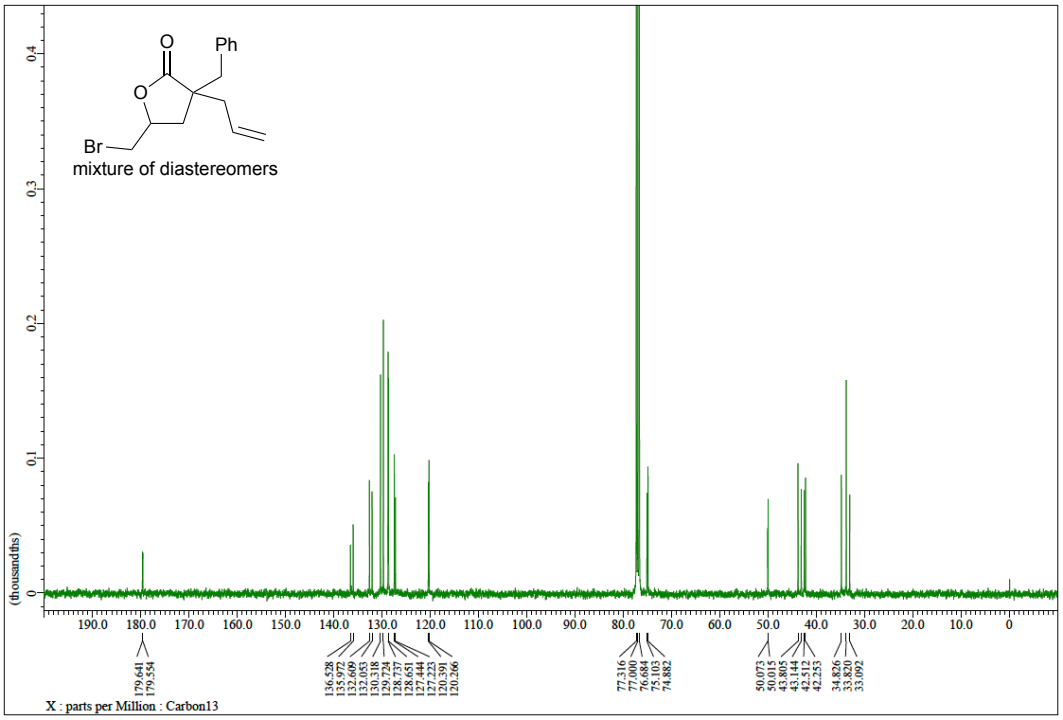

Ph
O
O
Br
major
abundance
X : parts per Million : Proton

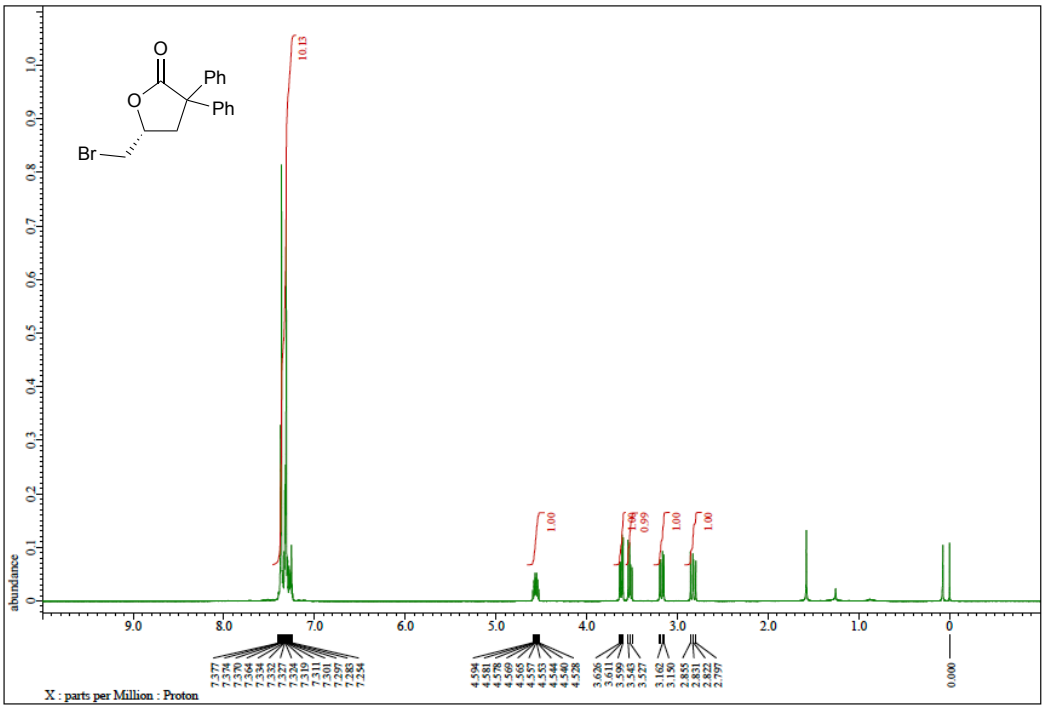

Ph
O
O
Br
major
(millionths)
X : parts per Million : Carbon13

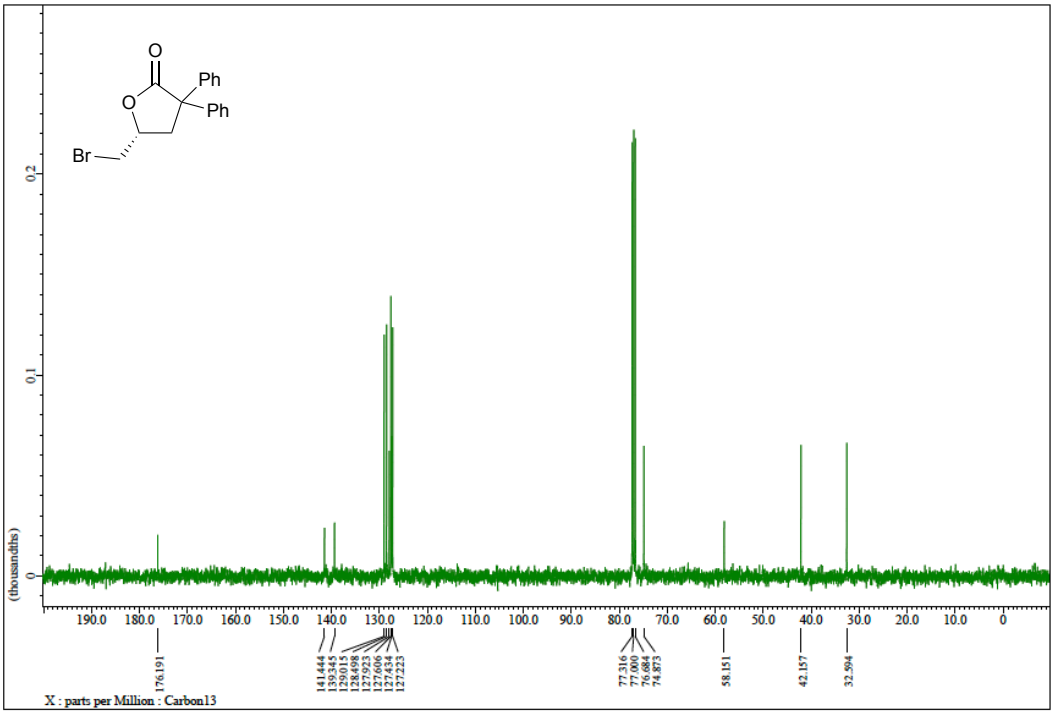

Ph
O
O
Br
minor
abundance
X : parts per Million : Proton

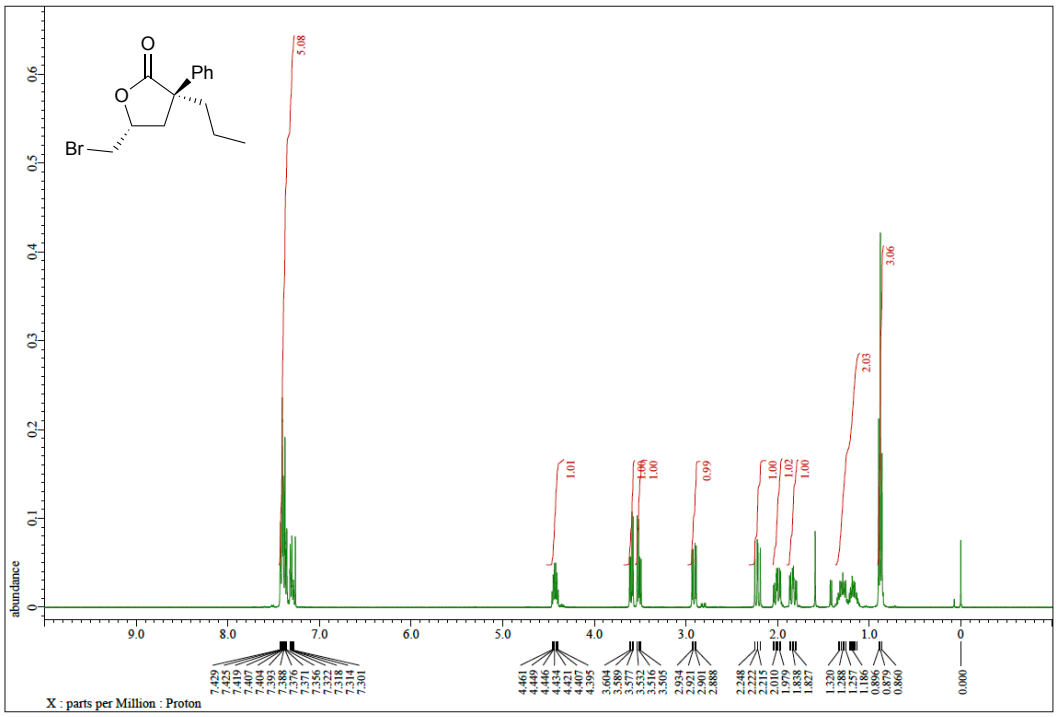

Ph
O
O
Br
minor
(millionths)
X : parts per Million : Carbon13

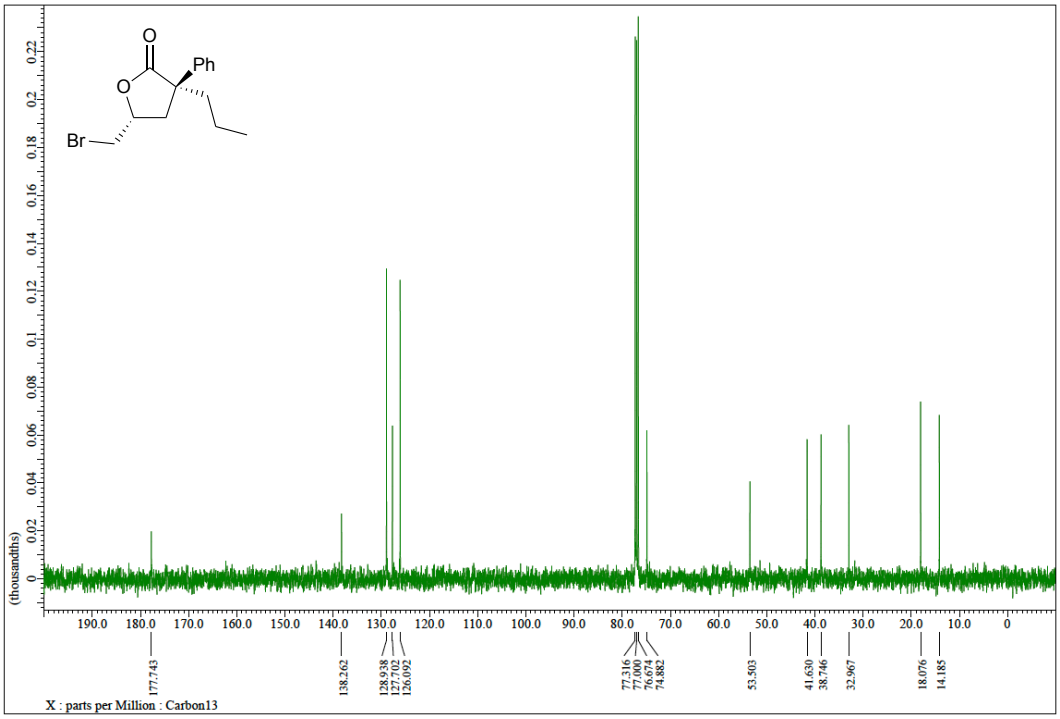

O
Ph
O
Br
mixture of diastereomers
abundance
X : parts per Million : Proton

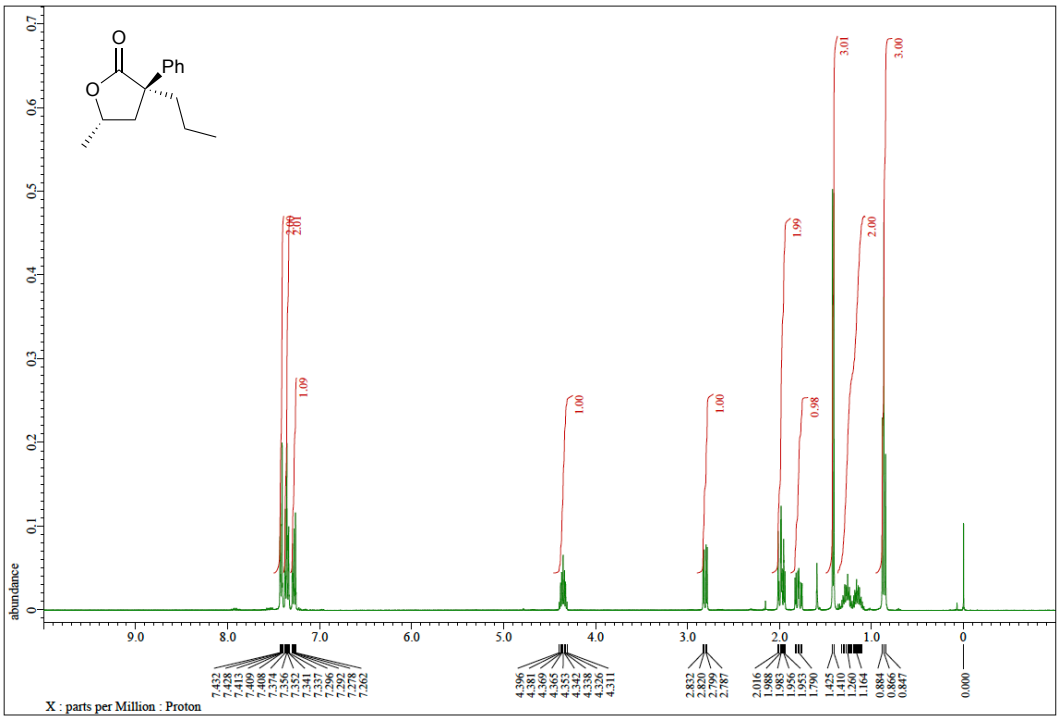

O
Ph
O
Br
mixture of diastereomers
(thousandths)
X : parts per Million : Carbon13

