Supporting Information

Transfer Hydrogenation of gem-Diester-substituted Cyclopropenes Enables the Synthesis of γ-Amino-acid Derivatives and γ-Lactams Bearing Multiple Stereocenters

Shouang Lan,[†,§] Siyu Shi,[‡,§] Chao Xu,[†] Chunyun Jang,[†] Jinggong Liu,[ǂ] Shuang Yang,[†] Xinqiang Fang*[,†]

[‡]Fujian Normal University, Fuzhou, 350108, China.

[†]State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, University of Chinese Academy of Sciences, Fuzhou 350100, China.

[ǂ]State Key Laboratory of Traditional Chinese Medicine Syndrome, The Second Affiliated Hospital of Guangzhou University of Chinese Medicine, Guangzhou 510120, China.

[§]These authors contributed equally to this work.

xqfang@fjirsm.ac.cn

Table of Contents

I. General Information

Commercially available materials were used as received, unless otherwise noted, all reactions and manipulations involving air- or moisture-sensitive compounds were performed using standard Schlenk technique. All solvents were purified and dried using typical procedures. Proton nuclear magnetic resonance (^{1}H NMR) spectra were

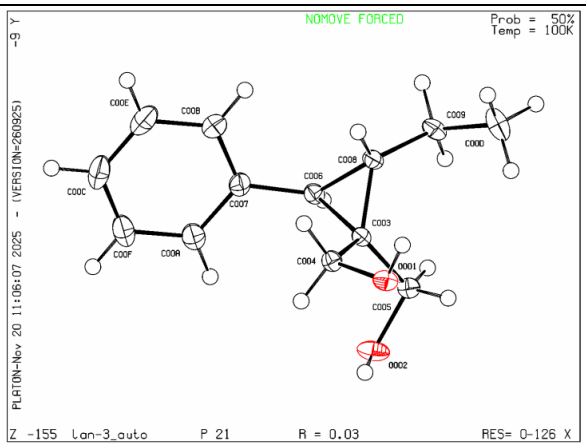
recorded on a Bruker AVANCE III HD400 (400 MHz) spectrometer, a JEOL ECZ600S (600 MHz) and a JEOL ECZ400S (400 MHz). Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) , chloroform (δ = 7.26 ppm). 1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets), m (multiplet), 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 AVANCE III HD400 (101 MHz) spectrometer , JEOL ECZ600S (151 MHz) and a JEOL ECZ400S (101 MHz). High resolution mass spectral analysis (HRMS) was performed on Thermo Fisher Scientific Q Exactive Plus Hybrid Quadrupole-Orbitrap Mass Spectrometer. X-ray crystallography analysis was performed on Agilent Super Nova X-ray diffractionmeter. Analytical thin-layer chromatography (TLC) was carried out on WFH-203 F254 pre-coated silica gel plate (0.2 mm thickness). Visualization was performed using a UV lamp or 2,4-Dinitrophenylhydrazine or potassium permanganate stain or phosphomolybdic acid.

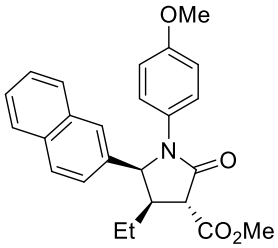
II. X-Ray Crystallographic Analysis

Method for single crystals cultivation: a pure solid sample (10–20 mg) was dissolved in dichloromethane/ethyl acetate (1 mL) in a vial at room temperature, and petroleum ether/hexane (1 mL) was added into the above solution slowly while keeping the sample completely dissolved. The vial was properly sealed with parafilm and kept at room temperature to allow the slow evaporation of the solvents until a single crystal was obtained.

2a'

50% probability level





5j

50% probability level

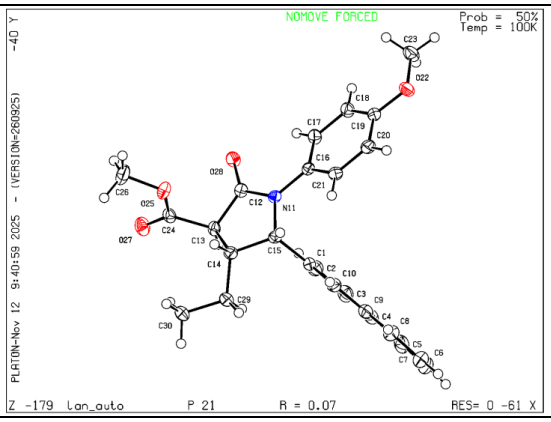


Table S1: Crystal data and structure refinement for 2a'

Identification code	**2a'**
Empirical formula	$C_{13}H_{18}O_2$
Formula weight	206.27
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.6463(3)
b/Å	5.90560(10)
c/Å	10.8390(3)
α/°	90
β/°	105.744(3)
γ/°	90
Volume/Å^3	594.30(3)

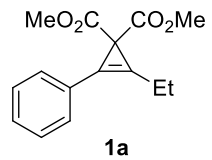
Z	2
ρcalcg/cm^3	1.153
μ/mm^{-1}	0.602
F(000)	224.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.476 to 149.17
Index ranges	-12 ≤ h ≤ 12, -6 ≤ k ≤ 7, -13 ≤ l ≤ 10
Reflections collected	5222
Independent reflections	2197 [R_{int} = 0.0160, R_{sigma} = 0.0154]
Data/restraints/parameters	2197/1/139
Goodness-of-fit on F^2	1.087
Final R indexes [I>=2σ (I)]	R1 = 0.0285, wR2 = 0.0771
Final R indexes [all data]	R1 = 0.0286, wR2 = 0.0772
Largest diff. peak/hole / e Å^{-3}	0.19/-0.14
Flack parameter	0.06(8)

Table S2: Crystal data and structure refinement for 5j

Identification code	**5j**
Empirical formula	$C_{25}H_{25}NO_4$
Formula weight	403.46
Temperature/K	100(2)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.3579(2)
b/Å	11.4992(2)
c/Å	10.7787(2)
α/°	90
β/°	93.485(2)
γ/°	90

Volume/Å^3	1034.02(4)
Z	2
ρcalcg/cm^3	1.296
μ/mm^{-1}	0.707
F(000)	428.0
Crystal size/mm^3	0.1 × 0.1 × 0.1
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.218 to 153.034
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 14, -13 ≤ l ≤ 13
Reflections collected	22915
Independent reflections	4188 [Rint = 0.1592, Rsigma = 0.0644]
Data/restraints/parameters	4188/1/275
Goodness-of-fit on F^2	1.064
Final R indexes [I>=2σ (I)]	R_1 = 0.0696, wR_2 = 0.1850
Final R indexes [all data]	R_1 = 0.0703, wR_2 = 0.1855
Largest diff. peak/hole / e Å^{-3}	0.45/-0.37
Flack parameter	0.2(3)

III. Typical Procedures for the Preparation of Substrates



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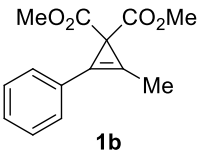

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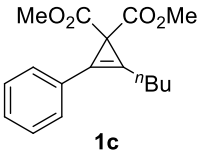

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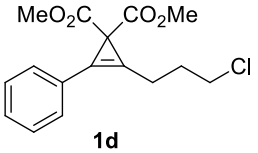

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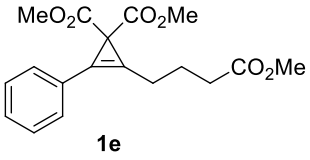

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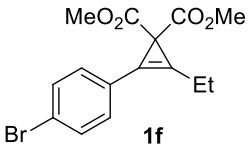

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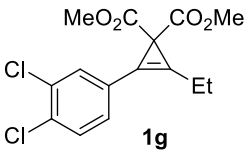

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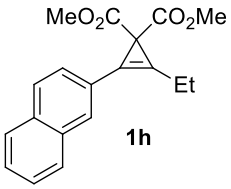

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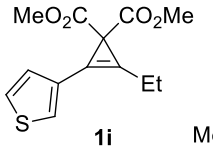
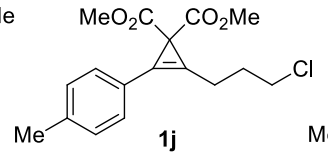


1i



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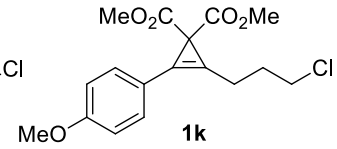

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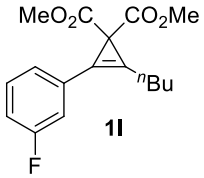

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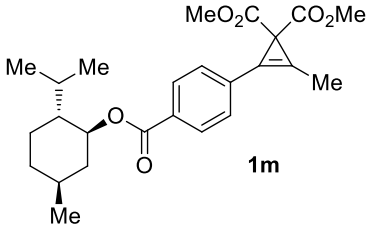

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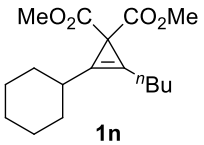

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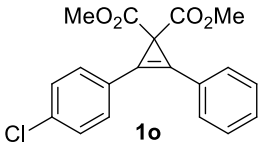

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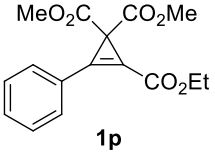

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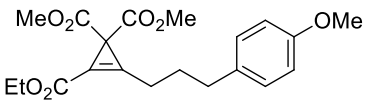

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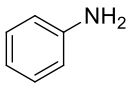

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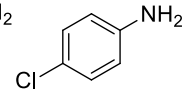

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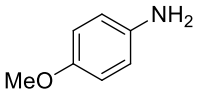

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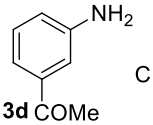

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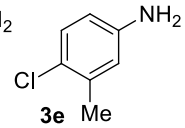

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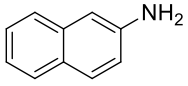

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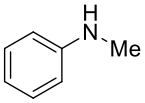

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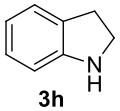

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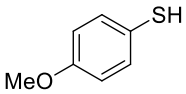

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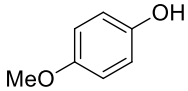

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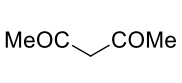
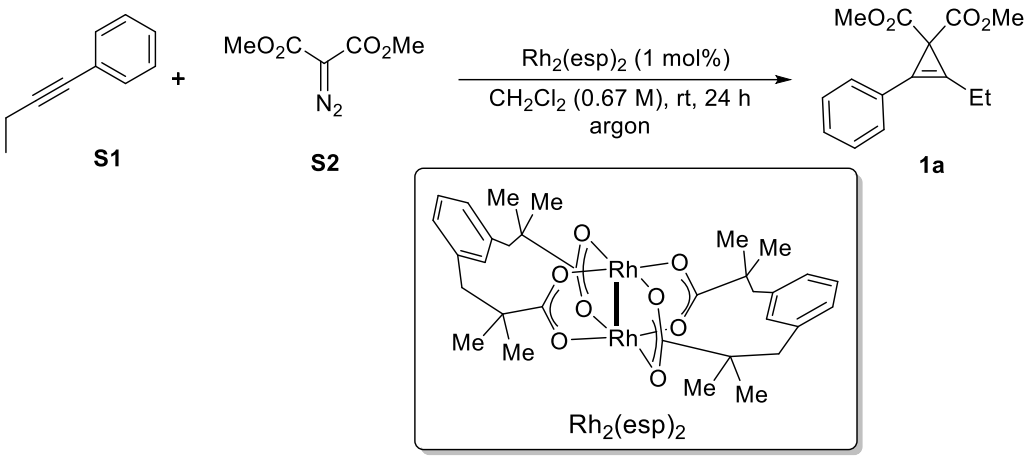


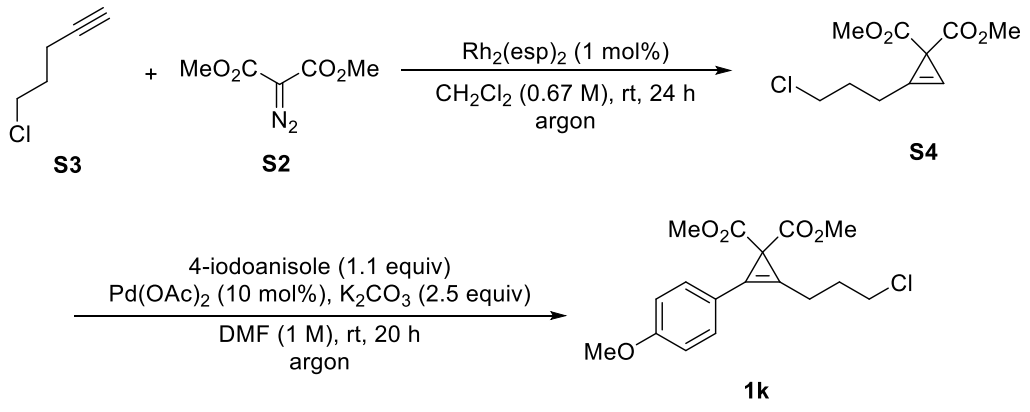
3k

1. Typical procedures for the preparation of substrates 1a−1i, 1l−1n



A 100 mL three-necked flask equipped with a stir bar was charged with $Rh_2(esp)_2$ (76 mg, 0.1 mmol) in air. The flask was sealed, evacuated, and refilled with argon (three cycles). A solution of alkene **S1** (1.302 g, 10 mmol) in CH_2Cl_2 (7 mL) was then added. The resulting mixture was cooled in a water/ice bath for 5 minutes. Subsequently, a solution of diazodimethylmalonate **S2** (2.055 g, 13 mmol) in CH_2Cl_2 (8 mL) was added via a syringe pump (0.6 mL/h) at room temperature. After stirring for 24 h, the mixture was quenched with a saturated aqueous thiourea solution (5 mL) and diluted with CH_2Cl_2 (25 mL). The mixture was stirred for an additional 30 minutes, transferred to a separatory funnel, and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1) to afford the product **1a** (803 mg, 31% yield) as an amorphous white solid.

2. Typical procedures for the preparation of substrates 1j, 1k, 1o

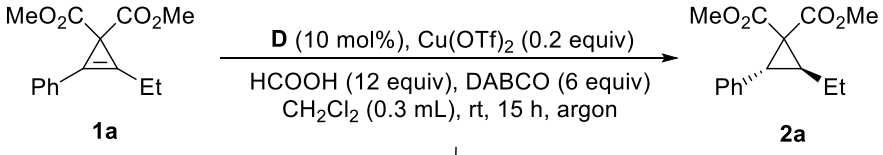


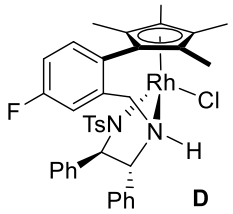
A 100 mL three-necked flask equipped with a stir bar was charged with $Rh_2(esp)_2$ (76 mg, 0.1 mmol) in air. The flask was sealed, evacuated, and refilled with argon (three cycles). A solution of alkene **S3** (1.026 g, 10 mmol) in CH_2Cl_2 (7 mL) was then added. The resulting mixture was cooled in a water/ice bath for 5 minutes. Subsequently, a solution of diazodimethylmalonate **S2** (2.055 g, 13 mmol) in CH_2Cl_2 (8 mL) was added via a syringe pump (0.6 mL/h) at room temperature. After stirring for 24 h, the mixture was quenched with a saturated aqueous thiourea solution (5 mL) and diluted with CH_2Cl_2 (25 mL). The mixture was stirred for an additional 30 minutes, transferred to a separatory funnel, and the aqueous layer was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1) to afford the product **S4** (1.877 g, 81% yield) as a colorless oil.

An oven-dried 25 mL Schlenk tube was charged with palladium acetate (224.5 mg, 1.0 mmol), 4-iodoanisole (2.574 g, 11 mmol), **S4** (2.327 g, 10 mmol), and anhydrous potassium carbonate (3.455 g, 25 mmol) under argon atmosphere. N,N-dimethylformamide (10 mL) was added, and the mixture was stirred at room temperature. After 20 h, TLC analysis indicated complete consumption of the starting material. The mixture was filtered through a short pad of silica gel (eluted with diethyl ether). The ethereal filtrate was washed sequentially with saturated aqueous ammonium chloride solution, water, and brine. The organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The crude residue was purified by preparative column chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1,) to afford **1k** (1.097 g, 32% yield) as a yellow oil.

2. Substrates 3a–3k are commercially available compounds

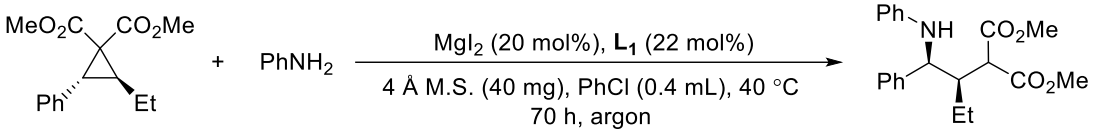
IV. Typical Procedures for Asymmetric Transfer Hydrogenation of gem-Diester-substituted Cyclopropenes

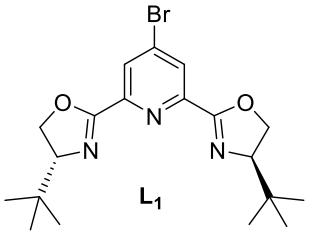




The mixture of HCOOH (45.2 μL, 1.2 mmol) and DABCO (67.3 mg, 0.6 mmol) in CH_2Cl_2 (0.3 mL) was added to **1a** (26.0 mg, 0.1 mmol), $Cu(OTf)_2$ (7.6 mg, 0.02 mmol) and the catalyst **D** (7.3 mg, 0.01 mmol). After stirring at room temperature for 15 h under argon atmosphere, the reaction mixture was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1) to afford the product **2a** (23.8 mg, 91% yield, 12:1 dr, 99% ee) as a colorless oil.

V. Typical Procedures for Asymmetric Ring-Opening of Tetrasubstituted Cyclopropanes with Nucleophiles

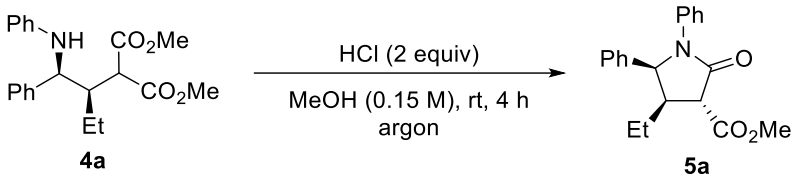




In a nitrogen-filled glovebox, an oven-dried 10 mL sealed tube was charged sequentially with MgI_2 (5.6 mg, 0.02 mmol), ligand **L1** (9.8 mg, 0.022 mmol), powdered 4 Å molecular sieves (40 mg), and a magnetic stir bar. PhCl (0.3 mL) was added, and the mixture was stirred inside the glovebox for 1 h to yield a yellow suspension. Separately, the mixture of **2a** (26.2 mg, 0.1 mmol, 99% ee) and **3a** (11.9 μL, 0.12 mmol) in PhCl (0.1 mL) was added. The tube was then sealed, removed from the glovebox, and stirred at 40 ºC until TLC analysis (about 70 h) indicated complete

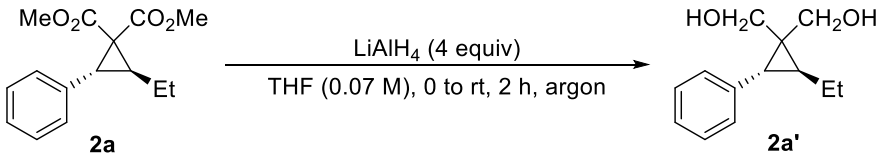
consumption of the cyclopropane **2a**. The mixture was then directly filtered under positive air pressure through a 2 cm silica gel plug, eluting with ethyl acetate (50 mL). The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1) to afford the product **4a** (30.5 mg, 86% yield, >20:1 dr, 99% ee) as a colorless oil.

VI. Typical Procedure for the Asymmetric Ring-Closing Reaction of 4a



HCl (2 M, 0.1 mL, 0.2 mmol) was added to **4a** (35.5 mg, 0.1 mmol) in MeOH (0.67 mL) under argon atmosphere. After stirred at room temperature for 4 h, the reaction was quenched with aqueous $NaHCO_3$ solution and extracted with CH_2Cl_2 (3×10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 5:1) to afford product **5a** (29.3 mg, 91% yield, >20:1 dr, 99% ee) as a amorphous white solid.

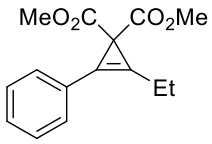
VII. Typical procedure of the synthesis of compound 2a'



A solution of diester **2a** (78.7 mg, 0.3 mmol) in THF (4.5 mL) was cooled to 0 °C in an ice bath. Lithium aluminum hydride ($LiAlH_4$, 45.5 mg, 12 mmol) was added in several small portions. The mixture was then allowed to warm gradually to room temperature and stirred for 2 h, at which point TLC analysis indicated complete consumption of the starting material. The reaction was carefully quenched by sequential addition of water (5 mL) and HCl (5 mL, 2 M). The resulting mixture was transferred to a separatory funnel, the layers were separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced

pressure. The residue was purified by flash chromatography (petroleum ether/ethyl acetate, v:v = 1:1) to afford product **2a'** (59.0 mg, 95% yield, >20:1 dr, 99% ee) as a amorphous white solid.

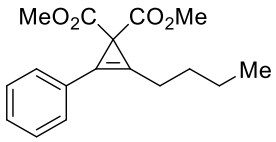
VIII. Characterizations of New Compounds



1a

Dimethyl 2-ethyl-3-phenylcycloprop-2-ene-1,1-dicarboxylate (1a):

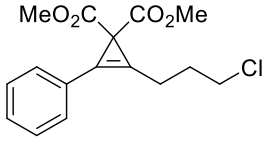
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 15:1), amorphous white solid, mp 45–47 ºC, 803 mg, 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.52 (m, 2H), 7.42–7.34 (m, 3H), 3.71 (s, 6H), 2.74 (q, *J* = 7.5 Hz, 2H), 1.35 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 129.7, 129.5, 128.9, 125.1, 110.2, 104.3, 52.3, 35.1, 18.3, 11.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{16}O_4Na$ 283.0941; Found 283.0937. IR (KBr thin film, cm^{-1}): ν 2953, 1722, 1597, 1434, 1232, 1059, 974, 761, 691, 554.



1c

Dimethyl 2-butyl-3-phenylcycloprop-2-ene-1,1-dicarboxylate (1c):

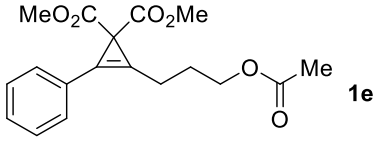
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 346 mg, 12% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.42–7.33 (m, 3H), 3.70 (s, 6H), 2.71 (t, *J* = 7.4 Hz, 2H), 1.78–1.70 (m, 2H), 1.50–1.41 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 129.7, 129.4, 128.9, 125.1, 109.3, 104.4, 52.2, 35.1, 29.3, 24.3, 22.5, 13.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{20}O_4Na$ 311.1254; Found 311.1248. IR (KBr thin film, cm^{-1}): ν 2954, 2872, 1724, 1490, 1434, 1235, 1059, 974, 759, 690.



1d

Dimethyl 2-(3-chloropropyl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (1d):

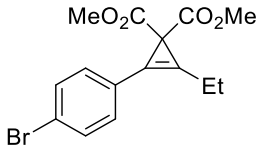
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 570 mg, 18% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54–7.52 (m, 2H), 7.46–7.36 (m, 3H), 3.72 (s, 6H), 3.66 (t, *J* = 6.3 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.26–2.15 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 129.8, 129.1, 124.8, 107.4, 105.9, 52.4, 44.0, 35.1, 30.00, 21.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{17}O_4ClNa$ 331.0708 (100.0%), 333.0678 (32.0%); Found 331.0701 (100.0%), 333.0674 (32.0%). IR (KBr thin film, cm^{-1}): ν 2952, 1720, 1434, 1235, 1059, 971, 836, 761, 690, 653.



1e

Dimethyl 2-(3-acetoxypropyl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (1e):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 337 mg, 10% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.0 Hz, 2H), 7.48–7.35 (m, 3H), 4.18 (t, *J* = 6.3 Hz, 2H), 3.72 (s, 6H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.14–2.07 (m, 2H), 2.05 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 171.2, 129.82, 129.76, 129.0, 124.8, 107.9, 105.5, 63.6, 52.4, 35.1, 26.5, 21.5, 21.1. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{20}O_6Na$; 355.1152 Found 355.1150. IR (KBr thin film, cm^{-1}): ν 2955, 1728, 1598, 1435, 1233, 1062, 917, 758, 692, 535.

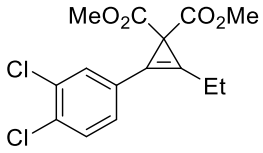


1f

Dimethyl 2-(4-bromophenyl)-3-ethylcycloprop-2-ene-1,1-dicarboxylate (1f):

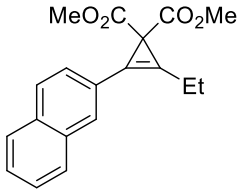
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 503 mg, 15% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55–7.53(m, 2H), 7.40–7.38 (m, 2H), 3.71 (s, 6H), 2.73 (q, *J* = 7.3 Hz, 2H), 1.34 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 132.2, 131.2, 124.1, 123.8, 111.3, 103.6, 52.4, 35.1, 18.4, 11.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for

$C_{15}H_{15}O_4BrNa$ 361.0046 (100.0%), 363.0025 (97.3%); Found 361.0043 (100.0%), 363.0022 (97.3%).. IR (KBr thin film, cm^{-1}): ν 2951, 1720, 1585, 1434, 1233, 1058, 973, 827, 762, 692, 558.



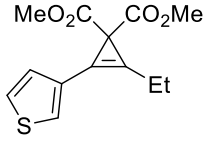
1g

Dimethyl 2-(3,4-dichlorophenyl)-3-ethylcycloprop-2-ene-1,1-dicarboxylate (1g): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous white solid, mp 37–40 ºC, 720 mg, 22% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.47 (d, *J* = 8.3 Hz, 1H), 7.35 (d, *J* = 8.3 Hz, 1H), 3.72 (s, 6H), 2.74 (q, *J* = 7.5 Hz, 2H), 1.34 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 133.7, 133.3, 131.2, 131.0, 128.7, 125.2, 112.7, 102.8, 52.5, 35.2, 18.3, 11.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{14}O_4Cl_2Na$ 351.0161 (100.0%), 353.0132 (63.9%); Found 351.0160 (100.0%), 353.0134 (63.9%).. IR (KBr thin film, cm^{-1}): ν 2953, 1884, 1719, 1464, 1381, 1243, 1028, 976, 822, 696.



1h

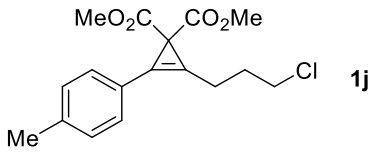
Dimethyl 2-ethyl-3-(naphthalen-2-yl)cycloprop-2-ene-1,1-dicarboxylate (1h): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous white solid, mp 83–86 ºC, 819 mg, 26% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.87–7.82 (m, 3H), 7.64 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.53–7.49 (m, 2H), 3.73 (s, 6H), 2.81 (q, *J* = 7.5 Hz, 2H), 1.40 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.6, 133.6, 133.3, 129.6, 128.7, 128.5, 127.9, 127.2, 126.8, 126.5, 122.4, 110.7, 104.5, 52.3, 35.3, 18.4, 11.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{18}O_4Na$ 333.1097; Found 333.1092. IR (KBr thin film, cm^{-1}): ν 2951, 2855, 1724, 1434, 1244, 935, 824, 746, 659, 479.



1i

Dimethyl 2-ethyl-3-(thiophen-3-yl)cycloprop-2-ene-1,1-dicarboxylate (1i):

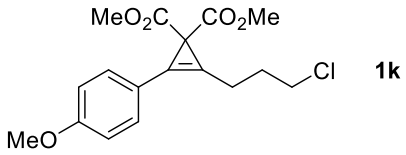
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 93.0 mg, 3% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 2.9, 1.0 Hz, 1H), 7.35 (dd, *J* = 5.0, 3.0 Hz, 1H), 7.25 (dd, *J* = 5.1, 1.2 Hz, 1H), 3.71 (s, 6H), 2.69 (q, *J* = 7.5 Hz, 2H), 1.32 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 128.1, 127.6, 126.8, 126.0, 107.6, 99.6, 52.3, 35.2, 18.1, 11.7. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{14}O_4NaS$ Caculated 289.0505; Found 289.0500. IR (KBr thin film, cm^{-1}): ν 2954, 1729, 1435, 1264, 1062, 733, 703, 634, 448, 419.



1j

Dimethyl 2-(3-chloropropyl)-3-(p-tolyl)cycloprop-2-ene-1,1-dicarboxylate (1j):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 680 mg, 21% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.0 Hz, 2H), 7.28–7.24 (m, 2H), 3.73 (s, 6H), 3.67 (t, *J* = 6.3 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 2.26–2.19 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 171.5, 140.2, 129.8, 121.9, 106.1, 105.8, 52.4, 44.0, 35.0, 30.1, 21.9, 21.7. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{19}O_4ClNa$ 345.0864 (100.0%), 347.0835 (32.0%); Found 345.0858 (100.0%), 347.0830 (32.0%). IR (KBr thin film, cm^{-1}): ν 2952, 1722, 1434, 1236, 1060, 971, 818, 727, 651, 596.

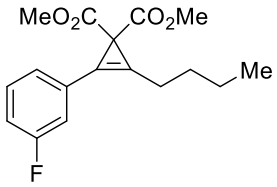


1k

Dimethyl 2-(3-chloropropyl)-3-(4-methoxyphenyl)cycloprop-2-ene-1,1-dicarboxylate (1k):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 3:1), yellow oil, 1.04 g, 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 3.83 (s, 3H), 3.70 (s, 6H), 3.65 (t, *J* = 6.3 Hz, 2H), 2.89 (t, *J* = 7.0 Hz, 2H), 2.22–2.15 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 160.8,

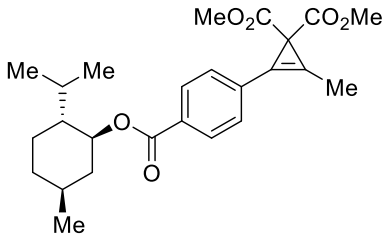
131.4, 117.2, 114.6, 105.4, 104.5, 55.5, 52.4, 44.0, 35.0, 30.1, 21.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{17}H_{20}O_5Cl$ 339.0994 (100.0%), 341.0964 (32.0%); Found 339.0998 (100.0%), 341.0970 (32.0%). IR (KBr thin film, cm^{-1}): ν 2923, 2850, 1723, 1604, 1241, 1061, 970, 834, 646, 526.



1l

Dimethyl 2-butyl-3-(3-fluorophenyl)cycloprop-2-ene-1,1-dicarboxylate (1l):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 962 mg, 31% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35–7.30 (m, 1H), 7.26–7.24 (m, 1H), 7.17–7.15 (m, 1H), 7.03–6.98 (m, 1H), 3.66 (s, 6H), 2.67 (t, J = 7.4 Hz, 2H), 1.72–1.65 (m, 2H), 1.44–1.35 (m, 2H), 0.91 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 162.8 (C-F, $^1J_{C\text{-}F}$ = 248.5 Hz), 130.5 (C-F, $^3J_{C\text{-}F}$ = 9.1 Hz), 127.1 (C-F, $^3J_{C\text{-}F}$ = 8.1 Hz), 125.3 (C-F, $^4J_{C\text{-}F}$ = 2.0 Hz), 116.4 (C-F, $^2J_{C\text{-}F}$ = 22.2 Hz), 116.2 (C-F, $^2J_{C\text{-}F}$ = 22.2 Hz), 110.9, 103.6 (C-F, $^4J_{C\text{-}F}$ = 3.0 Hz), 52.2, 35.1, 29.1, 24.2, 22.4, 13.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ –112.2. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{19}O_4FNa$ 329.1160; Found 329.1158. IR (KBr thin film, cm^{-1}): ν 2955, 2872, 1724, 1583, 1267, 1238, 1060, 870, 787, 633.

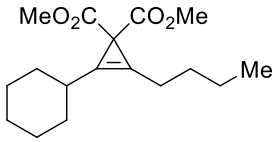


1m

Dimethyl 2-(4-((((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)-3-methylcycloprop-2-ene-1,1-dicarboxylate (1m):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous white solid, mp 76–79 ºC, 619 mg, 14% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.3 Hz, 2H), 7.58 (d, J = 8.3 Hz, 2H), 4.93 (td, J = 10.9, 4.3 Hz, 1H), 3.72 (s, 6H), 2.40 (s, 3H), 2.13–2.10 (m, 1H), 1.92 (dq, J = 6.9, 4.4 Hz, 1H), 1.74

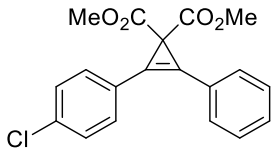
–1.72 (m, 2H), 1.60–1.52 (m, 2H), 1.18–1.06 (m, 2H), 0.92 (t, J = 7.3 Hz, 7H), 0.78 (d, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.1, 165.6, 131.4, 130.1, 129.5, 129.2, 108.3, 104.5, 75.3, 52.4, 47.4, 41.1, 35.2, 34.4, 31.6, 26.7, 23.8, 22.2, 20.9, 16.7, 9.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{36}O_6Na$ 451.2091; Found 451.2090. $[\alpha]_D^{19}$: –24.9 (c 0.3, $CHCl_3$); IR (KBr thin film, cm^{-1}): ν 2955, 2873, 1743, 1708, 1606, 1439, 1270, 955, 788, 695.



1n

Dimethyl 2-butyl-3-cyclohexylcycloprop-2-ene-1,1-dicarboxylate (1n):

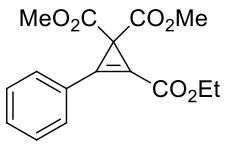
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 362 mg, 12% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 6H), 2.53 (s, 1H), 2.43 (t, J = 7.4 Hz, 2H), 1.86–1.83 (m, 2H), 1.68–1.66 (m, 2H), 1.60–1.50 (m, 3H), 1.39–1.22 (m, 7H), 0.89 (t, J = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 108.8, 104.5, 52.0, 34.8, 33.8, 30.5, 29.1, 26.0, 25.4, 23.4, 22.4, 13.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{26}O_4Na$ 317.1723; Found 317.1721. IR (KBr thin film, cm^{-1}): ν 2929, 2855, 1722, 1433, 1228, 1187, 1060, 978, 838, 738.



1o

Dimethyl 2-(4-chlorophenyl)-3-phenylcycloprop-2-ene-1,1-dicarboxylate (1o):

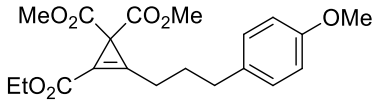
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous white solid, mp 70–73 ºC, 1.20 g, 35% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.4 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.52–7.45 (m, 5H), 3.73 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 136.2, 131.4, 130.39, 130.35, 129.5, 129.2, 125.1, 124.0, 107.3, 105.6, 52.61, 35.09. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{15}O_4ClNa$ 365.0551 (100.0%), 367.0522 (32.0%); Found 365.0552 (100.0%), 367.0523 (32.0%). IR (KBr thin film, cm^{-1}): ν 2951, 1879, 1716, 1611, 1512, 1239, 1033, 977, 760, 698.



1p

2-ethyl 1,1-dimethyl 3-phenylcycloprop-2-ene-1,1,2-tricarboxylate (1p):

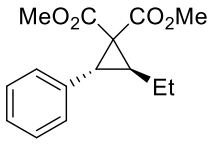
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), amorphous white solid, mp 107–110 ºC, 1.67 g, 55% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.79 (m, 2H), 7.56–7.47 (m, 3H), 4.39 (q, *J* = 7.2 Hz, 2H), 3.75 (s, 6H), 1.40 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 157.7, 132.7, 132.3, 129.3, 123.1, 120.1, 98.7, 62.3, 52.9, 36.5, 14.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{16}O_6Na$ 327.0839; Found 327.0843. IR (KBr thin film, cm^{-1}): ν 2952, 1862, 1755, 1432, 1282, 1189, 1034, 851, 780, 692.



1q

2-ethyl 1,1-dimethyl 3-(3-(4-methoxyphenyl)propyl)cycloprop-2-ene-1,1,2-tricarboxylate (1q):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 2.59 g, 69% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.5 Hz, 2H), 6.80 (d, *J* = 8.5 Hz, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.75 (s, 3H), 3.71 (s, 6H), 2.66 (t, *J* = 7.3 Hz, 4H), 2.01–1.93 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.4, 157.9, 157.2, 133.0, 129.4, 124.1, 113.8, 98.9 , 62.1, 55.2, 52.5, 36.2, 33.8, 28.1, 24.3, 14.1. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{24}O_7Na$ 399.1414; Found 399.1410. IR (KBr thin film, cm^{-1}): ν 2951, 1716, 1611,1512, 1435, 1239, 1062, 833, 760, 518.

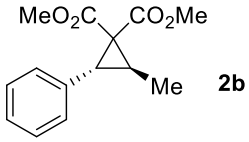


2a

Dimethyl (2*S*,3*R*)-2-ethyl-3-phenylcyclopropane-1,1-dicarboxylate (2a):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 23.8 mg, 91% yield, 12:1 dr. 1H NMR (400 MHz, CDCl3) δ 7.28–7.24 (m, 2H), 7.22–7.18 (m, 3H), 3.79 (s, 3H), 3.38 (s, 3H), 3.09 (d, *J* = 8.2 Hz, 1H),

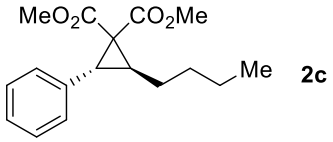
2.49 (dd, J = 15.3, 7.6 Hz, 1H), 1.64–1.49 (m, 2H), 1.07 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.7, 167.8, 135.4, 128.7, 128.2, 127.3, 52.8, 52.4, 42.9, 37.2, 32.8, 21.1, 13.3. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{18}O_4Na$ 285.1097; Found 285.1098. $[\alpha]_D^{21}$: +43.5 (c 0.4, $CHCl_3$); HPLC analysis: 99% ee (Chiralcel ODH, 0.2:99.8 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 19.8 min, R_t (minor) = 17.3 min. IR (KBr thin film, cm^{-1}): ν 2954, 1724, 1603, 1434, 1294, 1244, 1145, 922, 802, 697.



2b

Dimethyl (2*S*,3*R*)-2-methyl-3-phenylcyclopropane-1,1-dicarboxylate (2b):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 22.5 mg, 91% yield, 7:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.24 (m, 2H), 7.22–7.18 (m, 3H), 3.80 (s, 3H), 3.38 (s, 3H), 3.06 (d, J = 8.1 Hz, 1H), 2.60–2.53 (m, 1H), 1.27 (d, J = 6.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.7, 135.3, 128.6, 128.3, 127.3, 52.8, 52.4, 43.3, 38.0, 25.4, 12.6. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{14}H_{16}O_4Na$ 271.0941; Found 271.0940. $[\alpha]_D^{21}$: +57.1 (c 0.3, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IG, 0.8:99.2 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 16.8 min, R_t (minor) = 21.0 min. IR (KBr thin film, cm^{-1}): ν 2953, 1724, 1646, 1435, 1292, 1140, 904, 741, 697, 545.

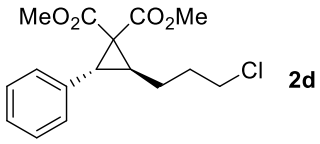


2c

Dimethyl (2*S*,3*R*)-2-butyl-3-phenylcyclopropane-1,1-dicarboxylate (2c):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 27.4 mg, 94% yield, 5:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.18 (m, 5H), 3.79 (s, 3H), 3.38 (s, 3H), 3.08 (d, J = 8.2 Hz, 1H), 2.50 (d, J = 14.1, 7.0Hz, 1H), 1.60–1.56 (m, 1H), 1.49–1.36 (m, 5H), 0.91 (t, J = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.8, 167.8, 135.4, 128.7, 128.3, 127.3, 52.8, 52.4, 42.9, 37.3,

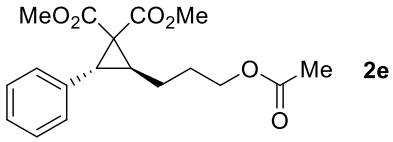
31.21, 31.18, 27.3, 22.4, 14.2. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{22}O_4Na$ 313.1410; Found 313.1408. $[\alpha]_D^{22}$: +16.4 (c 1.3, $CHCl_3$); HPLC analysis: 99% ee (Chiralcel OD-H, 0.1:99.9 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 30.6 min, R_t (minor) = 24.0 min. IR (KBr thin film, cm^{-1}): ν 2953, 1724, 1604, 1434, 1320, 1227, 1079, 908, 697, 585.



2d

Dimethyl (2*S*,3*R*)-2-(3-chloropropyl)-3-phenylcyclopropane-1,1-dicarboxylate (2d):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 23.3 mg, 75% yield, 8:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.22 (m, 3H), 7.18 (d, *J* = 7.2 Hz, 2H), 3.81 (s, 3H), 3.60 (t, *J* = 6.3 Hz, 2H), 3.39 (s, 3H), 3.12 (d, *J* = 8.1 Hz, 1H), 2.51 (dd, *J* = 15.1 Hz, 7.5 Hz, 1H), 2.00–1.92 (m, 2H), 1.75–1.69 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 167.5, 134.9, 128.6, 128.4, 127.5, 53.0, 52.5, 44.4, 42.9, 37.0, 31.9, 30.1, 24.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{19}O_4ClNa$ 333.0864 (100.0%), 335.0835 (32.0%); Found 333.0869 (100.0%), 335.0841 (32.0%). $[\alpha]_D^{22}$: +6.5 (c 6.7, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IC, 0.8:99.2 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 15.7 min, R_t (minor) = 17.4 min. IR (KBr thin film, cm^{-1}): ν 2952, 1724, 1603, 1499, 1434, 1254, 923, 798, 742, 699.

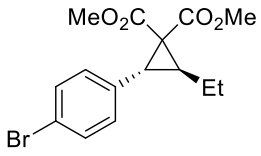


2e

Dimethyl (2*S*,3*R*)-2-(3-acetoxypropyl)-3-phenylcyclopropane-1,1-dicarboxylate (2e):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 21.5 mg, 64% yield, 10:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26–7.21 (m, 3H), 7.18 (d, *J* = 7.1 Hz, 2H), 4.11 (t, *J* = 6.4 Hz, 2H), 3.80 (s, 3H), 3.39 (s, 3H), 3.10 (d, *J* = 8.1 Hz, 1H), 2.53 (dd, *J* = 15.2, 7.6 Hz, 1H), 2.05 (s, 3H), 1.85–1.78

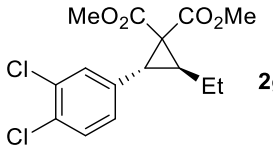
(m, 2H), 1.69–1.59 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.3, 168.6, 167.6, 135.0, 128.6, 128.3, 127.5, 64.0, 52.9, 52.5, 42.9, 37.2, 30.5, 28.1, 24.3, 21.1. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{18}H_{22}O_6Na$ 357.1309; Found 357.1304. $[\alpha]_D^{22}$: +9.3 (c 0.3, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IG, 2:98 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 34.0 min, R_t (minor) = 42.3 min. IR (KBr thin film, cm^{-1}): ν 2953, 1724, 1603, 1435, 1227, 963, 804, 758, 742, 698.



2f

Dimethyl (2*R*,3*S*)-2-(4-bromophenyl)-3-ethylcyclopropane-1,1-dicarboxylate (2f):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 31.5 mg, 92% yield, 6:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 3.79 (s, 3H), 3.43 (s, 3H), 3.00 (d, *J* = 8.1 Hz, 1H), 2.43 (dd, *J* = 15.3, 7.6 Hz, 1H), 1.58–1.49 (m, 2H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 167.6, 134.5, 131.4, 130.4, 121.3, 52.9, 52.6, 43.0, 36.5, 32.9, 21.1, 13.3. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{17}BrO_4Na$ 363.0202 (100.0%), 365.0182 (97.3%); Found 363.0201 (100.0%), 365.0180 (97.3%).. $[\alpha]_D^{22}$: +27.7 (c 1.7, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IG, 0.5:99.5 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 26.8 min, R_t (minor) = 25.8 min. IR (KBr thin film, cm^{-1}): ν 2950, 1724, 1632, 1491, 1435, 1294, 837, 744, 699, 619.

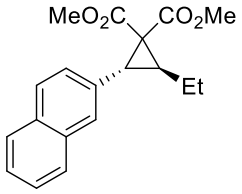


2g

Dimethyl (2*R*,3*S*)-2-(3,4-dichlorophenyl)-3-ethylcyclopropane-1,1-dicarboxylate (2g):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 31.0 mg, 94% yield, 5:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.3 Hz, 1H), 7.29 (d, *J* = 1.9 Hz, 1H), 7.03 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.80 (s, 3H), 3.48 (s, 3H), 2.99 (d, *J* = 8.1 Hz, 1H), 2.40 (dd, *J* = 15.2, 7.6 Hz, 1H), 1.56–1.46 (m,

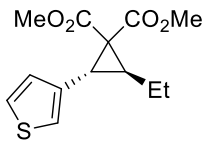
2H), 1.06 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 167.4, 135.9, 132.4, 131.5, 130.8, 130.2, 128.1, 53.0, 52.7, 43.0, 35.9, 33.0, 21.1, 13.3. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{15}H_{16}Cl_2O_4Na$ 353.0318 (100.0%), 355.0288 (63.9%); Found 353.0317 (100.0%), 355.0287 (63.9%).. $[\alpha]_D^{22}$: +33.5 (c 0.9, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IG, 1:99 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 9.7 min, R_t (minor) = 12.5 min. IR (KBr thin film, cm^{-1}): ν 2953, 1724, 1558, 1476, 1435, 1244, 1218, 1031, 823, 681.



2h

Dimethyl (2*S*,3*R*)-2-ethyl-3-(naphthalen-2-yl)cyclopropane-1,1-dicarboxylate (2h):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 29.6 mg, 95% yield, 8:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.73 (m, 3H), 7.64 (s, 1H), 7.47–7.42 (m, 2H), 7.33 (d, *J* = 8.5 Hz, 1H), 3.82 (s, 3H), 3.33 (s, 3H), 3.24 (d, *J* = 8.2 Hz, 1H), 2.62 (dd, *J* = 15.3, 7.6 Hz, 1H), 1.65–1.59 (m, 2H), 1.12 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.8, 167.8, 133.30, 132.98, 132.7, 127.9, 127.7, 127.4, 126.9, 126.2, 125.9, 52.8, 52.4, 43.1, 37.4, 33.1, 21.2, 13.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{19}H_{20}O_4Na$ 335.1254; Found 335.1250. $[\alpha]_D^{22}$: +35.3 (c 0.3, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IC, 3:97 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 4.5 min, R_t (minor) = 5.0 min. IR (KBr thin film, cm^{-1}): ν 2952, 1724, 162, 1246, 1215, 1144, 909, 820, 745, 644.

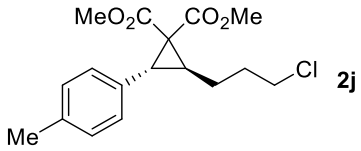


2i

Dimethyl (2*S*,3*S*)-2-ethyl-3-(thiophen-3-yl)cyclopropane-1,1-dicarboxylate (2i):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 21.0 mg, 78% yield, 5:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd,

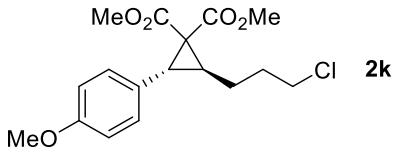
J = 5.0, 3.0 Hz, 1H), 7.03–7.01 (m, 1H), 6.92 (d, *J* = 4.9 Hz, 1H), 3.78 (s, 3H), 3.46 (s, 3H), 3.00 (d, *J* = 8.0 Hz, 1H), 2.39 (dd, *J* = 15.2, 7.6 Hz, 1H), 1.56–1.50 (m, 2H), 1.04 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.8, 136.5, 128.1, 125.4, 122.5, 52.8, 52.5, 42.8, 34.0, 32.4, 20.9, 13.3. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{16}O_4NaS$ 291.0662; Found 291.0666. $[\alpha]_D^{22}$: +31.2 (c 1.3, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IG, 1.5:98.5 ^{i}PrOH/hexanes, 0.9 mL/min, 220 nm), R_t (major) = 12.1 min, R_t (minor) = 13.0 min. IR (KBr thin film, cm^{-1}): ν 2951, 1723, 1435, 1293, 1206, 1093, 921, 806, 761, 633.



2j

Dimethyl (2*S*,3*R*)-2-(3-chloropropyl)-3-(p-tolyl)cyclopropane-1,1-dicarboxylate (2j):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 19.4 mg, 60% yield, 12:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (s, 4H), 3.80 (s, 3H), 3.60–3.57 (m, 2H), 3.41 (s, 3H), 3.08 (d, *J* = 8.2 Hz, 1H), 2.47 (dd, *J* = 15.4, 7.4 Hz, 1H), 2.30 (s, 3H), 2.00–1.90 (m, 2H), 1.74–1.67 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 168.6, 167.6, 137.1, 131.8, 129.1, 128.4, 52.9, 52.5, 44.4, 42.8, 36.9, 31.9, 30.2, 24.9, 21.2. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{21}ClO_4Na$ 347.1021 (100.0%), 349.0991 (32.0%); Found 347.1020 (100.0%), 349.0990 (32.0%).. $[\alpha]_D^{22}$: +6.7 (c 0.4, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IC, 0.8:99.2 ^{i}PrOH/hexanes, 0.8 mL/min, 220 nm), R_t (major) = 21.1 min, R_t (minor) = 23.7 min. IR (KBr thin film, cm^{-1}): ν 2951, 1724, 1518, 1435, 1294, 1253, 927, 820, 713, 650.

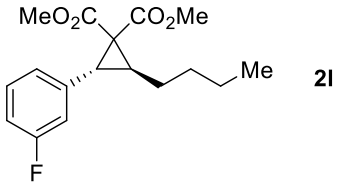


2k

Dimethyl (2*S*,3*R*)-2-(3-chloropropyl)-3-(4-methoxyphenyl)cyclopropane-1,1-dicarboxylate (2k):

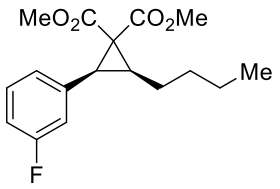
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v =

15:1), yellow oil, 17.5 mg, 51% yield, 10:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, *J* = 8.2 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 3.59 (t, *J* = 6.3 Hz, 2H), 3.42 (s, 3H), 3.07 (d, *J* = 8.2 Hz, 1H), 2.46 (dd, *J* = 15.1, 7.5 Hz, 1H), 1.99–1.90 (m, 2H), 1.73–1.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.6, 167.7, 158.9, 129.7, 126.8, 113.8, 55.4, 52.9, 52.5, 44.4, 42.8, 36.6, 31.9, 30.3, 24.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{21}O_5ClNa$ 363.0970 (100.0%), 365.0940 (32.0%); Found 363.0971 (100.0%), 365.0943 (32.0%).. $[\alpha]_D^{22}$: +35.3 (c 0.4, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IA, 4:96 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 8.6 min, R_t (minor) = 6.4 min. IR (KBr thin film, cm^{-1}): ν 2959, 2851, 1725, 1613, 1435, 1257, 1012, 922, 789, 661.



2l

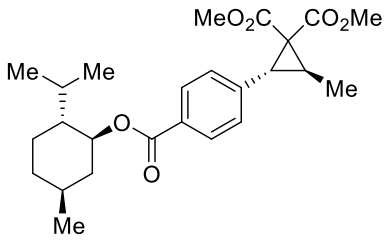
Dimethyl (2*S*,3*R*)-2-butyl-3-(3-fluorophenyl)cyclopropane-1,1-dicarboxylate (2l): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 22.2 mg, 72% yield, 3:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.18 (m, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.92–6.88 (m, 2H), 3.79 (s, 3H), 3.42 (s, 3H), 3.04 (d, *J* = 8.2 Hz, 1H), 2.45 (dd, *J* = 14.6, 7.1 Hz, 1H), 1.59–1.54 (m, 1H), 1.50–1.34 (m, 5H), 0.90 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.5, 167.5, 162.7 (C-F, $^{1}J_{C\text{-}F}$ = 247.5 Hz), 138.1 (C-F, $^{3}J_{C\text{-}F}$ = 7.1 Hz), 129.7 (C-F, $^{3}J_{C\text{-}F}$ = 9.1 Hz), 124.4 (C-F, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 115.6 (C-F, $^{2}J_{C\text{-}F}$ = 21.2 Hz), 114.3 (C-F, $^{2}J_{C\text{-}F}$ = 21.2 Hz) , 52.8, 52.5, 43.0, 36.6 (C-F, $^{4}J_{C\text{-}F}$ = 2.0 Hz), 31.3, 31.1, 27.2, 22.4, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.5. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{21}O_4FNa$ 331.1316; Found 331.1316. $[\alpha]_D^{22}$: +21.7 (c 4.2, $CHCl_3$); HPLC analysis: 99% ee (Chiralcel OD-H, 0.3:99.7 ^{i}PrOH/hexanes, 0.8 mL/min, 220 nm), R_t (major) = 12.1 min, R_t (minor) = 11.0 min. IR (KBr thin film, cm^{-1}): ν 2954, 2861, 1725, 1614, 1588, 1435, 1292, 931, 773, 688.



2l'

Dimethyl (2*S*,3*S*)-2-butyl-3-(3-fluorophenyl)cyclopropane-1,1-dicarboxylate (2l'):

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24–7.20 (m, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.95–6.91 (m, 2H), 3.79 (s, 3H), 3.64 (s, 3H), 3.08 (d, *J* = 10.0 Hz, 1H), 1.99–1.93 (m, 1H), 1.75–1.67 (m, 2H), 1.51–1.38 (m, 2H), 1.37–1.25 (m, 2H), 0.87 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.2, 167.2, 162.6 (C-F, $^1J_{C\text{-}F}$ = 246.4 Hz), 136.7 (C-F, $^3J_{C\text{-}F}$ = 8.1 Hz), 129.6 (C-F, $^3J_{C\text{-}F}$ = 9.1 Hz), 125.5 (C-F, $^4J_{C\text{-}F}$ = 3.0 Hz), 116.7 (C-F, $^2J_{C\text{-}F}$ = 22.2 Hz) , 114.0 (C-F, $^2J_{C\text{-}F}$ = 20.2 Hz), 53.1, 52.2, 37.8, 34.4 (C-F, $^4J_{C\text{-}F}$ = 2.0 Hz), 33.5, 31.8, 24.8, 22.7, 14.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ –113.4. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{17}H_{21}O_4FNa$ 331.1316; Found 331.1315. $[\alpha]_D^{22}$: –34.5 (c 0.1, $CHCl_3$); HPLC analysis: 99% ee (Chiralcel OD-H, 0.3:99.7 ^{i}PrOH/hexanes, 0.8 mL/min, 220 nm), R_t (major) = 12.4 min, R_t (minor) = 13.2 min. IR (KBr thin film, cm^{-1}): ν 2954, 2859, 1726, 1587, 1435, 1320, 1261, 1139, 954, 687.

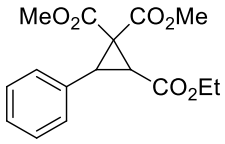


2m

Dimethyl (2*R*,3*S*)-2-(4-((((1*S*,2*R*,5*S*)-2-isopropyl-5-methylcyclohexyl)oxy)carbonyl)phenyl)-3-methylcyclopropane-1,1-dicarboxylate (2m):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 38.8 mg, 90% yield, 5:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 4.90 (td, *J* = 10.9, 4.3 Hz, 1H), 3.81 (s, 3H), 3.42 (s, 3H), 3.07 (d, *J* = 8.1 Hz), 2.61–2.54 (m, 1H), 2.12–2.09 (m, 1H), 1.98–1.91 (m, 1H), 1.73–1.71 (m, 2H), 1.56–1.50 (m, 2H), 1.28 (d, *J* = 6.3 Hz, 3H), 1.16–1.03 (m, 2H), 0.96–0.87 (m, 7H), 0.77 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

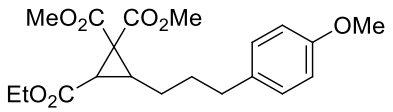
168.3, 167.5, 166.0, 140.4, 129.8, 129.5, 128.6, 75.0, 52.9, 52.6, 47.4, 43.5, 41.1, 37.7, 34.4, 31.6, 26.5, 25.6, 23.7, 22.2, 20.9, 16.6, 12.7. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{36}O_6Na$ 453.2248; Found 453.2243. $[\alpha]_D^{22}$: 1.0 (c 4.1, $CHCl_3$); IR (KBr thin film, cm^{-1}): ν 2953, 2870, 1711, 1611, 1260, 1220, 982, 866, 789, 634.



trans-**2p**

2-ethyl 1,1-dimethyl 3-phenylcycloprop-2-ene-1,1,2-tricarboxylate (*trans*-2p):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 27.5 mg, 90% yield, 5:1 dr. ^1H NMR (400 MHz, $CDCl_3$) δ 7.29–7.25 (m, 5H), 4.25–4.17 (m, 2H), 3.82 (s, 3H), 3.64 (d, *J* = 7.6 Hz, 1H), 3.48 (s, 3H), 3.24 (d, *J* = 7.5 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.2, 166.6, 165.8, 133.0, 128.7, 128.5, 127.9, 61.8, 53.3, 53.0, 44.2, 36.1, 31.3, 14.3. HRMS (ESI-Quadrupole-Orbitrap) m/z: [M + Na]+ Calcd for $C_{16}H_{18}O_6Na$ 329.0996; Found 329.1005. $[\alpha]_D^{26}$: +24.8 (c 1.6, $CHCl_3$); HPLC analysis: 92% ee (Chiralpak IC, 3:97 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 34.2 min, R_t (minor) = 37.5 min. IR (KBr thin film, cm^{-1}): ν 2196, 2018, 1734, 1437, 1264, 1038, 895, 735, 702 464.



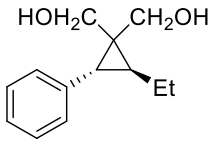
2q

2-Ethyl 1,1-dimethyl 3-(3-(4-methoxyphenyl)propyl)cyclopropane-1,1,2-tricarboxylate (2q):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 20:1), yellow oil, 14.7 mg, 39% yield, 1:1 dr. *trans*-**2q:** ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 4.19–4.07 (m, 2H), 3.78 (s, 3H), 3.73–3.72 (m, 6H), 2.61–2.55 (m, 3H), 2.34 (dd, *J* = 14.4, 7.2 Hz, 1H), 1.75–1.62 (m, 2H), 1.58–1.47 (m, 2H), 1.25 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 167.3, 167.0, 157.9, 134.1, 129.4, 113.9, 61.5, 55.4, 53.2, 53.0, 42.1, 34.4, 33.0, 32.8, 30.9, 25.6, 14.3. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for

$C_{20}H_{26}O_7Na$ 401.1571; Found 401.1574. $[\alpha]_D^{22}$: +0.6 (c 4.0, $CHCl_3$); HPLC analysis: 89% ee (Chiralpak IG, 15:85 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 15.3 min, R_t (minor) = 18.4 min. IR (KBr thin film, cm^{-1}): ν 2953, 1728, 1512, 1435, 1244, 1178, 812, 735, 702, 519.

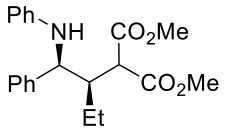
cis-**2q:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 4.17–4.10 (m, 2H), 3.78 (s, 3H), 3.75–3.73 (m, 6H), 2.60–2.56 (m, 3H), 2.01–1.77 (m, 4H), 1.63 (dd, *J* = 16.9, 9.0 Hz, 1H), 1.24 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 168.4, 165.7, 157.8, 134.5, 129.4, 113.9, 61.2, 55.4, 53.4, 52.6, 39.2, 34.8, 33.3, 31.6, 30.7, 23.5, 14.3. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{26}O_7Na$ 401.1571; Found 401.1570. $[\alpha]_D^{22}$: +5.8 (c 1.4, $CHCl_3$); HPLC analysis: 74% ee (Chiralpak IG, 5:95 ^{i}PrOH/hexanes, 0.5 mL/min, 220 nm), R_t (major) = 37.7 min, R_t (minor) = 35.9 min. IR (KBr thin film, cm^{-1}): ν 2955, 1731, 1612, 1512, 1436, 1375, 812, 736, 704, 516.



2a'

((2*S*,3*R*)-2-Ethyl-3-phenylcyclopropane-1,1-diyl)dimethanol (2a'):

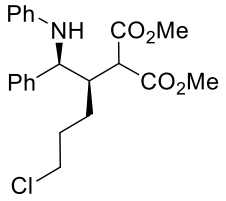
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 1:1), amorphous white solid, mp 67–69 ºC, 58.7 mg, 95% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.24–7.18 (m, 3H), 3.96 (d, *J* = 11.4 Hz, 1H), 3.88 (d, *J* = 11.4 Hz, 1H), 3.54 (d, *J* = 11.6 Hz, 1H), 3.40 (d, *J* = 11.6 Hz, 1H), 2.17 (br, 2H), 1.99 (d, *J* = 6.1 Hz, 1H), 1.72–1.61 (m, 1H), 1.56–1.45 (m, 1H), 1.39–1.34 (m, 1H), 1.10 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 138.4, 128.9, 128.5, 126.5, 67.5, 66.7, 34.9, 33.3, 28.9, 22.1, 14.5. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{18}O_2Na$ 229.1199; Found 229.1198. $[\alpha]_D^{22}$: –60.2 (c 0.1, $CHCl_3$); HPLC analysis: 99% ee (Chiralcel OD-H, 15:85 ^{i}PrOH/hexanes, 1 mL/min, 220 nm), R_t (major) = 6.2 min, R_t (minor) = 5.5 min. IR (KBr thin film, cm^{-1}): ν 3288, 2922, 1447, 1260, 1068, 1015, 941, 801, 741, 696.



