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Synthesis of Amino Acids and Peptides with Bulky Side Chains via Ligand-Enabled Carboxylate-Directed γ-C(sp^3)−H Arylation

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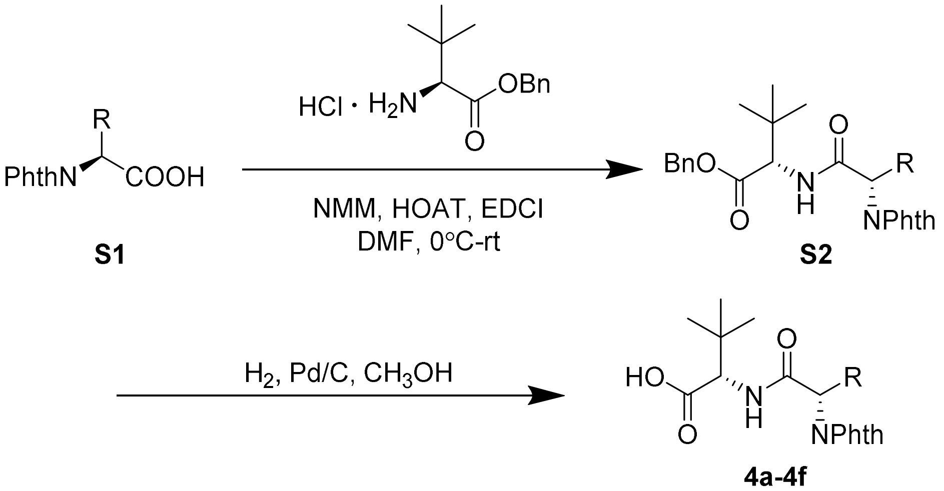
1. General Information

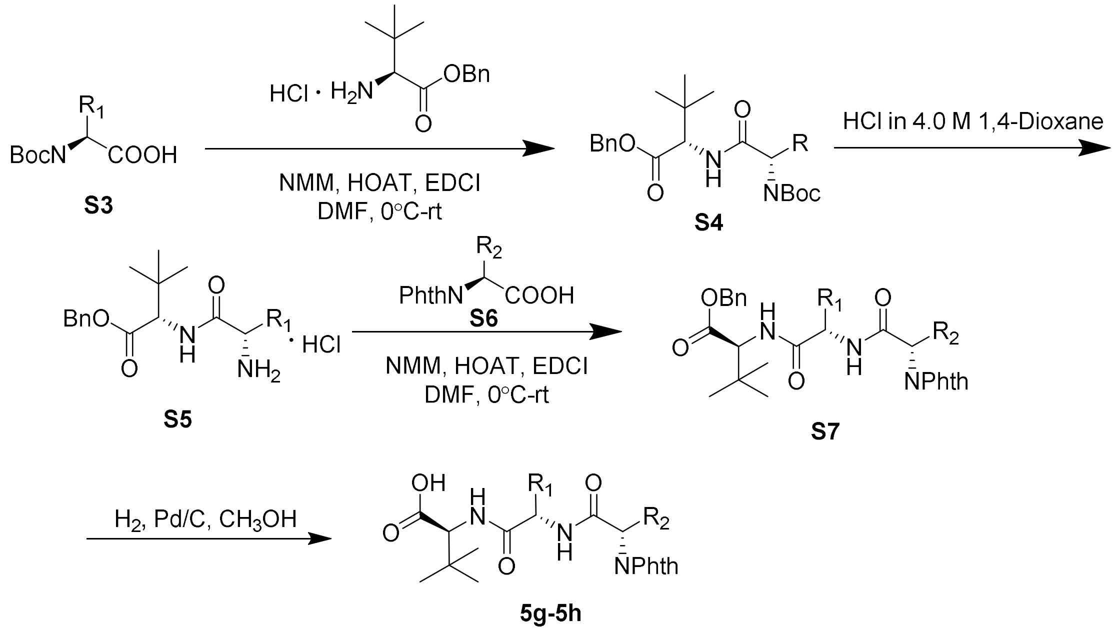
$Pd(OAc)_2$ (Laajoo), K_2CO_3 (Aladdin) were purchased from above mentioned company and used without additional purification. Other chemical reagents were commercially available and directly used without any further purification. NMR spectra were recorded on a Bruker Avance operating for ^1H NMR at 400 MHz, ^{13}C NMR at 100 MHz, using TMS as internal standard. The peaks were internally referenced to TMS (0.00 ppm) or residual undeuterated solvent signal (77.16 ppm for ^{13}C NMR). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, b = broad. Mass spectroscopy data of the products were collected on an HRMS-TOF instrumentor a low-resolution MS instrument using EI ionization. High pressure liquid chromatography (HPLC) analyses were performed on an Agilent 1100 instrument using a chiral stationary phase column (Daicel Co. CHIRALPAK). The chiral HPLC methods were calibrated with the corresponding racemic mixtures.

2. Experimental Section

2.1 General procedure for the preparation of short peptides

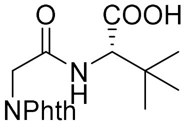


To a solution of L-*tert*-leucine benzyl ester hydrochloride (1.288 g, 5 mmol) and 4-methylmorpholine (NMM, 0.94 mL, 0.86 g, 8.5 mmol) in DMF (30 mL) was added **S1** (5 mmol) and 1-Hydroxy-7-azabenzotriazole (HOAt, O.75 g, 5.5 mmol). The mixture was cooled in an ice bath and subsequently 1-ethyl-3-(3- (dimethylamino)propyl)carbodiimide hydrochloride (EDCI, 1.15 g, 6 mmol) was added in one portion. After 1.5 h at 0 °C and 6 h at room temperature, the mixture waspartitioned between H_2O (200 mL) and EtOAc (30 mL). The aqueous phase wasextracted with EtOAc (30 mL X 3). The organic phase was washed successively with H_2O, 0.5 N HCl solution, saturated aqueous $NaHCO_3$ solution and brine, then it was dried over anhydrous Na_2SO_4, filtered, and the residue was purified by silica gel column chromatography, give the ester as a white solid, the benzyl ester was added to a hydrogenator in which palladium on activated carbon (10% Pd/C), MeOH (30 mL). After filled with hydrogen gas, the suspension was stirred overnight at room temperature. The reaction mixture was then filtered through a pad of Celite to remove the catalyst, and the solvents were removed under vacuum. The resulting residue was was purified by silica gel column chromatography[1].

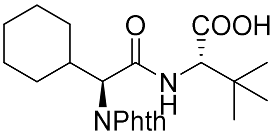


To a solution of L-*tert*-leucine benzyl ester hydrochloride (1.288 g, 5 mmol) and 4-methylmorpholine (NMM, 0.94 mL, 0.86 g, 8.5 mmol) in DMF (30 mL) was added **S3** (5 mmol) and 1-Hydroxy-7-azabenzotriazole (HOAt, O.75 g, 5.5 mmol). The mixture was cooled in an ice bath and subsequently 1-ethyl-3-(3- (dimethylamino)propyl)carbodiimide hydrochloride (EDCI, 1.15 g, 6 mmol) was added in one portion. After 1.5 h at 0 °C and 6 h at room temperature, the mixture waspartitioned between H_2O (200 mL) and EtOAc (30 mL). The aqueous phase wasextracted with EtOAc (30 mL X 3). The organic phase was washed successively with H_2O, 0.5 N HCl solution, saturated aqueous $NaHCO_3$ solution and brine, then it was dried over anhydrous Na_2SO_4, filtered, and the residue was purified by silica gel column chromatography, give the ester as a white solid **S4**, Adding **S4** to the round bottom flask in 10 mL HCl in 4 M 1.4-Dioxane, stirring at room temperature 4 h. the solvents were removed under vacuum to obtain **S5**.

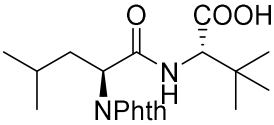
S5 and 4-methylmorpholine (NMM, 0.94 mL,) in DMF (30 mL) was added **S6** and 1-hydroxy-7-azabenzotriazole (HOAt,). The mixture was cooled in an ice bath and subsequently 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride (EDCI) was added in one portion. After 1.5 h at 0 °C and 6 h at room temperature, the mixture waspartitioned between H_2O (200 mL) and EtOAc (30 mL). The aqueous phase was extracted with EtOAc (30 mL X 3). The organic phase was washed successively with H_2O, 0.5 N HCl solution, saturated aqueous $NaHCO_3$ solution and brine, then it was dried over anhydrous Na_2SO_4, filtered, and the residue was purified by silica gel column chromatography, give the ester as a white solid **S7**, the benzyl ester was added to a hydrogenator in which palladium on activated carbon (10% Pd/C), MeOH (30 mL). After filled with hydrogen gas, the suspension was stirred overnight at room temperature. The reaction mixture was then filtered through a pad of Celite to remove the catalyst, and the solvents were removed under vacuum. The resulting residue was purified by silica gel column chromatography[1].



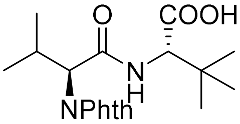
R = hydrogen, Compound **4a**, a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.84 (m, 2H), 7.71 (m, 2H), 6.96 (d, *J* = 9.3 Hz, 1H), 4.52 – 4.39 (m, 3H), 0.98 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 174.30, 168.08, 166.70, 134.41, 132.04, 123.78, 60.59, 40.76, 34.93, 26.65. **HRMS** (EI-TOF) calcd for $C_{16}H_{18}N_2O_5$ (M-H$^+$): 317.1143, found: 317.1140.



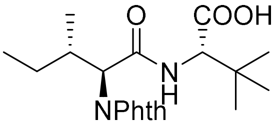
R = cyclohexyl, Compound **4b**, a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.81 (m, 2H), 7.79 – 7.73 (m, 2H), 7.70 (d, *J* = 9.0 Hz, 1H), 4.52 (d, *J* = 11.4 Hz, 1H), 4.32 (d, *J* = 8.9 Hz, 1H), 2.56 – 2.42 (m, 1H), 1.89 – 1.72 (m, 2H), 1.64 (d, *J* = 11.2 Hz, 2H), 1.45 (d, *J* = 12.8 Hz, 1H), 1.32 – 1.07 (m, 4H), 1.01 (s, 9H), 0.91 – 0.79 (m, 1H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 175.66 , 169.16 , 168.73 , 134.62 , 131.32 , 123.92 , 62.23 , 60.59 , 36.69 , 34.32 , 30.36 , 29.59 , 26.78 , 26.06 , 25.48 , 25.41 . **HRMS** (EI-TOF) calcd for $C_{22}H_{28}N_2O_5$ (M-H$^+$): 399.1925, found: 399.1927.



R = isobutyl, Compound **4c**, a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 – 7.77 (m, 2H), 7.82 – 7.65 (m, 2H), 6.92 (d, *J* = 9.0 Hz, 1H), 4.93 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.40 (d, *J* = 9.0 Hz, 1H), 2.44 – 2.25 (m, 1H), 1.93 – 1.79 (m, 1H), 1.52 – 1.36 (m, 1H), 0.98 (s, 9H), 0.92 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ175.03, 169.49 , 168.30 , 134.45 , 131.50 , 123.74 , 60.43, 53.65 , 37.65 , 34.72 , 26.55 , 25.26 , 23.04 , 21.32 . **HRMS** (EI-TOF) calcd for $C_{20}H_{26}N_2O_5$ (M-H$^+$): 373.1769, found: 373.1772.

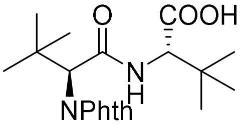


R = isopropyl, Compound **4d**, a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 – 7.81 (m, 2H), 7.77 – 7.68 (m, 3H), 4.38 (d, *J* = 11.4 Hz, 1H), 4.25 (d, *J* = 8.8 Hz, 1H), 2.89 – 2.75 (m, 1H), 1.07 (d, *J* = 6.6 Hz, 3H), 0.95 (s, 9H), 0.80 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 175.20, 169.33 , 168.74 , 134.65 , 131.31 , 124.00 , 63.42 , 60.85 , 34.32 , 28.00 , 26.74 , 19.83 , 19.57 . **HRMS** (EI-TOF) calcd for $C_{19}H_{24}N_2O_5$ (M-H$^+$): 359.1612, found: 359.1614.

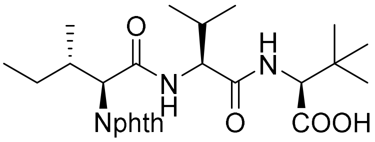


R = sec-butyl, Compound **4e**, a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.81 (m, 2H), 7.78 – 7.72 (m, 2H), 7.65 (d, 1H), 4.51 (d, *J* = 11.6 Hz, 1H), 4.32 (d, *J* = 8.8 Hz, 1H), 2.75 – 2.59 (m, 1H), 1.39

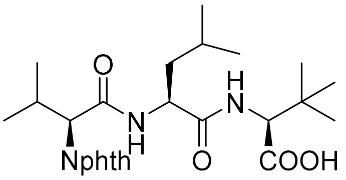
– 1.28 (m, 2H), 1.04 (d, *J* = 6.9 Hz, 3H), 1.01 (s, 9H), 0.82 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 175.03 , 169.99 , 168.83 , 134.72 , 131.28 , 124.00 , 61.90 , 61.05 , 34.24 , 33.35 , 26.72 , 25.51 , 15.70 , 10.10 . **HRMS** (EI-TOF) calcd for $C_{20}H_{26}N_2O_5$ (M-H$^+$): 373.1769, found: 373.1770.



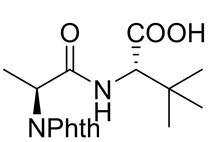
R = *tert*-butyl, Compound **4f**, a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.21 (d, *J* = 7.7 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.80 – 7.76 (m, 2H), 4.87 (s, 1H), 4.27 (d, *J* = 7.7 Hz, 1H), 1.13 (s, 9H), 1.01 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 176.12 , 168.36 , 134.78 , 131.23 , 123.96 , 65.79 , 61.71 , 36.71 , 33.83 , 28.28 , 26.88 . **HRMS** (EI-TOF) calcd for $C_{20}H_{26}N_2O_5$ (M-H$^+$): 373.1769, found: 373.1772.



R₁ = isopropyl, **R₂** = sec-butyl, Compound **4g**, a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.82 (m, 2H), 7.76 – 7.73 (m, 2H), 7.71 (d, *J* = 8.4 Hz, 1H), 6.97 (d, *J* = 9.3 Hz, 1H), 4.53 (d, *J* = 11.3 Hz, 1H), 4.32 (dd, *J* = 20.0, 8.7 Hz, 1H), 2.85 – 2.54 (m, 1H), 2.19 – 1.91 (m, 1H), 1.37 – 1.29 (m, 1H), 1.03 (d, *J* = 6.7 Hz, 3H), 0.89 (d, *J* = 5.4 Hz, 3H), 0.87 (d, *J* = 5.2 Hz, 3H), 0.83 (s, 9H), 0.82 (t, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.88 , 171.28 , 170.14 , 168.64 , 134.69 , 131.37 , 123.92 , 61.46 , 60.19 , 59.34 , 34.85 , 33.18 , 30.40 , 26.43 , 25.59 , 19.40 , 18.22 , 15.85 , 10.22 . **HRMS** (EI-TOF) calcd for $C_{25}H_{35}N_3O_6$ (M-H$^+$): 472.2453, found: 472.2455.



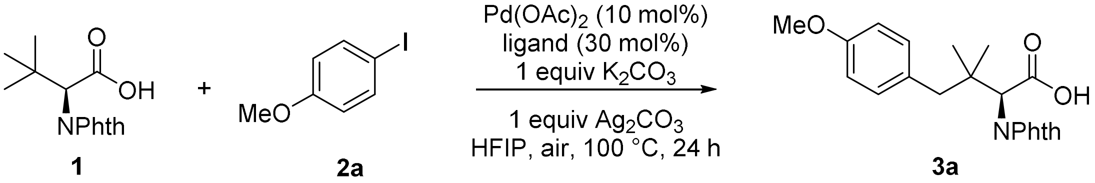
R₁ = isobutyl, **R₂** = isopropyl, Compound **4h**, a white solid.^{1}H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.82 (m, 2H), 7.79 – 7.72 (m, 2H), 7.50 – 7.40 (m, 1H), 6.95 – 6.84 (m, 1H), 4.53 – 4.42 (m, 2H), 4.28 (d, *J* = 9.2 Hz, 1H), 2.93 – 2.78 (m, 1H), 1.78 – 1.53 (m, 3H), 1.09 (d, *J* = 6.6 Hz, 3H), 0.92 (d, *J* = 5.6 Hz, 3H), 0.88 (d, *J* = 5.6 Hz, 3H), 0.85 (d, *J* = 6.6 Hz, 3H), 0.81 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 174.03 , 171.59 , 169.58 , 168.54 , 134.66 , 131.39 , 123.90 , 62.75 , 60.17 , 52.14 , 40.08 , 34.79 , 27.77 , 26.44 , 24.90 , 23.07 , 21.96 , 19.91 , 19.55 . **HRMS** (EI-TOF) calcd for $C_{25}H_{35}N_3O_6$ (M-H$^+$): 472.2453, found: 472.2455.



R = methyl, Compound **4i**, a white solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 – 7.83 (m, 2H), 7.77 – 7.66 (m, 2H), 6.78 (d, *J* = 9.2 Hz, 1H), 4.97 (q, *J* = 7.3 Hz, 1H), 4.43 (d, *J* = 9.3 Hz, 1H), 1.70 (d, *J* = 7.4 Hz, 3H), 0.96 (s, 9H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 174.92 , 169.57 , 168.03 , 134.53 , 131.80 , 123.78 , 60.50 , 49.87 , 34.93 , 26.62 , 15.52 . **HRMS** (EI-TOF) calcd for $C_{17}H_{12}N_2O_5$ (M-H$^+$): 331.1299, found: 371.1297.

2.2 Optimization of Reaction Conditions

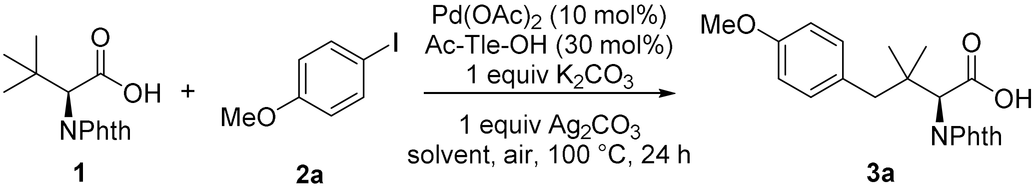
Table S1. Screening of ligands



entry	Ligand	yield
1	Ac-Gly-OH	trace
2	Ac-Leu-OH	10%
3	Ac-Ile-OH	trace
4	Ac-Ala-OH	trace
5	Ac-Val-OH	trace
6	Ac-Tle-OH	15%

Reaction Conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), Pd(OAc)$_2$ (0.01 mmol), Ag$_2$CO$_3$ (0.1 mmol), K$_2$CO$_3$ (0.1mmol), ligand (0.03 mmol), HFIP (1.0 mL), air for 24 h at 100 °C. Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

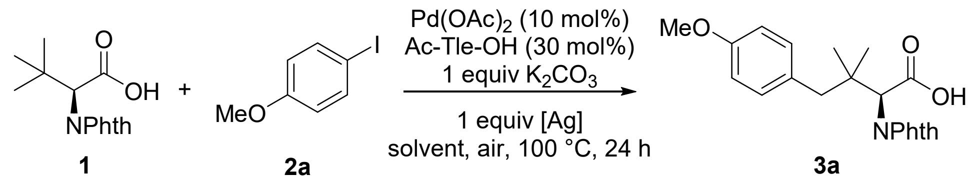
Table S2. Screening of solvents



entry	solvent	yield
1	HFIP	15%
2	HOAc	N.R
3	TFA	trace
4	*t*-BuOH	trace
5	DCE	N.R
6	PhMe	N.R
7	1.4-dioxane	N.R

Reaction Conditions: **1a** (0.10 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (0.01 mmol), Ag_2CO_3 (0.1 mmol), K_2CO_3 (0.1mmol), Ac-Tle-OH (0.03 mmol), solvent (1.0 mL), air for 24 h at 100 °C. Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

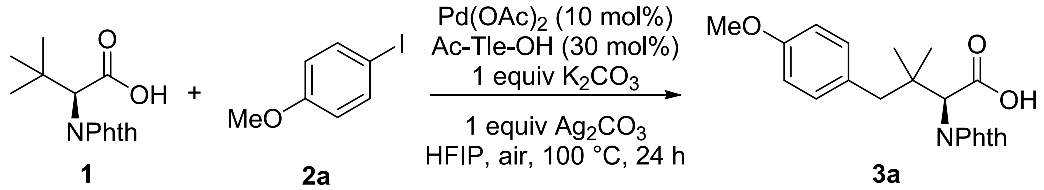
Table S3. Screening of Silver Salts



entry	[Ag]	yield
1	Ag_2CO_3	15%
2	AgOAc	trace
3	Ag_2NO_3	trace
4	Ag_2O	trace
5	AgOTf	trace
6	Ag_3PO_4	40%
7	None	trace

Reaction Conditions: **1** (0.10 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (0.01 mmol), Oxidant (0.1 mmol), K_2CO_3 (0.1mmol), Ac-Tle-OH (0.03 mmol), HFIP (1.0 mL), air for 24 h at 100 °C. Yield was determined by ^1H NMR using 1,3,5-trimethoxybenzene as an internal standard.

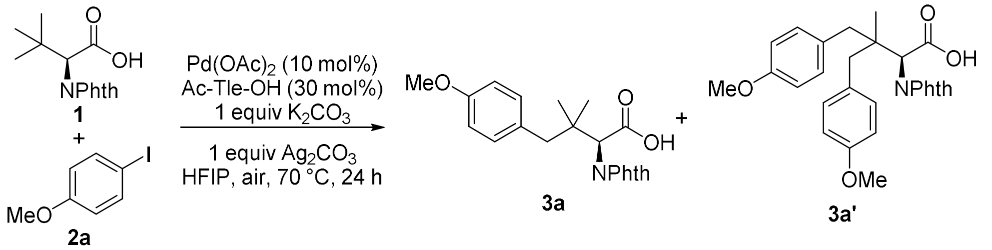
Table S4. Investigation of Temperature



entry	T/°C	yield
1	120	38%
2	100	40%
3	90	43%
4	70	46%
5	60	40%

Reaction Conditions: **1** (0.10 mmol), **2a** (0.15 mmol), $Pd(OAc)_2$ (0.01 mmol), Ag_3PO_4 (0.1 mmol), K_2CO_3 (0.1mmol), Ac-Tle-OH (0.03 mmol), HFIP (1.0 mL), air for 24 h . Yield was determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard.

Table S5. Screening the Equivalents of 2a

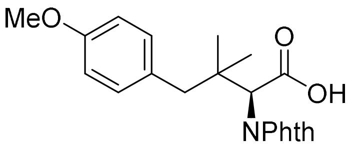


entry	**2a**	yield/**3a**	yield/**3a'**
1	1.0 equiv	38%	N.R
2	2.0 equiv	48%	6%
3	3.0 equiv	56%	15%
4	4.0 equiv	55%	11%
5	5.0 equiv	53%	14%
6[a]	3.0 equiv	57%	14%

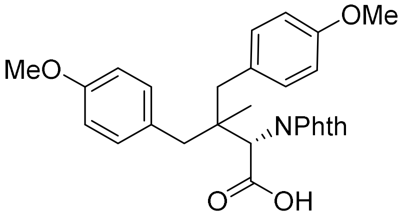
Reaction Conditions: **1a** (0.10 mmol), **2a**, Pd(OAc)$_2$ (0.01 mmol), Ag$_3$PO$_4$ (0.1 mmol), K$_2$CO$_3$(0.1mmol), Ac-Tle-OH (0.03 mmol), HFIP (1.0 mL), air for 24 h at 70 °C. Yield was determined by ^{1}H NMR using1,3,5-trimethoxybenzene as an internal standard. [a]D-Ac-Tle-OH was used as ligand.

2.3 Palladium-Catalyzed Carboxylate-Directed γ-C(sp^3)-H Arylation with Different Aryl Iodides.

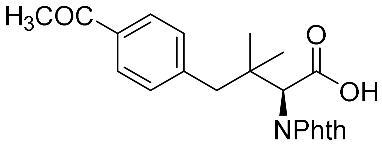
General Procedure A: To an oven-dried 50 mL Schlenk tube were added substrate **1** (0.30 mmol), **2** (0.90 mmol), Pd(OAc)$_2$ (6.6 mg, 0.030 mmol), Ac-Tle-OH (0.09 mmol), Ag$_3$PO$_4$ (125.4 mg, 0.30 mmol), K$_2$CO$_3$ (41.4 mg, 0.30 mmol), HFIP (3.0 mL). The mixture was stirred for 24 h at 70 °C followed by cooling. HCOOH (25uL) was then added and the resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The residue was purified by preparative TLC using PE/EtOAc/HCOOH as the eluent to afford the product **3.** Characterization data for products are reported as follows:



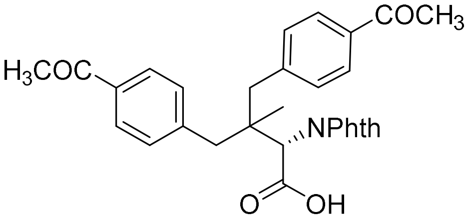
The title compound **3a** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3a** was obtained as a white solid (64.0 mg, 58%).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 – 7.82 (m, 2H), 7.79 – 7.70 (m, 2H), 7.09 (d, *J* = 8.6 Hz ,2H), 6.82 (d, *J* = 8.6 Hz ,2H), 4.86 (s, 1H), 3.79 (s, 3H), 3.01 (d, *J* = 13.3 Hz, 1H), 2.83 (d, *J* = 13.3 Hz, 1H), 1.17 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$)δ 172.84, 168.21 , 158.29 , 134.44 , 131.98 , 131.76 , 129.98 , 123.81 , 113.47 , 59.25 , 55.33 , 44.68 , 39.48 , 24.89 , 24.76 . **HRMS** (EI-TOF) calcd for $C_{22}H_{21}NO_5$ (M-H$^+$): 366.1347, found: 366.1347.



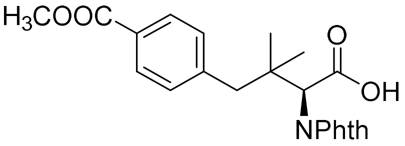
The title compound **3a’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%).**3a’** was obtained as a white solid (13.7 mg, 10%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 – 7.78 (m, 2H), 7.76 – 7.70 (m, 2H), 7.16 (d, *J* = 8.5 Hz, 2H), 7.07 (d, *J* = 8.5 Hz, 2H), 6.90 – 6.78 (m, 4H), 5.02 (s, 1H), 3.7997 (s, 3H), 3.7993 (s, 3H), 3.47 (d, *J* = 13.7 Hz, 1H), 3.39 (d, *J* = 13.4 Hz, 1H), 3.18 (d, *J* = 13.5 Hz, 1H), 2.54 (d, *J* = 13.6 Hz, 1H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.82 , 168.25 , 158.38 , 158.11 , 134.40 , 132.30 , 131.71 , 131.67 , 130.07 , 129.58 , 123.74 , 113.81 , 113.31 , 56.65 , 55.31 ,55.26, 42.75 , 42.39 , 42.04 , 22.74 . **HRMS** (EI-TOF) calcd for $C_{28}H_{27}NO_6$ (M-H$^+$): 472.1765, found: 472.1767.



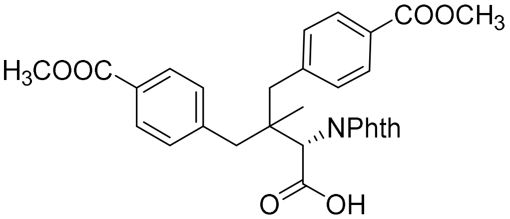
The title compound **3b** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3b** was obtained as a white solid (62.6 mg, 55%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.82 (m, 4H), 7.82 – 7.70 (m, 2H), 7.27 (d, *J* = 9.0 Hz ,2H), 4.83 (s, 1H), 3.17 (d, *J* = 12.8 Hz, 1H), 2.97 (d, *J* = 12.8 Hz, 1H), 2.60 (s, 3H), 1.16 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 198.33, 171.77, 168.22, 144.04, 135.50, 134.56, 131.71, 128.15, 123.89, 59.30, 45.17, 39.52, 26.71, 25.00, 24.84. **HRMS** (EI-TOF) calcd for $C_{22}H_{21}NO_5$ (M-H$^+$): 378.1347, found: 378.1349.



The title compound **3b'** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%).**3b'** was obtained as a white solid (19.4mg, 13%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.87 (m, 4H), 7.85 – 7.81 (m, 2H), 7.74 (m, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 4.88 (s, 1H), 3.70 (d, *J* = 13.3 Hz, 1H), 3.58 (d, *J* = 13.2 Hz, 1H), 3.25 (d, *J* = 13.0 Hz, 1H), 2.60 (s, 3H), 2.59(s, 3H), 2.56 (d, *J* = 13.5 Hz, 1H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.48 , 198.39 , 168.23 , 167.95 , 143.90 , 143.43 , 135.76 , 135.55 , 134.61 , 131.63 , 131.61 , 130.99 , 128.61 , 128.18 , 123.87 , 56.46 , 43.50 , 43.08 , 42.82 , 26.70 , 23.01 . **HRMS** (EI-TOF) calcd for $C_{30}H_{27}NO_6$ (M-H$^+$):496.1765, found: 496.1766.

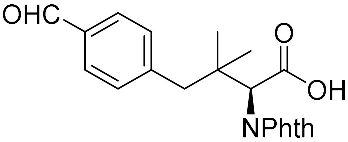


The title compound **3c** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3c** was obtained as a white solid (71.1 mg, 60%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.9 Hz, 2H), 7.92 – 7.85 (m, 2H), 7.80 – 7.70 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 4.82 (s, 1H), 3.90 (s, 3H), 3.15 (d, *J* = 12.9 Hz, 1H), 2.96 (d, *J* = 12.8 Hz, 1H), 1.15 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.70 , 168.20 , 167.34 , 143.65 , 134.55 , 131.72 , 131.13 , 129.32 , 128.41 , 123.89 , 59.36 , 52.17 , 45.18 , 39.51 , 24.95 , 24.82 . **HRMS** (EI-TOF) calcd for $C_{22}H_{21}NO_6$ (M-H$^+$):394.1296, found: 394.1296.

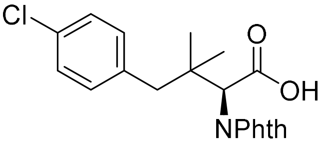


The title compound **3c'** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%).**3c'** was obtained as a white solid (14.3mg, 9%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 4H), 7.88 – 7.80 (m, 2H), 7.76 – 7.69 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 4.89 (s, 1H), 3.9097 (s, 3H), 3.9007 (s, 3H), 3.68 (d, *J* = 13.3 Hz, 1H), 3.56 (d, *J* = 13.1 Hz, 1H), 3.27 (d, *J* = 13.0 Hz, 1H), 2.57 (d, *J* = 13.2 Hz, 1H), 0.89 (s, 3H). ^{13}C

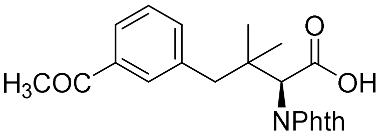
NMR (101 MHz, $CDCl_3$) δ 172.07 , 168.21 , 167.34 , 167.24 , 143.54 , 143.08 , 134.56 , 131.65 , 131.47 , 130.82 , 129.78 , 129.32 , 128.79 , 128.48 , 123.86 , 53.57 , 52.22, 52.19, 43.51 , 43.08 , 42.76 , 22.94 . **HRMS** (EI-TOF) calcd for $C_{30}H_{27}NO_8$ (M-H^+): 528.1664, found: 528.1664.



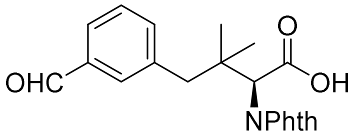
The title compound **3d** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3d** was obtained as a white solid (64.1 mg, 58%).^{1}H NMR (400 MHz, $CDCl_3$) δ 9.98 (s, 1H), 7.92 – 7.82 (m, 2H), 7.80 (d, *J* = 7.9 Hz, 2H), 7.78 – 7.74 (m, 2H), 7.35 (d, *J* = 7.8 Hz, 2H), 4.84 (s, 1H), 3.19 (d, *J* = 12.8 Hz, 1H), 3.00 (d, *J* = 12.8 Hz, 1H), 1.16 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.32 , 171.82 , 168.17 , 145.64 , 134.86 , 134.55 , 131.71 , 131.65 , 129.50 , 123.87 , 59.23 , 45.28 , 39.52 , 24.99 , 24.84 . **HRMS** (EI-TOF) calcd for $C_{21}H_{19}NO_5$ (M+Na^+): 388.1155, found: 388.1152.



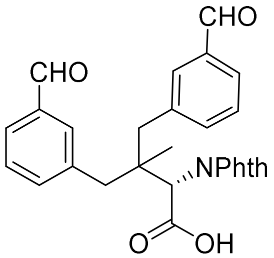
The title compound **3e** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3e** was obtained as a white solid (60.1 mg, 54%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.75 (m, 2H), 7.79 – 7.71 (m, 2H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 4.83 (s, 1H), 3.05 (d, *J* = 13.1 Hz, 1H), 2.87 (d, *J* = 13.1 Hz, 1H), 1.14 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.13 , 168.18 , 136.40 , 134.51 , 132.31 , 131.65 , 128.13 , 123.84 , 59.20 , 44.54 , 39.32 , 24.82 , 24.65 . **HRMS** (EI-TOF) calcd for $C_{20}H_{18}ClNO_4$ (M-H^+): 370.0851, found: 370.0850.



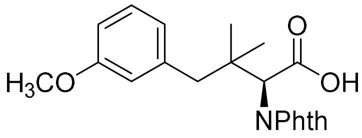
The title compound **3f** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3f** was obtained as a white solid (68.7 mg, 60%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.84 – 7.79 (m, 1H), 7.79 – 7.73 (m, 3H), 7.39 (m,2H), 4.84 (s, 1H), 3.16 (d, *J* = 13.1 Hz, 1H), 2.97 (d, *J* = 13.1 Hz, 1H), 2.59 (s, 3H), 1.15 (s, 3H), 1.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.72, 172.12, 168.21, 138.61, 136.93, 135.90, 134.55, 131.71, 130.77, 128.28, 126.70, 123.90, 59.33, 45.00, 39.41, 26.83, 24.83, 24.77. **HRMS** (EI-TOF) calcd for $C_{22}H_{21}NO_5$ (M-H^+): 378.1347, found: 378.1347.



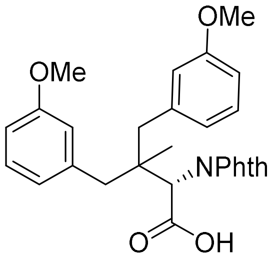
The title compound **3g** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3g** was obtained as a white solid (61.8 mg, 56%) ^{1}H NMR (400 MHz, CDCl$_3$) δ 9.99 (s, 1H), 7.97 – 7.84 (m, 2H), 7.81 – 7.73 (m, 3H), 7.69 (m, 1H), 7.51 – 7.43 (m, 2H), 4.85 (s, 1H), 3.19 (d, *J* = 13.1 Hz, 1H), 3.00 (d, *J* = 13.1 Hz, 1H), 1.16 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 192.79 , 172.02 , 168.20 , 137.26 , 136.30 , 134.59 , 132.12 , 131.70 , 128.76 , 128.22 , 123.92 , 59.30 , 44.80 , 39.41 , 24.87 , 24.78. **HRMS** (EI-TOF) calcd for $C_{21}H_{19}NO_5$ (M+Na$^+$): 388.1155, found: 388.1157.



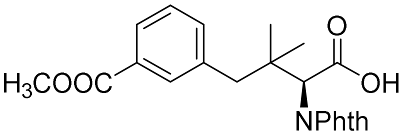
The title compound **3g’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%).**3g’** was obtained as a white solid (15.2mg, 10%).^{1}H NMR (400 MHz, CDCl$_3$) δ 10.01 (s, 1H), 9.97 (s, 1H), 7.87 – 7.82 (m, 2H), 7.81 – 7.72 (m, 5H), 7.64 – 7.61 (m, 1H), 7.57 – 7.43 (m, 4H), 4.89 (s, 1H), 3.74 (d, *J* = 13.3 Hz, 1H), 3.60 (d, *J* = 13.3 Hz, 1H), 3.32 (d, *J* = 13.3 Hz, 1H), 2.61 (d, *J* = 13.4 Hz, 1H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 192.73 , 192.67 , 168.23 , 138.97 , 138.53 , 137.57 , 136.88 , 136.55 , 136.37 , 134.65 , 132.19 , 131.61 , 129.28 , 128.92 , 128.83 , 128.50 , 123.92 , 43.17 , 42.69 , 42.55 , 22.79 . **HRMS** (EI-TOF) calcd for $C_{28}H_{23}NO_6$ (M-H$^+$): 468.1452, found: 468.1454.



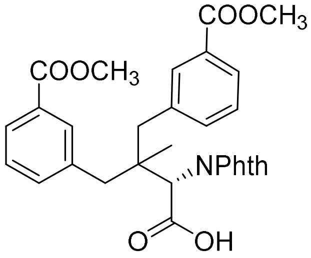
The title compound **3h** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3h** was obtained as a white solid (50.7 mg, 46%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.95 – 7.80 (m, 2H), 7.78 – 7.68 (m, 2H), 7.19 (t, *J* = 7.9 Hz, 1H), 6.77 (m,2H), 6.72 (m,1H), 4.86 (s, 1H), 3.78 (s, 3H), 3.04 (d, *J* = 13.1 Hz ,1H), 2.88 (d, *J* = 13.1 Hz 1H), 1.19 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.67 , 168.20 , 159.28 , 139.54 , 134.44 , 131.74 , 128.89 , 123.81 , 123.63 , 116.92 , 111.75 , 59.29 , 55.29 , 45.54 , 39.41 , 25.08 , 24.90 . **HRMS** (EI-TOF) calcd for $C_{21}H_{21}NO_5$ (M-H$^+$): 366.1347, found: 366.1350.



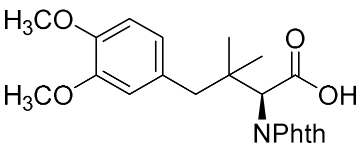
The title compound **3h'** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3h'** was obtained as a white solid (10.0mg, 7%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 – 7.78 (m, 2H), 7.79 – 7.66 (m, 2H), 7.29 – 7.11 (m, 2H), 6.87 – 6.73 (m, 5H), 6.68 (s, 1H), 5.03 (s, 1H), 3.78 (s, 3H), 3.74 (s, 3H), 3.52 (d, *J* = 13.6 Hz, 1H), 3.43 (d, *J* = 13.2 Hz, 1H), 3.19 (d, *J* = 13.3 Hz, 1H), 2.60 (d, *J* = 13.4 Hz, 1H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.64 , 168.19 , 159.51 , 159.22 , 139.57 , 139.18 , 134.42 , 131.69 , 129.34 , 128.78 , 124.01 , 123.77 , 123.21 , 117.21 , 116.52 , 112.24 , 111.67 , 55.30 , 55.23 , 43.55 , 43.21 , 42.63 , 23.11 . **HRMS** (EI-TOF) calcd for $C_{28}H_{27}NO_6$ (M-H$^+$): 472.1765, found: 472.1763.



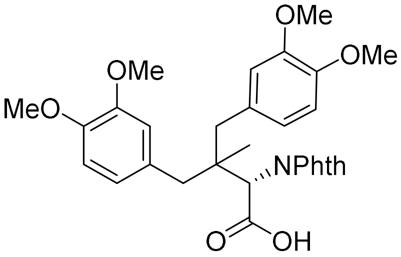
The title compound **3i** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3i** was obtained as a white solid (81.8 mg, 69%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.84 (m, 3H), 7.84 – 7.79 (m, 1H), 7.78 – 7.71 (m, 2H), 7.46 – 7.29 (m, 2H), 4.80 (s, 1H),3.88 (s, 3H),3.12 (d, *J* = 13.1 Hz, 1H), 2.95 (d, *J* = 13.1 Hz, 1H), 1.13 (s, 3H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.17 , 168.27 , 167.48 , 138.44 , 135.69 , 134.48 , 132.07 , 131.72 , 129.83 , 128.06 , 127.73 , 123.84 , 59.42 , 52.26 , 44.88 , 39.37 , 24.81 , 24.70. **HRMS** (EI-TOF) calcd for $C_{22}H_{21}NO_6$ (M-H$^+$): 394.1296, found: 394.1295.



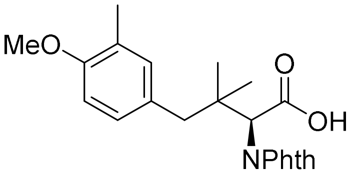
The title compound **3i'** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3i'** was obtained as a white solid (15.8mg, 10%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 (d, *J* = 7.7 Hz, 3H), 7.86 – 7.80 (m, 2H), 7.76 – 7.70 (m, 3H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.31 (m, 3H), 4.90 (s, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.69 (d, *J* = 13.4 Hz, 1H), 3.56 (d, *J* = 13.3 Hz, 1H), 3.27 (d, *J* = 13.3 Hz, 1H), 2.58 (d, *J* = 13.4 Hz, 1H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.40 , 168.23 , 167.45 , 167.32 , 138.23 , 137.84 , 136.08 , 135.31 , 134.52 , 132.33 , 131.89 , 131.64 , 130.18 , 129.93 , 128.59 , 128.19 , 128.10 , 127.81 , 123.84 , 56.42 , 52.27 , 43.17 , 42.68 , 42.58 , 22.75 . **HRMS** (EI-TOF) calcd for $C_{30}H_{27}NO_8$ (M-H$^+$): 528.1664, found: 528.1664.



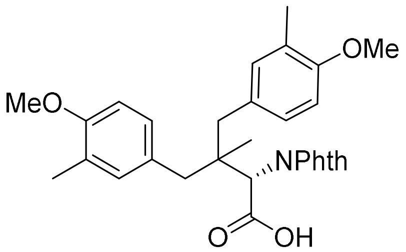
The title compound **3j** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3j** was obtained as a white solid (60.2 mg, 50%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 – 7.80 (m, 2H), 7.78 – 7.71 (m, 2H), 6.78 (d, *J* = 8.0 Hz, 1H), 6.77 – 6.63 (m, 2H), 4.82 (s, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.01 (d, *J* = 13.3 Hz, 1H), 2.81 (d, *J* = 13.3 Hz, 1H), 1.17 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.24 , 168.24 , 148.40 , 147.71 , 134.46 , 131.75 , 130.49 , 123.81 , 123.18 , 114.45 , 110.89 , 59.25 , 56.01 , 55.95 , 45.15 , 39.49 , 25.06 , 24.84. **HRMS** (EI-TOF) calcd for C$_{22}$H$_{23}$NO$_6$ (M-H$^+$): 396.1452, found: 396.1455.



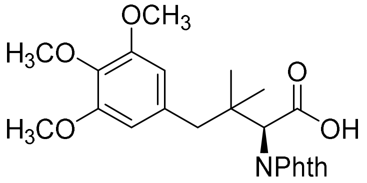
The title compound **3j’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3j’** was obtained as a white solid (8.0 mg, 5%).^{1}H NMR (400 MHz, CDCl$_3$ δ 7.86 – 7.81 (m, 2H), 7.76 – 7.70 (m, 2H), 6.86 – 6.74 (m, 4H), 6.71 (d, *J* = 8.2 Hz, 1H), 6.63 (s, 1H), 4.99 (s, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.84 (s, 3H), 3.79 (s, 3H), 3.47 (d, *J* = 13.7 Hz, 1H), 3.39 (d, *J* = 13.5 Hz, 1H), 3.09 (d, *J* = 13.4 Hz, 1H), 2.56 (d, *J* = 13.6 Hz, 1H), 0.92 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.26 , 168.23 , 148.67 , 148.29 , 147.89 , 147.60 , 134.44 , 131.71 , 130.06 , 123.77 (d, *J* = 3.7 Hz), 123.58 , 122.83 , 114.79 , 114.03 , 111.16 , 110.80 , 56.04 , 55.93 , 55.89 , 42.95 , 42.78 , 42.63 , 23.07 . **HRMS** (EI-TOF) calcd for C$_{30}$H$_{31}$NO$_8$ (M-H$^+$): 532.1977, found: 532.1977.



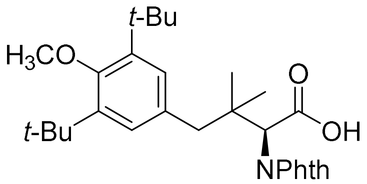
The title compound **3k** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3k** was obtained as a white solid (51.0 mg, 45%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 – 7.84 (m, 2H), 7.79 – 7.73 (m, 2H), 7.00 – 6.89 (m, 2H), 6.73 (d, *J* = 8.1 Hz, 1H), 4.87 (s, 1H), 3.81 (s, 3H), 2.96 (d, *J* = 13.3 Hz, 1H), 2.80 (d, *J* = 13.3 Hz, 1H), 2.18 (s, 3H), 1.18 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.28 , 168.20 , 156.41 , 134.43 , 133.44 , 131.73 , 129.47 , 129.16 , 125.87 , 123.80 , 109.49 , 59.31 , 55.39 , 44.65 , 39.44 , 24.88 , 24.74 , 16.39 . **HRMS** (EI-TOF) calcd for C$_{22}$H$_{23}$NO$_5$ (M-H$^+$): 380.1503, found: 380.1503.



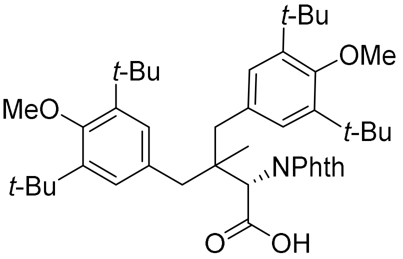
The title compound **3k'** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3k'** was obtained as a white solid (10.5 mg, 7%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.78 (m, 2H), 7.78 – 7.69 (m, 2H), 7.10 – 6.93 (m, 3H), 6.87 (s, 1H), 6.74 (dd, J = 8.2, 5.9 Hz, 2H), 5.03 (s, 1H), 3.81 (s ,3H), 3.80 (s ,3H), 3.40 (d, J = 13.7 Hz, 1H), 3.34 (d, J = 13.4 Hz, 1H), 3.10 (d, J = 13.4 Hz, 1H), 2.55 (d, J = 13.7 Hz, 1H), 2.19 (s ,3H), 2.15 (s ,3H), 0.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.77 , 168.26 , 156.56 , 156.29 , 134.37 , 133.81 , 133.20 , 131.74 , 129.67 , 129.53 , 129.23 , 128.86 , 126.24 , 125.70 , 123.72 , 109.82 , 109.41 , 56.82 , 55.40 , 55.34 , 42.73 , 42.42 , 42.02 , 22.83 , 16.44 , 16.38 . **HRMS** (EI-TOF) calcd for $C_{30}H_{31}NO_6$ (M-H$^+$): 500.2078, found: 500.2080.



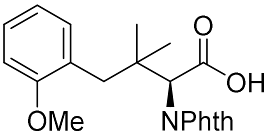
The title compound **3l** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3l** was obtained as a white solid (74.9 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 – 7.79 (m, 2H), 7.79 – 7.67 (m, 2H), 6.37 (s, 2H), 4.83 (s, 1H), 3.82 (s, 3H), 3.81 (s ,6H), 3.00 (d, J = 13.1 Hz, 1H), 2.82 (d, J = 13.2 Hz, 1H), 1.18 (s, 3H), 1.06 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.76 , 168.21 , 152.67 , 136.70 , 134.48 , 133.64 , 131.70 , 123.80 , 108.23 , 61.00 , 59.35 , 56.25 , 45.82 , 39.44 , 25.20 , 24.92 . **HRMS** (EI-TOF) calcd for $C_{23}H_{25}NO_7$ (M-H$^+$): 426.1558, found: 426.1559.



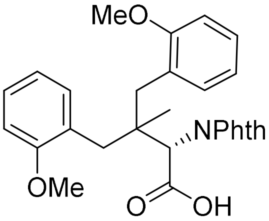
The title compound **3m** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3m** was obtained as a white solid (69.0 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.85 (m, 2H), 7.77 – 7.72 (m, 2H), 7.01 (s, 2H), 4.82 (s, 1H), 3.66 (s, 3H), 2.97 (d, J = 13.1 Hz, 1H), 2.78 (d, J = 13.1 Hz, 1H), 1.40 (s, 18H), 1.19 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.30 , 168.19 , 157.95 , 142.74 , 134.41 , 131.77 , 131.62 , 129.25 , 123.81 , 64.29 , 59.21 , 45.57 , 39.47 , 35.70 , 32.30 , 24.92 , 24.78 . **HRMS** (EI-TOF) calcd for $C_{29}H_{37}NO_5$ (M-H$^+$): 478.2599, found: 478.2598.



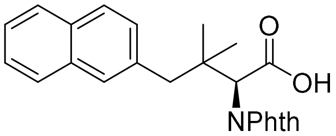
The title compound **3m’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3m’** was obtained as a white solid (11.5 mg, 5%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.89 – 7.78 (m, 2H), 7.75 – 7.69 (m, 2H), 7.09 (s, 2H), 7.02 (s, 2H), 4.74 (s, 1H), 3.67 (s ,3H), 3.66 (s ,3H), 3.38 (dd, *J* = 13.5, 4.7 Hz, 2H), 2.93 (d, *J* = 13.3 Hz, 1H), 2.51 (d, *J* = 13.5 Hz, 1H), 1.41 (s ,18H), 1.39 (s ,18H),), 0.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.37 , 168.22 , 157.97 , 142.76 , 134.43 , 131.77 , 131.61 , 129.25 , 123.82 , 64.30 , 59.17 , 45.56 , 39.50 , 35.71 , 32.30 , 24.93 , 24.77 . **HRMS** (EI-TOF) calcd for $C_{44}H_{59}NO_6$ (M-H$^+$): 696.4269, found:.696.4269.



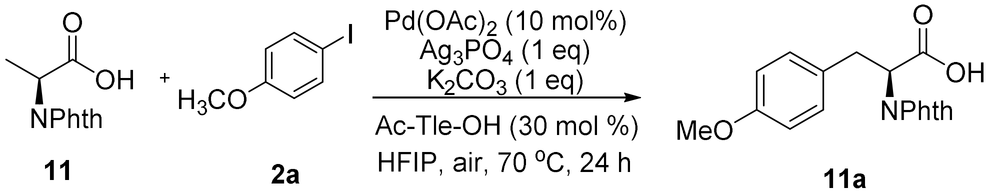
The title compound **3n** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3n** was obtained as a white solid (65.8 mg, 60%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 – 7.78 (m, 2H), 7.77 – 7.65 (m, 2H), 7.22 (m, 1H), 7.13 (m, 1H), 6.93 – 6.84 (m, 2H), 4.91 (s, 1H), 3.76 (s, 3H), 3.29 (d, *J* = 13.1 Hz, 1H), 2.80 (d, *J* = 13.1 Hz, 1H), 1.28 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.62 , 168.19 , 158.21 , 134.33 , 133.14 , 131.79 , 127.88 , 126.65 , 123.71 , 120.16 , 110.65 , 58.68 , 55.08 , 40.00 , 39.26 , 25.21 , 25.02 . **HRMS** (EI-TOF) calcd for $C_{22}H_{21}NO_5$ (M-H$^+$): 366.1347, found: 366.1340.



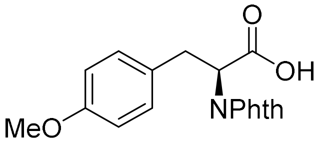
The title compound **3n’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3n’** was obtained as a white solid (11.3 mg, 8%)^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.79 (m, 2H), 7.78 – 7.58 (m, 2H), 7.22 – 7.11 (m, 3H), 7.02 – 6.76 (m, 5H), 5.00 (s, 1H), 3.79-3.76 (d, *J* = 12.0 Hz, 1H), 3.77 (s, 3H), 3.72 (d, *J* = 12.0 Hz, 1H), 3.68(s, 3H), 3.24 (d, *J* = 13.3 Hz, 1H), 2.54 (d, *J* = 13.7 Hz, 1H), 0.69 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.65, 168.29 , 158.60 , 158.15 , 134.25 , 133.57 , 133.34 , 131.90 , 128.03 , 127.58 , 127.46 , 126.62 , 123.62 , 120.35 , 120.00 , 110.70 , 110.66 , 57.15 , 55.28 , 54.99 , 43.92 , 36.80 , 36.00 , 22.24 . **HRMS** (EI-TOF) calcd for $C_{20}H_{23}NO_4$ (M-H$^+$): 472.1765, found: 472.1762.



The title compound **3o** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **3o** was obtained as a white solid (54.6 mg, 47%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.93 – 7.85 (m, 2H), 7.84 – 7.77 (m, 2H), 7.78 – 7.74 (m, 3H), 7.66 – 7.62 (m, 1H), 7.48 – 7.40 (m, 2H), 7.33 (dd, *J* = 8.4, 1.8 Hz, 1H), 4.93 (s, 1H), 3.23 (d, *J* = 13.1 Hz, 1H), 3.09 (d, *J* = 13.1 Hz, 1H), 1.22 (s, 3H), 1.11 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.22 , 168.11 , 135.46 , 134.37 , 133.26 , 132.15 , 131.62 , 129.57 , 129.44 , 127.62 , 127.55 , 127.21 , 125.82 , 125.35 , 123.74 , 59.50 , 45.29 , 39.69 , 24.84 , 24.71 . **HRMS** (EI-TOF) calcd for $C_{24}H_{21}NO_4$ (M-H$^+$): 386.1398, found: 386.1401.



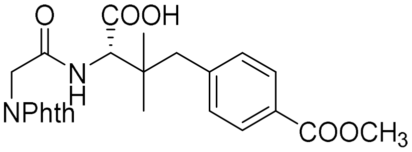
General Procedure A: To an oven-dried 50 mL Schlenk tube were added substrate **11** (0.30 mmol), **2a** (0.90 mmol), Pd(OAc)$_2$ (6.6 mg, 0.030 mmol), Ac-Tle-OH (0.09 mmol), Ag$_3$PO$_4$ (125.4 mg, 0.30 mmol), K$_2$CO$_3$ (41.4 mg, 0.30 mmol), HFIP (3.0 mL). The mixture was stirred for 24 h at 70 °C followed by cooling. HCOOH (25uL) was then added and the resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The residue was purified by preparative TLC using PE/EtOAc/HCOOH as the eluent to afford the product **11a.** Characterization data for products are reported as follows:



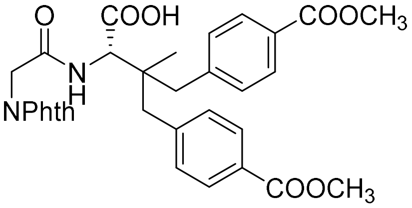
The title compound **11a** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **11a** was obtained as a white solid (49.5 mg, 51%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.83 – 7.73 (m, 2H), 7.70 – 7.61 (m, 2H), 7.07 (d, *J* = 8.5 Hz, 1H), 6.71 (d, *J* = 8.6 Hz, 1H), 5.17 (t, *J* = 8.3 Hz, 1H), 3.69 (s, 1H), 3.53 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (101 MHz, CDCl3) δ 174.25 , 167.59, 157.46, 134.26 , 131.57 , 129.93 , 128.53 , 123.65 , 114.09 , 55.22 , 53.37 , 33.63. **11a** is a known compound.[1]

2.4 Palladium-Catalyzed Carboxylate-Directed γ-C(sp^3)-H Arylation of Different Peptides.

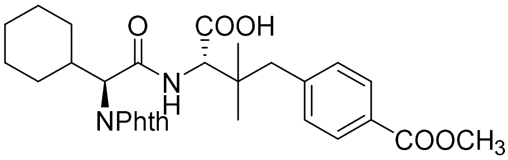
General Procedure B: To an oven-dried 50 mL Schlenk tube were added substrate **4** (0.10 mmol), **2c** (0.30 mmol), Pd(OAc)$_2$ (3.3 mg, 0.015 mmol), Ac-Tle-OH (0.030 mmol), Ag$_2$SO$_4$ (31.2 mg, 0.10 mmol), K$_2$CO$_3$ (13.8 mg, 0.10 mmol) and HFIP (1.0 mL). The mixture was stirred for 24 h at 70 °C followed by cooling. HCOOH (25uL) was then added and the resulting mixture was filtered through a celite pad and concentrated in *vacuo*. The residue was purified by preparative TLC using PE/EtOAc/HCOOH as the eluent to afford the product **5.** Characterization data for products are reported as follows:



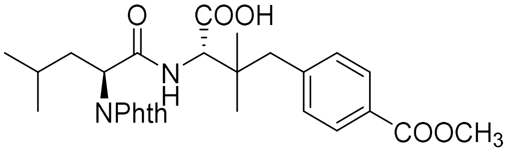
The title compound **5a** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 2: 1: 1%). **5a** was obtained as a white solid (19.0 mg, 42%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.87 (d, *J* = 7.6 Hz, 2H), 7.82 – 7.78 (m, 2H), 7.72 – 7.59 (m, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.79 – 6.58 (b, 1H), 4.59 – 4.36 (m, 3H), 3.87 (s, 3H), 2.66 (s, 2H), 0.99 (s, 3H). 0.97 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.94 , 168.09 , 167.37 , 167.12 , 143.17 , 134.43 , 131.91 , 131.00 , 129.25, 128.21 , 123.74 , 60.21 , 52.20 , 44.55 , 40.71 , 38.49 , 23.66 , 23.22 . **HRMS** (EI-TOF) calcd for $C_{24}H_{24}N_2O_7$ (M-H$^+$): 451.1511, found: 451.1512.



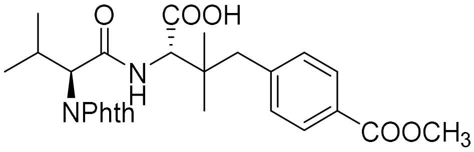
The title compound **5a'**was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 2: 1: 1%). **5a'** was obtained as a white solid (6.4 mg, 11%).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.88 (d, *J* = 4.4 Hz, 2H), 7.86 (d, *J* = 4.3 Hz, 2H), 7.81 – 7.76 (m, 2H), 7.66 – 7.59 (m, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 4.53 (d, *J* = 8.6 Hz, 1H), 4.47 (d, *J* = 16.3 Hz, 1H), 4.35 (d, *J* = 16.3 Hz, 1H), 3.88 (s, 3H), 3.87 (s, 3H), 3.00 (d, *J* = 13.1 Hz, 1H), 2.87 (d, *J* = 13.1 Hz, 1H), 2.72 (d, *J* = 13.2 Hz, 1H), 2.51 (d, *J* = 13.1 Hz, 1H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.74 , 168.03 , 167.54 – 167.11 (m), 142.54 , 142.40 , 134.45 , 131.92 , 131.28 , 131.09 , 129.52 , 129.48 , 128.66 , 128.60 , 126.02 , 123.79 , 58.08 , 52.23 , 52.21 , 42.48 , 41.80 , 40.71 , 21.91 . **HRMS** (EI-TOF) calcd for $C_{32}H_{30}N_2O_9$ (M-H$^+$): 585.1878, found: 585.1877.



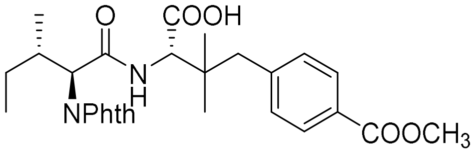
The title compound **5b** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **5b** was obtained as a white solid (18.7mg, 35%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.9 Hz, 2H), 7.89 – 7.82 (m, 2H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.76 – 7.70 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.54 (d, *J* = 11.2 Hz, 1H), 4.42 (d, *J* = 8.7 Hz, 1H), 3.90 (s, 3H), 2.70 (s, 2H), 2.60 – 2.45 (m, 1H), 1.86 (d, *J* = 12.7 Hz, 1H), 1.76 (d, *J* = 12.6 Hz, 1H), 1.64 (d, *J* = 10.9 Hz, 2H), 1.47 (d, *J* = 12.9 Hz, 1H), 1.32 – 1.07 (m, 4H), 0.97 – 0.91 (s, 6H), 0.90 – 0.82 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.72 , 169.40 , 168.76 , 167.27 , 143.02 , 134.69 , 131.30 , 130.95 , 129.34 , 128.42 , 123.94 , 62.09 , 60.04 , 52.22 , 44.77 , 38.09 , 36.77 , 30.50 , 29.55 , 26.03 , 25.50 , 25.40 , 23.86 , 23.42 . **HRMS** (EI-TOF) calcd for $C_{30}H_{34}N_2O_7$ (M-H$^+$): 533.2293, found: 533.2293.



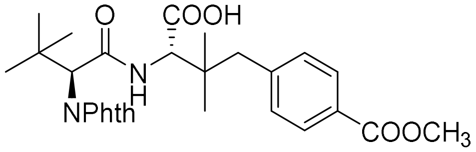
The title compound **5c** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **5c** was obtained as a white solid (23.9mg, 47%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.1 Hz, 2H), 7.90 – 7.84 (m, 2H), 7.80 – 7.70 (m, 2H), 7.22 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 9.0 Hz, 1H), 4.94 (dd, *J* = 11.1, 5.0 Hz, 1H), 4.55 (d, *J* = 9.0 Hz, 1H), 3.90 (s, 3H), 2.68 (s, 2H), 2.39 – 2.26 (m, 1H), 1.91 – 1.80 (m, 1H), 1.53 – 1.36 (m, 1H), 0.92(d, *J* = 2.0 Hz, 6H) 0.91(s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.53 , 169.61 , 168.29 , 167.17 , 143.02 , 134.56 , 131.45 , 130.89 , 129.23 , 128.28 , 123.78 , 59.86 , 53.45 , 52.11 , 44.48 , 38.53 , 37.58 , 25.23 , 23.70 , 23.30 , 23.08 , 21.29 . **HRMS** (EI-TOF) calcd for $C_{28}H_{32}N_2O_7$ (M-H$^+$): 507.2137, found: 507.2136.



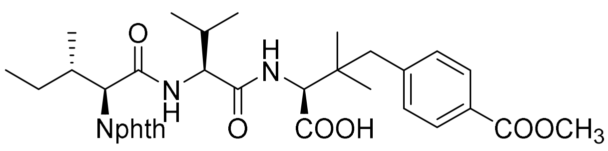
The title compound **5d** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **5d** was obtained as a white solid (20.7mg, 42%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 8.0 Hz, 2H), 7.89 – 7.84 (m, 2H), 7.77 – 7.73 (m, 2H), 7.70 (d, *J* = 9.1 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 2H), 4.47 (d, *J* = 2.7 Hz, 1H), 4.45 (s, 1H), 3.90 (s, 3H), 2.93 – 2.82 (m, 1H), 2.70 (s, 2H), 1.10 (d, *J* = 6.6 Hz, 3H), 0.94 (s, 3H). 0.93 (s, 3H), 0.85 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.63 , 169.50 , 168.69 , 167.27 , 143.01 , 134.70 , 131.36 , 130.97 , 129.35 , 128.48 , 123.94 , 63.25 , 60.08 , 52.20 , 44.77 , 38.12 , 28.03 , 23.87 , 23.45 , 19.99 , 19.60 . **HRMS** (EI-TOF) calcd for $C_{27}H_{30}N_2O_7$ (M-H$^+$): 493.1980, found: 493.1979.



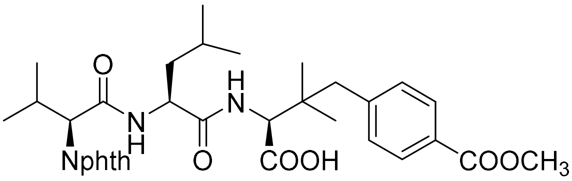
The title compound **5e** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **5e** was obtained as a white solid (23.4mg, 46%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.89 – 7.84 (m, 2H), 7.78 – 7.70 (m, 3H), 7.22 (d, *J* = 8.0 Hz, 2H), 4.55 (d, *J* = 11.6 Hz, 1H), 4.45 (d, *J* = 8.7 Hz, 1H), 3.91 (s, 3H), 2.71 (s, 2H), 1.41 – 1.30 (m, 2H), 1.06 (d, *J* = 6.7 Hz, 3H), 0.96 (s, 3H), 0.94 (s, 3H), 0.84 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.19 , 169.51 , 168.60 , 167.11 , 142.84 , 134.57 , 131.27 , 130.85 , 129.25 , 128.41 , 123.81 , 61.80 , 53.43 , 52.07 , 44.71 , 37.92 , 33.22 , 25.48 , 23.81 , 23.42 , 15.84 , 10.07 . **HRMS** (EI-TOF) calcd for $C_{28}H_{32}N_2O_7$ (M-H$^+$): 507.2137, found: 507.2137.



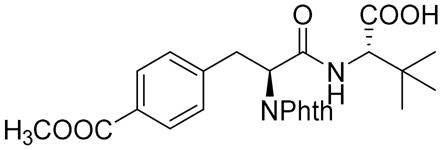
The title compound **5f** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **5f** was obtained as a white solid (24.9mg, 49%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.7 Hz, 1H), 7.97 – 7.86 (m, 4H), 7.80 – 7.75 (m, 2H), 7.27 – 7.25 (d, *J* = 9.8 Hz, 2H), 5.02 (s, 1H), 4.32 (d, *J* = 7.6 Hz, 1H), 3.89 (s, 3H), 3.03 (d, *J* = 12.9 Hz, 1H), 2.84 (d, *J* = 12.9 Hz, 1H), 1.16 (s, 3H), 1.04 (s, 9H), 0.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.69 , 168.33 , 167.34 , 143.47 , 134.89 , 131.22 , 129.13 , 128.16 , 124.03 , 64.51 , 61.78 , 52.11 , 45.58 , 40.26 , 33.77 , 26.89 , 24.95 , 24.58 . **HRMS** (EI-TOF) calcd for $C_{28}H_{32}N_2O_7$ (M-H$^+$): 507.2137, found: 507.2137.



The title compound **5g** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **5g** was obtained as a white solid (20.6mg, 34%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.9 Hz, 2H), 7.78 – 7.70 (m, 3H), 7.67 – 7.60 (m, 2H), 7.05 – 6.95 (m, 3H), 4.56 (d, *J* = 11.6 Hz, 1H), 4.43 (d, *J* = 9.1 Hz, 1H), 4.29 (t, *J* = 7.9 Hz, 1H), 3.91 (s, 3H), 2.75 – 2.65 (m, 1H), 2.51 (d, *J* = 13.0 Hz, 1H), 2.43 (d, *J* = 13.0 Hz, 1H), 2.31 – 2.18 (m, 1H), 1.40 – 1.30 (m, 2H), 1.06 (d, *J* = 6.7 Hz, 3H), 1.00 (d, *J* = 5.6 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H), 0.83 (t, 3H), 0.75 (s, 3H) 0.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.00 , 170.15 , 168.61 , 167.26 , 143.08 , 134.58 , 131.19 , 130.84 , 129.19 , 128.20 , 123.84 , 61.72 , 59.46 , 52.19 , 44.30 , 38.50 , 33.27 , 29.91 , 26.70 , 25.54 , 23.51 , 22.96 , 19.66 , 18.28 , 15.87 , 10.22 . **HRMS** (EI-TOF) calcd for $C_{33}H_{41}N_3O_8$ (M-H$^+$): 606.2821, found: 606.2823.

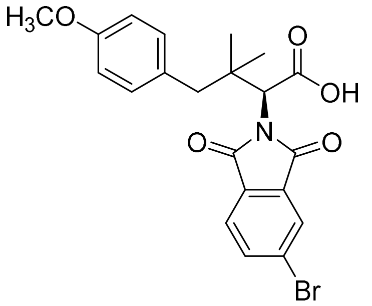


The title compound **5h** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **5h** was obtained as a white solid (13.9 mg, 23%).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.73 – 7.66 (m, 2H), 7.66 – 7.57 (m, 3H), 7.17 (d, *J* = 9.1 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 2H), 4.61 – 4.31 (m, 3H), 3.90 (s, 3H), 2.88 – 2.69 (m, 1H), 2.51 (d, *J* = 12.9 Hz, 1H), 2.44 (d, *J* = 13.0 Hz, 1H), 1.72 – 1.61 (m, 3H), 1.09 (d, *J* = 6.5 Hz, 3H), 0.95 (d, *J* = 5.6 Hz, 3H), 0.89 (d, *J* = 5.6 Hz, 3H), 0.83 (d, *J* = 6.6 Hz, 3H), 0.76 (s, 3H), 0.74(s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.55 , 170.06 , 168.52 , 167.21 , 142.96 , 134.58 , 131.12 , 130.74 , 128.23 , 123.82 , 63.05 ,60.57, 53.57 , 52.14 , 44.49 , 39.50 , 38.32 , 27.94 , 26.42 , 24.94 , 23.57 , 23.11 , 21.92 , 19.81 , 19.52 . **HRMS** (EI-TOF) calcd for $C_{33}H_{41}N_3O_8$ (M-H$^+$): 606.2821, found: 606.2824.

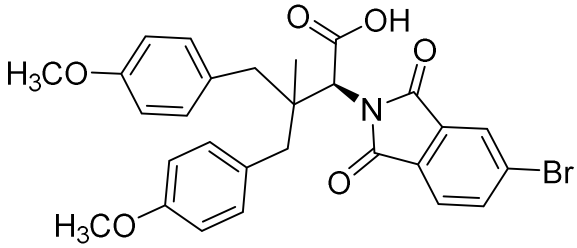


The title compound **5i** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **5i** was obtained as a white solid (31.5mg, 67%). ^{1}H NMR (400 MHz, CDCl$_3$)) δ 7.80 (d, *J* = 8.0 Hz, 2H), 7.77 – 7.71 (m, 2H), 7.69 – 7.63 (m, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.89 (d, *J* = 9.1 Hz, 1H), 5.19 (dd, *J* = 9.8, 6.8 Hz, 1H), 4.45 (d, *J* = 9.1 Hz, 1H), 3.81 (s, 3H), 3.62 (d, *J* = 4.4 Hz, 1H), 3.60 (s, 1H), 0.95 (s, 9H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.51 , 168.44 , 167.98 , 166.96 , 142.05 , 134.57 , 131.14 , 129.97 , 129.01 , 128.82 , 123.75 , 77.36 , 60.51 , 55.60 , 52.16 , 34.86, 26.55 . **HRMS** (EI-TOF) calcd for $C_{25}H_{26}N_2O_7$ (M-H$^+$): 465.1667, found: 465.1667.