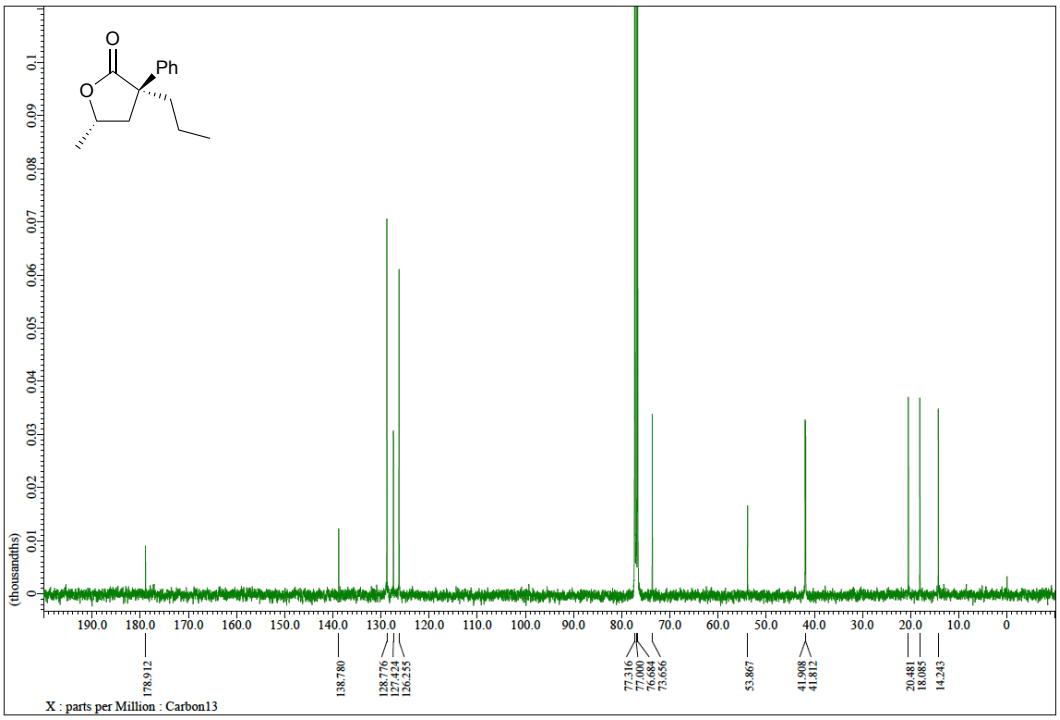

O
Ph
Ph
O
Br
abundance
X : parts per Million : Proton

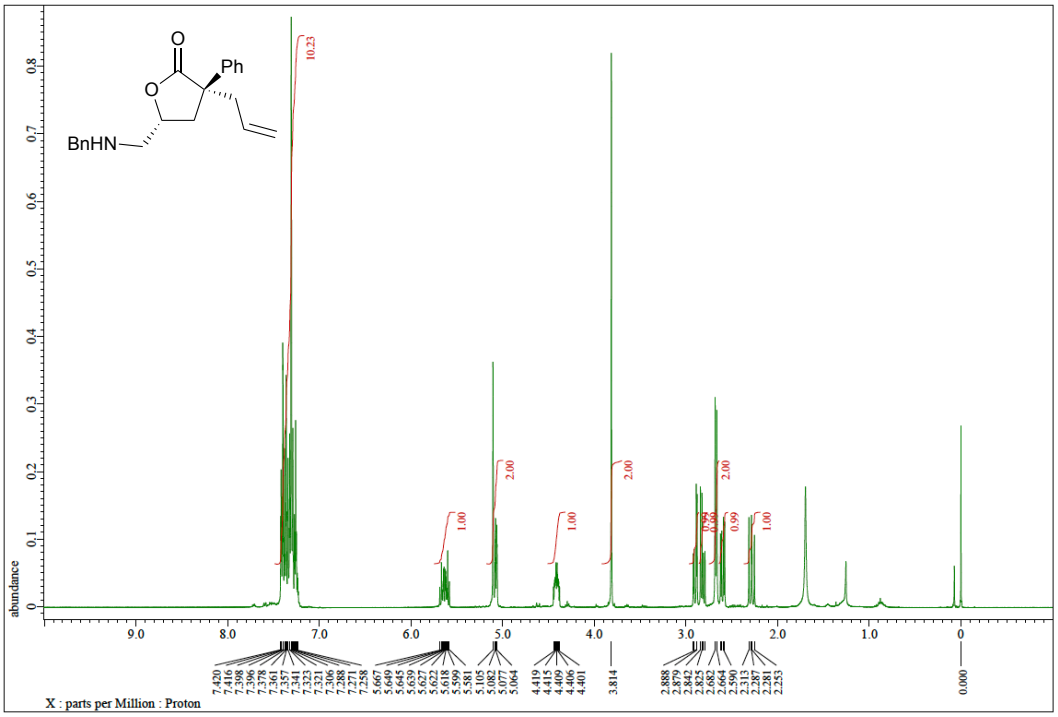

O
Ph
Ph
O
Br
(thousandths)
X : parts per Million : Carbon13

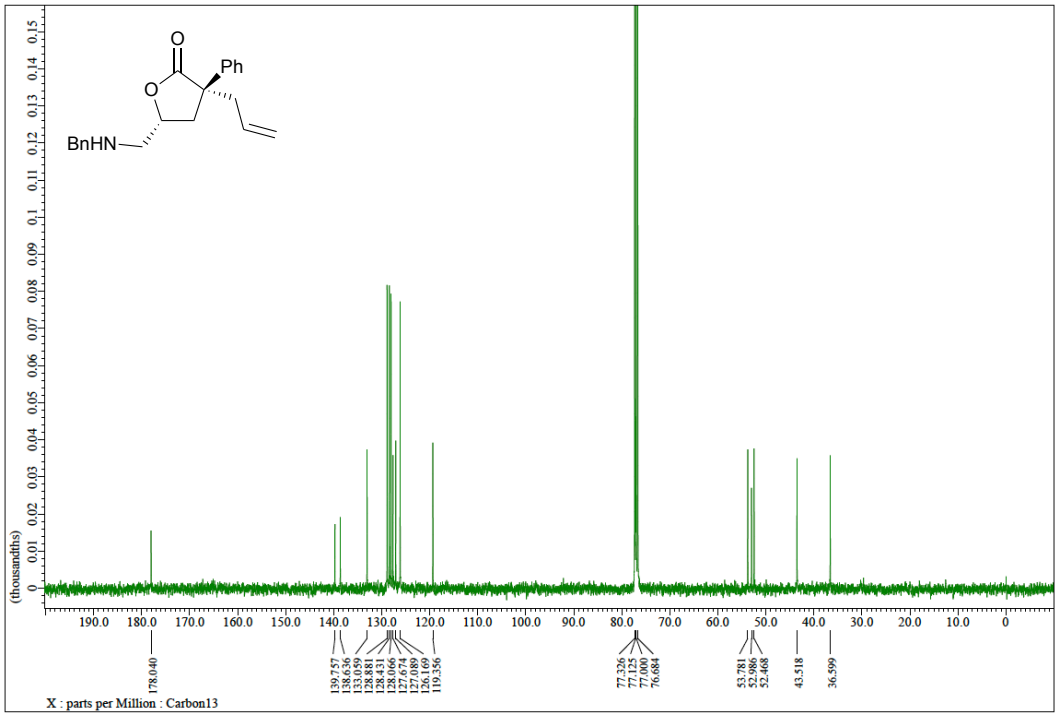

O
Ph
O
Br
abundance
X : parts per Million : Proton

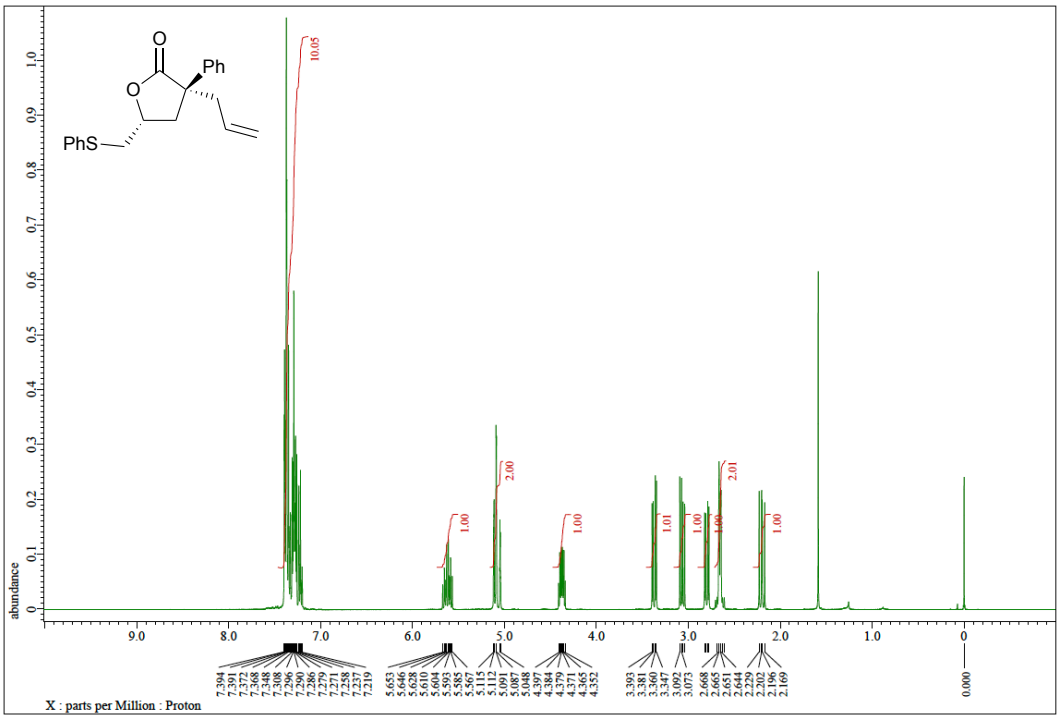

O
Ph
O
Br
(thousandths)
X : parts per Million : Carbon13

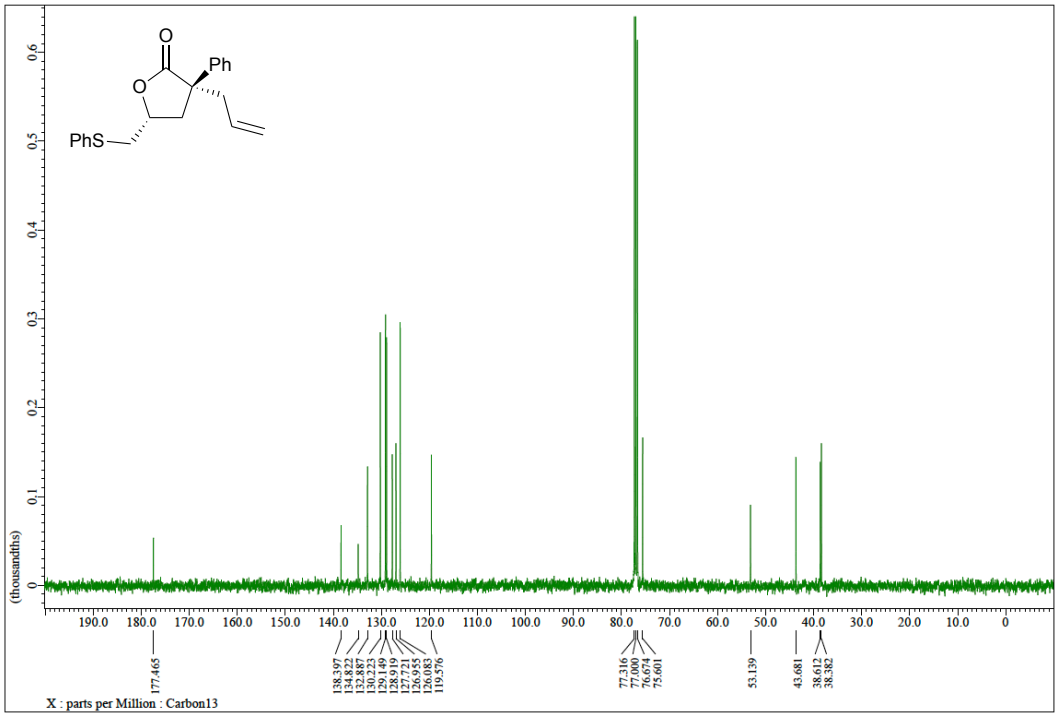

O
Ph
O
abundance
X : parts per Million : Proton

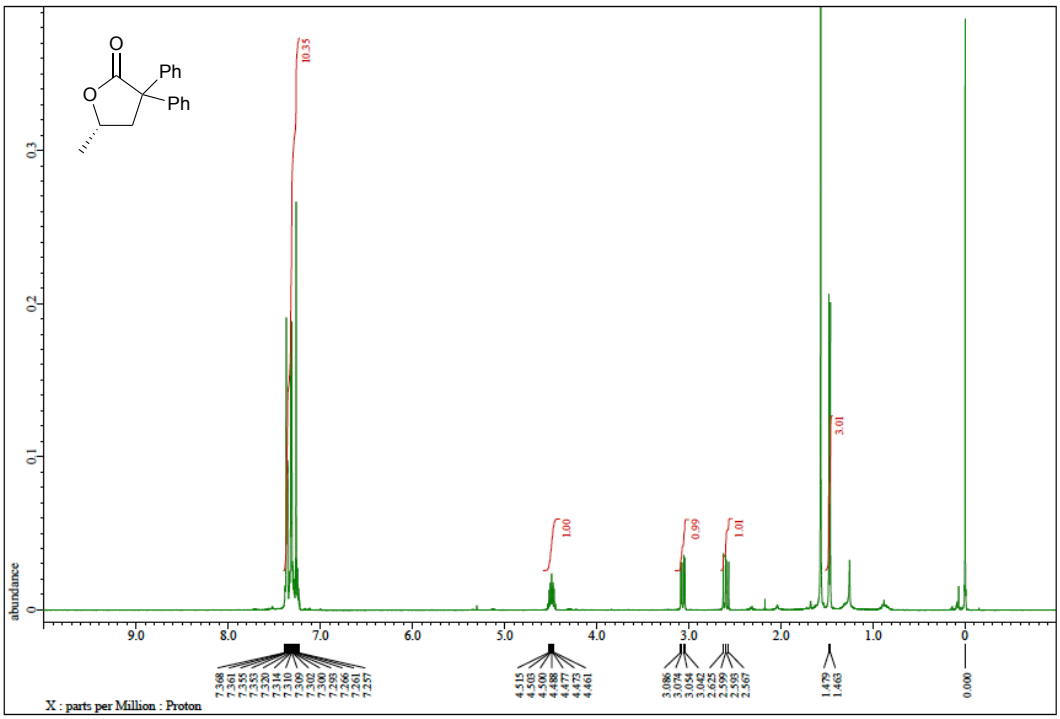

O
Ph
O
(thousandths)
X : parts per Million : Carbon13

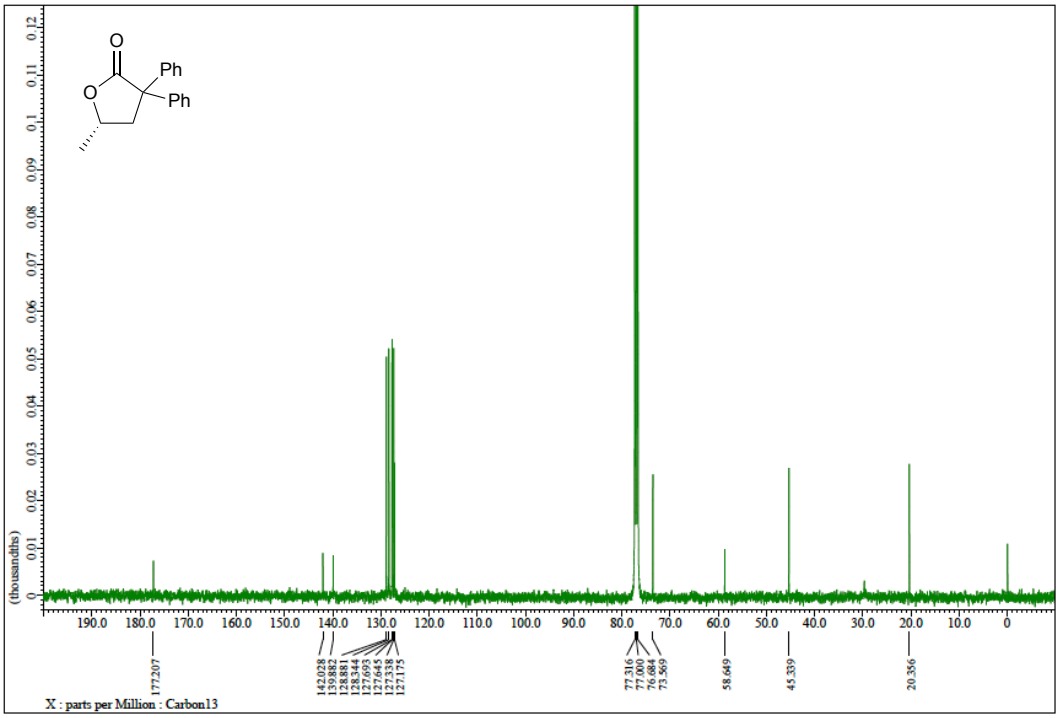

O
O
Ph
BnHN
abundance
X : parts per Million : Proton

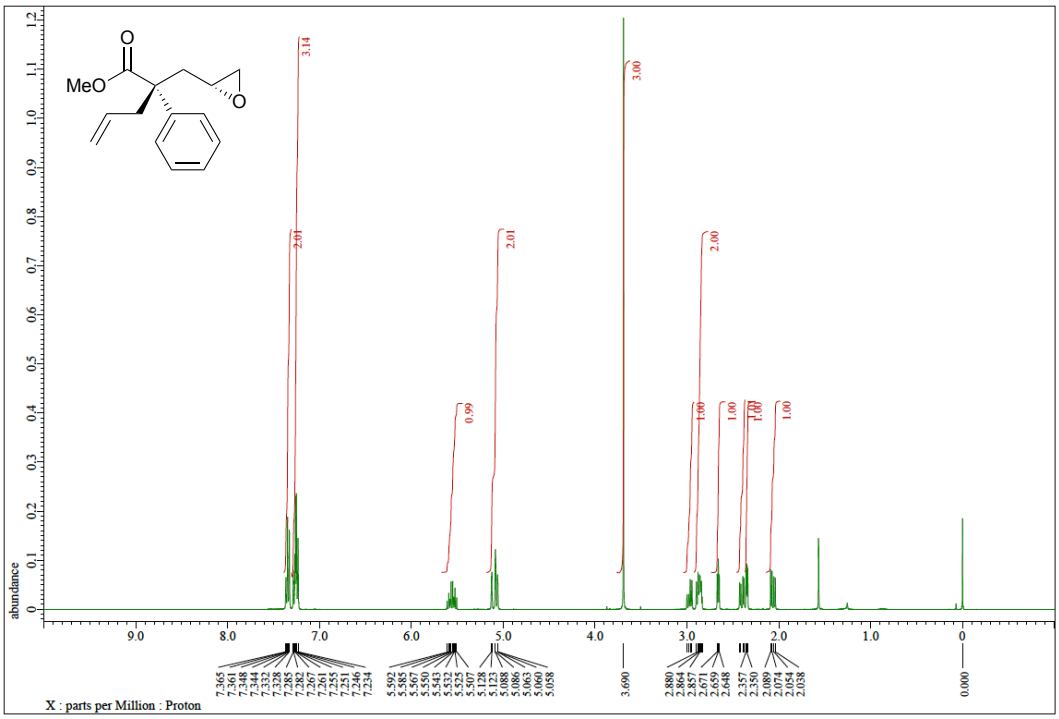

O
O
Ph
BnHN
(thousandths)
X : parts per Million : Carbon13

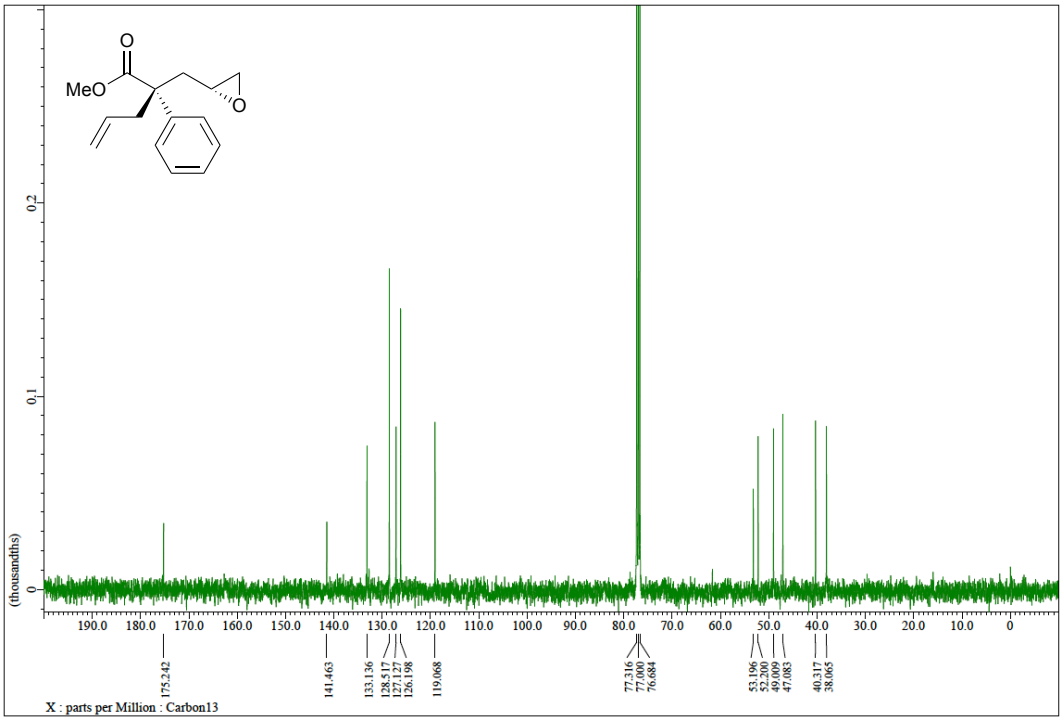

O
Ph
O
PhS
abundance
X : parts per Million : Proton

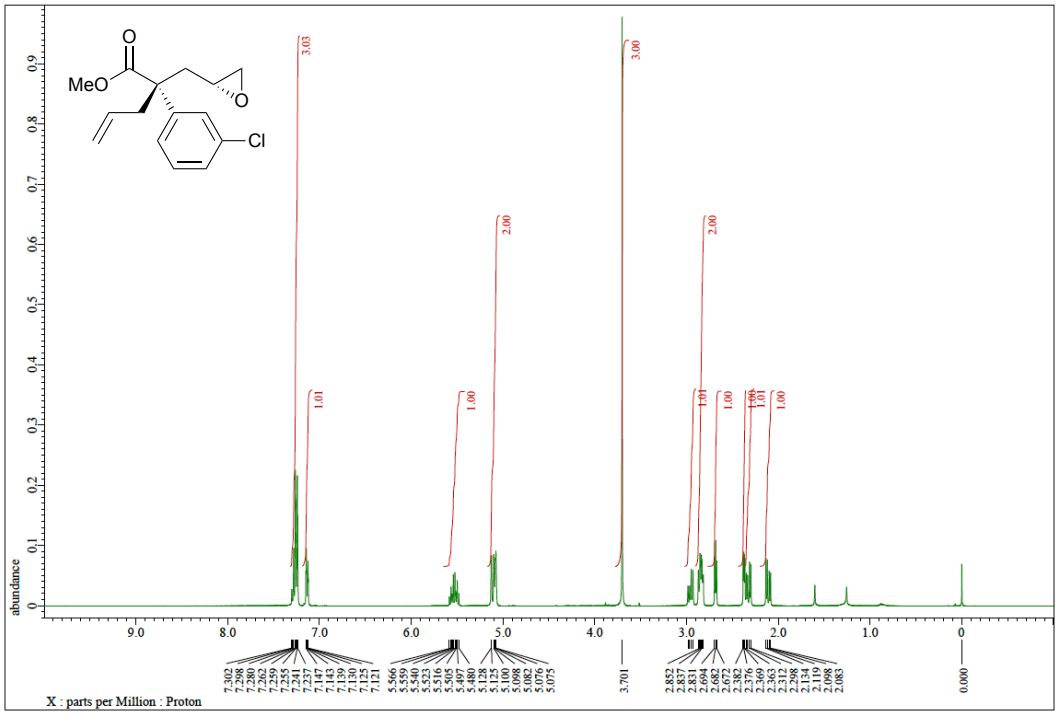

