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electronic supplementary information

Catalyst-Controlled Diastereoselectivity Reversal in Formation of Dihydropyrans

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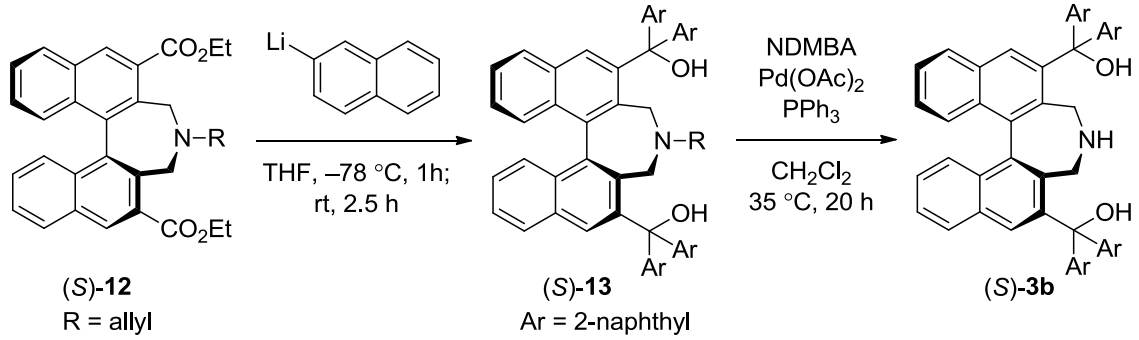
General Information.

Infrared (IR) spectra were recorded on a Shimadzu IRPrestige-21 spectrometer. ^{1}H NMR spectra were measured on a JEOL JNM-FX400 (400 MHz) spectrometer and a JEOL JNM-ECA500 (500 MHz) spectrometer. Data were reported as follows: chemical shifts in ppm from the residual solvent as an internal standard (δ 7.26 for $CDCl_3$ and δ 0.00 for TMS), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, AB q = AB quartet, m = multiplet, br = broad, and app = apparent), and coupling constants (Hz). ^{13}C NMR spectra were measured a JEOL JNM-FX400 (100 MHz) spectrometer on a JEOL JNM-FX500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts were reported in ppm from the residual solvent as an internal standard (δ 77.16 for $CDCl_3$). High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using Daicel CHIRALPAK AD-3, IB-3, IC, IC-3, and IG, 4.6 mm × 25 cm column. High-resolution mass spectra (HRMS) were performed on Thermo Scientific Exactive Plus. Optical rotations were measured on a JASCO DIP-1000 digital polarimeter. For thin layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm) were used. The products were purified by flash column chromatography on silica gel 60 (Merck 1.09386.9025, 230-400 mesh). For purification with preparative thin layer chromatography (PLC), Merck precoated PLC plates (silica gel 60 GF_{254}, 0.5 mm) were used. In experiments requiring dry solvents, tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were purchased from Kanto Chemical Co. Inc. as "Dehydrated". Commercially available aldehydes were distilled and stored under argon atmosphere at –20 °C. β,γ-Unsaturated α-keto carboxylic acids,[1] *tert*-butyl (*E*)-2-oxo-4-phenylbut-3-enoate, [1] catalysts (*S*)-**10,** [2] (*S*)-**3a**[2] and (*S*)-**4**[3] were prepared according to the literature procedure.

Preparation of Catalyst (*S*)-3b

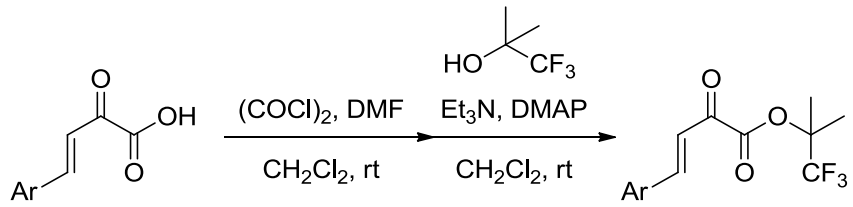


To a solution of 2-naphthyllithium (4.2 mmol) in THF (15 mL) was added a solution of (*S*)-**12** (316 mg, 0.7 mmol) in THF (2 mL) at –78 °C. After stirring for 1 h at –78 °C, the reaction mixture was warmed up to room temperature and stirred for 2.5 h. The reaction mixture was quenched by saturated NH_4Cl aq. After extraction with ethyl acetate, the organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The residue was roughly purified by column chromatography on silica gel and used for the next reaction.

A mixture of (*S*)-**13** (620 mg, *ca.* 0.7 mmol), *N*,*N*-dimethylbarbituric acid (NDMBA, 328 mg, 2.1 mmol), $Pd(OAc)_2$ (15.7 mg, 0.07 mmol) and triphenylphosphine (73.5 mg, 0.28 mmol) in CH_2Cl_2 (11 mL) was stirred at 35 °C for 20 h under argon atmosphere. After addition of CH_2Cl_2, the organic layer was washed with saturated $NaHCO_3$, dried over Na_2SO_4 and concentrated. The resulting residue was purified by column chromatography on silica gel to give (*S*)-**3b** (289 mg, 0.34 mmol, 48% yield over 2 steps).

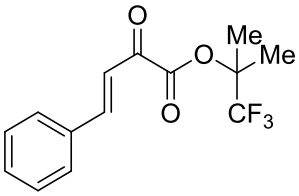
Catalyst (*S*)-3b. $[\alpha]_D^{19}$ = 179.3 (*c* 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.33 (38H, m), 4.08 (2H, br s), 2.87 (2H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 144.3, 142.7, 137.8, 134.0, 132.9, 132.6, 131.9, 131.0, 130.3, 129.0, 128.6, 128.3, 127.8, 127.5, 126.9, 126.2, 126.0, 125.8, 83.6, 45.0 (1 peak overlapped); IR (neat) 896, 858, 818, 747, 731 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{64}H_{46}O_2N$: 860.3523 ($[M + H]^+$), Found: 860.3514 ($[M + H]^+$)

General Procedure for Preparation of β,γ-Unsaturated α-Keto Esters



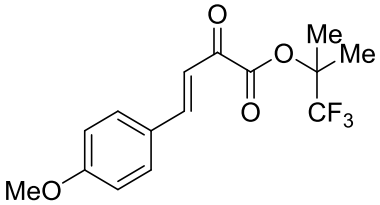
To a solution of β,γ-unsaturated α-keto carboxylic acid (3 mmol) and a catalytic amount of DMF in dry CH_2Cl_2 (7 mL) was added oxalyl chloride (0.66 mL, 7.7 mmol) dropwise at 0 °C under argon atmosphere. After stirring at room temperature for 5 h, the reaction mixture was concentrated to give a crude acid chloride. The crude mixture was diluted with CH_2Cl_2 (10 mL) and added to a solution of Et_3N (0.54 mL, 3.9 mmol), 2-trifluoromethyl-2-propanol (0.36 mL, 3.3 mmol) and DMAP (36 mg, 0.3 mmol) in CH_2Cl_2 (10 mL) at 0 °C. The reaction mixture was warmed up to room temperature and stirred overnight. After slow addition of 1 N HCl aq., the mixture was diluted with EtOAc. The organic layer was washed with brine, dried (Na_2SO_4) and concentrated. The residue was purified by flash column chromatography on silica gel to afford the corresponding product.

2,2,2-Trifluoro-1,1-dimethylethyl (*E*)-2-oxo-4-phenylbut-3-enoate



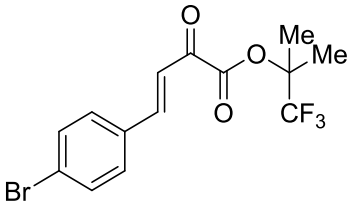
40% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (1H, d, J = 16.2 Hz), 7.62 (2H, d, J = 6.5 Hz), 7.49-7.42 (3H, m), 7.25 (1H, d, J = 15.9 Hz, $CHCl_3$ overlapped), 1.82 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.9, 159.9, 148.9, 133.9, 131.8, 129.1, 129.0, 124.5 (q, J = 282.5 Hz), 120.2, 82.4 (q, J = 30.2 Hz), 19.2; IR (neat) 1738, 1697, 1606, 1260, 1164, 1133, 1076, 741 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{14}H_{13}O_3F_3Na$: 309.0709 ([M + Na]$^+$), Found: 309.0710 ([M + Na]$^+$).

2,2,2-Trifluoro-1,1-dimethylethyl (*E*)-4-(4-methoxyphenyl)-2-oxobut-3-enoate



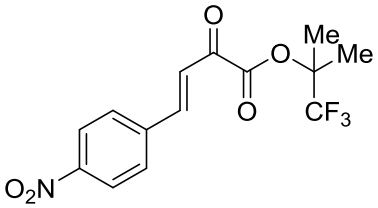
51% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (1H, d, J = 16.2 Hz), 7.58 (2H, d, J = 8.5 Hz), 7.12 (1H, dd, J = 16.2, 1.1 Hz), 6.94 (2H, d, J = 8.8 Hz), 3.87 (3H, s), 1.81 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.7, 162.8, 160.2, 148.8, 131.1, 126.7, 124.6 (q, J = 282.5 Hz), 117.9, 114.7, 82.3 (q, J = 30.2 Hz), 55.5, 19.2; IR (neat) 1739, 1682, 1592, 1512, 1261, 1160, 1142, 1082, 1024, 837 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{15}H_{15}O_4F_3Na$: 339.0815 ([M + Na]$^+$), Found: 339.0823 ([M + Na]$^+$).

2,2,2-Trifluoro-1,1-dimethylethyl (*E*)-4-(4-bromophenyl)-2-oxobut-3-enoate



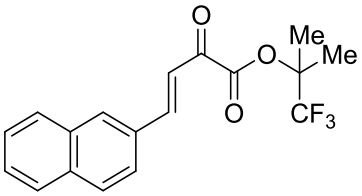
91% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (1H, d, J = 16.2 Hz), 7.57 (2H, d, J = 8.5 Hz), 7.48 (2H, d, J = 8.5 Hz), 7.25 (1H, d, J = 15.9 Hz), 1.81 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.6, 159.7, 147.3, 132.8, 132.5, 130.3, 126.3, 124.5 (q, J = 282.5 Hz), 120.7, 82.6 (q, J = 30.2 Hz), 19.2; IR (neat) 1741, 1691, 1604, 1583, 1261, 1196, 1163, 1140, 1087, 1065, 1006, 825, 772 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{14}H_{12}O_3{}^{79}BrF_3Na$: 386.9814 ([M + Na]$^+$), Found: 386.9818 ([M + Na]$^+$), Calcd. for $C_{14}H_{12}O_3{}^{81}BrF_3Na$: 388.9794 ([M + Na]$^+$), Found: 388.9800 ([M + Na]$^+$).

2,2,2-Trifluoro-1,1-dimethylethyl (*E*)-4-(4-nitrophenyl)-2-oxobut-3-enoate



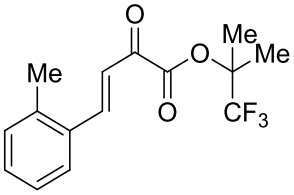
40% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.29 (2H, d, J = 9.1 Hz), 7.85 (1H, d, J = 16.2 Hz), 7.78 (2H, d, J = 8.8 Hz), 7.39 (1H, d, J = 16.2 Hz), 1.82 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.2, 159.2, 149.2, 145.1, 139.8, 129.5, 124.44 (q, J = 282.5 Hz), 124.35, 123.6, 82.9 (q, J = 30.2 Hz), 19.2; IR (neat) 1742, 1697, 1612, 1596, 1517, 1344, 1260, 1161, 1135, 1080, 905, 848, 728, 650 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{14}H_{12}O_5NF_3Na$: 354.0560 ([M + Na]$^+$), Found: 354.0561 ([M + Na]$^+$).

2,2,2-Trifluoro-1,1-dimethylethyl (*E*)-4-(naphthalen-2-yl)-2-oxobut-3-enoate



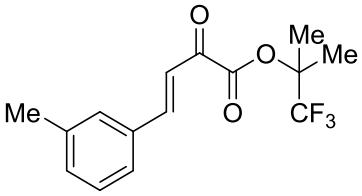
53% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (1H, s), 7.99 (1H, d, J = 16.2 Hz), 7.90-7.84 (3 H, m), 7.73 (1H, d, J = 8.5 Hz), 7.58-7.52 (2H, m), 7.36 (1H, d, J = 16.2 Hz), 1.83 (6H s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.8, 160.0, 148.9, 134.9, 133.2, 132.1, 131.4, 129.0, 128.9, 128.1, 127.9, 127.0, 124.5 (q, J = 283.8 Hz), 123.4, 120.3, 82.5 (q, J = 30.2 Hz), 19.2; IR (neat) 1758, 1689, 1583, 1236, 1163, 1133, 1096, 822, 785, 750 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{18}H_{15}O_3F_3Na$: 359.0866 ([M + Na]$^+$), Found: 359.0879 ([M + Na]$^+$).

2,2,2-Trifluoro-1,1-dimethylethyl (*E*)-2-oxo-4-(*o*-tolyl)but-3-enoate



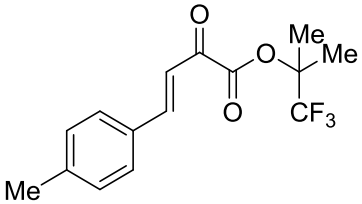
35% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (1H, d, J = 16.2 Hz), 7.66 (1H, d, J = 7.9 Hz), 7.35 (1H, app t, J = 6.8 Hz), 7.27-7.24 (2H, m), 7.16 (1H, d, J = 16.2 Hz), 2.47 (3H, s), 1.82 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 182.2, 160.2, 146.4, 139.1, 132.8, 131.5, 131.2, 126.8, 126.6, 124.5 (q, J = 282.5 Hz), 121.3, 82.5 (q, J = 30.6 Hz), 19.7, 19.2; IR (neat) 1739, 1608, 1594, 1255, 1164, 1134, 1077, 749 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{15}H_{15}O_3F_3Na$: 323.0866 ([M + Na]$^+$), Found: 323.0865 ([M + Na]$^+$).

2,2,2-Trifluoro-1,1-dimethylethyl (*E*)-2-oxo-4-(*m*-tolyl)but-3-enoate



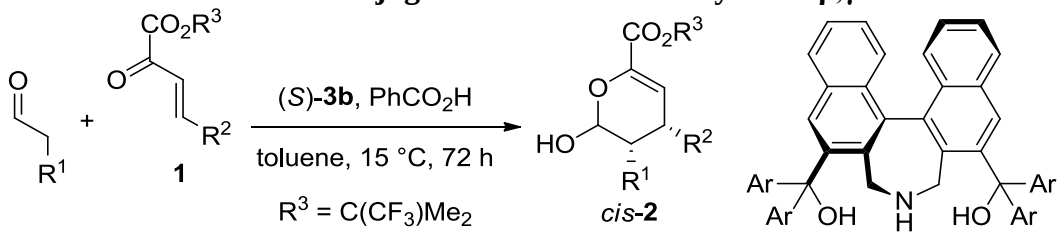
59% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (1H, d, J = 16.2 Hz), 7.43-7.42 (2H, m), 7.32 (1H, app t, J = 7.8 Hz), 7.28 (1H, d, J = 7.4 Hz), 7.23 (1H, d, J = 16.2 Hz), 2.40 (3H, s), 1.82 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.9, 160.0, 149.2, 138.9, 133.9, 132.7, 129.7, 129.0, 126.3, 124.5 (q, J = 282.5 Hz), 120.1, 82.4 (q, J = 30.6 Hz), 21.3, 19.2; IR (neat) 1738, 1600, 1583, 1227, 1162, 1131, 1074, 985, 766 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{15}H_{15}O_3F_3Na$: 323.0866 ([M + Na]$^+$), Found: 323.0882 ([M + Na]$^+$).

2,2,2-Trifluoro-1,1-dimethylethyl (*E*)-2-oxo-4-(*p*-tolyl)but-3-enoate



72% yield; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (1H, d, J = 15.9 Hz), 7.52 (2H, d, J = 7.9 Hz), 7.24 (2H, d, J = 8.2 Hz), 7.20 (1H, d, J = 16.2 Hz), 2.40 (3H, s), 1.81 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 181.9, 160.0, 149.0, 142.7, 131.2, 129.9, 129.1, 124.5 (q, J = 282.5 Hz), 119.3, 82.3 (q, J = 30.2 Hz), 21.6, 19.2; IR (neat) 1736, 1691, 1615, 1604, 1263, 1163, 1077, 987, 819, 774 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{15}H_{15}O_3F_3Na$: 323.0866 ([M + Na]$^+$), Found: 323.0855 ([M + Na]$^+$).

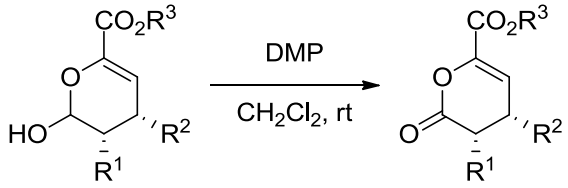
General Procedure for Conjugate Addition of Aldehydes to β,γ-Unsaturated α-Keto Esters



(*S*)-**3b** (Ar = 2-Naphthyl)

To a solution of the amine catalyst (*S*)-**3b** (0.01 mmol) and benzoic acid (0.01 mmol) in toluene (100 μL) was added the β,γ-unsaturated α-keto ester **1** (0.1 mmol) at 15 °C. To the mixture was added a solution of an aldehyde (0.5 mmol) in toluene (200 μL) slowly over 66.7 h (3 μL/h) with a syringe pump and the resulting mixture was stirred for 5.3 h. After concentration, the residue was purified by flash column chromatography on silica gel to afford a diastereomixture of the corresponding product. To stabilize the product and determine the enantiomeric excess, the obtained hemiacetal *cis*-**2** was immediately oxidized to *cis*-**6** after determination of the isolated yield and the diastereomeric ratio.

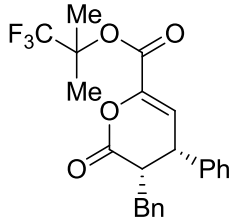
Typical Procedure for Oxidation of *cis*-2



cis-**2** $R^3 = C(CF_3)Me_2$ *cis*-**6**

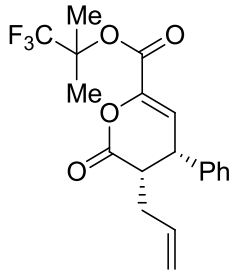
To a solution of *cis*-**2** (0.074 mmol) in CH_2Cl_2 (1.5 mL) was added the Dess-Martin periodinane (DMP, 0.30 mmol) in one portion at room temperature. The reaction mixture was stirred at room temperature until complete consumption of *cis*-**2** was observed by TLC analysis (30 min ~ 1 h). The reaction mixture was quenched by a saturated Na_2SO_3 aq. and $NaHCO_3$ aq. After extraction with CH_2Cl_2, the organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to afford the corresponding product.

2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-2-oxo-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate



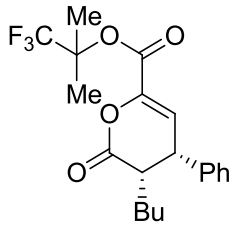
dr = 14/1, ee = 99/9% ee; $[\alpha]_D^{25}$ = 254.4 (*c* 0.69, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.31 (3H, m), 7.31-7.27 (2H, m), 7.25-7.22 (1H, m), 7.07-7.02 (4H, m), 6.61 (1H, d, *J* = 6.8 Hz), 3.63 (1H, app t, *J* = 6.8 Hz), 3.34-3.29 (2H, m), 2.40 (1H, dd, *J* = 15.7, 10.6 Hz), 1.75 (3H, s), 1.73 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 158.0, 141.6, 138.0, 135.6, 129.3, 128.9, 128.6, 128.5, 128.4, 126.8, 124.6 (q, *J* = 282.5 Hz), 119.4, 81.9 (q, *J* = 29.8 Hz), 44.7, 40.6, 32.0, 19.2; IR (neat) 1776, 1743, 1332, 1268, 1164, 1135, 1105, 752, 697 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{23}H_{21}O_4F_3Na$: 441.1284 ([M + Na]$^+$), Found: 441.1289 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak IC, hexane/*i*-PrOH = 10/1, flow rate = 1.0 mL/min, retention time; major diastereomer 8.1 min and 9.9 min (major), minor diastereomer 10.7 min and 12.2 min (major).

2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-allyl-2-oxo-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate



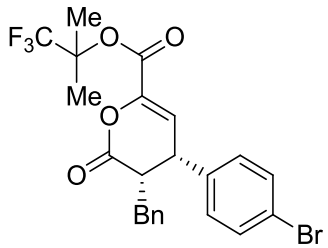
dr = >20/1, ee = 97/-% ee; $[\alpha]_D^{22}$ = 223.8 (*c* 0.83, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.29 (3H, m), 7.10 (2H, dd, *J* = 7.8, 1.6 Hz), 6.67, (1H, d, *J* = 6.8 Hz), 5.83-5.74 (1H, m), 5.11 (1H, d, *J* = 10.2 Hz), 5.03 (1H, dd, *J* = 17.1, 1.3 Hz), 3.82 (1H, app t, *J* = 6.9 Hz), 2.96 (1H, ddd, *J* = 8.5, 7.2, 5.6 Hz), 2.58-2.52 (1H, m), 1.89 (1H, app dt, *J* = 14.7 Hz, 7.9 Hz), 1.76 (3H, s), 1.75 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 158.0, 141.8, 135.5, 134.6, 129.2, 128.4, 128.3, 124.6 (q, *J* = 282.5 Hz), 119.1, 118.0, 81.9 (q, *J* = 29.8 Hz), 43.2, 41.0, 30.4, 19.2; IR (neat) 1778, 1746, 1335, 1262, 1167, 1137, 1109, 756, 699 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{19}H_{19}O_4F_3Na$: 391.1128 ($[M + Na]^+$), Found: 391.1135 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak IC, hexane/*i*-PrOH = 10/1, flow rate = 1.0 mL/min, retention time; major diastereomer 7.7 min and 9.8 min (major).

2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-butyl-2-oxo-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate



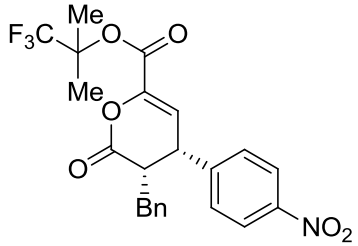
dr = 4/1, ee = 98/56% ee; ^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.38-7.29 (3H, m), 7.11-7.08 (2H, m), 6.65 (1H, d, *J* = 6.5 Hz), 3.80 (1H, app t, *J* = 6.9 Hz), 2.82 (1H, app q, *J* = 7.0 Hz), 1.76 (6H, s), 1.72-1.59 (1H, m), 1.43-1.12 (5H, m), 0.85 (3H, t, *J* = 7.1 Hz); minor diastereomer δ 7.38-7.29 (3H, m), 7.15 (2H, d, *J* = 7.0 Hz), 6.46 (1H, d, *J* = 4.6 Hz), 3.66 (1H, app dd, *J* = 6.9, 4.5 Hz), 2.74 (1H, app dd, *J* =12.6, 7.2 Hz), 1.75 (6H, s), 1.72-1.59 (1H, m), 1.43-1.12 (5H, m), 0.86 (3H, t, *J* = 7.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer δ 168.5, 158.1, 141.8, 135.9, 129.2, 128.2, 128.1, 124.6 (q, *J* = 282.5 Hz), 119.1, 81.8 (q, *J* = 29.8 Hz), 43.3, 41.6, 29.3, 25.9, 22.4, 19.2, 13.8; minor diastereomer δ 168.0, 157.9, 141.2, 139.6, 129.3, 128.0, 127.4, 124.6 (q, *J* = 282.5 Hz), 117.9, 81.8 (q, *J* = 29.8 Hz), 45.6, 43.0, 29.4, 28.8, 22.4, 13.8 (1 peaks overlapped); IR (neat) 1777, 1744, 1334, 1259, 1165, 1136, 1104, 755, 699 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{20}H_{23}O_4F_3Na$: 407.1441 ($[M + Na]^+$), Found: 407.1446 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak IG, hexane/*i*-PrOH = 10/1, flow rate = 1.0 mL/min, retention time; major diastereomer 8.6 min (major) and 11.0 min, minor diastereomer 7.3 min and 8.1 min (major).