4a

Dimethyl 2-((1*S*,2*R*)-1-phenyl-1-(phenylamino)butan-2-yl)malonate (4a):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 30.7 mg, 86% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.32–7.29 (m, 2H), 7.22 (dd, *J* = 7.2, 7.2 Hz, 1H), 7.10–7.04 (m, 2H), 6.64–6.62 (dd, *J* = 7.3, 7.3 Hz, 1H), 6.48 (d, *J* = 8.2 Hz, 2H), 4.82 (dd, *J* = 7.9, 3.2 Hz, 1H), 4.33 (d, *J* = 8.0 Hz, 1H), 3.72 (s, 3H), 3.62 (d, *J* = 5.7 Hz, 1H), 3.53 (s, 3H), 2.61–2.56 (m, 1H), 1.59–1.53 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 169.6, 147.1, 141.9, 129.2, 128.6, 127.1, 127.0, 117.5, 113.5, 56.0, 52.8, 52.7, 52.6, 47.3, 19.1, 13.1. HRMS (ESI-Quadrupole-Orbitrap) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{25}O_4NNa$ 378.1676; Found 378.1671. $[\alpha]_D^{22}$: +7.1 (c 3.0, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IA, 2:98 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 8.0 min, R_t (minor) = 7.4 min. IR (KBr thin film, cm^{-1}): ν 2953, 1732, 1695, 1600, 1497, 1259, 883, 748, 691, 505.

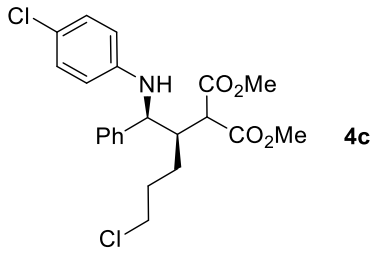


4b

Dimethyl 2-((1*S*,2*R*)-5-chloro-1-phenyl-1-(phenylamino)pentan-2-yl)malonate (4b):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 36.9 mg, 91% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.5 Hz, 2H), 7.17–7.12 (m, 3H), 6.84 (d, *J* = 8.2 Hz, 2H), 6.74 (dd, *J* = 7.3, 7.2 Hz, 1H), 4.71 (d, *J* = 4.3 Hz, 1H), 3.76 (s, 3H), 3.66 (s, 3H), 3.53–3.48 (m, 1H), 3.36 (ddd, *J* = 12.6, 9.1, 3.7 Hz, 1H), 3.01–2.96 (m, 1H), 1.90–1.75 (m, 2H), 1.68–1.48 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 169.3, 151.8, 140.6, 129.1, 128.5, 128.0, 126.8, 119.4, 117.6, 61.6, 53.1, 52.7, 52.6, 47.7, 40.5, 23.4, 22.2. HRMS (ESI-Quadrupole-Orbitrap) m/z: [M + H]$^+$ Calcd for $C_{22}H_{27}O_4NCl$

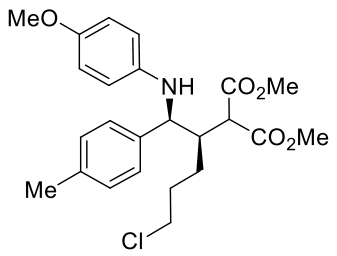
404.1623 (100.0%), 406.1594 (32.0%); Found 404.1621 (100.0%), 406.1604 (32.0%).. $[\alpha]_D^{22}$: +2.0 (c 1.7, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IG, 2:98 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 9.8 min, R_t (minor) = 12.9 min. IR (KBr thin film, cm^{-1}): ν 2926, 1732, 1598, 1501, 1426, 1264, 896, 735, 703, 564.



4c

Dmethyl 2-((1*S*,2*R*)-5-chloro-1-((4-chlorophenyl)amino)-1-phenylpentan-2-yl)malonate (4c):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 30.6 mg, 70% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27–7.22 (m, 4H), 7.18–7.15 (m, 1H), 7.09–7.05 (m, 2H), 6.78–6.74 (m, 2H), 4.59 (d, *J* = 4.8 Hz,1H), 3.76 (s, 3H), 3.67–3.65 (m, 4H), 3.43–3.30 (m, 2H), 3.00–2.90 (m, 1H), 1.92–1.76 (m, 2H), 1.72–1.66 (m, 1H), 1.55–1.48 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.7, 169.2, 150.5, 140.3, 129.0, 128.6, 128.0, 127.1, 124.5, 119.3, 62.1, 53.0, 52.7, 52.6, 48.6, 40.7, 23.5, 22.4. $[\alpha]_D^{22}$: +18.0 (c 0.3, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IC, 0.5:99.5 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 16.1 min, R_t (minor) = 14.1 min. IR (KBr thin film, cm^{-1}): ν 2950, 2852, 1731, 1595, 1495, 1434, 1244, 811, 704, 611.

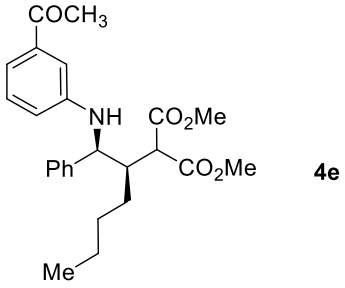


4d

Dimethyl 2-((1*S*,2*R*)-5-chloro-1-((4-methoxyphenyl)amino)-1-(p-tolyl)pentan-2-yl)malonate (4d):

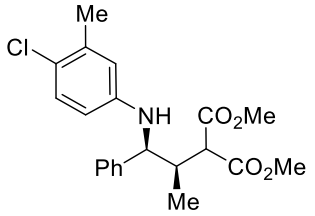
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 27.2 mg, 61% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d,

J = 8.0 Hz, 2H), 6.96 (d, *J* = 8.0 Hz, 2H), 6.86–6.82 (m, 2H), 6.65–6.61 (m, 2H), 4.12 (d, *J* = 7.7 Hz, 1H), 3.75 (s, 3H), 3.67 (s, 3H), 3.62 (s, 3H), 3.40 (d, *J* = 5.8 Hz, 1H), 3.28–3.23 (m, 1H), 3.07–3.01 (m, 1H), 2.69–2.62 (m, 1H), 2.22 (s, 3H), 1.91–1.77 (m, 3H), 1.65–1.58 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 169.4, 154.7, 146.3, 137.9, 136.4, 128.9, 128.6, 123.4, 113.9, 65.7, 55.4, 54.0, 52.9, 52.5, 52.3, 42.9, 25.4, 24.7, 21.2. $[\alpha]_D^{22}$: +19.7 (c 0.8, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IG, 5:95 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 13.2 min, R_t (minor) = 21.8 min. IR (KBr thin film, cm^{-1}): ν 2923, 2852, 1731, 1508, 1435, 1285, 1238, 805, 717, 559.



4e

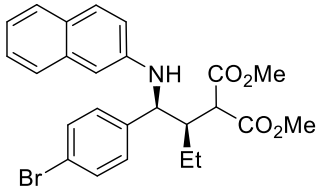
Dimethyl 2-((1*S*,2*R*)-1-((3-acetylphenyl)amino)-1-phenylhexan-2-yl)malonate (4e): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 30.6 mg, 72% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.4 Hz, 2H), 7.32–7.28 (m, 2H), 7.23–7.19 (m, 2H), 7.15–7.11 (m, 2H), 6.62 (dd, *J* = 8.0, 2.4 Hz, 1H), 4.84 (dd, *J* = 8.0, 3.1 Hz), 4.56 (d, *J* = 8.0 Hz, 1H), 3.73 (s, 3H), 3.59 (d, *J* = 5.6 Hz, 1H), 3.55 (s, 3H), 2.65–2.60 (m, 1H), 2.48 (s, 3H), 1.58–1.45 (m, 2H), 1.19–1.00 (m, 3H), 0.88–0.85 (m, 1H), 0.75 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 169.9, 169.6, 147.4, 141.3, 138.1, 129.5, 128.7, 127.3, 126.9, 117.9, 117.7, 113.0, 58.2, 53.1, 52.7, 52.6, 45.3, 30.4, 26.8, 25.7, 22.6, 13.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{31}O_5NNa$ 448.2094; Found 448.2091. $[\alpha]_D^{22}$: +26.1 (c 1.6, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IA, 3:97 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 33.4 min, R_t (minor) = 21.4 min. IR (KBr thin film, cm^{-1}): ν 2922, 2853, 1742, 1683, 1456, 1358, 1258, 789, 687, 587.



4f

Dimethyl 2-((1*S*,2*R*)-1-((4-chloro-3-methylphenyl)amino)-1-phenylpropan-2-yl)malonate (4f):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 37.2 mg, 95% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31–7.29 (m, 4H), 7.25–7.21 (m, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.40 (d, *J* = 2.6 Hz, 1H), 6.25 (dd, *J* = 8.6, 2.7 Hz, 1H), 4.63 (d, *J* = 3.8 Hz, 1H), 4.18 (br, 1H), 3.72 (s, 3H), 3.68 (s, 3H), 3.56 (d, *J* = 8.1 Hz, 1H), 2.84–2.75 (m, 1H), 2.21 (s, 3H), 0.94 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.5, 169.3, 145.8, 141.3, 136.6, 129.5, 128.7, 127.3, 126.8, 122.8, 116.0, 112.2, 58.6, 54.9, 52.8, 52.7, 39.9, 20.4, 11.2. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{25}O_4NCl$ 390.1467 (100.0%), 392.1437 (32.0%); Found 390.1466 (100.0%), 392.1432 (32.0%).. $[\alpha]_D^{22}$: –44.0 (c 0.2, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IC, 1:99 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 9.3 min, R_t (minor) = 12.0 min. IR (KBr thin film, cm^{-1}): ν 3422, 2951, 2924, 1738, 1583, 1451, 1268, 819, 702, 622.

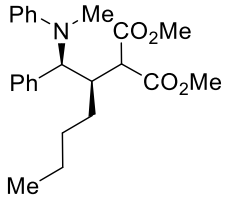


4g

Dimethyl 2-((1*S*,2*R*)-1-(4-bromophenyl)-1-(naphthalen-2-ylamino)butan-2-yl)malonate (4g):

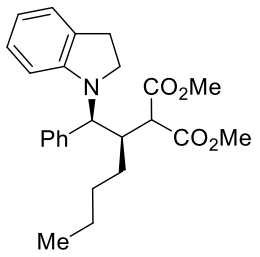
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 41.0 mg, 85% yield, 6:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, *J* = 12.0, 8.5 Hz, 2H), 7.47–7.43 (m, 3H), 7.34–7.27 (m, 3H), 7.18–7.14 (m, 1H), 6.90–6.88 (m, 1H), 6.49 (s, 1H), 4.93 (dd, *J* = 6.3, 1.0 Hz, 1H), 4.55 (d, *J* = 7.6 Hz, 1H), 3.74 (s, 3H), 3.66 (d, *J* = 5.3 Hz, 1H), 3.49 (s, 3H), 2.61–2.57 (m, 1H), 1.68–1.62 (m, 1H), 1.56–1.49 (m, 1H), 0.85 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ

170.0, 169.4, 144.3, 140.9, 135.0, 131.8, 129.0, 128.8, 127.7, 127.6, 126.4, 126.2, 122.3, 121.0, 117.9, 105.9, 57.6, 52.8, 52.7, 52.5, 47.2, 18.9, 13.0. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{25}H_{27}O_4NBr$ 484.1118 (100.0%), 486.1098 (97.3%); Found 484.1116 (100.0%), 486.1092 (97.3%). $[\alpha]_D^{22}$: –63.5 (c 0.3, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IC, 1.5:98.5 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 7.7 min, R_t (minor) = 8.4 min. IR (KBr thin film, cm^{-1}): ν 2925, 1729, 1630, 1435, 1264, 808, 734, 702, 620, 472.



4h

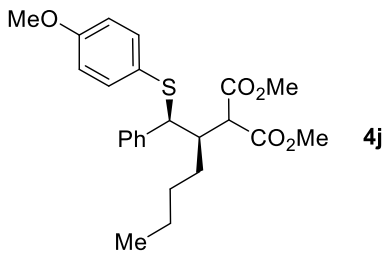
Dimethyl 2-((1*S*,2*R*)-1-(methyl(phenyl)amino)-1-phenylhexan-2-yl)malonate (4h): Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 31.8 mg, 80% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23–7.19 (m, 5H), 7.09–7.07 (m, 2H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.81–6.77 (m, 1H), 5.02 (d, *J* = 11.7 Hz, 1H), 3.93 (d, *J* = 6.0 Hz, 1H), 3.65 (s, 3H), 3.59 (s, 3H), 3.22–3.16 (m, 1H), 2.37 (s, 3H), 1.56–1.48 (m, 1H), 1.36–1.29 (m, 1H), 1.23–1.07 (m, 4H), 0.74 (t, *J* =7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.9, 169.6, 150.5, 136.3, 128.9, 128.2, 128.1, 127.5, 118.7, 116.2, 67.3, 52.7, 52.29, 52.25, 39.1, 32.0, 29.0, 28.9, 23.0, 13.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{31}O_4NNa$ Caculated 420.2145; Found 420.2140. $[\alpha]_D^{22}$: +18.3 (c 0.2, $CHCl_3$); HPLC analysis: 98% ee (Chiralcel OD-H, 0.3:99.7 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 16.4 min, R_t (minor) = 15.5 min. IR (KBr thin film, cm^{-1}): ν 2953, 2871, 1729, 1596, 1497, 1433, 1254, 792, 748, 699.



4i

Dimethyl 2-((1*S*,2*R*)-1-(indolin-1-yl)-1-phenylhexan-2-yl)malonate (4i):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 37.2 mg, 91% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.23 (m, 5H), 7.11–7.08 (m, 1H), 6.94 (d, *J* = 7.1 Hz, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.61–6.58 (m, 1H), 4.92 (d, *J* = 11.8 Hz, 1H), 3.83 (d, *J* = 6.6 Hz, 1H), 3.63 (s, 3H), 3.53 (s, 3H), 3.44–3.38 (m, 1H), 3.22–3.14 (m, 1H), 2.93–2.69 (m, 3H), 1.45–1.28 (m, 2H), 1.24–1.06 (m, 4H), 0.75 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 169.7, 150.7, 136.1, 129.7, 128.9, 128.3, 127.6, 127.1, 124.5, 117.6, 108.0, 61.6, 53.1, 52.2, 52.0, 46.6, 39.8, 29.3, 28.3, 28.1, 22.9, 13.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{31}O_4NNa$ Caculated 432.2145; Found 432.2140. $[\alpha]_D^{22}$: –45.6 (c 0.3, $CHCl_3$); HPLC analysis: 97% ee (Chiralpak IA, 1:99 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 13.6 min, R_t (minor) = 10.2 min. IR (KBr thin film, cm^{-1}): ν 2952, 2928, 1728, 1472, 1434, 1250, 917, 827, 740, 641.

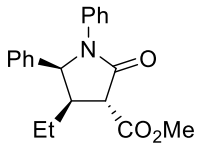


4j

Dimethyl 2-((1*S*,2*R*)-1-((4-methoxyphenyl)thio)-1-phenylhexan-2-yl)malonate (4j):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 10:1), yellow oil, 31.2 mg, 72% yield, 6:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 2H), 7.20–7.14 (m, 3H), 7.13–7.09 (m, 2H), 6.72–6.68 (d, *J* = 8.7 Hz, 2H), 4.16 (d, *J* = 9.2 Hz, 1H), 4.11 (d, *J* = 5.1 Hz, 1H), 3.76 (s, 3H), 3.74 (s, 3H), 3.72 (s, 3H), 2.71–2.65 (m, 1H), 1.56–1.36 (m, 2H), 1.11–1.02 (m, 3H), 0.98–0.92 (m, 1H), 0.70 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 169.9, 169.4, 159.6, 141.2, 135.7, 128.8, 128.2, 127.2, 125.0, 114.4, 59.2, 55.4, 53.6, 52.6, 52.4, 43.7, 30.4, 30.0, 22.8, 13.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{30}O_5SNa$ Caculated 453.1706; Found 453.1700. $[\alpha]_D^{22}$: –41.8 (c 0.3, $CHCl_3$); HPLC analysis: 96% ee (Chiralpak IA, 2:98 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t

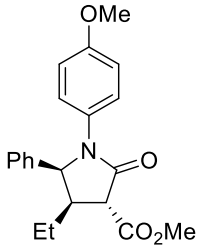
(major) = 5.6 min, R_t (minor) = 6.7 min. IR (KBr thin film, cm^{-1}): ν 2953, 2859, 1731, 1592, 1493, 1285, 1243, 827, 700, 641.



5a

Methyl (3*R*,4*R*,5*S*)-4-ethyl-2-oxo-1,5-diphenylpyrrolidine-3-carboxylate (5a):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), amorphous white solid, mp 76–79 ºC, 29.3 mg, 91% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48–7.46 (m, 2H), 7.37–7.30 (m, 3H), 7.25–7.17 (m, 4H), 7.08–7.05 (m, 1H), 5.23 (d, *J* = 8.1 Hz, 1H), 3.84 (s, 3H), 3.58 (d, *J* = 11.7 Hz, 1H), 3.20–3.12 (m, 1H), 1.27–1.19 (m, 1H), 0.93–0.88 (m, 1H), 0.85–0.81 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 170.8, 169.7, 138.2, 137.1, 129.1, 128.9, 128.5, 127.1, 125.3, 121.7, 66.4, 54.4, 52.9, 43.8, 23.6, 12.1. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{21}O_3NNa$ 346.1414; Found 346.1412. $[\alpha]_D^{22}$: +39.8 (c 0.4, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IA, 15:85 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 17.6 min, R_t (minor) = 7.7min. IR (KBr thin film, cm^{-1}): ν 2963, 2930, 1746, 1682, 1499, 1269, 1212, 811, 725, 698.

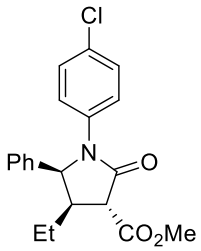


5b

Methyl (3*R*,4*R*,5*S*)-4-ethyl-1-(4-methoxyphenyl)-2-oxo-5-phenylpyrrolidine-3-carboxylate (5b)：

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), amorphous white solid, mp 91–94 ºC, 25.2 mg, 71% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) 7.35–7.29 (m, 5H), 7.16 (d, *J* = 7.2 Hz, 2H), 6.75 (d, *J* = 8.9 Hz, 2H), 5.15 (d, *J* = 8.1 Hz, 1H), 3.84 (s, 3H), 3.71 (s, 3H), 3.56 (d, *J* = 11.6 Hz, 1H), 3.20–3.12 (m, 1H), 1.25–1.16 (m, 1H), 0.93–0.85 (m, 1H), 0.82 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 169.4, 157.1, 137.3, 131.3, 129.0, 128.4, 127.2,

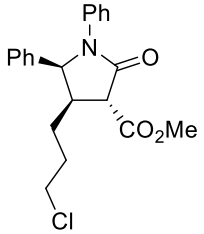
123.7, 114.1, 66.9, 55.5, 54.3, 52.9, 43.9, 23.7, 12.1. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{23}O_4NNa$ 376.1519; Found 376.1517. $[\alpha]_D^{22}$: +14.5 (c 1.7, $CHCl_3$); HPLC analysis: 99% ee (Chiralcel OD-H, 25:75 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 11.9 min, R_t (minor) = 10.1 min. IR (KBr thin film, cm^{-1}): ν 2957, 1739, 1683, 1509, 1463, 1238, 824, 732, 701, 516.



5c

Methyl (3*R*,4*R*,5*S*)-1-(4-chlorophenyl)-4-ethyl-2-oxo-5-phenylpyrrolidine-3-carboxylate (5c):

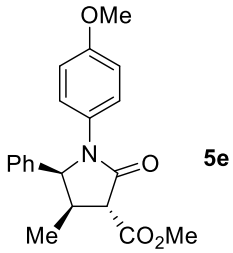
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), amorphous white solid, mp 97–99 ºC, 29.0 mg, 81% yield, >20:1 dr. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.36–7.30 (m, 3H), 7.19 (d, *J* = 8.8 Hz, 2H), 7.15 (d, *J* = 7.4 Hz, 2H), 5.20 (d, *J* = 8.1 Hz, 1H), 3.84 (s, 3H), 3.56 (d, *J* = 11.6 Hz, 1H), 3.18–3.12 (m, 1H), 1.24–1.19 (m, 1H), 0.92–0.86 (m, 1H), 0.83 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 169.8, 136.8, 136.7, 130.5, 129.2, 129.0, 128.7, 127.0, 122.8, 66.3, 54.4, 53.0, 43.8, 23.6, 12.0. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}O_3NCl$ 358.1204 (100.0%), 360.1175 (32.0%); Found 358.1200 (100.0%), 360.1172 (32.0%). $[\alpha]_D^{22}$: +12.7 (c 1.3, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IA, 25:75 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 22.9 min, R_t (minor) = 79.1 min. IR (KBr thin film, cm^{-1}): ν 2921, 2850, 1738, 1693, 1594, 1494, 1221, 837, 721, 703, 665.



5d

Methyl (3*R*,4*R*,5*S*)-4-(3-chloropropyl)-2-oxo-1,5-diphenylpyrrolidine-3-carboxylate (5d):

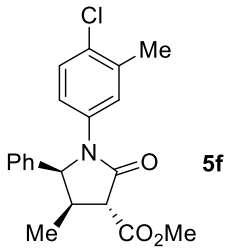
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow oil, 19.5 mg, 52% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.9 Hz, 2H), 7.38–7.30 (m, 3H), 7.24–7.18 (m, 4H), 7.10–7.06 (m, 1H), 5.23 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 3.59 (d, *J* = 11.7 Hz, 1H), 3.44–3.34 (m, 2H), 3.30–3.21 (m, 1H), 1.74–1.61 (m, 2H), 1.40–1.31 (m, 1H), 1.04–0.94 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 169.2, 138.1, 136.8, 129.3, 129.0, 128.7, 127.1, 125.5, 121.8, 66.3, 54.4, 53.1, 44.4, 41.3, 30.4, 27.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{23}O_3NCl$ 372.1361 (100.0%), 374.1331 (32.0%); Found 372.1367 (100.0%), 374.1333 (32.0%). $[\alpha]_D^{22}$: +25.7 (c 0.7, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IC, 25:75 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 26.2 min, R_t (minor) = 11.4 min. IR (KBr thin film, cm^{-1}): ν 2924, 2855, 1740, 1697, 1498, 1260, 801, 702, 692, 509.



5e

Methyl (3*R*,4*R*,5*S*)-1-(4-methoxyphenyl)-4-methyl-2-oxo-5-phenylpyrrolidine-3-carboxylate (5e):

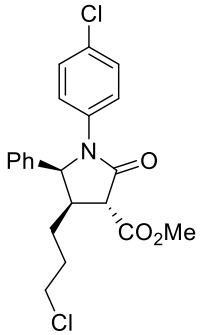
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), amorphous white solid, mp 99–101ºC, 30.7 mg, 90% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.30 (m, 5H), 7.16–7.14 (m, 2H), 6.78–6.74 (m, 2H), 5.12 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 3.47 (d, *J* = 11.6 Hz, 1H), 3.33–3.23 (m, 1H), 0.74 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 169.3, 157.0, 136.8, 131.4, 129.1, 128.4, 127.0, 123.4, 114.1, 67.1, 55.5, 55.1, 52.9, 36.9, 15.1. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{21}O_4NNa$ 362.1362; Found 362.1361. $[\alpha]D^{22}$: +33.0 (c 0.2, $CHCl_3$); HPLC analysis: 99% ee (Chiralcel OD-H, 15:85 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 19.2 min, R_t (minor) = 16.3 min. IR (KBr thin film, cm^{-1}): ν 2960, 2920, 1738, 1683, 1515, 1254, 836, 782, 730, 525.



5f

Methyl (3*R*,4*R*,5*S*)-1-(4-chloro-3-methylphenyl)-4-methyl-2-oxo-5-phenylpyrrolidine-3-carboxylate (5f):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow oil, 31.8 mg, 89% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 2.5 Hz, 1H), 7.38–7.31 (m, 3H), 7.17–7.11 (m, 4H), 5.15 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 3.46 (d, *J* = 11.8 Hz, 1H), 3.31–3.21 (m, 1H), 2.27 (s, 3H), 0.75 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.8, 169.6, 136.8, 136.7, 136.4, 130.8, 129.3, 129.2, 128.6, 126.8, 124.0, 120.0, 66.6, 55.2, 53.0, 36.8, 20.5, 15.0. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{20}H_{21}O_3NCl$ 358.1204 (100.0%), 360.1175 (32.0%); Found 358.1207 (100.0%), 360.1176 (32.0%). $[\alpha]_D^{22}$: +40.0 (c 0.1, $CHCl_3$); HPLC analysis: 99% ee (Chiralcel OD-H, 10:90 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 6.3 min, R_t (minor) = 7.7 min. IR (KBr thin film, cm^{-1}): ν 2919, 2849, 1740, 1680, 1483, 1388, 1259, 811, 698, 611.

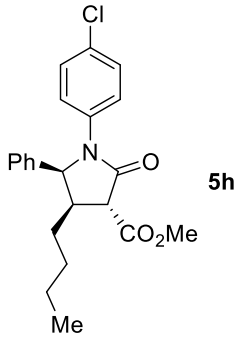


5g

Dethyl (3*R*,4*R*,5*S*)-1-(4-chlorophenyl)-4-(3-chloropropyl)-2-oxo-5-phenylpyrrolidine-3-carboxylate (5g):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow oil, 24.8 mg, 61% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.33 (m, 5H), 7.20–7.15 (m, 4H), 5.20 (d, *J* = 8.0 Hz, 1H), 3.86 (s, 3H), 3.58 (d, *J* = 11.7 Hz, 1H), 3.44–3.34 (m, 2H), 3.29–3.20 (m, 1H), 1.75–1.61 (m, 2H), 1.40–1.31

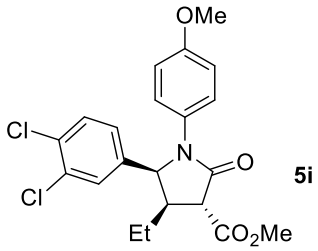
(m, 1H), 1.03–0.94 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) 170.3, 169.3, 136.7, 136.3, 130.7, 129.4, 129.0, 128.9, 127.0, 122.8, 66.1, 54.3, 53.2, 44.3, 41.2, 30.3, 27.8. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}O_3Cl_2N$ 406.0971 (100.0%), 408.0942 (63.9%); Found 406.0974 (100.0%), 408.0946 (63.9%). $[\alpha]_D^{22}$: +26.9 (c 0.5, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IC, 25:75 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 12.3 min, R_t (minor) = 8.1 min. IR (KBr thin film, cm^{-1}): ν 2924, 2854, 1740, 1698, 1494, 1456, 1260, 800, 760, 660, 510.



5h

Methyl (3*R*,4*R*,5*S*)-4-butyl-1-(4-chlorophenyl)-2-oxo-5-phenylpyrrolidine-3-carboxylate (5h):

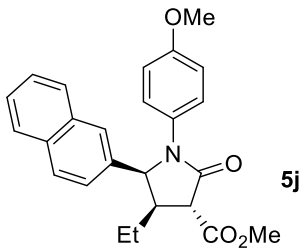
Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), yellow oil, 31.9 mg, 83% yield, >20:1 dr. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45–7.42 (m, 2H), 7.37–7.31 (m, 3H), 7.20–7.17 (m, 2H), 7.17–7.14 (m, 2H), 5.18 (d, *J* = 8.0 Hz, 1H), 3.84 (s, 3H), 3.56 (d, *J* = 11.8 Hz, 1H), 3.25–3.17 (m, 1H), 1.24–1.09 (m, 5H), 0.91–0.85 (m, 1H), 0.78 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 169.8, 136.8, 136.7, 130.5, 129.2, 129.0, 128.7, 127.0, 122.8, 66.3, 54.5, 53.0, 42.0, 30.0, 29.6, 22.6, 13.9. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{22}H_{25}O_3NCl$ 386.1517 (100.0%), 388.1488 (32.0%); Found 386.1512 (100.0%), 388.1480 (32.0%). $[\alpha]_D^{22}$: +23.7 (c 1.6, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IA, 25:75 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 24.4 min, R_t (minor) = 5.5 min. IR (KBr thin film, cm^{-1}): ν 2928, 2859, 1741, 1697, 1494, 1264, 829, 733, 701, 671.



5i

Methyl (3*R*,4*R*,5*S*)-5-(3,4-dichlorophenyl)-4-ethyl-1-(4-methoxyphenyl)-2-oxopyrrolidine-3-carboxylate (5i):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), amorphous white solid, mp 130–133ºC, 33.7 mg, 80% yield, >20:1 dr. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 1H), 7.29–7.26 (m, 3H), 7.00 (dd, *J* = 8.3, 1.7 Hz, 1H), 6.78 (d, *J* = 9.1 Hz, 2H), 5.13 (d, *J* = 8.2 Hz, 1H), 3.84 (s, 3H), 3.73 (s, 3H), 3.51 (d, *J* = 11.4 Hz, 1H), 3.20–3.15 (m, 1H), 1.23–1.17 (m, 1H), 0.96–0.88 (m, 1H), 0.84 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 169.1, 157.4, 137.8, 133.5, 132.7, 131.1, 130.6, 129.2, 126.5, 123.9, 114.3, 65.9, 55.5, 54.0, 53.1, 43.4, 23.9, 12.1. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + H]^+$ Calcd for $C_{21}H_{22}O_4NCl_2$ 422.0920 (100.0%), 424.0891 (63.9%); Found 422.0925 (100.0%), 424.0890 (63.9%). $[\alpha]_D^{22}$: +9.3 (c 0.5, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IA, 25:75 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 13.2 min, R_t (minor) = 9.1 min. IR (KBr thin film, cm^{-1}): ν 2926, 1741, 1690, 1512, 1470, 1248, 830, 735, 701, 674.



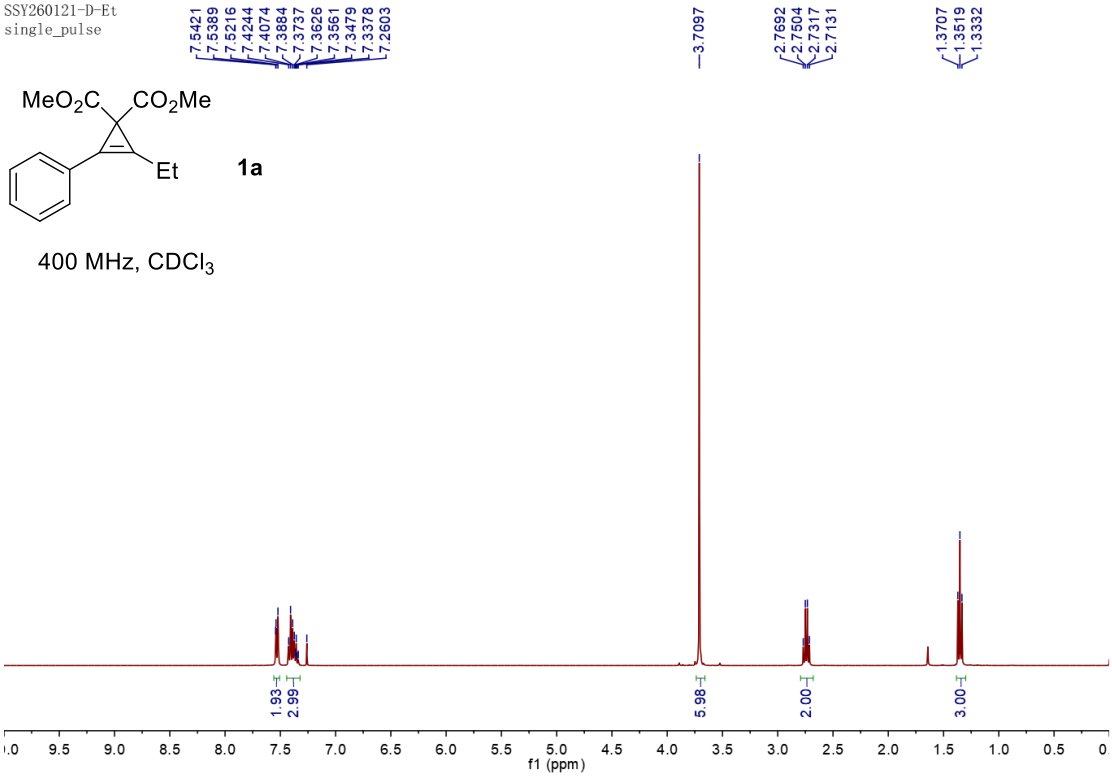
5j

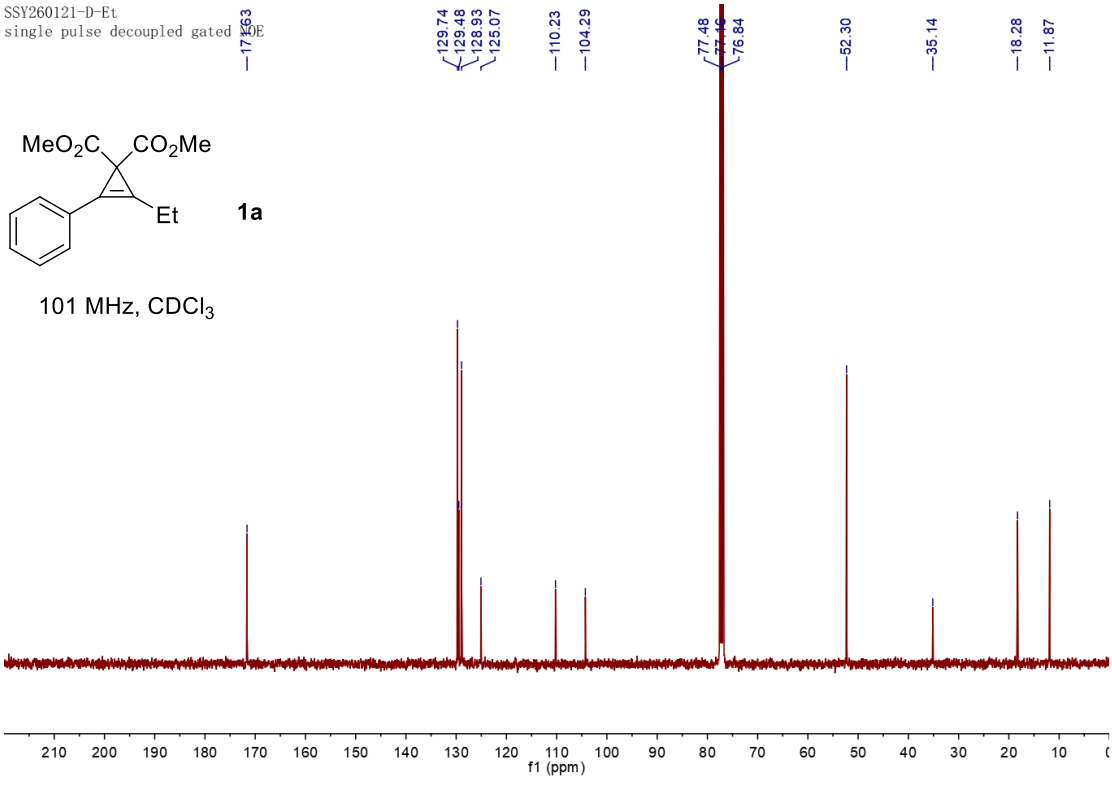
Methyl (3*R*,4*R*,5*S*)-4-ethyl-1-(4-methoxyphenyl)-5-(naphthalen-2-yl)-2-oxopyrrolidine-3-carboxylate (5j):

Purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, v:v = 5:1), amorphous white solid, mp 140–143ºC, 30.4 mg, 75% yield, >20:1 dr. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2H), 7.80–7.78 (m, 1H), 7.63 (s, 1H), 7.51–7.48

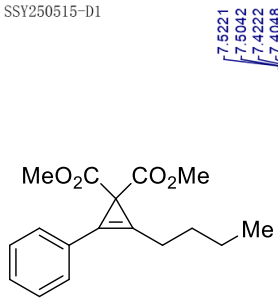
(m, 2H), 7.36–7.35 (m, 2H), 7.28 (d, *J* = 8.5 Hz, 1H), 6.72 (d, *J* = 9.1 Hz, 2H), 5.32 (d, *J* = 8.2 Hz, 1H), 3.86 (s, 3H), 3.69 (s, 3H), 3.66 (d, *J* = 11.6 Hz, 1H), 3.27–3.22 (m, 1H), 1.25–1.20 (m, 1H), 0.92–0.86 (m, 1H), 0.82 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.9, 169.5, 157.2, 134.9, 133.33, 133.26, 131.2, 129.0, 128.0, 127.9, 126.8, 126.5, 123.8, 114.1, 67.1, 55.4, 54.4, 53.0, 44.0, 23.8, 12.1. HRMS (ESI-Quadrupole-Orbitrap) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{25}O_4NNa$ Caculated 426.1676; Found 426.1675. $[\alpha]_D^{22}$: +8.2 (c 0.4, $CHCl_3$); HPLC analysis: 99% ee (Chiralpak IA, 25:75 ^{i}PrOH/hexanes, 1 mL/min, 254 nm), R_t (major) = 24.9 min, Rt (minor) = 11.3 min. IR (KBr thin film, cm^{-1}): ν 2925, 2854, 1729, 1682, 1513, 1432, 1242, 841, 780, 650.

NMR Spectra of New Compounds





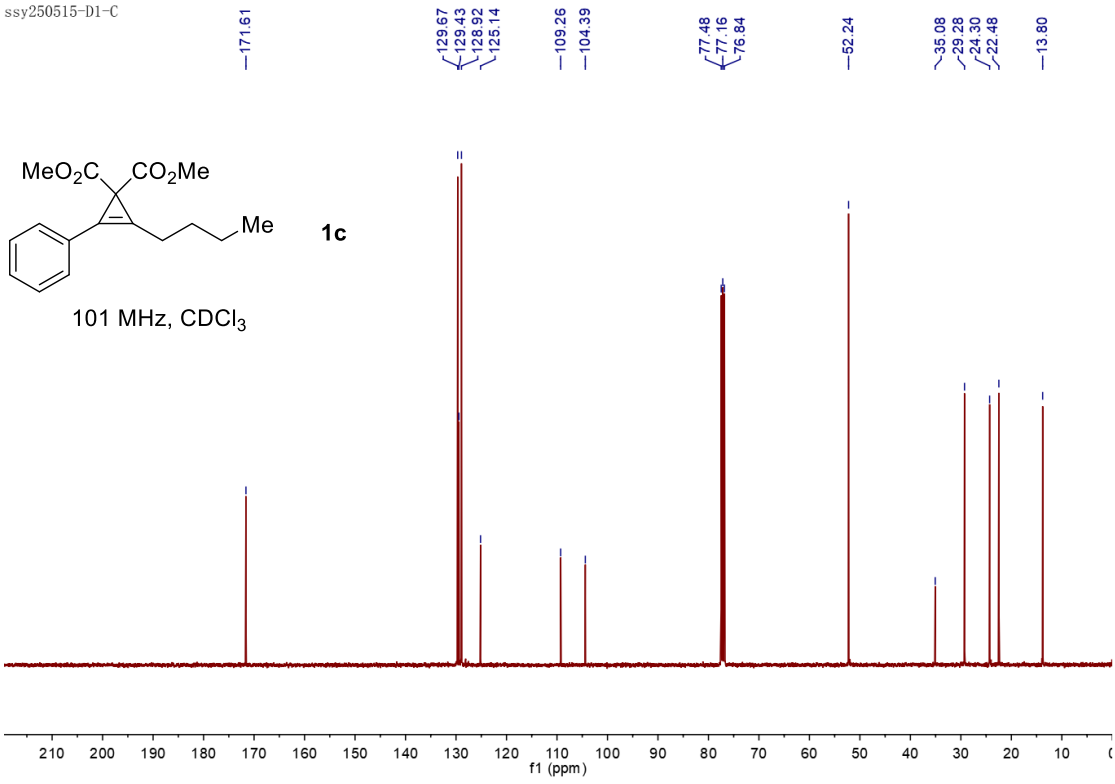
SSY250515-D1



1c

400 MHz, $CDCl_3$

ssy250515-D1-C



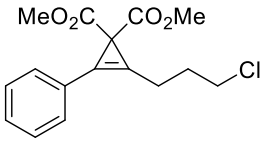
1c

101 MHz, $CDCl_3$

SSY250523-D-Cl
single_pulse

7.5440
7.5406
7.5246
7.4482
7.4440
7.4275
7.4084
7.4005
7.3824
7.2663
7.2602

3.7182
3.6768
3.6655
3.6610
3.6500
3.6452
2.9489
2.9312
2.9135
2.2484
2.2318
2.2150
2.1984
2.1813

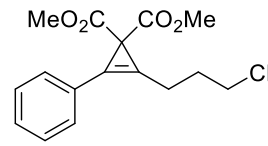


1d

400 MHz, $CDCl_3$

ssy250524-D-Cl-C

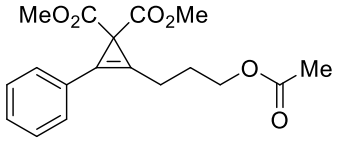
171.4325
129.8325
129.0722
124.7777
107.4033
105.9418
77.4775
77.1560
76.8424
52.4311
43.9763
35.0558
30.0022
21.8892



1d

101 MHz, $CDCl_3$

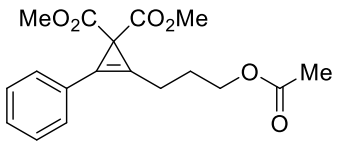
SSY251014-D-YX
single_pulse



1e

400 MHz, $CDCl_3$

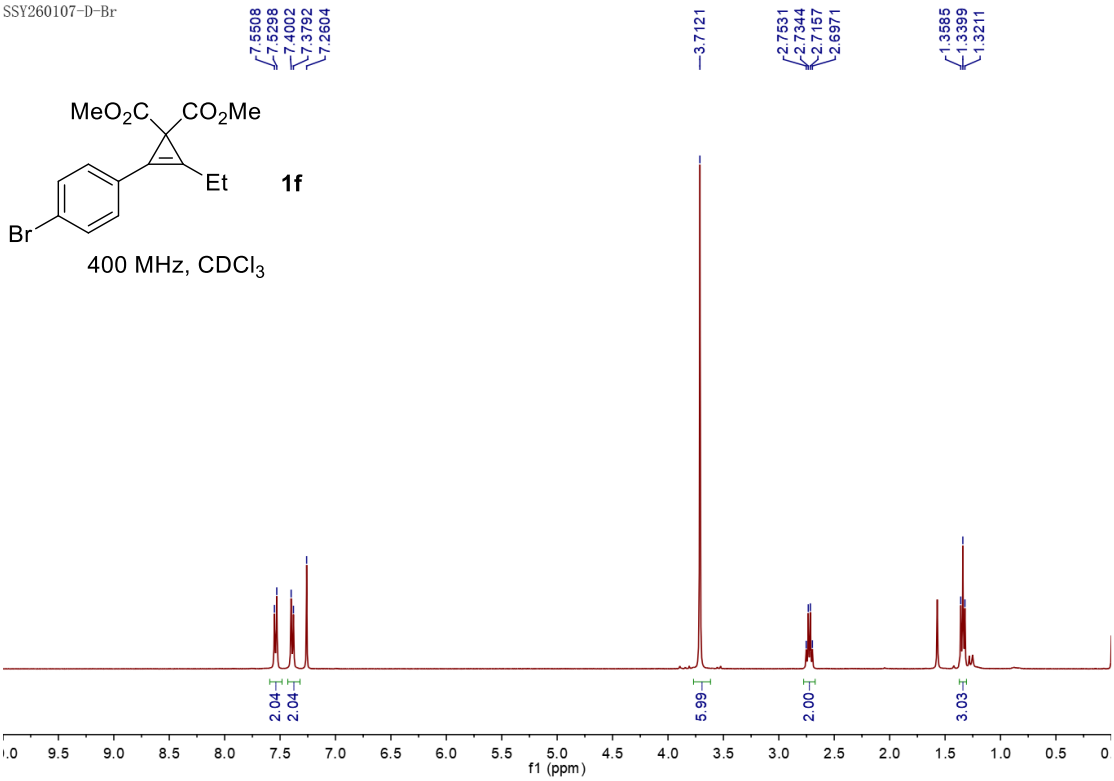
SSY251012-D-YX-C-5h
single pulse decoupled gated NOE

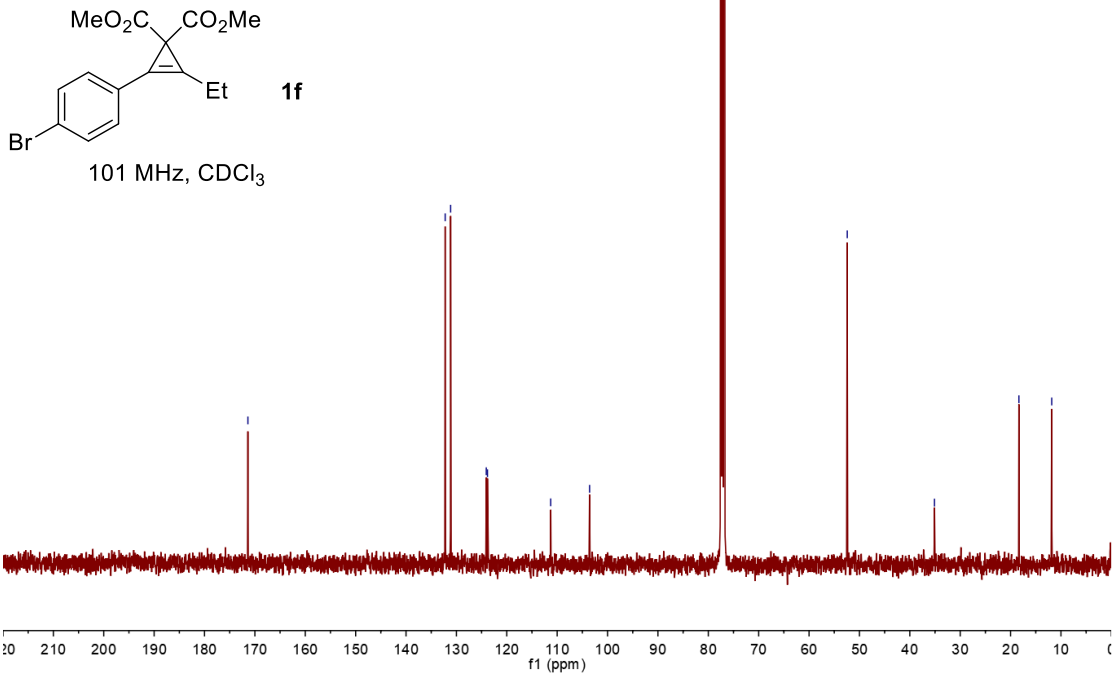


1e

151 MHz, $CDCl_3$

SSY260107-D-Br



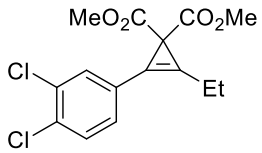


1f

400 MHz, $CDCl_3$

101 MHz, $CDCl_3$

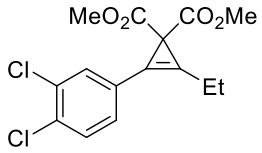
SSY251010-69



1g

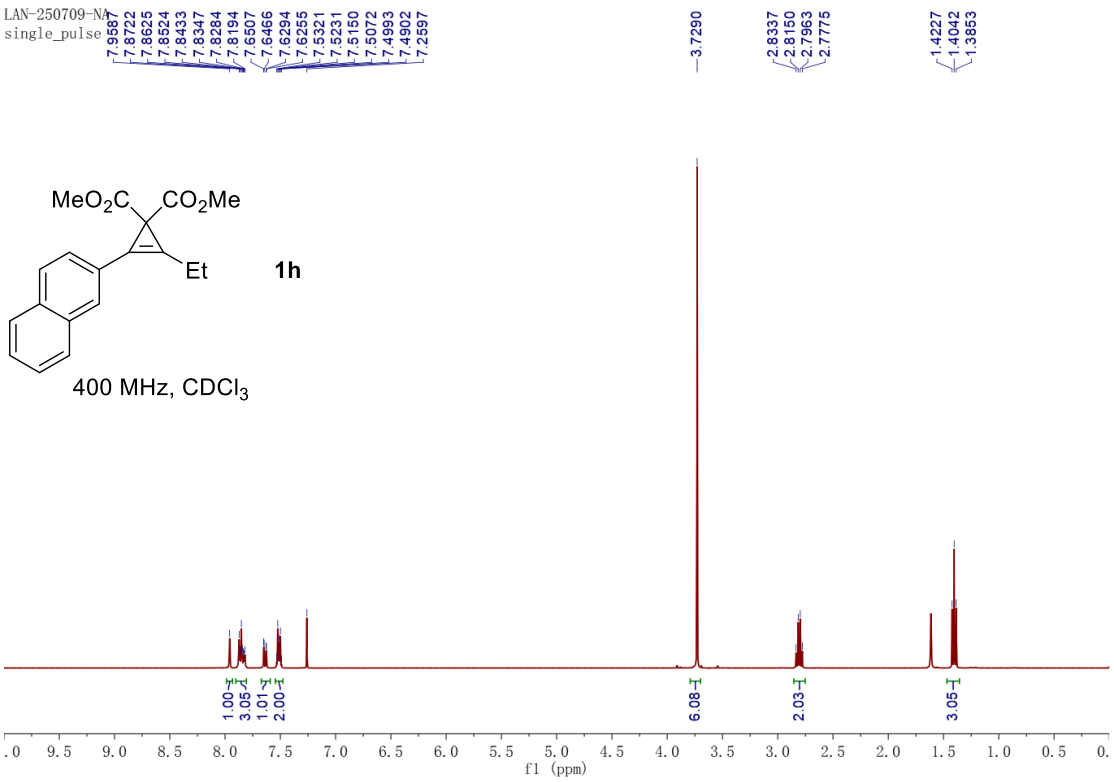
400 MHz, $CDCl_3$

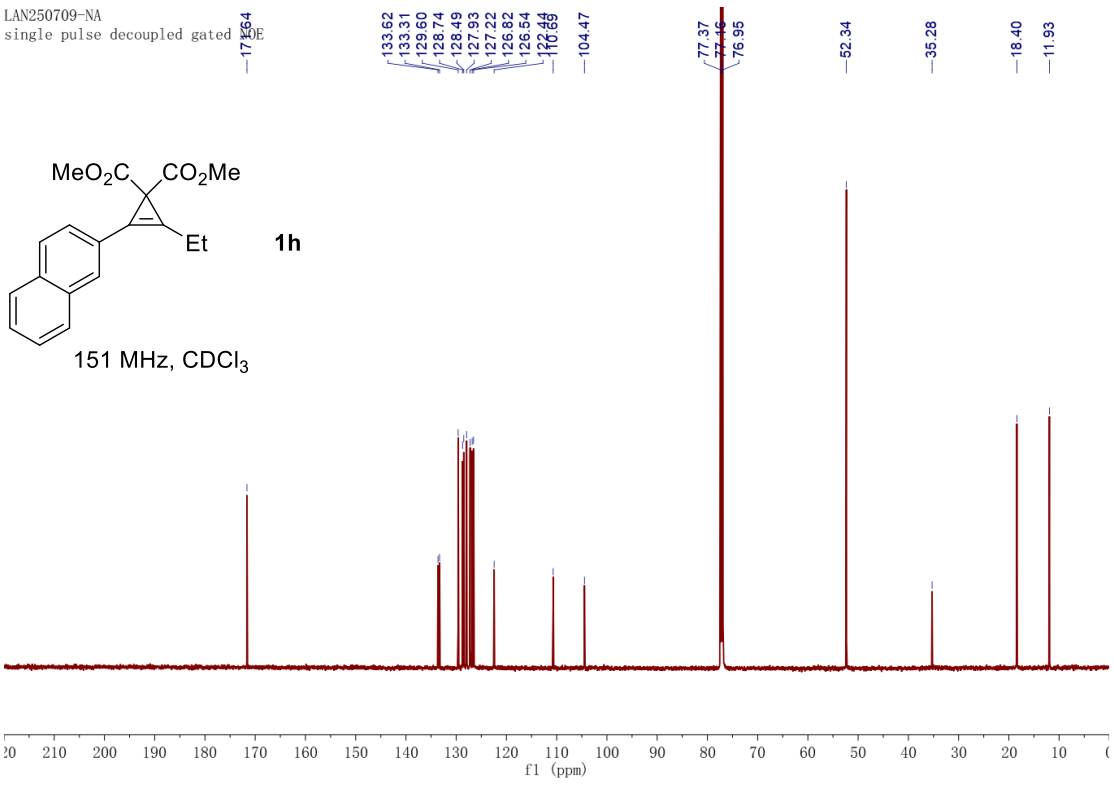
SSY251011-D-2Cl
single pulse decoupled gated NOE

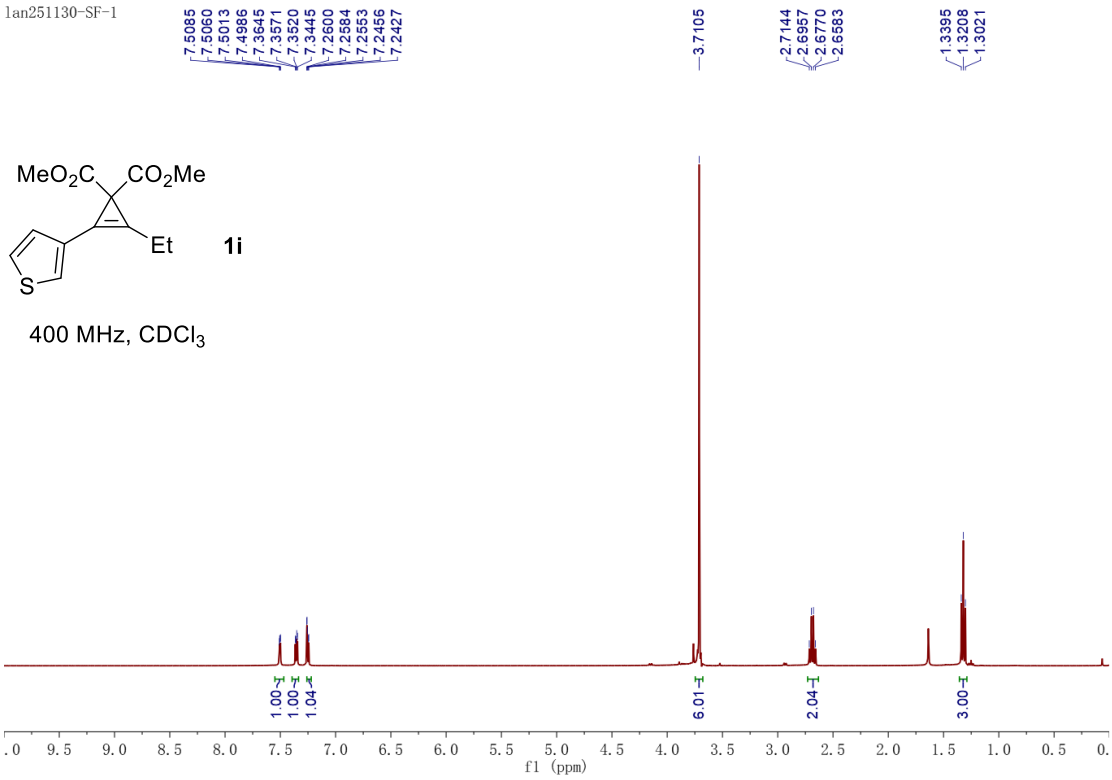


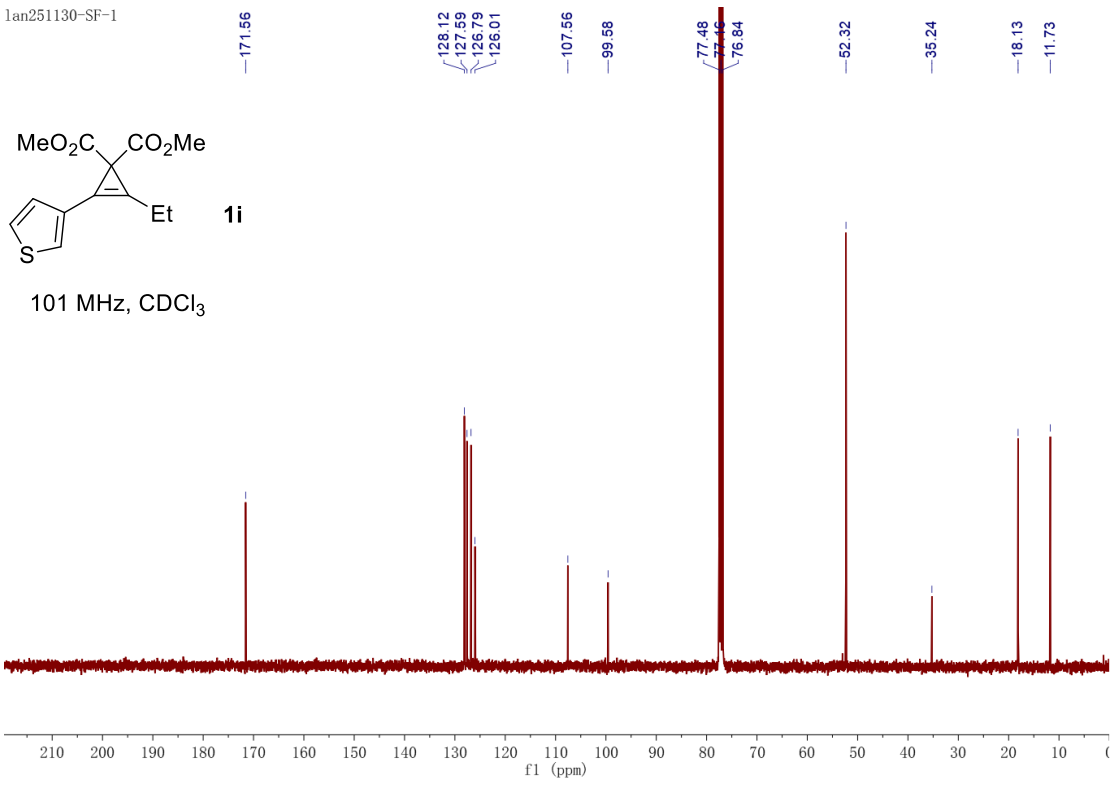
1g

151 MHz, $CDCl_3$

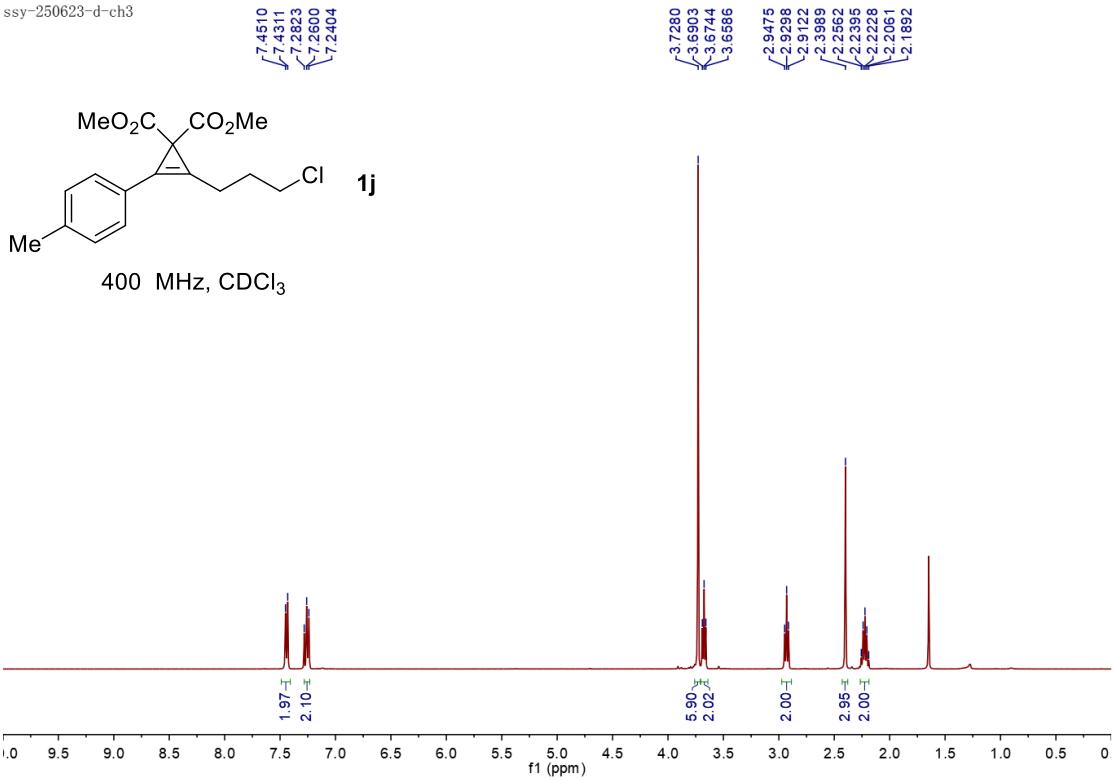

LAN-250709-NA
single_pulse
7.9587
7.8722
7.8625
7.8524
7.8433
7.8347
7.8284
7.8194
7.6507
7.6466
7.6294
7.6255
7.5321
7.5231
7.5150
7.5072
7.4993
7.4902
7.2597
3.7290
2.8337
2.8150
2.7963
2.7775
1.4227
1.4042
1.3853
MeO2C
CO2Me
Et
1h
400 MHz, CDCl3
1.00
3.05
1.01
2.00
6.08
2.03
3.05
f1 (ppm)


LAN250709-NA
single pulse decoupled gated DE
133.62
133.31
129.60
128.74
128.49
127.93
127.22
126.82
126.54
104.47
77.37
77.46
76.95
52.34
35.28
18.40
11.93
MeO2C
CO2Me
Et
1h
151 MHz, CDCl3
f1 (ppm)

