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SUPPORTING INFORMATION

Asymmetric Synthesis of Benzothiazolopyrimidines with High Catalytic Efficiency and Stereoselectivity under Bifunctional Phosphonium Salt System

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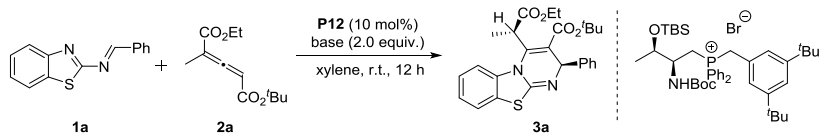
1. General Information

All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$, CD_3OD or DMSO-d_6 on a Brüker Advance 400 spectrometer. Chemical shifts (δ) were given in parts per million (ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublet), br s (broad singlet). Coupling constants (*J*) were reported in Hertz (Hz). All high resolution mass spectra were obtained on a Thermo LTQ mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatographic separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel. Enantiomeric excess was determined by HPLC analysis using chiral column described below in detail. Optical rotations were measured with polarimeter. The absolute configurations of the [4 + 2] cyclization products were assigned on the basis of X-ray crystallographic analysis of the single crystal of compound **4e**.

All phosphonium salt catalysts used in this study were prepared via a P-alkylation reaction of our previously reported organophosphines according to the known procedures.[1]

2. Optimization of Reaction Conditions

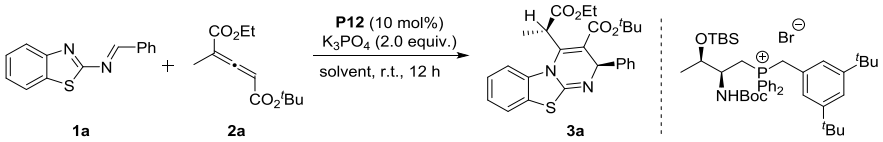
***Table S1*:** Screening of the bases in xylene.[a]



Entry	Base	Yield (%)	ee (%)	*dr*
1	K_2CO_3	80	78	>20:1
2	Cs_2CO_3	90	55	>20:1
3	K_3PO_4	81	80	>20:1
4	K_2HPO_4	trace	--	--
5	$K_3PO_4 \cdot 7H_2O$	60	77	>20:1
6	$(NH_4)_2CO_3$	50	45	>20:1
7	NaOAc	10	34	>20:1

[a] Reactions were performed with **1a** (0.1 mmol), **2a** (0.12 mmol), **P12** (10 mol%) and corresponding base in toluene (0.5 mL) at room temperature. The *dr* values were determined by ^{1}H NMR and ee values were determined by HPLC analysis. Isolated yield.

***Table S2*:** Screening of the solvent.[a]

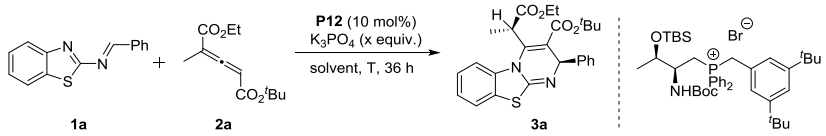


Entry	Solvent	Yield (%)	ee (%)	*dr*
1	Xylene	81	80	>20:1
2	Toluene	79	77	>20:1
3	DCM	89	44	>20:1
4	EA	95	31	18:1
5	MeCN	73	57	>20:1
6	MTBE	60	54	19:1
7	Et_2O	44	73	>20:1
8	Hexane	80	82	>20:1
9	Acetone	81	30	>20:1

[a] Reactions were performed with **1a** (0.1 mmol), **2a** (0.12 mmol), **P12** (10 mol%)

and K_3PO_4 (0.2 mmol) in corresponding solvent (0.5 mL) at room temperature. The *dr* values were determined by ^{1}H NMR and ee values were determined by HPLC analysis. Isolated yield.

***Table S3*:** Screening of the temperature and equivalents of base.[a]



Entry	T (^{o}C)	K_3PO_4 (x equiv.)	Yield (%)	ee (%)	*dr*
1	r.t.	2	80	82	>20:1
2	0	2	77	85	>20:1
3	-10	2	78	84	>20:1
4	-20	2	74	82	>20:1
5	-10	4	91	90	>20:1
6	-10	6	90	87	>20:1
7[b]	-10	4	82	73	>20:1

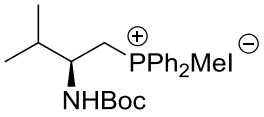
[a] Reactions were performed with **1a** (0.1 mmol), **2a** (0.12 mmol), **P12** (10 mol%) and K_3PO_4 (0.2 mmol) in corresponding solvent (0.5 mL) at corresponding temperature. The *dr* values were determined by ^{1}H NMR and ee values were determined by HPLC analysis. Isolated yield.[b] 5 mol% **P12** was used.

3. Preparation of the Catalysts

A. General procedures for preparation of phosphonium salts

The catalysts **P1-5** are known compounds, and their characterization data were in agreement with those reported in the literature. The phosphonium bromides **P6-12** were prepared according to the reported procedures[1] and fully characterized.

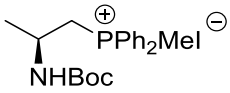
(*S*)-(2-((*tert*-butoxycarbonyl)amino)-3-methylbutyl)(methyl)diphenylphosphonium iodide (P6)



A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.90 (m, 2H), 7.79-7.70 (m, 6H), 7.70-7.63 (m, 2H), 5.94 (d, *J* = 10.4 Hz, 1H), 4.69-4.59 (m, 1H), 3.85-3.76 (m, 1H),

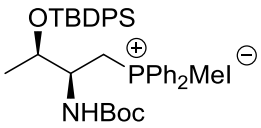
2.79 (d, *J* = 14.0 Hz, 3H), 2.11-2.03 (m, 1H), 1.70 (s, 1H), 1.33 (s, 9H), 0.93 (dd, *J* = 6.7, 0.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5 , 134.9 (d, *J* = 2.7 Hz), 134.6 (d, *J* = 2.9 Hz), 132.5 (d, *J* = 10.3 Hz), 132.3 (d, *J* = 9.8 Hz), 130.4 (d, *J* = 12.5 Hz), 130.2 (d, *J* = 12.6 Hz), 119.7 (dd, *J* = 150.7, 85.7 Hz), 79.7, 51.1 (d, J = 5.3 Hz), 34.5 (d, J = 13.1 Hz), 28.3, 27.2 (d, J = 52.2 Hz), 19.4, 18.1, 8.6 (d, J = 54.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.18; HRMS (ESI) m/z calcd for $C_{23}H_{33}NO_2PI$ $[M-I]^+$ = 386.2249, found = 386.2247.

(*S*)-(2-((*tert*-butoxycarbonyl)amino)propyl)(methyl)diphenylphosphonium iodide (P7)



A white solid; ^{1}H NMR (400 MHz, MeOD) δ 7.32-7.27 (m, 2H), 7.21-7.10 (m, 4H), 7.08-7.01 (m, 4H), 3.49-3.44 (m, 1H), 2.73-2.61 (m, 2H), 2.10 (d, *J* = 14.2 Hz, 3H), 0.70 (dd, *J* = 6.7, 2.5 Hz, 3H), 0.59 (s, 9H). ^{13}C NMR (100 MHz, MeOD) δ 156.5, 135.4 (d, *J* = 2.9 Hz), 133.3 (d, *J* = 10.0 Hz), 133.0 (d, *J* = 10.0 Hz), 131.1, 130.9, 122.6, 120.7 (d, *J* = 15.5 Hz), 120.8, 79.8 (d, *J* = 88.7 Hz), 43.1, 31.0 (d, *J* = 52.0 Hz), 28.4, 23.6 (d, *J* = 14.8 Hz), 6.9 (d, *J* = 54.8 Hz). ^{31}P NMR (162 MHz, MeOD) δ 21.33. HRMS (ESI) m/z calcd for $C_{21}H_{29}NO_2PI$ $[M-I]^+$ = 358.1936, found = 358.1934.

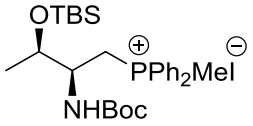
((2*S*,3*R*)-2-((*tert*-butoxycarbonyl)amino)-3-((*tert*-butyldiphenylsilyl)oxy)butyl)(methyl)diphenylphosphonium iodide (P8)



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.60 (m, 8H), 7.59-7.54 (m, 6H), 7.34-7.28 (m, 6H), 5.77 (d, *J* = 10.0 Hz, 1H), 4.14 (s, 2H), 3.80-3.71 (m, 1H), 3.06 (td, *J* = 14.5, 4.3 Hz, 1H), 2.77 (dd, *J* = 13.8, 3.6 Hz, 3H), 1.24 (s, 9H), 1.13 (d, *J* = 5.0 Hz, 3H), 0.98 (d, *J* = 3.0 Hz, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 135.6, 135.5, 134.6, 134.5, 133.1 (d, *J* = 40.0 Hz), 132.3, 132.2, 132.1, 130.2, 130.1, 130.0, 129.8 (d, *J* = 3.0 Hz), 127.8, 127.6, 119.5, 118.6, 79.8, 71.4 (d, *J* = 14.1 Hz), 50.5, 28.1,

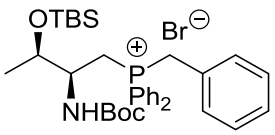
26.9, 24.1 (d, *J* = 55.4 Hz), 19.1, 18.6, 8.2 (d, *J* = 53.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.91. HRMS (ESI) m/z calcd for $C_{38}H_{49}NO_3PSiI$ $[M-I]^+$ = 626.3214, found = 626.3210.

((2*S*,3*R*)-2-((*tert*-butoxycarbonyl)amino)-3-((*tert*-butyldimethylsilyl)oxy)butyl)(methyl)diphenylphosphonium iodide (P9)



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.72 (m, 6H), 7.65-7.61 (m, 4H), 5.90 (d, *J* = 8.7 Hz, 1H), 4.12-3.87 (m, 3H), 3.33 (t, *J* = 14.5 Hz, 9H), 2.83 (d, *J* = 14.0 Hz, 3H), 1.29 (s, 9H), 1.20 (d, *J* = 6.0 Hz, 3H), 0.82 (s, 9H), 0.04 (s, 3H), 0.00 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 134.8 (d, *J* = 3.0 Hz), 134.6 (d, *J* = 3.0 Hz), 132.3 (d, *J* = 10.0 Hz), 132.3 (d, *J* = 10.0 Hz), 130.3 (d, *J* = 13.0 Hz), 130.1 (d, *J* = 12.0 Hz), 120.7, 119.3 (d, *J* = 85.2 Hz), 79.9, 70.1 (d, *J* = 14.3 Hz), 50.8, 28.2, 25.8, 23.76, 18.6, 17.9, 8.6 (d, *J* = 54.3 Hz), -4.6 (d, *J* = 9.5 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.91. HRMS (ESI) m/z calcd for $C_{28}H_{45}NO_3PSiI$ $[M-I]^+$ = 502.2091, found = 502.2095.

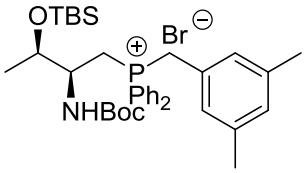
benzyl((2*S*,3*R*)-2-((*tert*-butoxycarbonyl)amino)-3-((*tert*-butyldimethylsilyl)oxy)butyl)diphenylphosphonium bromide (P10)



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.84 (m, 2H), 7.74-7.70 (m, 4H), 7.61-7.51 (m, 4H), 7.14-7.12 (m, 1H), 7.05 (t, *J* = 7.4 Hz, 2H), 6.94-6.93 (m, 2H), 6.08 (d, *J* = 8.9 Hz, 1H), 5.10 (t, *J* = 14.8 Hz, 1H), 4.49 (dd, *J* = 25.1, 12.6 Hz, 1H), 4.29 (t, *J* = 14.5 Hz, 1H), 3.93 (d, *J* = 6.0 Hz, 2H), 3.04 (t, *J* = 14.6 Hz, 1H), 1.24 (s, 9H), 1.15 (d, *J* = 5.8 Hz, 3H), 0.74 (d, *J* = 2.2 Hz, 9H), -0.00 (d, *J* = 2.6 Hz, 3H), -0.05 (d, *J* = 2.3 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 134.6 (d, *J* = 3.0 Hz), 134.5 (d, *J* = 3.0Hz), 133.9 (d, *J* = 7.4 Hz), 130.5 (d, *J* = 5.5 Hz), 129.9, 129.8, 129.7,

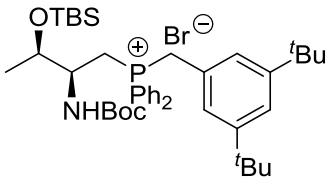
128.7 (d, *J* = 3.0 Hz), 128.1 (d, *J* = 4.0 Hz), 127.5 (d, *J* = 9.0 Hz), 117.7 (d, *J* = 28.0 Hz), 116.9 (d, *J* = 31.0 Hz), 79.5, 69.7 (d, *J* = 14.0 Hz), 50.2 (d, *J* = 5.0 Hz), 30.4 (d, *J* = 45.0 Hz), 28.2, 25.7, 20.9 (d, *J* = 52.0 Hz), 17.7 (d, *J* = 14.0 Hz), -4.7 (d, *J* = 16.0 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.22. HRMS (ESI) m/z calcd for $C_{34}H_{48}NO_3PSiBr$ $[M\text{-}Br]^+$ = 577.3141, found = 577.3136.

((2*S*,3*R*)-2-((*tert*-butoxycarbonyl)amino)-3-((*tert*-butyldimethylsilyl)oxy)butyl)(3, 5-dimethylbenzyl)diphenylphosphonium bromide (P11)



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90-7.85 (m, 2H), 7.74-7.69 (m, 4H), 7.62-7.55 (m, 4H), 6.76 (s, 1H), 6.44 (s, 2H), 6.13 (s, 1H), 4.94-4.87 (m, 1H), 4.39 (d, *J* = 11.4 Hz, 1H), 4.18 (t, *J* = 14.5 Hz, 1H), 3.93 (s, 2H), 3.03 (t, *J* = 14.6 Hz, 1H), 2.02 (s, 6H), 1.26 (d, *J* = 2.0 Hz, 9H), 1.17-1.15 (m, 3H), 0.75 (d, *J* = 1.9 Hz, 9H), 0.01 (d, *J* = 2.1 Hz, 3H), -0.04 (d, *J* = 1.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 138.3 (d, *J* = 3.4 Hz), 134.5,134.0 (d, *J* = 4.1 Hz), 134.0 (d, *J* = 4.1 Hz) 129.8 (d, *J* = 5.3 Hz), 129.7, 129.6, 129.5, 128.3 (d, *J* = 5.6 Hz), 127.0 (d, *J* = 8.9 Hz), 117.9 (d, *J* = 8.5 Hz), 117.1 (d, *J* = 11.0 Hz), 79.5, 69.8 (d, *J* = 13.8 Hz), 50.3, 30.5 (d, *J* = 45.5 Hz), 28.3, 25.7, 21.4, 20.9, 17.8, 0.1, -4.7 (d, *J* = 20.6 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.14. HRMS (ESI) m/z calcd for $C_{36}H_{52}NO_3PSiBr$ $[M\text{-}Br]^+$ = 605.3454, found = 605.3449.

((2*S*,3*R*)-2-((*tert*-butoxycarbonyl)amino)-3-((*tert*-butyldimethylsilyl)oxy)butyl)(3, 5-di-tert-butylbenzyl)diphenylphosphonium bromide (P12)



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, *J* = 12.4, 7.8 Hz, 2H), 7.79-7.74 (m, 4H), 7.66-7.59 (m, 5H), 7.42 (s, 2H), 5.95 (d, *J* = 9.0 Hz, 1H), 5.64 (t, *J*

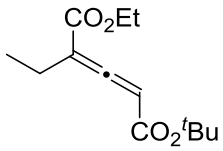
= 15.2 Hz, 1H), 4.63-4.50 (m, 2H), 3.99-3.93 (m, 2H), 3.12 (t, *J* = 14.5 Hz, 1H), 1.26 (s, 9H), 1.16 (d, *J* = 5.9 Hz, 3H), 0.74 (s, 9H), 0.02 (s, 3H), -0.04 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 135.3 (d, *J* = 21.0 Hz), 134.1, 133.9 (d, *J* = 9.2 Hz), 132.1 (d, *J* = 30.7 Hz), 131.2 (d, *J* = 8.8 Hz), 130.8, 130.4 (d, *J* = 5.1 Hz), 130.3 (d, *J* = 4.8 Hz), 124.0, 122.1, 121.3 , 116.7 (d, *J* = 18.0 Hz), 115.9 (d, *J* = 19.5 Hz), 79.8, 69.8 (d, *J* = 13.8 Hz), 50.2, 30.4 (d, *J* = 46.3 Hz), 28.3, 25.7, 21.5 (d, *J* = 51.3 Hz), 17.8, 17.62, 0.0, -4.7, -4.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.32. HRMS (ESI) m/z calcd for $C_{42}H_{64}NO_3PSiBr$ $[M-Br]^+$ = 689.4939, found = 689.4940.

4. General Procedure for the Synthesis of Substrates

General procedure for preparing allenoates:

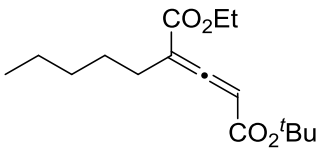
All 2-benzothiazolimines and allenoates were prepared from the corresponding literature procedure.[2,3] Unknown compounds **2a**, **2c** and **2e-f** were fully characterized.

5-(*tert*-butyl) 1-ethyl 2-ethylpenta-2,3-dienedioate (2a)



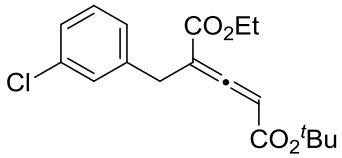
A colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (t, *J* = 3.1 Hz, 1H), 4.27-4.16 (m, 2H), 2.42-2.28 (m, 2H), 1.47 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ217.8, 165.6, 163.6, 106.5, 94.0, 81.7, 61.5, 28.2, 21.8, 14.3, 12.4. HRMS (ESI) *m/z* calcd for $C_{13}H_{20}O_4$ $[M+Na]^+$ = 263.1259, found = 263.1257;

5-(*tert*-butyl) 1-ethyl 2-pentylpenta-2,3-dienedioate (2c)



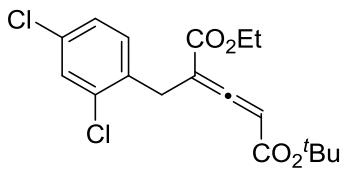
A colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.82 (t, *J* = 2.8 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 2.39-2.21 (m, 2H), 1.46 (d, *J* = 5.2 Hz, 9H), 1.34-1.20 (m, 8H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.1, 165.6, 163.6, 104.8, 93.5, 81.7, 61.5, 31.2, 28.2 (d, *J* = 11.5 Hz), 27.5, 22.5, 14.3, 14.1. HRMS (ESI) *m/z* calcd for $C_{16}H_{26}O_4$ $[M+Na]^+$ = 305.1729, found = 305.1726;

5-(*tert*-butyl) 1-ethyl 2-(3-chlorobenzyl)penta-2,3-dienedioate (2e)



A colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.32 (m, 1H), 7.27 (d, *J* = 3.3 Hz, 1H), 7.25-7.21 (m, 1H), 5.86 (t, *J* = 2.5 Hz, 1H), 4.27 (qd, *J* = 7.1, 0.9 Hz, 2H), 3.68 (ddd, *J* = 41.5, 15.2, 2.6 Hz, 2H), 1.54 (s, 9H), 1.32 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 218.5, 165.0, 163.0, 139.9, 134.2, 129.7, 129.2, 127.3, 127.1, 103.9, 94.1, 82.1, 61.8, 34.7, 28.2, 14.3. HRMS (ESI) *m/z* calcd for $C_{18}H_{21}ClO_4$ $[M+Na]^+$ = 359.1026, found = 359.1026;

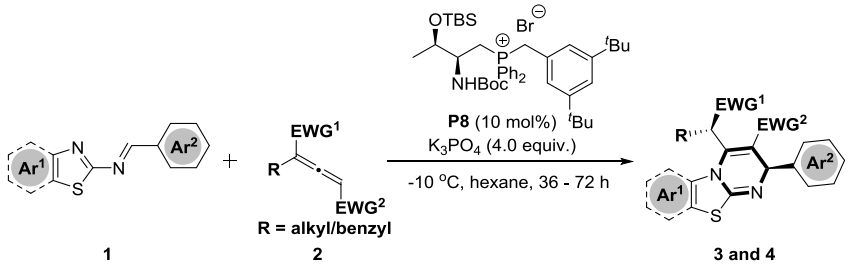
5-(*tert*-butyl) 1-ethyl 2-(2,4-dichlorobenzyl)penta-2,3-dienedioate (2f)



A colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, *J* = 2.0 Hz, 1H), 7.27-7.26 m, 1H), 7.15 (dd, *J* = 8.3, 2.0 Hz, 1H), 5.76 (t, *J* = 2.7 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.74 (ddd, *J* = 44.9, 15.6, 2.7 Hz, 2H), 1.43 (s, 9H), 1.26 (t, *J* = 7.1 Hz, 3H). ^{13}C

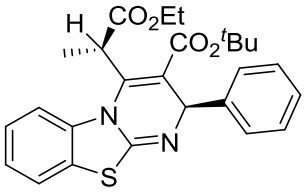
NMR (100 MHz, $CDCl_3$) δ 217.2, 163.7, 161.7, 134.0, 133.0, 132.13, 130.8, 128.2, 125.9, 101.7, 93.2, 80.8, 60.7, 30.8, 27.0, 13.1. HRMS (ESI) *m/z* calcd for $C_{18}H_{20}Cl_2O_4$ $[M+Na]^+$ = 393.0636, found = 393.0634;

5. General Procedure for the Asymmetric Synthesis of 3 and 4.



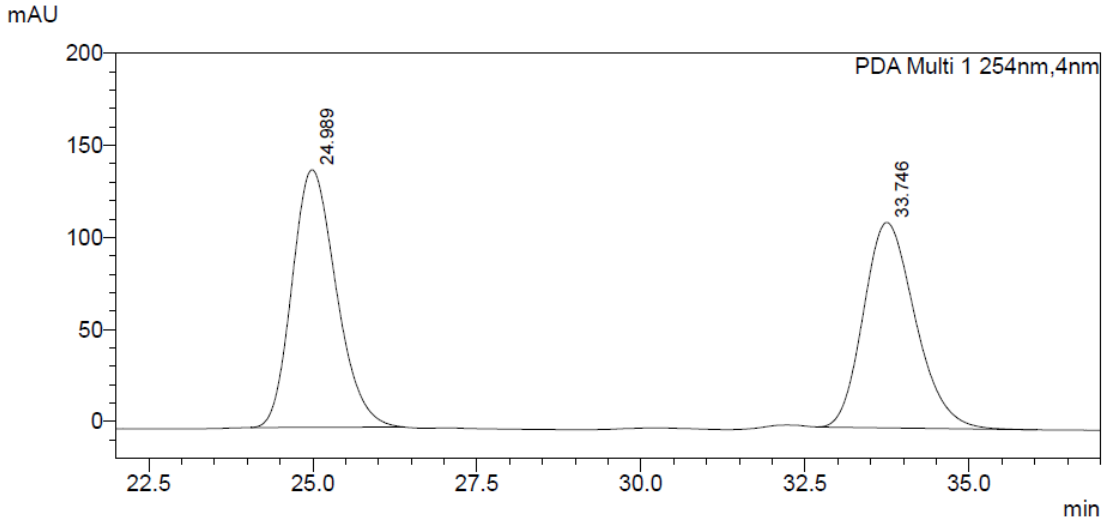
To a flame-dried round bottle flask with a magnetic stirring bar were added the 2-benzothiazolimines (0.1 mmol), allenoates (0.12 mmol), phosphonium salt **P12** (0.01 mmol) and K_3PO_4 (0.4 mmol), followed by the addition of Hexane (0.5 mL). The reaction mixture was stirred at -10 ^oC for 36-72 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford products **3/4** .

<u>*tert*-butyl(*R*)-4-((*S*)-1-ethoxy-1-oxopropan-2-yl)-2-phenyl-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (3a)</u>



White foam, (42.2 mg), 91% yield; $[\alpha]^{25}_D$ = +83.3 (*c* 0.40, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.41 (m 2H), 7.34-7.32 (m, 1H), 7.29-7.27 (m, 1H), 7.26-7.25 (m, 1H), 7.23-7.19 (m, 1H), 7.19-7.16 (m, 2H), 7.14-7.09 (m, 1H), 5.91 (s, 1H), 4.32-4.25 (m, 3H), 1.59 (s, 1H), 1.50 (d, *J* = 6.9 Hz, 3H), 1.40 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 164.7, 146.8, 141.3, 135.5, 128.5, 127.4, 126.9, 126.6, 125.7, 125.1, 124.5, 122.9, 115.1, 81.7, 61.4, 61.3, 39.2, 27.9,

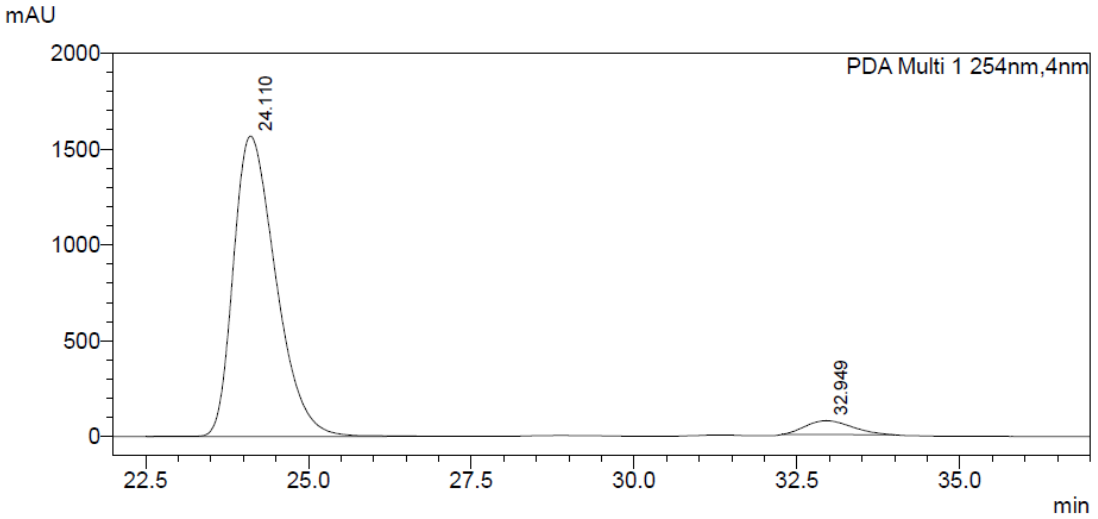
16.1, 14.2. HRMS (ESI) *m/z* calcd for $C_{26}H_{28}N_2O_4S$ $[M+Na]^+$ = 487.1667, found = 487.1665; The ee value was 90%, t_R (major) = 24.1 min, t_R (minor) = 32.9 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 0.5 mL/min).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	24.989	139865	55.644	6552927	51.655
2	33.746	111489	44.356	6133136	48.345
Total		251354	100.000	12686063	100.000

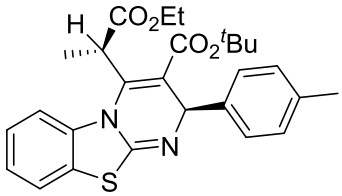


Peak Table

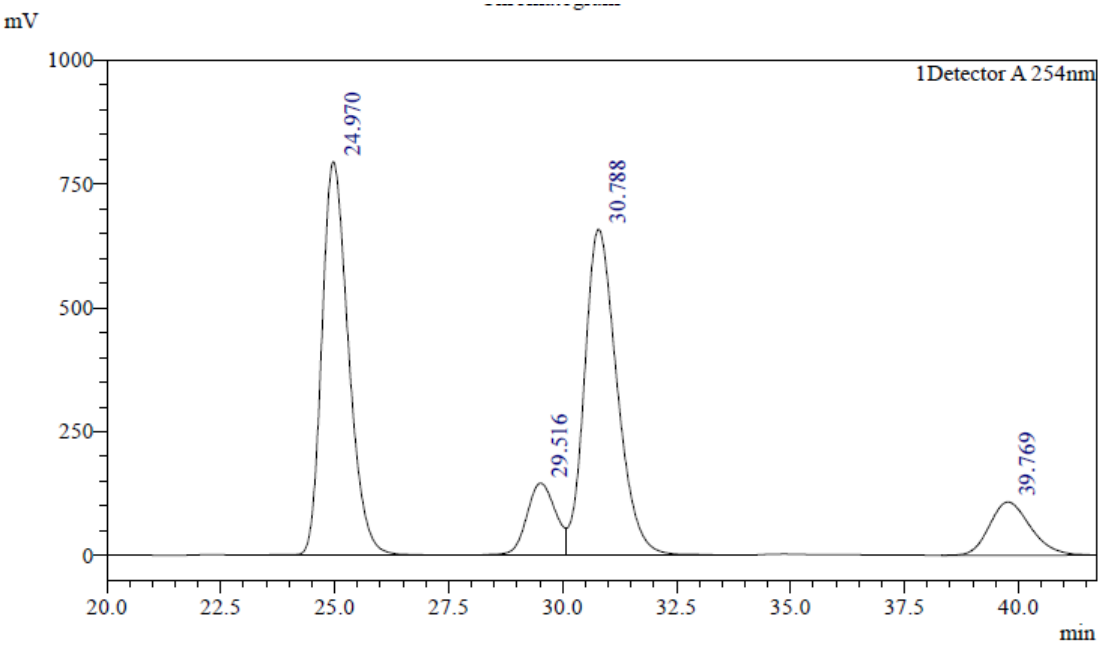
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	24.110	1568449	95.582	71047252	95.176
2	32.949	72498	4.418	3601246	4.824
Total		1640946	100.000	74648498	100.000

<u>*tert*-butyl(*R*)-4-((*S*)-1-ethoxy-1-oxopropan-2-yl)-2-(p-tolyl)-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (3b)</u>



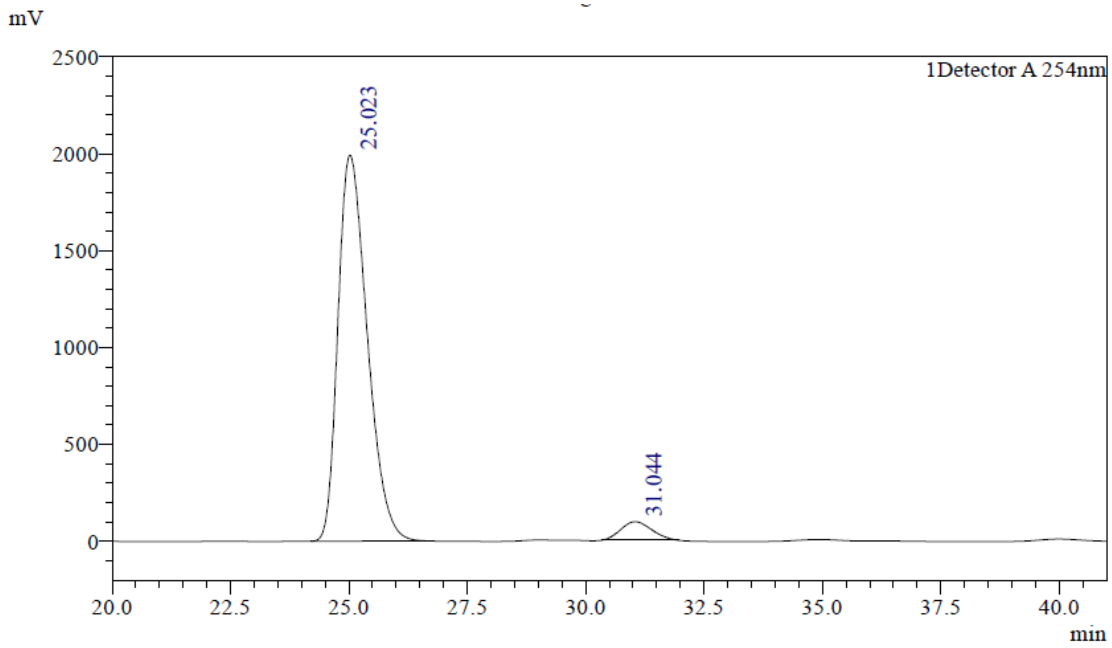
White foam, (43.0 mg), 90% yield; $[\alpha]^{25}_{D}$ = +94.4 (*c* 0.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33-7.30 (m, 3H), 7.19-7.13 (m, 2H), 7.12-7.06 (m, 3H), 5.89 (s, 1H), 4.31-4.26 (m, 3H), 2.28 (s, 3H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.40 (s, 9H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 164.8, 157.3, 146.7, 138.5, 136.9, 135.6, 129.1, 126.8, 125.6, 125.1, 124.4, 122.8, 115.0, 110.6, 81.5, 61.3, 61.2, 39.1, 27.9, 21.1, 16.1, 14.2. HRMS (ESI) *m/z* calcd for $C_{27}H_{30}N_2O_4S$ $[M+Na]^+$ = 501.1824, found = 501.1820; The ee value was 90%, t_R (major) = 25.0 min, t_R (minor) = 31.0 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 0.5 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	24.970	794397	46.565	32176126	41.214
2	29.516	145832	8.548	6449098	8.261
3	30.788	658325	38.589	32709433	41.897
4	39.769	107448	6.298	6736825	8.629
Total		1706002	100.000	78071483	100.000

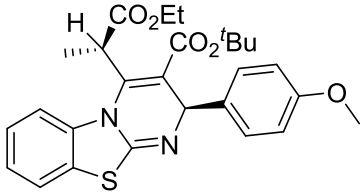


Peak Table

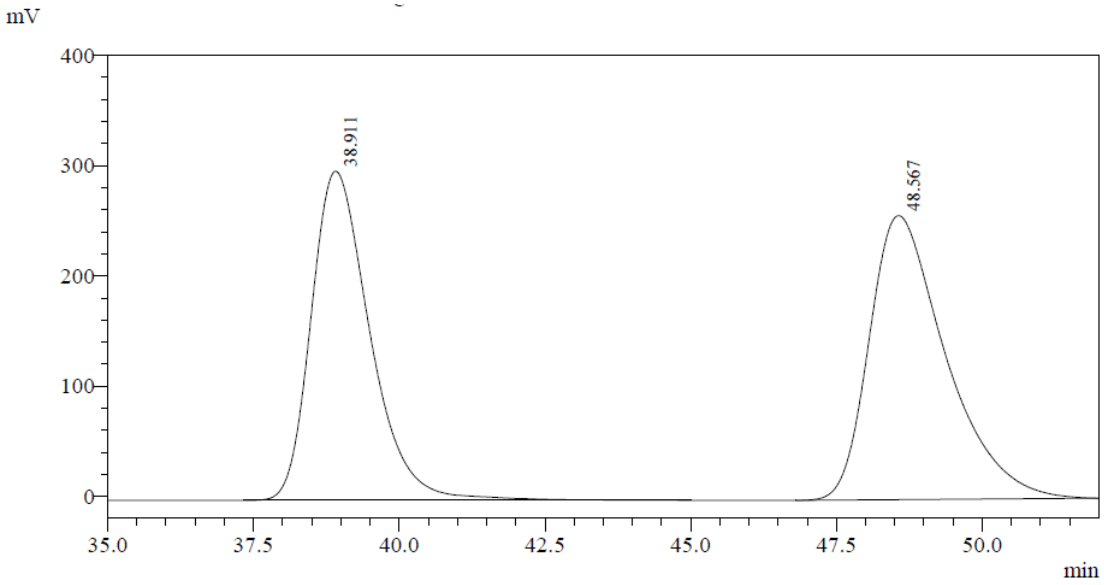
Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	25.023	1991227	95.456	85535250	95.165
2	31.044	94785	4.544	4346053	4.835
Total		2086012	100.000	89881303	100.000

tert-butyl(_R_)-4-((_S_)-1-ethoxy-1-oxopropan-2-yl)-2-(4-methoxyphenyl)-2_H_-benzo[4,5]thiazolo[3,2-_a_]pyrimidine-3-carboxylate (3c)



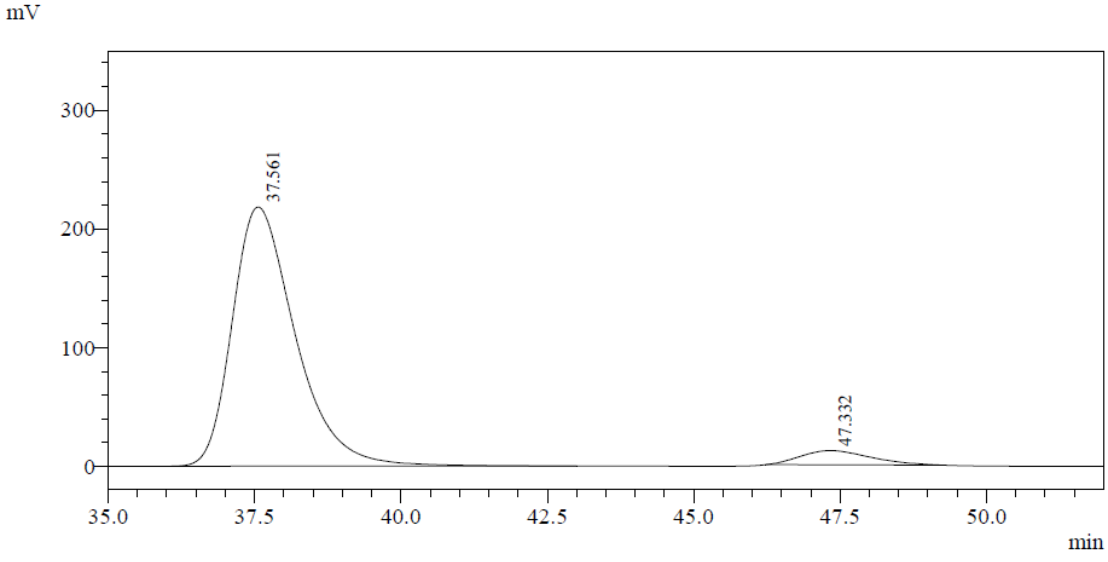
White foam, (41.5 mg), 84% yield; $[\alpha]^{25}_{D}$ = +138.1 (*c* 0.55, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.32 (m, 3H), 7.21-7.12 (m, 3H), 6.82-6.78 (m, 2H), 5.85 (s, 1H), 4.28 (dd, *J* = 13.5, 6.8 Hz, 3H), 3.75 (s, 3H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.39 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 164.8, 157.4, 158.9, 146.6, 135.6, 133.6, 128.1, 125.7, 125.1, 124.5, 122.9, 115.0, 113.8, 111.0, 81.6, 61.4, 60.9, 55.2, 39.2, 28.0, 16.1, 14.2. HRMS (ESI) *m/z* calcd for $C_{27}H_{30}N_2O_5S$ $[M+Na]^+$ = 517.1773, found = 517.1755; The ee value was 89%, t_R (major) = 37.6 min, t_R (minor) = 47.3 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	38.911	298515	53.676	20943188	47.135
2	48.567	257629	46.324	23489045	52.865
Total		556143	100.000	44432233	100.000

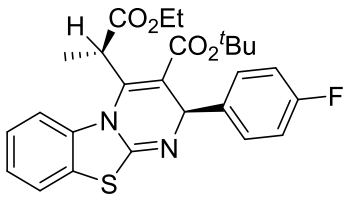


Peak Table

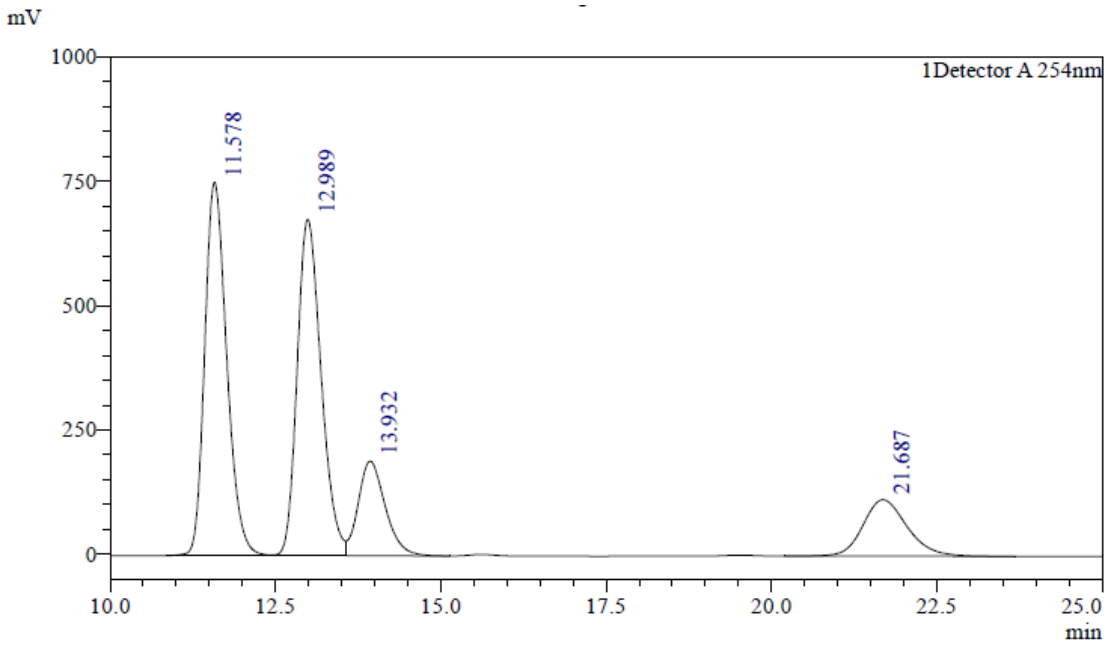
Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	37.561	218488	94.810	16380279	94.276
2	47.332	11961	5.190	994455	5.724
Total		230449	100.000	17374734	100.000

<u>*tert*-butyl(*R*)-4-((*S*)-1-ethoxy-1-oxopropan-2-yl)-2-(4-fluorophenyl)-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (3d)</u>



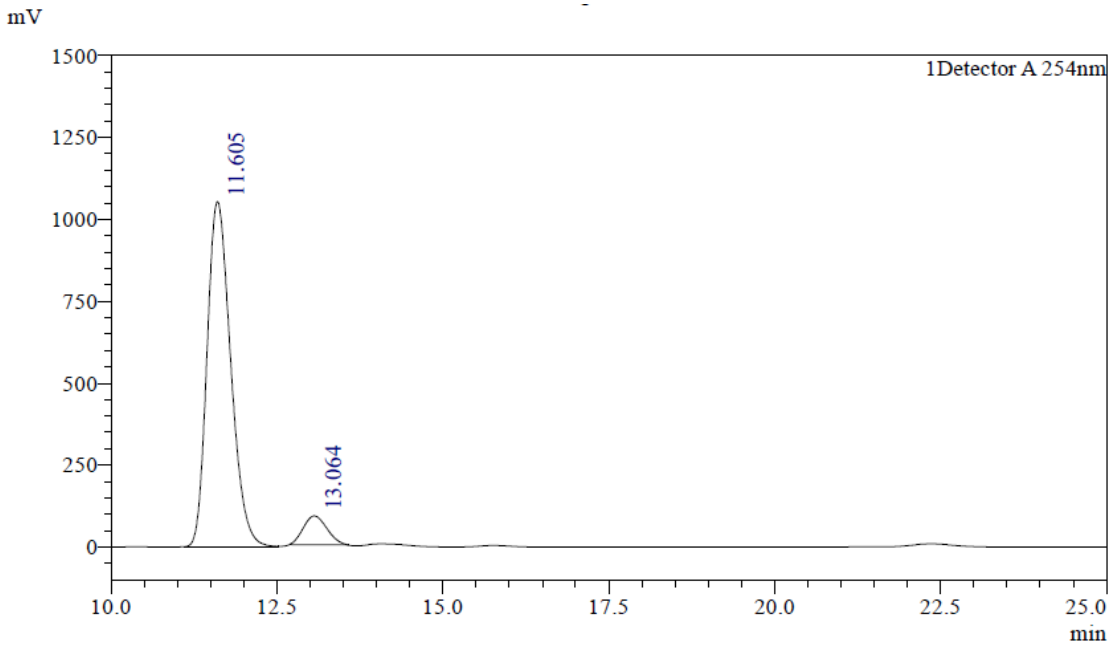
White foam, (44.8 mg), 93% yield; $[\alpha]^{25}_{D}$ = +129.0 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.33 (m, 3H), 7.18-7.16 (m, 2H), 7.15-7.10 (m, 1H), 6.94 (ddd, *J* = 9.8, 5.9, 2.6 Hz, 2H), 5.87 (s, 1H), 4.34-4.22 (m, 3H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.39 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 164.9, 163.6, 161.1, 157.8, 147.2, 137.6 (d, *J* = 3.0 Hz), 135.7, 128.8 (d, *J* = 8.0 Hz), 125.3, 124.8, 124.6 (d, *J* = 281.0 Hz), 115.6, 115.3 (d, *J* = 14.0 Hz), 110.6, 81.9, 61.6, 61.1, 39.4, 28.2, 16.3, 14.5. HRMS (ESI) *m/z* calcd for $C_{26}H_{27}FN_2O_4S$ $[M+Na]^+$ = 505.1573, found = 505.1571; The ee value was 85%, t_R (major) = 11.6 min, t_R (minor) = 13.0 min (Chiralcel IC, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.578	750950	43.365	17388276	38.495
2	12.989	676871	39.087	17073093	37.797
3	13.932	190395	10.995	5419662	11.998
4	21.687	113487	6.553	5289126	11.709
Total		1731703	100.000	45170157	100.000

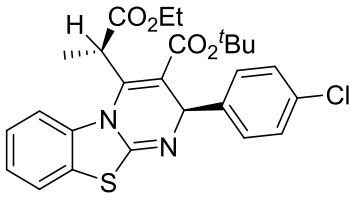


Peak Table

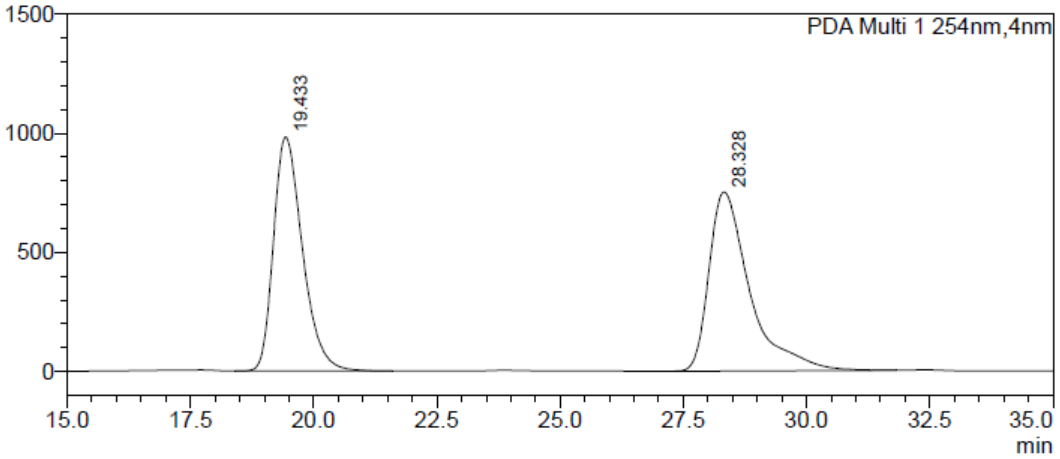
Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.605	1053359	92.281	26099105	92.300
2	13.064	88106	7.719	2177382	7.700
Total		1141466	100.000	28276487	100.000

tert-butyl(_R_)-2-(4-chlorophenyl)-4-((_S_)-1-ethoxy-1-oxopropan-2-yl)-2_H_-benzo[4,5]thiazolo[3,2-_a_]pyrimidine-3-carboxylate (3e)



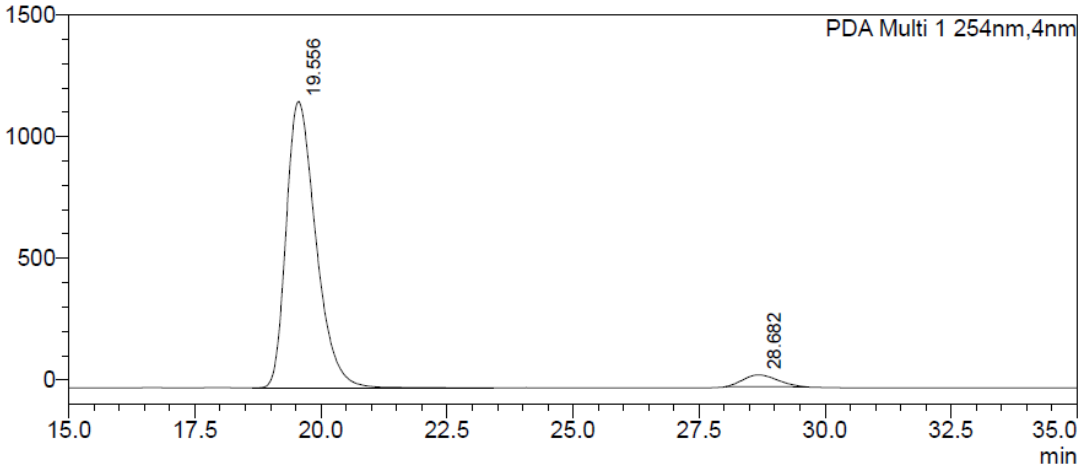
White foam, (44.3 mg), 89% yield; $[\alpha]^{25}_{D}$ = +98.2 (*c* 0.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.34 (m, 3H), 7.25-7.22 (m, 2H), 7.18-7.11 (m, 3H), 5.87 (s, 1H), 4.28 (dd, *J* = 13.4, 6.6 Hz, 3H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.40 (s, 9H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 164.6, 157.6, 147.3, 140.2, 135.5, 133.1, 128.6, 128.3, 125.7, 125.1, 124.6, 122.9, 115.1, 109.9, 81.7, 61.4, 61.0, 39.2, 28.0, 16.1, 14.3. HRMS (ESI) *m/z* calcd for $C_{26}H_{27}ClN_2O_4S$ $[M+Na]^+$ = 521.1278, found = 521.1427; The ee value was 91%, t_R (major) = 19.6 min, t_R (minor) = 28.7 min (Chiralcel IC, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	19.433	983422	56.666	40210957	48.131
2	28.328	752055	43.334	43334659	51.869
Total		1735478	100.000	83545616	100.000