2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-4-(4-bromophenyl)-2-oxo-3,4-dihydro-2*H*-pyran-6-carboxylate



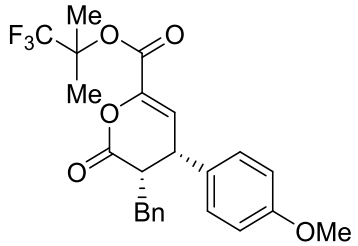
dr = >20/1, ee = 99/38% ee; $[\alpha]_D^{25}$ = 193.9 (*c* 0.85, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (2H, d, *J* = 8.5 Hz), 7.30 (2H, t, *J* = 7.2 Hz), 7.26-7.23 (1H, $CHCl_3$ overlapped, m), 7.05 (2H, d, *J* = 7.1 Hz), 6.88 (2H, d, *J* = 8.5 Hz), 6.56 (1H, d, *J* = 6.8 Hz), 3.59 (1H, app t, *J* = 6.8 Hz), 3.31-3.26 (2H, m), 2.37 (1H, dd, *J* = 15.9, 10.8 Hz), 1.74 (3H, s), 1.73 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.9, 157.8, 141.8, 137.6, 134.6, 132.4, 130.1, 128.8, 128.7, 126.9, 124.6 (q, *J* = 282.5 Hz), 122.5, 118.7, 82.0 (q, *J* = 29.8 Hz), 44.4, 40.0, 32.0, 19.2; IR (neat) 1774, 1747, 1335, 1269, 1166, 1135, 1107, 1010, 823 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{23}H_{20}O_4{}^{79}BrF_3Na$: 519.0389 ($[M + Na]^+$), Found: 519.0392 ($[M + Na]^+$), Calcd. for $C_{23}H_{20}O_4{}^{81}BrF_3Na$: 521.0369 ($[M + Na]^+$), Found: 521.0368 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak AD-3, hexane/*i*-PrOH = 10/1, flow rate = 0.75 mL/min, retention time; major diastereomer 18.9 min (major) and 19.9 min, minor diastereomer 17.1 min and 26.6 min (major).

2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-4-(4-nitrophenyl)-2-oxo-3,4-dihydro-2*H*-pyran-6-carboxylate



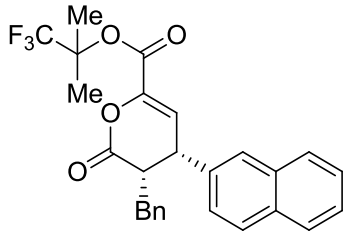
dr = 10/1 (The product slightly epimerized under the oxidation conditions.); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (2H, d, *J* = 8.7 Hz), 7.33-7.27 (3H, m), 7.18 (2H, d, *J* = 8.7 Hz), 7.03 (2H, d, *J* = 6.8 Hz), 6.56 (1H, d, *J* = 7.0 Hz), 3.76 (1H, app t, *J* = 7.0 Hz), 3.39-3.30 (2H, m), 2.37-2.30 (1H, m), 1.76 (3H, s), 1.74 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.5, 157.6, 147.9, 143.1, 142.4, 137.1, 129.5, 128.9, 128.7, 127.1, 124.6 (q, *J* = 282.5 Hz), 124.4, 117.6, 82.2 (q, *J* = 30.2 Hz), 44.1, 40.1, 32.0, 19.2; IR (neat) 1777, 1744, 1521, 1346, 1269, 1163, 1134, 1105, 852, 753, 737, 698 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{23}H_{20}O_6NF_3Na$: 486.1135 ($[M + Na]^+$), Found: 486.1133 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak IC, hexane/*i*-PrOH = 3/1, flow rate = 1.0 mL/min, retention time; major diastereomer 27.7 min and 57.4 min (major), minor diastereomer 17.4 min (major) and 29.8 min.

2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-4-(4-methoxyphenyl)-2-oxo-3,4-dihydro-2*H*-pyran-6-carboxylate



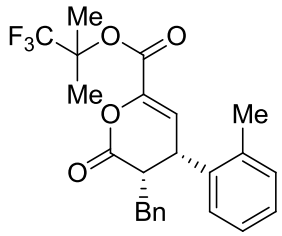
dr = >20/1 (Diastereomers could be separated by silica gel column chromatography.), ee = 98/8% ee; $[\alpha]_D^{25}$ = 269.8 (*c* 1.30, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (2H, t, *J* = 7.1 Hz), 7.25-7.21 (1H, m), 7.07 (2H, d, *J* = 7.0 Hz), 6.94 (2H, d, *J* = 8.7 Hz), 6.87 (2H, d, *J* = 8.7 Hz), 6.59 (1H, d, *J* = 7.0 Hz), 3.81 (3H, s), 3.57 (1H, t, *J* = 6.9 Hz), 3.29-3.21 (2H, m), 2.44-2.37 (1H, m), 1.74 (3H, s), 1.73 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.4, 159.6, 158.0, 141.3, 138.1, 129.6, 128.9, 128.6, 127.3, 126.7, 124.6 (q, *J* = 282.5 Hz), 119.8, 114.6, 81.8 (q, *J* = 29.8 Hz), 55.3, 44.9, 39.8, 32.0, 19.2; IR (neat) 1776, 1745, 1513, 1335, 1253, 1166, 1137, 1107, 1035, 830, 756, 700 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{24}H_{23}O_5F_3Na$: 471.1390 ($[M + Na]^+$), Found: 471.1392 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak IC-3, hexane/*i*-PrOH = 10/1, flow rate = 1.0 mL/min, retention time; major diastereomer 15.1 min and 23.3 min (major), minor diastereomer 22.3 min (major) and 25.7 min.

2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-4-(naphthalen-2-yl)-2-oxo-3,4-dihydro-2*H*-pyran-6-carboxylate



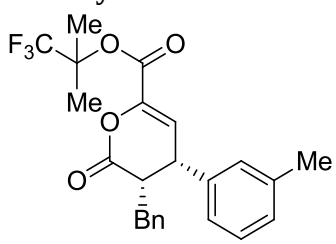
dr = >20/1, ee = 98/43% ee; $[\alpha]_D^{16}$ = 386.6 (*c* 0.91, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.83 (2H, m), 7.81-7.78 (1H, m), 7.53-7.50 (2H, m). 7.45 (1H, s), 7.32-7.23 (3H, m, $CHCl_3$ overlapped), 7.12 (1H, dd, *J* = 8.5, 1.7 Hz), 7.04 (2H, d, *J* = 7.0 Hz), 6.65 (1H, d, *J* = 6.8 Hz), 3.79 (1H, app t, *J* = 6.8 Hz), 3.38-3.27 (2H, m), 2.43 (1H, dd, *J* = 14.4, 9.3 Hz), 1.76 (3H, s), 1.73 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 158.0, 141.6, 138.0, 133.4, 133.1, 132.9, 129.2, 128.9, 128.6, 127.8, 127.7, 126.8, 126.7, 126.6, 125.7, 124.6 (q, *J* = 282.7 Hz), 119.3, 81.9 (q, *J* = 30.2 Hz), 44.6, 40.8, 32.1, 19.2 (aromatic 1 peak overlapped); IR (neat) 1777, 1745, 1333, 1268, 1167, 1137, 1107, 821, 754 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{27}H_{23}O_4F_3Na$: 491.1441 ($[M + Na]^+$), Found: 491.1440 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak IG, hexane/*i*-PrOH = 10/1, flow rate = 1.0 mL/min, retention time; major diastereomer 13.5 min and 18.3 min (major), minor diastereomer 12.8 min (major) and 14.8 min.

2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-2-oxo-4-(*o*-tolyl)-3,4-dihydro-2*H*-pyran-6-carboxylate



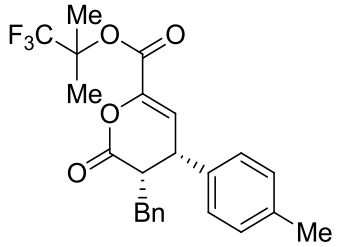
dr = 2.4/1; ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer δ 7.32-7.27 (1H, m), 7.25-7.14 (6H, m), 6.88-6.86 (1H, m), 6.50 (1H, d, *J* = 6.5 Hz), 3.87-3.83 (1H, m), 3.36 (1H, dd, *J* = 14.5, 5.1 Hz), 3.32-3.28 (1H, m), 2.55 (1H, dd, *J* = 14.5, 9.9 Hz), 1.92 (3H, s), 1.73 (3H, s), 1.71 (3H, s); minor diastereomer δ 7.32-7.27 (1H, m), 7.25-7.14 (4H, m), 7.13-7.11 (1H, m), 7.09-7.06 (2H, m), 7.02-7.01 (1H, m), 6.44 (1H, dd, *J* = 5.5, 1.0 Hz), 3.87-3.83 (1H, m), 3.10 (1H, dd, *J* = 13.5, 5.5 Hz), 3.01-2.97 (1H, m), 2.86 (1H, dd, *J* = 13.3, 8.5 Hz), 1.87 (3H, s), 1.79 (3H, s), 1.77 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer δ 168.8, 158.0, 141.1, 137.8, 136.3, 134.7, 131.1, 128.72, 128.65, 128.0, 127.3, 126.9, 126.8, 124.6 (q, *J* = 282.5 Hz), 118.5, 81.8 (q, *J* = 30.2 Hz), 43.6, 35.5, 32.1, 19.4, 19.2; minor diastereomer δ 167.8, 157.7, 141.9, 137.2, 136.7, 135.4, 131.3, 129.4, 128.8, 127.9, 127.2, 127.0, 126.5, 124.6 (q, *J* = 282.5 Hz), 116.9, 81.9 (q, *J* = 30.2 Hz), 47.3, 37.1, 36.2, 19.3, 18.9 (1 peak overlapped); IR (neat) 1775, 1746, 1334, 1271, 1166, 1136, 1111, 753, 727 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{24}H_{23}O_4F_3Na$: 455.1441 ($[M + Na]^+$), Found: 455.1443 ($[M + Na]^+$); HPLC analysis: Daicel Chiralpak IG, hexane/*i*-PrOH = 10/1, flow rate = 1.0 mL/min, retention time; major diastereomer 10.8 min 11.4 min (major), minor diastereomer 8.5 min and 9.1 min (major).

2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-2-oxo-4-(*m*-tolyl)-3,4-dihydro-2*H*-pyran-6-carboxylate



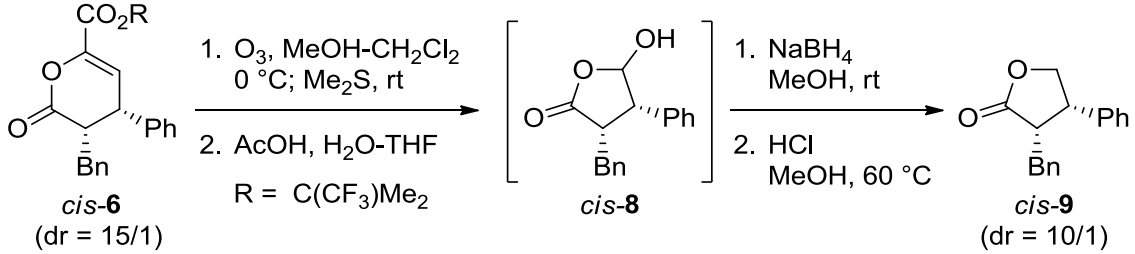
dr = 4.1/1; ^{1}H NMR (500 MHz, $CDCl_3$) major diastereomer δ 7.30-7.27 (2H, m), 7.25-7.22 (2H, m), 7.14 (1H, d, J = 7.4 Hz), 7.05 (2H, d, J = 7.4 Hz), 6.81 (2H, t, J = 9.4 Hz), 6.60 (1H, d, J = 6.8 Hz), 3.60-3.56 (1H, m), 3.28-3.23 (2H, m), 2.40 (1H, dd, J = 15.9, 10.0 Hz), 2.34 (3H, s), 1.75 (3H, s), 1.73 (3H, s); minor diastereomer δ 7.30-7.22 (4H, m), 7.20-7.17 (2H, m), 7.10 (1H, d, J = 7.7 Hz), 6.85-6.79 (2H, m), 6.42 (1H, d, J = 4.8 Hz), 3.10 (1H, app q, J = 6.5 Hz), 3.04 (1H, dd, J = 13.9, 6.2 Hz), 2.96-2.89 (1H, m), 2.79-2.72 (1H, m), 2.32 (3H, s), 1.763 (3H, s), 1.756 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) major diastereomer δ 168.3, 158.0, 141.5, 139.0, 138.1, 135.5, 129.2, 129.10, 129.06, 128.9, 128.6, 126.7, 125.5, 124.6 (q, J = 282.5 Hz), 119.5, 81.8 (q, J = 29.8 Hz), 44.6, 40.6, 32.0, 21.4, 19.2; minor diastereomer δ 167.8, 157.8, 141.1, 139.2, 139.1, 137.3, 129.23, 129.21, 128.8, 128.7, 128.0, 127.1, 124.6 (q, J = 282.5 Hz), 124.4, 117.5, 81.9 (q, J = 29.8 Hz), 47.4, 41.6, 35.7 21.4, 19.2; IR (neat) 1778, 1745, 1335, 1269, 1166, 1137, 1108, 699 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{24}H_{23}O_4F_3Na$: 455.1441 ([M + Na]$^+$), Found: 455.1444 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak IC, hexane/*i*-PrOH = 10/1, flow rate = 1.0 mL/min, retention time; major diastereomer 8.0 min and 9.9 min (major), minor diastereomer 10.9 min (major) and 12.0 min.

2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-2-oxo-4-(*p*-tolyl)-3,4-dihydro-2*H*-pyran-6-carboxylate



dr = 20/1, ee = 98/7% ee; $[\alpha]_D^{21}$ = 312.7 (*c* 0.61, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.27 (2H, m), 7.25-7.21 (1H, m), 7.16 (2H, d, J = 7.7 Hz), 7.06 (2H, d, J = 7.1 Hz), 6.91 (2H, d, J = 8.2 Hz), 6.60 (1H, d, J = 7.1 Hz), 3.58 (1H, app t, J = 6.8 Hz), 3.28-3.22 (2H, m), 2.43-2.38 (1H, m), 2.35 (3H, s), 1.74 (3H, s), 1.72 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.3, 158.0, 141.4, 138.3, 138.1, 132.5, 129.9, 128.9, 128.6, 128.3, 126.7, 124.6 (q, J = 282.5 Hz), 119.7, 81.8 (q, J = 30.2 Hz), 44.8, 40.2, 32.0, 21.1, 19.2; IR (neat) 1777, 1745, 1335, 1270, 1165, 1136, 1106, 820, 756, 734, 714, 700 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{24}H_{23}O_4F_3Na$: 455.1441 ([M + Na]$^+$), Found: 455.1445 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak IB-3, hexane/*i*-PrOH = 10/1, flow rate = 1.0 mL/min, retention time; major diastereomer 6.4 min and 7.0 min (major), minor diastereomer 7.5 min (major) and 11.5 min.

Synthesis of γ-Lactone *cis*-9

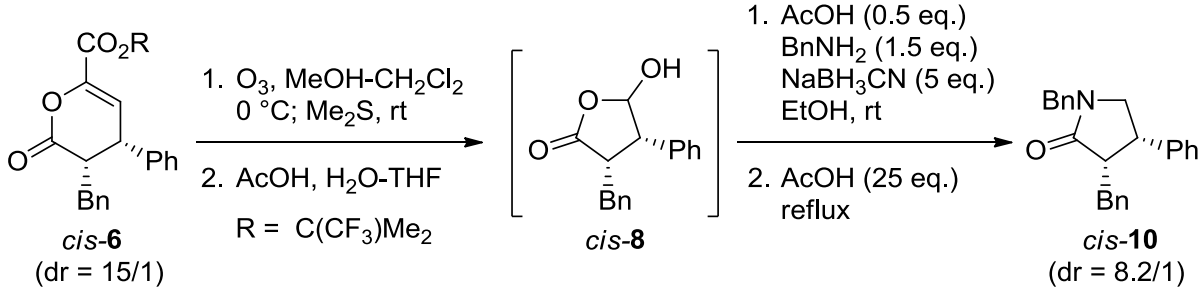


To a solution of *cis*-**6** (16 mg, 0.038 mmol) in CH_2Cl_2 (1 mL) and MeOH (2 mL), ozone was bubbled at 0 °C until complete consumption of *cis*-**6** was observed by TLC analysis (around 5 min). The mixture was then flushed with nitrogen and added dimethyl sulfide (30 μL, 0.4 mmol). The reaction mixture was gradually warmed up to room temperature and stirred overnight. All volatiles were removed *in vacuo*. The crude mixture was diluted with THF (1 mL). After addition of acetic acid (1.8 μL, 0.03 mmol) and water (50 μL) were added to the solution and stirred for 1 h at room temperature. The reaction mixture was diluted with EtOAc, dried over Na_2SO_4 and concentrated. The residue was dissolved in MeOH (0.4 mL). Sodium borohydride (7.2 mg, 0.19 mmol) was added to the solution. After stirring for 1 h, HCl (0.5 M in MeOH, 750 mL, 0.38 mmol) was added to the reaction mixture carefully. After stirring 1 h at

60 °C, the reaction mixture was quenched by a saturated $NaHCO_3$ aq. After extraction with EtOAc, the organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to afford *cis*-**9** (6.7 mg, 0.027 mmol).

γ-Lactone *cis*-9. dr = 20/1 (Diastereomers could be separated by PLC.), ee = 99% ee; $[\alpha]_D^{18}$ = 193.1 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.32 (3H, m), 7.24-7.17 (3H, m), 7.04-7.02 (2H, m), 6.93 (2H, d, *J* = 7.3 Hz), 4.57 (1H, dd, *J* = 9.2, 5.8 Hz), 4.46 (1H, d, *J* = 9.4 Hz), 3.60 (1H, app t, *J* = 6.9 Hz), 3.29-3.23 (1H, m), 3.13 (1H, dd, *J* = 14.7, 3.9 Hz), 2.29 (1H, dd, *J* = 14.7, 10.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 178.0, 138.71, 138.66, 128.9, 128.7, 128.4, 127.9, 127.8, 126.4, 73.0, 46.2, 44.6, 31.6; IR (neat) 1771, 1143, 710, 698 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{17}H_{16}O_2Na$: 275.1043 ([M + Na]$^+$), Found: 275.1039 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak IG, hexane/*i*-PrOH = 10/1, flow rate = 1.0 mL/min, retention time; major diastereomer 14.4 min and 15.5 min (major).

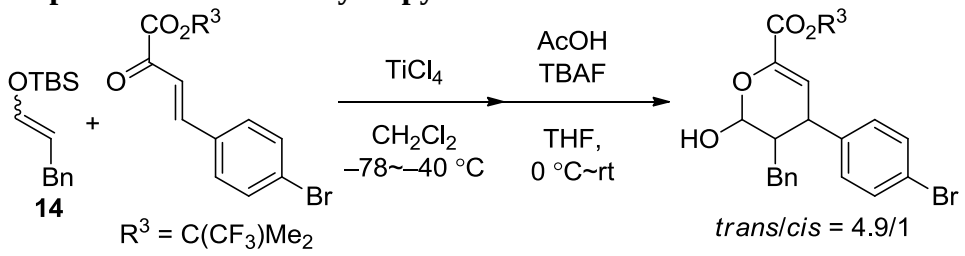
Synthesis of γ-Lactam *cis*-10



To a solution of *cis*-**6** (28.3 mg, 0.068 mmol) in CH_2Cl_2 (1 mL) and MeOH (2 mL), ozone was bubbled at 0 °C until complete consumption of *cis*-**6** was observed by TLC analysis (around 5 min). The mixture was then flushed with nitrogen and added dimethyl sulfide (43 μL, 0.57 mmol). The reaction mixture was gradually warmed up to room temperature and stirred overnight. All volatiles were removed *in vacuo*. The crude mixture was diluted with THF (1 mL). After addition of acetic acid (2.0 μL, 0.033 mmol) and water (100 μL), the mixture was stirred for 1 h at room temperature. The reaction mixture was diluted with EtOAc, dried over Na_2SO_4 and concentrated. The residue was dissolved in EtOH (1.3 mL). Acetic acid (2.0 μL, 0.033 mmol) and sodium cyanoborohydride (21.2 mg, 0.34 mmol) were added to the solution followed by benzylamine (11.1 μL, 0.1 mmol). After stirring for 1 h, acetic acid (96.6 mL, 1.75 mmol) and EtOH (2.5 mL) was added to the reaction mixture carefully. The mixture was refluxed for 3 h. The reaction mixture was quenched by a saturated $NaHCO_3$ aq. After extraction with EtOAc, the organic layer was dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to afford *cis*-**10** (18.3 mg, 0.053 mmol).

γ-Lactam *cis*-10. dr = 8.2/1, ee = 98% ee; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.27 (5H, m), 7.24-7.12 (6H, m), 6.90-6.85 (4H, m), 4.66 (1H, d, *J* = 14.2 Hz), 4.49 (1H, d, *J* = 14.2 Hz), 3.61 (1H, dd, *J* = 9.9, 6.8 Hz), 3.41 (1H, td, *J* = 7.4, 1.7 Hz), 3.23-3.16 (3H, m), 2.32 (1H, dd, *J* = 15.4, 11.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 175.0, 140.5, 139.7, 136.2, 128.8, 128.7, 128.6, 128.4, 128.0, 127.9, 127.7, 127.1, 125.9, 52.1, 48.5, 47.1, 40.9, 31.9; IR (neat) 1686, 1495, 1454, 1428, 699 cm^{-1}; HRMS (ESI-MS) Calcd. for $C_{24}H_{23}ONNa$: 364.1672 ([M + Na]$^+$), Found: 364.1689 ([M + Na]$^+$); HPLC analysis: Daicel Chiralpak IG, hexane/*i*-PrOH = 10/1, flow rate = 1.0 mL/min, retention time; major diastereomer 27.4 min (major) and 33.0 min.

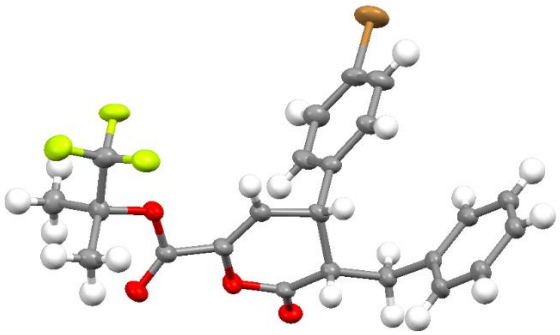
Preparation of *trans*-Dihydropyran



To a solution of 2,2,2-trifluoro-1,1-dimethylethyl (*E*)-4-(4-bromophenyl)-2-oxobut- 3-enoate (73 mg, 0.20 mmol) in anhydrous CH_2Cl_2 (4 mL) was added $TiCl_4$ (1M in CH_2Cl_2, 200 µL, 0.20 mmol) at –78 °C. After stirring for 15 min, silyl enol ether **14** (74.4 mg, 0.30 mmol) was added. The reaction mixture was stirred at –78 °C for 1 h. The reaction mixture was warmed up to –40 °C and stirred for 30 min. The reaction mixture was quenched with a saturated $NaHCO_3$ aq. After extraction with EtOAc, the organic layer was dried over Na_2SO_4 and concentrated. The crude mixture was diluted with THF (2 mL). Acetic acid (34.3 µL, 0.60 mmol) and TBAF (1 M in THF, 400 µL, 0.40 mmol) were added to the solution at 0 °C. The reaction mixture was warmed up to rt and stirred for 1 h. After addition of AcOEt, the organic layer was washed with brine, dried over Na_2SO_4 and concentrated. The resulting residue was purified by column chromatography on silica gel to give the product (71.3 mg, 0.14 mmol).

Crystal Structure Analysis of Dihydropyranone 7

Single crystals of **7** for X-ray diffraction experiments were grown from THF and hexane at room temperature. The data were collected at –150 °C on a Rigaku R-AXIS RAPID IP diffractometer with graphite-monochromated Cu Kα radiation (λ = 1.5419 Å). The crystal structure was solved by direct methods using SIR97[4] and refined in SHELXL-97[5] by full matrix least-squares using anisotropic thermal displacement parameters for all non-hydrogen atoms. Crystallographic data for **7**: $C_{23}H_{20}BrF_3O_4$, colorless blocks, 0.36×0.28×0.10 mm^3, monoclinic, $P2_1$, a = 12.6188(4), b = 5.81849(17), c = 15.3547(4) Å, V = 1092.17(5) $Å^3$, ρ_{calcd} = 1.512 gcm^{-3}, Z = 2, $2\theta_{max}$ = 136.56°, μ = 3.041 mm^{-1}. A total of 9822 reflections were measured. R = 0.0431, and Rw = 0.1086 for 3559 observed reflections with $I > 2.0\sigma(I)$. Flack parameter = –0.036(15). CCDC-1585733 (**7**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



ORTEP diagram of dihydropyranone **7**

References

1 Y. Matsumura, T. Suzuki, A. Sakakura and K. Ishihara, *Angew*. *Chem*., *Int*. *Ed*., 2014, **53**, 6131.
2 T. Kano, M. Ueda, J. Takai and K. Maruoka, *J*. *Am*. *Chem*. *Soc*., 2006, **128**, 6046.
3 T. Ooi, M. Kameda and K. Maruoka, *J*. *Am*. *Chem*. *Soc*., 2003, **125**, 5139.
4 SIR97, Program for the solution of crystal structures: A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 1999, 32, 115.Ooi, M. Kameda and K. Maruoka, *J*. *Am*. *Chem*. *Soc*., 2003, **125**, 5139.
5 G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement; University of Göttingen: Göttingen, Germany, 1997.