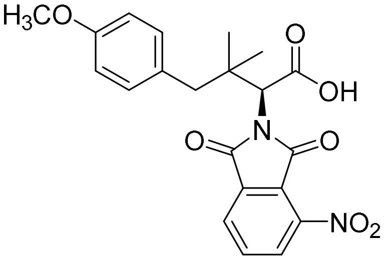
2.5 Palladium-Catalyzed Carboxylate-Directed γ-C(sp^3)-H Arylation of Tle with Different Protecting Groups.



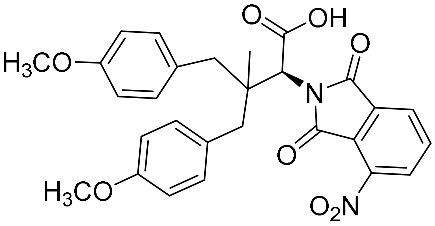
The title compound **7a** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%).**7a** was obtained as a white solid (54.3mg, 61%).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.99 (s, 1H), 7.87 (d, *J* = 7.7, 1H), 7.72 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 4.83 (s, 1H), 3.79 (s, 3H), 3.00 (d, *J* = 13.3 Hz, 1H), 2.81 (d, *J* = 13.3 Hz, 1H), 1.16 (s, 3H), 0.99 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.09 , 167.22 , 166.68 , 158.17 , 137.32 , 134.29 , 133.23 , 131.82 , 130.11 , 129.69 , 129.31 , 127.04 , 125.04 , 123.67 , 113.36 , 55.20 , 44.56 , 39.34 , 28.01 , 24.78 , 24.64 . **HRMS** (EI-TOF) calcd for $C_{21}H_{20}BrNO_5$ (M-H$^+$): 444.0452, found: 444.0452.



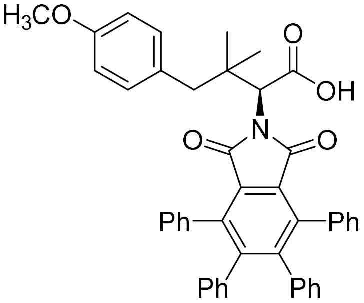
The title compound **7a’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%).**7a’** was obtained as a white solid (16.1mg, 15%).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.96 (s, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.69 (d, *J* = 7.9 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.82 (dd, *J* = 8.5, 2.4 Hz, 4H), 4.98 (s, 1H), 3.79 (s, 3H), 3.78(s, 3H), 3.44 (d, *J* = 13.7 Hz, 1H), 3.35 (d, *J* = 13.5 Hz, 1H), 3.12 (d, *J* = 13.5 Hz, 1H), 2.54 (d, *J* = 13.7 Hz, 1H), 0.85 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 173.30 , 167.42 , 166.89 , 158.48 , 158.23 , 137.42 , 133.36 , 132.30 , 131.72 , 130.23 , 129.95 , 129.50 , 129.42 , 127.11 , 125.11 , 113.87 , 113.40 , 56.96 , 55.34 , 55.30 , 42.80 , 42.47 , 42.09 , 22.78 . **HRMS** (EI-TOF) calcd for $C_{28}H_{26}BrNO_6$ (M-H$^+$): 550.0871, found: 550.0870.



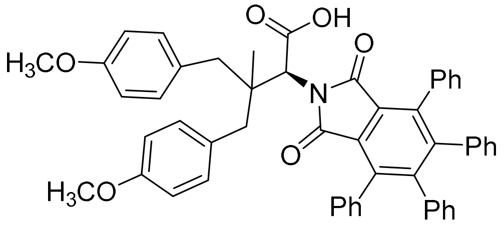
The title compound **7b** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%).**7b** was obtained as a pale yellow solid (38.3mg, 46%).^{1}H NMR (400 MHz, CDCl$_3$) δ 8.13 (d, *J* = 7.7 Hz, 2H), 7.93 (t, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.83 (d, *J* = 8.2 Hz, 2H), 4.88 (s, 1H), 3.79 (s, 3H), 3.04 (d, *J* = 13.4 Hz, 1H), 2.81 (d, *J* = 13.3 Hz, 1H), 1.20 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.33 , 165.70 , 162.74 , 158.39 , 145.40 , 135.78 , 133.77 , 131.92 , 129.60 , 129.06 , 127.58 , 123.47 , 113.58 , 59.57 , 55.34 , 44.84 , 39.49 , 25.01 , 24.88 . **HRMS** (EI-TOF) calcd for $C_{21}H_{20}N_2O_7$ (M-H$^+$): 411.1198, found: 411.1201.



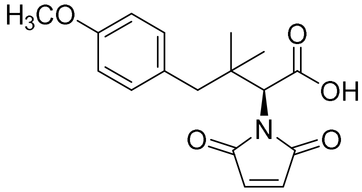
The title compound **7b’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7b’** was obtained as a pale yellow solid (8.5mg, 8%).^{1}H NMR (400 MHz, CDCl$_3$) δ 8.19 – 8.02 (m, 2H), 7.91 (t, *J* = 7.8 Hz, 1H), 7.15 (d, *J* = 8.2 Hz, 2H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.81 (m, 4H), 4.99 (s, 1H), 3.79 (s, 3H), 3.77（s, 3H） 3.43 (d, *J* = 13.7 Hz, 1H), 3.37 (d, *J* = 13.5 Hz, 1H), 3.06 (d, *J* = 13.5 Hz, 1H), 2.53 (d, *J* = 13.7 Hz, 1H), 0.91 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.97 , 165.71 , 162.70 , 158.36 , 158.15 , 145.21 , 135.58 , 133.62 , 132.16 , 131.50 , 129.62 , 129.20 , 128.84 , 127.36 , 123.29 , 113.80 , 113.31 , 57.26 , 55.21 , 55.16 , 42.68 , 42.41 , 41.93 , 22.76 . **HRMS** (EI-TOF) calcd for $C_{28}H_{26}N_2O_8$ (M-H$^+$): 517.1616, found: 517.1617.



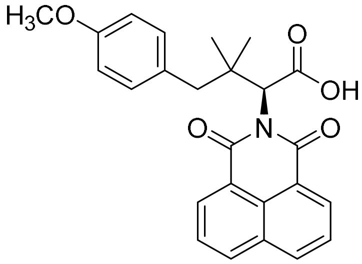
The title compound **7c** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7c** was obtained as a white solid (71.2mg, 53%).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.24 (s, 1H), 7.21 – 7.16 (m, 6H), 7.12 (d, 4H), 7.03 (d, *J* = 8.3 Hz, 2H), 6.89 – 6.86 (m, 6H), 6.79 (d, 2H), 6.75 – 6.70 (m, 3H), 4.74 (s, 1H), 3.76 (s, 3H), 2.92 (d, *J* = 13.3 Hz, 1H), 2.75 (d, *J* = 13.3 Hz, 1H), 1.09 (s, 3H), 0.98 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.72 , 167.09 , 158.16 , 148.34 , 139.78 , 138.12 , 135.57 , 131.97 , 130.82 (d, *J* = 2.1 Hz), 130.10 , 130.07 , 127.85 , 127.58 , 127.40 , 127.12 , 126.44 , 113.41 , 59.42 , 55.31 , 44.70 , 39.35 , 24.82 (d, *J* = 9.8 Hz). **HRMS** (EI-TOF) calcd for $C_{45}H_{37}NO_5$ (M-H$^+$): 670.2599, found: 670.2602.



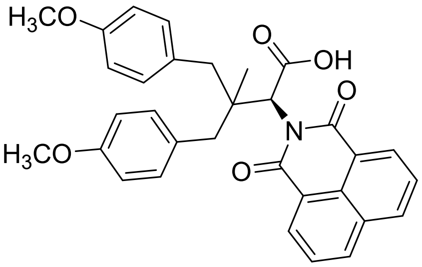
The title compound **7c’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7c’** was obtained as a white solid (23.3mg, 15%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 (s, 1H), 7.15 – 7.03 (m, 10H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.89 – 6.85 (m, 7H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.75 – 6.69 (m, 6H), 4.71 (s, 1H), 3.78 (s, 3H), 3.72 (s, 3H), 3.41 (d, *J* = 13.7 Hz, 1H), 3.37 (d, *J* = 13.7 Hz, 1H), 2.78 (d, *J* = 13.6 Hz, 1H), 2.37 (d, *J* = 13.8 Hz, 1H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.64 , 158.20 , 158.07 , 139.67 , 138.15 , 135.58 , 132.32 , 131.52 , 130.81 , 130.80 , 130.38 , 130.06 , 129.75 , 127.89 , 127.55 , 127.40 , 127.10 , 126.41 , 113.86 , 113.32 , 56.73 , 55.34 , 55.24 , 42.80 , 42.56 , 41.57 , 23.24 . **HRMS** (EI-TOF) calcd for $C_{52}H_{43}NO_6$ (M-H$^+$): 776.3017, found: 776.3013.



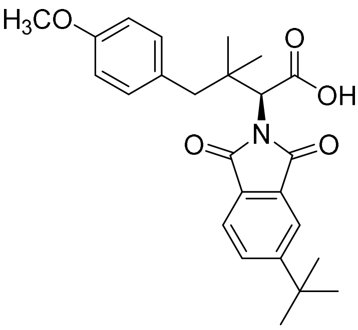
The title compound **7d** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7d** was obtained as a white solid (22.2mg, 15%).^{1}H NMR (400 MHz, CDCl3) δ 7.07 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.76 (s, 2H), 4.65 (s, 1H), 3.79 (s, 3H), 2.95 (d, *J* = 13.3 Hz, 1H), 2.77 (d, *J* = 13.3 Hz, 1H), 1.11 (s, 3H), 0.96 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 172.68, 170.48 , 158.32 , 134.37 , 131.94 , 129.84 , 113.50 , 55.34 , 53.57 , 44.58 , 39.24 , 24.82 , 24.66 . **HRMS** (EI-TOF) calcd for $C_{17}H_{19}NO_5$ (M-H$^+$): 316.1190, found: 316.1189.



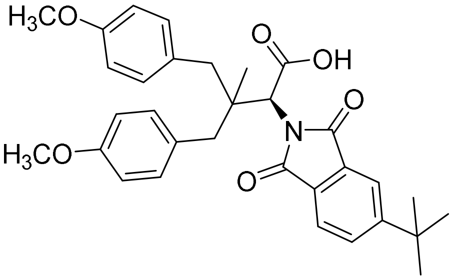
The title compound **7e** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7e** was obtained as a white solid (36.7mg, 44%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 – 8.43 (m, 2H), 8.19 (d, *J* = 8.2 Hz, 2H), 7.73 (m, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.1 Hz, 2H), 5.75 (s, 1H), 3.77 (s, 3H), 3.10 (d, *J* = 13.3 Hz, 1H), 2.86 (d, *J* = 13.2 Hz, 1H), 1.19 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.24 , 164.61 , 164.34 , 158.10 , 134.35 , 132.21 , 132.06 , 131.81 , 131.60 , 130.38 , 128.21 , 127.15 , 122.51 , 122.21 , 113.31 , 59.18 , 55.27 , 45.02 , 39.82 , 25.04 , 25.00 . **HRMS** (EI-TOF) calcd for $C_{25}H_{23}NO_5$ (M-H$^+$): 416.1503, found: 416.1502.



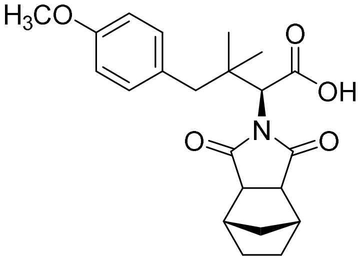
The title compound **7e’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7e’** was obtained as a white solid (10.4mg, 10%).^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, *J* = 7.2 Hz, 1H), 8.51 (d, *J* = 7.3 Hz, 1H), 8.28 – 8.13 (m, 2H), 7.78 – 7.64 (m, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H),6.85 (d, *J* = 8.1 Hz, 2H), 6.78 (d, *J* = 8.2 Hz, 1H), 5.79 (s, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.71 (d, *J* = 13.7 Hz, 1H), 3.56 (d, *J* = 13.7 Hz, 1H), 2.90 – 2.66 (d, *J* = 13.7 Hz, 1H),, 2.45 (d, *J* = 13.7 Hz, 1H), 0.98 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.96 , 164.76 , 164.50 , 158.29 , 157.98 , 134.32 , 132.40 , 131.65 , 130.69 , 130.06 , 128.23 , 127.17 , 127.13 , 122.59 , 122.24 , 113.81 , 113.19 , 56.73 , 55.27 , 55.24 , 43.26 , 42.97 , 42.02 , 22.68 . **HRMS** (EI-TOF) calcd for $C_{32}H_{29}NO_6$ (M-H$^+$): 522.1922, found: 522.1920.



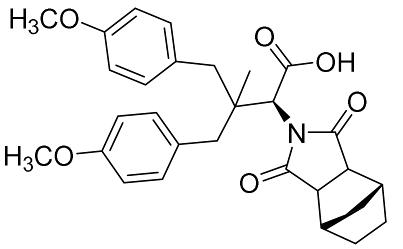
The title compound **7f** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7f** was obtained as a white solid (32.2mg, 38%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.83 – 7.74 (m, 2H), 7.09 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.1 Hz, 2H), 4.86 (s, 1H), 3.79 (s, 3H), 3.01 (d, *J* = 13.3 Hz, 1H), 2.86 (d, *J* = 13.3 Hz, 1H), 1.37 (s, 9H), 1.17 (s, 3H), 1.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.69 , 168.63 , 168.22 , 159.11 , 158.20 , 131.97 , 131.91 , 131.46 , 130.02 , 129.02 , 123.63 , 113.40 , 59.21 , 55.28 , 44.60 , 39.43 , 35.89 , 31.23 , 24.77 (d, *J* = 11.8 Hz). **HRMS** (EI-TOF) calcd for $C_{25}H_{29}NO_5$ (M-H$^+$): 422.1973, found: 422.1976.



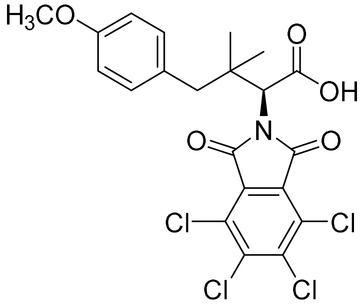
The title compound **7f’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7f’** was obtained as a white solid (16.9mg, 16%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.75 (s, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.83 (t, *J* = 7.7 Hz, 4H), 5.01 (s, 1H), 3.80 (s, 3H), 3.79 (s, 3H), 3.45 (d, *J* = 13.7 Hz, 1H), 3.37 (d, *J* = 13.5 Hz, 1H), 3.19 (d, *J* = 13.5 Hz, 1H), 2.55 (d, *J* = 13.7 Hz, 1H), 1.37 (s, 9H), 0.86 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.77 , 168.59 , 168.15 , 158.98 , 158.31 , 158.04 , 132.21 , 131.80 , 131.63 , 131.34 , 130.07 , 129.53 , 128.92 , 123.46 , 120.78 , 113.71 , 113.22 , 56.51 , 55.20 , 55.15 , 42.67 , 42.33 , 41.98 , 35.78 , 31.13 , 22.63 . **HRMS** (EI-TOF) calcd for $C_{32}H_{35}NO_6$ (M-H$^+$): 528.2391, found: 528.2393.



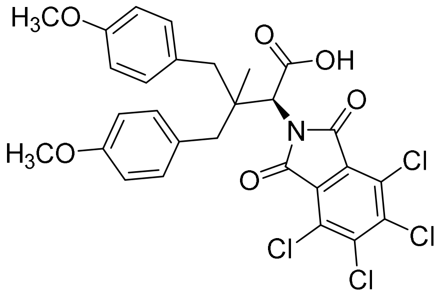
The title compound **7g** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%).**7g** was obtained as a white solid (47.7mg, 62%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, *J* = 8.2 Hz, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 4.63 (s, 1H), 3.78 (s, 3H), 3.15 (s, 2H), 2.96 (d, *J* = 13.3 Hz, 1H), 2.81 – 2.73 (m, 3H), 1.71 – 1.44 (m, 5H), 1.36 (m, 1H), 1.09 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.41 , 178.18 , 172.09 , 158.12 , 131.81 , 129.82 , 113.31 , 60.49 , 55.19 , 48.90 , 44.41 , 42.66 , 39.55 , 39.37 , 39.04 , 24.77 , 24.63 . **HRMS** (EI-TOF) calcd for $C_{22}H_{27}NO_5$ (M-H$^+$): 384.1816, found: 384.1816.



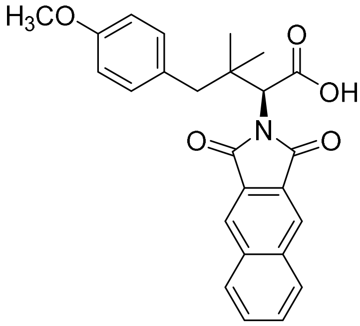
The title compound **7g’** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7g’** was obtained as a white solid (8.8mg, 9%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 8.2 Hz, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 6.82 (t, *J* = 7.7 Hz, 4H), 4.75 (s, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.40 (t, *J* = 12.5 Hz, 1H), 3.17 – 3.04 (s, 2H), 2.95 (d, *J* = 13.5 Hz, 1H), 2.76 (s, 2H), 2.47 (d, *J* = 13.7 Hz, 1H), 1.58 – 1.21 (m, 6H), 0.83 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.57 , 178.16, 172.22 , 158.27 , 158.04 , 132.16 , 131.48 , 130.04 , 129.43 , 113.72 , 113.23 , 55.21 , 55.13 , 48.83 , 42.63 , 42.34 , 41.87 , 39.56 , 39.39 , 24.66 , 22.71 . **HRMS** (EI-TOF) calcd for $C_{29}H_{33}NO_6$ (M-H$^+$): 490.2235, found: 490.2237.



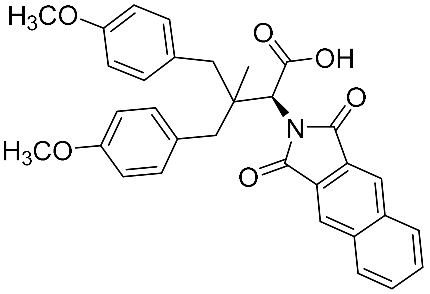
The title compound **7h** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7h** was obtained as a white solid (47.5mg, 47%).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.08 (d, *J* = 8.2 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 4.85 (s, 1H), 3.79 (s, 3H), 3.04 (d, *J* = 13.4 Hz, 1H), 2.78 (d, *J* = 13.4 Hz, 1H), 1.20 (s, 3H), 1.01 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.24 , 163.50 , 158.39 , 140.71 , 131.87 , 130.18 , 129.57 , 127.28 , 113.59 , 59.51 , 55.33 , 44.94 , 39.47 , 25.03 , 24.97 . **HRMS** (EI-TOF) calcd for $C_{21}H_{17}Cl_4NO_5$ (M-H$^+$): 501.9788, found: 501.9789.



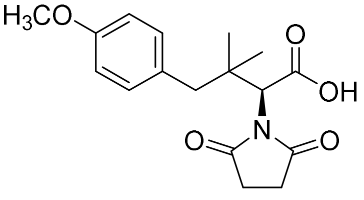
The title compound **7h'** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7h'** was obtained as a white solid (9.8mg, 8%).^{1}H NMR (400 MHz, CDCl$_3$) δ 7.15 (d, *J* = 8.2 Hz, 2H), 7.02 (d, *J* = 8.3 Hz, 2H), 6.81 (t, *J* = 9.2 Hz, 4H), 4.96 (s, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.40 (m, 2H), 3.03 (d, *J* = 13.5 Hz, 1H), 2.52 (d, *J* = 13.8 Hz, 1H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 172.21 , 163.47 , 158.32 , 158.15 , 140.51 , 132.15 , 131.42 , 129.97 , 129.56 , 129.22 , 127.13 , 113.79 , 113.31 , 57.32 , 55.22 , 55.14 , 42.70 , 42.49 , 41.94 , 22.83 . **HRMS** (EI-TOF) calcd for $C_{28}H_{23}Cl_4NO_5$ (M-H$^+$): 608.0206, found: 608.0209.



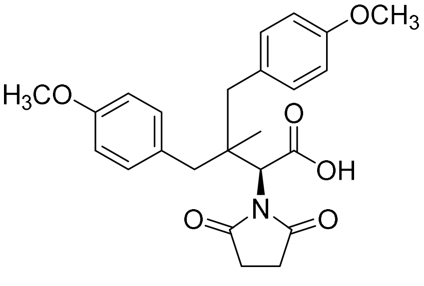
The title compound **7i** was prepared under the optimized conditions and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%).**7i** was obtained as a white solid (24.2mg, 29%).^{1}H NMR (400 MHz, CDCl3) δ 8.34 (s, 2H), 8.03 (m, 2H), 7.76 – 7.61 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 2H), 6.81 (d, *J* = 7.8 Hz, 2H), 4.95 (s, 1H), 3.78 (s, 3H), 3.05 (d, *J* = 13.3 Hz, 1H), 2.87 (d, *J* = 13.3 Hz, 1H), 1.21 (s, 3H), 1.04 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 173.14 , 167.96 , 158.22 , 135.66 , 131.98 , 130.42 , 130.01 , 129.45 , 127.26 , 125.38 , 113.42 , 59.43 , 55.29 , 44.64 , 39.62 , 24.89 , 24.74 . **HRMS** (EI-TOF) calcd for $C_{25}H_{23}NO_5$ (M-H$^+$): 416.1503, found: 416.1505.



The title compound **7i'** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7i'** was obtained as a white solid (8.4mg, 8%)^{1}H NMR (400 MHz, CDCl3) δ 8.32 (s, 2H), 8.13 – 7.93 (m, 2H), 7.76 – 7.61 (m, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 2H), 6.82 (m, 4H), 5.07 (s, 1H), 3.79 (s, 6H), 3.49 (d, *J* = 13.7 Hz, 1H), 3.44 (d, *J* = 13.4 Hz, 1H), 3.17 (d, *J* = 13.5 Hz, 1H), 2.54 (d, *J* = 13.6 Hz, 1H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, CDCl3) δ 172.99 , 168.03 , 158.44 , 158.16 , 135.70 , 132.35 , 131.75 , 130.44 , 130.18 , 129.68 , 129.45 , 127.33 , 125.32 , 113.86 , 113.34 , 56.88 , 55.31 (d, *J* = 4.0 Hz), 42.97 , 42.51 , 42.07 , 22.80 . **HRMS** (EI-TOF) calcd for $C_{32}H_{29}NO_6$ (M-H$^+$): 522.1922, found: 522.1923.

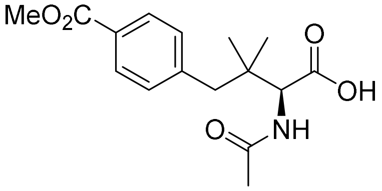


The title compound **7j** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7j** was obtained as a white solid (43.1mg, 45%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.07 (d, *J* = 8.3 Hz, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 4.69 (s, 1H), 3.79 (s, 3H), 2.93 (d, *J* = 13.3 Hz, 1H), 2.78 (s, 3H), 2.73 (d, *J* = 13.3 Hz, 1H), 1.10 (s, 3H), 0.94 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 177.20, 172.30, 158.21 , 131.92 , 129.81 , 113.42 , 59.58 , 55.30 , 43.79 (d, *J* = 149.7 Hz), 39.21, 28.17 , 24.77 , 24.61. **HRMS** (EI-TOF) calcd for $C_{17}H_{21}NO_5$ (M-H$^+$): 318.1347, found: 318.1346.

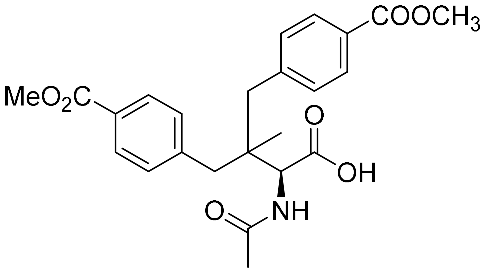


The title compound **7j'** was prepared following General Procedure A and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7j'** was obtained as a white solid (18.7mg, 14%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.13 (d, *J* = 8.6 Hz, 2H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.85 – 6.78 (m, 4H), 4.78 (s, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.43 – 3.32 (m, 2H), 2.94 (d, *J* = 11.2 Hz, 1H), 2.72 (s, 4H), 2.45

(d, *J* = 13.6 Hz, 1H), 0.82 (s, 3H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 177.18 , 158.36 , 158.15 , 132.27 , 131.61 , 130.04 , 129.57 , 127.55 , 113.80 , 113.34 , 55.27 , 42.52 , 41.97 , 28.17 , 26.69 , 22.63 . **HRMS** (EI-TOF) calcd for $C_{24}H_{27}NO_6$ (M-H$^+$): 424.1765, found: 424.1766.



The title compound **7kc** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7k** was obtained as a white solid (15.2 mg, 16%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.94 (d, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.24 (d, *J* = 10.8 Hz, 1H), 4.60 (d, *J* = 9.2 Hz, 1H), 3.90 (s, 3H), 2.72 (s, 2H), 2.07 (s, 3H), 0.95 (s, 6H). ^{13}C NMR (101 MHz, CDCl$_3$) δ 171.33 , 167.38 , 143.24 , 131.07 , 129.41 , 128.52 , 52.31 , 44.89 , 38.38 , 23.79 , 23.44 (d, *J* = 4.3 Hz). **HRMS** (EI-TOF) calcd for $C_{16}H_{20}NO_4$ (M-H+):307.1347, found: 306.1347.



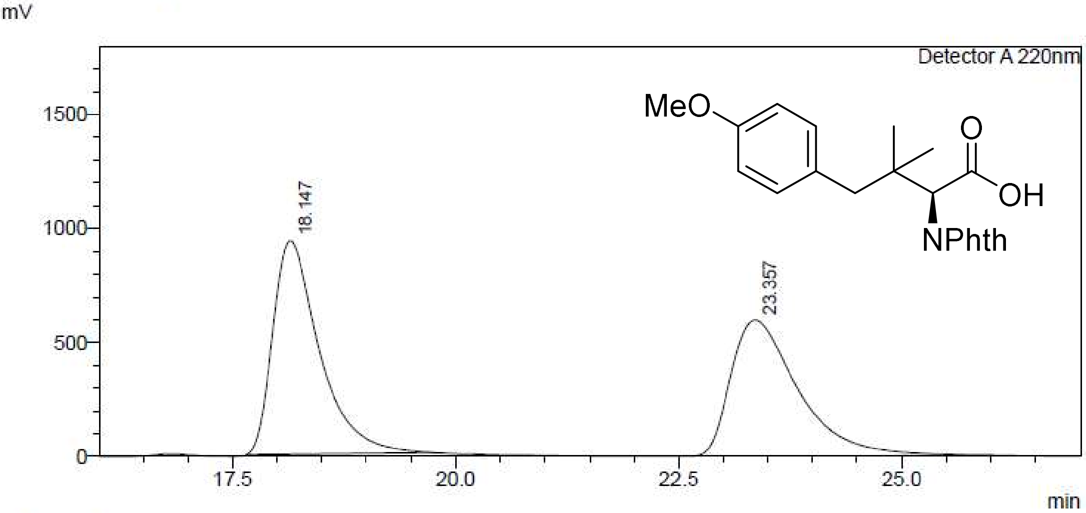
The title compound **7kc’** was prepared following General Procedure B and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7kc’** was obtained as a white solid (7.4 mg, 6%). ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.97 (dd, *J* = 8.2, 3.2 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.16 (d, *J* = 9.0 Hz, 1H), 4.57 (d, *J* = 9.1 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.08 (d, *J* = 13.1 Hz, 1H), 2.96 (d, *J* = 13.2 Hz, 1H), 2.82 (d, *J* = 13.4 Hz, 1H), 2.65 (d, *J* = 13.2 Hz, 1H), 1.94 (s, 3H), 0.93 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.24 , 167.19 , 167.13 , 142.62 , 131.29 , 131.04 , 129.59 , 129.54 , 128.80 , 128.76, 128.75, 52.29 , 42.62 , 41.54 , 29.47 , 27.36 , 23.23 , 22.14 . **HRMS** (EI-TOF) calcd for $C_{24}H_{26}NO_6$ (M-H+):440.1715, found: 440.1715.

2.6 Gram-Scale Synthesis of 3a

Gram-scale synthesis was carried out following the general procedure as described in Section 2.3 using **1** (10 mmol, 2.61 g). **3a** was obtained in 59% yield, 2.18 g. Enantiomeric excess was determined by HPLC with a Daicel Chiralpak AD-H, *n*-hexane/2-propanol = 50/50, v = 0.5 mL·min^{-1}, λ = 254 nm, t (minor) = 18.020 min, t (major) = 22.609 min, 99% ee.

3a: AD-H, hexane/*i*PrOH = 50/50, rate = 0.5 mL/min, 254 nm

<Chromatogram>



<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.147	33978373	935451	52.077		M	
2	23.357	31268572	594979	47.923		M	
Total		65246945	1530430				

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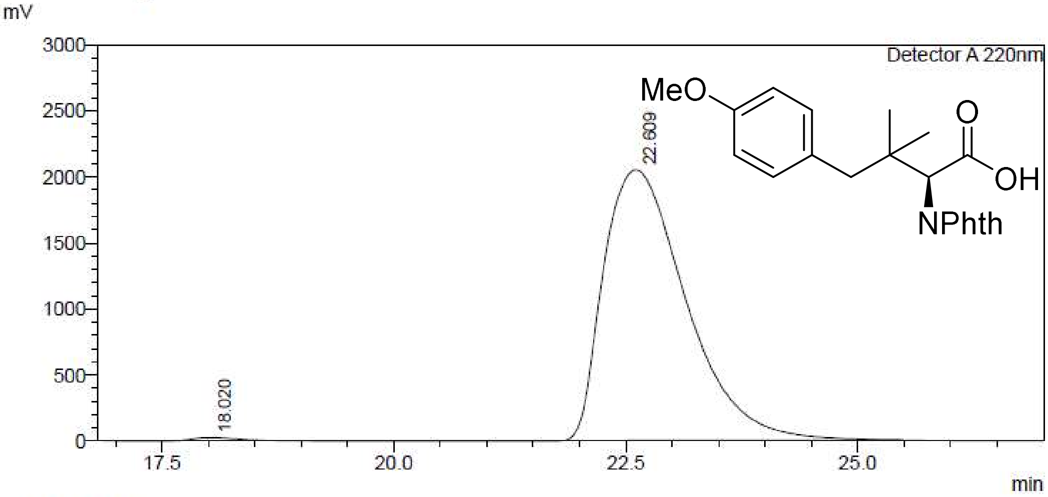


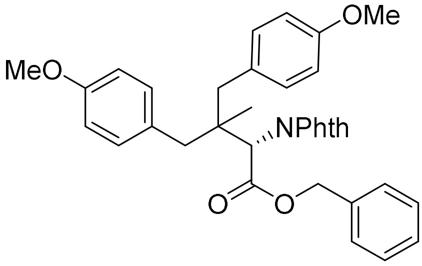
<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.020	734544	23555	0.577		M	
2	22.609	126571320	2045365	99.423		M	
Total		127305863	2068920				

3a’ was obtained in 12% yield, 0.59 g. Attempts to determined the ee value using HPLC failed after trying different types of chiral column. Then **3a’** was converted to the corresponding benzyl ester **11** to determine the ee value.

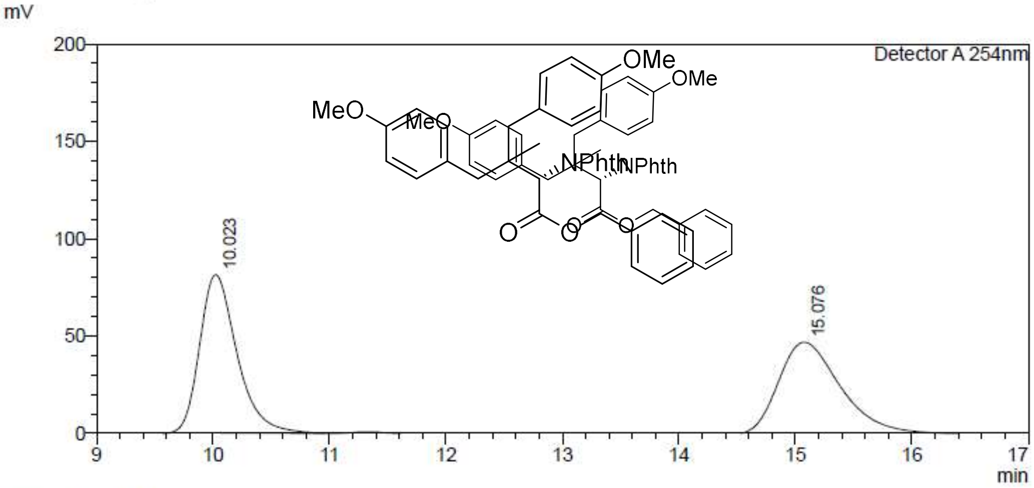
Preparation of Benzyl Ester 12



3a’ (47.3 mg, 0.1 mmol), $KHCO_3$ (20 mg, 0.2 mmol) and benzyl bromide (24 uL) in 2 mL DMF was stirred at rt for 2 h. Then the mixture was partitioned between H_2O (20 mL) and EtOAc (10 mL), The organic phase was dried over anhydrous Na_2SO_4, filtered, and the residue was purified by silica gel column chromatography, giving the benzyl ester **12** as a white solid (53.5mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.76 (m, 2H), 7.76 – 7.67 (m, 2H), 7.31 (s, 5H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.90 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 5.32 (d, *J* = 12.3 Hz, 1H), 5.08 (d, *J* = 12.2 Hz, 1H), 4.77 (s, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.44 (dd, *J* = 13.6, 8.7 Hz, 2H), 2.92 (d, *J* = 13.5 Hz, 1H), 2.44 (d, *J* = 13.5 Hz, 1H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.31 , 168.24 , 158.31 , 158.14 , 135.58 , 134.34 , 132.29 , 131.84 , 131.58 , 130.20 , 129.71 , 128.63 , 128.59 , 128.44 , 123.65 , 113.72 , 113.31 , 67.21 , 57.06 , 55.33 , 55.26 , 42.88 , 42.21 , 41.83 , 23.00 . **HRMS** (EI-TOF) calcd for $C_{35}H_{33}NO_6$ ($M+Na^+$): 586.2200, found: 586.2197. Enantiomeric excess was determined by HPLC with a Daicel Chiralpak IC, *n*-hexane/2-propanol = 70/30, v = 0.8 mL·min^{-1}, λ = 254 nm, t (minor) = 9.864 min, t (major) = 14.573 min, 96.2% ee.

12: IC, hexane/*i*PrOH = 70/30, rate = 0.8 mL/min, 254 nm

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.023	1803333	81233	49.714		M	
2	15.076	1824107	47675	50.286			
Total		3627441	128908				

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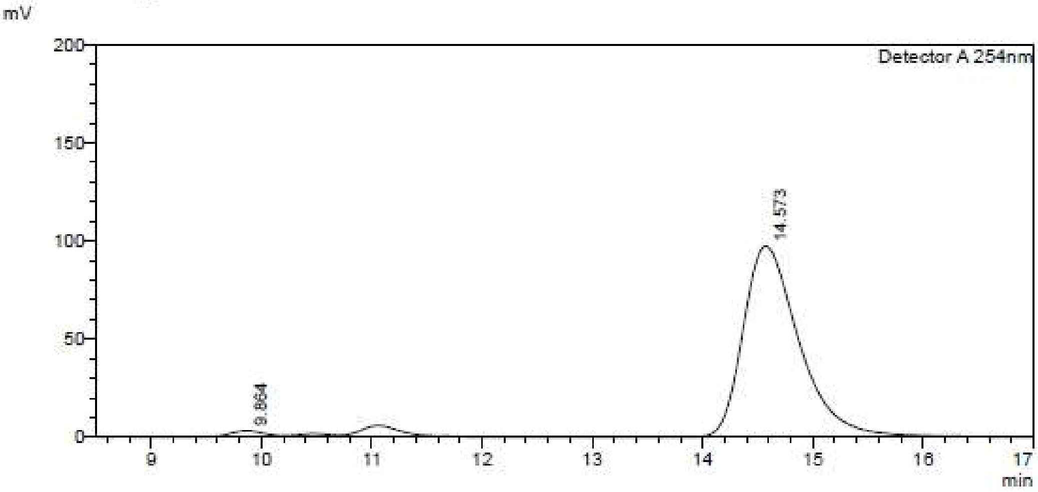


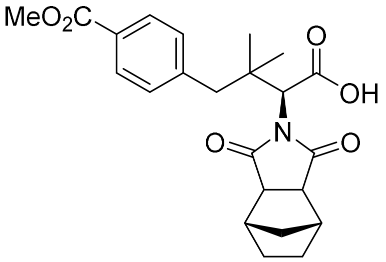
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.864	66449	3102	1.891			
2	14.573	3446735	97255	98.109			
Total		3513184	100357				

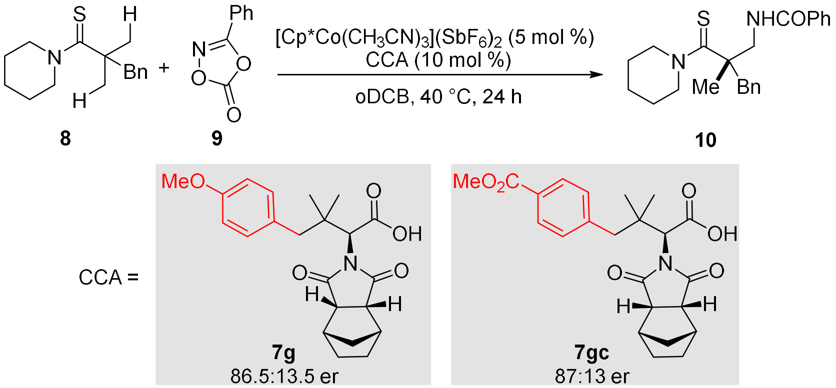
2.7 Co(III)-Catalyzed Enantioselective C(sp^3)-H amidation of Thioamide 8

2.7.1 Preparation of Chiral Acid 7gc



The title compound **7gc** was prepared under the optimized conditions and purified by preparative TLC (petroleum ether: ethyl acetate: formic acid = 3: 1: 1%). **7gc** was obtained as a white solid (70.6mg, 57%)^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 4.61 (s, 1H), 3.90 (s, 3H), 3.17 (s, 2H), 3.10 (d, *J* = 12.9 Hz, 1H), 2.88 (d, *J* = 12.8 Hz, 1H), 2.78 (s, 2H), 1.70 – 1.48 (m, 5H), 1.41 – 1.29 (m, 1H), 1.07 (s, 3H), 0.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 178.57 , 171.73 , 167.37 , 143.64 , 131.09 , 129.28 , 128.29 , 52.21 , 49.02 , 45.01 , 42.79 , 39.67 , 39.48 , 39.17 , 24.98 , 24.76 . **HRMS** (EI-TOF) calcd for $C_{23}H_{27}NO_6$ (M-H$^+$): 412.1765, found: 412.1768.

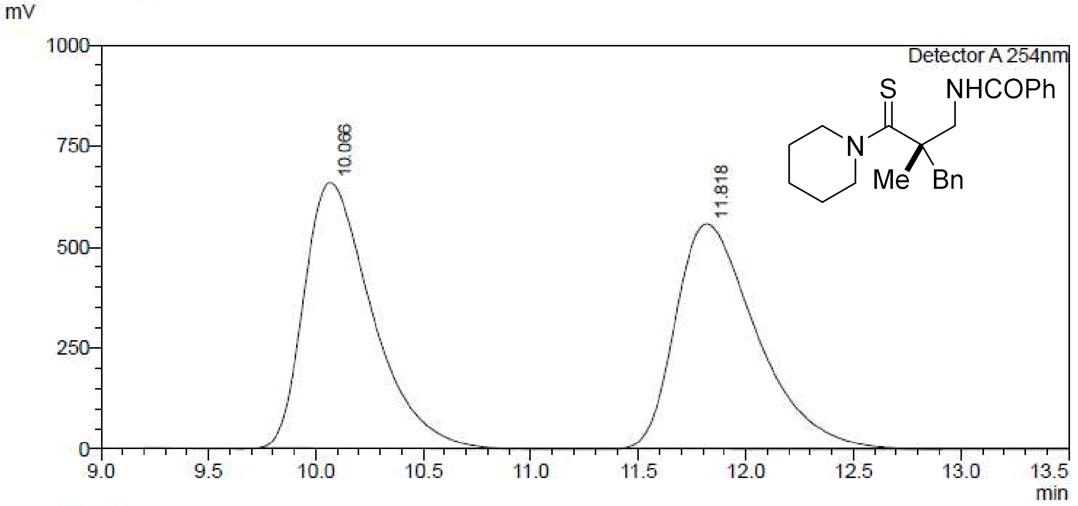
2.7.2 Co(III)-Catalyzed Enantioselective C(sp3)-H amidation of Thioamide 8



To an oven-dried 50 mL Schlenk tube were added **8** (0.05 mmol), **9** (0.06 mmol), $Cp^*Co(CH_3CN)_3](SbF_6)_2$ (0.0025 mmol), and chiral amino acid (0.005 mmol) in the o-DCB (0.05ml) under N_2 atmosphere. The title compound **10**^{3} was purified by preparative TLC (petroleum ether: ethyl acetate = 3: 1). **10** was isolated as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (brs, 1H), 7.80 – 7.75 (m, 2H), 7.51 – 7.36 (m, 3H), 7.34 – 7.20 (m, 5H), 4.20 – 4.03 (m, 4H), 4.03 – 3.83 (m, 2H), 3.19 (d, *J* = 14.2 Hz, 1H), 2.98 (d, *J* = 14.2 Hz, 1H), 1.83 – 1.73 (m, 6H), 1.39 (s, 3H). **7g** as chiral ligand: **10** (15.2mg, 76%, 86.5:13.5 er); **7gc** as chiral ligand: **10** (13.3mg, 69%, 87:13 er).

HPLC Spectra for 10: AD-H, hexane/*i*PrOH = 70/30, rate = 1 mL/min, 254 nm

<Chromatogram>



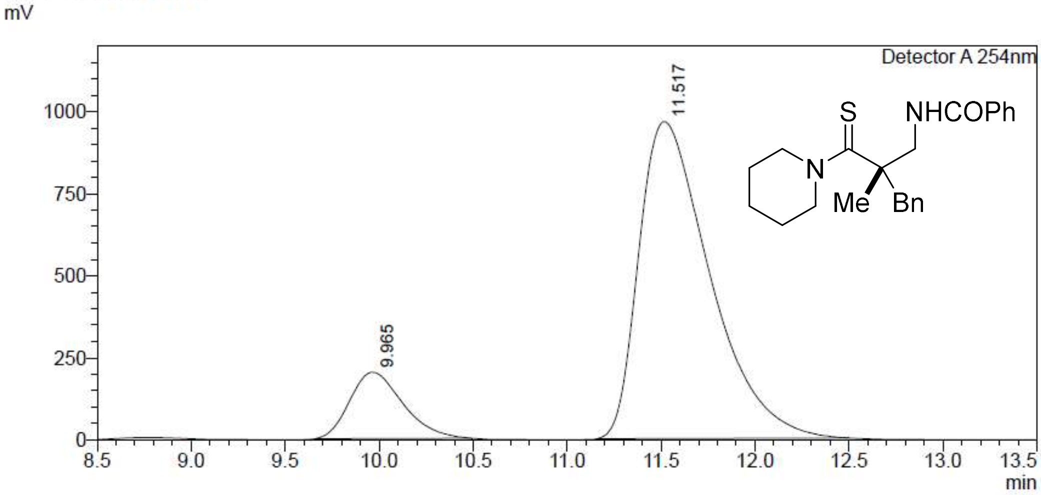
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.066	14503431	657873	49.740		M	
2	11.818	14654958	557287	50.260		M	
Total		29158389	1215159				

7g as chiral ligand

<Chromatogram>



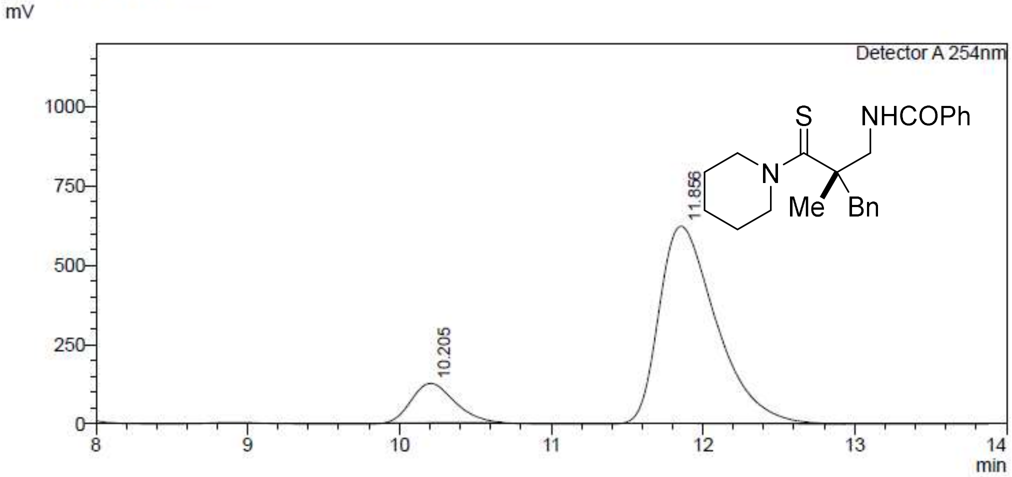
<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.965	3963192	201926	13.509		M	
2	11.517	25373702	965599	86.491		M	
Total		29336894	1167524				

7gc as chiral ligand

<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.205	2450332	123850	13.110		M	
2	11.856	16240060	620983	86.890		M	
Total		18690392	744833				

3. References

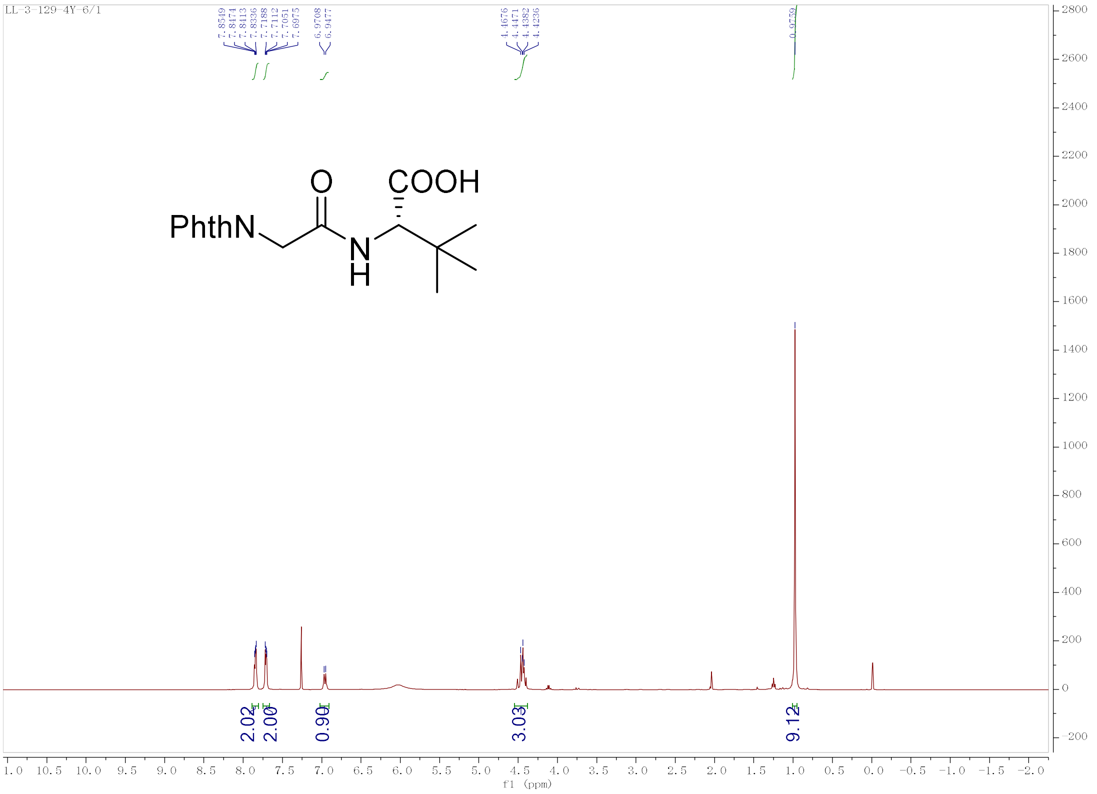
[1] Gong, W.; Zhang, G.-F.; Liu, T.; Giri, R.; Yu, J.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 16940.

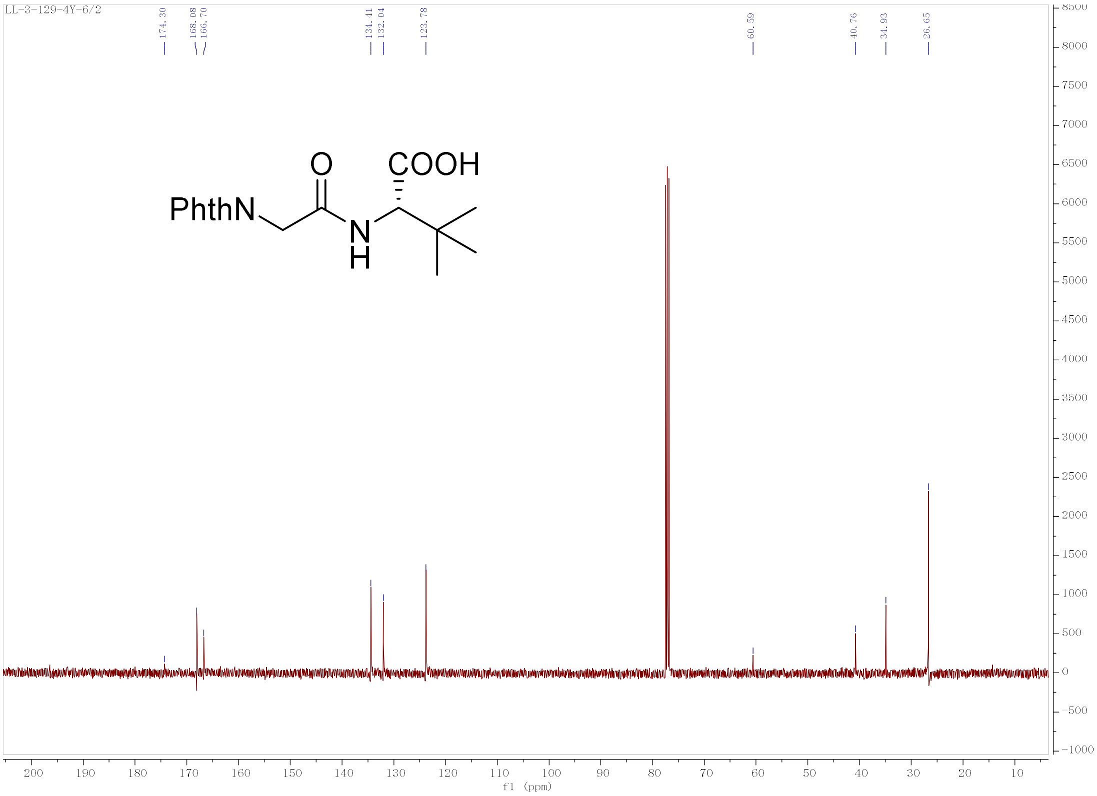
[2] Adly, F. G.; Gardinar, M. G.; Ghanem, A. *Chem. Eur. J.* **2016**, 22, 3447.

[3] Fukagawa, S.; Kato, Y.; Tanaka, R.; Kojima, M.; Yoshino, T.; Matsunaga, S, *Angew. Chem. Int. Ed.* **2019**, *131*,1165;

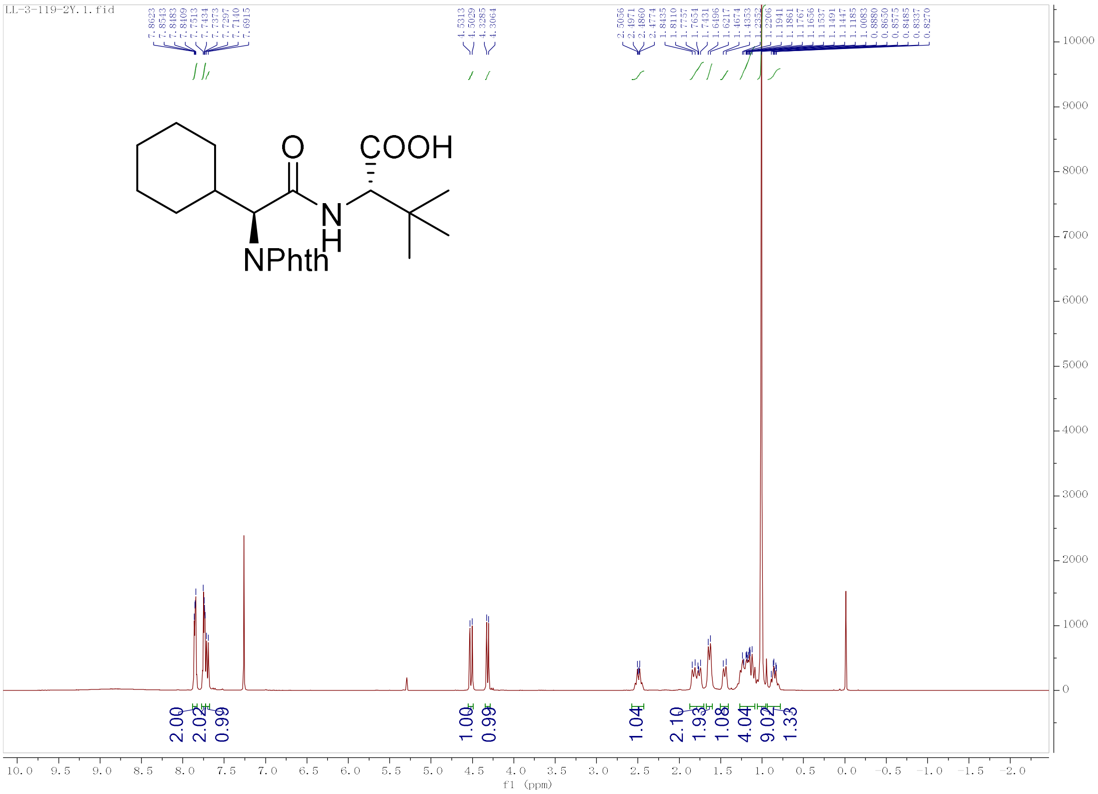
4. NMR Spectra

4a





4b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7.7140
7.6915
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4.5029
4.3285
4.3064
2.5056
2.4971
2.4860
2.4774
1.8435
1.8110
1.7757
1.7654
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1.6496
1.6217
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1.4353
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1.1941
1.1861
1.1767
1.1656
1.1537
1.1491
1.1447
1.1185
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0.8485
0.8337
0.8270
O
COOH
N
H
NPhth
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2.02
0.99
1.00
0.99
1.04
2.10
1.93
1.08
4.04
9.02
1.33
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
10.0
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
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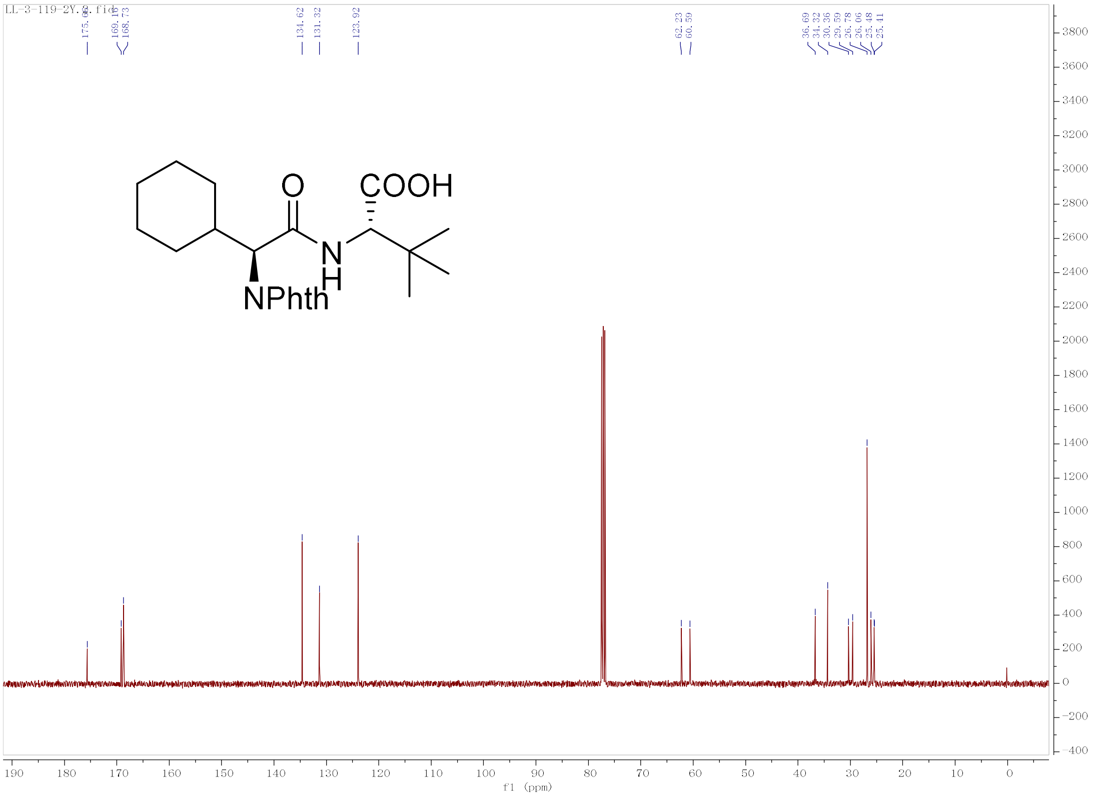
-1.5
-2.0
f1 (ppm)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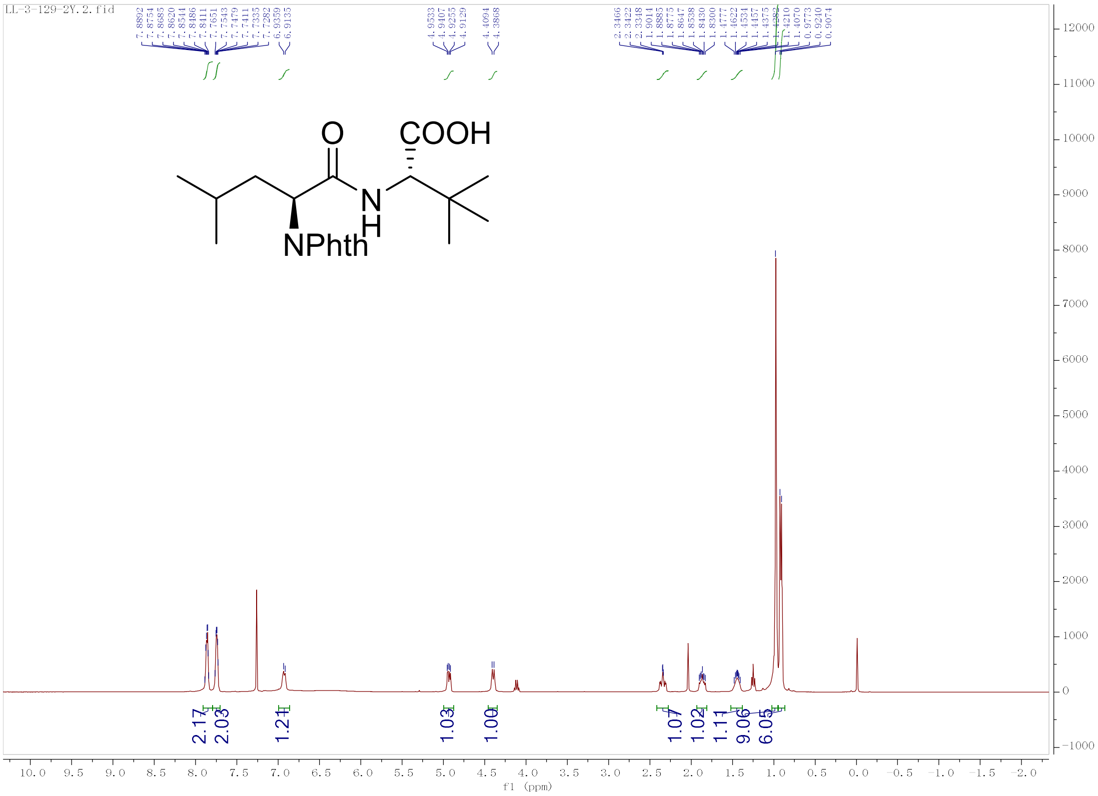
131.32
123.92
62.23
60.59
36.69
34.32
30.36
29.59
26.78
26.06
25.48
25.41
O
COOH
N
H
NPhth
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

4c



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7.7411
7.7335
7.7282
6.9359
6.9135
4.9533
4.9407
4.9255
4.9129
4.4094
4.3868
2.3466
2.3422
2.3348
1.9014
1.8885
1.8775
1.8647
1.8538
1.8430
1.8300
1.4777
1.4622
1.4534
1.4457
1.4375
1.4210
1.4070
0.9773
0.9240
0.9074
O
COOH
N
H
NPhth
2.17
2.03
1.21
1.03
1.00
1.07
1.02
1.11
9.06
6.05
10.0
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
-0.5
-1.0
-1.5
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f1 (ppm)
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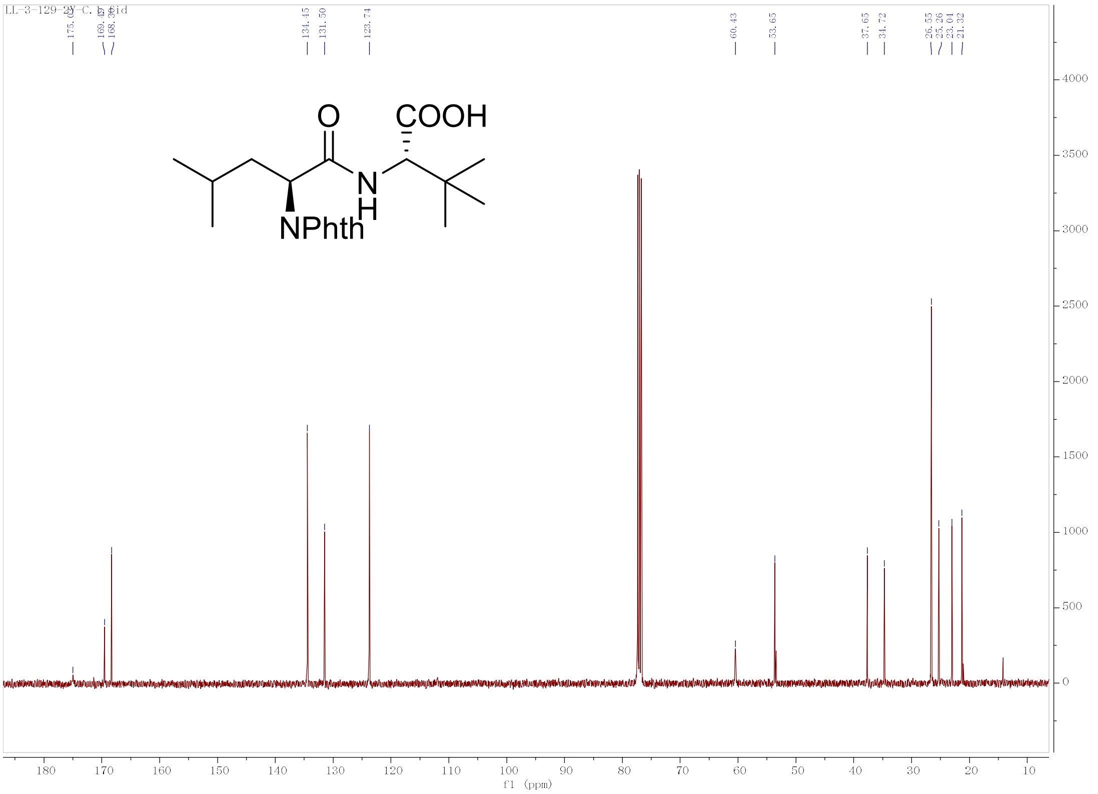
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000



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168.36
134.45
131.50
123.74
60.43
53.65
37.65
34.72
26.55
25.26
23.04
21.32
O
COOH
N
H
NPhth
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
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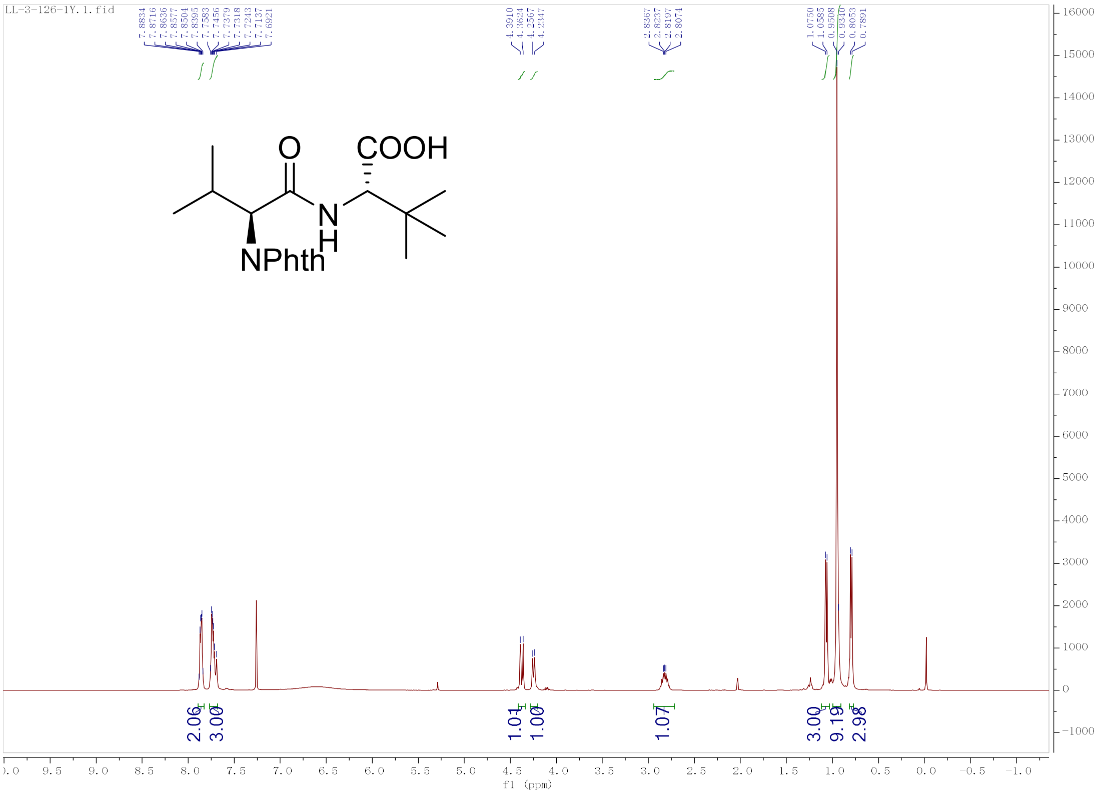
3500
3000
2500
2000
1500
1000
500
0