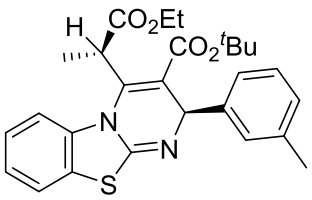


Peak Table

PDA Ch1 254nm

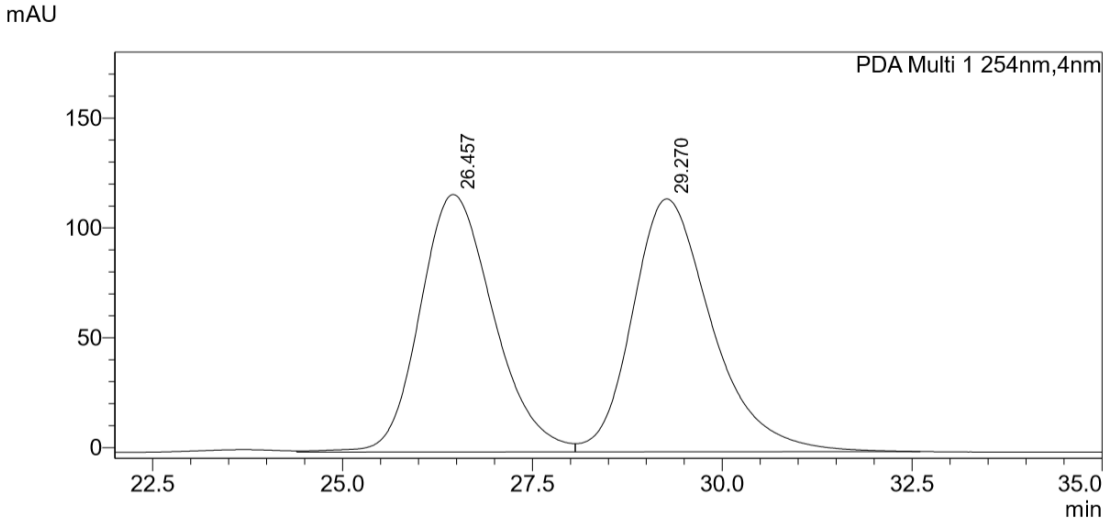
Peak#	Ret. Time	Height	Height%	Area	Area%
1	19.556	1177492	96.064	48331101	95.492
2	28.682	48239	3.936	2281423	4.508
Total		1225731	100.000	50612524	100.000

<u>*tert*-butyl(*R*)-4-((*S*)-1-ethoxy-1-oxopropan-2-yl)-2-(*m*-tolyl)-2*H*-benzo[4,5]thiazolo[3,2-a]pyrimidine-3-carboxylate (3f)</u>



White foam, (43.0 mg), 90% yield; $[\alpha]^{25}_{D}$ = +33.2 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 7.20-7.09 (m, 5H), 7.03 (d, *J* =

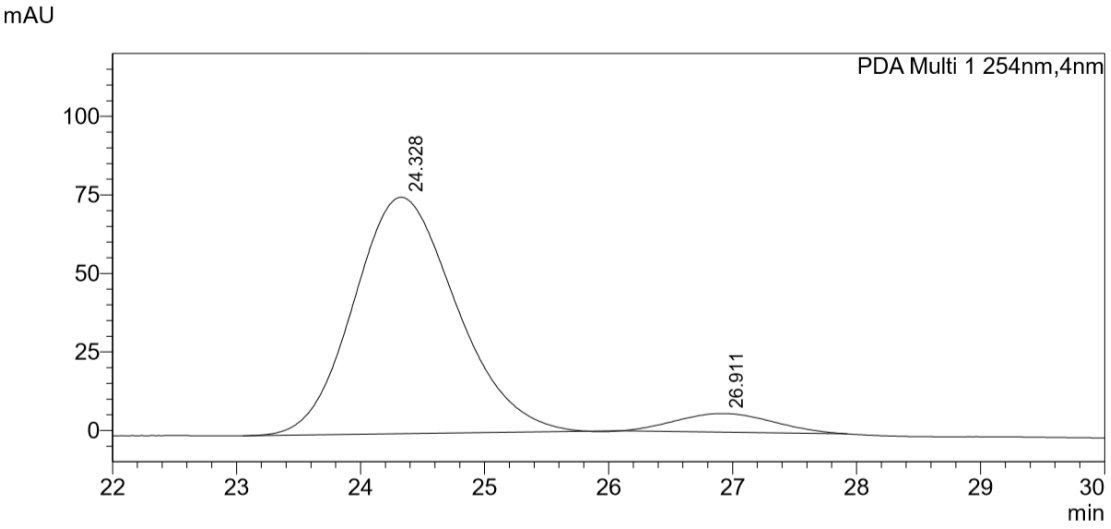
7.3 Hz, 1H), 5.89 (s, 1H), 4.31-4.21 (m, 3H), 2.30 (s, 3H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.40 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 165.1, 157.7, 146.9, 141.7, 138.2, 135.9, 128.5, 128.4, 128.1, 125.9, 125.3, 124.7, 124.0, 123.1, 115.2, 110.9, 81.8, 61.8, 61.6, 39.4, 28.2, 21.8, 16.4, 14.5. HRMS (ESI) *m/z* calcd for $C_{27}H_{30}N_2O_4S$ $[M+Na]^+$ = 501.1824, found = 501.1822; The ee value was 86%, t_R (major) = 24.3 min, t_R (minor) = 26.9 min (Chiralcel IC, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	26.457	117200	50.441	7892729	48.560
2	29.270	115149	49.559	8360974	51.440
Total		232348	100.000	16253703	100.000

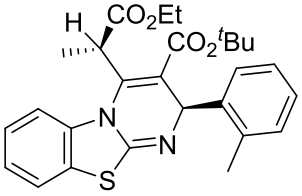


Peak Table

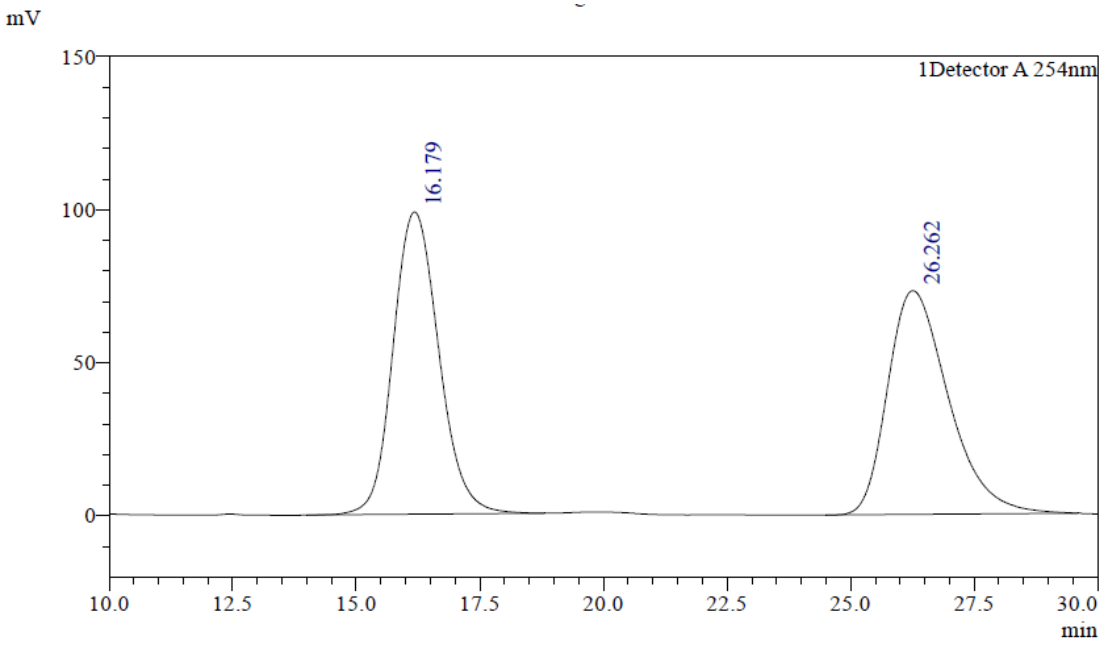
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	24.328	75293	92.657	4337639	92.988
2	26.911	5967	7.343	327116	7.012
Total		81260	100.000	4664754	100.000

<u>*tert*-butyl(*R*)-4-((*S*)-1-ethoxy-1-oxopropan-2-yl)-2-(*o*-tolyl)-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (3g)</u>



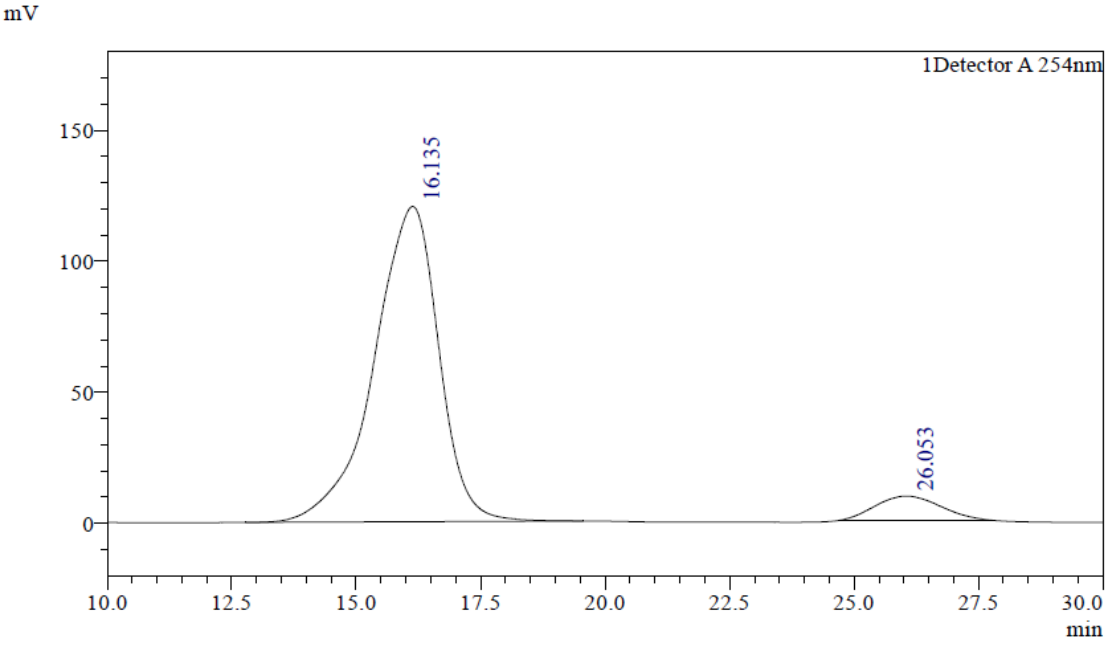
White foam, (36.8 mg), 77% yield; $[\alpha]^{25}_{D}$ = +96.8 (*c* 0.47, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.24-7.22 m, 1H), 7.19-7.07 (m, 5H), 6.04 (s, 1H), 4.38-4.29 (m, 3H), 2.62 (s, 3H), 1.53 (d, *J* = 6.9 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 164.8, 160.8, 158.4, 157.0, 146.6, 141.5, 132.0, 128.4, 127.4, 126.9, 115.5 (d, *J* = 9.0 Hz), 112.7, 112.4, 110.5, 110.4, 110.2, 81.6, 61.8, 61.4, 39.1, 28.0, 16.1, 14.2. HRMS (ESI) *m/z* calcd for $C_{27}H_{30}N_2O_4S$ $[M+Na]^+$ = 501.1824, found = 501.1820; The ee value was 86%, t_R (major) = 16.1 min, t_R (minor) = 26.1 min (Chiralcel IC, λ = 254 nm, 2% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.179	98772	57.460	6365696	50.384
2	26.262	73126	42.540	6268787	49.616
Total		171897	100.000	12634483	100.000

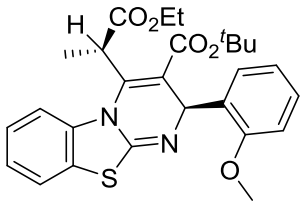


Peak Table

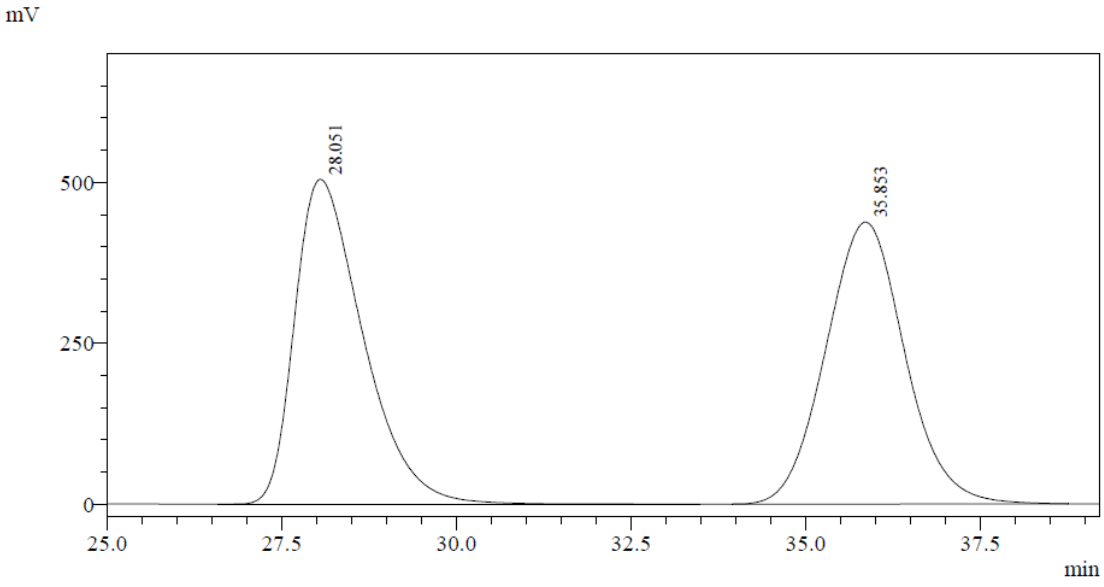
Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.135	120354	92.936	10896037	92.902
2	26.053	9149	7.064	832464	7.098
Total		129502	100.000	11728501	100.000

tert-butyl(_R_)-4-((_S_)-1-ethoxy-1-oxopropan-2-yl)-2-(2-methoxyphenyl)-2_H_-benzo[4,5]thiazolo[3,2-_a_]pyrimidine-3-carboxylate (3h)



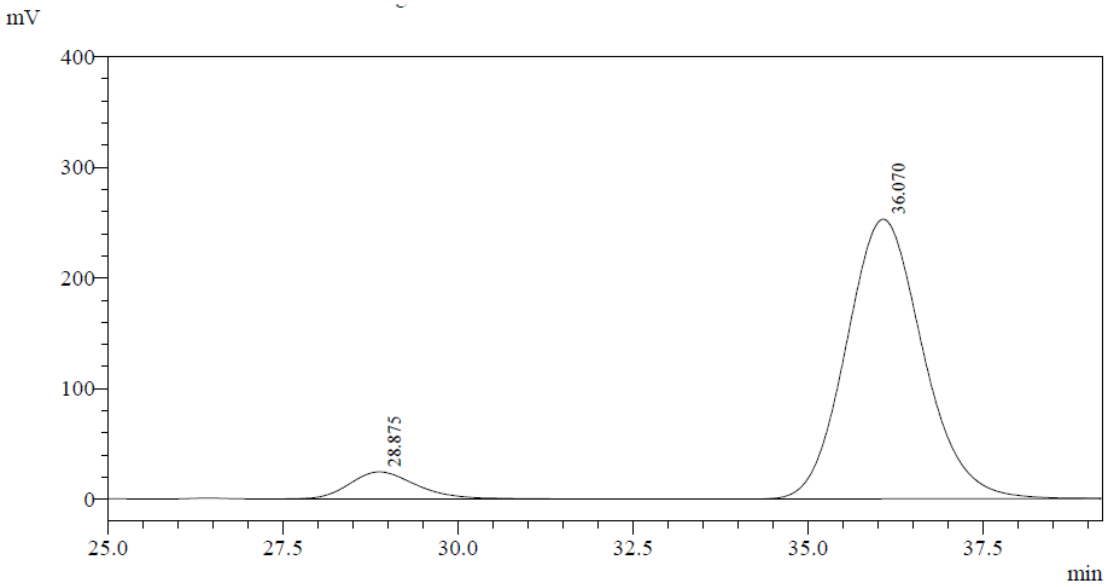
White foam, (36.5 mg), 74% yield; $[\alpha]^{25}_{D}$ = +148.8 (*c* 0.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (td, *J* = 8.0, 1.4 Hz, 2H), 7.24-7.15 (m, 3H), 7.09 (td, *J* = 7.5, 1.2 Hz, 1H), 6.89 (d, *J* = 7.8 Hz, 1H), 6.82 (td, *J* = 7.5, 0.8 Hz, 1H), 6.24 (s, 1H), 4.30-4.26 (m, 3H), 3.88 (s, 3H), 1.52 (d, *J* = 6.9 Hz, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.8, 164.9, 157.5, 147.2, 135.9, 129.5, 129.0, 128.2, 125.8, 125.4, 124.4, 123.0, 120.7, 114.8, 114.1, 111.1, 81.3, 61.6, 57.1, 56.0, 39.4, 28.1, 27.2, 16.5, 14.5. HRMS (ESI) *m/z* calcd for $C_{27}H_{30}N_2O_5S$ $[M+Na]^+$ = 517.1773, found = 517.1772; The ee value was 84%, t_R (major) = 36.1 min, t_R (minor) = 28.9 min (Chiralcel IG, λ = 254 nm, 12% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	28.051	504884	53.550	34478374	50.008
2	35.853	437944	46.450	34467595	49.992
Total		942828	100.000	68945969	100.000

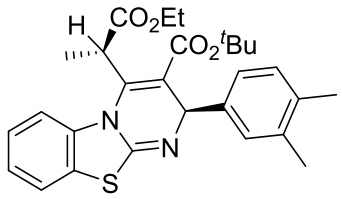


Peak Table

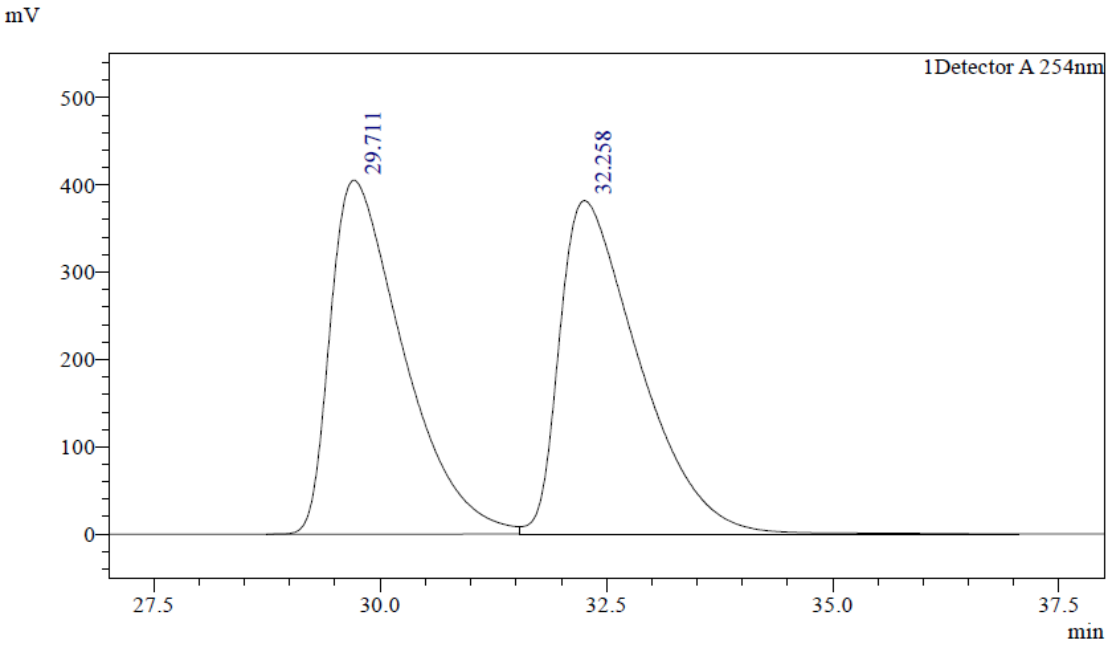
Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	28.875	24449	8.816	1638334	7.852
2	36.070	252881	91.184	19227982	92.148
Total		277330	100.000	20866316	100.000

<u>*tert*-butyl(*R*)-2-(3,4-dimethylphenyl)-4-((*S*)-1-ethoxy-1-oxopropan-2-yl)-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (3i)</u>



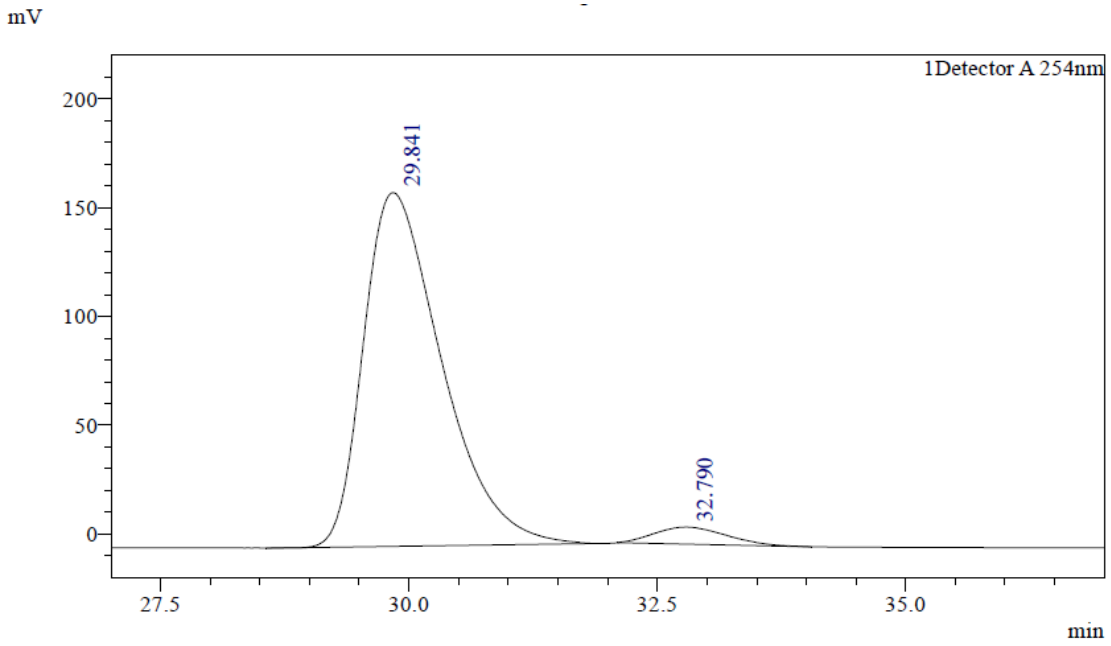
White foam, (38.4 mg), 78% yield; $[\alpha]^{25}_{D}$ = +125.1 (*c* 0.43, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.21-7.10 (m, 5H), 7.01 (d, *J* = 7.8 Hz, 1H), 5.87 (s, 1H), 4.30-4.26 (m, 3H), 2.21 (s, 3H), 2.19 (s, 3H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.40 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 164.9, 157.3, 146.6, 138.9, 136.5, 135.7, 135.6, 129.5, 128.5, 125.6, 125.1, 124.3, 124.0, 122.8, 114.9, 110.7, 81.5, 61.3, 61.2, 39.1, 28.0, 19.9, 19.4, 16.1, 14.3. HSRMS (ESI) *m/z* calcd for $C_{28}H_{32}N_2O_4S$ $[M+Na]^+$ = 515.1980, found = 515.1970; The ee value was 92%, t_R (major) = 29.8 min, t_R (minor) = 32.8 min (Chiralcel IE, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	29.711	405132	51.489	22788558	49.315
2	32.258	381708	48.511	23421377	50.685
Total		786840	100.000	46209935	100.000

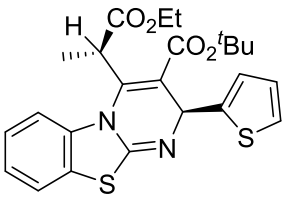


Peak Table

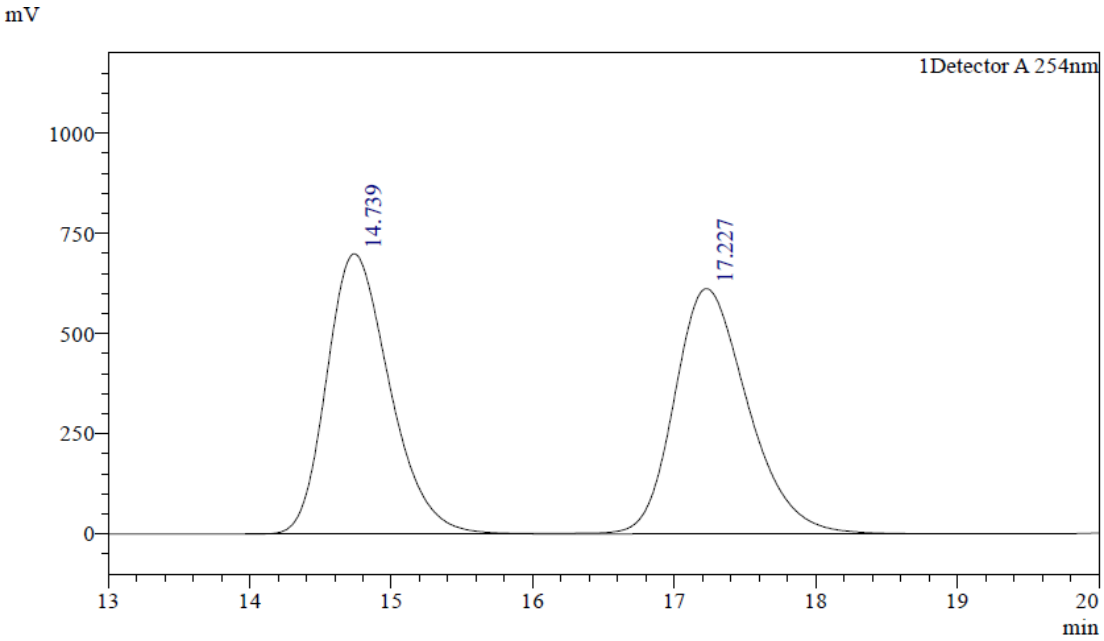
Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	29.841	8912493	162575	95.458	95.800
2	32.790	390752	7736	4.542	4.200
Total		9303245	170311	100.000	100.000

<u>*tert*-butyl(*R*)-4-((*S*)-1-ethoxy-1-oxopropan-2-yl)-2-(thiophen-2-yl)-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (3j)</u>



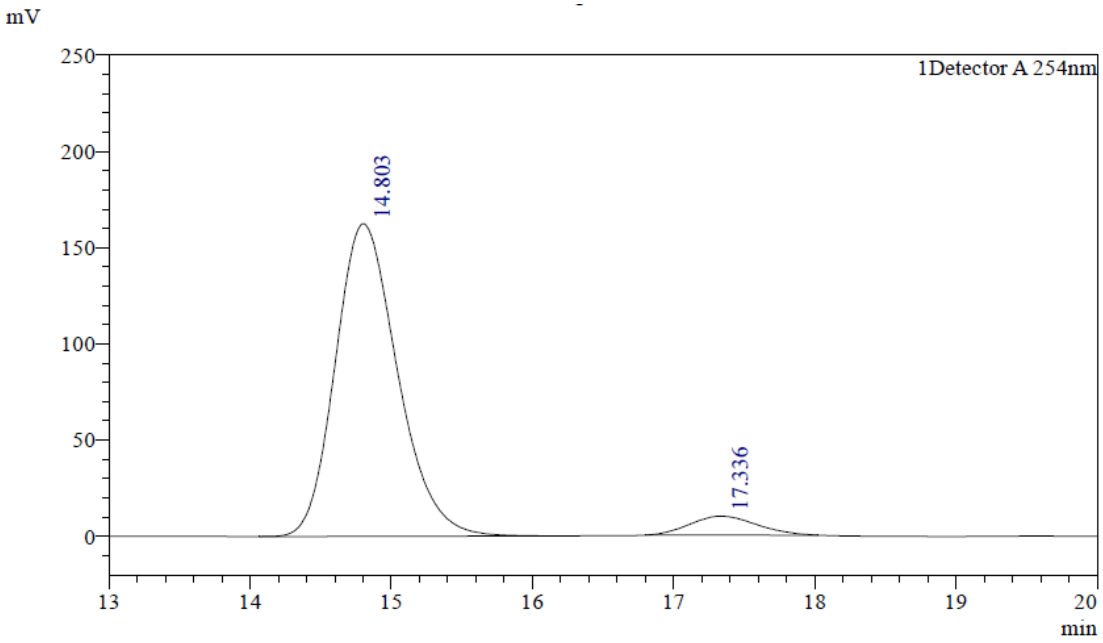
White foam, (42.3 mg), 90% yield; $[\alpha]^{25}_{D}$ = +167.7 (*c* 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.35 (m, 1H), 7.21-7.11 (m, 4H), 6.97 (d, *J* = 3.5 Hz, 1H), 6.86 (dd, *J* = 5.0, 3.6 Hz, 1H), 6.12 (s, 1H), 4.36 (d, *J* = 5.7 Hz, 1H), 4.21 (dd, *J* = 14.0, 7.0 Hz, 2H), 1.48 (d, *J* = 6.9 Hz, 3H), 1.46 (s, 9H), 1.24 (t, *J* = 7.1 Hz,3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 164.2, 158.9, 147.1, 145.4, 135.5, 126.3, 125.7, 125.0, 124.6, 124.5, 124.1, 122.9, 115.2, 110.8, 81.8, 61.4, 57.2, 39.1, 28.0, 16.1, 14.2. HRMS (ESI) *m/z* calcd for $C_{24}H_{26}N_2O_4S_2$ $[M+Na]^+$ = 493.1232, found = 493.1223; The ee value was 88%, t_R (major) = 14.8 min, t_R (minor) = 17.3 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.739	698608	53.321	21624621	49.446
2	17.227	611597	46.679	22109499	50.554
Total		1310205	100.000	43734120	100.000

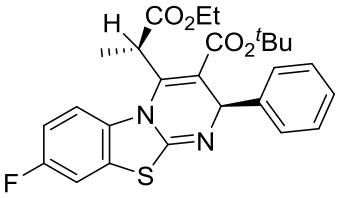


Peak Table

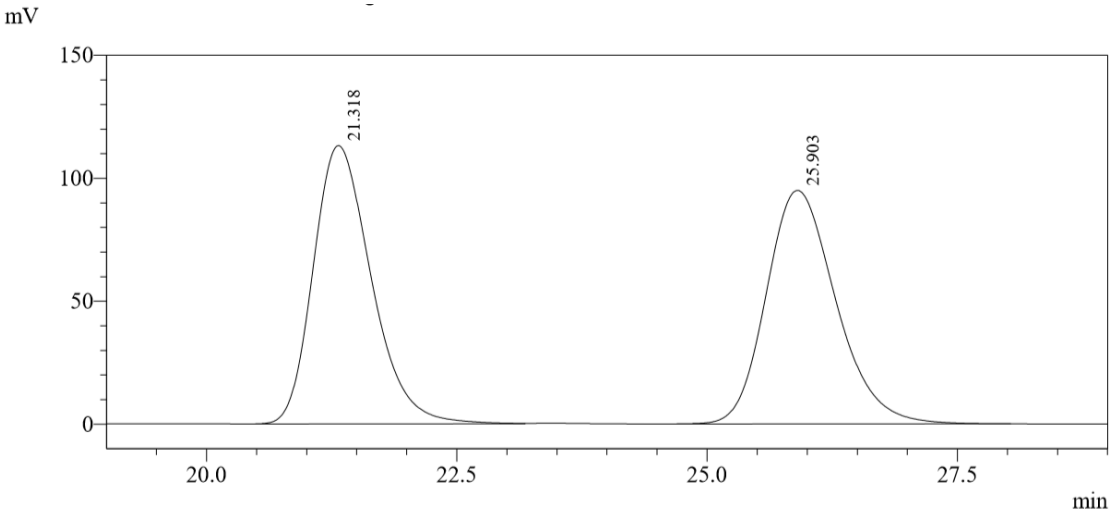
Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.803	162275	94.307	4966967	93.902
2	17.336	9797	5.693	322564	6.098
Total		172072	100.000	5289531	100.000

tert-butyl(_R_)-4-((_S_)-1-ethoxy-1-oxopropan-2-yl)-8-fluoro-2-phenyl-2_H_-benzo[4,5]thiazolo[3,2-_a_]pyrimidine-3-carboxylate (3k)



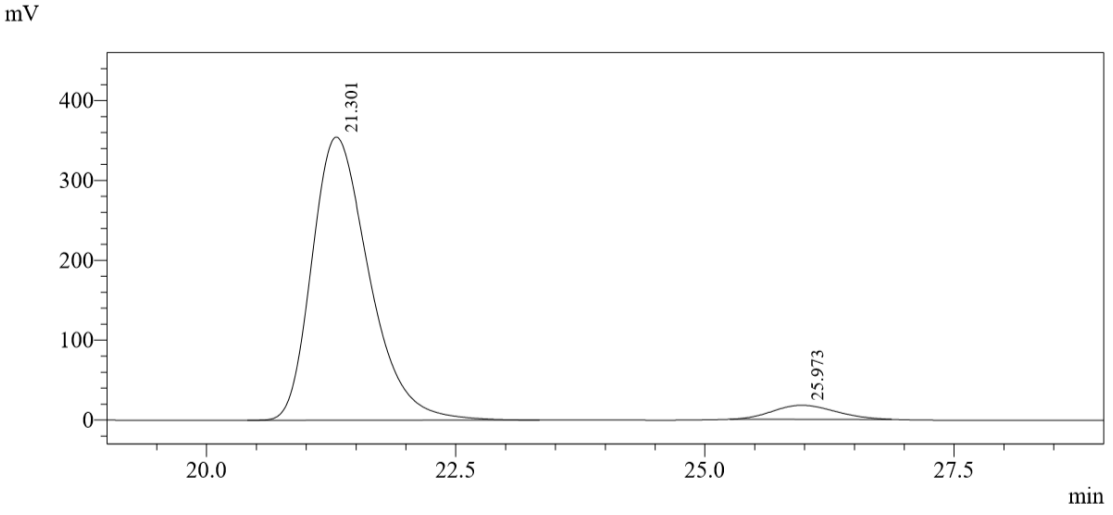
White foam, (44.8 mg), 93% yield; $[\alpha]^{25}_{D}$ = +191.2 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (m, 2H), 7.28-7.26 (m, 1H), 7.24-7.18 (m, 2H), 7.08 (ddd, *J* = 10.3, 8.3, 3.5 Hz, 2H), 6.86 (td, *J* = 8.7, 2.7 Hz, 1H), 5.90 (s, 1H), 4.29-4.19 (m, 3H), 1.48 (d, *J* = 6.9 Hz, 3H), 1.38 (s, 9H), 1.28 (t, *J* = 7.2 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 165.0, 161.1, 158.0 (d, *J* = 118 Hz), 146.9, 141.6, 132.2, 128.7, 127.7, 127.1, 127.0 (d, *J* = 98.1 Hz), 115.8 (d, *J* = 8.0 Hz), 112.9 (d, *J* = 240.0 Hz), 110.7, 110.5, 81.9, 61.9, 61.7, 39.4, 28.2, 16.3, 14.4. HRMS (ESI) *m/z* calcd for $C_{27}H_{31}FN_2O_4S$ $[M+Na]^+$ = 505.1573, found = 505.1571; The ee value was 90%, t_R (major) = 21.3 min, t_R (minor) = 26.0 min (Chiralcel IC, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 0.5 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.318	113146	54.377	4566190	49.847
2	25.903	94930	45.623	4594284	50.153
Total		208076	100.000	9160475	100.000

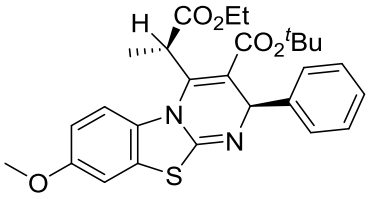


Peak Table

Detector A 254nm

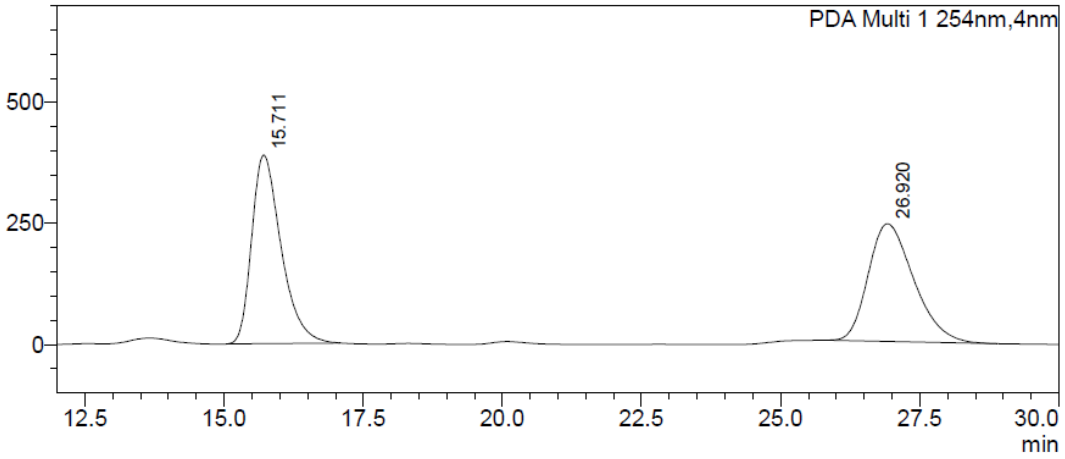
Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.301	354474	95.273	14121367	94.813
2	25.973	17588	4.727	772521	5.187
Total		372061	100.000	14893888	100.000

<u>*tert*-butyl(*R*)-4-((*S*)-1-ethoxy-1-oxopropan-2-yl)-8-methoxy-2-phenyl-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (3l)</u>



White foam, (45.0 mg), 91% yield; $[\alpha]^{25}_{D}$ = +87.6 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.3 Hz, 2H), 7.29-7.19 (m, 3H), 7.08 (d, *J* = 8.9 Hz, 1H),

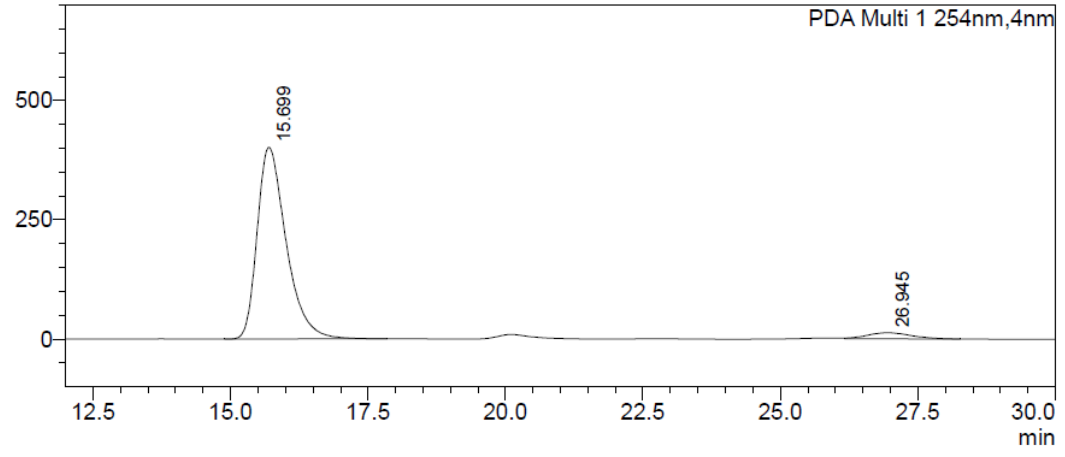
6.90 (d, *J* = 2.6 Hz, 1H), 6.70 (dd, *J* = 8.9, 2.6 Hz, 1H), 5.91 (s, 1H), 4.32-4.21 (m, 3H), 3.78 (s, 3H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.39 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 164.9, 161.5, 157.0, 147.1, 141.6, 129.4, 128.4, 127.3, 126.9, 126.5, 115.8, 111.5, 109.5 108.5, 81.4, 61.3, 55.8, 39.1, 31.6, 28.0, 22.7, 16.0, 14.2. HRMS (ESI) *m/z* calcd for $C_{27}H_{30}N_2O_5S$ $[M+Na]^+$ = 517.1773, found = 517.1754; The ee value was 91%, t_R (major) = 15.7 min, t_R (minor) = 26.7 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.711	389633	61.574	14321161	50.871
2	26.920	243150	38.426	13830537	49.129
Total		632784	100.000	28151698	100.000

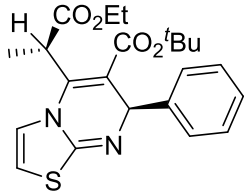


Peak Table

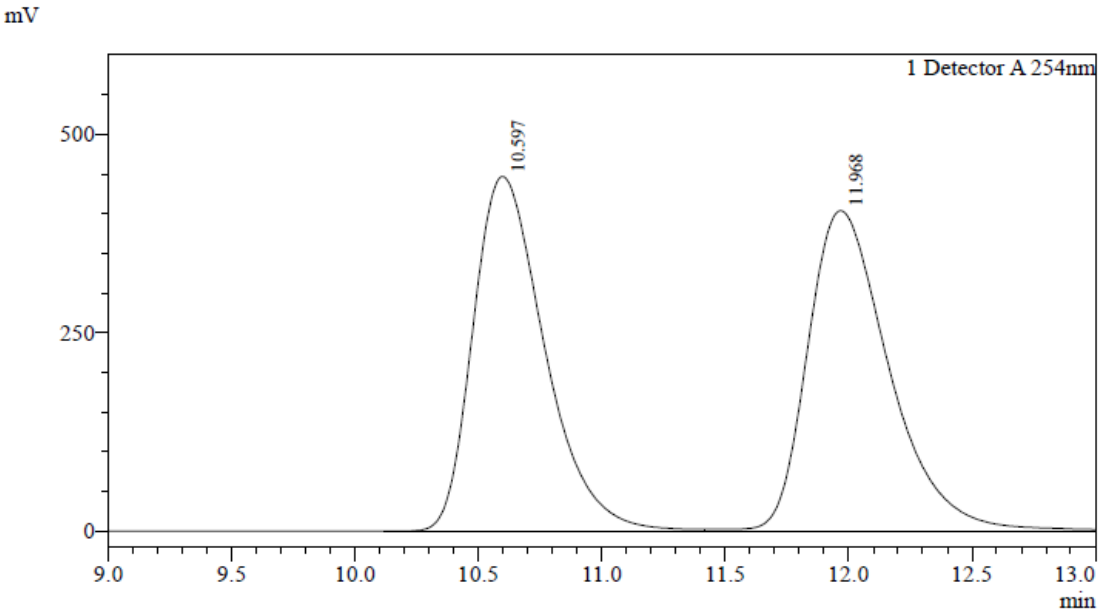
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.699	402206	96.871	14750116	95.360
2	26.945	12991	3.129	717726	4.640
Total		415198	100.000	15467842	100.000

tert-butyl(_R_)-5-((_S_)-1-ethoxy-1-oxopropan-2-yl)-7-phenyl-7_H_-thiazolo[3,2-_a_]pyrimidine-6-carboxylate (3m)



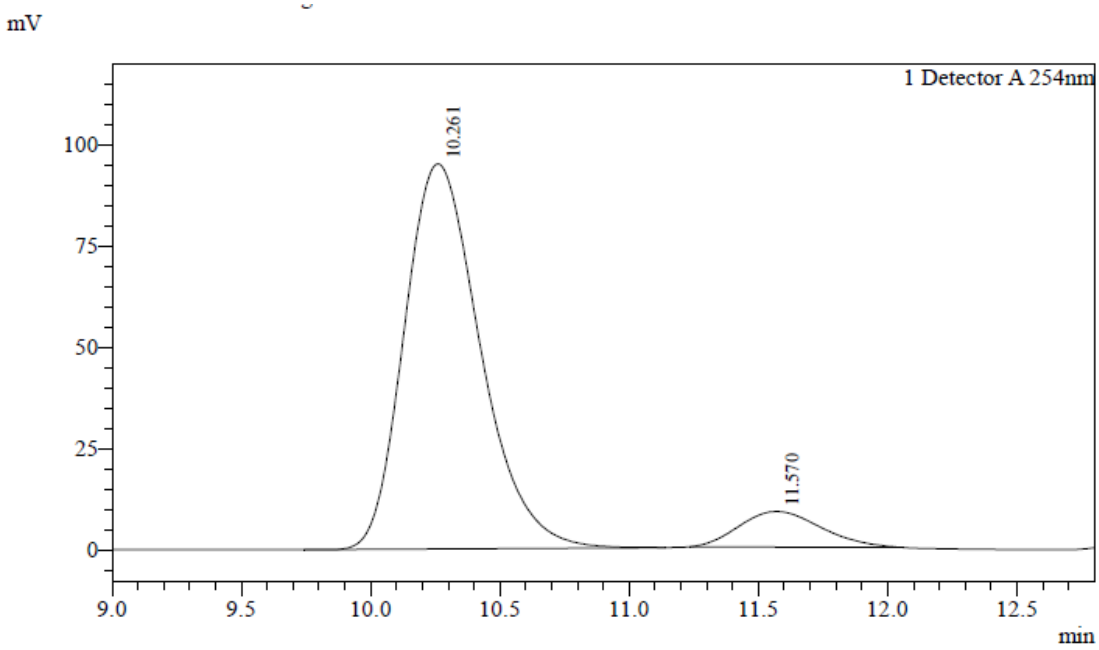
Light yellow solid, (37.7 mg), 91% yield; $[\alpha]^{25}_{D}$ = +54.0 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.34-7.30 (m, 3H), 6.44 (d, *J* = 5.3 Hz, 1H), 5.88 (d, *J* = 5.2 Hz, 1H), 5.70 (s, 1H), 4.32-4.25 (m, 1H), 4.24-4.19 (m, 1H), 1.62 (s, 2H), 1.45 (t, *J* = 6.0 Hz, 3H), 1.34 (d, *J* = 7.2 Hz, 3H), 1.31 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 165.9, 156.9, 144.7, 143.4, 128.7, 127.6, 127.4, 121.3, 105.7, 102.2, 81.8, 62.1, 62.0, 38.3, 28.2, 14.4, 13.8. HRMS (ESI) *m/z* calcd for $C_{22}H_{26}N_2O_4S$ $[M+Na]^+$ = 437.1511, found = 437.1509; The ee value was 80%, t_R (major) = 10.3 min, t_R (minor) = 11.6 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.597	446871	52.537	9044646	49.252
2	11.968	403716	47.463	9319320	50.748
Total		850586	100.000	18363966	100.000

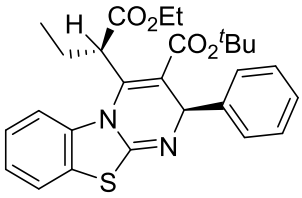


Peak Table

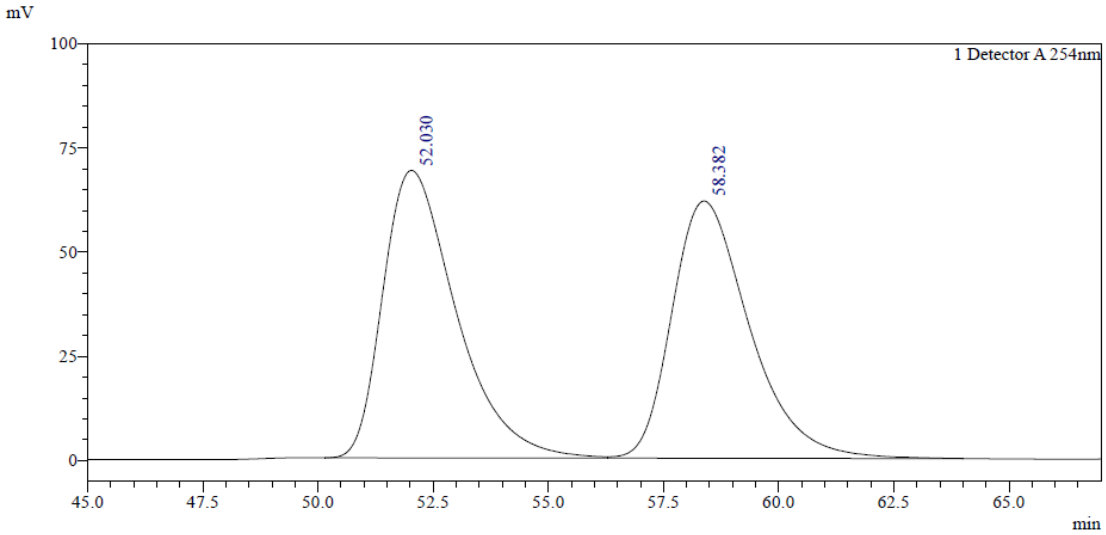
Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.261	94977	91.544	1940665	90.926
2	11.570	8774	8.456	193660	9.074
Total		103751	100.000	2134324	100.000

tert-butyl(_R_)-4-((_S_)-1-ethoxy-1-oxobutan-2-yl)-2-phenyl-2_H_-benzo[4,5]thiazolo[3,2-_a_]pyrimidine-3-carboxylate (4a)