O
Ph
O
PhS
(thousandths)
X : parts per Million : Carbon13

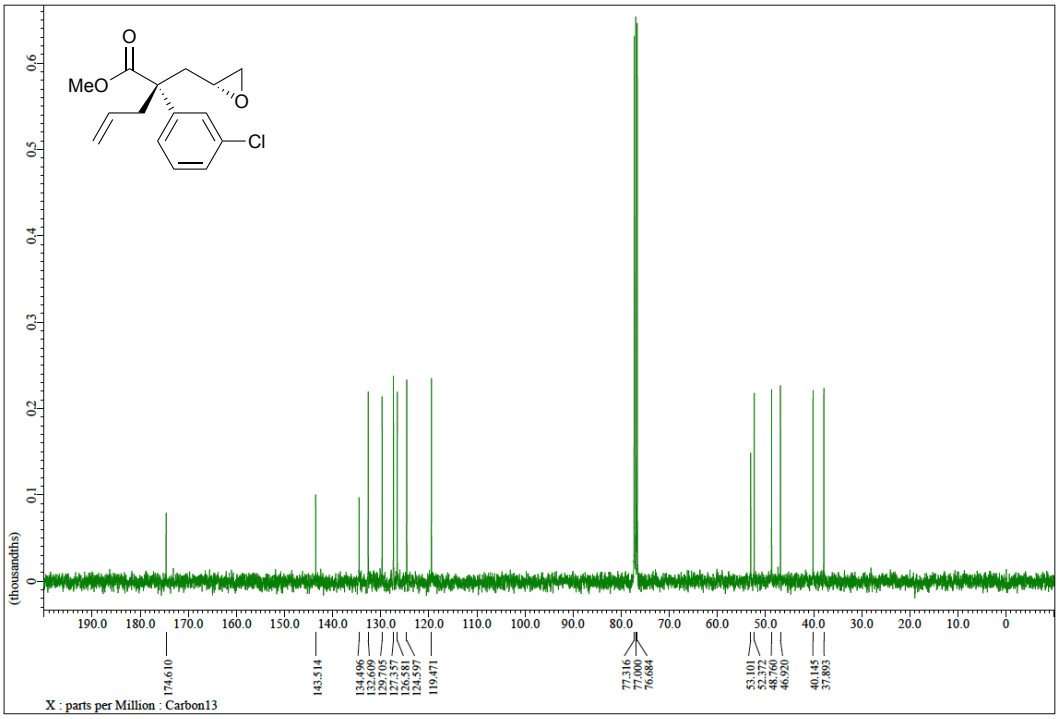

O
Ph
O
Ph
10.35
1.00
0.99
1.01
3.01
abundance
X : parts per Million : Proton

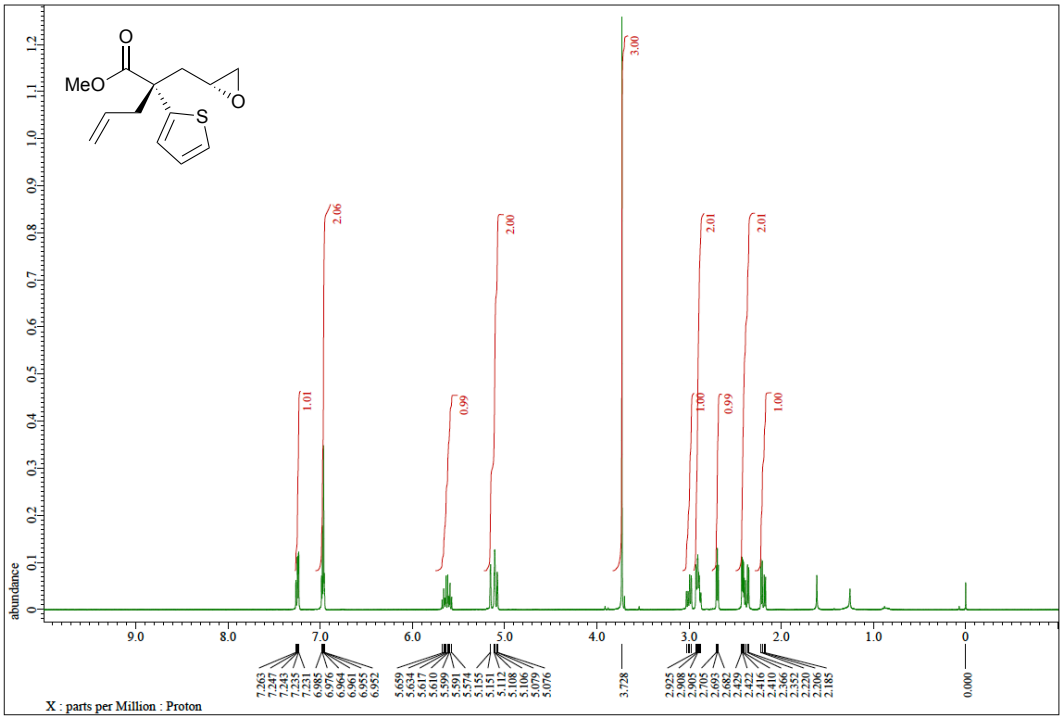

O
Ph
O
Ph
(thousandths)
X : parts per Million : Carbon13

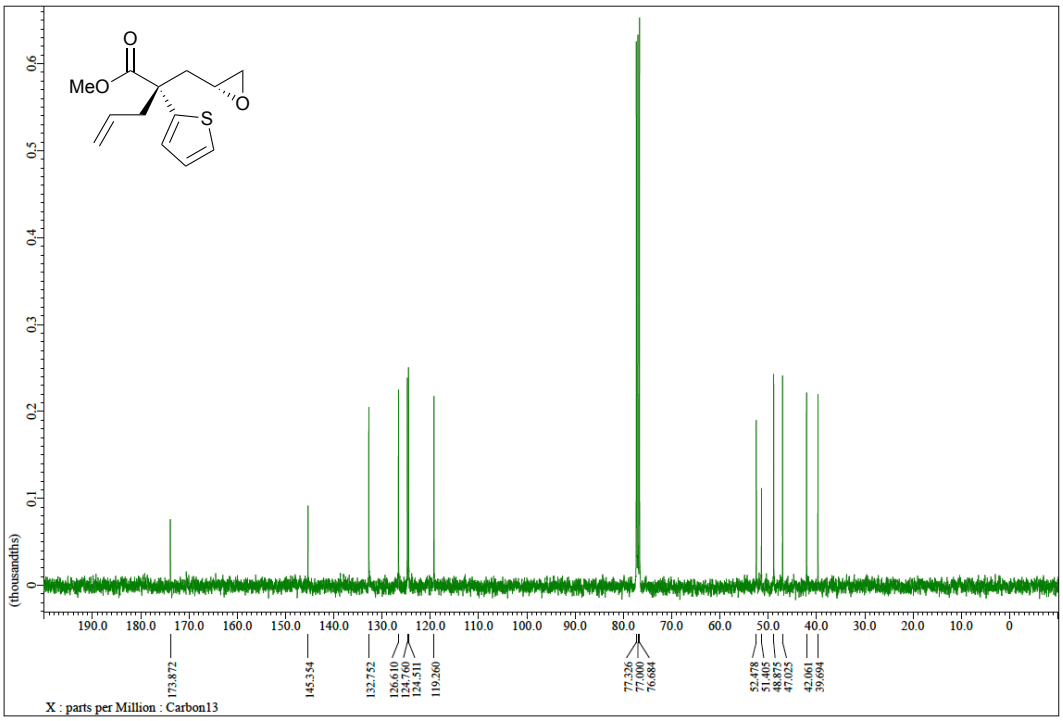

MeO
O
O
abundance
X : parts per Million : Proton


MeO
O
O
(thousandths)
X : parts per Million : Carbon13

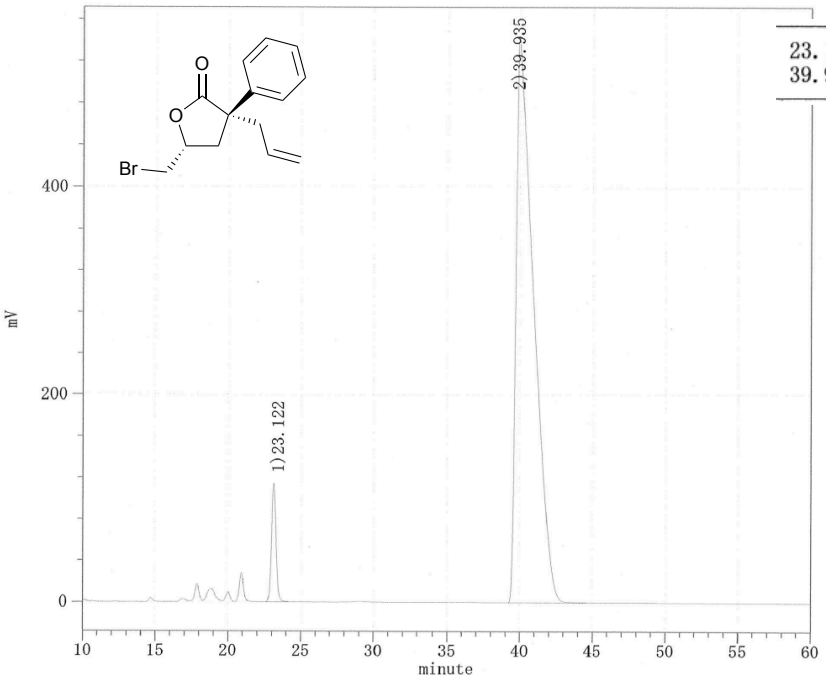

MeO
O
O
Cl
abundance
X : parts per Million : Proton


MeO
O
O
Cl
(thousandths)
X : parts per Million : Carbon13

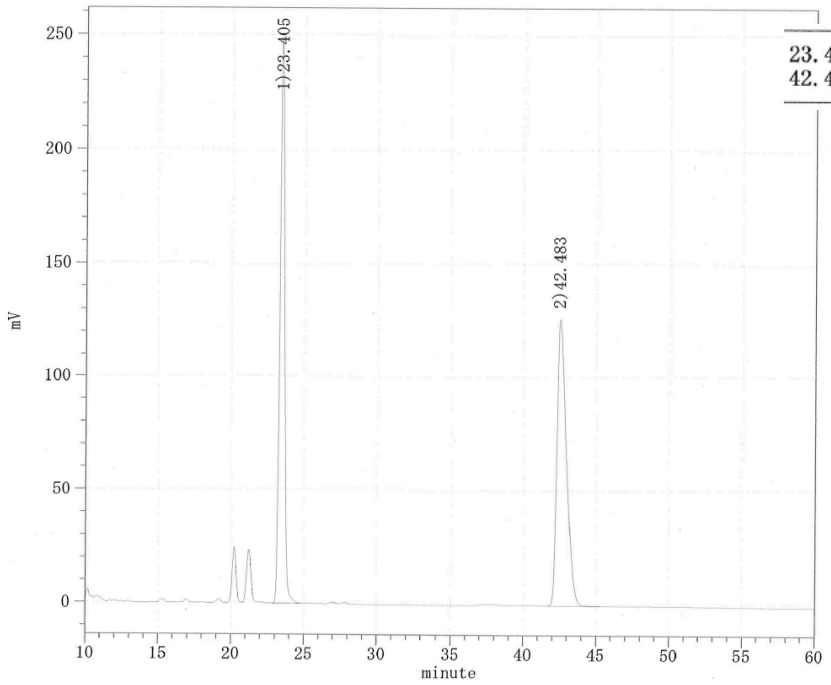

MeO
O
O
S
abundance
X : parts per Million : Proton


MeO
O
O
S
(thousandths)
X : parts per Million : Carbon13

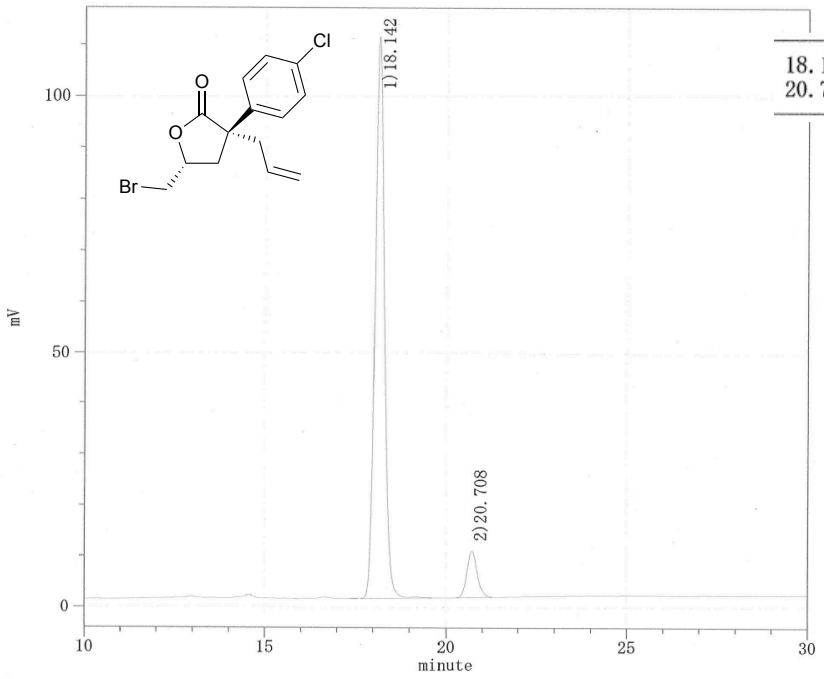
HPLC Charts



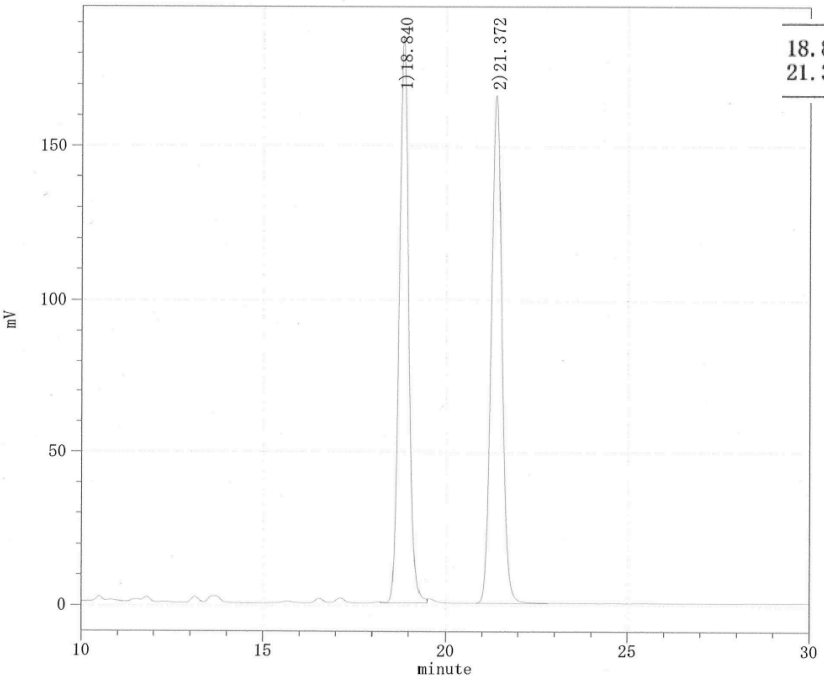
23.122	2488290	5.2083
39.935	45287160	94.7917



