Supporting Information

Stereoselective Construction of a Key Hydroindole Precursor of Epidithiodiketopiperazine (ETP) Natural Products

Minghao Feng,[†] and Xuefeng Jiang*,[†]

[†]*Shanghai Key Laboratory of Green Chemistry and Chemical Process, Department of Chemistry, East China Normal University, 3663 North Zhongshan Road, Shanghai 200062, P. R. China*
xfjiang@chem.ecnu.edu.cn

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I. General information

NMR spectrum:

^{1}H and ^{13}C NMR spectra were collected on 400 MHz NMR spectrometers (Bruker AVANCE) using $CDCl_3$. Chemical shifts are reported in parts per million (ppm). Chemical shifts for protons are reported in parts per million downfield and are referenced to residual deuterium in the NMR solvent ($CHCl_3$ = δ 7.26, DMSO = δ 2.50, Acetone = δ 2.05). Chemical shifts for carbon are reported in parts per million downfield and are referenced to the carbon resonances of the solvent ($CDCl_3$ = δ 77.0, DMSO = δ 39.52, Acetone = δ 206.26, 29.84). Data are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

Mass spectroscopy:

Mass spectra were in general recorded on a Shimadzu GCMS-QP2010 Ultra and a HP 5989A mass selective detector.

Chromatography:

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

IR:

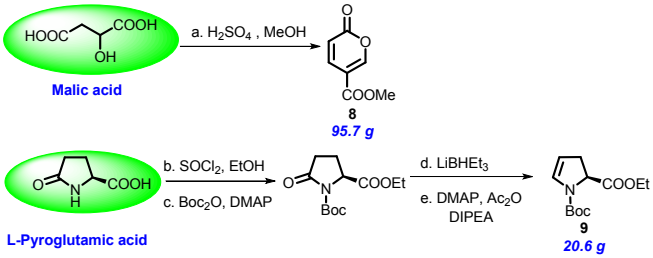
TENSOR (27) Series FT-IR Spectrometers.

Optical rotation values:

The $[\alpha]_D$ was recorded using PolAAr 3005 High Accuracy Polarimeter.

II. Synthesis of Diene 8 and Dienophile 9

Both diene 8 and dienophile 9 could be easily synthesized from the naturally abundant starting materials respectively in 95.7 grams and 20.6 grams under our optimized procedure,[1] which laid the foundation for affording the key intermediate in large scale

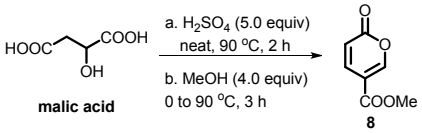


Conditions: (a) H_2SO_4 (5.0 equiv), 90 °C, 2 h, then MeOH (4.0 equiv), 0 to 90 °C, 3 h, 67%; (b) $SOCl_2$ (1.1 equiv), EtOH, 0 °C to rt, 2 h, 95%; (c) Boc_2O (1.1 equiv), DMAP (0.1 equiv), EtOAc, rt, 1 h, 90%; (d) $LiBHEt_3$ (1.1 equiv), toluene, -78 °C, 1 h; (e) DMAP (0.1 equiv), DIPEA (6.0 equiv), Ac_2O (2.0 equiv), toluene, reflux, 10 h, 83% over 2 steps.

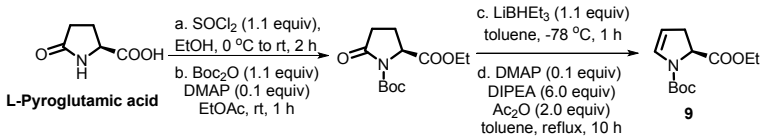
Reference：

1 (a) Chen, J.; Chen, Z.; Hu, G.; Li, Q.; Zhu, W.; Liu, Z.; Pei, Q.; Shen, J. *Arch. Pharm.* **2013**, *346*, 654. (b) Dieter, R. K.; Sharma. R. R. *J. Org. Chem.* **1996**, *61,* 4180.

III. Experimental Section



Diene **8** 500 mL concentrated H_2SO_4 (9.30 mol, 5.0 equiv) was added to 250.00 g malic acid (1.86 mol, 1.0 equiv) carefully. The mixture was heated to 90 °C with stirring, then the system was kept at the same temperature for 2 hours. After cooled to 0 °C, 300 mL MeOH (7.44 mol, 4.0 equiv) was added dropwise over 0.5 h, then the mixture was reacted at 90 °C for additional 2.5 h. After cooled to room temperature, the mixture was poured to 200 mL cold water and stirred for 0.5 h. The mixture was then flitered, the obtained solid product was washed by cold water. The crude product was purified by recrystallization from EtOAc to give the Diene **8** 70.4 g as slight yellow solid (95.7 g, 0.62 mol, 67% yield). R_f = 0.3 (Ethyl Acetate: Petroleum Ether = 10:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 2.6, 1.1 Hz, 1H), 7.77 (dd, *J* = 9.8, 2.6 Hz, 1H), 6.32 (dd, *J* = 9.8, 1.0 Hz, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.33, 159.70, 58.08, 141.54, 115.22, 111.87, 52.39.



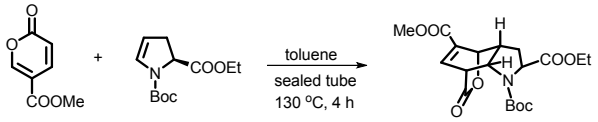
Dienophile **9**. To a stirred solution of L-pyroglutamic acid (50.00 g, 0.387 mol, 1.0 equiv) in EtOH (500 mL) at 0 °C, $SOCl_2$ (31.0 mL, 0.426 mol, 1.1 equiv) was added dropwise. The system was stirred at room temperature for 2 hours. Then the reaction was quenched with sat. aq. NH_4Cl and extracted with EtOAc (3×100 mL). The combined organic phases were washed with brine (2 ×50 mL), dried over Na_2SO_4 and concentrated. The obtained residue was analytically pure L-pyroglutamic acid ethyl ester (57.77g, 0.368 mol, 95% yield).

The obtained L-pyroglutamic acid ethyl ester was dissolved in EtOAc (500 mL), Boc_2O (88.3 g, 0.405 mol, 1.1 equiv) and DMAP (4.50 g, 36.8 mmol, 0.1 equiv) was added, the reaction was quenched with sat. aq. NH_4Cl after stirring for 1 h at room temperature. Then the mixture was extracted with EtOAc (3×100 mL). The combined organic phases were washed with brine (2×50 mL), dried over Na_2SO_4 and concentrated. The obtained residue was analytically pure N-Boc-L-pyroglutamic acid ethyl ester (84.98 g, 0.330 mol, 90% yield).

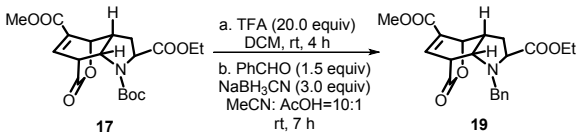
To a solution of N-Boc-L-pyroglutamic acid ethyl ester (25.71 g, 100 mmol, 1.0 equiv) in dry toluene (150 mL) at -78 °C, $LiBHEt_3$ (1.0 M in THF, 110 mL, 1.1 equiv) was added dropwise over 45 minutes. The reaction was stirred at the same temperature for additional 1 h before quenched with sat. aq. NH_4Cl. The mixture was extracted with EtOAc (3×100 mL). The combined organic phases were washed with brine (2×50 mL), dried over Na_2SO_4 and concentrated. The obtained crude yellow residue was used in the next step without further purification.

The crude alcohol was then dissolved in dry toluene (250 mL). DMAP (1.22g, 10 mmol, 0.1 equiv), DIPEA (99.1 mL, 600 mmol, 6.0 equiv), Ac_2O (18.8 mL，200 mmol, 2.0 equiv) was added in sequence. The reacting system was stirred at reflux temperature for 10 hours before quenched with sat. aq. NH_4Cl and extracted with EtOAc (3×100 mL). The combined organic phases were washed with brine (2×50 mL), dried over Na_2SO_4 and concentrated. The crude mixture so-obtained could be purified by flash column chromatography to give the analytically

pure dienophile **9** as yellow liquid (20.6 g, 84 mmol, 84% over 2 steps). R_f = 0.5 (Ethyl Acetate: Petroleum Ether = 10:1); $[\alpha]^{30}_D$ = -77.9 (c = 1.02, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 – 6.31 (m, 1H), 4.92 (d, *J* = 19.4 Hz, 1H), 4.59 (ddd, *J* = 31.5, 11.9, 5.1 Hz, 1H), 4.32 – 4.07 (m, 2H), 3.06 (dd, *J* = 30.3, 18.0 Hz, 1H), 2.64 (t, *J* = 18.9 Hz, 1H), 1.46 (d, *J* = 18.8 Hz, 8H), 1.27 (dd, *J* = 14.5, 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.95 (171.66), 151.46, 130.02, 104.98, 80.80, 61.16, 58.41 (57.91), 35.50 (57.91), 28.29 (28.18), 14.22 (14.10) (pair of rotomers).



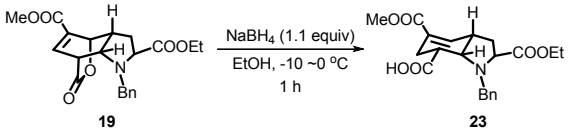
Compound **17**. To a stirred solution of diene **8** (14.0 g, 91 mmol, 1.0 equiv) in toluene (100 mL) was added dienophile **9** (24.10 g, 100 mmol, 1.1 equiv) in one portion. Then sealed the operator and kept the mixture at 130°C for 4 h. Then the mixture was concentrated. The obtained crude yellow residue was used in the next step without further purification. The crude mixture so-obtained could be purified by flash column chromatography to give the analytically pure compound **17** as a white solid (31.28 g, 79.17 mmol, 87% yield). R_f = 0.3 (Ethyl Acetate: Petroleum Ether = 3:1); $[\alpha]^{29}_D$ = -131.8 (c = 1.34, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.24 (m, 1H), 5.42 (s, 1H), 4.58 – 4.42 (m, 2H), 4.24 – 4.09 (m, 3H), 3.79 (s, 3H), 2.82 (dt, *J* = 18.2, 9.1 Hz, 1H), 2.51 – 2.38 (m, 1H), 2.16 – 2.05 (m, 1H), 1.39-1.50 (m, 9H), 1.25 (t, *J* = 7.0 Hz, 3H);^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 169.9, 162.4, 154.5, 139.5, 138.1, 81.4, 75.2, 63.2, 61.3, 59.6, 52.3, 46.5, 41.1, 28.4, 28.2, 28.0, 14.2; IR (neat) 2979, 1715, 1637, 1447, 1374, 1258, 1196, 1127, 1026, 965, 915, 737 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{25}NO_8$ [*M*+Na^+] 418.1472, Found 418.1471.



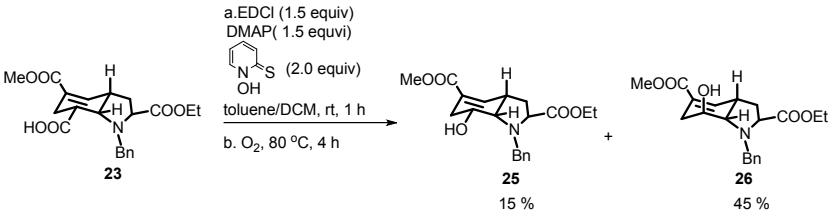
Compound **19**. The crude compound **17** was dissolved in DCM (200 mL).Then TFA (135 ml, 1.82 moL, 20.0 equiv) was added dropwise. The mixture was stirred at room temperature for 4 hours. Then the reaction was quenched with a sat. aq. $NaHCO_3$ solution (200 mL) and extracted with CH_2Cl_2 (3×100 mL). The combined organic phases were washed with brine (2×50 mL), dried over Na_2SO_4 and concentrated. The obtained residue was used for the next step without further purification.

The crude amine was dissolved in MeCN (200 mL) and glacial acetic acid (20 mL). Then PhCHO (13.3 ml, 132 mmol, 1.5 equiv), $NaBH_3CN$ (16.60 g, 264 mmol, 3.0 equiv) were added in sequence. The mixture was kept at ambient temperature for 7 hours. Then the reaction was quenched with sat. aq. NH_4Cl solution and extracted with EtOAc (3×100 mL). The combined organic phases were washed with brine (2×50 mL), dried over Na_2SO_4. After concentrated under reduced pressure, the obtained crude yellow residue could be used in the next step without further purification. The crude mixture so-obtained could be purified by flash column chromatography to

give the analytically pure compound **19** as a white solid. R_f = 0.3 (Ethyl Acetate: Petroleum Ether = 3:1); $[\alpha]^{29}_D$ = -77.3 (c = 1.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.16 (m, 6H), 5.36 (s, 1H), 4.14 – 4.01 (m, 2H), 3.95 (d, *J* = 13.0 Hz, 1H), 3.81 – 3.69 (m, 4H), 3.65 – 3.52 (m, 3H), 2.77 (dd, *J* = 9.1 Hz, 9.1 Hz , 1H), 2.15 (dt, *J* = 12.9, 8.3 Hz, 1H), 1.88 (dd, *J* = 13.0, 9.0 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 170.7, 162.6, 139.1, 138.8, 137.5, 129.0, 128.4, 127.5, 75.6, 65.4, 62.3, 60.4, 52.3, 47.4, 43.0, 28.4, 14.4; IR (neat) 2955, 1770, 1721, 1635, 1446, 1367, 1257, 1188, 1097, 1026, 967, 747, 705 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{23}NO_6$ [*M*+H$^+$] 386.1598, Found 386. 1617.



Carboxylic acid **23**. The crude compound **19** was dissolved in 500 mL EtOH. The solution was cooled down to -10 °C. Then $NaBH_4$ (3.79 g, 100.1 mmol, 1.1 equiv) was added in portions. The mixture was kept at 0 °C for 1 hour. The reaction was quenched with a sat. aq. NH_4Cl solution and extracted with EtOAc (3×100 mL). The combined organic phases were washed with brine (2 ×50 mL), dried over Na_2SO_4 and concentrated. The crude product was then purified by flash column chromatography, affording the carboxylic acid **23** as yellow solid (29.53g, 76.4 mmol, 84% over 4 steps). R_f = 0.3 (Ethyl Acetate: Petroleum Ether = 1:1); $[\alpha]^{29}_D$ = 4.5 (c = 0.69, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 15.33 (s, 1H), 7.44 – 7.26 (m, 5H), 6.82 (t, *J* = 2.8 Hz, 1H), 4.28 – 4.07 (m, 4H), 3.85 (dd, *J* = 10.1, 6.6 Hz, 1H), 3.74 (m, 4H), 3.42 (dd, *J* = 16.7, 2.9 Hz, 1H), 3.37 – 3.23 (m, 1H), 2.80 – 2.71 (m, 1H), 2.16 (dd, *J* = 13.0, 7.4 Hz, 1H), 2.06 – 1.90 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 170.7, 162.6, 139.1, 138.8, 137.5, 129.0, 128.4, 127.5, 75.6, 65.4, 62.3, 60.4, 52.3, 47.4, 43.0, 28.4, 14.4; IR (neat) 2948, 2410, 2254, 1713, 1441, 1372, 1204, 1104, 1149, 1102, 871, 752, 703 cm^{-1}. HRMS (ESI) Calcd for $C_{21}H_{25}NO_6$ [*M*+H$^+$] 388.1755, Found 388.1742.