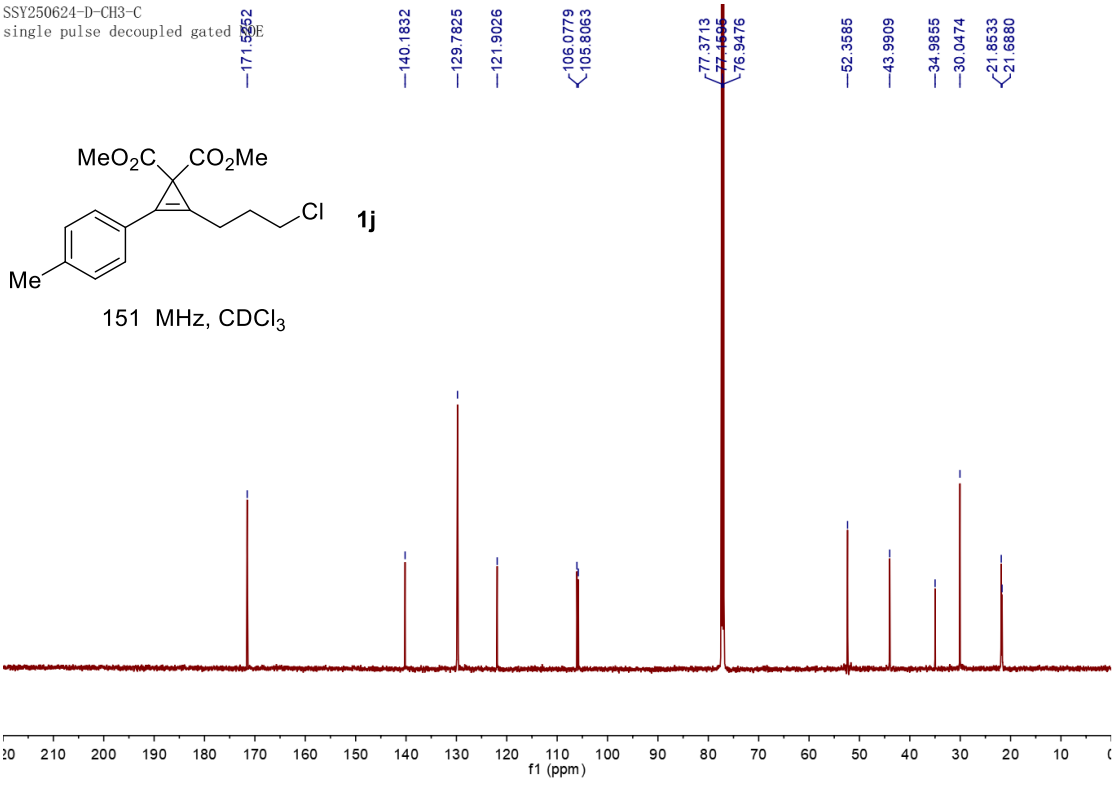

lan251130-SF-1
7.5085
7.5060
7.5013
7.4986
7.3645
7.3571
7.3520
7.3445
7.2600
7.2584
7.2553
7.2456
7.2427
3.7105
2.7144
2.6957
2.6770
2.6583
1.3395
1.3208
1.3021
MeO2C
CO2Me
Et
S
1i
400 MHz, CDCl3
1.00
1.00
1.04
6.01
2.04
3.00
f1 (ppm)


lan251130-SF-1
171.56
128.12
127.59
126.79
126.01
107.56
99.58
77.48
77.16
76.84
52.32
35.24
18.13
11.73
MeO2C
CO2Me
Et
S
1i
101 MHz, CDCl3
f1 (ppm)

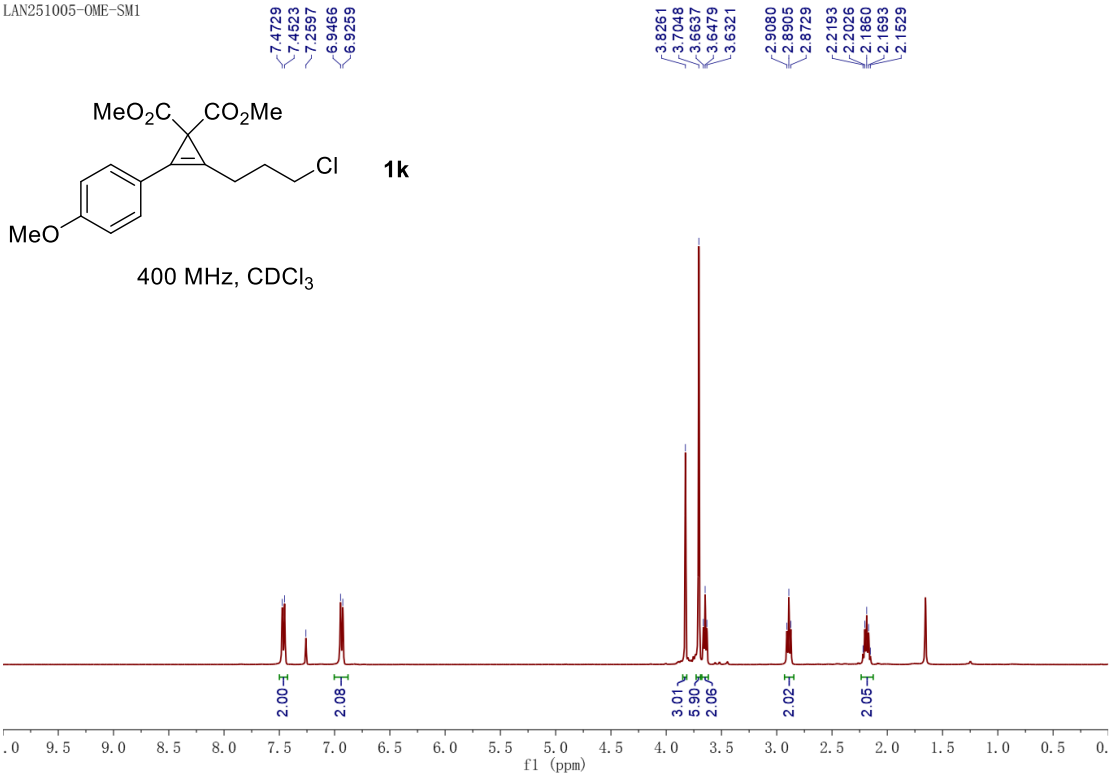
ssy-250623-d-ch3



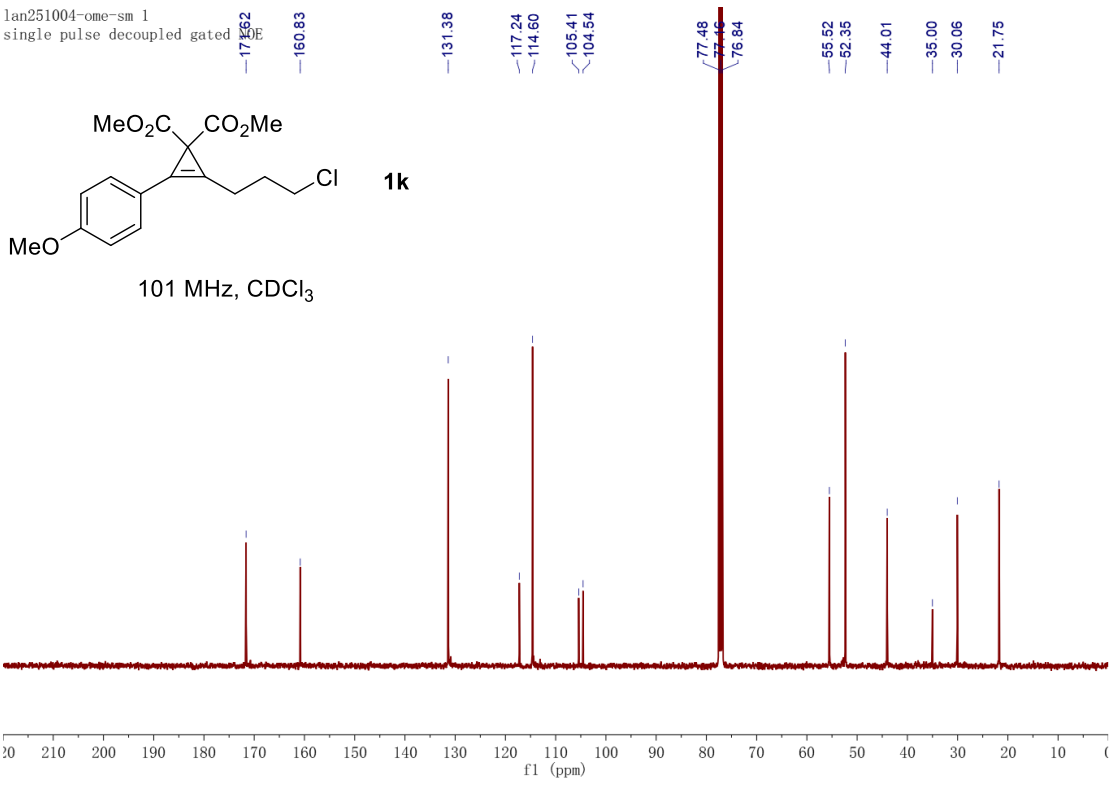
SSY250624-D-CH3-C
single pulse decoupled gated DE

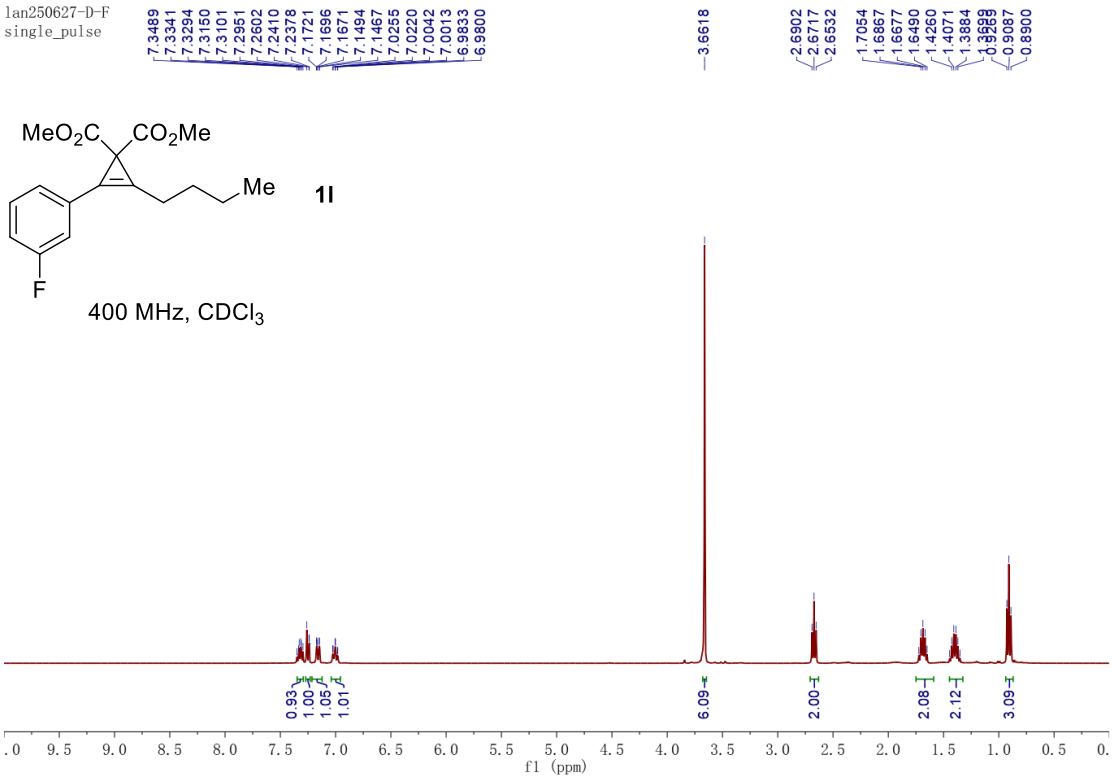


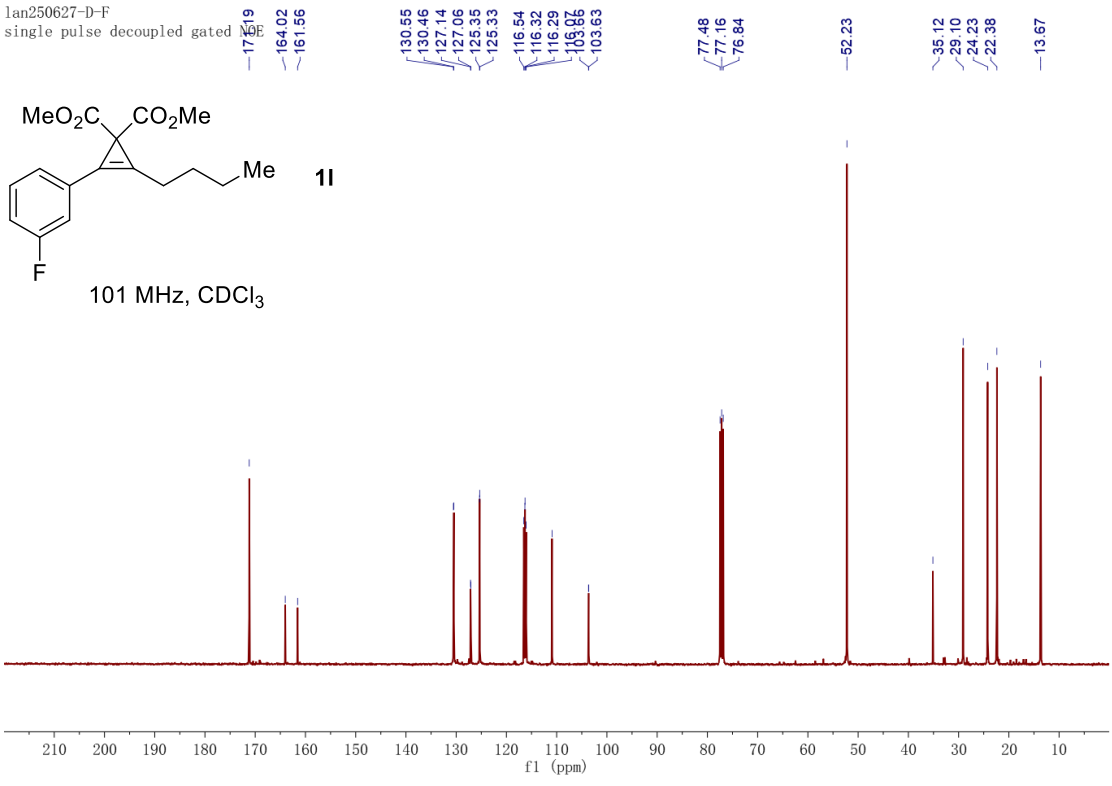
LAN251005-OME-SM1



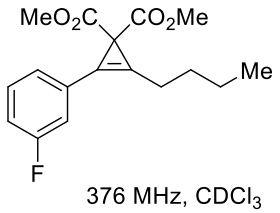
lan251004-ome-sm 1
single pulse decoupled gated NOE




lan250627-D-F
single_pulse
7.3489
7.3341
7.3294
7.3150
7.3101
7.2951
7.2602
7.2410
7.2378
7.1721
7.1696
7.1671
7.1494
7.1467
7.0255
7.0220
7.0042
7.0013
6.9833
6.9800
3.6618
2.6902
2.6717
2.6532
1.7054
1.6867
1.6677
1.6490
1.4260
1.4071
1.3884
0.9087
0.8900
MeO2C
CO2Me
Me
F
1l
400 MHz, CDCl3
0.93
1.00
1.05
1.01
6.09
2.00
2.08
2.12
3.09
f1 (ppm)

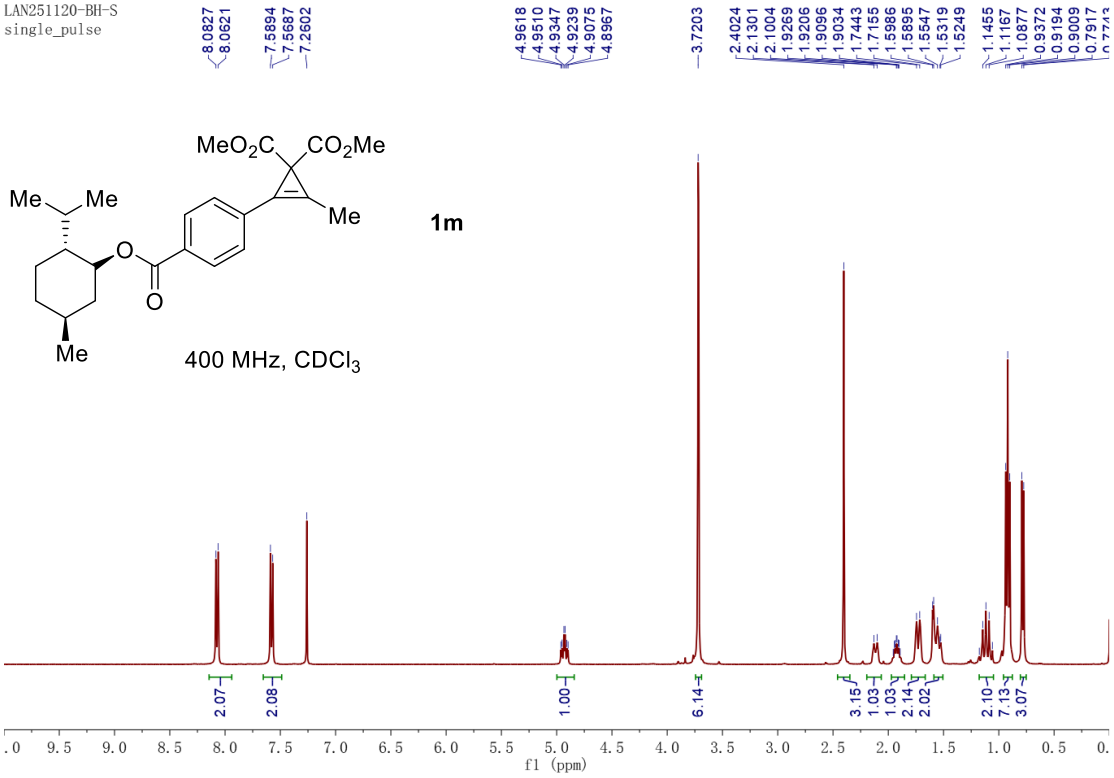

lan250627-D-F
single pulse decoupled gated NOE
175.19
164.02
161.56
130.55
130.46
127.14
127.06
125.35
125.33
116.54
116.32
116.29
116.07
103.86
103.63
77.48
77.16
76.84
52.23
35.12
29.10
24.23
22.38
13.67
MeO2C
CO2Me
Me
F
1l
101 MHz, CDCl3
f1 (ppm)

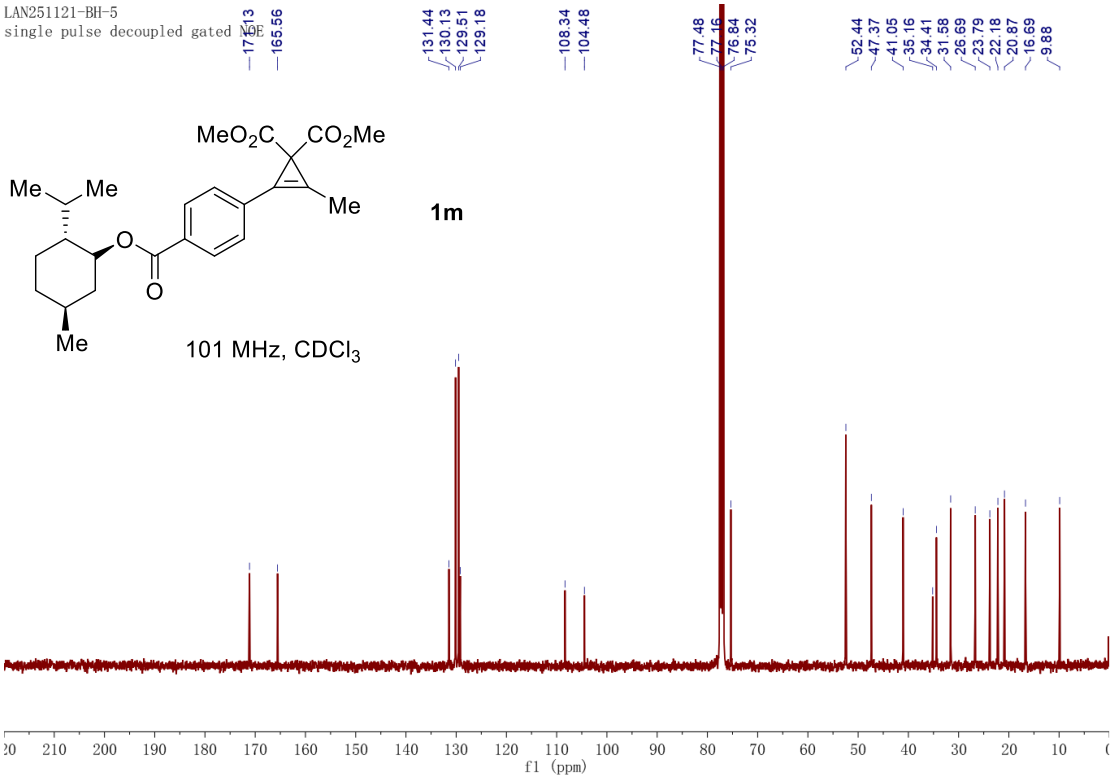
lan250627-D-F
single_pulse

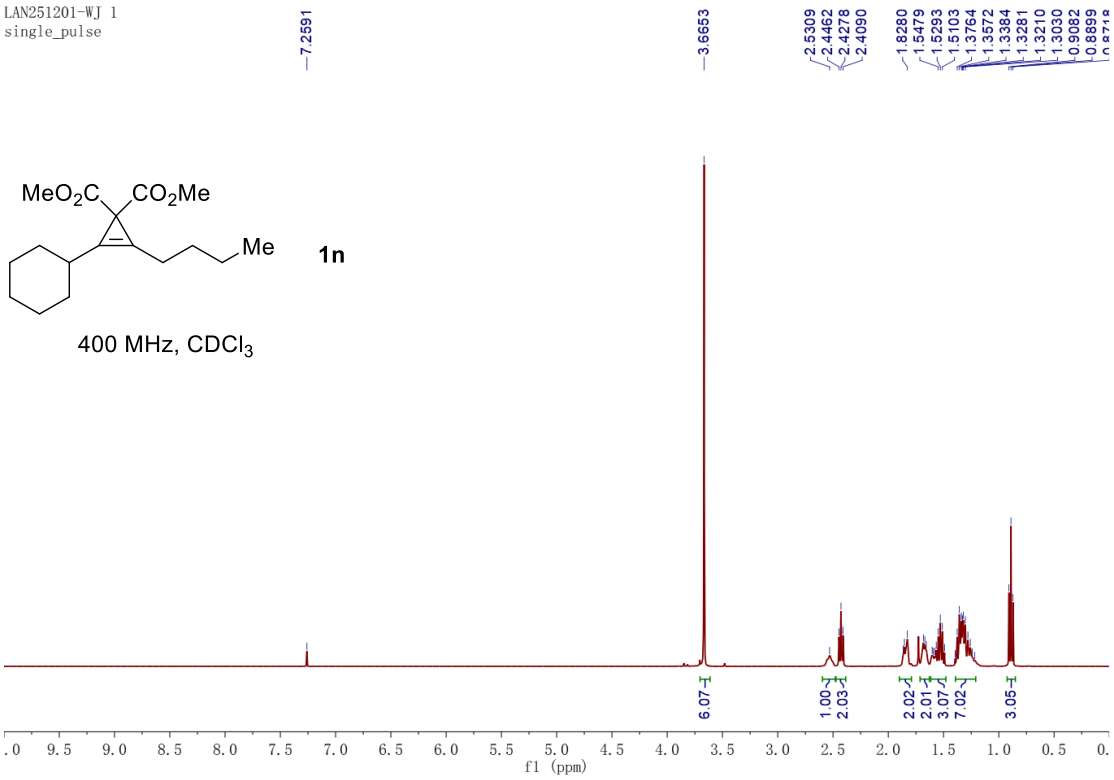


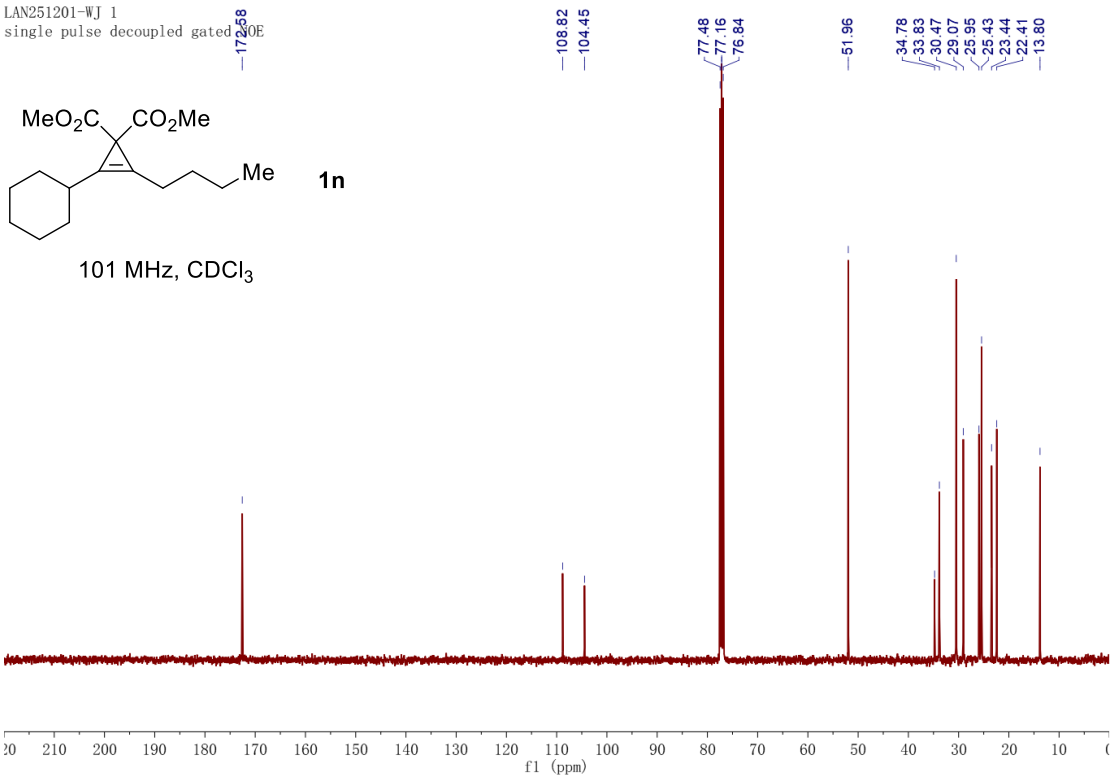
1l

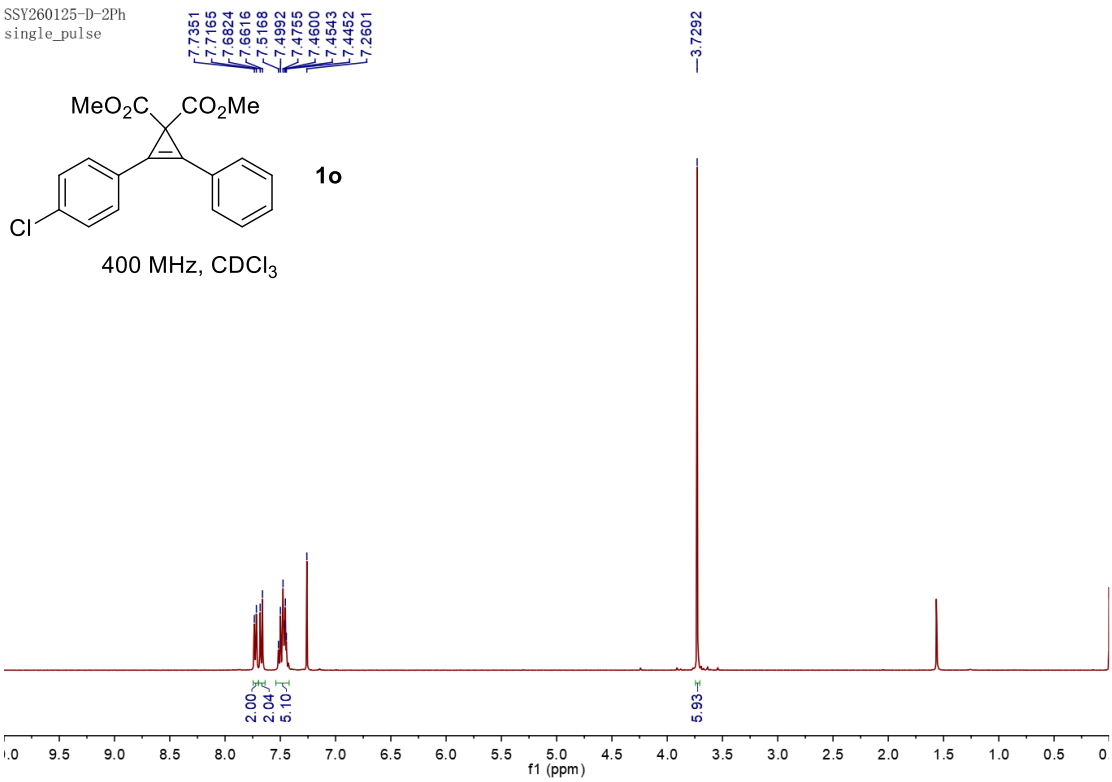
376 MHz, $CDCl_3$

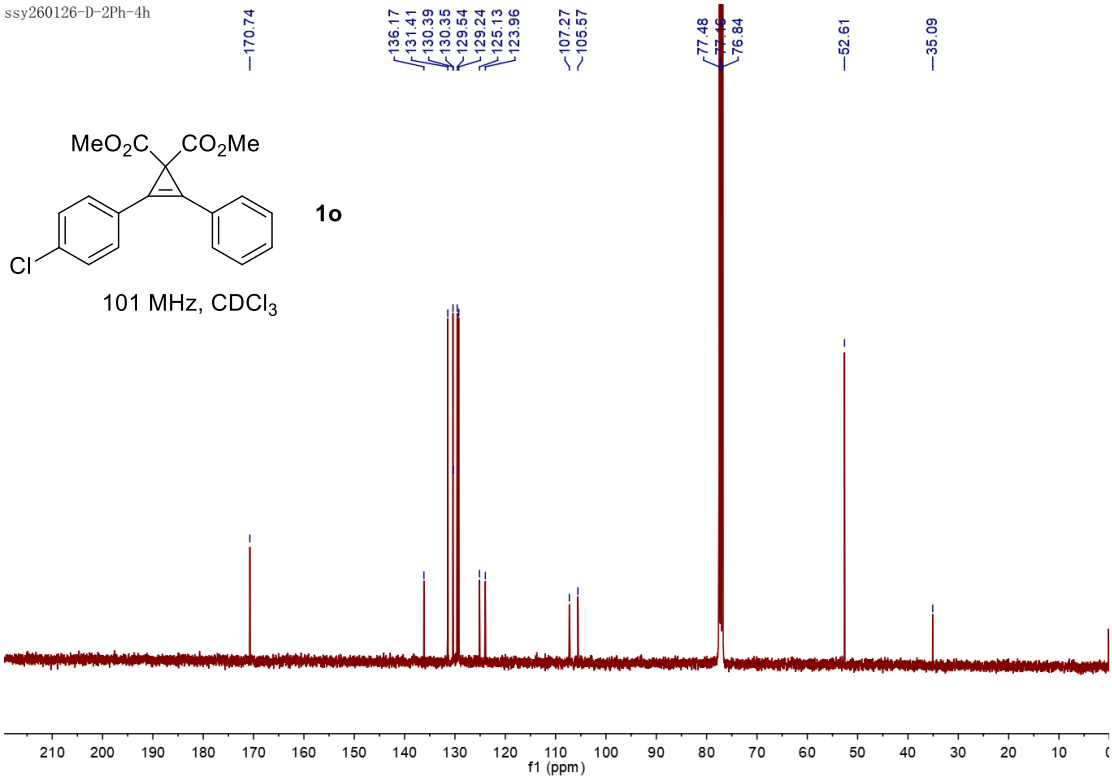

LAN251120-BH-S
single_pulse
MeO2C
CO2Me
Me
Me
Me
O
O
Me
1m
400 MHz, CDCl3
f1 (ppm)

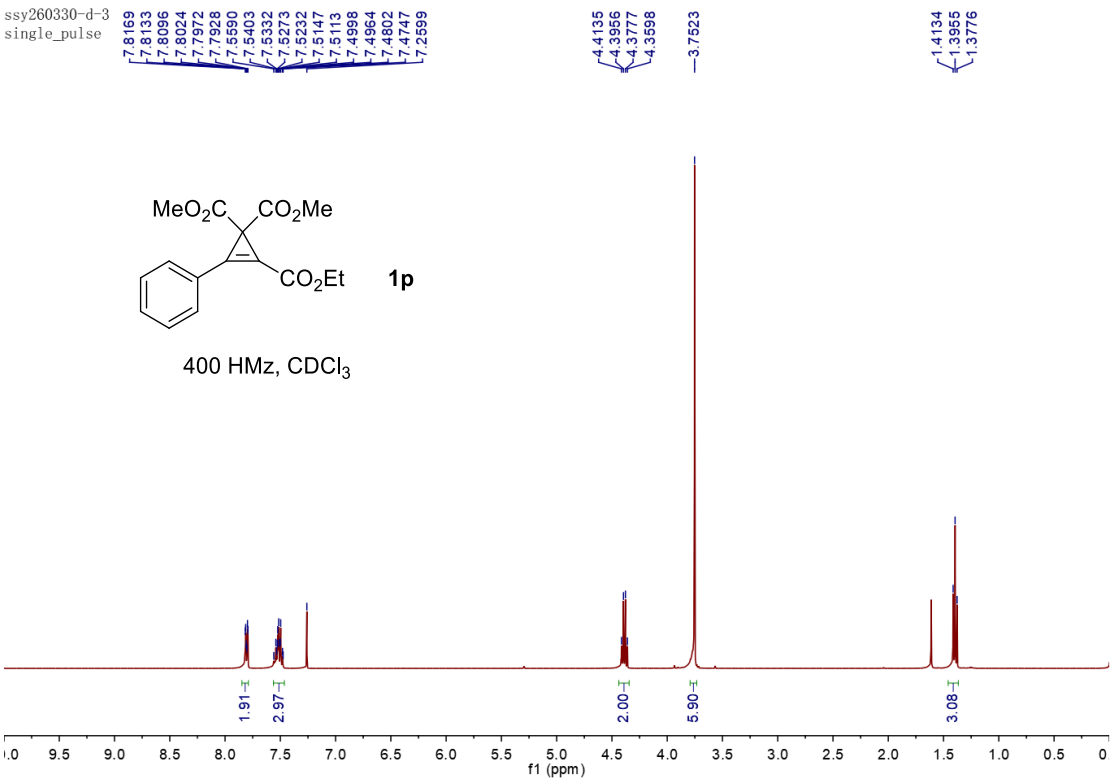

LAN251121-BH-5
single pulse decoupled gated NOE
MeO2C
CO2Me
Me
Me
Me
O
O
Me
1m
101 MHz, CDCl3
f1 (ppm)

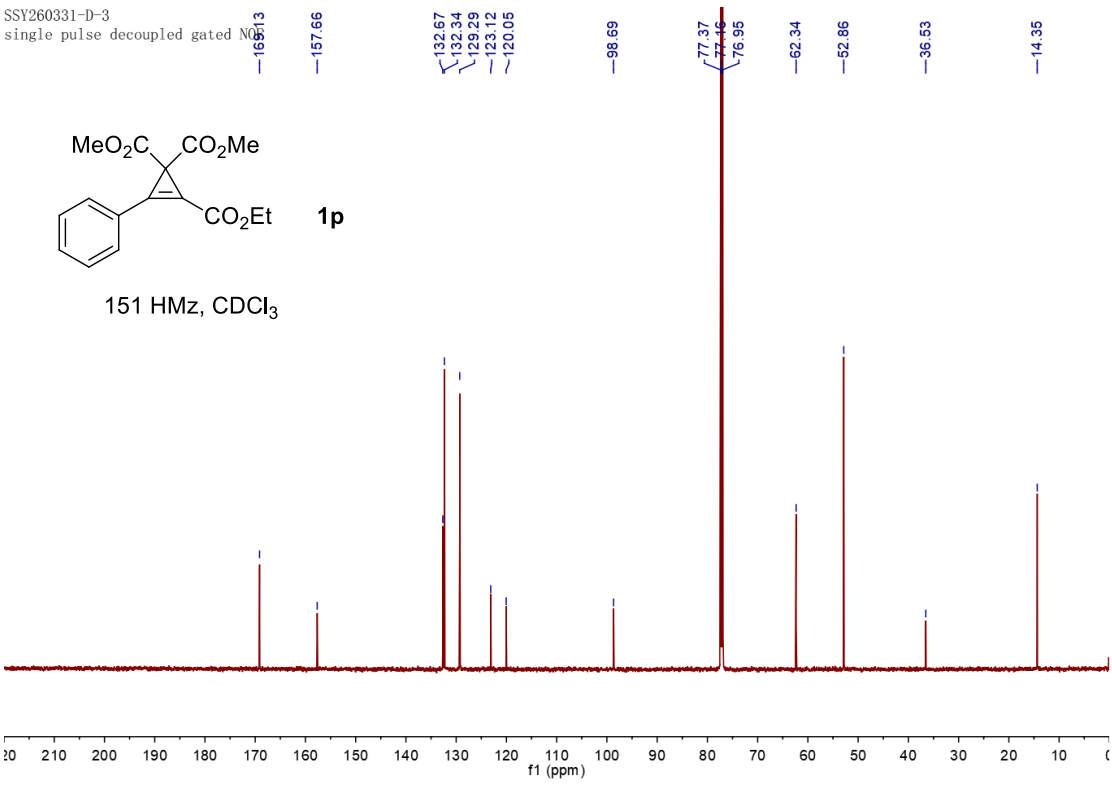

LAN251201-WJ 1
single_pulse
7.2591
3.6653
2.5309
2.4462
2.4278
2.4090
1.8280
1.5479
1.5293
1.5103
1.3764
1.3572
1.3384
1.3281
1.3210
1.3030
0.9082
0.8899
MeO2C
CO2Me
Me
1n
400 MHz, CDCl3
6.07
1.00
2.03
2.02
2.01
3.07
7.02
3.05
f1 (ppm)


LAN251201-WJ 1
single pulse decoupled gated DE
172.68
108.82
104.45
77.48
77.16
76.84
51.96
34.78
33.83
30.47
29.07
25.95
25.43
23.44
22.41
13.80
MeO2C
CO2Me
Me
1n
101 MHz, CDCl3
f1 (ppm)


SSY260125-D-2Ph
single_pulse
7.7351
7.7165
7.6824
7.6616
7.5168
7.4992
7.4755
7.4600
7.4543
7.4452
7.2601
3.7292
MeO2C
CO2Me
Cl
1o
400 MHz, CDCl3
2.00
2.04
5.10
5.93
f1 (ppm)

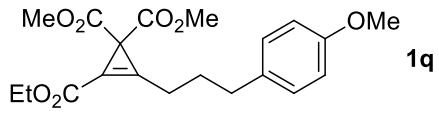

ssy260126-D-2Ph-4h
170.74
136.17
131.41
130.39
130.35
129.54
129.24
125.13
123.96
107.27
105.57
77.48
77.16
76.84
52.61
35.09
MeO2C
CO2Me
Cl
1o
101 MHz, CDCl3
f1 (ppm)


ssy260330-d-3
single_pulse
7.8169
7.8133
7.8096
7.8024
7.7972
7.7928
7.5590
7.5403
7.5332
7.5273
7.5232
7.5147
7.5113
7.4998
7.4964
7.4802
7.4747
7.2599
4.4135
4.3956
4.3777
4.3598
3.7523
1.4134
1.3955
1.3776
MeO2C
CO2Me
CO2Et
1p
400 HMz, CDCl3
1.91
2.97
2.00
5.90
3.08
f1 (ppm)


SSY260331-D-3
single pulse decoupled gated NOE
169.13
157.66
132.67
132.34
129.29
123.12
120.05
98.69
77.37
77.16
76.95
62.34
52.86
36.53
14.35
MeO2C
CO2Me
CO2Et
1p
151 HMz, CDCl3
f1 (ppm)

SSY251228-D
single_pulse

7.2602 7.0884 7.0672 6.8132 6.7919 4.3090 4.2912 4.2733 4.2554 3.7498 3.7093 2.6758 2.6579 2.6393 2.0072 1.9891 1.9704 1.9521 1.9341 1.3176 1.2999 1.2819

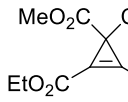


1q

400 HMz, $CDCl_3$

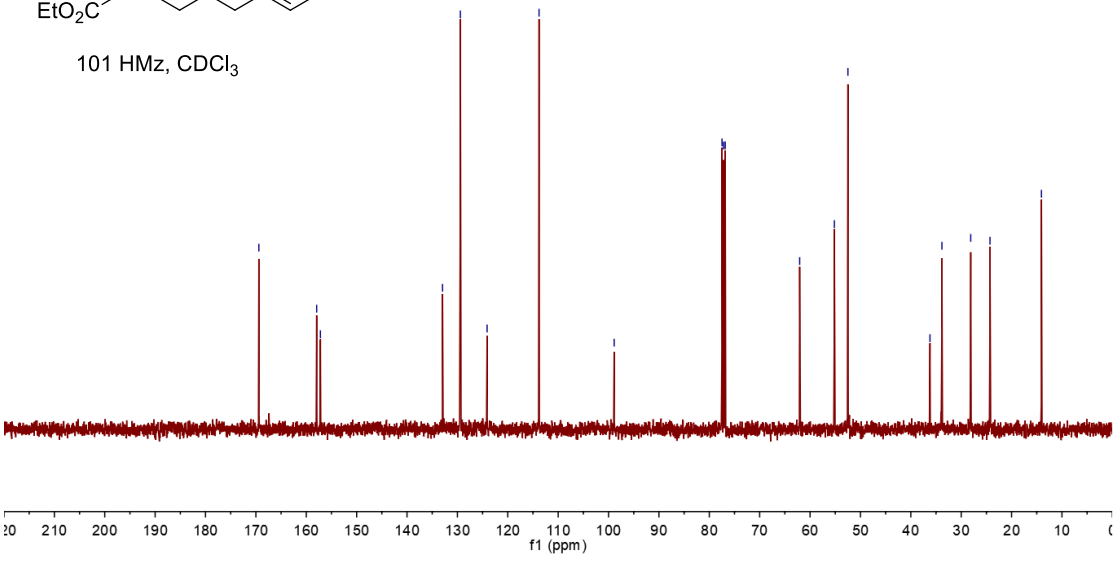
SSY251228-D-C
single pulse decoupled gated NOE

169.41 157.94 157.19 132.95 129.41 124.11 113.79 98.88 77.48 77.16 76.84 62.06 55.17 52.49 36.20 33.83 28.11 24.28 14.07

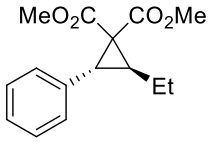


1q

101 HMz, $CDCl_3$



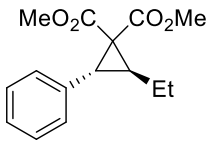
lan250331-1
single_pulse



2a

400 MHz, $CDCl_3$

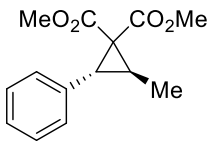
lan250331-1
single pulse decoupled gated NOE



2a

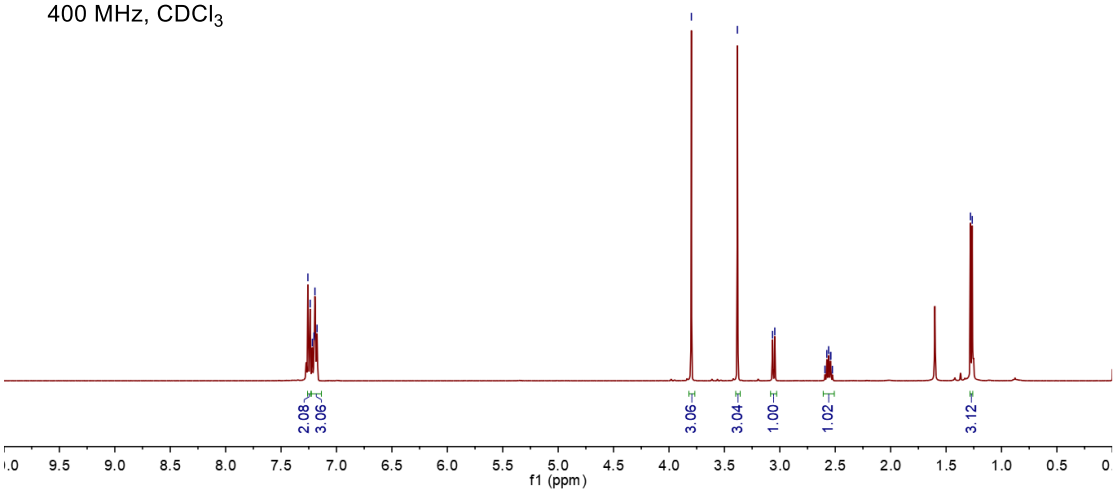
101 MHz, $CDCl_3$

SSY250920-Me-03
single_pulse

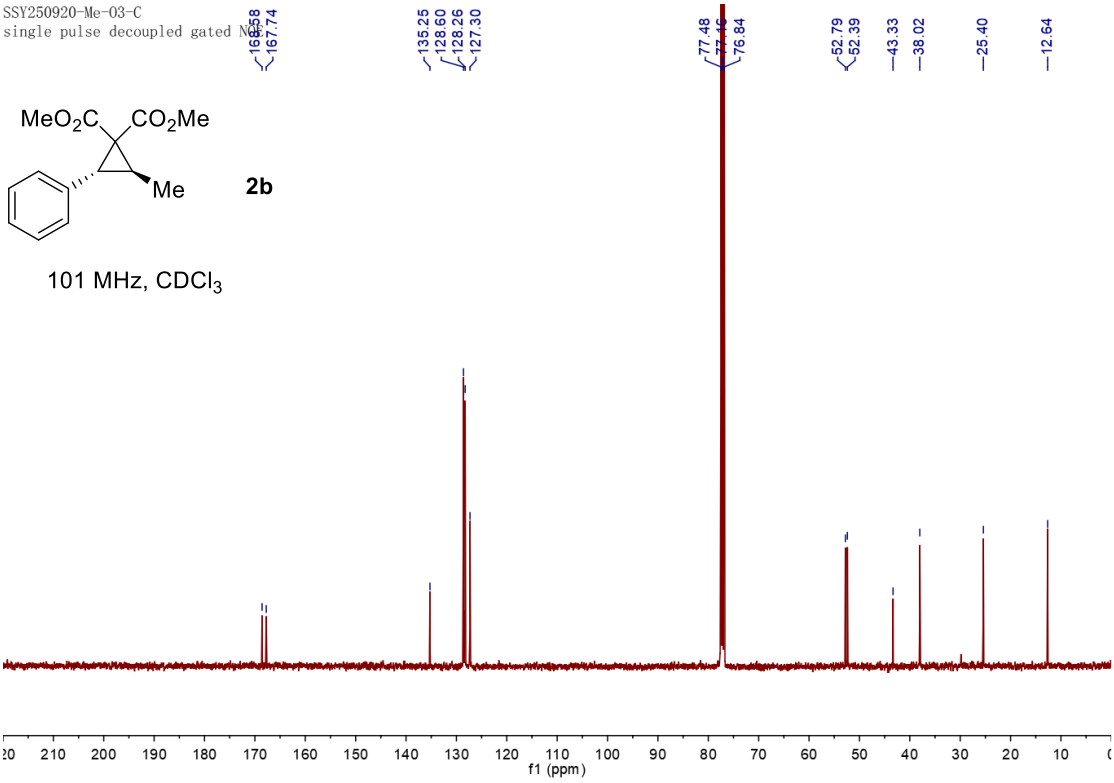


2b

400 MHz, $CDCl_3$



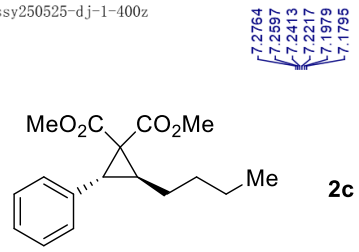
SSY250920-Me-03-C
single pulse decoupled gated NOE



2b

101 MHz, $CDCl_3$

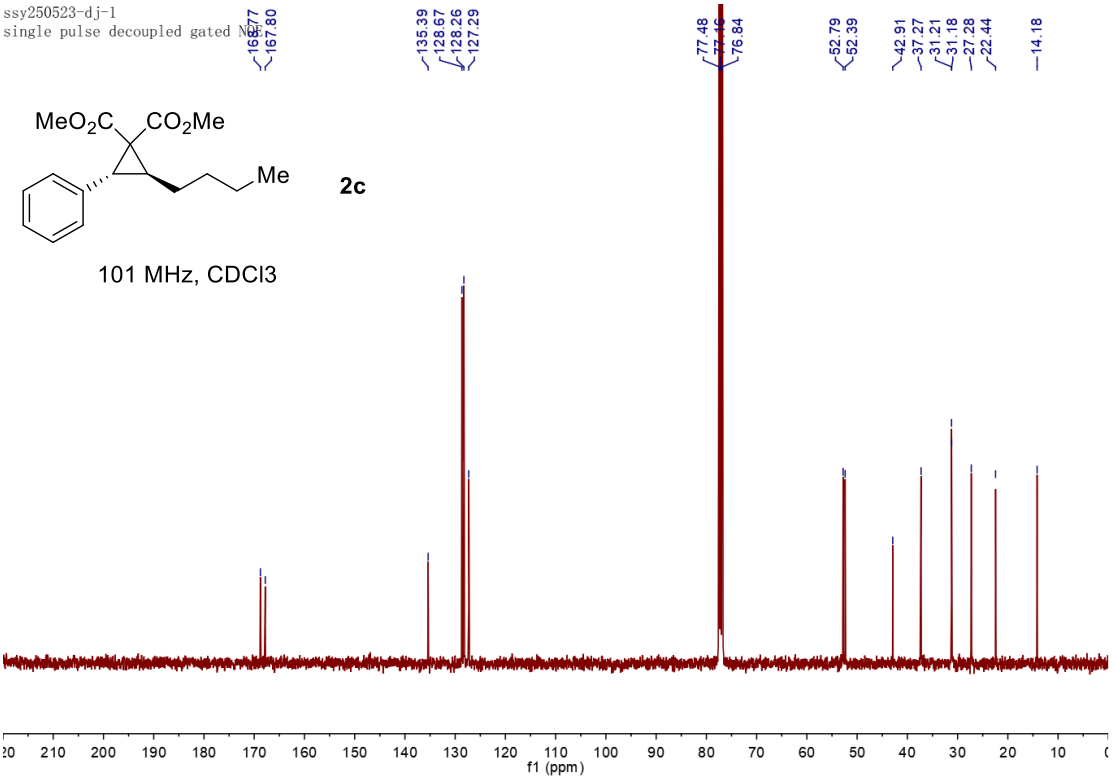
ssy250525-dj-1-400z



2c

400 MHz, CDCl3

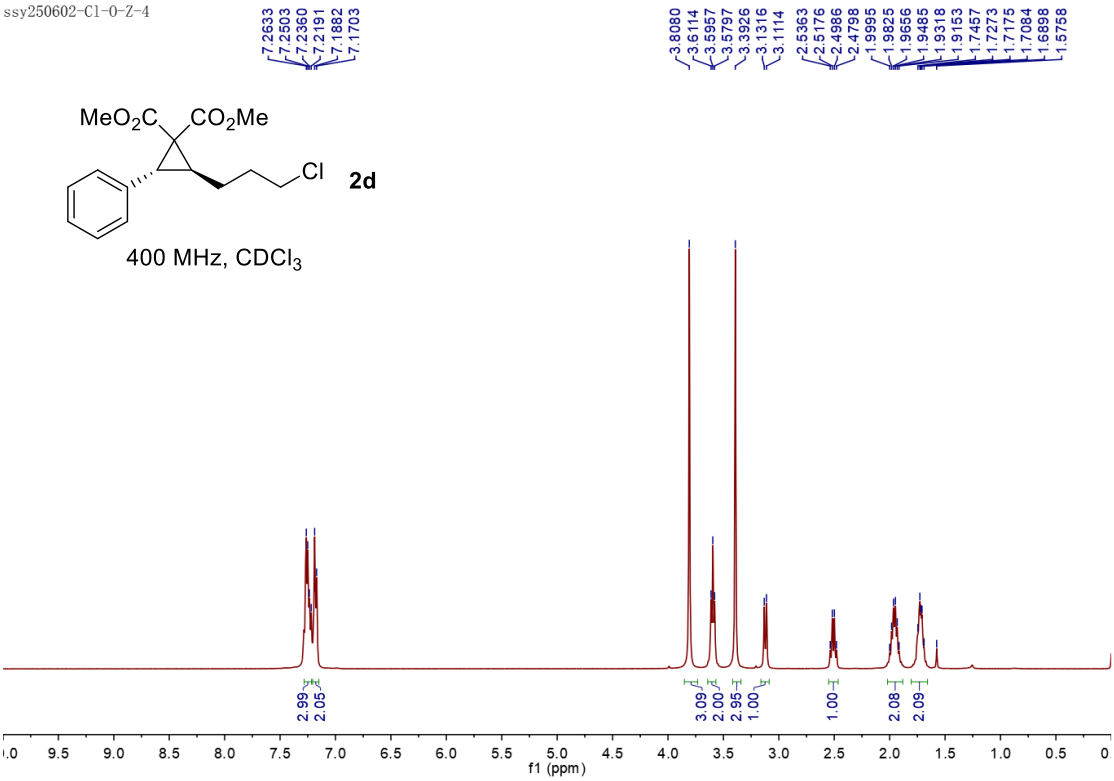
ssy250523-dj-1
single pulse decoupled gated NOE



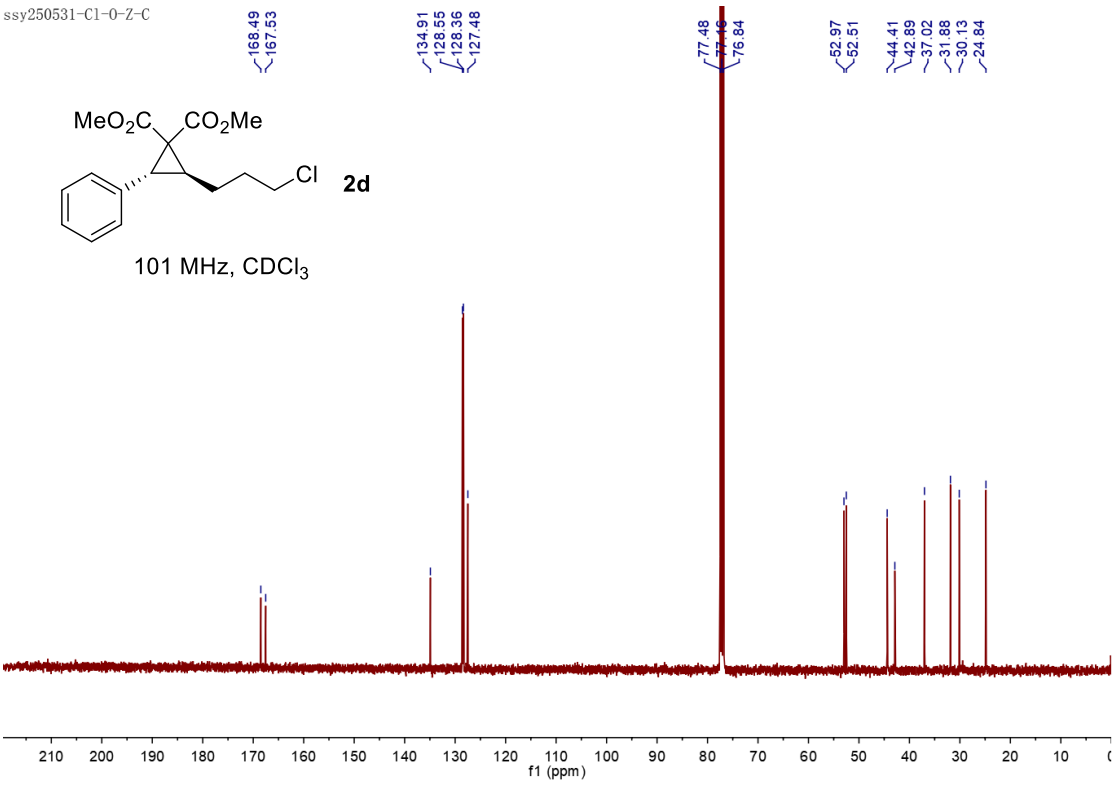
2c

101 MHz, CDCl3

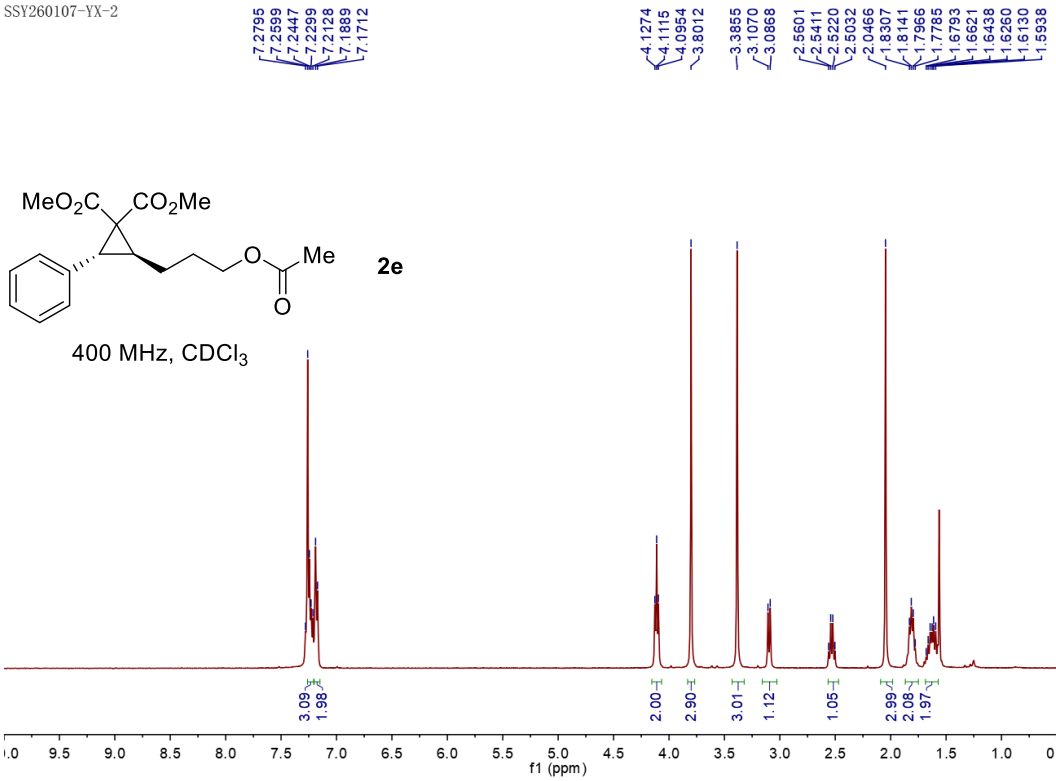
ssy250602-Cl-O-Z-4



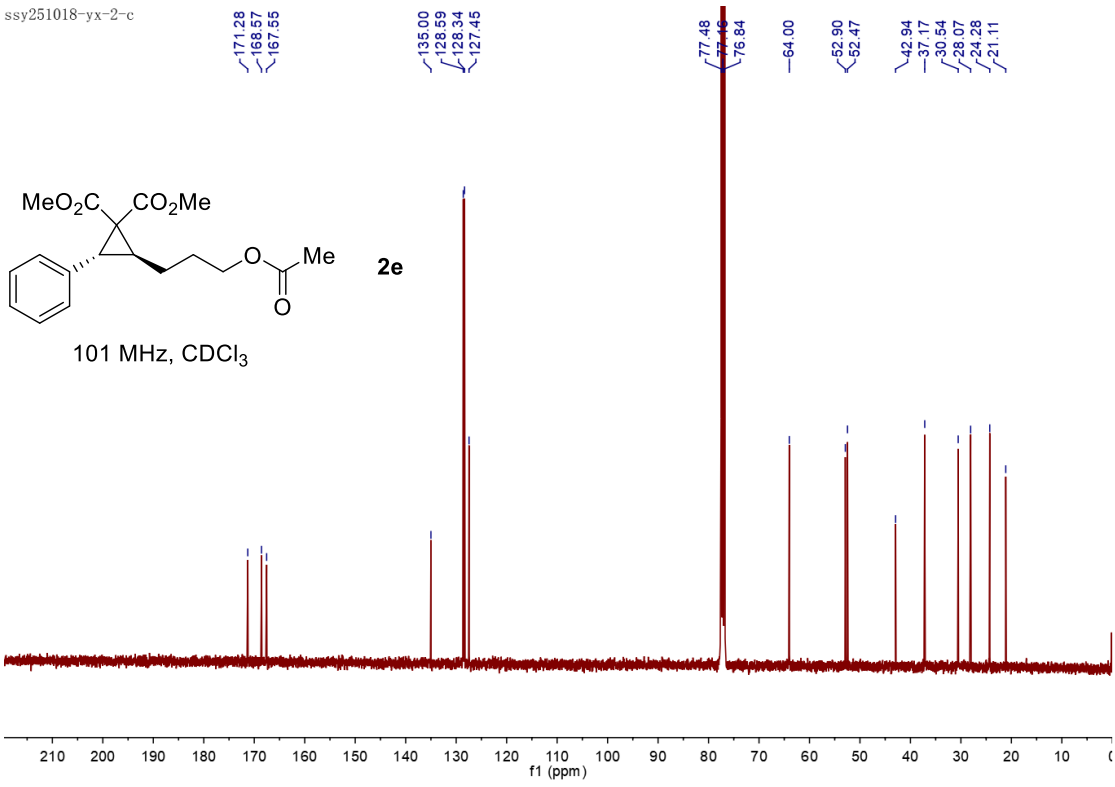
ssy250531-Cl-O-Z-C



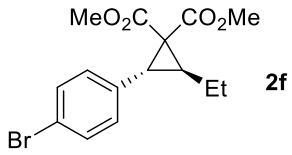
SSY260107-YX-2



ssy251018-yx-2-c



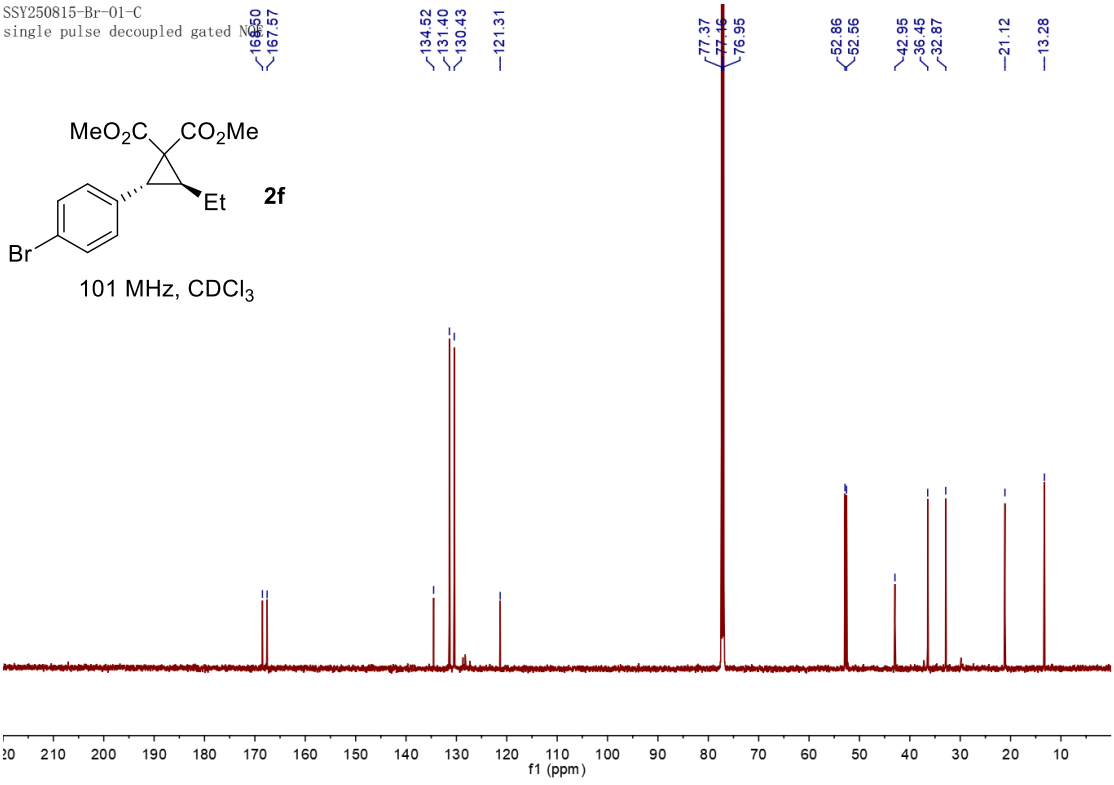
SSY250816-Br-01
single_pulse



2f

400 MHz, $CDCl_3$

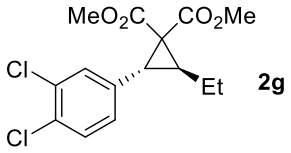
SSY250815-Br-01-C
single pulse decoupled gated NOE