4d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7.8395
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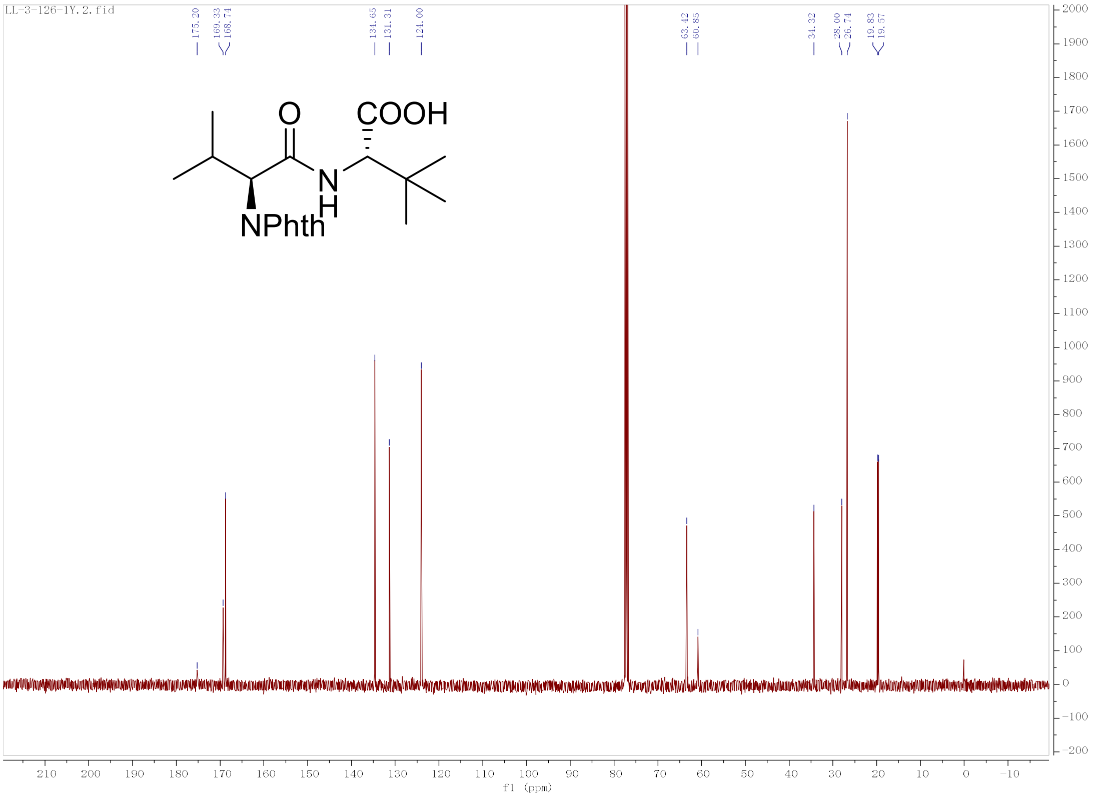
7.7379
7.7318
7.7243
7.7137
7.6921
4.3910
4.3624
4.2567
4.2347
2.8367
2.8237
2.8197
2.8074
1.0750
1.0585
0.9508
0.9340
0.8053
0.7891
O
COOH
N
H
NPhth
2.06
3.00
1.01
1.00
1.07
3.00
9.19
2.98
f1 (ppm)
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
−1000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168.74
134.65
131.31
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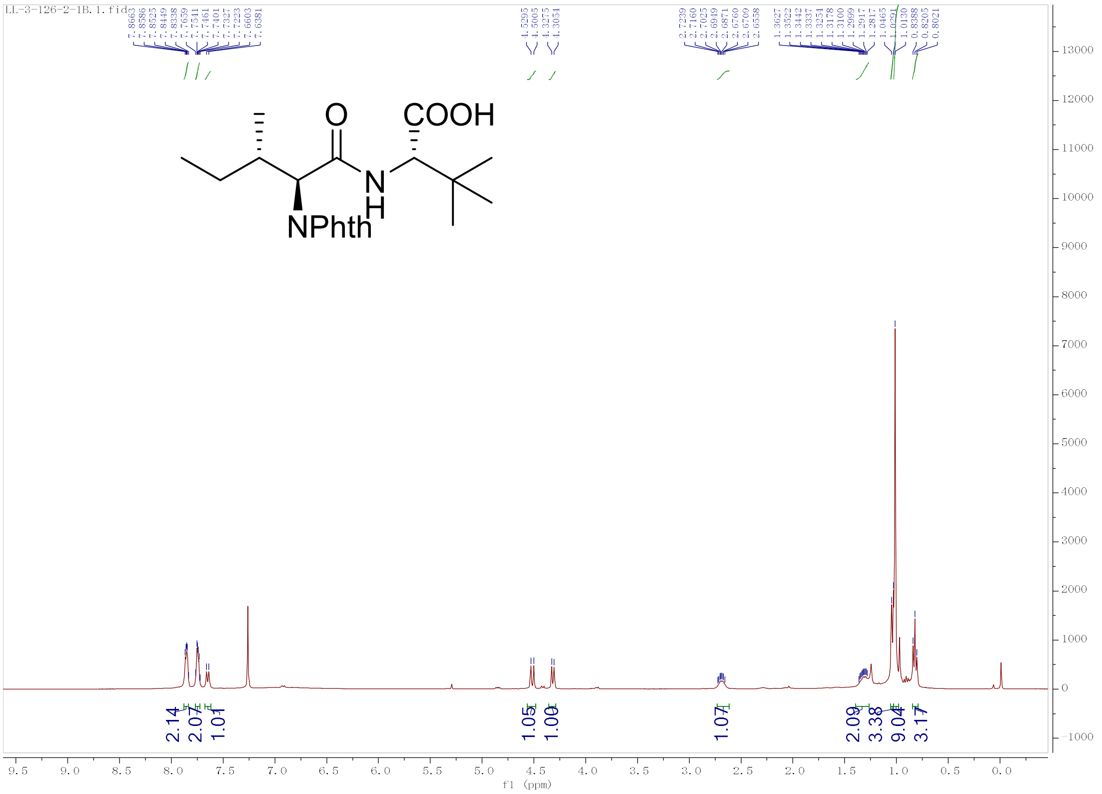
63.42
60.85
34.32
28.00
26.74
19.83
19.57
O
COOH
N
H
NPhth
f1 (ppm)
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
−200

4e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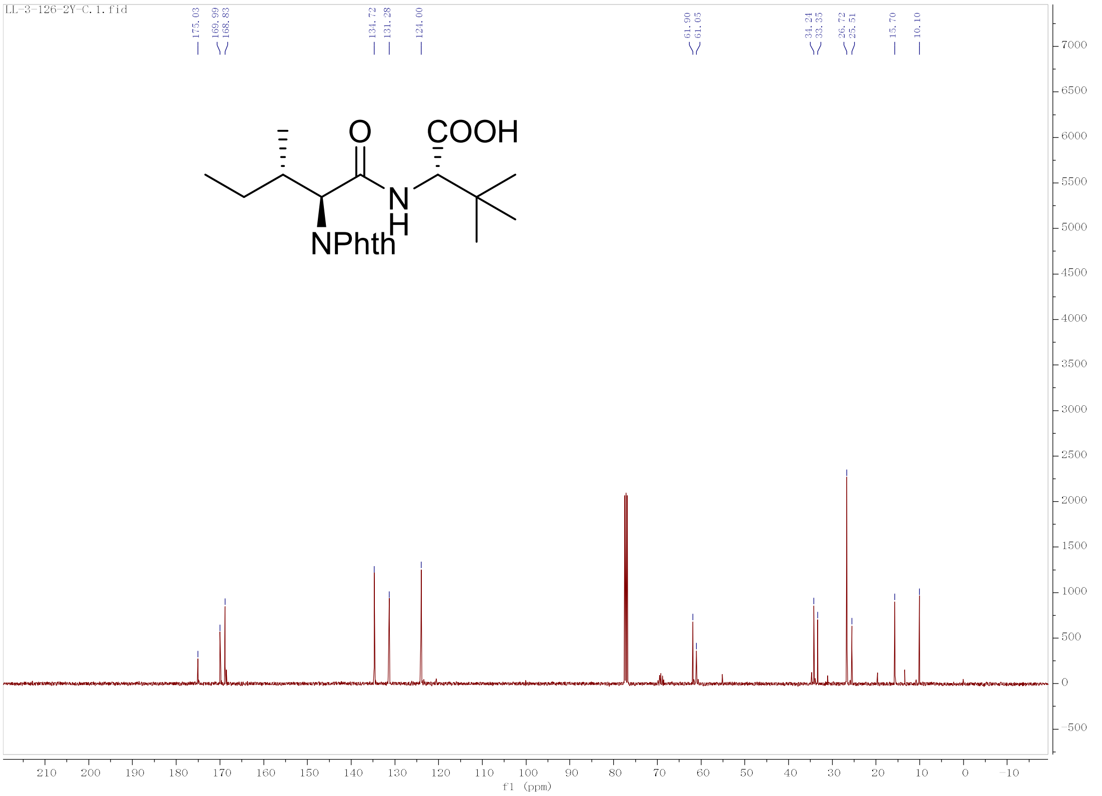
7.8338
7.7659
7.7541
7.7461
7.7401
7.7327
7.7223
7.6603
7.6381
4.5295
4.5005
4.3275
4.3051
2.7239
2.7160
2.7025
2.6949
2.6871
2.6760
2.6709
2.6558
1.3627
1.3522
1.3442
1.3337
1.3251
1.3178
1.3100
1.2999
1.2917
1.2817
1.0465
1.0291
1.0130
0.8388
0.8205
0.8021
O
COOH
N
H
NPhth
2.14
2.07
1.01
1.05
1.00
1.07
2.09
3.38
9.04
3.17
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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)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61.90
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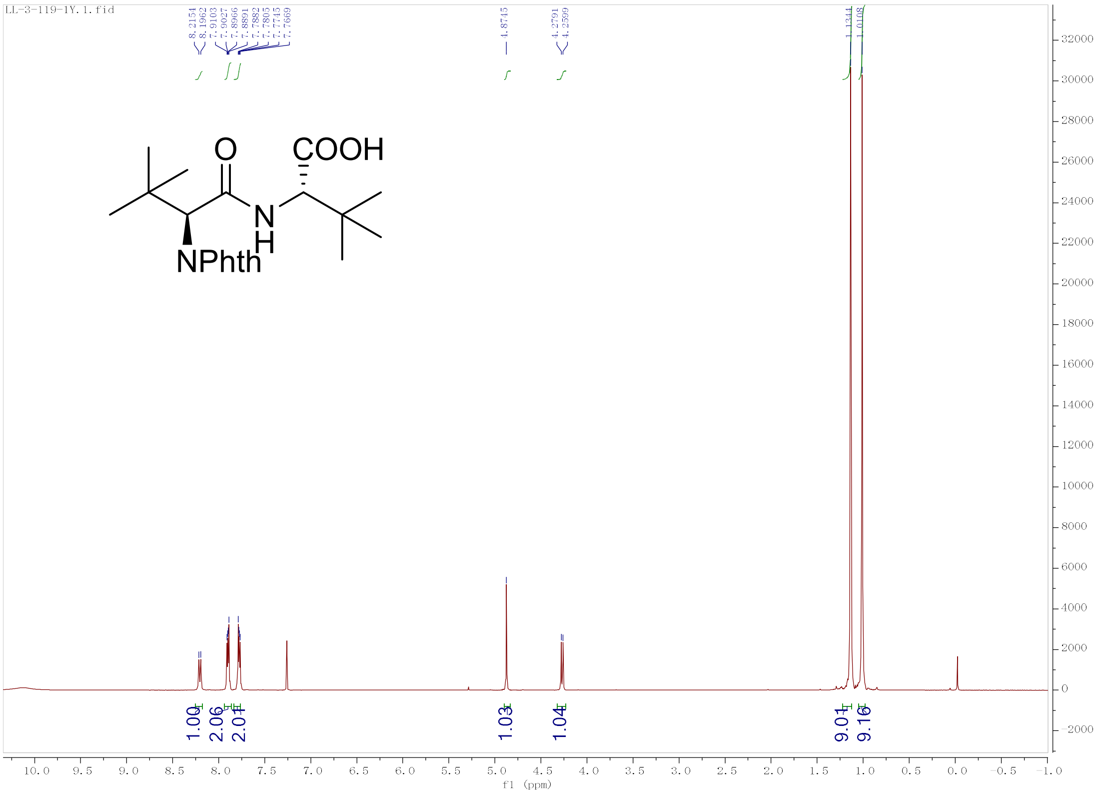
34.21
33.35
26.72
25.51
15.70
10.10
O
COOH
N
H
NPhth
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4f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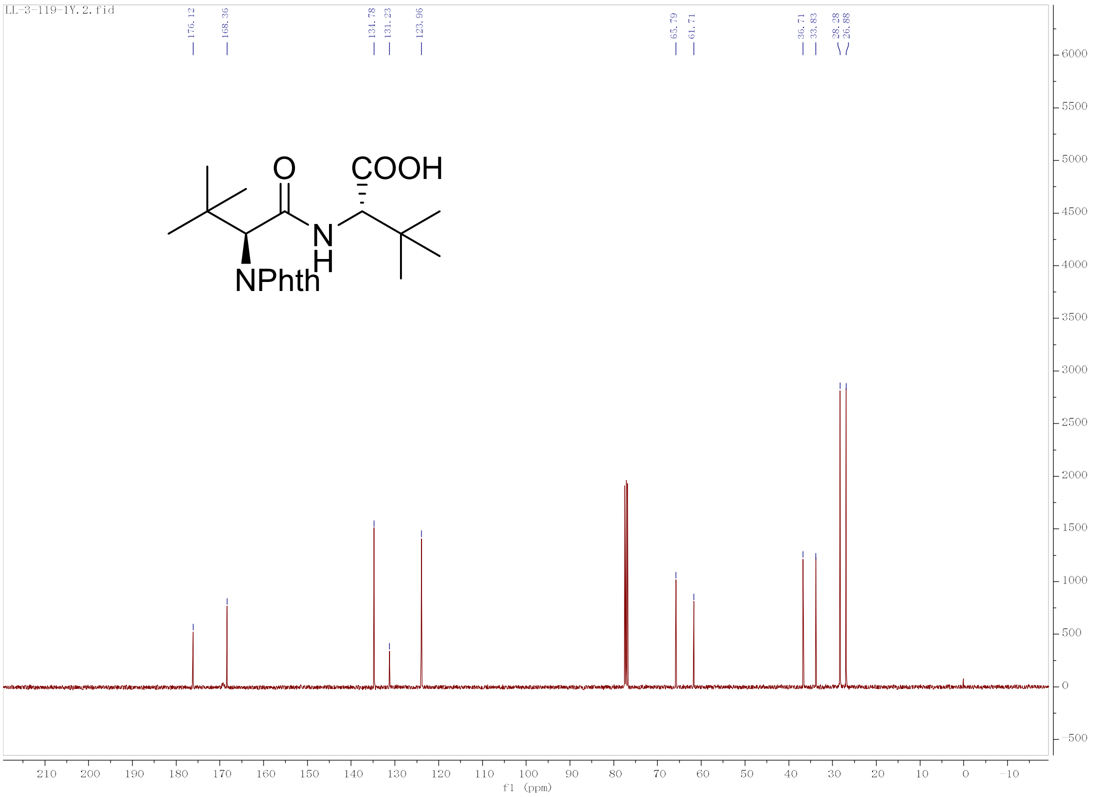
7.7805
7.7745
7.7669
4.8745
4.2791
4.2599
1.1344
1.0108
O
COOH
N
H
NPhth
1.00
2.06
2.01
1.03
1.04
9.01
9.16
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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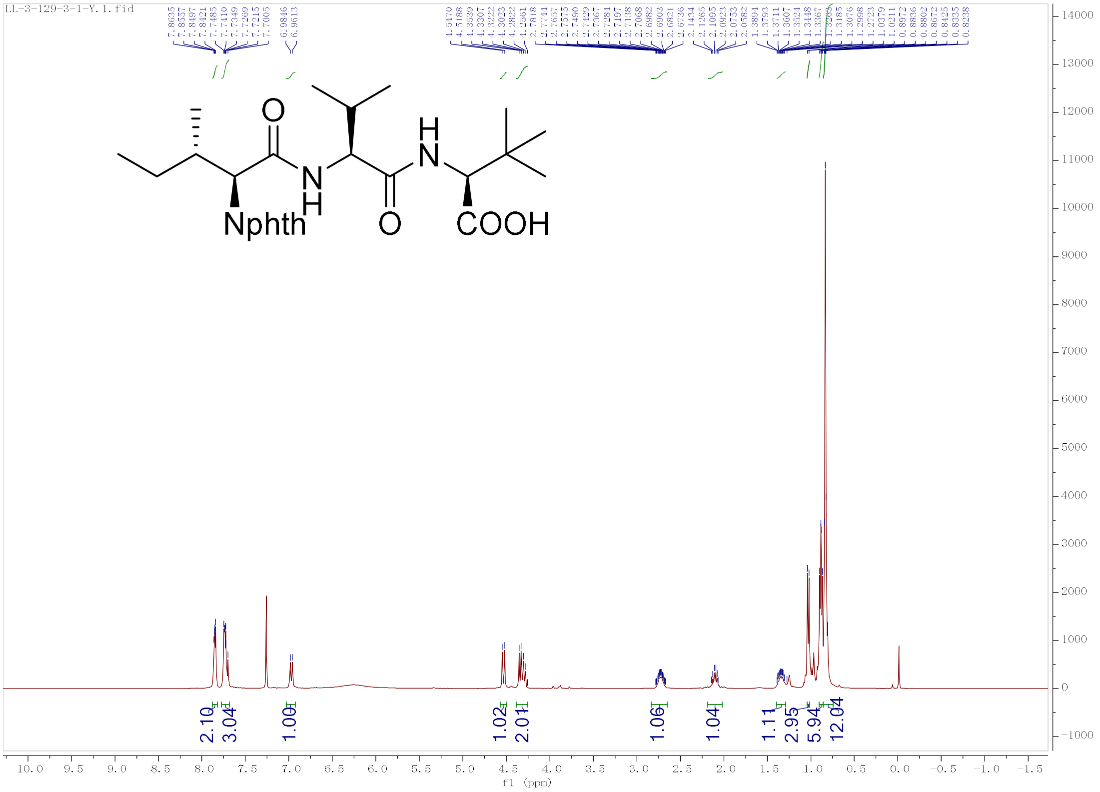
168.36
134.78
131.23
123.96
65.79
61.71
36.71
33.83
28.28
26.88
O
COOH
N
H
NPhth
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

4g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7.7269
7.7215
7.7005
6.9846
6.9613
4.5470
4.5188
4.3539
4.3307
4.3222
4.3023
4.2822
4.2561
2.7818
2.7744
2.7657
2.7575
2.7490
2.7429
2.7367
2.7284
2.7197
2.7138
2.7068
2.6982
2.6903
2.6821
2.6736
2.1434
2.1265
2.1095
2.0923
2.0753
2.0582
1.3894
1.3793
1.3711
1.3607
1.3524
1.3448
1.3367
1.3263
1.3185
1.3076
1.2998
1.2723
1.0379
1.0211
0.8972
0.8836
0.8802
0.8672
0.8425
0.8335
0.8238
O
N
H
Nphth
H
N
O
COOH
2.10
3.04
1.00
1.02
2.01
1.06
1.04
1.11
2.95
5.94
12.04
10.0
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
-0.5
-1.0
-1.5
f1 (ppm)
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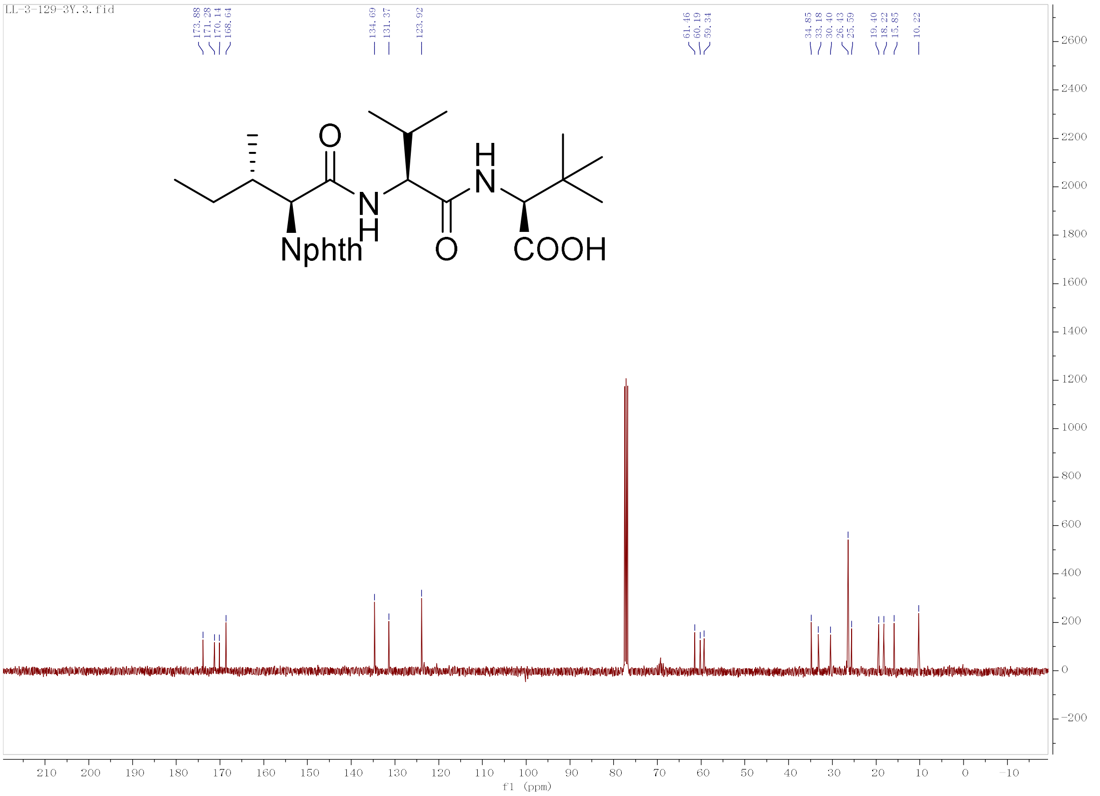
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000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131.37
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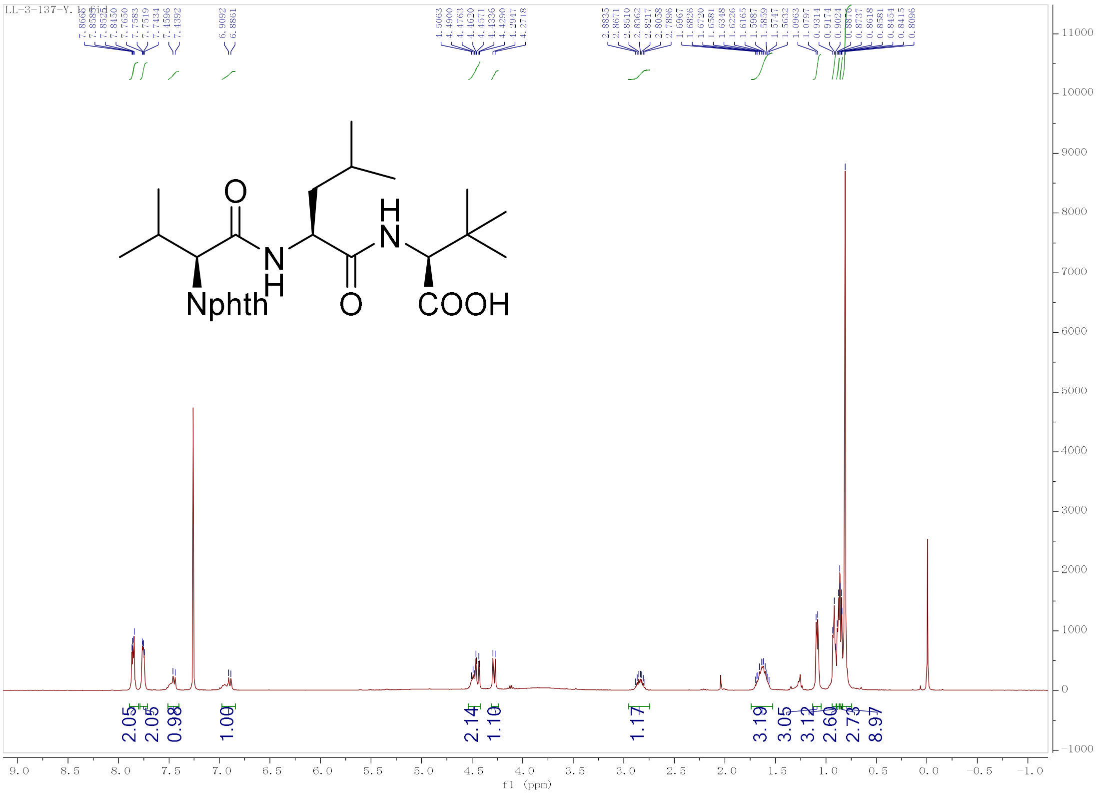
59.34
34.85
33.18
30.40
26.43
25.59
19.40
18.22
15.83
10.22
O
N
H
Nphth
H
N
O
COOH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

4h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7.4596
7.4392
6.9092
6.8861
4.5063
4.4900
4.4763
4.4620
4.4571
4.4336
4.4290
4.2947
4.2718
2.8835
2.8671
2.8510
2.8362
2.8217
2.8058
2.7896
1.6967
1.6826
1.6720
1.6581
1.6348
1.6226
1.6165
1.5987
1.5859
1.5747
1.5632
1.0963
1.0797
0.9314
0.9174
0.9024
0.8876
0.8737
0.8618
0.8581
0.8454
0.8415
0.8096
O
N
H
H
N
Nphth
O
COOH
2.05
2.05
0.98
1.00
2.14
1.10
1.17
3.19
3.05
3.12
2.60
2.73
8.97
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
-0.5
-1.0
f1 (ppm)
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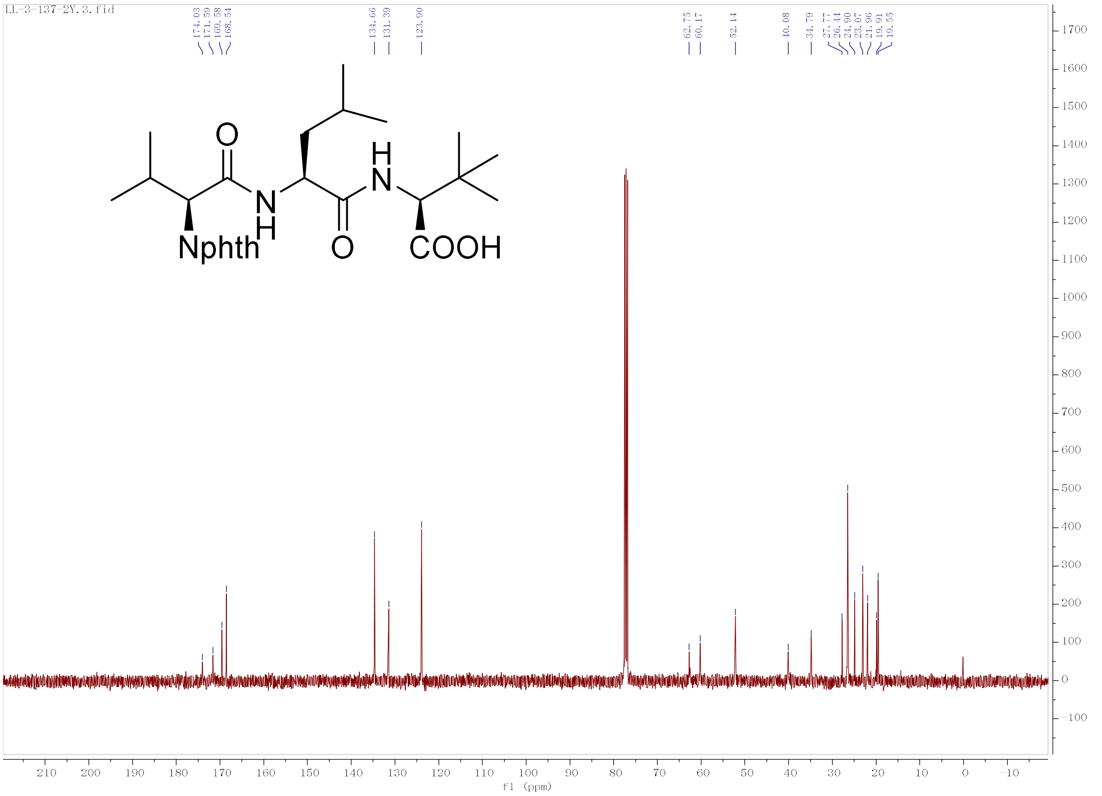
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000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169.58
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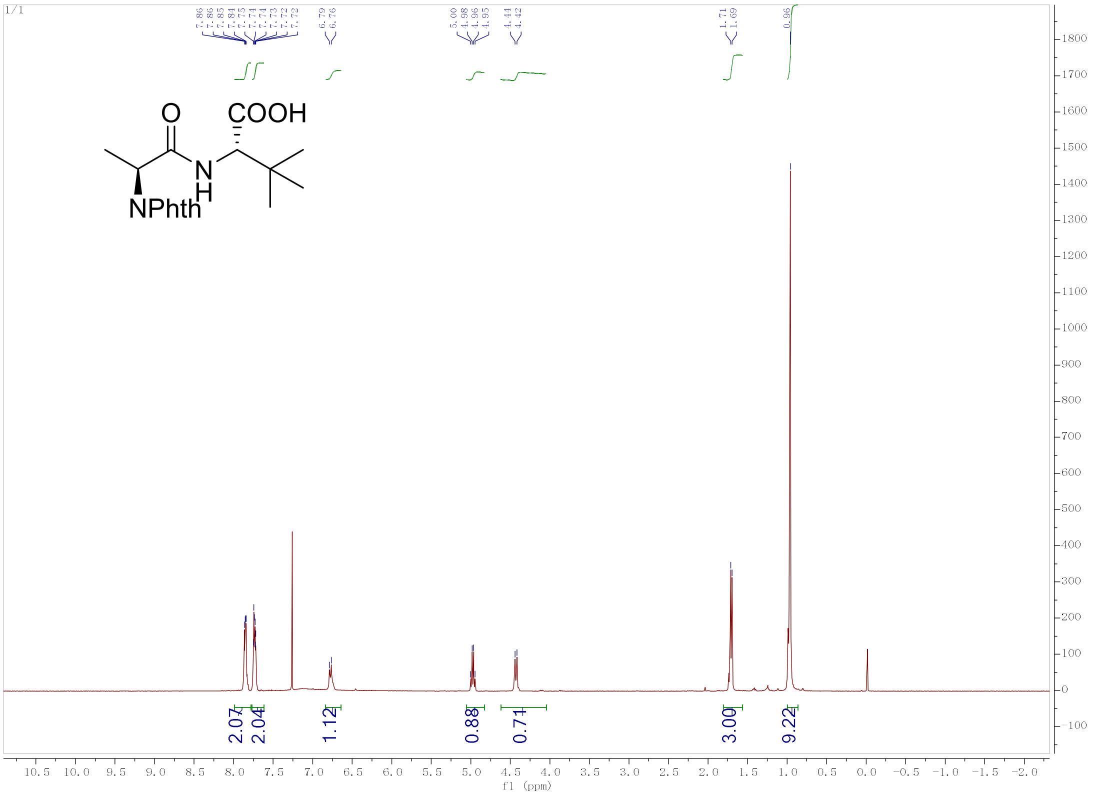
131.39
123.90
62.75
60.17
52.14
40.08
34.79
27.77
26.44
24.90
23.07
21.96
19.91
19.55
O
N
H
H
N
Nphth
O
COOH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

4i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7.86
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7.75
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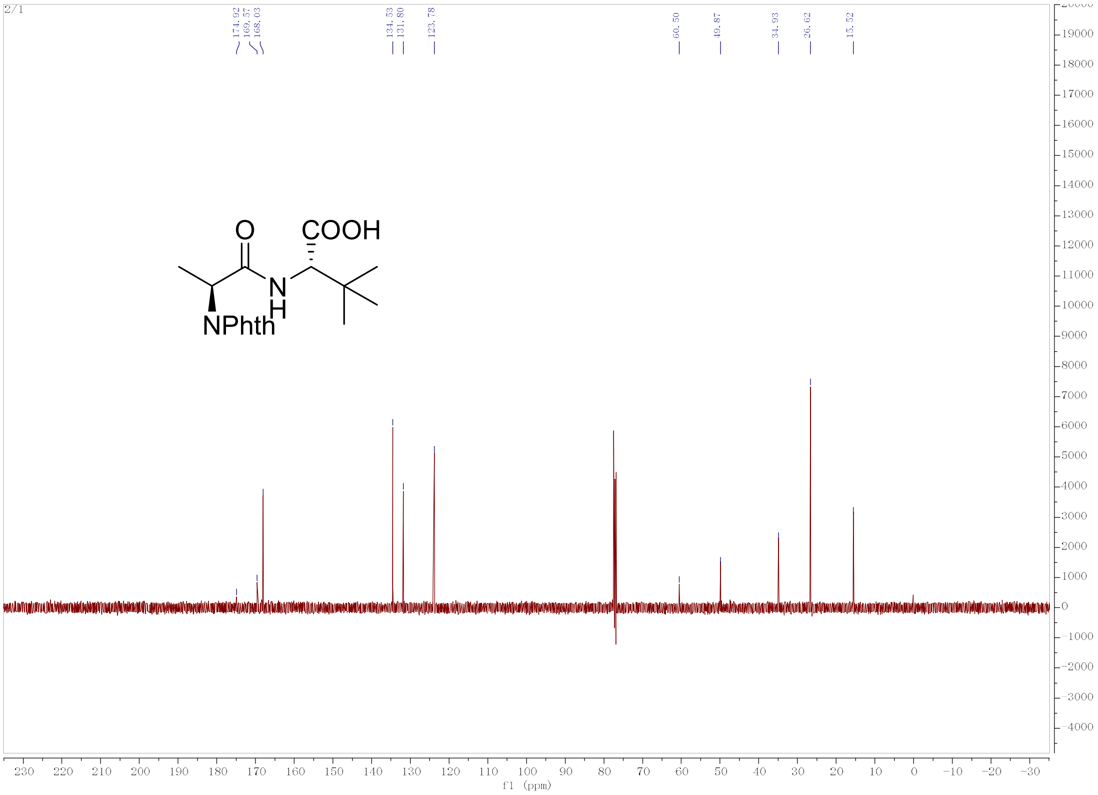
7.74
7.73
7.72
7.72
6.79
6.76
5.00
4.98
4.96
4.95
4.44
4.42
1.71
1.69
0.96
O
COOH
N
H
NPhth
2.07
2.04
1.12
0.88
0.74
3.00
9.22
f1 (ppm)


2/1
174.92
169.57
168.03
134.53
131.80
123.78
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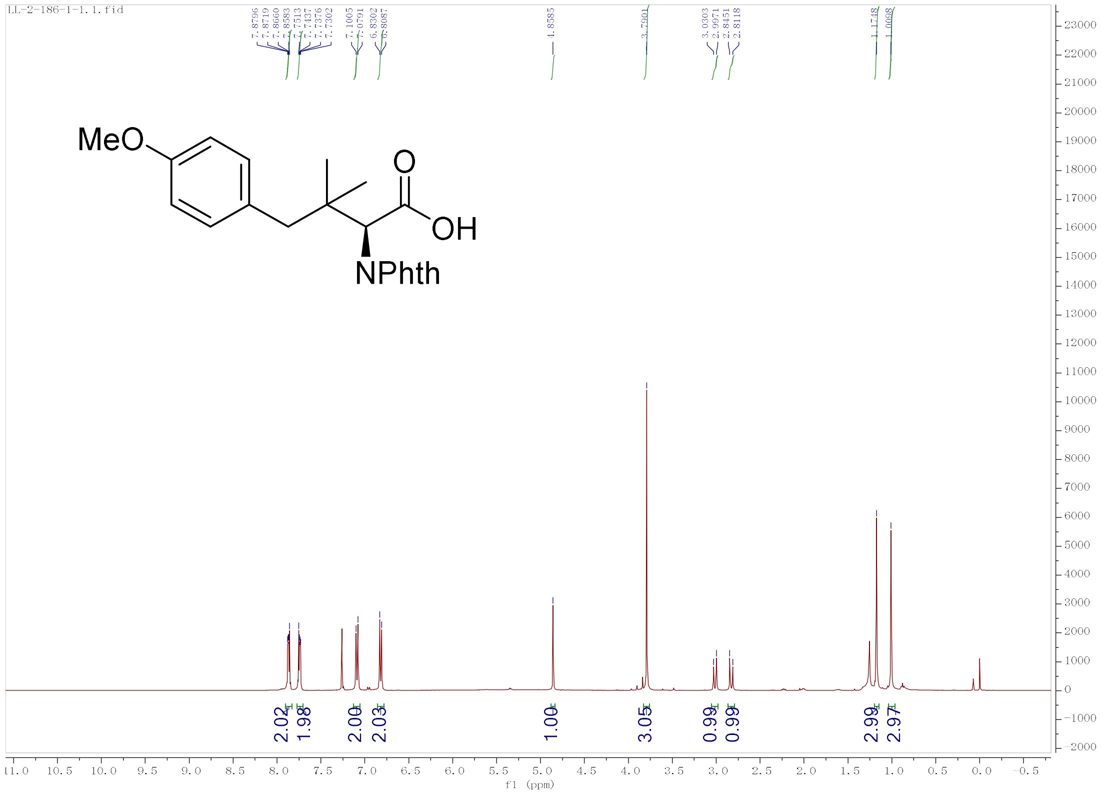
49.87
34.93
26.62
15.52
O
COOH
N
H
NPhth
f1 (ppm)

3a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7.7513
7.7437
7.7376
7.7302
7.1005
7.0791
6.8302
6.8087
4.8585
3.7901
3.0303
2.9971
2.8451
2.8118
1.1748
1.0098
MeO
O
OH
NPhth
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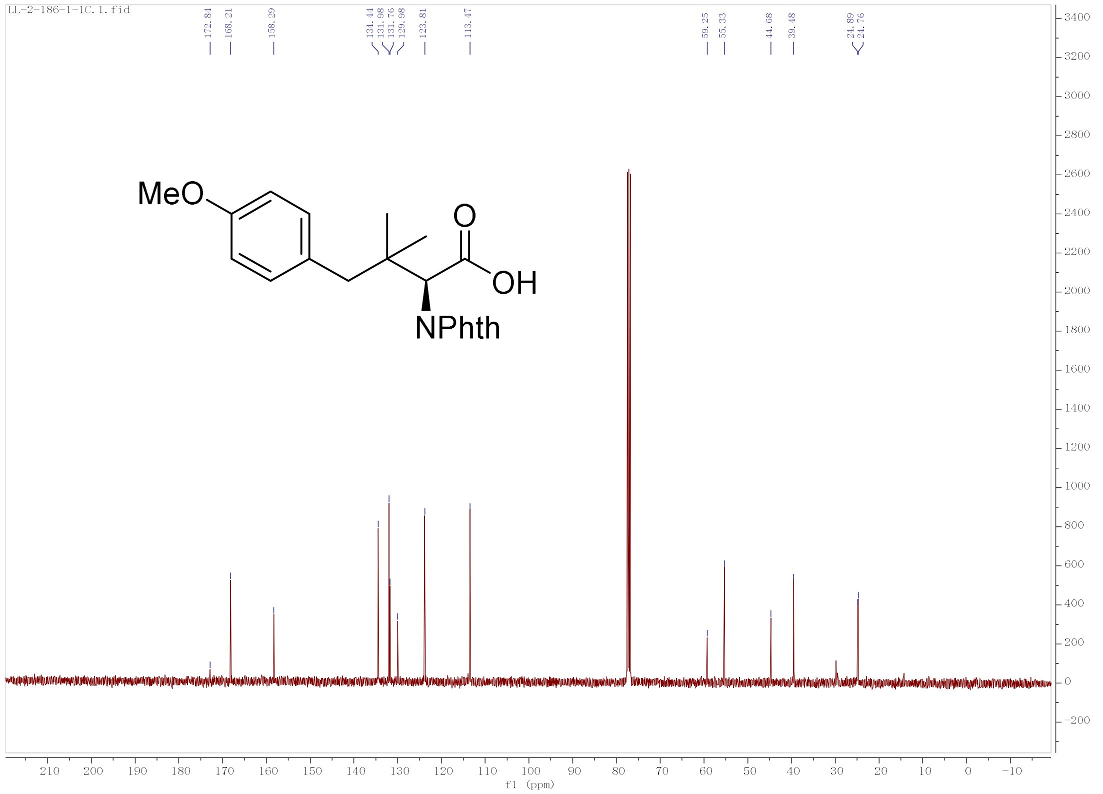
1.98
2.00
2.03
1.00
3.05
0.99
0.99
2.99
2.97
f1 (ppm)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158.29
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131.98
131.76
129.98
123.81
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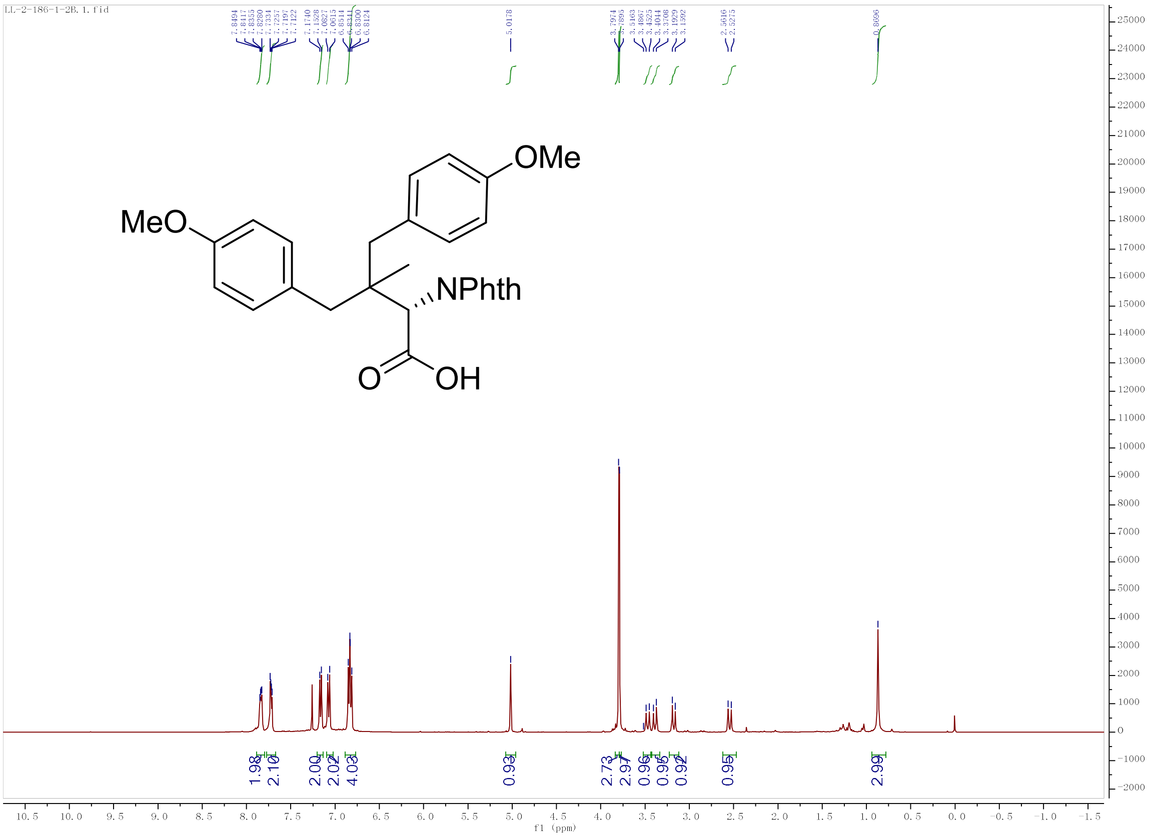
59.25
55.33
44.68
39.48
24.89
24.76
MeO
O
OH
NPhth
f1 (ppm)

3a’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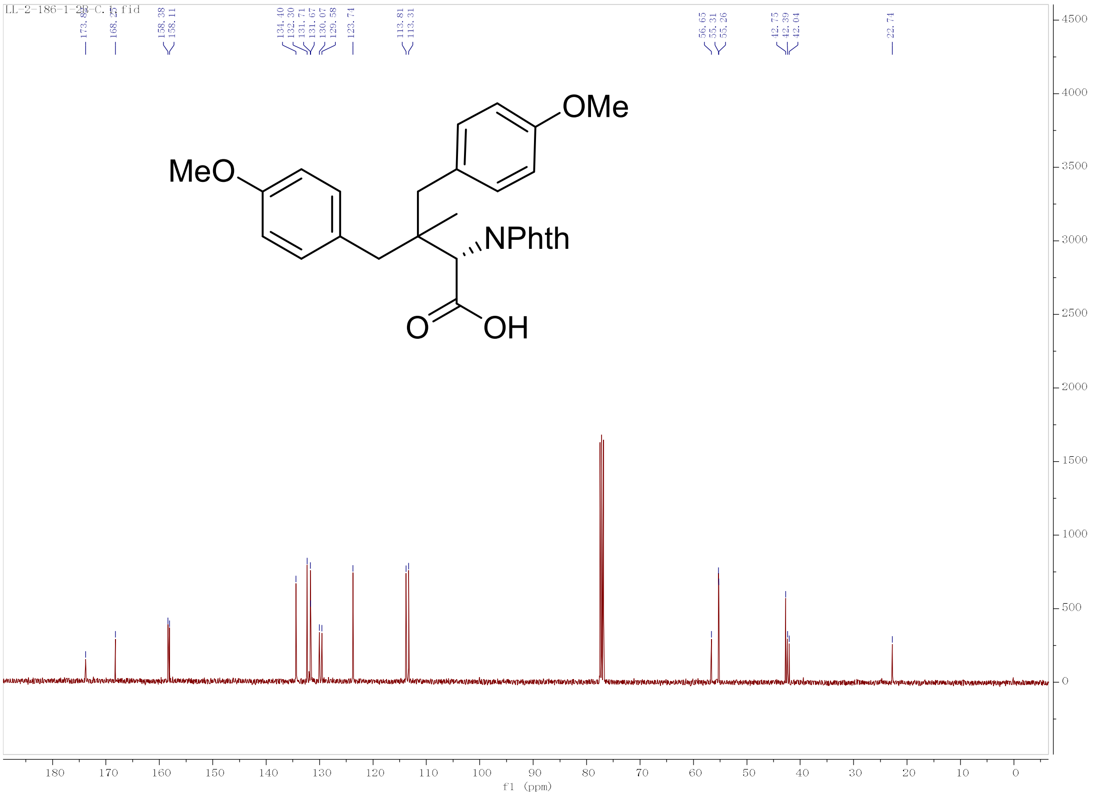
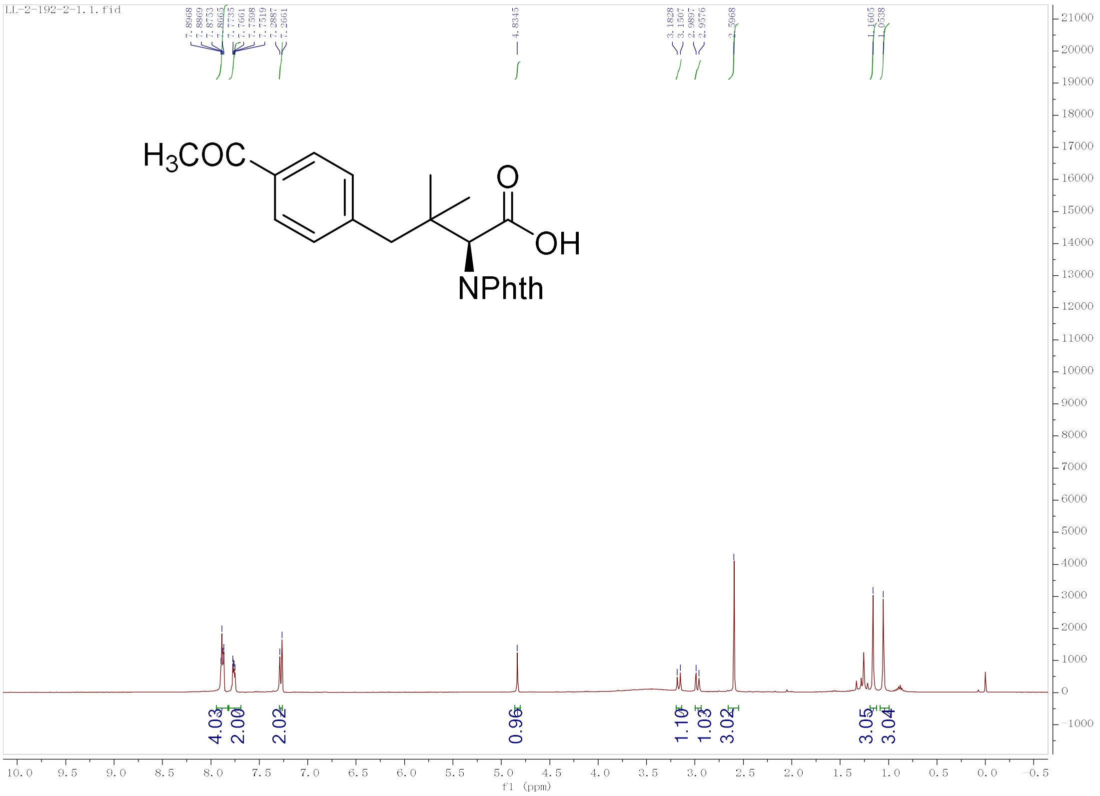
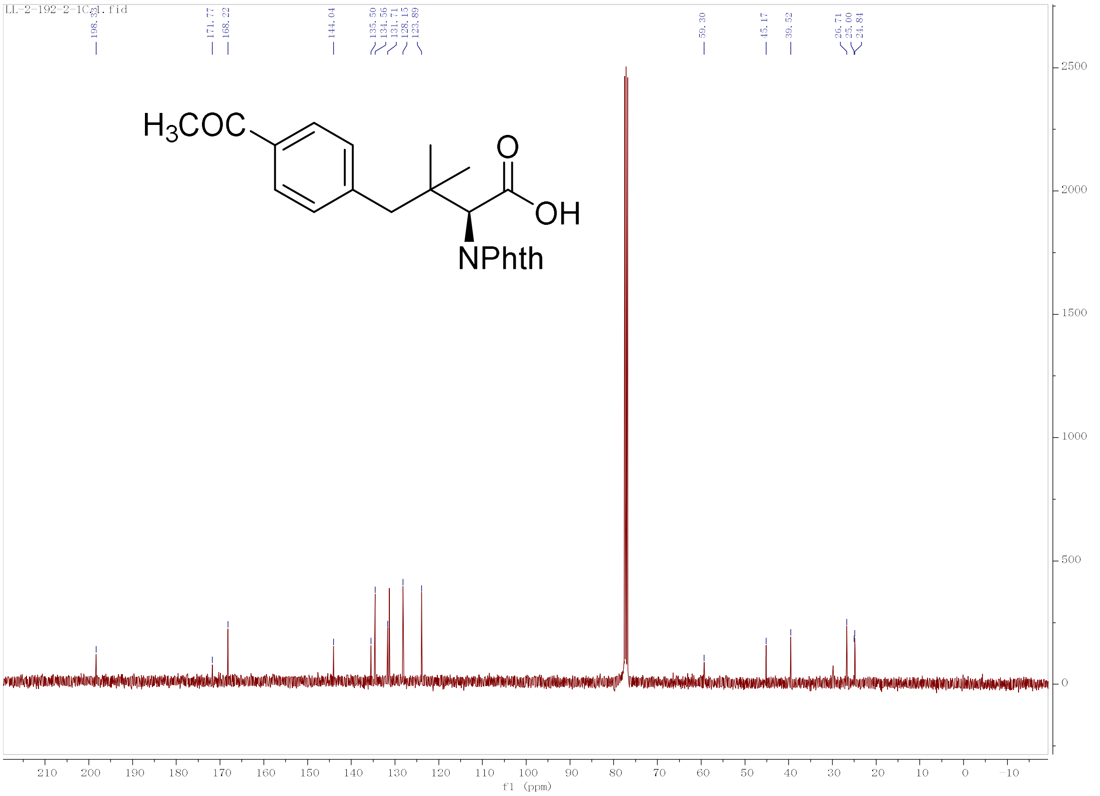
7.8417
7.8355
7.8280
7.7334
7.7257
7.7197
7.7122
7.1740
7.1528
7.0827
7.0615
6.8514
6.8341
6.8300
6.8124
5.0178
3.7974
3.7895
3.5163
3.4867
3.4525
3.4044
3.3708
3.1929
3.1592
2.5616
2.5275
0.8696
MeO
OMe
NPhth
O
OH
1.98
2.10
2.00
2.02
4.03
0.93
2.73
2.97
0.96
0.95
0.92
0.95
2.99
f1 (ppm)

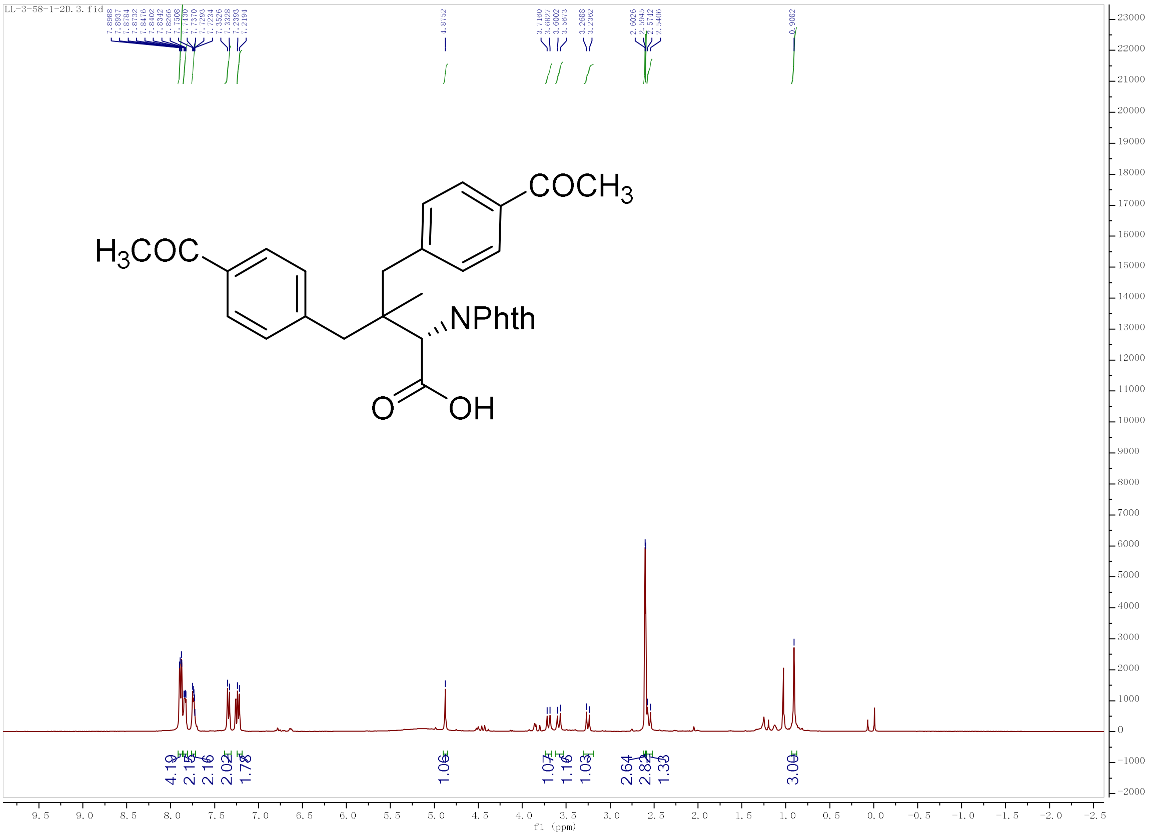

LL-2-186-1-2B-C.1.fid
173.85
168.25
158.38
158.11
134.40
132.30
131.71
131.67
130.07
129.58
123.74
113.81
113.31
56.65
55.31
55.26
42.75
42.39
42.04
22.74
MeO
OMe
NPhth
O
OH
f1 (ppm)

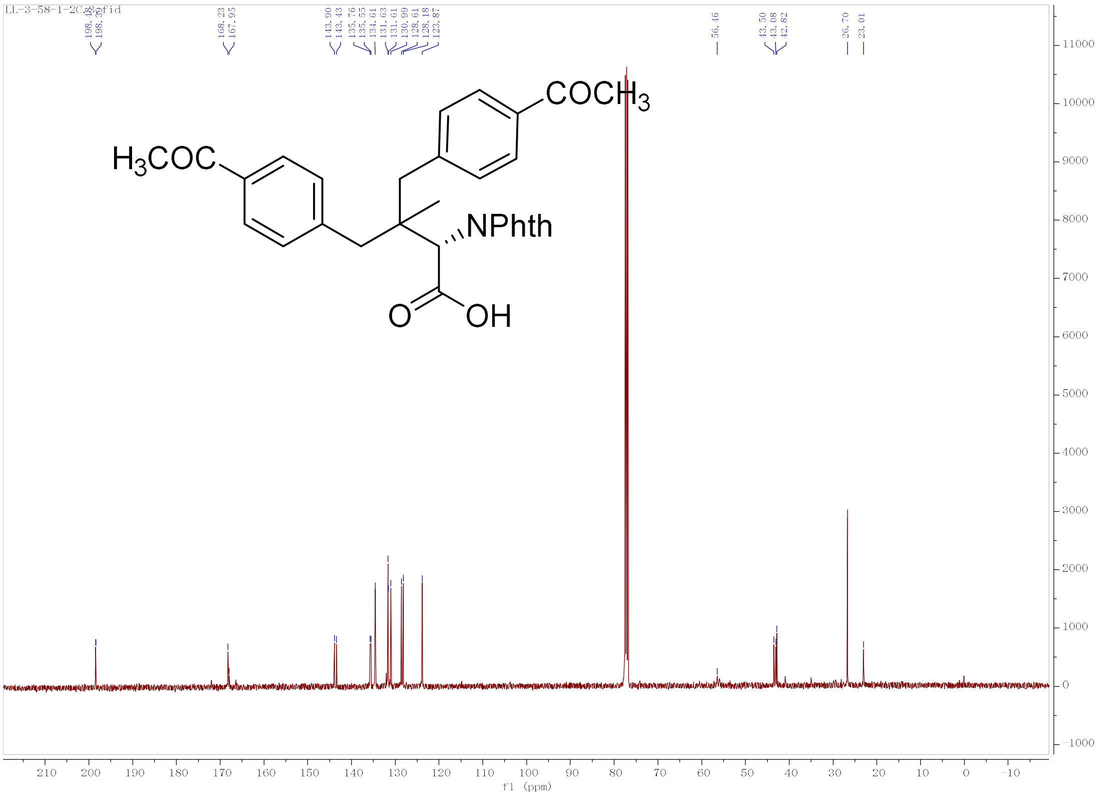
3b


LL-2-192-2-1.1.fid
7.8968
7.8869
7.8753
7.8665
7.7735
7.7661
7.7598
7.7519
7.2887
7.2661
4.8345
3.1828
3.1567
2.9897
2.9576
2.5968
1.1605
1.0538
H3COC
O
OH
NPhth
4.03
2.00
2.02
0.96
1.10
1.03
3.02
3.05
3.04
f1 (ppm)

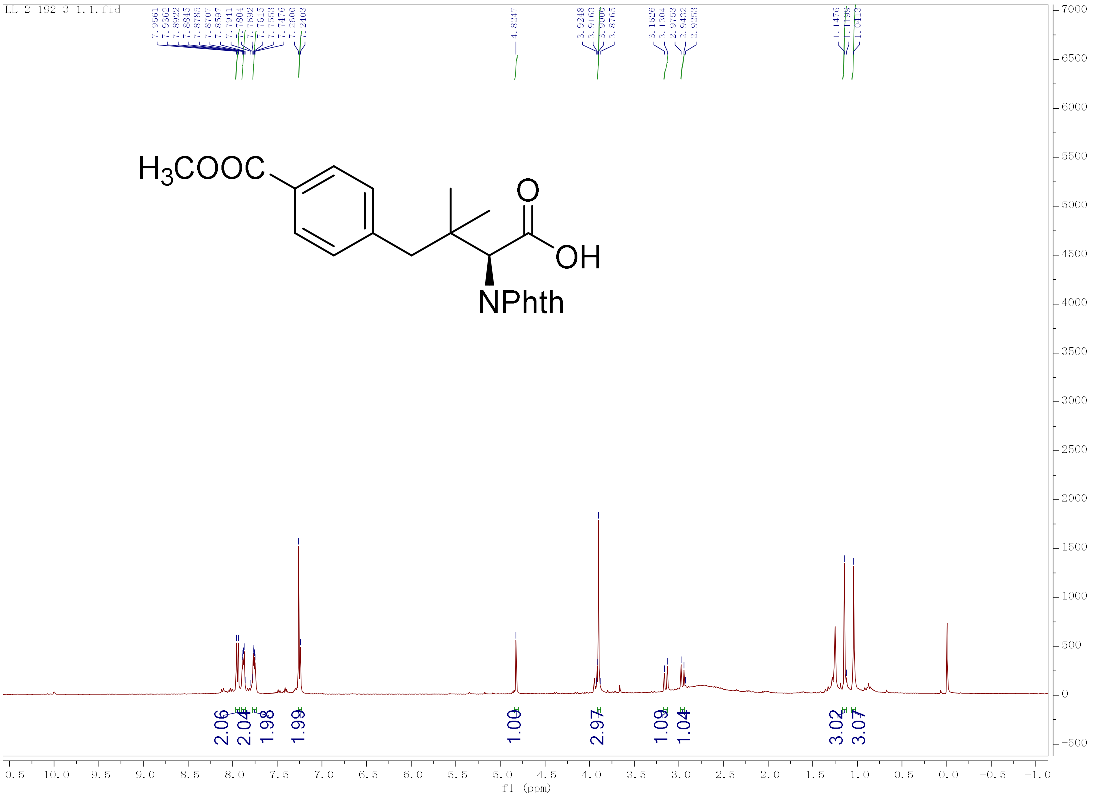

LL-2-192-2-1C.1.fid
198.3
171.77
168.22
144.04
135.50
134.56
131.71
128.15
123.89
59.30
45.17
39.52
26.71
25.00
24.81
H3COC
O
OH
NPhth
f1 (ppm)

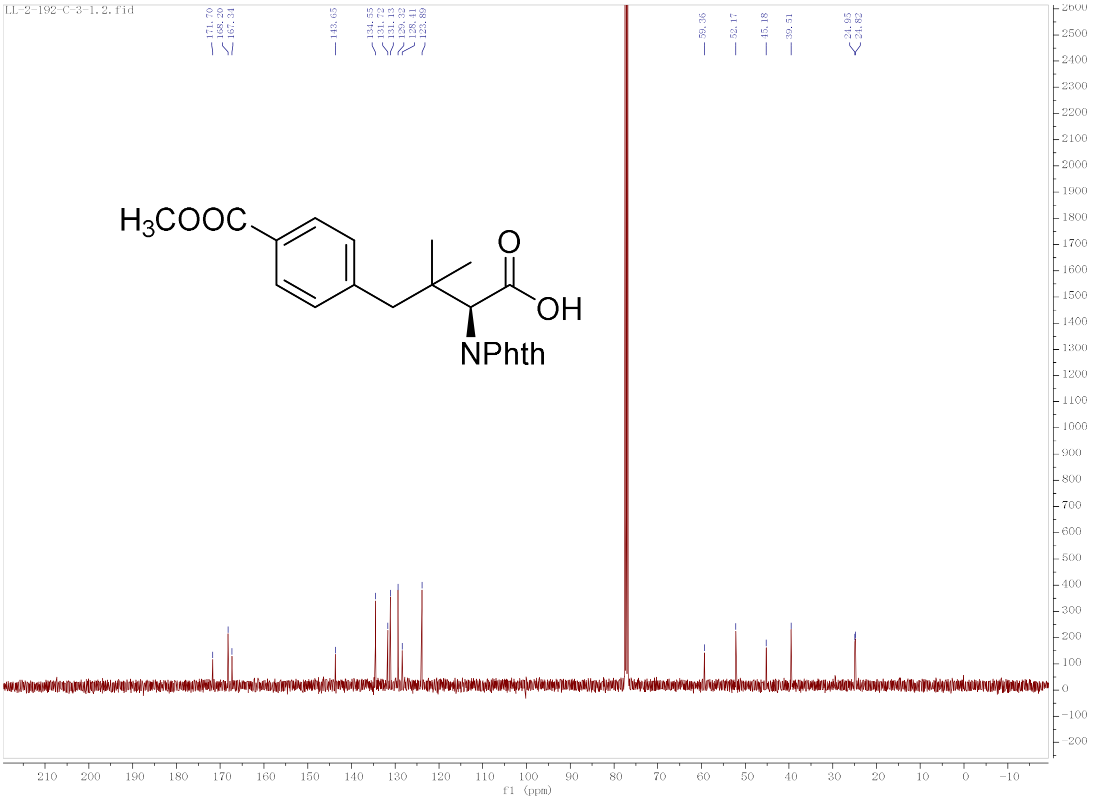
3b’


LL-3-58-1-2D.3.fid
7.8988
7.8937
7.8784
7.8732
7.8476
7.8402
7.8342
7.8266
7.7508
7.7430
7.7370
7.7293
7.7234
7.3526
7.3328
7.2393
7.2194
4.8752
3.7160
3.6827
3.6002
3.5673
3.2688
3.2362
2.6026
2.5945
2.5742
2.5406
0.9082
H3COC
COCH3
NPhth
O
OH
4.19
2.15
2.16
2.02
1.78
1.06
1.07
1.16
1.03
2.64
2.82
1.33
3.00
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
-0.5
-1.0
-1.5
-2.0
-2.5
f1 (ppm)
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

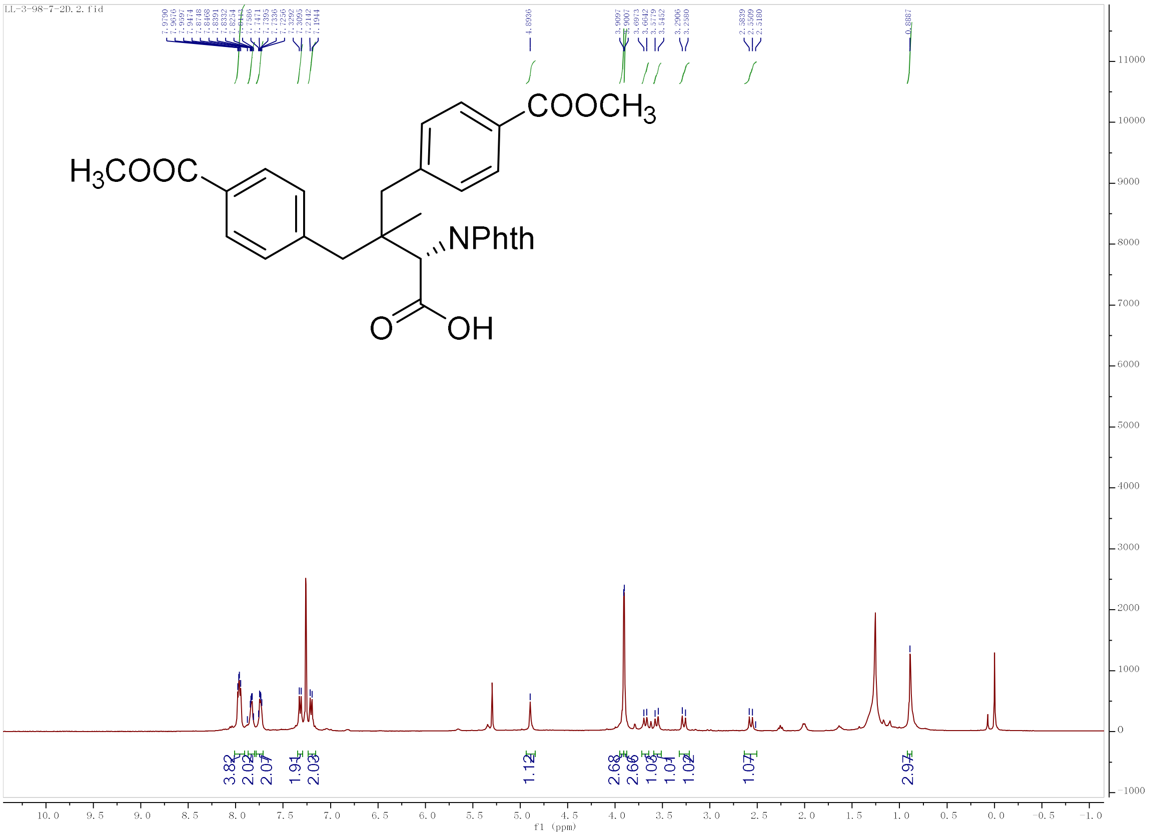

LL-3-58-1-2C.3.fid
198.48
198.39
168.23
167.95
143.90
143.43
135.76
135.55
134.61
131.63
131.61
130.99
128.61
128.18
123.87
56.46
43.50
43.08
42.82
26.70
23.01
H3COC
COCH3
NPhth
O
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

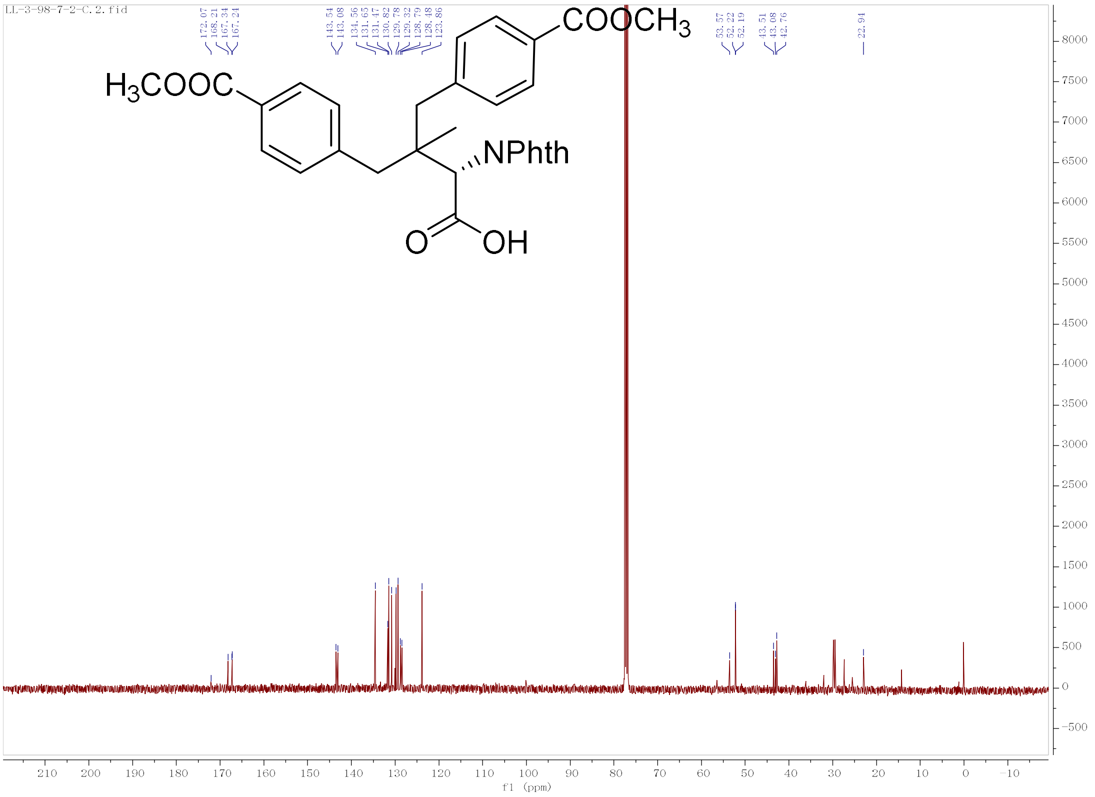
3c


LL-2-192-3-1.1.fid
7.9561
7.9362
7.8922
7.8845
7.8785
7.8707
7.8597
7.7941
7.7804
7.7692
7.7615
7.7553
7.7476
7.2600
7.2403
4.8247
3.9248
3.9163
3.9000
3.8765
3.1626
3.1304
2.9753
2.9432
2.9253
1.1476
1.1199
1.0413
H3COOC
O
OH
NPhth
2.06
2.04
1.98
1.99
1.00
2.97
1.09
1.04
3.02
3.07
0.5
10.0
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
-0.5
-1.0
f1 (ppm)
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

