Supporting Information

Asymmetric synthesis of aryl/vinyl alkyl carbinol esters via Ni-catalyzed reductive arylation/vinylation of 1-chloro-1-alkanol esters

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I. Experimental Section

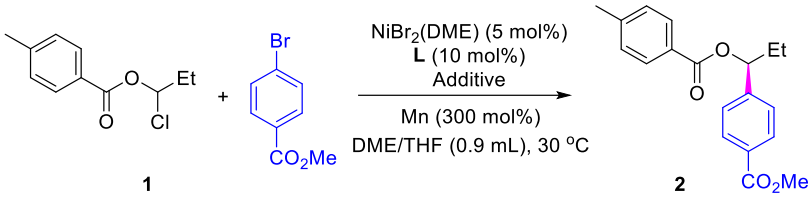
Part 1. General Information

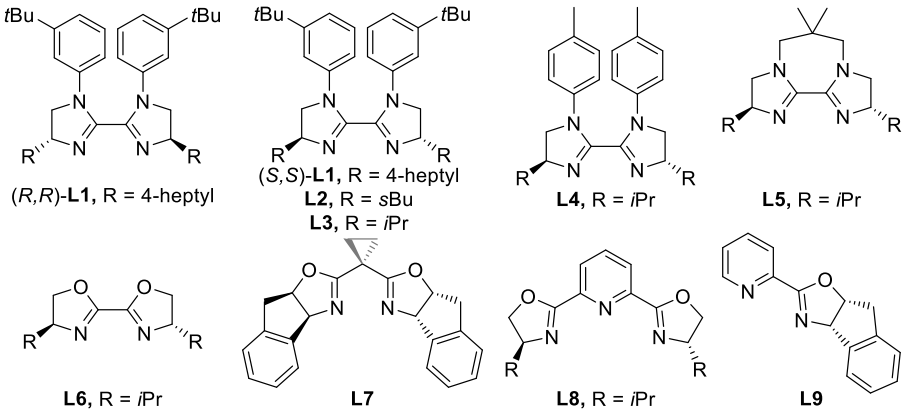
Commercial reagents were purchased from Adamas, Aldrich, Bide, Energy Chemical, TCI and Leyan. Column chromatography was performed using silica gel 200-300 mesh (purchased from Qingdao-Haiyang Co., China) as the solid support. All NMR spectra were recorded on JEOL (400 MHz) spectrometers and Bruker Avance (600 MHz) spectrometer at STP. Data for ^{1}H NMR spectra are reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. NMR spectra are internally referenced to residual proton solvent signals (note: $CDCl_3$ referenced at 7.26 ppm for ^{1}H NMR and 77.0 ppm for ^{13}C NMR). Coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doublet of doublets); ddd (doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets). High resolution mass spectra were measured on Bruker MicroTOF II ESI-TOF mass spectrometer, Agilent Technologies 6230 TOF LC/MS spectrometer in electrospray ionization (ESI^+) mode or direct analysis in real time mode ($DART^+$). Optical rotations were taken on JASCO P1030. Enantiomeric excesses were determined by chiral HPLC using a Shimadzu instrument using Daicel chiral columns. Melting point was recorded on a micro melting point apparatus (X-4, YUHUA Co., Ltd, Gongyi, China).

Part 2. Optimization Experiments

General procedure of optimization experiments: To a flame-dried tube equipped with a stir bar was added the appropriate ligand (0.015 mmol, 10 mol%) and methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv). The tube was transferred into a N_2-filled glovebox, Mn (24.7 mg, 0.45 mmol, 3.0 equiv), $NiBr_2$(DME) (2.3 mg, 5 mol%) and additives were added. The tube was sealed, removed from the glovebox and charged with the solvent. The mixture was stirred at 800 rpm, ensuring that the reductant was uniformly suspended. After 5 min, 1-chloropropyl 4-methylbenzoate **1** (63.8 mg, 0.3 mmol, 2.0 equiv) was added to the tube with a syringe over 1 min. The mixture was stirred vigorously (800 rpm) at 30 °C for 40 h. After that, the mixture was loaded directly onto a silica gel column (eluted with 0−5% EtOAc/Petroleum ether) to give the target molecule, the yield was determined by ^{1}H NMR, and the enantioselectivity was determined by HPLC analysis using Daicel Chiralcel columns.

Table S1 Optimization of the reaction conditions [a,b]



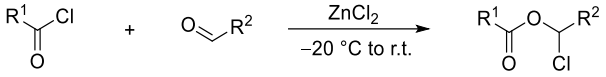


Entry	Ligand	Solvent	Additive (equiv.)	Yield %	e.e.%
1	(*R*, *R*)-**L1**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	95 (92)[c]	94
2	(*S*, *S*)-**L1**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	93	−94
3	**L2**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	94	−90
4	**L3**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	95	−89
5	**L4**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	90	−87
6	**L5**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	82	−62
7	**L6**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	36	−54
8	**L7**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	9	−17
9	**L8**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	50	−56
10	**L9**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	49	−6
11	**L3**	DME	LiI (2.5) TBAI (0.5)	92	−81
12	**L3**	THF	LiI (2.5) TBAI (0.5)	45	−89
13	**L3**	Acetone/THF (1/2)	LiI (2.5) TBAI (0.5)	56	−87
14	**L3**	DME/THF (2/1)	LiI (2.5) TBAI (0.5)	96	−88
15	**L3**	DME/THF (1/9)	LiI (2.5) TBAI (0.5)	81	−89
16	**L3**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	93	−88
17	(*R*, *R*)-**L1**	DME/THF (1/2)	-	Trace	-
18	(*R*, *R*)-**L1**	DME/THF (1/2)	LiI (2.5)	70	93
19	(*R*, *R*)-**L1**	DME/THF (1/2)	TBAI (0.5)	20	92
20	(*R*, *R*)-**L1**	DME/THF (1/2)	LiI (2.5) TEAI (0.5)	65	92
21	(*R*, *R*)-**L1**	DME/THF (1/2)	LiI (2.5) TBAC (0.5)	62	92
22	(*R*, *R*)-**L1**	DME/THF (1/2)	LiI (2.5) TBAB (0.5)	85	92
23	(*R*, *R*)-**L1**	DME/THF (1/2)	LiCl (2.5) TBAC (0.5)	7	-
24[d]	(*R*, *R*)-**L1**	DME/THF (1/2)	LiI (2.5) TBAI (0.5)	66	92

[*a*] Reactions conducted under N_2 on 0.15 mmol scale for 40 h, ee was determined by chiral HPLC analysis [*b*] NMR yield using 2,5-dimethyl furan as the internal standard. [*c*] Isolated yield. [*d*] Zn instead of Mn.

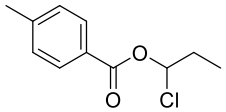
Part 3. Substrate Preparation

***a. General procedure for preparation of 1-chloro-1-alkanol esters* (GP A).**



The 1-chloro-1-alkanol esters were prepared according to the literature reported.[1, 2] To a round-bottom flask equipped with a stir bar was charged with $ZnCl_2$ (10 mol%). The flask was placed under a nitrogen atmosphere by evacuating and backfilling the flask (three cycles), followed by the addition of DCM and acyl chloride (0.5 M, 1.0 equiv), then the resulting solution was cooled to –20 °C and stirred for 5 min. After that, the aldehyde (1 M in DCM, 1.0 equiv) was added dropwise to the above mixture over 20 min. The reaction mixture was stirred for 2-12 hours at r.t., then quenched with $NaHCO_3$ (5% aq), extracted with DCM. The organic phase were collected, dried over $MgSO_4$, concentrated under reduced pressure. The crude material was purified by flash column chromatography on silica gel to give desire compound (isolated yield: ~50%).

1-Chloropropyl 4-methylbenzoate (1)



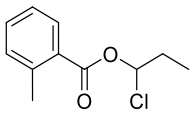
1 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.91 (m, 2H), 7.32 – 7.18 (m, 2H), 6.64 (t, *J* = 5.6 Hz, 1H), 2.42 (s, 3H), 2.21 – 2.14 (m, 2H), 1.13 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3, 144.7, 130.0, 129.2, 126.2, 85.7, 31.6, 21.7, 9.2.

HRMS (ESI) calculated for: $C_{11}H_{14}ClO_2^+$ ($[M+H]^+$) m/z 213.0677, found 213.0662.

1-Chloropropyl 2-methylbenzoate (SM1)



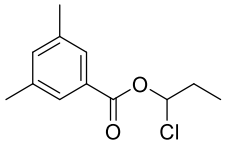
SM1 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.45 (td, *J* = 7.5, 1.5 Hz, 1H), 7.31 – 7.21 (m, 2H), 6.64 (t, *J* = 5.6 Hz, 1H), 2.64 (s, 3H), 2.21 – 2.14 (m, 2H), 1.14 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.9, 141.2, 132.8, 131.9, 130.9, 128.0, 125.8, 85.6, 31.6, 21.8, 9.2.

HRMS (ESI) calculated for: $C_{11}H_{14}ClO_2^+$ ($[M+H]^+$) m/z 213.0677, found 213.0662.

1-Chloropropyl 3,5-dimethylbenzoate (SM2)



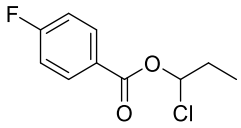
SM2 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 1.6 Hz, 2H), 7.25 – 7.22 (m, 1H), 6.64 (t, *J* = 5.7 Hz, 1H), 2.37 (d, *J* = 0.9 Hz, 6H), 2.22 – 2.15 (m, 2H), 1.14 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.6, 138.2, 135.4, 128.8, 127.6, 85.7, 31.6, 21.1, 9.3.

HRMS (ESI) calculated for: $C_{12}H_{16}ClO_2^+$ ($[M+H]^+$) m/z 227.0834, found 227.0842.

1-Chloropropyl 4-fluorobenzoate (SM3)



SM3 was prepared by ***GP A*** as a colorless oil.

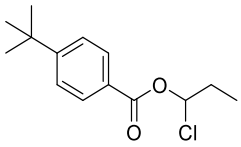
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 – 8.07 (m, 2H), 7.17 – 7.11 (m, 2H), 6.62 (t, *J* = 5.7 Hz, 1H), 2.21 – 2.14 (m, 2H), 1.13 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.2 (d, *J* = 255.4 Hz), 163.3, 132.6 (d, *J* = 9.5 Hz), 125.2 (d, *J* = 3.1 Hz), 115.8 (d, *J* = 22.1 Hz), 85.7, 31.6, 9.2.

^{19}F NMR (565 MHz, $CDCl_3$) δ −103.18.

HRMS (ESI) calculated for: $C_{10}H_{10}ClFO_2^+$ $[M]^+$ m/z 216.0348, found 216.0341.

1-Chloropropyl 4-(*tert*-butyl)benzoate (SM4)



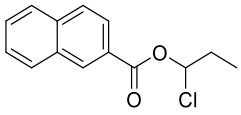
SM4 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H), 7.51 – 7.46 (m, 2H), 6.64 (t, *J* = 5.7 Hz, 1H), 2.22 – 2.14 (m, 2H), 1.34 (s, 9H), 1.13 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.3, 157.6, 129.9, 126.1, 125.5, 85.6, 35.2, 31.6, 31.0, 9.2.

HRMS (ESI) calculated for: $C_{14}H_{19}ClNaO_2^+$ ($[M+Na]^+$) m/z 277.0966, found 277.0982.

1-Chloropropyl 2-naphthoate (SM5)



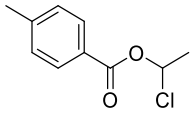
SM5 was prepared by ***GP A*** as a yellow oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (t, *J* = 1.1 Hz, 1H), 8.08 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.97 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.63 –7.55 (m, 2H), 6.72 (t, *J* = 5.7 Hz, 1H), 2.29 –2.21 (m 2H), 1.19 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.5, 135.8, 132.3, 131.8, 129.4, 128.7, 128.4, 127.8, 126.8, 126.1, 125.1, 85.9, 31.7, 9.3.

HRMS (ESI) calculated for: $C_{14}H_{14}ClO_2^+$ ($[M+H]^+$) m/z 249.0677, found 249.0662.

1-Chloroethyl 4-methylbenzoate (SM6)



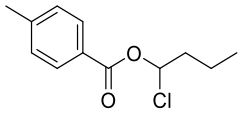
SM6 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.29 – 7.23 (m, 2H), 6.79 (q, *J* = 5.8 Hz, 1H), 2.42 (s, 3H), 1.92 (d, *J* = 5.8 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 144.7, 130.0, 129.2, 126.1, 81.2, 25.3, 21.7.

HRMS (ESI) calculated for: $C_{10}H_{12}ClO_2^+$ ($[M+H]^+$) m/z 199.0521, found 199.0549.

1-Chlorobutyl 4-methylbenzoate (SM7)



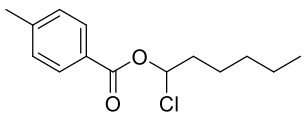
SM7 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 7.9 Hz, 2H), 6.69 (t, *J* = 5.9 Hz, 1H), 2.42 (s, 3H), 2.24 – 2.08 (m, 2H), 1.62 – 1.56 (m, 2H), 1.00 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 144.6, 130.0, 129.2, 126.2, 84.4, 40.3, 21.7, 18.3, 13.4.

HRMS (ESI) calculated for: $C_{12}H_{16}ClO_2^+$ ($[M+H]^+$) m/z 227.0834, found 227.0835.

1-Chlorohexyl 4-methylbenzoate (SM8)



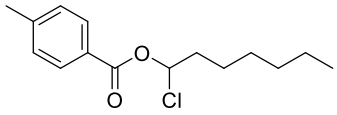
SM8 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.2 Hz, 2H), 6.67 (t, *J* = 5.9 Hz, 1H), 2.42 (s, 3H), 2.15 (dtd, *J* = 11.3, 7.6, 5.9 Hz, 2H), 1.59 – 1.52 (m, 2H), 1.39 – 1.30 (m, 4H), 0.95 – 0.84 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 144.6, 130.0, 129.2, 126.2, 84.7, 38.3, 31.0, 24.6, 22.4, 21.7, 13.9.

HRMS (ESI) calculated for: $C_{14}H_{19}ClNaO_2^+$ ($[M+Na]^+$) m/z 277.0966, found 277.0947.

1-Chloroheptyl 4-methylbenzoate (SM9)



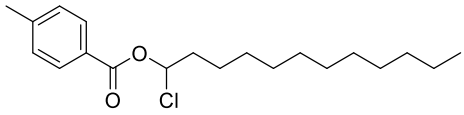
SM9 was prepared by ***GP A*** as a white oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 6.67 (t, *J* = 5.9 Hz, 1H), 2.42 (s, 3H), 2.19 – 2.11 (m, 2H), 1.57 – 1.51 (m, 2H), 1.42 – 1.35 (m, 2H), 1.34 – 1.26 (m, 4H), 0.92 – 0.86 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.37, 144.7, 130.0, 129.2, 126.2, 84.7, 38.3, 31.6, 28.5, 24.85, 22.5, 21.7, 14.0.

HRMS (ESI) calculated for: $C_{15}H_{21}ClNaO_2^+$ ($[M+Na]^+$) m/z 291.1123, found 291.1106.

1-Chlorododecyl 4-methylbenzoate (SM10)



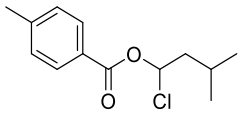
SM10 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.90 (m, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 6.67 (t, *J* = 5.9 Hz, 1H), 2.42 (s, 3H), 2.22 – 2.04 (m, 2H), 1.58 – 1.50 (m, 2H), 1.40 – 1.21 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 144.6, 130.0, 129.2, 126.2, 84.7, 38.3, 31.9, 29.6, 29.5, 29.4, 29.3, 28.9, 24.9, 22.7, 21.7, 14.1.

HRMS (ESI) calculated for: $C_{20}H_{31}ClNaO_2^+$ ($[M+Na]^+$) m/z 361.1905, found 361.1889.

1-Chloro-3-methylbutyl 4-methylbenzoate (SM11)



SM11 was prepared by ***GP A*** as a colorless oil.

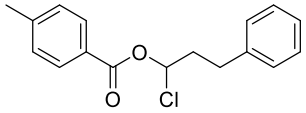
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.30 – 7.23 (m, 2H), 6.74 (dd, *J* = 7.2, 5.8 Hz, 1H),

2.42 (s, 3H), 2.12 (dt, *J* = 14.1, 7.0 Hz, 1H), 2.05 – 2.01 (m, 5.8 Hz, 1H), 1.93 – 1.89 (m, 1H), 0.99 (t, *J* = 6.4 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.4, 144.7, 130.0, 129.3, 126.2, 83.7, 47.0, 25.1, 22.3, 22.2, 21.7.

HRMS (ESI) calculated for: $C_{13}H_{17}ClNaO_2^+$ ($[M+Na]^+$) m/z 263.0809, found 263.0784.

1-Chloro-3-phenylpropyl 4-methylbenzoate (SM12)



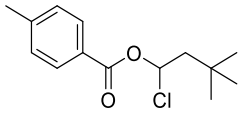
SM12 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.34 – 7.30 (m, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 7.24 – 7.20 (m, 3H), 6.66 (t, *J* = 5.8 Hz, 1H), 2.93 – 2.88 (m, 2H), 2.55 – 2.46 (m, 2H), 2.43 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 144.7, 140.0, 130.0, 129.3, 128.6, 128.4, 126.3, 126.0, 84.0, 39.7, 31.1, 21.7.

HRMS (ESI) calculated for: $C_{17}H_{18}ClO_2^+$ m/z ($[M+H]^+$) 289.0990, found 289.0991.

1-Chloro-3,3-dimethylbutyl 4-methylbenzoate (SM13)



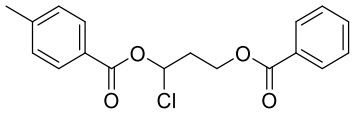
SM13 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.29 – 7.23 (m, 2H), 6.82 (dd, *J* = 9.1, 2.9 Hz, 1H), 2.42 (s, 3H), 2.33 (dd, *J* = 14.7, 9.1 Hz, 1H), 2.08 (dd, *J* = 14.7, 2.9 Hz, 1H), 0.99 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.2, 144.7, 130.1, 129.3, 126.1, 82.9, 51.8, 30.8, 29.7, 21.7.

HRMS (ESI) calculated for: $C_{14}H_{19}O_2^+$ ($[M-Cl^-]^+$) m/z 219.1380, found 219.1379.

3-(Benzoyloxy)-1-chloropropyl 4-methylbenzoate (SM14)

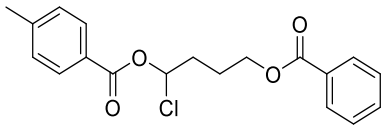


SM14 was prepared by ***GP A*** as a white oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.97 – 7.92 (m, 2H), 7.59 – 7.54 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 5.9 Hz, 1H), 4.58 (t, *J* = 6.1 Hz, 2H), 2.74 – 2.59 (m, 2H), 2.42 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 164.1, 144.9, 133.1, 130.1, 129.7, 129.6, 129.3, 128.4, 125.8, 81.8, 60.4, 37.6, 21.7.

4-(Benzoyloxy)-1-chlorobutyl 4-methylbenzoate (SM15)



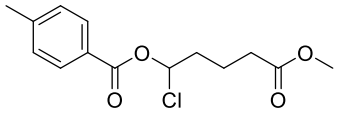
SM15 was prepared by ***GP A*** as a white oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 – 8.03 (m, 2H), 7.98 – 7.92 (m, 2H), 7.57 (tq, *J* = 7.2, 1.2 Hz, 1H), 7.47 – 7.43 (m, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 6.78 (t, *J* = 5.7 Hz, 1H), 4.42 (td, *J* = 6.3, 1.4 Hz, 2H), 2.42 (s, 3H), 2.37 – 2.31 (m, 2H), 2.12 – 2.05 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 164.2, 144.8, 133.0, 130.0, 130.0, 129.6, 129.3, 128.4, 125.9, 84.0, 63.9, 35.1, 24.3, 21.8.

HRMS (ESI) calculated for: $C_{19}H_{19}ClNaO_4^+$ ($[M+Na]^+$) m/z 369.0864, found 369.0870.

1-Chloro-5-methoxy-5-oxopentyl 4-methylbenzoate (SM16)

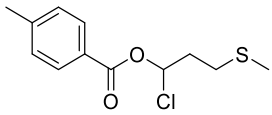


SM16 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.28 – 7.23 (m, 2H), 6.69 (t, *J* = 5.7 Hz, 1H), 3.68 (s, 3H), 2.44 – 2.40 (m, 5H), 2.25 – 2.16 (m, 2H), 1.91 (p, *J* = 7.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.3, 164.2, 144.8, 130.0, 129.3, 126.0, 83.9, 51.7, 37.5, 33.1, 21.7, 20.2.

1-Chloro-3-(methylthio)propyl 4-methylbenzoate (SM17)



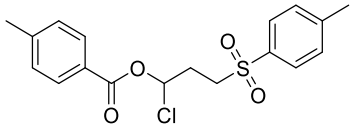
SM17 was prepared by ***GP A*** as a colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 7.7 Hz, 2H), 6.80 (t, *J* = 5.8 Hz, 1H), 2.72 (t, *J* = 7.4 Hz, 2H), 2.50 – 2.39 (m, 5H), 2.14 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 164.1, 144.8, 130.0, 129.3, 125.9, 83.3, 37.8, 29.2, 21.7, 15.6.

HRMS (ESI) calculated for: $C_{12}H_{15}ClNaO_2S^+$ ($[M+Na]^+$) m/z 281.0373, found 281.0345.

1-Chloro-3-tosylpropyl 4-methylbenzoate (SM18)



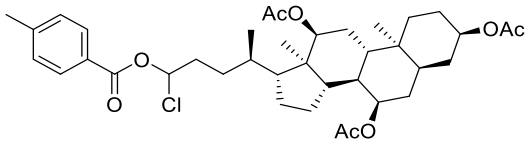
SM18 was prepared by ***GP A*** as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 – 7.86 (m, 2H), 7.84 – 7.80 (m, 2H), 7.41 – 7.37 (m, 2H), 7.28 – 7.24 (m, 2H), 6.74 (t, *J* = 5.2 Hz, 1H), 3.43 – 3.34 (m, 2H), 2.59 – 2.52 (m, 2H), 2.46 (s, 3H), 2.43 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 163.6, 145.2, 145.2, 135.6, 130.1, 130.1, 129.4, 128.1, 125.5, 81.9, 51.7, 31.7, 21.8, 21.7.

HRMS (ESI) calculated for: $C_{18}H_{19}ClNaO_4S^+$ ([M+Na]$^+$) m/z 389.0585, found 389.0575

(3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-17-((2R,5R)-5-Chloro-5-((4-methylbenzoyl)oxy)pentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,7,12-triyl triacetate (SM19)



SM19 was prepared by ***GP A*** as a white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.27 – 7.25 (m, 2H), 6.67 – 6.59 (m, 1H), 5.09 (t, *J* = 2.4 Hz, 1H), 4.91 – 4.89 (m, 1H), 4.60 – 4.54 (m, 1H), 2.42 (s, 3H), 2.25 – 2.12 (m, 4H), 2.09 – 2.00 (m, 8H), 1.96 – 1.92 (m, 1H), 1.91 – 1.83 (m, 2H), 1.80 – 1.72 (m, 2H), 1.70 – 1.57 (m, 7H), 1.54 – 1.38 (m, 4H), 1.33 – 1.22 (m, 2H), 1.14 – 1.02 (m, 2H), 0.91 (s, 3H), 0.87 (d, *J* = 6.6 Hz, 3H), 0.73 (d, *J* = 1.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 170.5, 170.5, 170.3, 170.3, 164.3, 130.0, 129.3, 129.3, 126.1, 85.1, 84.8, 75.4, 74.1, 70.7, 47.3, 47.3, 45.0, 43.4, 40.9, 37.7, 35.0, 34.8, 34.7, 34.6, 34.4, 34.3, 31.2, 30.8, 30.7, 28.9, 27.2, 27.2, 26.9, 25.6, 22.8, 22.5, 21.7, 21.6, 21.5, 21.4, 17.9, 17.8, 12.2.

HRMS (ESI) calculated for: $C_{38}H_{53}ClNaO_8^+$ ([M+Na]$^+$) m/z 695.3321, found 695.3340.

b. Synthesis of Ligands.

Chiral bisimidazoline ligands were prepared according to the reported procedure.[3]

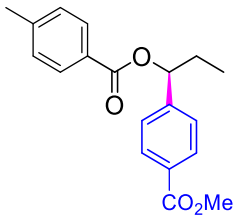
Part 4. Cross-Coupling Reactions and Product Characterization

General procedure for reductive enantioselective reductive cross-coupling reactions*:* To a

flame-dried tube with a stir bar was added aryl halide (0.15 mmol, 1.0 equiv), (*R,R*)-**L1** (9 mg, 10 mol%). The tube was transferred into an N_2-filled glovebox, Mn (24.7 mg, 0.45 mmol, 3.0 equiv), $NiBr_2$(DME) (2.3 mg, 5 mol%), LiI (50.2 mg, 2.5 equiv) and TBAI (27.7 mg, 0.5 equiv) were added. The tube was sealed, removed from the glovebox and charged with THF/DME (2:1, 0.9 mL). The mixture was stirred vigorously, ensuring that the reductant was uniformly suspended. After 5 min, 1-chloropropyl 4-methylbenzoate (63.8 mg, 2.0 equiv) was added to the tube by a syringe over 1 min. The mixture was stirred vigorously at 30 °C for 40 h. After that, the mixture was loaded directly onto a silica gel column (eluted with EtOAc/Petroleum ether) to give the target molecule.

The absolute stereochemistry was assigned by comparing the optical rotation of compound **3** with the literature reported measurement.[4] A *S*-configuration was determined for **3** accordingly, and was applied to all the products reported in this work.

(*S*)-1-(4-(Methoxycarbonyl)phenyl)propyl 4-methylbenzoate (2)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **2** as an off-white solid (43.1 mg, 92% yield, 94% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 8.547 min, t_R (major) = 6.437 min.

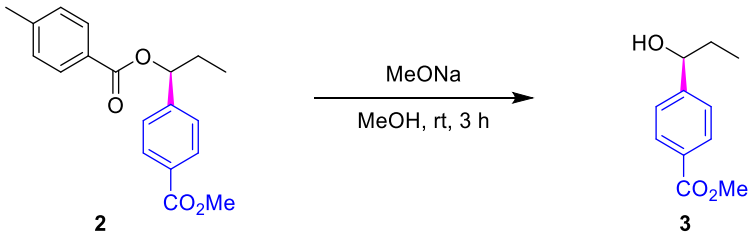
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 7.94 (m, 4H), 7.50 – 7.43 (m, 2H), 7.25 (d, J = 7.9 Hz, 2H), 5.94 (dd, J = 7.4, 6.0 Hz, 1H), 3.90 (s, 3H), 2.41 (s, 3H), 2.11 – 1.90 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 165.8, 145.9, 143.8, 129.7, 129.6, 129.5, 129.1, 127.4, 126.2, 77.0, 52.0, 29.5, 21.6, 9.8.

HRMS (ESI) calculated for $C_{19}H_{20}NaO_4^+$ ([M+Na]$^+$) m/z 335.1254, found 335.1257.

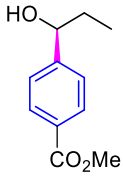
M.P. 68.3 – 69.2 ºC.

$[\alpha]_D^{25}$ = +44 (*c* 0.50, $CHCl_3$).



Scheme S1 Deprotection of the ester **2**

Methyl (*S*)-4-(1-hydroxypropyl)benzoate (3)[4]



(*S*)-1-(4-(Methoxycarbonyl)phenyl)propyl 4-methylbenzoate (31.2 mg, 0.1mmol) was added to a stirred solution of MeONa in MeOH (1 mL, 0.15 M). The mixture was stirred at rt for 3 h. Then the reaction mixture was concentrated to give a residue. The crude mixture was purified by flash column chromatograph to afford **3** as a colorless oil (31.2 mg, 77% yield, 94% ee).

Chiral HPLC (CHIRALPAK AD-H), *i*PrOH-hexane 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 16.149 min, t_R (major) = 17.970 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.94 (m, 2H), 7.41 (d, J = 8.2 Hz, 2H), 4.67 (t, J = 6.5 Hz, 1H), 3.91 (s, 3H), 2.03 (s, 1H), 1.85 – 1.72 (m, 2H), 0.92 (t, J = 7.4 Hz, 3H).

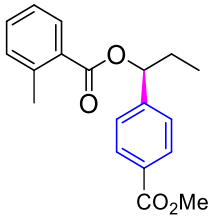
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 149.7, 129.6, 129.1, 125.8, 75.3, 52.1, 31.9, 9.9.

HRMS (ESI) calculated for $C_{11}H_{14}O_3^+$ ($[M+H]^+$) m/z 195.1016, found 195.1014.

$[\alpha]_D^{20}$ = −21 (*c* 0.50, CH_2Cl_2).

$[\alpha]_D^{20}$ = +24.4 (*c* 1.09, CH_2Cl_2) for methyl (*R*)-4-(1-hydroxypropyl)benzoate in the literature.

(*S*)-1-(4-(Methoxycarbonyl)phenyl)propyl 2-methylbenzoate (4)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 2-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **4** as a colorless oil (43.1 mg, 92% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.50 mL/min, 240 nm, t_R (minor) = 15.656 min, t_R (major) = 14.783 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.01 (m, 2H), 7.99 (dd, J = 7.8, 1.5 Hz, 1H), 7.51 – 7.45 (m, 2H), 7.41 (td, J = 7.5, 1.5 Hz, 1H), 7.30 – 7.22 (m, 2H), 5.93 (dd, J = 7.3, 6.1 Hz, 1H), 3.91 (s, 3H), 2.58 (s,

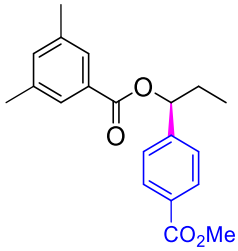
3H), 2.12 – 1.91 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 166.7, 145.8, 140.3, 132.1, 131.7, 130.5, 129.8, 129.6, 129.5, 126.4, 125.7, 77.2, 52.1, 29.5, 21.8, 9.9.

HRMS (ESI) calculated for $C_{19}H_{20}NaO_4^+$ ([M+Na]$^+$) m/z 335.1254, found 335.1253.

$[\alpha]_D^{25}$ = +17 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)propyl 3,5-dimethylbenzoate (5)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 3,5-dimethylbenzoate (68.0 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **5** as an off-white solid (42.0 mg, 86% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 6.741 min, t_R (major) = 5.577 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 2H), 7.69 (d, J = 1.7 Hz, 2H), 7.51 – 7.44 (m, 2H), 7.20 (s, 1H), 5.94 (dd, J = 7.4, 5.9 Hz, 1H), 3.90 (s, 3H), 2.37 (s, 6H), 2.12 – 1.91 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H).

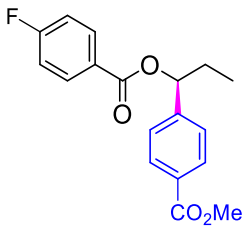
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 166.1, 145.8, 138.1, 134.7, 130.0, 129.7, 129.5, 127.3, 126.3, 77.1, 52.1, 29.5, 21.1, 9.8.

HRMS (ESI) calculated for $C_{20}H_{22}NaO_4^+$ ([M+Na]$^+$) m/z 349.1411, found 349.1413.

M.P. 62.3 – 63.1 ºC.

$[\alpha]_D^{25}$ = +48 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)propyl 4-fluorobenzoate (6)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-fluorobenzoate (65 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **6** as a colorless oil (41.7 mg, 88% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 14.839

min, t_R (major) = 6.414 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 – 8.06 (m, 2H), 8.05 – 7.99 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.16 – 7.08 (m, 2H), 5.93 (dd, *J* = 7.4, 6.1 Hz, 1H), 3.90 (s, 3H), 2.11 – 1.90 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H).

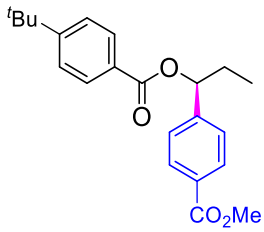
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 165.8 (d, *J* = 254.2 Hz), 164.8, 145.5, 132.2 (d, *J* = 9.4 Hz), 129.8, 129.7, 126.4 (d, *J* = 2.9 Hz), 126.3, 115.6 (d, *J* = 22.0 Hz), 77.5, 52.1, 29.4, 9.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ −105.36.

HRMS (ESI) calculated for $C_{18}H_{17}FNaO_4^+$ ([M+Na]$^+$) m/z 339.1004, found 339.1003.

$[\alpha]_D^{25}$ = +31 (*c* 1.00, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)propyl 4-(*tert*-butyl)benzoate (7)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-(*tert*-butyl)benzoate (76.4 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **7** as a colorless oil (48.4 mg, 91% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 6.229 min, t_R (major) = 5.584 min.

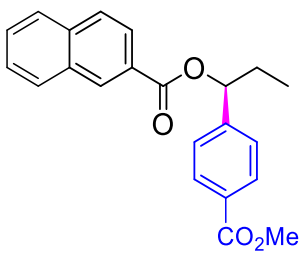
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.99 (m, 4H), 7.51 – 7.44 (m, 4H), 5.95 (dd, *J* = 7.4, 5.9 Hz, 1H), 3.90 (s, 3H), 2.10 – 1.90 (m, 2H), 1.34 (s, 9H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 165.8, 156.8, 145.9, 129.7, 129.5, 129.5, 127.4, 126.2, 125.4, 77.0, 52.1, 35.1, 31.1, 29.5, 9.8.

HRMS (ESI) calculated for $C_{22}H_{26}NaO_4^+$ ([M+Na]$^+$) m/z 377.1724, found 377.1722.

$[\alpha]_D^{25}$ = +78 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)propyl 2-naphthoate (8)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 2-naphthoate (74.6 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **8** as an

off-white solid (45.0 mg, 86% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 14.295 min, t_R (major) = 8.978 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (t, *J* = 1.1 Hz, 1H), 8.10 (dd, *J* = 8.6, 1.7 Hz, 1H), 8.06 – 8.02 (m, 2H), 8.00 – 7.95 (m, 1H), 7.89 (dd, *J* = 8.4, 5.5 Hz, 2H), 7.60 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.56 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.54 – 7.50 (m, 2H), 6.04 – 5.99 (m, 1H), 3.91 (s, 3H), 2.19 – 2.09 (m, 1H), 2.05 – 1.99 (m, 1H), 1.01 (*t*, *J* = 7.4 Hz, 3H).

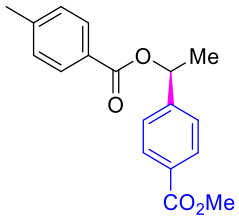
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 165.9, 145.7, 135.6, 132.4, 131.1, 129.8, 129.6, 129.3, 128.3, 128.2, 127.7, 127.4, 126.7, 126.3, 125.2, 77.4, 52.1, 29.5, 9.8.

HRMS (ESI) calculated for $C_{22}H_{20}NaO_4^+$ ([M+Na]$^+$) m/z 371.1254, found 371.1249.

M.P. 113.1 – 113.9 °C.

$[\alpha]_D^{25}$ = +121 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)ethyl 4-methylbenzoate (9)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloroethyl 4-methylbenzoate (59.6 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **9** as a colorless oil (41.0 mg, 92% yield, 93% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 13.100 min, t_R (major) = 7.092 min.

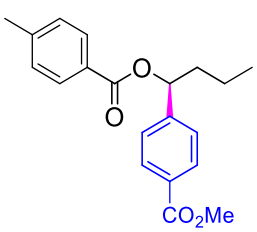
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 8.01 – 7.95 (m, 2H), 7.52 – 7.47 (m, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.14 (q, *J* = 6.6 Hz, 1H), 3.91 (s, 3H), 2.41 (s, 3H), 1.67 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 165.7, 147.0, 143.8, 129.9, 129.6, 129.5, 129.1, 127.4, 125.8, 72.1, 52.1, 22.4, 21.6.

HRMS (ESI) calculated for $C_{18}H_{18}NaO_4^+$ ([M+Na]$^+$) m/z 321.1098, found 321.1098

$[\alpha]_D^{25}$ = +64 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)butyl 4-methylbenzoate (10)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and

1-chlorobutyl 4-methylbenzoate (68.0 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **10** as an off-white solid (45.0 mg, 92% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 15.732 min, t_R (major) = 12.030 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 7.94 (m, 4H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.28 – 7.22 (m, 2H), 6.01 (dd, *J* = 7.9, 5.7 Hz, 1H), 3.90 (s, 3H), 2.41 (s, 3H), 2.08 – 2.00 (m, 1H), 1.89 – 1.83 (m, 1H), 1.48 – 1.33 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).

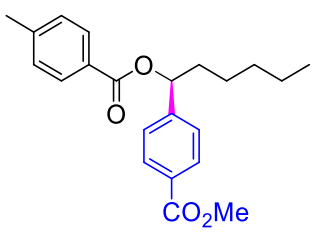
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 165.8, 146.2, 143.8, 129.8, 129.6, 129.5, 129.1, 127.4, 126.2, 75.7, 52.1, 38.6, 21.6, 18.7, 13.8.

HRMS (ESI) calculated for $C_{20}H_{22}NaO_4^+$ ([M+Na]$^+$) m/z 349.1411, found 349.1445.

M.P. 78.5 – 79.2 °C.

$[\alpha]_D^{25}$ = +62 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)hexyl 4-methylbenzoate (11)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chlorohexyl 4-methylbenzoate (76.4 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **11** as a colorless oil (46.0 mg, 87% yield, 93% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 7.057 min, t_R (major) = 5.312 min.

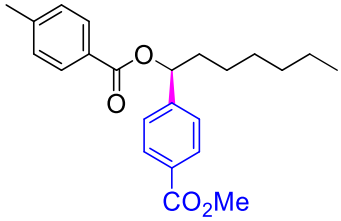
^{1}H NMR (600 MHz, $CDCl_3$) δ8.05 – 8.00 (m, 2H), 8.00 – 7.96 (m, 2H), 7.47 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 6.00 (dd, *J* = 7.7, 5.8 Hz, 1H), 3.90 (s, 3H), 2.41 (s, 3H), 2.09 – 1.99 (m, 1H), 1.92 – 1.86 (m, 1H), 1.35 – 1.25 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 165.8, 146.2, 143.7, 129.8, 129.6, 129.5, 129.1, 127.4, 126.2, 75.9, 52.0, 36.4, 31.4, 25.0, 22.4, 21.6, 13.9.

HRMS (ESI) calculated for $C_{22}H_{26}NaO_4^+$ ([M+Na]$^+$) m/z 377.1724, found 377.1724

$[\alpha]_D^{25}$ = +54 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)heptyl 4-methylbenzoate (12)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloroheptyl 4-methylbenzoate (80.6 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **12** as a colorless oil (46.0 mg, 83% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 6.779 min, t_R (major) = 5.139 min.

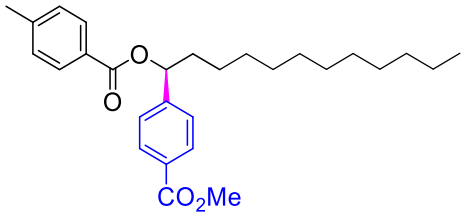
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.99 – 7.94 (m, 2H), 7.47 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 7.8 Hz, 2H), 5.99 (dd, J = 7.8, 5.8 Hz, 1H), 3.90 (s, 3H), 2.41 (s, 3H), 2.07 – 2.01 (m, 1H), 1.92 – 1.86 (m, 1H), 1.37 – 1.20 (m, 8H), 0.86 (t, J = 6.9 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 165.8, 146.2, 143.7, 129.8, 129.6, 129.5, 129.1, 127.4, 126.2, 75.9, 52.0, 36.5, 31.6, 29.0, 25.3, 22.5, 21.6, 14.0.

HRMS (ESI) calculated for $C_{23}H_{28}NaO_4^+$ ([M+Na]$^+$) m/z 391.1880, found 391.1877.

$[\alpha]_D^{25}$ = +47 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)dodecyl 4-methylbenzoate (13)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chlorododecyl 4-methylbenzoate (101.7 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **13** as a colorless oil (52.0 mg, 79% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.5 mL/min, 240 nm, t_R (minor) = 18.667 min, t_R (major) = 11.545 min.

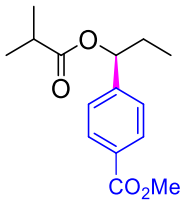
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 7.92 (m, 4H), 7.47 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 5.99 (dd, J = 7.8, 5.8 Hz, 1H), 3.90 (s, 3H), 2.41 (s, 3H), 2.07 – 1.97 (m, 1H), 1.91 – 1.86 (m, 1H), 1.43 – 1.21 (m, 18H), 0.87 (t, J = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.8, 165.8, 146.2, 143.7, 129.8, 129.6, 129.5, 129.1, 127.5, 126.2, 75.9, 52.0, 36.5, 31.9, 29.6, 29.5, 29.4, 29.3, 25.4, 22.6, 21.6, 14.1.

HRMS (ESI) calculated for $C_{28}H_{38}NaO_4^+$ ([M+Na]$^+$) m/z 461.2663, found 461.2674.

$[\alpha]_D^{25}$ = +42 (*c* 0.50, $CHCl_3$).

Methyl (S)-4-(1-(isobutyryloxy)propyl)benzoate (14)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl isobutyrate (49.4 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **14** as a colorless oil (30.6 mg, 77% yield, 84% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.5 mL/min, 240 nm, t_R (minor) = 12.215 min, t_R (major) = 11.048 min.

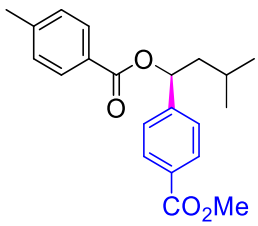
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 7.95 (m, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 5.68 (dd, *J* = 7.5, 6.0 Hz, 1H), 3.90 (s, 3H), 2.59 (hept, *J* = 7.0 Hz, 1H), 1.94 – 1.77 (m, 2H), 1.19 (d, *J* = 7.0 Hz, 3H), 1.15 (d, *J* = 7.1 Hz, 3H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 176.2, 166.8, 146.0, 129.7, 129.5, 126.2, 76.3, 52.1, 34.1, 29.4, 18.9, 18.8, 9.7.

HRMS (ESI) calculated for $C_{15}H_{20}NaO_4^+$ ($[M+Na]^+$) m/z 287.1254, found 287.1252.

$[\alpha]_D^{25}$ = −15 (*c* 0.30, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)-3-methylbutyl 4-methylbenzoate (15)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloro-3-methylbutyl 4-methylbenzoate (72.2 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **15** as a colorless oil (28.1 mg, 55% yield, 93% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.5 mL/min, 240 nm, t_R (minor) = 15.013 min, t_R (major) = 13.108 min.

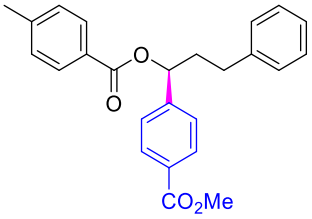
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.00 (m, 2H), 7.99 – 7.91 (m, 2H), 7.53 – 7.44 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.07 (dd, *J* = 9.1, 4.8 Hz, 1H), 3.90 (s, 3H), 2.41 (s, 3H), 2.05 – 1.98 (m, 1H), 1.75 – 1.66 (m, 2H), 0.98 (dd, *J* = 10.2, 6.3 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 165.8, 146.5, 143.8, 129.8, 129.6, 129.5, 129.1, 127.4, 126.2, 74.4, 52.0, 45.7, 24.8, 22.9, 22.2, 21.6.

HRMS (ESI) calculated for $C_{21}H_{24}NaO_4^+$ ($[M+Na]^+$) m/z 363.1567, found 363.1570

$[\alpha]_D^{25}$ = +63 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)-3-phenylpropyl 4-methylbenzoate (16)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloro-3-phenylpropyl 4-methylbenzoate (86.6 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **16** as a colorless oil (55.0 mg, 94% yield, 85% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 21.179 min, t_R (major) = 11.981 min.

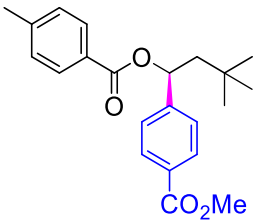
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.92 (m, 2H), 7.91 – 7.85 (m, 2H), 7.42 – 7.35 (m, 2H), 7.18 (dd, *J* = 7.7, 4.4 Hz, 4H), 7.12 – 7.05 (m, 3H), 5.93 (dd, *J* = 8.1, 5.3 Hz, 1H), 3.82 (s, 3H), 2.71 – 2.56 (m, 2H), 2.39 – 2.26 (m, 4H), 2.17 – 2.11 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.7, 165.7, 145.8, 143.9, 140.8, 129.9, 129.7, 129.1, 128.5, 128.3, 127.3, 126.2, 126.1, 75.3, 52.1, 38.0 , 31.7 , 21.7 .

HRMS (ESI) calculated for $C_{25}H_{25}O_4^+$ ($[M+H]^+$) m/z 389.1748, found 389.1743.

$[\alpha]_D^{25}$ = +49 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)-3,3-dimethylbutyl 4-methylbenzoate (17)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloro-3,3-dimethylbutyl 4-methylbenzoate (76.4 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **17** as a colorless oil (17.0 mg, 32% yield, 92% ee).

Chiral HPLC (CHIRALPAK IC-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 10.448 min, t_R (major) = 8.973 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.98 (m, 2H), 7.98 – 7.94 (m, 2H), 7.48 – 7.41 (m, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.12 (dd, *J* = 9.5, 2.8 Hz, 1H), 3.89 (s, 3H), 2.41 (s, 3H), 2.11 (dd, *J* = 14.9, 9.6 Hz, 1H), 1.68 (dd, *J* = 14.9, 2.9 Hz, 1H), 1.01 (s, 9H).

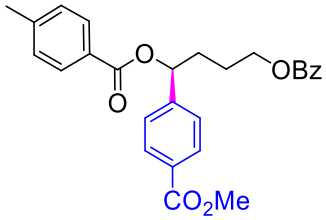
^{13}C NMR (151 MHz, $CDCl_3$) δ 16.8, 165.7, 147.7, 143.8, 129.9, 129.7, 129.4, 129.1, 127.4, 126.0,

74.0, 52.1, 50.2, 30.6, 30.0, 21.7.

HRMS (ESI) calculated for $C_{22}H_{26}NaO_4^+$ ([M+Na]$^+$) m/z 377.1724, found 377.1712.

$[\alpha]_D^{25}$ = +69 (*c* 0.50, $CHCl_3$).

(*S*)-4-(Benzoyloxy)-1-(4-(methoxycarbonyl)phenyl)butyl 4-methylbenzoate (18)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 4-(benzoyloxy)-1-chlorobutyl 4-methylbenzoate (104.0 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **18** as a colorless solid (60.0 mg, 90% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 22.185 min, t_R (major) = 15.762 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 – 8.00 (m, 4H), 8.00 – 7.94 (m, 2H), 7.58 – 7.53 (m, 1H), 7.52 – 7.48 (m, 2H), 7.45 – 7.40 (m, 2H), 7.26 (d, *J* = 2.4 Hz, 2H), 6.09 (dd, *J* = 7.8, 5.5 Hz, 1H), 4.36 (td, *J* = 6.5, 2.8 Hz, 2H), 3.90 (s, 3H), 2.41 (s, 3H), 2.25 – 2.16 (m, 1H), 2.13 – 2.07 (m, 1H), 1.98 – 1.80 (m, 2H).

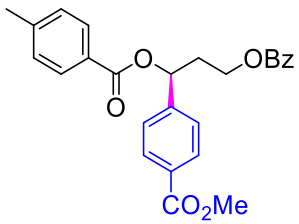
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 166.5, 165.7, 145.5, 143.9, 132.9, 130.1, 129.9, 129.8, 129.7, 129.5, 129.1, 128.3, 127.2, 126.2, 75.3, 64.3, 52.1, 33.0, 24.8, 21.6.

HRMS (ESI) calculated for $C_{27}H_{26}NaO_6^+$ ([M+Na]$^+$) m/z 469.1622, found 469.1620.

M.P. 66.7 – 67.2 °C.

$[\alpha]_D^{25}$ = +48 (*c* 0.50, $CHCl_3$).

(*S*)-3-(Benzoyloxy)-1-(4-(methoxycarbonyl)phenyl)propyl 4-methylbenzoate (19)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 3-(benzoyloxy)-1-chloropropyl 4-methylbenzoate (99.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **19** as a colorless oil (58.0 mg, 89% yield, 88% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 19.429 min, t_R (major) = 15.306 min.

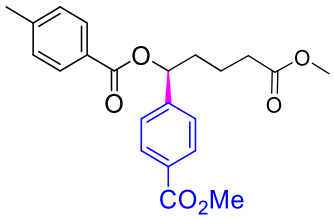
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 8.00 – 7.94 (m, 4H), 7.57 – 7.50 (m, 3H), 7.42 – 7.37 (m, 2H), 7.25 – 7.20 (m, 2H), 6.25 (dd, *J* = 8.0, 5.4 Hz, 1H), 4.53 – 4.37 (m, 2H), 3.90 (s, 3H), 2.62 – 2.49 (m, 1H), 2.46 – 2.34 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 166.3, 165.6, 145.1, 144.0, 132.9, 130.0, 129.9, 129.8, 129.7, 129.5, 129.1, 128.3, 127.0, 126.1, 73.0, 61.0, 52.1, 35.5, 21.6.

HRMS (ESI) calculated for $C_{26}H_{24}NaO_6^+$ ([M+Na]$^+$) m/z 455.1466, found 455.1464

$[\alpha]_D^{25}$ = +49 (*c* 0.50, $CHCl_3$).

(*S*)-5-Methoxy-1-(4-(methoxycarbonyl)phenyl)-5-oxopentyl 4-methylbenzoate (20)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloro-5-methoxy-5-oxopentyl 4-methylbenzoate (85.4 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **20** as a colorless oil (52.0 mg, 90% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 21.246 min, t_R (major) = 14.579 min.

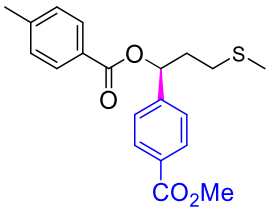
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 6.01 (dd, *J* = 7.9, 5.4 Hz, 1H), 3.90 (s, 3H), 3.64 (s, 3H), 2.41 (s, 3H), 2.36 (t, *J* = 7.4 Hz, 2H), 2.11 – 2.05 (m, 1H), 1.98 – 1.92 (m, 1H), 1.81 – 1.74 (m, 1H), 1.73 – 1.65 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.5, 166.7, 165.7, 145.6, 143.9, 129.9, 129.7, 129.7, 129.1, 127.2, 126.1, 75.3, 52.1, 51.5, 35.8, 33.5, 21.6, 20.8.

HRMS (ESI) calculated for $C_{22}H_{24}NaO_6^+$ ([M+Na]$^+$) m/z 407.1466, found 407.1475.

$[\alpha]_D^{25}$ = +59 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)-3-(methylthio)propyl 4-methylbenzoate (21)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloro-3-(methylthio)propyl 4-methylbenzoate (77.6 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to

afford **21** as a colorless oil (28.0 mg, 52% yield, 86% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 240 nm, t_R (minor) = 12.132 min, t_R (major) = 8.675 min.

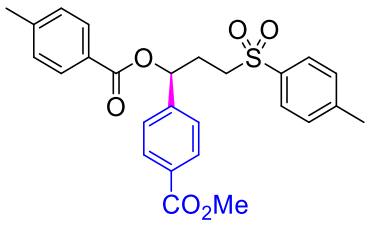
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.28 – 7.23 (m, 2H), 6.13 (dd, *J* = 8.0, 5.3 Hz, 1H), 3.90 (s, 3H), 2.59 – 2.52 (m, 2H), 2.42 (s, 3H), 2.38 – 2.32 (m, 1H), 2.20 – 2.13 (m, 1H), 2.10 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ166.7, 165.6, 145.3, 144.0, 129.9, 129.8, 129.7, 129.2, 127.1, 126.2, 74.6, 52.1, 36.0, 30.0, 21.7, 15.5.

HRMS (ESI) calculated for $C_{21}H_{25}O_4S^+$ ([M+H]$^+$) m/z 381.1131, found 381.1131.

$[\alpha]_D^{25}$ = +95 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxycarbonyl)phenyl)-3-tosylpropyl 4-methylbenzoate (22)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloro-3-tosylpropyl 4-methylbenzoate (110.1 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **22** as an off-white solid (30.0 mg, 43% yield, 87% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 20/80, 1.0 mL/min, 230 nm, t_R (minor) = 31.406 min, t_R (major) = 20.392 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 2H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 7.8 Hz, 2H), 6.05 (dd, *J* = 8.0, 5.0 Hz, 1H), 3.91 (s, 3H), 3.18 – 3.12 (m, 2H), 2.46 – 2.41 (m, 7H), 2.37 – 2.31 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.5, 165.3, 145.0, 144.4, 144.0, 135.7, 130.2, 130.1, 130.0, 129.7, 129.3, 128.0, 126.6, 126.0, 73.5, 52.6, 52.2, 29.6, 21.7, 21.6.

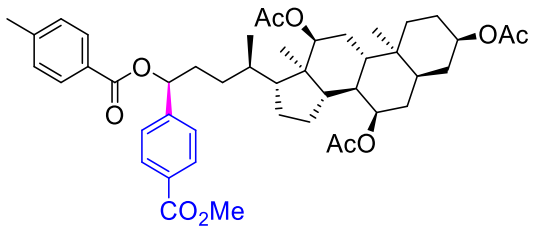
HRMS (ESI) calculated for $C_{26}H_{26}NaO_6S^+$ ([M+Na]$^+$) m/z 489.1343, found 489.1339.

M.P. 147.9 – 149.2 ºC.

$[\alpha]_D^{25}$ = +30 (*c* 0.30, $CHCl_3$).

(3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-17-((2*R*,5*S*)-5-(4-(Methoxycarbonyl)phenyl)-5-((4-methyl benzoyl)oxy)pentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,7,12-tr

iyl triacetate (23)



This compound was prepared according to the general procedure using methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and (3R,5S,7R,8R,9S,10S,12S,13R,14S,17R)-17-((2R)-5-chloro-5-((4-methylbenzoyl)oxy)pentan-2-yl)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthrene-3,7,12-triyl triacetate (202 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **23** as an off-white solid (80.0 mg, 69% yield, 84% de).

Chiral HPLC (CHIRALPAK AD-H), *i*PrOH-hexane 15/85, 1.0 mL/min, 240 nm, t_R (minor) = 52.844 min, t_R (major) = 45.760 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.92 (t, *J* = 6.8 Hz, 1H), 5.09 – 5.03 (m, 1H), 4.87 (q, *J* = 3.1 Hz, 1H), 4.58 – 4.53 (m, 1H), 3.89 (s, 3H), 2.40 (s, 3H), 2.10 (s, 3H), 2.05 (s, 3H), 2.03 – 1.98 (m, 5H), 1.96 – 1.85 (m, 3H), 1.84 – 1.70 (m, 5H), 1.68 – 1.63 (m, 1H), 1.61 – 1.55 (m, 3H), 1.53 – 1.43 (m, 3H), 1.38 – 1.34 (m, 2H), 1.27 – 1.15 (m, 2H), 1.08 – 0.95 (m, 3H), 0.89 (s, 3H), 0.80 (d, *J* = 6.7 Hz, 3H), 0.68 (s, 3H).

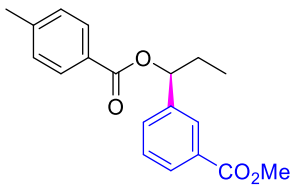
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.5, 170.4, 170.3, 166.7, 165.8, 145.9, 143.8, 129.8, 129.6, 129.6, 129.1, 127.3, 126.3, 76.3, 75.3, 74.0, 70.6, 52.1, 47.4, 45.0, 43.3, 40.9, 37.7, 34.8, 34.6, 34.6, 34.3, 33.0, 31.3, 31.2, 28.8, 27.1, 26.8, 25.5, 22.7, 22.5, 21.6, 21.5, 21.4, 21.4, 17.8, 12.2.

HRMS (ESI) calculated for $C_{46}H_{61}O_{10}^+$ ([M+H]$^+$) m/z 773.4260, found 773.4284.

M.P. 101.5 – 102.7 °C.

$[\alpha]_D^{25}$ = +180 (*c* 0.50, $CHCl_3$).

Methyl (*S*)-3-(1-((4-methylbenzoyl)oxy)propyl)benzoate (24)



This compound was prepared according to the general procedure using methyl 3-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **2** as a colorless oil (33.8 mg, 72% yield, 93% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 14.630

min, t_R (major) = 12.915 min.

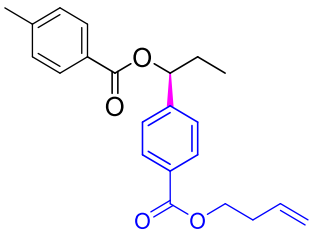
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (t, *J* = 1.8 Hz, 1H), 8.01 – 7.93 (m, 3H), 7.60 (dt, *J* = 7.7, 1.6 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 1H), 7.26 – 7.21 (m, 2H), 5.96 – 5.90 (m, 1H), 3.91 (s, 3H), 2.41 (s, 3H), 2.14 – 2.04 (m, 1H), 2.01 – 1.91 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 165.9, 143.7, 141.2, 131.1, 130.4, 129.7, 129.1, 129.0, 128.5, 127.6, 127.5, 77.2, 52.1, 29.5, 21.7, 9.9.

HRMS (ESI) calculated for $C_{19}H_{20}NaO_4^+$ ([M+Na]$^+$) m/z 335.1254, found 335.1249.

$[\alpha]_D^{25}$ = +45 (*c* 0.60, $CHCl_3$).

But-3-en-1-yl (S)-4-(1-((4-methylbenzoyl)oxy)propyl)benzoate (25)



This compound was prepared according to the general procedure using but-3-en-1-yl 4-bromobenzoate (38.3 mg, 0.15 mmol, 1.0 equiv) and 1-chlorobutyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **25** as a colorless oil (45.6 mg, 86% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 20.135 min, t_R (major) = 18.901 min.

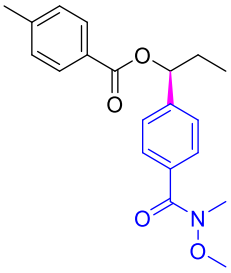
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 15.2, 7.9 Hz, 4H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.29 – 7.20 (m, 2H), 6.01 – 5.78 (m, 2H), 5.23 – 5.03 (m, 2H), 4.36 (t, *J* = 7.5 Hz, 2H), 2.51 (q, *J* = 6.7 Hz, 2H), 2.42 (S, 3H) , 2.00 (m, 2H), 0.97 (t, *J* = 7.3, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.2, 165.9, 145.9, 143.8, 134.0, 129.8, 129.7, 129.6, 129.1, 127.4, 126.2, 117.3, 77.0, 63.9, 33.1, 29.5, 21.7, 9.8.

HRMS (ESI) calculated for $C_{22}H_{25}O_4^+$ ([M+H]$^+$) m/z 353.1748, found 353.1754.

$[\alpha]_D^{25}$ = +53 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Methoxy(methyl)carbamoyl)phenyl)propyl 4-methylbenzoate (26)



This compound was prepared according to the general procedure using 4-bromo-*N*-methoxy-*N*-methylbenzamide (36.6 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **26** as a colorless oil (44.1 mg, 86% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 20/80, 0.5 mL/min, 240 nm, t_R (minor) = 12.460 min, t_R (major) = 13.452 min.

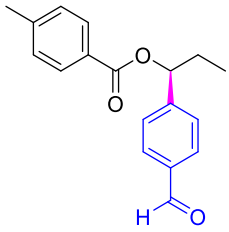
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 6.4 Hz, 2H), 7.44 – 7.40 (m, 2H), 7.24 (d, *J* = 11.6 Hz, 2H), 5.95 – 5.92 (m, 1H), 3.54 (s, 3H), 3.34(s, 3H), 2.41(s, 3H), 2.09 – 1.89 (m, 2H), 0.99 – 0.92 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 165.8, 143.7, 143.3, 133.4, 129.6, 129.1, 128.4, 127.5, 126.0, 77.0, 61.1, 46.0, 29.5, 21.6, 9.8.

HRMS (ESI) calculated for $C_{20}H_{23}NNaO_4^+$ ([M+Na]$^+$) m/z 364.1520, found 364.1511.

$[\alpha]_D^{25}$ = +55 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-Formylphenyl)propyl 4-methylbenzoate (27)



This compound was prepared according to the general procedure using 4-bromobenzaldehyde (27.8 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **27** as an off-white solid (13.6 mg, 32% yield, 94% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 10/90, 0.5 mL/min, 240 nm, t_R (minor) = 13.709 min, t_R (major) = 14.756 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 10.00 (s, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.94 (dd, *J* = 7.4, 5.9 Hz, 1H), 2.42 (s, 3H), 2.09 – 2.03 (m, 1H), 2.02 – 1.92 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H)..

^{13}C NMR (151 MHz, $CDCl_3$) δ 191.8, 165.8, 147.7, 143.9, 135.9, 130.0, 129.7, 129.2, 127.3, 126.9, 77.0, 29.5, 21.7, 9.8.

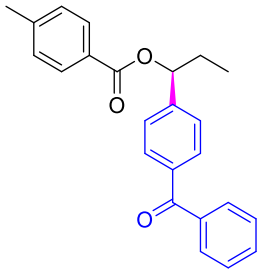
HRMS (ESI) calculated for $C_{18}H_{19}O_3^+$ ([M+H]$^+$) m/z 283.1329, found 283.1315.

M.P. 49.1 – 50.2 °C.

$[\alpha]_D^{25}$ = +82 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-Benzoylphenyl)propyl 4-methylbenzoate (28)

This compound was prepared according to the general procedure using (4-bromophenyl)(phenyl) -methanone (39.2 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl4-methylbenzoate (63.8 mg, 0.3 mmol,



2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **28** as a colorless oil (39.8 mg, 74% yield, 94% ee).

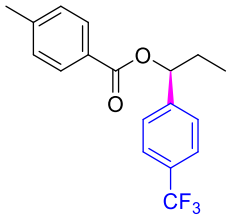
Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 16.655 min, t_R (major) = 24.302 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ, δ 8.00 (d, *J* = 8.2 Hz, 2H), 7.82 – 7.77 (m, 4H), 7.61 – 7.55 (m, 1H), 7.51 (d, *J* = 8.2 Hz, 2H), 7.49 – 7.45 (m, 2H), 7.29 – 7.23 (m, 2H), 5.97 (dd, *J* = 7.4, 6.0 Hz, 1H), 2.42 (s, 3H), 2.14 – 1.93 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 196.2, 165.9, 145.4, 143.8, 137.5, 137.0, 132.4, 130.3, 130.0, 129.7, 129.1, 128.2, 127.4, 126.2, 77.1, 29.5, 21.7, 9.9.

$[\alpha]_D^{25}$ = +63 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Trifluoromethyl)phenyl)propyl 4-methylbenzoate (29)



This compound was prepared according to the general procedure using 1-bromo-4-(trifluoromethyl)benzene (33.8 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **29** as an off-white solid (32.0 mg, 66% yield, 87% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.5 mL/min, 240 nm, t_R (minor) = 8.785 min, t_R (major) = 9.309 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.93 (dd, *J* = 7.5, 6.0 Hz, 1H), 2.42 (s, 3H), 2.12 – 2.02 (m, 1H), 2.00 – 1.91 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 144.8, 143.9, 129.9 (q, *J* = 32.5 Hz), 129.7, 129.1, 127.4, 126.6, 125.4 (q, *J* = 3.8 Hz), 124.1 (d, *J* = 272.0 Hz), 76.9, 29.6, 21.7, 9.8.

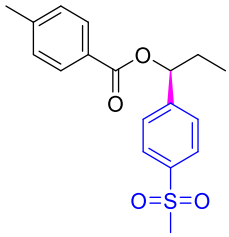
^{19}F NMR (565 MHz, $CDCl_3$) δ −62.55.

HRMS (ESI) calculated for $C_{18}H_{17}F_3O_2^+$ ($[M]^+$) m/z 322.1176, found 322.1166.

M.P. 54.5 – 55.5 °C.

$[\alpha]_D^{25}$ = +65 (*c* 0.30, $CHCl_3$).

(*S*)-1-(4-(Methylsulfonyl)phenyl)propyl 4-methylbenzoate (30)



This compound was prepared according to the general procedure using 1-bromo-4-(methylsulfonyl)benzene (35.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **30** as an off-white solid (46.0 mg, 92% yield, 94% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 20/80, 1.0 mL/min, 254 nm, t_R (minor) = 10.710 min, t_R (major) = 12.578 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.96 (m, 2H), 7.94 – 7.89 (m, 2H), 7.61 – 7.57 (m, 2H), 7.29 – 7.24 (m, 2H), 5.94 (dd, *J* = 7.5, 5.9 Hz, 1H), 3.03 (s, 3H), 2.42 (s, 3H), 2.12 – 2.02 (m, 1H), 2.00 – 1.94 (m, 1H), 0.99 (t, *J* = 7.4 Hz, 3H).

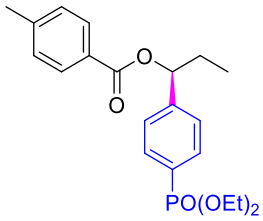
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 147.2, 144.1, 139.8, 129.6, 129.2, 127.6, 127.2, 127.1, 76.7, 44.5, 29.5, 21.7, 9.8.

HRMS (ESI) calculated for $C_{18}H_{20}NaO_4S^+$ ([M+Na]$^+$) m/z 355.0975, found 355.0970.

M.P. 109.5 – 110.7 ºC.

$[\alpha]_D^{25}$ = +64 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(Diethoxyphosphoryl)phenyl)propyl 4-methylbenzoate (31)



This compound was prepared according to the general procedure using diethyl (4-bromophenyl)phosphonate (44.0 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **31** as a colorless oil (52.2 mg, 89% yield, 89% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 20/80, 0.5 mL/min, 240 nm, t_R (minor) = 9.166 min, t_R (major) = 9.785 min.

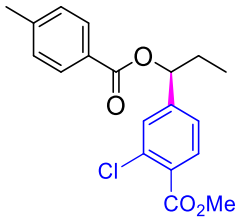
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.78 (dd, *J* = 13.1, 8.0 Hz, 2H), 7.48 (dd, *J* = 8.1, 3.9 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.93 – 5.91 (m, 1H), 4.18 – 4.02 (m, 4H), 2.41 (s, 3H), 2.04 (dq, *J* = 14.8, 7.4 Hz, 1H), 1.97 – 1.90 (m, 1H), 1.31 (t, *J* = 7.0 Hz, 6H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 145.4 (d, *J* = 3.0 Hz), 143.8, 132.0 (d, *J* = 10.4 Hz), 129.6, 129.1, 127.7 (d, *J* = 189.1 Hz), 127.4, 126.4 (d, *J* = 15.4 Hz), 77.0, 62.1 (d, *J* = 5.4 Hz), 29.5, 21.6, 16.3 (d, *J* = 6.6 Hz), 9.8.

HRMS (ESI) calculated for $C_{21}H_{27}NaO_5P^+$ ([M+Na]$^+$) m/z 413.1489, found 413.1487.

$[\alpha]_D^{25}$ = +46 (*c* 0.50, $CHCl_3$).

Methyl (*S*)-2-chloro-4-(1-((4-methylbenzoyl)oxy)propyl)benzoate (32)



This compound was prepared according to the general procedure using methyl 4-bromo-2-chlorobenzoate (37.4 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **32** as a colorless oil (27.1 mg, 52% yield, 94% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.5 mL/min, 240 nm, t_R (minor) = 26.977 min, t_R (major) = 18.218 min.

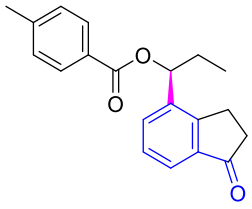
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 – 7.93 (m, 2H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.48 (d, *J* = 1.7 Hz, 1H), 7.33 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 2H), 5.87 (dd, *J* = 7.4, 5.9 Hz, 1H), 3.91 (s, 3H), 2.42 (s, 3H), 2.08 – 1.89 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 165.7, 146.1, 144.0, 134.0, 131.6, 129.6, 129.2, 129.1, 128.8, 127.2, 124.5, 76.2, 52.4, 29.4, 21.6, 9.7.

HRMS (ESI) calculated for $C_{19}H_{19}ClNaO_4^+$ ($[M+Na]^+$) m/z 369.0865, found 369.0850.

$[\alpha]_D^{25}$ = +42 (*c* 0.70, $CHCl_3$).

(*S*)-1-(1-Oxo-2,3-dihydro-1H-inden-4-yl)propyl 4-methylbenzoate (33)



This compound was prepared according to the general procedure using 4-bromo-2,3-dihydro-1H-inden-1-one (31.7 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **33** as an off-white solid (37.5 mg, 81% yield, 93% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 10/90, 0.5 mL/min, 240 nm, t_R (minor) = 14.864 min, t_R (major) = 15.865 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.70 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.66 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.3 Hz, 2H), 6.04 (dd, *J* = 7.7, 6.1 Hz, 1H), 3.42 (ddd, *J* = 17.2, 7.3, 4.4 Hz, 1H), 3.16 (ddd, *J* = 17.3, 7.4, 4.6 Hz, 1H), 2.79 – 2.66 (m, 2H), 2.41 (s, 3H), 2.17 – 1.93 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

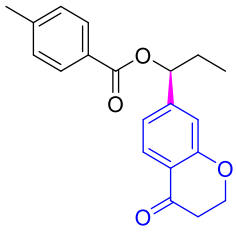
^{13}C NMR (151 MHz, $CDCl_3$) δ 206.8, 165.9, 152.4, 143.9, 138.9, 137.3, 131.8, 129.6, 129.2, 127.9, 127.3, 123.3, 74.2, 36.1, 28.6, 24.4, 21.7, 10.0.

HRMS (ESI) calculated for $C_{20}H_{20}NaO_3^+$ ([M+Na]$^+$) m/z 331.1305, found 331.1299.

M.P. 117.3 – 118.4 °C.

$[\alpha]_D^{25}$ = +101 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-Oxochroman-7-yl)propyl 4-methylbenzoate (34)



This compound was prepared according to the general procedure using 6-bromo-3,4-dihydronaphthalen-1(2H)-one (33.8 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **34** as a colorless oil (38.9 mg, 80% yield, 94% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 10/90, 0.5 mL/min, 240 nm, t_R (minor) = 21.856 min, t_R (major) = 19.450 min.

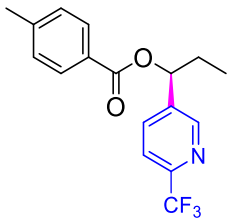
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.87 (d, *J* = 8.1 Hz, 1H), 7.26 (s, 2H), 7.04 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.99 (d, *J* = 1.5 Hz, 1H), 5.85 (dd, *J* = 7.4, 5.8 Hz, 1H), 4.55 – 4.48 (m, 2H), 2.78 (dd, *J* = 7.0, 5.9 Hz, 2H), 2.41 (s, 3H), 2.05 – 1.90 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

.**^{13}C NMR (101 MHz, $CDCl_3$)** δ 191.4, 165.8, 161.8, 149.6, 143.9, 129.7, 129.1, 127.4, 127.3, 120.6, 119.3, 76.8, 67.0, 37.6, 29.4, 21.7, 9.8.

HRMS (ESI) calculated for $C_{20}H_{20}NaO_4^+$ ([M+Na]$^+$) m/z 347.1254, found 347.1254.

$[\alpha]_D^{25}$ = +55 (*c* 0.50, $CHCl_3$).

(*S*)-1-(6-(Trifluoromethyl)pyridin-3-yl)propyl 4-methylbenzoate (35)



This compound was prepared according to the general procedure using 5-bromo-2-(trifluoromethyl)pyridine (33.9 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **35** as a colorless oil (27.2 mg, 56% yield, 94% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 0.3 mL/min, 240 nm, t_R (minor) = 21.498 min, t_R (major) = 22.362 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.79 (d, *J* = 2.1 Hz, 1H), 8.00 – 7.93 (m, 2H), 7.89 (dd, *J* = 8.1, 2.1 Hz, 1H), 7.67 (dd, *J* = 8.1, 0.8 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 5.98 (dd, *J* = 7.5, 6.0 Hz, 1H), 2.42 (s, 3H), 2.15 – 2.07 (m, 1H), 2.03 – 1.96 (m, 1H), 1.01 (t, *J* = 7.4 Hz, 3H).

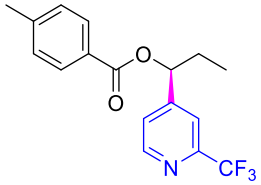
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 148.4, 147.6 (q, *J* = 34.8 Hz), 144.2, 139.6, 135.3, 129.7, 129.2, 126.9, 121.4 (d, *J* = 274.1 Hz), 120.3 (q, *J* = 3.0 Hz), 74.7, 29.4, 21.7, 9.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ −67.89.

HRMS (ESI) calculated for $C_{17}H_{16}F_3NNaO_2^+$ ([M+Na]$^+$) m/z 346.1026, found 346.1006。

$[\alpha]_D^{25}$ = +35 (*c* 1.00, $CHCl_3$).

(*S*)-1-(2-(Trifluoromethyl)pyridin-4-yl)propyl 4-methylbenzoate (36)



This compound was prepared according to the general procedure using 4-bromo-2-(trifluoromethyl)pyridine (30.8 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **36** as a colorless oil (28.6 mg, 59% yield, 93% ee).

Chiral HPLC (CHIRALPAK AD-H), *i*PrOH-hexane 10/90 0.5 mL/min, 240 nm, t_R (minor) = 10.015 min, t_R (major) = 10.699 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.70 (d, *J* = 5.0 Hz, 1H), 8.02 – 7.95 (m, 2H), 7.68 – 7.65 (m, 1H), 7.49 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 5.94 (dd, *J* = 7.6, 5.5 Hz, 1H), 2.43 (s, 3H), 2.09 – 1.95 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

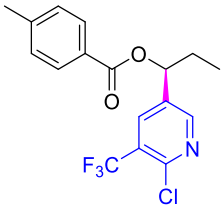
.**^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.7, 151.9, 150.2, 148.6 (q, *J* = 34.6 Hz), 144.4, 129.7, 129.3, 126.7, 123.7, 121.4 (q, *J* = 274.3 Hz), 117.8 (q, *J* = 2.7 Hz), 75.5, 29.3, 21.7, 9.6.

19F NMR (565 MHz, $CDCl_3$) δ −67.98.

HRMS (ESI) calculated for $C_{17}H_{16}F_3NNaO_2^+$ ([M+Na]$^+$) m/z 346.1026, found 346.1017.

$[\alpha]_D^{25}$ = +82 (*c* 0.20, $CHCl_3$).

(*S*)-1-(6-Chloro-5-(trifluoromethyl)pyridin-3-yl)propyl 4-methylbenzoate (37)



This compound was prepared according to the general procedure using 5-bromo-2-chloro-3-(trifluoromethyl)pyridine (39.1 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The

crude mixture was purified by flash column chromatograph to afford **37** as a colorless oil (28.0 mg, 52% yield, 93% ee).

Chiral HPLC (CHIRALPAK AD-H), *i*PrOH-hexane 10/90, 0.5 mL/min, 240 nm, t_R (minor) = 16.390 min, t_R (major) = 15.343 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.62 (d, *J* = 2.3 Hz, 1H), 8.02 (d, *J* = 2.3 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.24 (m, 2H), 5.94 (dd, *J* = 7.7, 6.0 Hz, 1H), 2.42 (s, 3H), 2.11 (dq, *J* = 14.9, 7.4 Hz, 1H), 1.97 (ddd, *J* = 13.9, 7.5, 6.2 Hz, 1H), 1.02 (t, *J* = 7.4 Hz, 3H).

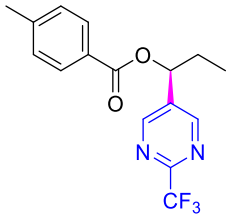
.**^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.7, 150.7, 148.3, 144.4, 135.6, 134.7 (q, *J* = 4.8 Hz), 129.7, 129.3, 126.7, 125.2 (d, *J* = 33.3 Hz), 122.0 (d, *J* = 273.1 Hz), 74.0, 29.2, 21.7, 9.7.

.**^{19}F NMR (565 MHz, $CDCl_3$)** δ −63.63.

HRMS (ESI) calculated for $C_{17}H_{15}ClF_3NNaO_2^+$ ($[M+Na]^+$) m/z 380.0636, found 380.0650.

$[\alpha]_D^{25}$ = +52 (*c* 0.30, $CHCl_3$).

(*S*)-1-(2-(Trifluoromethyl)pyrimidin-5-yl)propyl 4-methylbenzoate (38)



This compound was prepared according to the general procedure using methyl 5-bromo-2-(trifluoromethyl)pyrimidine (34.1 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **38** as a colorless oil (18.5 mg, 38% yield, 91% ee).

Chiral HPLC (CHIRALPAK **A**D-H), *i*PrOH-hexane 10/90, 0.5 mL/min, 240 nm, t_R (minor) = 12.215 min, t_R (major) = 13.073 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (s, 2H), 8.05 – 7.85 (m, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 5.98 (dd, *J* = 7.7, 5.9 Hz, 1H), 2.43 (s, 3H), 2.20 – 2.09 (m, 1H), 2.07 – 1.98 (m, 1H), 1.05 (t, *J* = 7.4 Hz, 3H).

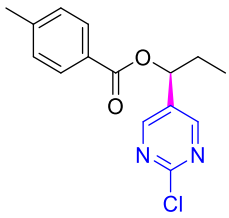
.**^{13}C NMR (151 MHz, $CDCl_3$)** δ 165.7, 156.2, 156.2 (q, *J* = 36.2 Hz), 144.6, 136.3, 129.7, 129.3, 126.4, 119.5 (q, *J* = 274.8 Hz), 72.8, 29.1, 21.7, 9.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ −70.27.

HRMS (ESI) calculated for $C_{16}H_{16}F_3N_2O_2^+$ ($[M+H]^+$) m/z 325.1159, found 325.1145.

$[\alpha]_D^{25}$ = +26 (*c* 0.20, $CHCl_3$).

(S)-1-(2-Chloropyrimidin-5-yl)propyl 4-methylbenzoate (39)



This compound was prepared according to the general procedure using 5-bromo-2-chloropyrimidine (29.0 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **39** as an off-white solid (21.8 mg, 50% yield, 91% ee).

Chiral HPLC (CHIRALPAK IC-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 20.690 min, t_R (major) = 19.202 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 2H), 7.92 (d, *J* = 6.8 Hz, 2H), 7.27 – 7.24 (m, 2H), 5.91 – 5.88 (m, 1H), 2.42 (s, 3H), 2.19 – 2.07 (m, 1H), 2.04 – 1.93 (M, 1H), 1.02 (t, *J* = 7.4 Hz, 3H).

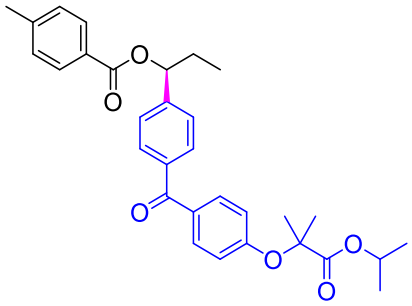
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.8, 160.9, 158.1, 144.4, 132.7, 129.7, 129.3, 126.6, 72.6, 28.9, 21.7, 9.7.

HRMS (ESI) calculated for $C_{15}H_{15}ClN_2NaO_2^+$ ([M+Na]$^+$) m/z 313.0715, found 313.0722

M.P. 111.4 – 111.9 °C.

$[\alpha]_D^{25}$ = +41 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(4-((1-Isopropoxy-2-methyl-1-oxopropan-2-yl)oxy)benzoyl)phenyl)propyl 4-methylbenzoate (40)



This compound was prepared according to the general procedure using isopropyl 2-(4-(4-bromobenzoyl) -phenoxy)-2-methylpropanoate (60.8 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **40** as a colorless oil (58.8 mg, 78% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 10/90, 0.5 mL/min, 240 nm, t_R (minor) = 12.641 min, t_R (major) = 14.731 min.

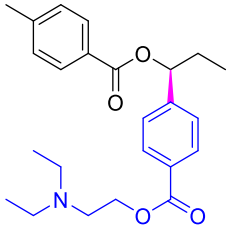
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.1 Hz, 2H), 7.82 – 7.70 (m, 4H), 7.49 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 6.2 Hz, 2H), 6.93 – 6.77 (m, 2H), 5.95 (dd, *J* = 7.4, 6.0 Hz, 1H), 5.09 – 5.05 (M, 1H), 2.41 (s, 3H), 2.14 – 1.93 (m, 2H), 1.65 (s, 6H), 1.19 (d, *J* = 6.2 Hz, 6H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.0, 173.1, 165.9, 159.5, 144.9, 143.8, 137.5, 132.0, 130.4, 129.9, 129.6, 129.4, 129.1, 126.1, 117.1, 79.3, 77.1, 69.2, 29.5, 25.3, 25.3, 21.6, 21.5, 9.8.

HRMS (ESI) calculated for $C_{31}H_{34}NaO_6^+$ ([M+Na]$^+$) m/z 525.2248, found 525.2228.

$[\alpha]_D^{25}$ = +57 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-((2-(Diethylamino)ethoxy)carbonyl)phenyl)propyl 4-methylbenzoate (41)



This compound was prepared according to the general procedure using 2-(diethylamino)ethyl 4-bromobenzoate (45.0 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **41** as a colorless oil (45.9 mg, 77% yield, 92% ee).

Chiral HPLC (CHIRALPAK IC-H), *i*PrOH-hexane 10/90, 0.5 mL/min, 240 nm, t_R (minor) = 21.424 min, t_R (major) = 22.681 min.

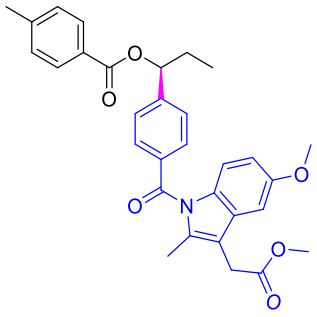
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 8.00 – 7.94 (m, 2H), 7.46 (d, *J* = 8.3 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.93 (dd, *J* = 7.4, 6.0 Hz, 1H), 4.38 (t, *J* = 6.2 Hz, 2H), 2.84 (t, *J* = 6.2 Hz, 2H), 2.62 (q, *J* = 7.1 Hz, 4H), 2.41 (s, 3H), 2.09 – 1.91 (m, 2H), 1.06 (t, *J* = 7.1 Hz, 6H), 0.96 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 165.8, 145.8, 143.8, 129.8, 129.7, 129.6, 129.1, 127.4, 126.2, 77.0, 63.4, 51.0, 47.8, 29.5, 21.7, 12.1, 9.8.

HRMS (ESI) calculated for $C_{24}H_{31}NNaO_4^+$ ([M+Na]$^+$) m/z 420.2146, found 420.2143.

$[\alpha]_D^{25}$ = +48 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(5-Methoxy-3-(2-methoxy-2-oxoethyl)-2-methyl-1H-indole-1-carbonyl)phenyl)propyl 4-methylbenzoate (42)



This compound was prepared according to the general procedure using methyl 2-(1-(4-bromobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl) -acetate (62.5 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **42** as an off-white solid (66.3 mg, 86% yield, 93% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 20/80, 0.5 mL/min, 240 nm, t_R (minor) = 23.605 min, t_R (major) = 27.547 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.3 Hz, 2H), 7.73 – 7.66 (m, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.96 (d, *J* = 2.6 Hz, 1H), 6.91 (d, *J* = 9.0 Hz, 1H), 6.65 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.00 (dd, *J* = 7.4, 5.8 Hz, 1H), 3.83 (s, 3H), 3.70 (s, 3H), 3.67 (s, 2H), 2.43 (s, 3H), 2.35 (s, 3H), 2.13 – 1.94 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H).

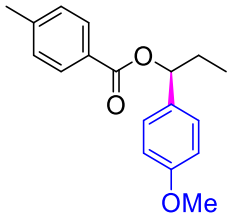
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.4, 169.0, 165.8, 155.9, 145.9, 143.9, 135.9, 134.9, 130.9, 130.5, 129.9, 129.7, 129.1, 127.4, 126.6, 115.0, 112.1, 111.5, 101.2, 76.8, 55.7, 52.1, 30.1, 29.6, 21.7, 13.3, 9.7.

HRMS (ESI) calculated for $C_{31}H_{32}NO_6^+$ ($[M+H]^+$) m/z 514.2225, found 514.2220.

M.P. 108.9 – 109.6 °C.

$[\alpha]_D^{25}$ = +51 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-Methoxyphenyl)propyl 4-methylbenzoate (43)



This compound was prepared according to the general procedure using 1-iodo-4-methoxybenzene (35.1 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **43** as a colorless oil (36.3 mg, 85% yield, 92% ee).

Chiral HPLC (CHIRALPAK IC-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 14.807 min, t_R (major) = 16.387 min.

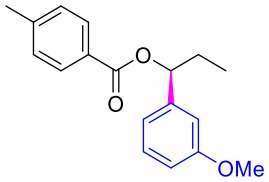
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.37 – 7.32 (m, 2H), 7.25 – 7.21 (m, 2H), 6.91 – 6.86 (m, 2H), 5.86 (t, *J* = 6.9 Hz, 1H), 3.79 (s, 3H), 2.40 (s, 3H), 2.09 – 2.03 (m, 1H), 1.96 – 1.90 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 159.1, 143.4, 132.8, 129.6, 129.0, 127.9, 127.9, 113.7, 77.4, 55.2, 29.4, 21.6, 10.0.

HRMS (ESI) calculated for $C_{18}H_{20}NaO_3^+$ ($[M+Na]^+$) m/z 307.1305, found 307.1310.

$[\alpha]_D^{25}$ = +34 (*c* 1.00, $CHCl_3$).

(*S*)-1-(3-Methoxyphenyl)propyl 4-methylbenzoate (44)



This compound was prepared according to the general procedure using 1-iodo-3-methoxybenzene (35.1 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **44** as a colorless oil (35.5 mg, 83% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.50 mL/min, 240 nm, t_R (minor) = 13.735 min, t_R (major) = 12.642 min.

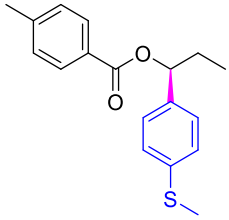
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.28 – 7.22 (m, 3H), 6.99 (dt, *J* = 7.6, 1.3 Hz, 1H), 6.95 (t, *J* = 2.1 Hz, 1H), 6.83 – 6.81 (m, 1H), 5.88 (dd, *J* = 7.4, 6.1 Hz, 1H), 3.80 (s, 3H), 2.41 (s, 3H), 2.08 – 2.01 (m, 1H), 1.98 – 1.90 (m, 1H), 0.96 (t, *J* = 7.4 , 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 159.6, 143.5, 142.4, 129.7, 129.4, 129.0, 127.8, 118.8, 112.9, 112.3, 77.5, 55.2, 29.6, 21.6, 9.9.

HRMS (ESI) calculated for $C_{18}H_{20}NaO_3^+$ ([M+Na]$^+$) m/z 307.1305, found 307.1308.

$[\alpha]_D^{25}$ = +53 (*c* 0.60, $CHCl_3$).

(*S*)-1-(4-(Methylthio)phenyl)propyl 4-methylbenzoate (45)



This compound was prepared according to the general procedure using (4-iodophenyl)(methyl)sulfane (37.5 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **45** as a colorless oil (38.8 mg, 86% yield, 93% ee).

Chiral HPLC (CHIRALPAK IC-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 254 nm, t_R (minor) = 19.187 min, t_R (major) = 22.205 min.

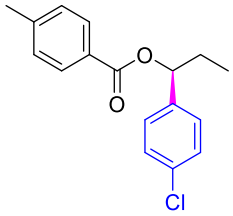
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.2 Hz, 2H), 7.35 – 7.32 (m, 2H), 7.25 – 7.21 (m, 4H), 5.86 (d, *J* = 6.1 Hz, 1H), 2.47 (s, 3H), 2.41 (s, 3H), 2.11 – 2.00 (m, 1H), 1.93 (q, *J* = 6.9 Hz, 1H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.9, 143.6, 137.9, 137.6, 129.6, 129.0, 127.7, 127.0, 126.6, 77.3, 29.4, 21.6, 15.8, 9.9.

HRMS (ESI) calculated for $C_{18}H_{20}NaO_2S^+$ ([M+Na]$^+$) m/z 323.1077, found 323.1072.

$[\alpha]_D^{25}$ = +44 (*c* 1.00, $CHCl_3$).

(*S*)-1-(4-Chlorophenyl)propyl 4-methylbenzoate (46)



This compound was prepared according to the general procedure using 1-chloro-4-iodobenzene (35.8 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **46** as an off-white solid (37.4 mg, 86% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.5 mL/min, 240 nm, t_R (minor) = 10.086 min, t_R (major) = 10.628 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ7.96 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.29 (m, 4H), 7.24 (d, *J* = 7.9 Hz, 2H), 5.86 (t, *J* = 6.8 Hz, 1H), 2.41 (s, 3H), 2.04 (dq, *J* = 14.7, 7.3 Hz, 1H), 1.92 (dt, *J* = 13.9, 7.1 Hz, 1H), 0.96 (t, *J* = 7.4 Hz, 3H).

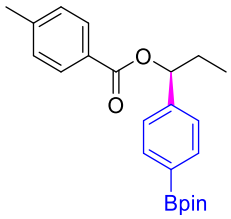
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 143.7, 139.3, 133.5, 129.6, 129.1, 128.6, 127.8, 127.5, 76.9, 29.5, 21.7, 9.9.

HRMS (ESI) calculated for $C_{17}H_{17}ClNaO_2^+$ ($[M+Na]^+$) m/z 311.0810, found 311.0808.

M.P. 64.5 – 65.8 °C.

$[\alpha]_D^{25}$ = +33 (*c* 1.00, $CHCl_3$).

(*S*)-1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propyl 4-methylbenzoate (47)



This compound was prepared according to the general procedure using 2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (49.5 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **47** as a colorless oil (31.4 mg, 55 % yield, 92% ee).

Chiral HPLC (CHIRALPAK IC-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 11.851 min, t_R (major) = 10.320 min.

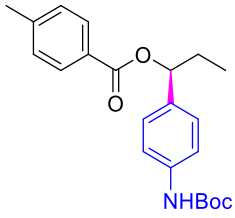
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.90 (dd, *J* = 7.3, 6.1 Hz, 1H), 2.41 (s, 3H), 2.08 – 2.02 (m, 1H), 1.98 – 1.92 (m, 1H), 1.33 (s, 12H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 143.8, 143.5, 134.9, 129.6, 129.0, 127.7, 125.7, 83.7, 77.6, 29.5, 24.8, 24.8, 21.6, 9.9.

HRMS (ESI) calculated for $C_{23}H_{29}BNaO_4^+$ ([M+Na]$^+$) m/z 403.2052, found 403.2062.

$[\alpha]_D^{25}$ = +44 (*c* 0.30, $CHCl_3$).

(*S*)-1-(4-((tert-Butoxycarbonyl)amino)phenyl)propyl 4-methylbenzoate (48)



This compound was prepared according to the general procedure using *tert*-butyl (4-iodophenyl)carbamate (47.9 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **48** as an off-white solid (39.9 mg, 72% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 10/90, 0.5 mL/min, 240 nm, t_R (minor) = 12.722 min, t_R (major) = 23.701 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.33 (s, 4H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.48 (s, 1H), 5.85 (t, *J* = 6.8 Hz, 1H), 2.40 (s, 3H), 2.07 – 2.01 (m, 1H), 1.97 – 1.86 (m, 1H), 1.51 (s, 9H), 0.94 (t, *J* = 7.4 Hz, 3H).

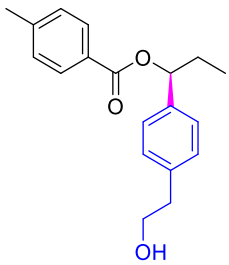
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 152.7, 143.5, 137.9, 135.3, 129.6, 129.0, 127.8, 127.3, 118.5, 80.5, 77.4, 29.4, 28.3, 21.6, 9.9.

HRMS (ESI) calculated for $C_{22}H_{27}NNaO_4^+$ ([M+Na]$^+$) m/z 392.1833, found 392.1825.

M.P. 106.1 – 106.9 °C.

$[\alpha]_D^{25}$ = +24 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-(2-Hydroxyethyl)phenyl)propyl 4-methylbenzoate (49)



This compound was prepared according to the general procedure using 2-(4-iodophenyl)ethan-1-ol (37.2 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **49** as a colorless oil (31.8 mg, 71% yield, 92% ee).

Chiral HPLC (CHIRALPAK IC-H), *i*PrOH-hexane 10/90, 0.5 mL/min, 240 nm, t_R (minor) = 26.157 min, t_R (major) = 25.058 min.

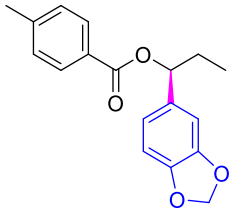
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.93 (m, 2H), 7.39 – 7.33 (m, 2H), 7.25 – 7.18 (m, 4H), 5.88 (dd, *J* = 7.5, 6.1 Hz, 1H), 3.84 (t, *J* = 6.5 Hz, 2H), 2.85 (t, *J* = 6.6 Hz, 2H), 2.41 (s, 3H), 2.06 (dt, *J* = 13.8, 7.4 Hz, 1H), 1.97 – 1.89 (m, 1H), 0.96 (t, *J* = 7.4 Hz, 3H).

.**^{13}C NMR (151 MHz, $CDCl_3$)** δ 166.0, 143.5, 139.0, 138.0, 129.6, 129.0, 129.0, 127.8, 126.7, 77.5, 63.5, 38.8, 29.5, 21.6, 10.0.

HRMS (ESI) calculated for $C_{19}H_{22}NaO_3^+$ ([M+Na]$^+$) m/z 321.1462, found 321.1464.

$[\alpha]_D^{25}$ = +47 (*c* 0.30, $CHCl_3$).

(*S*)-1-(Benzo[d][1,3]dioxol-5-yl)propyl 4-methylbenzoate (50)



This compound was prepared according to the general procedure using 5-iodobenzo[d][1,3]dioxole (37.2 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **50** as a colorless oil (31.8 mg, 71% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.5 mL/min, 240 nm, t_R (minor) = 15.709 min, t_R (major) = 13.756 min.

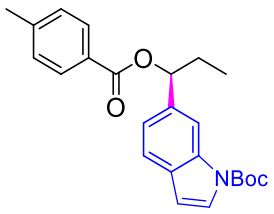
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98 – 7.93 (m, 2H), 7.25 – 7.20 (m, 2H), 6.91 (d, *J* = 1.7 Hz, 1H), 6.88 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.96 5.90 (m, 2H), 5.80 (t, *J* = 6.9 Hz, 1H), 2.40 (s, 3H), 2.07 – 1.99 (m, 1H), 1.92 – 1.85 (m, 1H), 0.94 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 147.7, 147.1, 143.5, 134.7, 129.6, 129.0, 127.8, 120.3, 108.1, 106.9, 101.0, 77.6, 29.5, 21.6, 10.0.

HRMS (ESI) calculated for $C_{18}H_{18}NaO_4^+$ ([M+Na]$^+$) m/z 321.1098, found 321.1090.

$[\alpha]_D^{25}$ = +22 (*c* 0.30, $CHCl_3$).

***tert*-Butyl (*S*)-6-(1-((4-methylbenzoyl)oxy)propyl)-1*H*-indole-1-carboxylate (51)**



This compound was prepared according to the general procedure using *tert*-butyl 6-iodo-1H-indole-1-carboxylate (51.5 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **51** as a colorless oil (40.2 mg, 68% yield, 90% ee)

Chiral HPLC (CHIRALPAK IC-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 13.526 min, t_R (major) = 21.453 min.

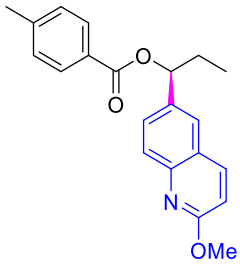
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (s, 1H), 8.03 – 7.96 (m, 2H), 7.58 (d, *J* = 3.7 Hz, 1H), 7.52 (d, *J* = 8.1 Hz, 1H), 7.31 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 3.7 Hz, 1H), 6.01 (t, *J* = 6.9 Hz, 1H), 2.40 (s, 3H), 2.19 – 2.11 (m, 1H), 2.01 (tt, *J* = 13.8, 7.4 Hz, 1H), 1.67 (s, 9H), 0.99 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 149.7, 143.4, 137.0, 135.1, 130.3, 129.7, 129.0, 127.9, 126.3, 121.4, 120.8, 113.5, 107.1, 83.7, 78.4, 29.9, 28.2, 21.6, 10.2.

HRMS (ESI) calculated for $C_{24}H_{27}NNaO_4^+$ ([M+Na]$^+$) m/z 416.1833, found 416.1840.

$[\alpha]_D^{25}$ = +40 (*c* 1.00, $CHCl_3$).

(*S*)-1-(2-Methoxyquinolin-6-yl)propyl 4-methylbenzoate (52)



This compound was prepared according to the general procedure using 6-iodo-2-methoxyquinoline (42.8 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **52** as an off-white solid (25.7 mg, 51% yield, 93% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 12.238 min, t_R (major) = 14.084 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.1 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.6 Hz, 1H), 7.73 (d, *J* = 2.0 Hz, 1H), 7.69 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.25 (d, *J* = 7.9 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.04 (t, *J* = 6.8 Hz, 1H), 4.06 (s, 3H), 2.41 (s, 3H), 2.17 – 2.11 (m, 1H), 2.08 – 1.97 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H).

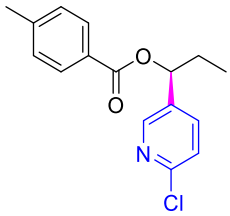
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 162.5, 146.3, 143.6, 138.7, 136.3, 129.7, 129.1, 127.8, 127.7, 127.5, 125.3, 124.7, 113.3, 77.5, 53.4, 29.5, 21.6, 10.0.

HRMS (ESI) calculated for $C_{21}H_{21}NNaO_3^+$ ([M+Na]$^+$) m/z 358.1414, found 358.1411.

M.P. 58.8 – 59.7 °C.

$[\alpha]_D^{25}$ = +104 (*c* 0.20, $CHCl_3$).

(*S*)-1-(6-Chloropyridin-3-yl)propyl 4-methylbenzoate (53)



This compound was prepared according to the general procedure using 2-chloro-5-iodopyridine (35.9 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **53** as an off-white solid (12.2 mg, 28% yield, 92% ee).

Chiral HPLC (CHIRALPAK AD-H), *i*PrOH-hexane 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 10.567 min, t_R (major) = 14.891 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.45 (d, *J* = 2.5 Hz, 1H), 7.98 – 7.88 (m, 2H), 7.68 (dd, *J* = 8.2, 2.5 Hz, 1H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.89 (dd, *J* = 7.5, 6.2 Hz, 1H), 2.41 (s, 3H), 2.13 – 2.03 (m, 1H), 1.99 – 1.90 (m, 1H), 0.98 (t, *J* = 7.4 Hz, 3H).

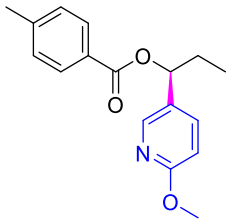
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 150.9, 148.2, 144.1, 137.0, 135.2, 129.6, 129.2, 127.1, 124.1, 74.6, 29.2, 21.7, 9.7.

HRMS (ESI) calculated for $C_{16}H_{16}ClNNaO_2^+$ ([M+Na]$^+$) m/z 312.0762, found 312.0770.

M.P. 68.1 – 68.9 °C.

$[\alpha]_D^{25}$ = +54 (*c* 0.30, $CHCl_3$).

(*S*)-1-(6-Methoxypyridin-3-yl)propyl 4-methylbenzoate (54)



This compound was prepared according to the general procedure using 5-iodo-2-methoxypyridine (35.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **54** as a colorless oil (22.3 mg, 52% yield, 92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.5 mL/min, 240 nm, t_R (minor) = 12.733 min, t_R (major) = 11.784 min.

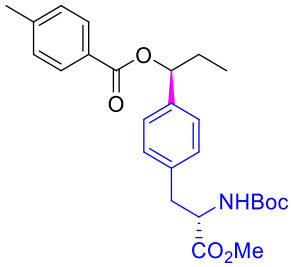
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.23 (d, *J* = 2.5 Hz, 1H), 7.97 – 7.90 (m, 2H), 7.63 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.22 (d, *J* = 8.0 Hz, 2H), 6.73 (d, *J* = 8.5 Hz, 1H), 5.86 (t, *J* = 6.9 Hz, 1H), 3.92 (s, 3H), 2.39 (s, 3H), 2.11 – 2.04 (m, 1H), 1.95 – 1.88 (m, 1H), 0.95 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 163.9, 145.5, 143.7, 137.1, 129.6, 129.0, 128.9, 127.5, 110.8, 75.2, 53.4, 29.1, 21.6, 9.9.

HRMS (ESI) calculated for $C_{17}H_{19}NNaO_3^+$ ([M+Na]$^+$) m/z 308.1258, found 308.1265

$[\alpha]_D^{25}$ = +30 (*c* 0.40, $CHCl_3$).

(*S*)-1-(4-((*S*)-2-((*tert*-Butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl)propyl 4-methylbenzoate (55)



This compound was prepared according to the general procedure using methyl (*S*)-2-((*tert*-butoxycarbonyl)amino)-3-(*p*-tolyl) -propanoate (44.0 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **55** as a colorless oil (41.0 mg, 60% yield, 93% de).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 240 nm, t_R (minor) = 24.873 min, t_R (major) = 22.533 min.

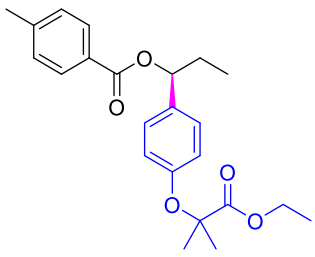
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 7.11 (dd, *J* = 8.2, 3.4 Hz, 2H), 5.90 – 5.87 (m, 1H), 4.98 (d, *J* = 8.4 Hz, 1H), 4.58 (q, *J* = 6.8 Hz, 1H), 3.69 (s, 3H), 3.11 – 3.08 (m, 1H), 3.04 – 2.99 (m, 1H), 2.40 (s, 3H), 2.06 – 2.00 (m, 1H), 1.95 – 1.88 (m, 1H), 1.40 (d, *J* = 5.2 Hz, 9H), 0.94 (t, *J* = 7.4 Hz, 3H).

.**^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.3, 165.9, 155.0, 143.5, 139.4, 135.5, 129.6, 129.3, 129.0, 127.7, 126.6, 79.9, 77.3, 54.3, 52.2, 38.0, 29.5, 28.2, 21.6, 9.9.

HRMS (ESI) calculated for $C_{26}H_{33}NNaO_6^+$ ([M+Na]$^+$) m/z 478.2201, found 478.2185.

$[\alpha]_D^{25}$ = +82 (*c* 0.50, $CHCl_3$).

(*S*)-1-(4-((1-Ethoxy-2-methyl-1-oxopropan-2-yl)oxy)phenyl)propyl 4-methylbenzoate (56)



This compound was prepared according to the general procedure using ethyl 2-(4-iodophenoxy)-2-methylpropanoate (50.1 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **56** as a colorless oil (45.0 mg, 78% yield, 91% ee).

Chiral HPLC (CHIRALPAK IC-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 230 nm, t_R (minor) = 25.450 min, t_R (major) = 24.266 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.6 Hz, 2H), 7.23 (d, *J* = 7.9 Hz,

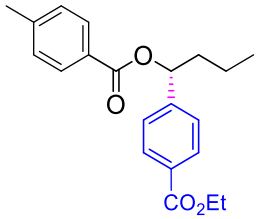
2H), 6.80 (d, J = 8.6 Hz, 2H), 5.86 (t, J = 6.8 Hz, 1H), 4.22 (q, J = 7.1 Hz, 2H), 2.40 (s, 3H), 2.03 (dp, J = 14.7, 7.4 Hz, 1H), 1.95 – 1.82 (m, 1H), 1.58 (d, J = 2.7 Hz, 6H), 1.22 (t, J = 7.1 Hz, 3H), 0.92 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.2, 166.0, 155.0, 143.5 134.2, 129.6, 129.0, 127.9, 127.4, 118.8, 79.1, 77.2, 61.4, 29.4, 25.4, 25.3, 21.6, 14.0, 10.0.

HRMS (ESI) calculated for $C_{23}H_{28}NaO_5^+$ ([M+Na]$^+$) m/z 407.1829, found 407.1813.

$[\alpha]_D^{25}$ = +29 (c 0.50, $CHCl_3$).

(*R*)-1-(4-(Ethoxycarbonyl)phenyl)butyl 4-methylbenzoate (57)



This compound was prepared according to the general procedure using (*S,S*)-**L1**, ethyl 4-bromobenzoate (34.4 mg, 0.15 mmol, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (68.0 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **57** as a colorless oil (47.0 mg, 92% yield, −93% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.5 mL/min, 240 nm, t_R (minor) = 13.859 min, t_R (major) = 16.787 min.

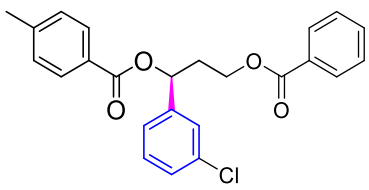
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, J = 8.1 Hz, 2H), 7.97 (d, J = 7.9 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.25 (d, J = 7.9 Hz, 2H), 6.08 – 5.96 (m, 1H), 4.36 (q, J = 7.1 Hz, 2H), 2.41 (s, 3H), 2.07 – 2.00 (m, 1H), 1.90 – 1.84 (m, 1H), 1.49 – 1.33 (m, 5H), 0.95 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.3, 165.8, 146.1, 143.8, 129.9, 129.7, 129.6, 129.1, 127.5, 126.2, 75.7, 60.9, 38.6, 21.7, 18.7, 14.3, 13.8.

HRMS (ESI) calculated for $C_{21}H_{24}NaO_4^+$ ([M+Na]$^+$) m/z 363.1567, found 363.1564.

$[\alpha]_D^{25}$ = −61 (c 0.50, $CHCl_3$).

(*S*)-3-(Benzoyloxy)-1-(3-chlorophenyl)propyl 4-methylbenzoate (58)



This compound was prepared according to the general procedure using 1-chloro-3-iodobenzene (35.8 mg, 0.15 mmol, 1.0 equiv) and 3-(benzoyloxy)-1-chloropropyl 4-methylbenzoate (99.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **58** as a colorless oil (50.3 mg, 82% yield, 87% ee).

Chiral HPLC (CHIRALCEL AD-H), *i*PrOH-hexane 10/90, 1.0 mL/min, 240 nm, t_R (minor) = 9.711 min, t_R (major) = 11.333 min.

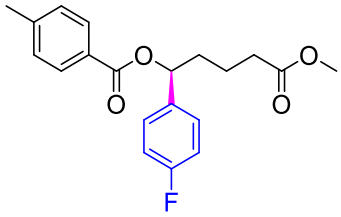
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.96 – 7.93 (m, 4H), 7.56 – 7.50 (m, 1H), 7.44 – 7.37 (m, 3H), 7.32 – 7.28 (m, 1H), 7.26 – 7.17 (m, 4H), 6.14 (dd, *J* = 8.1, 5.4 Hz, 1H), 4.47 – 4.37 (m, 2H), 2.54 – 2.48 (m, 1H), 2.42 – 2.32 (m, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 165.6, 144.0, 142.2, 134.6, 133.0, 130.0, 129.9, 129.7, 129.6, 129.2, 128.3, 127.0, 126.4, 124.5, 72.8, 61.1, 35.6, 21.7.

HRMS (ESI) calculated for $C_{24}H_{21}ClNaO_4^+$ ([M+Na]$^+$) m/z 431.1021, found 431.1023.

$[\alpha]_D^{25}$ = +26 (*c* 0.90, $CHCl_3$).

(*S*)-1-(4-Fluorophenyl)-5-methoxy-5-oxopentyl 4-methylbenzoate (59)



This compound was prepared according to the general procedure using methyl 1-fluoro-4-iodobenzene (33.3 mg, 0.15 mmol, 1.0 equiv) and 1-chloro-5-methoxy-5-oxopentyl 4-methylbenzoate (85.4 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **59** as a colorless oil (37.2 mg, 72% yield, 91% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 5/95, 0.5 mL/min, 210 nm, t_R (minor) = 17.734 min, t_R (major) = 16.456 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.92 (m, 2H), 7.43 – 7.35 (m, 2H), 7.26 – 7.21 (m, 2H), 7.07 – 6.99 (m, 2H), 5.95 (dd, *J* = 7.8, 5.8 Hz, 1H), 3.65 (s, 3H), 2.41 (s, 3H), 2.36 (t, *J* = 7.4 Hz, 2H), 2.11 – 2.03 (m, 1H), 1.95 – 1.90 (m, 1H), 1.80 – 1.72 (m, 1H), 1.70 – 1.64 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 173.5, 165.8, 162.3 (d, *J* = 246.3 Hz), 143.8, 136.3 (d, *J* = 3.2 Hz) 129.6, 129.1, 128.1 (d, *J* = 8.0 Hz), 127.4, 115.4 (d, *J* = 21.5 Hz), 75.2, 51.5, 35.8, 33.5, 21.6, 20.9.

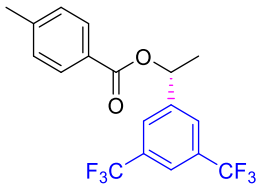
^{19}F NMR (565 MHz, $CDCl_3$) δ −114.23.

HRMS (ESI) calculated for $C_{20}H_{21}FNaO_4^+$ ([M+Na]$^+$) m/z 367.1317, found 367.1315.

$[\alpha]_D^{25}$ = +43 (*c* 0.20, $CHCl_3$).

(*R*)-1-(3,5-Bis(trifluoromethyl)phenyl)ethyl 4-methylbenzoate (60)

This compound was prepared according to the general procedure using (*S,S*)-**L1,** methyl 1-bromo-3,5-bis(trifluoromethyl)benzene (44.0 mg, 0.15 mmol, 1.0 equiv) and 1-chloroethyl



4-methylbenzoate (59.6 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **60** as a colorless oil (40.6 mg, 72% yield, −92% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 0/100, 0.5 mL/min, 240 nm, t_R (minor) = 35.830 min, t_R (major) = 37.689 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.88 (d, *J* = 1.6 Hz, 2H), 7.82 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.19 (q, *J* = 6.7 Hz, 1H), 2.43 (s, 3H), 1.71 (d, *J* = 6.7 Hz, 3H).

