SUPPORTING INFORMATION

Synergistically Activating Nucleophile Strategy Enabled Organocatalytic Asymmetric P-Addition of Cyclic Imines

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1. General information

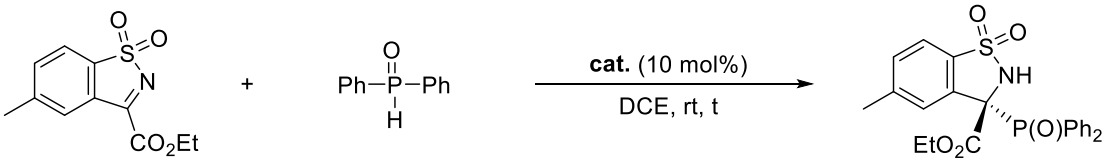
All the starting materials were obtained from commercial sources and used without further purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE III HD (400 MHz) spectrometer in $CDCl_3$. Chemical shifts (δ) are reported in ppm, and the residual solvent peak was used as an internal reference $CDCl_3$ [δ(^{1}H) = 7.26 ppm, δ (^{13}C) = 77.0 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). CD spectra were acquired using a J-1500 CD spectrometer and an Applied Photophysics Chirascan spectrometer. 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 excesses were determined by HPLC analysis using chiral column described below in detail. Optical rotations were measured with polarimeter.

All the cyclic imines **1**/**1'**, **6** listed in Figure S2 were synthesized following general procedures D,[4] E,[5] and F.[6] Phosphine oxides **2a**, **2g, 3a, 3b, 3c** and **3d** were obtained from commercial sources, and other phosphine oxides **2** were synthesized following the previous reported literature and listed in Figure S3.[3] All the 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] The structure and absolute configurations of products were assigned by optical rotation analysis of **5'b** and **5'j** (Figure S4), and CD analysis of compound **4a**, **5a**, **7a** and **7g** were tested and calculated (Figure S5-8).

2. Optimizations of reaction conditions

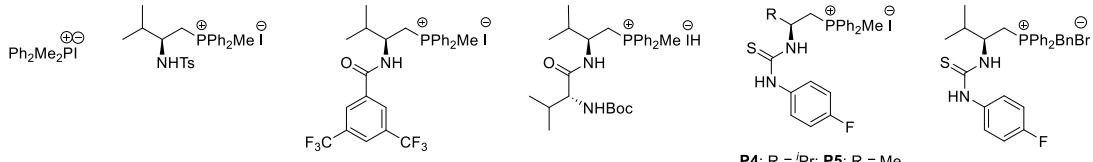
2.1 Optimization for asymmetric P-nucleophile addition to cyclic N-sulfonyl imines 1a with secondary phosphine oxides 2a

Table S1. The asymmetric **P**-nucleophile addition to cyclic ketimine **1a** with diphenylphosphine oxide **2a** catalyzed by different chiral phosphonium salts in DCE.[a]



1a + **2a** → **4a**

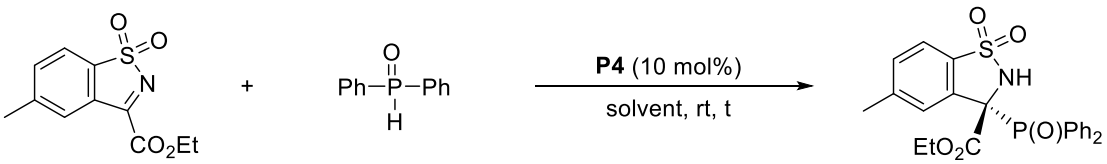
entry	cat.	base(x equiv.)	t (h)	yield (%)[b]	ee (%)[c]
1	**P0**	K_2CO_3(1.0)	1	98	0
2	**-**	-	2	83	0
3	**P1**	-	2	90	34
4	**P2**	-	2	92	53
5	**P3**	-	2	90	71
6	**P4**	**-**	**2**	**93**	**90**
7	**P5**	-	2	86	68
8	**P6**	-	2	92	86
9	**P7**	-	2	87	83



P0 **P1** **P2** **P3** **P4**: R = ^{i}Pr; **P5**: R = Me **P6**: R = ^{t}Bu **P7**

[a]Reactions were performed with **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (10 mol%) in solvent (1.0 mL) at room temperature. [b]Isolated yield. [c]The ee value was determined by HPLC analysis on a chiral stationary phase. Ts = 4-toluenesulfonyl. DCE = 1,2-dichloroethane.

Table S2. The asymmetric **P**-nucleophile addition to cyclic ketimine **1a** with diphenylphosphine oxide **2a** catalyzed by **P4** : screening solvents and other conditions.[a]



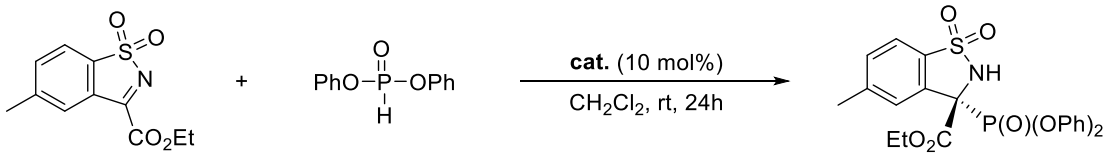
1a + **2a** → **4a**

entry	solvent	base(x equiv.)	t (h)	yield (%)[b]	ee (%)[c]
1	CH_2Cl_2	-	2	93	90
2	$CHCl_3$	-	2	94	73
3	Et_2O		2	89	88
4	toluene		2	88	93
5	hexane		4	90	75
6	**DCE**		**2**	**95**	**>99**
7[d]	DCE	K_2CO_3(1.0)	0.5	92	<5
8[e]	DCE	K_2CO_3(0.5)	1	96	75
9[f]	DCE	-	2.5	92	89

[a]Reactions were performed with **1a** (0.1 mmol), **2a** (0.12 mmol), **P4** (10 mol%) in solvent (1.0 mL) at room temperature. [b]Isolated yield. [c]The ee value was determined by HPLC analysis on a chiral stationary phase. [d]1.0 equivalent of K_2CO_3 was added. [e]0.5 equivalent of K_2CO_3 was added. [f]The catalyst loading was 5 mol%. Ts = 4-toluenesulfonyl. c

2.2 Optimization for asymmetric P-nucleophile addition to cyclic N-sulfonyl imines 1a with secondary phosphine oxides 3a

Table S3. The asymmetric **P**-nucleophile addition to cyclic ketimine **1a** with $(PhO)_2P(O)H$ **3a** catalyzed by different chiral phosphonium salts in CH_2Cl_2. [a]

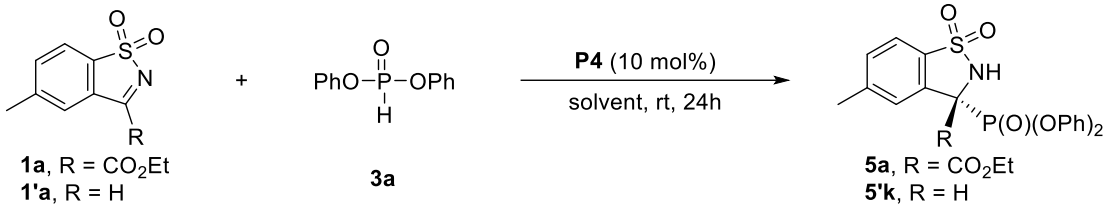


1a **3a** **5a**

entry	cat.	yield (%)[b]	ee (%)[c]
1	**P1**	90	2
2	**P2**	88	85
3	**P3**	91	62
4	**P4**	**92**	**88**
5	**P5**	90	70
6	**P6**	89	80
7	**P7**	92	38

[a]Reactions were performed with **1a** (0.1 mmol), **3a** (0.12 mmol), catalyst (10 mol%) in CH_2Cl_2 (2.0 mL) at room temperature. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase.

Table S4. The asymmetric **P**-nucleophile addition to cyclic ketimine **1a** with $(PhO)_2P(O)H$ **3a** catalyzed by **P4**: screening of the solvents, and catalyst Loading. [a]

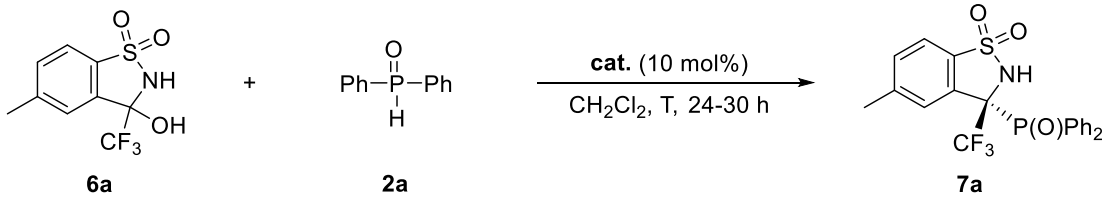


entry	ketimine	solvent	t (h)	yield (%)[b]	ee (%)[c]
1	**1a**	CH_2Cl_2	24	92	88
2	**1a**	$CHCl_3$	24	92	73
3	**1a**	DCE	24	95	91
4	**1a**	hexane	48	91	95
5	**1a**	**toluene**	**24**	**96**	**>99**
6[d]	**1a**	toluene	24	93	90
7	**1'a**	toluene	-	-	-
8[e]	**1'a**	toluene	54	91	88
9[e]	**1'a**	DCE	48	92	90
10[e]	**1'a**	CH_2Cl_2	48	95	98
11[d,e]	**1'a**	CH_2Cl_2	48	94	89

[a]Reactions were performed with **1a** (0.1 mmol), **3a** (0.12 mmol), **P4** (10 mol%) in solvent (2.0 mL) at room temperature. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]With 5 mol% catalyst **P4**. [e]2.0 equiv. of Cs_2CO_3 was added.

3.1 Optimization of reaction conditions for the asymmetric P-nucleophile addition to CF_3-substituted cyclic N-sulfonyl amines 6a with secondary phosphine oxides 2a

Table S5. The asymmetric **P**-nucleophile addition to cyclic ketimine **6a** with diphenylphosphine oxide **2a**: screening different chiral phosphonium salts and other conditions. [a]



entry	cat.	T (°C)	t (h)	yield (%)[b]	ee (%)[c]

1	**P1**	-30	24	90	4
2	**P2**	-30	24	93	4
3	**P3**	-30	24	89	24
4	**P4**	**-30**	**24**	**92**	**71**
5	**P5**	-30	24	92	56
6	**P6**	-30	24	90	0
7	**P7**	-30	24	92	23
8	**P4**	-50	24	90	63
9[d]	**P4**	**-30**	**30**	**93**	**94**
10[d]	**P4**	-78	48	92	92
11[d,e]	**P4**	-30	48	92	28

[a]Reactions were performed with **6a** (0.1 mmol), **2a** (0.12 mmol), catalyst (10 mol%) in CH_2Cl_2 (1.0 mL). [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]3.0 mL CH_2Cl_2 was used. [e]With 5 mol% catalyst **P4**.

3. Preparation of catalysts.

All the catalysts listed in Figure S1 were synthesized following general procedures A[1], B and C[2]. The catalysts **P1**-**P4** are known compounds, and their characterization data were in agreement with those reported in the literature.[1,2] Unknown compounds **P5**- **P7, P4-1, P4-2, P4-3 and P4-4** were fully characterized.

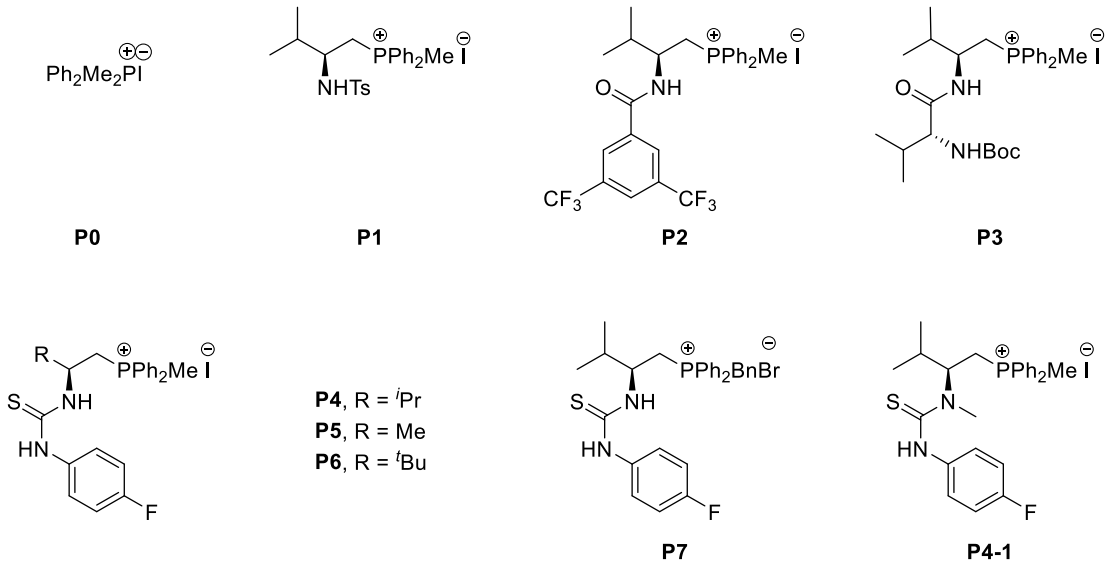
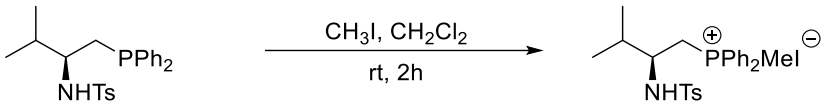


Figure S1. Phosphonium salt catalysts in this study.

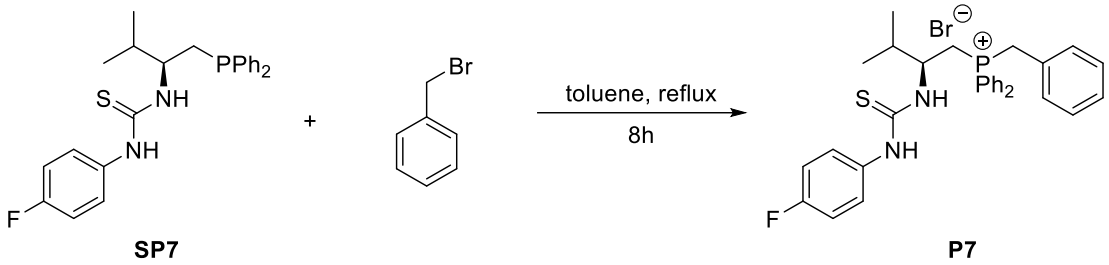
(1) General procedure A: preparation of phosphonium salt P1



SP1 **P1**

General procedure A: To a solution of phosphine **SP1** (1 mmol, 425 mg) in CH_2Cl_2 (10 mL) was slowly added the methyl iodide solution (4 mmol, 568 mg, 2.0 M in CH_2Cl_2). Then the mixture was allowed to stir at room temperature for 2 h. The reaction crude mixture was directly purified by flash chromatography dichloromethane/ methanol = 20/1 to afford the desired chiral phosphonium salt **P1** as a yellow solid (93% yield). The phosphonium salts **P2**-**P6** were prepared from the above procedure by using the corresponding phosphines as reactants.[1]

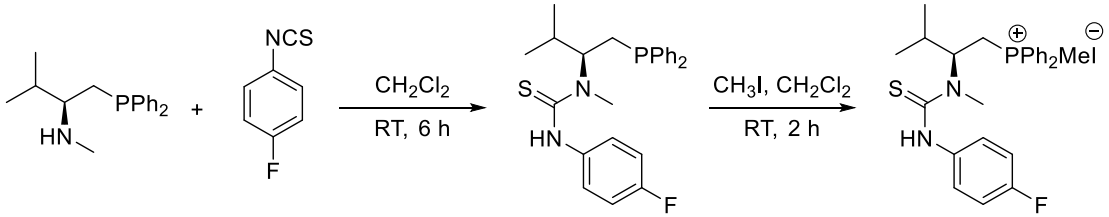
(2) General procedure B: preparation of phosphonium salt P7



SP7 **P7**

General procedure B: To a solution of phosphine **SP7** (1 mmol, 424 mg) in toluene was slowly added the benzyl bromide solution (1.2 mmol, 204 mg, 2.0 M in toluene). Then, the mixture was refluxed in toluene for 12 h. The reaction crude mixture was directly purified by flash chromatography dichloromethane/methanol = 20/1 to afford the desired chiral phosphonium salt **P7** as a white solid (95% yield).

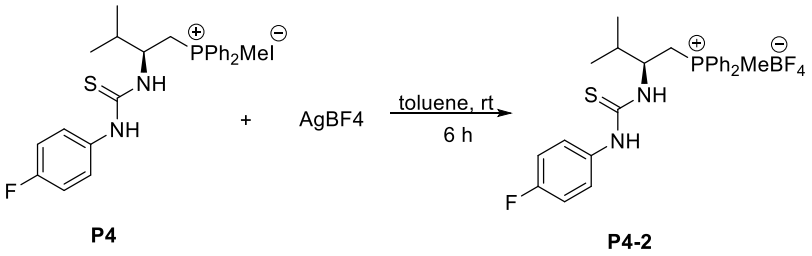
(3) General procedure C: preparation of phosphonium salts P4-1



A **B** **SP4-1** **P4-1**

General procedure C: To a solution of compound **A** (0.4 mmol, 114 mg) in anhydrous CH_2Cl_2 was cooled to 0 ºC, and a solution of **B** (0.48 mmol, 73.4 mg) in CH_2Cl_2 was added dropwise.[2] Then, the reaction mixture was stirred at room temperature for 6 hours. The reaction crude mixture was directly purified by flash chromatography (petroleum ether/ethyl acetate = 5/1) to afford **SP4-1** (95% yield) as a colorless solid.
To a solution of phosphine **SP4-1** (1.0 mmol, 438mg) in CH_2Cl_2 was slowly added the methyl iodide solution (4.0 mmol, 568 mg, 2.0 M in CH_2Cl_2). Then, the mixture was allowed to stir at room temperature for 24 h. The reaction crude mixture was directly purified by flash chromatography dichloromethane/methanol = 20/1 to afford the desired chiral phosphonium salt **P4-1** as a yellow solid (70% yield) was fully characterized.

(4) General procedure C: preparation of phosphonium salts P4-2

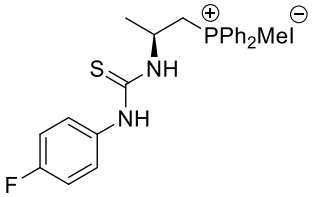


P4 **P4-2**

To a solution of chiral phosphonium salt P**4** (0.1 mmol) in anhydrous tolunne was quickly added $AgBF_4$ (0.3 mmol). Then, the mixture was allowed to stir at room temperature for 3 h. The reaction crude mixture was directly purified by flash chromatography dichloromethane/methanol = 20/1 to afford the desired chiral phosphonium salt **P4-2** as a yellow solid (85% yield). chiral phosphonium salt P**4-2, P4-3** and **P4-4** were fully characterized.

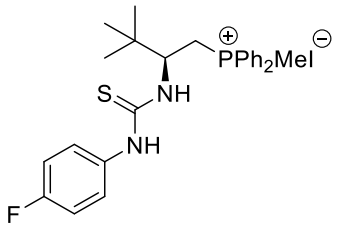
Characterization of the unknown phosphonium salts

(*S*)-(2-(3-(4-fluorophenyl)thioureido)propyl)(methyl)diphenylphosphonium iodide (P5)



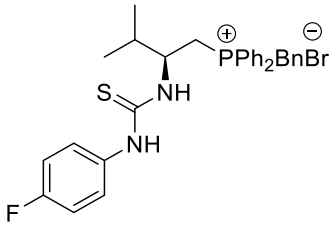
A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.71 (d, *J* = 8.8 Hz, 1H), 7.89 - 7.81 (m, 2H), 7.81 - 7.69 (m, 4H), 7.70 - 7.61 (m, 4H), 7.44 - 7.31 (m, 2H), 7.01 - 6.87 (m, 2H), 5.33 - 5.19 (m, 1H), 3.79 (dt, *J* = 15.5, 11.0 Hz, 1H), 3.11 - 2.97 (m, 1H), 2.85 (d, *J* = 13.9 Hz, 3H), 1.48 (dd, *J* = 6.6, 2.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.34, 160.12 (d, *J* = 242.9 Hz), 135.14 (d, *J* = 2.9 Hz), 134.88 (d, *J* = 2.9 Hz), 134.59 (d, *J* = 2.5 Hz), 132.39 (d, *J* = 10.2 Hz), 132.25 (d, *J* = 10.0 Hz), 130.52 (d, *J* = 6.4 Hz), 130.40 (d, *J* = 6.6 Hz), 126.11 (d, *J* = 8.0 Hz), 119.50 (d, *J* = 8.4 Hz), 118.65 (d, *J* = 8.7 Hz), 115.15 (d, *J* = 22.4 Hz), 45.22 (d, *J* = 4.1 Hz), 30.94 (d, *J* = 51.5 Hz), 23.64 (d, *J* = 14.0 Hz), 8.62 (d, *J* = 53.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.94; HRMS (ESI) m/z calcd for $C_{23}H_{25}N_2PSFI$ $[M\text{-}I]^+$ = 411.1460, found = 411.1466.

(*S*)-(2-(3-(4-fluorophenyl)thioureido)-3,3-dimethylbutyl)(methyl)diphenylphosphonium iodide (P6)



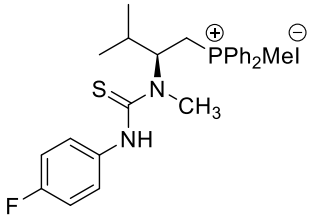
A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.88 (d, *J* = 9.8 Hz, 1H), 7.90 - 7.79 (m, 3H), 7.80 - 7.67 (m, 5H), 7.67 - 7.59 (m, 2H), 7.56 - 7.48 (m, 2H), 7.03 - 6.90 (m, 2H), 4.95 - 4.85 (m, 1H), 3.95 - 3.77 (m, 1H), 2.89 (d, *J* = 14.1 Hz, 3H), 2.75 (t, *J* = 14.8 Hz, 1H), 1.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.84, 160.21 (d, *J* = 242.7 Hz), 135.52 (d, *J* = 3.0 Hz), 135.04 (d, *J* = 2.6 Hz), 134.88 (d, *J* = 3.0 Hz), 132.55 (d, *J* = 9.5 Hz), 132.24 (d, *J* = 10.3 Hz), 130.61 (d, *J* = 7.7 Hz), 130.48 (d, *J* = 8.0 Hz), 126.18 (d, *J* = 8.1 Hz), 121.20, 120.35, 118.14, 117.28, 115.18 (d, *J* = 22.4 Hz), 56.29 (d, *J* = 4.5 Hz), 37.36 (d, *J* = 11.7 Hz), 26.32, 26.15 (d, *J* = 53.4 Hz), 8.09 (d, *J* = 53.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.13; HRMS (ESI) m/z calcd for $C_{26}H_{31}N_2PSFI$ $[M\text{-}I]^+$ = 453.1930, found = 453.1924.

(*S*)-benzyl(2-(3-(4-fluorophenyl)thioureido)-3-methylbutyl) diphenylphosphonium bromide (P7)



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.29 (s, 1H), 9.20 (d, *J* = 9.4 Hz, 1H), 7.78 - 7.68 (m, 3H), 7.65 - 7.49 (m, 7H), 7.42 - 7.34 (m, 2H), 7.22 - 7.18 (m, 1H), 7.13 (t, *J* = 7.6 Hz, 2H), 6.93 - 6.82 (m, 4H), 5.25 - 5.08 (m, 1H), 4.88 - 4.66 (m, 2H), 3.55 - 3.42 (m, 1H), 2.69 - 2.56 (m, 1H), 2.04 - 1.92 (m, 1H), 0.94 (t, *J* = 6.3 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.06, 159.71 (d, *J* = 242.3 Hz), 135.13 (d, *J* = 2.7 Hz), 135.03 (d, *J* = 2.7 Hz), 134.62 (d, *J* = 2.7 Hz), 133.36 (d, *J* = 2.7 Hz), 133.27 (d, *J* = 2.5 Hz), 130.38 (d, *J* = 5.7 Hz), 130.11 (d, *J* = 9.8 Hz), 129.99 (d, *J* = 10.1 Hz), 129.23 (d, *J* = 3.1 Hz), 129.02, 128.73 (d, *J* = 3.6 Hz), 128.21, 126.89 (d, *J* = 8.5 Hz), 125.48 (d, *J* = 8.0 Hz), 118.68, 117.86, 117.52, 116.69, 114.76 (d, *J* = 22.3 Hz), 52.66 (d, *J* = 4.3 Hz), 34.78 (d, *J* = 12.6 Hz), 28.91 (d, *J* = 44.8 Hz), 25.38 (d, *J* = 51.5 Hz), 18.41 (d, *J* = 18.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.29; HRMS (ESI) m/z calcd for $C_{31}H_{33}N_2PSFBr$ $[M\text{-}Br]^+$ = 515.2081, found = 515.2080.

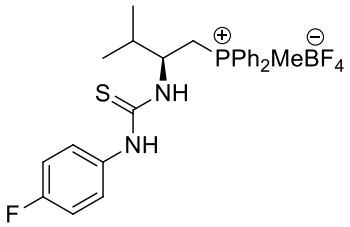
(*S*)-(2-(3-(4-fluorophenyl)-1-methylthioureido)propyl)(methyl)diphenylphosphonium iodide (P4-1)



A yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 - 7.88 (m, 4H), 7.78 - 7.59 (m, 6H), 7.33 - 7.29 (m, 1H), 7.08 - 6.88 (m, 2H), 6.75 - 6.61 (m, 1H), 5.85 (dd, *J* = 22.0, 6.8 Hz, 1H), 4.49 - 4.25 (m, 1H), 3.22 (s, 1H), 2.92 (dd, *J* = 22.0, 10.8 Hz, 3H), 2.80 (s, 1H), 1.63 (s, 1H), 1.31 - 1.20 (m, 3H), 1.05 - 0.92 (m, 3H), 0.91 - 0.85 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 183.05, 159.61, 135.44, 134.91, 132.67 (dd, *J* = 13.4, 10.0 Hz), 130.39, 130.26 (d, *J* = 1.5 Hz), 130.12, 128.60 (d, *J* = 8.2 Hz), 115.89, 115.26 (d, *J* = 22.5 Hz), 100.10, 60.51, 34.43, 32.79 (d, *J* = 12.8 Hz), 29.80, 19.67 (d, *J* = 145.9

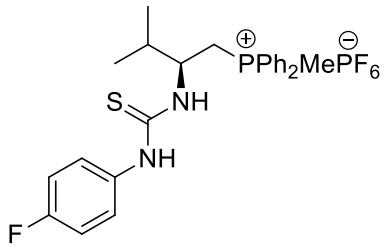
Hz), 15.95, 8.93 (d, *J* = 53.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.55; HRMS (ESI) m/z calcd for $C_{26}H_{31}N_2PSFI$ $[M\text{-}I]^+$ = 453.1924, found = 453.1920.

(*S*)-(2-(3-(4-fluorophenyl)thioureido)propyl)(methyl)diphenylphosphonium tetrafluoroborate (P4-2)



A white solid; ^{1}H NMR (400 MHz, CD_3OD) δ 7.87 - 7.57 (m, 10 H), 7.56 - 7.51 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 1H), 7.11 - 7.04 (m, 1H), 6.95 - 6.88 (m, 1H), 5.67 (d, *J* = 10.0 Hz, 1H), 3.30 - 3.21 (m, 2H), 3.11 - 3.00 (m, 1H), 2.72 - 2.65 (m, 3H), 2.36 (s, 1H), 1.03 (dd, *J* = 6.8, 2.8 Hz, 1H), 0.95 (d, *J* = 6.8 Hz, 3H), 0.65 (dd, *J* = 11.6, 7.2 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 160.97, 158.59, 156.81, 145.13, 140.16, 136.38 (d, *J* = 2.8 Hz), 135.90 (d, *J* = 3.0 Hz), 135.52 (dd, *J* = 10.6, 3.1 Hz), 135.30 (d, *J* = 3.0 Hz), 133.63 (d, *J* = 9.8 Hz), 133.40 - 132.91 (m), 127.70, 126.29 (d, *J* = 8.5 Hz), 123.10, 122.46 (d, *J* = 45.6 Hz), 121.80 (d, *J* = 7.5 Hz), 120.97 (dd, *J* = 85.7, 45.0 Hz), 117.16 (d, *J* = 23.3 Hz), 116.00 (d, *J* = 22.5 Hz), 55.60 (d, *J* = 4.9 Hz), 35.59 (d, *J* = 13.2 Hz), 33.98 (d, *J* = 11.0 Hz), 28.77 (d, *J* = 53.3 Hz), 25.90 (d, *J* = 53.7 Hz), 21.40, 17.94 (dd, *J* = 223.9, 87.6 Hz), 6.70 (dd, *J* = 101.3, 54.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.18; HRMS (ESI) *m/z* calcd for $C_{25}H_{29}BN_2PSF_5$ $[M\text{-}BF_4]^+$ = 439.1768, found = 439.1766.

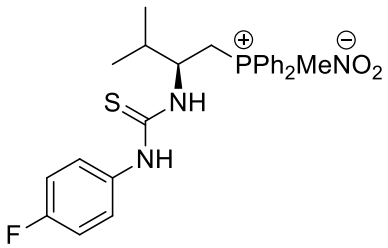
(*S*)-(2-(3-(4-fluorophenyl)thioureido)propyl)(methyl)diphenylphosphonium hexafluorophosphate(V) (P4-3)



A white solid; ^{1}H NMR (400 MHz, CD_3OD) δ 7.89 - 7.75 (m, 6H), 7.74 - 7.64 (m, 4H), 7.62 - 7.57 (m, 1H), 7.36 - 7.30 (m, 1H), 7.14 - 6.93 (m, 2H), 4.82 (s, 3H), 3.34 -

3.29 (m, 1H), 3.10 - 2.97 (m, 1H), 2.83 (d, *J* = 14.0 Hz, 1H), 2.72 (dd, *J* = 14.4, 3.6 Hz, 2H), 2.40 (s, 1H), 1.05 - 0.97 (m, 3H), 0.69 (dd, *J* = 10.8, 6.8 Hz, 3H); ^{13}C NMR (100 MHz, CD_3OD) δ 145.18, 140.04, 135.92 (d, *J* = 2.9 Hz), 135.63 (dd, *J* = 7.2 4.0 Hz), 133.55 (d, *J* = 9.8 Hz), 133.23 (dd, *J* = 10.1, 6.3 Hz), 131.47 - 130.79 (m), 128.10 (d, *J* = 8.3 Hz), 127.71, 122.10 (d, *J* = 86.2 Hz), 120.73 (d, *J* = 86.1 Hz), 116.68 (d, *J* = 23.1 Hz), 36.22 (d, *J* = 13.2 Hz), 33.96 (d, *J* = 10.9 Hz), 26.04 (d, *J* = 53.3 Hz), 21.42, 18.89 (d, *J* = 78.3 Hz), 17.15 (d, *J* = 128.6 Hz), 7.17 (dd, *J* = 54.9, 9.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.13; HRMS (ESI) *m/z* calcd for $C_{25}H_{29}N_2P_2SF_7$ $[M\text{-}BF_6]^+$ = 439.1768, found = 439.1768.

(*S*)-1-(4-fluorophenyl)-3-(1-(methyl(nitro)diphenylphosphoranyl)propan-2-yl)thiourea (P4-4)



A white solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 - 7.75 (m, 6H), 7.70 - 7.60 (m, 6H), 7.49 - 7.46 (m, 1H), 6.95 - 6.91 (m, 1H), 5.08 - 4.87 (m, 1H), 3.83 - 3.57 (m, 1H), 3.01 (d, *J* = 14.0 Hz, 1H), 2.91 - 2.81 (m, 3H), 2.37 (s, 1H), 2.09 - 2.00 (m, 1H), 1.249 - 1.19 (m, 1H), 0.99 (dd, *J* = 10.8, 6.8 Hz, 6H), 0.78 (d, *J* = 6.8 Hz, 1H), 0.65 (d, *J* = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 181.34, 160.06 (d, *J* = 242.5 Hz), 143.33, 139.27, 135.27 (dd, *J* = 40.1, 3.0 Hz), 135.07 (dd, *J* = 47.9, 2.9 Hz), 132.71 - 132.08 (m), 130.87 - 130.07 (m), 129.72, 126.47, 126.00 (d, *J* = 8.0 Hz), 121.51 (d, *J* = 85.7 Hz), 119.22 (dd, *J* = 166.6, 85.5 Hz), 117.36 (d, *J* = 84.5 Hz), 115.07 (d, *J* = 22.4 Hz), 53.15 (d, *J* = 4.5 Hz), 34.69 (d, *J* = 12.8 Hz), 32.90 (d, *J* = 12.2 Hz), 26.92 (d, *J* = 53.1 Hz), 20.51 (d, *J* = 224.6 Hz), 18.42, 8.86 (dd, *J* = 117.1, 53.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.16; HRMS (ESI) *m/z* calcd for $C_{25}H_{29}N_3O_2PSF$ $[M\text{-}NO_2]^+$ = 439.1768, found = 439.1760.

4. Preparation of cyclic imines 1/1' and 6 and phosphine oxides 2

All cyclic ketimines **1/1'** and **6** listed in Figure S2 were prepared following general procedures A[4], B[5] and C[6]. All the phosphine oxides **2** were listed in Figure S3. Phosphine oxides **2a**, **2f, 2g, 3a, 3b, 3c** and **3d** were obtained from commercial sources, other phosphine oxides were synthesized following the previous reported literature. All the cyclic imine**s 1/1'** and **6** and phosphine oxides **2** were known compounds.

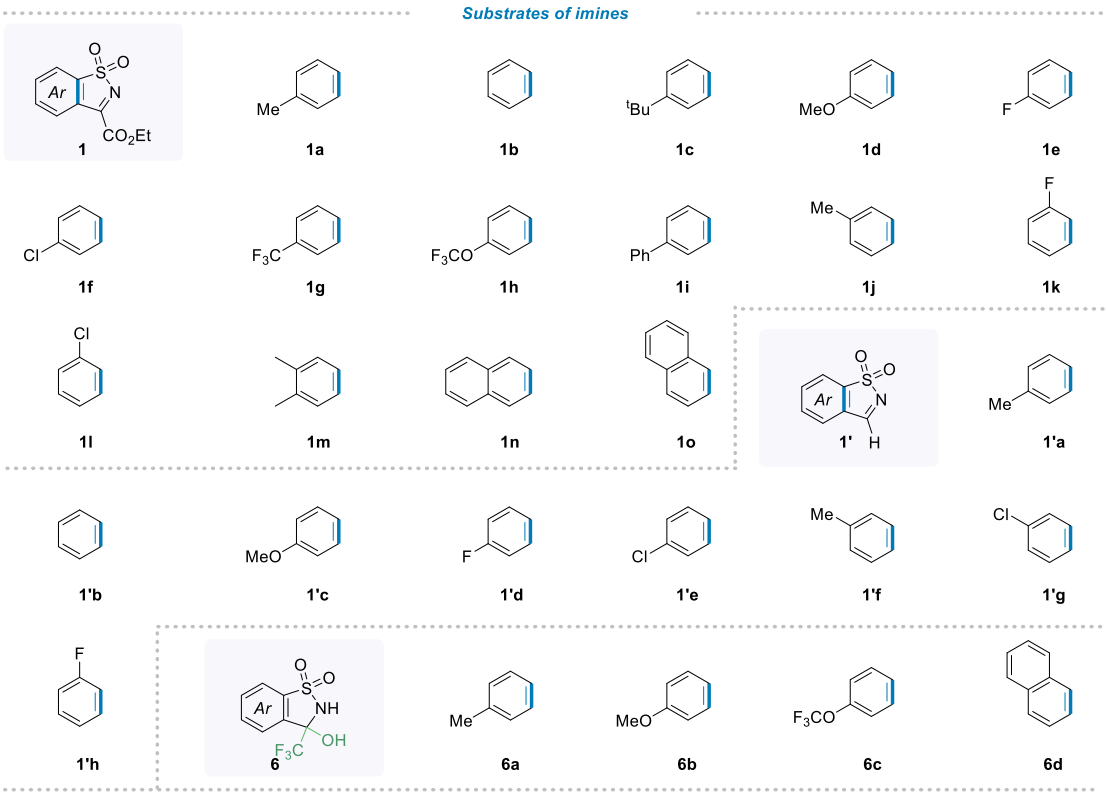


Figure S2. Substrates of cyclic imines **1/1'** and **6**

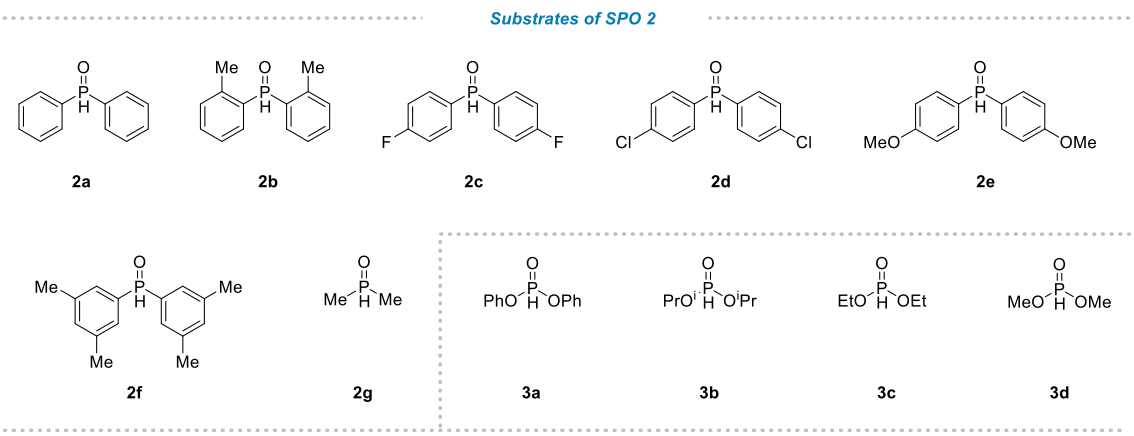
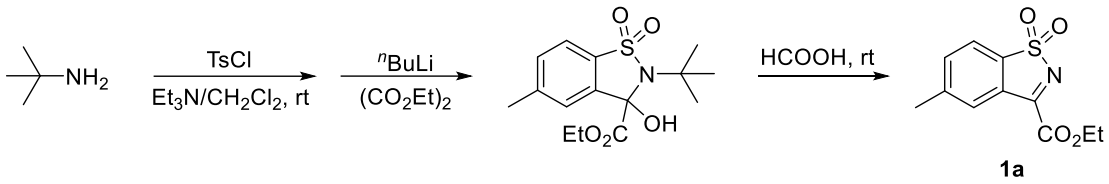


Figure S3. Substrates of phosphine oxides **2.**

4.1 Preparation of cyclic imines 1/1' and 6

(1) General procedure D: preparation of cyclic imines 1



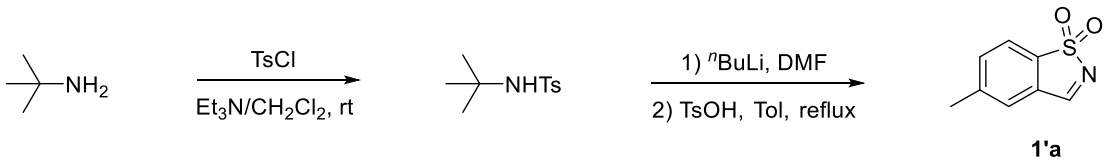
1a

General procedure D: To a solution of tert-butylamine (30 mmol, 2.9 g) and triethylamine (40 mmol, 4.1 g) in DCM in an ice bath was added arylsulfonyl chloride (20 mmol, 3.8 g) dropwise. The mixture was stirred at room temperature overnight. It was washed with saturated sodium carbonate and brine. The organic layer was separated, and the aqueous layer was extracted with DCM. The combined organic extracts were dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo to give the aryl sulfonamide as a solid without further purification.

n-butyllithium (30.75 mmol, 12.3 mL, 2.5 M in hexane) was added dropwise over a 20 minute period to a cold (0 ℃), mechanically stirred solution of the aryl sulfonamide (15 mmol) in anhydrous tetrahydrofuran (100 mL) under a dry nitrogen atmosphere. After stirring an additional 25 min at 0 ℃ a precipitate formed. The suspension was cooled further to -78 ℃ and diethyl oxalate (45 mmol, 6.6 g) was added. The cooling bath was removed and the suspension was stirred at ambient temperature for 2 h. The reaction was quenched with 5% HCl (40 mL) and added to water (200 mL). The organics were extracted with diethyl ether (200 mL). The diethyl ether phase was washed with brine (200 mL). The solvent was removed and the crude product was obtained used directly in the next step.

To the crude product obtained above, formic acid (25 mL) was added and the suspension was stirred at room temperature under a dry nitrogen atmosphere. After 5 min dissolution occurred. After 20 h the solution was concentrated and the resultant solid was dissolved in DCM and concentrated (three times) to remove traces of formic acid. This afforded the title compound as a white solid which was further purified by flash chromatography.

(2) General procedure E: preparation of cyclic imines 1'



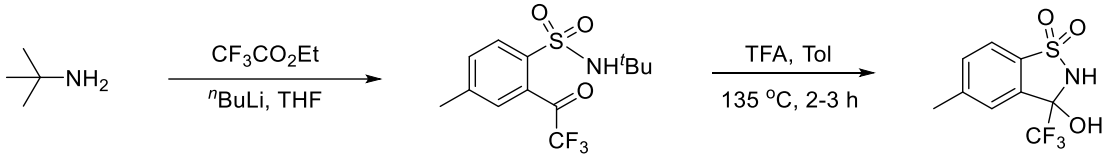
1'a

General procedure E: To a solution of tert-butylamine (30 mmol, 2.9 g) and triethylamine (40 mmol, 4.1 g) in CH_2Cl_2 in an ice bath was added arylsulfonyl chloride (20 mmol, 3.4 g) dropwise. The mixture was stirred at room temperature overnight. It was washed with saturated sodium carbonate and brine. The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo to give the aryl sulfonamide as a solid without further purification.

The N-tert-butylbenzenesulfonamide (20 mmol, 4.5 g) in tetrahydrofuran (100 mL) held at -78 ^oC under nitrogen atmosphere was added dropwise a 1.6 M solution of n-butyllithium in tetrahydrofuran (44 mmol, 27 mL). After stirred at -20 ^oC for 0.5 h, the yellow mixture was placed at -78 ^oC and dimethyl formamide (30 mmol, 15mL) was added. The solution was allowed to stir for 4 h, then warm slowly to room temperature. Saturated aqueous ammonium chloride (100 mL) was added, the mixture was transferred to a separatory funnel with EA, and the organic phase was separated. The aqueous phase was extracted with EA (3×50 mL) and the organic extracts were combined, washed with brine (80 mL), dried over anhydrous sodium sulfate. The resulting mixture was concentrated in vacuo and further purification was performed by a short silica gel column.

Subsequently, to a solution of the above crude product in toluene, p-toluenesulfonic acid (0.2 mmol, 40 mg) was added. The mixture was stirred at 110 ^oC for 5 h. The yellow oil was purified by a silica gel column eluted with PE/EA = 2/1 to give pure product as a yellow solid (58% yield).

(3) General procedure F: Preparation of *in situ* cyclic imine 6

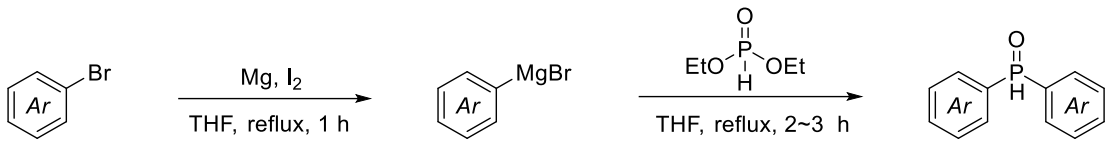


6a

General procedure F: n-Butyllithium (32 mmol, 13 mL, 2.5 M in hexance) was added dropwise over 20 minutes period to a cold (0 ℃), mechanically stirred solution of the aryl sulfonamide (15 mmol, 3.4 g) in anhydrous tetrahydrofuran (100 ml) under a dry nitrogen atmosphere. After stirring an additional 25 min at 0 °C a precipitate formed. The suspension was cooled further to -78 ℃ and ethyl trifluoroacetate (45 mmol, 6.4 g) was added dropwise over 10 minutes. The resulting mixture was allowed to stir for 4 h at -30 °C and 2 h at ambient temperature. The reaction was quenched with 5% HCl (40 ml) and extracted with ether (50×3 mL). The combined ether phase was washed with brine (200 mL), dried over anhydrous Na_2SO_4. The solvent was removed and the crude product was obtained which can be used directly in the next step or purified by column chromatography (DCM/PE = 1/3-1/1).

To the crude product obtained above, TFA (75 mol) in toluene (20 mL) was added and the resulting mixture was stirred at 135 °C in sealed tube. After 2-3 h the solution was concentrated and the resultant solid was dissolved in CH_2Cl_2 (150 mL) and washed with saturated $NaHCO_3$ (50×2 mL) to remove traces of TFA. Then the organic phase was washed with brine and dried over Na_2SO_4. The solvent was removed and the obtained crude product was further purified by flash chromatography (PE/EA = 8/1-3/1) to give pure product as a white solid (68% yield).