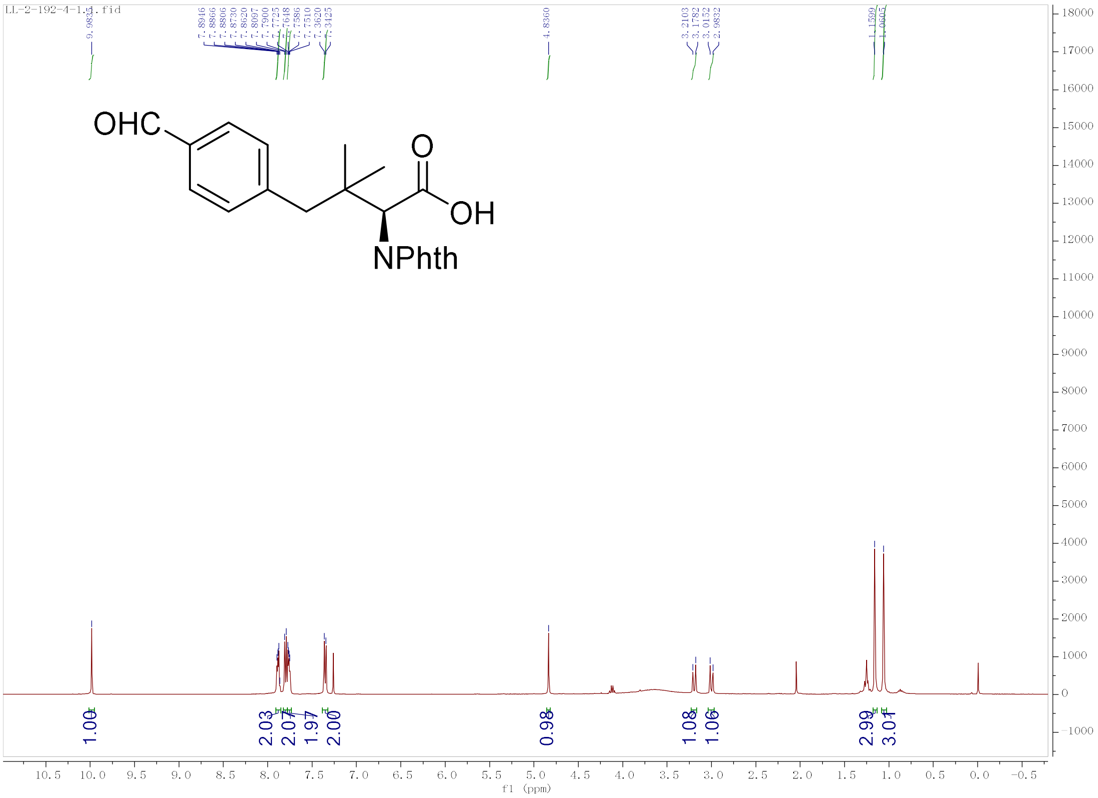

LL-2-192-C-3-1.2.fid
171.70
168.20
167.34
143.65
134.55
131.72
131.13
129.32
128.41
123.89
59.36
52.17
45.18
39.51
24.95
24.82
H3COOC
O
OH
NPhth
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2600
2500
2400
2300
2200
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200

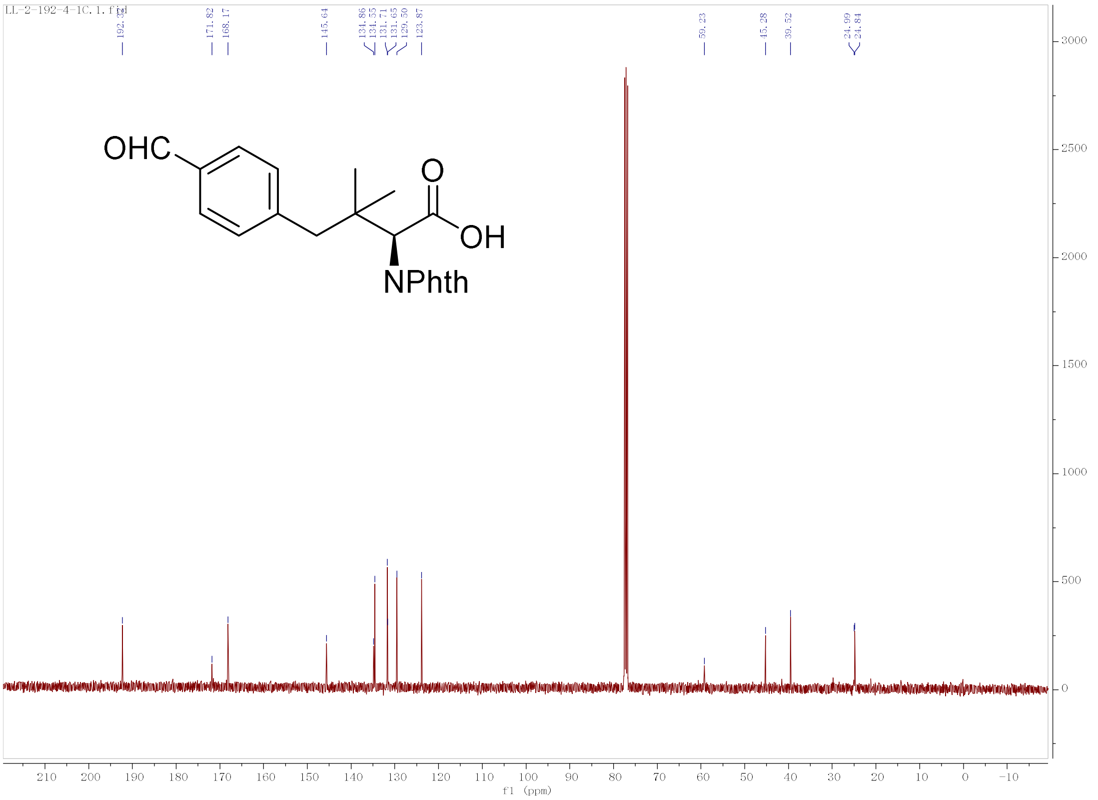
3c’


LL-3-98-7-2D.2.fid
7.9790
7.9676
7.9597
7.9474
7.8748
7.8468
7.8391
7.8332
7.8254
7.8113
7.7586
7.7471
7.7395
7.7336
7.7256
7.3292
7.3095
7.2142
7.1944
4.8936
3.9097
3.9007
3.6973
3.6642
3.5779
3.5452
3.2906
3.2580
2.5839
2.5509
2.5180
0.8887
COOCH3
H3COOC
NPhth
O
OH
3.82
2.02
2.07
1.91
2.08
1.12
2.68
2.66
1.03
1.01
1.02
1.07
2.97
f1 (ppm)

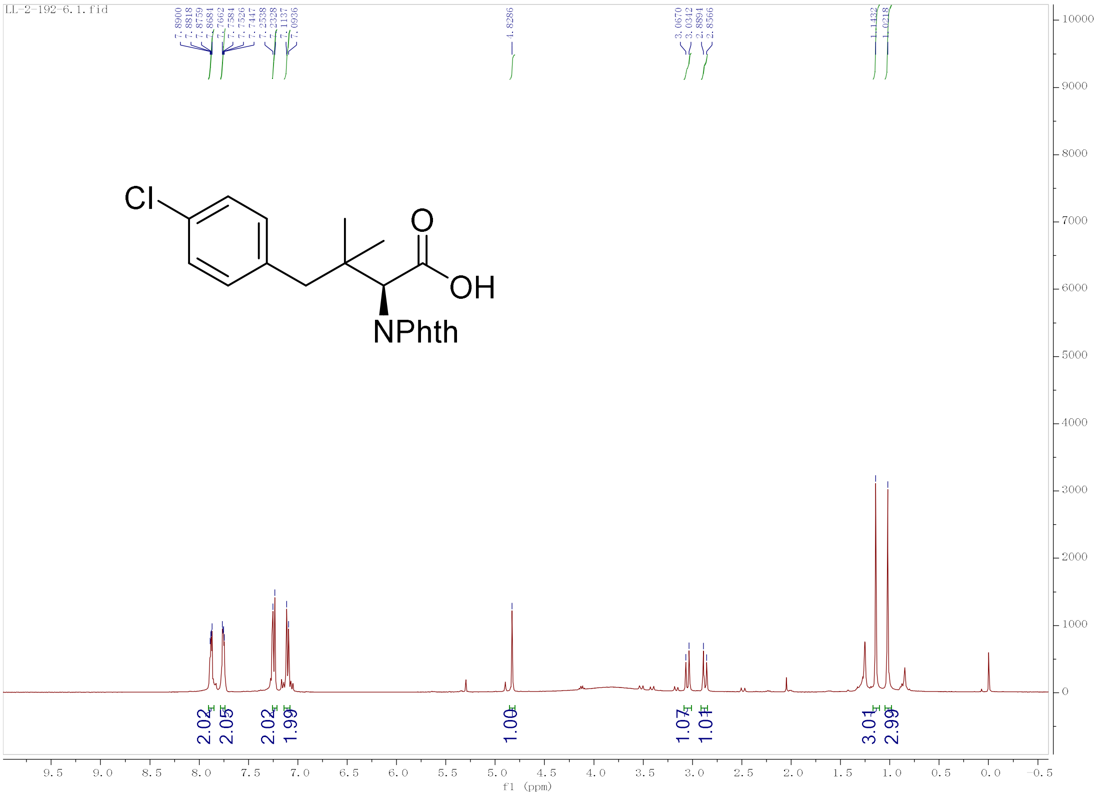

LL-3-98-7-2-C.2.fid
172.07
168.21
167.34
167.24
143.54
143.08
134.56
131.65
131.47
130.82
129.78
129.32
128.79
128.48
123.86
53.57
52.22
52.19
43.51
43.08
42.76
22.91
COOCH3
H3COOC
NPhth
O
OH
f1 (ppm)

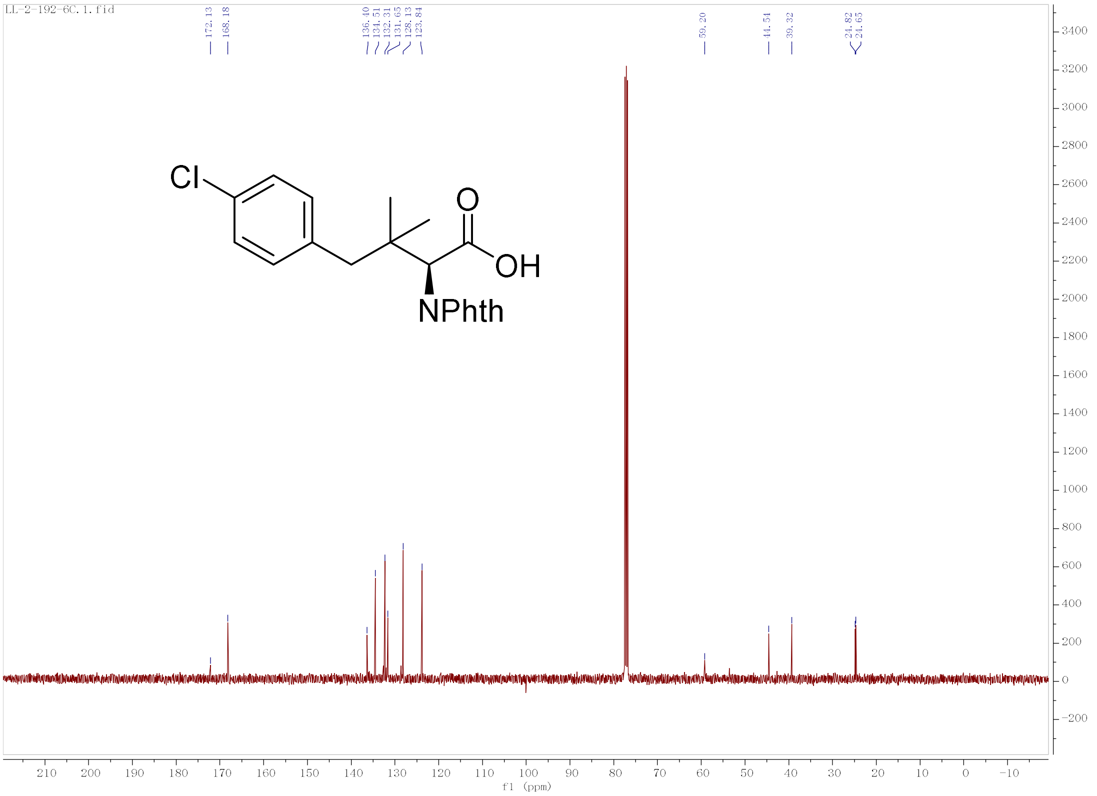
3d


LL-2-192-4-1.1.fid
9.9835
7.8946
7.8866
7.8806
7.8730
7.8620
7.8097
7.7900
7.7725
7.7648
7.7586
7.7510
7.3620
7.3425
4.8360
3.2103
3.1782
3.0152
2.9832
1.1599
1.0605
OHC
O
OH
NPhth
1.00
2.03
2.07
1.97
2.00
0.98
1.08
1.06
2.99
3.01
10.5
10.0
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
-0.5
f1 (ppm)
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

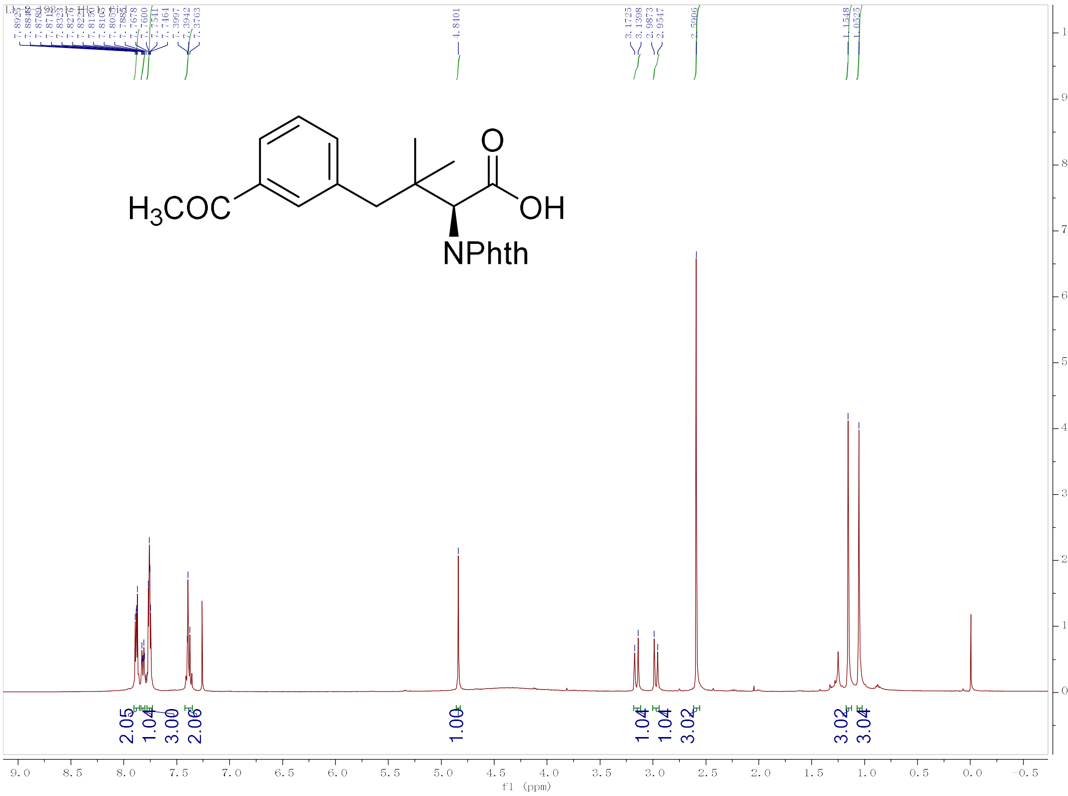

LL-2-192-4-1C.1.fid
192.32
171.82
168.17
145.64
134.86
134.55
131.71
131.65
129.50
123.87
59.23
45.28
39.52
24.99
24.84
OHC
O
OH
NPhth
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
3000
2500
2000
1500
1000
500
0

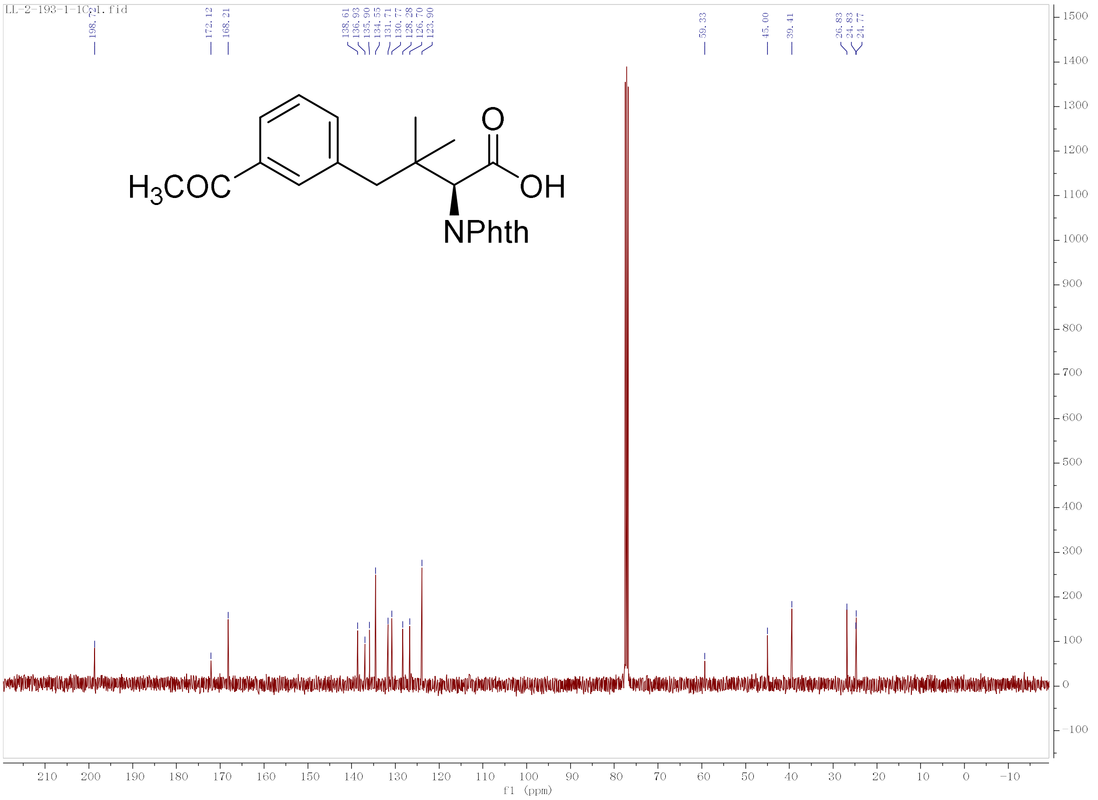
3e


LL-2-192-6.1.fid
7.8900
7.8818
7.8759
7.8684
7.7662
7.7584
7.7526
7.7447
7.2538
7.2328
7.1137
7.0936
4.8286
3.0670
3.0342
2.8894
2.8566
1.1432
1.0218
Cl
O
OH
NPhth
2.02
2.05
2.02
1.99
1.00
1.07
1.01
3.01
2.99
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
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
-0.5
f1 (ppm)

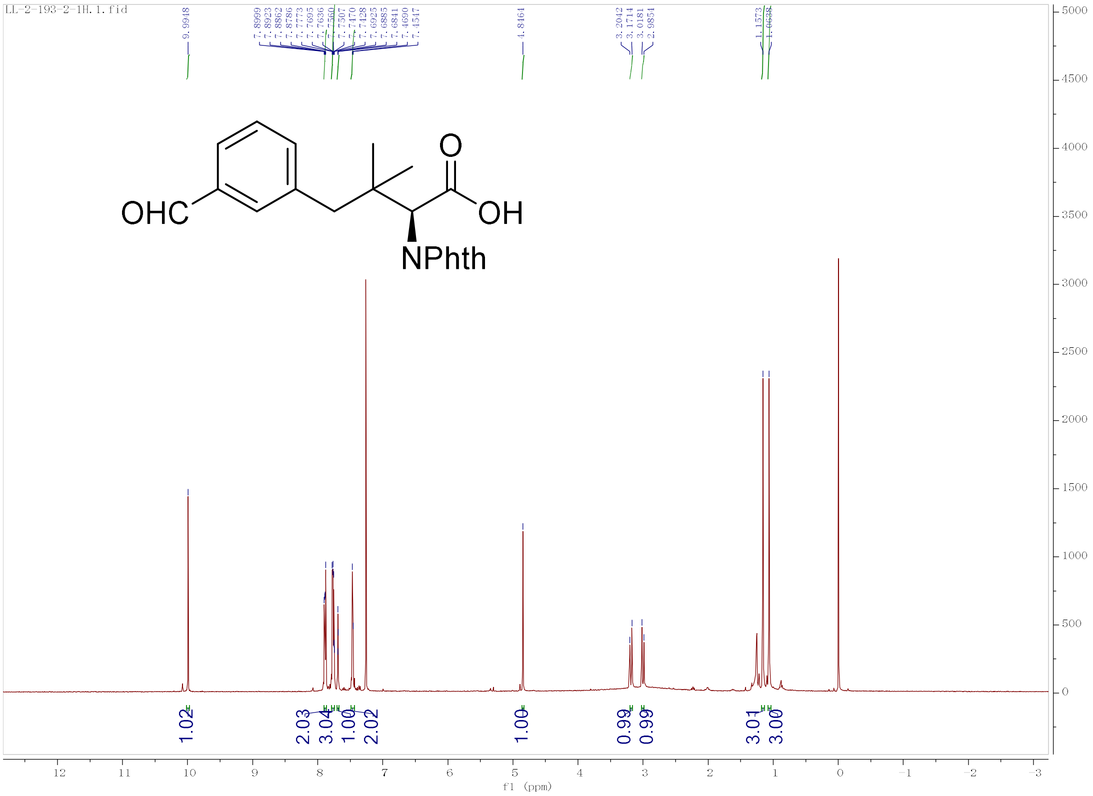

LL-2-192-6C.1.fid
172.13
168.18
136.40
134.51
132.31
131.65
128.13
123.84
59.20
44.51
39.32
24.82
24.65
Cl
O
OH
NPhth
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

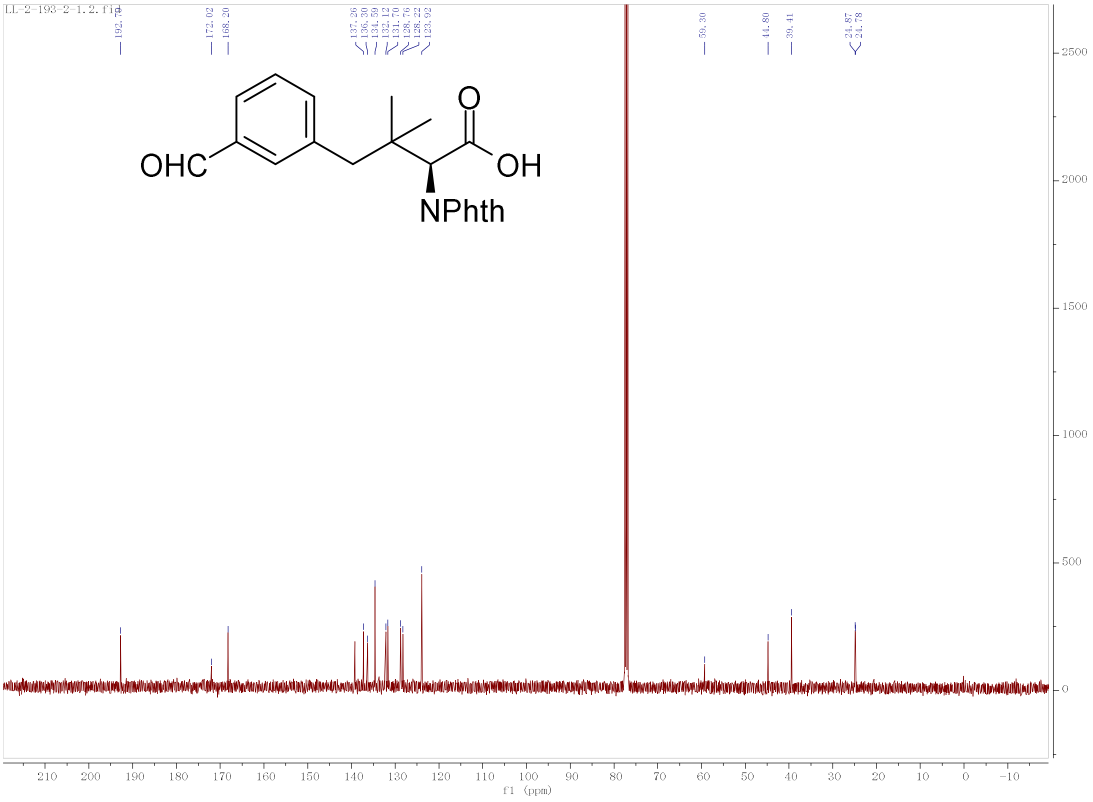
3f


LL-2-193-1-1H.1.fid
7.8925
7.8848
7.8789
7.8713
7.8323
7.8276
7.8221
7.8150
7.8105
7.8055
7.7882
7.7678
7.7600
7.7541
7.7464
7.3997
7.3942
7.3763
4.8401
3.1725
3.1398
2.9873
2.9547
2.5906
1.1518
1.0525
H3COC
O
OH
NPhth
2.05
1.04
3.00
2.06
1.00
1.04
1.04
3.02
3.02
3.04
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
-0.5
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

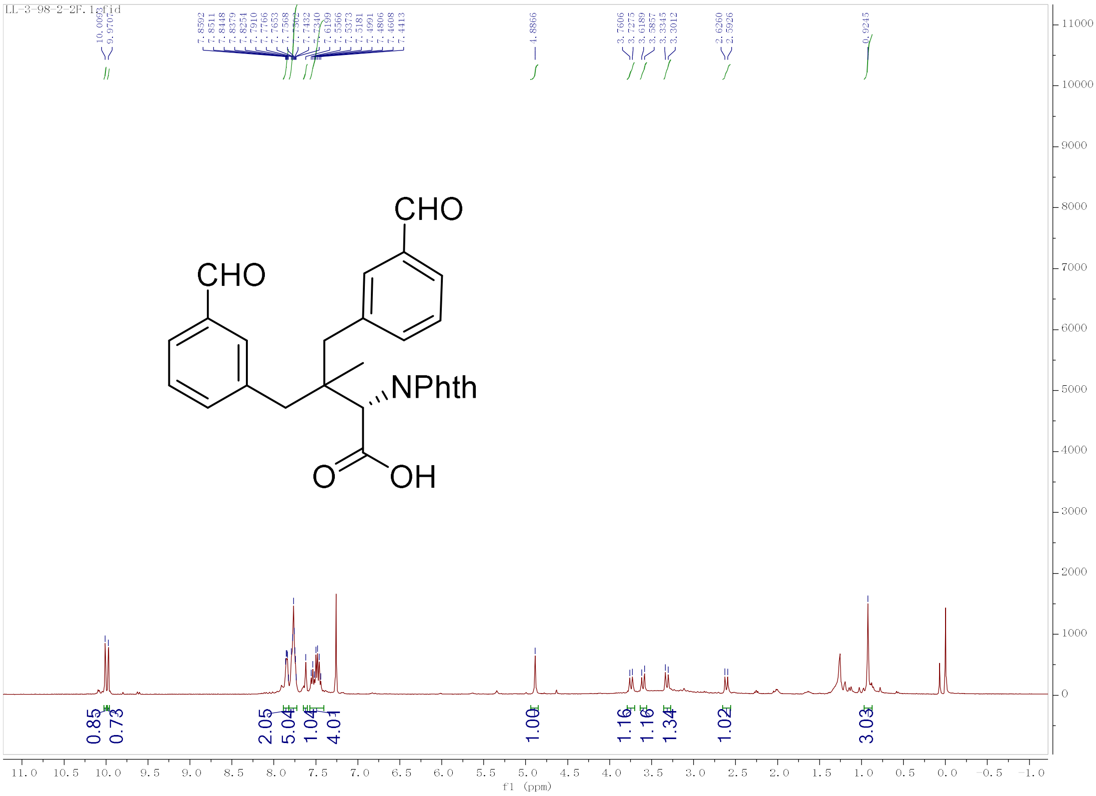

LL-2-193-1-1C.1.fid
198.72
172.12
168.21
138.61
136.93
135.90
134.55
131.71
130.77
128.28
126.70
123.90
59.33
45.00
39.41
26.83
24.83
24.77
H3COC
O
OH
NPhth
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

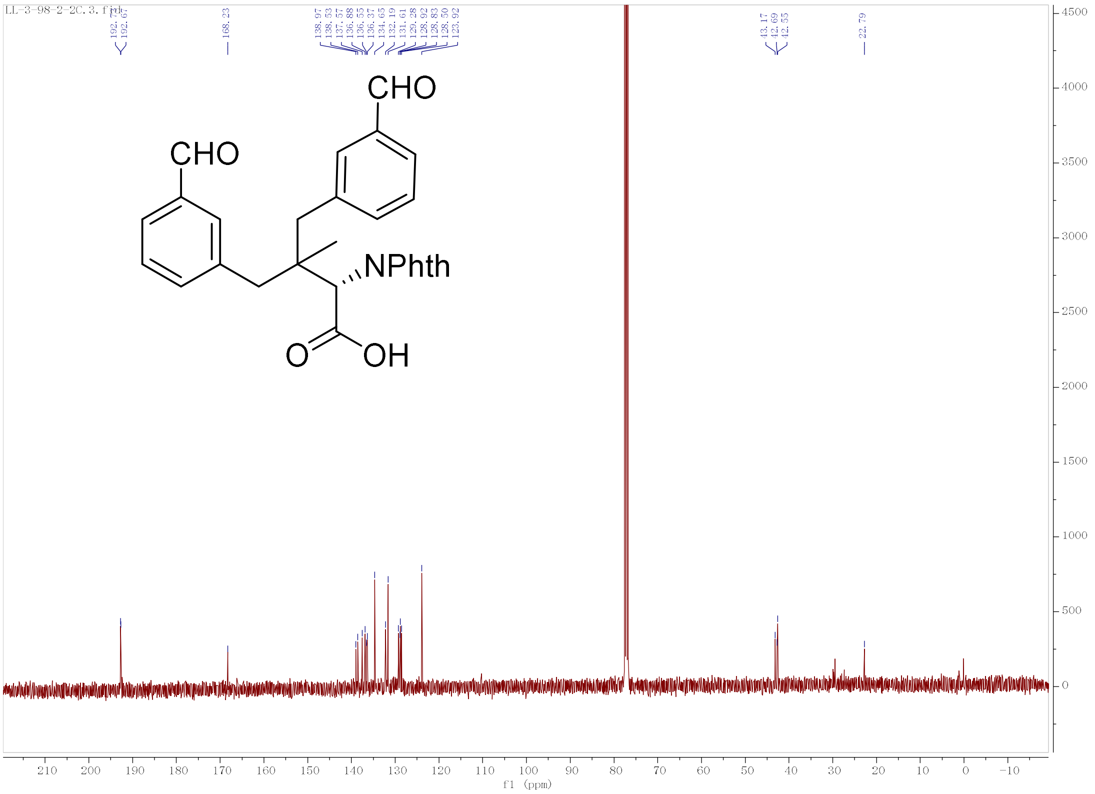
3g


LL-2-193-2-1H.1.fid
9.9948
7.8999
7.8923
7.8862
7.8786
7.7773
7.7695
7.7636
7.7560
7.7507
7.7470
7.7428
7.6925
7.6885
7.6841
7.4690
7.4547
4.8464
3.2042
3.1714
3.0181
2.9854
1.1573
1.0638
OHC
O
OH
NPhth
1.02
2.03
3.04
1.00
2.02
1.00
0.99
0.99
3.01
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0

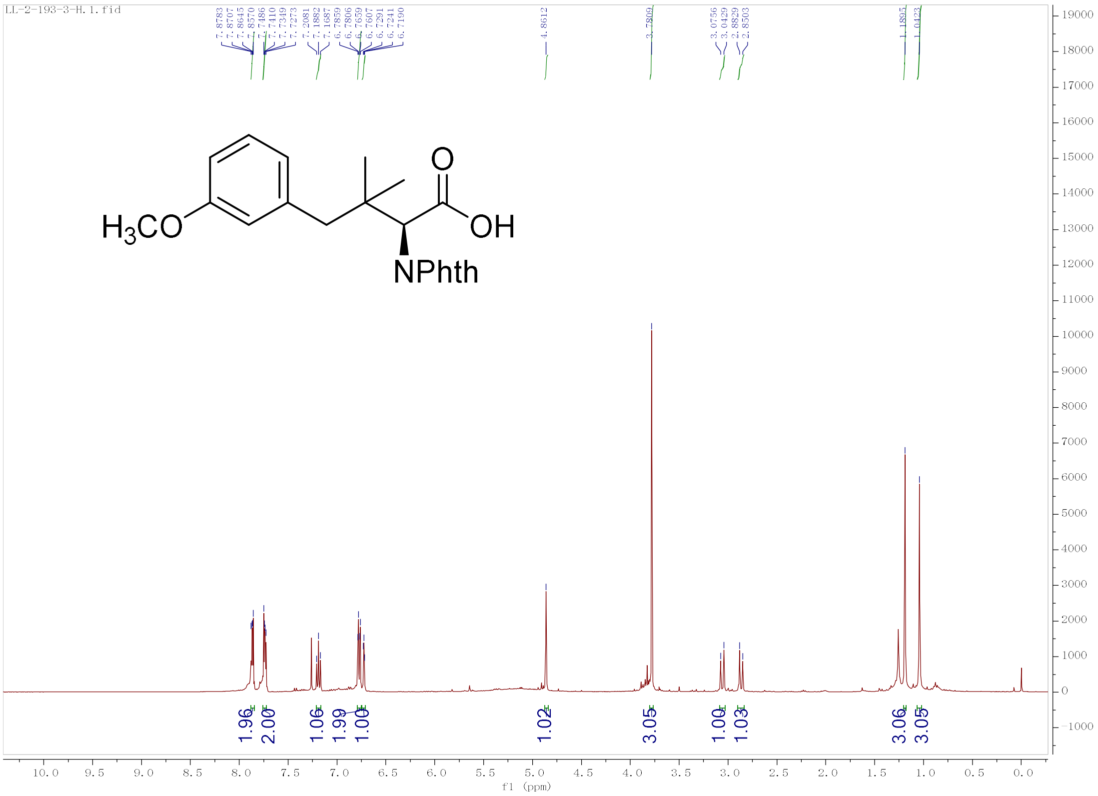

LL-2-193-2-1.2.fid
192.7
172.02
168.20
137.26
136.30
134.59
132.12
131.70
128.76
128.22
123.92
59.30
44.80
39.41
24.87
24.78
OHC
O
OH
NPhth
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
2500
2000
1500
1000
500
0

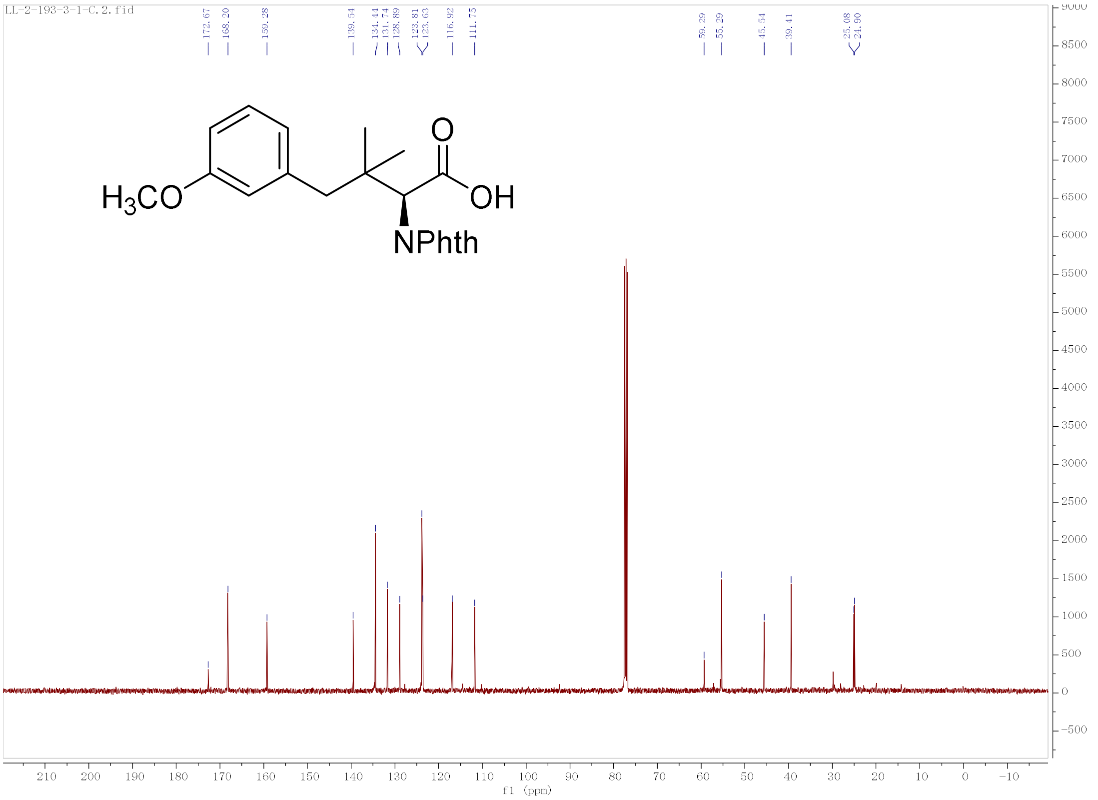
3g’


LL-3-98-2-2F.1.fid
10.0093
9.9707
7.8592
7.8511
7.8448
7.8379
7.8254
7.7910
7.7766
7.7653
7.7568
7.7502
7.7432
7.7340
7.6199
7.5566
7.5373
7.5181
7.4991
7.4806
7.4608
7.4413
4.8866
3.7606
3.7275
3.6189
3.5857
3.3345
3.3012
2.6260
2.5926
0.9245
CHO
CHO
NPhth
O
OH
0.85
0.73
2.05
5.04
1.04
4.01
1.00
1.16
1.16
1.34
1.02
3.03
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
11.0
10.5
10.0
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
-0.5
-1.0
f1 (ppm)

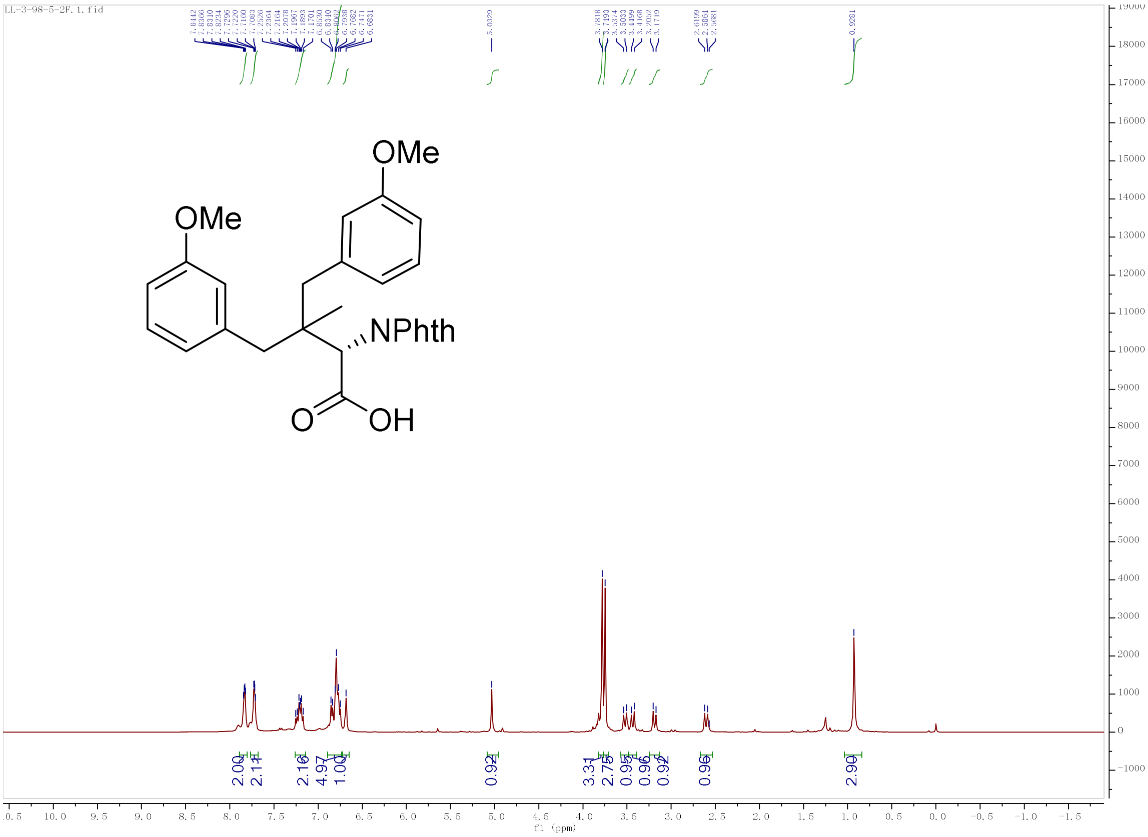

LL-3-98-2-2C.3.fid
192.73
192.67
168.23
138.97
138.53
137.57
136.88
136.55
136.37
134.65
132.19
131.61
129.28
128.92
128.83
128.50
123.92
43.17
42.69
42.55
22.79
CHO
CHO
NPhth
O
OH
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

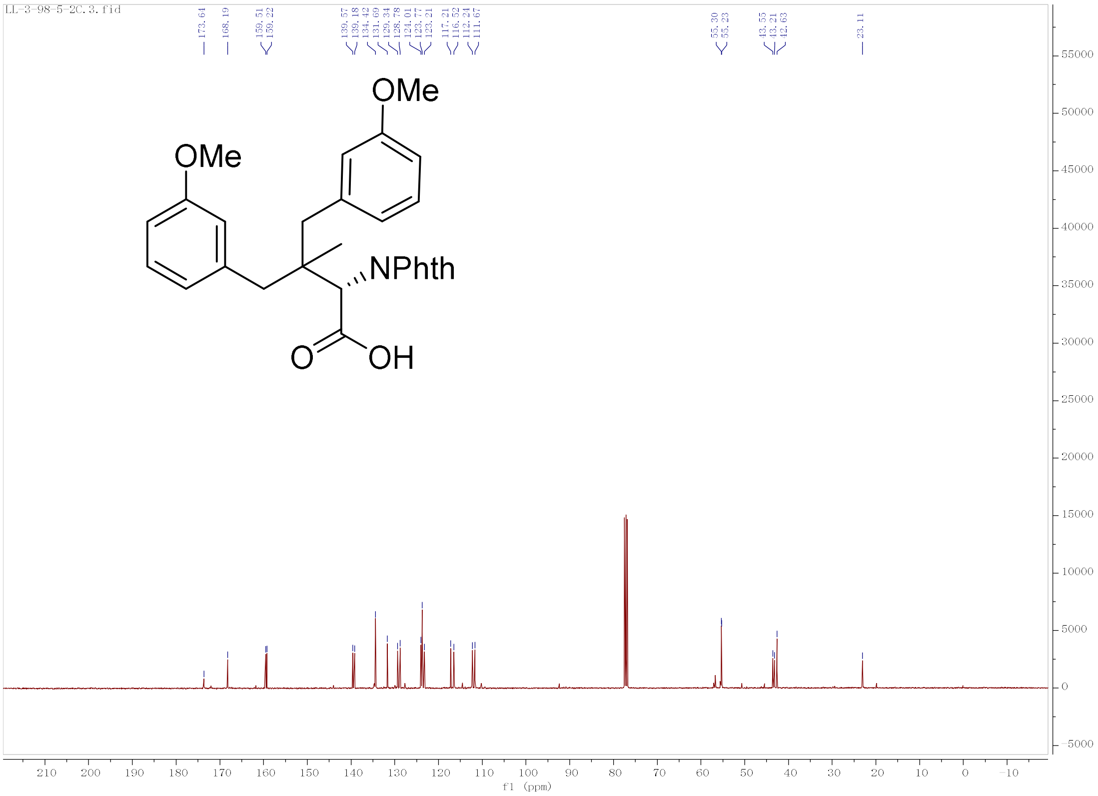
3h


LL-2-193-3-H.1.fid
7.8783
7.8707
7.8645
7.8570
7.7486
7.7410
7.7349
7.7273
7.2081
7.1882
7.1687
6.7859
6.7806
6.7659
6.7607
6.7291
6.7241
6.7190
4.8612
3.7809
3.0756
3.0429
2.8829
2.8503
1.1895
1.0423
H3CO
O
OH
NPhth
1.96
2.00
1.06
1.99
1.00
1.02
3.05
1.00
1.03
3.06
3.05
f1 (ppm)

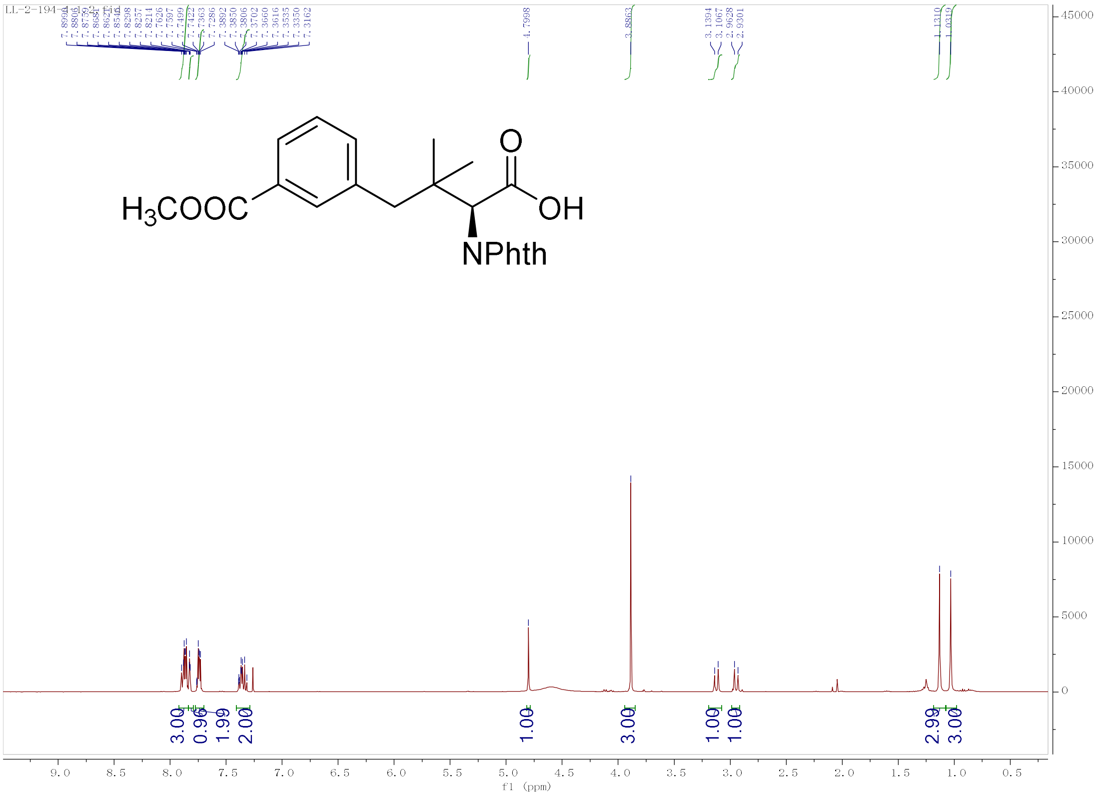

LL-2-193-3-1-C.2.fid
172.67
168.20
159.28
139.54
134.44
131.74
128.89
123.81
123.63
116.92
111.73
59.29
55.29
45.54
39.41
25.08
24.90
H3CO
O
OH
NPhth
f1 (ppm)

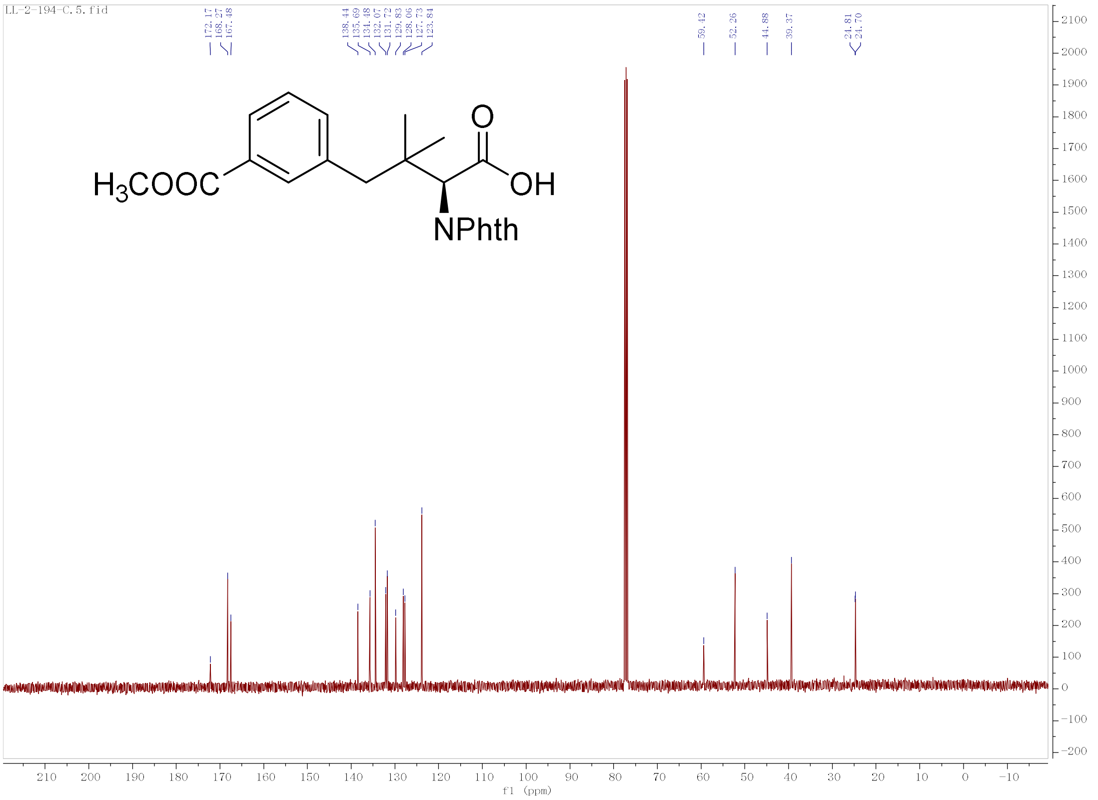
3h’


LL-3-98-5-2F.1.fid
7.8442
7.8366
7.8310
7.8234
7.7296
7.7220
7.7160
7.7083
7.2526
7.2364
7.2164
7.2078
7.1967
7.1893
7.1701
6.8530
6.8340
6.8062
6.7938
6.7682
6.7471
6.6831
5.0329
3.7818
3.7493
3.5374
3.5033
3.4499
3.4168
3.2052
3.1719
2.6199
2.5864
2.5681
0.9281
OMe
OMe
NPhth
O
OH
2.00
2.11
2.16
4.97
1.00
0.92
3.31
2.75
0.95
0.96
0.92
0.96
2.90
f1 (ppm)

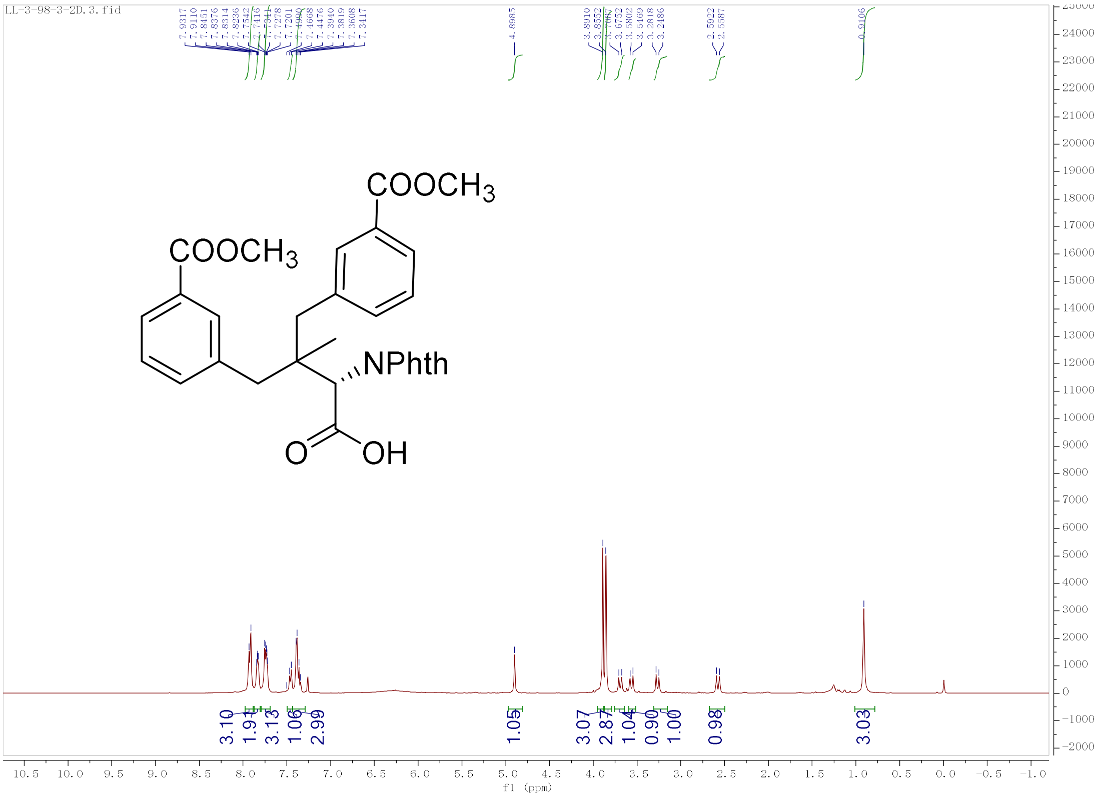

LL-3-98-5-2C.3.fid
173.64
168.19
159.51
159.22
139.57
139.18
134.42
131.69
129.34
128.78
124.01
123.77
123.21
117.21
116.52
112.24
111.67
55.30
55.23
43.55
43.21
42.63
23.11
OMe
OMe
NPhth
O
OH
f1 (ppm)

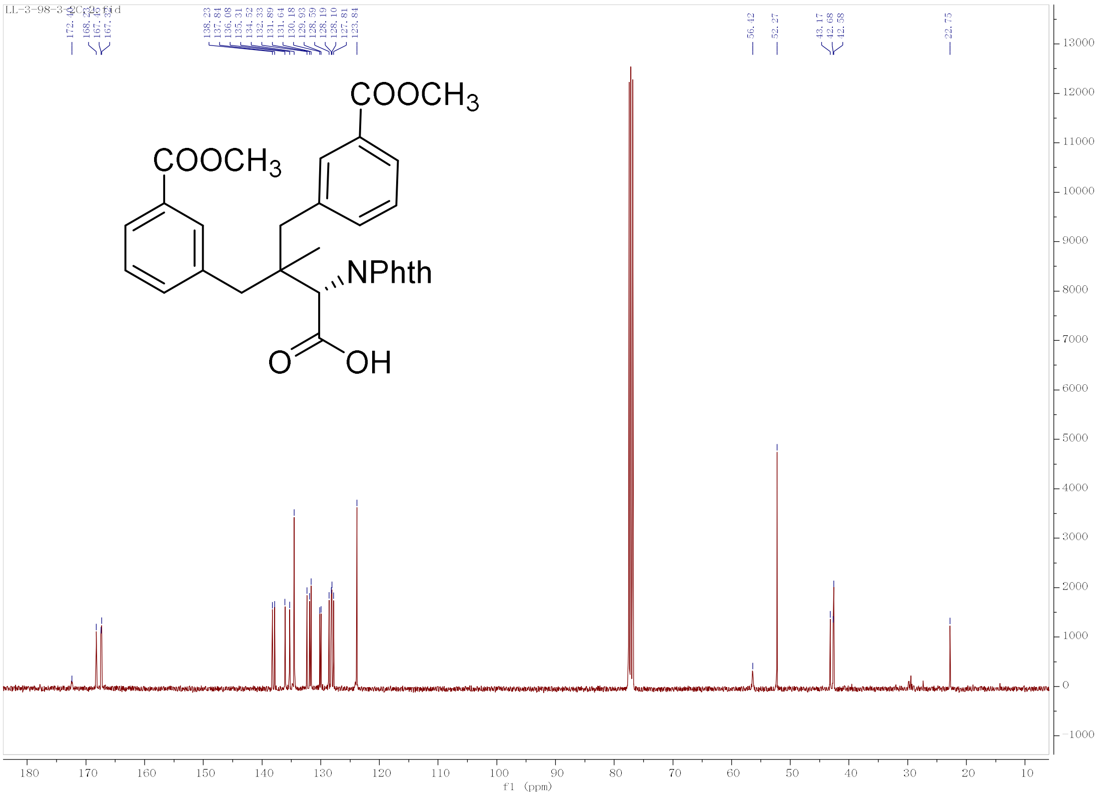
3i


LL-2-194-4-1.2.fid
7.8990
7.8806
7.8759
7.8681
7.8621
7.8546
7.8298
7.8257
7.8214
7.7626
7.7597
7.7499
7.7422
7.7363
7.7286
7.3892
7.3850
7.3806
7.3702
7.3660
7.3616
7.3535
7.3350
7.3162
4.7998
3.8863
3.1394
3.1067
2.9628
2.9301
1.1310
1.0319
H3COOC
O
OH
NPhth
3.00
0.96
1.99
2.00
1.00
3.00
1.00
1.00
2.99
3.00
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
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
f1 (ppm)

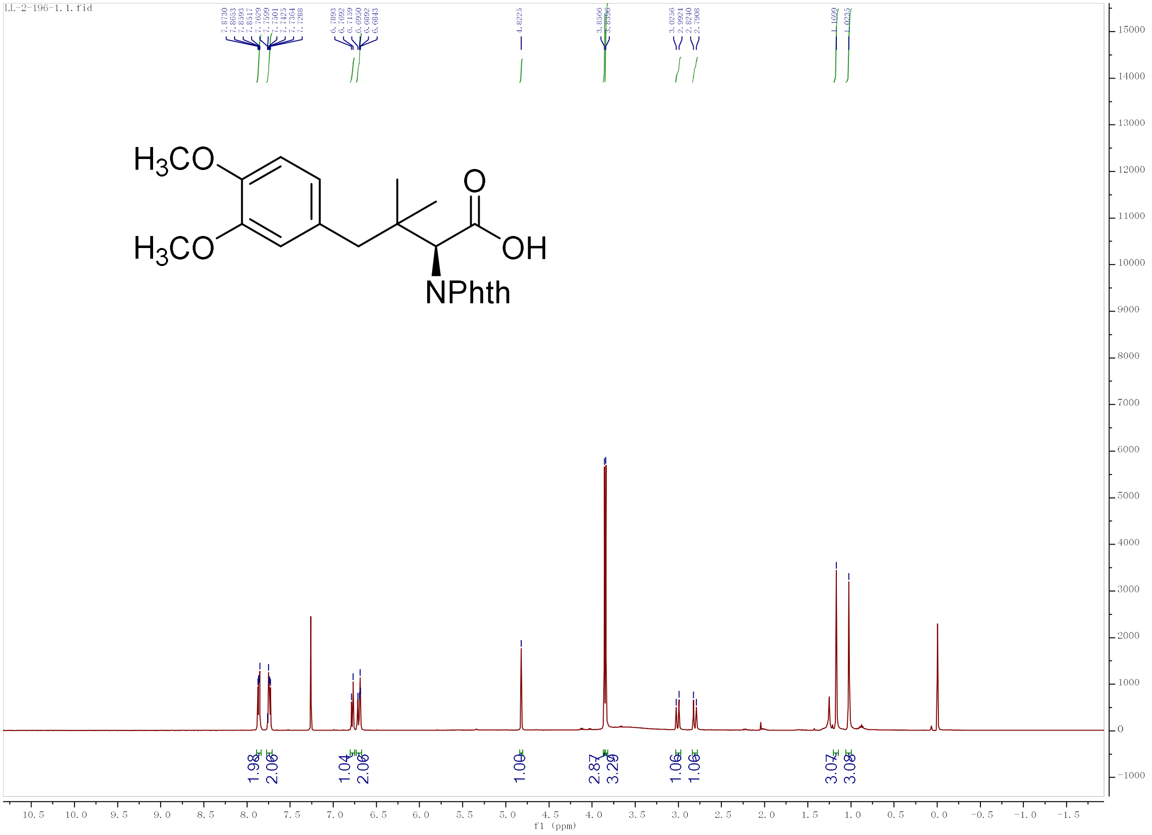

LL-2-194-C.5.fid
172.17
168.27
167.48
138.44
135.69
134.48
132.07
131.72
129.83
128.06
127.73
123.84
59.42
52.26
44.88
39.37
24.81
24.70
H3COOC
O
OH
NPhth
2100
2000
1900
1800
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
-200
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

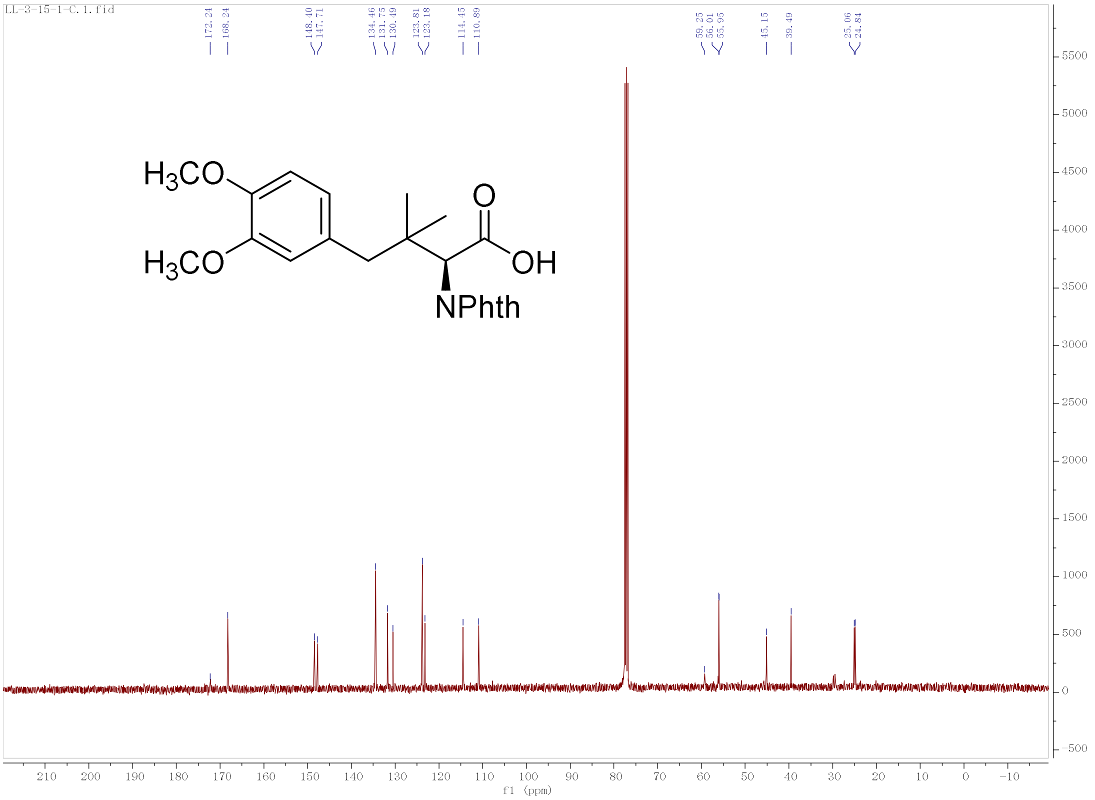
3i’


LL-3-98-3-2D.3.fid
7.9317
7.9110
7.8451
7.8376
7.8314
7.8236
7.7542
7.7416
7.7341
7.7278
7.7201
7.4990
7.4668
7.4476
7.3940
7.3819
7.3608
7.3417
4.8985
3.8910
3.8552
3.7087
3.6752
3.5802
3.5469
3.2818
3.2486
2.5922
2.5587
0.9106
COOCH3
COOCH3
NPhth
O
OH
3.10
1.94
3.13
1.06
2.99
1.05
3.07
2.87
1.04
0.90
1.00
0.98
3.03
10.5
10.0
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
-0.5
-1.0
f1 (ppm)
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

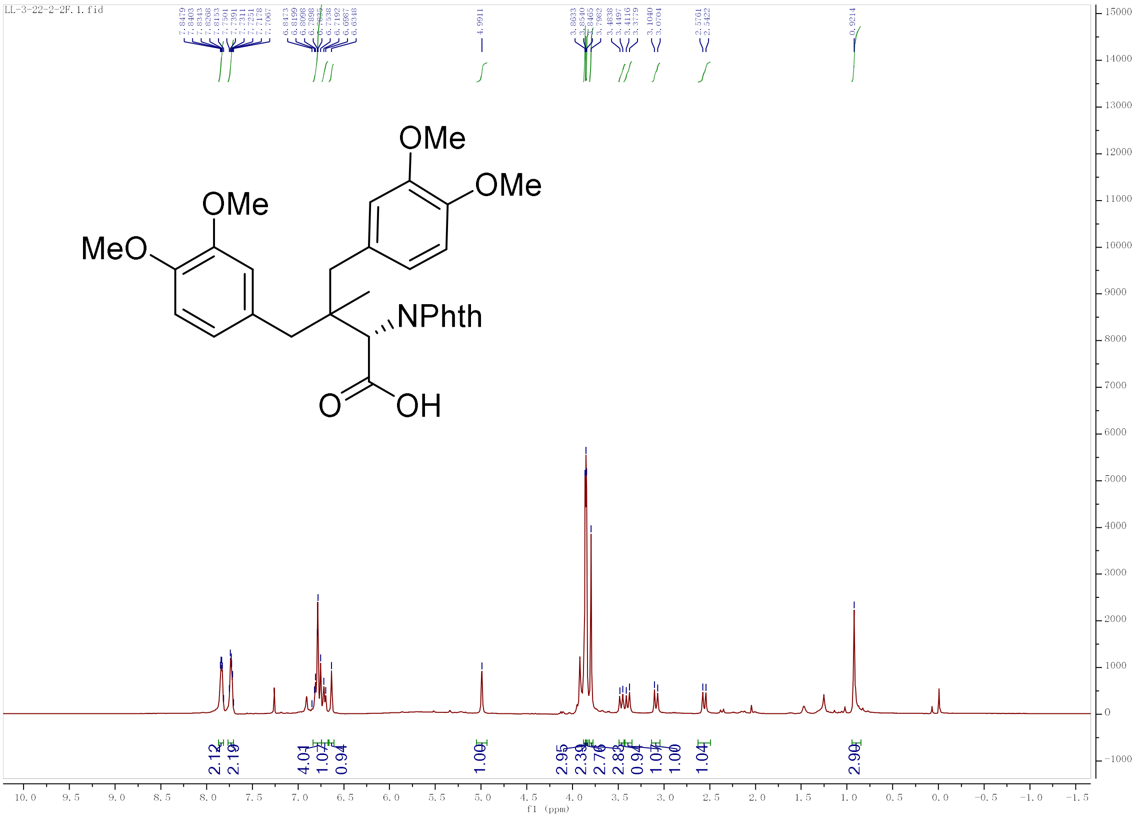

LL-3-98-3-2C.2.fid
172.42
168.23
167.41
167.37
138.23
137.84
136.08
135.31
134.52
132.33
131.89
131.64
130.18
129.93
128.59
128.19
128.10
127.81
123.84
56.42
52.27
43.17
42.68
42.58
22.75
COOCH3
COOCH3
NPhth
O
OH
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

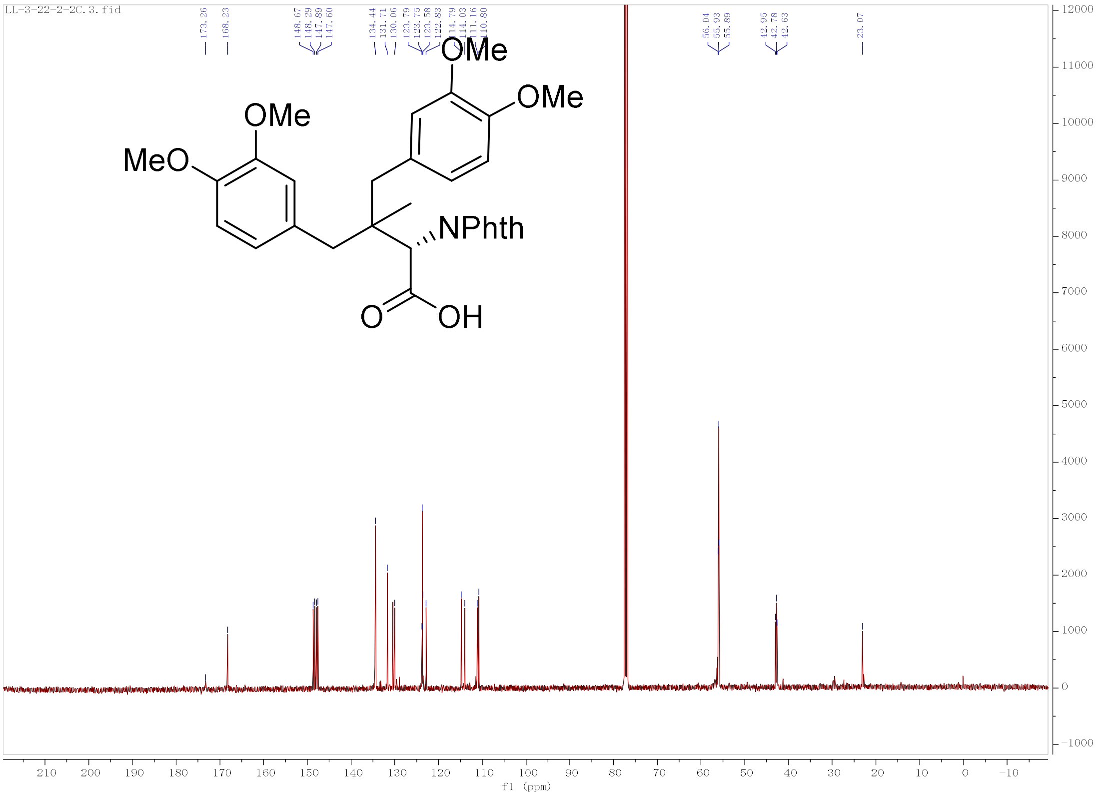
3j


LL-2-196-1.1.fid
7.8730 7.8653 7.8593 7.8517 7.7629 7.7599 7.7501 7.7425 7.7364 7.7288
6.7893 6.7692 6.7159 6.6950 6.6892 6.6843
4.8225
3.8566 3.8396
3.0256 2.9924 2.8240 2.7908
1.1699 1.0235
H3CO
H3CO
O
OH
NPhth
1.98 2.06 1.04 2.06 1.00 2.87 3.29 1.06 1.06 3.07 3.08
f1 (ppm)