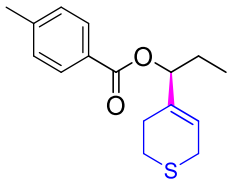
^{13}C NMR (151 MHz, $CDCl_3$) δ 165.6, 144.6, 144.2, 132.0 (q, *J* = 33.3 Hz), 129.7, 129.2, 126.9, 126.2 (d, *J* = 3.9 Hz), 123.2 (q, *J* = 272.9 Hz), 121.9 (dt, *J* = 7.5, 3.8 Hz), 71.3, 22.4, 21.7.

^{19}F NMR (565 MHz, $CDCl_3$) δ −62.83.

HRMS (ESI) calculated for $C_{18}H_{15}F_6O_2^+$ ($[M+H]^+$) m/z 377.0971, found 377.0979.

$[\alpha]_D^{25}$ = −65 (*c* 0.50, $CHCl_3$).

(*S*) -1-(3,6-Dihydro-2H-thiopyran-4-yl)propyl 4-methylbenzoate (61)



This compound was prepared according to the general procedure using 3,6-dihydro-2H-thiopyran-4-yl trifluoromethanesulfonate (37.2 mg, 0.15 mmol, 1.0 equiv) and 1-chlorobutyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **61** as a colorless oil (25.0 mg, 60% yield, 90% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 2/98, 0.5 mL/min, 240 nm, t_R (minor) = 18.318 min, t_R (major) = 19.630 min.

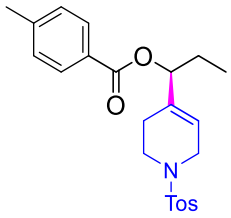
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 – 7.84 (m, 2H), 7.24 (d, *J* = 7.9 Hz, 2H), 5.95 (tt, *J* = 4.0, 1.8 Hz, 1H), 5.28 (t, *J* = 6.9 Hz, 1H), 3.30 – 3.07 (m, 2H), 2.79 – 2.67 (m, 2H), 2.44 – 2.28 (m, 5H), 1.88 – 1.70 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 143.5, 136.7, 129.6, 129.0, 127.8, 121.7, 80.0, 25.7, 25.3, 25.0, 24.8, 21.6, 9.9.

HRMS (ESI) calculated for $C_{16}H_{20}NaO_2S^+$ ($[M+Na]^+$) m/z 299.1077, found 299.1063.

$[\alpha]_D^{25}$ = +23 (*c* 0.20, $CHCl_3$).

(*S*) -1-(1-Tosyl-1,2,3,6-tetrahydropyridin-4-yl)propyl 4-methylbenzoate (62)



This compound was prepared according to the general procedure using 1-Tosyl-1,2,3,6-tetrahydropyridin-4-yl trifluoromethanesulfonate (57.8 mg, 0.15 mmol, 1.0 equiv) and 1-chlorobutyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **62** as a colorless oil (44.2 mg, 71% yield, 88% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 10/90, 0.5 mL/min, 240 nm, t_R (minor) = 28.104 min, t_R (major) = 30.808 min.

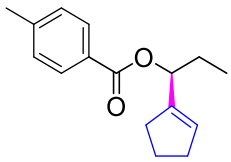
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 5.68 (t, *J* = 3.6 Hz, 1H), 5.26 (t, *J* = 6.8 Hz, 1H), 3.70 – 3.51 (m, 2H), 3.30 (dt, *J* = 11.3, 5.4 Hz, 1H), 3.07 (dt, *J* = 11.8, 5.9 Hz, 1H), 2.40 (s, 3H), 2.40 (s, 3H), 2.26 – 2.22(m, 2H), 1.80 – 1.66 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.7, 143.7, 143.6, 134.7, 133.0, 129.6, 129.5, 129.1, 127.6, 127.5, 119.8, 78.1, 44.5, 42.6, 25.5, 24.3, 21.6, 21.4, 9.7.

HRMS (ESI) calculated for $C_{23}H_{27}NNaO_4S^+$ ([M+Na]$^+$) m/z 436.1553, found 436.1536.

$[\alpha]_D^{25}$ = +58 (*c* 0.50, $CHCl_3$).

(*S*)-1-(Cyclopent-1-en-1-yl)propyl 4-methylbenzoate (63)



This compound was prepared according to the general procedure using cyclopent-1-en-1-yl trifluoromethanesulfonate (32.4 mg, 0.15 mmol, 1.0 equiv) and 1-chlorobutyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **63** as a colorless oil (29.8 mg, 81% yield, 85% ee).

Chiral HPLC (CHIRALCEL OD-H), hexane, 0.5 mL/min, 240 nm, t_R (minor) = 30.963 min, t_R (major) = 32.054 min.

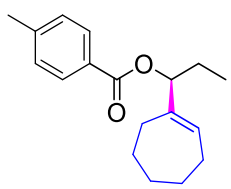
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 5.71 – 5.64 (m, 1H), 5.59 (t, *J* = 6.6 Hz, 1H), 2.41 (s, 3H), 2.38 – 2.30 (m, 4H), 1.93 – 1.85 (m, 2H), 1.84 – 1.77 (m, 2H), 0.93 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 143.4, 142.4, 129.6, 129.0, 128.0, 127.2, 74.8, 32.2, 31.6, 26.1, 23.1, 21.6, 9.7.

HRMS (ESI) calculated for $C_{16}H_{20}NaO_2^+$ ([M+Na]$^+$) m/z 267.1356, found 267.1357.

$[\alpha]_D^{25}$ = +3.1 (*c* 0.70, $CHCl_3$).

(*S*)-1-(Cyclohept-1-en-1-yl)propyl 4-methylbenzoate (64)



This compound was prepared according to the general procedure using cyclohept-1-en-1-yl trifluoromethanesulfonate (36.6 mg, 0.15 mmol, 1.0 equiv) and 1-chlorobutyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **64** as a colorless oil (20.8 mg, 51% yield, 88% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 0.5/99.5, 0.5 mL/min, 240 nm, t_R (minor) = 12.383 min, t_R (major) = 13.028 min.

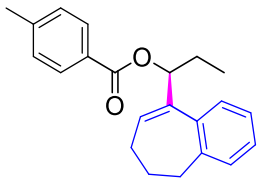
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.0 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 5.91 (t, *J* = 6.5 Hz, 1H), 5.25 (t, *J* = 6.9 Hz, 1H), 2.40 (s, 3H), 2.22 (dt, *J* = 6.8, 2.9 Hz, 2H), 2.18 – 2.08 (m, 2H), 1.73 (ddd, *J* = 45.1, 14.0, 7.0 Hz, 4H), 1.56 – 1.41 (m, 4H), 0.91 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 143.2, 141.7, 130.1, 129.5, 129.0, 128.2, 81.3, 32.6, 28.2, 28.1, 26.9, 26.8, 25.7, 21.6, 10.1.

HRMS (ESI) calculated for $C_{18}H_{24}NaO_2^+$ ($[M+Na]^+$) m/z 295.1669, found 295.1662.

$[\alpha]_D^{25}$ = +12 (*c* 0.60, $CHCl_3$).

(*S*)-1-(6,7-Dihydro-5H-benzo[7]annulen-9-yl)propyl 4-methylbenzoate (65)



This compound was prepared according to the general procedure using 6,7-dihydro-5H-benzo[7]annulen-9-yl trifluoromethanesulfonate (43.8 mg, 0.15 mmol, 1.0 equiv) and 1-chlorobutyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **65** as a colorless oil (32.8 mg, 68% yield, 89% ee).

Chiral HPLC (CHIRALCEL OD-H), *i*PrOH-hexane 1/99, 0.5 mL/min, 240 nm, t_R (minor) = 18.304 min, t_R (major) = 16.893 min.

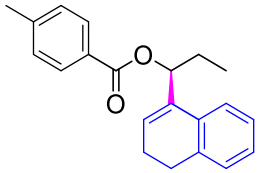
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.9 Hz, 2H), 7.60 (d, *J* = 7.7 Hz, 1H), 7.28 (d, *J* = 7.9 Hz, 3H), 7.24 – 7.18 (m, 2H), 6.28 (t, *J* = 7.3 Hz, 1H), 5.82 (t, *J* = 6.5 Hz, 1H), 2.63 – 2.51 (m, 2H), 2.43 (s, 3H), 2.10 (p, *J* = 7.1 Hz, 2H), 1.90 – 1.82 (m, 1H), 1.82 – 1.68 (m, 3H), 0.92 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 143.5, 141.4, 140.5, 138.4, 129.6, 129.1, 128.8, 128.0, 127.9, 127.0, 126.9, 126.1, 78.3, 34.7, 32.2, 27.6, 24.1, 21.7, 10.1.

HRMS (ESI) calculated for $C_{22}H_{25}O_2^+$ ([M+H]$^+$) m/z 321.1850, found 321.1837.

$[\alpha]_D^{25}$ = +84 (*c* 0.30, $CHCl_3$).

(*S*)-1-(3,4-Dihydronaphthalen-1-yl)propyl 4-methylbenzoate (66)



This compound was prepared according to the general procedure using 3,4-dihydronaphthalen-1-yl trifluoromethanesulfonate (41.7 mg, 0.15 mmol, 1.0 equiv) and 1-chlorobutyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **66** as a colorless oil (29.5 mg, 64% yield, 91% ee).

Chiral HPLC (CHIRALPAK AD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 254 nm, t_R (minor) = 10.072 min, t_R (major) = 14.579 min.

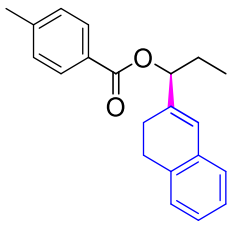
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 2H), 7.53 (d, *J* = 7.7 Hz, 1H), 7.25 – 7.21 (m, 3H), 7.16 (d, *J* = 4.5 Hz, 2H), 6.22 (t, *J* = 4.7 Hz, 1H), 5.97 (t, *J* = 6.5 Hz, 1H), 2.75 (t, *J* = 8.0 Hz, 2H), 2.42 (s, 3H), 2.34 – 2.24 (m, 4.6 Hz, 2H), 2.04 – 1.93 (m, 2H), 0.98 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 143.5, 136.8, 135.4, 132.8, 129.6, 129.0, 127.9, 127.8, 127.0, 126.8, 126.3, 123.2, 76.1, 28.2, 27.0, 22.8, 21.6, 10.1.

HRMS (ESI) calculated for $C_{21}H_{23}O_2^+$ ([M+H]$^+$) m/z 307.1693, found 307.1675.

$[\alpha]_D^{25}$ = +9 (*c* 0.30, $CHCl_3$).

(*S*)-1-(3,4-Dihydronaphthalen-2-yl)propyl 4-methylbenzoate (67)



This compound was prepared according to the general procedure using 3,4-dihydronaphthalen-2-yl trifluoromethanesulfonate (41.7 mg, 0.15 mmol, 1.0 equiv) and 1-chlorobutyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **67** as a colorless oil (33.2 mg, 72% yield, 88% ee).

Chiral HPLC (CHIRALPAK AD-H), *i*PrOH-hexane 2/98, 0. mL/min, 254 nm, t_R (minor) = 22.303 min, t_R (major) = 29.739 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 – 7.94 (m, 2H), 7.25 (d, *J* = 4.0 Hz, 2H), 7.16 – 7.07 (m, 3H), 7.05

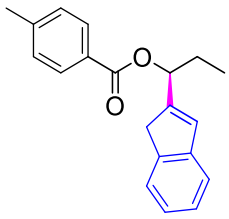
– 7.01 (m, 1H), 6.50 (d, J = 1.5 Hz, 1H), 5.53 (t, J = 6.7 Hz, 1H), 2.92 – 2.74 (m, 2H), 2.47 – 2.29 (m, 5H), 1.96 – 1.79 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 143.5, 138.5, 135.0, 133.8, 129.6, 129.1, 127.9, 127.2, 127.0, 126.5, 126.3, 124.5, 78.5, 27.9, 25.8, 23.3, 21.7, 9.8.

HRMS (ESI) calculated for $C_{21}H_{22}NaO_2^+$ ([M+Na]$^+$) m/z 329.1512, found 329.1501.

$[\alpha]_D^{25}$ = +34 (*c* 0.50, $CHCl_3$).

(*S*)-1-(1*H*-Inden-2-yl)propyl 4-methylbenzoate (68)



This compound was prepared according to the general procedure using 2-bromo-1*H*-indene (29.3 mg, 0.15 mmol, 1.0 equiv) and 1-chlorobutyl 4-methylbenzoate (63.8 mg, 0.3 mmol, 2.0 equiv). The crude mixture was purified by flash column chromatograph to afford **68** as a colorless oil (29.9 mg, 68% yield, 85% ee).

Chiral HPLC (CHIRALPAK AD-H), *i*PrOH-hexane 5/95, 1.0 mL/min, 254 nm, t_R (minor) = 13.195 min, t_R (major) = 16.901 min.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 7.4 Hz, 1H), 7.35 (d, J = 7.5 Hz, 1H), 7.26 (d, J = 7.9 Hz, 3H), 7.17 (dd, J = 8.1, 6.9 Hz, 1H), 6.84 (s, 1H), 5.96 (t, J = 6.6 Hz, 1H), 3.55 – 3.40 (m, 2H), 2.43 (s, 3H), 2.08 – 1.95 (m, 2H), 1.02 (t, J = 7.4 Hz, 3H).

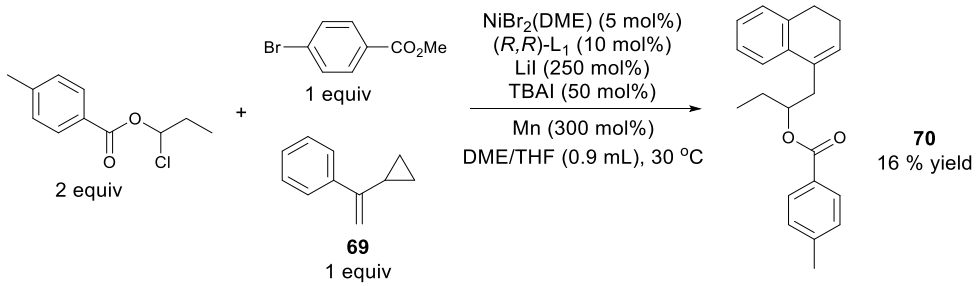
^{13}C NMR (151 MHz, $CDCl_3$) δ 166.0, 147.1, 144.2, 143.6, 143.0, 129.6, 129.1, 128.8, 127.7, 126.4, 124.6, 123.7, 121.0, 74.3, 38.2, 27.5, 21.6, 9.8.

HRMS (ESI) calculated for $C_{20}H_{20}NaO_2^+$ ([M+Na]$^+$) m/z 315.1356, found 315.1337.

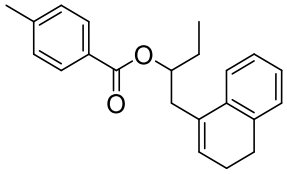
$[\alpha]_D^{25}$ = +20 (*c* 0.60, $CHCl_3$).

Part 5. Control Experiments and Other Possible Mechanism

Part 5.1 Radical clock reaction



1-(3,4-Dihydronaphthalen-1-yl)butan-2-yl 4-methylbenzoate (70)



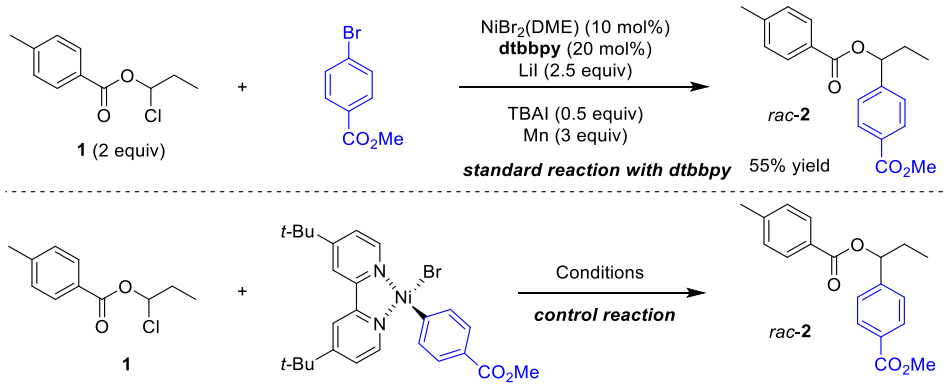
To a flame-dried tube with a stir bar was added the appropriate ligand (9 mg, 10 mol%) and methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv). The tube was transferred into an N_2-filled glovebox, $NiBr_2$(DME) (2.3 mg, 5 mol%), Mn (24.7 mg, 3.0 equiv), LiI (50.2 mg, 2.5 equiv), TBAI (27.7 mg, 0.5 equiv) were added. The tube was sealed, and removed from the glovebox. The tube was charged with THF/DME (2:1, 0.9 mL) and stirred vigorously, ensuring that the reductant was uniformly suspended. Then (1-cyclopropylvinyl) -benzene (21.6 mg, 1.0 equiv) and 1-chloropropyl 4-methylbenzoate (63.8 mg, 2.0 equiv) were added to the tube. The mixture was stirred vigorously at 30 °C for 40 h. After that, the mixture was loaded directly onto a silica gel column (eluted with 0-5% EtOAc/Petroleum ether) to give **2** (85% yield) and **74** (colorless oil, 7.6 mg, 16% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.9 Hz, 2H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 3H), 7.16 – 7.09 (m, 2H), 5.93 (t, *J* = 4.3 Hz, 1H), 5.25 – 5.19 (m, 1H), 2.96 (dd, *J* = 14.2, 6.5 Hz, 1H), 2.74 – 2.60 (m, 3H), 2.41 (s, 3H), 2.24 – 2.18 (m, 2H), 1.80 – 1.66 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.4, 143.3, 136.5, 134.5, 132.8, 129.5, 129.0, 128.0, 127.9, 127.5, 126.8, 126.6, 123.0, 74.5, 37.5, 28.3, 26.6, 23.1, 21.6, 9.6.

HRMS (ESI) calculated for $C_{22}H_{25}NaO_2^+$ ([M+H]$^+$) m/z 321.1850, found 321.1839.

Part 5.2 Stoichiometric reaction of Ar-Ni(II) with 1



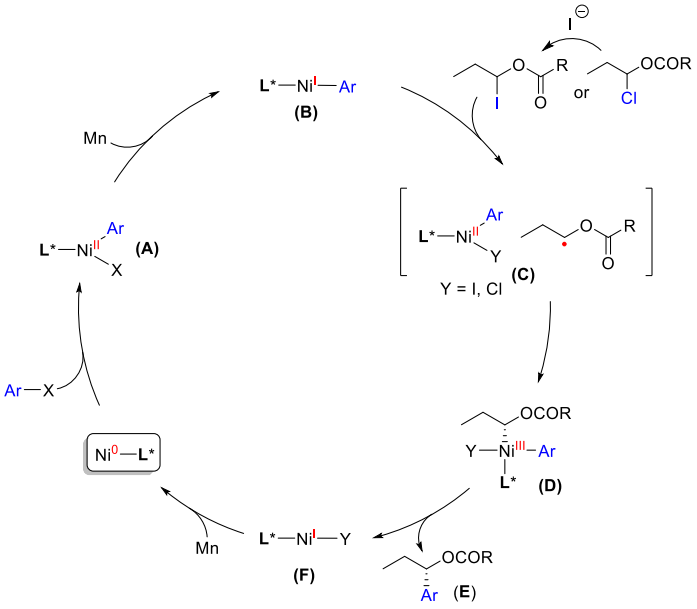
Condition	Mn	LiI	TBAI	*rac*-**2**
1	3 equiv	2.5 equiv	0.5 equiv	22%
2	-	2.5 equiv	0.5 equiv	36%

The reaction was conducted in an argon-filled glove box. To a reaction tube equipped with a magnetic stir bar was added Ar-Ni(L)Br (40.7 mg, 0.075 mmol), Mn (if needed, 3 equiv) and LiI (2.5 equiv),

TBAI (0.5 equiv), followed by DME and THF. The reaction tube was sealed and removed from the glove box, then 1-chloropropyl 4-methylbenzoate (32 mg, 2 equiv) was added to the mixture. The reaction mixture was stirred at 30 °C for 24 h. Then the reaction mixture was diluted with ethyl acetate (5 mL) and water (5 mL). The mixture was extracted with EtOAc (3 x 15 mL), the combined organic phases were washed with water and brine, then dried over $MgSO_4$ and concentrated. The reaction mixtures were analyzed by ^1H NMR with an internal standard.

Part 5.3 A possible sequential reduction (or double oxidative addition) mechanism

This mechanism starts with the oxidative addition of Ar−X to Ni(0), and the generated Ar−Ni(II)−X (**A**) is reduced to Ar−Ni(I) (**B**) by Mn(0). A second oxidative addition of an alkyl electrophile C(sp^3)−Y (Y = I or Cl) to (**B**) gives Ar−Ni(III)Y−C(sp^3) (**D**) via an in-cage radical/Ni rebound. The reductive elimination of (**D**) produced the desired product (**E**) and a Ni(I)−Y complex (**F**). The reduction of (**F**) to Ni(0) closes the catalytic cycle.

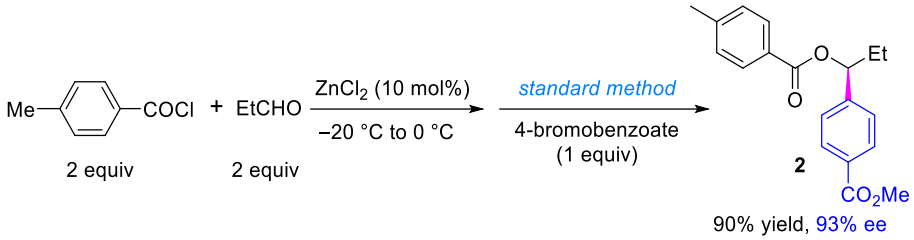


Part 6. Scale-Up Synthesis

To a flame-dried vial with a stir bar was added (*R,R*)-**L1** (299.5 mg, 0.5 mmol, 10 mol%) and methyl 4-bromobenzoate (1.08 g, 5.0 mmol, 1.0 equiv). The vial was transferred into an N_2-filled glovebox, Mn (824 mg, 15 mmol, 3.0 equiv), $NiBr_2$(DME) (77.2 mg, 0.25 mmol, 5 mol%), LiI (1.67 g, 12.5 mmol, 2.5 euuiv) and TBAI (923.5 mg, 2.5 mmol, 0.5 equiv) were added. The vial was sealed and removed from the glovebox. The vial was charged with solvent (THF/DME 2:1, 30 mL) and stirred vigorously, ensuring that the reductant was uniformly suspended. After 5 min, 1-chloropropyl

4-methylbenzoate **1** (2.13 g, 10 mmol, 2.0 equiv) was added to the vial with a syringe over 5 min. The mixture was stirred vigorously at 30 °C for 48 h. After the reaction was complete, the reaction mixture was concentrated under reduced pressure to remove about 20 mL solvent, the left mixture was loaded directly onto a silica gel column (eluted with 0-5% EtOAc/Petroleum ether) to give the target molecule **2** (1.33 g, 85% yield, 93% ee).

Part 7. One Pot Synthesis



To a round-bottom flask equipped with a stir bar was charged with $ZnCl_2$ (4 mg, 10 mol%). The flask was placed under a nitrogen atmosphere by evacuating and backfilling the flask (three cycles), followed by the addition of DCM (0.6 mL) and 4-methylbenzoyl chloride (46.4 mg, 0.3 mmol), then the resulting solution was cooled to –20 °C and stirred for 5 min. After that, propionaldehyde (1 M in DCM, 0.3 mmol) was added dropwise to the above mixture over 5 min. The reaction mixture was stirred for 3 hours at –20~0 ºC. Then the mixture was concentrated in vacuo to afford the residue which was used directly in the next step.

To a flame-dried tube with a stir bar was added methyl 4-bromobenzoate (32.3 mg, 0.15 mmol, 1.0 equiv), (*R*,*R*)-**L1** (9 mg, 10 mol%). The tube was transferred into an N_2-filled glovebox, Mn (24.7 mg, 0.45 mmol, 3.0 equiv), $NiBr_2$(DME) (2.3 mg, 5 mol %), LiI (50.2 mg, 2.5 equiv) and TBAI (27.7 mg, 0.5 equiv) were added. The tube was sealed, removed from the glovebox and charged with THF (0.3 mL). The mixture was stirred vigorously, ensuring that the reductant was uniformly suspended. After 5 min, the above crude 1-chloropropyl 4-methylbenzoate was dissolved in THF (0.3 mL) and transferred via syringe, rinsing with DME (0.3 mL). The mixture was stirred vigorously at 30 ℃ for 40 h. After that, the mixture was loaded directly onto a silica gel column (eluted with EtOAc/Petroleum ether) to give the target molecule (42.0 mg, 90% yield, 93% ee).

II. Reference

1. L. H. Ulich and R. Adams, *J. Am. Chem. Soc.* **1921**, *43*, 660–667.

2. Z.-P. Yang and G. C. Fu, *J. Am. Chem. Soc.* **2020**, *142*, 5870−5875.

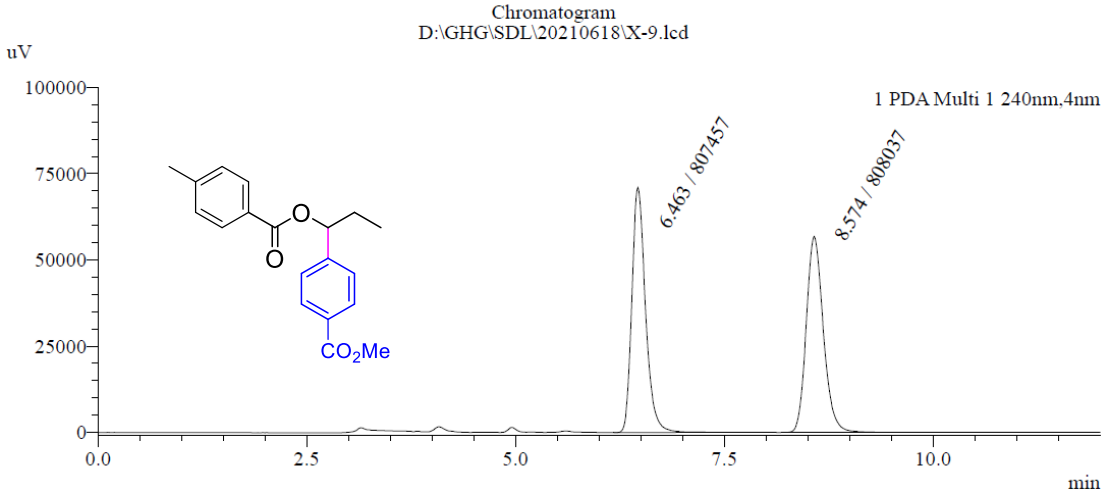
3. a) Y. He, C. Liu, L. Yu and S. Zhu, *Angew. Chem. Int. Ed*. **2020**, *59*, 21530 – 21534; b) X. Cheng, H. Lu, Z. Lu, *Nat. Commun*. **2019**, *10*, 3549.

4. a) M. Rouen, P. Chaumont, G. Barozzino-Consiglio, J. Maddaluno and A. Harrison-Marchand, *Chem. – Eur. J*., **2018**, 24, 9238−9242; b) Q. Wang, S. Li, C.-J. Hou, T.-T. Chu, X.-P. Hu, *Appl. Organomet. Chem.* **2019**, *33*, e5108.

5. a) R. Peters, Z.-q. Xin and F. Maier, *Chem. Asian J*. **2010**, *5*, 1770 – 1774; b) A. G. Myers, J. K. Barbay and B. Zhong, *J. Am. Chem. Soc.* **2001**, *123*, 7207–7219.

III. HPLC Traces

2: racemic

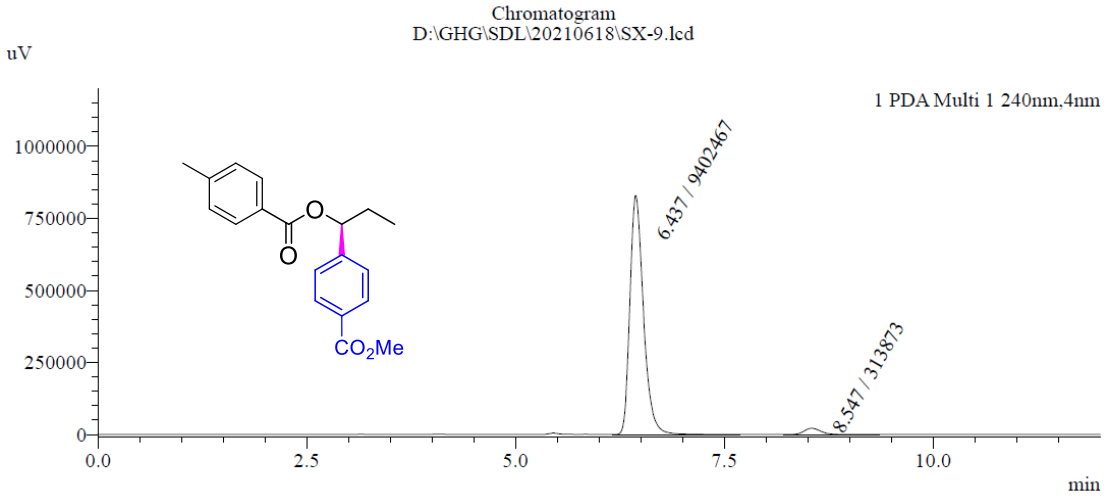


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	6.463	0.1702	807456.63	70960.74	49.9821
2	8.574	0.2160	808036.58	56757.54	50.0179

2: enantioenriched, 94% ee

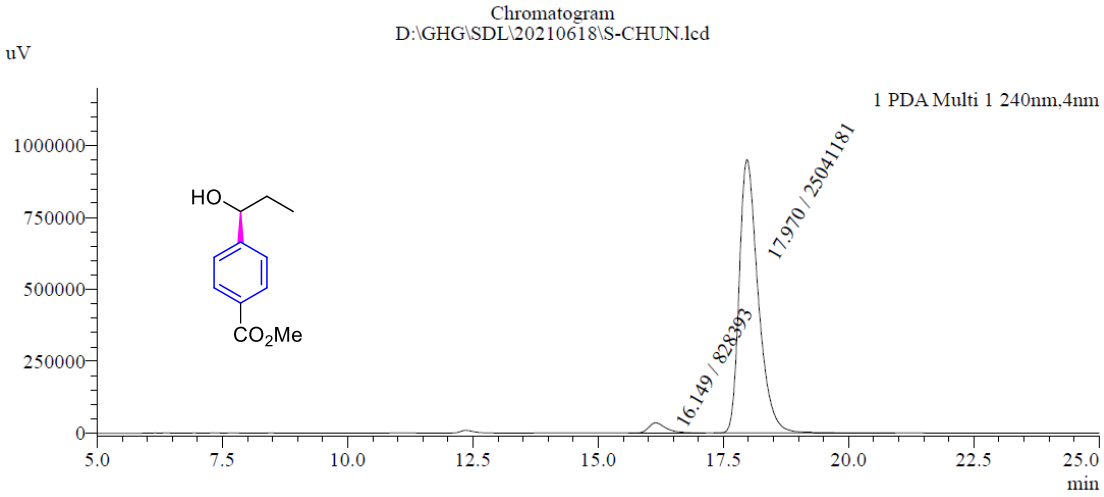


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	6.437	0.1699	9402467.22	828808.77	96.7696
2	8.547	0.2149	313873.15	22098.45	3.2304

3: enantioenriched, 94% ee

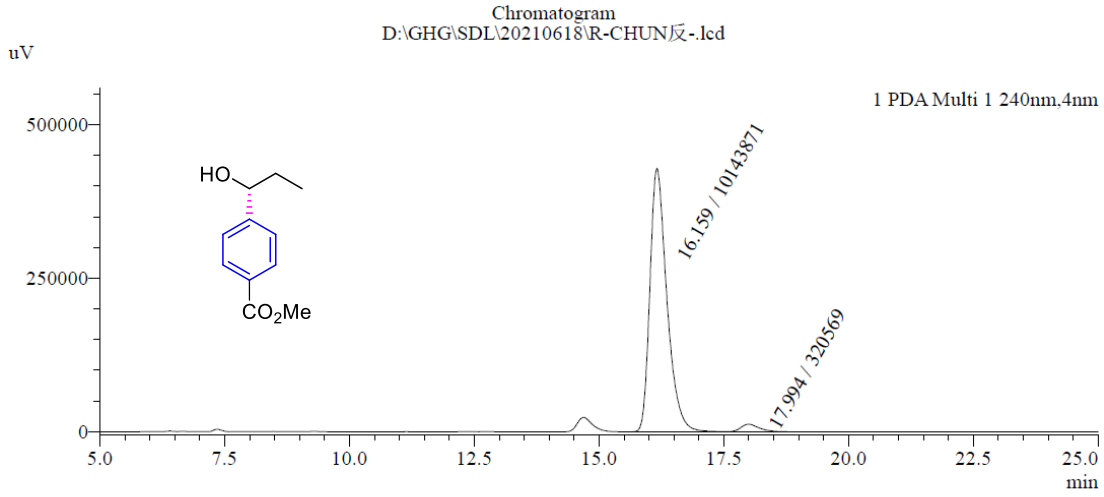


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	16.149	0.3494	828392.77	35151.98	3.2022
2	17.970	0.3931	25041180.87	949814.00	96.7978

(*R*)-3: enantioenriched, −94% ee

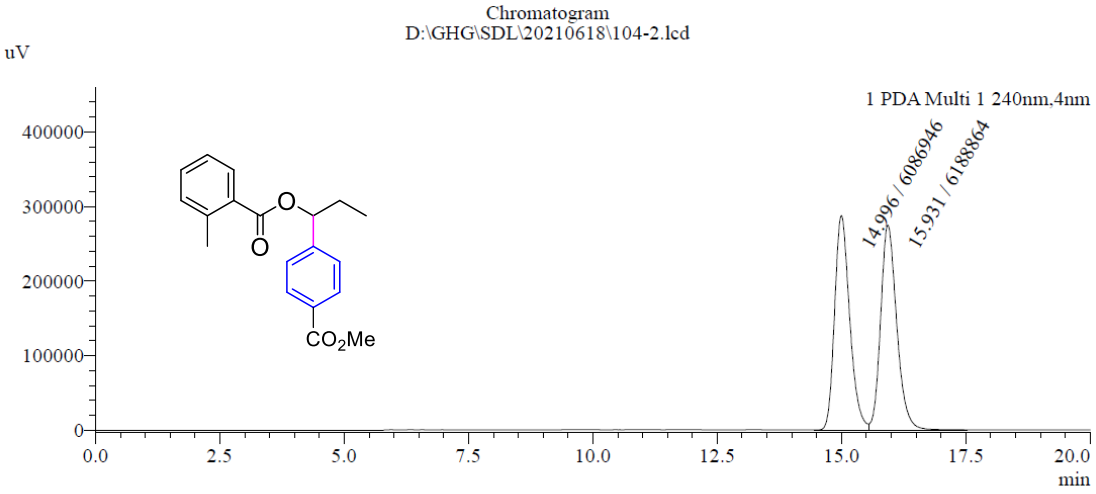


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	16.159	0.3528	10143871.45	429133.47	96.9366
2	17.994	0.3866	320569.20	12351.87	3.0634

4: racemic

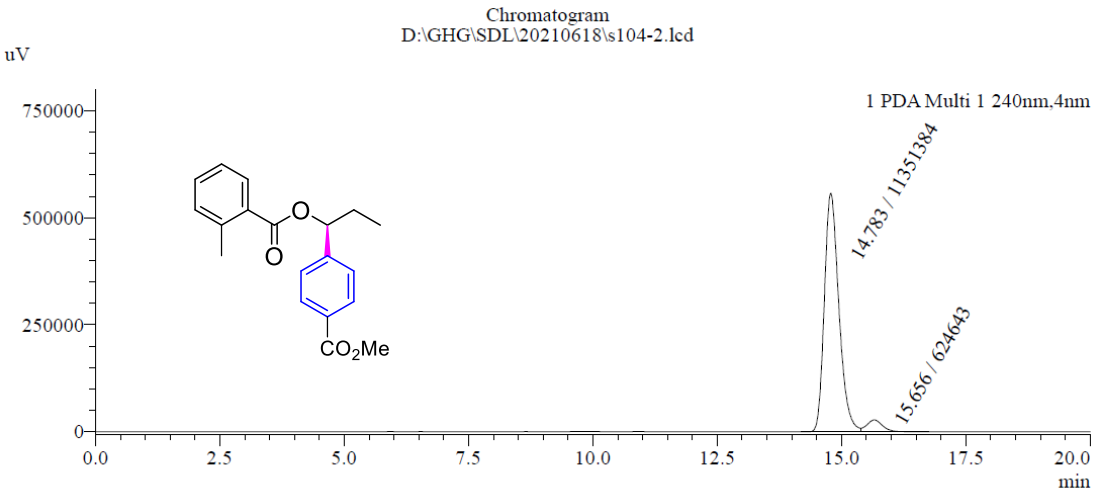


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	14.996	0.3220	6086946.30	287786.87	49.5849
2	15.931	0.3394	6188863.54	274801.44	50.4151

4: enantioenriched, 90% ee

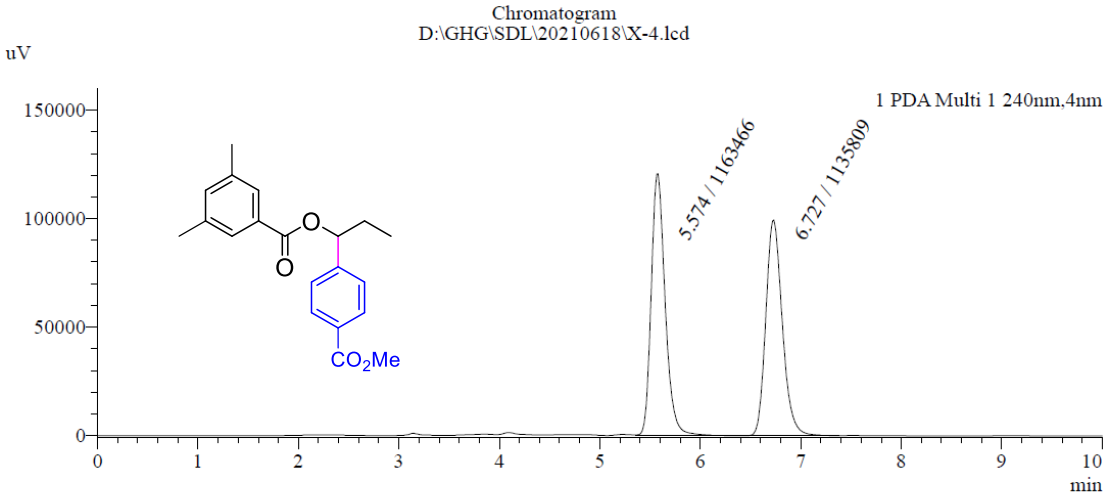


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	14.783	0.3091	11351383.98	557602.29	94.7842
2	15.656	0.3437	624642.81	27979.51	5.2158

5: racemic

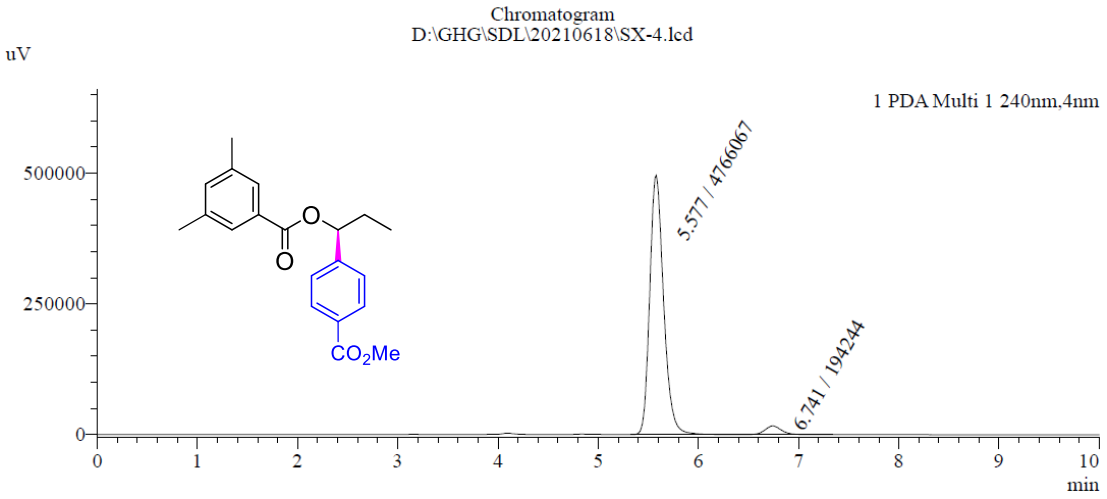


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	5.574	0.1440	1163466.00	120660.77	50.6014
2	6.727	0.1731	1135809.39	99386.92	49.3986

5: enantioenriched, 92% ee

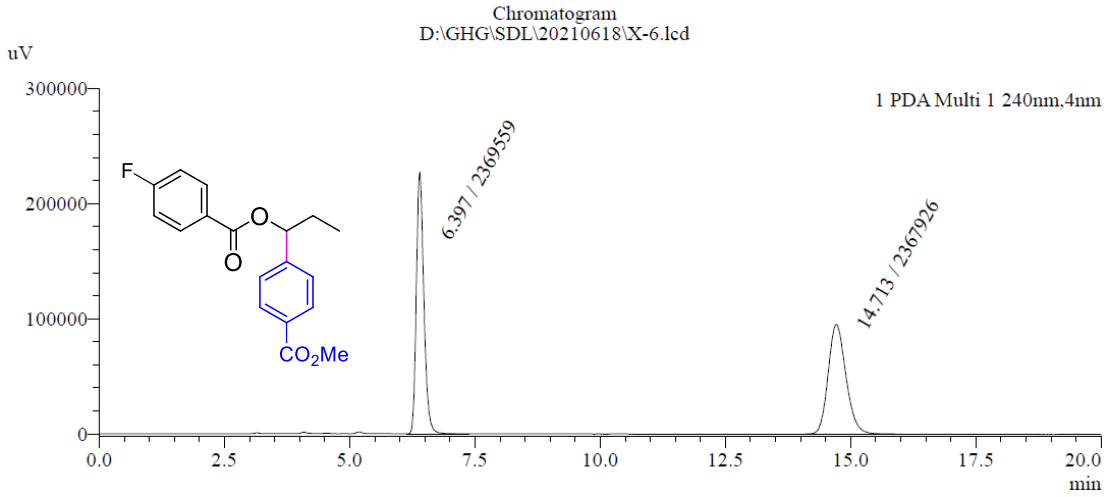


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	5.577	0.1444	4766066.68	496099.20	96.0840
2	6.741	0.1750	194244.26	16571.48	3.9160

6: racemic

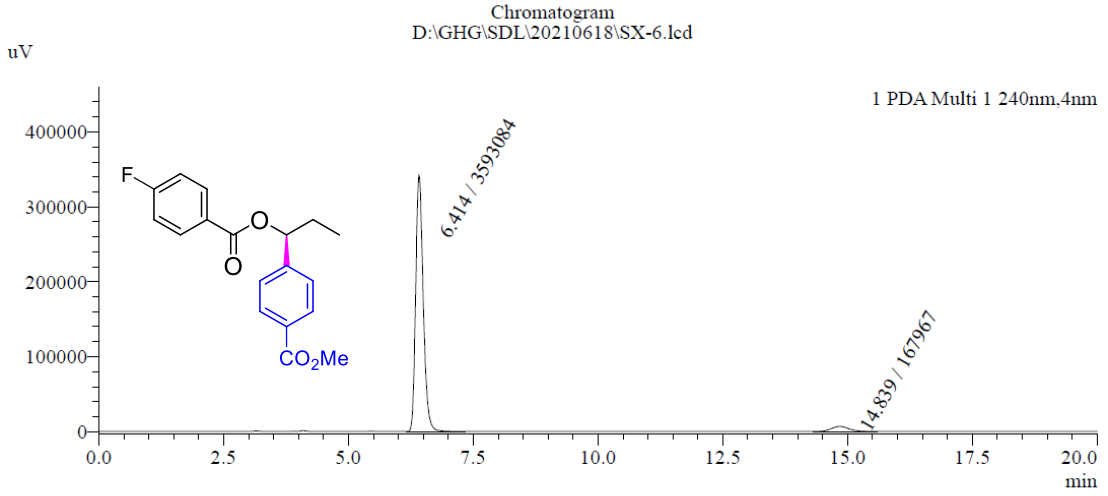


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	6.397	0.1575	2369559.46	226710.64	50.0172
2	14.713	0.3796	2367926.20	95205.44	49.9828

6: enantioenriched, 91% ee

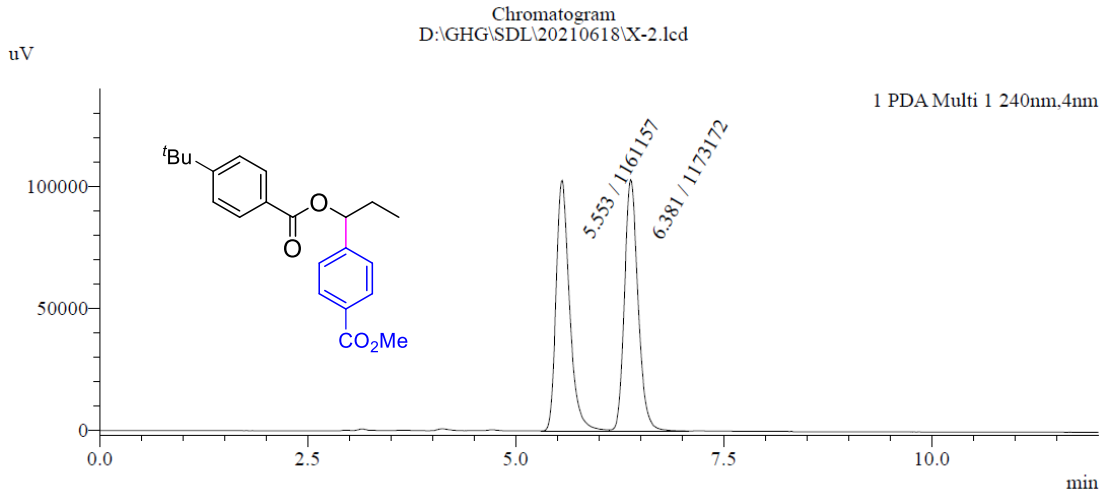


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	6.414	0.1584	3593084.17	342434.81	95.5340
2	14.839	0.3804	167966.84	6798.81	4.4660

7: racemic

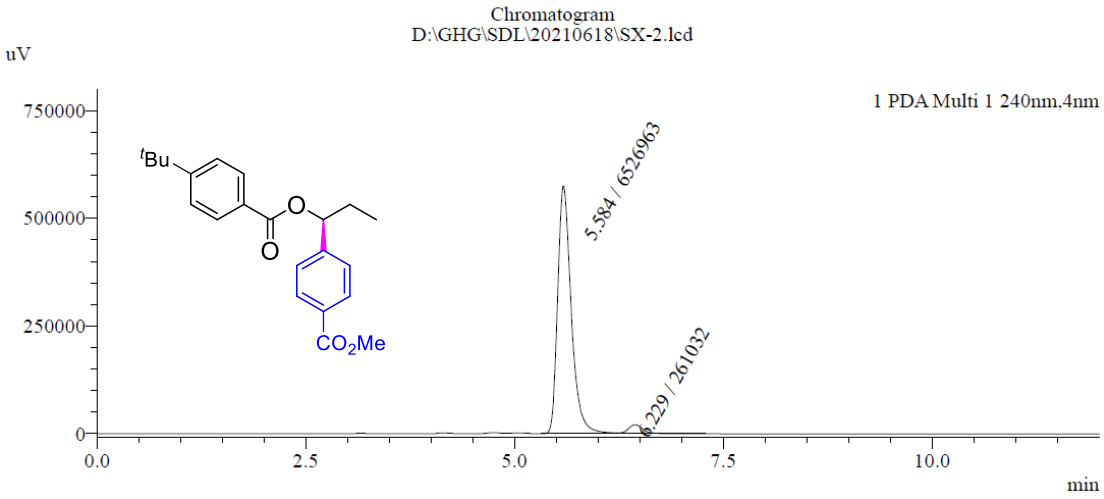


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	5.553	0.1673	1161157.01	102741.94	49.7427
2	6.381	0.1724	1173171.61	103088.90	50.2573

7: enantioenriched, 92% ee

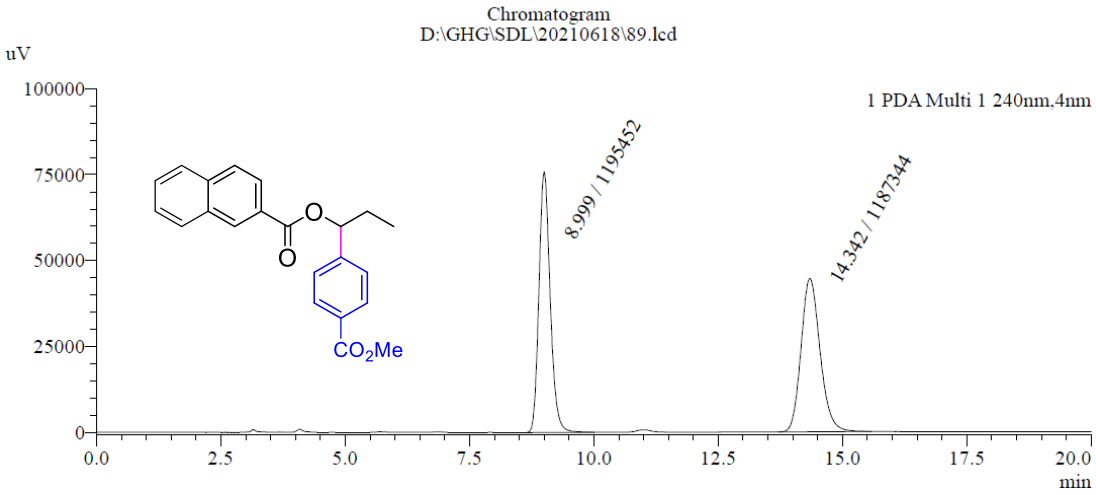


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	5.584	0.1680	6526963.13	575240.31	96.1545
2	6.229	--	261032.23	1812.74	3.8455

8: racemic

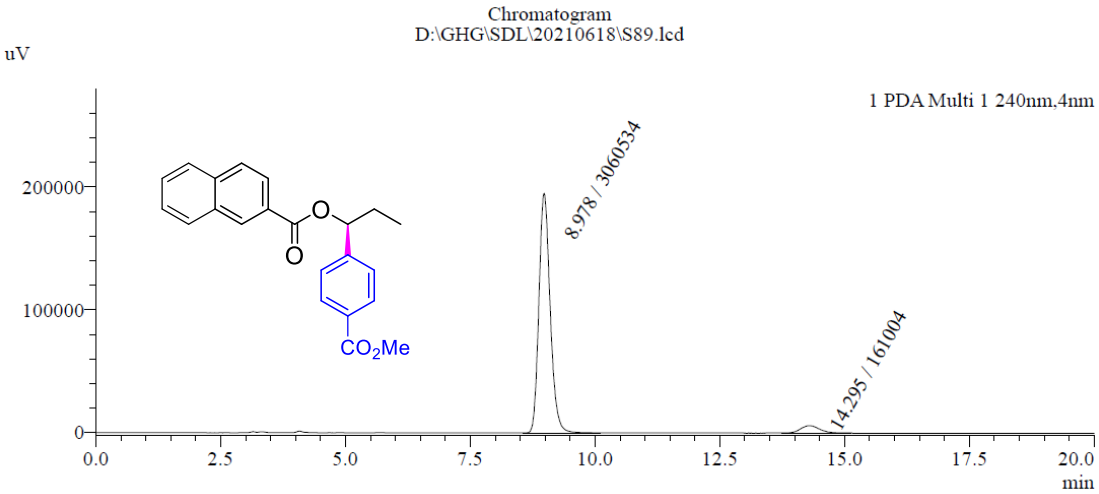


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	8.999	0.2389	1195451.79	75783.86	50.1701
2	14.342	0.4053	1187343.76	44646.75	49.8299

8: enantioenriched, 90% ee

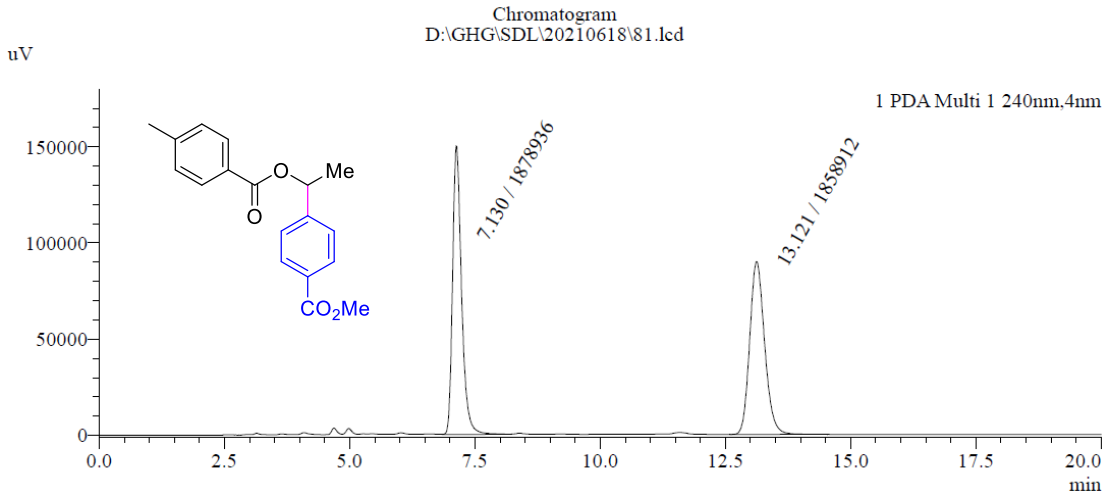


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	8.978	0.2380	3060533.56	194997.35	95.0023
2	14.295	0.4047	161004.14	6111.19	4.9977

9: racemic

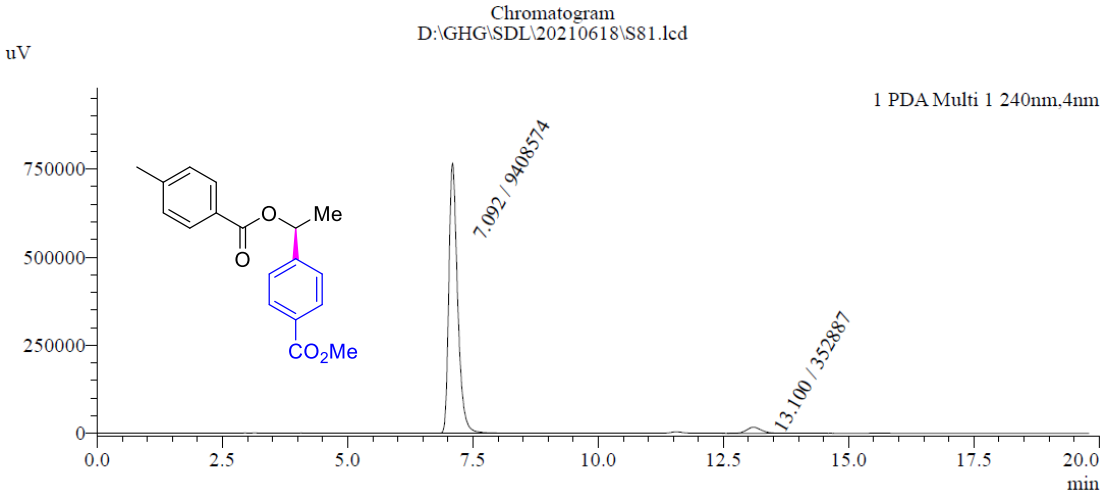


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	7.130	0.1849	1878935.81	150034.72	50.2679
2	13.121	0.3150	1858911.51	89907.14	49.7321

9: enantioenriched, 93% ee

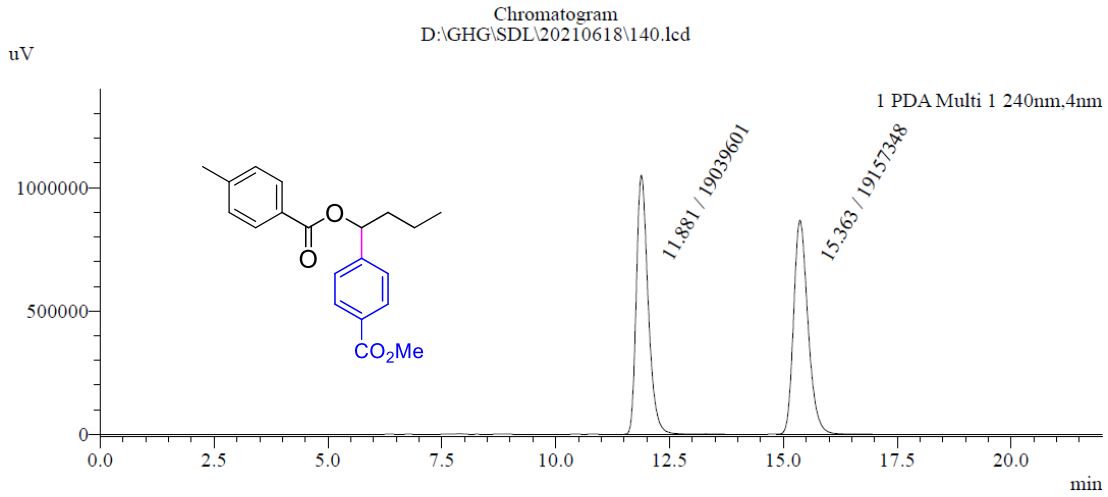


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	7.092	0.1828	9408573.79	765530.06	96.3849
2	13.100	0.3149	352887.43	17161.67	3.6151

10: racemic

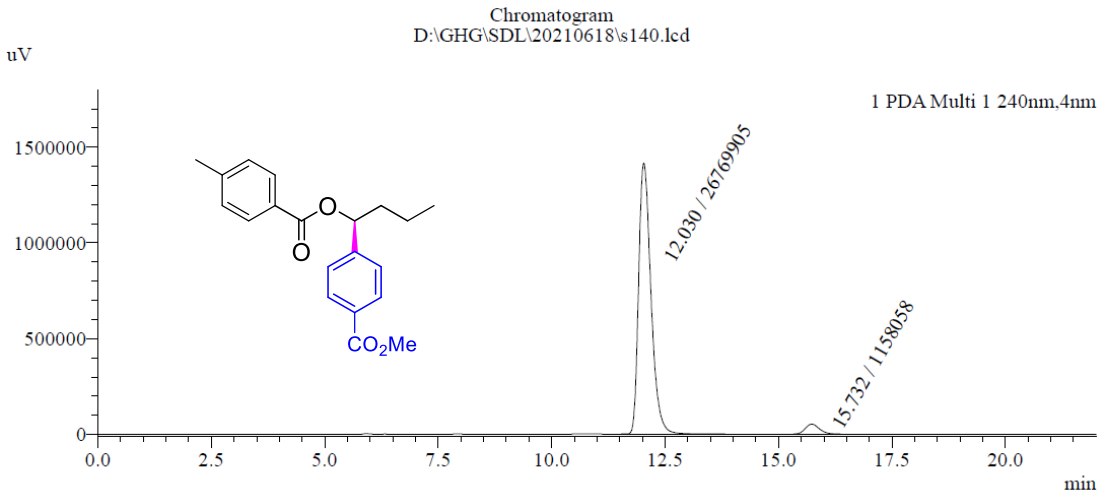


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	11.881	0.2720	19039601.22	1050821.53	49.8459
2	15.363	0.3335	19157347.54	868151.72	50.1541

10: enantioenriched, 92% ee

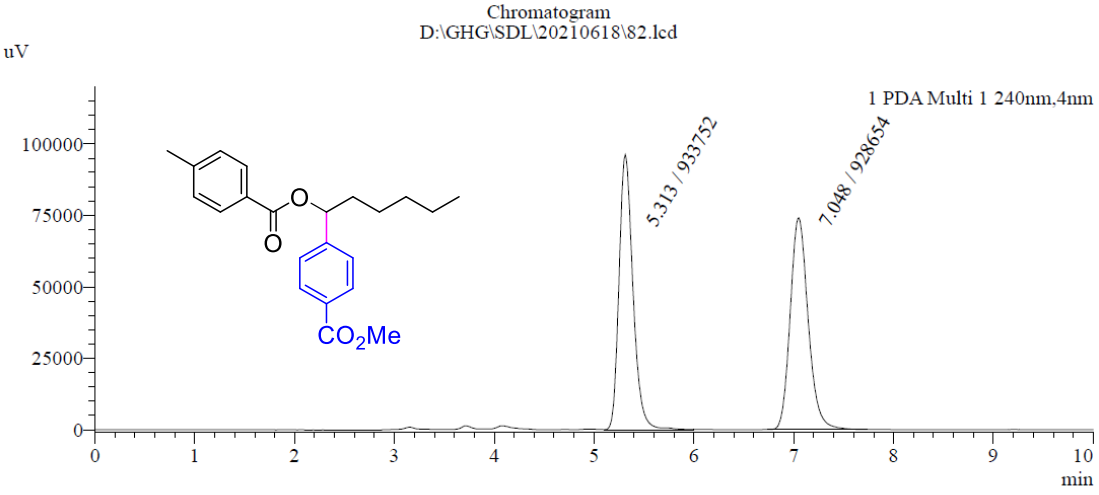


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.030	0.2864	26769904.54	1415503.45	95.8534
2	15.732	0.3348	1158058.13	52410.93	4.1466

11: racemic

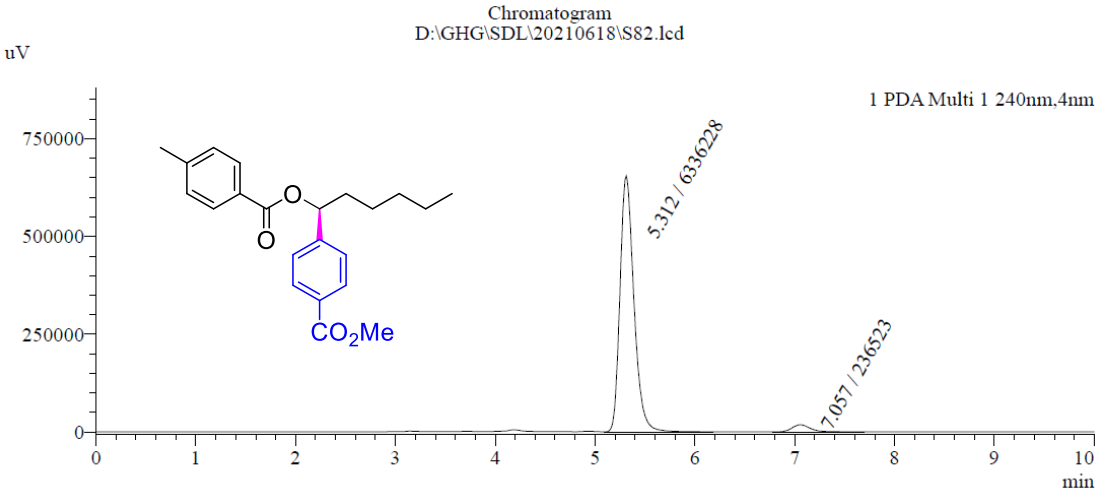


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	5.313	0.1454	933751.69	96227.58	50.1369
2	7.048	0.1899	928653.90	74060.73	49.8631

11: enantioenriched, 93% ee

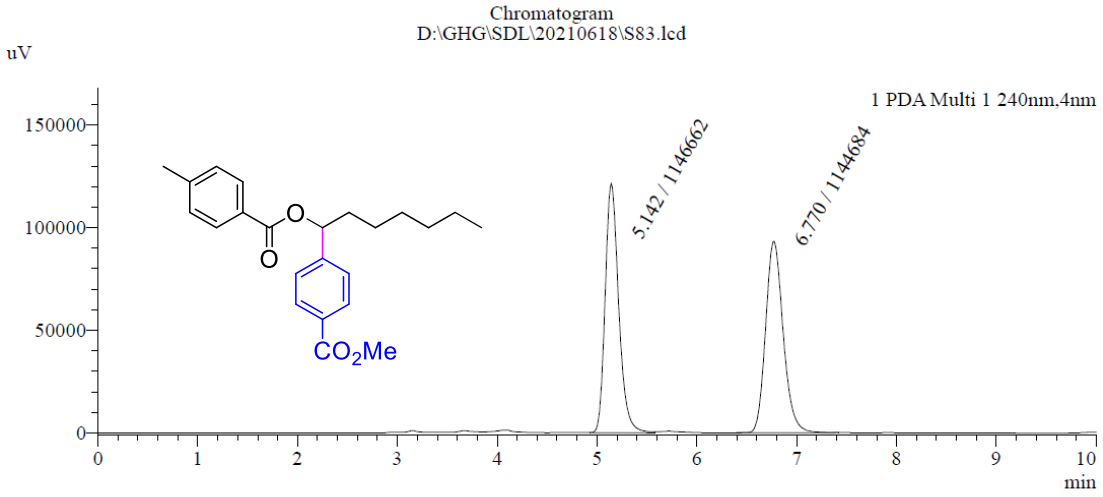


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	5.312	0.1457	6336227.81	654464.77	96.4015
2	7.057	0.1904	236522.76	18436.20	3.5985

12: racemic

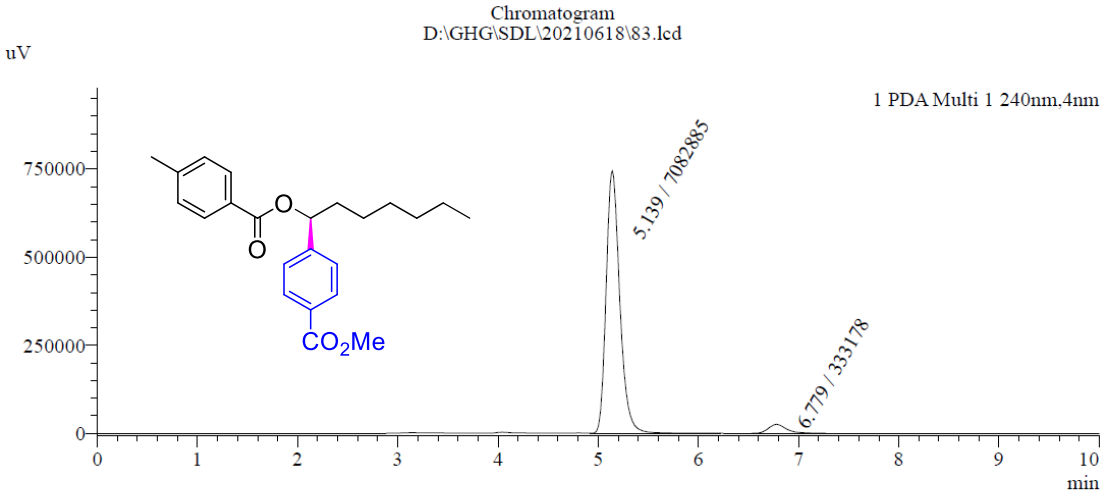


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	5.142	0.1423	1146662.30	121428.39	50.0432
2	6.770	0.1864	1144683.51	93323.02	49.9568

12: enantioenriched, 91% ee

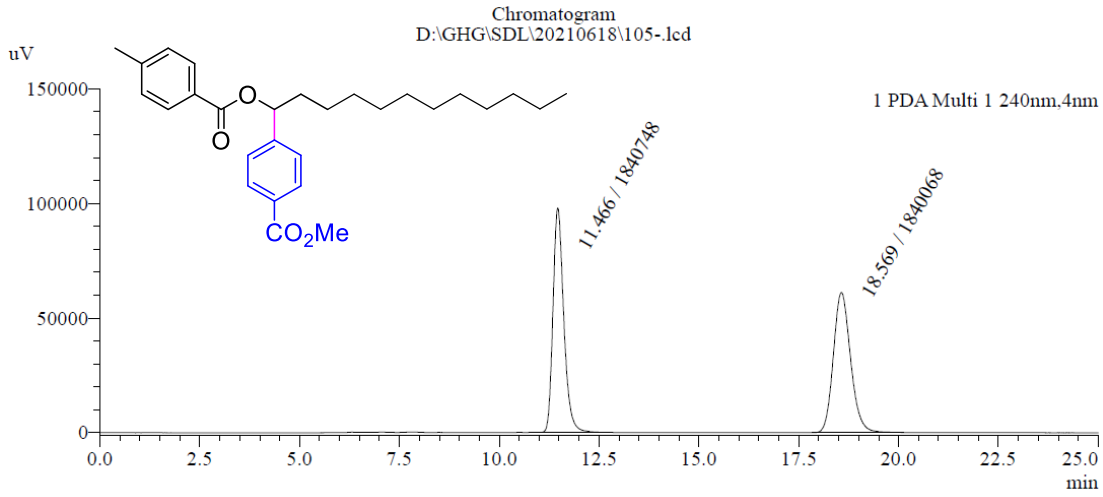


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	5.139	0.1428	7082885.39	745379.42	95.5074
2	6.779	0.1892	333177.57	25606.21	4.4926

13: racemic

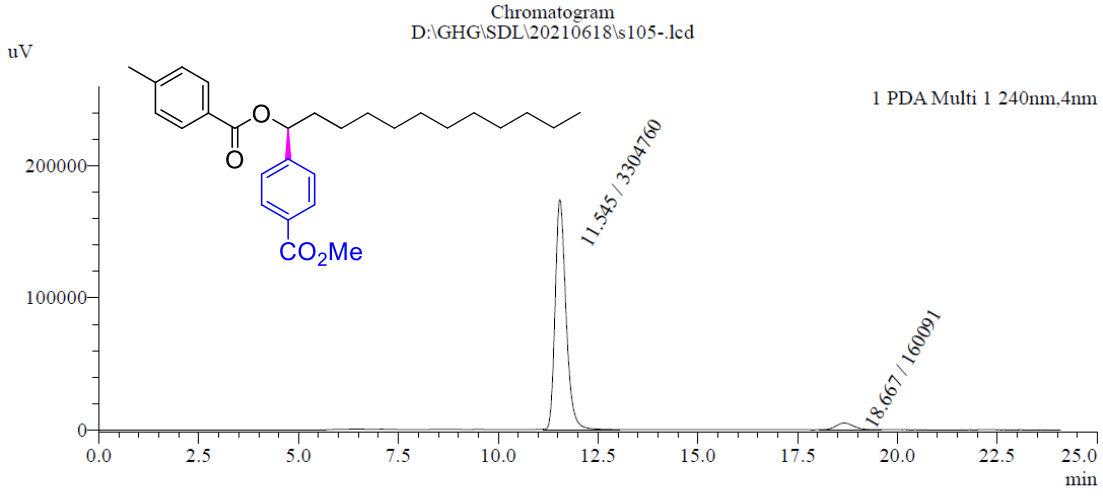


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	11.466	0.2820	1840747.70	97840.41	50.0092
2	18.569	0.4577	1840067.60	61146.96	49.9908

13: enantioenriched, 91% ee

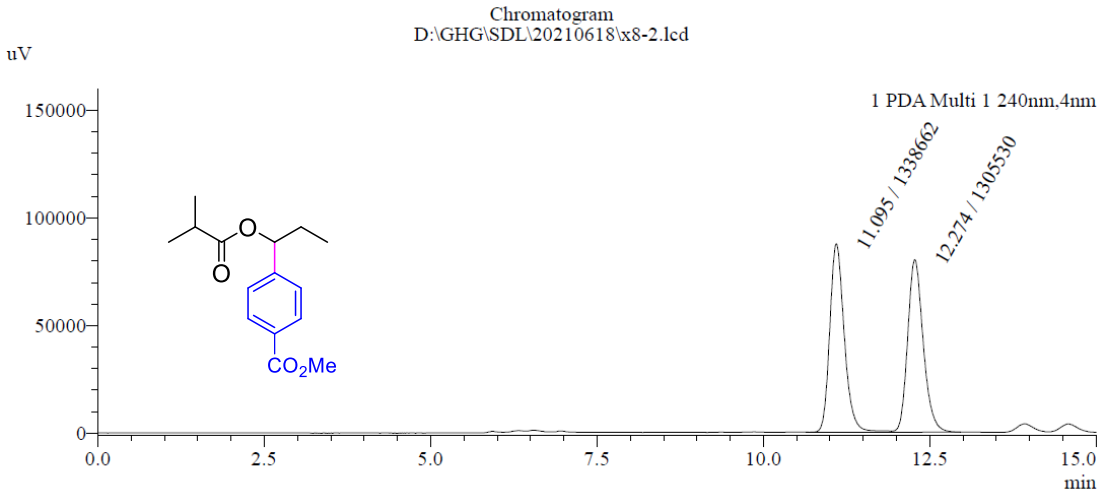


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	11.545	0.2839	3304760.46	174176.44	95.3796
2	18.667	0.4762	160091.24	5173.46	4.6204

14: racemic

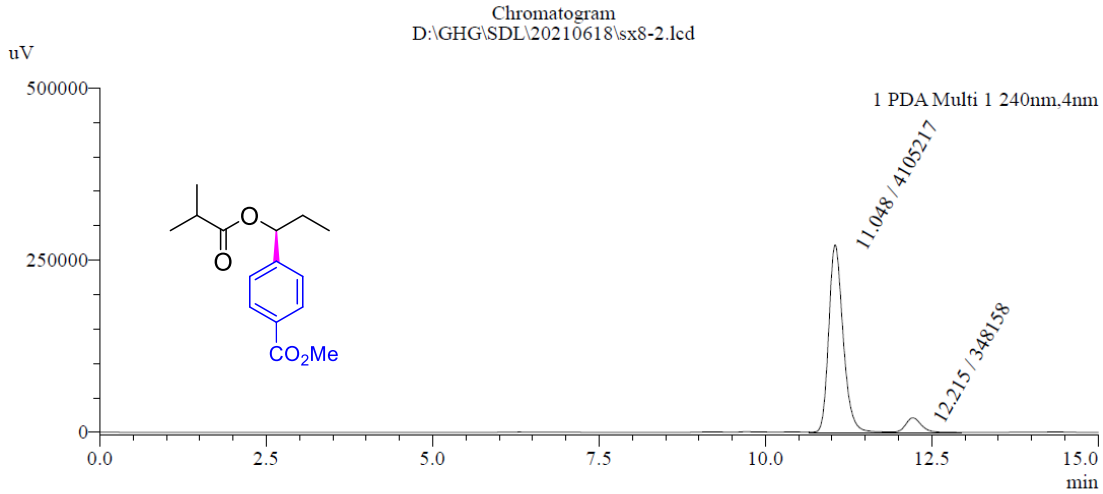


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	11.095	0.2276	1338662.36	87725.39	50.6265
2	12.274	0.2464	1305530.40	80170.34	49.3735

14: enantioenriched, 84% ee

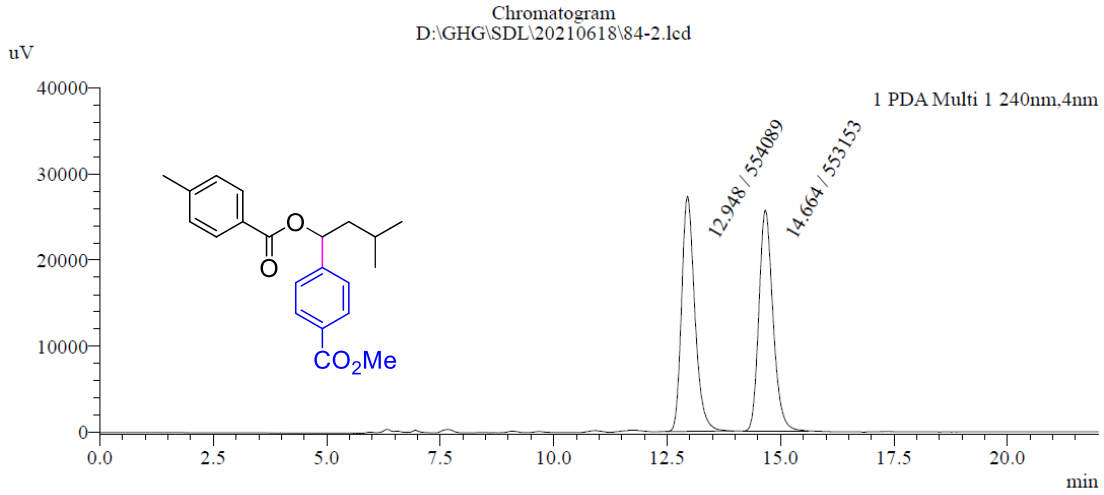


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	11.048	0.2263	4105216.77	272506.07	92.1822
2	12.215	0.2448	348158.16	21302.34	7.8178

15: racemic

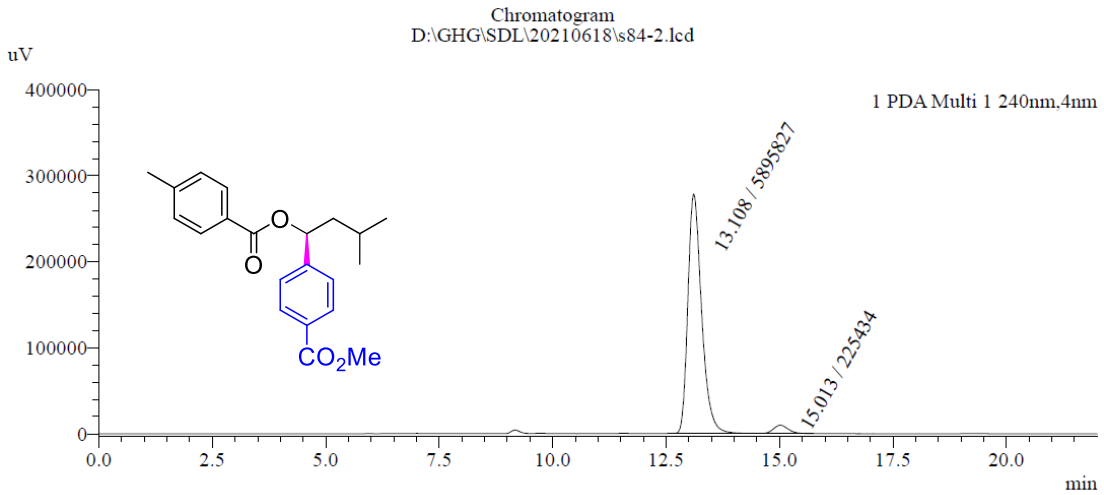


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.948	0.3054	554089.39	27269.66	50.0423
2	14.664	0.3271	553152.92	25639.07	49.9577

15: enantioenriched, 93% ee

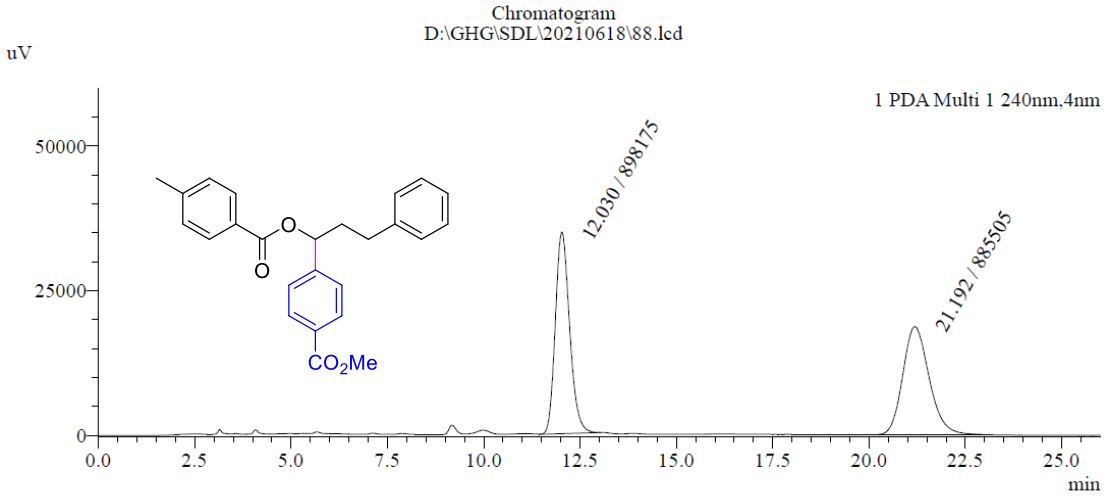


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.108	0.3165	5895826.93	278739.95	96.3172
2	15.013	0.3459	225434.04	9873.20	3.6828

16: racemic

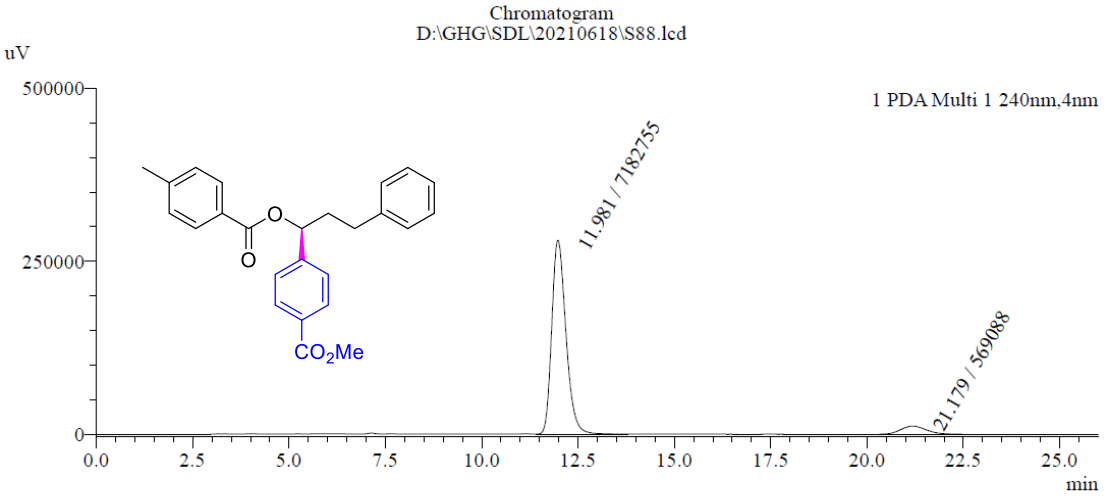


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.030	0.3936	898175.24	34850.64	50.3552
2	21.192	0.7255	885504.92	18651.37	49.6448

16: enantioenriched, 85% ee

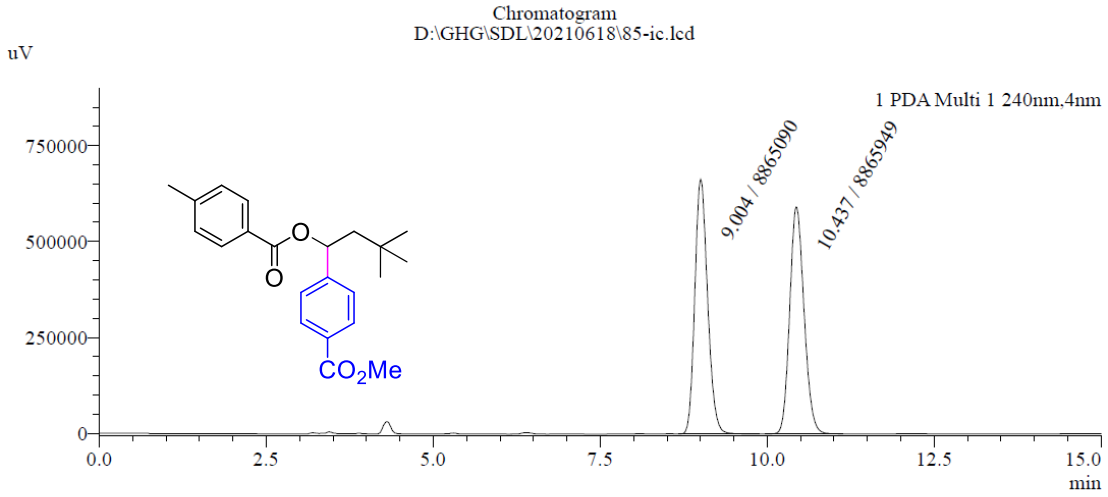


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	11.981	0.3887	7182755.29	280362.94	92.6587
2	21.179	0.7243	569087.55	12043.88	7.3413

17: racemic

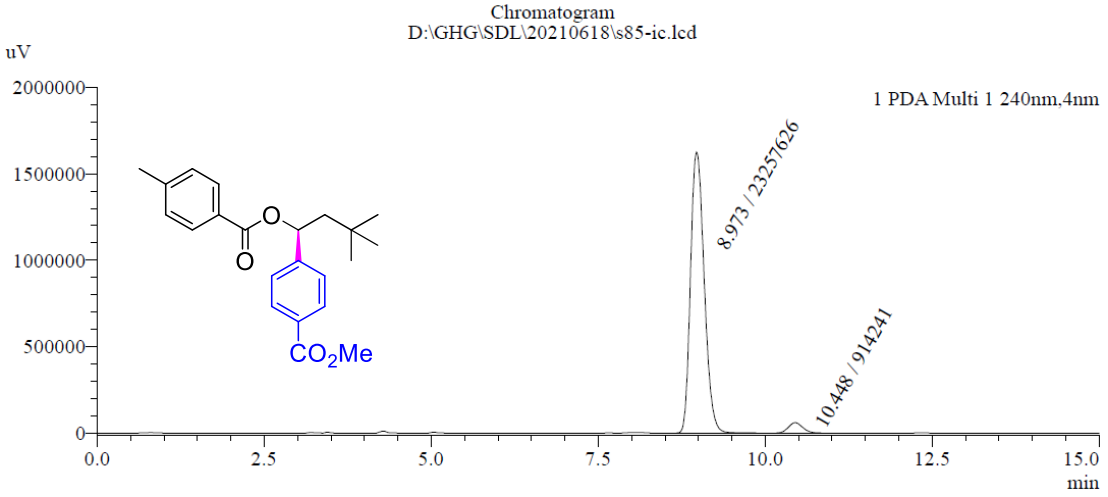


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	9.004	0.2050	8865090.28	664713.63	49.9976
2	10.437	0.2311	8865948.65	591708.35	50.0024

17: enantioenriched, 92% ee

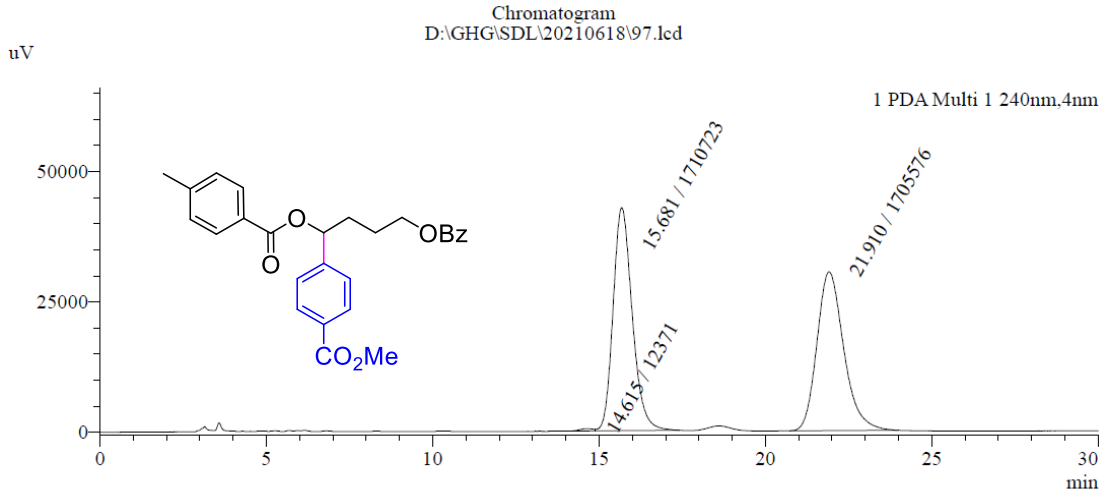


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	8.973	0.2222	23257625.54	1626248.69	96.2177
2	10.448	0.2320	914241.28	60868.76	3.7823

18: racemic

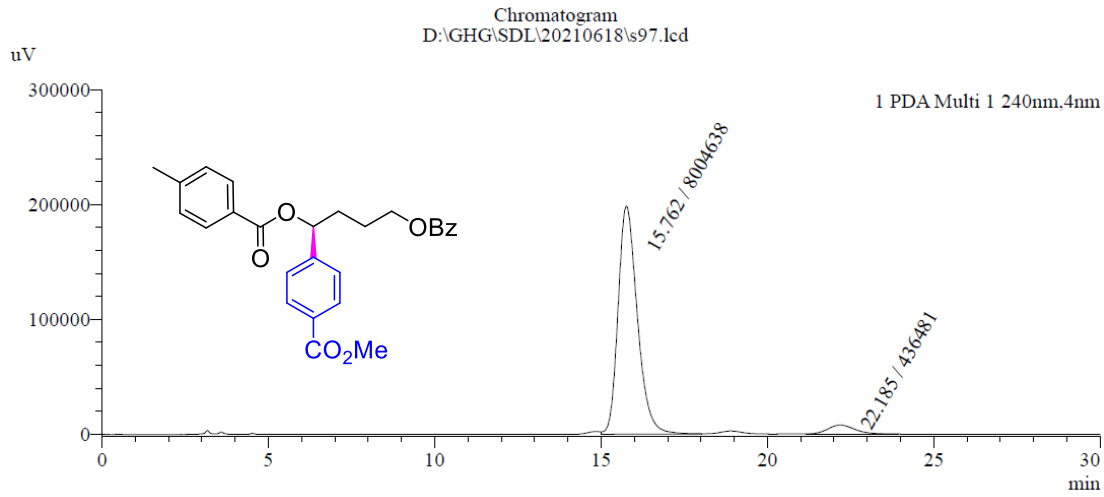


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	14.615	--	12370.65	452.66	0.3608
2	15.681	0.6069	1710722.93	42741.37	49.8947
3	21.910	0.8480	1705576.35	30413.00	49.7445

18: enantioenriched, 90% ee

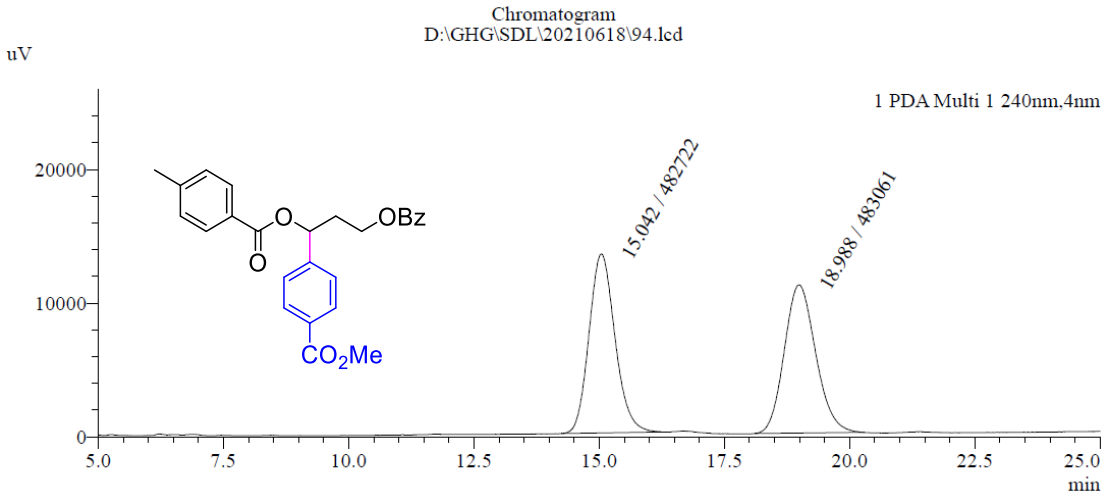


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	15.762	0.6095	8004638.48	198534.31	94.8291
2	22.185	0.8620	436481.45	7761.48	5.1709

19: racemic

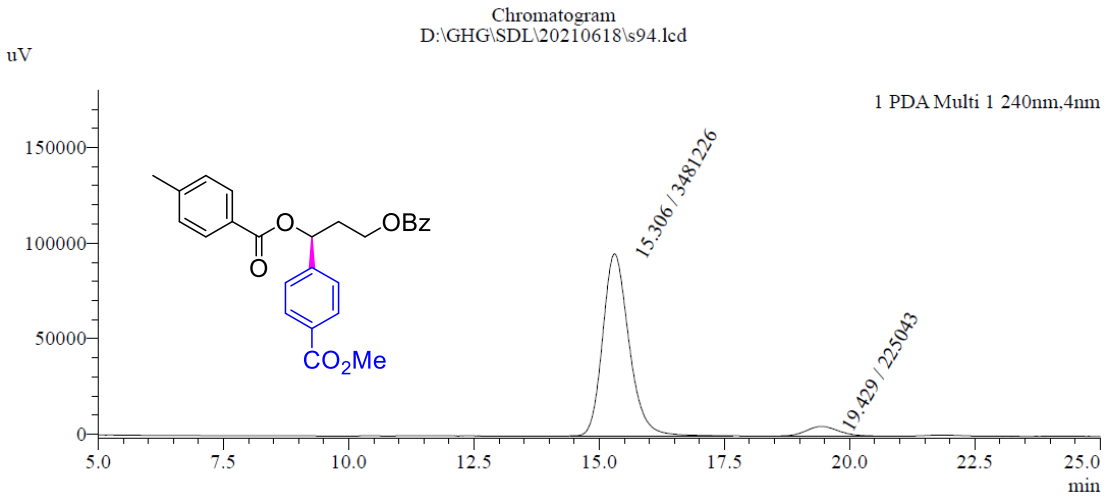


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	15.042	0.5527	482721.94	13387.08	49.9824
2	18.988	0.6731	483061.41	11073.95	50.0176

19: enantioenriched, 88% ee

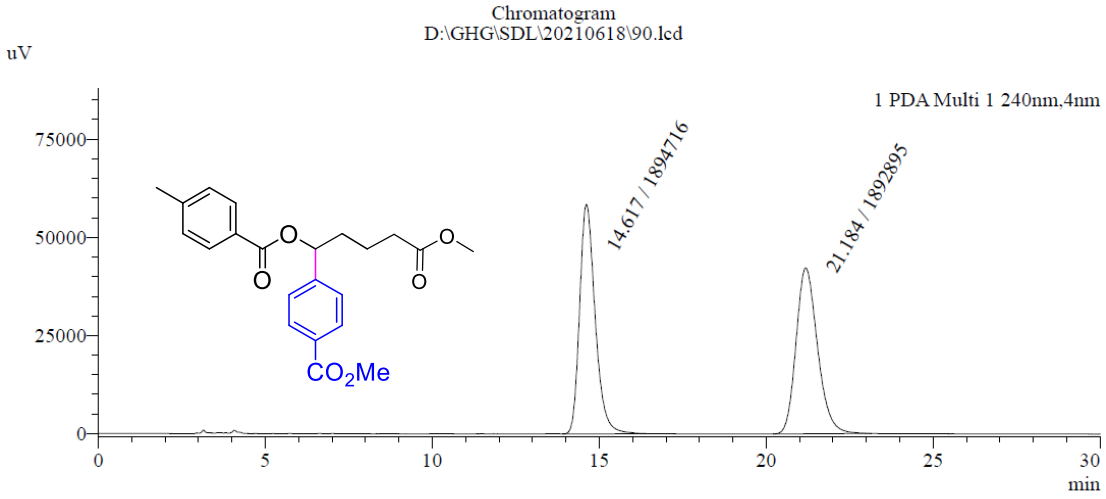


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	15.306	0.5491	3481226.39	95344.29	93.9280
2	19.429	0.6951	225043.30	5020.78	6.0720

20: racemic

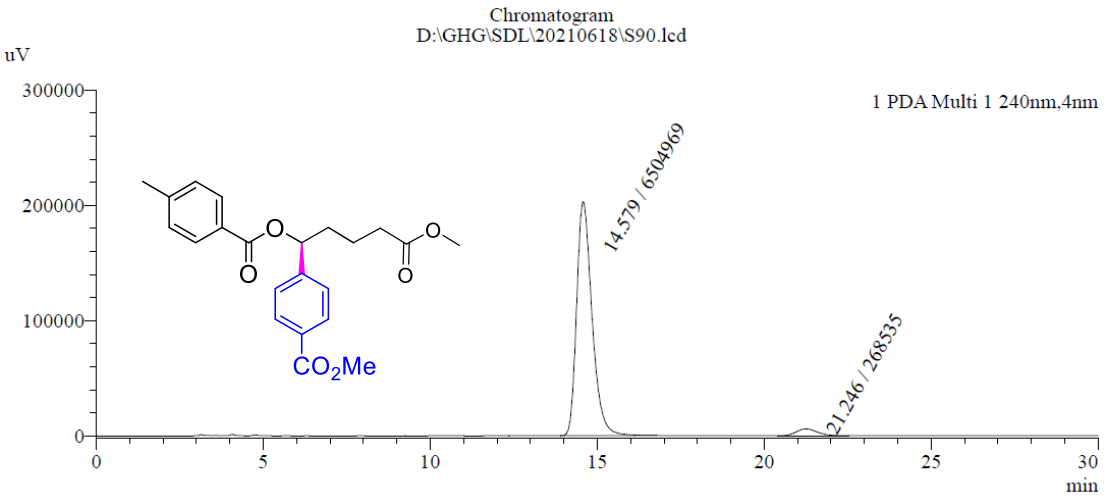


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	14.617	0.4863	1894716.02	58510.19	50.0240
2	21.184	0.6813	1892895.25	42286.63	49.9760

20: enantioenriched, 92% ee

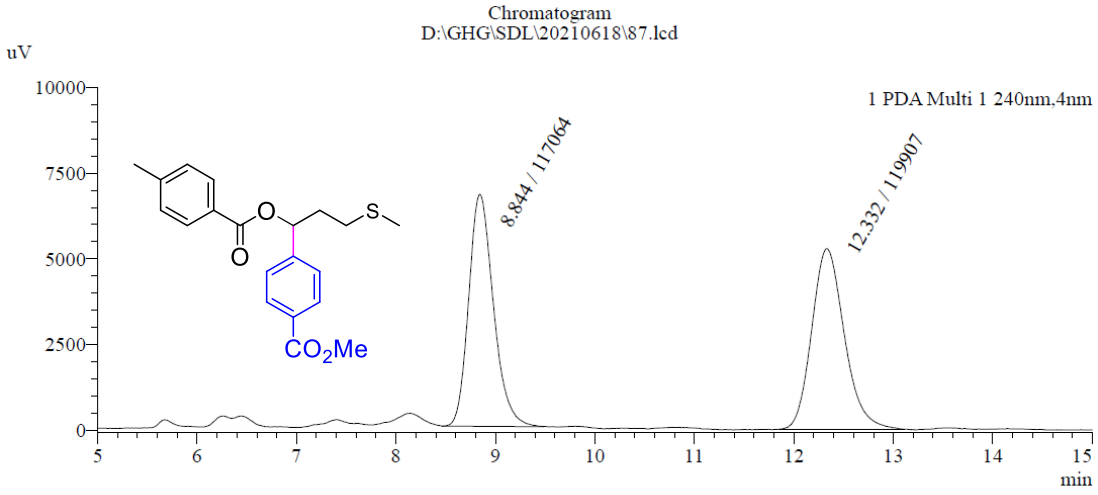


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	14.579	0.4819	6504968.97	203054.85	96.0355
2	21.246	0.6879	268535.46	6007.25	3.9645

21: racemic

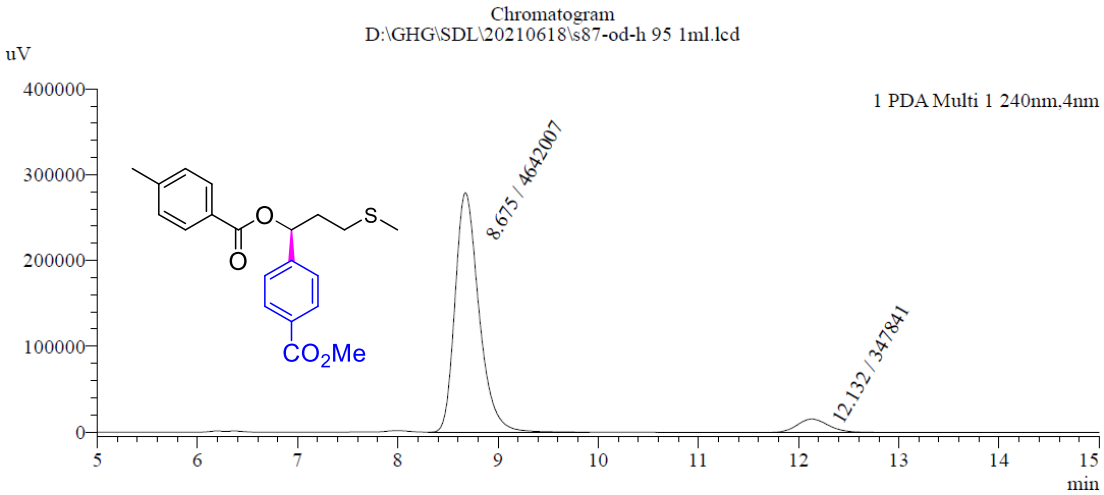


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	8.844	0.2631	117063.66	6763.65	49.4001
2	12.332	0.3467	119907.04	5260.53	50.5999

21: enantioenriched, 86% ee

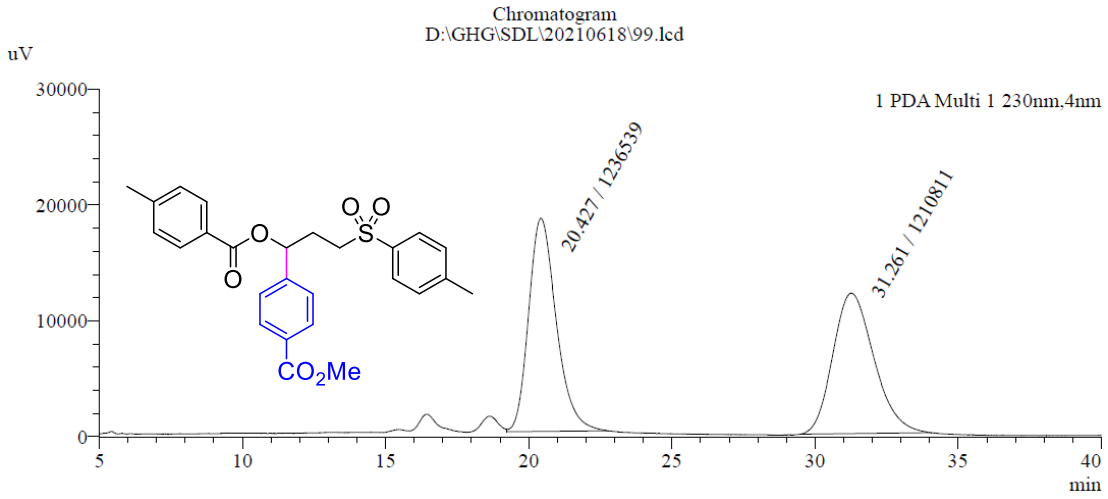


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	8.675	0.2493	4642006.97	279404.23	93.0290
2	12.132	0.3370	347840.55	15701.00	6.9710

22: racemic

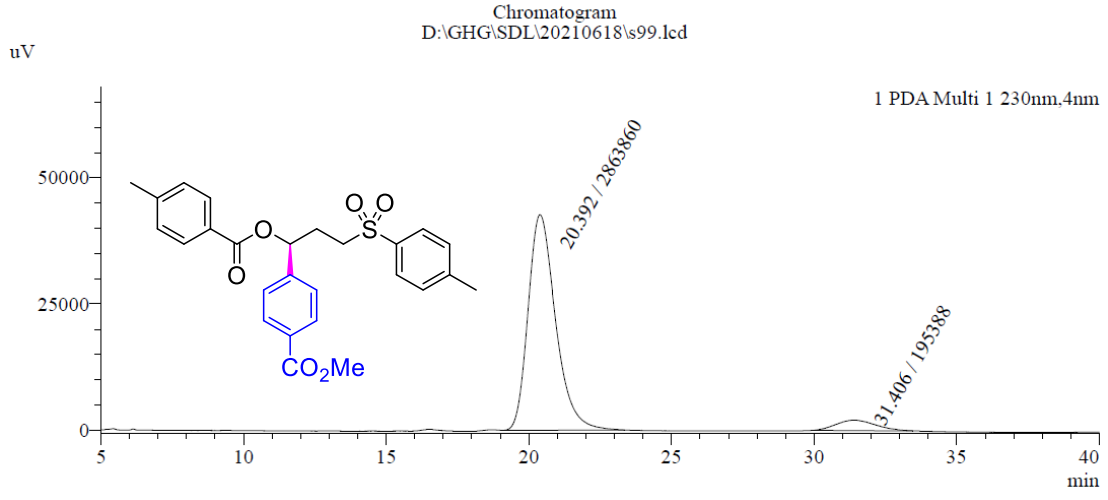


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	20.427	1.0202	1236539.20	18386.28	50.5256
2	31.261	1.5407	1210811.17	12132.23	49.4744

22: enantioenriched, 87% ee

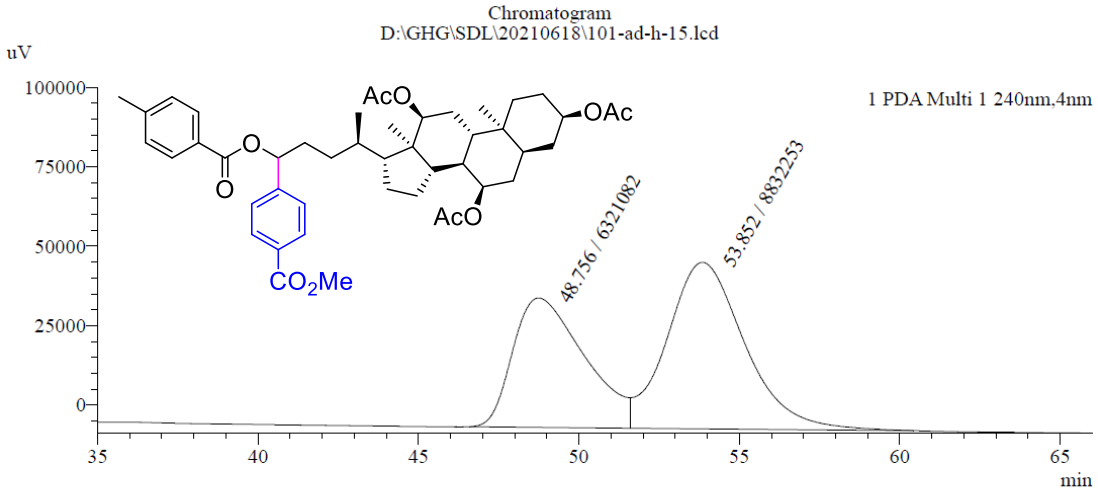


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	20.392	1.0127	2863860.23	42684.11	93.6132
2	31.406	1.5275	195387.69	2038.68	6.3868

23: racemic

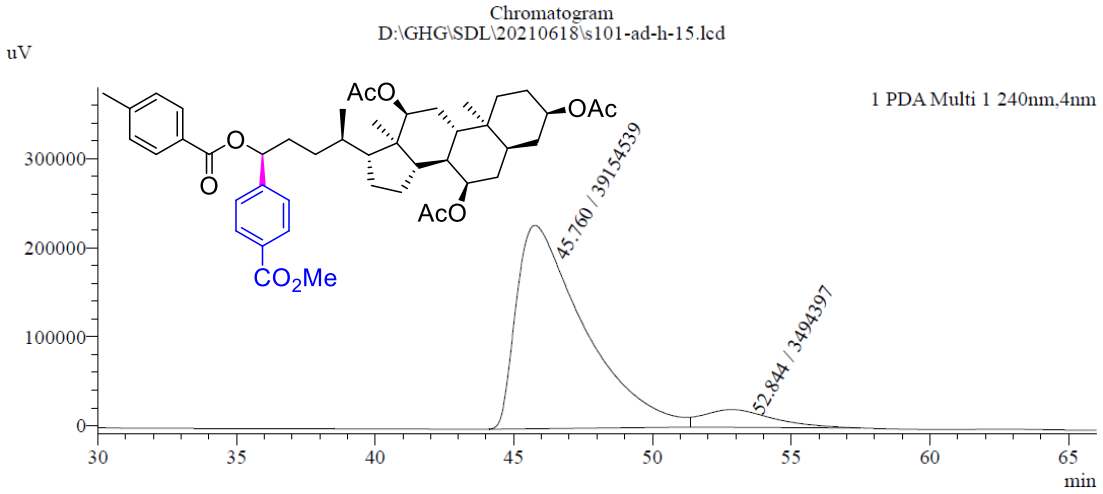


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	48.756	2.4876	6321081.78	40708.47	41.7141
2	53.852	2.5224	8832252.77	52412.25	58.2859

23: enantioenriched, 84% de

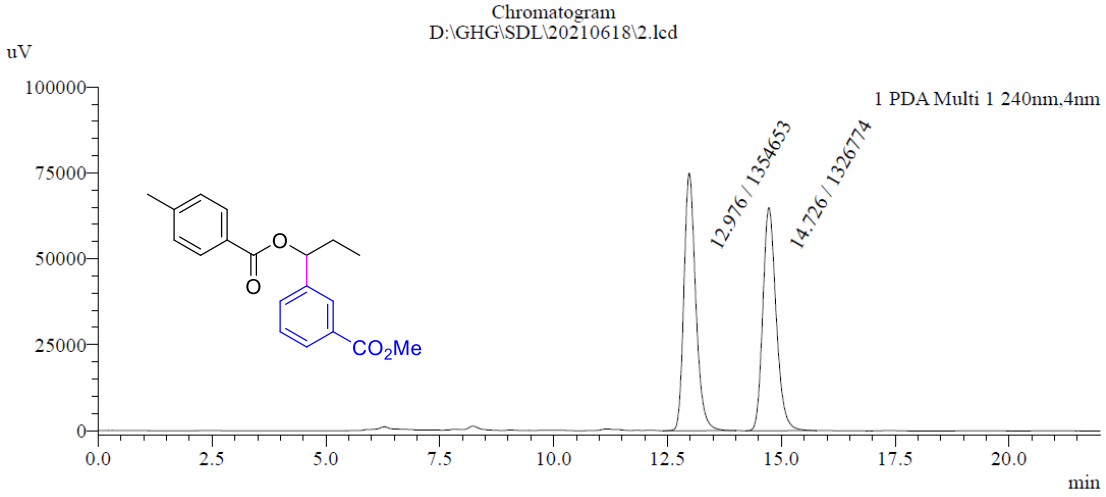


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	45.760	2.5400	39154539.10	228420.42	91.8066
2	52.844	--	3494397.15	19864.11	8.1934