2f

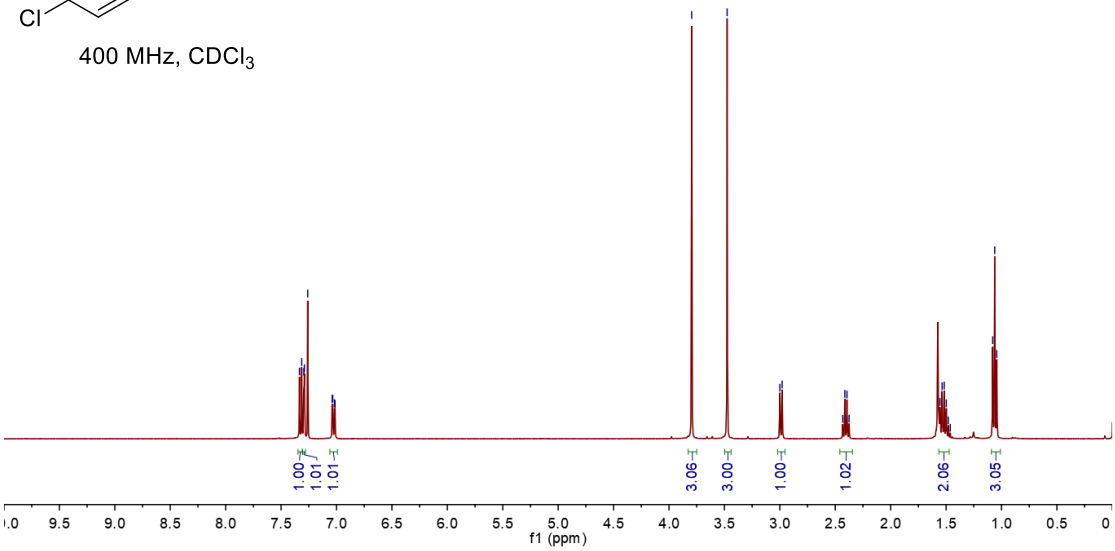
101 MHz, $CDCl_3$

ssy251013-2cl-o2
single_pulse

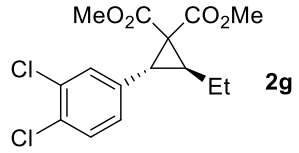


2g

400 MHz, $CDCl_3$



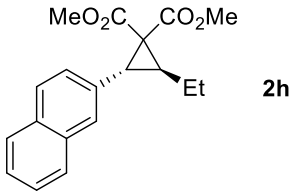
ssy251013-2Cl-0Z-C



2g

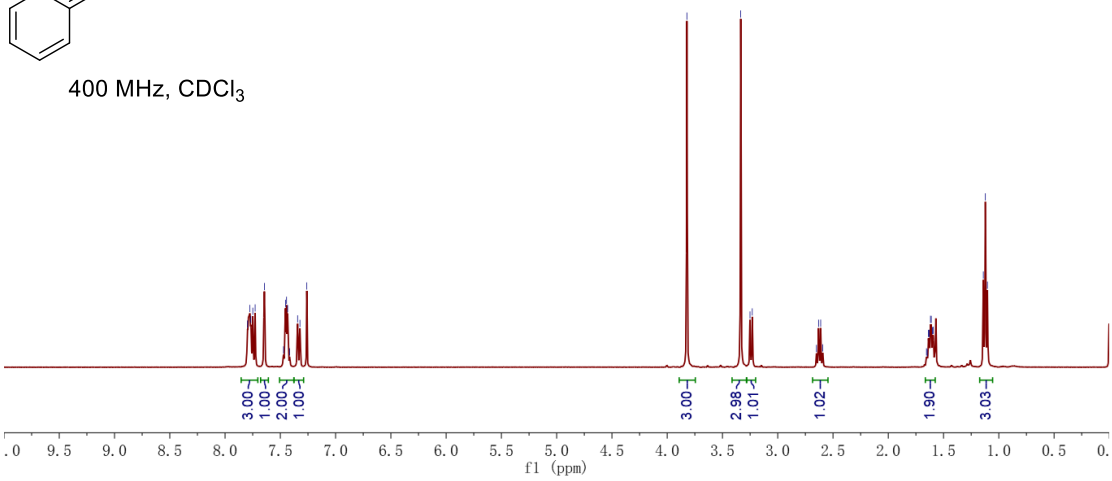
101 MHz, $CDCl_3$

LAN251012-NA2

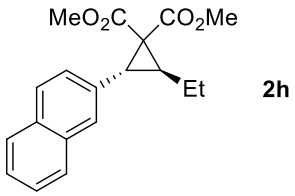


2h

400 MHz, $CDCl_3$

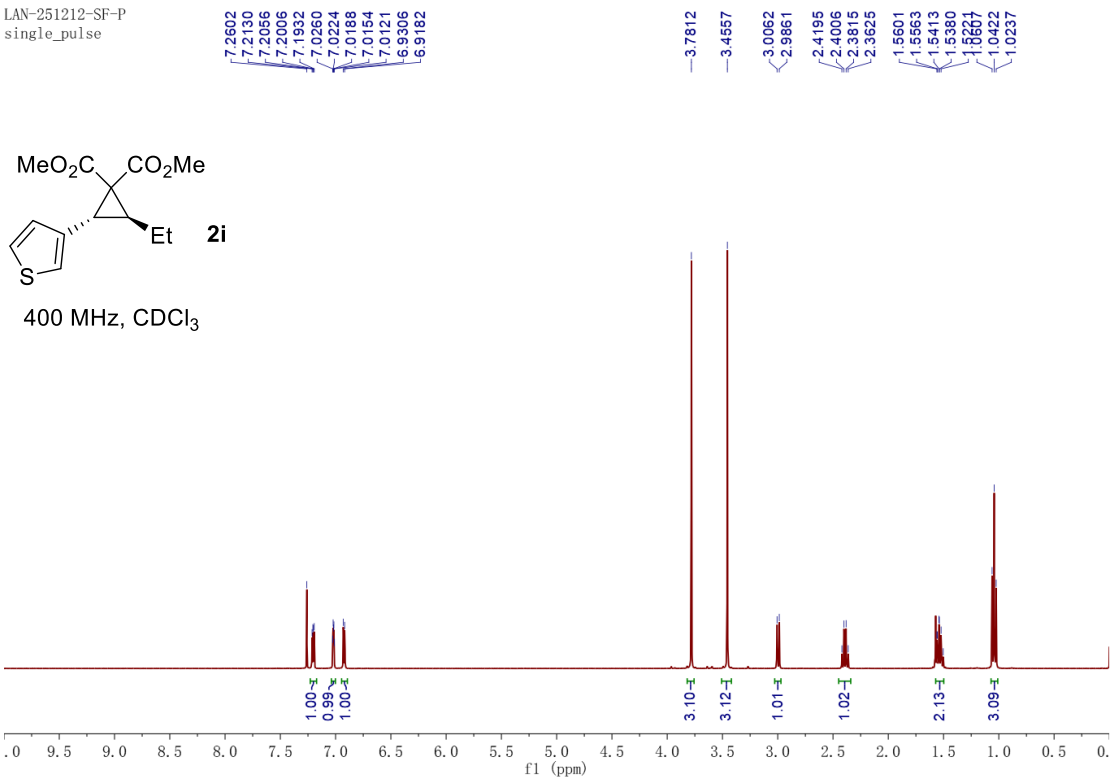


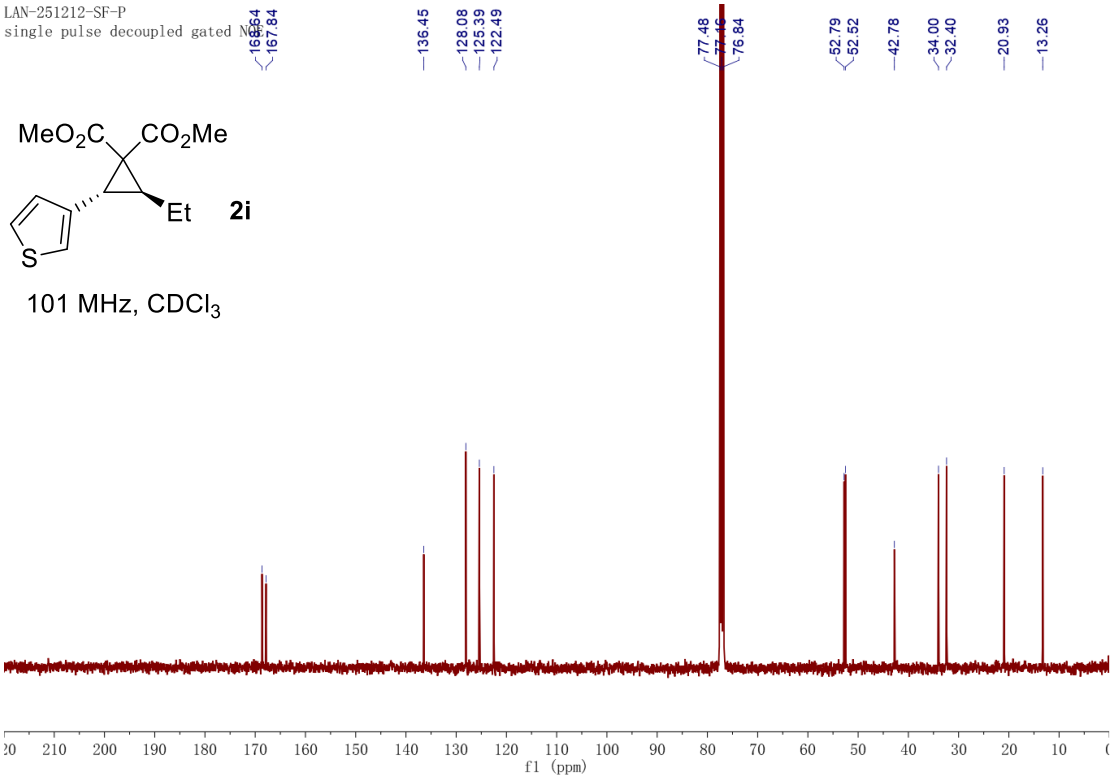
LAN251011-NA2
single pulse decoupled gated NOE



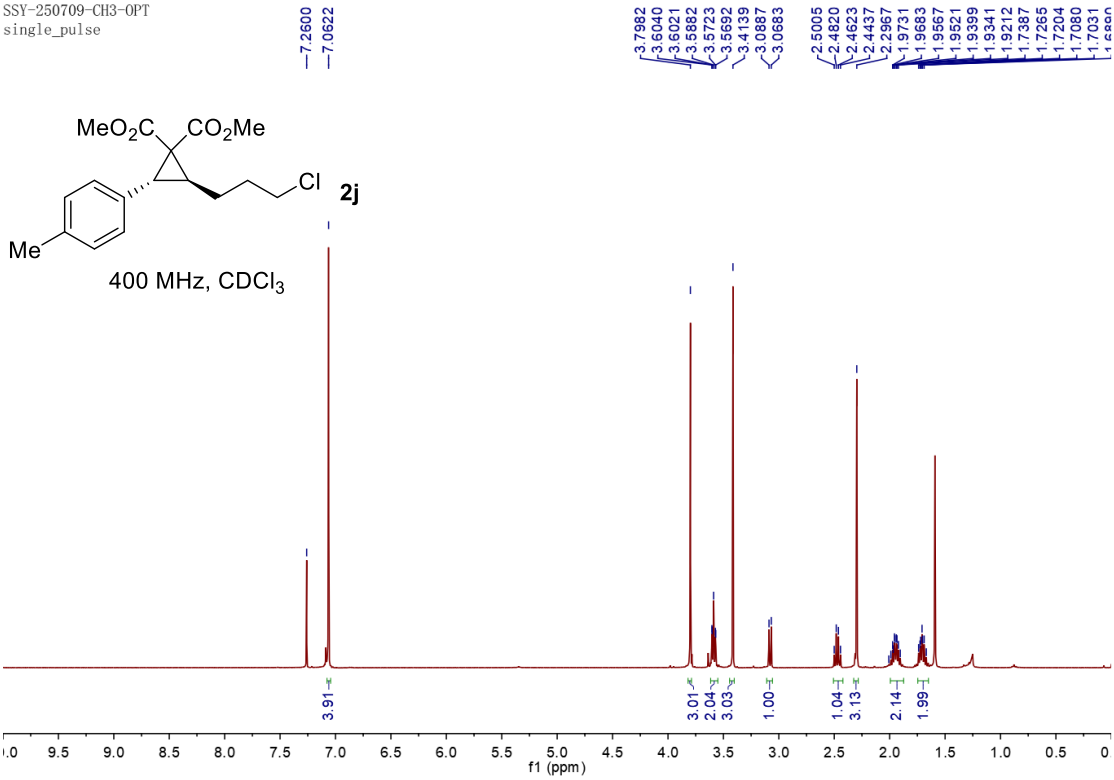
2h

151 MHz, $CDCl_3$

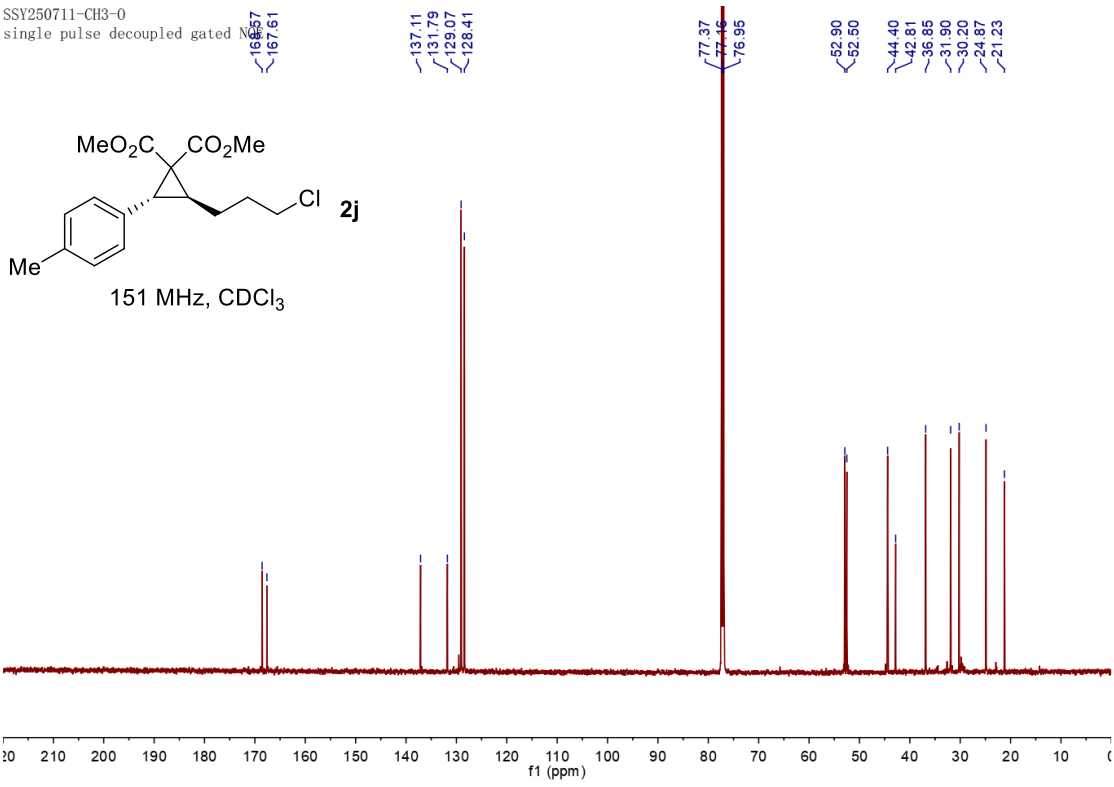

LAN-251212-SF-P
single_pulse
7.2602
7.2130
7.2056
7.2006
7.1932
7.0260
7.0224
7.0188
7.0154
7.0121
6.9306
6.9182
3.7812
3.4557
3.0062
2.9861
2.4195
2.4006
2.3815
2.3625
1.5601
1.5563
1.5413
1.5380
1.0422
1.0237
MeO2C
CO2Me
Et
2i
S
400 MHz, CDCl3
1.00
0.99
1.00
3.10
3.12
1.01
1.02
2.13
3.09
f1 (ppm)


LAN-251212-SF-P
single pulse decoupled gated NOE
168.54
167.84
136.45
128.08
125.39
122.49
77.48
77.16
76.84
52.79
52.52
42.78
34.00
32.40
20.93
13.26
MeO2C
CO2Me
Et
2i
S
101 MHz, CDCl3
f1 (ppm)

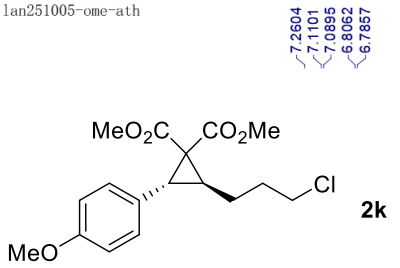
SSY-250709-CH3-OPT
single_pulse



SSY250711-CH3-O
single pulse decoupled gated NOE



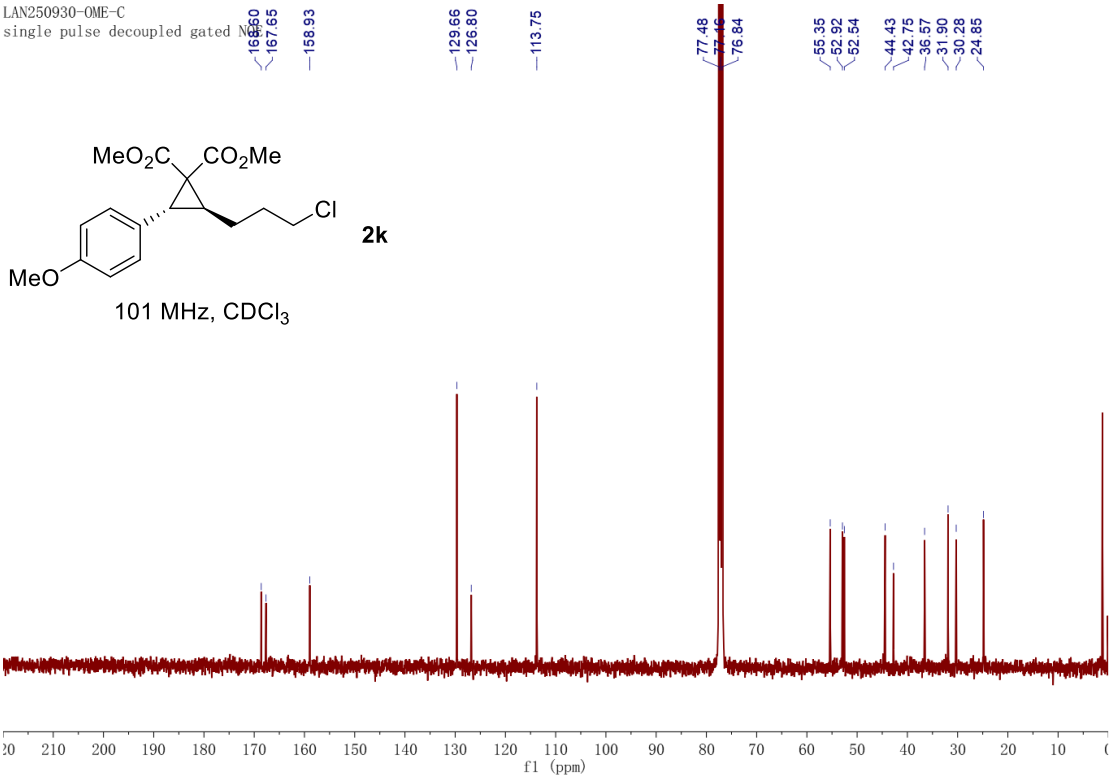
lan251005-ome-ath



2k

400 MHz, $CDCl_3$

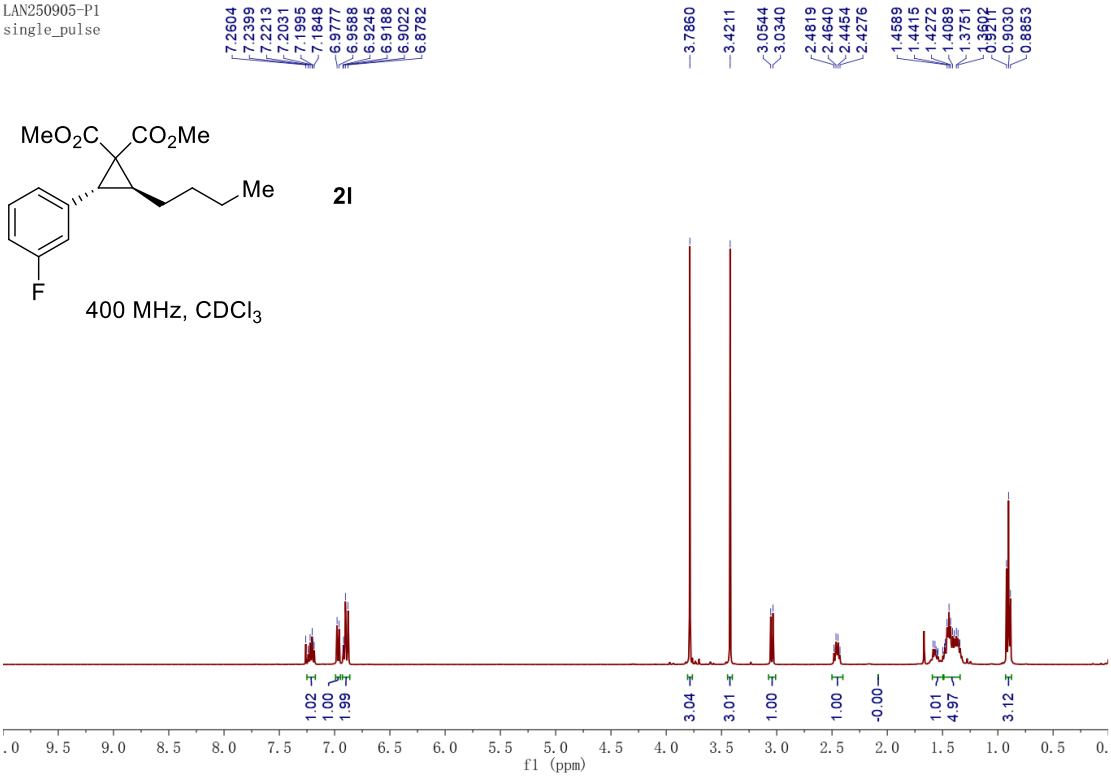
LAN250930-OME-C
single pulse decoupled gated NOE



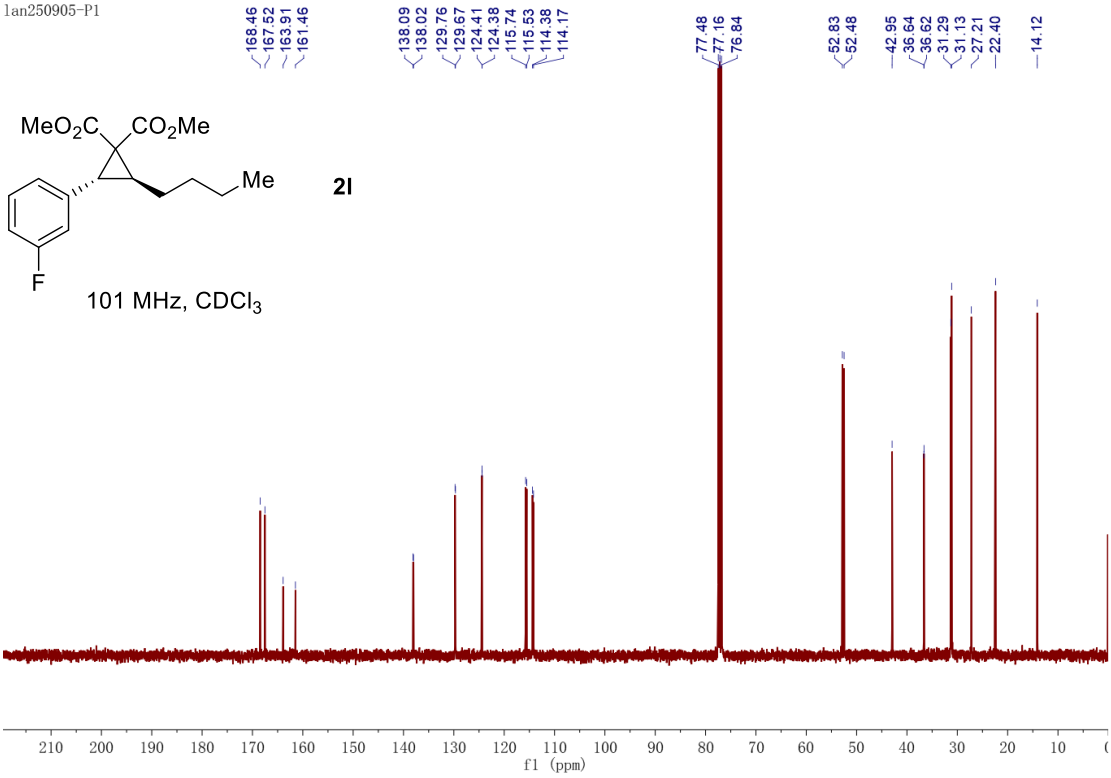
2k

101 MHz, $CDCl_3$

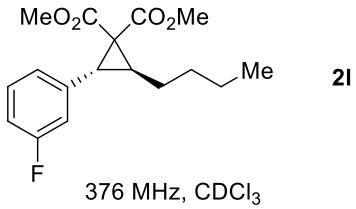
LAN250905-P1
single_pulse



lan250905-P1

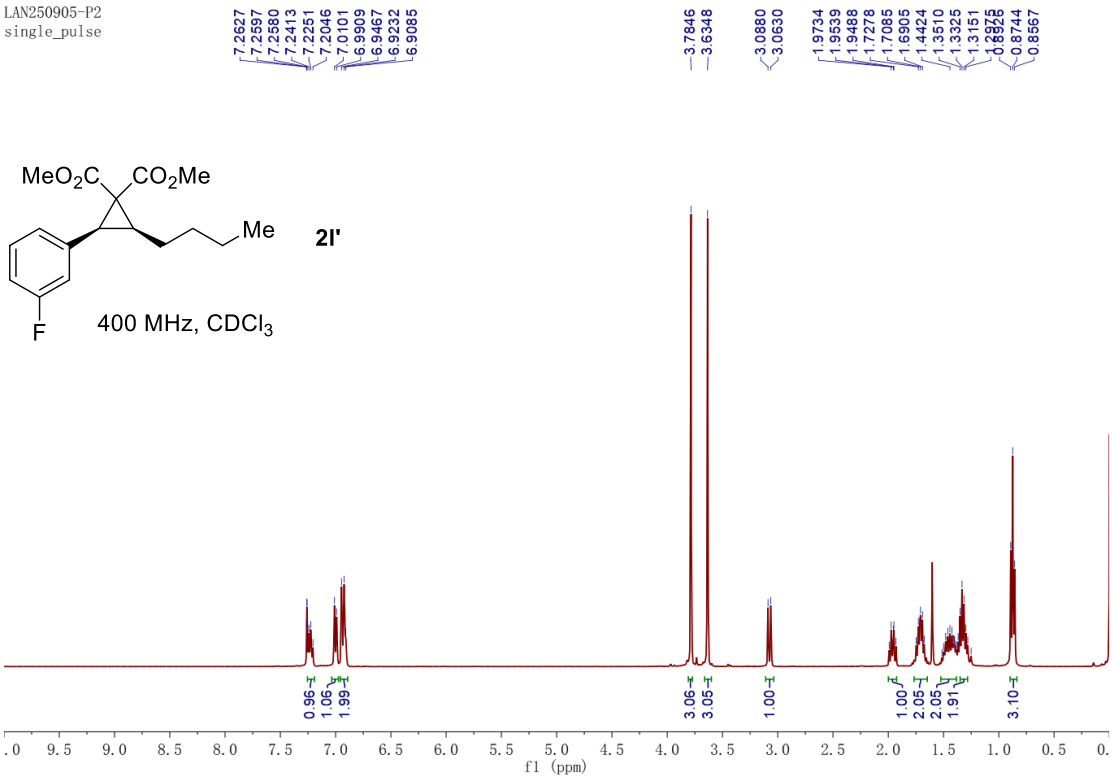


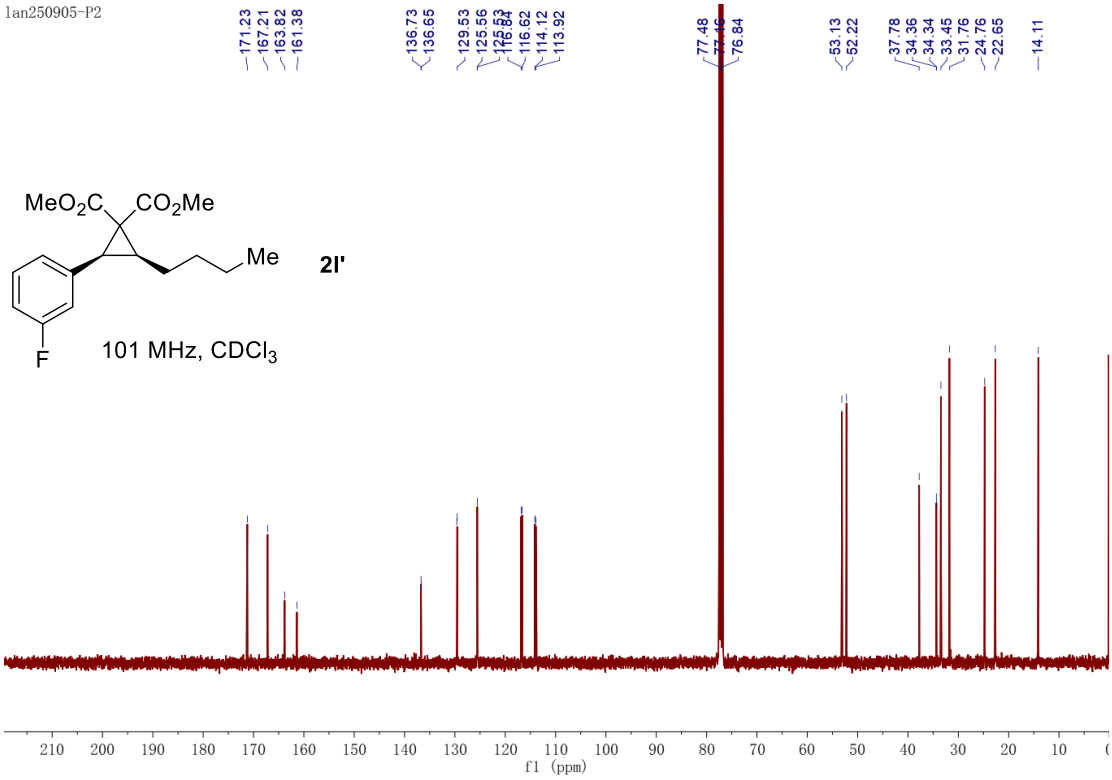
SSY260113-F1



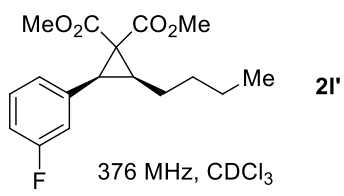
2l

376 MHz, $CDCl_3$


LAN250905-P2
single_pulse
7.2627
7.2597
7.2580
7.2413
7.2251
7.2046
7.0101
6.9909
6.9467
6.9232
6.9085
3.7846
3.6348
3.0880
3.0630
1.9734
1.9539
1.9488
1.7278
1.7085
1.6905
1.4424
1.3510
1.3325
1.3151
0.8926
0.8744
0.8567
MeO2C
CO2Me
Me
F
2l'
400 MHz, CDCl3
0.96
1.06
1.99
3.06
3.05
1.00
1.00
2.05
2.05
1.91
3.10
f1 (ppm)

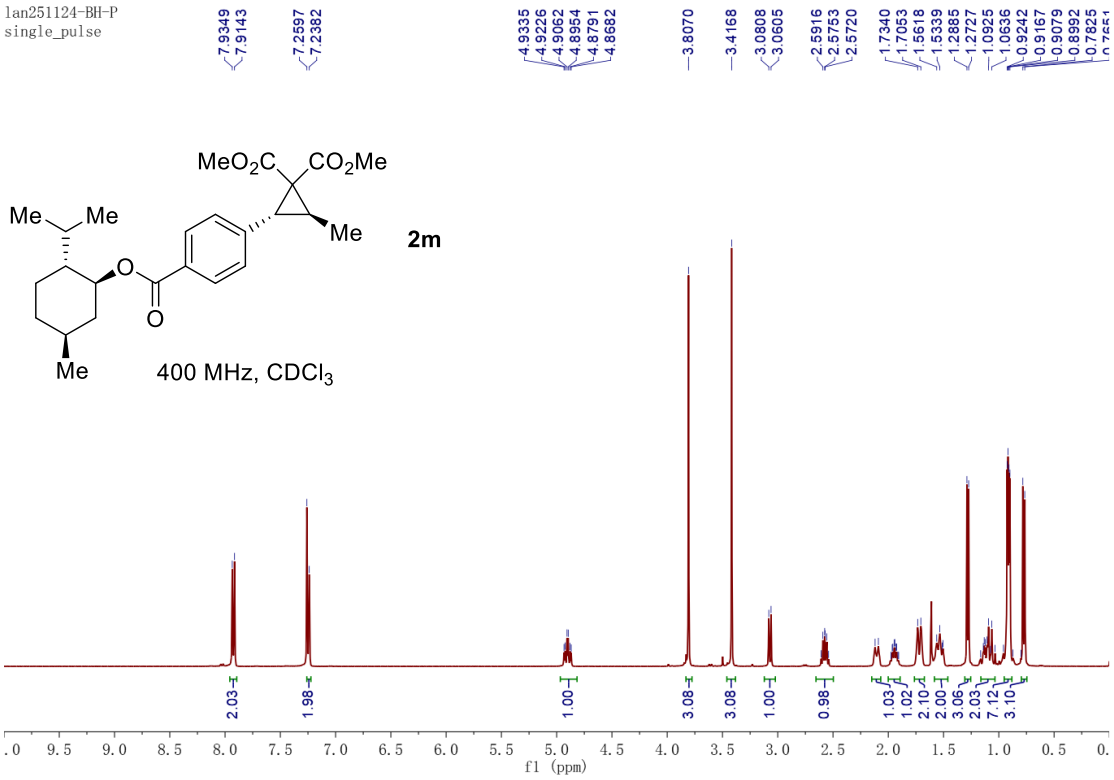

lan250905-P2
171.23
167.21
163.82
161.38
136.73
136.65
129.53
125.56
116.62
114.12
113.92
77.48
77.16
76.84
53.13
52.22
37.78
34.36
34.34
33.45
31.76
24.76
22.65
14.11
MeO2C
CO2Me
Me
F
2l'
101 MHz, CDCl3
f1 (ppm)

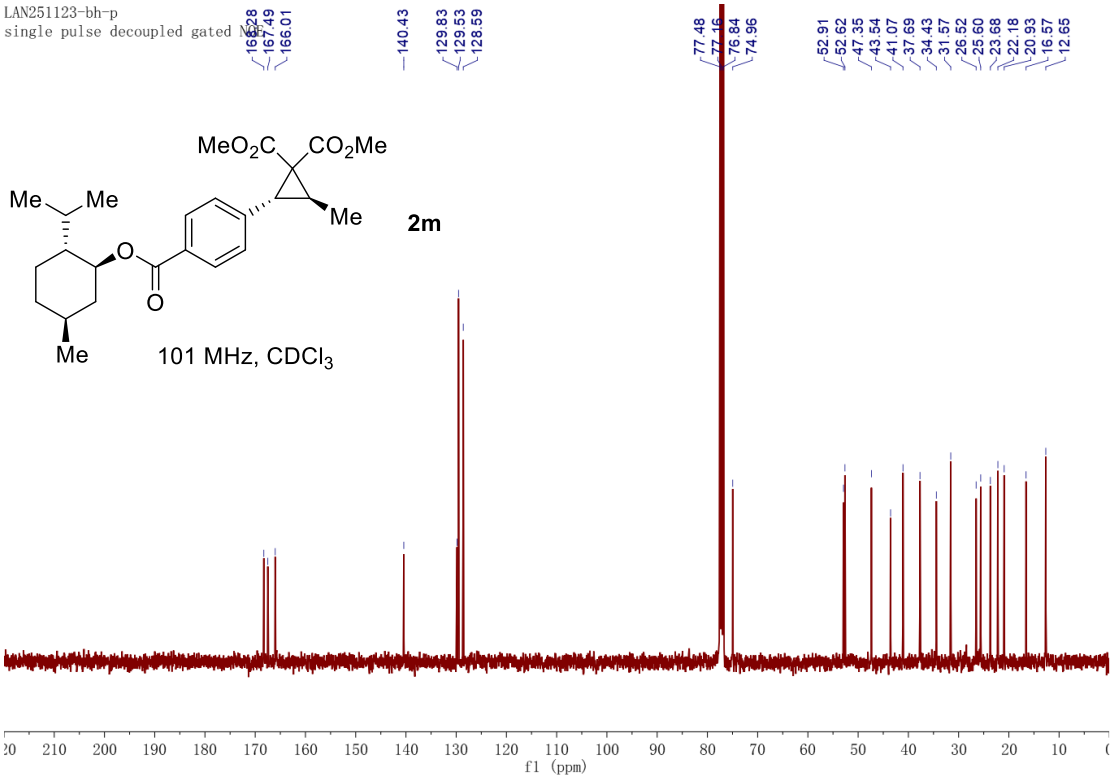
SSY260113-F2



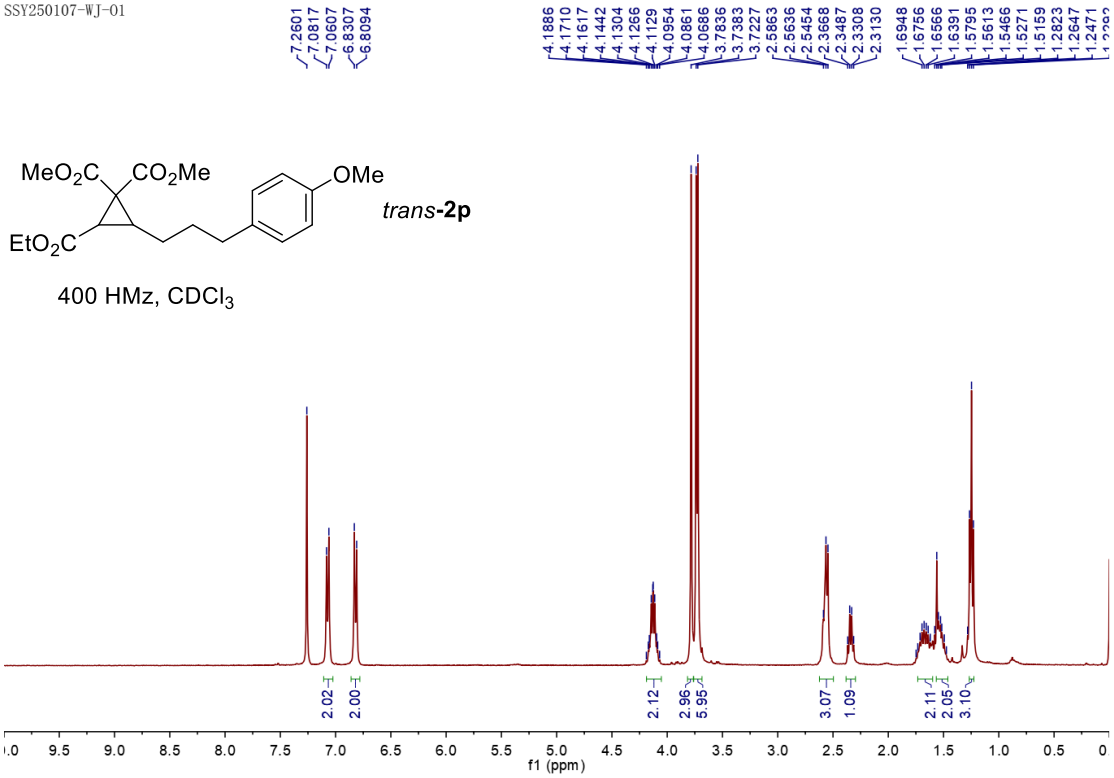
2l'

376 MHz, $CDCl_3$

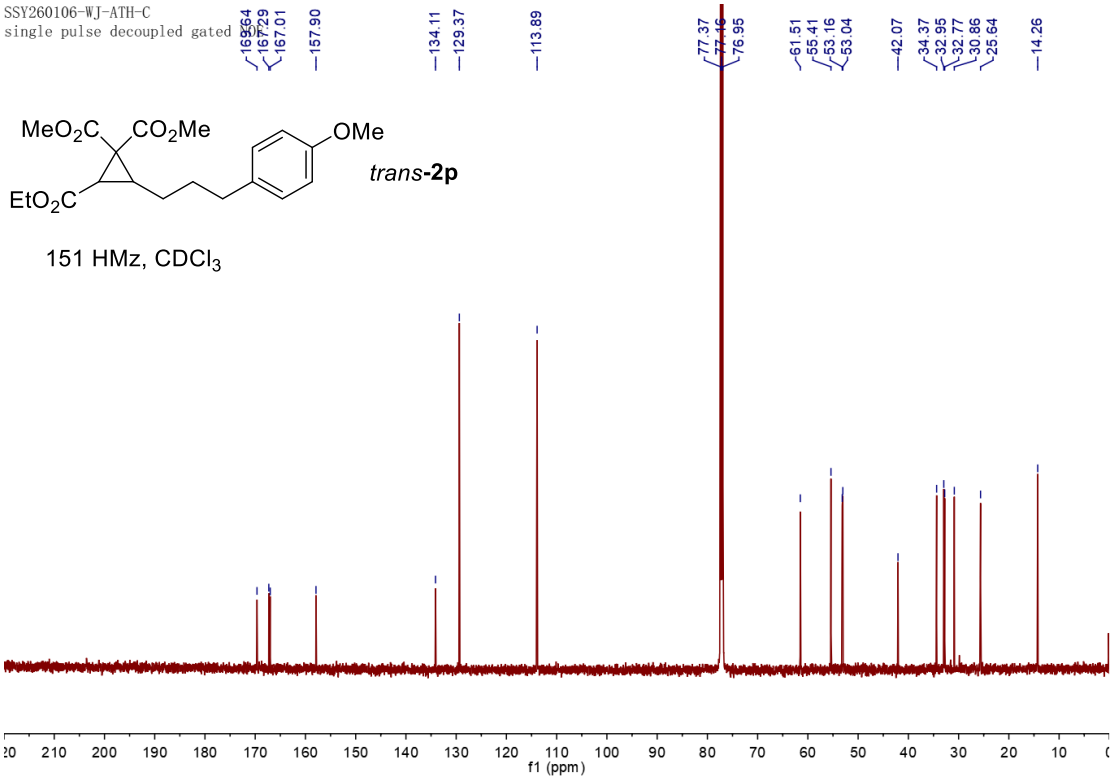

lan251124-BH-P
single_pulse
7.9349
7.9143
7.2597
7.2382
4.9335
4.9226
4.9062
4.8954
4.8791
4.8682
3.8070
3.4168
3.0808
3.0605
2.5916
2.5753
2.5720
1.7340
1.7053
1.5618
1.5339
1.2885
1.2727
1.0925
1.0636
0.9242
0.9167
0.9079
0.8992
0.7825
MeO2C
CO2Me
Me
Me
Me
O
O
Me
2m
400 MHz, CDCl3
2.03
1.98
1.00
3.08
3.08
1.00
0.98
1.03
1.02
2.10
2.00
3.06
2.03
7.12
3.10
f1 (ppm)


LAN251123-bh-p
single pulse decoupled gated
166.28
167.49
166.01
140.43
129.83
129.53
128.59
77.48
77.16
76.84
74.96
52.91
52.62
47.35
43.54
41.07
37.69
34.43
31.57
26.52
25.60
23.68
22.18
20.93
16.57
12.65
MeO2C
CO2Me
Me
Me
Me
O
O
Me
2m
101 MHz, CDCl3
f1 (ppm)

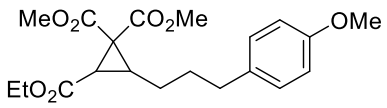
SSY250107-WJ-01



SSY260106-WJ-ATH-C
single pulse decoupled gated

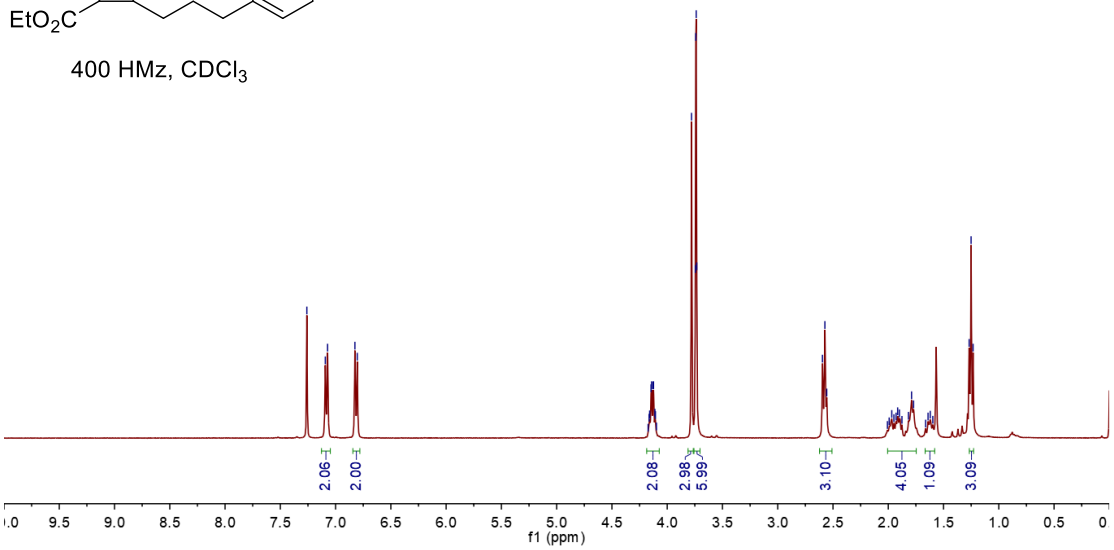


SSY260117-20

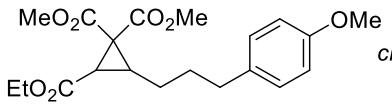


cis-**2p**

400 HMz, $CDCl_3$

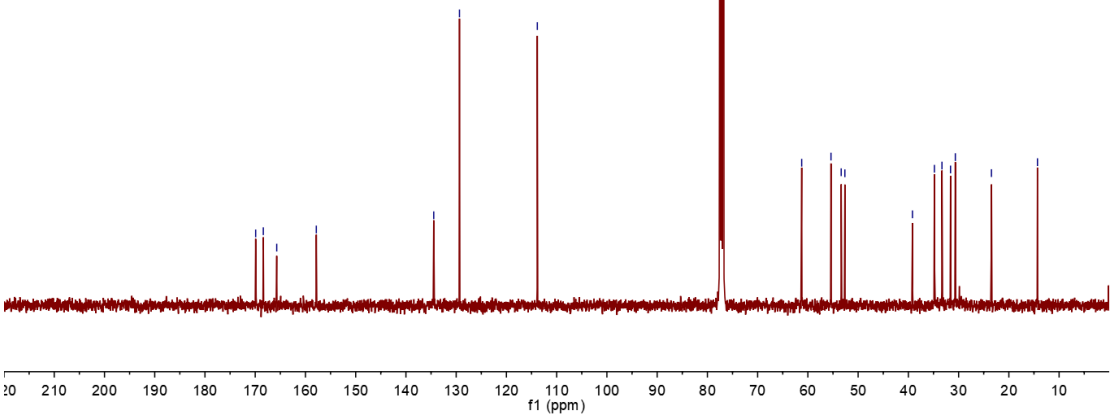


SSY250117-20-C
single pulse decoupled gated

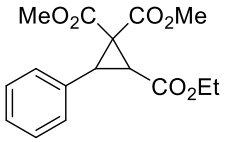


cis-**2p**

101 HMz, $CDCl_3$

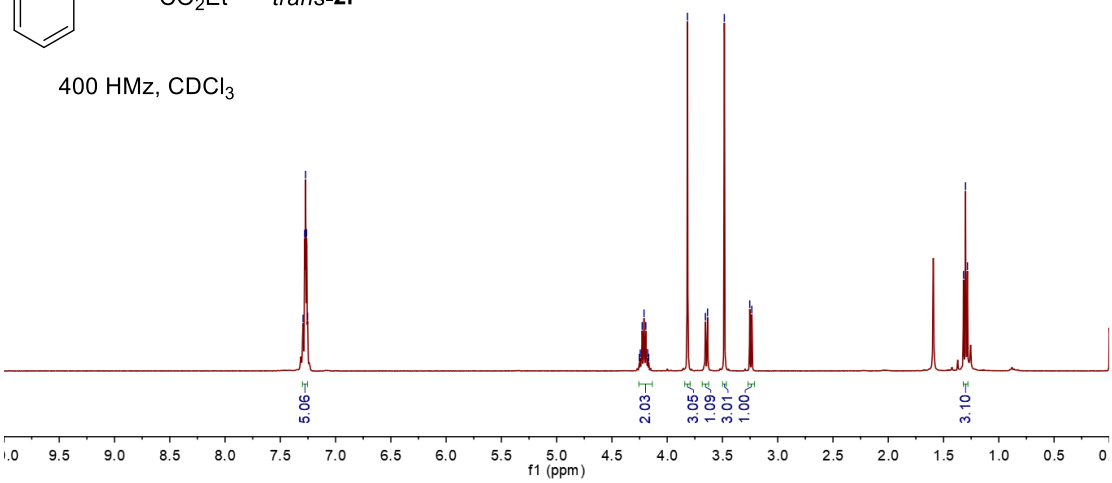


ssy260401-01-1
single_pulse

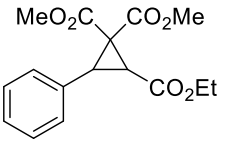


trans-**2r**

400 HMz, $CDCl_3$

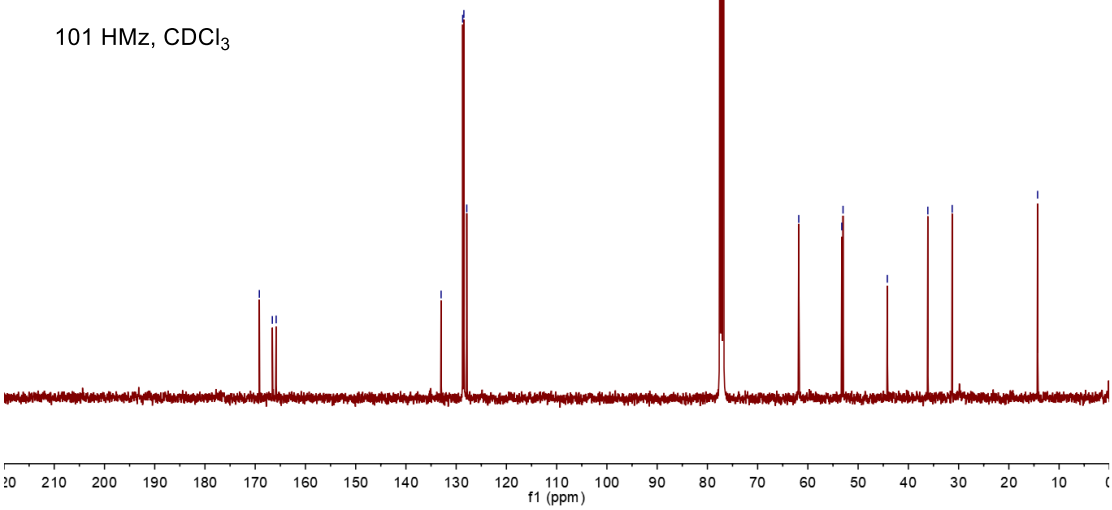


ssy260401-01-1-C
single pulse decoupled gated

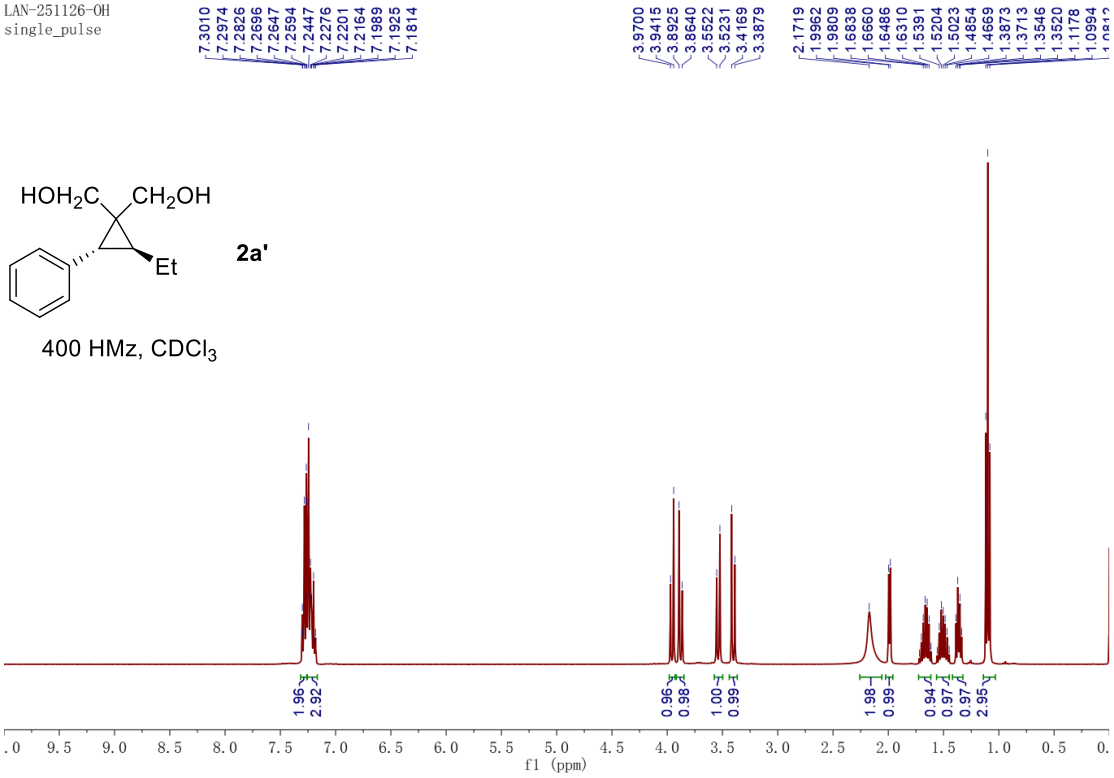


trans-**2r**

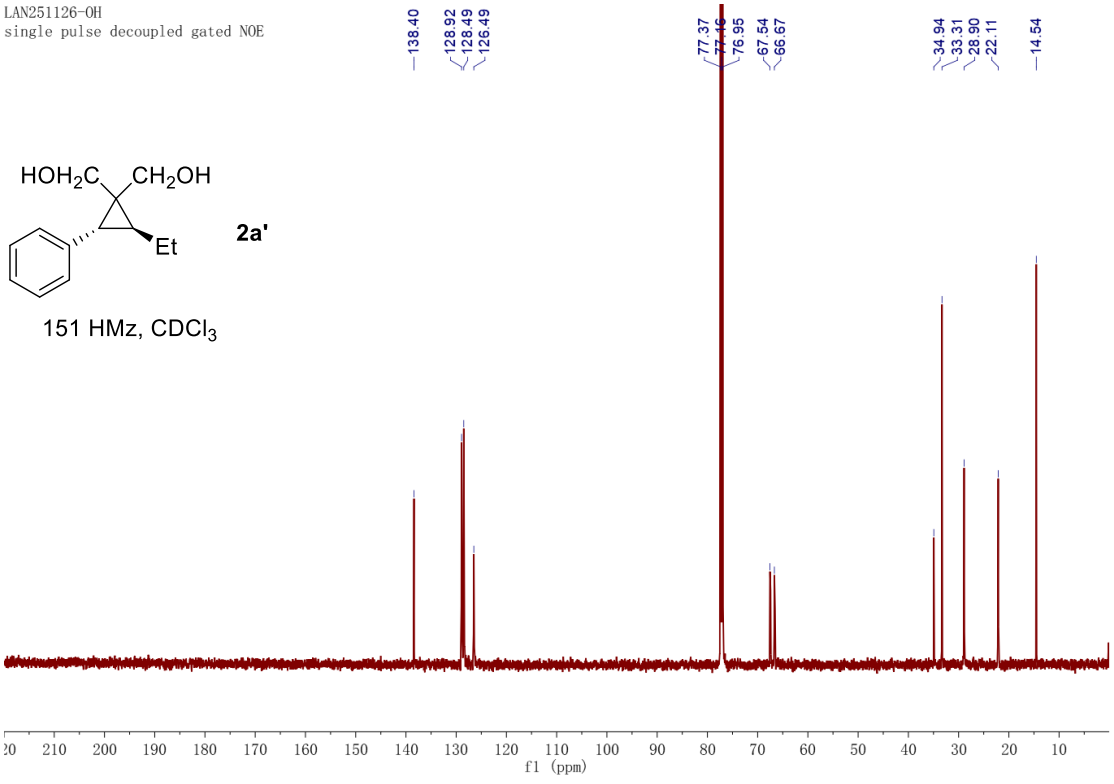
101 HMz, $CDCl_3$



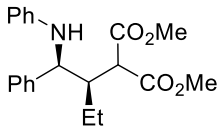
LAN-251126-OH
single_pulse



LAN251126-OH
single pulse decoupled gated NOE



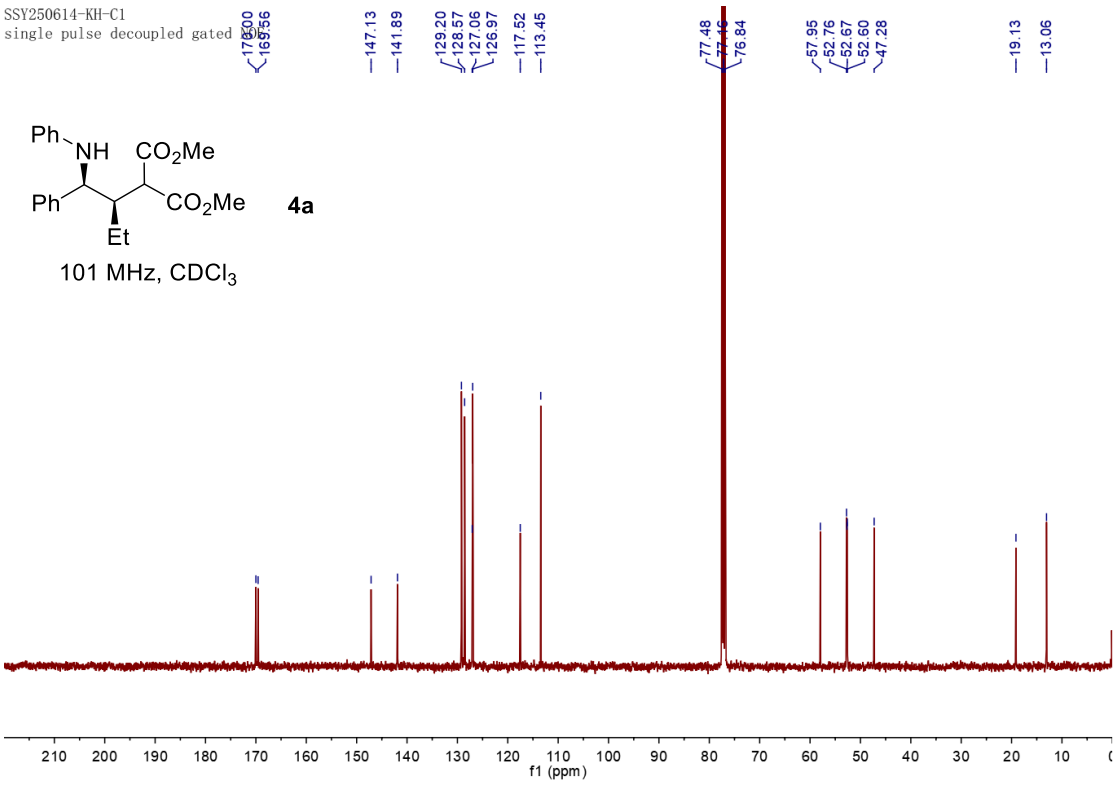
SSY250614-KH-C
single_pulse



4a

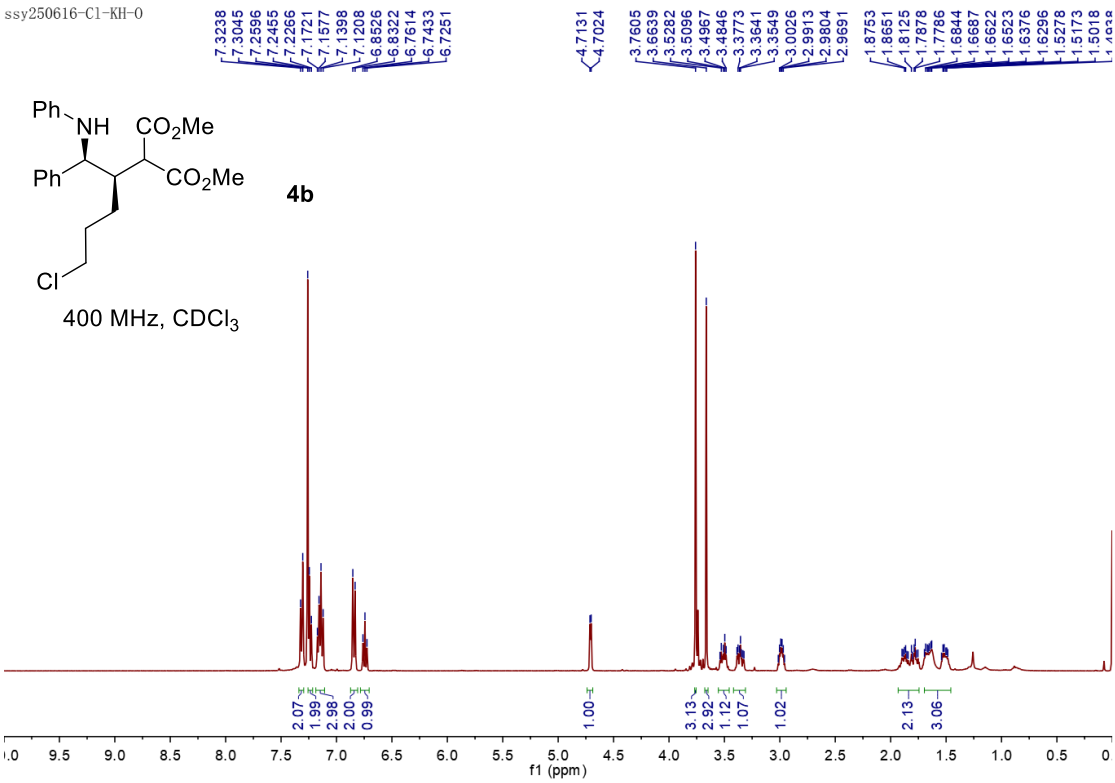
400 MHz, $CDCl_3$

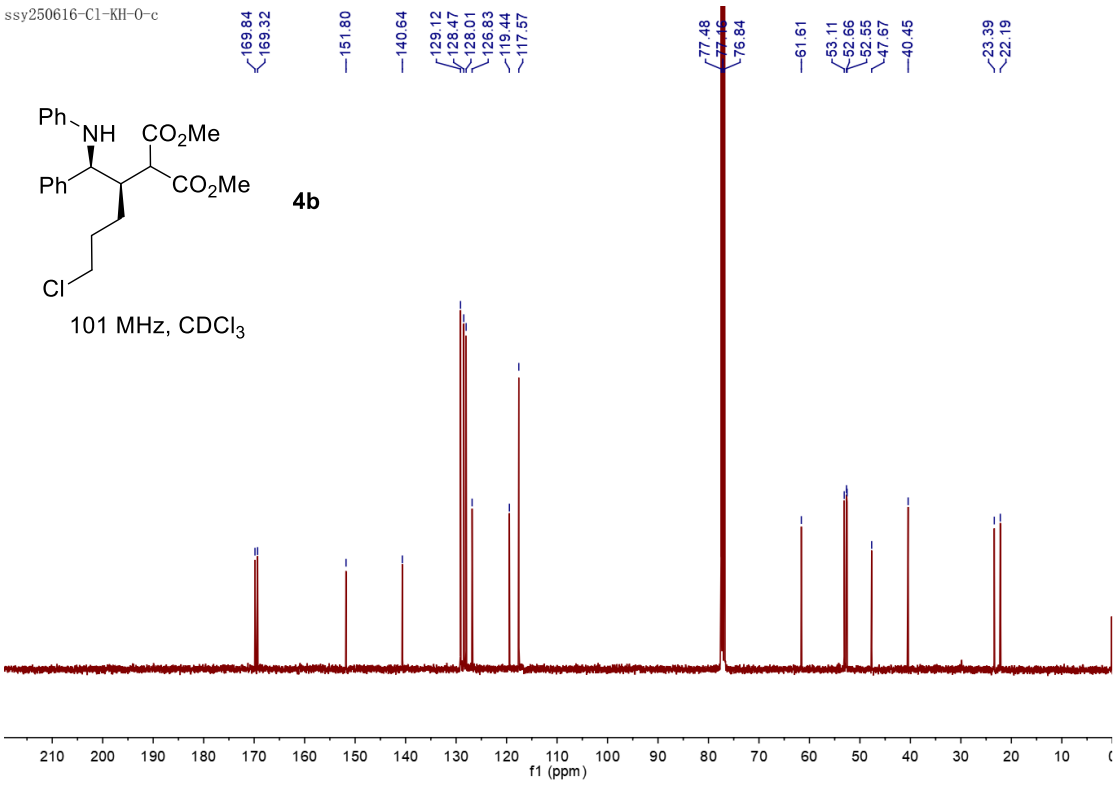
SSY250614-KH-C1
single pulse decoupled gated