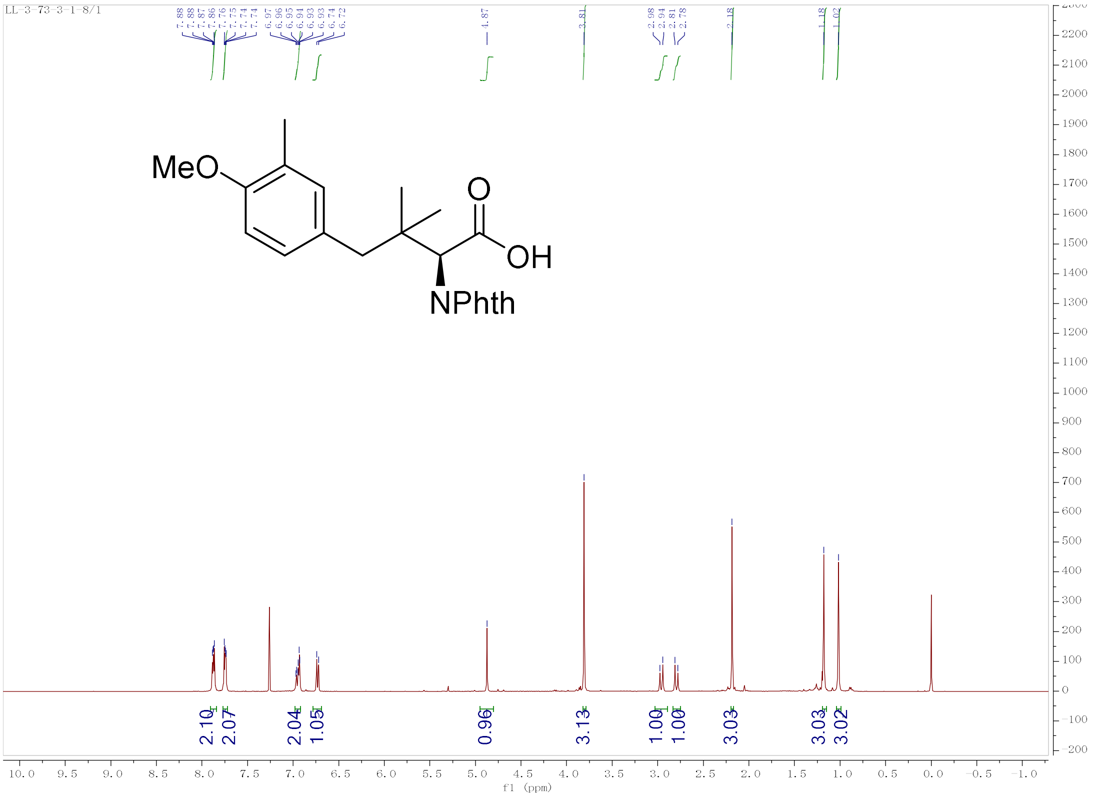

LL-3-15-1-C.1.fid
172.24 168.24 148.40 147.71 134.46 131.75 130.49 123.81 123.18 114.45 110.89 59.25 56.01 55.95 45.15 39.49 25.06 24.84
H3CO
H3CO
O
OH
NPhth
f1 (ppm)

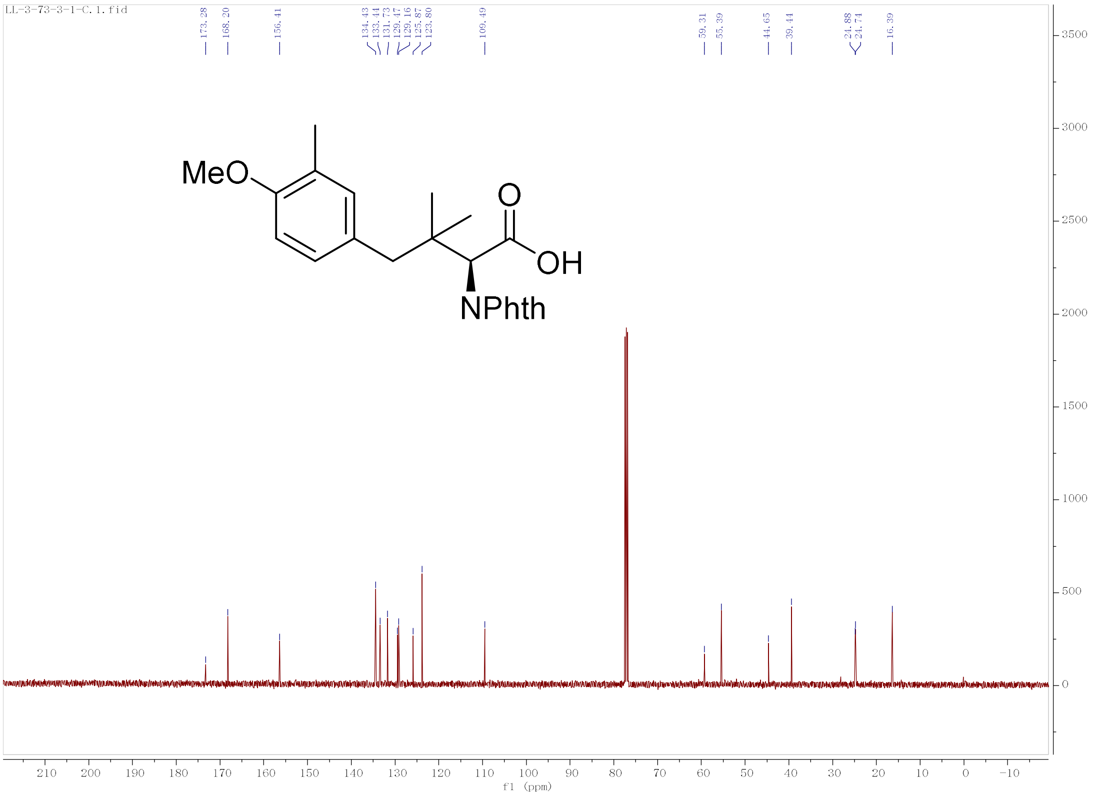
3j'


LL-3-22-2-2F.1.fid
7.8479
7.8403
7.8343
7.8268
7.8153
7.7501
7.7391
7.7311
7.7251
7.7178
7.7067
6.8473
6.8199
6.8098
6.7898
6.7835
6.7538
6.7192
6.6987
6.6348
4.9911
3.8633
3.8540
3.8465
3.7982
3.4838
3.4497
3.4116
3.3779
3.1040
3.0704
2.5761
2.5422
0.9214
OMe
OMe
OMe
MeO
NPhth
O
OH
2.12
2.19
4.01
1.07
0.94
1.00
2.95
2.39
2.76
2.83
0.94
1.07
1.00
1.04
2.90
10.0
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
-0.5
-1.0
-1.5
f1 (ppm)
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

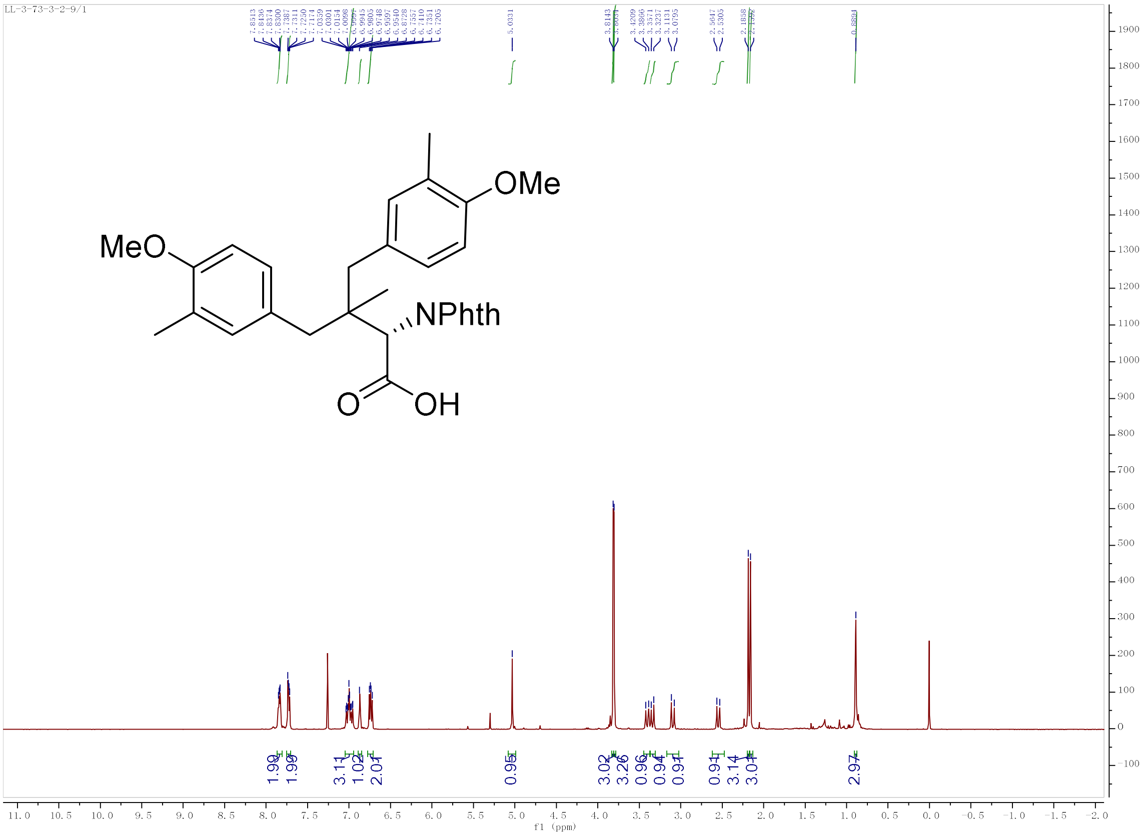

LL-3-22-2-2C.3.fid
173.26
168.23
148.67
148.29
147.89
147.60
134.44
131.71
130.06
123.79
123.75
123.58
122.83
114.79
114.03
111.16
110.80
56.04
55.93
55.89
42.95
42.78
42.63
23.07
OMe
OMe
OMe
MeO
NPhth
O
OH
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

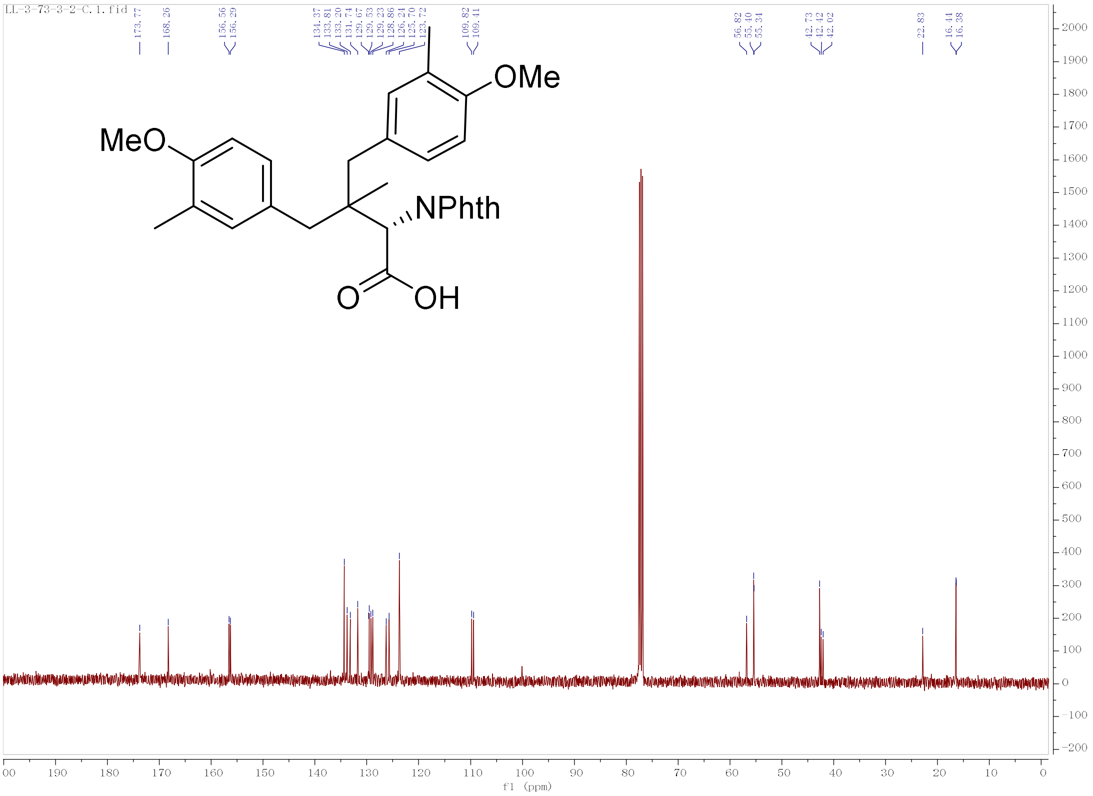
3k


LL-3-73-3-1-8/1
7.88
7.88
7.87
7.86
7.76
7.75
7.74
7.74
6.97
6.96
6.95
6.94
6.93
6.93
6.74
6.72
4.87
3.81
2.98
2.94
2.81
2.78
2.18
1.18
1.02
MeO
O
OH
NPhth
2.10
2.07
2.04
1.05
0.96
3.13
1.00
1.00
3.03
3.03
3.02
10.0 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 -0.5 -1.0
f1 (ppm)
2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

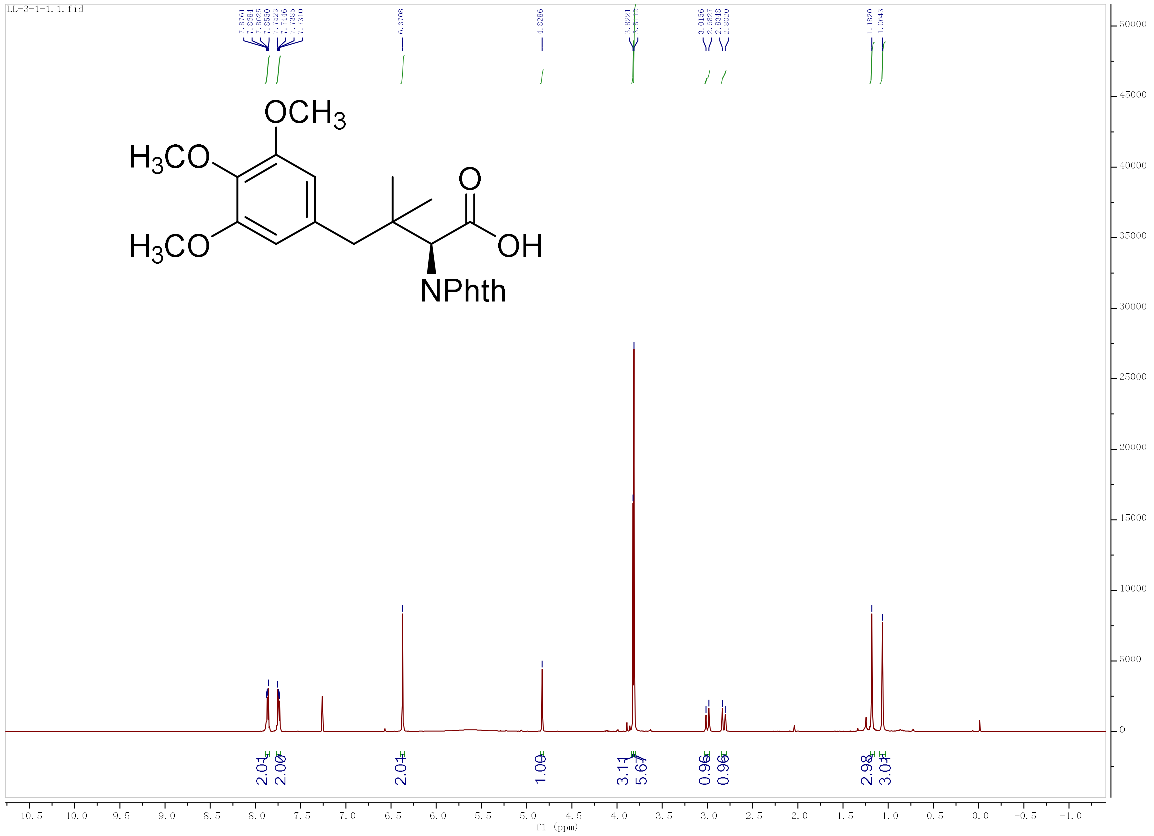

LL-3-73-3-1-C.1.fid
173.28
168.20
156.41
134.43
133.44
131.73
129.47
129.16
125.87
123.80
109.49
59.31
55.39
44.65
39.44
24.88
24.74
16.39
MeO
O
OH
NPhth
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
3500 3000 2500 2000 1500 1000 500 0

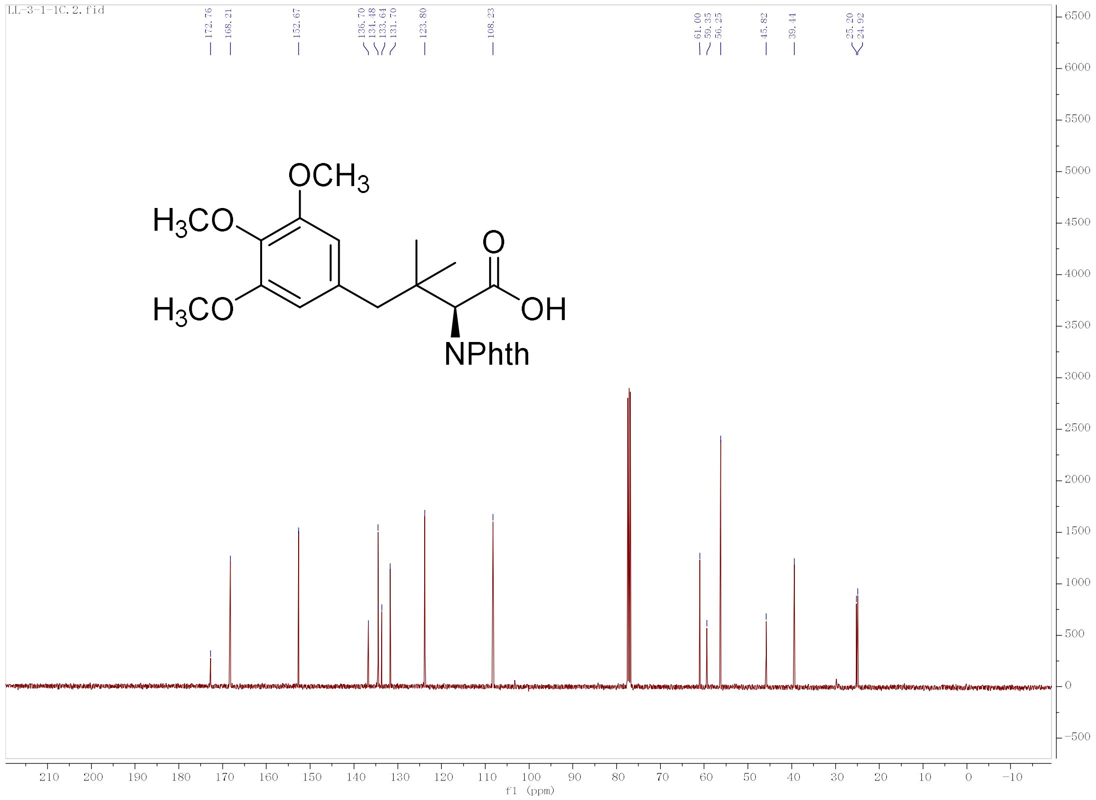
3k’


LL-3-73-3-2-9/1
OMe
MeO
NPhth
O
OH
1.99
1.99
3.11
1.02
2.04
0.95
3.02
3.26
0.96
0.94
0.94
0.91
3.14
3.04
2.97
f1 (ppm)

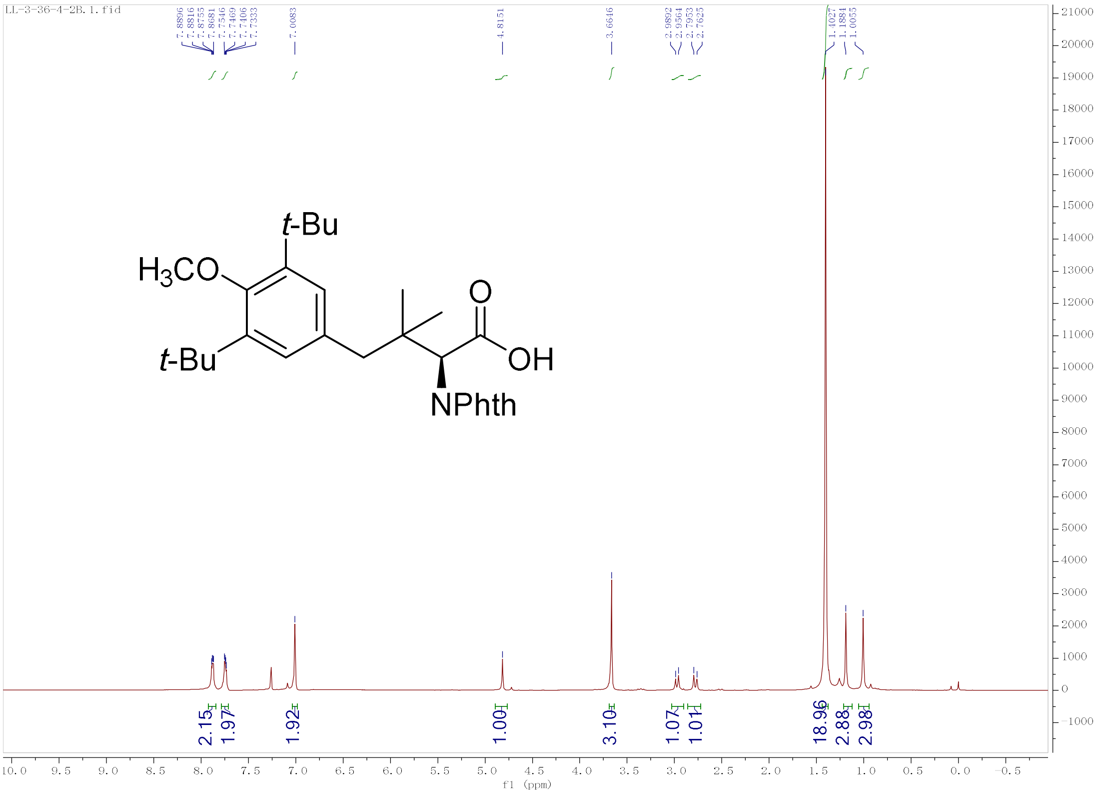

LL-3-73-3-2-C.1.fid
173.77
168.26
156.56
156.29
134.37
133.81
133.20
131.74
129.67
129.53
129.23
128.86
126.21
125.70
123.72
109.82
109.41
56.82
55.40
55.31
42.73
42.42
42.02
22.83
16.44
16.38
OMe
MeO
NPhth
O
OH
f1 (ppm)

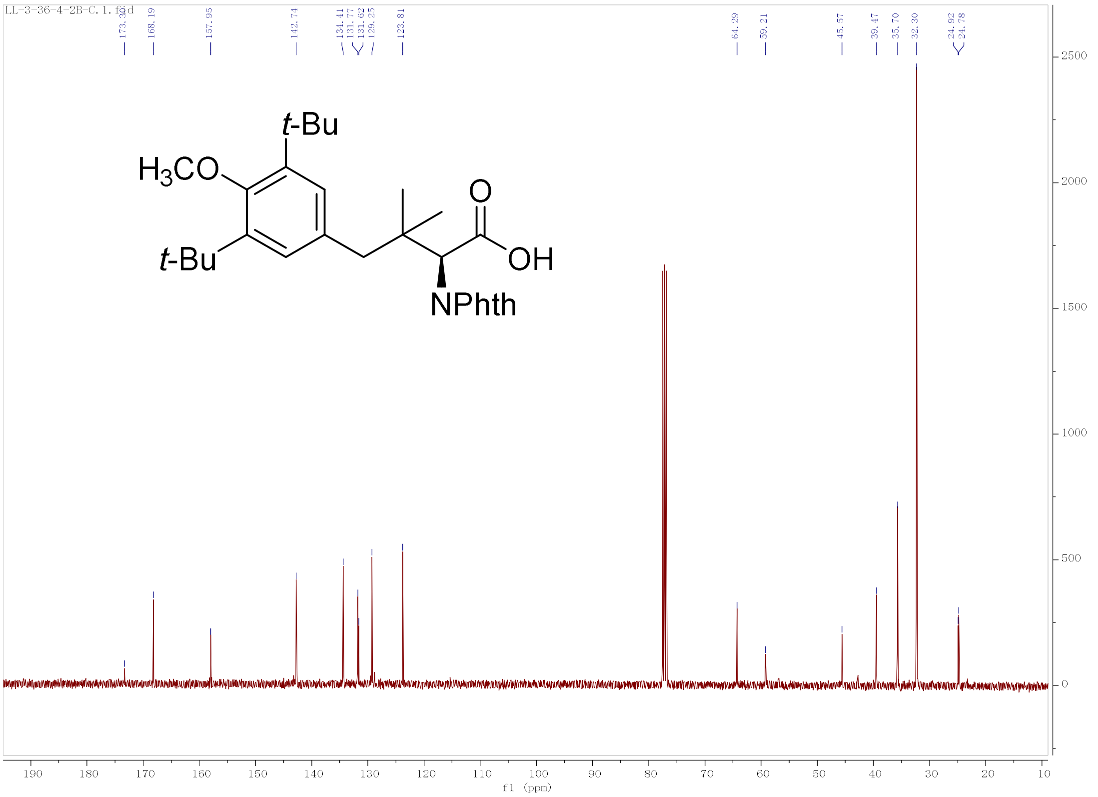
3l


LL-3-1-1.1.fid
7.8761
7.8684
7.8625
7.8550
7.7523
7.7446
7.7385
7.7310
6.3708
4.8286
3.8221
3.8112
3.0156
2.9827
2.8348
2.8020
1.1820
1.0643
OCH3
H3CO
H3CO
O
OH
NPhth
2.04
2.00
2.04
1.00
3.11
5.67
0.96
0.96
2.98
3.04
f1 (ppm)

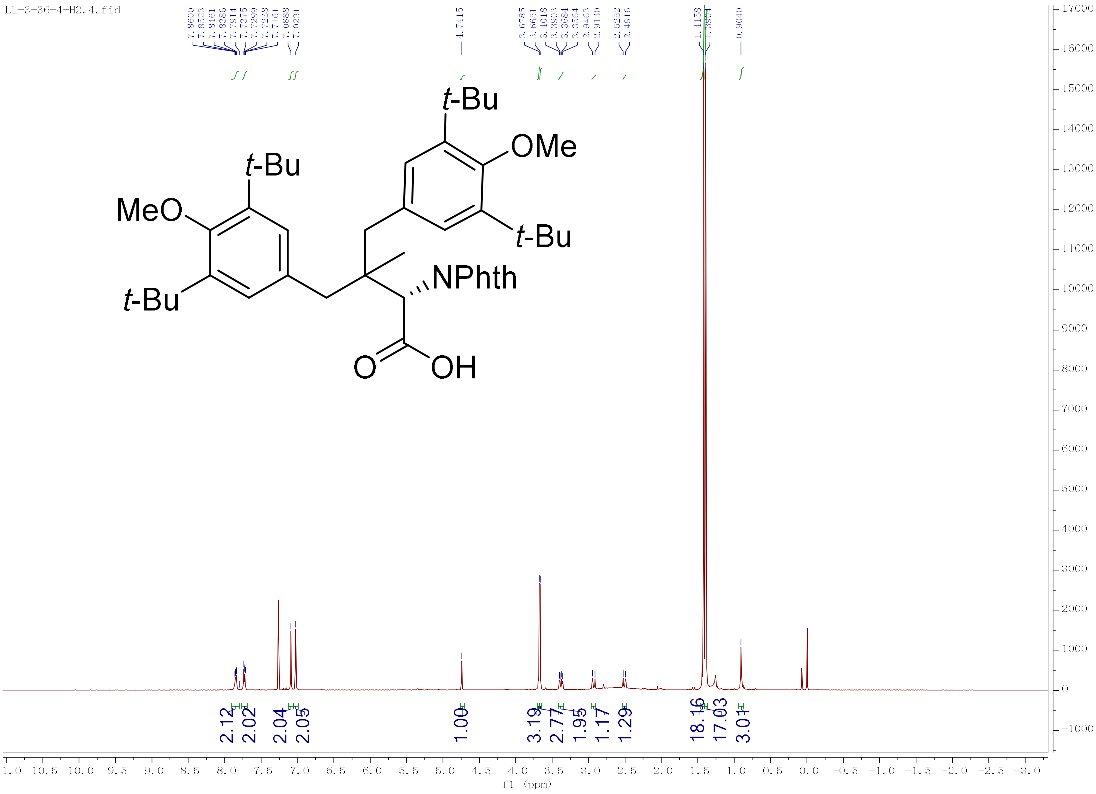

LL-3-1-1C.2.fid
172.76
168.21
152.67
136.70
134.48
133.64
131.70
123.80
108.23
61.00
59.35
56.25
45.82
39.44
25.20
24.92
OCH3
H3CO
H3CO
O
OH
NPhth
f1 (ppm)

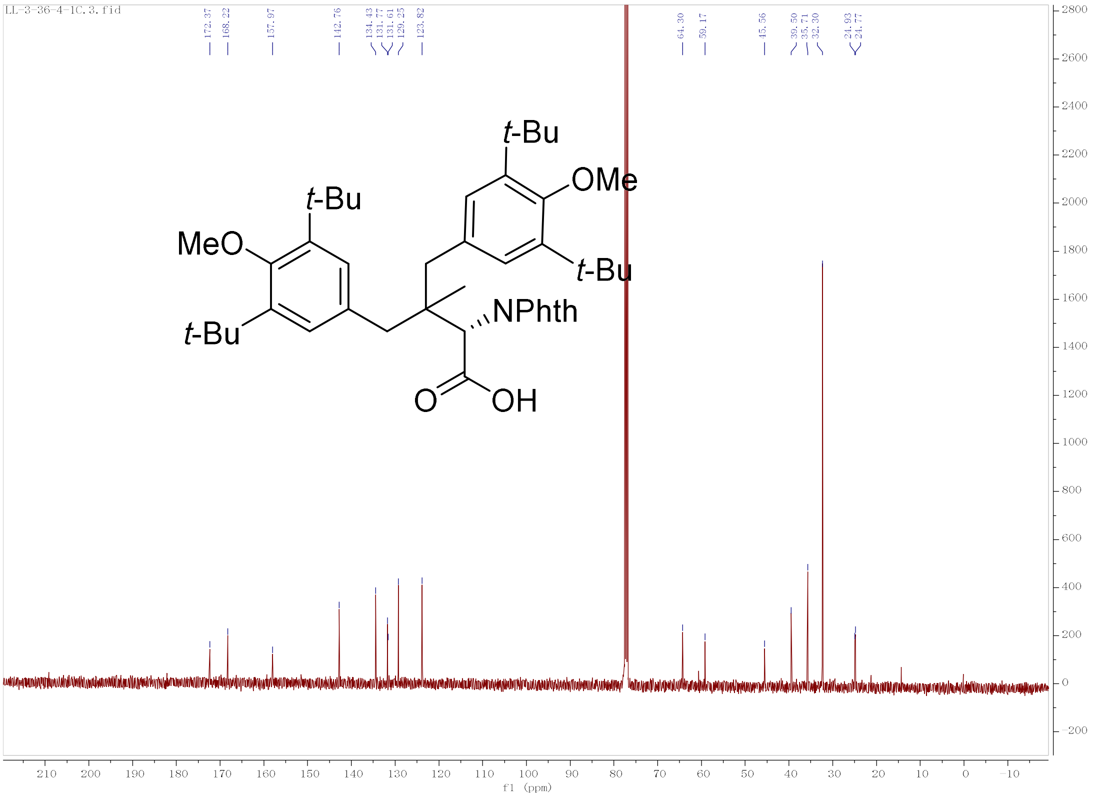
3m


LL-3-36-4-2B.1.fid
7.8896
7.8816
7.8755
7.8681
7.7546
7.7469
7.7406
7.7333
7.0083
4.8151
3.6646
2.9892
2.9564
2.7953
2.7625
1.4027
1.1884
1.0055
t-Bu
H3CO
t-Bu
O
OH
NPhth
2.15
1.97
1.92
1.00
3.10
1.07
1.01
18.96
2.88
2.98
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
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
-0.5
f1 (ppm)

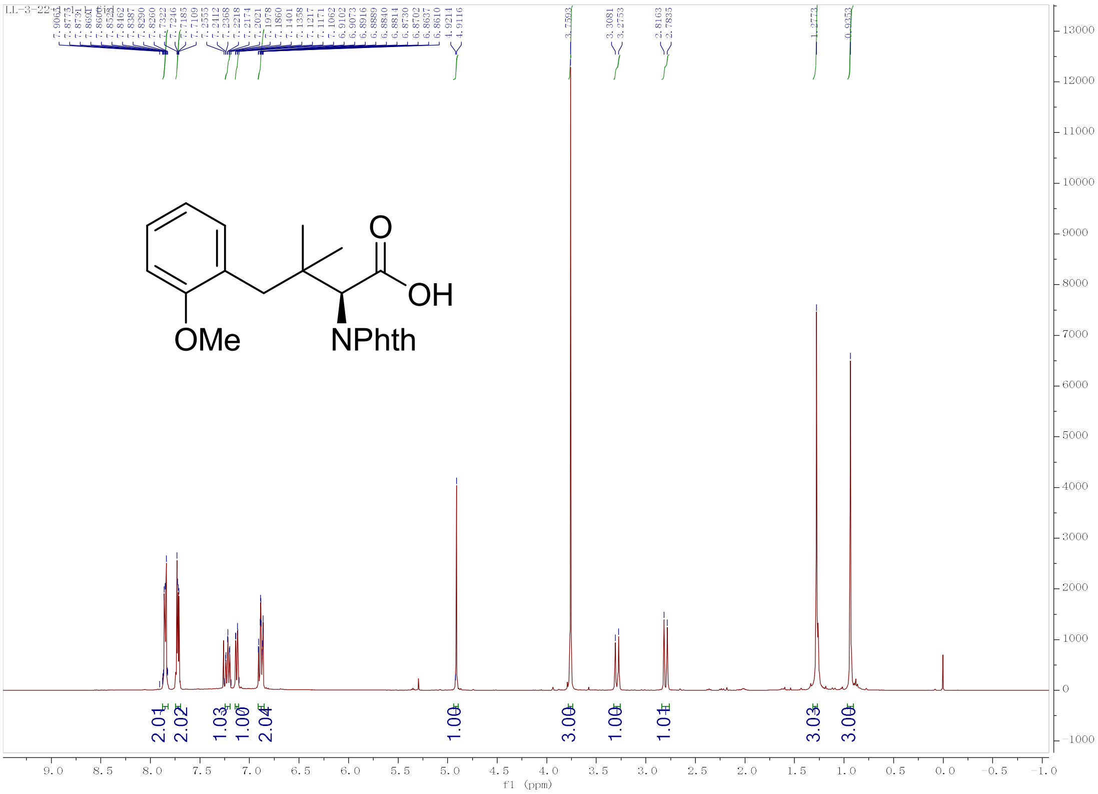

LL-3-36-4-2B-C.1.fid
173.3
168.19
157.95
142.74
134.41
131.77
131.62
129.25
123.81
64.29
59.21
45.57
39.47
35.70
32.30
24.92
24.78
t-Bu
H3CO
t-Bu
O
OH
NPhth
2500
2000
1500
1000
500
0
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

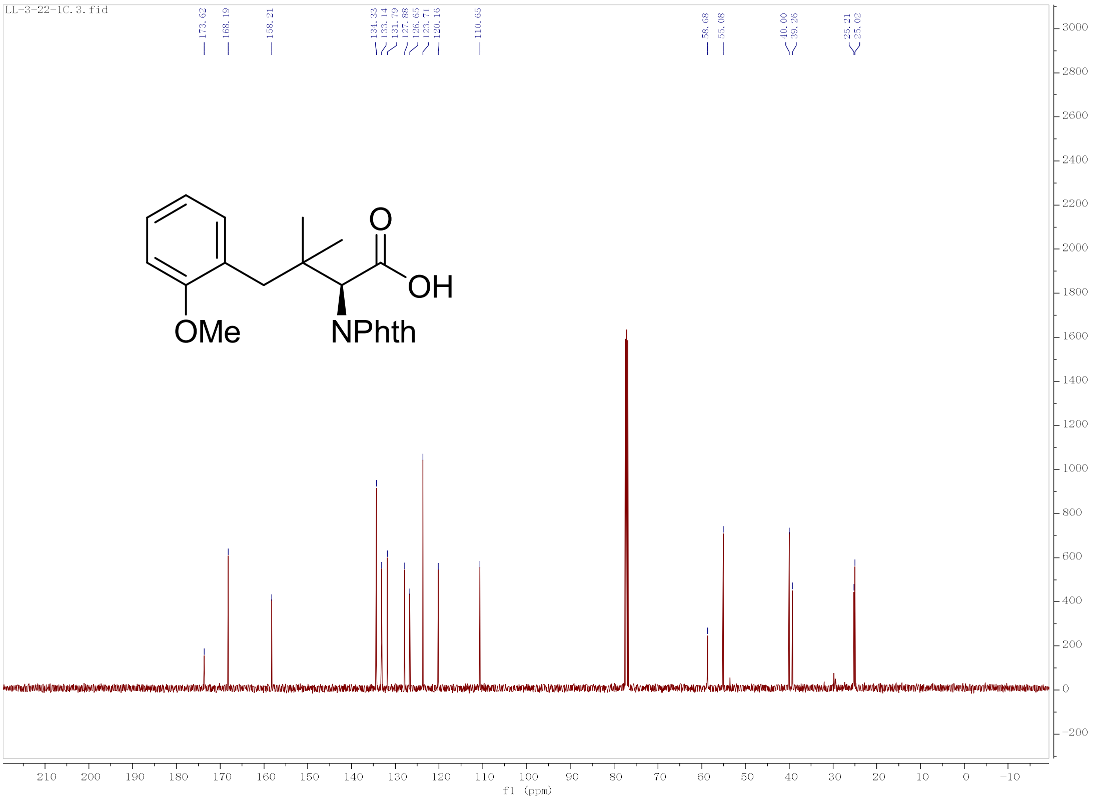
3m'


LL-3-36-4-H2.4.fid
7.8600
7.8523
7.8461
7.8386
7.7914
7.7375
7.7299
7.7238
7.7161
7.0888
7.0231
4.7415
3.6785
3.6651
3.4018
3.3903
3.3684
3.3564
2.9463
2.9130
2.5252
2.4916
1.4158
1.3901
0.9040
t-Bu
OMe
t-Bu
MeO
t-Bu
t-Bu
NPhth
O
OH
2.12
2.02
2.04
2.05
1.00
3.19
2.77
1.95
1.17
1.29
18.16
17.03
3.01
f1 (ppm)

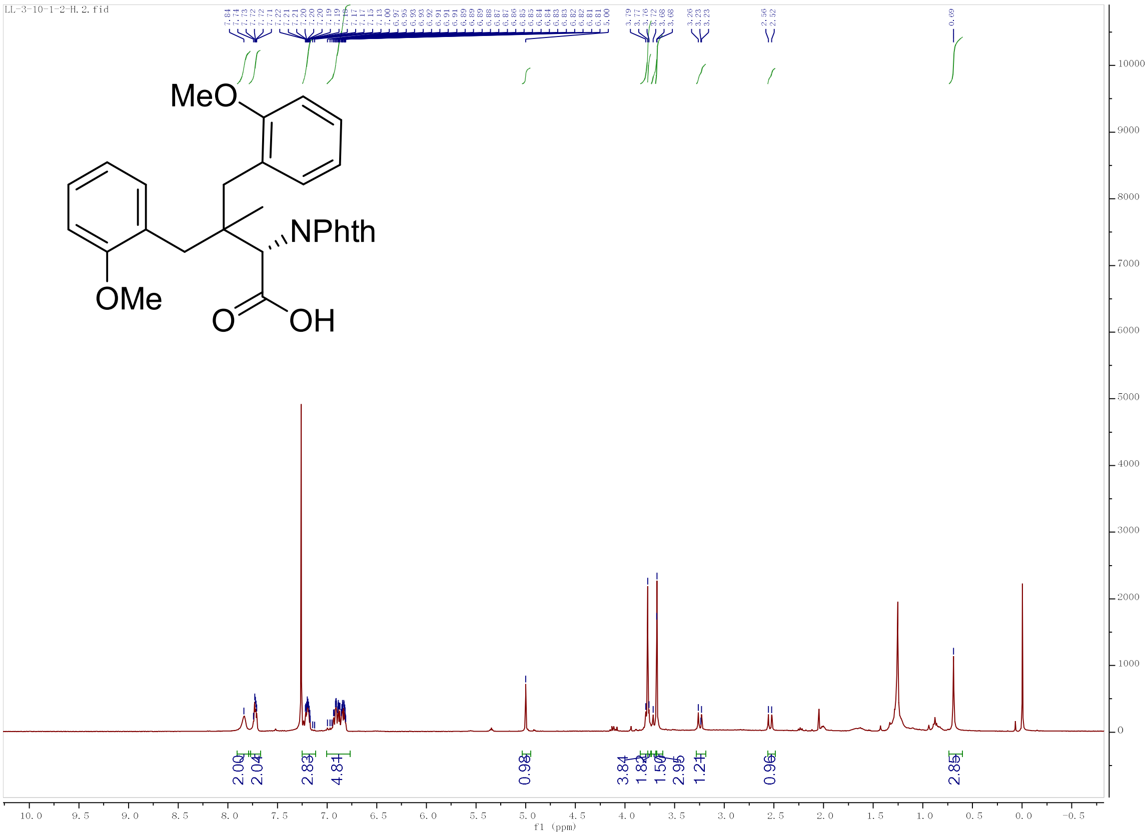

LL-3-36-4-1C.3.fid
172.37
168.22
157.97
142.76
134.43
131.77
131.61
129.25
123.82
64.30
59.17
45.56
39.50
35.71
32.30
24.93
24.77
t-Bu
OMe
t-Bu
MeO
t-Bu
t-Bu
NPhth
O
OH
f1 (ppm)

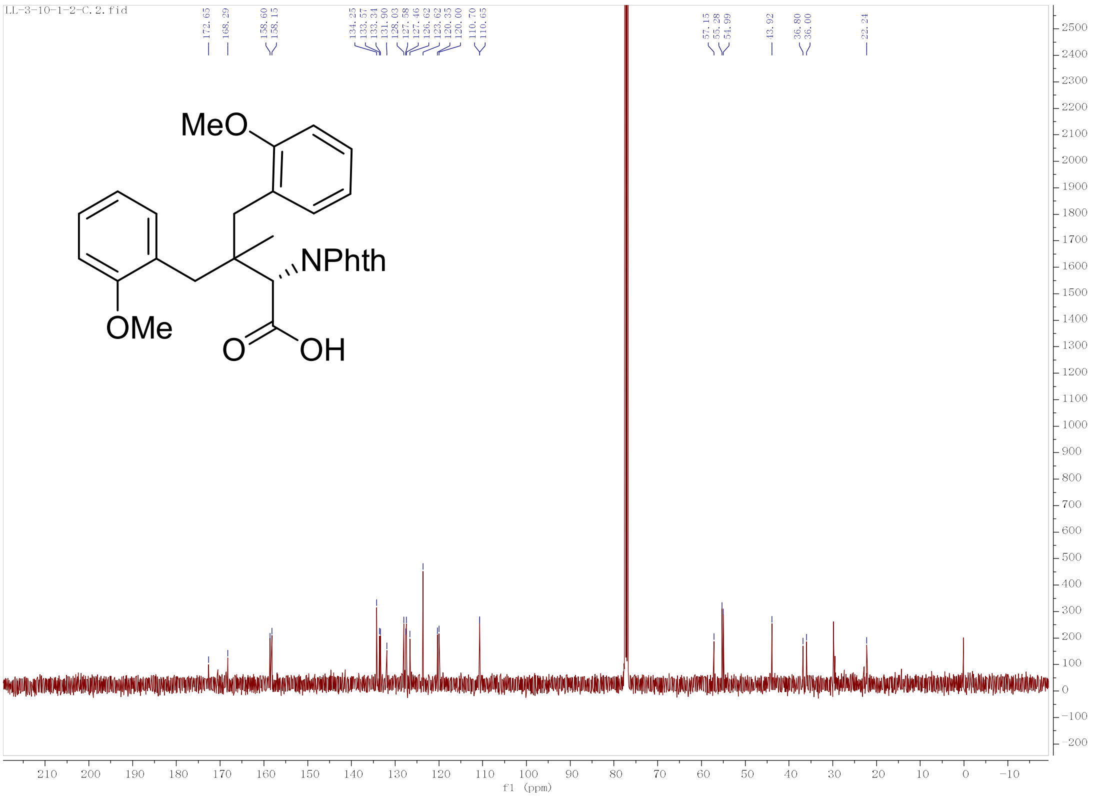
3n


LL-3-22-1.1.1.fid
7.9063
7.8773
7.8731
7.8691
7.8606
7.8523
7.8462
7.8387
7.8290
7.8260
7.7322
7.7246
7.7185
7.7109
7.2555
7.2412
7.2368
7.2218
7.2174
7.2021
7.1978
7.1860
7.1401
7.1358
7.1217
7.1171
7.1062
6.9102
6.9073
6.8916
6.8889
6.8840
6.8814
6.8730
6.8702
6.8637
6.8610
4.9214
4.9116
3.7593
3.3081
3.2753
2.8163
2.7835
1.2773
0.9352
OMe
O
OH
NPhth
2.01
2.02
1.03
1.00
2.04
1.00
3.00
1.00
1.01
3.03
3.00
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
-0.5
-1.0
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

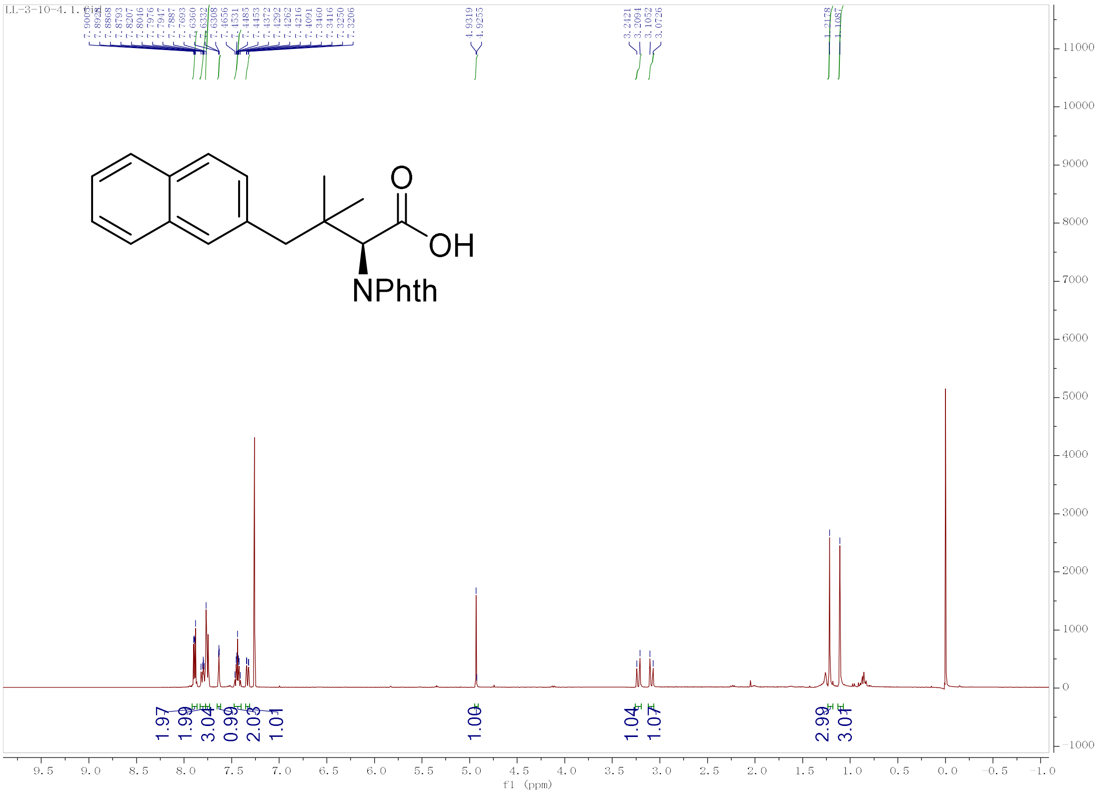

LL-3-22-1C.3.fid
173.62
168.19
158.21
134.33
133.14
131.79
127.88
126.65
123.71
120.16
110.65
58.68
55.08
40.00
39.26
25.21
25.02
OMe
O
OH
NPhth
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

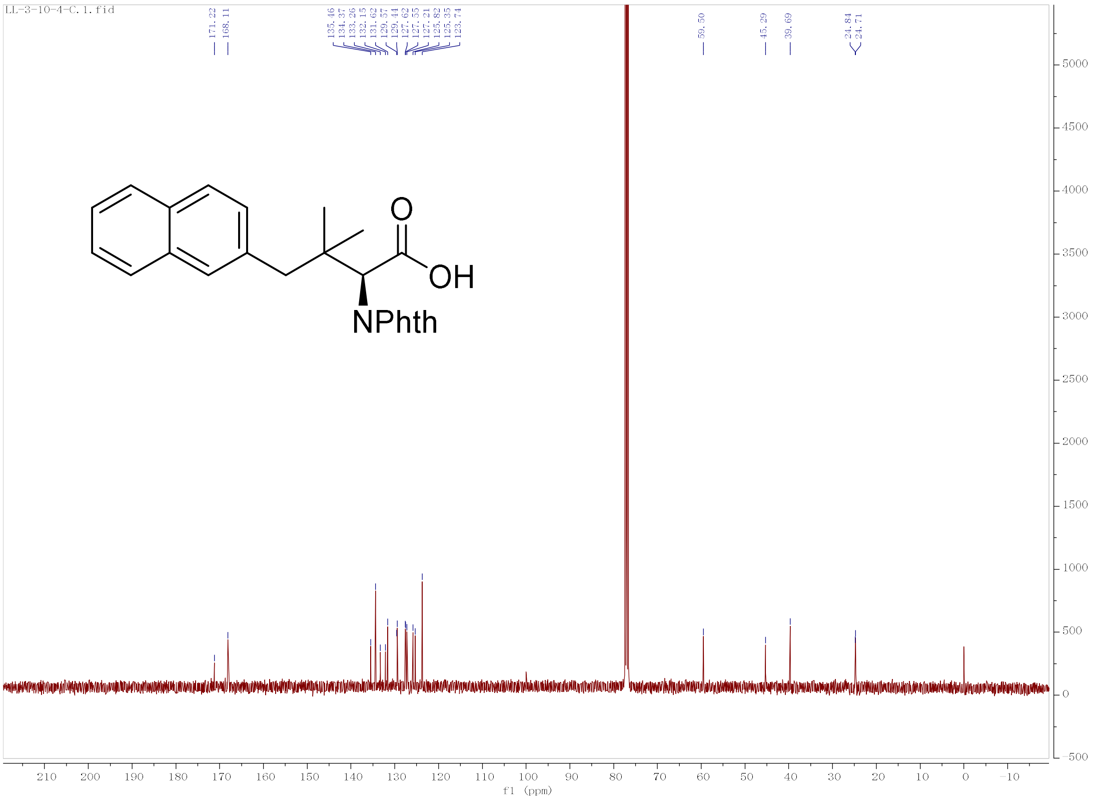
3n’


LL-3-10-1-2-H.2.fid
7.84 7.74 7.73 7.72 7.72 7.71 7.22 7.21 7.21 7.20 7.20 7.20 7.19 7.19 7.18 7.17 7.17 7.15 7.13 7.00 6.97 6.95 6.93 6.93 6.92 6.91 6.91 6.91 6.89 6.89 6.89 6.88 6.87 6.87 6.86 6.85 6.85 6.84 6.84 6.83 6.83 6.82 6.82 6.81 6.81 5.00
3.79 3.77 3.76 3.72 3.68 3.68 3.26 3.23 3.23 2.56 2.52 0.69
MeO
NPhth
OMe
O
OH
2.00 2.04 2.83 4.81 0.98 3.84 1.82 1.50 2.95 1.24 0.96 2.85
10.0 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 -0.5
f1 (ppm)
10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0

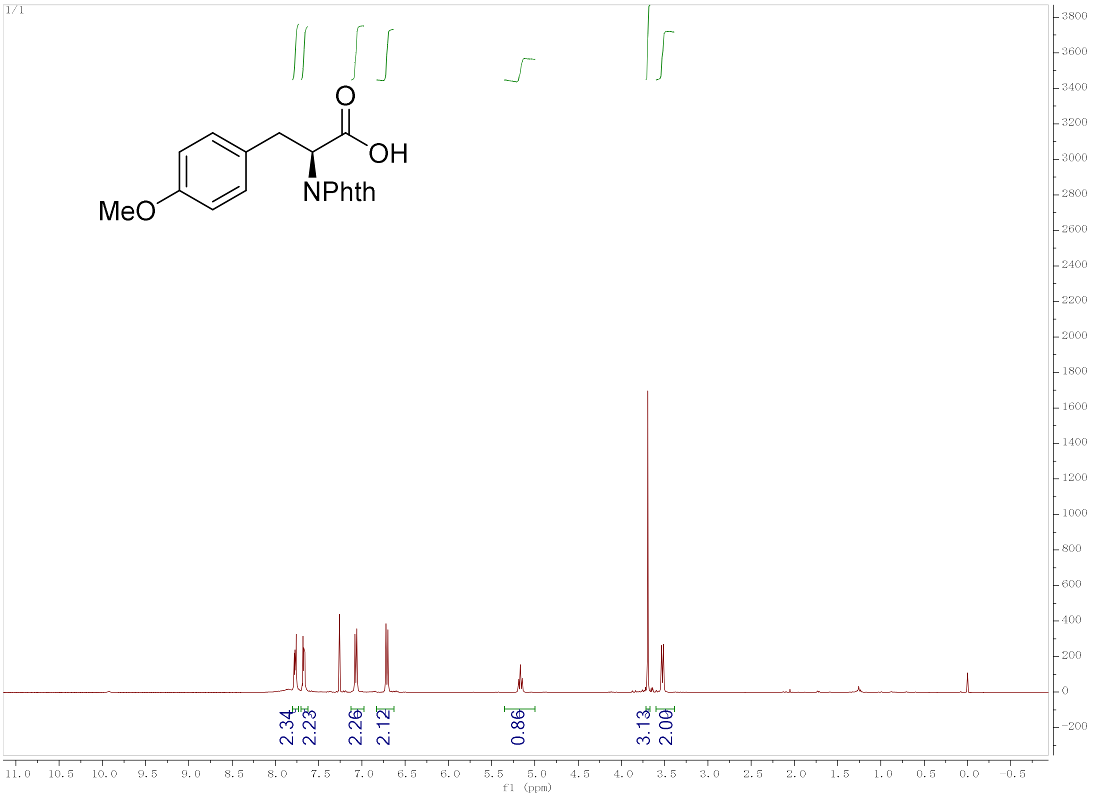

LL-3-10-1-2-C.2.fid
172.65 168.29 158.60 158.15 134.25 133.57 133.34 131.90 128.03 127.58 127.46 126.62 123.62 120.35 120.00 110.70 110.65 57.15 55.28 54.99 43.92 36.80 36.00 22.24
MeO
NPhth
OMe
O
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2500 2400 2300 2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

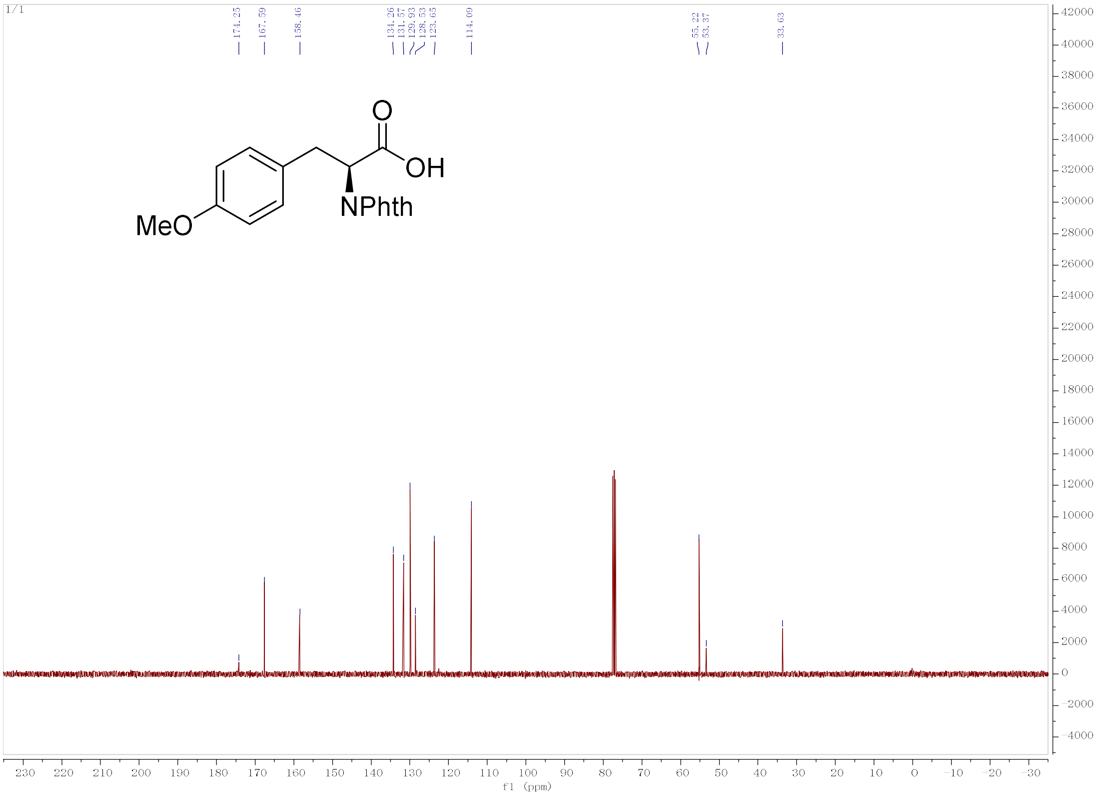
3o


LL-3-10-4.1.fid
7.9005
7.8928
7.8868
7.8793
7.8207
7.8046
7.7976
7.7947
7.7887
7.7693
7.6360
7.6332
7.6308
7.4656
7.4531
7.4485
7.4453
7.4372
7.4292
7.4262
7.4216
7.4091
7.3460
7.3416
7.3250
7.3206
4.9319
4.9255
3.2421
3.2094
3.1052
3.0726
1.2178
1.1087
O
OH
NPhth
1.97
1.99
3.04
0.99
2.03
1.01
1.00
1.04
1.07
2.99
3.01
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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
-0.5
-1.0
f1 (ppm)

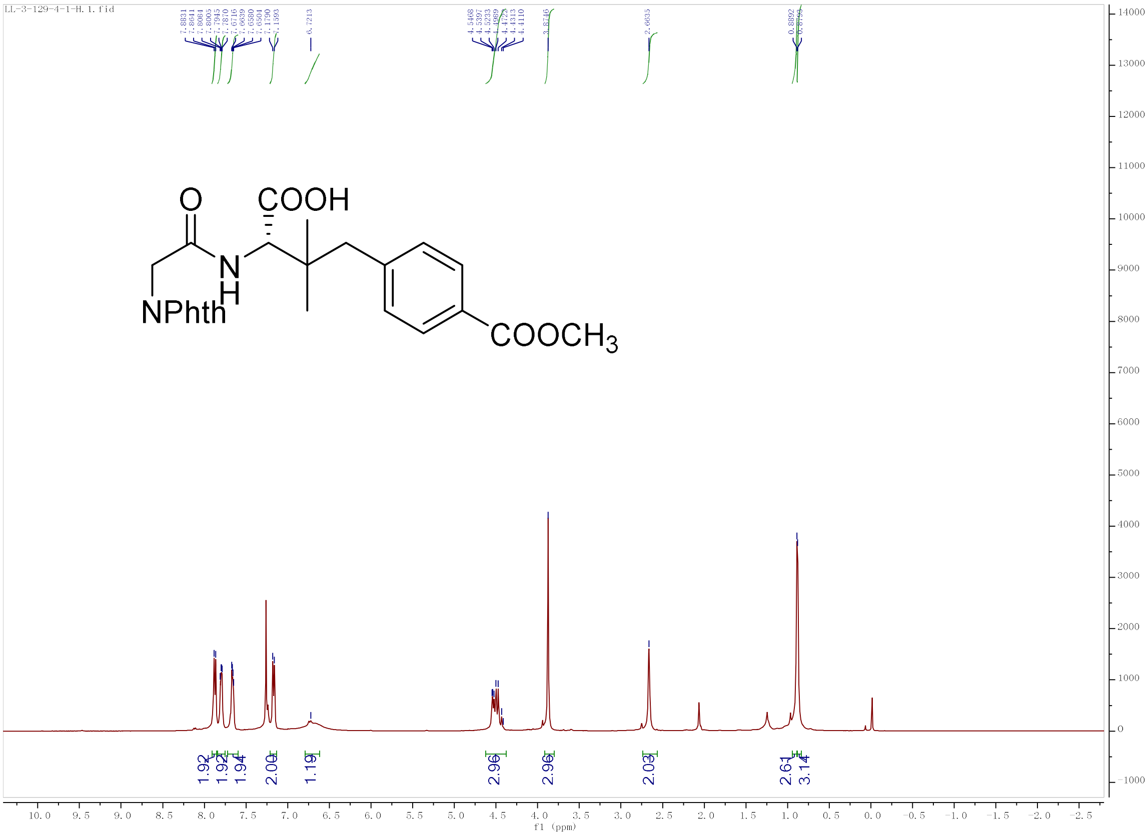

LL-3-10-4-C.1.fid
171.22
168.11
135.46
134.37
133.26
132.15
131.62
129.57
129.44
127.62
127.55
127.21
125.82
125.35
123.74
59.50
45.29
39.69
24.84
24.71
O
OH
NPhth
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

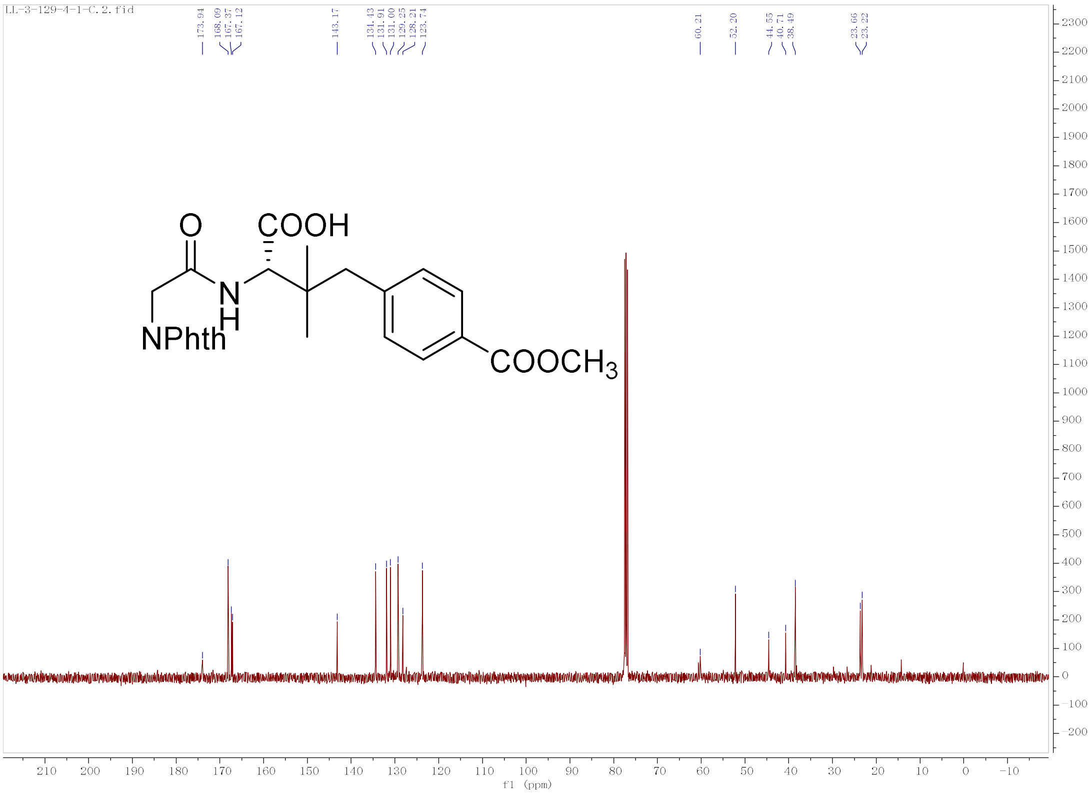
11a


1/1
MeO
O
OH
NPhth
2.34
2.23
2.26
2.12
0.86
3.13
2.00
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
11.0
10.5
10.0
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
-0.5
f1 (ppm)

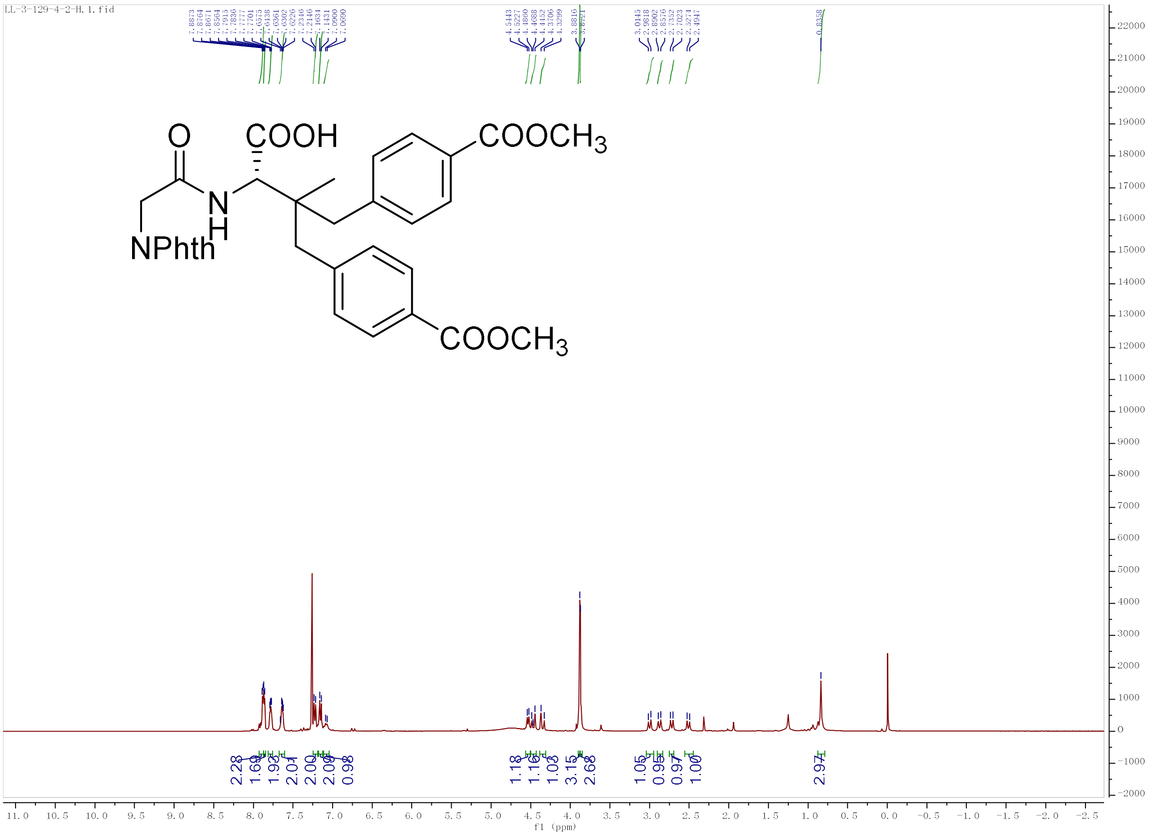

1/1
174.25
167.59
158.46
134.26
131.57
129.93
128.53
123.65
114.09
55.22
53.37
33.63
MeO
O
OH
NPhth
42000
40000
38000
36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
-4000
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)