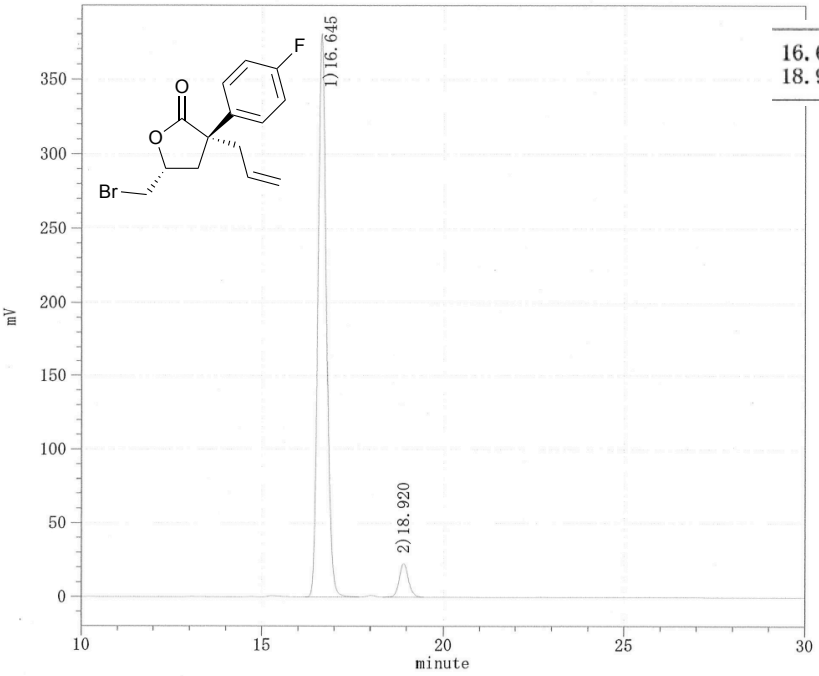
23.405	5722582	49.9166
42.483	5741707	50.0834



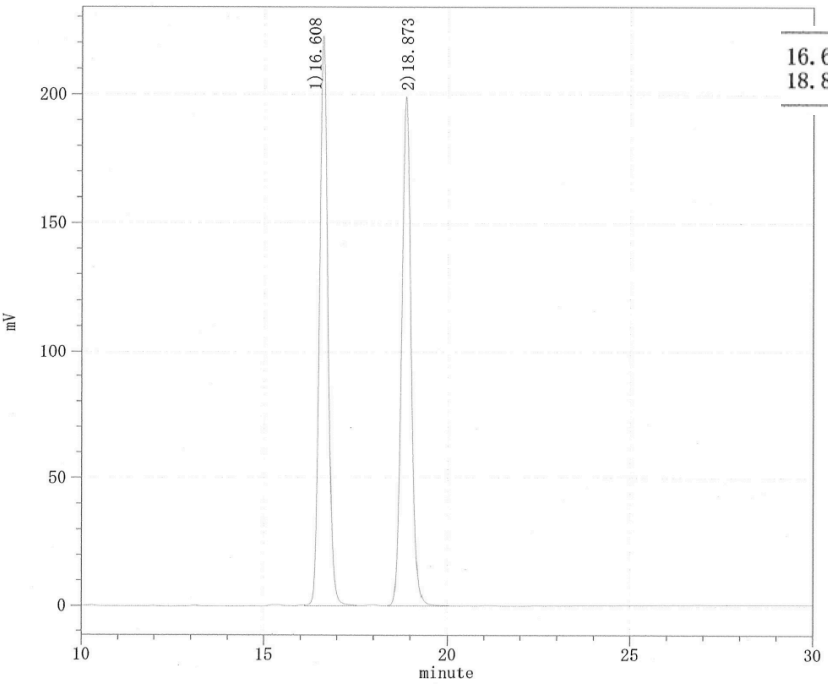
18.142	1983408	91.6163
20.708	181500	8.3837



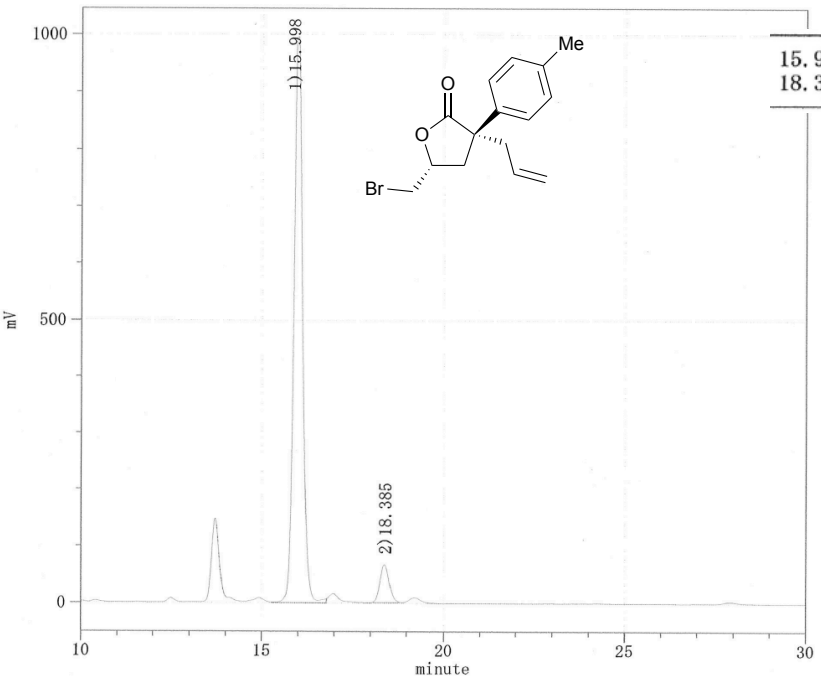
18.840	3419249	50.0712
21.372	3409525	49.9288



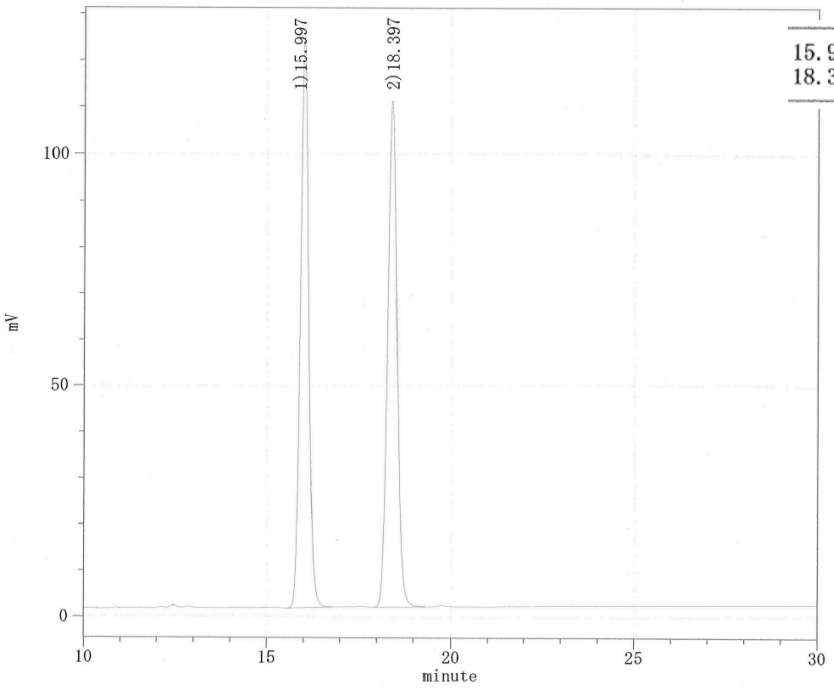
16.645	6269444	93.6692
18.920	423729	6.3308



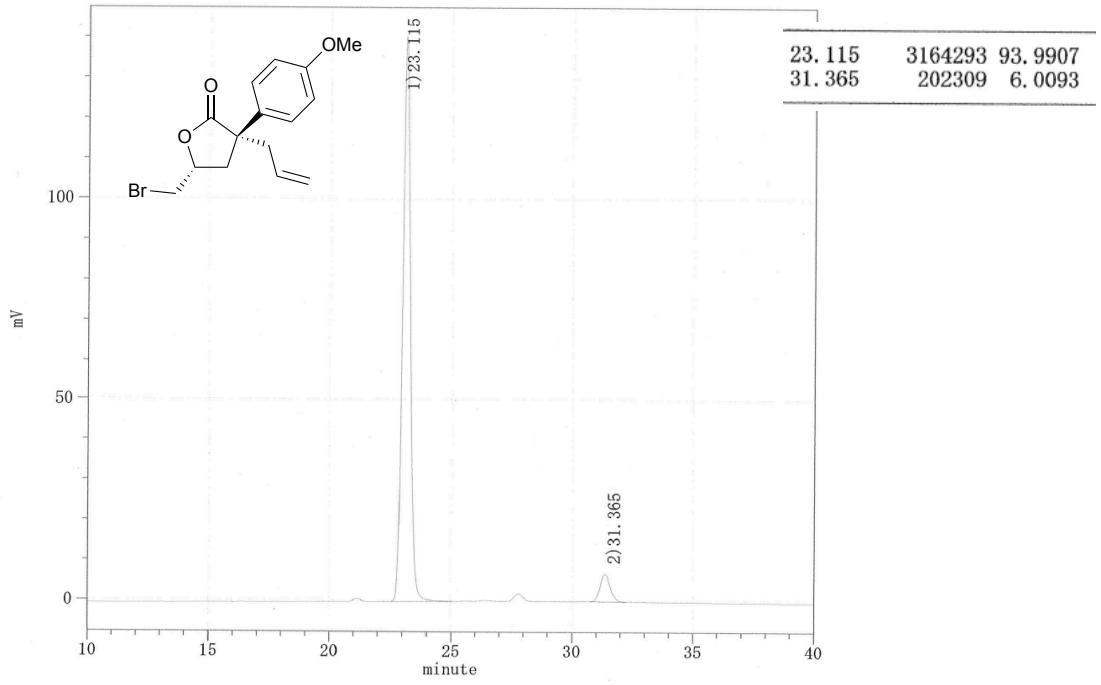
16.608	3651323	50.0215
18.873	3648191	49.9785



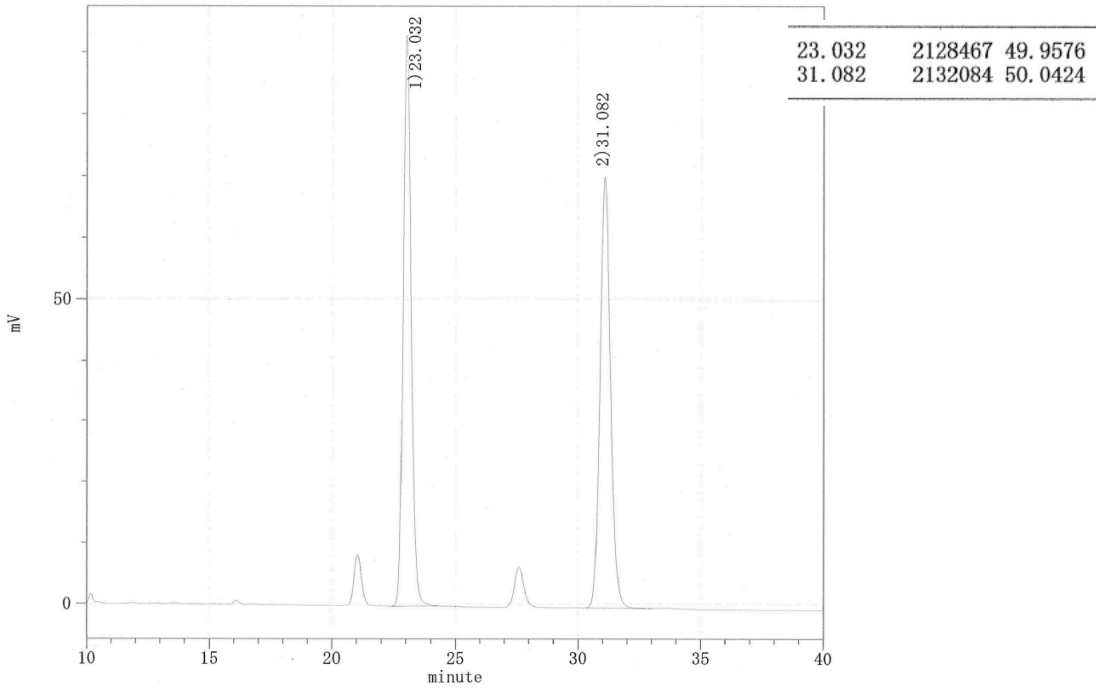
15.998	16950031	93.5142
18.385	1175589	6.4858



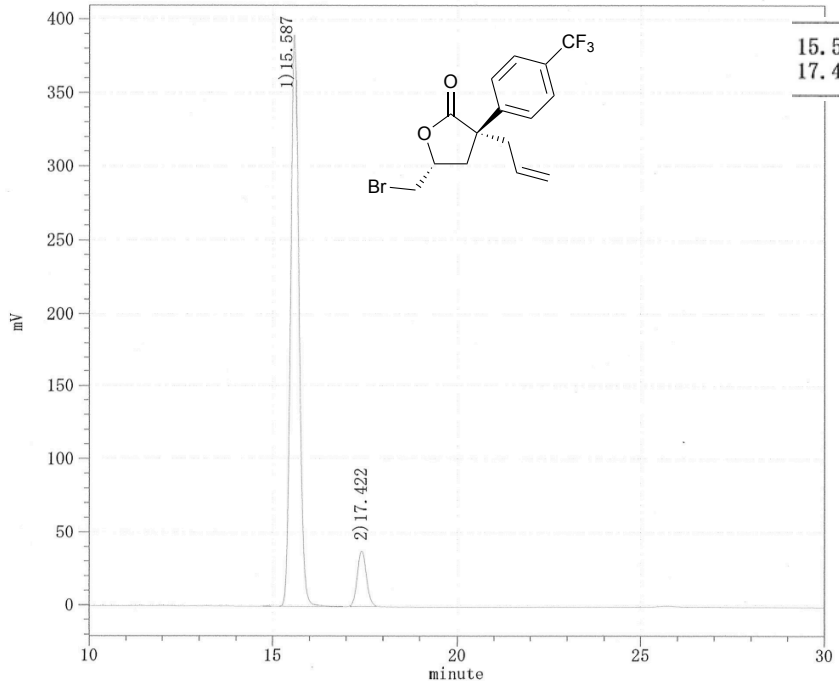
15.997	1960574	50.0294
18.397	1958267	49.9706



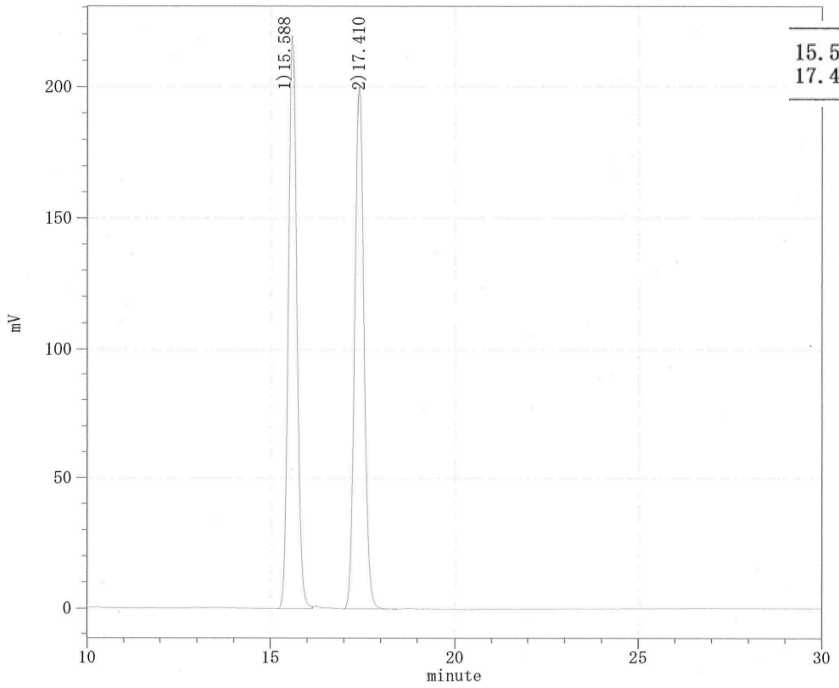
23.115	3164293	93.9907
31.365	202309	6.0093



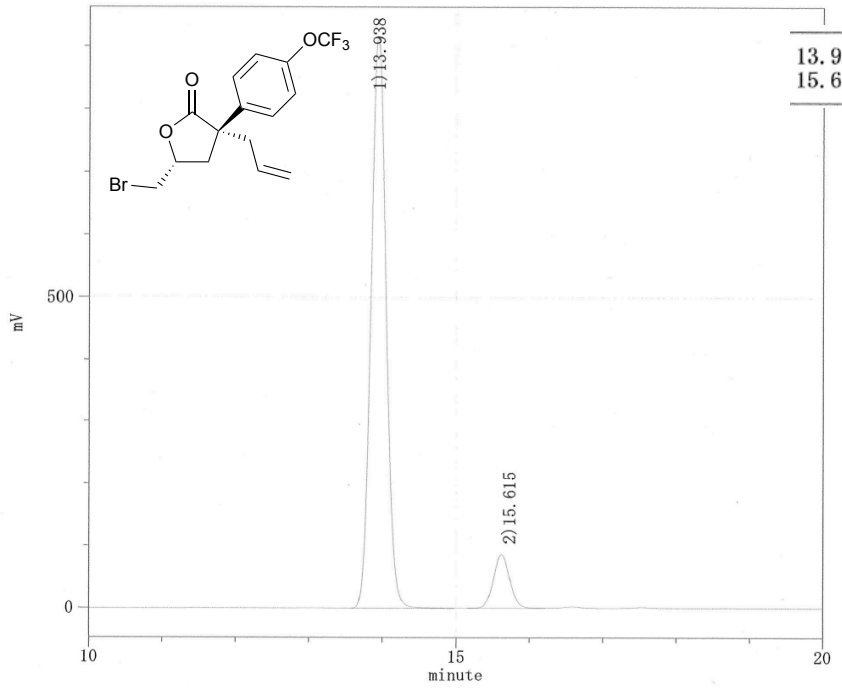
23.032	2128467	49.9576
31.082	2132084	50.0424



