Supplementary Information

Asymmetric Synthesis of γ-Lactams under Low-loading *N*-Heterocylic Carbenes Catalysis

Yuxia Zhang,[†,§] Ye Zhang,[†,§] Jingcheng Guo,[†,§] Jinna Han,[†] Xiangui Zhou,[†] Zhenqian Fu,*[,†]

[†] Key Laboratory of Flexible Electronics & Institute of Advanced Materials, Nanjing Tech University, 30 South Puzhu Road, Nanjing 211816, China.

E-mail: iamzqfu@njtech.edu.cn

I: General Information

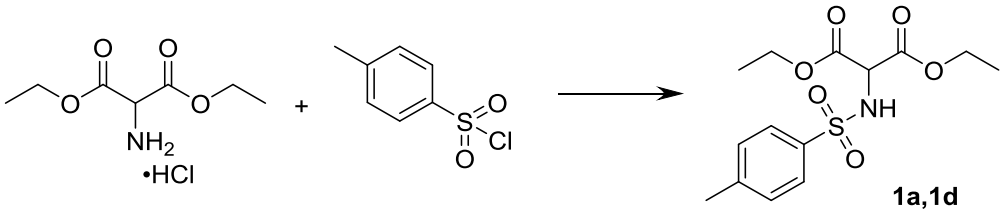
Commercially available materials were purchased from Alfa Aesar and Sigma-Aldrich. Toluene and DCM was dried over Pure Solv solvent purification system. THF was distilled over sodium. Other solvents were dried over 4Å molecular sieve prior use. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker (400 MHz) (100 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on a Waters Q–TOF Permier Spectrometer. The determination of enantiomeric excess was performed *via* chiral HPLC analysis using Shimadzu LC-20AD HPLC workstation. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Optical rotations were measured using a 1 mL cell with a 1 dm path length on a Jasco P-1030 polarimeter and are reported as follows: $[\alpha]^{rt}_{D}$ (*c* is in gm per 100 mL solvent). Analytical thin-layer chromatography (TLC) was carried out on Merck 60 F254 pre-coated silica gel plate (0.2 mm thickness).

II. General procedure

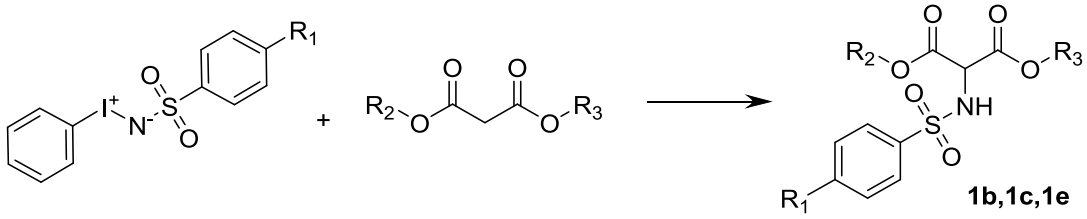
a) General procedure for the synthesis of enals 1

1a-1h, **1l**, **1n, 1o, 1q, 1s** and **1t** were purchased. Enals **1i-1k, 1m, 1p, 1r, 1u-1x** were synthesized according to the literature. [1-5] To a dried 50 mL flask was added formylmethylene)triphenylphosphorane (1.521 g, 5 mmol), aldehydes (7 mmol) and 25 mL toluene. The mixture was refluxed overnight (detected by TLC), and then the solvent was removed under reduced pressure. The residue was purified by silica column chromatography to afford the product **1**.

b) General procedure for the synthesis of *N*-Ts diethyl aminomalonate 2



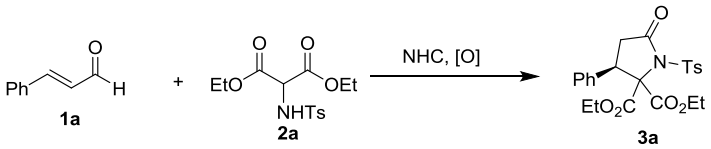
2a and **2d** were synthesized according to the literature.[6] p-Toluenesulfonyl chloride (3.8 g, 20 mmol) was added to a suspension of diethyl aminomalonate hydrochloride (4.22 g, 20 mmol) in 10 mL pyridine at 0 ℃. The mixture was warmed to room temperature and stirred for 12h (detected by TLC). Upon completion of the reaction, to the mixture was poured into 50 mL ice water with stirring. The precipitated solid was filtered off and washed with water, and then recrystallization from EA/PE afforded the product **2a** (5.3g, 80%yield).



2b, **2c** and **2e** were synthesized according to the literature. [7,8] $Cu(OTf)_2$ (0.1 mmol), 1,10-phen (0.1 mmol), and powdered 4Å MS (600 mg) were added to a solution of dry CH_2Cl_2 (5 mL) at 0℃. After stirring for 1 h at the same temperature, 1,3-dicarbonyl compound (1.0 mmol) and PhI=NTs or PhI=NNs [9] (2 mmol) was added to the mixture and then the reaction mixture was stirred at room temperature until the reaction completed (detected by TLC). The crude product was filtered through Celite, washed with EtOAc (30 mL), evaporated to dryness, and purified by silica gel flash column chromatography (eluent: n-hexane/EtOAc 4:1) to give the products **2**.

c) Experimental data of other Lewis acids

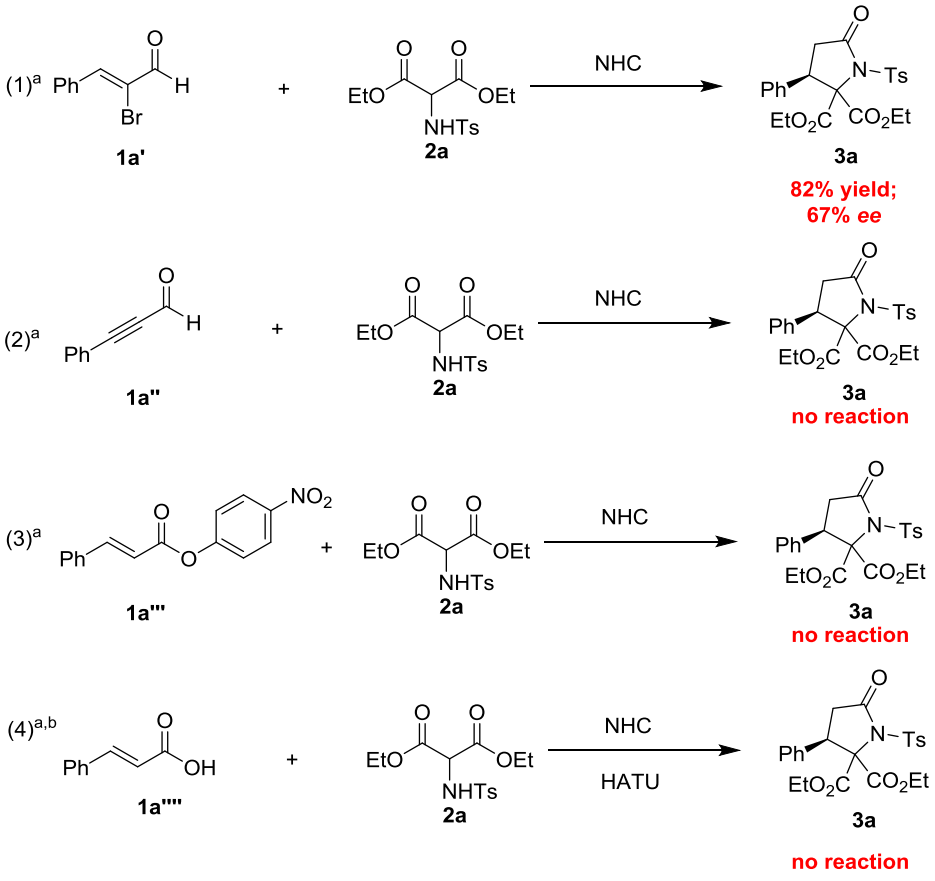
Table S1. Experimental data of other Lewis acids



Entry[a]	Lewis acid	Yield[%][b]	ee[%][c]
1	$Cu(OTf)_2$	-	-
2	$Zn(OTf)_2$	15	49
3	$Sc(OTf)_3$	68	49
4	$Ti(O^iPr)_4$	45	99
5	$Mg(OTf)_2$	62	99
6	/	88	48

[a] Standard condition: **1a** (0.3 mmol), **2a** (0.2 mmol), NHC **D** (2 mol%), NaO^tBu (0.047 mmol), K_2CO_3 (0.093 mmol), [O] (0.24 mmol), Lewis acid (0.04 mmol), 4Å MS (100 mg), DCM (1 mL), 0 ℃ to rt (ice water mixture). [b] Isolated yields after column chromatography. [c] Determined by chiral HPLC.

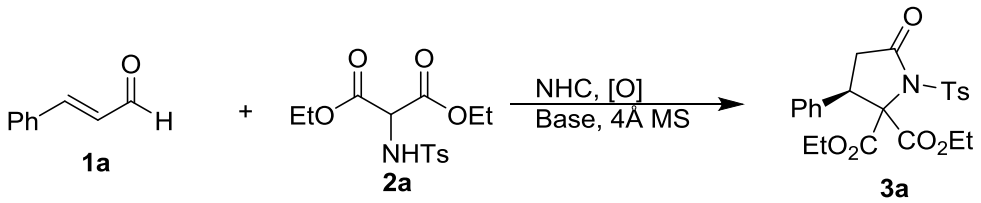
d) Experimental data of other acyazolium precursors



[a] Reaction conditions: **1** (0.3 mmol), **2a** (0.2 mmol), **NHC D** (2 mol%), NaO^tBu (0.047 mmol), K_2CO_3 (0.093 mmol), LiCl (0.2 mmol),4Å MS (100 mg), DCM (1 mL), 0°C to rt (ice water mixture).); yields (after SiO_2 chromatography purification) were based on 1; Determined by chiral HPLC. [b] HATU (0.04 mmol) was used.

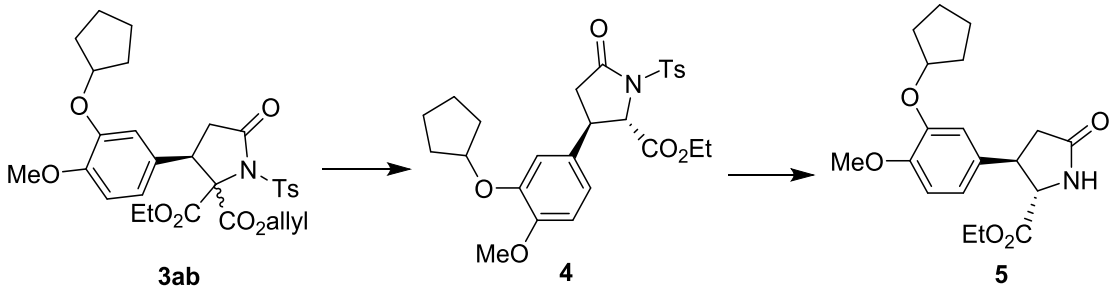
Scheme S1. Experimental data of other acyazolium precursors

e) General procedure for the reactions of 1a with 2a to synthesize product 3 (3a as an example)



To a dried 10 mL Schlenk tube equipped with a magnetic stir bar was added **2a** (0.2 mmol, 65.8 mg), NHC **D** pre-catalyst (0.004 mmol, 1.7 mg), 3,3',5,5'-tetra-tert-butyldiphenoquinone (0.24 mmol, 98.0 mg), LiCl (0.2 mmol, 8.4 mg), NaO^tBu (0.047 mmol, 4.5 mg), K_2CO_3 (0.093mmol, 13.0 mg) and MS 4Å (100.0 mg). To this mixture was added dry DCM (1.0 mL), and **1a** (0.3 mmol, 38 uL) via a micro syringe, then the reaction mixture was stirred for 12h at ice-water (detected by TLC). The solvent was remover under reduced pressure, and then the residue was purified by column chromatography (silica gel, Petroleum ether/EtOAc, 5:1, v/v) to afford the product **3a**.

f) General procedure for the reactions of 3ab to synthesize product 4 and 5 [3]



To an ovendried, 10-mL round-bottomed flask equipped with a magnetic stir bar were added $Pd_2(dba)_3$- $CHCl_3$ (16.8 mg, 0.016 mmol, 10 mol%), PPh_3 (2.2 mg, 0.008 mmol, 5 mol%), HCO_2NH_4 (20.4 mg, 0.32 mmol, 2.0 equiv) and CH_3CN (2.0 mL) and the mixture was stirred at room temperature for 10 min. Compound **3ab** (93.6 mg, 0.16 mmol, 1.0 equiv) in CH_3CN (2 mL) was added to the mixture, and then the reaction was heated to 90 ℃ with vigorous stirring for 2 h (detected by TLC). After the reaction was completed, the reaction mixture was concentrated under reduced pressure, and then purified by column chromatography (silica gel, Petroleum ether/EtOAc, 3:1, v/v) to afford the product **4**. The relative stereo-chemistry of compound **4** was assigned based on the work of Romo's group.[3]

Under Ar atmosphere, to an 25-mL round-bottomed flask equipped with a magnetic stir bar were added SmI_2 (5.77 mL of 0.1M in THF, 0.577 mmol, 6.0 equiv) , and **4** (48.2 mg, 0.096 mmol, 1.0 equiv) at 0 ℃. The reaction mixture was warmed to room temperature and stirred for 30 min (detected by TLC). After the reaction was completed, the reaction mixture was quenched with saturated $NaHCO_3$ and extracted

with EtOAc (3 × 20 mL). The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated under reduced pressure. And then the crude residue was purified by column chromatography (silica gel, Petroleum ether/EtOAc, 1:1, v/v) to afford the product **5**.

g) Stereochemistry determination 3a via X-ray crystallographic analysis

Product 3a was was crystallized as a colorless crystal *via* vaporization of a hexane/ethyl acetate solution, and its absolute configuration was determined by x-ray structure analaysis. CCDC 2061718 contains the supplementary crystallographic data that can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

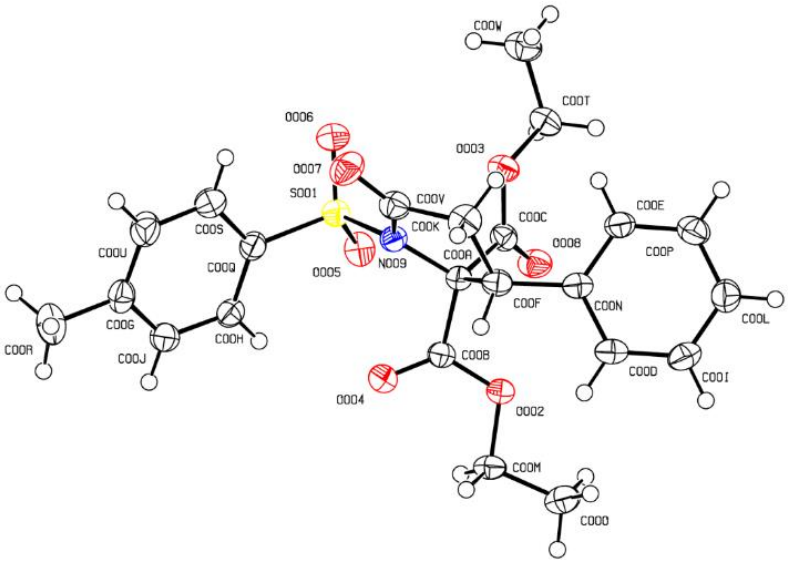


Figure S1 Crystal structure of compound **3a** (displacement ellipsoids are drawn at the 30% probability) (grey atom, C; red atom, O; blue atom, N; yellow atom, S)

Flack parameter

Flack x determined using 1844 quotients [(I+)-(I-)]/[(I+)+(I-)]
(Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
;

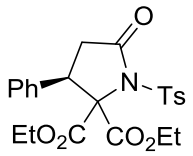
_refine_ls_abs_structure_Flack	0.02(7)
_refine_ls_extinction_coef	.
_refine_ls_extinction_method	none
_refine_ls_goodness_of_fit_ref	1.031
_refine_ls_hydrogen_treatment	constr
_refine_ls_matrix_type	full
_refine_ls_number_parameters	292
_refine_ls_number_reflns	5040
_refine_ls_number_restraints	1
_refine_ls_R_factor_all	0.0561

_refine_ls_R_factor_gt 0.0491
_refine_ls_restrained_S_all 1.031
_refine_ls_shift/su_max 0.000
_refine_ls_shift/su_mean 0.000
_refine_ls_structure_factor_coef Fsqd
_refine_ls_weighting_details
'w=1/[\s^2^(Fo^2^)+(0.0485P)^2^+0.1456P] where P=(Fo^2^+2Fc^2^)/3'
_refine_ls_weighting_scheme calc
_refine_ls_wR_factor_gt 0.1202
_refine_ls_wR_factor_ref 0.1275
_refine_special_details ?
_olex2_refinement_description

III. Characterizations of products, reference

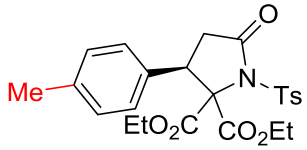
Structure of known compounds **1i**,[1] **1j**,[2] **1k**,[2] **1m**,[2] **1p**,[3] **1r**,[4] **1u- 1w**,[6] **1x**,[10] **2a**,[6] **2b**,[7] **2c**,[8] **2d**,[6] **2e**,[8] **3a**,[11] **3b**,[11] **3f**,[11] **3z**[8] and **5**[12] were confirmed by NMR spectral comparison with literature data. The compounds not reported before, ^{1}H NMR and ^{13}C NMR characterization and the corresponding spectra are provided.

a) Characterizations of Products



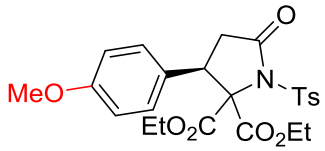
3a

Diethyl (*R*)-5-oxo-3-phenyl-1-tosylpyrrolidine-2,2-dicarboxylate (3a): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (81.7 mg, 89% yield) as a white solid: mp 123.0-125.2 ℃; $[\alpha]_D^{25}$ (c 0.561, $CHCl_3$) = -66.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.4 Hz, 2H), 7.35-7.29 (m, 5H), 7.13-7.10 (m, 2H), 4.46-4.40 (m, 2H), 4.07 (t, J = 8.4 Hz, 1H), 3.97-3.89 (m, 1H), 3.84-3.76 (m, 1H), 2.94-2.83 (m, 2H), 2.45 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.2 Hz, 3H); HRMS(ESI) calcd for $C_{23}H_{26}NO_7S$ $(M+H)^+$: 460.1424, Found: 460.1411; 94% *ee* as determined by HPLC (Chiralcel ASH, 90:10 hexanes/*i*-PrOH, 0.8 mL/min), tr (major) = 37.0 min, tr (minor) = 41.7 min.



3b

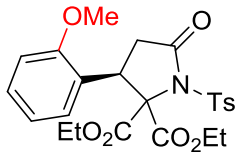
Diethyl (*R*)-5-oxo-3-(p-tolyl)-1-tosylpyrrolidine-2,2-dicarboxylate (3b): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (87.1 mg, 92% yield) as a white solid: mp 158.4-161.8 ℃; $[\alpha]_D^{25}$ (c 0.726, $CHCl_3$) = -41.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.10 (d, J = 8.0 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 4.45-4.40 (m, 2H), 4.03 (t, J = 8.4 Hz, 1H), 3.98-3.92 (m, 1H), 3.88-3.80 (m, 1H), 2.92-2.80 (m, 2H), 2.45 (s, 3H), 2.32 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H); HRMS(ESI) calcd for $C_{24}H_{28}NO_7S$ $(M+H)^+$: 474.1581, Found: 474.1570; 92% *ee* as determined by HPLC (Chiralcel ASH, 90:10 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 42.6 min, tr (minor) = 51.4 min.



3c

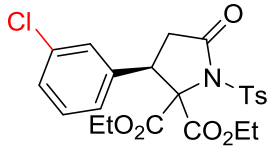
Diethyl (*R*)-3-(4-methoxyphenyl)-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3c): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (84.1 mg, 86% yield) as a white solid: mp 125.6-128.4 ℃; $[\alpha]_D^{25}$ (c 0.583,

$CHCl_3$) = -64.3; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.0 Hz, 2H), 7.34 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.8 Hz, 2H), 6.82 (d, J = 8.8 Hz, 2H), 4.46-4.38 (m, 2H), 4.03-3.94 (m, 2H), 3.90-3.82 (m, 1H), 3.78 (s, 3H), 2.91 - 2.80 (m, 2H), 2.45 (s, 3H), 1.39 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.4, 167.3, 165.2, 159.8, 145.4, 135.4, 130.1, 129.6, 129.1, 127.2, 113.9, 77.5, 63.2, 62.7, 55.4, 46.4, 36.6, 21.8, 14.1, 13.7; HRMS(ESI) calcd for $C_{24}H_{28}NO_8S$ $(M+H)^+$: 490.1530, Found: 490.1521; 89% *ee* as determined by HPLC (Chiralcel ASH, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 32.8 min, tr (minor) = 45.8 min.



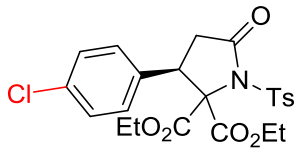
3d

Diethyl (*R*)-3-(2-methoxyphenyl)-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3d): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (96.9 mg, 99% yield) as a white solid: mp 153.1-154.2 ℃; $[\alpha]_D^{25}$ (c 0.549, $CHCl_3$) = -31.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.09 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.28-7.24 (m, 1H), 7.00 (dd, J = 7.2, 1.2 Hz, 1H), 6.86 (t, J = 7.6 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 4.45-4.34 (m, 3H), 3.98-3.90 (m, 1H), 3.73-3.65 (m, 1H), 3.55 (s, 3H), 2.89-2.76 (m, 2H), 2.44 (s, 3H), 1.39 (t, J = 6.8 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.9, 167.3, 165.3, 158.1, 145.1, 135.7, 130.2, 129.9, 129.1, 128.9, 124.5, 120.4, 110.8, 77.1, 63.0, 62.4, 54.9, 42.6, 35.8, 21.8, 14.0, 13.6; HRMS(ESI) calcd for $C_{24}H_{28}NO_8S$ $(M+H)^+$: 490.1530, Found: 490.1522; 90% *ee* as determined by HPLC (Chiralcel AD, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 18.4 min, tr (minor) = 25.3 min.



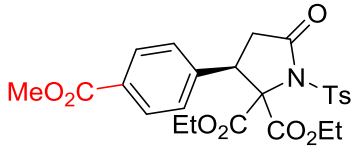
3e

Diethyl (*R*)-3-(3-chlorophenyl)-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3e): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (64.1 mg, 65% yield) as a white solid: mp 157.1-158.4 ℃; $[\alpha]_D^{25}$ (c 0.423, $CHCl_3$) = -47.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.4 Hz, 2H), 7.47-7.44 (m, 1H), 7.35 (d, J = 8.4 Hz, 2H), 7.27-7.26 (m, 1H), 7.18 (t, J = 8.0 Hz, 1H), 7.05 (d, J = 7.6 Hz, 1H), 4.44 (q, J = 7.2 Hz, 2H), 4.06-3.97 (m, 2H), 3.95-3.87 (m, 1H), 2.85 (d, J = 8.4 Hz, 2H), 2.45 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.04 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.7, 167.1, 165.0, 145.5, 137.8, 135.3, 131.8, 131.6, 130.2, 130.0, 129.1, 127.2, 122.6, 77.3, 63.5, 62.9, 46.3, 36.2, 21.9, 14.1, 13.6; HRMS(ESI) calcd for $C_{23}H_{25}ClNO_7S$ $(M+H)^+$: 494.1035, Found: 494.1027; 90% *ee* as determined by HPLC (Chiralcel ODH, 85:Q5 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 40.8 min, tr (minor) = 31.5 min.



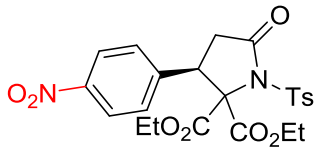
3f

Diethyl (*R*)-3-(4-chlorophenyl)-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3f): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (54.3 mg, 55% yield) as a white solid: mp 160.0-161.9 ℃; $[\alpha]_D^{25}$ (c 0.290, $CHCl_3$) = -60.3; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.06 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 7.06 (d, J = 8.4 Hz, 2H), 4.43 (q, J = 6.0 Hz, 2H), 4.05 (t, J = 8.4 Hz, 1H), 4.01-3.95 (m, 1H), 3.91-3.83 (m, 1H), 2.91-2.79 (m, 2H), 2.45 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.03 (t, J = 7.2 Hz, 3H); HRMS(ESI) calcd for $C_{23}H_{25}ClNO_7S$ $(M+H)^+$: 494.1035, Found: 494.1027; 93% *ee* as determined by HPLC (Chiralcel AD, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 24.2 min, tr (minor) = 22.6 min.



3g

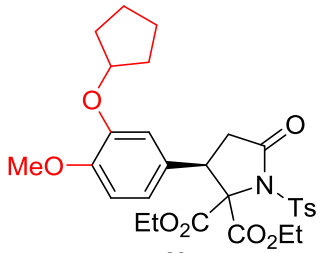
Diethyl (*R*)-3-(4-(methoxycarbonyl)phenyl)-5-oxo-1-tosylpyrrolidine-2,2-dicarbox ylate (3g): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (88.0 mg, 85% yield) as a white solid: mp 140.9-143.5 ℃; $[\alpha]_D^{25}$ (c 0.568, $CHCl_3$) = -35.2; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.07 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.4 Hz, 2H), 4.44 (q, J = 7.2 Hz, 2H), 4.14 (t, J = 8.0 Hz, 1H), 4.00-3.91 (m, 4H), 3.86-3.78 (m, 1H), 2.89 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.8, 167.1, 166.5, 165.0, 145.5, 140.8, 135.3, 130.4, 130.0, 129.8, 129.1, 128.6, 77.3, 63.5, 62.8, 52.4, 46.6, 36.3, 21.9, 14.1, 13.6; HRMS(ESI) calcd for $C_{25}H_{28}NO_9S$ $(M+H)^+$: 518.1479, Found: 532.1471; 95% *ee* as determined by HPLC (Chiralcel IA, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 47.3 min, tr (minor) = 33.1 min.



3h

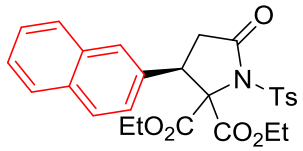
Diethyl (*R*)-3-(4-nitrophenyl)-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3h): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product (69.6 mg, 69% yield) as a white solid: mp 53.1-55.2 ℃; $[\alpha]_D^{25}$ (c 0.915, $CHCl_3$) = 30.1; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.16 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.8 Hz, 2H), 4.45 (q, J = 6.8 Hz, 2H), 4.20 (t, J = 8.0 Hz, 1H), 4.06-3.98 (m, 1H), 3.93-3.85 (m, 1H), 2.97-2.83 (m,

2H), 2.47 (s, 3H), 1.41 (t, *J* = 7.2 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.3, 167.0, 164.9, 145.7, 143.1, 135.1, 130.0, 129.6, 129.2, 123.7, 77.1, 63.8, 63.1, 46.2, 36.3, 21.9, 14.0, 13.7; HRMS(ESI) calcd for $C_{23}H_{25}N_2O_9S$ $(M+H)^+$: 505.1275, Found: 505.1266; 89% *ee* as determined by HPLC (Chiralcel AD, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 58.9 min, tr (minor) = 42.6 min.



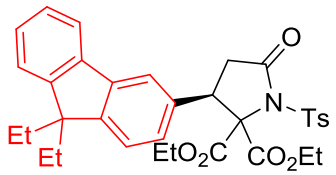
3i

Diethyl (*R*)-3-(3-(cyclopentyloxy)-4-methoxyphenyl)-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3i): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (91.7 mg, 77% yield) as a colorless oil; $[\alpha]_D^{25}$ (c 0.448, $CHCl_3$) = -83.8; ^{1}H NMR (400 MHz, CDCl3) δ = 8.08 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.4 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.55 (d, *J* = 2.0 Hz, 1H), 4.52-4.48 (m, 1H), 4.46-4.38 (m, 2H), 4.01-3.93 (m, 2H), 3.85-3.77 (m, 4H), 2.93 (dd, *J* = 17.2, 8.8 Hz, 1H), 2.78 (dd, *J* = 17.2, 7.2 Hz, 1H), 2.44 (s, 3H), 1.79-1.76 (m, 6H), 1.54 (d, *J* = 4.8 Hz, 2H), 1.40 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.5, 167.5, 165.0, 150.4, 150.1, 145.3, 142.2, 140.7, 135.6, 134.2, 130.0, 129.1, 127.6, 127.0, 126.9, 123.1, 123.0, 120.0, 119.5, 77.8, 63.3, 62.5, 56.2, 47.3, 36.8, 32.7, 32.6, 21.9, 14.1, 13.7, 8.5, 8.4; HRMS(ESI) calcd for $C_{29}H_{35}NNaO_9S$ $(M+Na)^+$: 596.1925, Found: 596.1933; 89% *ee* as determined by HPLC (Chiralcel ODH, 90:10 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 26.2 min, tr (minor) = 32.7 min.



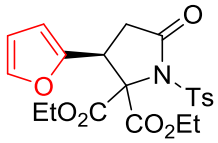
3j

Diethyl (*R*)-3-(naphthalen-2-yl)-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3j): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (85.6 mg, 84% yield) as a white solid: mp 128.9-130.6 ℃; $[\alpha]_D^{25}$ (c 0.713, $CHCl_3$) = -38.6; ^{1}H NMR (400 MHz, CDCl3) δ = 8.09 (d, *J* = 8.4 Hz, 2H), 7.82-7.72 (m, 3H), 7.58 (s, 1H), 7.51-7.48 (m, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.23-7.19 (m, 1H), 4.47 (q, *J* = 7.2 Hz, 2H), 4.26 (t, *J* = 8.4 Hz, 1H), 3.89-3.81 (m, 1H), 3.75-3.67 (m, 1H), 3.06-2.92 (m, 2H), 2.47 (s, 1H), 1.42 (t, *J* = 7.2 Hz, 3H), 0.78 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.3, 167.3, 165.2, 145.4, 135.4, 133.2, 133.1, 133.0, 130.1, 129.1, 128.4, 127.9, 127.8, 127.7, 126.8, 126.7, 125.9, 77.6, 63.4, 62.7, 47.1, 36.5, 21.9, 14.1, 13.4; HRMS(ESI) calcd for $C_{27}H_{28}NO_7S$ $(M+H)^+$: 510.1581, Found: 510.1574; 92% *ee* as determined by HPLC (Chiralcel AsH, 90:10 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 42.6 min, tr (minor) = 51.4 min.



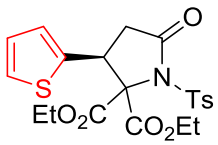
3k

Diethyl (*R*)-3-(9,9-diethyl-9H-fluoren-3-yl)-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3k): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (112.2 mg, 93% yield) as a white solid: mp 143.5-145.9 ℃; $[\alpha]_D^{25}$ (c 0.768, $CHCl_3$) = -48.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.10 (d, J = 8.4 Hz, 2H), 7.69-7.66 (m, 1H), 7.61 (d, J = 8.0 Hz, 1H), 7.36 -7.31 (m, 5H), 7.07 (dd, J = 8.0, 1.6 Hz, 1H), 7.02 (s, 1H), 4.50-4.40 (m, 2H), 4.16 (t, J = 8.4 Hz, 1H), 4.03-3.95 (m, 1H), 3.82-3.74 (m, 1H), 2.95 (d, J = 8.4 Hz, 2H), 2.46 (s, 3H), 2.00-1.86 (m, 4H), 1.41 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H), 0.27 (q, J = 7.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.5, 167.5, 165.0, 150.4, 150.1, 145.3, 142.2, 140.7, 135.6, 134.2, 130.0, 129.1, 127.6, 127.0, 126.9, 123.1, 123.0, 120.0, 119.5, 77.8, 63.3, 62.5, 56.2, 47.3, 36.8, 32.7, 32.6, 21.9, 14.1, 13.7, 8.6, 8.5; HRMS(ESI) calcd for $C_{34}H_{38}NO_7S$ $(M+H)^+$: 604.2363, Found: 604.2360; 89% *ee* as determined by HPLC (Chiralcel AD, 90:10 hexanes/*i*-PrOH, 0.8 mL/min), tr (major) = 23.0 min, tr (minor) = 25.3 min.



3l

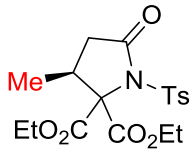
Diethyl (*S*)-3-(furan-2-yl)-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3l): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (81.8 mg, 91% yield) as a white solid: mp 108.3-109.4 ℃; $[\alpha]_D^{25}$ (c 0.414, $CHCl_3$) = -96.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, J = 8.4 Hz, 2H), 7.36-7.35 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 6.33 (dd, J = 3.2, 2.0 Hz, 1H), 6.19 (d, J = 3.2 Hz, 1H), 4.43 (q, J = 7.2 Hz, 2H), 4.19 (t, J = 9.2 Hz, 1H), 4.22-4.10 (m, 1H), 4.06-3.98 (m, 1H), 2.92 (dd, J = 17.2, 10.0 Hz, 1H), 2.76 (dd, J = 16.8, 8.4 Hz, 1H), 2.44 (s, 3H), 1.40 (t, J = 7.2 Hz, 3H), 1.14 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 166.8, 165.1, 148.6, 145.4, 143.0, 135.3, 130.0, 129.1, 110.8, 109.2, 76.2, 63.4, 63.0, 41.3, 34.3, 21.8, 14.0, 13.7; HRMS(ESI) calcd for $C_{21}H_{24}NO_8S$ $(M+H)^+$: 450.1217, Found: 450.1210; 87% *ee* as determined by HPLC (Chiralcel ASH, 90:10 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 36.6 min, tr (minor) = 42.5 min.



3m

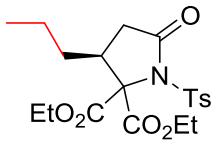
Diethyl (*S*)-5-oxo-3-(thiophen-2-yl)-1-tosylpyrrolidine-2,2-dicarboxylate (3m): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave

the product (77.2 mg, 83% yield) as a white solid: mp 113.6-115.9 ℃; $[\alpha]_D^{25}$ (c 0.493, $CHCl_3$) = -81.2; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.26-7.27 (m, 1H), 6.92-6.98 (m, 2H), 4.41-4.48 (m, 2H), 4.30 (t, J = 9.2 Hz, 1H), 3.94-4.11 (m, 2H), 2.98 (dd, J = 16.8, 10.4 Hz, 1H), 2.89 (dd, J = 16.8, 8.8 Hz, 1H), 2.44 (s, 3H), 1.41 (t, J = 7.2 Hz, 3H), 1.07 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 171.2, 167.0, 165.1, 145.5, 137.4, 135.2, 130.0, 129.0, 127.3, 127.1, 126.0, 77.0, 63.4, 62.9, 42.5, 37.6, 21.9, 14.1, 13.7; HRMS(ESI) calcd for $C_{21}H_{24}NO_7S_2(M+H)^+$: 466.0989, Found: 466.0979; 88% *ee* as determined by HPLC (Chiralcel ASH, 90:10 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 36.2 min, tr (minor) = 41.9 min.



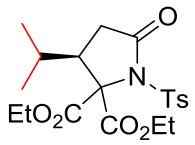
3n

Diethyl (*S*)-3-methyl-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3n): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (56.4 mg, 71% yield) as a white solid: mp 95.5-97.3 ℃; $[\alpha]_D^{25}$ (c 0.379, $CHCl_3$) = -343.0; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, J = 7.6 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 4.40-4.30 (m, 4H), 2.78-2.69 (m, 1H), 2.55 (dd, J = 16.8, 8.0 Hz, 1H), 2.42 (s, 3H), 2.32 (dd, J = 16.8, 10.4 Hz, 1H), 1.37-1.32 (m, 6H), 1.19 (d, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.5, 167.4, 165.8, 145.3, 135.4, 129.9, 129.0, 76.2, 62.9, 62.8, 38.2, 36.9, 21.8, 15.7, 14.2; HRMS(ESI) calcd for $C_{18}H_{24}NO_7S$ $(M+H)^+$: 398.1268, Found: 398.1259; 98% *ee* as determined by HPLC (Chiralcel AD, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 12.1 min, tr (minor) = 14.6 min.



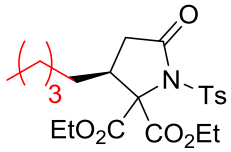
3o

Diethyl (*S*)-5-oxo-3-propyl-1-tosylpyrrolidine-2,2-dicarboxylate (3o): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (62.9 mg, 74% yield) as a white solid: mp 136.0-137.5 ℃; $[\alpha]_D^{25}$ (c 0.390, $CHCl_3$) = -89.7; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.41-4.33 (m, 4H), 2.63-2.52 (m, 2H), 2.43 (s, 3H), 2.33 (td, J = 14.4, 4.4 Hz, 1H), 1.85-1.80 (m, 1H), 1.36 (td, J = 7.2, 2.8 Hz, 7H), 1.29-1.20 (m, 2H), 0.90 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.4, 167.4, 165.9, 145.3, 135.4, 129.9, 129.0, 75.8, 62.9, 62.8, 42.0, 36.5, 32.5, 21.8, 20.8, 14.1, 14.0, 13.9; HRMS(ESI) calcd for $C_{20}H_{27}NNaO_7S$ $(M+Na)^+$: 448.1400, Found: 448.1454; 99% *ee* as determined by HPLC (Chiralcel ASH, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 16.7 min, tr (minor) = 19.5 min.



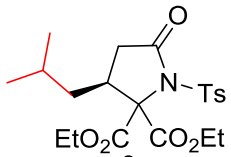
3p

Diethyl (*R*)-3-isopropyl-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3p): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (49.3 mg, 58% yield) as a white solid: mp 79.2-80.4 ℃; $[\alpha]_D^{25}$ (c 0.346, $CHCl_3$) = -28.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.43-4.27 (m, 4H), 2.61-2.54 (m, 1H), 2.48 (dd, J = 16.8, 7.6 Hz, 1H), 2.41 (s, 3H), 2.23 (dd, J = 16.8, 12.4 Hz, 1H), 1.77-1.70 (m, 1H), 1.34 (td, J = 11.2, 7.2 Hz, 6H), 1.02 (d, J = 6.4 Hz, 3H), 0.83 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.1, 167.8, 165.6, 145.3, 135.4, 129.6, 129.1, 75.9, 63.2, 62.9, 50.8, 35.3, 29.5, 21.8, 21.3, 21.1, 14.0, 13.9; HRMS(ESI) calcd for $C_{20}H_{28}NO_7S$ $(M+H)^+$: 426.1581, Found: 426.1589; 98% *ee* as determined by HPLC (Chiralcel AD, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 12.7 min, tr (minor) = 11.5 min.



3q

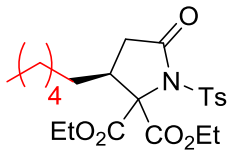
Diethyl (*S*)-5-oxo-3-pentyl-1-tosylpyrrolidine-2,2-dicarboxylate (3q): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (77.0 mg, 85% yield) as a white solid: mp 71.6-74.6 ℃; $[\alpha]_D^{25}$ (c 0.142, $CHCl_3$) = -228.9; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 4.41-4.32 (m, 4H), 2.59-2.52 (m, 2H), 2.43 (s, 3H), 2.33 (dd, J = 19.2, 13.6 Hz, 1H), 1.85 (s, 1H), 1.35 (td, J = 7.2, 1.6 Hz, 6H), 1.28-1.23 (m, 7H), 0.86 (t, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.4, 167.5, 165.9, 145.3, 135.4, 129.9, 129.0, 75.8, 62.9, 62.8, 42.2, 36.5, 31.5, 30.3, 27.2, 22.4, 21.8, 14.2, 14.1, 14.0; HRMS(ESI) calcd for $C_{22}H_{31}NNaO_7S$ $(M+Na)^+$: 476.1713, Found: 476.1702; 96% *ee* as determined by HPLC (Chiralcel AD, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 11.1 min, tr (minor) = 12.5 min.



3r

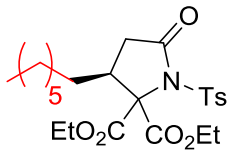
Diethyl (*S*)-3-isobutyl-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3r): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (61.5 mg, 70% yield) as a white solid: mp 79.2-80.4 ℃; $[\alpha]_D^{25}$ (c 0.457, $CHCl_3$) = -60.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 4.35 (q, J = 7.2 Hz, 4H), 2.68-2.59 (m, 1H), 2.53 (dd, J = 16.8, 8.4 Hz, 1H), 2.41 (s, 3H), 2.32 (dd, J = 16.8, 11.6 Hz, 1H), 1.67-1.60 (m, 1H), 1.54-1.45 (m, 1H), 1.34 (td, J = 7.2, 4.0 Hz, 6H), 1.24-1.17 (m, 1H), 0.89 (d, J = 6.4 Hz, 3H), 0.81 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.5, 167.4,

165.9, 145.3, 135.4, 129.9, 129.0, 75.7, 62.8, 40.1, 39.3, 36.6, 26.0, 23.6, 21.8, 21.3, 14.1, 14.0; HRMS(ESI) calcd for $C_{21}H_{30}NO_7S$ $(M+H)^+$: 440.1737, Found: 440.1729; 95% *ee* as determined by HPLC (Chiralcel ODH, 90:10 hexanes/*i*-PrOH, 0.8 mL/min), tr (major) = 14.8 min, tr (minor) = 18.0 min.



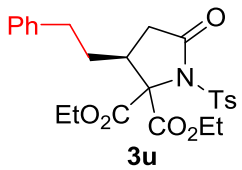
3s

Diethyl (*S*)-3-hexyl-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3s): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (78.5 mg, 84% yield) as a colorless oil; $[\alpha]_D^{25}$ (c 0.579, $CHCl_3$) = -64.8; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, *J* = 8.4 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 4.37-4.29 (m, 4H), 2.56-2.49 (m, 2H), 2.39 (s, 3H), 2.34-2.25 (m, 1H), 1.85-1.82 (m, 1H), 1.32 (td, *J* = 6.8, 1.2 Hz, 6H), 1.25-1.20 (m, 9H), 0.83 (td, *J* = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.5, 167.4, 165.9, 145.3, 135.4, 129.9, 129.0, 75.8, 62.9, 62.8, 42.1, 36.5, 31.6, 30.4, 29.0, 27.5, 22.6, 21.8, 14.2, 14.1, 14.0; HRMS(ESI) calcd for $C_{23}H_{34}NO_7S$ $(M+H)^+$: 468.2050, Found: 468.2055; 93% *ee* as determined by HPLC (Chiralcel IA, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 9.9 min, tr (minor) = 10.8 min.



3t

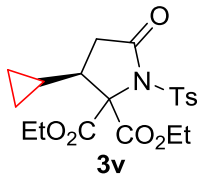
Diethyl (*S*)-3-heptyl-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3t): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (78.9 mg, 82% yield) as a colorless oil; $[\alpha]_D^{25}$ (c 0.628, $CHCl_3$) = -63.7; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.02 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 4.41-4.27 (m, 4H), 2.57-5.51 (m, 2H), 2.41 (s, 3H), 2.31 (dd, *J* = 19.6, 14.0 Hz, 1H), 1.86-1.73 (m, 1H), 1.35-1.31 (m, 6H), 1.27-1.22 (m, 11H), 0.85 (t, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.4, 167.4, 165.8, 145.3, 135.4, 129.9, 129.0, 75.8, 62.9, 62.8, 42.2, 36.5, 31.9, 31.8, 31.7, 30.4, 29.2, 29.1, 27.5, 22.6, 21.8, 14.1, 14.0; HRMS(ESI) calcd for $C_{24}H_{36}NO_7S$ $(M+H)^+$: 482.2207, Found: 482.2210; 95% *ee* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 11.0 min, tr (minor) = 12.6 min.