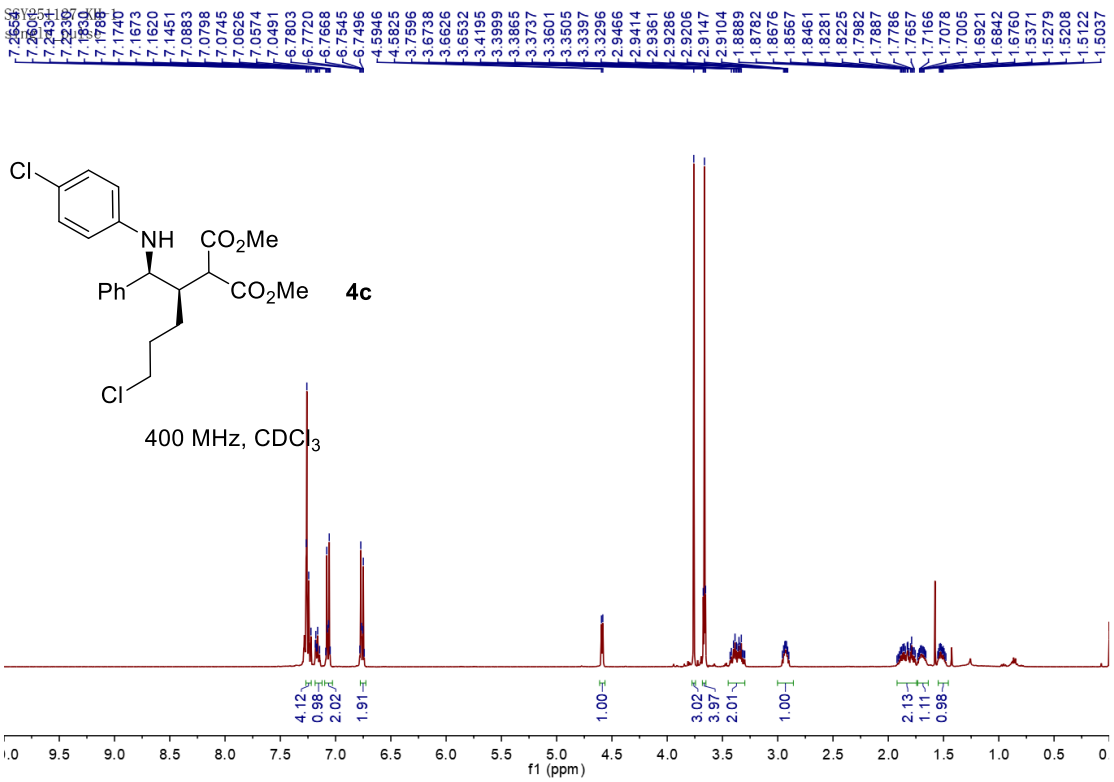


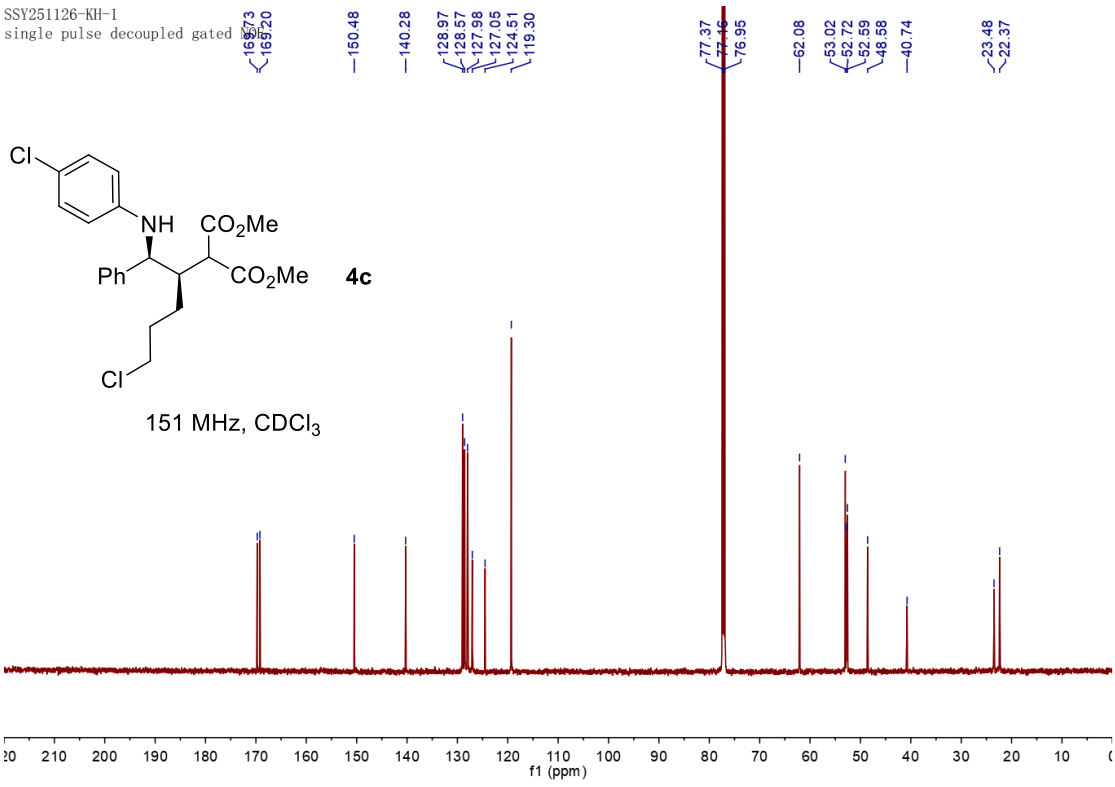
4a

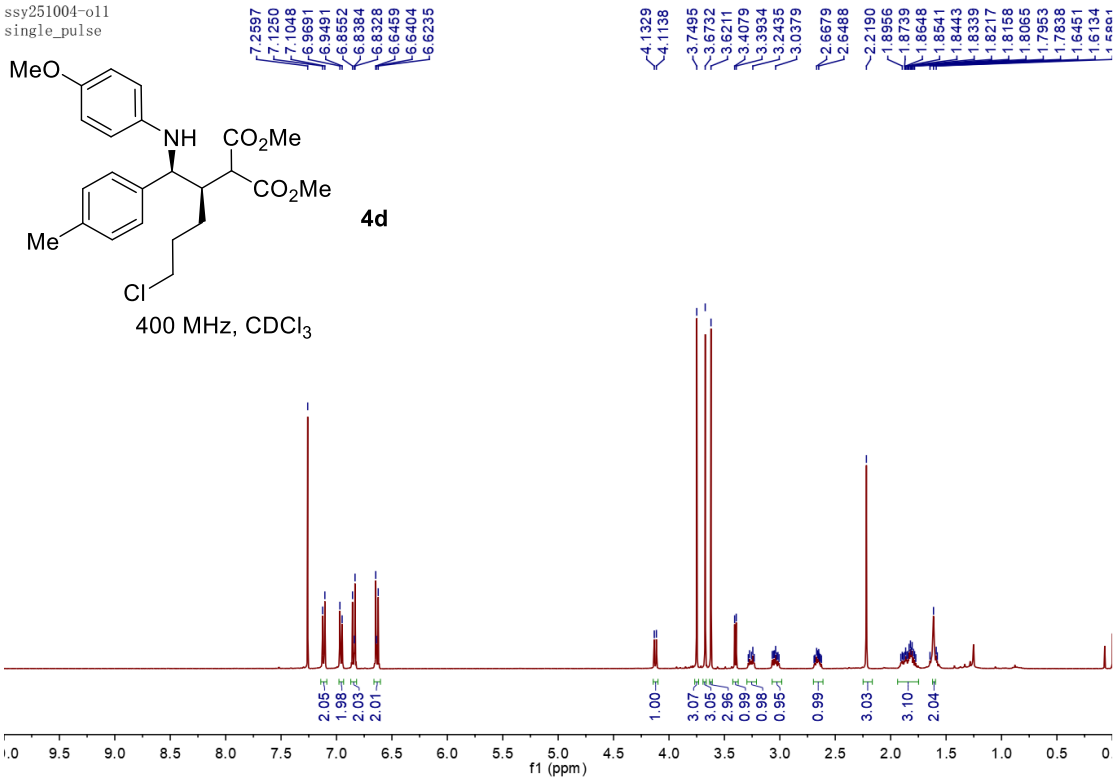
101 MHz, $CDCl_3$

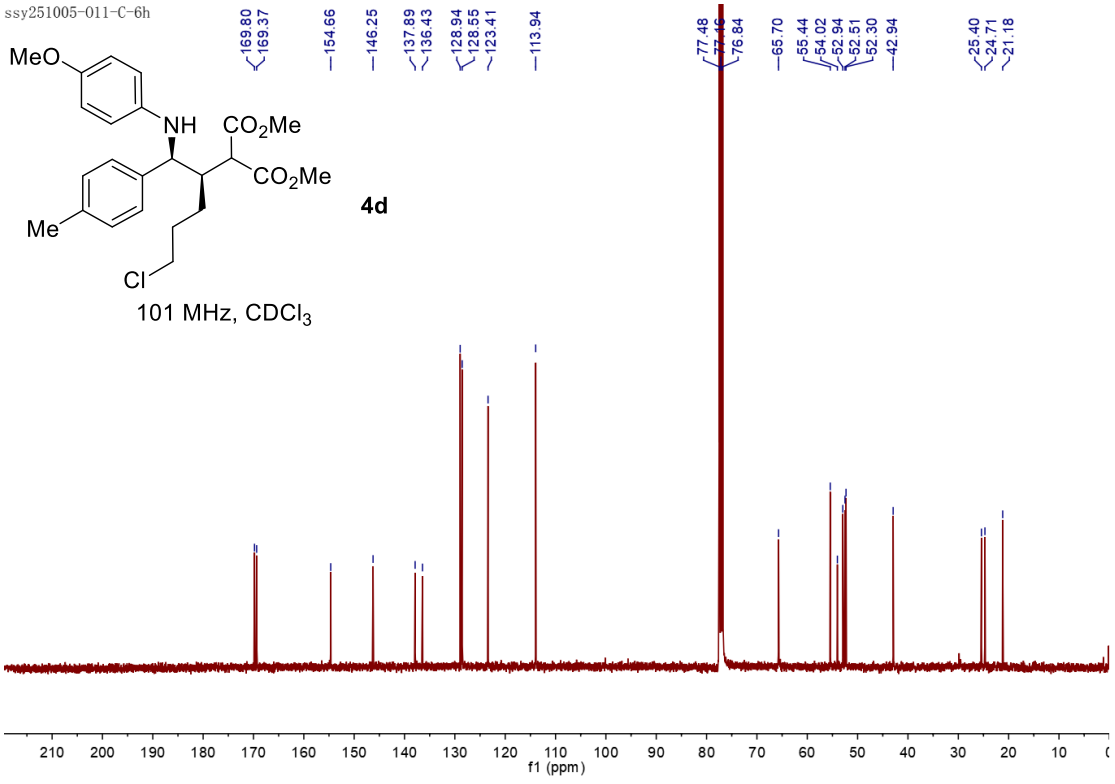

ssy250616-Cl-KH-0
Ph
NH
CO2Me
Ph
CO2Me
Cl
4b
400 MHz, CDCl3
f1 (ppm)

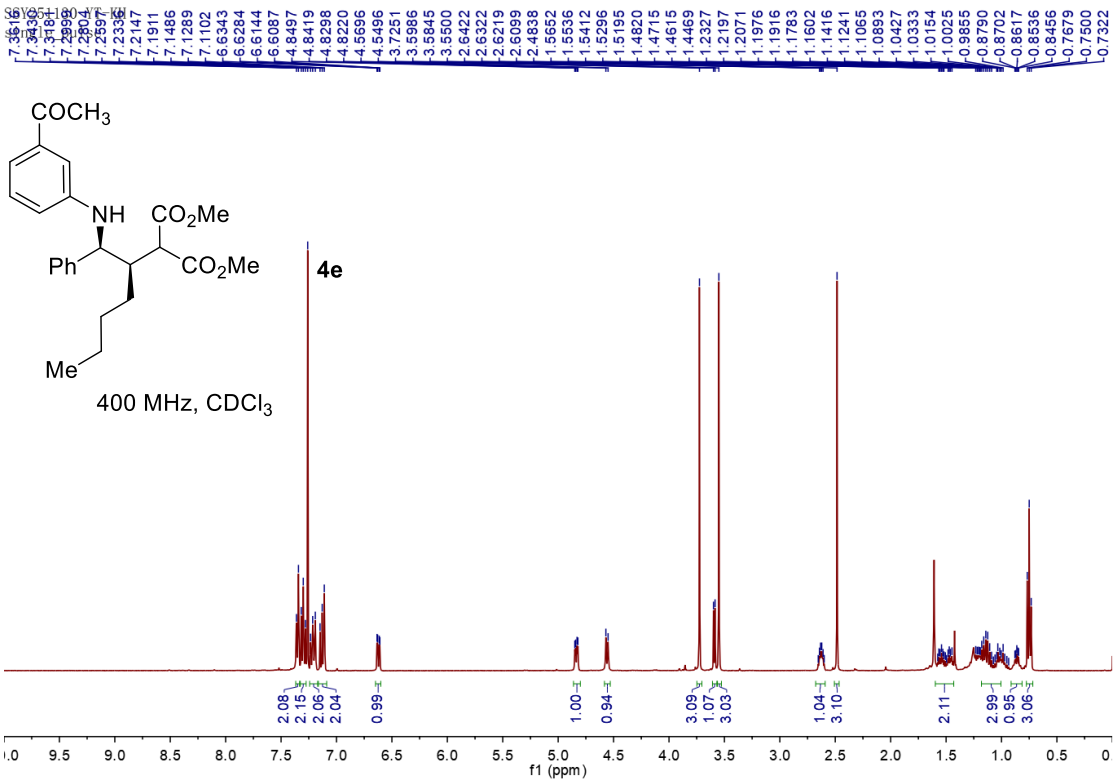

ssy250616-Cl-KH-0-c
Ph
NH
CO2Me
Ph
CO2Me
Cl
4b
101 MHz, CDCl3
f1 (ppm)

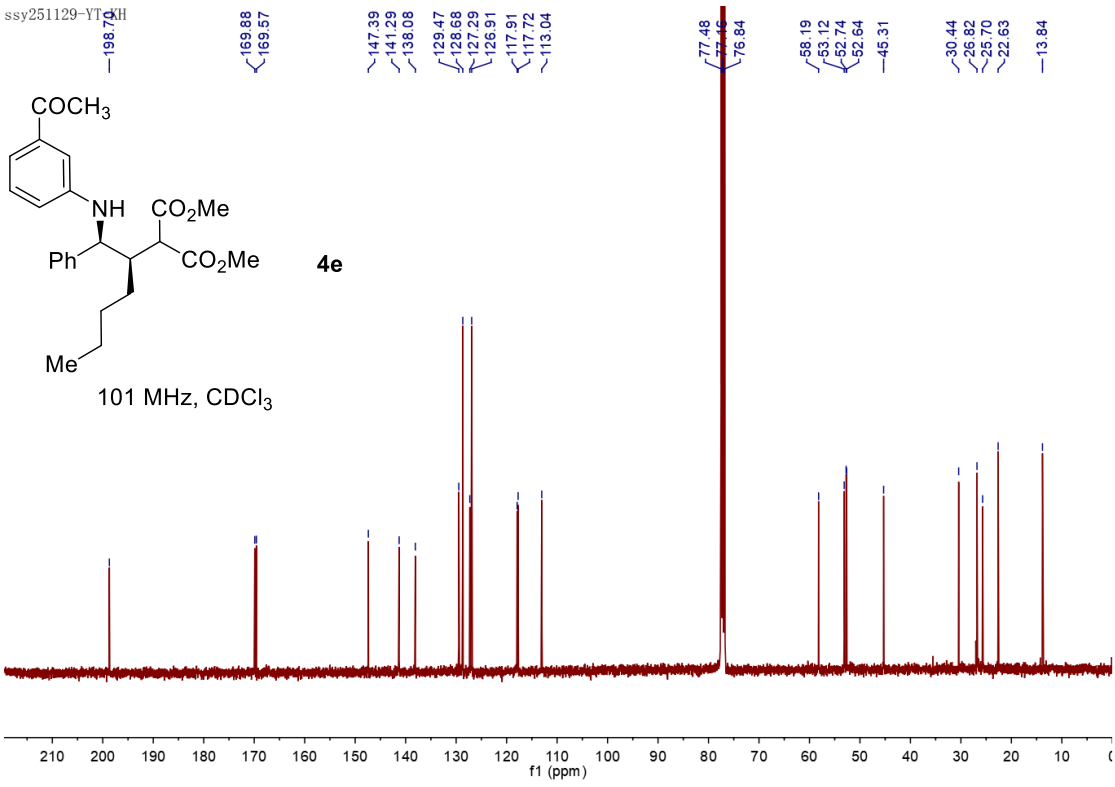

Cl
NH
CO2Me
Ph
CO2Me
4c
Cl
400 MHz, CDCl3
f1 (ppm)


SSY251126-KH-1
single pulse decoupled gated NOE
Cl
NH
CO2Me
Ph
CO2Me
4c
Cl
151 MHz, CDCl3
f1 (ppm)

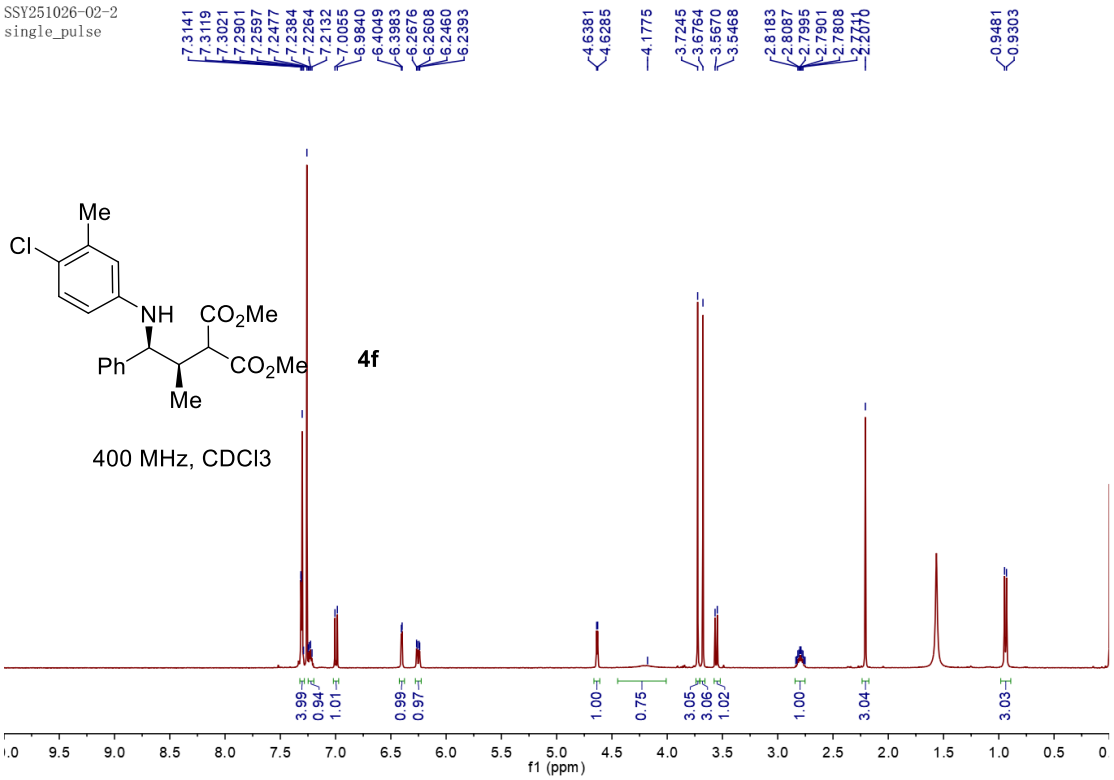

ssy251004-o11
single_pulse
MeO
NH
CO2Me
CO2Me
Me
Cl
4d
400 MHz, CDCl3
f1 (ppm)


ssy251005-011-C-6h
MeO
NH
CO2Me
CO2Me
Me
Cl
4d
101 MHz, CDCl3
f1 (ppm)

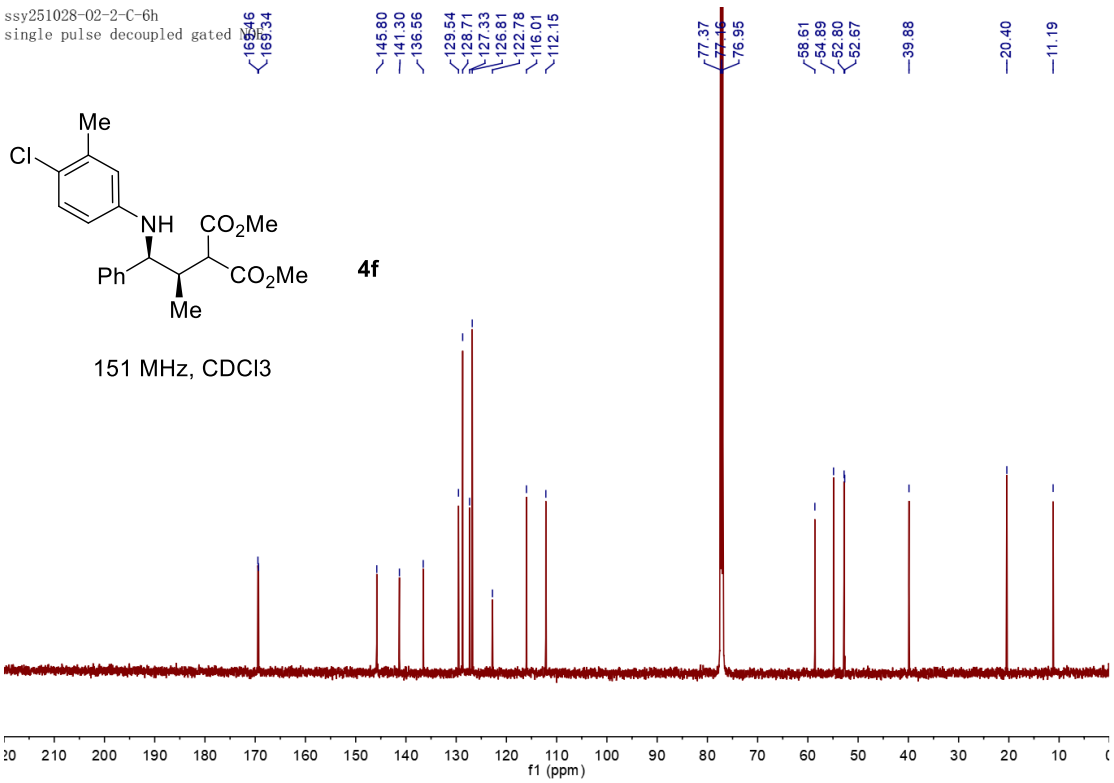

COCH3
NH
CO2Me
Ph
CO2Me
Me
4e
400 MHz, CDCl3
f1 (ppm)

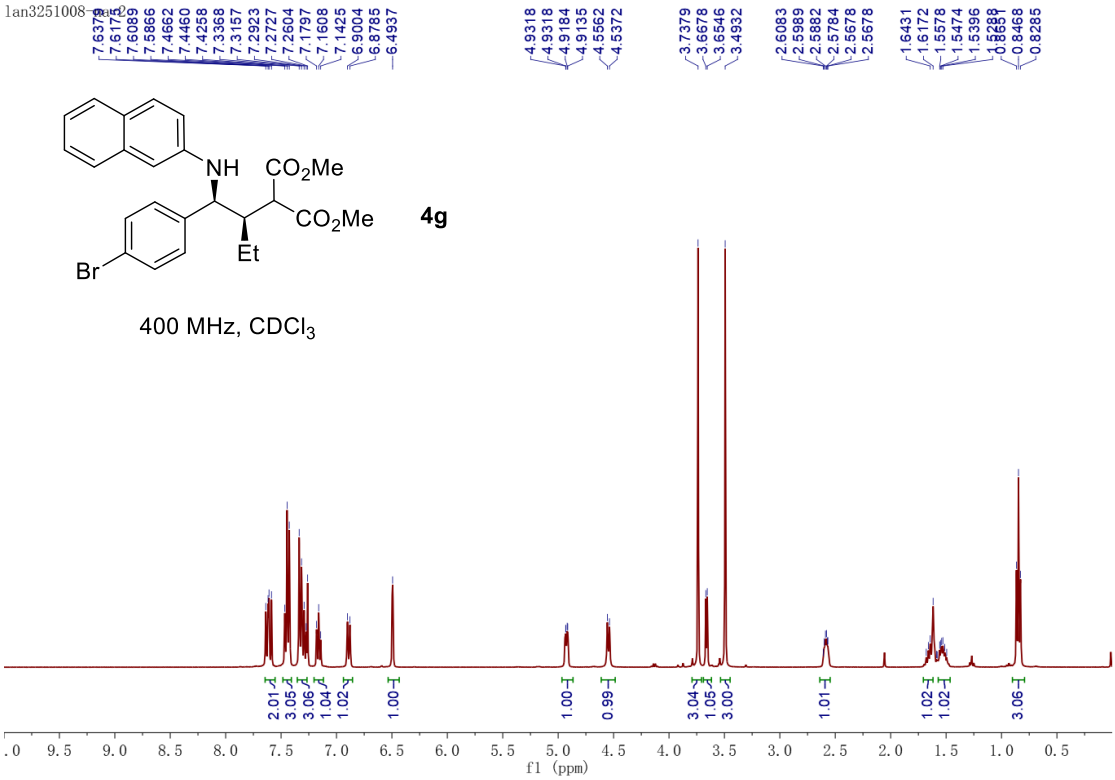

COCH3
NH
CO2Me
Ph
CO2Me
Me
4e
101 MHz, CDCl3
f1 (ppm)

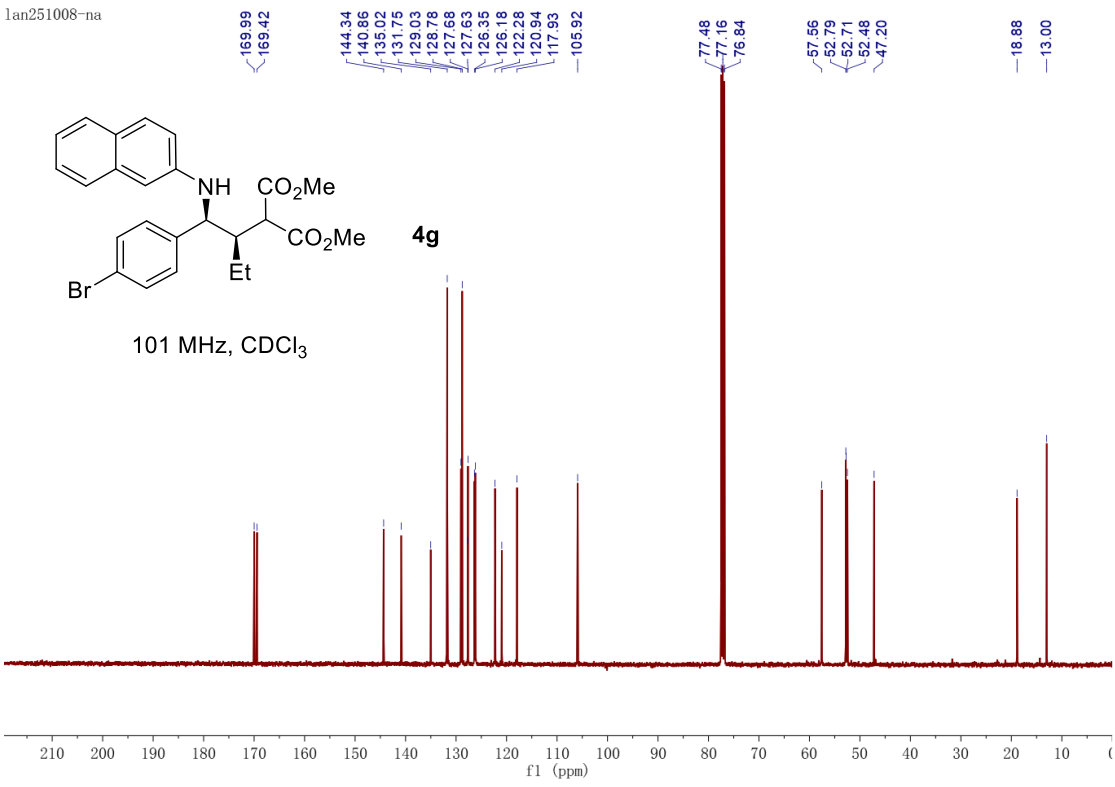
SSY251026-02-2
single_pulse



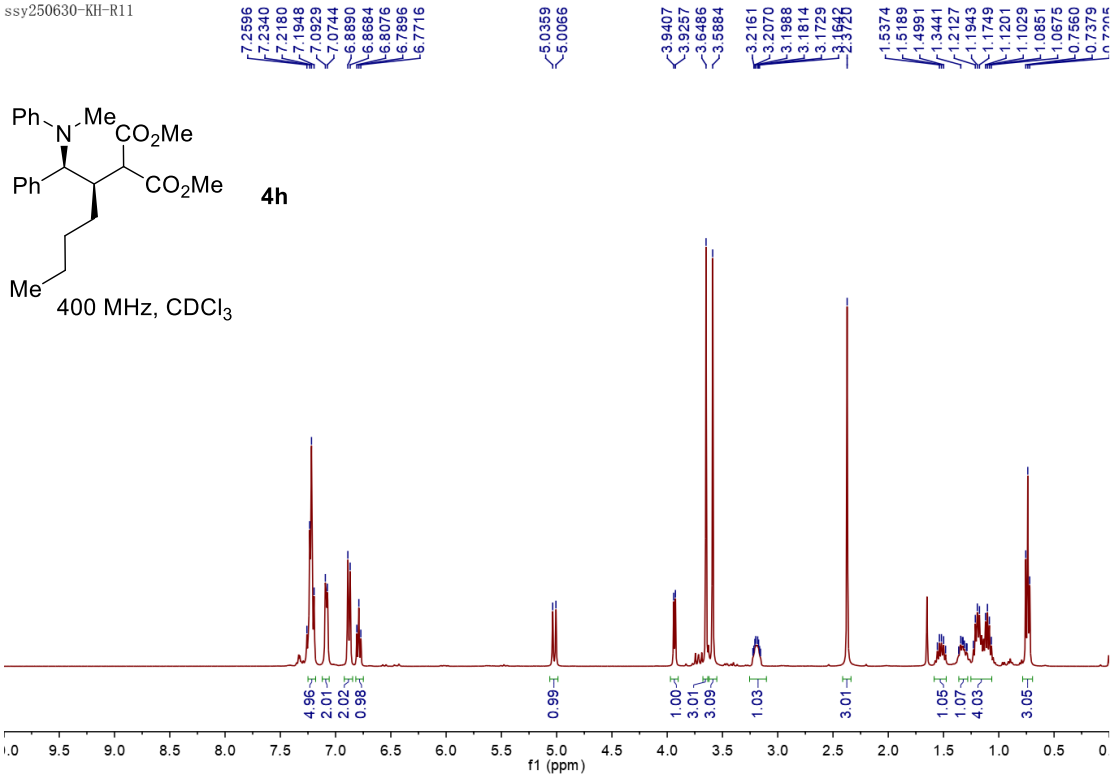
ssy251028-02-2-C-6h
single pulse decoupled gated



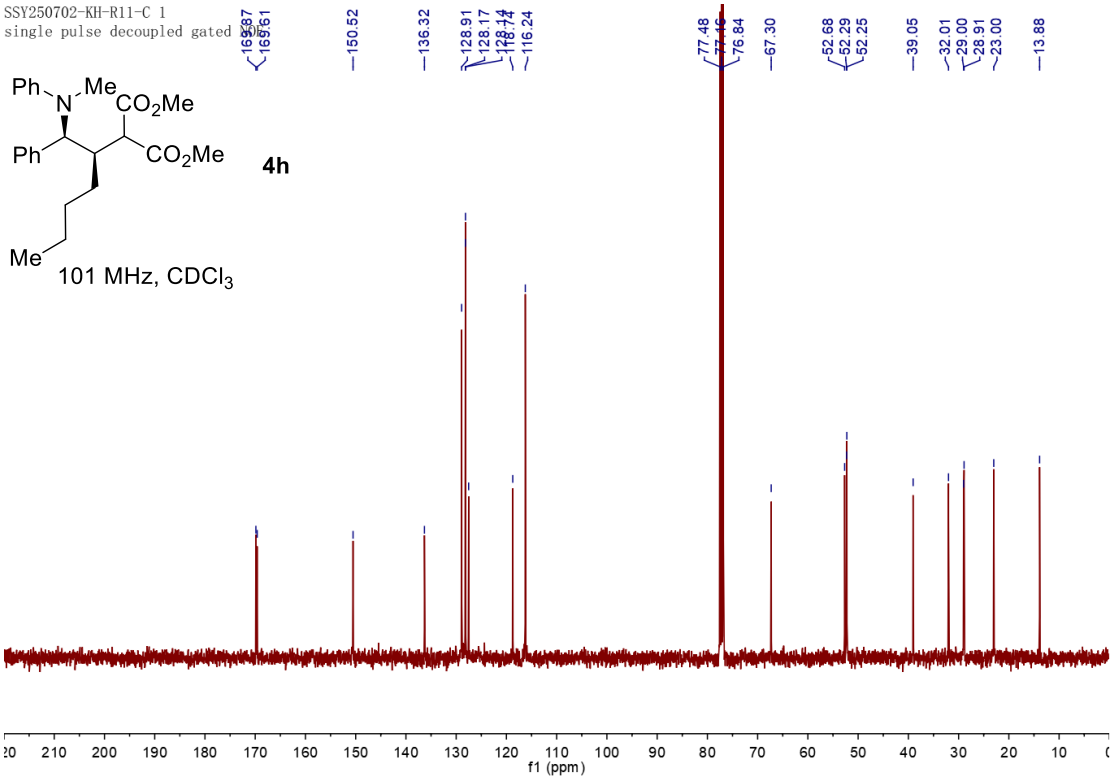

lan3251008-na-2
NH
CO2Me
CO2Me
Et
Br
4g
400 MHz, CDCl3
f1 (ppm)

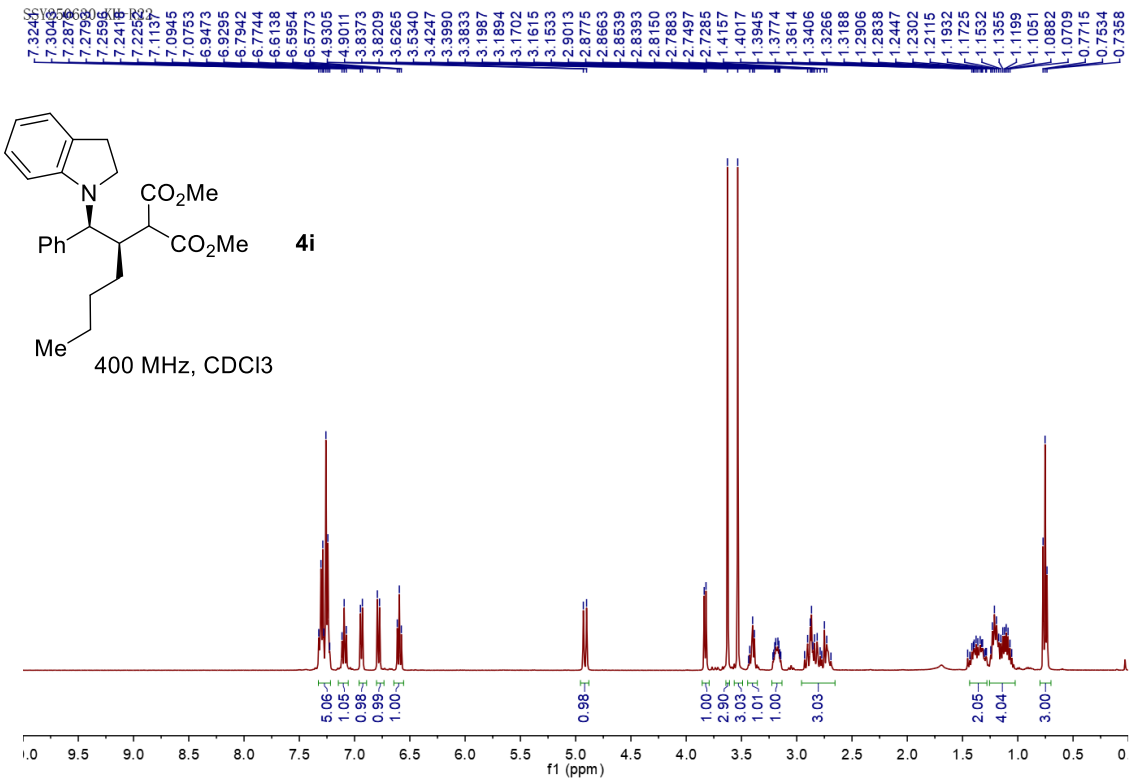

lan251008-na
NH
CO2Me
CO2Me
Et
Br
4g
101 MHz, CDCl3
f1 (ppm)

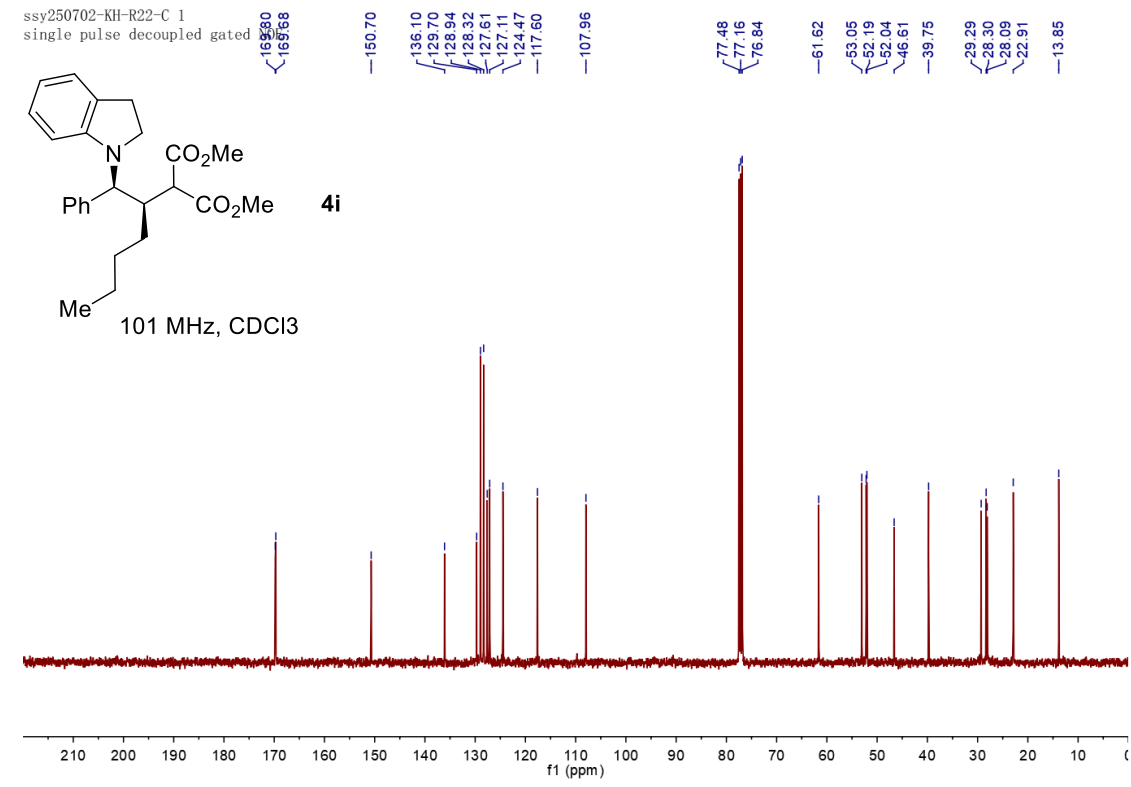
ssy250630-KH-R11

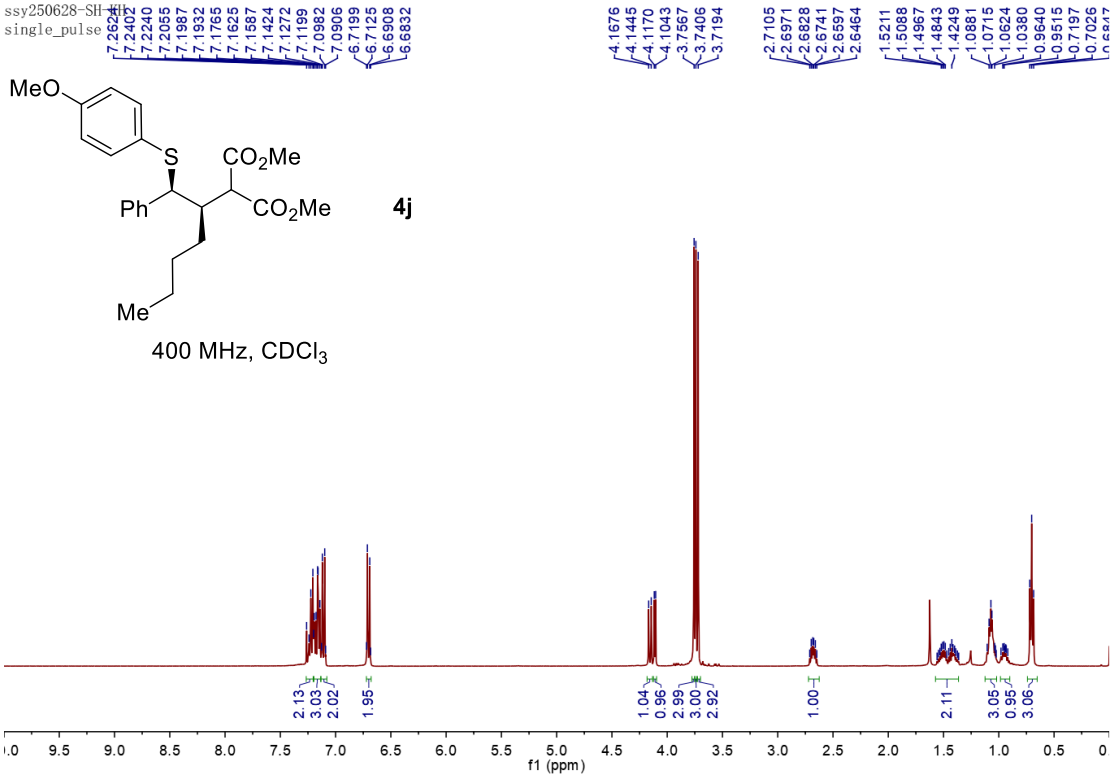


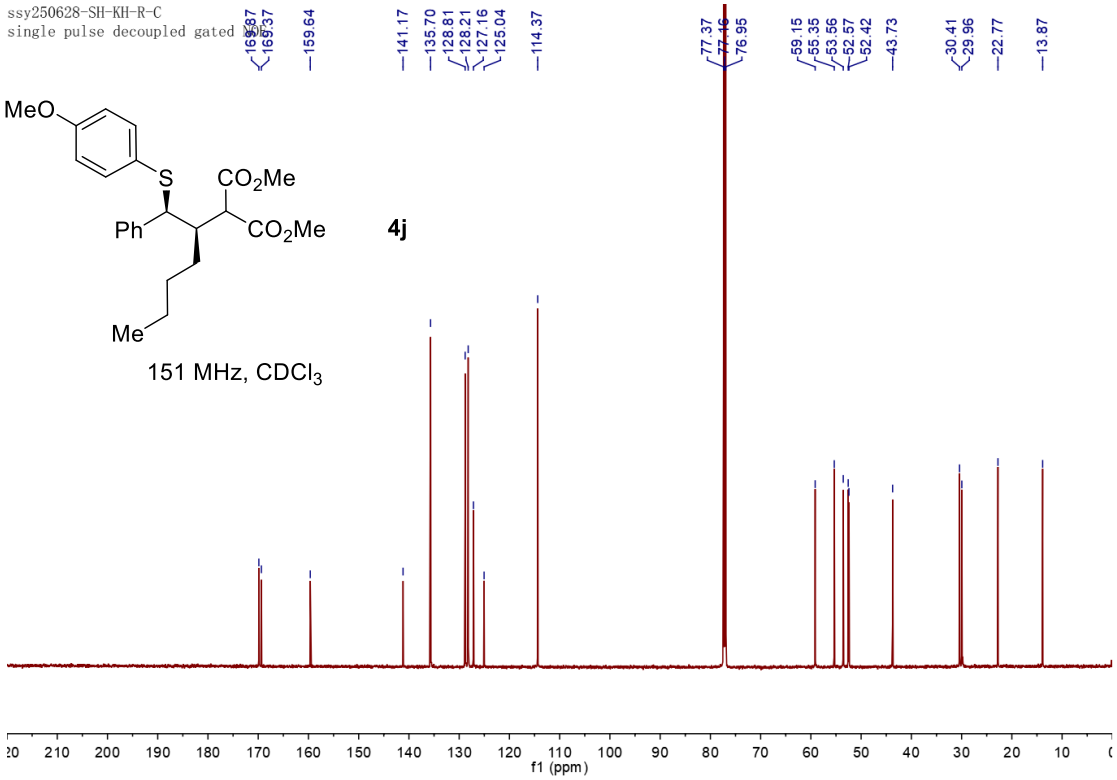
SSY250702-KH-R11-C 1
single pulse decoupled gated

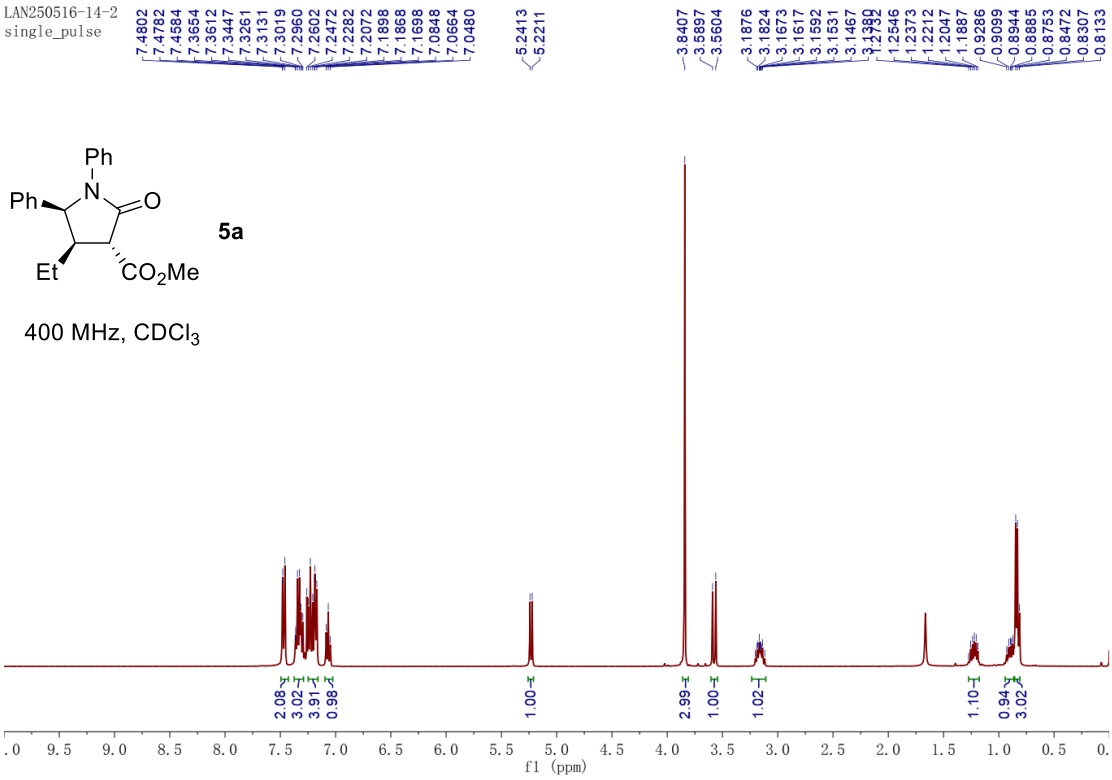


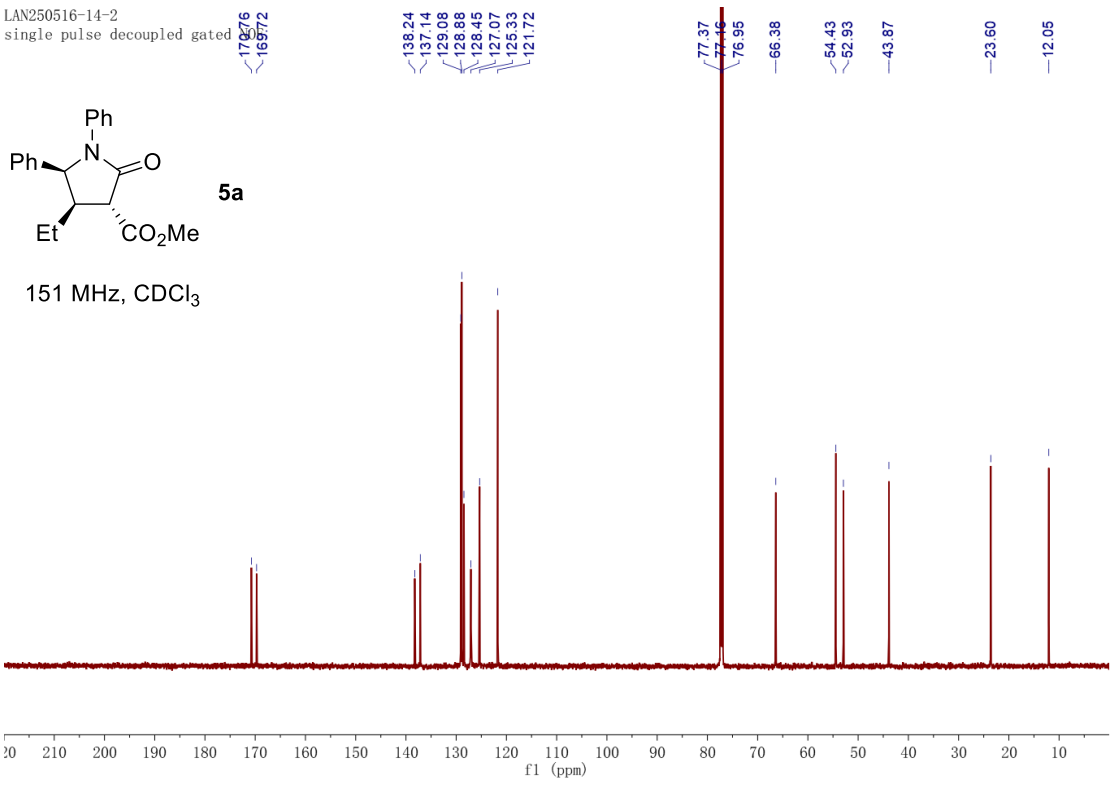

CO2Me
CO2Me
Ph
Me
4i
400 MHz, CDCl3
f1 (ppm)


ssy250702-KH-R22-C 1
single pulse decoupled gated
CO2Me
CO2Me
Ph
Me
4i
101 MHz, CDCl3
f1 (ppm)

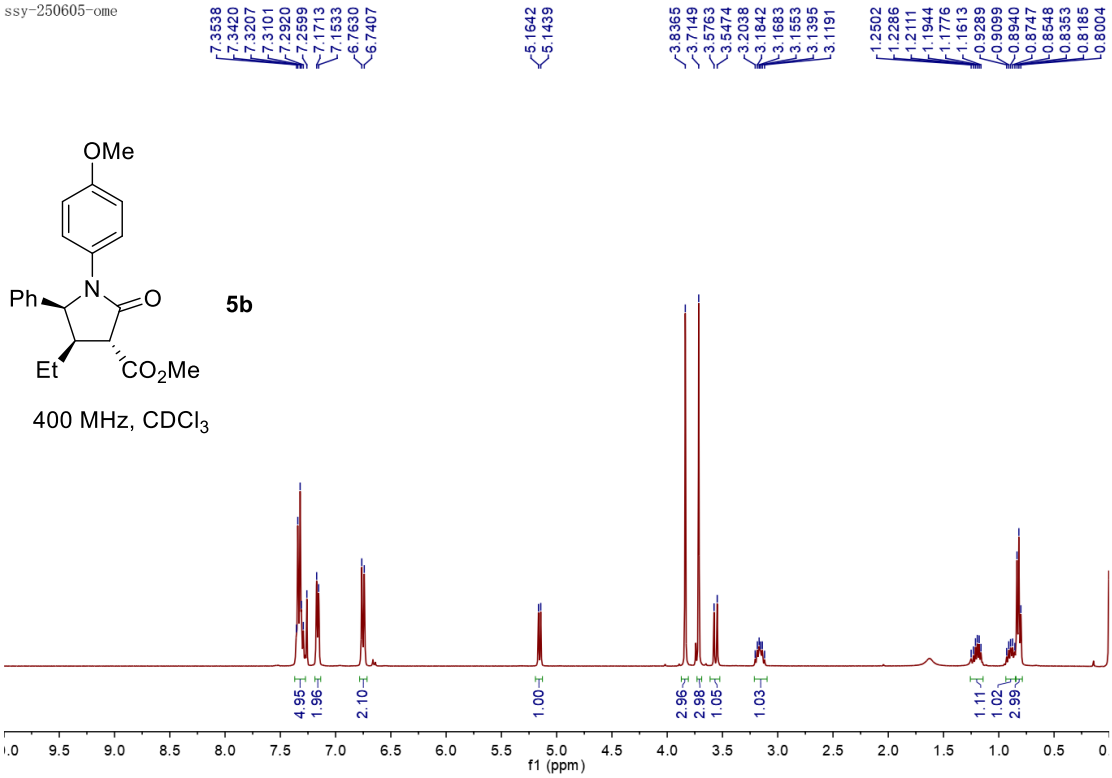

ssy250628-SH-KH
single_pulse
MeO
S
CO2Me
Ph
CO2Me
Me
4j
400 MHz, CDCl3
f1 (ppm)


ssy250628-SH-KH-R-C
single pulse decoupled gated
MeO
S
CO2Me
Ph
CO2Me
Me
4j
151 MHz, CDCl3
f1 (ppm)