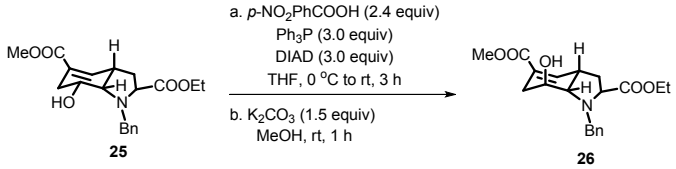


Alcohol **25** and **26**. To the solution of carboxylic acid **23** (505.0 mg, 1.30 mmol, 1.0 equiv) in toluene (40 mL) and DCM (8 mL) was added DMAP (249.0 mg, 1.96 mmol, 1.5 equiv), EDCl (374.0 mg, 1.95 mmol, 1.5 equiv), 2-mercaptopyridine-N-oxide (442.0 mg, 2.61 mmol, 2.0 equiv) in sequence. After the reaction mixture was stirred at room temperature for 1 hour, oxygen was bubbled through the solution at 80 °C for 4 hours. Then the *t*-BuSH (2.94 ml, 26.07 mmol, 20.0 eq) was added to the reaction mixture, the solution was kept at room temperature for additional 1 h before quenched with a sat. aq. NH_4Cl solution and extracted with EtOAc (3×10 mL). The solvent was removed in vacuum and the residue was purified by flash column chromatography to give **26**

(209.5 mg, 0.58 mmol, 45%) as a yellow oil and **25** (70.3 mg, 0.20 mmol, 15%) as a yellow oil.

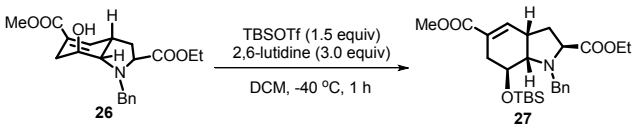
Alcohol **25** R_f = 0.5 (Ethyl Acetate: Petroleum Ether = 2:1); $[\alpha]^{30}_D$ = 24.0 (c = 0.70, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 5H), 6.93 (t, *J* = 3.0 Hz, 1H), 4.26 – 4.10 (m, 2H), 4.03 – 3.87 (m, 3H), 3.73 (s, 3H), 3.69 (d, *J* = 7.3 Hz, 1H), 3.45 – 3.33 (m, 2H), 3.22 – 3.07 (m, 1H), 2.95 (dd, *J* = 17.6, 2.9 Hz, 1H), 2.14 (dd, *J* = 17.6, 2.3 Hz, 1H), 2.07 (dd, *J* = 12.3, 7.6 Hz, 1H), 1.84 (td, *J* = 12.6, 7.5 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.5, 170.7, 162.6, 139.1, 138.8, 137.5, 129.0, 128.4, 127.5, 75.6, 65.4, 62.3, 60.4, 52.3, 47.4, 43.0, 28.4, 14.4; ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.1, 167.5, 138.9, 138.1, 128.9, 128.6, 127.6, 125.7, 62.0, 61.4, 60.5, 53.3, 51.7, 36.5, 34.7, 28.0, 14.3; IR (neat) 3439, 2948, 2254, 1719, 1654, 1444, 1369, 1256, 1190, 108, 1028, 923, 858, 749, 704 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{25}NO_5$ [*M*+H$^+$] 360.1805, Found 360.1797.

Alcohol **26** R_f = 0.2 (Ethyl Acetate: Petroleum Ether = 2:1); $[\alpha]^{30}_D$ = -15.0 (c = 1.22, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.10 (m, 5H), 6.85 (s, 1H), 4.14 (d, *J* = 14.1 Hz, 1H), 4.10 – 3.98 (m, 2H), 3.87 – 3.74 (m, 2H), 3.65 (s, *J* = 1.7 Hz, 3H), 3.63 – 3.54 (m, 1H), 3.32 – 3.17 (m, 2H), 2.56 – 2.45 (m, 1H), 2.30 (dd, *J* = 16.7, 7.0 Hz, 1H), 2.09 (dd, *J* = 12.6, 8.1 Hz, 1H), 1.80 – 1.69 (m, 1H), 1.14 (t, *J* = 7.1, 3H); ^{13}C NMR (100 MHz, $CDCl_3$):173.8, 167.2, 140.7, 139.4, 128.2, 128.1, 126.3, 70.2, 62.4, 60.2, 54.2, 51.7, 37.7, 34.7, 29.2, 14.2; IR (neat) 3499, 2947, 1716, 1444,1369, 1252, 1186, 1095, 1034, 747, 702 cm^{-1}; HRMS (ESI) Calcd for $C_{20}H_{25}NO_5$ [*M*+H$^+$] 350.1805, Found 360.1797.



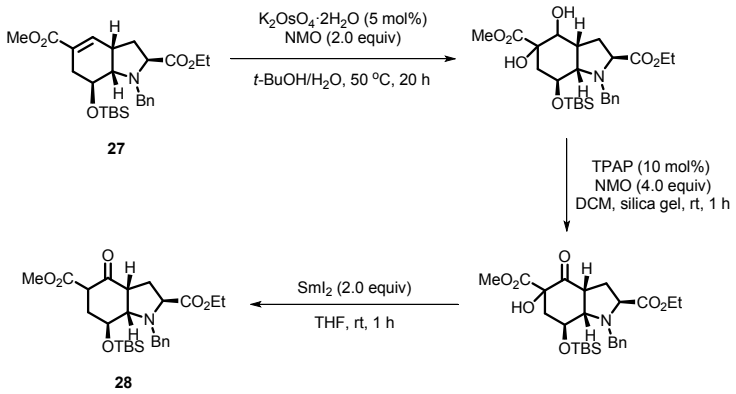
Conversion from **25** to **26**. A solution of **25** (70.3 mg, 0.195 mmol, 1.0 equiv) in THF (3 mL) was treated with PPh_3 (122.7 mg, 0.468 mmol, 2.4 equiv), *p*-nitrobenzoic acid (97.7 mg, 0.585 mmol, 3.0 equiv) and DIAD (115 μL, 20.0 mg, 0.585 mmol, 3.0 equiv) at 0 °C. The reaction mixture was stirred at room temperature for 2.5 h, hereupon all volatiles were removed in vacuum. The crude product was purified by flash chromatography.

The obtained product was dissolved in MeOH (1.0 mL), K_2CO_3 (40.5 mg, 0.292 mmol, 1.5 equiv) was added in one portion. After stirred at room temperature for 1 h, the reaction was quenched with a sat. aq. NH_4Cl solution and extracted with EtOAc (3×3 mL). The combined organic phases were then washed by sat. aq. NaCl and dried over Na_2SO_4. The solvent was removed in vacuum and the residue was purified by flash column chromatography to give **26** (46.4 mg, 0.129 mmol, 66% yield).



TBS protected product **27**. To a solution of alcohol **26** (300.0 mg, 0.835 mmol, 1.0 equiv) in dry DCM (20 mL), 2,6-lutidine (0.29 mL, 2.54 mmol, 3.0 equiv) was added. After the mixture was then cooled to -40 °C, TBSOTf (0.26 mL, 1.25 mmol, 1.5 equiv) was added dropwise. The

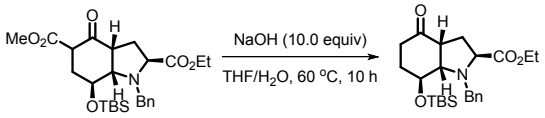
reaction was stirred at the same temperature for 1 h, and then quenched with sat. aq. NH_4Cl. The aqueous phase was separated and extracted with DCM (3×10 mL). The combined organic phases were then washed by sat. aq. NaCl and dried over Na_2SO_4 then concentrated. Purification by flash column chromatography afforded the TBS protected product **27** as yellow oil (336.2 mg, 0.71 mmol, 85% yield). R_f = 0.3 (Ethyl Acetate: Petroleum Ether = 20:1); $[\alpha]^{30}_D$ = -30.2 (c = 1.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.18 (m, 5H), 6.90 (d, *J* = 3.9 Hz, 1H), 4.15 (d, *J* = 13.8 Hz, 1H), 4.12 – 4.01 (m, 3H), 3.82 (d, *J* = 13.8 Hz, 1H), 3.75 (s, 3H), 3.60 (dd, *J* = 8.1, 2.0 Hz, 1H), 3.38 (d, *J* = 4.7 Hz, 1H), 3.27 – 3.17 (m, 1H), 2.50 – 2.43 (m, 1H), 2.41 (s, 1H), 2.15 (ddd, *J* = 12.8, 8.9, 2.1 Hz, 1H), 1.80 (d, *J* = 12.9 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.84 (s, 9H), 0.06 (d, *J* = 1.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.94, 167.72, 141.17, 139.09, 128.40, 128.18, 126.94, 125.50, 77.32, 77.00, 76.68, 69.43, 64.65, 61.97, 60.05, 53.57, 51.63, 37.26, 34.31, 28.79, 25.78, 17.97, 14.22, -4.46, -4.68; IR (neat) 2950, 2860, 1800, 1722, 1656, 1451, 1370, 1256, 1186, 1152, 1095, 960, 836, 777, 700 cm^{-1}; HRMS (ESI) Calcd for $C_{26}H_{39}NO_5Si$ [*M*+H$^+$] 474.2670, Found 474.2690.



β-methoxycarbonyl ketone **28**. The TBS protected compound **27** (290.0 mg, 0.612 mmol, 1.0 equiv) was dissolved in *t*BuOH/H_2O (10 mL/10 mL), then NMO (143.0 mg, 1.224 mmol, 2.0 equiv) and K_2OsO_4•$2H_2O$ (11.0 mg, 0.0306 mmol, 5 mol%) were added. The system was stirred at 50 °C for 20 h before cooled to room temperature. To the mixture 5 mL of EtOAc was added, then the aqueous phase was separated. The aqueous phase was extracted with EtOAc (3×10 mL).The combined organic phases were then washed by sat. aq. NaCl and dried over Na_2SO_4 then concentrated. The obtained diol was used for the next step without further purification.

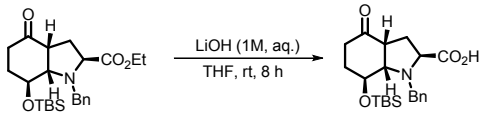
To the solution of so-obtained diol in dry DCM (30 mL), NMO (287 mg, 2.45 mmol, 4.0 equiv) and silica gel (290 mg) was added, the mixture was stirred at room temperature for 20 minutes. Then TPAP (43 mg, 0.122 mmol, 20 mol%) was added in one portion, and the reaction was then stirred for additional 1 hour at room temperature. Then the mixture was filtered through a pad of silica gel. The filtrate was concentrated to give the crude product.

The so-obtained crude product was then dissolved in a small amount of dry THF, SmI_2 (0.1 M in THF, 12.2 mL, 2.0 equiv) was added dropwise in 20 minutes. The system was then stirred for 1 hour and quenched with 5 mL of 0.1M HCl (aq.). The aqueous was extracted with EtOAc (3 ×10 mL).The combined organic phases were then washed by sat. aq. NaCl and dried over Na_2SO_4 then concentrated. Purification by flash column chromatography afforded the mixture of inseparable diastereoisomers **28** as yellow oil (105 g, 0.214 mmol, 35% yield over 3 steps). R_f = 0.5 (Ethyl Acetate: Petroleum Ether = 20:1).



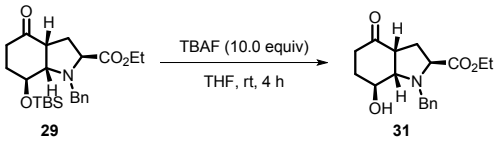
28 **29**

Compound **29**. To the solution of *β*-methoxycarbonyl ketone **28** (30.0 mg, 0.0612 mmol, 1.0 equiv) in THF/H_2O (2.5 mL/2.5 mL), NaOH (24.5 mg, 0.612 mmol, 10.0 equiv) was added. The mixture was stirred at 60 °C for 10 hours. After diluted with 5 mL EtOAc, the reaction was quenched with sat. aq. NH_4Cl. The aqueous phase was separated and extracted with EtOAc (3×5 mL). The combined organic phases were then dried over Na_2SO_4 and concentrated. Purification by flash column chromatography afforded compound **29** as yellow oil (11.0 mg, 0.0257 mmol, 42% yield) and recovered *β*-methoxycarbonyl ketone **28** (5.5 mg, 0.0112 mmol, 18%). R_f = 0.6 (Ethyl Acetate: Petroleum Ether = 10:1); $[\alpha]^{30}_D$ = -12.0 (c = 0.03, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 5H), 4.09 (q, *J* = 7.1 Hz, 2H), 3.99 (s, 1H), 3.85 (dd, *J* = 48.2, 13.8 Hz, 2H), 3.70 – 3.59 (m, 2H), 3.08 (dd, *J* = 15.2, 7.5 Hz, 1H), 2.71 – 2.56 (m, 1H), 2.51 – 2.39 (m, 1H), 2.37 – 2.22 (m, 2H), 1.88 (ddd, *J* = 13.0, 8.7, 2.9 Hz, 1H), 1.84 – 1.75 (m, 1H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.88 (s, 9H), 0.07 (t, *J* = 5.0 Hz, 9H), 0.07 (d, *J* = 10.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.48, 173.71, 138.70, 128.32, 127.20, 69.00, 66.69, 62.02, 60.23, 52.68, 48.64, 33.39, 30.18, 26.11, 25.71, 18.01, 14.23, -4.79, -4.85; IR (neat) 2951, 1720, 1455, 1365, 1259, 1092, 1028, 806, 698 cm^{-1}; HRMS (EI) Calcd for $C_{24}H_{40}NO_4Si$ 431.2492, Found 431.2494.