24: racemic

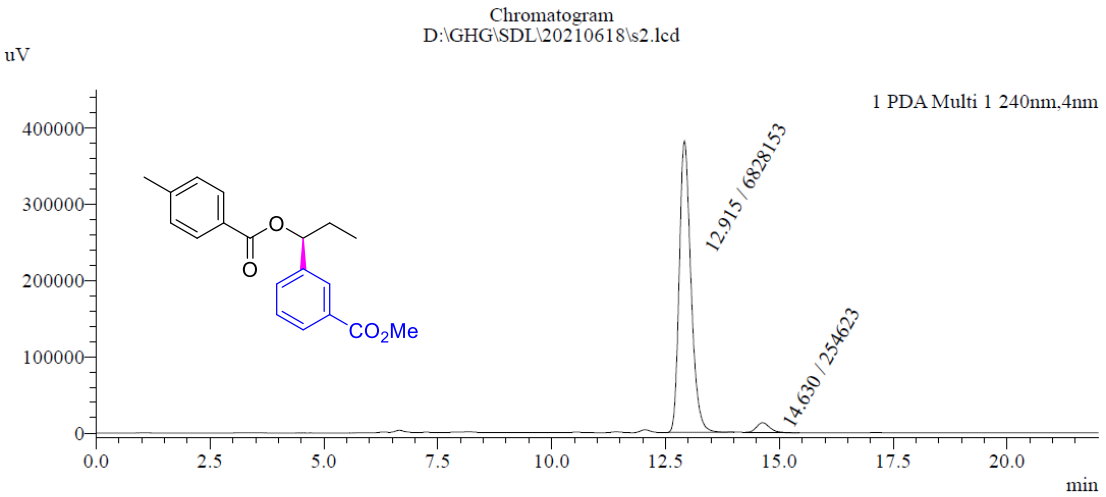


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.976	0.2705	1354652.89	75056.92	50.5199
2	14.726	0.3087	1326773.99	64984.00	49.4801

24: enantioenriched, 93% ee

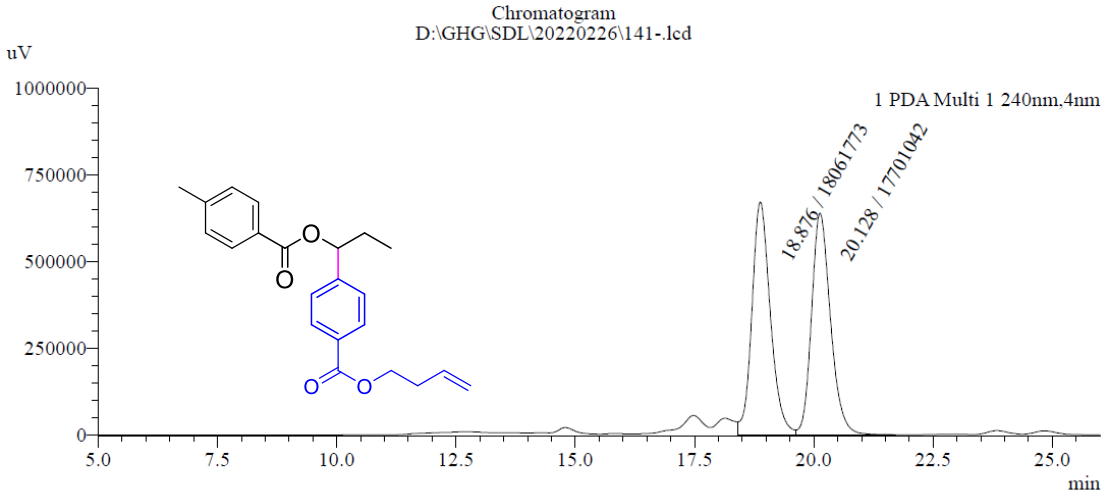


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.915	0.2704	6828152.65	382316.60	96.4050
2	14.630	0.3067	254623.04	12713.33	3.5950

25: racemic

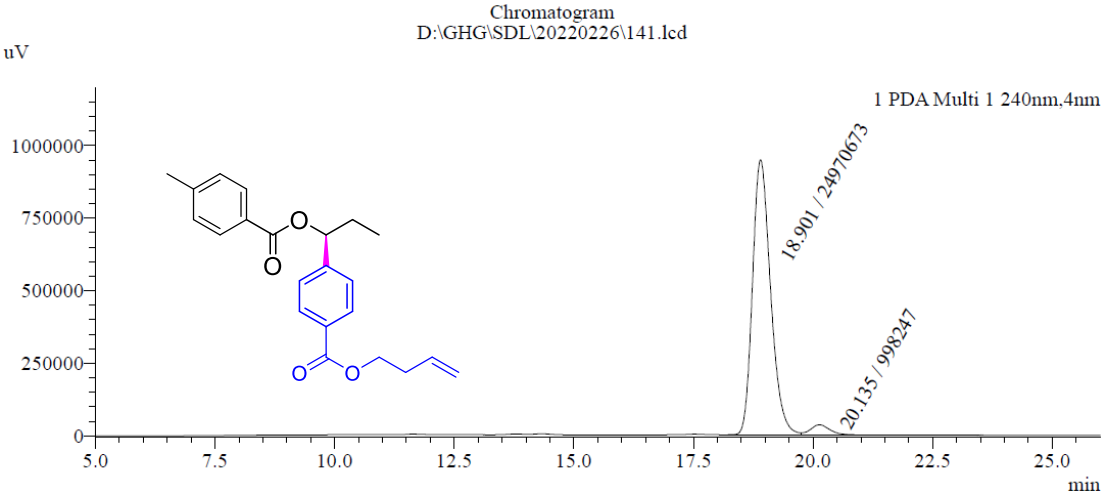


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	18.876	0.4024	18061772.91	671136.75	50.5043
2	20.128	0.4173	17701042.16	638963.63	49.4957

25: enantioenriched, 92% ee

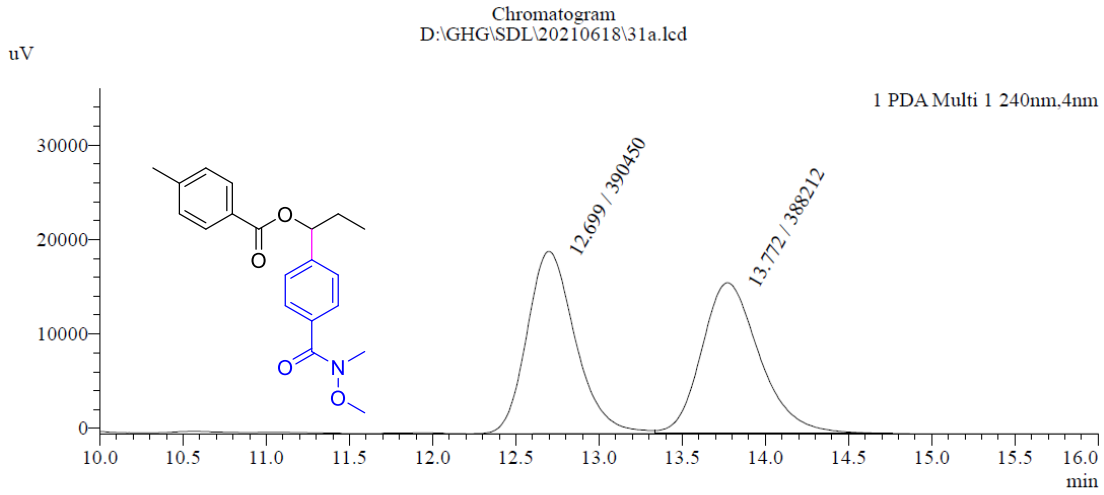


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	18.901	0.4003	24970673.49	948642.83	96.1560
2	20.135	0.4268	998246.92	35281.42	3.8440

26: racemic

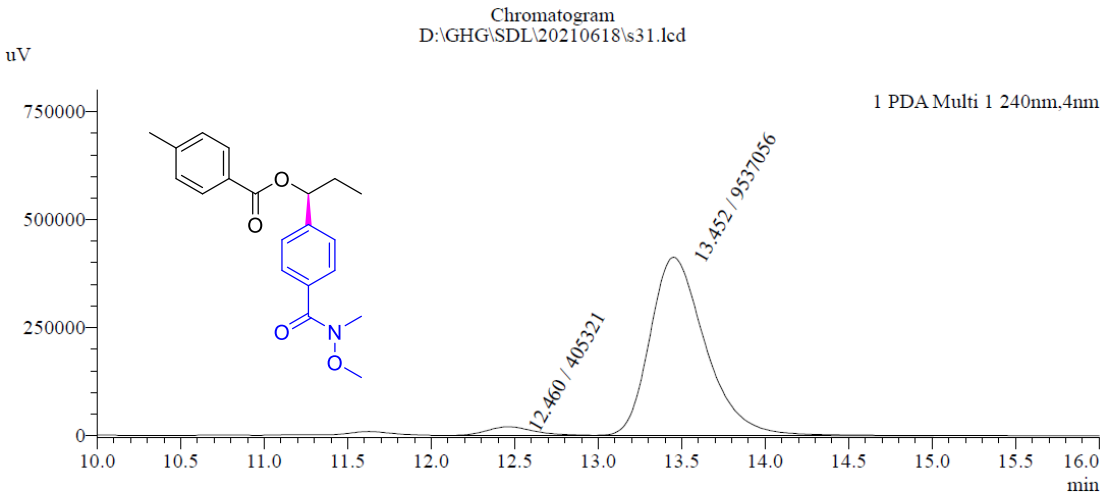


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.699	0.3056	390450.49	19313.56	50.1437
2	13.772	0.3657	388212.00	15985.18	49.8563

26: enantioenriched, 92% ee

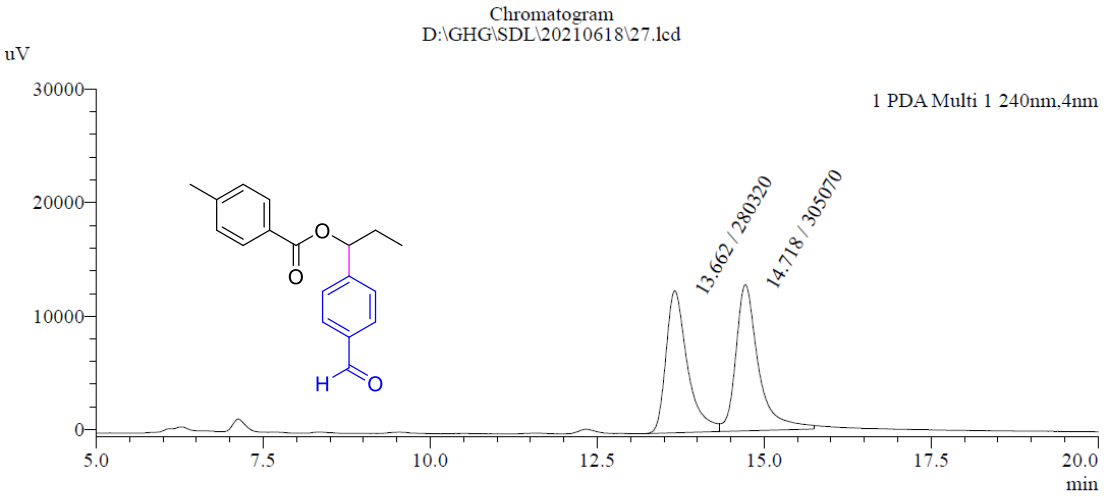


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.460	0.2965	405320.88	20372.98	4.0767
2	13.452	0.3469	9537055.52	412592.75	95.9233

27: racemic

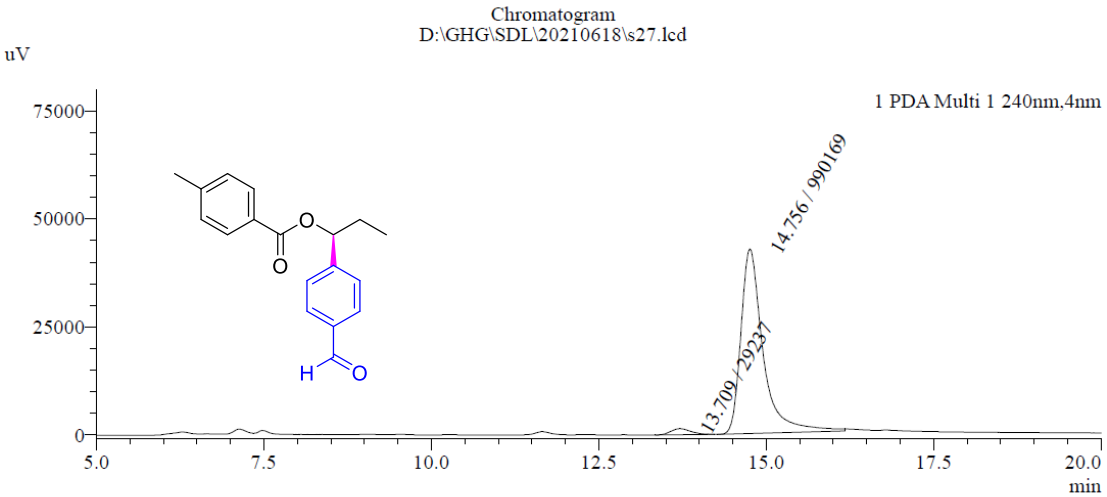


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.662	0.3231	280320.49	12503.64	47.8861
2	14.718	0.3237	305069.89	12885.37	52.1139

27: enantioenriched, 94% ee

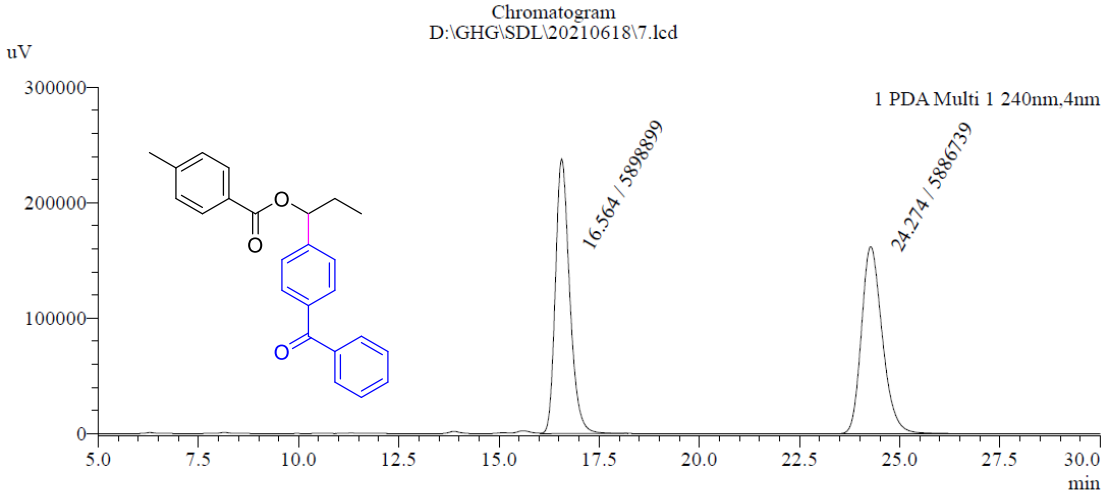


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.709	0.3192	29236.81	1414.40	2.8680
2	14.756	0.3189	990168.91	42709.72	97.1320

28: racemic

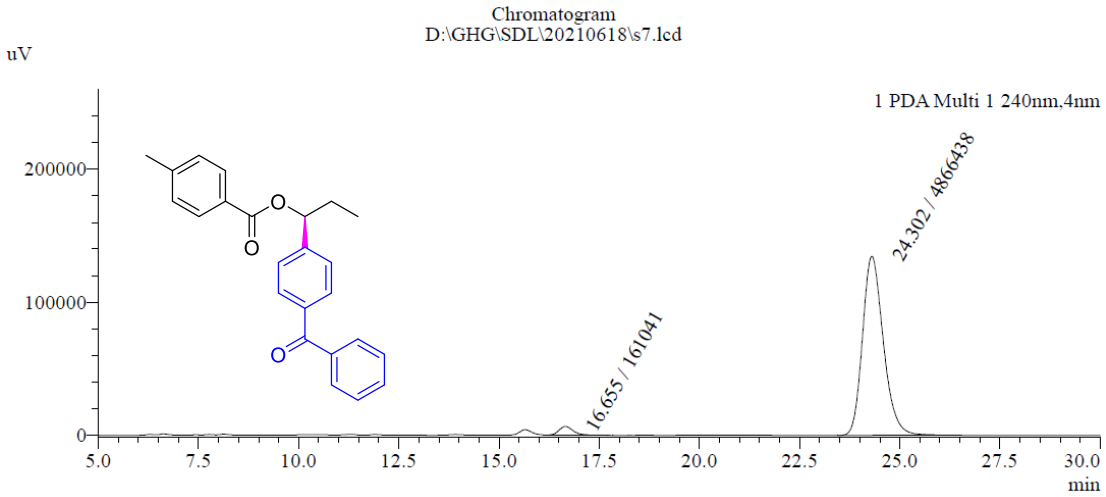


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	16.564	0.3741	5898898.59	237883.62	50.0516
2	24.274	0.5508	5886738.92	162137.38	49.9484

28: enantioenriched, 94% ee

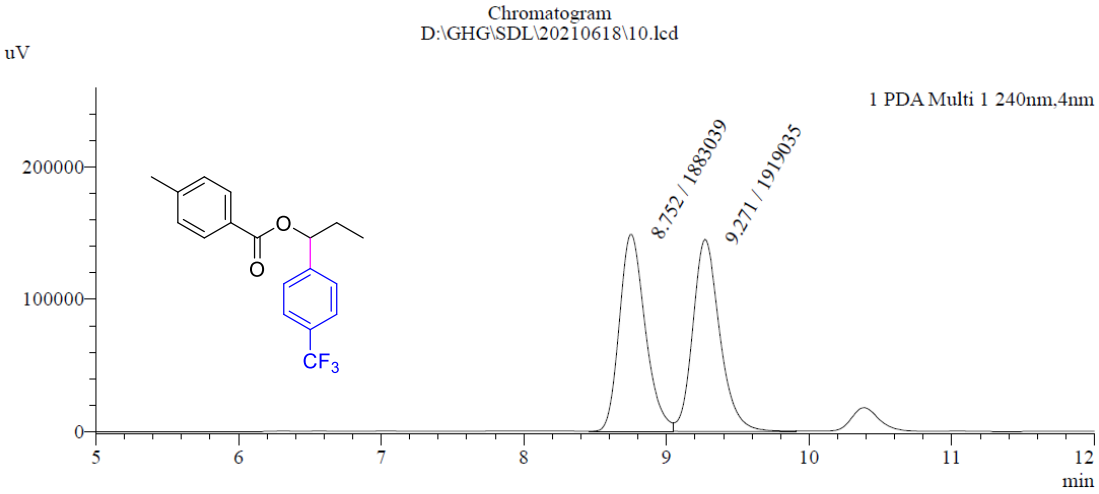


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	16.655	0.3727	161041.18	6560.56	3.2032
2	24.302	0.5495	4866438.32	134462.57	96.7968

29: racemic

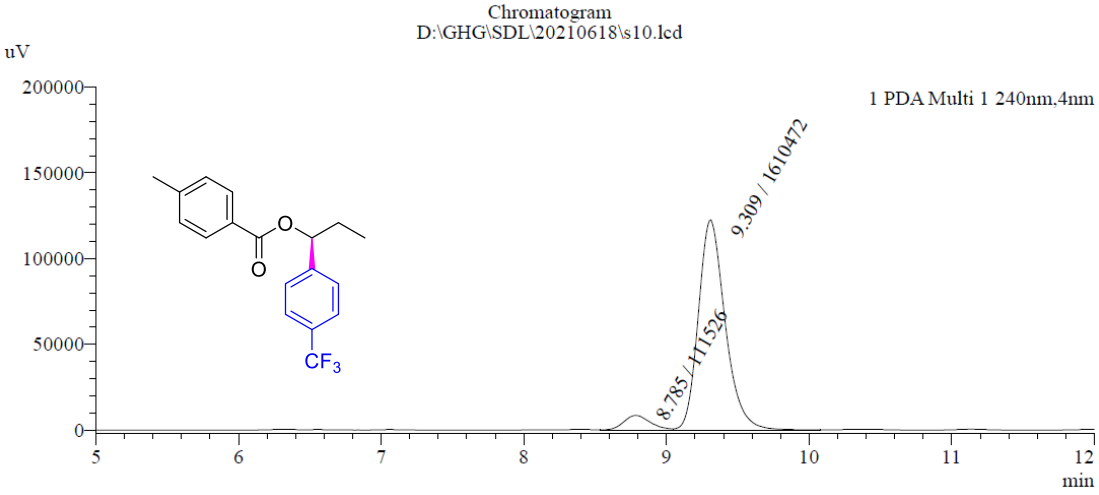


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	8.752	0.1921	1883039.46	149119.65	49.5266
2	9.271	0.1978	1919034.88	145294.12	50.4734

29: enantioenriched, 87% ee

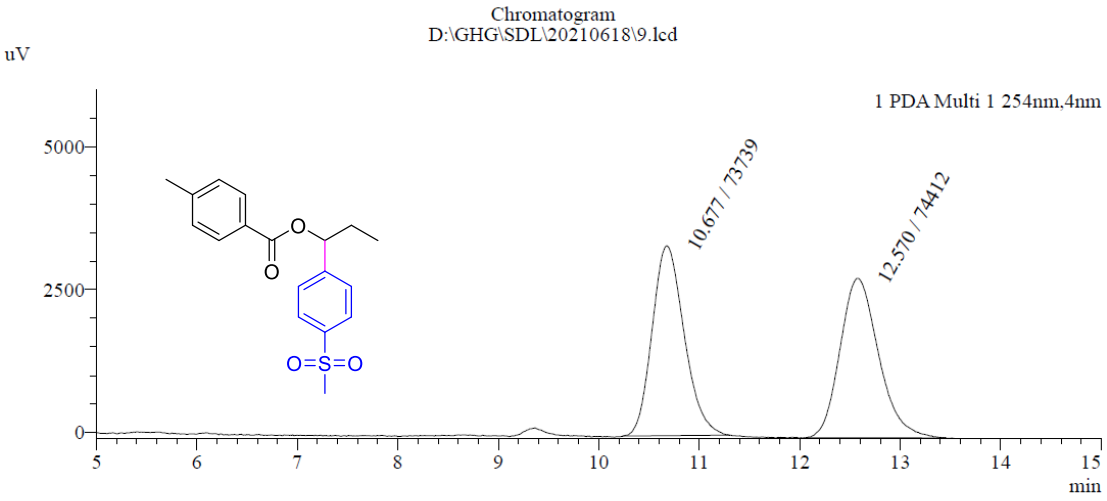


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	8.785	0.1976	111525.99	8590.24	6.4765
2	9.309	0.1978	1610472.26	122337.16	93.5235

30: racemic

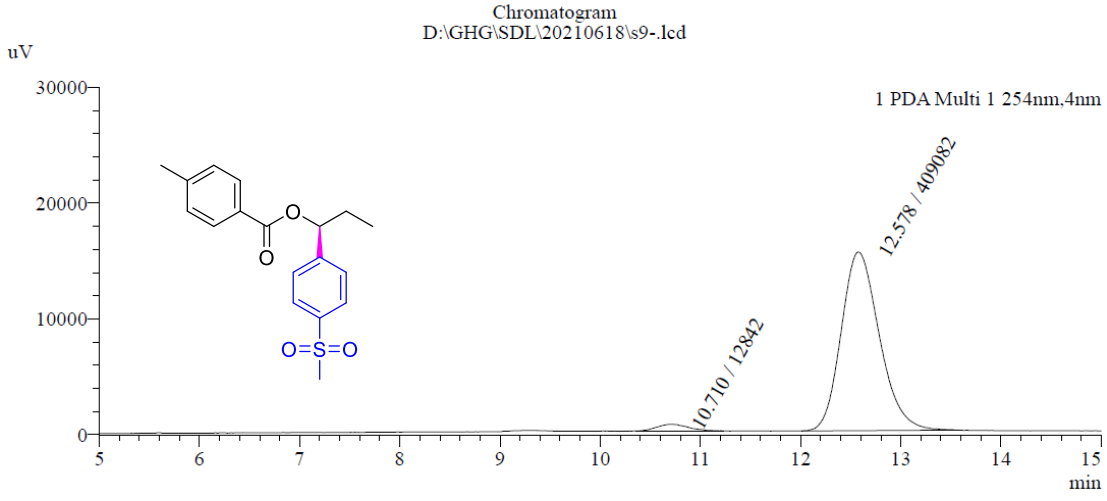


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.677	0.3420	73739.27	3324.15	49.7729
2	12.570	0.4075	74412.26	2784.74	50.2271

30: enantioenriched, 94% ee

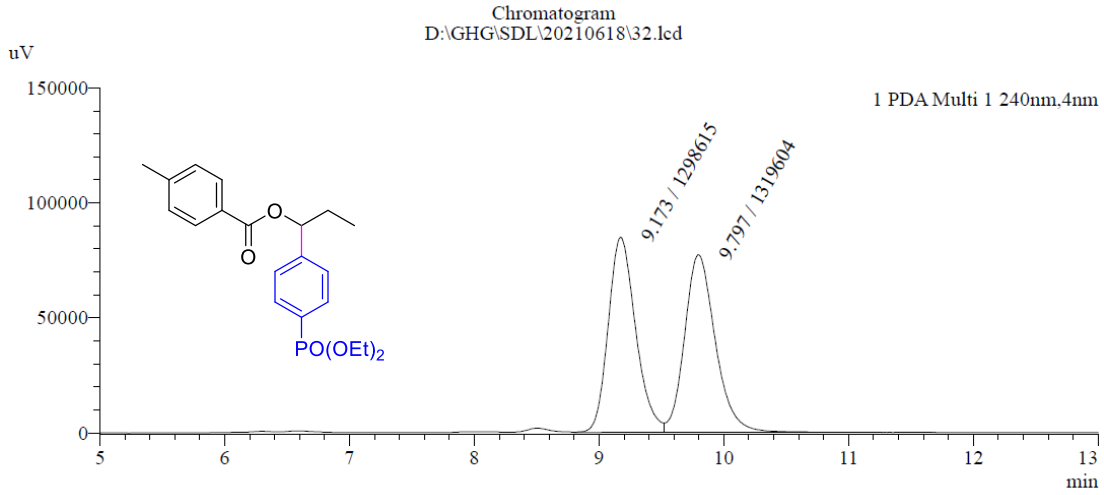


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.710	0.3356	12841.96	591.86	3.0437
2	12.578	0.4057	409082.25	15433.72	96.9563

31: racemic

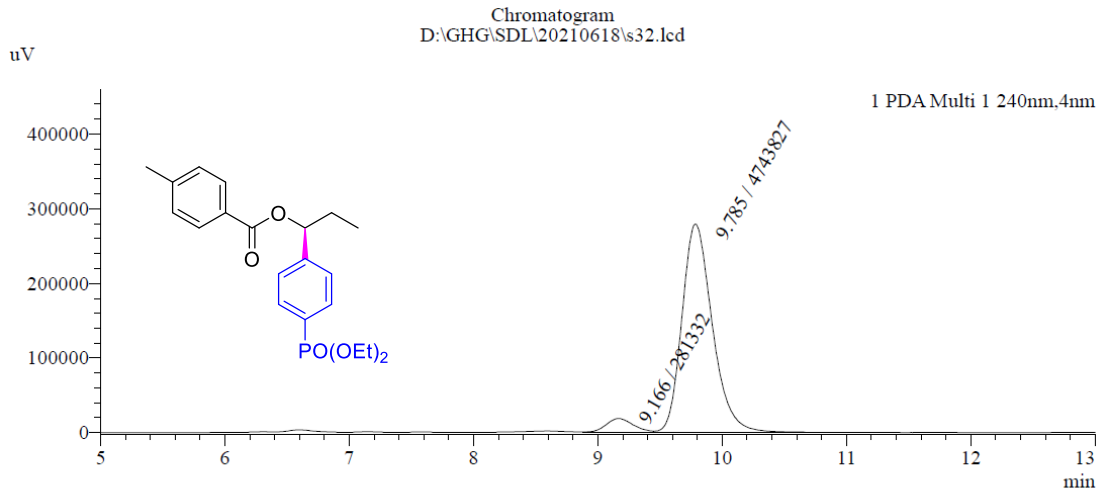


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	9.173	0.2333	1298614.85	84832.56	49.5992
2	9.797	0.2573	1319604.47	77213.11	50.4008

31: enantioenriched, 89% ee

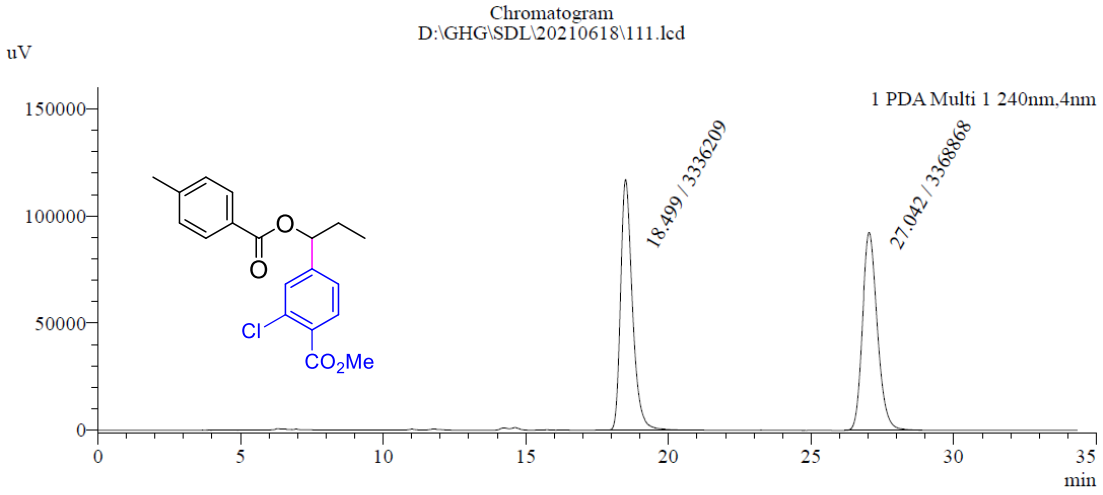


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	9.166	0.2344	281331.64	18470.79	5.5985
2	9.785	0.2566	4743826.79	279236.18	94.4015

32: racemic

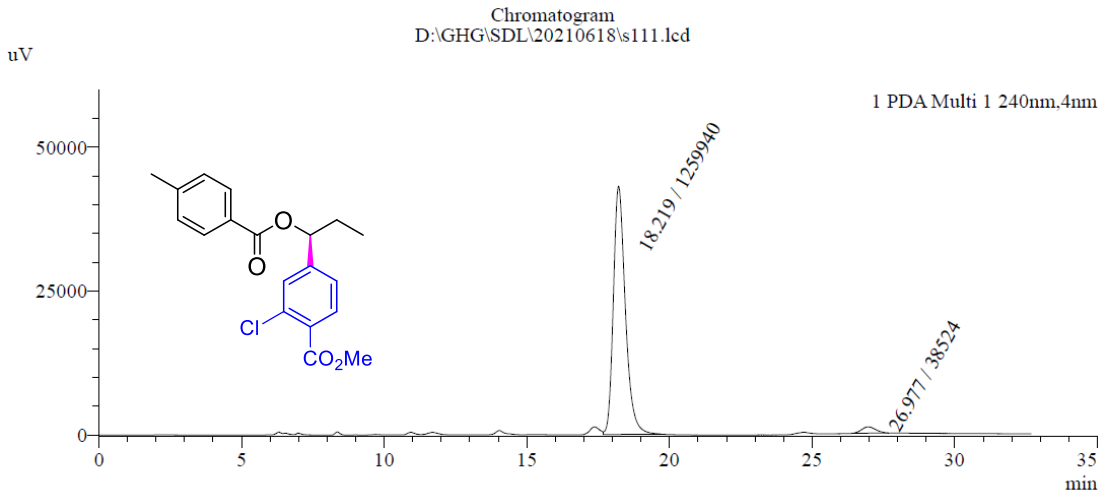


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	18.499	0.4246	3336209.24	116896.57	49.7565
2	27.042	0.5538	3368867.91	92409.74	50.2435

32: enantioenriched, 94% ee

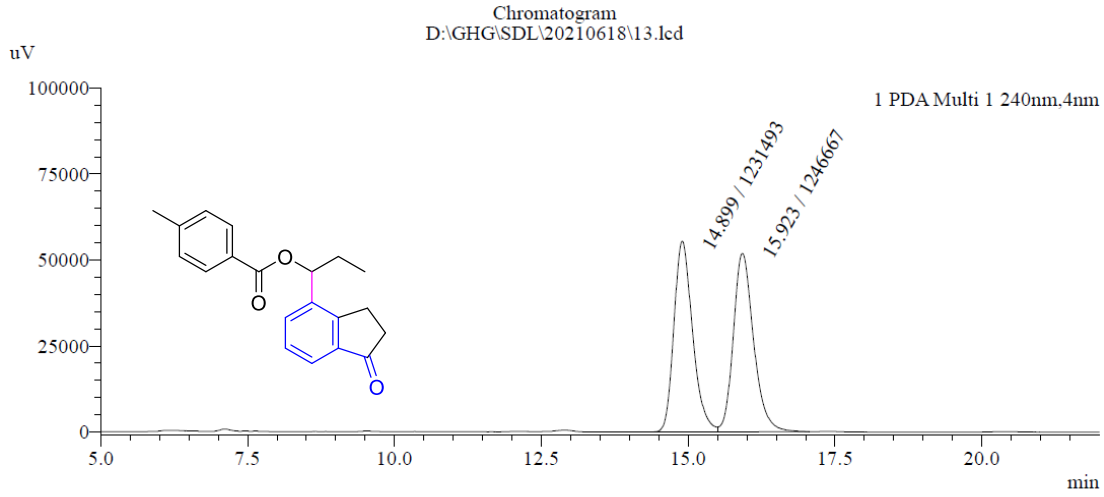


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	18.219	0.4346	1259939.78	43155.26	97.0331
2	26.977	0.5480	38524.40	1114.29	2.9669

33: racemic

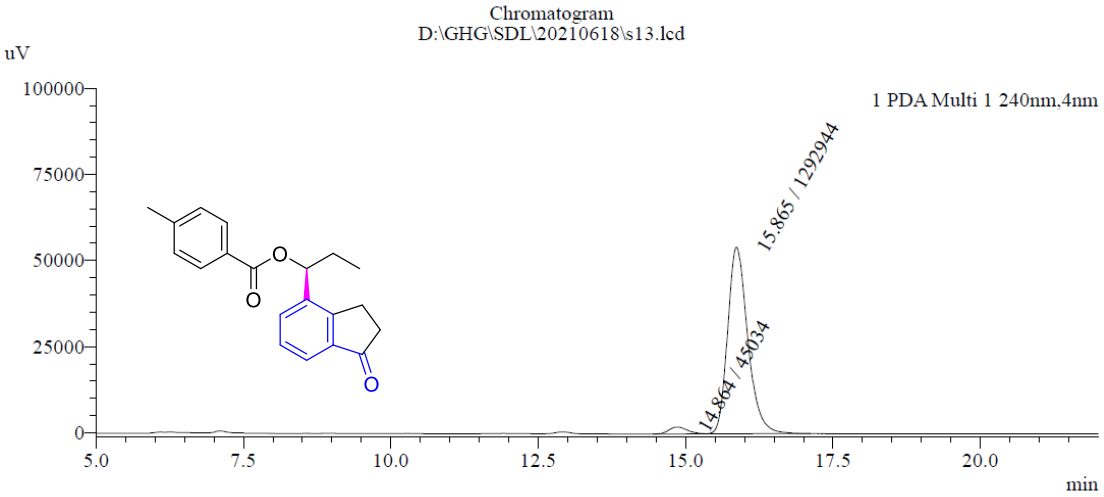


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	14.899	0.3358	1231492.68	55470.77	49.6938
2	15.923	0.3602	1246667.27	51855.65	50.3062

33: enantioenriched, 93% ee

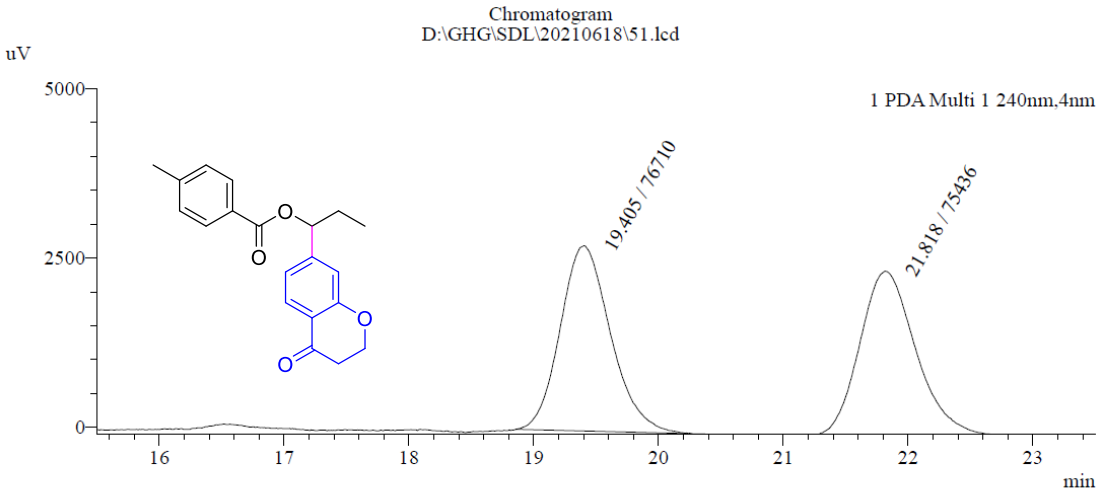


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	14.864	0.3375	45033.85	2059.72	3.3658
2	15.865	0.3582	1292944.02	54240.34	96.6342

34: racemic

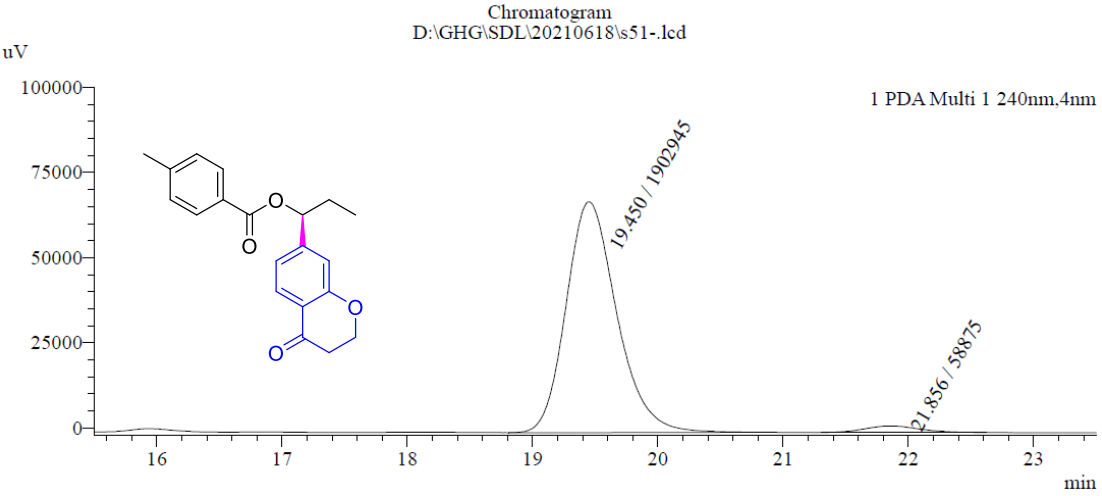


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	19.405	0.4282	76710.11	2735.19	50.4186
2	21.818	0.4756	75436.33	2424.03	49.5814

34: enantioenriched, 94% ee

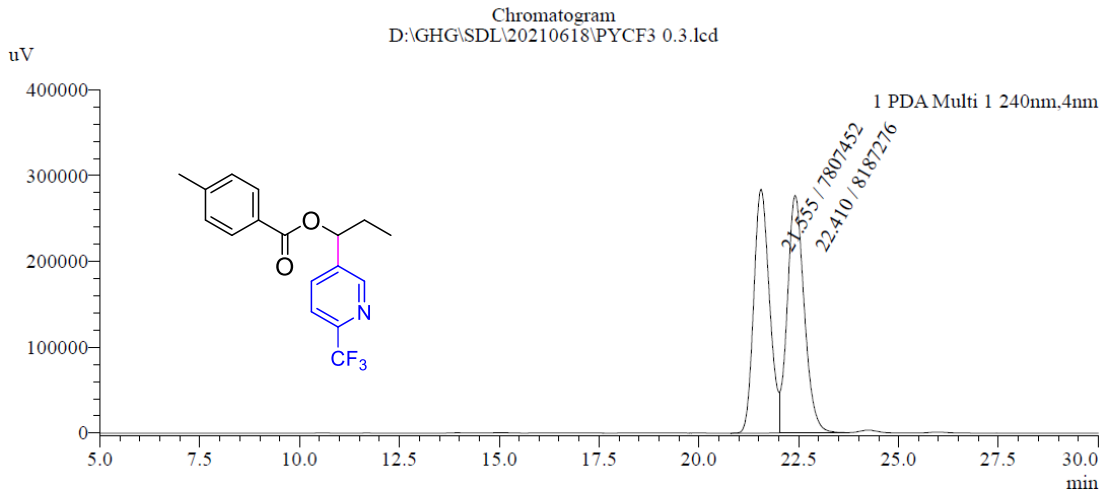


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	19.450	0.4252	1902945.15	67735.57	96.9989
2	21.856	0.4713	58875.32	1932.33	3.0011

35: racemic

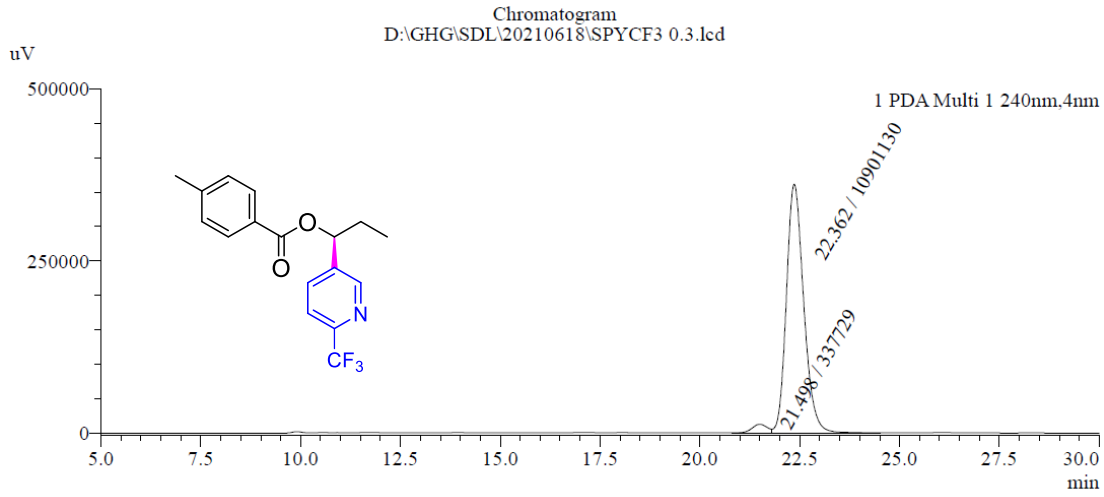


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	21.555	0.4285	7807451.63	284209.64	48.8127
2	22.410	0.4490	8187275.79	276939.16	51.1873

35: enantioenriched, 94% ee

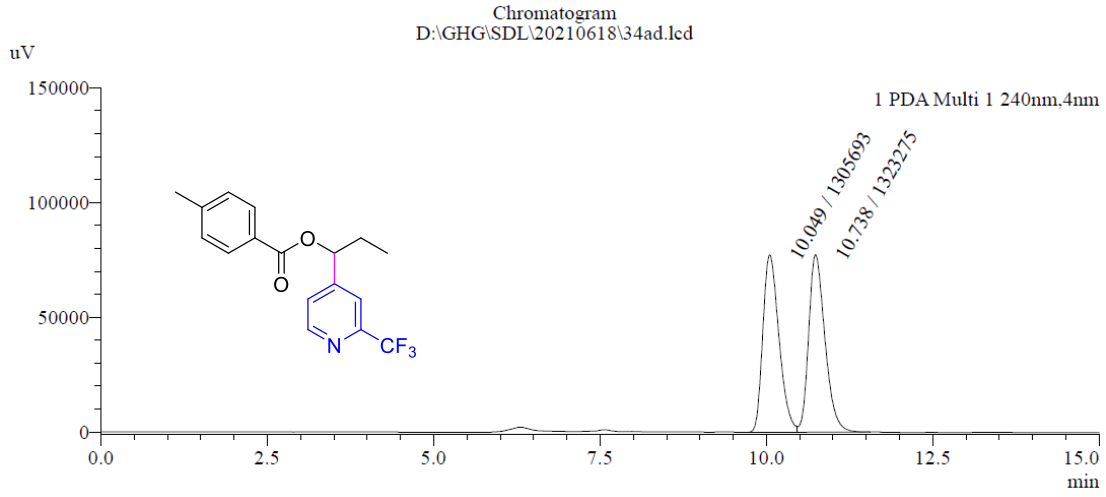


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	21.498	0.4537	337728.81	12568.82	3.0050
2	22.362	0.4576	10901129.68	361162.89	96.9950

36: racemic

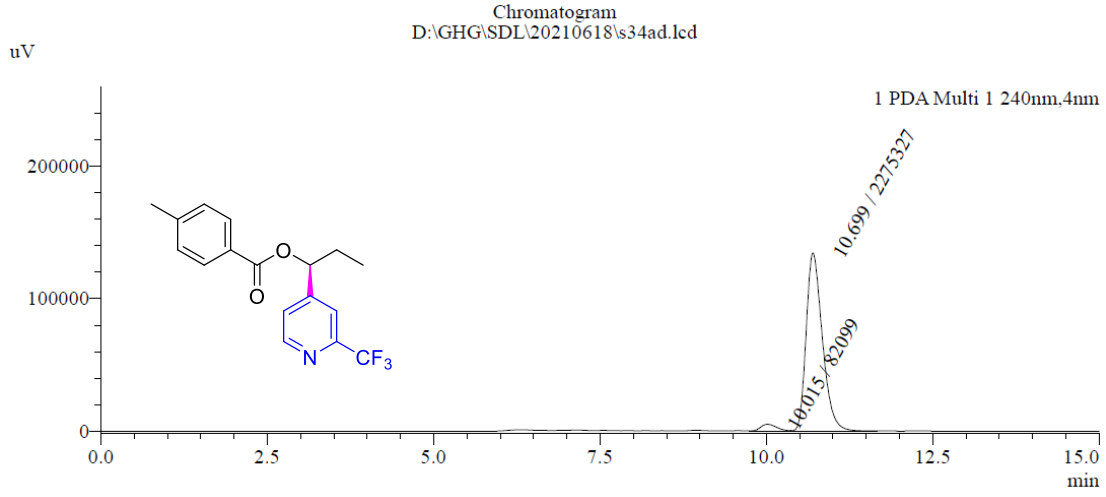


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.049	0.2618	1305693.07	77289.95	49.6656
2	10.738	0.2599	1323275.47	77343.25	50.3344

36: enantioenriched, 93% ee

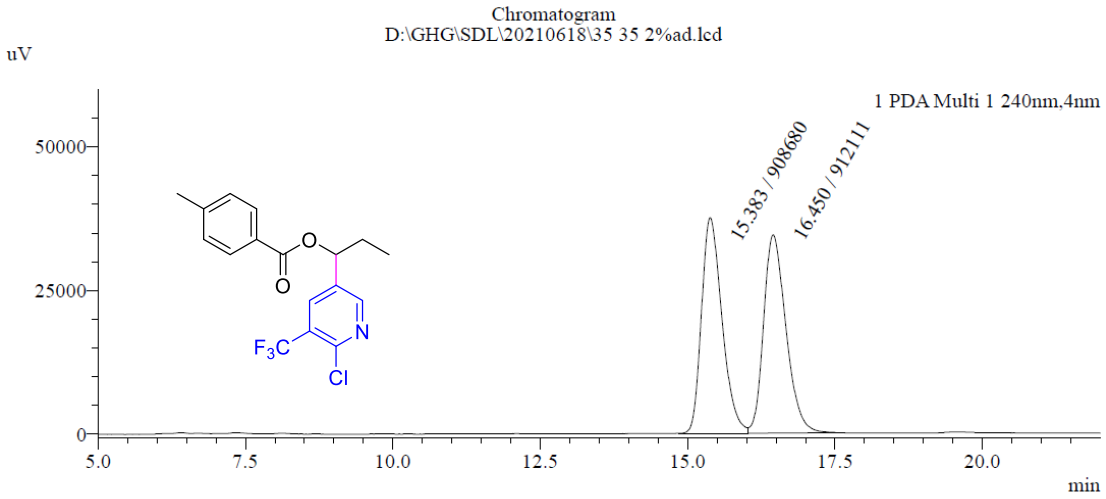


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.015	0.2575	82098.97	5040.92	3.4826
2	10.699	0.2579	2275326.90	134389.58	96.5174

37: racemic

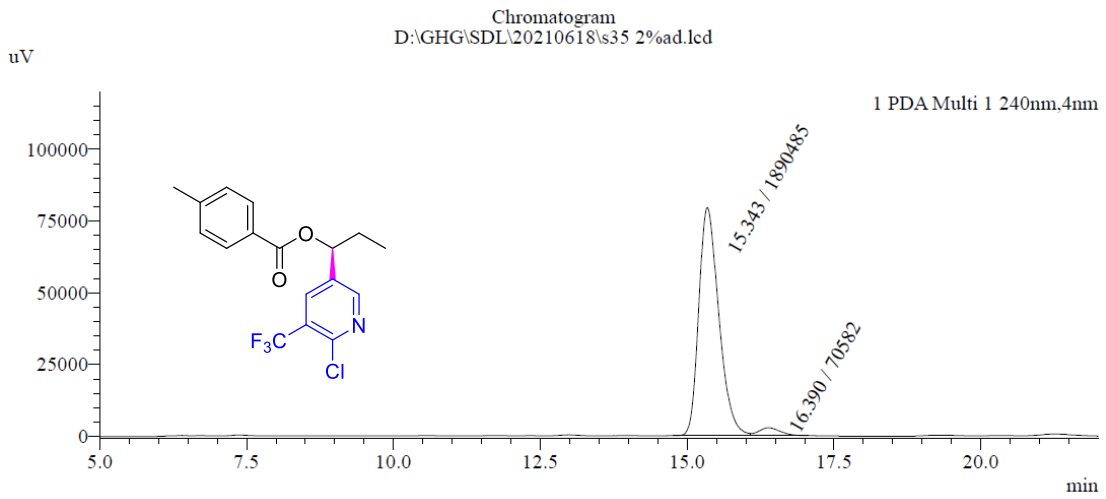


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	15.383	0.3711	908679.59	37518.30	49.9058
2	16.450	0.4038	912111.14	34484.11	50.0942

37: enantioenriched, 93% ee

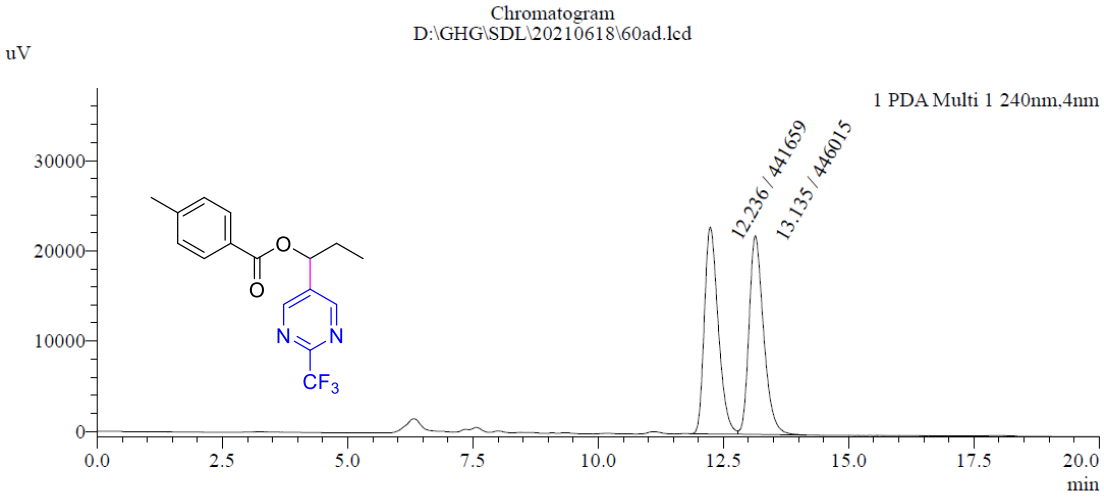


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	15.343	0.3637	1890484.94	79416.42	96.4008
2	16.390	0.4018	70582.47	2757.15	3.5992

38: racemic

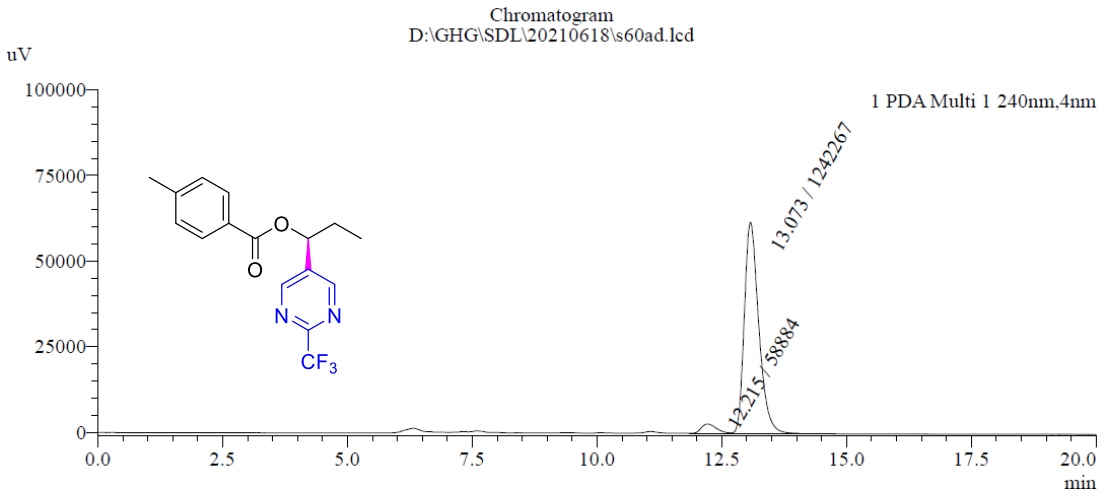


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.236	0.2954	441658.81	22923.05	49.7546
2	13.135	0.3052	446015.14	22002.25	50.2454

38: enantioenriched, 91% ee

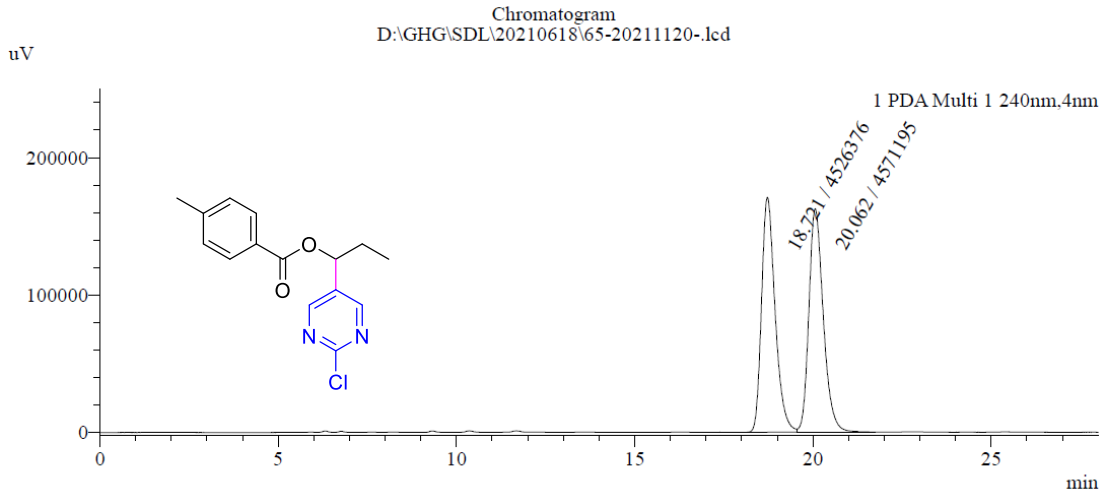


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.215	0.3354	58884.23	2748.51	4.5255
2	13.073	0.3042	1242266.87	61581.18	95.4745

39: racemic

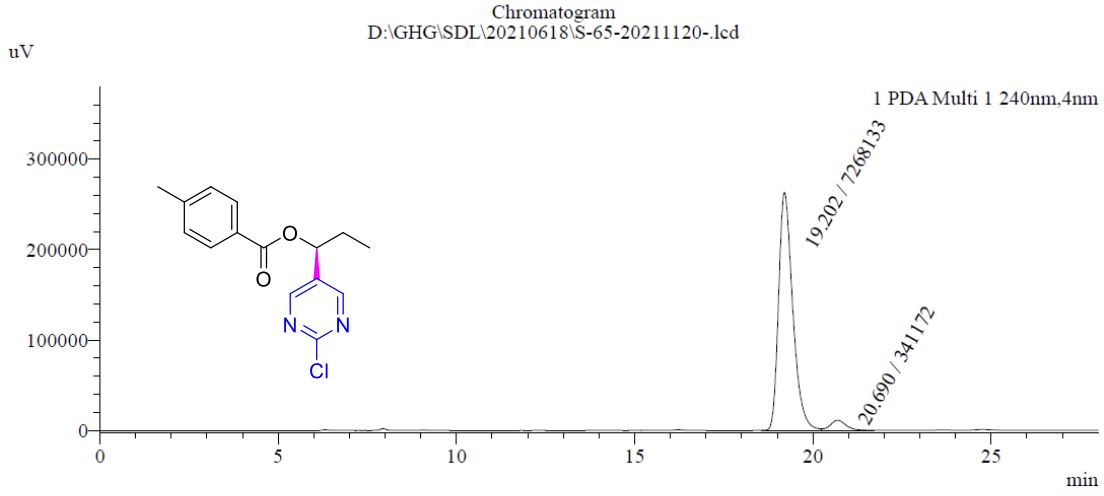


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	18.721	0.3999	4526376.36	170919.69	49.7537
2	20.062	0.4238	4571195.02	162534.44	50.2463

39: enantioenriched, 91% ee

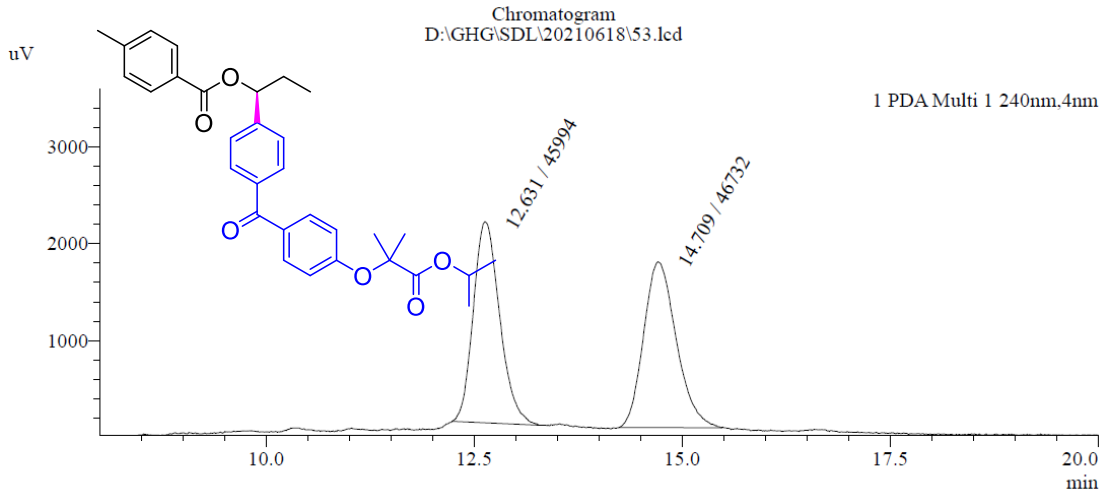


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	19.202	0.4163	7268132.91	262910.49	95.5164
2	20.690	0.4553	341172.17	11224.16	4.4836

40: racemic

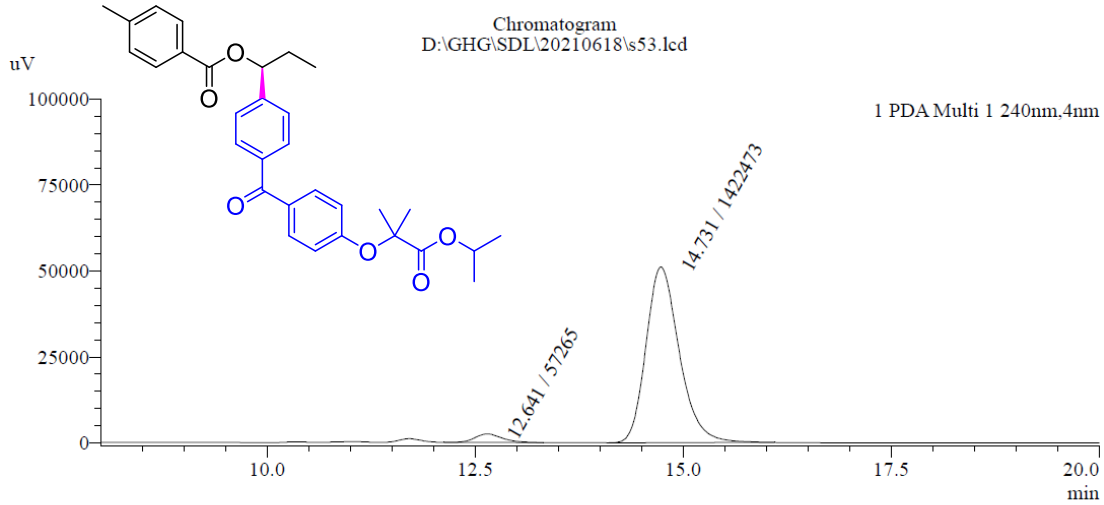


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.631	0.3394	45993.77	2081.31	49.6021
2	14.709	0.4195	46731.60	1711.54	50.3979

40: enantioenriched, 92% ee

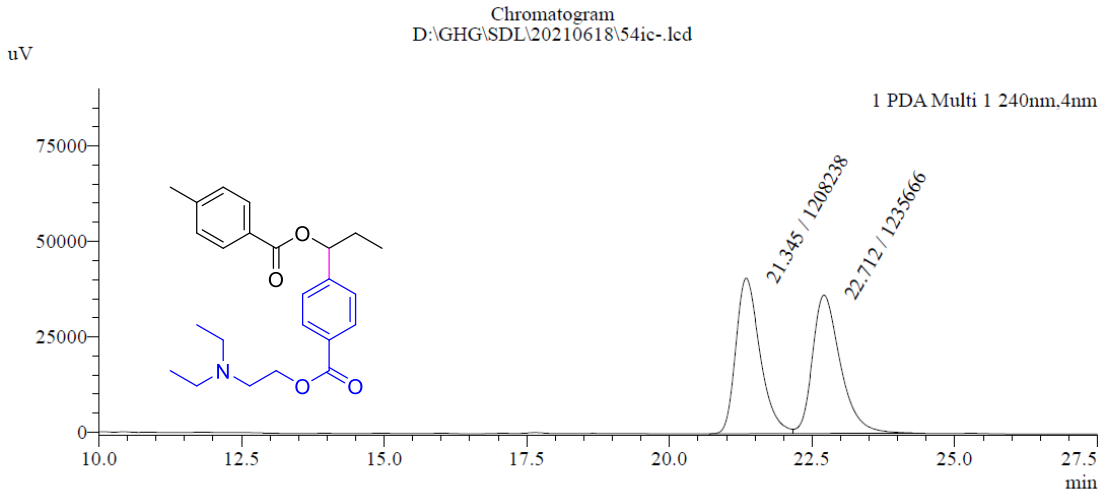


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.641	0.3477	57265.21	2480.28	3.8700
2	14.731	0.4203	1422472.85	51075.86	96.1300

41: racemic

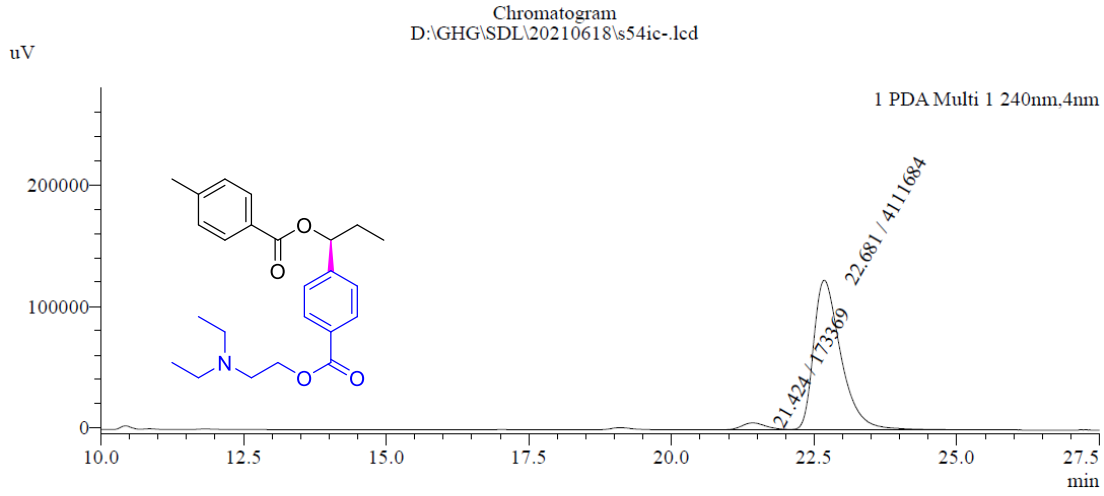


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	21.345	0.4491	1208238.11	40747.27	49.4389
2	22.712	0.5072	1235665.65	36274.00	50.5611

41: enantioenriched, 92% ee

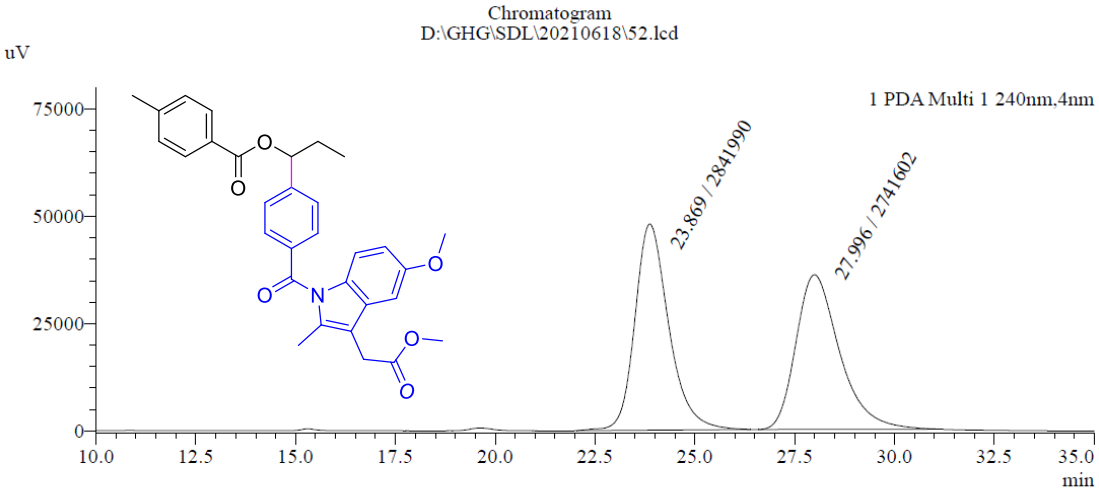


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	21.424	0.4605	173369.30	5772.07	4.0459
2	22.681	0.4971	4111683.82	123057.67	95.9541

42: racemic

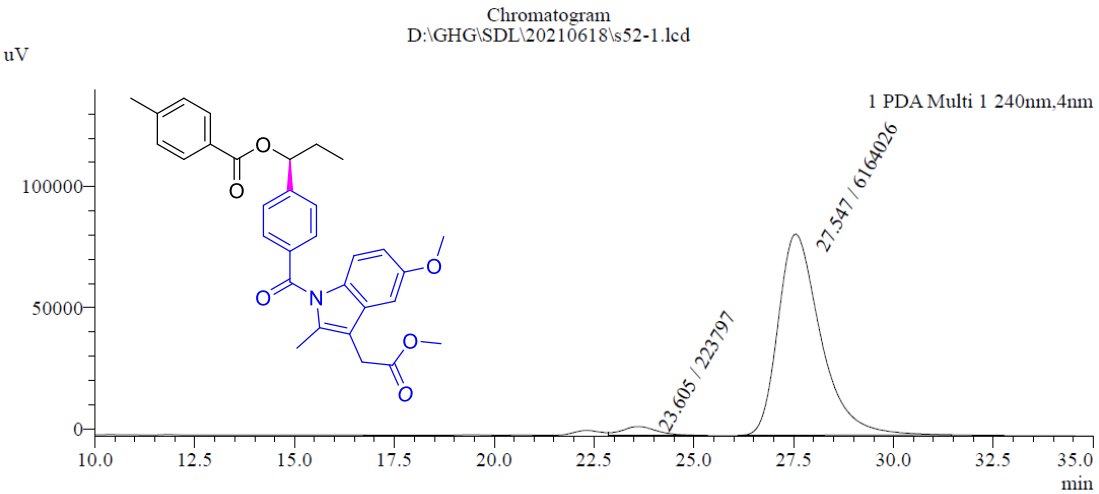


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	23.869	0.8748	2841990.28	48061.79	50.8990
2	27.996	1.1379	2741601.86	36030.68	49.1010

42: enantioenriched, 93% ee

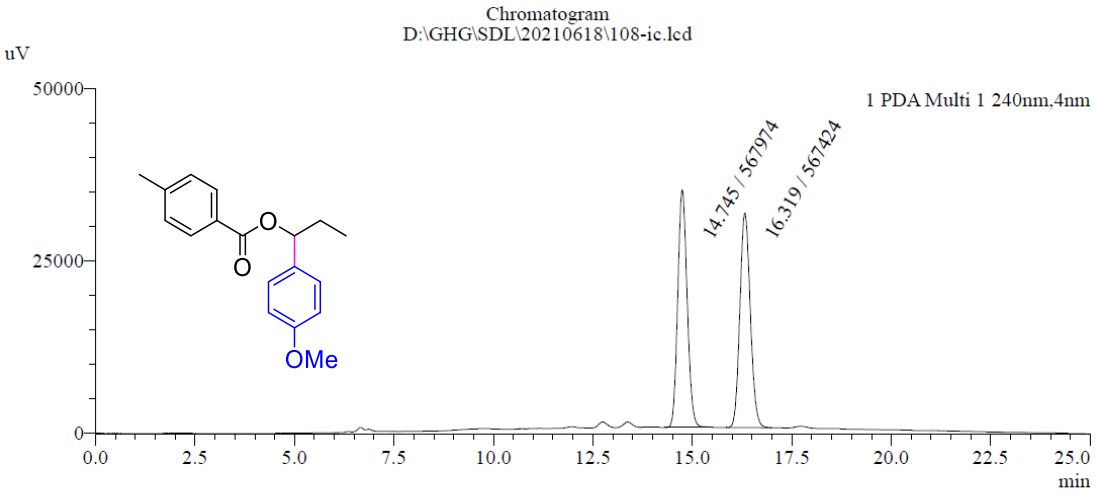


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	23.605	0.9269	223797.39	3702.23	3.5035
2	27.547	1.0965	6164025.50	83056.55	96.4965

43: racemic

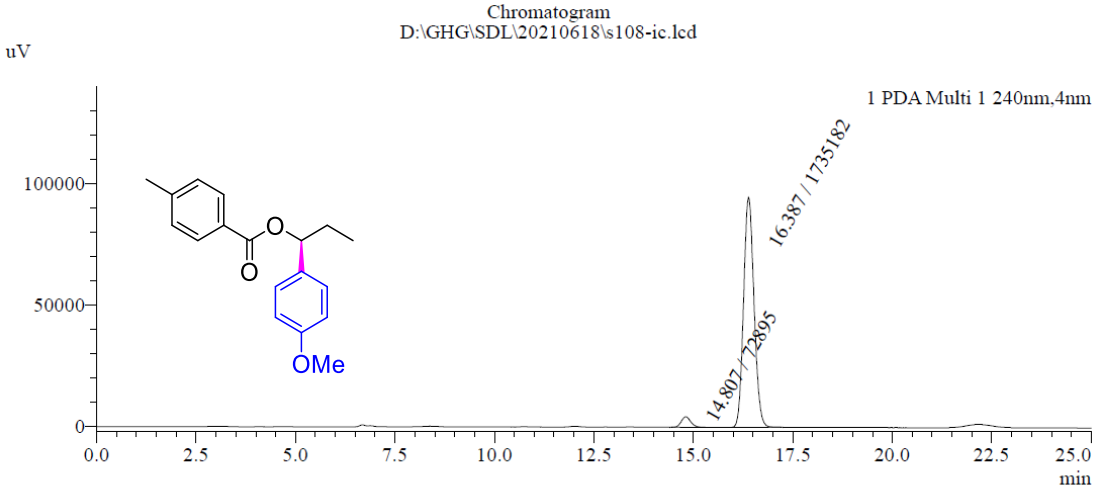


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	14.745	0.2545	567973.53	34467.11	50.0242
2	16.319	0.2822	567424.38	31131.60	49.9758

43: enantioenriched, 92% ee

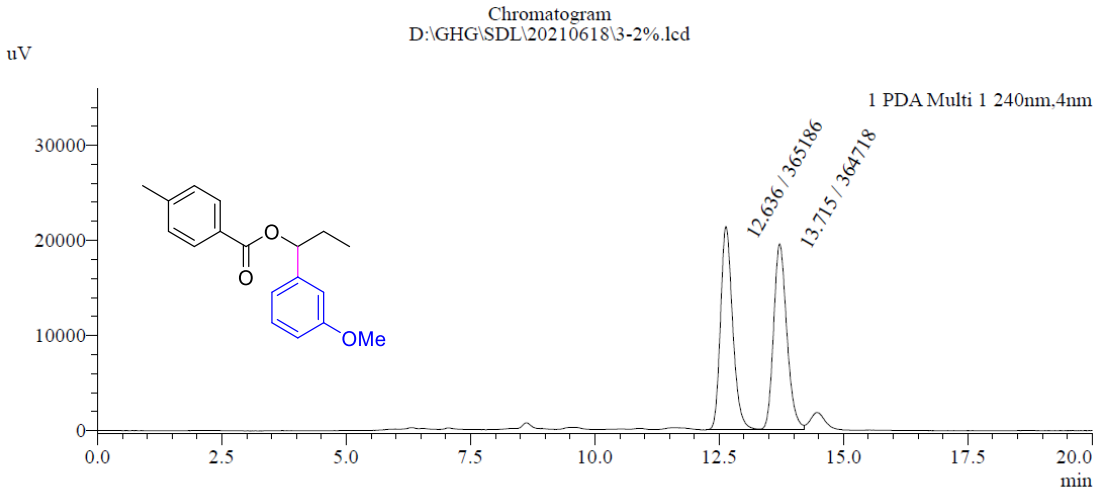


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	14.807	0.2568	72894.50	4360.18	4.0316
2	16.387	0.2835	1735182.19	94724.21	95.9684

44: racemic

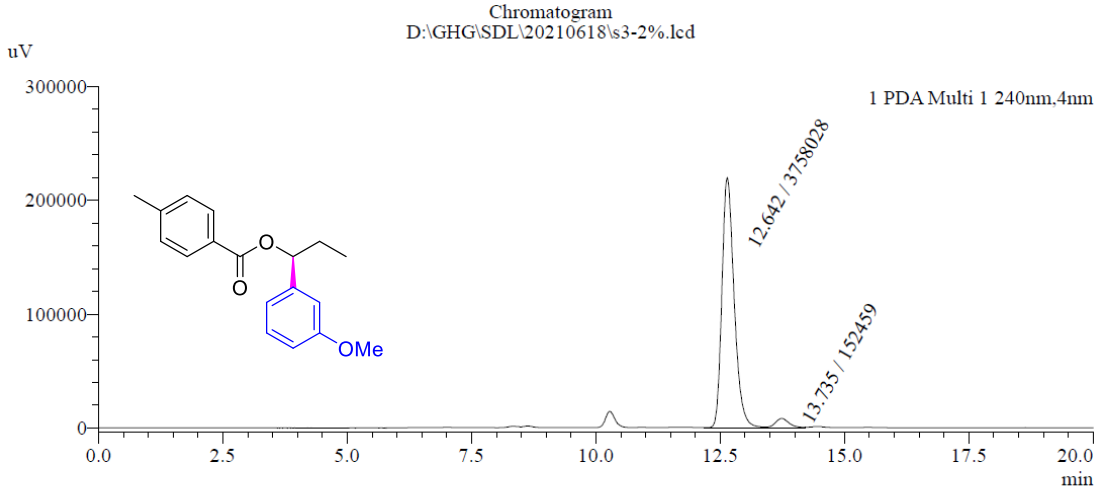


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.636	0.2577	365186.16	21381.72	50.0321
2	13.715	0.2823	364718.25	19577.80	49.9679

44: enantioenriched, 92% ee

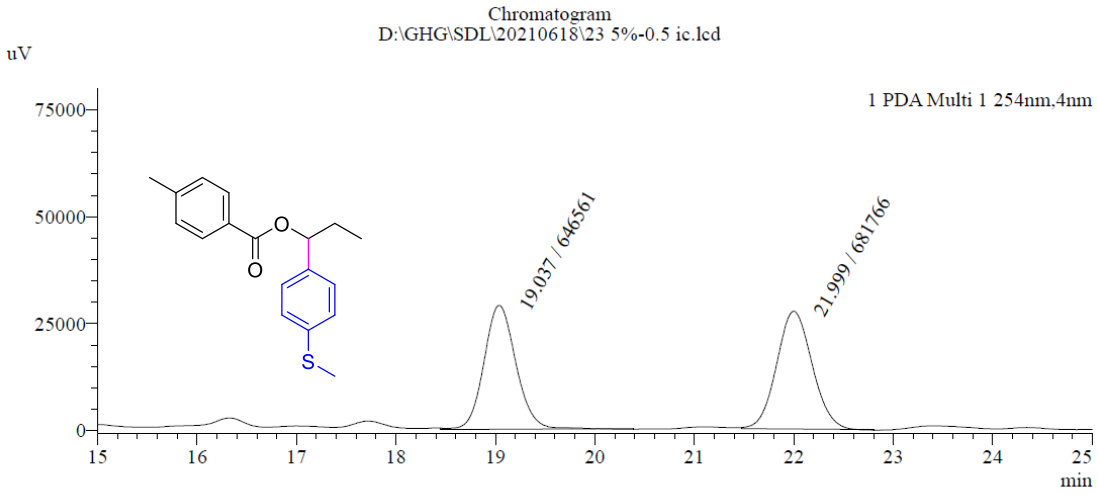


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.642	0.2583	3758027.87	219655.12	96.1013
2	13.735	0.2816	152458.82	8093.64	3.8987

45: racemic

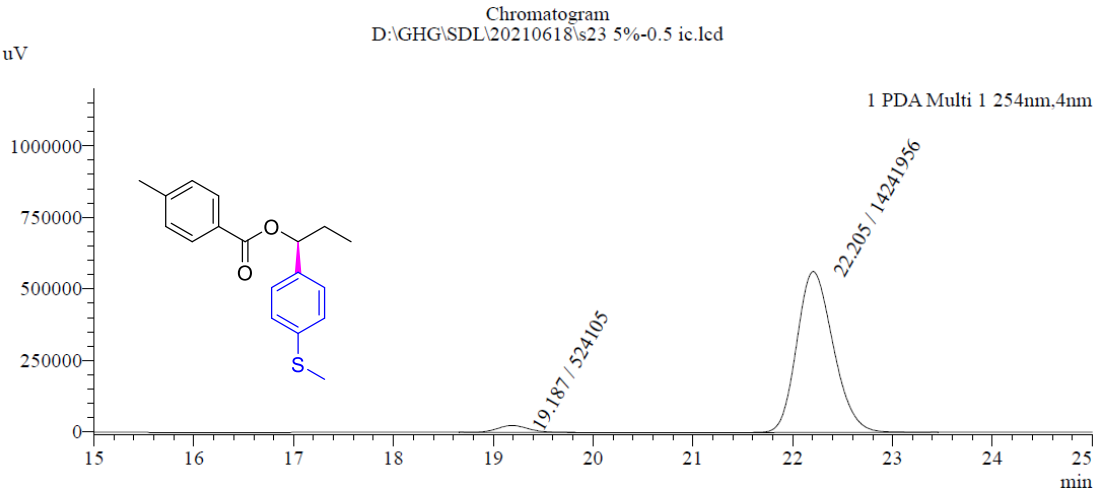


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	19.037	0.3406	646560.67	28955.14	48.6748
2	21.999	0.3849	681765.89	27510.48	51.3252

45: enantioenriched, 93% ee

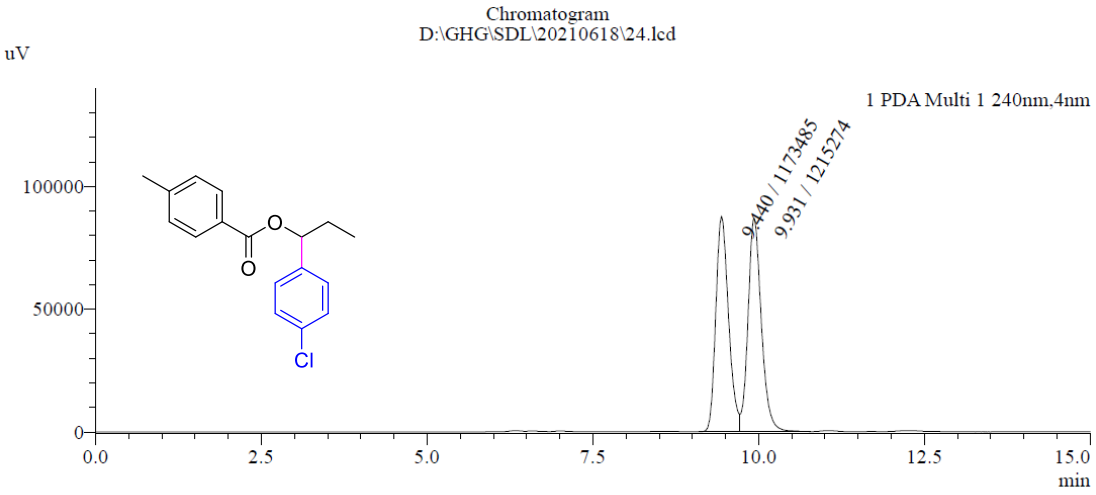


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	19.187	0.3350	524105.21	24274.11	3.5494
2	22.205	0.3922	14241956.43	562156.32	96.4506

46: racemic

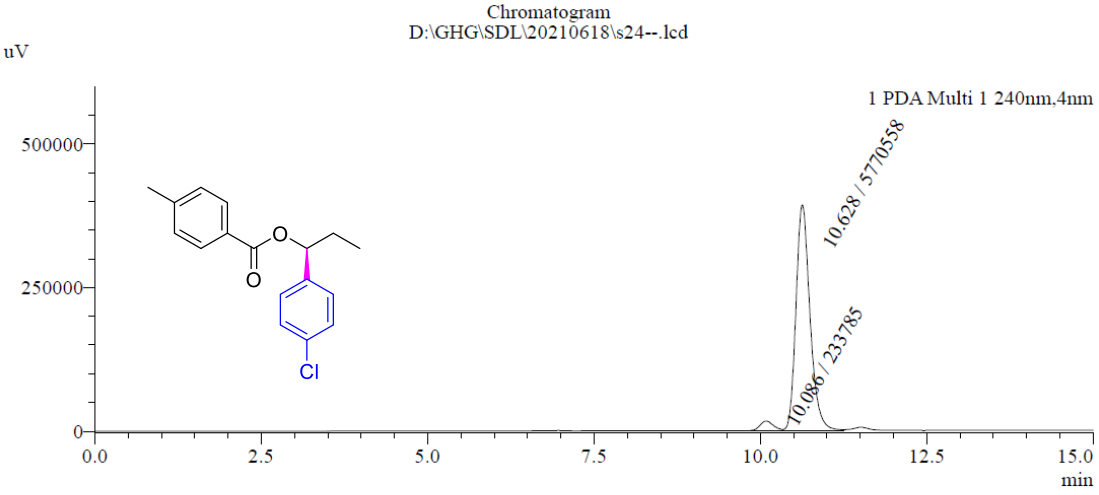


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	9.440	0.2052	1173484.85	87559.55	49.1253
2	9.931	0.2091	1215273.80	86920.05	50.8747

46: enantioenriched, 92% ee

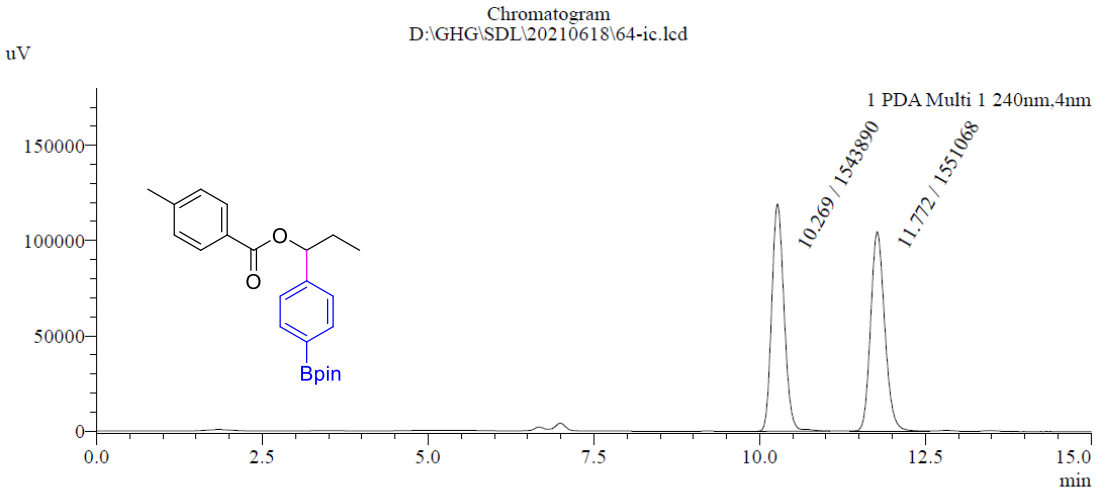


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.086	0.2171	233784.97	16707.83	3.8936
2	10.628	0.2206	5770557.86	393308.95	96.1064

47: racemic

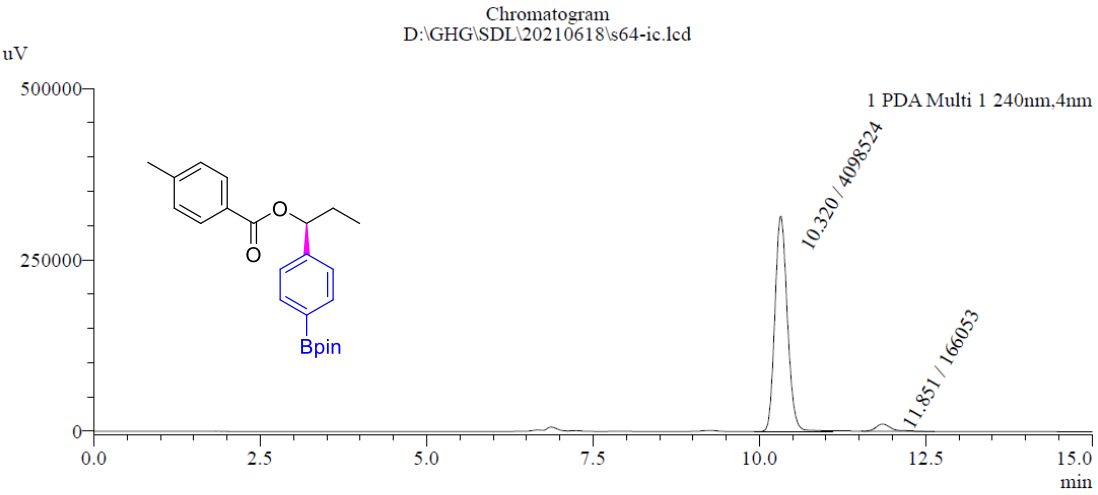


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.269	0.1987	1543889.79	119309.44	49.8840
2	11.772	0.2269	1551068.21	104623.00	50.1160

47: enantioenriched, 92% ee

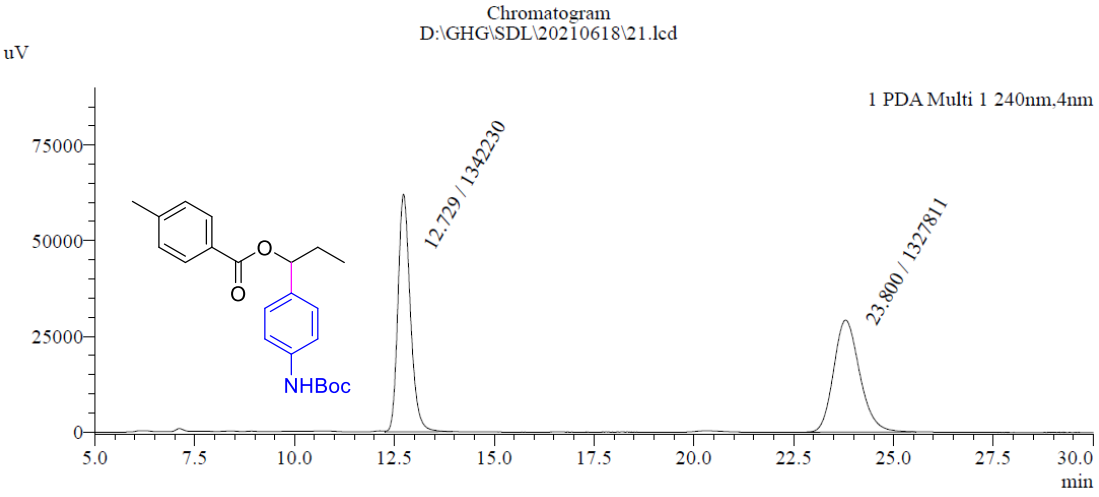


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.320	0.2002	4098524.40	314045.80	96.1062
2	11.851	0.2280	166053.22	10416.64	3.8938

48: racemic

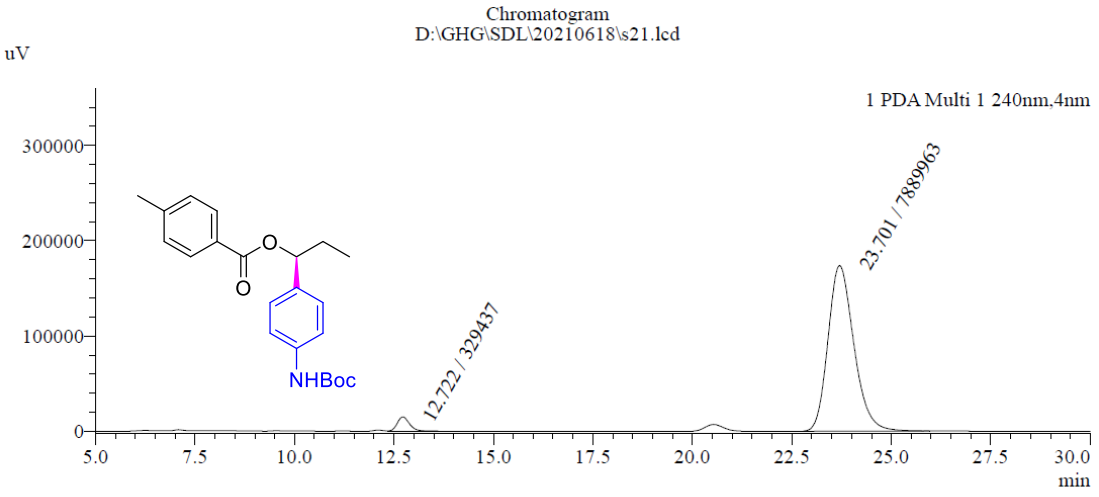


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.729	0.3253	1342229.72	62092.46	50.2700
2	23.800	0.6924	1327811.32	29285.78	49.7300

48: enantioenriched, 92% ee

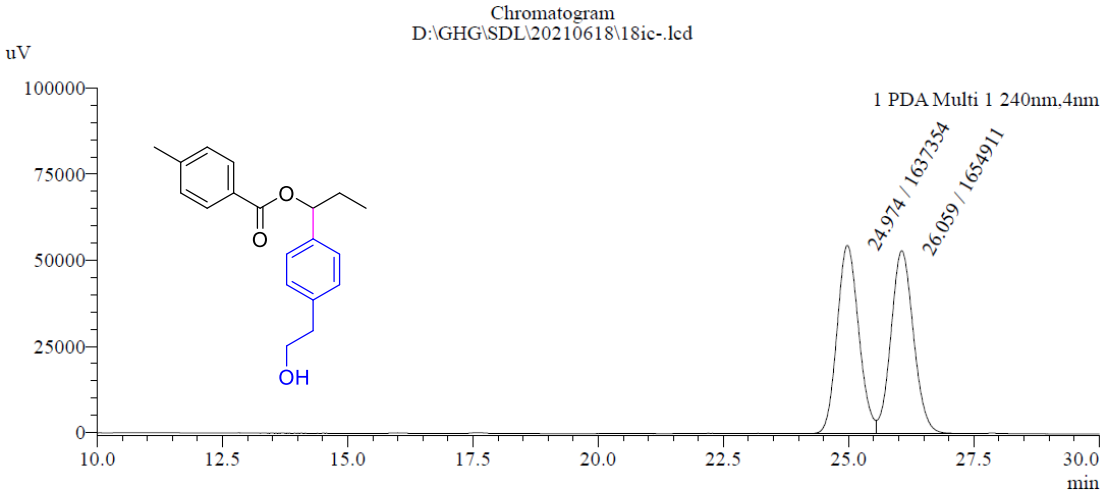


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.722	0.3260	329436.55	15151.10	4.0080
2	23.701	0.6893	7889962.85	174036.16	95.9920

49: racemic

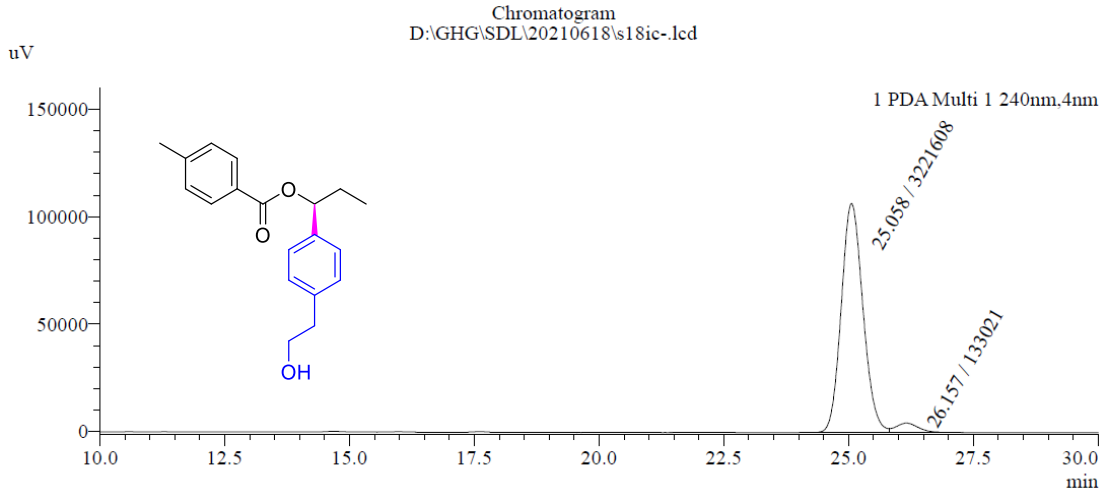


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	24.974	0.4658	1637353.86	54598.78	49.7334
2	26.059	0.4811	1654911.01	53020.13	50.2666

49: enantioenriched, 92% ee

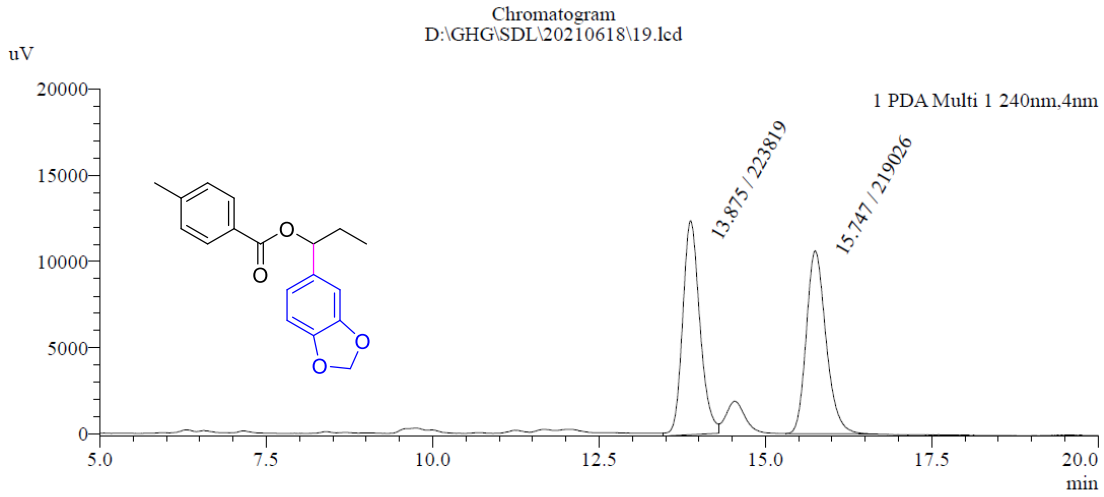


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	25.058	0.4676	3221608.35	106477.25	96.0347
2	26.157	0.5097	133020.93	4303.36	3.9653

50: racemic

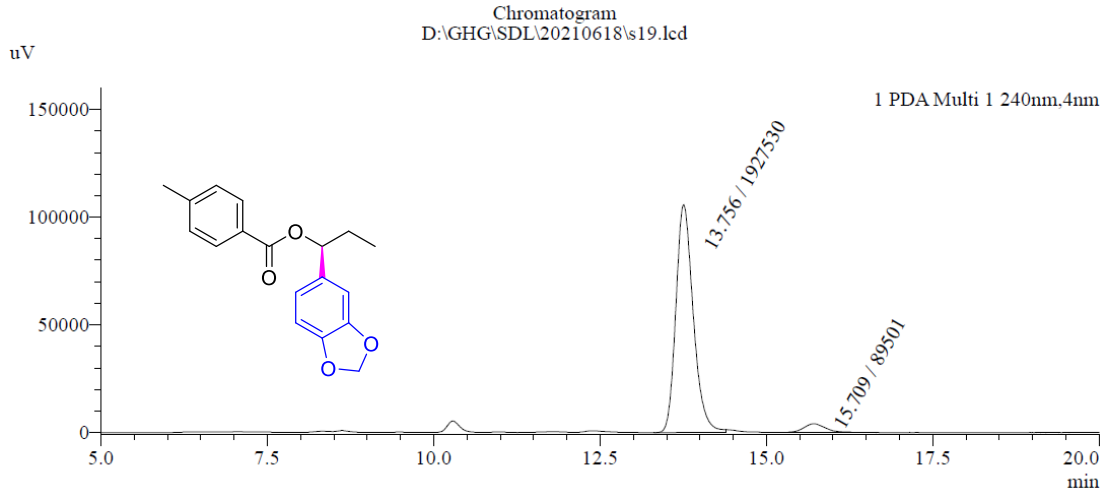


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.875	0.2721	223818.80	12403.02	50.5412
2	15.747	0.3130	219025.52	10596.12	49.4588

50: enantioenriched, 91% ee

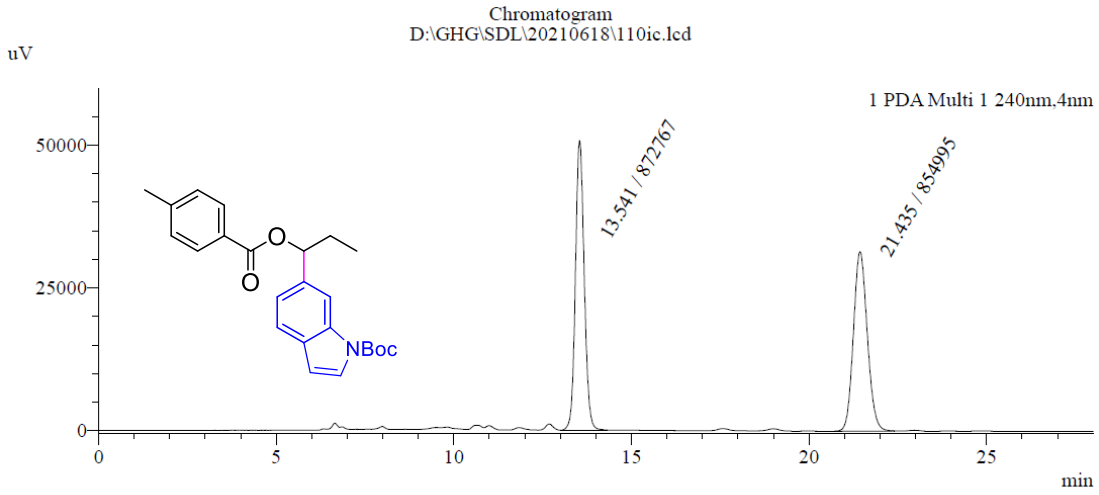


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.756	0.2747	1927530.25	105670.98	95.5628
2	15.709	0.3393	89500.52	3986.93	4.4372

51: racemic

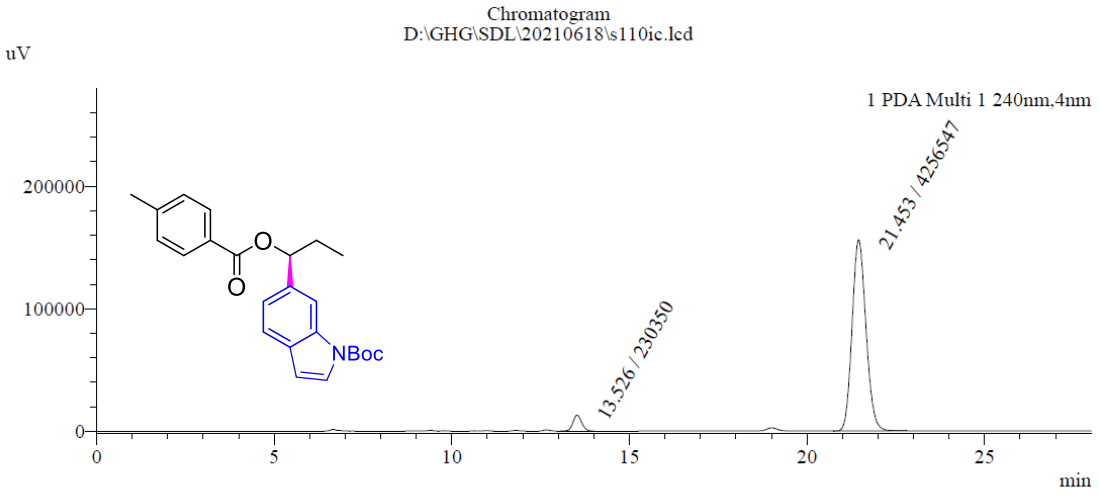


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.541	0.2615	872767.16	50763.89	50.5143
2	21.435	0.4184	854995.07	31454.69	49.4857

51: enantioenriched, 90% ee

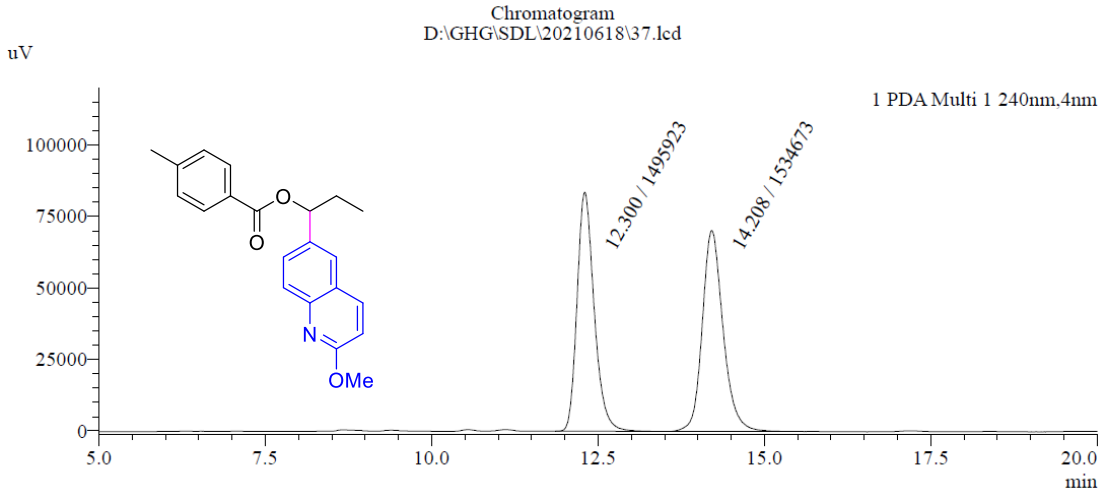


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.526	0.2637	230350.18	13212.32	5.1338
2	21.453	0.4197	4256546.61	156152.51	94.8662

52: racemic

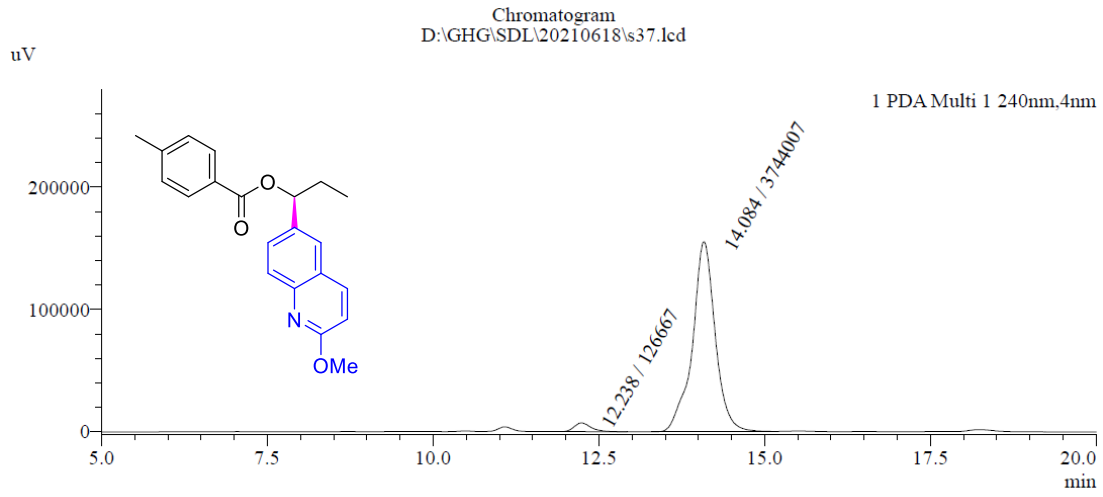


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.300	0.2686	1495922.60	83641.69	49.3607
2	14.208	0.3225	1534673.05	70349.47	50.6393

52: enantioenriched, 93% ee

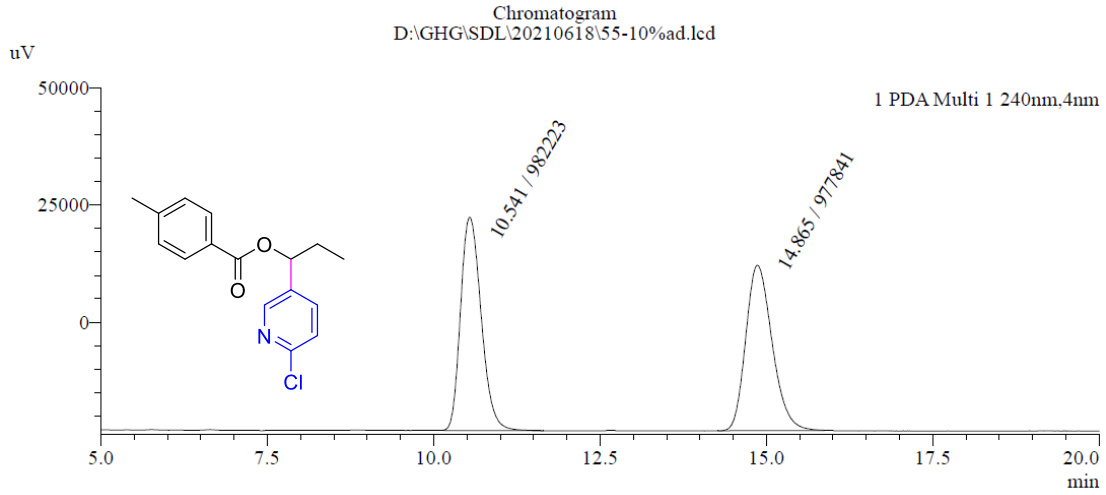


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	12.238	0.2652	126667.00	7110.86	3.2725
2	14.084	0.3330	3744006.57	155435.10	96.7275