4.2 General procedure G: Preparation of phosphine oxides 2

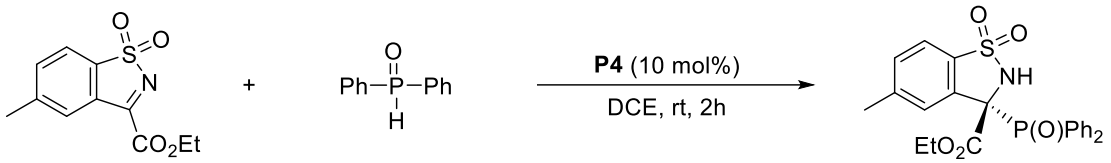


2

General procedure G: Aryl bromide (10 mol, 1.6 g) in THF was added slowly to a stirred THF solution of I_2 (0.1 mol, 0.25 g), and heated under reflux for 1 hour. Then diethyl phosphate (3 mol, 0.42 g) in THF was added slowly under the cooling of an ice-water bath. The mixture thus obtained was heated under reflux for 1 hour. The resulting reaction mixture was cooled to 0 °C, and hydrochloric acid (50 mL, 6 M) was added slowly upon stirring. The solution was evaporated under reduced pressure at 40 °C. The residue was extracted with EA (150 mL). The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo, The crude product was purified by column chromatography on silica gel using PE/EA (1:1) as eluents.

5. Representative procedure for asymmetric P-nucleophile addition

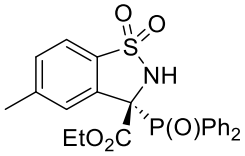
5.1 Representative procedure for asymmetric P-nucleophile addition to cyclic N-sulfonyl imines 1 with secondary phosphine oxides 2



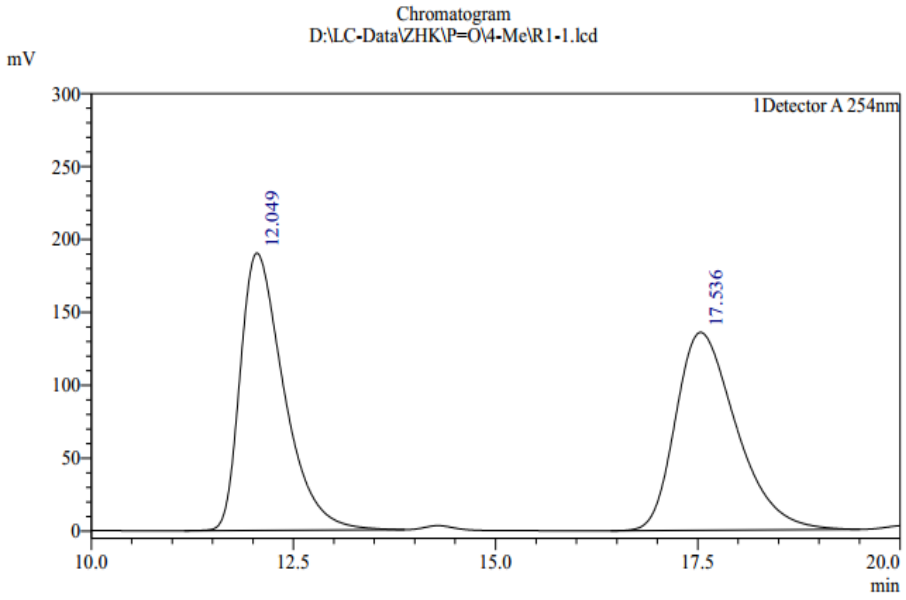
1a **2a** **4a**

Representative procedure for 4a: To a flame-dried round bottle flask with a magnetic stirring bar were added cyclic ketimine **1a** (0.10 mmol, 25.3 mg), phosphine oxide **2a** (0.12 mmol, 24.2 mg), phosphonium salt **P4** (0.01 mmol, 5.7 mg), and DCE (1.0 mL). The reaction mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate = 3:1) to afford **4a** (96% yield) as a white solid.

(*S*)-ethyl 3-(diphenylphosphoryl)-5-methyl-2,3-dihydrobenzo[d] isothiazole-3-carboxylate1,1-dioxide (4a)



A white solid; m.p. = 185 - 187 °C; 43.7 mg, 96% yield; $[\alpha]^{25}_D$ = -70.67 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 - 8.13 (m, 1H), 8.12 - 8.05 (m, 2H), 7.64 - 7.56 (m, 3H), 7.55 - 7.49 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.43 - 4.38 (m, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.30 - 7.23 (m, 3H), 6.00 (d, *J* = 4.0 Hz, 1H), 4.29 - 4.06 (m, 2H), 2.49 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.56 (d, *J* = 2.7 Hz), 144.64 (d, *J* = 1.9 Hz), 133.09 (d, *J* = 2.8 Hz), 132.82 (d, *J* = 2.8 Hz), 132.56 (dd, *J* = 16.7, 8.7 Hz), 131.85 (d, *J* = 1.6 Hz), 131.72 (d, *J* = 3.1 Hz), 131.43 (d, *J* = 2.4 Hz), 128.79 (d, *J* = 11.7 Hz), 128.42 (d, *J* = 2.4Hz), 128.36, 128.18 (d, *J* = 12.3 Hz), 127.45 (d, *J* = 13.8 Hz), 126.48, 120.90 (d, *J* = 1.3 Hz), 70.02 (d, *J* = 71.4Hz), 64.46, 21.97, 13.83; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.18; HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_5PS$ $[M+H]^+$ = 456.1035, found = 456.1038; The ee value was >99%, t_R (minor) = 12.1 min, t_R (major) = 16.9 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

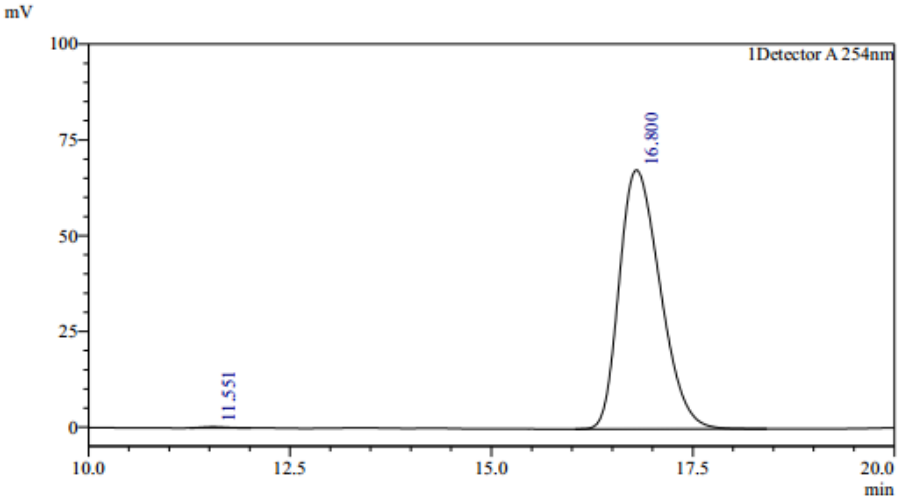


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	12.049	7140364	190166	58.353	50.112
2	17.536	7108546	135720	41.647	49.888
Total		14248910	325886	100.000	100.000

Racemic **4a**



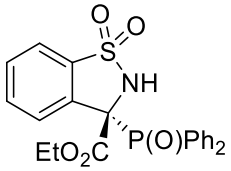
Peak Table

Detector A 254nm

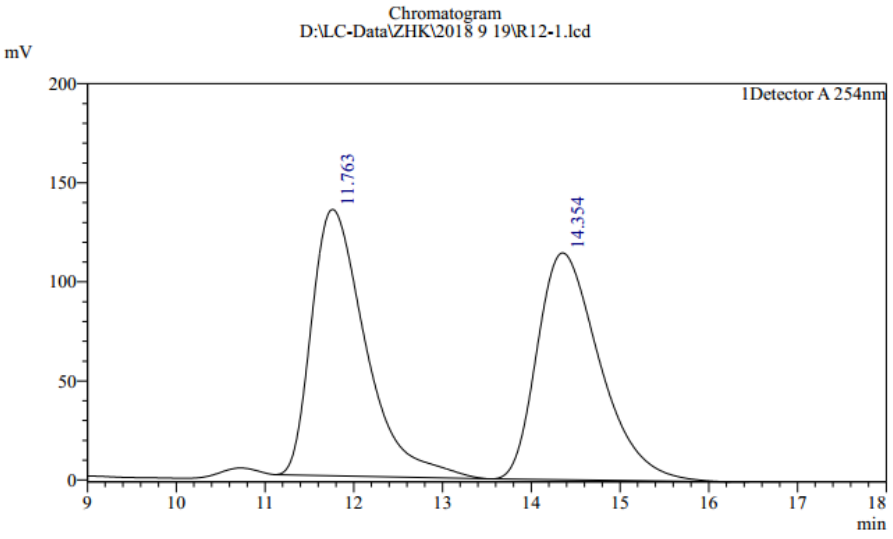
Peak#	Ret. Time	Area	Height	Height%	Area%
1	11.551	5567	272	0.401	0.233
2	16.800	2386681	67601	99.599	99.767
Total		2392247	67873	100.000	100.000

Enantiomerically enriched **4a**

(*S*)-ethyl 3-(diphenylphosphoryl)-2,3-dihydrobenzo[d]isothiazole -3-carboxylate 1,1-dioxide (4b)



A white solid; m.p. = 178 - 180 °C; 42.3 mg, 96% yield; $[\alpha]^{25}_{D}$ = -13.32 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.6 Hz, 1H), 8.14 - 8.06 (m, 2H), 7.73 - 7.68 (m, 1H), 7.67 - 7.53 (m, 7H,) 7.47 - 7.40(m, 1H), 7.32 - 7.25 (m, 2H), 5.94 (d, *J* = 3.6 Hz, 1H), 4.29 - 4.10 (m, 2H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.63 (d, *J* = 2.6 Hz), 134.37 (d, *J* = 3.2 Hz), 133.51 (d, *J* = 1.7 Hz), 133.27 (d, *J* = 2.9 Hz), 132.99 (d, *J* = 2.8 Hz), 132.65 (dd, *J* = 18.7, 8.6 Hz), 131.26 (d, *J* = 2.3 Hz), 130.92 (d, *J* = 1.8 Hz), 128.93 (d, *J* = 11.7 Hz), 128.56 (d, *J* = 2.5 Hz), 128.33 (d, *J* = 12.3 Hz), 127.41 (d, *J* = 2.1 Hz), 126.38, 121.32 (d, *J* = 1.5 Hz), 70.29 (d, *J* = 70.8 Hz), 64.67, 13.94; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.13; HRMS (ESI) m/z calcd for $C_{22}H_{21}NO_5PS$ $[M+H]^+$ = 478.0878, found = 478.0870; The ee value was >99%, t_R (minor) = 10.6 min, t_R (major) = 14.8 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

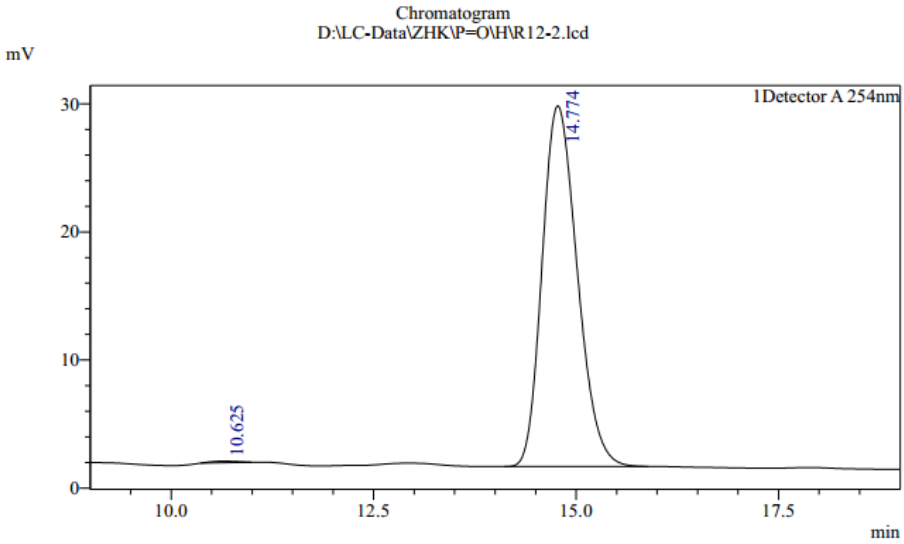


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	11.763	5698761	134415	53.996	50.374
2	14.354	5614092	114518	46.004	49.626
Total		11312853	248933	100.000	100.000

Racemic **4b**



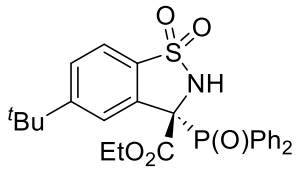
Peak Table

Detector A 254nm

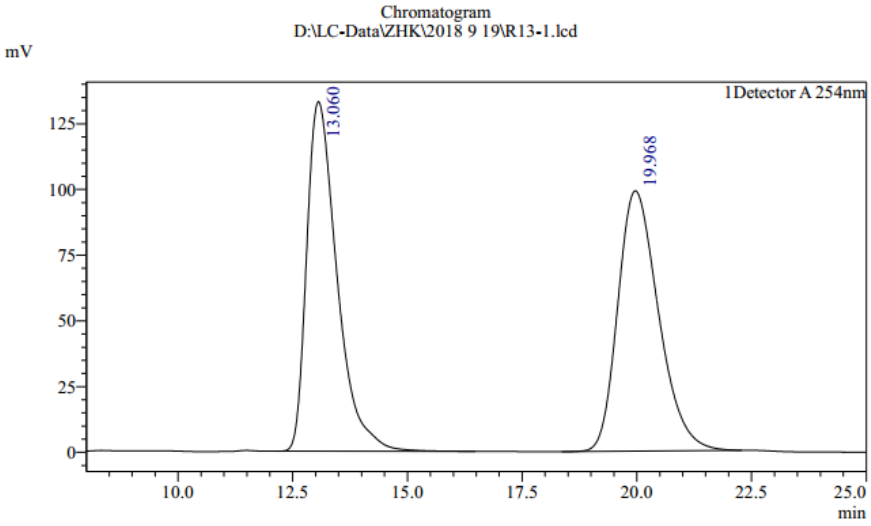
Peak#	Ret. Time	Area	Height	Height%	Area%
1	10.625	2822	123	0.437	0.331
2	14.774	849237	28167	99.563	99.669
Total		852059	28291	100.000	100.000

Enantiomerically enriched **4b**

(*S*)-ethyl 5-(tert-butyl)-3-(diphenylphosphoryl)-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (4c)



A white solid; m.p. = 117 - 119 °C; 46.2 mg, 93% yield; $[\alpha]^{25}_D$ = -63.67 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 - 8.30 (m, 1H), 8.13 - 8.04 (m, 2H), 7.70 - 7.61 (m, 3H), 7.60 - 7.53 (m, 2H), 7.54 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.44 - 7.38 (m, 1H), 7.31 - 7.24 (m, 2H), 5.83 (s, 1H), 4.29 - 4.21 (m, 2H), 1.37 (s, 9H), 1.20 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.72 (d, *J* = 2.8 Hz), 157.80 (d, *J* = 1.8 Hz), 133.20 (d, *J* = 2.8 Hz), 132.87 (d, *J* = 2.8 Hz), 132.63 (dd, *J* = 14.5, 8.5 Hz), 131.44 (d, *J* = 3.2 Hz), 131.38 (d, *J* = 2.4 Hz), 128.90 (d, *J* = 11.8 Hz), 128.59, 128.26 (d, *J* = 12.2 Hz), 128.01 (d, *J* = 1.5 Hz), 127.59 (d, *J* = 4.5 Hz), 126.53, 125.65 (d, *J* = 2.7 Hz), 120.82 (d, *J* = 1.3 Hz), 70.18 (d, *J* = 70.9 Hz), 64.43, 35.70, 31.20, 13.97; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.13; HRMS (ESI) m/z calcd for $C_{26}H_{28}NO_5PS$ $[M+Na]^+$ = 498.1504, found = 498.1505; The ee value was >99%, t_R (minor) = 13.8 min, t_R (major) = 19.4 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

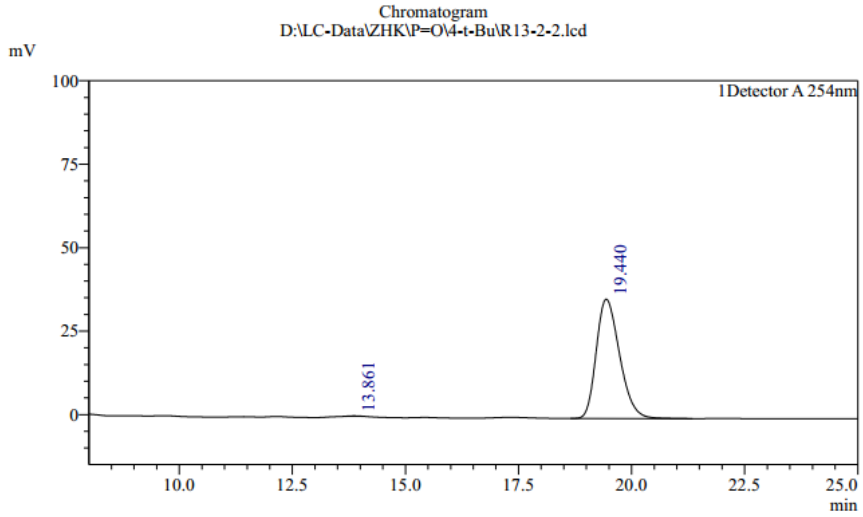


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.060	6128099	133008	57.320	50.020
2	19.968	6123221	99036	42.680	49.980
Total		12251320	232045	100.000	100.000

Racemic **4c**



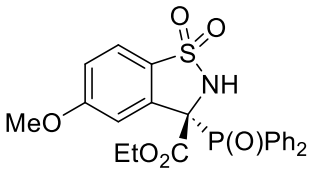
Peak Table

Detector A 254nm

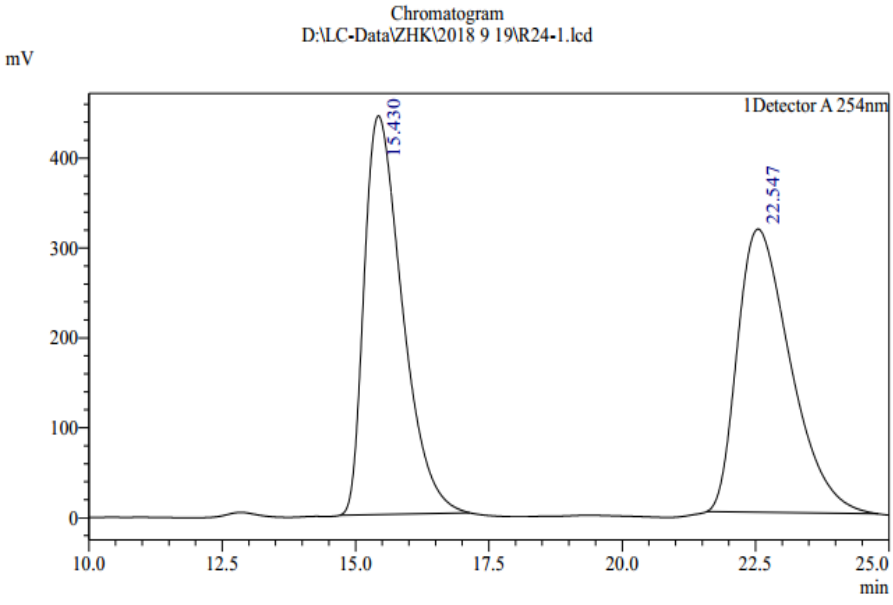
Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.861	2616	150	0.417	0.203
2	19.440	1286874	35768	99.583	99.797
Total		1289490	35917	100.000	100.000

Enantiomerically enriched **4c**

(*S*)-ethyl 3-(diphenylphosphoryl)-5-methoxy-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (4d)



A white solid; m.p. = 125 - 126 °C; 42.9 mg, 91% yield; $[\alpha]^{25}_{D}$ = -52.67 (*c* 1.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 - 8.05 (m, 2H), 7.82 - 7.78 (m, 1H), 7.68 - 7.59 (m, 3H), 7.58 - 7.51 (m, 2H), 7.49 - 7.41 (m, 2H), 7.34 - 7.27 (m, 2H), 7.05 (dd, *J* = 8.8, 1.6 Hz, 1H), 5.94 (d, *J* = 4.0 Hz, 1H), 4.28 - 4.14 (m, 2H), 3.93 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.43 (d, *J* = 2.5 Hz), 163.62 (d, *J* = 1.6 Hz), 133.87 (d, *J* = 2.2 Hz), 133.20 (d, *J* = 2.6 Hz), 132.96 (d, *J* = 2.7 Hz), 132.61 (dd, *J* = 18.4, 8.6 Hz), 128.87 (d, *J* = 11.7 Hz), 128.32, 128.31 (d, *J* = 12.3 Hz), 127.42 (d, *J* = 15.3 Hz), 126.45, 126.37 (d, *J* = 3.0 Hz), 122.45, 118.95 (d, *J* = 1.1 Hz), 111.38 (d, *J* = 2.1 Hz), 69.86 (d, *J* = 70.8 Hz), 64.54, 56.26, 13.91; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.18; HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_6PS$ $[M+H]^+$ = 472.0984, found = 472.0981; The ee value was >99%, t_R (minor) = 16.0 min, t_R (major) = 19.1 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

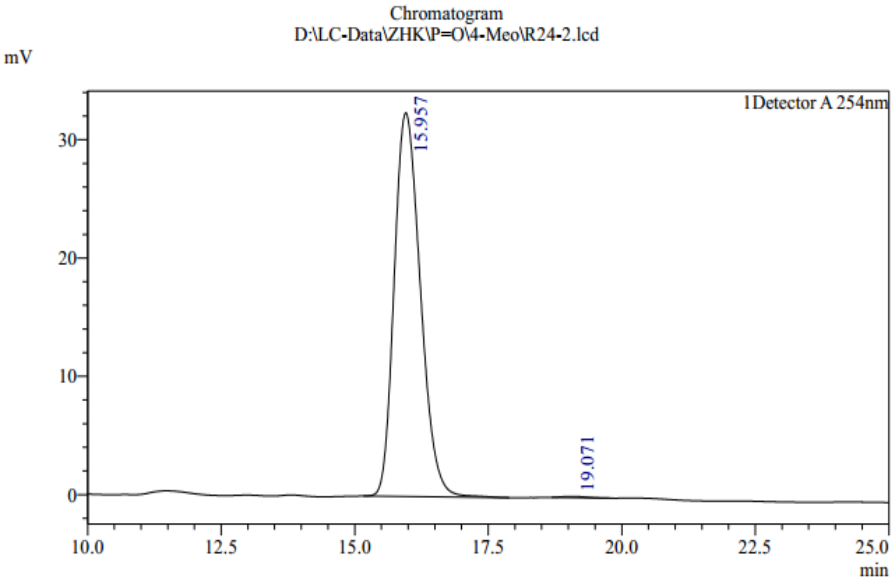


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	15.430	22048437	443406	58.456	50.233
2	22.547	21843527	315127	41.544	49.767
Total		43891964	758533	100.000	100.000

Racemic **4d**



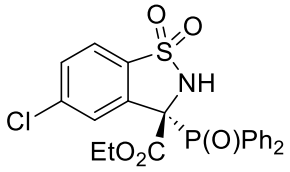
Peak Table

Detector A 254nm

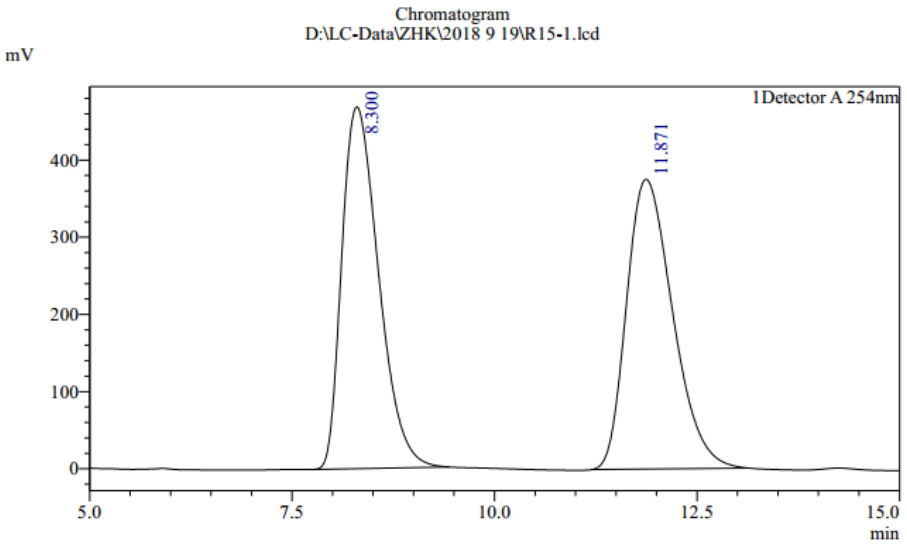
Peak#	Ret. Time	Area	Height	Height%	Area%
1	15.957	1105712	32439	99.682	99.718
2	19.071	3129	103	0.318	0.282
Total		1108841	32542	100.000	100.000

Enantiomerically enriched **4d**

(*S*)-ethyl 5-chloro-3-(diphenylphosphoryl)-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (4e)



A white solid; m.p. = 139 - 141 °C; 44.7 mg, 94% yield; $[\alpha]^{25}_{D}$ = -34.22 (*c* 0.2, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 - 8.36 (m, 1H), 8.14 - 8.05 (m, 2H), 7.70 - 7.61 (m, 3H), 7.61 - 7.54 (m, 2H), 7.53 - 7.43 (m, 3H), 7.36 - 7.28 (m, 2H), 6.01 (d, *J* = 4.0 Hz, 1H), 4.30 - 4.14 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.15 (d, *J* = 2.2 Hz), 140.09 (d, *J* = 2.1 Hz), 133.40 (d, *J* = 2.7 Hz), 133.27 (d, *J* = 2.4 Hz), 133.17 (d, *J* = 2.8 Hz), 132.85 (d, *J* = 3.1 Hz), 132.63 (dd, *J* = 25.8, 8.6 Hz), 131.47 (d, *J* = 1.6 Hz), 128.98 (d, *J* = 11.9 Hz), 128.54, 128.45 (d, *J* = 12.4 Hz), 128.06, 127.10 (d, *J* = 4.9 Hz), 126.08, 122.34 (d, *J* = 1.3 Hz), 69.90 (d, *J* = 69.3 Hz), 64.95, 13.91; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.10; HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_5PSCl$ $[M+H]^+$ = 476.0488, found = 476.0493; The ee value was >99%, t_R (minor) = 8.3 min, t_R (major) = 12.0 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

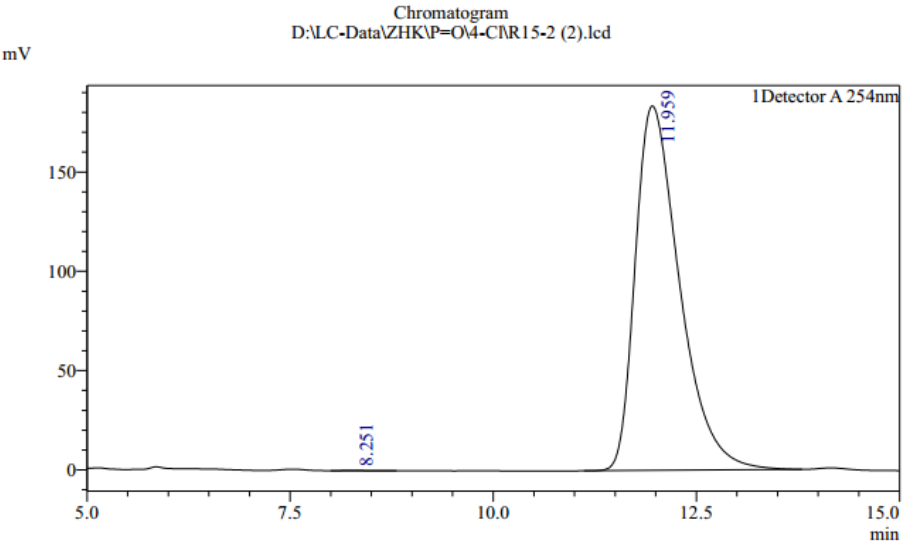


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	8.300	14820184	468775	55.525	49.892
2	11.871	14884317	375491	44.475	50.108
Total		29704501	844266	100.000	100.000

Racemic **4e**



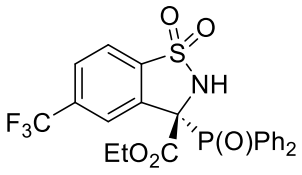
Peak Table

Detector A 254nm

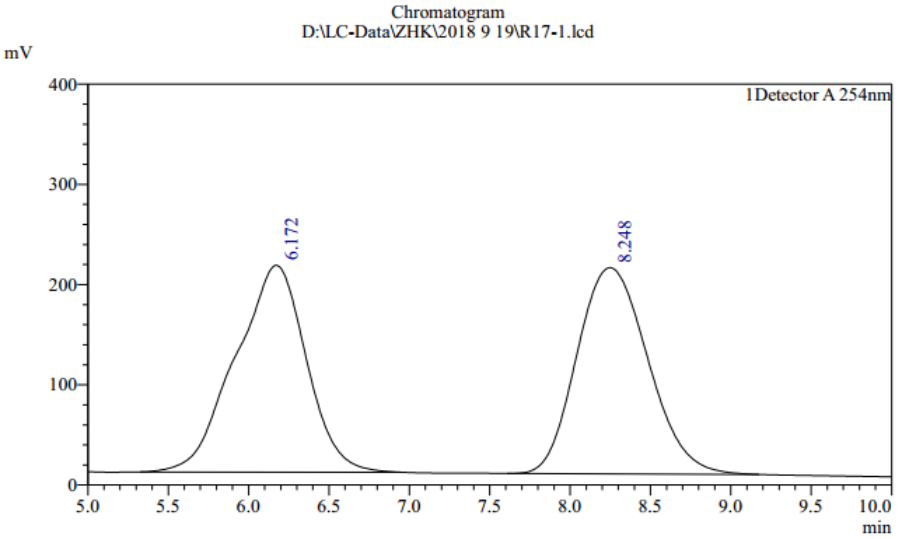
Peak#	Ret. Time	Area	Height	Height%	Area%
1	8.251	2673	153	0.083	0.038
2	11.959	6977098	183521	99.917	99.962
Total		6979771	183674	100.000	100.000

Enantiomerically enriched **4e**

(*S*)-ethyl 3-(diphenylphosphoryl)-5-(trifluoromethyl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (4f)



A white solid; m.p. = 112 - 113 °C; 45.8 mg, 90% yield; $[\alpha]^{25}_{D}$ = -42.37 (*c* 0.9, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.14 - 8.06 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.73 - 7.65 (m, 2H), 7.65 - 7.55 (m, 4H), 7.48 - 7.42 (m, 1H), 7.31 (m, 2H), 6.09 (d, *J* = 3.6 Hz, 1H), 4.30 - 4.15 (m, 2H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.03 (d, *J* = 2.2 Hz), 137.41, 135.61 (d, *J* = 1.9 Hz), 135.28 (d, *J* = 1.8 Hz), 133.50 (d, *J* = 2.8 Hz), 133.25 (d, *J* = 2.8 Hz), 132.61 (dd, *J* = 23.4, 8.6 Hz), 132.57, 129.05 (d, *J* = 12.0 Hz), 128.50 (d, *J* = 12.4 Hz), 126.96 (d, *J* = 3.8 Hz), 126.15 (dd, *J* = 3.6, 2.6 Hz), 125.91, 124.37, 122.08 (d, *J* = 1.5 Hz), 121.66, 118.94, 70.23 (d, *J* = 68.9 Hz), 65.03, 13.84; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.21; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.73; HRMS (ESI) m/z calcd for $C_{23}H_{19}NO_5PSF_3$ $[M+Na]^+$ = 510.0752, found = 510.0744; The ee value was >99%, t_R (minor) = 6.2 min, t_R (major) = 8.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

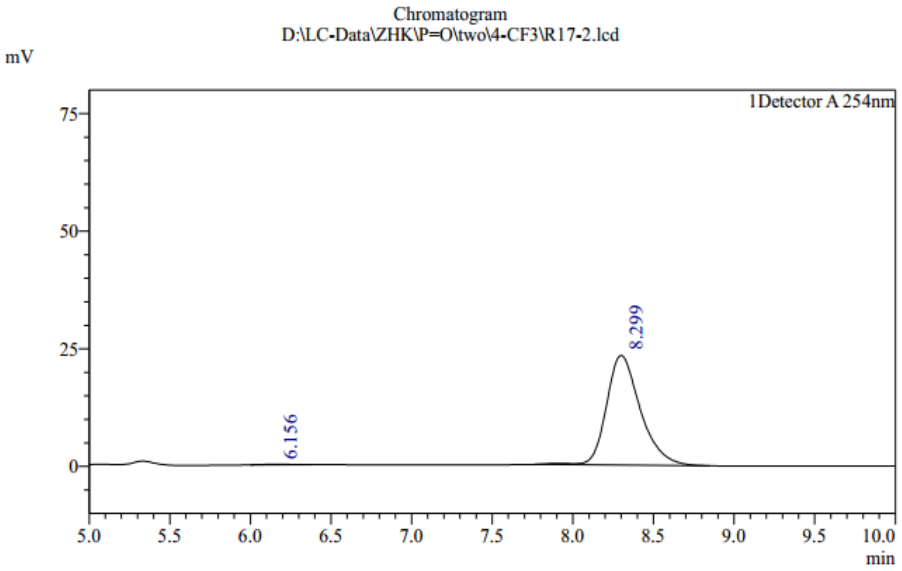


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	6.172	6335493	206418	50.086	50.025
2	8.248	6329172	205708	49.914	49.975
Total		12664665	412126	100.000	100.000

Racemic **4f**



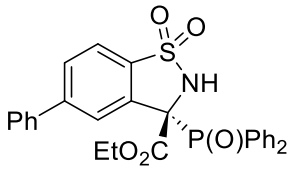
Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	6.156	1322	105	0.448	0.385
2	8.299	342242	23332	99.552	99.615
Total		343564	23437	100.000	100.000

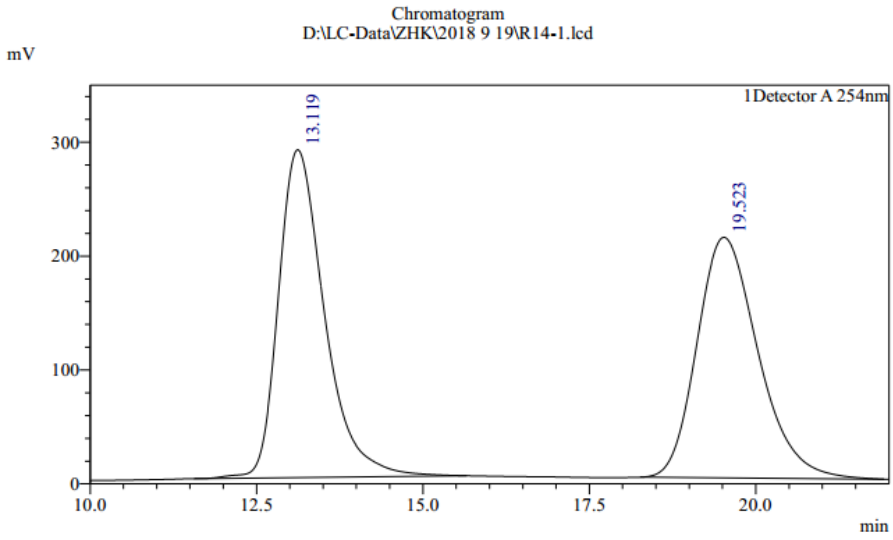
Enantiomerically enriched **4f**

(*S*)-ethyl 3-(diphenylphosphoryl)-5-phenyl-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (4g)



A white solid; m.p. = 165 - 167 °C; 46.5 mg, 90% yield; $[\alpha]^{25}_{D}$ = -78.33 (*c* 1.2, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.61 - 8.55 (m, 1H), 8.18 - 8.09 (m, 2H), 7.81 - 7.76 (m, 1H), 7.70 - 7.63 (m, 6H), 7.62 - 7.56 (m, 2H), 7.55 - 7.49 (m, 2H), 7.48 - 7.41 (m, 2H), 7.30 - 7.27 (m, 2H), 5.97 (d, *J* = 3.2 Hz, 1H), 4.37 - 4.11 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.63 (d, *J* = 2.6 Hz), 146.77, 138.88, 133.29 (d, *J* = 2.7 Hz), 133.02 (d, *J* = 2.8 Hz), 132.91 (d, *J* = 3.2 Hz), 132.66 (dd, *J* = 19.4, 8.6 Hz), 132.10 (d, *J* = 2.2 Hz), 129.90 (d, *J* = 1.6 Hz), 129.28, 129.01, 128.90, 128.41 (d, *J* = 12.3 Hz), 128.34, 127.79, 127.45 (d, *J* = 9.2 Hz), 126.74 (d, *J* = 2.6 Hz), 126.45, 121.63, 70.27 (d, *J* = 70.6 Hz), 64.71, 13.98; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.25; HRMS (ESI) m/z calcd for $C_{28}H_{24}NO_5PS$ $[M+H]^+$ = 518.1191, found = 518.1186; The ee value was >99%, t_R (minor) = 13.8 min, t_R (major) = 19.4 min (Chiralcel IC, λ = 254

nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

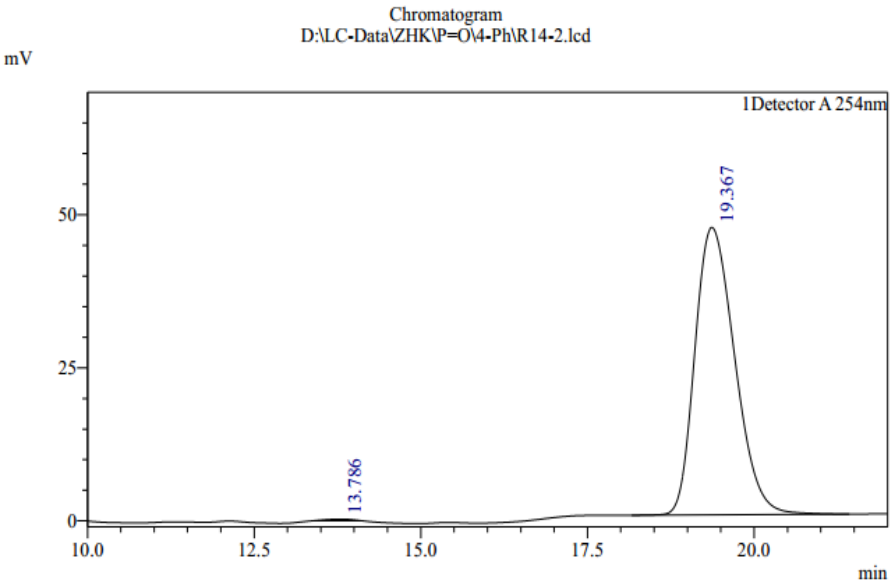


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.119	13831731	287817	57.673	50.603
2	19.523	13502138	211233	42.327	49.397
Total		27333869	499050	100.000	100.000

Racemic **4g**



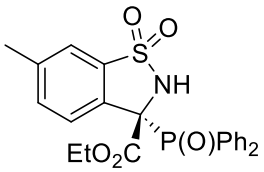
Peak Table

Detector A 254nm

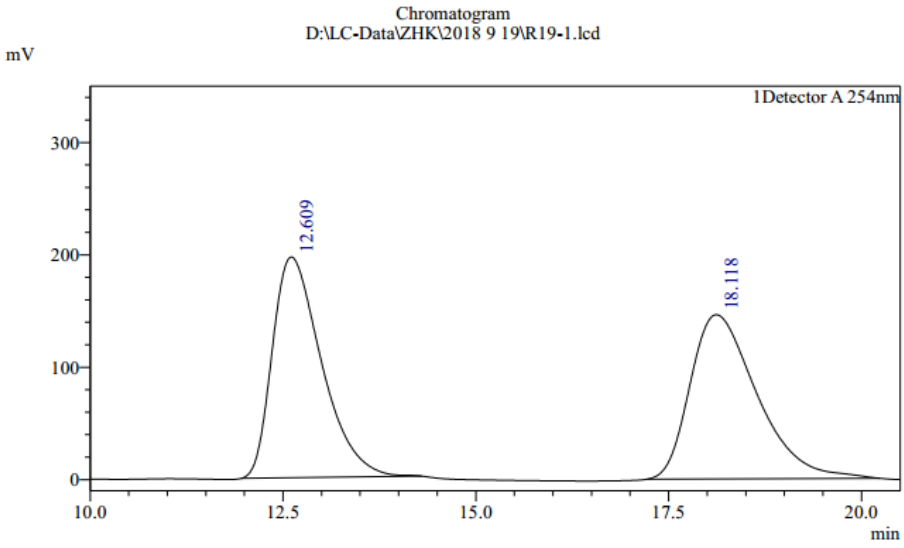
Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.786	8451	291	0.616	0.429
2	19.367	1960423	46971	99.384	99.571
Total		1968874	47262	100.000	100.000

Enantiomerically enriched **4g**

(*S*)-ethyl 3-(diphenylphosphoryl)-6-methyl-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (4h)



A white solid; m.p. = 147 - 149 °C; 42.3 mg, 93% yield; $[\alpha]^{25}_{D}$ = -34.72 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, *J* = 8.0, 1.2 Hz, 1H), 8.13 - 8.05 (m, 2H), 7.66 - 7.59 (m, 3H), 7.58 - 7.48 (m, 3H), 7.46 - 7.41 (m, 1H), 7.40 - 7.36 (m, 1H), 7.32 - 7.26 (m, 2H), 5.94 (d, *J* = 4.0 Hz, 1H), 4.28 - 4.10 (m, 2H), 2.42 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.80 (d, *J* = 3.0 Hz), 141.81 (d, *J* = 1.9 Hz), 134.68 (d, *J* = 1.7 Hz), 134.39 (d, *J* = 3.2 Hz), 133.16 (d, *J* = 2.7 Hz), 132.90 (d, *J* = 2.8 Hz), 132.62 (dd, *J* = 28.7, 8.7 Hz), 128.86 (d, *J* = 11.7 Hz), 128.52, 128.42 (d, *J* = 2.5 Hz), 128.28 (d, *J* = 12.3 Hz), 128.14 (d, *J* = 2.5 Hz), 127.56 (d, *J* = 2.8 Hz), 126.53, 121.17 (d, *J* = 1.4 Hz), 70.05 (d, *J* = 71.7 Hz), 64.52, 21.41, 13.91; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.96 ; HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_5PS$ $[M+H]^+$ = 456.1035, found = 456.1038; The ee value was >99%, t_R (minor) = 12.5 min, t_R (major) = 17.7 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

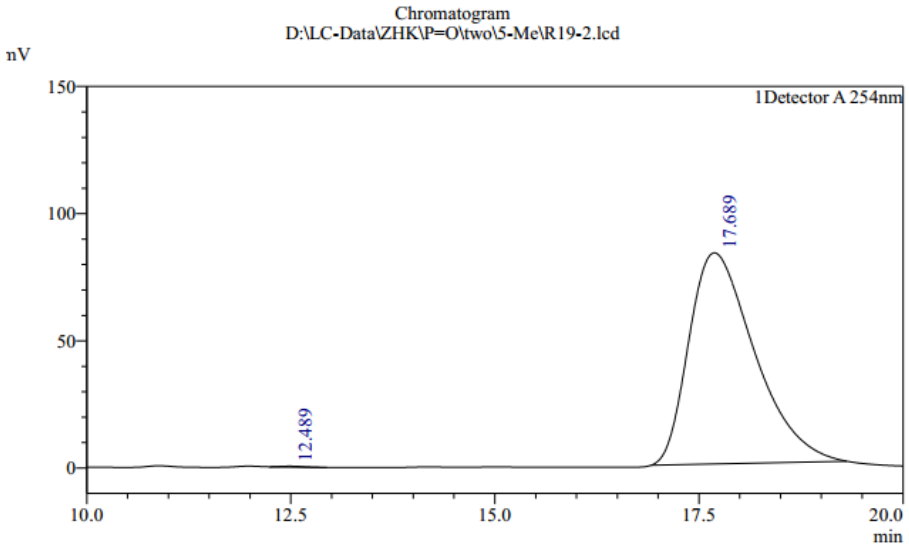


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	12.609	8717887	196415	57.348	49.774
2	18.118	8797097	146083	42.652	50.226
Total		17514984	342497	100.000	100.000

Racemic **4h**



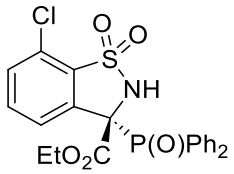
Peak Table

Detector A 254nm

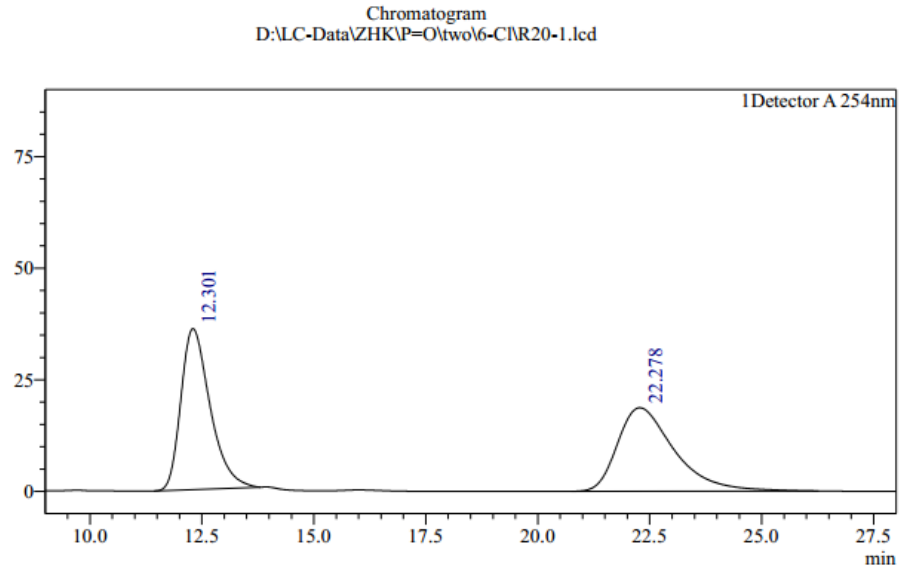
Peak#	Ret. Time	Area	Height	Height%	Area%
1	12.489	6125	332	0.399	0.132
2	17.689	4648277	82985	99.601	99.868
Total		4654403	83317	100.000	100.000