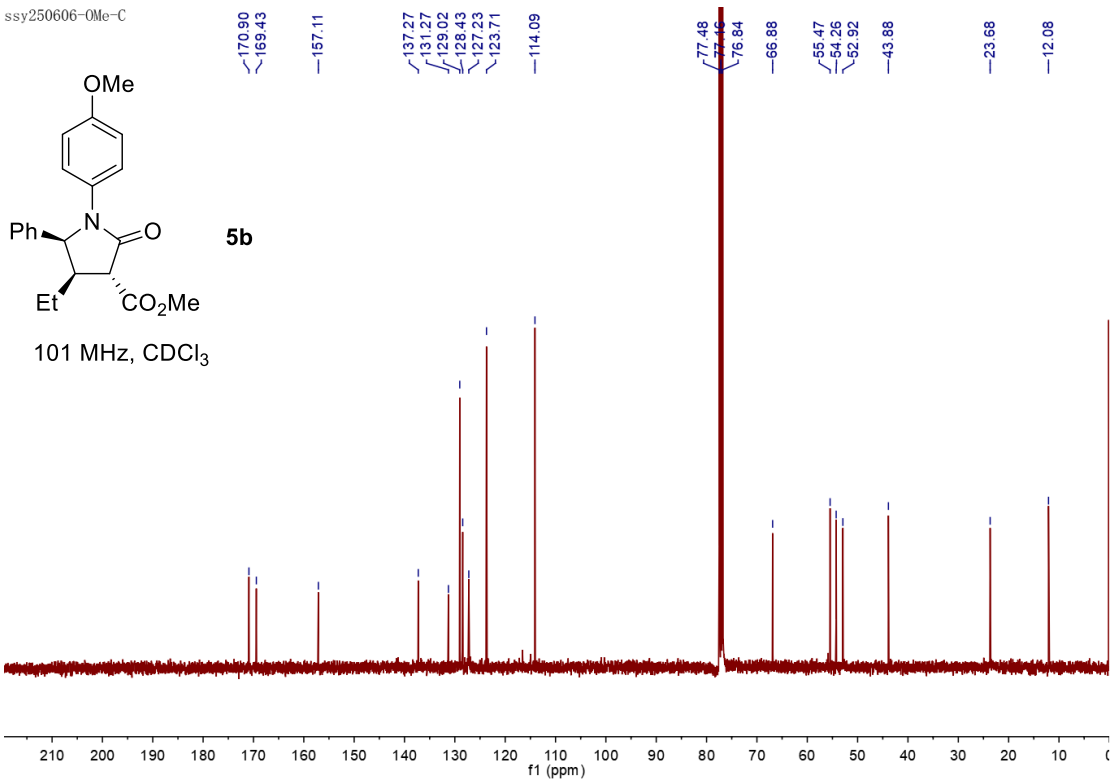

LAN250516-14-2
single_pulse
7.4802
7.4782
7.4584
7.3654
7.3612
7.3447
7.3261
7.3131
7.3019
7.2960
7.2602
7.2472
7.2282
7.2072
7.1898
7.1868
7.1698
7.0848
7.0664
7.0480
5.2413
5.2211
3.8407
3.5897
3.5604
3.1876
3.1824
3.1673
3.1617
3.1592
3.1531
3.1467
3.1380
3.1232
1.2546
1.2373
1.2212
1.2047
1.1887
0.9286
0.9099
0.8944
0.8885
0.8753
0.8472
0.8307
0.8133
Ph
N
O
Ph
Et
CO2Me
5a
400 MHz, CDCl3
2.08
3.02
3.91
0.98
1.00
2.99
1.00
1.02
1.10
0.94
3.02
f1 (ppm)


LAN250516-14-2
single pulse decoupled gated
170.76
169.72
138.24
137.14
129.08
128.88
128.45
127.07
125.33
121.72
77.37
77.16
76.95
66.38
54.43
52.93
43.87
23.60
12.05
Ph
N
O
Ph
Et
CO2Me
5a
151 MHz, CDCl3
f1 (ppm)

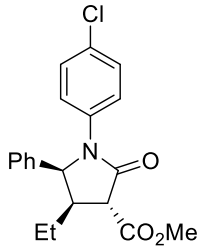
ssy-250605-ome



ssy250606-OMe-C



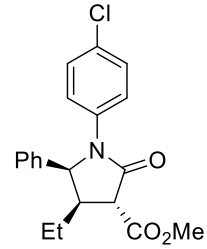
SSY250914-Cl-CH
single_pulse



5c

600 MHz, $CDCl_3$

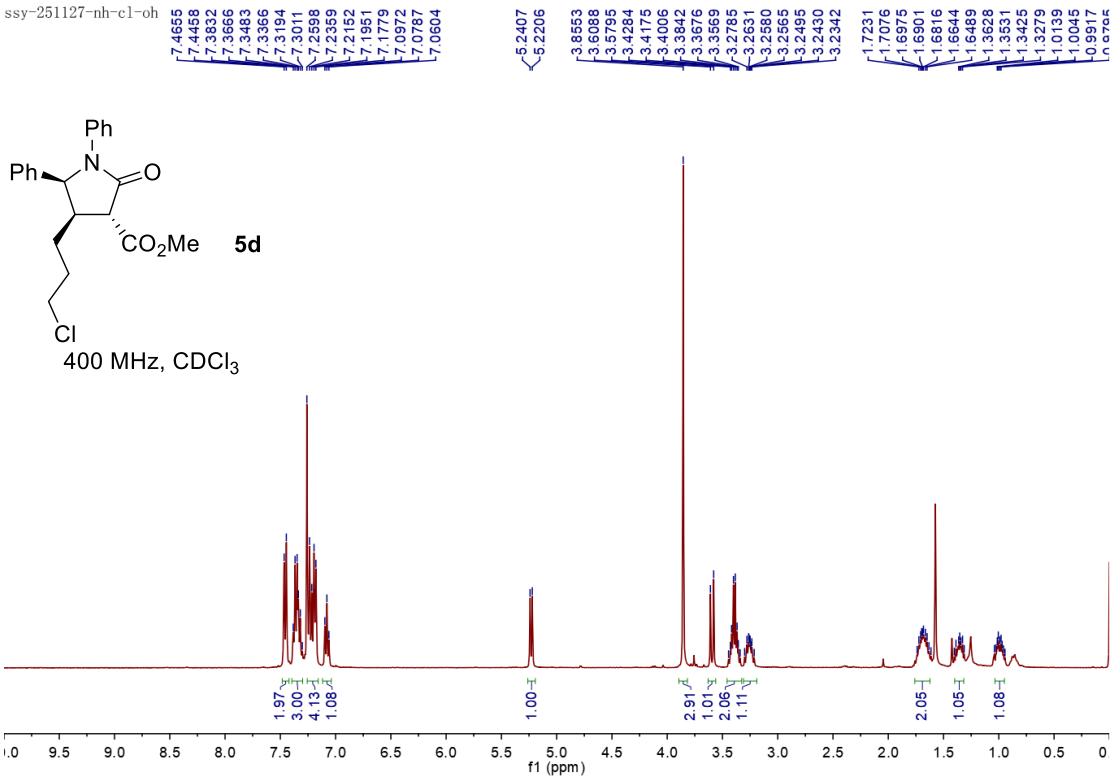
ssy250909-cl-ch-11



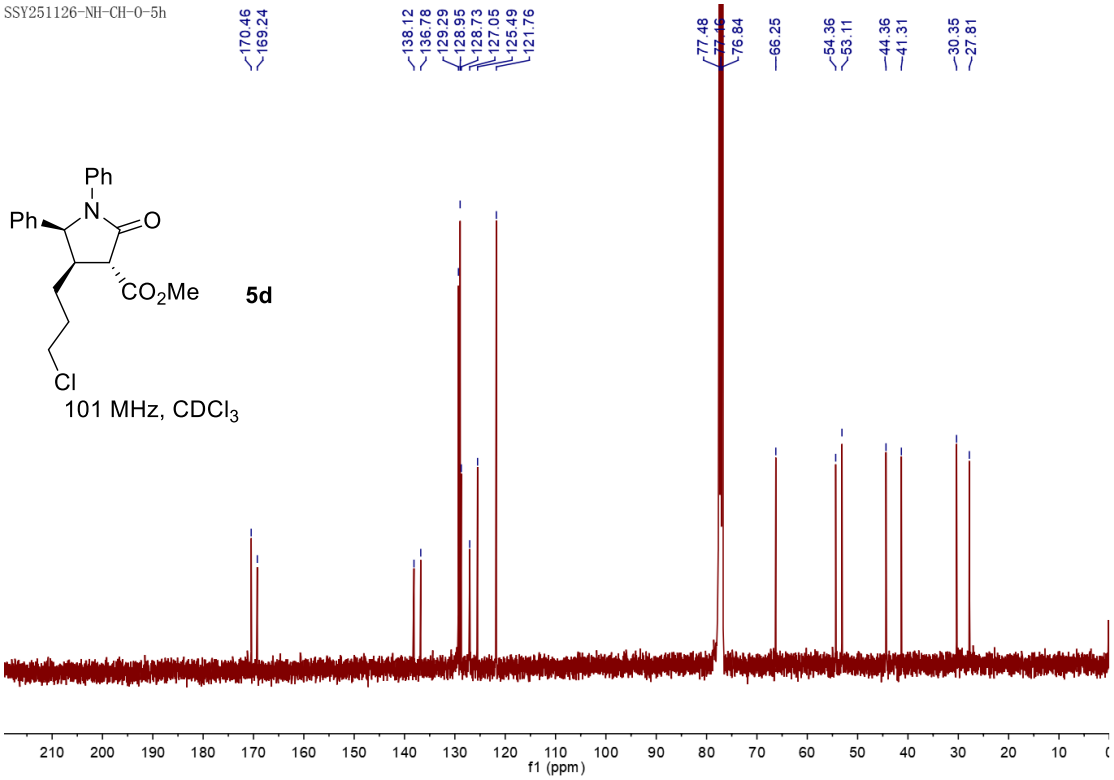
5c

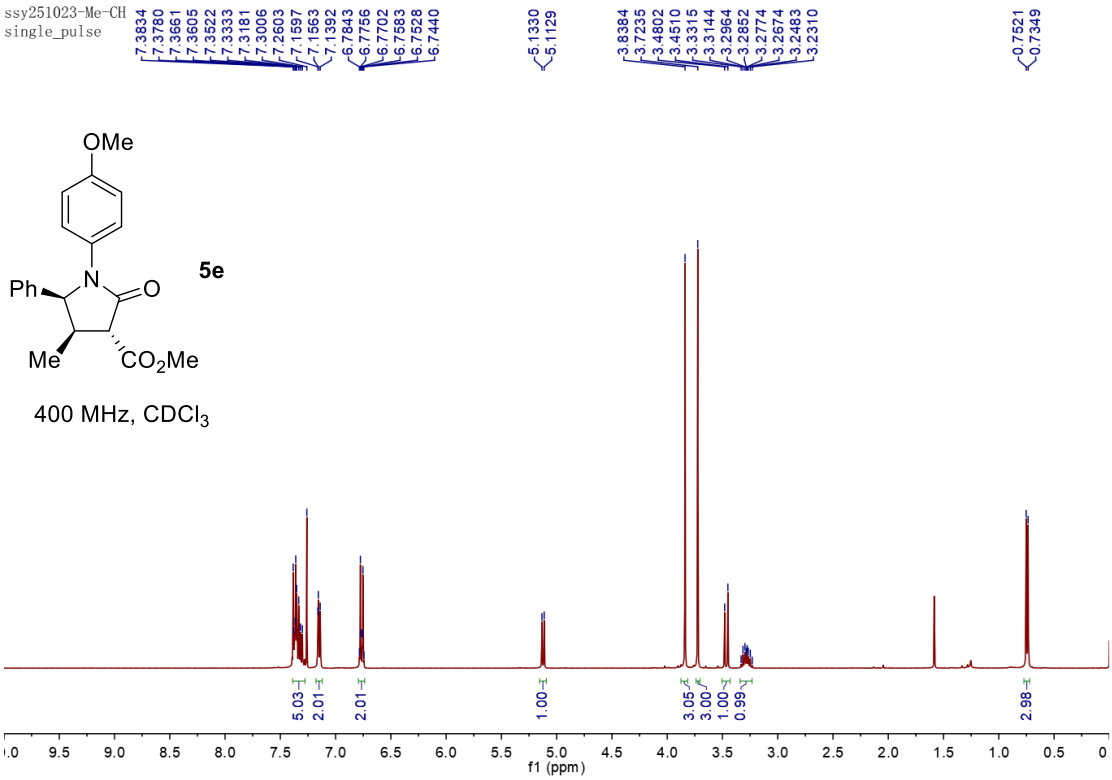
101 MHz, $CDCl_3$

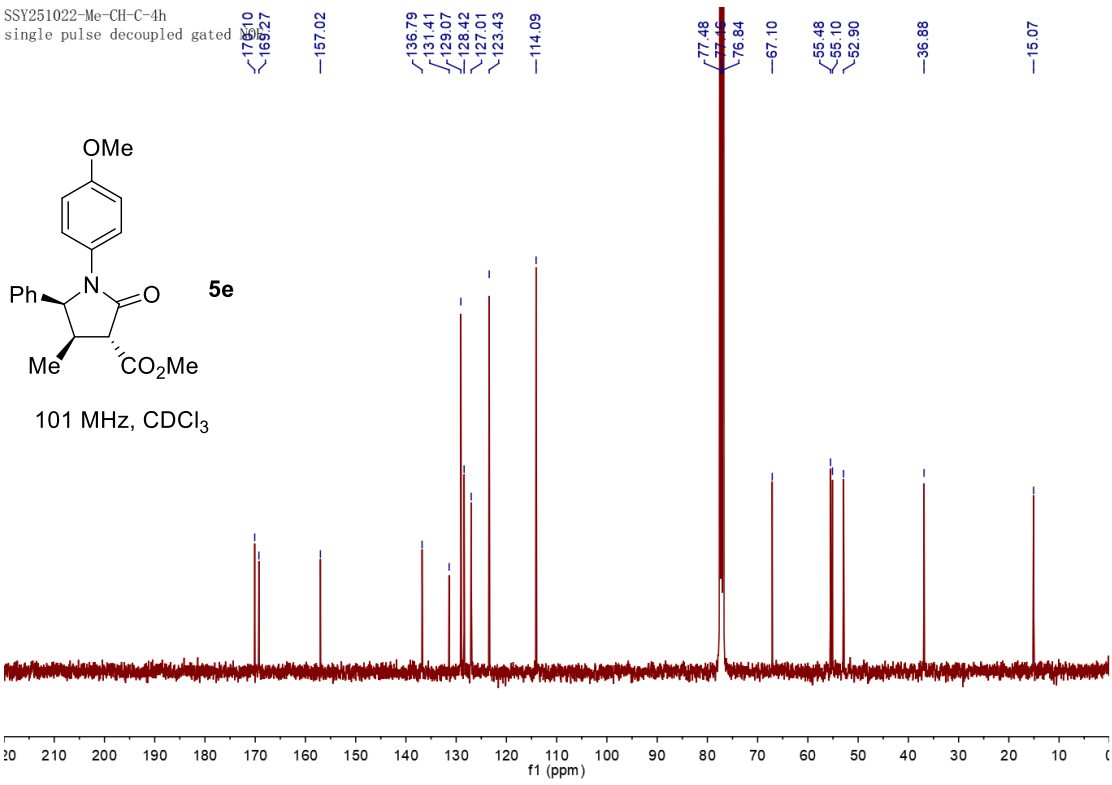
ssy-251127-nh-cl-oh



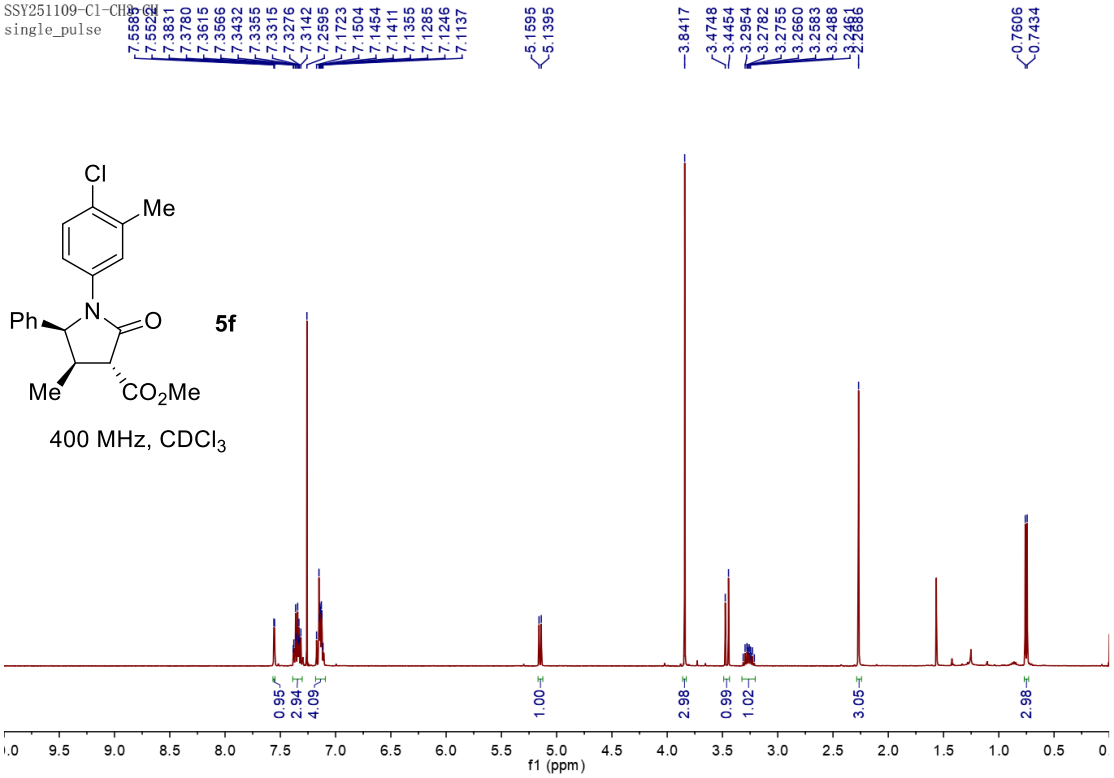
SSY251126-NH-CH-O-5h



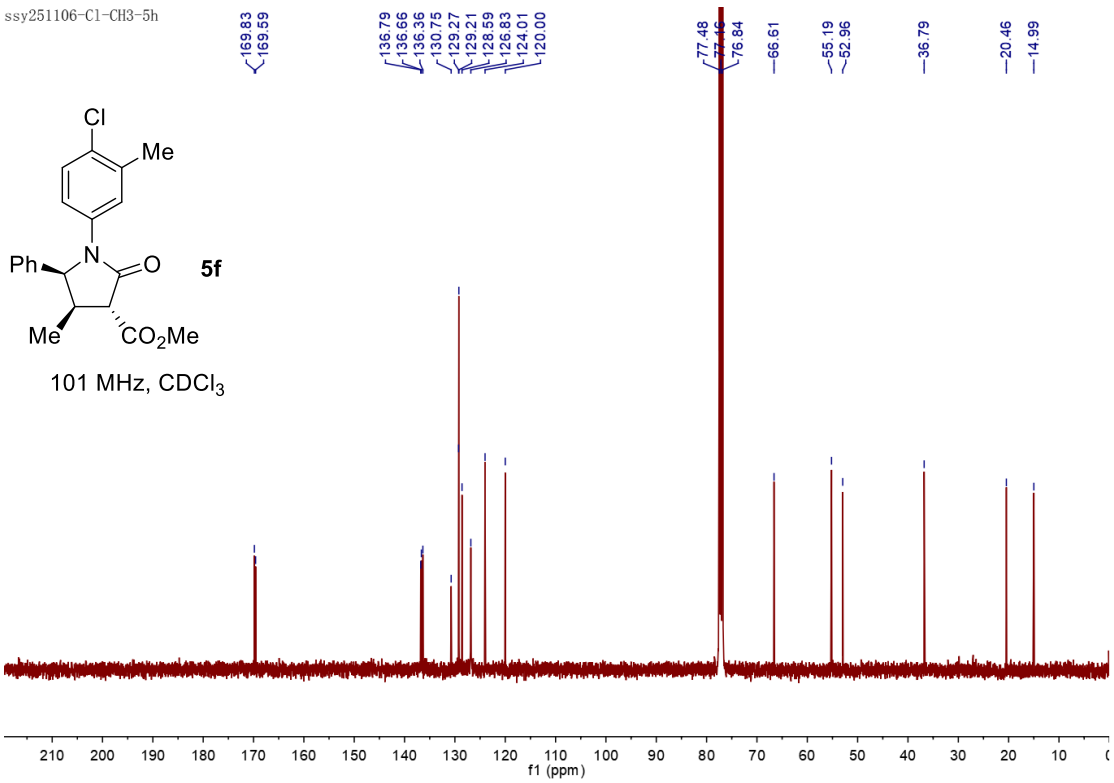

ssy251023-Me-CH
single_pulse
7.3834
7.3780
7.3661
7.3605
7.3522
7.3333
7.3181
7.3006
7.2603
7.1597
7.1563
7.1392
6.7843
6.7756
6.7702
6.7583
6.7528
6.7440
5.1330
5.1129
3.8384
3.7235
3.4802
3.4510
3.3315
3.3144
3.2964
3.2852
3.2774
3.2674
3.2483
3.2310
0.7521
0.7349
OMe
Ph
N
O
Me
CO2Me
5e
400 MHz, CDCl3
5.03
2.01
2.01
1.00
3.05
3.00
1.00
0.99
2.98
f1 (ppm)


SSY251022-Me-CH-C-4h
single pulse decoupled gated NOE
170.10
169.27
157.02
136.79
131.41
129.07
128.42
127.01
123.43
114.09
77.48
77.16
76.84
67.10
55.48
55.10
52.90
36.88
15.07
OMe
Ph
N
O
Me
CO2Me
5e
101 MHz, CDCl3
f1 (ppm)

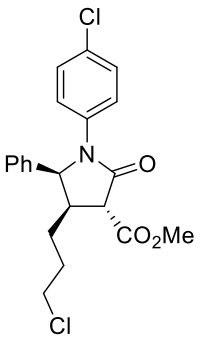
SSY251109-Cl-CH3-CH
single_pulse



ssy251106-Cl-CH3-5h



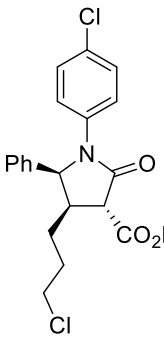
ssy-251127-o6-ch



5g

400 MHz, $CDCl_3$

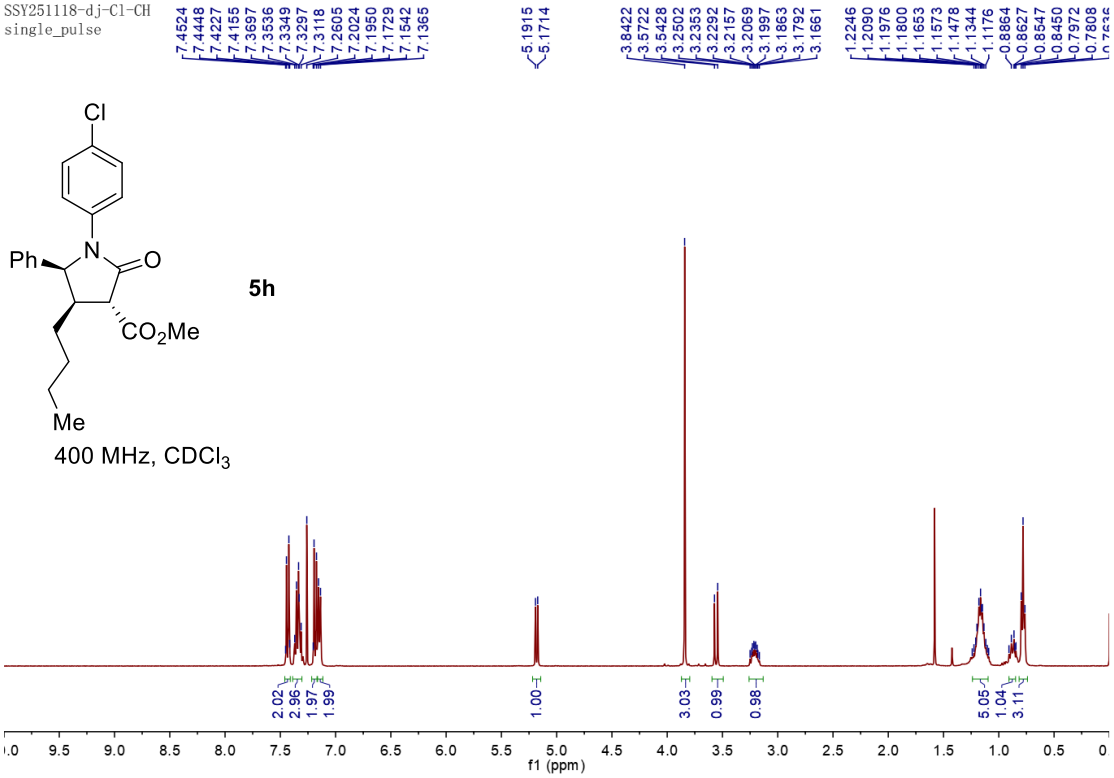
ssy251123-06-CH



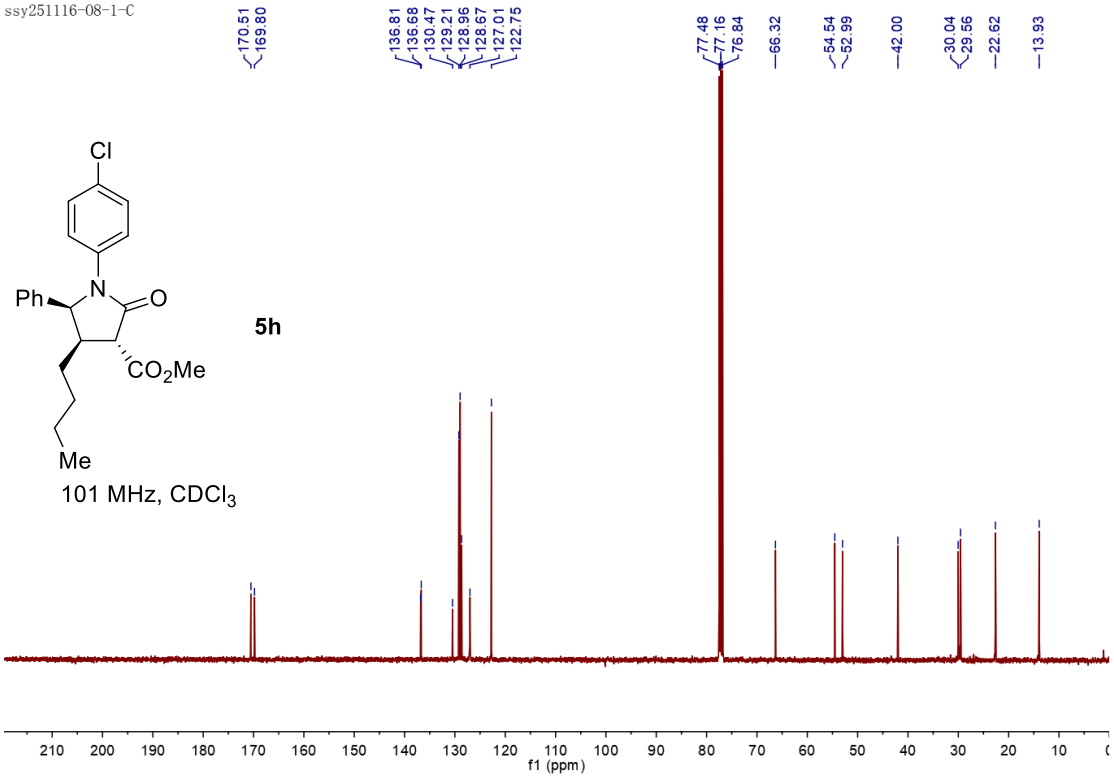
5g

101 MHz, $CDCl_3$

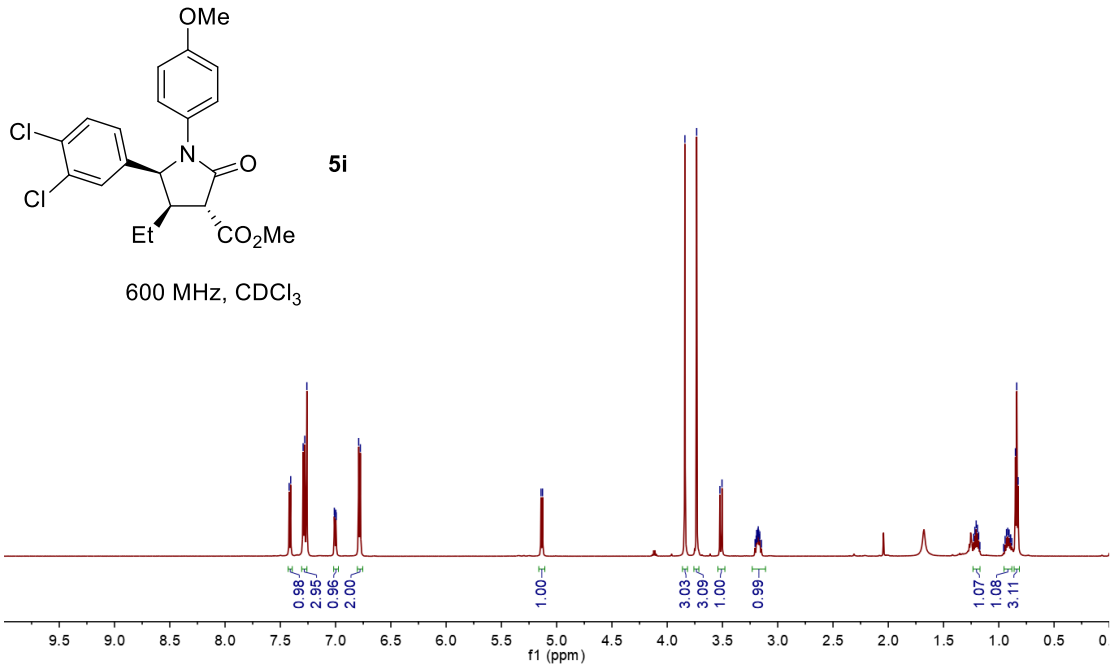
SSY251118-dj-Cl-CH
single_pulse



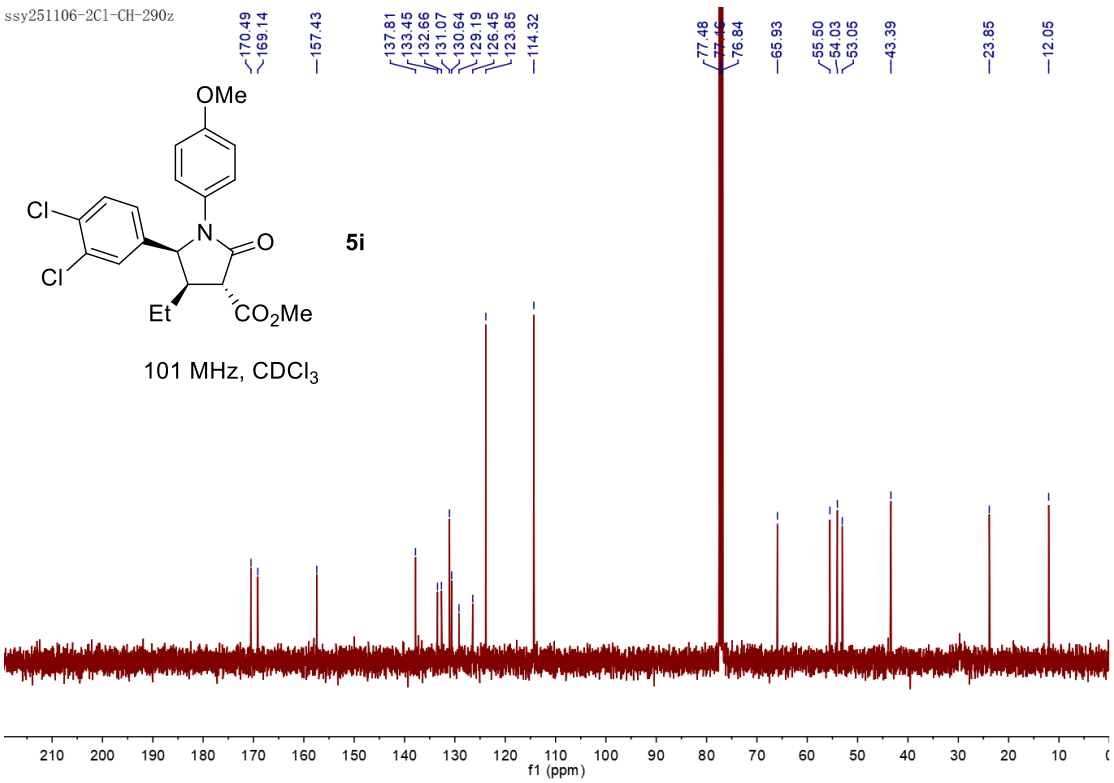
ssy251116-08-1-C

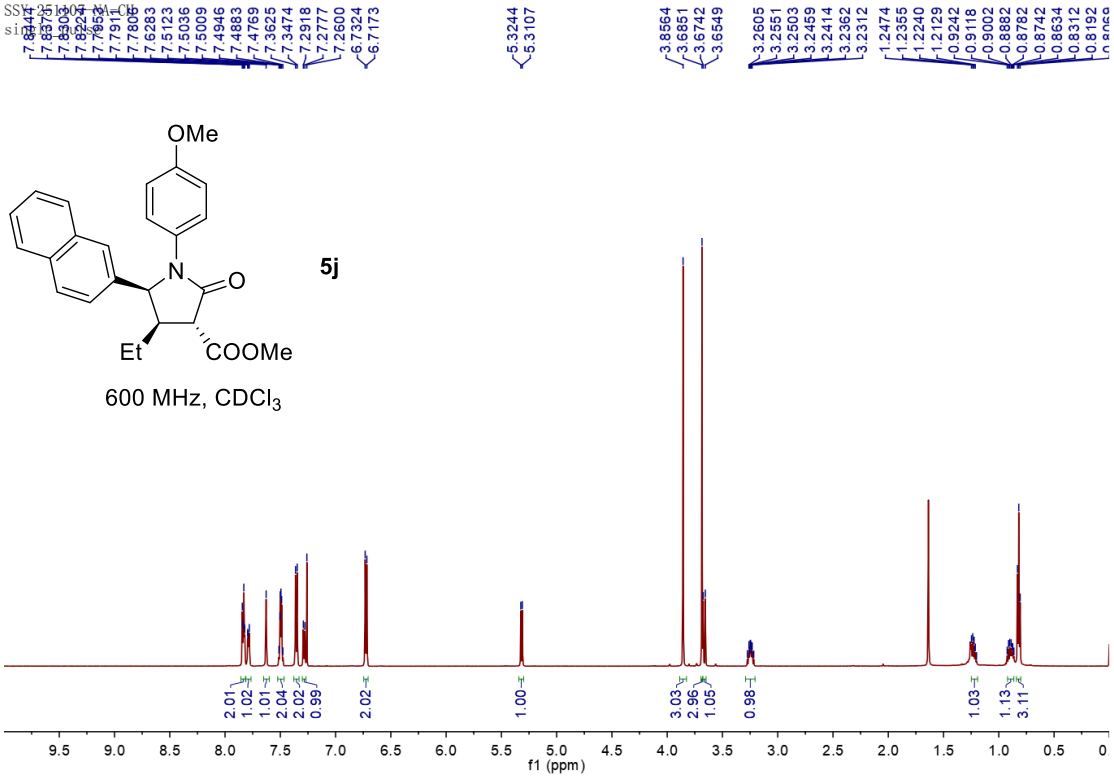


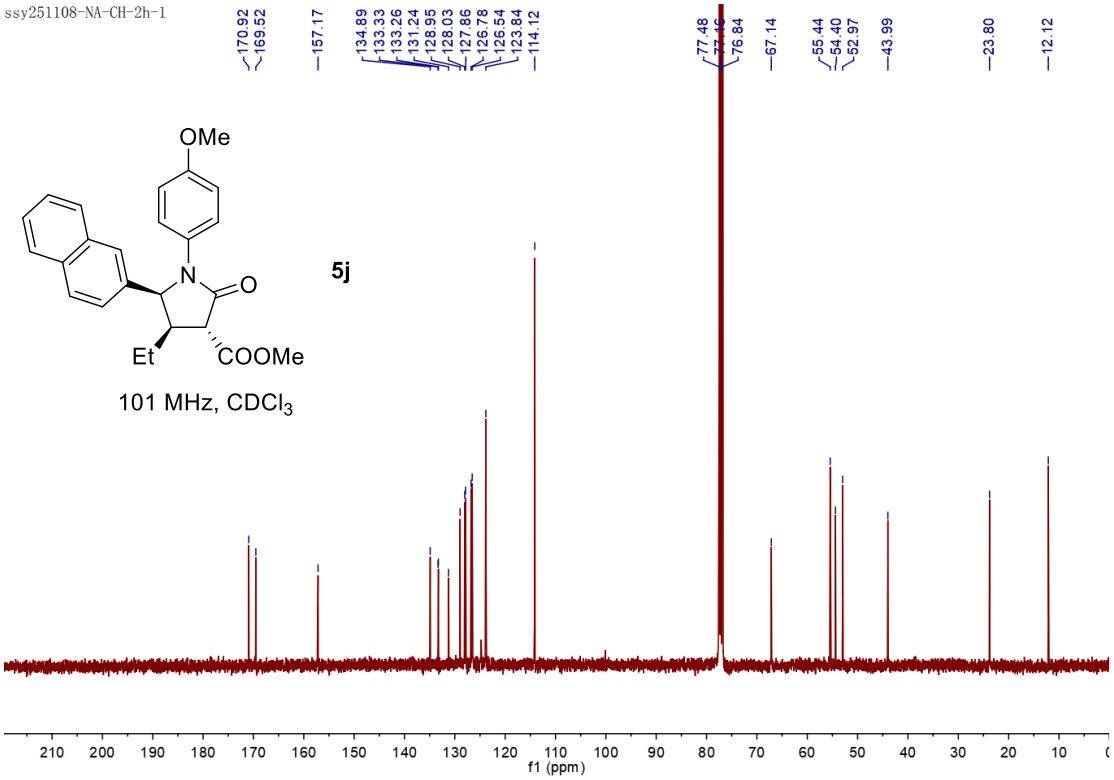
SSY251104-2Cl-CH
single_pulse



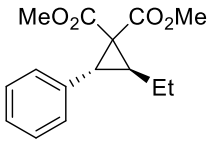
ssy251106-2Cl-CH-290z




OMe
N
O
Et
COOMe
5j
600 MHz, CDCl3
f1 (ppm)


ssy251108-NA-CH-2h-1
OMe
N
O
Et
COOMe
5j
101 MHz, CDCl3
f1 (ppm)

X. HPLC Spectra for ee Determination.



2a

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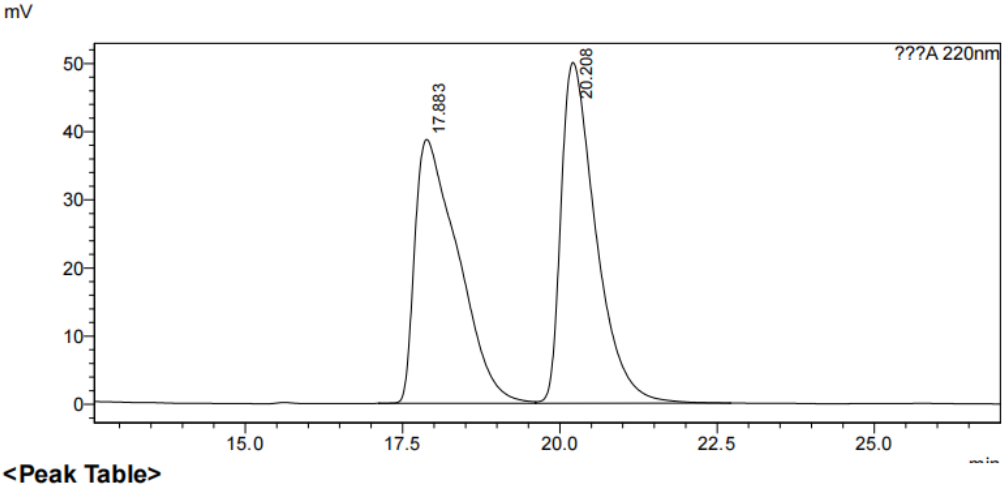
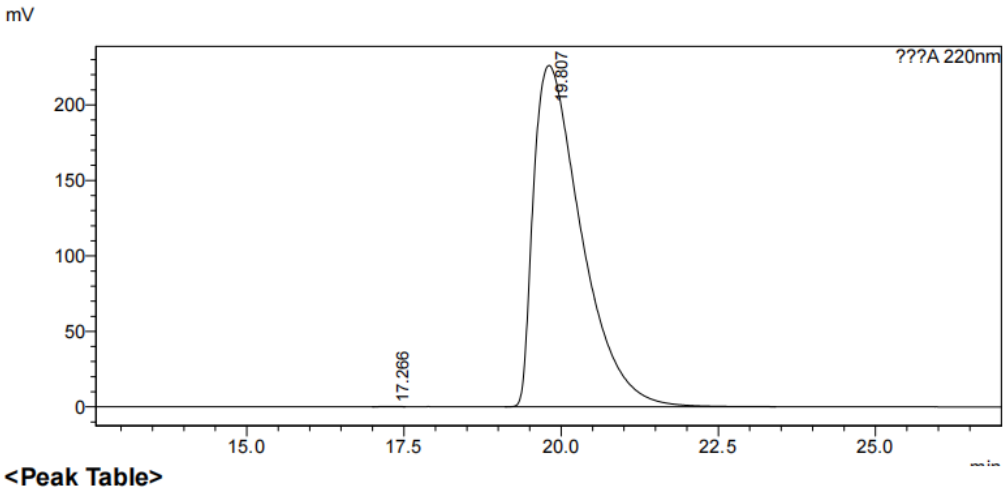


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.883	1854898	38707	49.038			
2	20.208	1927674	49998	50.962		V	
Total		3782572	88705				

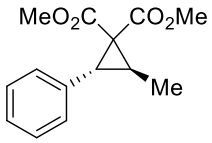
<Chromatogram>



<Peak Table>

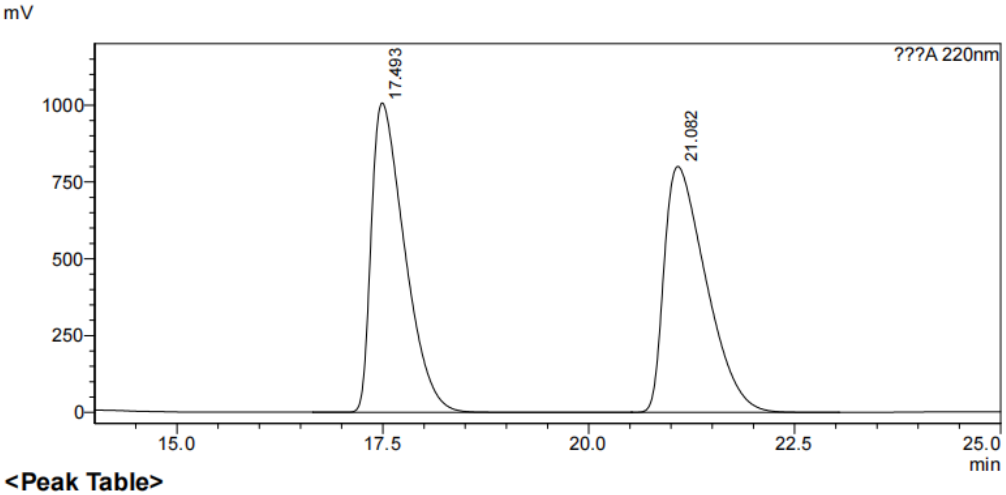
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.266	917	57	0.008		M	
2	19.807	11993814	226080	99.992			
Total		11994731	226137				



2b

<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.493	28376984	1007545	50.024			
2	21.082	28349659	800387	49.976		V	
Total		56726643	1807932				

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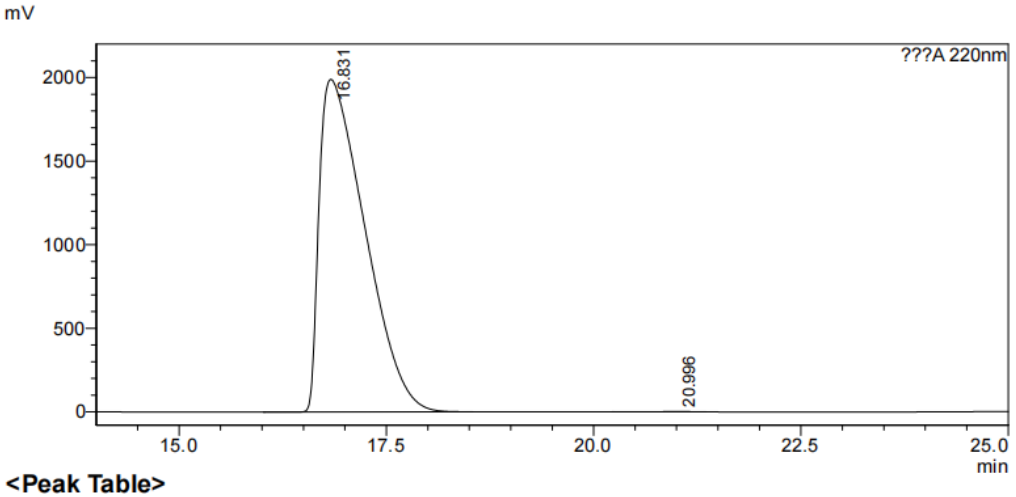
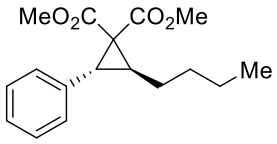


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.831	76294045	1989892	99.943		M	
2	20.996	43173	1920	0.057		M	
Total		76337218	1991812				



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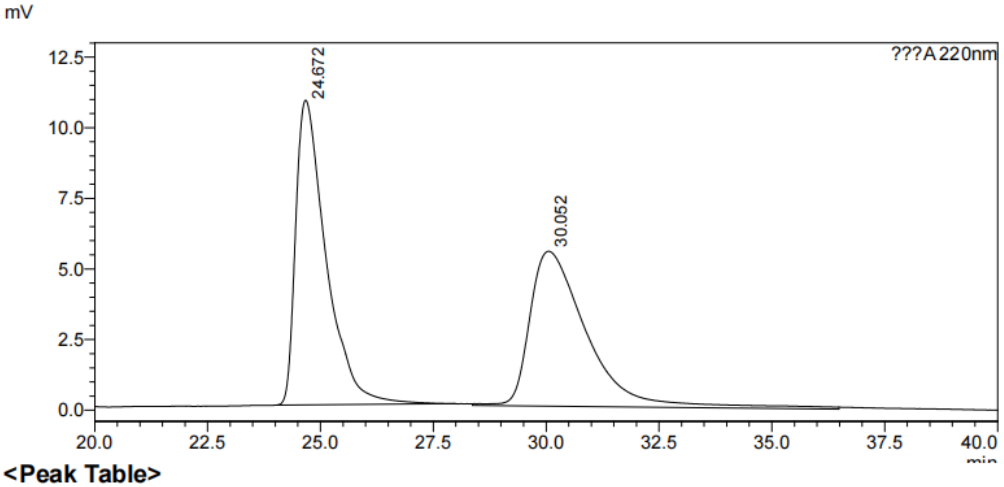
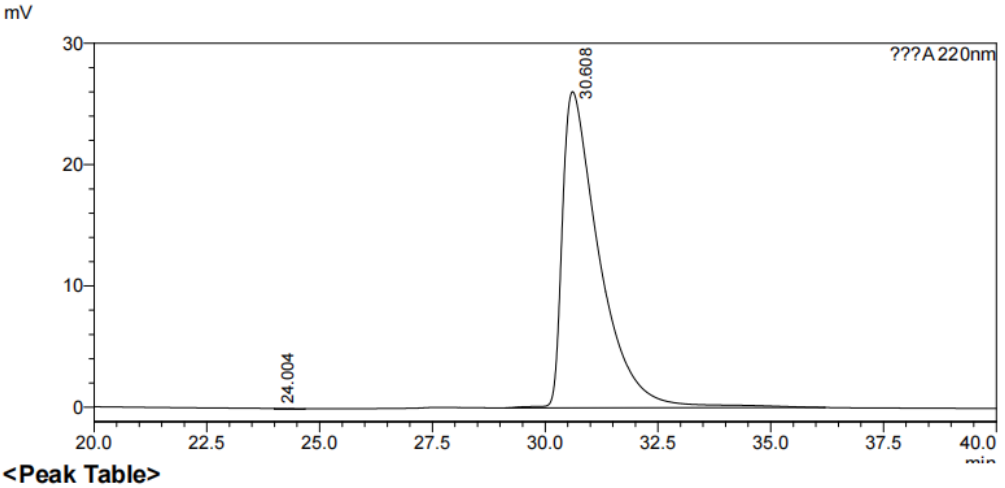


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.672	507565	10788	51.111		M	
2	30.052	485505	5482	48.889		M	
Total		993069	16270				

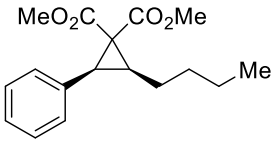
<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	24.004	2125	61	0.142		M	
2	30.608	1490945	26063	99.858		M	
Total		1493071	26124				



2c'

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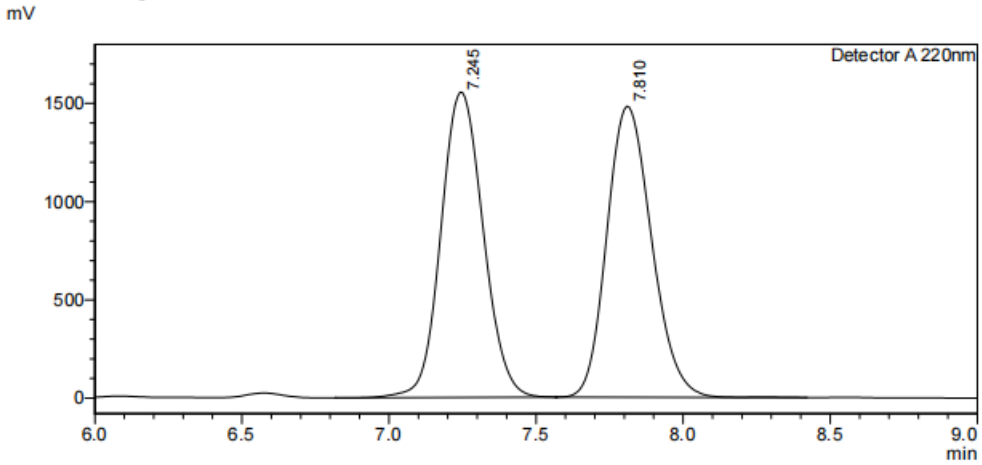
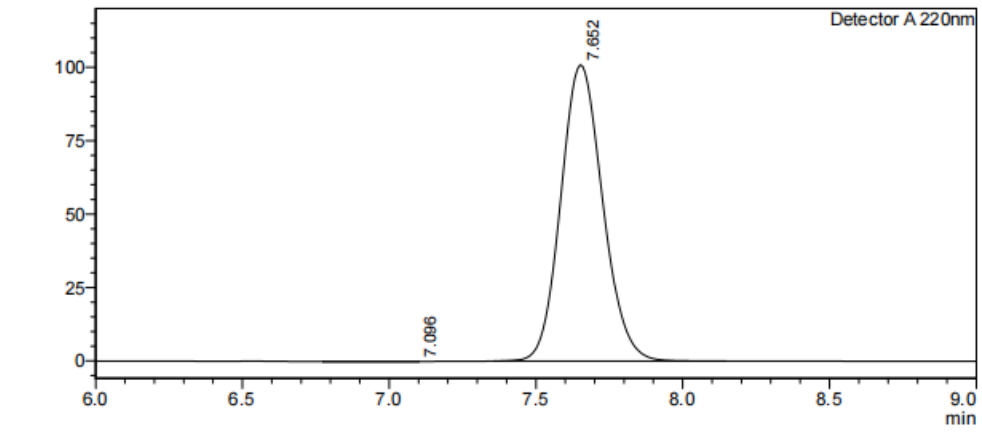


<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.245	15543142	1553691	49.805			
2	7.810	15664749	1480711	50.195		M	
Total		31207891	3034402				

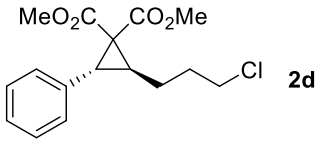
<Chromatogram>



<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.096	1981	115	0.197		M	
2	7.652	1002797	100923	99.803		M	
Total		1004778	101039				



2d

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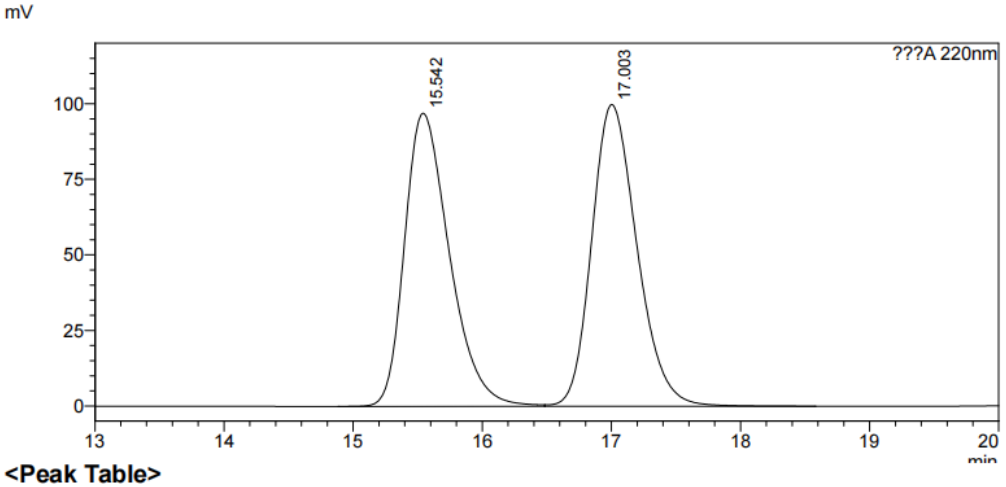
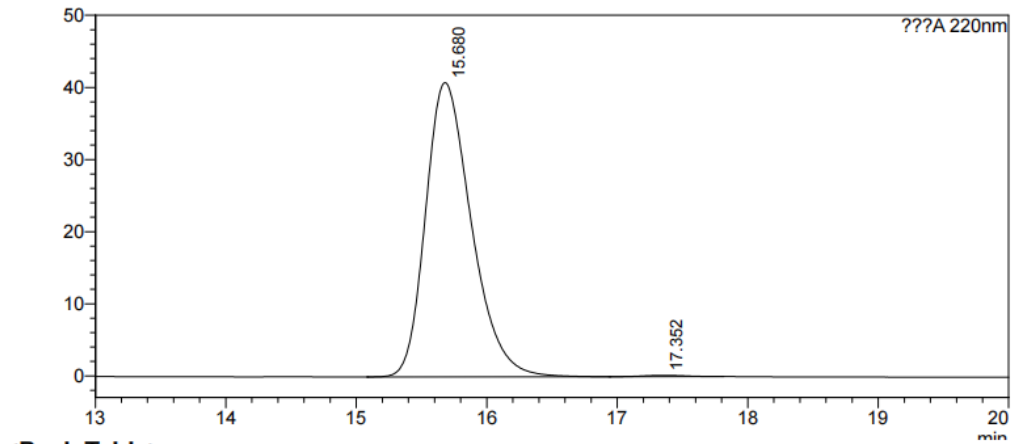


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.542	2345637	96987	49.084			
2	17.003	2433209	99828	50.916		V	
Total		4778846	196815				

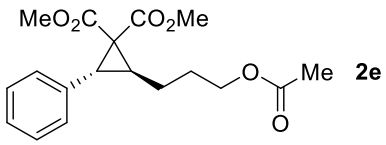
<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.680	997425	40800	99.592			
2	17.352	4082	182	0.408			
Total		1001507	40983				



2e

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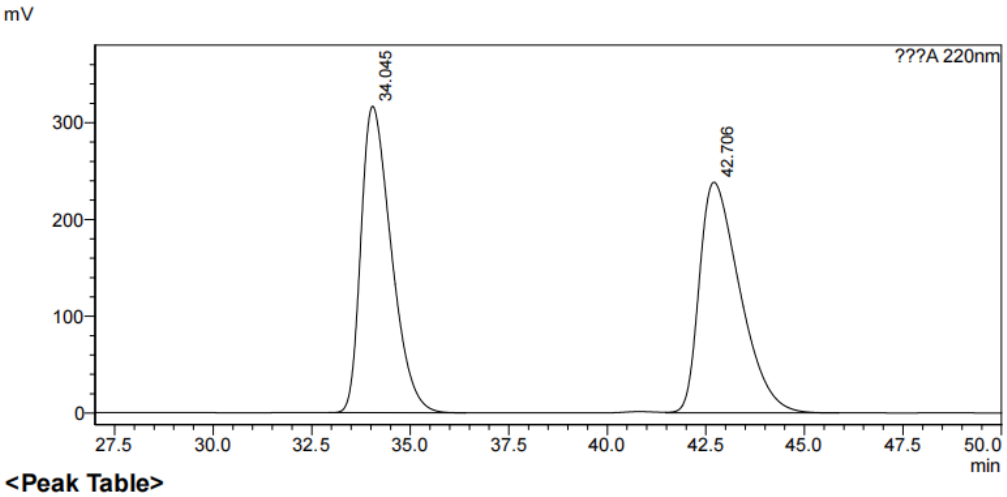
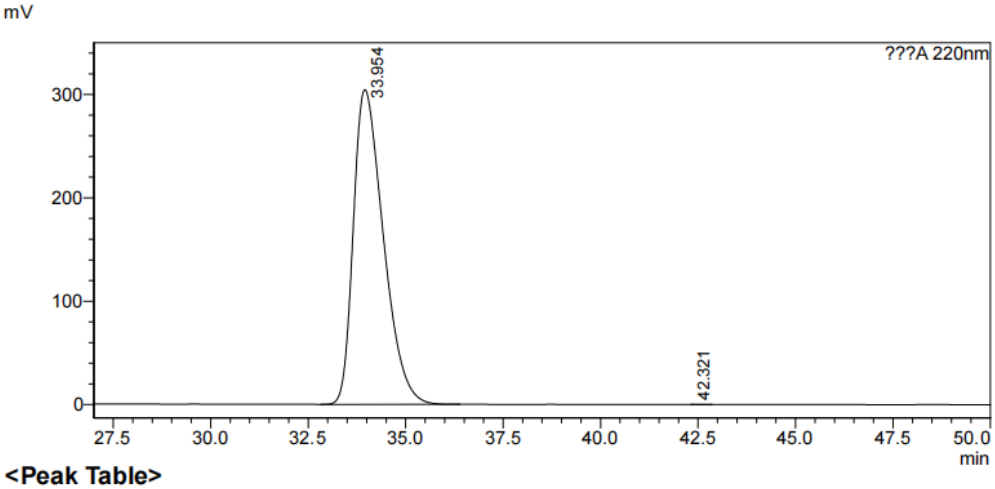


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.045	16940677	316574	49.842			
2	42.706	17048102	238295	50.158			
Total		33988779	554869				

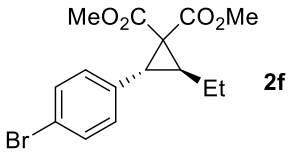
<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	33.954	16295189	304462	99.977			
2	42.321	3747	127	0.023		M	
Total		16298936	304590				



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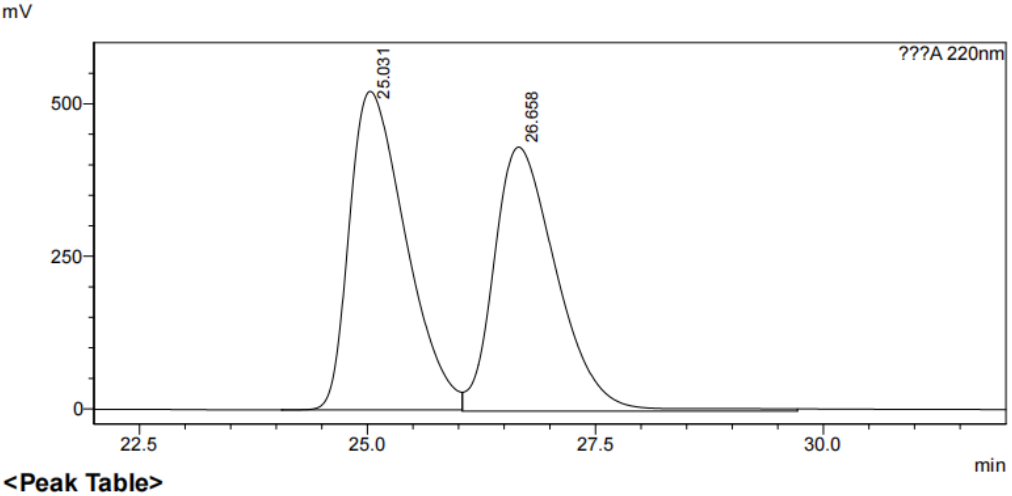
<Chromatogram>

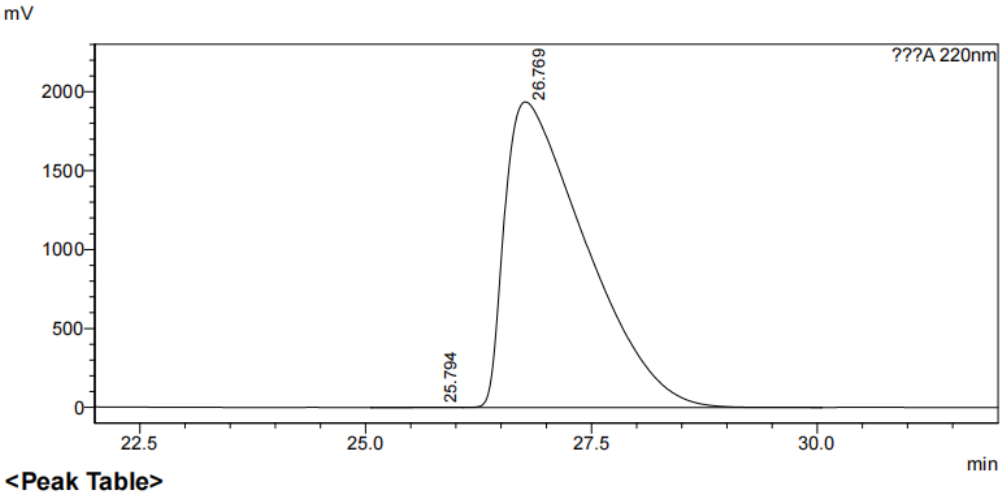


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	25.031	22396323	522082	51.832			
2	26.658	20812732	432570	48.168		M	
Total		43209055	954653				