NMR Spectra

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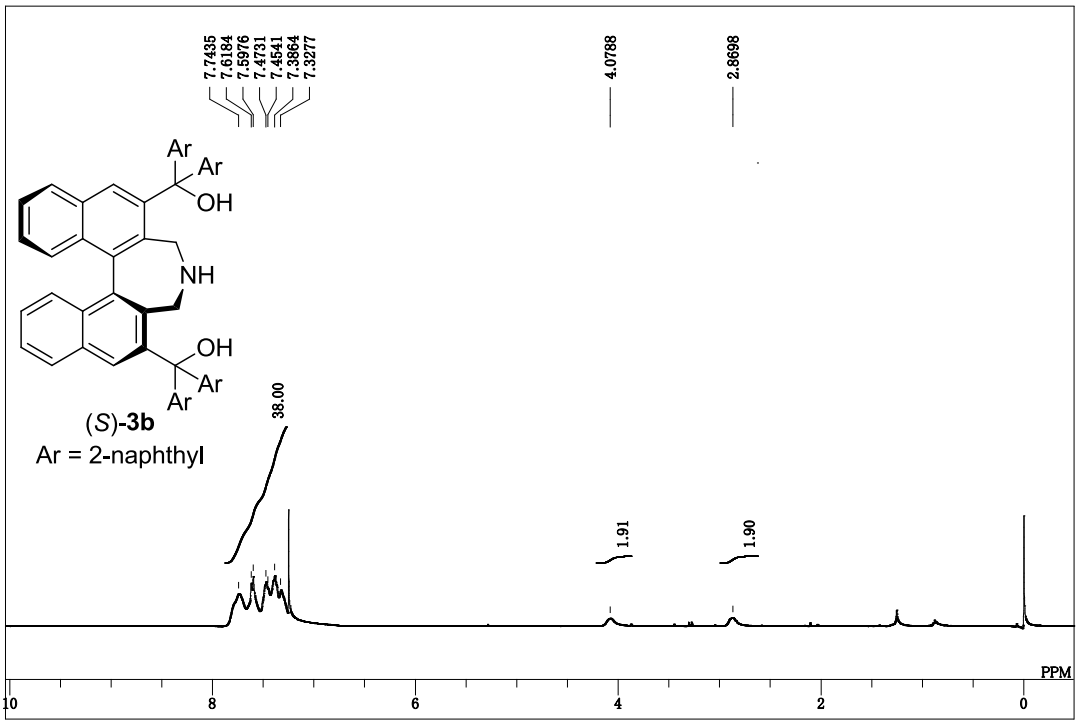
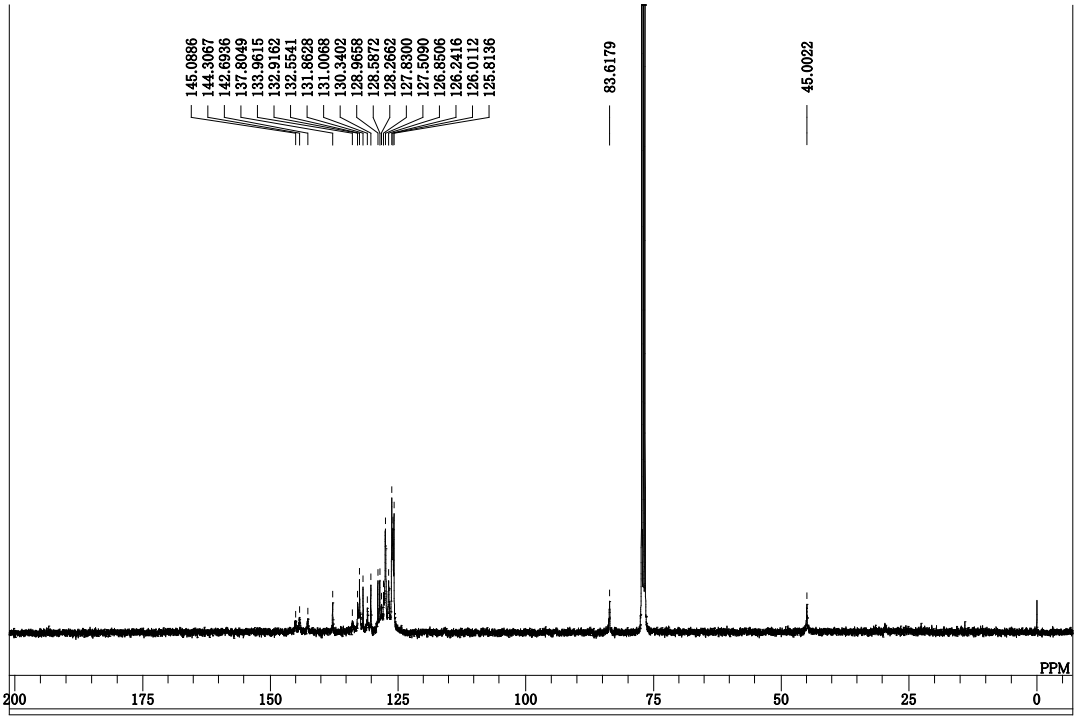
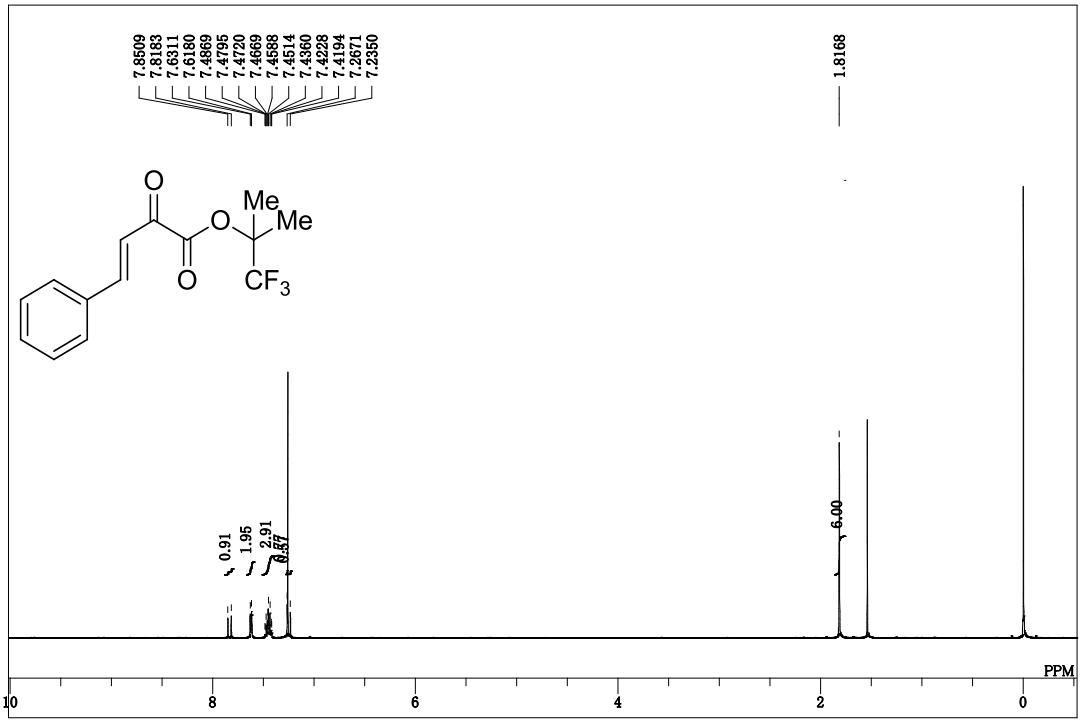
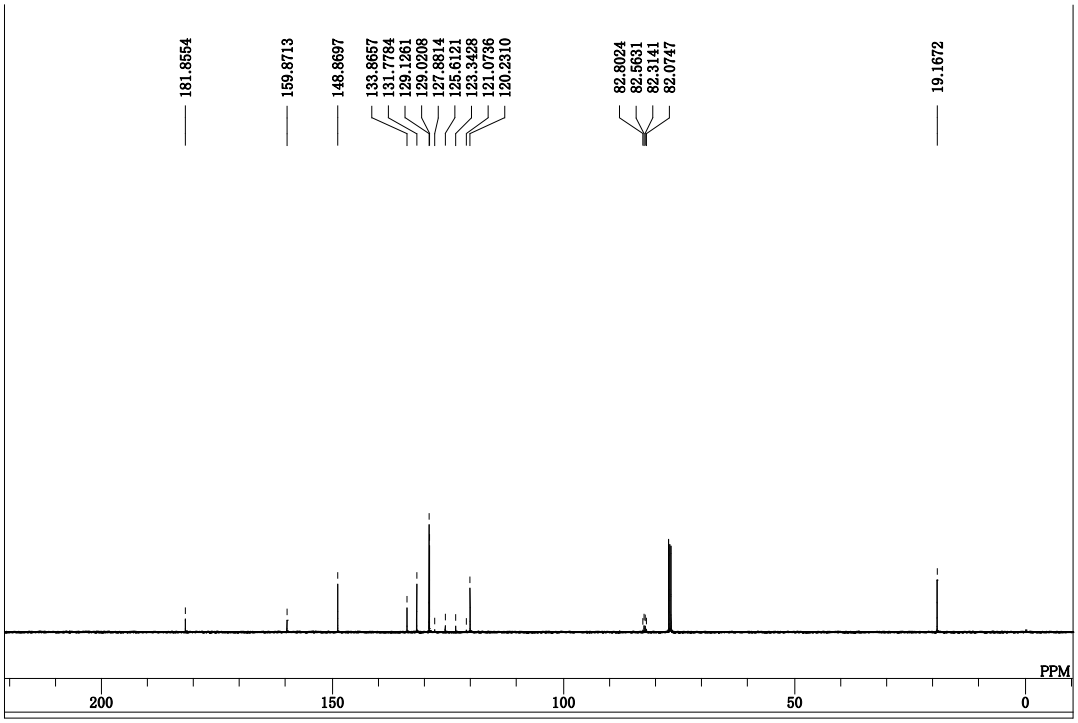




2,2,2-Trifluoro-1,1-dimethylethyl (*E*)-2-oxo-4-phenylbut-3-enoate





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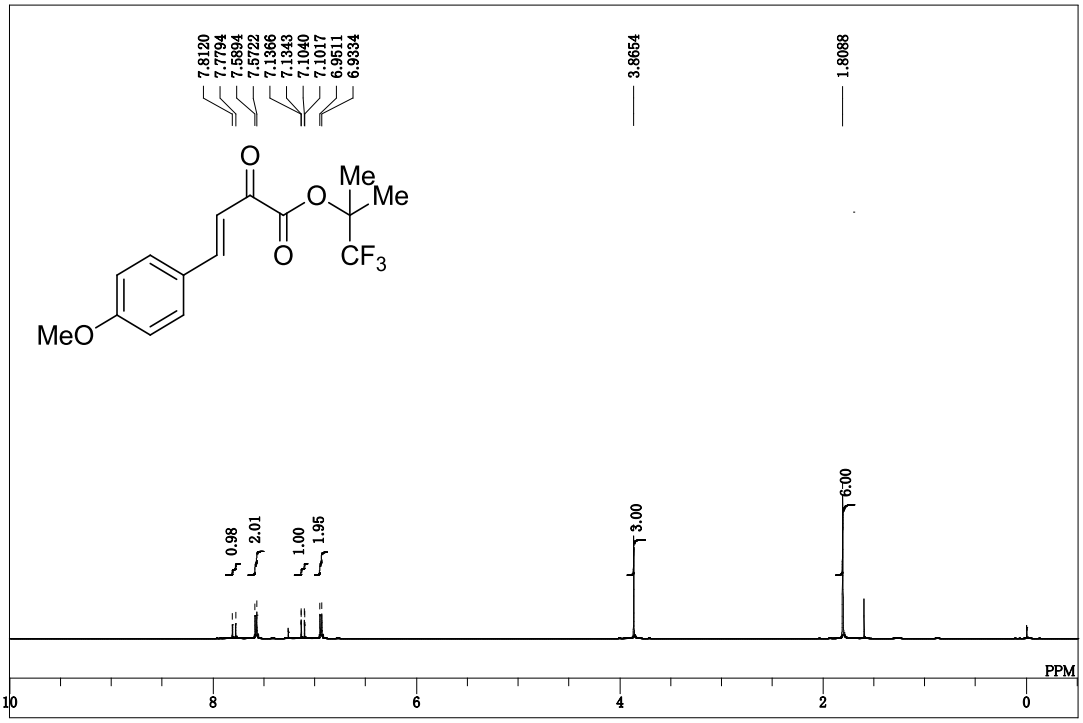

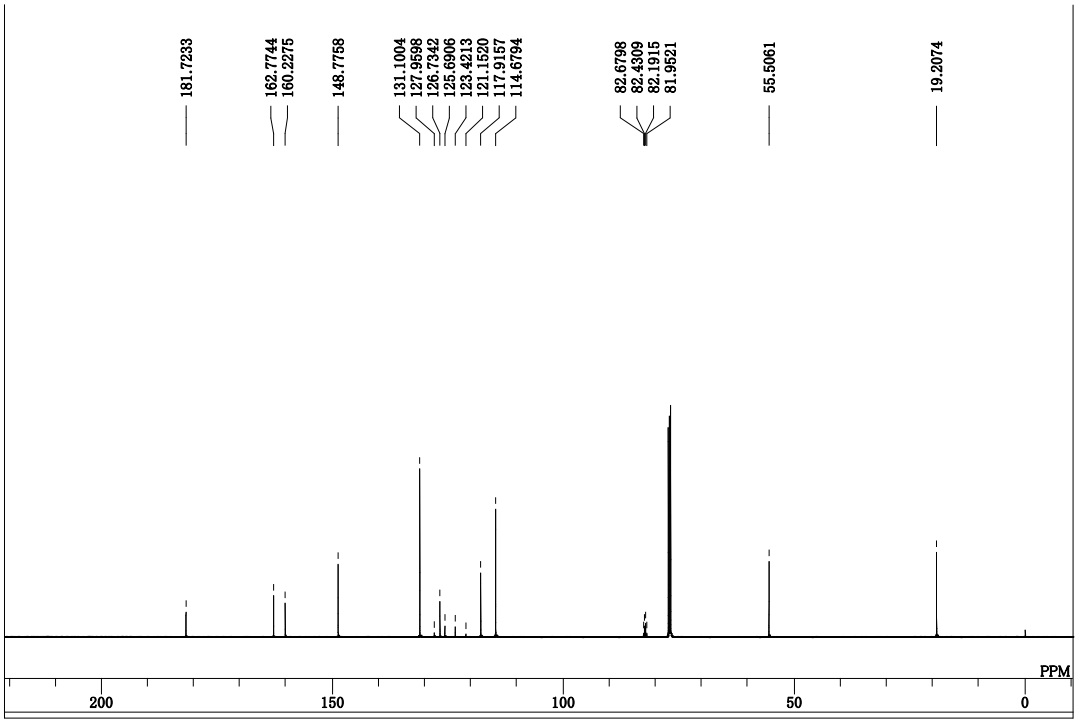

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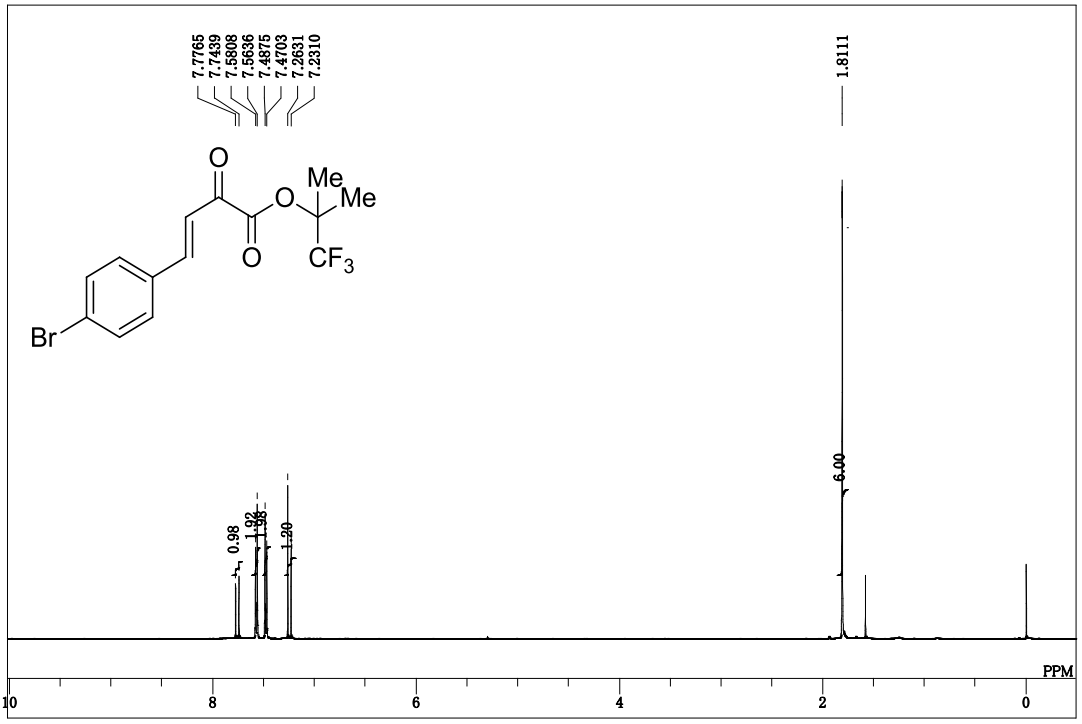

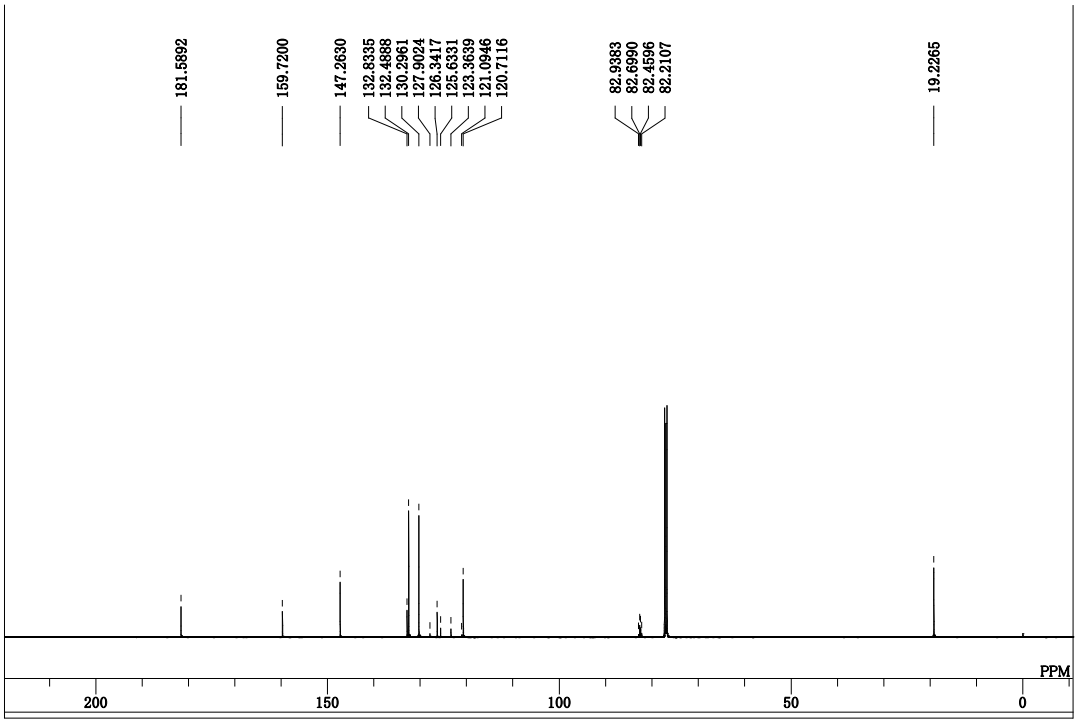

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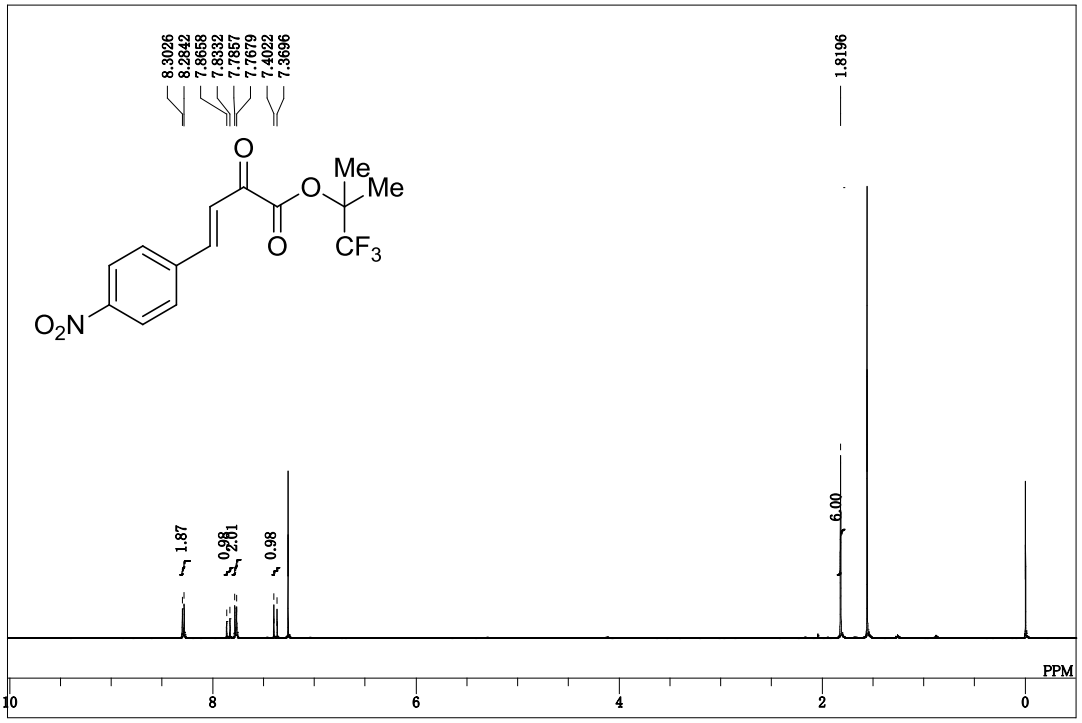