53: racemic

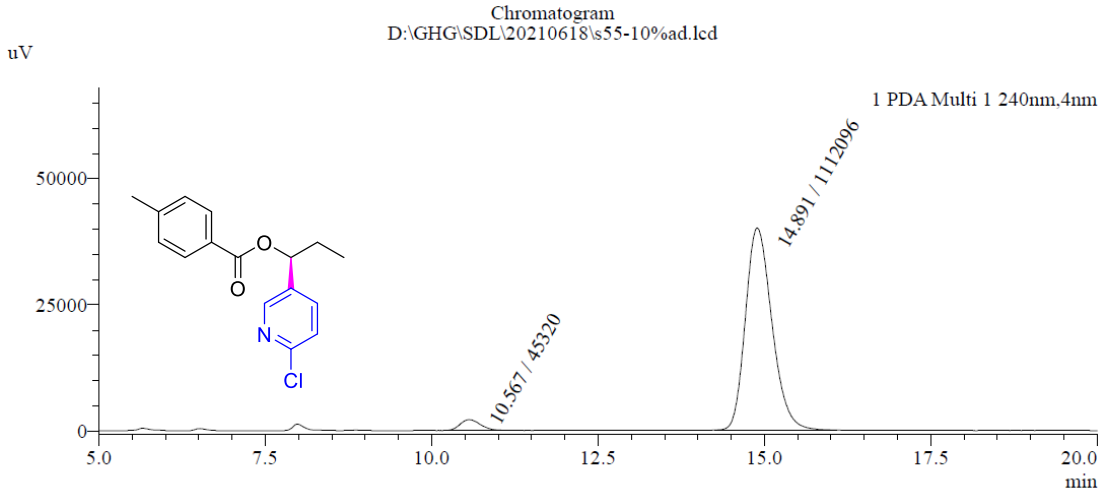


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.541	0.3352	982223.33	45490.77	50.1118
2	14.865	0.4262	977841.47	35293.83	49.8882

53: enantioenriched, 92% ee

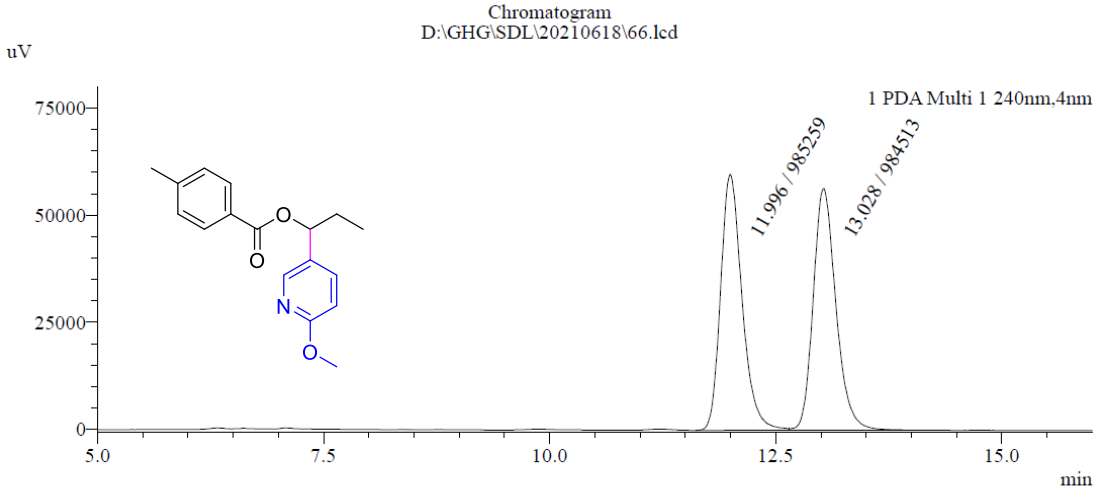


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.567	0.3364	45320.24	2117.28	3.9156
2	14.891	0.4268	1112095.62	40022.85	96.0844

54: racemic

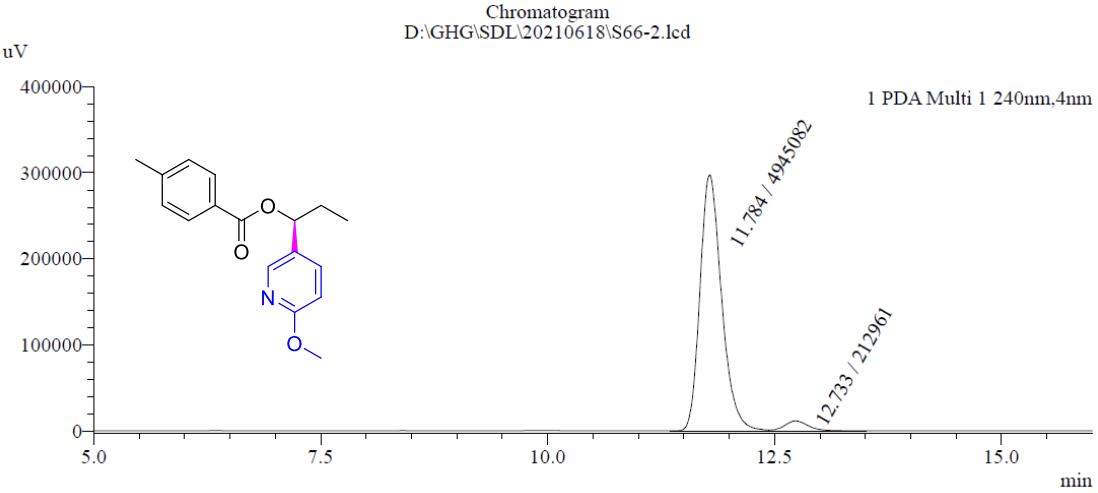


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	11.996	0.2480	985259.42	59667.86	50.0189
2	13.028	0.2631	984513.12	56391.61	49.9811

54: enantioenriched, 92% ee

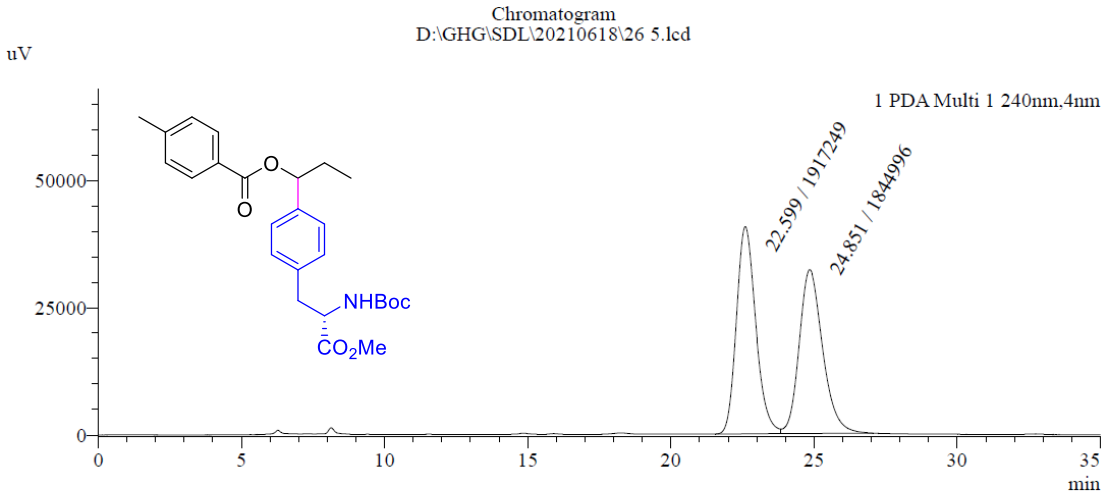


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	11.784	0.2514	4945082.45	297502.16	95.8713
2	12.733	0.2715	212960.98	11652.57	4.1287

55: racemic

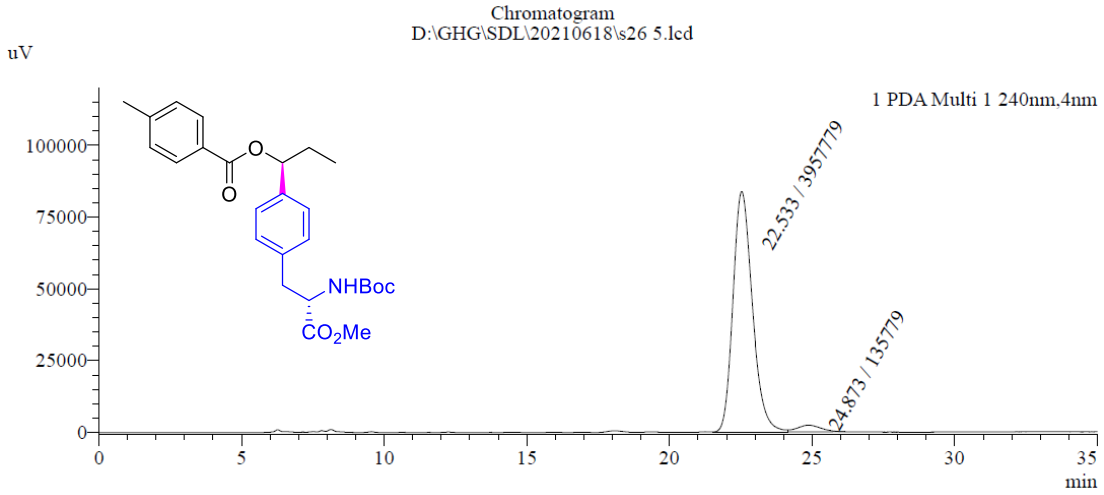


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	22.599	0.7189	1917249.21	40724.75	50.9602
2	24.851	0.8644	1844996.15	32207.90	49.0398

55: enantioenriched, 93% de

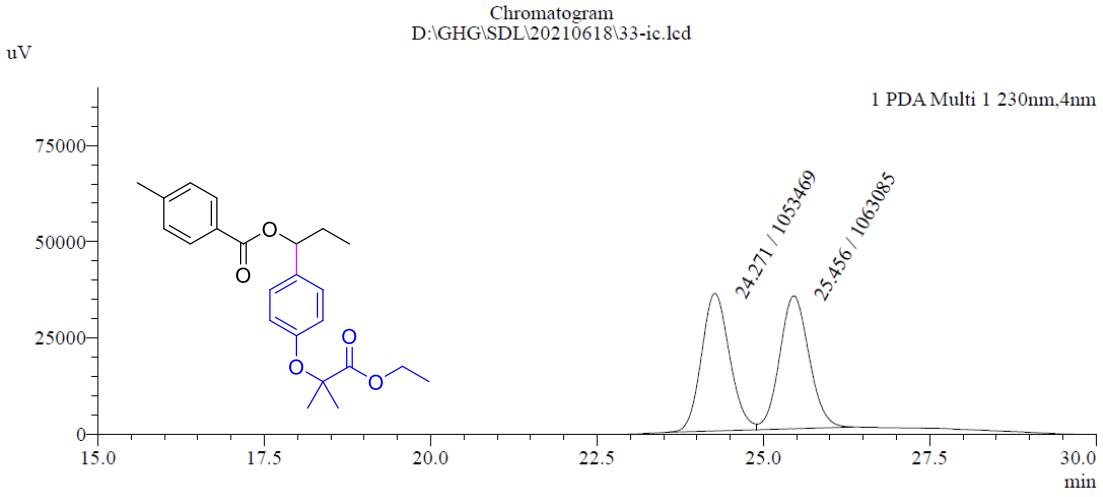


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	22.533	0.7199	3957779.01	83663.17	96.6831
2	24.873	0.9219	135778.79	2321.57	3.3169

56: racemic

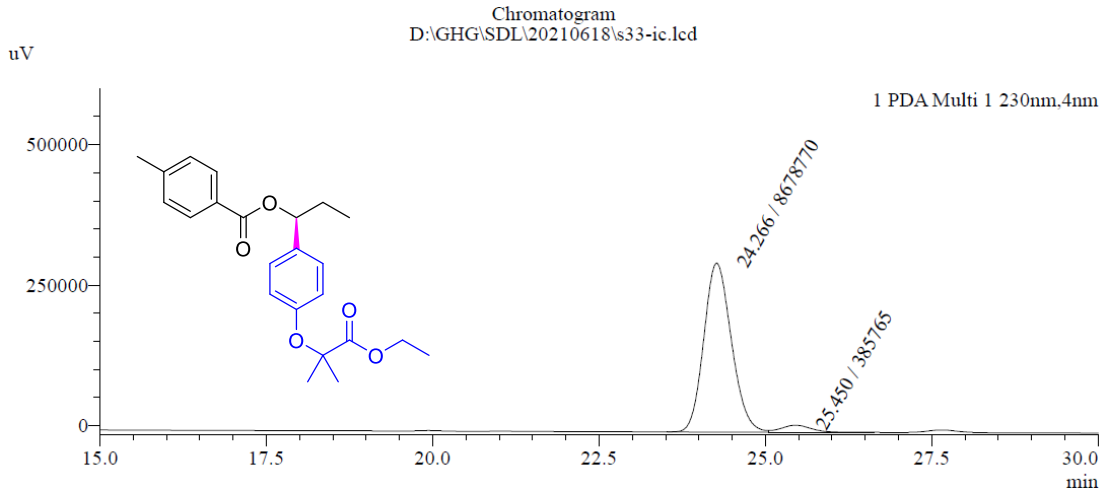


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	24.271	0.4559	1053468.96	35682.85	49.7728
2	25.456	0.4739	1063084.81	34524.11	50.2272

56: enantioenriched, 91% ee

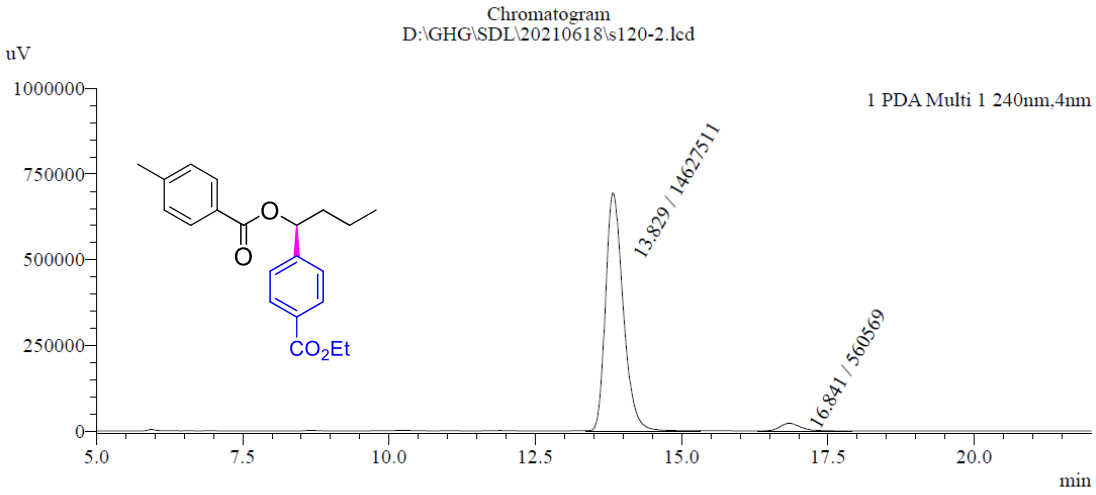


Peak Table

PDA Ch1 230nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	24.266	0.4468	8678770.27	300518.03	95.7442
2	25.450	0.4766	385765.42	12533.92	4.2558

(*S*)-57: enantioenriched, 93% ee

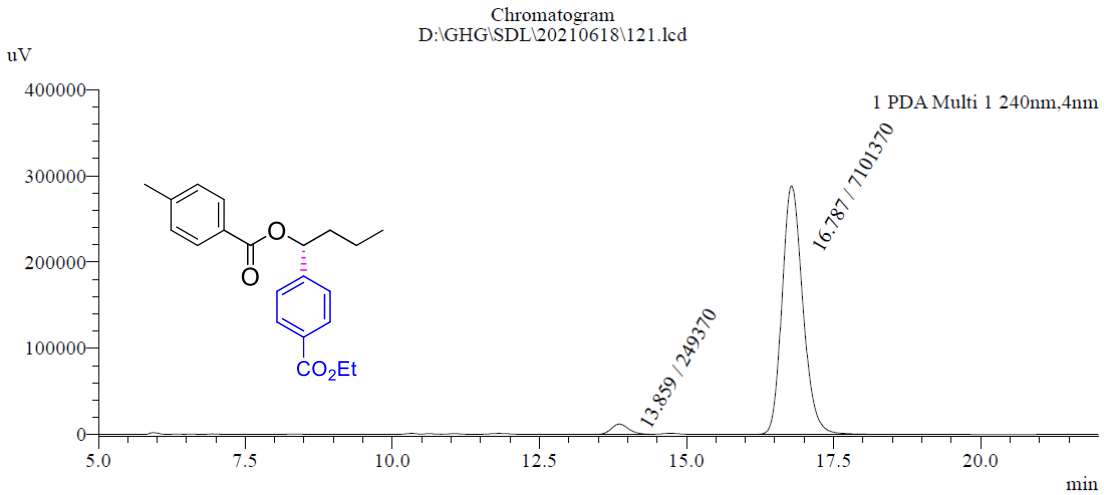


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.829	0.3186	14627511.15	694688.83	96.3091
2	16.841	0.3726	560569.48	22410.41	3.6909

57: enantioenriched, -93% ee

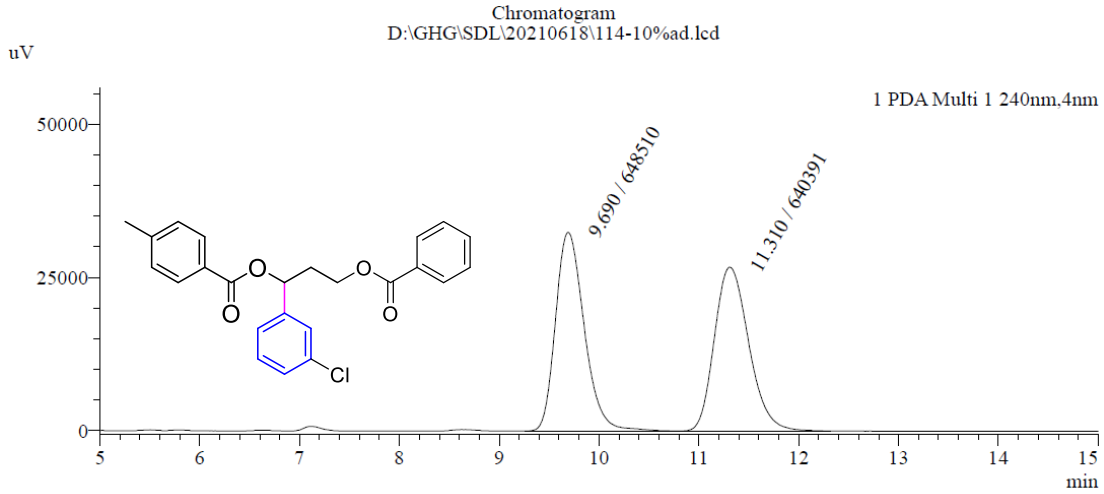


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.859	0.3163	249370.28	12026.50	3.3925
2	16.787	0.3745	7101370.31	288524.27	96.6075

58: racemic

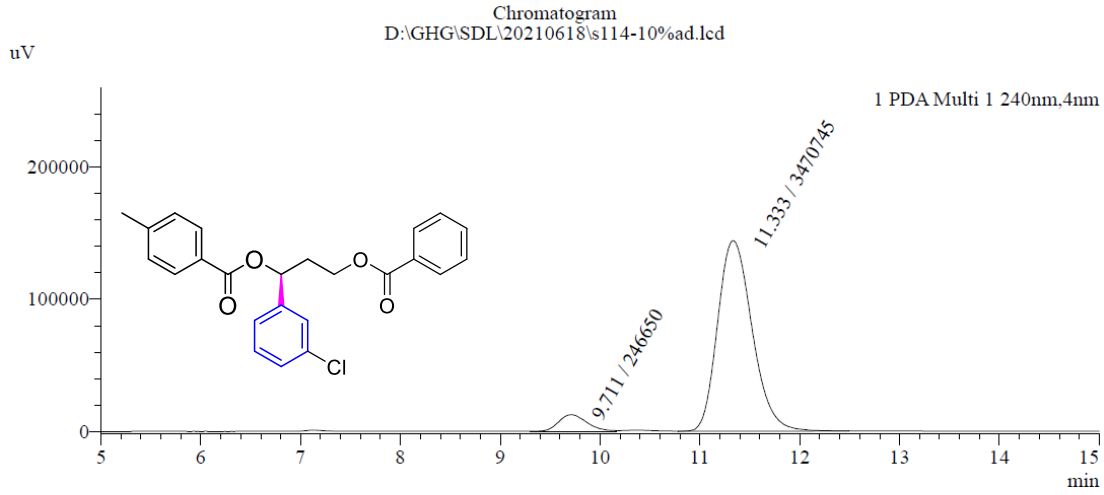


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	9.690	0.3052	648509.60	32445.81	50.3150
2	11.310	0.3711	640390.60	26755.43	49.6850

58: enantioenriched, 87% ee

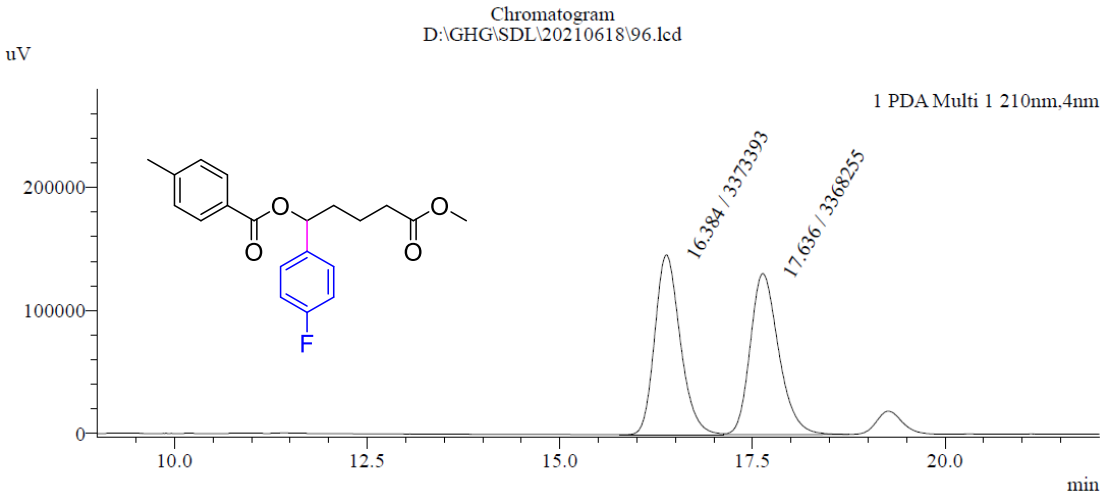


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	9.711	0.3056	246649.56	12505.64	6.6350
2	11.333	0.3730	3470744.89	144055.52	93.3650

59: racemic

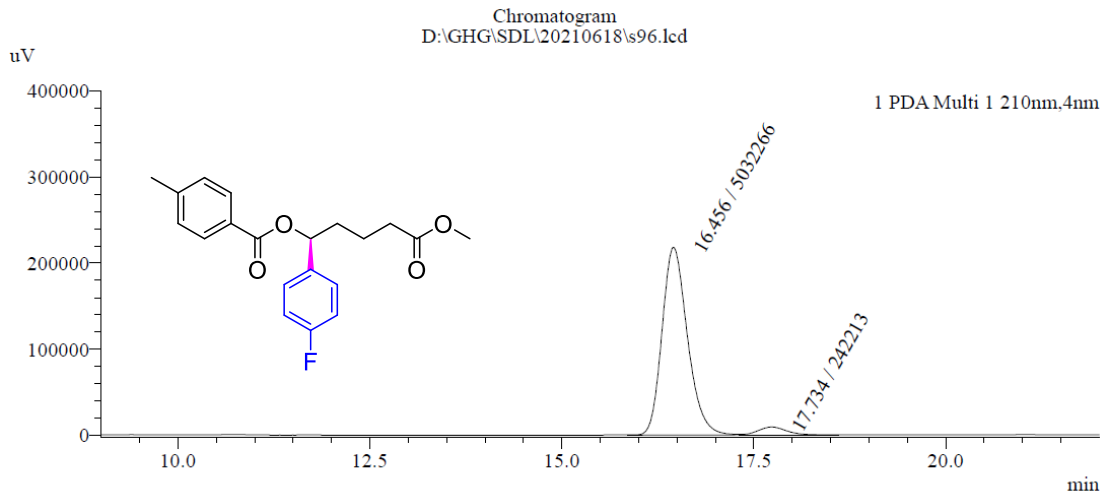


Peak Table

PDA Ch1 210nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	16.384	0.3511	3373393.33	146358.84	50.0381
2	17.636	0.3906	3368254.54	131007.56	49.9619

59: enantioenriched, 91% ee

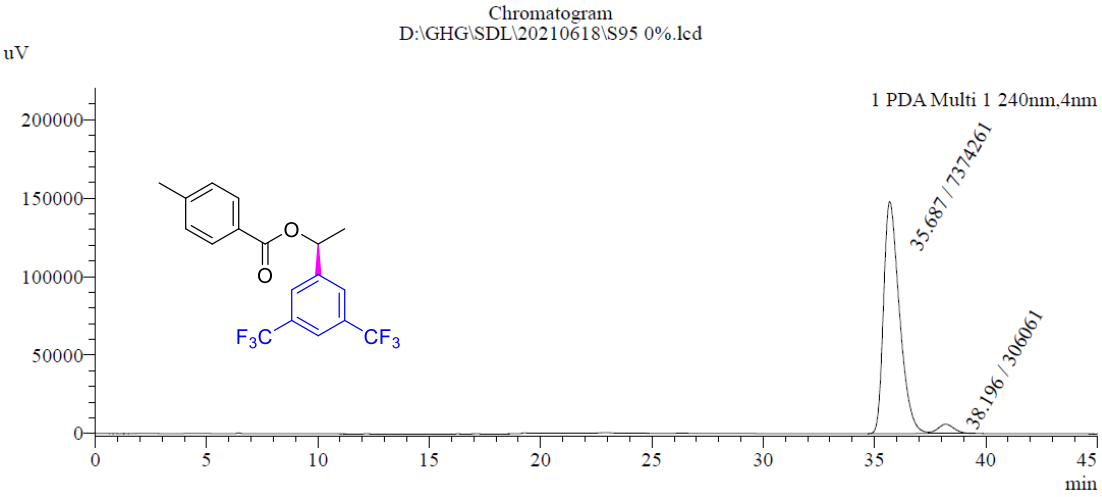


Peak Table

PDA Ch1 210nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	16.456	0.3511	5032265.53	217900.64	95.4078
2	17.734	0.3922	242213.17	9301.55	4.5922

(*S*)-60: enantioenriched, 92% ee

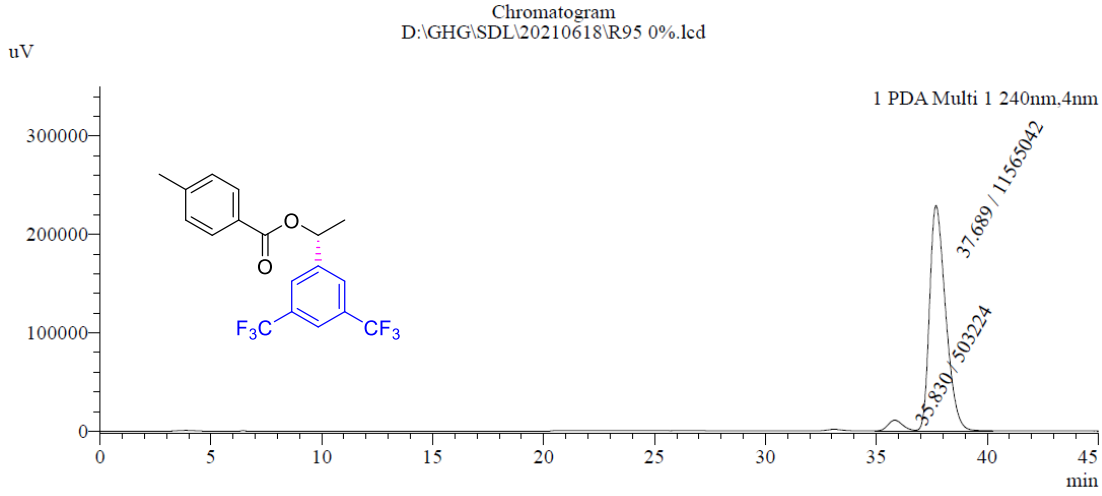


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	35.687	0.7601	7374261.47	147784.40	96.0150
2	38.196	0.7871	306060.64	5956.23	3.9850

60: enantioenriched, −92% ee

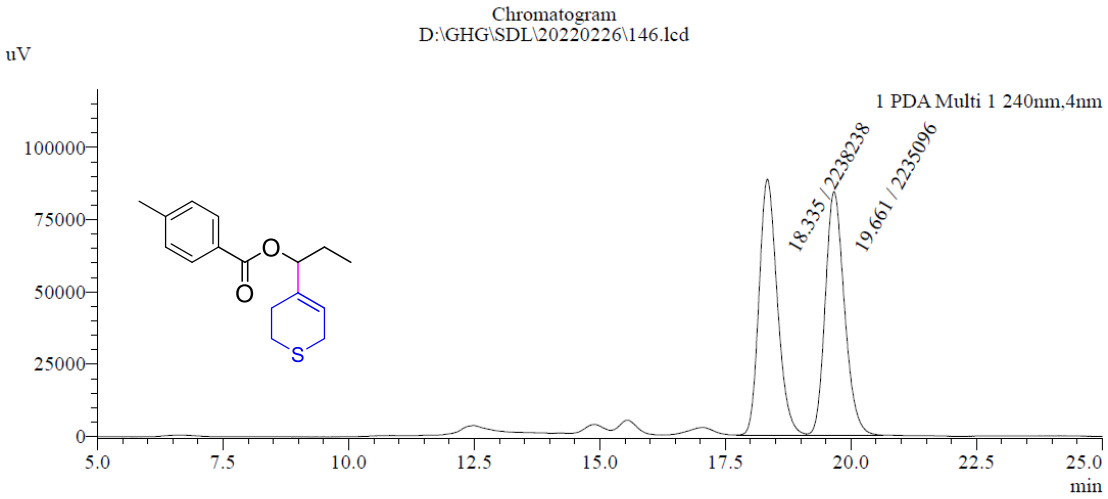


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	35.830	0.7225	503223.78	10843.41	4.1698
2	37.689	0.7767	11565042.49	228964.60	95.8302

61: racemic

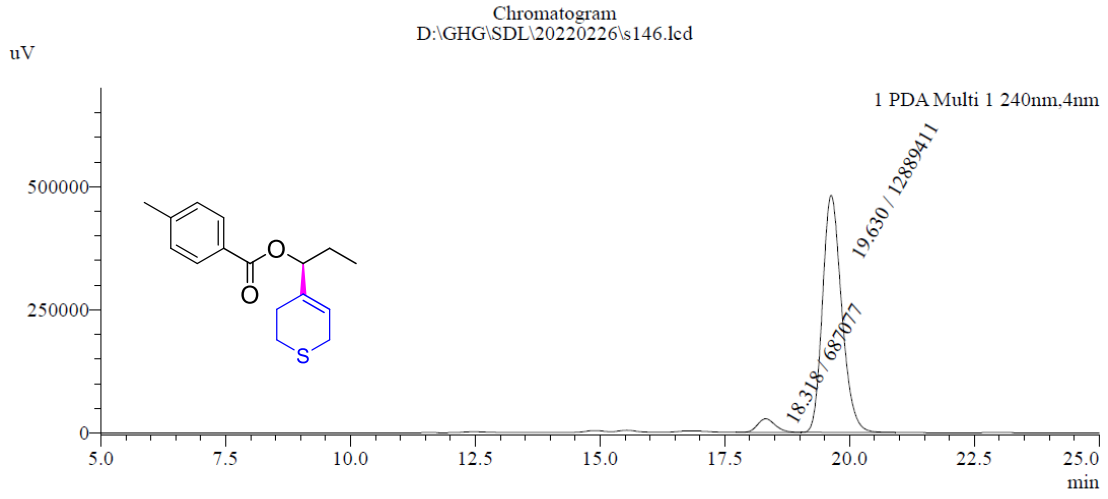


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	18.335	0.3872	2238237.77	88486.32	50.0351
2	19.661	0.4064	2235096.27	84135.09	49.9649

61: enantioenriched, 90% ee

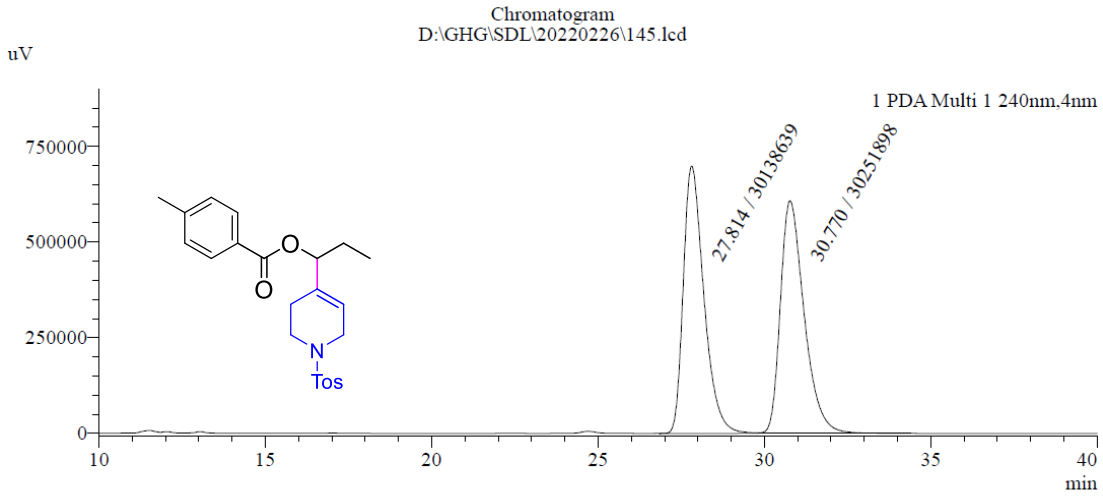


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	18.318	0.3825	687076.80	27640.42	5.0608
2	19.630	0.4096	12889411.24	481312.54	94.9392

62: racemic

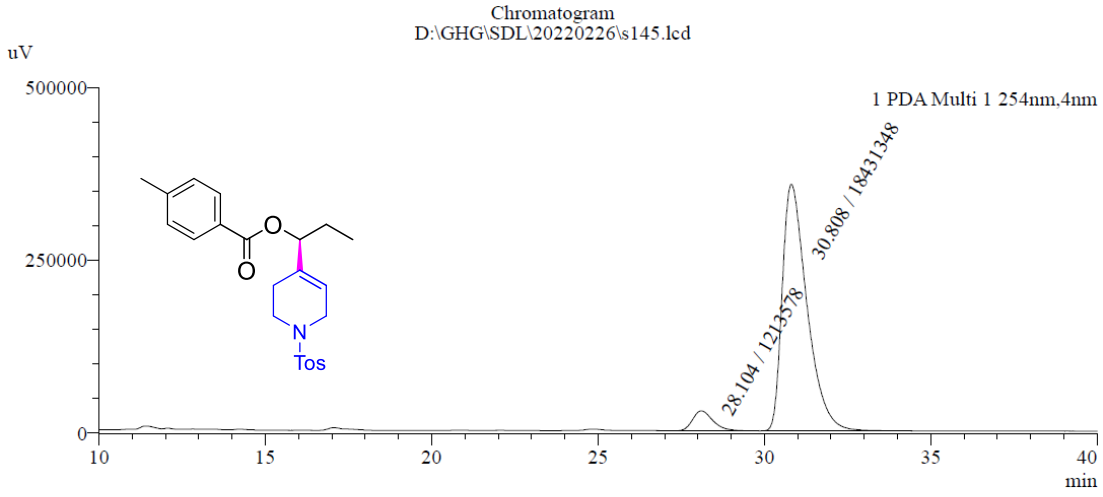


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	27.814	0.6502	30138638.73	698855.40	49.9062
2	30.770	0.7484	30251898.10	608150.44	50.0938

62: enantioenriched, 88% ee

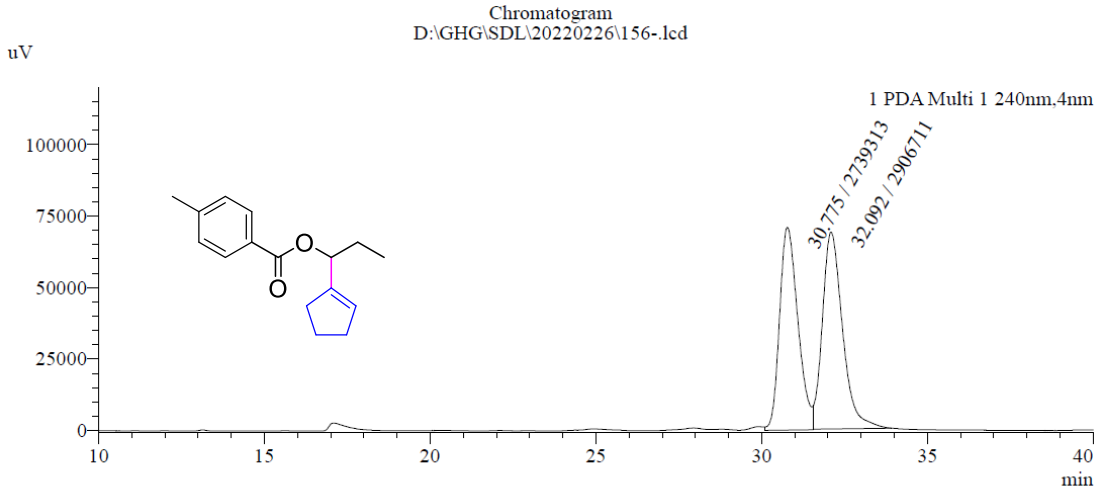


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	28.104	0.6435	1213578.20	28763.79	6.1776
2	30.808	0.7813	18431347.61	356716.22	93.8224

63: racemic

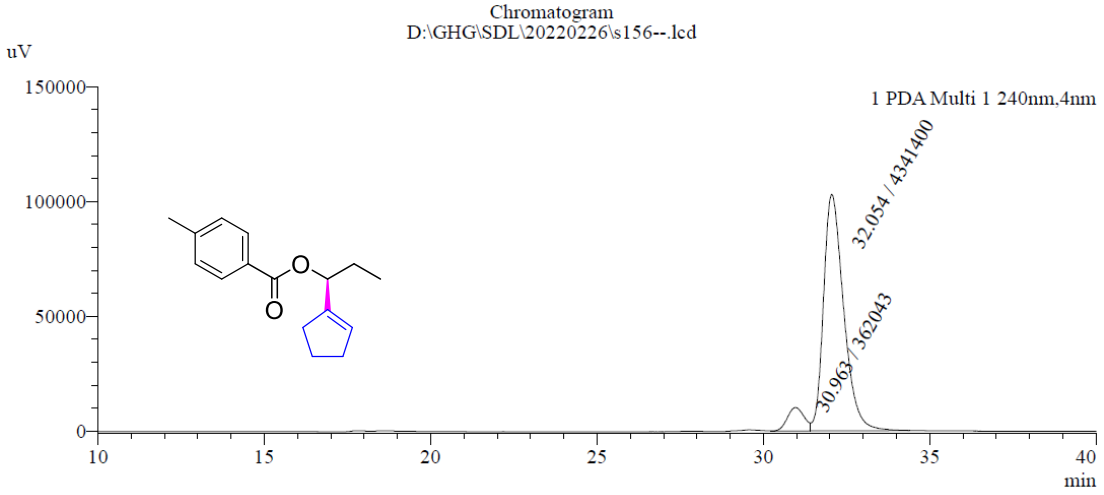


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	30.775	0.5941	2739312.87	70913.74	48.5176
2	32.092	0.6324	2906711.41	68786.95	51.4824

63: enantioenriched, 85% ee

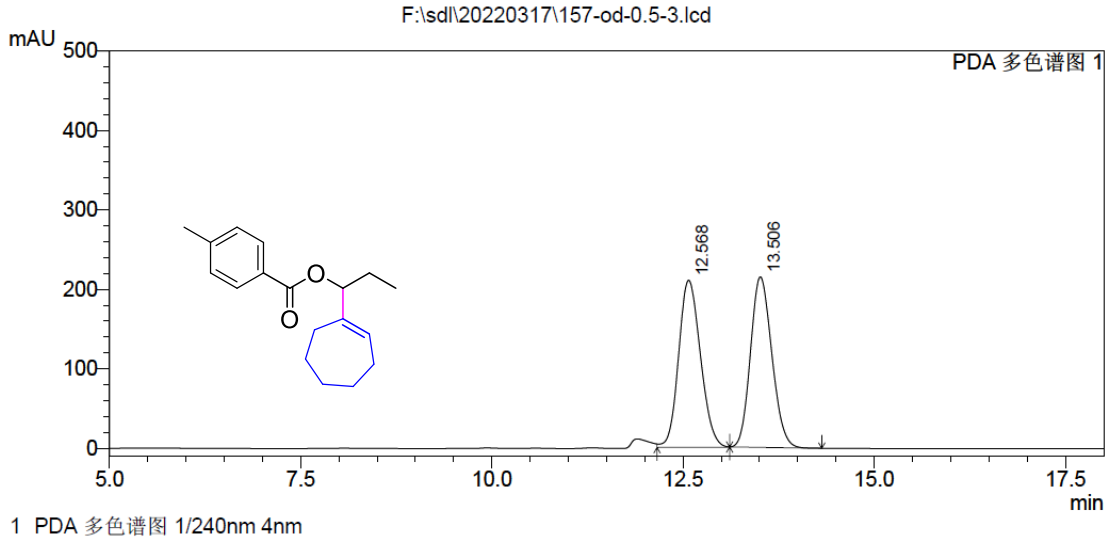


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	30.963	0.5795	362042.79	10267.38	7.6974
2	32.054	0.6361	4341399.95	102968.69	92.3026

64: racemic

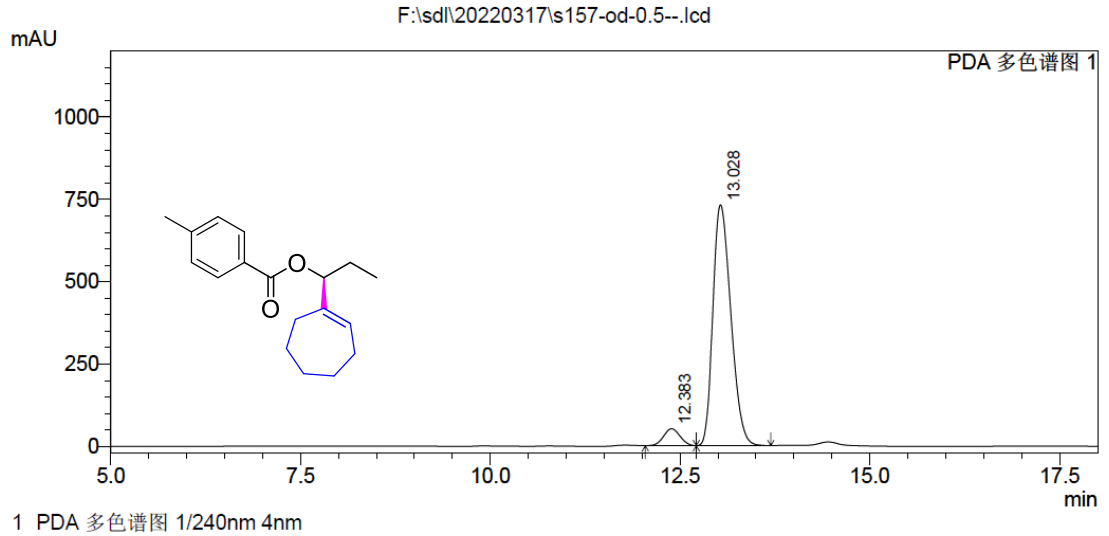


1 PDA 多色谱图 1/240nm 4nm

Ch1 240nm 4nm

Peak#	Ret.Time[min]	Width[min]	Area	Height[mAU]	Area %
1	12.568	0.308	4185939	210548	50.086
2	13.506	0.303	4171567	214720	49.914
总计			8357506		100.000

64: enantioenriched, 88% ee

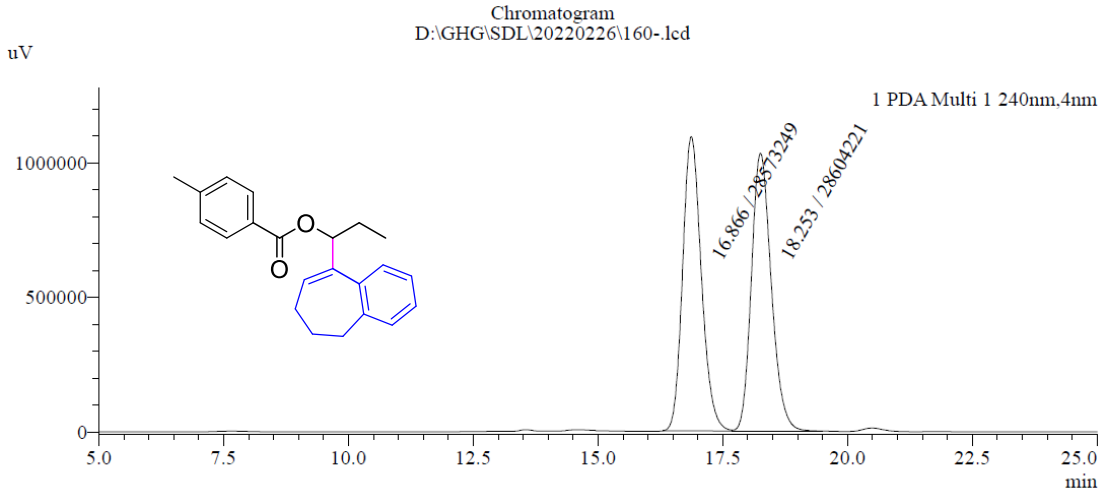


1 PDA 多色谱图 1/240nm 4nm

Ch1 240nm 4nm

Peak#	Ret.Time[min]	Width[min]	Area	Height[mAU]	Area %
1	12.383	0.238	778756	51500	6.075
2	13.028	0.258	12040457	731451	93.925
总计			12819213		100.000

65: racemic

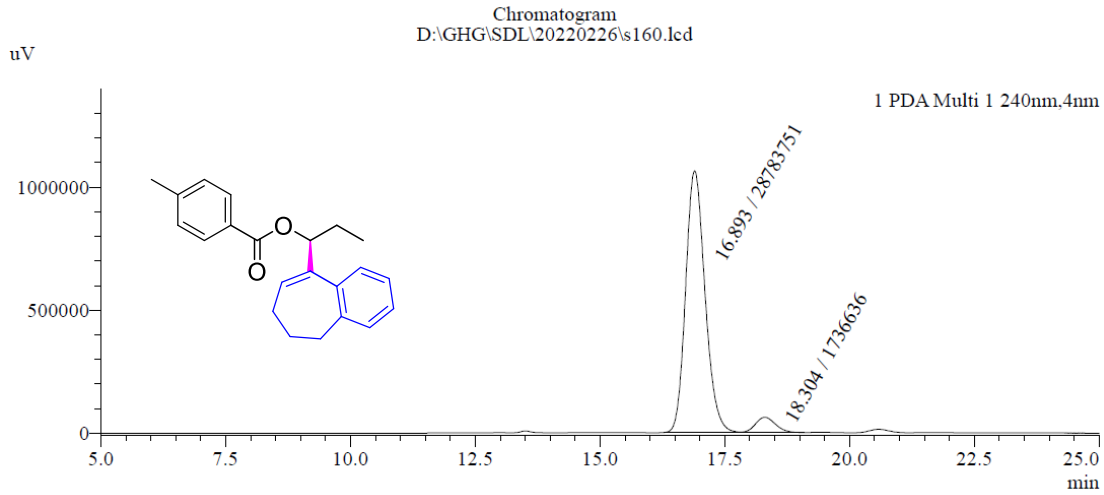


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	16.866	0.3998	28573248.80	1094880.54	49.9729
2	18.253	0.4237	28604220.54	1032835.08	50.0271

65: enantioenriched, 89% ee

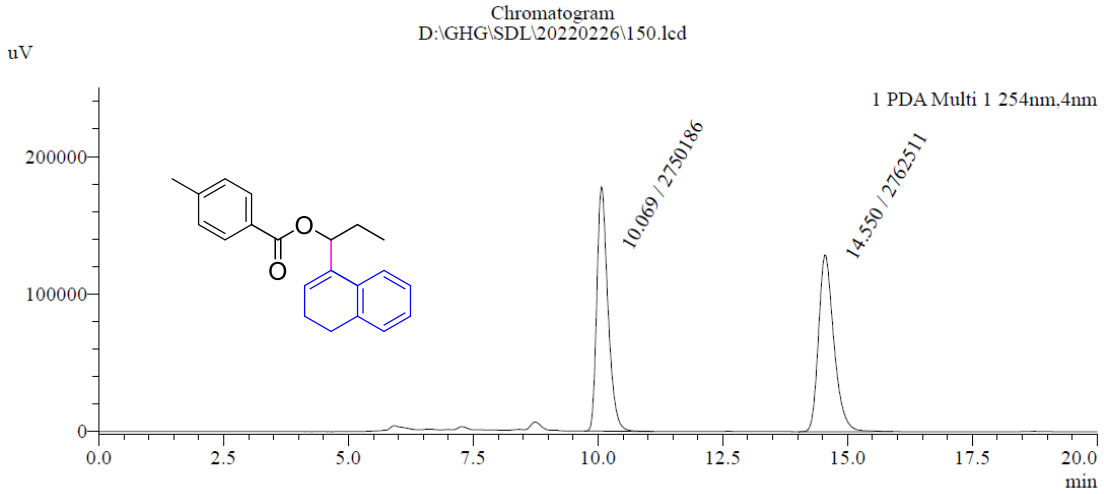


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	16.893	0.4142	28783750.73	1064273.04	94.3099
2	18.304	0.4318	1736636.03	62309.54	5.6901

66: racemic

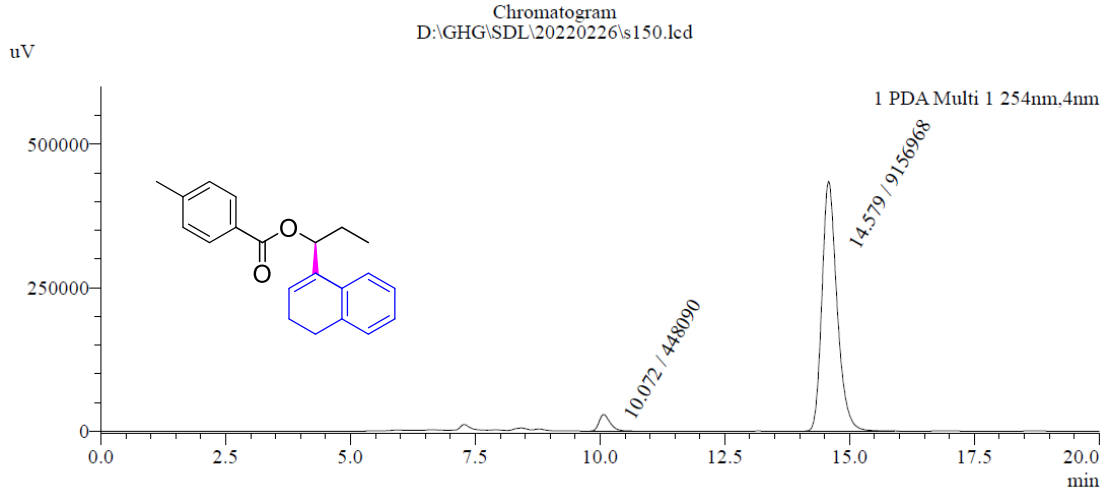


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.069	0.2336	2750185.66	177521.79	49.8882
2	14.550	0.3212	2762510.57	128515.31	50.1118

66: enantioenriched, 91% ee

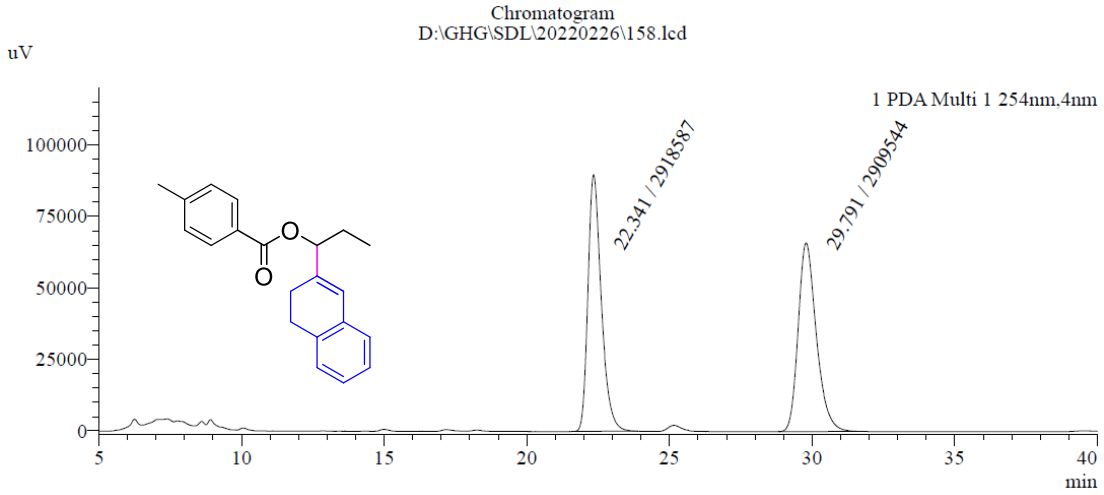


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	10.072	0.2328	448089.74	28979.25	4.6651
2	14.579	0.3139	9156968.01	435506.65	95.3349

67: racemic

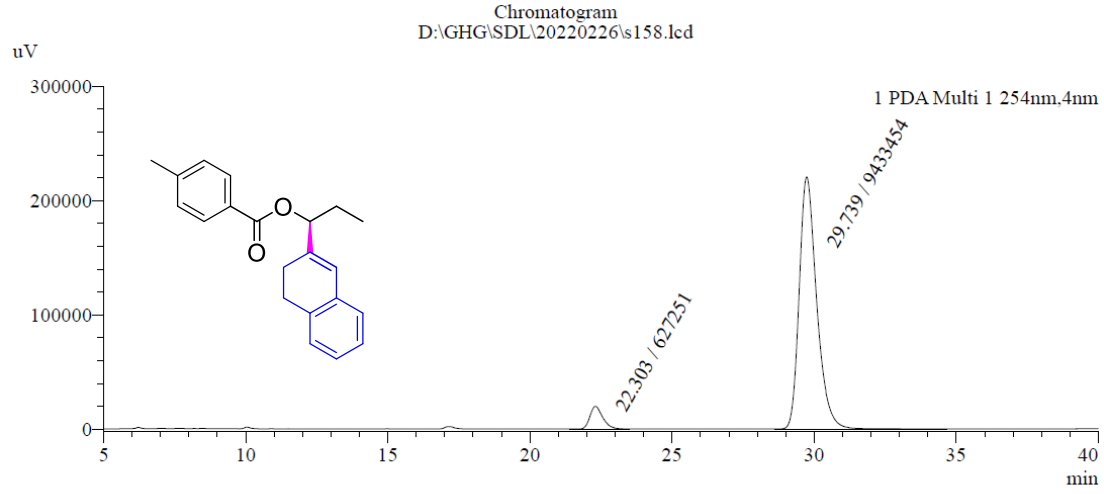


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	22.341	0.4858	2918586.55	89761.92	50.0776
2	29.791	0.6618	2909544.49	65993.79	49.9224

67: enantioenriched, 88% ee

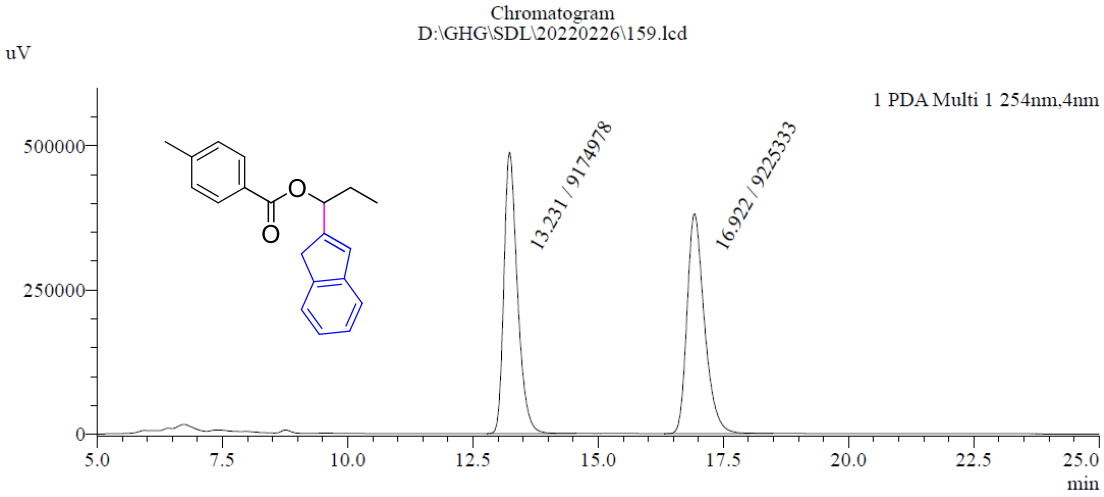


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	22.303	0.4733	627251.09	19910.44	6.2347
2	29.739	0.6351	9433453.77	220584.48	93.7653

68: racemic

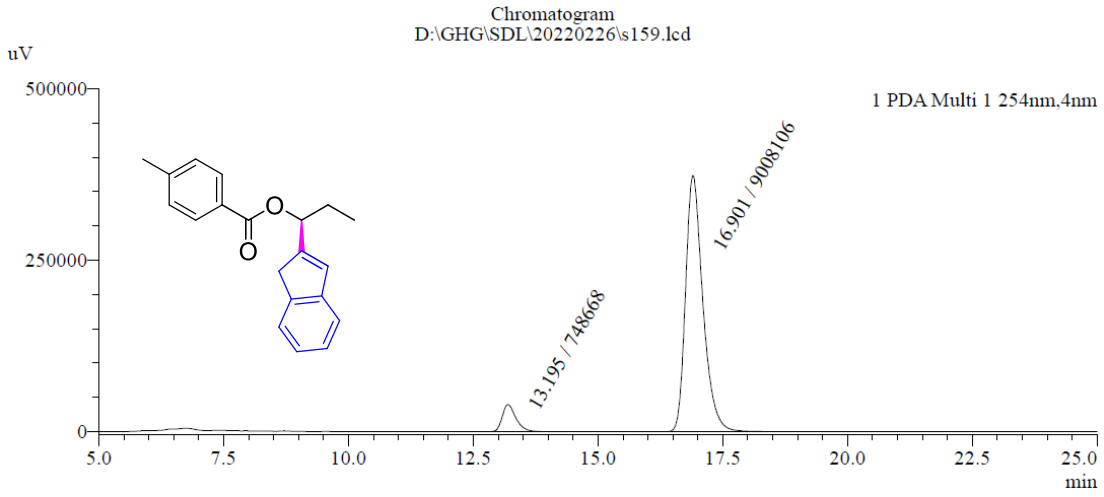


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.231	0.2811	9174978.44	487707.02	49.8632
2	16.922	0.3620	9225332.84	380916.82	50.1368

68: enantioenriched, 85% ee



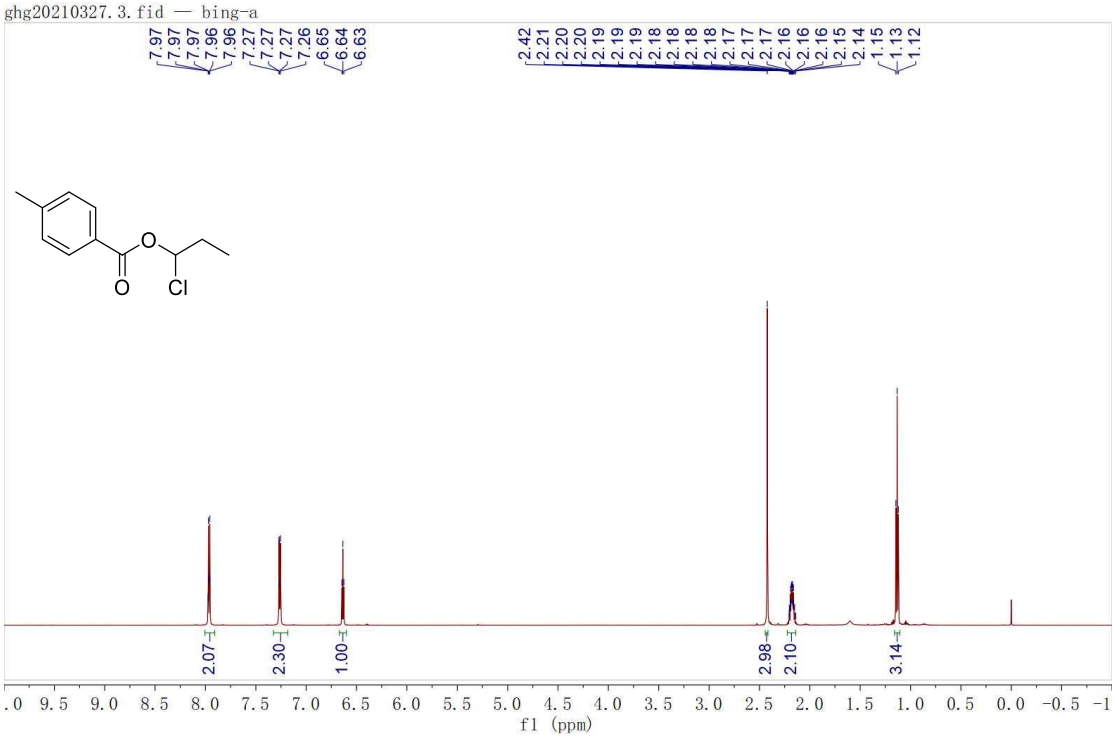
Peak Table

PDA Ch1 254nm

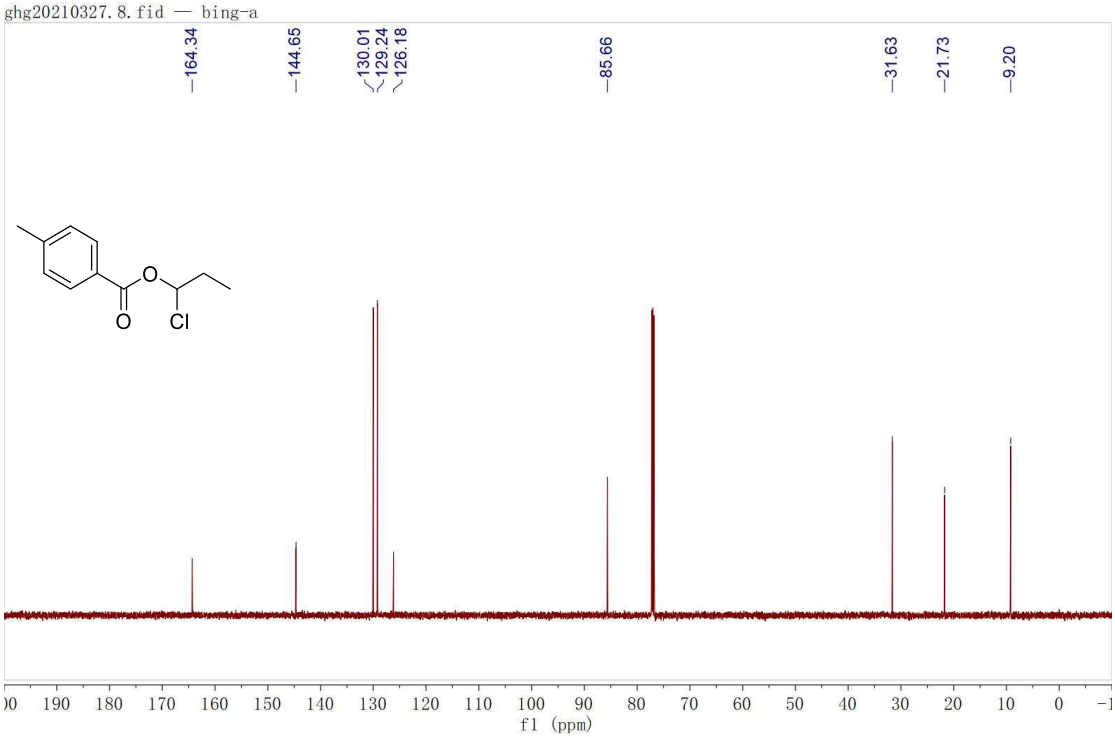
Peak#	Ret. Time [min]	Width [min]	Area [uV*s]	Height [uV]	Area %
1	13.195	0.2840	748668.06	39530.39	7.6733
2	16.901	0.3608	9008106.06	372872.33	92.3267

IV. NMR Data

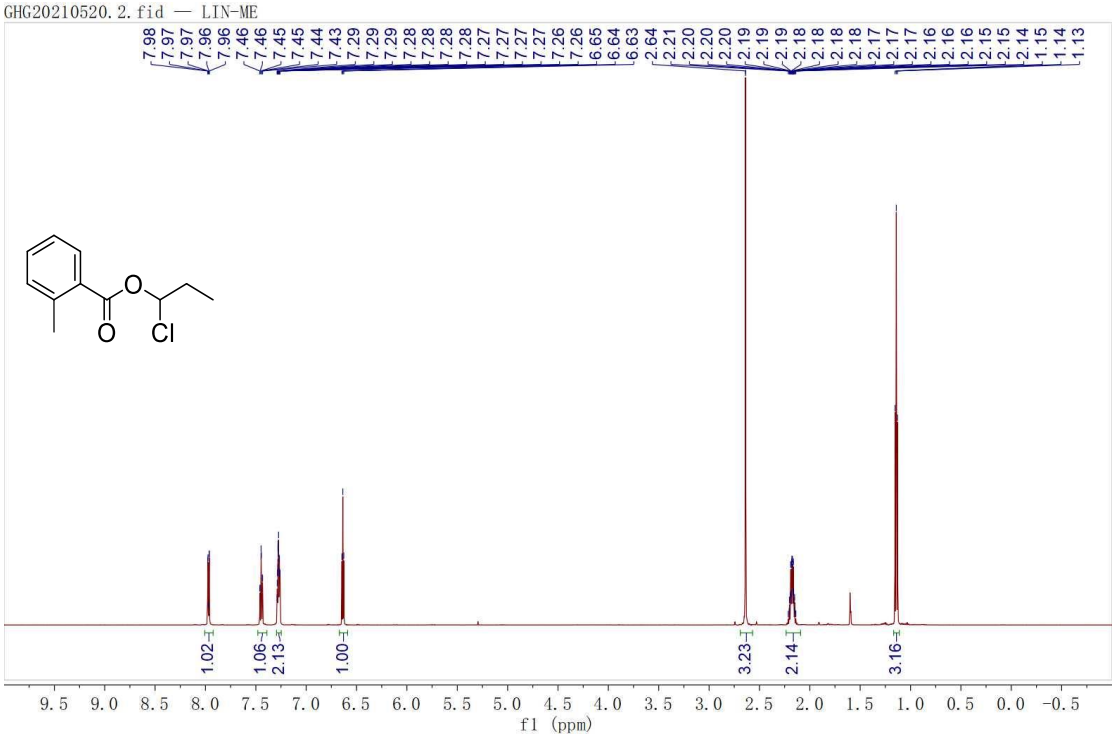
1, ^{1}H-NMR (600 MHZ, $CDCl_3$)



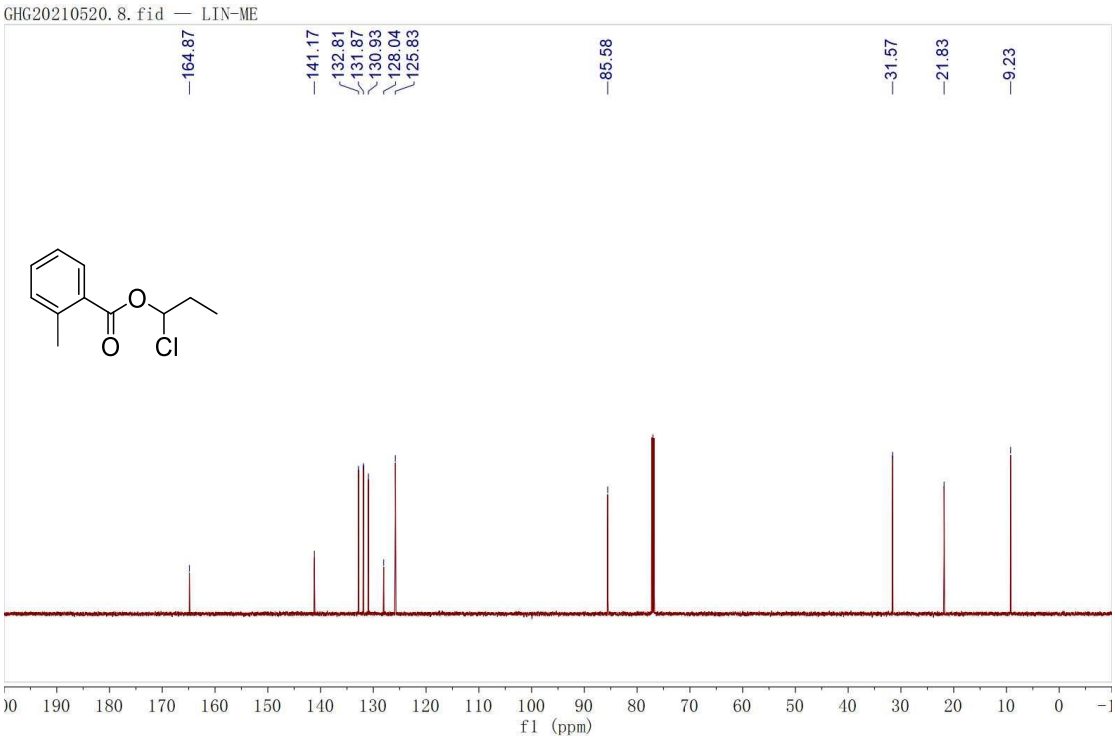
1, ^{13}C NMR (151 MHz, $CDCl_3$)



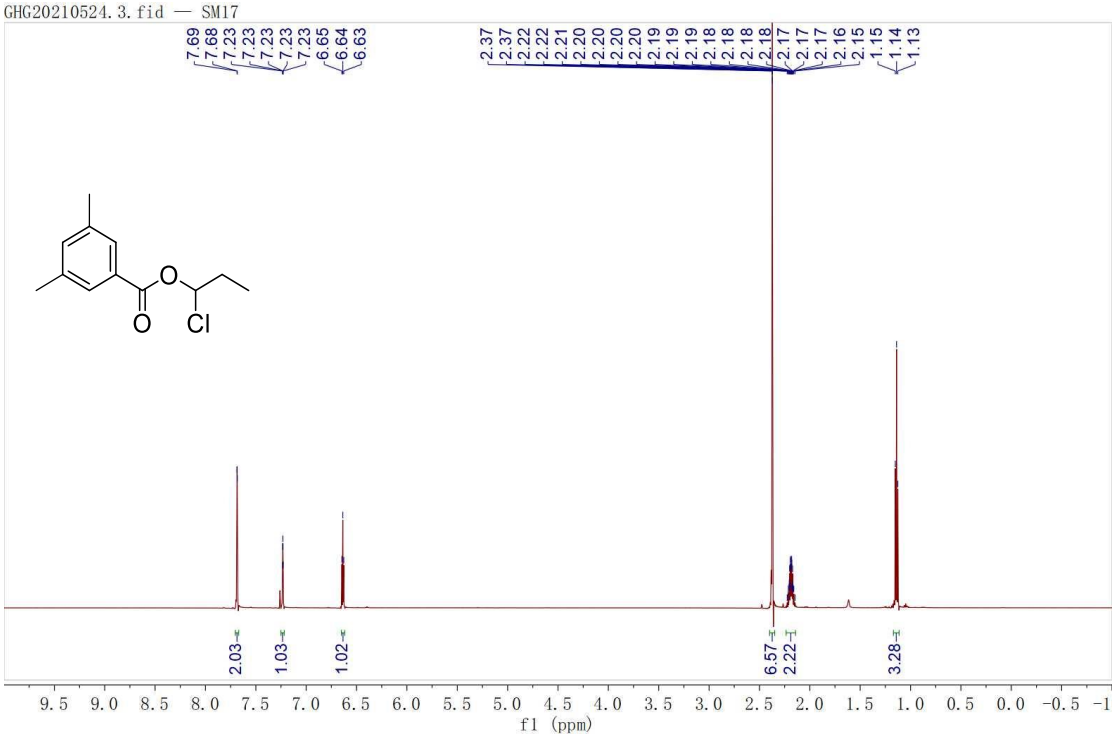
SM1, ^{1}H-NMR (600 MHZ, $CDCl_3$)



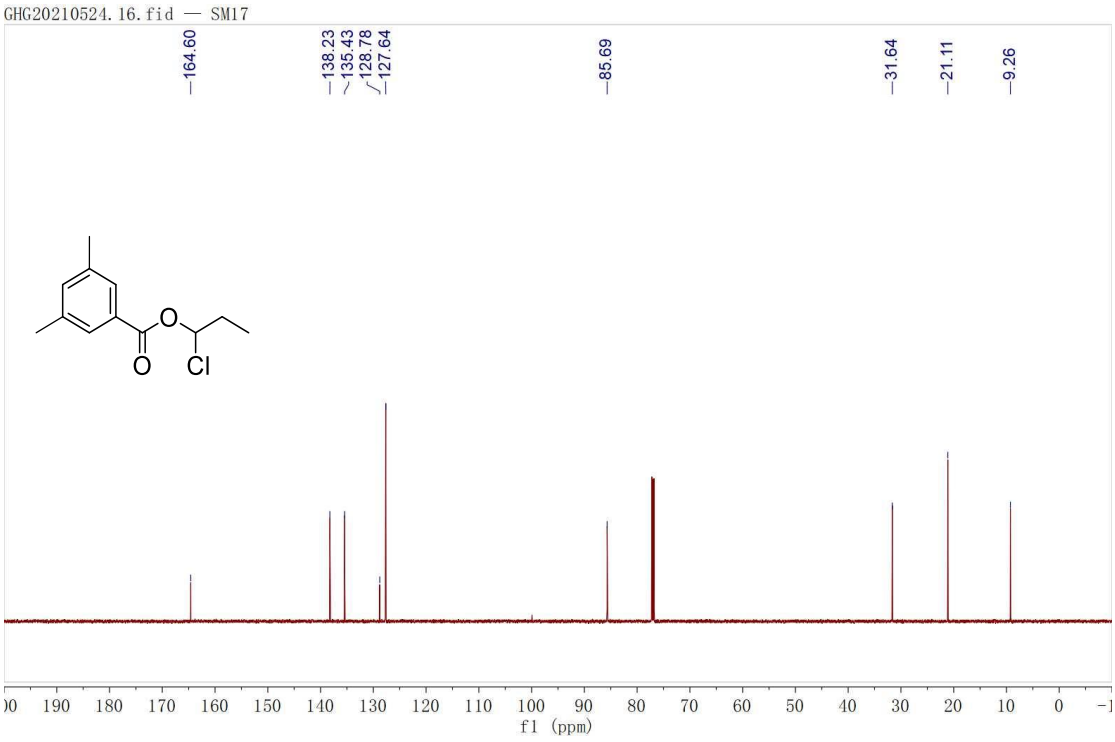
SM1, ^{13}C NMR (151 MHz, $CDCl_3$)



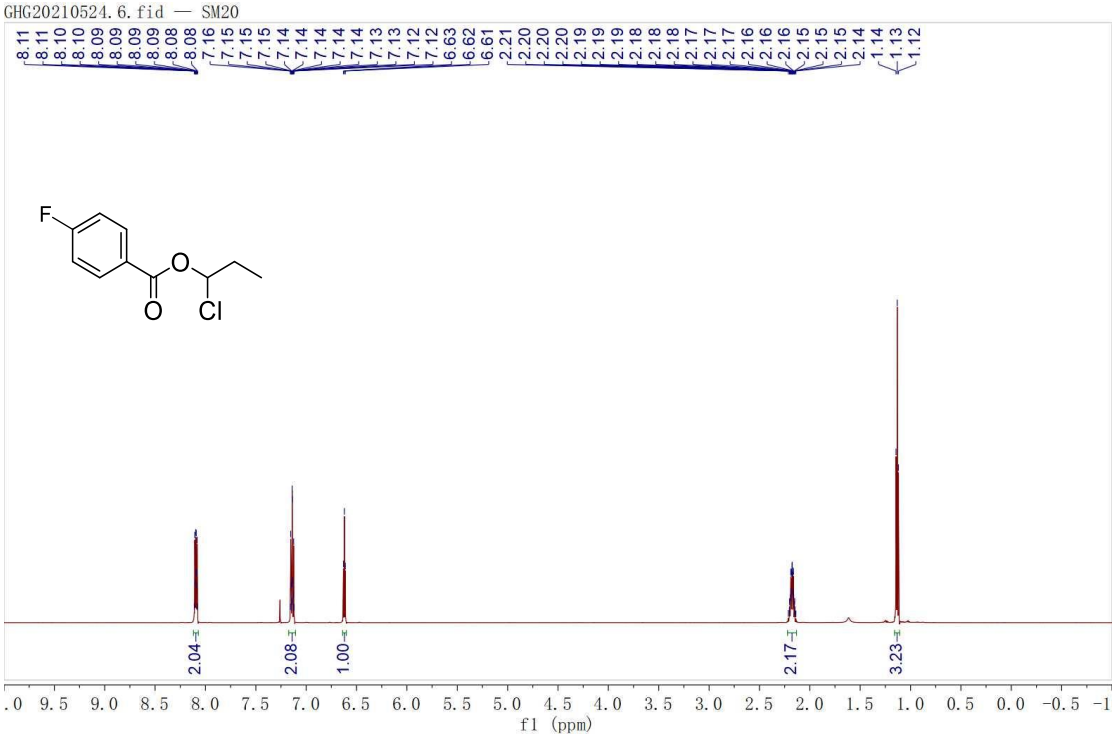
SM2, ^{1}H-NMR (600 MHZ, $CDCl_3$)



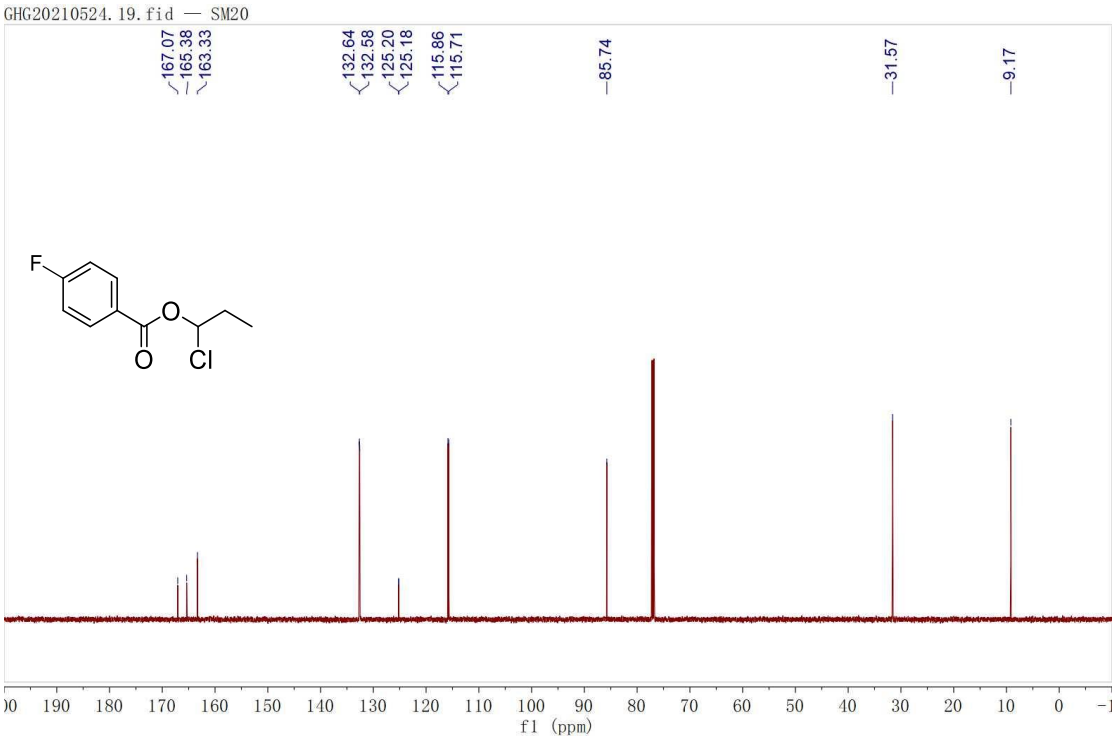
SM2, ^{13}C NMR (151 MHz, $CDCl_3$)



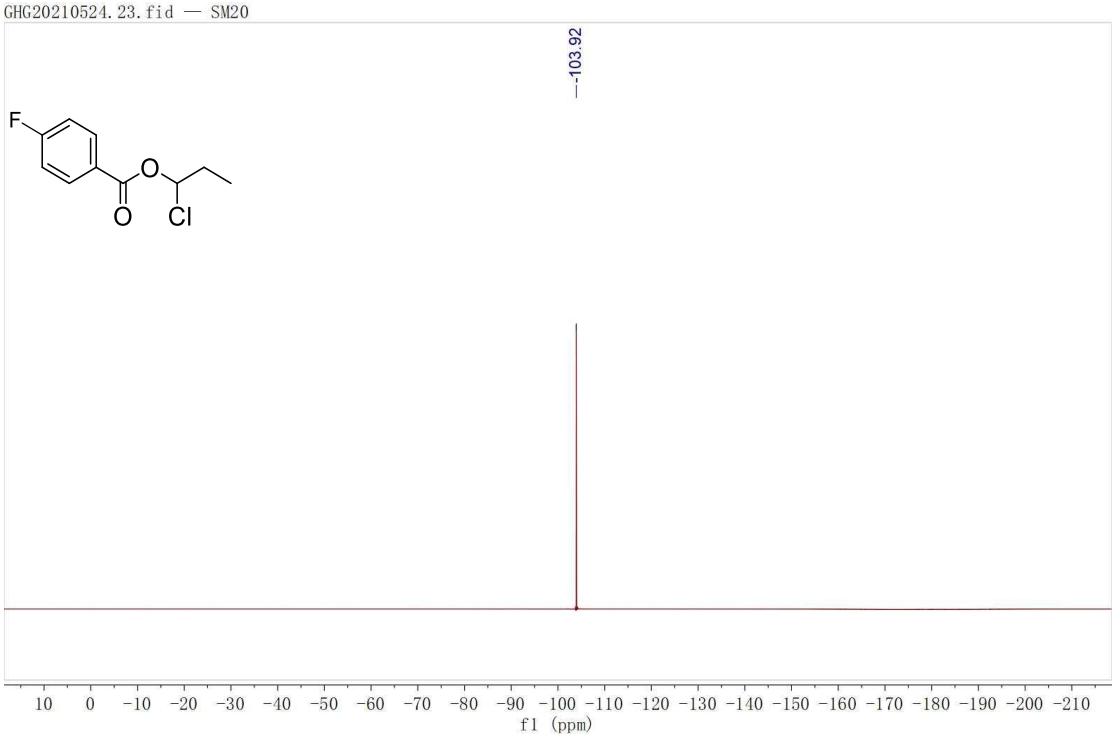
SM3, ^{1}H-NMR (600 MHZ, $CDCl_3$)



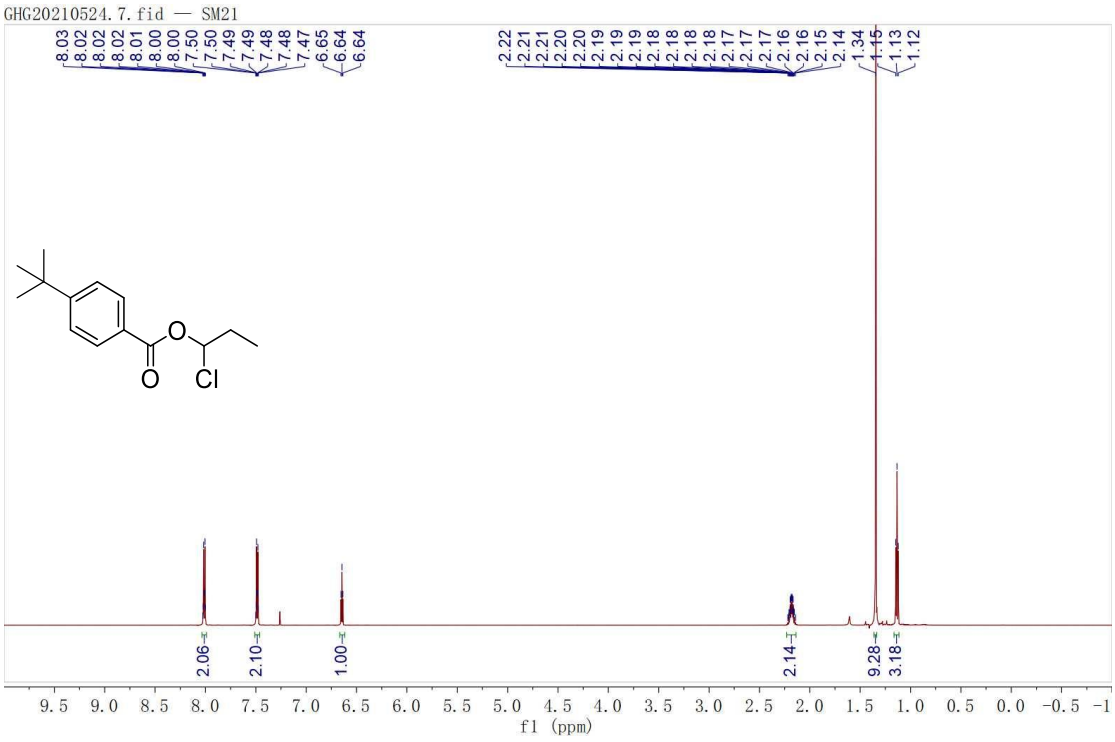
SM3, ^{13}C NMR (151 MHz, $CDCl_3$)



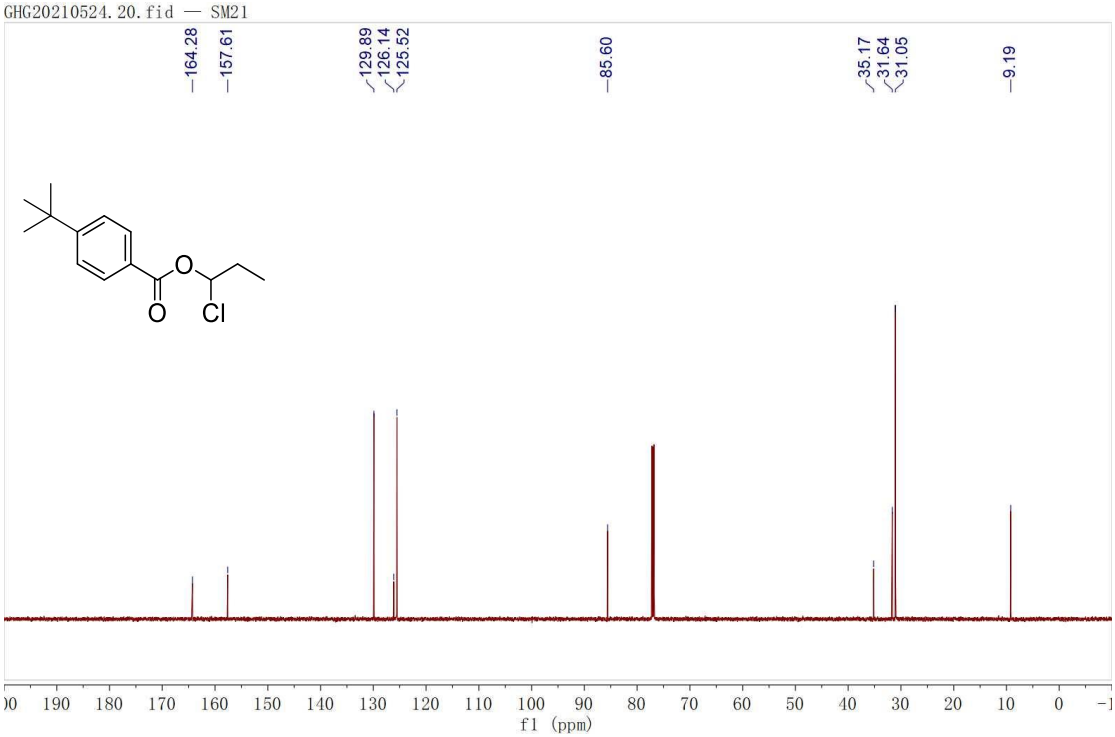
SM3, ^{19}F NMR (565 MHz, $CDCl_3$)



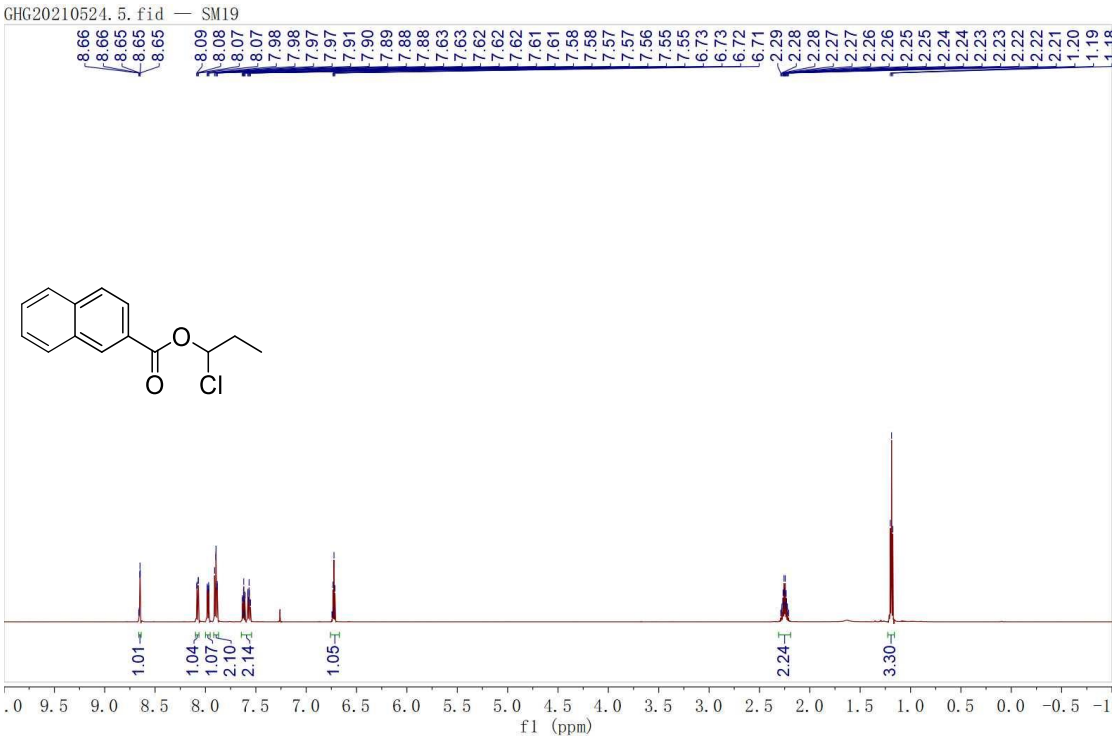
SM4, ^{1}H-NMR (600 MHZ, $CDCl_3$)



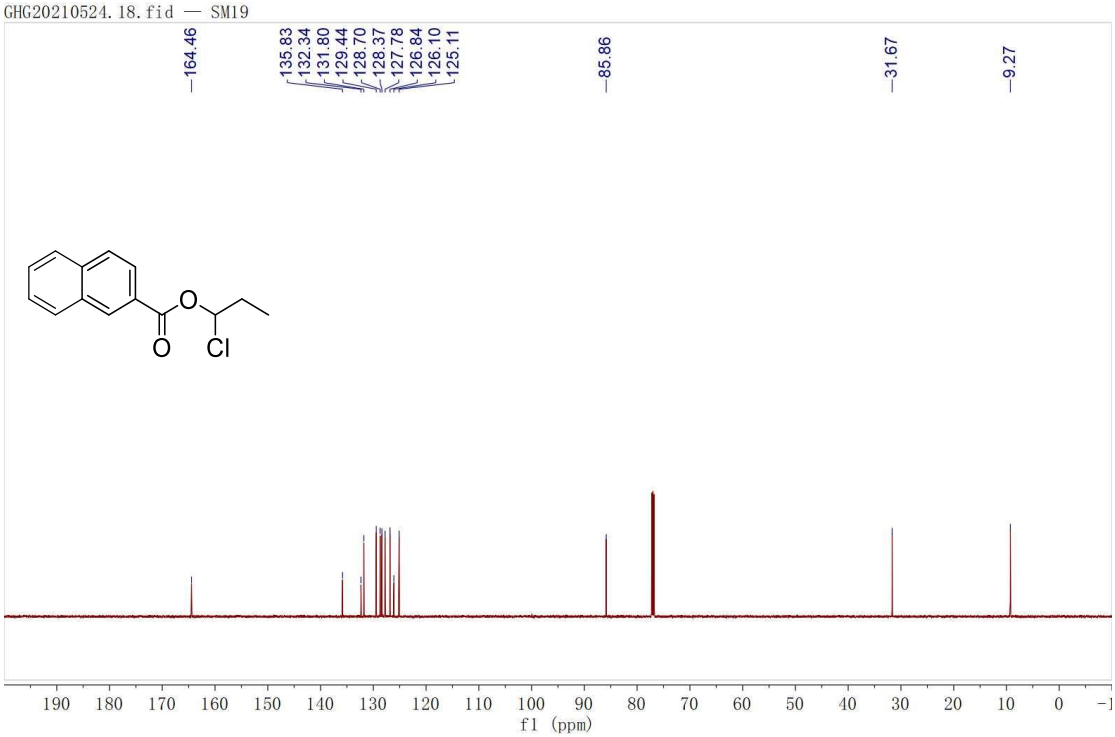
SM4, ^{13}C NMR (151 MHz, $CDCl_3$)



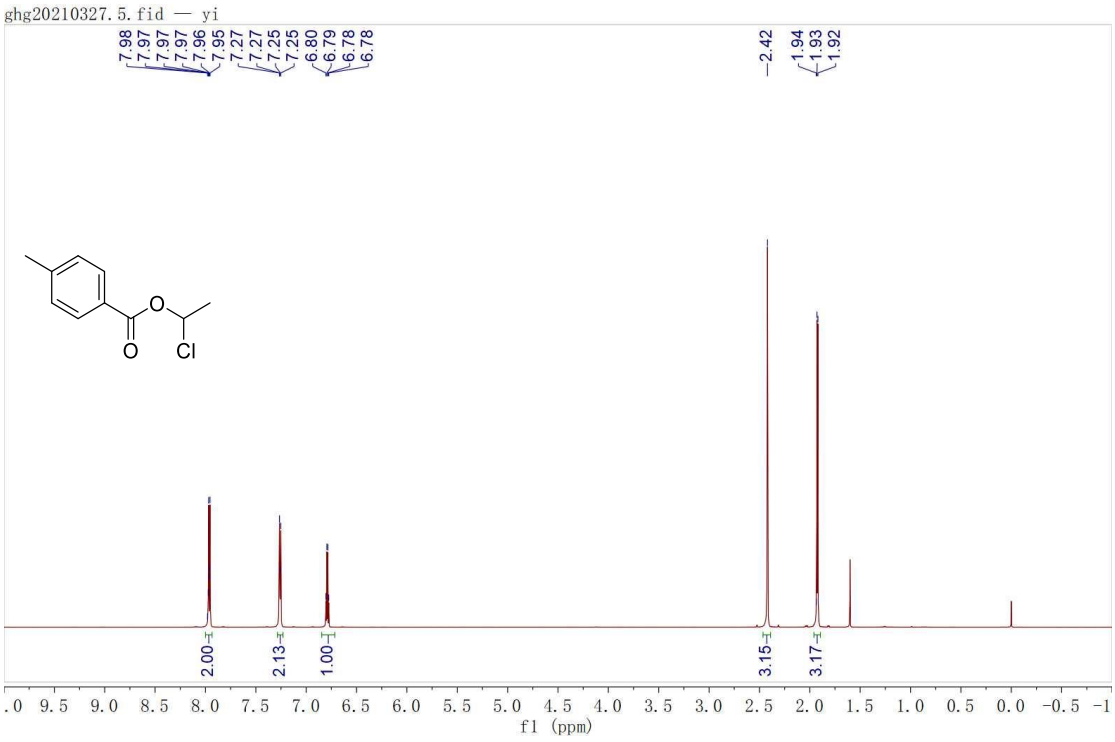
SM5, ^{1}H-NMR (600 MHZ, $CDCl_3$)



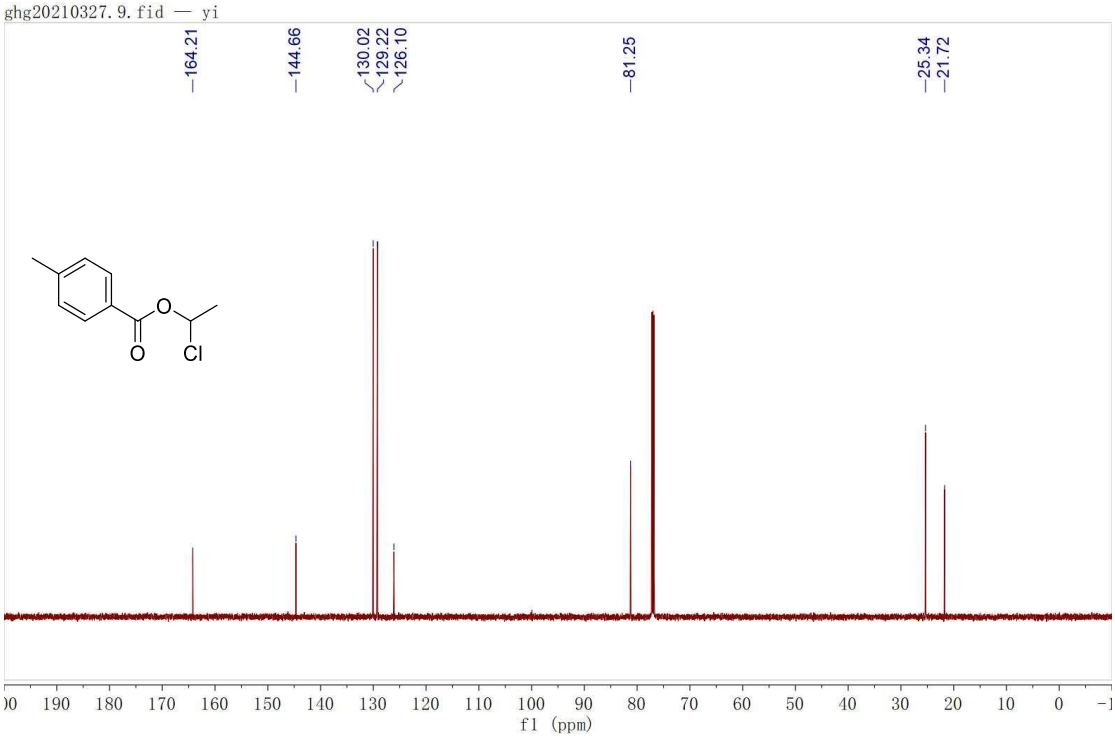
SM5, ^{13}C NMR (151 MHz, $CDCl_3$)



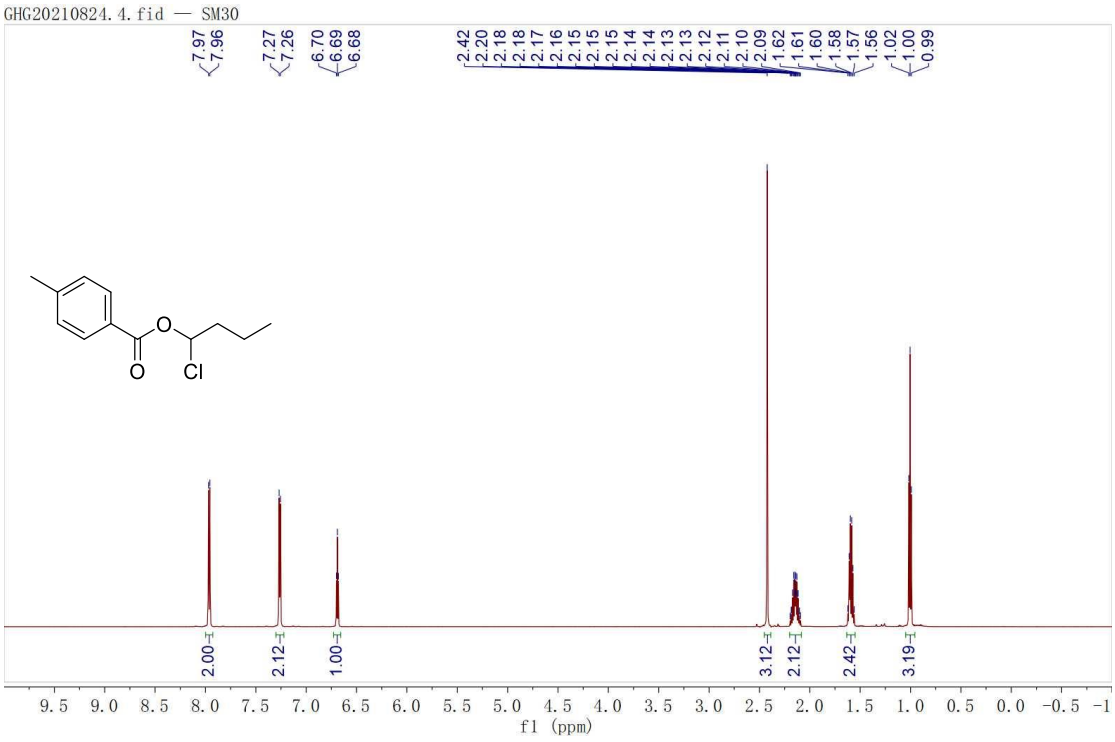
SM6, ^{1}H-NMR (600 MHZ, $CDCl_3$)



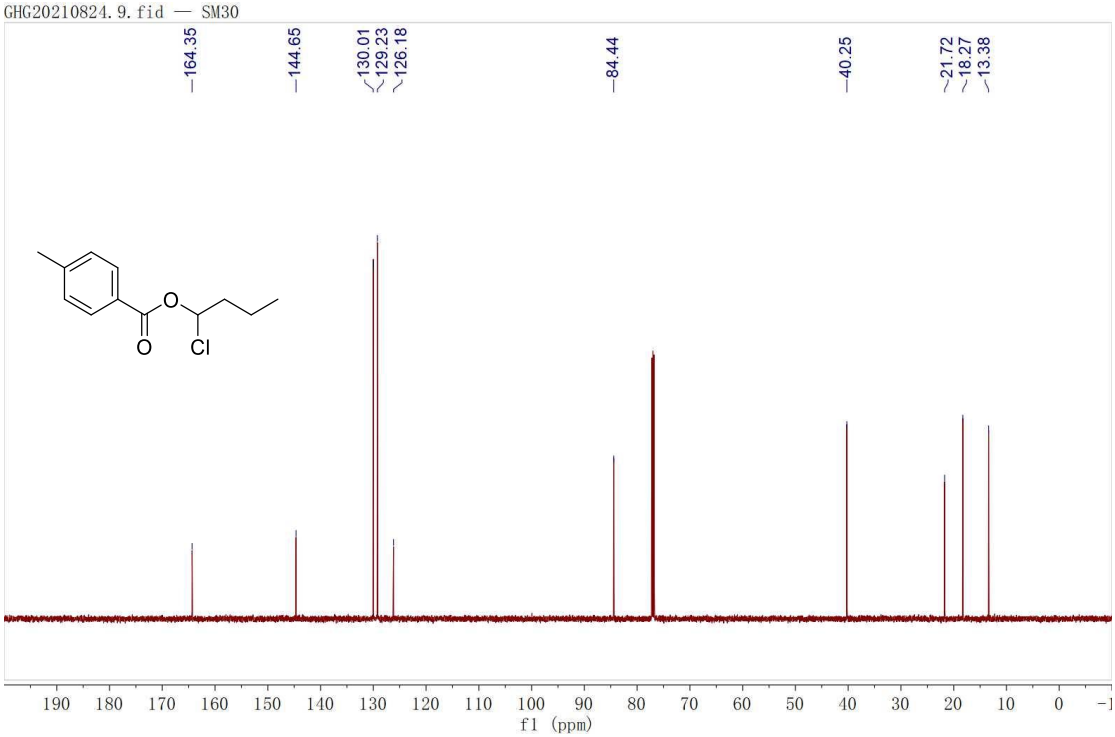
SM6, ^{13}C NMR (151 MHz, $CDCl_3$)



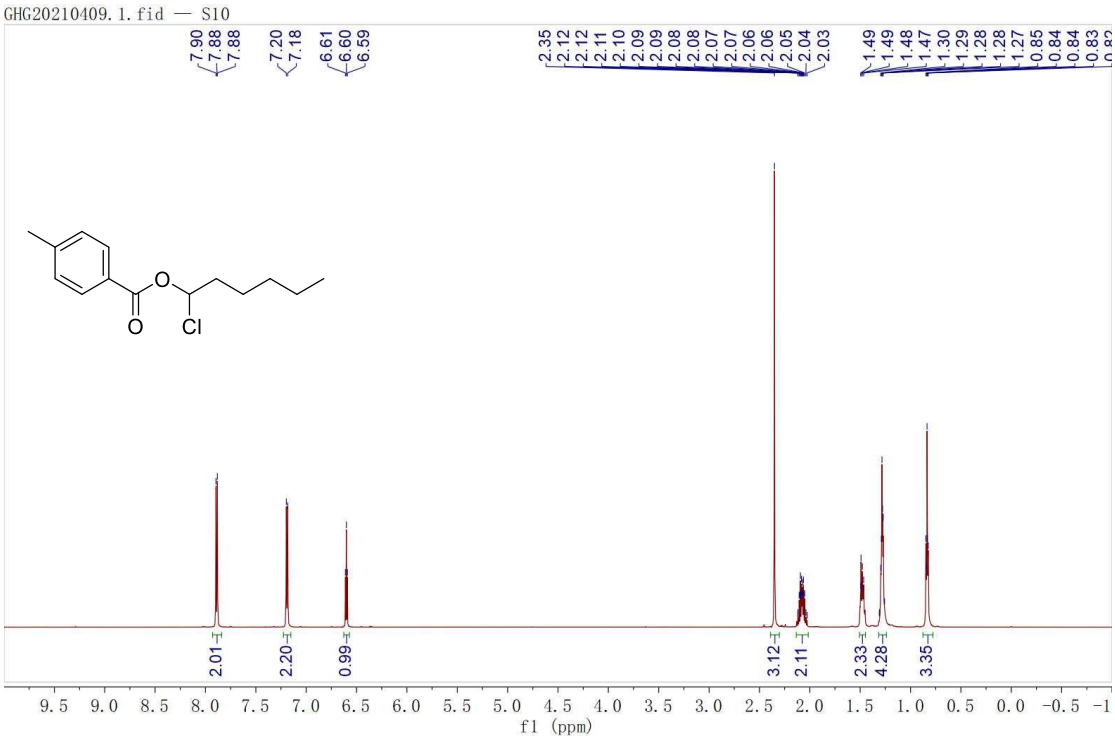
SM7, ^{1}H-NMR (600 MHZ, $CDCl_3$)



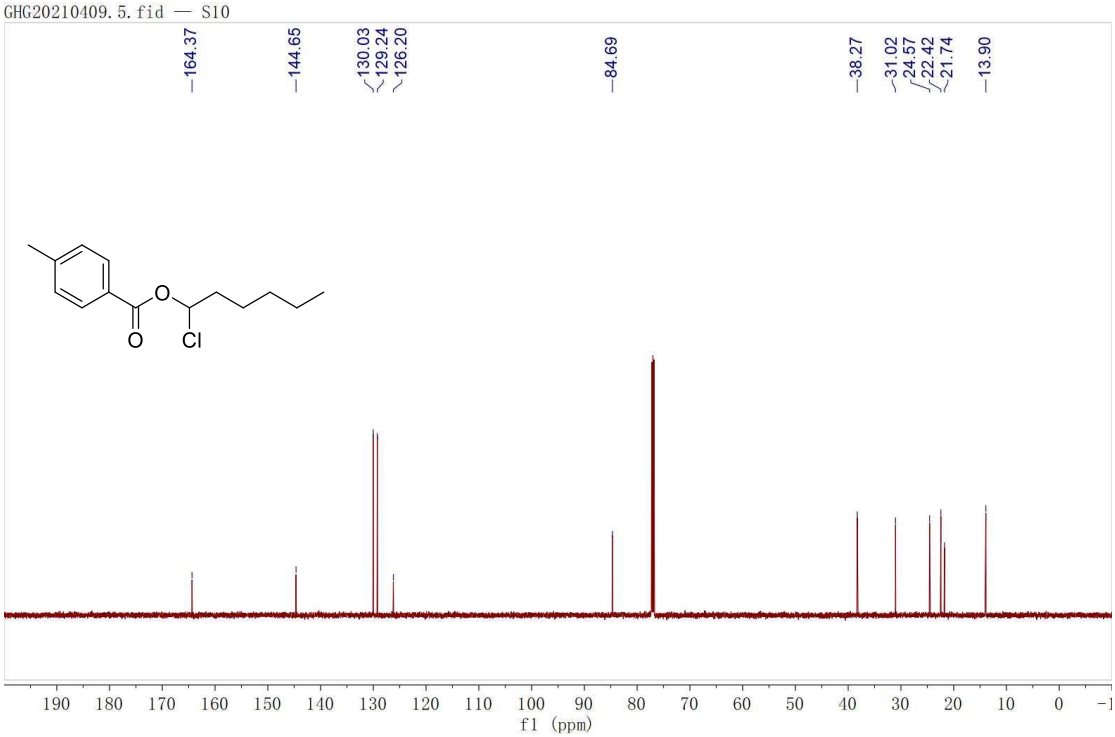
SM7, ^{13}C NMR (151 MHz, $CDCl_3$)