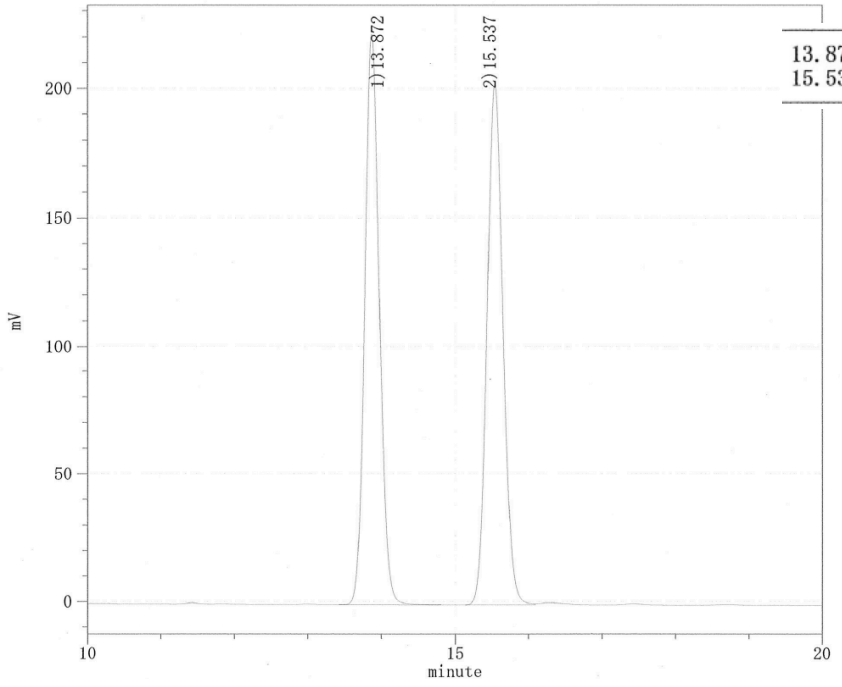
15.587	6129383	90.5402
17.422	640408	9.4598



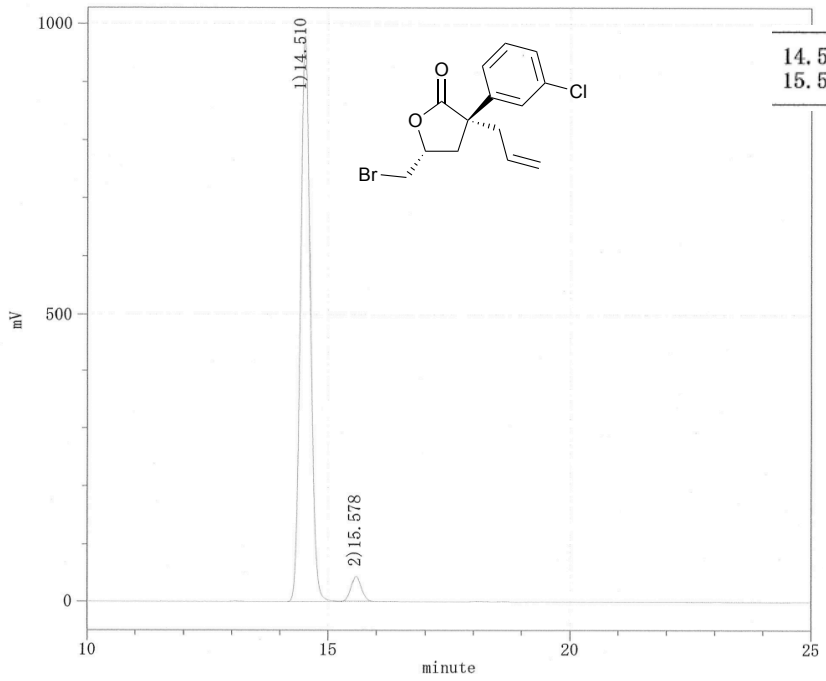
15.588	3462136	49.9364
17.410	3470949	50.0636



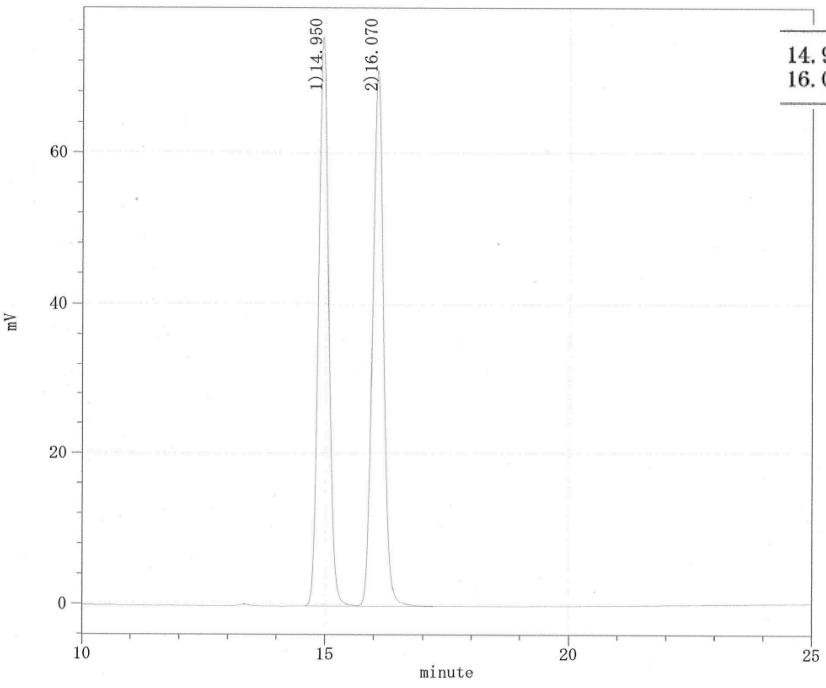
13.938	12992960	90.5355
15.615	1358277	9.4645



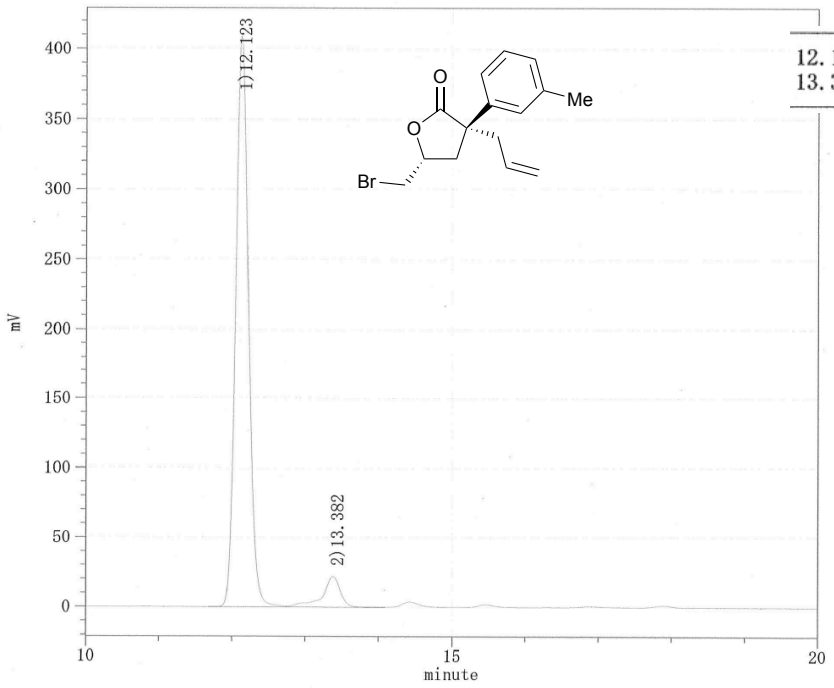
13.872	3062116	49.9751
15.537	3065170	50.0249



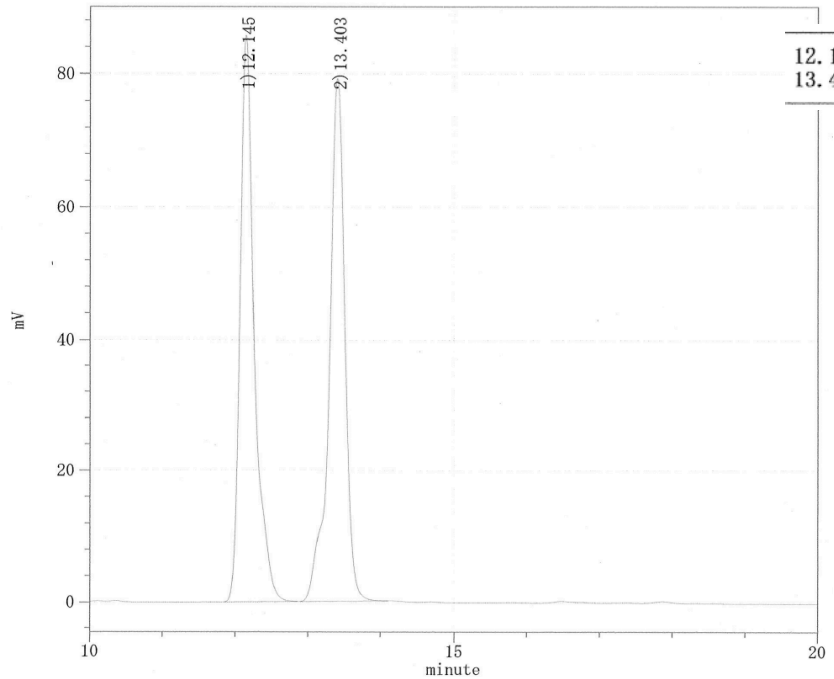
14.510	13954506	95.7315
15.578	622212	4.2685



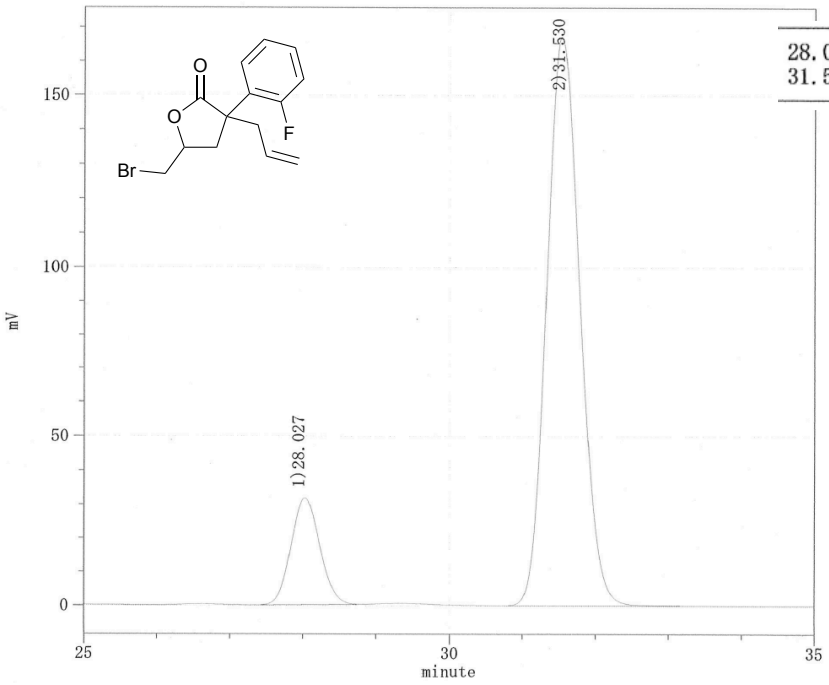
14.950	1103439	49.7507
16.070	1114496	50.2493



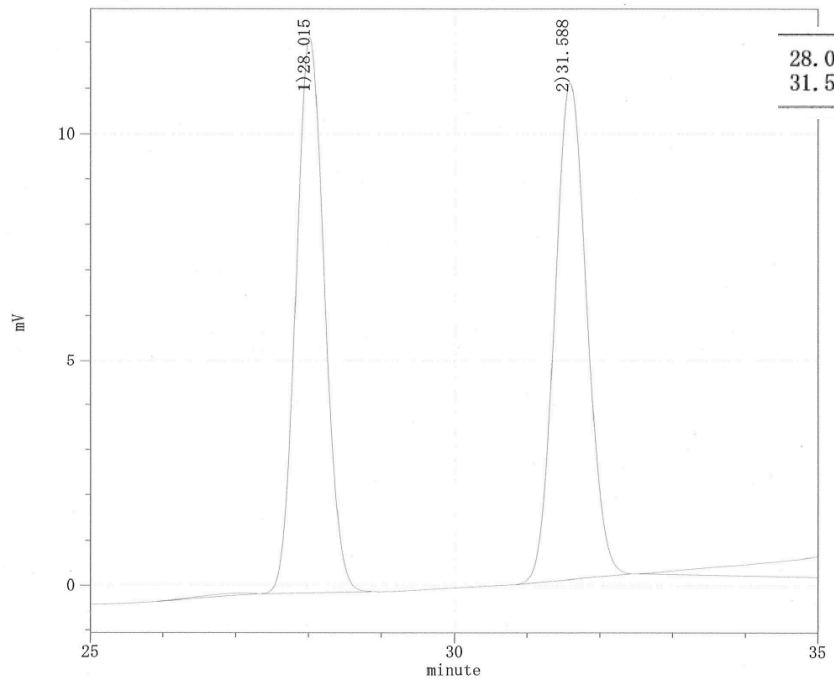
12.123	4971495	92.8436
13.382	383204	7.1564



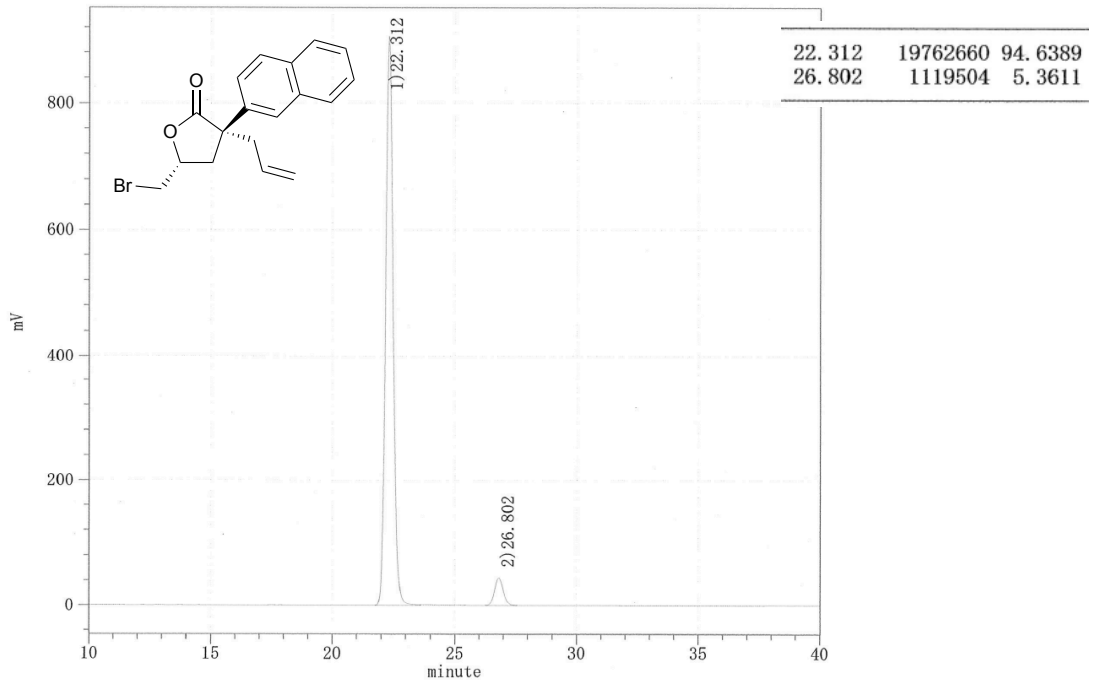
12.145	1163106	50.0443
13.403	1161045	49.9557



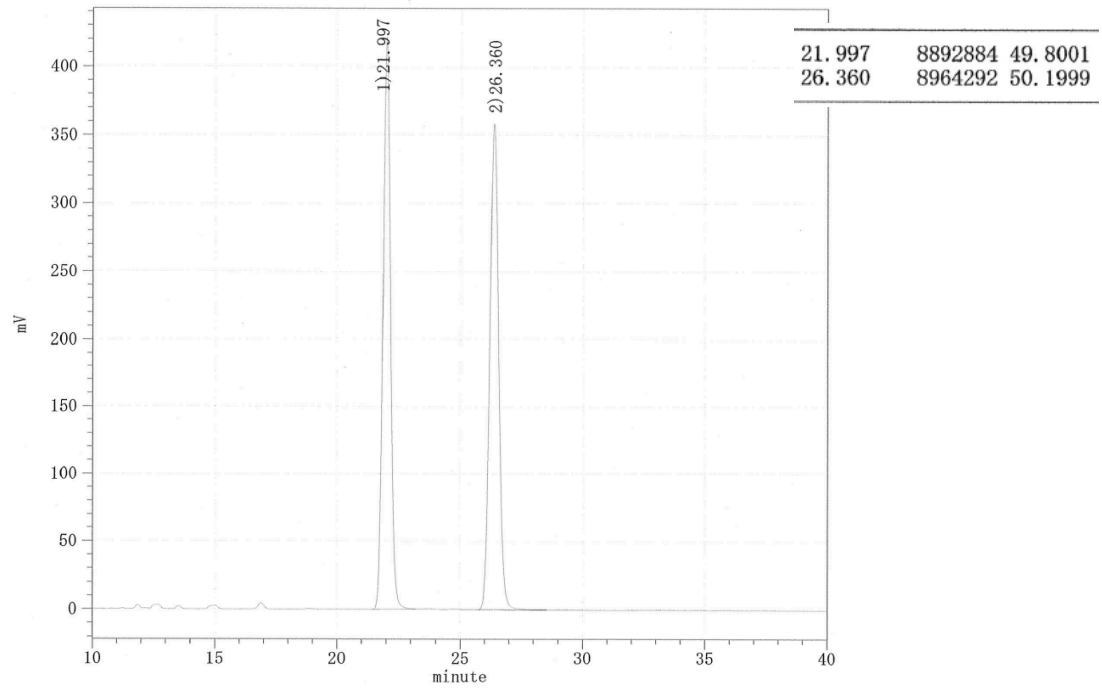
28.027	866361	14.1077
31.530	5274677	85.8923