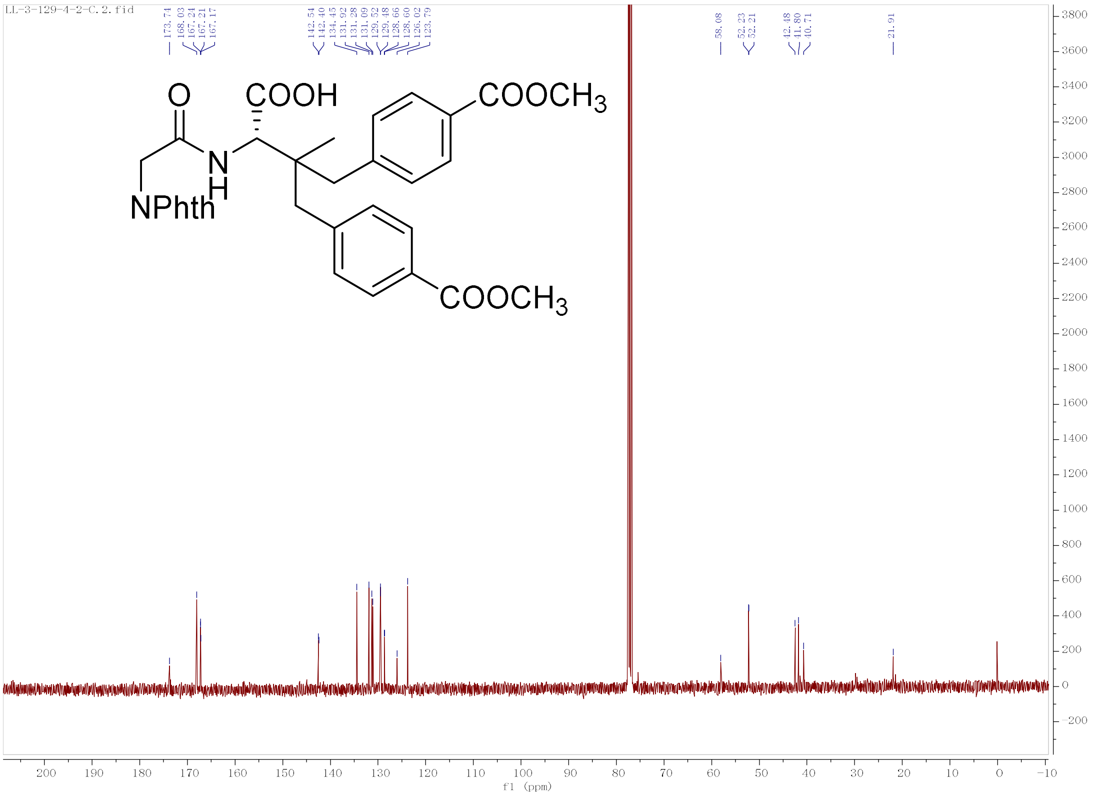
5a


LL-3-129-4-1-H.1.fid
7.8831
7.8641
7.8084
7.8005
7.7945
7.7870
7.6716
7.6639
7.6580
7.6504
7.1790
7.1593
6.7213
4.5468
4.5397
4.5233
4.4989
4.4722
4.4313
4.4110
3.8746
2.6635
0.8892
0.8793
O
COOH
N
H
NPhth
COOCH3
1.92
1.92
1.94
2.00
1.19
2.96
2.96
2.03
2.61
3.14
f1 (ppm)

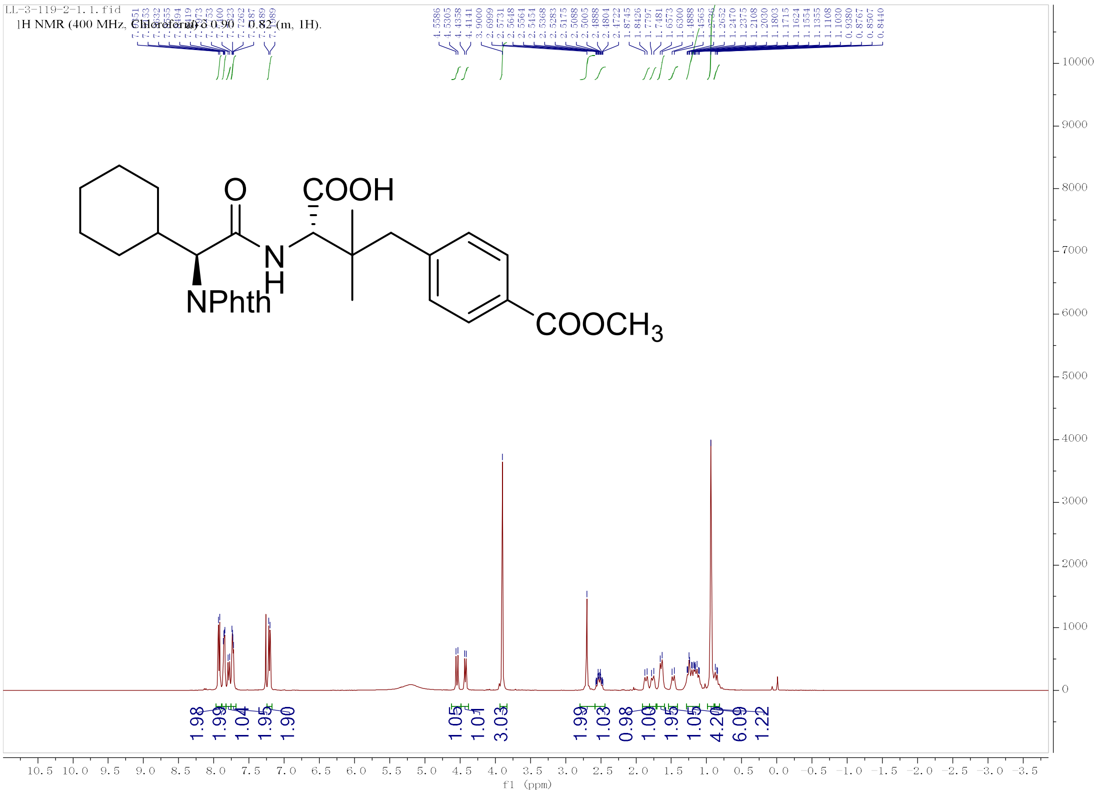

LL-3-129-4-1-C.2.fid
173.94
168.09
167.37
167.12
143.17
134.43
131.91
131.00
129.25
128.21
123.74
60.21
52.20
44.55
40.71
38.49
23.66
23.22
O
COOH
N
H
NPhth
COOCH3
f1 (ppm)

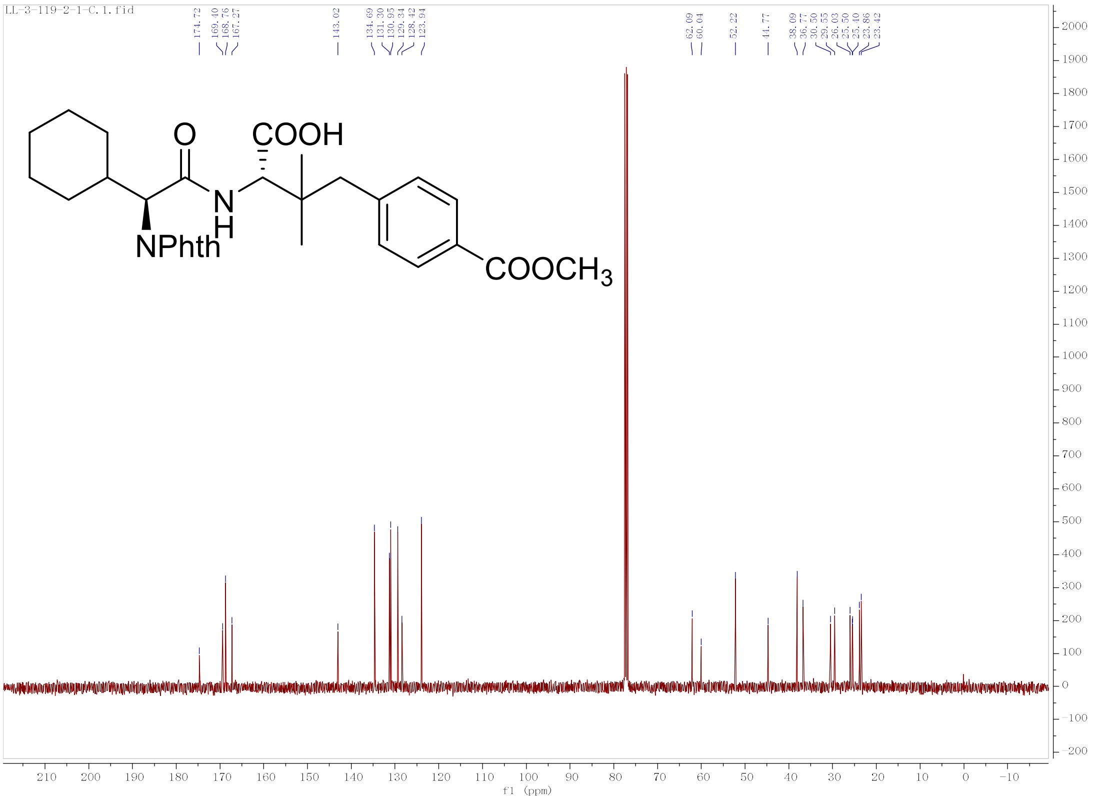
5a’


LL-3-129-4-2-H.1.fid
7.8873
7.8764
7.8671
7.8564
7.7915
7.7836
7.7777
7.7701
7.6575
7.6438
7.6361
7.6302
7.6226
7.2346
7.2146
7.1634
7.1431
7.0900
7.0690
4.5443
4.5227
4.4860
4.4688
4.4452
4.3706
4.3299
3.8816
3.8721
3.0145
2.9818
2.8902
2.8576
2.7352
2.7023
2.5274
2.4947
0.8358
O
COOH
N
H
NPhth
COOCH3
COOCH3
2.28
1.69
1.93
2.01
2.00
2.09
0.98
1.18
1.16
1.03
3.15
2.68
1.05
0.95
0.97
1.00
2.97
f1 (ppm)

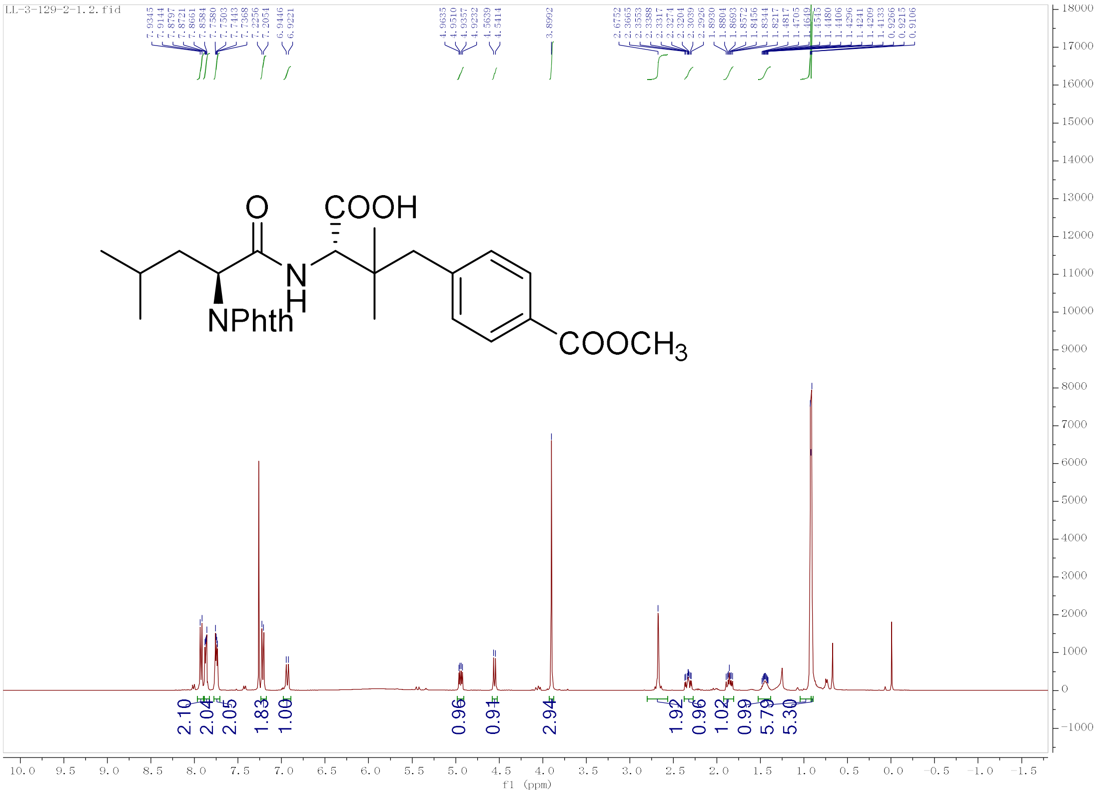

LL-3-129-4-2-C.2.fid
173.74
168.03
167.24
167.21
167.17
142.54
142.40
134.45
131.92
131.28
131.09
129.52
129.48
128.66
128.60
126.02
123.79
58.08
52.23
52.21
42.48
41.80
40.71
21.91
O
COOH
N
H
NPhth
COOCH3
COOCH3
f1 (ppm)

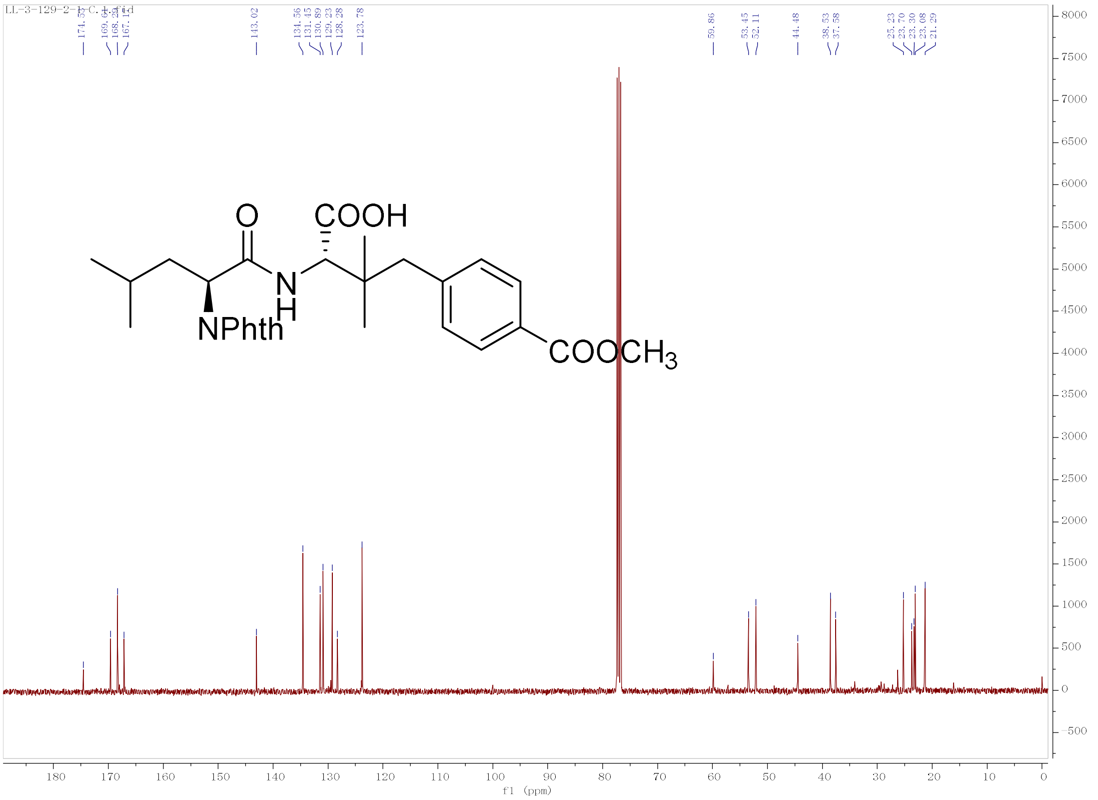
5b


LL-3-119-2-1.1.fid
1H NMR (400 MHz, Chloroform-d) δ 0.90 – 0.82 (m, 1H).
O
COOH
N
H
NPhth
COOCH3
1.98
1.99
1.04
1.95
1.90
1.05
1.01
3.03
1.99
1.03
0.98
1.00
1.95
1.05
4.20
6.09
1.22
f1 (ppm)

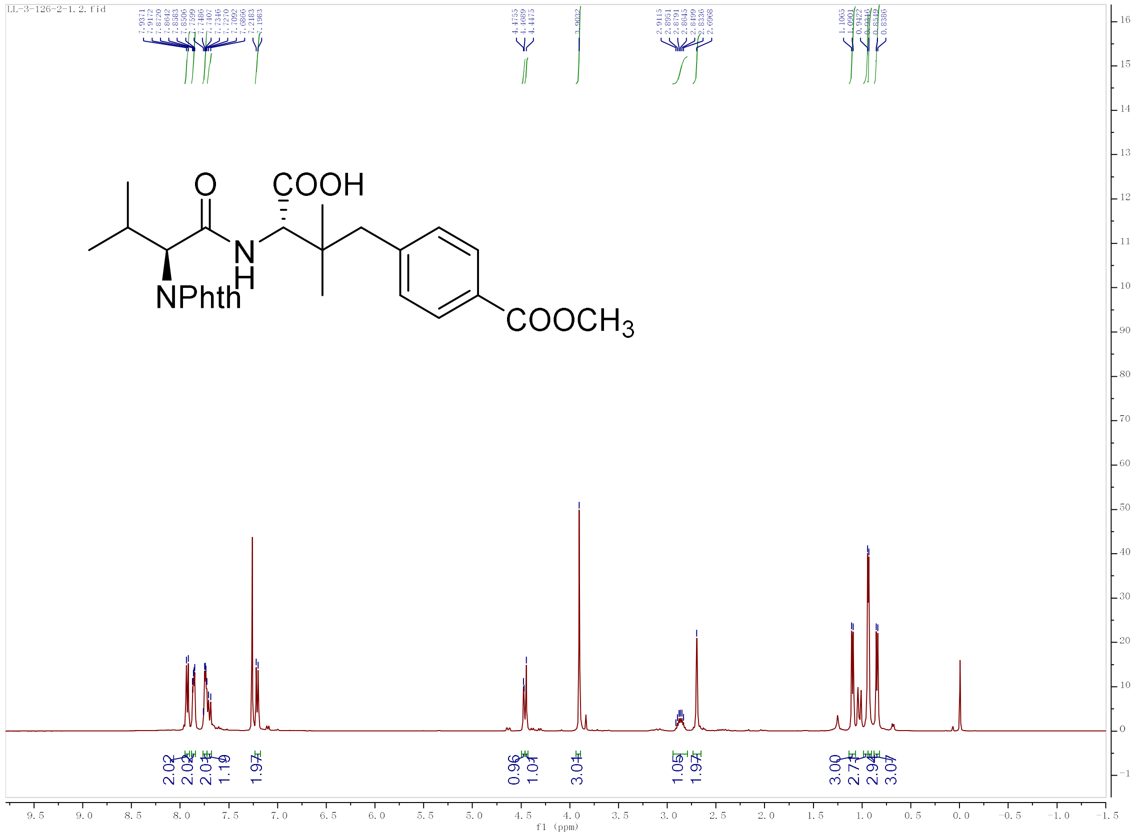

LL-3-119-2-1-C.1.fid
174.72
169.40
168.76
167.27
143.02
134.69
131.30
130.95
129.34
128.42
123.94
62.09
60.04
52.22
44.77
38.09
36.77
30.50
29.55
26.03
25.50
25.10
23.86
23.42
O
COOH
N
H
NPhth
COOCH3
f1 (ppm)

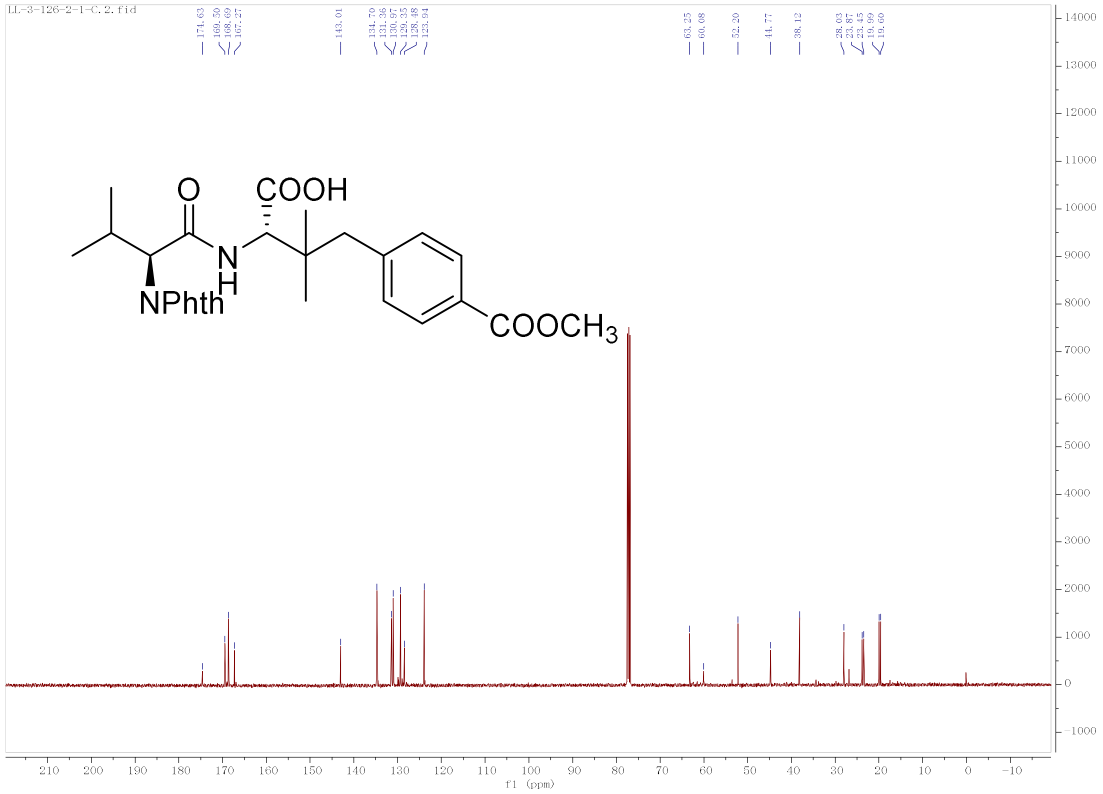
5c


LL-3-129-2-1.2.fid
7.9345 7.9144 7.8797 7.8721 7.8661 7.8584 7.7580 7.7503 7.7443 7.7368 7.2256 7.2054 6.9446 6.9221
4.9635 4.9510 4.9357 4.9232 4.5639 4.5414
3.8992
2.6752 2.3665 2.3553 2.3388 2.3317 2.3274 2.3204 2.3039 2.2926 1.8930 1.8804 1.8693 1.8572 1.8456 1.8344 1.8217 1.4817 1.4705 1.4649 1.4545 1.4480 1.4406 1.4296 1.4241 1.4209 1.4133 0.9266 0.9215 0.9106
O
COOH
N
H
NPhth
COOCH3
2.10 2.04 2.05 1.83 1.00 0.96 0.91 2.94 1.92 0.96 1.02 0.99 5.79 5.30
10.0 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 -0.5 -1.0 -1.5
f1 (ppm)
18000 17000 16000 15000 14000 13000 12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

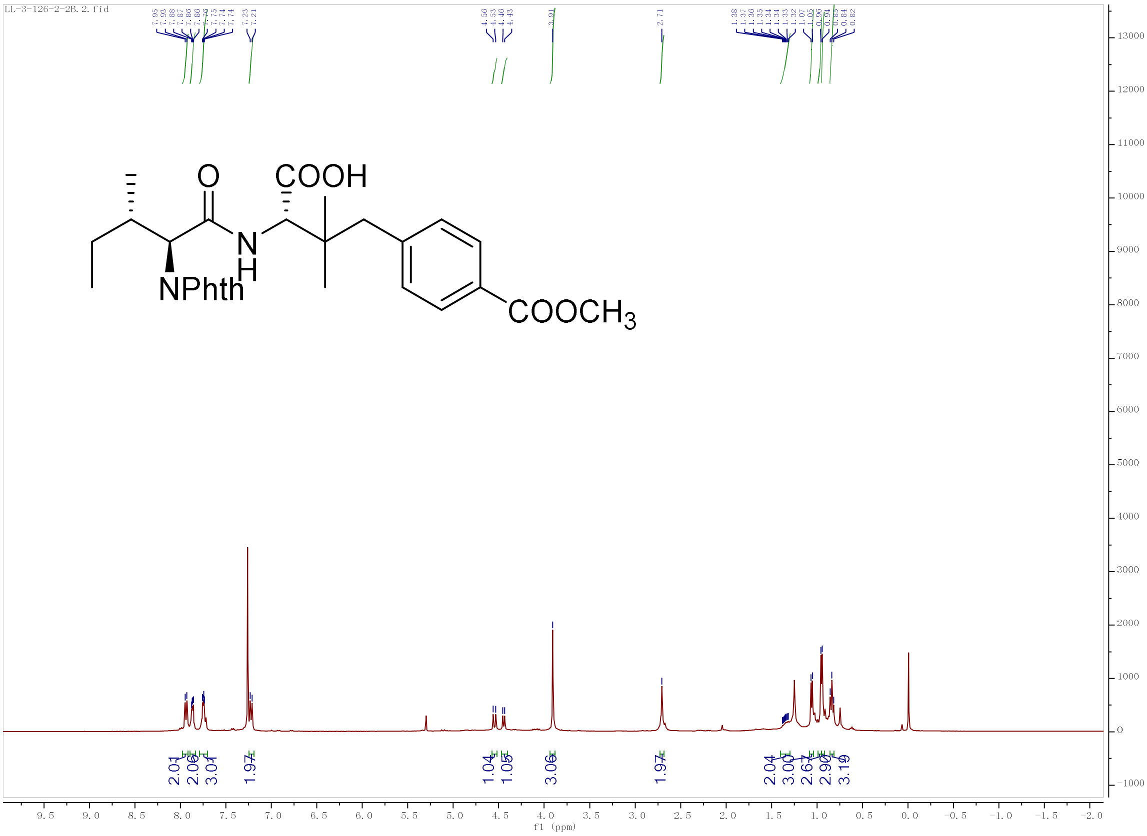

LL-3-129-2-1-C.1.fid
174.53 169.61 168.29 167.14
143.02
134.56 131.45 130.89 129.23 128.28
123.78
59.86
53.45 52.11
44.48
38.53 37.58
25.23 23.70 23.30 23.08 21.29
O
COOH
N
H
NPhth
COOCH3
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

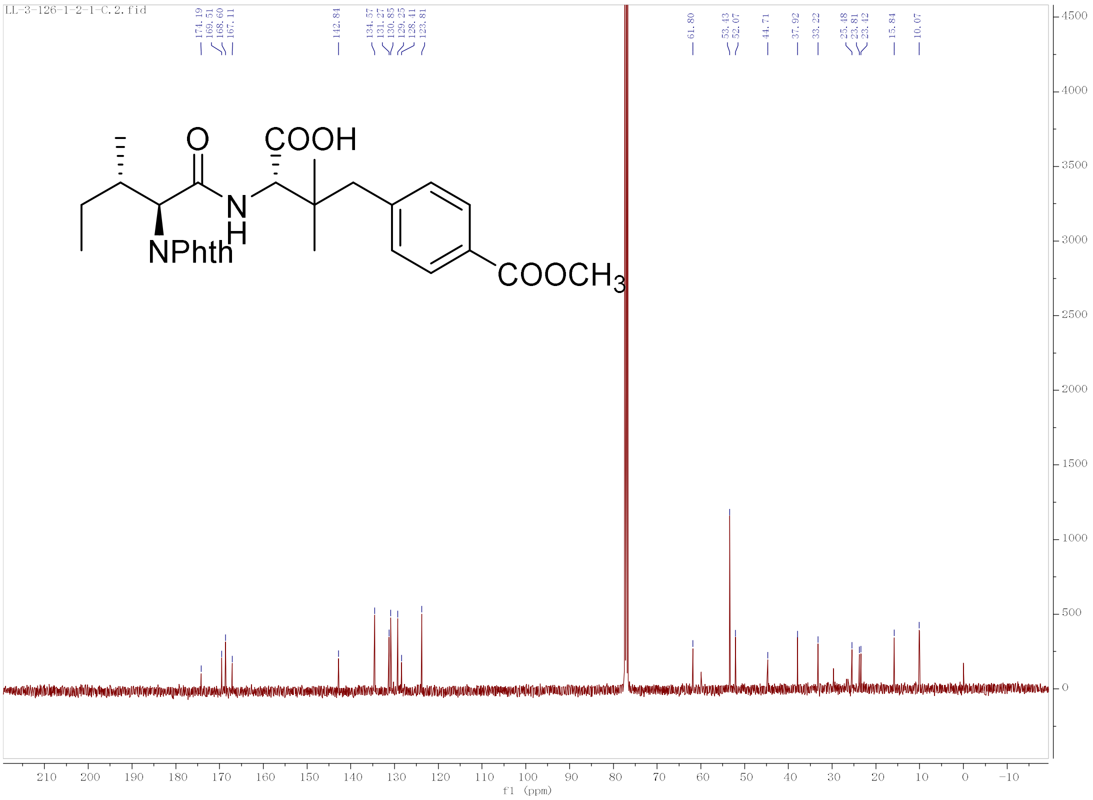
5d


LL-3-126-2-1.2.fid
7.9371
7.9172
7.8720
7.8642
7.8583
7.8506
7.7599
7.7486
7.7407
7.7346
7.7270
7.7092
7.6866
7.2183
7.1983
4.4755
4.4689
4.4475
3.9032
2.9115
2.8951
2.8791
2.8645
2.8499
2.8336
2.6968
1.1065
1.0901
0.9422
0.9316
0.8549
0.8386
O
COOH
N
H
NPhth
COOCH3
2.02
2.02
2.01
1.19
1.97
0.96
1.01
3.04
1.05
1.97
3.00
2.74
2.94
3.07
f1 (ppm)

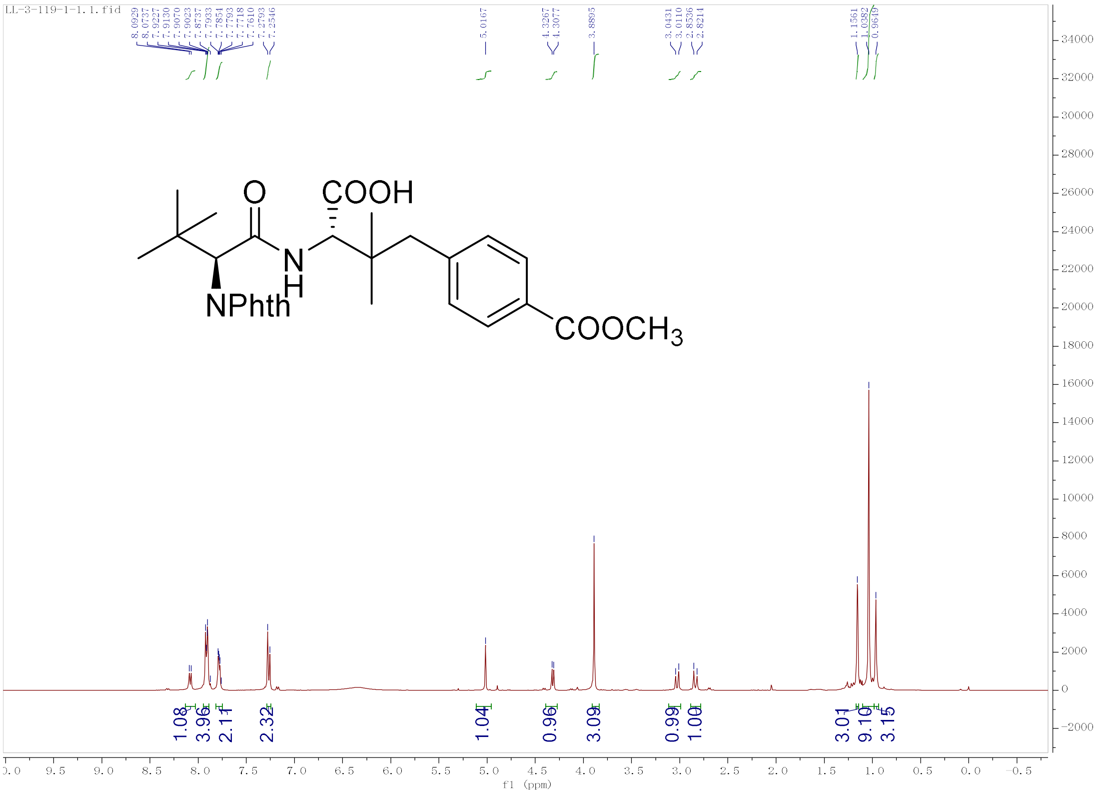

LL-3-126-2-1-C.2.fid
171.63
169.50
168.69
167.27
143.01
134.70
131.36
130.97
129.35
128.48
123.94
63.25
60.08
52.20
44.77
38.12
28.03
23.87
23.45
19.99
19.60
O
COOH
N
H
NPhth
COOCH3
f1 (ppm)

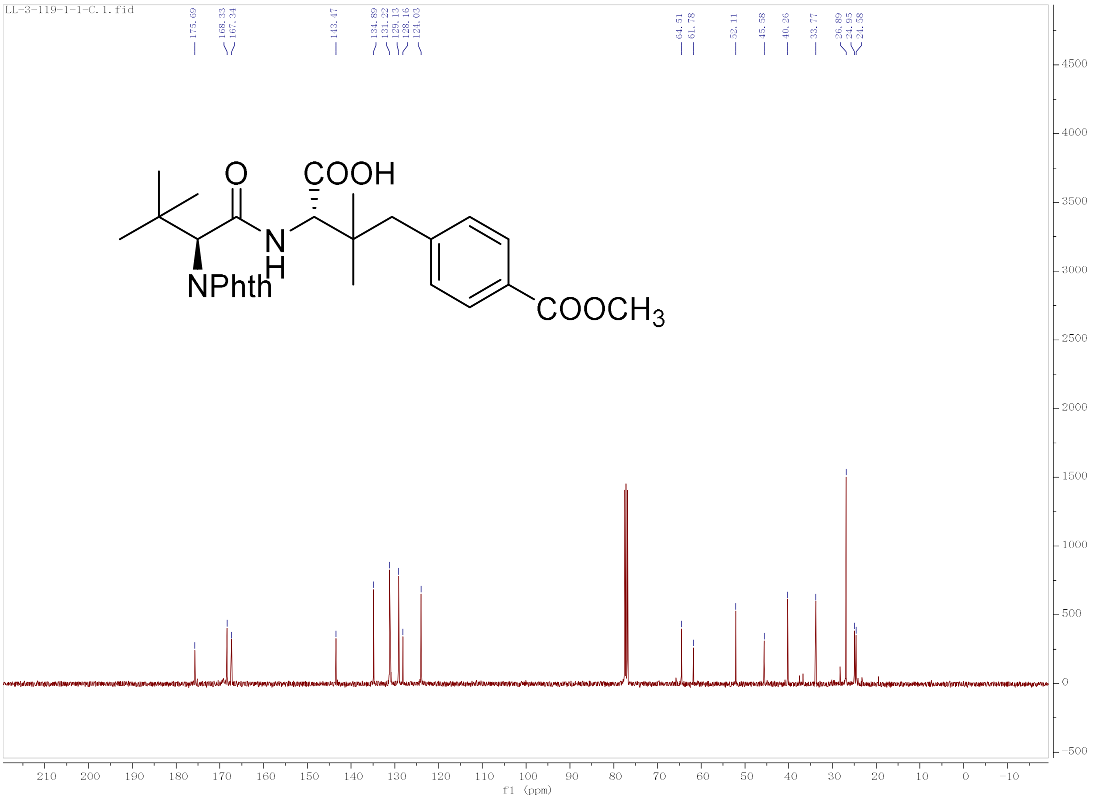
5e


LL-3-126-2-2B.2.fid
7.95
7.93
7.88
7.87
7.86
7.86
7.76
7.75
7.74
7.74
7.23
7.21
4.56
4.53
4.46
4.43
3.91
2.71
1.38
1.37
1.36
1.35
1.34
1.34
1.33
1.32
1.07
1.05
0.96
0.94
0.85
0.84
0.82
O
COOH
N
H
NPhth
COOCH3
2.01
2.06
3.04
1.97
1.04
1.05
3.06
1.97
2.04
3.00
2.67
2.90
3.19
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
-0.5
-1.0
-1.5
-2.0
f1 (ppm)
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

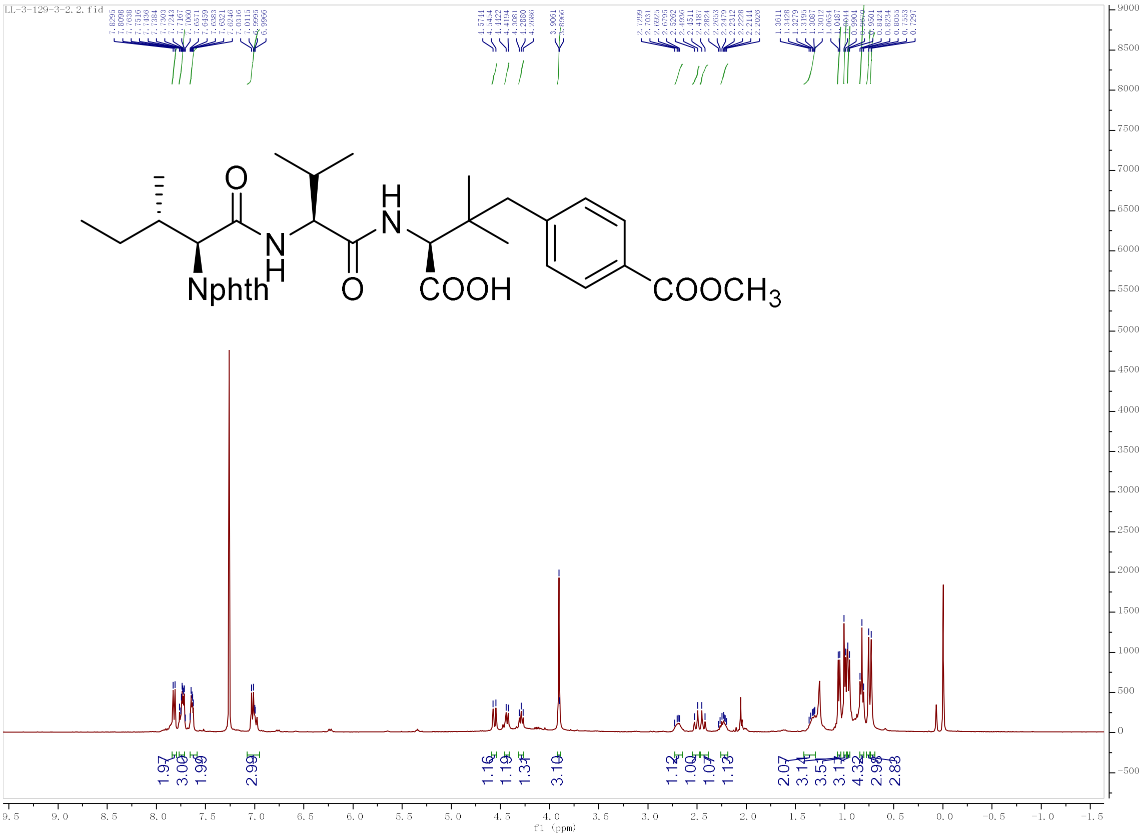

LL-3-126-1-2-1-C.2.fid
174.19
169.51
168.60
167.11
142.84
134.57
131.27
130.85
129.25
128.41
123.81
61.80
53.43
52.07
44.71
37.92
33.22
25.48
23.81
23.42
15.84
10.07
O
COOH
N
H
NPhth
COOCH3
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
4500
4000
3500
3000
2500
2000
1500
1000
500
0

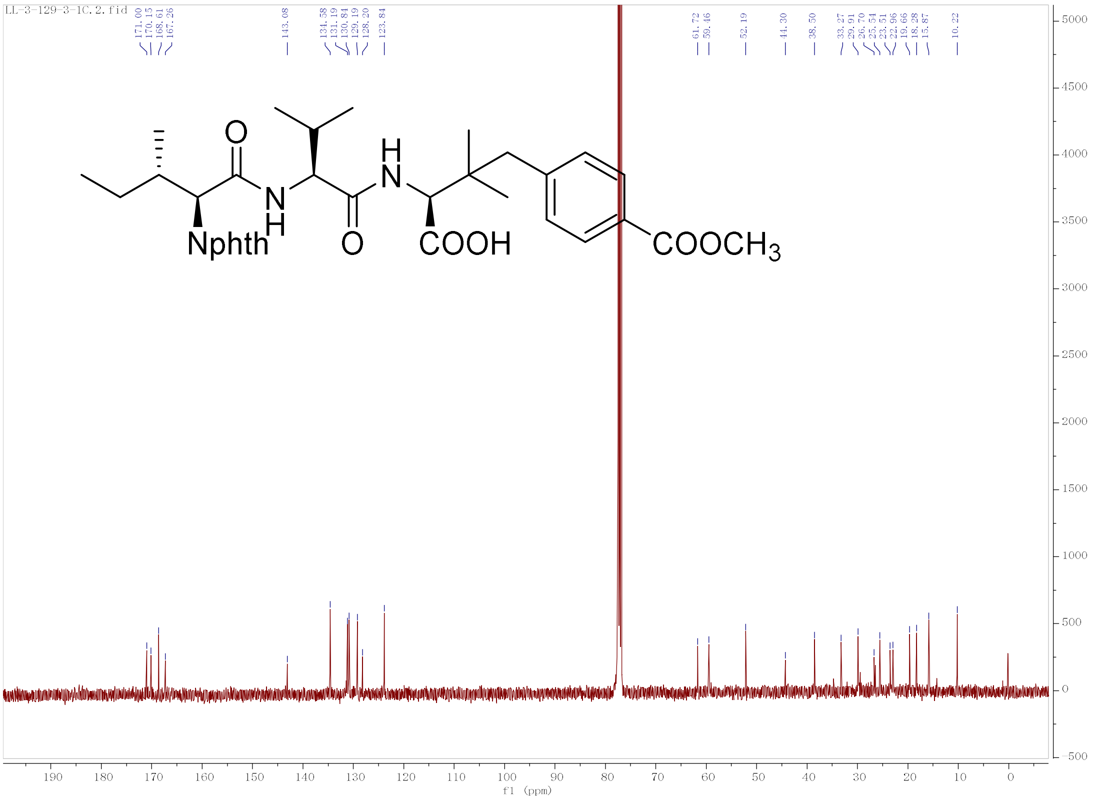
5f


LL-3-119-1-1.1.fid
8.0929
8.0737
7.9227
7.9130
7.9070
7.9023
7.8737
7.7933
7.7854
7.7793
7.7718
7.7610
7.2793
7.2546
5.0167
4.3267
4.3077
3.8895
3.0431
3.0110
2.8536
2.8214
1.1561
1.0382
0.9619
O
COOH
N
H
NPhth
COOCH3
1.08
3.96
2.11
2.32
1.04
0.96
3.09
0.99
1.00
3.01
9.10
3.15
f1 (ppm)

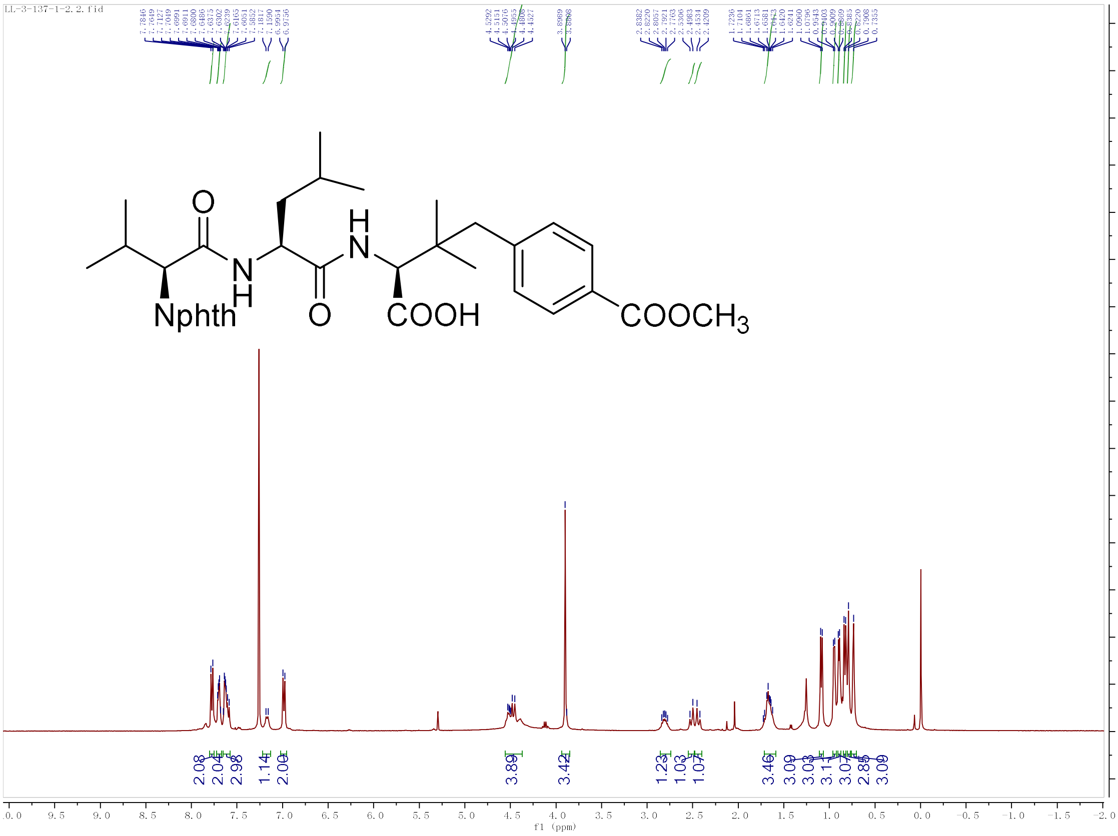

LL-3-119-1-C.1.fid
175.69
168.33
167.34
143.47
134.89
131.22
129.13
128.16
124.03
64.51
61.78
52.11
45.58
40.26
33.77
26.89
24.95
24.58
O
COOH
N
H
NPhth
COOCH3
f1 (ppm)

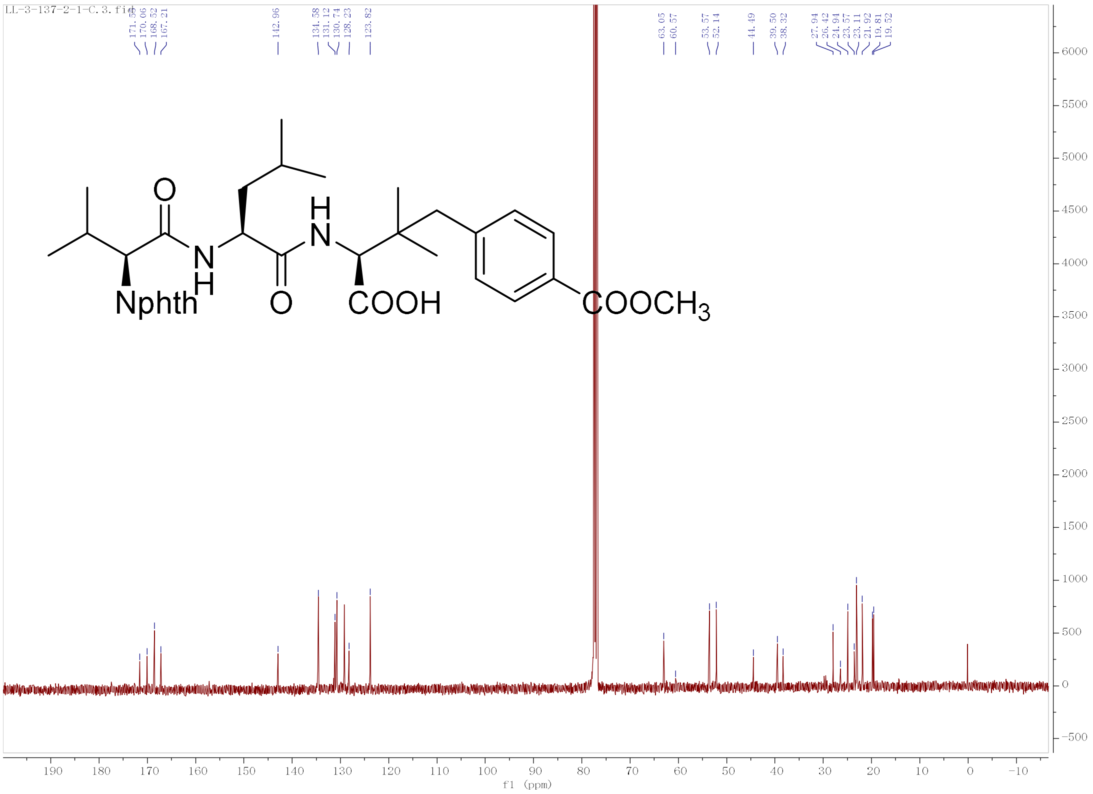
5g


LL-3-129-3-2.2.fid
7.8295 7.8098 7.7638 7.7516 7.7436 7.7384 7.7303 7.7243 7.7167 7.7060 7.6571 7.6459 7.6383 7.6321 7.6246 7.0316 7.0115 6.9995 6.9966
4.5744 4.5454 4.4422 4.4194 4.3081 4.2880 4.2686 3.9061 3.8966
2.7299 2.7031 2.6925 2.6795 2.5262 2.4936 2.4511 2.4187 2.2824 2.2653 2.2479 2.2312 2.2228 2.2144 2.2026
1.3611 1.3428 1.3279 1.3195 1.3087 1.3012 1.0654 1.0487 1.0044 0.9904 0.9670 0.9501 0.8424 0.8234 0.8055 0.7553 0.7297
O
H
N
N
H
Nphth
O
COOH
COOCH3
1.97
3.00
1.99
2.99
1.16
1.19
1.31
3.10
1.12
1.00
1.07
1.13
2.07
3.14
3.51
3.17
4.32
2.98
2.83
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 -0.5 -1.0 -1.5
f1 (ppm)
9000 8500 8000 7500 7000 6500 6000 5500 5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

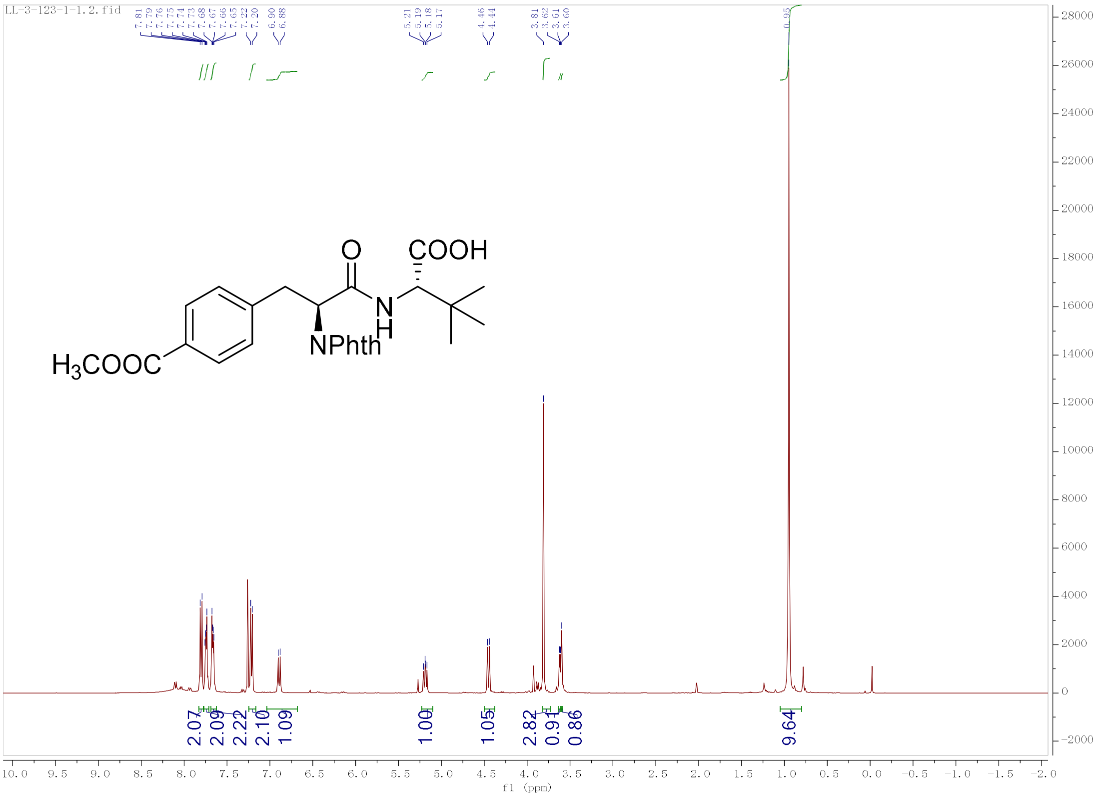

LL-3-129-3-1C.2.fid
171.00 170.15 168.61 167.26
143.08
134.58 131.19 130.81 129.19 128.20
123.84
61.72 59.46
52.19
44.30
38.50
33.27 29.91 26.70 25.54 23.51 22.96 19.66 18.28 15.87
10.22
O
H
N
N
H
Nphth
O
COOH
COOCH3
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
5000 4500 4000 3500 3000 2500 2000 1500 1000 500 0 -500

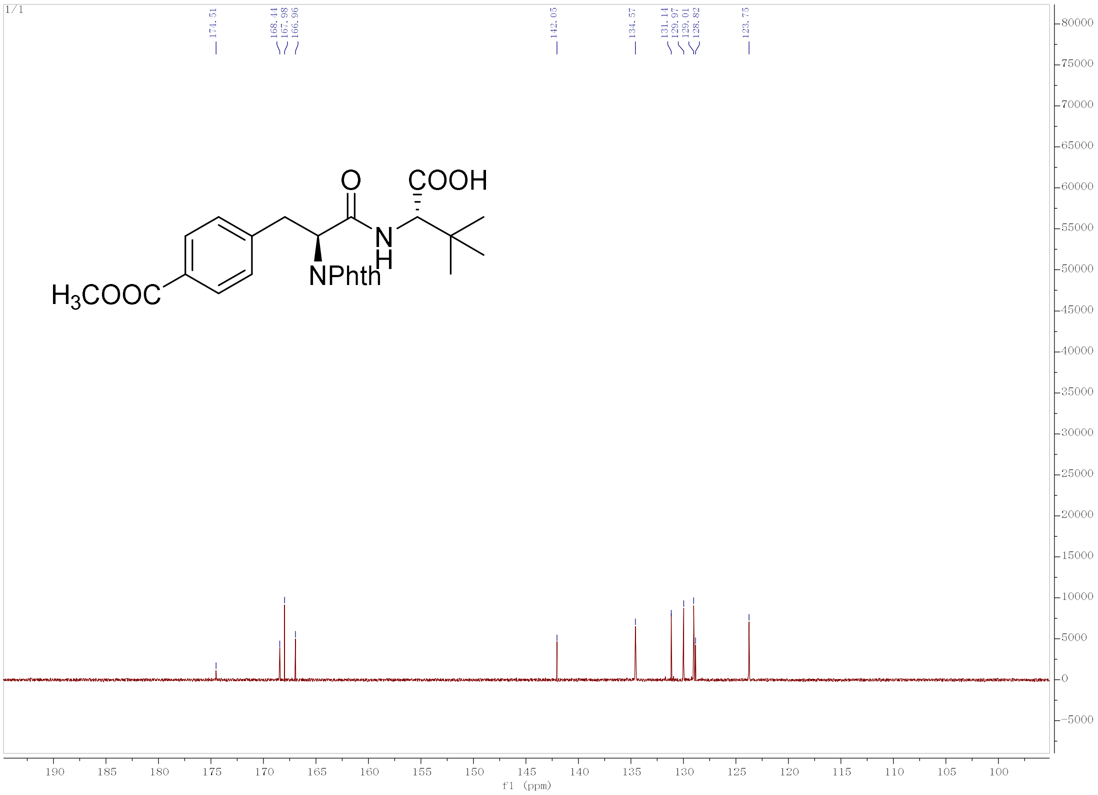
5h


LL-3-137-1-2.2.fid
7.7846 7.7649 7.7127 7.7049 7.6991 7.6911 7.6800 7.6486 7.6375 7.6302 7.6239 7.6165 7.6051 7.5852 7.1817 7.1590 6.9954 6.9756
4.5292 4.5151 4.5076 4.4955 4.4808 4.4527
3.8989 3.8898
2.8382 2.8220 2.8057 2.7921 2.7763 2.5306 2.4983 2.4534 2.4209
1.7236 1.7104 1.6861 1.6713 1.6581 1.6473 1.6420 1.6241 1.0960 1.0796 0.9543 0.9403 0.9009 0.8869 0.8385 0.8220 0.7908 0.7355
O
H
N
N
H
Nphth
O
COOH
COOCH3
2.08
2.04
2.98
1.14
2.00
3.89
3.42
1.23
1.03
1.07
3.46
3.09
3.03
3.11
3.07
2.85
3.09
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
10.0 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 -0.5 -1.0 -1.5 -2.0
f1 (ppm)

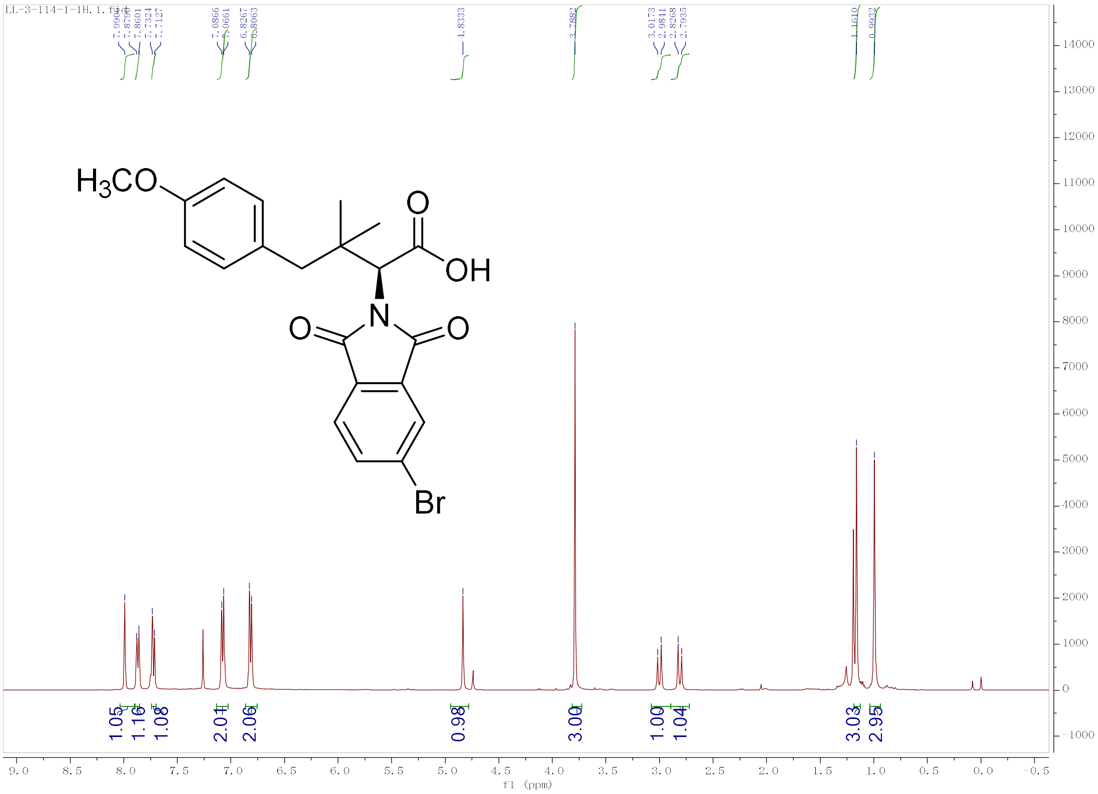

LL-3-137-2-1-C.3.fid
171.59 170.06 168.52 167.21
142.96
134.58 131.12 130.74 128.23
123.82
63.05 60.57
53.57 52.14
44.49
39.50 38.32
27.94 26.42 24.94 23.57 23.11 21.92 19.81 19.52
O
H
N
N
H
Nphth
O
COOH
COOCH3
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

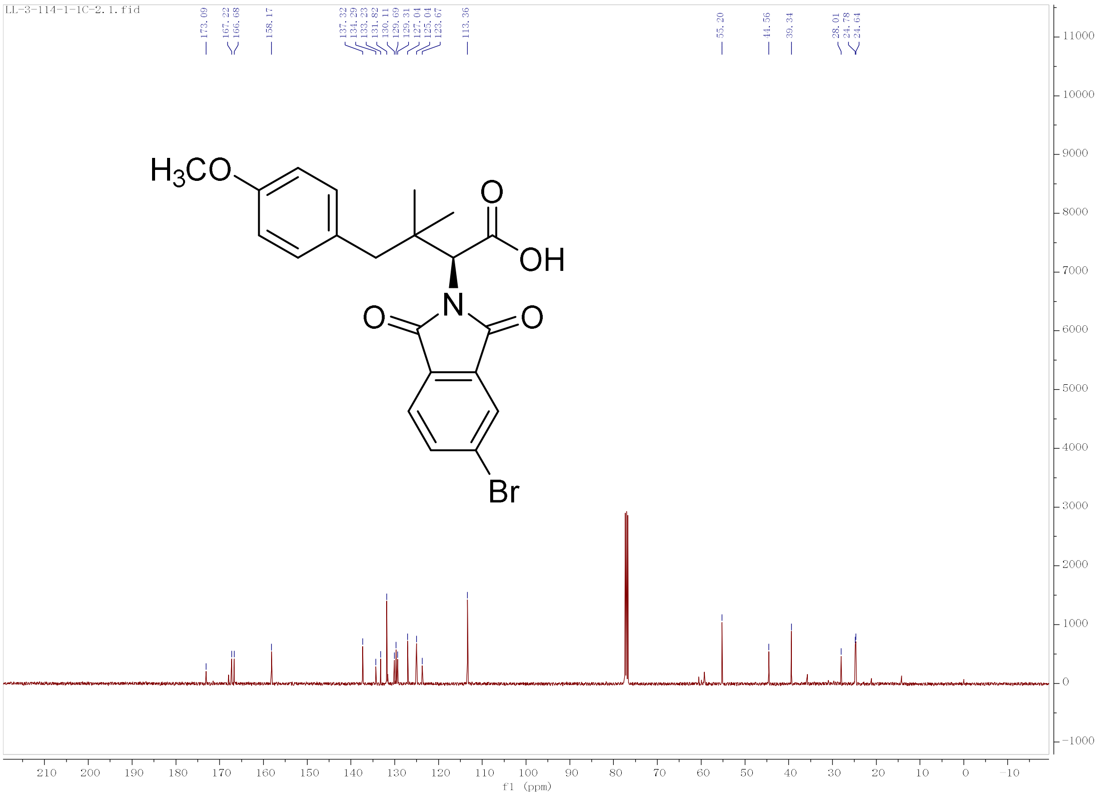
5i


LL-3-123-1-1.2.fid
7.81
7.79
7.76
7.75
7.74
7.73
7.68
7.67
7.66
7.65
7.22
7.20
6.90
6.88
5.21
5.19
5.18
5.17
4.46
4.44
3.81
3.62
3.61
3.60
0.95
O
COOH
N
H
NPhth
H3COOC
2.07
2.09
2.22
2.10
1.09
1.00
1.05
2.82
0.91
0.86
9.64
10.0
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
-0.5
-1.0
-1.5
-2.0
f1 (ppm)
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000

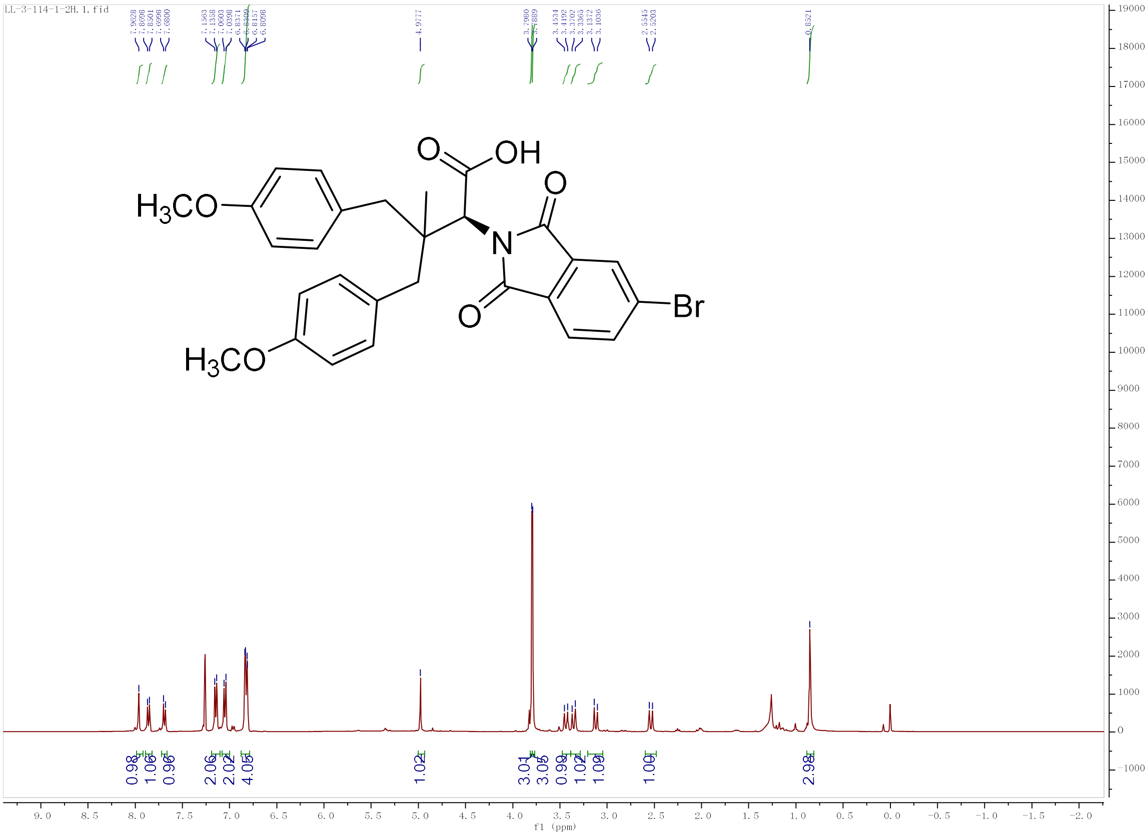

1/1
174.51
168.44
167.98
166.96
142.05
134.57
131.14
129.97
129.01
128.82
123.75
O
COOH
N
H
NPhth
H3COOC
190
185
180
175
170
165
160
155
150
145
140
135
130
125
120
115
110
105
100
f1 (ppm)
80000
75000
70000
65000
60000
55000
50000
45000
40000
35000
30000
25000
20000
15000
10000
5000
0
-5000

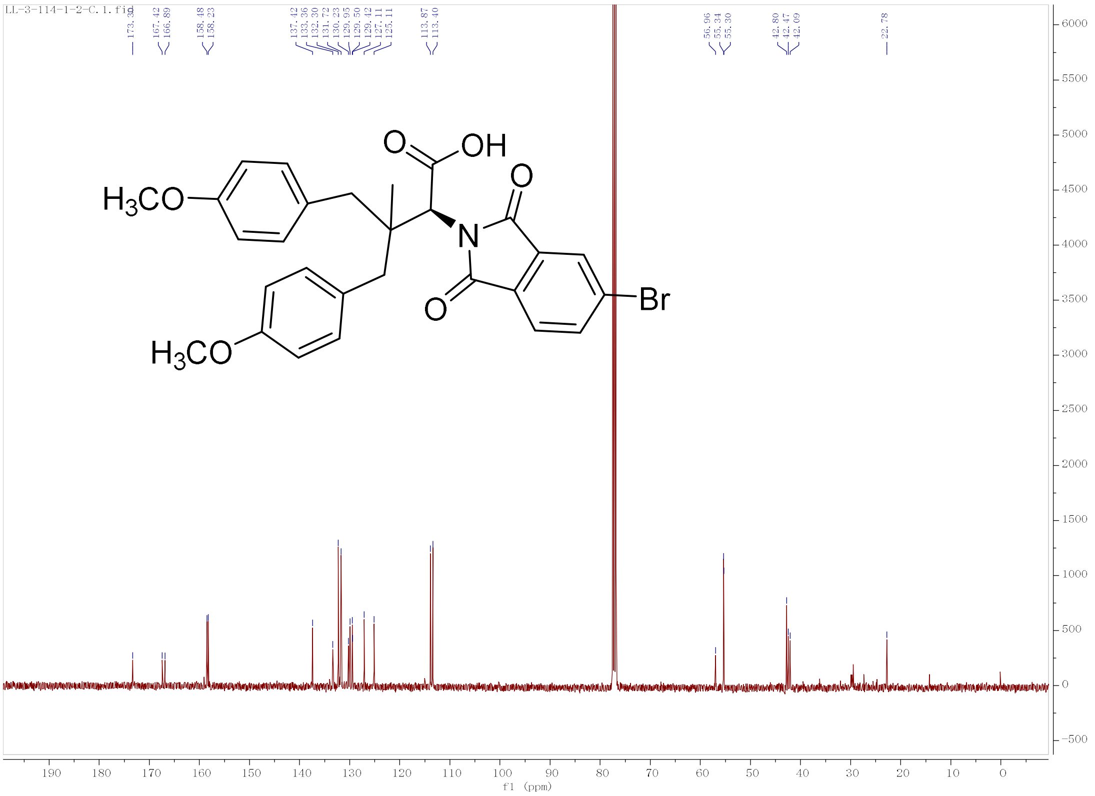
7a


LL-3-114-1-1H.1.fid
7.9904
7.8790
7.8601
7.7324
7.7127
7.0866
7.0661
6.8267
6.8063
4.8333
3.7882
3.0173
2.9841
2.8268
2.7935
1.1610
0.9932
H3CO
O
OH
N
O
O
Br
1.05
1.16
1.08
2.01
2.06
0.98
3.00
1.00
1.04
3.03
2.95
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
-0.5
f1 (ppm)
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