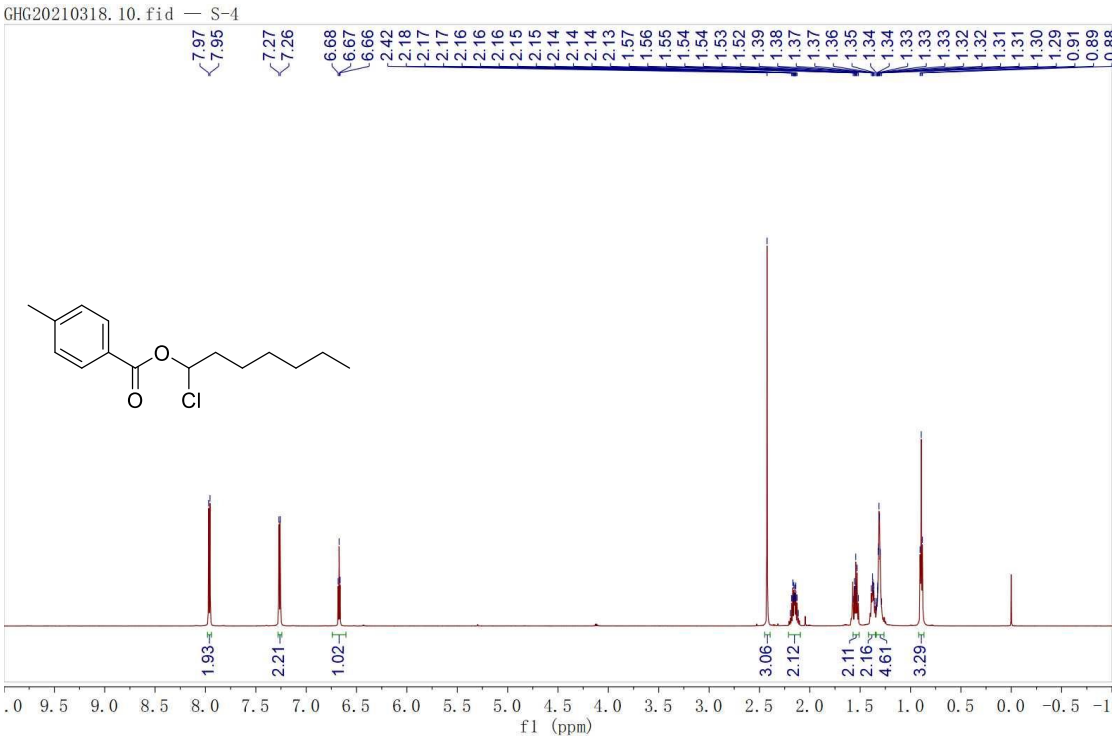
SM8, ^{1}H-NMR (600 MHZ, $CDCl_3$)



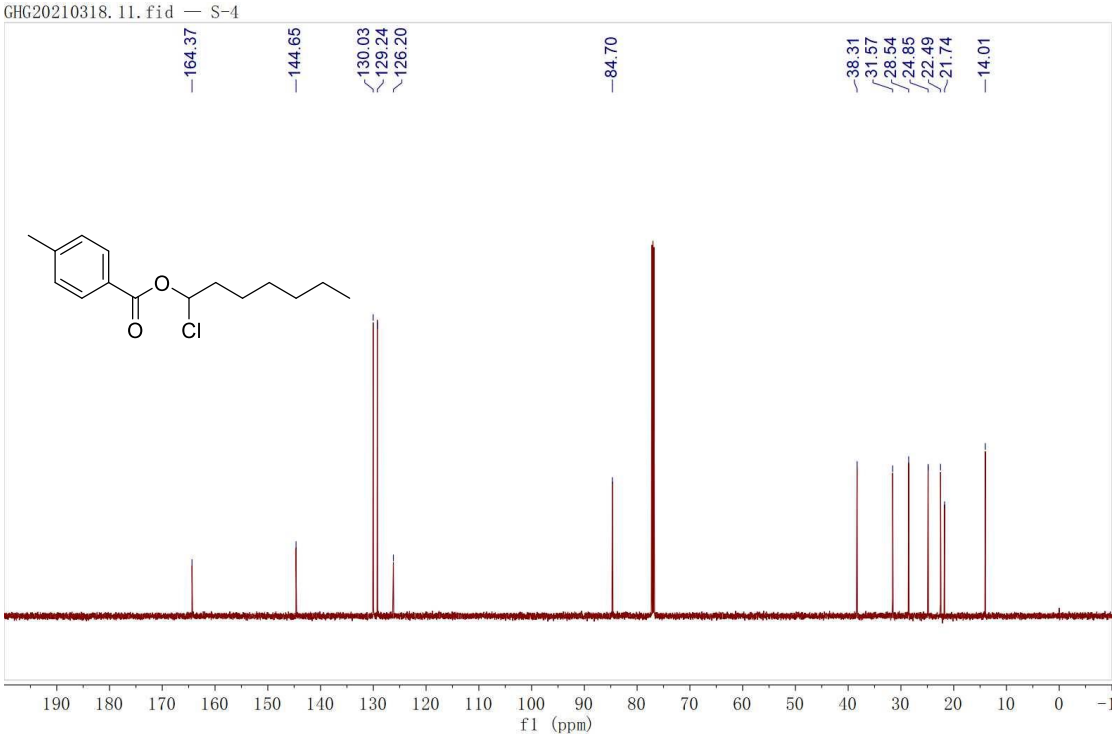
SM8, ^{13}C NMR (151 MHz, $CDCl_3$)



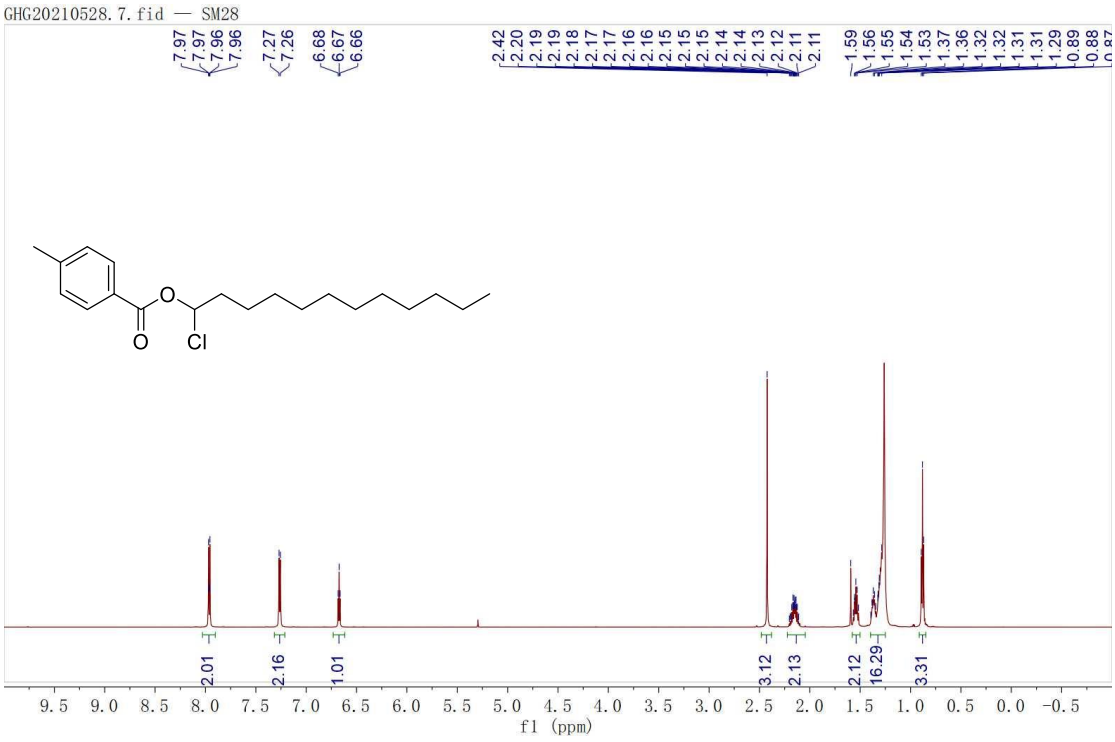
SM9, ^{1}H-NMR (600 MHZ, $CDCl_3$)



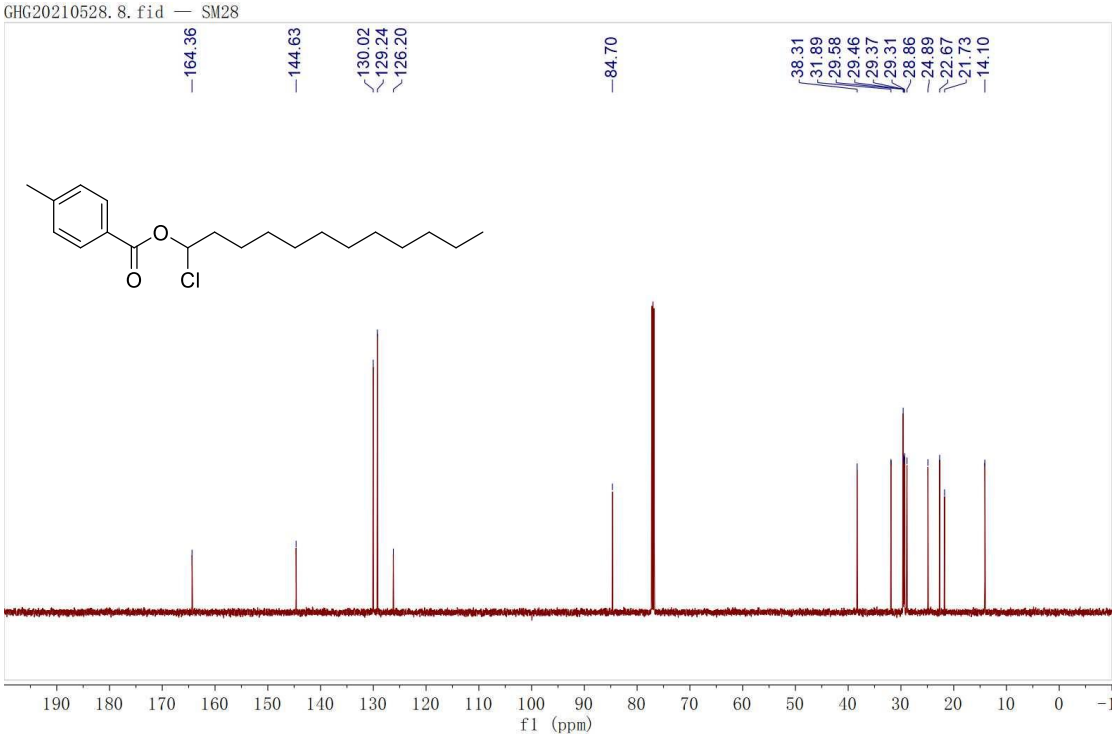
SM9, ^{13}C NMR (151 MHz, $CDCl_3$)



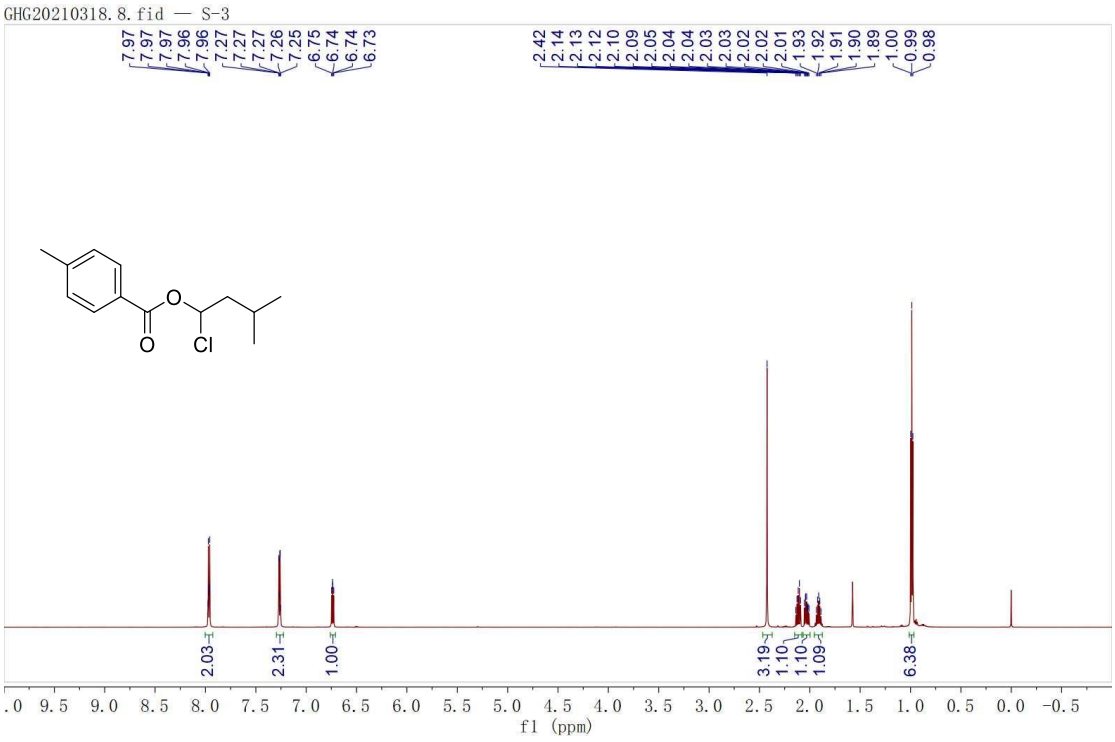
SM10, ^{1}H-NMR (600 MHZ, $CDCl_3$)



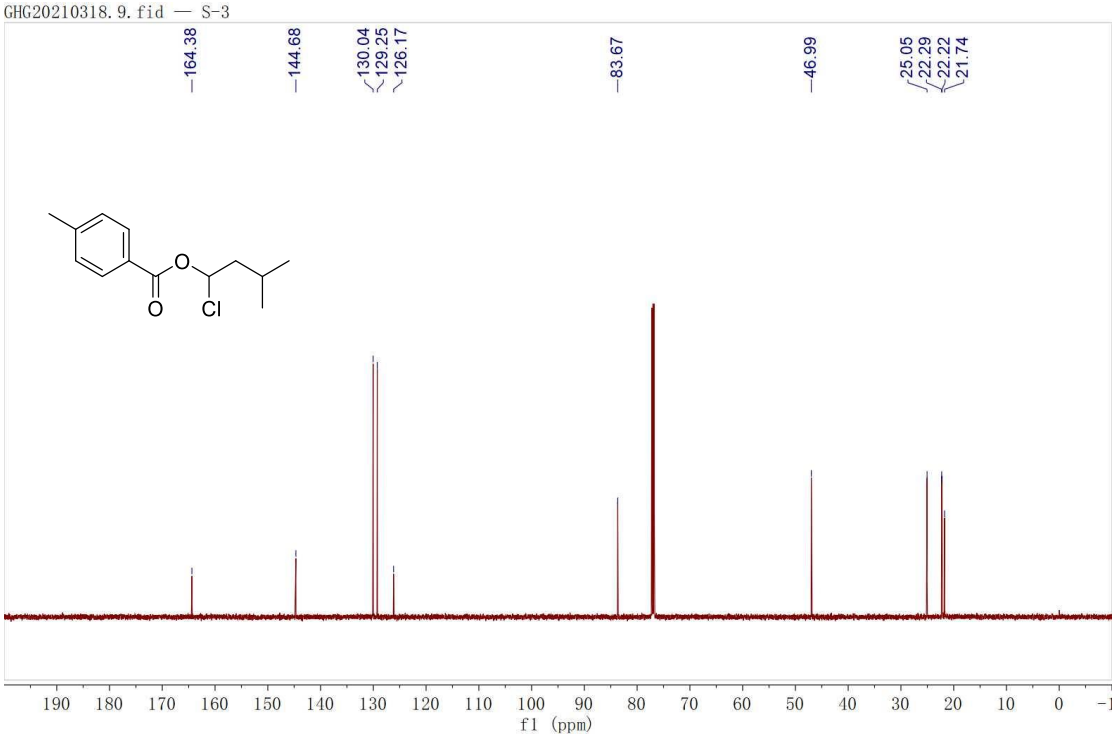
SM10, ^{13}C NMR (151 MHz, $CDCl_3$)



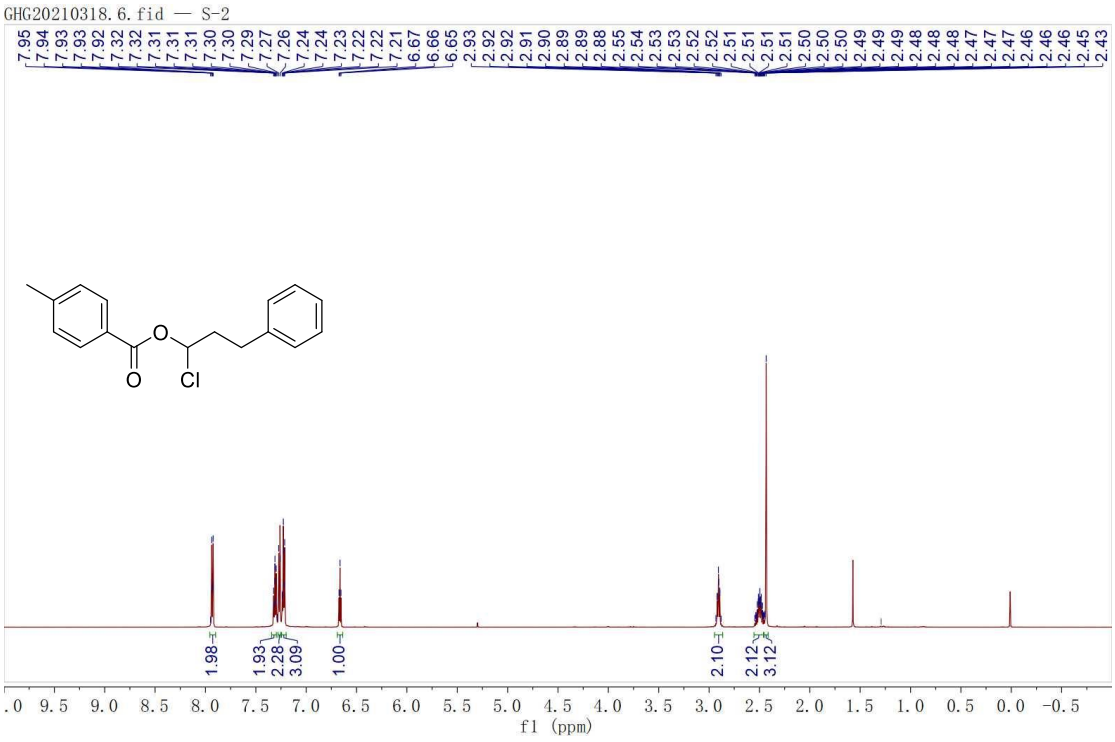
SM11, ^{1}H-NMR (600 MHZ, $CDCl_3$)



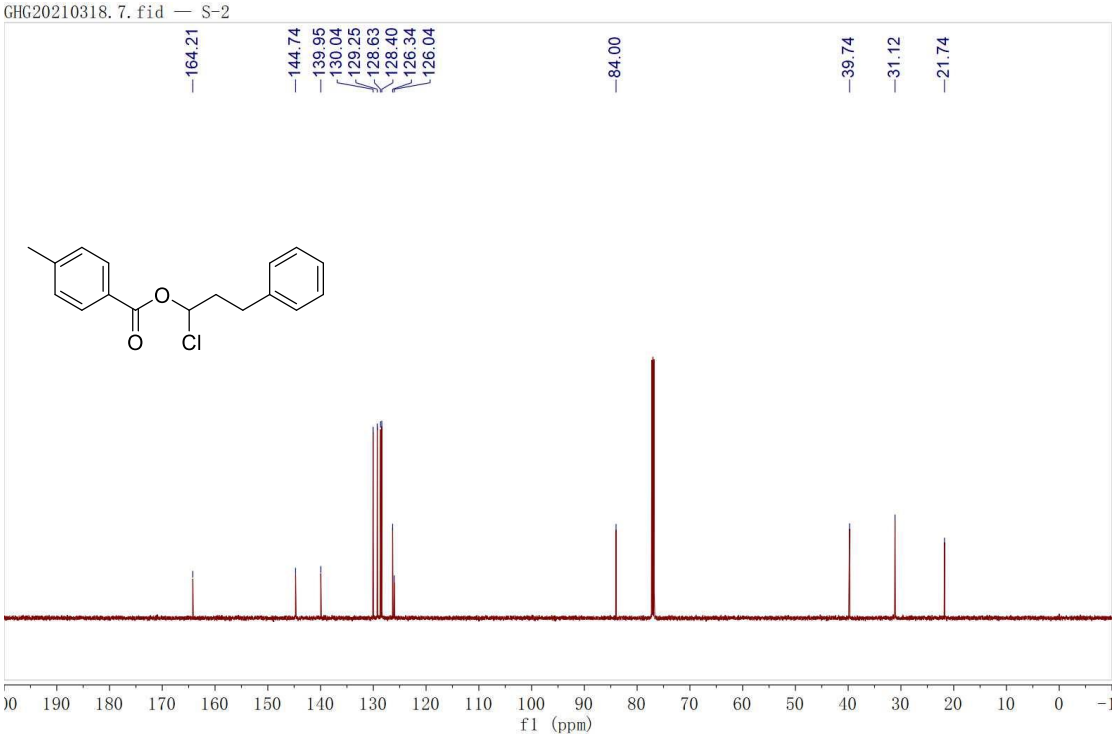
SM11, ^{13}C NMR (151 MHz, $CDCl_3$)



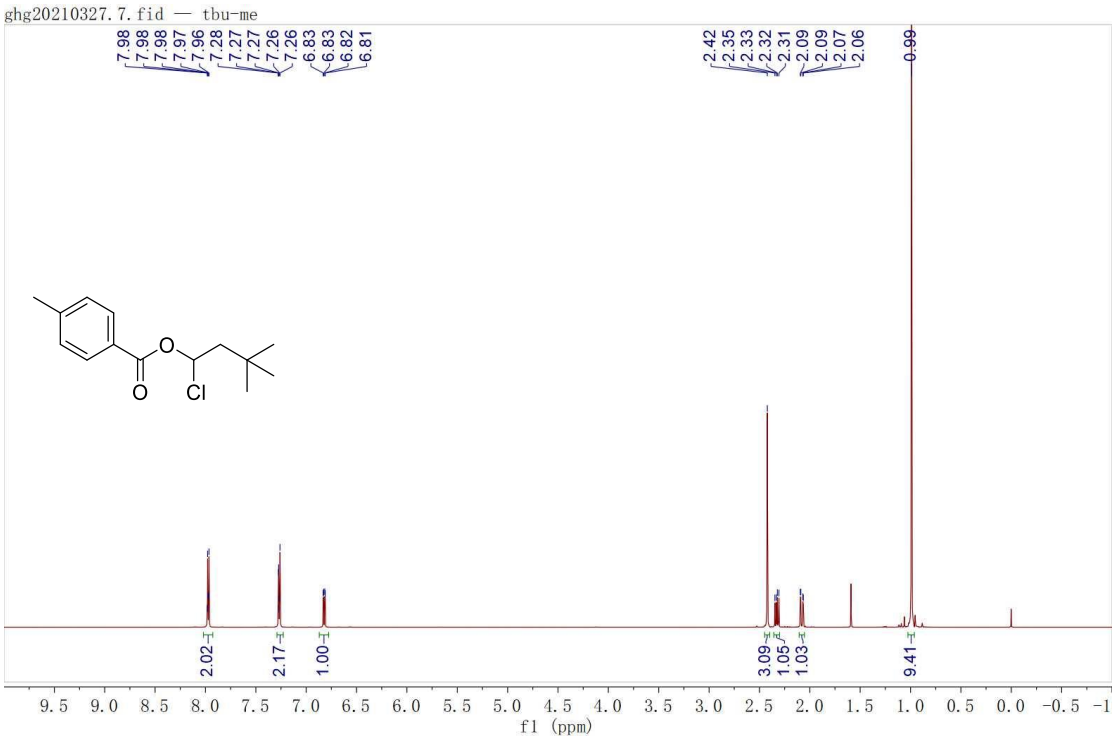
SM12, ^{1}H-NMR (600 MHZ, $CDCl_3$)



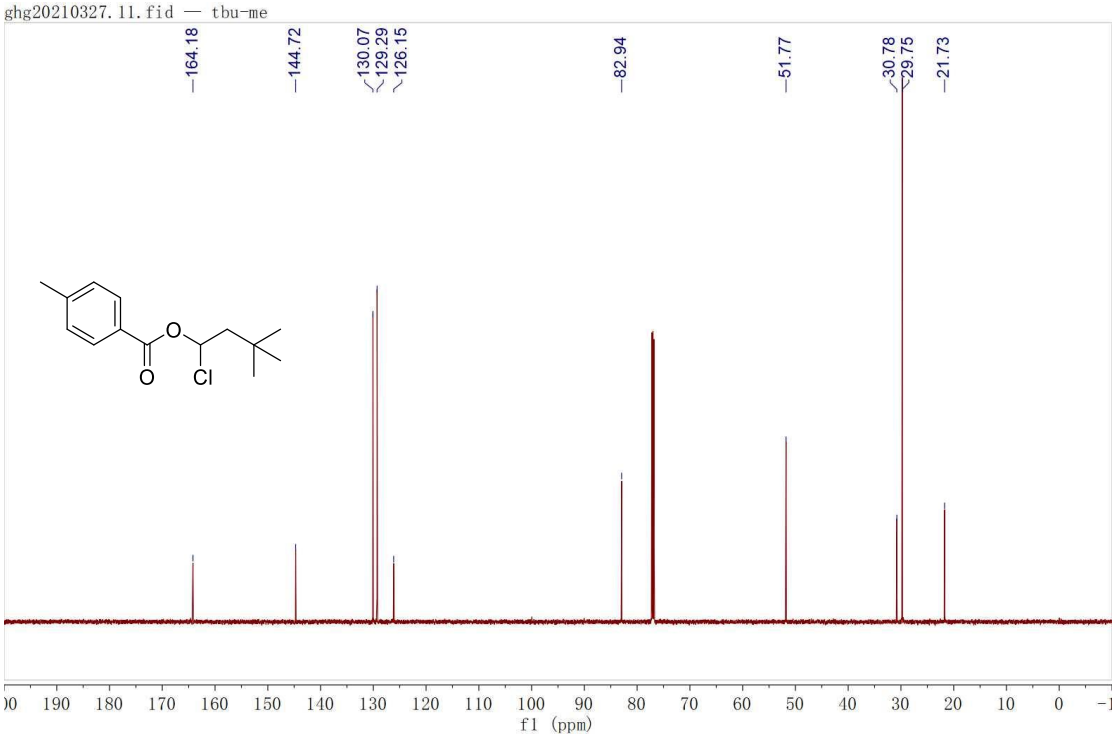
SM12, ^{13}C NMR (151 MHz, $CDCl_3$)



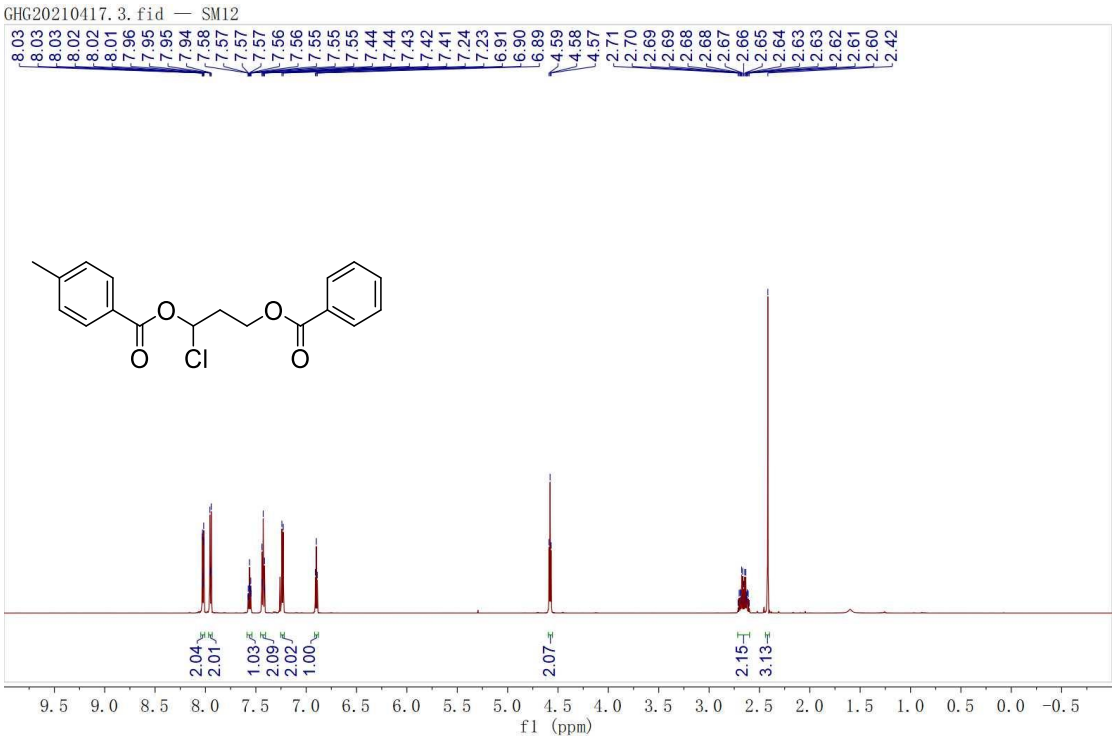
SM13, ^{1}H-NMR (600 MHZ, $CDCl_3$)



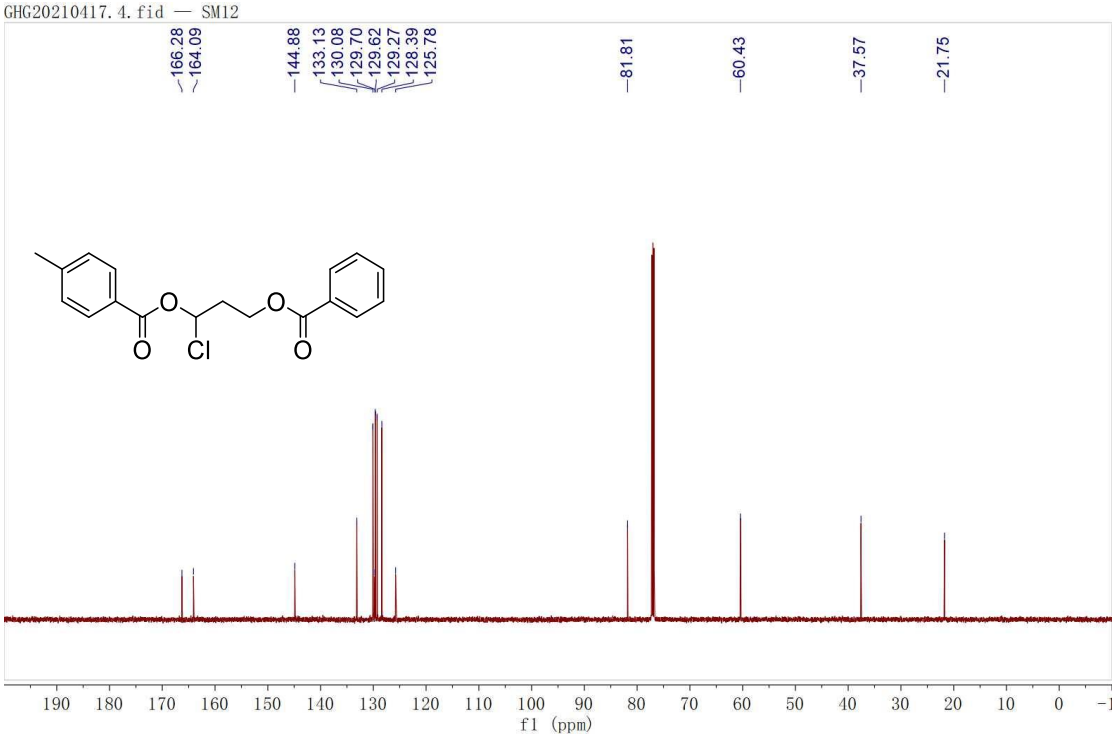
SM13, ^{13}C NMR (151 MHz, $CDCl_3$)



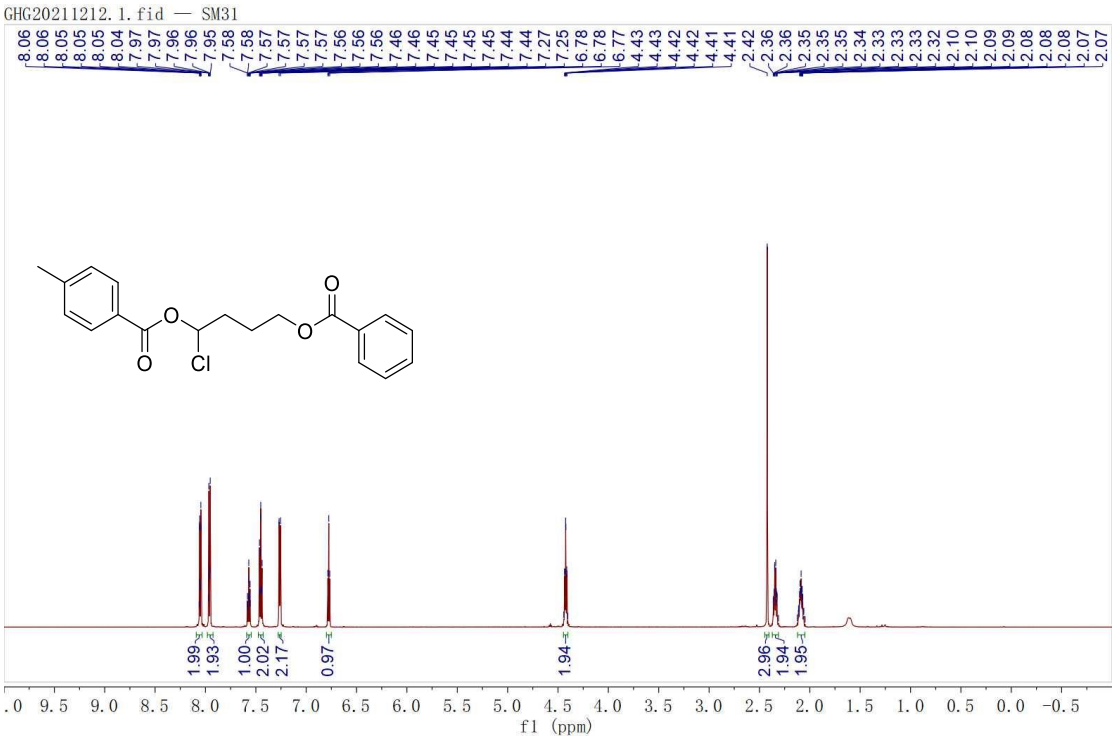
SM14, ^{1}H-NMR (600 MHZ, $CDCl_3$)



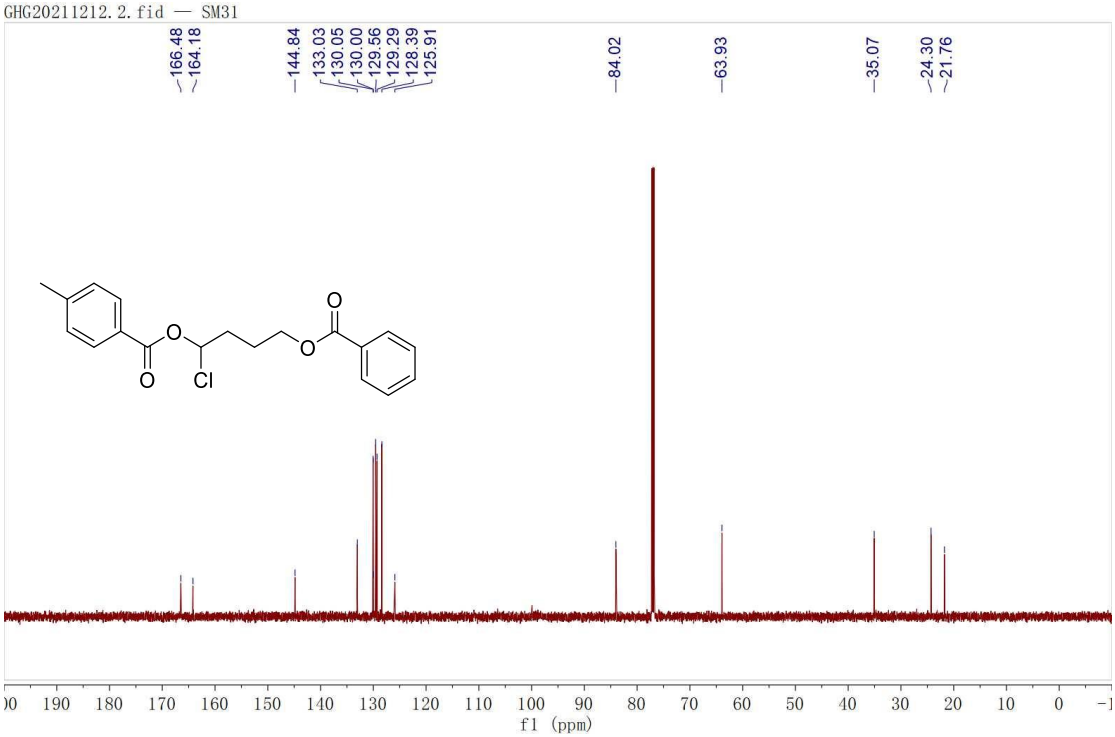
SM14, ^{13}C NMR (151 MHz, $CDCl_3$)



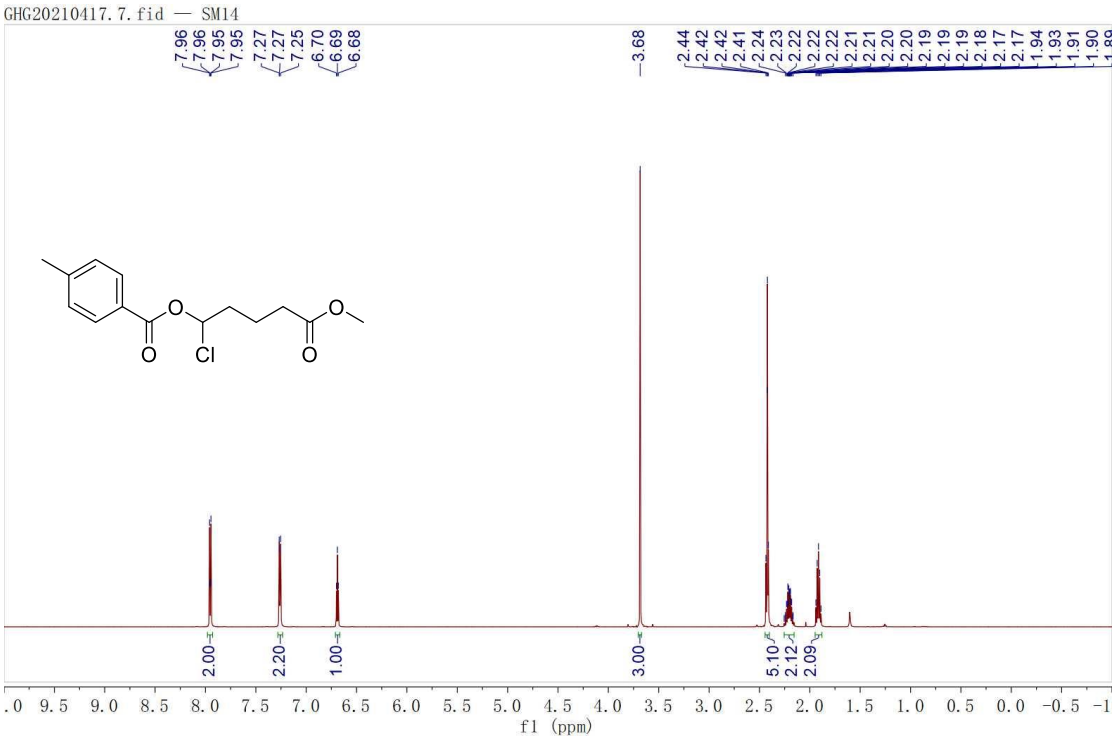
SM15, ^{1}H-NMR (600 MHZ, $CDCl_3$)



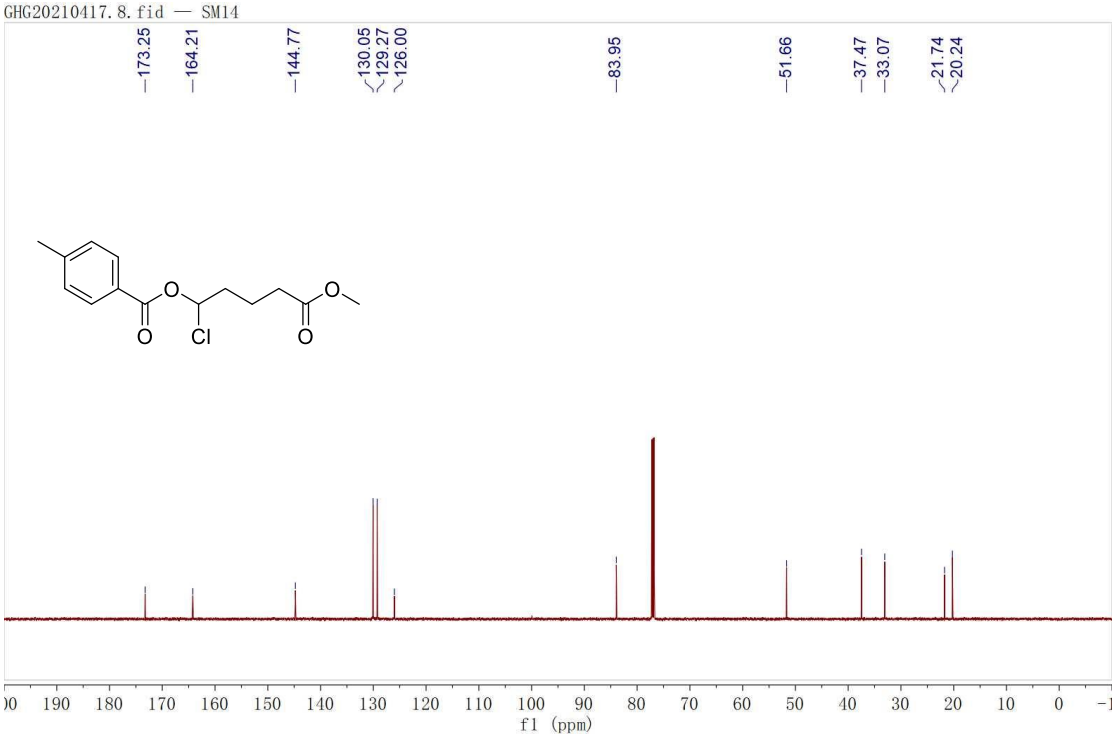
SM15, ^{13}C NMR (151 MHz, $CDCl_3$)



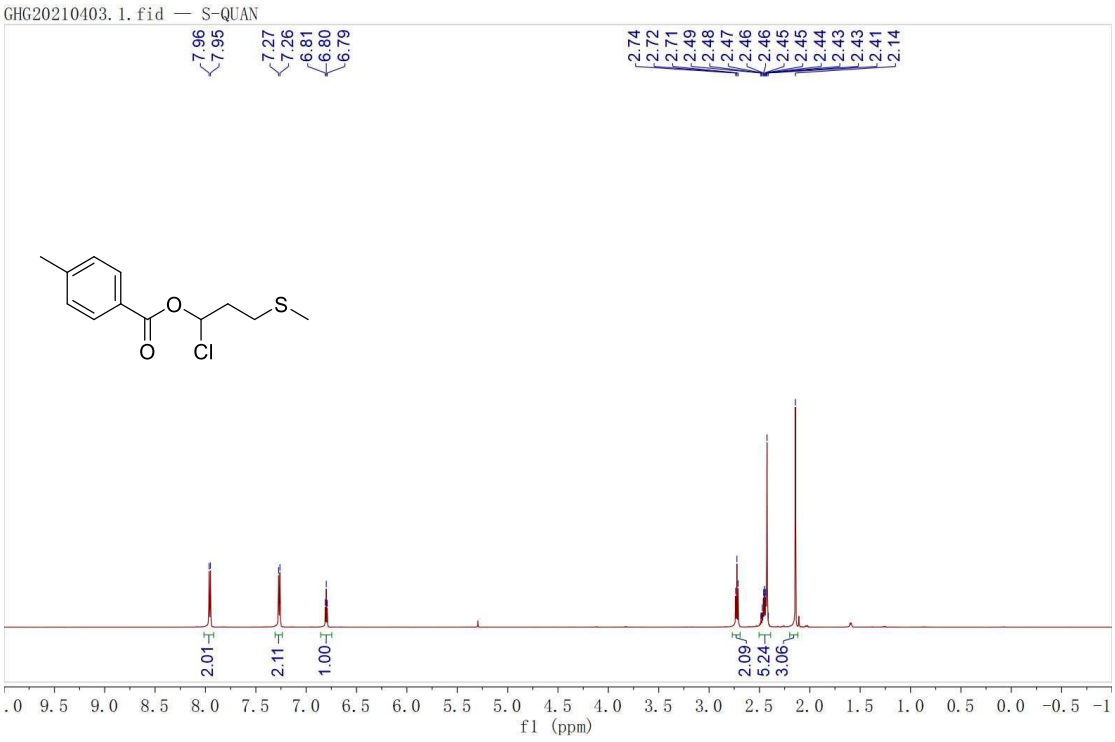
SM16, ^{1}H-NMR (600 MHZ, $CDCl_3$)



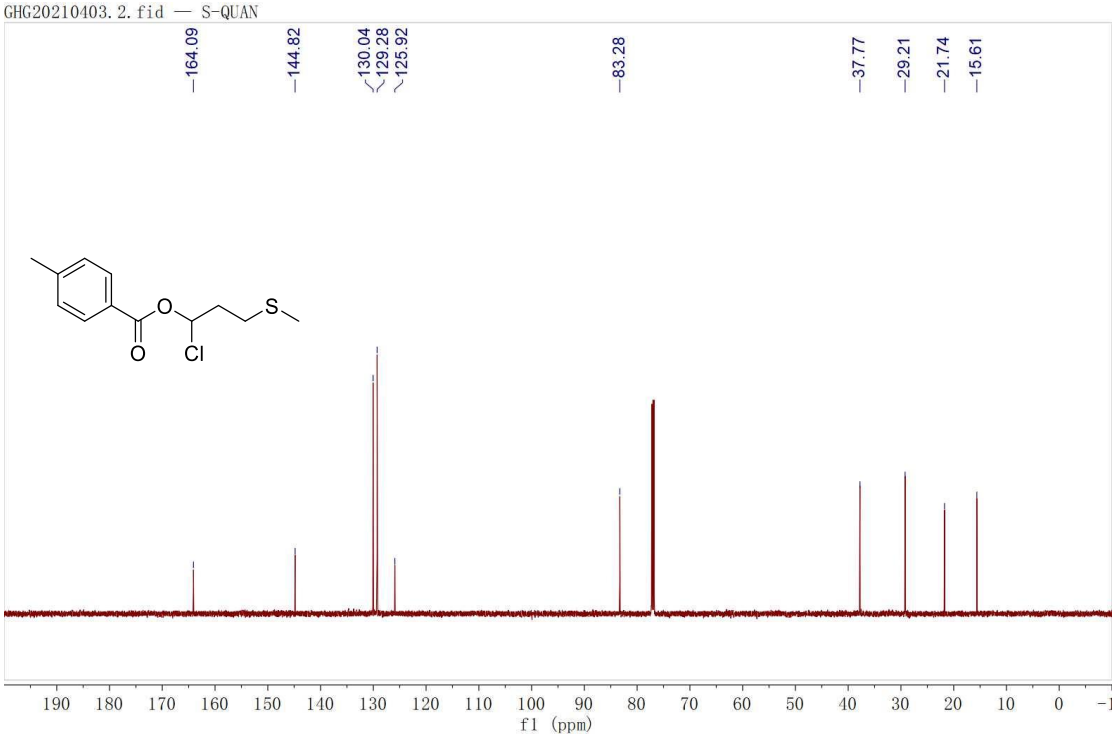
SM16, ^{13}C NMR (151 MHz, $CDCl_3$)



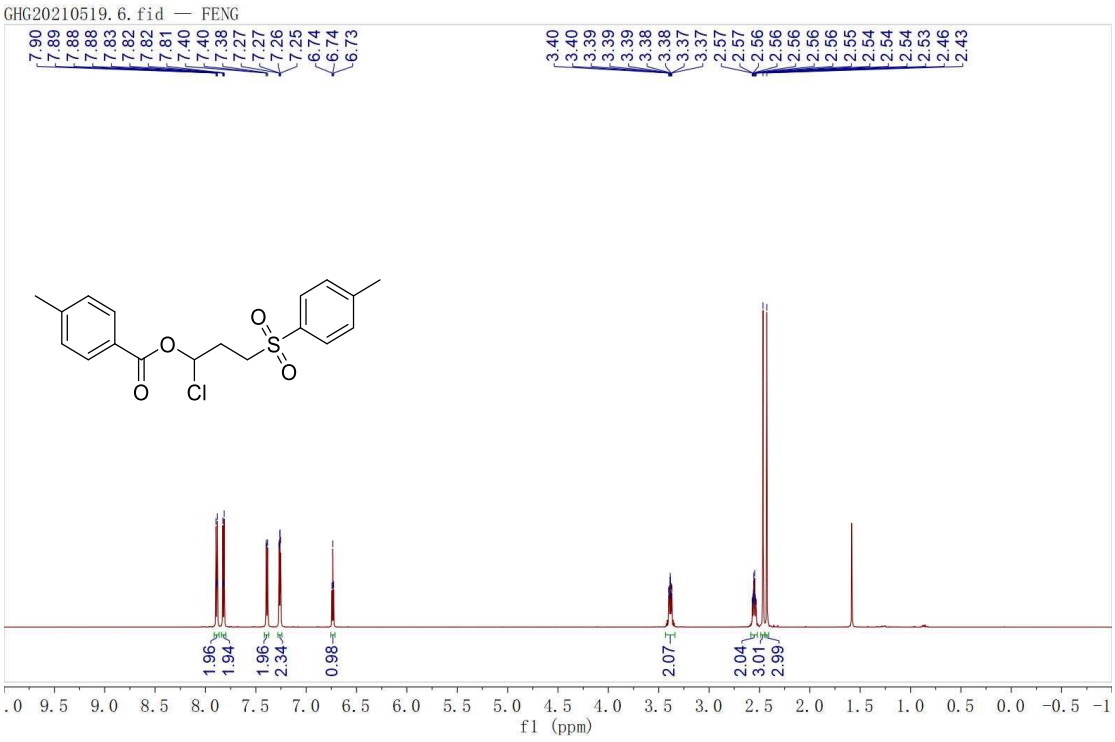
SM17, ^{1}H-NMR (600 MHZ, $CDCl_3$)



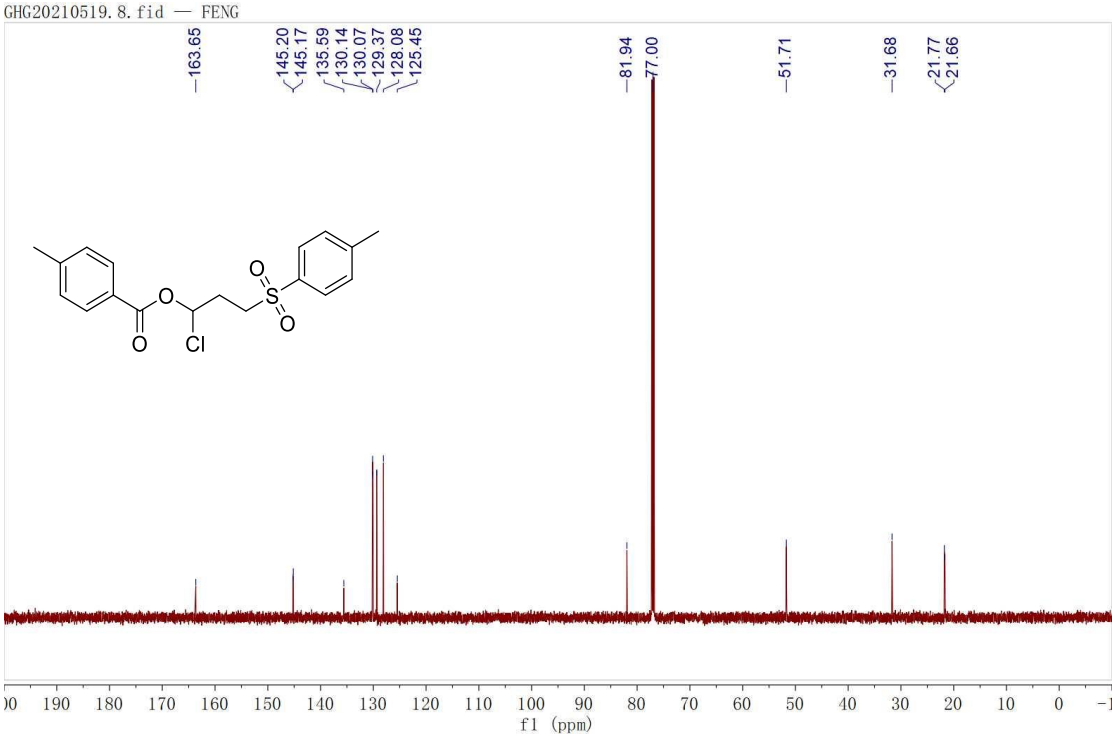
SM17, ^{13}C NMR (151 MHz, $CDCl_3$)



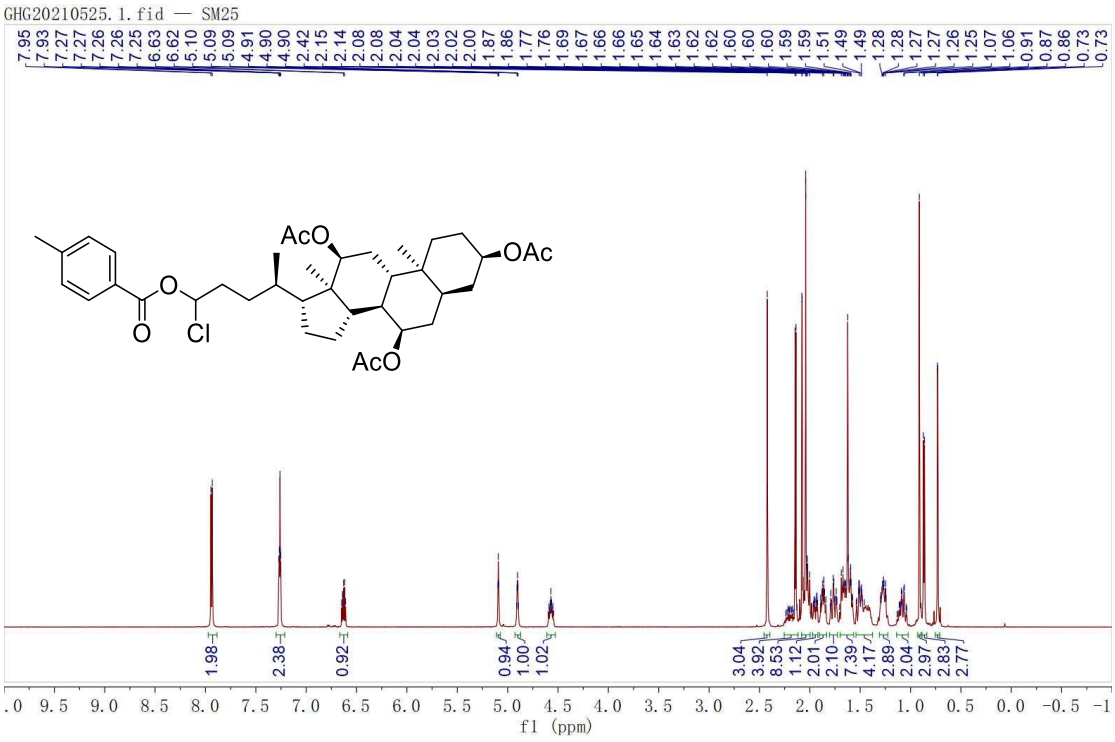
SM18, ^{1}H-NMR (600 MHZ, $CDCl_3$)



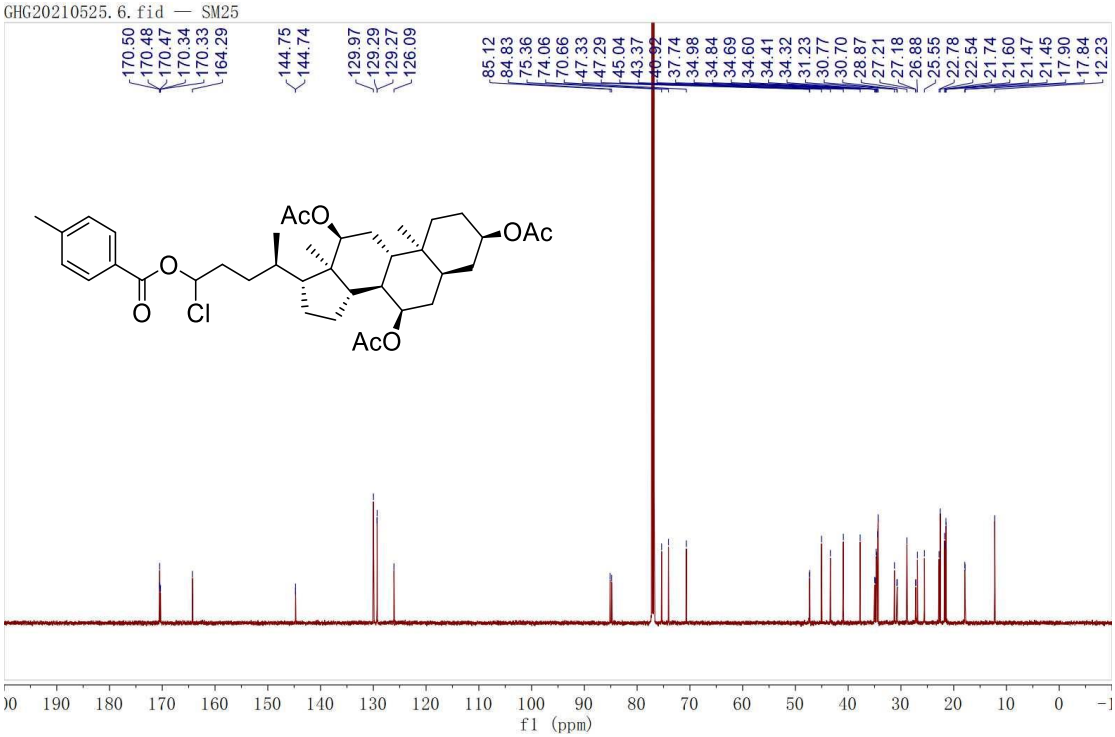
SM18, ^{13}C NMR (151 MHz, $CDCl_3$)



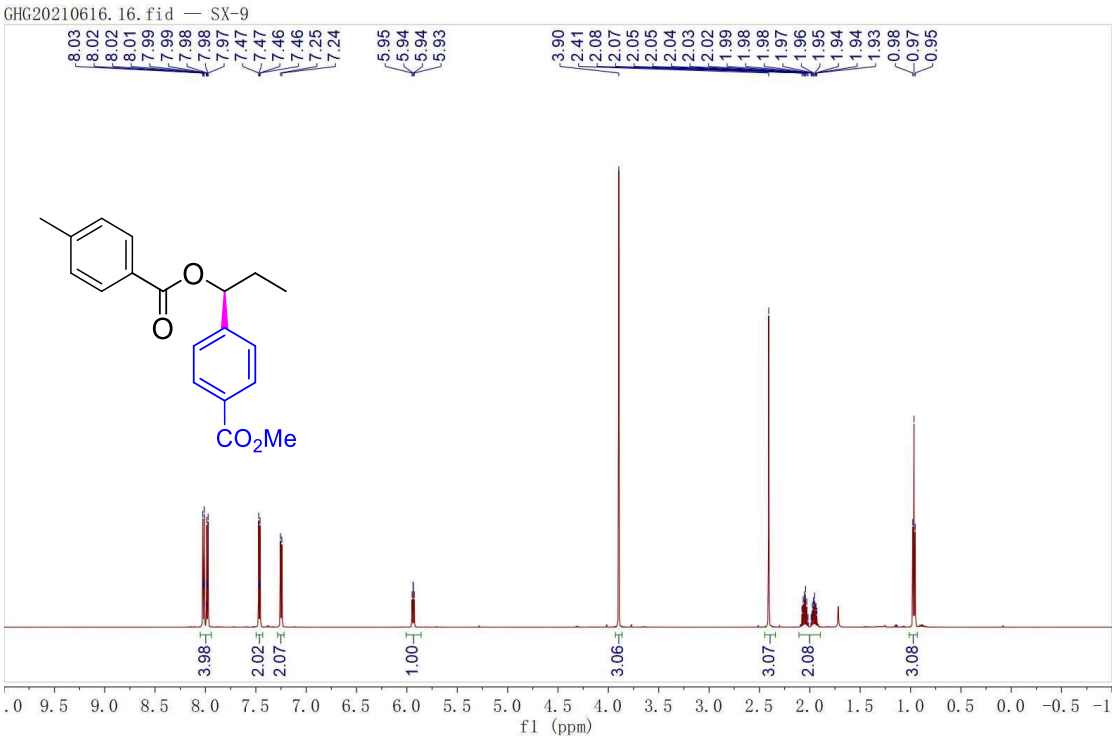
SM19, ^{1}H-NMR (600 MHZ, $CDCl_3$)



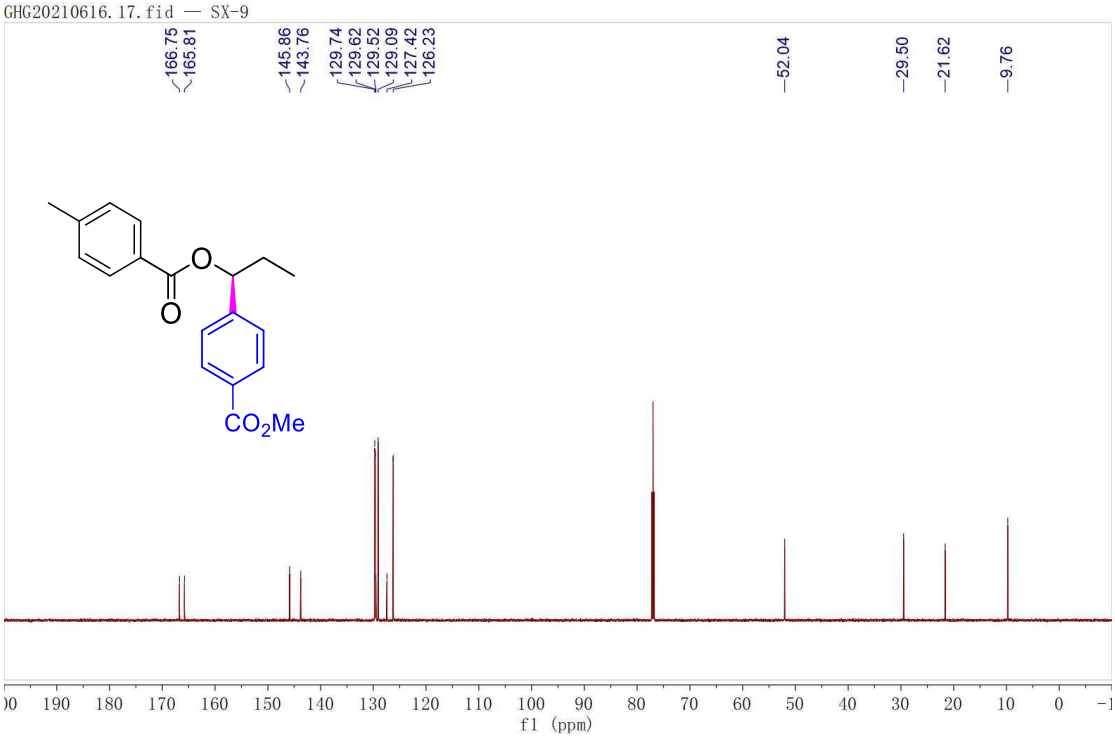
SM19, ^{13}C NMR (151 MHz, $CDCl_3$)



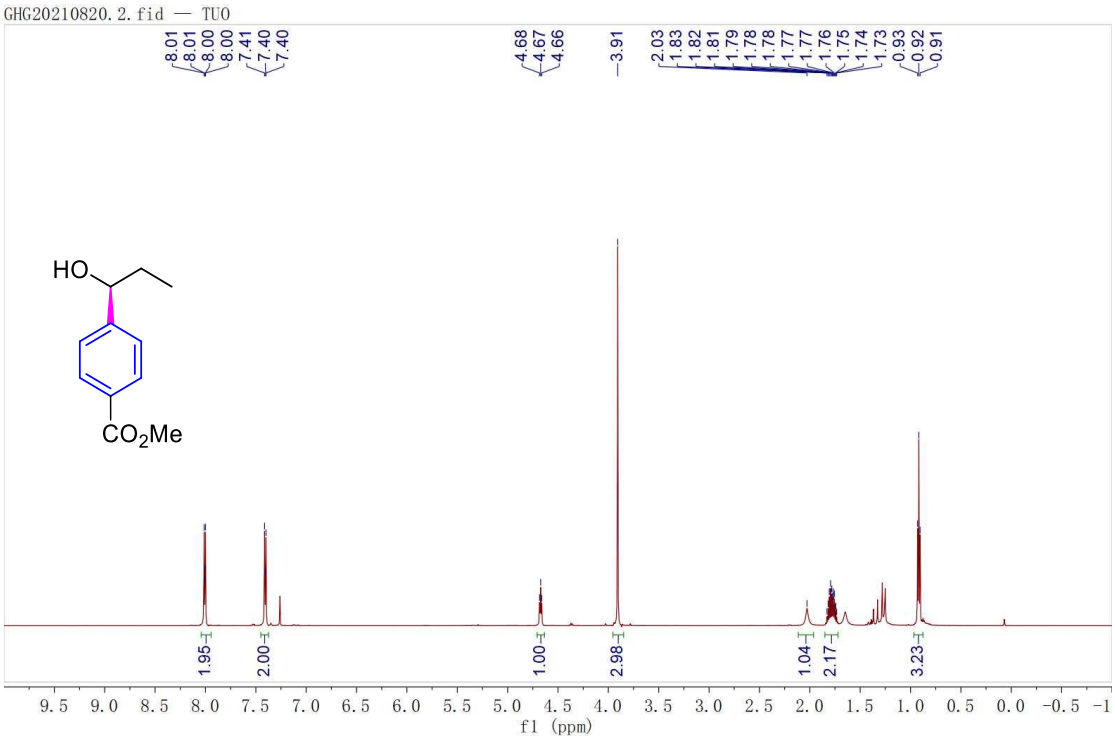
2, ^{1}H-NMR (600 MHZ, $CDCl_3$)



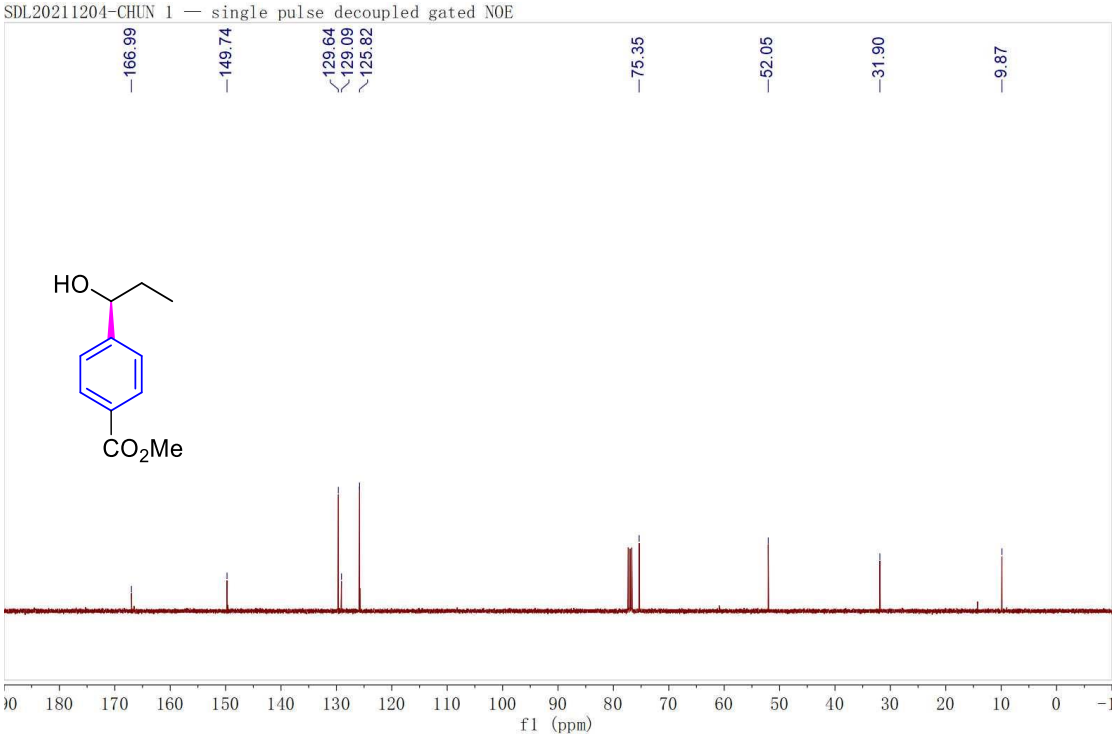
2, ^{13}C NMR (151 MHz, $CDCl_3$)



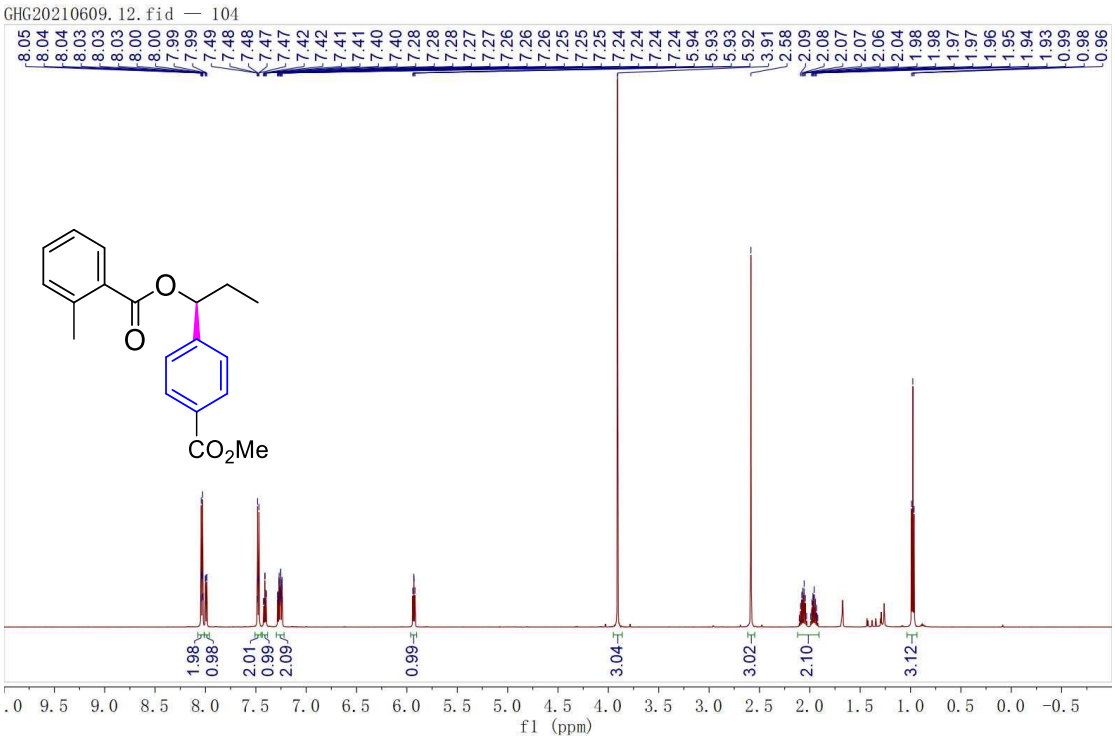
3, ^{1}H-NMR (600 MHZ, $CDCl_3$)



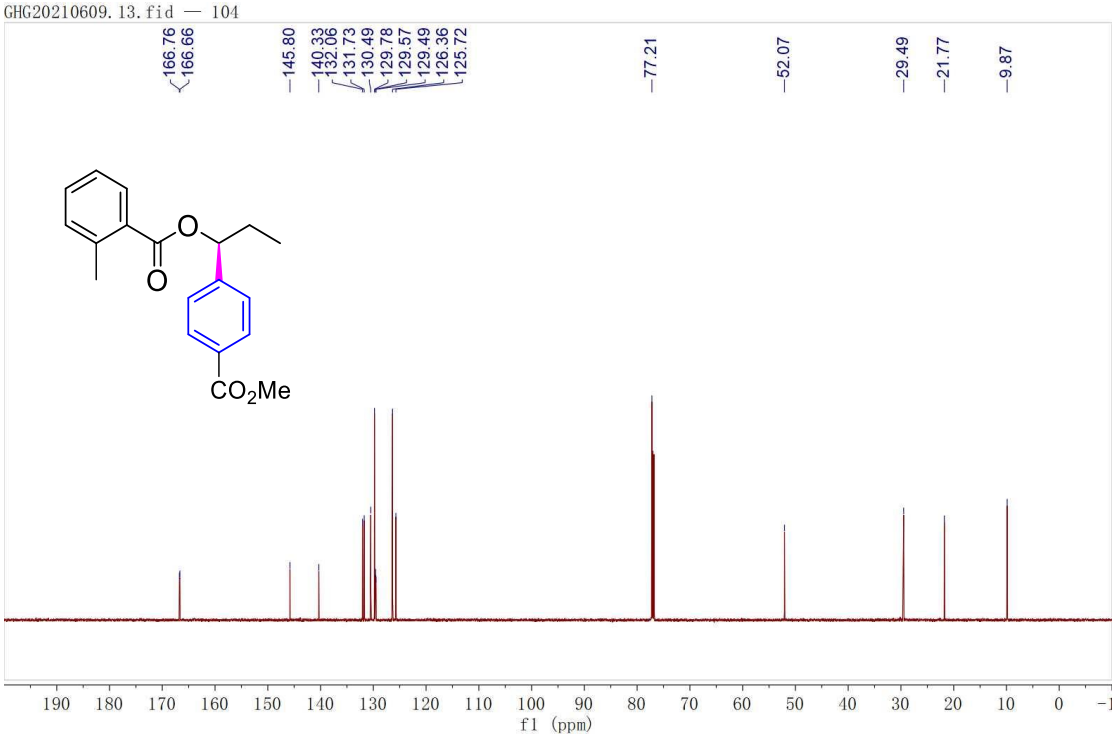
3, ^{13}C NMR (101 MHz, $CDCl_3$)



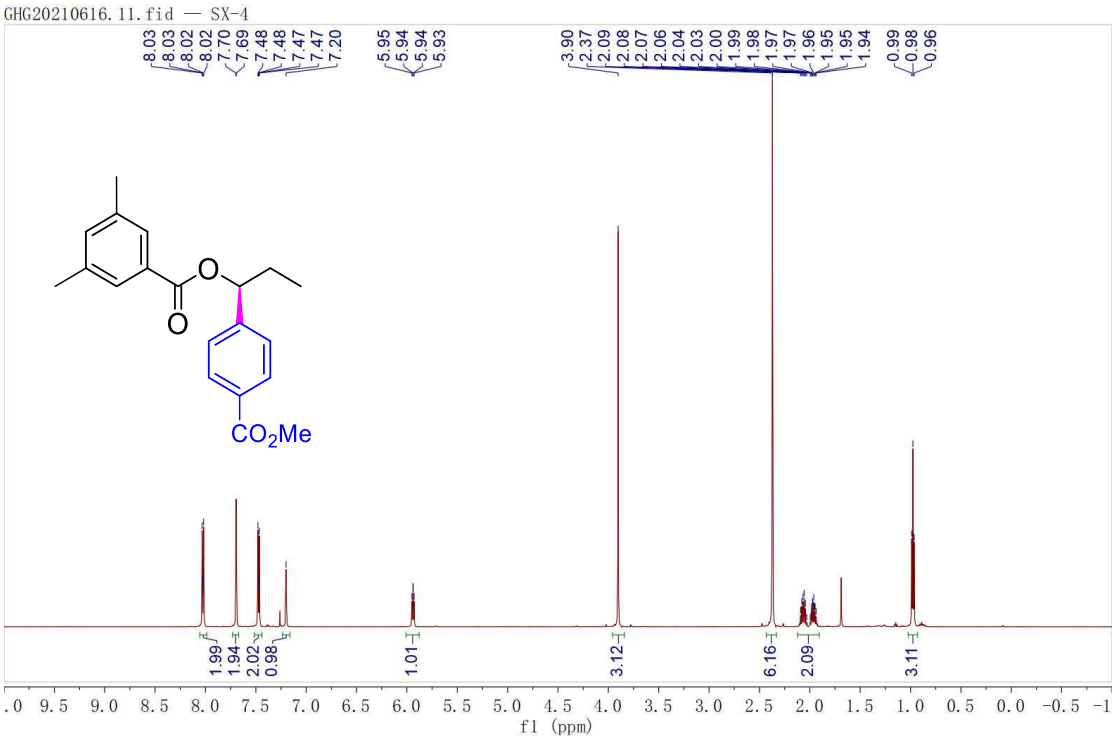
4, ^{1}H-NMR (600 MHZ, $CDCl_3$)



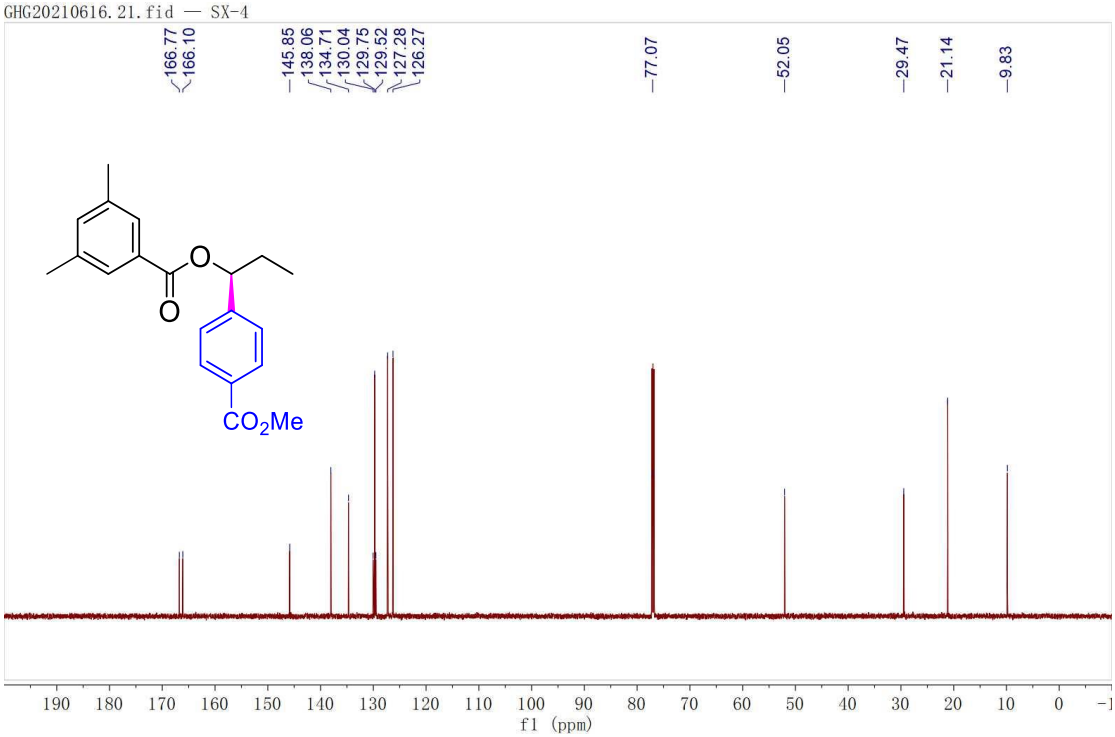
4, ^{13}C NMR (151 MHz, $CDCl_3$)



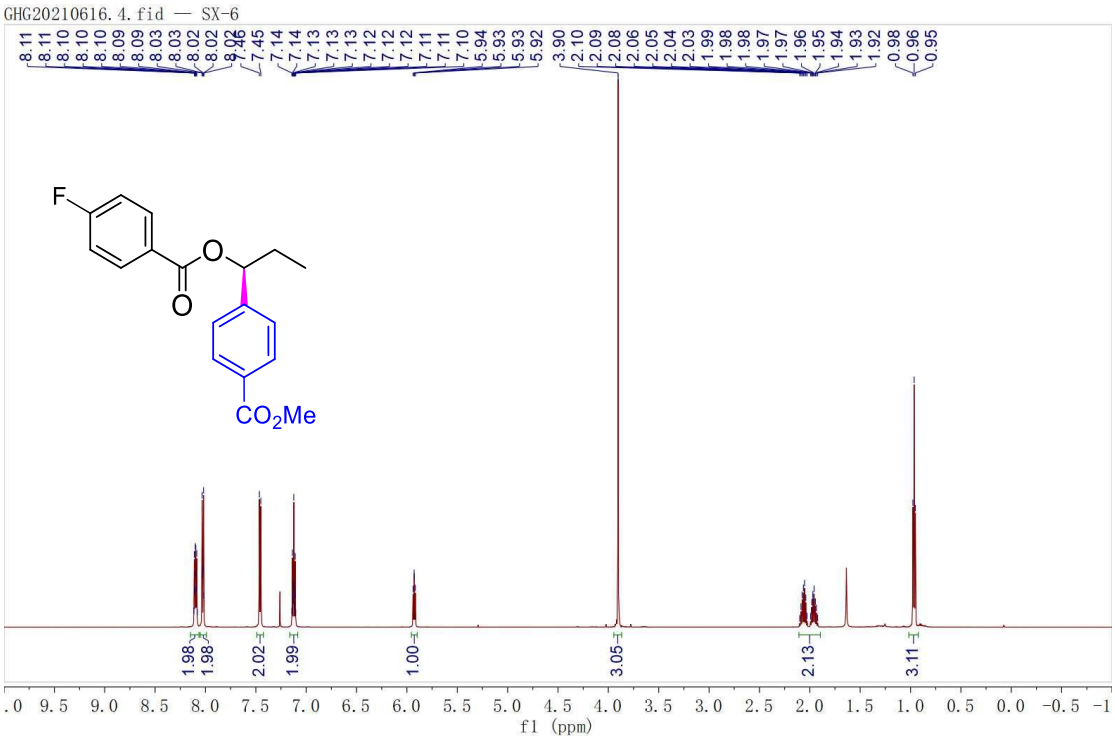
5, ^{1}H-NMR (600 MHZ, $CDCl_3$)



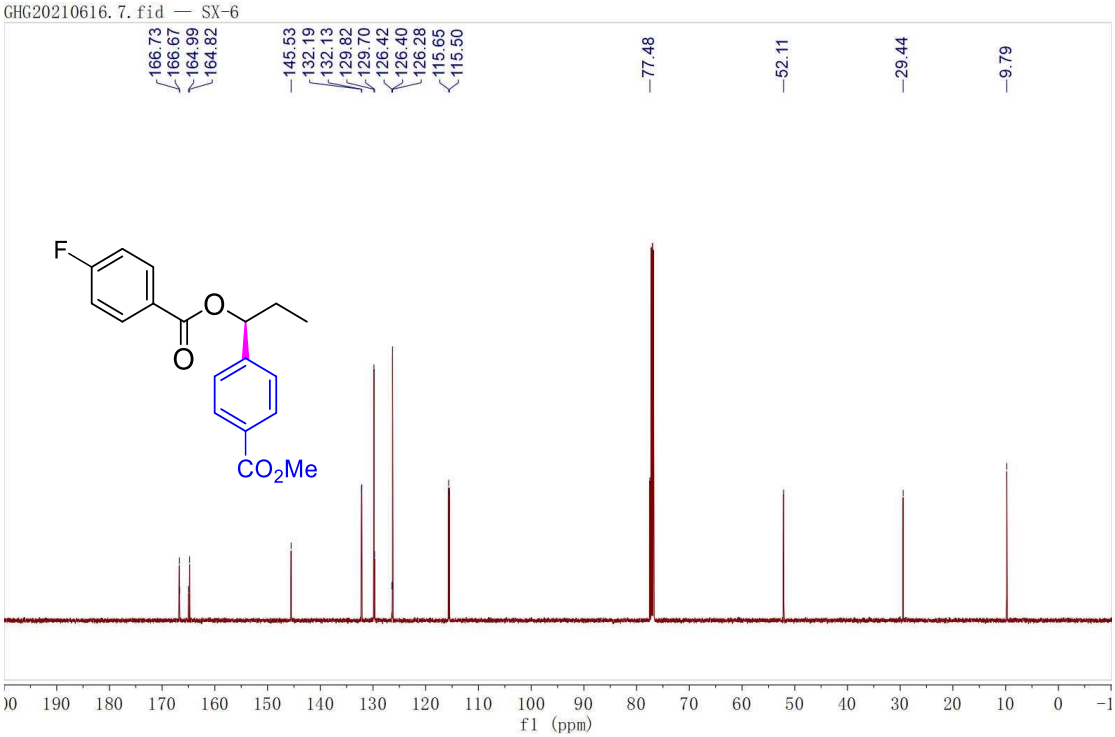
5, ^{13}C NMR (151 MHz, $CDCl_3$)



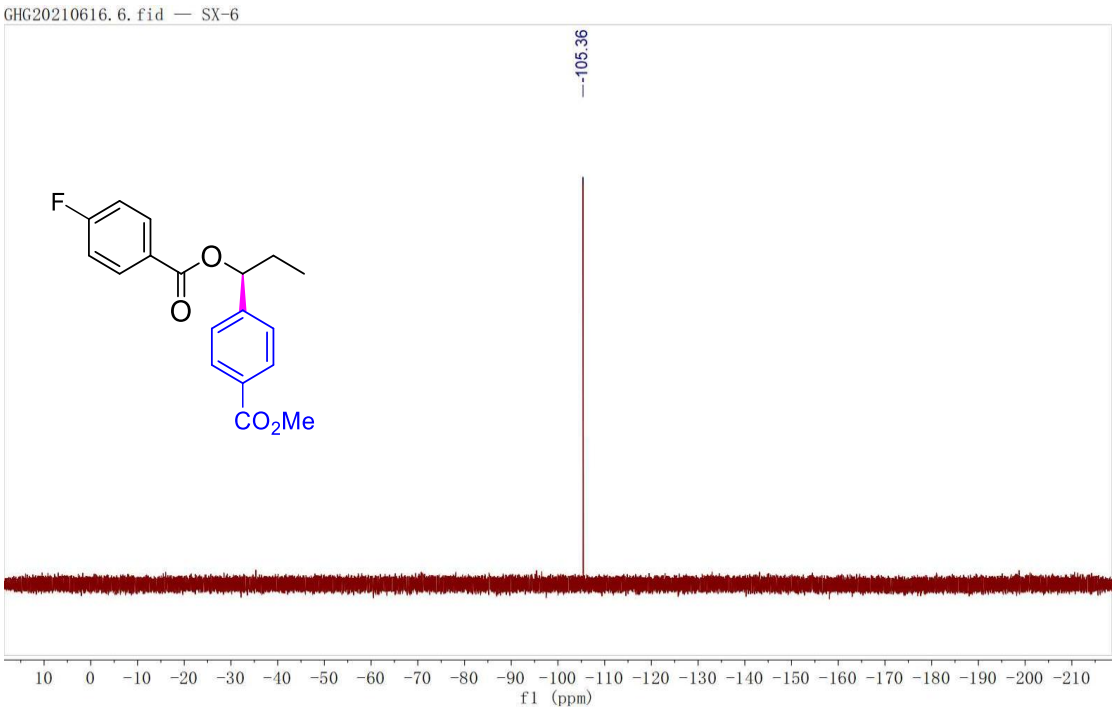
6, ^{1}H-NMR (600 MHZ, $CDCl_3$)



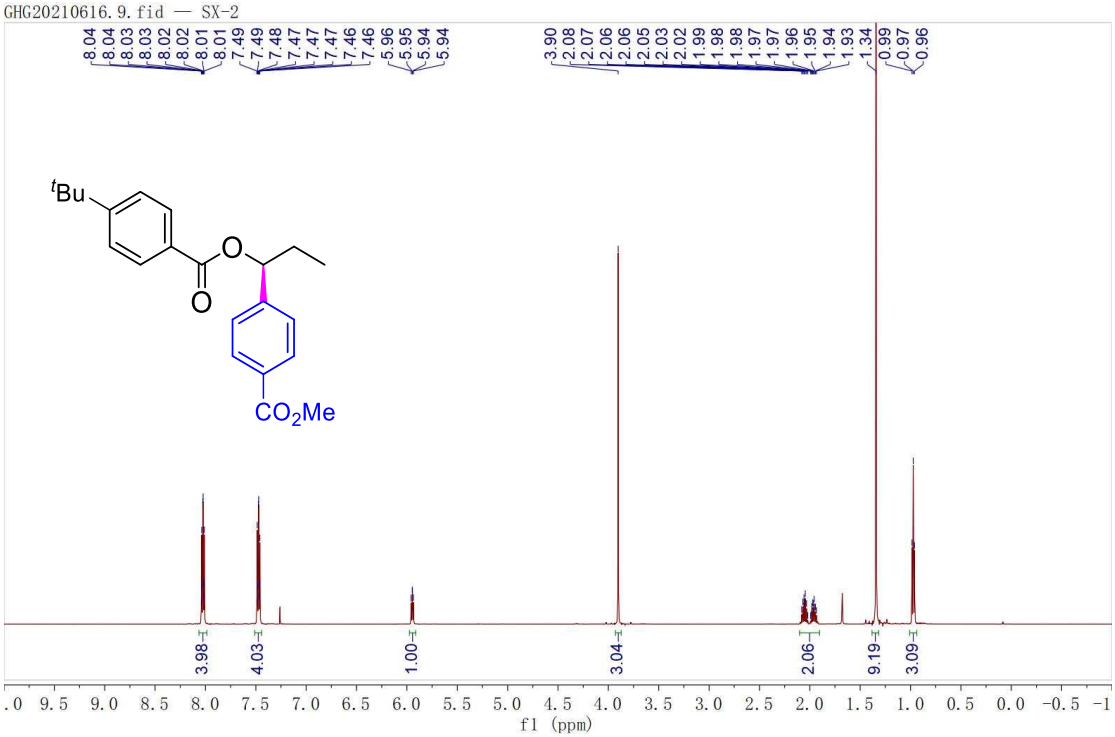
6, ^{13}C NMR (151 MHz, $CDCl_3$)



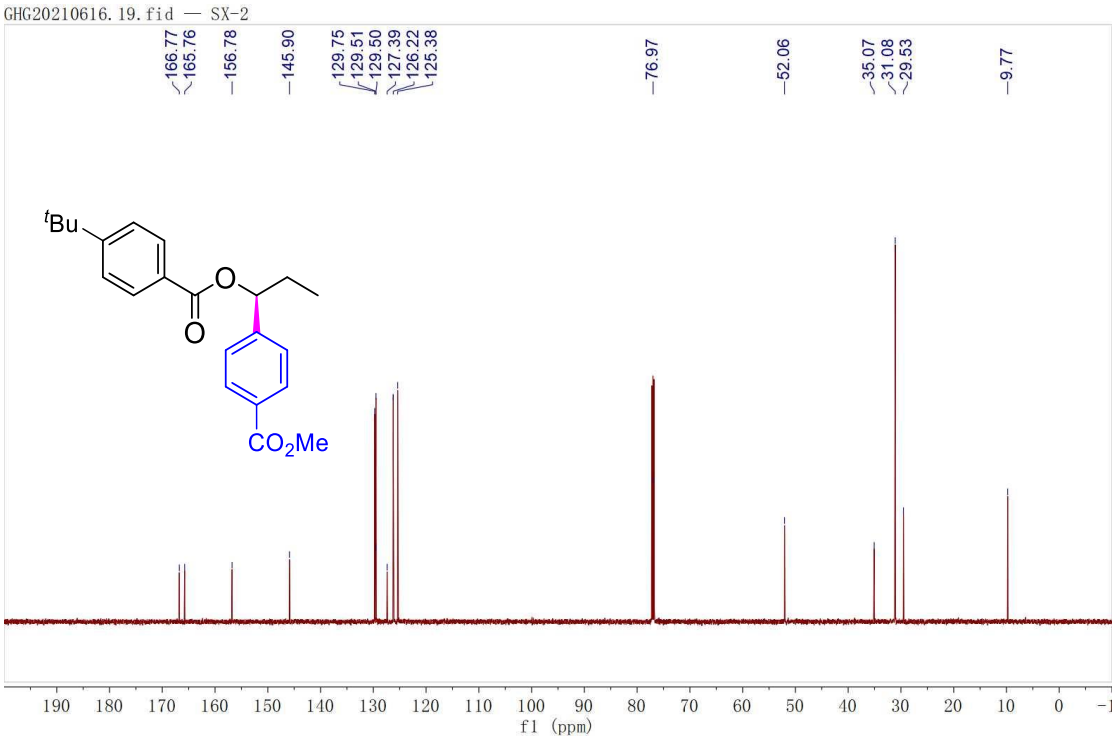
6, ^{19}F NMR (565 MHz, $CDCl_3$)



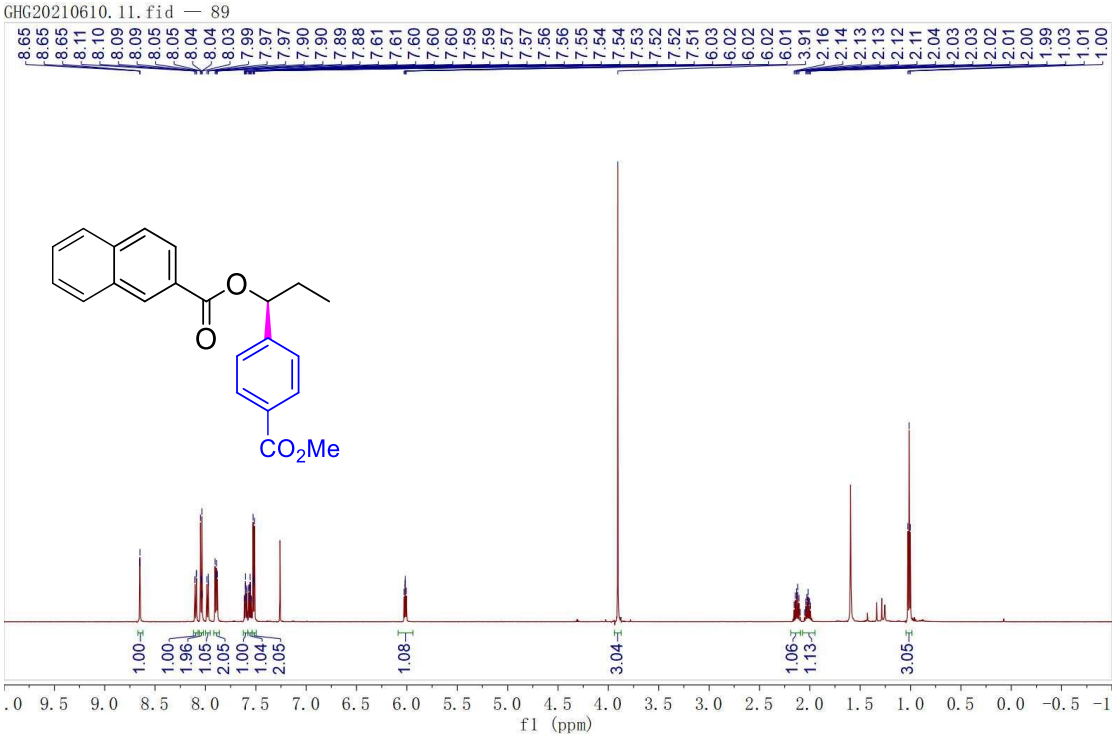
7, ^{1}H-NMR (600 MHZ, $CDCl_3$)



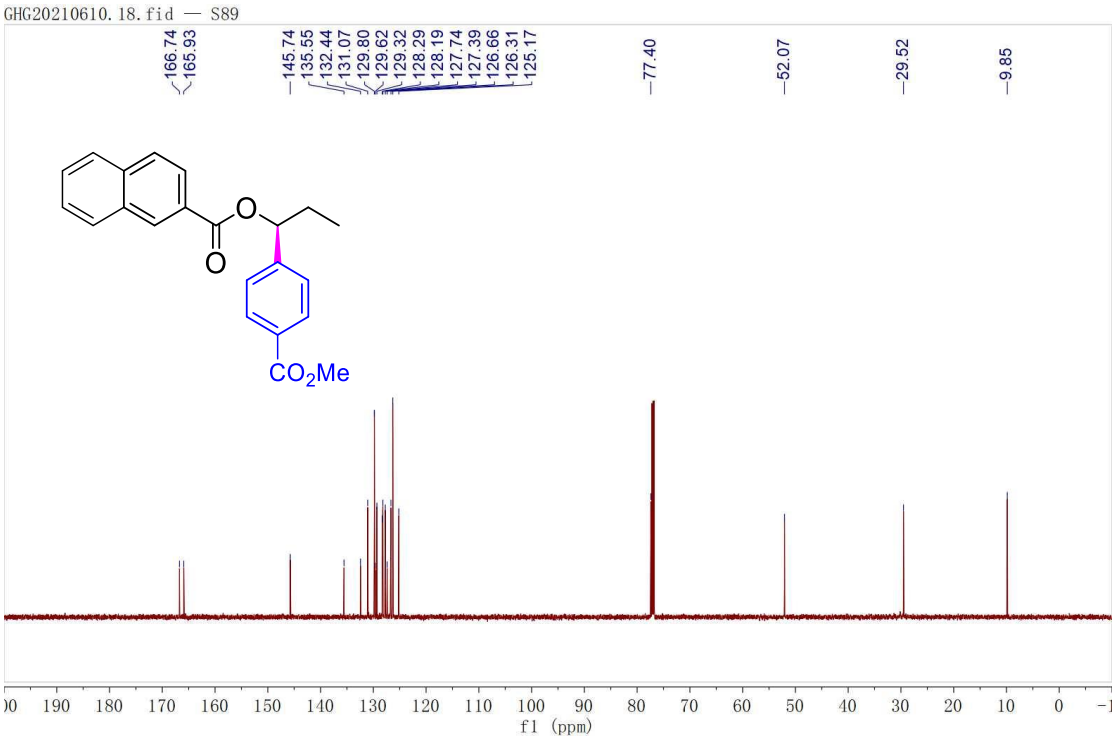
7, ^{13}C NMR (151 MHz, $CDCl_3$)



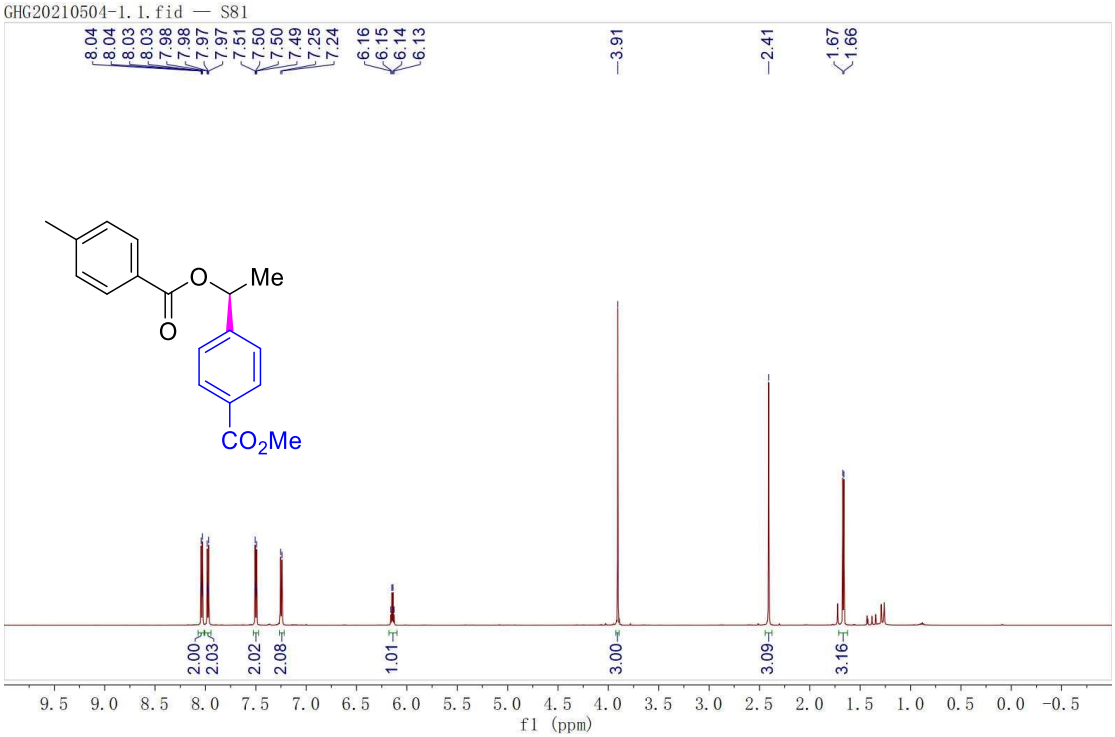
8, ^{1}H-NMR (600 MHZ, $CDCl_3$)



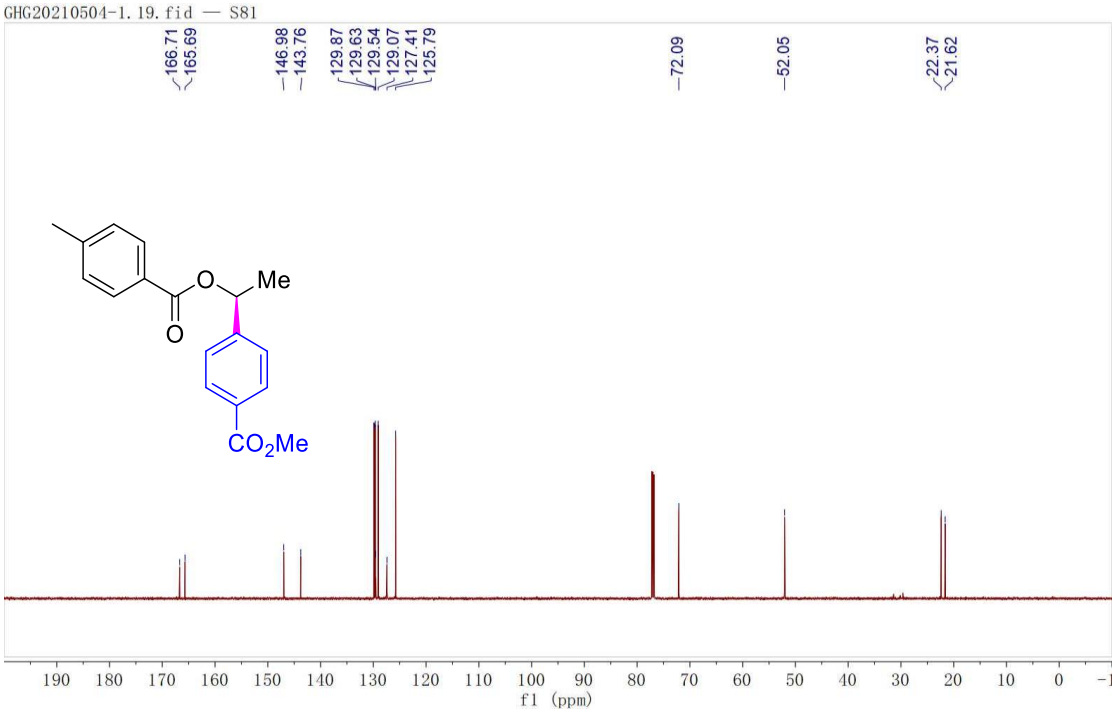
8, ^{13}C NMR (151 MHz, $CDCl_3$)



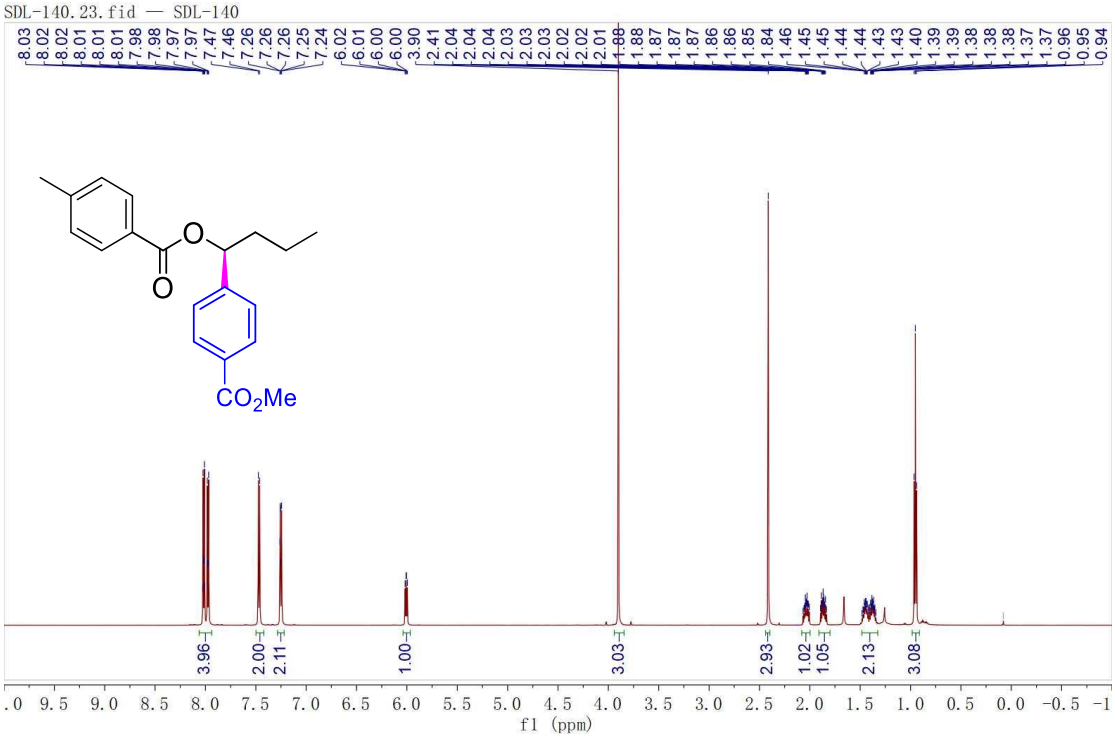
9, ^{1}H-NMR (600 MHZ, $CDCl_3$)



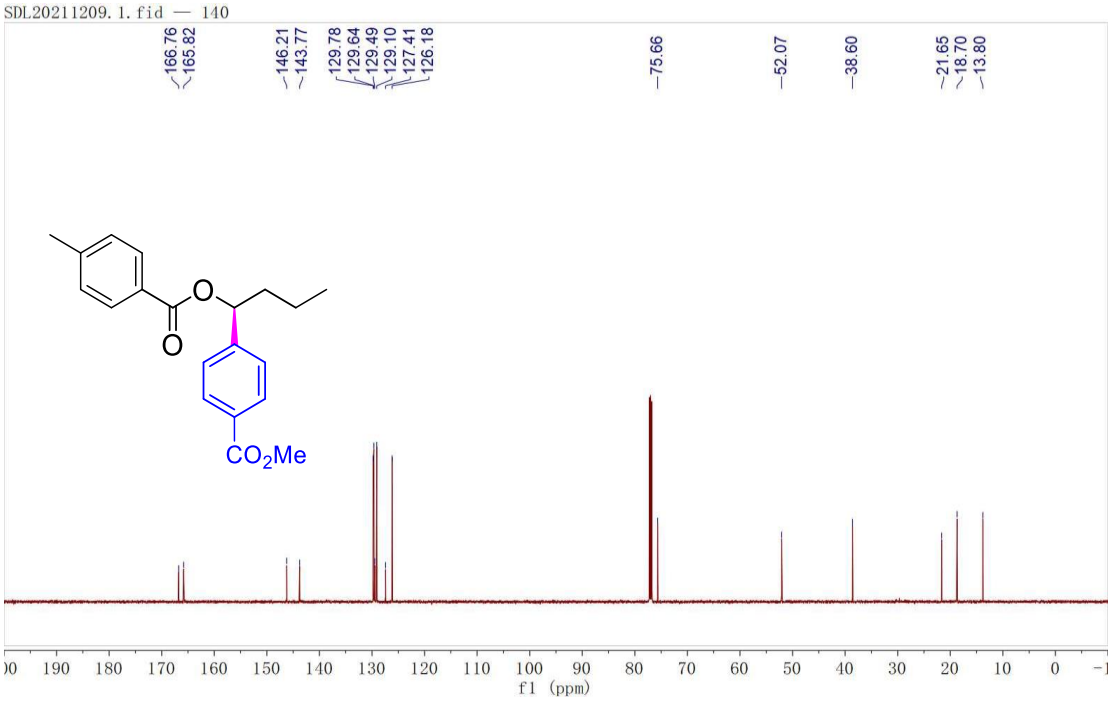
9, ^{13}C NMR (151 MHz, $CDCl_3$)