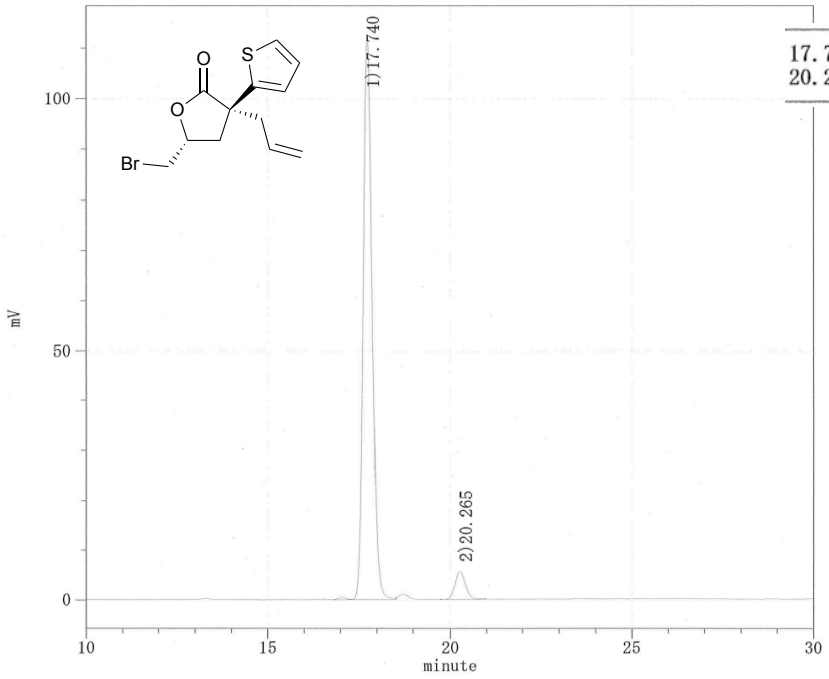
28.015	335545	49.9492
31.588	336228	50.0508



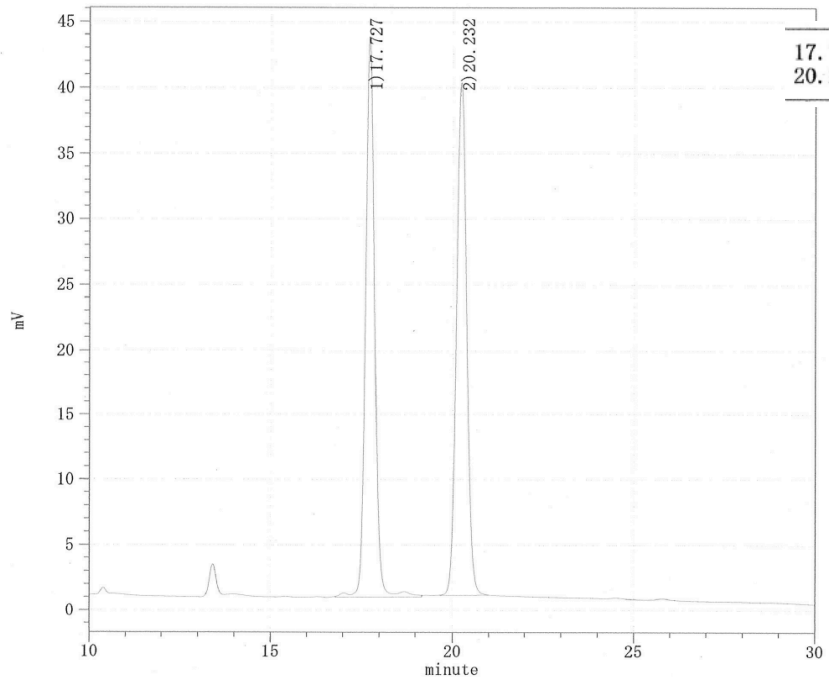
22.312	19762660	94.6389
26.802	1119504	5.3611



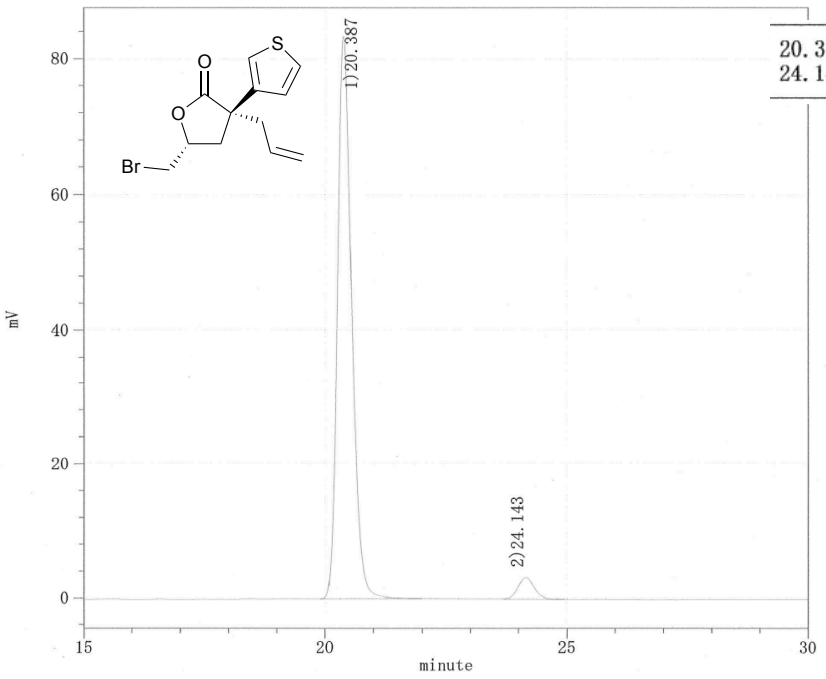
21.997	8892884	49.8001
26.360	8964292	50.1999



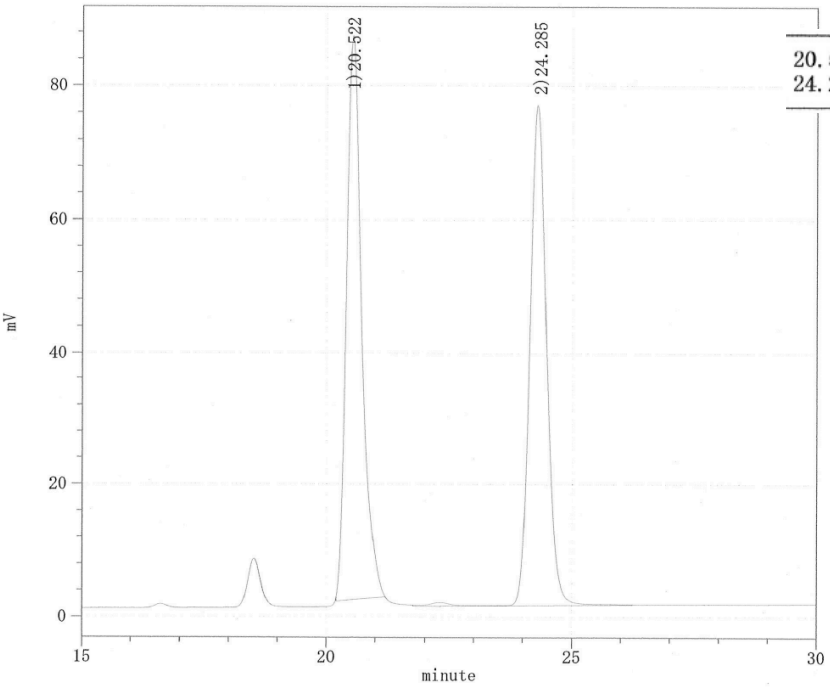
17.740	1944711	94.7617
20.265	107500	5.2383



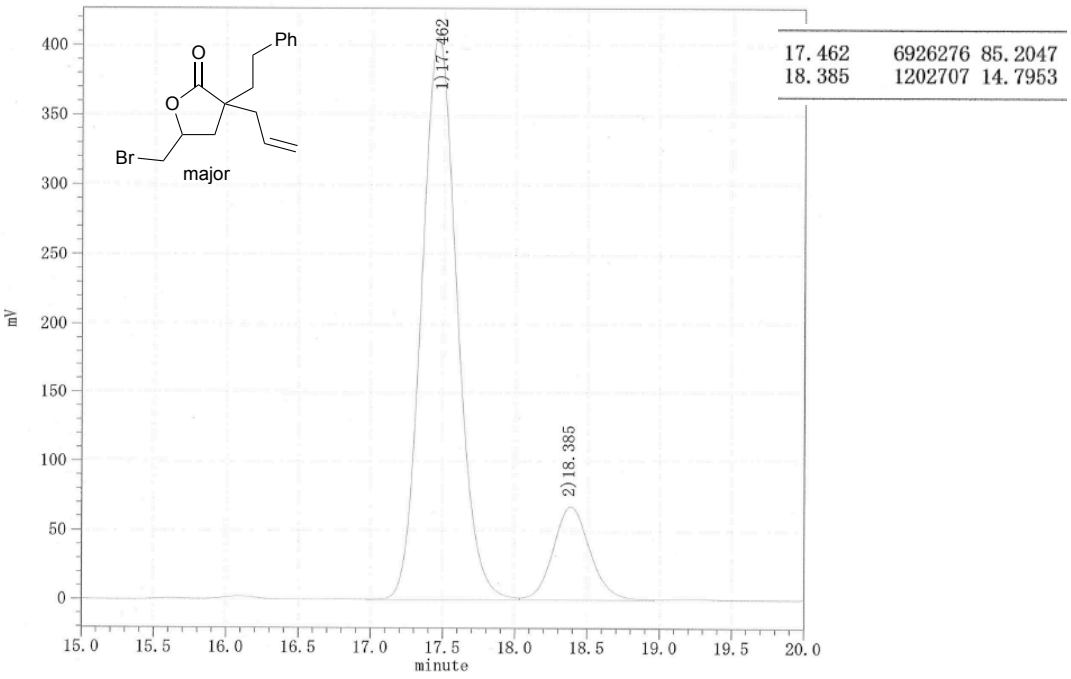
17.727	762288	50.1391
20.232	758059	49.8609



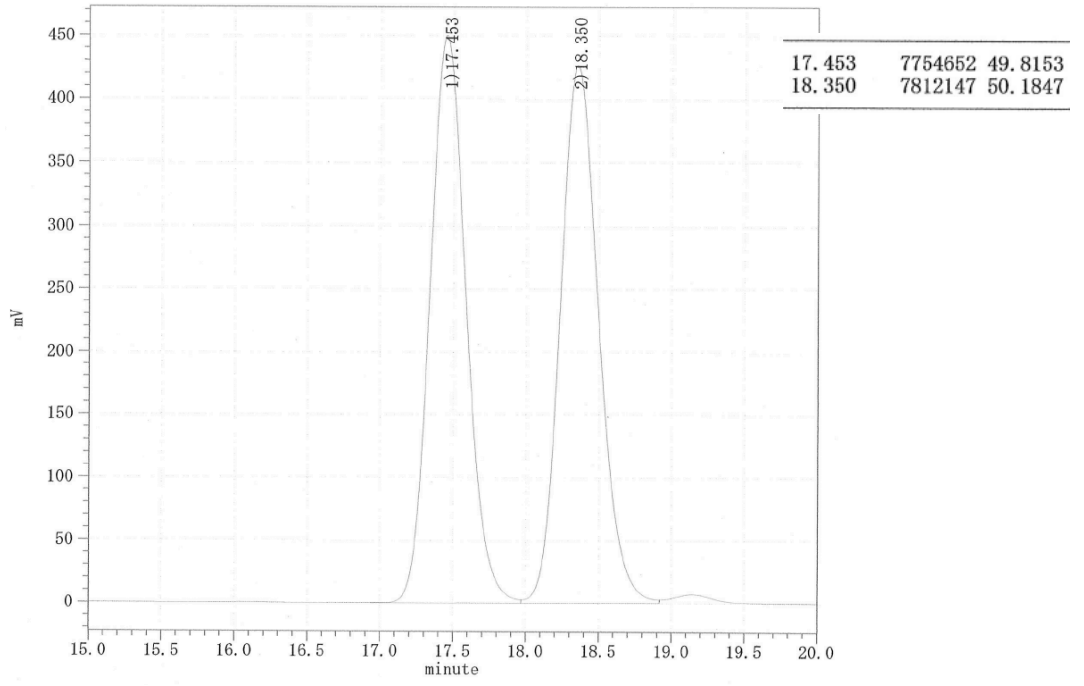
20.387	1706661	95.7562
24.143	75638	4.2438



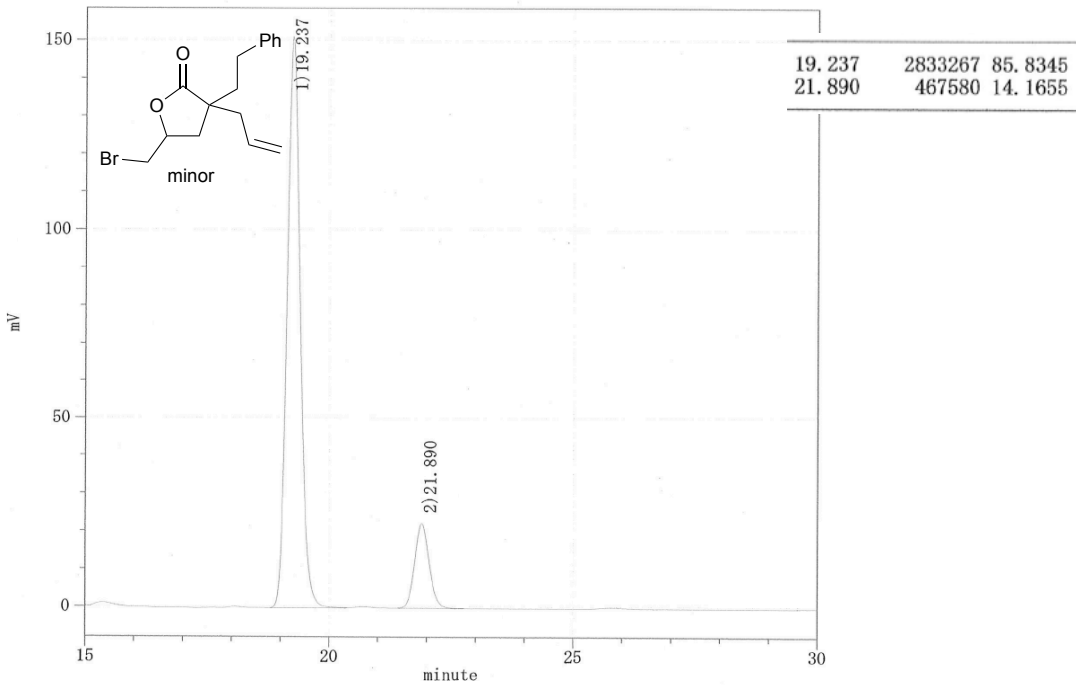
20.522	1825740	50.2212
24.285	1809660	49.7788



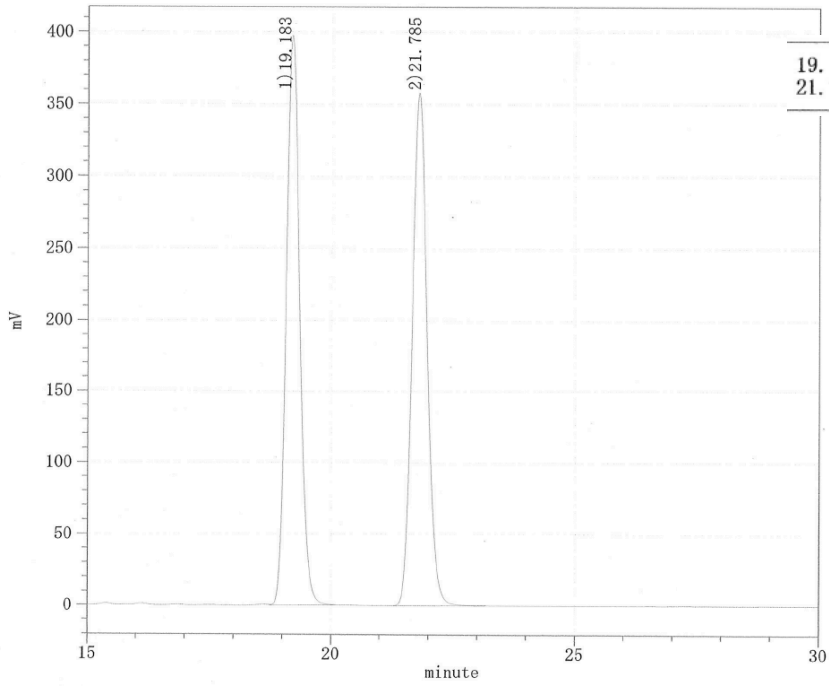
17.462	6926276	85.2047
18.385	1202707	14.7953



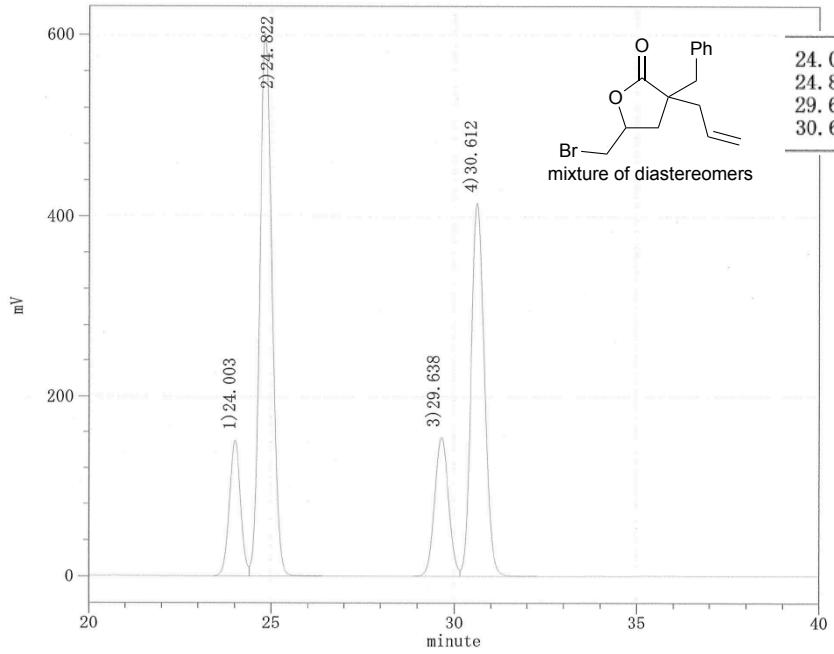
17.453	7754652	49.8153
18.350	7812147	50.1847