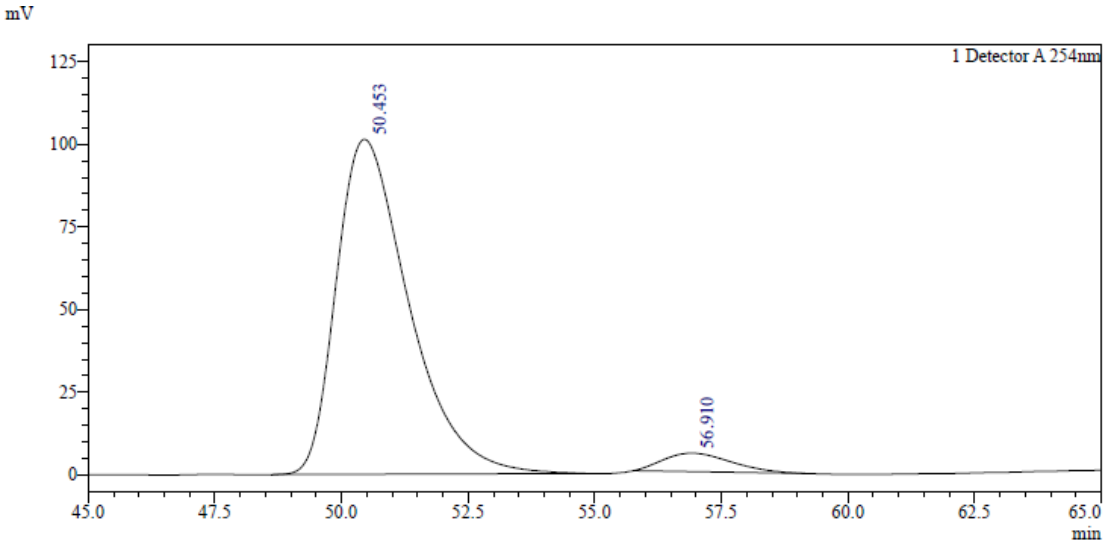
White foam, (42.5 mg), 89% yield; $[\alpha]^{25}_{D}$ = +88.4 (*c* 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.3 Hz, 2H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.21-7.17 (m, 2H), 7.15-7.11 (m, 1H), 7.10-7.08 (m, 2H), 7.07-7.01 (m, 1H), 5.89 (s, 1H), 4.29- 4.18 (m, 2H), 3.98 (d, *J* = 5.4 Hz, 1H), 2.21-2.14 (m, 1H), 1.89-1.81 (m, 1H), 1.34 (s, 1H), 1.32 (s, 9H), 1.26 (t, *J* = 7.2 Hz, 3H), 0.58 (t, *J* = 7.5 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 164.9, 157.5, 146.4, 141.7, 135.9, 128.6, 127.5, 127.2, 125.8, 125.43, 124.7, 123.1, 115.7, 110.8, 81.7, 62.0, 61.4, 46.7, 28.2, 24.7, 14.5, 11.9. HRMS (ESI) *m/z* calcd for $C_{27}H_{30}N_2O_5S$ $[M+Na]^+$ = 501.1824, found = 501.1820; The ee value was 90%, t_R (major) = 50.5 min, t_R (minor) = 56.9 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	52.030	7655227	68987	52.796	51.397
2	58.382	7238949	61679	47.204	48.603
Total		14894176	130666	100.000	100.000

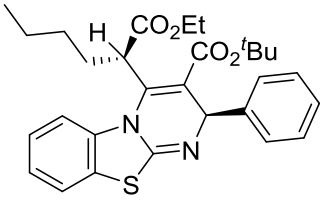


Peak Table

Detector A 254nm

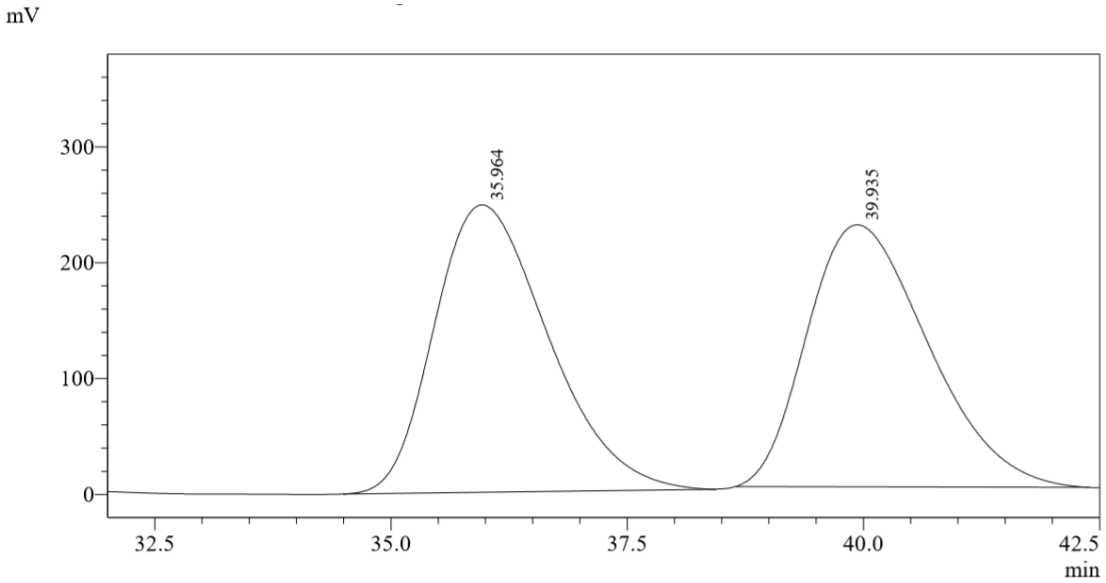
Peak#	Ret. Time	Area	Height	Height%	Area%
1	50.453	10110645	101359	94.737	95.008
2	56.910	531262	5631	5.263	4.992
Total		10641907	106990	100.000	100.000

<u>*tert*-butyl(*R*)-4-((*S*)-1-ethoxy-1-oxohexan-2-yl)-2-phenyl-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (4b)</u>



White foam, (48.0 mg), 92% yield; $[\alpha]^{25}_{D}$ = +138.1 (*c* 0.40, $CHCl_3$); ^{1}H NMR (400

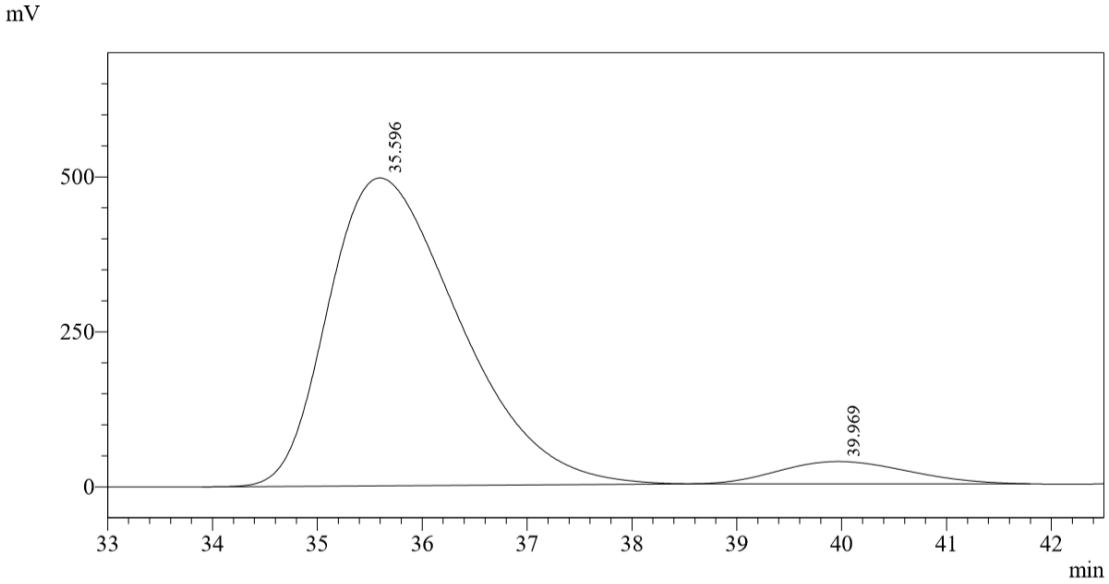
MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.6 Hz, 2H), 7.36 (d, *J* = 7.2 Hz, 1H), 7.29-7.18 (m, 3H), 7.19-7.11 (m, 3H), 5.97 (s, 1H), 4.51 (dd, *J* = 10.8, 4.2 Hz, 1H), 4.40-4.28 (m, 2H), 4.10 (dd, *J* = 13.6, 4.2 Hz, 1H), 2.22-2.15 (m, 1H), 1.96-1.86 (m, 1H), 1.40 (s, 9H), 1.34 (t, *J* = 7.2 Hz, 3H), 1.09-0.99 (m, 3H), 0.90-0.84 (m, 1H), 0.73 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 164.7, 157.5, 146.2, 141.1, 135.6, 128.4, 127.4, 127.0, 125.7, 125.2, 124.6, 122.9, 115.4, 81.6, 61.5, 61.3, 44,7, 30.8, 29.1, 28.0, 22.2, 14.3, 13.7. HRMS (ESI) *m/z* calcd for $C_{29}H_{34}N_2O_4S$ $[M+Na]^+$ = 529.2173, found = 529.2135; The ee value was 87%, t_R (major) = 35.6 min, t_R (minor) = 40.0 min (Chiralcel IC, λ = 254 nm, 2% *i*-PrOH/hexanes, flow rate = 0.5 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	35.964	247993	52.301	20817849	50.820
2	39.935	226171	47.699	20145640	49.180
Total		474164	100.000	40963489	100.000

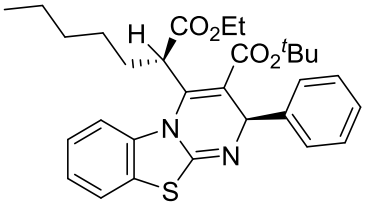


Peak Table

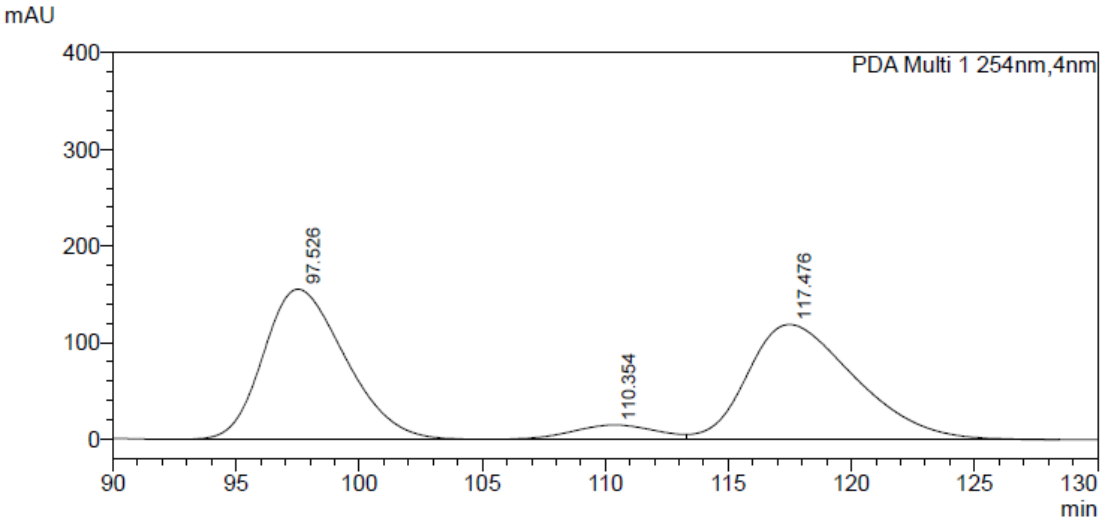
Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	35.596	496485	93.257	43148787	93.346
2	39.969	35899	6.743	3075884	6.654
Total		532384	100.000	46224671	100.000

<u>*tert*-butyl(*R*)-4-((*S*)-1-ethoxy-1-oxoheptan-2-yl)-2-phenyl-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (4c)</u>



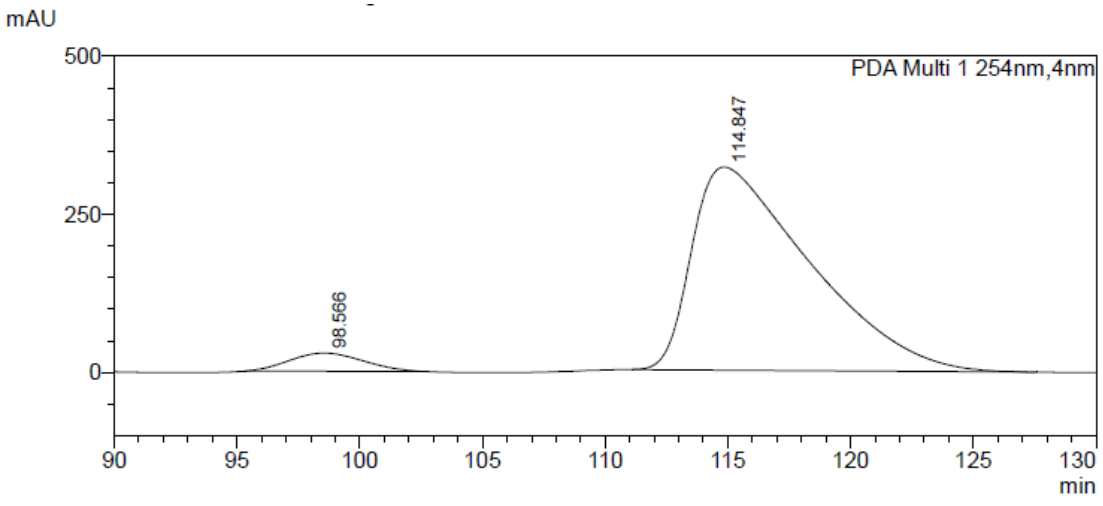
White foam, (47.3 mg), 91% yield; $[\alpha]^{25}_{D}$ = +199.8 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 7.2 Hz, 2H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.29-7.25 (m, 2H), 7.22-7.20 (m, 1H), 7.19-7.16 (m, 2H), 7.14-7.09 (m, 1H), 5.96 (s, 1H), 4.39-4.26 (m, 2H), 4.10 (d, *J* = 5.8 Hz, 1H), 2.21-2.13 (m, 1H), 1.97-1.88 (m, 1H), 1.39 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.16-1.07 (m, 3H), 0.99-0.88 (m, 3H), 0.71 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 165.2, 157.7, 146.8, 141.9, 136.2, 128.8, 127.7, 127.4, 126.0, 125.7, 124.9, 123.3, 115.8, 111.0, 81.9, 62.3, 61.70, 44.9, 31.6, 31.5, 28.4, 27.1, 22.8, 14.7, 14.3. HRMS (ESI) *m/z* calcd for $C_{31}H_{40}N_2O_4S$ $[M+H]^+$ = 521.2474, found = 521.2467; The ee value was 89%, t_R (major) = 114.8 min, t_R (minor) = 98.6 min (Chiralcel IG, λ = 254 nm, 2% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	97.526	155285	53.774	35877931	47.604
2	110.354	14644	5.071	3429293	4.550
3	117.476	118846	41.155	36059840	47.846
Total		288774	100.000	75367064	100.000

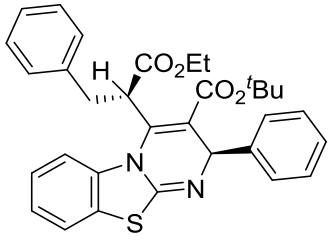


Peak Table

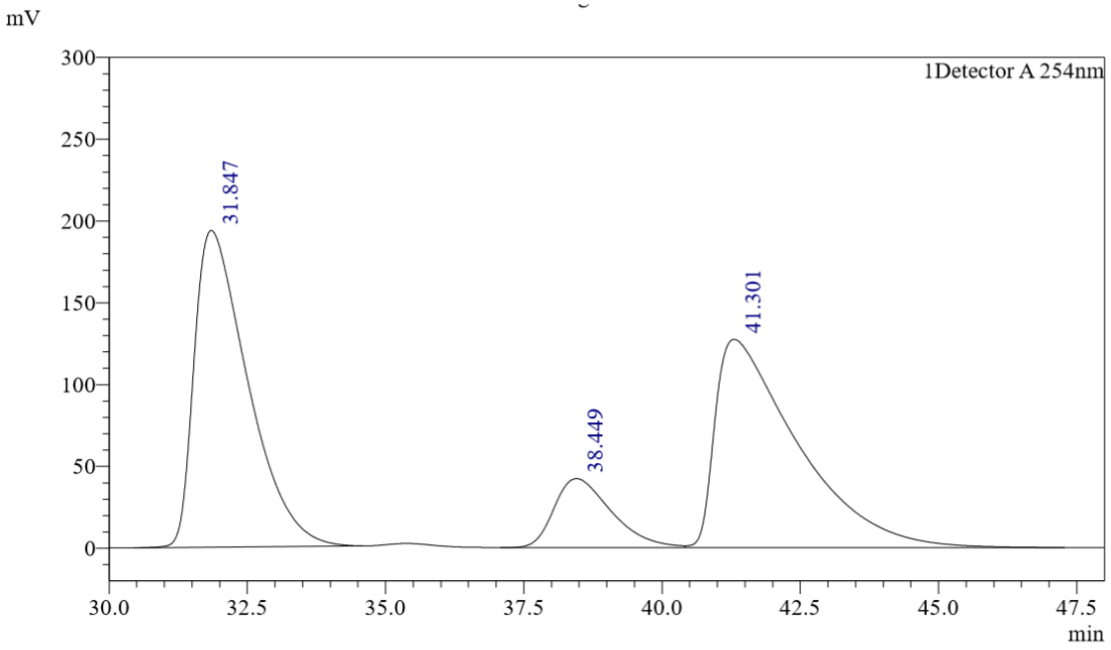
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	98.566	28785	8.227	6058249	5.338
2	114.847	321109	91.773	107440870	94.662
Total		349894	100.000	113499119	100.000

<u>*tert*-butyl(*R*)-4-((*S*)-1-ethoxy-1-oxo-3-phenylpropan-2-yl)-2-phenyl-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (4d)</u>



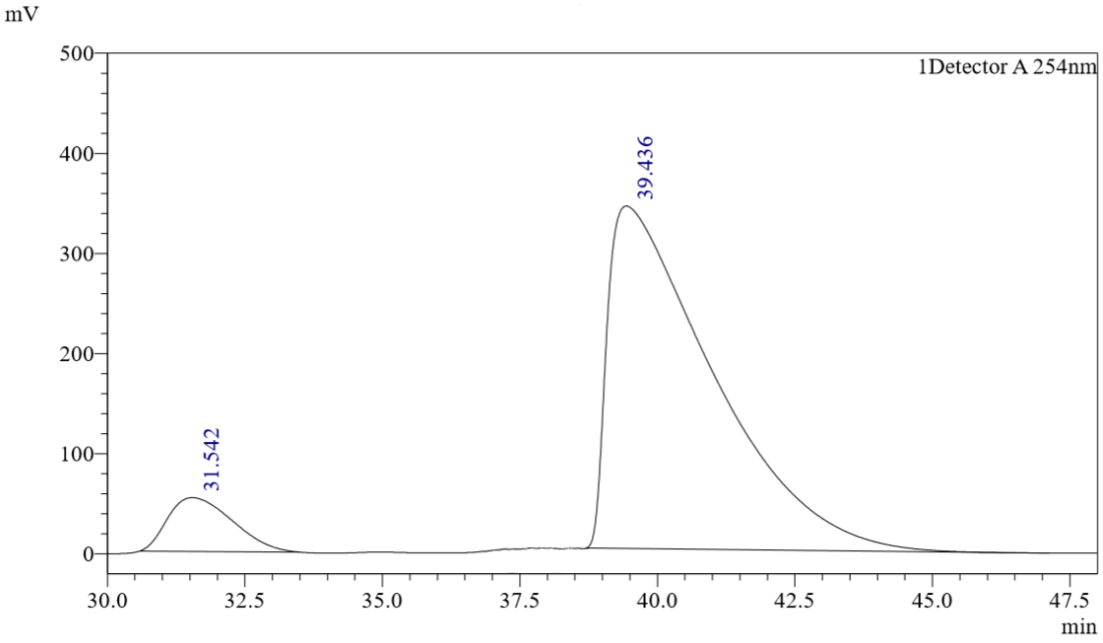
White foam, (47.5 mg), 88% yield; $[\alpha]^{25}_{D}$ = +194.4 (*c* 0.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.26-7.15 (m, 3H), 7.15-7.07 (m, 3H), 7.06-7.00 (m, 4H), 6.81-6.71 (m, 2H), 5.94 (s, 1H), 4.51 (dd, *J* = 10.8, 4.2 Hz, 1H), 4.46-4.28 (m, 2H), 3.55 (dd, *J* = 13.6, 4.2 Hz, 1H), 3.11 (dd, *J* = 13.6, 10.9 Hz, 1H), 1.47 (s, 9H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.60, 164.92, 157.0, 145.8, 141.5, 137.3, 135.3, 128.5, 128.3, 128.1, 127.2, 126.9, 126.7, 125.7, 125.0, 124.1, 122.4, 115.3, 110.5, 81.5, 61.5, 61.3, 45.9, 36.8, 28.1, 14.3. HRMS (ESI) *m/z* calcd for $C_{32}H_{32}N_2O_4S$ $[M+Na]^+$ = 563.1980, found = 563.1980; The ee value was 82%, t_R (major) = 39.4 min, t_R (minor) = 31.5 min (Chiralcel IE, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	31.847	193597	53.330	13049612	44.539
2	38.449	42125	11.604	3033857	10.355
3	41.301	127293	35.065	13216045	45.107
Total		363015	100.000	29299514	100.000

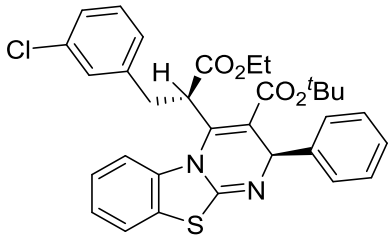


Peak Table

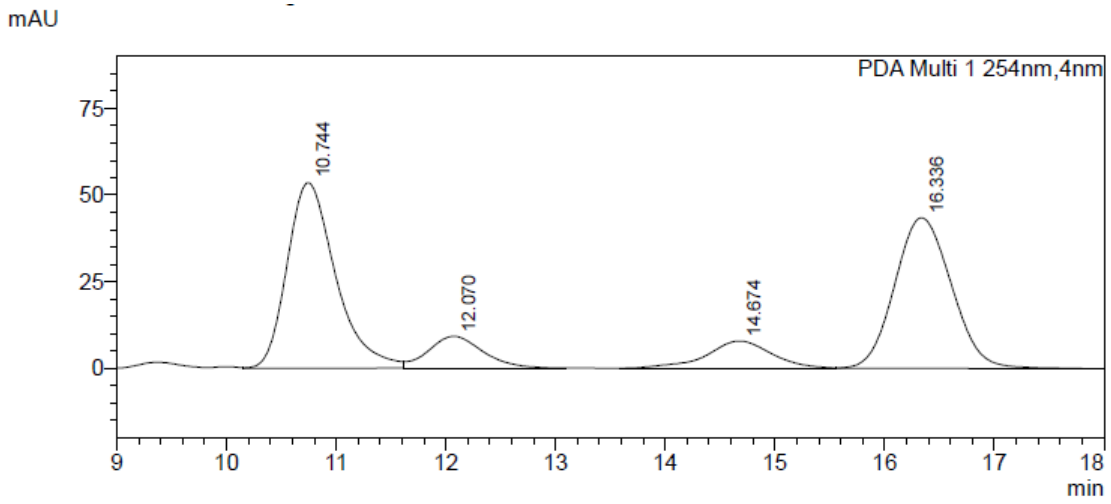
Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	31.542	53746	13.585	4399162	8.792
2	39.436	341868	86.415	45636842	91.208
Total		395614	100.000	50036004	100.000

tert-butyl(_R_)-4-((_S_)-3-(3-chlorophenyl)-1-ethoxy-1-oxopropan-2-yl)-2-phenyl-2_H_-benzo[4,5]thiazolo[3,2-_a_]pyrimidine-3-carboxylate (4e)



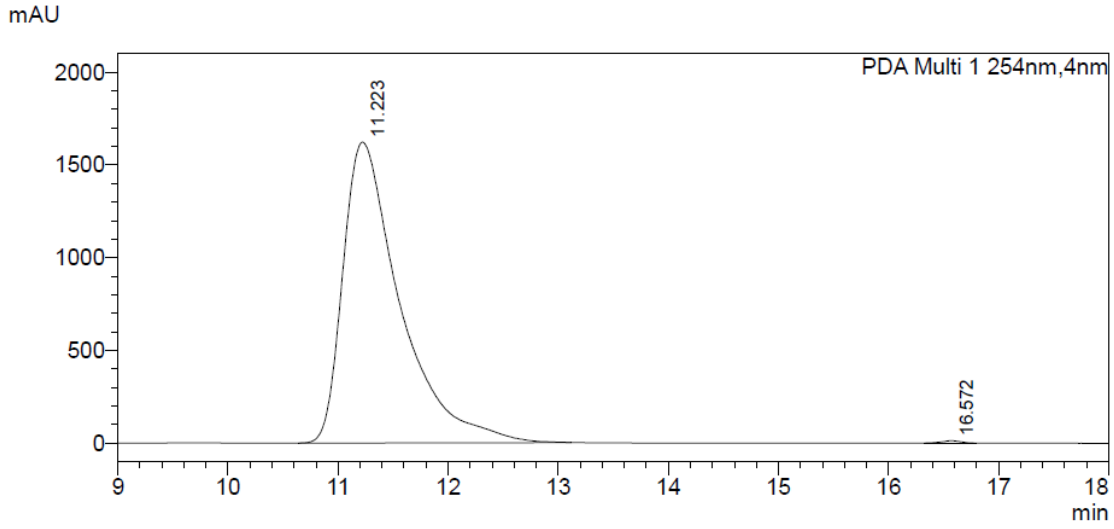
Yellow solid, (54.9 mg), 93% yield; $[\alpha]^{25}_{D}$ = +119.3 (*c* 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.25 (t, *J* = 1.7 Hz, 1H), 7.23-7.16 (m, 4H), 7.13 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.09-7.06 (m, 2H), 7.04-6.99 (m, 2H), 6.67-6.63 (m, 2H), 5.93 (s, 1H), 4.50 (dd, *J* = 10.8, 4.2 Hz, 1H), 4.44-4.33 (m, 2H), 3.51 (dd, *J* = 13.6, 4.3 Hz, 1H), 3.11 (dd, *J* = 13.6, 10.9 Hz, 1H), 1.47 (s, 9H), 1.36 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 164.8, 157.0, 145.7, 141.3, 139.4, 135.1, 134.3, 129.8, 128.3, 128.0, 127.2, 127.1, 126.9, 126.8, 125.7, 125.1, 124.4, 122.8, 115.2, 110.5, 81.7, 61.6, 61.2, 45.5, 36.5, 28.1, 14.3; HRMS (ESI) *m/z* calcd for $C_{32}H_{31}ClN_2O_4S$ $[M+Na]^+$ = 597.1591, found = 597.1569; The ee value was 99.5%, t_R (major) = 11.2 min, t_R (minor) = 16.6 min (Chiralcel IC, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.744	53522	46.912	1648028	42.723
2	12.070	9175	8.042	315354	8.175
3	14.674	7905	6.929	332028	8.607
4	16.336	43487	38.117	1562083	40.495
Total		114090	100.000	3857493	100.000

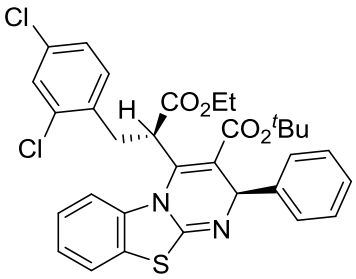


Peak Table

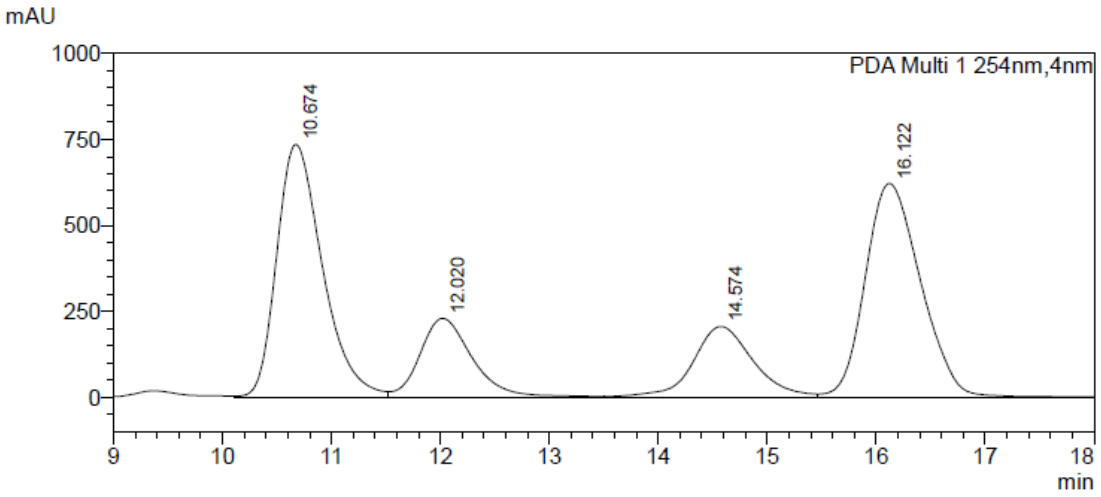
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.223	1621276	99.220	58446809	99.746
2	16.572	12742	0.780	148945	0.254
Total		1634017	100.000	58595754	100.000

<u>*tert*-butyl(*R*)-4-((*S*)-3-(2,4-dichlorophenyl)-1-ethoxy-1-oxopropan-2-yl)-2-phenyl-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (4f)</u>



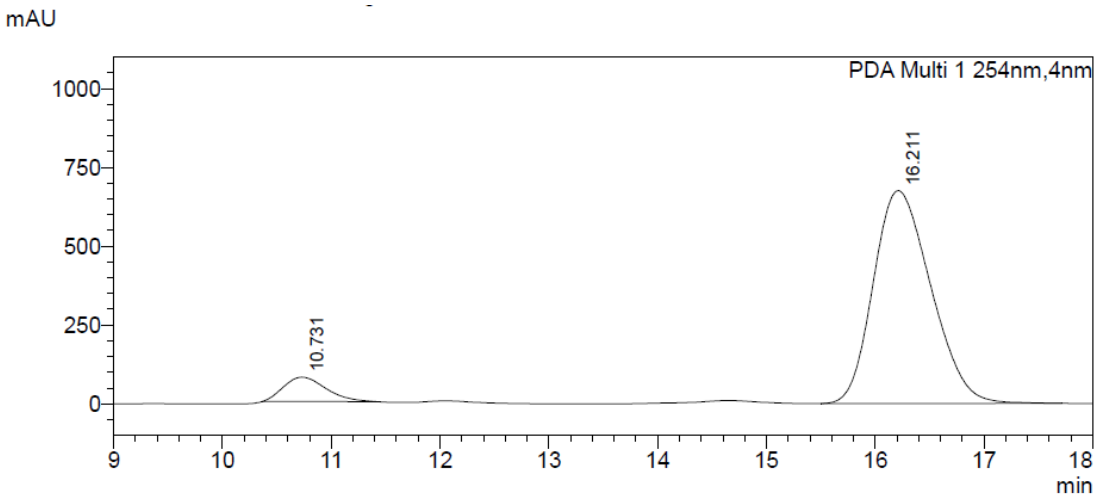
Yellow solid, (57.7 mg), 95% yield; $[\alpha]^{25}_{D}$ = +148.7 (*c* 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.26-7.22 (m, 2H), 7.20-7.16 (m, 2H), 7.14-7.00 (m, 5H), 6.84 (d, *J* = 8.2 Hz, 1H), 5.94 (s, 1H), 4.69 (dd, *J* = 10.5, 4.4 Hz, 1H), 4.44-4.32 (m, 2H), 3.65 (dd, *J* = 13.5, 4.4 Hz, 1H), 3.21 (dd, *J* = 13.5, 10.5 Hz, 1H), 1.46 (s, 9H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 165.2, 157.6, 146.2, 141.6, 135.5, 134.7, 134.1, 134.0, 132.2, 129.4, 128.7, 127.9, 127.7, 127.3, 126.0, 125.9, 124.9, 122.8, 116.0, 111.2, 82.2, 62.0, 61.7, 43.6, 34.5, 28.5, 14.7. HRMS (ESI) *m/z* calcd for $C_{32}H_{30}Cl_2N_2O_4S$ $[M+Na]^+$ = 631.1201, found = 631.1192; The ee value was 84%, t_R (major) = 16.2 min, t_R (minor) = 10.7 min (Chiralcel IG, λ = 254 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.674	735089	41.026	21460730	36.334
2	12.020	229495	12.808	7665313	12.978
3	14.574	205701	11.480	7899797	13.375
4	16.122	621481	34.685	22038563	37.313
Total		1791765	100.000	59064404	100.000

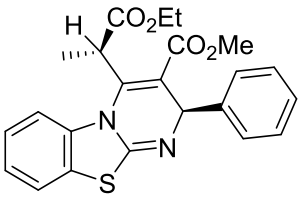


Peak Table

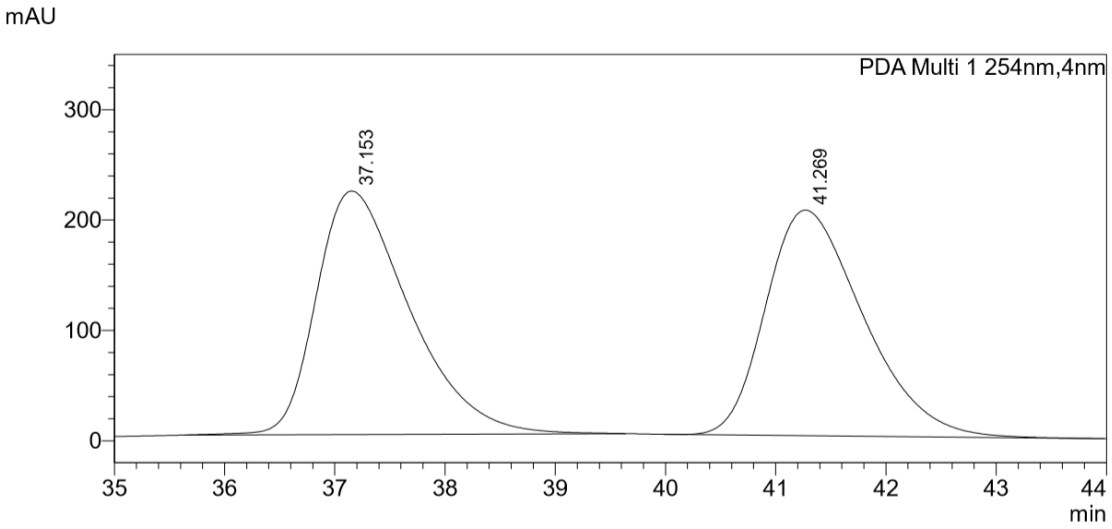
PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.731	77164	10.254	2098829	7.789
2	16.211	675366	89.746	24845533	92.211
Total		752530	100.000	26944362	100.000

methyl(*R*)-4-((*S*)-1-ethoxy-1-oxopropan-2-yl)-2-phenyl-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (4g)



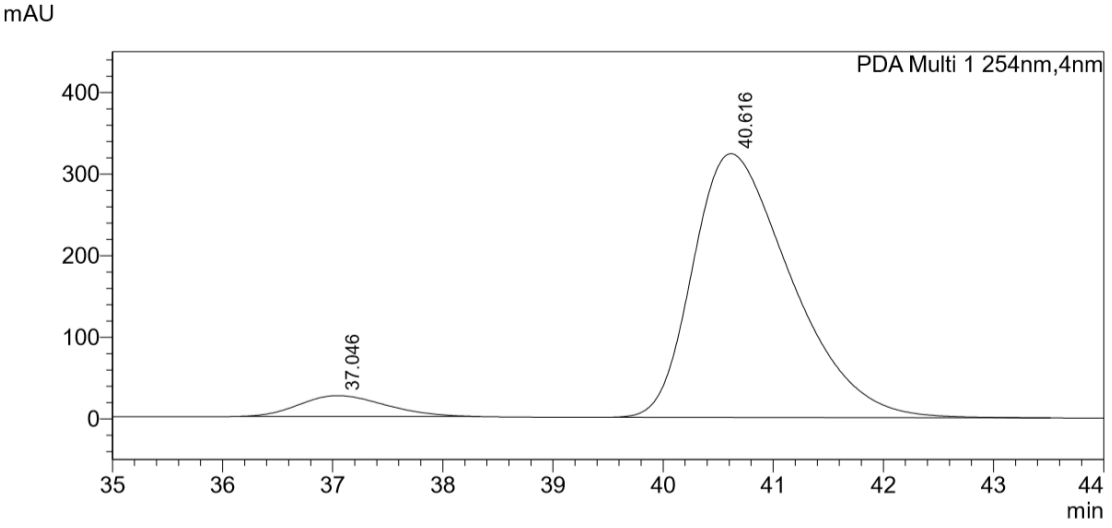
White foam, (38.4 mg), 91% yield; $[\alpha]^{25}_{D}$ = +33.2 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ7.42 (d, *J* = 7.2 Hz, 2H), 7.34 (dd, *J* = 8.0, 7.5 Hz, 1H), 7.30-7.27 (m, 2H), 7.25 (s, 1H), 7.24-7.21 (m, 2H), 7.20-7.11 (m, 2H), 6.02 (s, 1H), 4.36-4.26 (m, 3H), 3.71 (s, 3H), 1.46 (d, *J* = 6.8Hz, 3H), 1.33 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 166.1, 157.2, 148.1, 141.0, 135.5, 128.6, 127.5, 127.0, 125.7, 124.7, 122.9, 115.1, 108.4, 100.0, 61.4, 51.9, 39.5, 29.7, 16.3, 14.3. HRMS (ESI) *m/z* calcd for $C_{23}H_{22}N_2O_4S$ $[M+Na]^+$ = 445.1198, found = 445.1195; The ee value was 87%, t_R (major) = 40.6 min, t_R (minor) = 37.0 min (Chiralcel IE, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	37.153	220609	51.896	12953130	50.620
2	41.269	204489	48.104	12635641	49.380
Total		425098	100.000	25588771	100.000

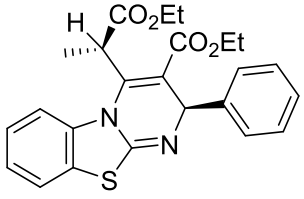


Peak Table

PDA Ch1 254nm

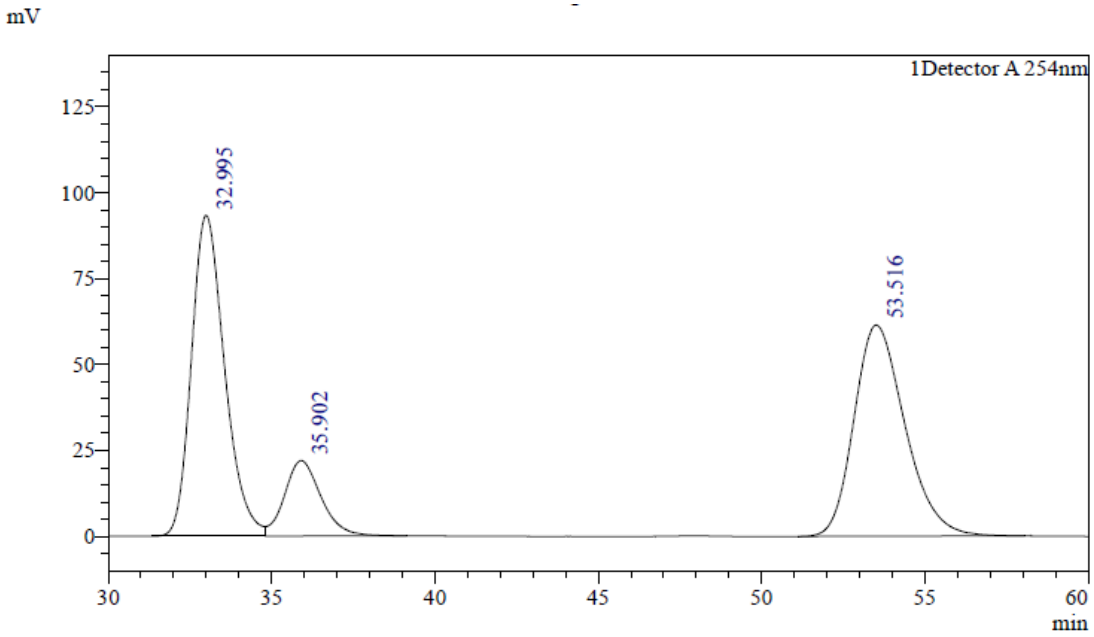
Peak#	Ret. Time	Height	Height%	Area	Area%
1	37.046	25548	7.322	1392768	6.473
2	40.616	323388	92.678	20123993	93.527
Total		348936	100.000	21516761	100.000

ethyl(*R*)-4-((*S*)-1-ethoxy-1-oxopropan-2-yl)-2-phenyl-2*H*-benzo[4,5]thiazolo[3,2-*a*]pyrimidine-3-carboxylate (4h)



White foam, (38.8 mg), 89% yield; $[\alpha]^{25}_{D}$ = +129.0 (*c* 0.60, $CHCl_3$); ^{1}H NMR (400

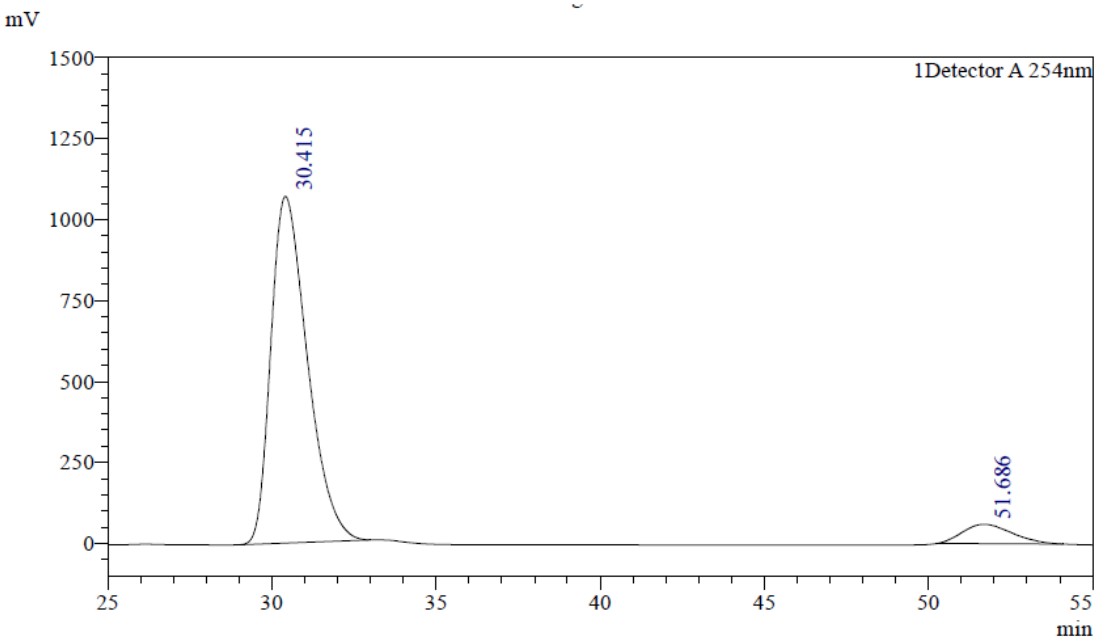
MHz, $CDCl_3$) δ 7.42-7.40 (m, 2H), 7.33 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.28-7.24 (m, 2H), 7.22-7.09 (m, 4H), 6.02 (s, 1H), 4.34-4.23 (m, 3H), 4.22-4.12 (m, 2H), 1.47 (d, *J* = 6.9 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 165.6, 157.4, 147.7, 141.1, 135.5, 128.5, 127.5, 127.0, 125.7, 125.2, 124.6, 122.9, 115.1, 108.9, 61.5, 61.0, 39.4, 31.6, 22.7, 16.2, 14.2. HRMS (ESI) *m/z* calcd for $C_{24}H_{24}N_2O_4S$ $[M+Na]^+$ = 459.1354, found = 459.1357; The ee value was 86%, t_R (major) = 30.4 min, t_R (minor) = 51.7 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	32.995	93349	52.836	6590998	44.065
2	35.902	21909	12.400	1701542	11.376
3	53.516	61419	34.764	6664738	44.558
Total		176678	100.000	14957278	100.000

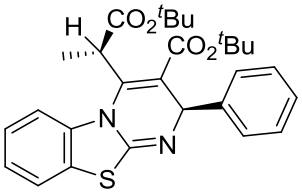


Peak Table

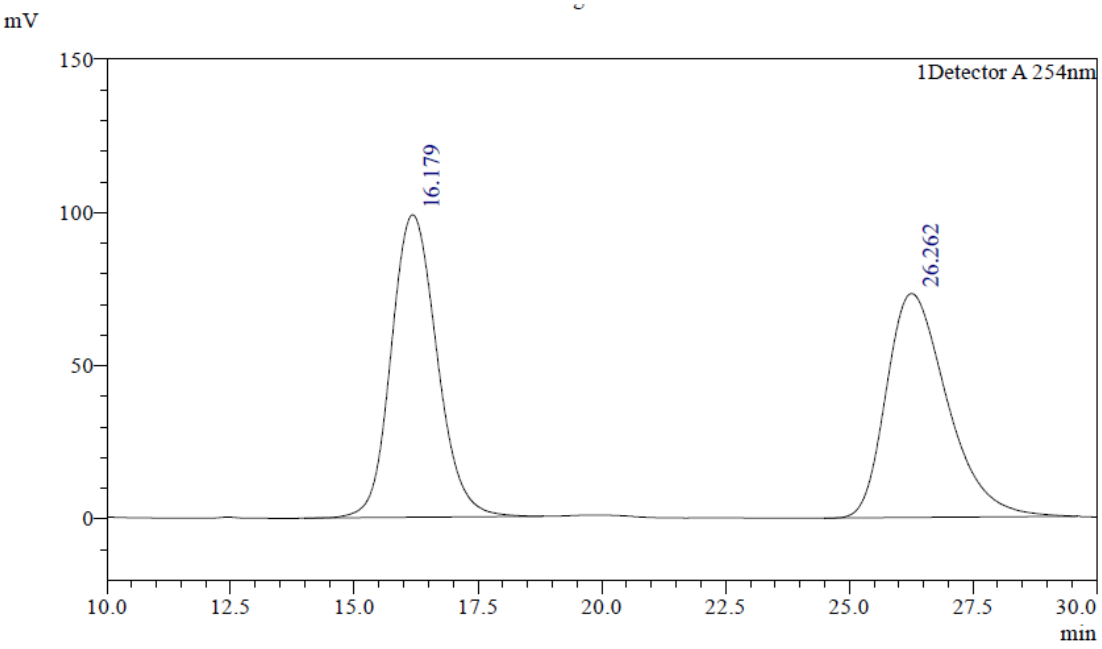
Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	30.415	1070050	94.715	82792805	92.923
2	51.686	59710	5.285	6305473	7.077
Total		1129761	100.000	89098279	100.000

tert-butyl(_R_)-4-((_S_)-1-(_tert_-butoxy)-1-oxopropan-2-yl)-2-phenyl-2_H_-benzo[4,5]thiazolo[3,2-_a_]pyrimidine-3-carboxylate (4i)



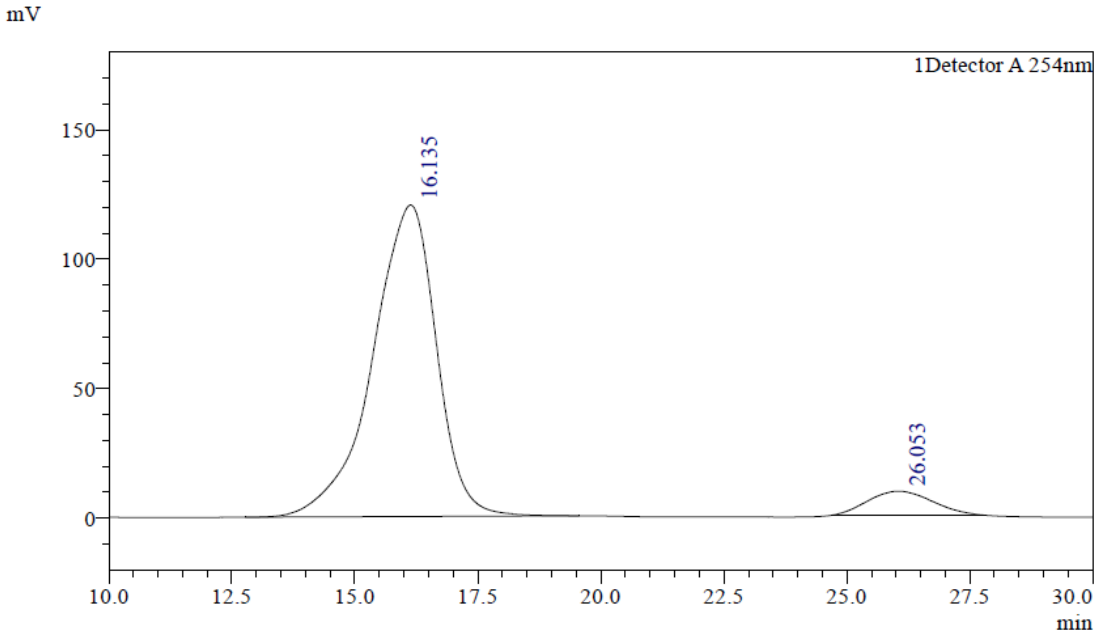
White foam, (45.7 mg), 90% yield; $[\alpha]^{25}_{D}$ = +107.9 (*c* 0.45, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41-7.39 (m, 2H), 7.34 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.27 (t, *J* = 1.8 Hz, 1H), 7.25-7.20 (m, 3H), 7.19-7.09 (m, 2H), 5.91 (s, 1H), 4.24 (s, 1H), 1.48-1.45 (m, 12H), 1.40 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 164.5, 157.2, 147.7, 141.9, 135.8, 128.4, 127.3, 127.0, 125.6, 125.1, 124.3, 122.9, 114.8, 110.1, 81.7, 81.2, 61.8, 40.1, 28.2, 28.0, 15.8. HRMS (ESI) *m/z* calcd for $C_{28}H_{32}N_2O_4S$ $[M+Na]^+$ = 515.1980, found = 515.1972; The ee value was 86%, t_R (major) = 16.1 min, t_R (minor) = 26.0 min (Chiralcel IC, λ = 254 nm, 2% *i*-PrOH/hexanes, flow rate = 0.5 mL/min).



Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.179	98772	57.460	6365696	50.384
2	26.262	73126	42.540	6268787	49.616
Total		171897	100.000	12634483	100.000



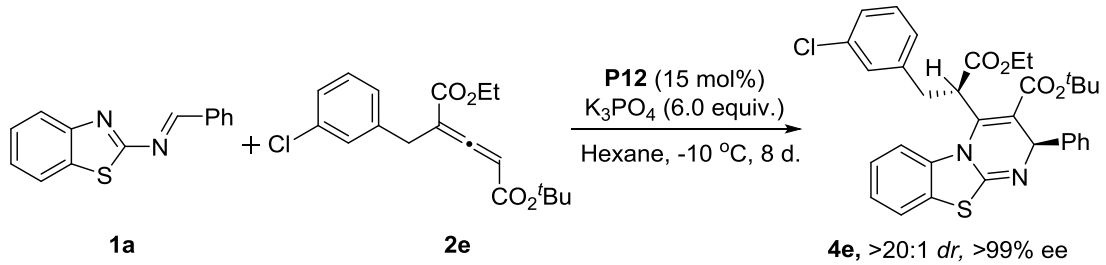
Peak Table

Detector A 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.135	120354	92.936	10896037	92.902
2	26.053	9149	7.064	832464	7.098
Total		129502	100.000	11728501	100.000

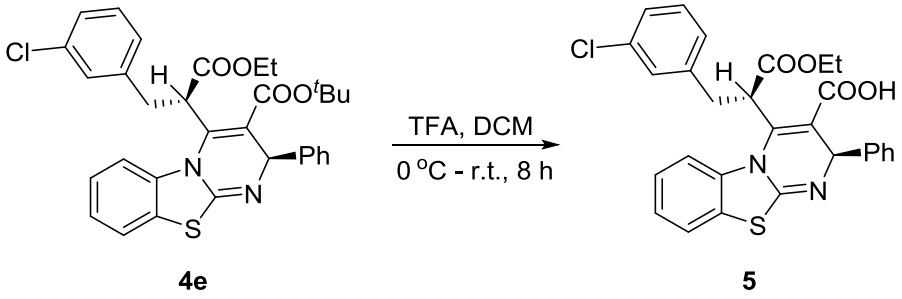
6. Scale-up Synthesis and Synthetic Elaboration of Product

(i). General procedure of scale-up synthesis



To a flame-dried round bottle flask with a magnetic stirring bar were added 2-benzothiazolimine **1a** (1.0 g, 4.20 mmol), allenoate **2e** (1.20 mmol), phosphonium salt **P12** (0.15 mmol) and K_3PO_4 (6.00 mmol), followed by the addition of Hexane. The reaction mixture was stirred at -10 ^oC for 8 days. The reaction was added H_2O (10 mL), and the mixture was extracted with DCM (10 mL x 3), dried over Na_2SO_4, the solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel to afford **4e** (1.61 g, 67% yield, >99% ee, >20:1 dr) as a yellow solid.

(ii). Synthetic elaboration of product



To a solution of **4e** (57.5 mg, 0.1 mmol) in DCM (5.0 mL) was added TFA (18.9 mg, 0.5 mmol) at 0 ℃. Then, the mixture was allowed to stir under nitrogen atmosphere at room temperature for 8 h. After stirring for 8 h, the reaction mixture was quenched with saturated aqueous NaCl, the aqueous phase was extracted three times with DCM. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduce pressure. The residue was purified by silica gel column chromatography to afford the desired product **5** as a light-yellow oil (45.2 mg, >99% ee, >20:1 dr).

Yellow oil; $[\alpha]^{25}_{D}$ = +97.2 (*c* 0.50, $CHCl_3$);^{1}H NMR (400 MHz, DMSO) δ 7.38 (d, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 3H), 7.16-6.98 (m, 5H), 6.71 (d, *J* = 9.0 Hz, 2H), 5.91 (s, 1H), 4.25 (dd, *J* = 17.7, 11.2 Hz, 3H), 3.33 (dd, *J* = 13.2, 4.1 Hz, 2H), 3.27-3.08 (m, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, DMSO) δ 170.6, 156.0, 142.7, 141.0, 135.7, 133.3, 130.1, 128.5, 128.3, 127.5, 127.4, 127.2, 126.7, 126.1, 124.2, 124.0, 123.2, 114.7, 62.0, 60.9, 45.3, 36.3, 14.6. HRMS (ESI) *m/z* calcd for $C_{28}H_{23}N_2O_4S$ $[M+Na]^+$ = 541.0965, found = 541.0940.

7. Mechanistic Studies and Proposed Mechanism

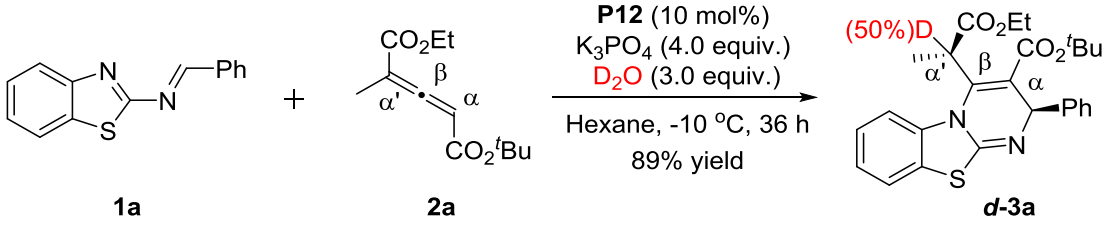


Figure S1. Deuterium-labeling Experiment.

(i). General procedure of *d*-3a

To a flame-dried round bottle flask with a magnetic stirring bar were added the2-benzothiazolimine **1a** (0.10 mmol), allenoate **2a** (1.20 mmol), phosphonium salt **P12** (0.10 mmol) and K_3PO_4 (4.00 mmol), followed by the addition of hexane and deuterium oxide (24 μL, 1.20 mmol). The reaction mixture was stirred at -10 ℃ for 36 h. Then, the aqueous phase was extracted three times with DCM. The combined organic phase was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give ***d*-3a** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.41 (m 2H), 7.34-7.32 (m, 1H), 7.30-7.25 (m, 2H), 7.22-7.21 (m, 1H), 7.17-7.16 (m, 2H), 7.14-7.08 (m, 1H), 5.91 (s, 1H), 4.31-4.25 (m, 2.5H), 1.68 (s, 1H), 1.50 (d, *J* = 6.9 Hz, 3H), 1.42 (s, 1H), 1.39 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H); HRMS (ESI) *m/z* calcd for $C_{27}H_{27}DN_2O_4S$ $[M+Na]^+$ = 488.1730, found = 488.1726.

(ii). Control Experiments and Mechanism

The methylated catalysts **P12-1** was prepared and used for the [4 + 2] reaction to test the reactivities and enantioselectivities. The results were displayed in ***Figure S2*** When methylated catalysts were used, the enantioselectivities decreased. The result clearly verify the significance of the hydrogen bonding in the catalytic system. On the basis of the experiments, the deuterium-labeling experiment, our previous research and the absolute configuration, a plausible mechanism was presented.

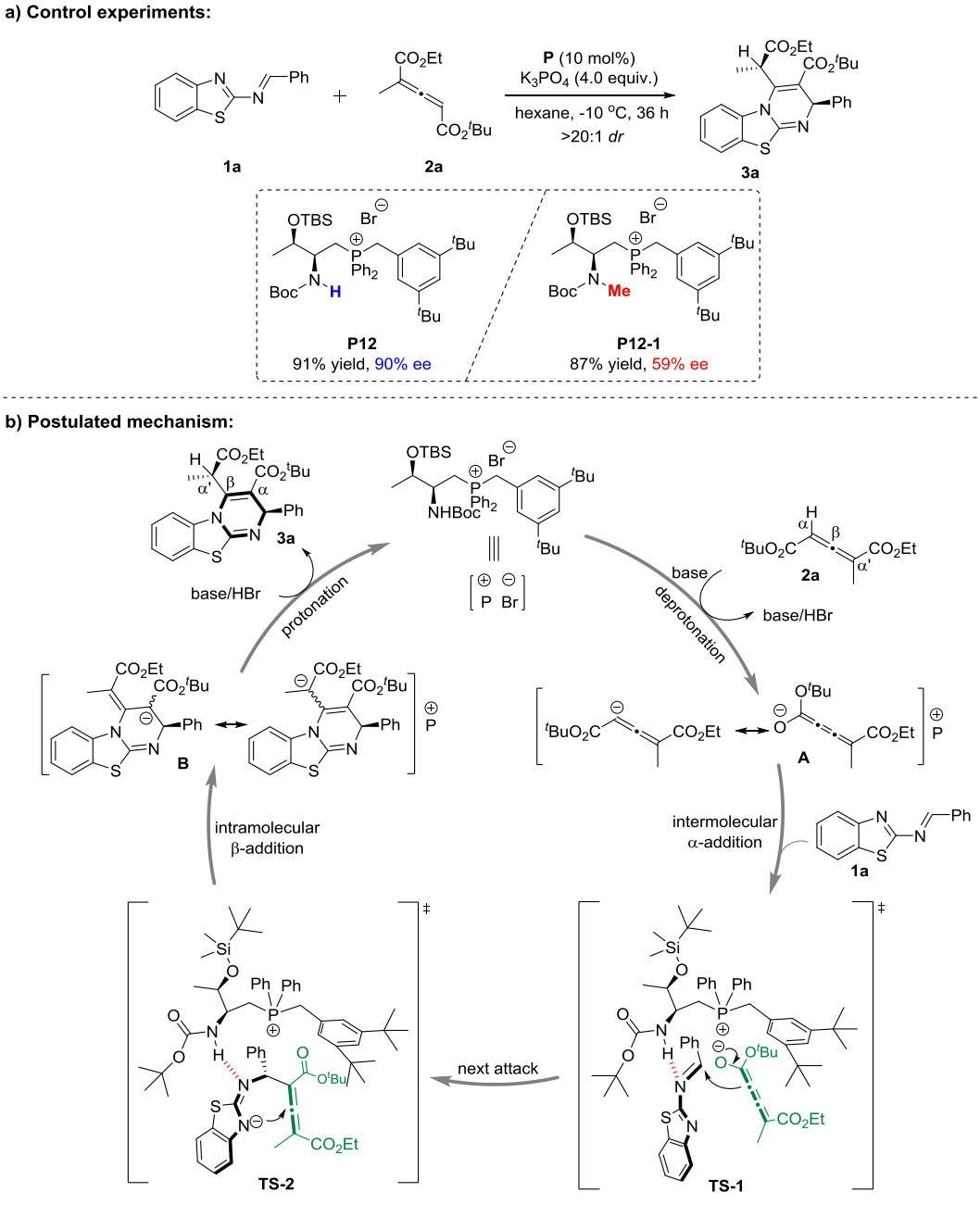
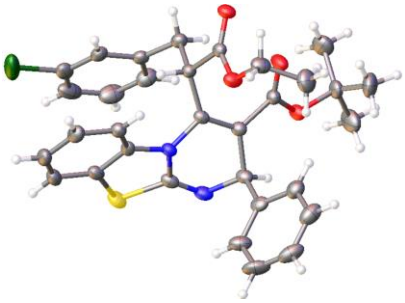


Figure S2. Control experiments and postulated mechanism.

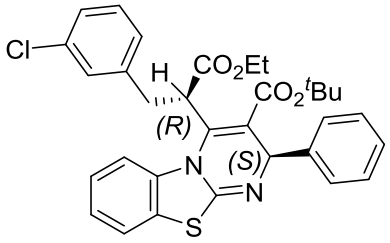
8. Crystal Structure of Product 4e.

the X-ray crystal of **4e** was obtained (Table S4). CCDC 1966944 contains the supplementary crystallographic data of the adduct **4e** for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table S4. Crystal data and structure refinement for **4e**.



X-ray structure of **4e**
CCDC (1966944)



4e

Identification code	WTL-LDM-150K
Empirical formula	$C_{32}H_{31}ClN_2O_4S$
Formula weight	575.10
Temperature/K	150.01(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.29029(17)
b/Å	20.9516(4)
c/Å	8.39594(16)
α /°	90
β /°	97.0201(18)
γ /°	90
Volume/Å^3	1447.40(5)
Z	2
ρ calcg/cm^3	1.320
μ /mm^{-1}	2.165
F(000)	604.0
Crystal size/mm^3	0.6 × 0.3 × 0.3
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°8.44 to 143.534	
Index ranges	-9 ⩽ h ⩽ 10, -25 ⩽ k ⩽ 25, -10 ⩽ l ⩽ 6
Reflections collected	13708

Independent reflections	5560 [Rint = 0.0453, Rsigma = 0.0483]
Data/restraints/parameters	5560/1/365
Goodness-of-fit on F^2	1.048
Final R indexes [I>=2σ (I)]	R_1 = 0.0536, wR_2 = 0.1369
Final R indexes [all data]	R_1 = 0.0554, wR_2 = 0.1404
Largest diff. peak/hole / e $Å^{-3}$	0.26/-0.41
Flack parameter	-0.021(10)

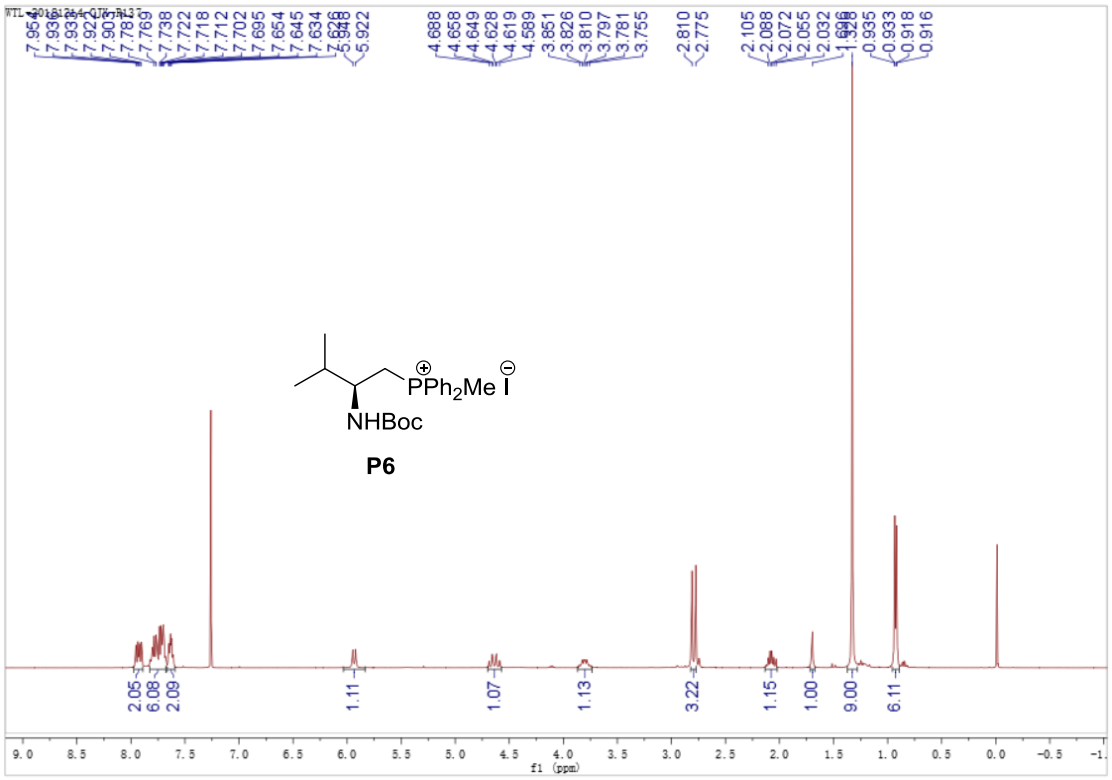
9. Reference

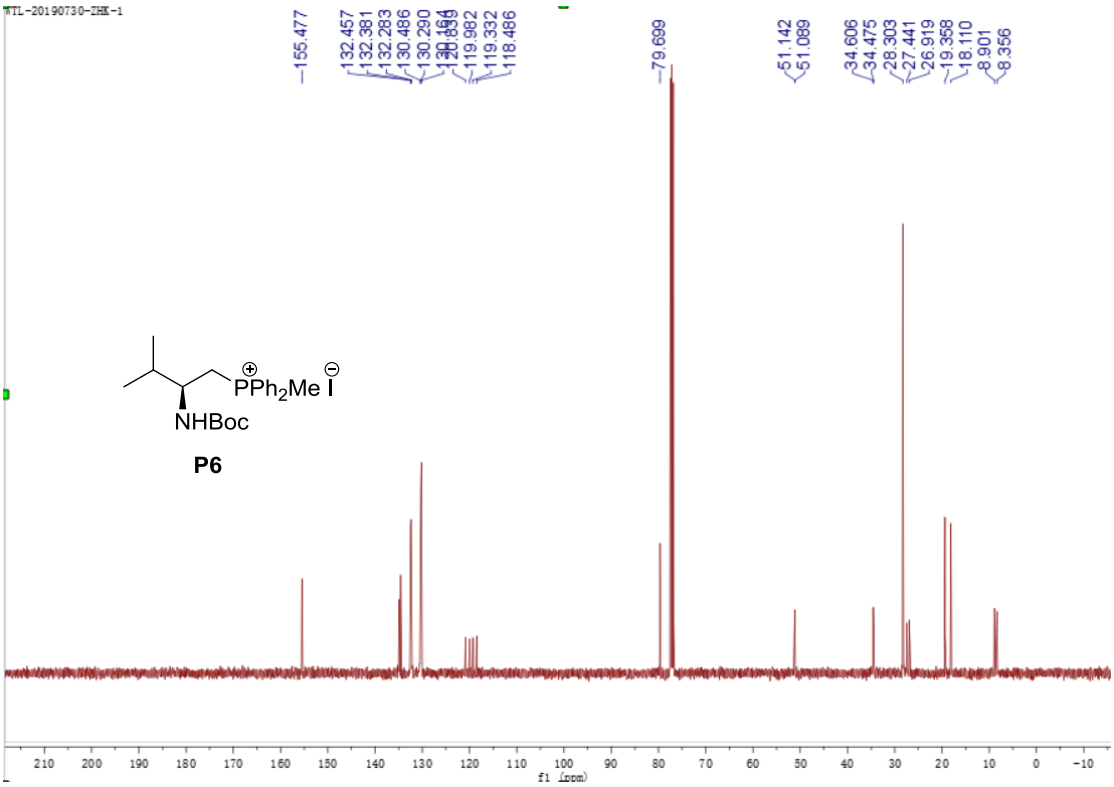
[1] (a) X. Han, Y. Wang, F. Zhong and Y. Lu, *J. Am. Chem. Soc.*, 2011, **133**, 1726; (b) X. Han, F. Zhong, Y. Wang and Y. Lu, *Angew. Chem., Int. Ed.*, 2012, **51**, 767; (c) F. Zhong, X. Han, Y. Wang and Y. Lu, *Chem. Sci.*, 2012, **3**, 1231; (d) F. Zhong, X. Han, Y. Wang and Y. Lu, *Angew. Chem., Int. Ed*., 2011, **50**, 7837; (e) F. Zhong, J. Luo, G.-Y. Chen, X. Dou and Y. Lu, *J. Am. Chem. Soc.*, 2012, **134**, 10222; (f) F. Zhong, X. Dou, X. Han, W. Yao, Q, Zhu, Y. Meng and Y. Lu, *Angew. Chem., Int. Ed.*, 2013, **52**, 943.

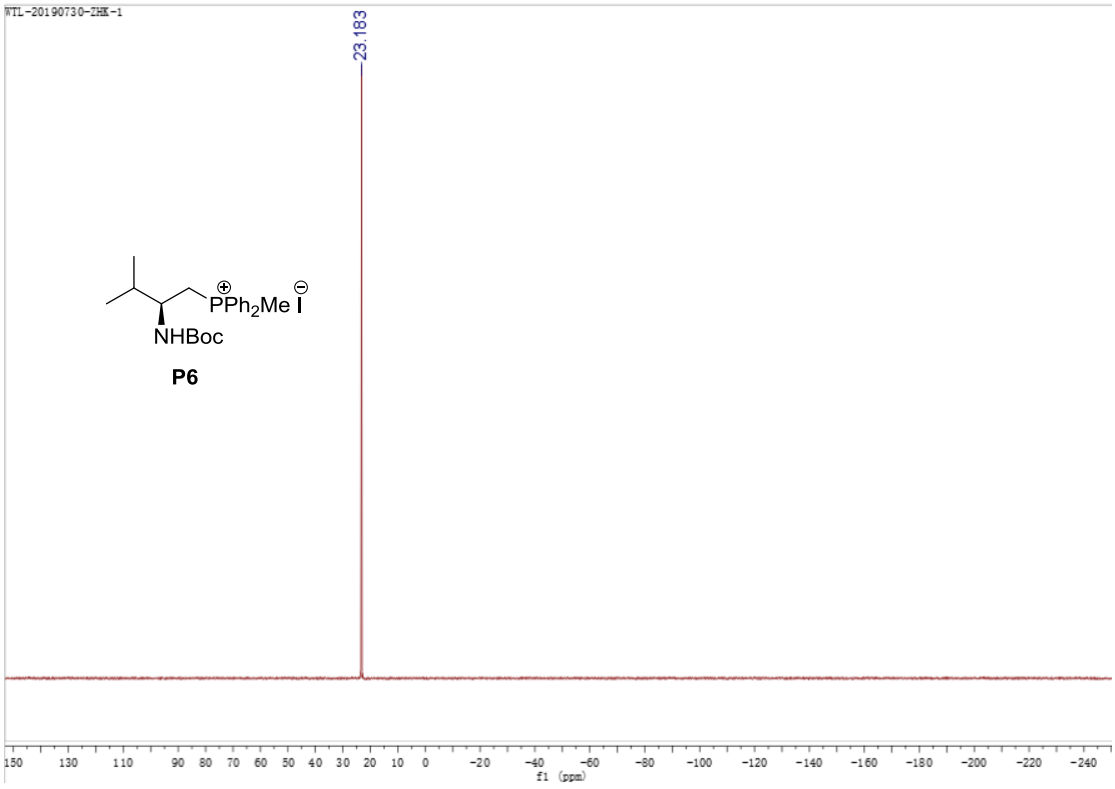
[2] (a) Q. Ni, X. Song, J. Xiong, G. Raabe and D. Enders, *Chem. Commun*., 2015, **51**, 1263; (b) L. Jarrige, D. Glavaˇc, G. Levitre, P. Retailleau, G. Bernadat, L. Neuville and G. Masson, *Chem. Sci*., 2019, **10**, 3765.

[3] (a) T. Hashimoto, Y. Naganawa and K. Maruoka, *J. Am. Chem. Soc*., 2009, **131**, 6614; (b) T. Hashimoto, K. Sakata, F. Tamakuni, M. J. Dutton and K. Maruoka, *Nat. Chem*. , 2013, **5**, 240.