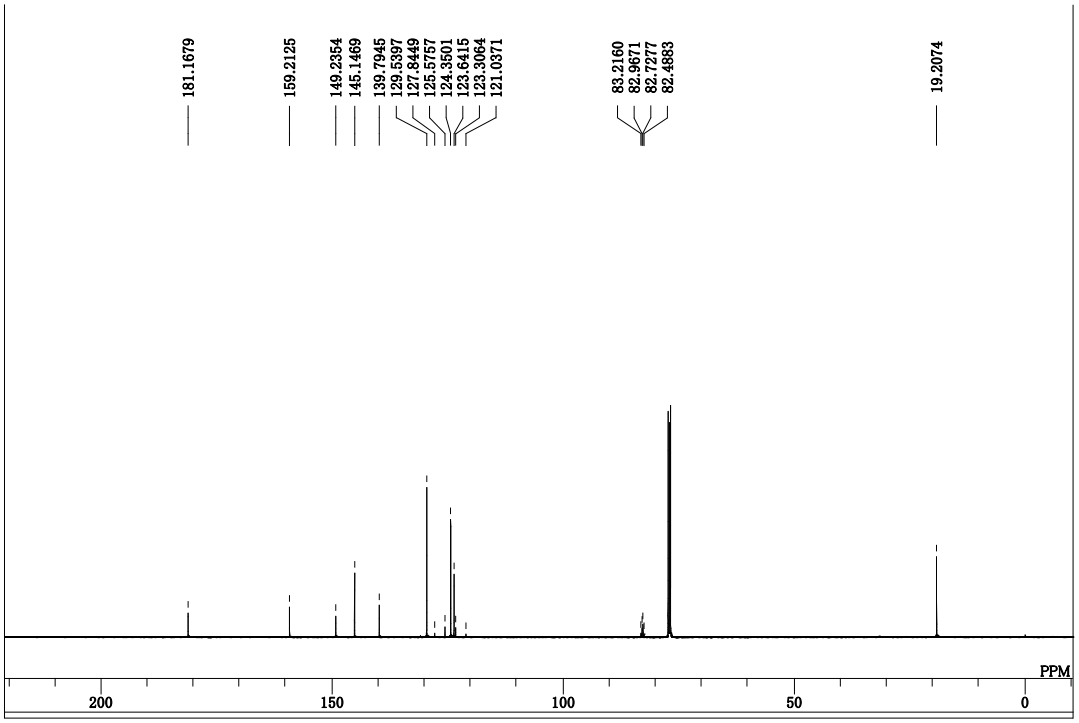

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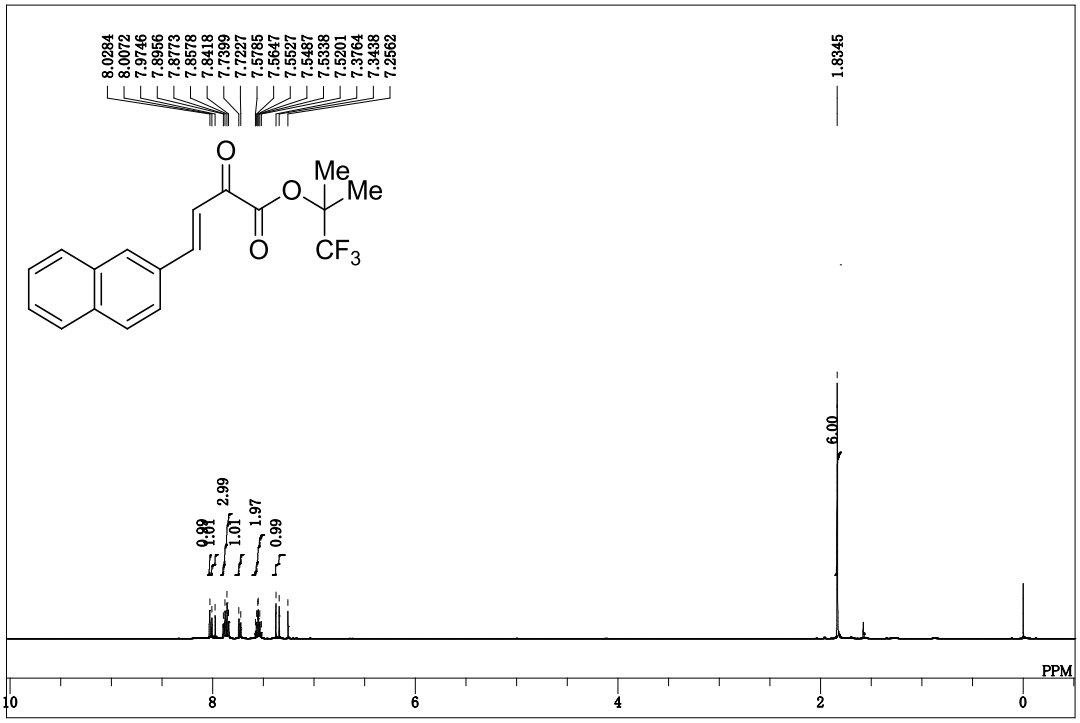

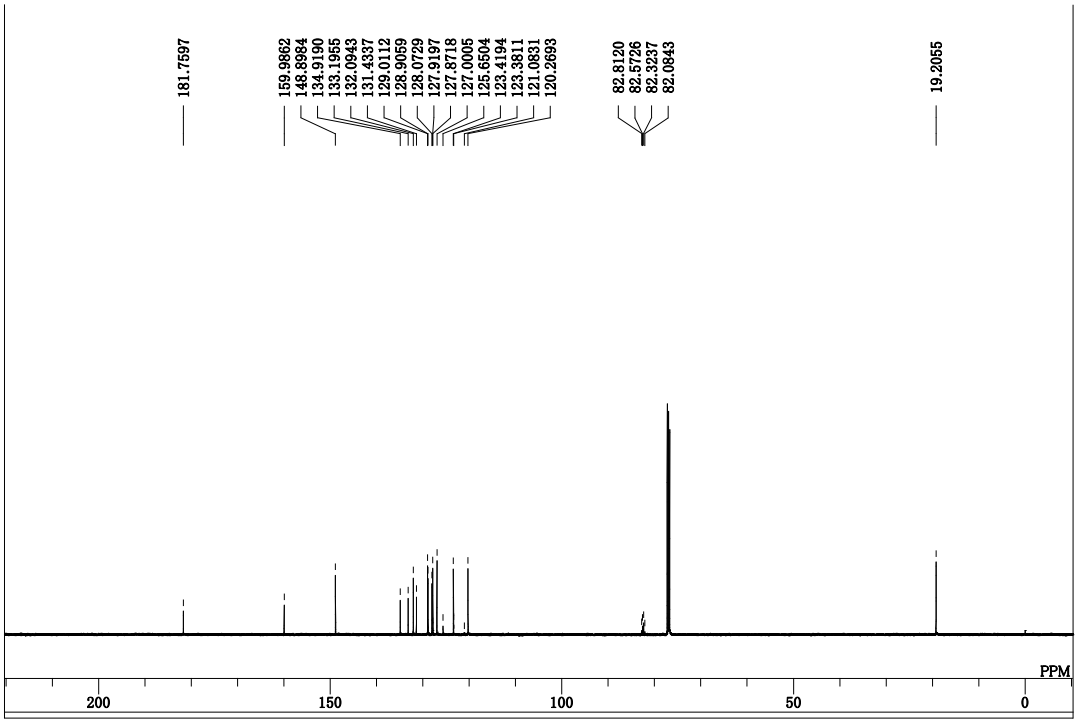

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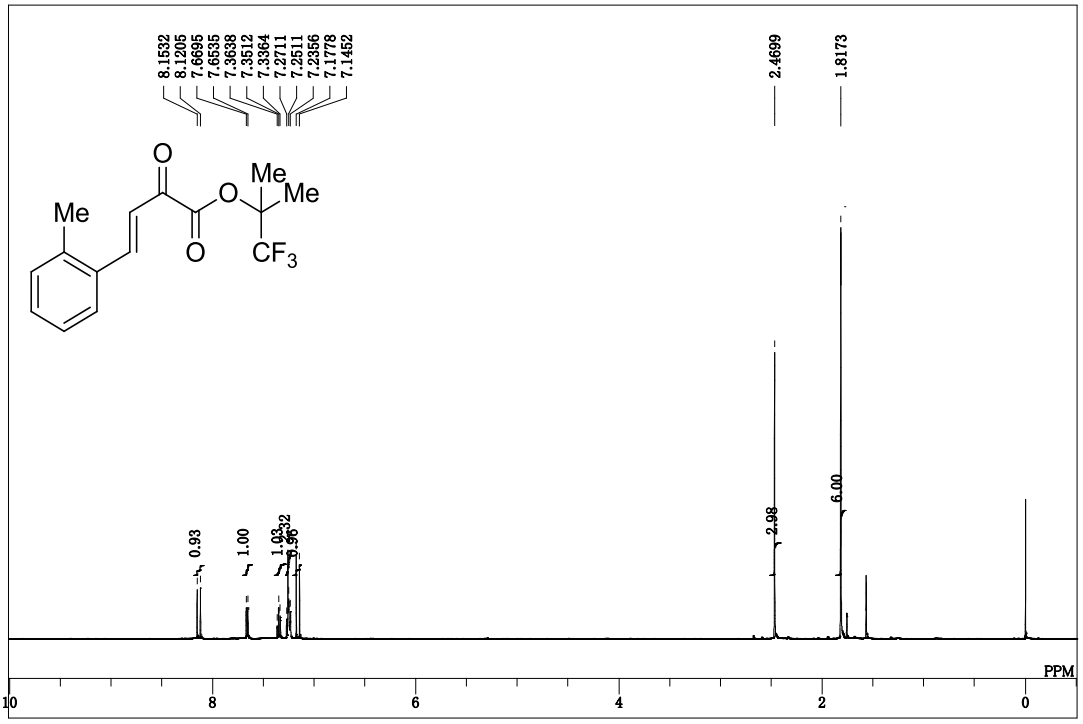

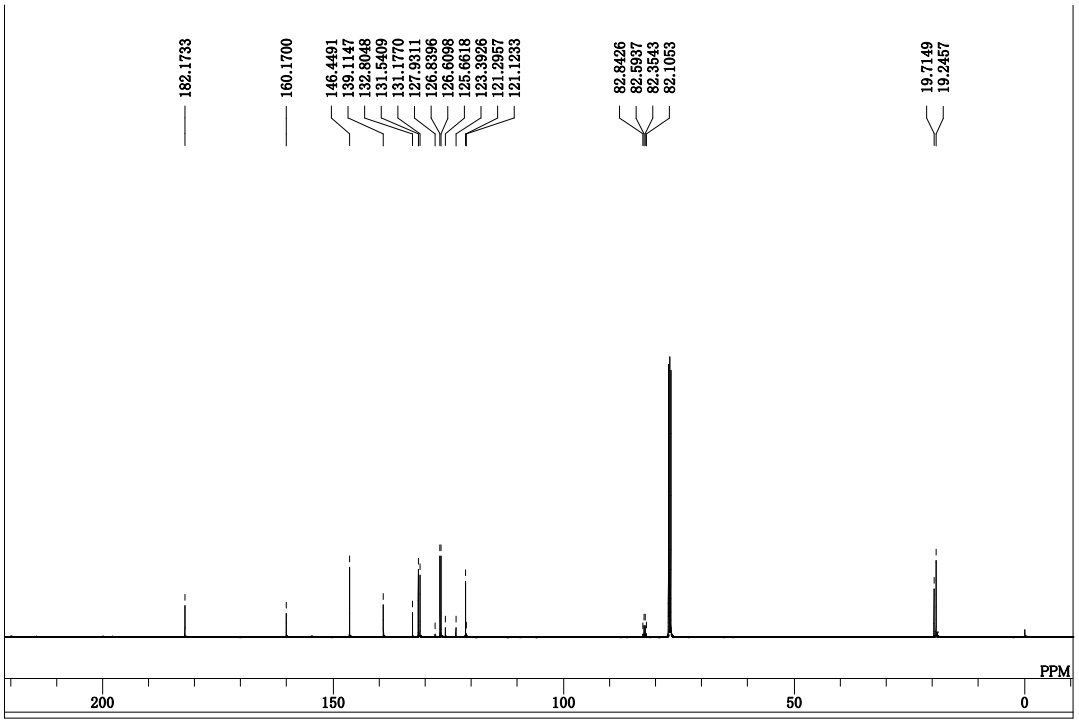

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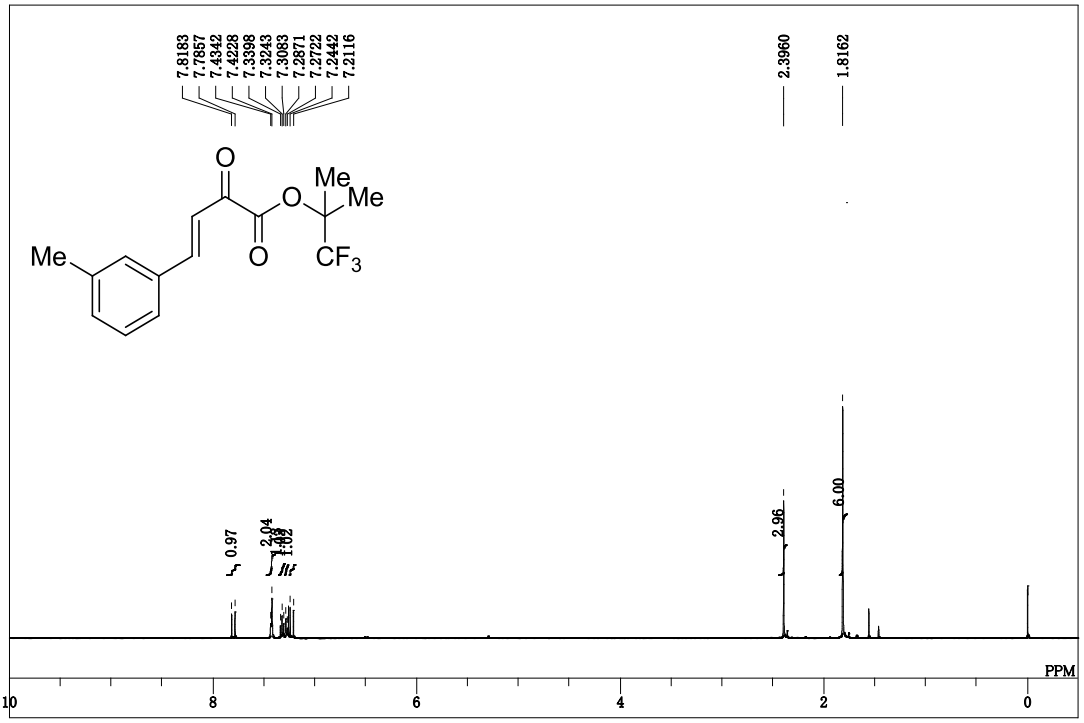

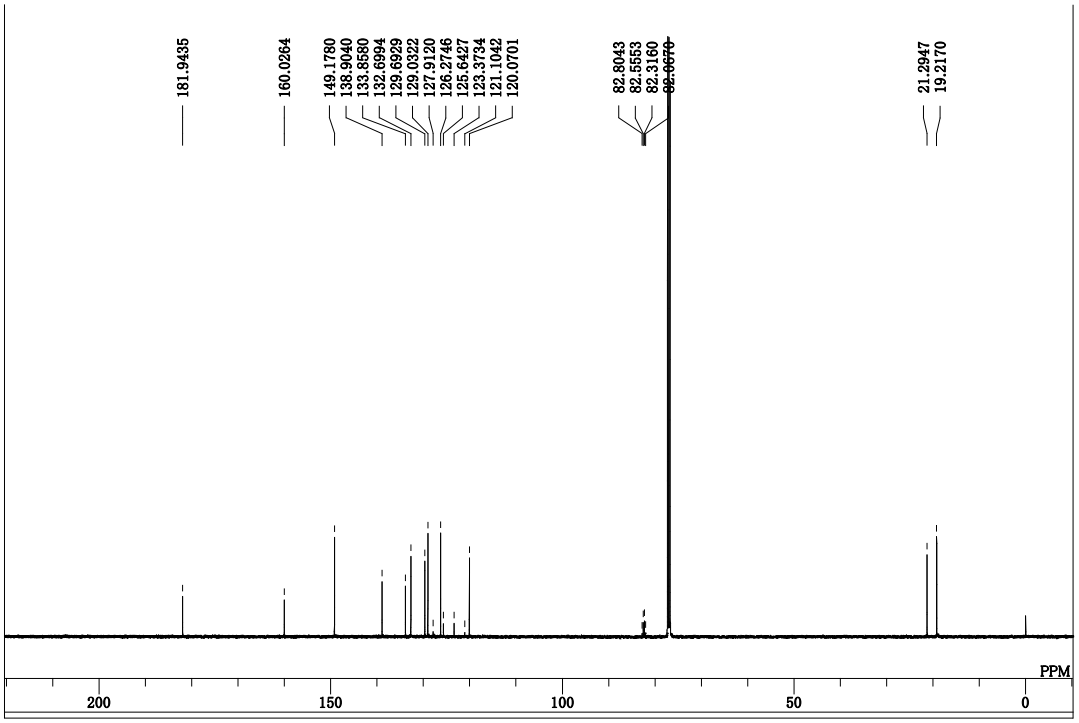

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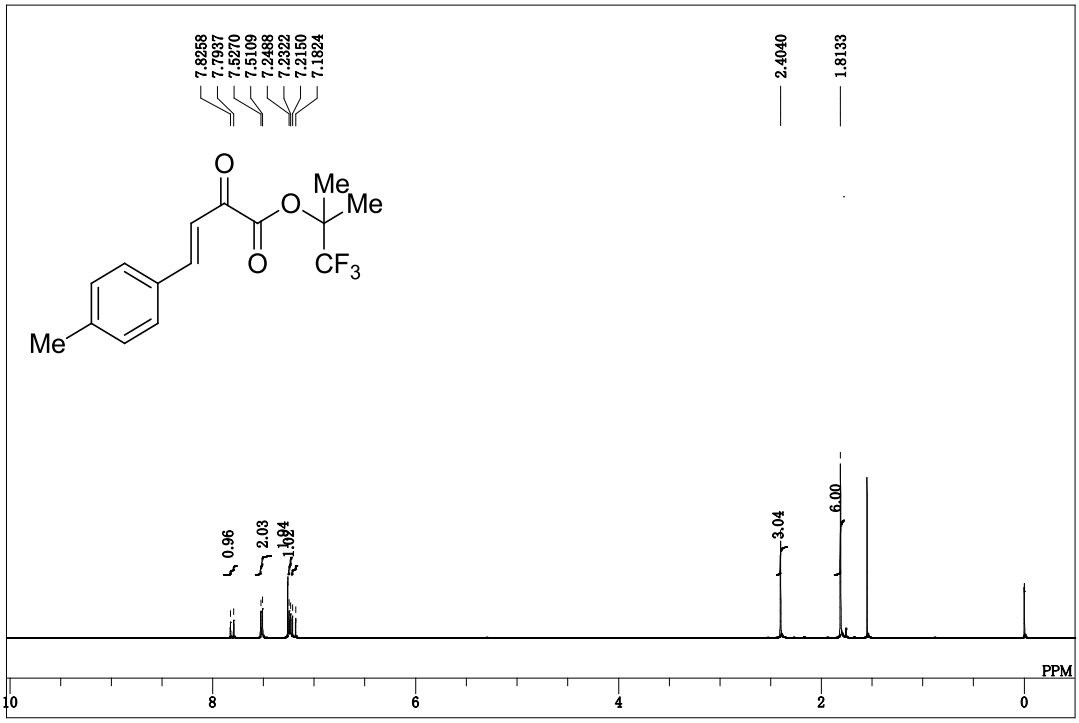

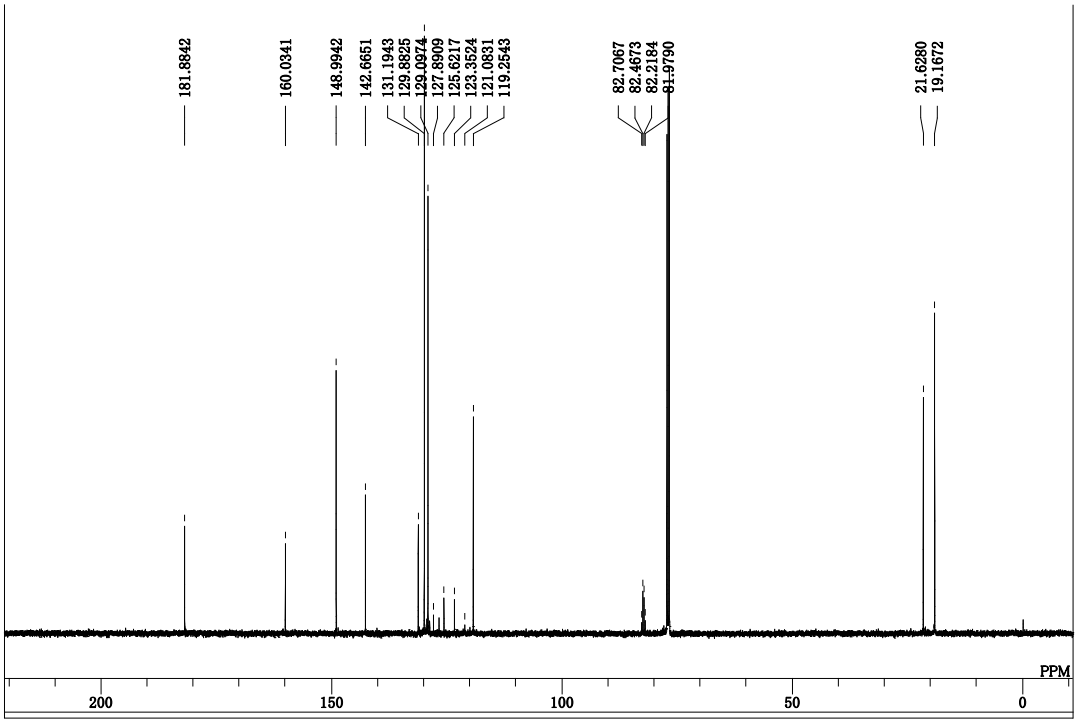

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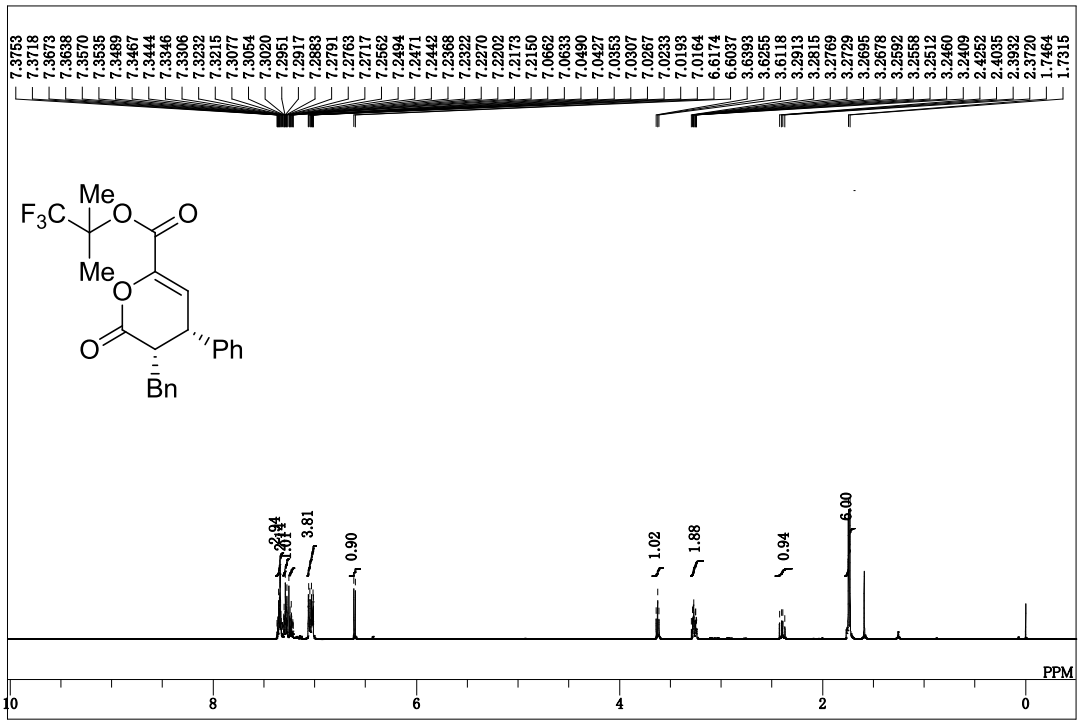