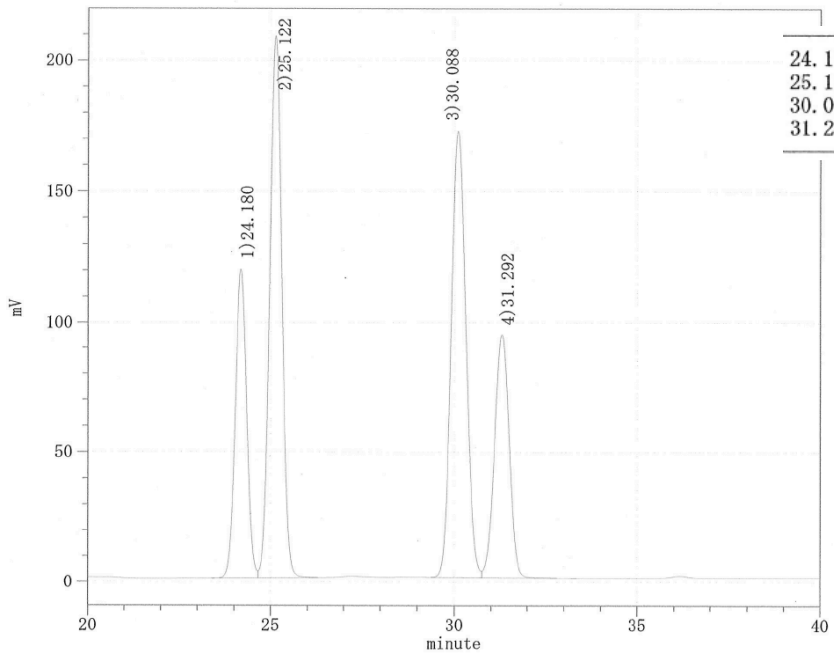
19.237	2833267	85.8345
21.890	467580	14.1655



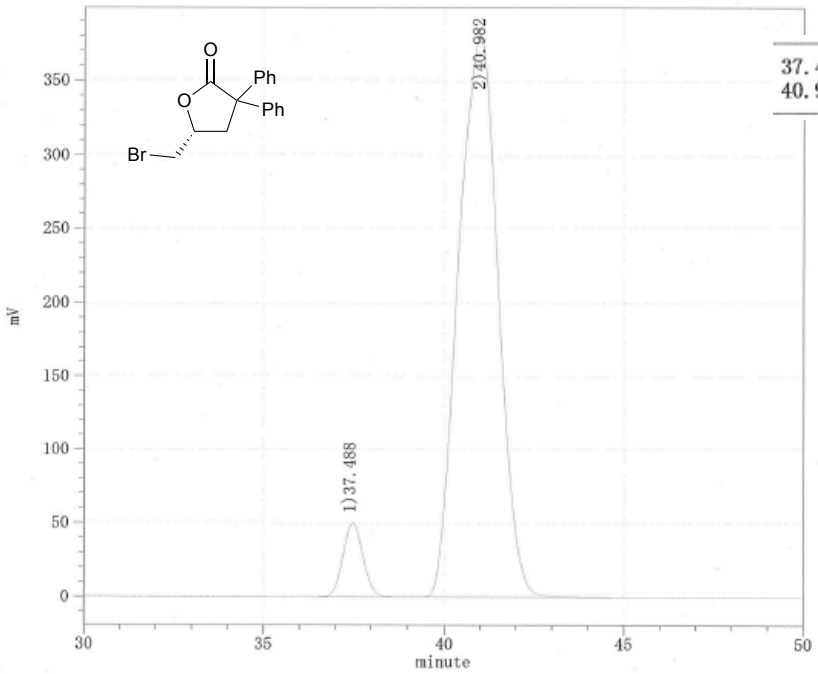
19.183	7628798	49.7984
21.785	7690565	50.2016



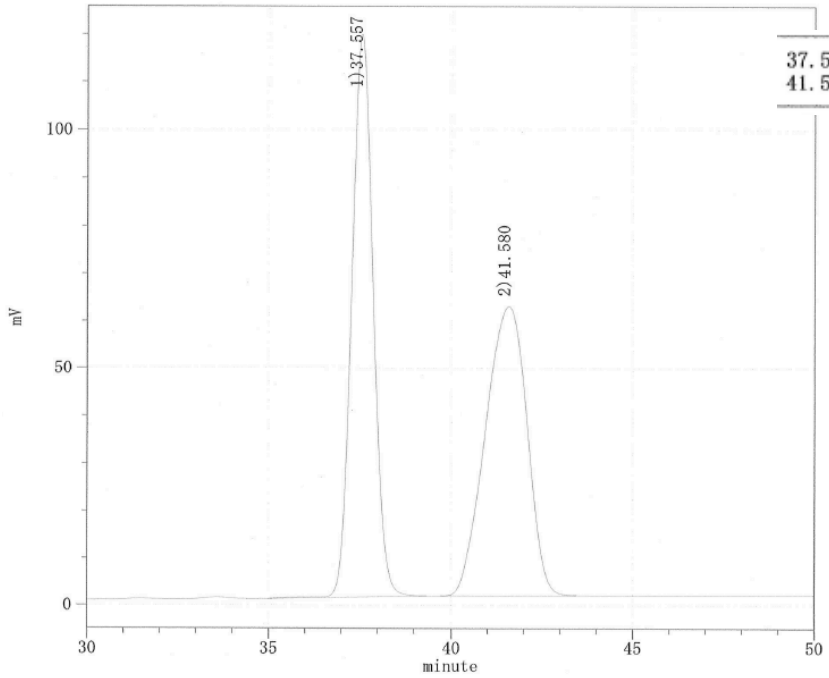
24.003	3236400	10.1723
24.822	14042430	44.1366
29.638	4068587	12.7879
30.612	10468400	32.9031



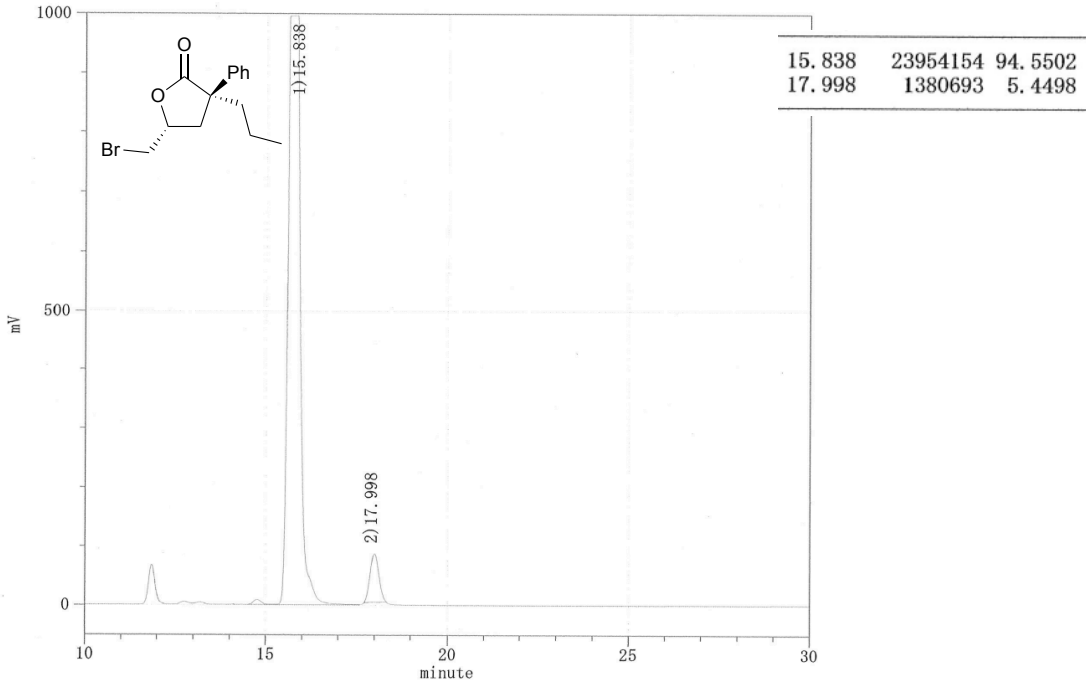
24.180	2585298	17.5728
25.122	4763417	32.3779
30.088	4752169	32.3014
31.292	2611066	17.7479



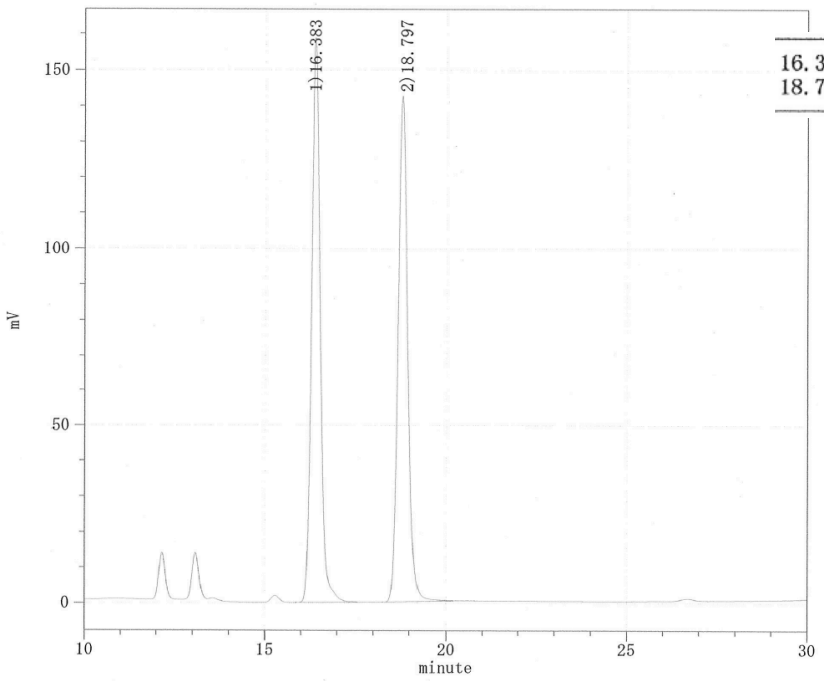
37.488	1940378	6.2359
40.982	29176070	93.7641



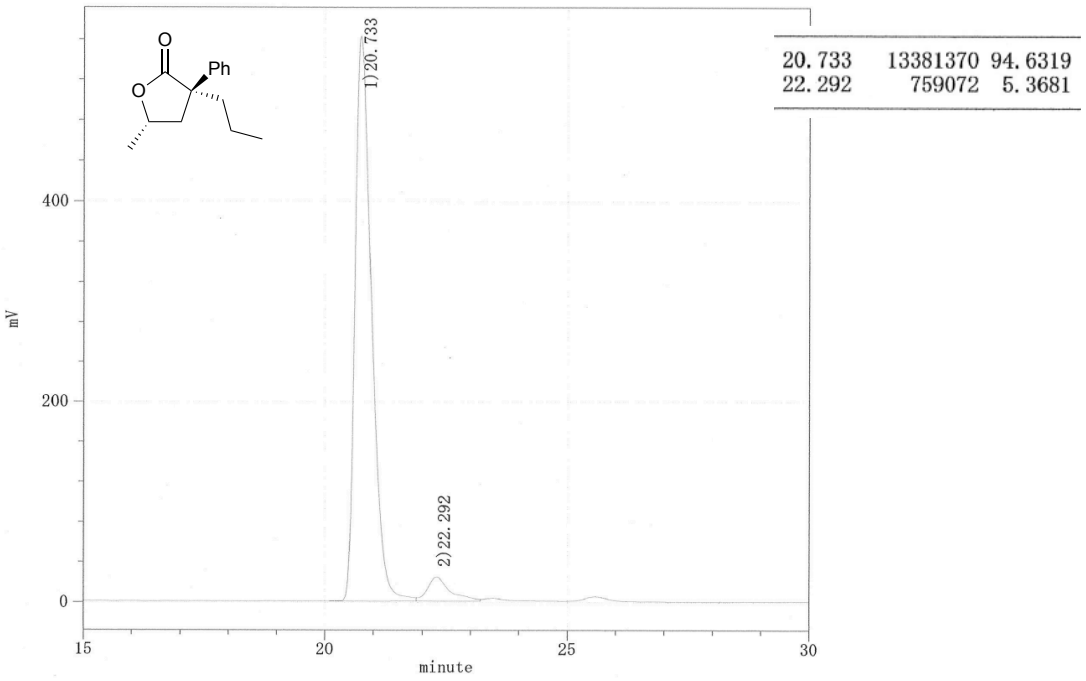
37.557	4853260	49.8802
41.580	4876573	50.1198



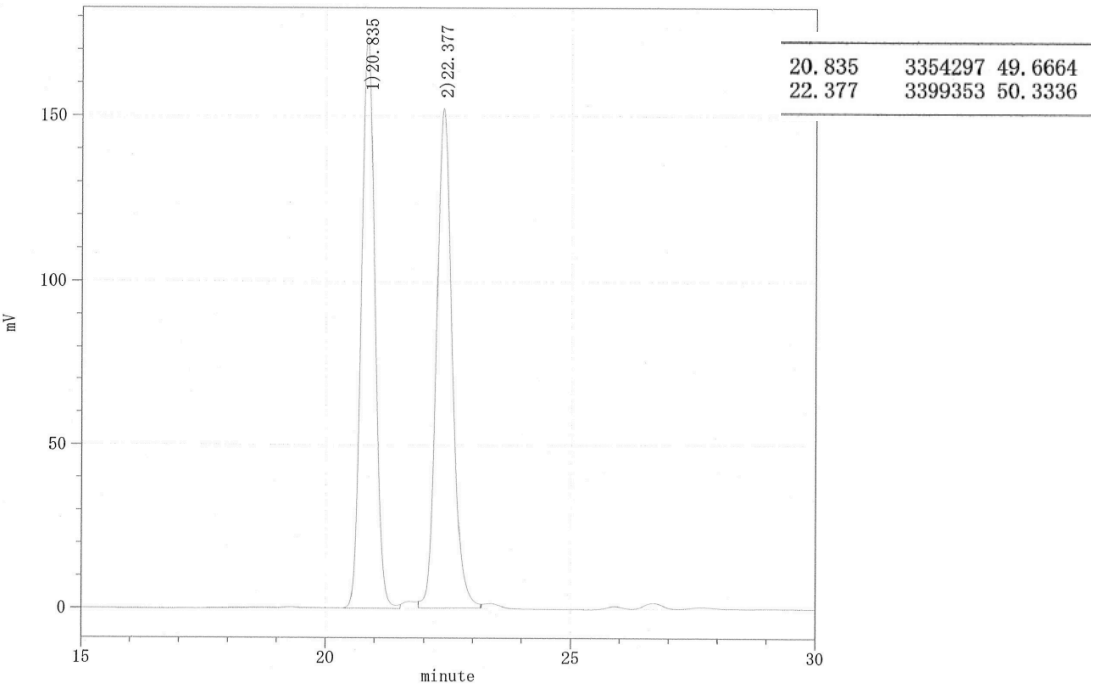
15.838	23954154	94.5502
17.998	1380693	5.4498



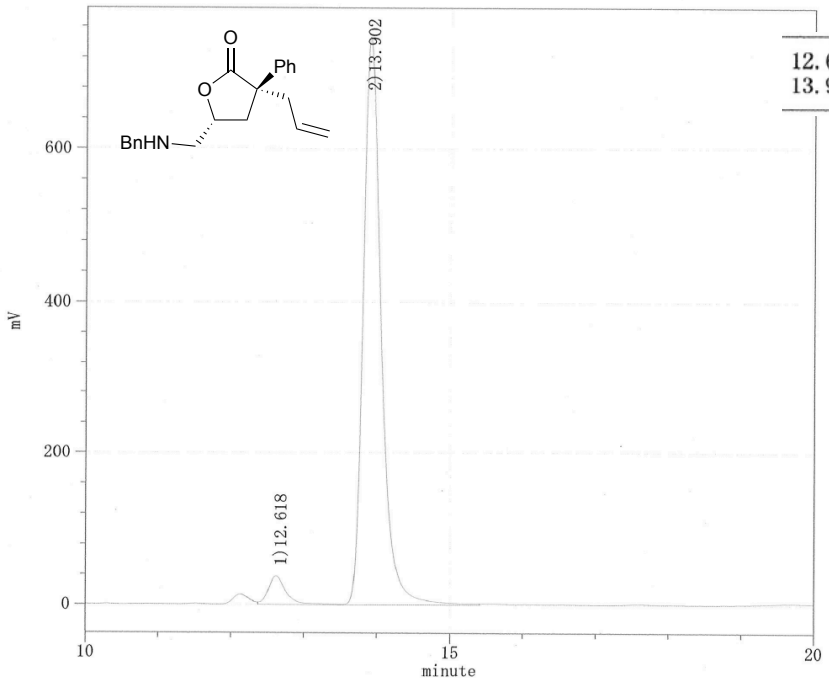
16.383	2709067	50.3605
18.797	2670284	49.6395



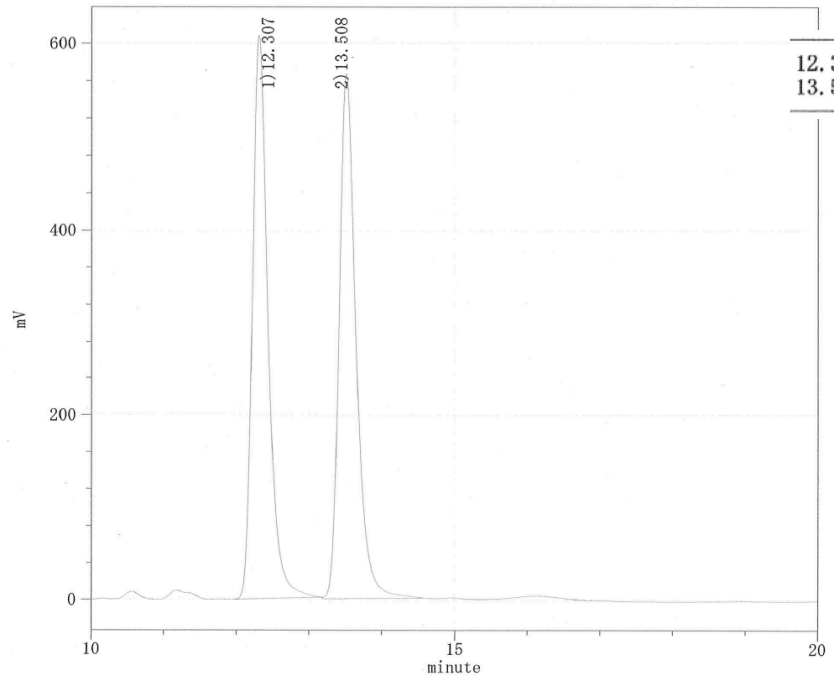
20.733	13381370	94.6319
22.292	759072	5.3681