3u

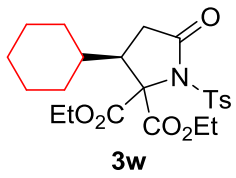
Diethyl (*S*)-5-oxo-3-phenethyl-1-tosylpyrrolidine-2,2-dicarboxylate (3u): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (76.0 mg, 78% yield) as a colorless oil; $[\alpha]_D^{25}$ (c 0.542, $CHCl_3$) = -83.0; ^{1}H

NMR (400 MHz, $CDCl_3$) δ = 8.03 (d, J = 8.4 Hz, 2H), 7.31 (d, J = 8.0 Hz, 2H), 7.27-7.24 (m, 2H), 7.20-7.16 (m, 1H), 7.11-7.09 (m, 2H), 4.40-4.18 (m, 4H), 2.76-2.69 (m, 1H), 2.58-2.48 (m, 3H), 2.44-2.34 (m, 4H), 2.29-2.20 (m, 1H), 1.64-1.55 (m, 1H), 1.35 (t, J = 7.2 Hz, 3H), 1.25 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.2, 167.2, 165.9, 145.3, 140.0, 135.4, 129.9, 129.0, 128.7, 128.3, 126.6, 75.6, 63.0, 62.9, 40.9, 36.3, 33.4, 31.8, 21.8, 14.2, 14.0; HRMS(ESI) calcd for $C_{25}H_{30}NO_7S$ $(M+H)^+$: 488.1737, Found: 488.1746; 99% *ee* as deterined by HPLC (Chiralcel ID, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 48.2 min, tr (minor) = 36.3 min.



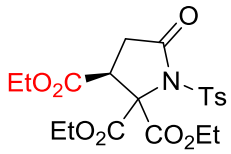
3v

Diethyl (*R*)-3-cyclopropyl-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3v): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (66.9 mg, 79% yield) as a white solid: mp 132.1-134.6 ℃; $[\alpha]_D^{25}$ (c 0.503, $CHCl_3$) = -84.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 4.43-4.27 (m, 4H), 2.57 (dd, J = 17.2, 8.4 Hz. 1H), 2.41-2.35 (m, 4H), 2.18 (dd, J = 17.6, 8.4 Hz, 1H), 1.35 (td, J = 7.2, 1.6 Hz, 6H), 0.92-0.84 (m, 1H), 0.59-0.49 (m, 2H), 0.32-0.26 (m, 1H), 0.14-0.08 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.2, 167.6, 165.6, 145.3, 135.6, 130.0, 129.0, 76.4, 63.1, 62.9, 46.9, 36.4, 21.8, 14.1, 14.0, 12.2, 4.8, 3.4; HRMS(ESI) calcd for $C_{20}H_{26}NO_7S$ $(M+H)^+$: 424.1424, Found: 424.1416; 96% *ee* as determined by HPLC (Chiralcel IB, 90:10 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 16.6 min, tr (minor) = 19.9 min.



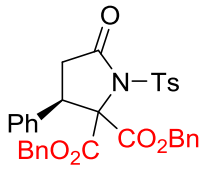
3w

Diethyl (*R*)-3-cyclohexyl-5-oxo-1-tosylpyrrolidine-2,2-dicarboxylate (3w): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (67.9 mg, 73% yield) as a white solid: mp 99.8-103.6 ℃; $[\alpha]_D^{25}$ (c 0.523, $CHCl_3$) = -52.6; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.40-4.30 (m, 4H), 2.68-2.60 (m, 1H), 2.46 (dd, J = 16.8, 7.6 Hz, 1H), 2.41 (s, 3H), 2.21 (dd, J = 16.8, 12.8 Hz, 1H), 2.08 (d, J = 12.4 Hz, 1H), 1.68-1.41 (m, 5H), 1.34 (q, J = 6.8 Hz, 6H), 1.20-1.06 (m, 3H), 0.84 (qd, J = 12.0, 2.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.1, 167.8, 165.7, 145.3, 135.4, 129.6, 129.1, 75.8, 63.2, 62.8, 49.7, 38.7, 34.9, 31.3, 31.0, 26.0, 25.9, 25.7, 21.8, 14.1, 13.9; HRMS(ESI) calcd for $C_{23}H_{32}NO_7S$ $(M+H)^+$: 466.1894, Found: 466.1985; 99% *ee* as determined by HPLC (Chiralcel IA, 90:10 hexanes/*i*-PrOH, 0.8 mL/min), tr (major) = 22.5 min, tr (minor) = 21.5 min.



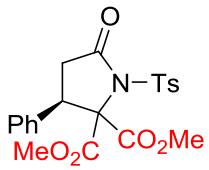
3x

Triethyl (*S*)-5-oxo-1-tosylpyrrolidine-2,2,3-tricarboxylate (3x): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:10) gave the product (57.4 mg, 63% yield) as a white solid: mp 177.2-179.3 ℃; $[\alpha]_D^{25}$ (c 0.243, $CHCl_3$) = -123.5; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.00 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.47-4.29 (m, 4H), 4.17 (q, J = 7.2 Hz, 2H), 3.69 (dd, J = 11.2, 8.0 Hz, 1H), 2.79 (dd, J = 17.2, 10.8 Hz, 1H), 2.53 (dd, J = 17.6, 8.0 Hz, 1H), 2.41 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 170.2, 167.8, 166.6, 165.5, 145.5, 135.3, 129.8, 129.3, 74.9, 63.8, 63.6, 62.0, 47.1, 32.6, 21.8, 14.0, 13.9, 13.9; HRMS(ESI) calcd for $C_{20}H_{25}NNaO_9S$ $(M+Na)^+$: 478.1142, Found: 478.1134; 99% *ee* as determined by HPLC (Chiralcel ODH, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 14.3 min, tr (minor) = 17.9 min.



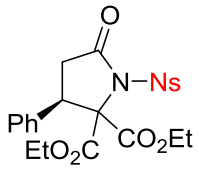
3y

Dibenzyl (*R*)-5-oxo-3-phenyl-1-tosylpyrrolidine-2,2-dicarboxylate (3y): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product (72.3 mg, 62% yield) as a white solid: mp 104.8-106.6 ℃; $[\alpha]_D^{25}$ (c 0.258, $CHCl_3$) = -94.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (d, J = 8.0 Hz, 2H), 7.35-7.19 (m, 11H), 7.12 (t, J = 7.2 Hz, 2H), 7.02 (d, J = 6.4 Hz, 2H), 6.87 (d, J = 7.6 Hz, 2H), 5.36 (dd, J = 28.8, 12.0 Hz, 2H), 4.93 (d, J = 12.4 Hz, 1H), 4.71 (d, J = 12.4 Hz, 1H), 3.97 (t, J = 8.8 Hz, 1H), 2.88 (dd, J = 17.2, 9.6 Hz, 1H), 2.77 (dd, J = 17.2, 8.8 Hz, 1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.1, 167.1, 165.2, 145.5, 135.1, 134.7, 134.6, 134.4, 130.1, 129.9, 129.1, 128.9, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.4, 68.9, 68.4, 58.8, 47.2, 36.2, 21.9; HRMS(ESI) calcd for $C_{33}H_{29}NNaO_7S$ $(M+Na)^+$: 606.1557, Found: 606.1548; 91% *ee* as determined by HPLC (Chiralcel ASH, 85:15 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 32.4 min, tr (minor) = 45.8 min.



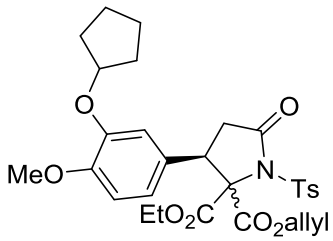
3z

Dimethyl (*R*)-5-oxo-3-phenyl-1-tosylpyrrolidine-2,2-dicarboxylate (3z): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product (73.3 mg, 85% yield) as a white solid: mp 185.4-186.9 ℃; $[\alpha]_D^{25}$ (c 0.183, $CHCl_3$) = -73.2; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H),7.31-729 (m, 3H), 7.09-7.07 (m, 2H), 4.03 (t, J = 8.8 Hz, 1H), 3.95 (s, 3H), 3.40 (s, 3H), 2.95-2.84 (m, 2H), 2.44 (s, 3H); HRMS(ESI) calcd for $C_{21}H_{22}NO_7S$ $(M+H)^+$: 432.1111, Found: 432.1097; 90% *ee* as determined by HPLC (Chiralcel AD, 70:30 hexanes/*i*-PrOH, 0.5 mL/min), tr (major) = 14.4 min, tr (minor) = 34.0 min.



3aa

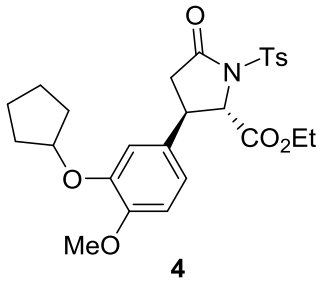
Diethyl (*R*)-1-((4-nitrophenyl)sulfonyl)-5-oxo-3-phenylpyrrolidine-2,2-dicarboxylate (3aa): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (87.3 mg, 89% yield) as a white solid: mp 166.7-169.8 ℃; $[\alpha]_D^{25}$ (c 0.284, $CHCl_3$) = -114.4; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.43-8.36 (m, 4H), 7.33-7.27 (m, 3H), 7.10-7.07 (m, 2H), 4.44 (q, J = 7.2 Hz, 2H), 4.08 (t, J = 8.4 Hz, 1H), 3.98-3.90 (m, 1H), 3.83-3.75 (m, 1H), 2.97-2.85 (m, 2H), 1.40 (t, J = 6.8 Hz, 3H), 0.963 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.4, 167.2, 165.1, 150.9, 143.7, 135.4, 131.6, 129.0, 128.8, 128.4, 123.6, 78.0, 63.7, 63.1, 46.8, 36.5, 14.1, 13.6; HRMS(ESI) calcd for $C_{22}H_{23}N_2O_9S$ $(M+H)^+$: 491.1124, Found: 491.1131; 94% *ee* as determined by HPLC (Chiralcel ADH, 90:10 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 57.5 min, tr (minor) = 45.9 min.



3ab

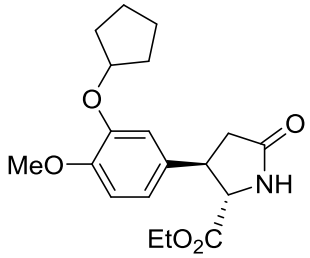
Ethyl (3*R*)-2-(but-3-enoyl)-3-(3-(cyclopentyloxy)-4-methoxyphenyl)-5-oxo-1-tosylpyrrolidine-2-carboxylate (3ab): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:5) gave the product (93.6 mg, 80% yield) as a colorless oil; $[\alpha]_D^{25}$ (c 0.167, $CHCl_3$) = -22.1; ^1H NMR (400 MHz, $CDCl_3$) δ = 8.05 (d, J = 2.0 Hz, 2H), 7.30 (d, J = 2.0 Hz, 2H), 6.71 (d, J = 5.6 Hz, 1H), 6.63-6.59 (m, 1H), 6.51 (d, J = 2.4 Hz, 1H), 5.62-5.52 (m, 1H), 5.33-5.29 (m, 1H), 5.19-5.11 (m, 1H), 4.86-4.82 (m, 1H), 4.46-4.40 (m, 2H), 4.01-3.97 (m, 2H), 3.86-3.81 (m, 1H), 3.79 (s, 3H), 2.97-2.87 (m, 1H), 2.82-2.74 (m, 1H), 2.43 (s, 3H), 1.79-1.74 (m, 6H), 1.55-1.51 (m, 2H), 1.39 (t, J = 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.6, 167.2, 165.0, 150.2, 147.7, 145.3, 135.5, 130.9, 130.1, 129.1, 128.0, 120.7, 118.9, 114.5, 111.4, 80.5, 77.7, 67.6, 67.1, 63.4, 62.7, 56.1, 46.6, 37.0, 32.9, 24.3, 24.2, 21.8, 14.1, 13.7; HRMS(ESI) calcd for $C_{30}H_{36}NO_9S$ $(M+H)^+$: 586.2105, Found: 586.2115; 89% *ee* as determined by

HPLC (Chiralcel ASH, 98:2 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 62.2 min, tr (minor) = 5.8 min.



4

Ethyl (2*S*, 3*R*)-3-(3-(cyclopentyloxy)-4-methoxyphenyl)-5-oxo-1-tosylpyrrolidine-2-carboxylate (4): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:3) gave the product (48.2 mg, 60% yield) as a colorless oil; $[\alpha]_D^{25}$ (c 0.173, $CHCl_3$) = +63.4; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95-7.91 (m, 2H), 7.33-7.30 (m, 2H), 6.78-6.74 (m, 1H), 6.65-6.62 (m, 2H), 4.77 (q, *J* = 2.8 Hz, 1H), 4.66-4.62 (m, 1H), 4.35-4.21 (m, 2H), 3.82 (t, *J* = 2.8 Hz, 3H), 3.45 (dt, *J* = 8.8, 3.2 Hz, 1H), 3.01-2.93 (m, 1H), 2.56-2.49 (m, 1H), 2.44 (t, *J* = 2.8 Hz, 3H), 1.89-1.80 (m, 6H), 1.60-1.56 (m, 2H), 1.51 (dt, *J* = 6.8, 3.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ = 172.2, 170.3, 149.7, 148.3, 145.5, 134.9, 133.3, 129.5, 129.1, 118.4, 112.3, 112.2, 80.5, 67.2, 62.4, 56.2, 41.2, 38.6, 32.9, 32.8, 24.2, 21.9, 14.2; HRMS(ESI) calcd for $C_{26}H_{32}NO_7S$ $(M+H)^+$: 502.1894, Found: 502.1895; 90% *ee* as determined by HPLC (Chiralcel ODH, 80:20 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 12.5 min, tr (minor) = 15.9 min.



5

Ethyl (2*S*, 3*R*)-3-(3-(cyclopentyloxy)-4-methoxyphenyl)-5-oxopyrrolidine-2-carboxylate (5): Flash column chromatography on silica gel (ethyl acetate/petroleum ether, 1:1) gave the product (25.0 mg, 75% yield) as a colorless oil; $[\alpha]_D^{25}$ (c 0.150, $CHCl_3$) = +74.0; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.83-6.77 (m, 3H), 6.51 (br, 1H), 4.77-4.73 (m, 1H), 4.24-4.14 (m, 3H), 3.82 (s, 3H), 3.65-3.59 (m, 1H), 2.83 (dd, *J* = 17.6, 9.6 Hz, 1H), 2.49 (dd, *J* = 17.6, 6.8 Hz, 1H), 1.93-1.79 (m, 6H), 1.63-1.55 (m, 2H), 1.24 (t, *J* = 7.2 Hz, 3H); HRMS(ESI) calcd for $C_{19}H_{26}NO_5$ $(M+H)^+$: 348.1805, Found: 348.1813; 89% *ee* as determined by HPLC (Chiralcel ODH,80:20 hexanes/*i*-PrOH, 1.0 mL/min), tr (major) = 9.2 min, tr (minor) = 11.0 min.

b) References

(1) L. D. Hawkins, Preparation of Trisubstituted Benzene Compounds for Treating Congestive Heart Failure, US 4971959 [A] 1990.

(2) D. H. Liu, Z. L. Hu, Y. X. Zhang, Z. Q. Fu and Huang, W, Access to Enantioenriched Spiro-ϵ-Lactam Oxindoles by an N-Heterocyclic Carbene-Catalyzed [4+3] Annulation of Flexible Oxotryptamines with Enals, *Chem. Eur. J.*, 2019, **25**, 11223.

(3) J. Sabbatani and N. Maulide, Temporary Generation of a Cyclopropyl Oxocarbenium Ion Enables Highly Diastereoselective Donor-Acceptor Cyclopropane Cycloaddition, *Angew. Chem. Int. Ed.*, 2016, **55**, 6780.

(4) C. Guo, M. Saifuddin, T. Saravanan, M. Sharifi and G. J. Poelarends, Biocatalytic Asymmetric Michael Additions of Nitromethane to α, β-Unsaturated Aldehydes *via* Enzyme-bound Iminium Ion Intermediates, *ACS Catal*., 2019, **9**, 4369.

(5) A. Bouisseau, M. Gao and M. C. Willis, Traceless Rhodium-Catalyzed Hydroacylation using Alkyl Aldehydes: the Enantioselective Synthesis of β-aryl Ketones, *Chem. Eur. J.*, 2016, **22**, 15624.

(6) C. B. Miao, A. Q. Zheng, L. J. Zhou, X. Lyu and H. T. Yang, Copper-catalyzed Annulation of Oxime Acetates with α-amino Acid Ester Derivatives: Synthesis of 3-sulfonamido/imino 4-pyrrolin-2-ones, *Org. Lett.*, 2020, **22**, 3381.

(7) T. M. U. Ton, F. Himawan, J. W. W. Chang and P. W. H. Chan, Copper (II) Triflate Catalyzed Amination of 1,3-dicarbonyl Compounds, *Chem. Eur. J.*, 2012, **18**, 12020.

(8) S. Vellalath, K. N. Van and D. Romo, Direct Catalytic Asymmetric Synthesis of n-Heterocycles from Commodity Acid Chlorides by Employing α, β-unsaturated Acylammonium Salts, *Angew. Chem. Int. Ed.*, 2013, **52**, 13688.

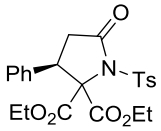
(9) T. N. Nguyen and J. A. May, Branched Amine Synthesis via Aziridine or Azetidine Opening with Organotrifluoroborates by Cooperative Brønsted/Lewis Acid Catalysis: an Acid-dependent Divergent Mechanism, *Org. Lett.*, 2018, **20**, 3618.

(10) F. Yin, A. Garifullina and F. Tanaka, Synthesis of Pyrrolidine-3-carboxylic Acid Derivatives via Asymmetric Michael Addition Reactions of Carboxylate-Substituted Enones, *Org. Biomol. Chem*., 2017, **15**, 6089.

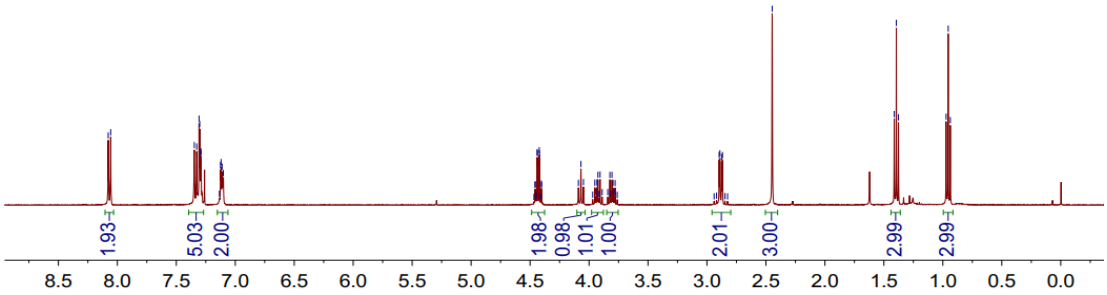
(11) J. J. Cheng, P. Chen, J. H. Zheng, C. J. Pan and Y. F. Yuan, Method for N-heterocyclic Carbene-Catalyzed Synthesis of Polysubstituted Pyrrolidone Compounds, CN 106916093[A], 2017.

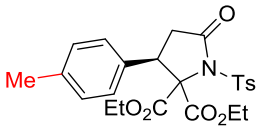
(12) Z. Q. Fu, J. F. Xu, T. S. Zhu, W. W. Yi Leong and Y. R. Chi, β-Carbon Activation of Saturated Carboxylic Esters through N-heterocyclic Carbene Organocatalysis, *Nature Chem.*, 2013, **5**, 835.

(5) Ⅳ: ^{1}H, ^{13}C NMR and HPLC dates of products

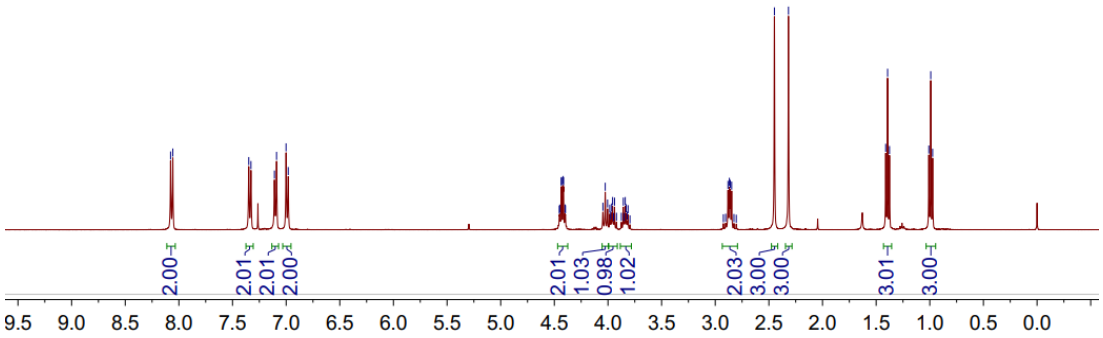


3a

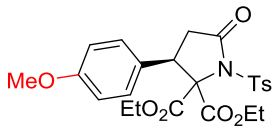




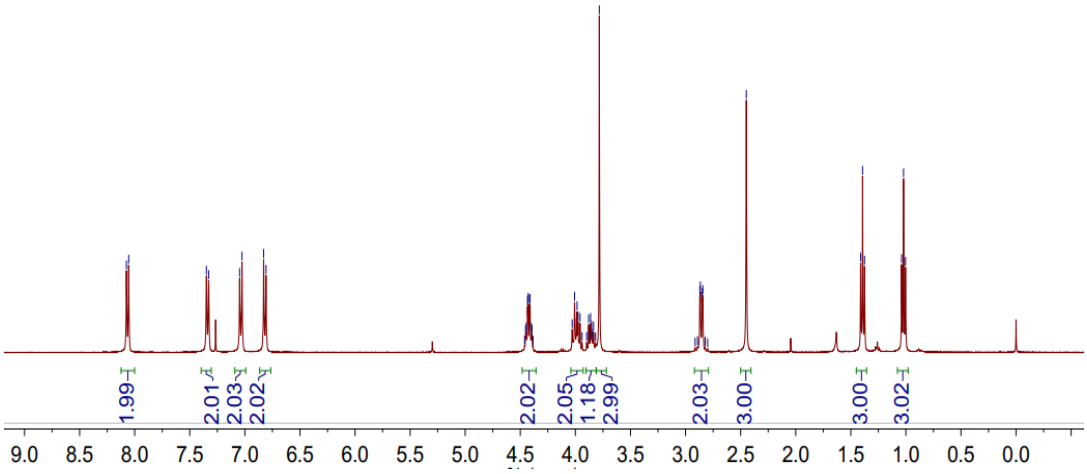
3b



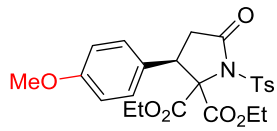

8.075
8.055
7.349
7.329
7.048
7.026
6.830
6.808
4.461
4.452
4.447
4.434
4.429
4.417
4.411
4.399
4.394
4.384
4.029
4.007
3.985
3.975
3.958
3.940
3.898
3.880
3.871
3.862
3.853
3.844
3.835
3.817
3.783
2.913
2.891
2.870
2.865
2.849
2.843
2.822
2.449
1.411
1.393
1.375
1.039
1.021
1.003


MeO
N
Ts
O
EtO2C
CO2Et

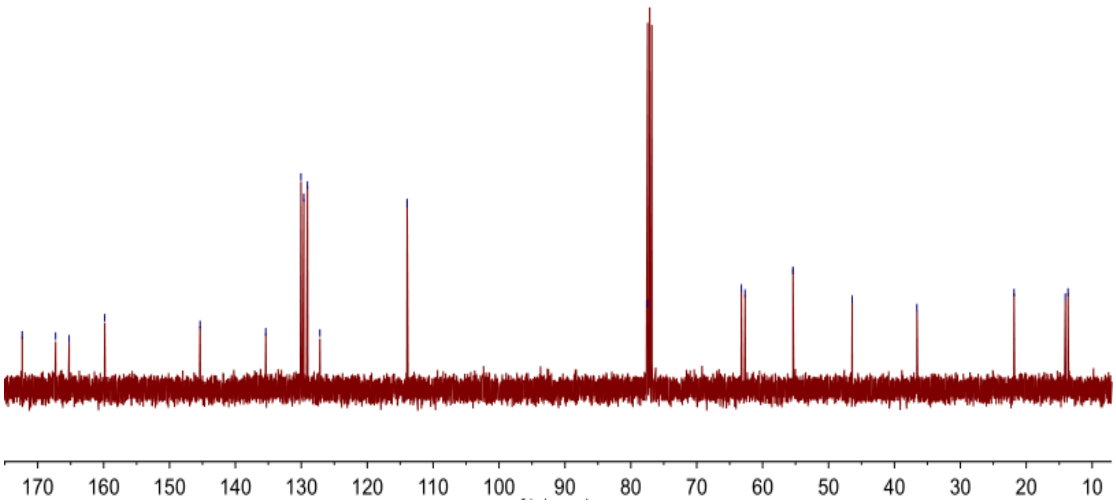
3c

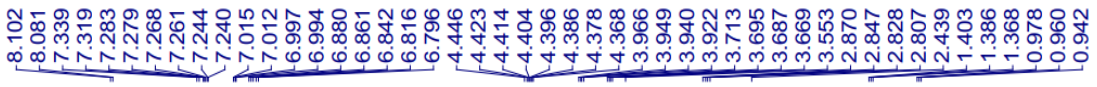

1.99
2.01
2.03
2.02
2.02
2.05
1.18
2.99
2.03
3.00
3.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

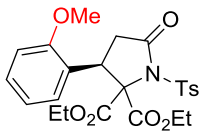

172.364
167.293
165.240
159.835
145.373
135.396
130.054
129.633
129.081
127.182
113.943
77.495
63.228
62.664
55.395
46.414
36.583
21.853
14.077
13.658


MeO
N
Ts
O
EtO2C
CO2Et

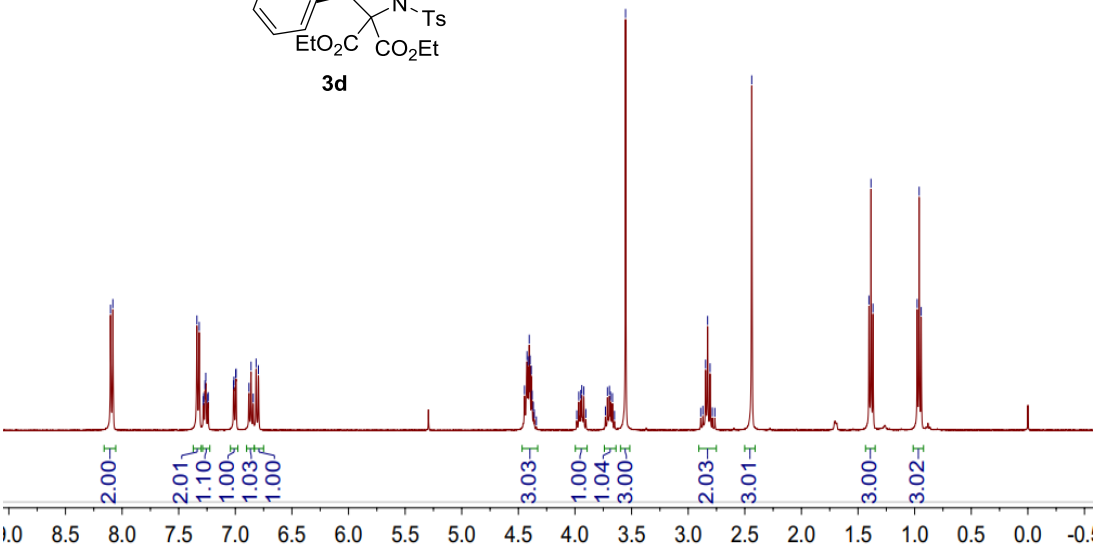
3c


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

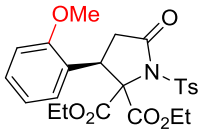

8.102
8.081
7.339
7.319
7.283
7.279
7.268
7.261
7.244
7.240
7.015
7.012
6.997
6.994
6.880
6.861
6.842
6.816
6.796
4.446
4.423
4.414
4.404
4.396
4.386
4.378
4.368
3.966
3.949
3.940
3.922
3.713
3.695
3.687
3.669
3.553
2.870
2.847
2.828
2.807
2.439
1.403
1.386
1.368
0.978
0.960
0.942


OMe
O
N
Ts
EtO2C
CO2Et

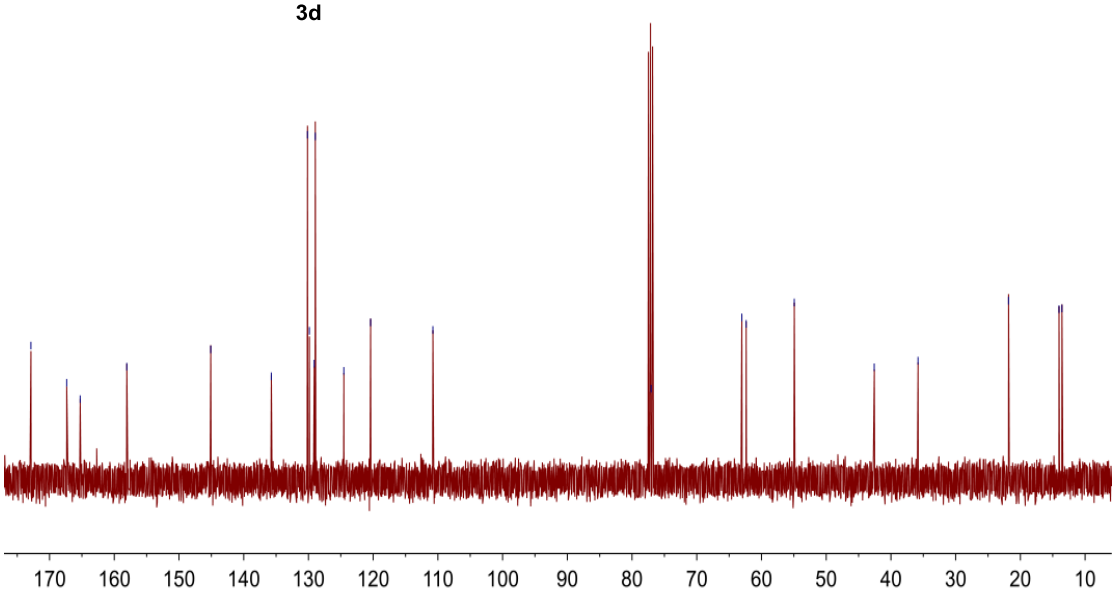
3d


2.00
2.01
1.10
1.00
1.03
1.00
3.03
1.00
1.04
3.00
2.03
3.01
3.00
3.02
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

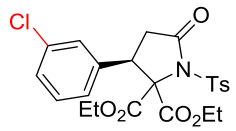

172.878
167.348
165.265
158.063
145.100
135.738
130.151
129.851
129.112
128.946
124.530
120.395
110.774
77.054
63.047
62.372
54.932
42.577
35.811
21.829
14.028
13.583


OMe
O
N
Ts
EtO2C
CO2Et

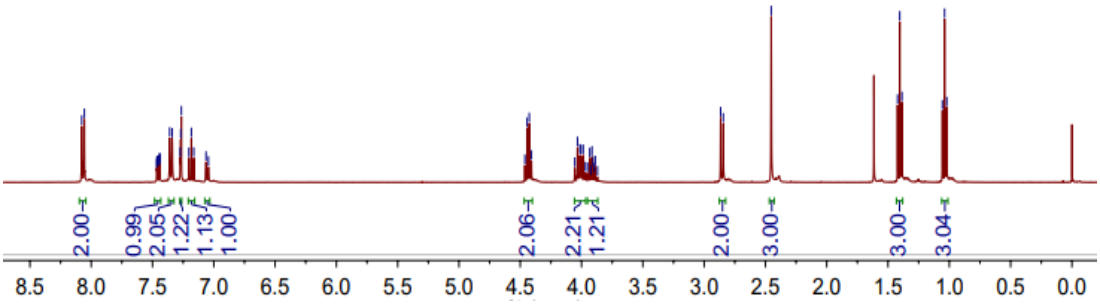
3d


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

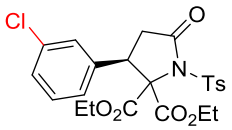

8.077
8.056
7.442
7.360
7.339
7.274
7.269
7.265
7.203
7.183
7.163
7.063
4.462
4.444
4.427
4.409
4.055
4.033
4.013
4.005
3.987
3.933
3.915
3.906
2.844
2.453
1.422
1.404
1.387
1.057
1.039
1.021


Cl
O
N
Ts
EtO2C
CO2Et

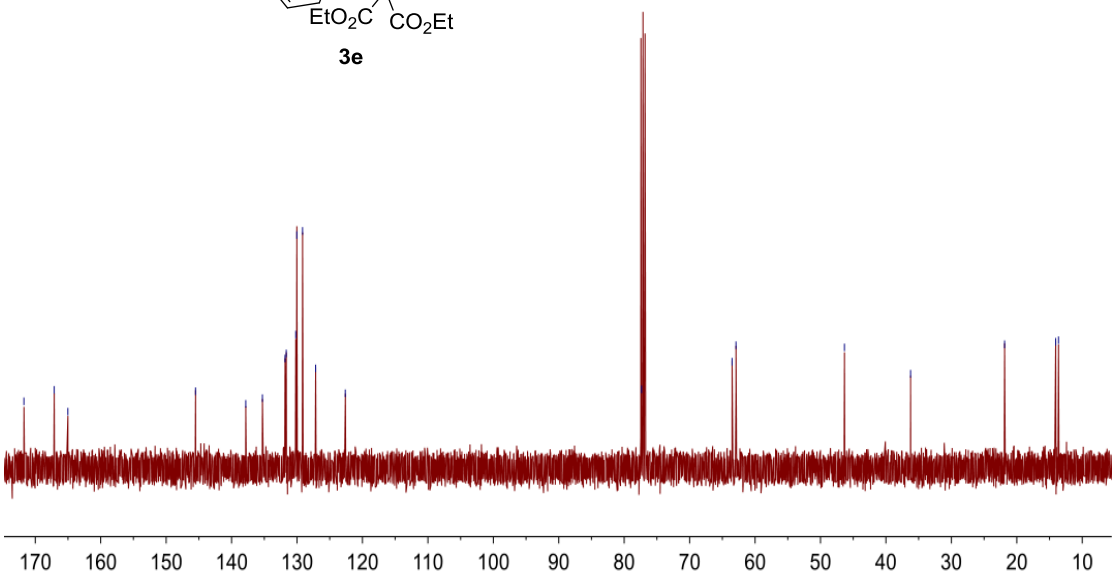
3e

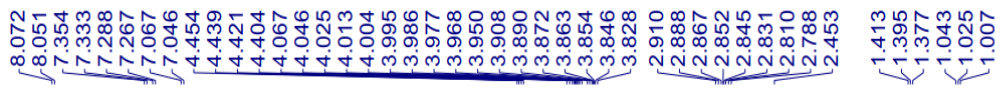

2.00
0.99
2.05
1.22
1.13
1.00
2.06
2.21
1.21
2.00
3.00
3.00
3.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

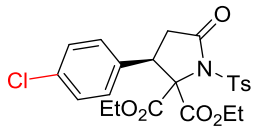

171.735
167.108
165.024
145.509
137.830
135.288
131.826
131.646
130.193
130.031
129.154
127.161
122.619
77.349
63.510
62.918
46.343
36.231
21.865
14.060
13.624


Cl
O
N
Ts
EtO2C
CO2Et

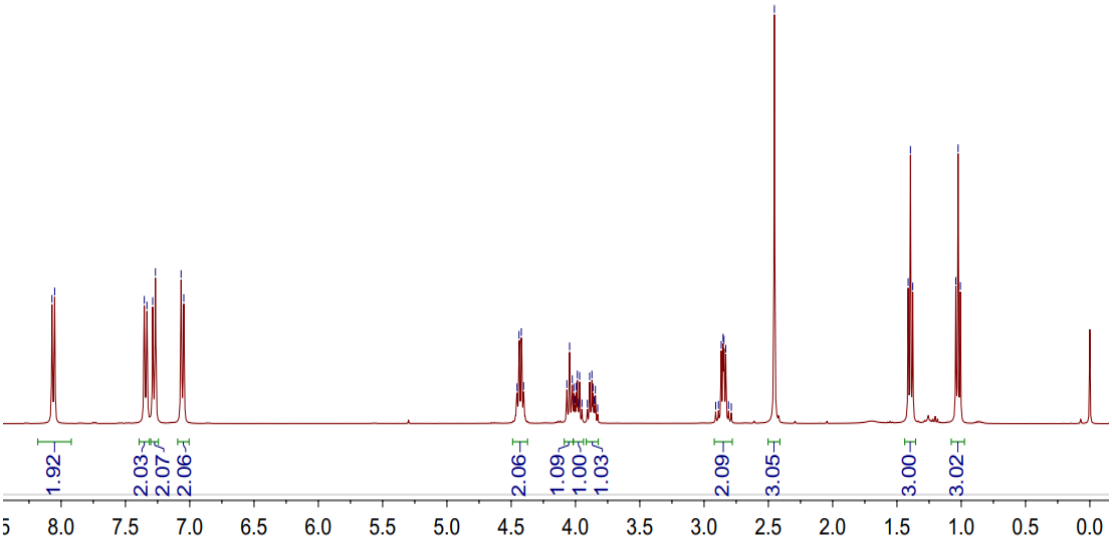
3e


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

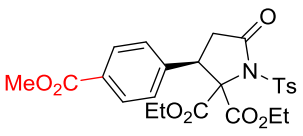

8.072
8.051
7.354
7.333
7.288
7.267
7.067
7.046
4.454
4.439
4.421
4.404
4.067
4.046
4.025
4.013
4.004
3.995
3.986
3.977
3.968
3.950
3.908
3.890
3.872
3.863
3.854
3.846
3.828
2.910
2.888
2.867
2.852
2.845
2.831
2.810
2.788
2.453
1.413
1.395
1.377
1.043
1.025
1.007


Cl
O
N
Ts
EtO2C
CO2Et

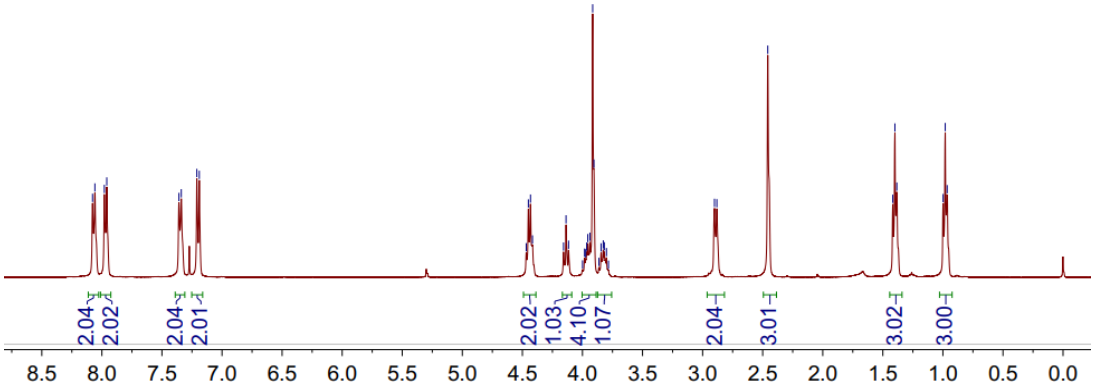
3f


1.92
2.03
2.07
2.06
2.06
1.09
1.00
1.03
2.09
3.05
3.00
3.02
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

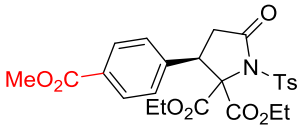

8.078
8.058
7.979
7.959
7.359
7.339
7.210
7.189
4.468
4.450
4.433
4.416
4.157
4.137
4.116
3.982
3.973
3.965
3.956
3.938
3.915
3.905
3.845
3.827
3.818
2.881
2.458
1.417
1.399
1.384
0.998
0.981
0.965


MeO2C
O
N
Ts
EtO2C
CO2Et

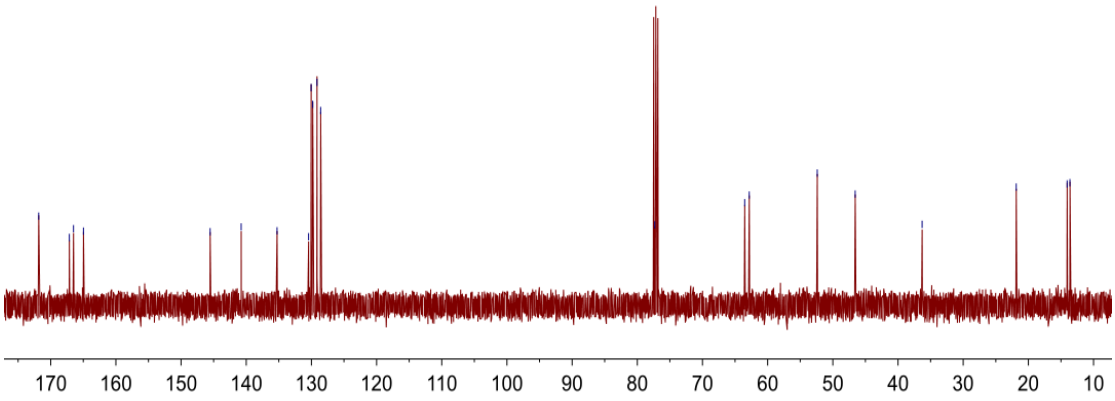
3g

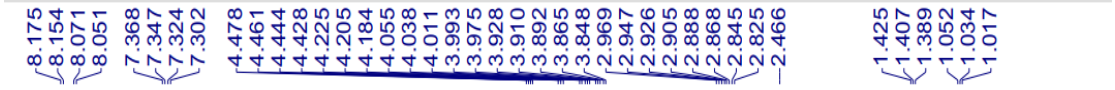

2.04
2.02
2.04
2.01
2.02
1.03
4.10
1.07
2.04
3.01
3.02
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

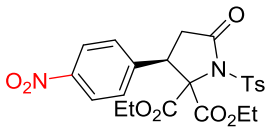

171.842
167.138
166.505
164.971
145.540
140.771
135.273
130.430
130.044
129.806
129.143
128.580
77.316
63.523
62.825
52.393
46.569
36.304
21.861
14.052
13.621