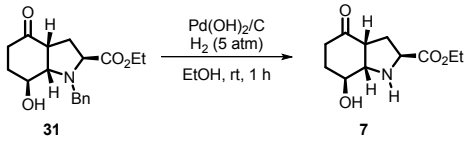
29 **30**

Carboxylic acid **30**. To a stirred solution of compound **29** (10.0 mg, 0.023 mmol, 1.0 equiv) in THF (1 mL) was added LiOH (1.0 M aq., 0.25 mL) in one portion, and the resulting mixture was stirred at ambient temperature for 8 h. The reaction was then quenched with aq. $KHSO_4$ solution (1 M) until pH = 3, and then extracted with EtOAc (3 × 3 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. The resulting crude product could be purified by flash column chromatography to give the carboxylic acid **30** as a white solid (8.9 mg, 0.022 mmol, 95% yield). R_f = 0.3 (DCM: MeOH = 20:1); $[\alpha]^{31}_D$ = -31.4 (c = 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.19 (m, 5H), 4.04 – 3.84 (m, 3H), 3.78 – 3.70 (m, 1H), 3.61 (d, *J* = 7.3 Hz, 1H), 3.11 (dd, *J* = 15.5, 7.7 Hz, 1H), 2.69 – 2.57 (m, 1H), 2.55 – 2.44 (m, 1H), 2.30 (ddd, *J* = 32.7, 14.1, 5.5 Hz, 2H), 2.06 – 1.92 (m, 1H), 1.86 – 1.76 (m, 1H), 0.89 (s, 9H), 0.07 (d, *J* = 9.1 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.33, 177.56, 138.57, 128.45, 128.35, 127.32, 68.92, 66.78, 61.74, 52.71, 48.60, 33.31, 30.37, 29.69, 26.09, 25.73, 18.02, -4.76, -4.82; IR (neat) 2934, 2858, 1710, 1630, 1458, 1373, 1255, 1088, 1022, 837, 760, 737, 700; HRMS (EI) Calcd for $C_{22}H_{33}NO_4Si$ 403.2179, Found 403.2184.



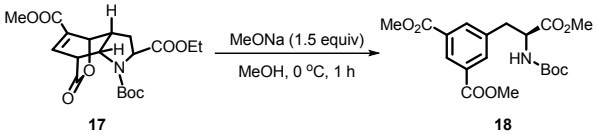
29 31

Alcohol **31**. 10 mg compound **29** (0.0232 mmol, 1.0 equiv) was dissolved in 1 mL THF at room temperature, TBAF (1.0 M in THF, 0.23 mL, 0.23 mmol, 10.0 equiv) was added in dropwise. The mixture was stirred at room temperature for 4 hours, then quenched with sat. aq. NH_4Cl and extracted with EtOAc (3×3 mL). The combined organic phases were dried over Na_2SO_4 and concentrated. The crude product was then purified by flash column chromatography to give the alcohol **31** as white solid (6.6 mg, 0.0213 mmol, 95% yield). R_f = 0.3 (Ethyl Acetate: Petroleum Ether = 3:1); $[\alpha]^{31}_D$ = -47.3 (c = 0.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.16 (m, 6H), 4.18 – 3.97 (m, 4H), 3.90 – 3.59 (m, 3H), 3.15 (dd, *J* = 15.5, 7.8 Hz, 1H), 2.64 (ddd, *J* = 17.1, 10.2, 7.0 Hz, 1H), 2.55 – 2.43 (m, 1H), 2.43 – 2.33 (m, 1H), 2.20 (tdd, *J* = 10.1, 6.3, 2.3 Hz, 1H), 1.96 (ddd, *J* = 25.6, 16.1, 7.7 Hz, 2H), 1.76 (s, 1H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.97, 173.75, 138.76, 128.41, 128.26, 127.24, 68.64, 67.98, 61.81, 60.33, 52.86, 48.47, 34.05, 29.85, 26.68, 14.24; IR (neat) 3471, 2943, 1715, 1453, 1366, 1193, 1077, 1027, 946, 750, 702 cm $^{-1}$; HRMS (ESI) Calcd for $C_{18}H_{23}NO_4$ [*M*+Na^+] 340.1519, Found 340.1508.



31 7

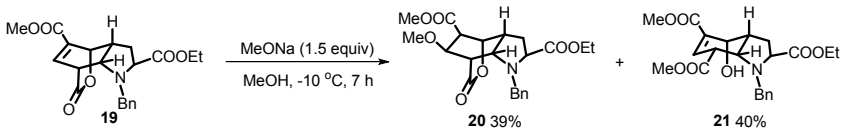
Monomer **7**. The obtained alcohol **31** (6.6 mg, 0.0213 mmol, 1.0 equiv) was dissolved in 0.5 mL EtOH in a reaction tube, to which $Pd(OH)_2$/C (5 wt.%, 0.66 mg) was added. Then the tube was transferred to a Parr pressure reactor. The Parr reactor was charged with 5 atm of H_2 gas. After the mixture was stirred for 4 h at 30 °C, the gas was ventilated, and the residue was diluted with Et_2O. Filtration through a short column of silica gel, evaporation afforded the analytically pure compound **7** (yellow oil, 4.7 mg, 0.0209 mmol, 98%). R_f = 0.3 (Ethyl Acetate); $[\alpha]^{31}_D$ = 52.0 (c = 0.06, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 (q, *J* = 7.1 Hz, 2H), 3.86 – 3.72 (m, 2H), 3.61 (t, *J* = 6.4 Hz, 1H), 2.87 (dd, *J* = 14.0, 6.9 Hz, 1H), 2.77 – 2.59 (m, 2H), 2.38 – 2.29 (m, 1H), 2.28 – 2.17 (m, 1H), 1.99 – 1.87 (m, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 210.25, 175.17, 68.88, 66.18, 61.40, 57.55, 49.44, 35.65, 31.29, 28.21, 14.18; IR (neat) 3426, 2928, 1716, 1435, 1369, 126, 1082, 1029, 865, 802 cm $^{-1}$, Calcd for $C_{11}H_{17}NO_4$ 227.1158, Found 227.1153.



17 18

C-N bond cleavage product **18**.To a solution of compound **17** (50 mg, 0.125 mmol, 1.0 equiv) in MeOH (3 mL) at 0 °C, MeONa (10.2 mg, 0.188 mmol, 1.5 equiv) was added. The system was stirred at 0 °C for 1 h before quenched with sat. aq. NH_4Cl. The mixture was then extracted with EtOAc (3×5 mL). The combined organic phases were washed with brine (2×1 mL), dried over Na_2SO_4 and concentrated. Purification by flash column chromatography afforded the C-N bond

cleavage product **18** as yellow oil (43.8 mg, 0.110 mmol, 88% yield). R_f = 0.3 (Ethyl Acetate: Petroleum Ether = 3:1); $[\alpha]^{31}_D$ = 40.3 (c = 0.13, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.00 (s, 2H), 5.04 (d, *J* = 7.2 Hz, 1H), 4.60 (d, *J* = 6.6 Hz, 1H), 3.93 (s, 6H), 3.74 (s, 3H), 3.27 (dd, *J* = 13.5, 5.3 Hz, 1H), 3.12 (dd, *J* = 13.6, 6.1 Hz, 1H), 1.51 – 1.34 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.75, 165.05, 153.88, 136.23, 133.66, 129.81, 128.44, 79.15, 53.33, 51.43, 51.35, 36.99, 27.20; IR (neat) 3341, 2961, 1723, 1604, 1520, 1442, 1327, 1246, 1167, 1056, 1003, 863, 758 cm^{-1}; HRMS (ESI) Calcd for $C_{19}H_{25}NO_8$ [*M*+Na^+] 418.1472, Found 418.1497.

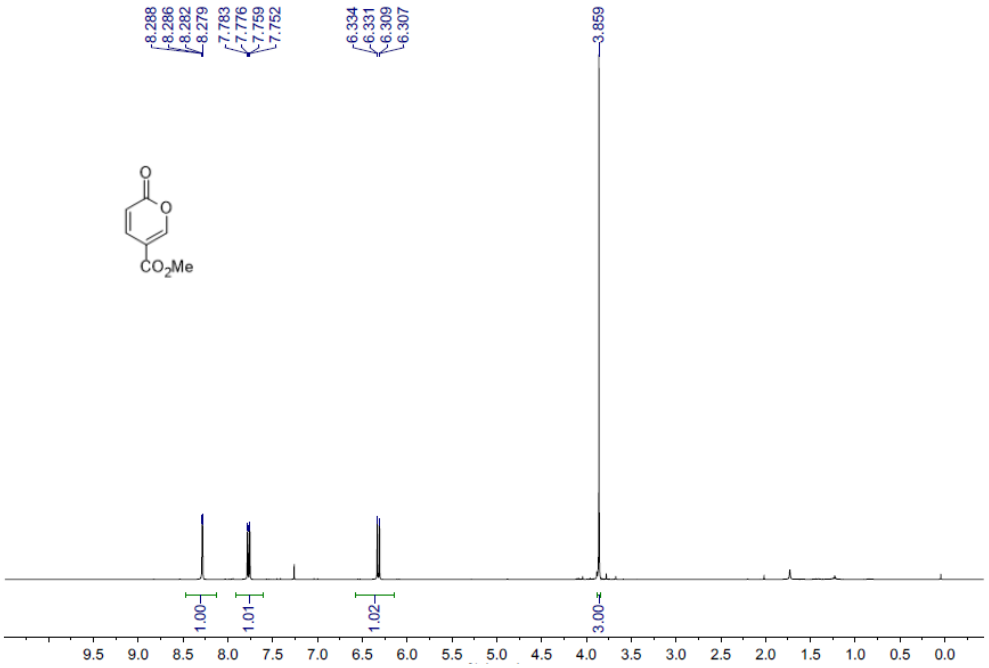


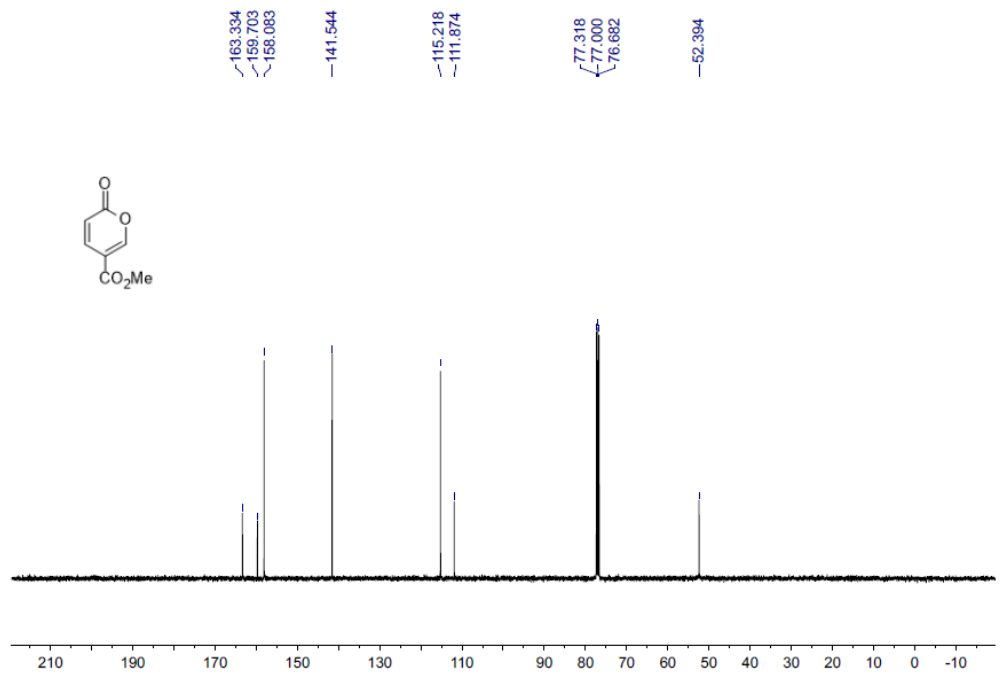
Compound **20** and **21**. To a solution of compound **19** (40 mg, 0.104 mmol, 1.0 equiv) in MeOH (1.5 mL) at -10 °C, MeONa (8.4 mg, 0.156 mmol, 1.5 equiv) was added. The system was stirred at -10 °C for 7 h before quenched with sat. aq. NH_4Cl. The mixture was then extracted with EtOAc (3×5 mL). The combined organic phases were washed with brine (2×1 mL), dried over Na_2SO_4 and concentrated. Purification by flash column chromatography afforded the compound **20** (yellow oil, 16.9 mg, 0.0406 mmol, 39% yield) and compound **21** (yellow oil, 17.5 mg, 0.0416 mmol, 40% yield).

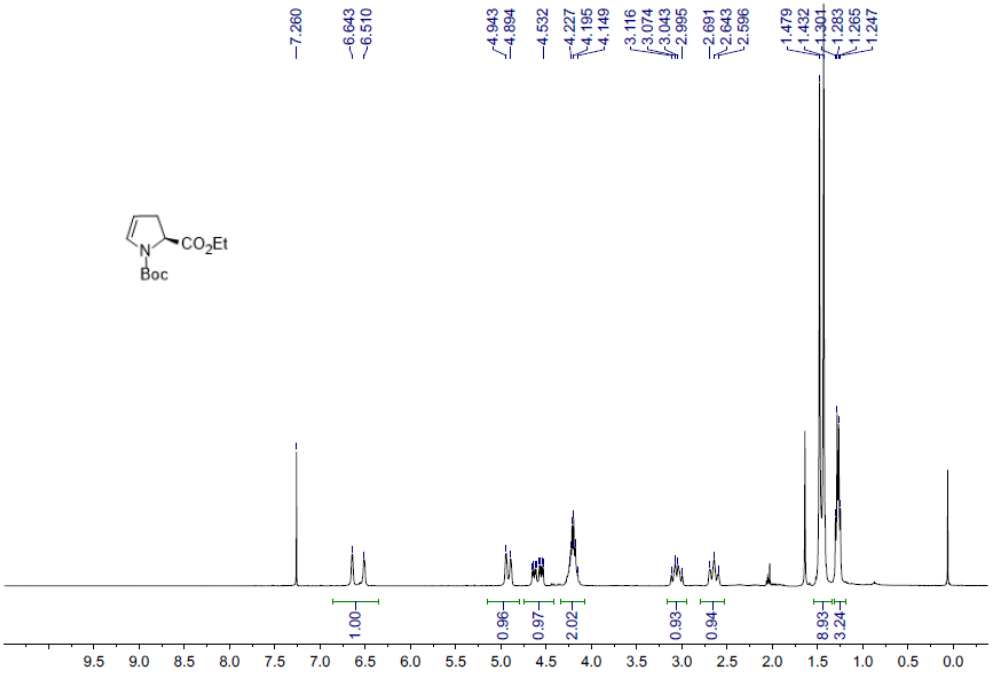
Compound **20**: R_f = 0.5 (Ethyl Acetate: Petroleum Ether = 3:1); $[\alpha]^{31}_D$ = -31.2 (c = 0.07, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.19 (m, 5H), 4.72 (d, *J* = 3.5 Hz, 1H), 4.22 – 3.89 (m, 4), 3.76 (s, 3H), 3.66 – 3.58 (m, 2H), 3.47 (d, *J* = 7.7 Hz, 1H), 3.36 (s, 3H), 3.26 (s, 1H), 3.05 (t, *J* = 4.1 Hz, 1H), 2.61 (dd, *J* = 18.4, 9.2 Hz, 1H), 2.14 (dt, *J* = 12.9, 8.4 Hz, 1H), 1.94 (dd, *J* = 12.9, 9.1 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.48, 170.42, 170.13, 137.65, 128.87, 128.30, 127.34, 75.84, 61.98, 60.43, 60.33, 60.24, 56.74, 52.75, 52.55, 50.87, 45.77, 37.20, 29.86, 14.26; IR (neat) 2927, 2858, 1727, 1454, 1382, 1247, 1200, 1085, 1026, 912, 737 cm^{-1}; HRMS (EI) Calcd for $C_{22}H_{27}NO_7$ 417.1788, Found 417.1785.