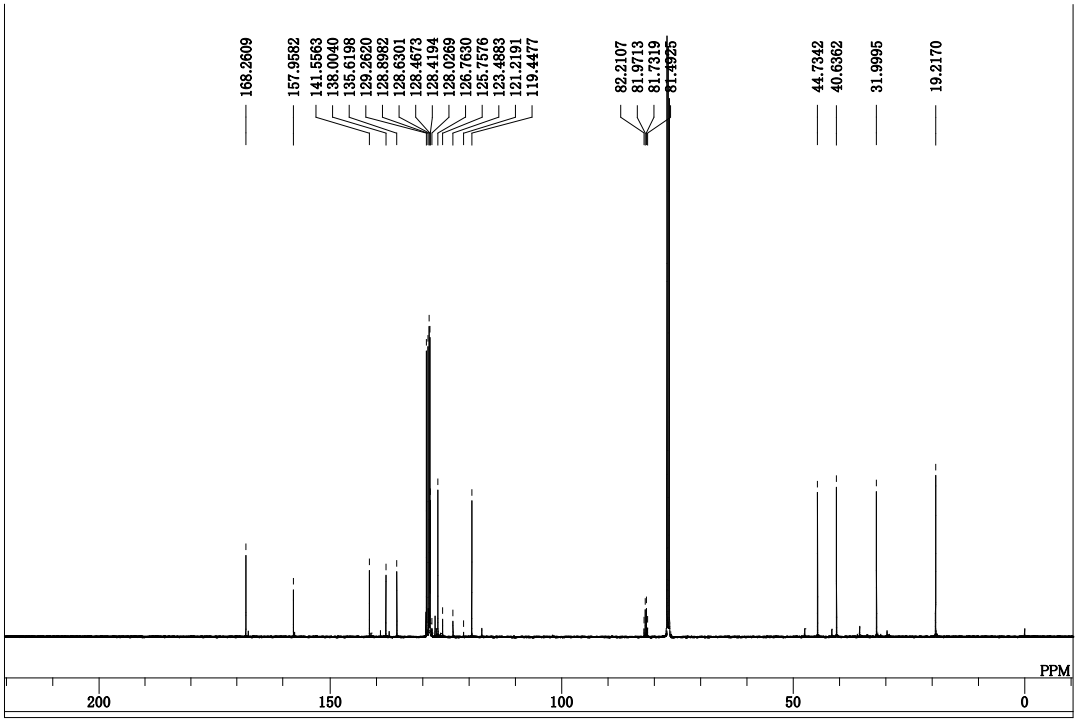

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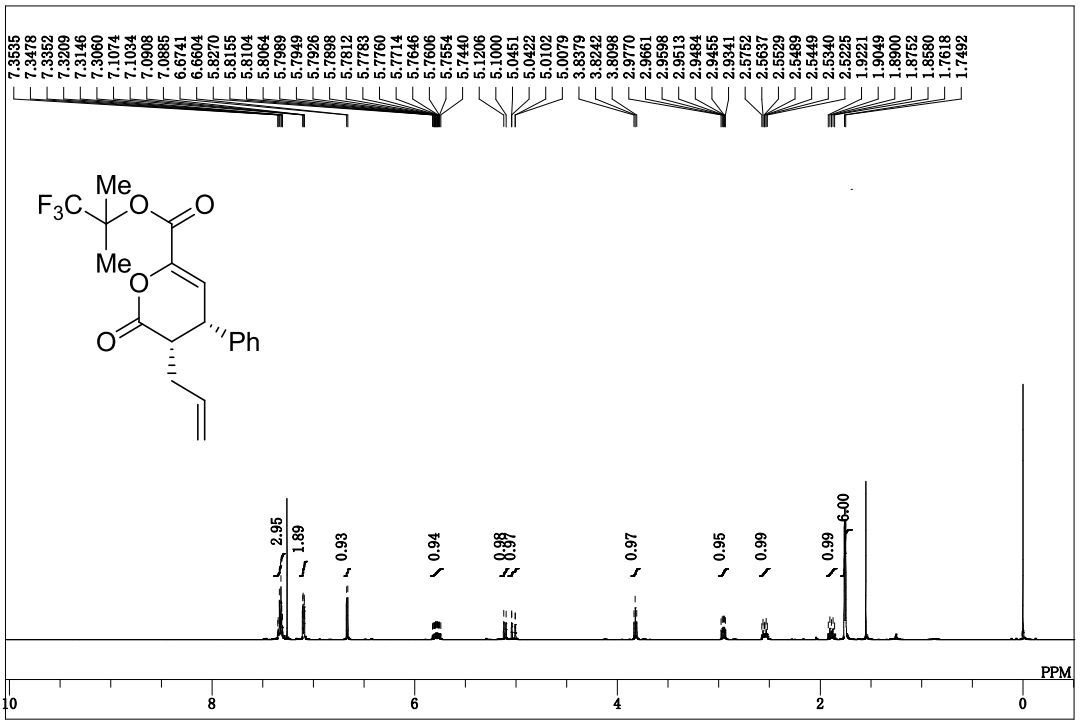

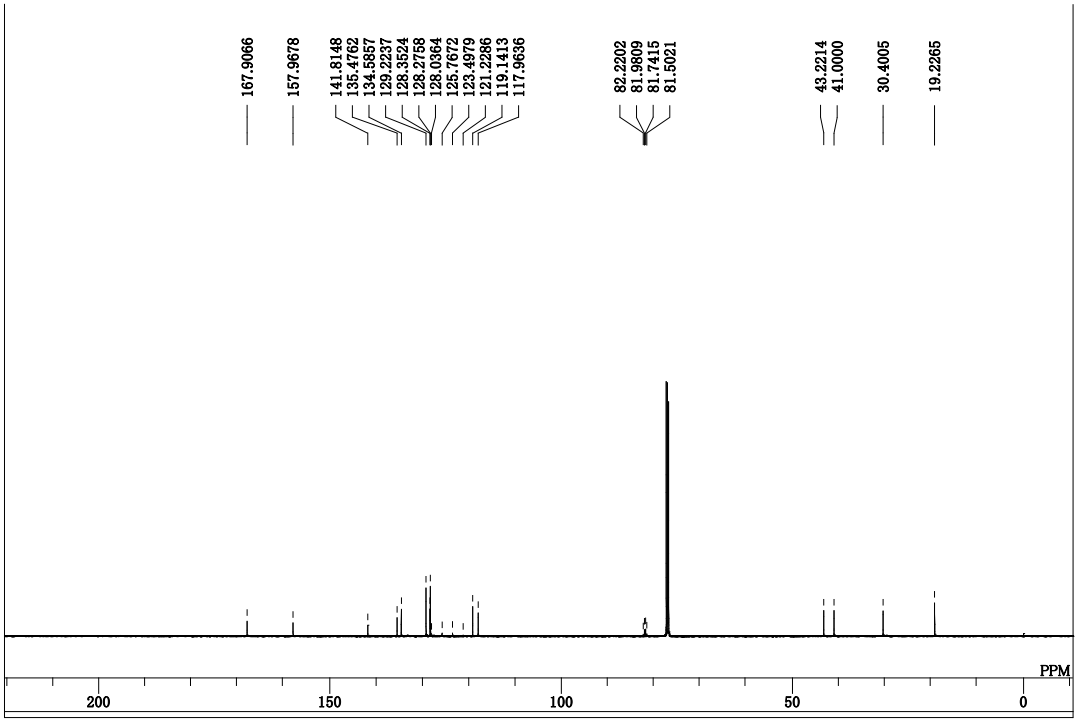

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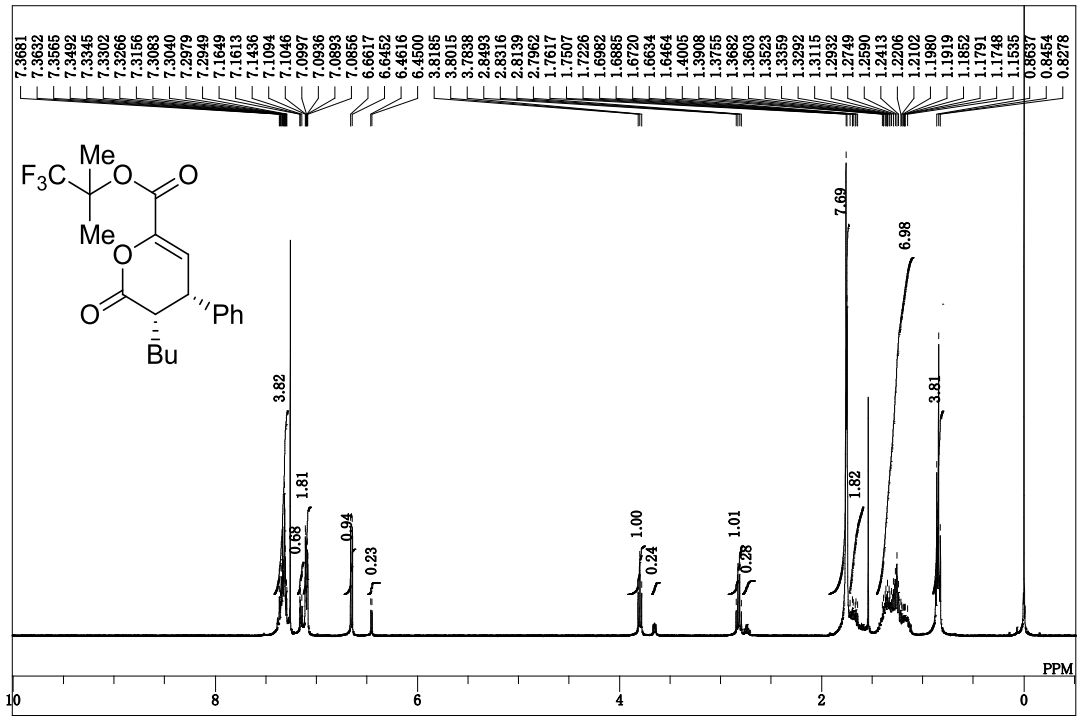

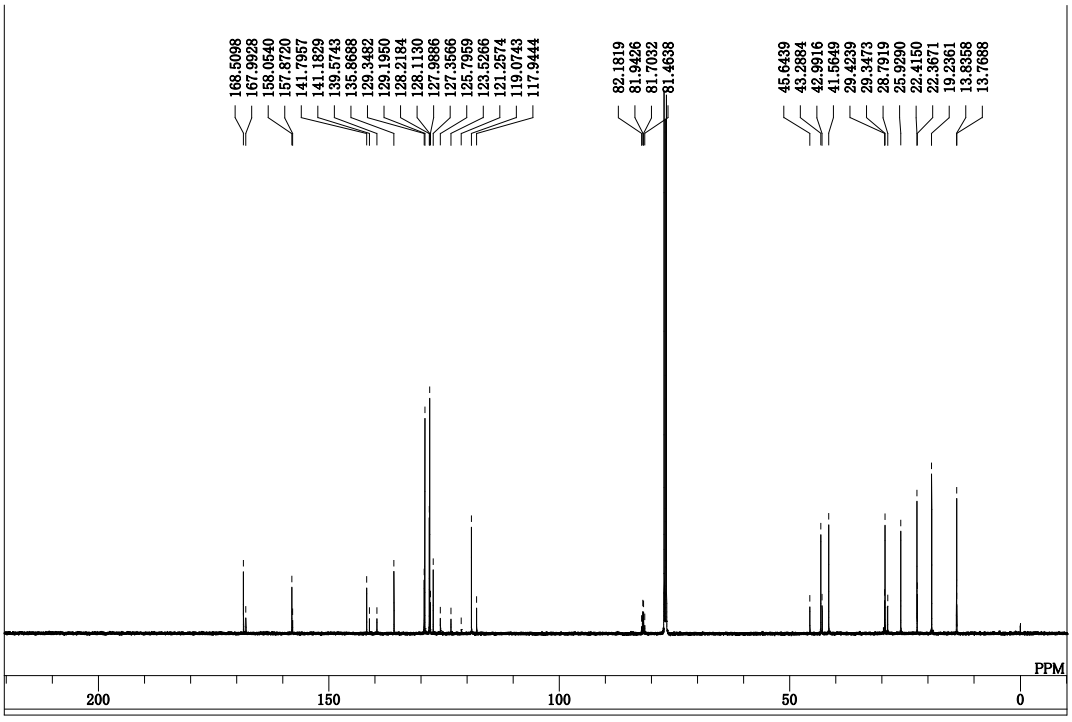

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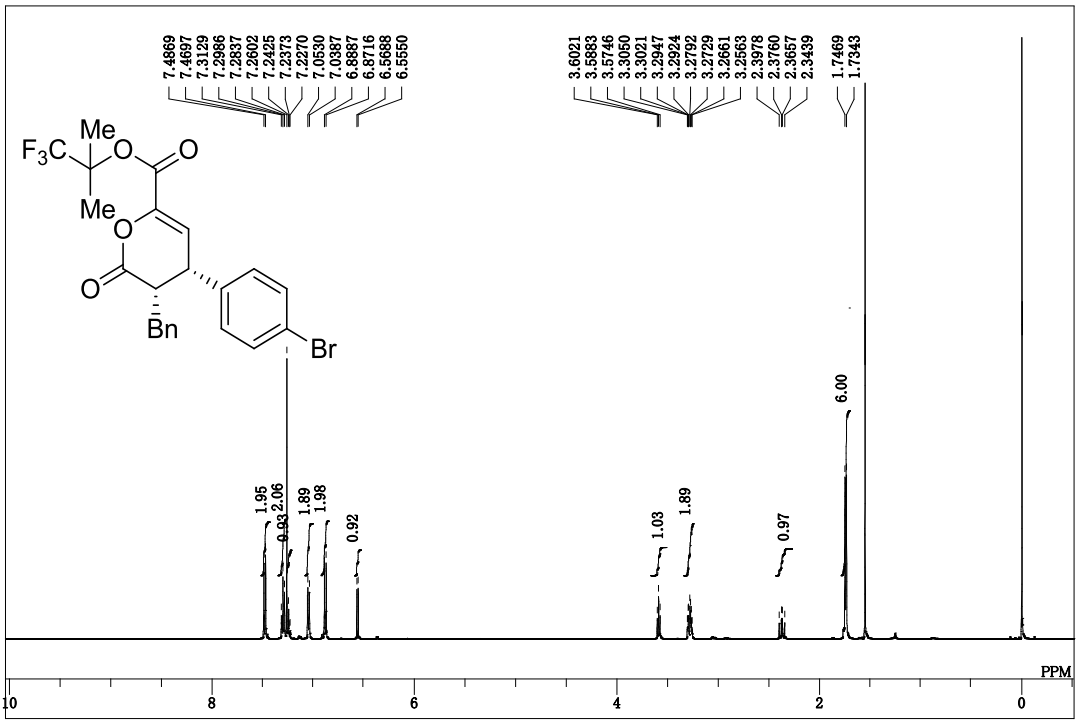

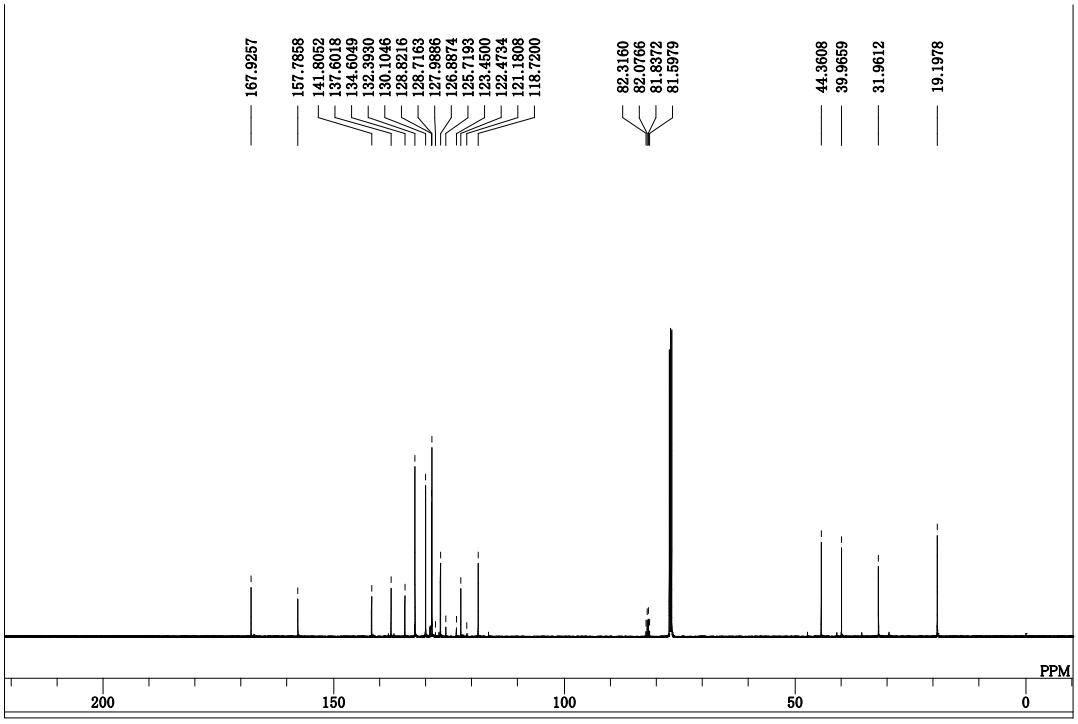

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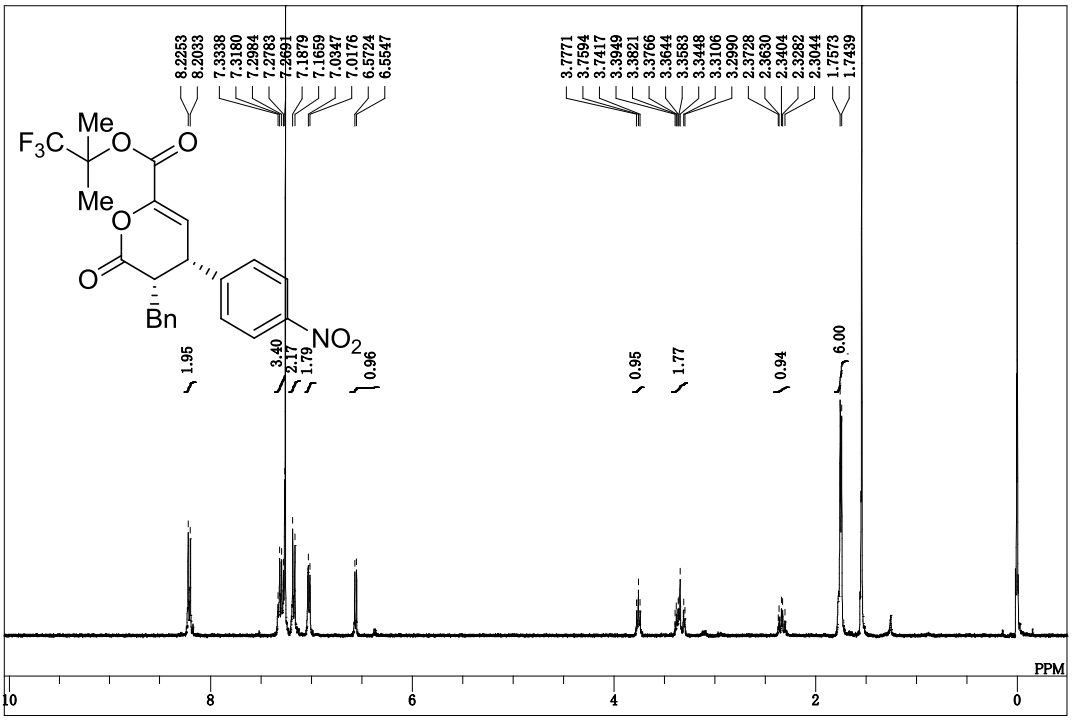

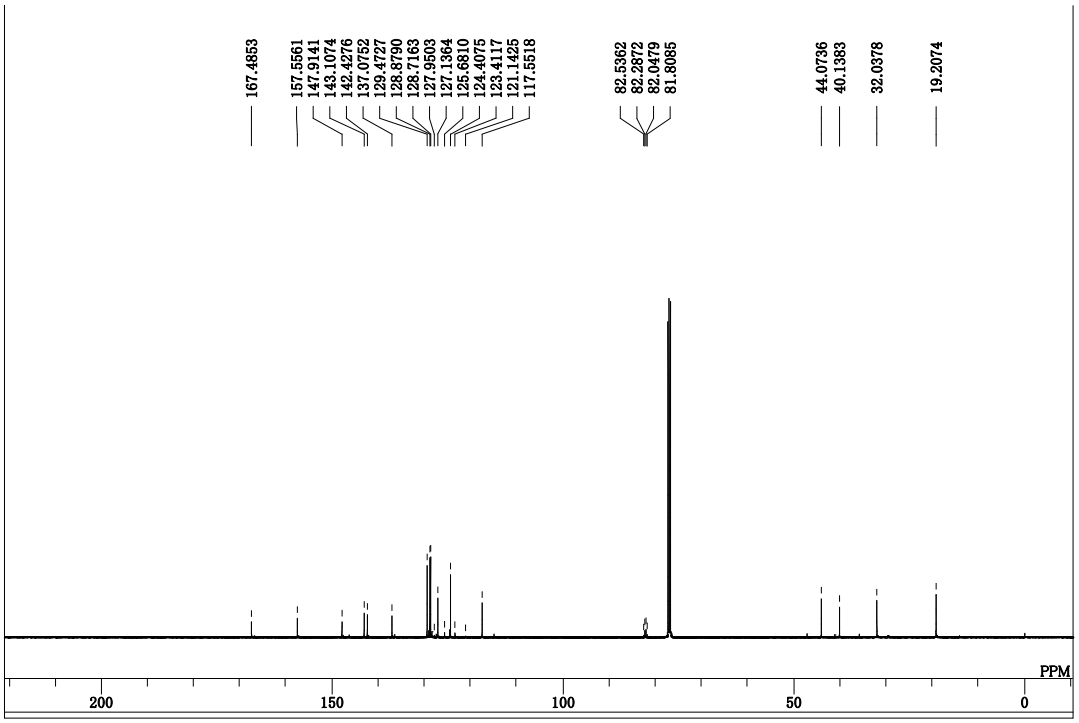

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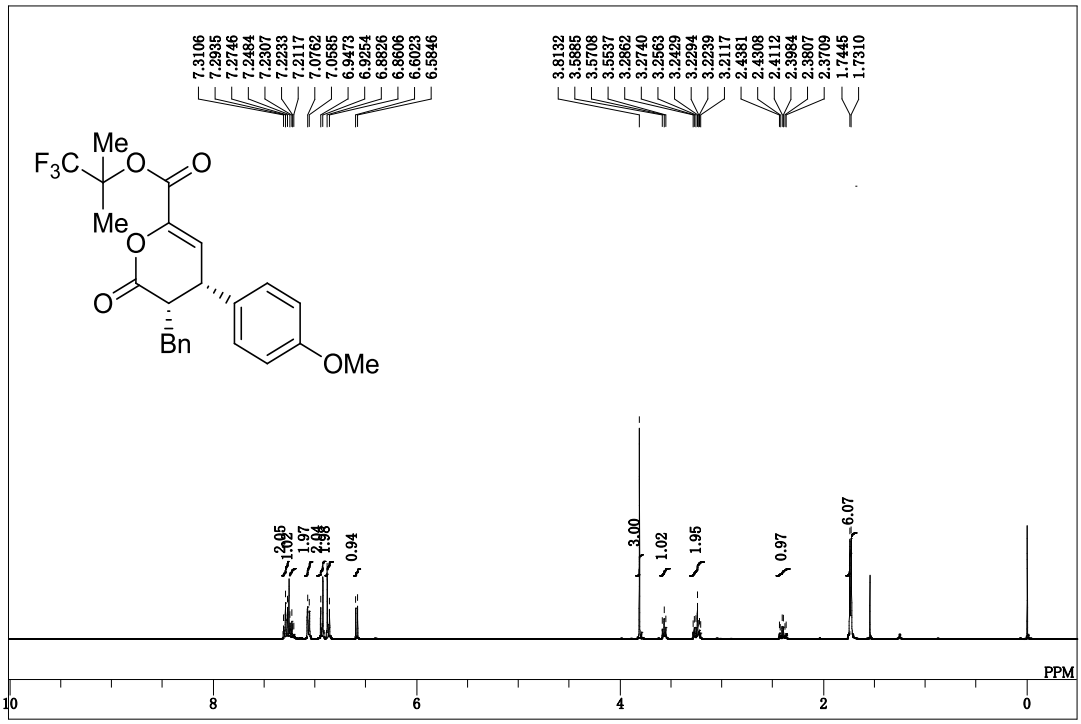