MeO2C
O
N
Ts
EtO2C
CO2Et

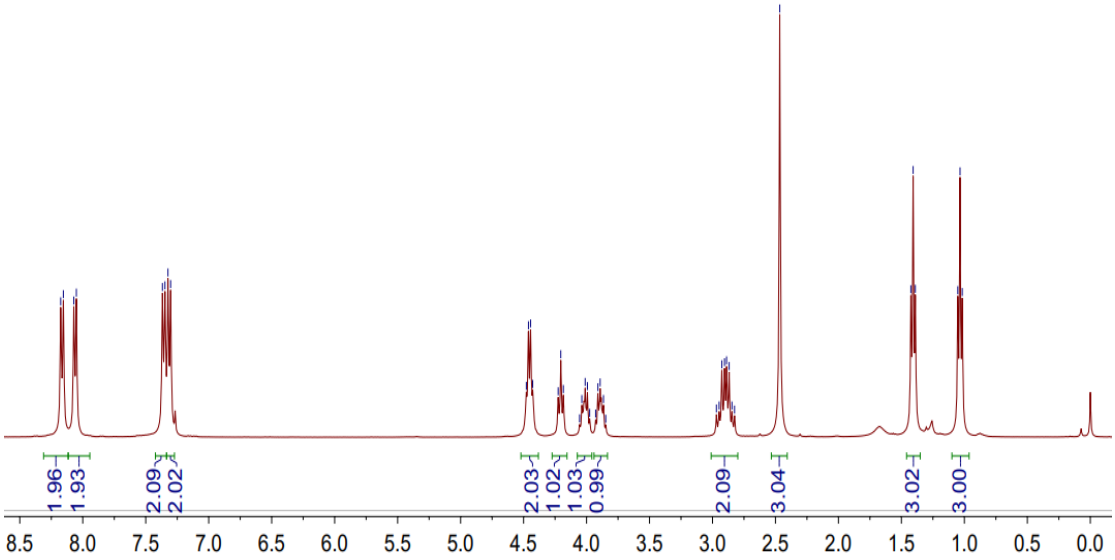
3g

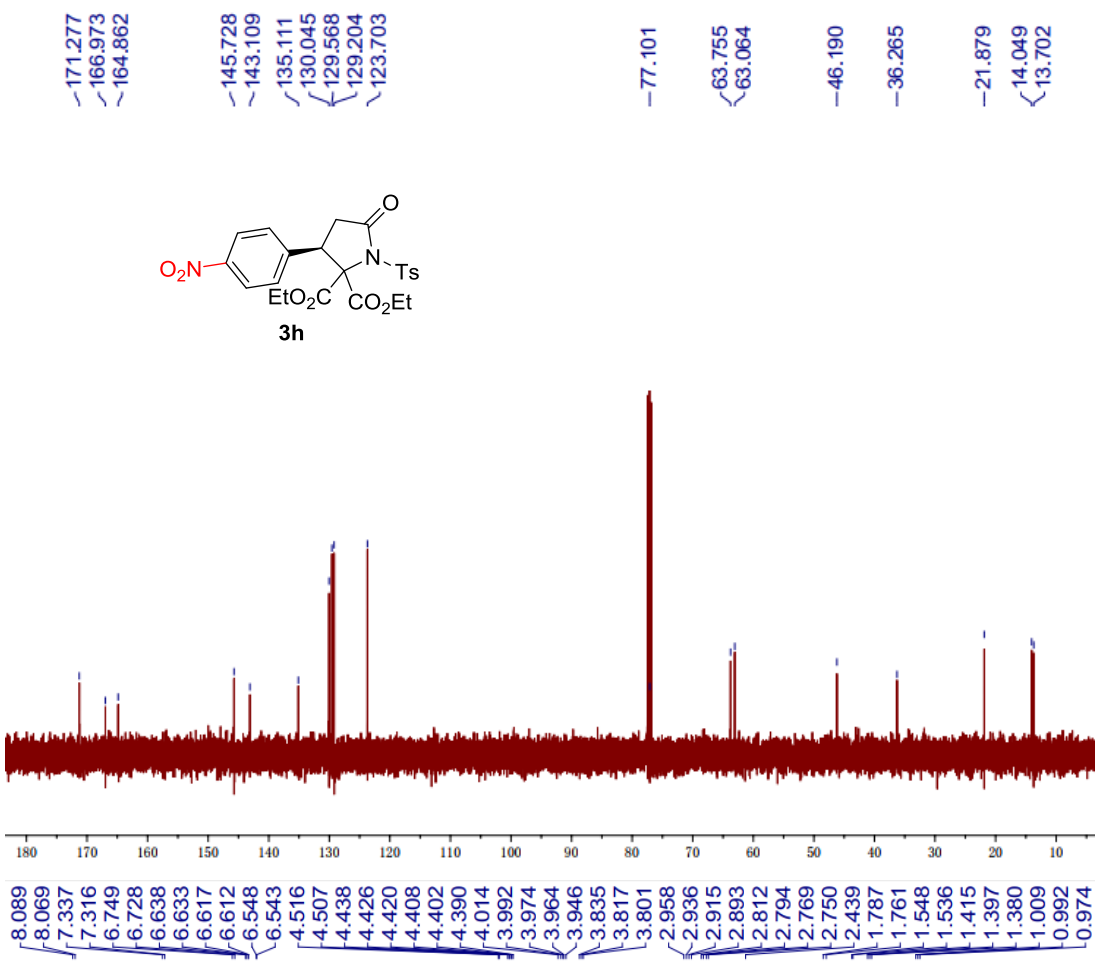

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

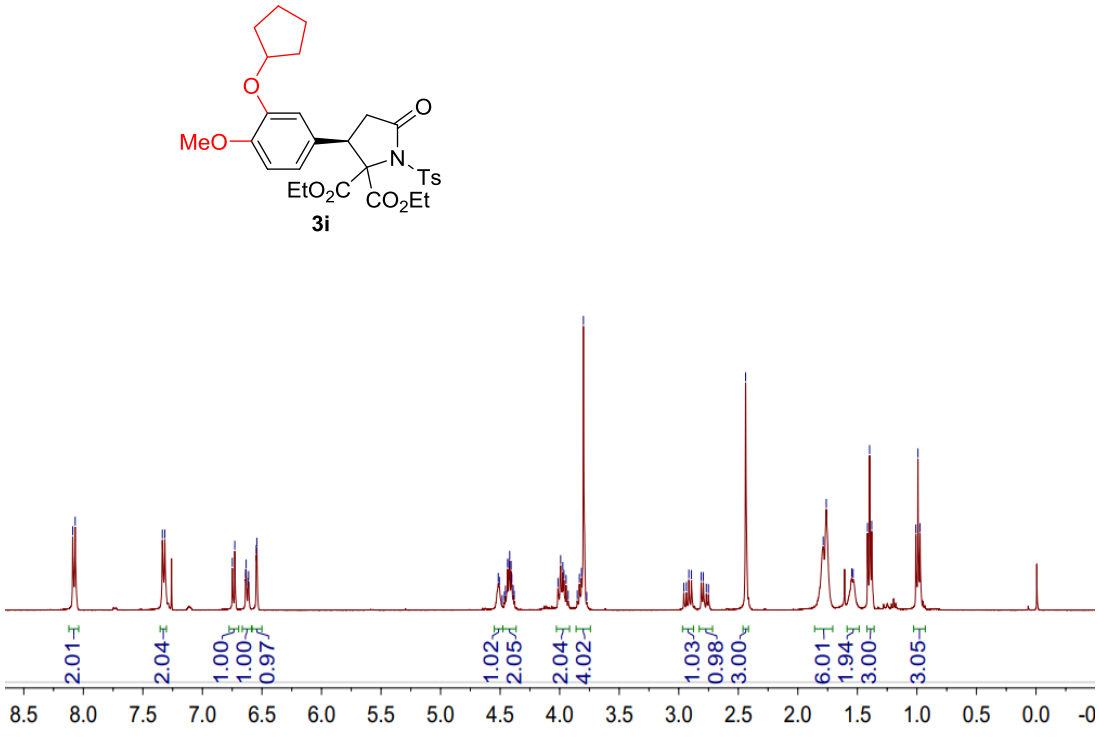

8.175
8.154
8.071
8.051
7.368
7.347
7.324
7.302
4.478
4.461
4.444
4.428
4.225
4.205
4.184
4.055
4.038
4.011
3.993
3.975
3.928
3.910
3.892
3.865
3.848
2.969
2.947
2.926
2.905
2.888
2.868
2.845
2.825
2.466
1.425
1.407
1.389
1.052
1.034
1.017

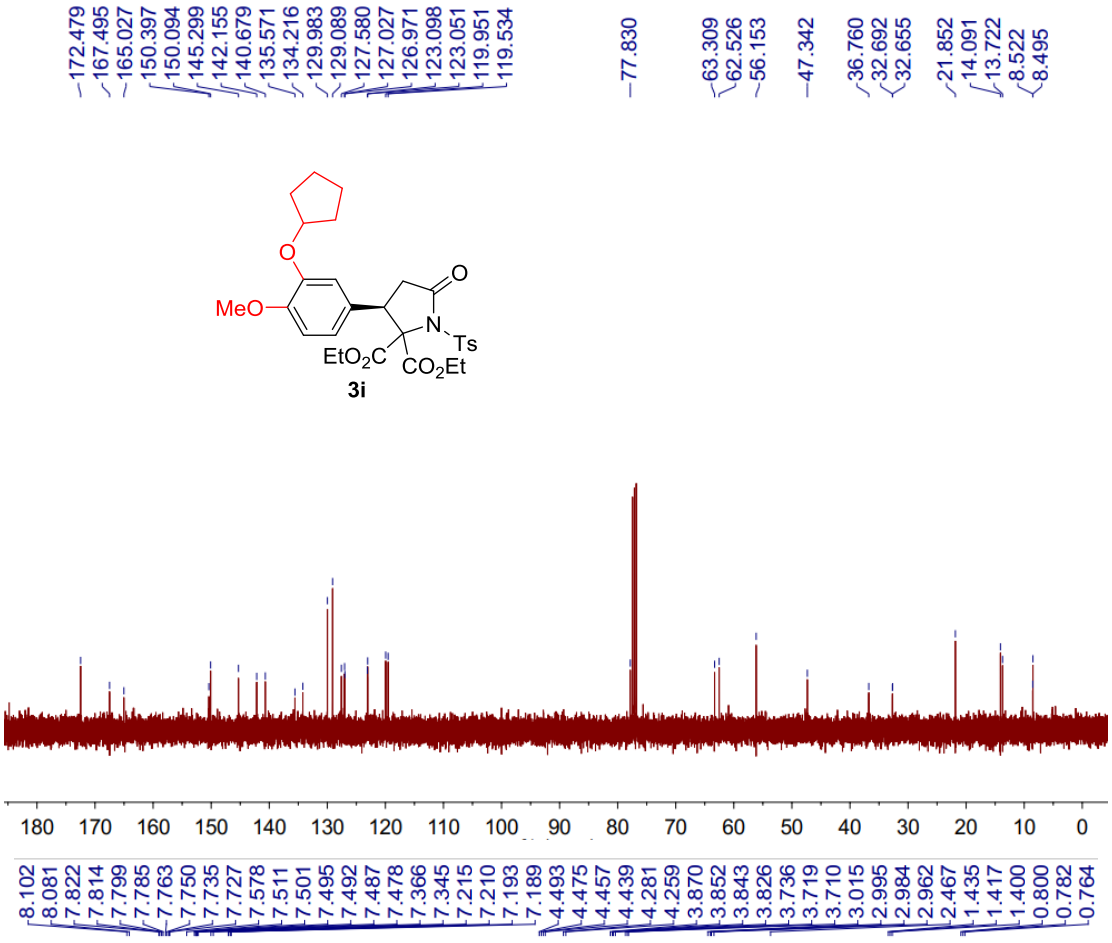

O2N
O
N
Ts
EtO2C
CO2Et

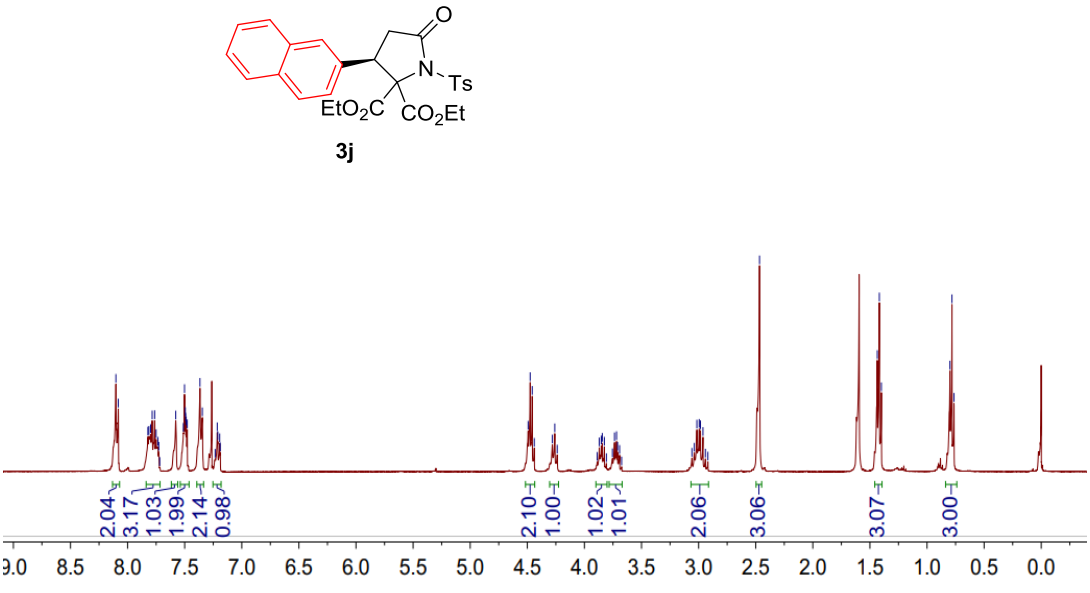
3h

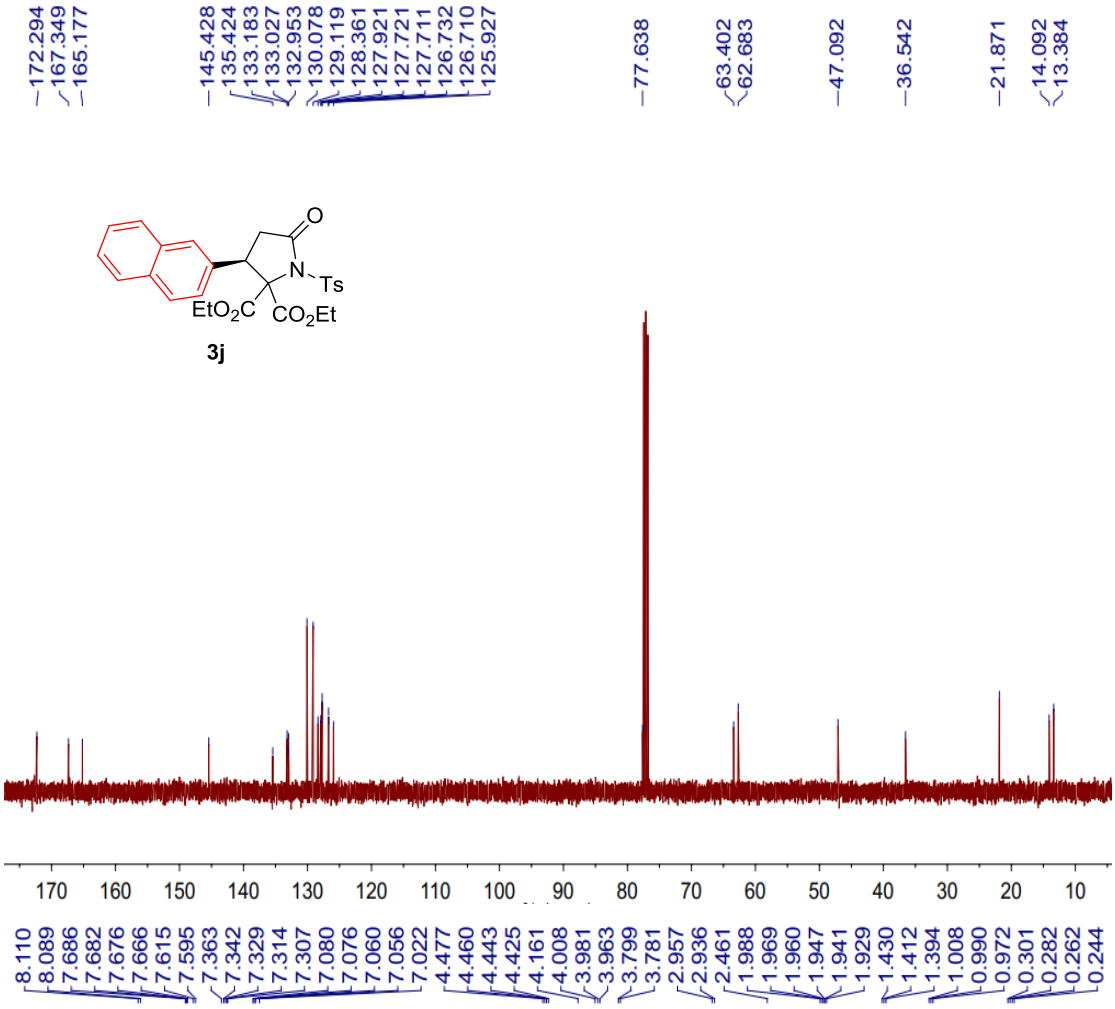

1.96
1.93
2.09
2.02
2.03
1.02
1.03
0.99
2.09
3.04
3.02
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

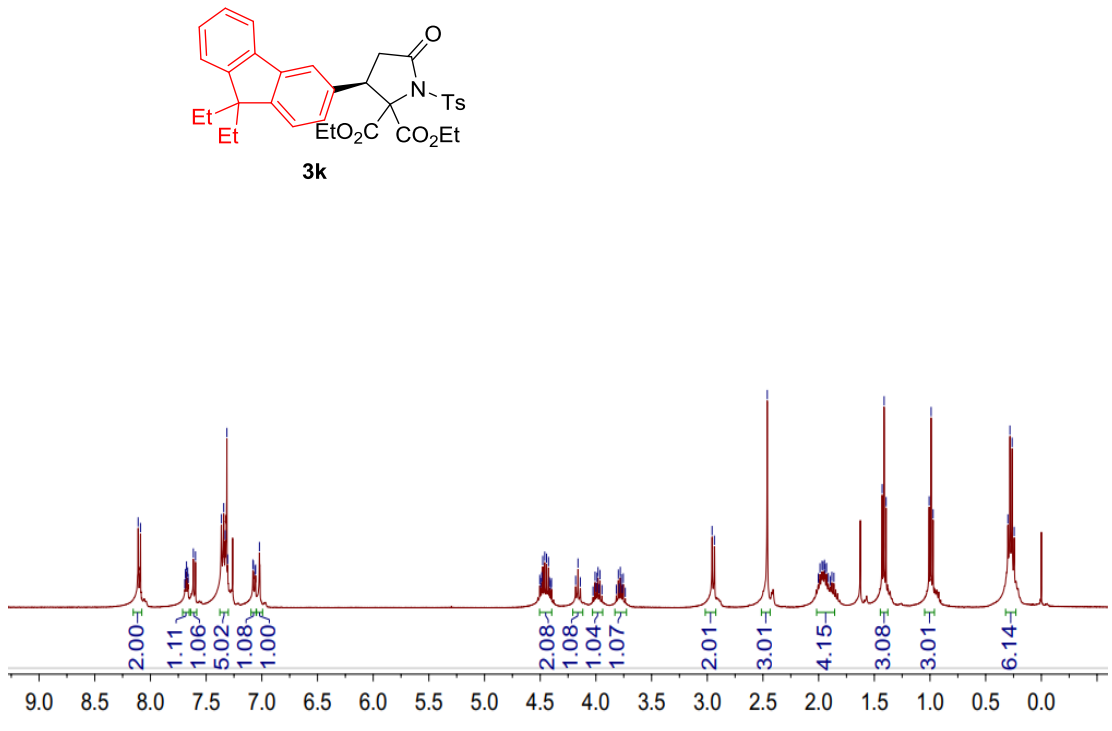

171.277
166.973
164.862
145.728
143.109
135.111
130.045
129.568
129.204
123.703
77.101
63.755
63.064
46.190
36.265
21.879
14.049
13.702
O
O2N
N
Ts
EtO2C
CO2Et
3h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
8.089
8.069
7.337
7.316
6.749
6.728
6.638
6.633
6.617
6.612
6.548
6.543
4.516
4.507
4.438
4.426
4.420
4.408
4.402
4.390
4.014
3.992
3.974
3.964
3.946
3.835
3.817
3.801
2.958
2.936
2.915
2.893
2.812
2.794
2.769
2.750
2.439
1.787
1.761
1.548
1.536
1.415
1.397
1.380
1.009
0.992
0.974

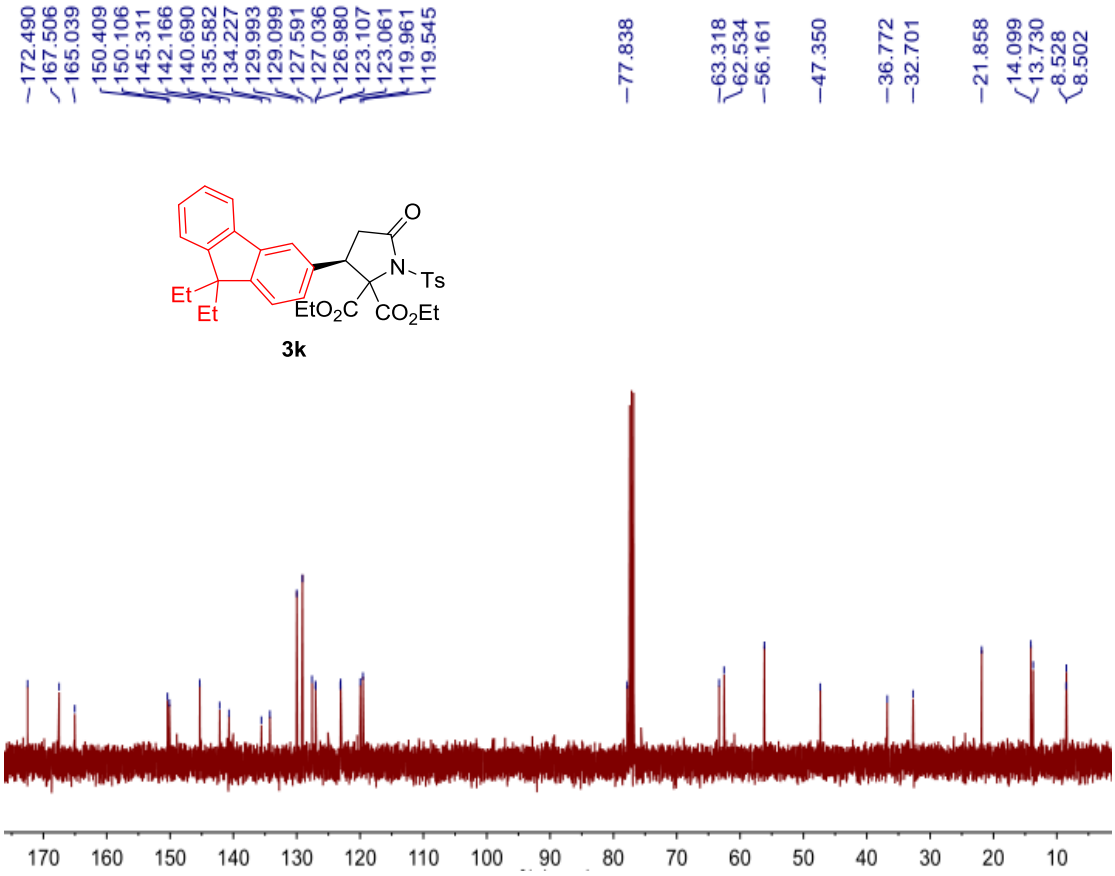

O
MeO
O
N
Ts
EtO2C
CO2Et
3i
2.01
2.04
1.00
1.00
0.97
1.02
2.05
2.04
4.02
1.03
0.98
3.00
6.01
1.94
3.00
3.05
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0


172.479
167.495
165.027
150.397
150.094
145.299
142.155
140.679
135.571
134.216
129.983
129.089
127.580
127.027
126.971
123.098
123.051
119.951
119.534
77.830
63.309
62.526
56.153
47.342
36.760
32.692
32.655
21.852
14.091
13.722
8.522
8.495
MeO
O
O
N
Ts
EtO2C
CO2Et
3i
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
8.102
8.081
7.822
7.814
7.799
7.785
7.763
7.750
7.735
7.727
7.578
7.511
7.501
7.495
7.492
7.487
7.478
7.366
7.345
7.215
7.210
7.193
7.189
4.493
4.475
4.457
4.439
4.281
4.259
3.870
3.852
3.843
3.826
3.736
3.719
3.710
3.015
2.995
2.984
2.962
2.467
1.435
1.417
1.400
0.800
0.782
0.764

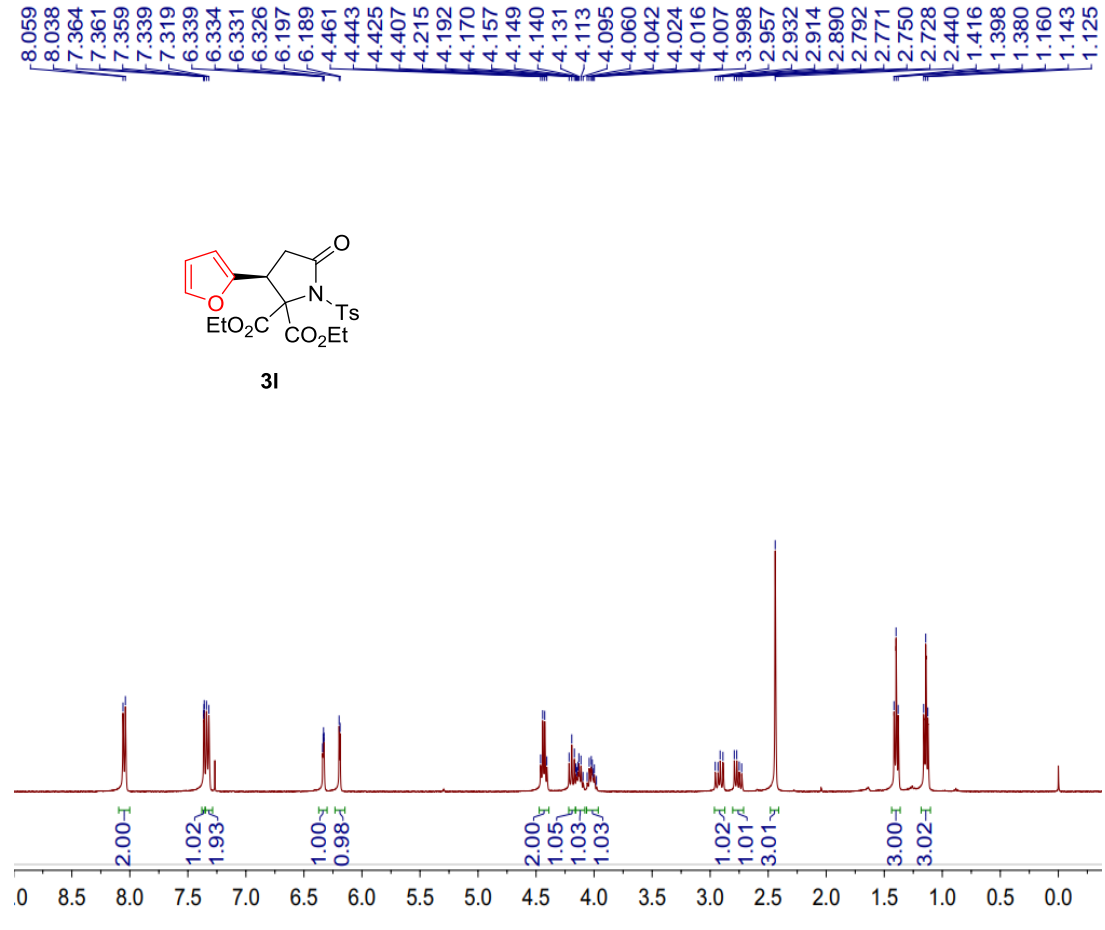

O
N
Ts
EtO2C
CO2Et
3j
2.04
3.17
1.03
1.99
2.14
0.98
2.10
1.00
1.02
1.01
2.06
3.06
3.07
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


172.294
167.349
165.177
145.428
135.424
133.183
133.027
132.953
130.078
129.119
128.361
127.921
127.721
127.711
126.732
126.710
125.927
77.638
63.402
62.683
47.092
36.542
21.871
14.092
13.384
O
N
Ts
EtO2C
CO2Et
3j
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
8.110
8.089
7.686
7.682
7.676
7.666
7.615
7.595
7.363
7.342
7.329
7.314
7.307
7.080
7.076
7.060
7.056
7.022
4.477
4.460
4.443
4.425
4.161
4.008
3.981
3.963
3.799
3.781
2.957
2.936
2.461
1.988
1.969
1.960
1.947
1.941
1.929
1.430
1.412
1.394
1.008
0.990
0.972
0.301
0.282
0.262
0.244

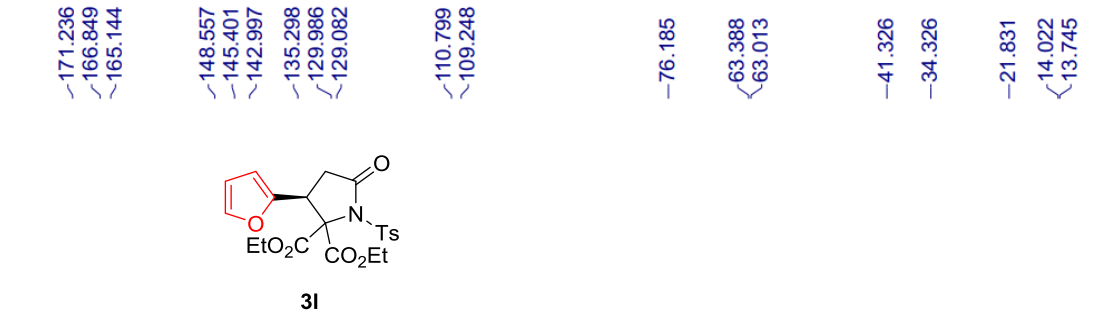

O
N
Ts
Et
Et
EtO2C
CO2Et
3k
2.00
1.11
1.06
5.02
1.08
1.00
2.08
1.08
1.04
1.07
2.01
3.01
4.15
3.08
3.01
6.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0


172.490
167.506
165.039
150.409
150.106
145.311
142.166
140.690
135.582
134.227
129.993
129.099
127.591
127.036
126.980
123.107
123.061
119.961
119.545
77.838
63.318
62.534
56.161
47.350
36.772
32.701
21.858
14.099
13.730
8.528
8.502
Et
Et
EtO2C
CO2Et
N
Ts
O
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

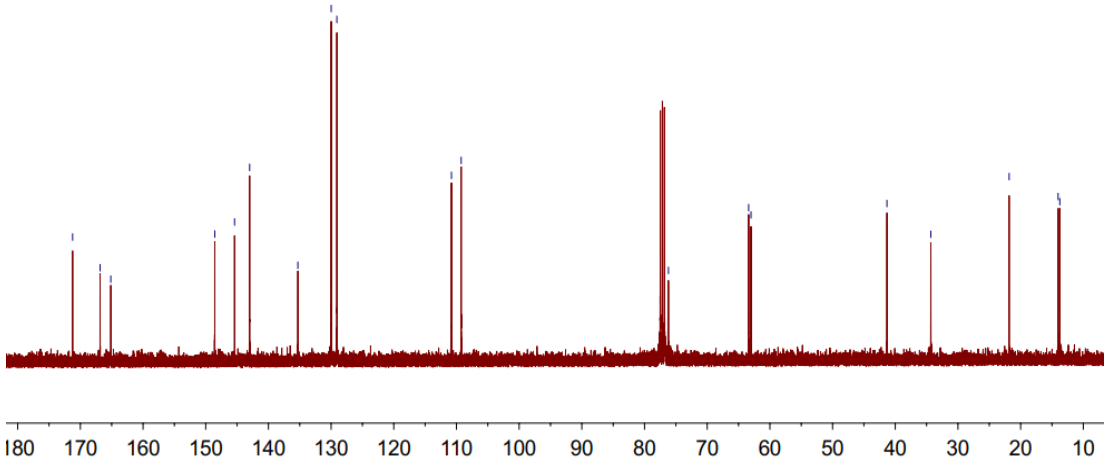
3k


8.059
8.038
7.364
7.361
7.359
7.339
7.319
6.339
6.334
6.331
6.326
6.197
6.189
4.461
4.443
4.425
4.407
4.215
4.192
4.170
4.157
4.149
4.140
4.131
4.113
4.095
4.060
4.042
4.024
4.016
4.007
3.998
2.957
2.932
2.914
2.890
2.792
2.771
2.750
2.728
2.440
1.416
1.398
1.380
1.160
1.143
1.125
O
N
Ts
EtO2C
CO2Et
2.00
1.02
1.93
1.00
0.98
2.00
1.05
1.03
1.03
1.02
1.01
3.01
3.00
3.02
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

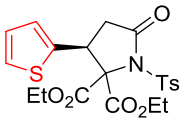
3l


171.236
166.849
165.144
148.557
145.401
142.997
135.298
129.986
129.082
110.799
109.248
76.185
63.388
63.013
41.326
34.326
21.831
14.022
13.745
O
N
Ts
O
EtO2C
CO2Et

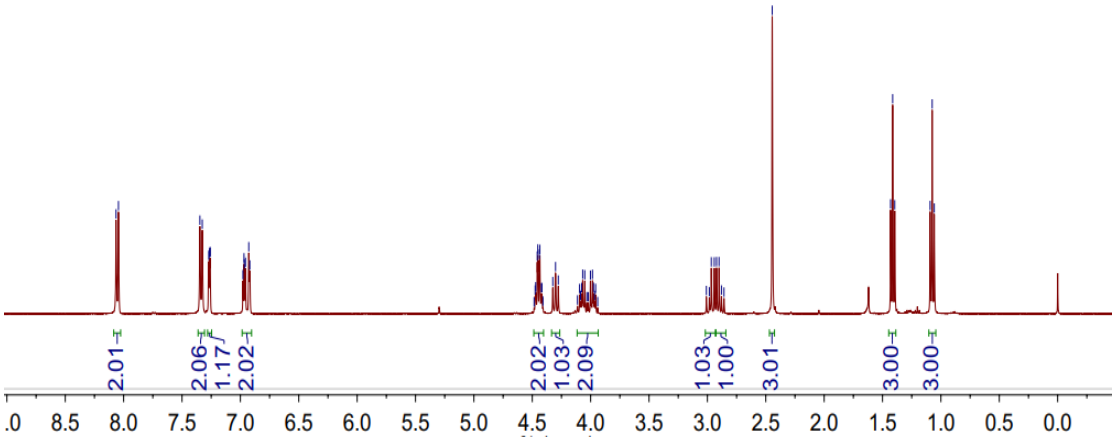
3l

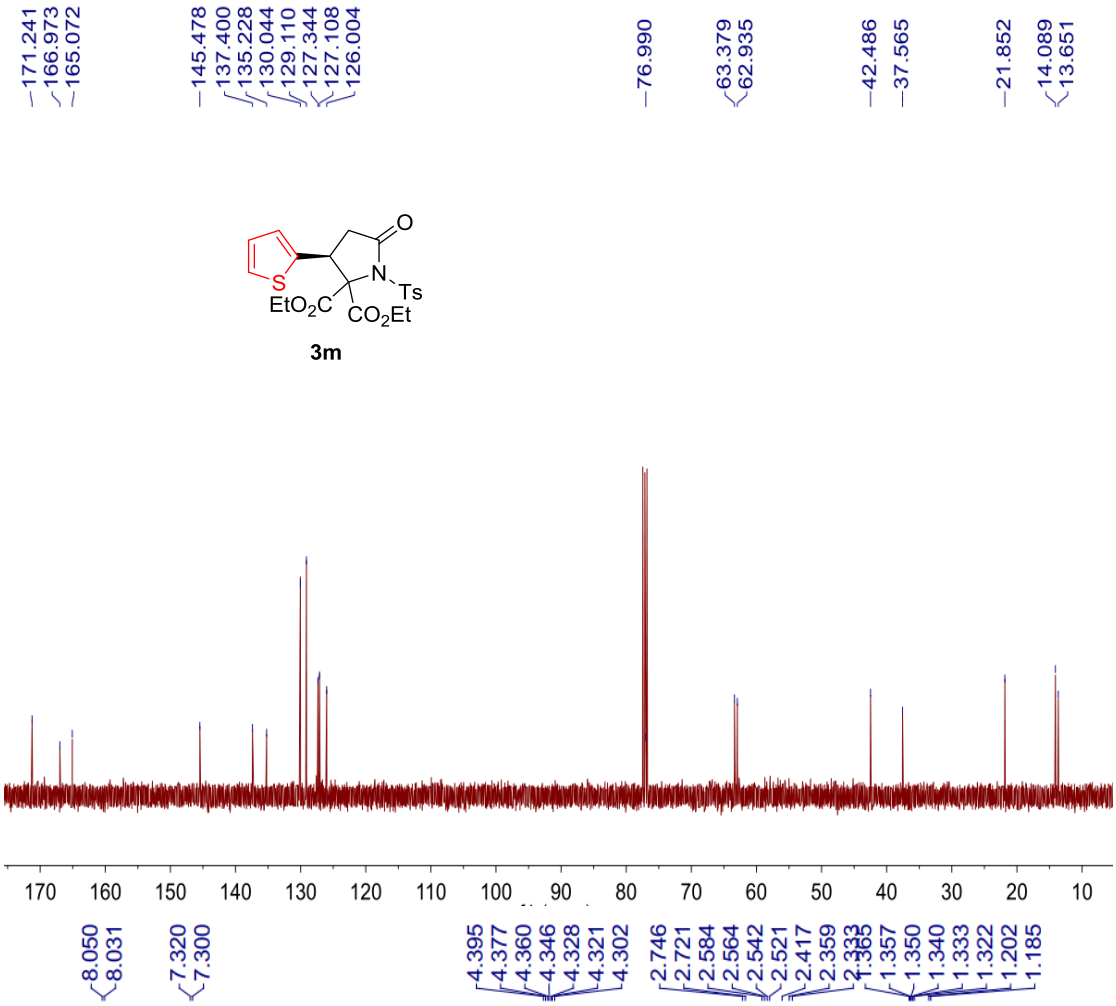

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

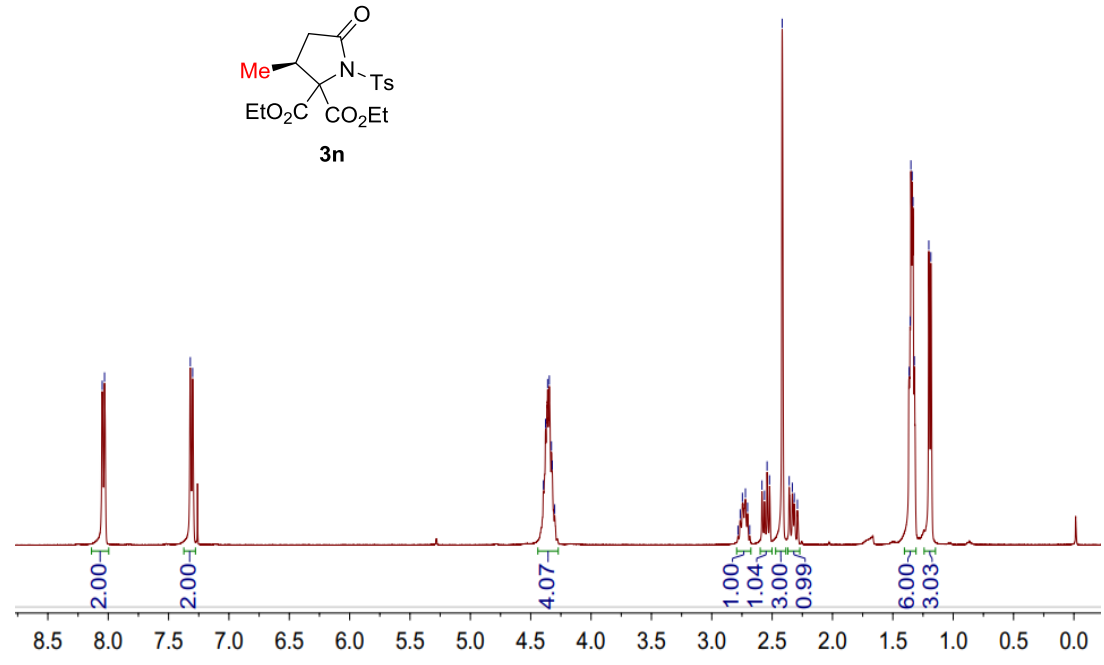

8.065
8.044
7.347
7.326
7.271
7.264
7.261
7.259
6.978
6.969
6.966
6.957
6.928
6.919
4.475
4.471
4.457
4.453
4.440
4.435
4.422
4.417
4.324
4.301
4.277
4.095
4.077
4.068
4.050
4.002
3.984
3.975
3.957
3.009
2.983
2.967
2.941
2.922
2.900
2.880
2.445
1.431
1.413
1.395
1.093
1.075
1.057