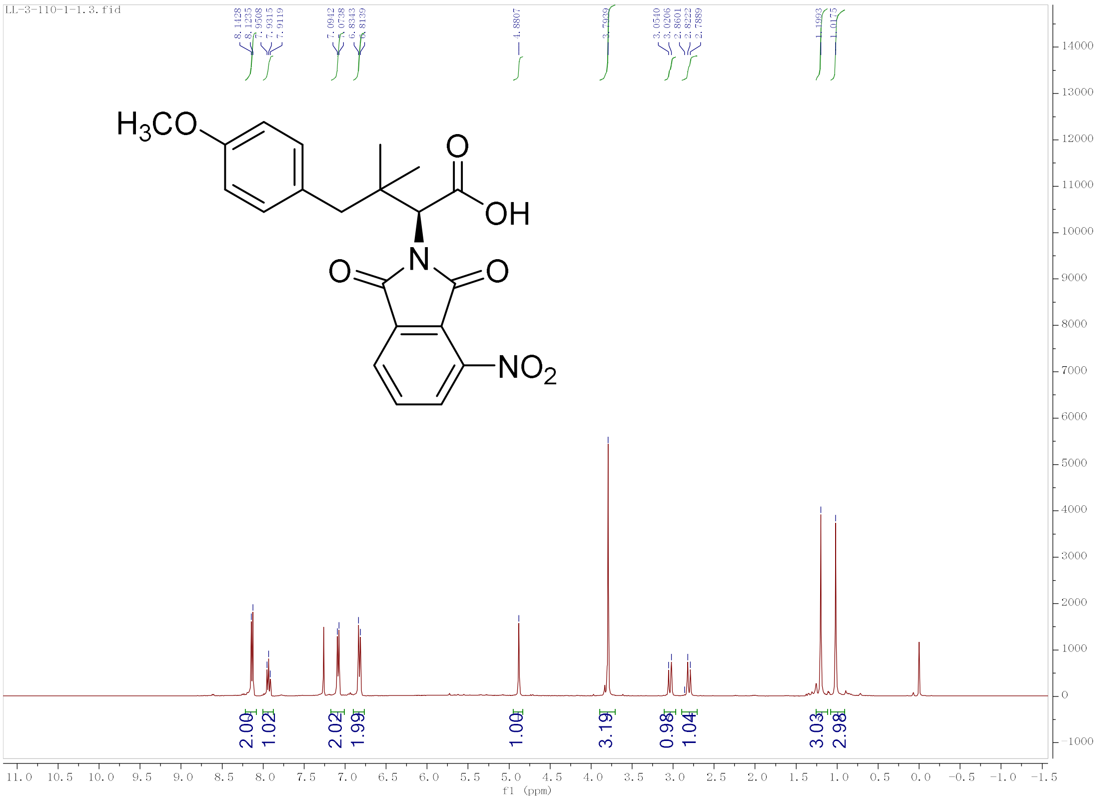

LL-3-114-1-1C-2.1.fid
173.09
167.22
166.68
158.17
137.32
134.29
133.23
131.82
130.11
129.69
129.31
127.04
125.04
123.67
113.36
55.20
44.56
39.34
28.01
24.78
24.64
H3CO
O
OH
N
O
O
Br
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

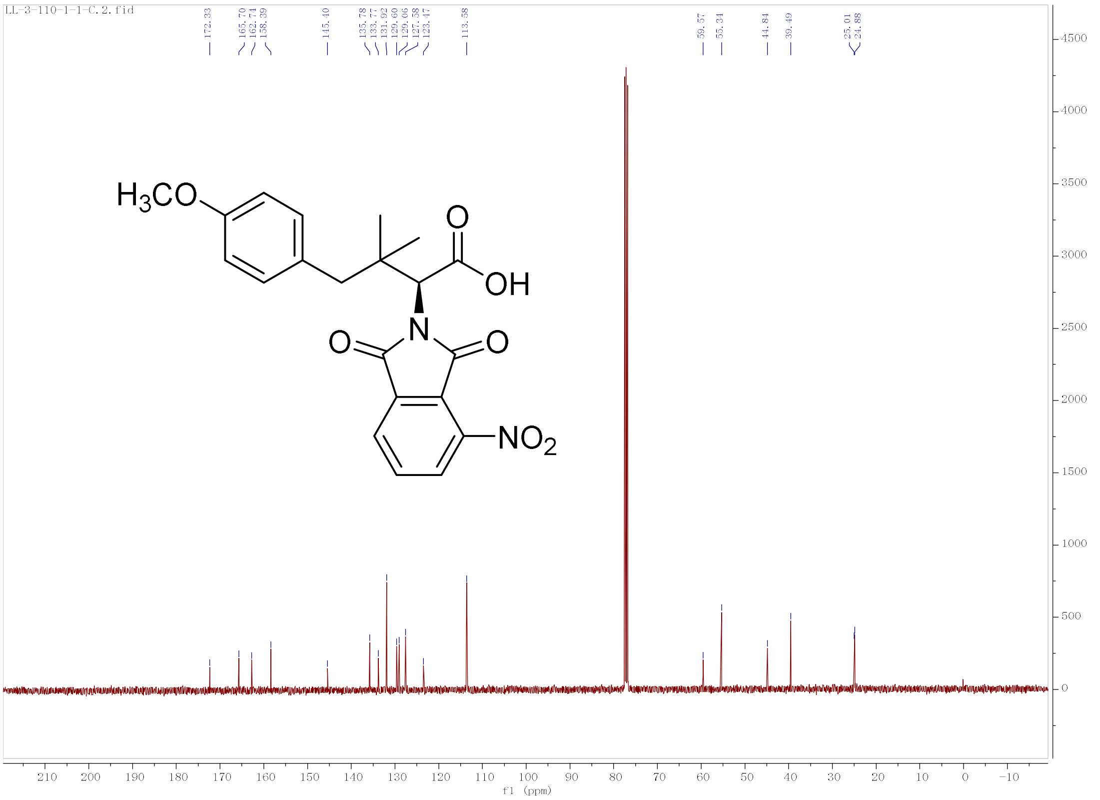
7a’


LL-3-114-1-2H.1.fid
7.9628
7.8698
7.8501
7.6998
7.6800
7.1563
7.1358
7.0603
7.0398
6.8371
6.8309
6.8157
6.8098
4.9777
3.7980
3.7889
3.4534
3.4192
3.3702
3.3365
3.1372
3.1036
2.5545
2.5203
0.8521
0.98
1.06
0.96
2.06
2.02
4.05
1.02
3.01
3.05
0.99
1.02
1.09
1.00
2.98
H3CO
H3CO
O
OH
O
N
O
Br
f1 (ppm)

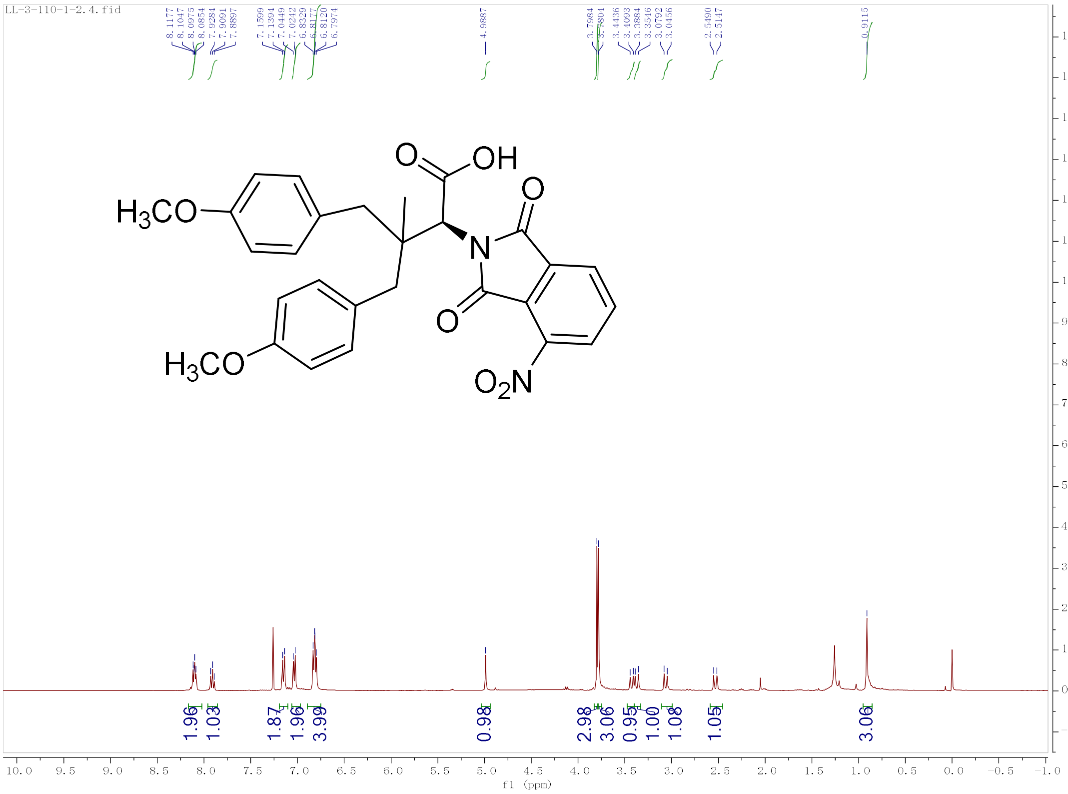

LL-3-114-1-2-C.1.fid
173.30
167.42
166.89
158.48
158.23
137.42
133.36
132.30
131.72
130.23
129.95
129.50
129.42
127.11
125.11
113.87
113.40
56.96
55.34
55.30
42.80
42.47
42.09
22.78
H3CO
H3CO
O
OH
O
N
O
Br
f1 (ppm)

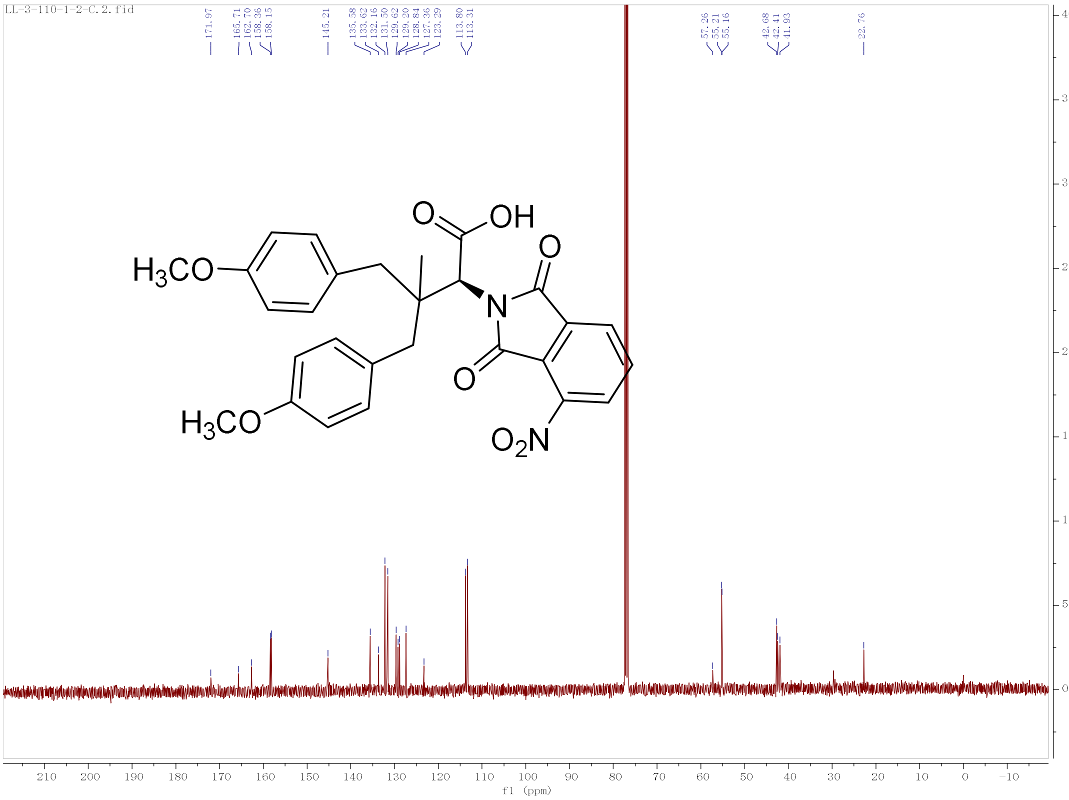
7b


LL-3-110-1-1.3.fid
8.1428
8.1235
7.9508
7.9315
7.9119
7.0942
7.0738
6.8343
6.8139
4.8807
3.7939
3.0540
3.0206
2.8601
2.8222
2.7889
1.1993
1.0175
H3CO
O
OH
N
O
O
NO2
2.00
1.02
2.02
1.99
1.00
3.19
0.98
1.04
3.03
2.98
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
11.0
10.5
10.0
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
-0.5
-1.0
-1.5
f1 (ppm)

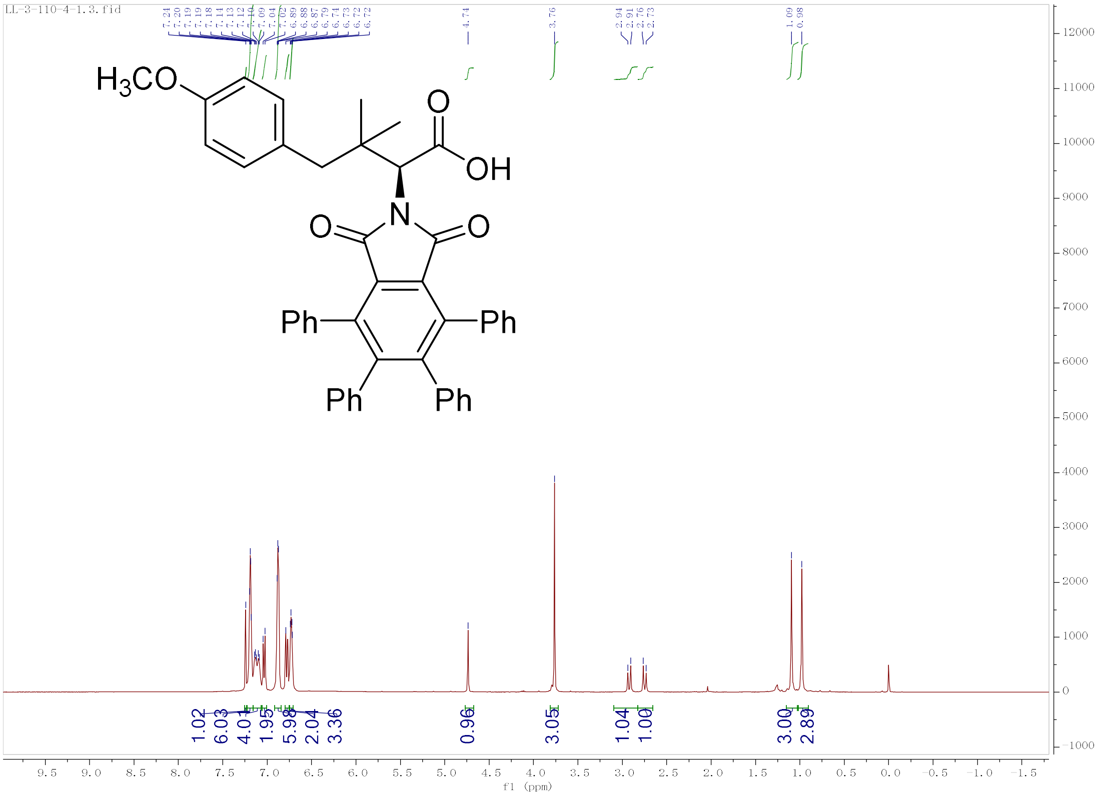

LL-3-110-1-1-C.2.fid
172.33
165.70
162.74
158.39
145.40
135.78
133.77
131.92
129.60
129.06
127.58
123.47
113.58
59.57
55.34
44.84
39.49
25.01
24.88
H3CO
O
OH
N
O
O
NO2
4500
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

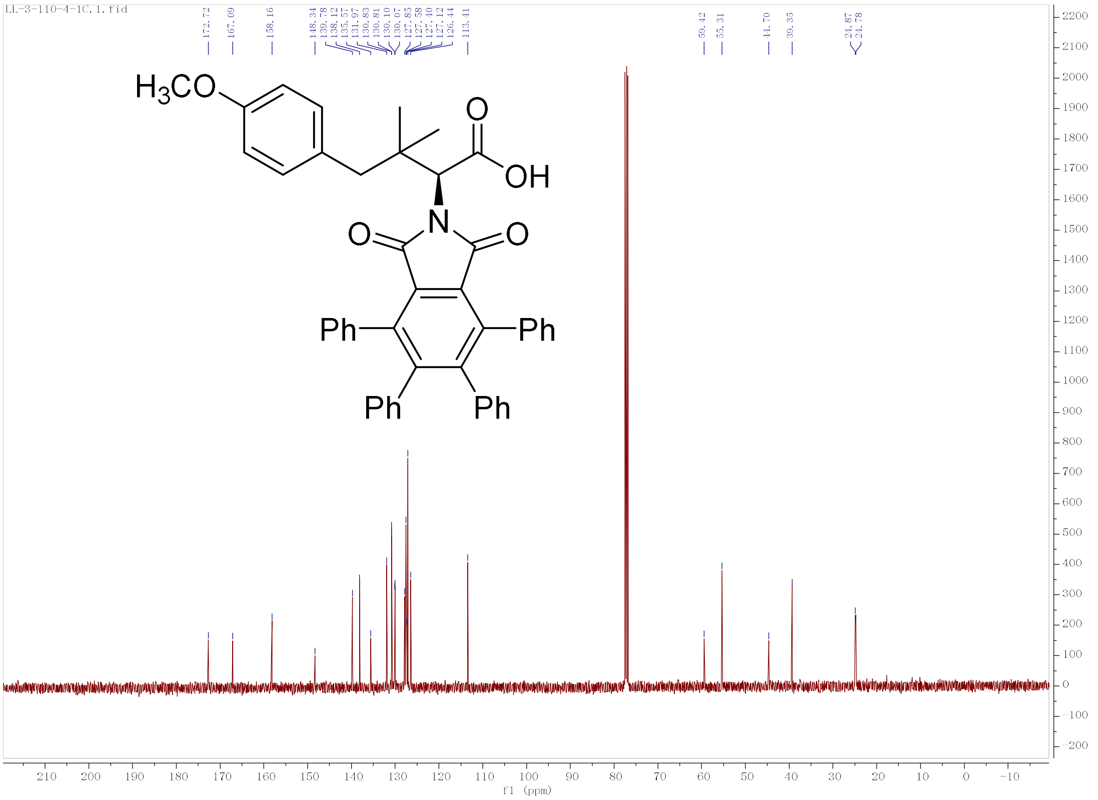
7b’


LL-3-110-1-2.4.fid
8.1177
8.1047
8.0975
8.0854
7.9284
7.9091
7.8897
7.1599
7.1394
7.0449
7.0242
6.8329
6.8177
6.8120
6.7974
4.9887
3.7984
3.7804
3.4436
3.4093
3.3884
3.3546
3.0792
3.0456
2.5490
2.5147
0.9115
H3CO
H3CO
O
OH
O
N
O
O2N
1.96
1.03
1.87
1.96
3.99
0.98
2.98
3.06
0.95
1.00
1.08
1.05
3.06
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
10.0
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
-0.5
-1.0
f1 (ppm)

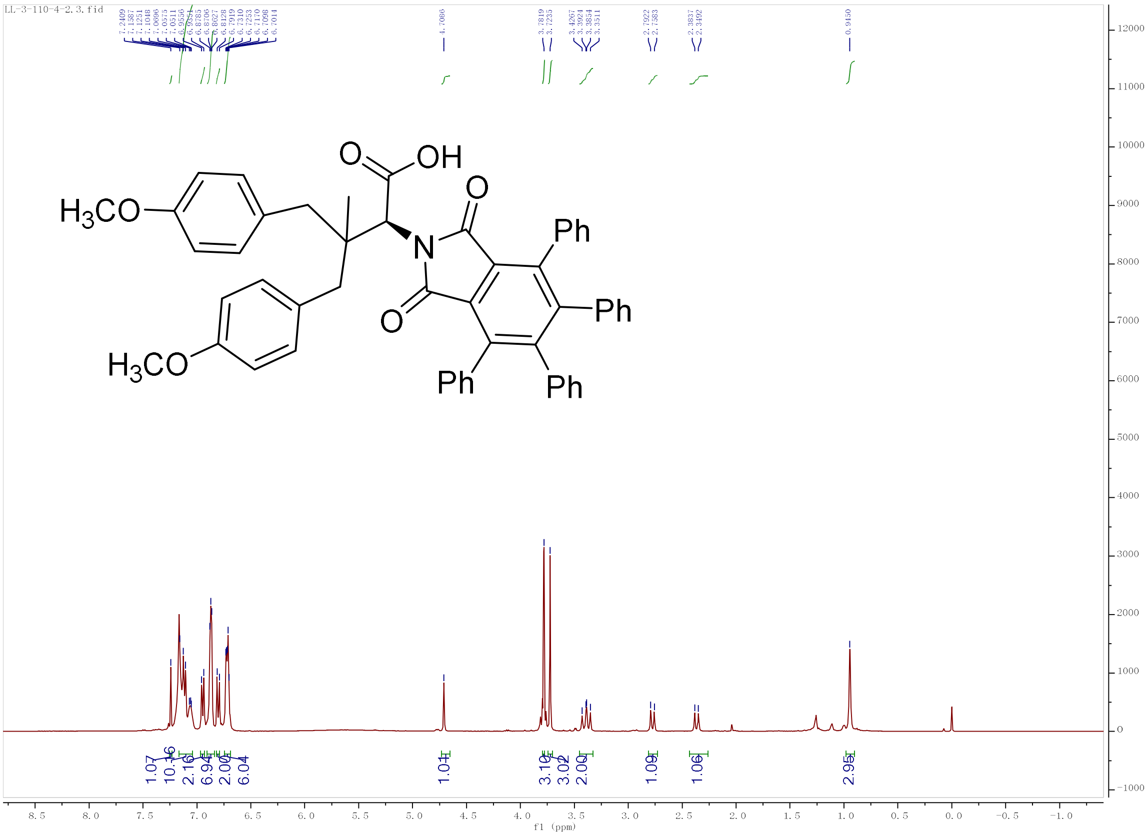

LL-3-110-1-2-C.2.fid
171.97
165.71
162.70
158.36
158.15
145.21
135.58
133.62
132.16
131.50
129.62
129.20
128.84
127.36
123.29
113.80
113.31
57.26
55.21
55.16
42.68
42.41
41.93
22.76
H3CO
H3CO
O
OH
O
N
O
O2N
4000
3500
3000
2500
2000
1500
1000
500
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

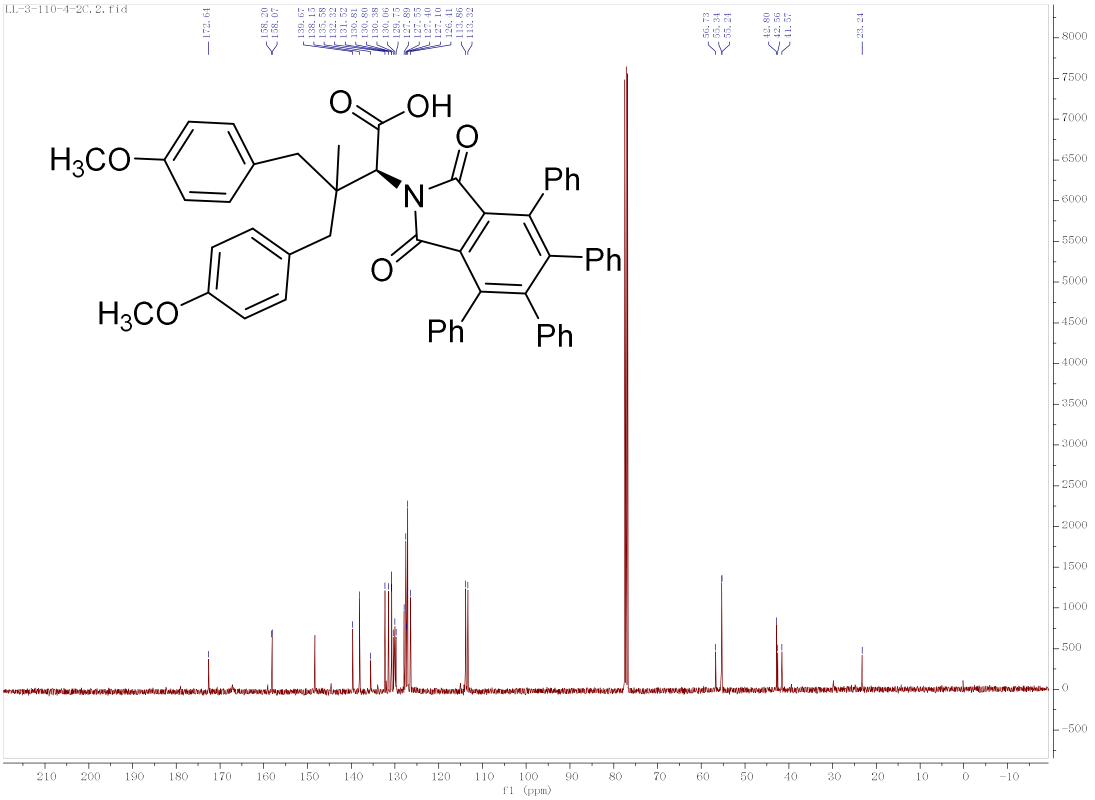
7c


LL-3-110-4-1.3.fid
7.24 7.20 7.19 7.19 7.18 7.14 7.13 7.12 7.10 7.09 7.04 7.02 6.89 6.88 6.87 6.79 6.74 6.73 6.72 6.72
4.74
3.76
2.94 2.91 2.76 2.73
1.09 0.98
H3CO
O
OH
N
O
O
Ph
Ph
Ph
Ph
1.02 6.03 4.01 1.95 5.98 2.04 3.36
0.96
3.05
1.04 1.00
3.00 2.89
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 -0.5 -1.0 -1.5
f1 (ppm)
12000 11000 10000 9000 8000 7000 6000 5000 4000 3000 2000 1000 0 -1000

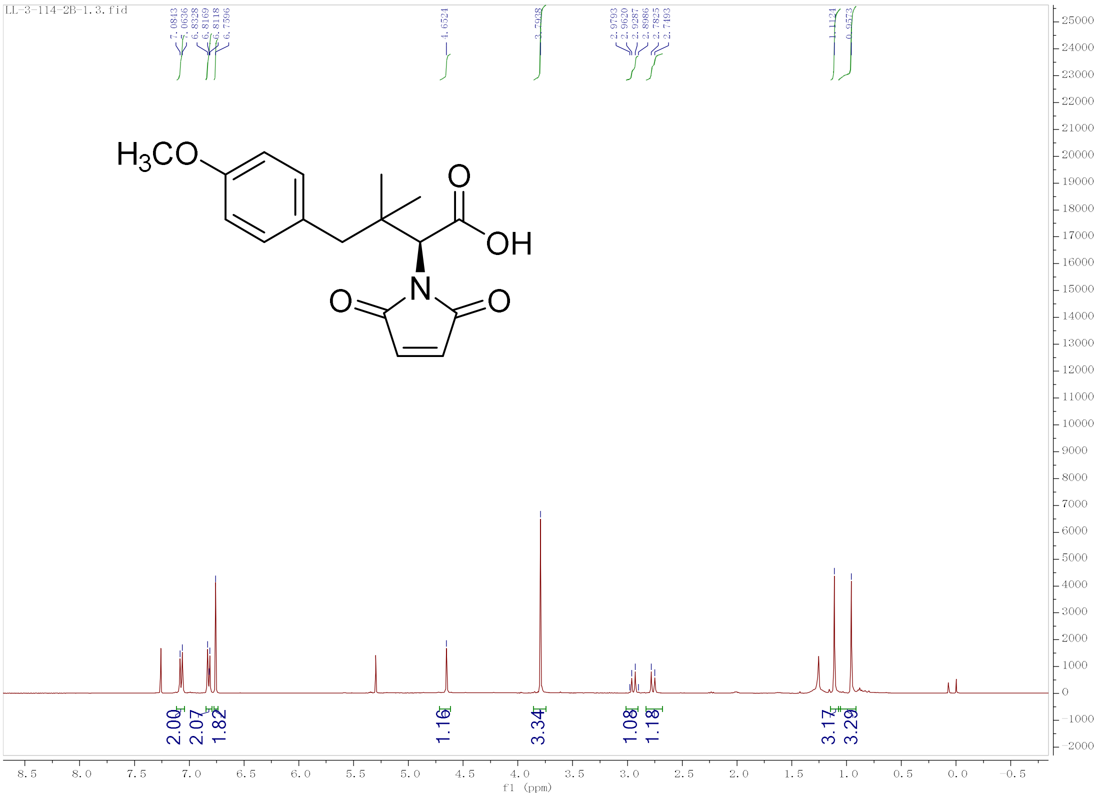

LL-3-110-4-1C.1.fid
172.72
167.09
158.16
148.34 139.78 138.12 135.57 131.97 130.83 130.81 130.10 130.07 127.85 127.58 127.40 127.12 126.44
113.41
59.42
55.31
44.70
39.35
24.87 24.78
H3CO
O
OH
N
O
O
Ph
Ph
Ph
Ph
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
2200 2100 2000 1900 1800 1700 1600 1500 1400 1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 -100 -200

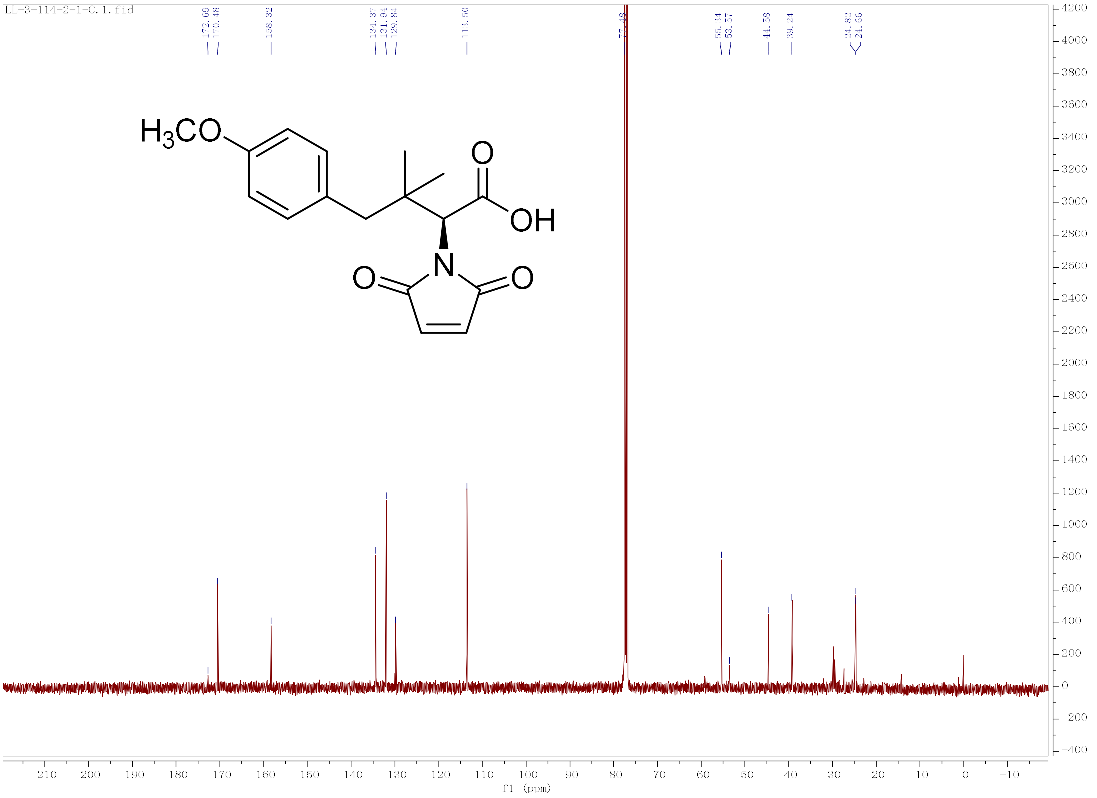
7c’


LL-3-110-4-2.3.fid
7.2409
7.1587
7.1251
7.1048
7.0696
7.0575
7.0511
6.9556
6.9351
6.8785
6.8706
6.8627
6.8128
6.7919
6.7310
6.7253
6.7170
6.7098
6.7014
4.7066
3.7819
3.7235
3.4267
3.3924
3.3854
3.3511
2.7922
2.7583
2.3837
2.3492
0.9150
H3CO
H3CO
O
OH
O
N
O
Ph
Ph
Ph
Ph
1.07
10.16
2.16
6.94
2.00
6.04
1.04
3.10
3.02
2.00
1.09
1.06
2.95
f1 (ppm)

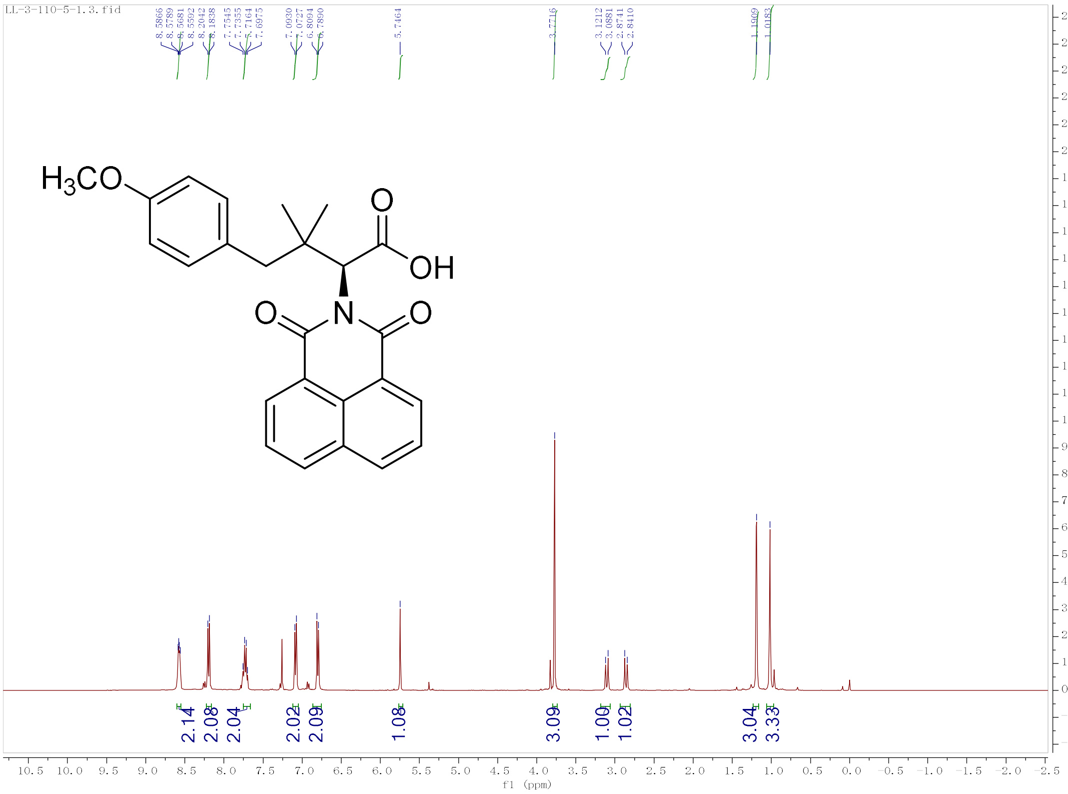

LL-3-110-4-2C.2.fid
172.61
158.20
158.07
139.67
138.15
135.58
132.32
131.52
130.81
130.80
130.38
130.06
129.75
127.89
127.55
127.40
127.10
126.41
113.86
113.32
56.73
55.34
55.24
42.80
42.56
41.57
23.24
H3CO
H3CO
O
OH
O
N
O
Ph
Ph
Ph
Ph
f1 (ppm)

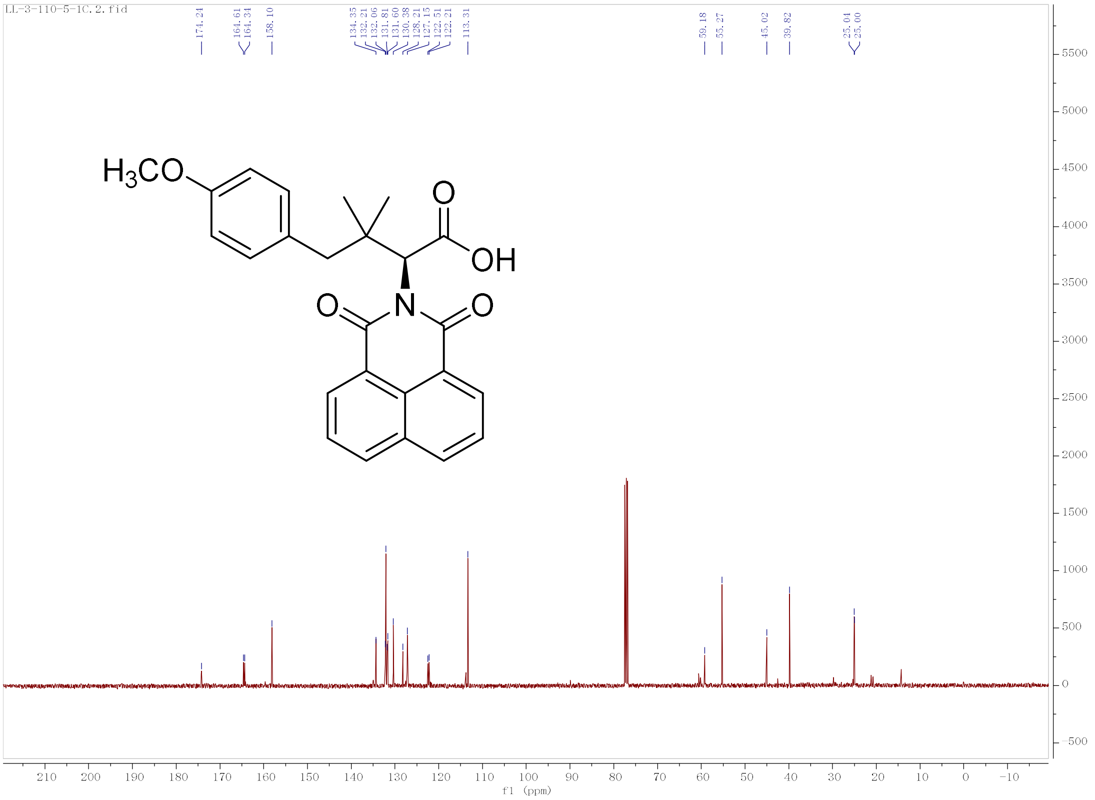
7d


LL-3-114-2B-1.3.fid
7.0843
7.0636
6.8328
6.8169
6.8118
6.7596
4.6524
3.7938
2.9793
2.9620
2.9287
2.8986
2.7825
2.7493
1.1124
0.9573
H3CO
O
OH
N
O
O
2.00
2.07
1.82
1.16
3.34
1.08
1.18
3.17
3.29
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
-0.5
f1 (ppm)
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

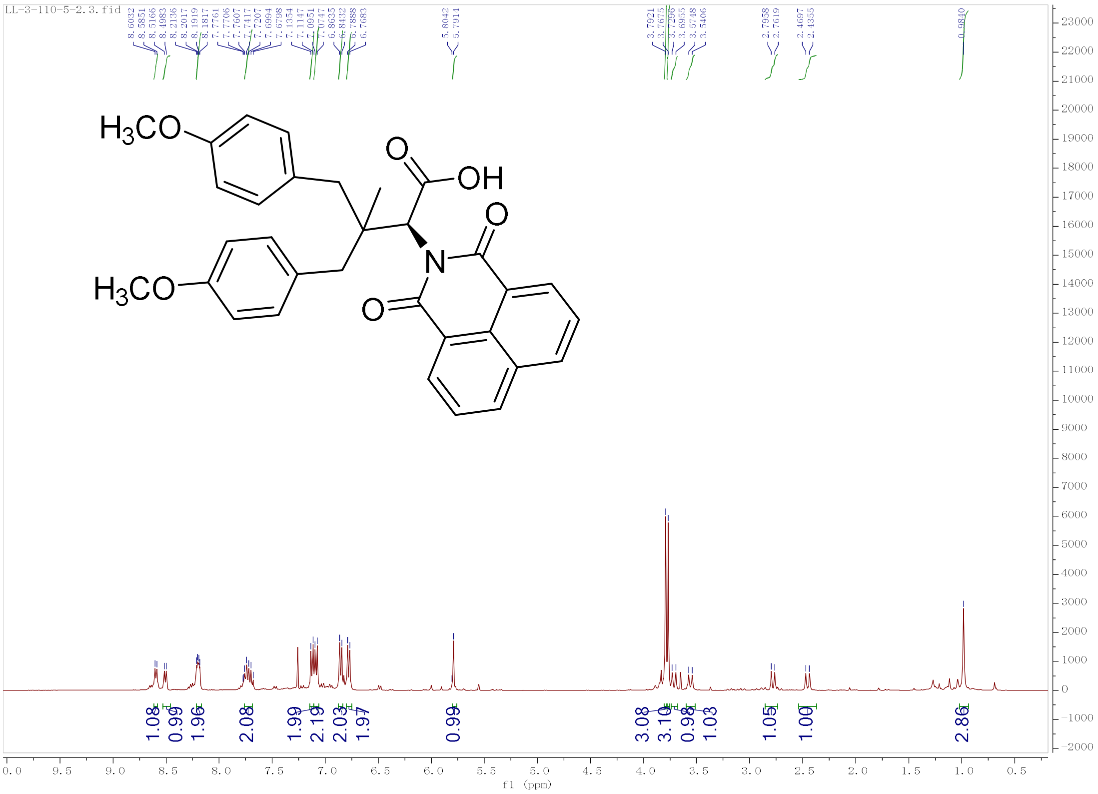

LL-3-114-2-1-C.1.fid
172.69
170.48
158.32
134.37
131.94
129.84
113.50
77.48
55.34
53.57
44.58
39.24
24.82
24.66
H3CO
O
OH
N
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
4200
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200
-400

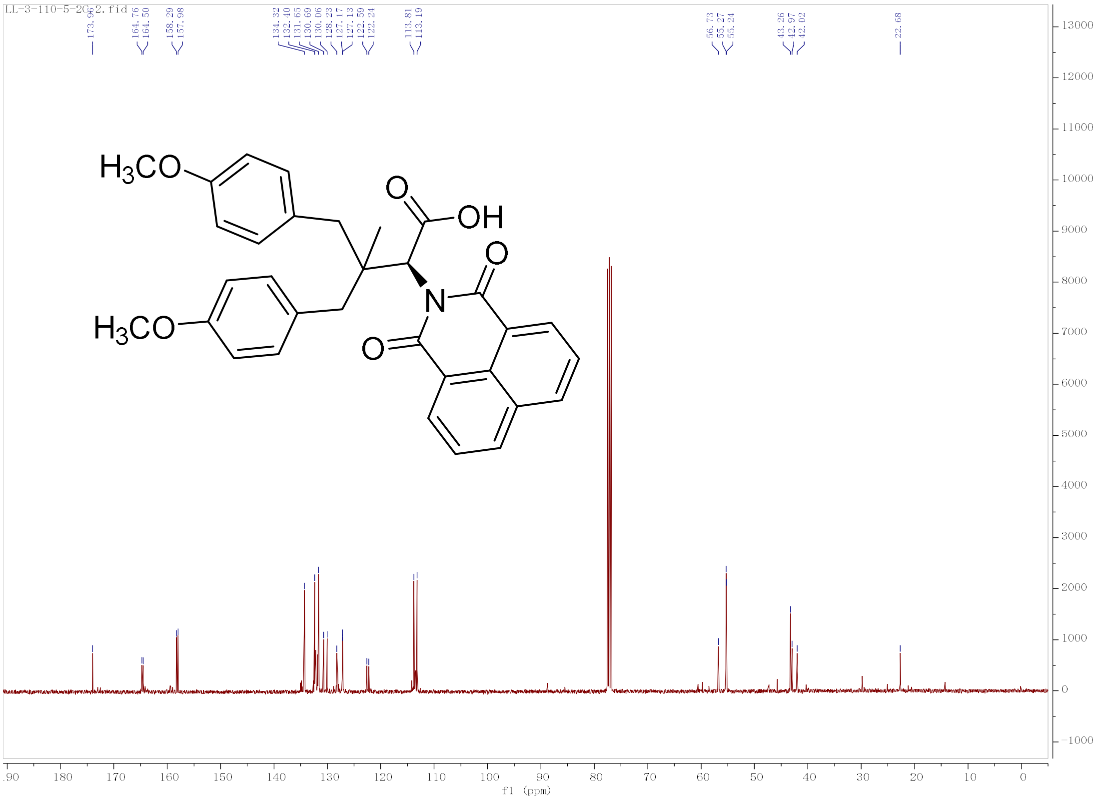
7e


LL-3-110-5-1.3.fid
8.5866
8.5789
8.5681
8.5592
8.2042
8.1838
7.7545
7.7355
7.7164
7.6975
7.0930
7.0727
6.8094
6.7890
5.7464
3.7716
3.1212
3.0881
2.8741
2.8410
1.1909
1.0183
H_3CO
O
OH
O
N
O
2.14
2.08
2.04
2.02
2.09
1.08
3.09
1.00
1.02
3.04
3.33
25000
24000
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000
10.5
10.0
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
-0.5
-1.0
-1.5
-2.0
-2.5
f1 (ppm)

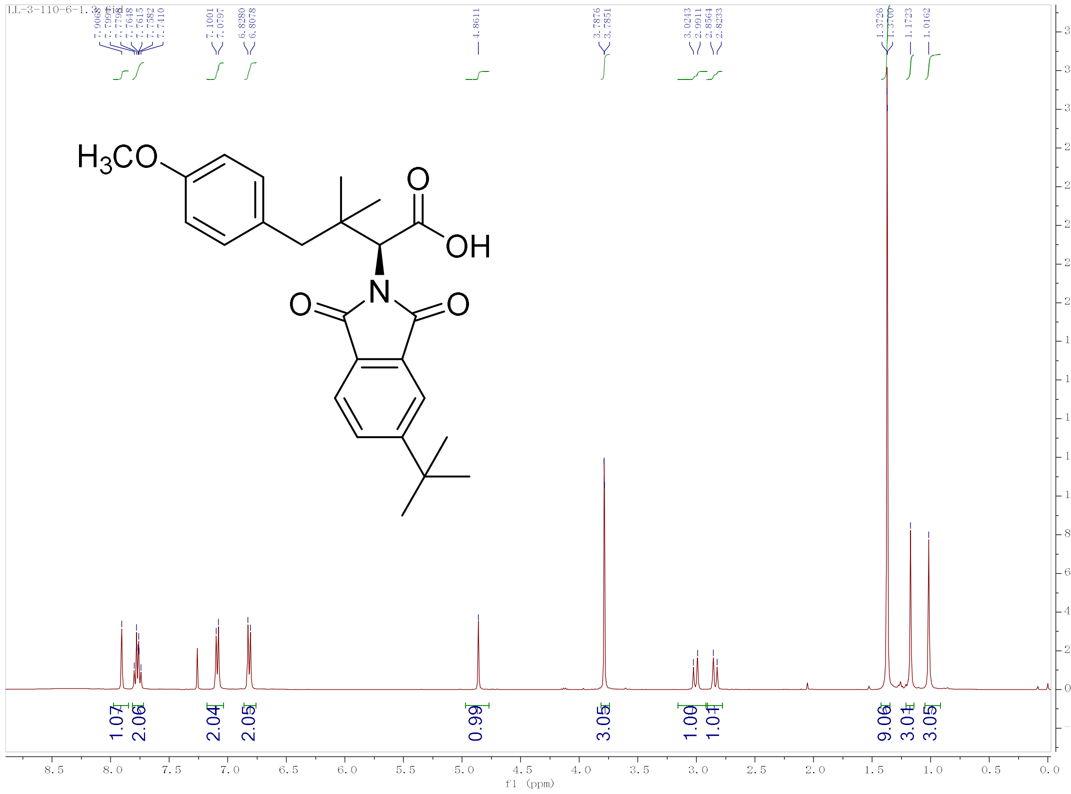

LL-3-110-5-1C.2.fid
174.24
164.61
164.34
158.10
134.35
132.21
132.06
131.81
131.60
130.38
128.21
127.15
122.51
122.21
113.31
59.18
55.27
45.02
39.82
25.04
25.00
H_3CO
O
OH
O
N
O
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

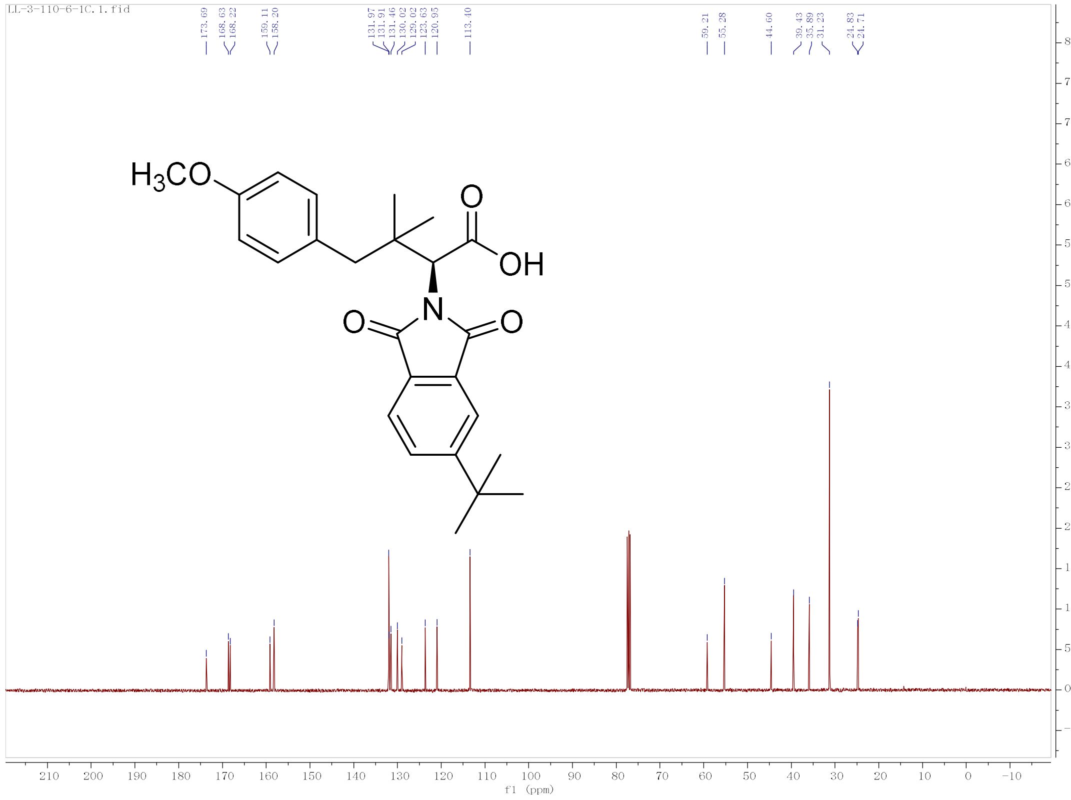
7e’


LL-3-110-5-2.3.fid
8.6032
8.5851
8.5166
8.4983
8.2136
8.2017
8.1919
8.1817
7.7761
7.7706
7.7607
7.7417
7.7207
7.6904
7.6798
7.1354
7.1147
7.0951
7.0747
6.8635
6.8132
6.7888
6.7683
5.8042
5.7914
3.7921
3.7675
3.7296
3.6955
3.5748
3.5406
2.7958
2.7619
2.4697
2.4355
0.9840
H3CO
H3CO
O
OH
O
N
O
1.08
0.99
1.96
2.08
1.99
2.19
2.03
1.97
0.99
3.08
3.10
0.98
1.03
1.05
1.00
2.86
f1 (ppm)

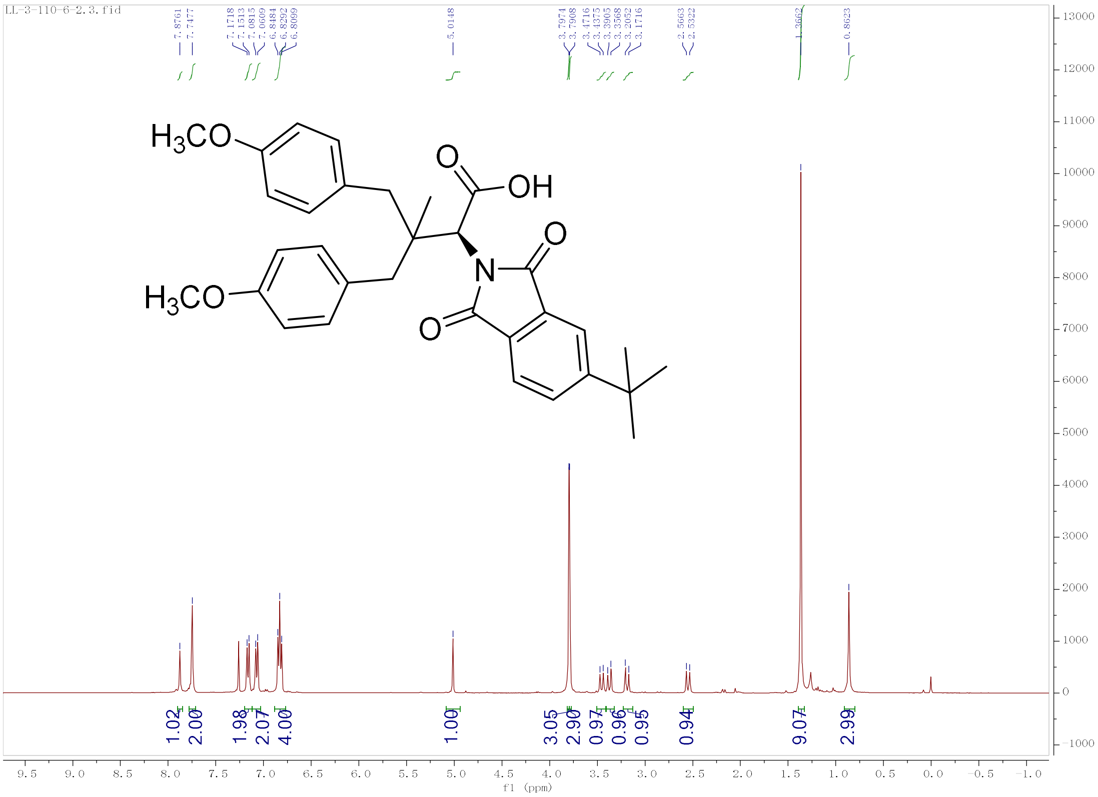

LL-3-110-5-2C-2.fid
173.96
164.76
164.50
158.29
157.98
134.32
132.40
131.65
130.69
130.06
128.23
127.17
127.13
122.59
122.24
113.81
113.19
56.73
55.27
55.21
43.26
42.97
42.02
22.68
H3CO
H3CO
O
OH
O
N
O
f1 (ppm)

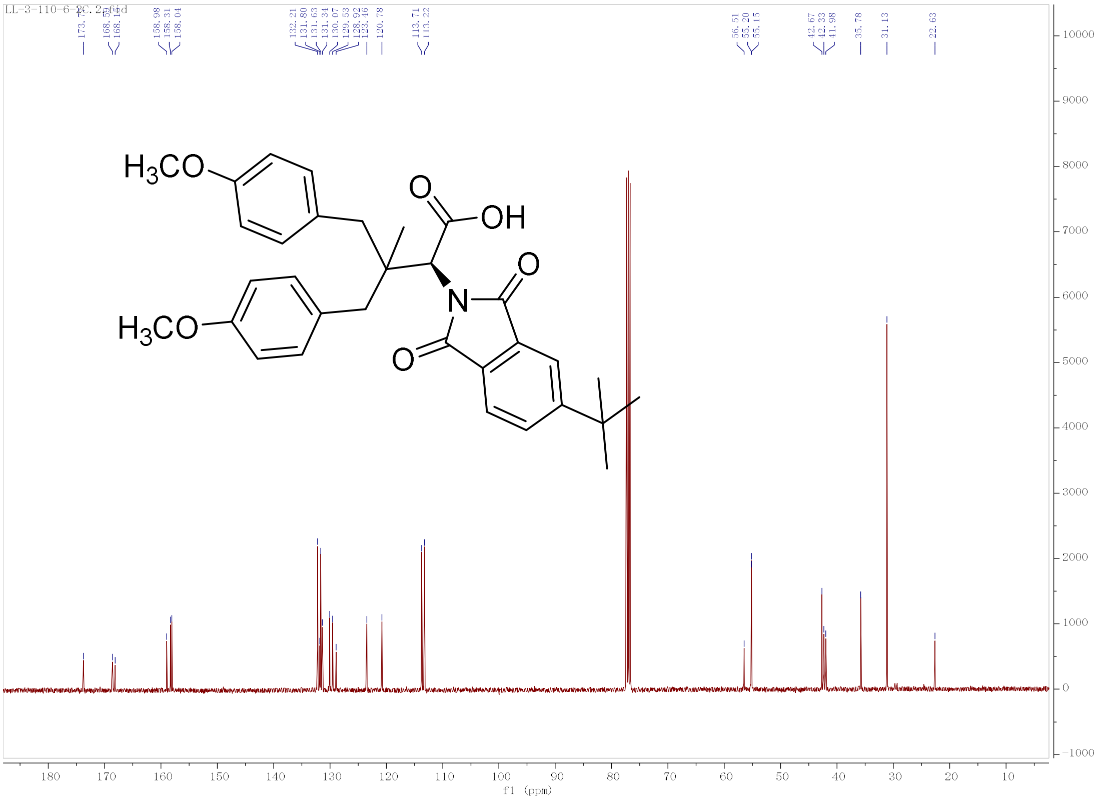
7f


LL-3-110-6-1.3.fid
7.9068
7.7991
7.7798
7.7648
7.7615
7.7582
7.7410
7.1001
7.0797
6.8280
6.8078
4.8611
3.7876
3.7851
3.0243
2.9911
2.8564
2.8233
1.3726
1.3700
1.1723
1.0162
H3CO
O
OH
N
O
O
1.07
2.06
2.04
2.05
0.99
3.05
1.00
1.01
9.06
3.01
3.05
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
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)

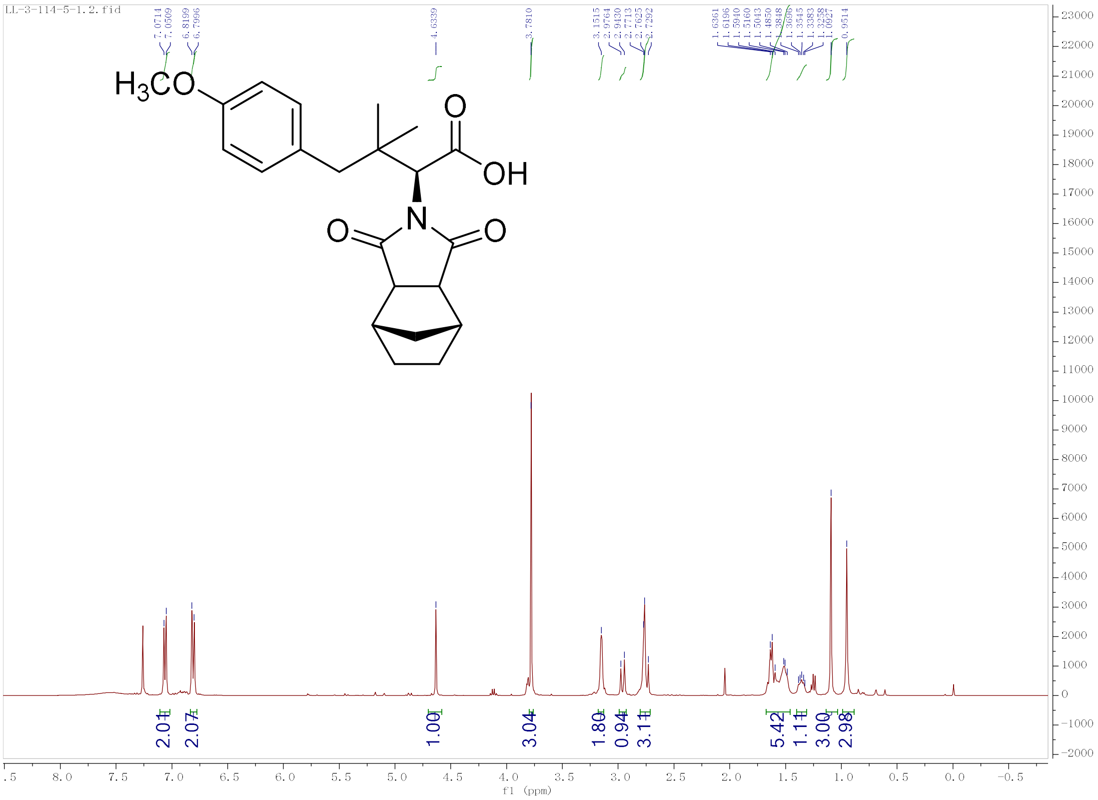

LL-3-110-6-1C.1.fid
173.69
168.63
168.22
159.11
158.20
131.97
131.91
131.46
130.02
129.02
123.63
120.95
113.40
59.21
55.28
44.60
39.43
35.89
31.23
24.83
24.71
H3CO
O
OH
N
O
O
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

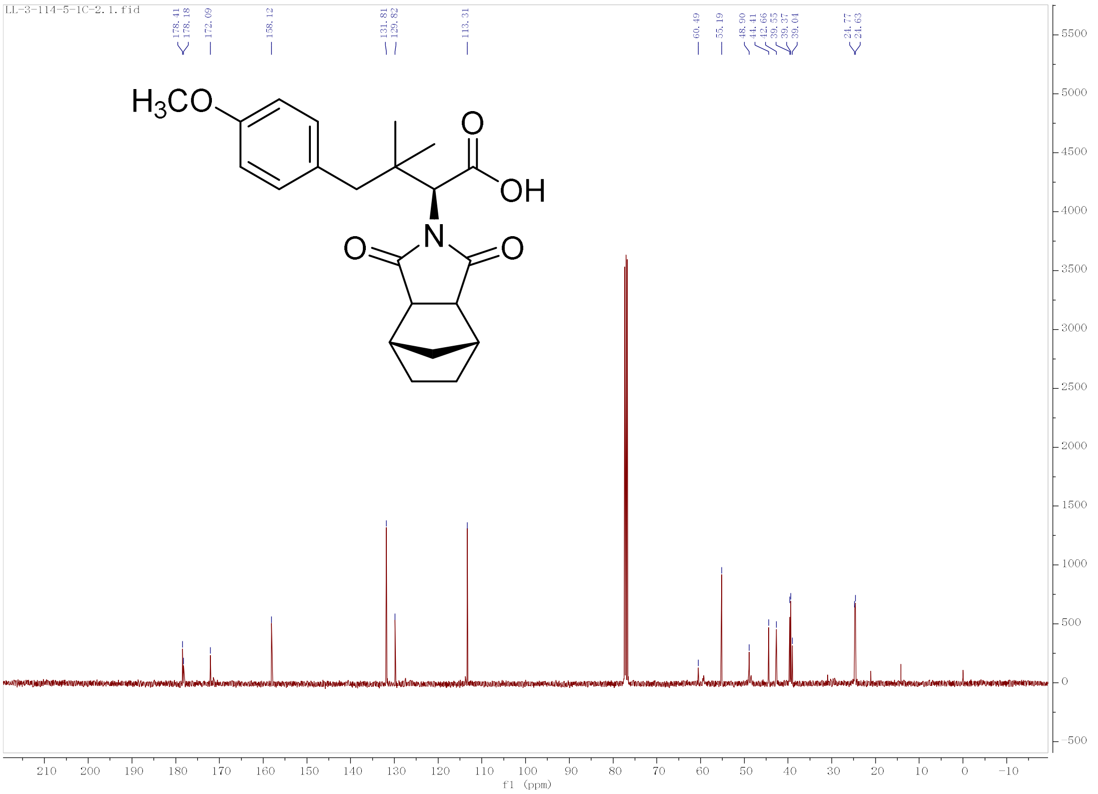
7f'


LL-3-110-6-2.3.fid
7.8761
7.7477
7.1718
7.1513
7.0815
7.0609
6.8484
6.8292
6.8099
5.0148
3.7974
3.7908
3.4716
3.4375
3.3905
3.3568
3.2052
3.1716
2.5663
2.5322
1.3662
0.8623
H_3CO
H_3CO
O
OH
O
N
O
1.02
2.00
1.98
2.07
4.00
1.00
3.05
2.90
0.97
0.96
0.95
0.94
9.07
2.99
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
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
-0.5
-1.0
f1 (ppm)

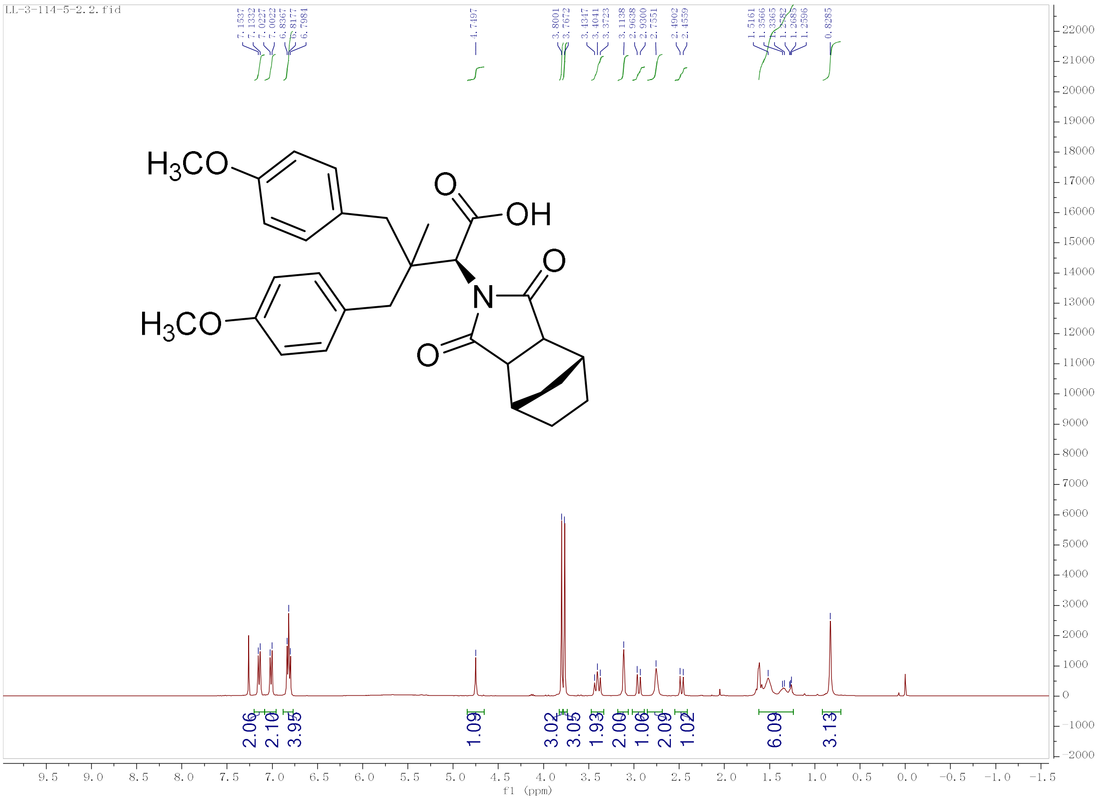

LL-3-110-6-2C.2.fid
173.7
168.5
168.1
158.98
158.31
158.04
132.21
131.80
131.63
131.34
130.07
129.53
128.92
123.46
120.78
113.71
113.22
56.51
55.20
55.15
42.67
42.33
41.98
35.78
31.13
22.63
H_3CO
H_3CO
O
OH
O
N
O
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

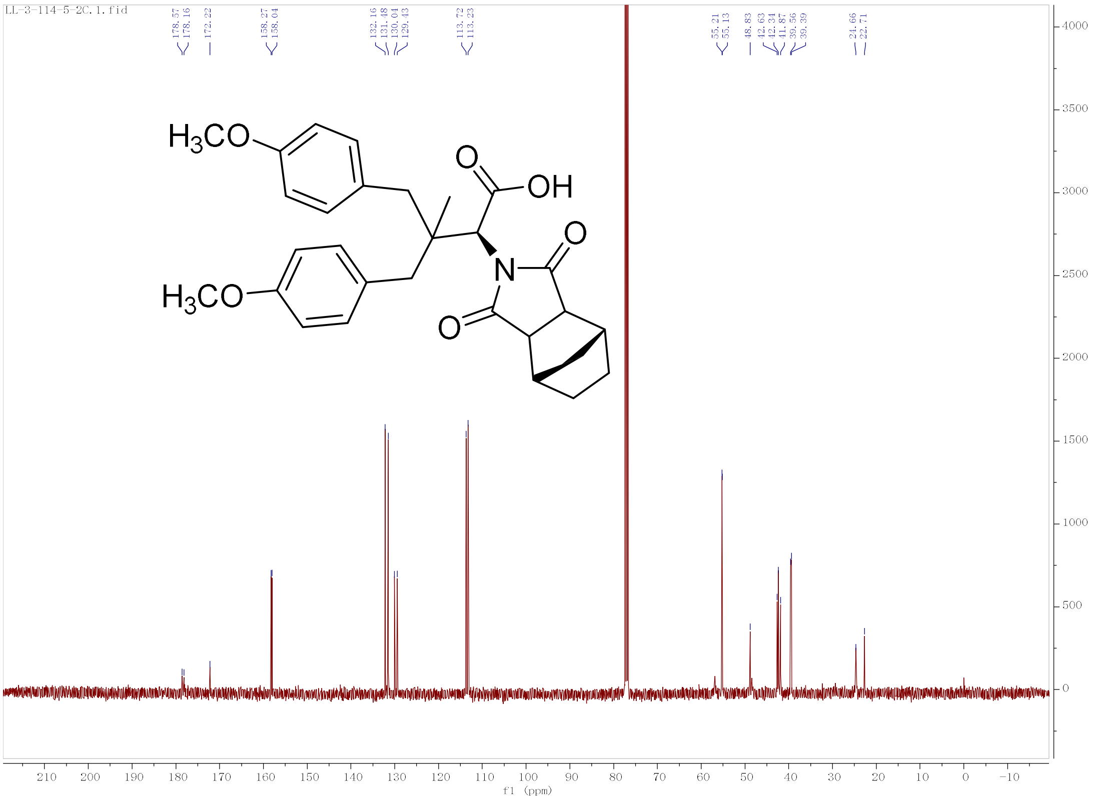
7g


LL-3-114-5-1.2.fid
7.0714
7.0509
6.8199
6.7996
4.6339
3.7810
3.1515
2.9764
2.9430
2.7713
2.7625
2.7292
1.6361
1.6196
1.5940
1.5160
1.5043
1.4850
1.3848
1.3696
1.3545
1.3383
1.3258
1.0927
0.9514
H3CO
O
OH
N
O
O
2.01
2.07
1.00
3.04
1.80
0.94
3.11
5.42
1.11
3.00
2.98
.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
-0.5
f1 (ppm)
23000
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