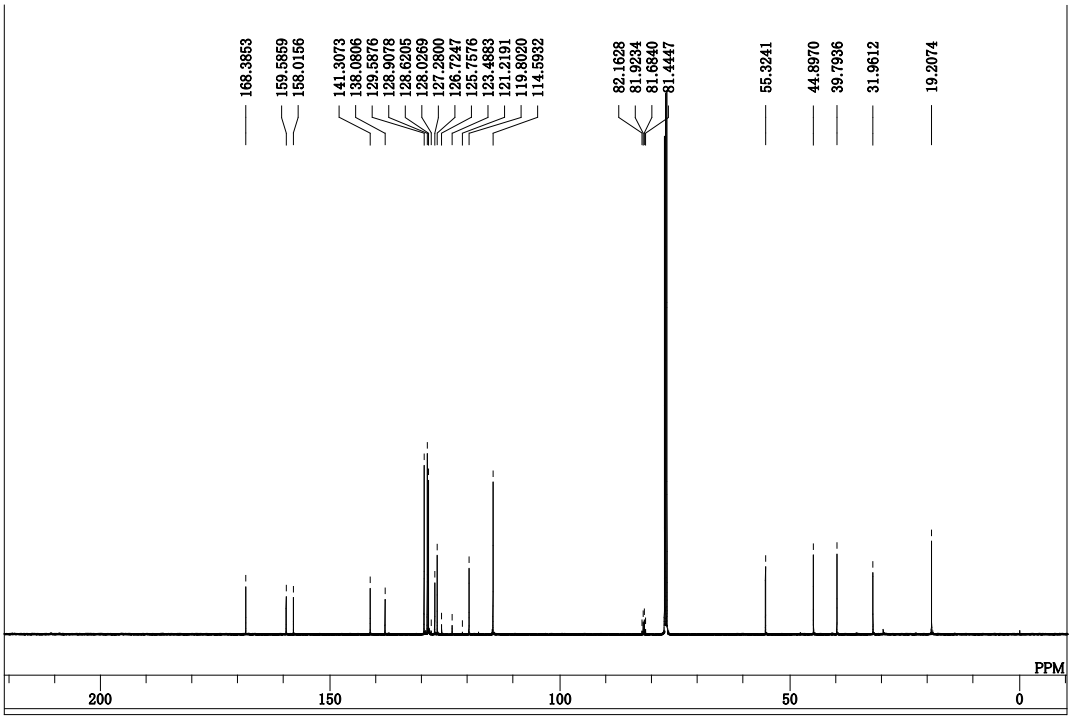

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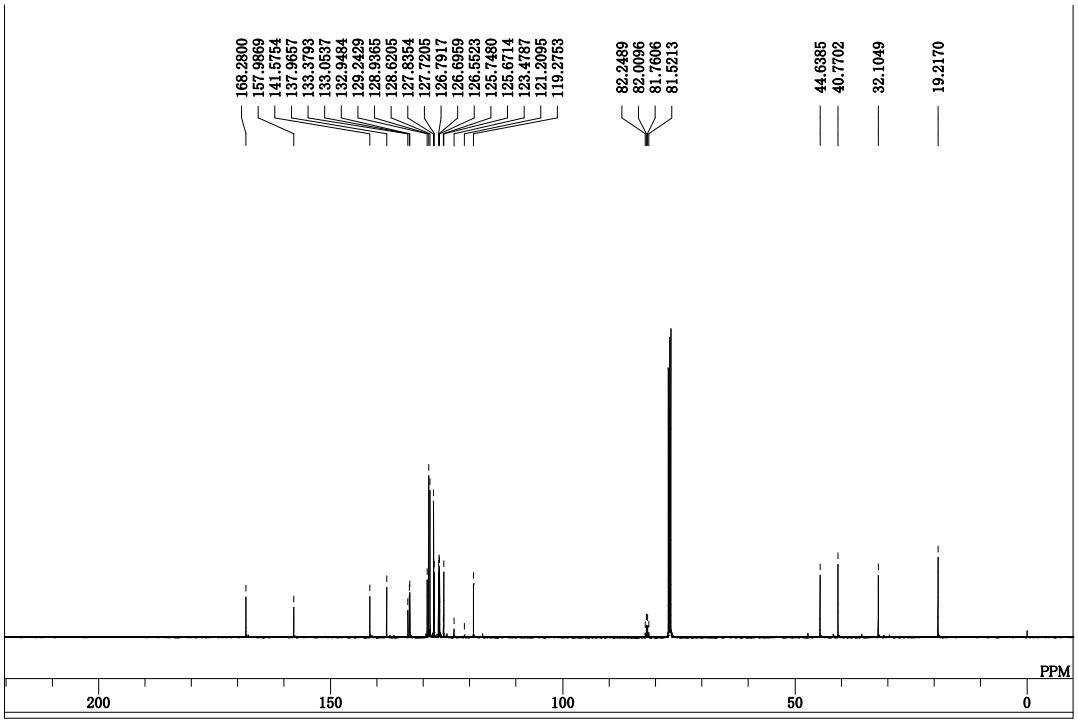

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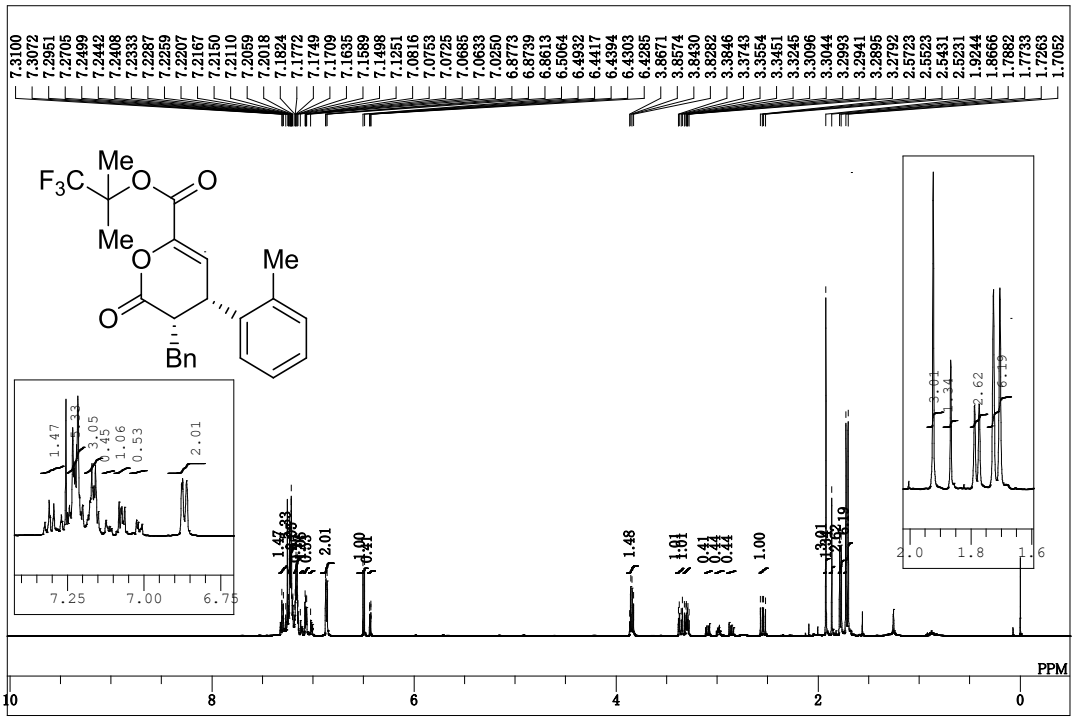

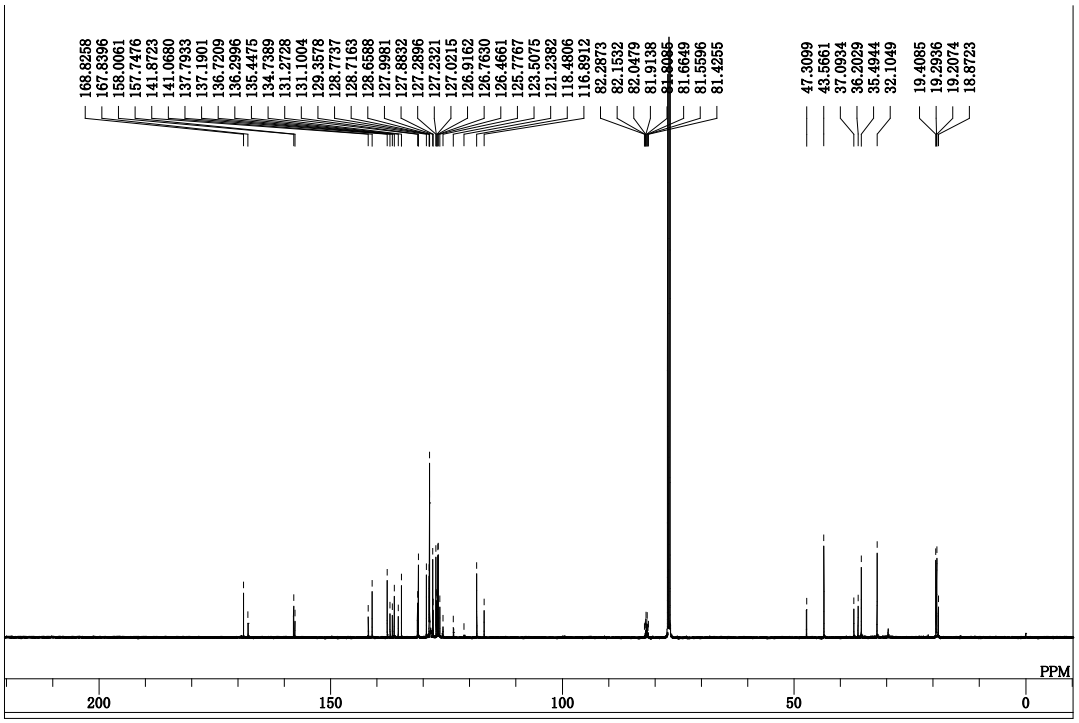

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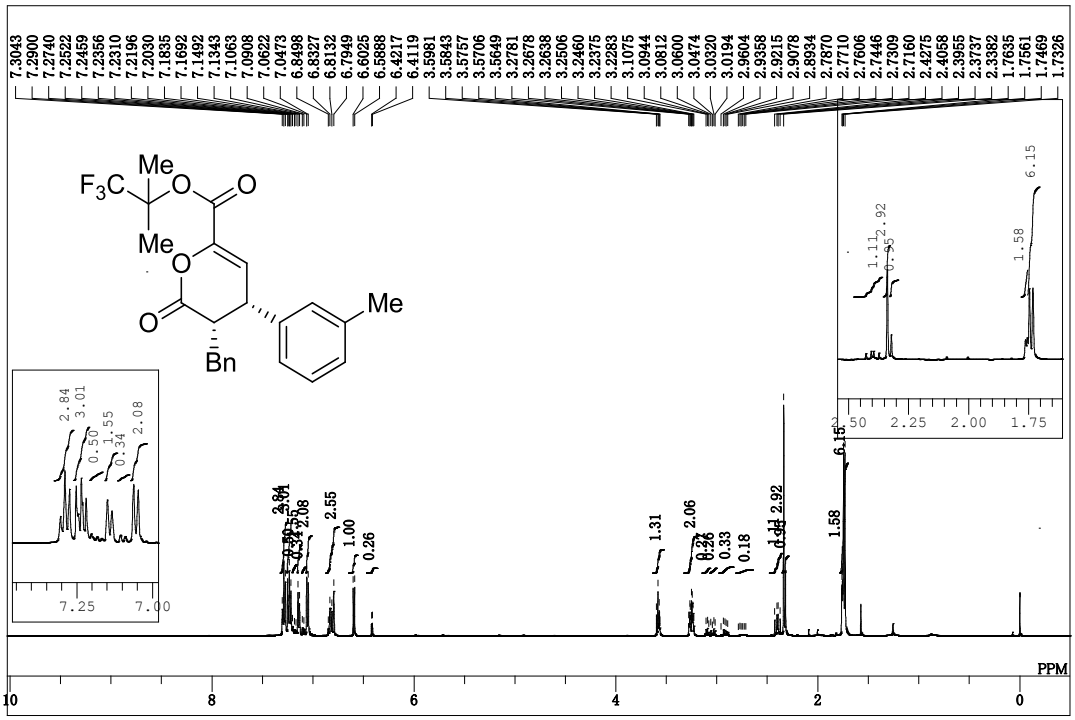

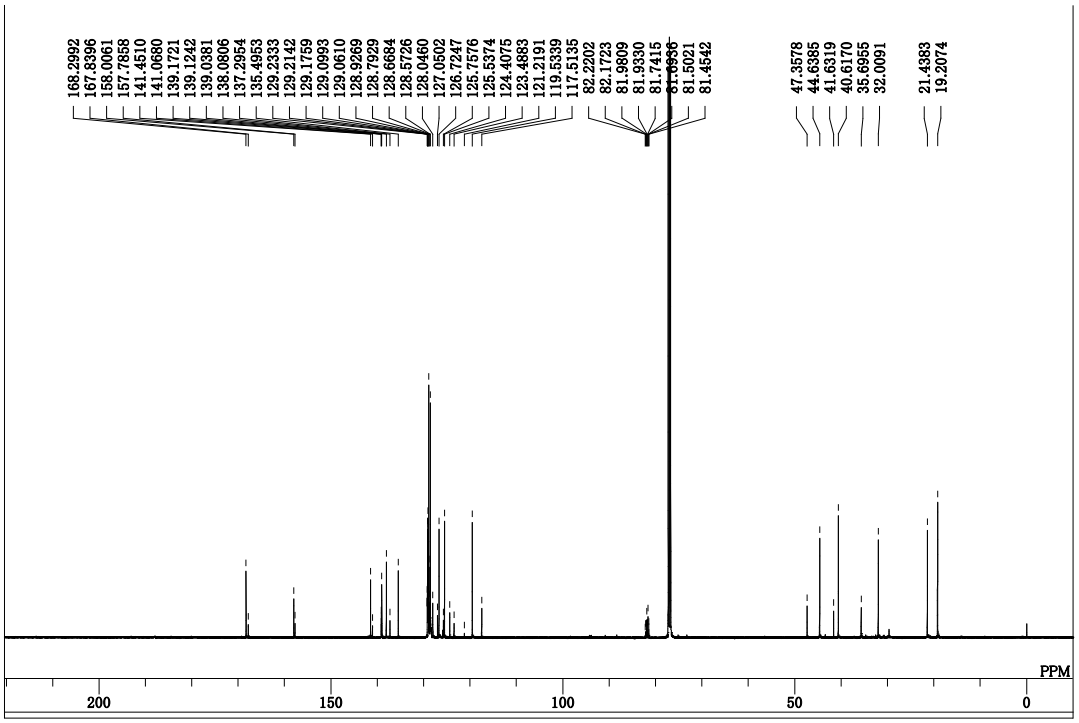

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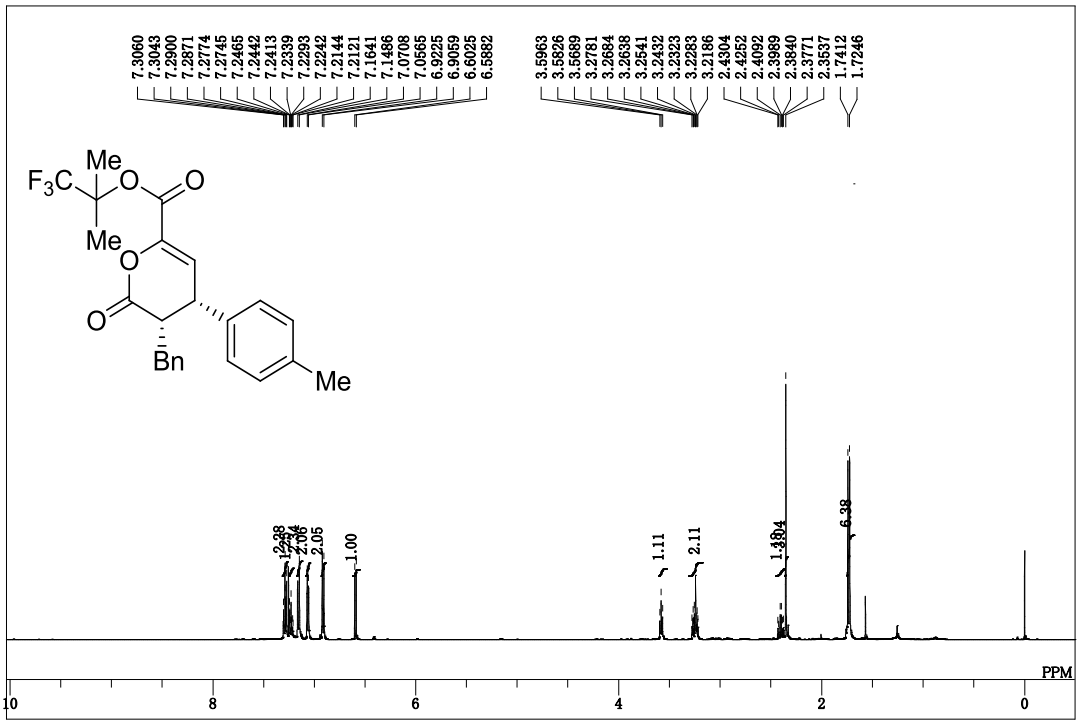
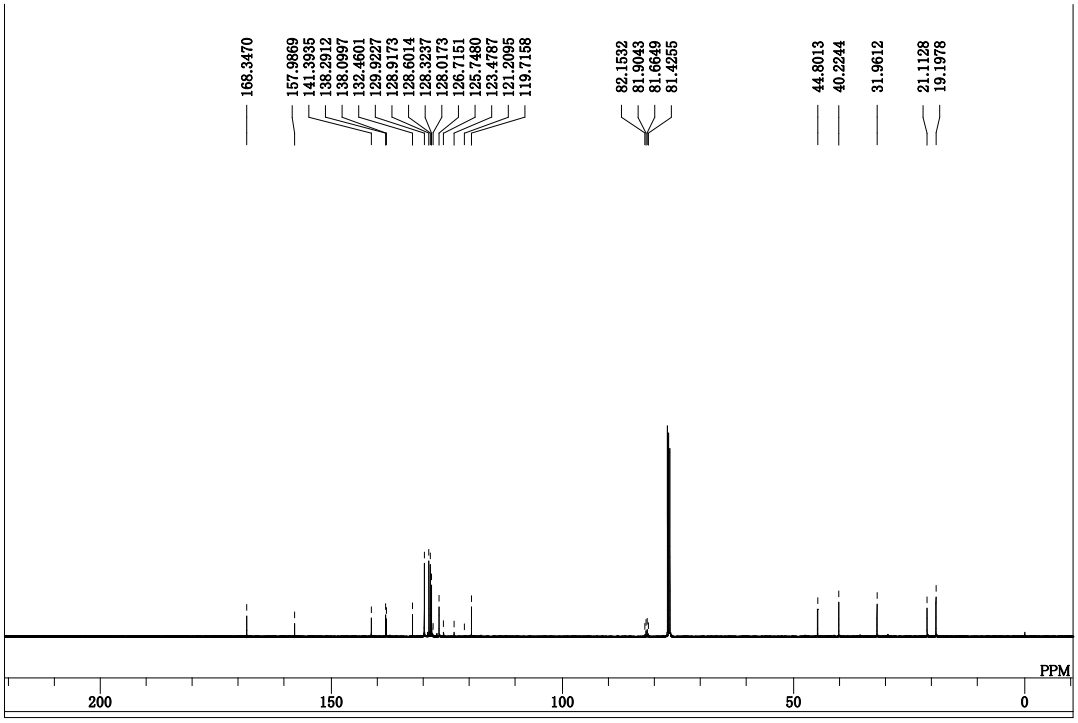
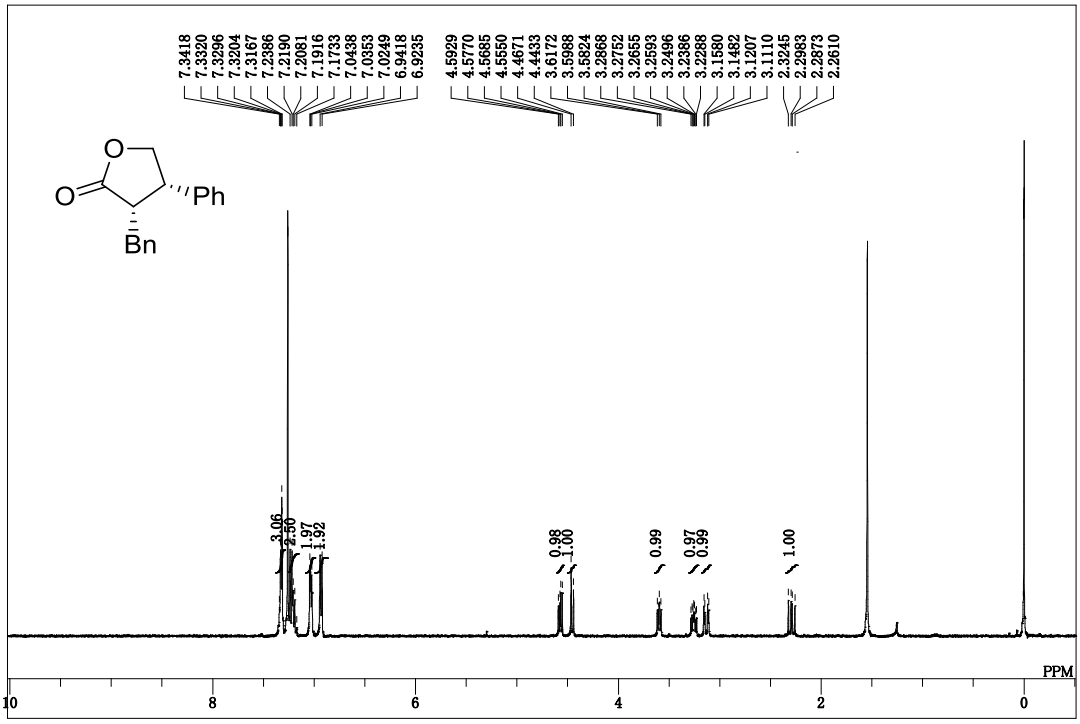
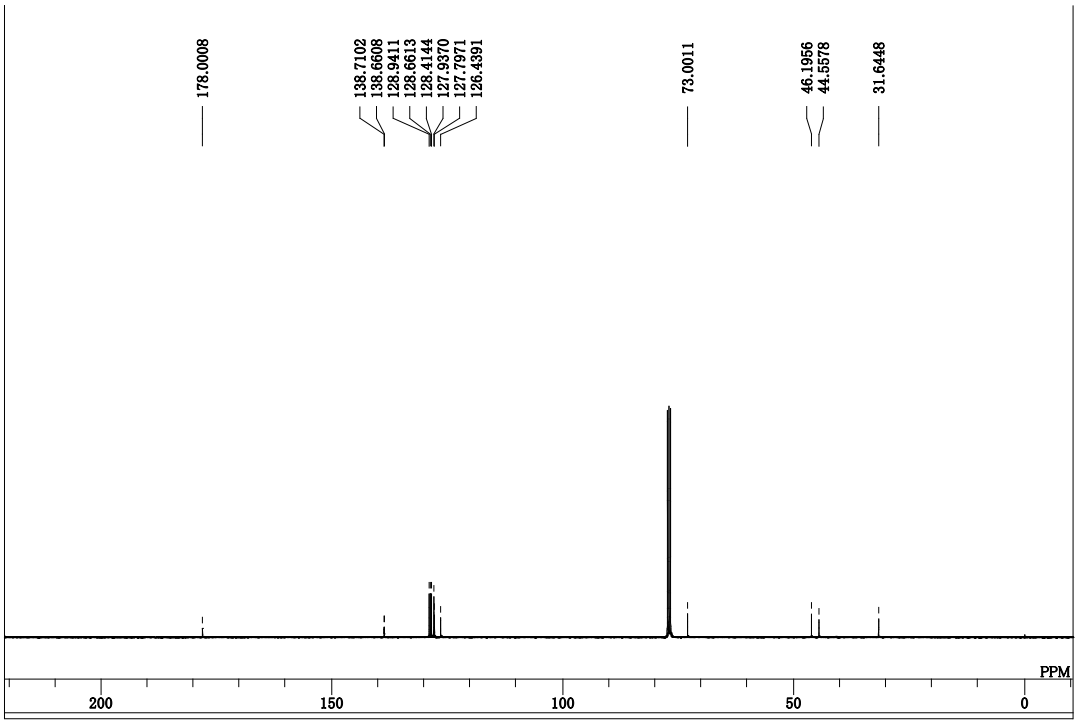