Enantiomerically enriched **4h**

(*S*)-ethyl 7-chloro-3-(diphenylphosphoryl)-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (4i)



A white solid; m.p. = 131 - 133 °C; 44.7 mg, 94% yield; $[\alpha]^{25}_{D}$ = -42.32 (*c* 0.8, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 - 8.29 (m, 1H), 8.16 - 8.05 (m, 2H), 7.70 - 7.54 (m, 6H), 7.53 - 7.44 (m, 2H), 7.36 - 7.29 (m, 2H), 6.05 (d, *J* = 4.4 Hz, 1H), 4.28 - 4.07 (m, 2H), 1.14 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.27 (d, *J* = 2.4 Hz), 134.51 (d, *J* = 1.8 Hz), 133.91 (d, *J* = 2.0 Hz), 133.39 (d, *J* = 2.8 Hz), 133.29 (d, *J* = 2.8 Hz), 132.62 (dd, *J* = 19.5, 8.7 Hz), 132.30 (d, *J* = 3.2 Hz), 131.65 (d, *J* = 1.7 Hz), 128.98 (d, *J* = 11.8 Hz), 128.79 (d, *J* = 1.7 Hz), 128.48 (d, *J* = 12.3 Hz), 128.15, 127.16 (d, *J* = 3.0 Hz), 126.89 (d, *J* = 2.5 Hz), 126.10, 69.35 (d, *J* = 69.7 Hz), 64.88, 13.92; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.58 ; HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_5PSCl$ $[M+H]^+$ = 476.0488, found = 476.0481; The ee value was 98%, t_R (minor) = 14.6 min, t_R (major) = 23.0 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

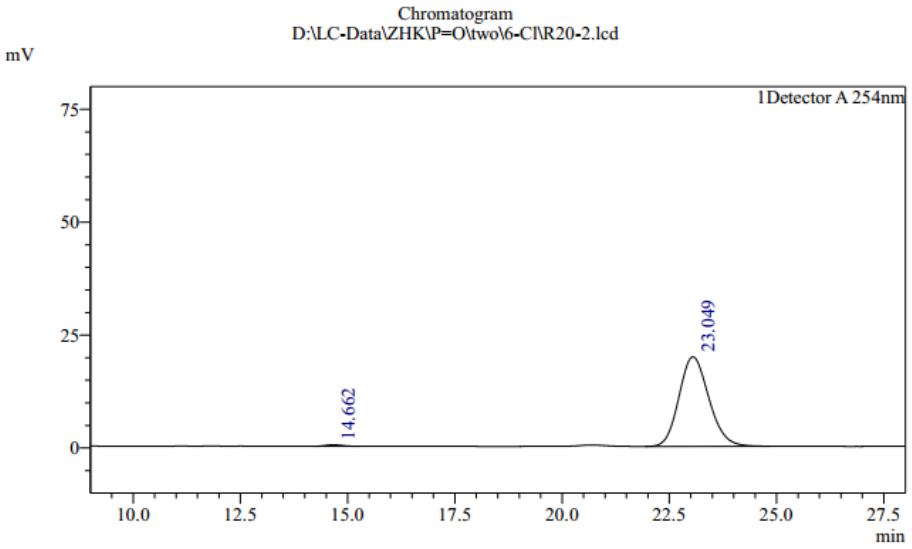


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	12.301	1638270	36081	65.856	49.872
2	22.278	1646665	18707	34.144	50.128
Total		3284935	54787	100.000	100.000

Racemic **4i**



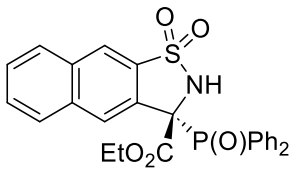
Peak Table

Detector A 254nm

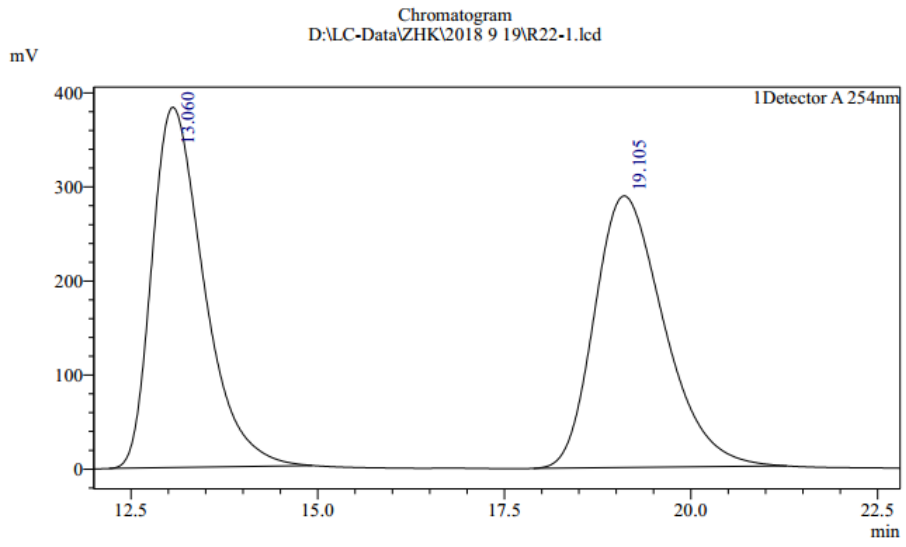
Peak#	Ret. Time	Area	Height	Height%	Area%
1	14.662	8846	334	1.656	0.912
2	23.049	960788	19812	98.344	99.088
Total		969633	20146	100.000	100.000

Enantiomerically enriched **4i**

(*S*)-ethyl 3-(diphenylphosphoryl)-2,3-dihydronaphtho[2,3-d] isothiazole-3-carboxylate 1,1-dioxide (4j)



A white solid; m.p. = 116 - 118 °C; 45.2 mg, 92% yield; $[\alpha]^{25}_{D}$ = -37.43 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 - 8.83 (m, 1H), 8.21 - 8.06 (m, 4H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.74 - 7.53 (m, 7H), 7.41 - 7.34 (m, 1H), 7.25 - 7.18 (m, 2H), 6.06 (d, *J* = 4.0 Hz, 1H), 4.33 - 4.13 (m, 2H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.98 (d, *J* = 3.1 Hz), 135.38 (d, *J* = 2.1 Hz), 133.23 (d, *J* = 2.6 Hz), 132.89 (d, *J* = 2.8 Hz), 132.67 (dd, *J* = 19.3, 8.6 Hz), 131.88 (d, *J* = 2.6 Hz), 129.42, 129.21 (d, *J* = 5.3 Hz), 128.93 (d, *J* = 11.7 Hz), 128.53 (d, *J* = 3.3 Hz), 128.47, 128.31 (d, *J* = 12.3 Hz), 127.63 (d, *J* = 12.5 Hz), 126.64, 126.20 (d, *J* = 2.6 Hz), 122.10 (d, *J* = 1.0 Hz), 70.05 (d, *J* = 71.5 Hz), 64.70, 13.98; ^{31}P NMR (162 MHz, $CDCl_3$) δ 27.95; HRMS (ESI) m/z calcd for $C_{26}H_{22}NO_5PS$ $[M+H]^+$ = 492.1035, found = 492.1028; The ee value was 95%, t_R (minor) = 14.9 min, t_R (major) = 21.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

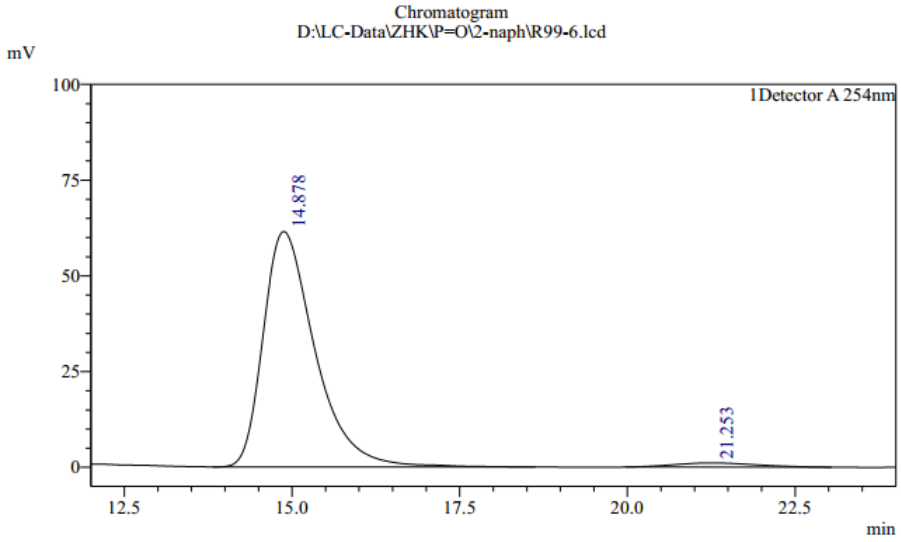


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.060	18565269	383108	57.020	49.737
2	19.105	18761516	288774	42.980	50.263
Total		37326785	671882	100.000	100.000

Racemic **4j**



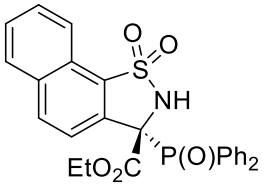
Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	14.878	3310077	61484	98.252	97.255
2	21.253	93432	1094	1.748	2.745
Total		3403509	62578	100.000	100.000

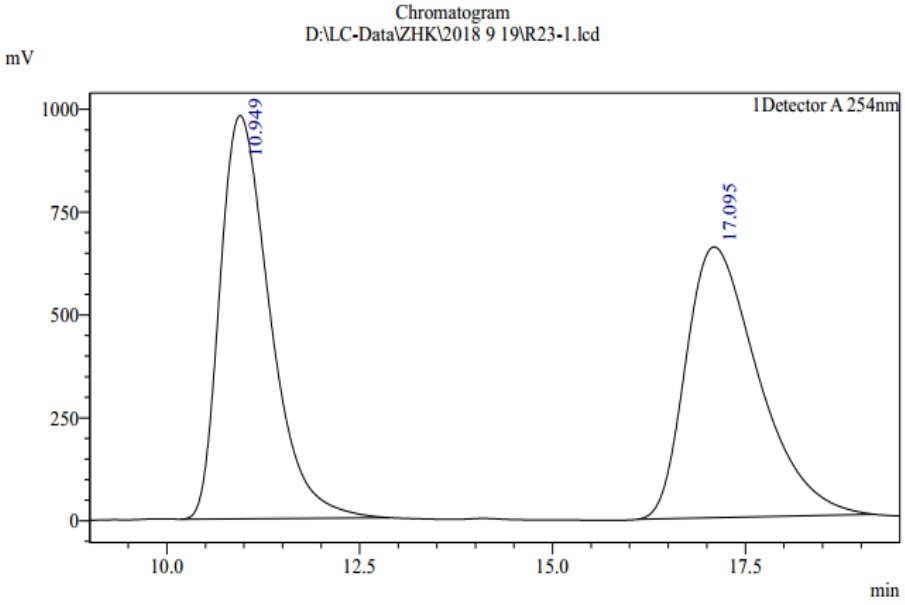
Enantiomerically enriched **4j**

(*S*)-ethyl 3-(diphenylphosphoryl)-2,3-dihydronaphtho[2,1-d] isothiazole-3-carboxylate 1,1-dioxide (4k)



A white solid; m.p. = 175 - 177 ºC; 44.2 mg, 90% yield; $[\alpha]^{25}_{D}$ = -102.33 (*c* 1.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 - 8.39 (m, 1H), 8.24 - 8.18 (m, 1H), 8.18 - 8.09 (m, 3H), 7.98 - 7.93 (m, 1H), 7.69 - 7.61 (m, 5H), 7.60 - 7.54 (m, 2H), 7.39 - 7.32 (m, 1H), 7.24 - 7.28 (m, 2H), 6.13 (d, *J* = 4.0 Hz, 1H), 4.30 - 4.14 (m, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.66 (d, *J* = 2.5 Hz), 134.14 (d, *J* = 1.3 Hz), 133.99 (d, *J* = 1.1 Hz), 133.23 (d, *J* = 2.8 Hz), 132.99 (d, *J* = 2.8 Hz), 132.61 (dd, *J* = 15.6, 8.7 Hz), 131.02 (d, *J* = 2.3 Hz), 130.00 (d, *J* = 4.0 Hz), 129.17, 128.90 (d, *J* = 11.8 Hz), 128.60 (d, *J* = 19.2 Hz), 128.27 (d, *J* = 12.3 Hz), 127.45 (d, *J* = 17.3 Hz), 126.32, 124.98 (d, *J* = 1.5 Hz), 123.73 (d, *J* = 1.7 Hz), 122.99, 70.72 (d, *J* = 70.8 Hz), 70.01, 64.69, 13.94; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.32; HRMS (ESI) m/z calcd for $C_{26}H_{22}NO_5PS$ $[M+H]^+$ = 492.1035, found = 492.1036; The ee value was >99%, t_R (minor) = 11.4 min, t_R (major) = 16.7 min (Chiralcel IC, λ = 254 nm, 40% *i*-

PrOH/hexanes, flow rate = 1.0 mL/min).

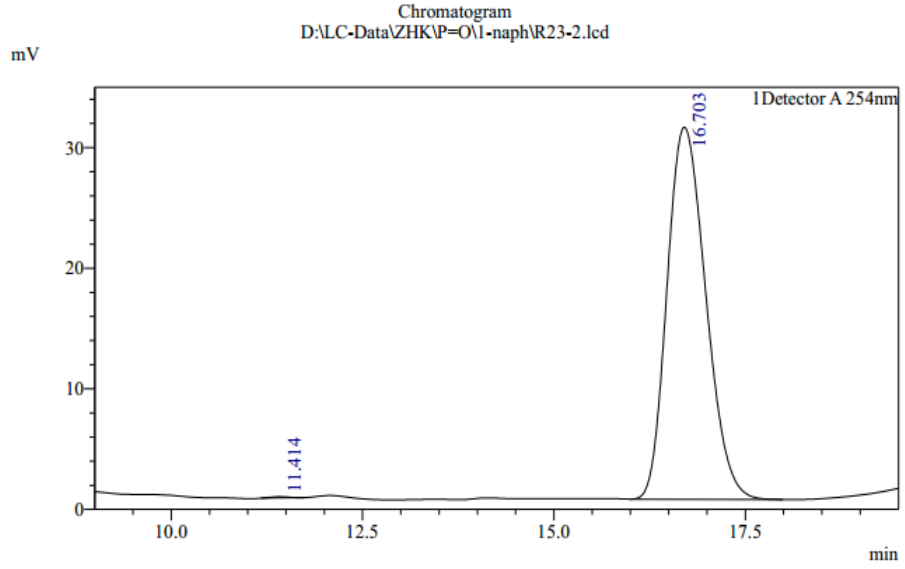


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	10.949	44066617	979623	59.823	50.576
2	17.095	43063403	657919	40.177	49.424
Total		87130020	1637542	100.000	100.000

Racemic **4k**



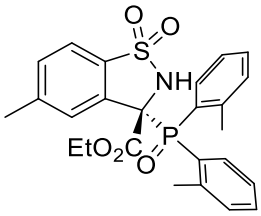
Peak Table

Detector A 254nm

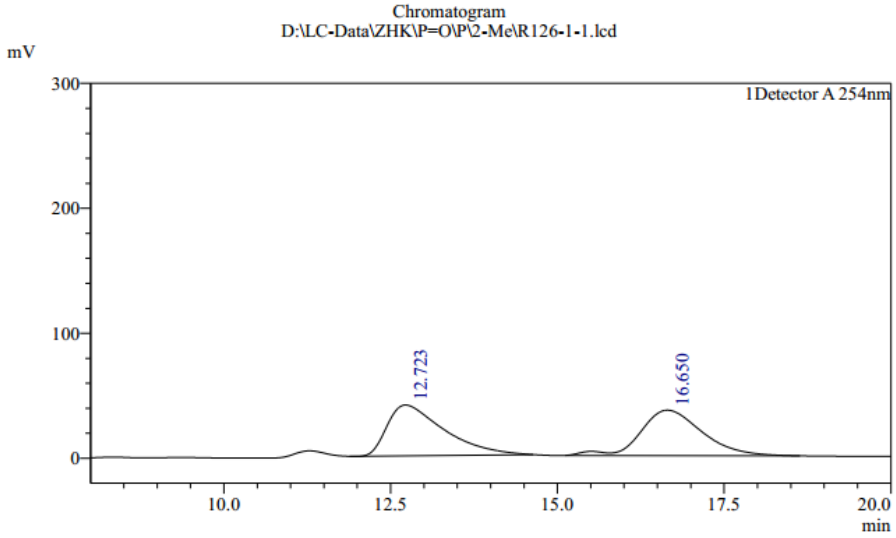
Peak#	Ret. Time	Area	Height	Height%	Area%
1	11.414	1567	101	0.326	0.144
2	16.703	1084544	30855	99.674	99.856
Total		1086111	30956	100.000	100.000

Enantiomerically enriched **4k**

(*S*)-ethyl 3-(di-o-tolylphosphoryl)-5-methyl-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (4l)



A white solid; m.p. = 171 - 173 °C; 44.4 mg, 92% yield; $[\alpha]^{25}_{D}$ = -41.00 (*c* 1.1, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.67 - 7.7.58 (m, 1H), 7.54 - 7.38 (m, 3H), 7.33 - 7.24 (m, 3H), 7.23 - 7.16 (m, 1H), 7.07 - 6.94 (m, 2H), 5.97 (d, *J* = 5.6 Hz, 1H), 4.36 - 4.23 (m, 2H), 2.51 (s, 3H), 2.42 (s, 3H), 1.98 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.12 (d, *J* = 3.1 Hz), 144.46 (d, *J* = 1.9 Hz), 144.05 (dd, *J* = 20.4, 9.0 Hz), 134.32 (d, *J* = 11.0 Hz), 132.84 (d, *J* = 11.2 Hz), 132.50 (dd, *J* = 7.3, 2.7 Hz), 132.27 (d, *J* = 1.3 Hz), 132.12 (d, *J* = 11.9 Hz), 131.98 (d, *J* = 1.6 Hz), 131.88 (d, *J* = 3.1 Hz), 130.43 (d, *J* = 10.4 Hz), 129.69, 129.44 (d, *J* = 2.3 Hz), 128.72, 126.70, 125.71, 125.49 (d, *J* = 12.2 Hz), 125.01 (d, *J* = 12.7 Hz), 121.10 (d, *J* = 1.3 Hz), 70.01 (d, *J* = 71.4 Hz), 64.73, 22.03, 21.71 (d, *J* = 3.8 Hz), 21.11 (d, *J* = 2.9 Hz), 13.84; ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.35; HRMS (ESI) m/z calcd for $C_{25}H_{26}NO_5PS$ $[M+H]^+$ = 484.1348, found = 484.1347; The ee value was >99%, t_R (minor) = 10.7 min, t_R (major) = 15.6min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

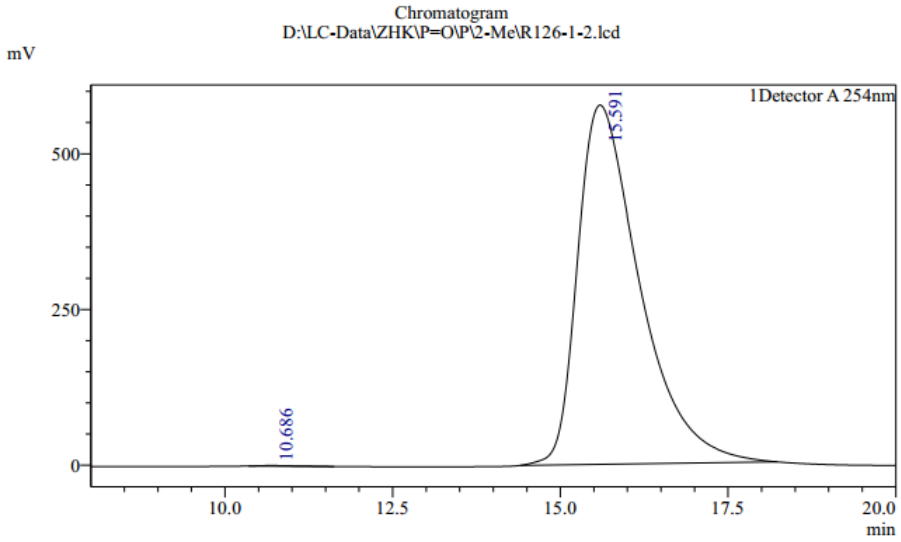


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	12.723	2400607	40620	52.767	50.685
2	16.650	2335744	36359	47.233	49.315
Total		4736351	76979	100.000	100.000

Racemic **4l**



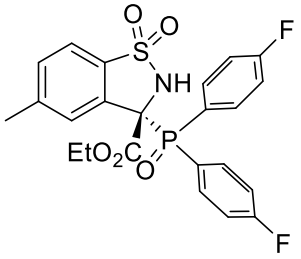
Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	10.686	38261	1022	0.177	0.103
2	15.591	37154116	576604	99.823	99.897
Total		37192377	577626	100.000	100.000

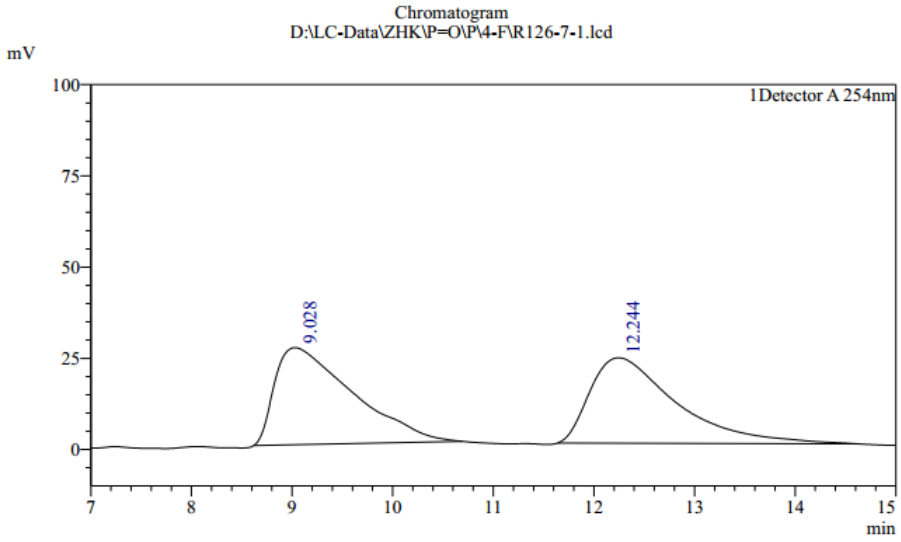
Enantiomerically enriched **4l**

(*S*)-ethyl -(bis(4-fluorophenyl)phosphoryl)-5-methyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (4m)



A white solid; m.p. = 163 - 167 ºC; 46.2 mg, 94% yield; $[\alpha]^{25}_{D}$ = -47.67 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 - 8.05 (m, 3H), 7.67 - 7.55 (m, 2H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.31 - 7.22 (m, 2H), 7.02 - 6.93 (m, 2H), 5.94 (d, *J* = 4.4 Hz, 1H), 4.32 - 4.15 (m, 2H), 2.53 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.17 (dd, *J* = 13.3, 3.3 Hz), 166.53 (d, *J* = 2.7 Hz), 164.63 (dd, *J* = 12.7, 3.5 Hz), 144.97 (d, *J* = 2.0 Hz), 135.27 (q, *J* = 9.8 Hz), 132.17 (d, *J* = 1.9 Hz), 131.82 (d, *J* = 3.2 Hz), 131.24 (d, *J* = 2.3 Hz), 128.38 (d, *J* = 2.6 Hz), 124.21 (d, *J* = 3.3 Hz), 123.23 (dd, *J* = 6.9, 3.6 Hz), 122.14 (d, *J* = 3.5 Hz), 121.18 (d, *J* = 1.6 Hz), 116.53 (dd, *J* = 21.3, 12.8 Hz), 115.90 (dd, *J* = 21.4, 13.5 Hz), 70.14 (d, *J* = 73.6 Hz), 64.78, 22.09, 14.01; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.92; ^{19}F NMR (376 MHz, $CDCl_3$) δ -

103.99; HRMS (ESI) m/z calcd for $C_{23}H_{20}NO_5PSF_2$ $[M+H]^+$ = 492.0846, found = 492.0849; The ee value was 94%, t_R (minor) = 9.8 min, t_R (major) = 13.2 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

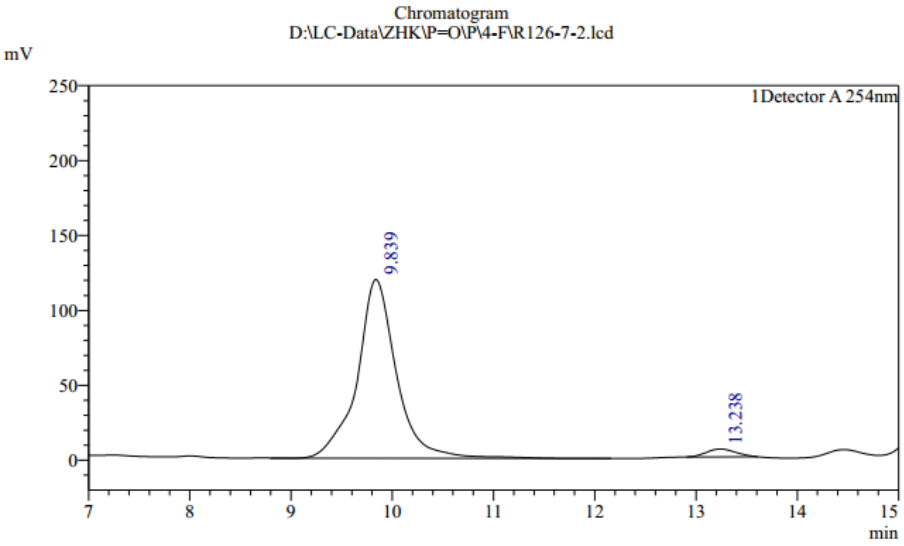


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	9.028	1426741	26615	53.224	50.596
2	12.244	1393144	23391	46.776	49.404
Total		2819885	50006	100.000	100.000

Racemic **4m**



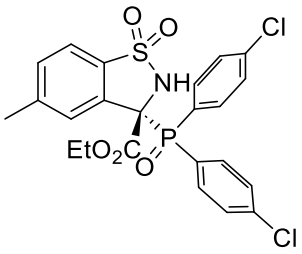
Peak Table

Detector A 254nm

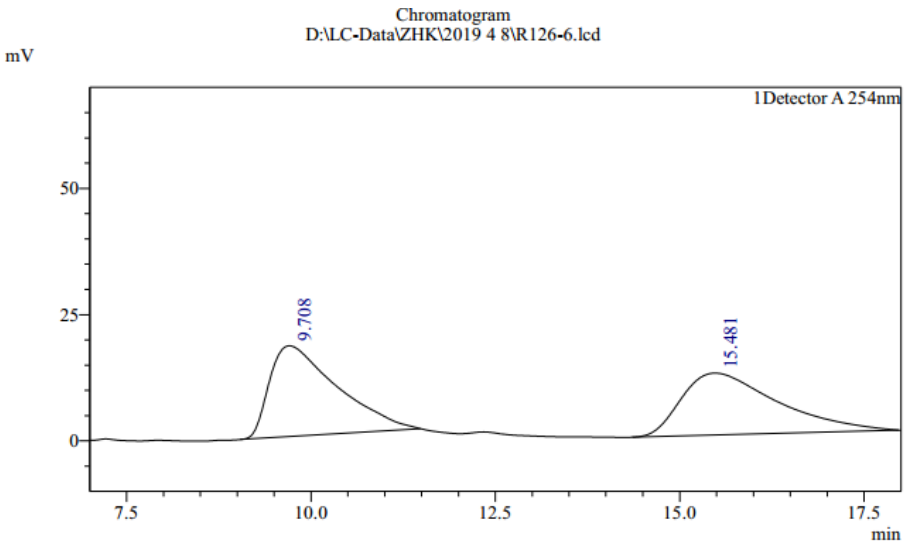
Peak#	Ret. Time	Area	Height	Height%	Area%
1	9.839	3219598	119272	95.810	96.836
2	13.238	105200	5216	4.190	3.164
Total		3324798	124488	100.000	100.000

Enantiomerically enriched **4m**

(*S*)-ethyl 3-(bis(4-chlorophenyl)phosphoryl)-5-methyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (4n)



A white solid; m.p. = 148 - 150 °C; 48.6 mg, 93% yield; $[\alpha]^{25}_{D}$ = -44.80 (*c* 1.4, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.06 - 7.97 (m, 2H), 7.59 - 7.47 (m, 5H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.30 - 7.22 (m, 2H), 6.05 (d, *J* = 4.0 Hz, 1H), 4.30 - 4.4.13 (m, 2H), 2.51 (s, 3H), 1.17 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.34 (d, *J* = 2.8 Hz), 144.97 (d, *J* = 1.9 Hz), 140.24 (d, *J* = 3.6 Hz), 139.94 (d, *J* = 3.6 Hz), 133.94 (dd, *J* = 19.6, 9.4 Hz), 132.18 (d, , *J* = 1.7 Hz), 131.76 (d, *J* = 3.3 Hz), 130.99 (d, *J* = 2.4 Hz), 129.36 (d, *J* = 12.4 Hz), 128.76 (d, *J* = 12.9 Hz), 128.32 (d, *J* = 2.5 Hz), 126.64, 125.66 (d, *J* = 2.2 Hz), 124.60, 121.18 (d, *J* = 1.6 Hz), 69.93 (d, *J* = 73.9 Hz), 64.75, 22.05, 13.97; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.89; HRMS (ESI) m/z calcd for $C_{23}H_{20}NO_5PSCl_2$ $[M+H]^+$ = 524.0255, found = 524.0253; The ee value was 99%, t_R (minor) = 8.6 min, t_R (major) = 15.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

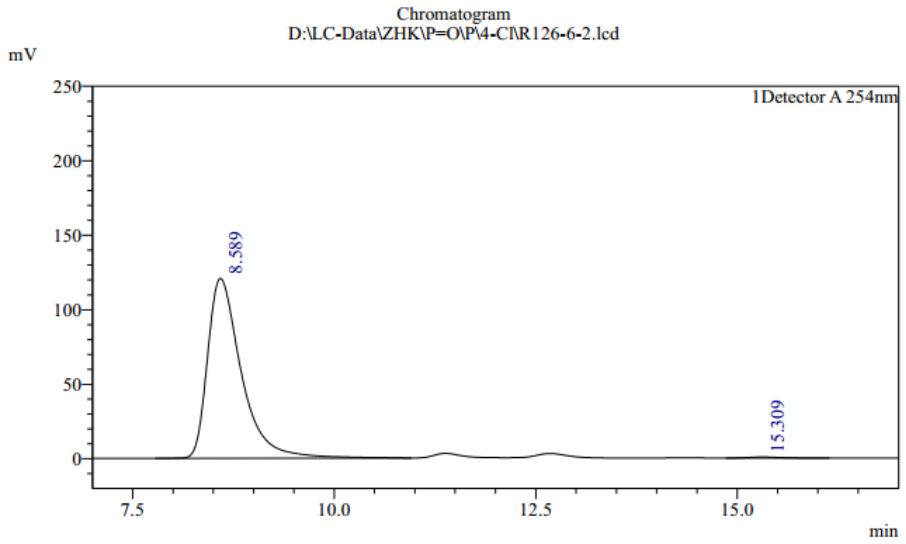


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	9.708	1137330	17981	59.456	50.661
2	15.481	1107634	12262	40.544	49.339
Total		2244964	30243	100.000	100.000

Racemic **4n**



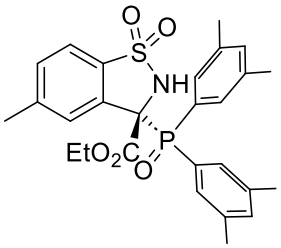
Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	8.589	3527411	120798	99.410	99.437
2	15.309	19958	717	0.590	0.563
Total		3547369	121515	100.000	100.000

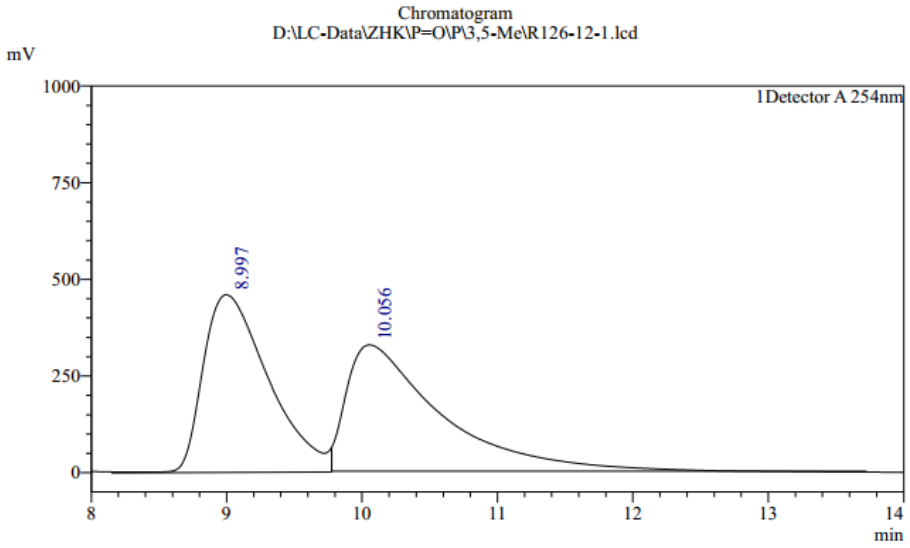
Enantiomerically enriched **4n**

(*S*)-ethyl 3-(bis(3,5-dimethylphenyl)phosphoryl)-5-methyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (4o)



A white solid; m.p. = 155 - 157 ºC; 47.0 mg, 92% yield; $[\alpha]^{25}_{D}$ = -35.00 (*c* 1.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.63 (d, *J* = 11.2 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.25 - 7.16 (m, 3H), 7.03 (s, 1H), 5.79 (d, *J* = 3.2 Hz, 1H), 4.31 - 4.13 (m, 2H), 2.50 (s, 3H), 2.39 (s, 6H), 2.18 (s, 6H), 1.16 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.73 (d, *J* = 2.9 Hz), 144.60 (d, *J* = 1.8 Hz), 138.53 (d, *J* = 12.5 Hz), 137.87 (d, *J* = 13.0 Hz), 134.82 (d, *J* = 3.0 Hz), 134.45 (d, *J* = 2.9 Hz), 131.84 (dd, *J* = 8.1, 2.5 Hz), 131.69 (d, *J* = 1.7 Hz), 130.25 (d, *J* = 8.6 Hz), 130.00 (d, *J* = 8.4 Hz), 128.52 (d, *J* = 2.5 Hz), 128.36, 127.34 (d, *J* = 11.3 Hz), 126.25, 120.77 (d, *J* = 1.4 Hz), 70.11 (d, *J* = 70.0 Hz), 64.38, 22.02, 21.52, 21.24, 13.89; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.24; HRMS (ESI) m/z calcd for $C_{27}H_{30}NO_5PS$ $[M+H]^+$ =

512.1661, found = 512.1162; The ee value was 96%, t_R (minor) = 9.8 min, t_R (major) = 12.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

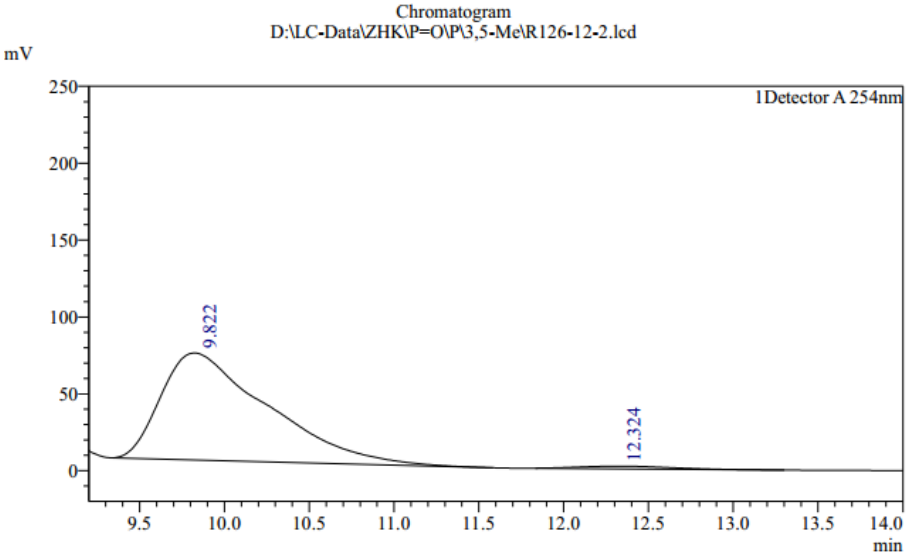


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	8.997	15426703	459541	58.455	49.477
2	10.056	15752627	326607	41.545	50.523
Total		31179330	786149	100.000	100.000

Racemic **4o**



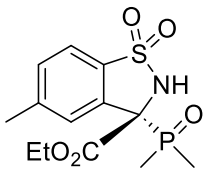
Peak Table

Detector A 254nm

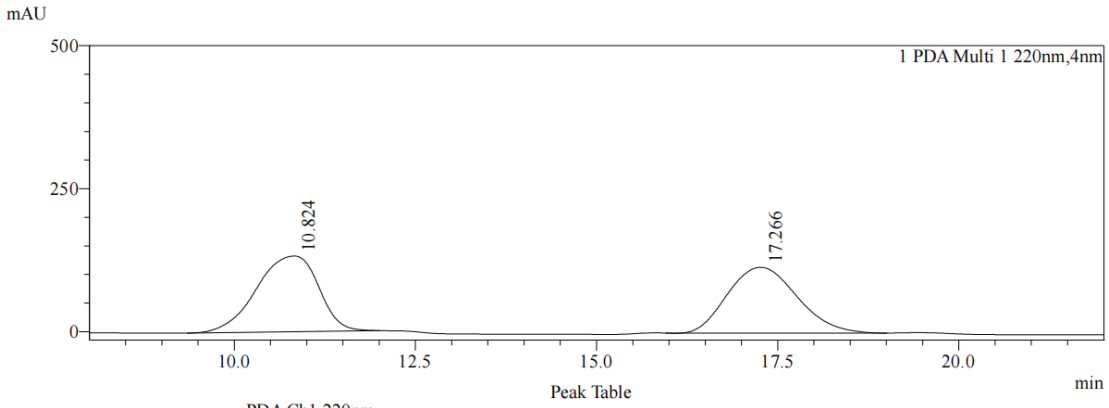
Peak#	Ret. Time	Area	Height	Height%	Area%
1	9.822	3052516	69569	97.583	97.925
2	12.324	64683	1723	2.417	2.075
Total		3117199	71292	100.000	100.000

Enantiomerically enriched **4o**

(*S*)-ethyl 3-(dimethylphosphoryl)-5-methyl-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (4p)



A white solid; m.p. = 94 - 97 °C; 31.4 mg, 95% yield; $[\alpha]^{25}_{D}$ = -10.68 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 4.49 - 4.36 (m, 2H), 2.52 (s, 3H), 1.63 (d, *J* = 12.8 Hz, 3H), 1.41 - 1.35 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.71 (d, *J* = 1.5 Hz), 145.35 (d, *J* = 1.6 Hz), 132.26 (d, *J* = 1.8 Hz), 131.74 (d, *J* = 3.0 Hz), 131.19 (d, *J* = 1.8 Hz), 127.97 (d, *J* = 2.2 Hz), 121.41 (d, *J* = 1.2 Hz), 68.74 (d, *J* = 67.8 Hz), 64.85, 22.12, 14.18, 13.25 (d, *J* = 68.4 Hz), 12.32 (d, *J* = 71.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 51.96; HRMS (ESI) m/z calcd for $C_{13}H_{18}NO_5PS$ $[M+Na]^+$ = 354.0541, found = 354.0546; The ee value was 96%, t_R (major) = 9.8 min, t_R (minor) = 17.3 min (Chiralcel IC, λ = 220 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min)

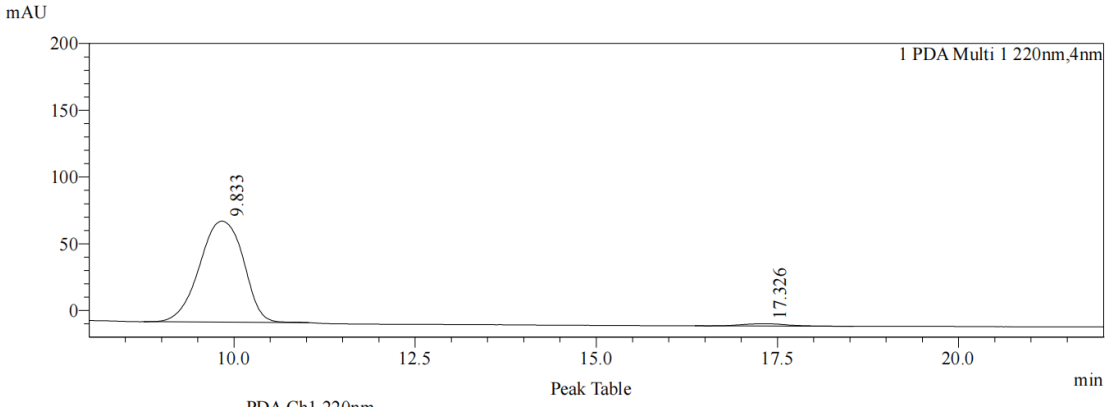


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	10.824	132325	53.501	7895435	50.692
2	17.266	115009	46.499	7679829	49.308
Total		247334	100.000	15575264	100.000

Racemic **4p**



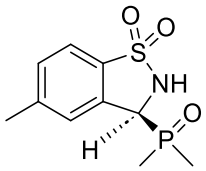
Peak Table

PDA Ch1 220nm

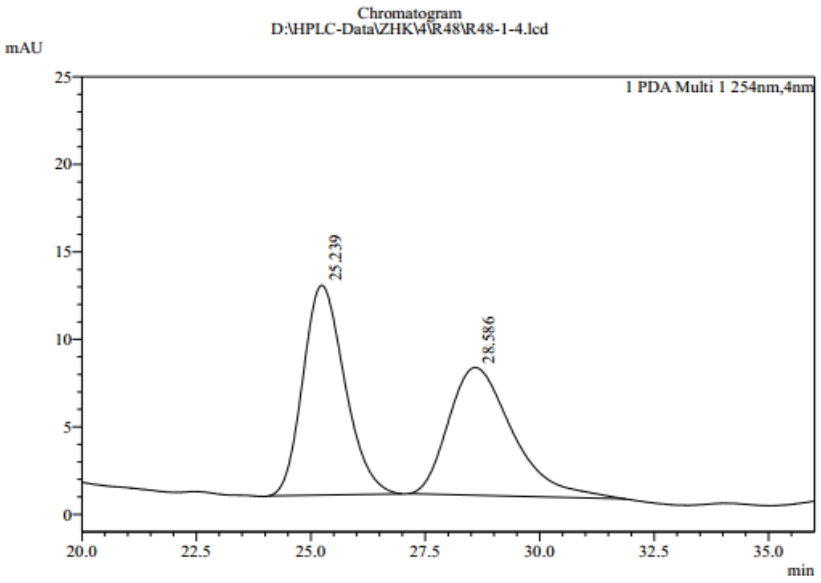
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.833	75626	97.827	3194965	97.795
2	17.326	1680	2.173	72039	2.205
Total		77306	100.000	3267005	100.000

Enantiomerically enriched **4p**

(*R*)-3-(dimethylphosphoryl)-5-methyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (4q)



A white solid; m.p. = 85 - 87 °C; 23.6 mg, 91% yield; $[\alpha]^{25}_{D}$ = -15.00 (*c* 1.0, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.54 (s, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 5.11 (d, *J* = 9.2 Hz, 1H), 2.44 (s, 3H), 1.58 (d, *J* = 13.2 Hz, 3H), 1.09 (d, *J* = 12.8 Hz, 3H); ^{13}C NMR (100 MHz, DMSO) δ 143.32 (d, *J* = 2.0 Hz), 134.05 (d, *J* = 2.3 Hz), 132.59 (d, *J* = 9.8 Hz), 130.64 (d, *J* = 1.4 Hz), 125.89 (d, *J* = 2.2 Hz), 120.79 (d, *J* = 1.3 Hz), 55.91 (d, *J* = 75.5 Hz), 21.28, 14.63 (d, *J* = 67.9 Hz), 10.65 (d, *J* = 67.4 Hz); ^{31}P NMR (162 MHz, DMSO) δ 46.20; HRMS (ESI) m/z calcd for $C_{10}H_{14}NO_3PS$ $[M+Na]^+$ = 282.0330, found = 282.0327; The ee value was 99%, t_R (minor) = 23.6 min, t_R (major) = 29.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

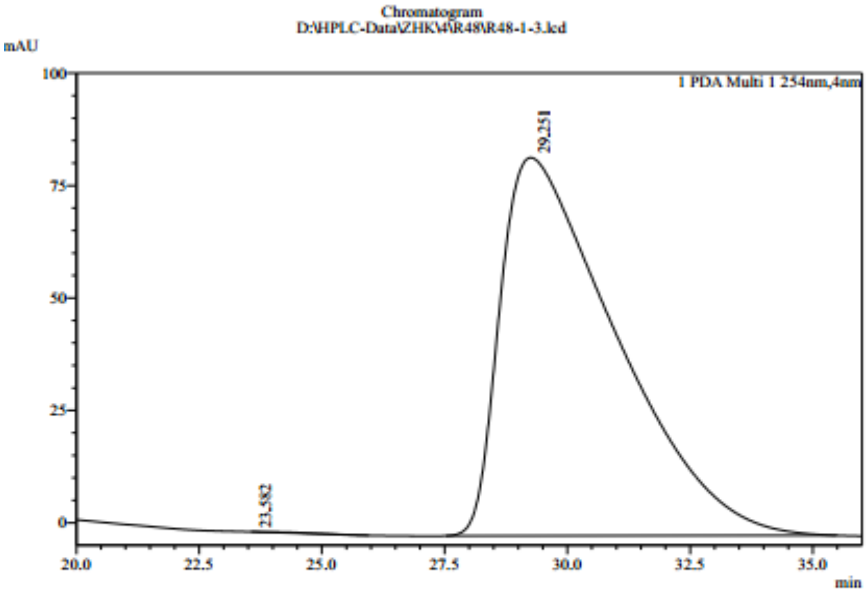


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	25.239	11983	62.126	762490	51.730
2	28.586	7305	37.874	711479	48.270
Total		19288	100.000	1473969	100.000

Racemic **4q**



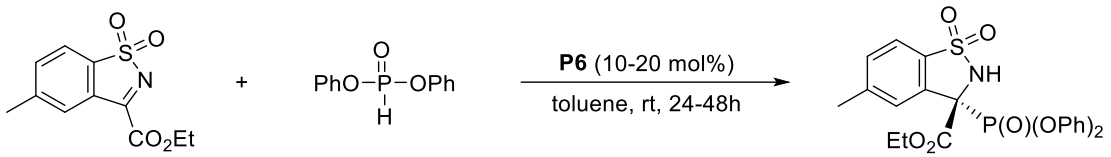
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	23.582	9	0.010	7928	0.057
2	29.251	84078	99.990	13823393	99.943
Total		84087	100.000	13831321	100.000

Enantiomerically enriched **4q**

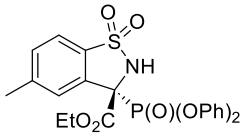
5.2 Representative procedure for asymmetric P-nucleophile addition to cyclic N-sulfonyl imines 1/1' with secondary phosphine oxides 3



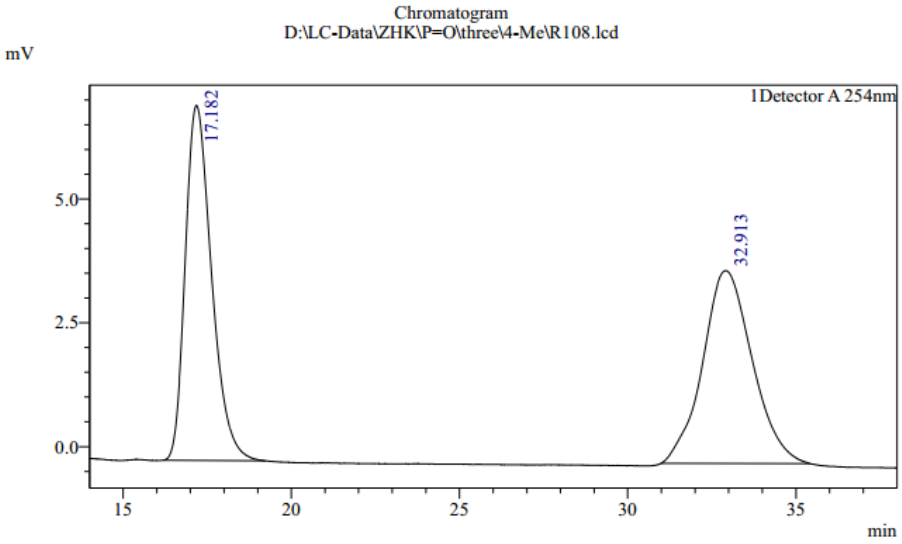
1a **3a** **5a**

Representative procedure 5a: To a flame-dried round bottle flask with a magnetic stirring bar were added cyclic ketimine **1a** (0.10 mmol, 25.3mg), Phosphine Oxide **3a** (0.12 mmol, 28.1 mg), phosphonium salt **P4** (0.01 mmol, 5.7 mg), and toluene (2.0 mL). The reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate = 3:1) to afford **5a** (93% yield) as a white solid.