10. NMR Spectra



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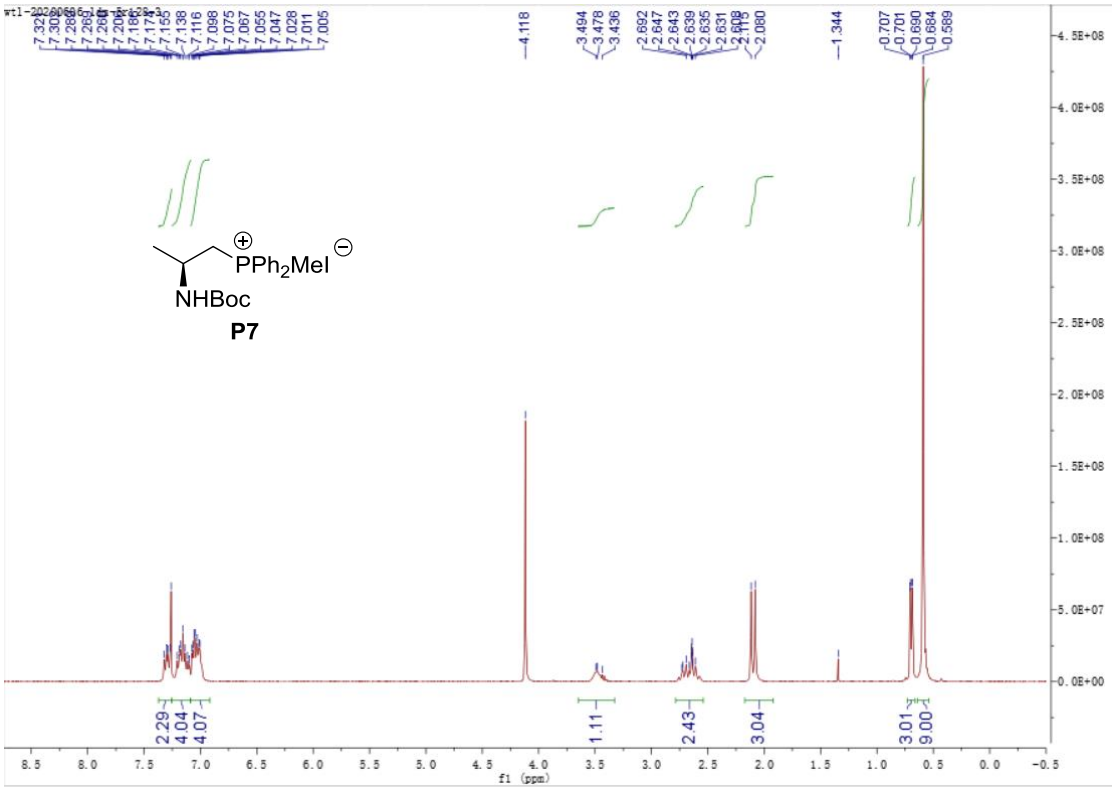
P6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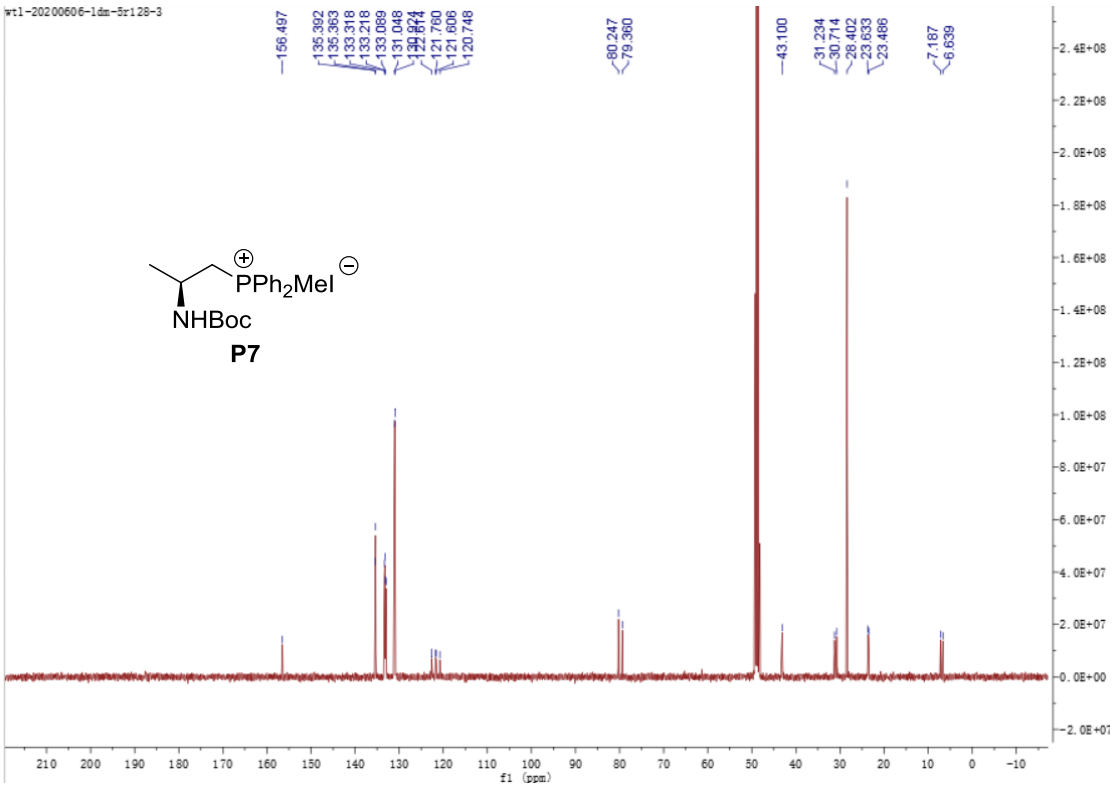
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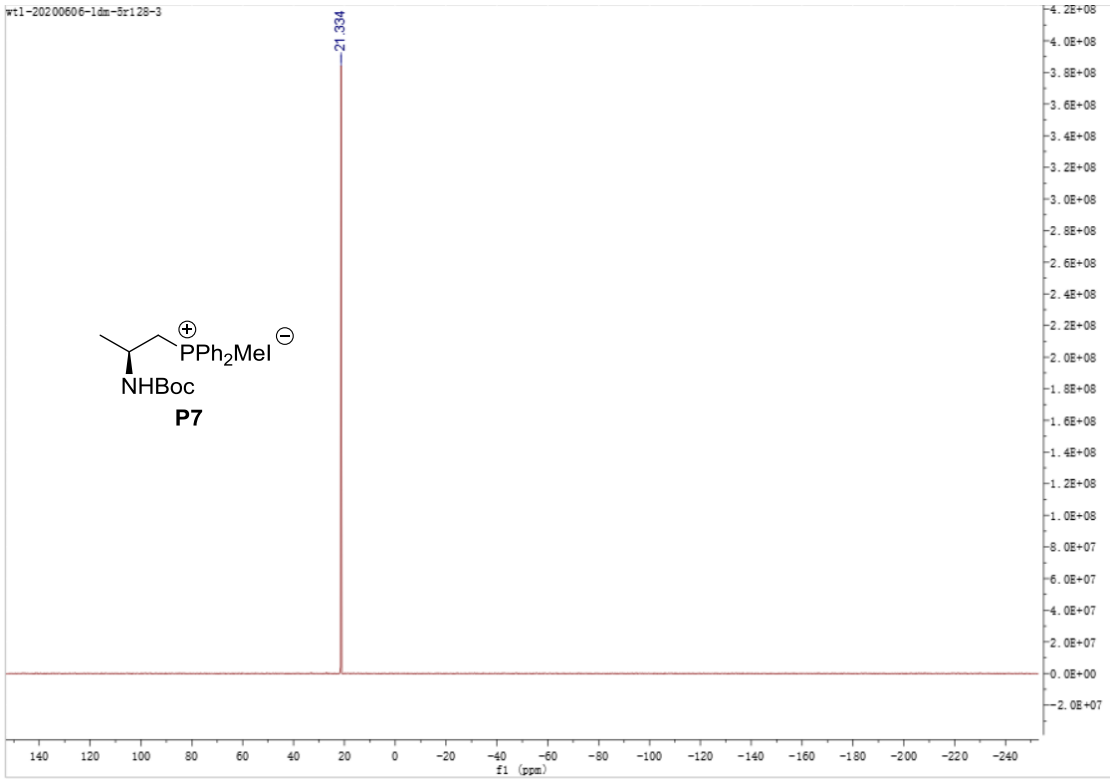
P7
f1 (ppm)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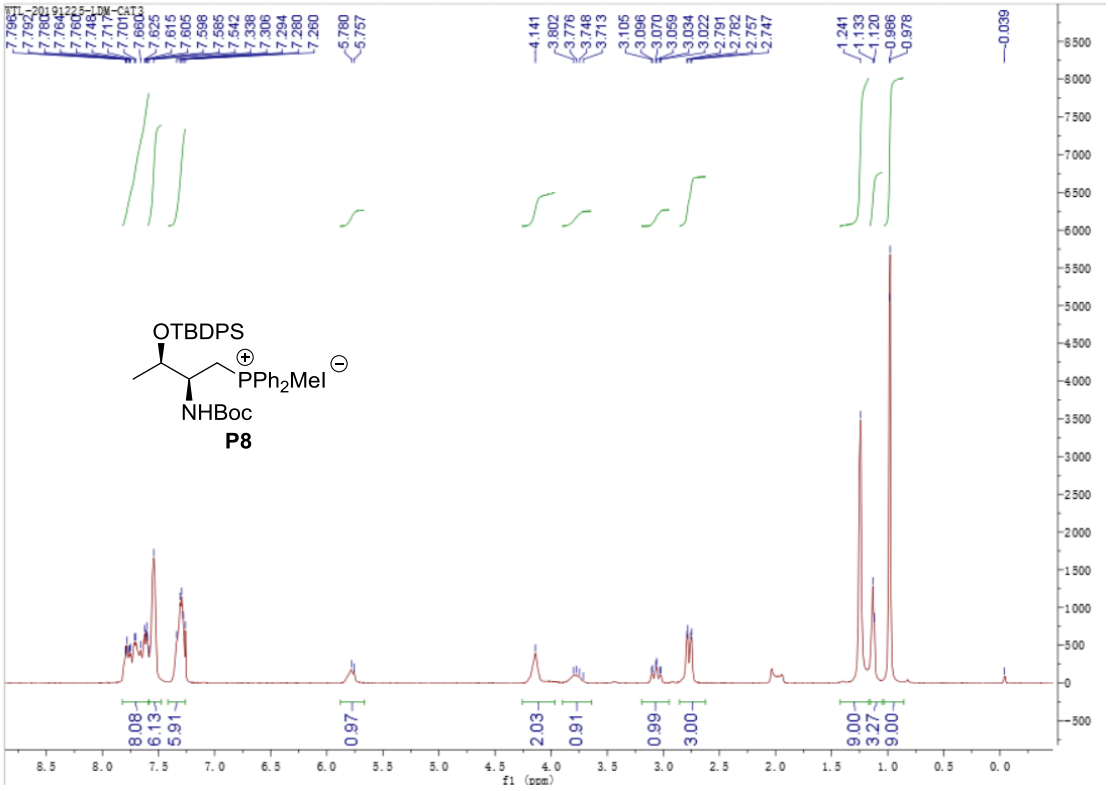
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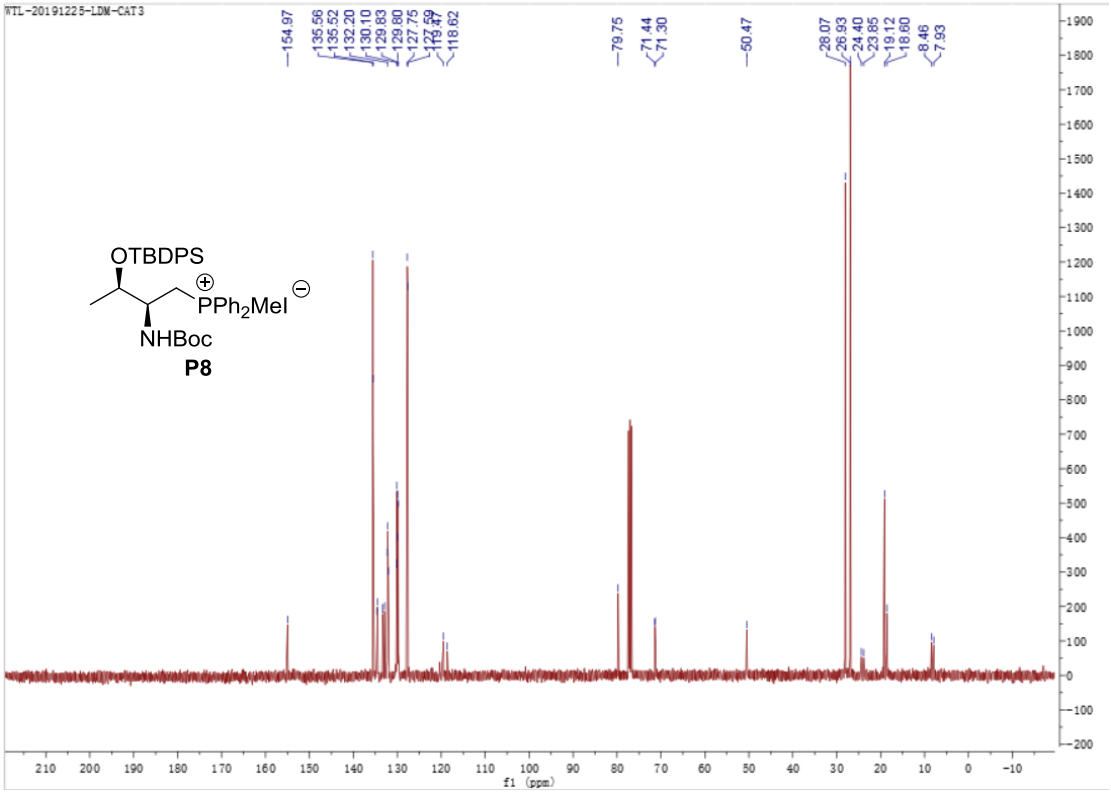
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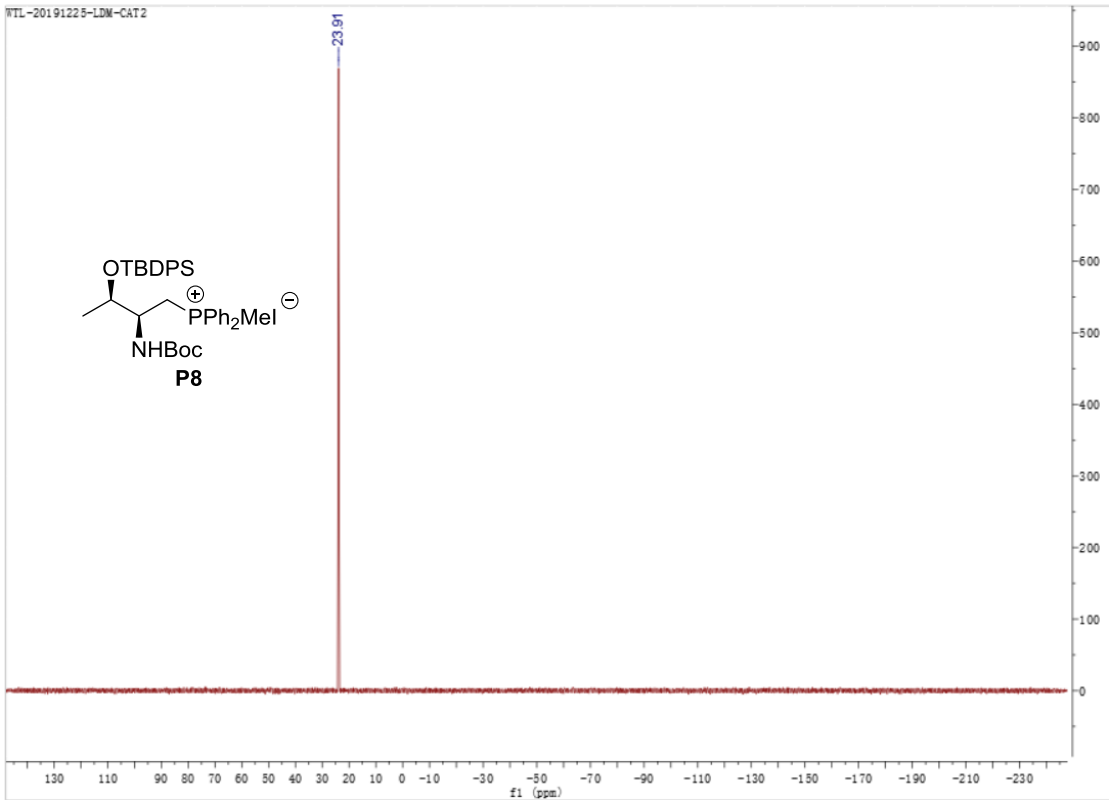
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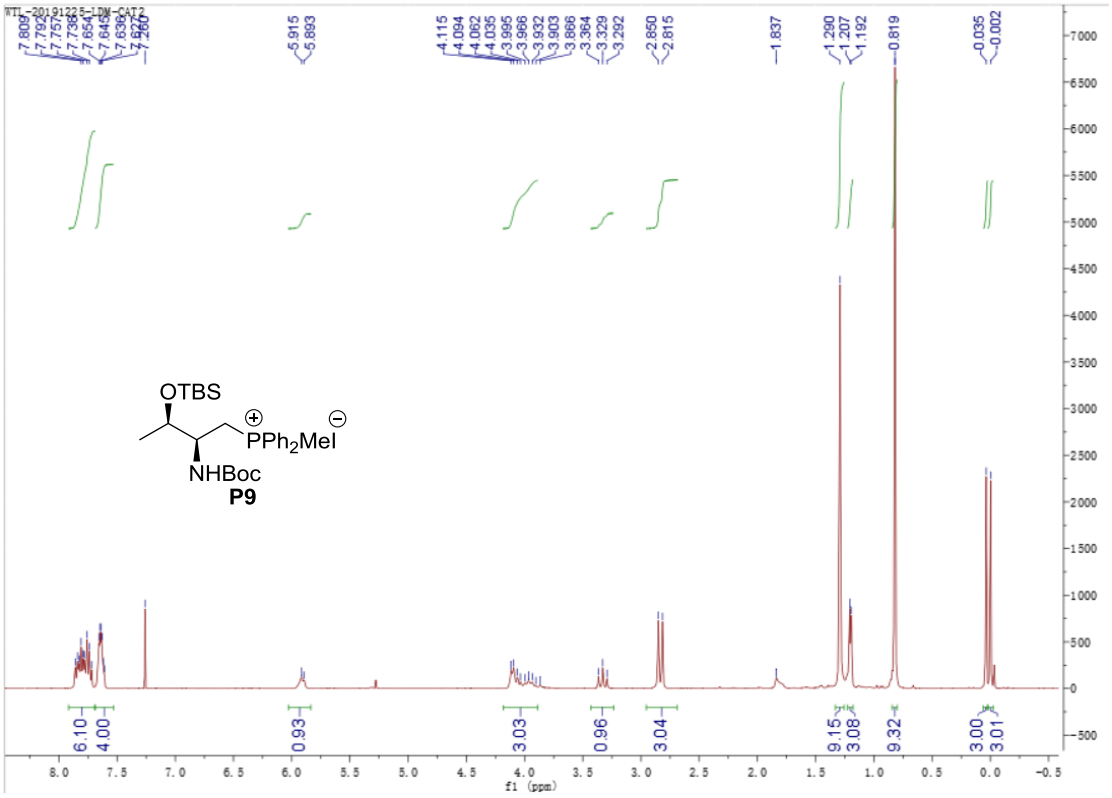
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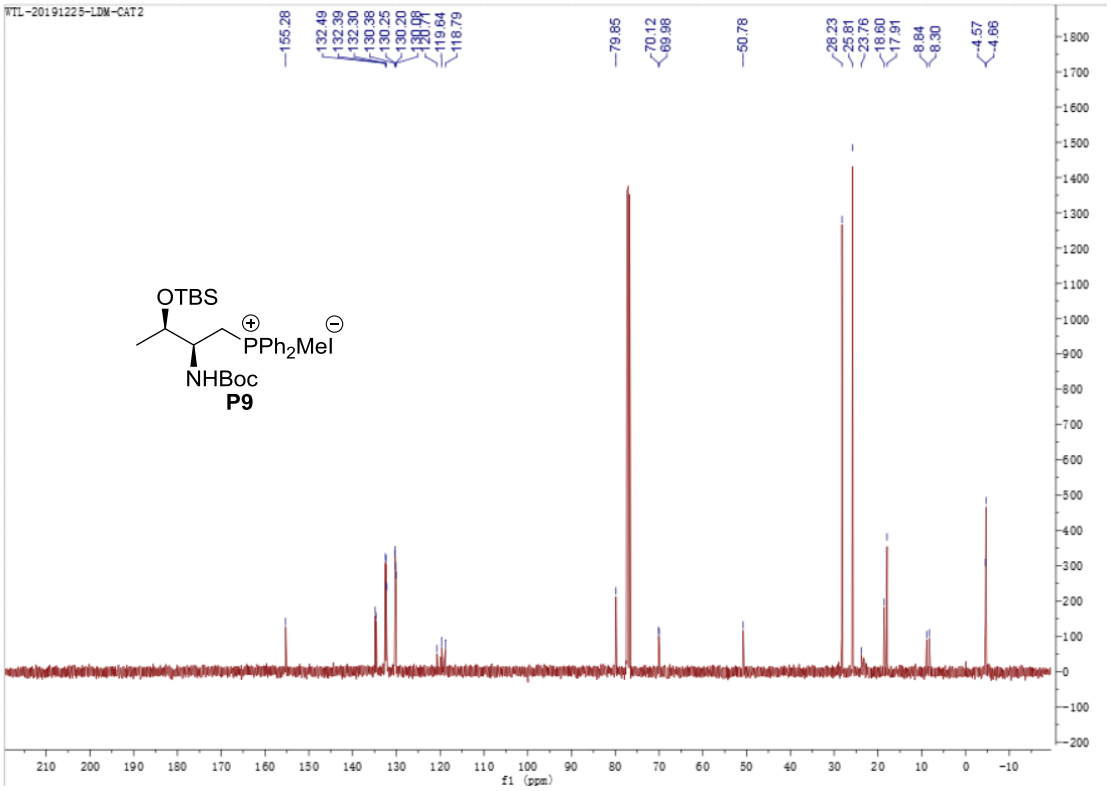
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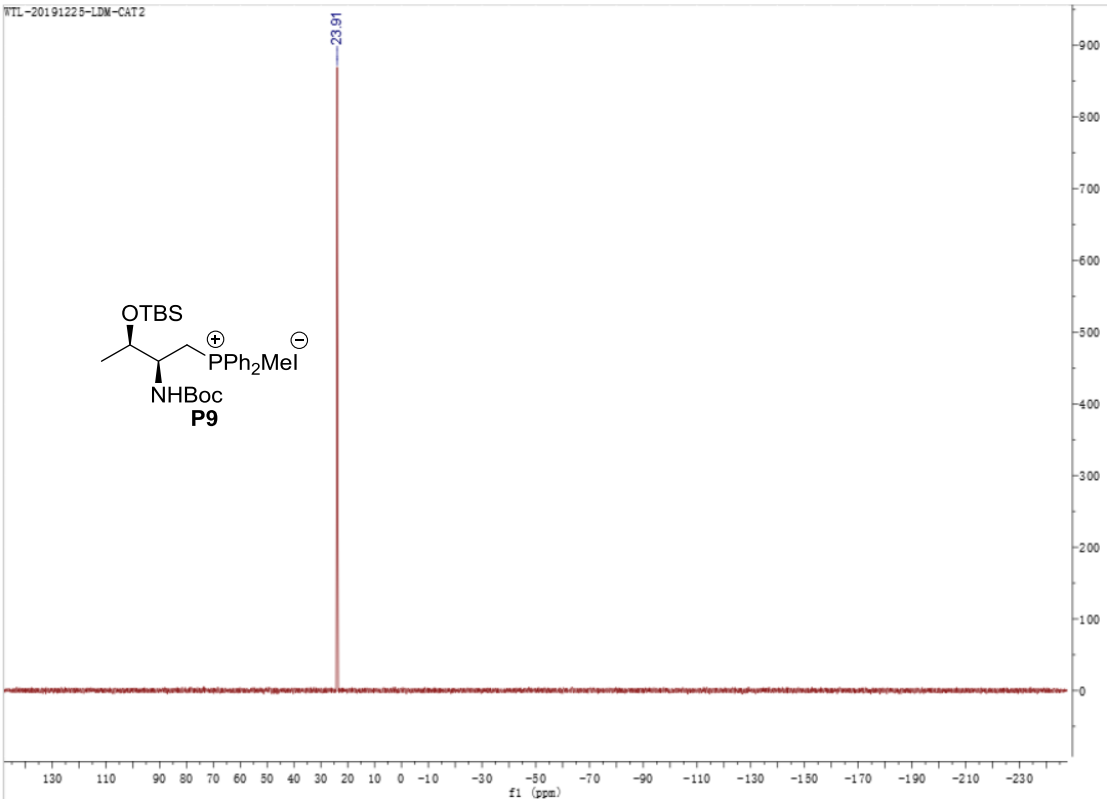
f1 (ppm)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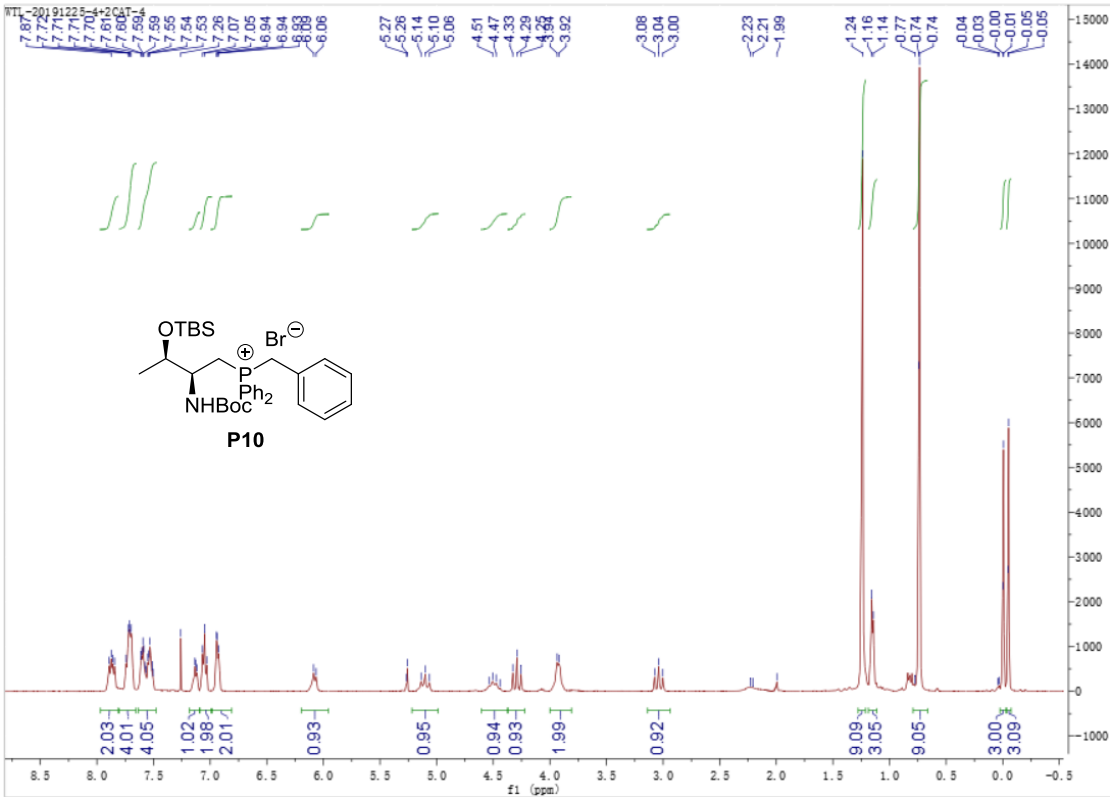
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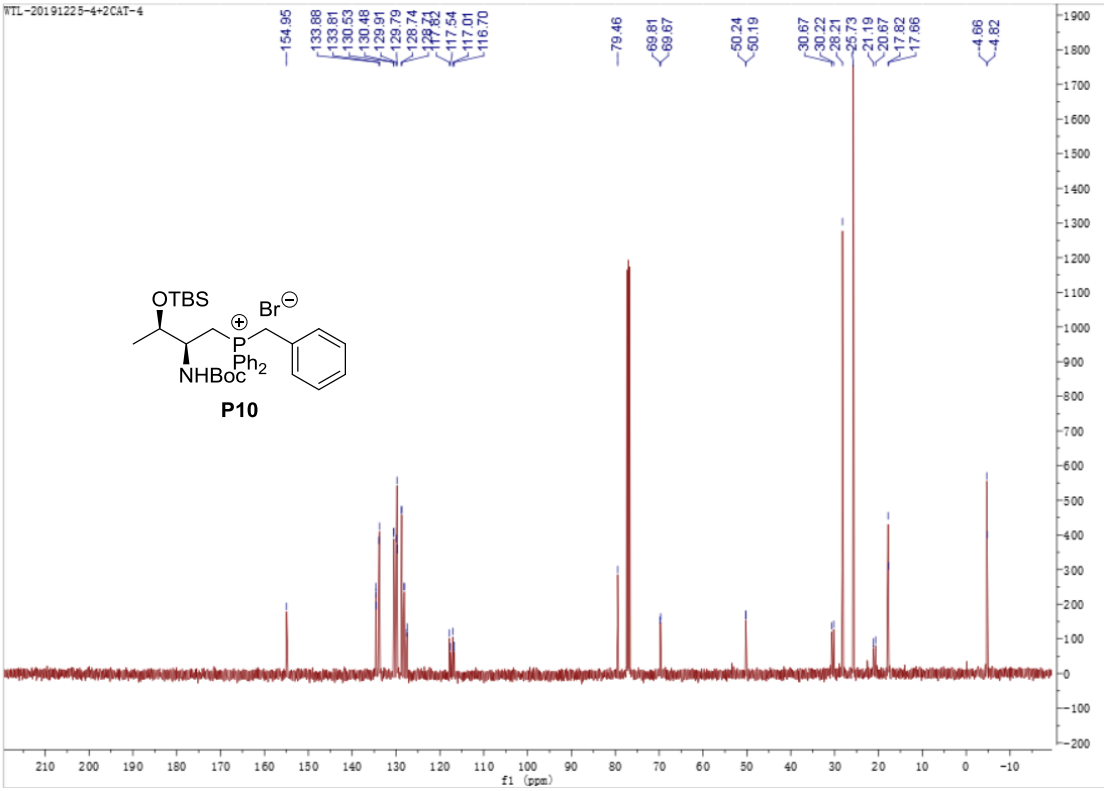
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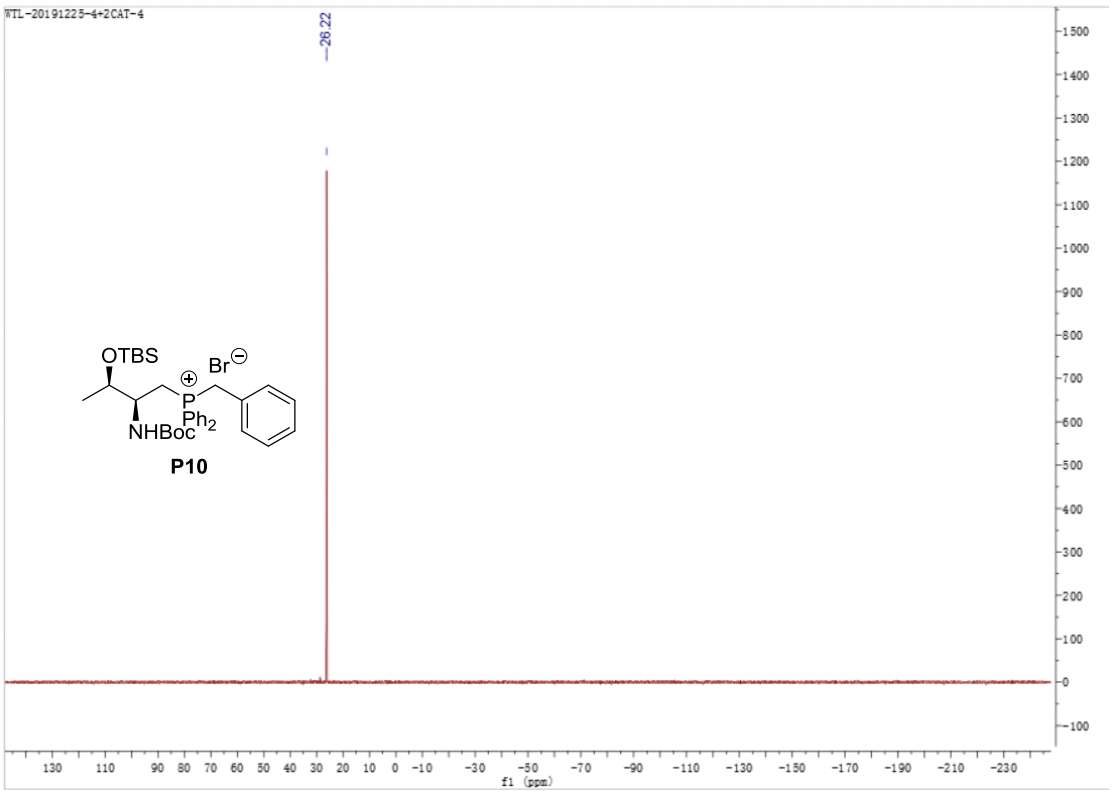
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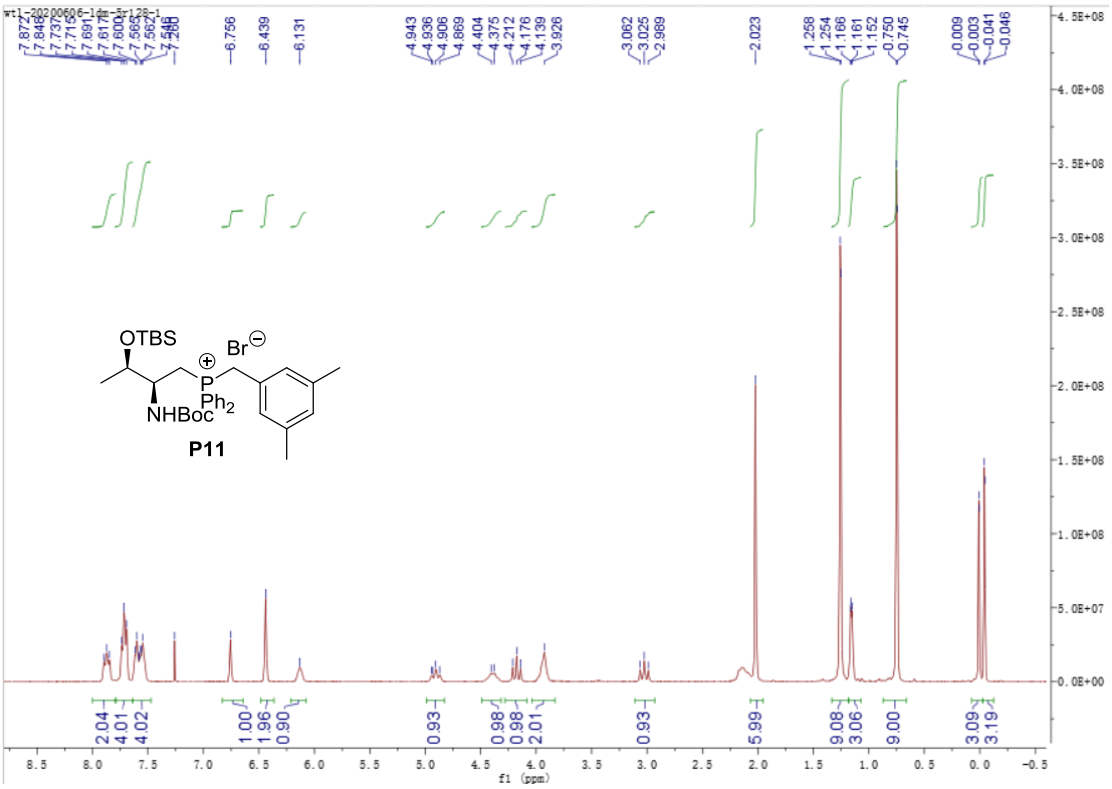
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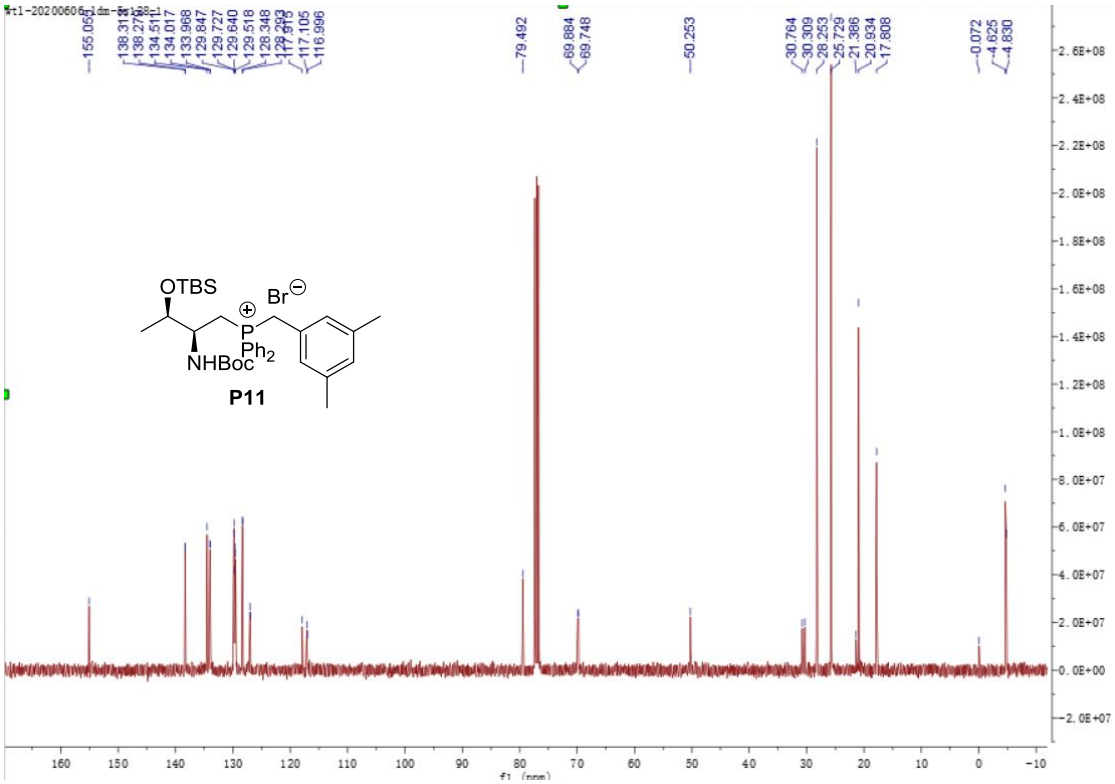
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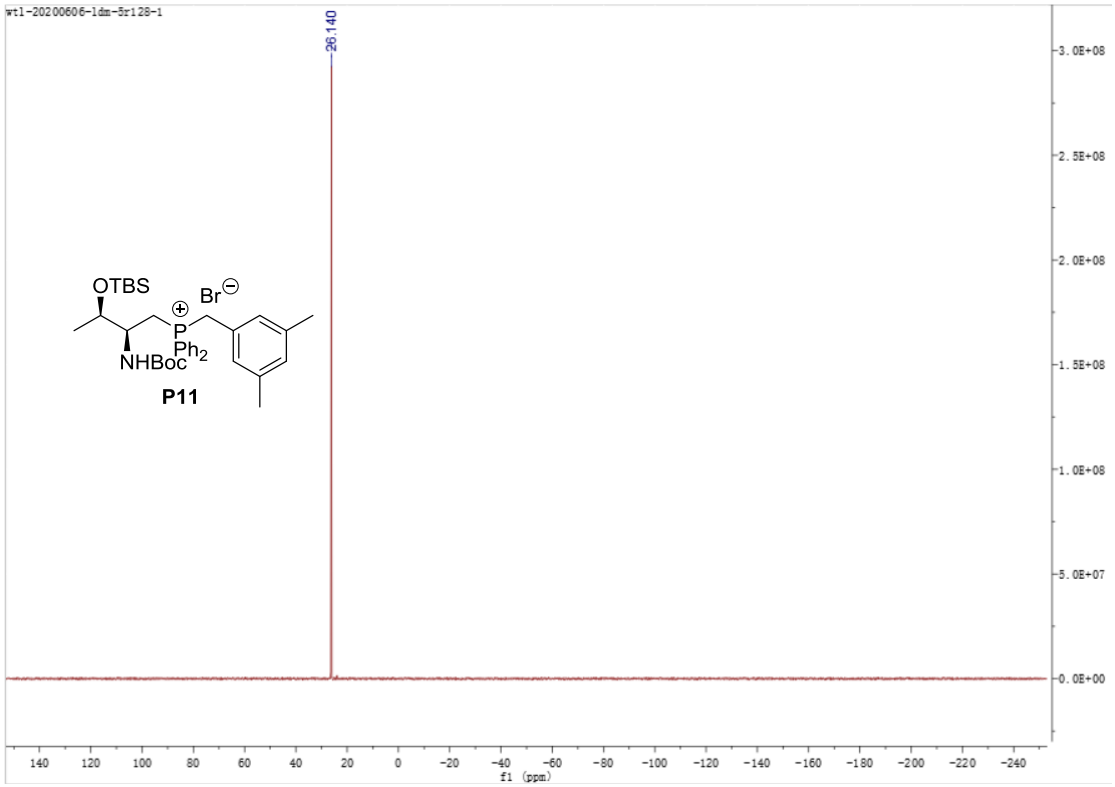
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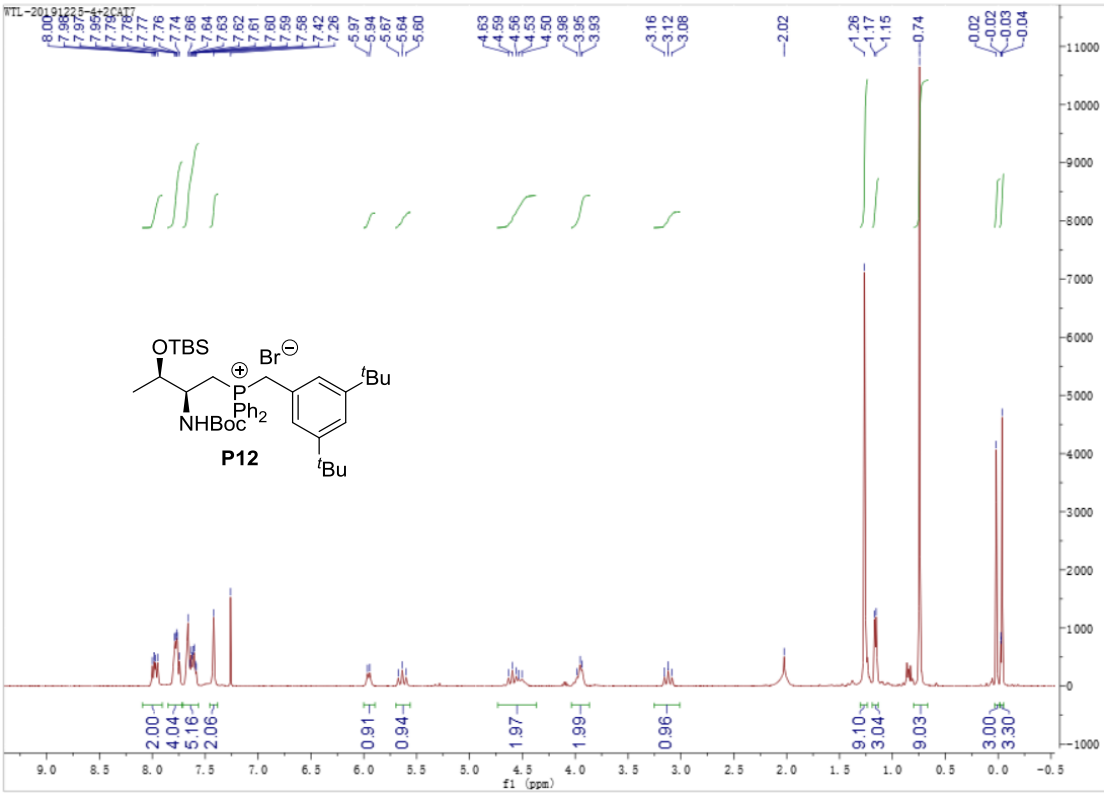
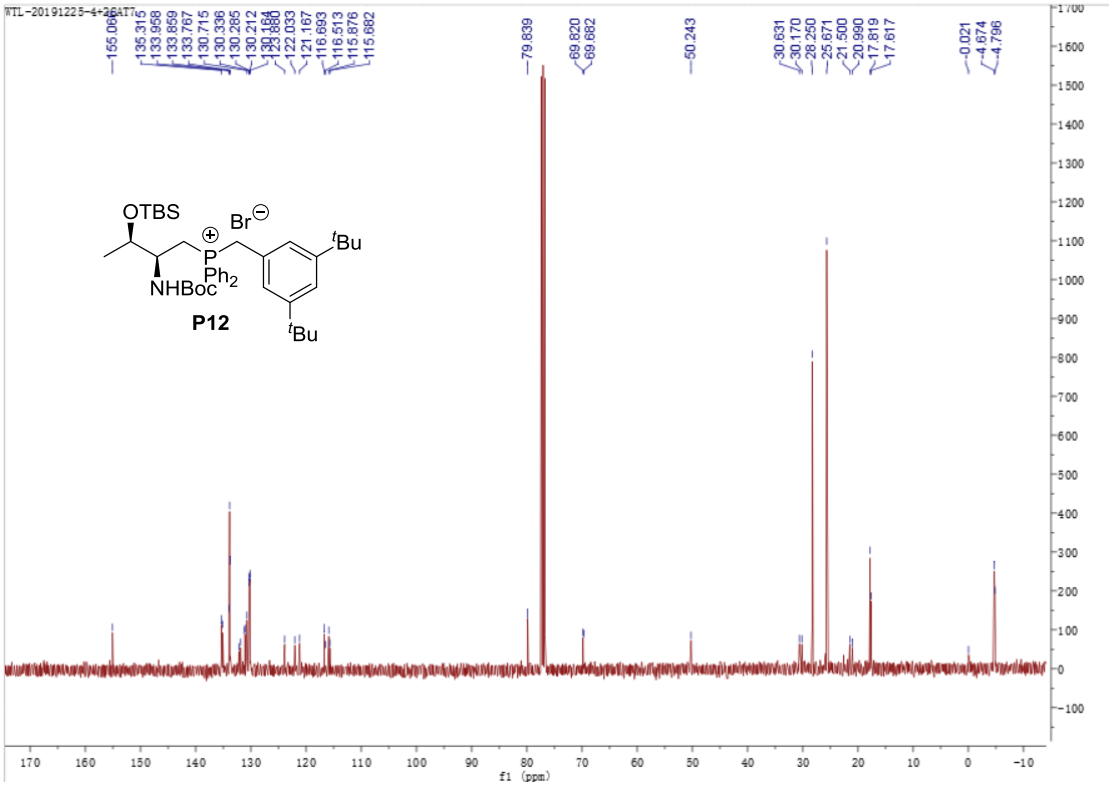
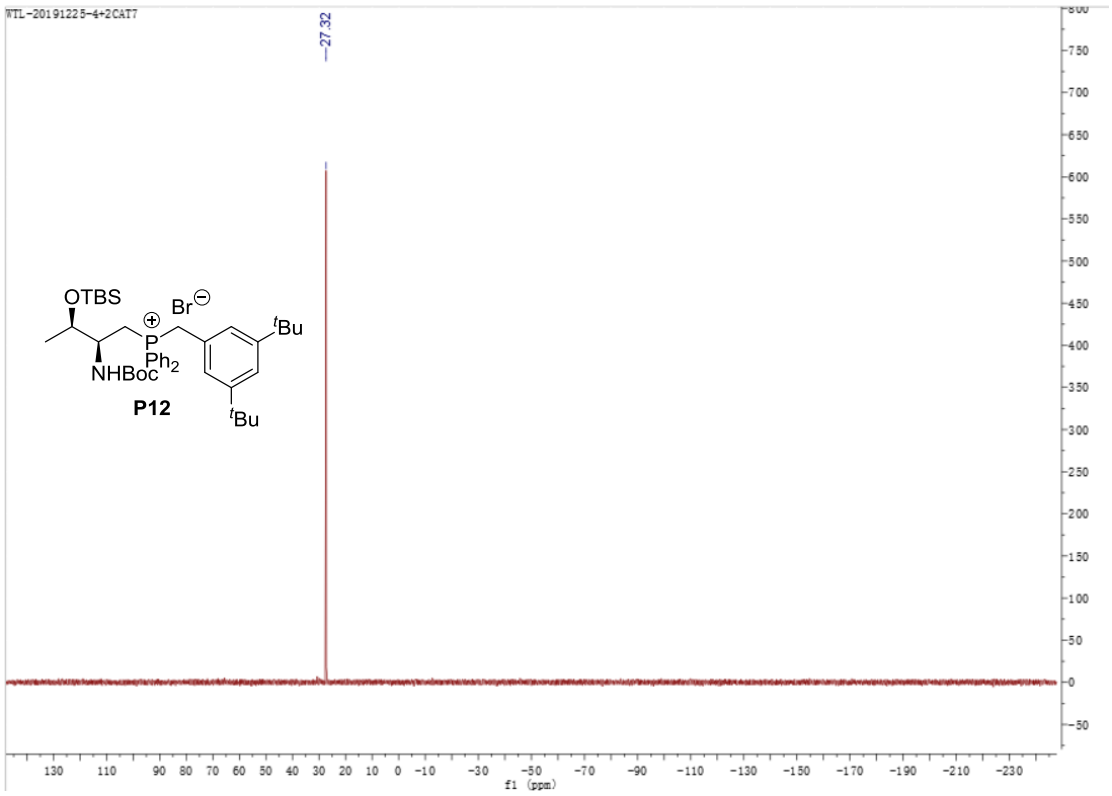
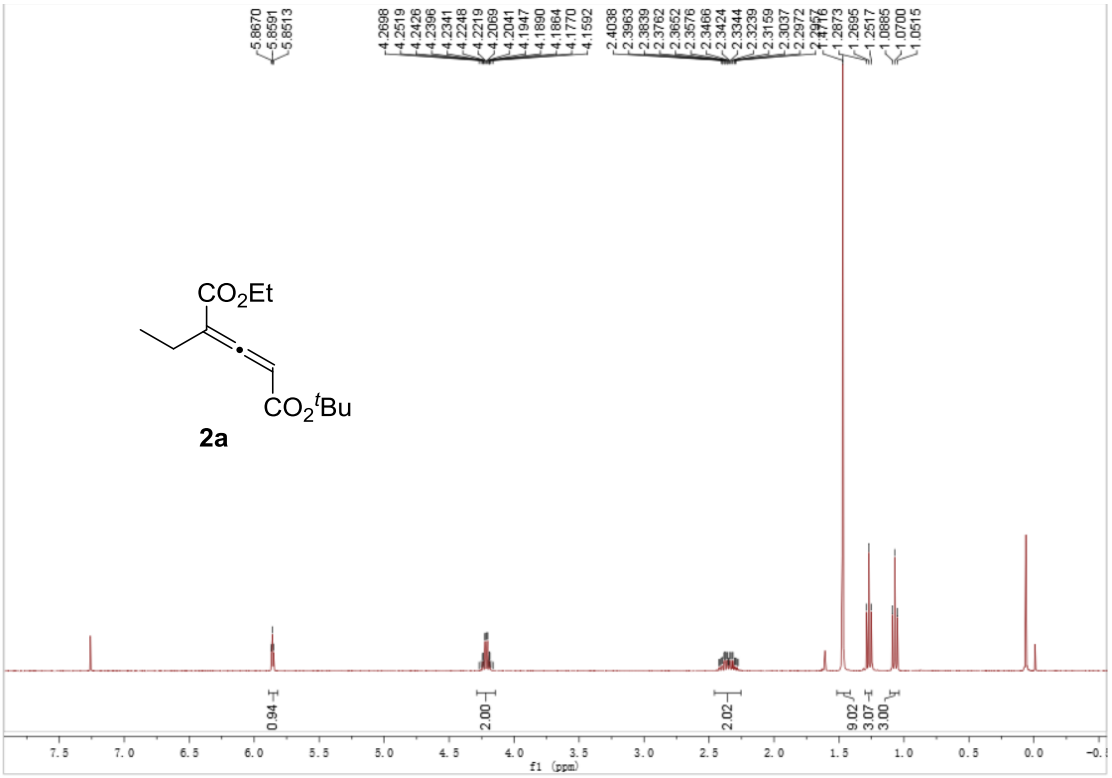
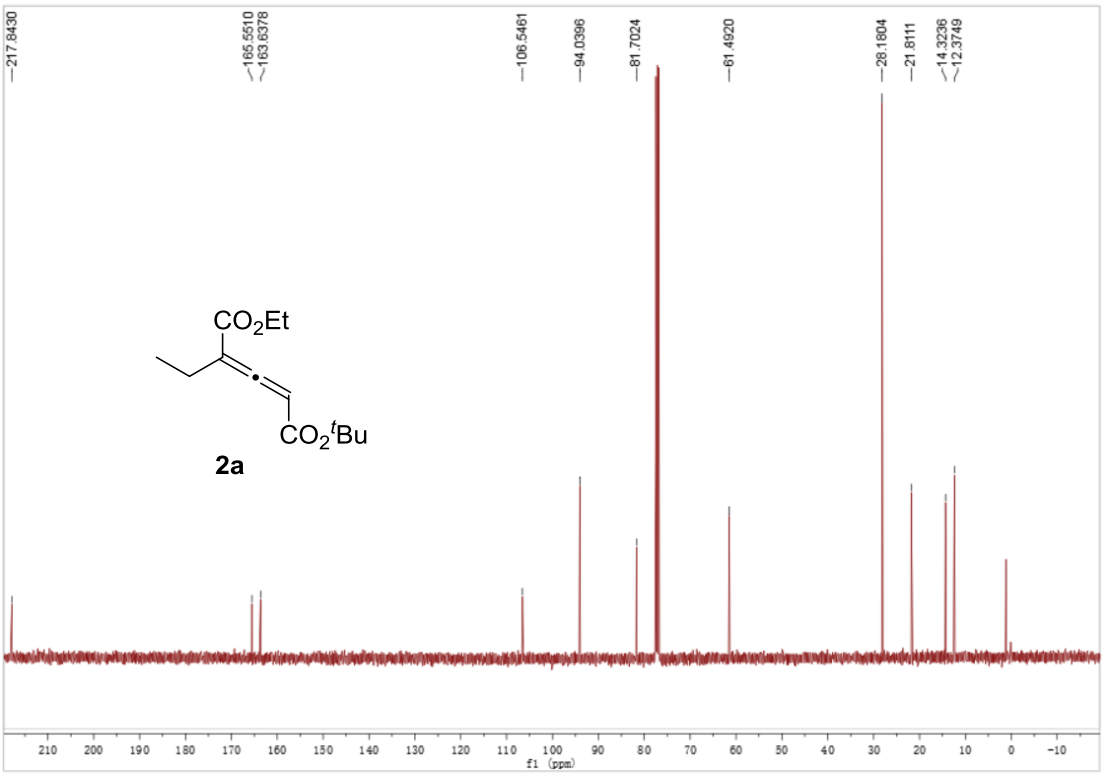
P11
f1 (ppm)

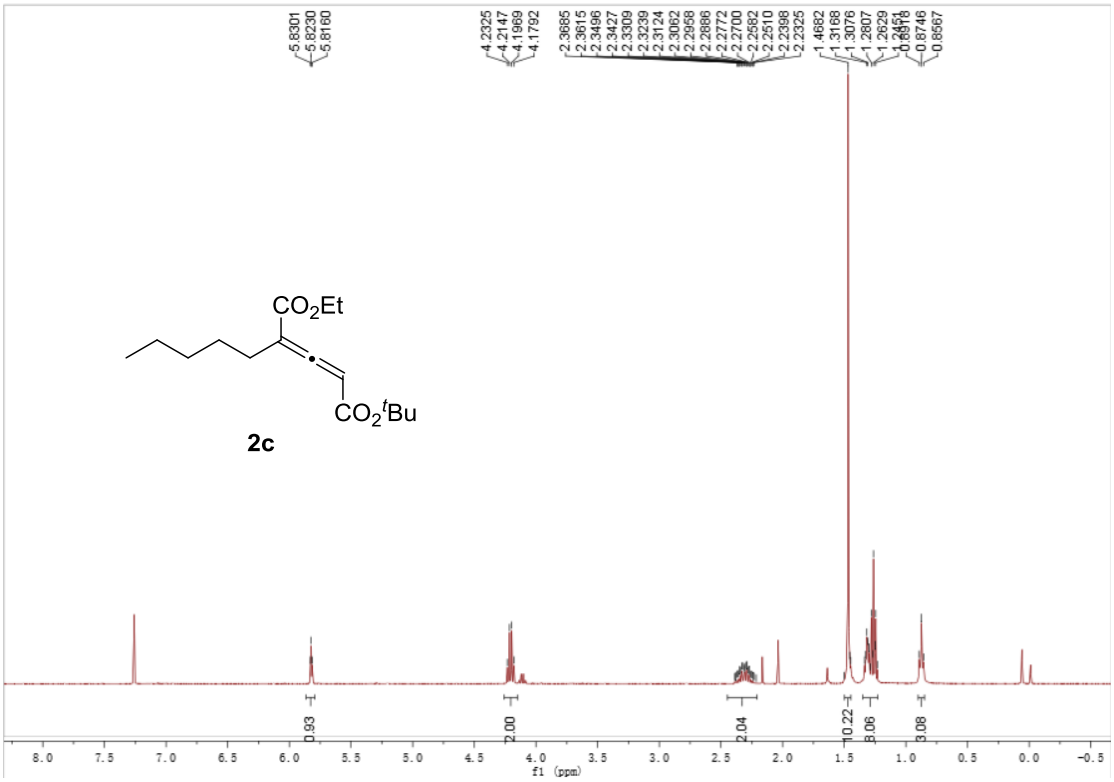

OTBS
Br
P
Ph2
NHBoc
tBu
tBu
P12
f1 (ppm)

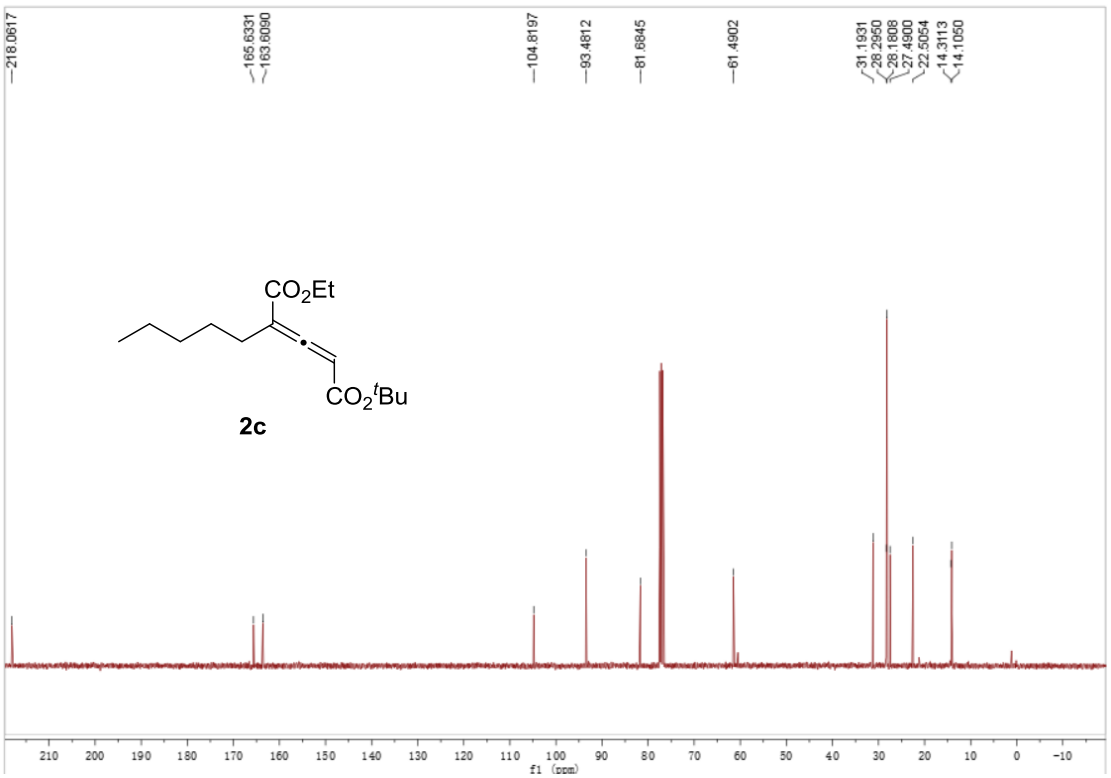

OTBS
Br
P
Ph2
NHBoc
tBu
tBu
P12
f1 (ppm)

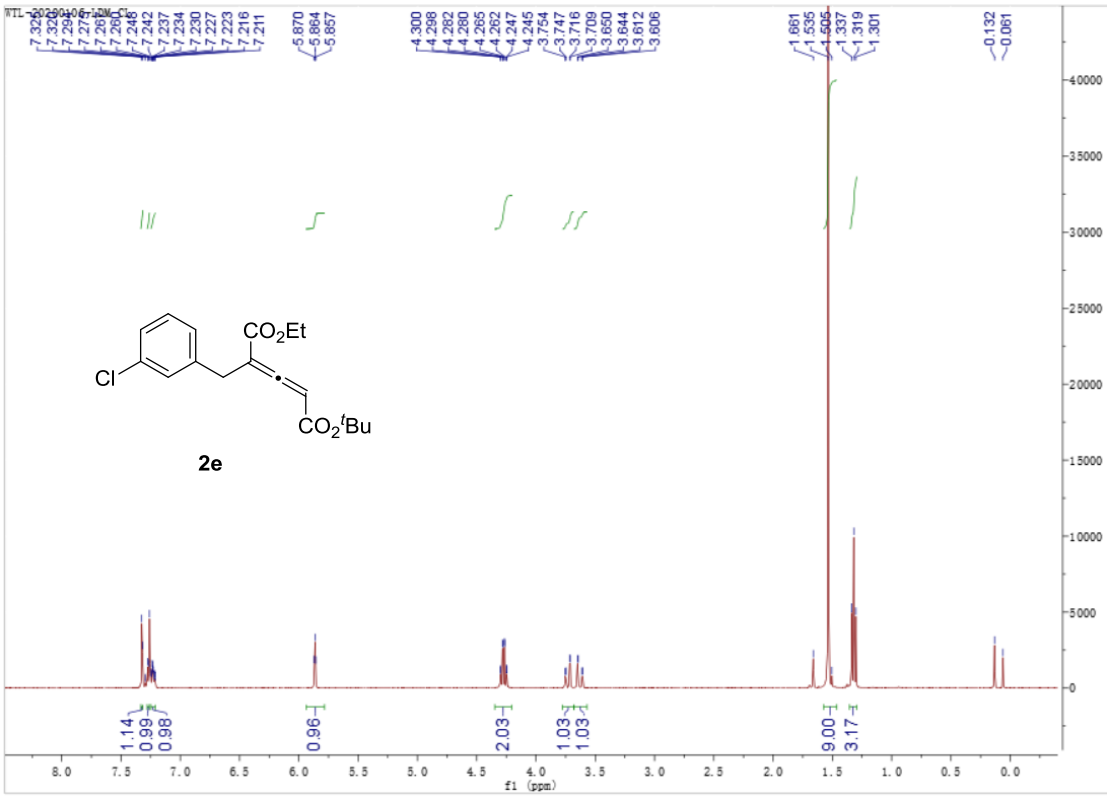

WTL-20191225-4+2CAT7
27.32
OTBS
Br
tBu
P
Ph2
NHBoc
tBu
P12

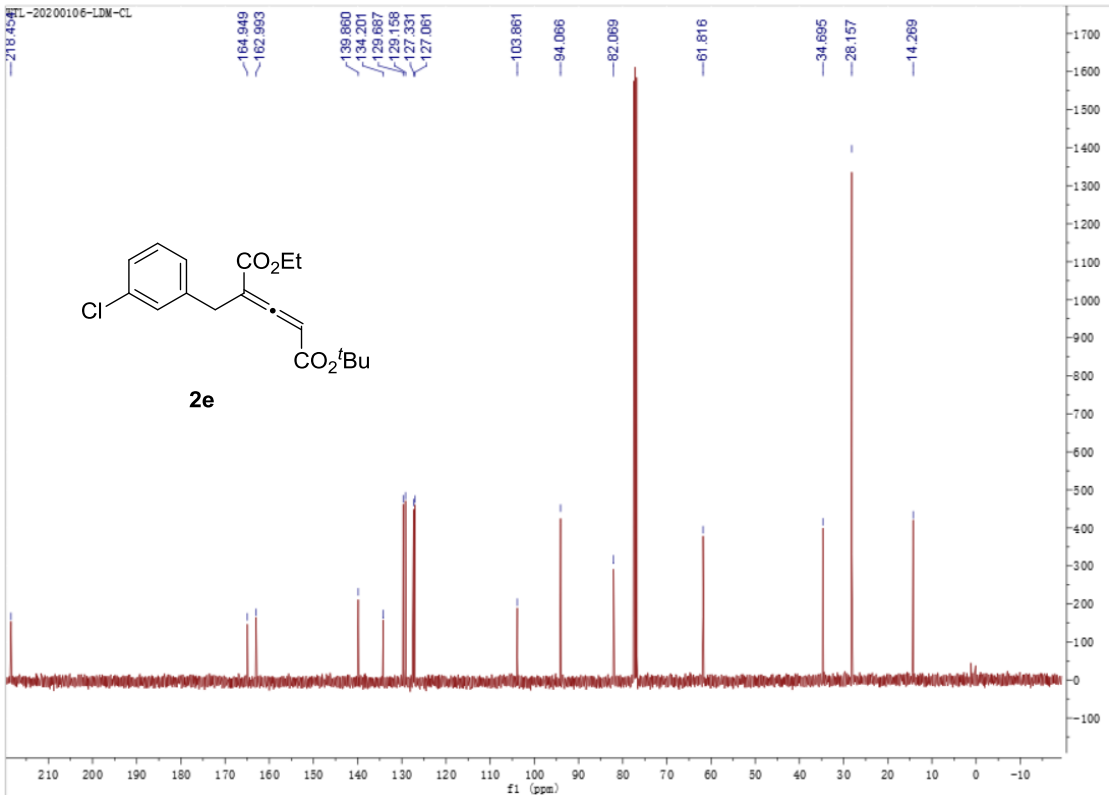

CO2Et
CO2tBu
2a


217.8430
165.5510
163.6378
106.5461
94.0396
81.7024
61.4920
28.1804
21.8111
14.3236
12.3749
CO2Et
CO2tBu
2a
f1 (ppm)

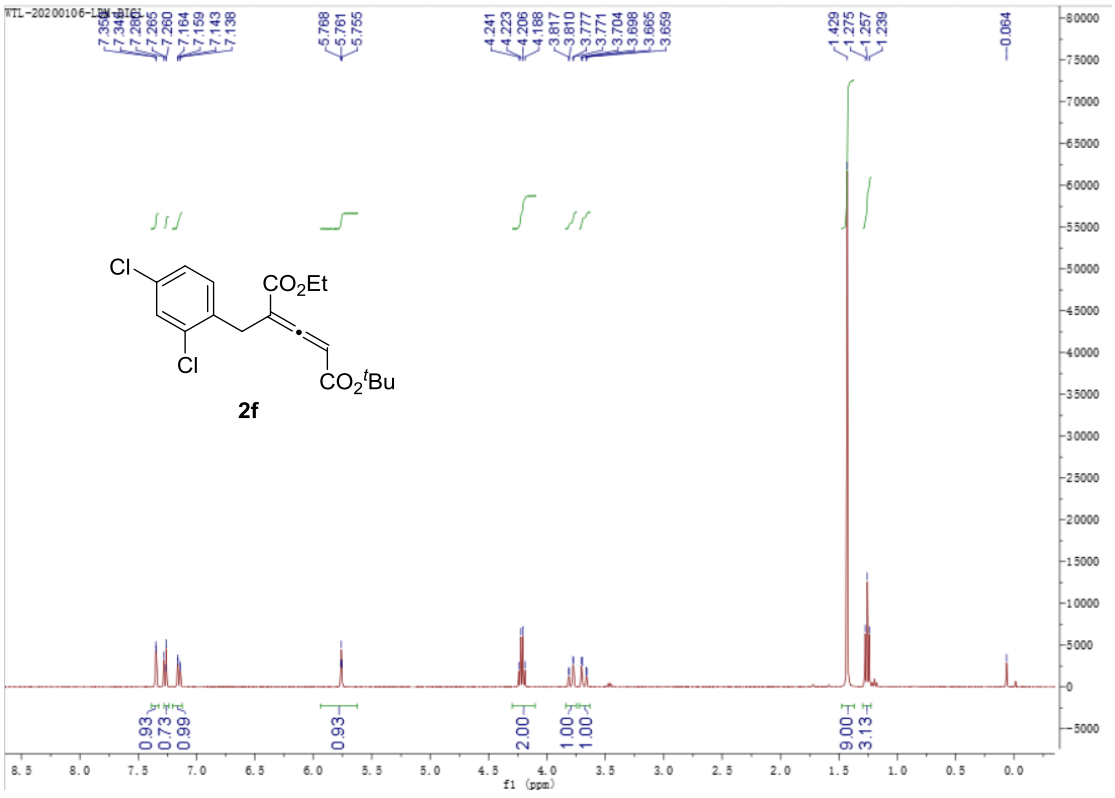

5.8301
5.8230
5.8160
4.2325
4.2147
4.1969
4.1792
2.3685
2.3615
2.3496
2.3427
2.3309
2.3239
2.3124
2.3062
2.2958
2.2886
2.2772
2.2700
2.2582
2.2510
2.2398
2.2325
1.4682
1.3168
1.3076
1.2807
1.2629
0.8746
0.8567
0.93
2.00
2.04
10.22
3.06
3.08
CO2Et
CO2tBu
2c
f1 (ppm)


218.0617
165.6331
163.6090
104.8197
93.4812
81.6845
61.4902
31.1931
28.2950
28.1808
27.4900
22.5054
14.3113
14.1050
CO2Et
CO2tBu
2c
f1 (ppm)

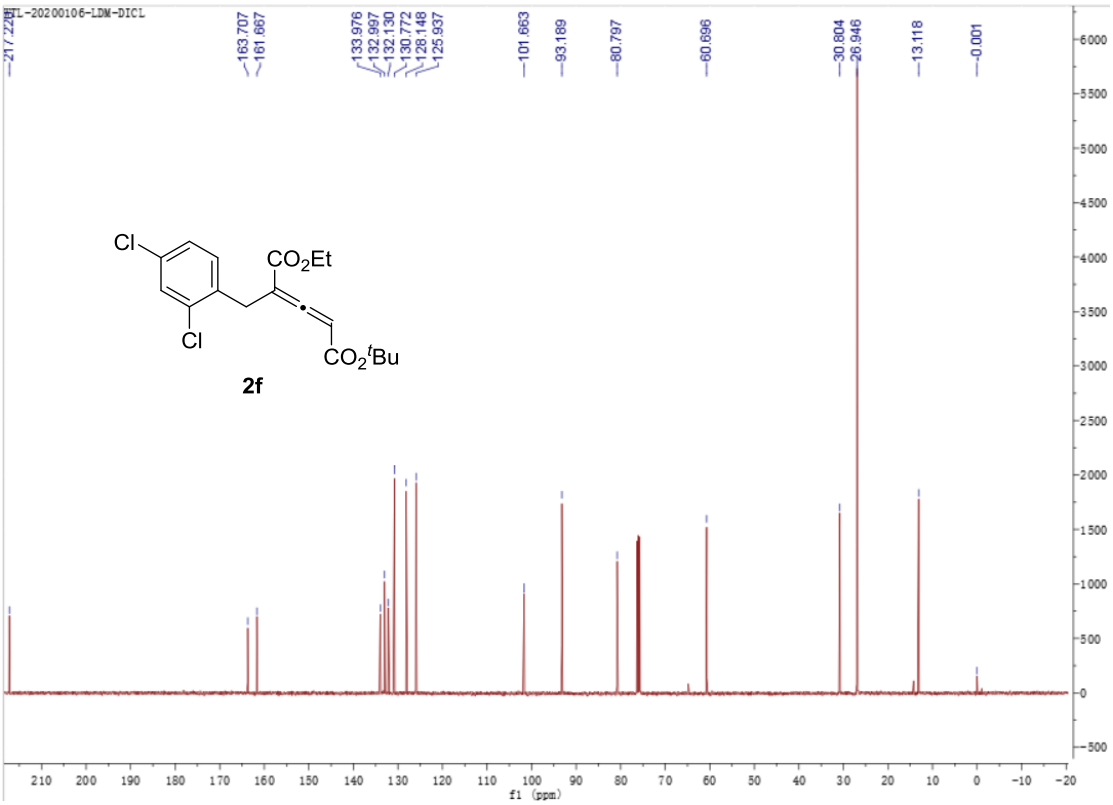

5.870
5.864
5.857
4.300
4.298
4.282
4.280
4.265
4.262
4.247
4.245
3.754
3.747
3.716
3.709
3.650
3.644
3.612
3.606
1.661
1.535
1.505
1.337
1.319
1.301
0.132
0.061
CO2Et
Cl
CO2tBu
2e
1.14
0.99
0.98
0.96
2.03
1.03
1.03
9.00
3.17
f1 (ppm)