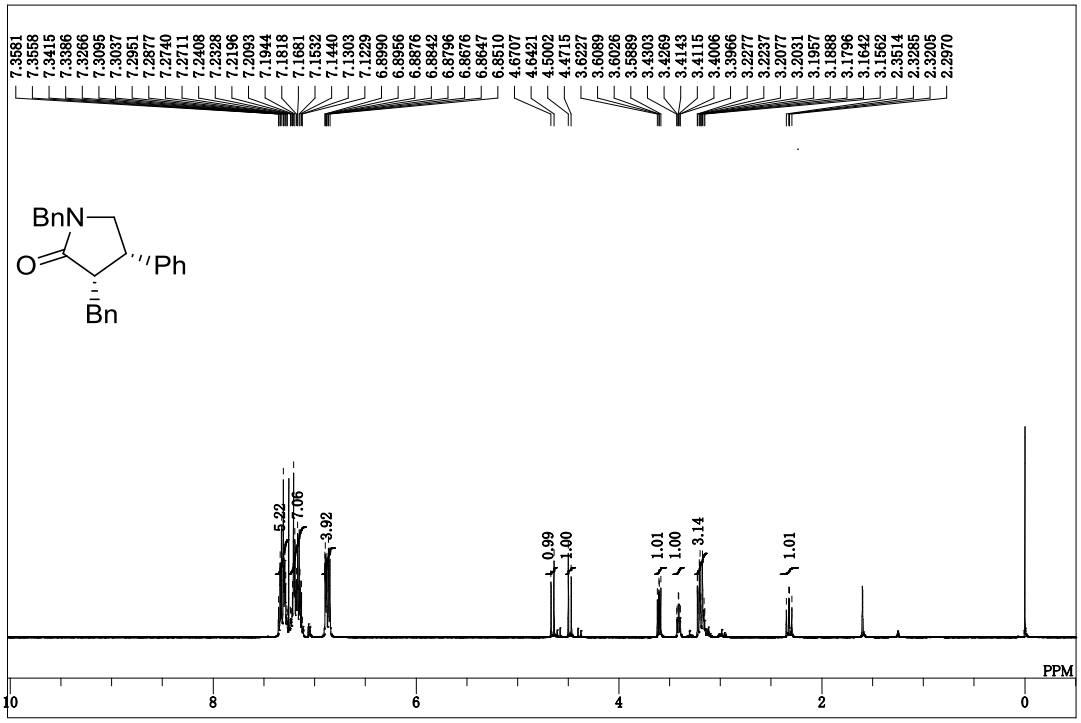


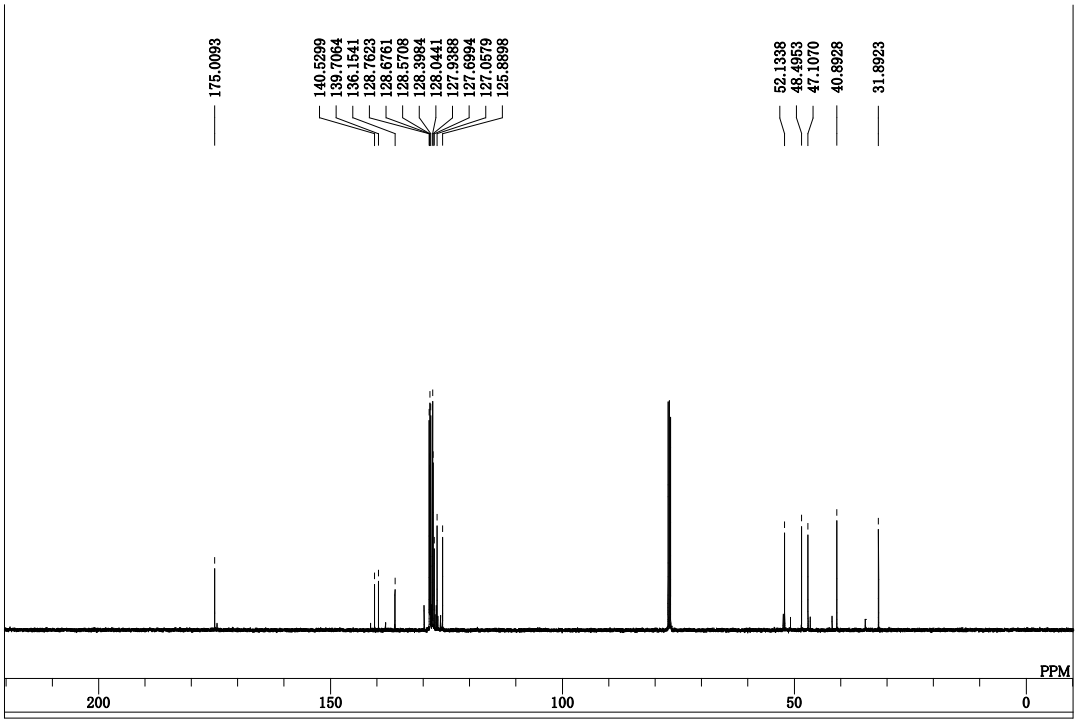
γ-Lactone *cis*-9





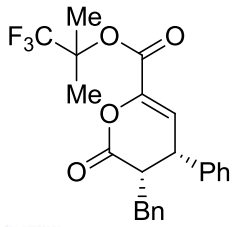
γ-Lactam *cis*-10

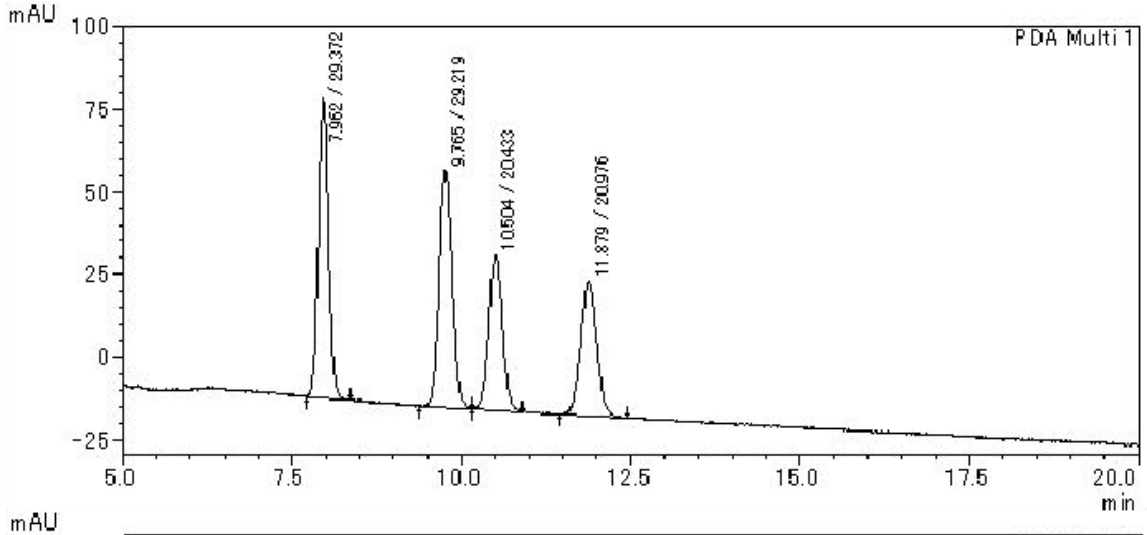


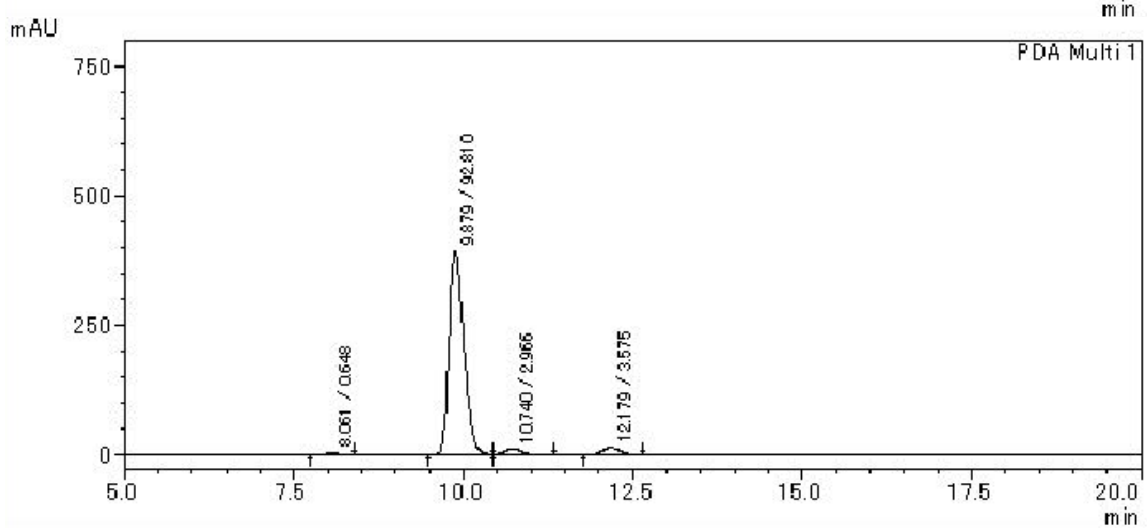


HPLC Data

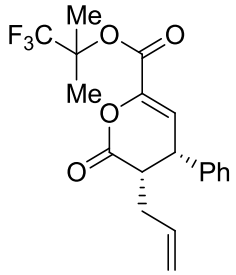
2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-2-oxo-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate

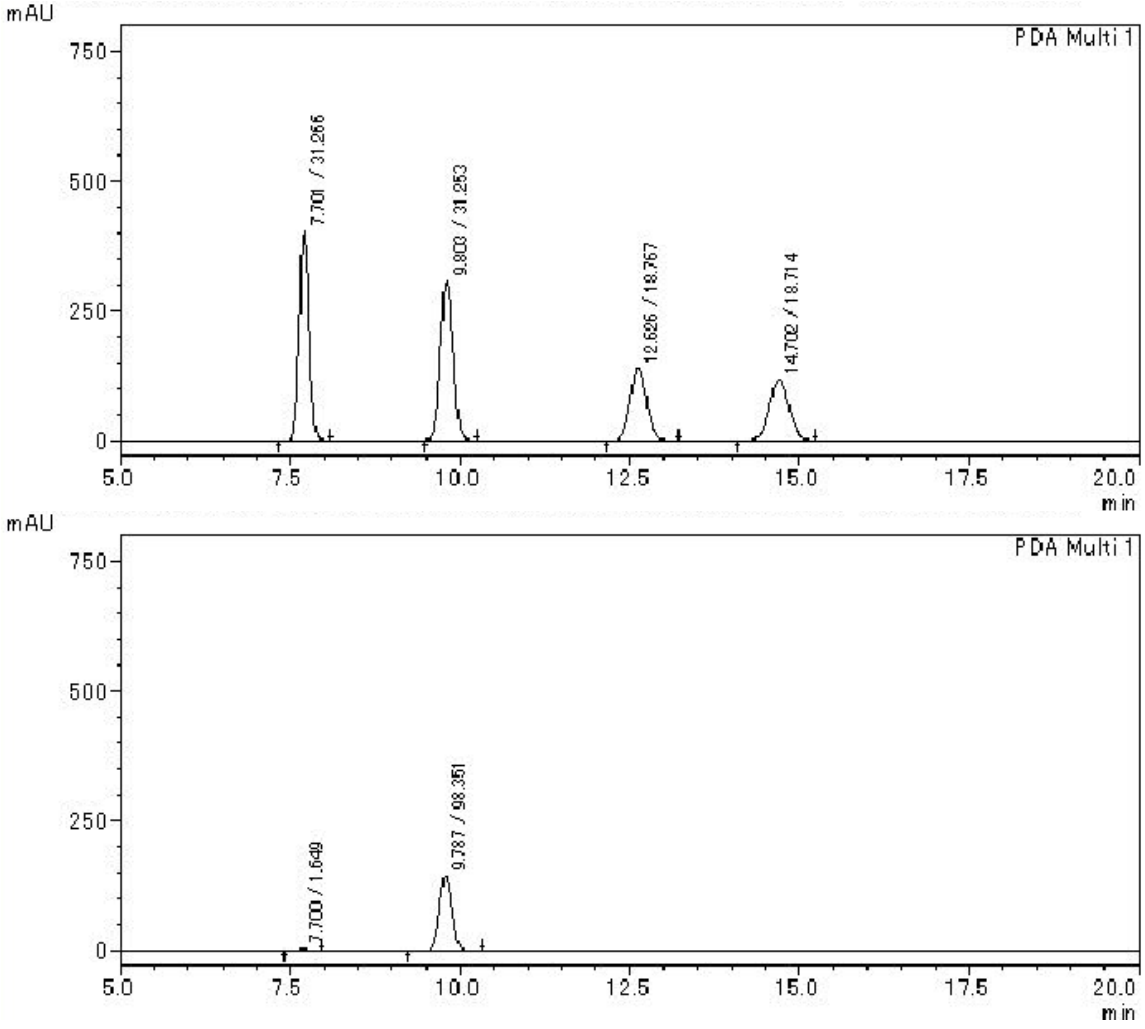




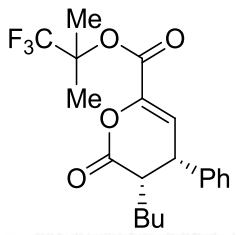


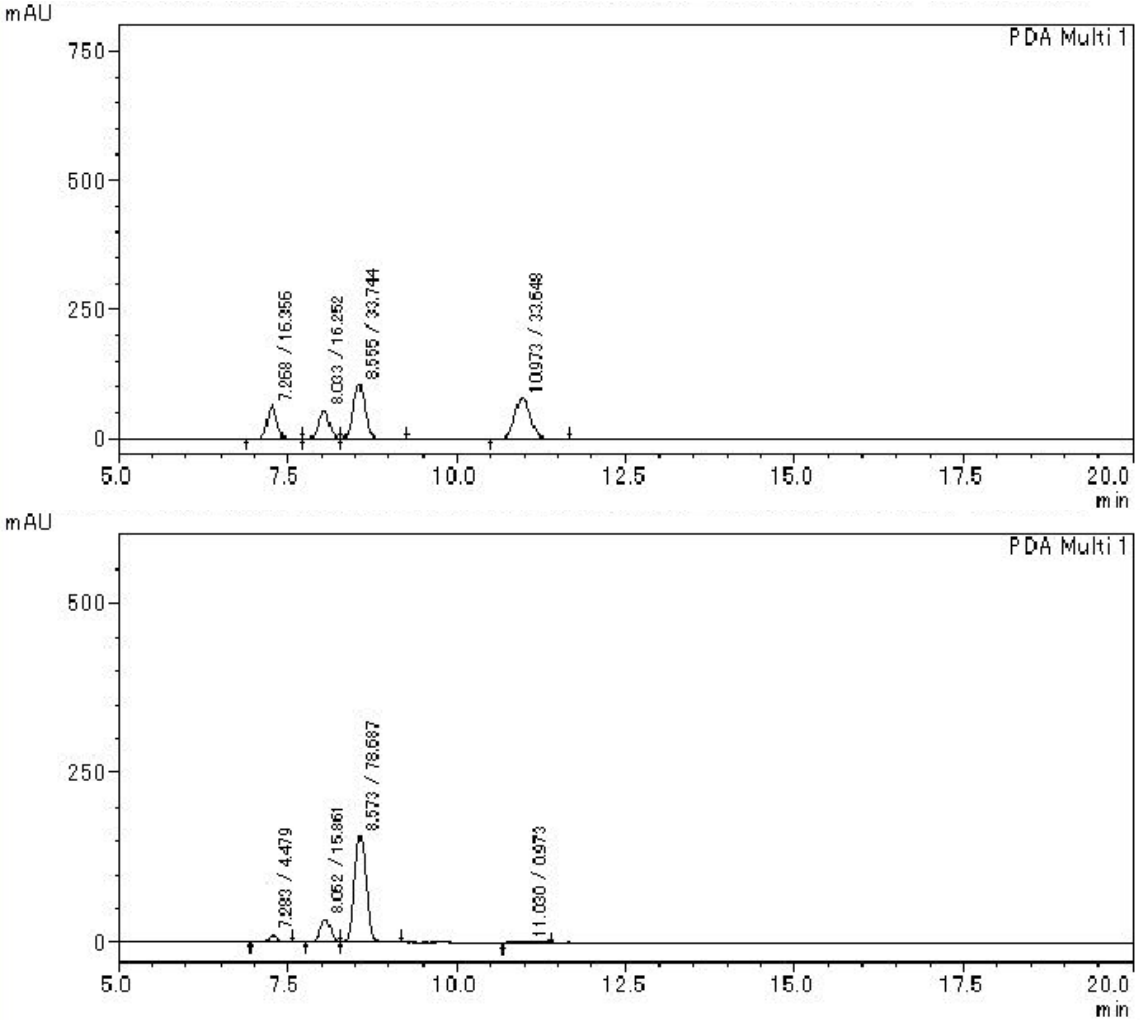
2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-allyl-2-oxo-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate



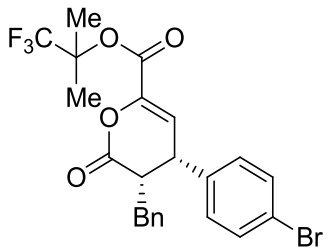


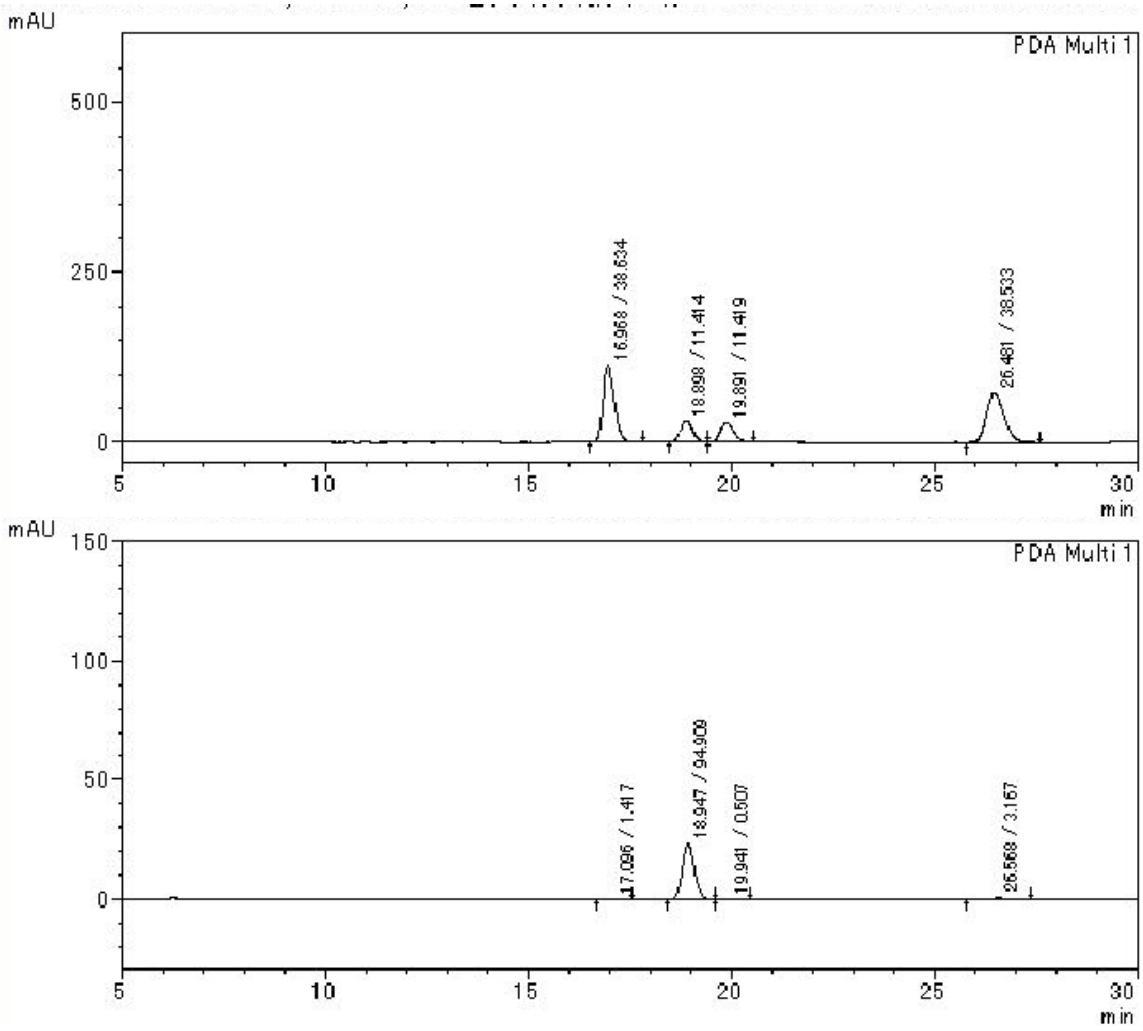
2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-butyl-2-oxo-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate



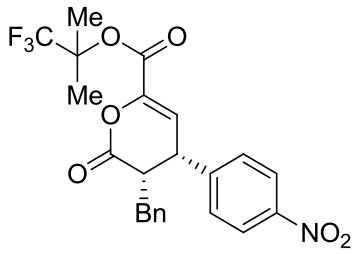


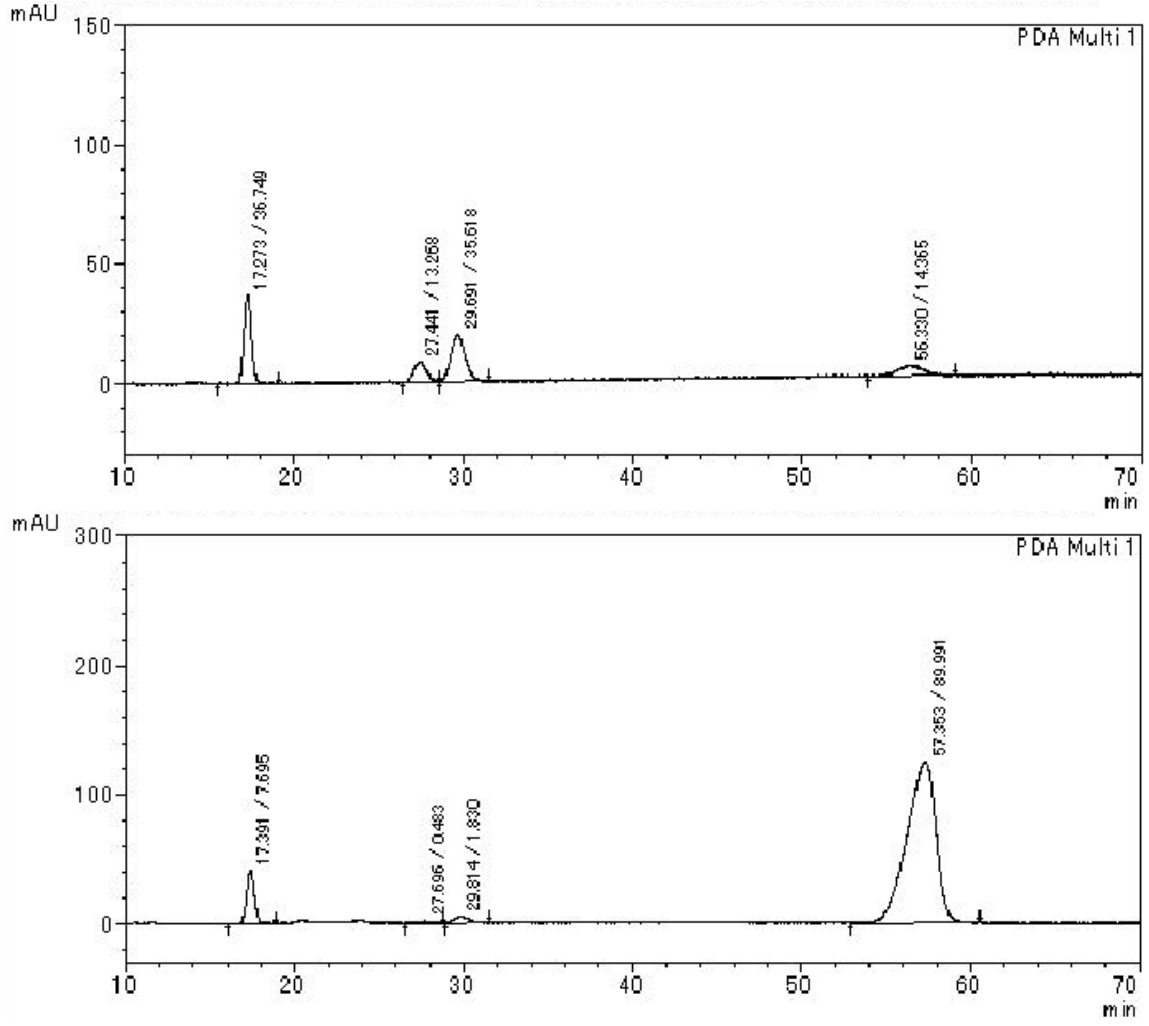
2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-4-(4-bromophenyl)-2-oxo-3,4-dihydro-2*H*-pyran-6-carboxylate