(*S*)-ethyl 3-(diphenoxyphosphoryl)-5-methyl-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (5a)



A white solid; m.p. = 135 - 137 ^oC; 45.3 mg, 93% yield; $[\alpha]^{25}_D$ = -14.37 (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.95 - 7.87 (m, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.35 - 7.27 (m, 2H), 7.24 - 7.14 (m, 5H), 7.11 - 7.05 (m, 1H), 7.01 - 6.94 (m, 2H), 6.09 (d, *J* = 5.2 Hz, 1H), 4.46 - 4.24 (m, 2H), 2.44 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.36 (d, *J* = 4.5 Hz), 150.50 (d, *J* = 9.6 Hz), 150.18 (d, *J* = 10.0 Hz), 145.02 (d, *J* = 2.7 Hz), 132.46 (d, *J* = 2.6 Hz), 132.14 (d, *J* = 5.1 Hz), 130.25 (d, *J* = 4.3 Hz), 129.91 (d, *J* = 0.6 Hz), 129.71, 127.86 (d, *J* = 3.0 Hz), 125.89 (d, *J* = 1.0 Hz), 125.57 (d, *J* = 0.7 Hz), 121.59 (d, *J* = 2.2 Hz), 120.58 (d, *J* = 4.4 Hz), 120.17 (d, *J* = 4.4 Hz), 67.62 (d, *J* = 166.5 Hz), 65.04, 22.01, 13.97; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.32; HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_7PS$ $[M+Na]^+$ = 510.0747, found = 510.0740; The ee value was >99%, t_R (minor) = 17.9 min, t_R (major) = 31.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

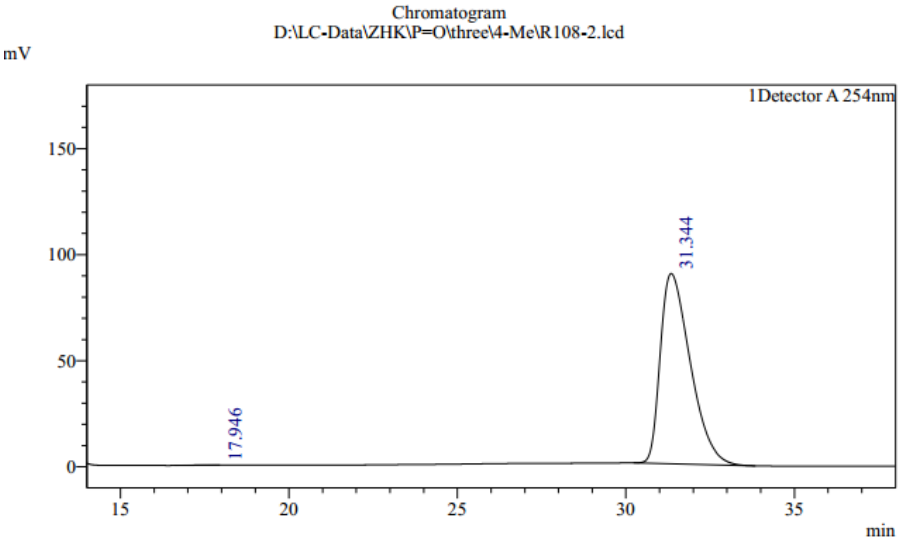


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	17.182	389504	7168	64.810	49.411
2	32.913	398787	3892	35.190	50.589
Total		788291	11060	100.000	100.000

Racemic **5a**



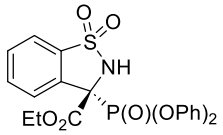
Peak Table

Detector A 254nm

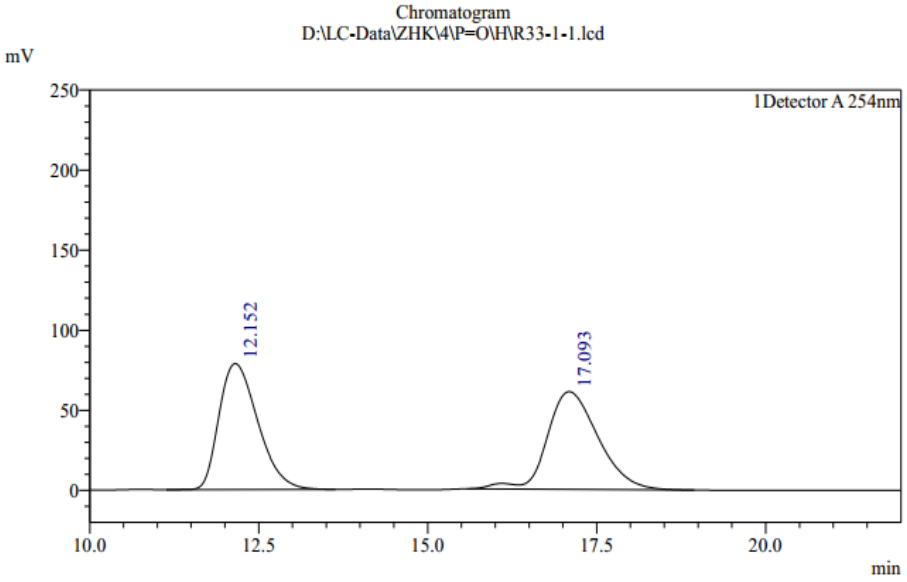
Peak#	Ret. Time	Area	Height	Height%	Area%
1	17.946	1867	0	0.000	0.034
2	31.344	5541532	89720	100.000	99.966
Total		5543398	89720	100.000	100.000

Enantiomerically enriched **5a**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (5b)



A white solid; m.p. = 98 - 100 °C; 45.4 mg, 96% yield; $[\alpha]^{25}_{D}$ = -32.18 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 - 8.11 (m, 1H), 7.88 - 7.79 (m, 1H), 7.72 -7.59 (m, 2H), 7.34 - 7.26 (m, 2H), 7.22 - 7.12 (m, 5H), 7.11 - 7.05 (m, 1H), 7.01 - 6.92 (m, 2H), 6.22 (d, *J* = 4.8 Hz, 1H), 4.40 - 4.27 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.27 (d, *J* = 4.5 Hz), 150.24 (dd, *J* = 26.7, 9.7 Hz), 134.79 (d, *J* = 5.0 Hz), 134.37 (d, *J* = 18.5 Hz), 133.71 (d, *J* = 2.7 Hz), 131.49 (d, *J* = 2.7 Hz), 130.00 (d, *J* = 4.5 Hz), 129.89 (d, *J* = 0.7 Hz), 129.74, 127.76 (d, *J* = 2.9 Hz), 125.89 (d, *J* = 1.0 Hz), 125.61 (d, *J* = 0.7 Hz), 121.84 (d, *J* = 2.2 Hz), 120.56 (d, *J* = 4.4 Hz), 120.15 (d, *J* = 4.4 Hz), 67.77 (d, *J* = 167.0 Hz), 65.10, 13.92; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.33; HRMS (ESI) m/z calcd for $C_{22}H_{20}NO_7PS$ $[M+Na]^+$ = 496.0590, found = 496.0588; The ee value was >99%, t_R (minor) = 12.8 min, t_R (major) = 16.2 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

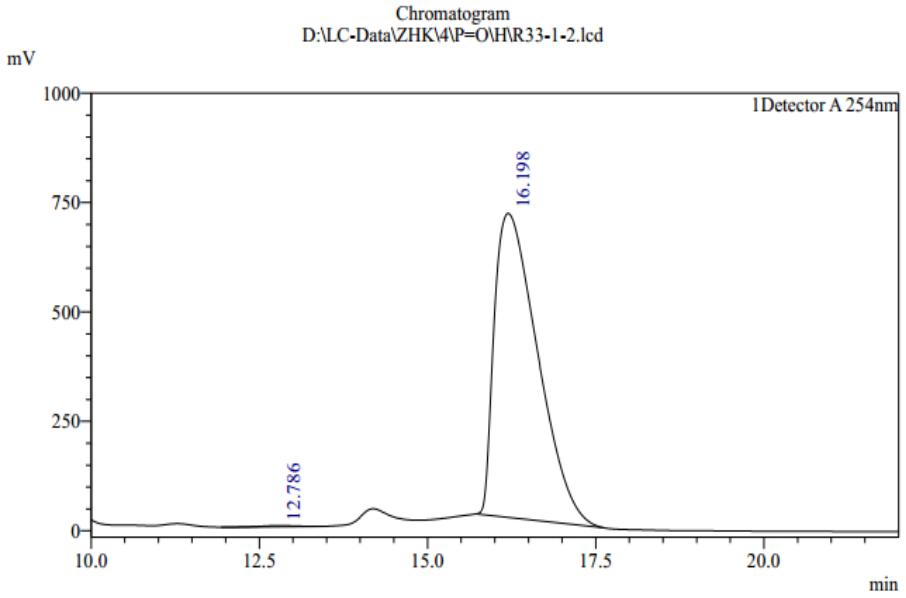


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	12.152	3144566	78698	56.327	49.474
2	17.093	3211375	61019	43.673	50.526
Total		6355941	139717	100.000	100.000

Racemic **5b**



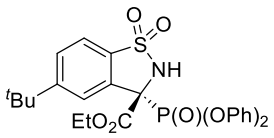
Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	12.786	75411	2330	0.334	0.242
2	16.198	31108919	694780	99.666	99.758
Total		31184329	697111	100.000	100.000

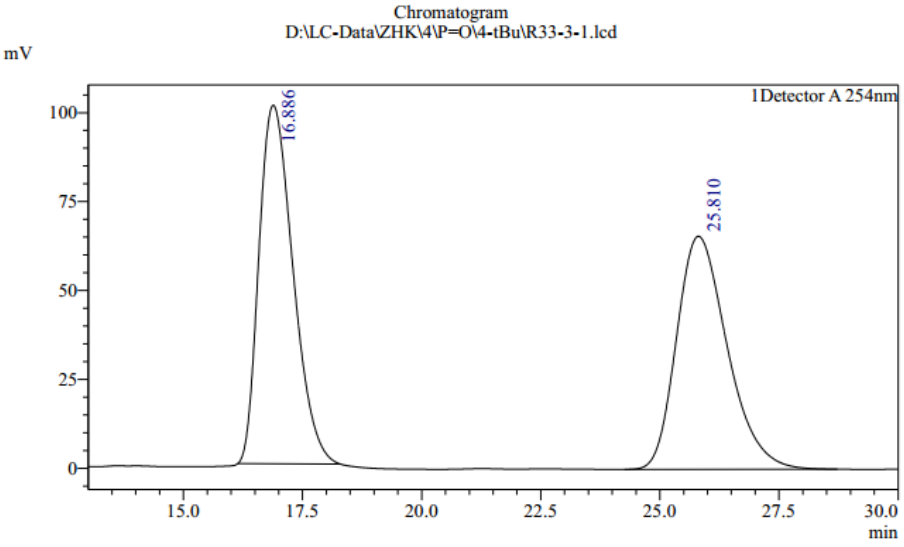
Enantiomerically enriched **5b**

(*S*)-ethyl 5-(tert-butyl)-3-(diphenoxyphosphoryl)-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (5c)



A white solid; m.p. = 106 - 107 ^{o}C; 48.7 mg, 92% yield; $[\alpha]^{25}_{D}$ = -45.17 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 - 8.11 (m, 1H), 7.75 (dd, *J* = 8.4, 0.4 Hz, 1H), 7.68 - 7.62 (m, 1H), 7.35 - 7.26 (m, 2H), 7.22 - 7.13 (m, 5H), 7.10 - 7.03 (m, 1H), 6.98 - 6.90 (m, 2H), 6.08 (s, 1H), 4.46 - 4.25 (m, 2H), 1.32 - 1.26 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.43 (d, *J* = 4.9 Hz), 158.11 (d, *J* = 2.4 Hz), 150.59 (d, *J* = 9.4 Hz), 150.14 (d, *J* = 10.0 Hz), 131.95 (d, *J* = 5.0 Hz), 129.94, 129.88, 129.67, 128.92 (d, *J* = 2.3 Hz), 125.93 (d, *J* = 0.9 Hz), 125.52, 124.85 (d, *J* = 3.0 Hz), 121.43 (d, *J* = 2.1 Hz), 120.63 (d, *J* = 4.4 Hz), 120.15 (d, *J* = 4.4 Hz), 67.73 (d, *J* = 166.1 Hz), 64.92, 35.70, 31.17, 14.01; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.41; HRMS (ESI) m/z calcd for $C_{26}H_{28}NO_7PS$ $[M+Na]^+$ = 552.1222, found = 552.1226; The ee value was >99%, t_R

(major) = 16.6 min, t_R (minor) = 25.5 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

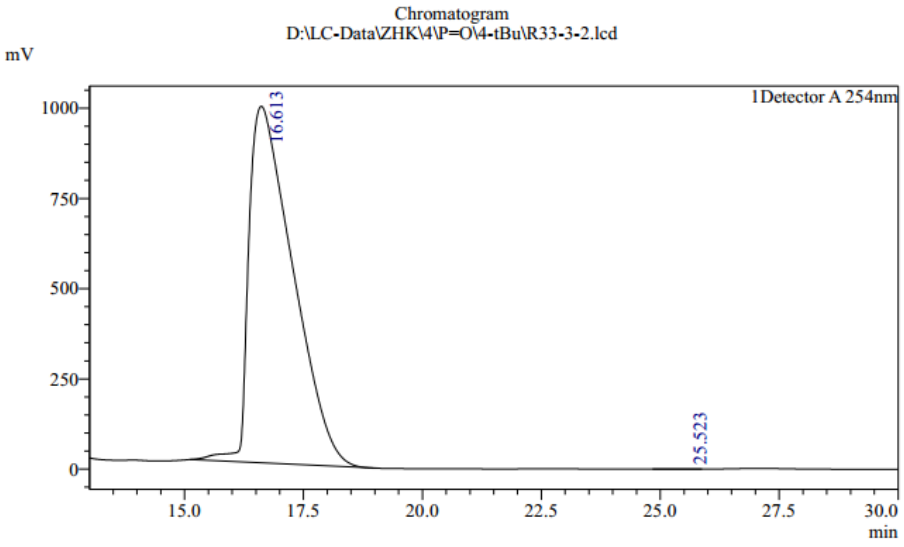


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	16.886	5003271	100797	60.600	50.801
2	25.810	4845440	65535	39.400	49.199
Total		9848712	166332	100.000	100.000

Racemic **5c**



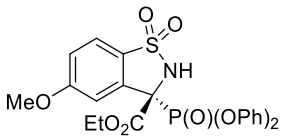
Peak Table

Detector A 254nm

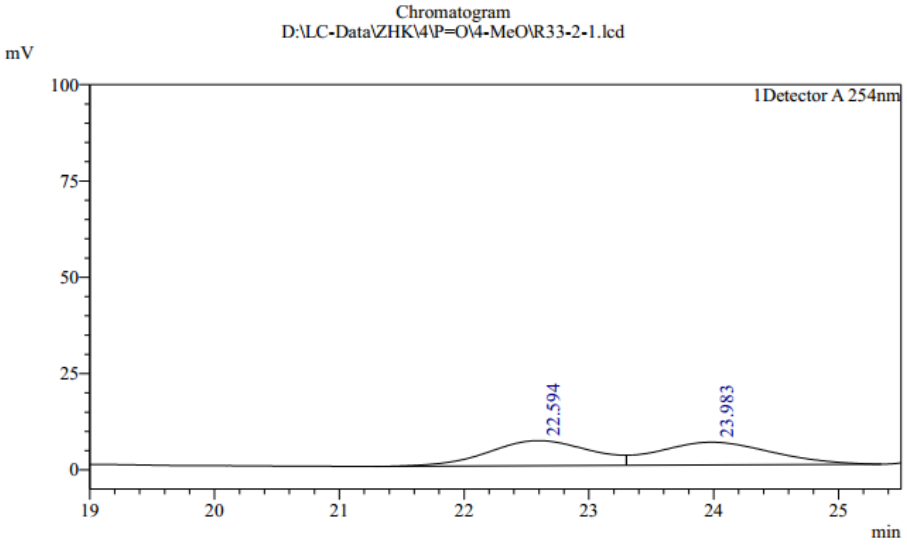
Peak#	Ret. Time	Area	Height	Height%	Area%
1	16.613	63677188	988092	99.988	99.993
2	25.523	4254	123	0.012	0.007
Total		63681442	988215	100.000	100.000

Enantiomerically enriched **5c**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-5-methoxy-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (5d)



A white solid; m.p. = 107 - 110 °C; 48.8 mg, 97% yield; $[\alpha]^{25}_{D}$ = -16.67 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.58 - 7.52(m, 1H), 7.34 - 7.29 (m, 2H), 7.23 - 7.16 (m, 5H), 7.14 - 7.08 (m, 2H), 7.04 - 6.98 (m, 2H), 6.05 (s, 1H), 4.41 - 4.28 (m, 2H), 3.84 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.26 (d, *J* = 4.3 Hz), 163.87 (d, *J* = 2.5 Hz), 150.55 (d, *J* = 9.8 Hz), 150.19 (d, *J* = 9.6 Hz), 132.54 (d, *J* = 4.4 Hz), 129.86 (d, *J* = 19.5Hz), 126.80 (d, *J* = 4.9 Hz), 125.95, 125.63, 123.16 (d, *J* = 2.1 Hz), 120.96, 120.61 (d, *J* = 4.4 Hz), 120.22 (d, *J* = 4.4 Hz), 118.78 (d, *J* = 2.3 Hz), 111.55 (d, *J* = 2.7 Hz), 67.46 (d, *J* = 166.3 Hz), 65.08, 56.16, 14.02; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.22; HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_8PS$ $[M+Na]^+$ = 526.0696, found = 526.0691; The ee value was >99%, t_R (minor) = 20.8 min, t_R (major) = 24.2 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

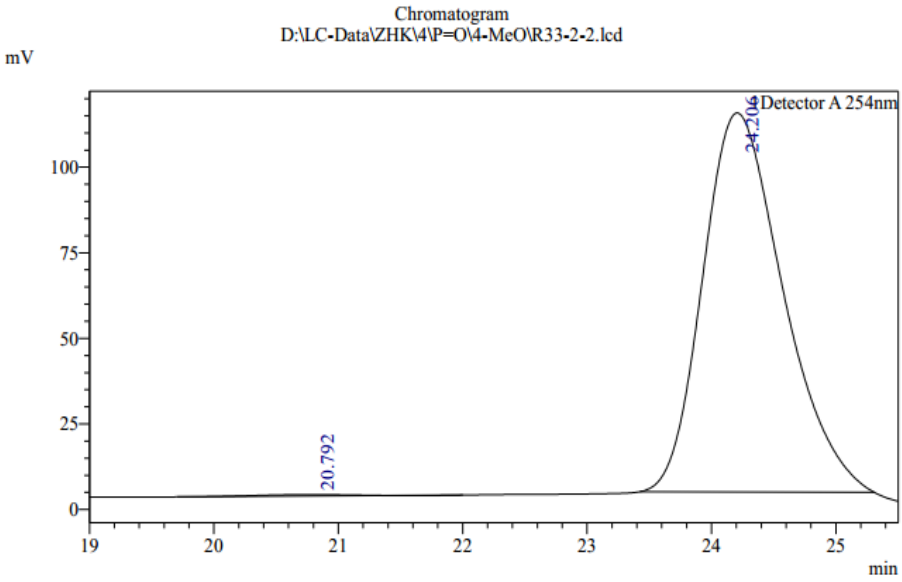


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	22.594	373113	6514	52.509	49.991
2	23.983	373254	5891	47.491	50.009
Total		746367	12405	100.000	100.000

Racemic **5d**



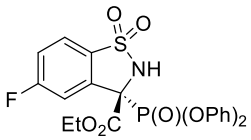
Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	20.792	21146	417	0.375	0.424
2	24.206	4961653	110722	99.625	99.576
Total		4982799	111139	100.000	100.000

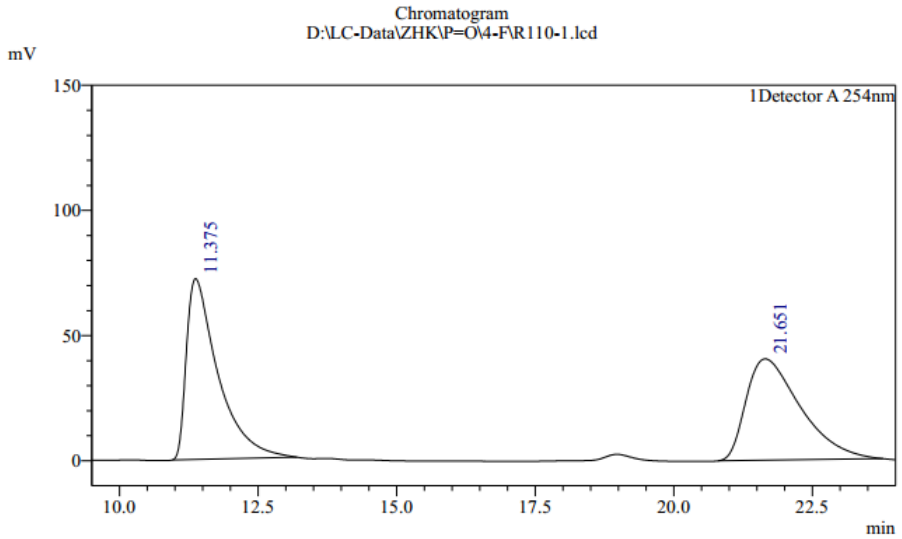
Enantiomerically enriched **5d**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-5-fluoro-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (5e)



A white solid; m.p. = 105 - 107 °C; 46.2 mg, 94% yield; $[\alpha]^{25}_{D}$ = -42.37 (*c* 0.9, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 - 7.78 (m, 2H), 7.37 - 7.27 (m, 3H), 7.25 - 7.09 (m, 6H), 7.07 - 7.01 (m, 2H), 6.35 (d, *J* = 4.4 Hz, 1H), 4.39 - 4.30 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.72 (d, *J* = 3.2 Hz), 164.75 (d, *J* = 3.9 Hz), 164.17 (d, *J* = 3.1 Hz), 150.14 (dd, *J* = 25.6, 9.6 Hz), 133.14 (dd, *J* = 10.3, 4.6 Hz), 130.86 (dd, *J* = 4.9, 2.7 Hz), 129.93 (d, *J* = 0.6 Hz), 129.85, 125.89 (dd, *J* = 19.5, 1.0 Hz), 124.04 (dd, *J* = 10.0, 2.3 Hz), 120.48 (d, *J* = 4.4 Hz), 120.08 (d, *J* = 4.4 Hz), 119.72 (d, *J* = 2.4 Hz), 119.48 (d, *J* = 2.4 Hz), 115.22 (d, *J* = 2.7 Hz), 114.96 (d, *J* = 2.7 Hz), 67.26 (dd, *J* = 167.0, 2.2 Hz), 65.37, 13.89; ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.64; ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.22; HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_7PSF$ $[M+Na]^+$ = 514.0491, found = 514.0487; The ee value was >99%, t_R (minor) = 12.8

min, t_R (major) = 20.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

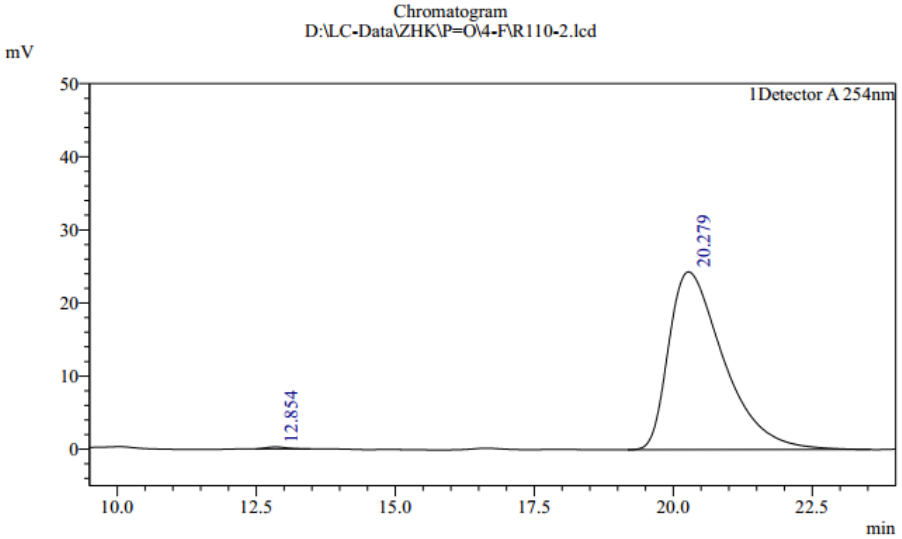


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	11.375	2866751	72190	64.055	50.875
2	21.651	2768088	40510	35.945	49.125
Total		5634839	112700	100.000	100.000

Racemic **5e**



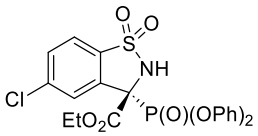
Peak Table

Detector A 254nm

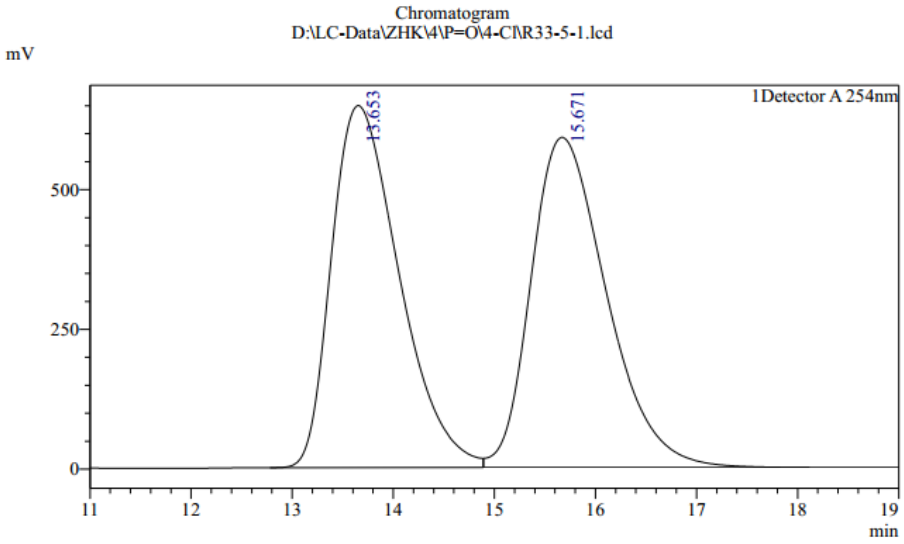
Peak#	Ret. Time	Area	Height	Height%	Area%
1	12.854	6244	257	1.044	0.371
2	20.279	1678689	24328	98.956	99.629
Total		1684933	24584	100.000	100.000

Enantiomerically enriched **5e**

(*S*)-ethyl 5-chloro-3-(diphenoxyphosphoryl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (5f)



A white solid; m.p. = 92 - 94 °C; 48.2 mg, 95% yield; $[\alpha]^{25}_{D}$ = -31.83 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 - 8.09 (m, 1H), 7.80 - 7.72 (m, 1H), 7.61 - 7.58 (m, 1H), 7.31 - 7.28 (m, 2H), 7.27 - 7.20 (m, 2H), 7.20 - 7.10 (m, 4H), 7.08 - 7.02 (m, 2H), 4.42 - 4.30 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.70 (d, *J* = 3.8 Hz), 150.28 (d, *J* = 9.5 Hz), 150.02 (d, *J* = 10.1 Hz), 140.24 (d, *J* = 3.2 Hz), 133.23 (d, *J* = 4.9 Hz), 132.02 (d, *J* = 4.5 Hz), 131.93 (d, *J* = 2.7 Hz), 129.83 (d, *J* = 7.7 Hz), 127.86 (d, *J* = 2.8 Hz), 125.92, 125.72, 122.87 (d, *J* = 2.2 Hz), 120.39 (d, *J* = 4.4 Hz), 119.98 (d, *J* = 4.4 Hz), 67.27 (d, *J* = 165.8 Hz), 65.34, 13.85; ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.44; HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_7PSCl$ $[M+Na]^+$ = 530.0192, found = 530.0195; The ee value was 98%, t_R (minor) = 13.0 min, t_R (major) = 16.8 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

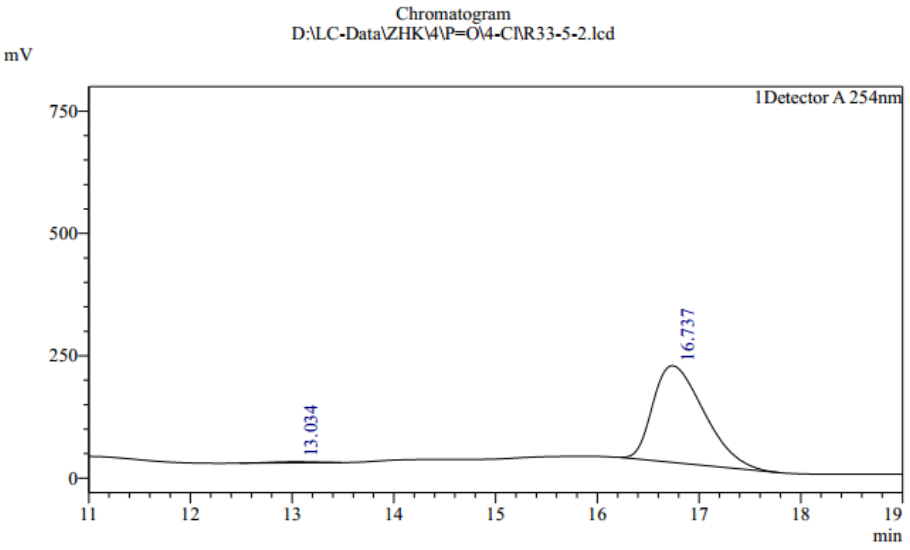


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.653	30154226	647798	52.306	49.565
2	15.671	30683470	590679	47.694	50.435
Total		60837695	1238477	100.000	100.000

Racemic **5f**



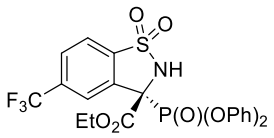
Peak Table

Detector A 254nm

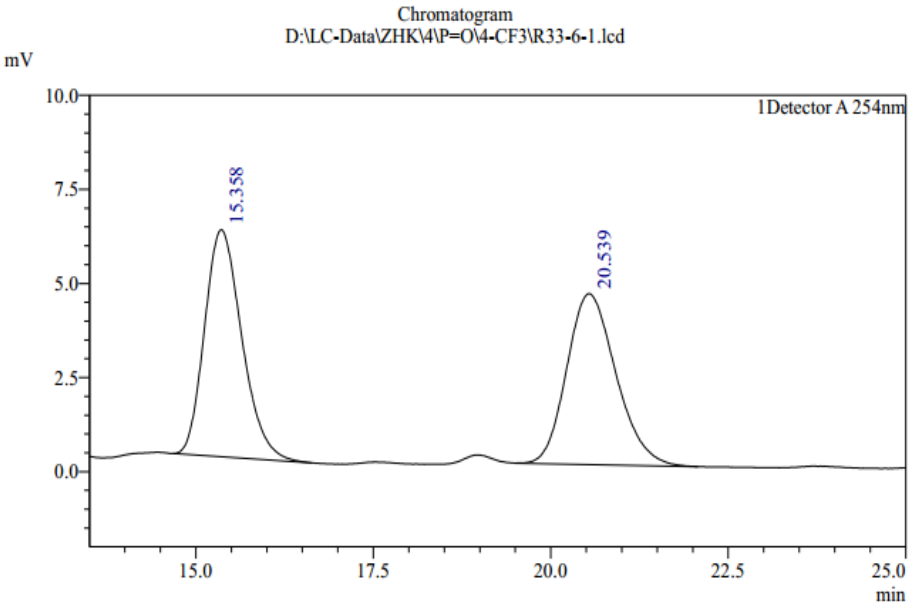
Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.034	63764	2000	1.003	0.916
2	16.737	6895016	197399	98.997	99.084
Total		6958779	199399	100.000	100.000

Enantiomerically enriched **5f**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-5-(trifluoromethyl)-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (5g)



A white solid; m.p. = 96 - 98 °C; 50.9 mg, 94% yield; $[\alpha]^{25}_{D}$ = -45.00 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (s, 1H), 7.99 - 7.86 (m 2H), 7.36 - 7.28 (m, 2H), 7.26 - 7.10 (m, 6H), 7.08 - 7.02 (m, 2H), 6.17 (s, 1H), 4.53 - 4.20 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.64 (d, *J* = 3.4 Hz), 150.41 (d, *J* = 9.6 Hz), 150.09 (d, *J* = 10.1 Hz), 137.97 (d, *J* = 4.8 Hz), 135.96 (d, *J* = 2.5 Hz), 135.63 (d, *J* = 2.5 Hz), 131.36 (d, *J* = 4.5 Hz),, 129.99 (d, *J* = 6.2 Hz), 128.72 (dd, *J* = 6.4, 3.0 Hz), 126.11 (d, *J* = 0.8 Hz), 125.89, 125.44 (dd, *J* = 7.2, 3.2 Hz), 124.25 (d, *J* = 2.8 Hz), 122.81 (d, *J* = 2.1 Hz), 120.45 (d, *J* = 4.4 Hz), 119.93 (d, *J* = 4.6 Hz), 67.65 (d, *J* = 165.2 Hz), 65.58, 13.90; ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.05; HRMS (ESI) m/z calcd for $C_{23}H_{19}NO_7PSF_3$ $[M+Na]^+$ = 564.0530, found = 564.0536; The ee value was 94%, t_R (minor) = 16.5 min, t_R (major) = 19.7 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

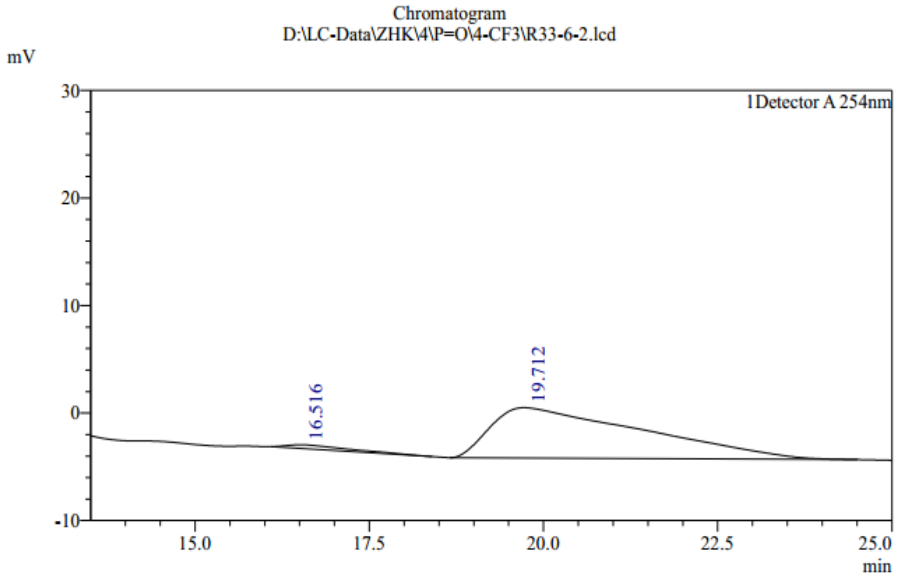


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	15.358	220482	6031	57.051	50.182
2	20.539	218887	4540	42.949	49.818
Total		439369	10571	100.000	100.000

Racemic **5g**



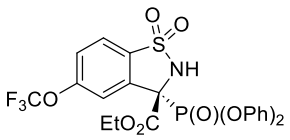
Peak Table

Detector A 254nm

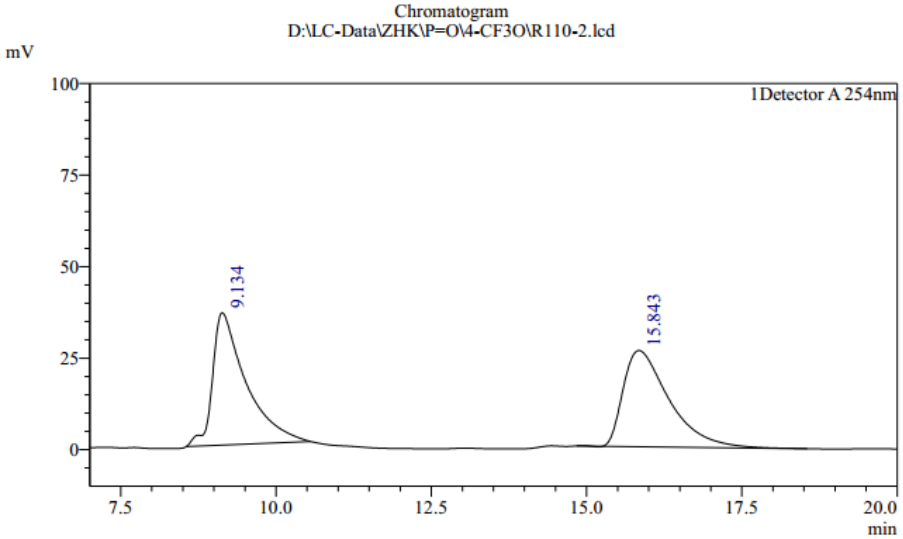
Peak#	Ret. Time	Area	Height	Height%	Area%
1	16.516	23749	345	6.855	3.205
2	19.712	717134	4682	93.145	96.795
Total		740883	5027	100.000	100.000

Enantiomerically enriched **5g**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-5-(trifluoromethoxy)-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (5h)



A white solid; m.p. = 85 - 88 °C; 50.1 mg, 90% yield; $[\alpha]^{25}_{D}$ = -31.67 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 - 8.01 (m, 1H), 7.89 - 8.85 (m, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.38 - 7.01 (m, 10H), 6.43 (d, *J* = 4.8 Hz, 1H), 4.43 - 4.27 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.61 (d, *J* = 3.8 Hz), 152.63 (dd, *J* = 3.0, 1.9 Hz), 150.13 (dd, *J* = 28.7, 9.6 Hz), 132.99 (d, *J* = 4.9 Hz), 132.71 (d, *J* = 4.6 Hz), 130.12 (d, *J* = 1.0 Hz), 129.92 (d, *J* = 0.6 Hz), 129.83, 129.46, 125.99 (d, *J* = 0.9 Hz), 125.79, 124.13, 123.69 (d, *J* = 2.2 Hz), 121.49, 120.61 (d, *J* = 4.9 Hz), 120.45 (d, *J* = 4.5 Hz), 119.97 (d, *J* = 4.5 Hz), 119.90, 118.90, 116.32, 115.39, 68.11 (dd, *J* = 165.4 Hz), 65.38, 13.75; ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.39; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.87; HRMS (ESI) m/z calcd for $C_{23}H_{19}NO_8PSF_3$ $[M+Na]^+$ = 580.0408, found = 580.0400; The ee value was >99%, t_R (minor) = 9.8 min, t_R (major) = 16.7 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

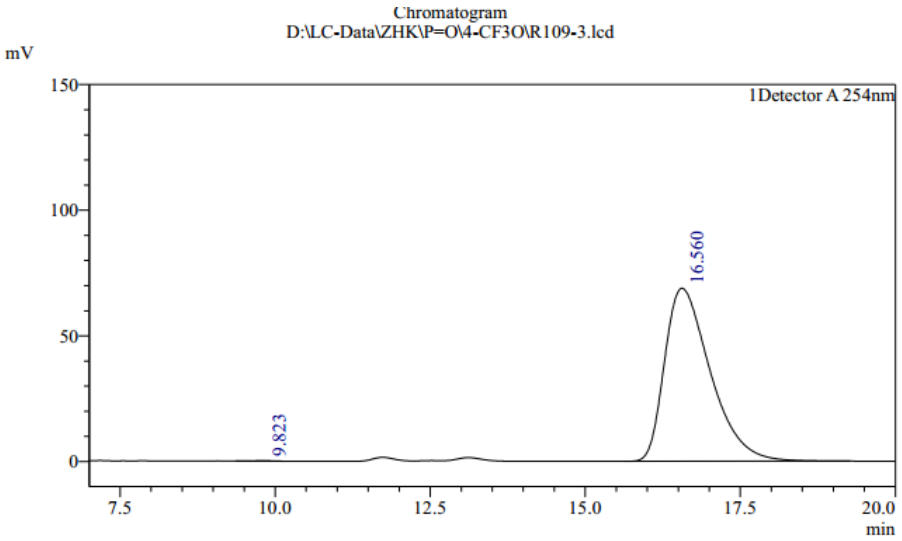


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	9.134	1353193	36130	57.923	50.099
2	15.843	1347839	26246	42.077	49.901
Total		2701032	62376	100.000	100.000