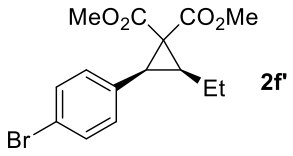
<Chromatogram>



<Peak Table>

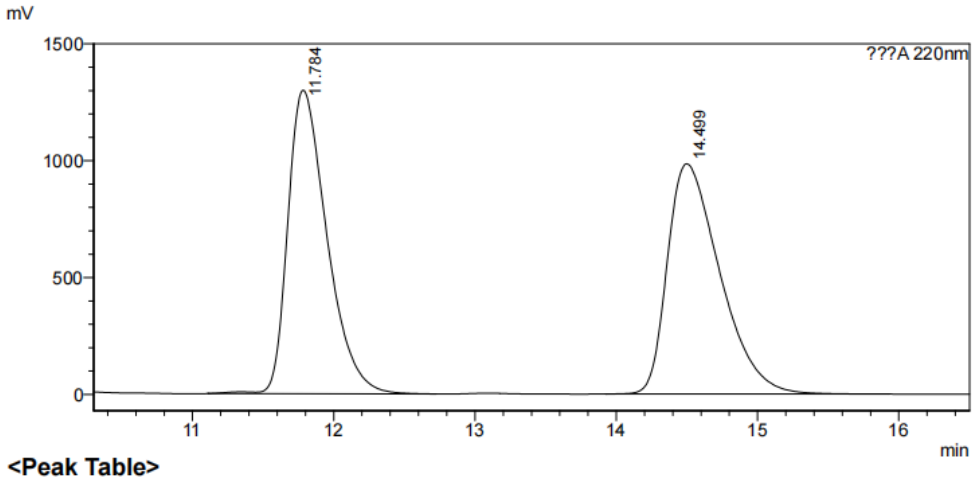
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	25.794	60490	1689	0.050			
2	26.769	120707783	1936524	99.950		V	
Total		120768273	1938212				



2f'

<Chromatogram>

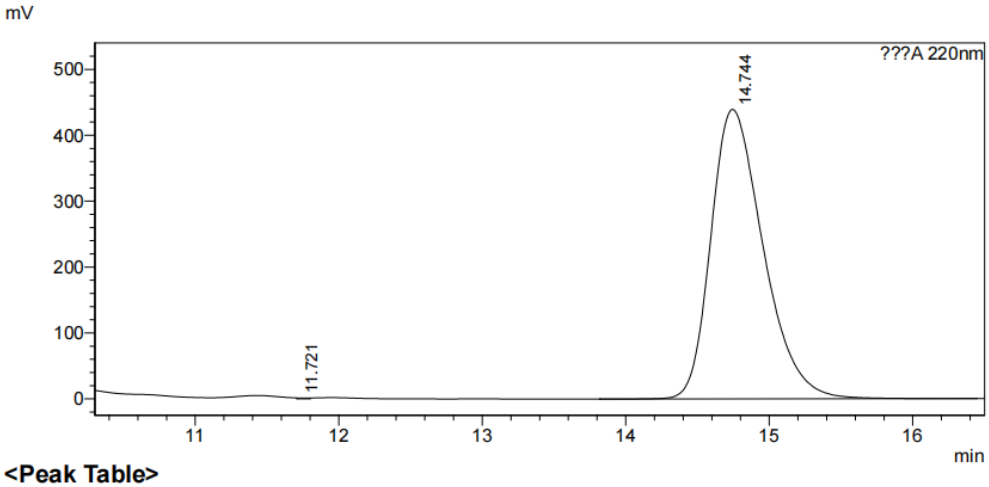


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.784	25050555	1298806	49.589		M	
2	14.499	25466282	984959	50.411		M	
Total		50516838	2283765				

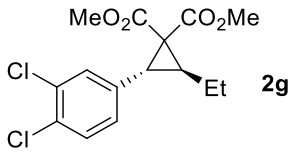
<Chromatogram>



<Peak Table>

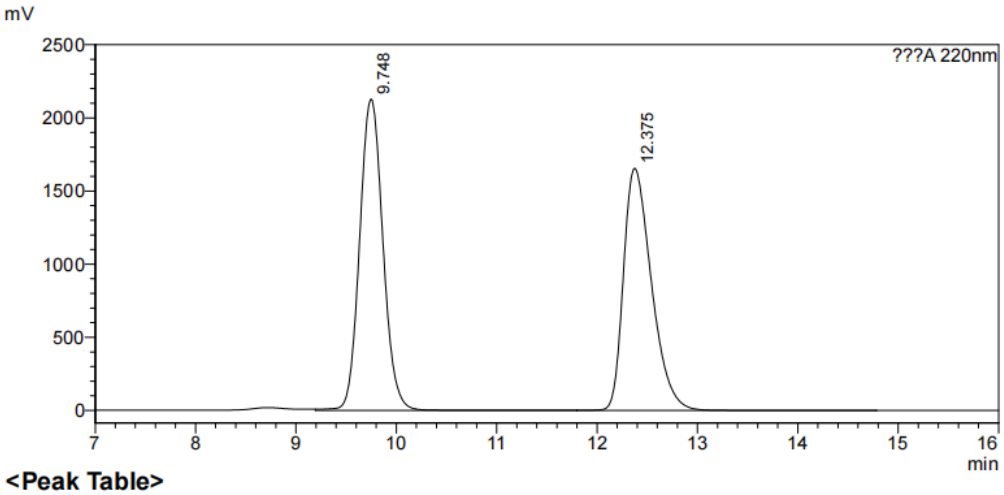
???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.721	7096	1384	0.064		M	
2	14.744	11156611	439399	99.936			
Total		11163706	440783				



2g

<Chromatogram>

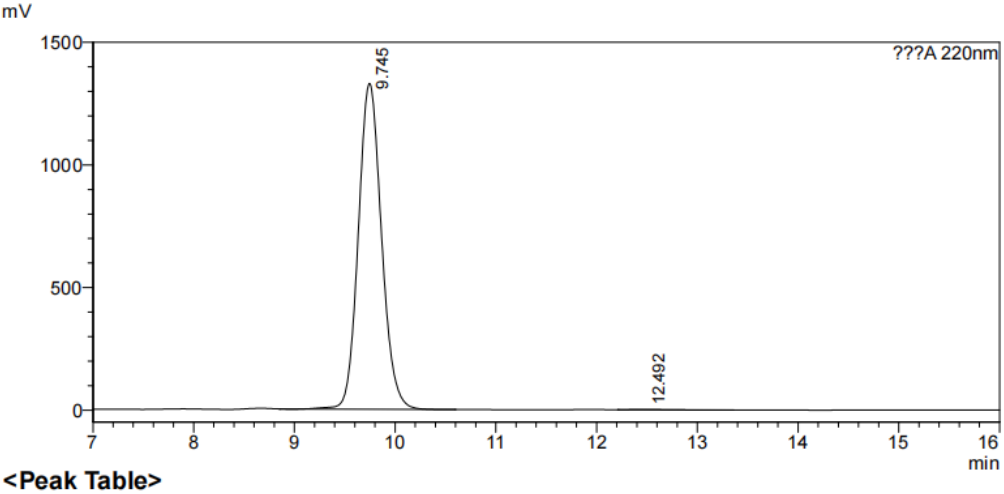


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.748	34470480	2128285	51.781			
2	12.375	32099691	1655375	48.219		SV	
Total		66570170	3783659				

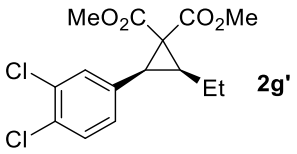
<Chromatogram>



<Peak Table>

???A 220nm

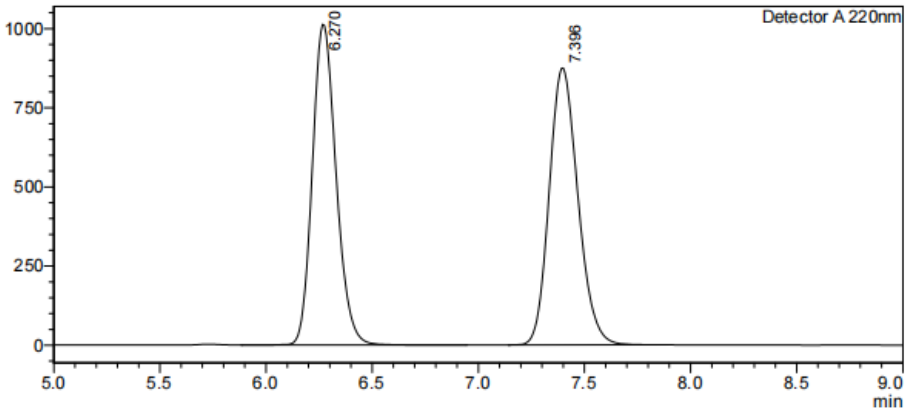
Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.745	21302914	1329104	99.784		M	
2	12.492	46159	1725	0.216			
Total		21349073	1330829				



2g'

<Chromatogram>

mV



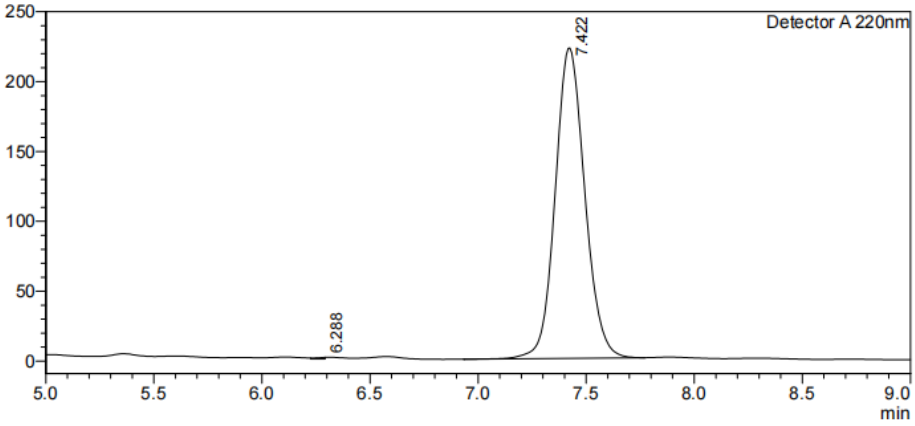
<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.270	7896214	1013205	48.982		M	
2	7.396	8224306	874489	51.018		M	
Total		16120520	1887694				

<Chromatogram>

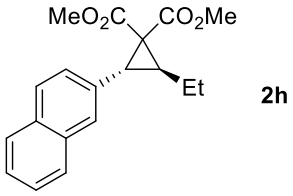
mV



<Peak Table>

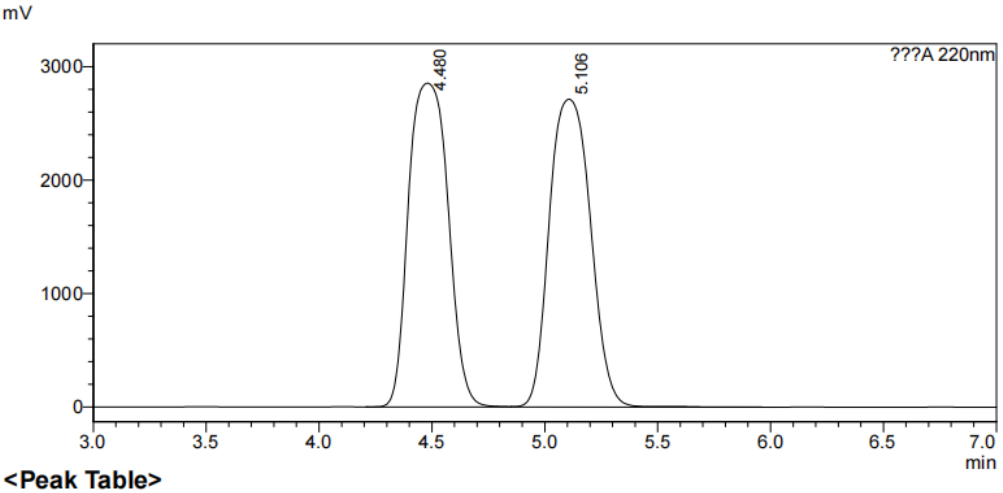
Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.288	3463	1039	0.163		M	
2	7.422	2115896	222219	99.837			
Total		2119360	223258				



2h

<Chromatogram>

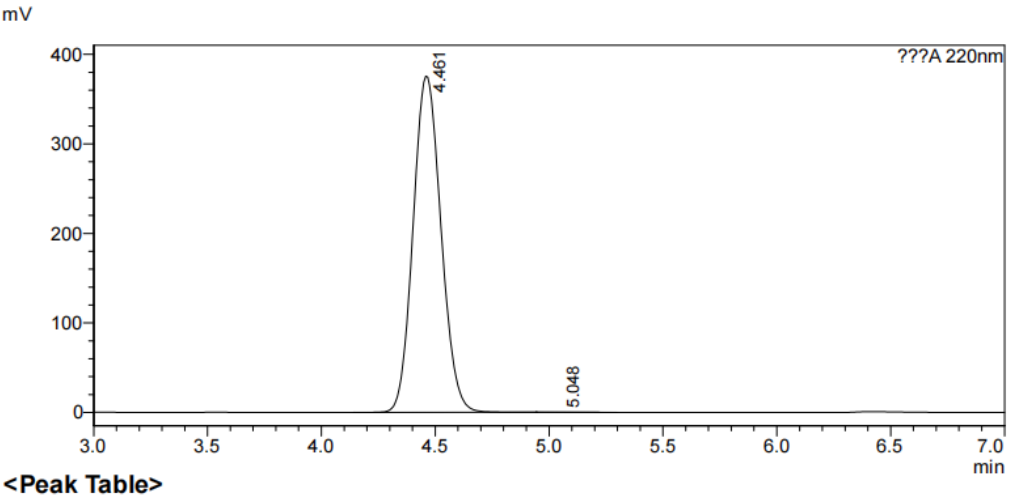


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.480	34909538	2853711	50.278			
2	5.106	34523174	2712825	49.722		V	
Total		69432712	5566535				

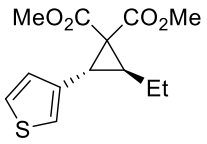
<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	4.461	3203304	375539	99.965		M	
2	5.048	1114	99	0.035		M	
Total		3204418	375638				



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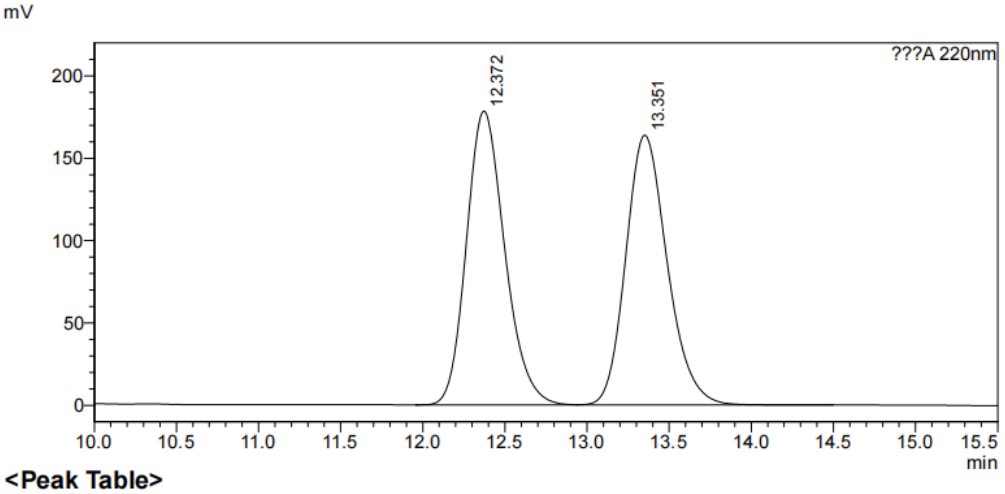
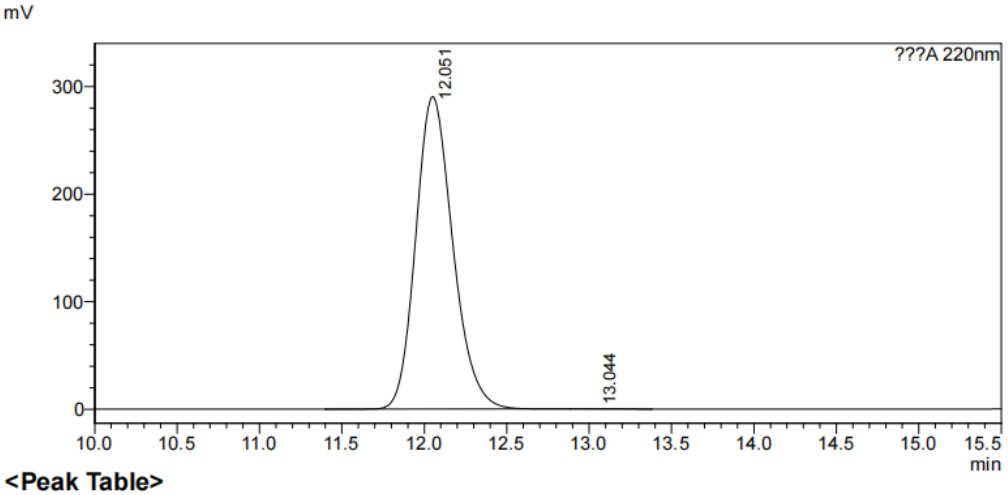


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.372	2899757	178405	50.178			
2	13.351	2879140	163851	49.822		V	
Total		5778897	342257				

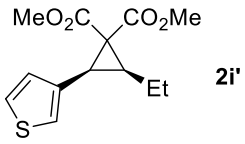
<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.051	4551207	290534	99.976			
2	13.044	1074	55	0.024		M	
Total		4552281	290590				



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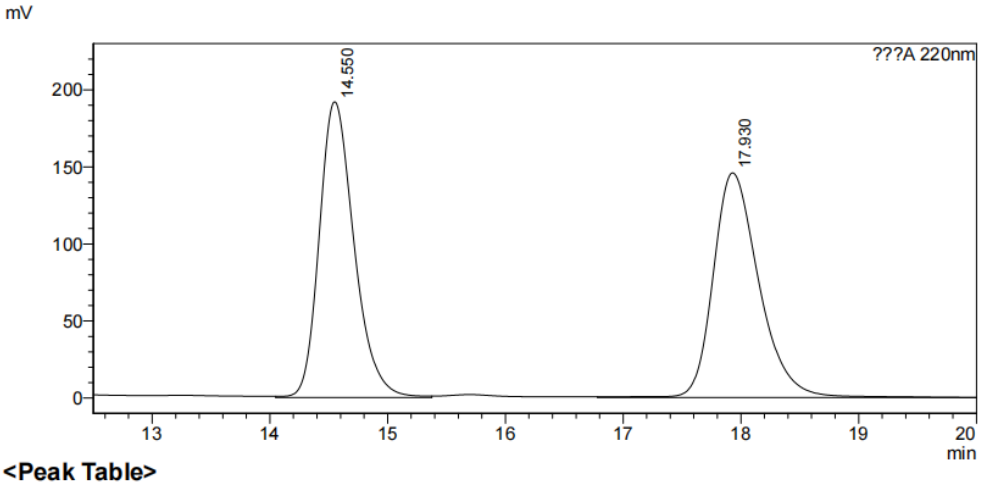

<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.550	3947060	191964	50.022			
2	17.930	3943557	145729	49.978			
Total		7890617	337694				

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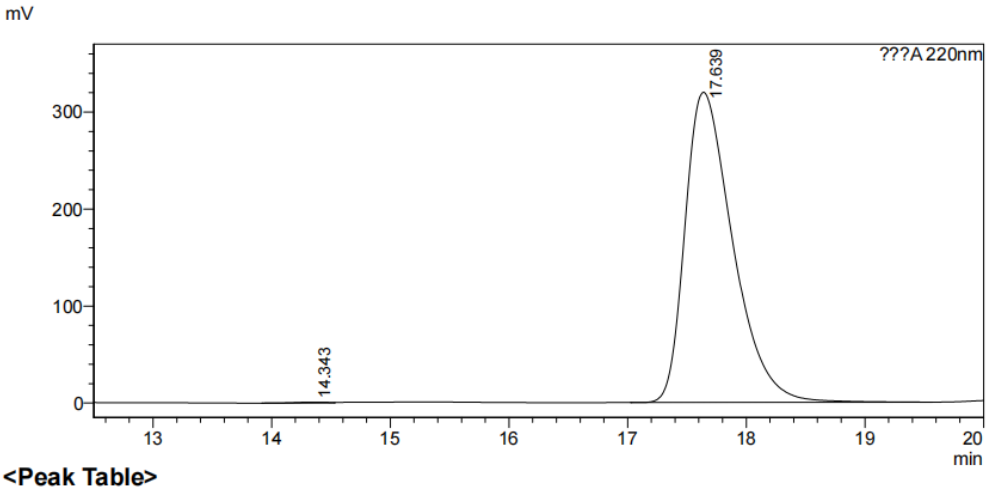
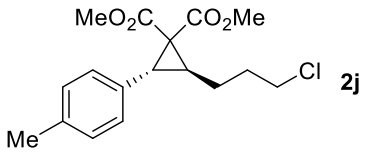


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.343	17473	876	0.195			
2	17.639	8951844	319861	99.805		M	
Total		8969317	320737				



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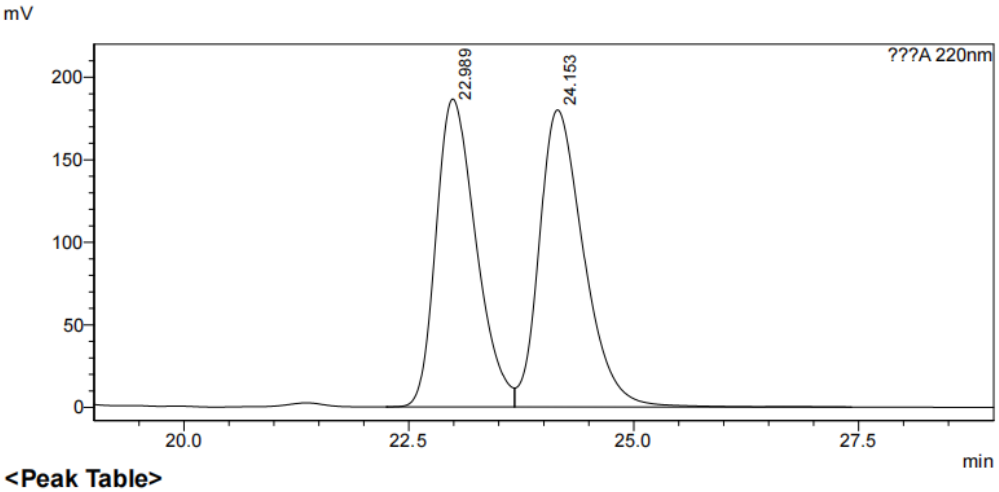

<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.989	5764901	186508	48.252			
2	24.153	6182622	179942	51.748		V	
Total		11947523	366450				

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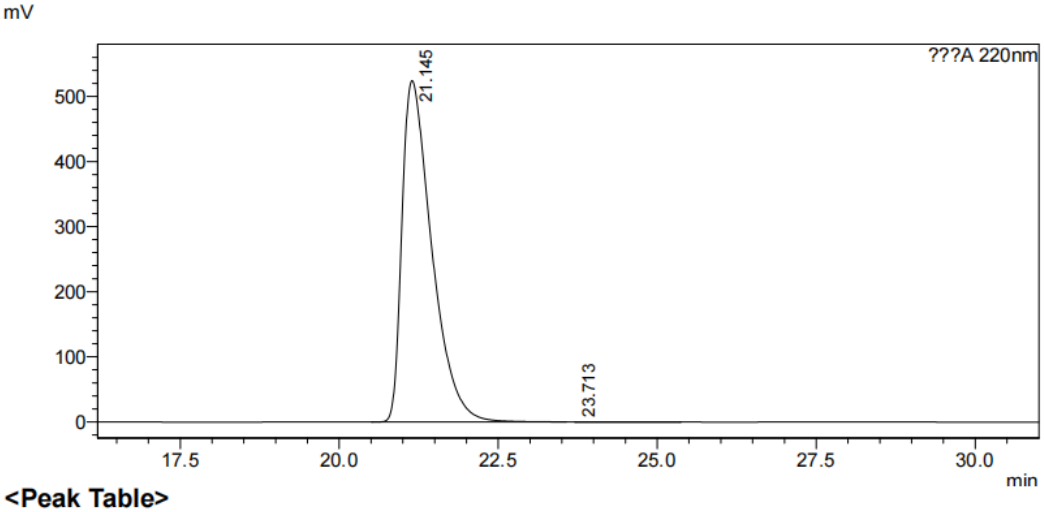
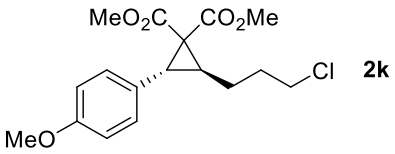


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.145	17131125	524318	99.864		M	
2	23.713	23352	291	0.136		M	
Total		17154476	524609				



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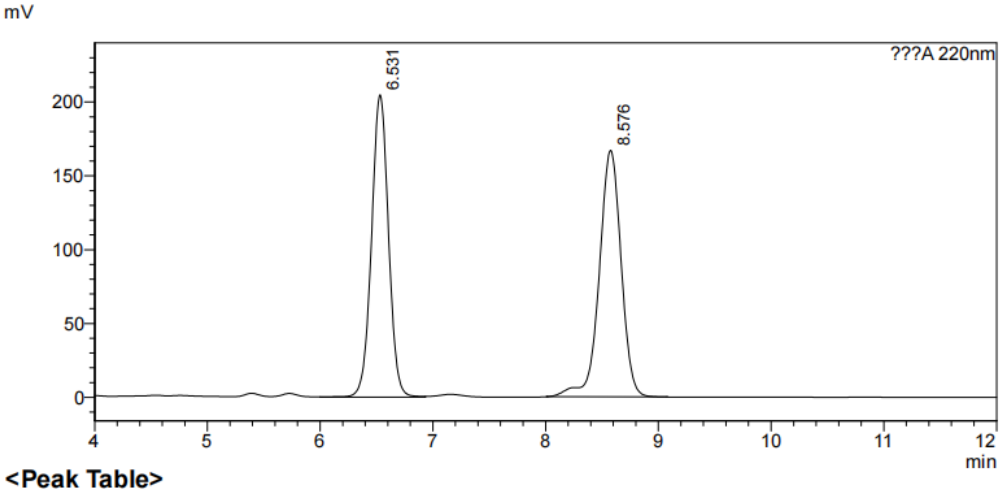
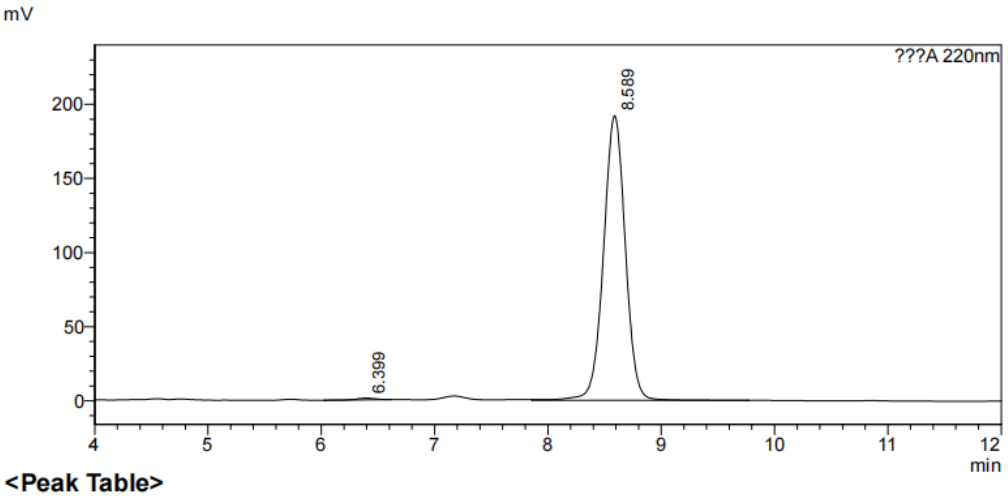


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.531	2143047	204858	48.683			
2	8.576	2258987	167045	51.317		M	
Total		4402034	371903				

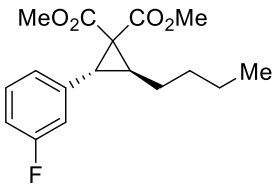
<Chromatogram>



<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.399	13326	1213	0.514		M	
2	8.589	2577030	192164	99.486			
Total		2590356	193376				



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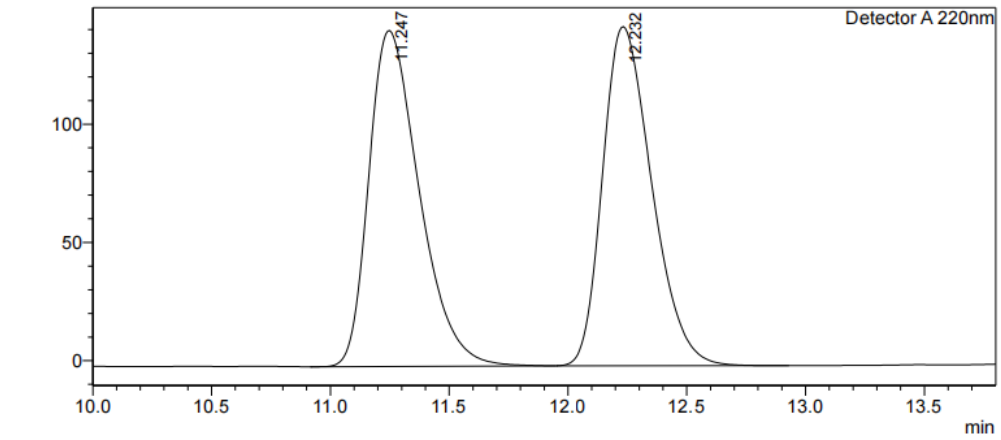
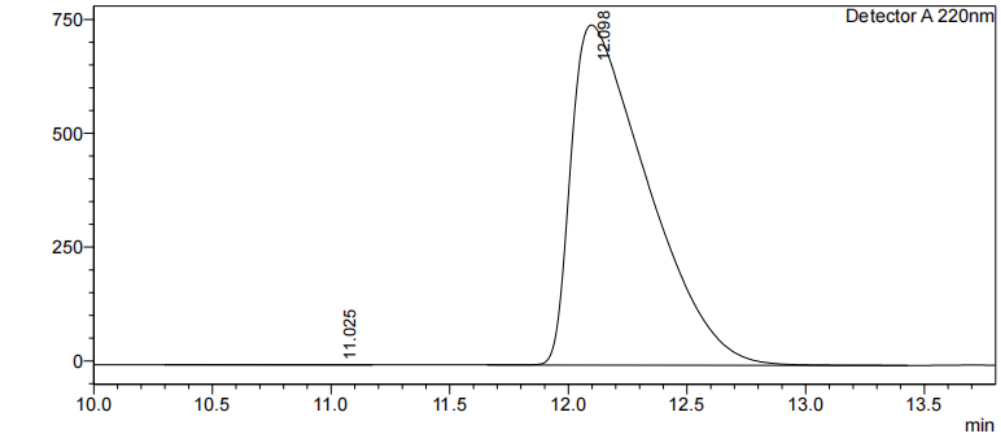


<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.247	2096388	141957	50.381		M	
2	12.232	2064669	143366	49.619		M	
Total		4161058	285322				

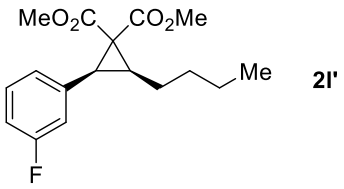
<Chromatogram>



<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.025	16836	566	0.100			
2	12.098	16789126	747003	99.900			
Total		16805962	747570				



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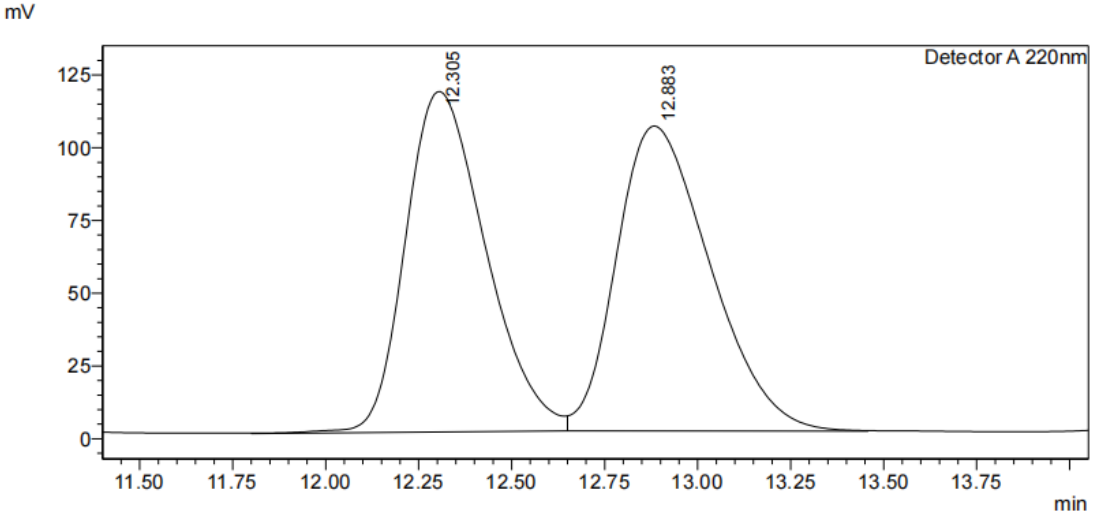
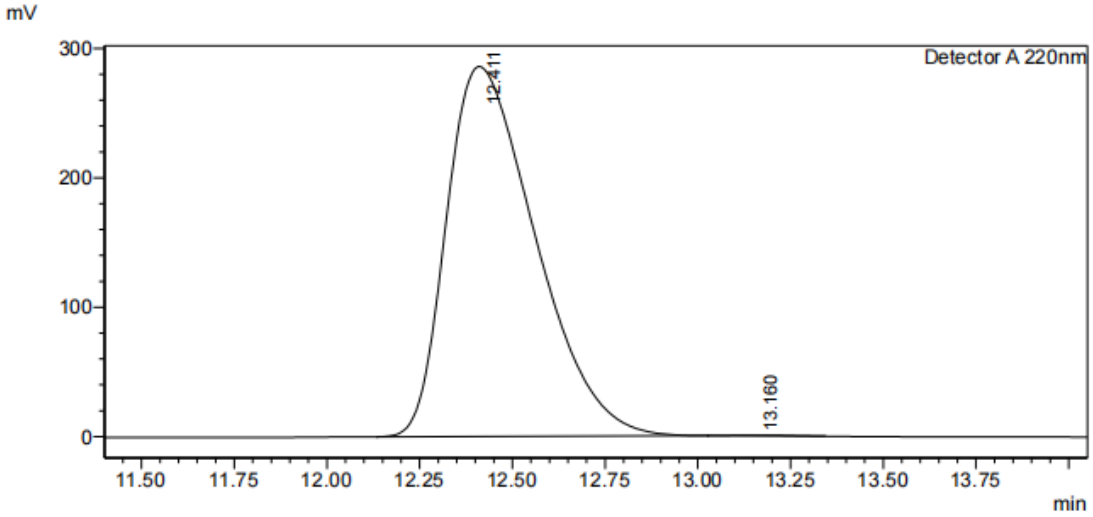


<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.305	1755211	117003	48.941		M	
2	12.883	1831151	104765	51.059		M	
Total		3586362	221768				

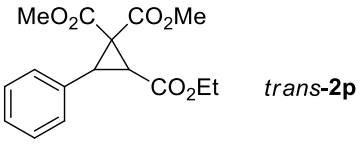
<Chromatogram>



<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	12.411	4764754	285929	99.871		M	
2	13.160	6166	585	0.129		M	
Total		4770920	286513				



trans-**2p**

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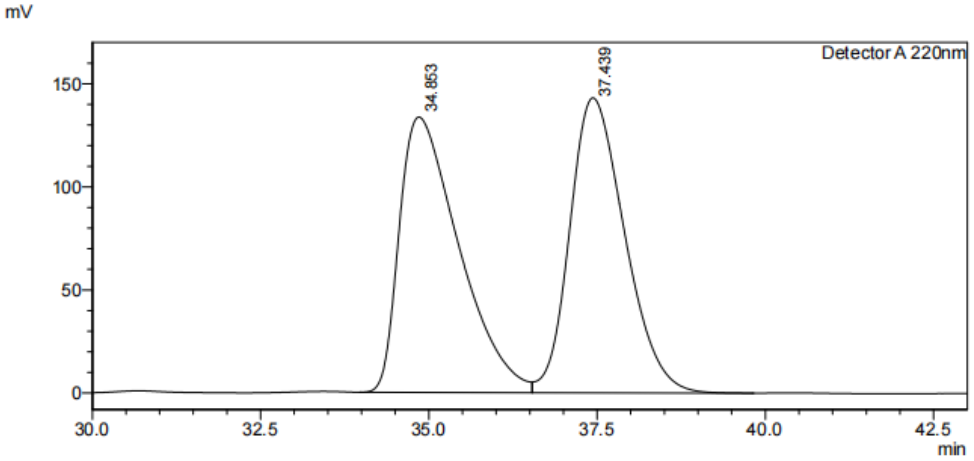

<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.853	8234867	133535	50.317			
2	37.439	8131114	143017	49.683		V	
Total		16365981	276552				

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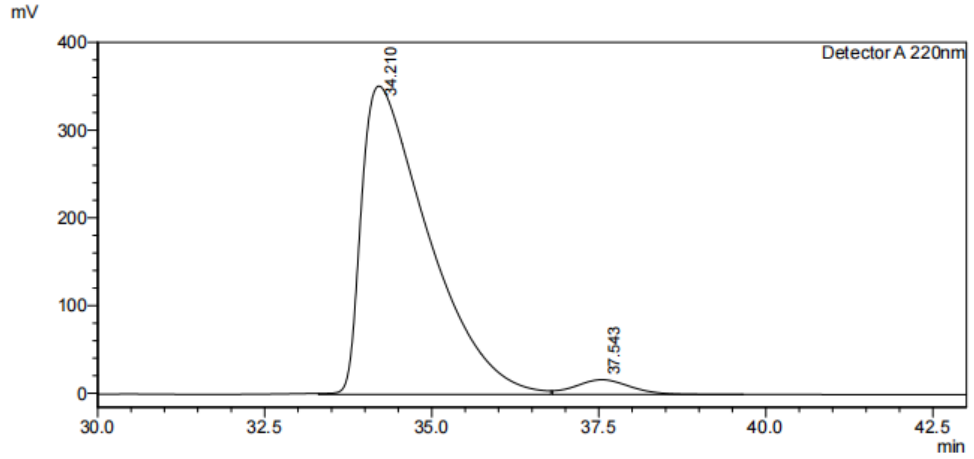
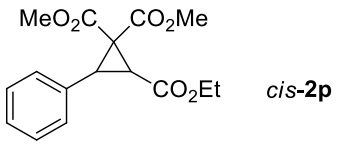


<Peak Table>

Detector A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	34.210	24578761	351741	96.180		M	
2	37.543	976290	16899	3.820		M	
Total		25555050	368640				



cis-**2p**

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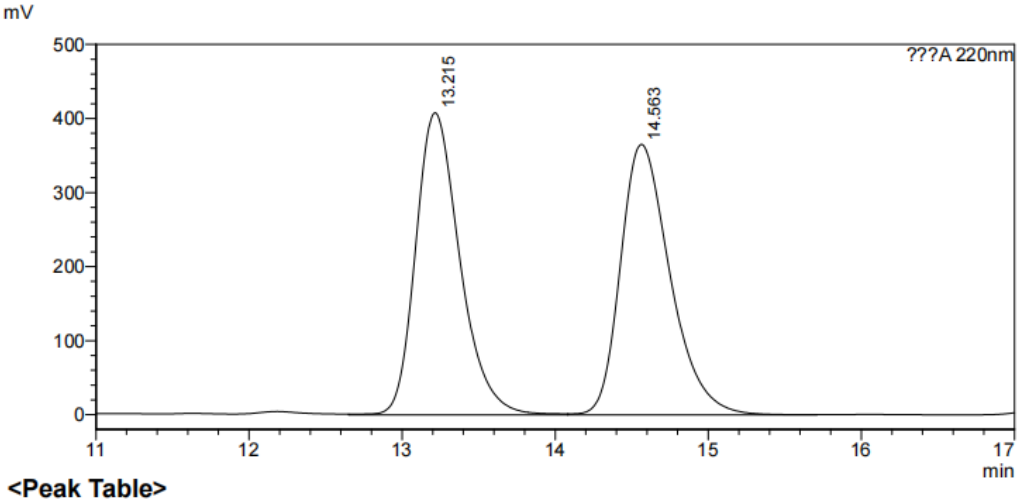

<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.215	8206054	408134	49.881			
2	14.563	8245335	365295	50.119		V	
Total		16451389	773429				

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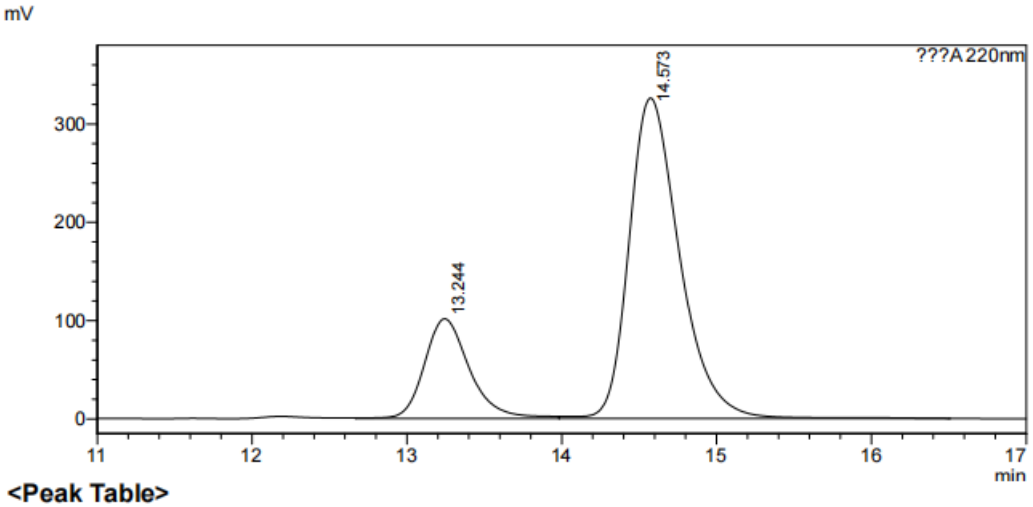
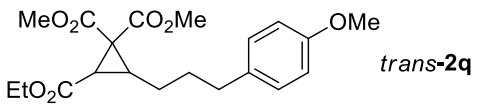


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.244	2069237	101417	21.791		M	
2	14.573	7426548	326036	78.209		M	
Total		9495785	427454				



trans-**2q**

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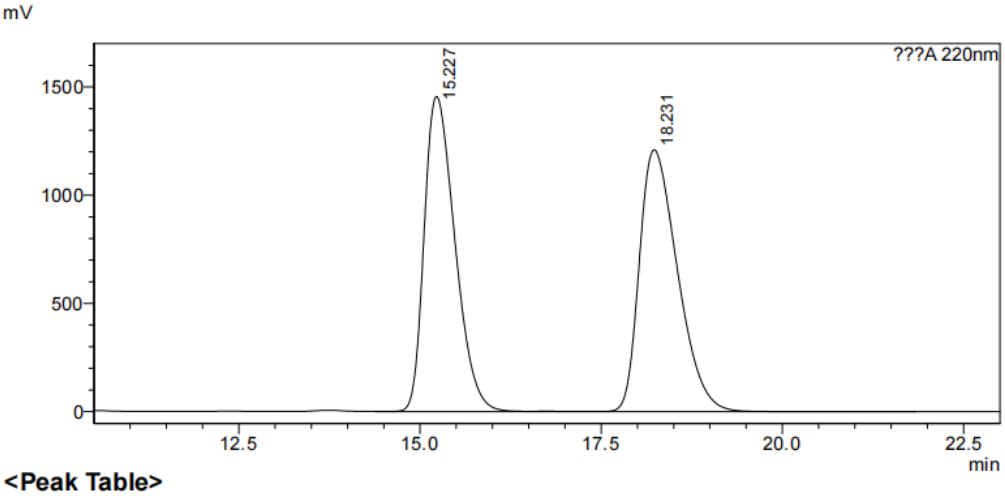

<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.227	43092066	1456569	49.283			
2	18.231	44346357	1209664	50.717		V	
Total		87438423	2666233				

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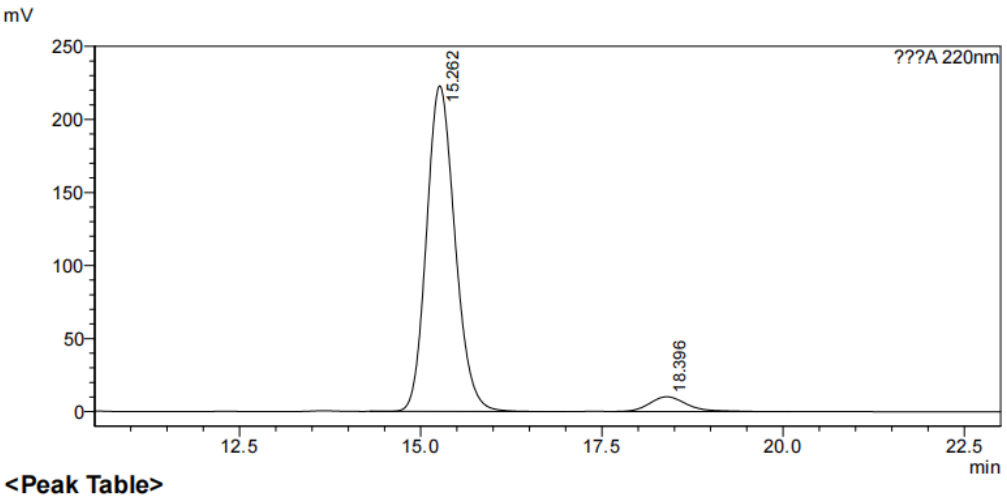
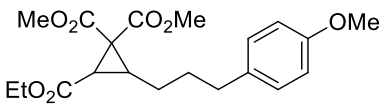


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.262	6085314	222842	94.315			
2	18.396	366775	10168	5.685			
Total		6452089	233010				



cis-**2q**

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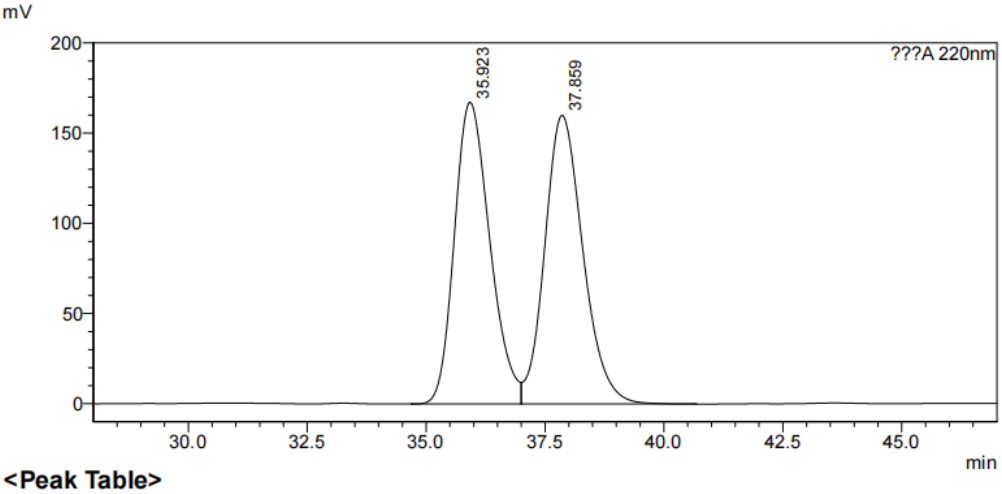

<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.923	8684981	167225	49.245			
2	37.859	8951136	160019	50.755		V	
Total		17636117	327244				

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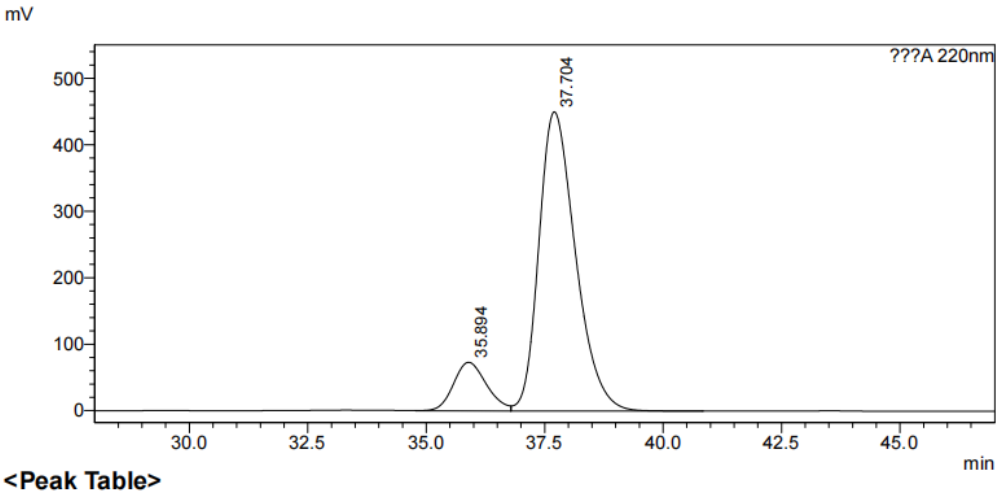
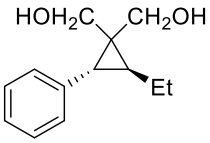


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	35.894	3554002	73072	12.795			
2	37.704	24221447	450039	87.205		V	
Total		27775449	523111				



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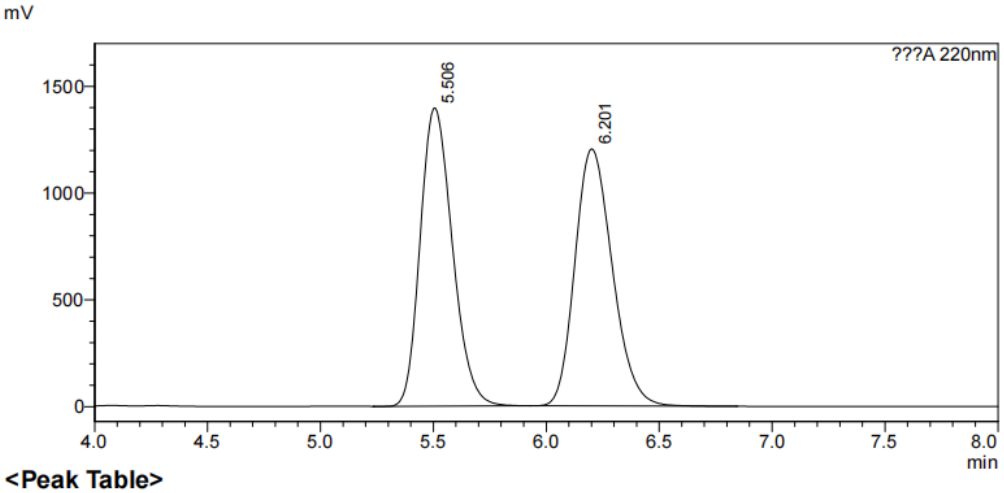

<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.506	13851642	1397247	49.930		M	
2	6.201	13890250	1205402	50.070		M	
Total		27741892	2602649				

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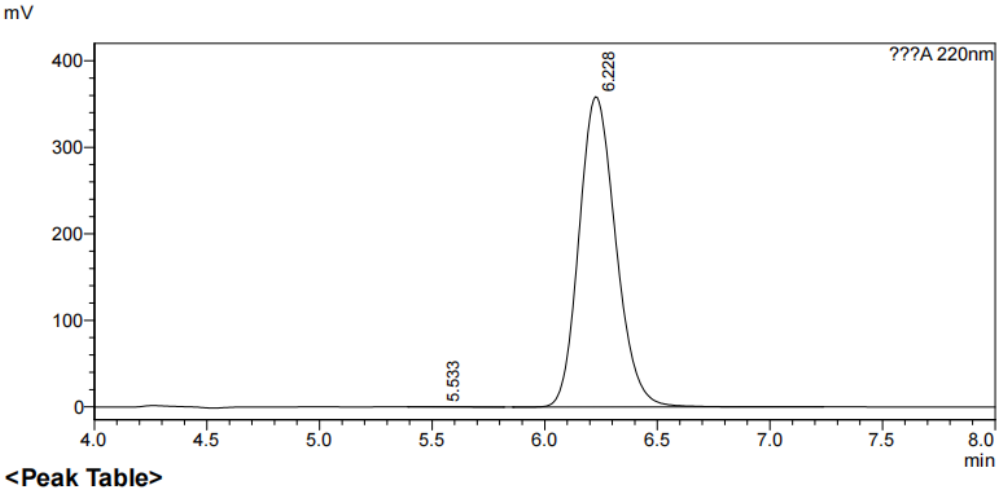
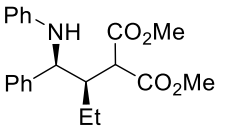


<Peak Table>

???A 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.533	1107	97	0.027		M	
2	6.228	4076172	358678	99.973		M	
Total		4077279	358775				



4a

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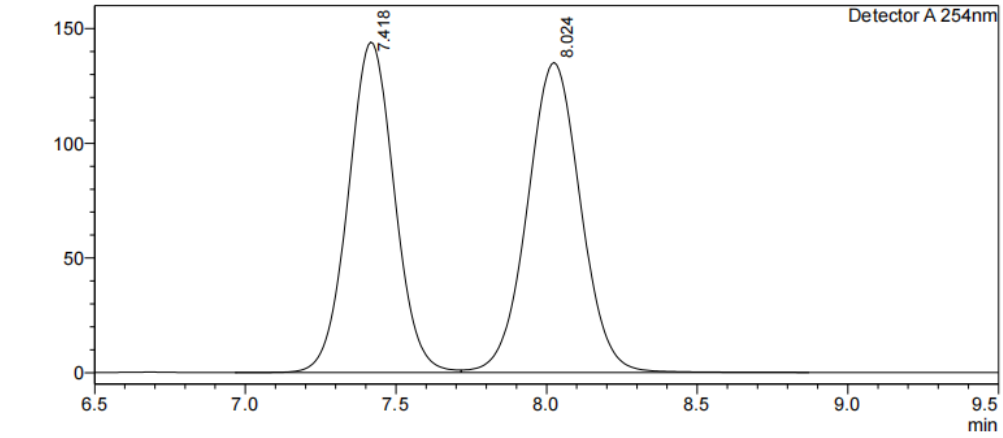

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.418	1535584	144145	48.010			
2	8.024	1662851	135109	51.990		V	
Total		3198435	279253				

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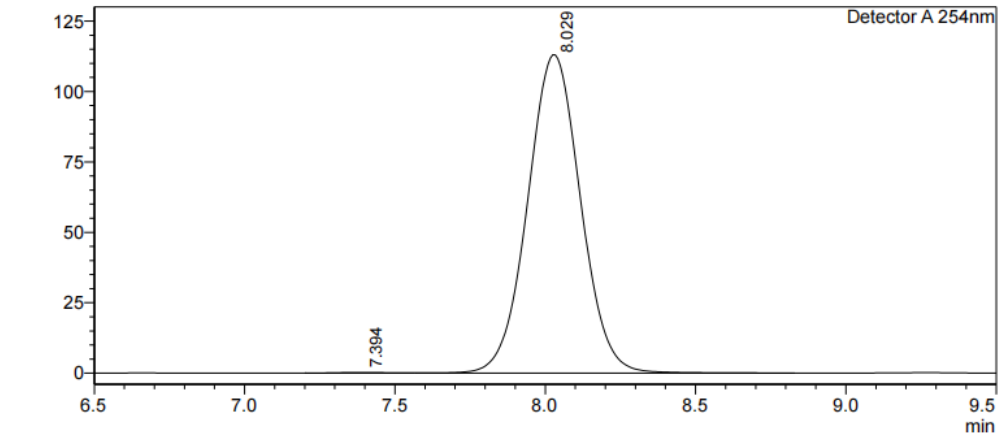
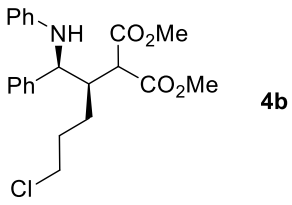


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.394	2803	213	0.202		V	
2	8.029	1385447	113021	99.798		V	
Total		1388250	113234				



4b

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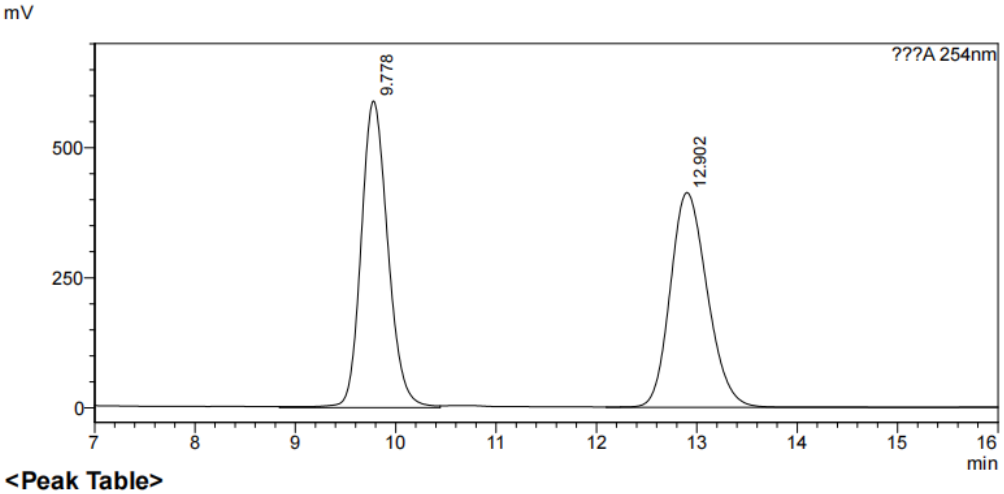

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.778	10922867	589133	50.636			
2	12.902	10648302	413003	49.364			
Total		21571170	1002135				

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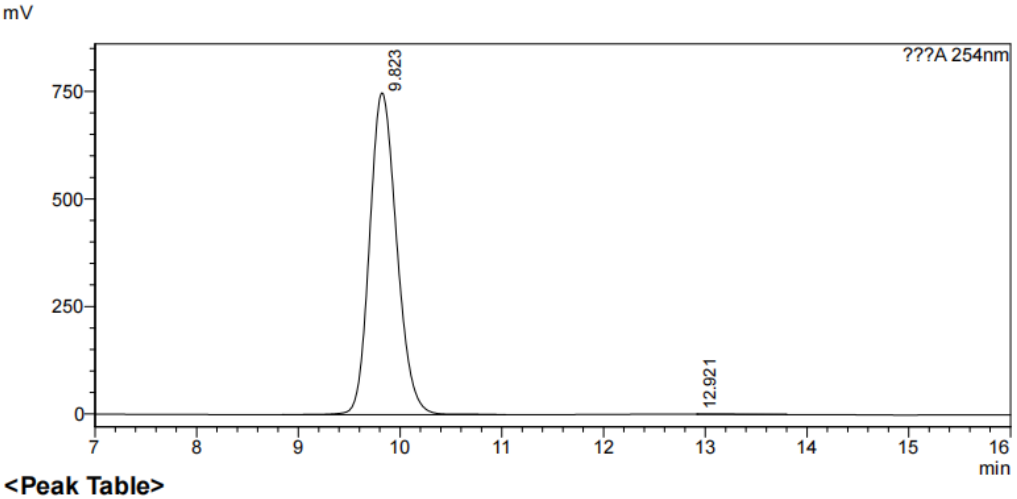
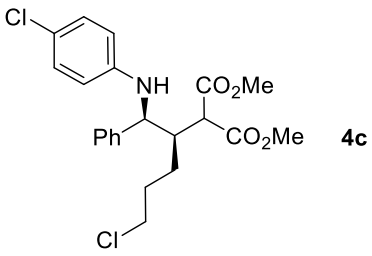


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.823	13862964	748113	99.995		M	
2	12.921	682	5	0.005		M	
Total		13863646	748118				



4c

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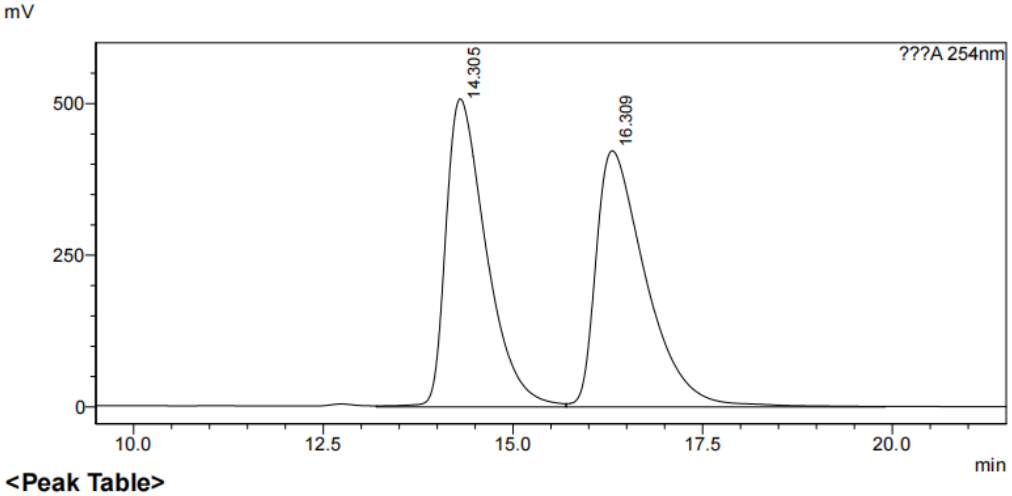
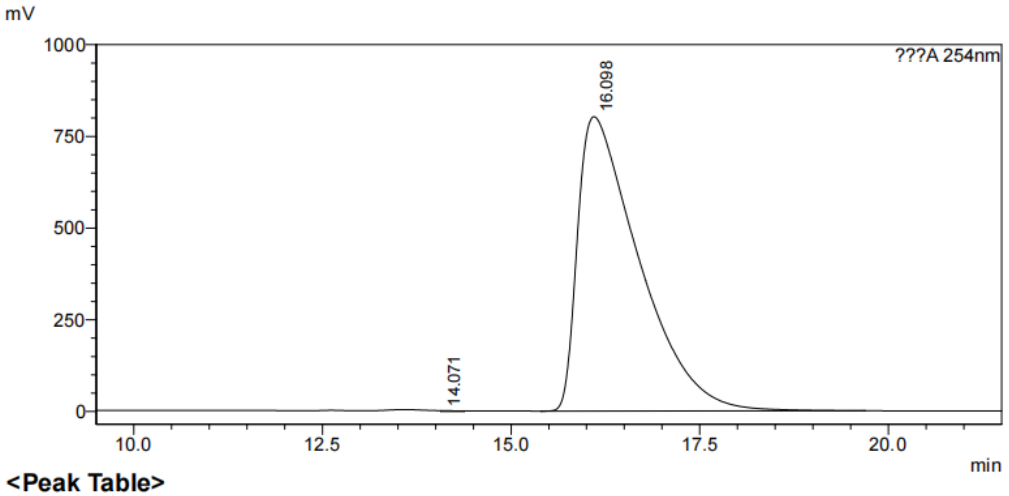