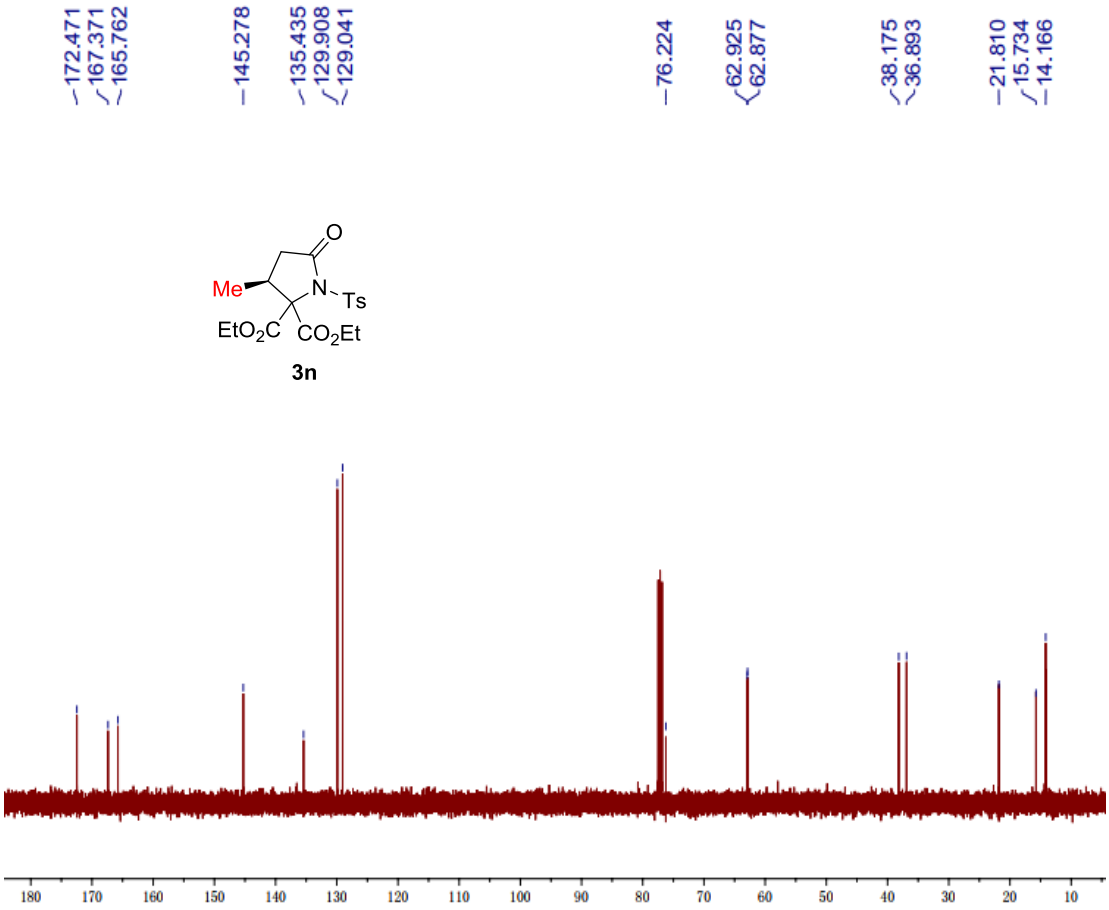

O
S
N
Ts
EtO2C
CO2Et

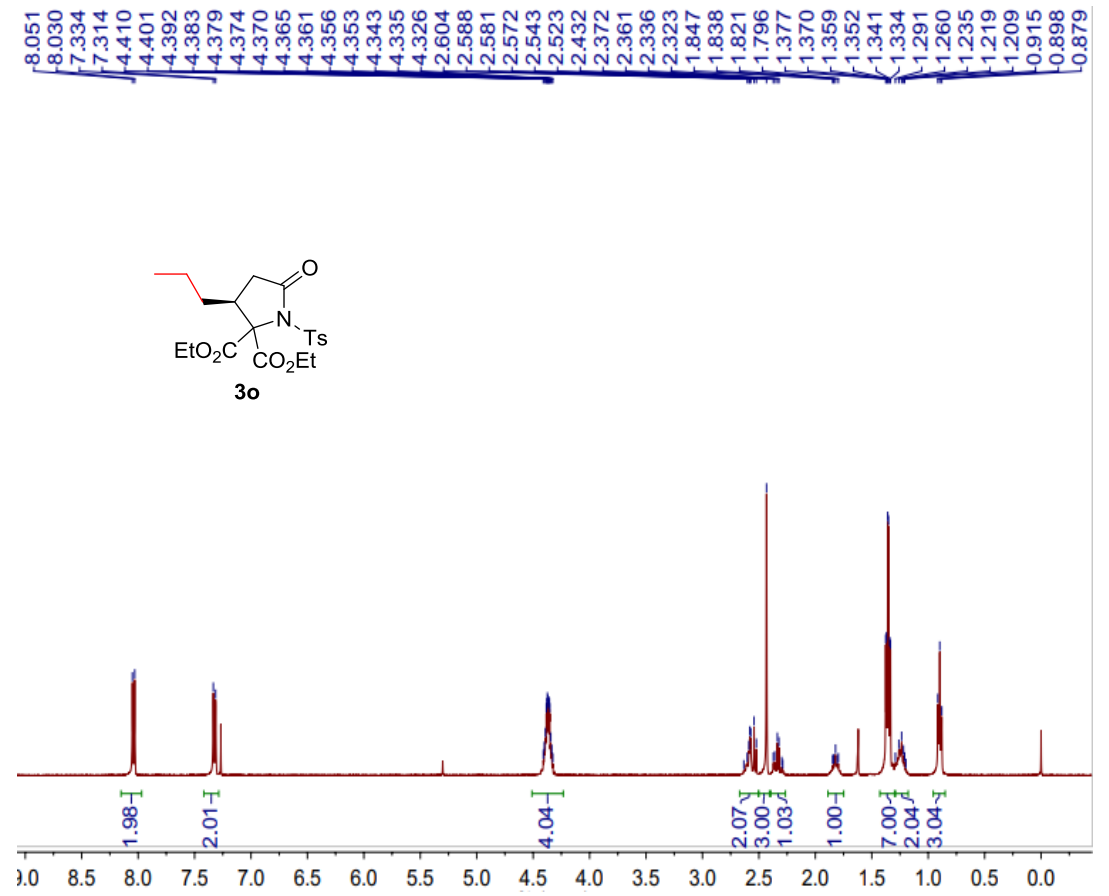
3m

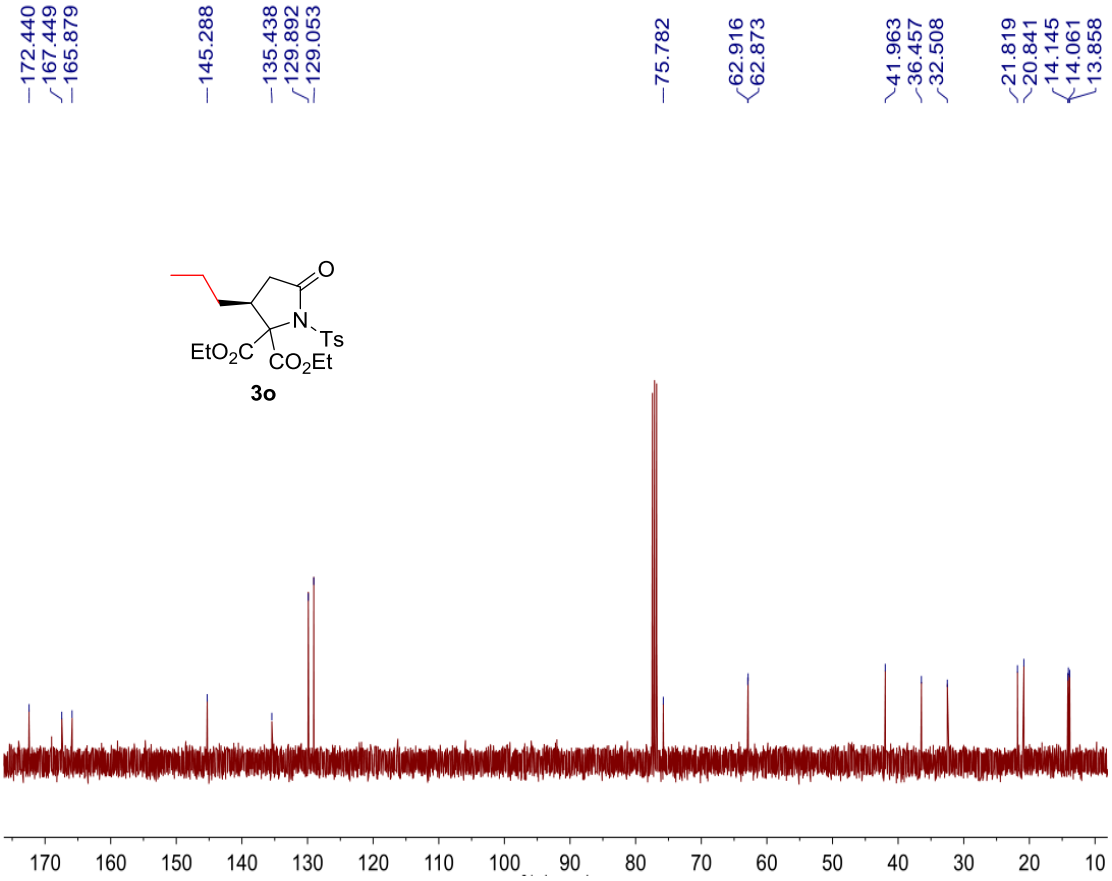

2.01
2.06
1.17
2.02
2.02
1.03
2.09
1.03
1.00
3.01
3.00
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

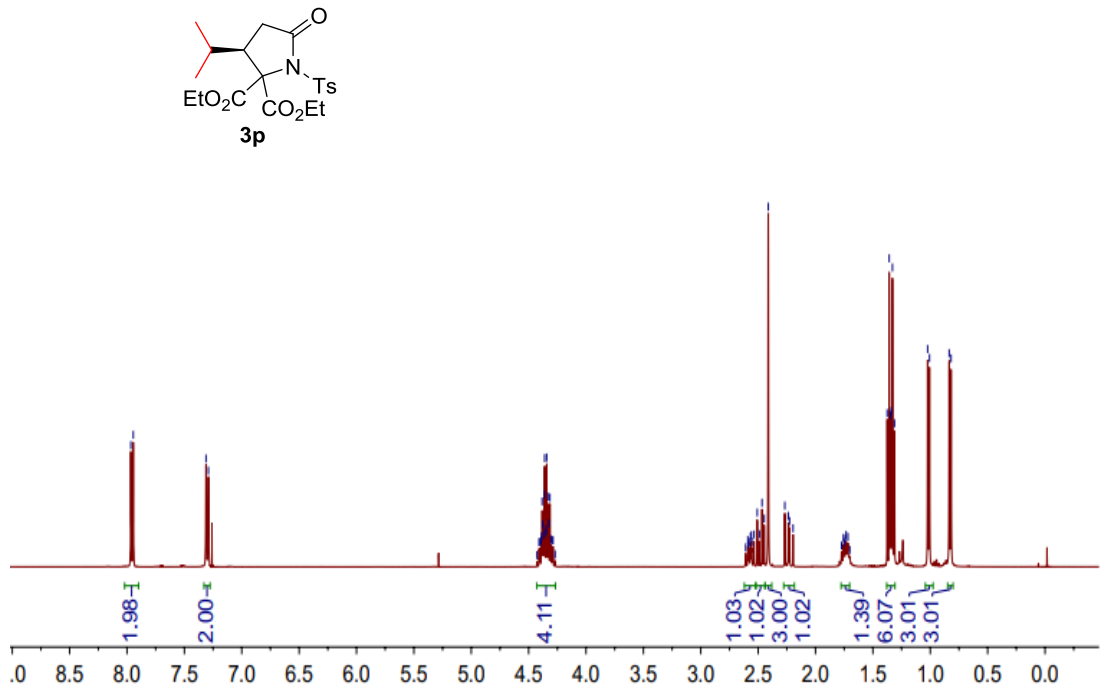

171.241
166.973
165.072
145.478
137.400
135.228
130.044
129.110
127.344
127.108
126.004
76.990
63.379
62.935
42.486
37.565
21.852
14.089
13.651
O
S
N
Ts
EtO2C
CO2Et
3m
8.050
8.031
7.320
7.300
4.395
4.377
4.360
4.346
4.328
4.321
4.302
2.746
2.721
2.584
2.564
2.542
2.521
2.417
2.359
1.357
1.350
1.340
1.333
1.322
1.202
1.185
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

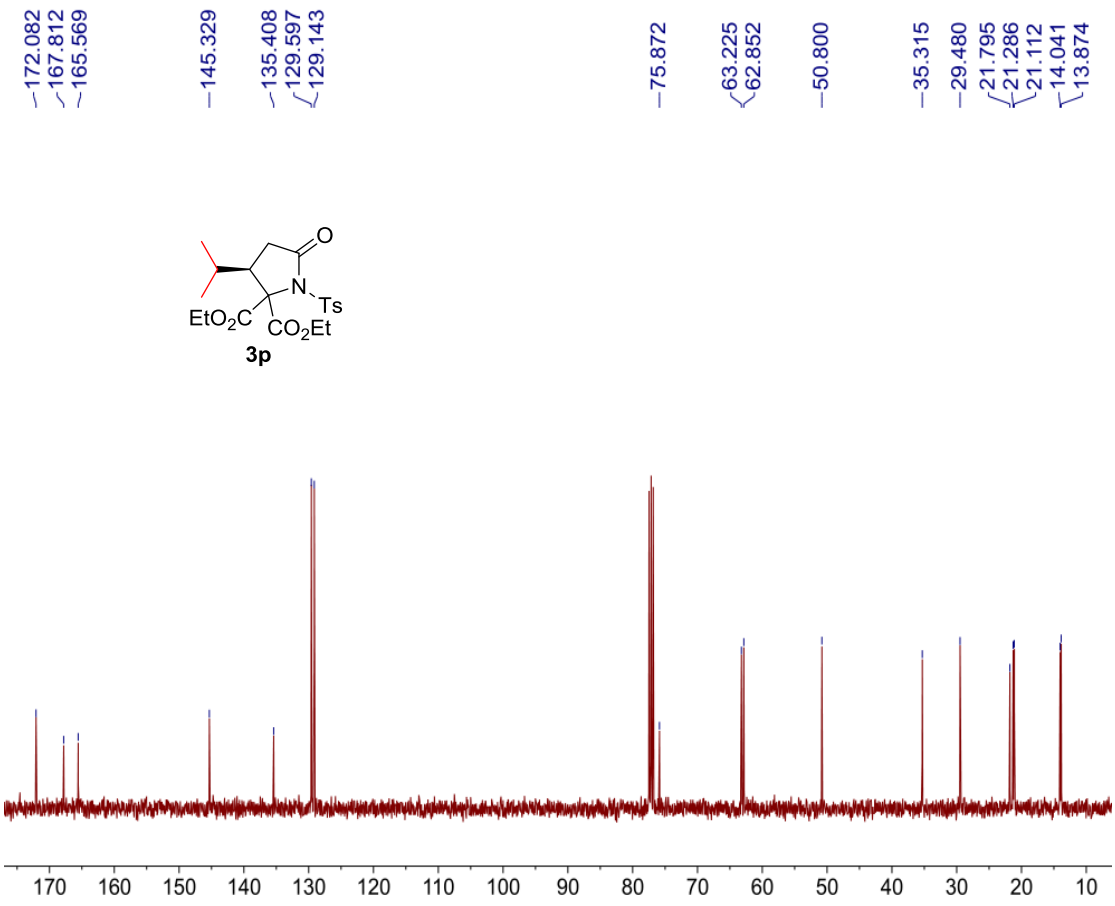

Me
O
N
Ts
EtO2C
CO2Et
3n
2.00
2.00
4.07
1.00
1.04
3.00
0.99
6.00
3.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

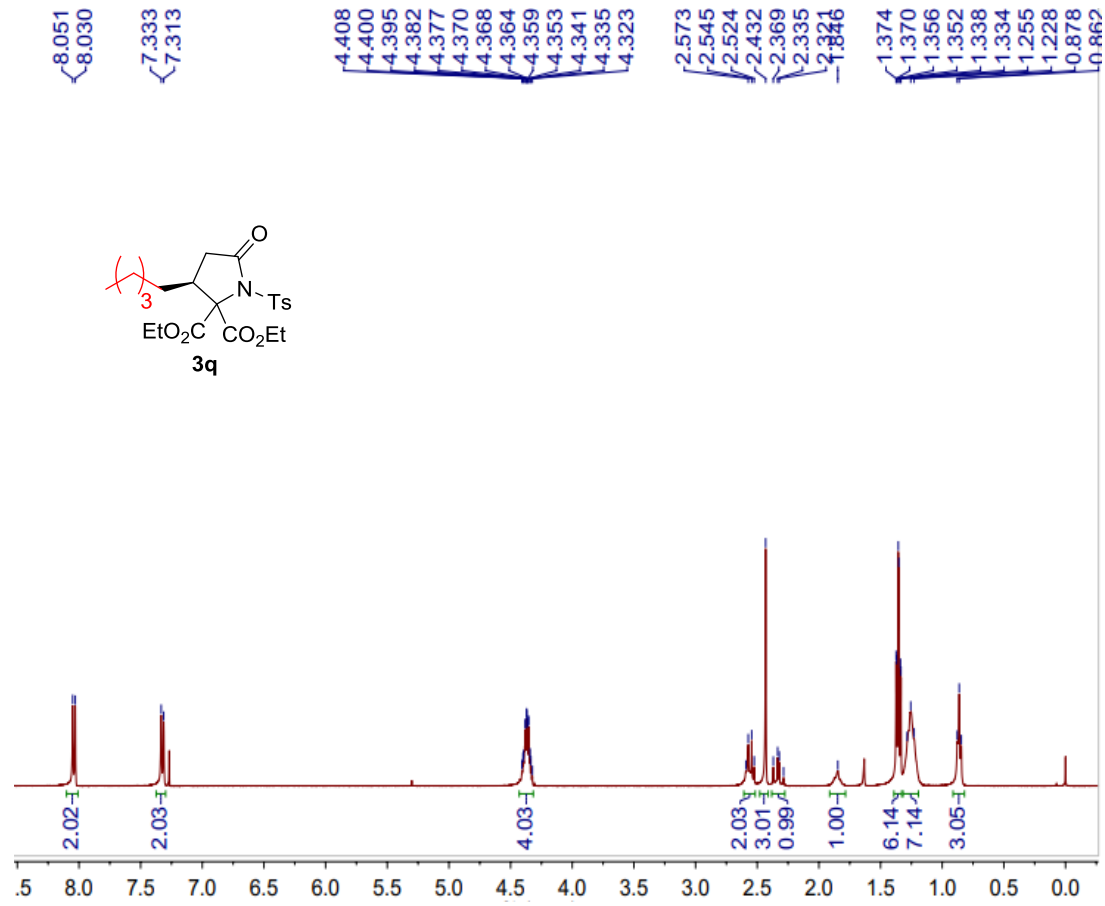

172.471
167.371
165.762
145.278
135.435
129.908
129.041
76.224
62.925
62.877
38.175
36.893
21.810
15.734
14.166
Me
N
Ts
O
EtO2C
CO2Et
3n

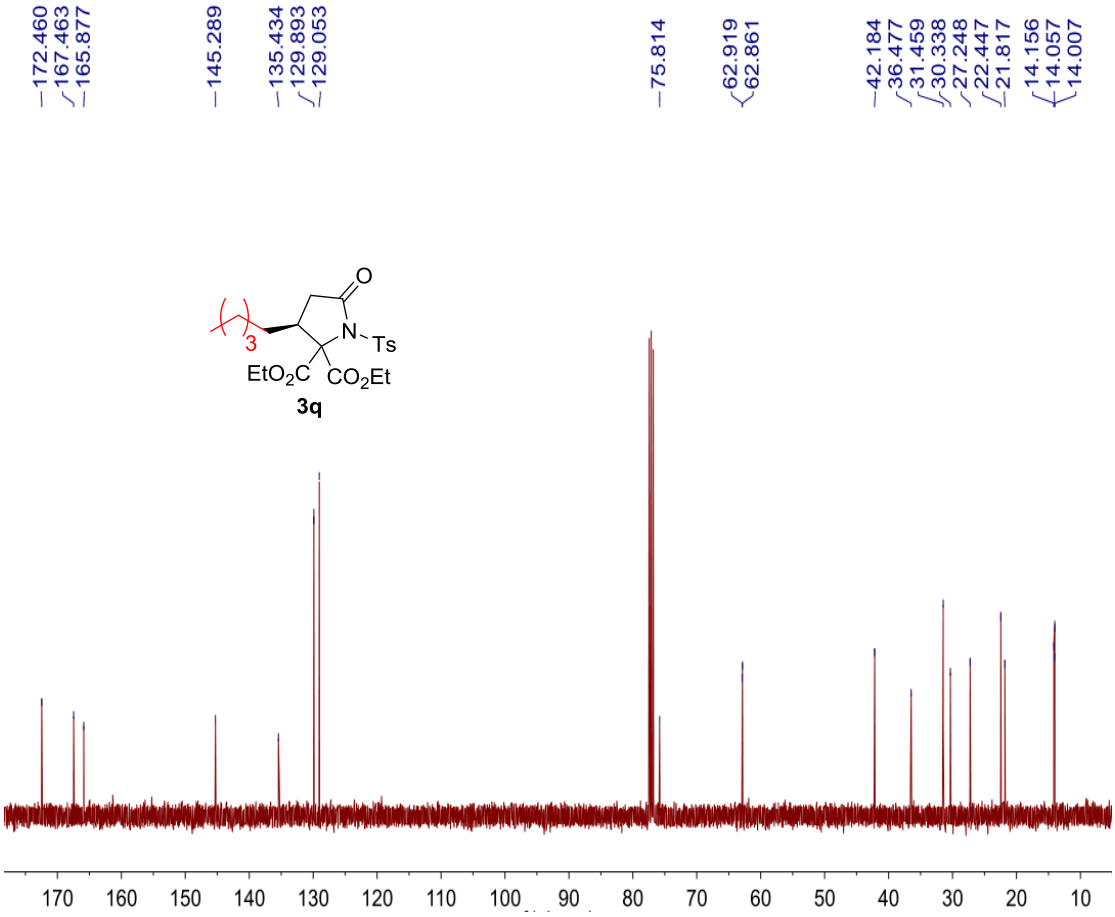

8.051
8.030
7.334
7.314
4.410
4.401
4.392
4.383
4.379
4.374
4.370
4.365
4.361
4.356
4.353
4.343
4.335
4.326
2.604
2.588
2.581
2.572
2.543
2.523
2.432
2.372
2.361
2.336
2.323
1.847
1.838
1.821
1.796
1.377
1.370
1.359
1.352
1.341
1.334
1.291
1.260
1.235
1.219
1.209
0.915
0.898
0.879
N
Ts
O
EtO2C
CO2Et
3o
1.98
2.01
4.04
2.07
3.00
1.03
1.00
7.00
2.04
3.04

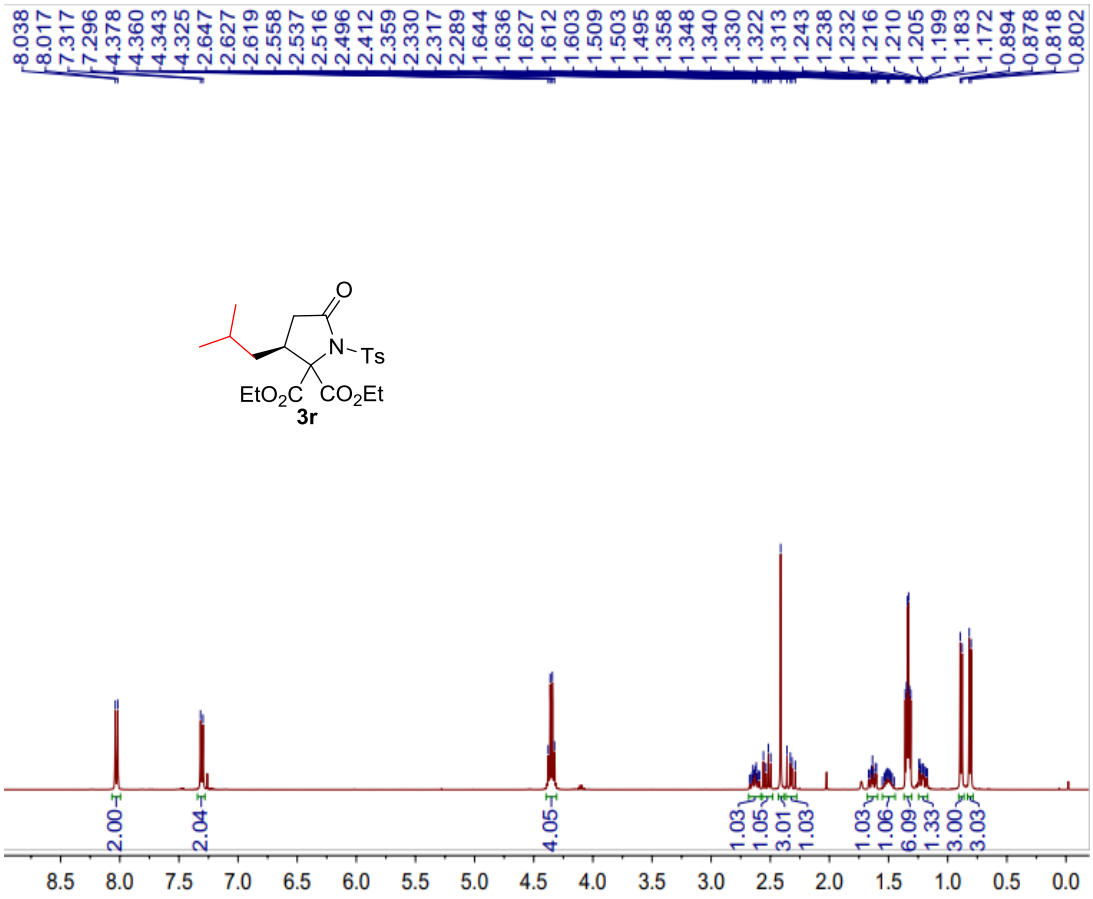

172.440
167.449
165.879
145.288
135.438
129.892
129.053
75.782
62.916
62.873
41.963
36.457
32.508
21.819
20.841
14.145
14.061
13.858
O
N
Ts
EtO2C
CO2Et
3o
7.967
7.946
7.311
7.290
4.391
4.388
4.383
4.378
4.370
4.364
4.360
4.350
4.347
4.342
4.332
4.324
4.314
4.305
4.296
4.287
2.590
2.566
2.559
2.536
2.508
2.489
2.466
2.447
2.412
2.268
2.237
2.226
2.196
1.757
1.741
1.734
1.717
1.376
1.358
1.348
1.340
1.330
1.312
1.023
1.007
0.835
0.819

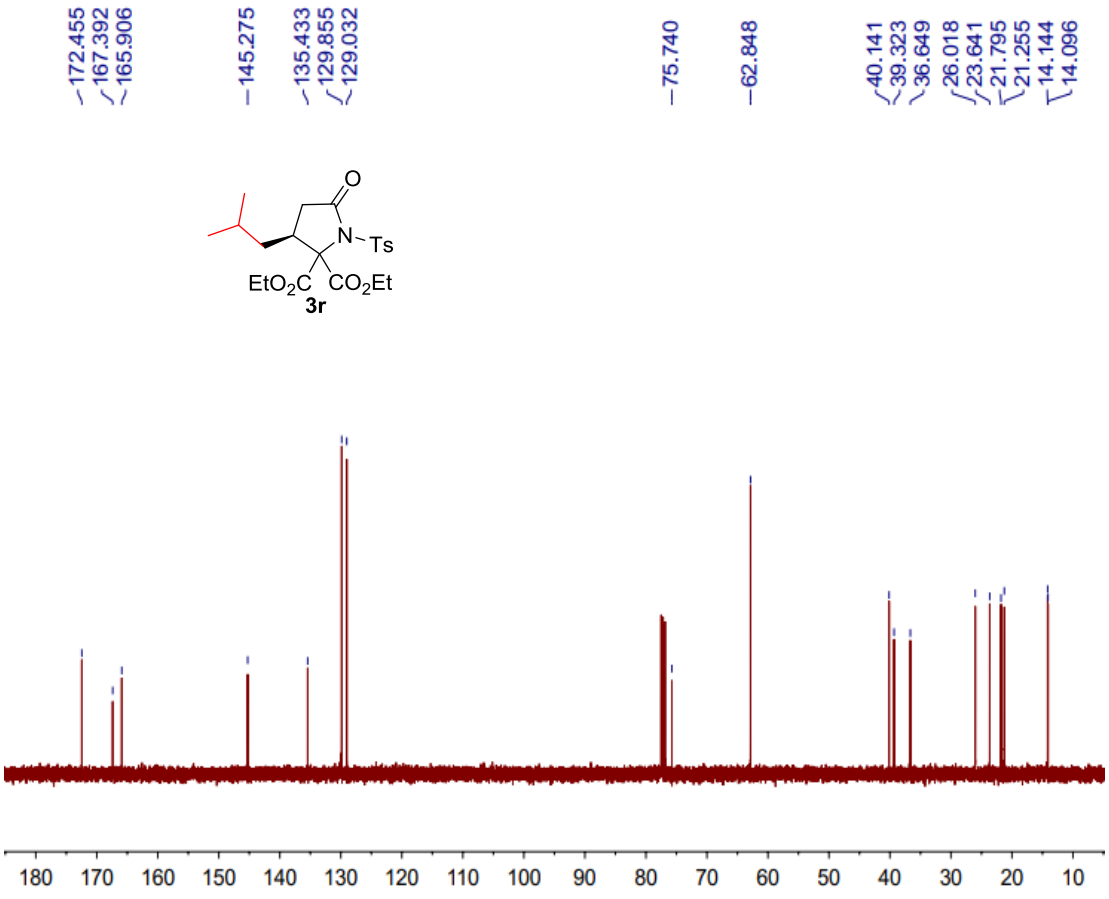

O
N
Ts
EtO2C
CO2Et
3p
1.98
2.00
4.11
1.03
1.02
3.00
1.02
1.39
6.07
3.01
3.01

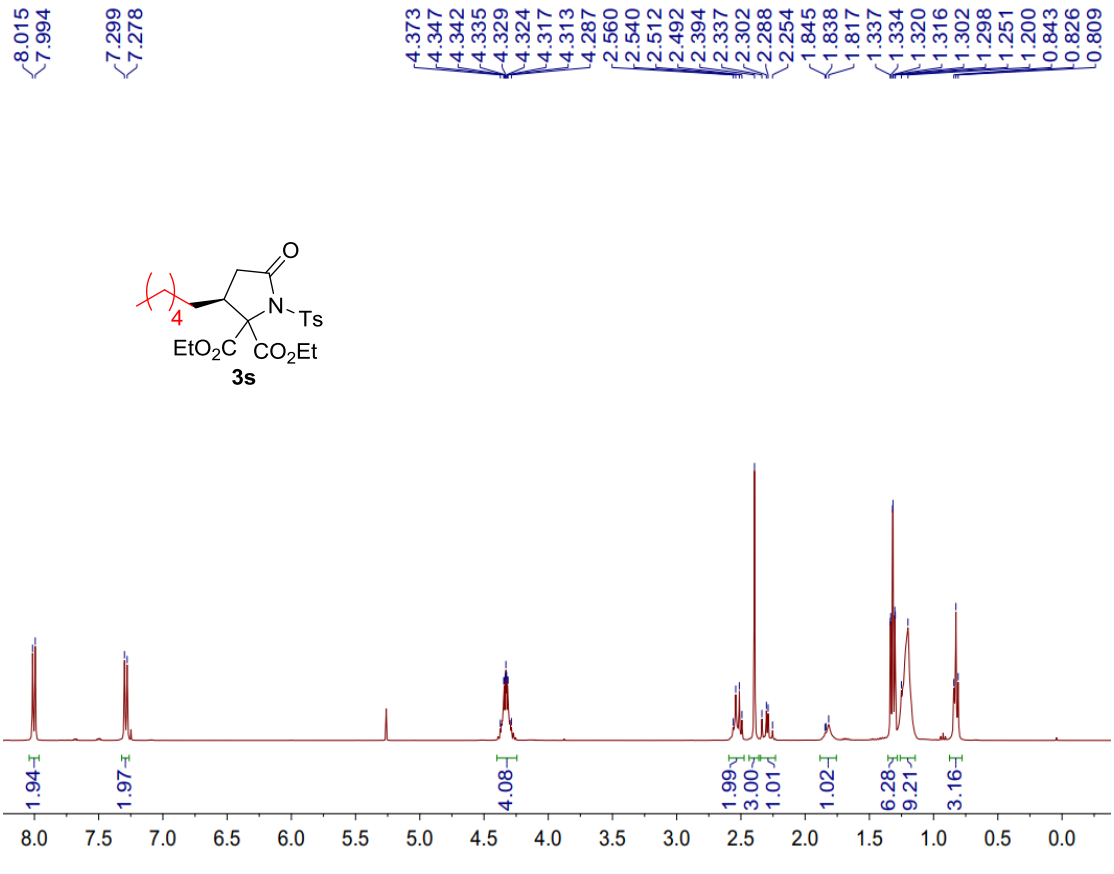

172.082
167.812
165.569
145.329
135.408
129.597
129.143
75.872
63.225
62.852
50.800
35.315
29.480
21.795
21.286
21.112
14.041
13.874
O
N
Ts
EtO2C
CO2Et
3p
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

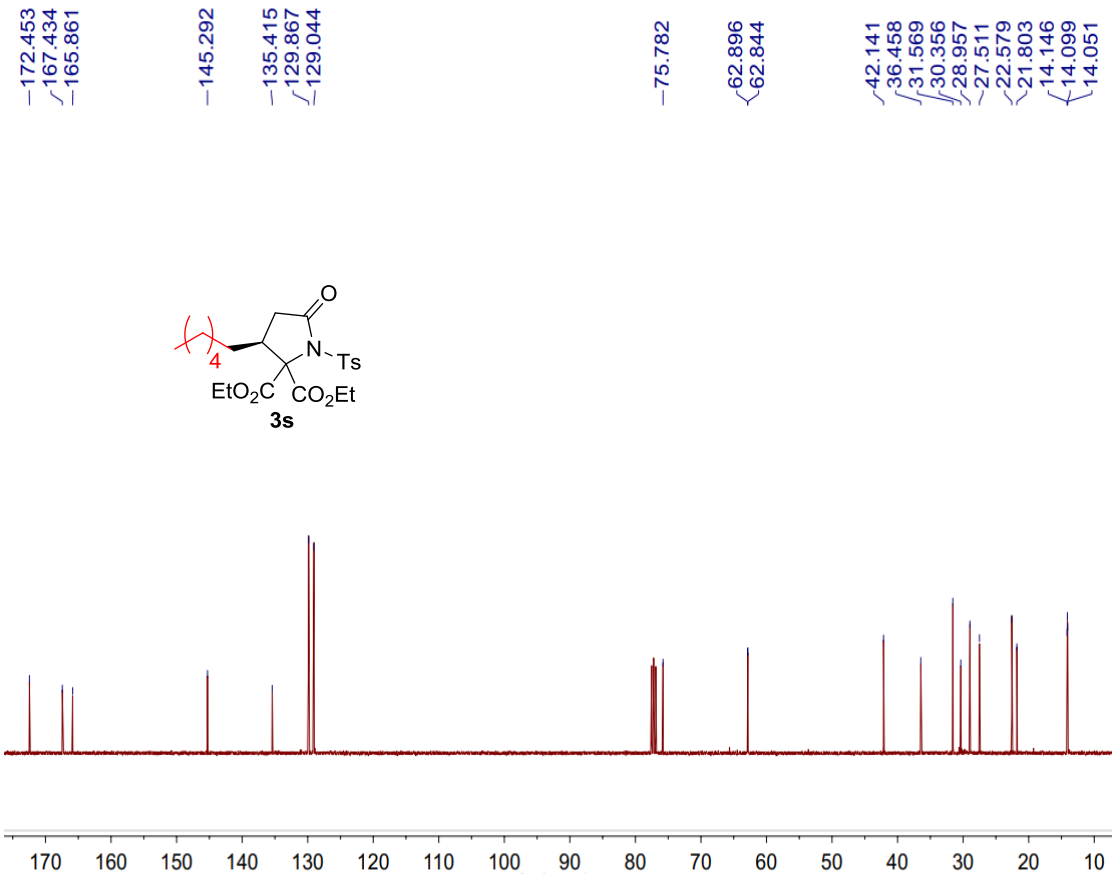

8.051
8.030
7.333
7.313
4.408
4.400
4.395
4.382
4.377
4.370
4.368
4.364
4.359
4.353
4.341
4.335
4.323
2.573
2.545
2.524
2.432
2.369
2.335
1.374
1.370
1.356
1.352
1.338
1.334
1.255
1.228
0.878
O
N
Ts
3
EtO2C
CO2Et
3q
2.02
2.03
4.03
2.03
3.01
0.99
1.00
6.14
7.14
3.05
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

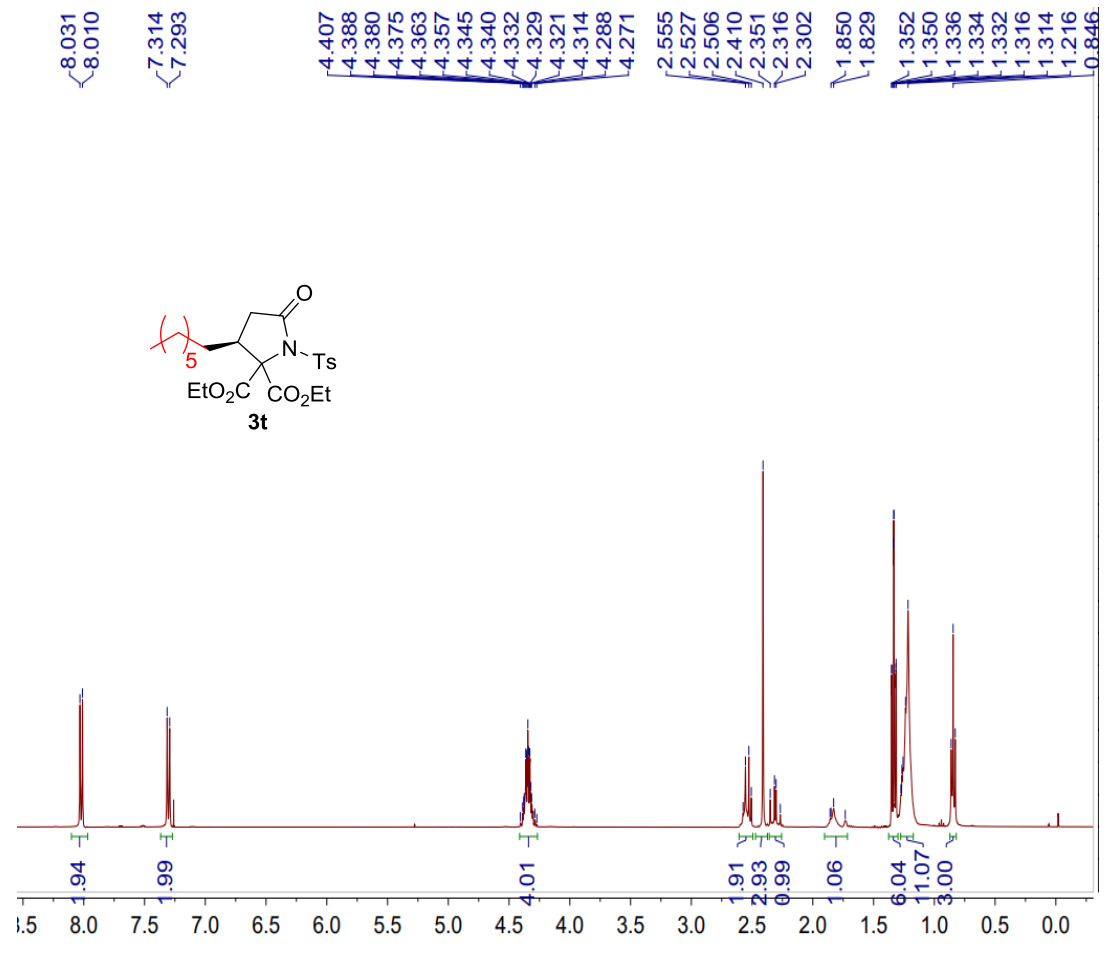

172.460
167.463
165.877
145.289
135.434
129.893
129.053
75.814
62.919
62.861
42.184
36.477
31.459
30.338
27.248
22.447
21.817
14.156
14.057
14.007
O
N
Ts
3
EtO2C
CO2Et
3q
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

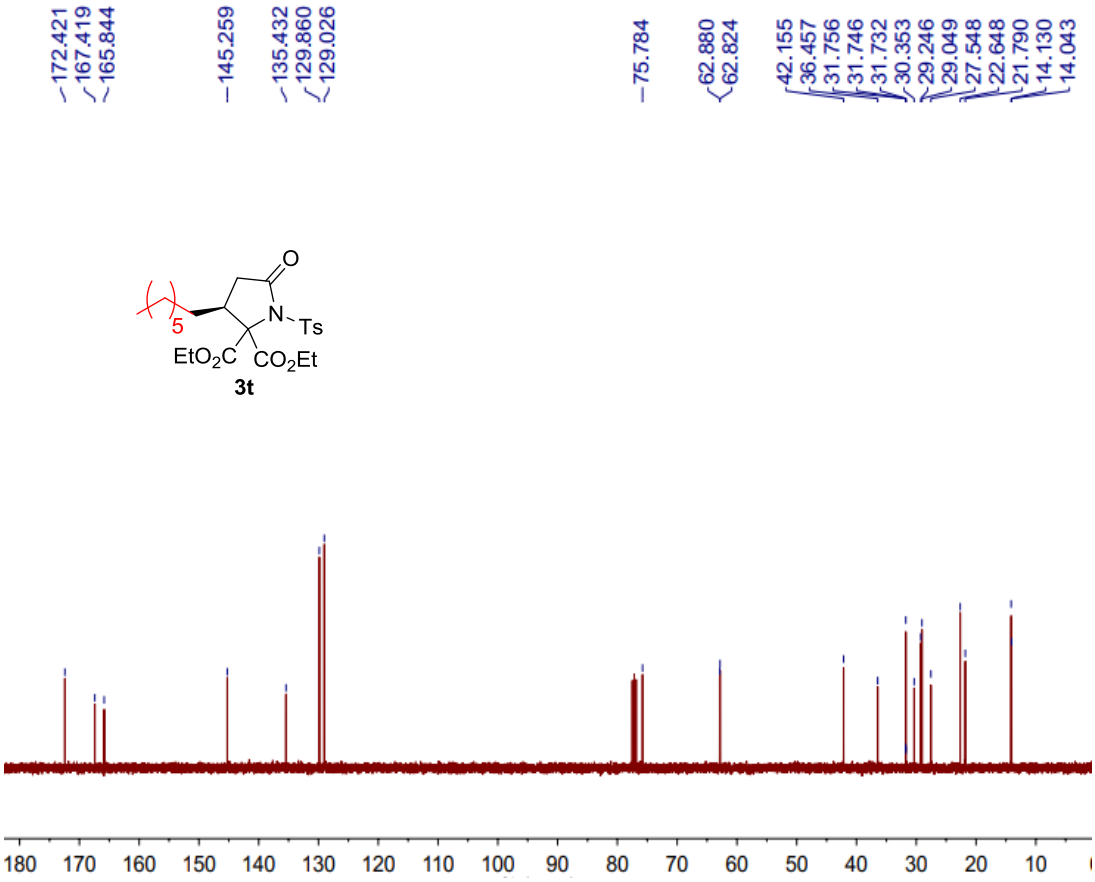

8.038
8.017
7.317
7.296
4.378
4.360
4.343
4.325
2.647
2.627
2.619
2.558
2.537
2.516
2.496
2.412
2.359
2.330
2.317
2.289
1.644
1.636
1.627
1.612
1.603
1.509
1.503
1.495
1.358
1.348
1.340
1.330
1.322
1.313
1.243
1.238
1.232
1.216
1.210
1.205
1.199
1.183
1.172
0.894
0.878
0.818
0.802
O
N
Ts
EtO2C
CO2Et
3r
2.00
2.04
4.05
1.03
1.05
3.01
1.03
1.03
1.06
6.09
1.33
3.00
3.03
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

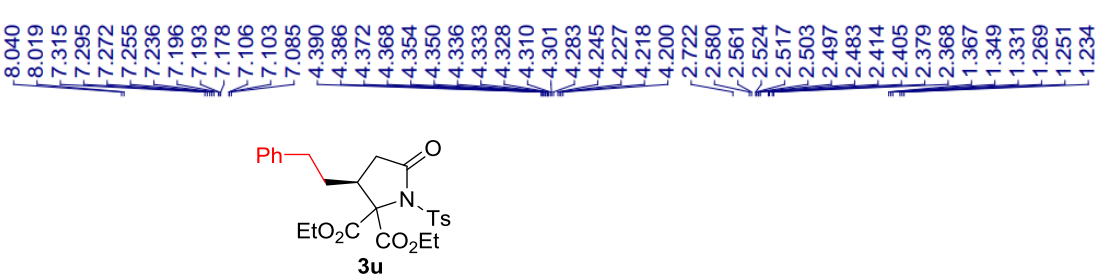

172.455
167.392
165.906
145.275
135.433
129.855
129.032
75.740
62.848
40.141
39.323
36.649
26.018
23.641
21.795
21.255
14.144
14.096
O
N
Ts
EtO2C
CO2Et
3r
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


8.015
7.994
7.299
7.278
4.373
4.347
4.342
4.335
4.329
4.324
4.317
4.313
4.287
2.560
2.540
2.512
2.492
2.394
2.337
2.302
2.288
2.254
1.845
1.838
1.817
1.337
1.334
1.320
1.316
1.302
1.298
1.251
1.200
0.843
0.826
0.809
4
O
N
Ts
EtO2C
CO2Et
3s
1.94
1.97
4.08
1.99
3.00
1.01
1.02
6.28
9.21
3.16
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