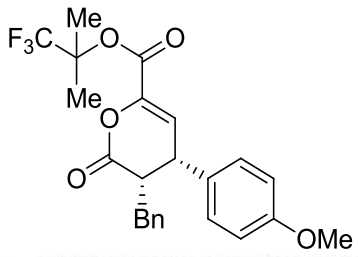


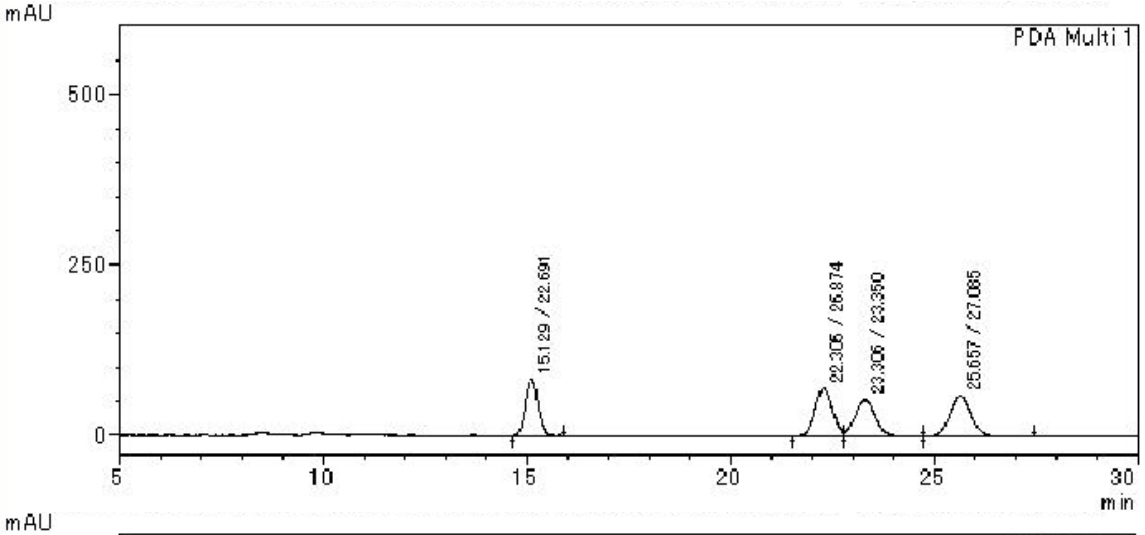
2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-4-(4-nitrophenyl)-2-oxo-3,4-dihydro-2*H*-pyran-6-carboxylate

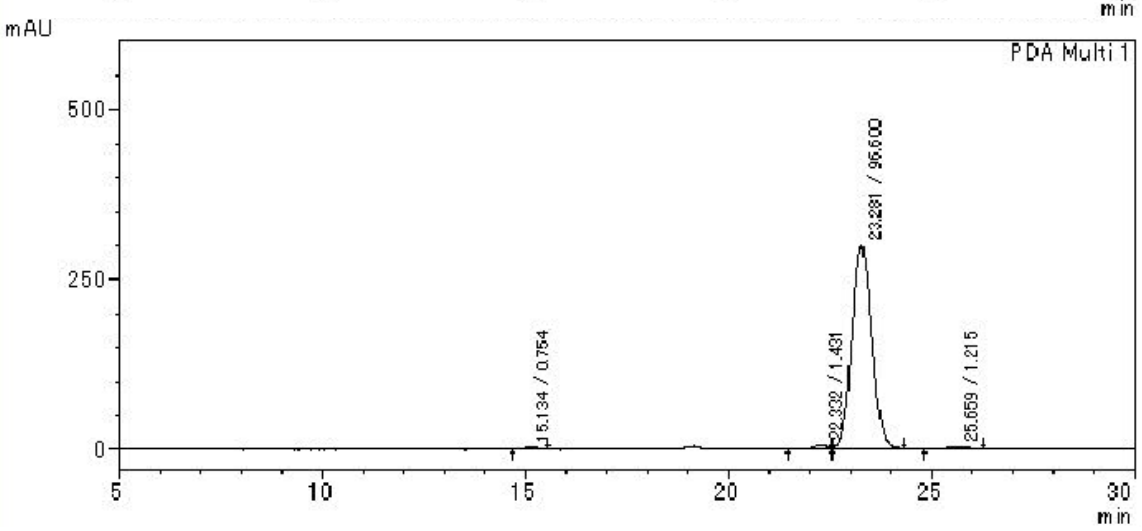




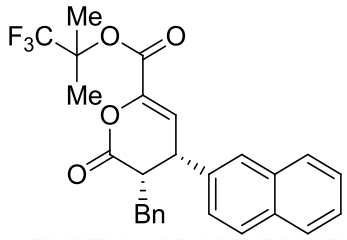
2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-4-(4-methoxyphenyl)-2-oxo-3,4-dihydro-2*H*-pyran-6-carboxylate

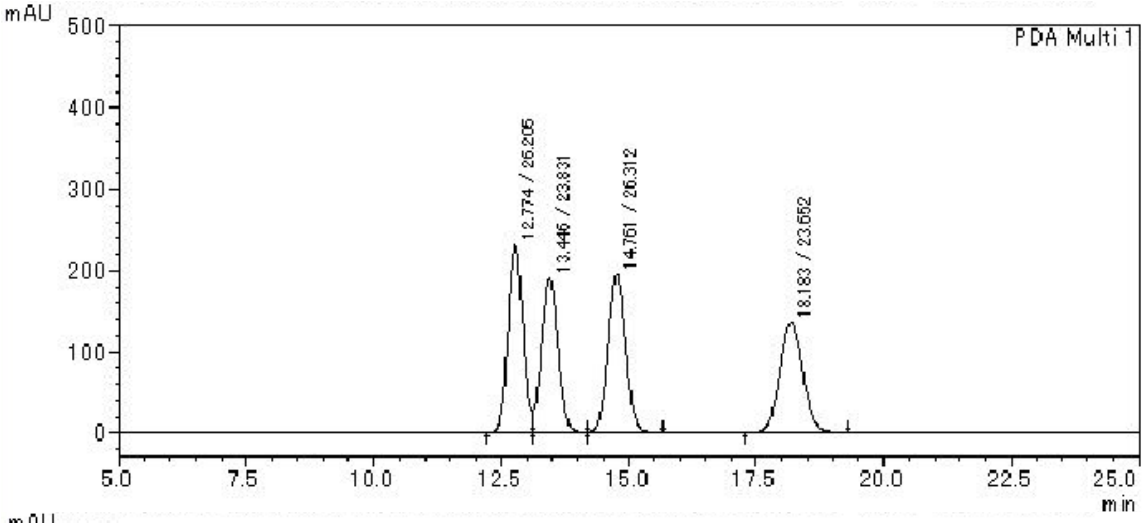


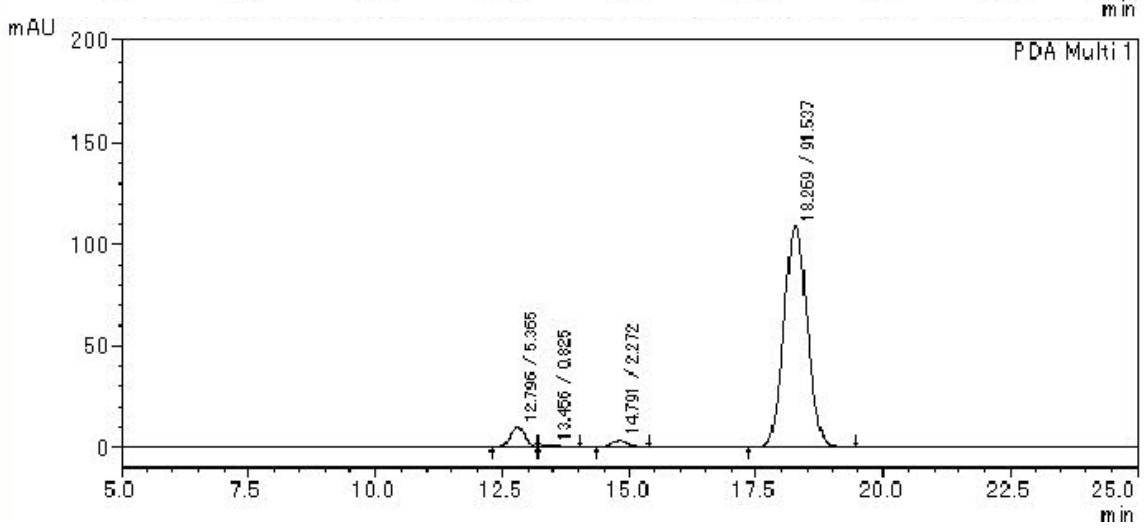




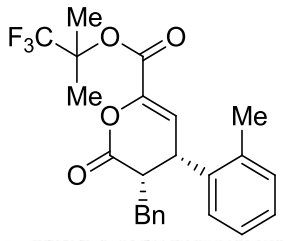
2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-4-(naphthalen-2-yl)-2-oxo-3,4-dihydro-2*H*-pyran-6-carboxylate

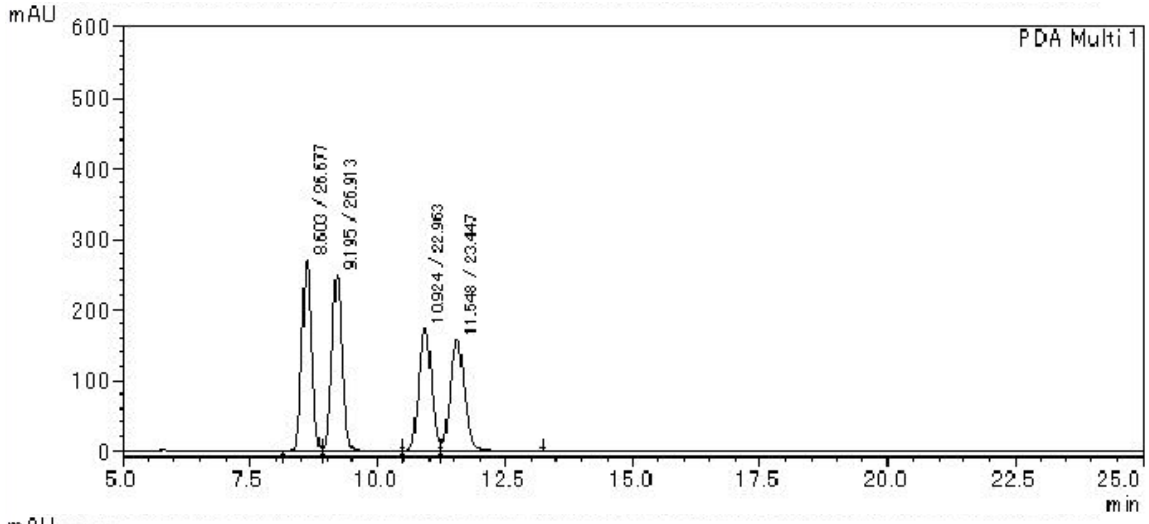


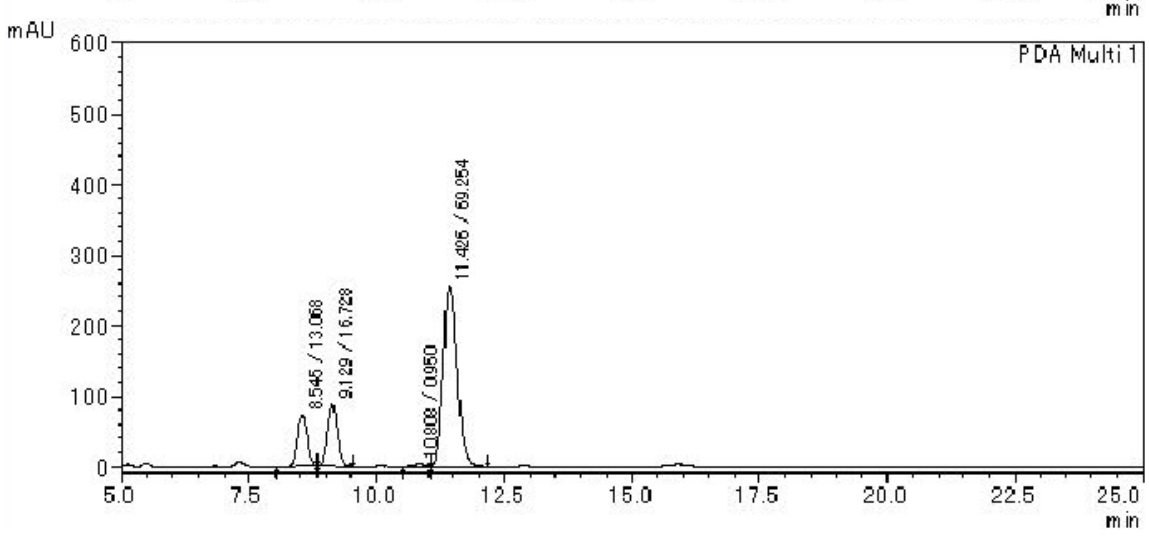




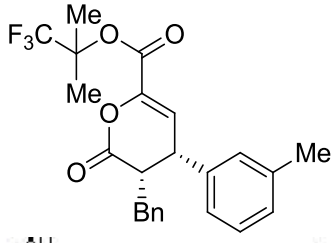
2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-2-oxo-4-(*o*-tolyl)-3,4-dihydro-2*H*-pyran-6-carboxylate

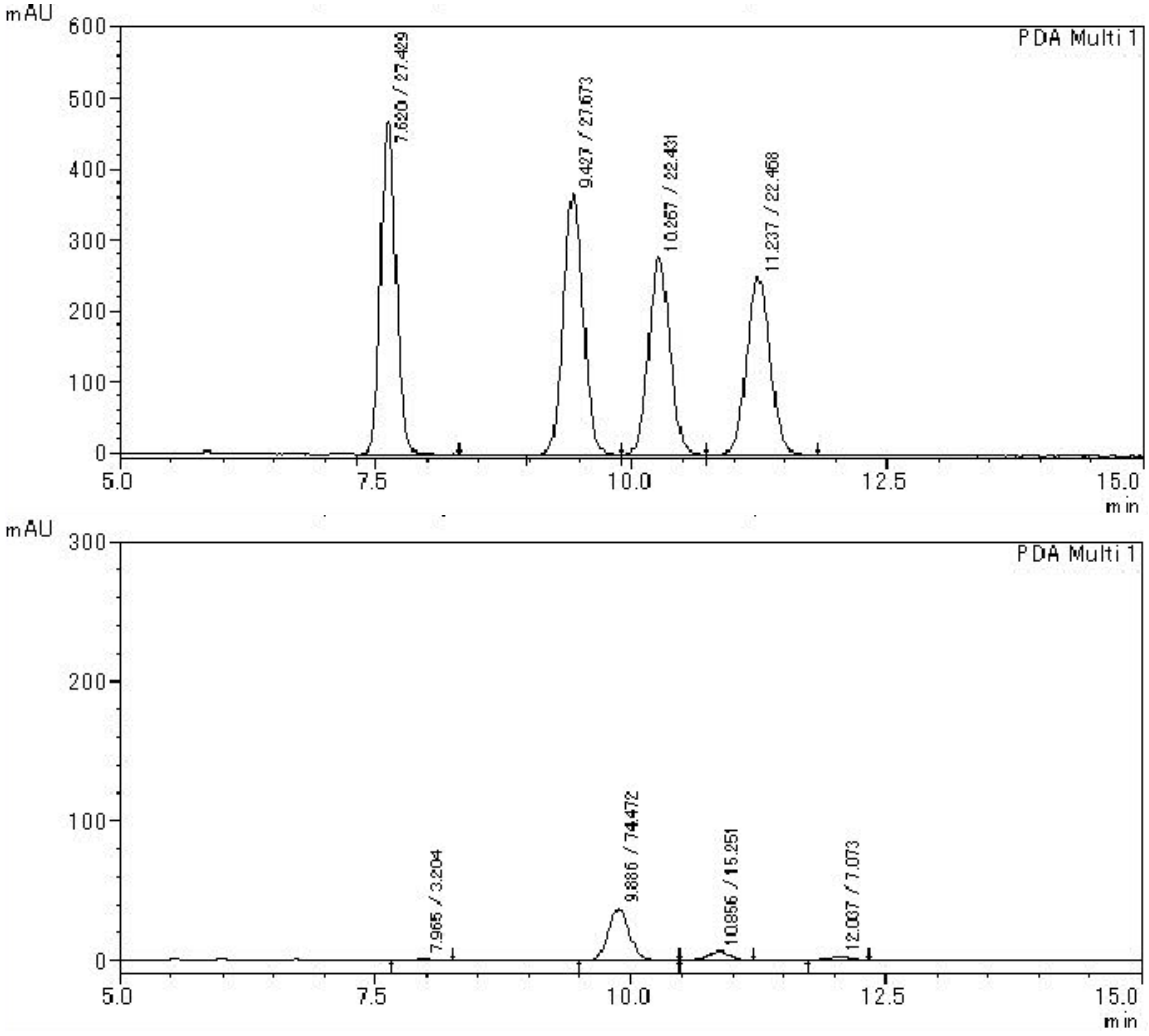




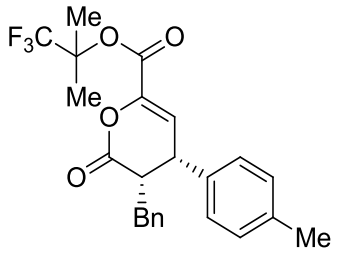


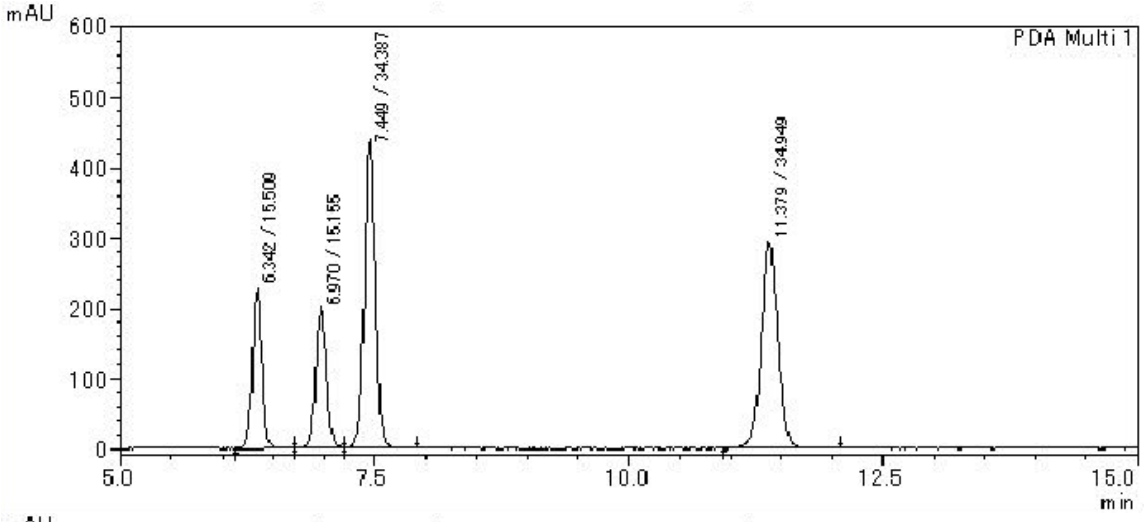
2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-2-oxo-4-(*m*-tolyl)-3,4-dihydro-2*H*-pyran-6-carboxylate

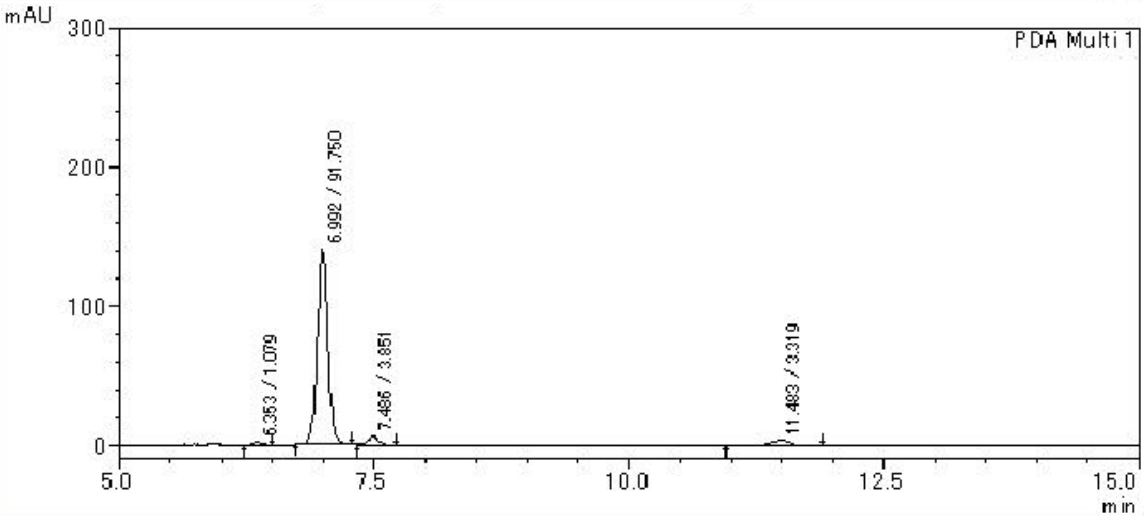




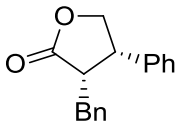
2,2,2-Trifluoro-1,1-dimethylethyl (3*S*,4*S*)-3-benzyl-2-oxo-4-(*p*-tolyl)-3,4-dihydro-2*H*-pyran-6-carboxylate

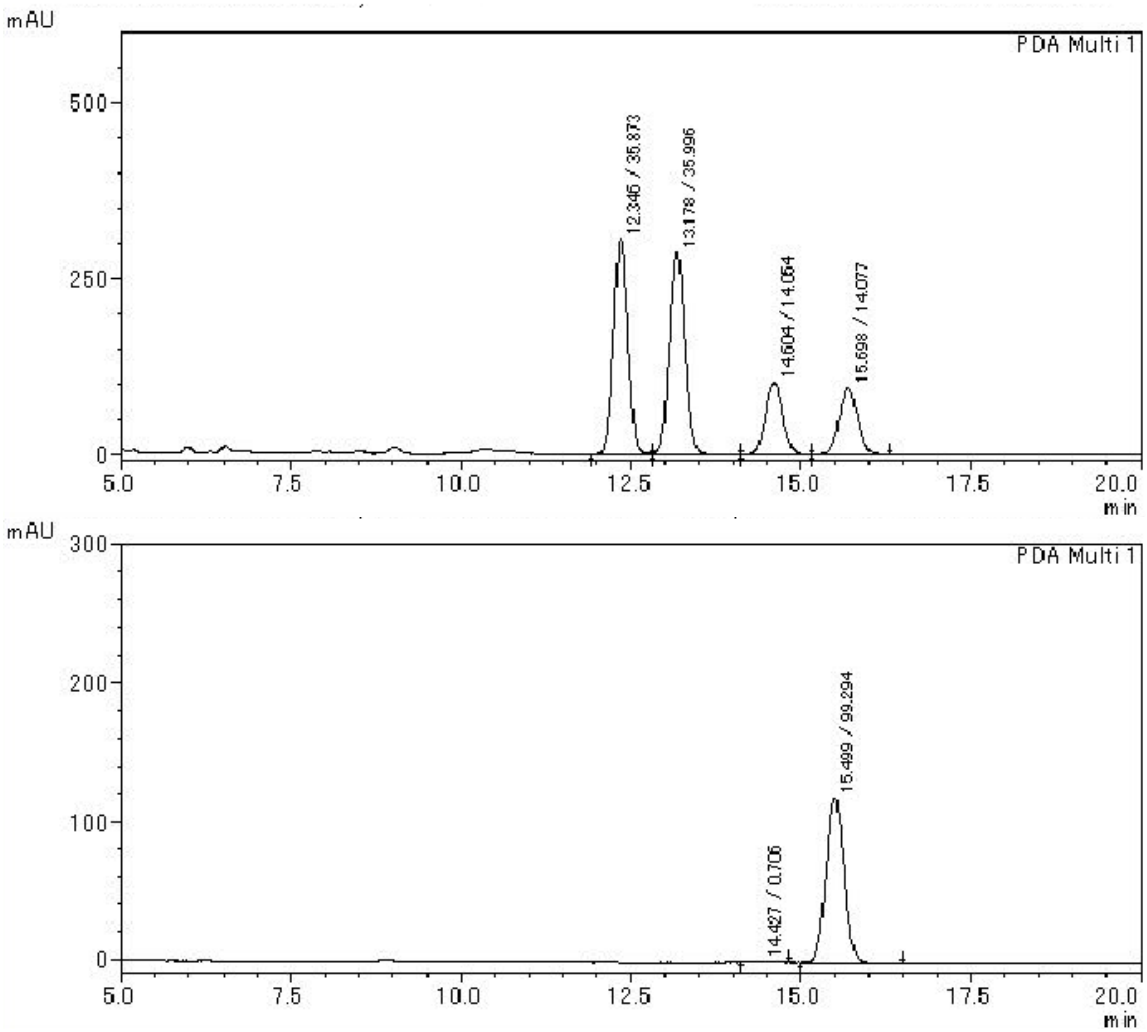






γ-Lactone *cis*-9





γ-Lactam *cis*-10