Compound **21**: R_f = 0.2 (Ethyl Acetate: Petroleum Ether = 3:1); $[\alpha]^{31}_D$ = -47.3 (c = 0.04, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 6.98 (d, *J* = 2.8 Hz, 1H), 4.97 (d, *J* = 3.5 Hz, 1H), 4.30 – 4.15 (m, 2H), 4.14 – 4.08 (m, 3H), 3.81 (d, *J* = 7.3 Hz, 1H), 3.78 (s, 3H), 3.49 – 3.38 (m, 1H), 3.33 (s, 3H), 2.93 (dd, *J* = 6.9, 3.5 Hz, 1H), 2.20 (dd, *J* = 13.1, 7.6 Hz, 1H), 1.97 (td, *J* = 13.2, 7.4 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.64, 170.82, 165.83, 141.43, 134.66, 131.41, 129.53, 129.13, 128.74, 71.87, 61.69, 61.30, 58.09, 57.31, 53.84, 52.10, 39.74, 36.97, 33.26, 14.16; IR (neat) 2932, 1726, 1452, 1388, 1267, 1197, 1153, 1087, 1026, 916, 737; HRMS (ESI) Calcd for $C_{22}H_{27}NO_7$ [*M*+H^+] 418.1866, Found 418.1839.

IV. ^{1}H and ^{13}C NMR Spectra of Compounds



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1.479
1.432
1.301
1.283
1.265
1.247
CO2Et
N
Boc
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0.97
2.02
0.93
0.94
8.93
3.24
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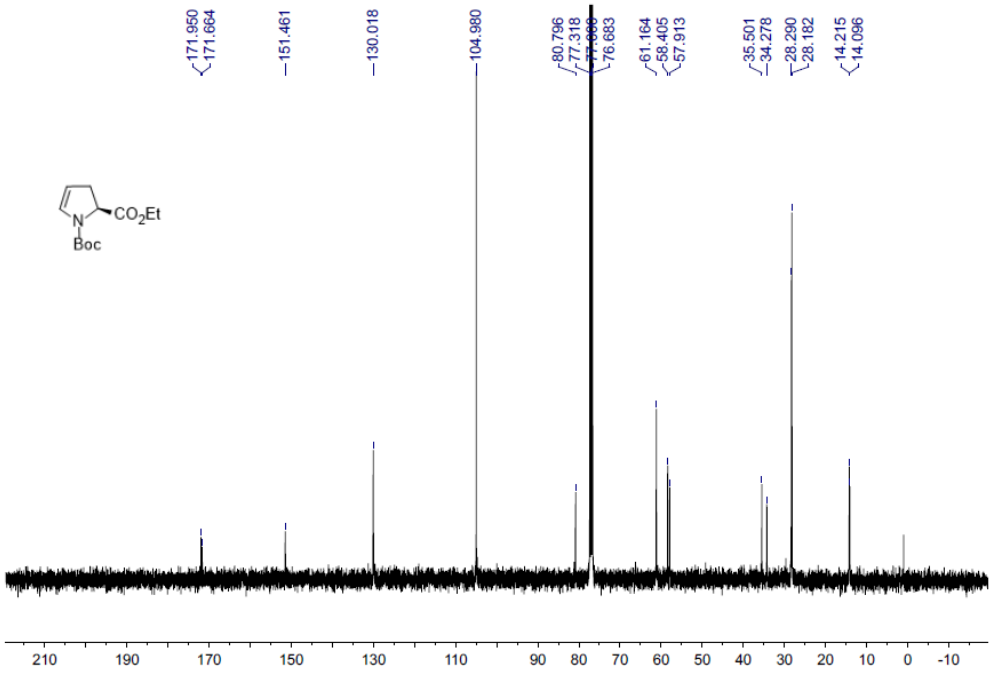
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Boc
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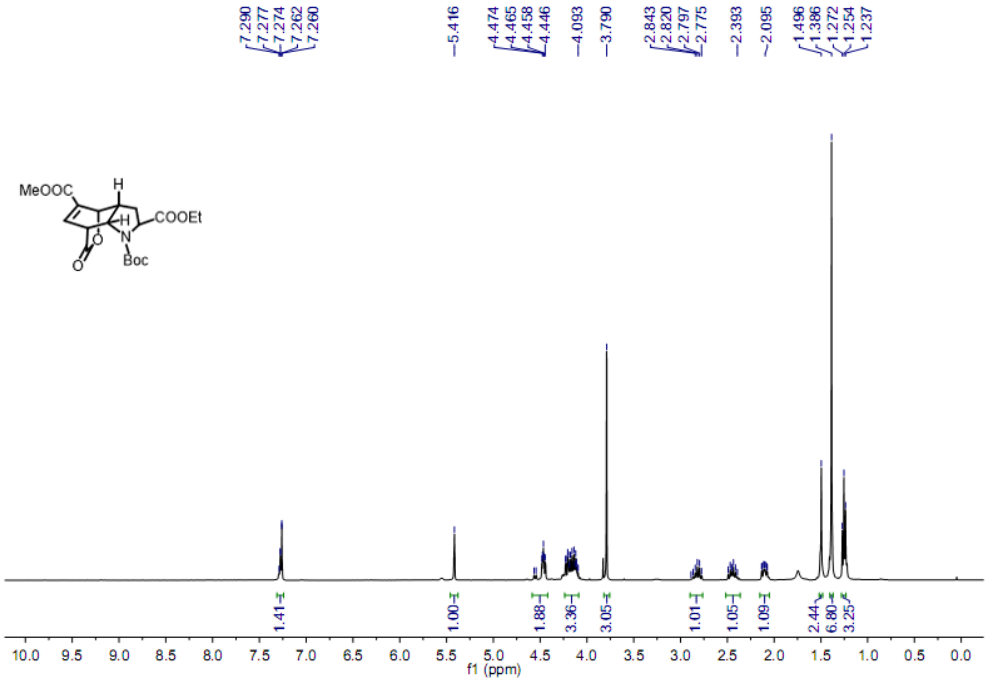
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2.095
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1.237
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COOEt
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3.05
1.01
1.05
1.09
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3.25
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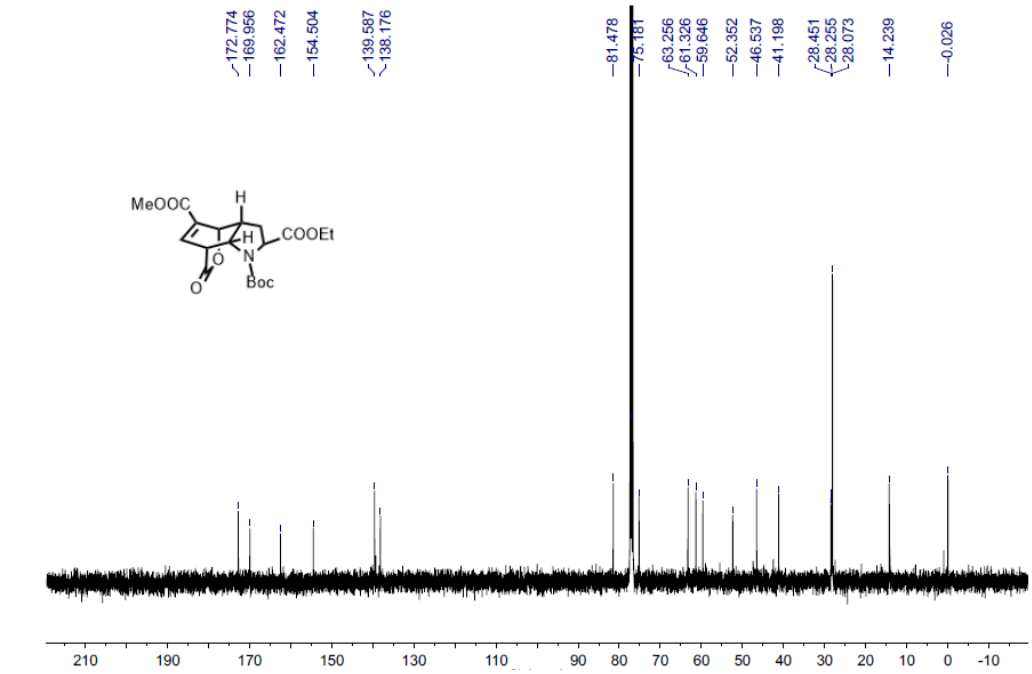
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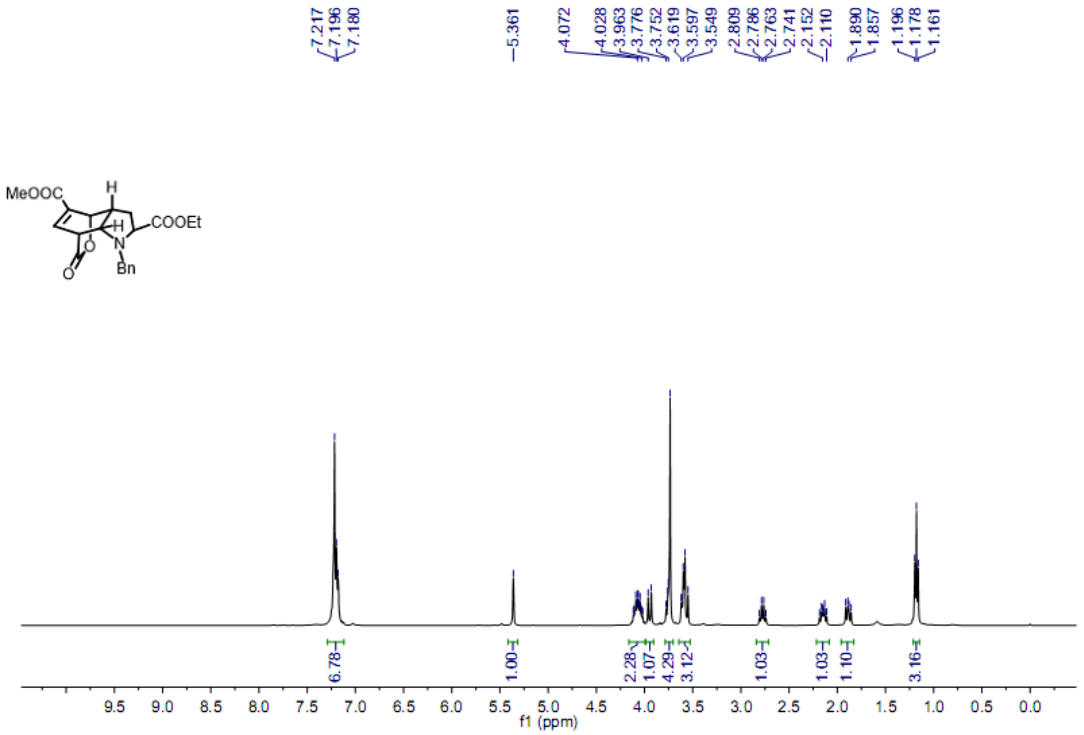
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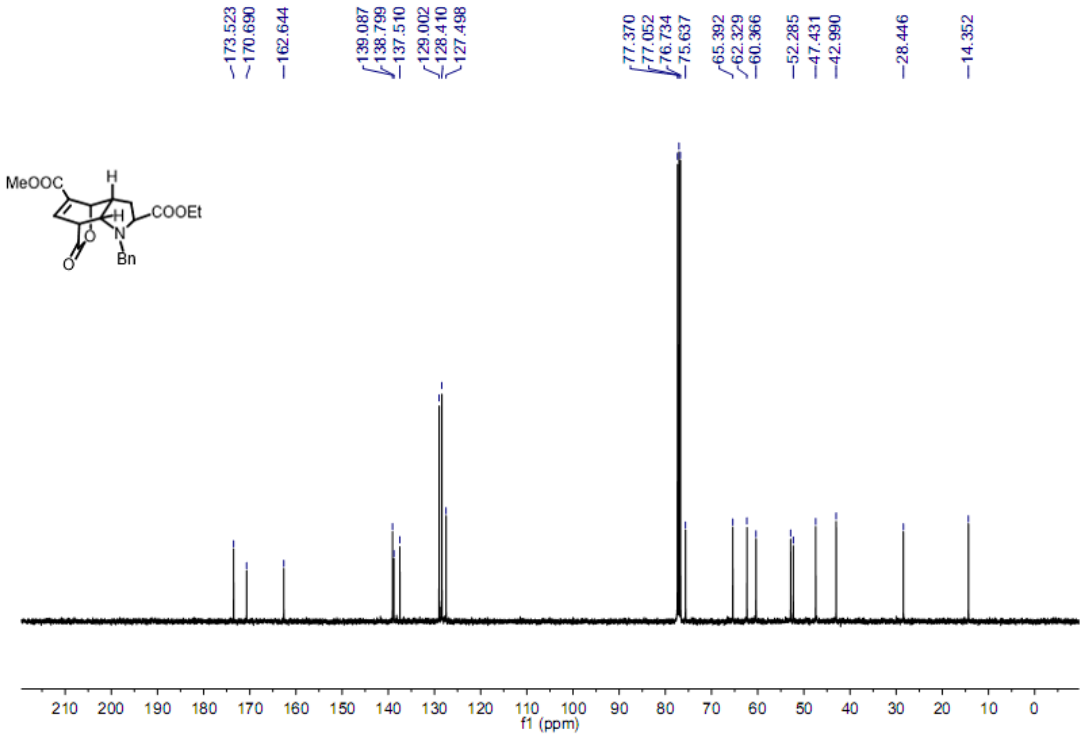
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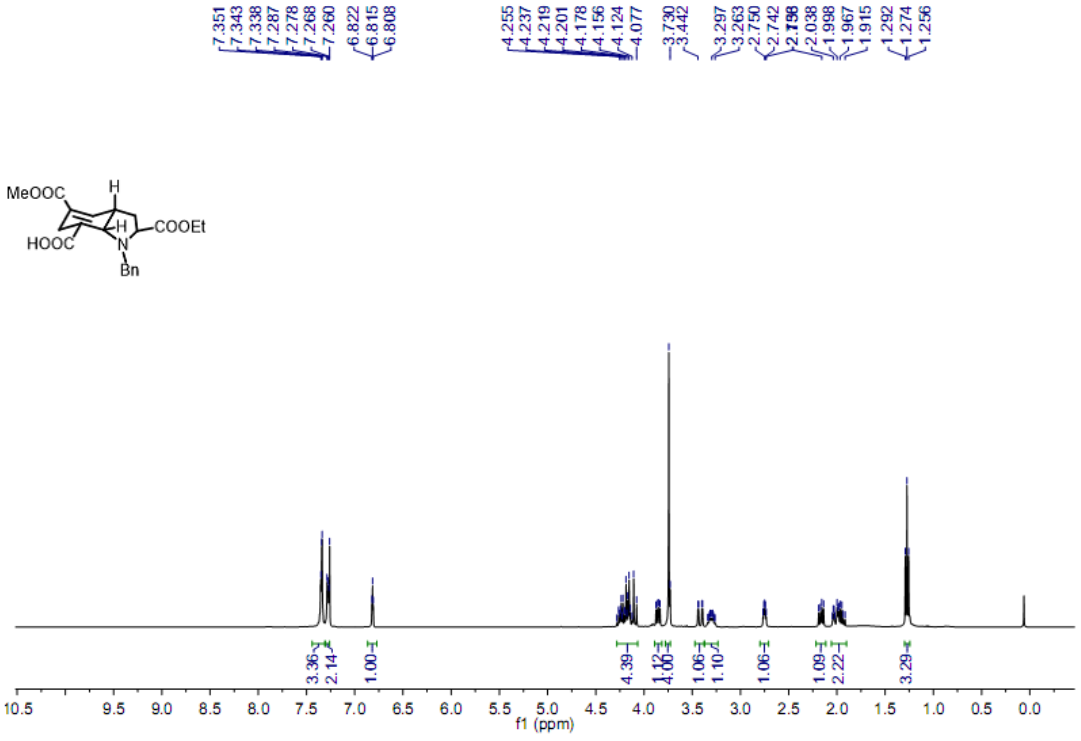
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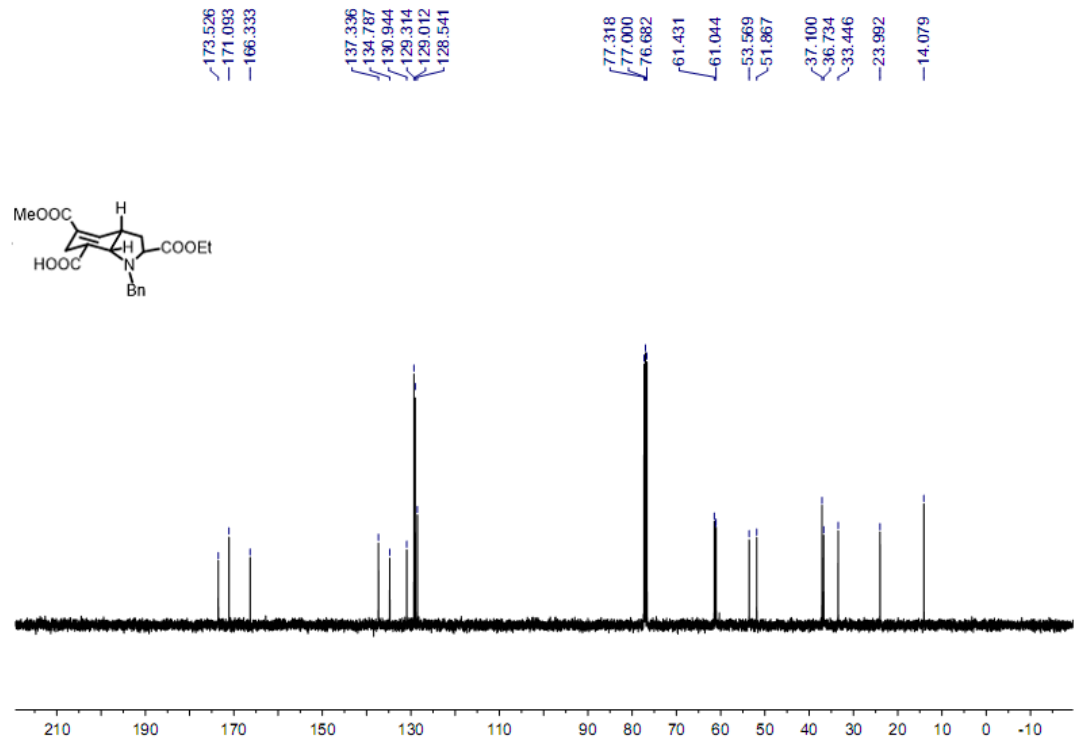
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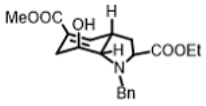
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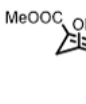
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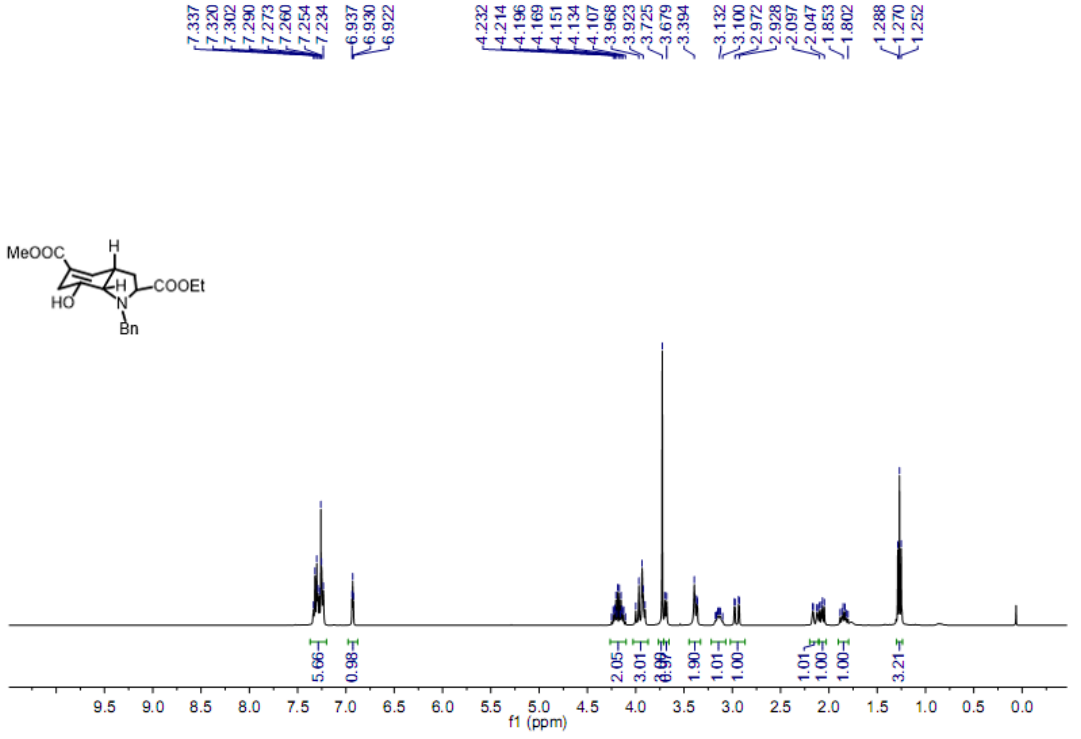
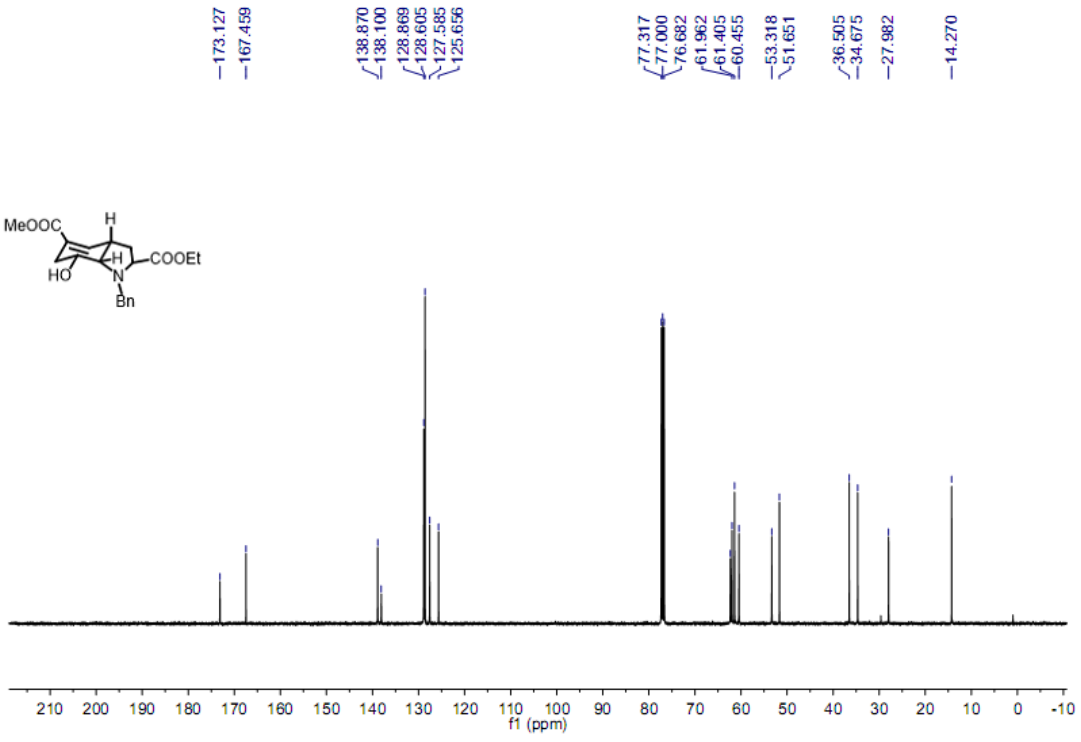
29.250
14.158