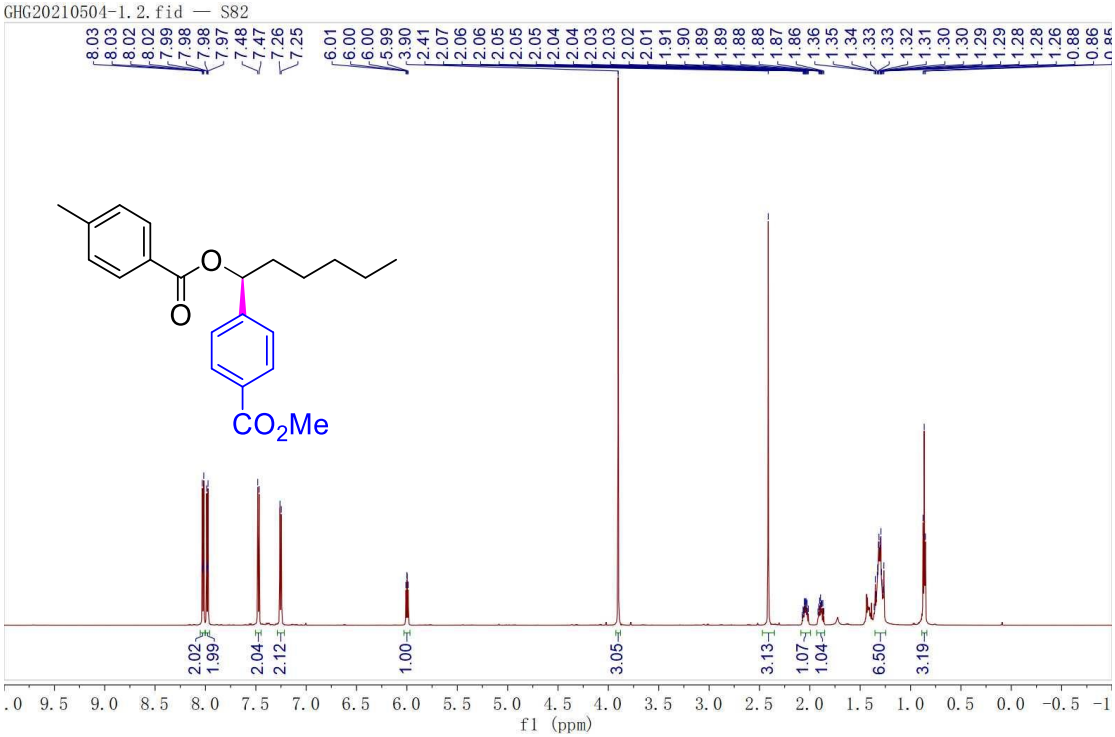
10, ^{1}H-NMR (600 MHZ, $CDCl_3$)



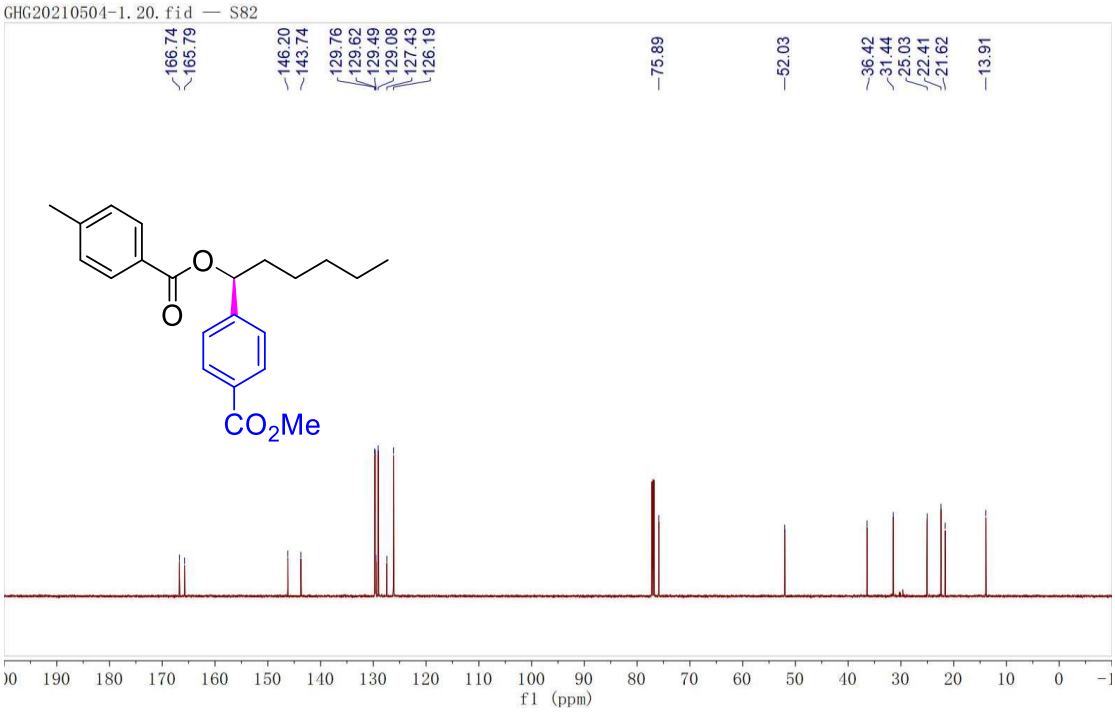
10, ^{13}C NMR (151 MHz, $CDCl_3$)



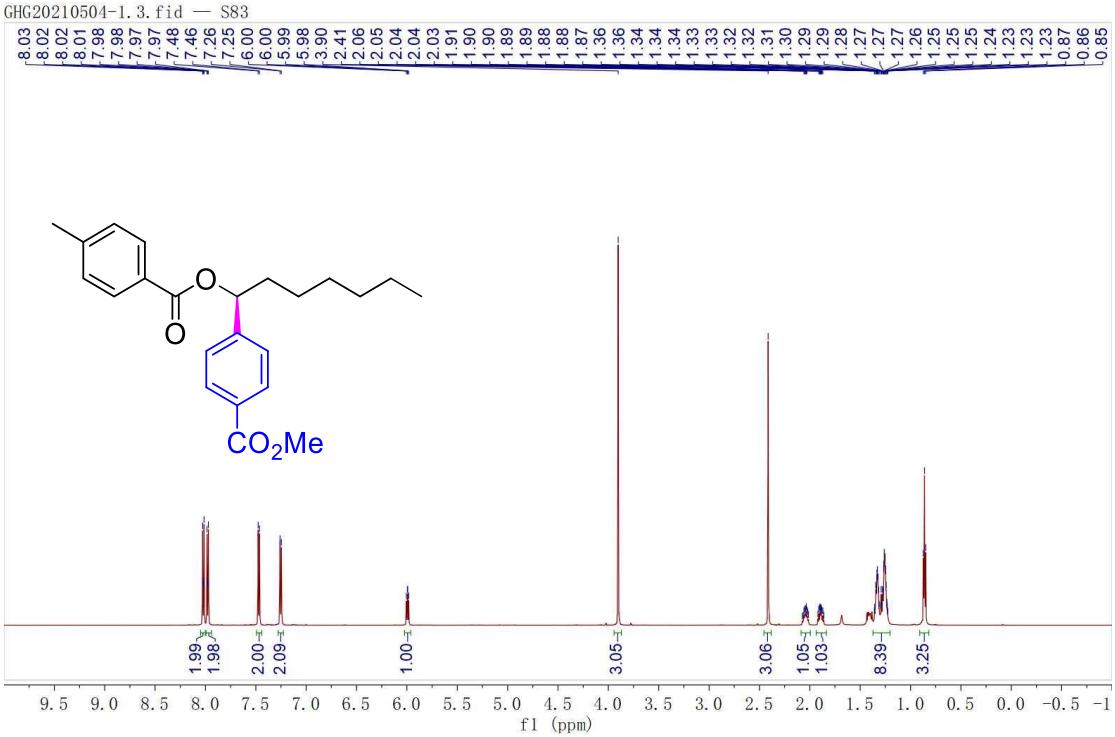
11, ^{1}H-NMR (600 MHZ, $CDCl_3$)



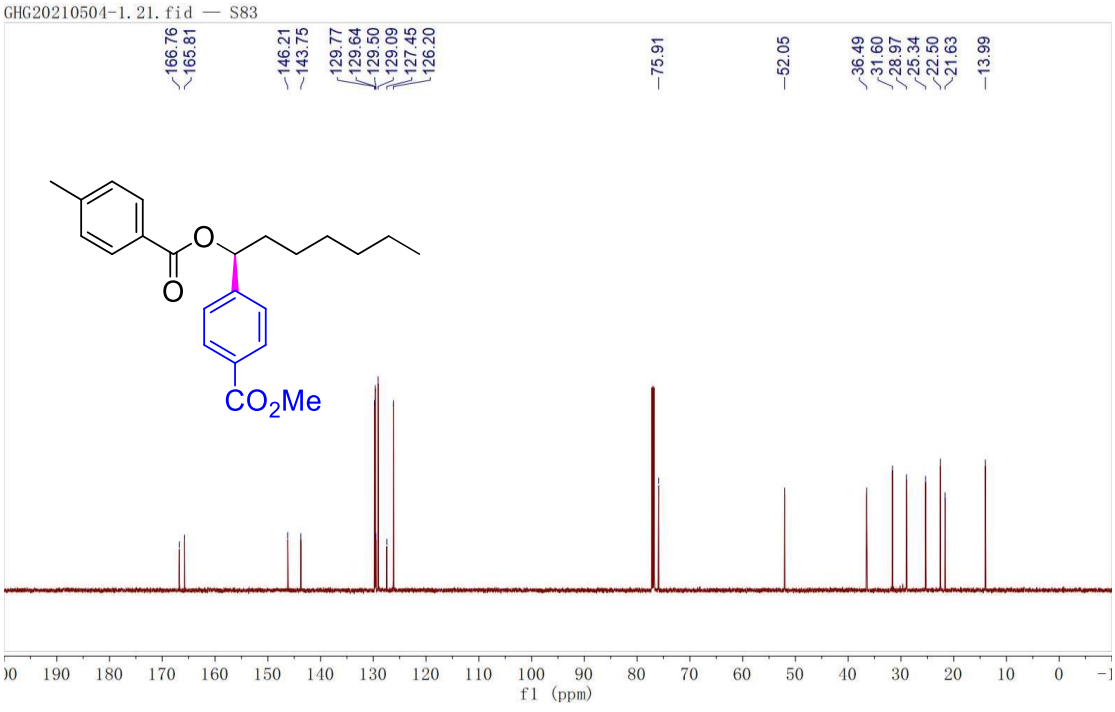
11, ^{13}C NMR (151 MHz, $CDCl_3$)



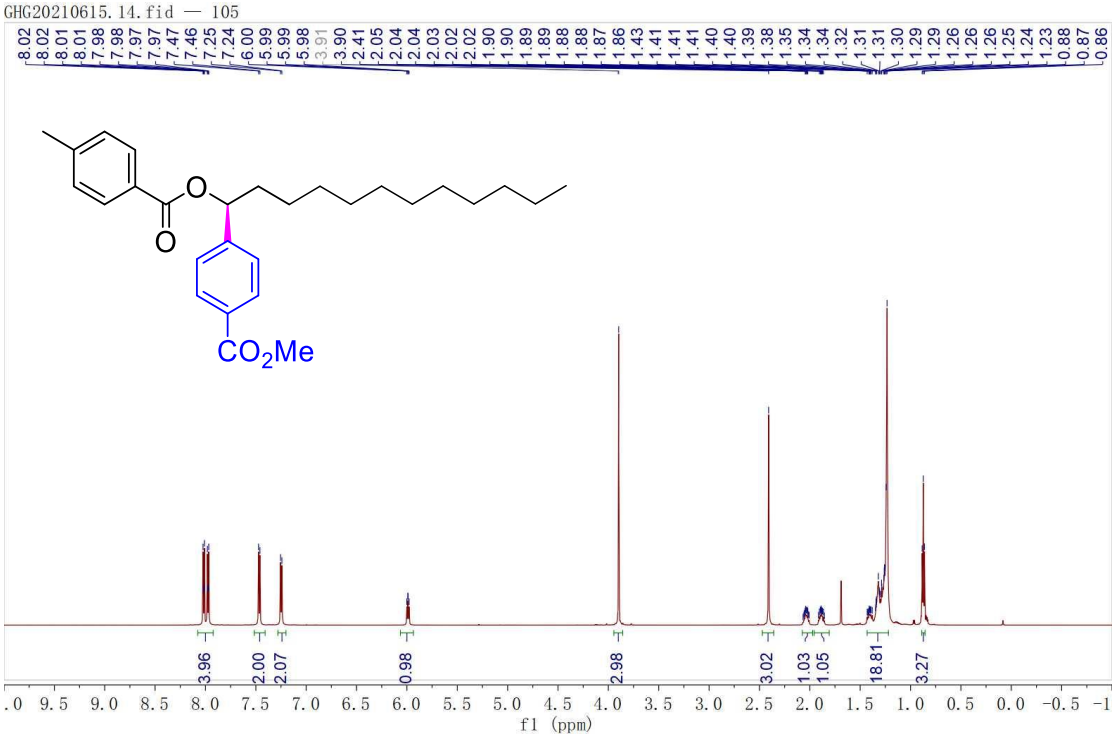
12, ^{1}H-NMR (600 MHZ, $CDCl_3$)



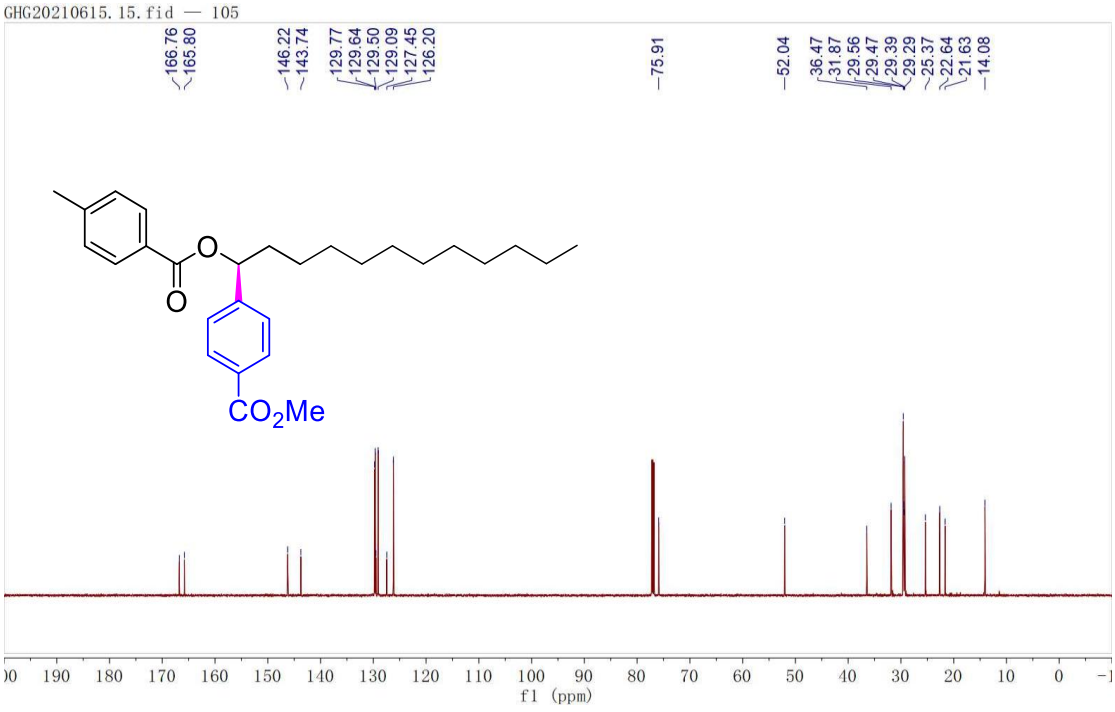
12, ^{13}C NMR (151 MHz, $CDCl_3$)



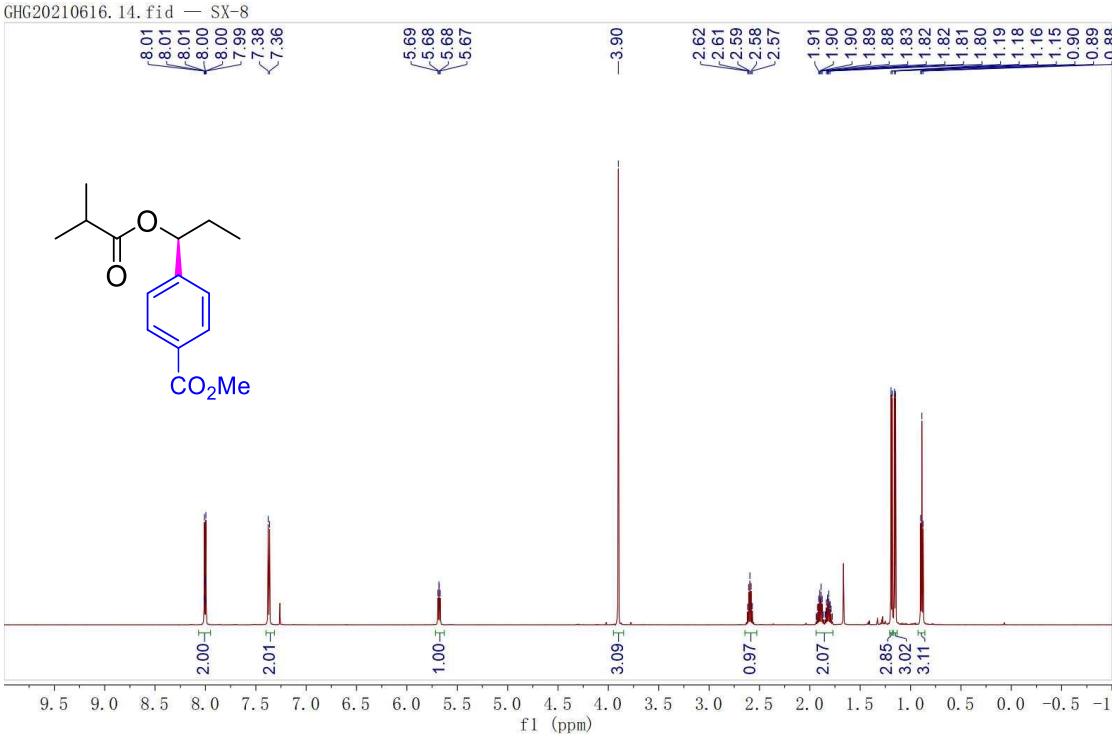
13, ^{1}H-NMR (600 MHZ, $CDCl_3$)



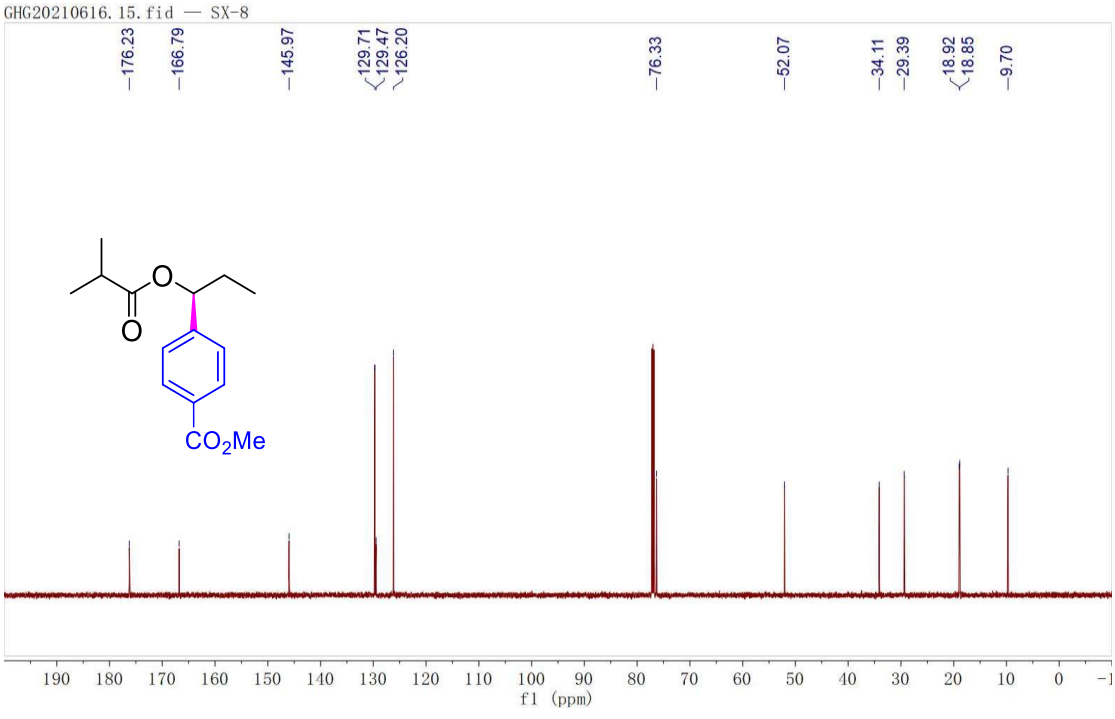
13, ^{13}C NMR (151 MHz, $CDCl_3$)



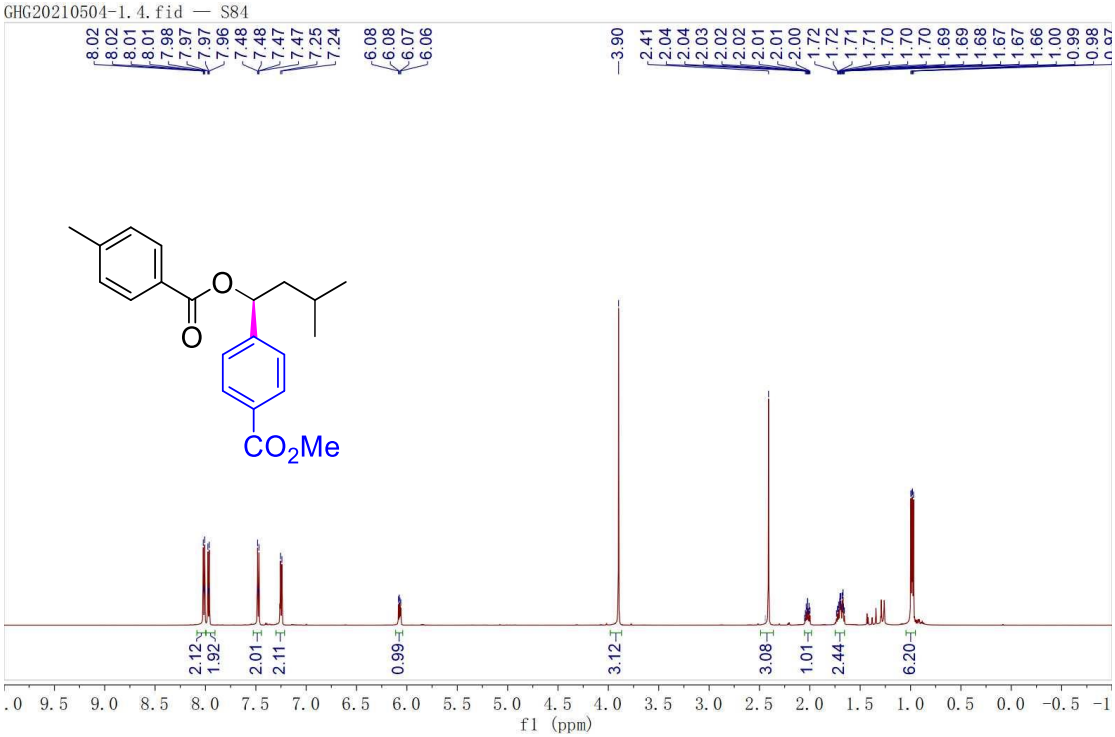
14, ^{1}H-NMR (600 MHZ, $CDCl_3$)



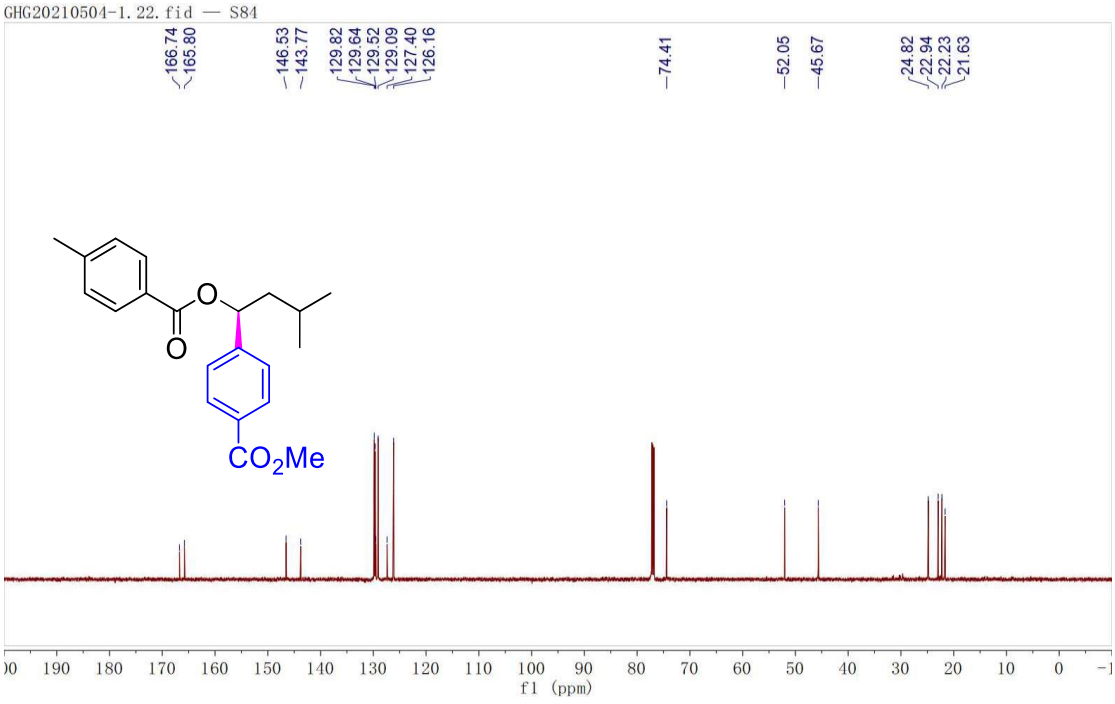
14, ^{13}C NMR (151 MHz, $CDCl_3$)



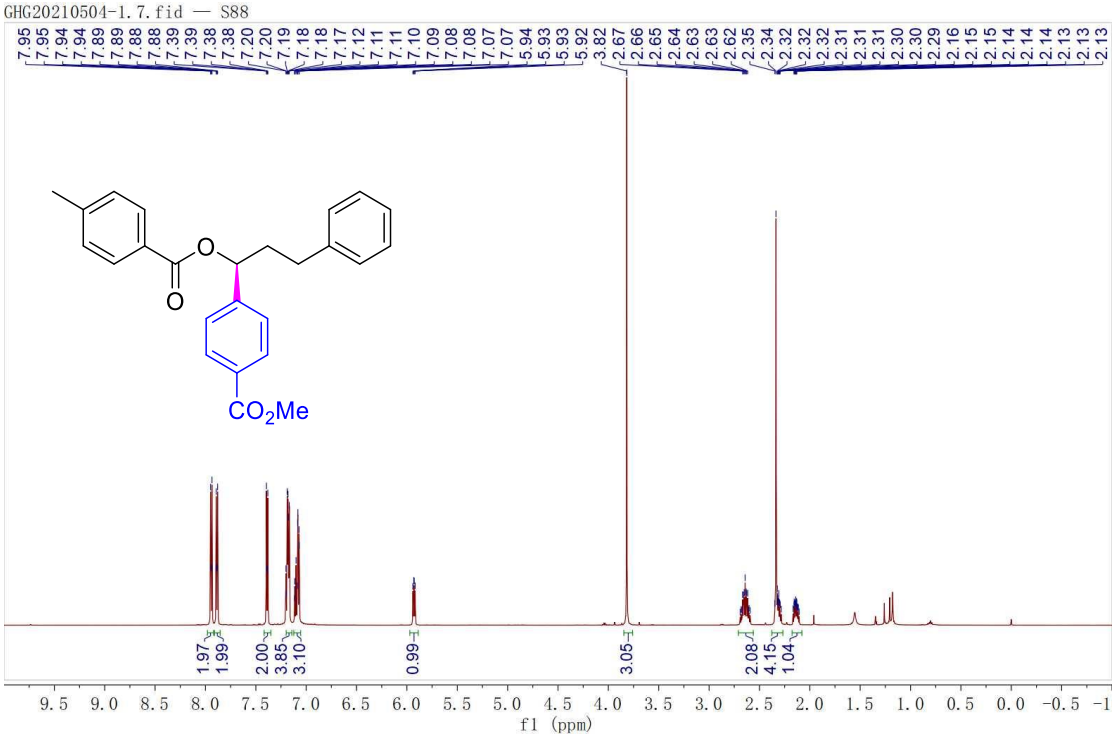
15, ^{1}H-NMR (600 MHZ, $CDCl_3$)



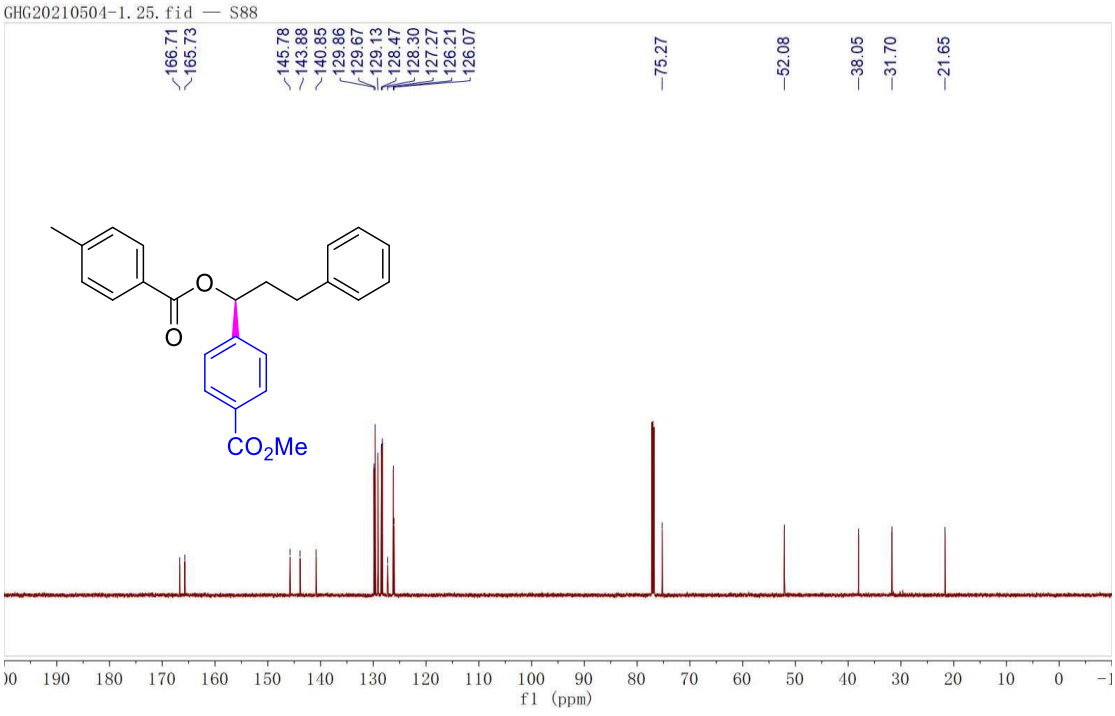
15, ^{13}C NMR (151 MHz, $CDCl_3$)



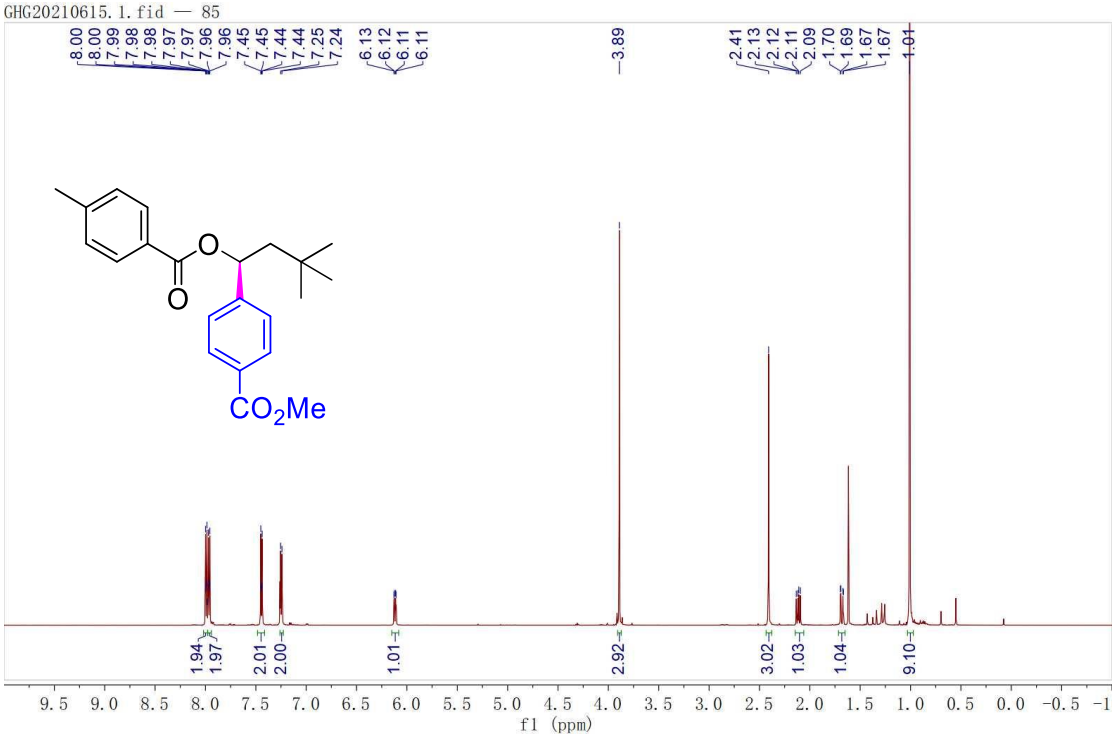
16, ^{1}H-NMR (600 MHZ, $CDCl_3$)



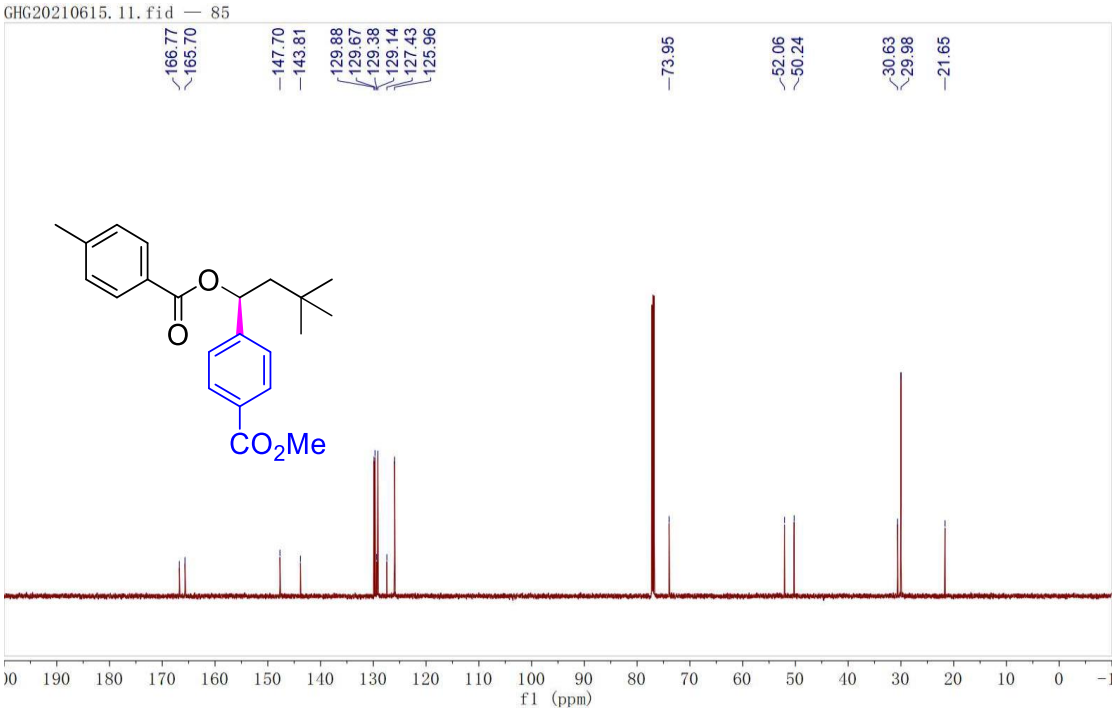
16, ^{13}C NMR (151 MHz, $CDCl_3$)



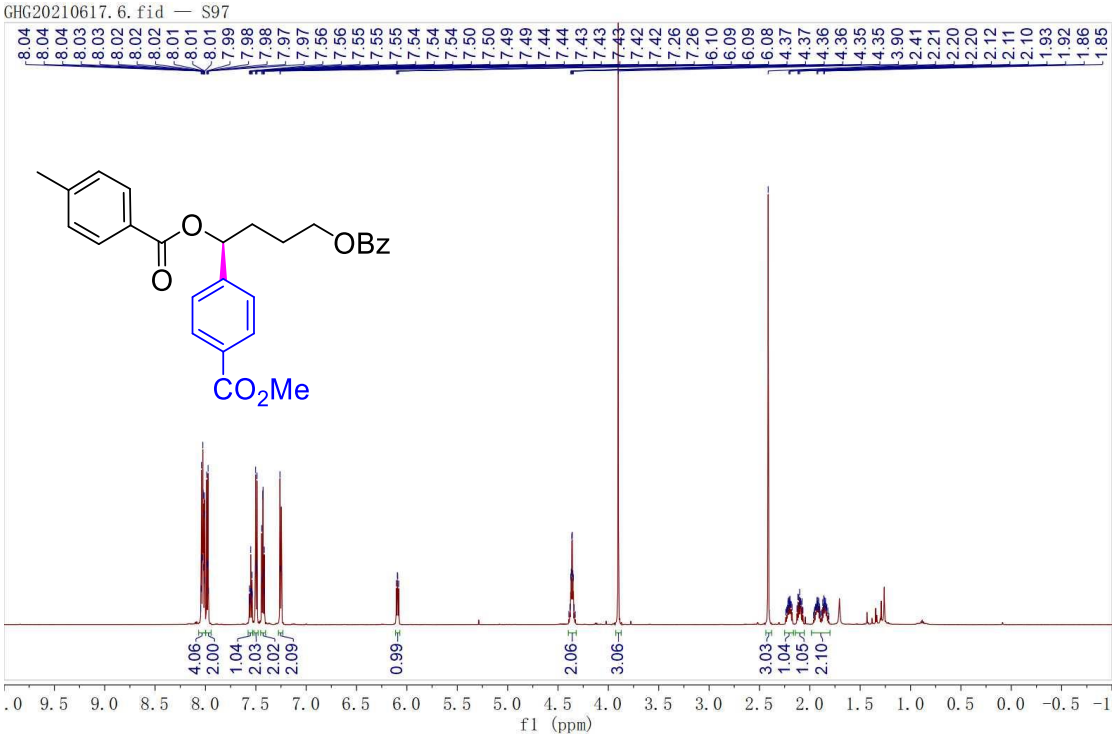
17, ^{1}H-NMR (600 MHZ, $CDCl_3$)



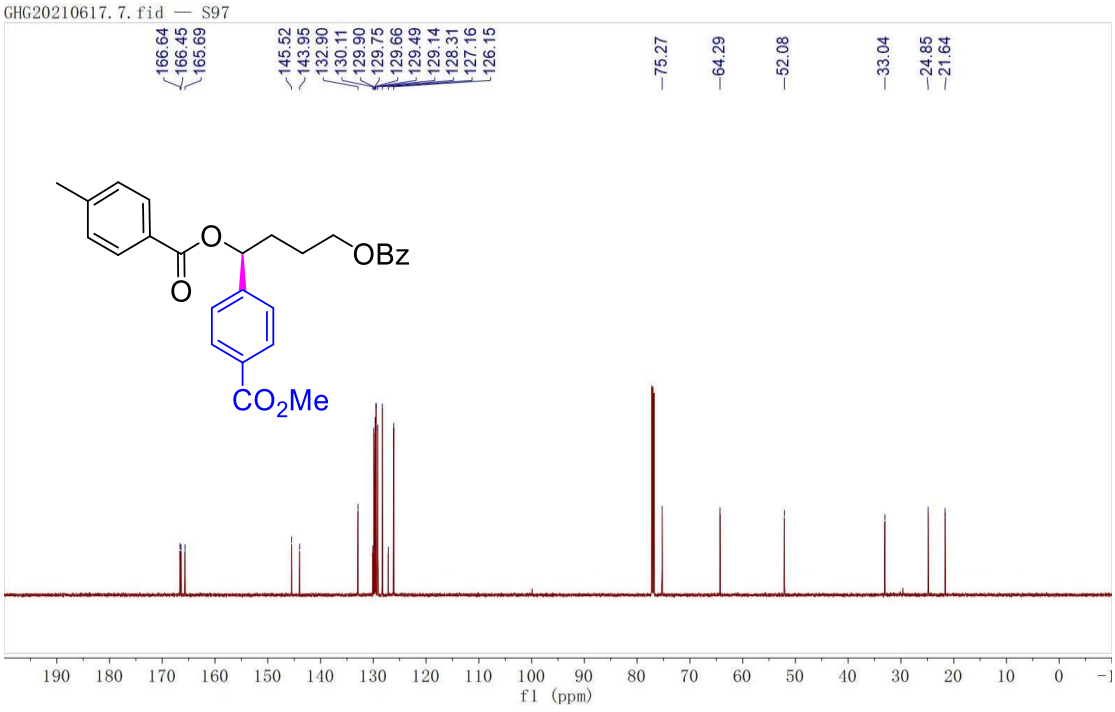
17, ^{13}C NMR (151 MHz, $CDCl_3$)



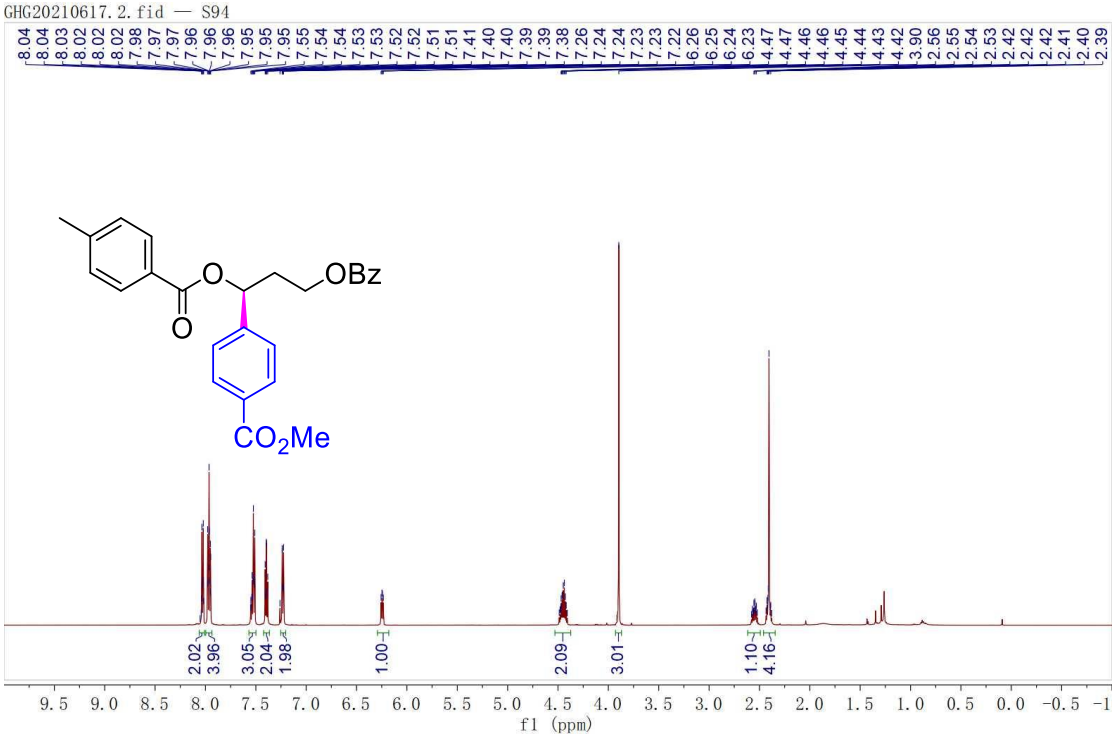
18, ^{1}H-NMR (600 MHZ, $CDCl_3$)



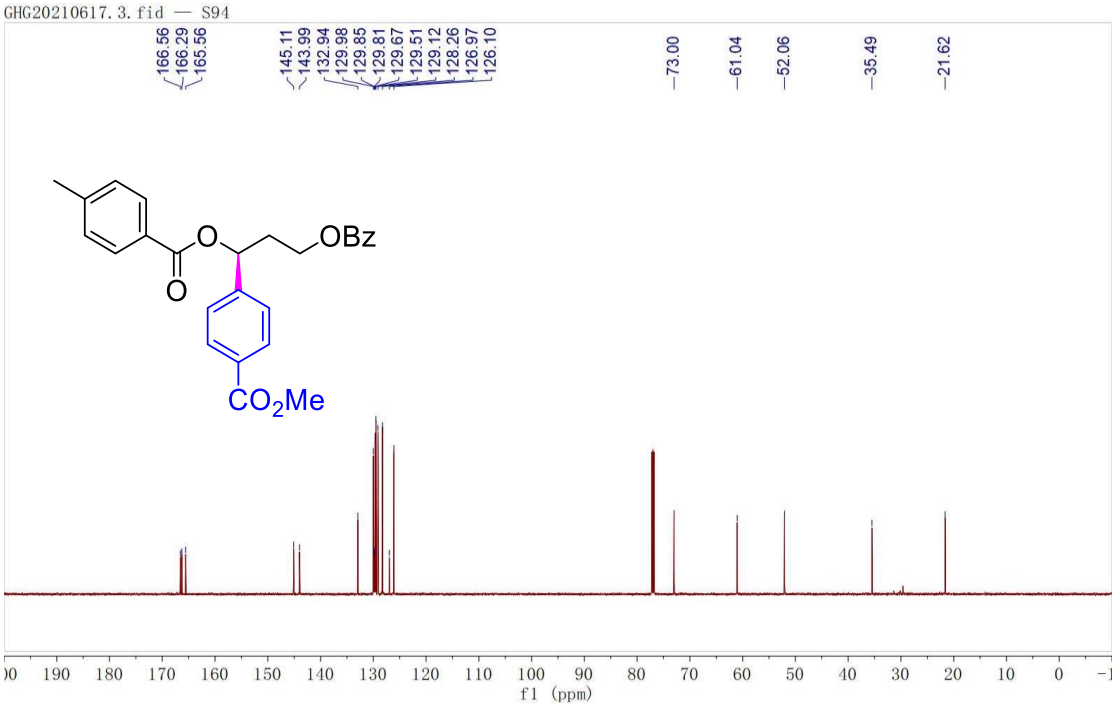
18, ^{13}C NMR (151 MHz, $CDCl_3$)



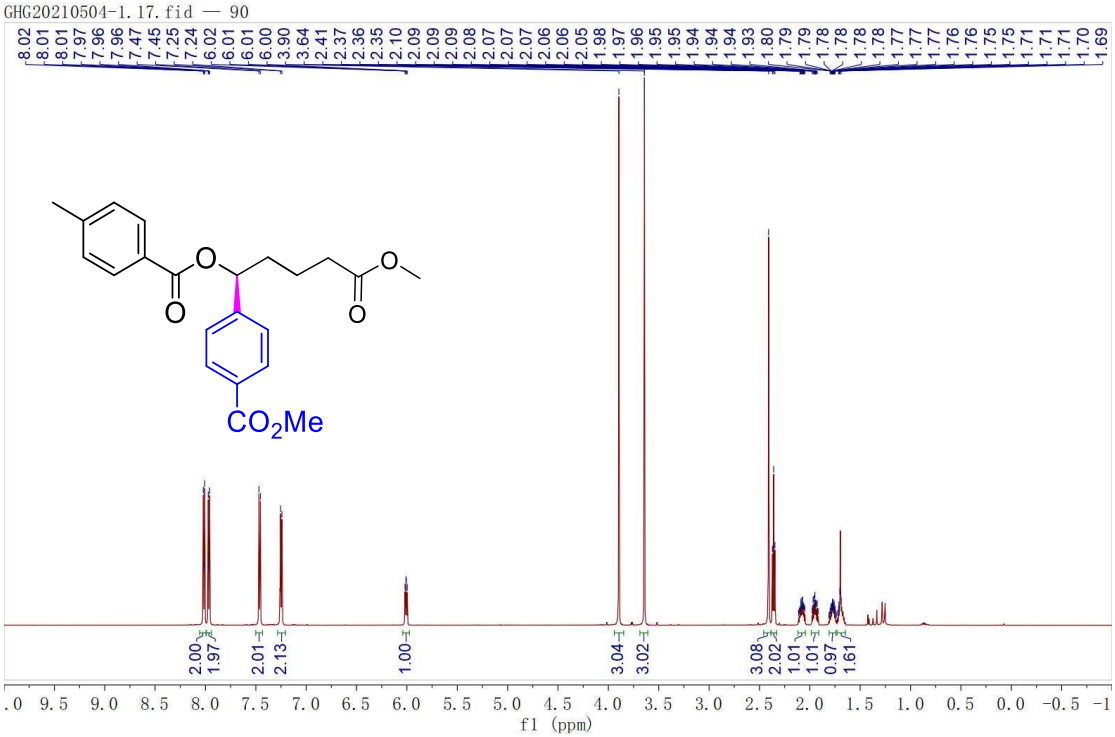
19, ^{1}H-NMR (600 MHZ, $CDCl_3$)



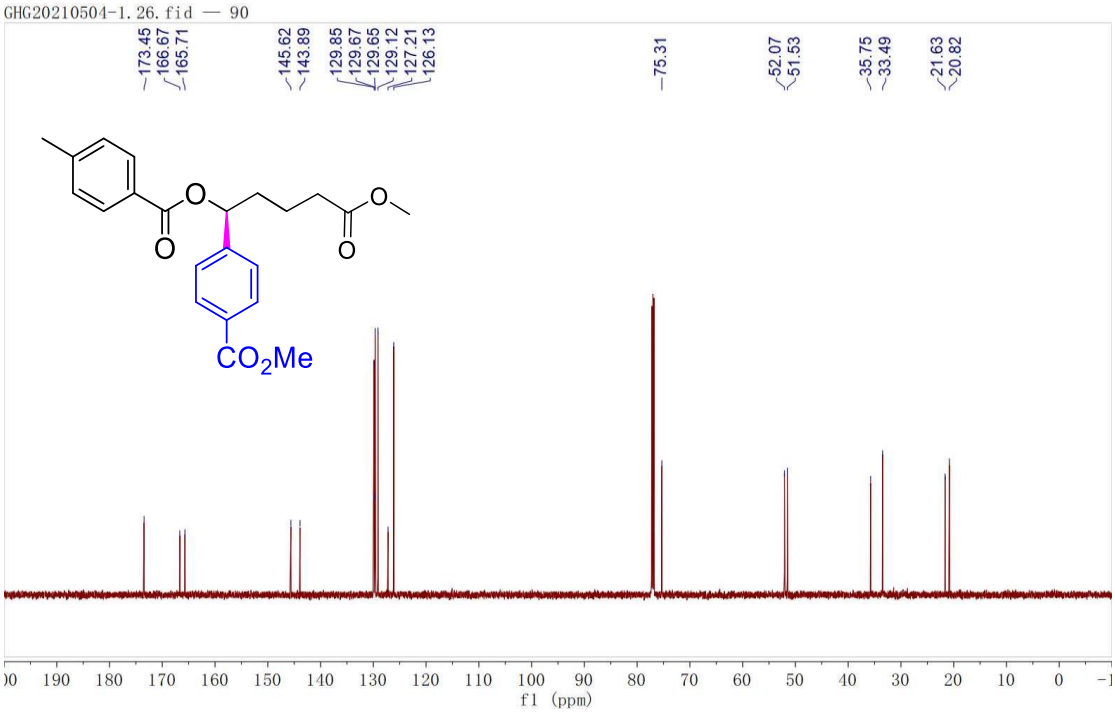
19, ^{13}C NMR (151 MHz, $CDCl_3$)



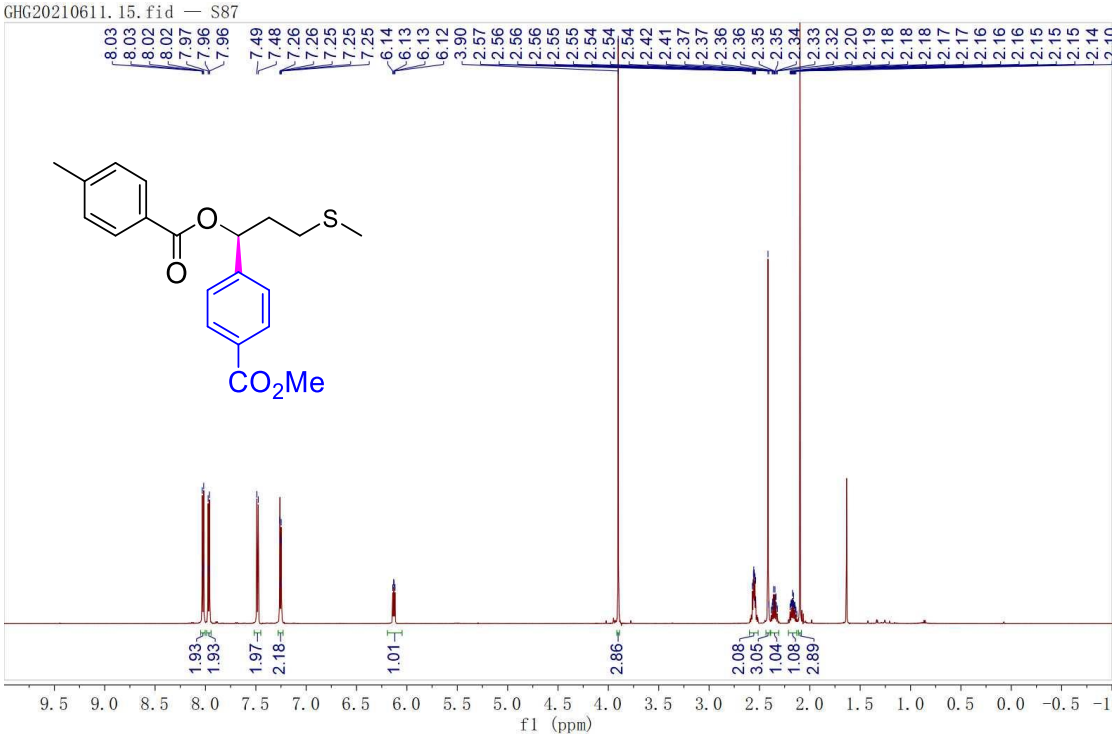
20, ^{1}H-NMR (600 MHZ, $CDCl_3$)



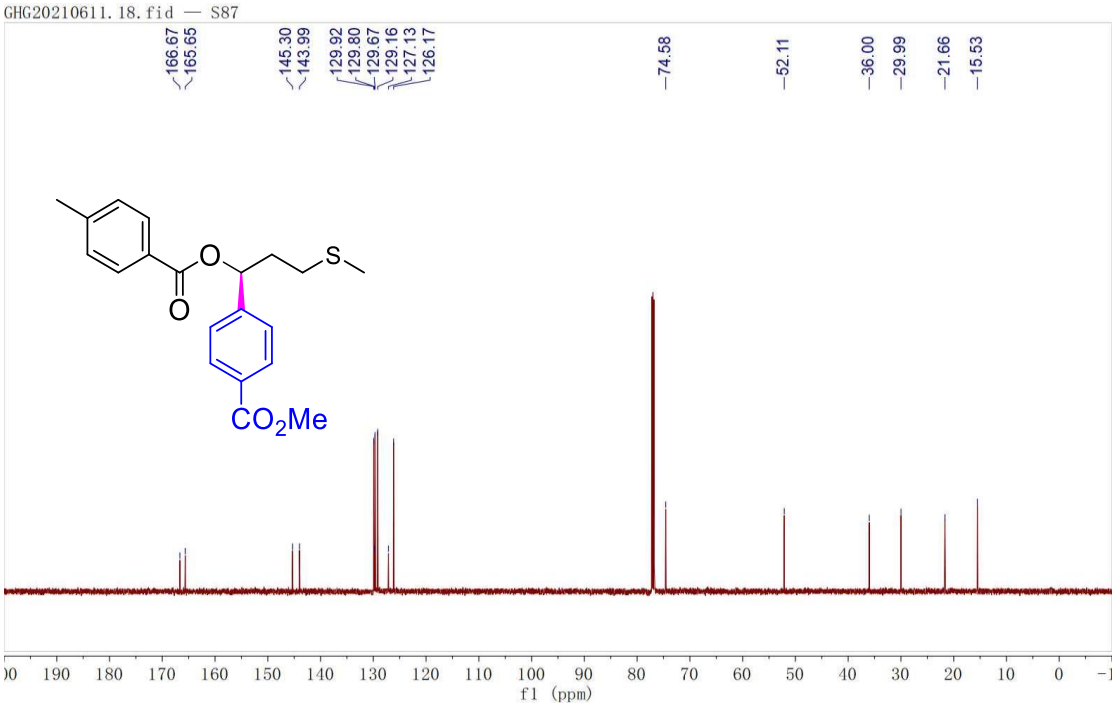
20, ^{13}C NMR (151 MHz, $CDCl_3$)



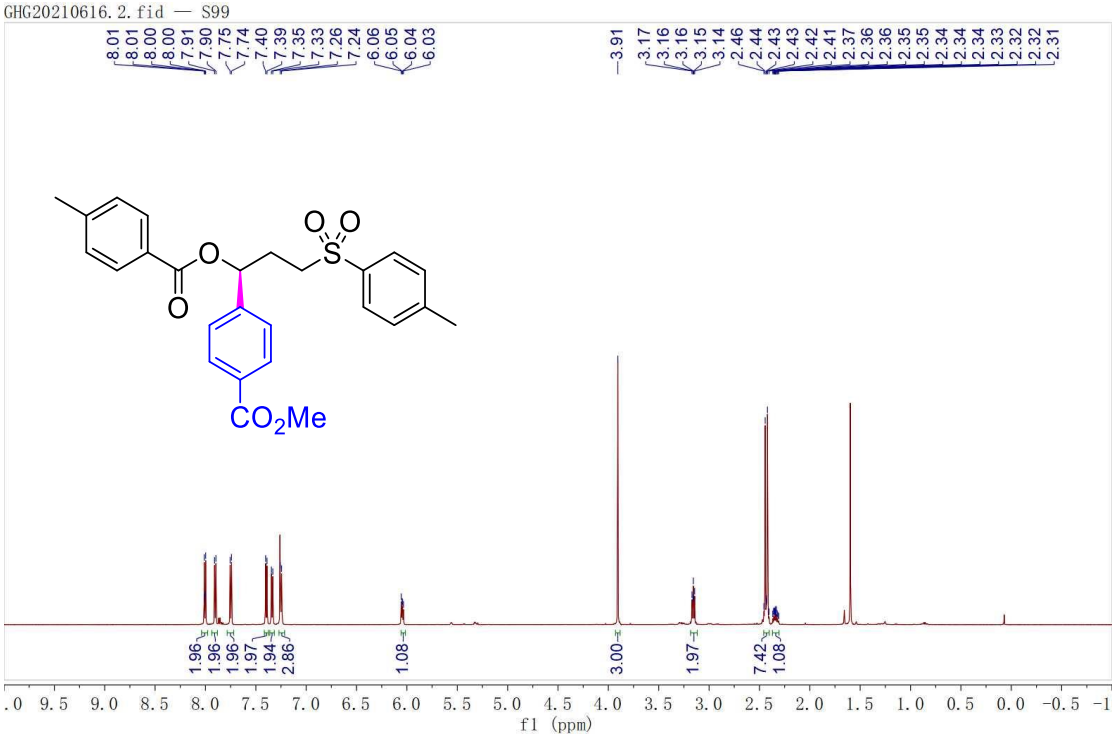
21, ^{1}H-NMR (600 MHZ, $CDCl_3$)



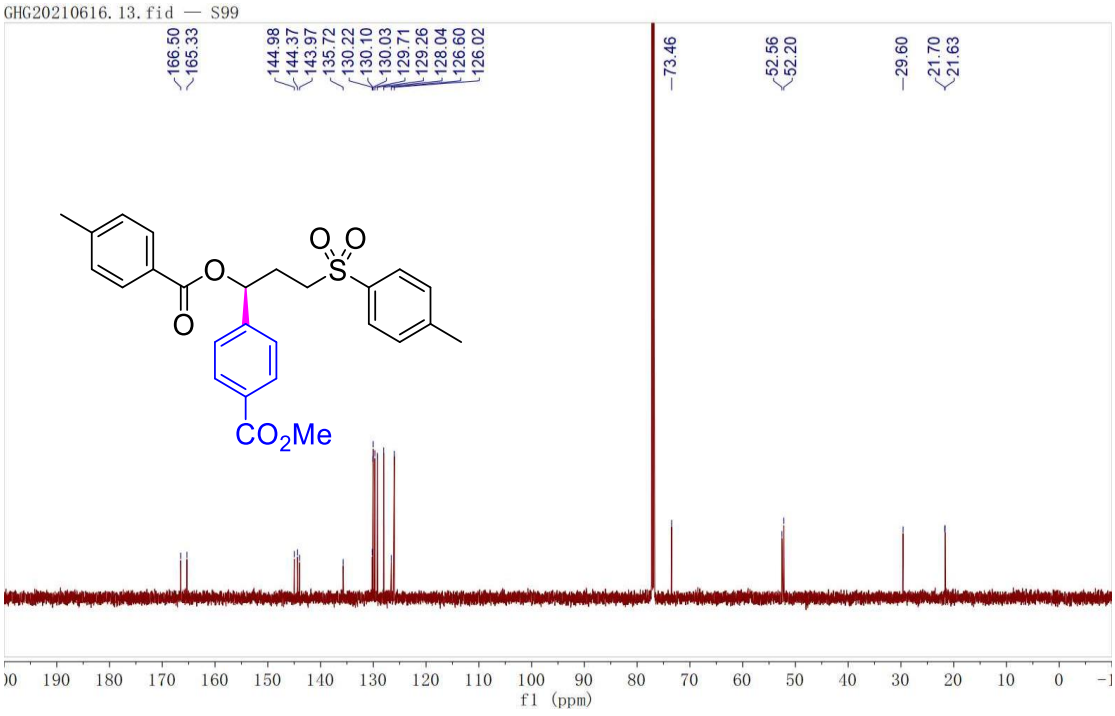
21, ^{13}C NMR (151 MHz, $CDCl_3$)



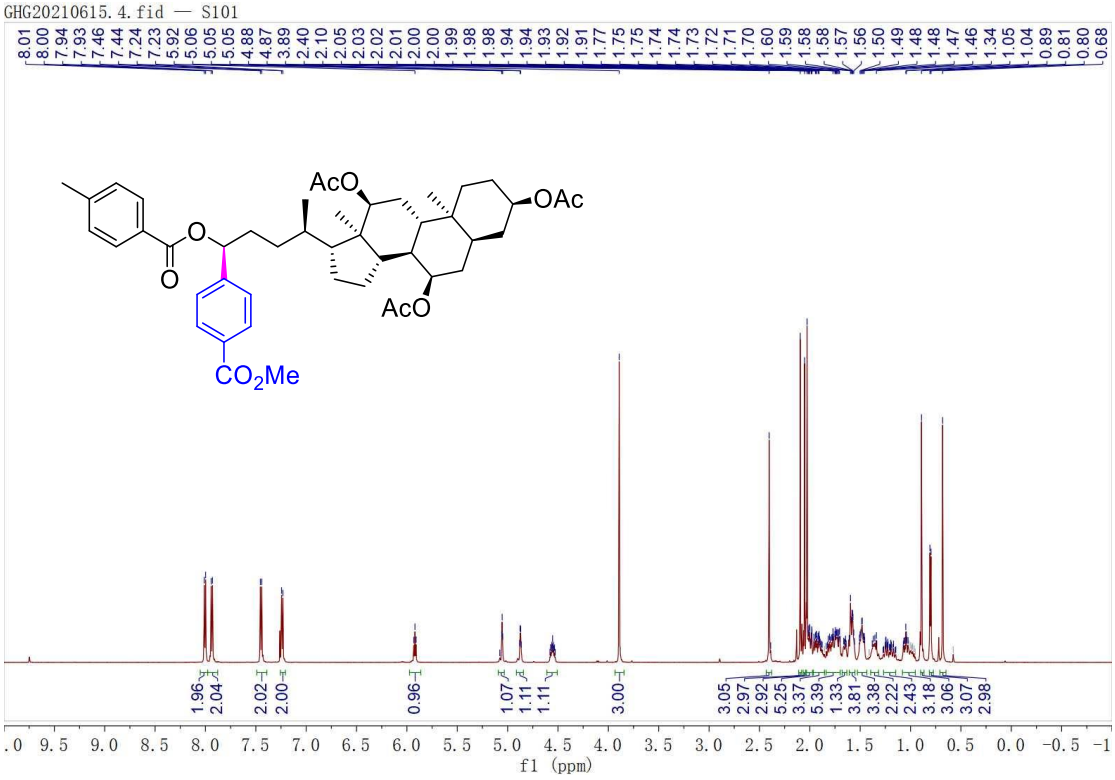
22, ^{1}H-NMR (600 MHZ, $CDCl_3$)



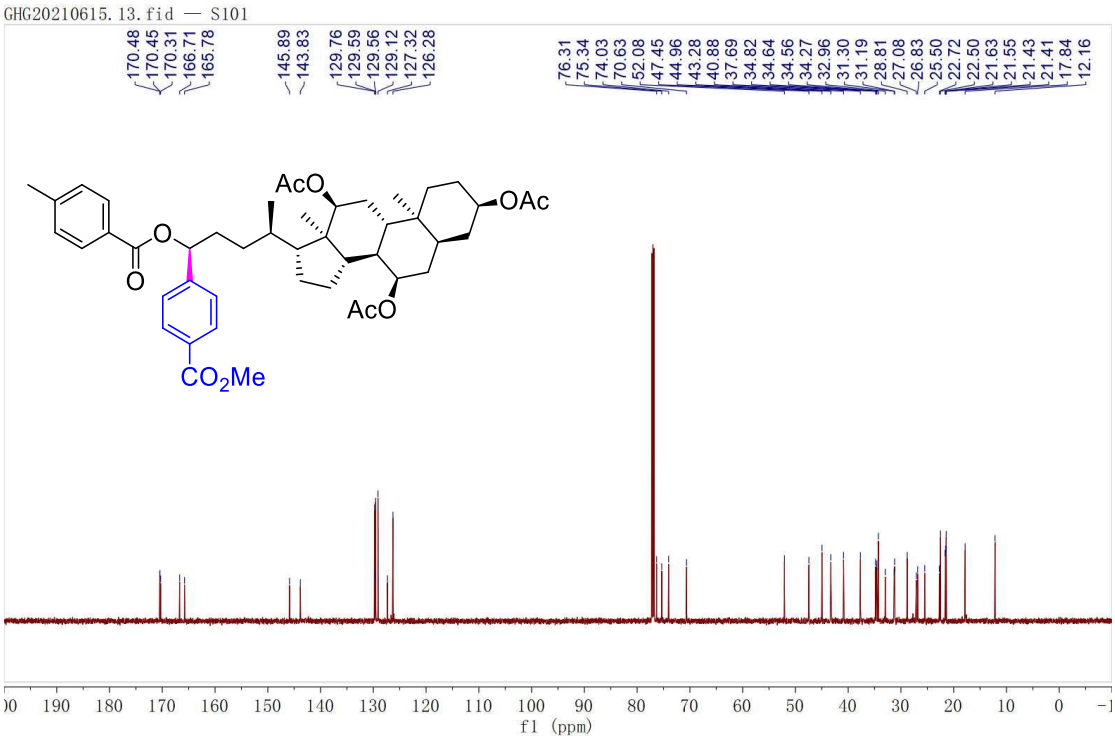
22, ^{13}C NMR (151 MHz, $CDCl_3$)



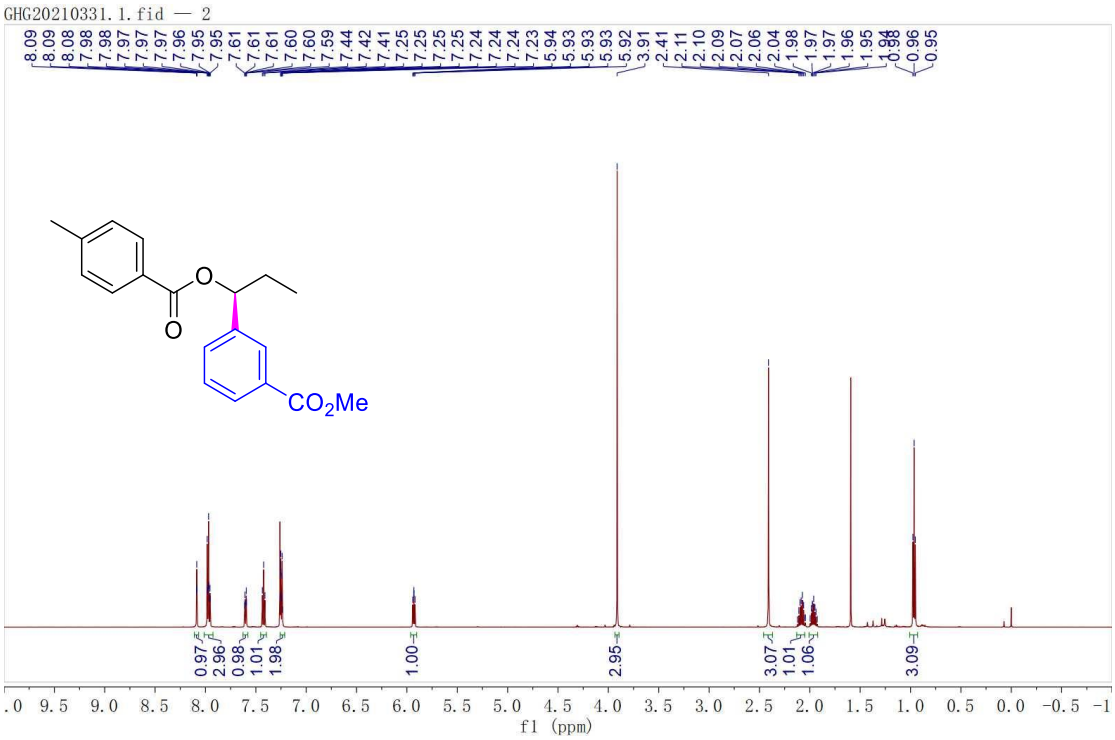
23, ^{1}H-NMR (600 MHZ, $CDCl_3$)



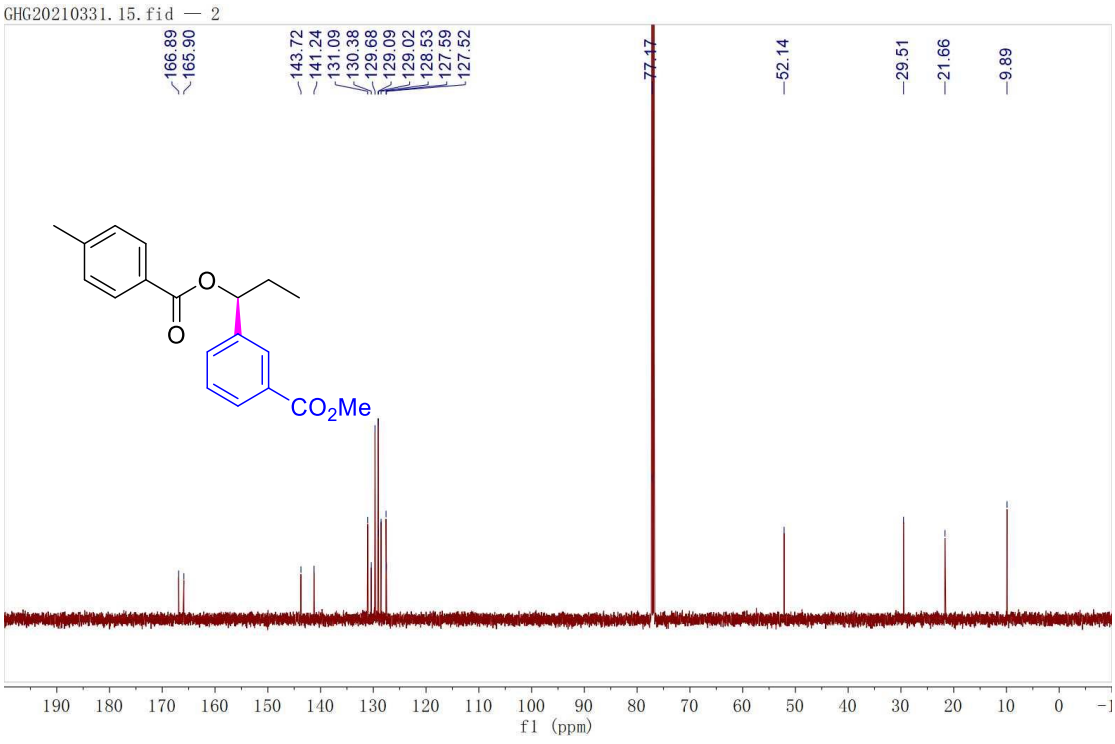
23, ^{13}C NMR (151 MHz, $CDCl_3$)



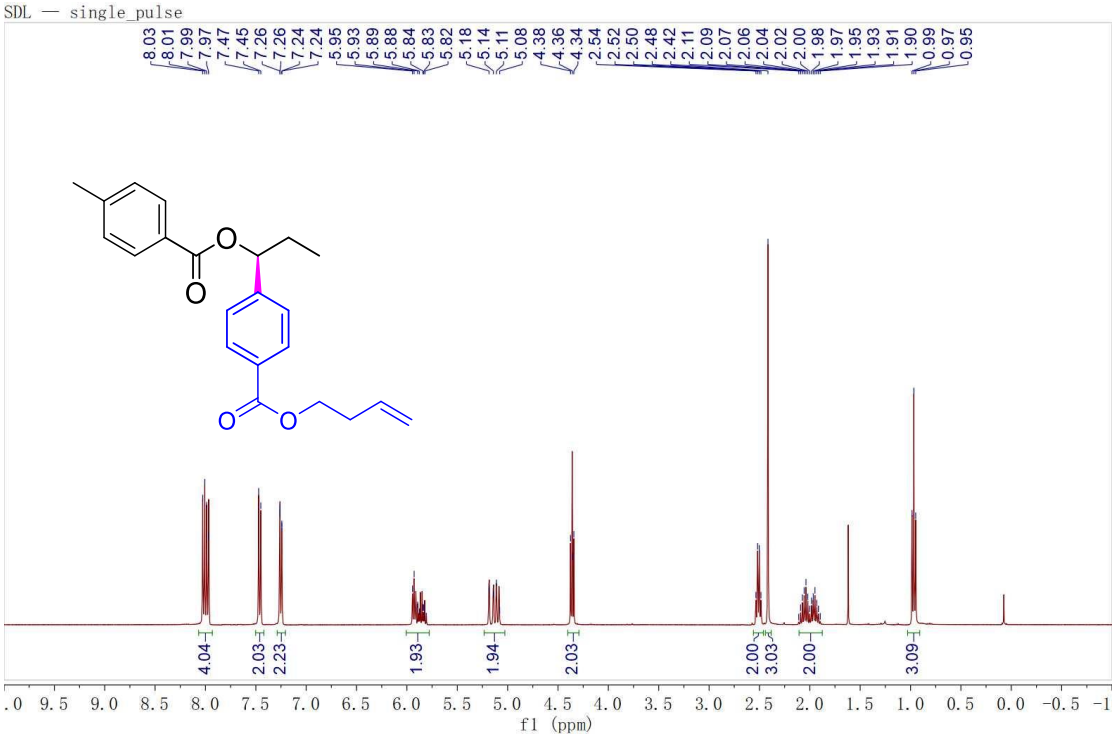
24, ^{1}H-NMR (600 MHZ, $CDCl_3$)



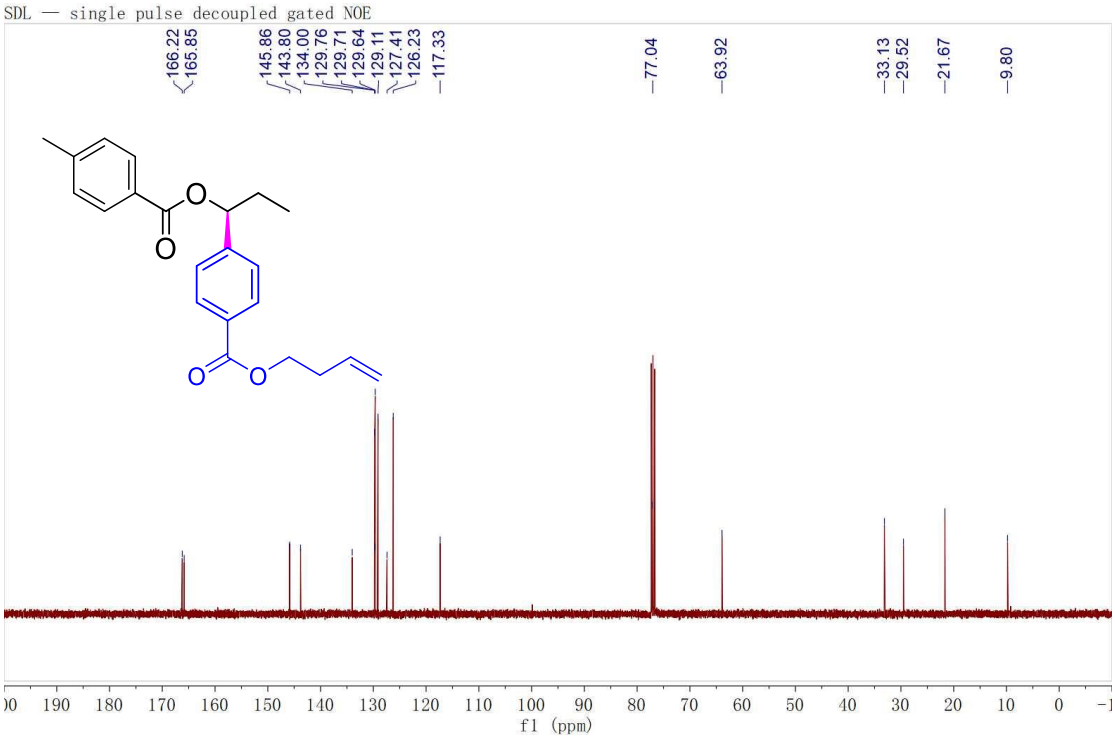
24, ^{13}C NMR (151 MHz, $CDCl_3$)



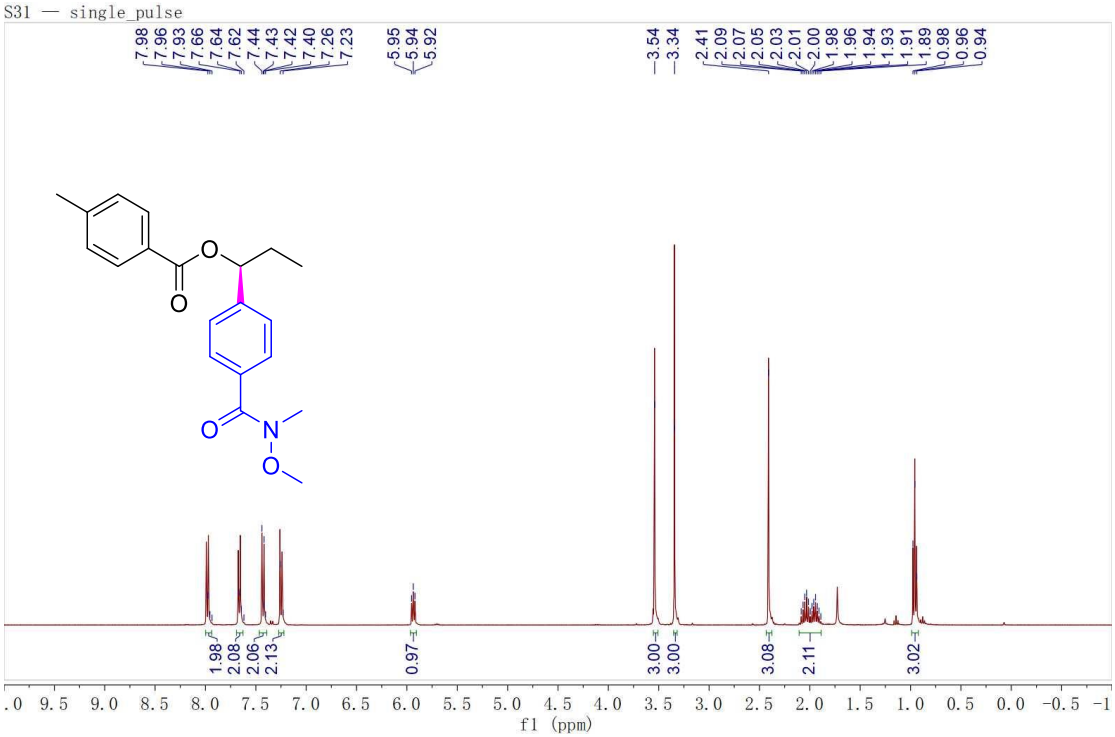
25, ^{1}H-NMR (400 MHZ, $CDCl_3$)



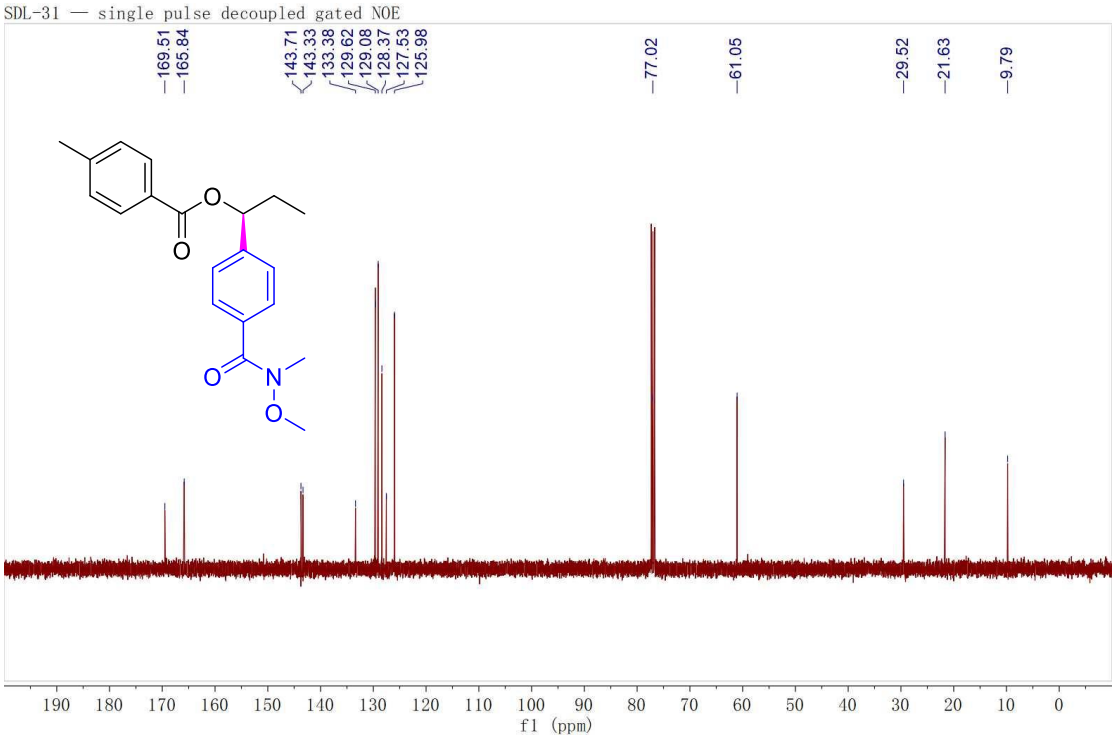
25, ^{13}C NMR (101 MHz, $CDCl_3$)



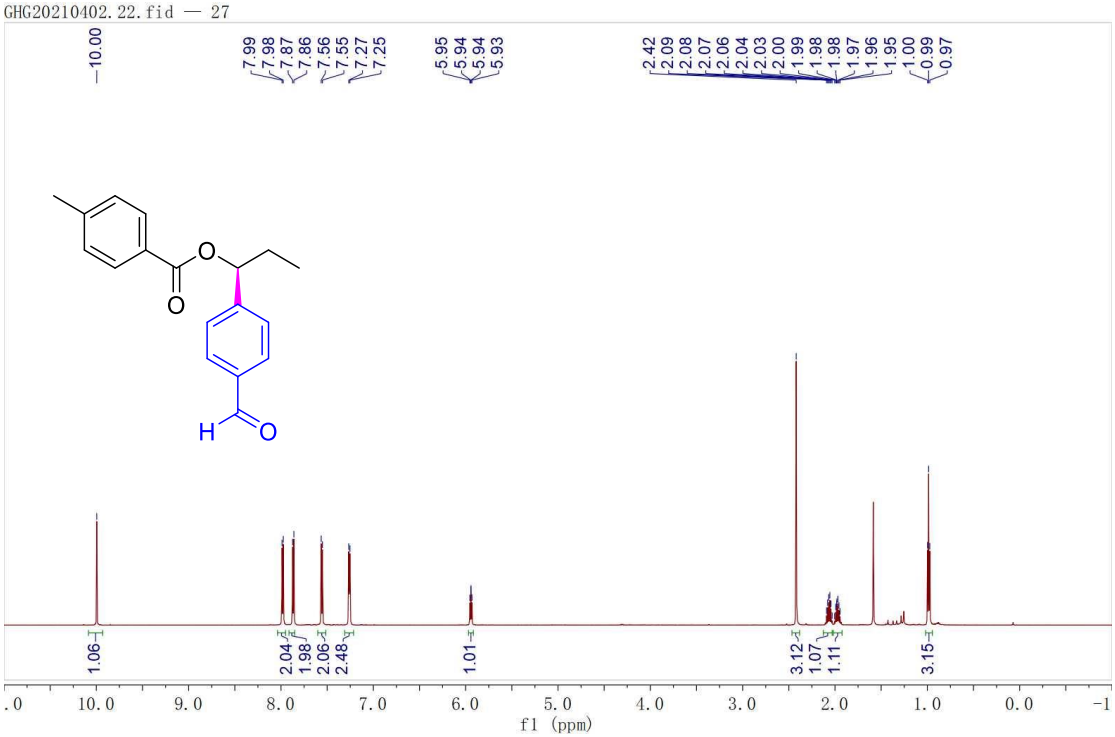
26, ^{1}H-NMR (400 MHZ, $CDCl_3$)



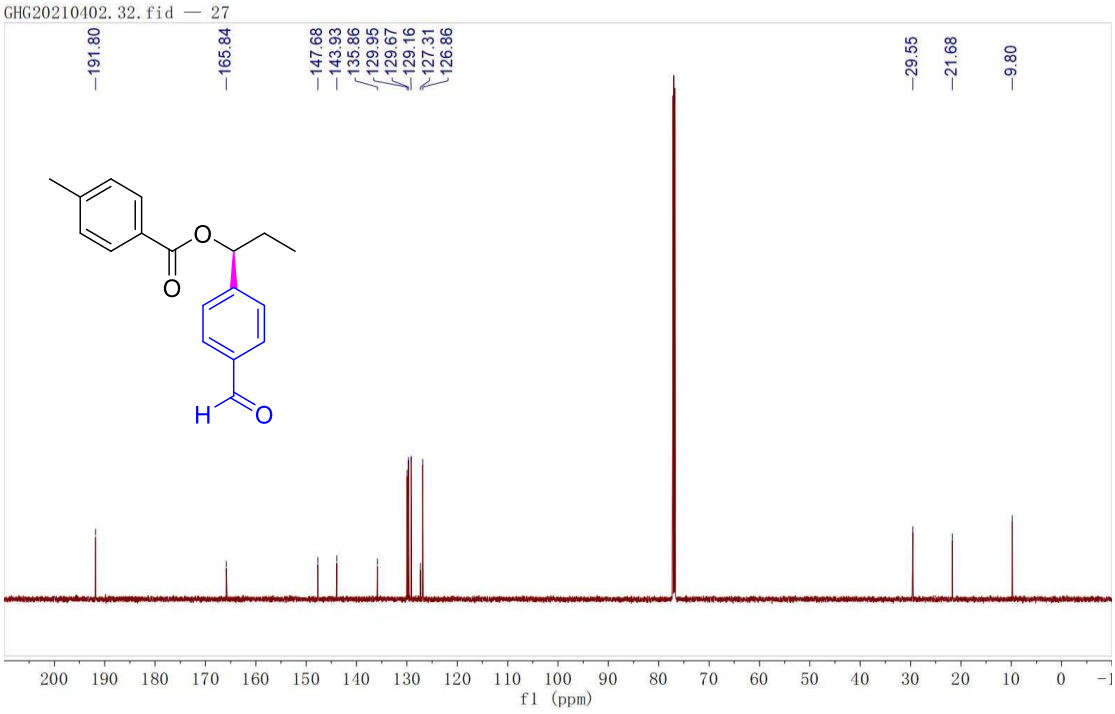
26, ^{13}C NMR (101 MHz, $CDCl_3$)



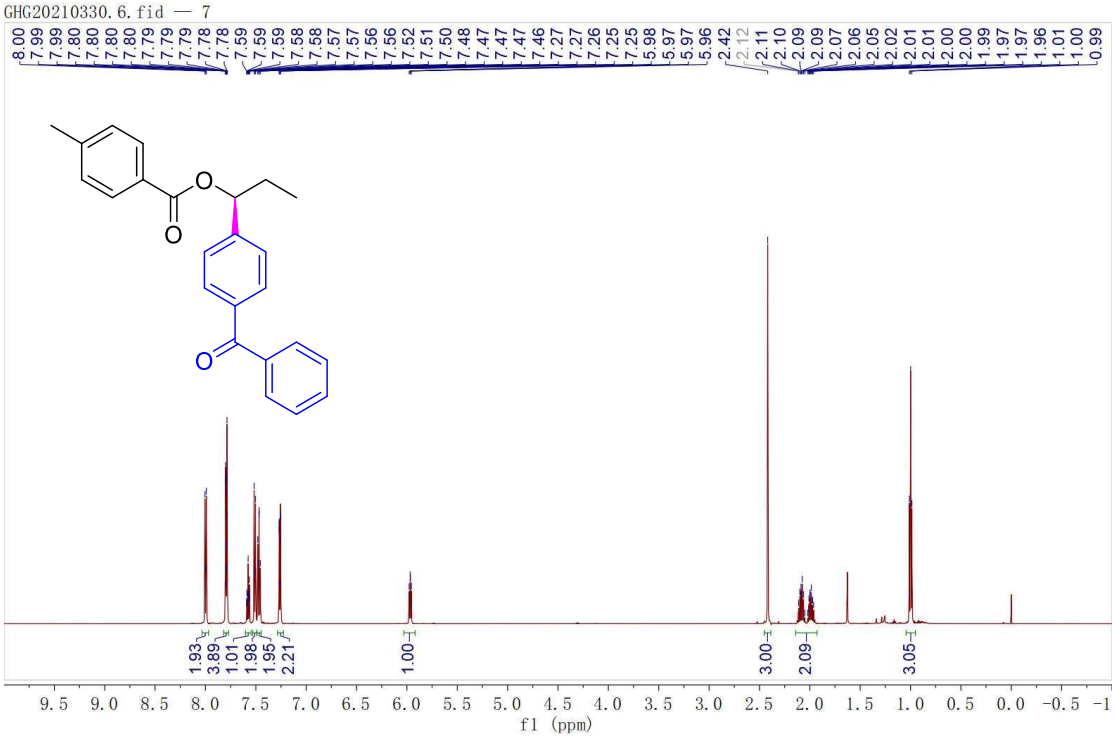
27, ^{1}H-NMR (600 MHZ, $CDCl_3$)



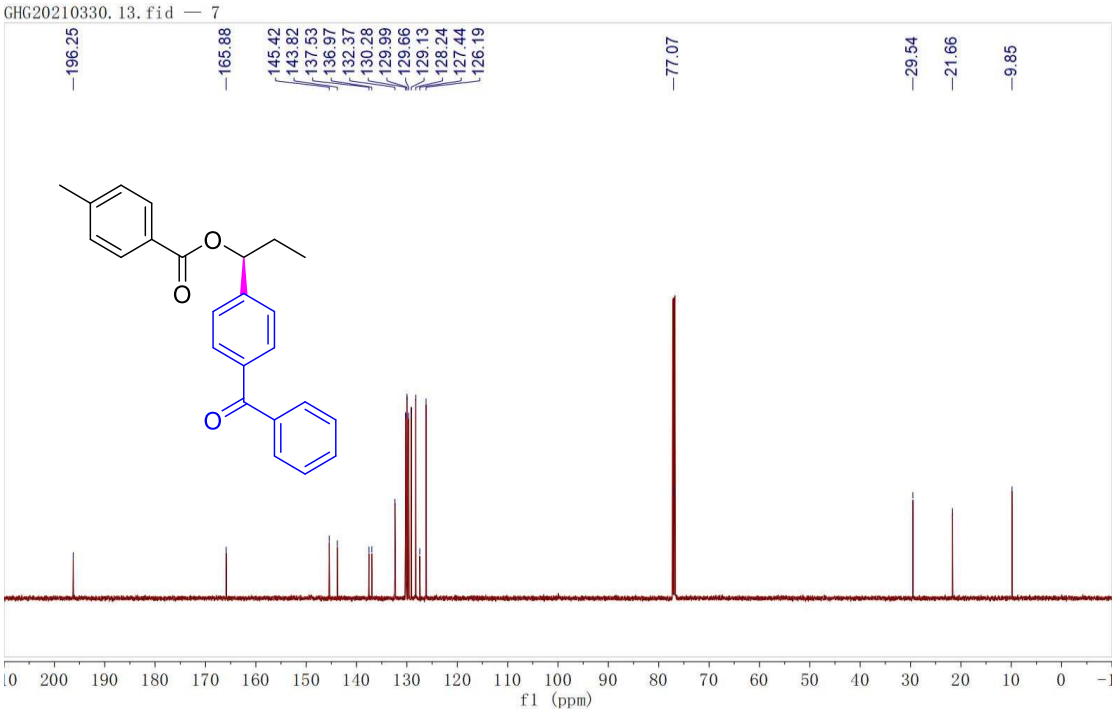
27, ^{13}C NMR (151 MHz, $CDCl_3$)



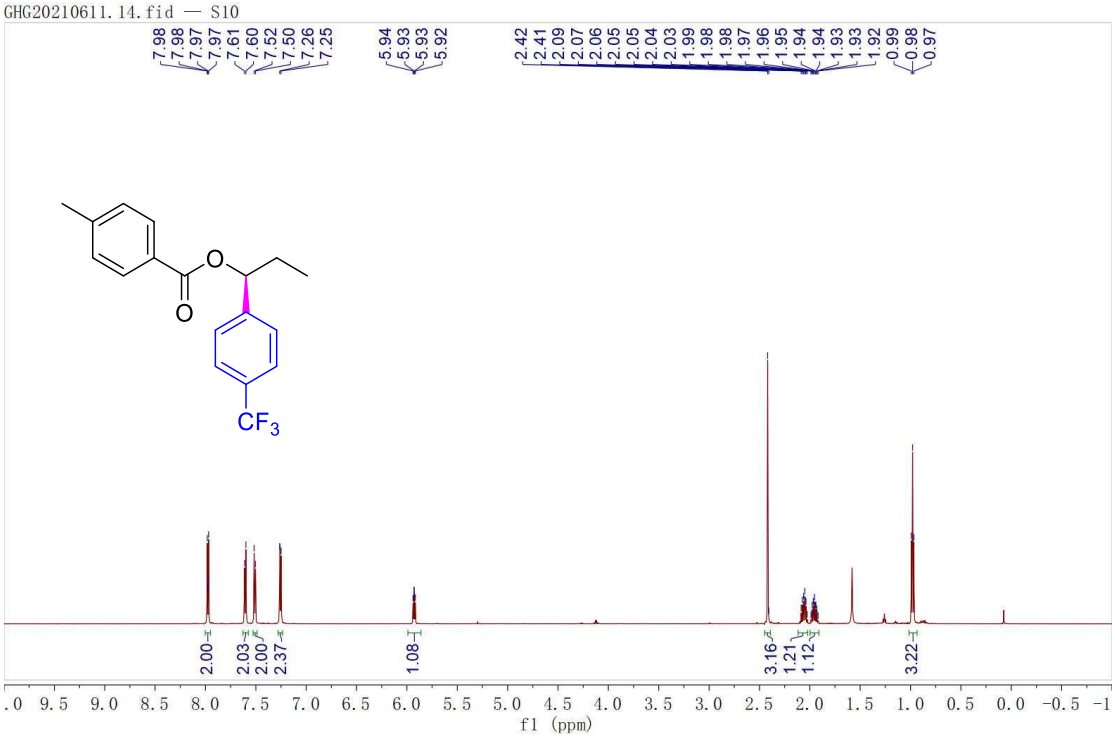
28, ^{1}H-NMR (600 MHZ, $CDCl_3$)



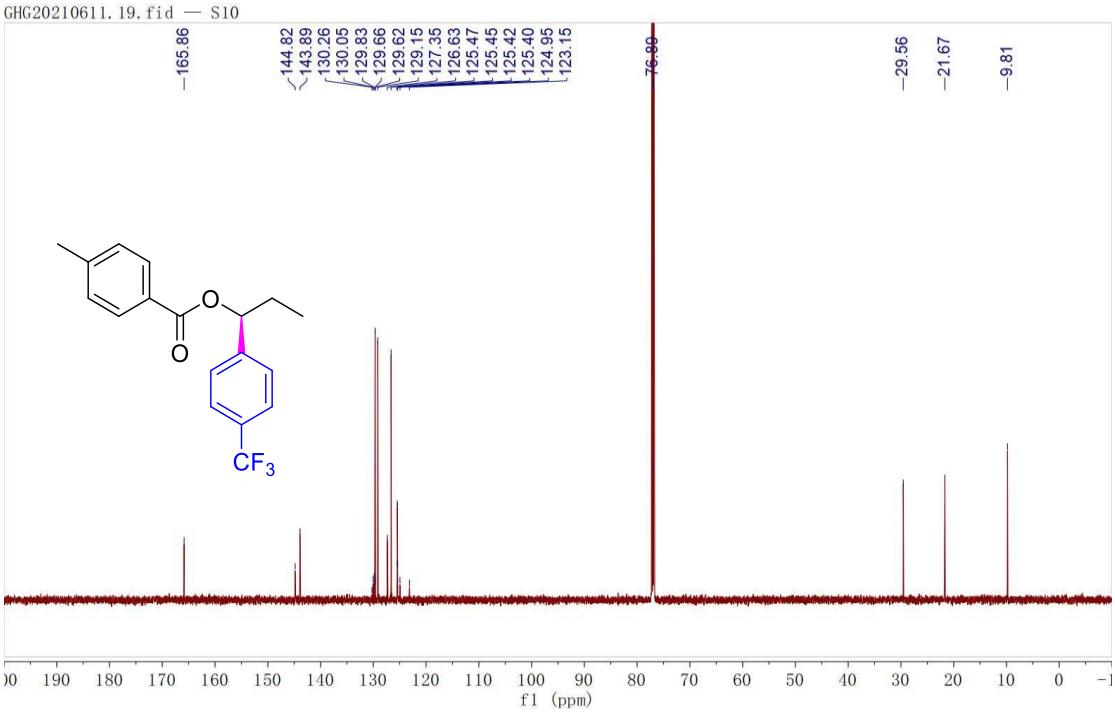
28, ^{13}C NMR (101 MHz, $CDCl_3$)



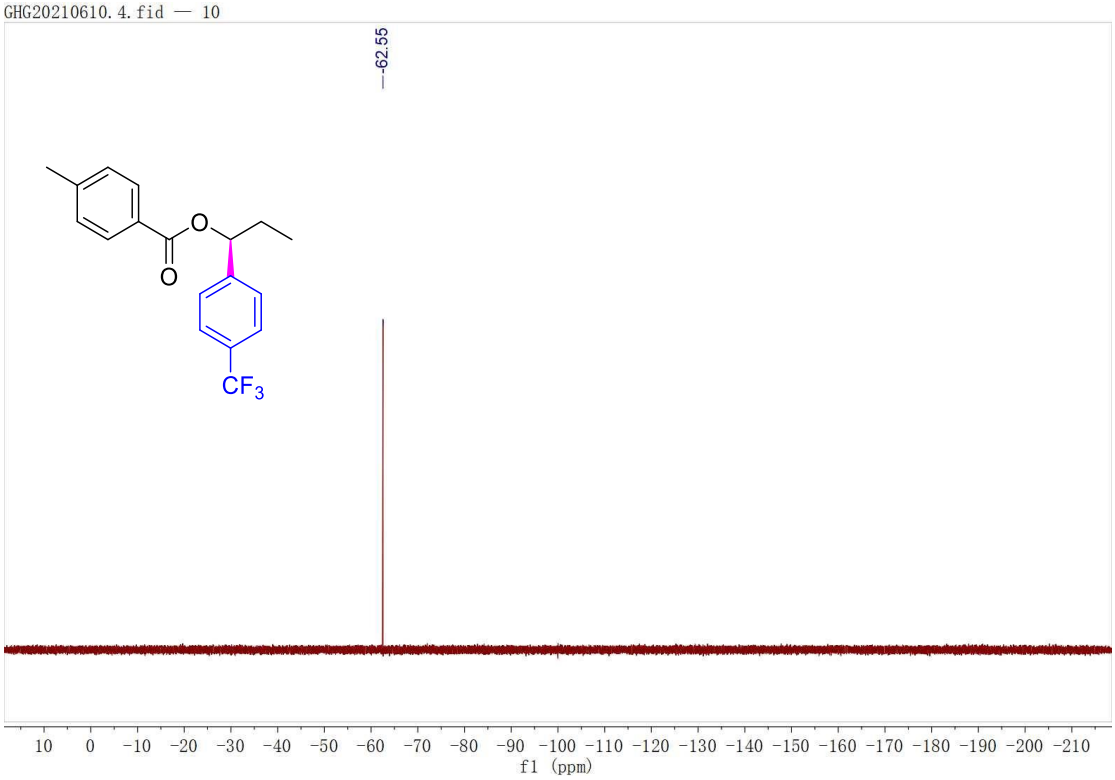
29, ^{1}H-NMR (600 MHZ, $CDCl_3$)



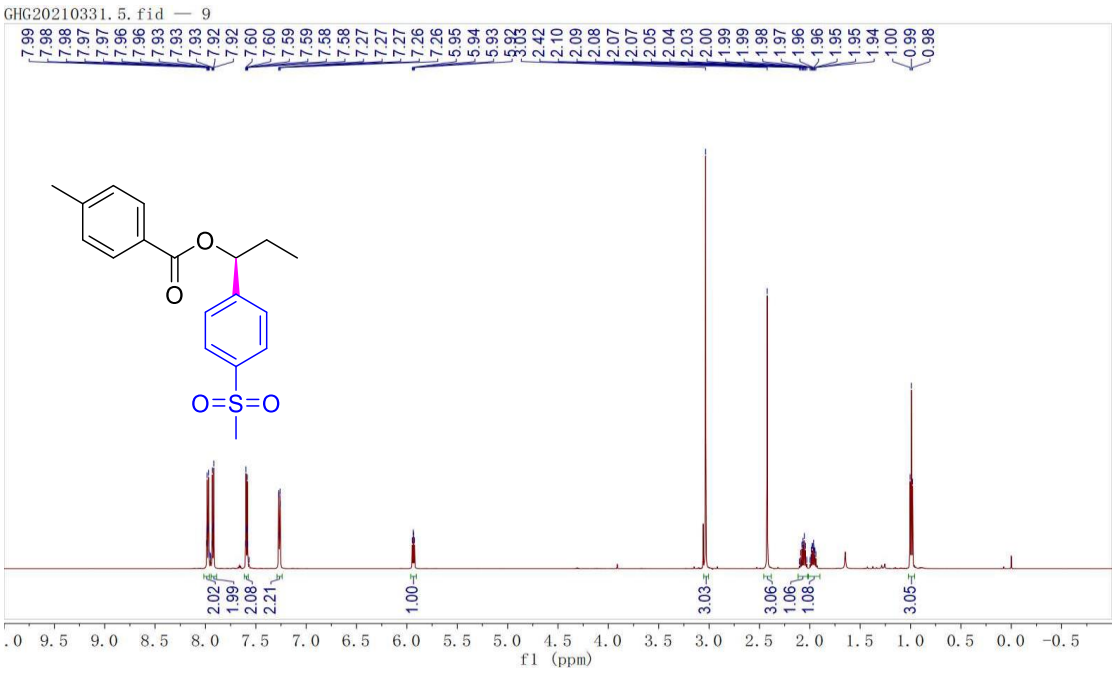
29, ^{13}C NMR (151 MHz, $CDCl_3$)



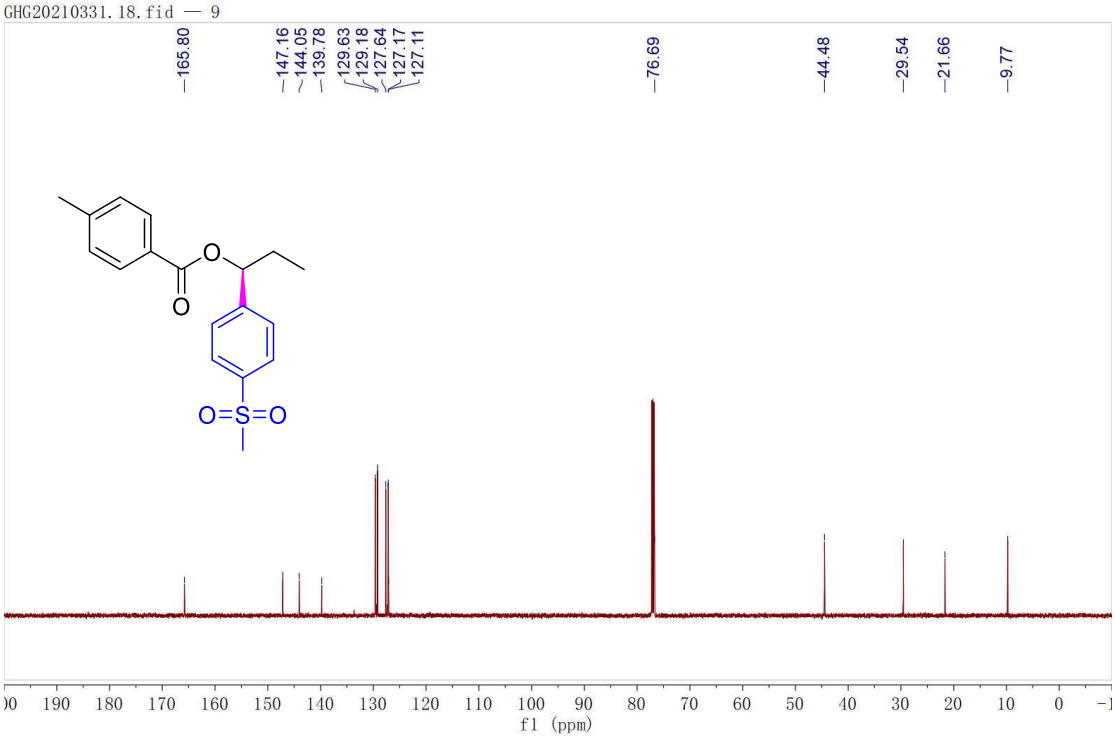
29, ^{19}F NMR (565 MHz, $CDCl_3$)



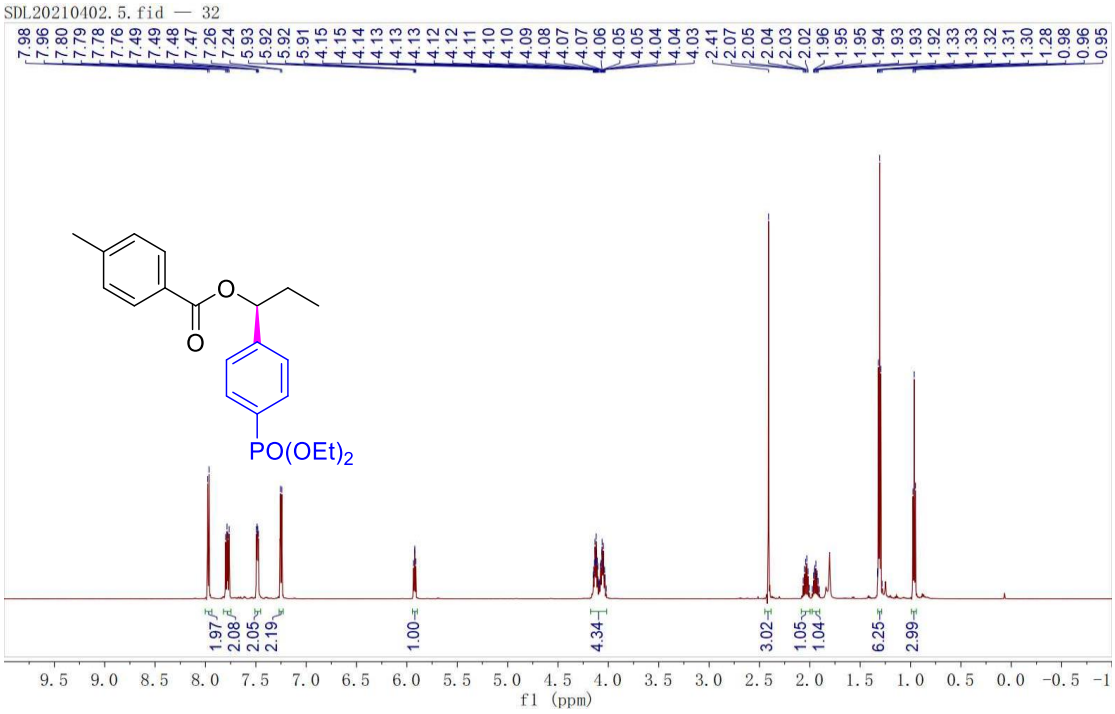
30, ^{1}H-NMR (600 MHZ, $CDCl_3$)