WTL-20200106-LDM-CL
218.454
164.949
162.993
139.860
134.201
129.687
129.158
127.331
127.061
103.861
94.066
82.069
61.816
34.695
28.157
14.269
CO2Et
Cl
CO2tBu
f1 (ppm)

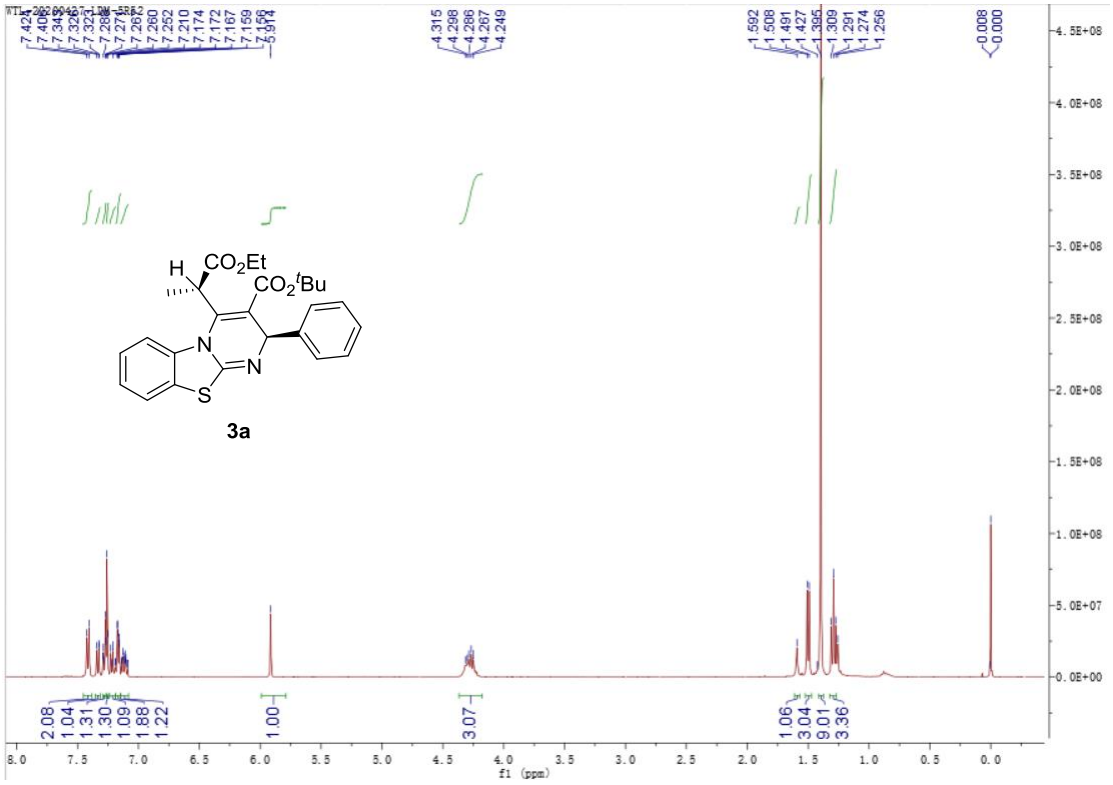
2e


7.356
7.344
7.286
7.265
7.260
7.164
7.159
7.143
7.138
5.768
5.761
5.755
4.241
4.223
4.206
4.188
3.817
3.810
3.777
3.771
3.704
3.698
3.665
3.659
1.429
1.275
1.257
1.239
0.064
Cl
CO2Et
Cl
CO2tBu
0.93
0.73
0.99
0.93
2.00
1.00
1.00
9.00
3.13
f1 (ppm)

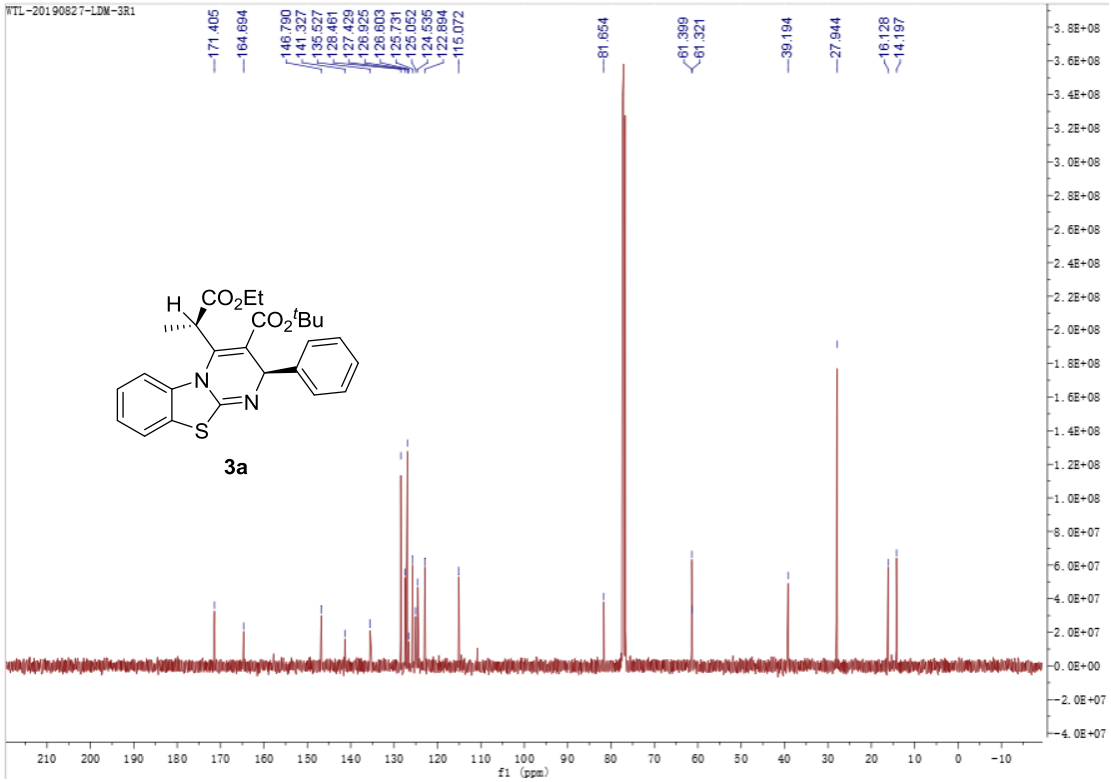
2f


WTL-20200106-LDM-DICL
163.707
161.867
133.976
132.997
132.130
130.772
128.148
125.937
101.863
93.189
80.797
60.696
30.804
26.946
13.118
0.001
Cl
Cl
CO2Et
CO2tBu
f1 (ppm)

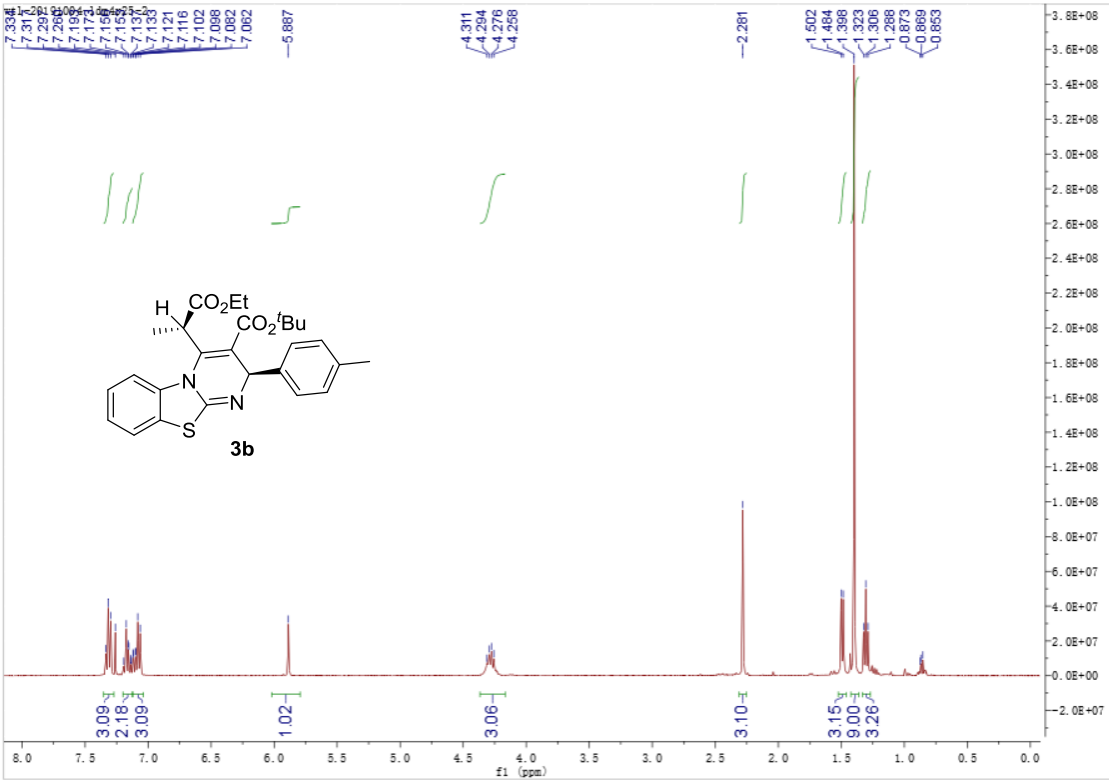
2f


4.315
4.298
4.286
4.267
4.249
1.592
1.508
1.491
1.427
1.395
1.309
1.291
1.274
1.256
0.008
0.000
H
CO2Et
CO2tBu
N
N
S
2.08
1.04
1.31
1.30
1.09
1.88
1.22
1.00
3.07
1.06
3.04
9.01
3.36
f1 (ppm)

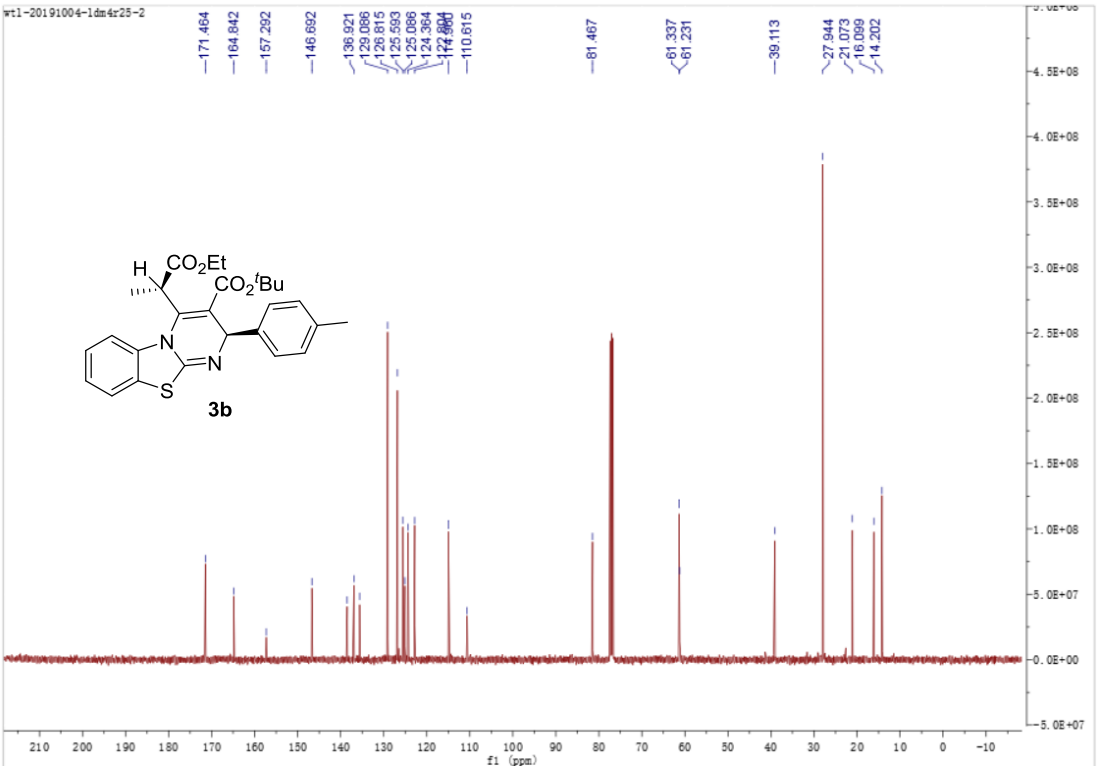
3a

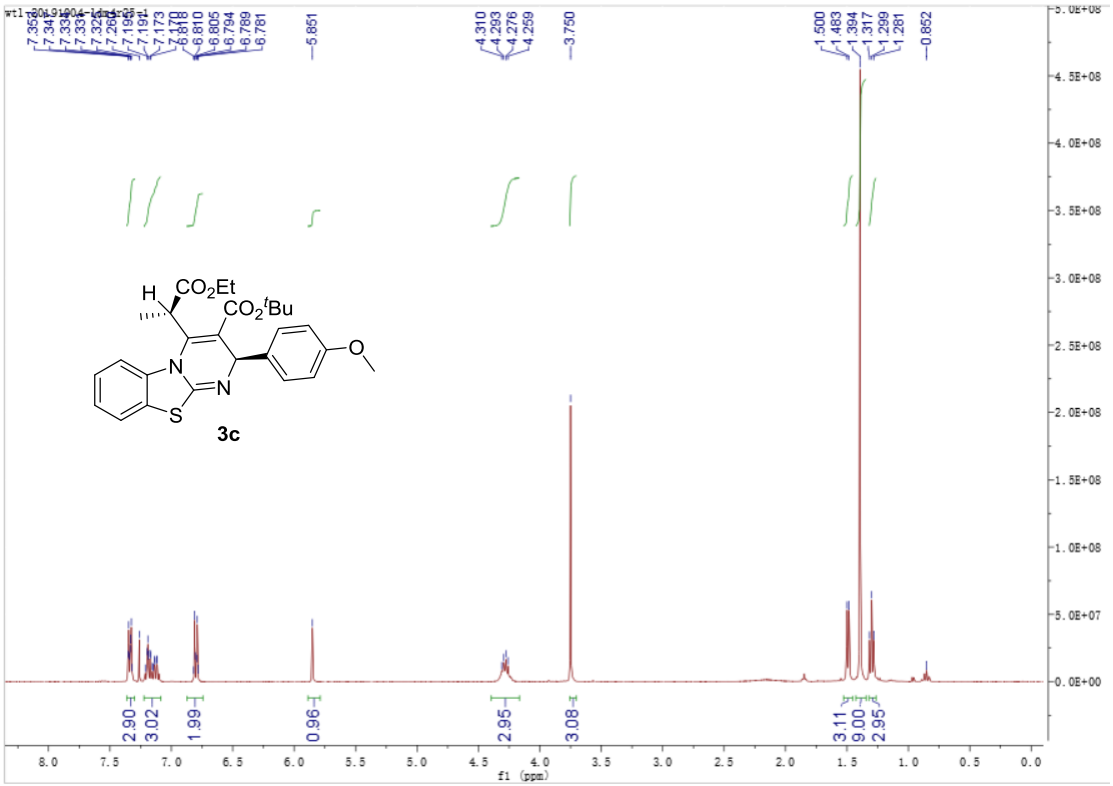

WTL-20190827-LDM-3R1
171.405
164.694
146.790
141.327
135.527
128.461
127.429
126.925
126.603
125.731
125.052
124.535
122.894
115.072
81.654
61.399
61.321
39.194
27.944
16.128
14.197
H
CO2Et
CO2tBu
N
N
S
f1 (ppm)

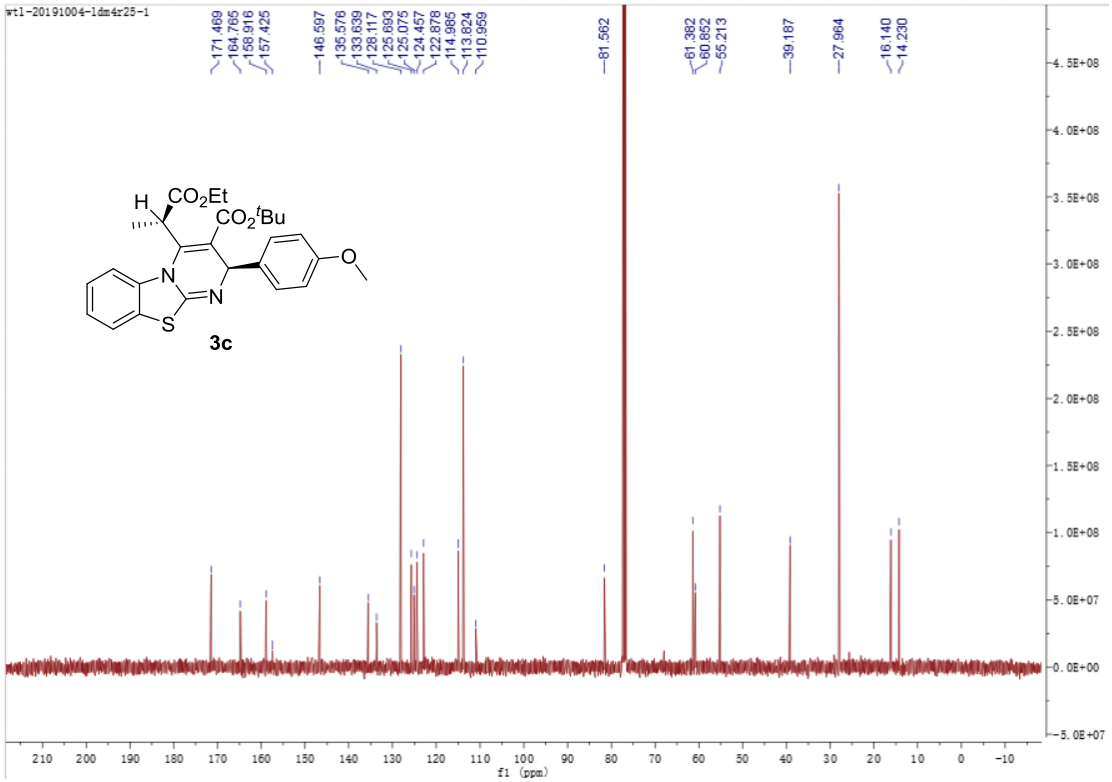
3a

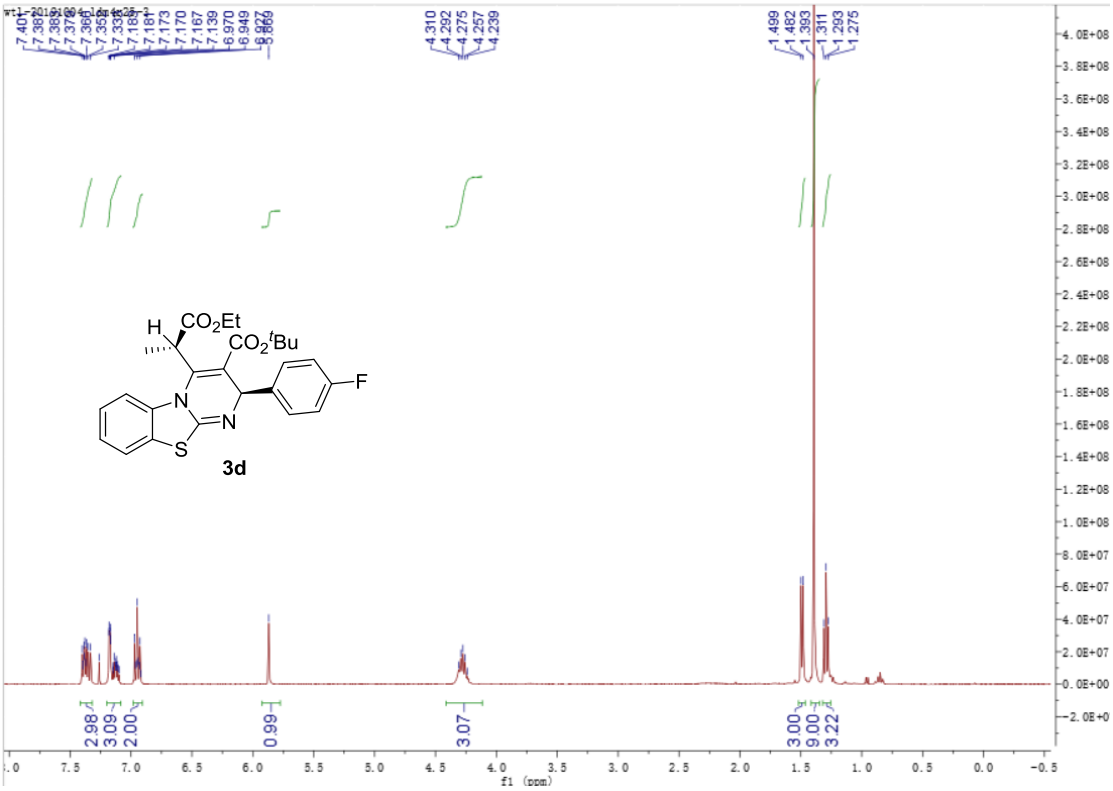

7.334
7.311
7.297
7.265
7.194
7.174
7.156
7.152
7.133
7.121
7.116
7.102
7.098
7.082
7.062
5.887
4.311
4.294
4.276
4.258
2.281
1.502
1.484
1.398
1.323
1.306
1.288
0.873
0.869
0.853
H
CO2Et
CO2tBu
N
N
S
3.09
2.18
3.09
1.02
3.06
3.10
3.15
9.00
3.26
f1 (ppm)

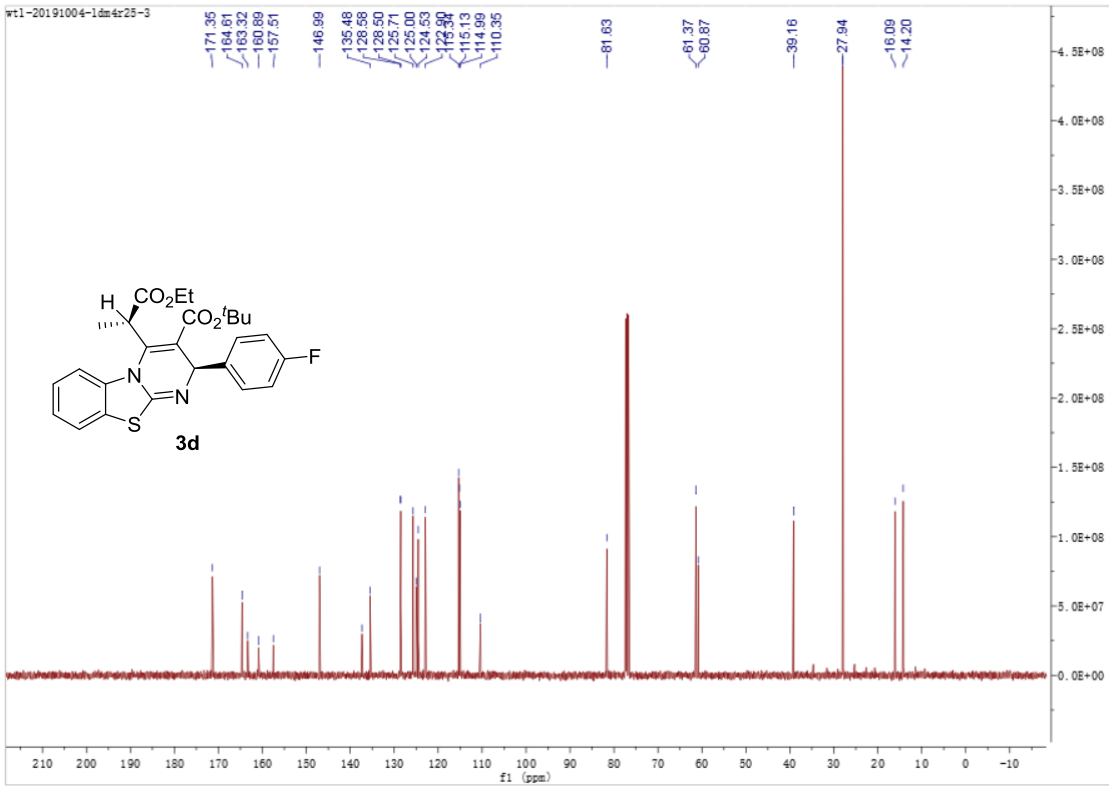
3b

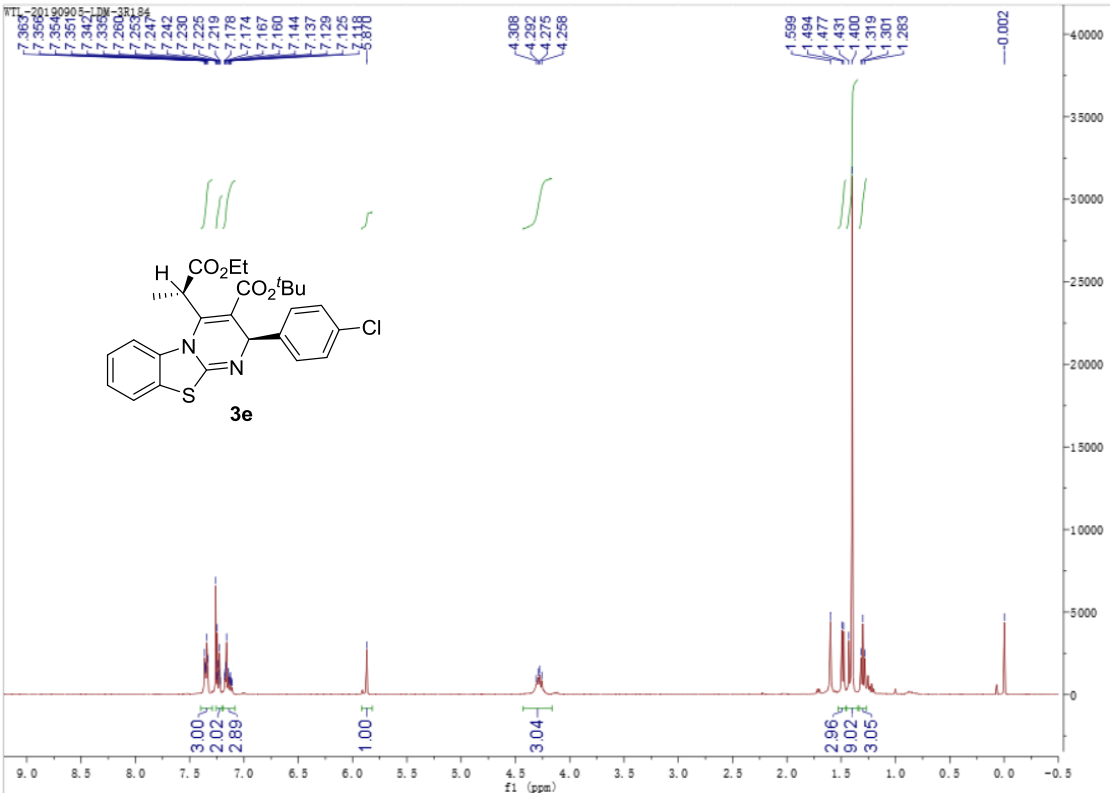

wtl-20191004-1dm4r25-2
171.464
164.842
157.292
146.692
136.921
129.086
126.815
125.593
125.086
124.364
110.615
81.467
61.337
61.231
39.113
27.944
21.073
16.099
14.202
H
CO2Et
CO2tBu
N
N
S
3b
f1 (ppm)

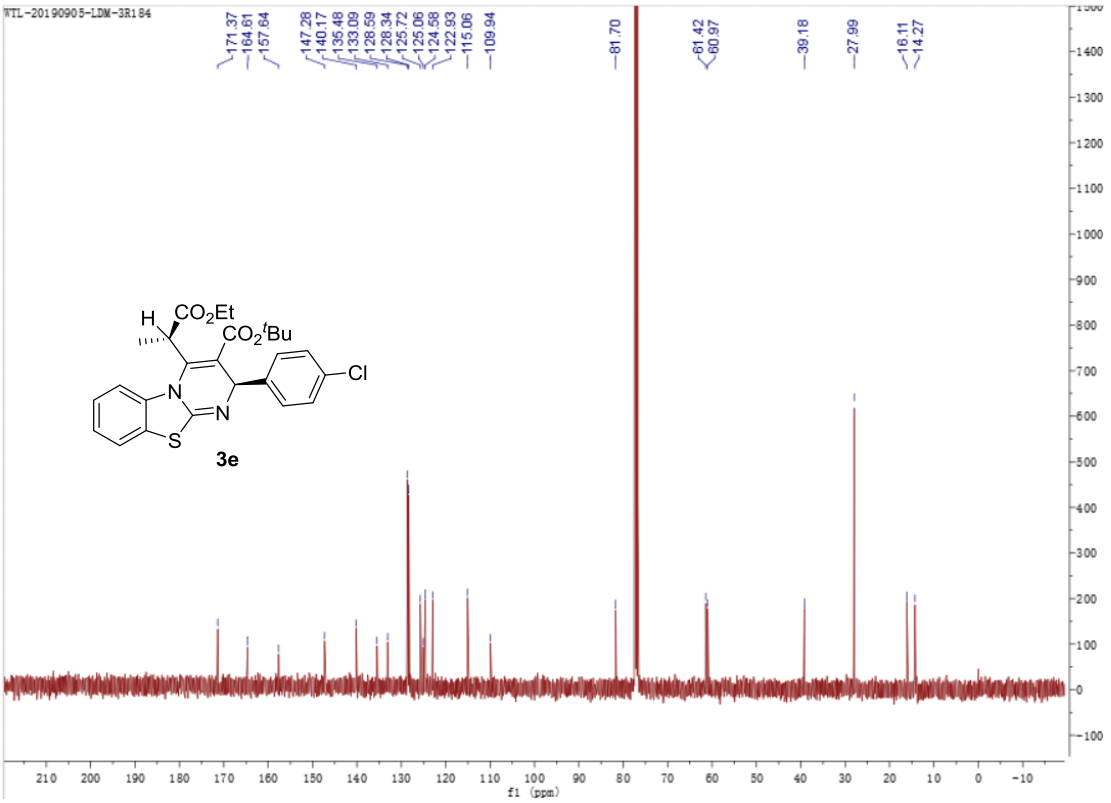

7.351
7.341
7.333
7.326
7.265
7.191
7.173
6.810
6.805
6.794
6.789
6.781
5.851
4.310
4.293
4.276
4.259
3.750
1.500
1.483
1.394
1.317
1.299
1.281
0.852
2.90
3.02
1.99
0.96
2.95
3.08
3.11
9.00
2.95
H
CO2Et
CO2tBu
N
N
S
O
3c
f1 (ppm)

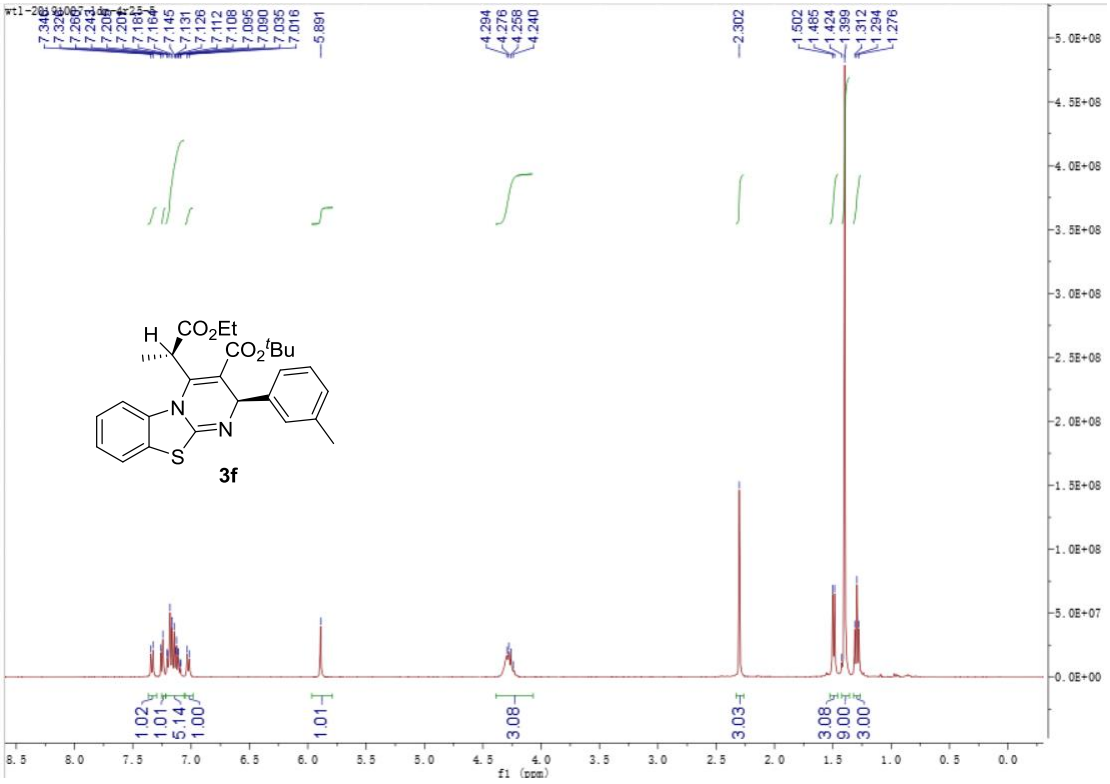

wt1-20191004-1dm4r25-1
171.469
164.765
158.916
157.425
146.597
135.576
133.639
128.117
125.693
125.075
124.457
122.878
114.985
113.824
110.959
81.562
61.382
60.852
55.213
39.187
27.964
16.140
14.230
H
CO2Et
CO2tBu
N
N
S
O
3c
f1 (ppm)

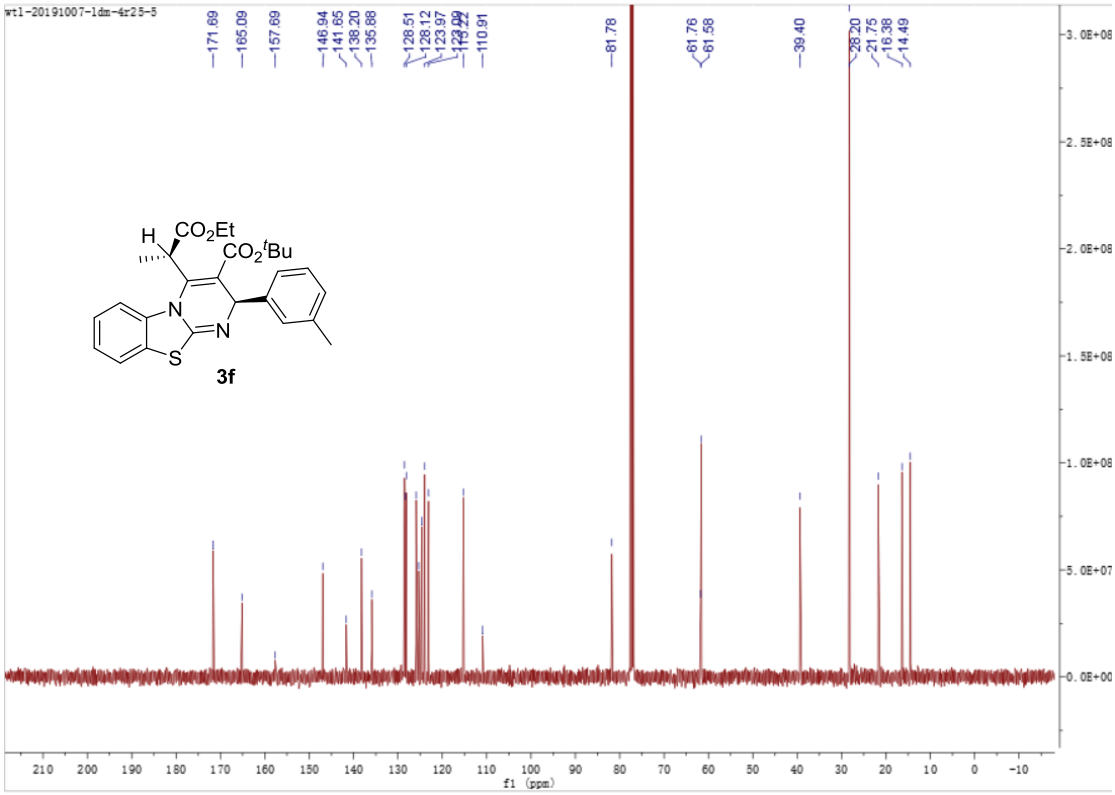

7.401
7.382
7.378
7.361
7.358
7.338
7.169
7.161
7.173
7.170
7.167
7.139
6.970
6.949
6.927
6.869
4.310
4.292
4.275
4.257
4.239
1.499
1.482
1.393
1.311
1.293
1.275
2.98
3.09
2.00
0.99
3.07
3.00
9.00
3.22
H
CO2Et
CO2tBu
N
N
S
F
3d
f1 (ppm)

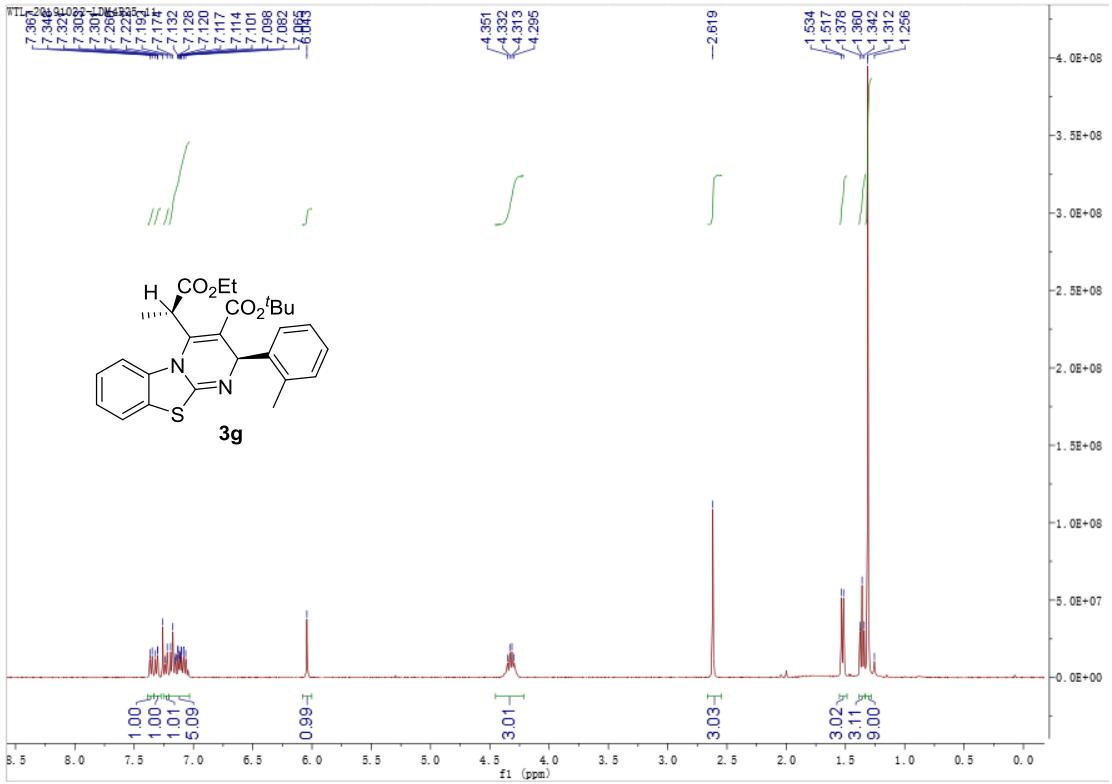

wtl-20191004-1dm4r25-3
171.35
164.61
163.32
160.89
157.51
146.99
135.48
128.58
128.50
125.71
125.00
124.53
115.13
114.99
110.35
81.63
61.37
60.87
39.16
27.94
16.09
14.20
H
CO2Et
CO2tBu
F
N
N
S
3d
f1 (ppm)

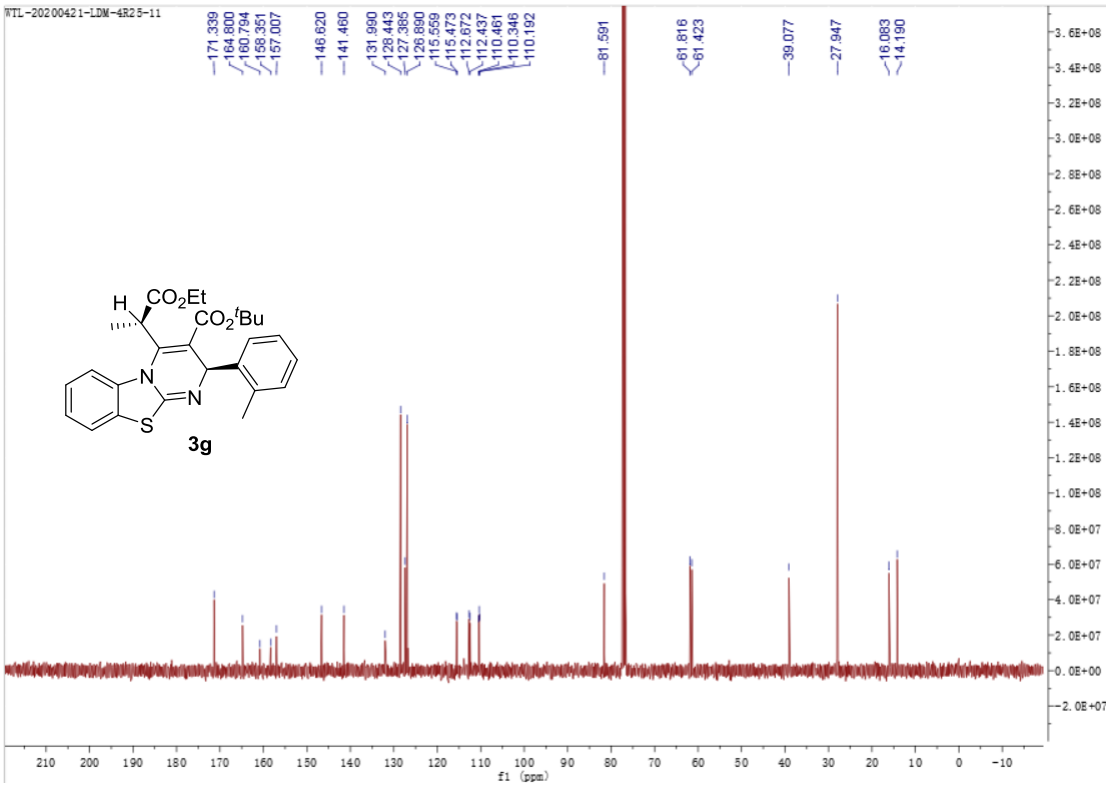

WTL-20190905-1DM-3R184
7.363
7.356
7.354
7.351
7.342
7.335
7.260
7.253
7.247
7.242
7.230
7.225
7.219
7.178
7.174
7.167
7.160
7.144
7.137
7.129
7.125
7.118
5.870
4.308
4.292
4.275
4.258
1.599
1.494
1.477
1.431
1.400
1.319
1.301
1.283
0.002
H
CO2Et
CO2tBu
Cl
N
N
S
3e
3.00
2.02
2.89
1.00
3.04
2.96
9.02
3.05
f1 (ppm)

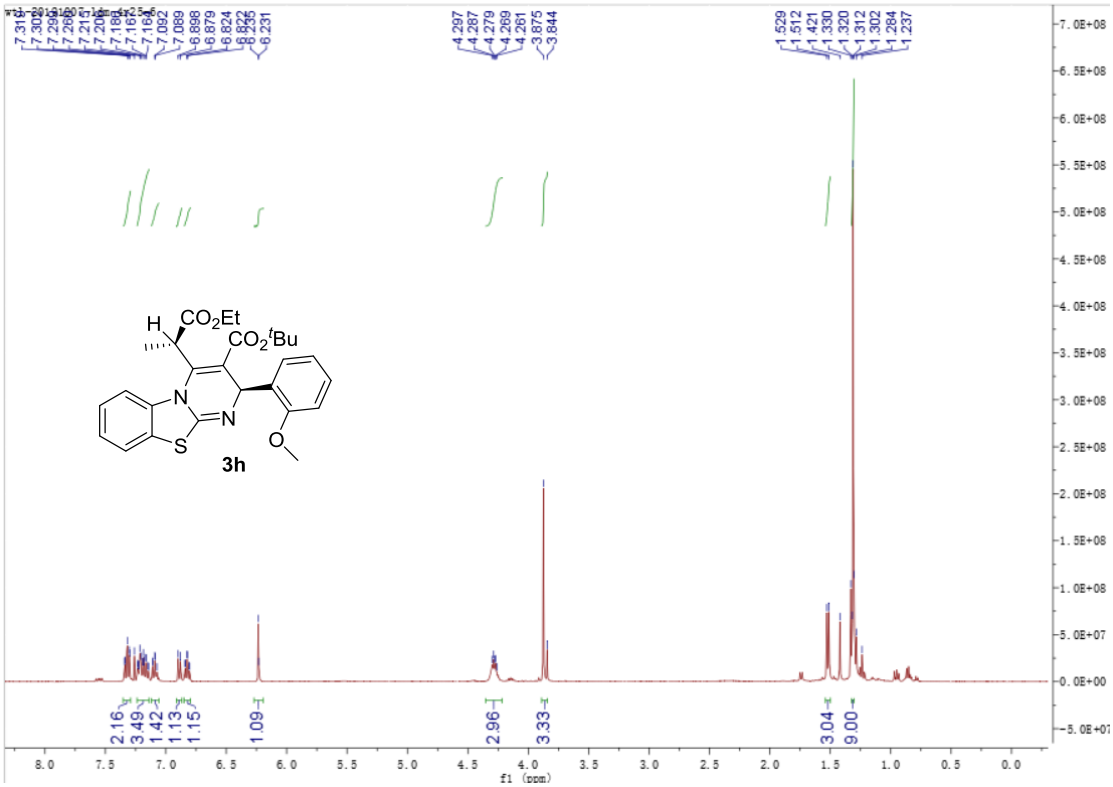

WTL-20190905-LDM-3R184
171.37
164.61
157.64
147.28
140.17
135.48
133.09
128.59
128.34
125.72
125.06
124.58
122.93
115.06
109.94
81.70
61.42
60.97
39.18
27.99
16.11
14.27
H
CO2Et
CO2tBu
N
N
S
Cl
3e
f1 (ppm)

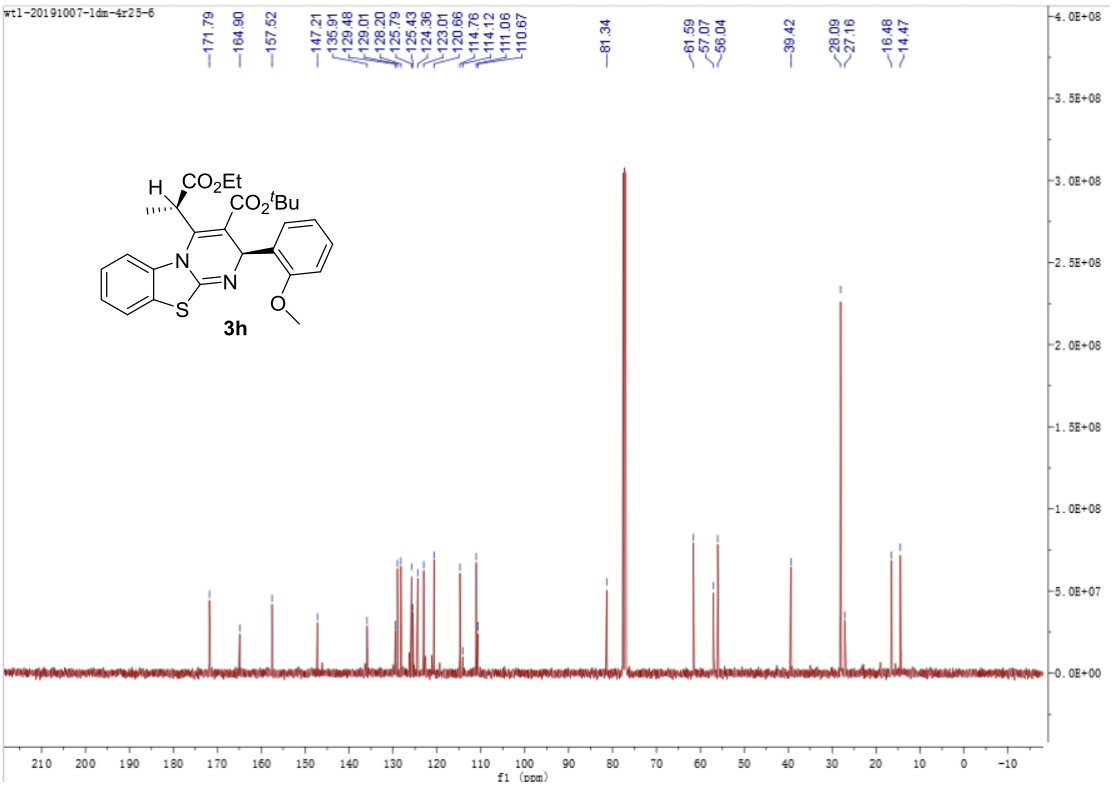

7.345
7.329
7.266
7.243
7.209
7.202
7.185
7.164
7.145
7.131
7.126
7.112
7.108
7.095
7.090
7.035
7.016
5.891
4.294
4.276
4.258
4.240
2.302
1.502
1.485
1.424
1.399
1.312
1.294
1.276
H
CO2Et
CO2tBu
N
N
S
3f
1.02
1.01
5.14
1.00
1.01
3.08
3.03
3.08
9.00
3.00
f1 (ppm)