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.305	18852248	507797	49.313			
2	16.309	19377289	422074	50.687		M	
Total		38229537	929871				

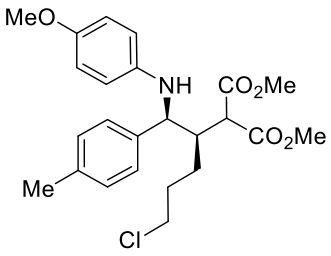
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.071	38166	2387	0.084		M	
2	16.098	45541978	802411	99.916		M	
Total		45580144	804798				



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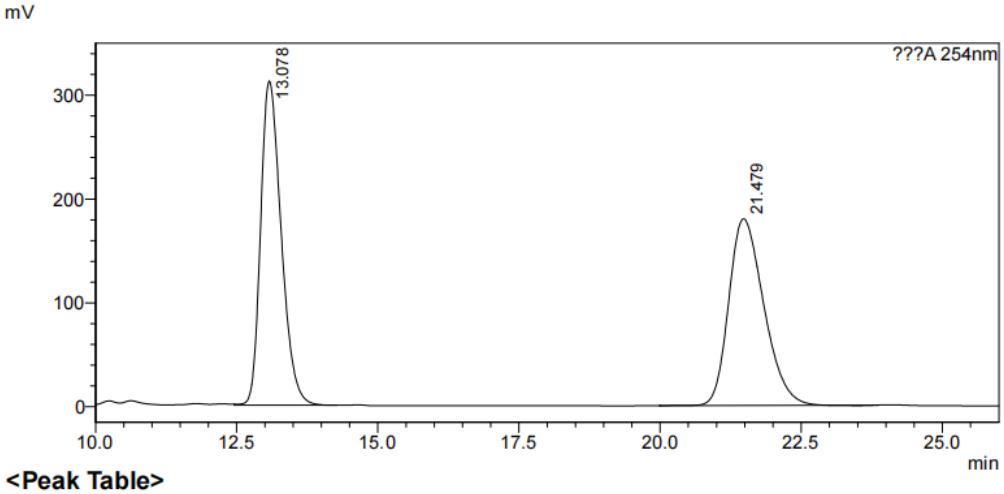

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.078	7908777	312233	50.498			
2	21.479	7752858	179725	49.502		M	
Total		15661634	491959				

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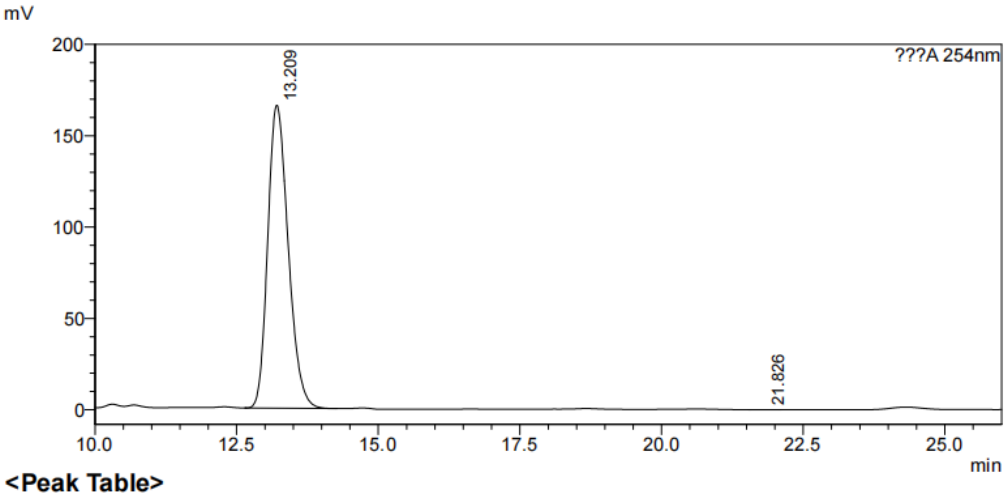
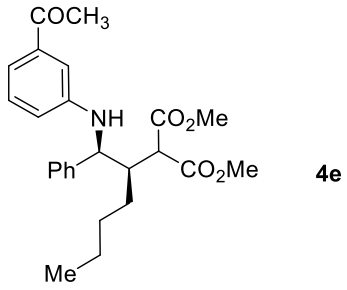


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	13.209	4169986	165942	99.990			
2	21.826	416	22	0.010		M	
Total		4170402	165963				



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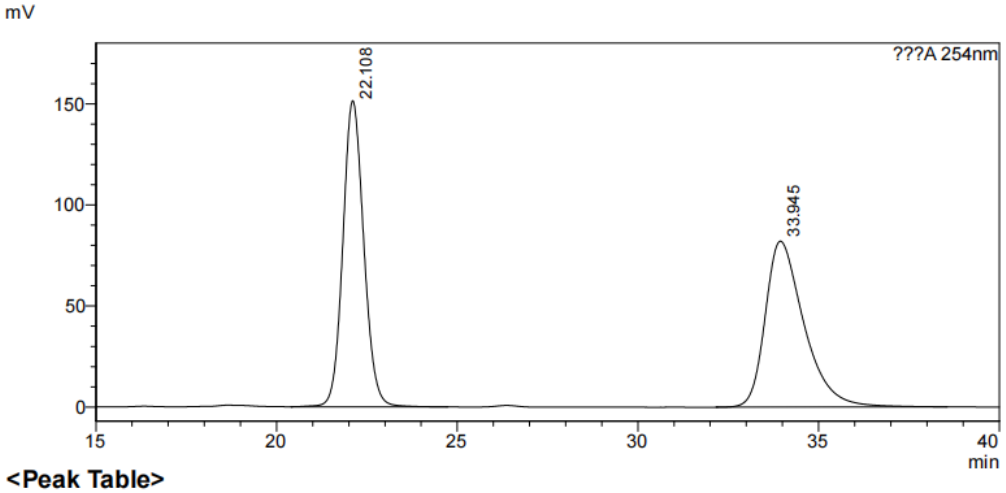

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	22.108	6105598	151477	49.885			
2	33.945	6133686	82103	50.115			
Total		12239284	233580				

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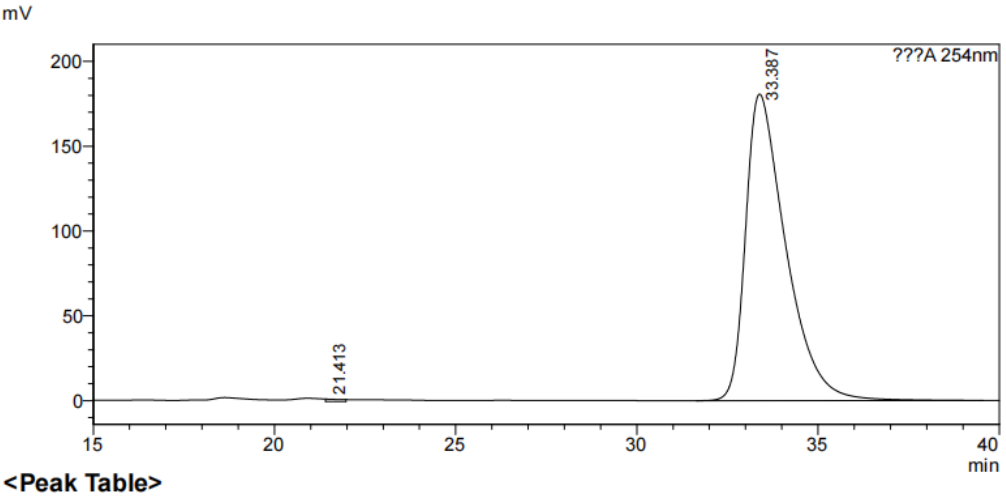
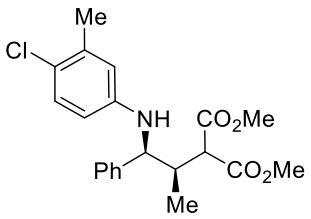


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	21.413	40550	1393	0.290		M	
2	33.387	13963848	180677	99.710			
Total		14004398	182070				



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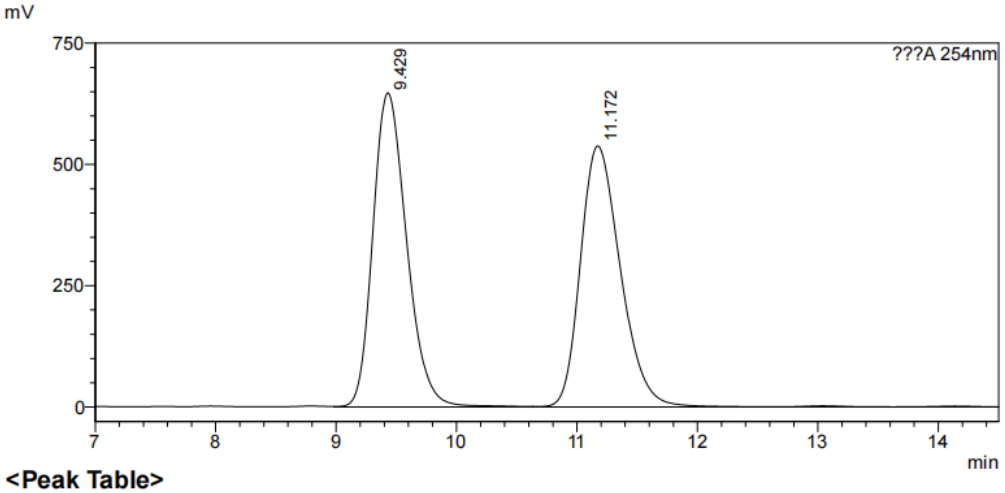

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.429	12620773	647201	50.207			
2	11.172	12516531	538180	49.793		V	
Total		25137304	1185381				

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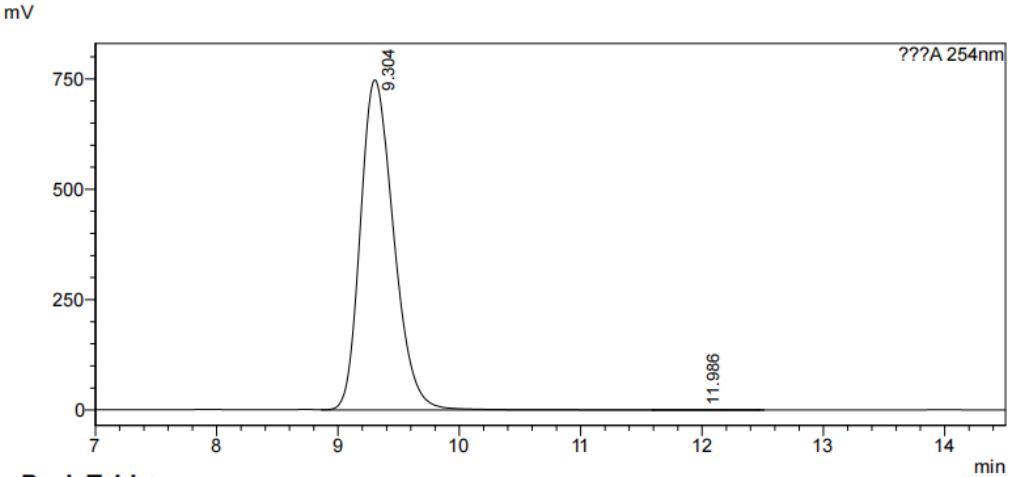
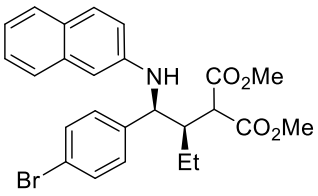


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.304	14323249	747766	99.974		S	
2	11.986	3744	157	0.026		T	
Total		14326993	747923				



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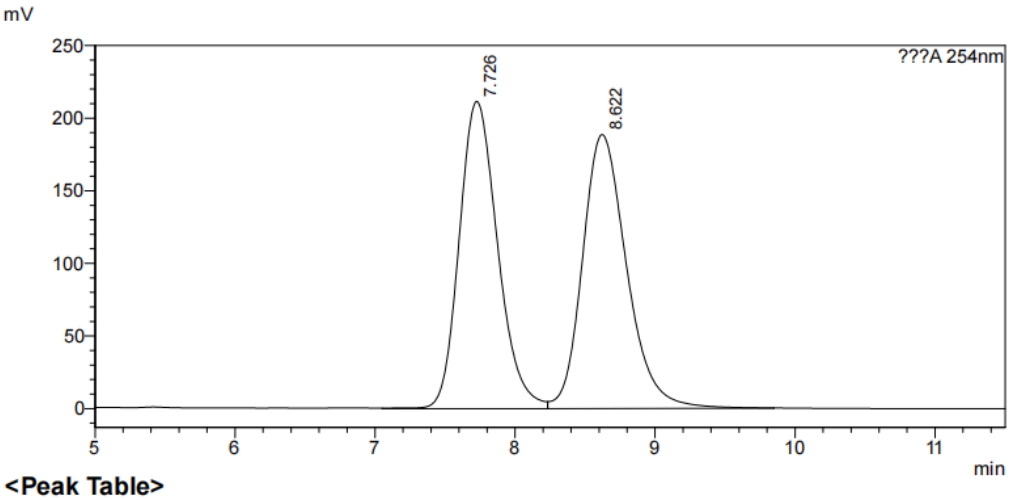
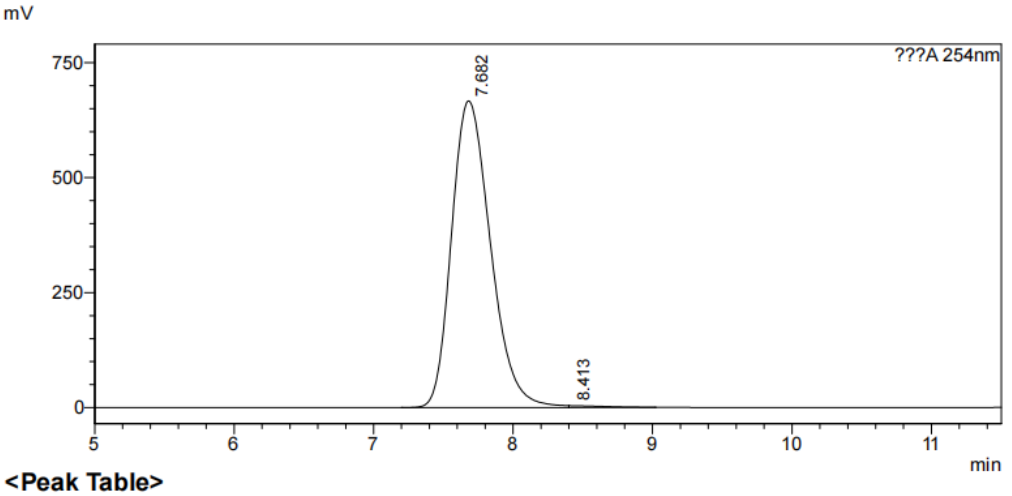


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.726	4038891	211659	49.417			
2	8.622	4134156	188685	50.583		M	
Total		8173047	400344				

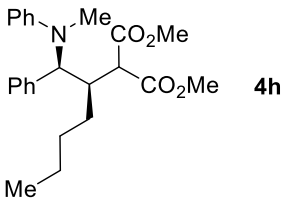
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.682	12956712	666814	99.473		M	
2	8.413	68671	4023	0.527		M	
Total		13025383	670837				



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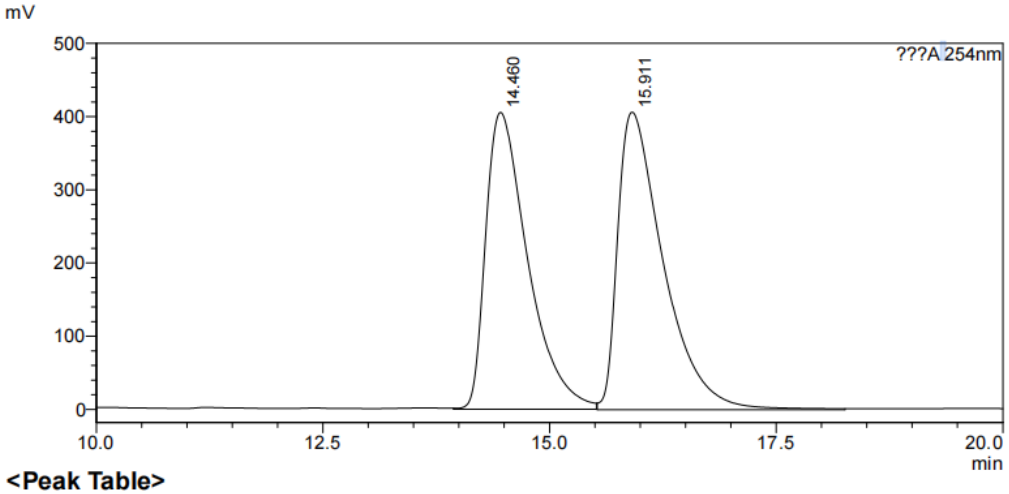
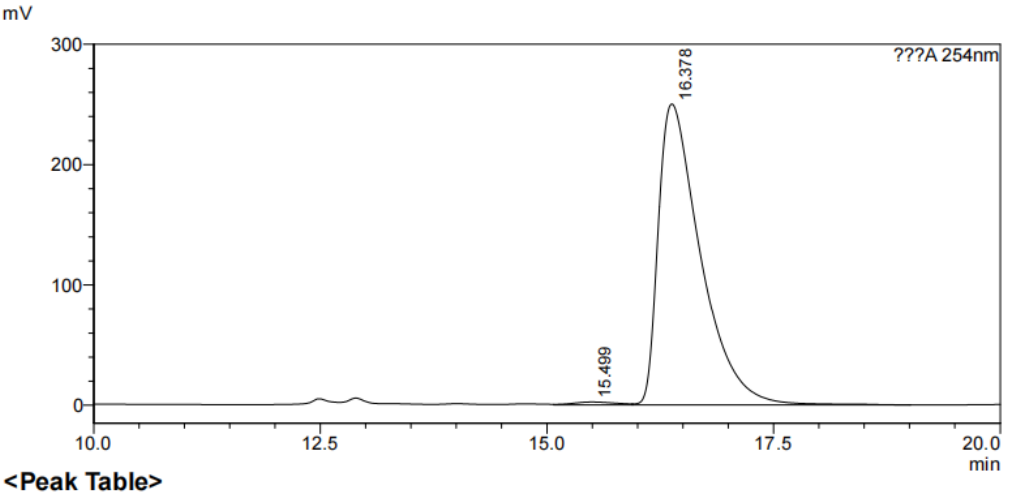


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	14.460	13085385	405660	47.920			
2	15.911	14221604	406318	52.080		M	
Total		27306989	811978				

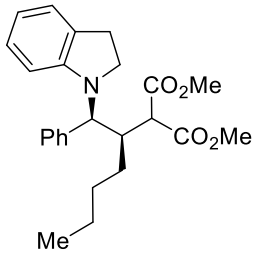
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	15.499	84056	2507	1.025			
2	16.378	8120175	250171	98.975		V	
Total		8204231	252678				



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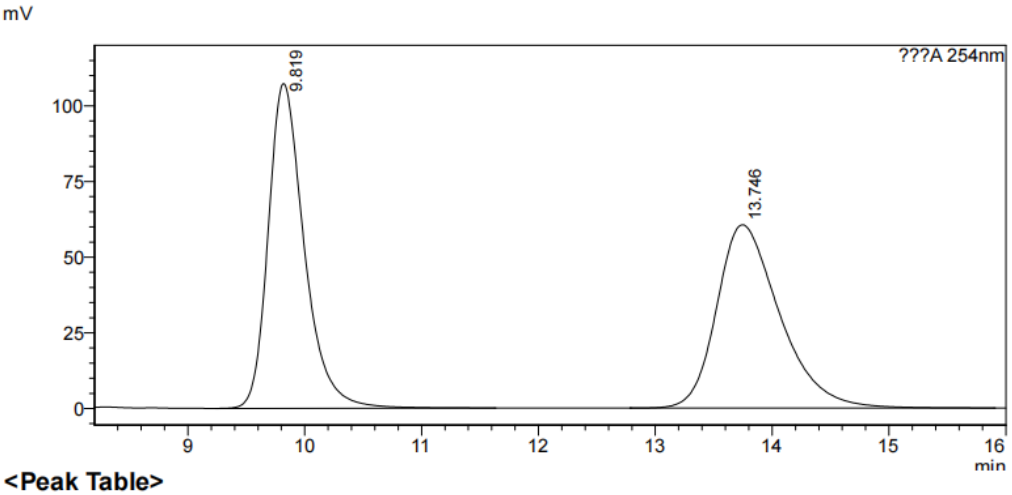

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.819	2301155	107334	50.253			
2	13.746	2277973	60567	49.747			
Total		4579127	167900				

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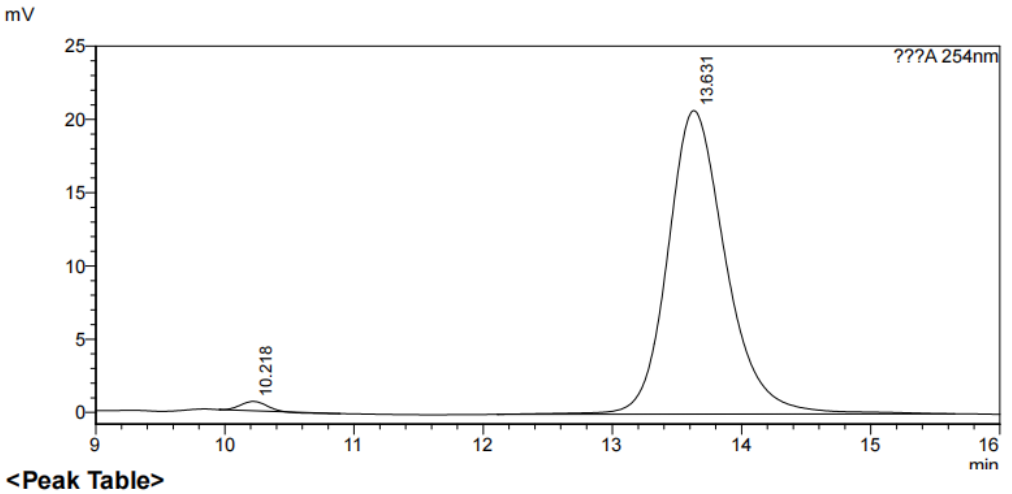
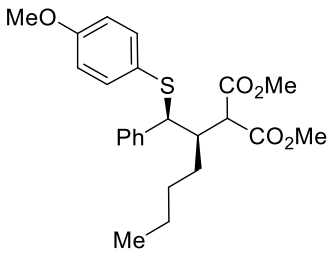


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.218	8335	636	1.268		M	
2	13.631	649089	20714	98.732			
Total		657424	21349				



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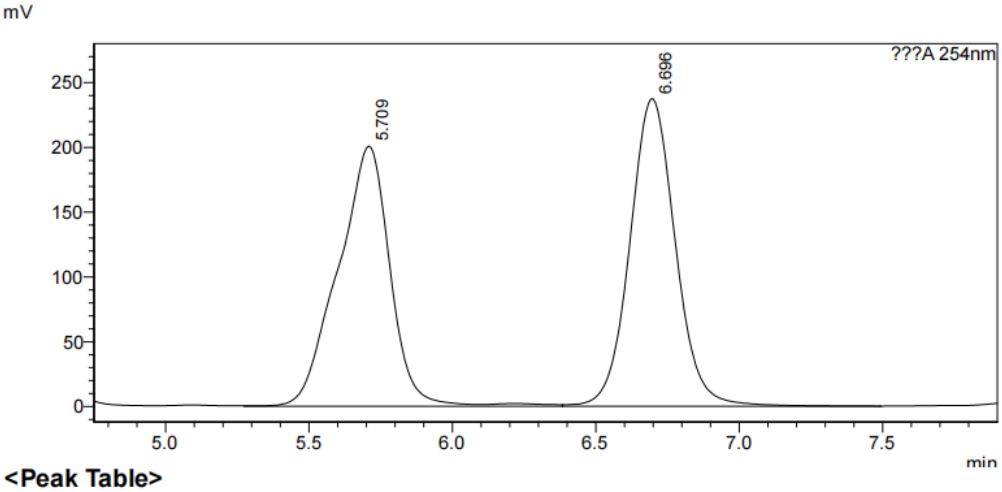

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.709	2545955	200956	49.174			
2	6.696	2631460	237418	50.826		V	
Total		5177415	438373				

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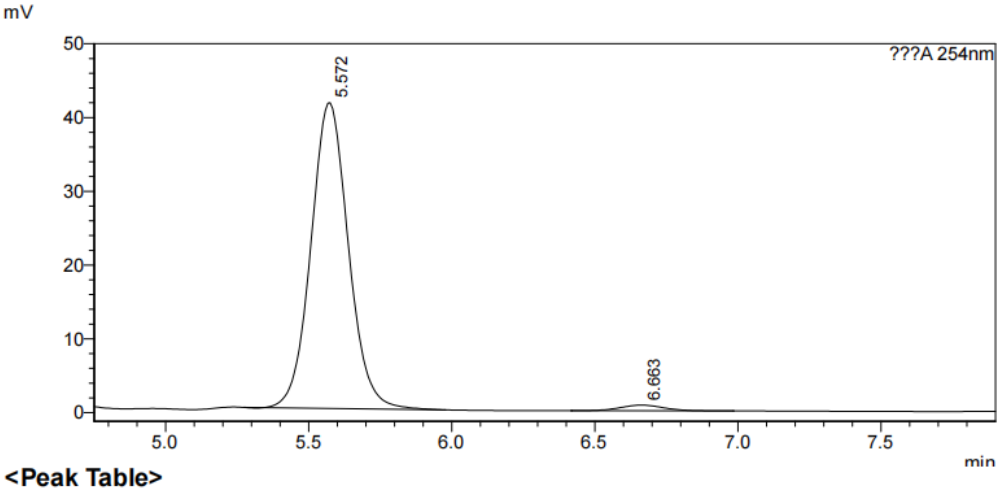
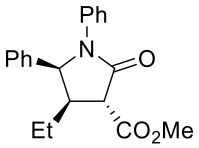


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.572	377830	41461	97.901		M	
2	6.663	8102	767	2.099			
Total		385932	42227				



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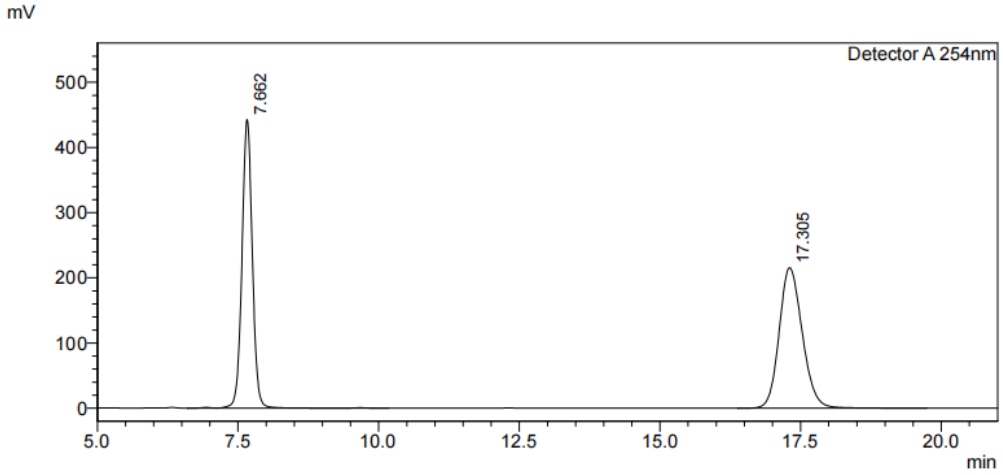

<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.662	5698914	442622	48.051		M	
2	17.305	6161258	215509	51.949		S	
Total		11860172	658131				

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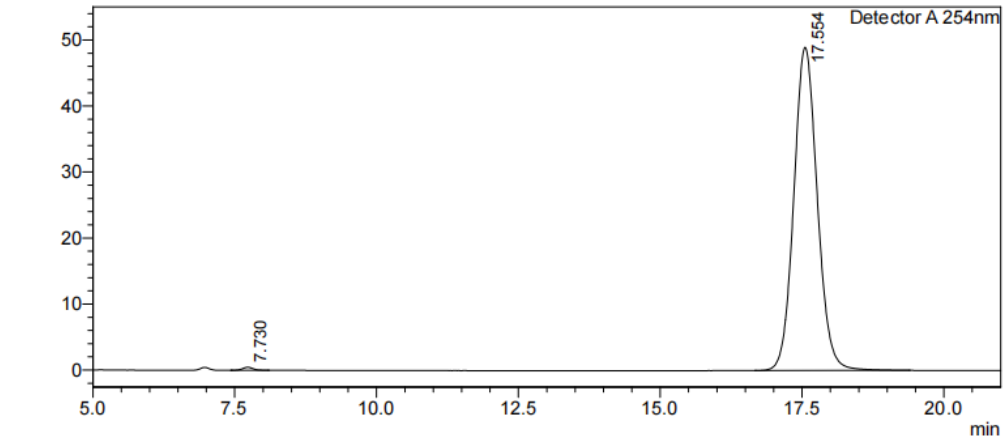
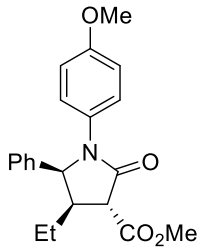


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	7.730	5888	457	0.416			
2	17.554	1409460	48979	99.584			
Total		1415348	49436				



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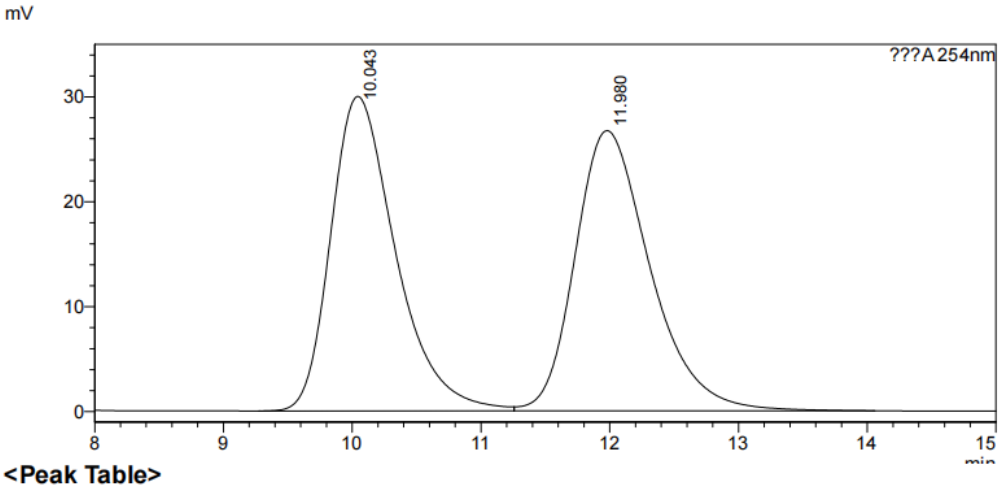

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.043	1050208	29975	49.281			
2	11.980	1080848	26707	50.719		V	
Total		2131056	56683				

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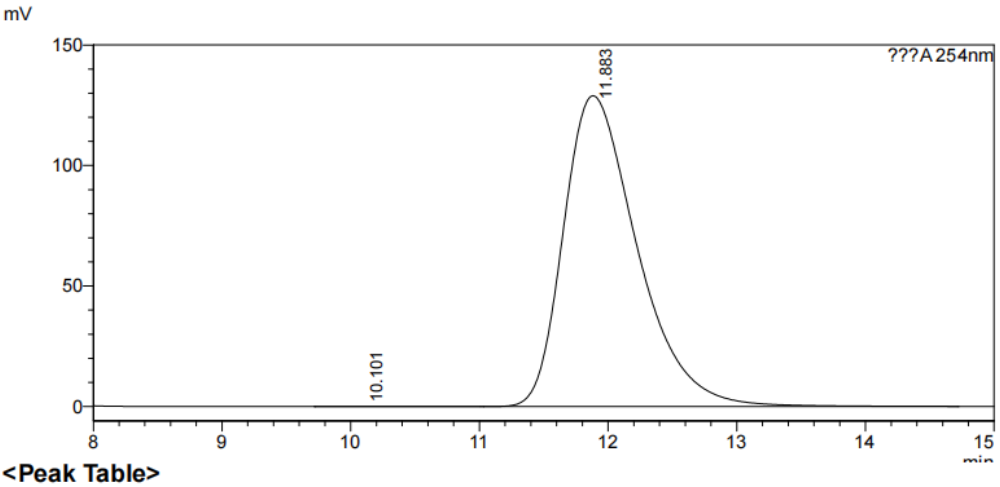
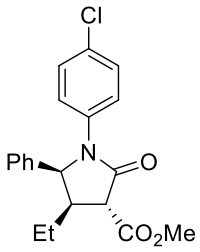


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	10.101	696	29	0.014		M	
2	11.883	5138429	128959	99.986			
Total		5139125	128988				



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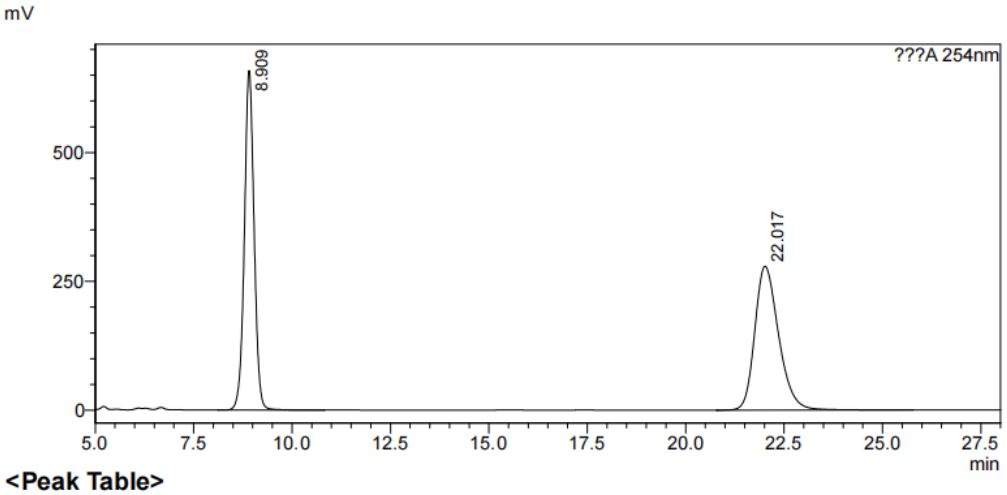

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.909	11340979	659241	49.018			
2	22.017	11795588	279159	50.982			
Total		23136567	938400				

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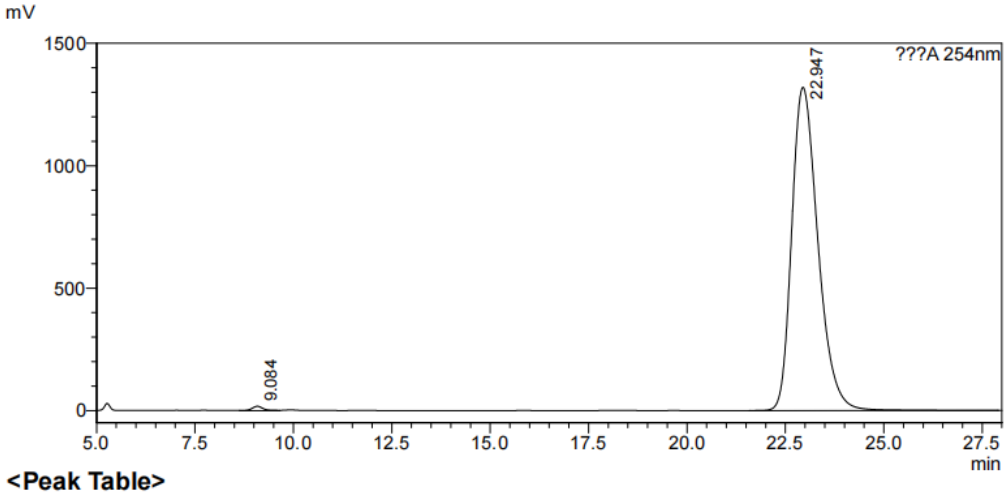
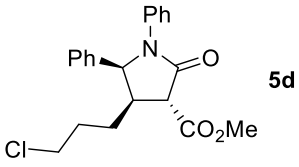


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.084	341869	17469	0.556			
2	22.947	61119036	1320566	99.444			
Total		61460904	1338034				



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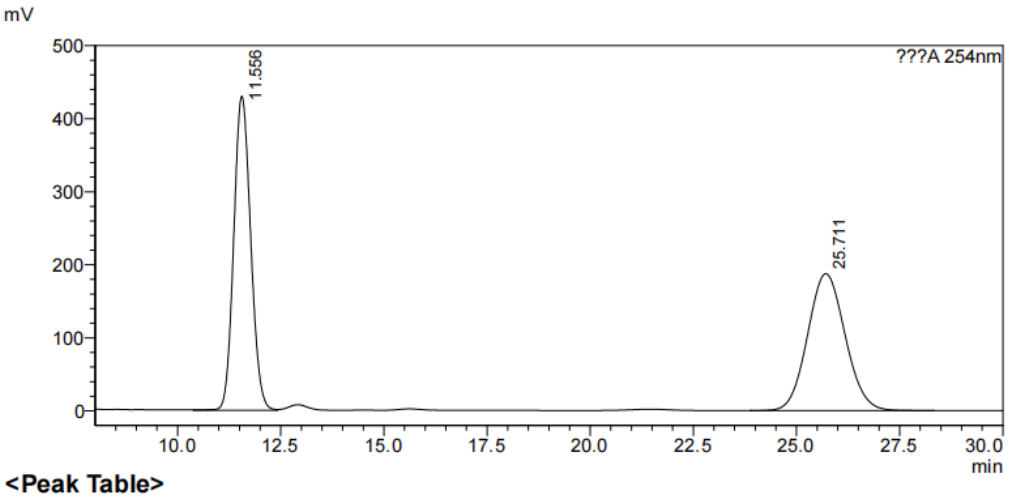
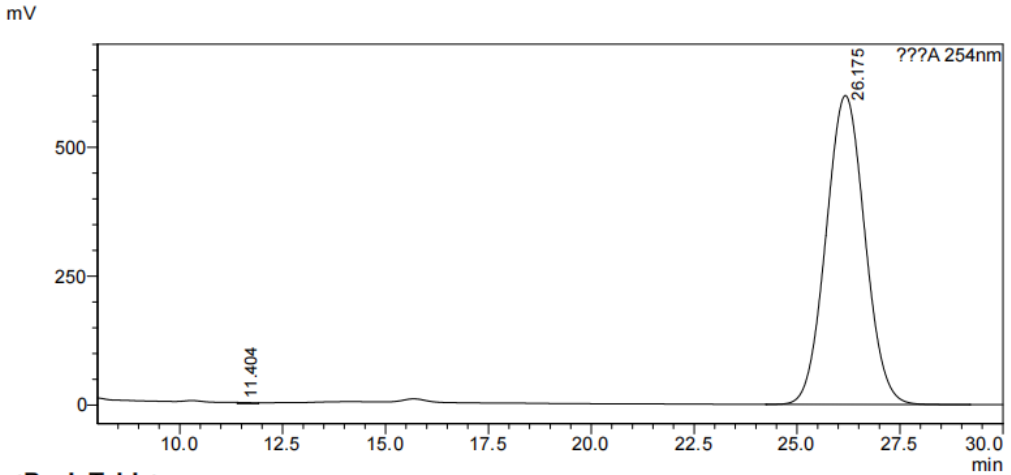


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.556	12312412	430261	50.959			
2	25.711	11848856	187306	49.041			
Total		24161268	617567				

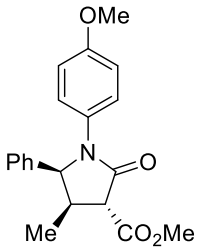
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.404	49512	1991	0.126		M	
2	26.175	39309746	599274	99.874			
Total		39359258	601264				



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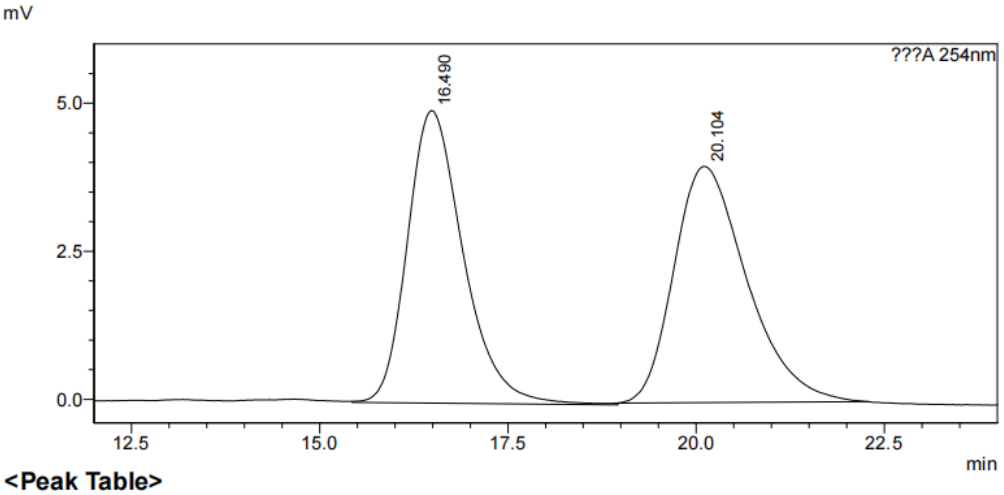

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.490	255741	4939	48.727		M	
2	20.104	269102	3987	51.273			
Total		524843	8926				

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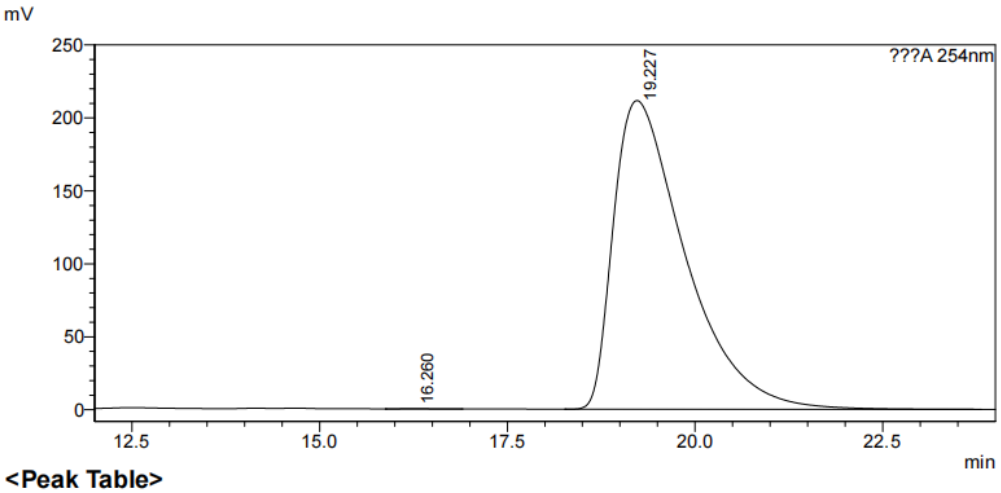
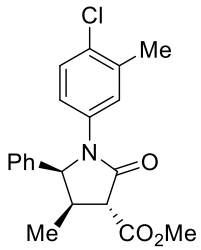


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	16.260	5176	174	0.037			
2	19.227	14098941	211527	99.963			
Total		14104116	211701				



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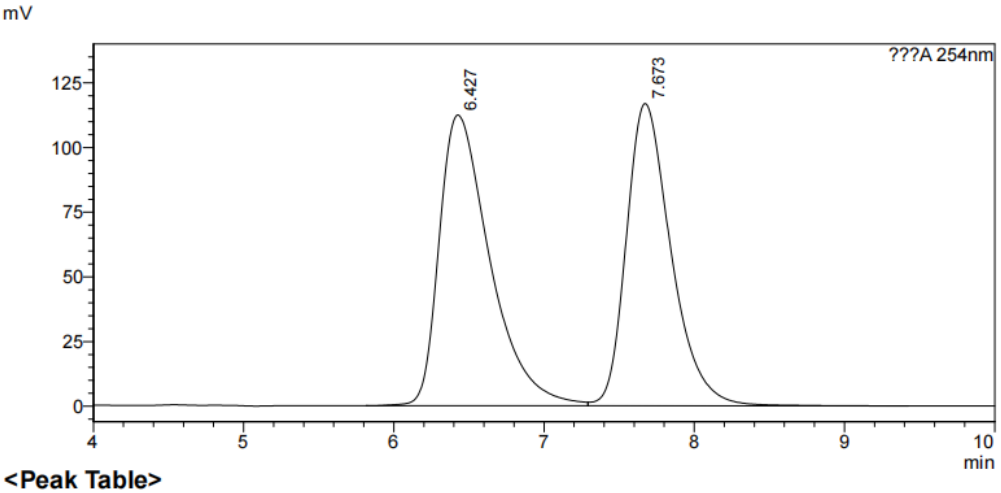

<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.427	2641975	112380	52.176			
2	7.673	2421607	116872	47.824		V	
Total		5063582	229252				

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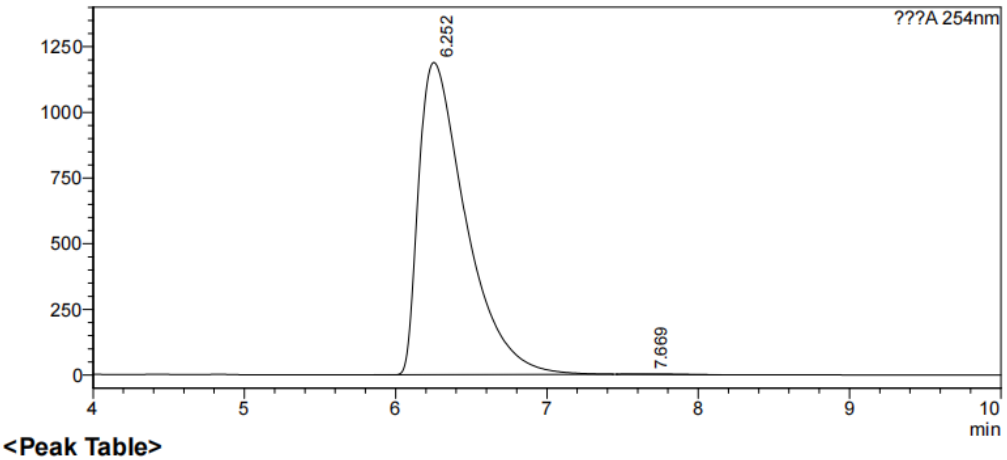
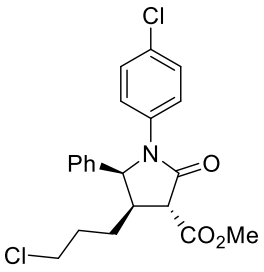


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	6.252	25721597	1188636	99.877		M	
2	7.669	31740	1508	0.123			
Total		25753337	1190145				



5g

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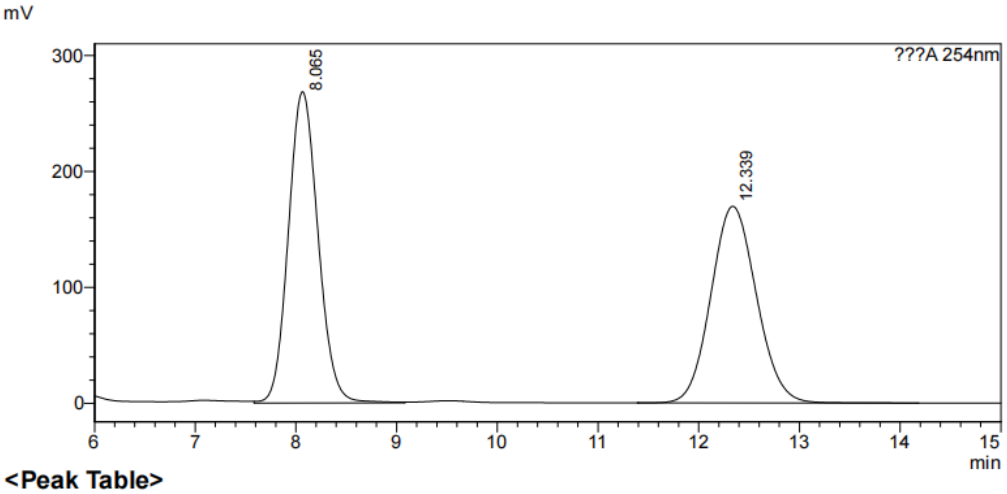
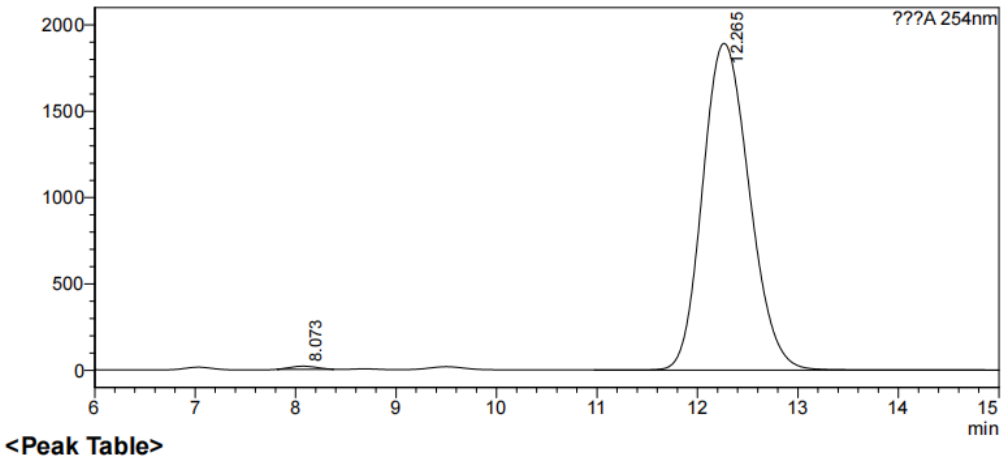


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.065	5512346	268540	50.845			
2	12.339	5329085	169598	49.155			
Total		10841431	438138				

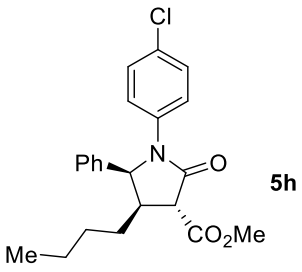
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	8.073	320053	17839	0.520		M	
2	12.265	61212165	1892564	99.480			
Total		61532218	1910403				



5h

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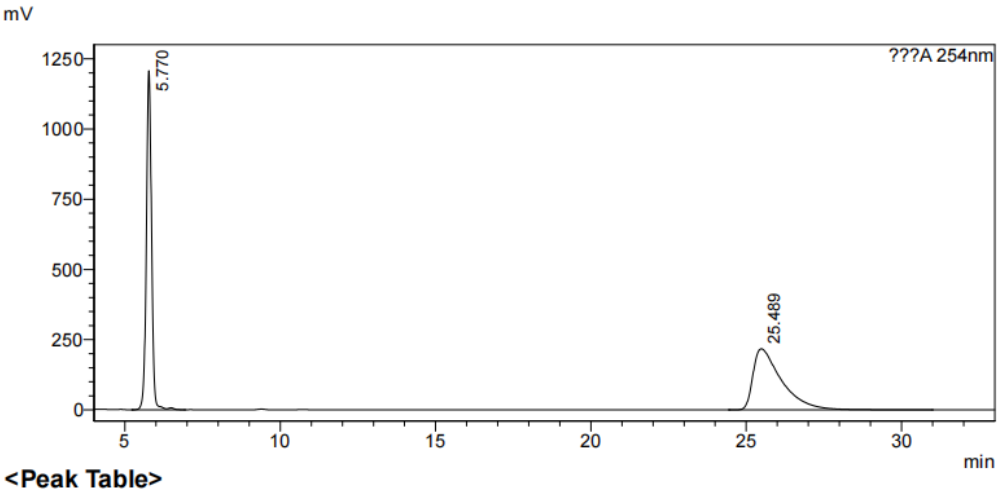
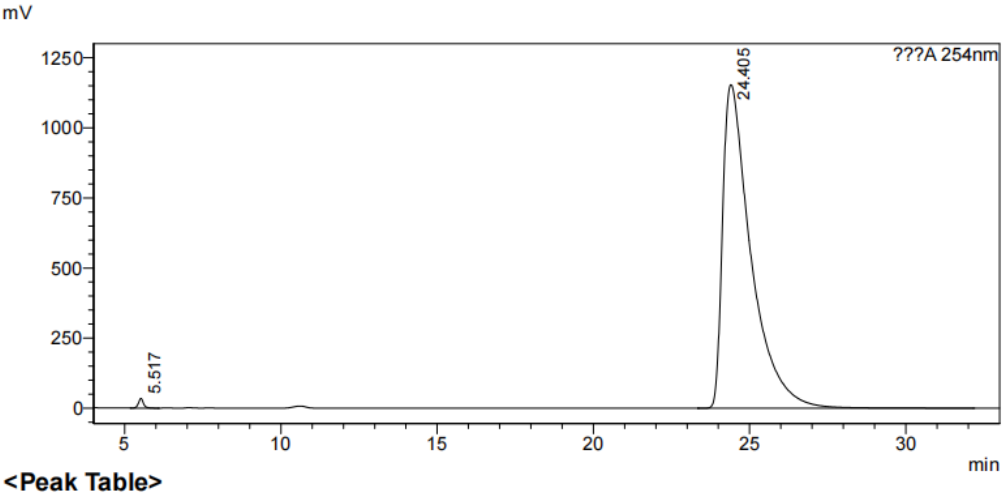


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.770	14007127	1207083	50.173		M	
2	25.489	13910505	217439	49.827			
Total		27917632	1424521				

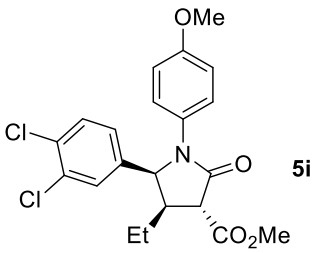
<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	5.517	408168	35063	0.557			
2	24.405	72886552	1153892	99.443		S	
Total		73294720	1188955				



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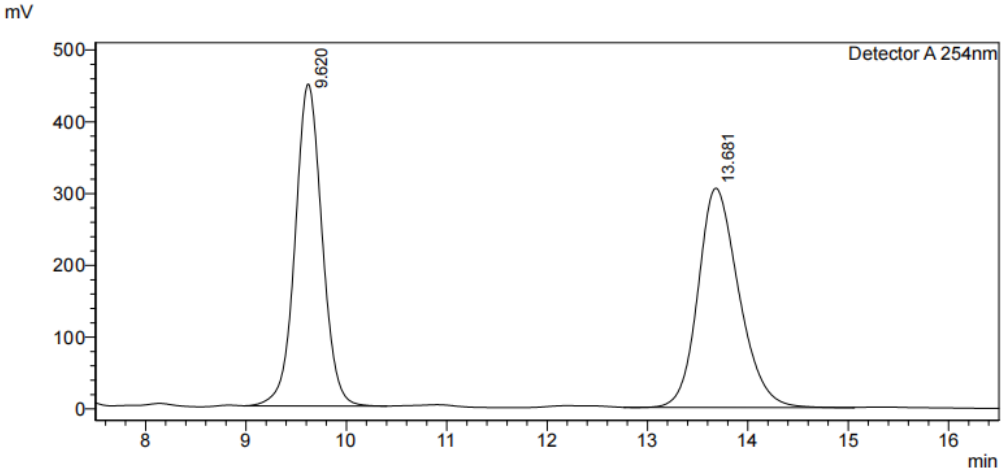
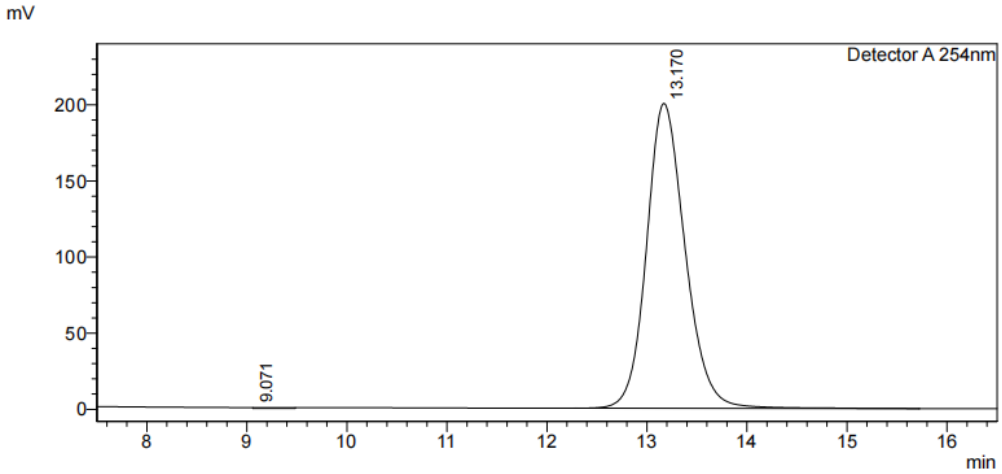


<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.620	8371914	448336	49.248			
2	13.681	8627611	305393	50.752		M	
Total		16999526	753728				

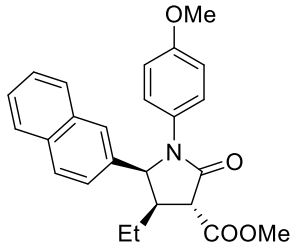
<Chromatogram>



<Peak Table>

Detector A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	9.071	11883	493	0.220		M	
2	13.170	5384495	200292	99.780			
Total		5396378	200785				



5j

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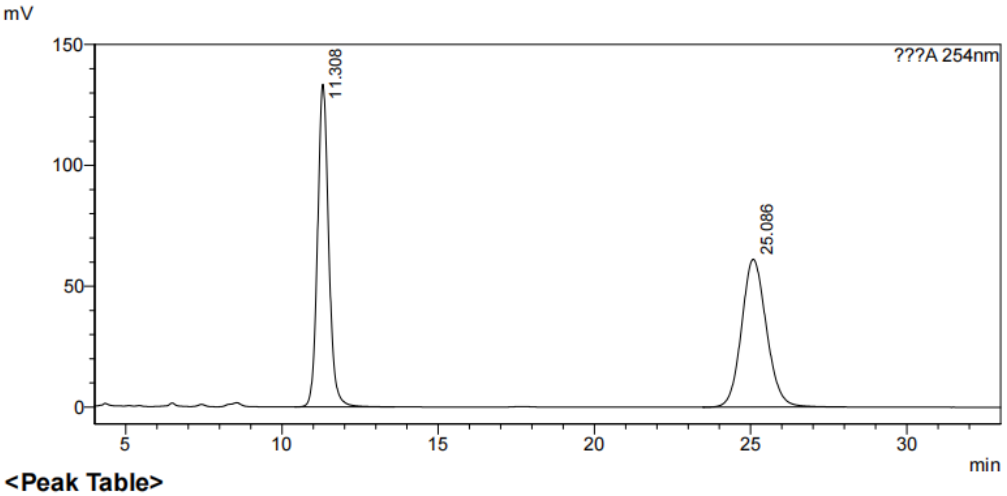
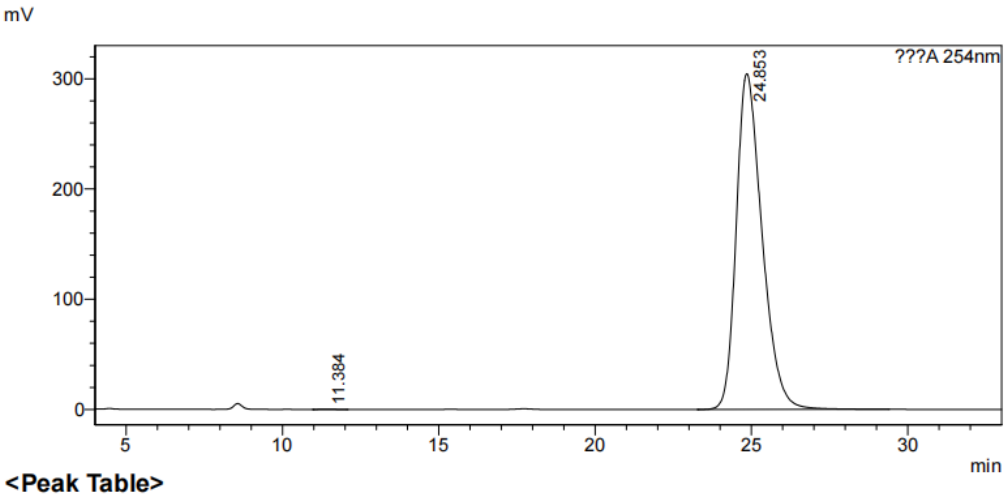


<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.308	3310705	133497	49.333			
2	25.086	3400215	61176	50.667			
Total		6710921	194673				

<Chromatogram>



<Peak Table>

???A 254nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.384	6186	227	0.035			
2	24.853	17499231	304590	99.965			
Total		17505418	304818				