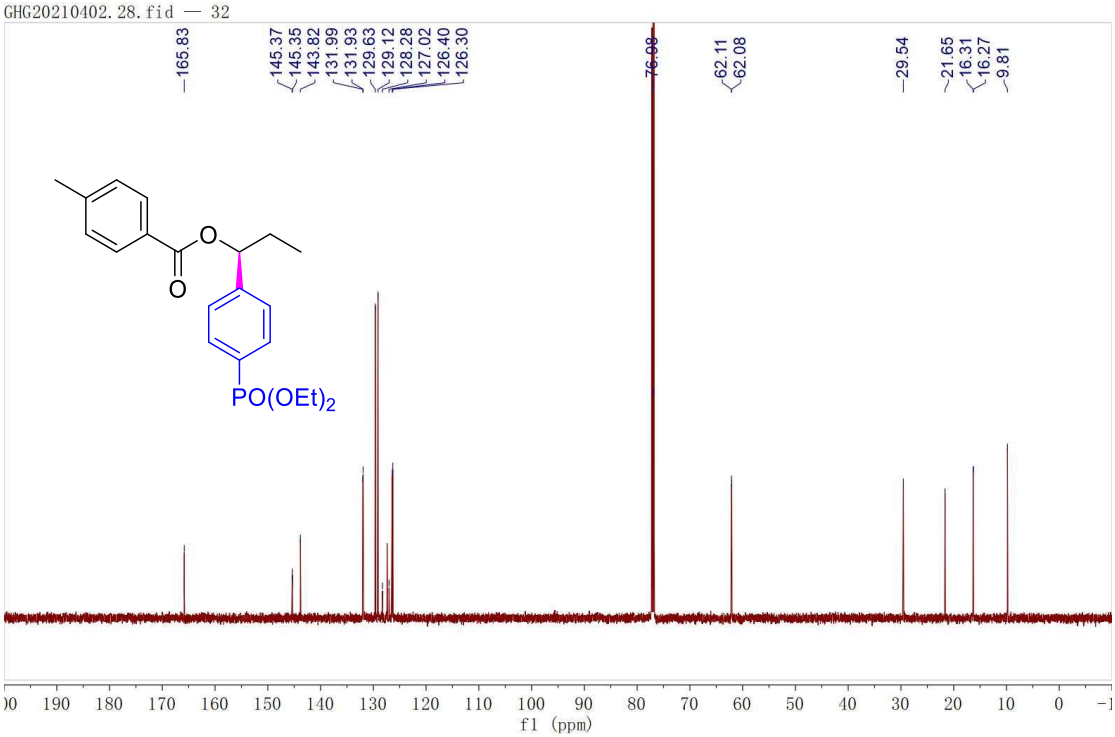
30, ^{13}C NMR (151 MHz, $CDCl_3$)



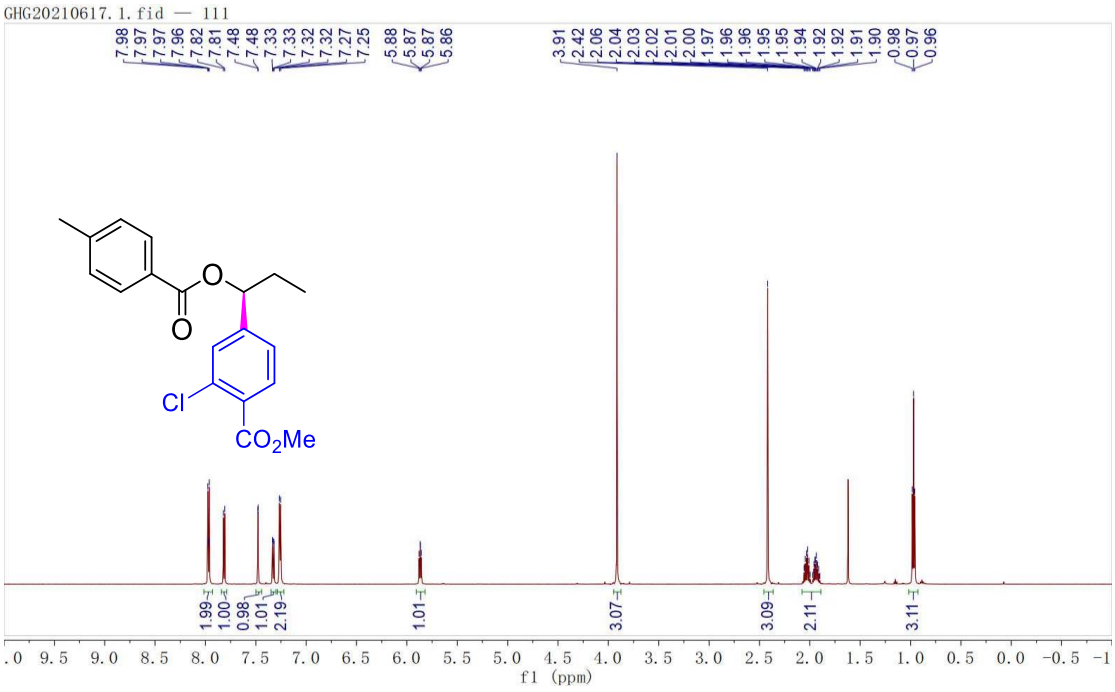
31, ^{1}H-NMR (600 MHZ, $CDCl_3$)



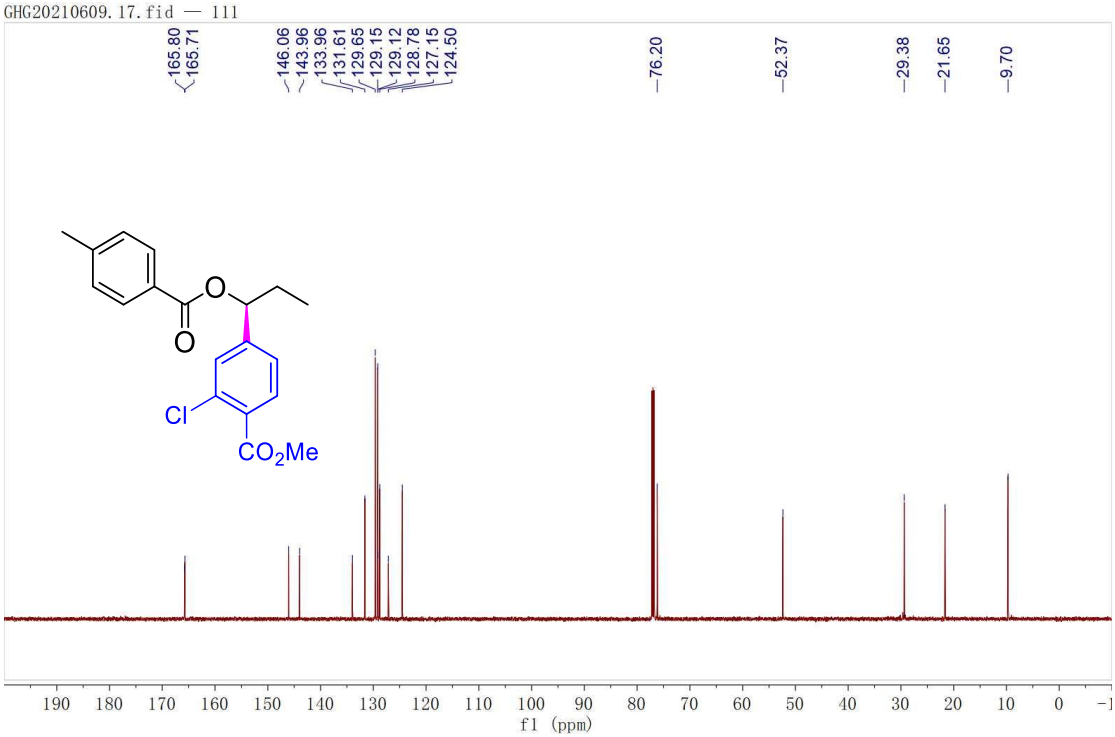
31, ^{13}C NMR (151 MHz, $CDCl_3$)



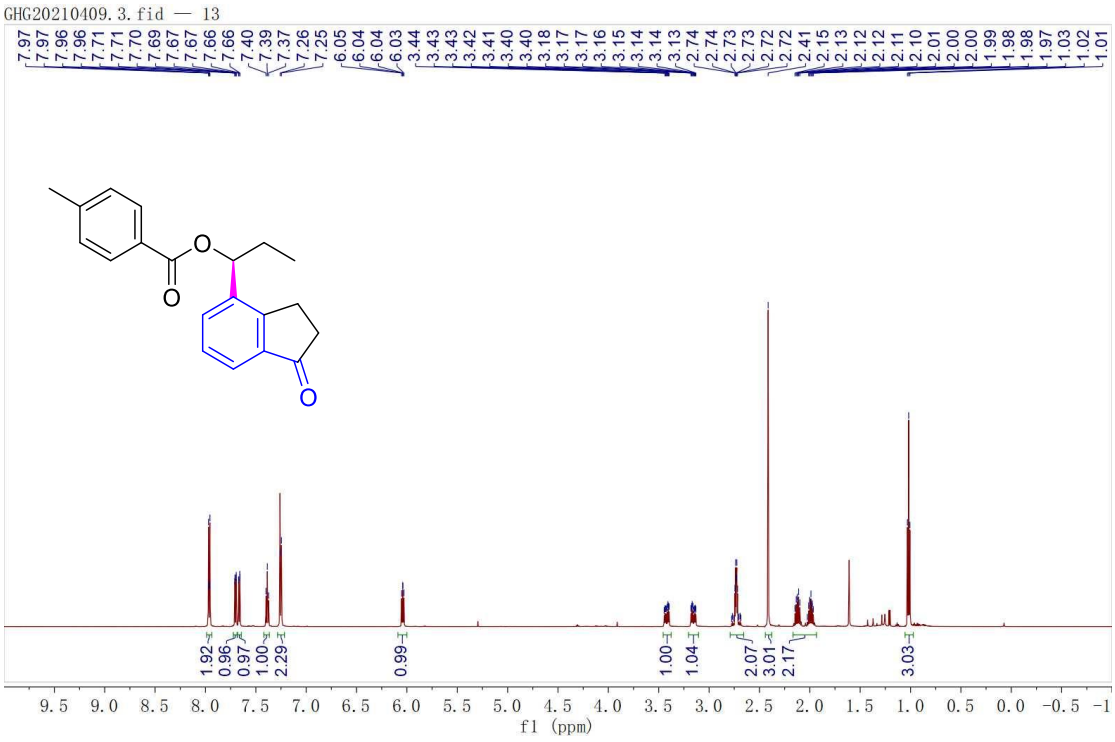
32, ^{1}H-NMR (600 MHZ, $CDCl_3$)



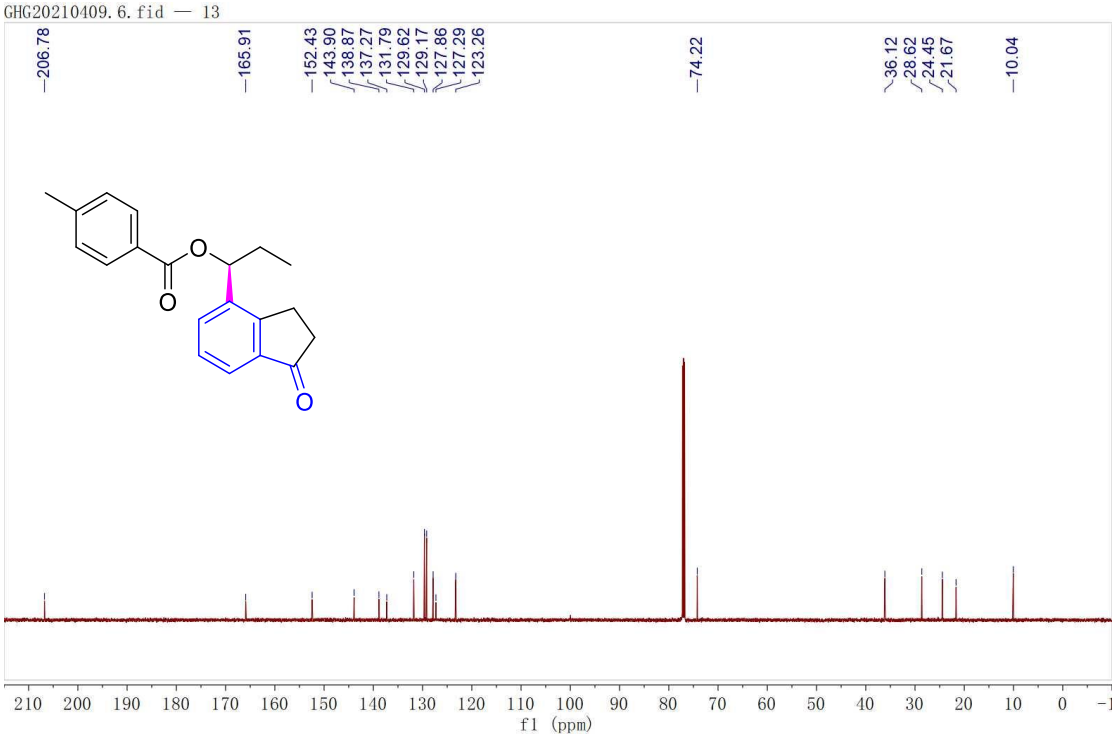
32, ^{13}C NMR (151 MHz, $CDCl_3$)



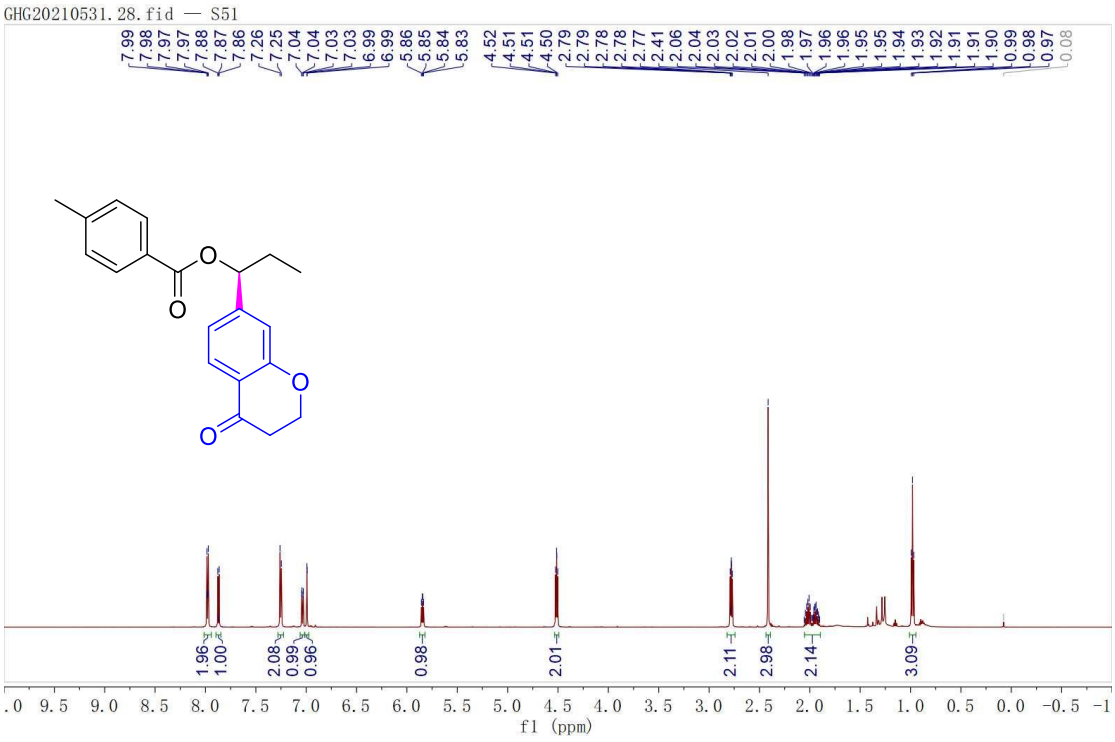
33, ^{1}H-NMR (600 MHZ, $CDCl_3$)



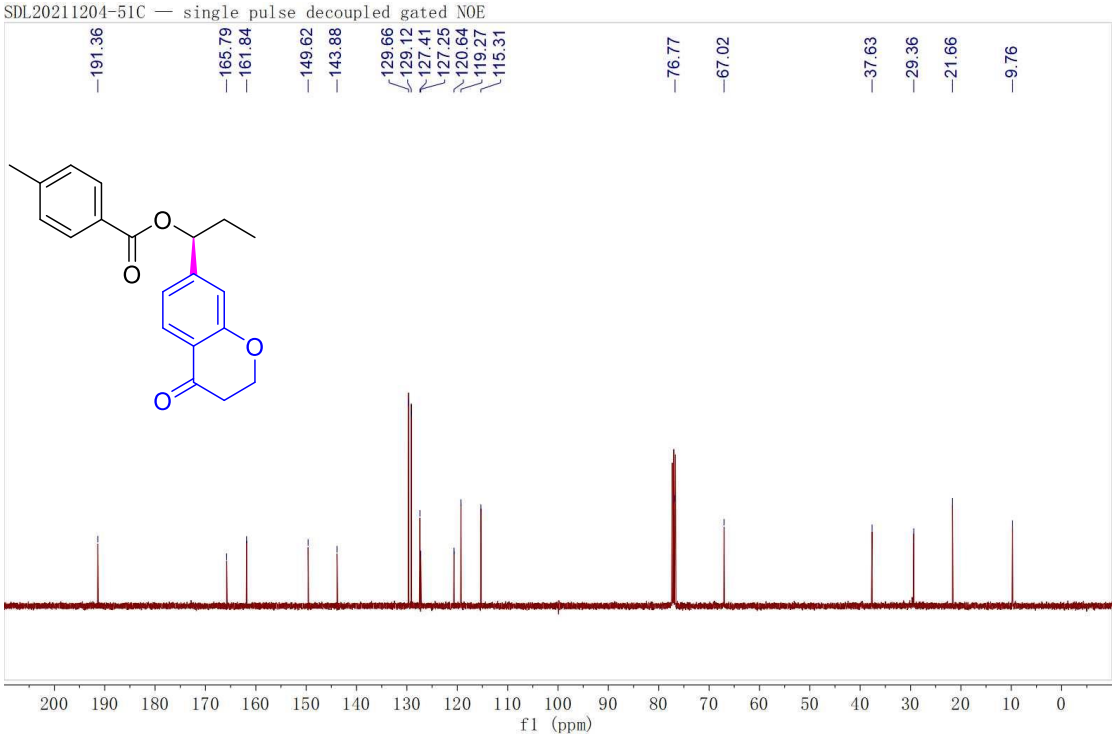
33, ^{13}C NMR (151 MHz, $CDCl_3$)



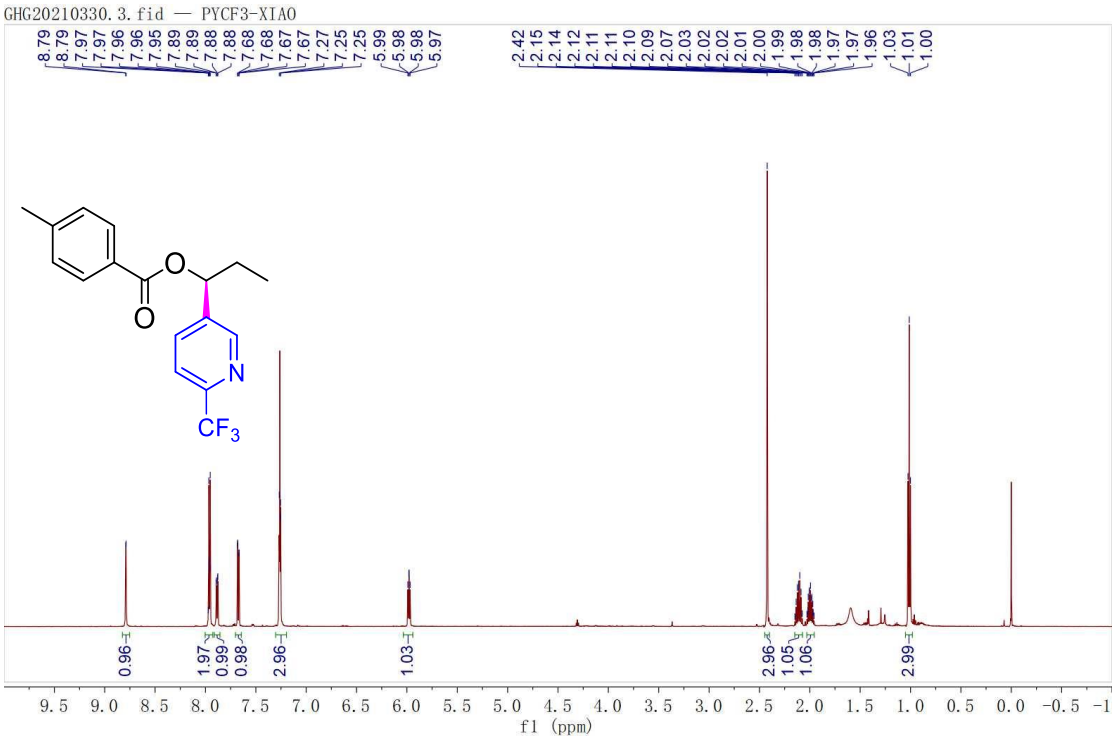
34, ^{1}H-NMR (600 MHZ, $CDCl_3$)



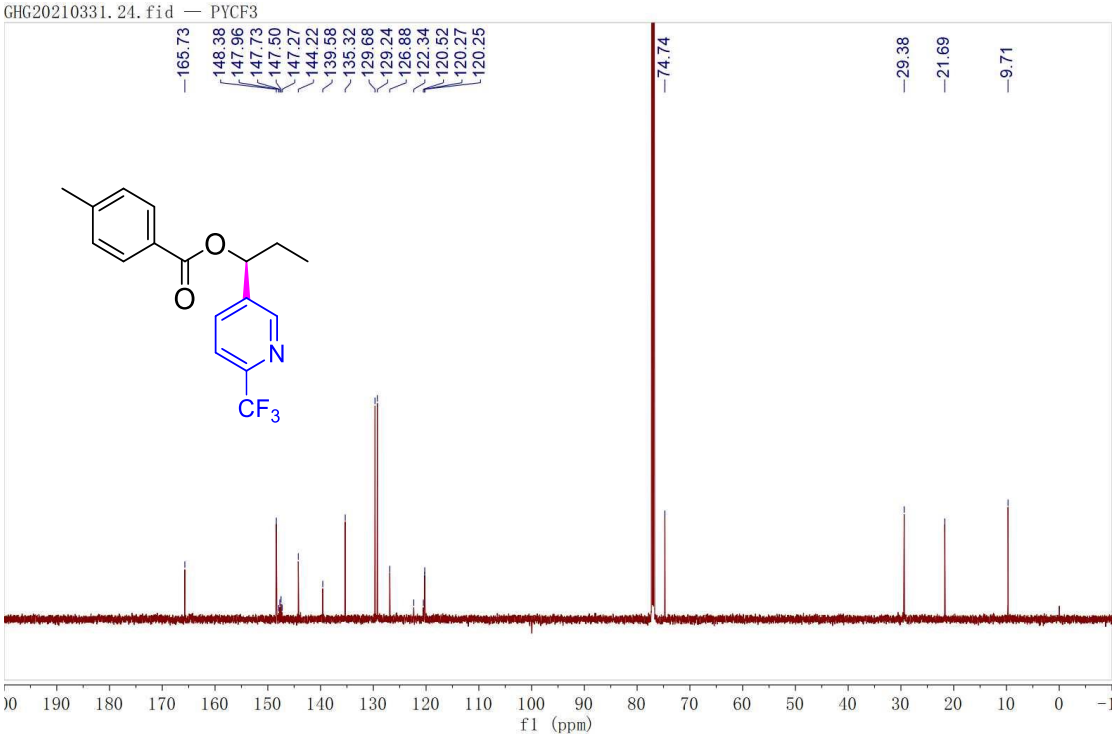
34, ^{13}C NMR (101 MHz, $CDCl_3$)



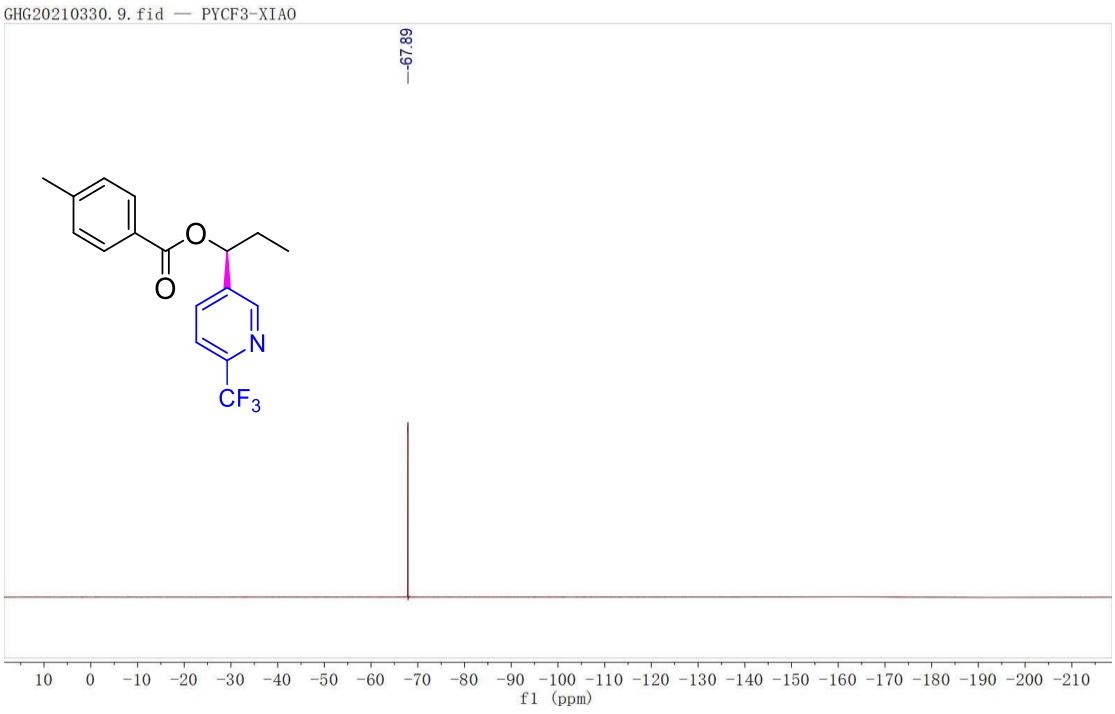
35, ^{1}H-NMR (600 MHZ, $CDCl_3$)



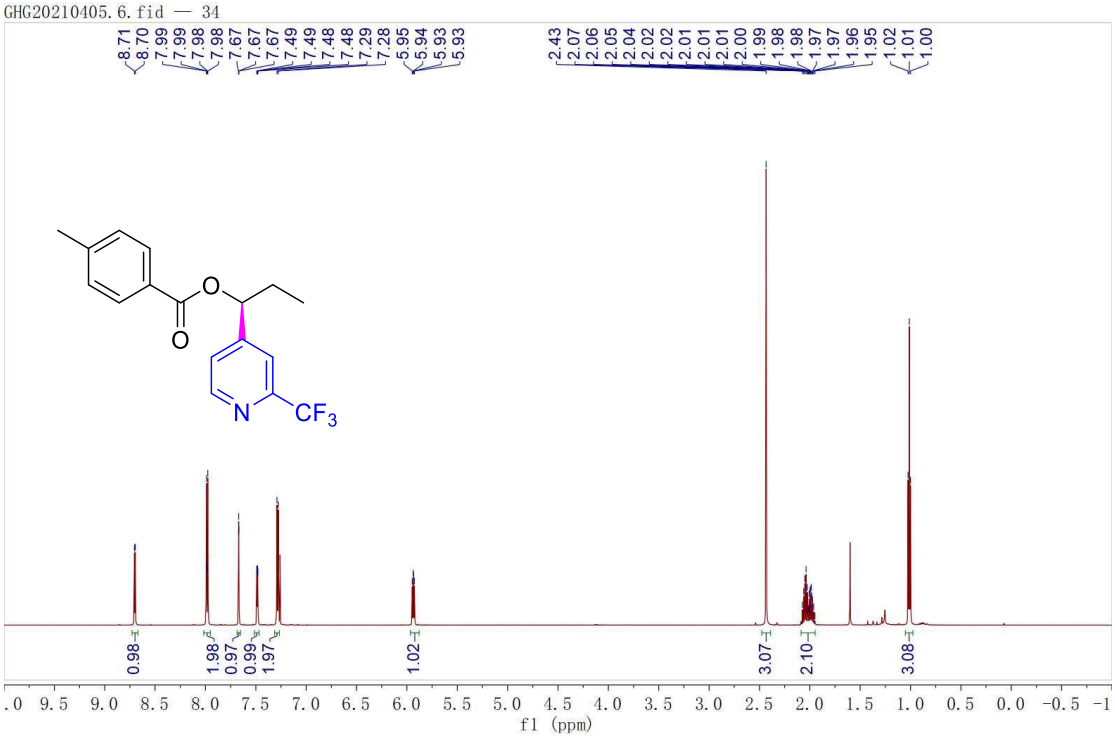
35, ^{13}C NMR (151 MHz, $CDCl_3$)



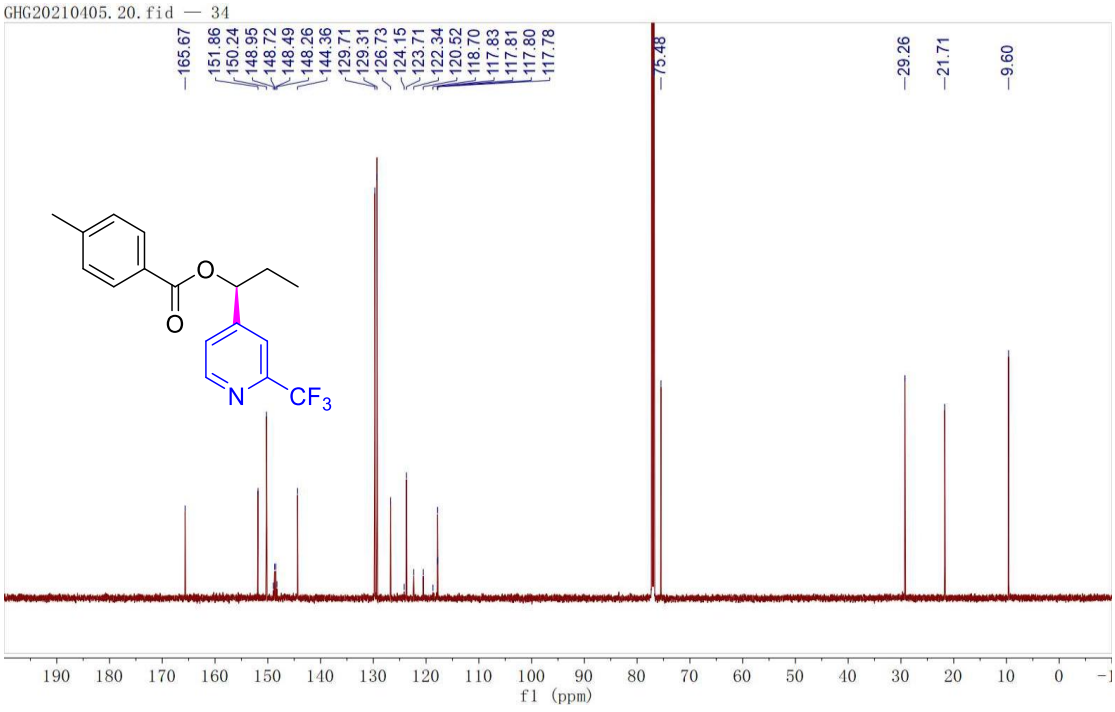
35, ^{19}F NMR (565 MHz, $CDCl_3$)



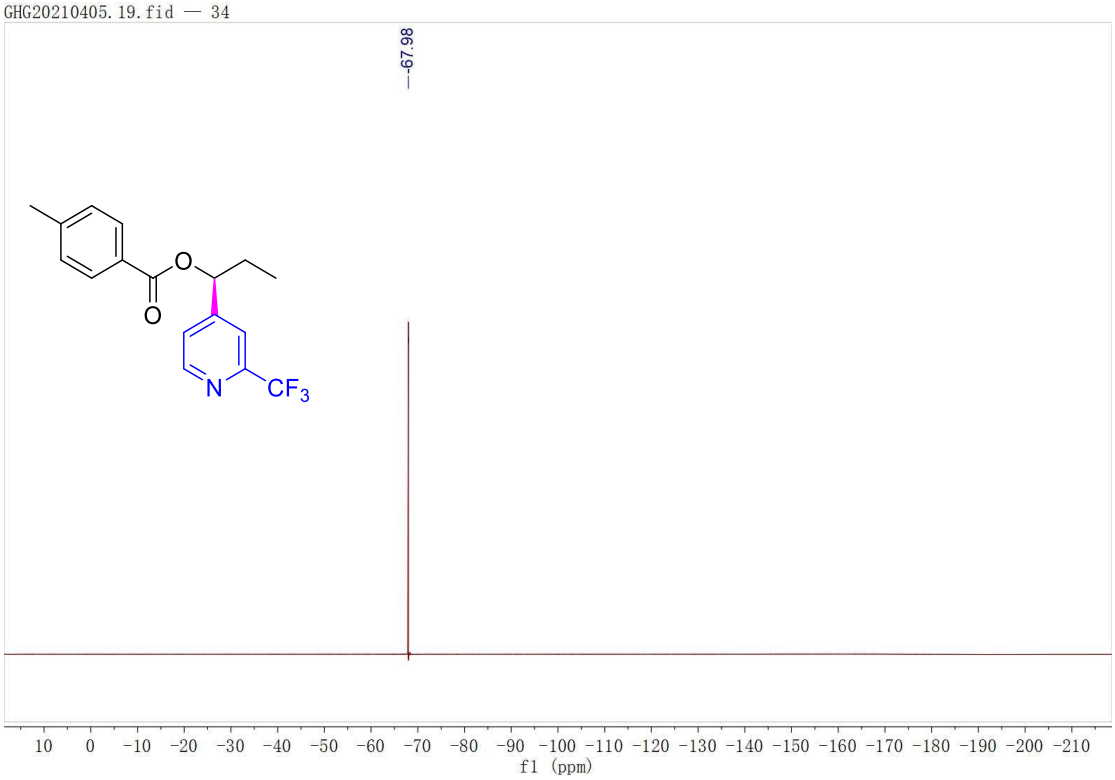
36, ^{1}H-NMR (600 MHZ, $CDCl_3$)



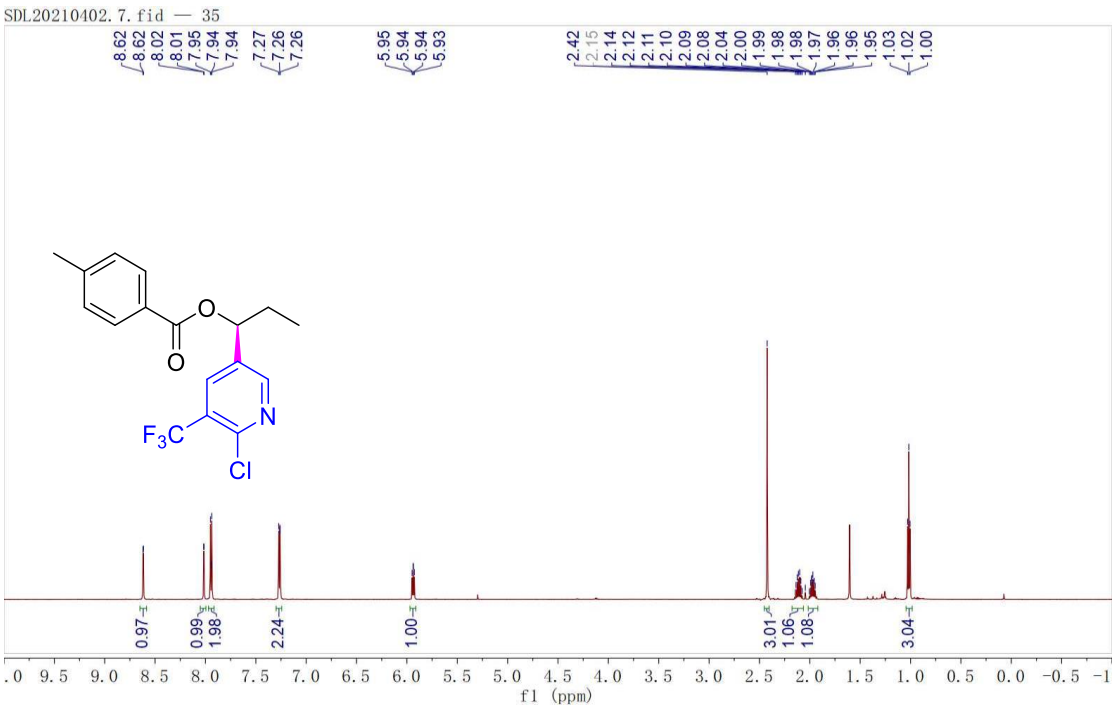
36, ^{13}C NMR (151 MHz, $CDCl_3$)



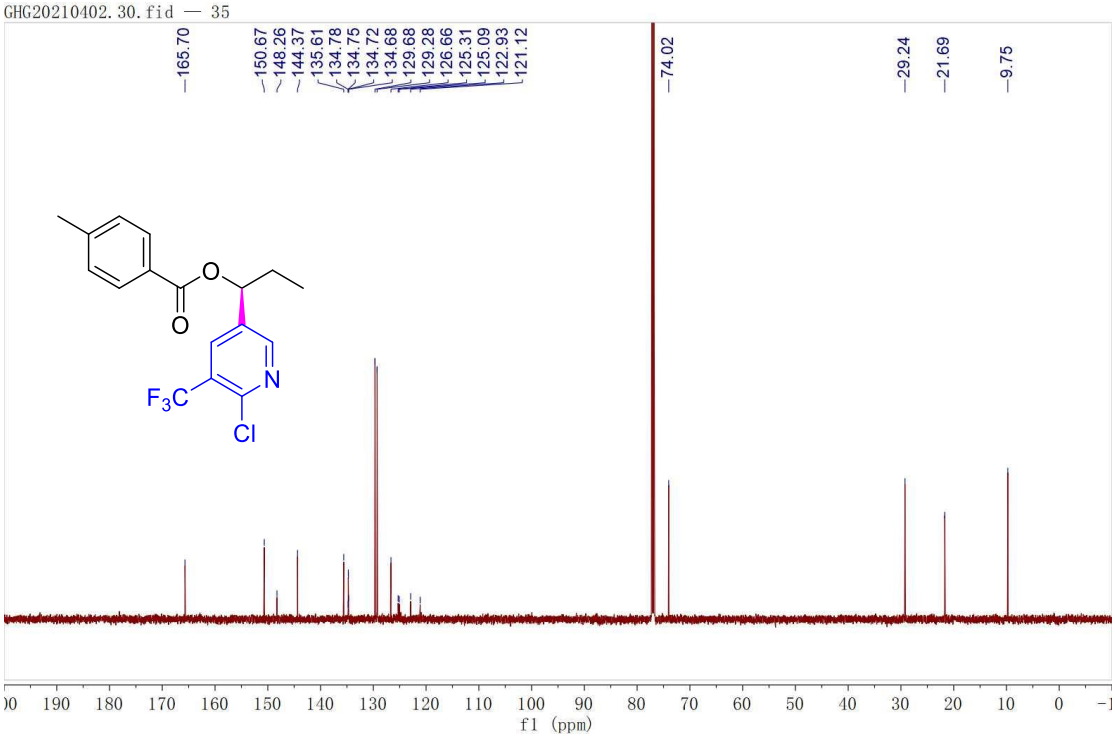
36, ^{19}F NMR (565 MHz, $CDCl_3$)



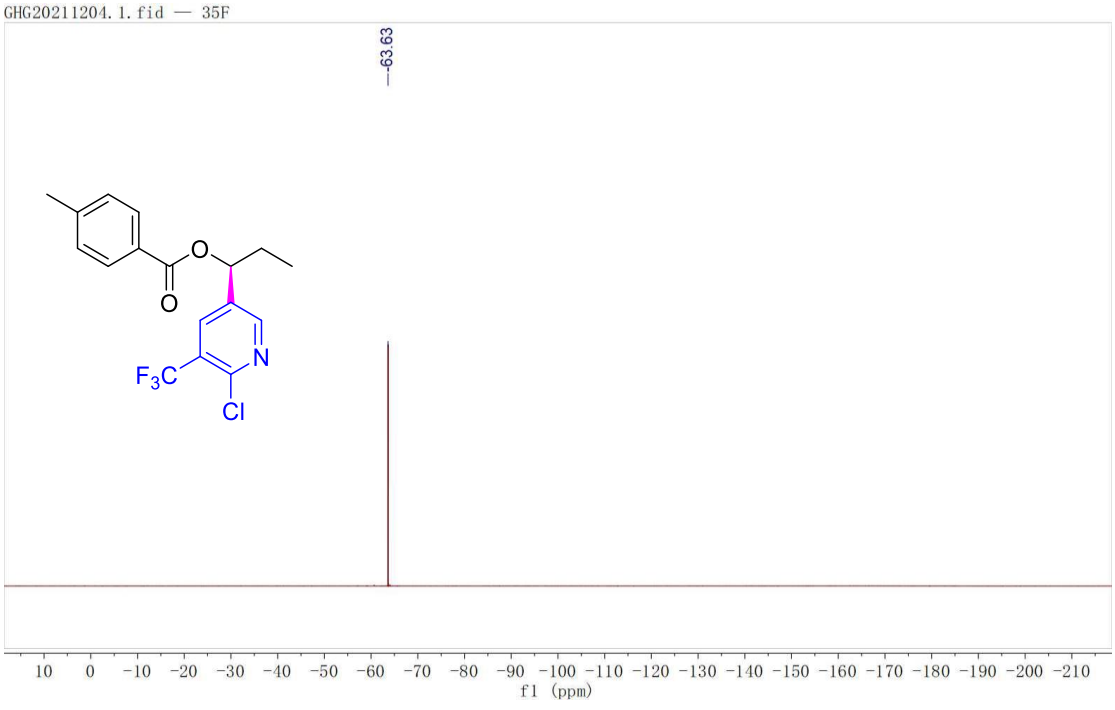
37, ^{1}H-NMR (600 MHZ, $CDCl_3$)



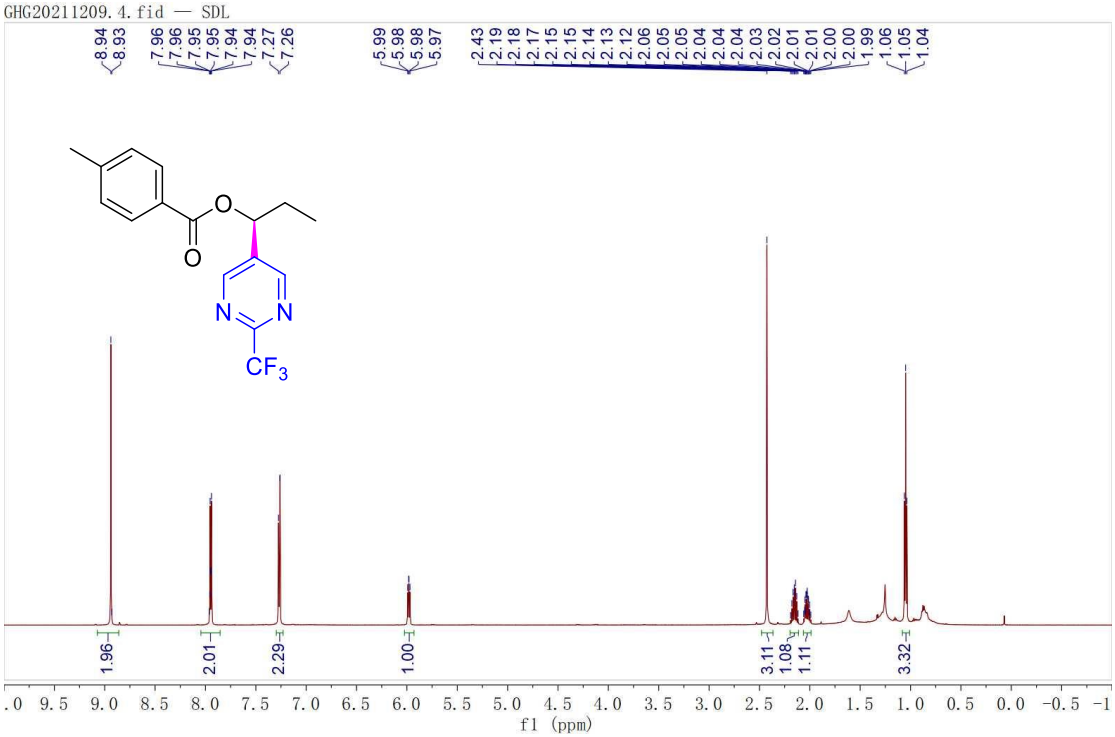
37, ^{13}C NMR (151 MHz, $CDCl_3$)



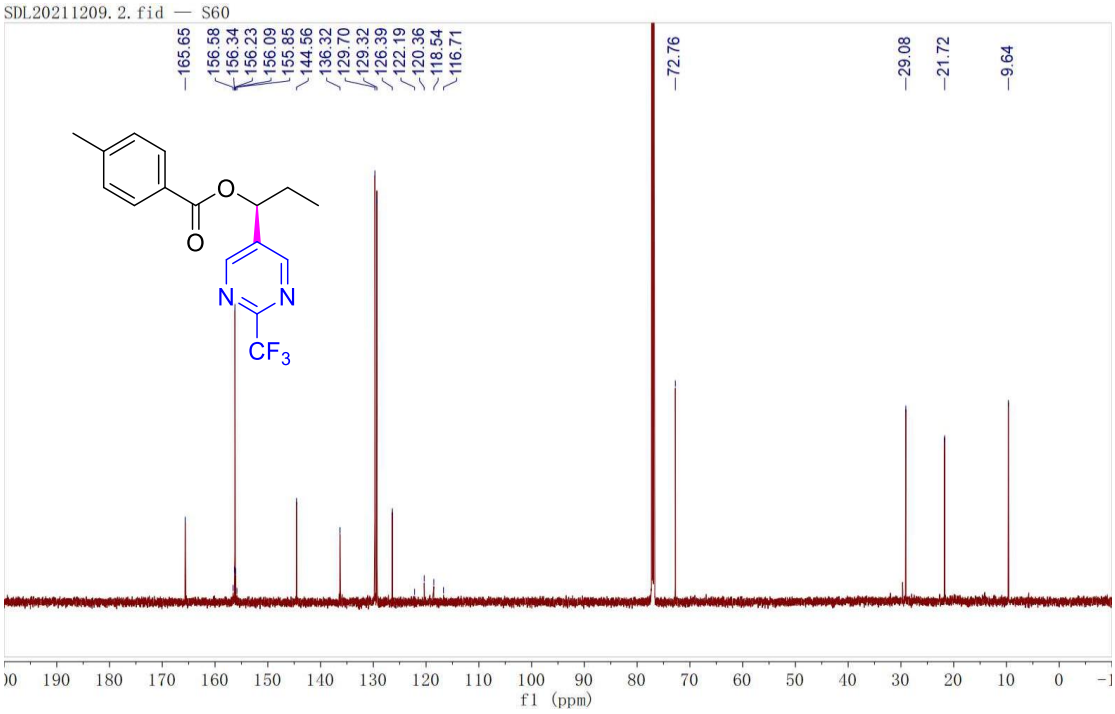
37, ^{19}F NMR (565 MHz, $CDCl_3$)



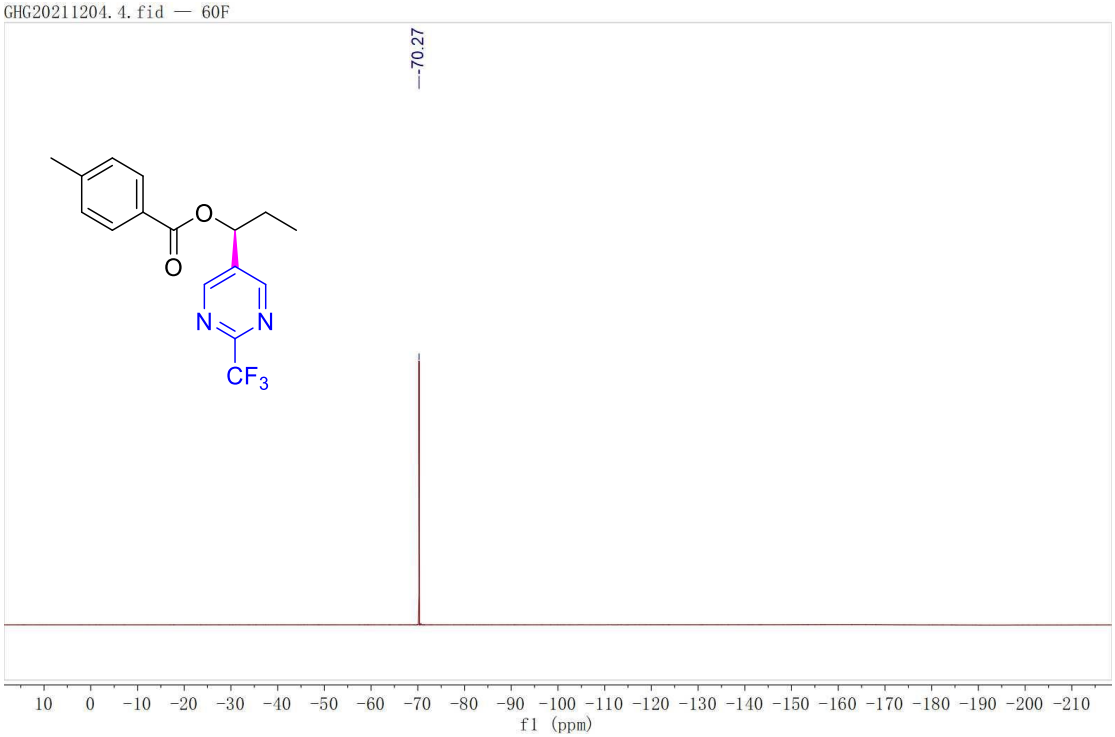
38, ^{1}H-NMR (600 MHZ, $CDCl_3$)



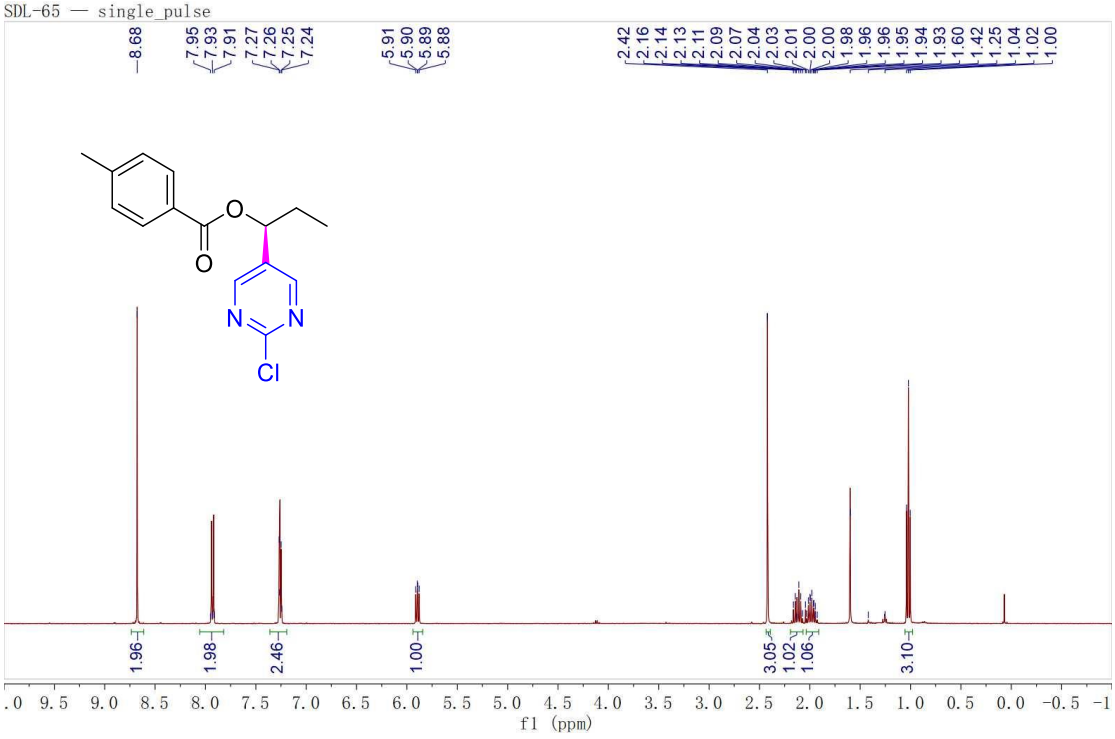
38, ^{13}C NMR (151 MHz, $CDCl_3$)



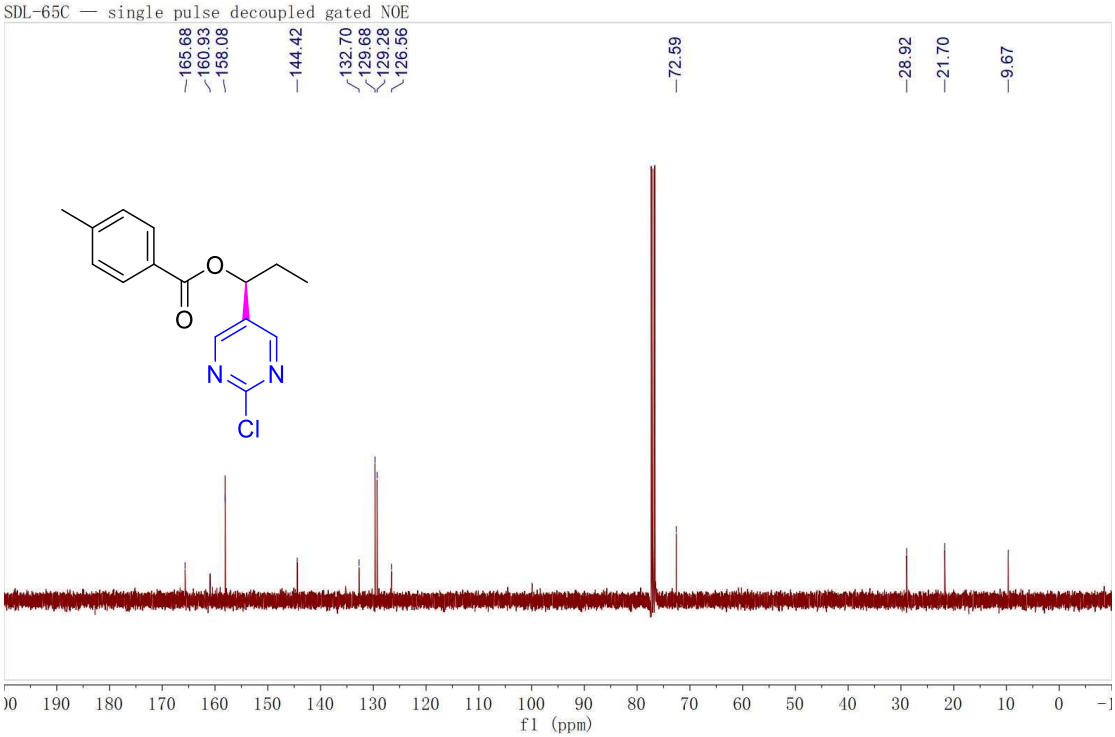
38, ^{19}F NMR (565 MHz, $CDCl_3$)



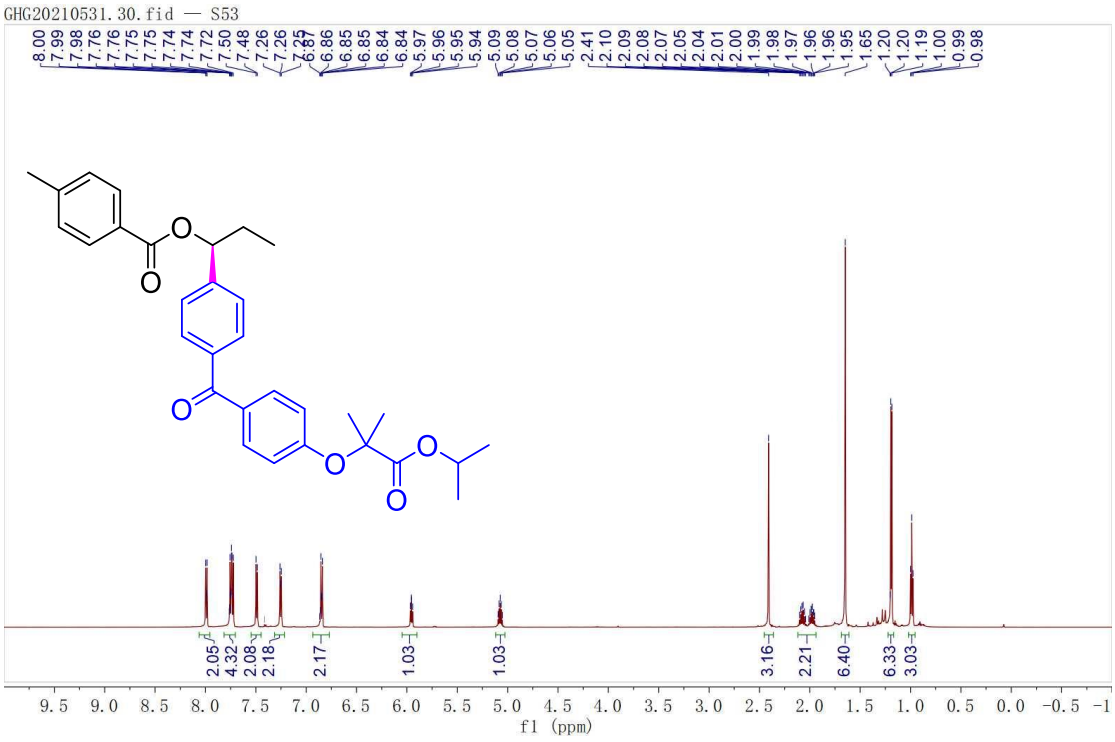
39, ^{1}H-NMR (400 MHZ, $CDCl_3$)



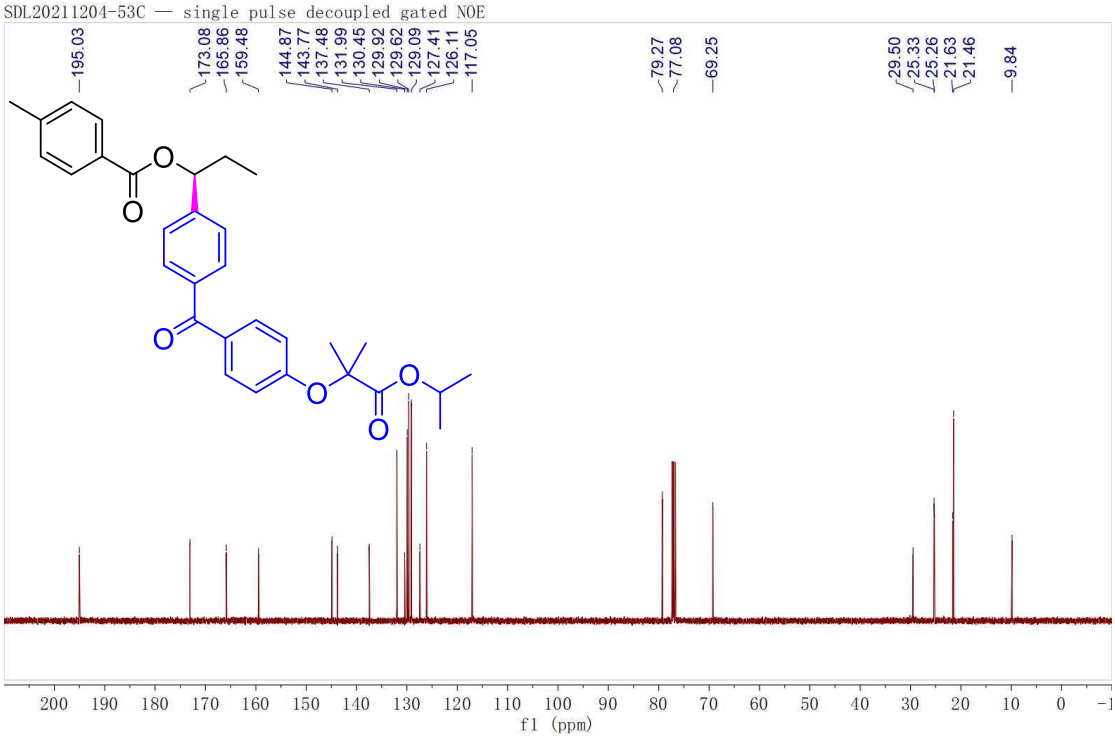
39, ^{13}C NMR (101 MHz, $CDCl_3$)



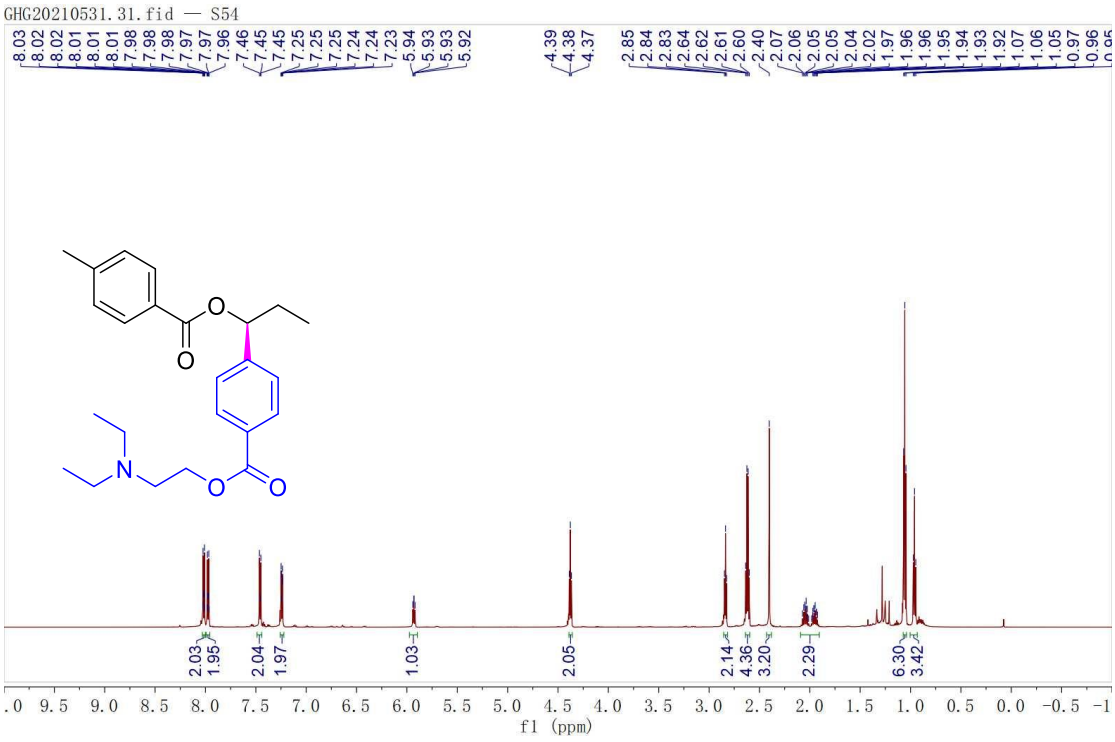
40, ^{1}H-NMR (600 MHZ, $CDCl_3$)



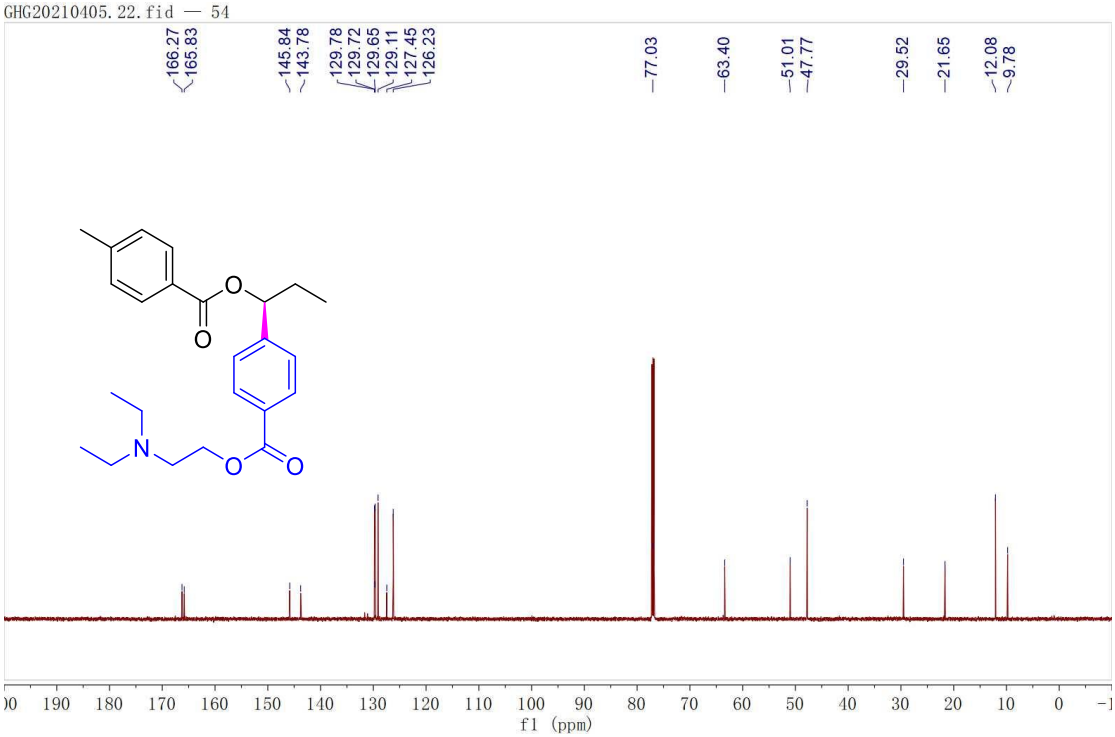
40, ^{13}C NMR (101 MHz, $CDCl_3$)



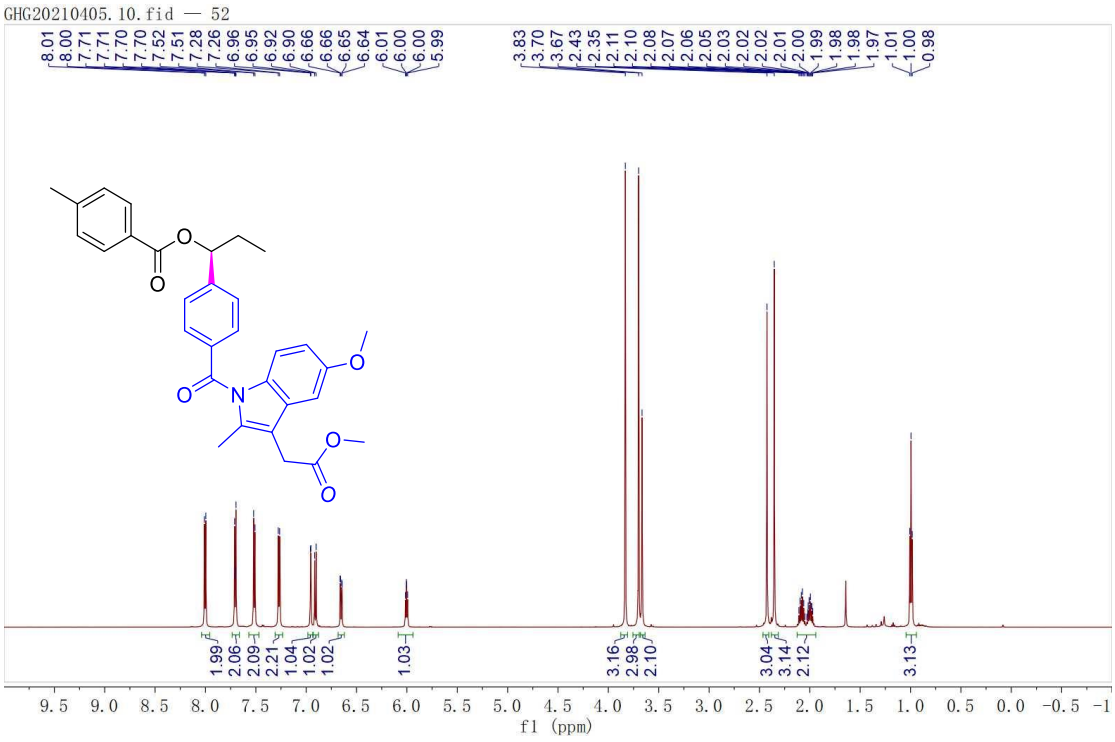
41, ^{1}H-NMR (600 MHZ, $CDCl_3$)



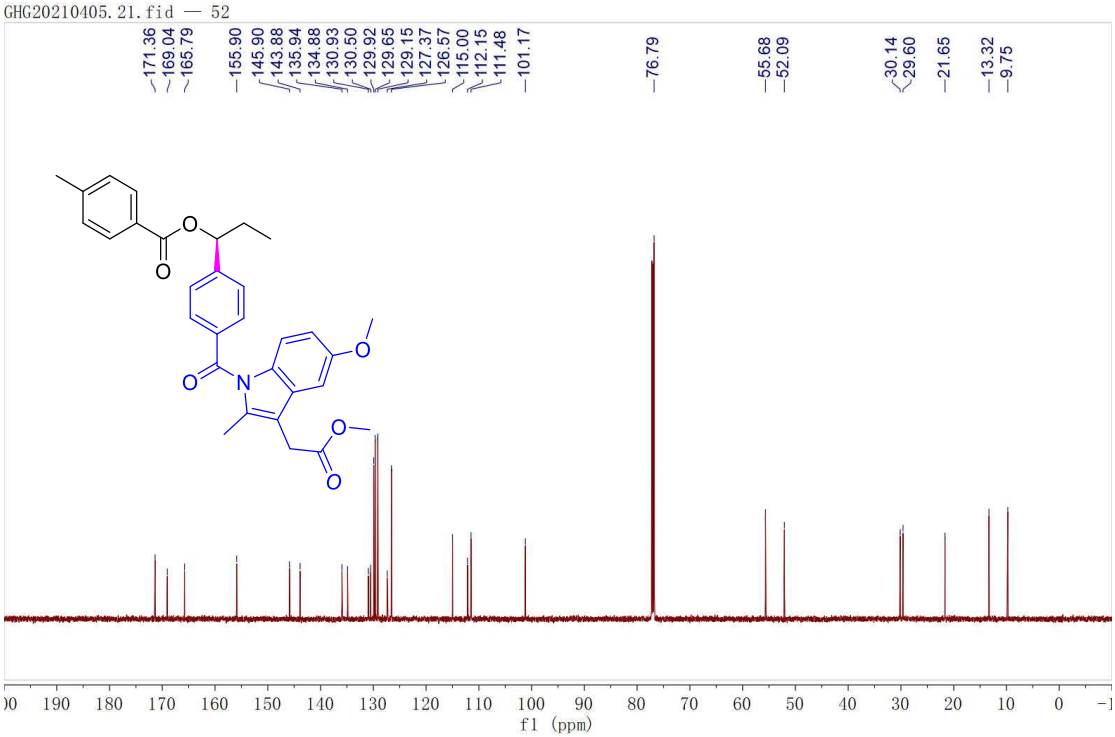
41, ^{13}C NMR (151 MHz, $CDCl_3$)



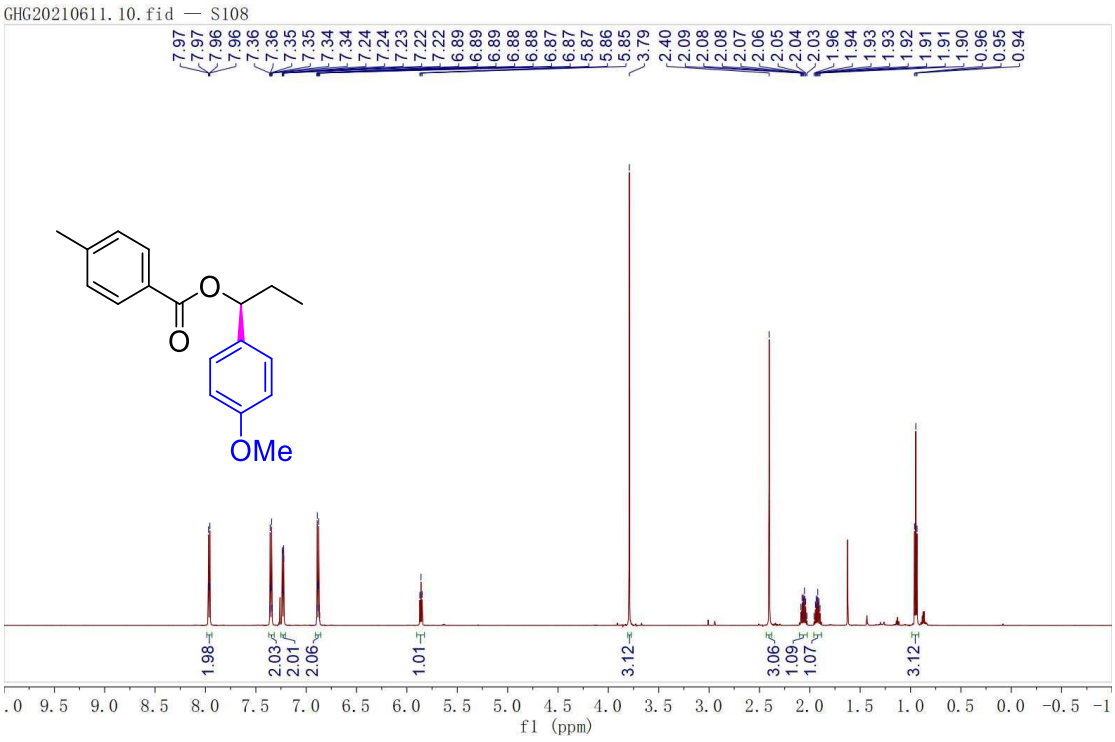
42, ^{1}H-NMR (600 MHZ, $CDCl_3$)



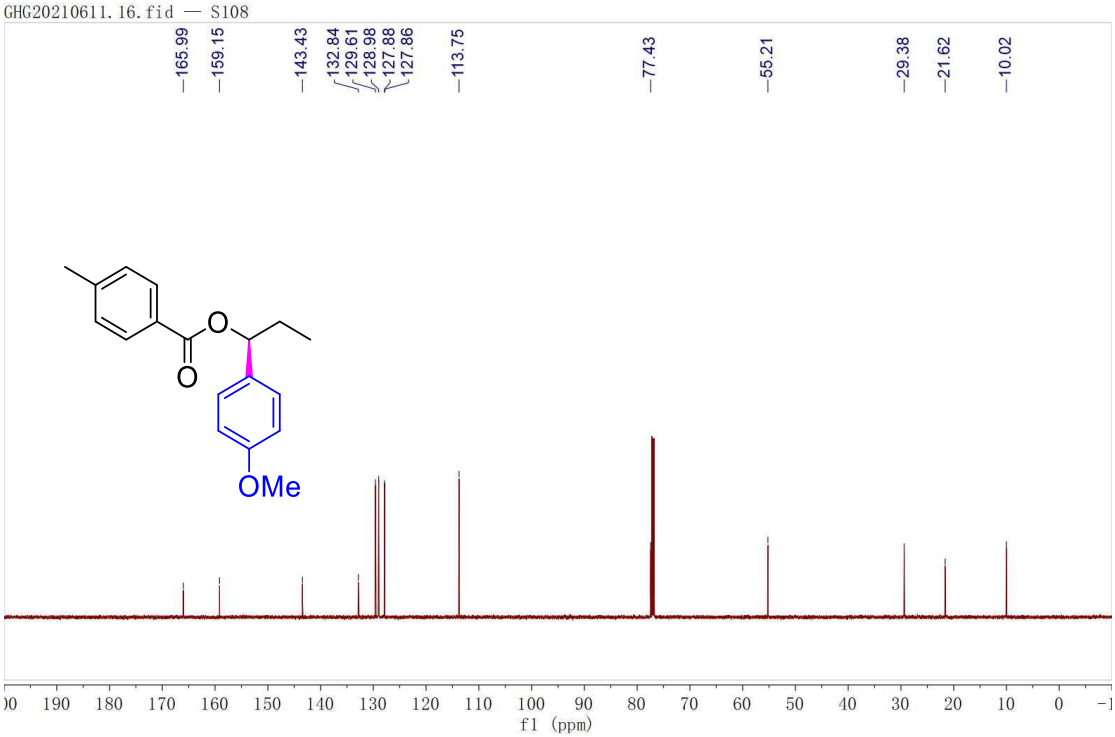
42, ^{13}C NMR (151 MHz, $CDCl_3$)



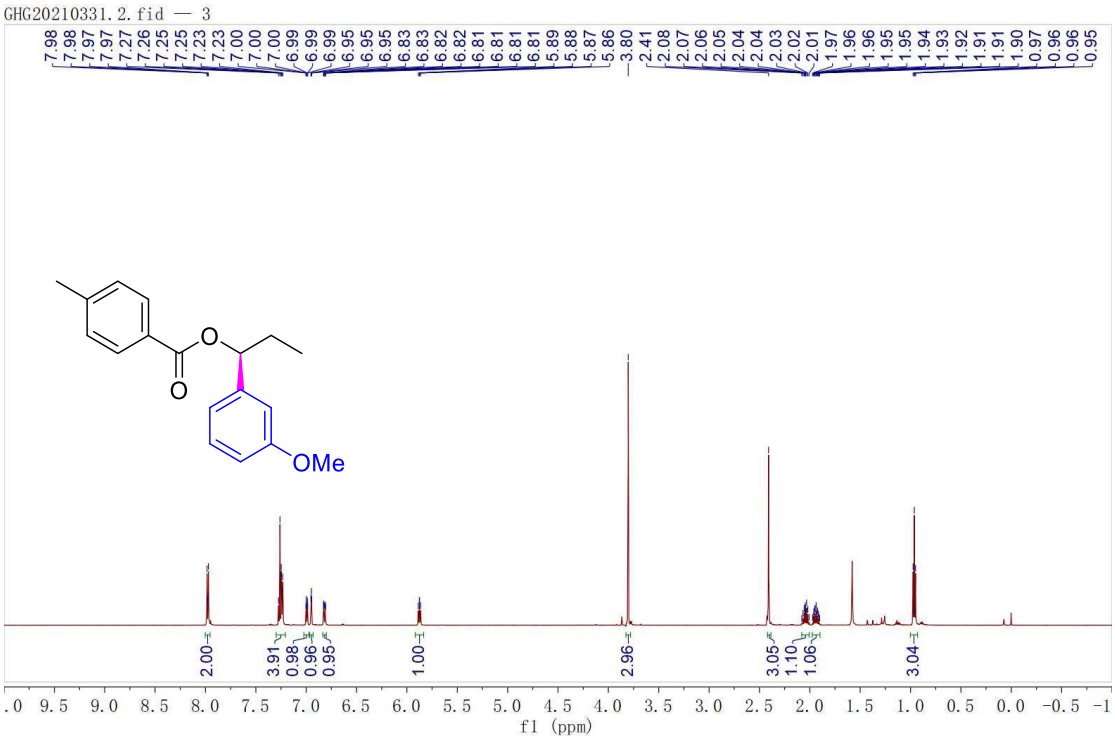
43, ^{1}H-NMR (600 MHZ, $CDCl_3$)



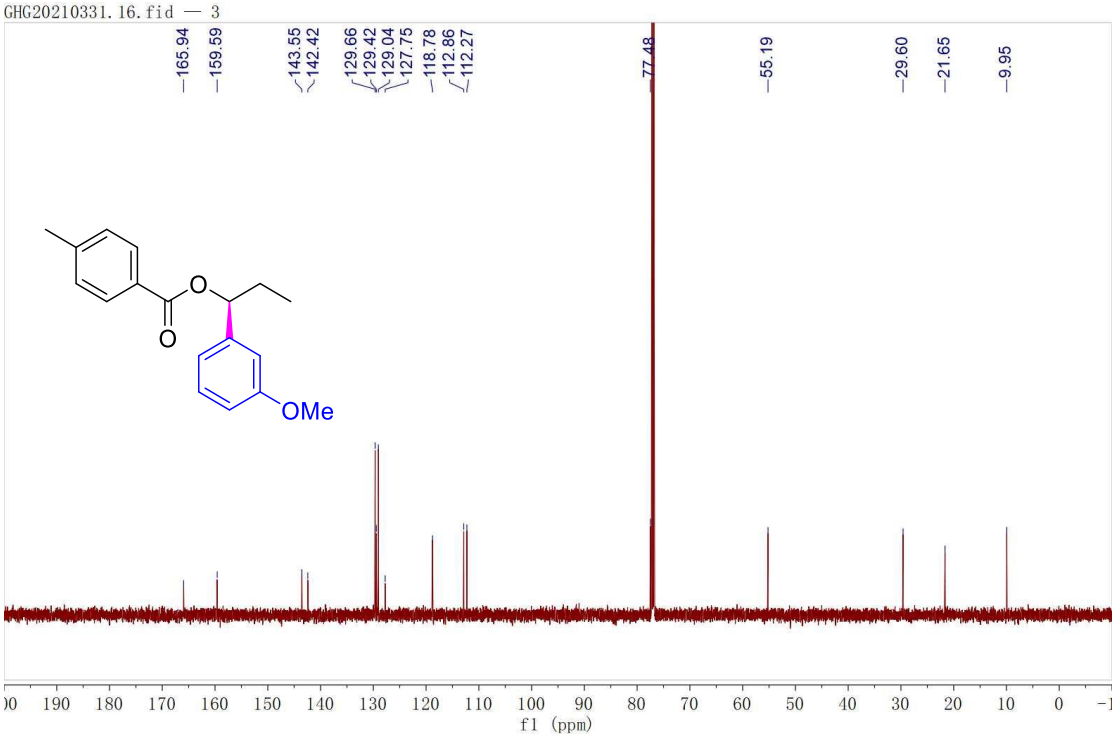
43, ^{13}C NMR (151 MHz, $CDCl_3$)



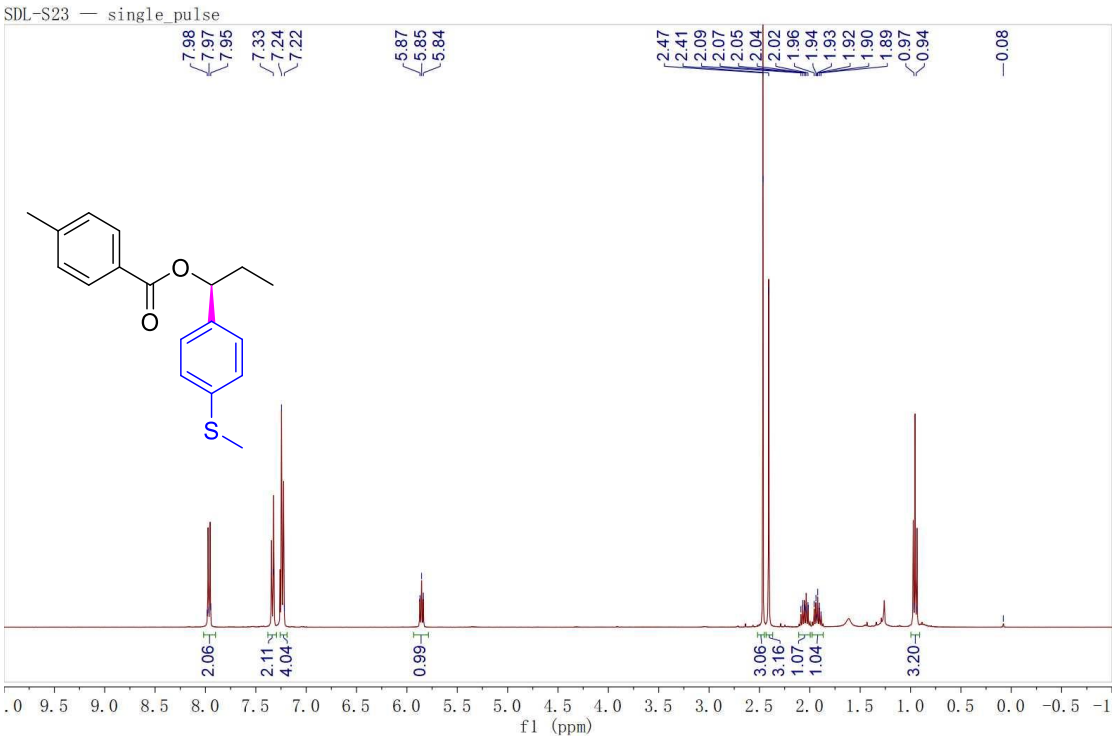
44, ^{1}H-NMR (600 MHZ, $CDCl_3$)



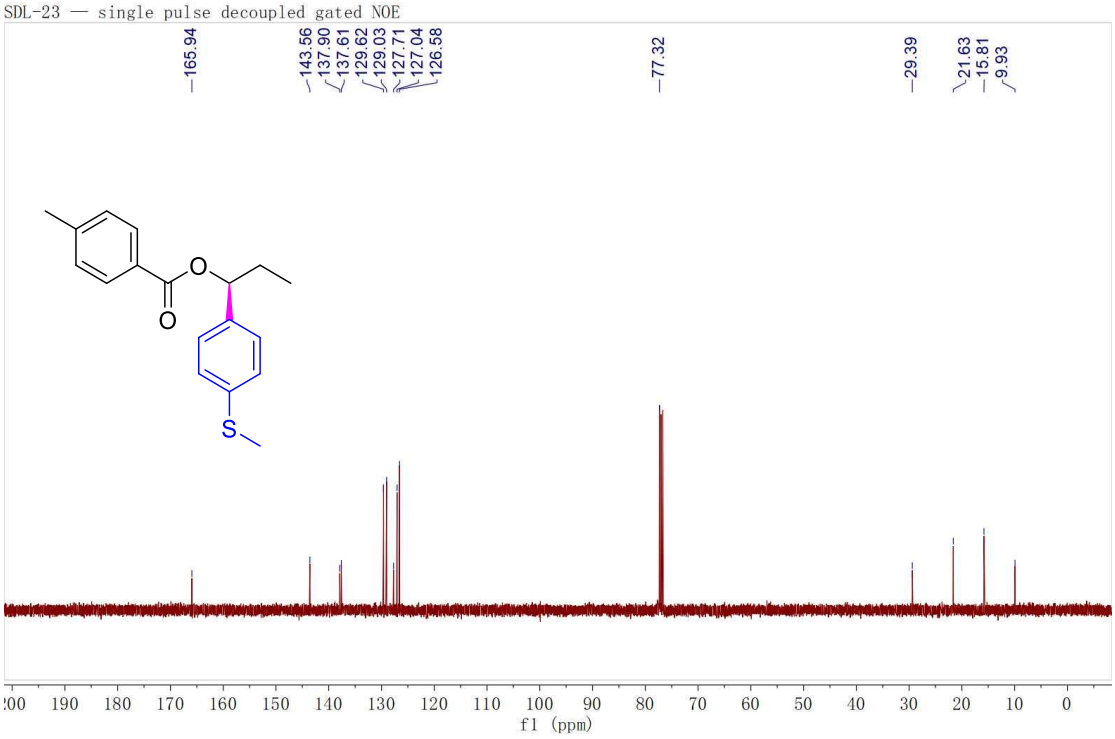
44, ^{13}C NMR (151 MHz, $CDCl_3$)



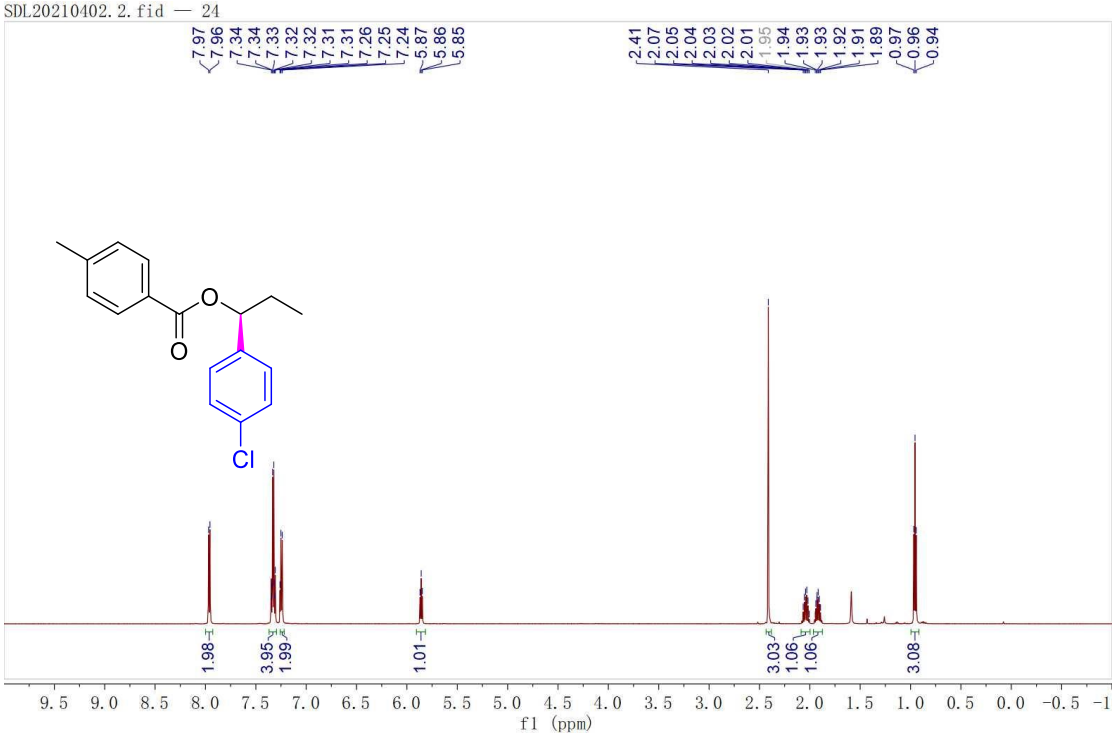
45, ^{1}H-NMR (400 MHZ, $CDCl_3$)



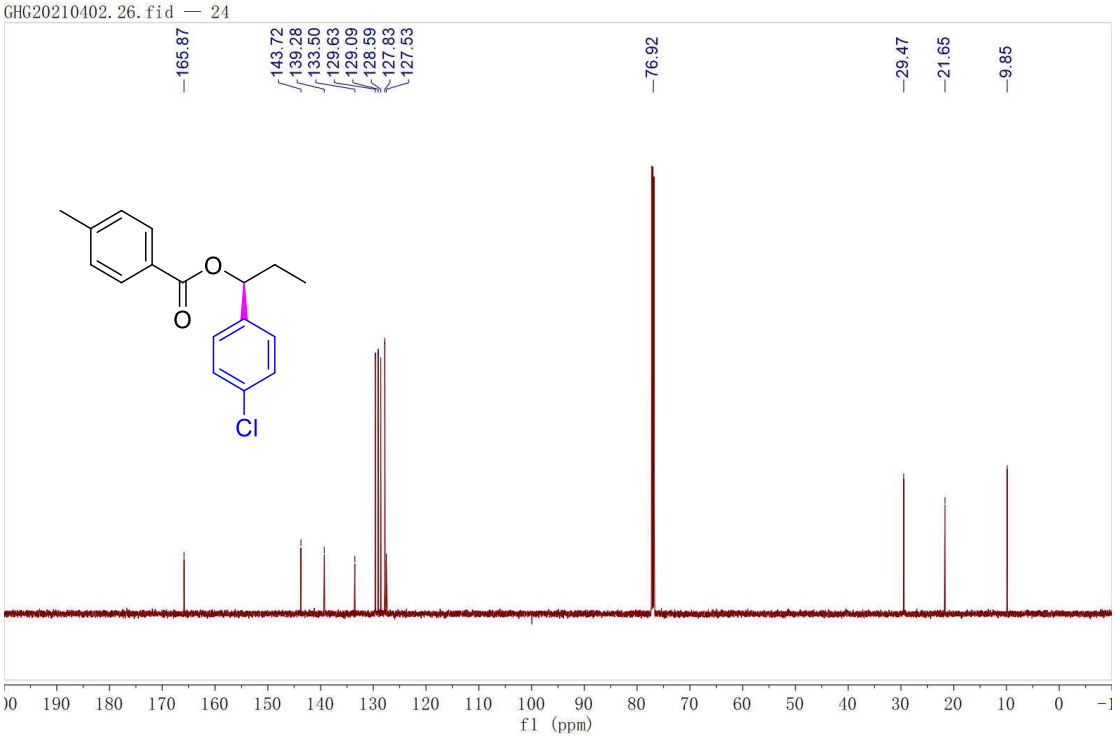
45, ^{13}C NMR (101 MHz, $CDCl_3$)



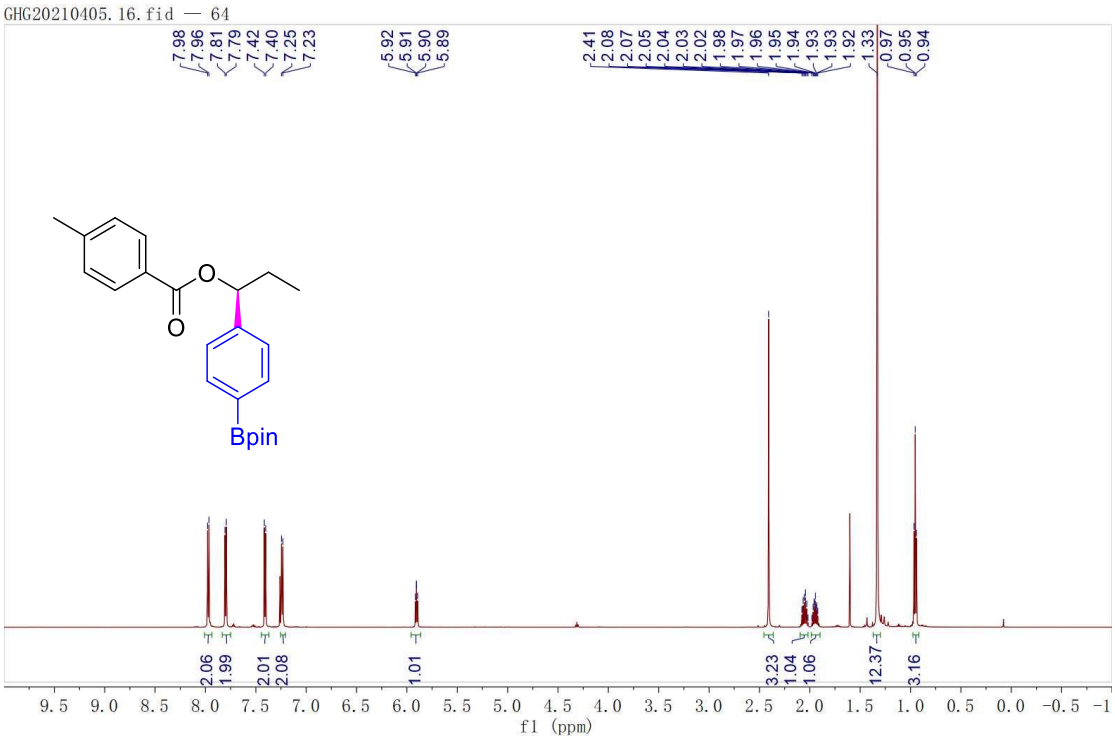
46, ^{1}H-NMR (600 MHZ, $CDCl_3$)



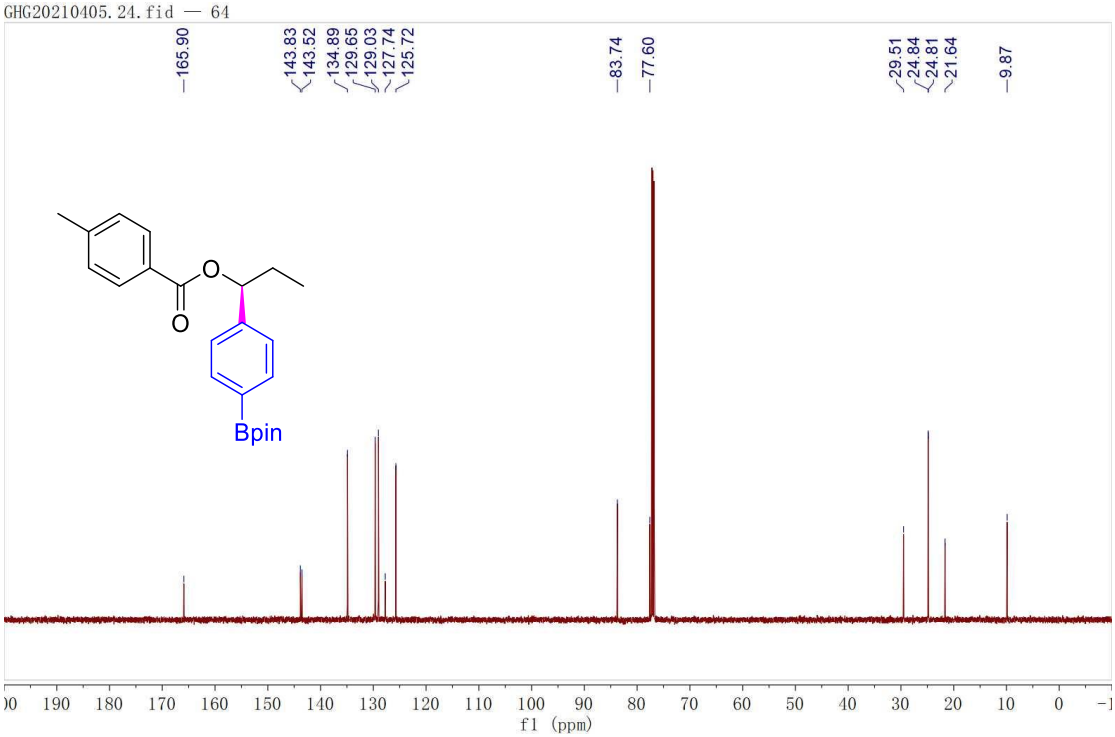
46, ^{13}C NMR (151 MHz, $CDCl_3$)



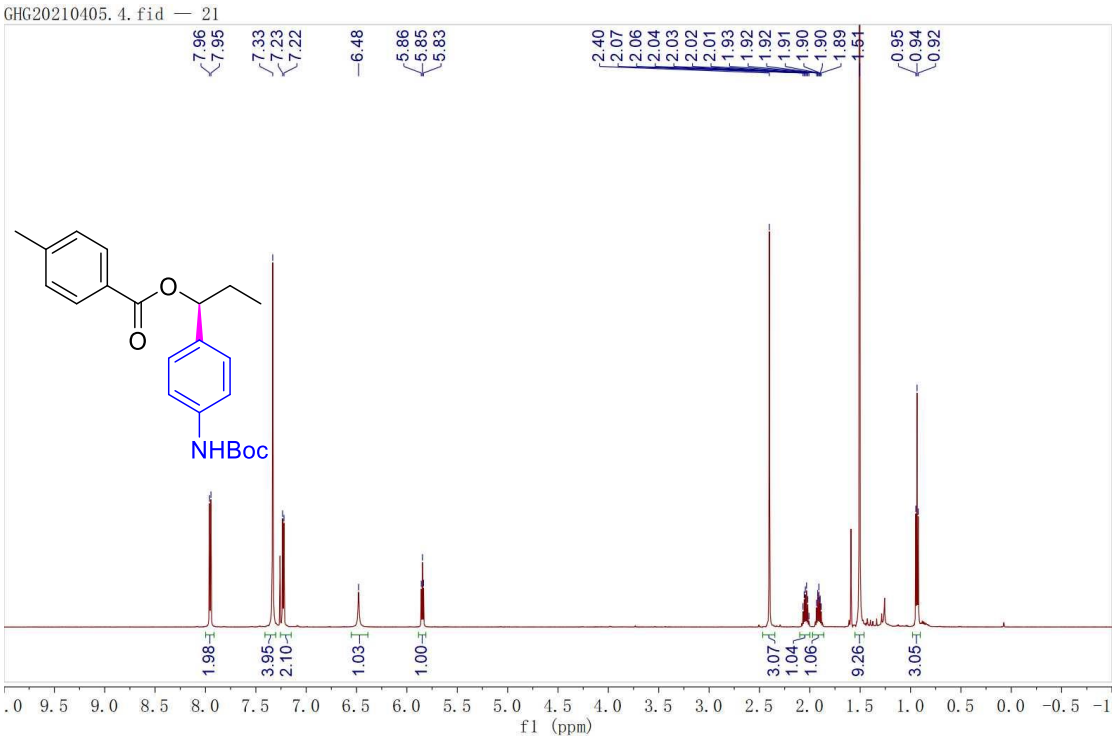
47, ^{1}H-NMR (600 MHZ, $CDCl_3$)



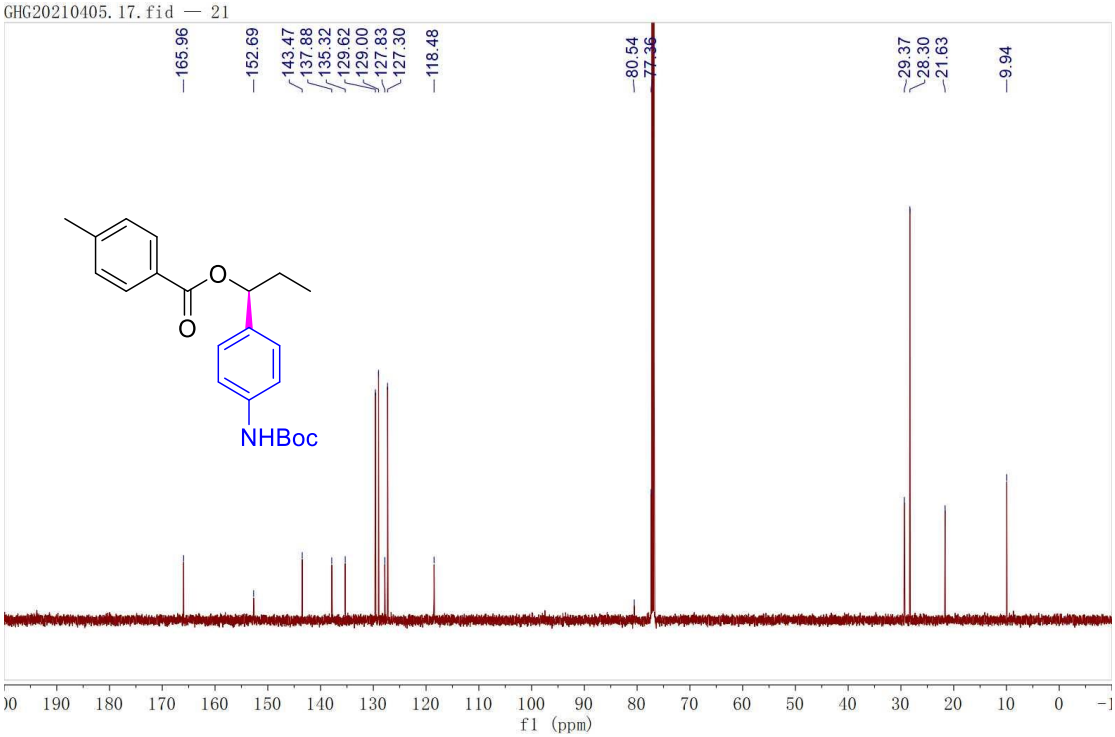
47, ^{13}C NMR (151 MHz, $CDCl_3$)



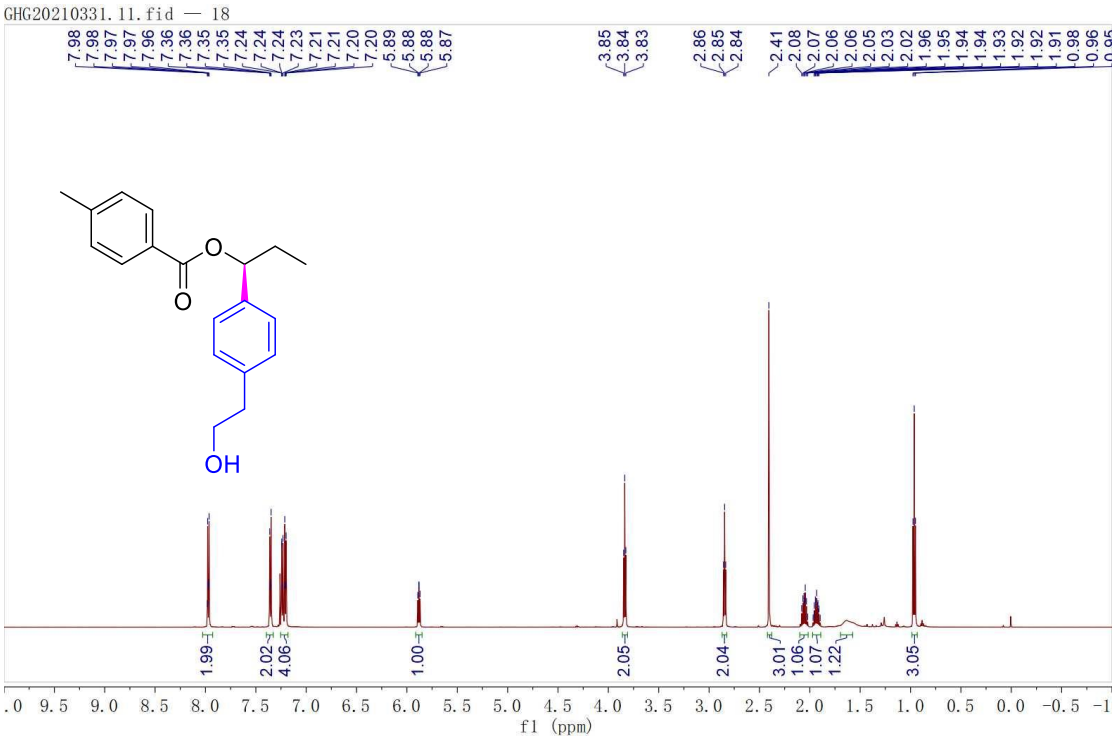
48, ^{1}H-NMR (600 MHZ, $CDCl_3$)



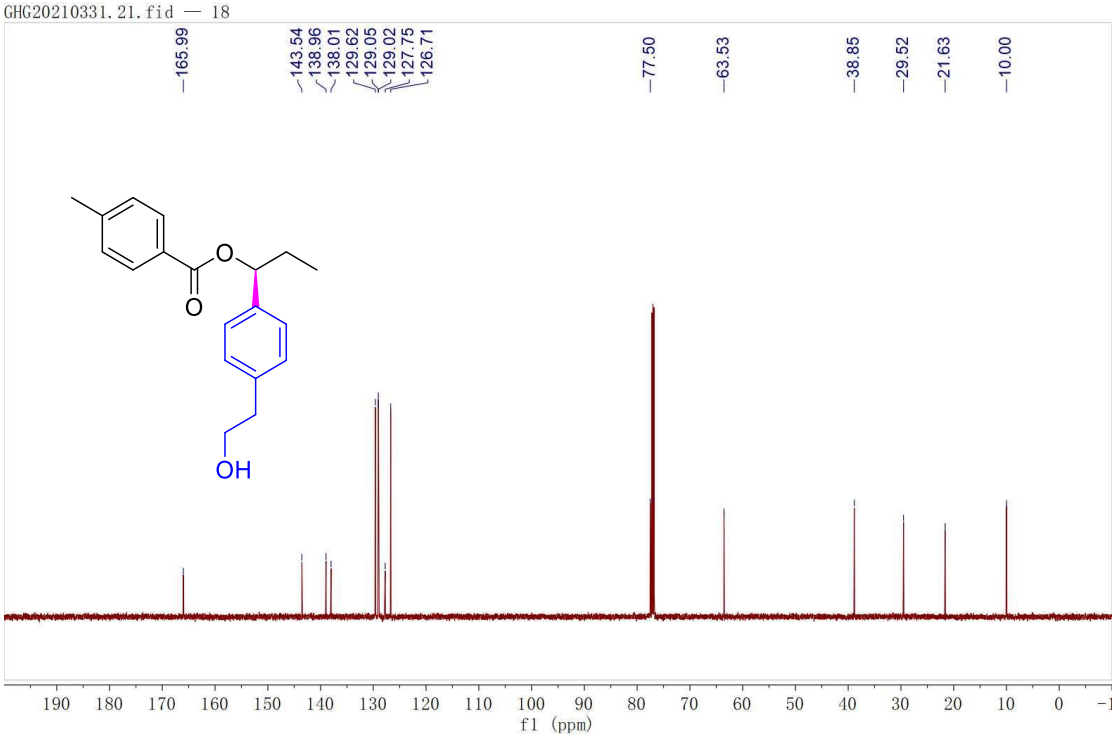
48, ^{13}C NMR (151 MHz, $CDCl_3$)



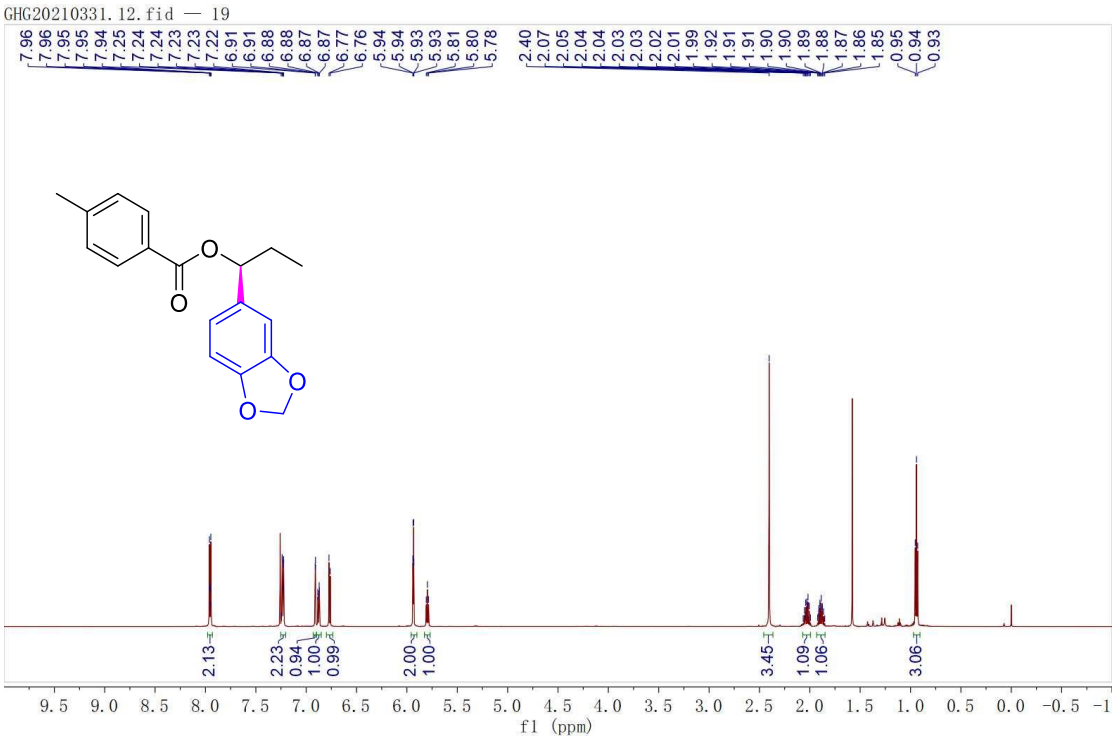
49, ^{1}H-NMR (600 MHZ, $CDCl_3$)