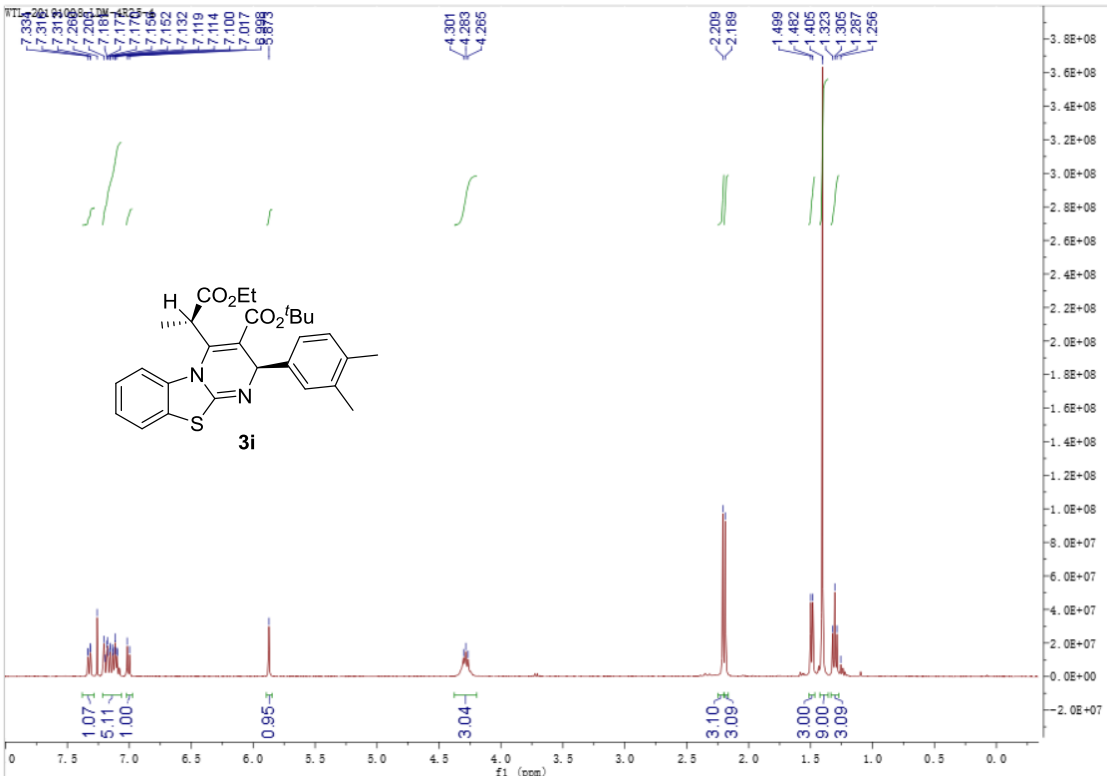

wtl-20191007-1dm-4r25-5
171.69
165.09
157.69
146.94
141.65
138.20
135.88
128.51
128.12
123.97
110.91
81.78
61.76
61.58
39.40
28.20
21.75
16.38
14.49
H
CO2Et
CO2tBu
N
N
S
3f
f1 (ppm)

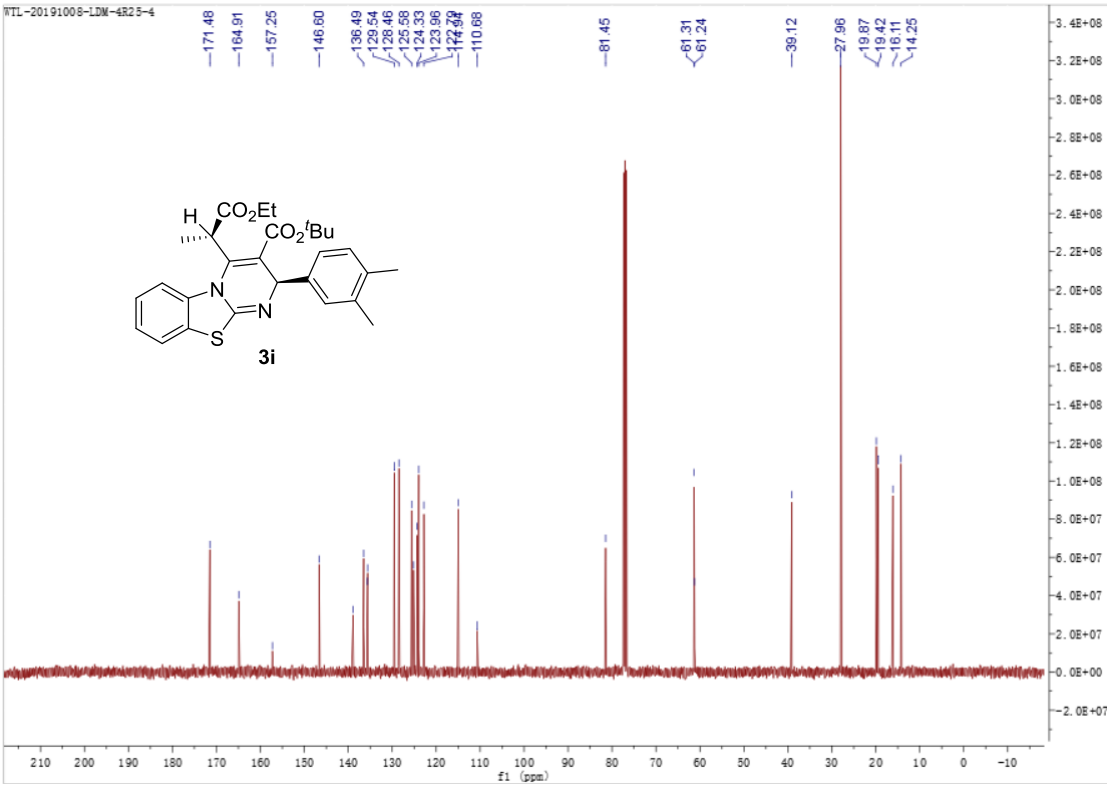

7.365
7.346
7.321
7.302
7.301
7.266
7.229
7.194
7.174
7.132
7.128
7.120
7.117
7.114
7.101
7.098
7.082
4.351
4.332
4.313
4.295
2.619
1.534
1.517
1.378
1.360
1.342
1.312
1.256
H
CO2Et
CO2tBu
N
N
S
3g
1.00
1.00
1.01
5.09
0.99
3.01
3.03
3.02
3.11
9.00
f1 (ppm)


WTL-20200421-LDM-4R25-11
171.339
164.800
160.794
159.351
157.007
146.620
141.460
131.990
129.443
127.385
126.890
115.559
115.473
112.672
112.437
110.461
110.346
110.192
81.591
61.816
61.423
39.077
27.947
16.083
14.190
H
CO2Et
CO2tBu
N
N
S
3g
f1 (ppm)


7.316
7.302
7.299
7.296
7.217
7.209
7.164
7.162
7.159
7.092
7.089
6.898
6.879
6.824
6.822
6.820
6.231
4.297
4.287
4.279
4.269
4.261
3.875
3.844
1.529
1.512
1.421
1.330
1.320
1.312
1.302
1.284
1.237
2.16
3.49
1.42
1.13
1.15
1.09
2.96
3.33
3.04
9.00
H
CO2Et
CO2tBu
N
N
S
O
3h
f1 (ppm)


wtl-20191007-1dm-4r25-6
171.79
164.90
157.52
147.21
135.91
129.48
129.01
128.20
125.79
125.43
124.36
123.01
120.66
114.76
114.12
111.06
110.67
81.34
61.59
57.07
56.04
39.42
28.09
27.16
16.48
14.47
H
CO2Et
CO2tBu
N
N
S
O
3h
f1 (ppm)


7.339
7.311
7.310
7.266
7.200
7.181
7.177
7.176
7.156
7.152
7.132
7.119
7.114
7.100
7.017
6.998
6.873
4.301
4.283
4.265
2.209
2.189
1.499
1.482
1.405
1.323
1.305
1.287
1.256
1.07
5.11
1.00
0.95
3.04
3.10
3.09
3.00
9.00
3.09
H
CO2Et
CO2tBu
N
N
S
3i
f1 (ppm)


WTL-20191008-LDM-4R25-4
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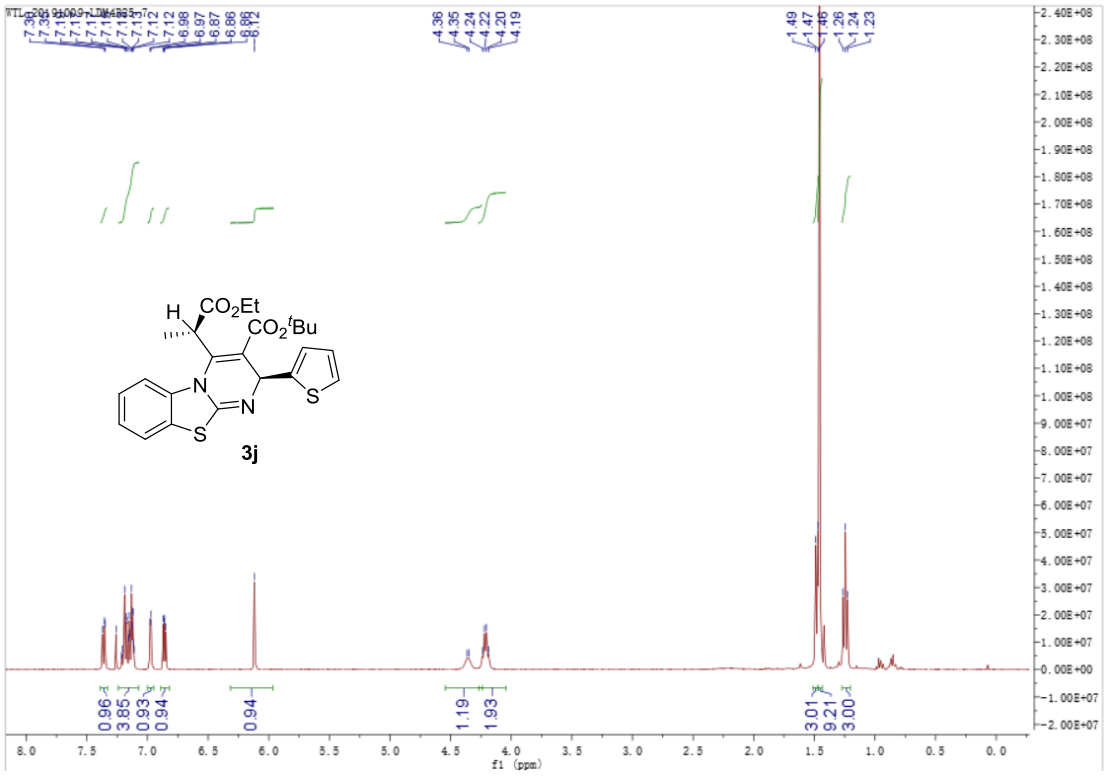
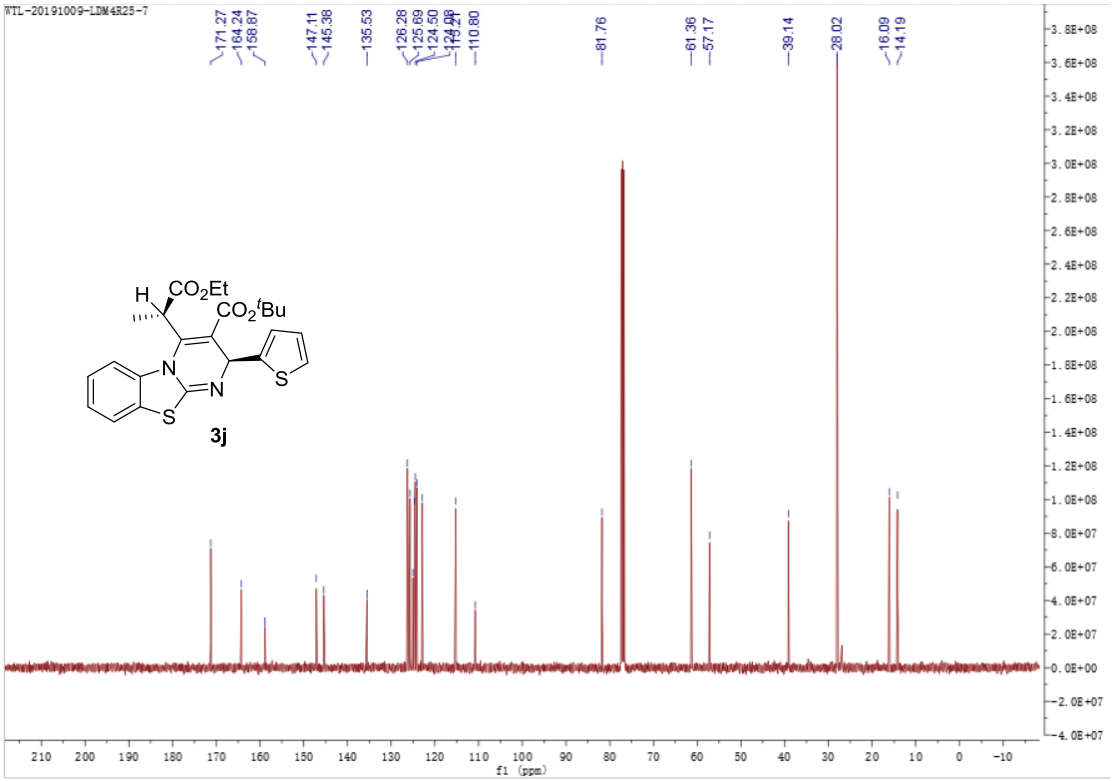
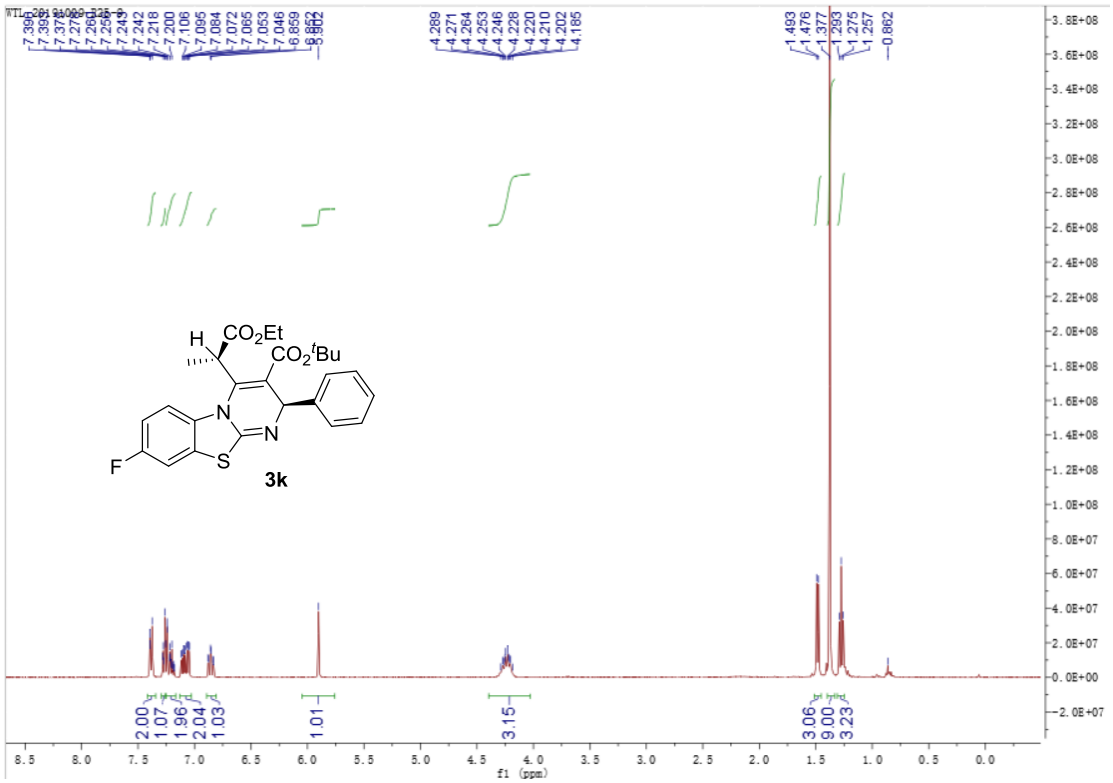
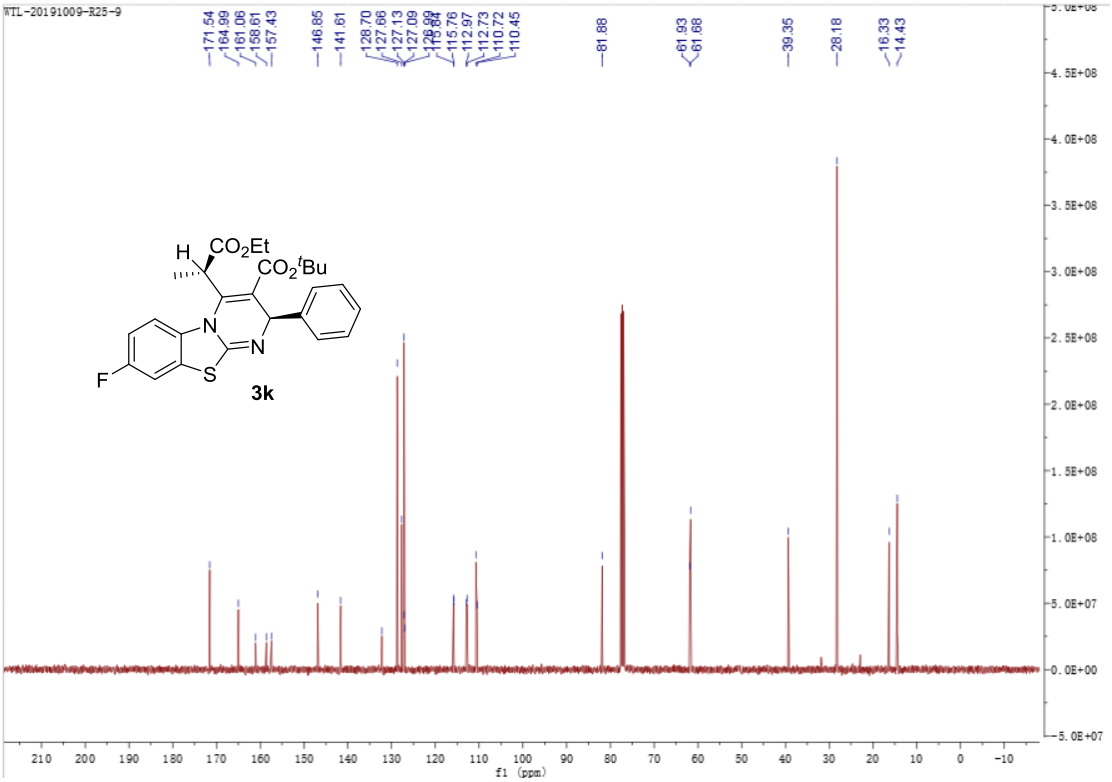
164.91
157.25
146.60
136.49
129.54
128.46
125.58
124.33
123.96
110.68
81.45
61.31
61.24
39.12
27.96
19.87
19.42
16.11
14.25
H
CO2Et
CO2tBu
N
N
S
3i
f1 (ppm)


4.36
4.35
4.24
4.22
4.20
4.19
1.49
1.47
1.46
1.26
1.24
1.23
H
CO2Et
CO2tBu
N
N
S
S
3j
0.96
3.85
0.93
0.94
0.94
1.19
1.93
3.01
9.21
3.00
f1 (ppm)


WTL-20191009-LDM4R25-7
171.27
164.24
158.87
147.11
145.38
135.53
126.28
125.69
124.50
110.80
81.76
61.36
57.17
39.14
28.02
16.09
14.19
H
CO2Et
CO2tBu
N
S
N
S
3j
f1 (ppm)


4.289
4.271
4.264
4.253
4.246
4.228
4.220
4.210
4.202
4.185
1.493
1.476
1.377
1.293
1.275
1.257
0.862
H
CO2Et
CO2tBu
N
N
S
F
3k
2.00
1.07
1.96
2.04
1.03
1.01
3.15
3.06
9.00
3.23
f1 (ppm)


WTL-20191009-R25-9
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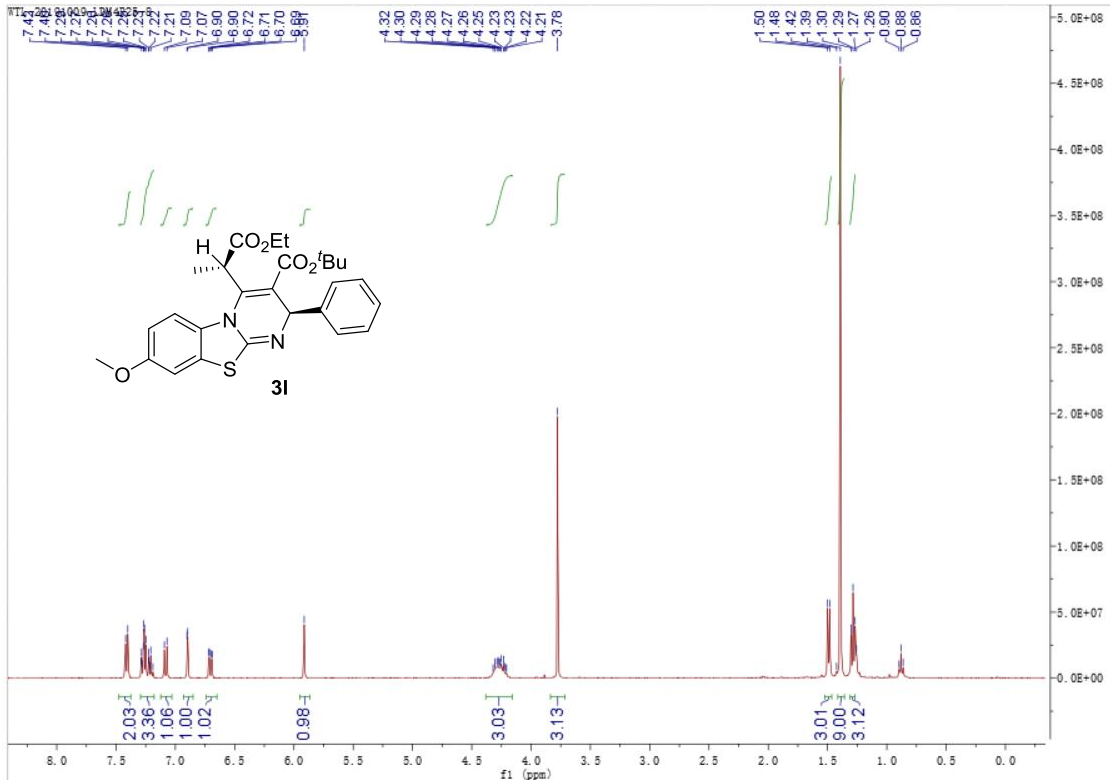
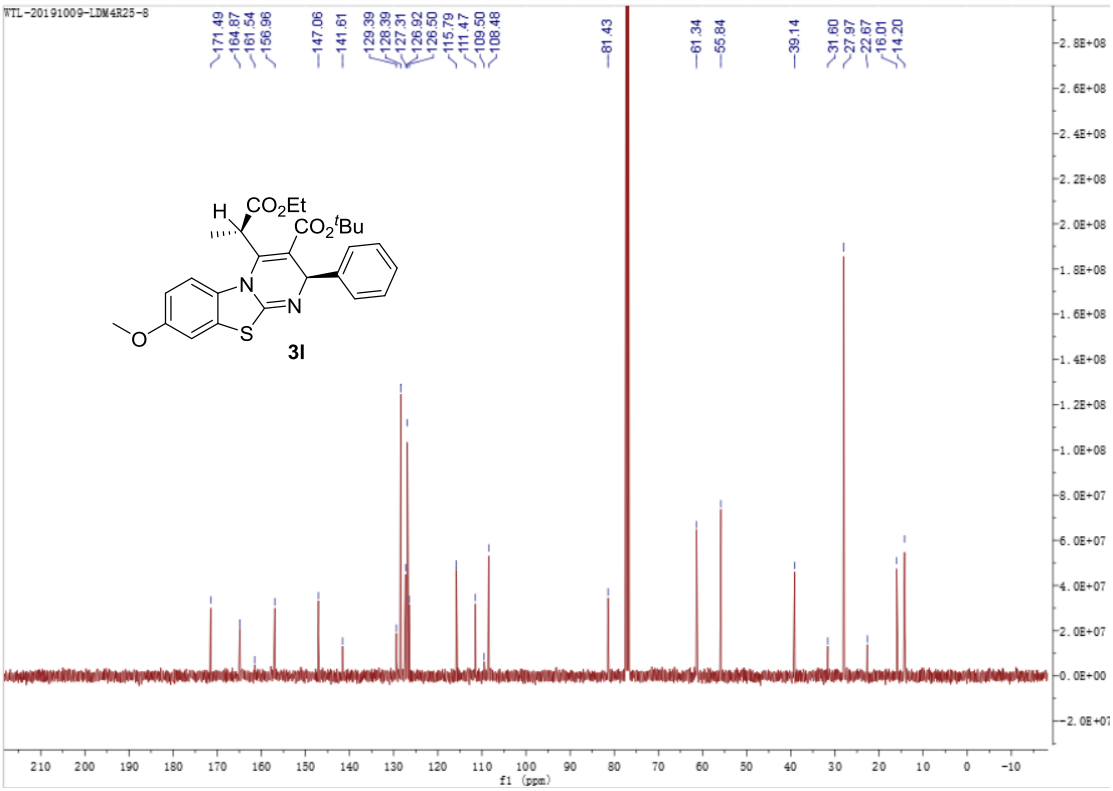
161.06
158.61
157.43
146.85
141.61
128.70
127.66
127.13
127.09
115.76
112.97
112.73
110.72
110.45
81.88
61.93
61.68
39.35
28.18
16.33
14.43
H
CO2Et
CO2tBu
N
N
S
F
3k
f1 (ppm)


4.32
4.30
4.29
4.28
4.27
4.26
4.25
4.23
4.22
4.21
3.78
1.50
1.48
1.42
1.39
1.30
1.29
1.27
1.26
0.90
0.88
0.86
2.03
3.36
1.06
1.00
1.02
0.98
3.03
3.13
3.01
9.00
3.12
H
CO2Et
CO2tBu
N
N
S
O
3l
f1 (ppm)


WTL-20191009-LDM4R25-8
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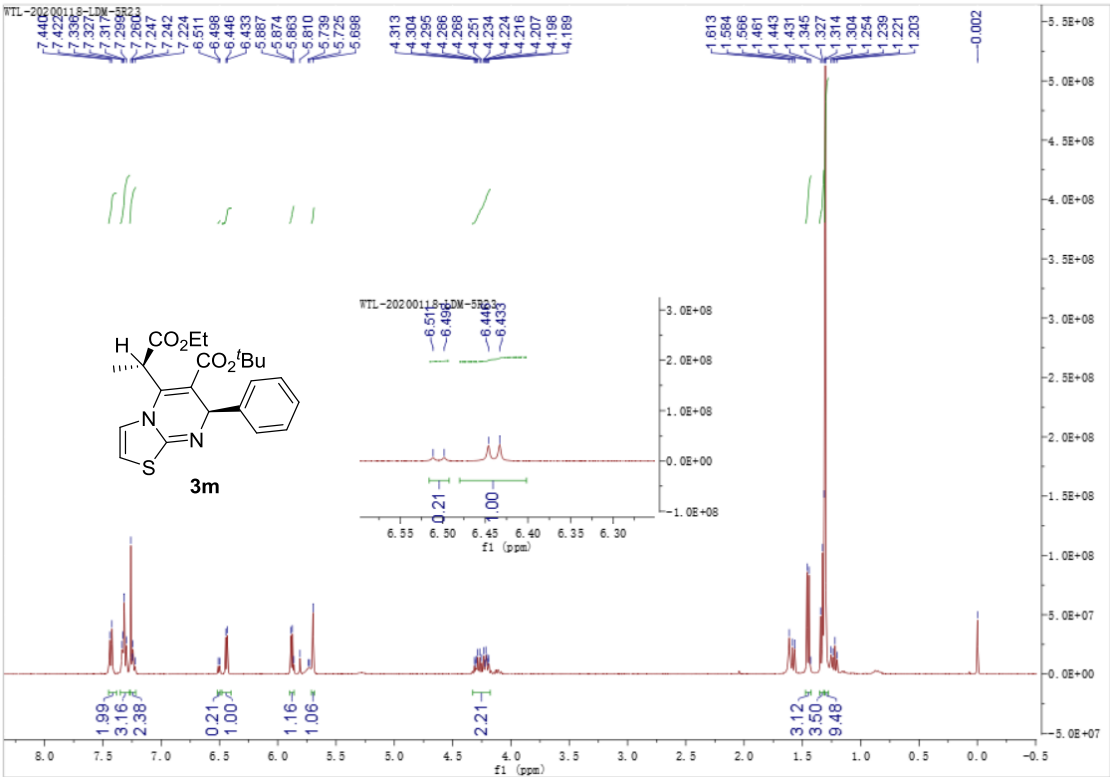
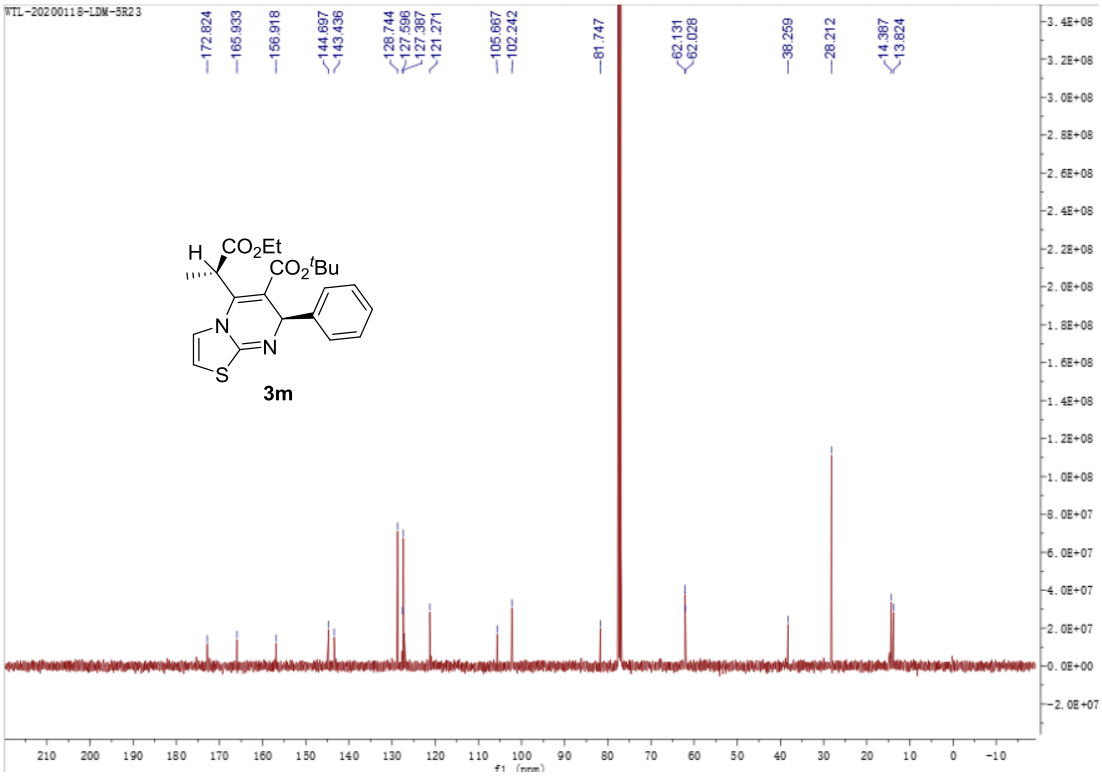
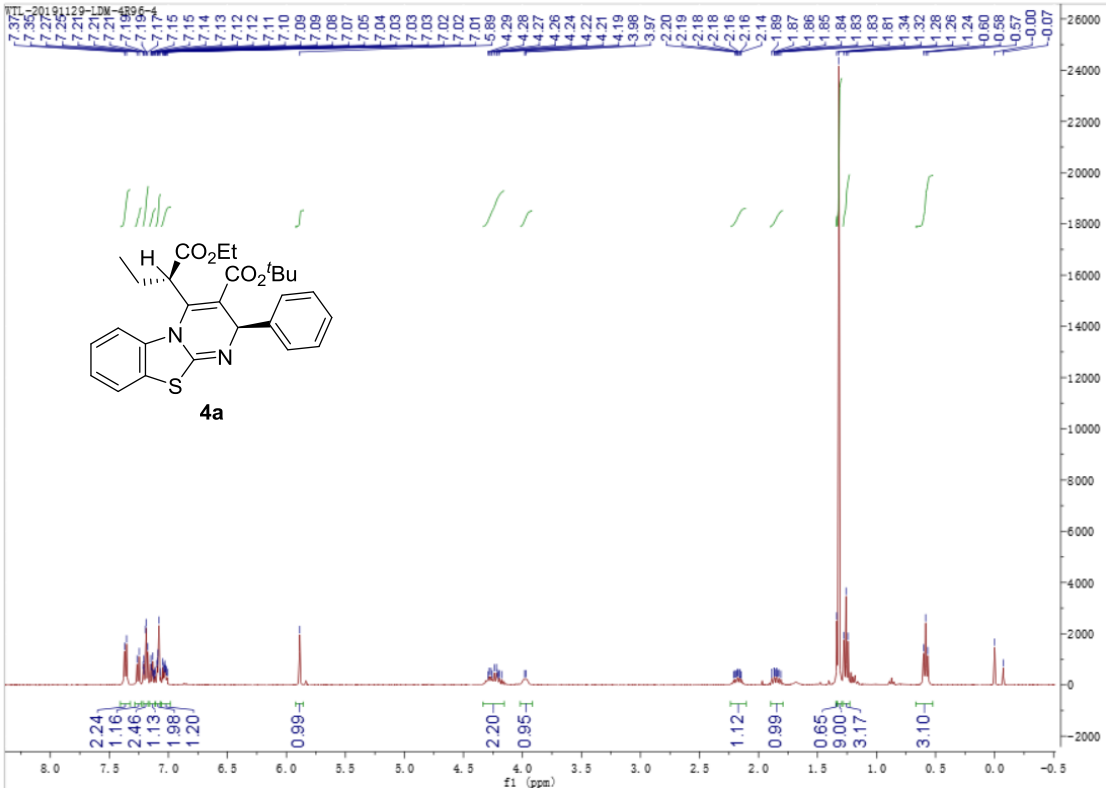
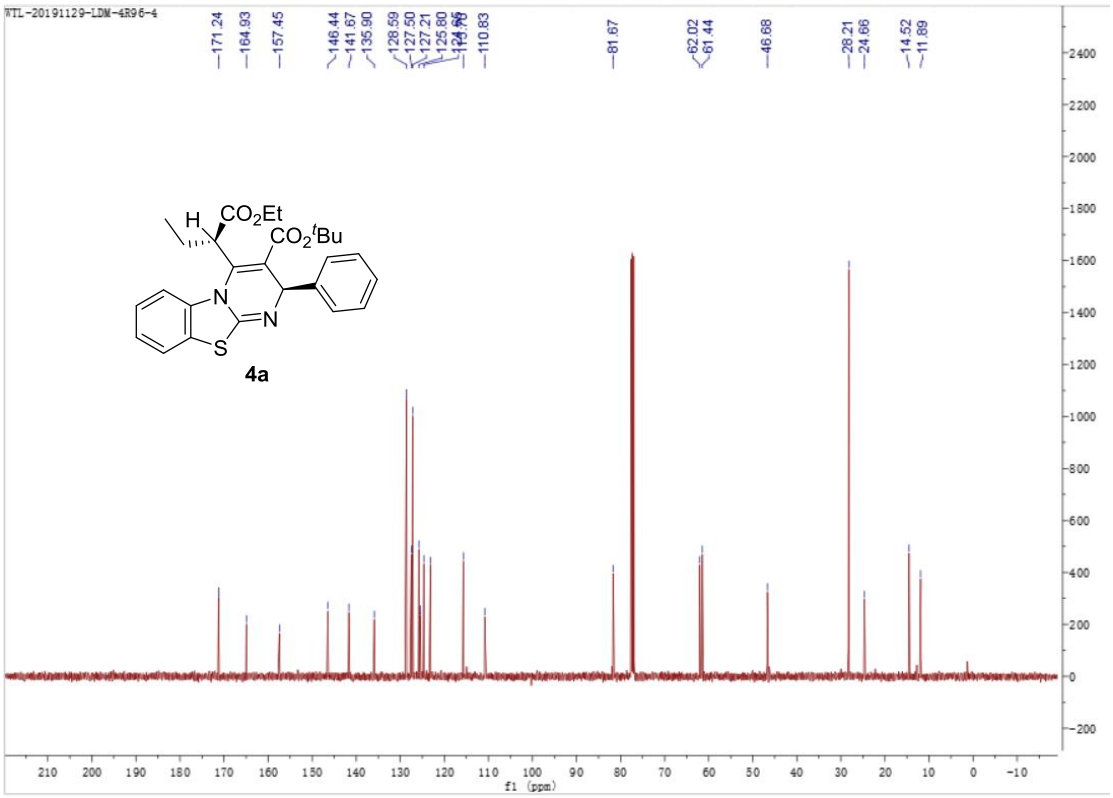
161.54
156.96
147.06
141.61
129.39
128.39
127.31
126.92
126.50
115.79
111.47
109.50
108.48
81.43
61.34
55.84
39.14
31.60
27.97
22.67
16.01
14.20
H
CO2Et
CO2tBu
N
N
S
O
3l
f1 (ppm)

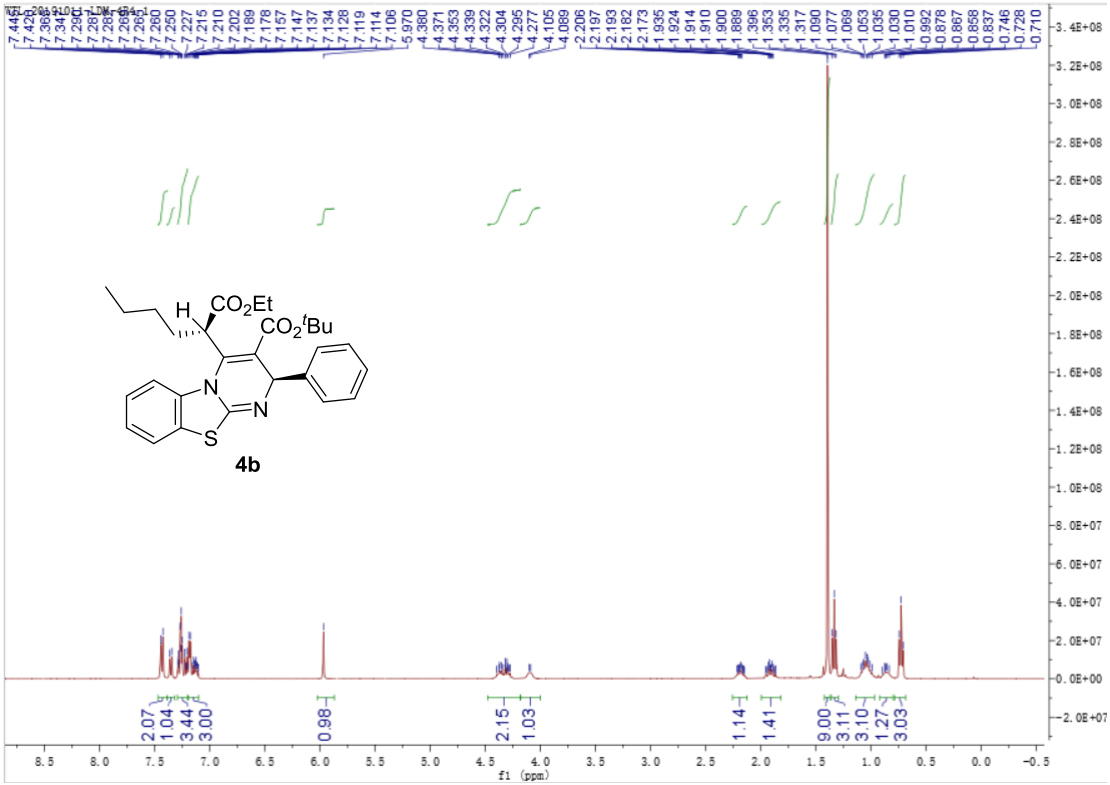

WTL-20200118-LDM-5R23
7.440
7.422
7.396
7.327
7.317
7.299
7.260
7.247
7.242
7.224
6.511
6.498
6.446
6.433
5.887
5.874
5.863
5.810
5.739
5.725
5.696
4.313
4.304
4.295
4.286
4.268
4.251
4.234
4.224
4.216
4.207
4.198
4.189
1.613
1.584
1.566
1.461
1.443
1.431
1.345
1.327
1.314
1.304
1.254
1.239
1.221
1.203
0.002
H
CO2Et
CO2tBu
N
N
S
3m
1.99
3.16
2.38
0.21
1.00
1.16
1.06
2.21
3.12
3.50
9.48
f1 (ppm)


WTL-20200118-LDM-5R23
172.824
165.933
156.918
144.697
143.436
128.744
127.596
127.387
121.271
105.667
102.242
81.747
62.131
62.028
38.259
28.212
14.387
13.824
H
CO2Et
CO2tBu
N
N
S
3m

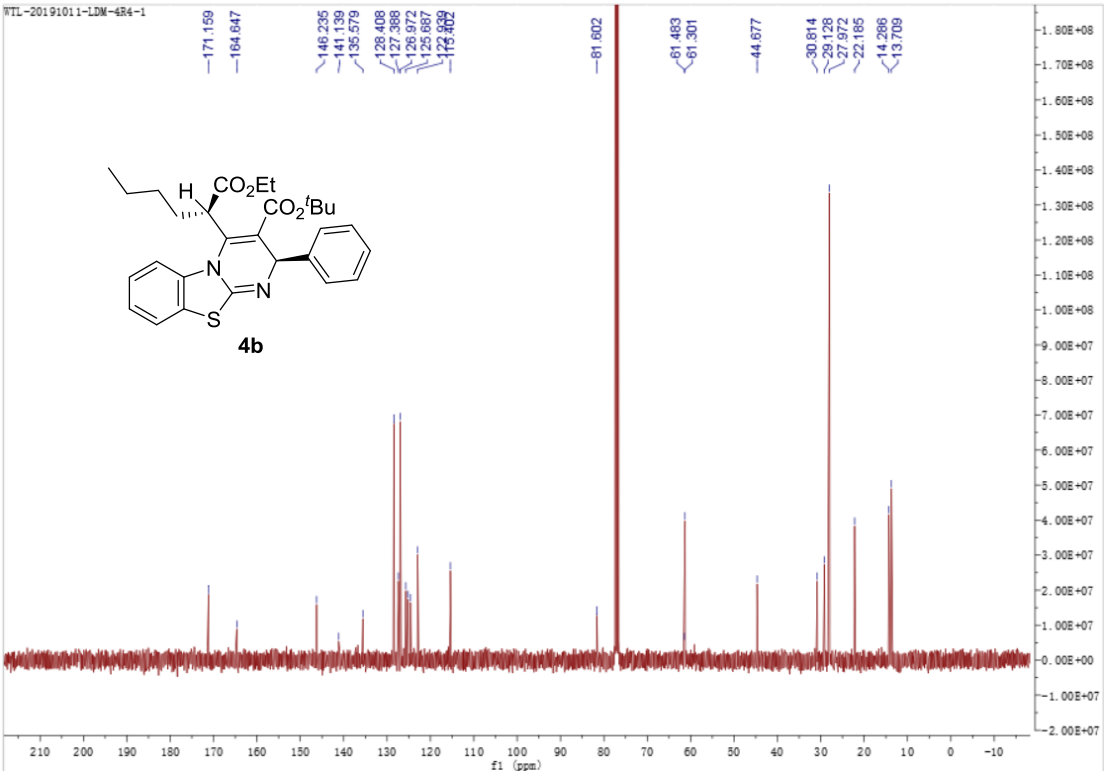

WTL-20191129-LDM-4R96-4
H
CO2Et
CO2tBu
N
N
S
4a
2.24
1.16
2.46
1.13
1.98
1.20
0.99
2.20
0.95
1.12
0.99
0.65
9.00
3.17
3.10
f1 (ppm)

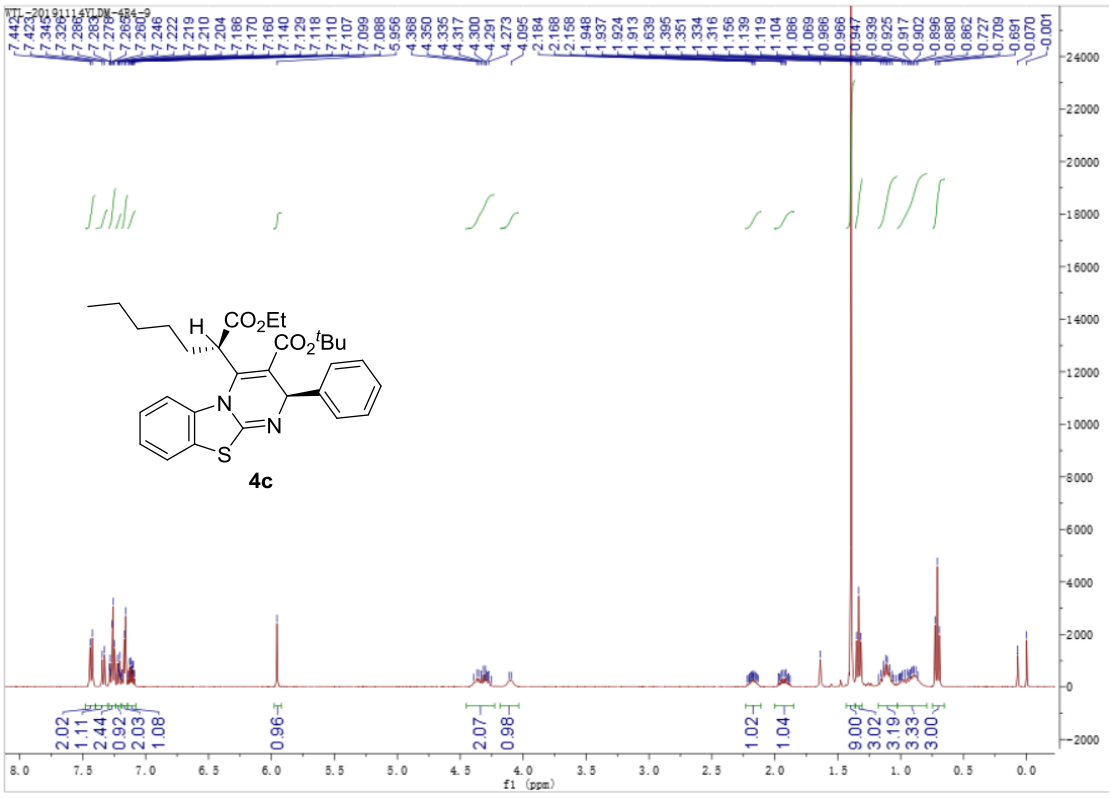

WTL-20191129-LDM-4R96-4
171.24
164.93
157.45
146.44
141.67
135.90
128.59
127.50
127.21
125.80
110.83
81.67
62.02
61.44
46.68
28.21
24.66
14.52
11.89
H
CO2Et
CO2tBu
N
N
S
f1 (ppm)