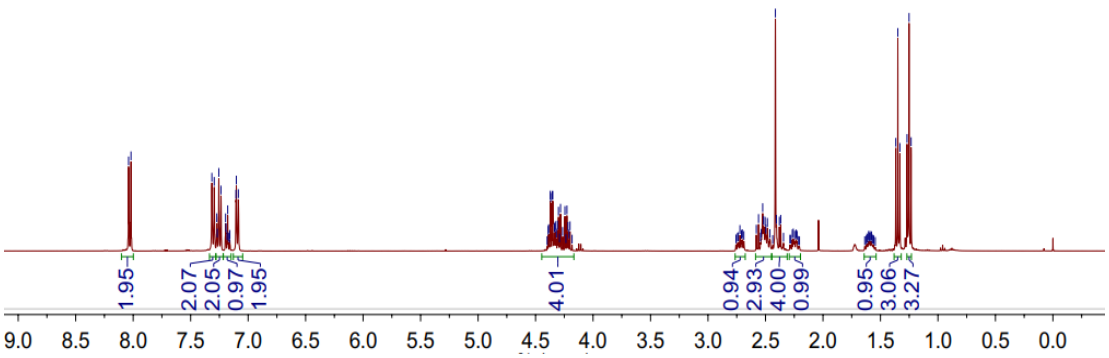

172.453
167.434
165.861
145.292
135.415
129.867
129.044
75.782
62.896
62.844
42.141
36.458
31.569
30.356
28.957
27.511
22.579
21.803
14.146
14.099
14.051
O
N
Ts
4
EtO2C
CO2Et
3s
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

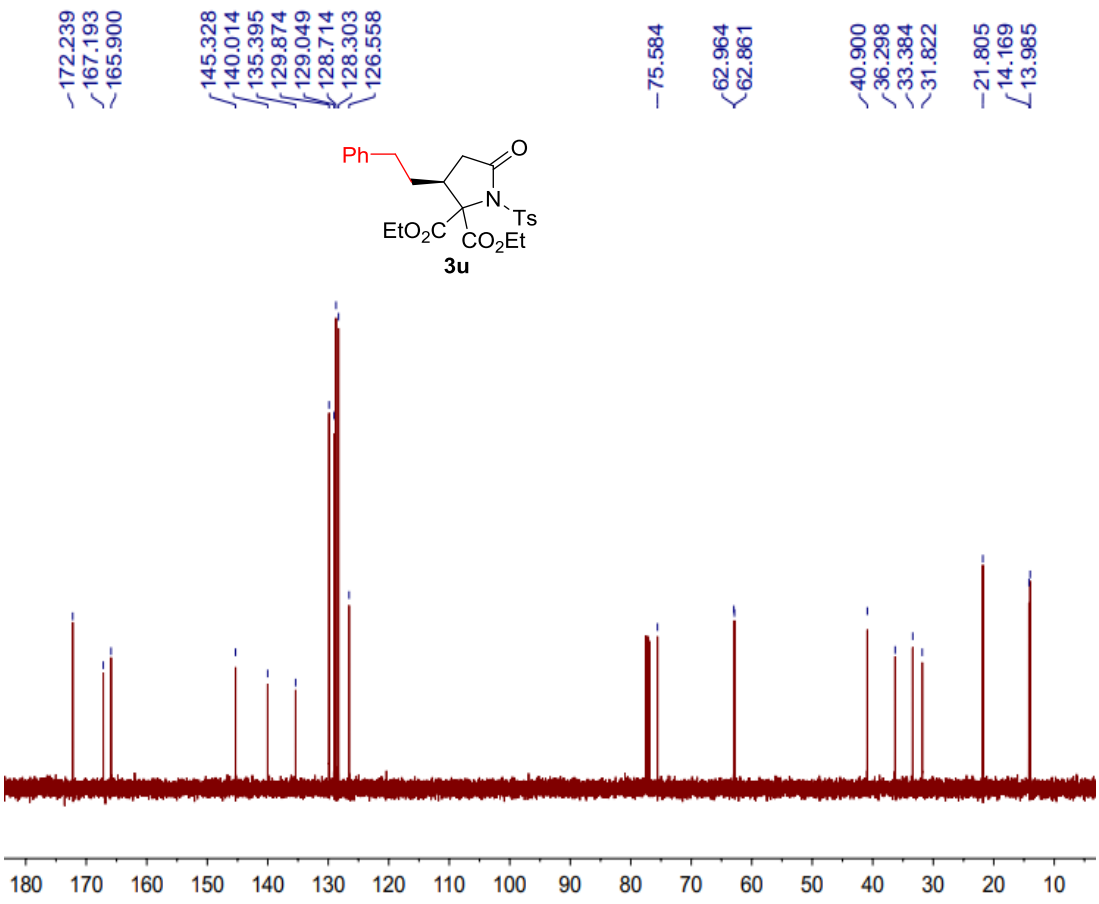

8.031
8.010
7.314
7.293
4.407
4.388
4.380
4.375
4.363
4.357
4.345
4.340
4.332
4.329
4.321
4.314
4.288
4.271
2.555
2.527
2.506
2.410
2.351
2.316
2.302
1.850
1.829
1.352
1.350
1.336
1.334
1.332
1.316
1.314
1.216
0.846
O
N
Ts
5
EtO2C
CO2Et
3t
1.94
1.99
4.01
1.91
2.93
0.99
1.06
6.04
11.07
3.00
8.0
7.5
7.0
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

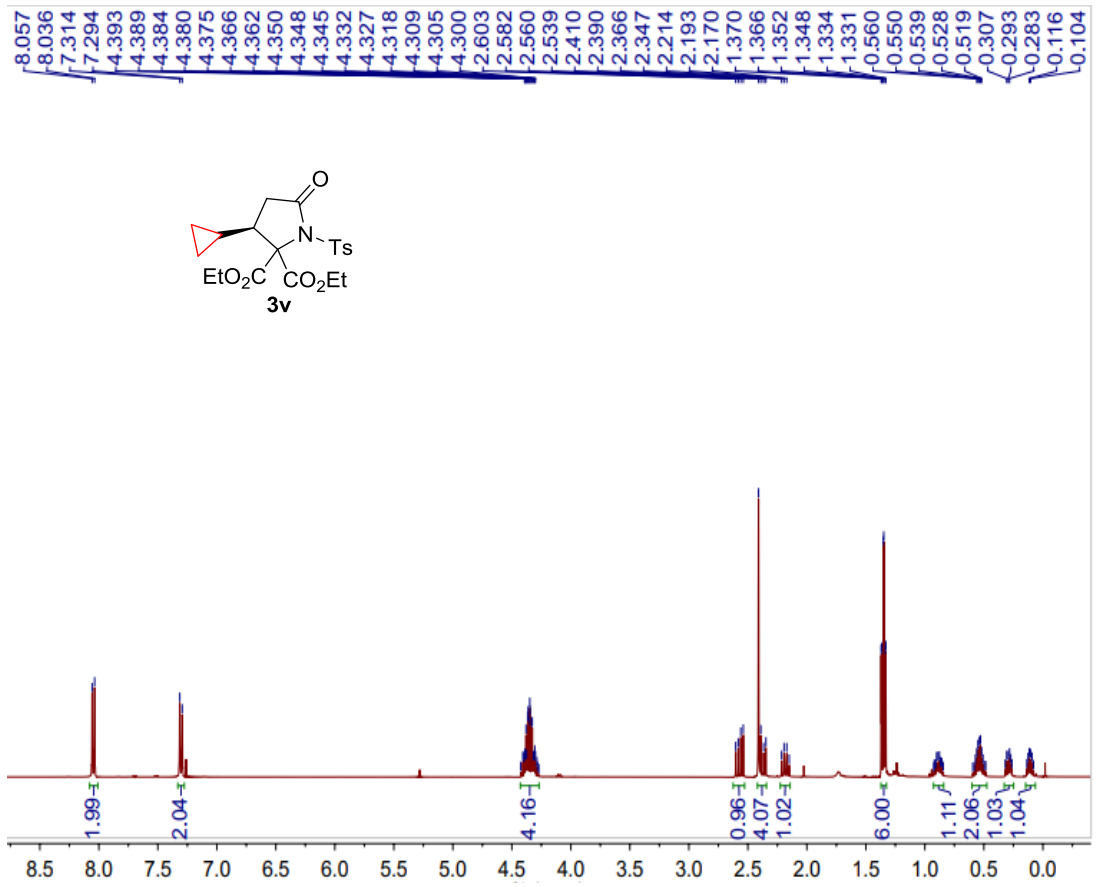

172.421
167.419
165.844
145.259
135.432
129.860
129.026
75.784
62.880
62.824
42.155
36.457
31.756
31.746
31.732
30.353
29.246
29.049
27.548
22.648
21.790
14.130
14.043
O
N
Ts
5
EtO2C
CO2Et
3t
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10

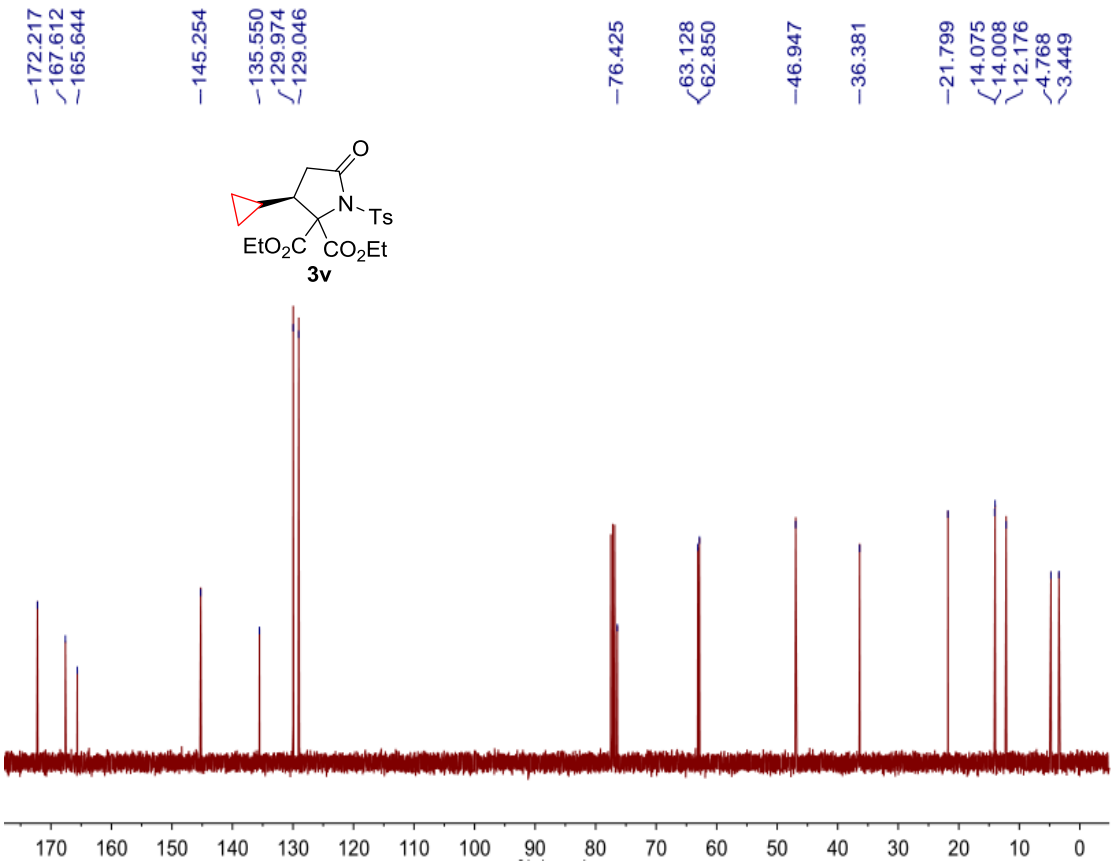

8.040
8.019
7.315
7.295
7.272
7.255
7.236
7.196
7.193
7.178
7.106
7.103
7.085
4.390
4.386
4.372
4.368
4.354
4.350
4.336
4.333
4.328
4.310
4.301
4.283
4.245
4.227
4.218
4.200
2.722
2.580
2.561
2.524
2.517
2.503
2.497
2.483
2.414
2.405
2.379
2.368
1.367
1.349
1.331
1.269
1.251
1.234

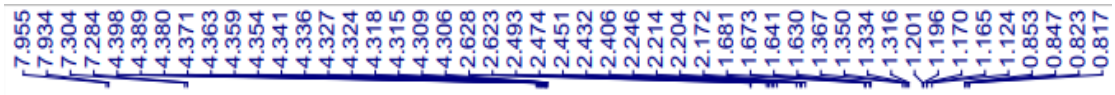
Ph
O
N
Ts
EtO2C
CO2Et
3u

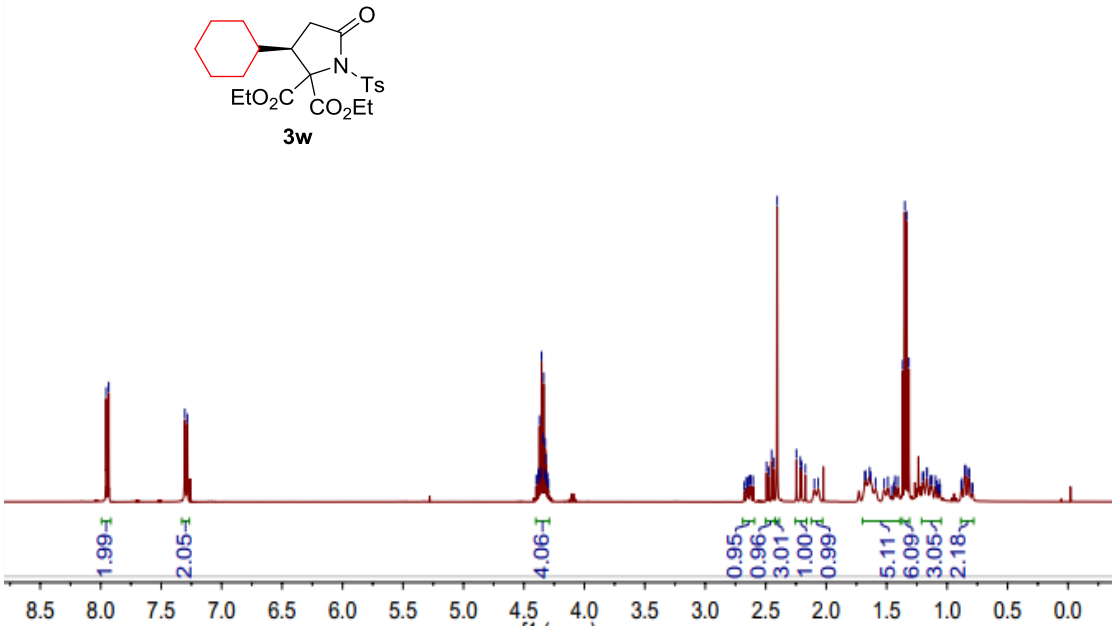

1.95
2.07
2.05
0.97
1.95
4.01
0.94
2.93
4.00
0.99
0.95
3.06
3.27
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

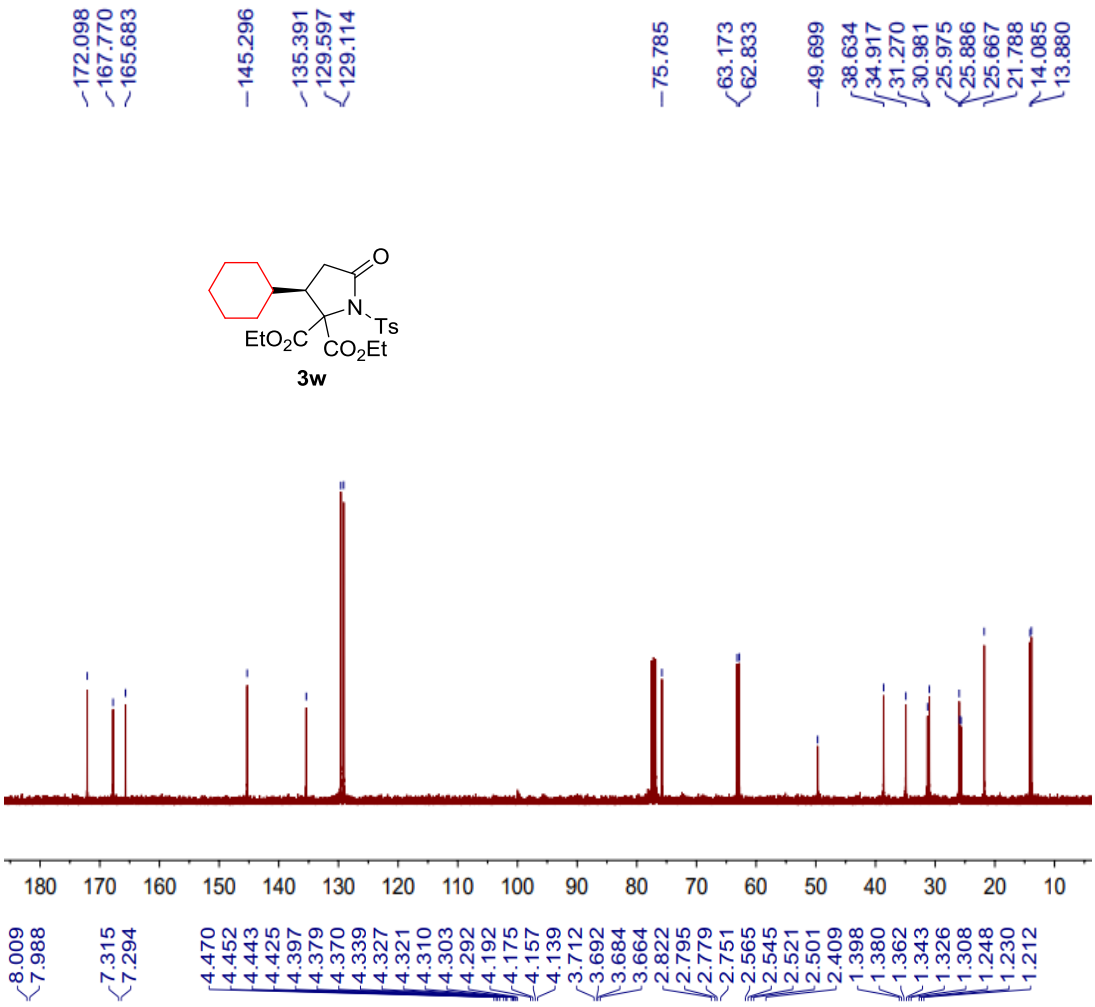

172.239
167.193
165.900
145.328
140.014
135.395
129.874
129.049
128.714
128.303
126.558
75.584
62.964
62.861
40.900
36.298
33.384
31.822
21.805
14.169
13.985
Ph
O
N
Ts
EtO2C
CO2Et
3u
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10


8.057
8.036
7.314
7.294
4.393
4.389
4.384
4.380
4.375
4.366
4.362
4.350
4.348
4.345
4.332
4.327
4.318
4.309
4.305
4.300
2.603
2.582
2.560
2.539
2.410
2.390
2.366
2.347
2.214
2.193
2.170
1.370
1.366
1.352
1.348
1.334
1.331
0.560
0.550
0.539
0.528
0.519
0.307
0.293
0.283
0.116
0.104
O
N
Ts
EtO2C
CO2Et
3v
1.99
2.04
4.16
0.96
4.07
1.02
6.00
1.11
2.06
1.03
1.04
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

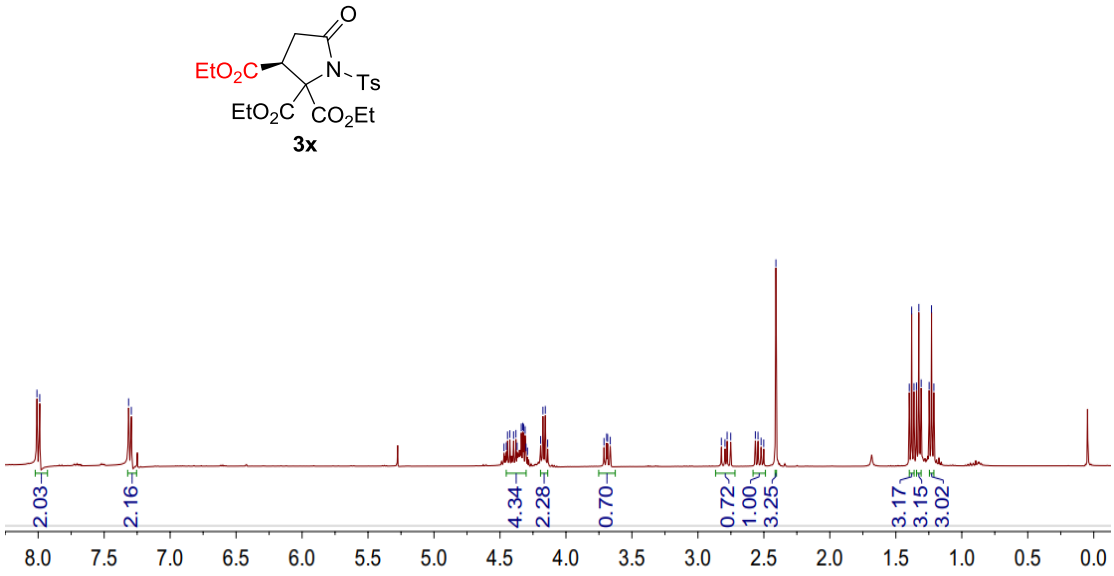

172.217
167.612
165.644
145.254
135.550
129.974
129.046
76.425
63.128
62.850
46.947
36.381
21.799
14.075
14.008
12.176
4.768
3.449
O
N
Ts
EtO2C
CO2Et
3v


7.955
7.934
7.304
7.284
4.398
4.389
4.380
4.371
4.363
4.359
4.354
4.341
4.336
4.327
4.324
4.318
4.315
4.309
4.306
2.628
2.623
2.493
2.474
2.451
2.432
2.406
2.246
2.214
2.204
2.172
1.681
1.673
1.641
1.630
1.367
1.350
1.334
1.316
1.201
1.196
1.170
1.165
1.124
0.853
0.847
0.823
0.817


O
N
Ts
EtO2C
CO2Et
3w
1.99
2.05
4.06
0.95
0.96
3.01
1.00
0.99
5.11
6.09
3.05
2.18

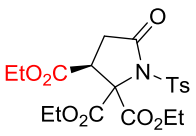

172.098
167.770
165.683
145.296
135.391
129.597
129.114
75.785
63.173
62.833
49.699
38.634
34.917
31.270
30.981
25.975
25.886
25.667
21.788
14.085
13.880
O
N
Ts
EtO2C
CO2Et
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
8.009
7.988
7.315
7.294
4.470
4.452
4.443
4.425
4.397
4.379
4.370
4.339
4.327
4.321
4.310
4.303
4.292
4.192
4.175
4.157
4.139
3.712
3.692
3.684
3.664
2.822
2.795
2.779
2.751
2.565
2.545
2.521
2.501
2.409
1.398
1.380
1.362
1.343
1.326
1.308
1.248
1.230
1.212

3w

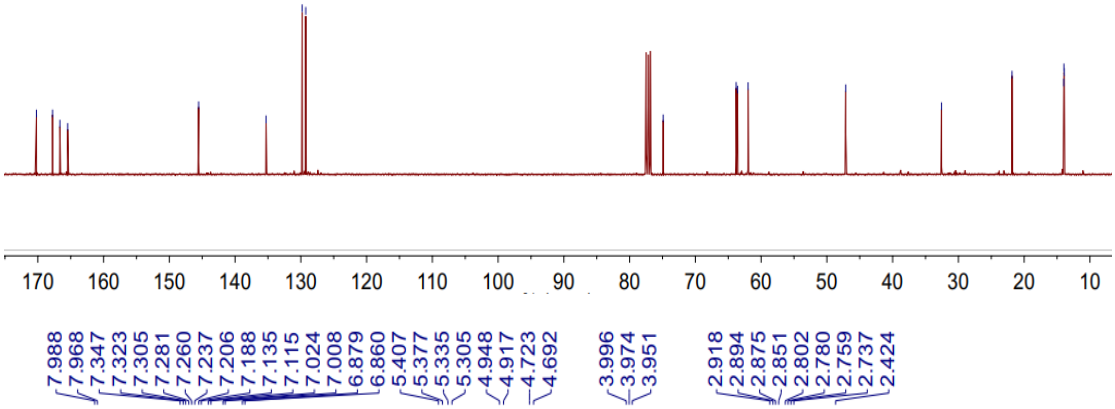

O
N
Ts
EtO2C
EtO2C
CO2Et
2.03
2.16
4.34
2.28
0.70
0.72
1.00
3.25
3.17
3.15
3.02
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0

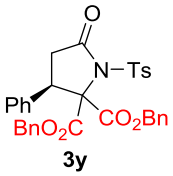
3x


170.210
167.760
166.643
165.460
145.546
135.291
129.802
129.256
74.896
63.799
63.584
61.987
47.134
32.570
21.847
13.976
13.950
13.902

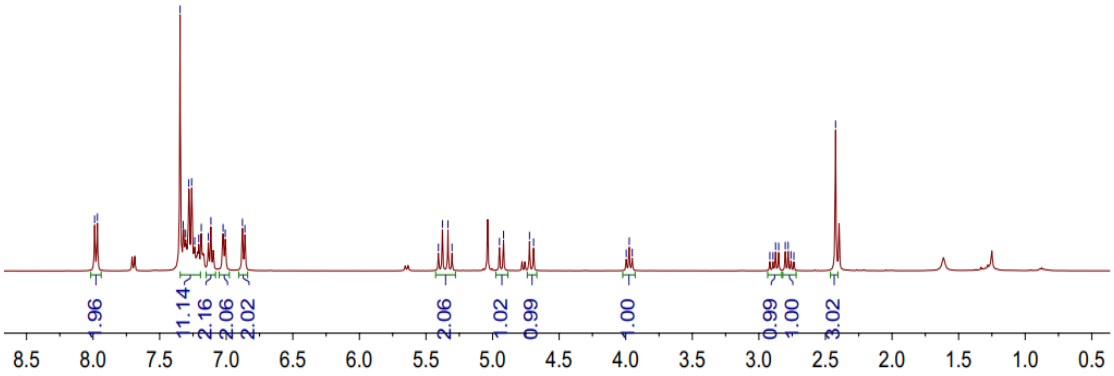

O
EtO2C
N
Ts
EtO2C
CO2Et

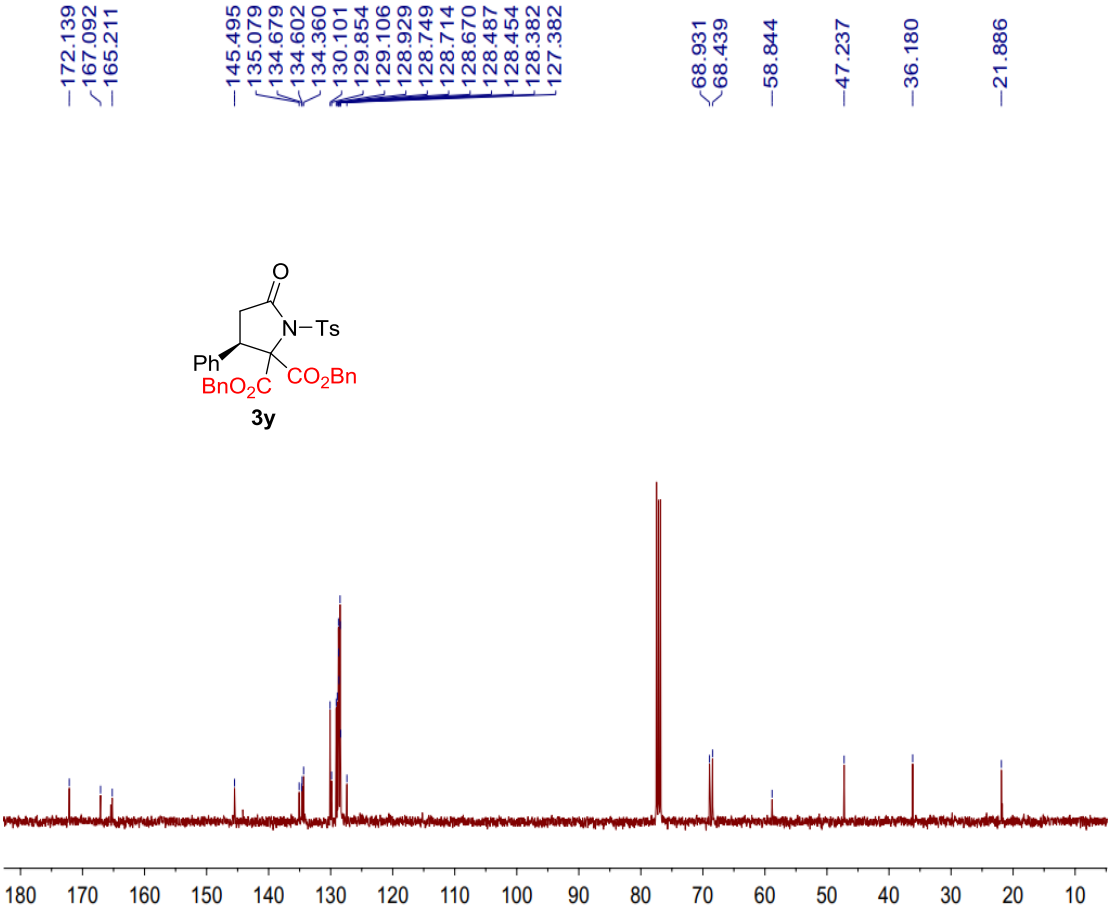
3x


170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
7.988
7.968
7.347
7.323
7.305
7.281
7.260
7.237
7.206
7.188
7.135
7.115
7.024
7.008
6.879
6.860
5.407
5.377
5.335
5.305
4.948
4.917
4.723
4.692
3.996
3.974
3.951
2.918
2.894
2.875
2.851
2.802
2.780
2.759
2.737
2.424


O
N–Ts
Ph
BnO2C
CO2Bn

3y

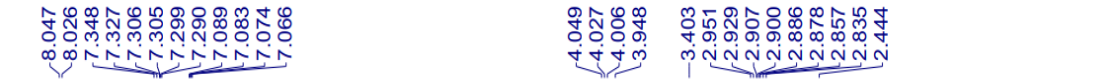

1.96
11.14
2.16
2.06
2.02
2.06
1.02
0.99
1.00
0.99
1.00
3.02
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

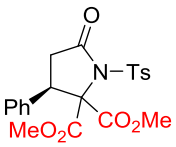

172.139
167.092
165.211
145.495
135.079
134.679
134.602
134.360
130.101
129.854
129.106
128.929
128.749
128.714
128.670
128.487
128.454
128.382
127.382
68.931
68.439
58.844
47.237
36.180
21.886

O
N–Ts
Ph
BnO2C
CO2Bn

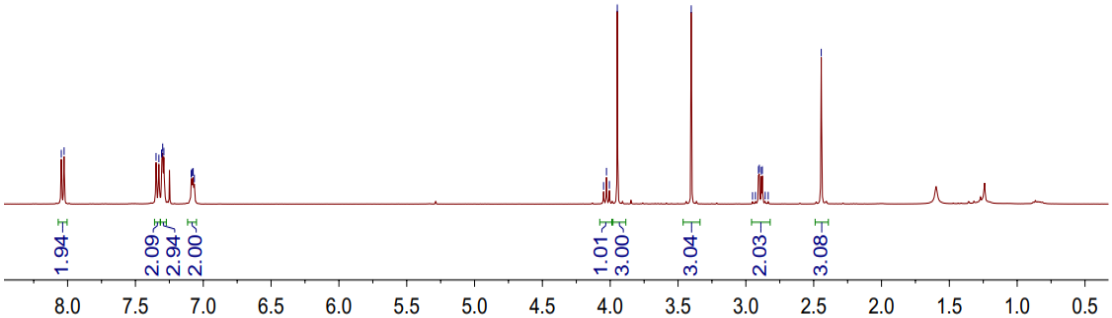
3y

180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

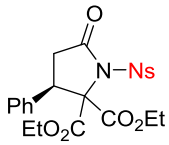

8.047
8.026
7.348
7.327
7.306
7.305
7.299
7.290
7.089
7.083
7.074
7.066
4.049
4.027
4.006
3.948
3.403
2.951
2.929
2.907
2.900
2.886
2.878
2.857
2.835
2.444


O
N–Ts
Ph
MeO2C
CO2Me

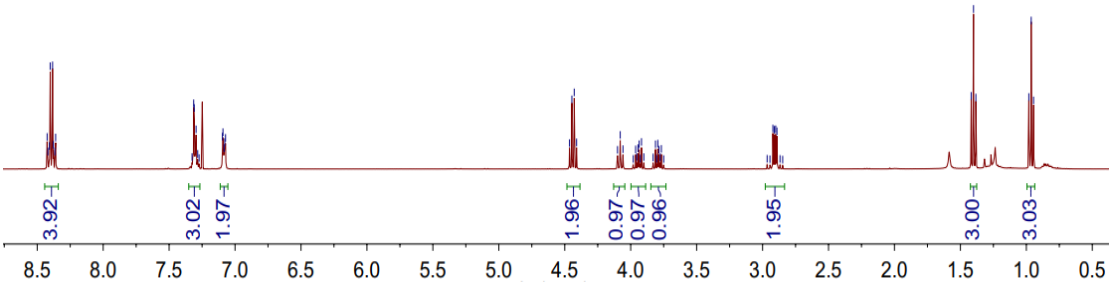
3z

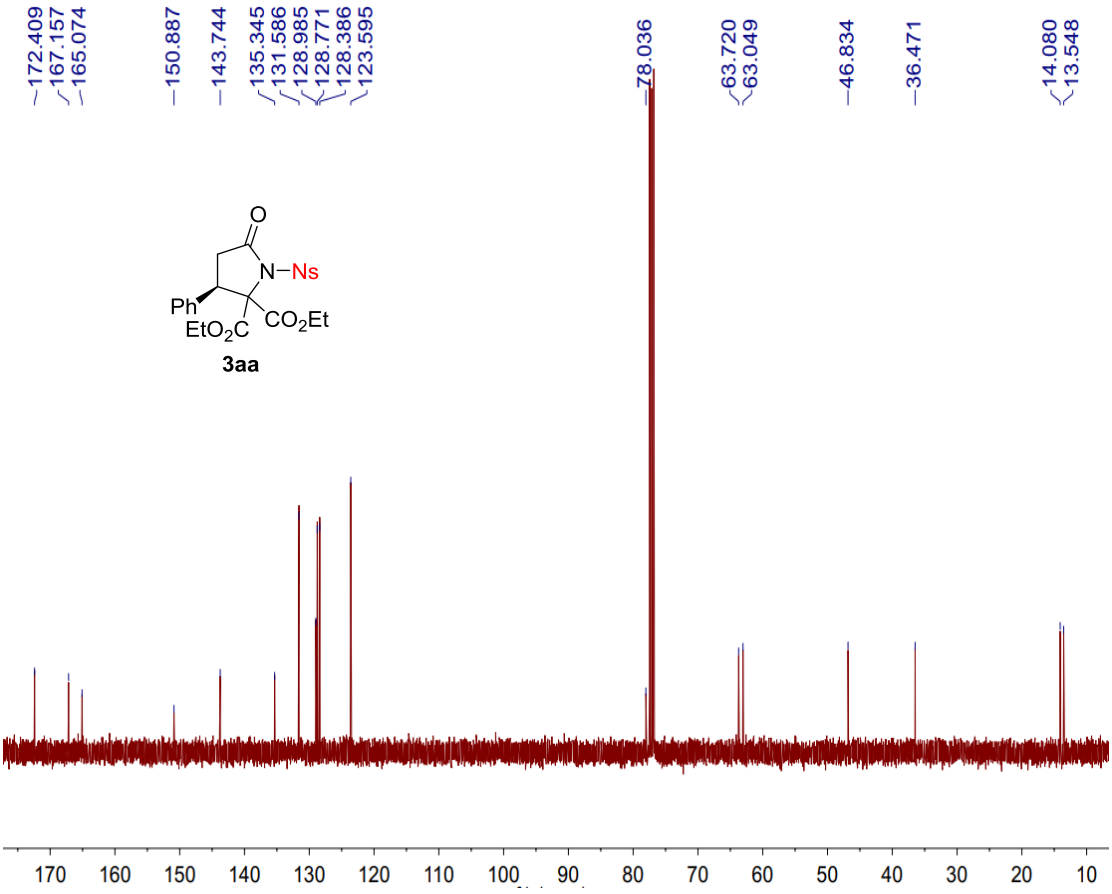

1.94
2.09
2.94
2.00
1.01
3.00
3.04
2.03
3.08
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5


8.425
8.419
8.408
8.402
8.384
8.378
8.366
8.360
7.326
7.314
7.310
7.295
7.283
7.273
7.096
7.092
7.083
7.078
7.072
4.464
4.446
4.428
4.410
4.100
4.079
4.059
3.963
3.954
3.945
3.936
3.927
3.918
3.900
3.830
3.812
3.803
3.794
3.785
3.776
3.768
2.965
2.922
2.911
2.901
2.891
1.418
1.401
1.383
0.981
0.963
0.945

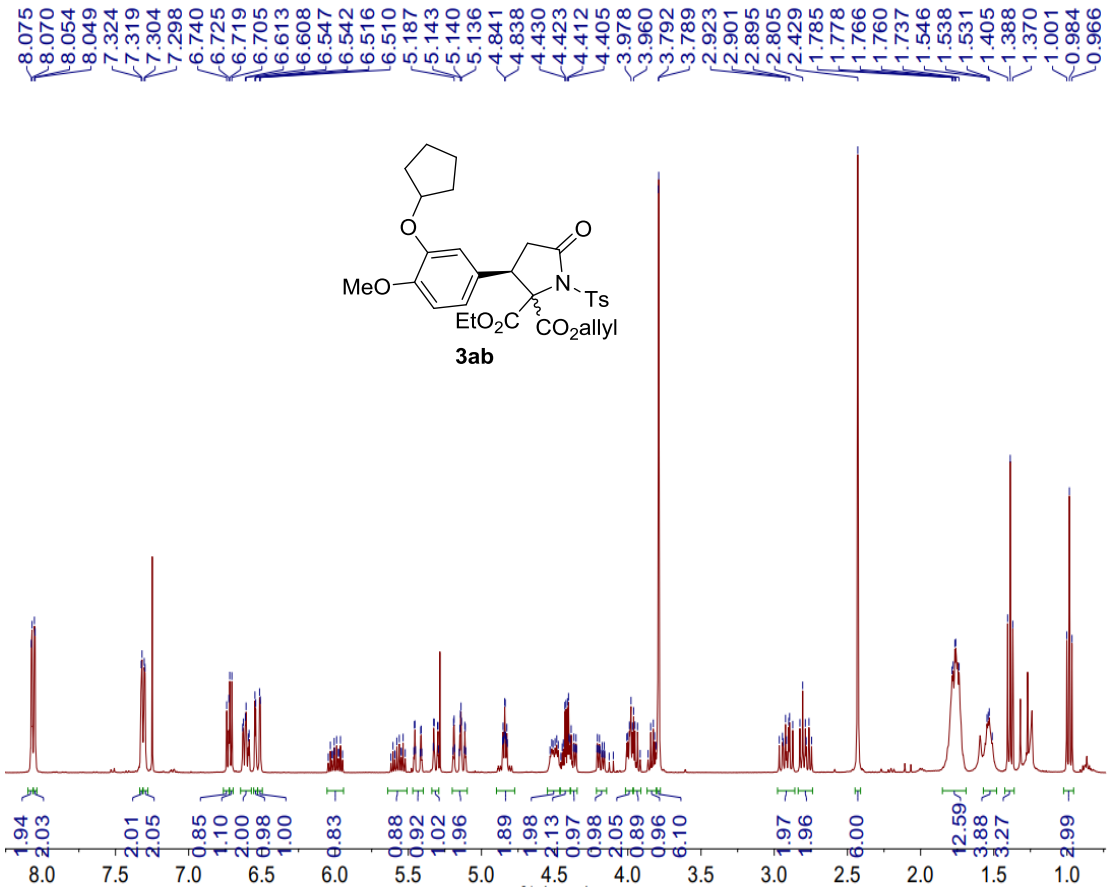

O
N–Ns
Ph
EtO2C
CO2Et

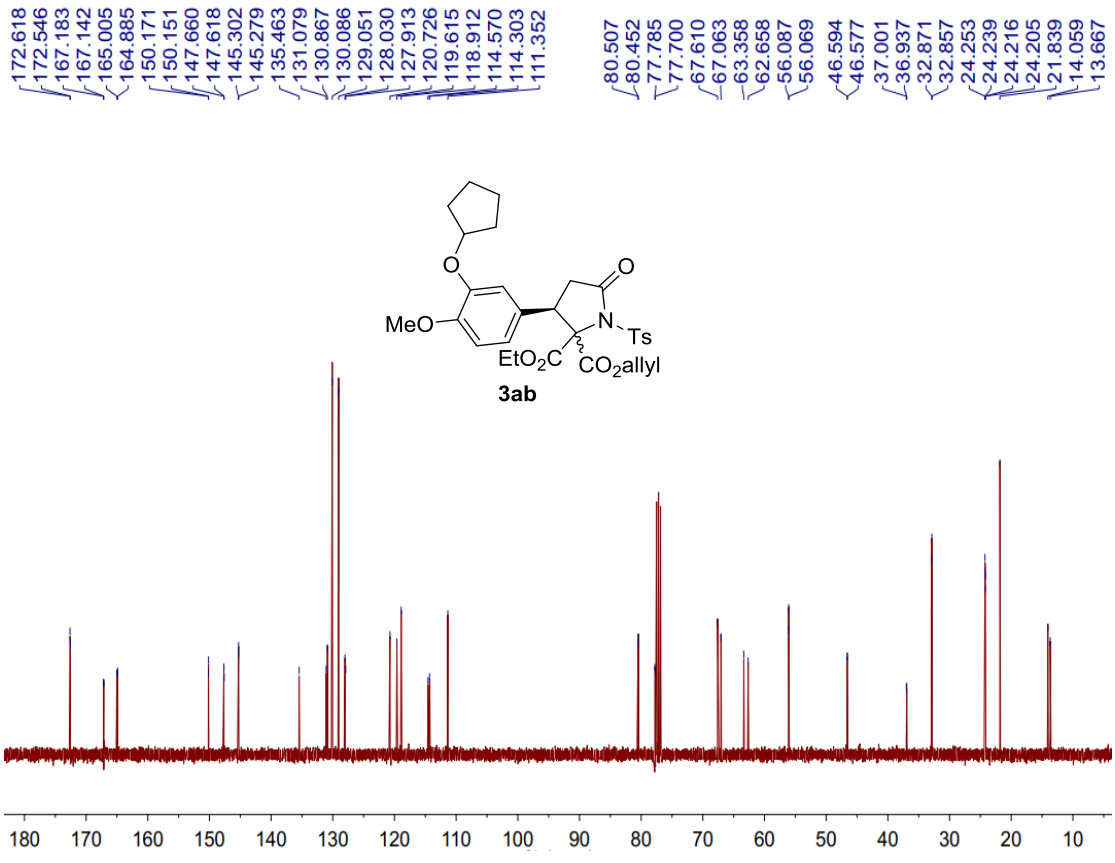
3aa


3.92
3.02
1.97
1.96
0.97
0.97
0.96
1.95
3.00
3.03
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

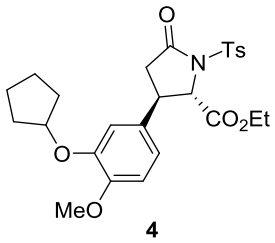

172.409
167.157
165.074
150.887
143.744
135.345
131.586
128.985
128.771
128.386
123.595
78.036
63.720
63.049
46.834
36.471
14.080
13.548
O
N–Ns
Ph
EtO2C
CO2Et
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