Racemic **5h**



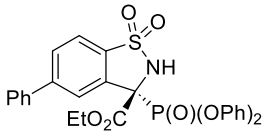
Peak Table

Detector A 254nm

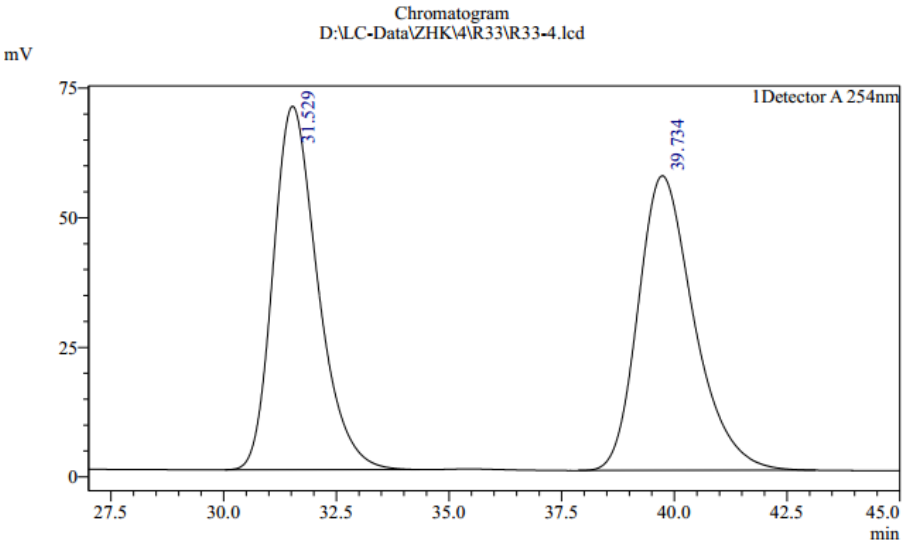
Peak#	Ret. Time	Area	Height	Height%	Area%
1	9.823	3082	136	0.197	0.087
2	16.560	3536166	68881	99.803	99.913
Total		3539248	69017	100.000	100.000

Enantiomerically enriched **5h**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-5-phenyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (5i)



A white solid; m.p. = 106 - 107 °C; 51.6 mg, 94% yield; $[\alpha]^{25}_{D}$ = -38.17 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 - 8.28 (m, 1H), 7.92 - 7.79 (m, 2H), 7.55 - 7.40 (m, 5H), 7.37 - 7.29 (m, 2H), 7.23 - 7.12 (m, 5H), 7.069 - 7.03 (m, 1H), 7.02 - 6.97 (m, 2H), 6.14 (d, *J* = 3.6 Hz, 1H), 4.48 - 4.21 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.30 (d, *J* = 4.3 Hz), 150.53 (d, *J* = 9.6 Hz), 150.20 (d, *J* = 9.9 Hz), 147.29 (d, *J* = 2.5 Hz), 138.83, 133.31 (d, *J* = 4.9 Hz), 130.75 (d, *J* = 4.3 Hz), 130.59 (d, *J* = 2.6 Hz), 129.99, 129.75, 129.30, 129.05, 127.67, 126.27 (d, *J* = 2.9 Hz), 125.99, 125.66, 122.20 (d, *J* = 2.0 Hz), 120.61 (d, *J* = 4.4 Hz), 120.17 (d, *J* = 4.5 Hz), 67.77 (d, *J* = 165.6 Hz), 65.18, 14.07; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.19; HRMS (ESI) m/z calcd for $C_{28}H_{24}NO_7PS$ $[M+Na]^+$ = 572.0898, found = 572.0899; The ee value was 98%, t_R (minor) = 30.1 min, t_R (major) = 40.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

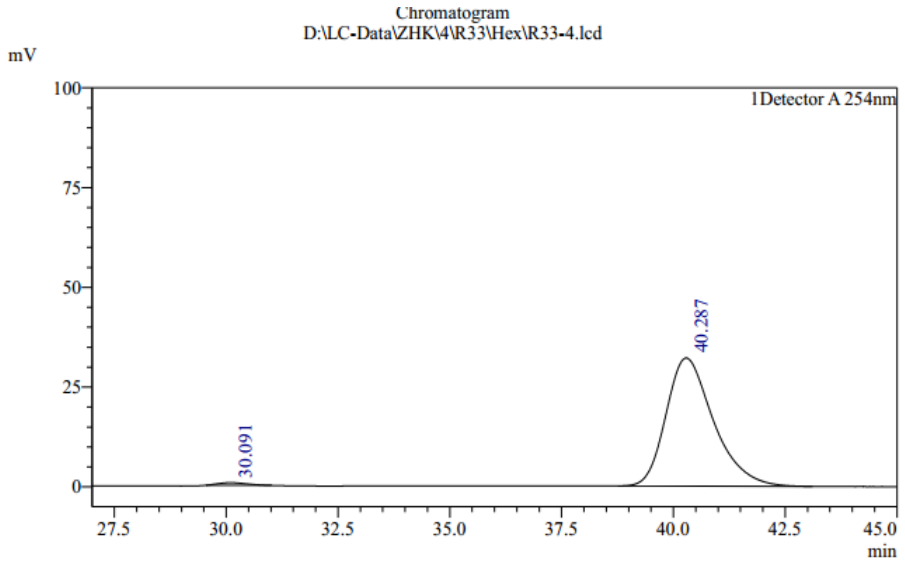


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	31.529	4832525	70114	55.230	49.665
2	39.734	4897674	56835	44.770	50.335
Total		9730199	126949	100.000	100.000

Racemic **5i**



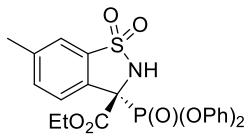
Peak Table

Detector A 254nm

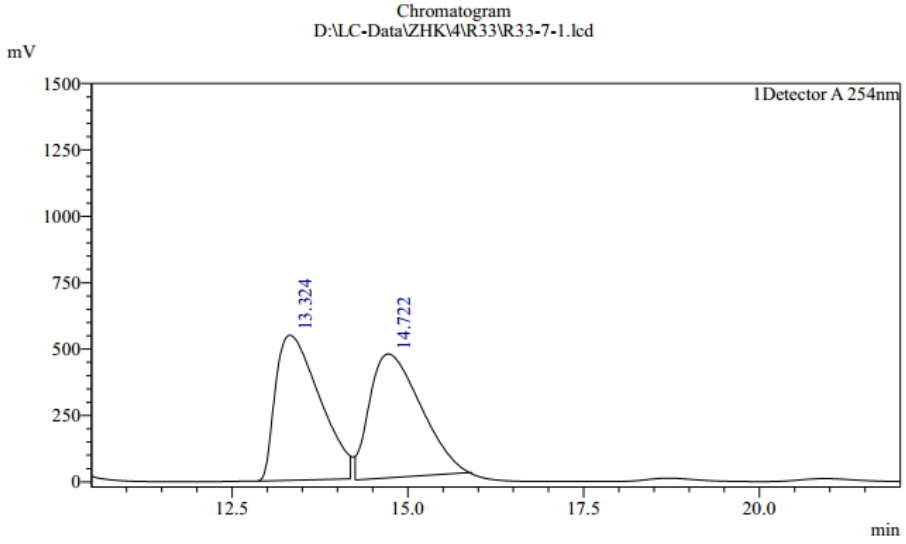
Peak#	Ret. Time	Area	Height	Height%	Area%
1	30.091	29579	662	2.021	1.230
2	40.287	2374886	32107	97.979	98.770
Total		2404466	32769	100.000	100.000

Enantiomerically enriched **5i**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-6-methyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (5j)



A white solid; m.p. = 98 - 99 °C; 45.8 mg, 94% yield; $[\alpha]^{25}_{D}$ = -33.47 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.62 (s, 1H), 7.48 (d, *J* = 8.0 Hz, 1H), 7.33 - 7.27 (m, 2H), 7.24 - 7.07 (m, 6H), 7.02 - 6.96 (m, 2H), 6.07 (d, *J* = 4.8 Hz, 1H), 4.40- 4.25 (m, 2H), 2.47 (d, *J* = 1.6 Hz, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.50 (d, *J* = 4.9 Hz), 150.47 (d, *J* = 9.5 Hz), 150.22 (d, *J* = 10.1 Hz), 142.53 (d, *J* = 2.8 Hz), 134.90 (d, *J* = 5.0 Hz), 134.86 (d, *J* = 2.6 Hz), 129.91, 129.77, 127.43 (d, *J* = 2.8 Hz), 127.31 (d, *J* = 4.8 Hz), 125.88, 125.58, 121.82 (d, *J* = 2.1 Hz), 120.63 (d, *J* = 4.4 Hz), 120.26 (d, *J* = 4.7 Hz), 67.61 (d, *J* = 167.6 Hz), 65.03, 21.46, 13.99; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.51; HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_7PS$ $[M+Na]^+$ = 510.0741, found = 510.0746; The ee value was >99%, t_R (minor) = 12.7 min, t_R (major) = 14.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

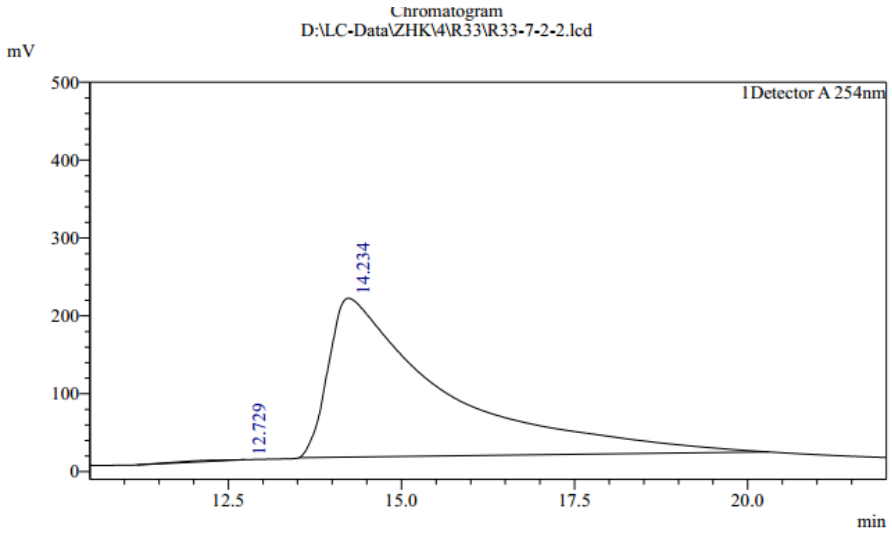


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.324	23895413	547220	53.967	50.255
2	14.722	23652744	466778	46.033	49.745
Total		47548157	1013997	100.000	100.000

Racemic **5j**



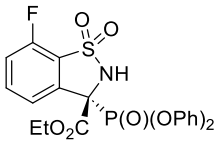
Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	12.729	84291	2	0.001	0.358
2	14.234	23453293	204022	99.999	99.642
Total		23537583	204024	100.000	100.000

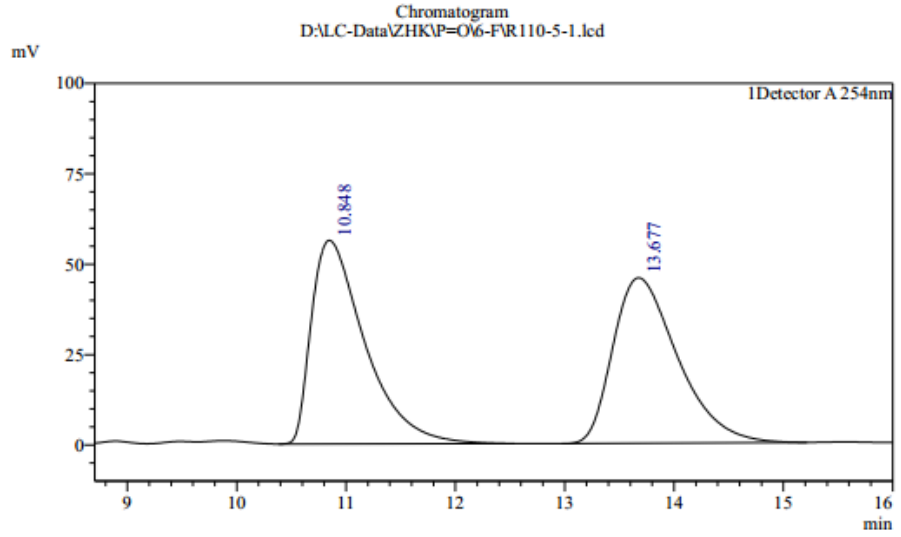
Enantiomerically enriched **5j**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-7-fluoro-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (5k)



A white solid; m.p. = 85 - 86 °C; 45.7 mg, 93% yield; $[\alpha]^{25}_{D}$ = -12.33 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 - 7.92 (m, 1H), 7.70 - 7.63 (m, 1H), 7.34 - 7.08 (m, 9H), 7.06 - 7.00 (m, 2H), 6.28 (d, *J* = 5.2 Hz, 1H), 4.38 - 4.29 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.91 (d, *J* = 3.8 Hz), 157.71 (d, *J* = 2.3 Hz), 155.13 (d, *J* = 2.2 Hz), 150.21 (dd, *J* = 29.6, 9.6 Hz), 136.19 (dd, *J* = 7.2, 2.7 Hz), 133.03 (dd, *J* = 3.9 1.5 Hz), 129.96 (d, *J* = 0.6 Hz), 129.85, 126.01 (d, *J* = 1.0 Hz), 125.75 (d, *J* = 0.8 Hz), 123.70 (d, *J* = 3.3 Hz), 123.63 - 123.40 (q, *J* = 2.5 Hz), 123.02 (dd, *J* = 20.1, 4.8 Hz), 120.53 (d, *J* = 4.4 Hz), 120.13 (d, *J* = 4.5 Hz), 118.35 (dd, *J* = 18.1, 2.4 Hz), 68.58, 67.75 (d, *J* = 167.0 Hz), 13.94; ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.73; ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.25; HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_7PSF$ $[M+Na]^+$ = 514.0491, found = 514.0498; The ee value was 99%, t_R

(major) = 9.4 min, t_R (minor) = 12.8 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

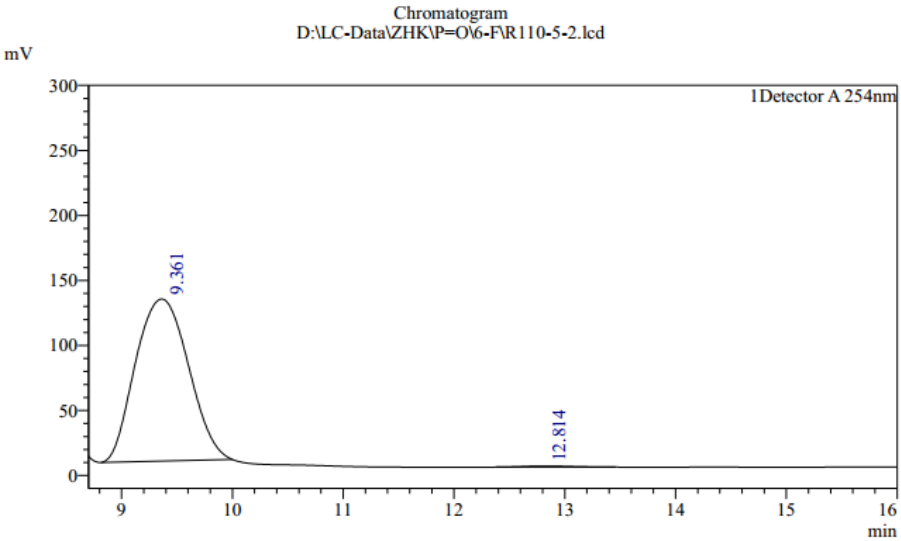


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	10.848	1919680	56314	55.168	50.440
2	13.677	1886184	45764	44.832	49.560
Total		3805863	102077	100.000	100.000

Racemic **5k**



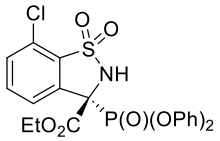
Peak Table

Detector A 254nm

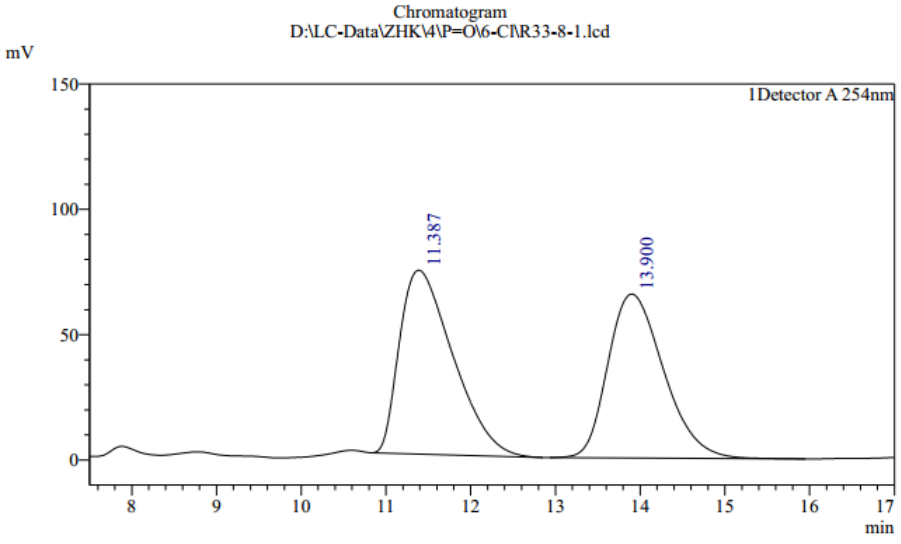
Peak#	Ret. Time	Area	Height	Height%	Area%
1	9.361	4151361	124584	99.324	99.398
2	12.814	25152	848	0.676	0.602
Total		4176513	125432	100.000	100.000

Enantiomerically enriched **5k**

(*S*)-ethyl 7-chloro-3-(diphenoxyphosphoryl)-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (5l)



A white solid; m.p. = 81 - 83 °C; 47.2 mg, 93% yield; $[\alpha]^{25}_{D}$ = -31.83 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.64 - 7.50 (m, 3H), 7.47 - 7.40 (m, 2H), 7.39 - 7.28 (m, 6H), 7.24 - 7.14 (m, 2H), 5.53 (d, *J* = 3.6 Hz, 1H), 4.18 - 3.98 (m, 2H), 1.10 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.65, 150.22 (dd, *J* = 31.9, 7.3 Hz), 135.89, 135.05, 132.95 (d, *J* = 8.9 Hz), 132.53 (d, *J* = 5.7 Hz), 131.73, 130.00, 129.82, 129.41, 126.05, 123.38, 120.92 (d, *J* = 4.7 Hz), 120.71 (d, *J* = 4.9 Hz), 63.26, 61.87 (d, *J* = 5.1 Hz), 13.87; ^{31}P NMR (162 MHz, $CDCl_3$) δ 3.81; HRMS (ESI) m/z calcd for $C_{22}H_{19}NO_7PS$ $[M+Na]^+$ = 530.0195, found = 530.0191; The ee value was 95%, t_R (major) = 9.4 min, t_R (minor) = 10.8 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

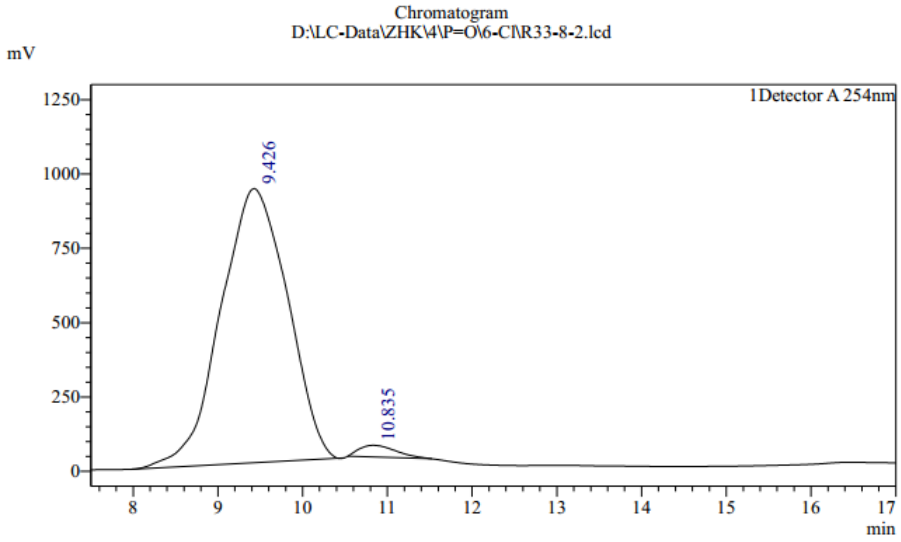


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	11.387	3216960	73343	52.858	51.827
2	13.900	2990155	65412	47.142	48.173
Total		6207115	138754	100.000	100.000

Racemic **5l**



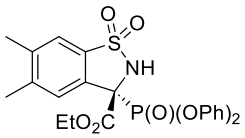
Peak Table

Detector A 254nm

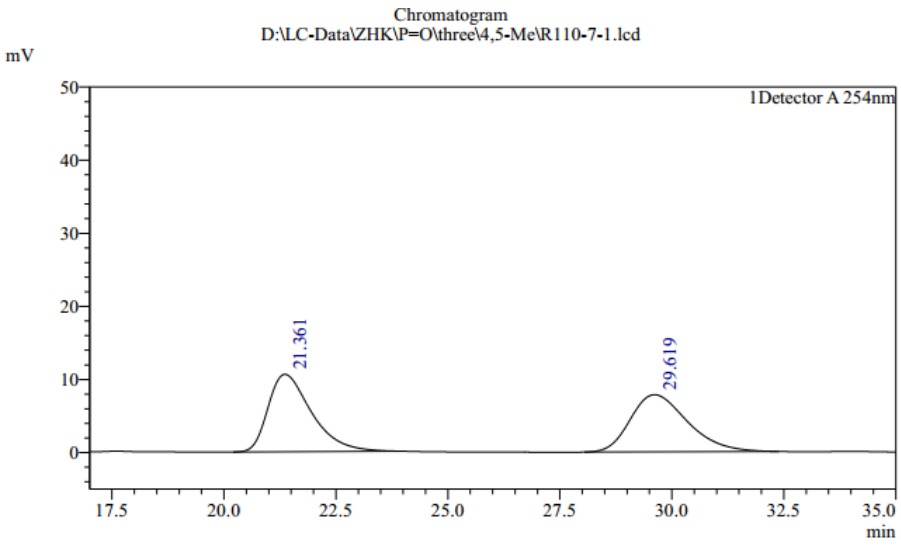
Peak#	Ret. Time	Area	Height	Height%	Area%
1	9.426	50565136	921394	95.927	97.690
2	10.835	1195769	39126	4.073	2.310
Total		51760906	960520	100.000	100.000

Enantiomerically enriched **5l**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-5,6-dimethyl-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (5m)



A white solid; m.p. = 147 - 149 ^{o}C; 46.1 mg, 92% yield; $[\alpha]^{25}_{D}$ = -31.67 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 - 7.81 (m, 1H), 7.57 (s, 1H), 7.33 - 7.27 (m, 2H), 7.23 - 7.13 (m, 5H), 7.13 - 7.06 (m, 1H), 7.04 - 6.98 (m, 2H), 6.08 (d, *J* = 5.2 Hz, 1H), 4.37 - 4.28 (m, 2H), 2.39 - 2.28 (m, 6H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.51 (d, *J* = 5.2 Hz), 150.36 (dd, *J* = 29.7, 9.7 Hz), 143.88 (d, *J* = 2.7 Hz), 141.28 (d, *J* = 2.8 Hz), 132.30 (d, *J* = 5.0 Hz), 129.85 (d, *J* = 0.6 Hz), 129.65, 127.94 (d, *J* = 2.9 Hz), 127.57 (d, *J* = 4.5 Hz), 125.80 (d, *J* = 1.0 Hz), 125.44 (d, *J* = 0.6 Hz) , 121.98 (d, *J* = 2.2 Hz), 120.58 (d, *J* = 4.4 Hz), 120.19 (d, *J* = 4.5 Hz), 67.49 (d, *J* = 167.3 Hz), 64.90 , 20.71, 20.14, 13.95; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.58; HRMS (ESI) m/z calcd for $C_{24}H_{24}NO_7PS$ $[M+Na]^+$ = 524.0898, found = 524.0892; The ee value was 98%, t_R (minor) = 23.3 min, t_R (major) = 30.9 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

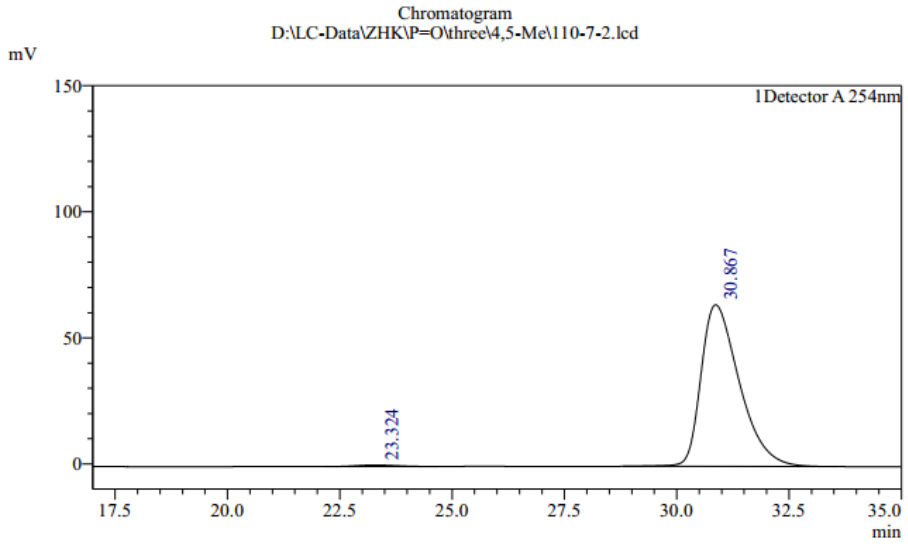


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	21.361	714649	10592	57.503	50.684
2	29.619	695353	7828	42.497	49.316
Total		1410002	18419	100.000	100.000

Racemic **5m**



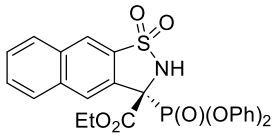
Peak Table

Detector A 254nm

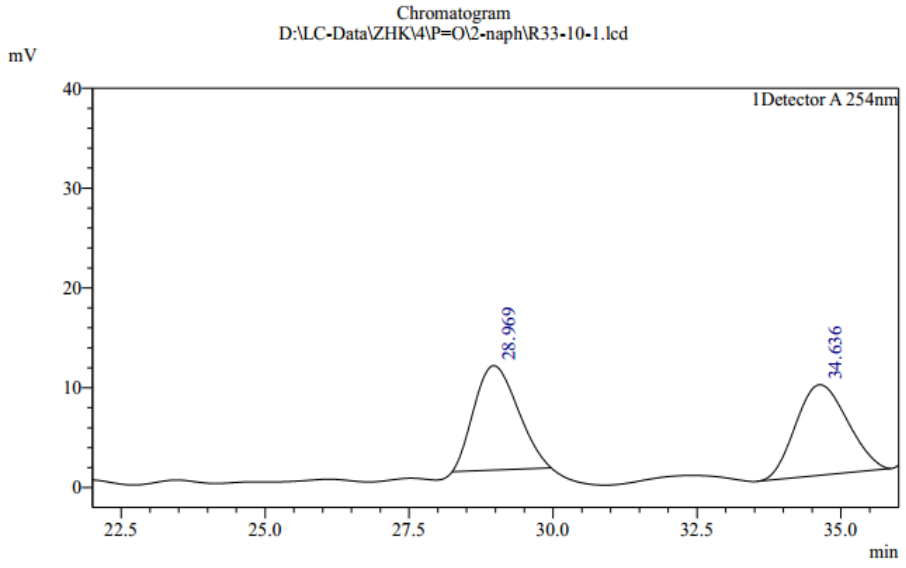
Peak#	Ret. Time	Area	Height	Height%	Area%
1	23.324	38442	613	0.947	0.998
2	30.867	3814681	64120	99.053	99.002
Total		3853123	64733	100.000	100.000

Enantiomerically enriched **5m**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-2,3-dihydronaphtho[2,3-d]isothiazole-3-carboxylate 1,1-dioxide (5n)



A white solid; m.p. = 107 - 108 °C; 48.1 mg, 92% yield; $[\alpha]^{25}_{D}$ = -57.67 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.0 Hz, 1H), 8.20 - 8.07(m, 2H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.81 - 7.67 (m, 2H), 7.33 - 7.28 (m, 2H), 7.22 - 7.10 (m, 5H), 7.09 - 6.97 (m, 3H), 5.30 (s, 1H), 4.45 - 4.29 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.36 (d, *J* = 4.2 Hz), 150.36 (d, *J* = 10.0 Hz), 150.23 (d, *J* = 10.0 Hz), 134.58 (d, *J* = 2.0 Hz), 134.33 (d, *J* = 1.5 Hz), 130.65 (d, *J* = 5.9 Hz), 129.91 , 129.74, 129.57, 129.43 (d, *J* = 4.5 Hz), 128.82 (d, *J* = 16.1 Hz), 125.76 (d, *J* = 28.9 Hz), 125.33 (d, *J* = 2.2 Hz), 123.30, 122.70 (d, *J* = 1.6 Hz), 120.64 (d, *J* = 4.4 Hz), 120.28 (d, *J* = 4.5 Hz), 67.96 (d, *J* = 167.1 Hz), 65.21, 14.01; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.20; HRMS (ESI) m/z calcd for $C_{26}H_{22}NO_7PS$ $[M+Na]^+$ = 546.0741, found $[M+Na]^+$ = 546.0743; The ee value was 94%, t_R (minor) = 26.6 min, t_R (major) = 35.1 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

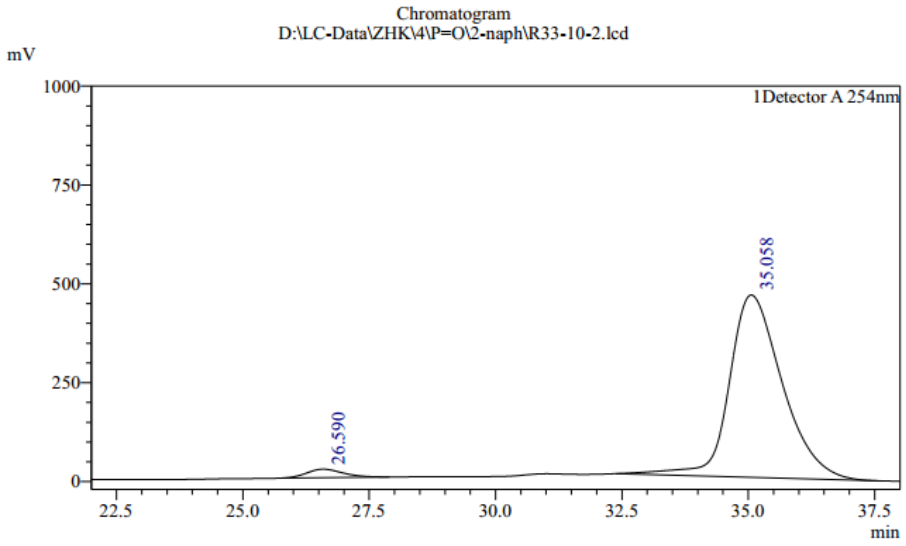


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	28.969	552454	10452	53.505	49.315
2	34.636	567801	9082	46.495	50.685
Total		1120254	19534	100.000	100.000

Racemic **5n**



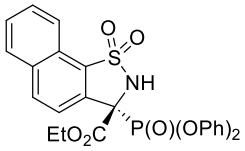
Peak Table

Detector A 254nm

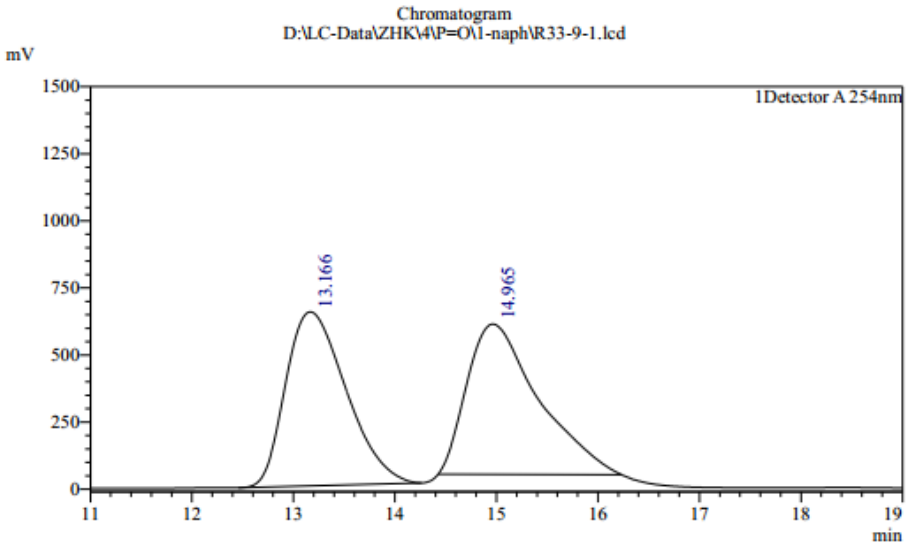
Peak#	Ret. Time	Area	Height	Height%	Area%
1	26.590	1084290	21519	4.459	3.115
2	35.058	33728690	461061	95.541	96.885
Total		34812981	482579	100.000	100.000

Enantiomerically enriched **5n**

(*S*)-ethyl 3-(diphenoxyphosphoryl)-2,3-dihydronaphtho[2,1-d]isothiazole-3-carboxylate 1,1-dioxide (5o)



A white solid; m.p. = 108 - 110 °C; 48.1 mg, 92% yield; $[\alpha]^{25}_{D}$ = -15.87 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 - 7.57 (m, 1H), 8.37 (s, 1H), 8.08 - 7.92 (m, 2H), 7.73 - 7.56 (m, 2H), 7.37 - 7.28 (m, 2H), 7.21 - 7.14 (m, 3H), 7.14 - 7.06 (m, 2H), 7.02 - 6.90 (m, 3H), 5.30 (s, 1H), 4.47 - 4.29 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.65 (d, *J* = 4.9 Hz), 150.47 (d, *J* = 9.6 Hz), 150.24 (d, *J* = 10.0 Hz), 135.33 (d, *J* = 2.8 Hz), 133.57 (d, *J* = 2.0 Hz), 132.00 (d, *J* = 4.2 Hz), 129.93, 129.67, 129.40, 129.22 (d, *J* = 11.6 Hz), 128.77, 128.06 (d, *J* = 4.1 Hz), 125.92, 125.51, 125.18, 122.71 (d, *J* = 1.6 Hz), 120.61 (d, *J* = 4.4 Hz), 120.14 (d, *J* = 4.5 Hz), 115.46, 67.52 (d, *J* = 167.1 Hz), 65.14, 14.03; ^{31}P NMR (162 MHz, $CDCl_3$) δ 4.57; HRMS (ESI) m/z calcd for $C_{26}H_{22}NO_7PS$ $[M+Na]^+$ = 546.0741, found = 546.0738; The ee value was 99%, t_R (minor) = 13.2 min, t_R (major) = 15.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

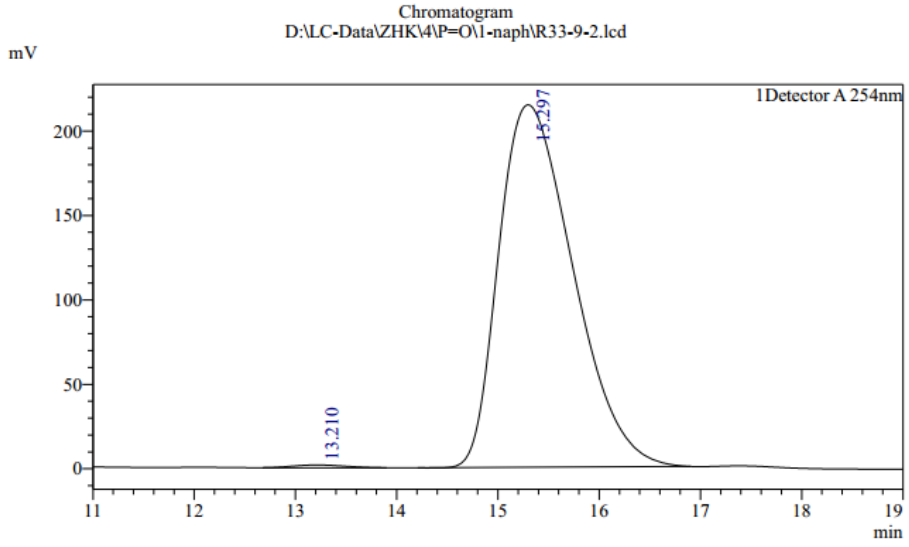


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.166	26827315	648949	53.671	49.420
2	14.965	27457531	560167	46.329	50.580
Total		54284847	1209116	100.000	100.000

Racemic **5o**



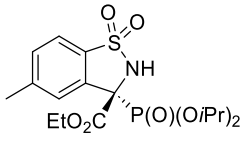
Peak Table

Detector A 254nm

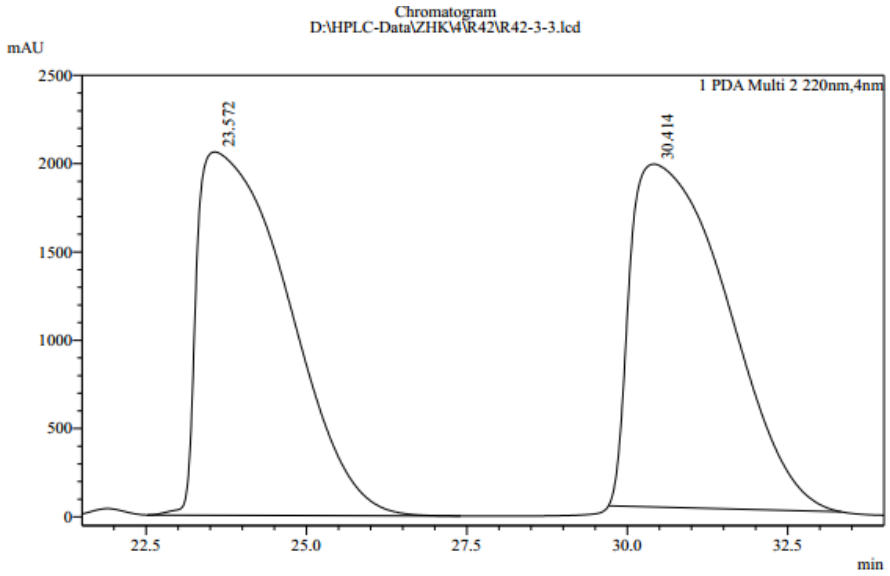
Peak#	Ret. Time	Area	Height	Height%	Area%
1	13.210	56820	1623	0.751	0.516
2	15.297	10947201	214629	99.249	99.484
Total		11004021	216253	100.000	100.000

Enantiomerically enriched **5o**

(*S*)-ethyl 3-(diisopropoxyphosphoryl)-5-methyl-2,3-dihydrobenzo[d] isothiazole-3-carboxylate 1,1-dioxide (5p)



A white solid; m.p. = 91 - 93 °C; 39.0 mg, 93% yield; $[\alpha]^{25}_{D}$ = -22.37 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.45 - 7.36 (m, 1H), 4.88 - 4.74 (m, 1H), 4.65 - 4.51 (m, 1H), 4.44 - 4.27 (m, 2H), 2.49 (s, 3H), 1.34 (dd, *J* = 7.2, 4.4 Hz, 6H), 1.28 (dd, *J* = 6.0, 2.8 Hz, 6H), 1.00 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.28 (d, *J* = 3.0 Hz), 144.52 (d, *J* = 2.5 Hz), 131.99 (dd, *J* = 17.5, 4.8 Hz), 131.47 (d, *J* = 4.7 Hz), 127.92 (d, *J* = 2.8 Hz), 121.21 (d, *J* = 1.9 Hz), 74.53 (dd, *J* = 17.0, 7.9 Hz), 67.96 (d, *J* = 160.3 Hz), 64.35, 24.22 (dd, *J* = 3.1, 0.2 Hz), 23.74 (d, *J* = 5.8 Hz), 23.16 (d, *J* = 5.6 Hz), 22.08, 14.08; ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.29; HRMS (ESI) m/z calcd for $C_{17}H_{26}NO_7PS$ $[M+Na]^+$ = 442.1054, found = 442.1048; The ee value was 91%, t_R (minor) = 23.8 min, t_R (major) = 28.1 min (Chiralcel IC, λ = 220 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

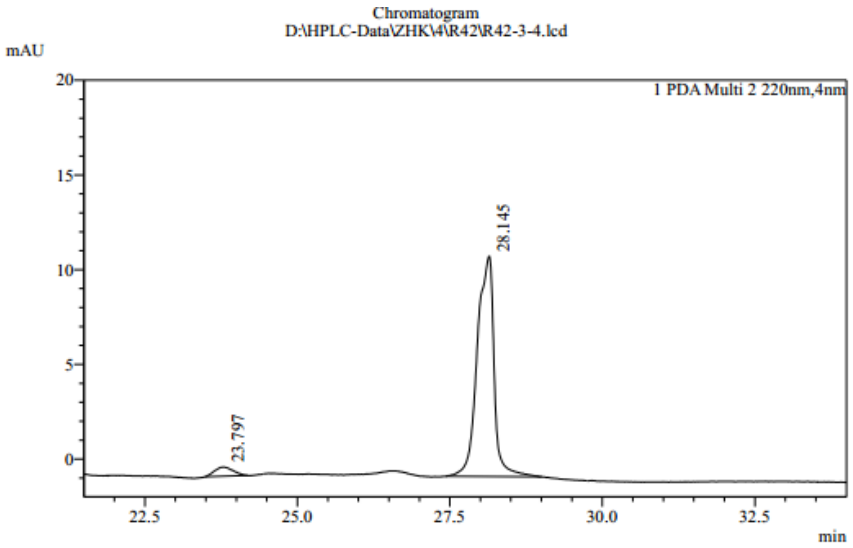


Peak Table

PDA Ch2 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	23.572	2056900	51.443	202623371	49.724
2	30.414	1941504	48.557	204872008	50.276
Total		3998404	100.000	407495379	100.000

Racemic **5p**



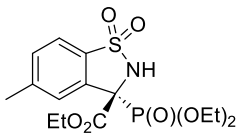
Peak Table

PDA Ch2 220nm

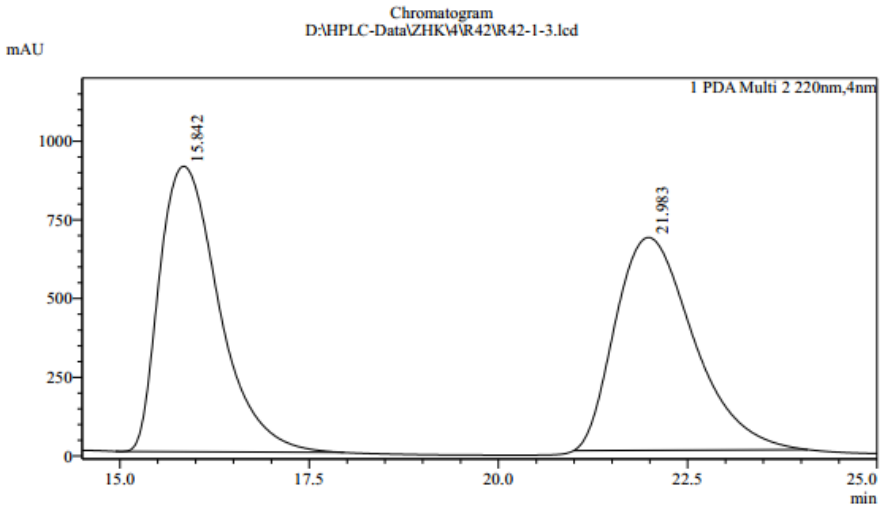
Peak#	Ret. Time	Height	Height%	Area	Area%
1	23.797	481	3.977	10305	4.407
2	28.145	11626	96.023	223556	95.593
Total		12107	100.000	233861	100.000

Enantiomerically enriched **5p**

(*S*)-ethyl 3-(diethoxyphosphoryl)-5-methyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (5q)



A white solid; m.p. = 85 - 87 °C; 36.8 mg, 94% yield; $[\alpha]^{25}_{D}$ = -22.37 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 - 7.82 (m, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.46 - 7.40 (m, 1H), 5.84 (s, 1H), 4.46 - 4.34 (m, 2H), 4.34 - 4.24 (m, 2H), 4.17 - 3.98 (m, 2H), 2.50 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H), 1.30 (td, *J* = 7.2, 0.8 Hz, 3H), 1.23 (td, *J* = 7.2, 0.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.10 (d, *J* = 2.9 Hz), 144.67 (d, *J* = 2.5 Hz), 132.10 (d, *J* = 2.8 Hz), 132.06 (d, *J* = 5.0 Hz), 131.51 (d, *J* = 4.4 Hz), 127.80 (d, *J* = 2.7 Hz), 121.33 (d, *J* = 2.0 Hz), 67.95 (d, *J* = 160.7 Hz), 65.96 (d, *J* = 7.3 Hz), 65.20 (d, *J* = 7.3 Hz), 64.60, 22.13, 16.55 (d, *J* = 5.4 Hz), 16.35 (d, *J* = 5.4 Hz), 14.12; ^{31}P NMR (162 MHz, $CDCl_3$) δ 12.05; HRMS (ESI) m/z calcd for $C_{15}H_{22}NO_7PS$ $[M+Na]^+$ = 414.0752, found = 414.0750; The ee value was 94%, t_R (major) = 16.5 min, t_R (minor) = 21.1 min (Chiralcel AS-H, λ = 220 nm, 30% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

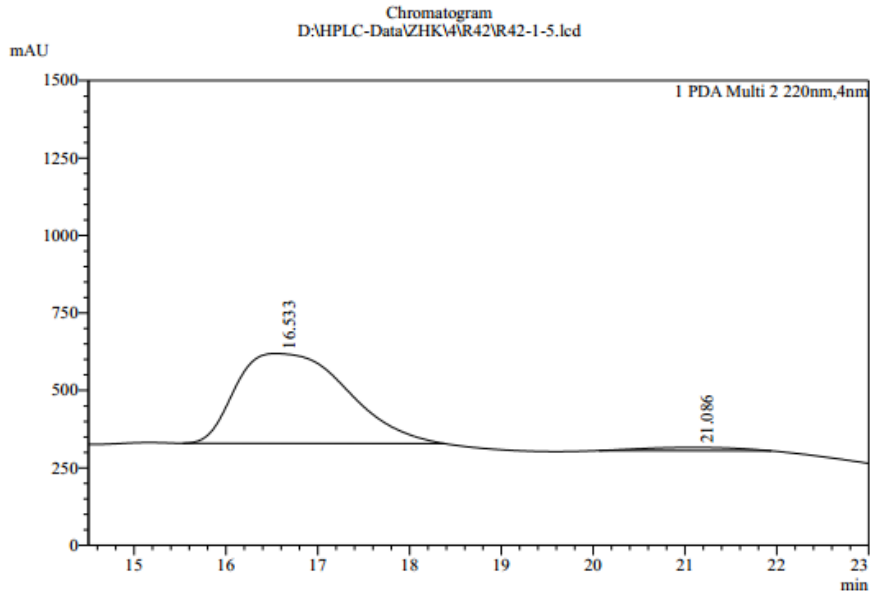


Peak Table

PDA Ch2 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.842	906673	57.278	49801409	50.544
2	21.983	676253	42.722	48728520	49.456
Total		1582926	100.000	98529929	100.000

Racemic **5q**



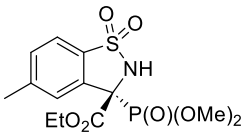
Peak Table

PDA Ch2 220nm

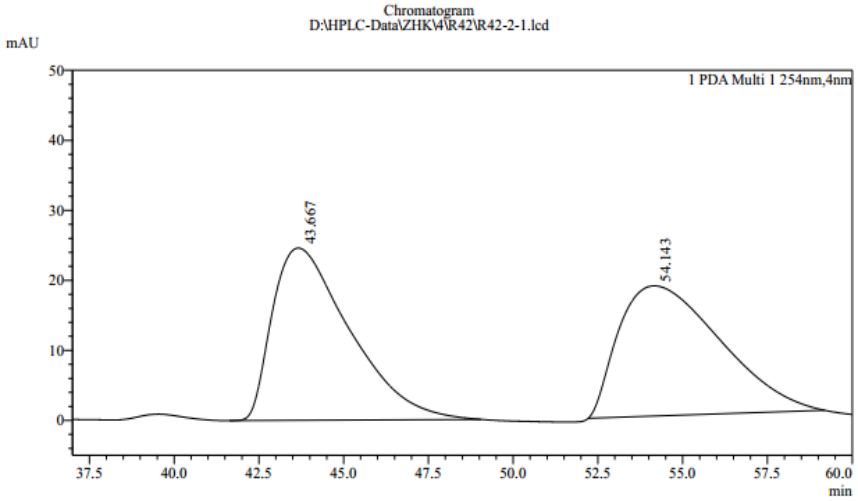
Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.533	289891	96.426	24386843	96.924
2	21.086	10745	3.574	773992	3.076
Total		300636	100.000	25160835	100.000

Enantiomerically enriched **5q**

(*S*)-ethyl 3-(dimethoxyphosphoryl)-5-methyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (5r)



A white solid; m.p. = 101 - 103 °C; 34.1 mg, 94% yield; $[\alpha]^{25}_{D}$ = -22.37 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.47 - 7.40 (m, 1H), 5.90 (s, 1H), 4.47 - 4.34 (m, 2H), 3.91 (d, *J* = 10.4 Hz, 3H), 3.76 (d, *J* = 10.8 Hz, 3H), 2.51 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.92 (d, *J* = 3.0 Hz), 144.85 (d, *J* = 2.6 Hz), 132.24 (d, *J* = 2.4 Hz), 131.97 (d, *J* = 4.6 Hz), 131.31 (d, *J* = 4.8 Hz), 127.55 (d, *J* = 2.6 Hz), 121.43 (d, *J* = 2.0 Hz), 67.89 (d, *J* = 162.5 Hz), 64.75, 56.40 (d, *J* = 7.5 Hz), 55.44 (d, *J* = 7.3 Hz), 22.13, 14.11; ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.46; HRMS (ESI) m/z calcd for $C_{13}H_{18}NO_7PS$ $[M+Na]^+$ = 386.0439, found = 386.0447; The ee value was 91%, t_R (minor) = 42.8 min, t_R (major) = 53.4 min (Chiralcel AS-H, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 0.8 mL/min).