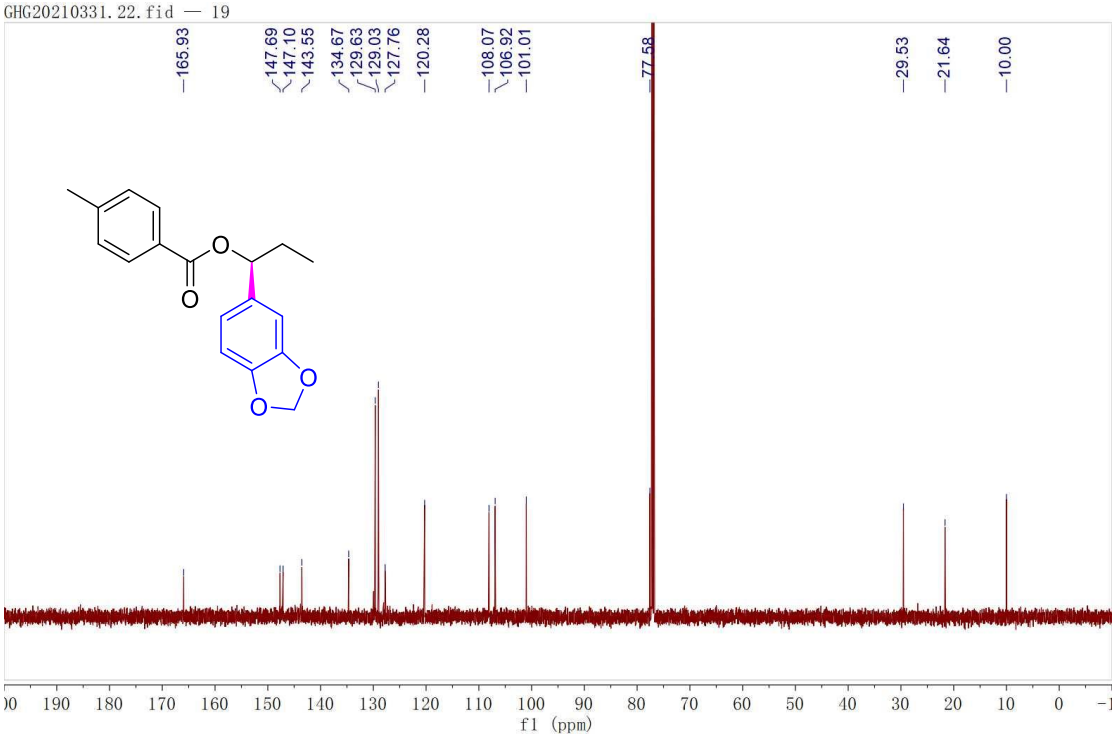
49, ^{13}C NMR (151 MHz, $CDCl_3$)



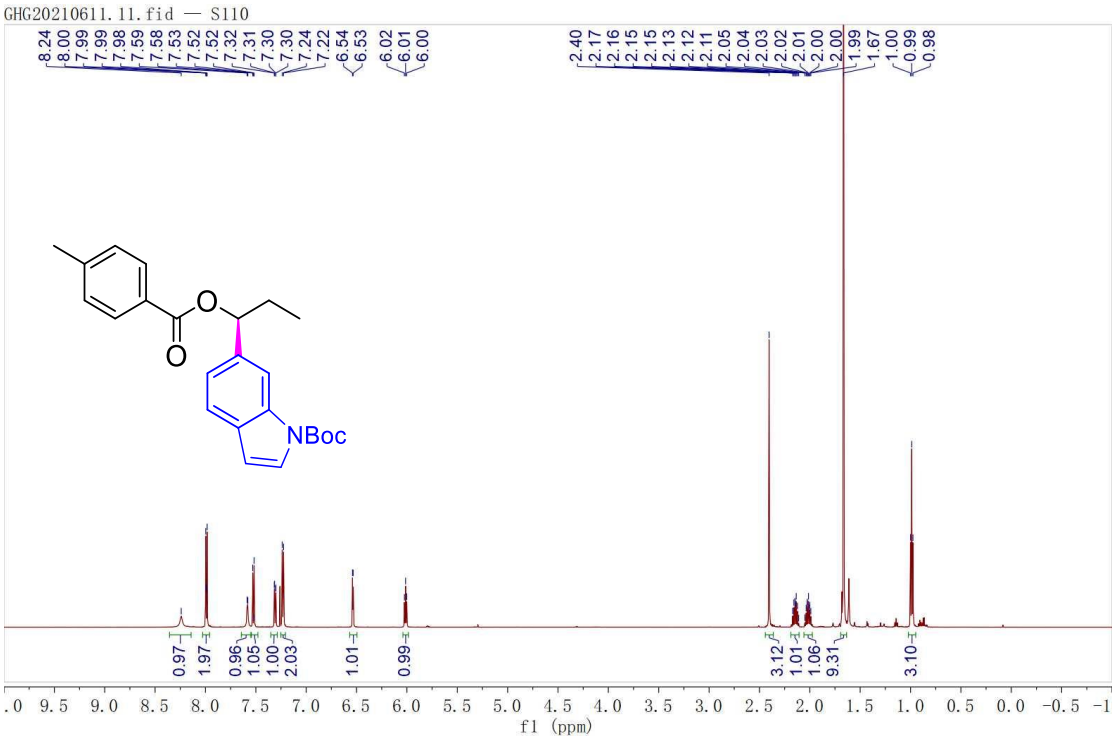
50, ^{1}H-NMR (600 MHZ, $CDCl_3$)



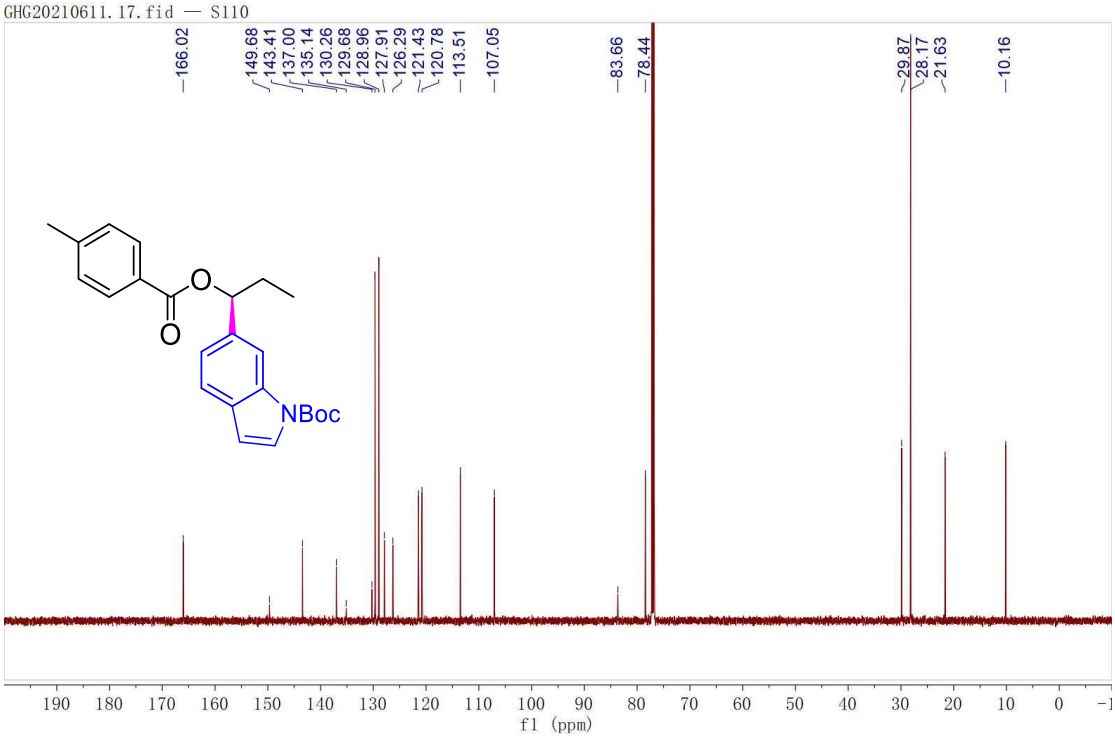
50, ^{13}C NMR (151 MHz, $CDCl_3$)



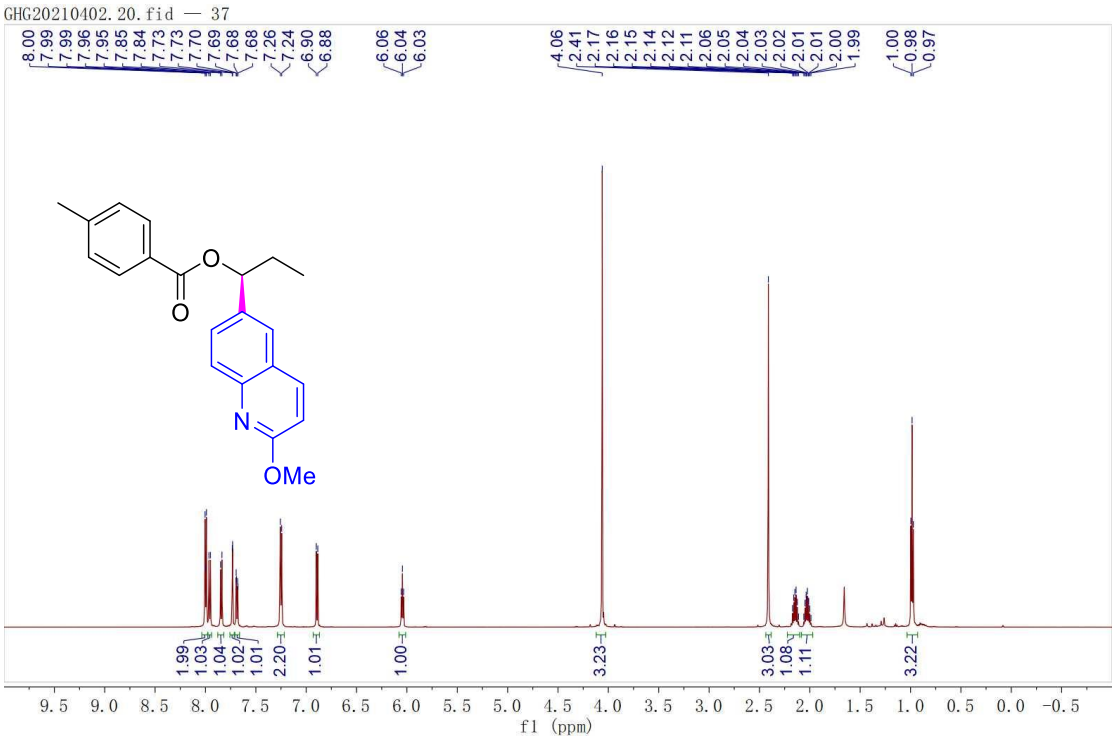
51, ^{1}H-NMR (600 MHZ, $CDCl_3$)



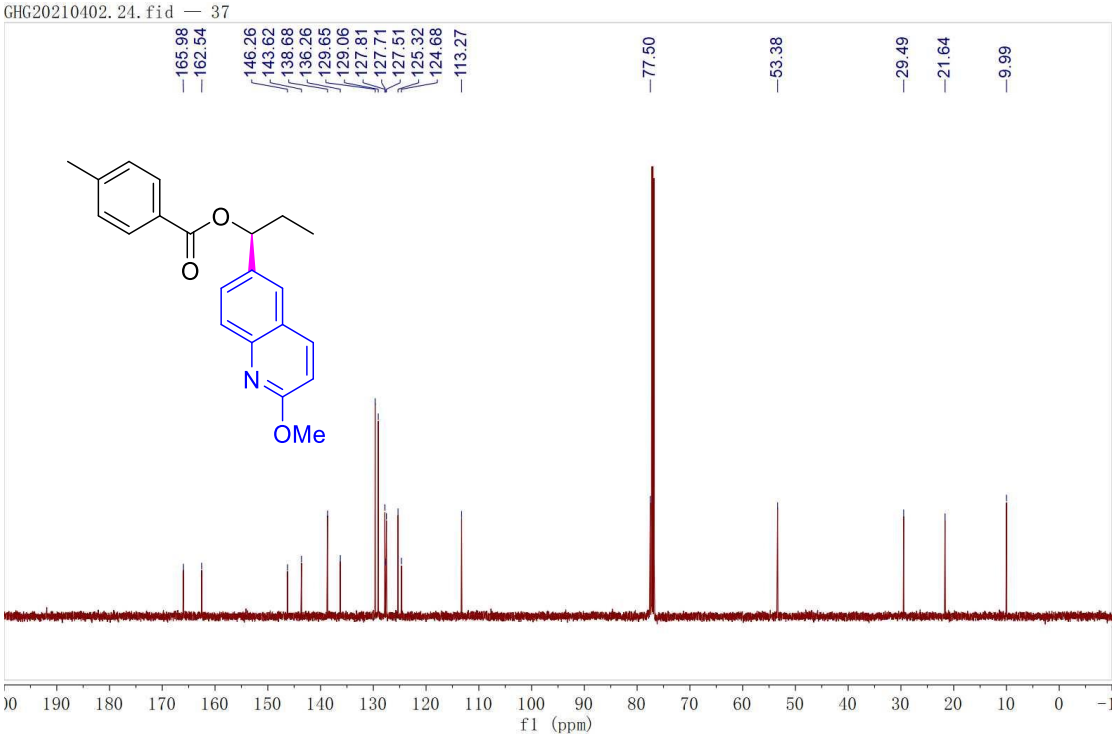
51, ^{13}C NMR (151 MHz, $CDCl_3$)



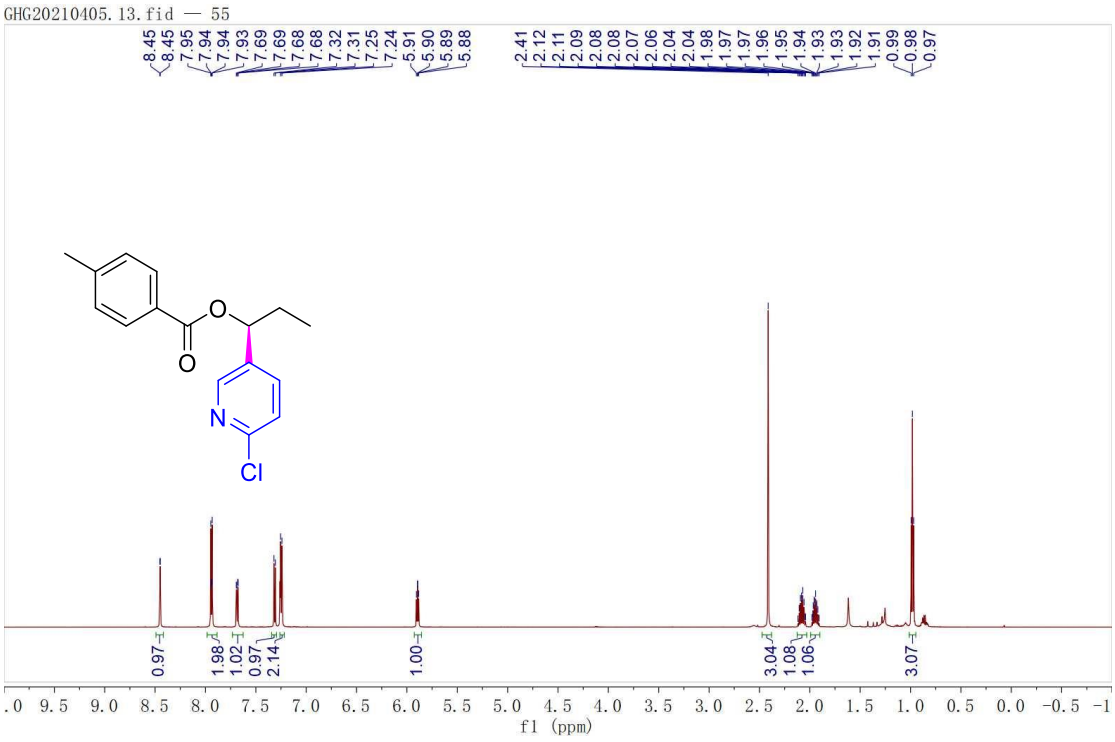
52, ^{1}H-NMR (600 MHZ, $CDCl_3$)



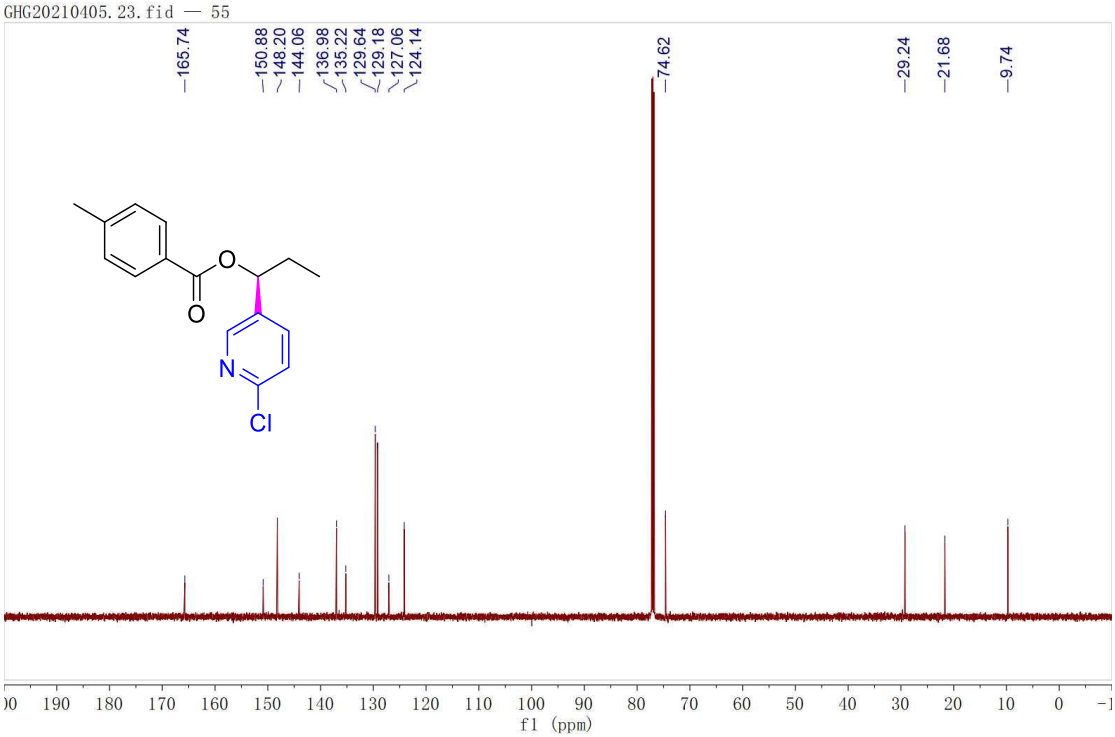
52, ^{13}C NMR (151 MHz, $CDCl_3$)



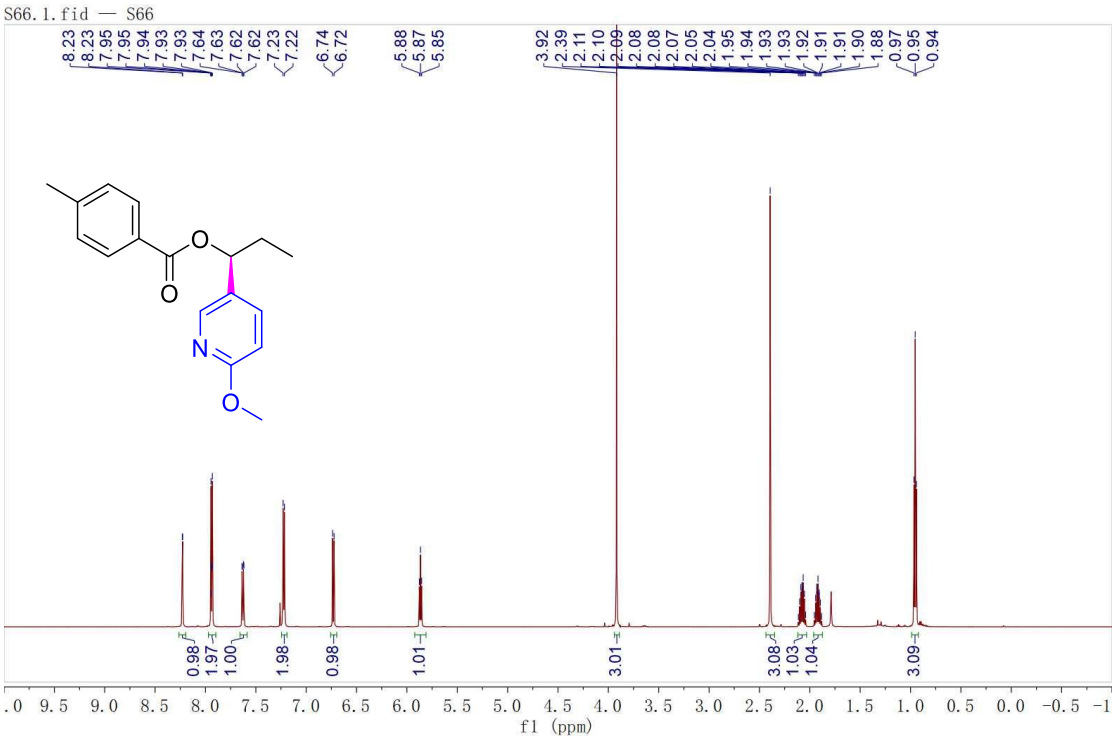
53, ^{1}H-NMR (600 MHZ, $CDCl_3$)



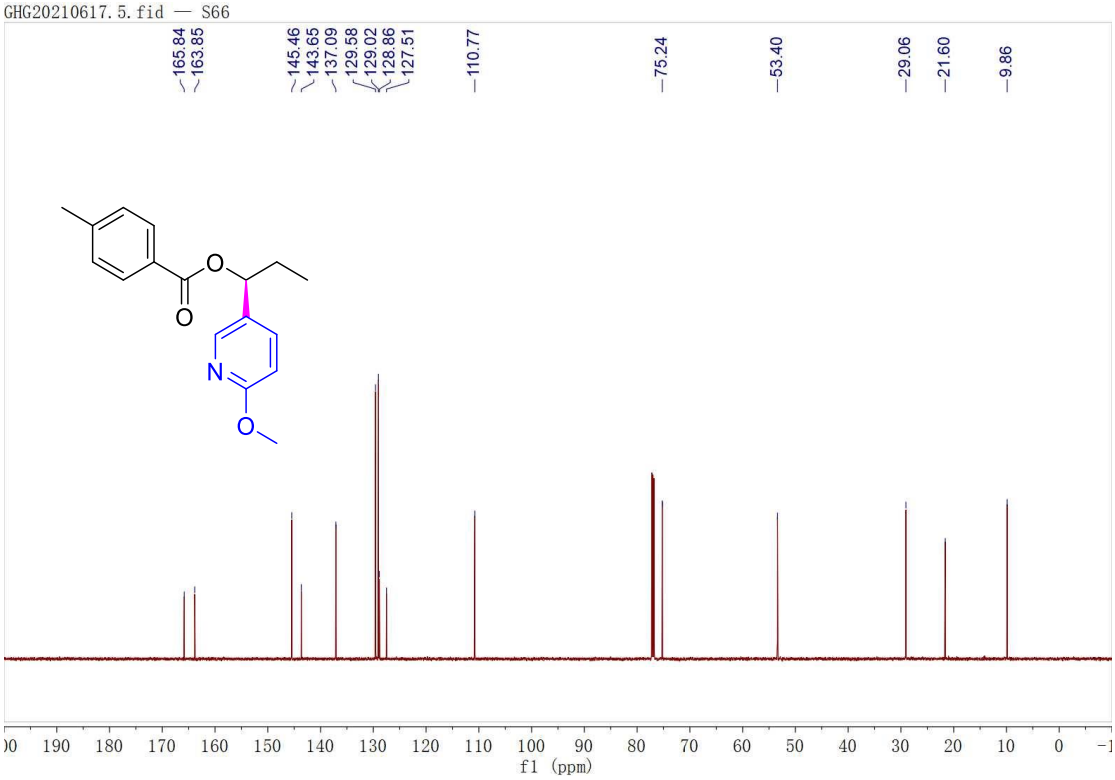
53, ^{13}C NMR (151 MHz, $CDCl_3$)



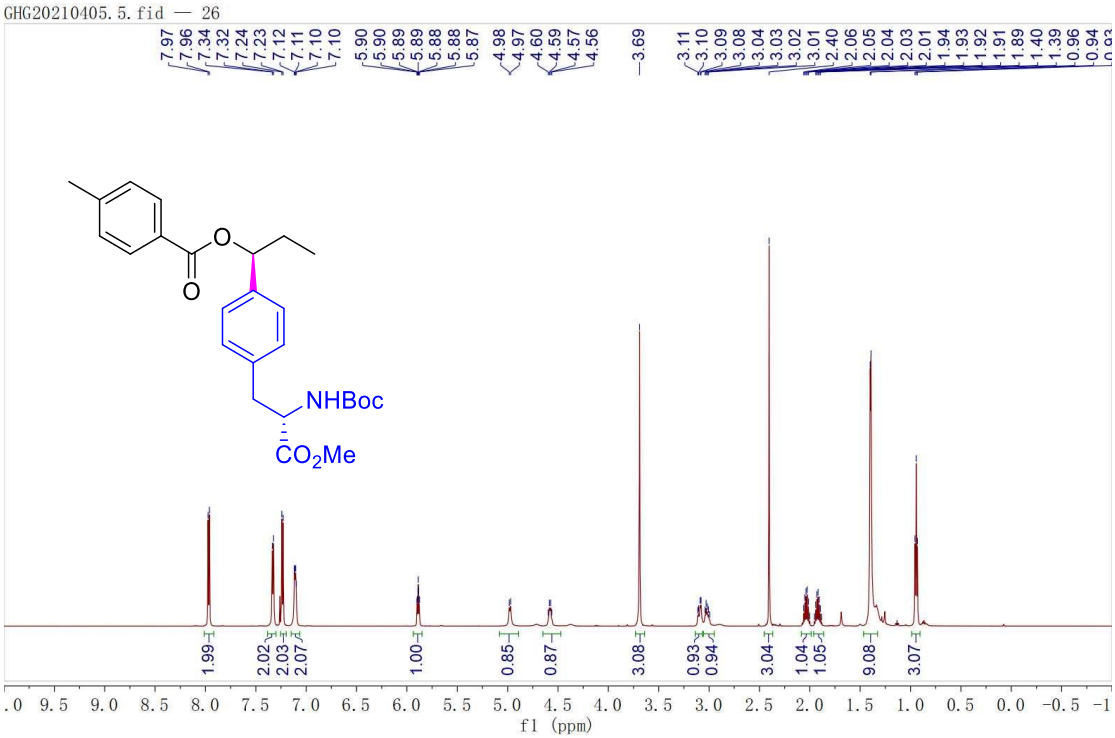
54, ^{1}H-NMR (600 MHZ, $CDCl_3$)



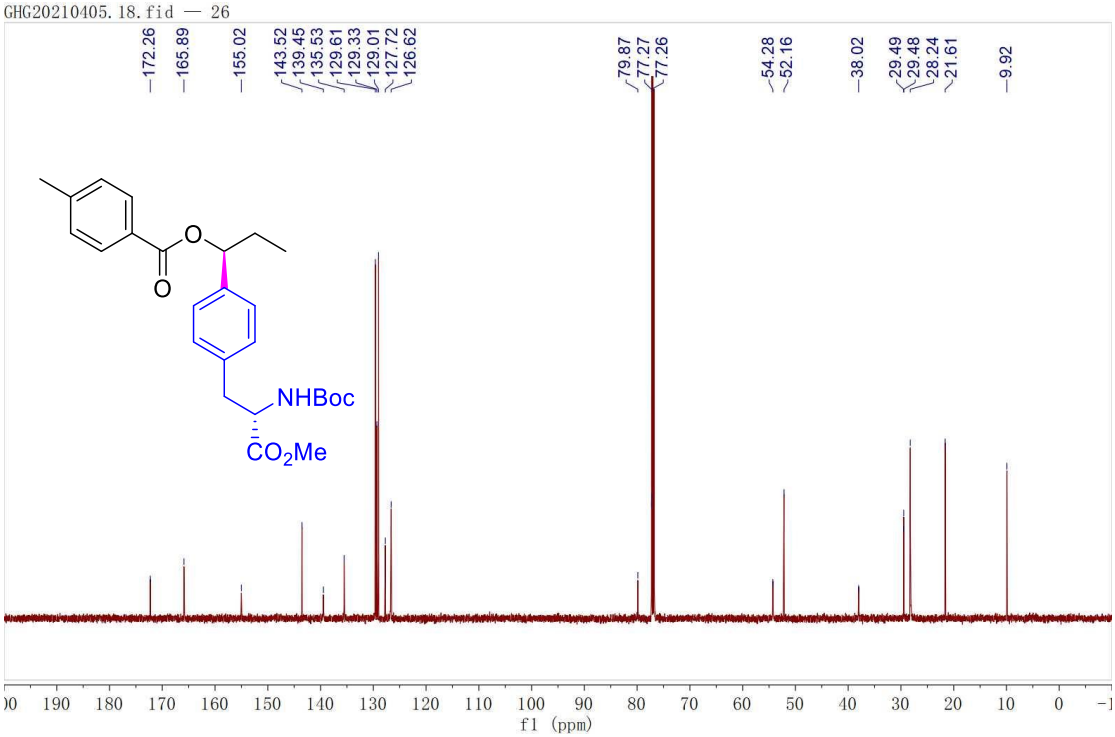
54, ^{13}C NMR (151 MHz, $CDCl_3$)



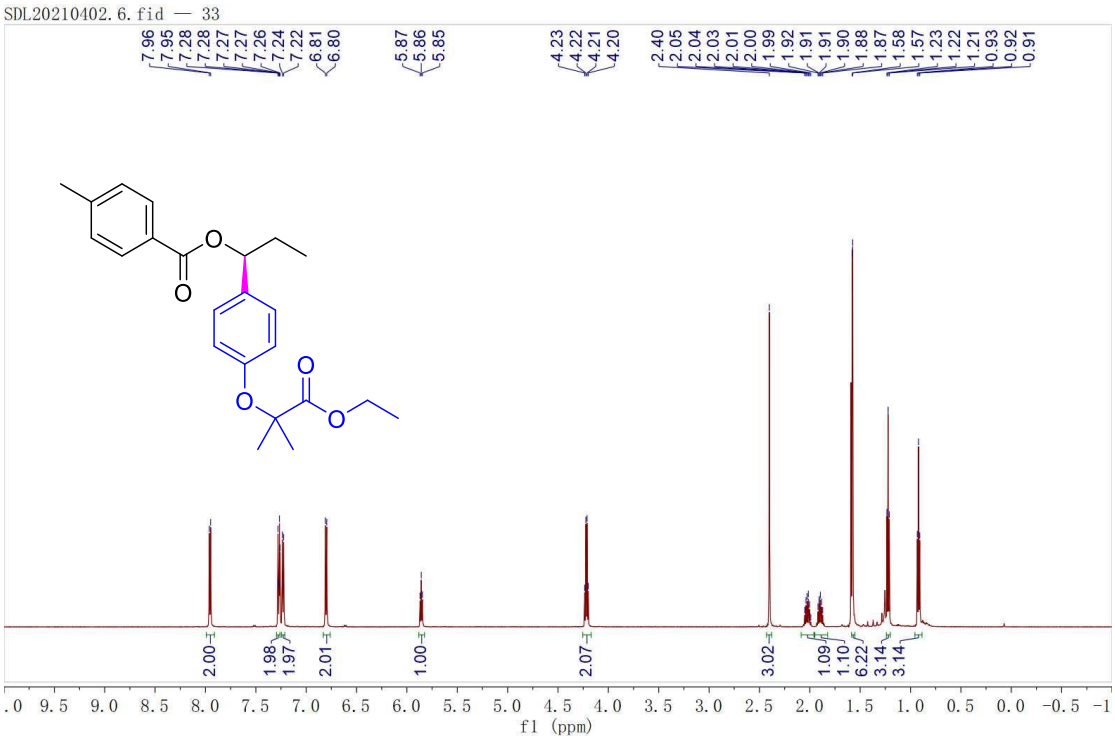
55, ^{1}H-NMR (600 MHZ, $CDCl_3$)



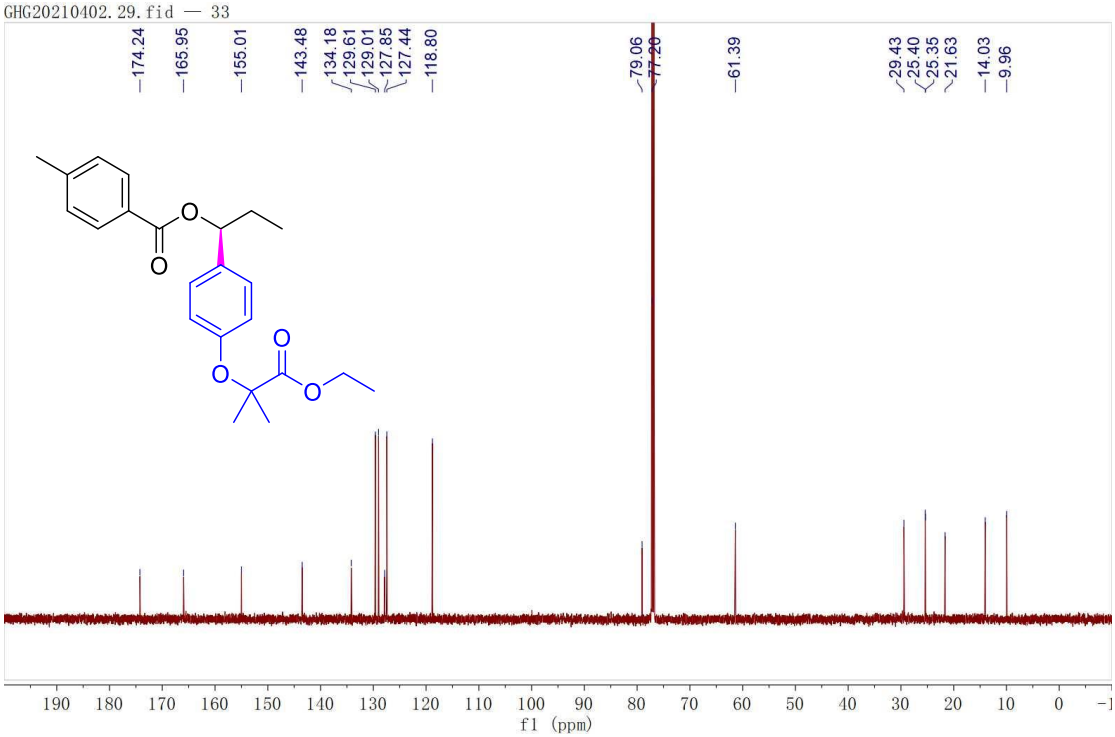
55, ^{13}C NMR (151 MHz, $CDCl_3$)



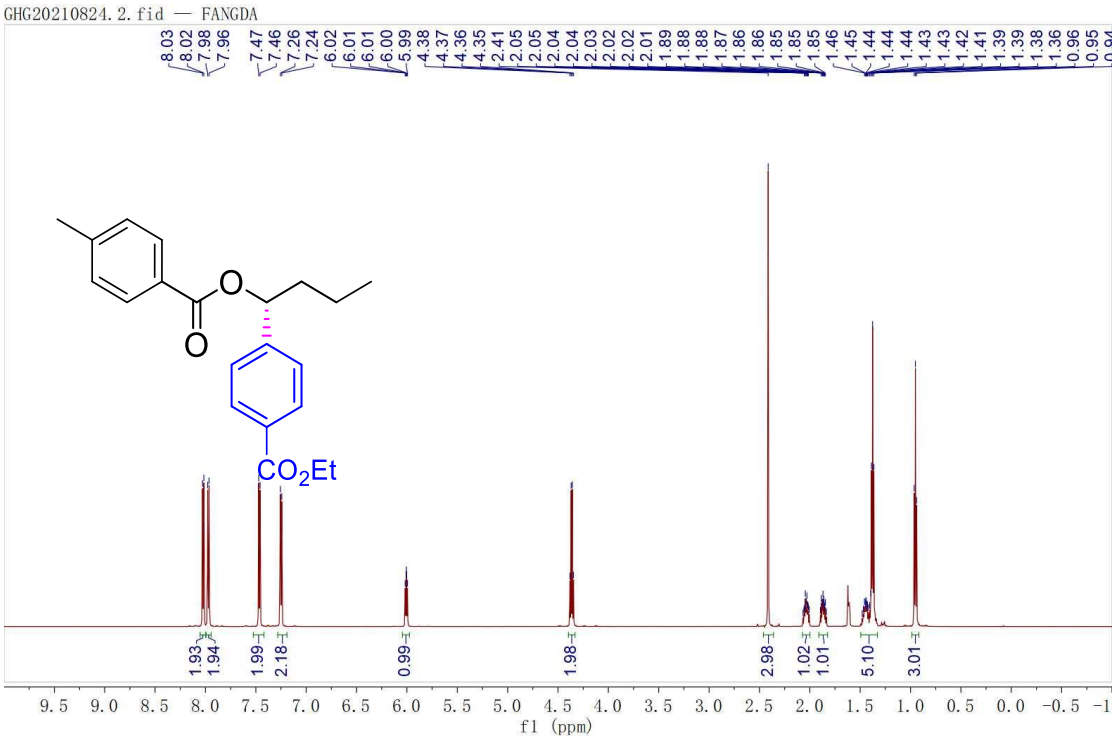
56, ^{1}H-NMR (600 MHZ, $CDCl_3$)



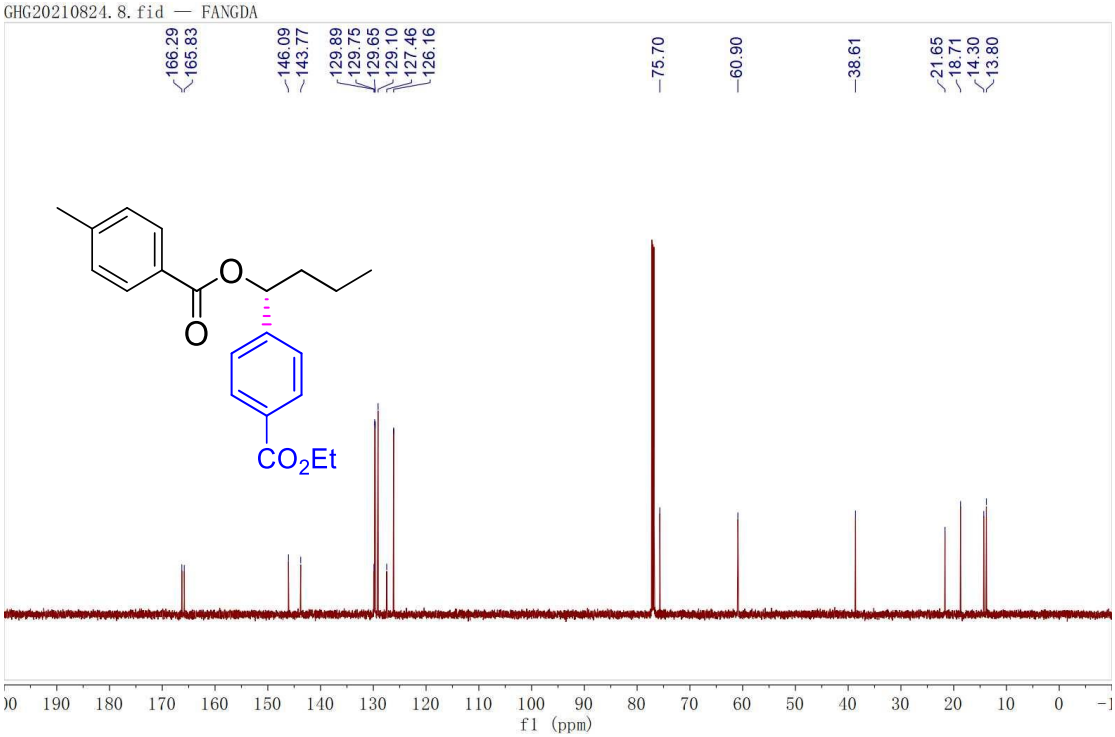
56, ^{13}C NMR (151 MHz, $CDCl_3$)



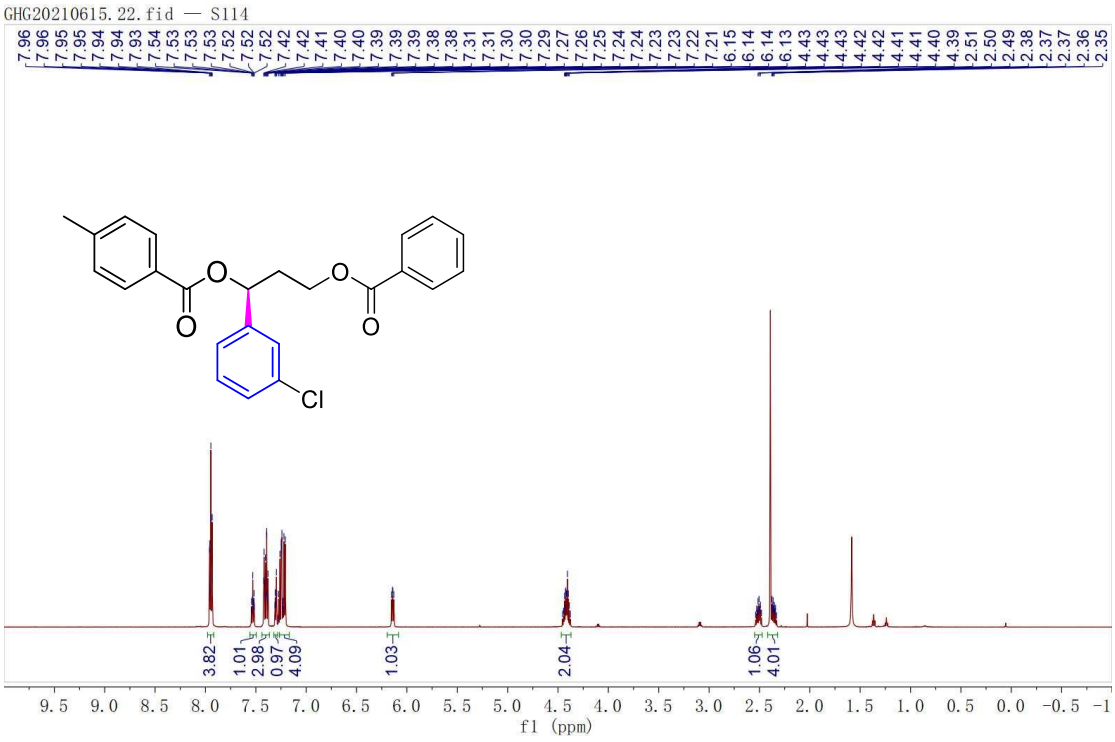
57, ^{1}H-NMR (600 MHZ, $CDCl_3$)



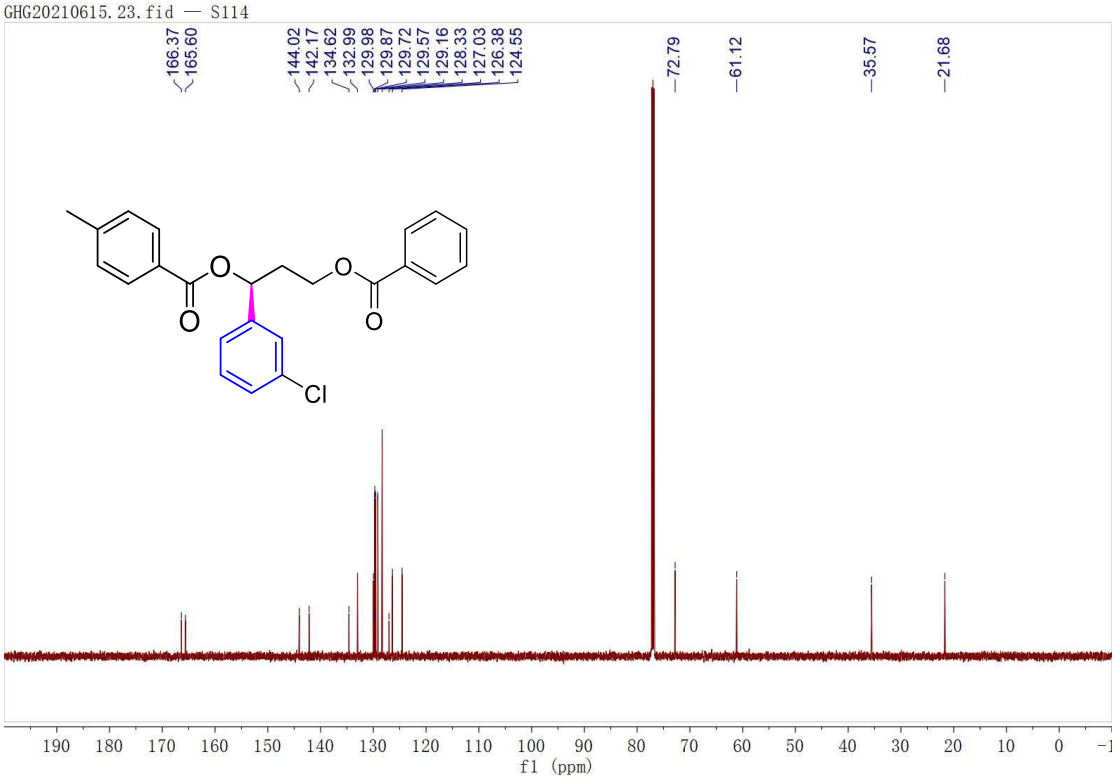
57, ^{13}C NMR (151 MHz, $CDCl_3$)



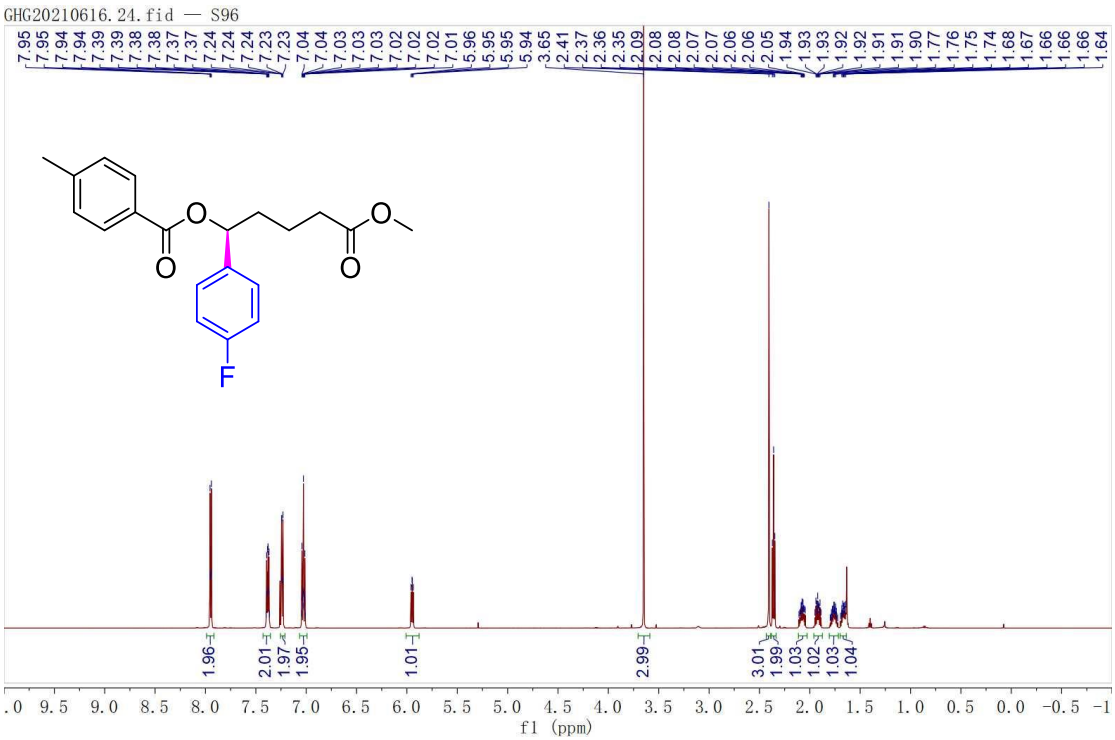
58, ^{1}H-NMR (600 MHZ, $CDCl_3$)



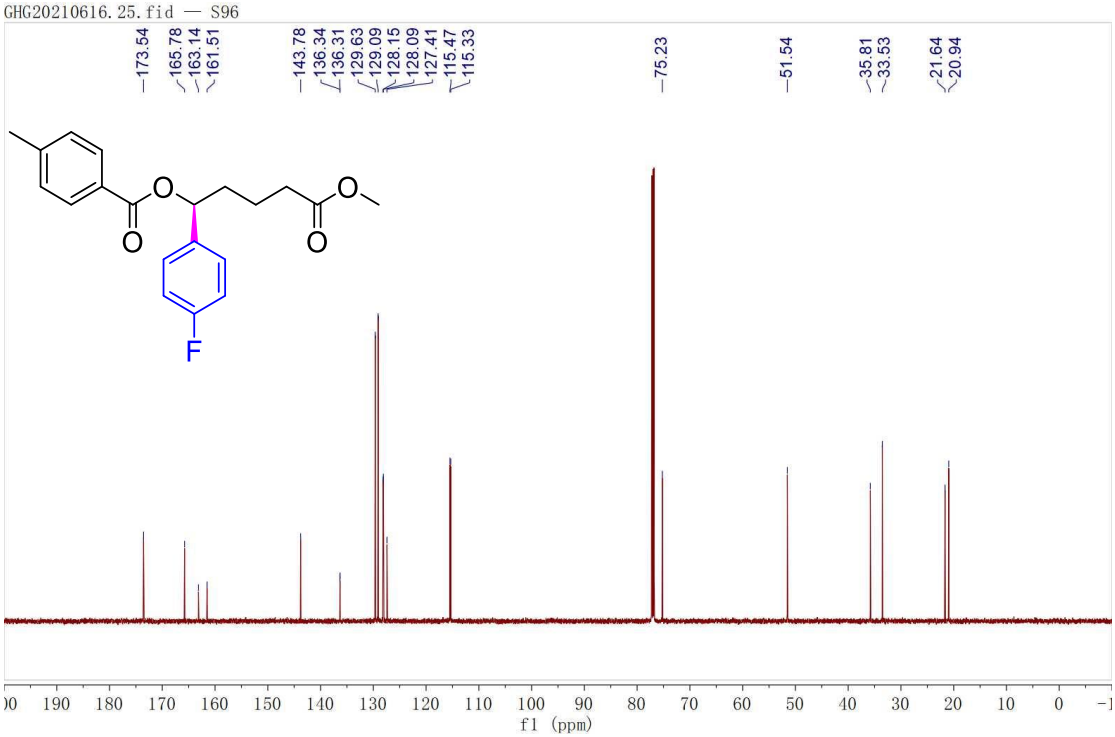
58, ^{13}C NMR (151 MHz, $CDCl_3$)



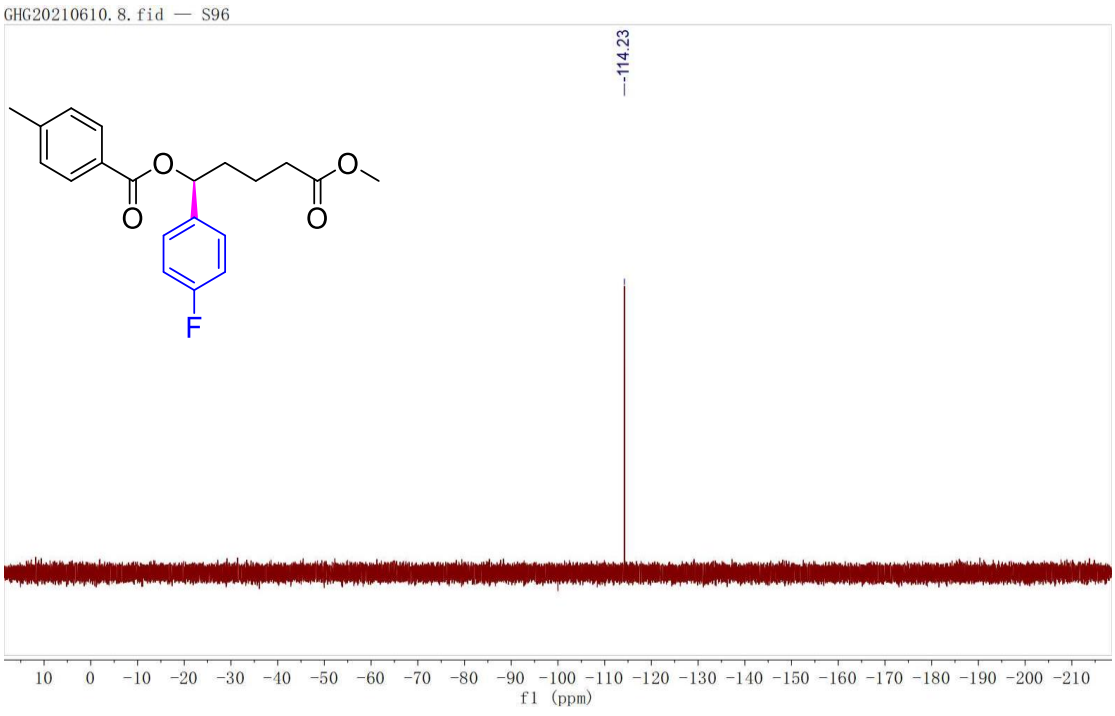
59, ^{1}H-NMR (600 MHZ, $CDCl_3$)



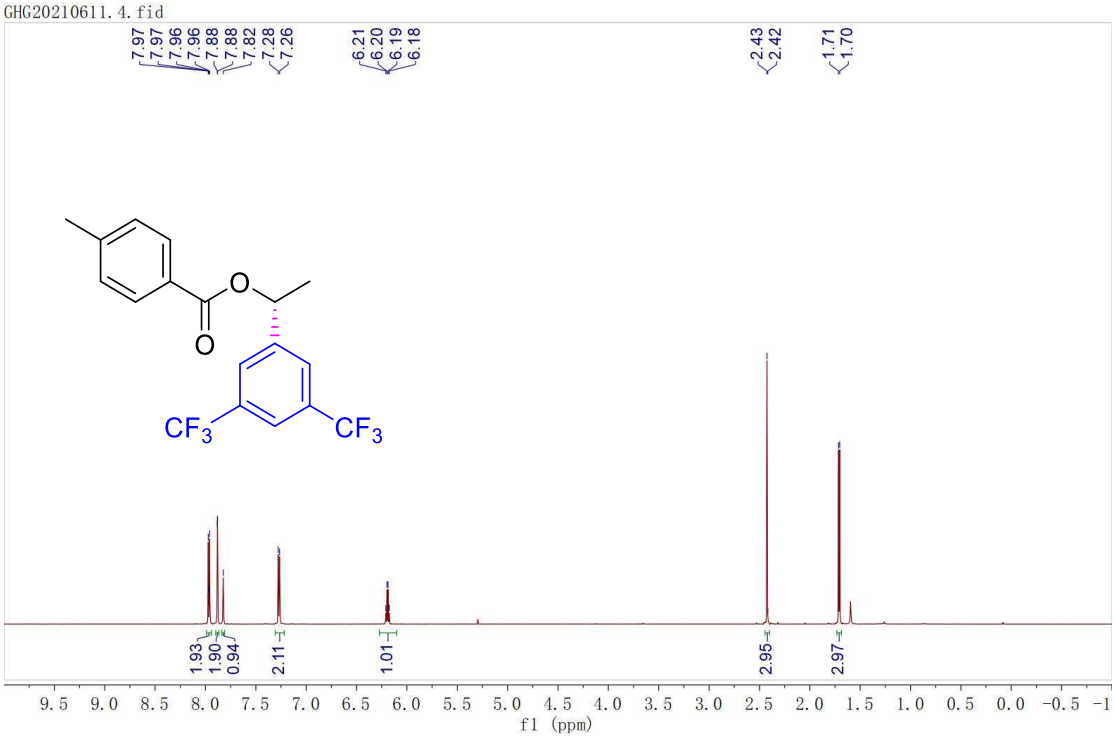
59, ^{13}C NMR (151 MHz, $CDCl_3$)



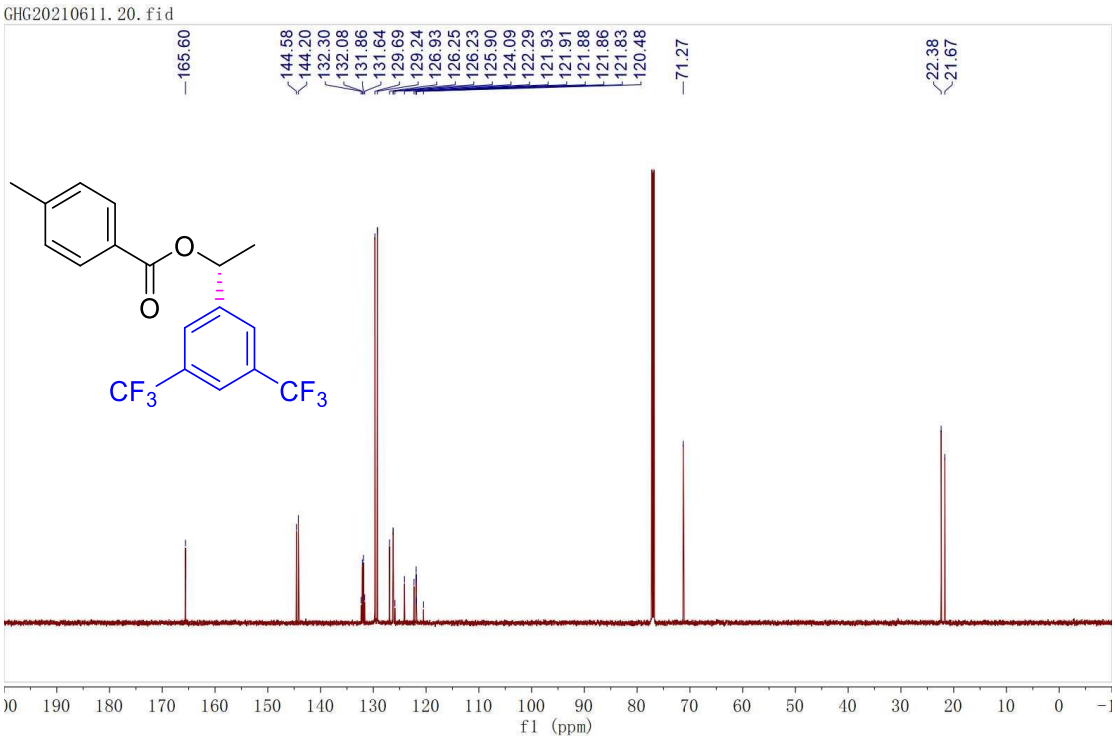
59, ^{9}F NMR (565 MHz, $CDCl_3$)



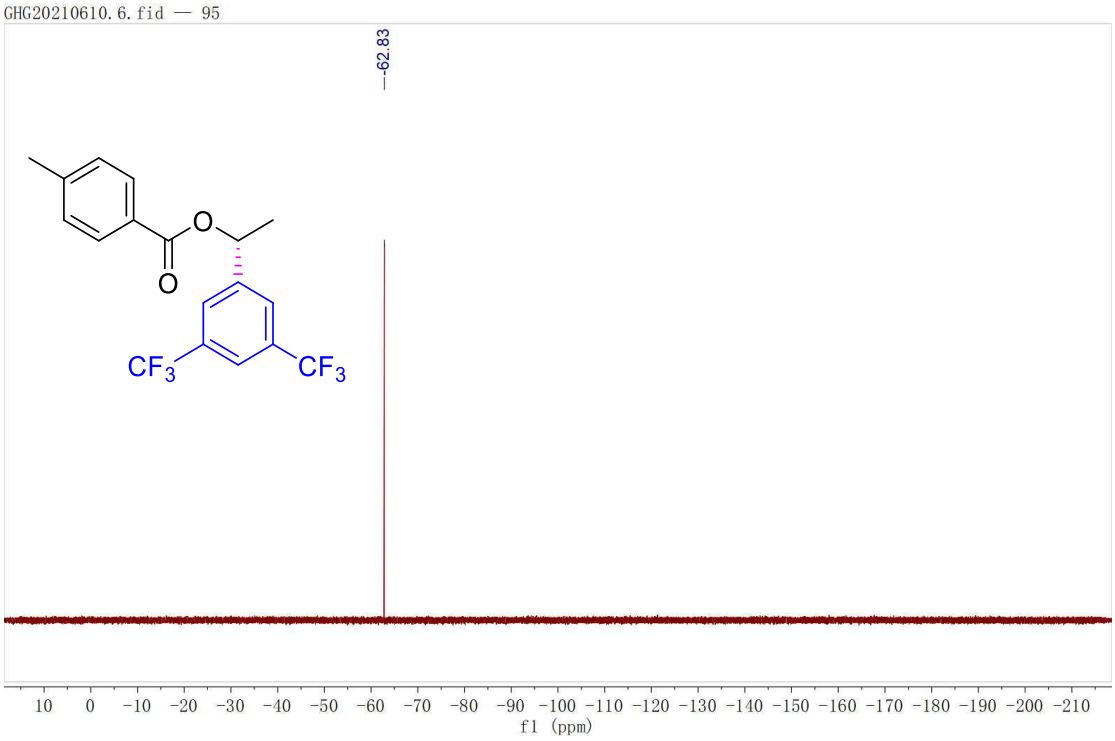
60, ^{1}H-NMR (600 MHZ, $CDCl_3$)



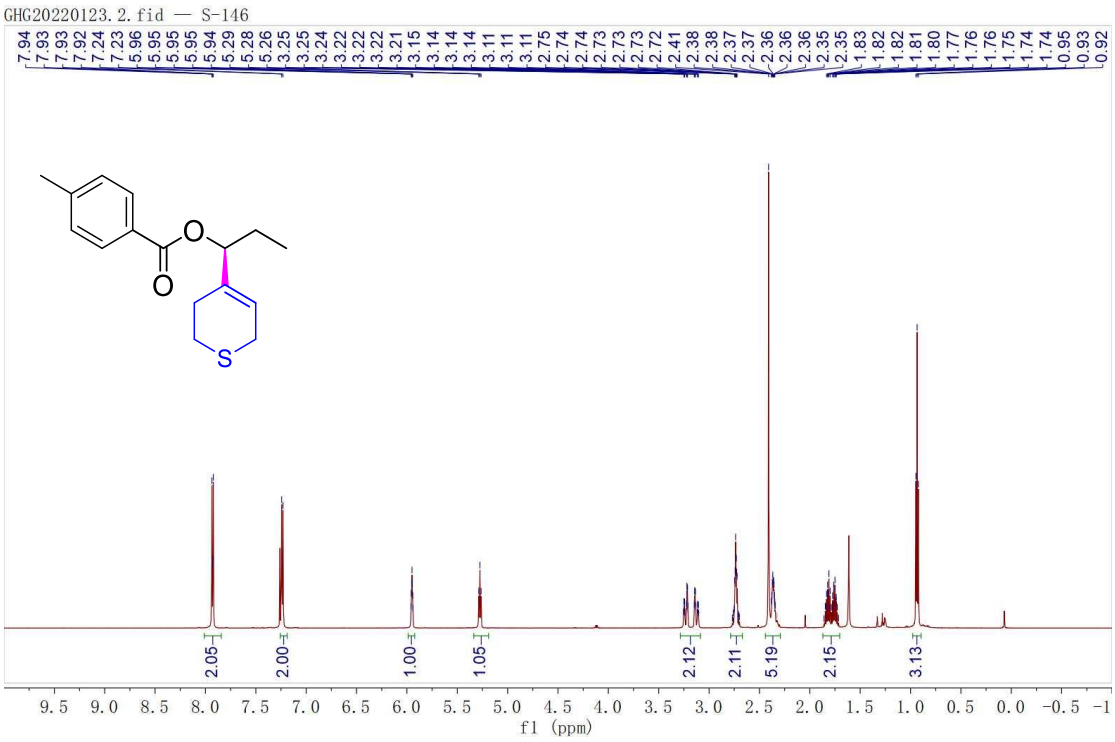
60, ^{13}C NMR (151 MHz, $CDCl_3$)



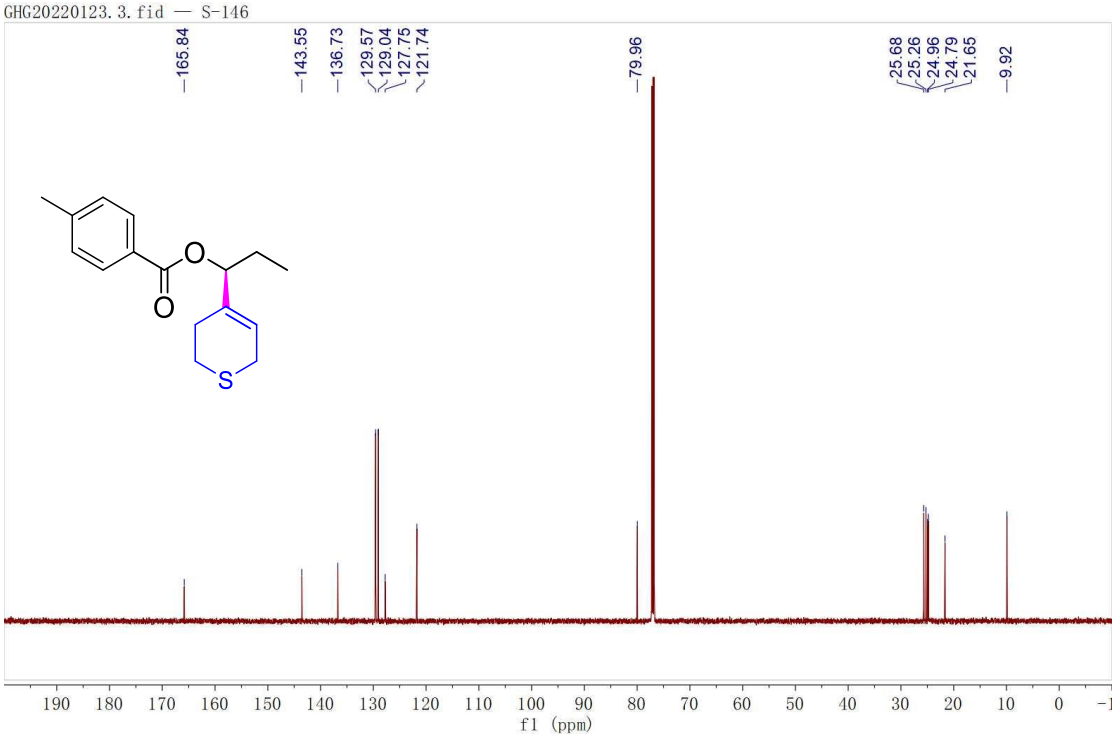
60, ^{9}F NMR (565 MHz, $CDCl_3$)



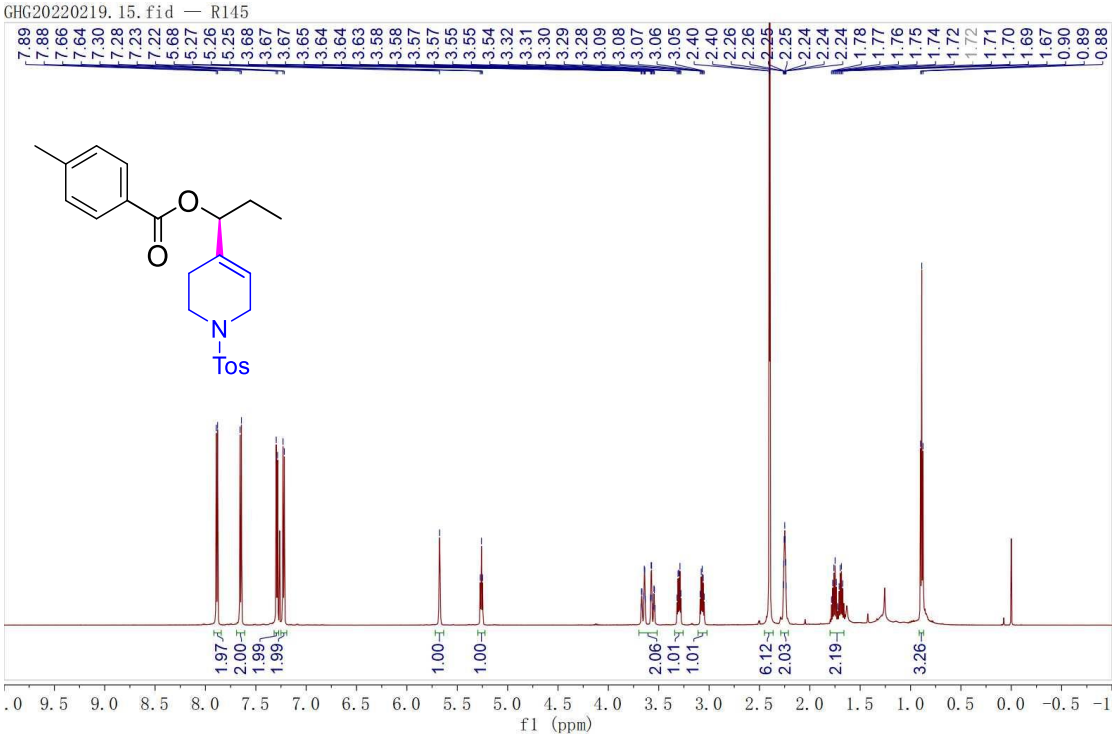
61, ^{1}H-NMR (600 MHZ, $CDCl_3$)



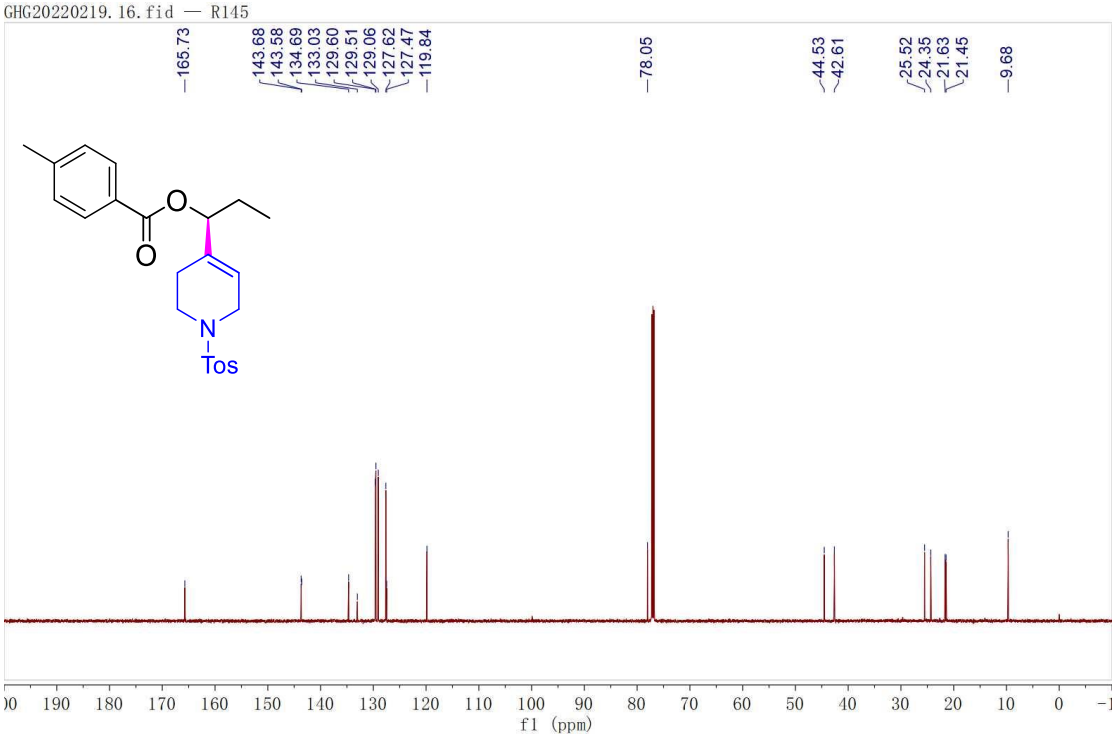
61, ^{13}C NMR (151 MHz, $CDCl_3$)



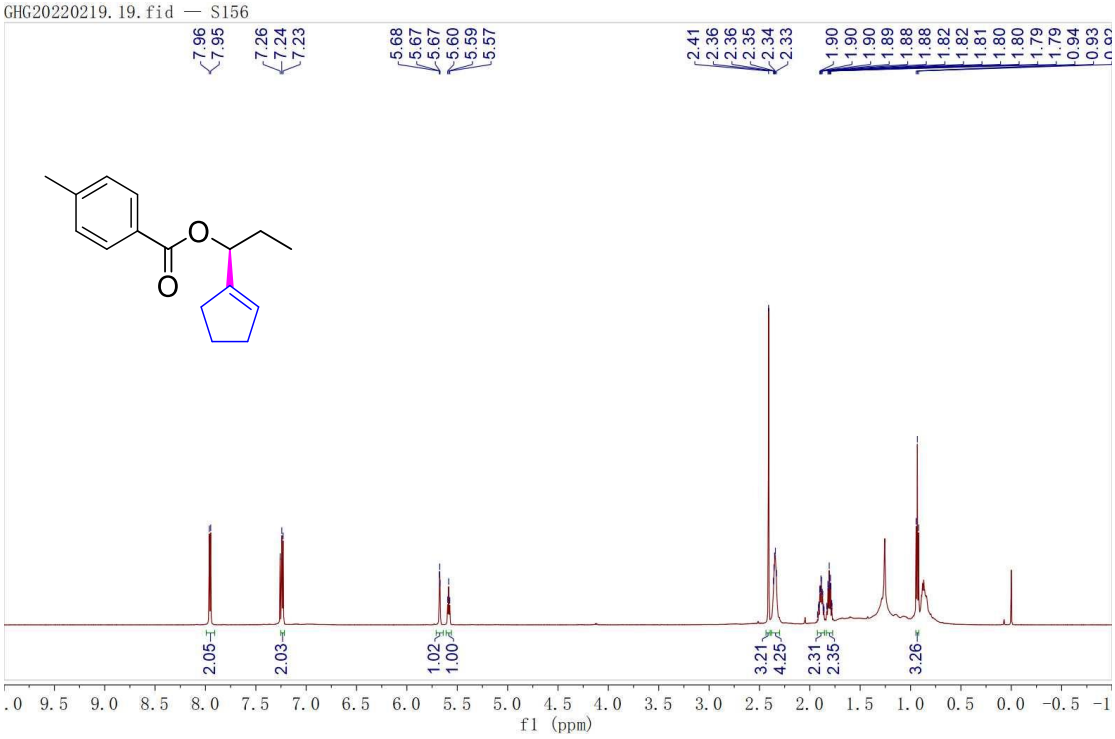
62, ^{1}H-NMR (600 MHZ, $CDCl_3$)



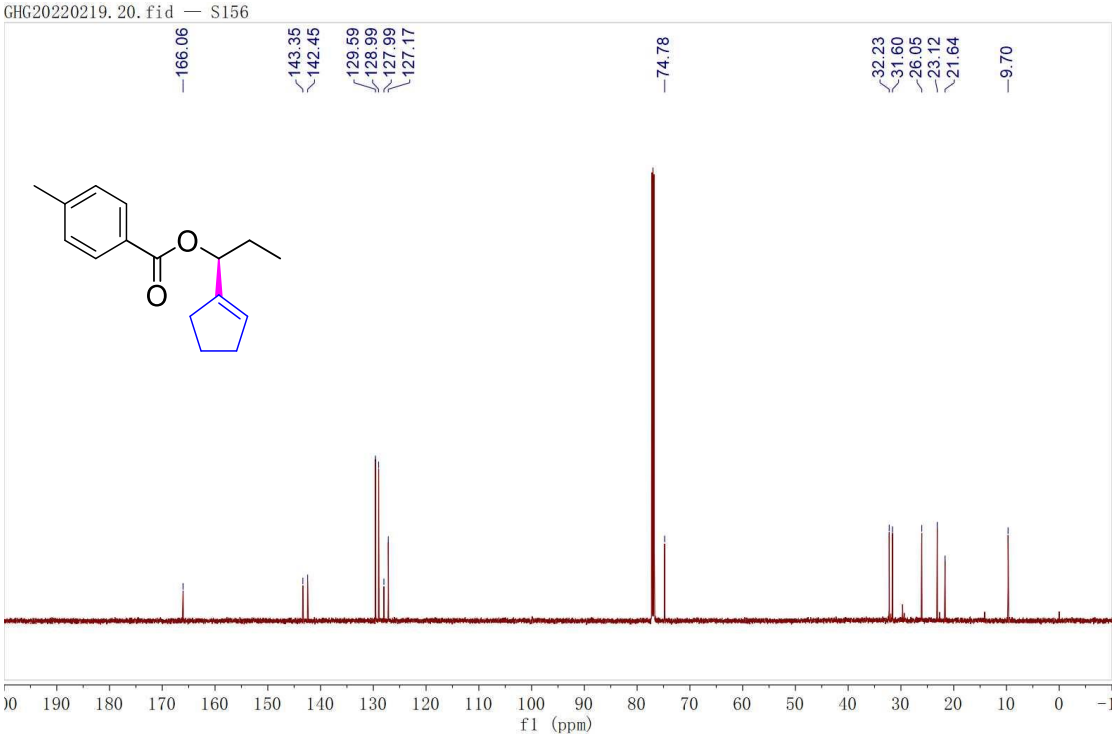
62, ^{13}C NMR (151 MHz, $CDCl_3$)



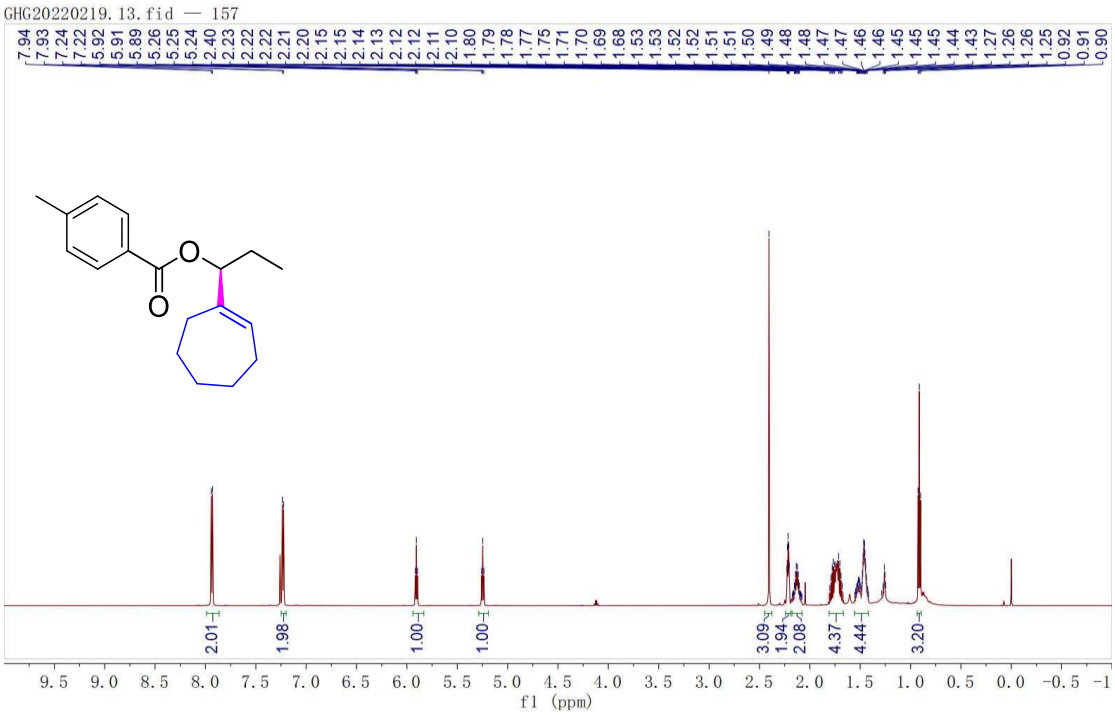
63, ^{1}H-NMR (600 MHZ, $CDCl_3$)



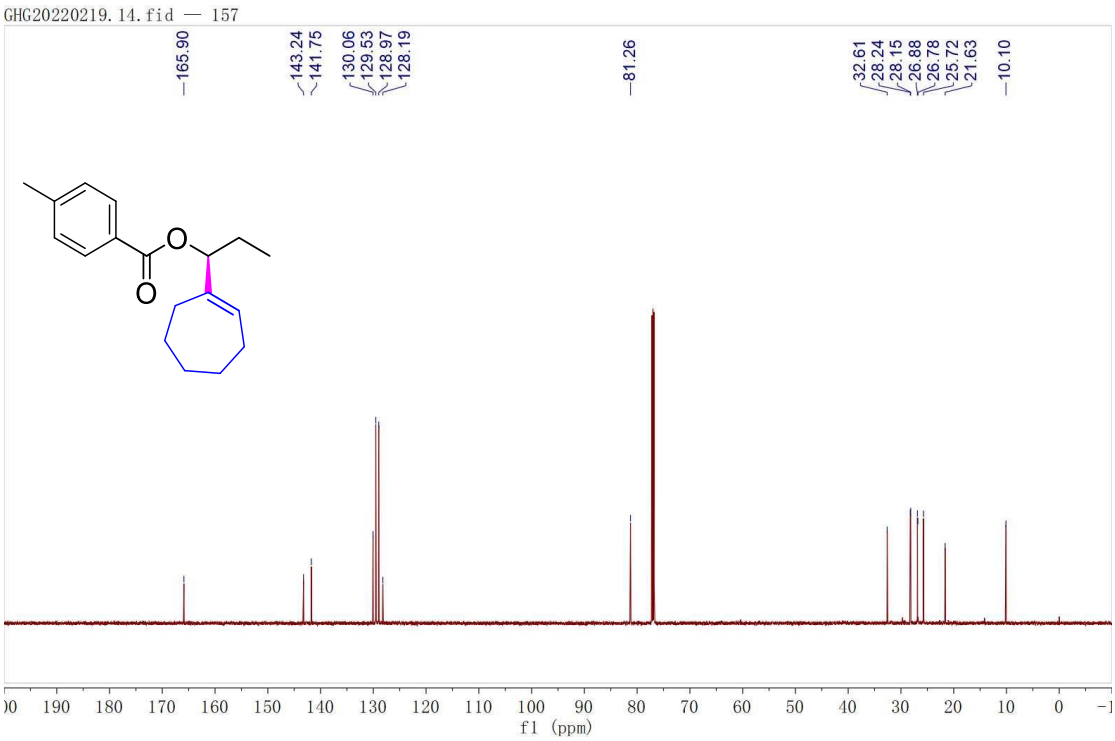
63, ^{13}C NMR (151 MHz, $CDCl_3$)



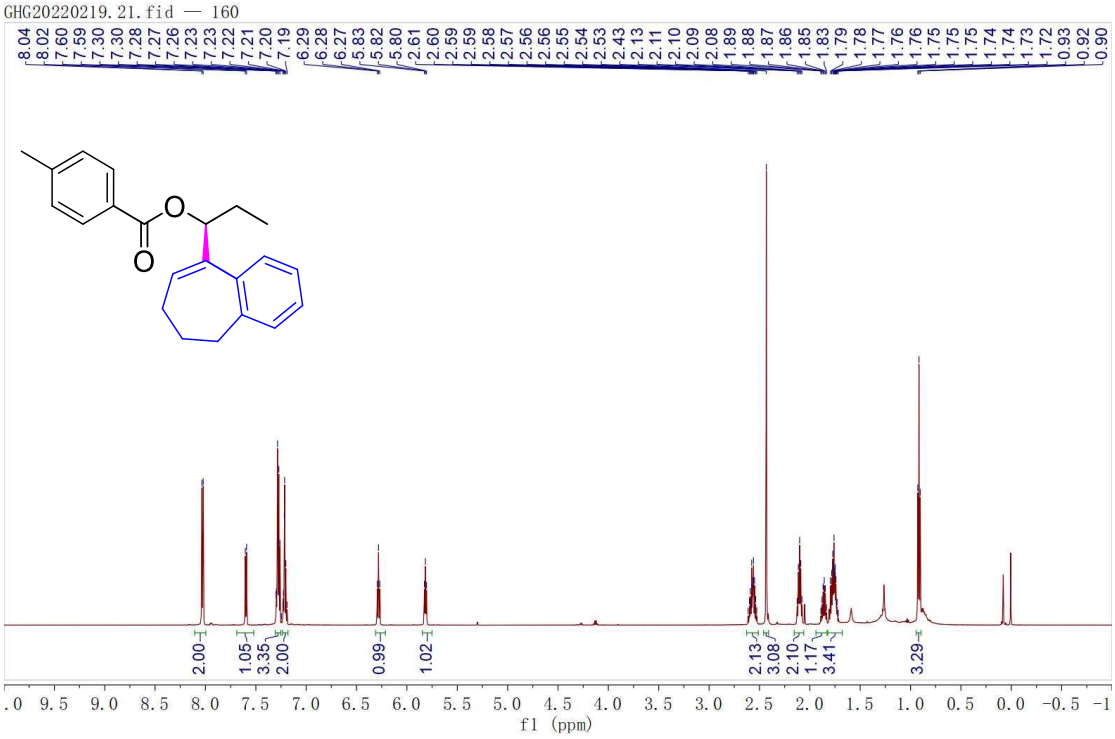
64, ^{1}H-NMR (600 MHZ, $CDCl_3$)



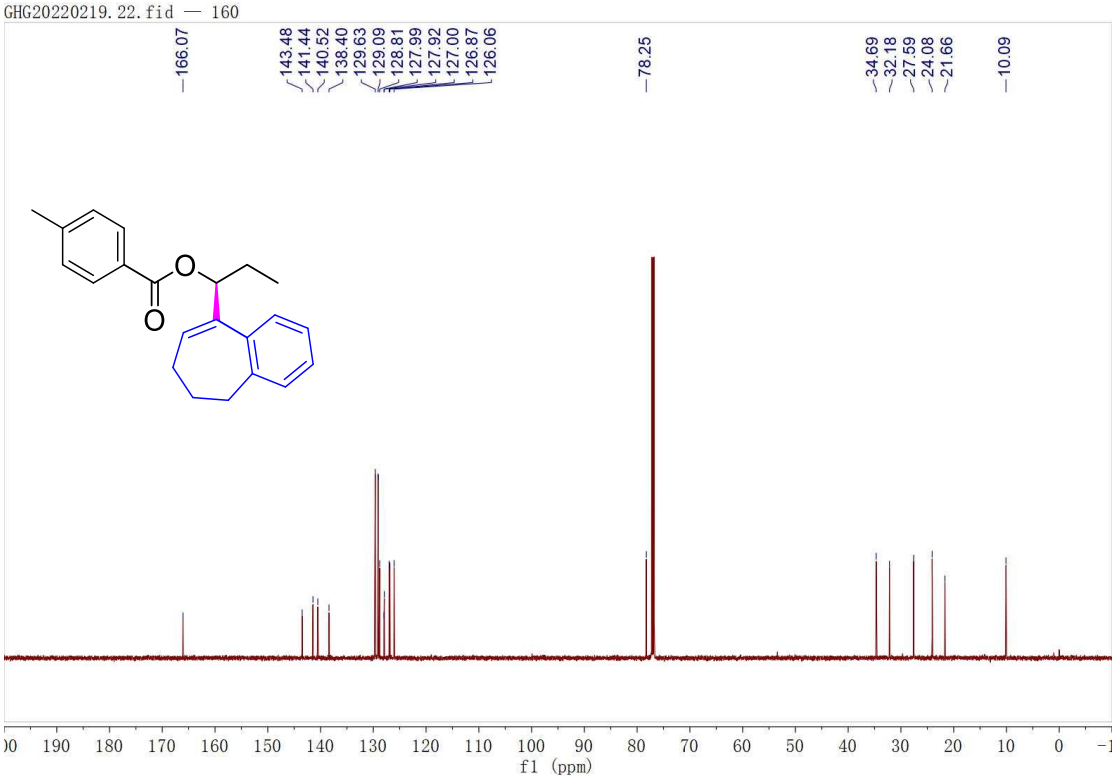
64, ^{13}C NMR (151 MHz, $CDCl_3$)



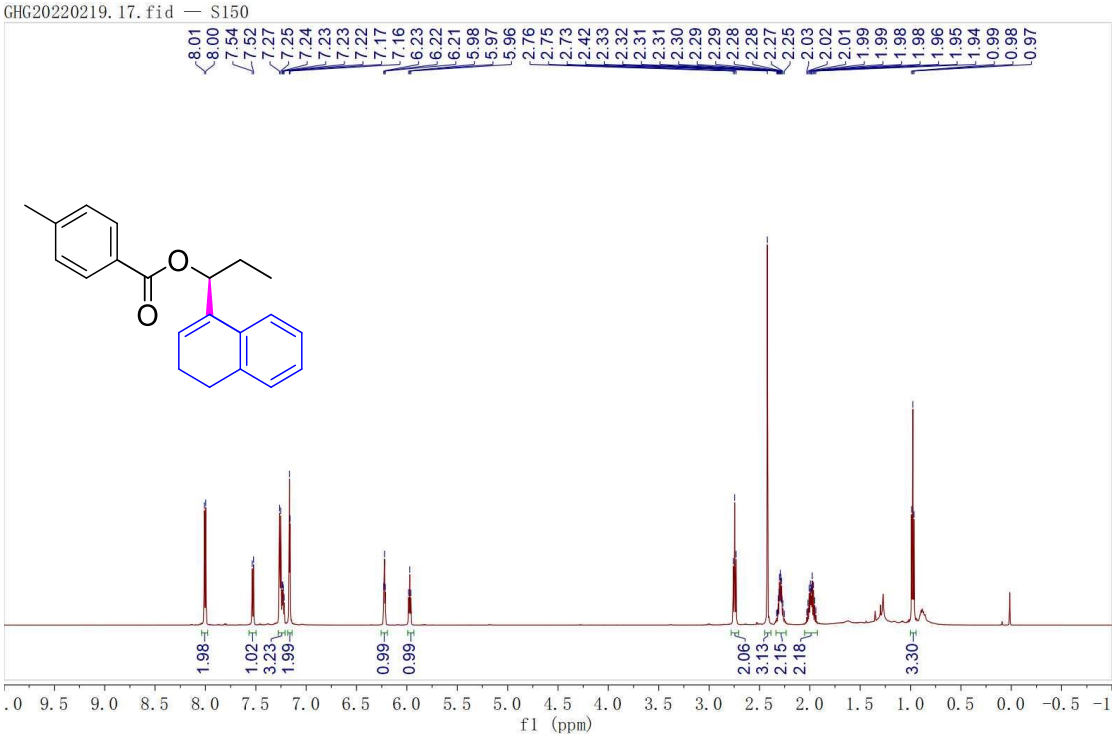
65, ^{1}H-NMR (600 MHZ, $CDCl_3$)



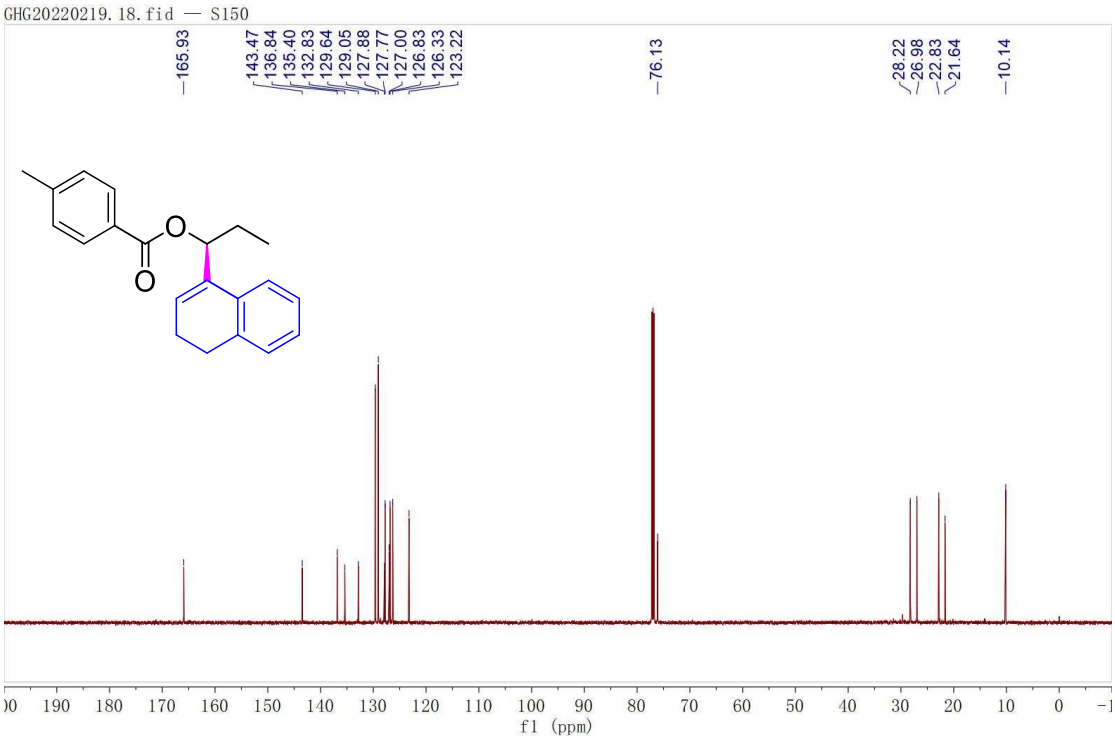
65, ^{13}C NMR (151 MHz, $CDCl_3$)



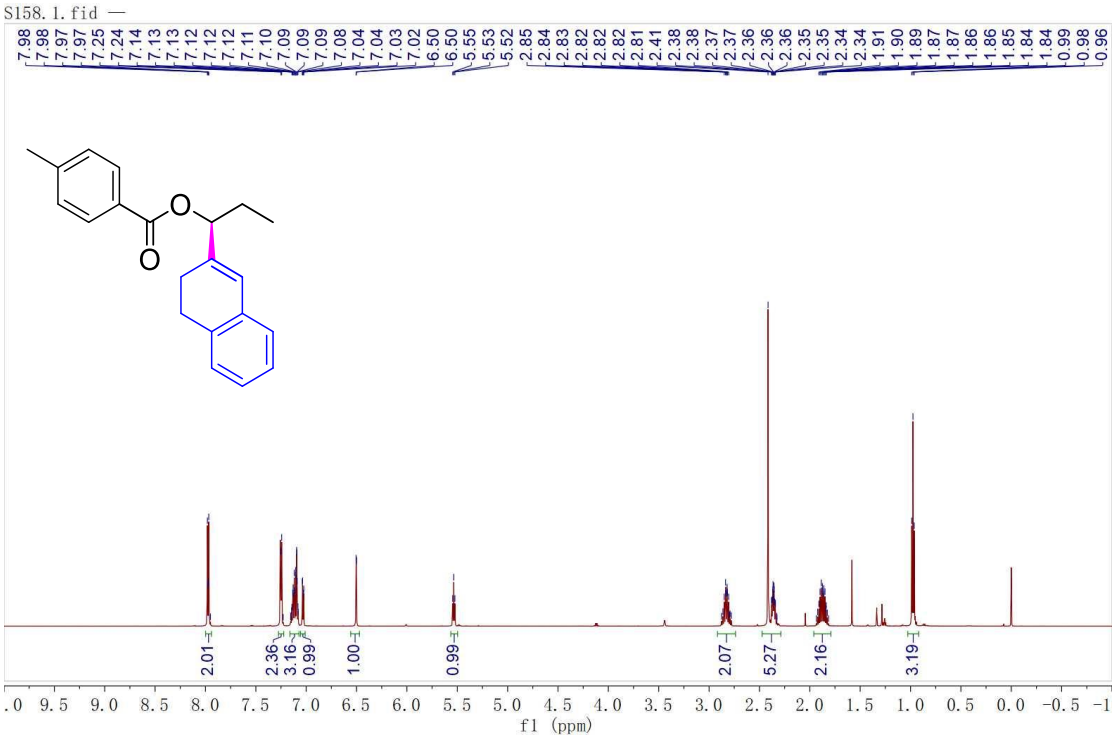
66, ^{1}H-NMR (600 MHZ, $CDCl_3$)



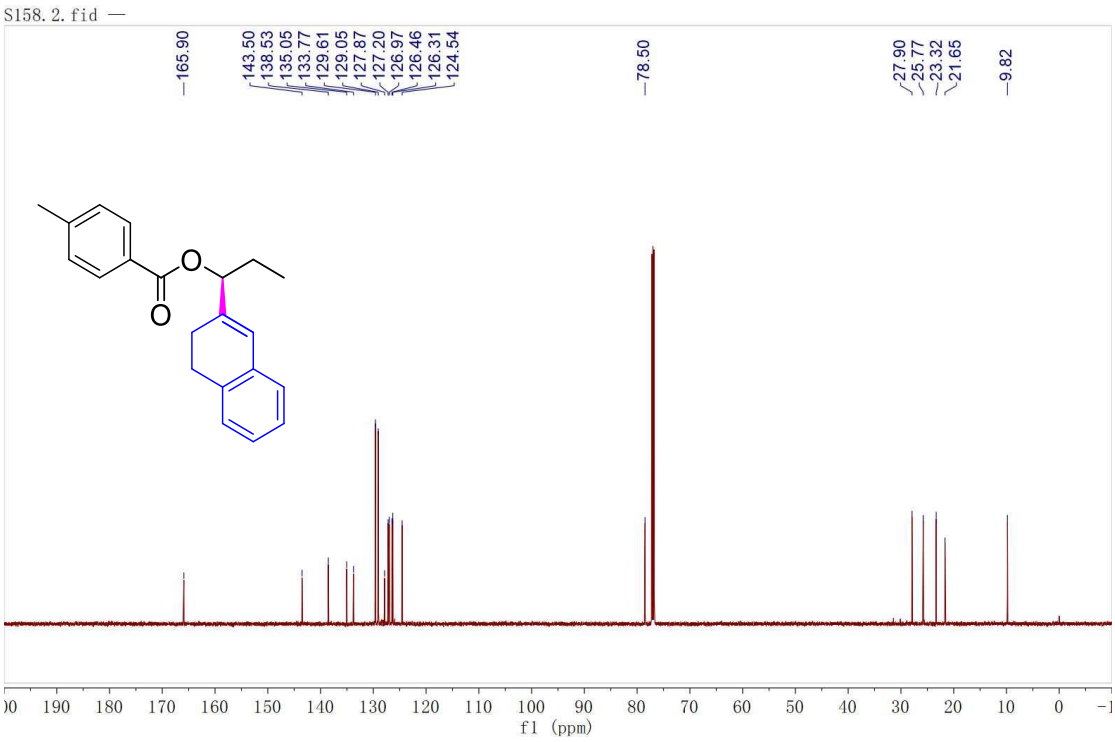
66, ^{13}C NMR (151 MHz, $CDCl_3$)



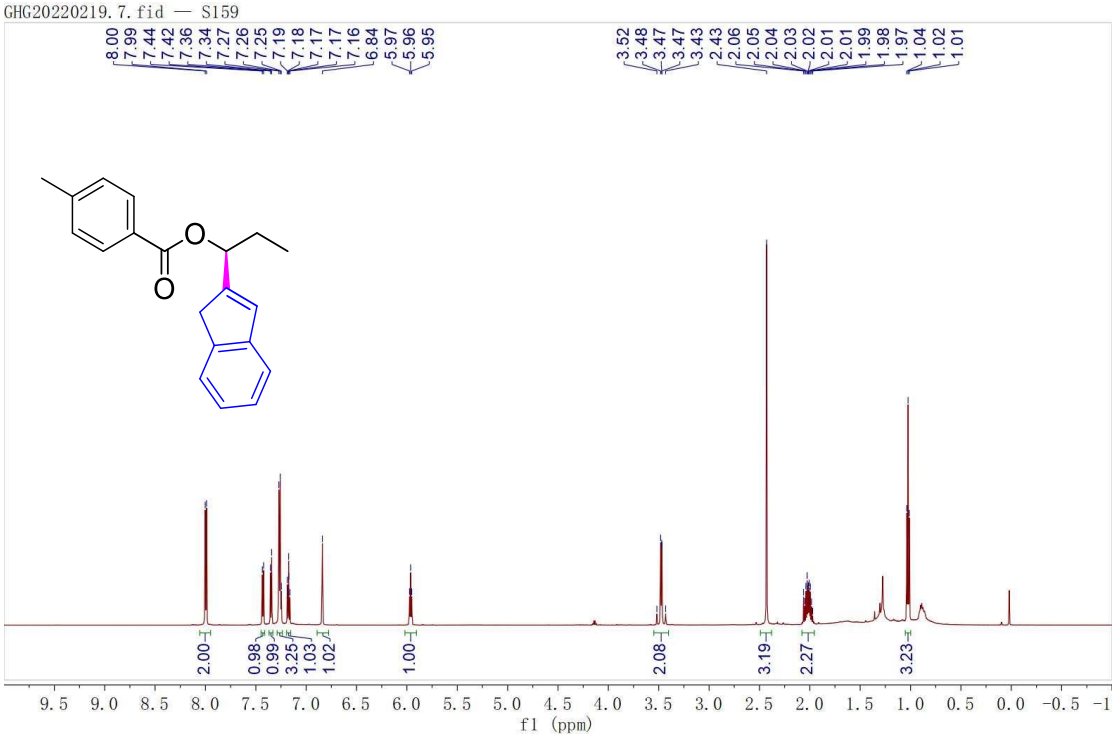
67, ^{1}H-NMR (600 MHZ, $CDCl_3$)



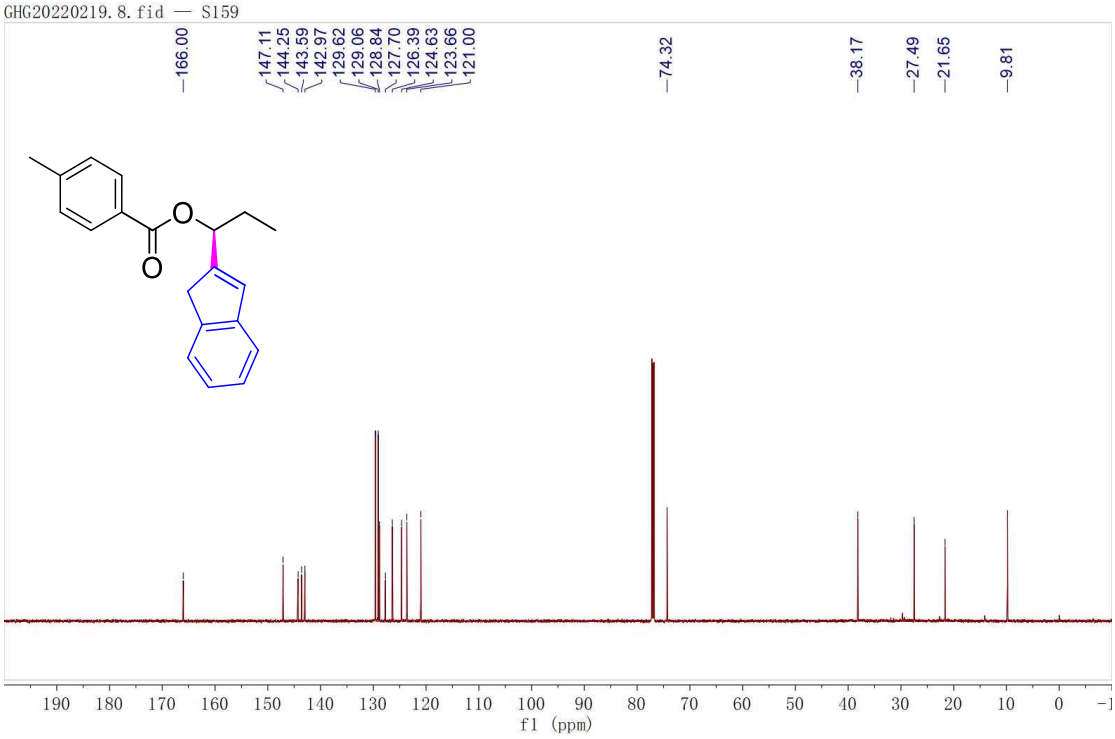
67, ^{13}C NMR (151 MHz, $CDCl_3$)



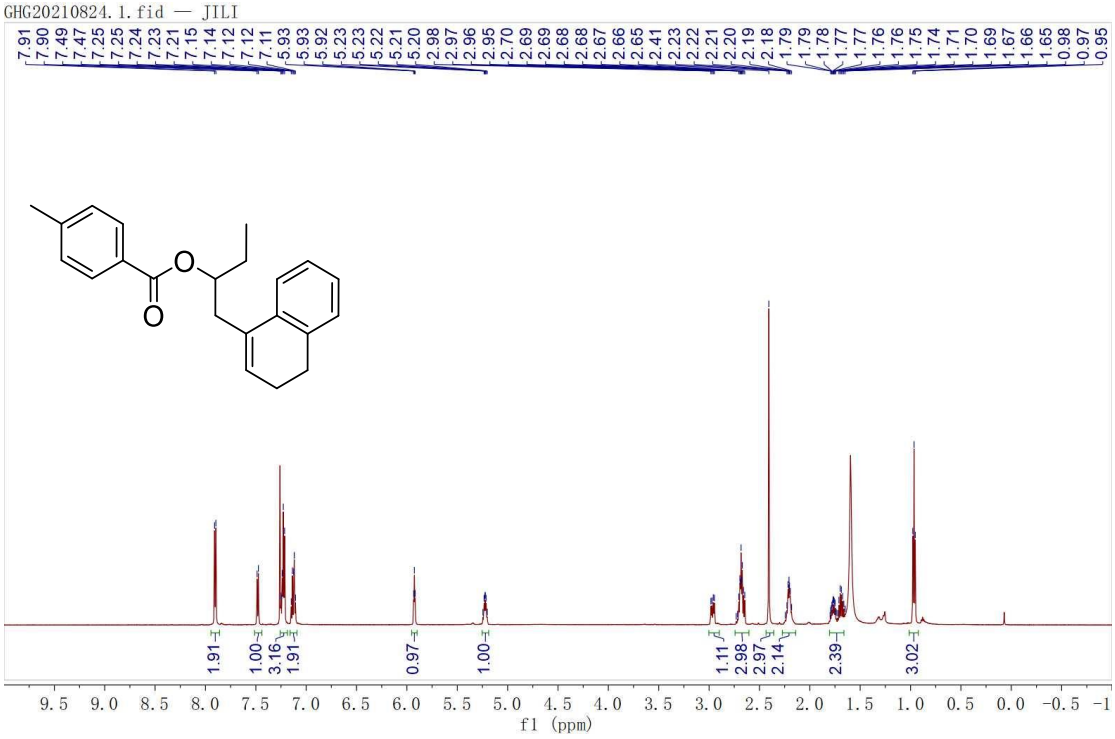
68, ^{1}H-NMR (600 MHZ, $CDCl_3$)



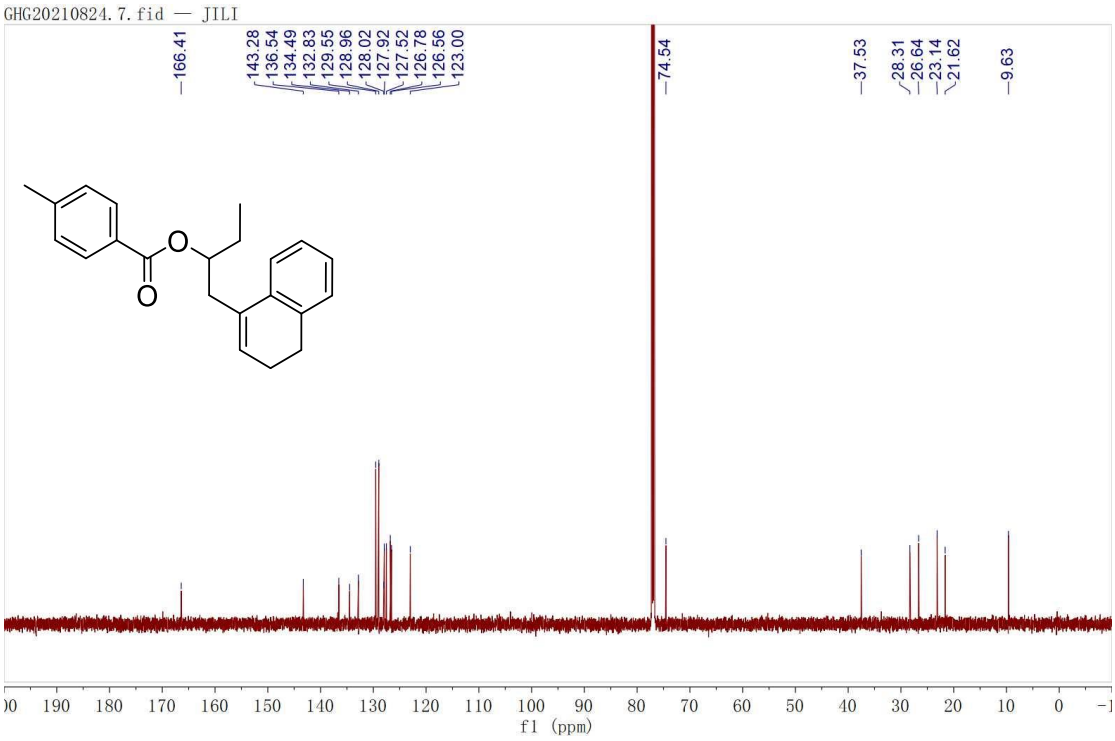
68, ^{13}C NMR (151 MHz, $CDCl_3$)



70, ^{1}H-NMR (600 MHZ, $CDCl_3$)



70 ^{13}C NMR (151 MHz, $CDCl_3$)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f1 (ppm)