7.337
7.320
7.302
7.290
7.273
7.260
7.254
7.234
6.937
6.930
6.922
4.232
4.214
4.196
4.169
4.151
4.134
4.107
3.968
3.923
3.725
3.679
3.394
3.132
3.100
2.972
2.928
2.097
2.047
1.853
1.802
1.288
1.270
1.252
MeOOC
H
HO
H
N
COOEt
Bn
5.66
0.98
2.05
3.01
1.90
1.01
1.00
1.01
1.00
1.00
3.21
f1 (ppm)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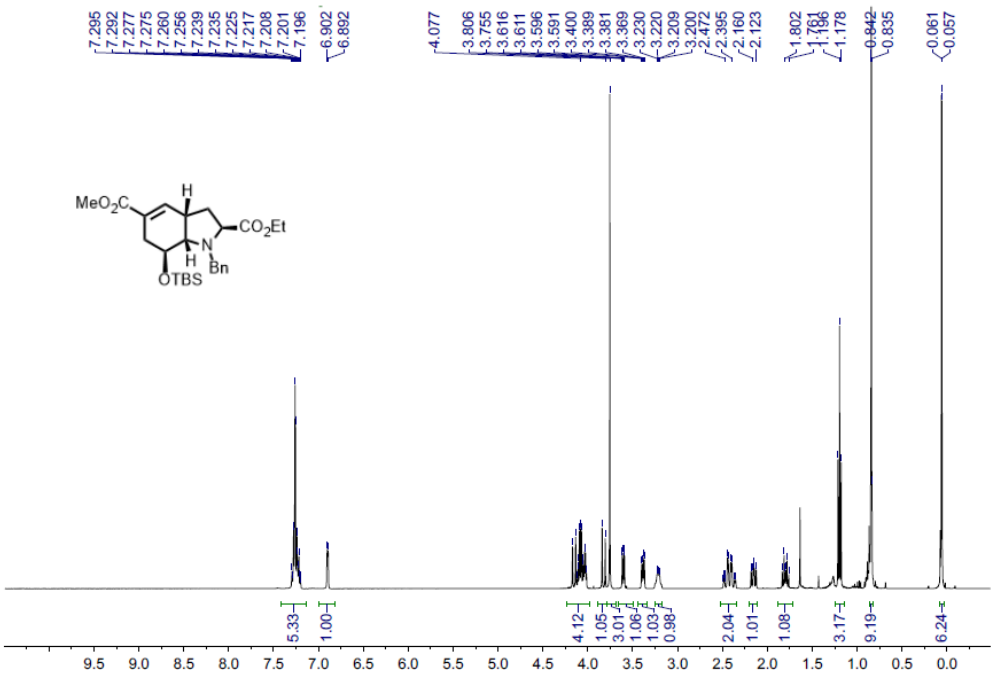
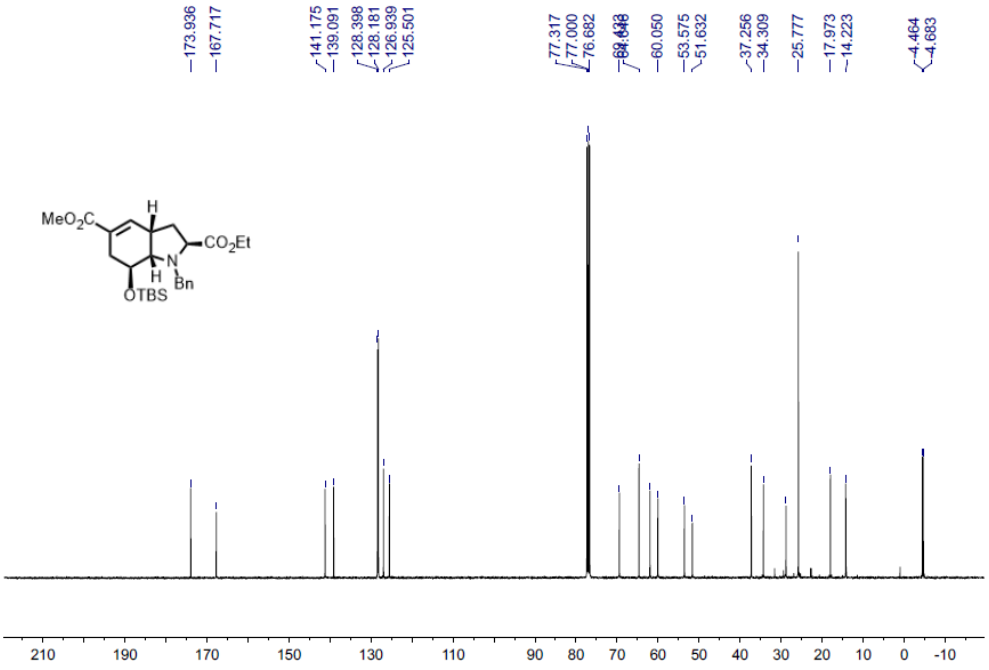
167.459
138.870
138.100
128.869
128.605
127.585
125.656
77.317
77.000
76.682
61.962
61.405
60.455
53.318
51.651
36.505
34.675
27.982
14.270
MeOOC
H
HO
H
N
COOEt
Bn
f1 (ppm)