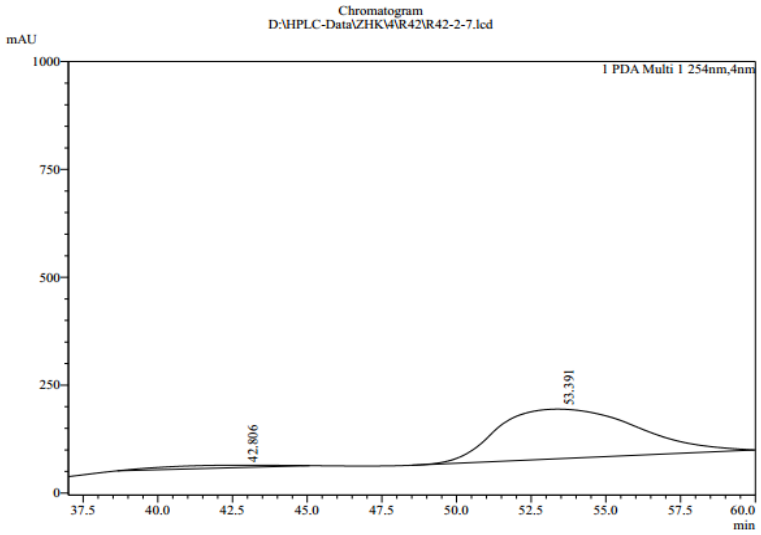


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	43.667	24599	56.924	3913970	50.174
2	54.143	18615	43.076	3886809	49.826
Total		43215	100.000	7800779	100.000

Racemic **5r**



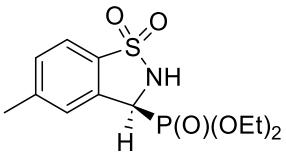
Peak Table

PDA Ch1 254nm

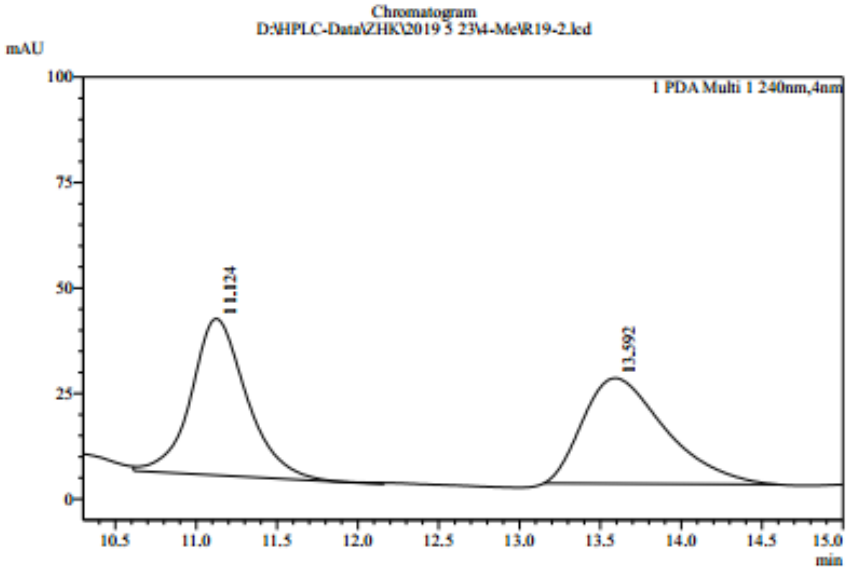
Peak#	Ret. Time	Height	Height%	Area	Area%
1	42.806	5312	4.413	1678774	4.315
2	53.391	115041	95.587	37226302	95.685
Total		120352	100.000	38905076	100.000

Enantiomerically enriched **5r**

(*S*)-diethyl (5-methyl-1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl) Phosphonate (5'a)



A white solid; m.p. = 90 - 92 °C; 29.3 mg, 92% yield; $[\alpha]^{25}_{D}$ = -36.33 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.52 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 6.00 - 5.87 (m, 1H), 5.00 (dd, *J* = 11.2, 4.8 Hz, 1H), 4.32 - 4.18 (m, 2H), 4.15 - 3.93 (m, 2H), 2.47 (s, 3H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.39 (d, *J* = 2.7Hz), 132.67 (d, *J* = 5.2 Hz), 132.45 (d, *J* = 5.6 Hz), 131.08 (d, *J* = 2.3 Hz), 126.17 (d, *J* = 2.8 Hz), 121.39 (d, *J* = 2.7Hz), 64.58 (d, *J* = 7.0 Hz), 64.17 (d, *J* = 7.2 Hz), 54.09 (d, *J* = 160.9 Hz), 21.98, 16.54 (d, *J* = 5.6 Hz), 16.38 (d, *J* = 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.85; HRMS (ESI) m/z calcd for $C_{12}H_{18}NO_5PS$ $[M+Na]^+$ = 342.0530, found = 342.0526; The ee value was 91%, t_R (major) = 11.2 min, t_R (minor) = 13.6 min (Chiralcel AS-H, λ = 240 nm, 40% *i*-PrOH/hexanes, flow rate = 0.6 mL/min).

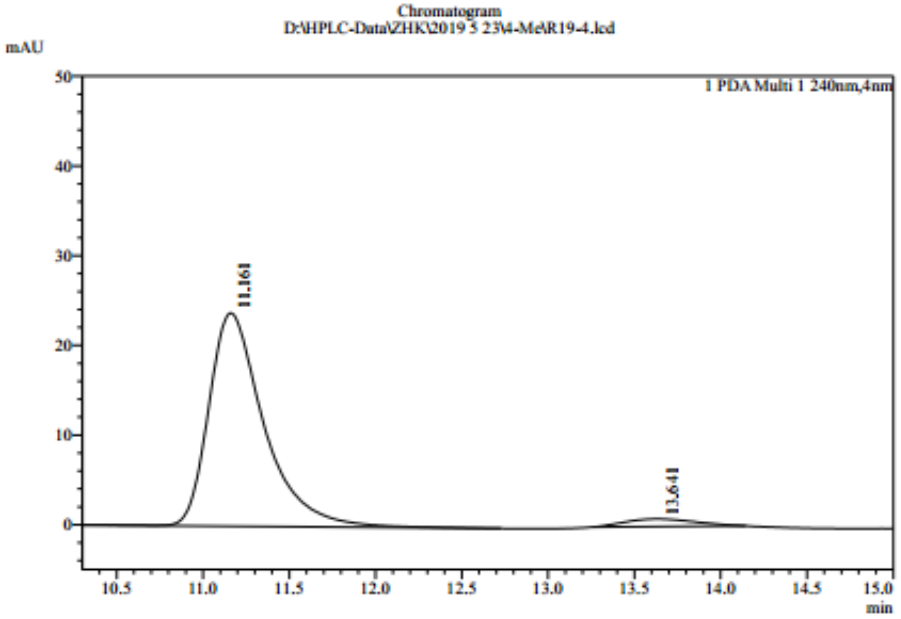


Peak Table

PDA Ch1 240nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.124	37126	59.778	893132	50.101
2	13.592	24981	40.222	889533	49.899
Total		62107	100.000	1782665	100.000

Racemic **5'a**



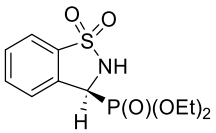
Peak Table

PDA Ch1 240nm

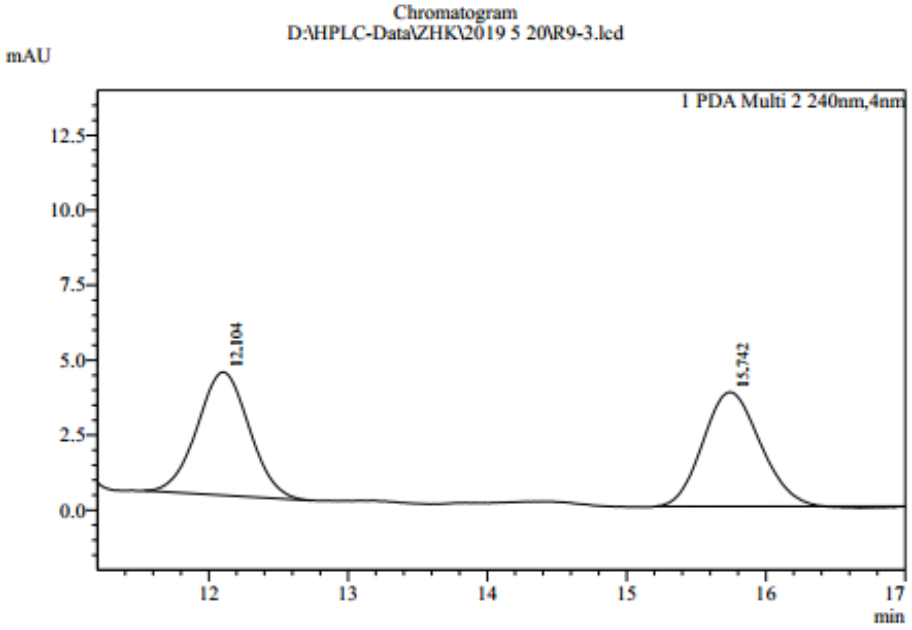
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.161	23755	96.570	529415	95.690
2	13.641	844	3.430	23843	4.310
Total		24599	100.000	553258	100.000

Enantiomerically enriched **5'a**

(*S*)-diethyl (1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl)phosphonate (5'b)



A white solid; m.p. = 92 - 94 °C; 28.4 mg, 93% yield; $[\alpha]^{25}_{D}$ = -33.33 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.74 (d, *J* = 7.6 Hz, 1H), 7.668 - 7.62(m, 1H), 7.61 - 7.54 (m, 1H), 6.27 - 6..14 (m, 1H), 5.07 (dd, *J* = 11.2, 4.4 Hz, 1H), 4.34 - 4.17 (m, 2H), 4.13 - 3.94 (m, 2H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.12 (d, *J* = 5.6 Hz), 133.26 (d, *J* = 2.4 Hz), 132.37 (d, *J* = 5.2 Hz), 130.05 (d, *J* = 2.6 Hz), 126.04 (d, *J* = 2.8 Hz), 121.66 (d, *J* = 1.9 Hz), 64.76 (d, *J* = 6.8 Hz), 64.11 (d, *J* = 7.1 Hz), 54.26 (d, *J* = 161.4 Hz), 16.52 (d, *J* = 5.4 Hz), 16.38 (d, *J* = 5.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.83; HRMS (ESI) m/z calcd for $C_{11}H_{16}NO_5PS$ $[M+Na]^+$ = 328.0379, found = 328.0369; The ee value was 90%, t_R (major) = 11.2 min, t_R (minor) = 16.3 min (Chiralcel AS-H, λ = 240 nm, 40% *i*-PrOH/hexanes, flow rate = 0.6 mL/min).

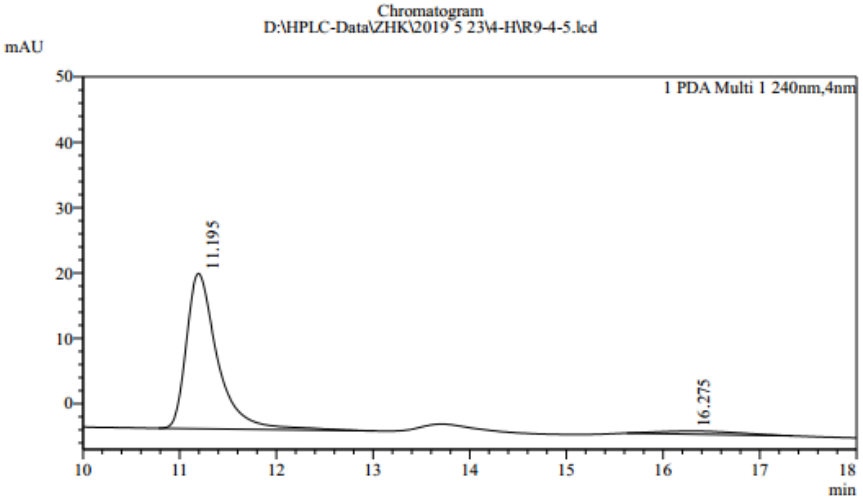


Peak Table

PDA Ch2 240nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.104	4112	51.888	106896	49.680
2	15.742	3813	48.112	108272	50.320
Total		7925	100.000	215168	100.000

Racemic **5'b**



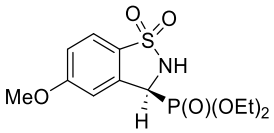
Peak Table

PDA Ch1 240nm

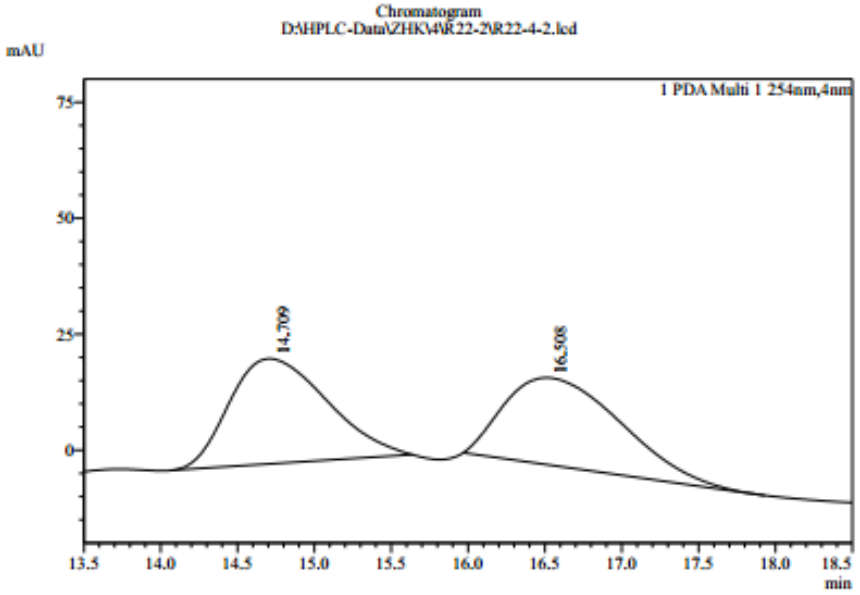
Peak#	Ret. Time	Height	Height%	Area	Area%
1	11.195	23720	98.028	533284	95.064
2	16.275	477	1.972	27687	4.936
Total		24197	100.000	560971	100.000

Enantiomerically enriched **5'b**

(*S*)-diethyl (5-methoxy-1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl) Phosphonate (5'c)



A white solid; m.p. = 99 - 101 °C; 31.8 mg, 95% yield; $[\alpha]^{25}_D$ = -18.17 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.4, 0.8 Hz, 1H), 7.19 (s, 1H), 7.12 - 7.7.0 (m, 1H), 4.98 (d, *J* = 11.6 Hz, 1H), 4.32 - 4.20(m, 2H), 4.15 - 3.95 (m, 2H), 3.89 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H), 1.22 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.69 (d, *J* = 2.8 Hz), 135.01 (d, *J* = 5.4 Hz), 127.12 (d, *J* = 5.6 Hz), 123.03 (d, *J* = 1.8 Hz), 117.52 (d, *J* = 2.4 Hz), 109.63 (d, *J* = 2.6 Hz), 64.55 (d, *J* = 6.9 Hz), 64.25 (d, *J* = 7.1 Hz), 56.07, 54.00 (d, *J* = 159.9 Hz), 16.57 (d, *J* = 5.5 Hz), 16.41 (d, *J* = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.62; HRMS (ESI) m/z calcd for $C_{12}H_{18}NO_6PS$ $[M+Na]^+$ = 358.0485, found = 358.0479; The ee value was 94%, t_R (minor) = 14.7 min, t_R (major) = 16.8 min (Chiralcel AS-H, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 0.6 mL/min).

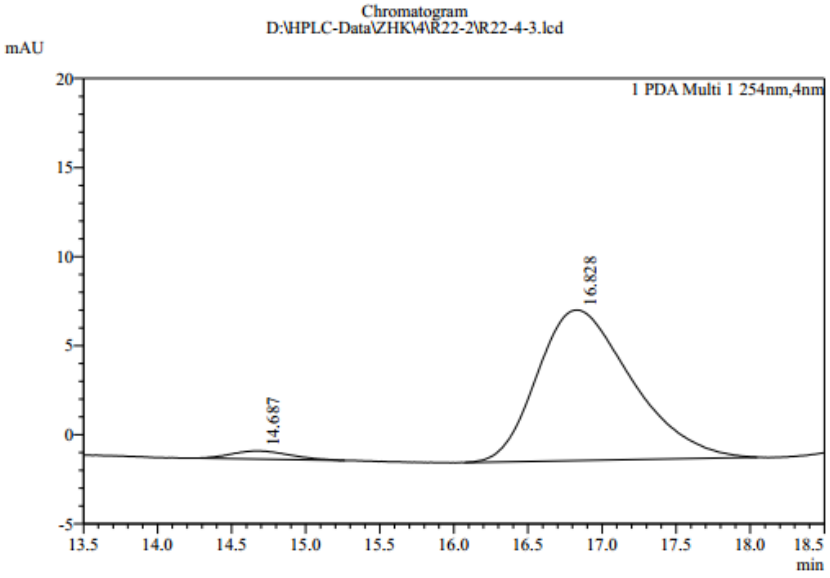


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.709	22690	54.823	1003933	50.067
2	16.508	18698	45.177	1001233	49.933
Total		41388	100.000	2005167	100.000

Racemic **5'c**



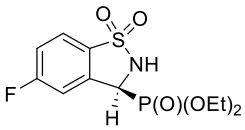
Peak Table

PDA Ch1 254nm

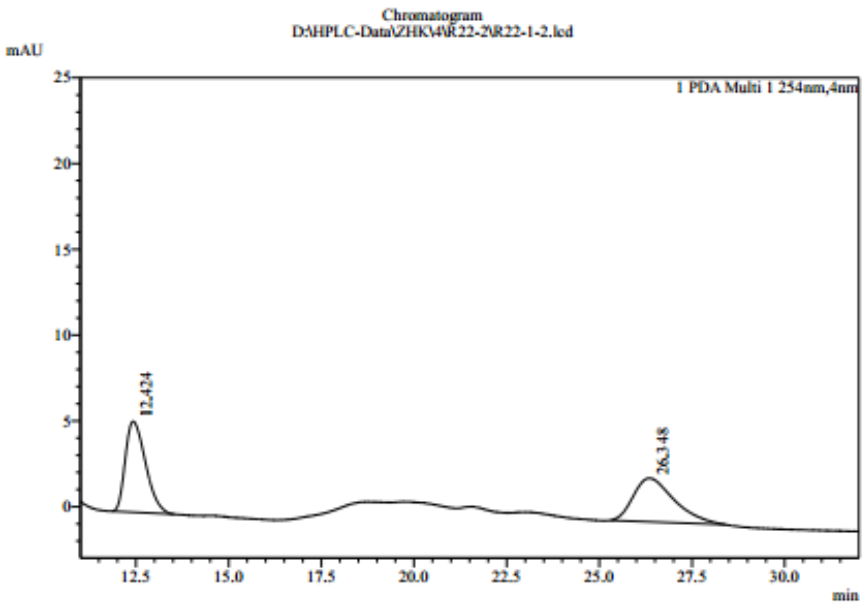
Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.687	455	5.106	12135	3.134
2	16.828	8449	94.894	375044	96.866
Total		8904	100.000	387178	100.000

Enantiomerically enriched **5'c**

(S)-diethyl (5-fluoro-1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl)phosphonate (5'd)



A white solid; m.p. = 95 - 97 °C; 29.4 mg, 91% yield; $[\alpha]^{25}_{D}$ = -15.47 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 - 7.61 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 1H), 7.28 - 7.19 (m, 1H), 6.36 - 5.85 (m, 1H), 5.05 (d, *J* = 12.0 Hz, 1H), 4.34 - 4.20 (m, 2H), 4.18 - 4.00 (m, 2H), 1.32 (t, *J* = 7.2 Hz, 3H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.81 (d, *J* = 2.5 Hz), 135.75 (d, *J* = 1.2 Hz), 121.79 (d, *J* = 3.1 Hz), 121.75 (d, *J* = 3.0 Hz), 116.97 (d, *J* = 2.4 Hz), 116.79 (d, *J* = 2.4 Hz), 65.00 (d, *J* = 7.0 Hz), 64.27 (d, *J* = 7.3 Hz), 54.29 (d, *J* = 162.7 Hz), 16.55 (d, *J* = 5.4 Hz), 16.42 (d, *J* = 5.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.11; ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.73; HRMS (ESI) m/z calcd for $C_{11}H_{15}NO_5PSF$ $[M+Na]^+$ = 346.0279, found = 346.0272; The ee value was >99%, t_R (major) = 12.9 min, t_R (minor) = 24.5 min (Chiralcel AS-H, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 0.6 mL/min).

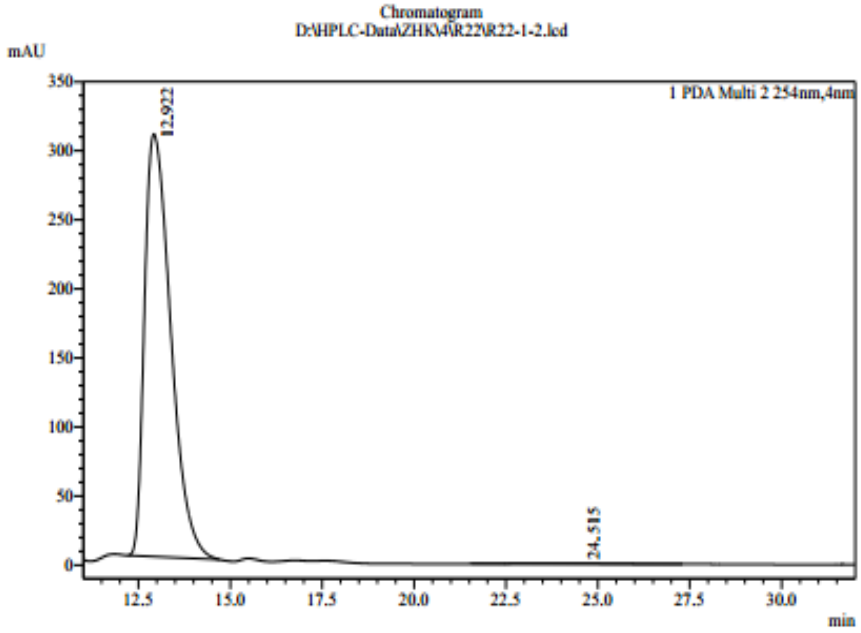


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.424	5292	67.588	201772	50.841
2	26.348	2538	32.412	195093	49.159
Total		7830	100.000	396866	100.000

Racemic **5'd**



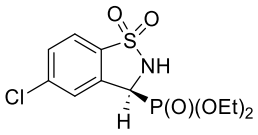
Peak Table

PDA Ch2 254nm

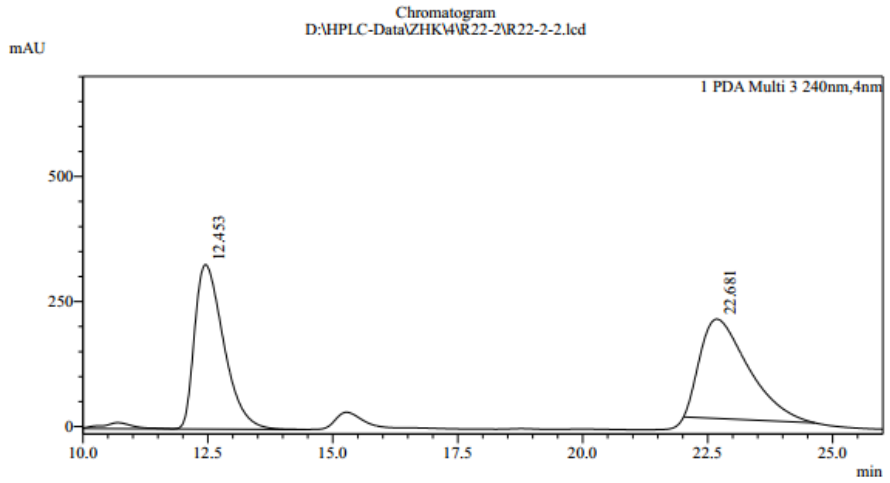
Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.922	305938	99.886	15174901	99.583
2	24.515	349	0.114	63557	0.417
Total		306287	100.000	15238457	100.000

Enantiomerically enriched **5'd**

(*S*)-diethyl (5-chloro-1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl)phosphonate (5'e)



A white solid; m.p. = 91 - 93 °C; 30.8 mg, 91% yield; $[\alpha]^{25}_{D}$ = -12.67 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 - 7.65 (m, 2H), 7.57 - 7.51 (m, 1H), 5.02 (d, *J* = 12.0 Hz, 1H), 4.30 - 4.20 (m, 2H), 4.20 - 4.09 (m, 3H), 1.29 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.74 (d, *J* = 3.0 Hz), 134.62 (d, *J* = 5.4 Hz), 133.75 (d, *J* = 5.3 Hz), 130.60 (d, *J* = 2.5 Hz), 126.17 (d, *J* = 2.7 Hz), 122.84 (d, *J* = 1.9 Hz), 64.69 (dd, *J* = 99.7, 7.9 Hz), 54.71, 53.08, 16.52 (d, *J* = 5.5 Hz), 16.43 (d, *J* = 5.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.34; HRM (ESI) m/z calcd for $C_{11}H_{15}NO_5PSCl$ $[M+Na]^+$ = 361.9984, found $[M+Na]^+$ = 361.9980; The ee value was 96%, t_R (minor) = 13.5 min, t_R (major) = 19.9 min (Chiralcel IC, λ = 240 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

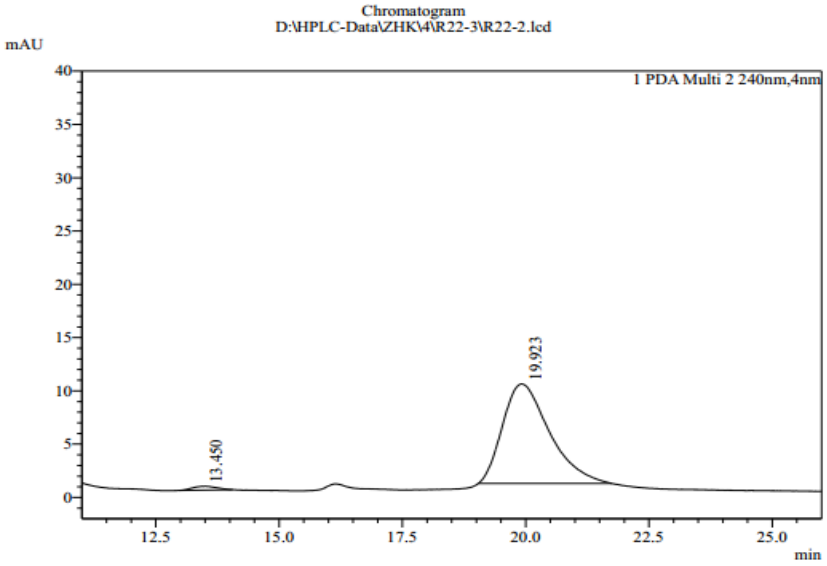


Peak Table

PDA Ch3 240nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	12.453	328357	62.316	13837779	50.729
2	22.681	198563	37.684	13440273	49.271
Total		526921	100.000	27278052	100.000

Racemic **5'e**



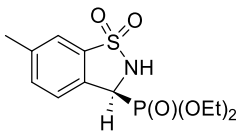
Peak Table

PDA Ch2 240nm

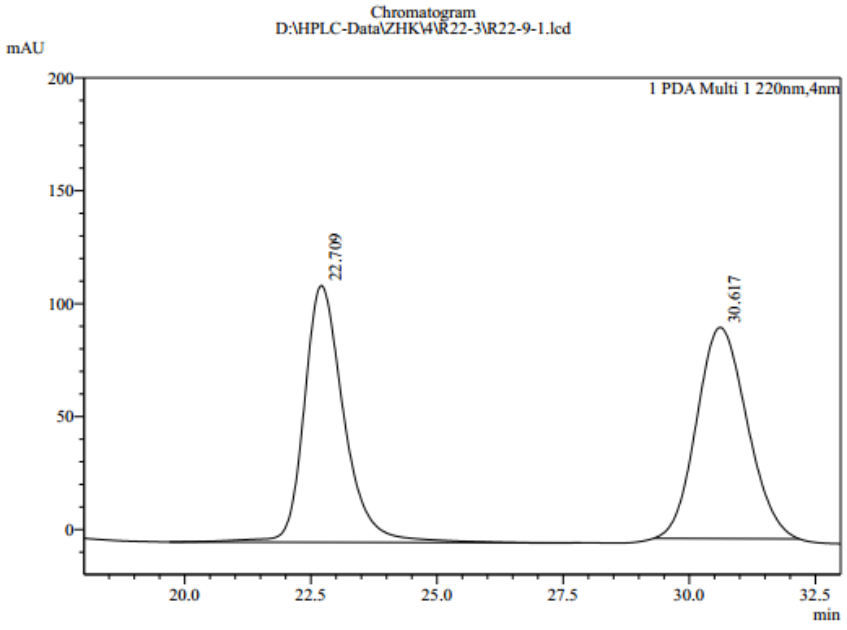
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.450	355	3.666	11913	1.886
2	19.923	9339	96.334	619648	98.114
Total		9694	100.000	631561	100.000

Enantiomerically enriched **5'e**

(*S*)-diethyl (6-methyl-1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl) Phosphonate (5'f)



A white solid; m.p. = 92- 94 ºC; 29.0 mg, 91% yield; $[\alpha]^{25}_{D}$ = -30.47 (*c* 0.5, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 - 7.58 (m, 2H), 7.46 (d, *J* = 8.0 Hz, 1H), 5.59 - 5.41 (m, 1H), 5.12 - 4.88 (m, 1H), 4.34 - 4.15 (m, 2H), 4.13 - 3.92 (m, 2H), 2.47 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.86 (d, *J* = 2.8 Hz), 135.10 (d, *J* = 5.7 Hz), 134.52 (d, *J* = 2.8 Hz), 129.44 (d, *J* = 5.3 Hz), 125.73 (d, *J* = 2.9 Hz), 121.63 (d, *J* = 1.8 Hz), 64.50 (d, *J* = 6.8 Hz), 64.15 (d, *J* = 7.2 Hz), 54.01 (d, *J* = 160.5 Hz), 21.45, 16.56 (d, *J* = 5.7 Hz), 16.41 (d, *J* = 5.5Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.86; HRMS (ESI) m/z calcd for $C12H18NO5PS$ $[M+Na]^+$ = 342.0530, found = 342.0526; The ee value was 90%, t_R (major) = 21.2 min, t_R (minor) = 28.7 min (Chiralcel AS-H, λ = 220 nm, 40% *i*-PrOH/hexanes, flow rate = 0.6 mL/min).

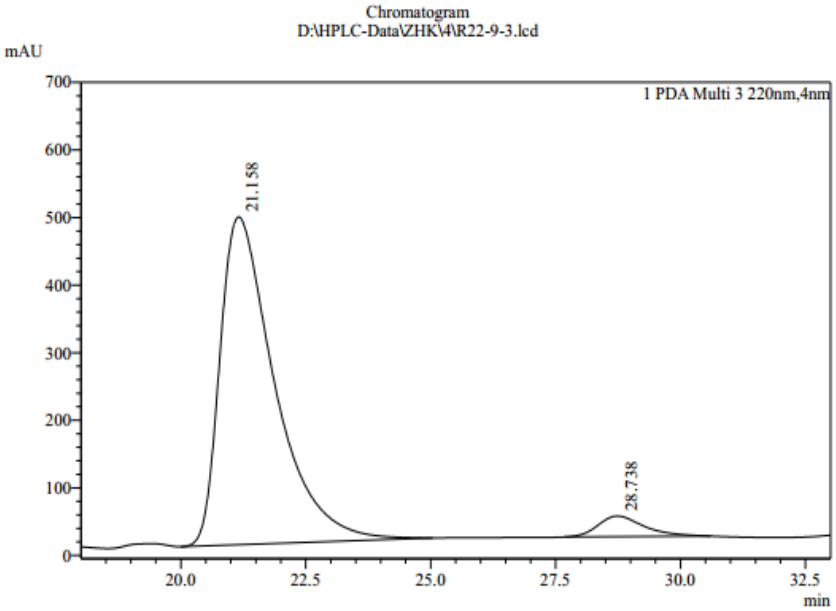


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	22.709	113726	54.868	6237783	48.944
2	30.617	93545	45.132	6506981	51.056
Total		207271	100.000	12744764	100.000

Racemic **5'f**



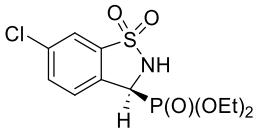
Peak Table

PDA Ch3 220nm

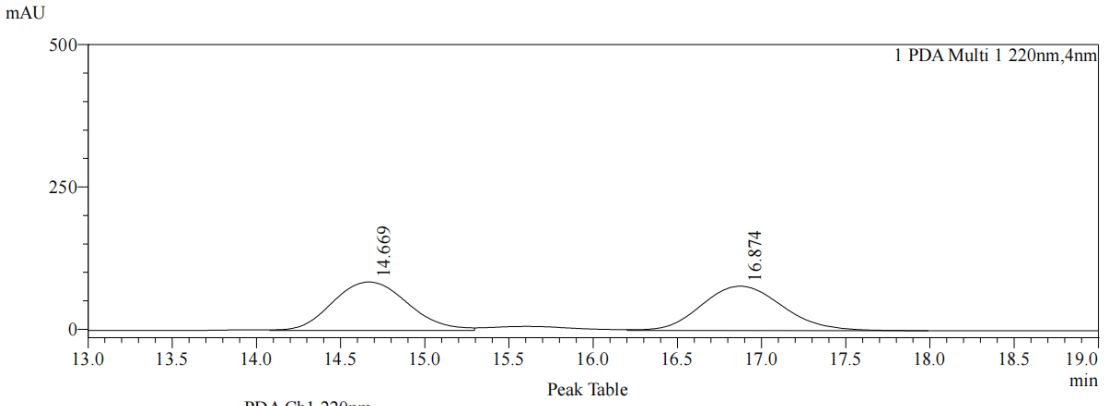
Peak#	Ret. Time	Height	Height%	Area	Area%
1	21.158	485099	94.087	36936207	94.950
2	28.738	30486	5.913	1964357	5.050
Total		515586	100.000	38900565	100.000

Enantiomerically enriched **5'f**

(*S*)-diethyl (6-chloro-1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl) phosphonate (5'g)



A white solid; m.p. = 87 - 89 °C; 30.5 mg, 90% yield; $[\alpha]^{25}_{D}$ = -34.18 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.56 - 7.47 (m, 1H), 6.29 (s, 1H), 5.10 (d, *J* = 10.0 Hz, 1H), 4.26 - 4.07 (m, 4H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.31 (d, *J* = 4.5 Hz), 134.06 (d, *J* = 2.6 Hz), 131.83 (d, *J* = 3.9 Hz), 131.52 (d, *J* = 2.9 Hz), 131.46 (d, *J* = 6.5 Hz), 120.30 (d, *J* = 2.3 Hz), 64.80 (d, *J* = 7.1 Hz), 64.00 (d, *J* = 7.2 Hz), 54.69 (d, *J* = 154.5 Hz), 16.42 (d, *J* = 2.4 Hz), 16.36 (d, *J* = 2.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.03; HRMS (ESI) m/z calcd for $C_{11}H_{15}NO_5PSCl$ $[M+Na]^+$ = 361.9984, found = 361.9980; The ee value was 99%, t_R (major) = 15.3 min, t_R (minor) = 17.3 min (Chiralcel AS-H, λ = 220 nm, 40% *i*-PrOH/hexanes, flow rate = 0.6 mL/min).

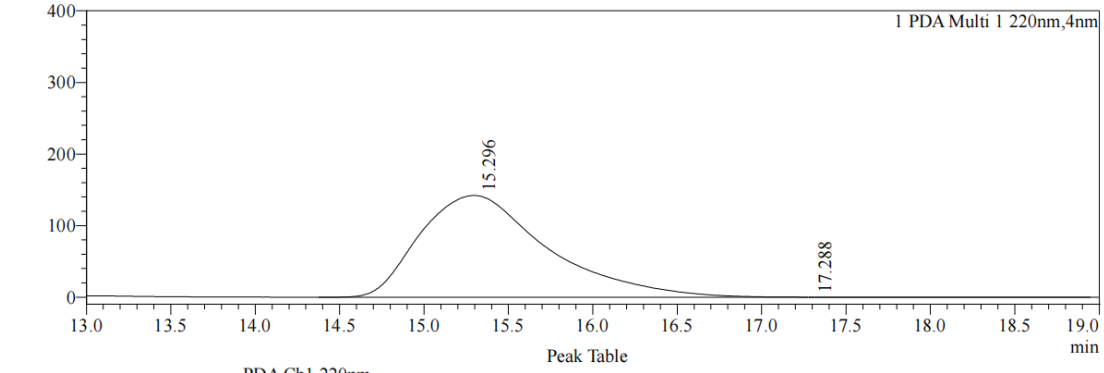


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	14.669	85255	52.202	2667639	50.330
2	16.874	78064	47.798	2632654	49.670
Total		163318	100.000	5300293	100.000

Racemic **5'g**



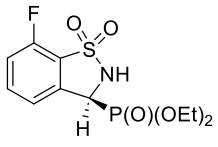
Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.296	142188	99.799	7501820	99.799
2	17.288	286	0.201	15086	0.201
Total		142474	100.000	7516906	100.000

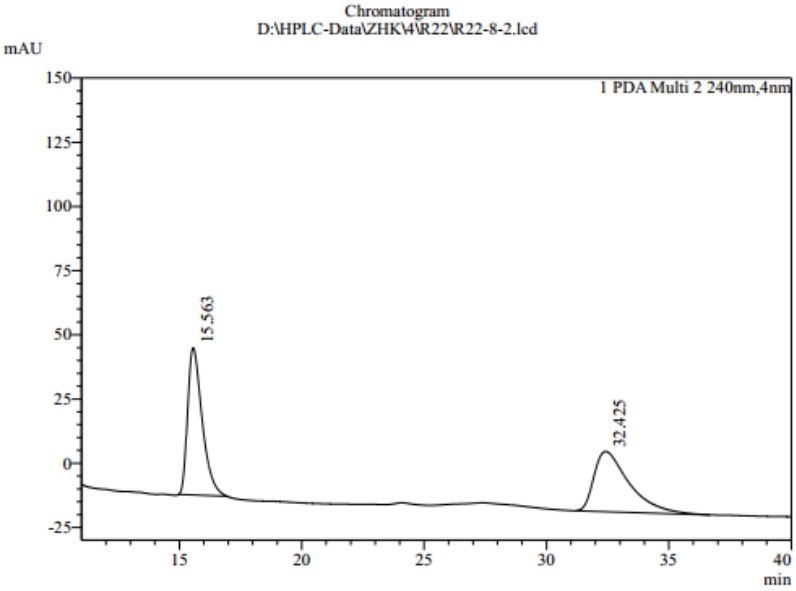
Enantiomerically enriched **5'g**

(*S*)-diethyl (7-fluoro-1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl) phosphonate (5'h)



A white solid; m.p. = 85 - 87 ^{o}C; 29.1 mg, 90% yield; $[\alpha]^{25}_{D}$ = -40.00 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.4, 4.4 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 1H), 7.32 - 7.23 (m,1H), 6.60 (s, 1H), 5.04 (d, *J* = 12.0 Hz, 1H), 4.33 - 4.20 (m, 2H), 4.19 - 4.07 (m, 2H), 1.32 - 1.29 (t, *J* = 7.2 Hz, 3H), 1.29 - 1.25 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR

(100 MHz, $CDCl_3$) δ 165.39 (dd, *J* = 253.5, 2.9 Hz), 135.72 (dd, *J* = 10.1, 5.7 Hz), 131.27 (dd, *J* = 5.2, 2.4 Hz), 123.91 (dd, *J* = 9.9, 1.8 Hz), 118.16 (d, *J* = 2.1 Hz), 118.04 (d, *J* = 2.2 Hz), 113.19 (dd, *J* = 24.9, 2.5 Hz), 65.19 (d, *J* = 7.1 Hz), 64.15 (dd, *J* = 24, 2.1 Hz), 53.93 (d, *J* = 162.6 Hz), 16.51 (d, *J* = 5.4 Hz), 16.43 (d, *J* = 5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 16.24; ^{19}F NMR (376 MHz, $CDCl_3$) δ -103.79; HRMS (ESI) m/z calcd for $C_{11}H_{15}NO_5PSF$ $[M+Na]^+$ = 346.0279, found = 346.0276; The ee value was 90%, t_R (major) = 15.7 min, t_R (minor) = 31.3 min (Chiralcel AS-H, λ = 240 nm, 40% *i*-PrOH/hexanes, flow rate = 0.6 mL/min).