3aa

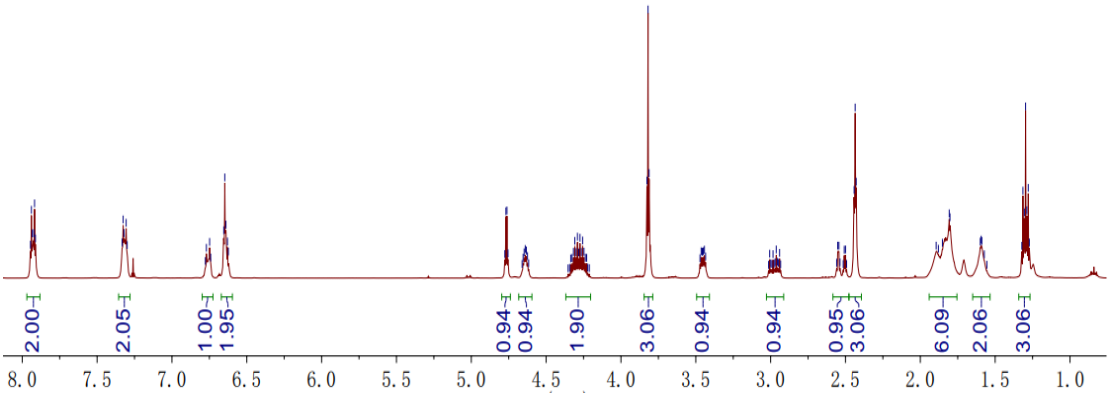

8.075
8.070
8.054
8.049
7.324
7.319
7.304
7.298
6.740
6.725
6.719
6.705
6.613
6.608
6.547
6.542
6.516
6.510
5.187
5.143
5.140
5.136
4.841
4.838
4.430
4.423
4.412
4.405
3.978
3.960
3.792
3.789
2.923
2.901
2.895
2.805
2.429
1.785
1.778
1.766
1.760
1.737
1.546
1.538
1.531
1.405
1.388
1.370
1.001
0.984
0.966
MeO
O
O
N
Ts
EtO2C
CO2allyl
3ab
1.94
2.03
2.01
2.05
0.85
1.10
2.00
6.98
1.00
0.83
0.88
0.92
1.02
1.96
1.89
1.98
2.13
0.97
0.98
2.05
0.89
0.96
6.10
1.97
1.96
6.00
12.59
3.88
3.27
2.99
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


172.618
172.546
167.183
167.142
165.005
164.885
150.171
150.151
147.660
147.618
145.302
145.279
135.463
131.079
130.867
130.086
129.051
128.030
127.913
120.726
119.615
118.912
114.570
114.303
111.352
80.507
80.452
77.785
77.700
67.610
67.063
63.358
62.658
56.087
56.069
46.594
46.577
37.001
36.937
32.871
32.857
24.253
24.239
24.216
24.205
21.839
14.059
13.667
MeO
O
O
N
Ts
EtO2C
CO2allyl
3ab
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

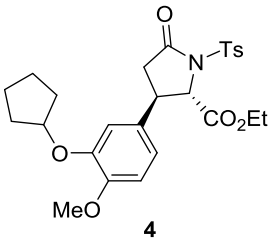

7.945
7.939
7.934
7.923
7.918
7.912
7.333
7.326
7.320
7.306
7.299
6.770
6.748
6.654
6.647
6.639
6.629
4.769
4.762
4.639
4.309
4.291
4.274
4.256
3.826
3.819
3.812
3.442
2.963
2.552
2.544
2.508
2.500
2.442
2.435
2.428
1.894
1.879
1.852
1.807
1.802
1.599
1.594
1.589
1.322
1.314
1.305
1.297
1.288
1.279
1.272


O
N
Ts
CO2Et
O
MeO

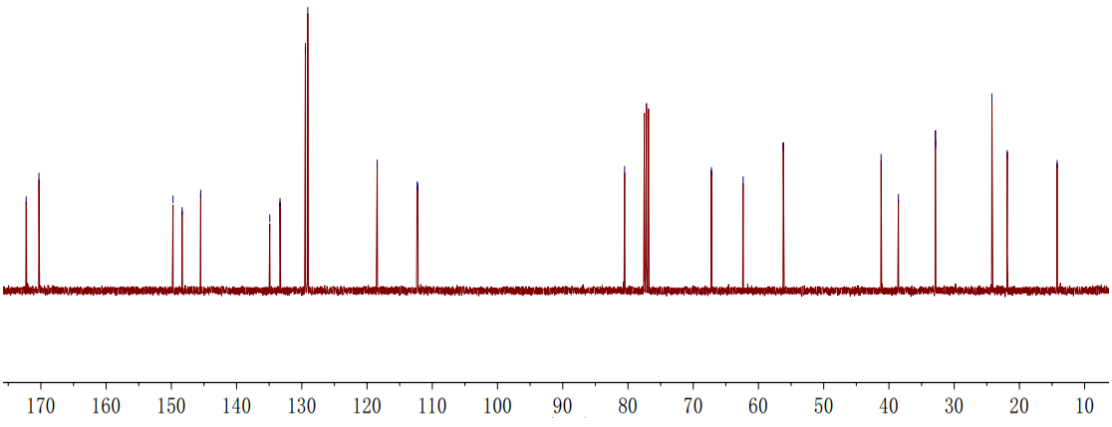
4

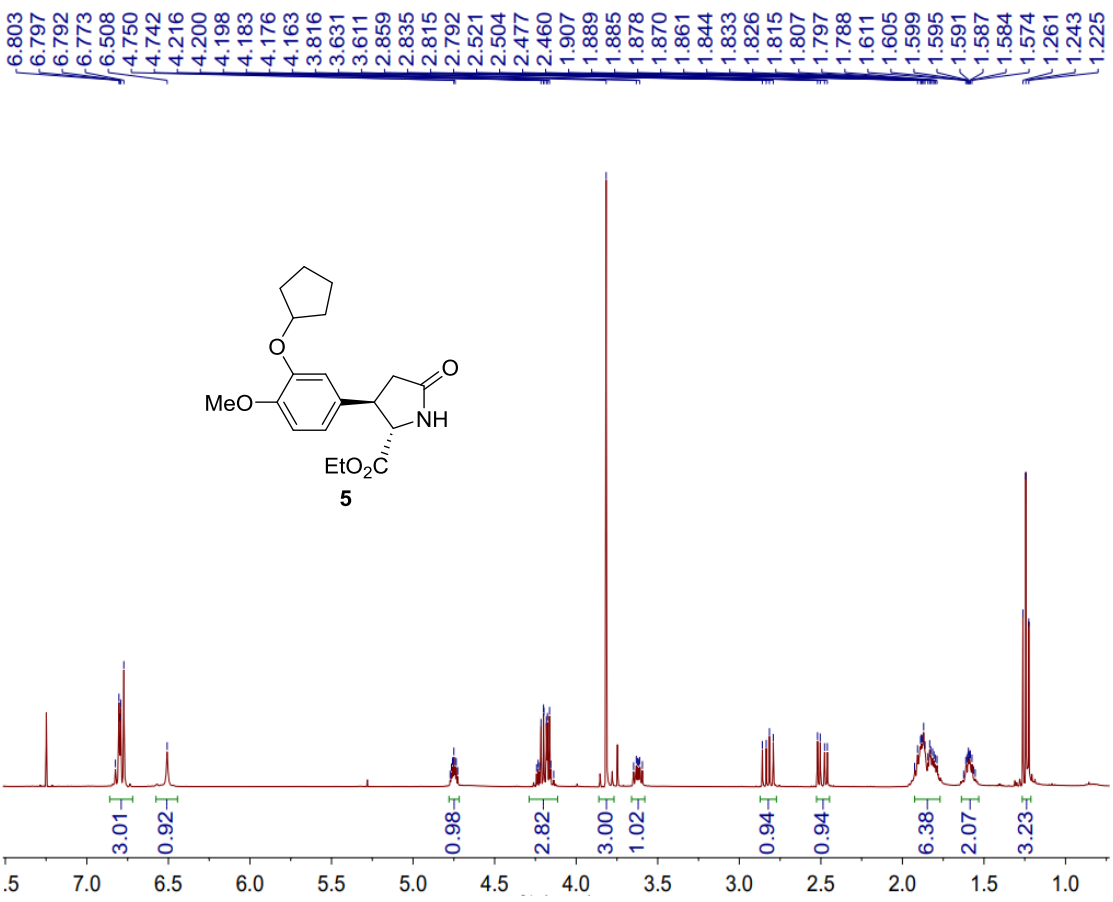

2.00
2.05
1.00
1.95
0.94
0.94
1.90
3.06
0.94
0.94
0.95
3.06
6.09
2.06
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0

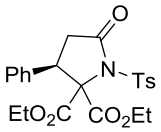

172.247
170.291
149.743
148.346
145.498
134.911
133.340
129.452
129.081
118.443
112.319
112.214
80.524
67.216
62.350
56.195
41.206
38.550
32.888
32.828
24.212
21.862
14.222


O
N
Ts
CO2Et
O
MeO

4

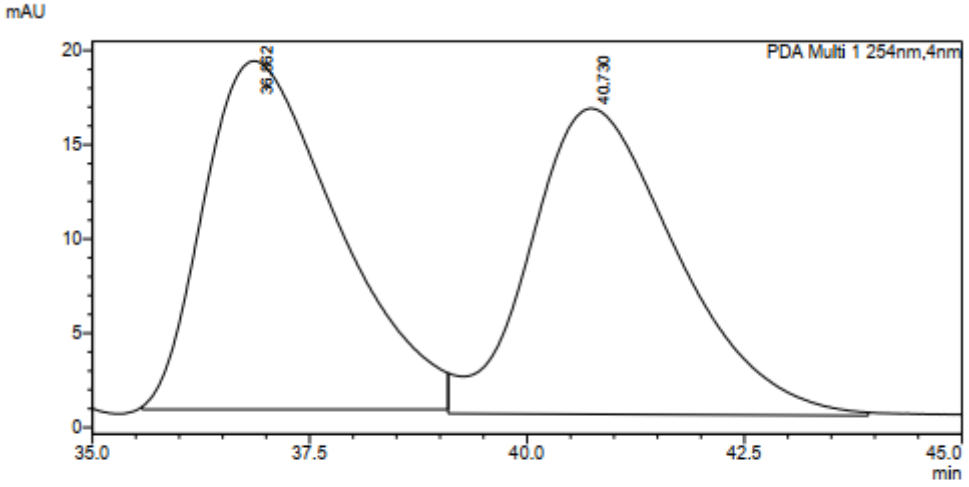

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10


6.803
6.797
6.792
6.773
6.508
4.750
4.742
4.216
4.200
4.198
4.183
4.176
4.163
3.816
3.631
3.611
2.859
2.835
2.815
2.792
2.521
2.504
2.477
2.460
1.907
1.889
1.885
1.878
1.870
1.861
1.844
1.833
1.826
1.815
1.807
1.797
1.788
1.611
1.605
1.599
1.595
1.591
1.587
1.584
1.574
1.261
1.243
1.225
O
MeO
O
NH
EtO2C
5
3.01
0.92
0.98
2.82
3.00
1.02
0.94
0.94
6.38
2.07
3.23
.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



3a

<Chromatogram>

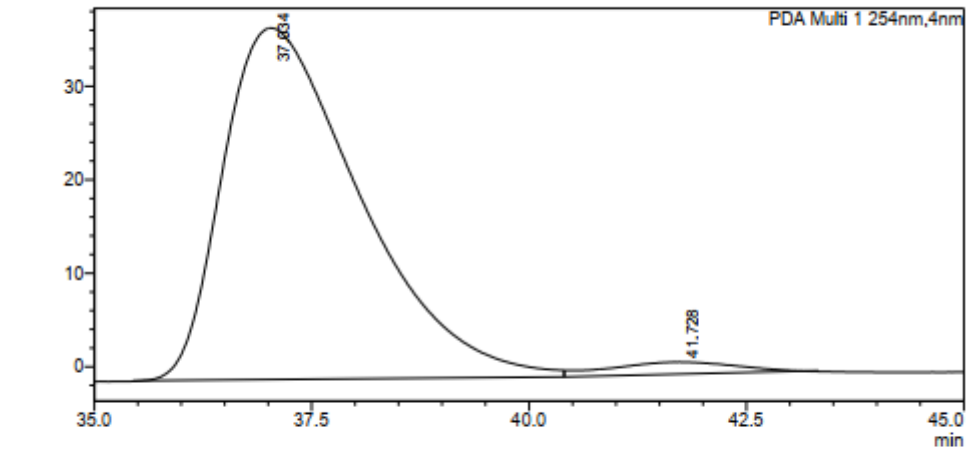


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	36.862	1975895	18481	50.859
2	40.730	1909170	16226	49.141
Total		3885064	34707	100.000

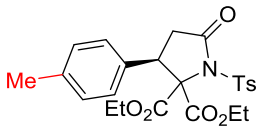
<Chromatogram>



<Peak Table>

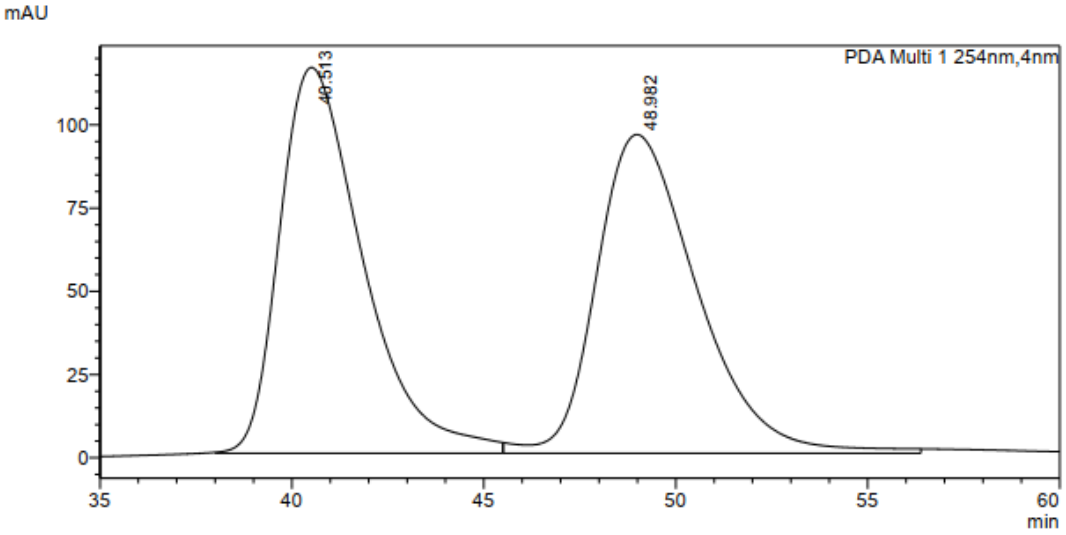
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	37.034	4122589	37592	96.935
2	41.728	130336	1285	3.065
Total		4252925	38876	100.000



3b

<Chromatogram>

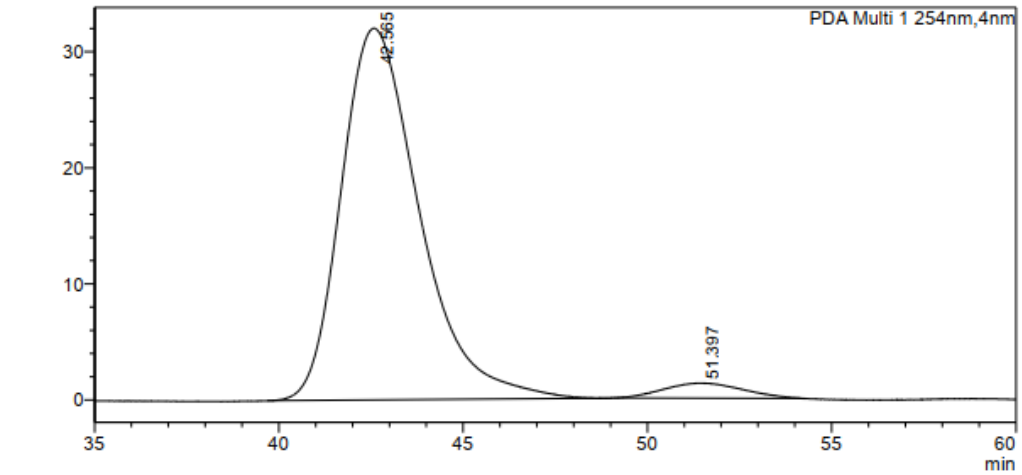


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	40.513	17495276	49.981	115880
2	48.982	17508852	50.019	95729
Total		35004127	100.000	211608

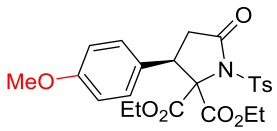
<Chromatogram>



<Peak Table>

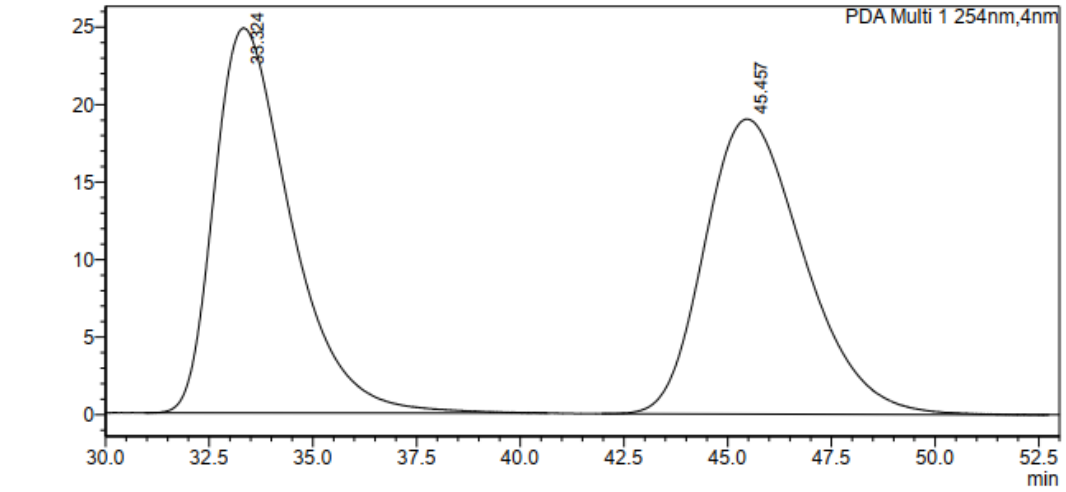
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	42.565	4724860	96.073	32007
2	51.397	193105	3.927	1295
Total		4917965	100.000	33301



3c

<Chromatogram>

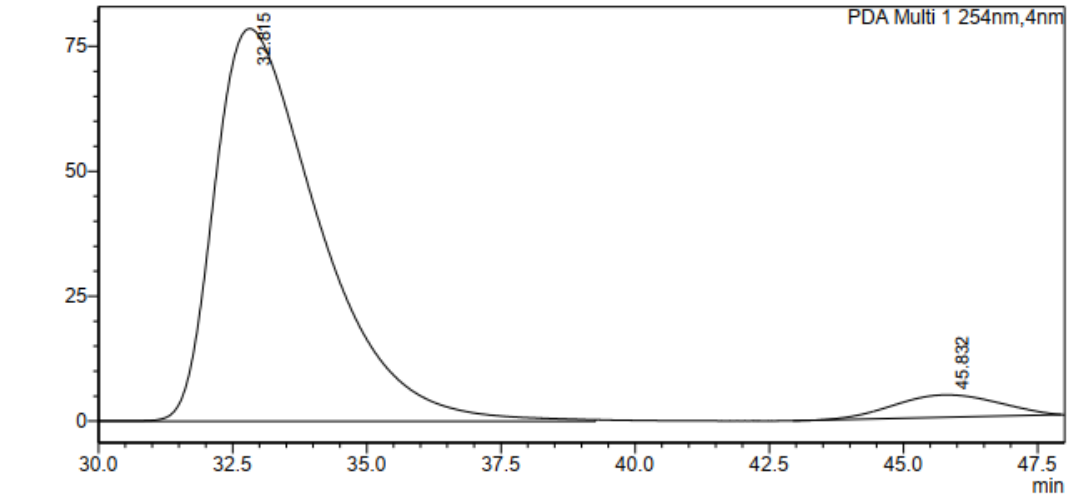


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	33.324	3190919	50.093	24831
2	45.457	3179040	49.907	19028
Total		6369960	100.000	43858

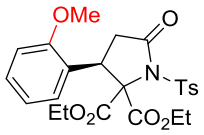
<Chromatogram>



<Peak Table>

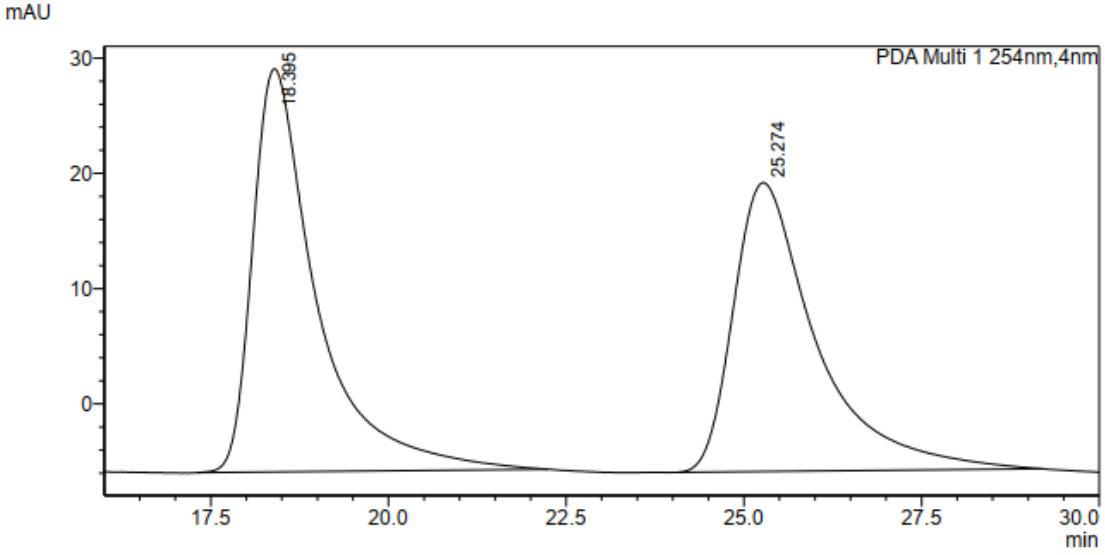
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	32.815	10668798	94.614	78581
2	45.832	607342	5.386	4476
Total		11276140	100.000	83058



3d

<Chromatogram>

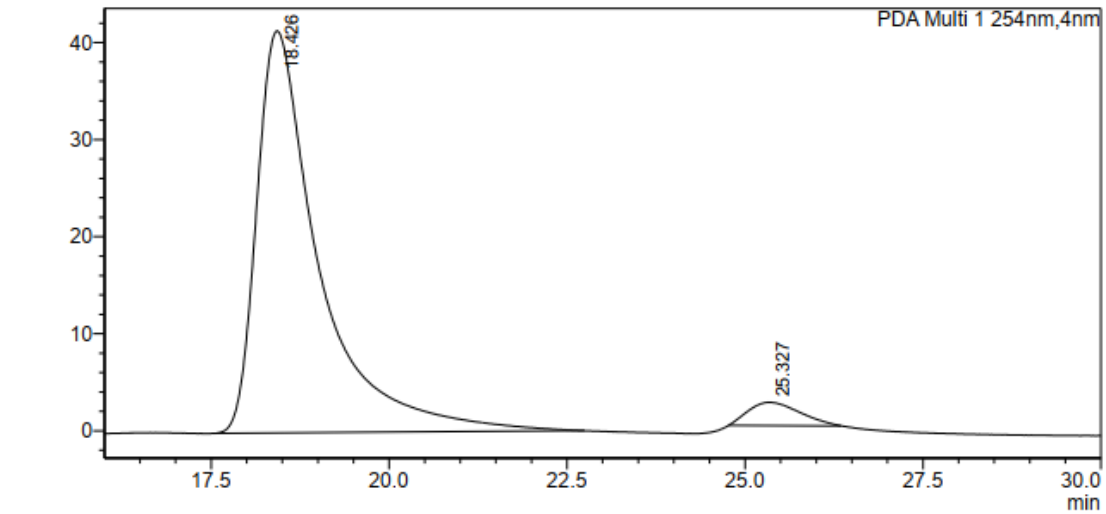


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	18.395	2200911	34963	51.908
2	25.274	2039111	25051	48.092
Total		4240021	60013	100.000

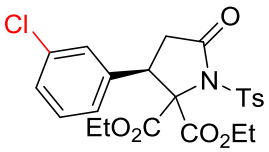
<Chromatogram>



<Peak Table>

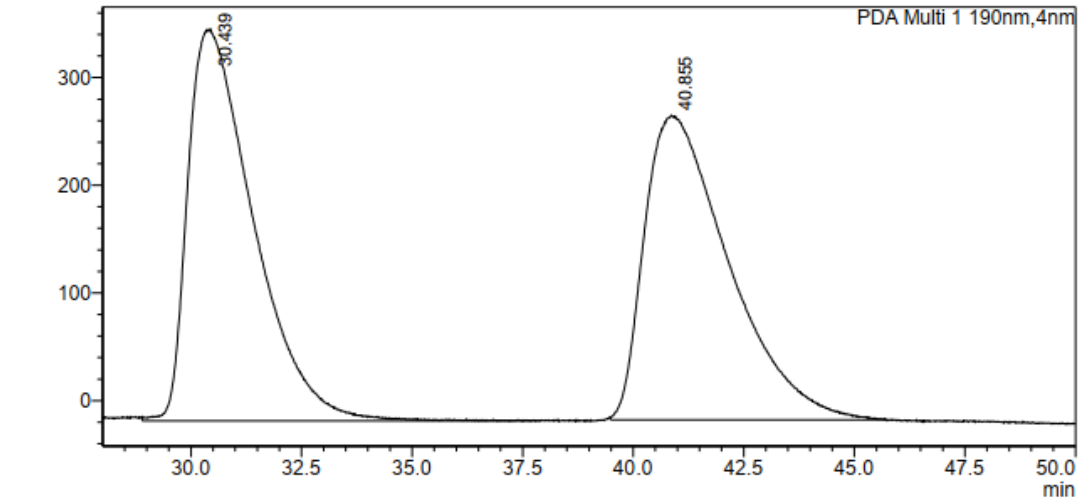
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	18.426	2525357	41420	95.440
2	25.327	120668	2391	4.560
Total		2646025	43811	100.000



3e

<Chromatogram>

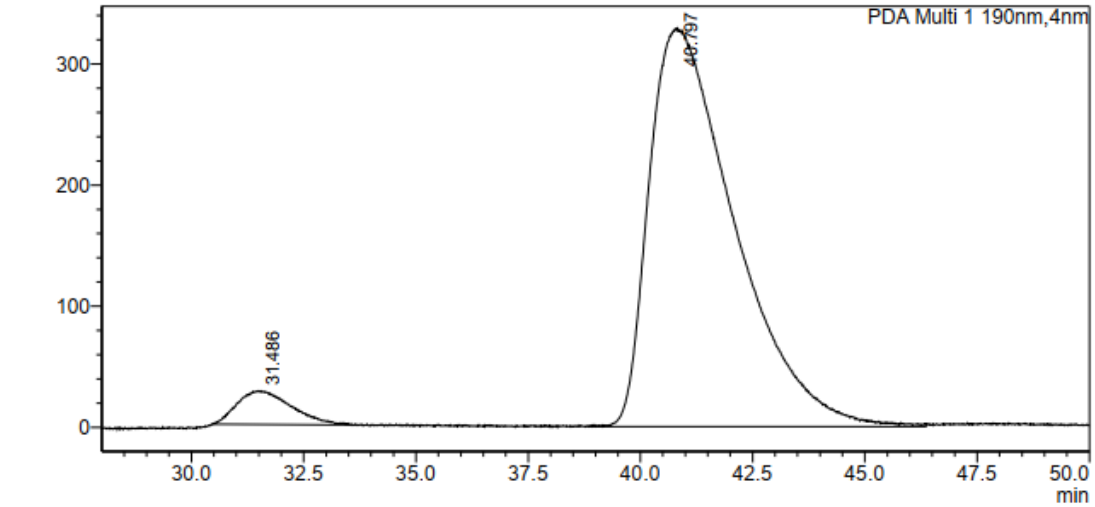


<Peak Table>

PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%	Height
1	30.439	37610210	50.094	363829
2	40.855	37469676	49.906	282481
Total		75079887	100.000	646310

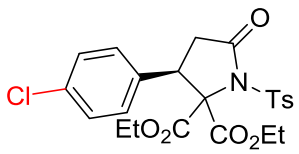
<Chromatogram>



<Peak Table>

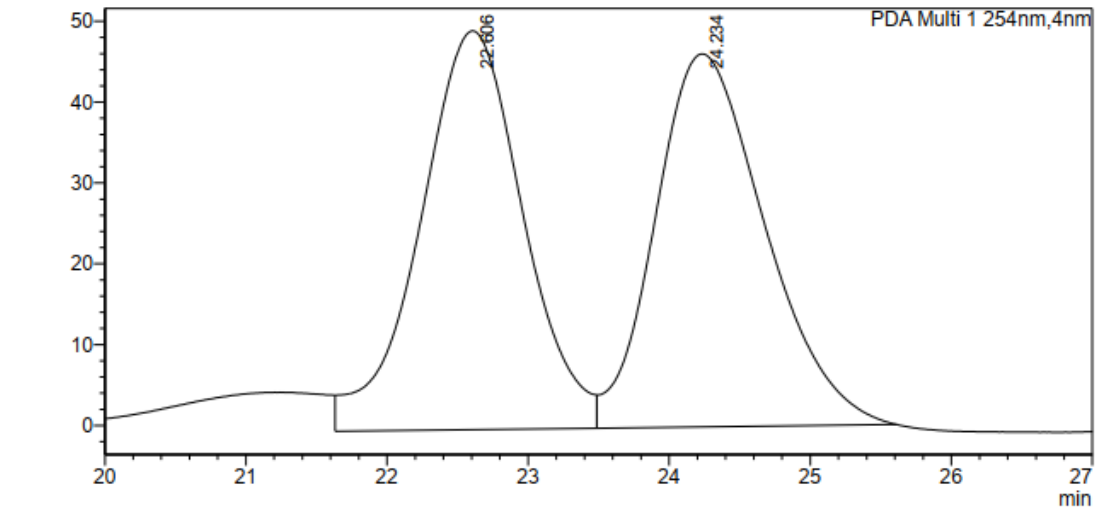
PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%	Height
1	31.486	2326632	5.081	27686
2	40.797	43462886	94.919	328492
Total		45789517	100.000	356178



3f

<Chromatogram>

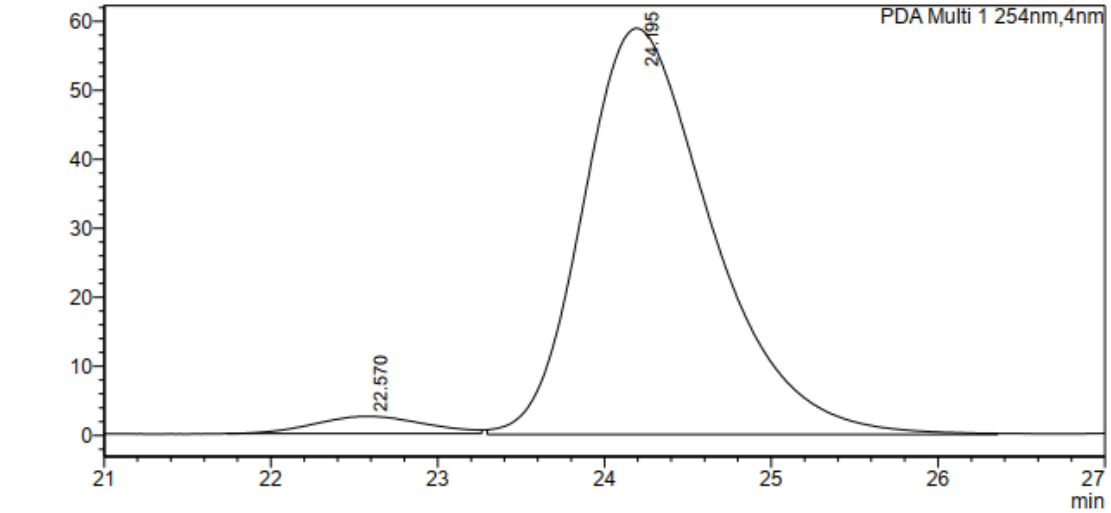


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	22.606	2499057	50.093	49334
2	24.234	2489790	49.907	46142
Total		4988847	100.000	95476

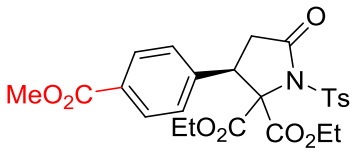
<Chromatogram>



<Peak Table>

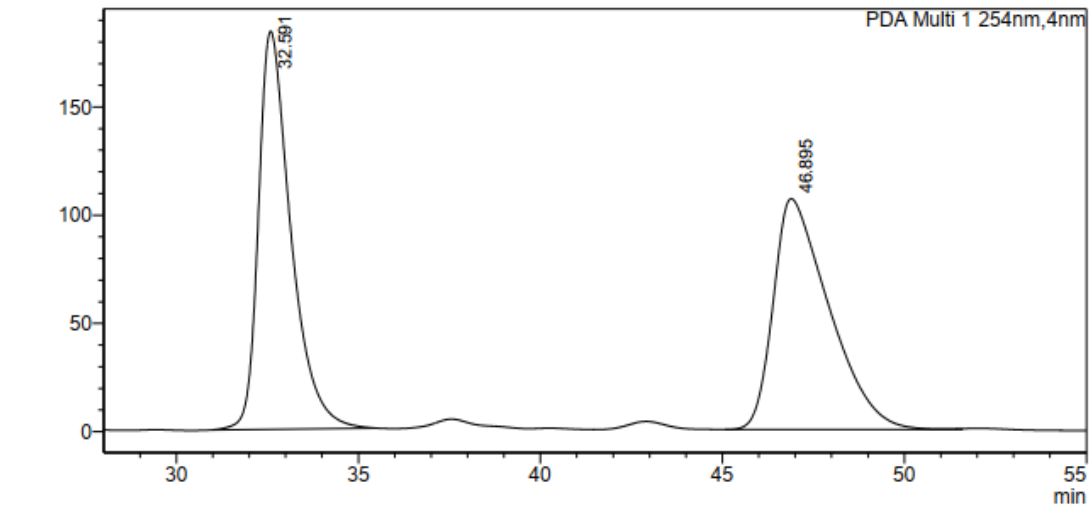
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	22.570	114887	3.511	2497
2	24.195	3157466	96.489	58859
Total		3272353	100.000	61356



3g

<Chromatogram>

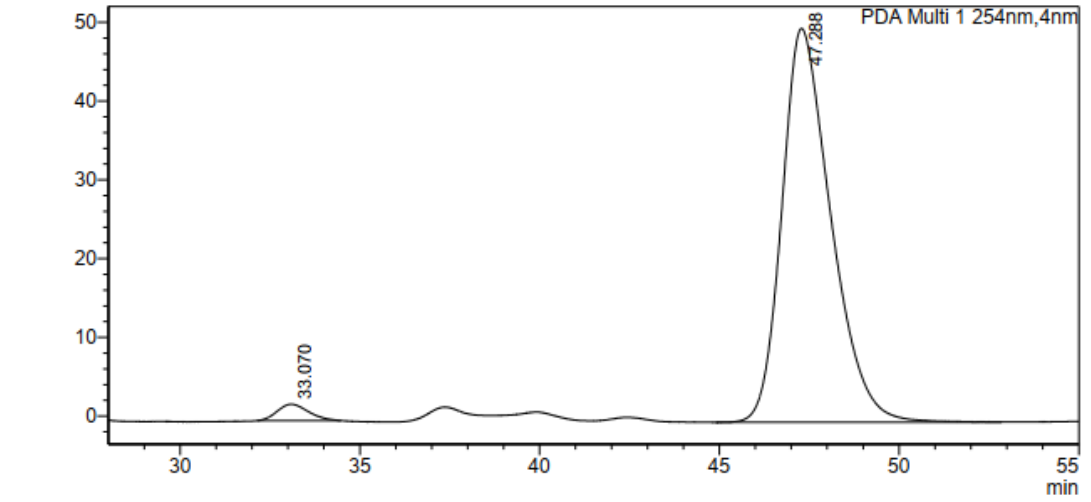


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	32.591	11405105	50.058	183846
2	46.895	11378724	49.942	106568
Total		22783830	100.000	290414

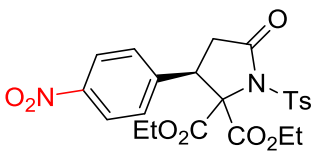
<Chromatogram>



<Peak Table>

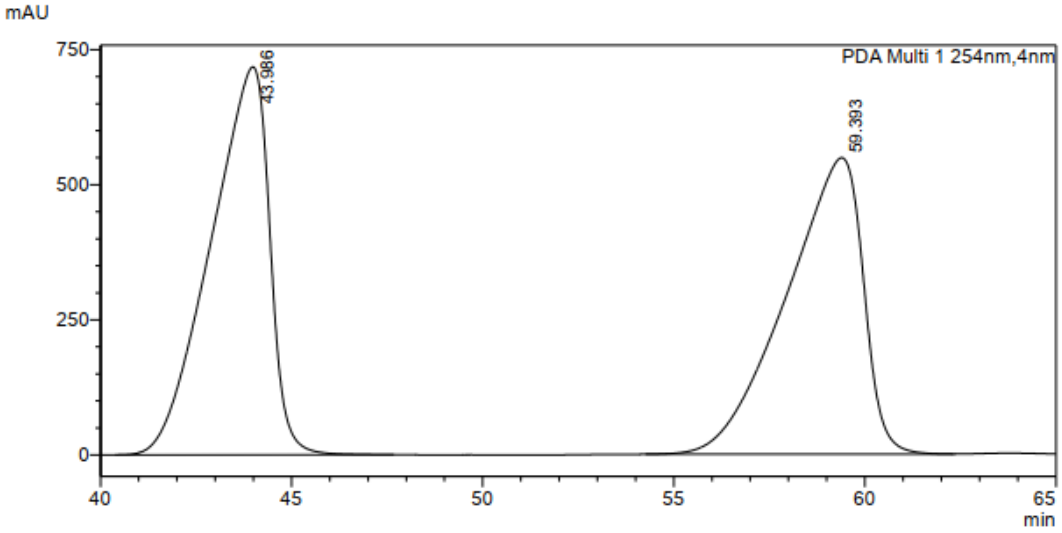
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	33.070	126245	2.593	2084
2	47.288	4742940	97.407	49996
Total		4869185	100.000	52080



3h

<Chromatogram>

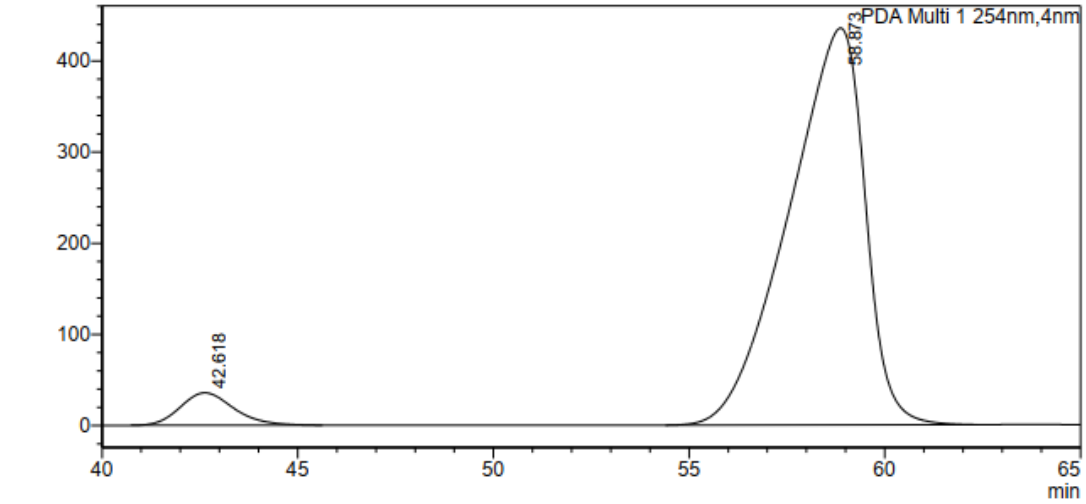


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	43.986	77022294	50.074	717790
2	59.393	76793221	49.926	548430
Total		153815515	100.000	1266220

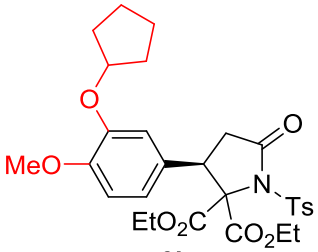
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

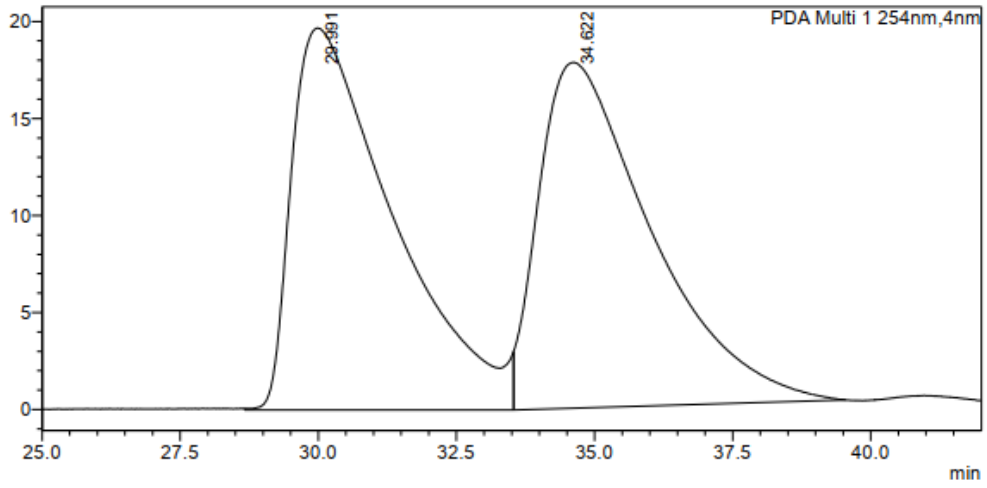
Peak#	Ret. Time	Area	Area%	Height
1	42.618	3398493	5.448	35608
2	58.873	58976695	94.552	435225
Total		62375188	100.000	470834



3i

<Chromatogram>

mAU



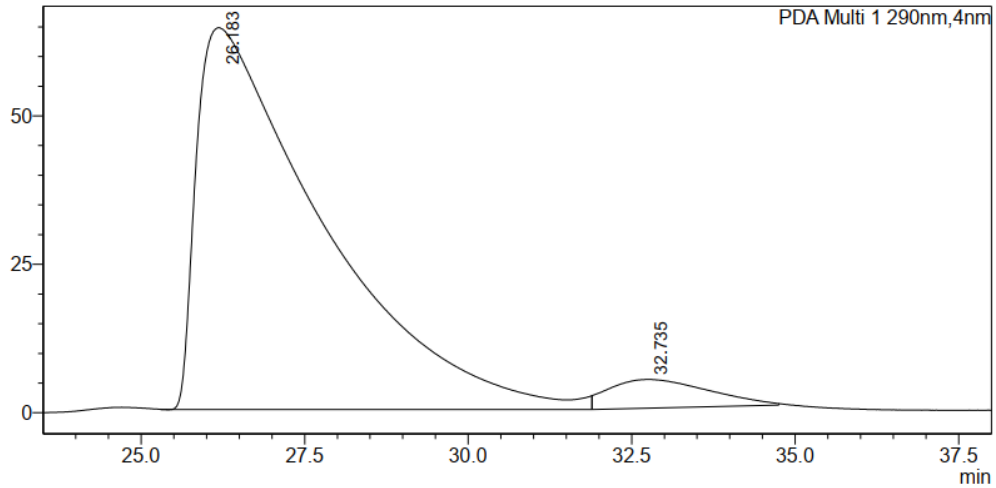
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	29.991	2516362	49.942	19689
2	34.622	2522225	50.058	17828
Total		5038587	100.000	37517