7.295
7.292
7.277
7.275
7.260
7.256
7.239
7.235
7.225
7.217
7.208
7.201
7.196
6.902
6.892
4.077
3.806
3.755
3.616
3.611
3.596
3.591
3.400
3.389
3.381
3.369
3.230
3.220
3.209
3.200
2.472
2.395
2.160
2.123
1.802
1.781
1.196
1.178
0.842
0.835
0.061
0.057
MeO2C
CO2Et
H
N
H
Bn
OTBS
5.33
1.00
4.12
1.05
3.01
1.06
1.03
0.98
2.04
1.01
1.08
3.17
9.19
6.24
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0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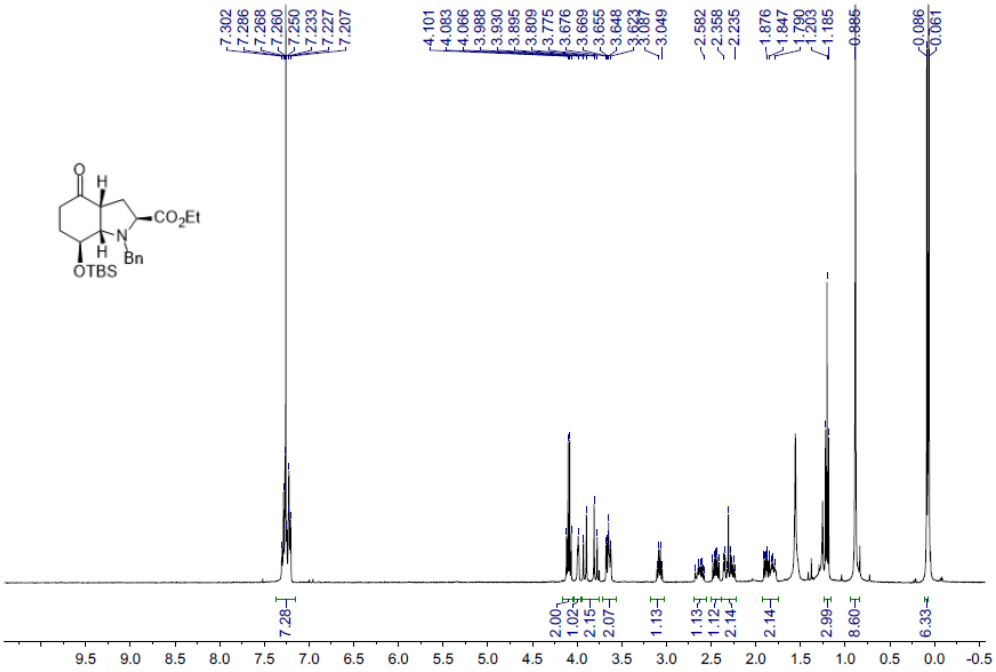
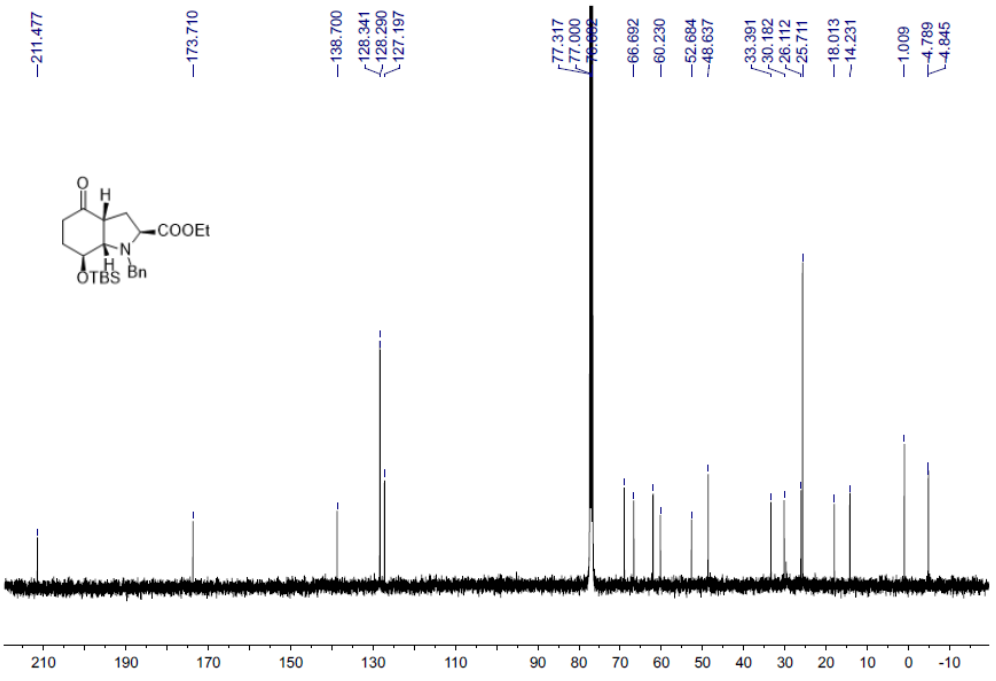
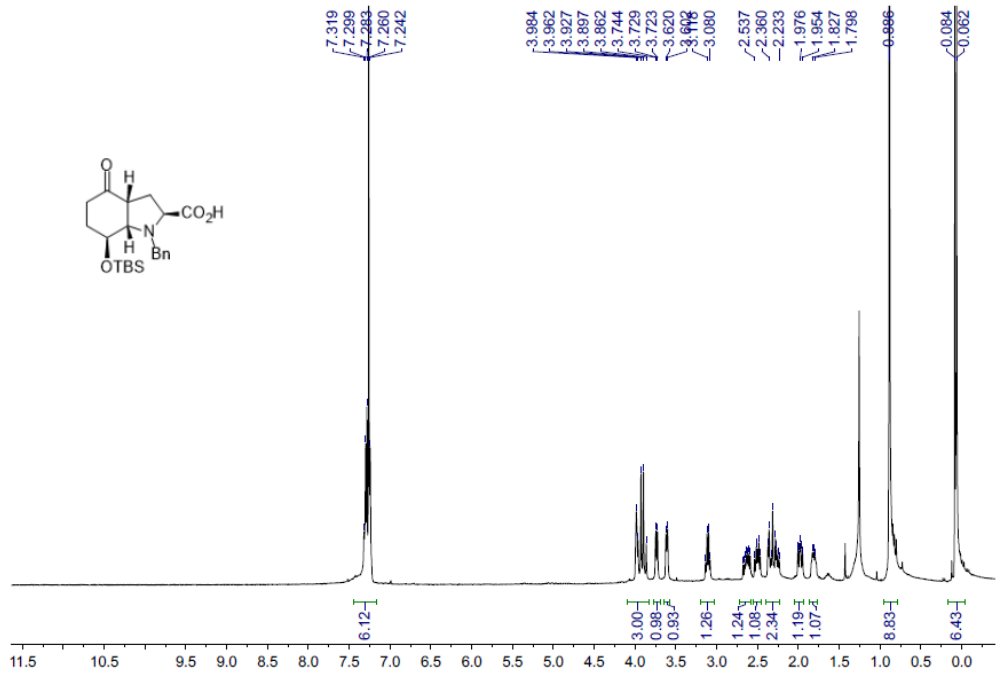
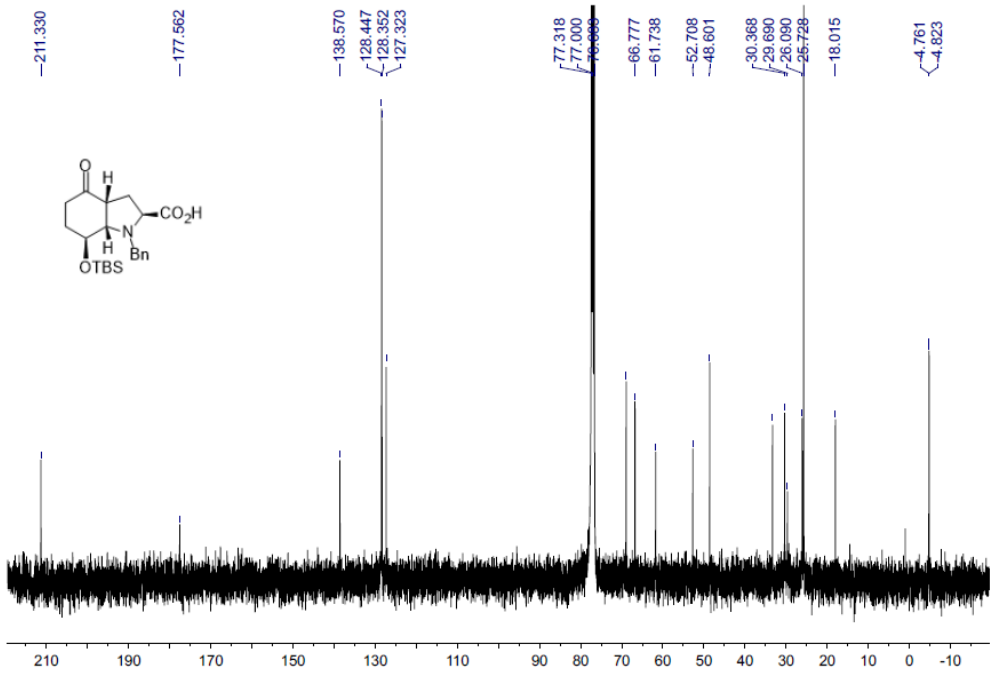
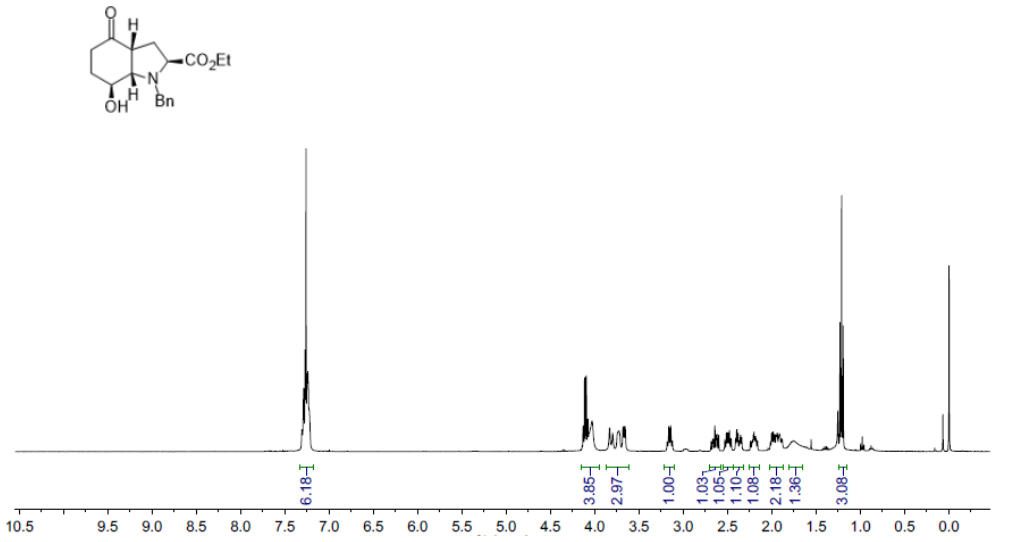
167.717
141.175
139.091
128.398
128.181
126.939
125.501
77.317
77.000
76.682
60.050
53.575
51.632
37.256
34.309
25.777
17.973
14.223
4.464
4.683
MeO2C
CO2Et
H
N
H
Bn
OTBS
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10

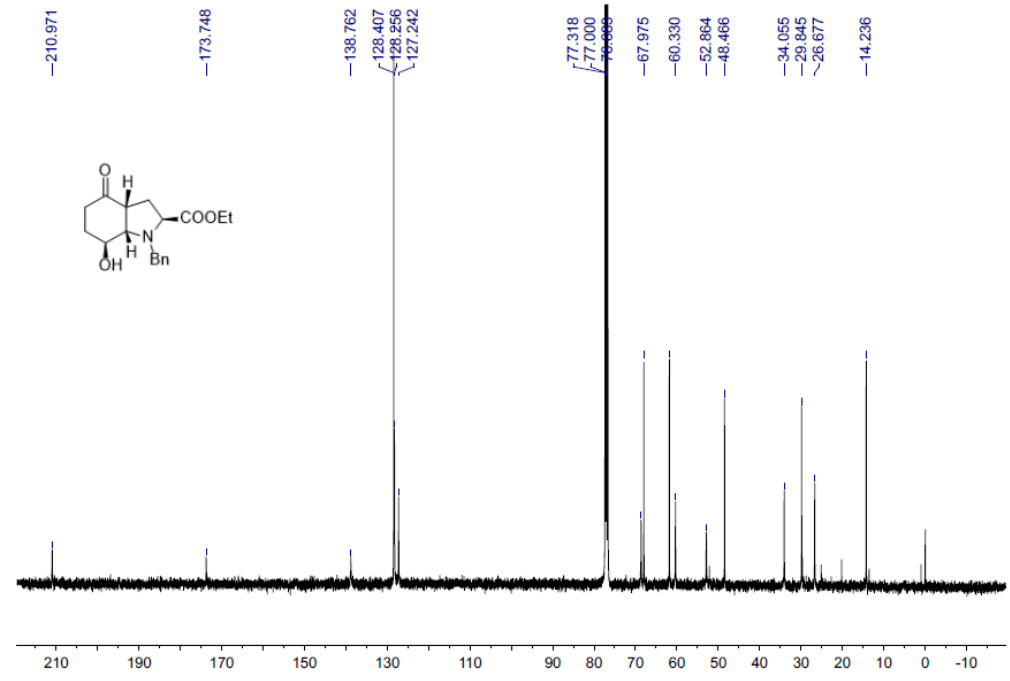

7.302
7.286
7.268
7.260
7.250
7.233
7.227
7.207
4.101
4.083
4.066
3.988
3.930
3.895
3.809
3.775
3.676
3.669
3.655
3.648
3.623
3.049
2.582
2.358
2.235
1.876
1.847
1.790
1.203
1.185
0.885
0.086
0.061
CO2Et
N
Bn
H
OTBS
7.28
2.00
1.02
2.15
2.07
1.13
1.13
1.12
2.14
2.14
2.99
8.60
6.33