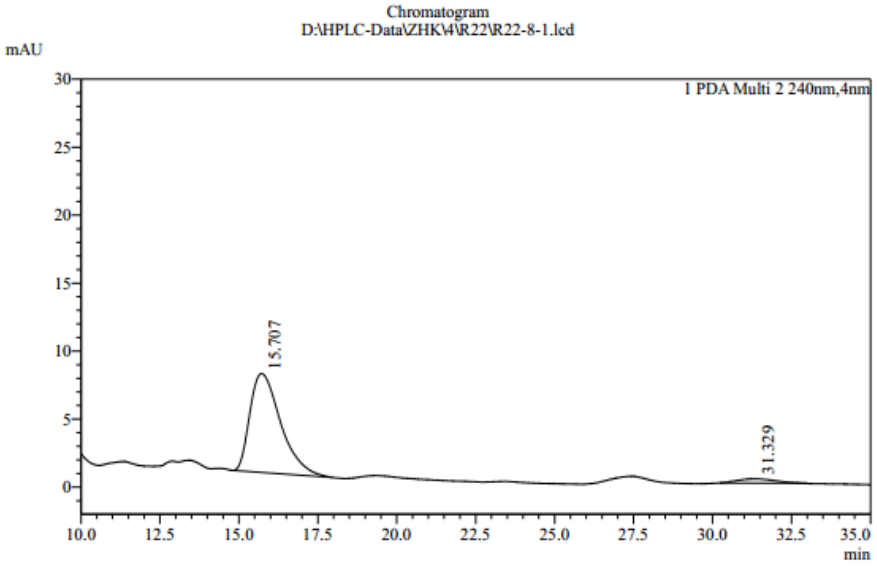


Peak Table

PDA Ch2 240nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.563	57312	70.995	2364546	50.289
2	32.425	23415	29.005	2337344	49.711
Total		80726	100.000	4701891	100.000

Racemic **5'h**



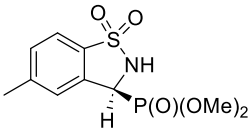
Peak Table

PDA Ch2 240nm

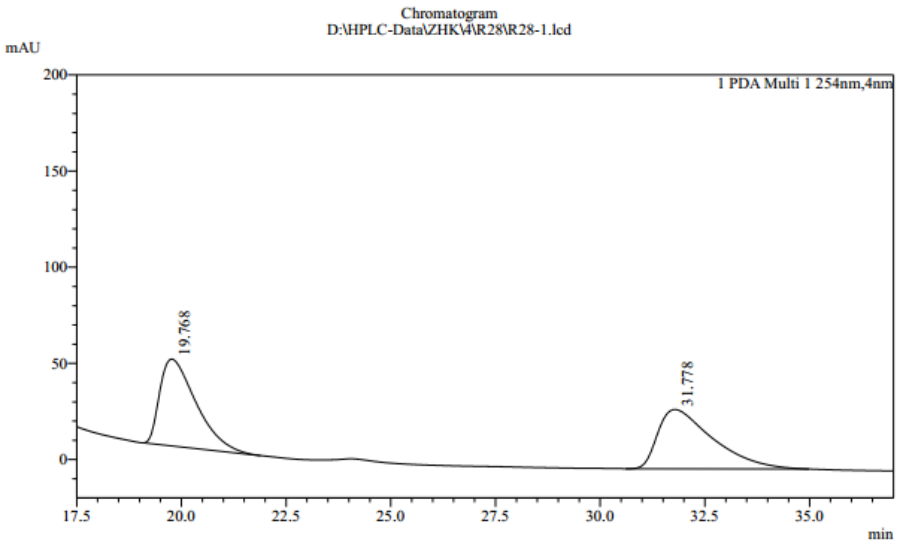
Peak#	Ret. Time	Height	Height%	Area	Area%
1	15.707	7269	95.871	493607	94.956
2	31.329	313	4.129	26219	5.044
Total		7582	100.000	519826	100.000

Enantiomerically enriched **5'h**

(*S*)-dimethyl (5-methyl-1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl) Phosphonate (5'i)



A white solid; m.p. = 89 - 91 °C; 27.1 mg, 93% yield; $[\alpha]^{25}_{D}$ = -20.50 (*c* 0.5, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.49 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 6.14 (s, 1H), 5.05 (d, *J* = 11.2 Hz, 1H), 3.87 (d, *J* = 10.4 Hz, 3H), 3.72 (d, *J* = 10.8 Hz, 3H), 2.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.56 (d, *J* = 4.8 Hz), 132.44 (d, *J* = 1.8 Hz), 132.38 (d, *J* = 2.4 Hz), 131.21 (d, *J* = 2.3 Hz), 126.14 (d, *J* = 2.8 Hz), 121.46 (d, *J* = 1.9 Hz), 55.07 (d, *J* = 7.0 Hz), 54.38 (d, *J* = 7.3 Hz), 53.77 (d, *J* = 162.6 Hz), 21.97; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.22; HRMS (ESI) m/z calcd for $C_{10}H_{14}NO_5PS$ $[M+Na]^+$ = 314.0217, found = 314.0211; The ee value was 98%, t_R (minor) = 20.3 min, t_R (major) = 31.6 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

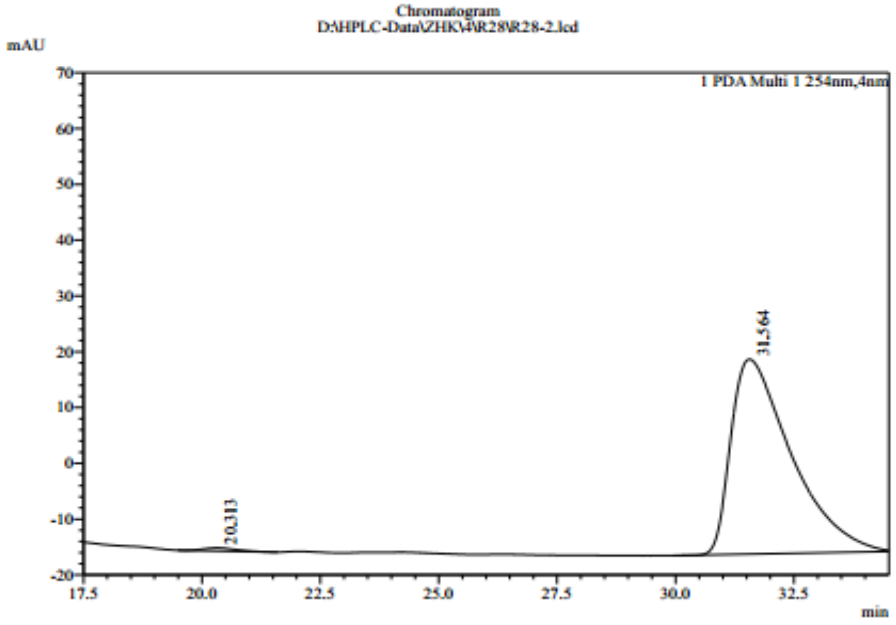


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	19.768	45179	59.430	2732101	49.258
2	31.778	30842	40.570	2814446	50.742
Total		76020	100.000	5546547	100.000

Racemic **5'i**



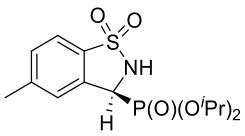
Peak Table

PDA Ch1 254nm

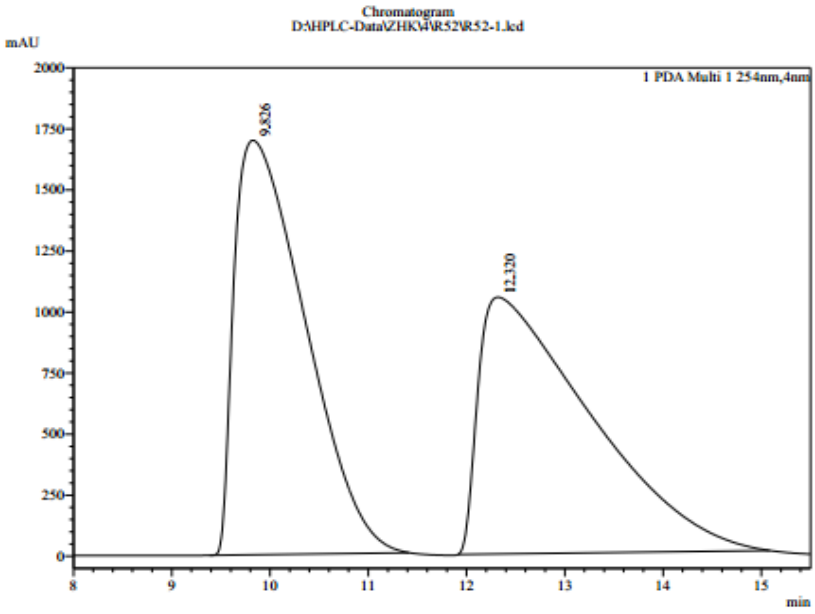
Peak#	Ret. Time	Height	Height%	Area	Area%
1	20.313	561	1.581	26587	0.852
2	31.564	34913	98.419	3093789	99.148
Total		35474	100.000	3120376	100.000

Enantiomerically enriched **5'i**

(*S*)-diisopropyl (5-methyl-1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl) Phosphonate (5'j)



A white solid; m.p. = 88 - 90 °C; 31.9 mg, 92% yield; $[\alpha]^{25}_D$ = -11.00 (*c* 0.3, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 5.46 (s, 1H), 4.93 (dd, *J* = 11.6, 2.8 Hz, 1H), 4.86 - 4.75 (m, 1H), 4.65 - 4.48 (m, 1H), 2.47 (s, 3H), 1.35 (d, *J* = 6.0 Hz, 3H), 1.30 (d, *J* = 2.8 Hz, 3H), 1.29 (d, *J* = 2.8 Hz, 3H), 1.03 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.35 (d, *J* = 2.6 Hz), 132.93 (d, *J* = 5.8 Hz), 132.52 (d, *J* = 5.7 Hz), 130.98 (d, *J* = 2.4 Hz), 126.11 (d, *J* = 2.8 Hz), 121.35 (d, *J* = 1.9 Hz), 73.38 (d, *J* = 14.5 Hz), 73.38, 54.47 (d, *J* = 159.5 Hz), 24.25 (d, *J* = 1.4 Hz), 24.22 (d, *J* = 1.6 Hz), 23.94 (d, *J* = 5.2 Hz), 23.51 (d, *J* = 5.1 Hz), 21.97; ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.85; HRMS (ESI) m/z calcd for $C_{14}H_{22}NO_5PS$ $[M+Na]^+$ = 370.0843, found = 370.0838; The ee value was 90%, t_R (minor) = 9.8 min, t_R (major) = 12.3 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

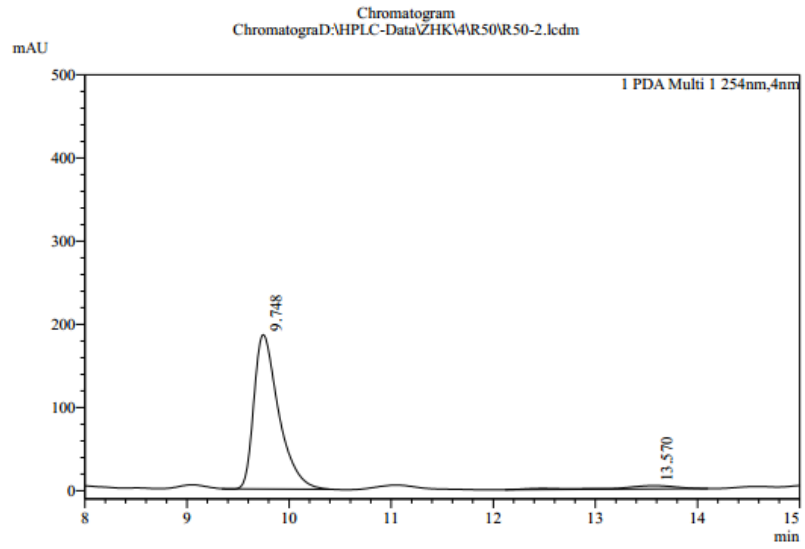


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.826	1696845	61.745	85262324	50.557
2	12.320	1051289	38.255	83382437	49.443
Total		2748133	100.000	168644761	100.000

Racemic **5'j**



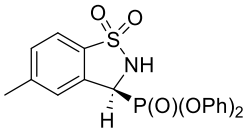
Peak Table

PDA Ch1 254nm

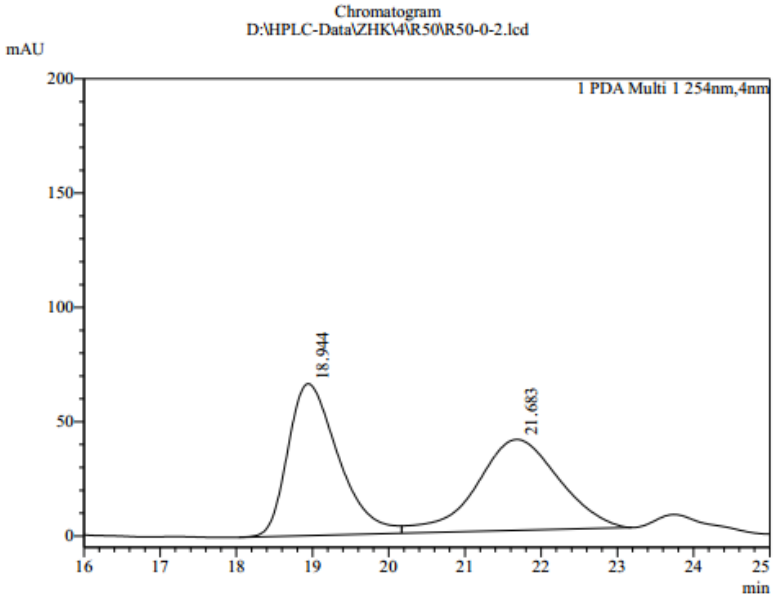
Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.748	185462	97.939	3128663	95.027
2	13.570	3902	2.061	163715	4.973
Total		189364	100.000	3292378	100.000

Enantiomerically enriched **5'j**

(*S*)-diphenyl (5-methyl-1,1-dioxido-2,3-dihydrobenzo[d]isothiazol-3-yl) Phosphonate (5'k)



A white solid; m.p. = 91 - 93 °C; 39.4 mg, 95% yield; $[\alpha]^{25}_{D}$ = -17.43 (*c* 0.3, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.33- 7.27 (m, 2H), 7.23 - 7.13 (m 5H), 7.12 - 7.05 (m, 1H), 7.01 - 6.93 (m, 2H), 5.73 (s, 1H), 5.30 (d, *J* = 9.2 Hz, 1H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.11 (d, *J* = 9.3 Hz), 149.85 (d, *J* = 9.3 Hz), 144.78 (d, *J* = 2.6 Hz), 132.45 (d, *J* = 6.2 Hz), 131.47 (d, *J* = 2.5 Hz), 131.30 (d, *J* = 5.1 Hz), 130.08, 129.77, 126.37 (d, *J* = 2.8 Hz), 125.98 (d, *J* = 0.9 Hz), 125.69, 121.61 (d, *J* = 2.0 Hz), 120.79 (d, *J* = 4.2 Hz), 120.46 (d, *J* = 4.3 Hz), 53.76 (d, *J* = 164.1 Hz), 21.86; ^{31}P NMR (162 MHz, $CDCl_3$) δ 9.37; HRMS (ESI) m/z calcd for $C_{22}H_{18}NO_5PS$ $[M+Na]^+$ = 438.0530, found = 438.0526; The ee value was 98%, t_R (minor) = 18.6 min, t_R (major) = 21.6 min (Chiralcel IC, λ = 254 nm, 40% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

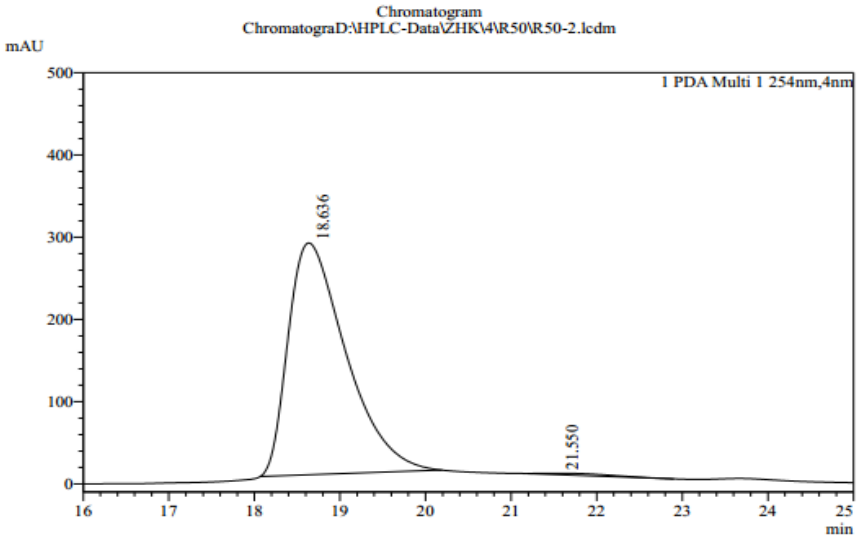


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	18.944	66385	62.533	3058001	50.489
2	21.683	39774	37.467	2998769	49.511
Total		106159	100.000	6056770	100.000

Racemic **5'k**



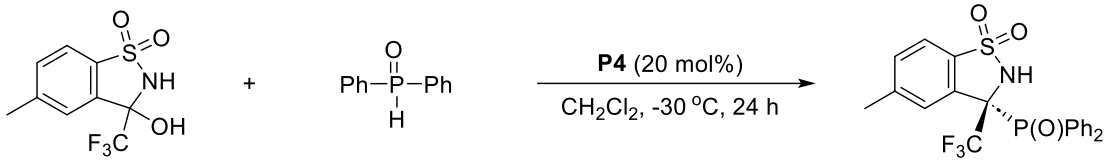
Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	18.636	281943	99.422	13254549	99.146
2	21.550	1640	0.578	114177	0.854
Total		283583	100.000	13368726	100.000

Enantiomerically enriched **5'k**

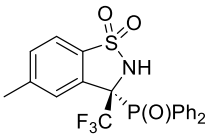
5.3 Representative procedure for the asymmetric P-nucleophile addition to CF_3-substituted cyclic N-sulfonyl amines 6 and phosphine oxide 2 and 3



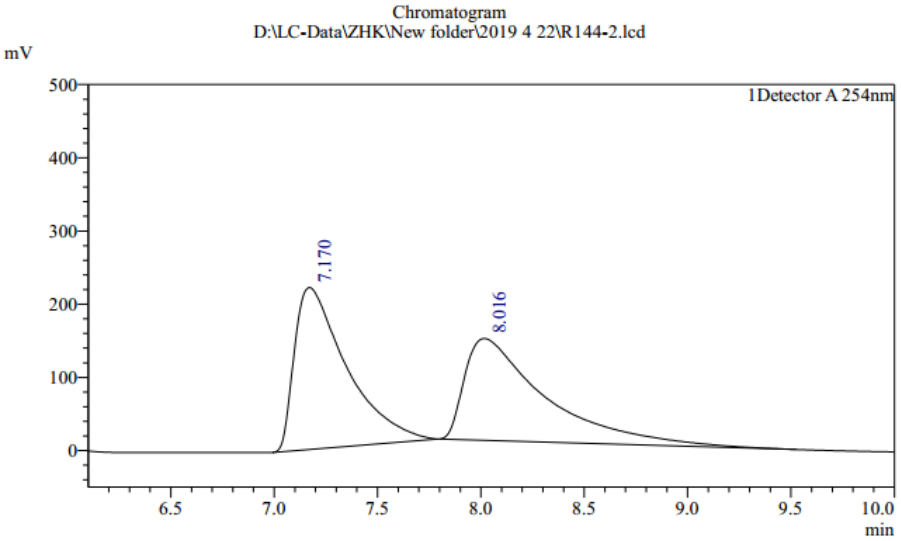
Representative procedure: To a flame-dried round bottle flask with a magnetic stirring bar were added the cyclic imine **6a** (0.1 mmol, 26.7 mg), Phosphine Oxide **2a** (0.12 mmol, 24.2 mg), and phosphonium salt **P4** (0.02 mmol, 11.3mg). followed by the addition of CH_2Cl_2 (1.0 ml). The reaction mixture was stirred at -30 °C for 24 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate = 3:1) to afford **7a** (92% yield) as a white solid.

Condition b: caried out room temperature.

(*S*)-3-(diphenylphosphoryl)-5-methyl-3-(trifluoromethyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (7a)



A white solid; m.p. = 85 - 87 °C; 41.5 mg, 92% yield; $[\alpha]^{25}_D$ = -12.32 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 - 8.04 (m, 2H), 7.98 - 7.86 (m, 3H), 7.55 - 7.47 (m, 2H), 7.47 - 7.27 (m, 6H), 7.00 (s, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.26, 133.07 (d, *J* = 2.6 Hz), 132.94 (d, *J* = 8.8 Hz), 132.83 (d, *J* = 2.6 Hz), 132.48 (d, *J* = 8.1 Hz), 129.07, 128.88 (d, *J* = 12.2 Hz), 128.66, 128.31 (d, *J* = 12.1 Hz), 127.62 (d, *J* = 8.9 Hz), 126.54 (d, *J* = 2.8 Hz), 125.33 (d, *J* = 7.3 Hz), 122.51 (dd, *J* = 6.7, 1.3 Hz), 121.27, 21.79; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.65; HRMS (ESI) m/z calcd for $C_{21}H_{17}NO_3PSF_3$ $[M+Na]^+$ = 474.0517, found = 474.0525; The ee value was 94%, t_R (minor) = 6.6 min, t_R (major) = 8.0 min (Chiralcel IC, λ = 254 nm, 30% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

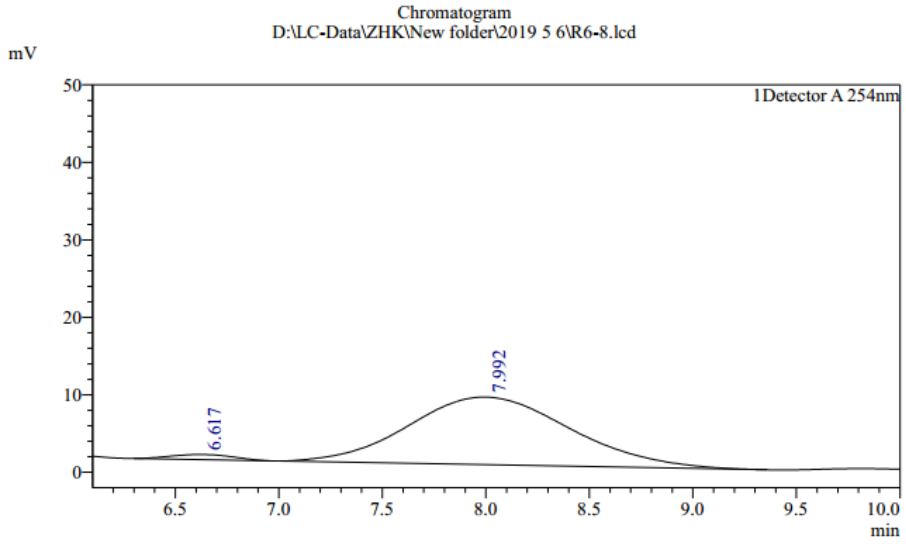


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	7.170	3881802	221096	61.397	50.879
2	8.016	3747666	139014	38.603	49.121
Total		7629469	360110	100.000	100.000

Racemic **7a**



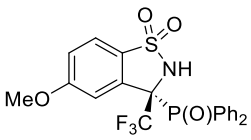
Peak Table

Detector A 254nm

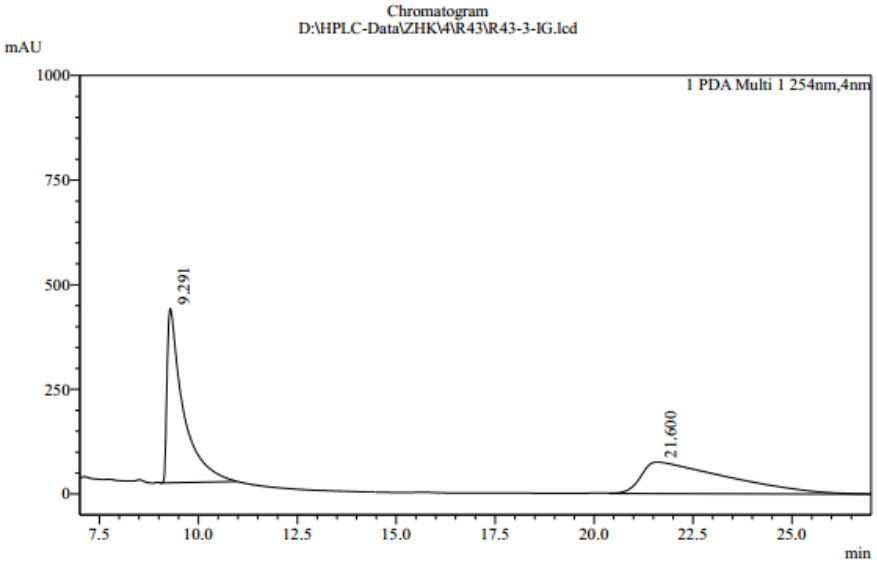
Peak#	Ret. Time	Area	Height	Height%	Area%
1	6.617	13975	669	7.114	2.857
2	7.992	475187	8728	92.886	97.143
Total		489163	9397	100.000	100.000

Enantiomerically enriched **7a**

(*S*)-3-(diphenylphosphoryl)-5-methoxy-3-(trifluoromethyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (7b)



A white solid; m.p. = 88 - 90 °C; 44.4 mg, 95% yield; $[\alpha]^{25}_{D}$ = -14.17 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.16 - 8.04 (m, 2H), 7.99 - 7.88 (m, 2H), 7.65 - 7.37 (m, 6H), 7.36 - 7.28 (m, 2H), 7.07 - 6.98 (m, 1H), 6.03 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.94 (d, *J* = 1.5 Hz), 133.46 (d, *J* = 2.8 Hz), 133.15 (d, *J* = 2.8 Hz), 132.99 (d, *J* = 8.9 Hz), 132.48 (d, *J* = 8.1 Hz), 131.56 (d, *J* = 1.5 Hz), 129.11 (d, *J* = 12.2 Hz), 128.66 (d, *J* = 12.1 Hz), 127.64 (d, *J* = 9.3 Hz), 127.05 (d, *J* = 2.7 Hz), 126.63, 123.09, 119.75 (d, *J* = 1.1 Hz), 110.35, 56.50; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.93; HRMS (ESI) m/z calcd for $C_{21}H_{17}NO_4PSF_3$ $[M+Na]^+$ = 490.0466, found = 490.0466; The ee value was >99%, t_R (major) = 8.4 min, t_R (minor) = 21.8 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

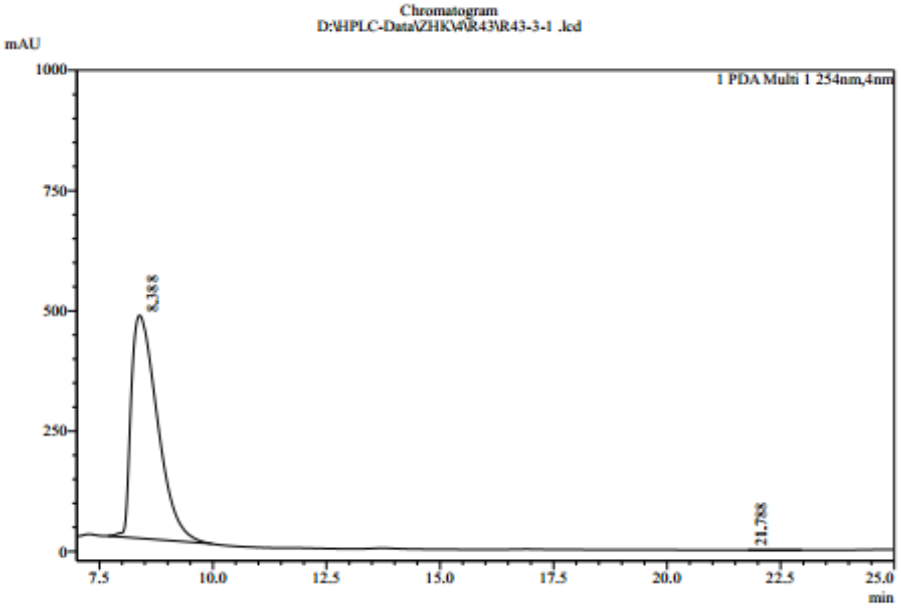


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.291	415708	84.680	11820782	50.992
2	21.600	75209	15.320	11360881	49.008
Total		490917	100.000	23181663	100.000

Racemic **7b**



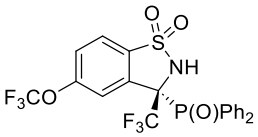
Peak Table

PDA Ch1 254nm

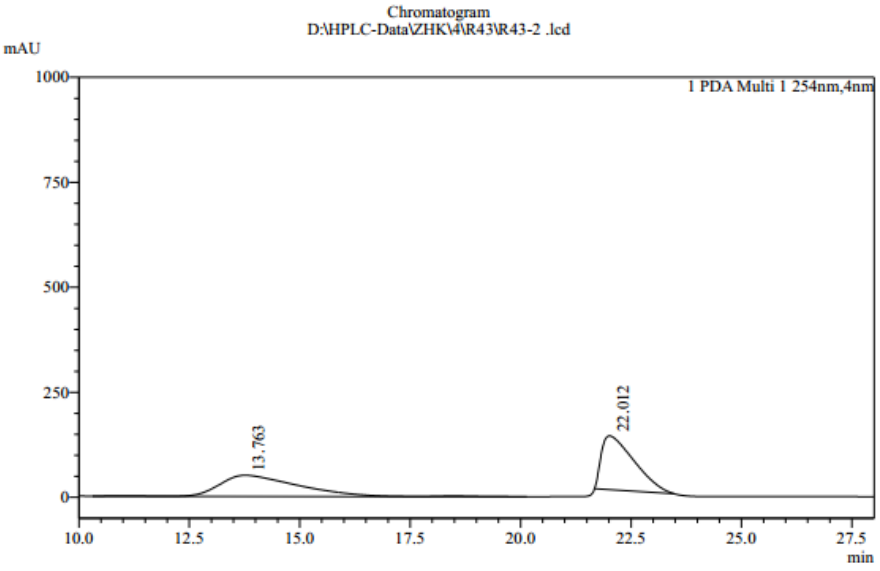
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.388	463398	100.000	18721825	99.997
2	21.788	1	0.000	576	0.003
Total		463400	100.000	18722402	100.000

Enantiomerically enriched **7b**

(*S*)-3-(diphenylphosphoryl)-5-(trifluoromethoxy)-3-(trifluoromethyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (7c)



A white solid; m.p. = 80 - 82 ºC; 47.9 mg, 92% yield; $[\alpha]^{25}_{D}$ = -17.17 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.66 (s, 1H), 7.73 - 7.63 (m, 5H), 7.58 - 7.43 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 132.67 (d, *J* = 2.8 Hz), 131.89, 131.62 (d, *J* = 9.3 Hz), 130.880, 130.77 (d, *J* = 11.3 Hz), 128.98 (d, *J* = 12.7 Hz), 120.75 (d, *J* = 6.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.59; HRMS (ESI) m/z calcd for $C_{21}H_{14}NO_4PSF_6$ $[M+Na]^+$ = 544.0183, found = 544.0194; The ee value was 98%, t_R (minor) = 13.7 min, t_R (major) = 21.5 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

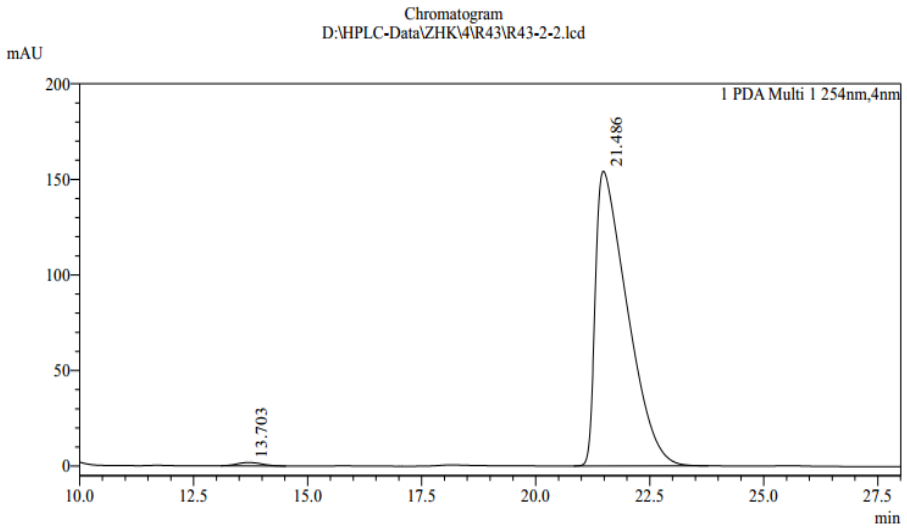


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.763	50252	28.190	6194062	48.282
2	22.012	128006	71.810	6634778	51.718
Total		178258	100.000	12828840	100.000

Racemic **7c**



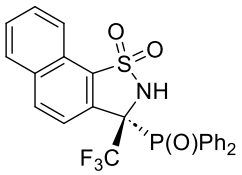
Peak Table

PDA Ch1 254nm

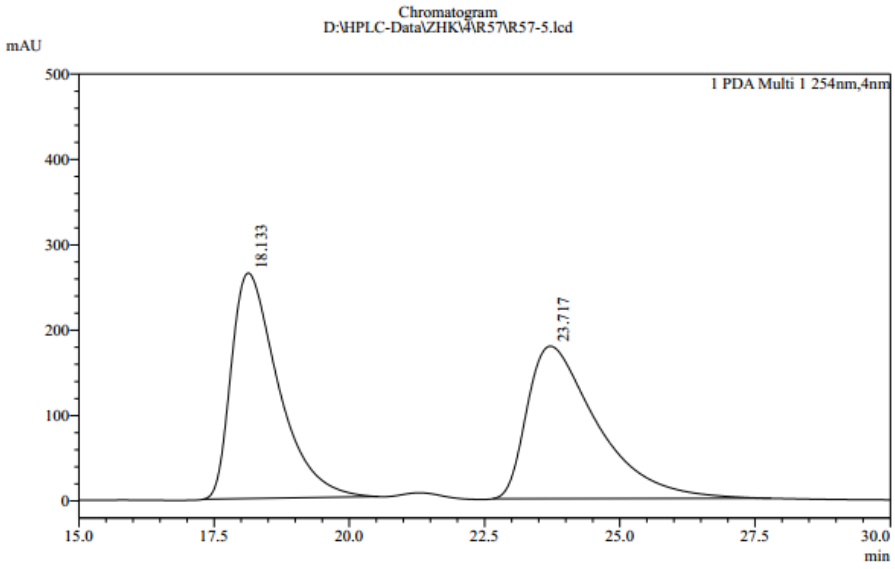
Peak#	Ret. Time	Height	Height%	Area	Area%
1	13.703	1756	1.126	65259	0.864
2	21.486	154115	98.874	7487308	99.136
Total		155870	100.000	7552567	100.000

Enantiomerically enriched **7c**

(*S*)-3-(diphenylphosphoryl)-3-(trifluoromethoxy)-2,3- dihydronaphtho[2,1-d]isothiazole 1,1-dioxide (7d)



A white solid; m.p. = 95 - 97 °C; 44.8 mg, 92% yield; $[\alpha]^{25}_{D}$ = -20.83 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO) δ 10.20 (s, 1H), 8.33 (d, *J* = 8.7 Hz, 1H), 8.21 - 8.05 (m, 5H), 7.84 - 7.63 (m, 7H), 7.35 - 7.18 (m, 3H); ^{13}C NMR (100 MHz, DMSO) δ 134.29, 133.65, 133.07 (d, *J* = 2.5 Hz), 132.72 (d, *J* = 2.3 Hz), 132.50 (d, *J* = 8.7 Hz), 131.77 (d, *J* = 8.0 Hz), 130.99 (d, *J* = 3.6 Hz), 129.63, 129.13, 128.95, 128.83, 128.16 (d, *J* = 11.7 Hz), 127.90, 127.75 (d, *J* = 1.2 Hz), 126.87, 123.81, 121.83 (d, *J* = 4.8 Hz); ^{31}P NMR (162 MHz, DMSO) δ 23.73; HRMS (ESI) m/z calcd for $C_{24}H_{17}NO_3PSF_3$ $[M+Na]^+$ = 510.0517, found = 510.0525; The ee value was 99%, t_R (minor) = 17.0 min, t_R (major) = 21.4min (Chiralcel IG, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

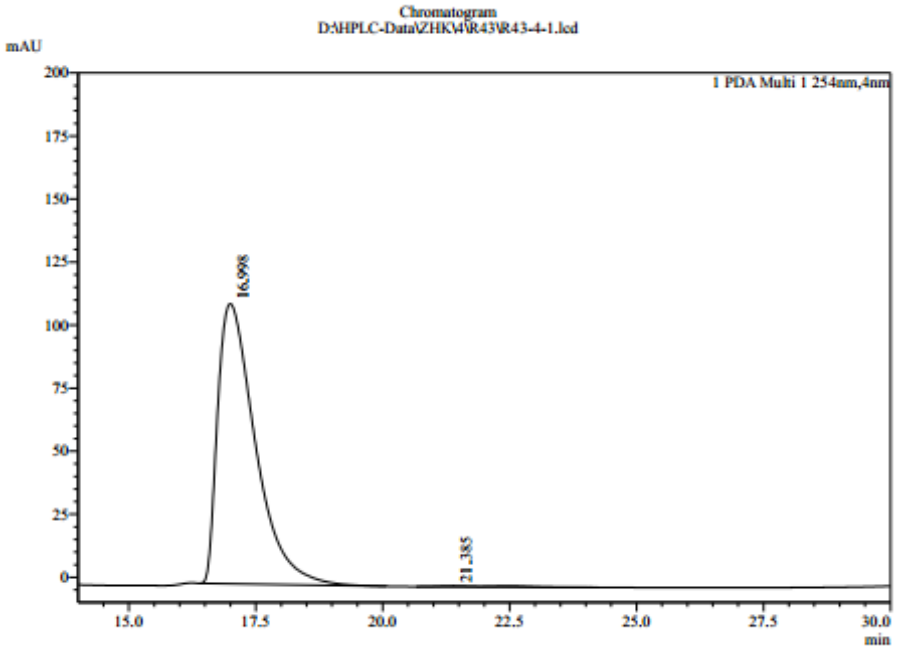


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	18.133	264142	59.673	15994126	49.778
2	23.717	178509	40.327	16136647	50.222
Total		442651	100.000	32130774	100.000

Racemic **7d**



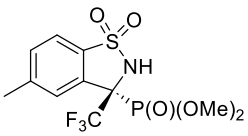
Peak Table

PDA Ch1 254nm

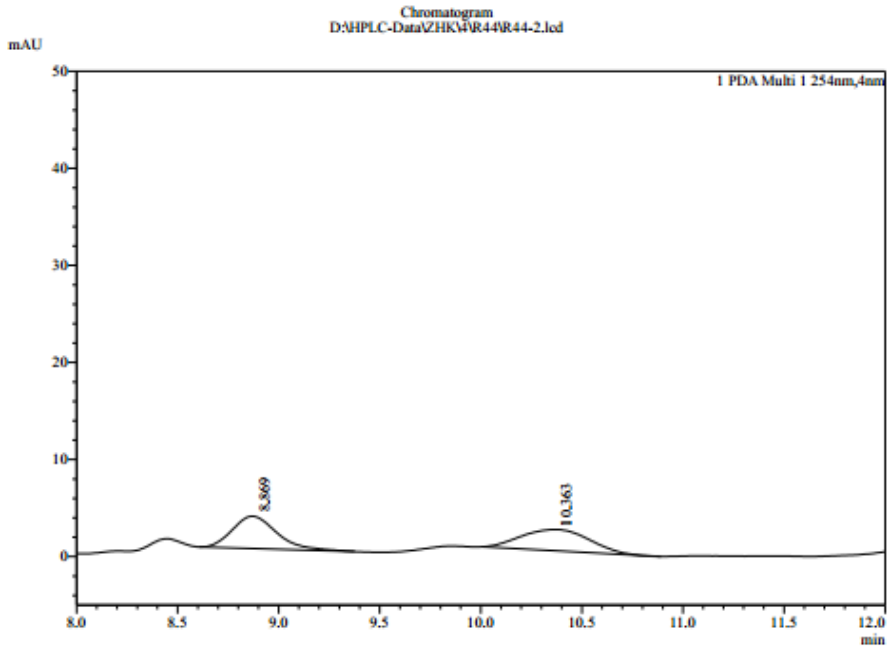
Peak#	Ret. Time	Height	Height%	Area	Area%
1	16.998	111067	99.678	5742991	99.339
2	21.385	358	0.322	38195	0.661
Total		111425	100.000	5781185	100.000

Enantiomerically enriched **7d**

(*S*)-dimethyl (5-methyl-1,1-dioxido-3-(trifluoromethyl)-2,3-dihydrobenzo[d]isothiazol-3-yl)phosphonate (7e)



A white solid; m.p. = 85 - 87 °C; 33.0 mg, 92% yield; $[\alpha]^{25}_{D}$ = -9.67 (*c* 0.7, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.0 Hz, 1H), 7.67 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 1H), 5.88 (d, *J* = 6.8 Hz, 1H), 3.90 (d, *J* = 10.8 Hz, 3H), 3.67 (d, *J* = 10.8 Hz, 3H), 2.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.36 (d, *J* = 2.1 Hz), 141.47, 133.94, 132.98 (d, *J* = 1.8 Hz), 126.83 (d, *J* = 2.1 Hz), 121.96 (d, *J* = 1.3 Hz), 55.65 (dd, *J* = 23.5, 6.8 Hz), 29.85, 22.11; ^{31}P NMR (162 MHz, $CDCl_3$) δ 12.99; HRMS (ESI) m/z calcd for $C_{11}H_{13}NO_5PSF_3$ $[M+Na]^+$ = 382.0102, found = 382.0998; The ee value was 99%, t_R (minor) = 8.4 min, t_R (major) = 11.1 min (Chiralcel IC, λ = 254 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

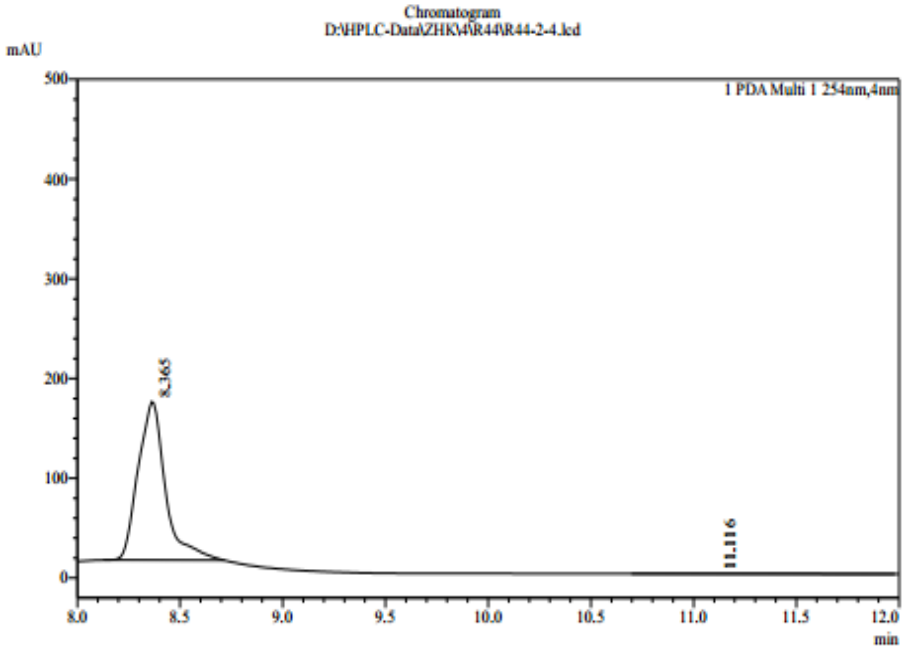


Peak Table

PDA Ch1 254nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.869	3334	60.532	50969	50.043
2	10.363	2174	39.468	50881	49.957
Total		5508	100.000	101850	100.000