<Chromatogram>

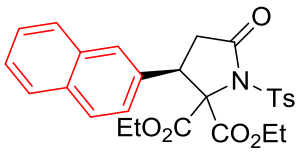
mAU



<Peak Table>

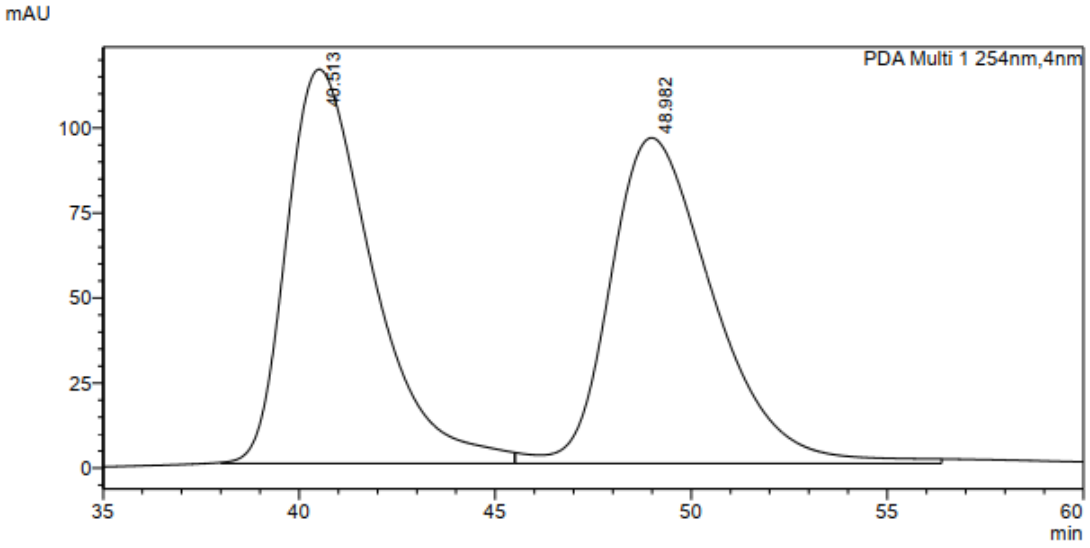
PDA Ch1 290nm

Peak#	Ret. Time	Area	Height	Area%
1	26.183	8627803	64273	94.435
2	32.735	508426	4830	5.565
Total		9136229	69104	100.000



3j

<Chromatogram>

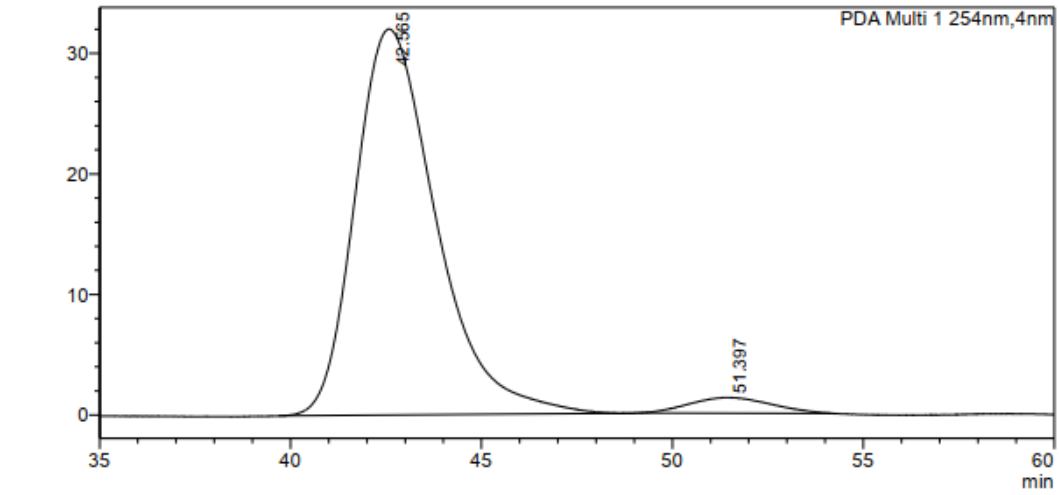


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	40.513	17495276	49.981	115880
2	48.982	17508852	50.019	95729
Total		35004127	100.000	211608

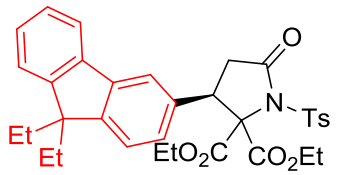
<Chromatogram>



<Peak Table>

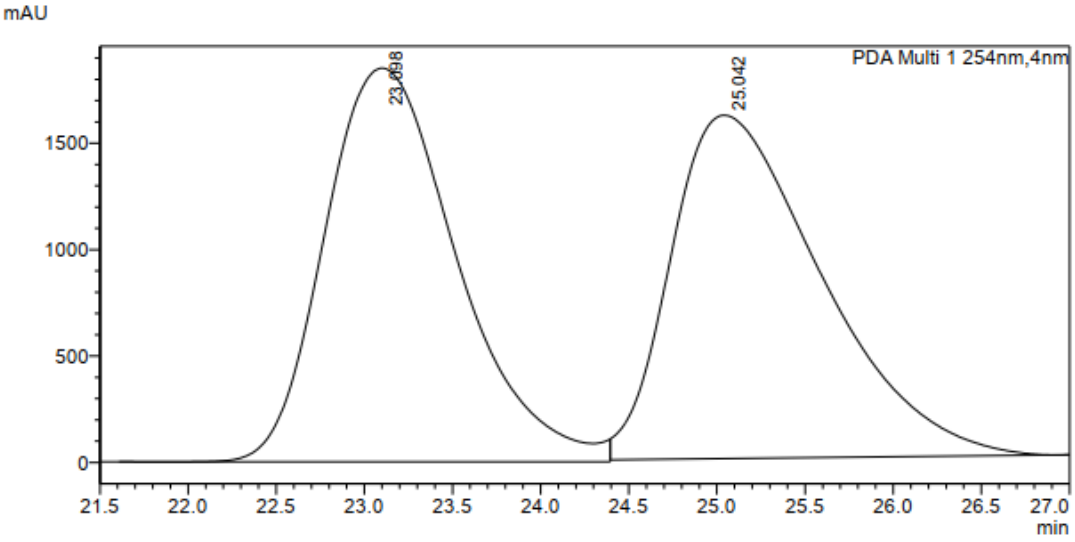
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	42.565	4724860	96.073	32007
2	51.397	193105	3.927	1295
Total		4917965	100.000	33301



3k

<Chromatogram>

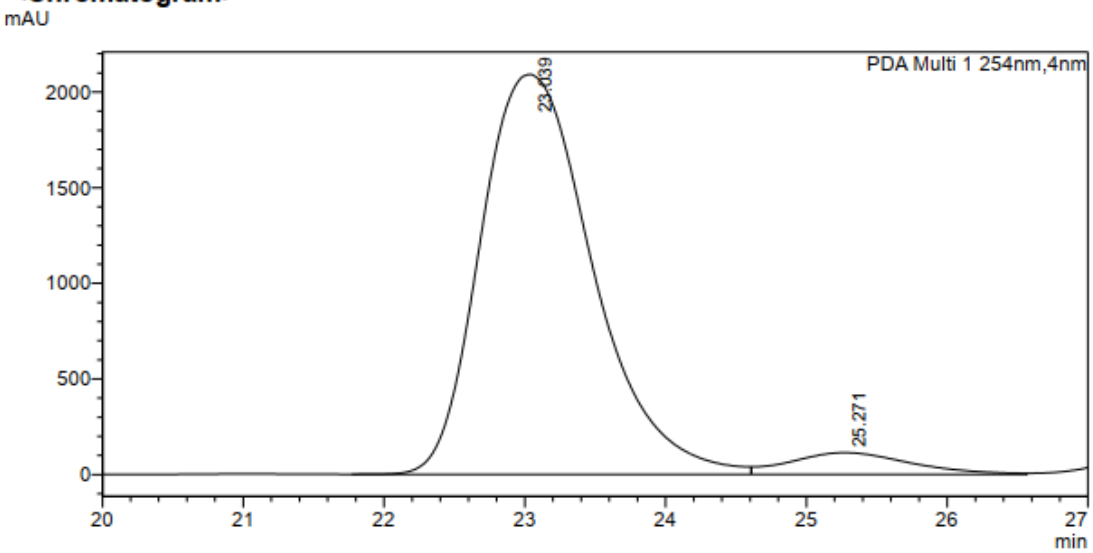


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	23.098	96205862	50.093	1849295
2	25.042	95847496	49.907	1613493
Total		192053359	100.000	3462787

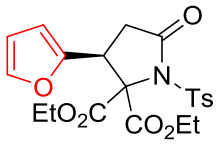
<Chromatogram>



<Peak Table>

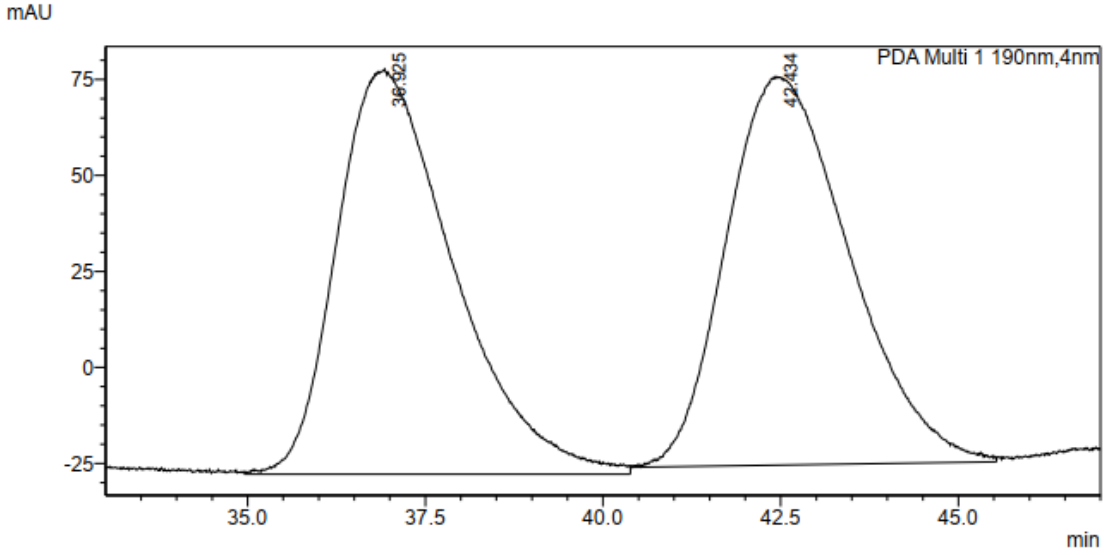
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	23.039	115754687	94.497	2091005
2	25.271	6741482	5.503	113492
Total		122496170	100.000	2204498



3l

<Chromatogram>

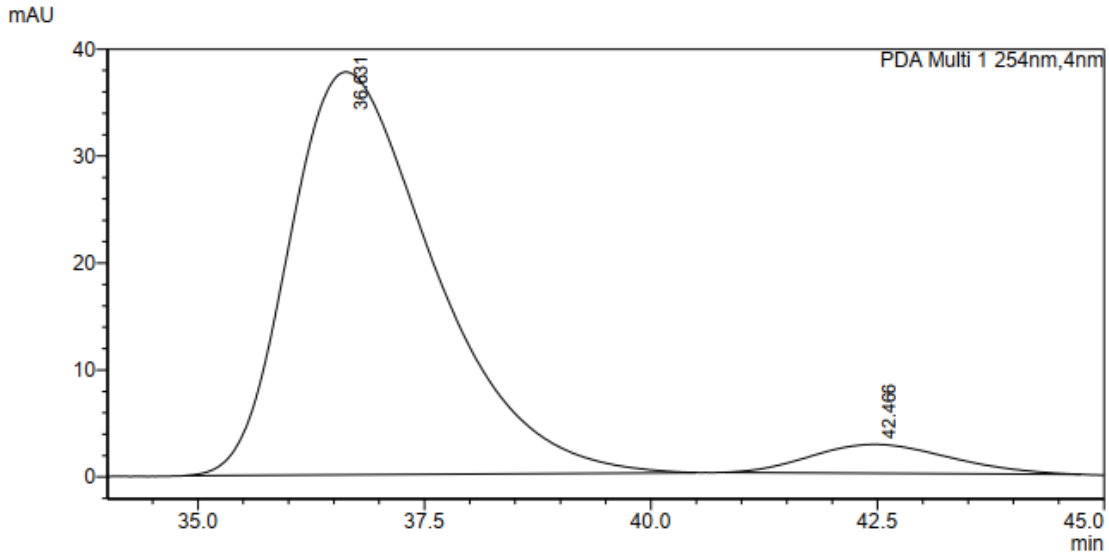


<Peak Table>

PDA Ch1 190nm

Peak#	Ret. Time	Area	Height	Area%
1	36.925	12029489	105441	49.661
2	42.434	12193820	101103	50.339
Total		24223309	206544	100.000

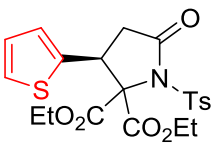
<Chromatogram>



<Peak Table>

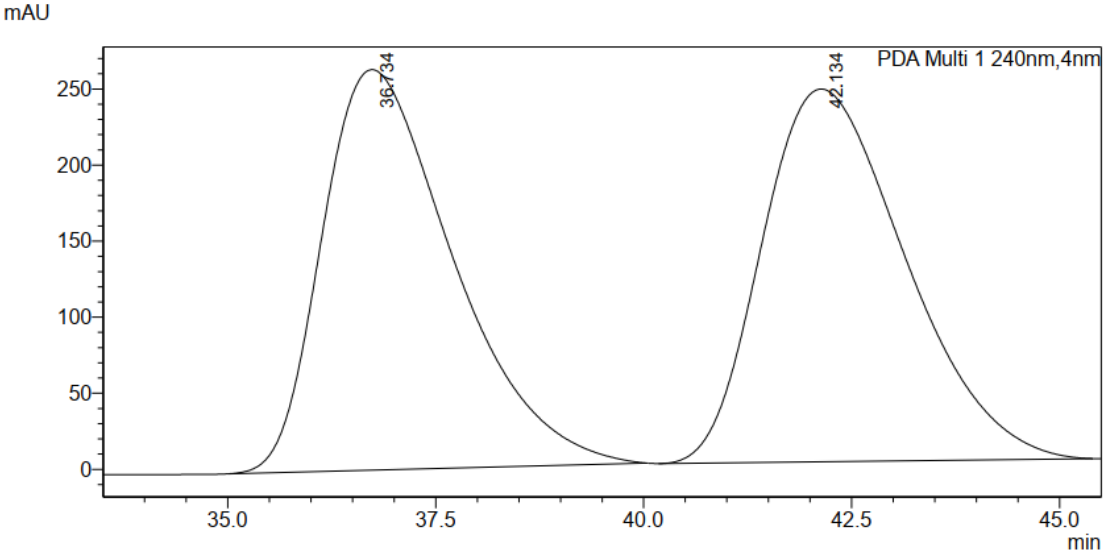
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	36.631	4170603	37665	93.546
2	42.466	287721	2695	6.454
Total		4458325	40360	100.000



3m

<Chromatogram>

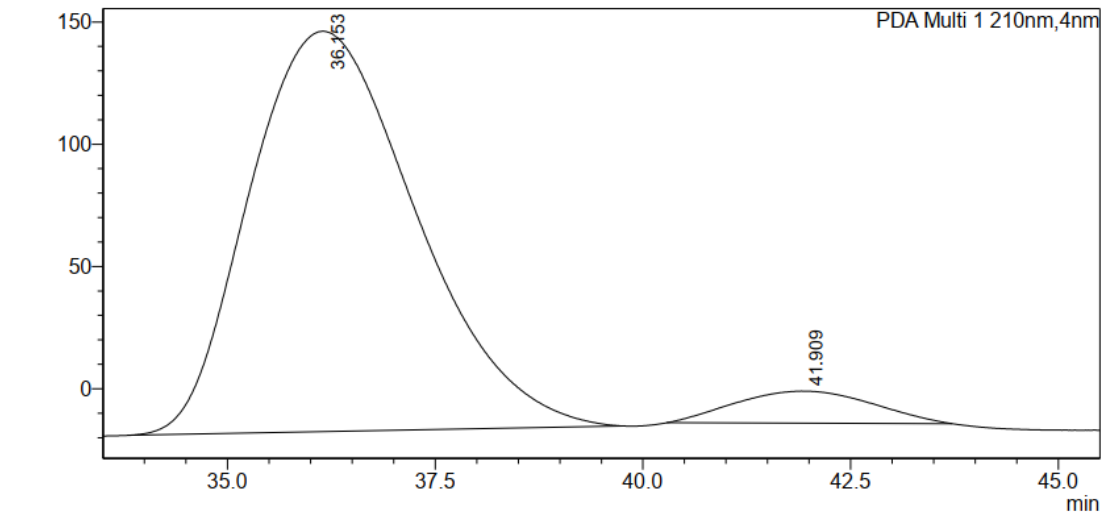


<Peak Table>

PDA Ch1 240nm

Peak#	Ret. Time	Area	Height	Area%
1	36.734	28772579	263220	49.538
2	42.134	29309605	244974	50.462
Total		58082184	508193	100.000

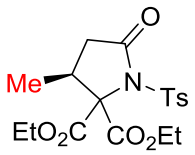
<Chromatogram>



<Peak Table>

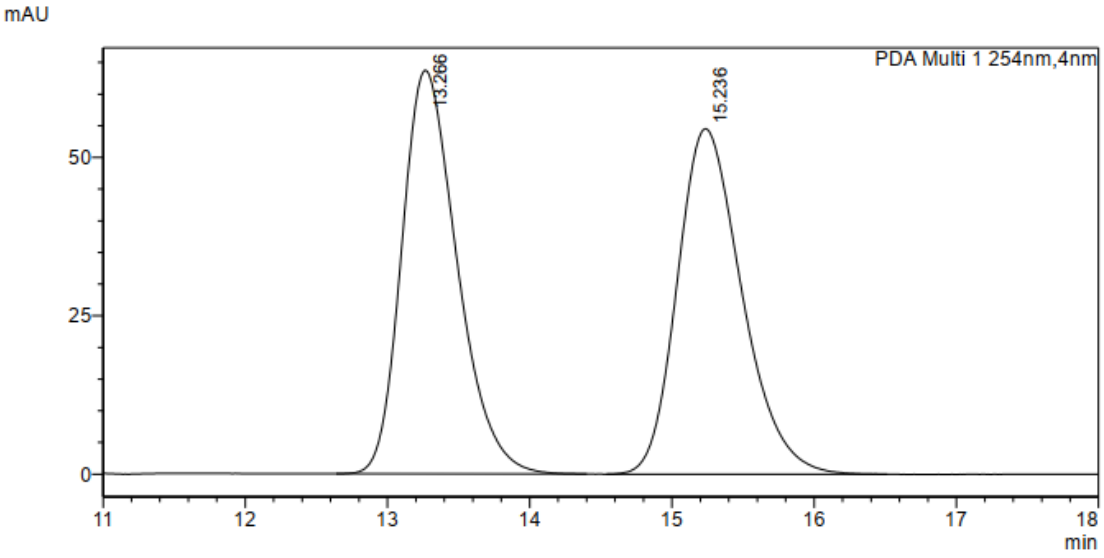
PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	36.153	22816748	163775	93.774
2	41.909	1514992	13118	6.226
Total		24331741	176893	100.000



3n

<Chromatogram>

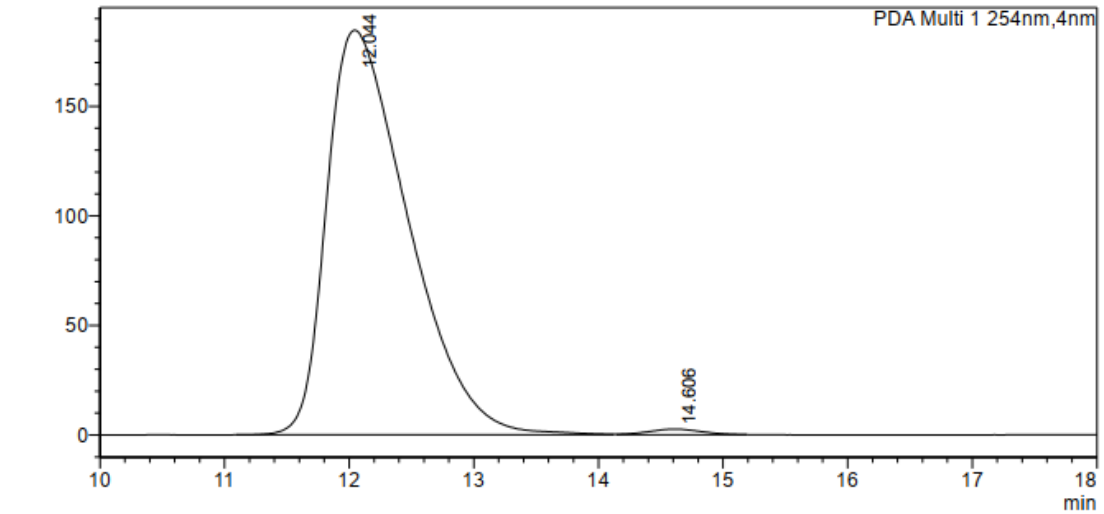


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	13.266	1724883	63700	50.022
2	15.236	1723376	54520	49.978
Total		3448259	118220	100.000

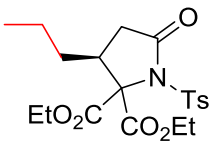
<Chromatogram>



<Peak Table>

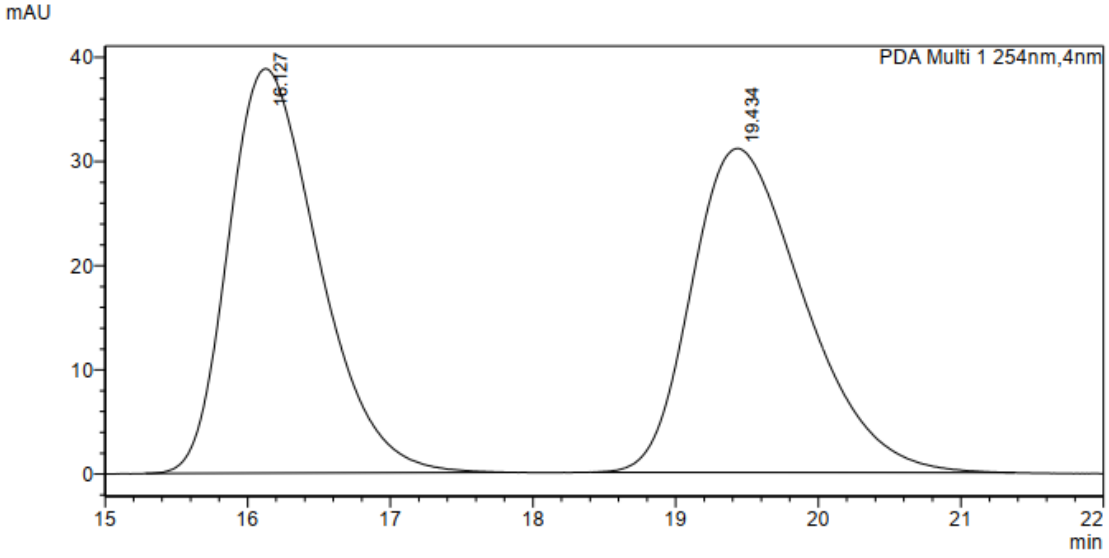
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	12.044	8413464	184687	99.081
2	14.606	78079	2600	0.919
Total		8491543	187286	100.000



3o

<Chromatogram>

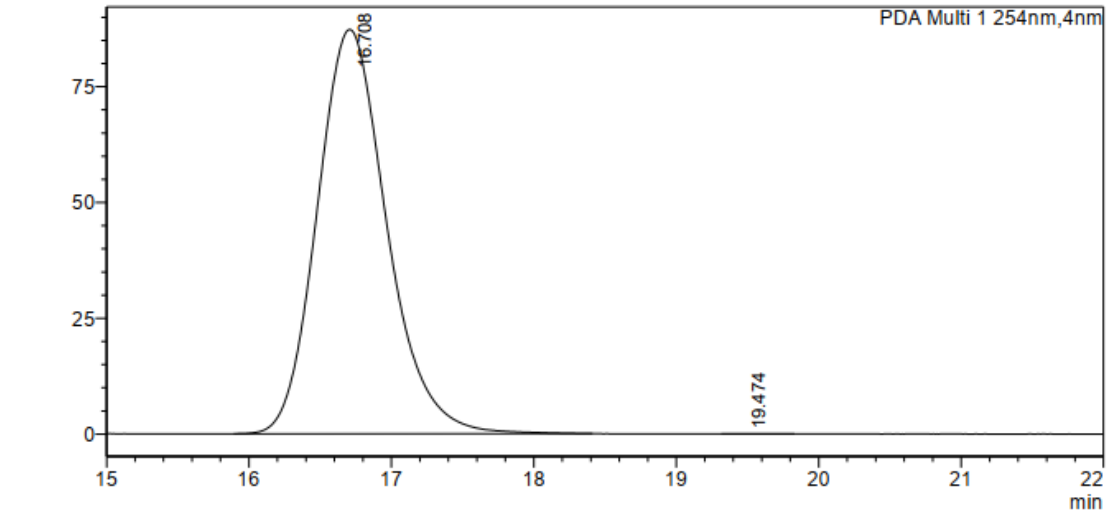


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16.127	1712095	38832	50.042
2	19.434	1709223	31104	49.958
Total		3421318	69936	100.000

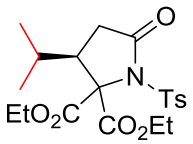
<Chromatogram>



<Peak Table>

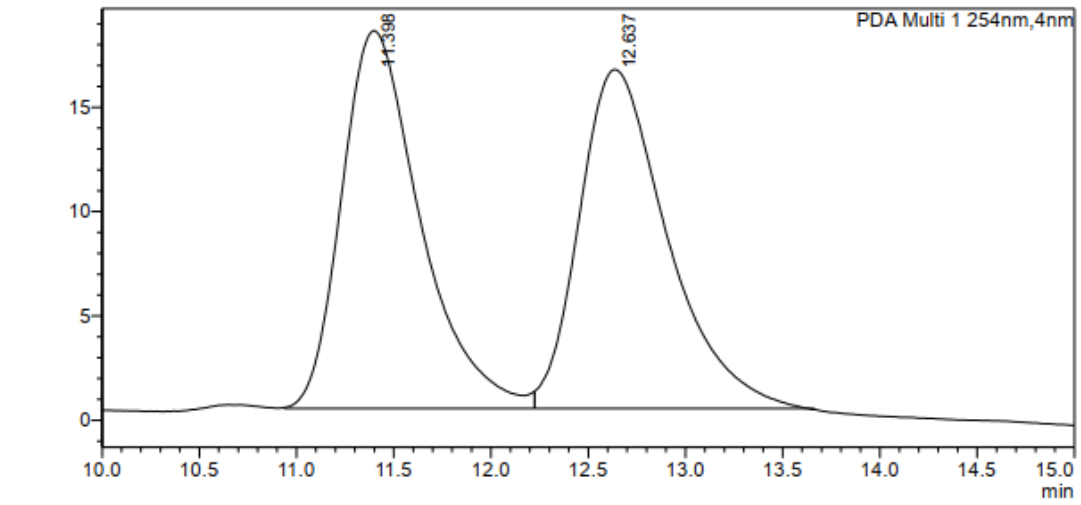
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	16.708	2964119	87282	99.997
2	19.474	87	16	0.003
Total		2964206	87298	100.000



3p

<Chromatogram>

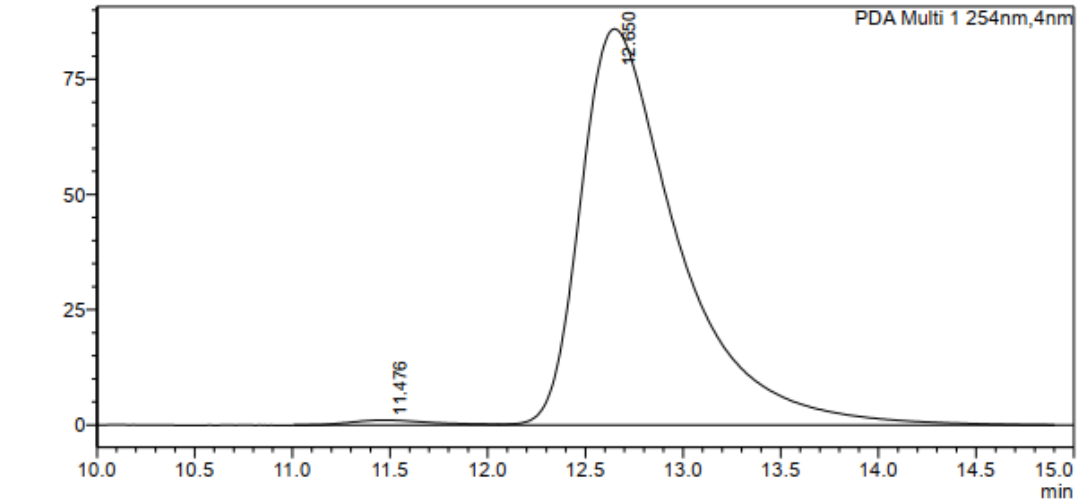


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	11.398	510330	49.982	18099
2	12.637	510705	50.018	16240
Total		1021035	100.000	34339

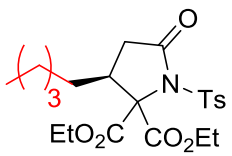
<Chromatogram>



<Peak Table>

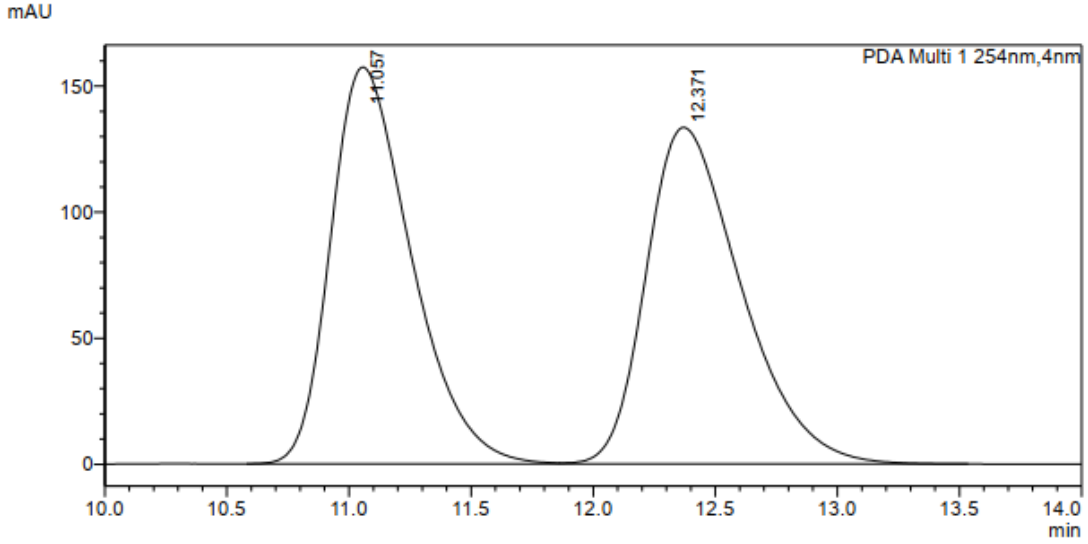
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	11.476	32270	1.069	1100
2	12.650	2986817	98.931	85943
Total		3019088	100.000	87042



3q

<Chromatogram>

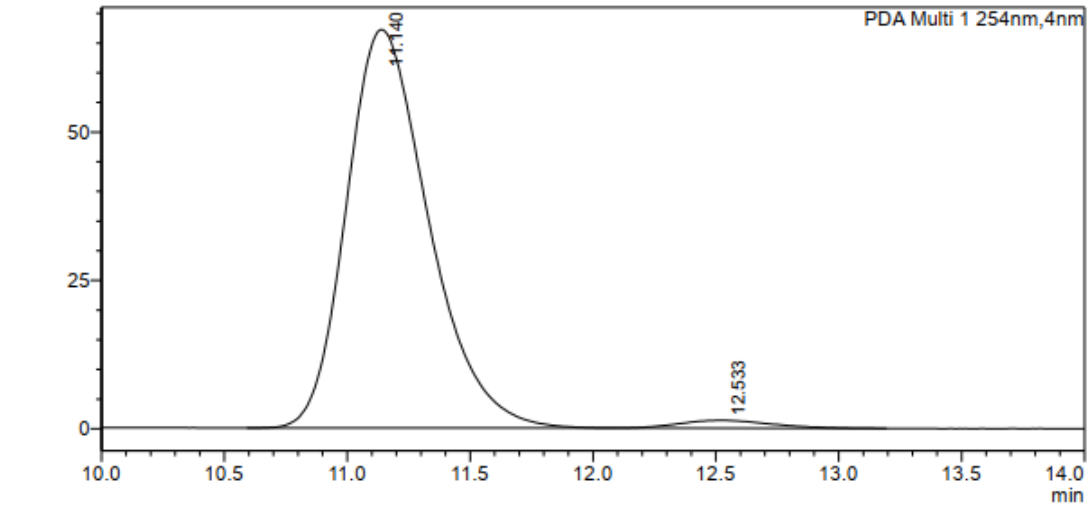


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	11.057	3619109	49.992	157343
2	12.371	3620195	50.008	133485
Total		7239303	100.000	290828

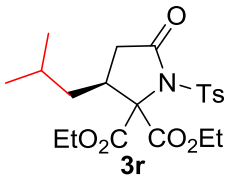
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

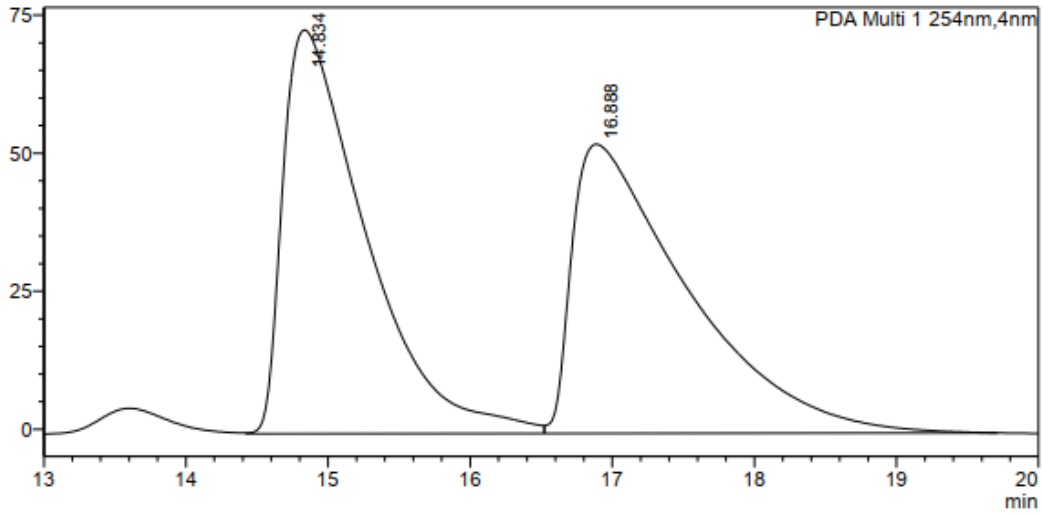
Peak#	Ret. Time	Area	Area%	Height
1	11.140	1564904	97.855	67142
2	12.533	34306	2.145	1321
Total		1599209	100.000	68462



3r

<Chromatogram>

mAU



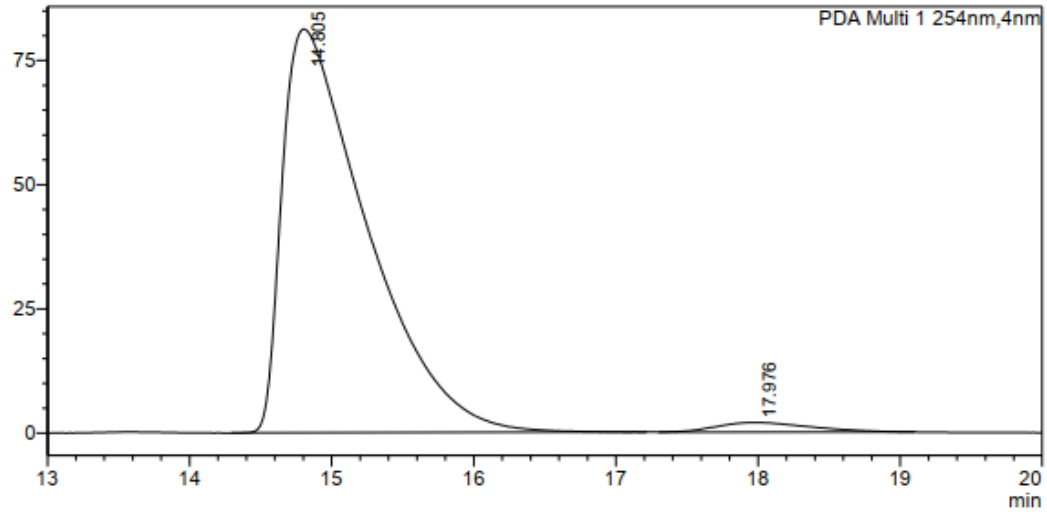
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.834	2971070	50.015	73117
2	16.888	2969251	49.985	52365
Total		5940322	100.000	125482

<Chromatogram>

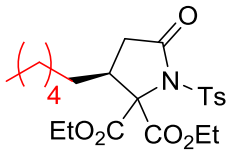
mAU



<Peak Table>

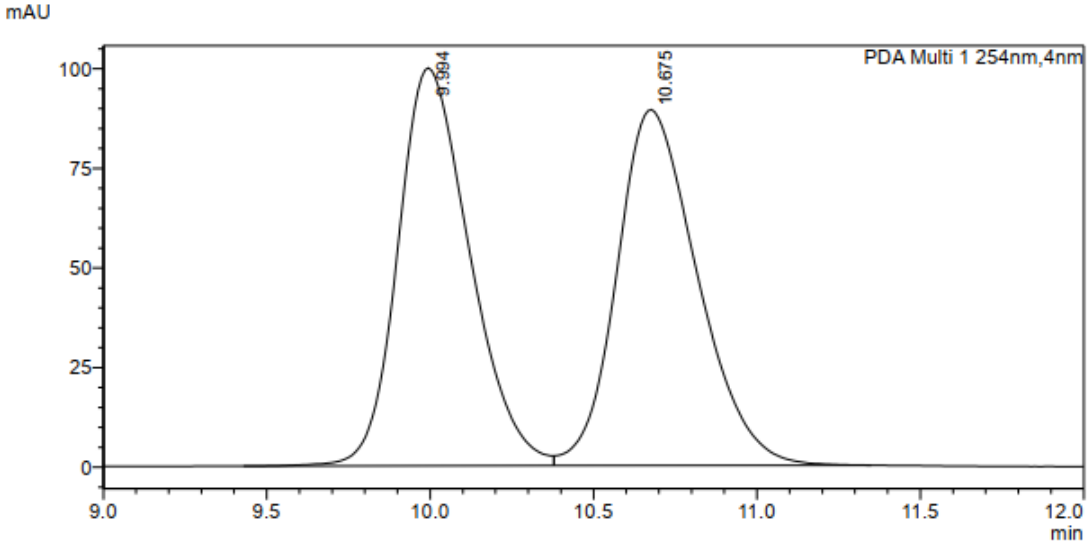
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	14.805	3376036	97.435	81247
2	17.976	88893	2.565	1929
Total		3464929	100.000	83176



3s

<Chromatogram>

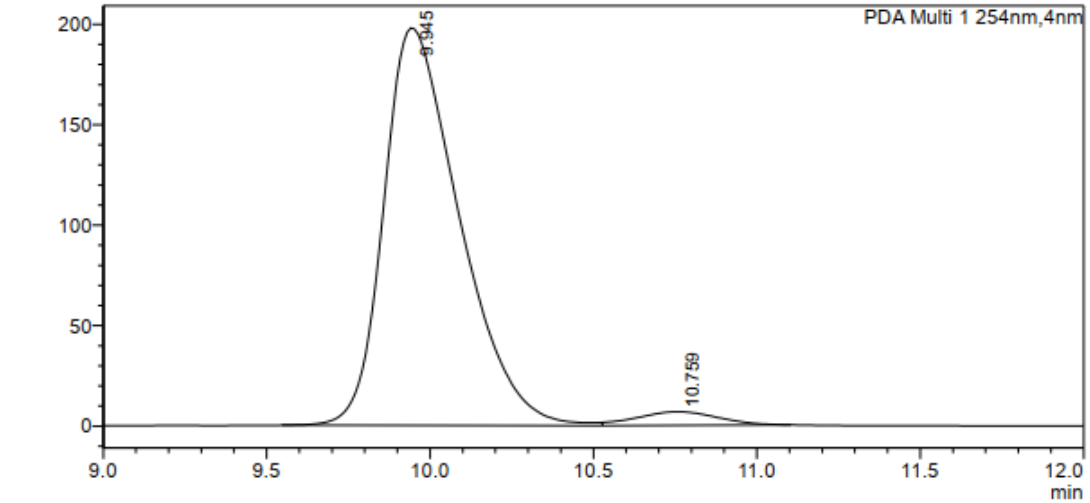


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	9.994	1529283	49.917	99876
2	10.675	1534348	50.083	89296
Total		3063631	100.000	189171

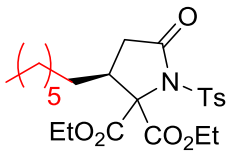
<Chromatogram>



<Peak Table>

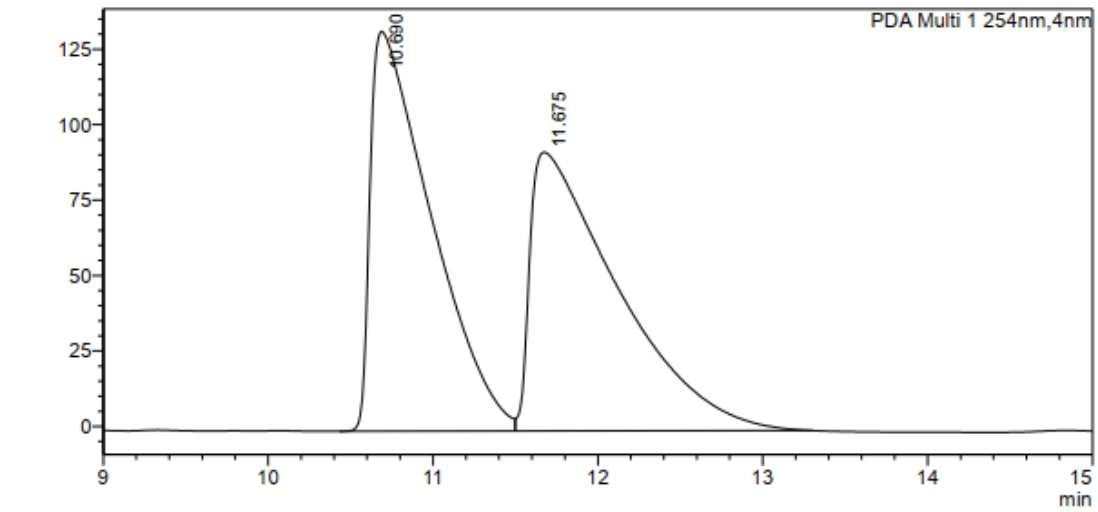
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	9.945	3190944	96.470	197852
2	10.759	116771	3.530	6784
Total		3307715	100.000	204636