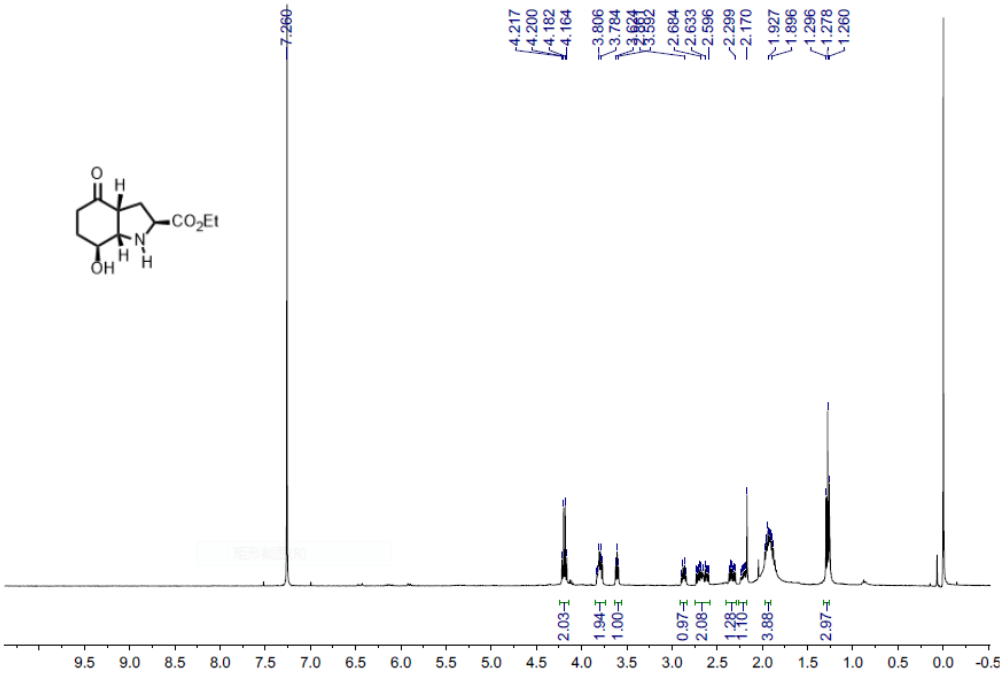

211.477
173.710
138.700
128.341
128.290
127.197
77.317
77.000
66.692
60.230
52.684
48.637
33.391
30.182
26.112
25.711
18.013
14.231
1.009
-4.789
-4.845
COOEt
N
Bn
H
OTBS

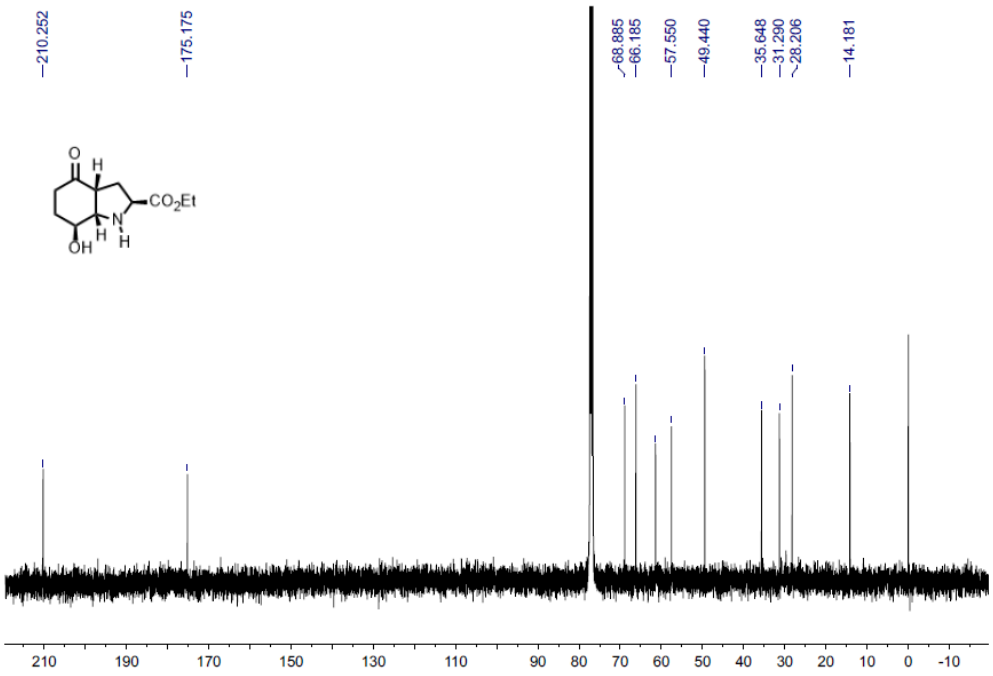

7.319
7.299
7.283
7.260
7.242
3.984
3.962
3.927
3.897
3.862
3.744
3.729
3.723
3.620
3.080
2.537
2.360
2.233
1.976
1.954
1.827
1.798
0.886
0.084
0.062
CO2H
N
H
Bn
OTBS
6.12
3.00
0.98
0.93
1.26
1.24
1.08
2.34
1.19
1.07
8.83
6.43

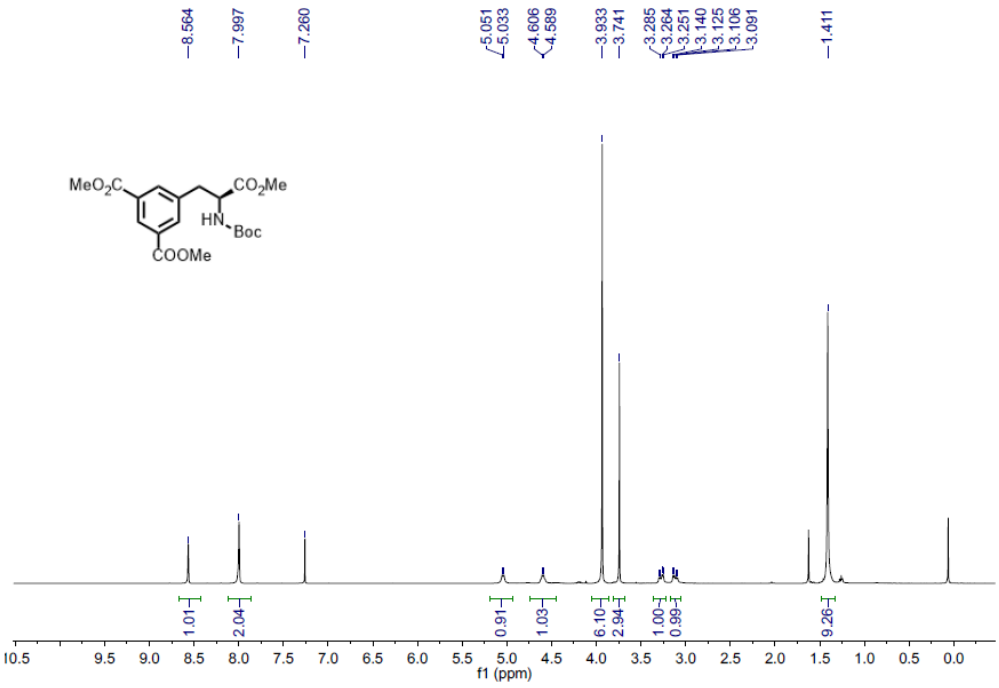

211.330
177.562
138.570
128.447
128.352
127.323
77.318
77.000
66.777
61.738
52.708
48.601
30.368
29.690
26.090
25.728
18.015
4.761
4.823
CO2H
N
H
Bn
OTBS

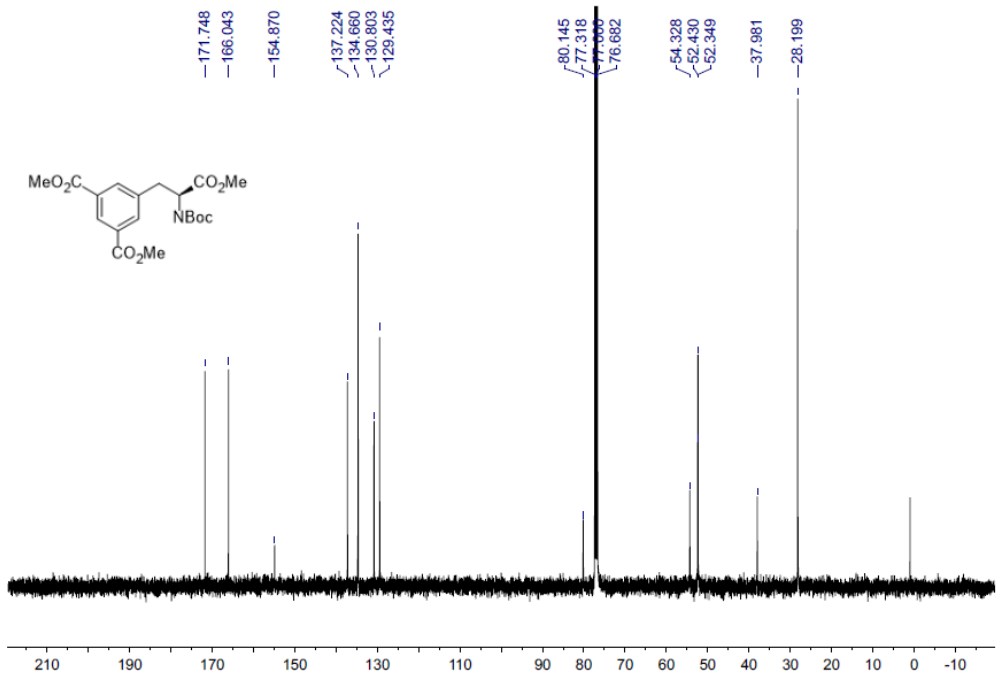

O
H
CO2Et
N
Bn
H
OH
6.18
3.85
2.97
1.00
1.03
1.05
1.10
1.08
2.18
1.36
3.08
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

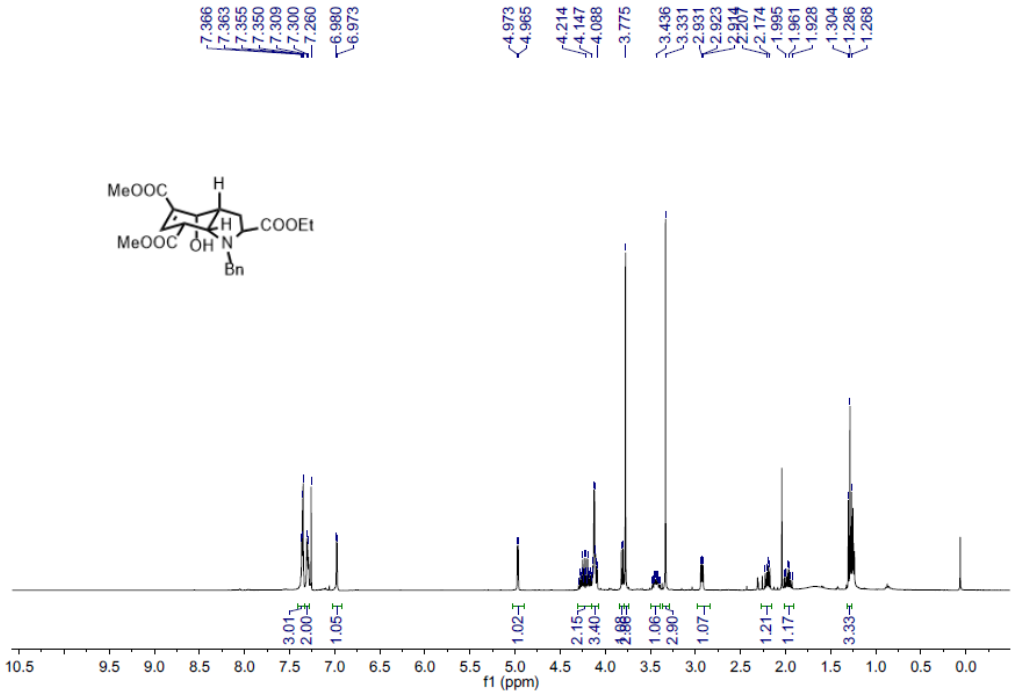

210.971
173.748
138.762
128.407
128.256
127.242
77.318
77.000
76.683
67.975
60.330
52.864
48.466
34.055
29.845
26.677
14.236
O
H
COOEt
N
Bn
H
OH
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10