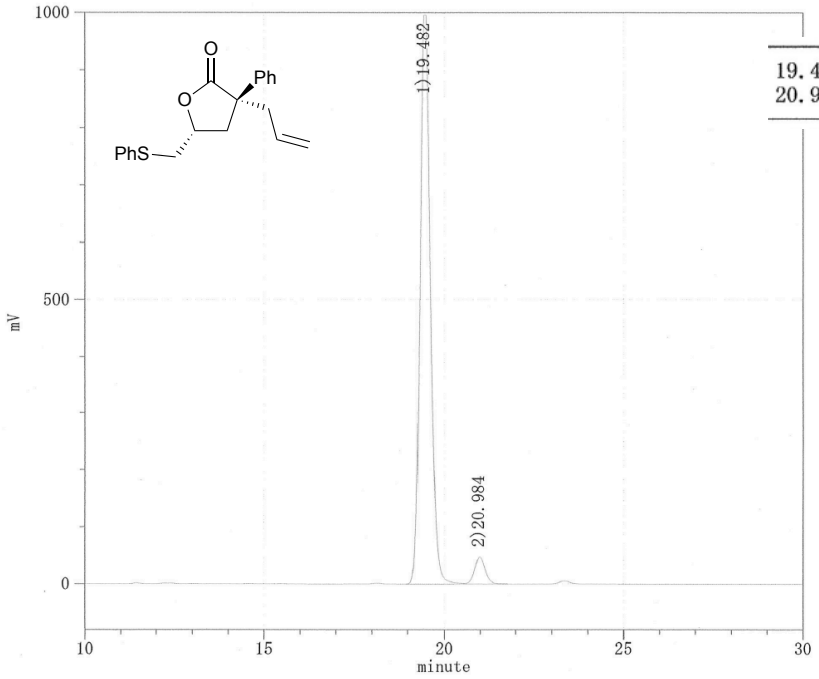
20.835	3354297	49.6664
22.377	3399353	50.3336



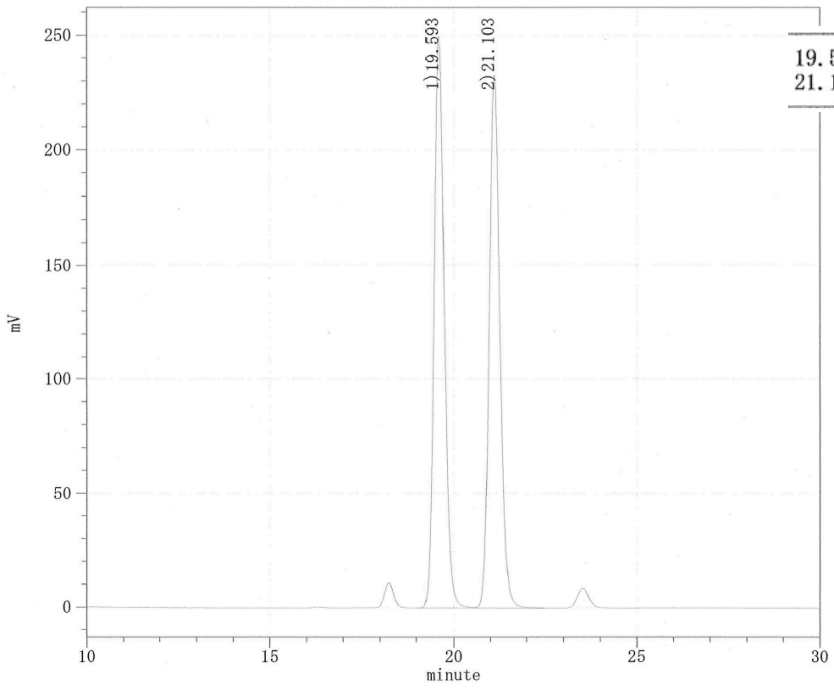
12.618	645499	4.7986
13.902	12806460	95.2014



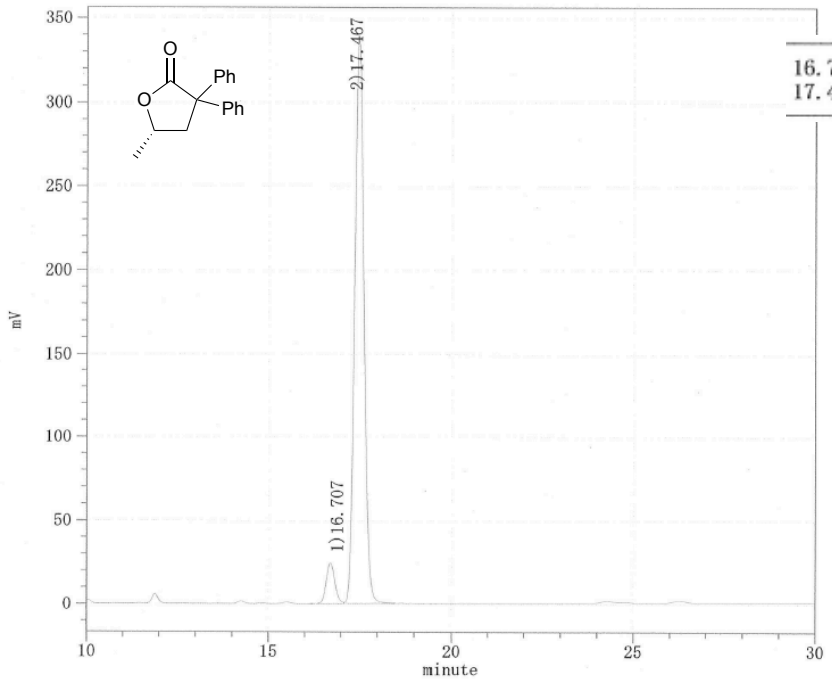
12.307	9086068	49.7662
13.508	9171447	50.2338



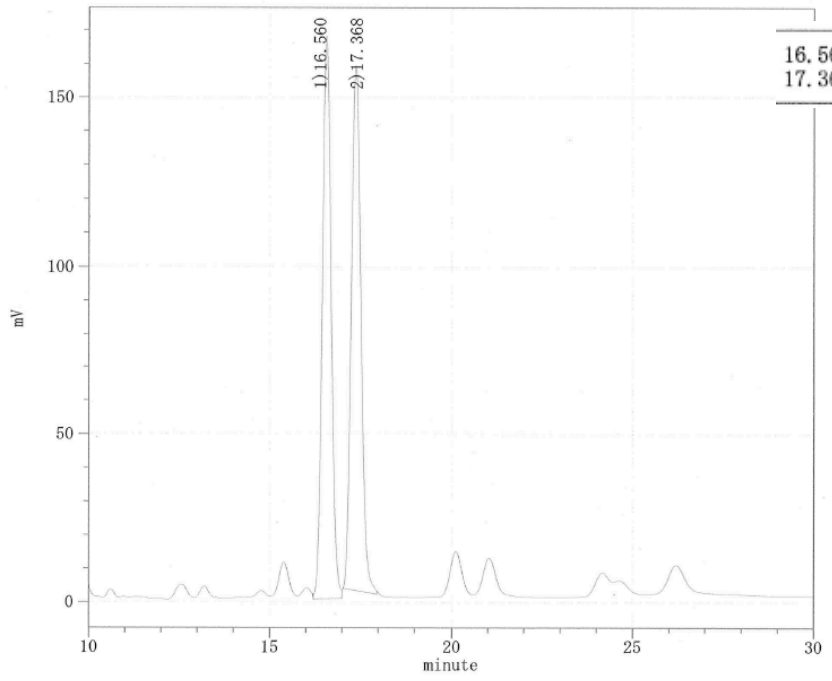
19.482	19786060	95.2720
20.984	981911	4.7280



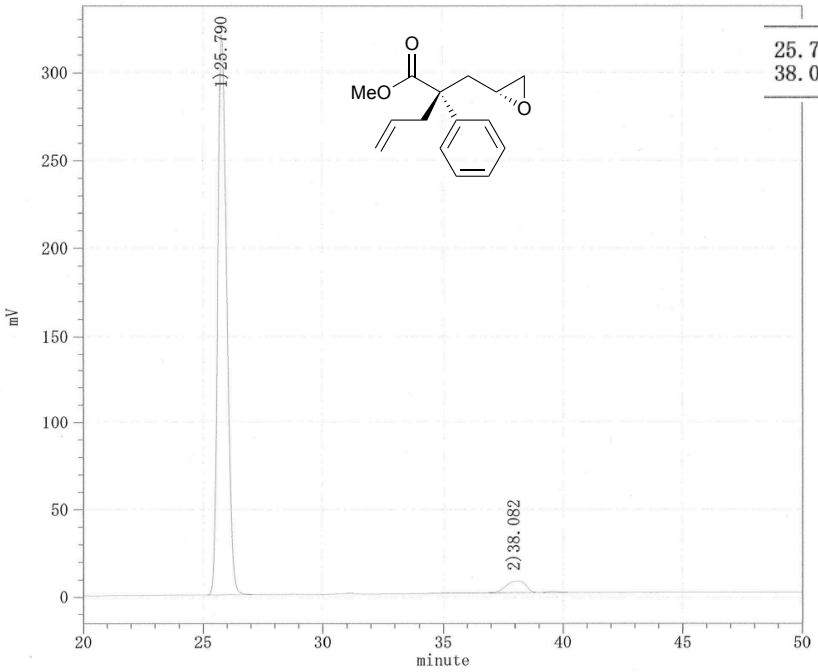
19.593	4790772	50.0525
21.103	4780716	49.9475



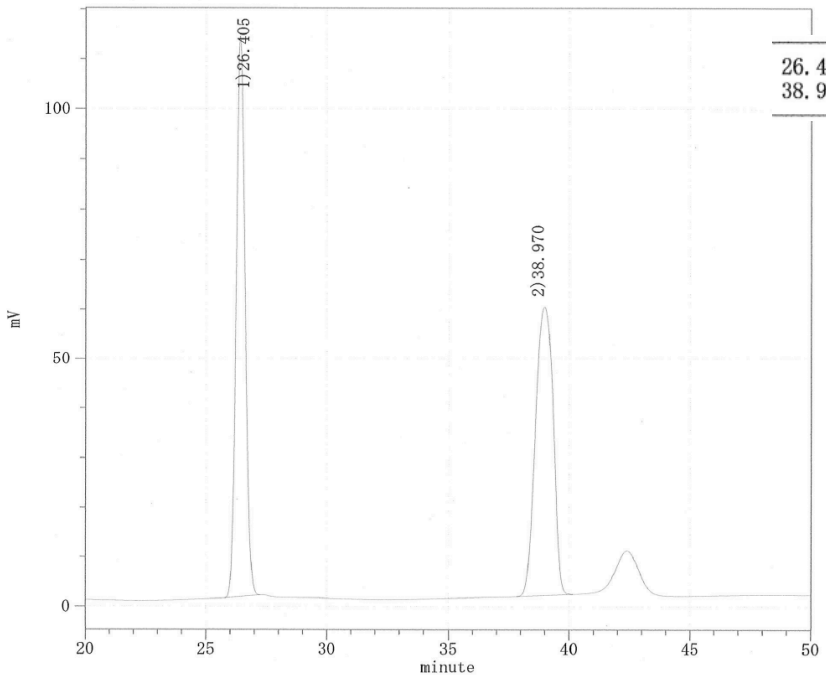
16.707	400385	6.3018
17.467	5953075	93.6982



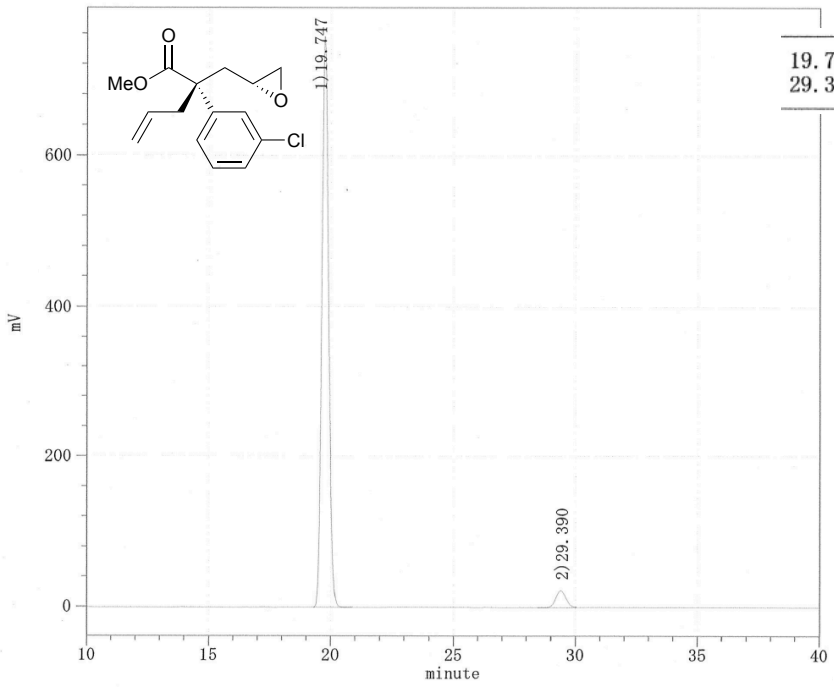
16.560	2895410	50.2121
17.368	2870946	49.7879



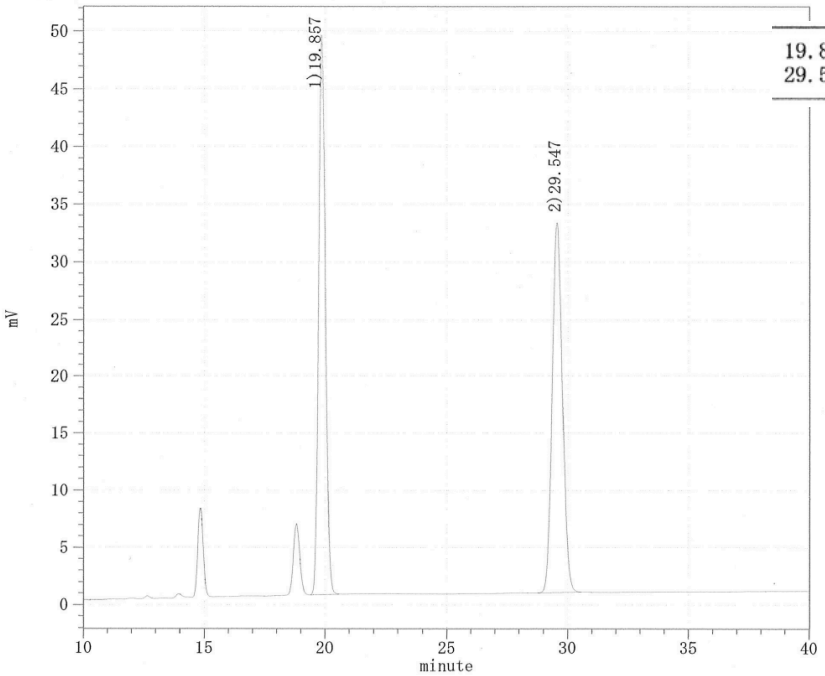
25.790	8339182	95.3322
38.082	408316	4.6678



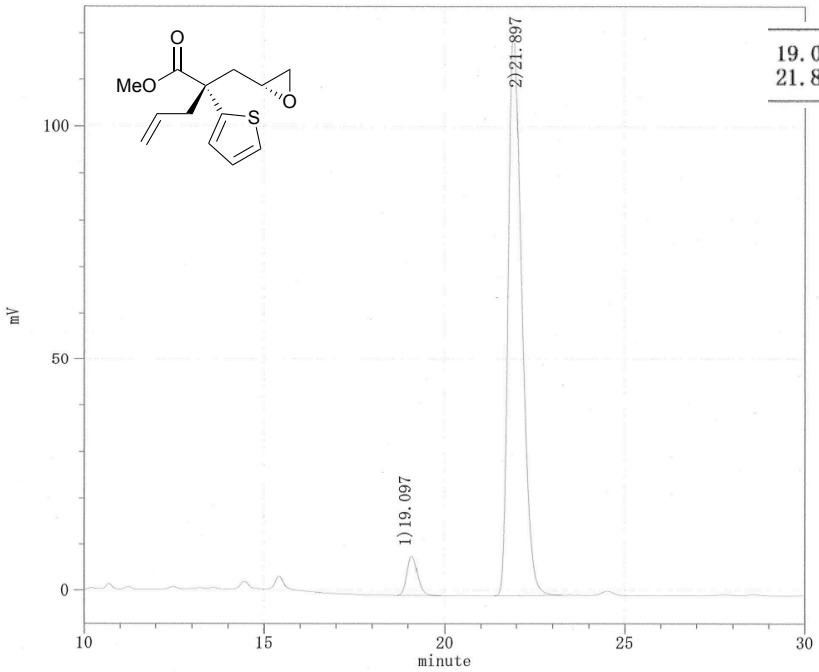
26.405	2943844	49.8189
38.970	2965251	50.1811



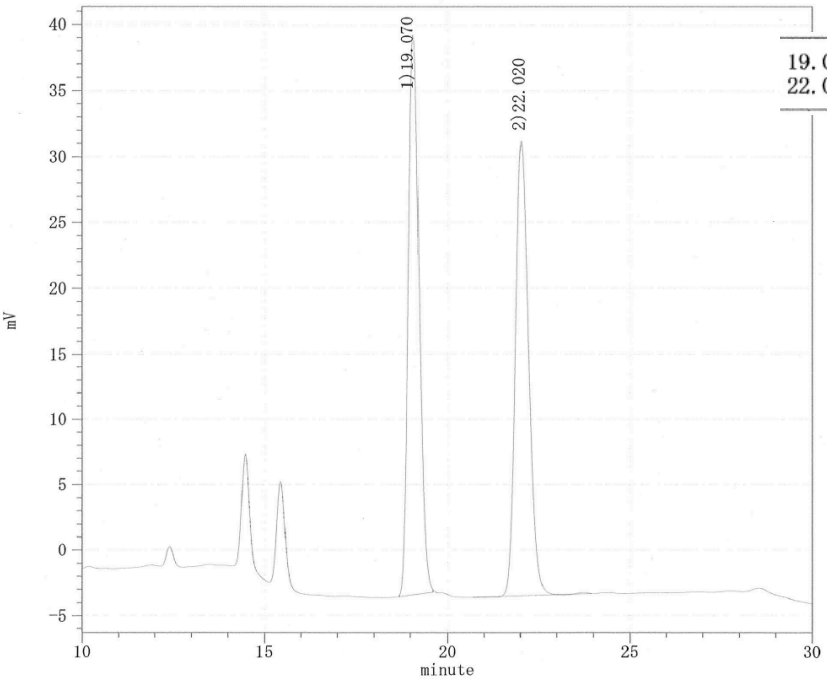
19.747	15134770	95.7681
29.390	668799	4.2319



19.857	961393	50.0351
29.547	960046	49.9649



19.097	165218	4.9441
21.897	3176483	95.0559



19.070	838531	49.1132
22.020	868814	50.8868