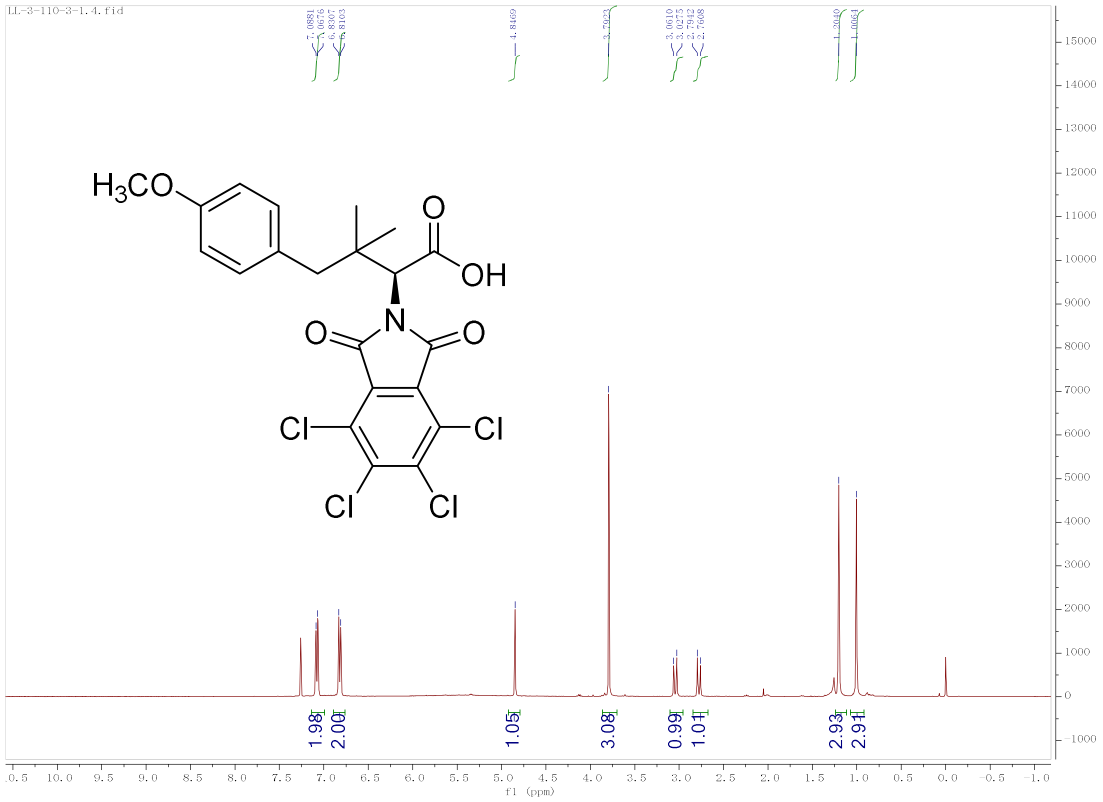

LL-3-114-5-1C-2.1.fid
178.41
178.18
172.09
158.12
131.81
129.82
113.31
60.49
55.19
48.90
44.41
42.66
39.55
39.37
39.04
24.77
24.63
H3CO
O
OH
N
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500

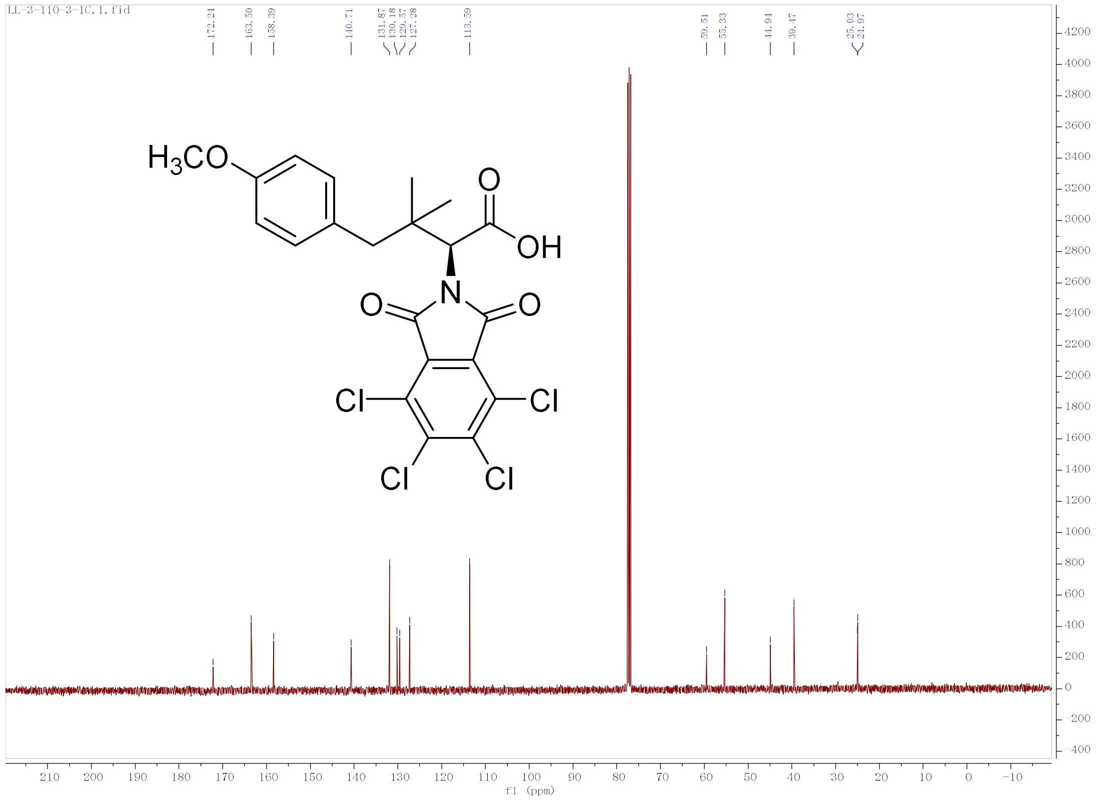
7g'


LL-3-114-5-2.2.fid
7.1537
7.1332
7.0227
7.0022
6.8367
6.8177
6.7984
4.7497
3.8001
3.7672
3.4347
3.4041
3.3723
3.1138
2.9638
2.9300
2.7551
2.4902
2.4559
1.5161
1.3566
1.3365
1.2782
1.2685
1.2596
0.8285
H3CO
H3CO
O
OH
O
N
O
2.06
2.10
3.95
1.09
3.02
3.05
1.93
2.00
1.06
2.09
1.02
6.09
3.13
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
-0.5
-1.0
-1.5
f1 (ppm)
22000
21000
20000
19000
18000
17000
16000
15000
14000
13000
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000
-2000

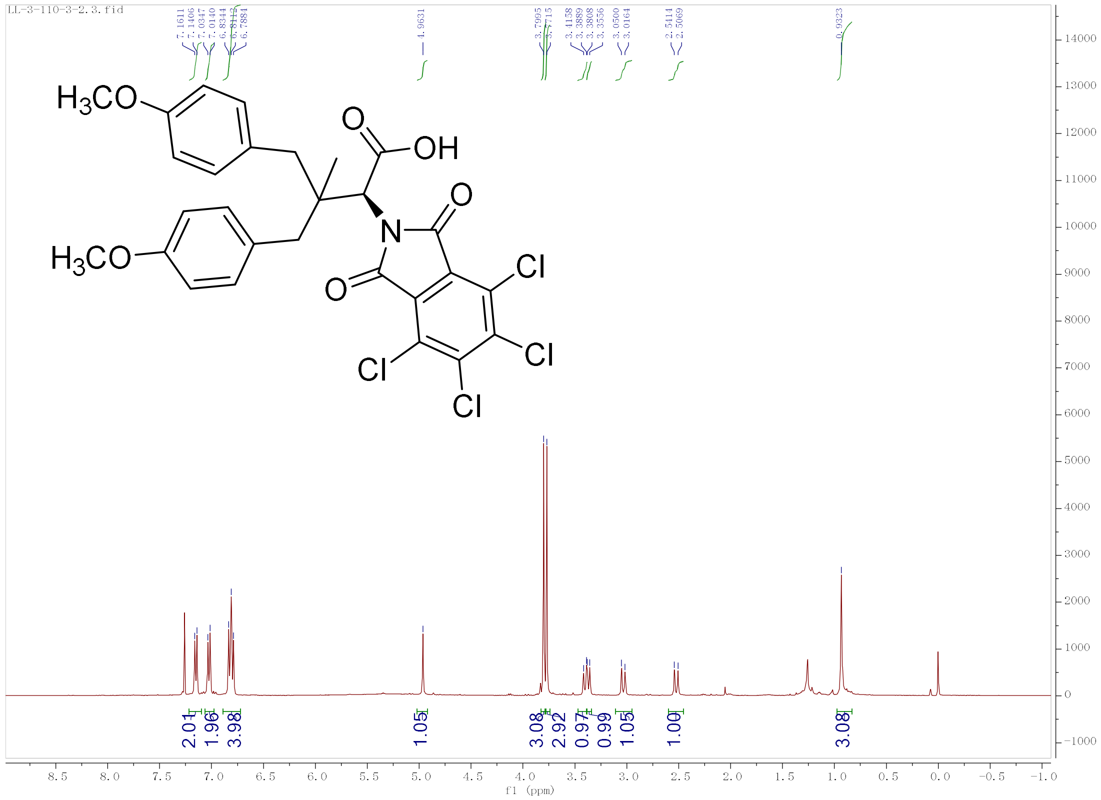

LL-3-114-5-2C.1.fid
178.57
178.16
172.22
158.27
158.04
132.16
131.48
130.04
129.43
113.72
113.23
55.21
55.13
48.83
42.63
42.34
41.87
39.56
39.39
24.66
22.71
H3CO
H3CO
O
OH
O
N
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
4000
3500
3000
2500
2000
1500
1000
500
0

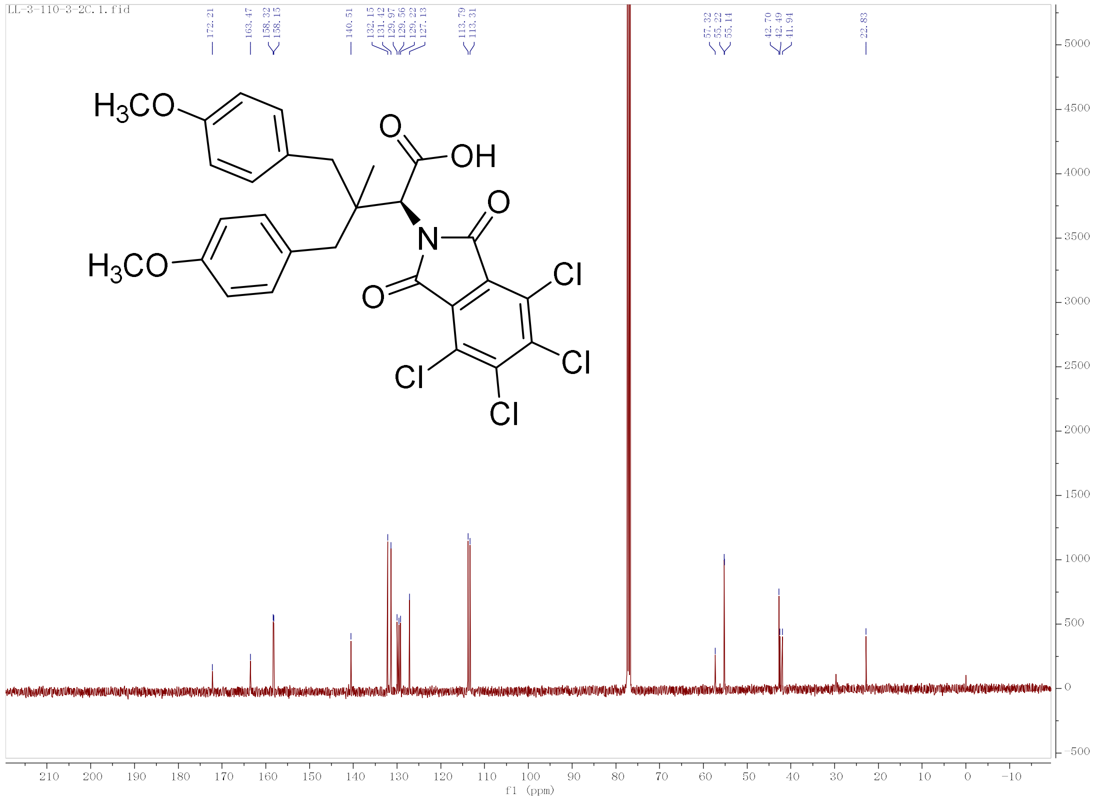
7h


LL-3-110-3-1.4.fid
7.0881
7.0676
6.8307
6.8103
4.8469
3.7923
3.0610
3.0275
2.7942
2.7608
1.2040
1.0064
1.98
2.00
1.05
3.08
0.99
1.01
2.93
2.91
H3CO
O
OH
N
O
O
Cl
Cl
Cl
Cl
f1 (ppm)

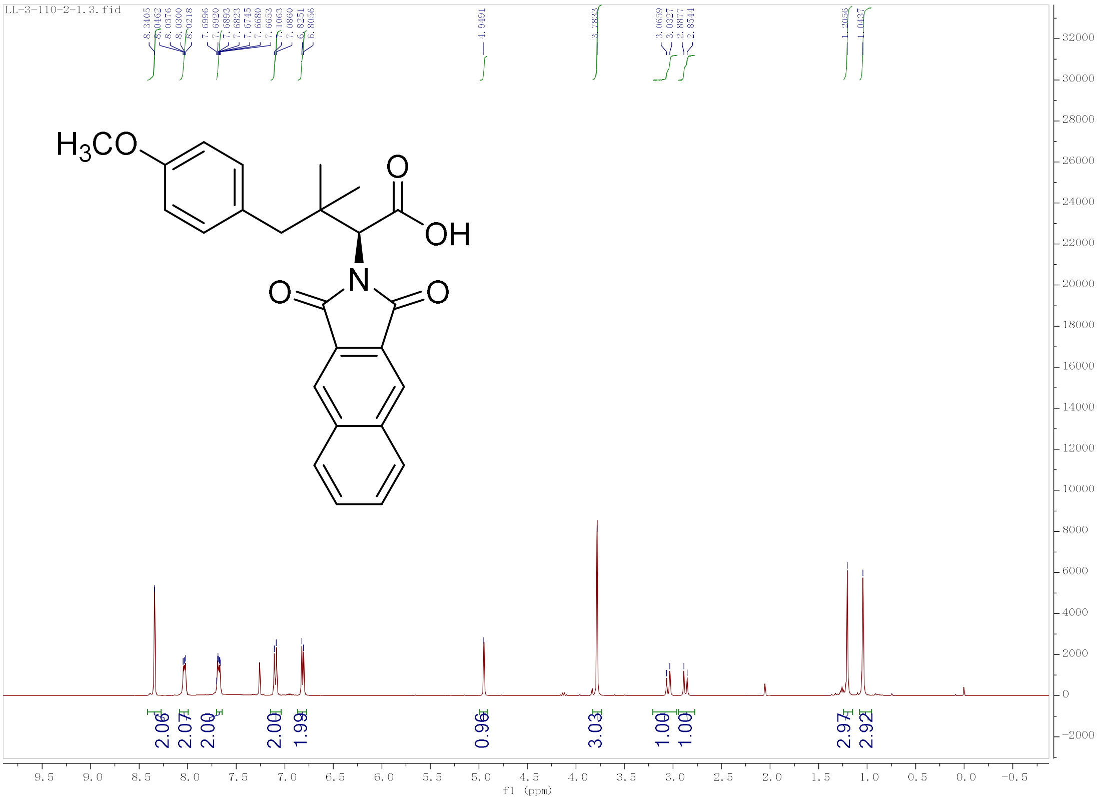

LL-3-110-3-1C.1.fid
172.24
163.50
158.39
140.71
131.87
130.18
129.57
127.28
113.59
59.51
55.33
44.94
39.47
25.03
24.97
H3CO
O
OH
N
O
O
Cl
Cl
Cl
Cl
f1 (ppm)

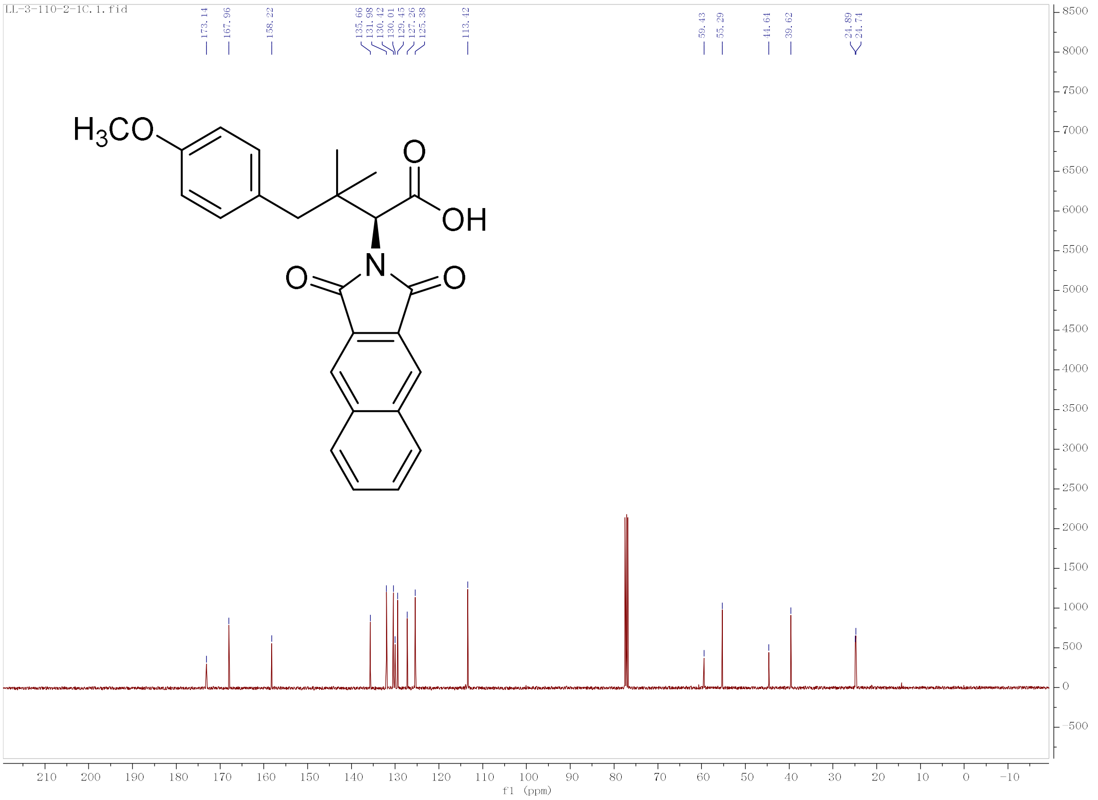
7h’


LL-3-110-3-2.3.fid
7.1611
7.1406
7.0347
7.0140
6.8344
6.8143
6.7884
4.9631
3.7995
3.7715
3.4158
3.3889
3.3808
3.3556
3.0500
3.0164
2.5411
2.5069
0.9323
H3CO
H3CO
O
OH
O
N
O
Cl
Cl
Cl
Cl
2.01
1.96
3.98
1.05
3.08
2.92
0.97
0.99
1.05
1.00
3.08
f1 (ppm)

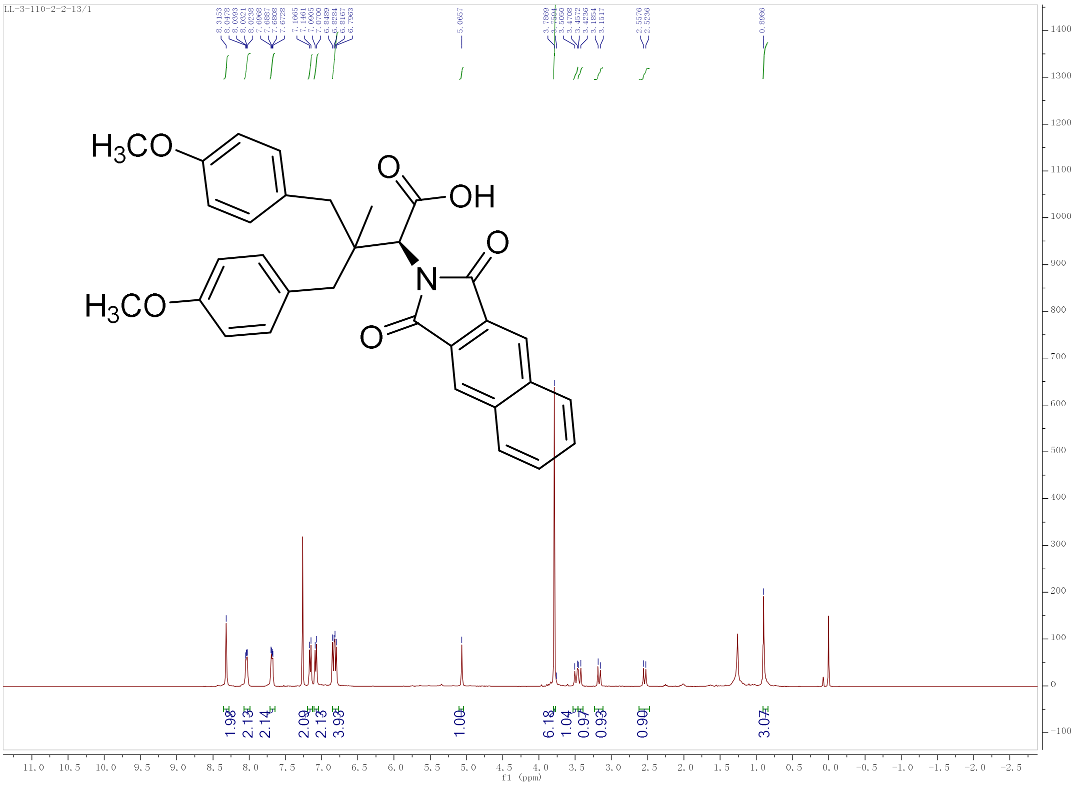

LL-3-110-3-2C.1.fid
172.21
163.47
158.32
158.15
140.51
132.15
131.42
129.97
129.56
129.22
127.13
113.79
113.31
57.32
55.22
55.14
42.70
42.49
41.91
22.83
H3CO
H3CO
O
OH
O
N
O
Cl
Cl
Cl
Cl
f1 (ppm)

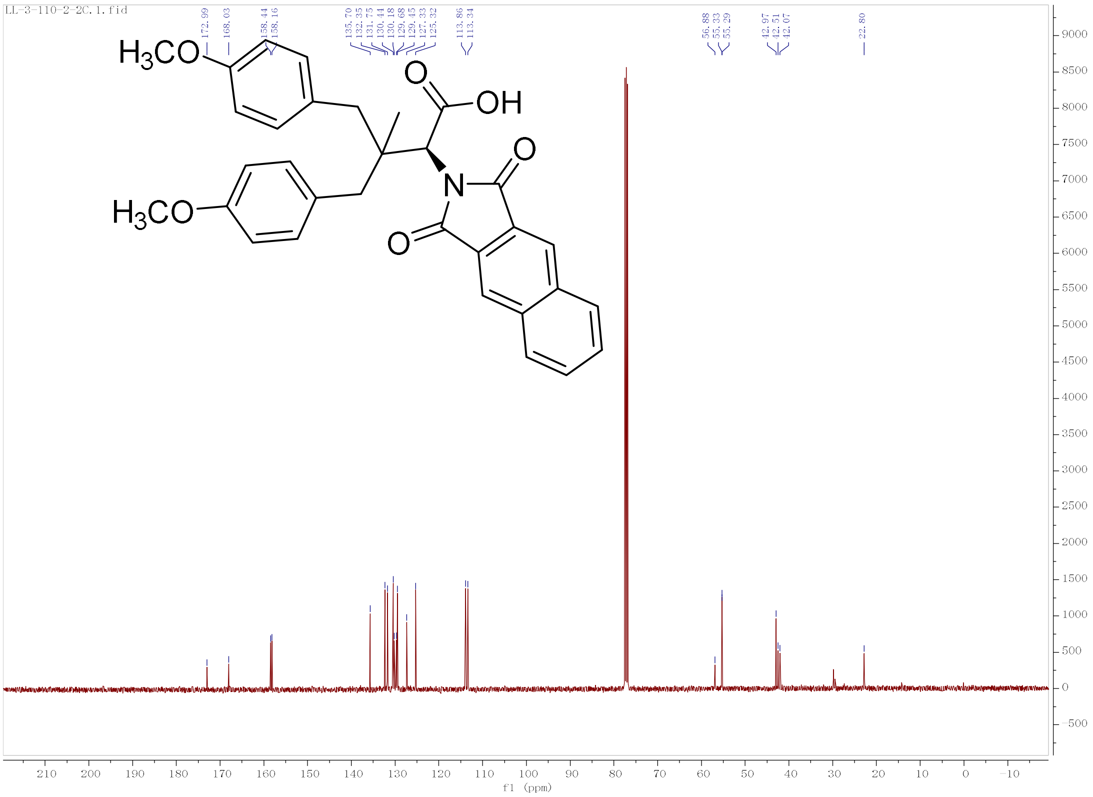
7i


LL-3-110-2-1.3.fid
8.3405
8.0462
8.0376
8.0300
8.0218
7.6996
7.6920
7.6893
7.6823
7.6745
7.6680
7.6653
7.1063
7.0860
6.8251
6.8056
4.9491
3.7833
3.0659
3.0327
2.8877
2.8544
1.2056
1.0437
H3CO
O
OH
N
O
O
2.06
2.07
2.00
2.00
1.99
0.96
3.03
1.00
1.00
2.97
2.92
f1 (ppm)

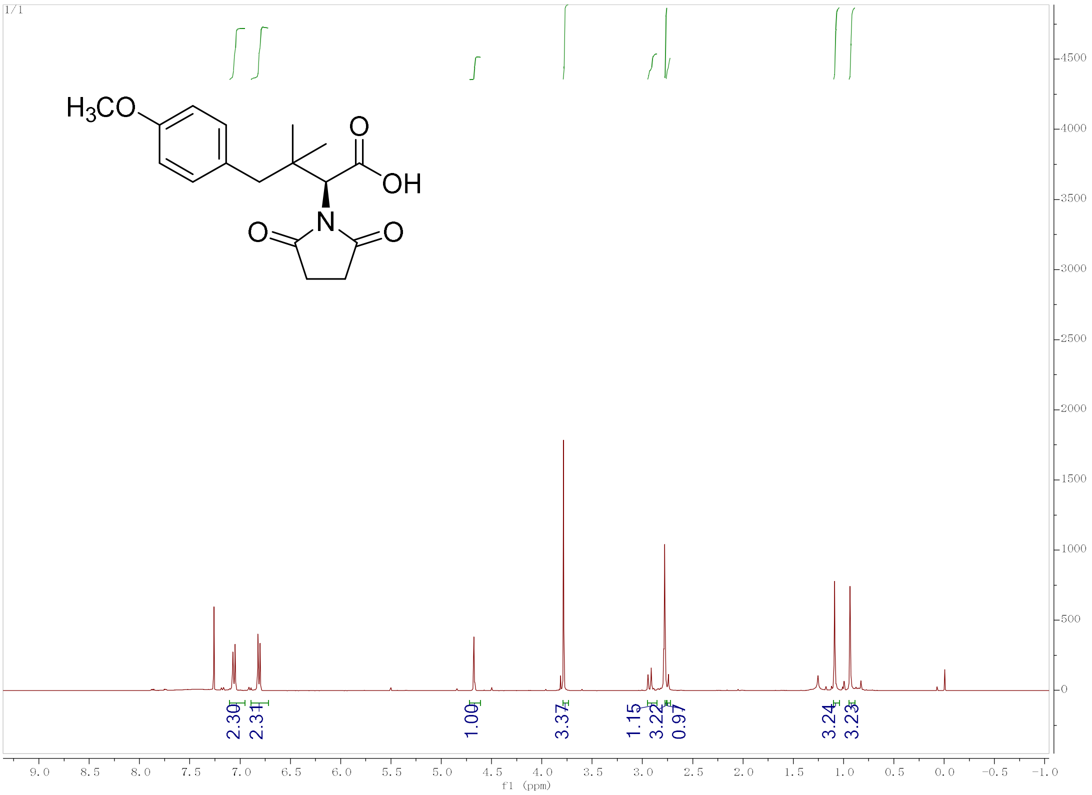

LL-3-110-2-1C.1.fid
173.14
167.96
158.22
135.66
131.98
130.42
130.01
129.45
127.26
125.38
113.42
59.43
55.29
44.64
39.62
24.89
24.74
H3CO
O
OH
N
O
O
f1 (ppm)

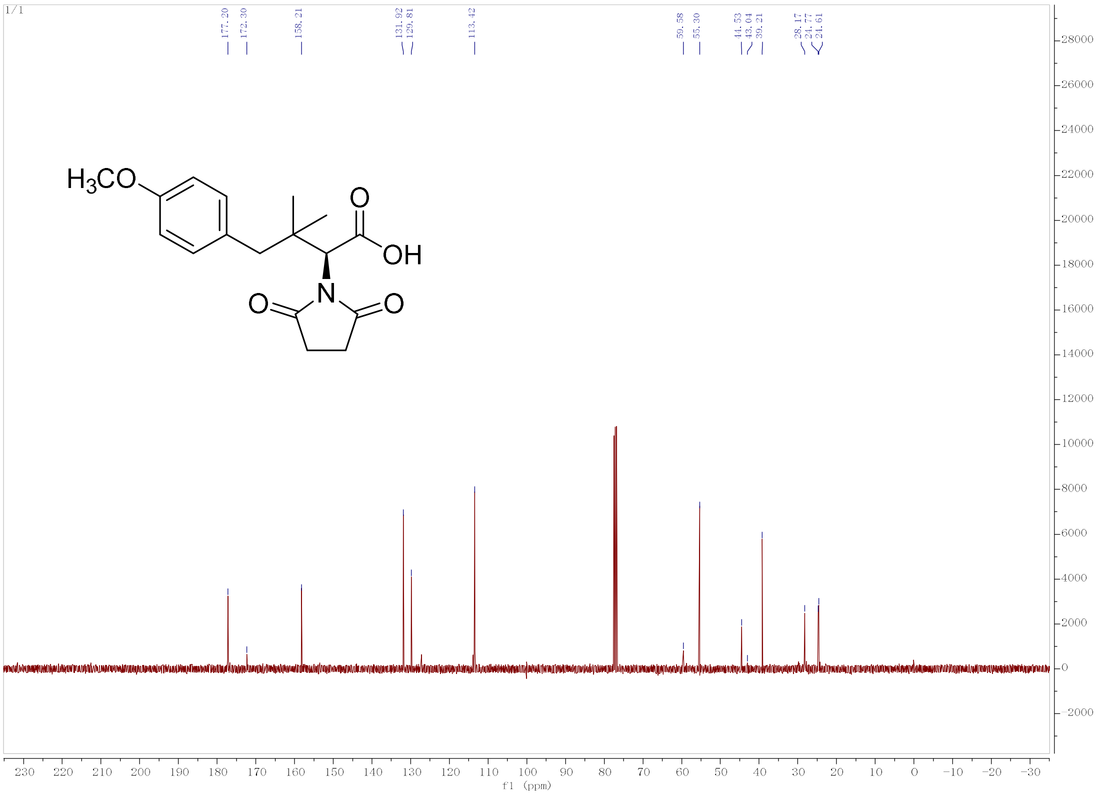
7i'


LL-3-110-2-2-13/1
8.3153
8.0478
8.0393
8.0321
8.0238
7.6968
7.6887
7.6808
7.6728
7.1665
7.1461
7.0905
7.0700
6.8489
6.8284
6.8167
6.7963
5.0657
3.7869
3.7504
3.5050
3.4708
3.4572
3.4236
3.1854
3.1517
2.5576
2.5236
0.8986
1.98
2.13
2.14
2.09
2.13
3.93
1.00
6.18
1.04
0.97
0.93
0.90
3.07
H3CO
H3CO
O
OH
O
N
O
f1 (ppm)

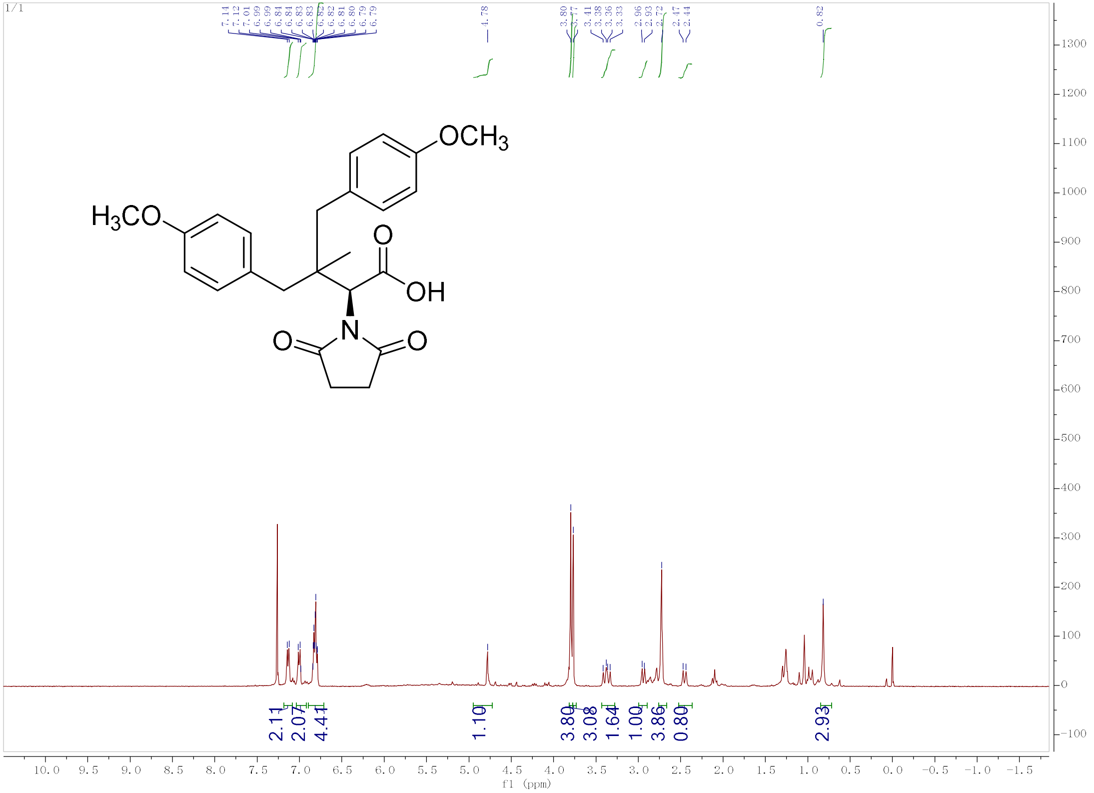

LL-3-110-2-2C.1.fid
172.99
168.03
158.44
158.16
135.70
132.35
131.75
130.44
130.18
129.68
129.45
127.33
125.32
113.86
113.34
56.88
55.33
55.29
42.97
42.51
42.07
22.80
H3CO
H3CO
O
OH
O
N
O
f1 (ppm)

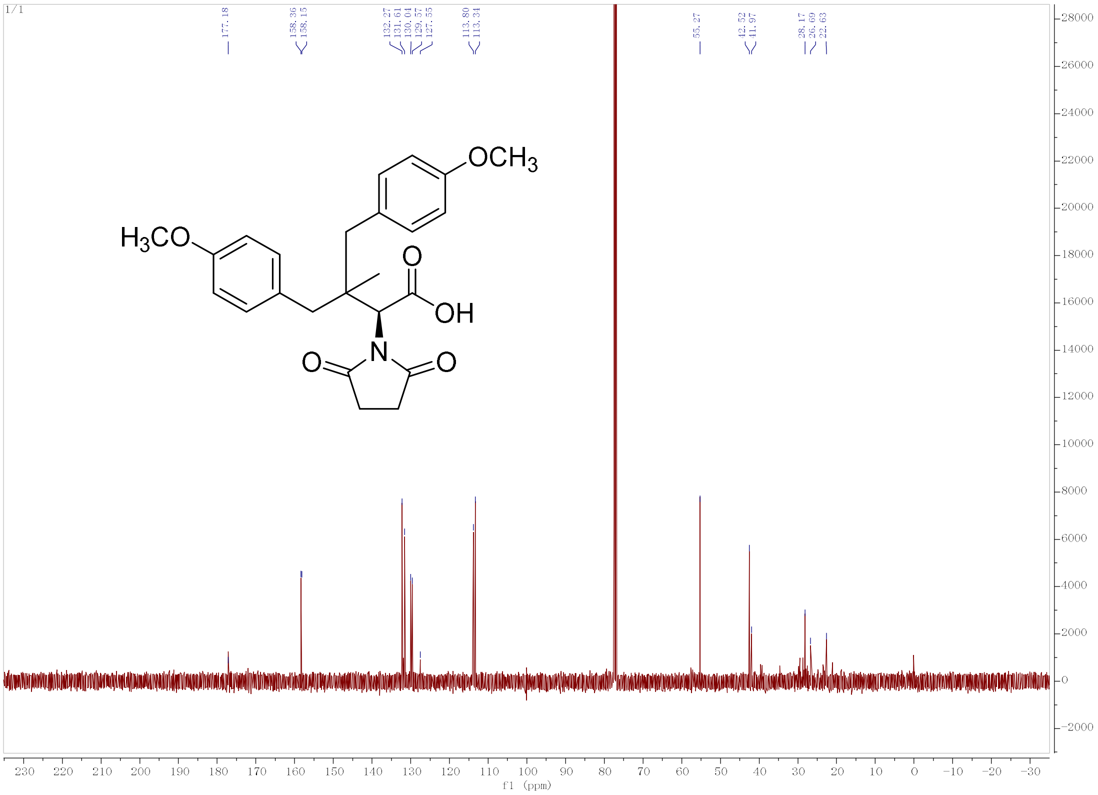
7j


1/1
H3CO
O
OH
N
O
O
2.30
2.31
1.00
3.37
1.15
3.22
0.97
3.24
3.23
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 -0.5 -1.0
f1 (ppm)
4500 4000 3500 3000 2500 2000 1500 1000 500 0

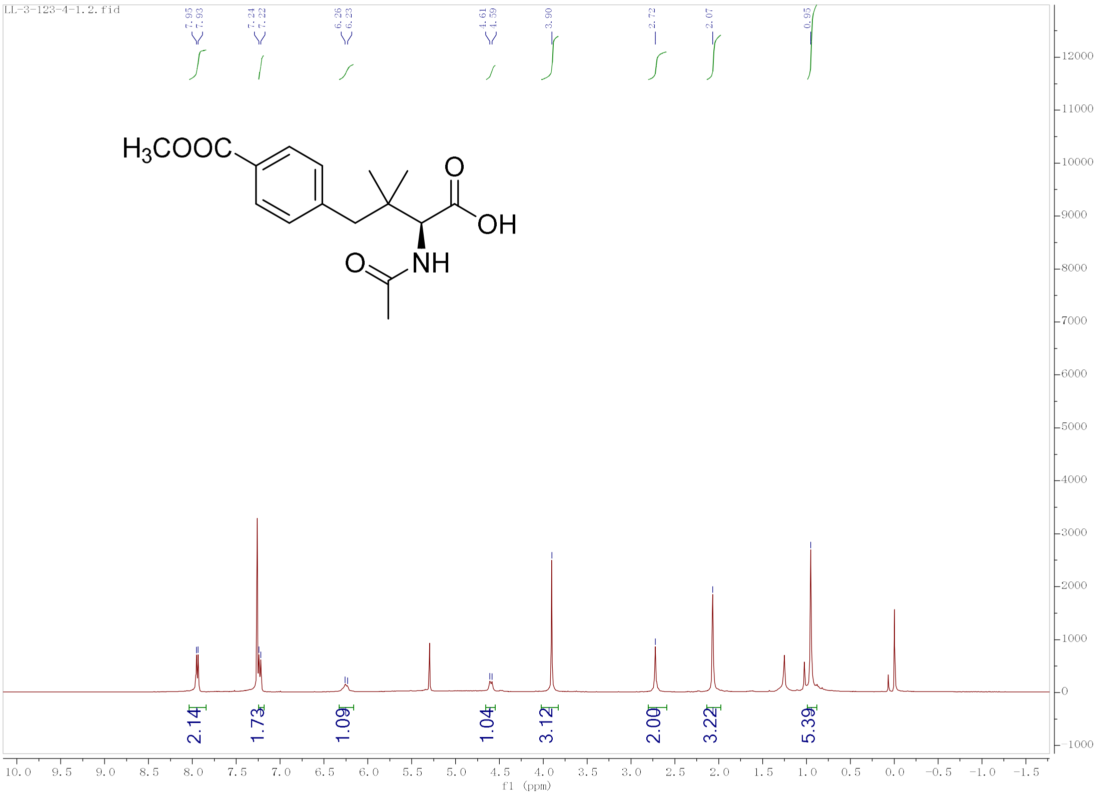

1/1
177.20
172.30
158.21
131.92
129.81
113.42
59.58
55.30
44.53
43.04
39.21
28.17
24.77
24.61
H3CO
O
OH
N
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
f1 (ppm)
28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 -2000

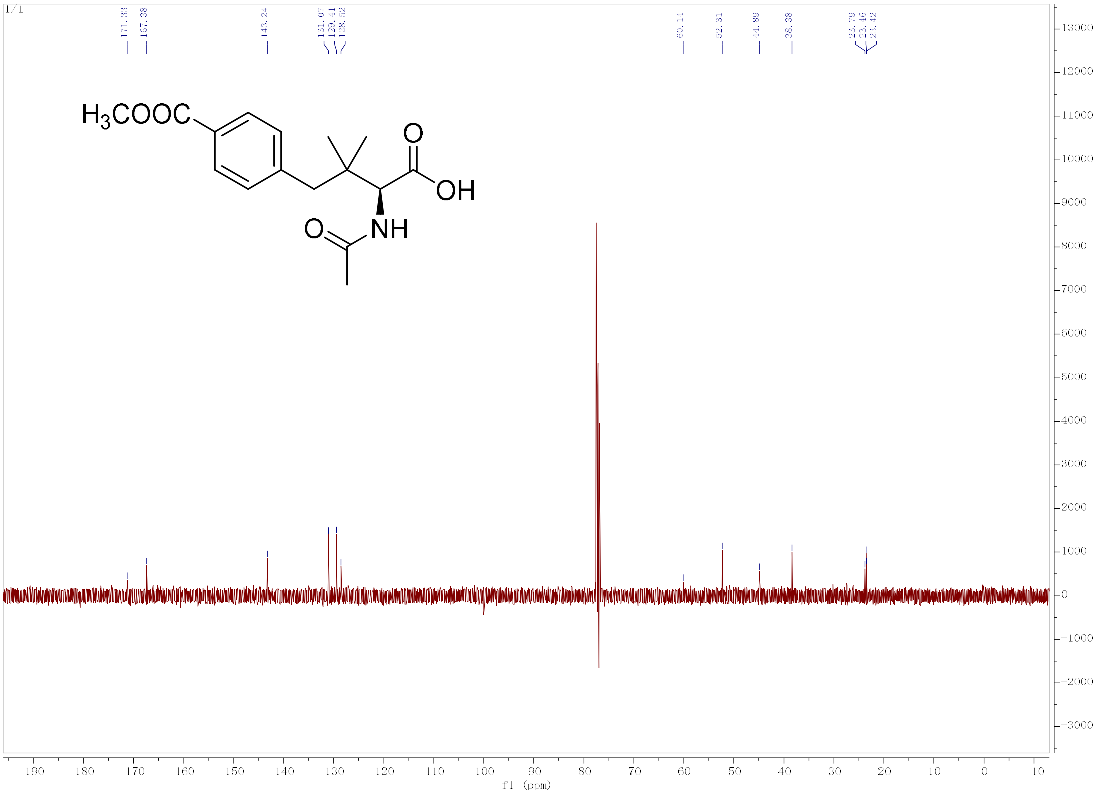
7j'


1/1
7.14 7.12 7.01 6.99 6.99 6.84 6.84 6.83 6.83 6.82 6.82 6.81 6.80 6.79 6.79
4.78
3.80 3.77 3.41 3.38 3.36 3.33 2.96 2.93 2.72 2.47 2.44
0.82
OCH3
H3CO
O
OH
N
O
O
2.11 2.07 4.41
1.10
3.80 3.08 1.64 1.00 3.86 0.80
2.93
10.0 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 −0.5 −1.0 −1.5
f1 (ppm)
1300 1200 1100 1000 900 800 700 600 500 400 300 200 100 0 −100

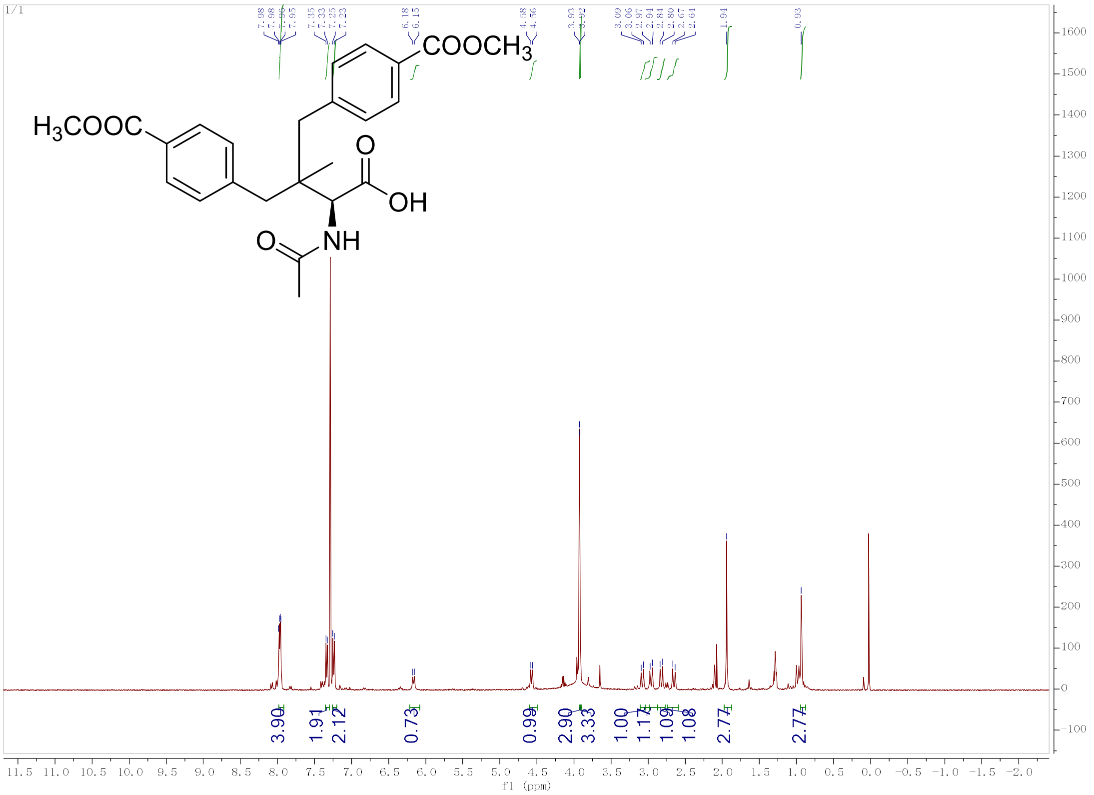

1/1
177.18
158.36 158.15
132.27 131.61 130.04 129.57 127.55
113.80 113.34
55.27
42.52 41.97
28.17 26.69 22.63
OCH3
H3CO
O
OH
N
O
O
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10 −20 −30
f1 (ppm)
28000 26000 24000 22000 20000 18000 16000 14000 12000 10000 8000 6000 4000 2000 0 −2000

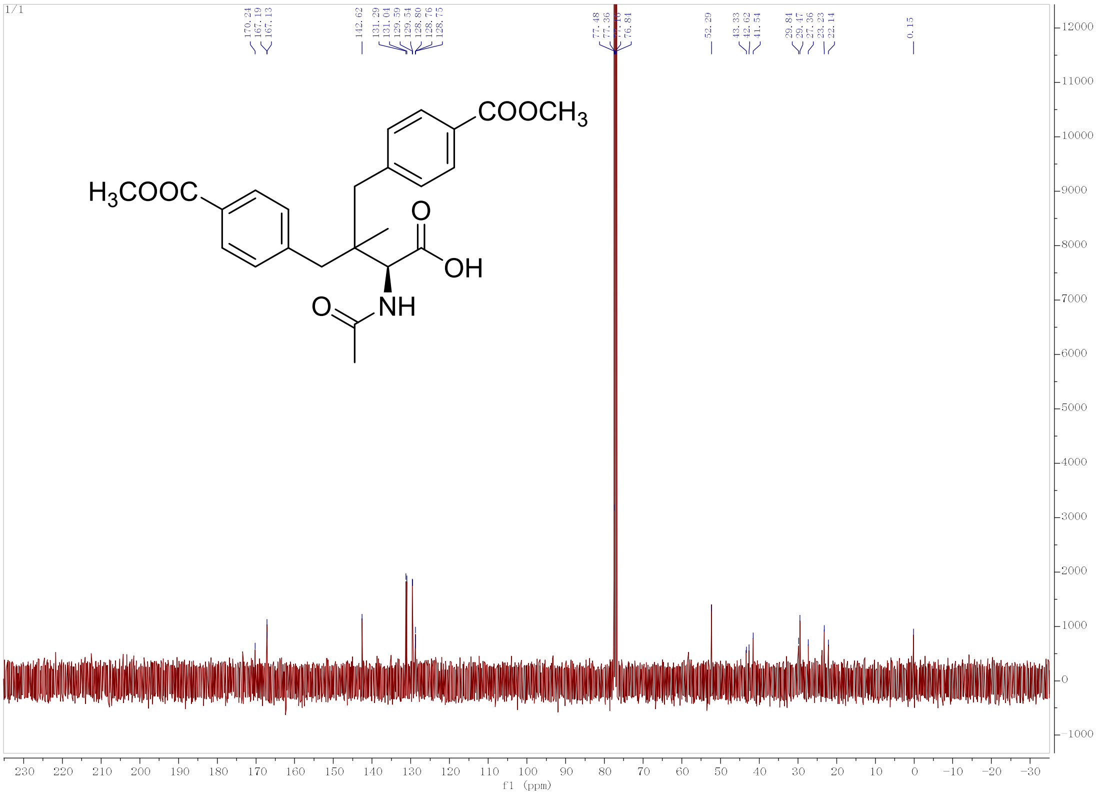
7kc


LL-3-123-4-1.2.fid
7.95
7.93
7.24
7.22
6.26
6.23
4.61
4.59
3.90
2.72
2.07
0.95
H3COOC
O
OH
O
NH
2.14
1.73
1.09
1.04
3.12
2.00
3.22
5.39
f1 (ppm)

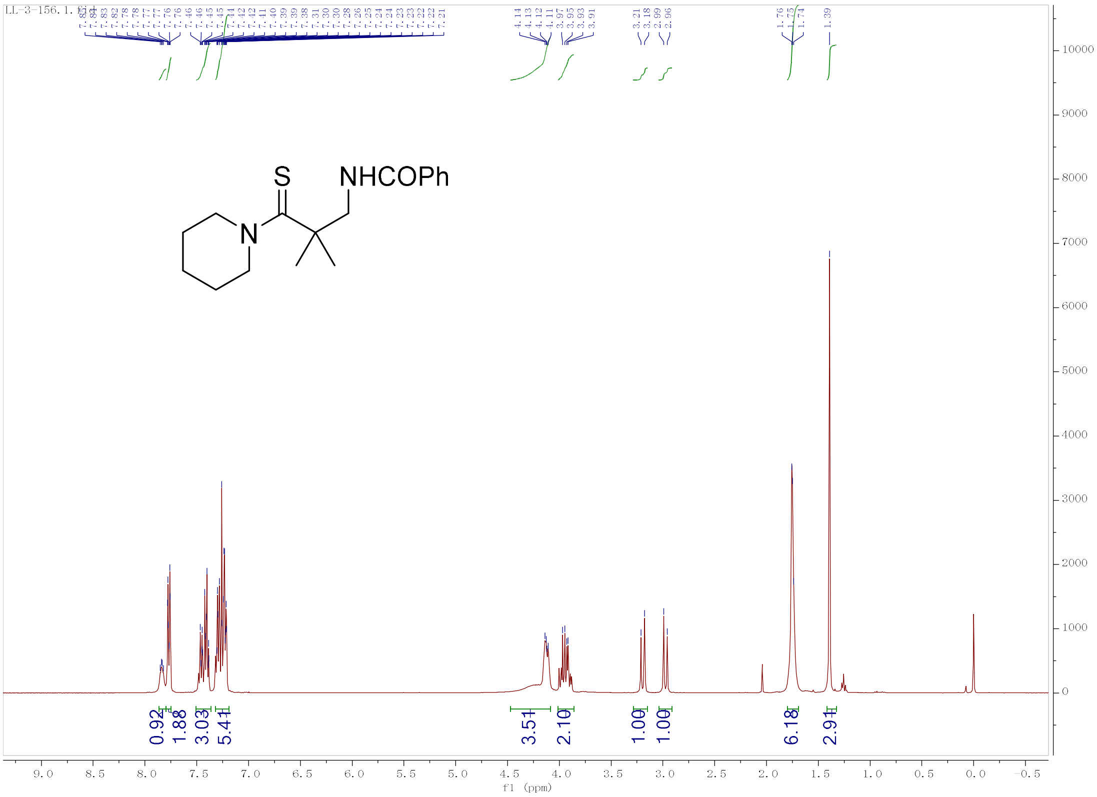

1/1
171.33
167.38
143.24
131.07
129.41
128.52
60.14
52.31
44.89
38.38
23.79
23.46
23.42
H3COOC
O
OH
O
NH
f1 (ppm)

7kc’

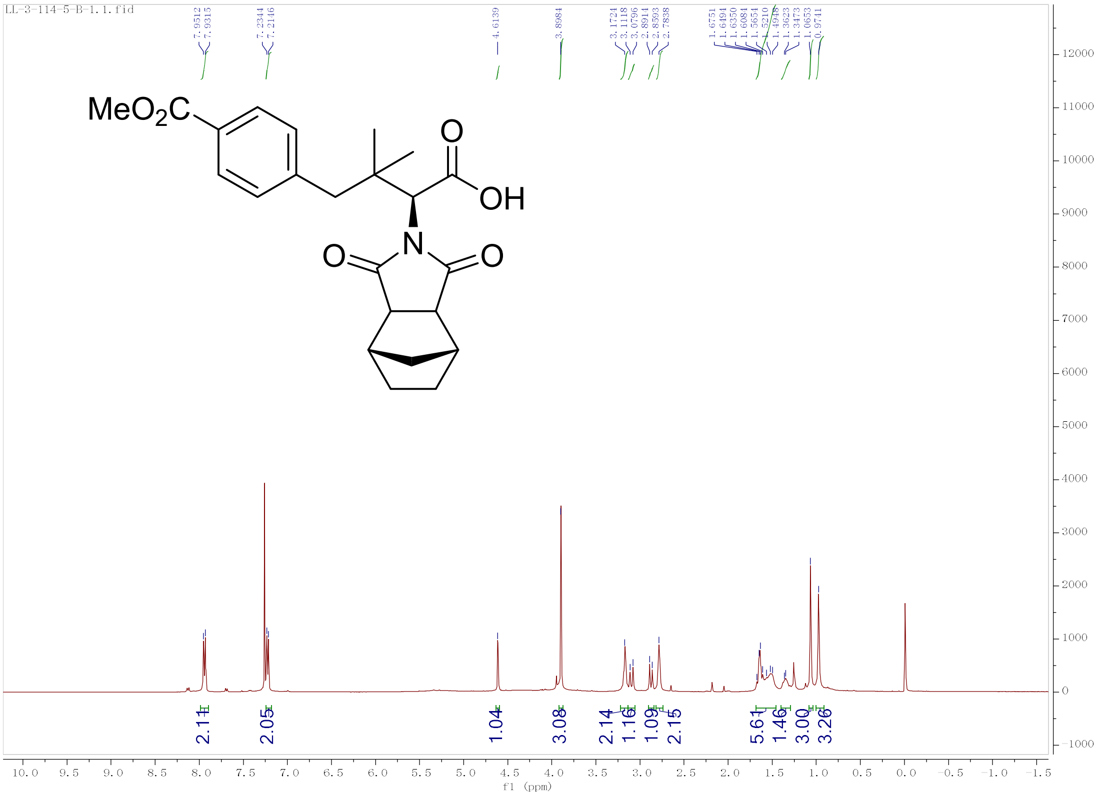

1/1
7.98
7.98
7.96
7.95
7.35
7.33
7.25
7.23
6.18
6.15
4.58
4.56
3.93
3.92
3.09
3.06
2.97
2.94
2.84
2.80
2.67
2.64
1.94
0.93
H_3COOC
$COOCH_3$
O
OH
O
NH
3.90
1.91
2.12
0.73
0.99
2.90
3.33
1.00
1.17
1.09
1.08
2.77
2.77
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
-2.0
f1 (ppm)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100

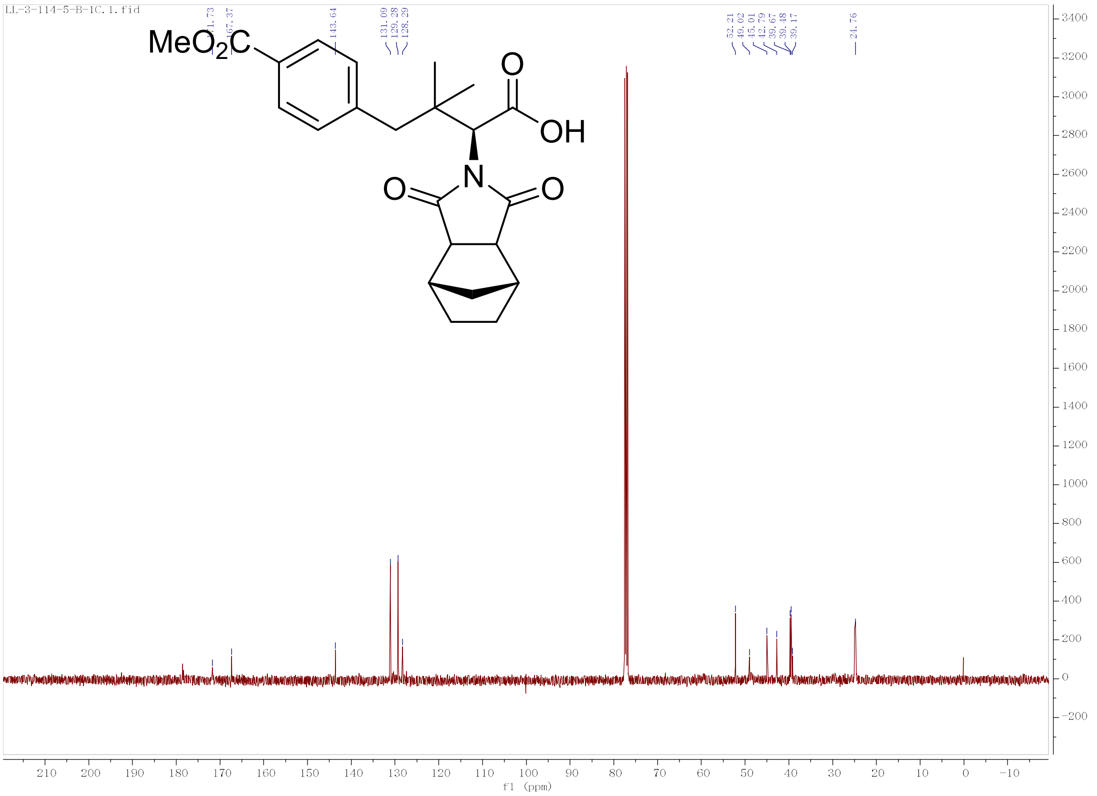

1/1
170.24
167.19
167.13
142.62
131.29
131.04
129.59
129.54
128.80
128.76
128.75
77.48
77.36
77.16
76.84
52.29
43.33
42.62
41.54
29.84
29.47
27.36
23.23
22.14
0.15
H_3COOC
$COOCH_3$
O
OH
O
NH
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
f1 (ppm)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000

10

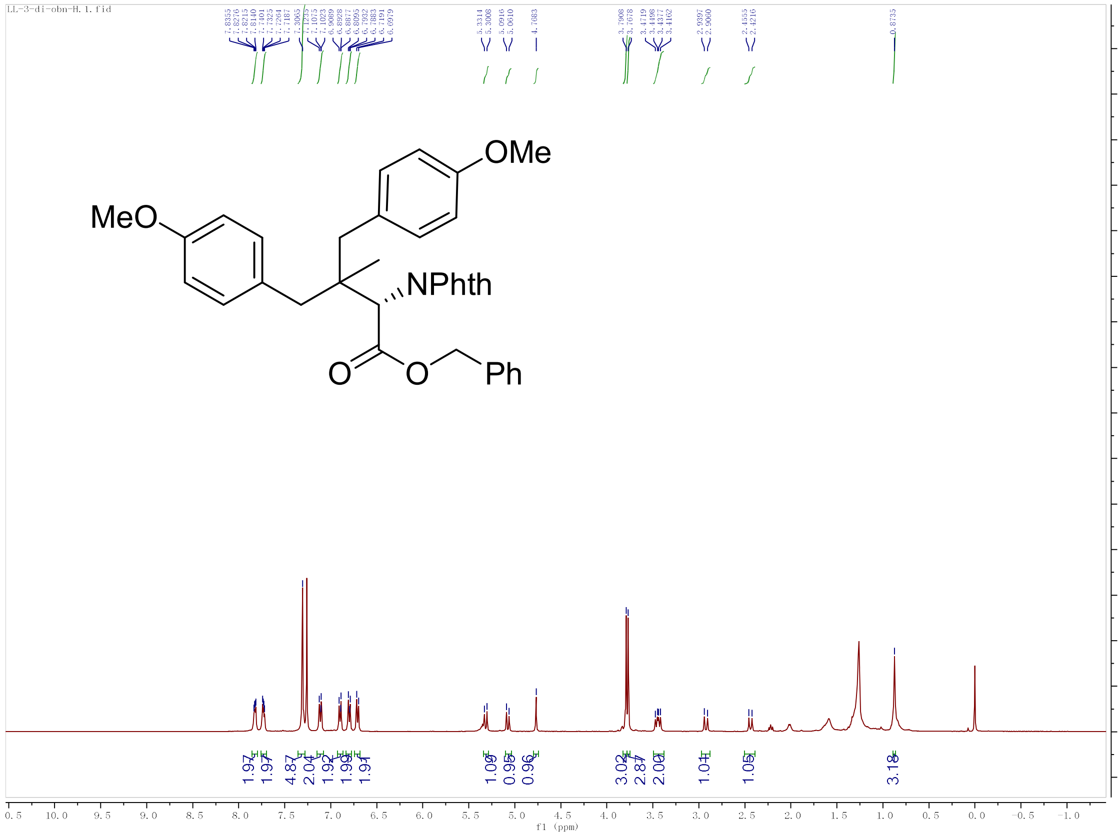

LL-3-156.1.fid
7.85
7.84
7.83
7.82
7.78
7.78
7.77
7.77
7.76
7.76
7.46
7.46
7.45
7.45
7.44
7.42
7.42
7.41
7.40
7.39
7.39
7.38
7.31
7.30
7.30
7.28
7.26
7.25
7.24
7.24
7.23
7.23
7.22
7.22
7.21
4.14
4.13
4.12
4.11
3.97
3.95
3.93
3.91
3.21
3.18
2.99
2.96
1.76
1.75
1.74
1.39
S
NHCOPh
N
0.92
1.88
3.03
5.41
3.51
2.10
1.00
1.00
6.18
2.91
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
-0.5
f1 (ppm)
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0

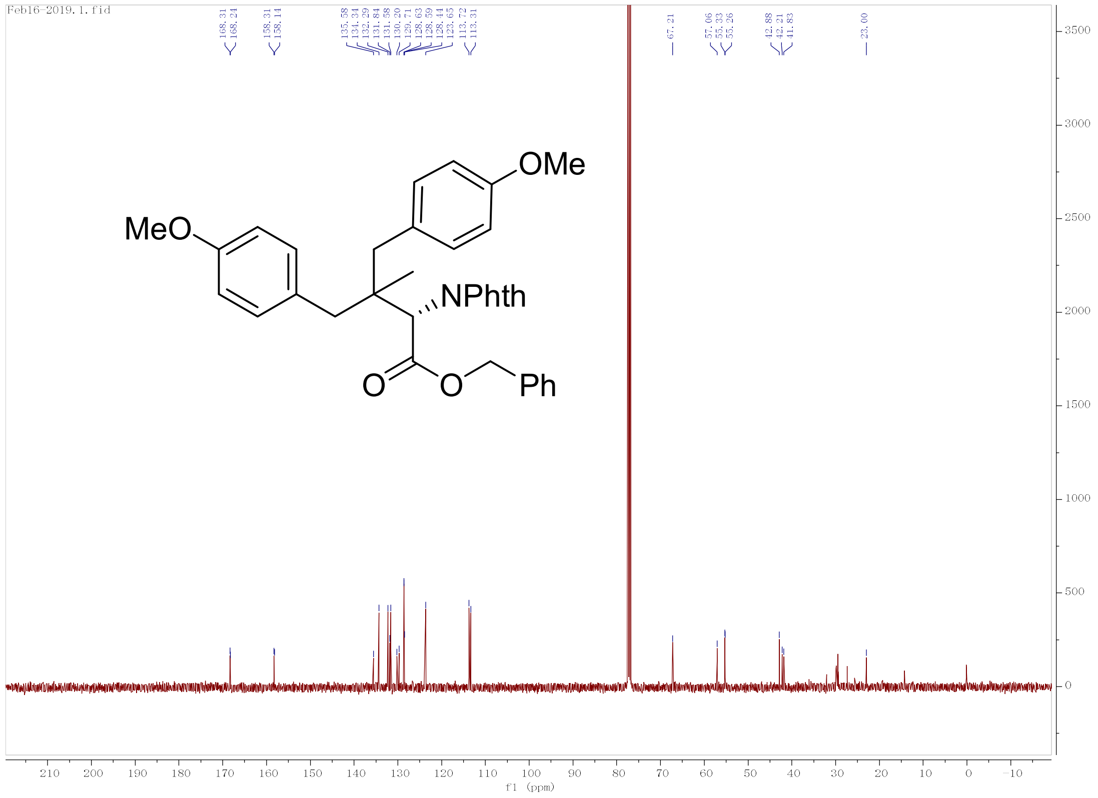
7gc


LL-3-114-5-B-1.1.fid
7.9512
7.9315
7.2344
7.2146
4.6139
3.8984
3.1724
3.1118
3.0796
2.8914
2.8593
2.7838
1.6751
1.6494
1.6350
1.6084
1.5654
1.5210
1.4948
1.3623
1.3473
1.0653
0.9741
MeO2C
O
OH
N
O
O
2.11
2.05
1.04
3.08
2.14
1.16
1.09
2.15
5.61
1.46
3.00
3.26
10.0
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
-0.5
-1.0
-1.5
f1 (ppm)
12000
11000
10000
9000
8000
7000
6000
5000
4000
3000
2000
1000
0
-1000


LL-3-114-5-B-1C.1.fid
1.73
167.37
143.64
131.09
129.28
128.29
52.21
49.02
45.01
42.79
39.67
39.48
39.17
24.76
MeO2C
O
OH
N
O
O
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
400
200
0
-200

12


LL-3-di-obn-H.1.fid
7.8355 7.8276 7.8215 7.8140 7.7401 7.7325 7.7264 7.7187 7.3065 7.1233 7.1075 7.1023 6.9089 6.8928 6.8877 6.8095 6.7932 6.7883 6.7191 6.6979
5.3314 5.3008 5.0916 5.0610 4.7683
3.7908 3.7678 3.4719 3.4498 3.4377 3.4162 2.9397 2.9060 2.4555 2.4216 0.8735
1.97 1.97 4.87 2.04 1.92 1.99 1.94 1.09 0.95 0.96 3.02 2.87 2.00 1.04 1.05 3.18
MeO
OMe
NPhth
O
O
Ph
f1 (ppm)


Feb16-2019.1.fid
168.31 168.24 158.31 158.14
135.58 134.34 132.29 131.84 131.58 130.20 129.71 128.63 128.59 128.44 123.65 113.72 113.31
67.21 57.06 55.33 55.26 42.88 42.21 41.83 23.00
MeO
OMe
NPhth
O
O
Ph
f1 (ppm)