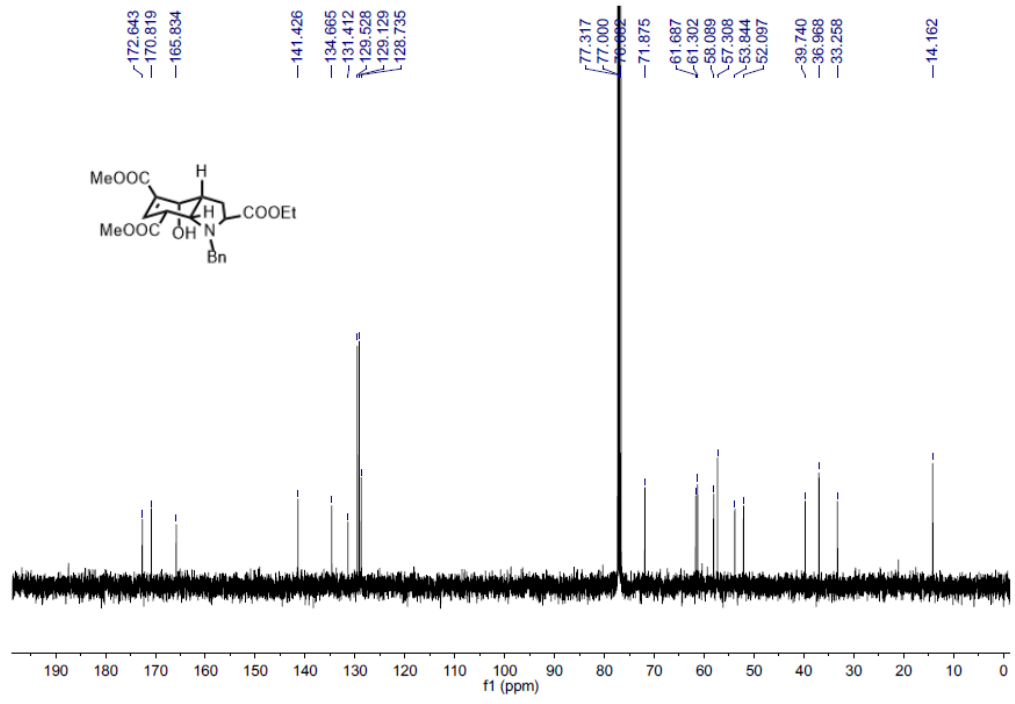

7.260
4.217
4.200
4.182
4.164
3.806
3.784
2.684
2.633
2.596
2.299
2.170
1.927
1.896
1.296
1.278
1.260
2.03
1.94
1.00
0.97
2.08
1.28
1.10
3.88
2.97
CO2Et
OH

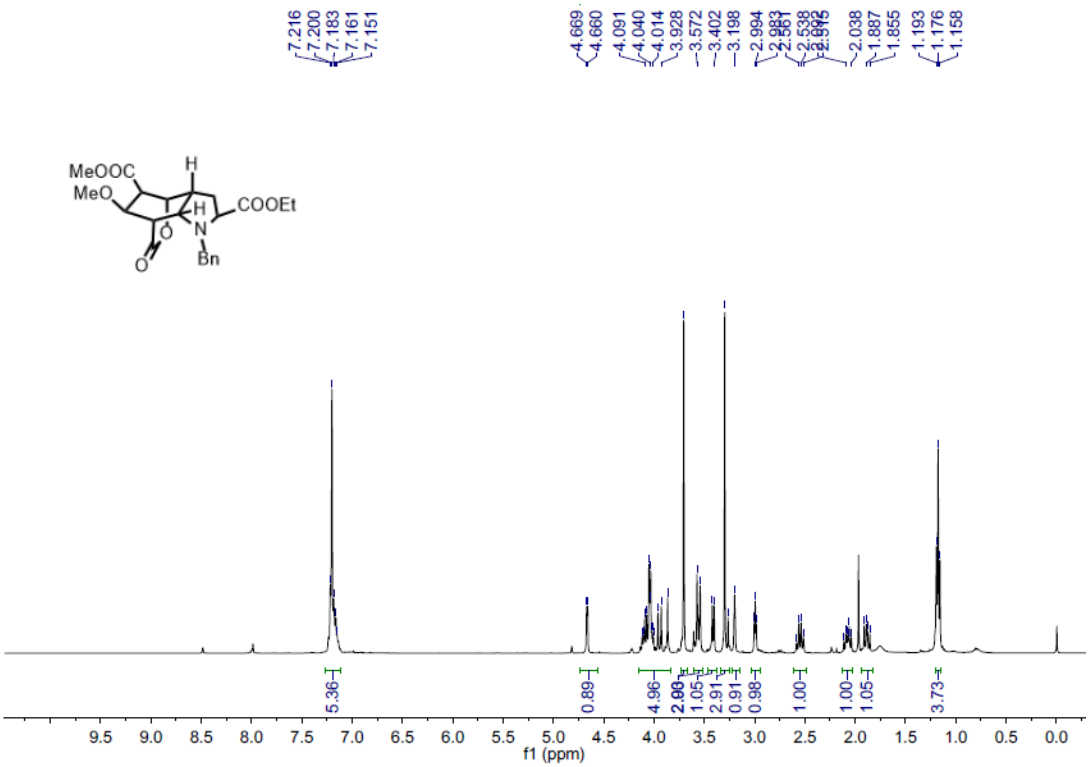

210.252
175.175
68.885
66.185
57.550
49.440
35.648
31.290
28.206
14.181
CO2Et
OH

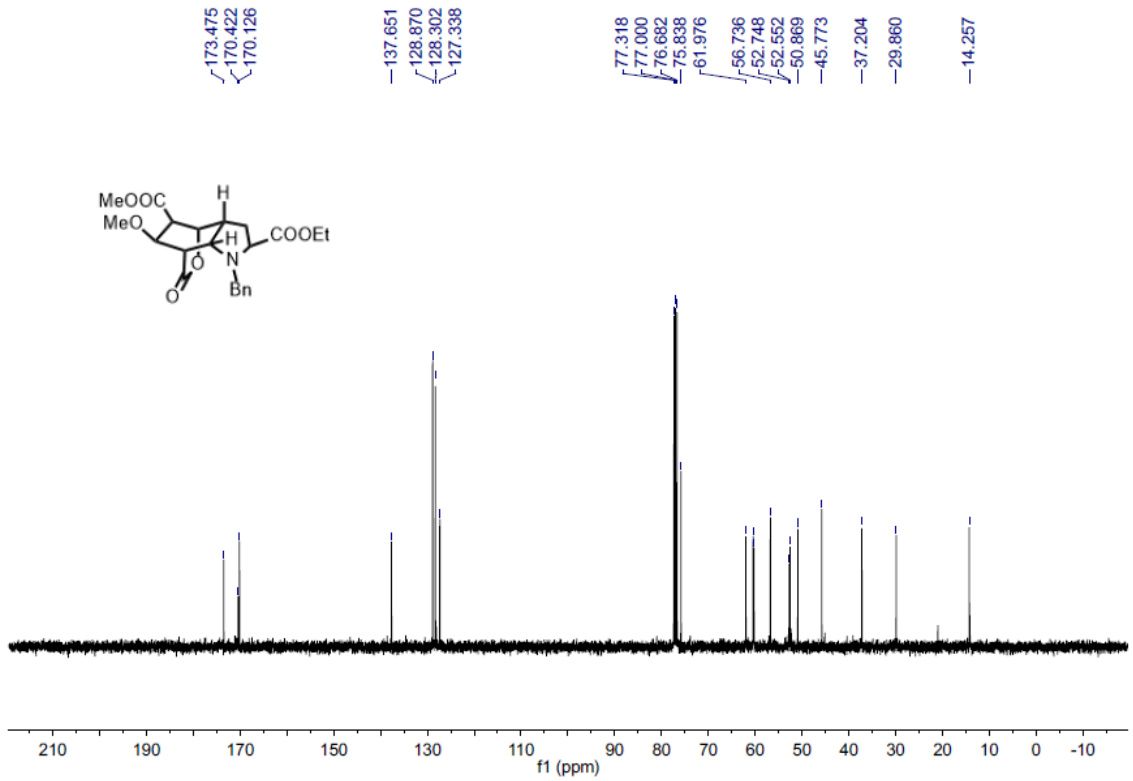

8.564
7.997
7.260
5.051
5.033
4.606
4.589
3.933
3.741
3.285
3.264
3.251
3.140
3.125
3.106
3.091
1.411
MeO2C
CO2Me
HN
Boc
COOMe
1.01
2.04
0.91
1.03
6.10
2.94
1.00
0.99
9.26
f1 (ppm)


171.748
166.043
154.870
137.224
134.660
130.803
129.435
80.145
77.318
77.000
76.682
54.328
52.430
52.349
37.981
28.199
MeO2C
CO2Me
NBoc
CO2Me

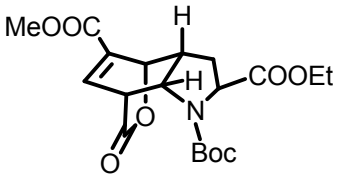

7.366
7.363
7.355
7.350
7.309
7.300
7.260
6.980
6.973
4.973
4.965
4.214
4.147
4.088
3.775
3.436
3.331
2.931
2.923
2.174
1.995
1.961
1.928
1.304
1.286
1.268
MeOOC
H
COOEt
MeOOC
OH
N
Bn
3.01
2.00
1.05
1.02
2.15
3.40
1.06
2.90
1.07
1.21
1.17
3.33
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


172.643
170.819
165.834
141.426
134.665
131.412
129.528
129.129
128.735
77.317
77.000
76.682
71.875
61.687
61.302
58.089
57.308
53.844
52.097
39.740
36.968
33.258
14.162
MeOOC
H
COOEt
MeOOC
OH
N
Bn
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeOOC
MeO
H
H
N
Bn
COOEt
O
O
7.216
7.200
7.183
7.161
7.151
4.669
4.660
4.091
4.040
4.014
3.928
3.572
3.402
3.198
2.994
2.983
2.561
2.538
2.038
1.887
1.855
1.193
1.176
1.158
5.36
0.89
4.96
2.00
1.05
2.91
0.91
0.98
1.00
1.00
1.05
3.73
f1 (ppm)


MeOOC
MeO
H
H
N
Bn
COOEt
O
O
173.475
170.422
170.126
137.651
128.870
128.302
127.338
77.318
77.000
76.682
75.838
61.976
56.736
52.748
52.552
50.869
45.773
37.204
29.860
14.257
f1 (ppm)

V. X-ray Crystal Data



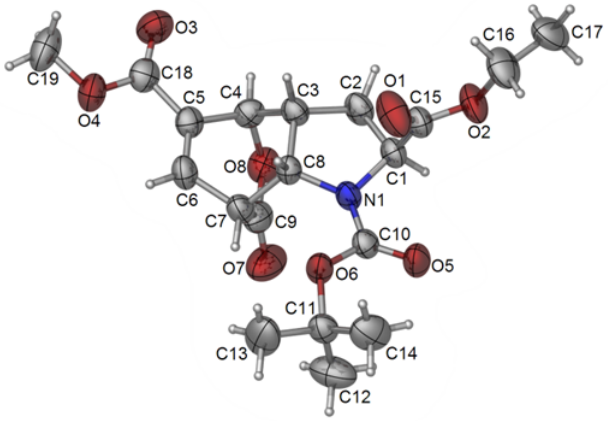


Table 1. Crystal Data and Structure Refinement for Compound **17**
CCDC-99583

Compound	**17**
Empirical formula	$C_{19}H_{25}NO_8$
Formula weight	395.40
Crystal system	Orthorhombic
Space group	*P2(1)2(1)2(1)*
a, Å	9.7254 (9)
b, Å	9.9683 (7)
c, Å	20.3950 (19)
α, °	90
β, °	90
γ, °	90
V, Å^3	1977.2(3)
Z	4
ρ_{calcd} (mg cm^{-3})	1.328
μ, mm^{-1}	0.104
F(000)	840
θ range (deg)	2.27 to 25.01
R_{int}	0.0383
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0367$, $wR_2 = 0.0892$
R indices (all data)	$R_1 = 0.0448$, $wR_2 = 0.0949$

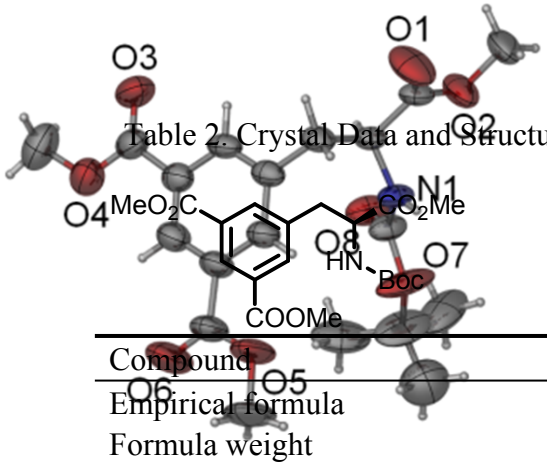


Table 2. Crystal Data and Structure Refinement for Compound **18**
CCDC-99586

Compound	18
Empirical formula	$C_{19}H_{25}NO_8$
Formula weight	395.40
Crystal system	triclinic
Space group	*P1*
a, Å	5.0916 (7)
b, Å	9.9171 (13)
c, Å	10.67050 (15)
α, °	81.115(4)
β, °	77.646(5)
γ, °	87.407(4)
V, Å^3	519.96(12)
Z	1
ρ_{calcd} (mg cm^{-3})	1.263
μ, mm^{-1}	0.099
F(000)	210
θ range (deg)	1.98 to 25.01
R_{int}	0.0319
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0763$, $wR_2 = 0.2046$
R indices (all data)	$R_1 = 0.0864$, $wR_2 = 0.2202$

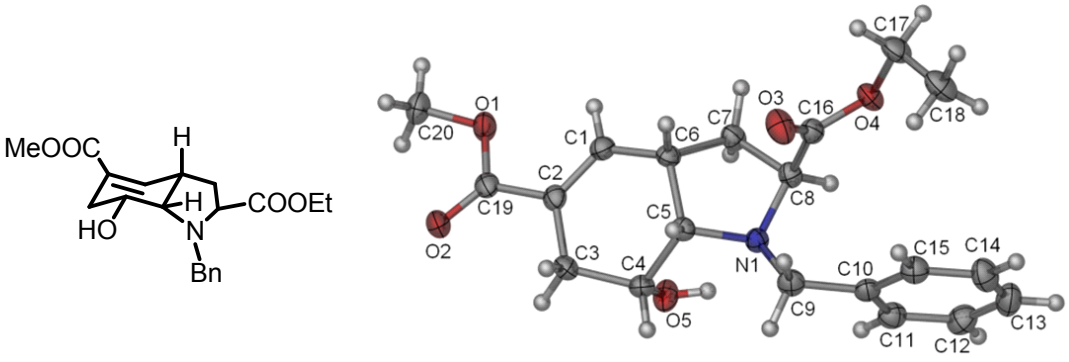


Table 3. Crystal Data and Structure Refinement for Compound **25**
CCDC-99587

Compound	25
Empirical formula	$C_{10}H_{25}NO_5$
Formula weight	359.41
Crystal system	Monoclinic
Space group	*P1*
a, Å	9.1672 (5)
b, Å	7.7813 (5)
c, Å	12.9980 (8)
α, °	90
β, °	90.487(2)
γ, °	90
V, Å^3	914.50(10)
Z	2
ρ_{calcd} (mg cm^{-3})	1.305
μ, mm^{-1}	0.094
F(000)	384
θ range (deg)	2.53 to 25.01
R_{int}	0.0188
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0247$, $wR_2 = 0.0648$
R indices (all data)	$R_1 = 0.0256$, $wR_2 = 0.0656$

All these data can be obtained free of charge from Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/ci.