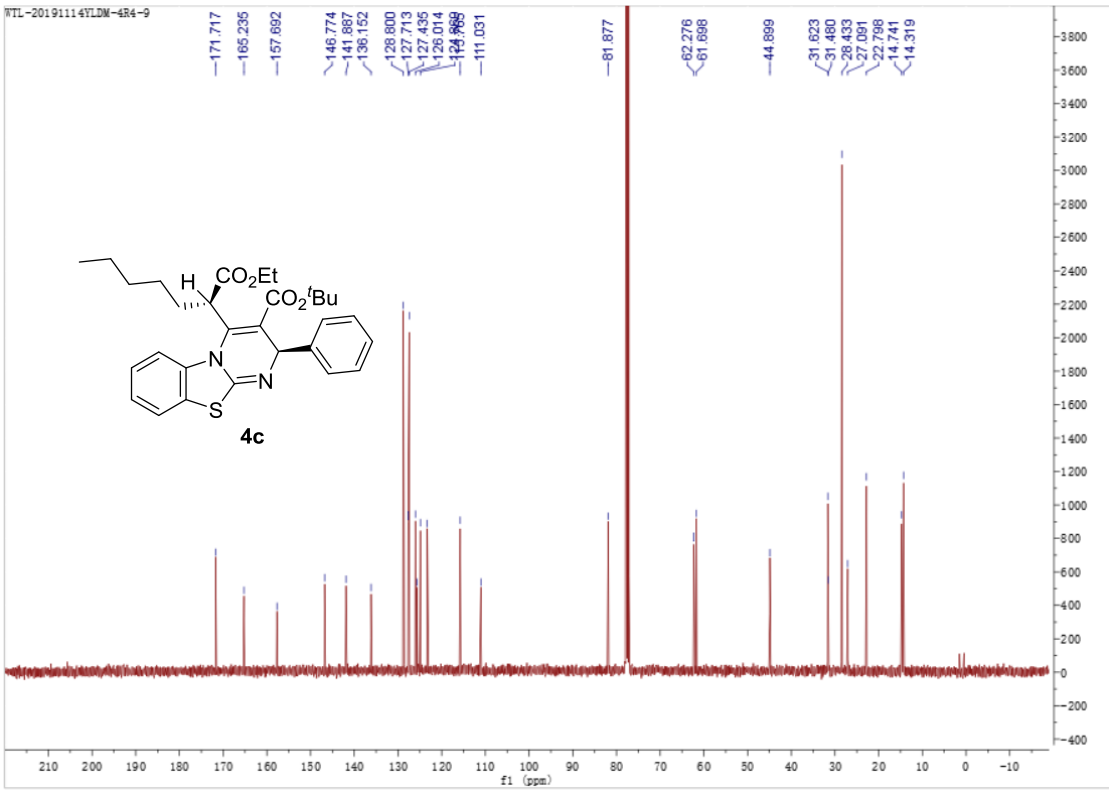
4a

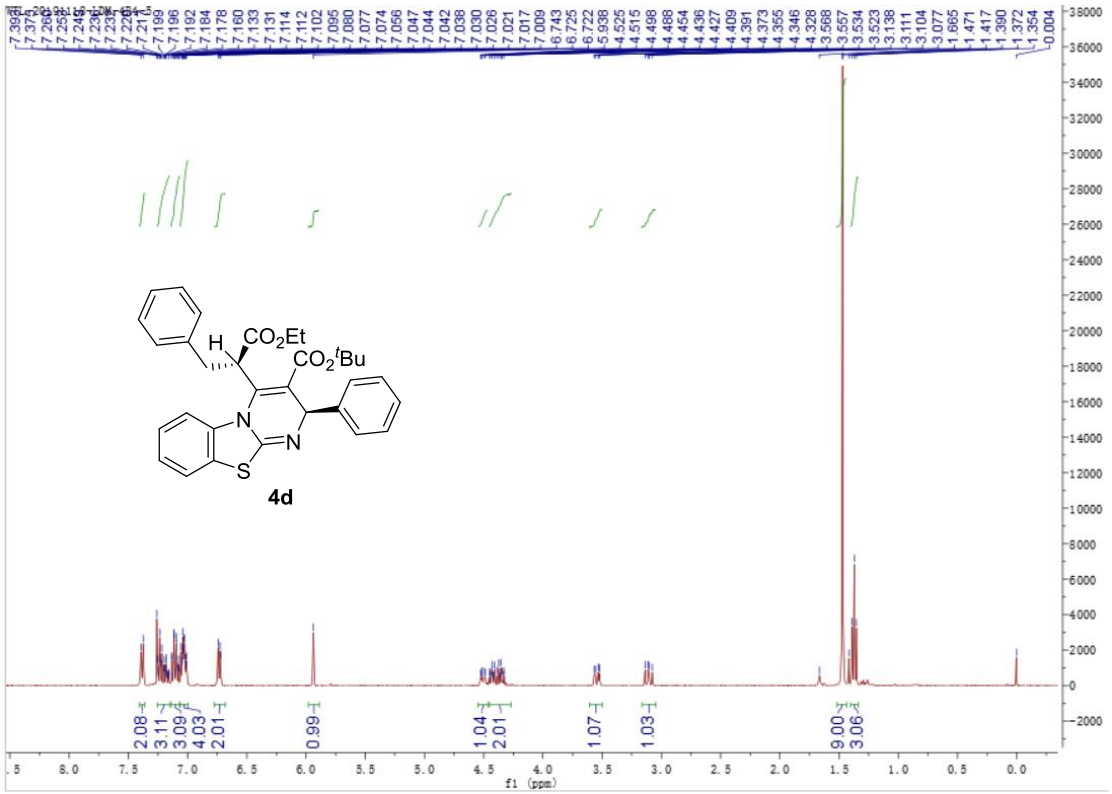

H
CO2Et
CO2tBu
N
N
S
2.07
1.04
3.44
3.00
0.98
2.15
1.03
1.14
1.41
9.00
3.11
3.10
1.27
3.03
f1 (ppm)

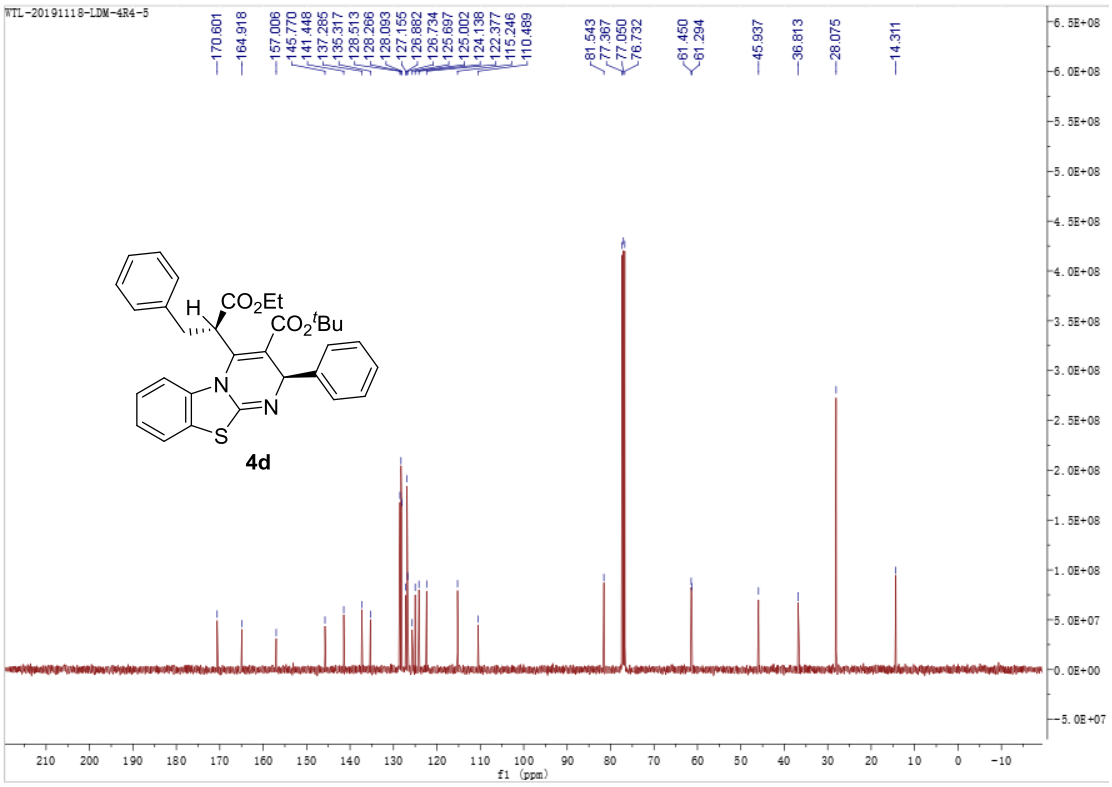
4b


WTL-20191011-LDM-4R4-1
171.159
164.647
146.235
141.139
135.579
128.408
127.388
126.972
125.687
81.602
61.483
61.301
44.677
30.814
29.126
27.972
22.185
14.286
13.709
H
CO2Et
CO2tBu
N
N
S
4b
f1 (ppm)

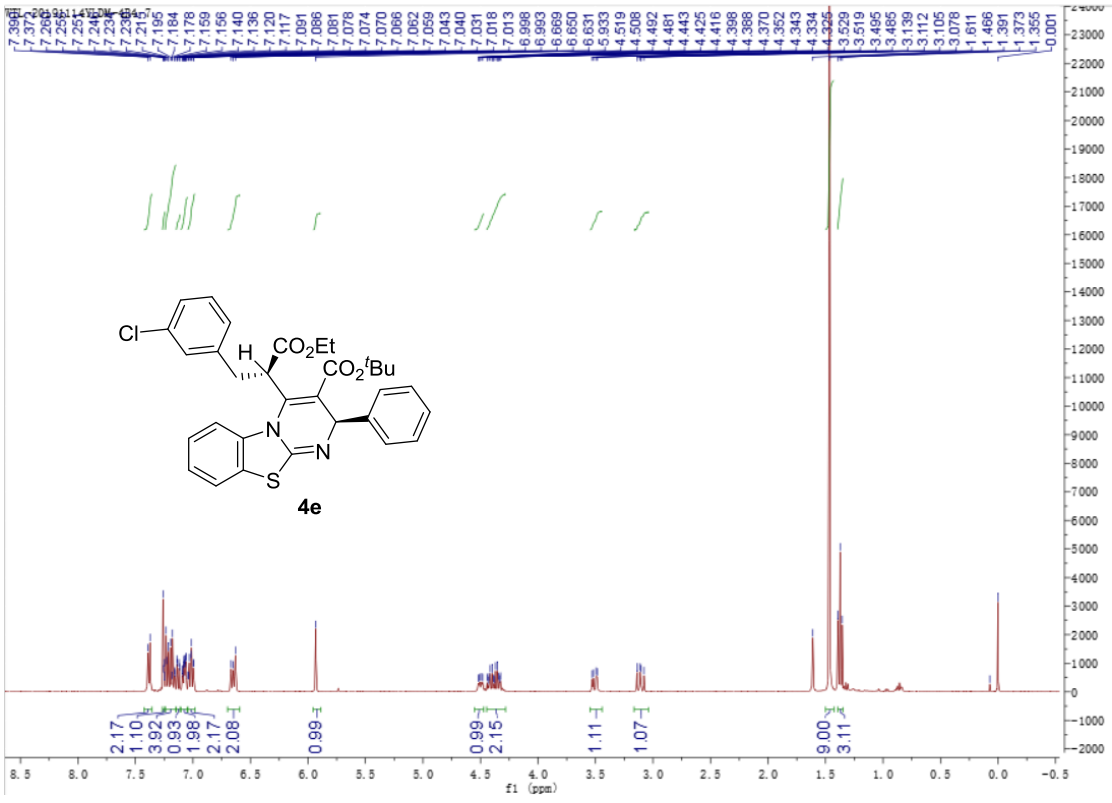

H
CO2Et
CO2tBu
N
N
S
4c
2.02
1.11
2.44
0.92
2.03
1.08
0.96
2.07
0.98
1.02
1.04
9.00
3.02
3.19
3.33
3.00
f1 (ppm)


WTL-20191114YLDM-4R4-9
171.717
165.235
157.692
146.774
141.887
136.152
128.800
127.713
127.435
126.014
111.031
81.877
62.276
61.698
44.899
31.623
31.480
28.433
27.091
22.798
14.741
14.319
H
CO2Et
CO2tBu
N
N
S
4c
f1 (ppm)

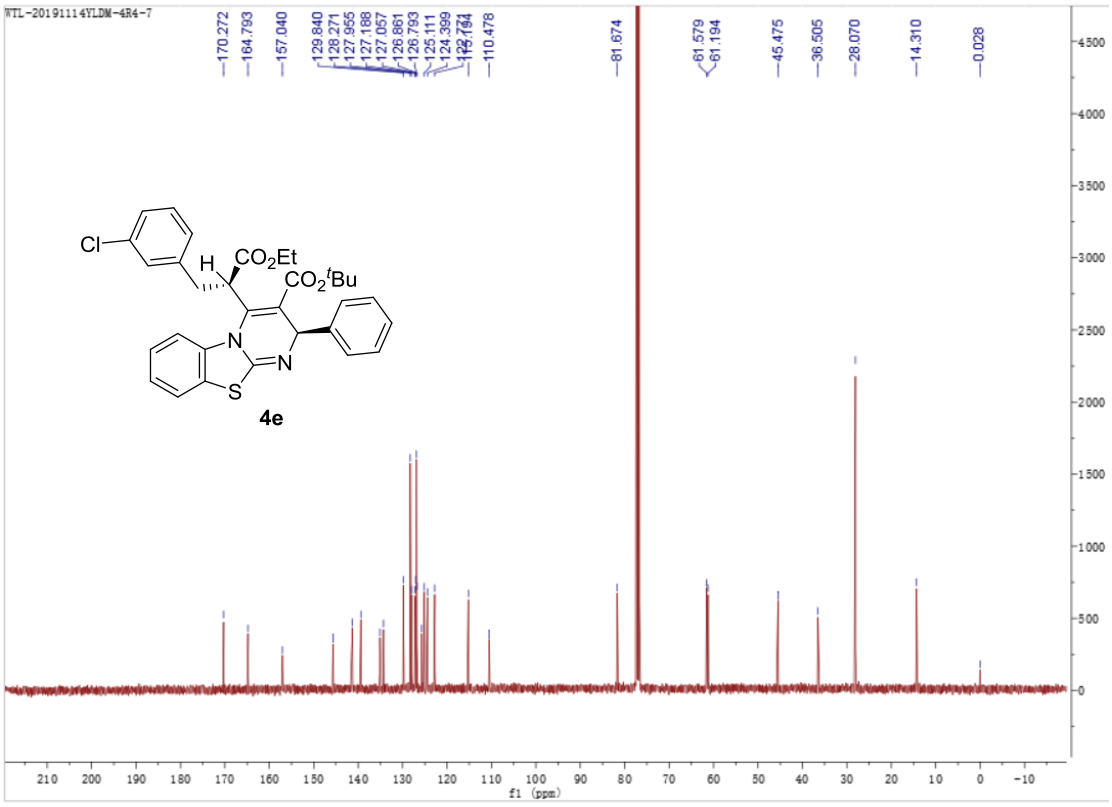

H
CO2Et
CO2tBu
N
N
S
4d
2.08
3.11
3.09
4.03
2.01
0.99
1.04
2.01
1.07
1.03
9.00
3.06
f1 (ppm)


WTL-20191118-LDM-4R4-5
170.601
164.918
157.006
145.770
141.448
137.285
135.317
128.513
128.266
128.093
127.155
126.882
126.734
125.697
125.002
124.138
122.377
115.246
110.489
81.543
77.367
77.050
76.732
61.450
61.294
45.937
36.813
28.075
14.311
H
CO2Et
CO2tBu
N
N
S
f1 (ppm)

4d


Cl
H
CO2Et
CO2tBu
N
N
S
2.17
1.10
3.92
0.93
1.98
2.17
2.08
0.99
0.99
2.15
1.11
1.07
9.00
3.11
f1 (ppm)

4e


WTL-20191114YLDM-4R4-7
170.272
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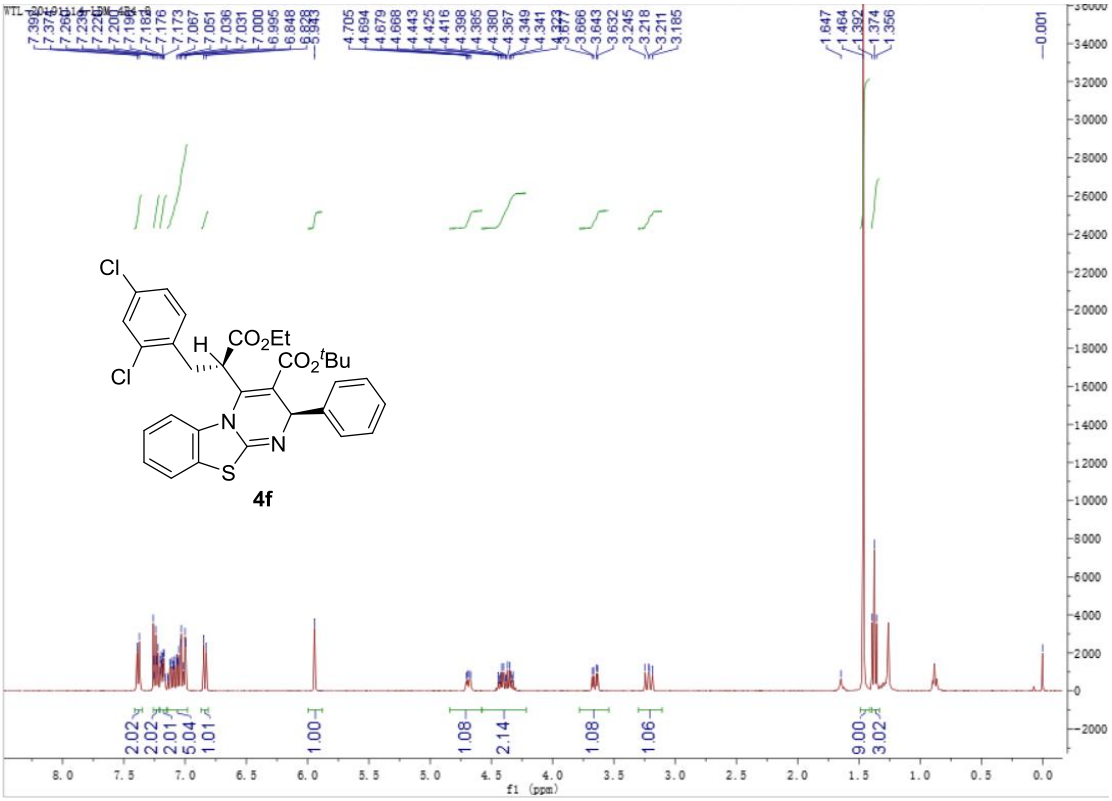
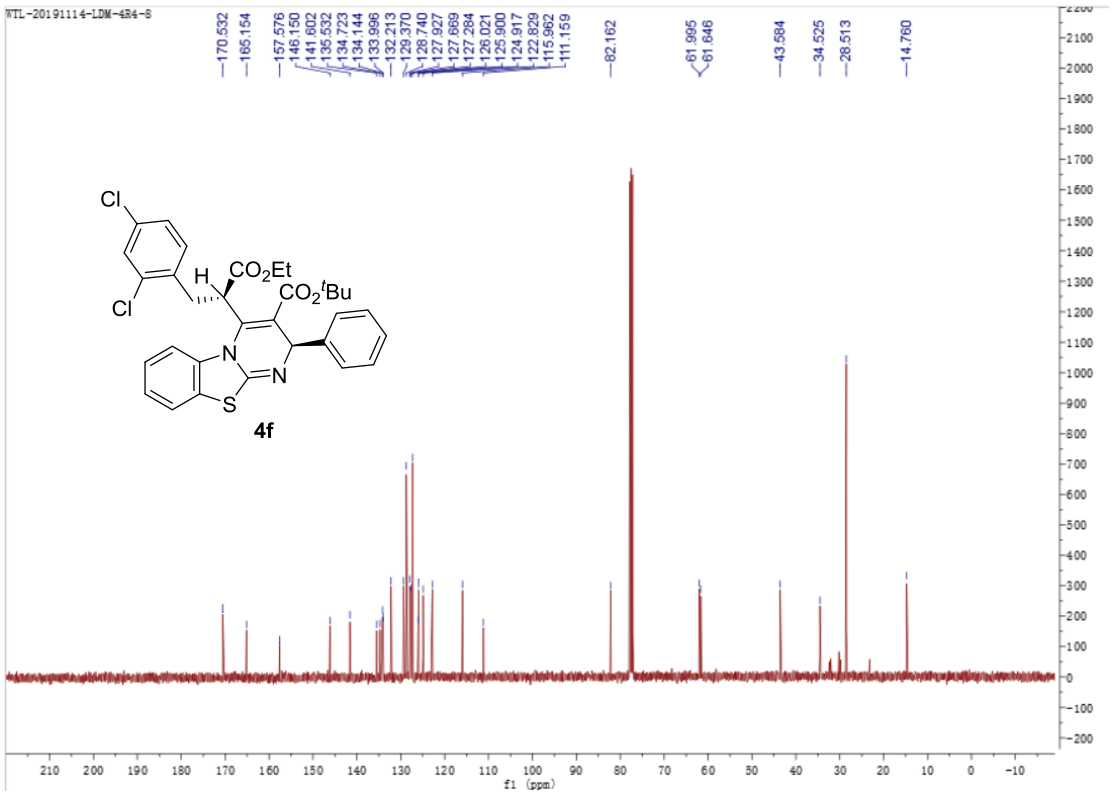
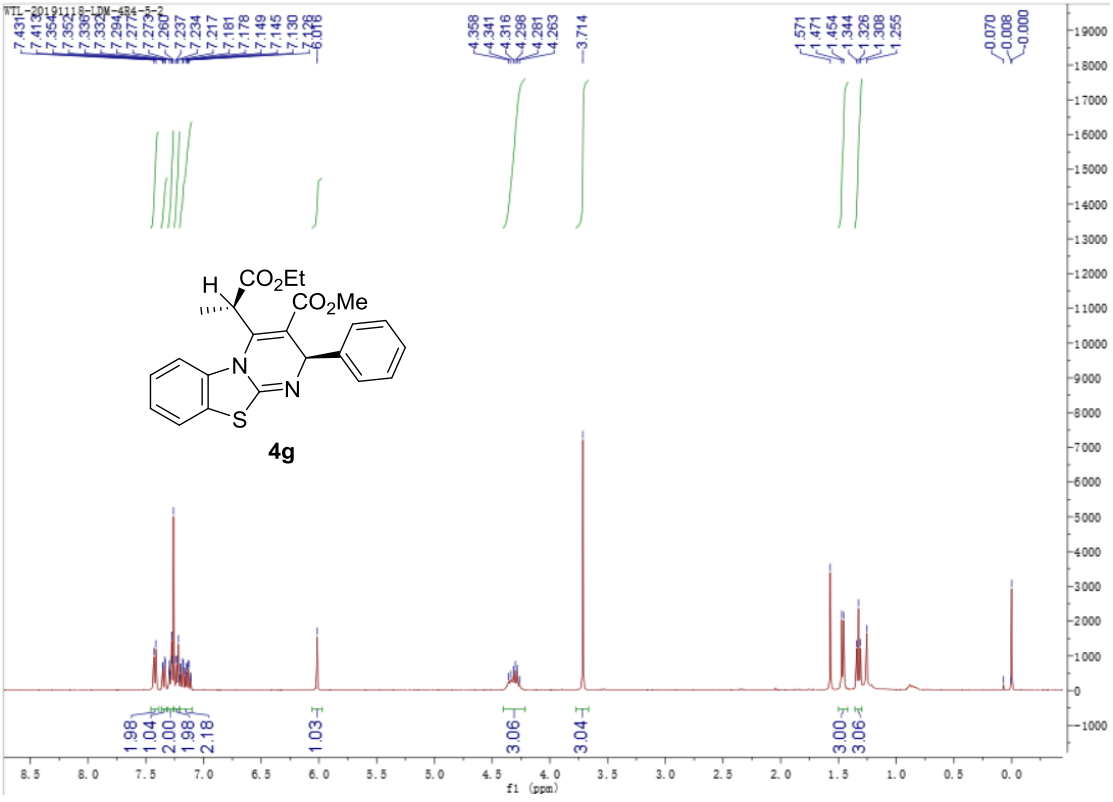
157.040
129.840
128.271
127.955
127.188
127.057
126.861
126.793
125.111
124.399
110.478
81.674
61.579
61.194
45.475
36.505
28.070
14.310
0.028
Cl
H
CO2Et
CO2tBu
N
N
S
4e
f1 (ppm)


7.399
7.374
7.260
7.239
7.220
7.200
7.196
7.162
7.176
7.173
7.067
7.051
7.036
7.031
7.000
6.995
6.848
6.828
5.943
4.705
4.694
4.679
4.668
4.443
4.425
4.416
4.398
4.380
4.367
4.349
4.341
3.677
3.666
3.643
3.632
3.245
3.218
3.211
3.185
1.647
1.464
1.392
1.374
1.356
0.001
Cl
Cl
H
CO2Et
CO2tBu
N
N
S
4f
2.02
2.02
2.01
5.04
1.01
1.00
1.08
2.14
1.08
1.06
9.00
3.02
f1 (ppm)


WTL-20191114-LDM-4R4-8
170.532
165.154
157.576
146.150
141.602
135.532
134.723
134.144
133.996
132.213
129.370
128.740
127.927
127.669
127.284
126.021
125.900
124.917
122.829
115.962
111.159
82.162
61.995
61.646
43.584
34.525
28.513
14.760
Cl
Cl
H
CO2Et
CO2tBu
N
N
S
f1 (ppm)

4f


7.431
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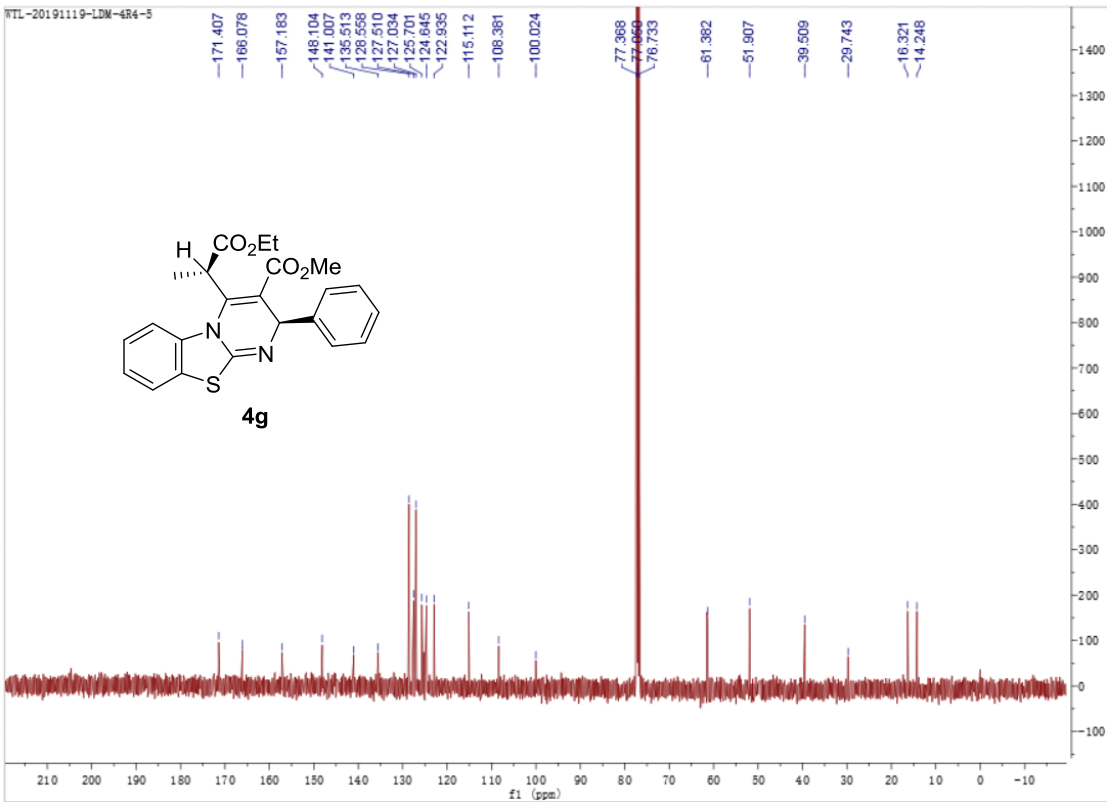
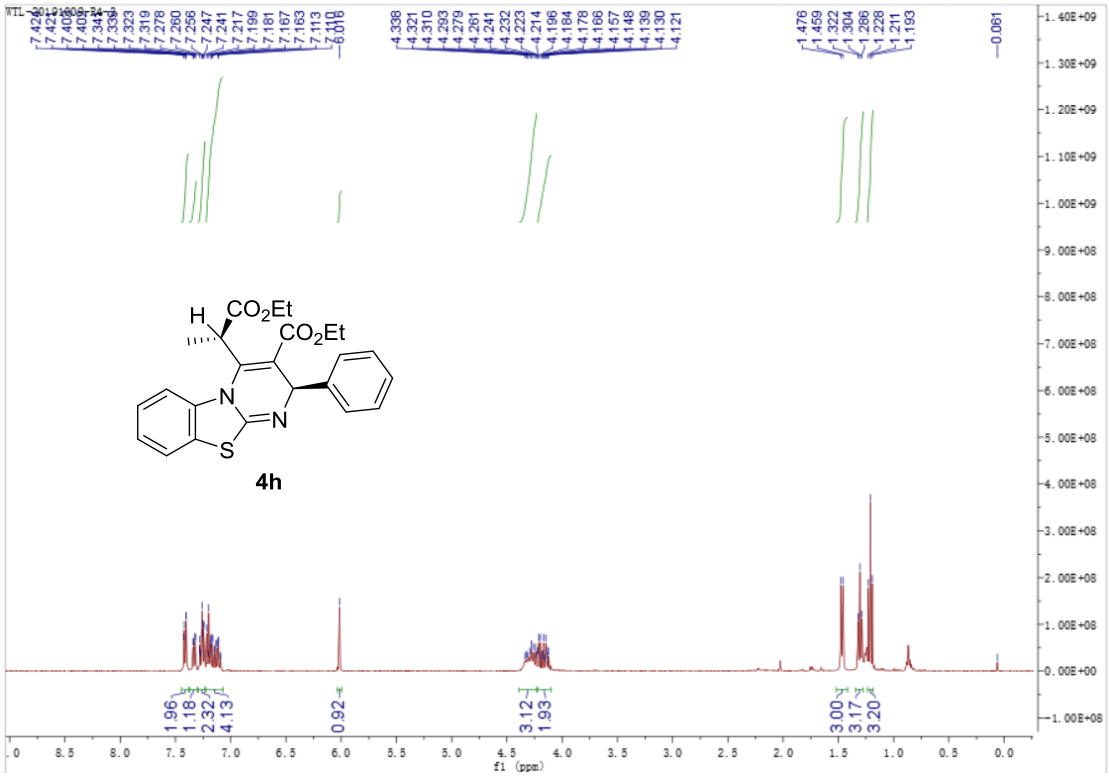
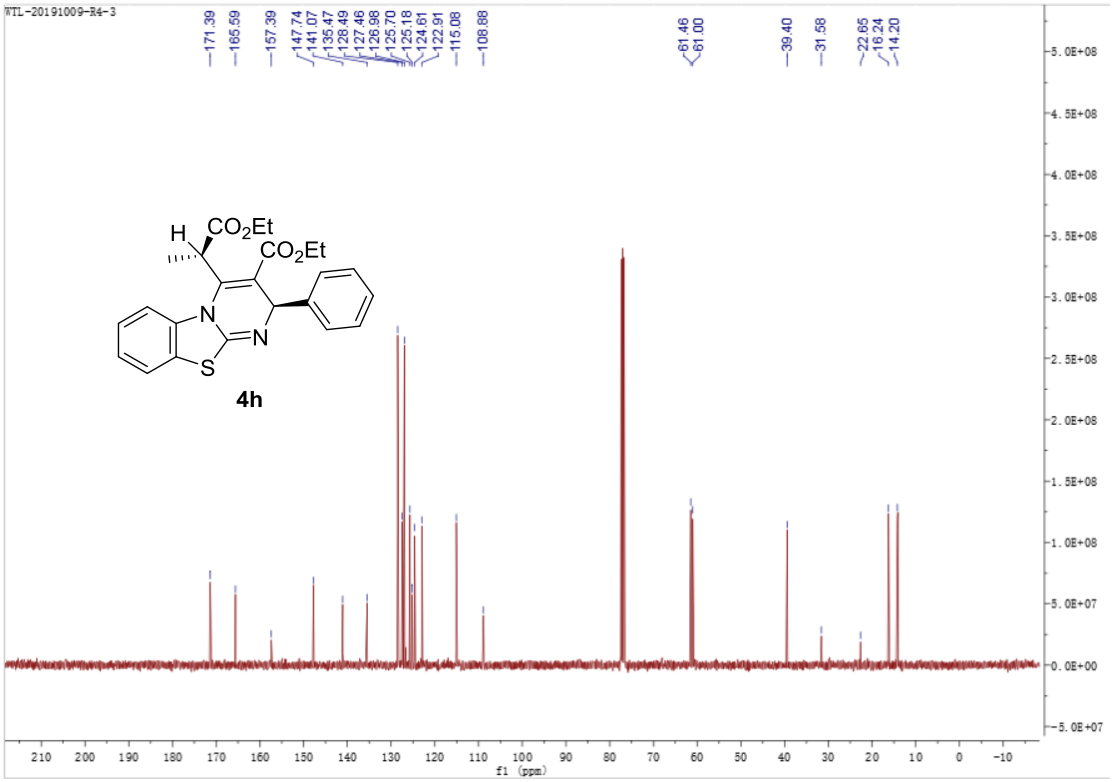
7.354
7.352
7.339
7.332
7.294
7.273
7.267
7.237
7.234
7.217
7.181
7.178
7.149
7.145
7.130
7.126
6.018
4.358
4.341
4.316
4.298
4.281
4.263
3.714
1.571
1.471
1.454
1.344
1.326
1.308
1.255
0.070
0.008
0.000
H
CO2Et
CO2Me
N
N
S
1.98
1.04
2.00
1.98
2.18
1.03
3.06
3.04
3.00
3.06
f1 (ppm)

4g


WTL-20191119-LDW-4R4-5
171.407
166.078
157.183
148.104
141.007
135.513
129.558
127.510
127.034
125.701
124.645
122.935
115.112
108.381
100.024
77.368
77.050
76.733
61.382
51.907
39.509
29.743
16.321
14.248
H
CO2Et
CO2Me
N
N
S
4g
f1 (ppm)


7.421
7.403
7.344
7.339
7.323
7.319
7.278
7.260
7.256
7.247
7.241
7.217
7.199
7.181
7.167
7.163
7.113
7.110
6.018
4.338
4.321
4.310
4.293
4.279
4.261
4.241
4.232
4.223
4.214
4.196
4.184
4.178
4.166
4.157
4.148
4.139
4.130
4.121
1.476
1.459
1.322
1.304
1.286
1.228
1.211
1.193
0.061
1.96
1.18
2.32
4.13
0.92
3.12
1.93
3.00
3.17
3.20
H
CO2Et
CO2Et
N
N
S
4h
f1 (ppm)


WTL-20191009-R4-3
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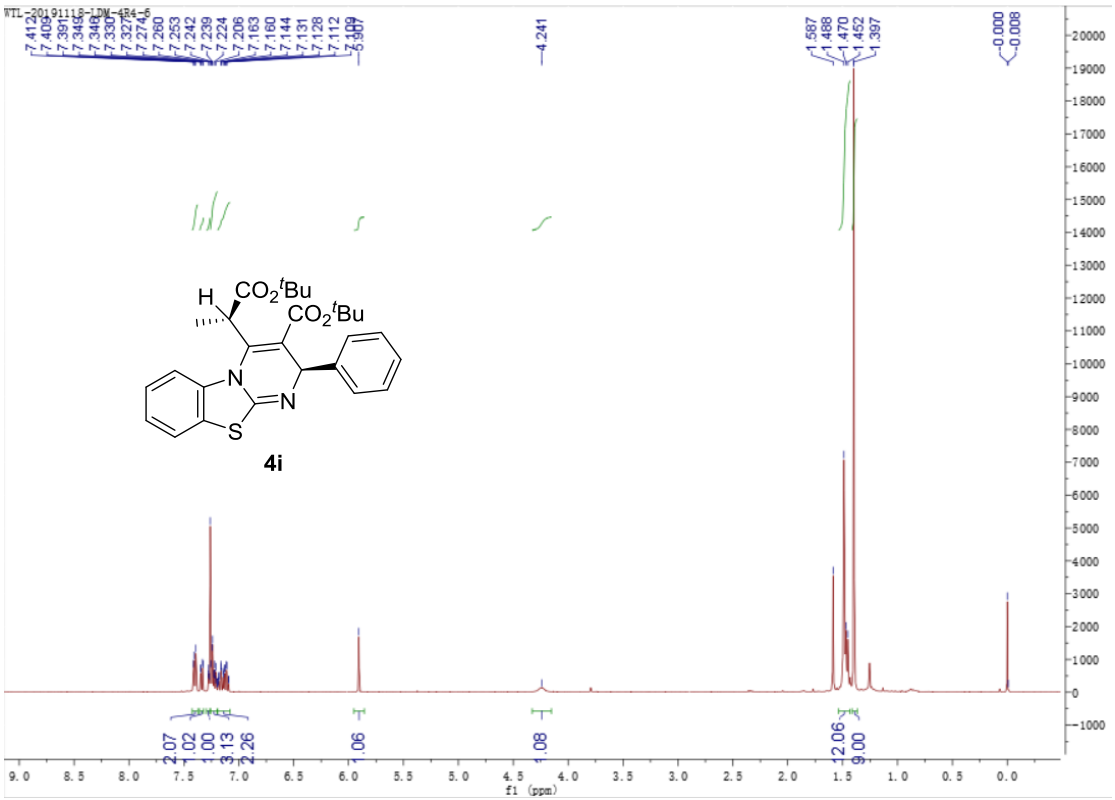
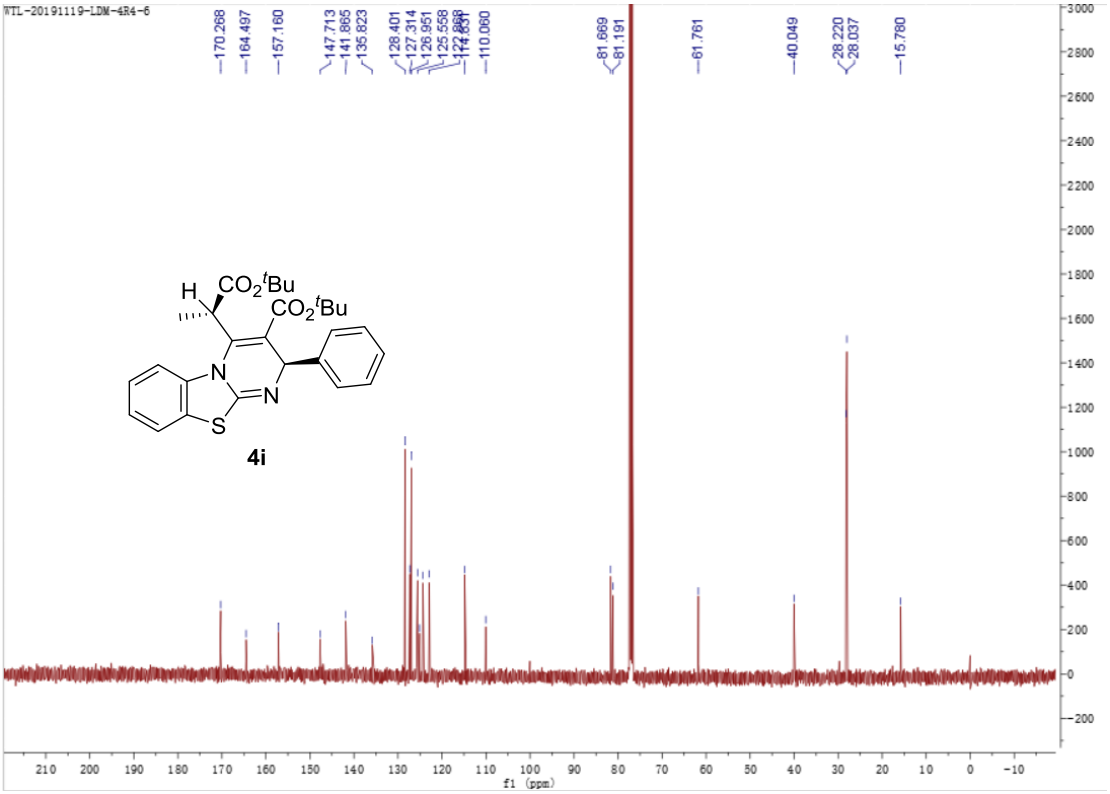
165.59
157.39
147.74
141.07
135.47
128.49
127.46
126.98
125.70
125.18
124.61
122.91
115.08
108.88
61.46
61.00
39.40
31.58
22.65
16.24
14.20
H
CO2Et
CO2Et
N
N
S
f1 (ppm)

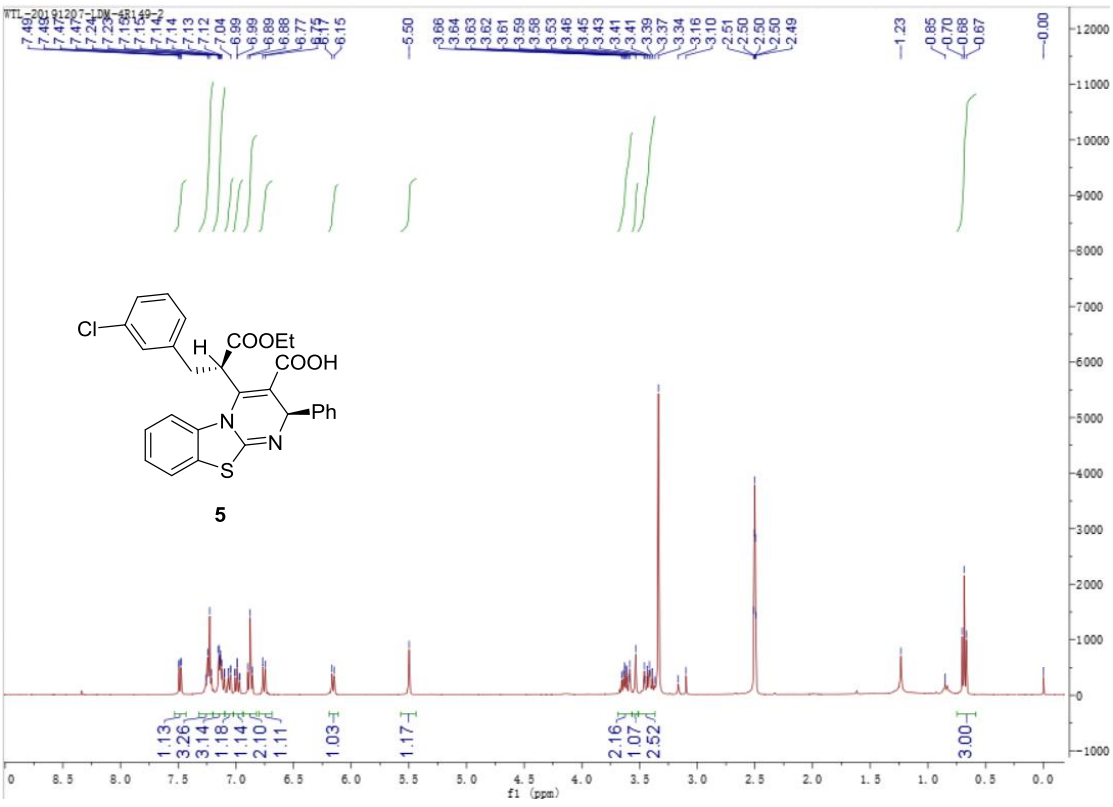
4h


7.412
7.409
7.391
7.345
7.330
7.327
7.274
7.260
7.253
7.242
7.239
7.224
7.206
7.163
7.160
7.144
7.131
7.128
7.112
7.109
7.107
5.307
4.241
1.587
1.488
1.470
1.452
1.397
0.000
-0.008
H
CO2tBu
CO2tBu
N
N
S
2.07
1.02
1.00
3.13
2.26
1.06
1.08
12.06
9.00
f1 (ppm)

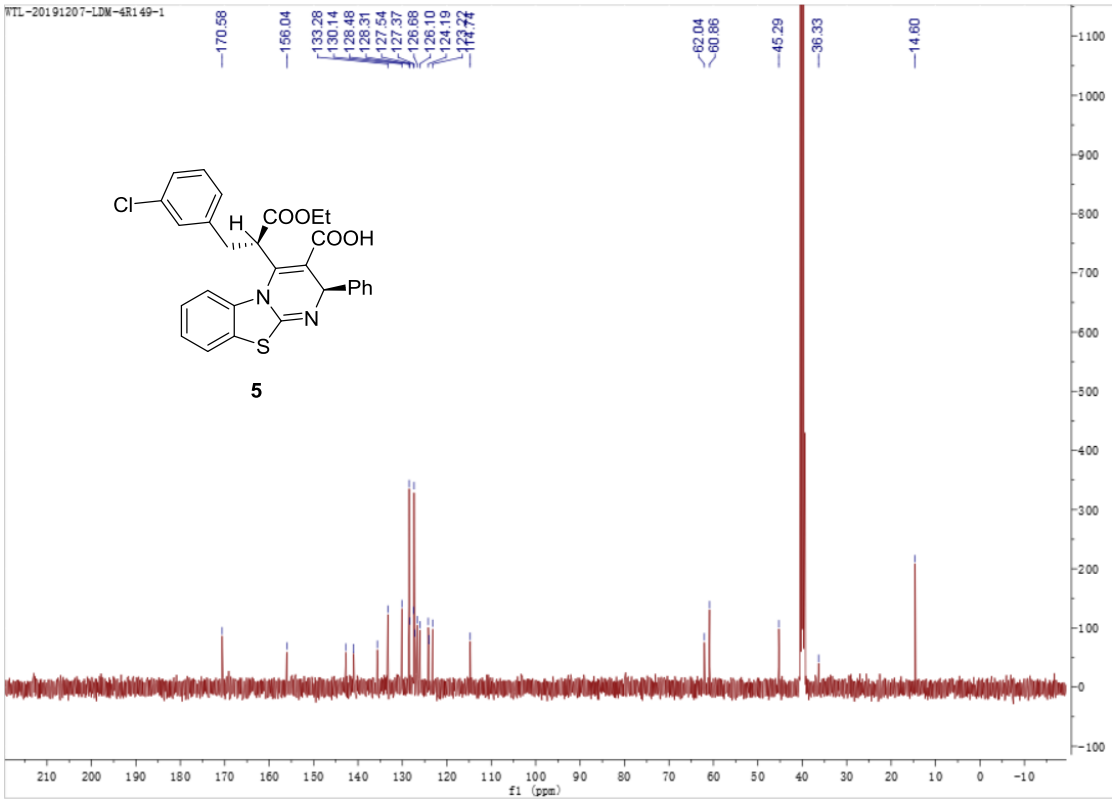
4i

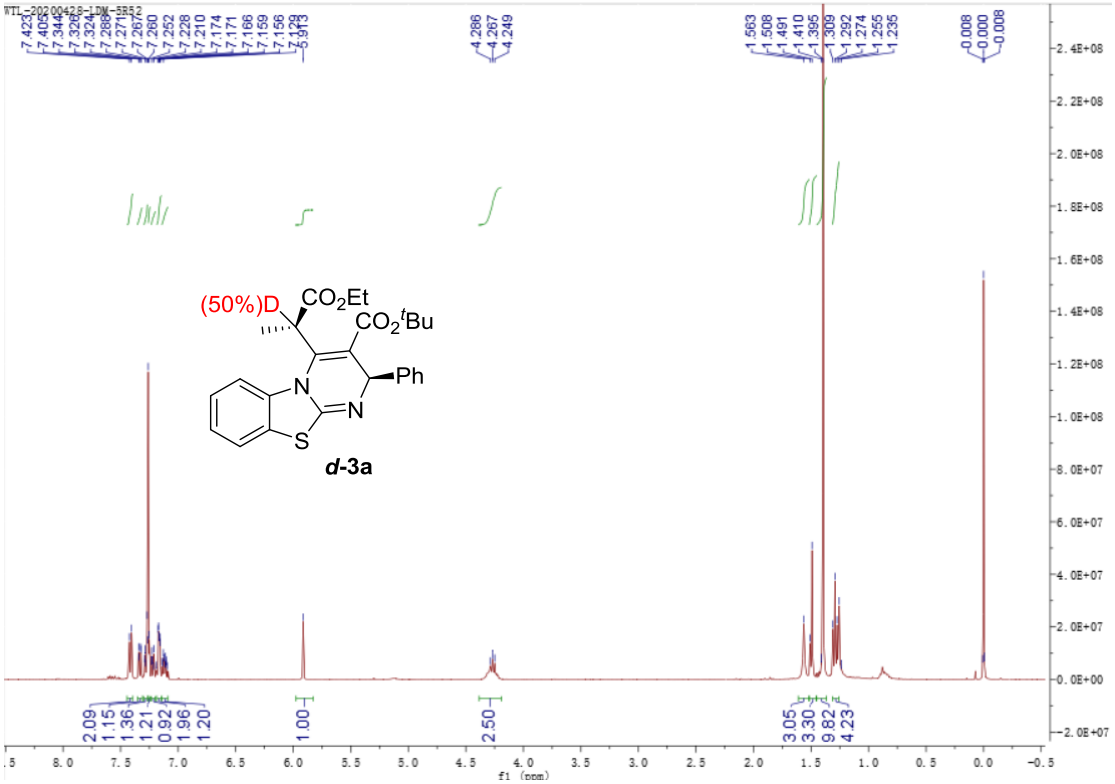

WTL-20191119-LDM-4R4-6
170.268
164.497
157.160
147.713
141.865
135.823
128.401
127.314
126.951
125.558
110.060
81.669
81.191
61.761
40.049
28.220
28.037
15.780
H
CO2tBu
CO2tBu
N
N
S
f1 (ppm)

4i


Cl
H
COOEt
COOH
Ph
N
N
S
f1 (ppm)

5


WTL-20191207-LDM-4R149-1
170.58
156.04
133.28
130.14
128.48
128.31
127.54
127.37
126.68
126.10
124.19
62.04
60.86
45.29
36.33
14.60
Cl
H
COOEt
COOH
Ph
N
N
S
5
f1 (ppm)


4.286
4.267
4.249
1.563
1.508
1.491
1.410
1.395
1.309
1.292
1.274
1.255
1.235
0.008
0.000
-0.008
(50%)D
CO2Et
CO2tBu
Ph
N
N
S
d-3a
2.09
1.15
1.36
1.21
0.92
1.96
1.20
1.00
2.50
3.05
3.30
9.82
4.23
f1 (ppm)