3t

<Chromatogram>

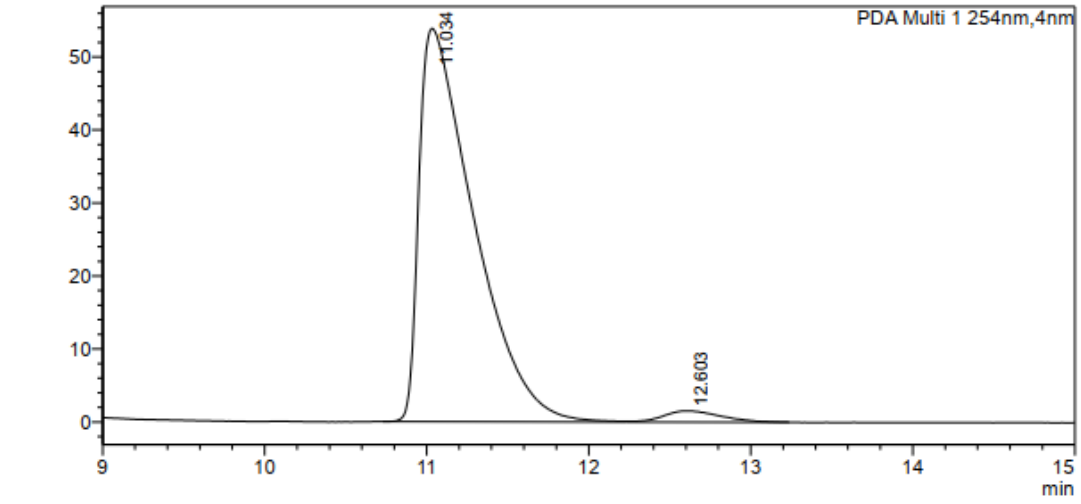


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	10.690	3413291	49.951	132536
2	11.675	3419998	50.049	92316
Total		6833289	100.000	224851

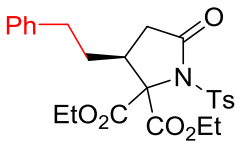
<Chromatogram>



<Peak Table>

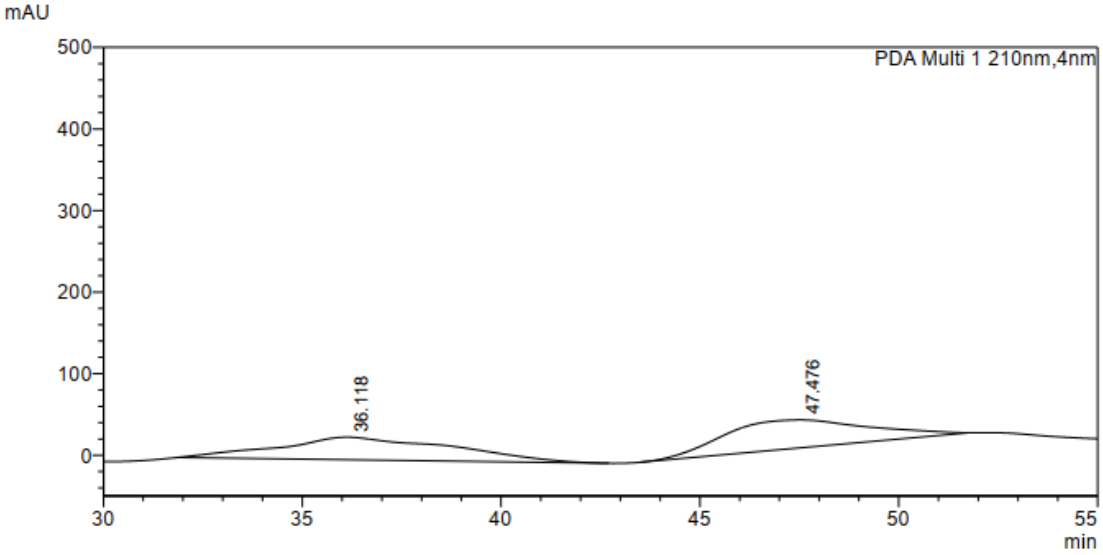
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	11.034	1267261	97.136	53859
2	12.603	37365	2.864	1519
Total		1304626	100.000	55378



3u

<Chromatogram>

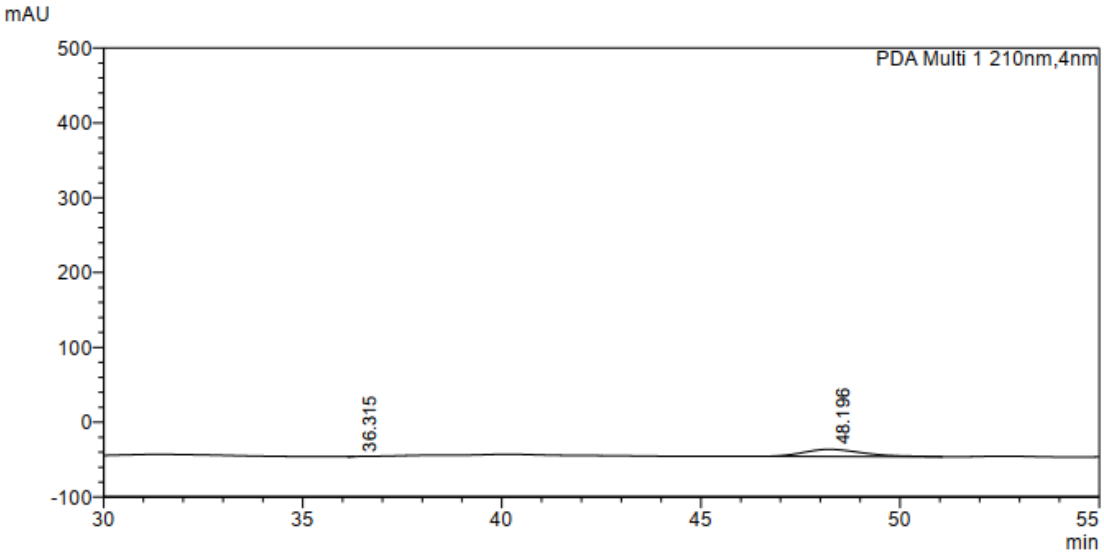


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	36.118	8542457	27671	48.910
2	47.476	8923279	34567	51.090
Total		17465736	62239	100.000

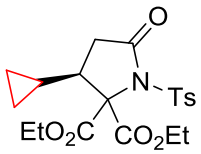
<Chromatogram>



<Peak Table>

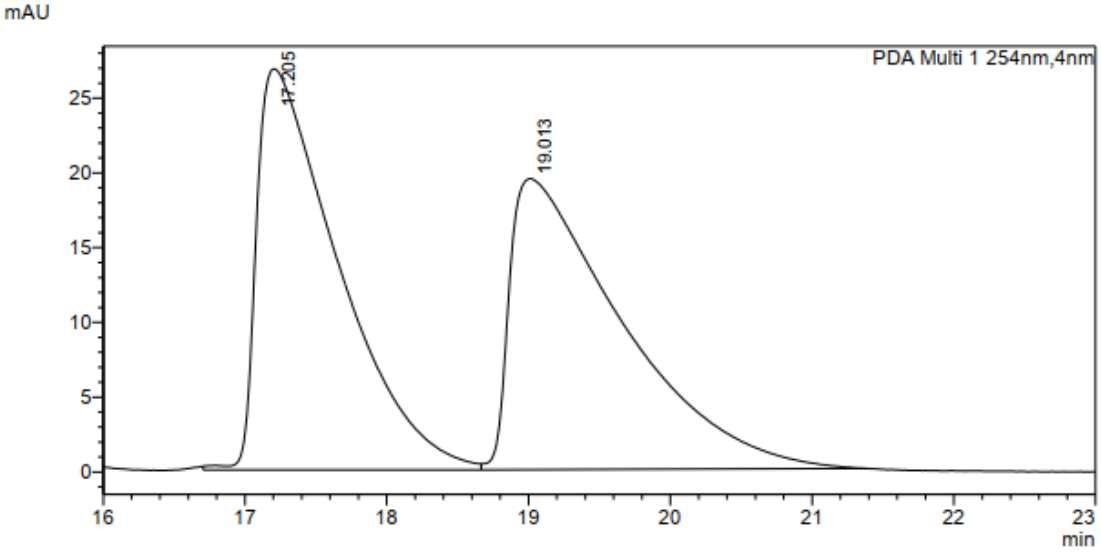
PDA Ch1 210nm

Peak#	Ret. Time	Area	Height	Area%
1	36.315	3251	-153	0.338
2	48.196	957486	9407	99.662
Total		960737	9254	100.000



3v

<Chromatogram>

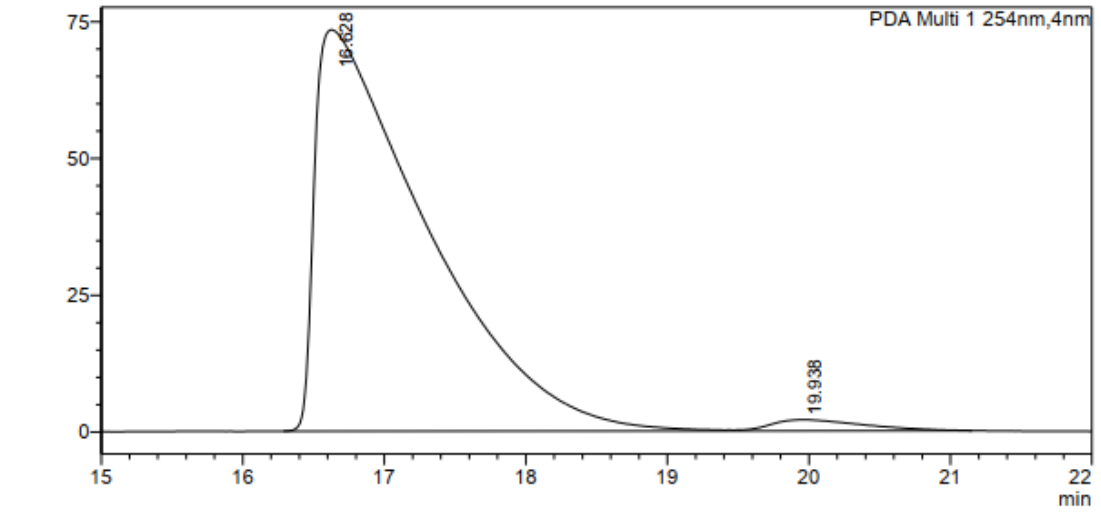


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	17.205	1070897	49.995	26811
2	19.013	1071097	50.005	19450
Total		2141994	100.000	46261

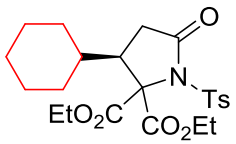
<Chromatogram>



<Peak Table>

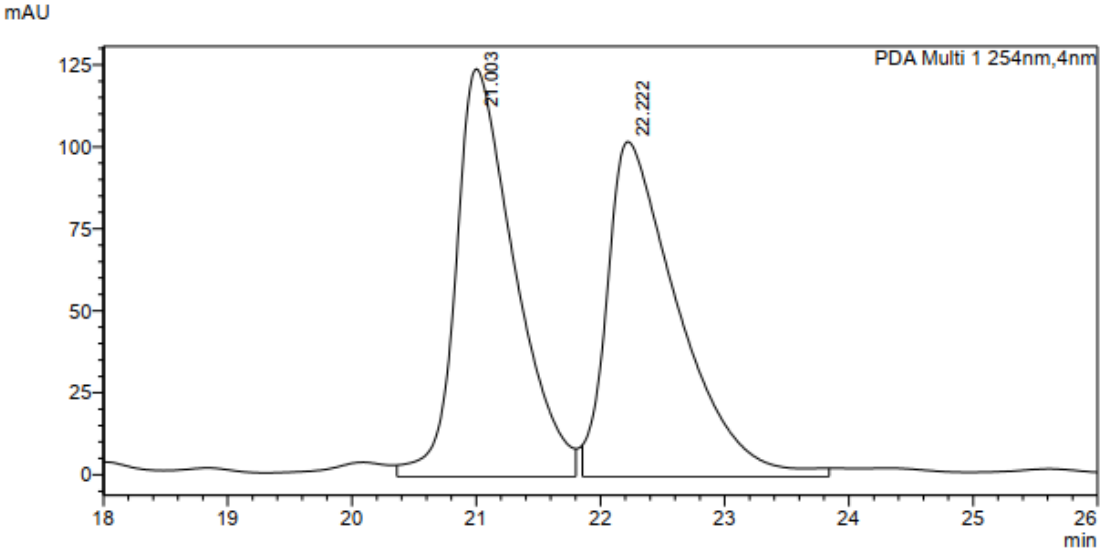
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	16.628	4036240	97.798	73353
2	19.938	90899	2.202	2018
Total		4127138	100.000	75371



3w

<Chromatogram>

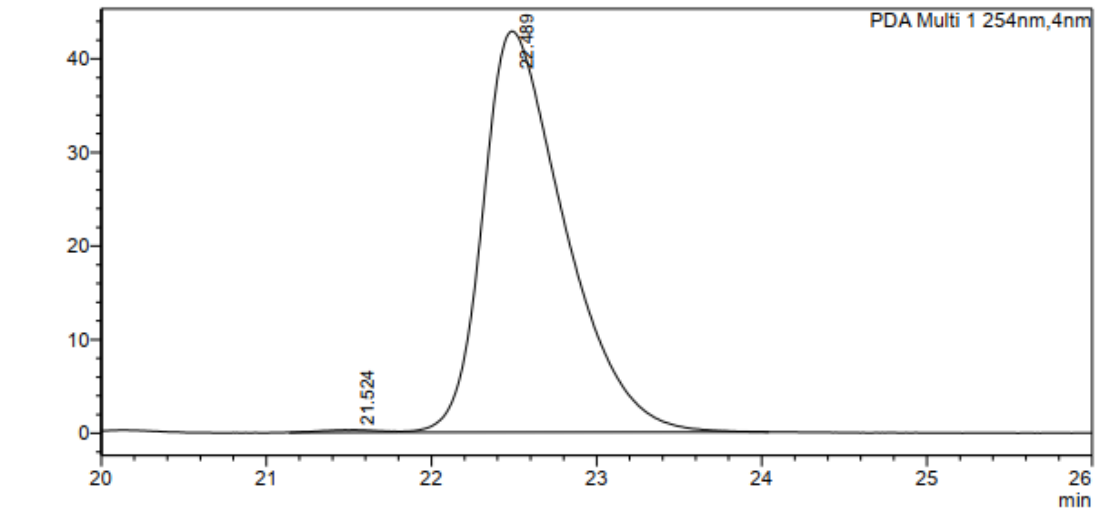


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	21.003	4062336	50.018	124205
2	22.222	4059441	49.982	102054
Total		8121777	100.000	226259

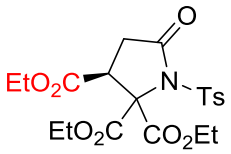
<Chromatogram>



<Peak Table>

PDA Ch1 254nm

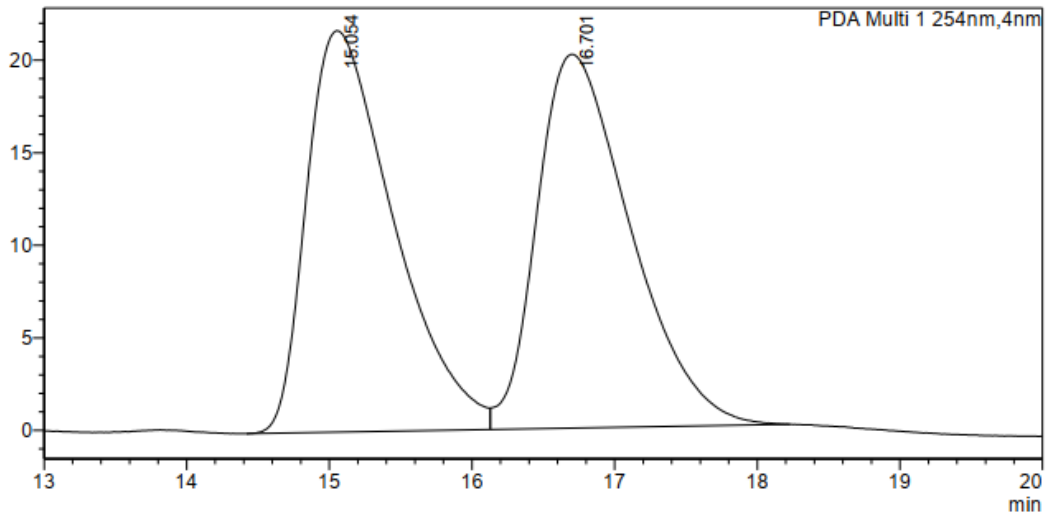
Peak#	Ret. Time	Area	Area%	Height
1	21.524	6512	0.438	269
2	22.489	1480926	99.562	42839
Total		1487438	100.000	43108



3x

<Chromatogram>

mAU



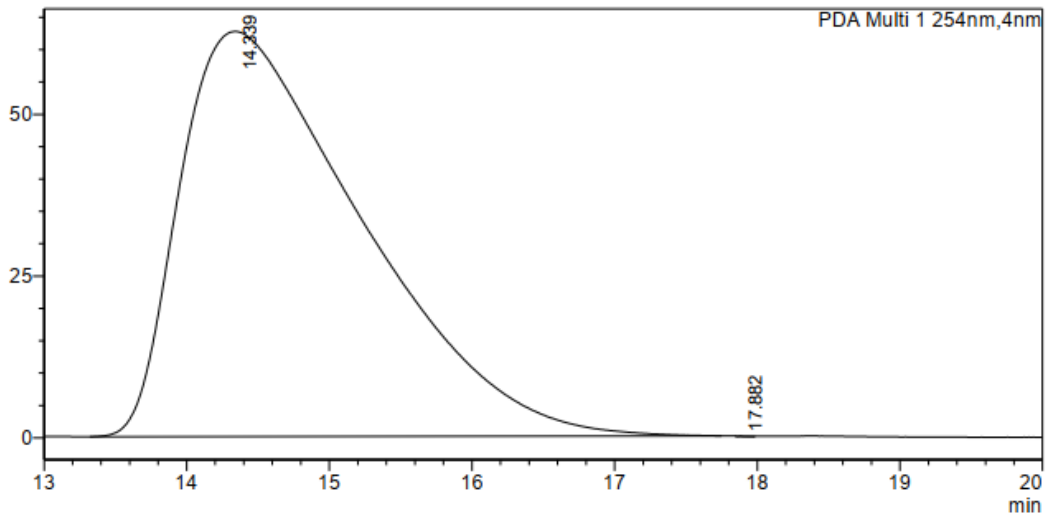
<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	15.054	920148	21689	49.937
2	16.701	922485	20198	50.063
Total		1842634	41887	100.000

<Chromatogram>

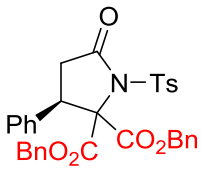
mAU



<Peak Table>

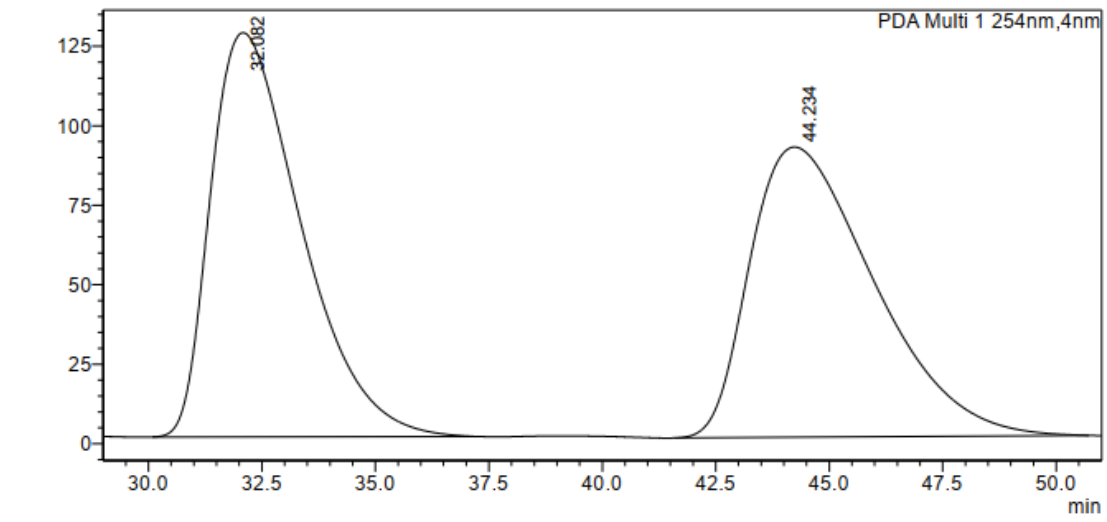
PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	14.339	5561406	62609	99.990
2	17.882	581	69	0.010
Total		5561987	62678	100.000



3y

<Chromatogram>

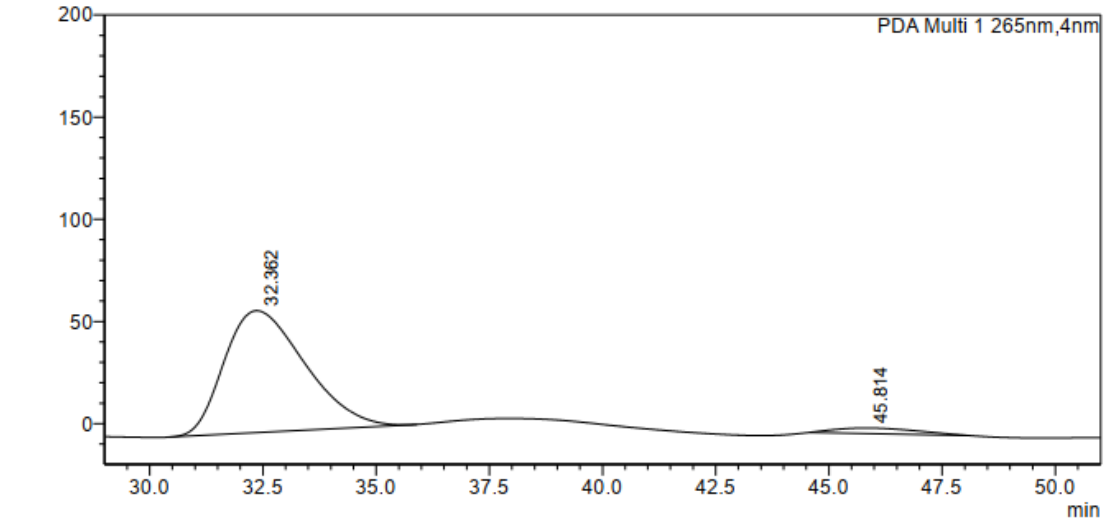


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Height	Area%
1	32.082	17627412	127117	50.380
2	44.234	17361651	91275	49.620
Total		34989063	218392	100.000

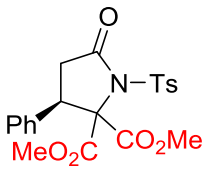
<Chromatogram>



<Peak Table>

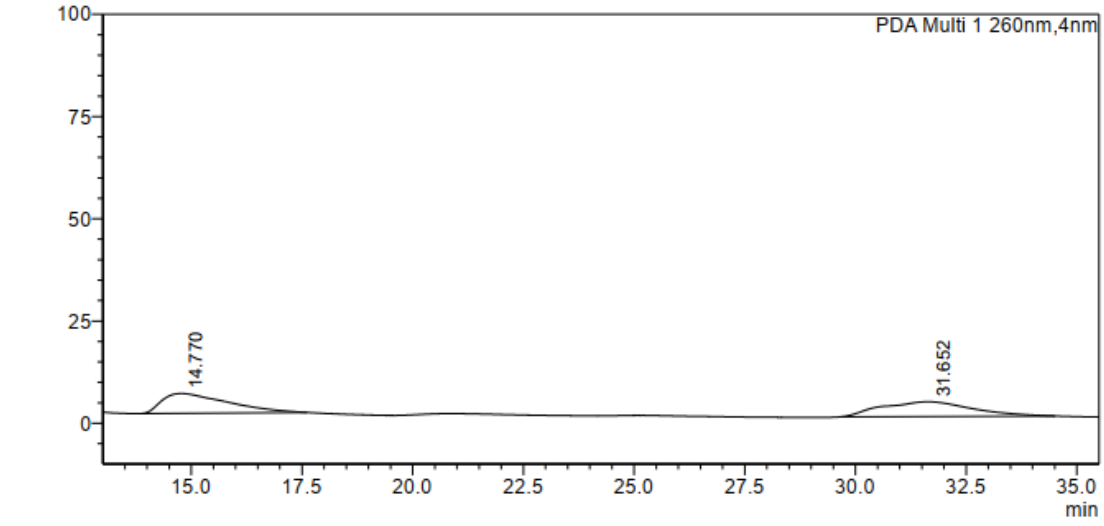
PDA Ch1 265nm

Peak#	Ret. Time	Area	Height	Area%
1	32.362	7398614	59673	95.609
2	45.814	339828	2683	4.391
Total		7738442	62356	100.000



3z

<Chromatogram>

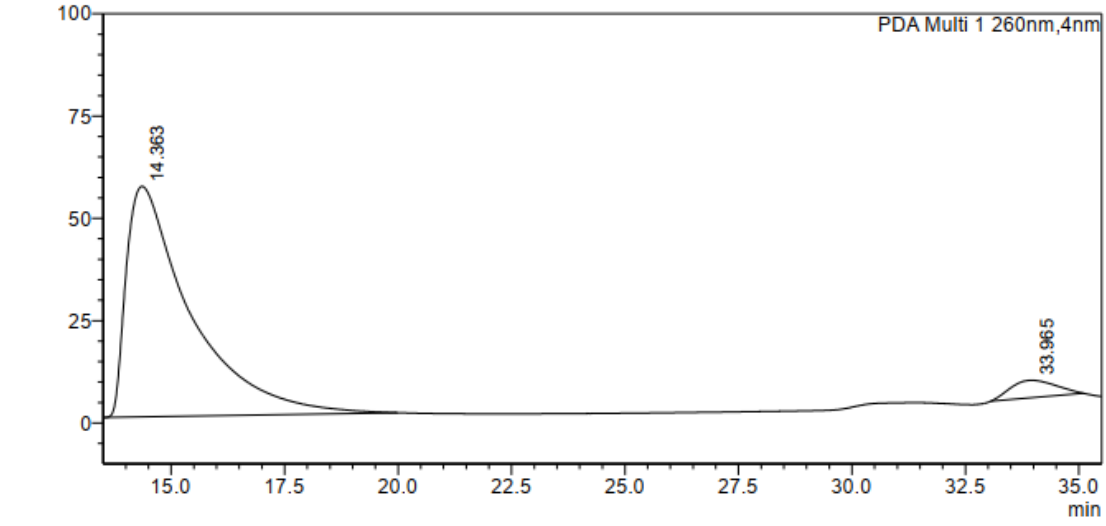


<Peak Table>

PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%
1	14.770	500560	4844	49.260
2	31.652	515594	3630	50.740
Total		1016154	8474	100.000

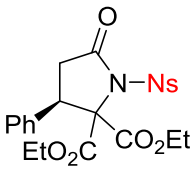
<Chromatogram>



<Peak Table>

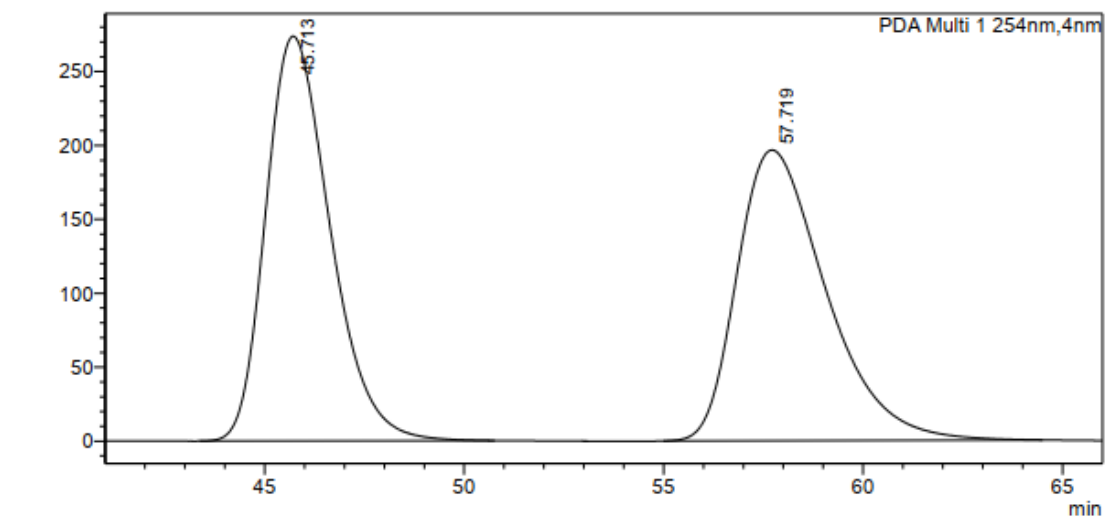
PDA Ch1 260nm

Peak#	Ret. Time	Area	Height	Area%
1	14.363	5562108	56344	94.897
2	33.965	299074	4269	5.103
Total		5861182	60613	100.000



3aa

<Chromatogram>

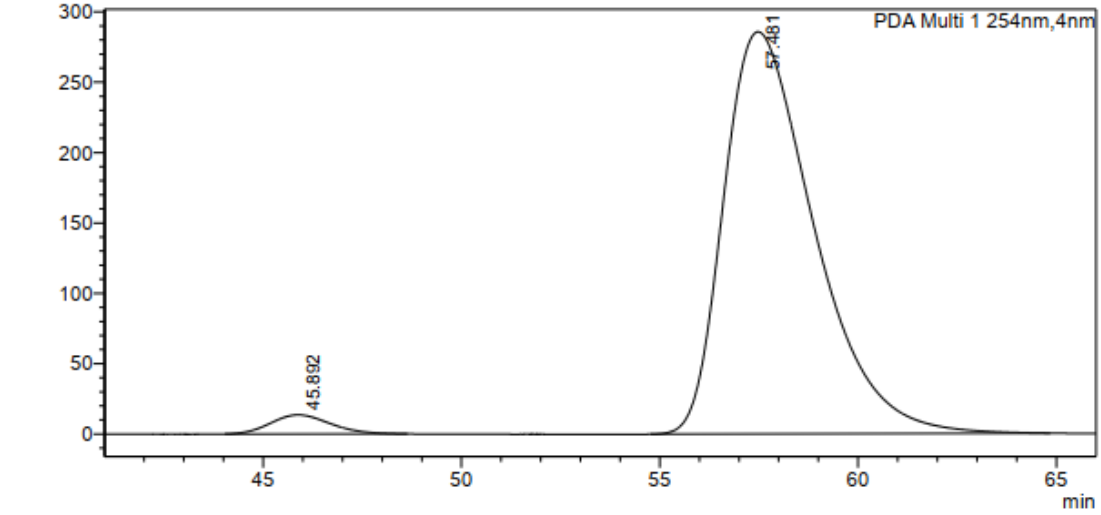


<Peak Table>

PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	45.713	30741470	50.203	273749
2	57.719	30493008	49.797	196632
Total		61234478	100.000	470381

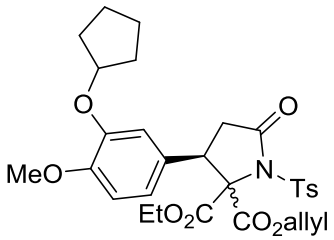
<Chromatogram>



<Peak Table>

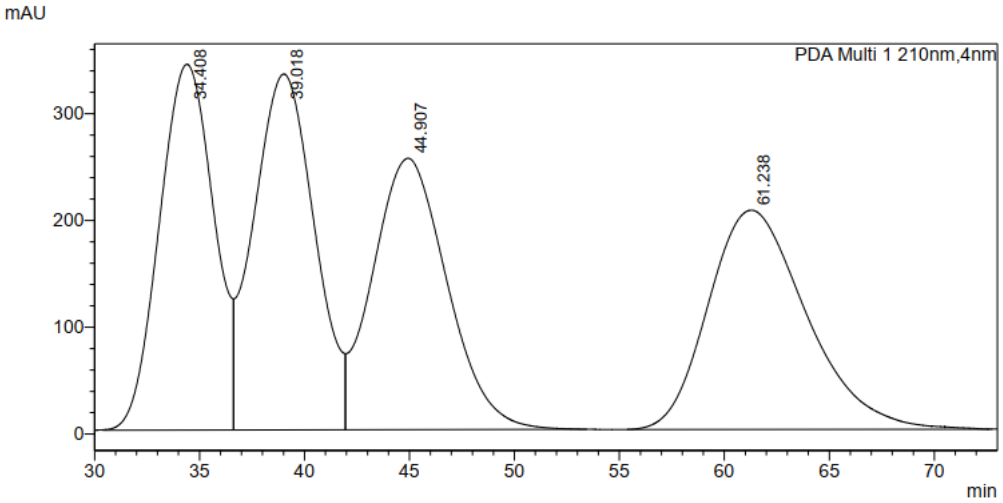
PDA Ch1 254nm

Peak#	Ret. Time	Area	Area%	Height
1	45.892	1412842	3.028	13497
2	57.481	45242511	96.972	285742
Total		46655354	100.000	299239



3ab

<Chromatogram>

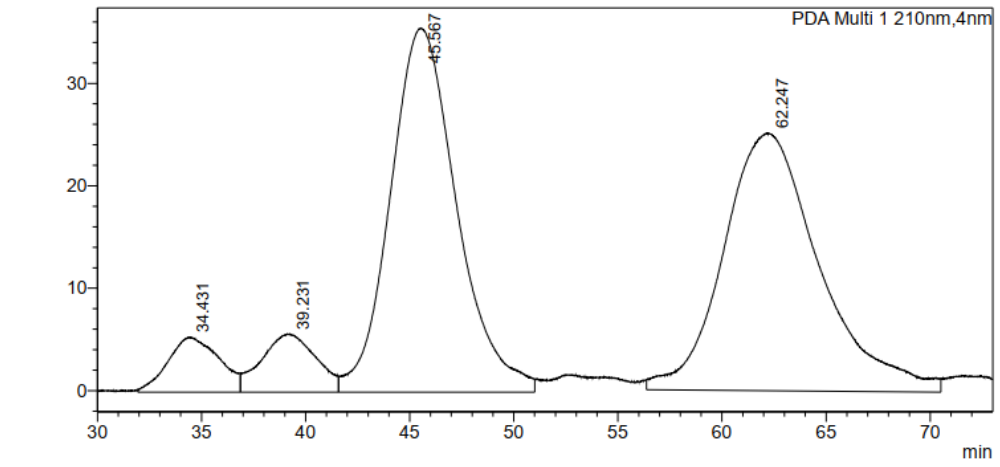


<Peak Table>

PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height
1	34.408	61749243	23.860	342565
2	39.018	67429389	26.055	333273
3	44.907	62764766	24.252	254098
4	61.238	66854968	25.833	205362
Total		258798366	100.000	1135298

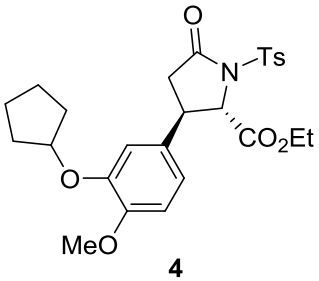
<Chromatogram>



<Peak Table>

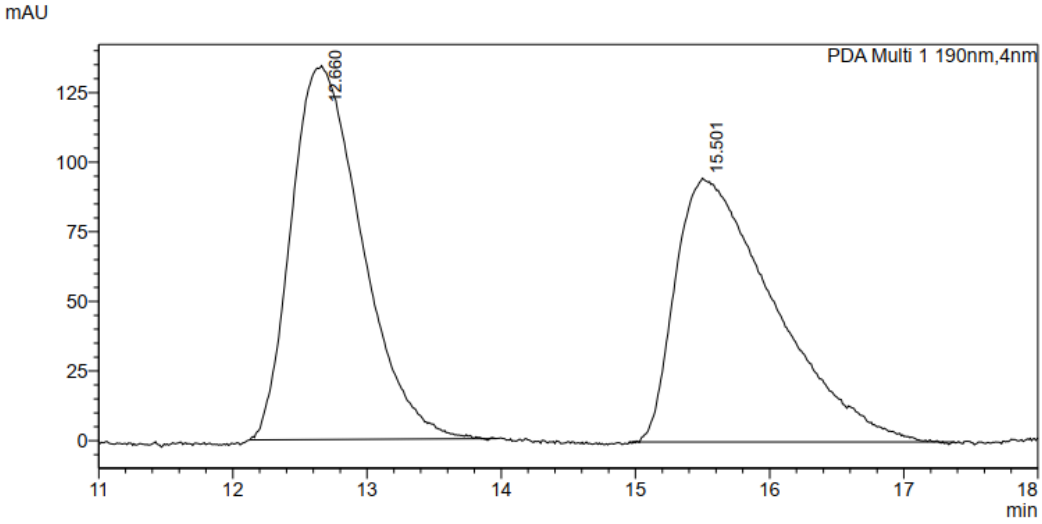
PDA Ch1 210nm

Peak#	Ret. Time	Area	Area%	Height
1	34.431	923894	5.165	5378
2	39.231	1032174	5.770	5702
3	45.567	7872224	44.007	35548
4	62.247	8060272	45.058	25150
Total		17888564	100.000	71778



4

<Chromatogram>

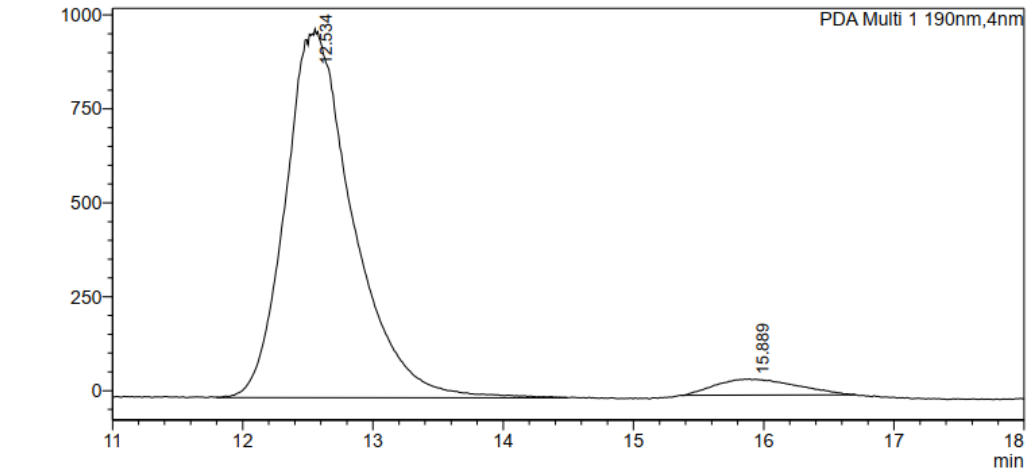


<Peak Table>

PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%	Height
1	12.660	4915040	50.257	134219
2	15.501	4864767	49.743	94678
Total		9779807	100.000	228897

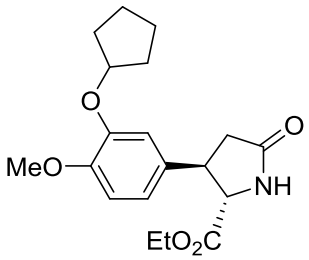
<Chromatogram>



<Peak Table>

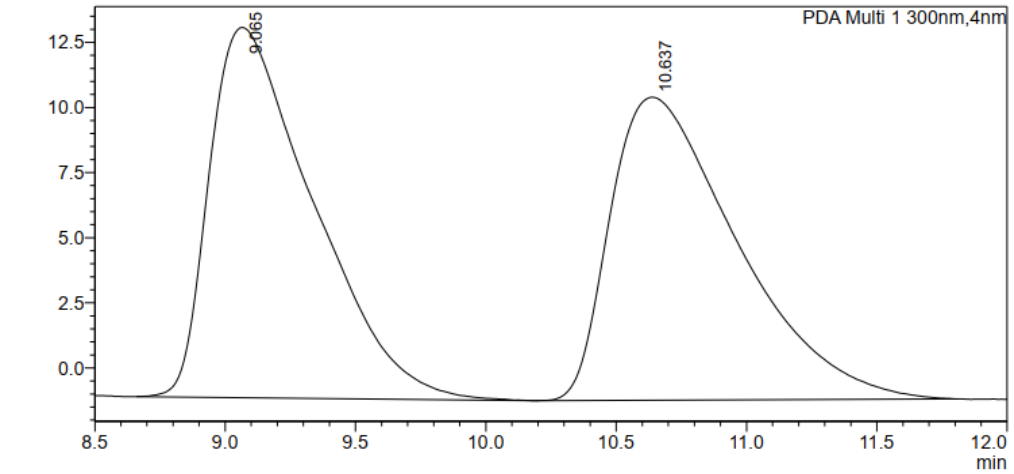
PDA Ch1 190nm

Peak#	Ret. Time	Area	Area%	Height
1	12.534	35339761	95.076	968628
2	15.889	1830430	4.924	42672
Total		37170191	100.000	1011300



5

<Chromatogram>

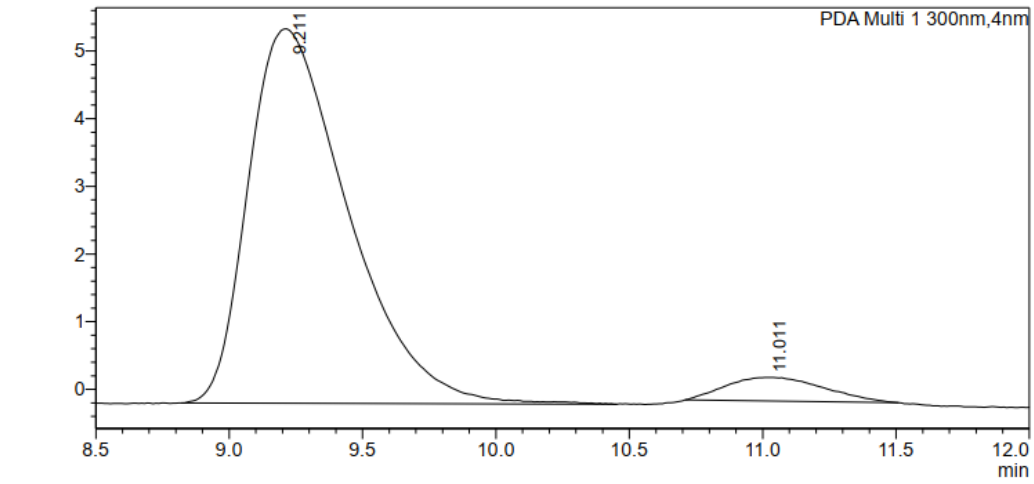


<Peak Table>

PDA Ch1 300nm

Peak#	Ret. Time	Area	Area%	Height
1	9.065	394691	50.059	14215
2	10.637	393768	49.941	11635
Total		788459	100.000	25850

<Chromatogram>



<Peak Table>

PDA Ch1 300nm

Peak#	Ret. Time	Area	Area%	Height
1	9.211	144009	94.150	5532
2	11.011	8947	5.850	349
Total		152956	100.000	5881