Racemic **7e**



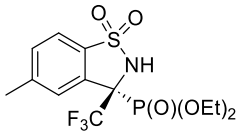
Peak Table

PDA Ch1 254nm

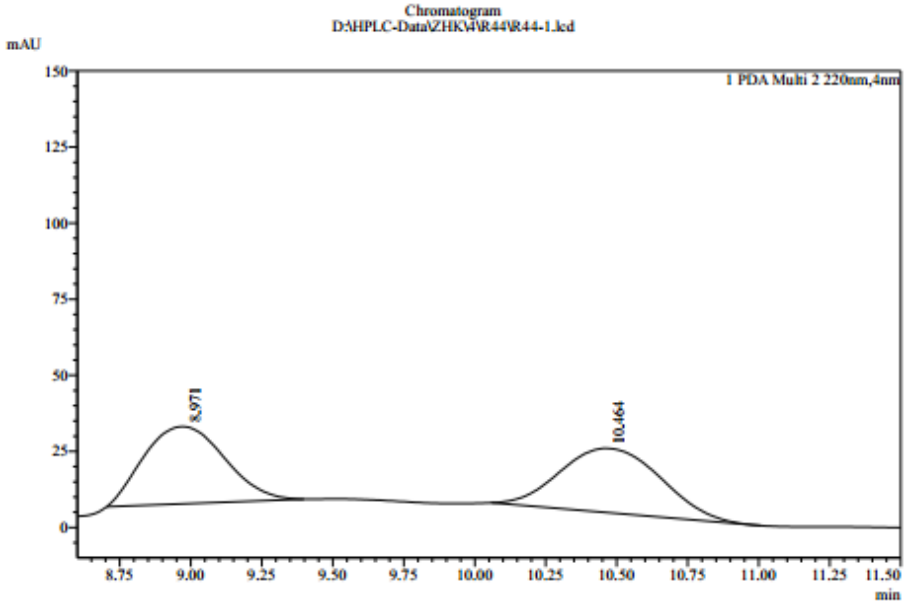
Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.365	158972	99.908	1470203	99.494
2	11.116	147	0.092	7484	0.506
Total		159119	100.000	1477687	100.000

Enantiomerically enriched **7e**

(*S*)-diethyl (5-methyl-1,1-dioxido-3-(trifluoromethyl)-2,3-dihydrobenzo[d]isothiazol-3-yl)phosphonate (7f)



A white solid; m.p. = 79 - 91 ºC; 35.2 mg, 91% yield; $[\alpha]^{25}_{D}$ = -10.50 (*c* 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 - 7.78 (m, 1H), 7.67 - 7.64 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 5.93 (s, 1H), 4.19 - 4.09 (m, 4H), 2.43 (d, *J* = 7.6 Hz, 3H), 1.36 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.20, 138.13, 130.33 (d, *J* = 4.2 Hz), 129.83, 128.92 (d, *J* = 10.0 Hz), 126.57, 67.20 (d, *J* = 32.0 Hz), 65.74 (d, *J* = 1.8 Hz), 62.19 (d, *J* = 5.7 Hz), 30.69, 29.83, 21.67, 16.41 (d, *J* = 6.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 10.55; HRMS (ESI) m/z calcd for $C_{13}H_{17}NO_5PSF_3$ $[M+Na]^+$ = 410.0415, found = 410.0410; The ee value was 90%, t_R (minor) = 9.4 min, t_R (major) = 10.4 min (Chiralcel IC, λ = 220 nm, 10% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

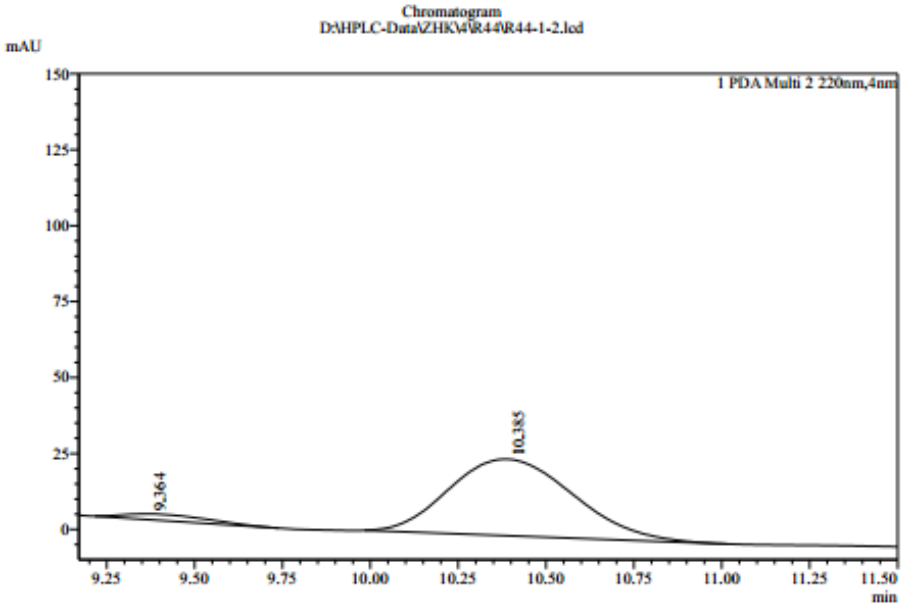


Peak Table

PDA Ch2 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	8.971	25322	54.547	503207	49.119
2	10.464	21101	45.453	521255	50.881
Total		46423	100.000	1024462	100.000

Racemic **7f**



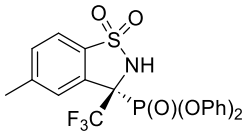
Peak Table

PDA Ch2 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	9.364	1852	6.854	32798	5.047
2	10.385	25168	93.146	617099	94.953
Total		27020	100.000	649897	100.000

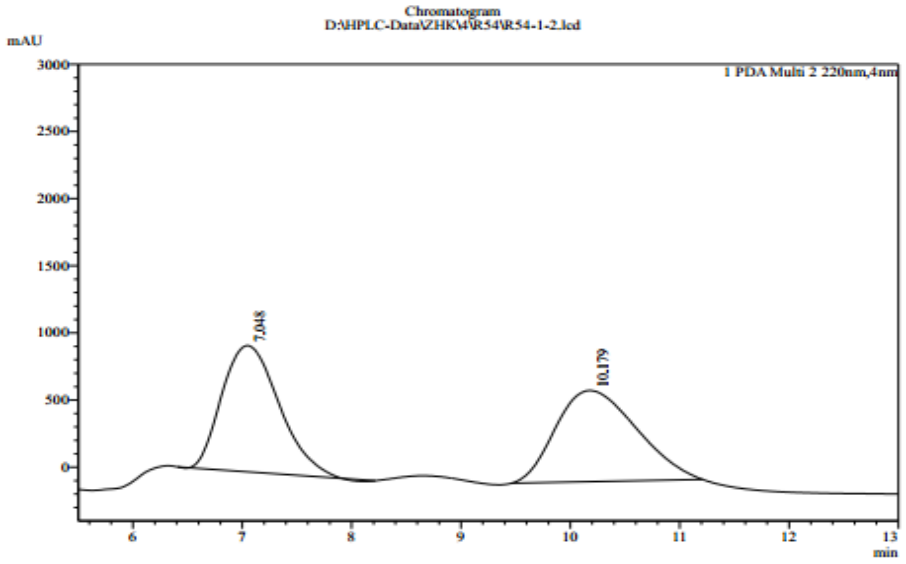
Enantiomerically enriched **7f**

(*S*)-diphenyl (5-methyl-1,1-dioxido-3-(trifluoromethyl)-2,3-dihydrobenzo[d]isothiazol-3-yl)phosphonate (7g)



A white solid; m.p. = 77 - 79 °C; 44.0 mg, 91% yield; $[\alpha]^{25}_D$ = -21.68 (*c* 0.6, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.0 Hz, 1H), 7.66 (s, 1H), 7.43 (dd, *J* = 8.1, 0.5 Hz, 1H), 7.38 - 7.30 (m, 2H), 7.24 - 7.20 (m, 1H), 7.18 - 7.11 (m, 3H), 7.09 - 7.03 (m, 1H), 6.93 - 6.81 (m, 3H), 6.04 (d, *J* = 6.8 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.75, 149.98 (dd, *J* = 84.6, 9.1 Hz), 145.48 (d, *J* = 2.3 Hz), 133.16 (d, *J* = 2.1 Hz), 132.78 (d, *J* = 5.4 Hz), 130.21 (d, *J* = 0.8 Hz), 129.72 (d, *J* = 8.2 Hz), 127.32, 126.41 (d, *J* = 1.1 Hz), 125.85, 122.02 (d, *J* = 1.4 Hz), 120.79, 120.49 (d, *J* = 4.3 Hz), 119.72 (d, *J* = 4.5 Hz), 115.43, 29.84, 21.83; ^{31}P NMR (162 MHz, $CDCl_3$) δ 1.60; HRMS (ESI) m/z calcd for $C_{21}H_{17}NO_5PSF_3$ $[M+Na]^+$ = 506.0415, found =

506.0420; The ee value was 97%, t_R (major) = 6.3 min, t_R (minor) = 9.9 min (Chiralcel IC, λ = 220 nm, 5% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

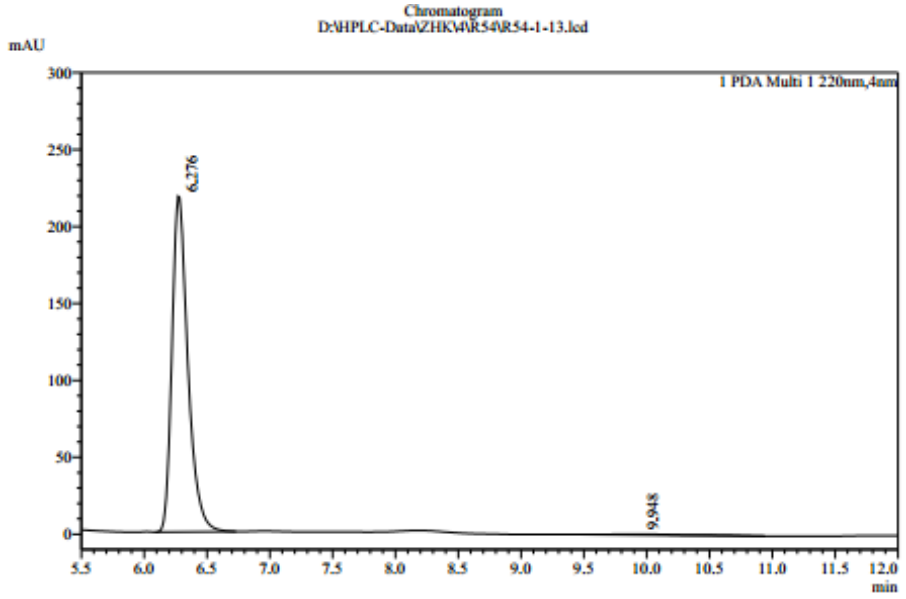


Peak Table

PDA Ch2 220nm

Peak#	Ret. Time	Height	Height%	Area	Area%
1	7.048	940511	58.063	34207078	49.448
2	10.179	679294	41.937	34971334	50.552
Total		1619805	100.000	69178412	100.000

Racemic **7g**



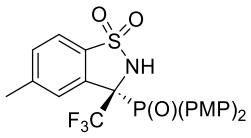
Peak Table

PDA Ch1 220nm

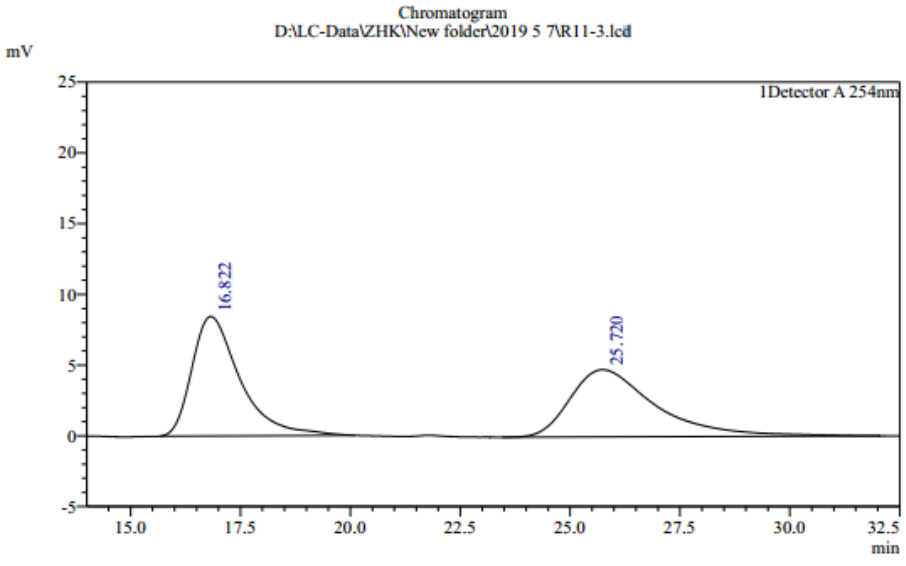
Peak#	Ret. Time	Height	Height%	Area	Area%
1	6.276	218164	99.736	1921702	98.549
2	9.948	577	0.264	28292	1.451
Total		218741	100.000	1949995	100.000

Enantiomerically enriched **7g**

(*S*)-3-(bis(4-methoxyphenyl)phosphoryl)-5-methyl-3-(trifluoromethyl)-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (7h)



A white solid; m.p. = 81 - 83 °C; 38.6 mg, 92% yield; $[\alpha]^{25}_{D}$ = -10.43 (*c* 0.7, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 - 7.91 (m, 2H), 7.82 - 7.75 (m, 3H), 7.54 (d, *J* = 8.0 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 1H), 7.05 - 6.98 (m, 2H), 6.84 - 6.75 (m, 2H), 5.37 (s, 1H), 3.87 (d, *J* = 1.6 Hz, 3H), 3.75 (d, *J* = 1.6 Hz, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.49 (d, *J* = 2.8 Hz), 163.09 (d, *J* = 2.9 Hz), 145.16 (d, *J* = 0.9 Hz), 134.77 (d, *J* = 10.0 Hz), 134.31 (d, *J* = 9.6 Hz), 132.49, 132.37 (d, *J* = 2.7 Hz), 129.60, 127.36, 121.43, 118.68 (d, *J* = 24.7 Hz), 117.68, 114.59 (d, *J* = 13.1 Hz), 114.06 (d, *J* = 13.1 Hz), 55.55, 55.41, 21.90; ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.26; HRMS (ESI) m/z calcd for $C_{23}H_{21}NO_5PSF_3$ $[M+Na]^+$ = 534.0728, found = 534.0720; The ee value was 99%, t_R (minor) = 15.5 min, t_R (major) = 24.6 min (Chiralcel IC, λ = 254 nm, 20% *i*-PrOH/hexanes, flow rate = 1.0 mL/min).

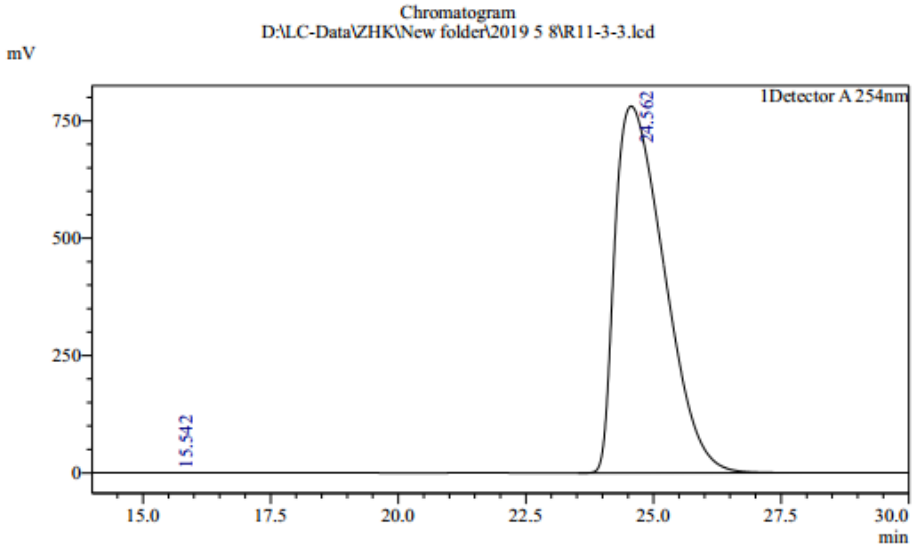


Peak Table

Detector A 254nm

Peak#	Ret. Time	Area	Height	Height%	Area%
1	16.822	642031	8446	64.040	50.108
2	25.720	639275	4743	35.960	49.892
Total		1281305	13189	100.000	100.000

Racemic **7h**



Peak Table

Detector A 254nm

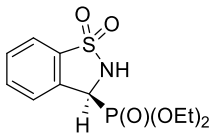
Peak#	Ret. Time	Area	Height	Height%	Area%
1	15.542	1741	56	0.007	0.003
2	24.562	52441698	781369	99.993	99.997
Total		52443438	781425	100.000	100.000

Enantiomerically enriched **7h**

6. Investigation of the absolute stereochemistry

6.1. Determination of absolute configuration of 5'

The absolute configuration of **5'b** and **5'j** were assigned to be *S* by comparing optical rotation of the same compounds reported in the literature (Scheme S4),[6] and the configuration of **5'a**, **5'c** - **5'i** and **5'k** were assigned by analogy.



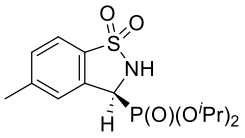
(*S*)-**5'b**

Found: **5'b** with 90% ee

$[\alpha]^{25}_D$ = -33.33 (*c* 0.60 $CHCl_3$)

Reported[1]: (*S*)-**5'b** with 94% ee

$[\alpha]^{20}_D$ = -38.93 (*c* 0.56 $CHCl_3$)



(*S*)-**5'j**

Found: **5'j** with 90% ee

$[\alpha]^{25}_D$ = -11.00 (*c* 0.30 $CHCl_3$)

Reported[1]: (*S*)-**5'j** with 94% ee

$[\alpha]^{20}_D$ = -57.33 (*c* 0.59 $CHCl_3$)

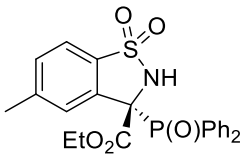
Figure S4. Optical rotation of **5'b** and **5'j** compared to reported

6.2. Determination of absolute configuration of 4, 5 and 7[7].

In order to confirm the absolute configuration of compounds **4**, **5** and **7**. For four compounds, geometry optimization e and ectronic circular dichroism (ECD) spectrum calculations were performed at the PBE0-D3(BJ)/ 6-311+G(d,p) / SMD

(dichloromethane) level of theory,[7b-7e] using Gaussian 09 program package.[7f] The calculated ECD curves were generated using Multiwfn 3.8 software.[7g]

A. Determination of absolute configuration of 4a



The absolute configuration (AC) of **4a** was confirmed as *S* and detailed method was elaborated as following: the CD spectrum experiment of **4a** from the catalytic reaction was obtained, at the same time, the ECD spectra of (*S*)-**4a** were calculated. As shown in Figure S5, the simulated spectra are in good agreement with the experimental spectral data, and the *S* configuration could be reliably assigned to compound **4a**.

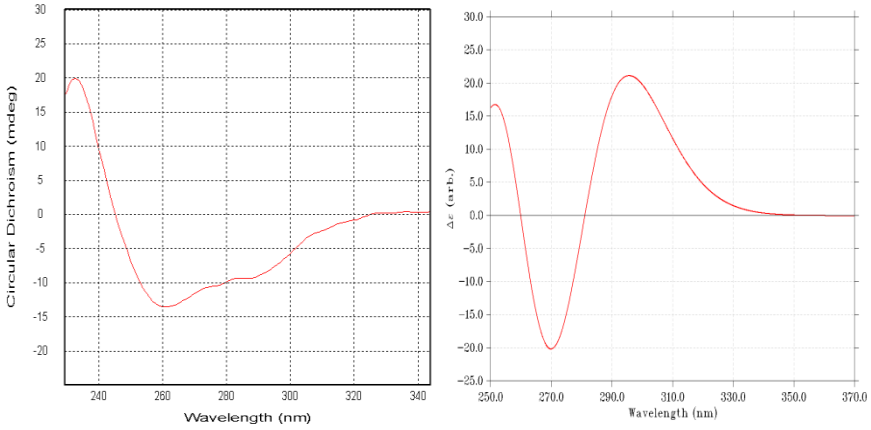
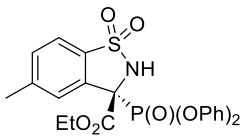


Figure S5. Experimental ECD spectra (left) and simulated spectra (right) proving *S*-conformer absolute configuration of **4a**.

B. Determination of absolute configuration of 5a



As shown in Scheme S6, the simulated spectra of (*S*)-**5a** are in good agreement with the experimental spectral data, and the *S* configuration could be reliably assigned to compound **5a**.

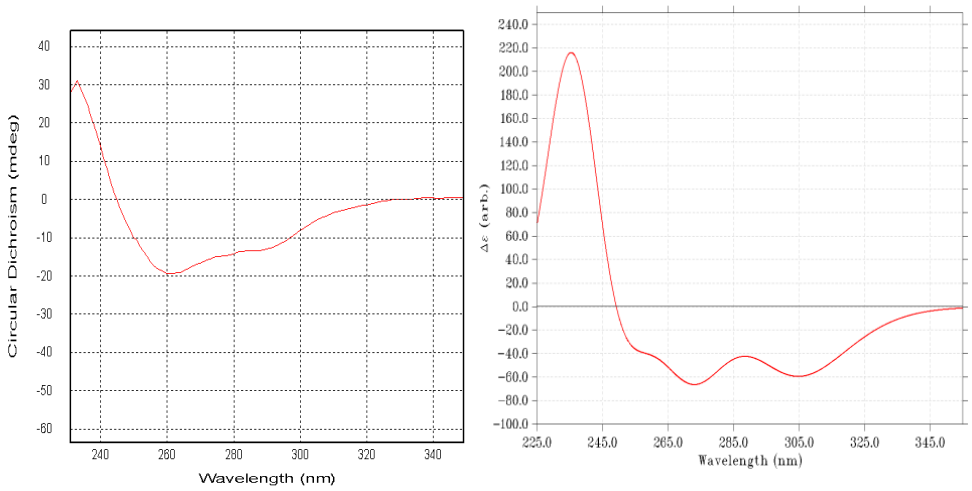
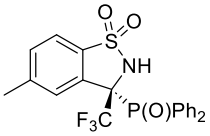


Figure S6. Experimental CD spectra (left) and simulated spectra (right) proving S-conformer 5a absolute configuration

C. Determination of absolute configuration of 7a

As shown in Scheme S7, the simulated spectra of (*S*)-**7a** are in good agreement with the experimental spectral data, and the *S* configuration could be reliably assigned to compound **7a**.



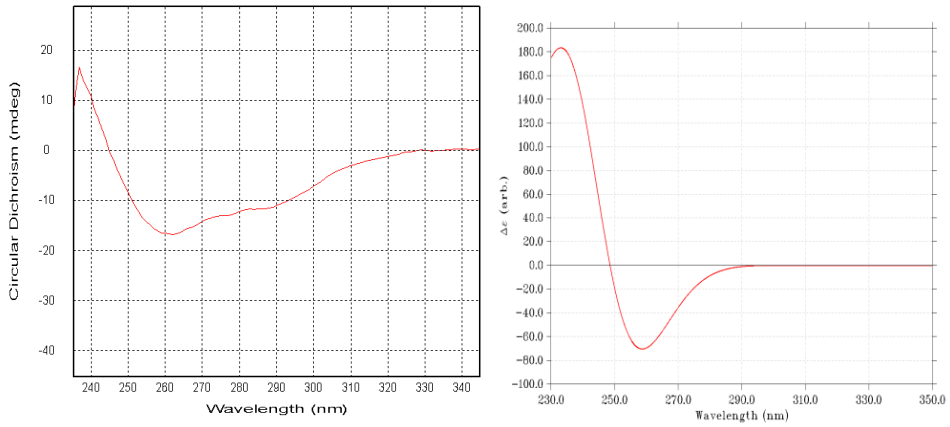


Figure S7. Experimental ECD spectra (left) and simulated spectra (right) proving *S*-conformer absolute configuration of **7a**.

D. Determination of absolute configuration of 7g

As shown in Scheme S8, the simulated spectra of (*S*)-**7g** are in good agreement with the experimental spectral data, and the *S* configuration could be reliably assigned to compound **7g**.

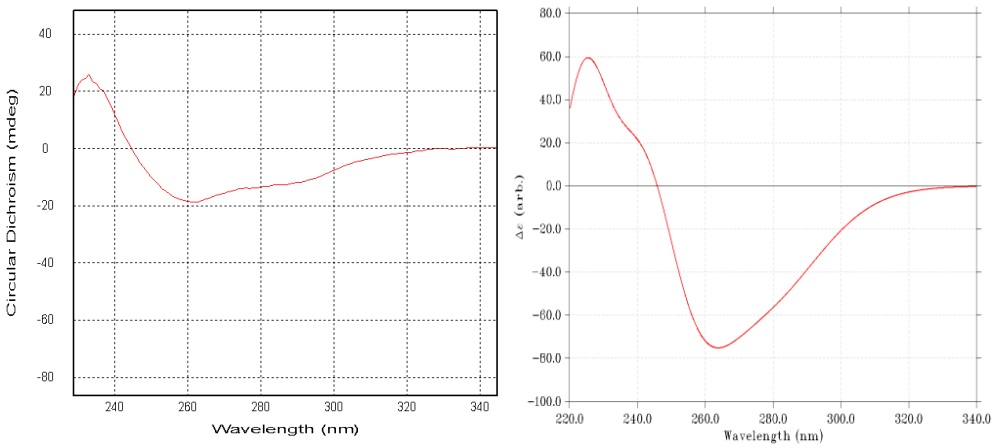


Figure S8. Experimental ECD spectra (left) and simulated spectra (right) proving *S*-conformer absolute configuration of **7g**.

6.3 Single crystal structure of catalyst P4

The absolute configuration of the catalyst **P4** was assigned as (*S*) by X-ray crystallographic analysis of a single crystal of **14** (Figure S9). CCDC 1935757 contains the supplementary crystallographic data of the chiral catalyst **P4** 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.

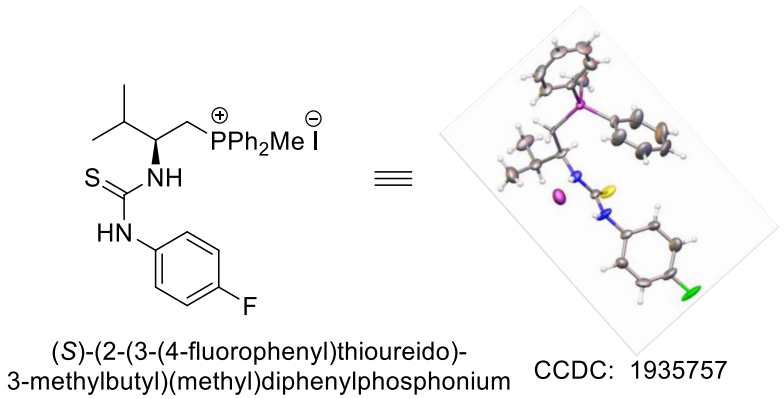


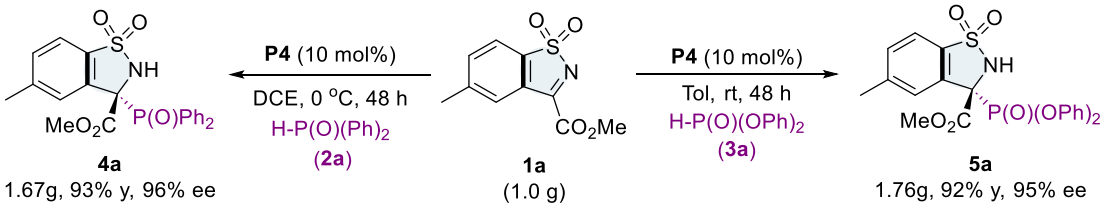
Figure S9. X-ray structure of **P4**

Table S6. Crystal data and structure refinement for **P4**

Identification code	catalyst **P4**
Empirical formula	$C_{25}H_{29}FIN_2PS$
Formula weight	566.43
Temperature/K	295.4(6)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	9.4752(4)
b/Å	11.6241(3)
c/Å	12.9271(6)
α/°	90
β/°	111.550(5)
γ/°	90
Volume/Å^3	1324.26(10)
Z	2
ρ_{calc}g/cm^3	1.421
μ/mm^{-1}	10.974
F(000)	572.0
Crystal size/mm^3	0.7 × 0.6 × 0.2
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.352 to 131.016
Index ranges	-11 ≤ h ≤ 11, -13 ≤ k ≤ 9, -12 ≤ l ≤ 15
Reflections collected	6569
Independent reflections	3343 [R_{int} = 0.1119, R_{sigma} = 0.0835]
Data/restraints/parameters	3343/1/283
Goodness-of-fit on F^2	1.131
Final R indexes [I>=2σ (I)]	R_1 = 0.0957, wR_2 = 0.2193
Final R indexes [all data]	R_1 = 0.0978, wR_2 = 0.2230
Largest diff. peak/hole / e Å^{-3}	2.88/-2.26
Flack parameter	0.009(16)

7. Gram-scale preparations and transformations

A. Procedure for the gram-scale synthesis of 4a and 5a



4a
1.67g, 93% y, 96% ee

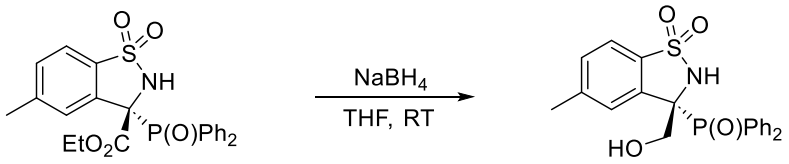
1a
(1.0 g)

5a
1.76g, 92% y, 95% ee

Gram-scale synthesis of 4a: To a flame-dried round bottle flask with a magnetic stirring bar were added the cyclic imine **1a** (4.0 mmol, 1012 mg), Phosphine Oxide **2a** (4.8 mmol, 969.6 mg), and phosphonium salt **P4** (0.4 mmol, 476 mg). followed by the addition of dry DCE (60.0 ml). The reaction mixture was stirred at 0 ºC for 48 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate = 3:1) to afford 4a (93% yield) as a white solid.

Gram-scale synthesis of 5a: To a flame-dried round bottle flask with a magnetic stirring bar were added the cyclic imine **1a** (4.0 mmol, 1012 mg), Phosphine Oxide **3a** (4.8 mmol, 1123.2 mg), and phosphonium salt **P6** (0.4 mmol, 226.4 mg). followed by the addition of toluene (40.0 mL). The reaction mixture was stirred at room temperature for 48 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel (CH_2Cl_2/ethyl acetate = 3:1) to afford **5a** (92% yield) as a white solid.

B. Preparation of compound 8[8]

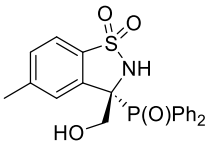


4a
(99% ee)

8
90% yield, 99% ee

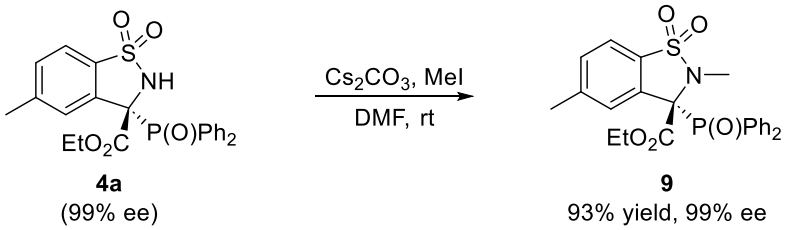
General procedure: To the solution of **4a** (0.2 mmol, 91.0 mg) in THF (5 mL) was added $NaBH_4$ (0.6 mmol, 22.8 mg) in three portions at 0 ºC. The resulting mixture was stirred for 0.5 hour at room temperature. Then, the reaction was quenched with saturated aqueous chloride ammonium (2 mL). The organic solvent was removed in vacuo and the aqueous layer was extracted with CH_2Cl_2 (5 mL x 3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and evaporated under vacuum. The residue was purified by flash chromatography over silica gel (CH_2Cl_2/ethyl acetate = 3:1) to afford the desired product **8**.

(*S*)-3-(diphenylphosphoryl)-3-(hydroxymethyl)-5-methyl-2,3-dihydrobenzo[d]isothiazole 1,1-dioxide (8)



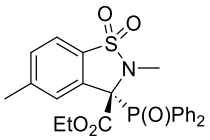
A white solide; m.p. = 142 - 144 ^{o}C; 74.3 mg, 90% yield, 99% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 - 7.47 (m, 5H), 7.47 - 7.30(m 3H), 7.16 - 6.95 (m, 5H), 5.86 (s, 1H), 5.32 (s, 1H), 3.92 - 3.54 (m, 1H), 2.21 (s, 1H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$:CD3OD = 1:1) δ 143.81 (d, *J* = 2.1 Hz), 143.65, 137.72, 132.88, 132.69 (d, *J* = 2.6 Hz), 132.55 (d, *J* = 3.0 Hz), 132.40 (dd, *J* = 12.9, 2.7 Hz), 132.01 (d, *J* = 3.7 Hz), 131.58 (dd, *J* = 56.4, 9.0 Hz), 130.39 (d, *J* = 1.9 Hz), 130.06 (d, *J* = 11.8 Hz), 129.90, 129.53, 128.57 (d, *J* = 13.0 Hz), 128.12 (dd, *J* = 66.8, 12.0 Hz), 126.18, 125.42 (d, *J* = 2.5 Hz), 125.18, 124.64, 120.42 (d, *J* = 1.6 Hz), 120.10, 64.03, 58.53, 56.23 (d, *J* = 84.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$:CD_3OD = 1:1) δ 35.78; HRMS (ESI) m/z calcd for $C_{21}H_{20}NO4PS$ $[M+Na]^+$ = 436.0748, found = 436.0740.

C. Preparation of compound 9[9]



General procedure: To the solution of **4a** (0.2 mmol, 91.0 mg) in DMF (5 mL) was added CH_3I (0.6 mmol), The resulting mixture was stirred for 0.5 hour at room temperature. Then, the reaction was added Cs_2CO_3 (0.2 mmol). The resulting mixture was stirred for 4 hours at room temperature. The reaction was quenched with saturated aqueous NaCl (2 mL). The mixture layer was extracted with CH_2Cl_2 (10 mL x 3). The combined organic layer was dried over anhydrous sodium sulfate, filtered and evaporated under vacuum. The residue was purified by flash chromatography over silica gel (CH_2Cl_2/ethyl acetate = 3:1) to afford the desired product **9**.

(*S*)-ethyl 3-(diphenylphosphoryl)-2,5-dimethyl-2,3-dihydrobenzo[d]isothiazole-3-carboxylate 1,1-dioxide (9)



A white solide, m.p. = 184 - 186 ^{o}C; 87.2 mg, 93% yield, 99% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 - 7.77 (m, 2H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.59 - 7.48 (m, 4H), 7.46 - 7.37 (m, 4H), 7.33 (d, *J* = 8.0 Hz, 1H), 6.88 (s, 1H), 4.42 - 4.17 (m, 2H), 2.90 (s, 3H), 2.21 (s, 3H), 1.27 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.15 (d, *J* = 6.8 Hz), 143.54 (d, *J* = 1.7 Hz), 133.40 (d, *J* = 8.7 Hz), 132.92 (d, *J* = 2.7 Hz), 132.78 (d, *J* = 2.9 Hz), 131.57 (d, *J* = 1.6 Hz), 130.88 (d, *J* = 3.4 Hz), 130.56 (d, *J* = 2.6 Hz), 129.40 (d, *J* = 16.4 Hz), 128.65 (d, *J* = 11.9 Hz), 128.41 (d, *J* = 19.6 Hz), 127.96 (d, *J* = 12.0 Hz), 127.21 (d, *J* = 3.0 Hz), 121.24 (d, *J* = 0.8 Hz), 73.93 (d, *J* = 73.5 Hz), 63.38, 27.18, 21.78, 14.08; ^{31}P NMR (162 MHz, $CDCl_3$) δ 31.85; HRMS (ESI) m/z calcd for $C_{24}H_{24}NO_5PS$ $[M+Na]^+$ = 492.1010, found = 492.1002.

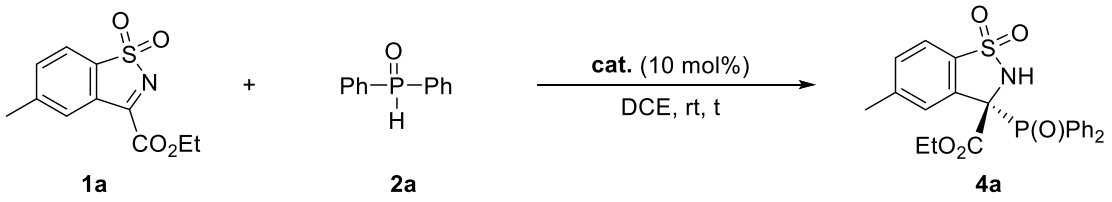
8. Mechanistic studies

8.1. Model reaction promoted by different catalysts

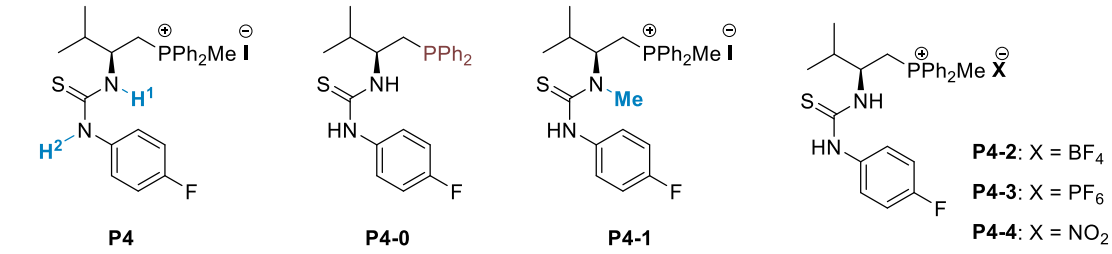
According to previous mechanistic results, we prepared the methylated phosphonium salt catalyst **P4-1**. As shown, employment of N-methylated catalyst **P4-1** led to the formation of the desired product **4a** in low yield with sharply decreased enantioselectivities (entry 2). Additionally, when methanol was used as solvent (entry 3), erosion of enantioselectivity was observed due to that the hydrogen-bond network was disrupted under polar system, Besides, when changed the optimal phosphonium salt catalyst P4 to its corresponding trivalent. phosphine (**P4-0**) under the standard conditions for the reaction, the yield and selectivity of the reaction decreased remarkably, giving nearly racemic product only with 35% isolated yield (entry 4). All these results indicated the importance of both hydrogen-bonding and ion-pair interactions in this phase-transfer system. Futhermore, we have also tested different negative ions with a neutral H-bonding trivalent phosphine catalyst (P4-0) under the standard conditions for the reaction. Not surprisingly, the yield and selectivity of the reaction decreased remarkably, giving nearly racemic product with moderate isolated

yield (entries 5-7), which indicated the synergistic effect between the hydrogen-bonding and ion pair of the bifunctional phosphonium salts. Additionally, the anions effect of the bifunctional phosphonium salt were investigated, the other types of bifunctional phosphonium salt catalysts with BF_4^- (**P4-2**) 、PF_6^- (**P4-3**) and NO_2^-(**P4-4**) were synthesized and applied in the model reaction under standard conditions, and the results shown that the enantioselectivities of this asymmetric P-addition reaction were dropped sharply (Table S7, entries 8-10). We speculated that mainly due to the steric hindrance and the tightness of ion pairs moiety in the catalyst.

Table S7. Asymmetric P-nucleophile addition to cyclic ketimine 1a with 2a promoted by different phosphonium salts[a]



Catalysts examined



entry	cat.	sol.	T (°C)	t (h)	yield (%)[b]	ee (%)[c]
1	**P4**	DCE	rt	2	95	>99
2	**P4-1**	DCE	rt	2	94	8
3	**P4**	MeOH	rt	0.5	92	0
4	**P4-0**	DCE	rt	24	35	<5
5[d]	**P4-0**	DCE	rt	24	83	<5
6[e]	**P4-0**	DCE	rt	24	72	<5
7[f]	**P4-0**	DCE	rt	24	67	0
8	**P4-2**	DCE	rt	2	80	<5
9	**P4-3**	DCE	rt	2	85	<5
10	**P4-4**	DCE	rt	2	90	12

[a]Reactions were performed with **1a** (0.1 mmol), **2a** (0.12 mmol), catalyst (0.01 mmol) in solvent (1.0

mL). [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]The NaI (0.1 mmol) was used. [e]The NaBr (0.1 mmol) was used. [f]The NaCl (0.1 mmol) was used.

8.2. ^{1}H NMR titration of 1a or 2a with catalyst P4

^{1}H NMR titration experiments were conducted on a Bruker spectrometer by recording the changes of ^{1}H NMR spectra of the catalyst **P4** after the corresponding targets addition. In a typical experiment, the catalyst **P4** (28.3 mg, 0.05 mmol) was dissolved with CD_3Cl (0.5 mL) in nuclear magnetic tube. Then, the ^{1}H NMR spectrum of catalyst **P4** was recorded. After that, the corresponding equivalent of substrate (**1a** or **2a**) was stepwise added to the NMR-tube and chemical shifts of the protons on the catalyst **P4** were recorded after each addition.

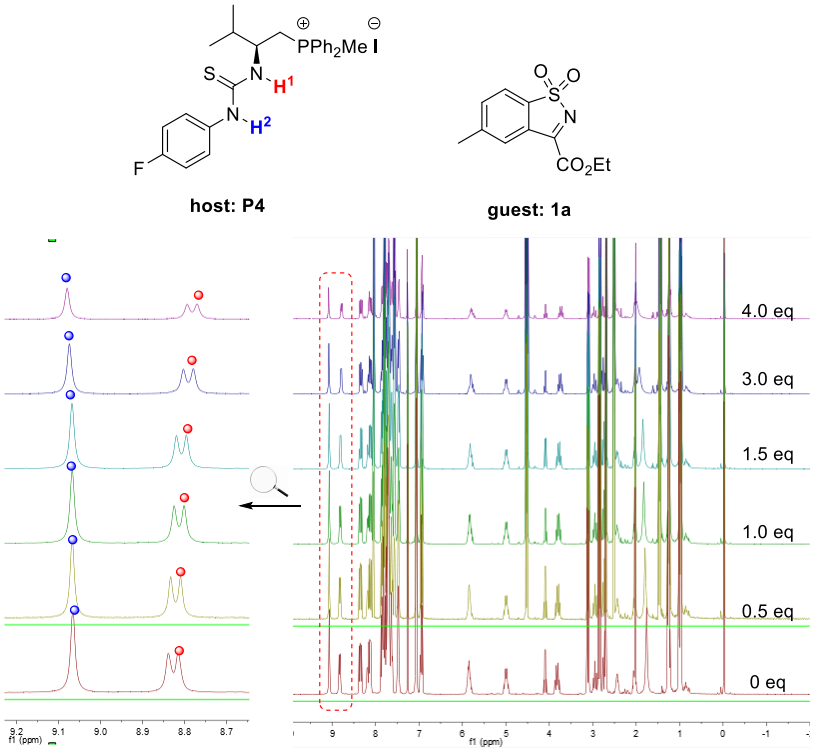


Figure S10. ^{1}H NMR spectrum of **P4** with **1a**

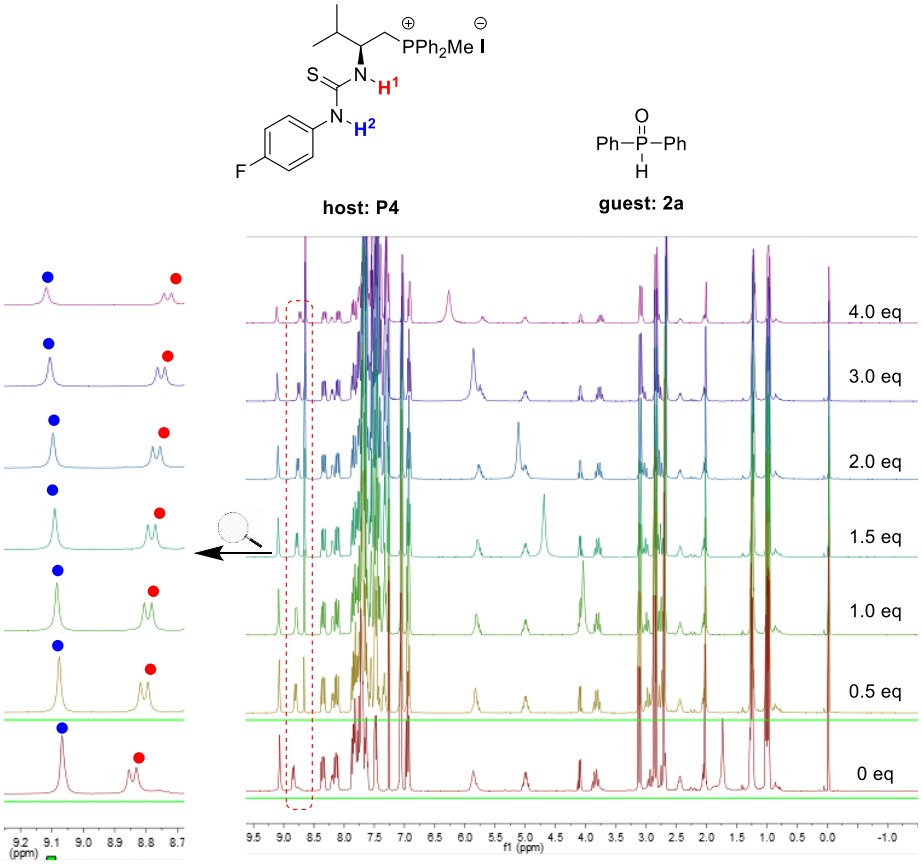


Figure S11. ^{1}H NMR spectrum of **P4** with **2a**

^{1}H NMR titration was conducted in chloroform-d, which was dried with potassium carbonate and degassed. The total concentration of the host (**P4**) and the guest (**1a**/**2a**) was 0.04 M. The proportion of the concentration of the host vs the total concentration varied from 0.2 equivalent to 0.8. The chemical shift of N-H^{1} of **P4** were recorded. 1:1 binding pattern could also be observed in the Job plot.

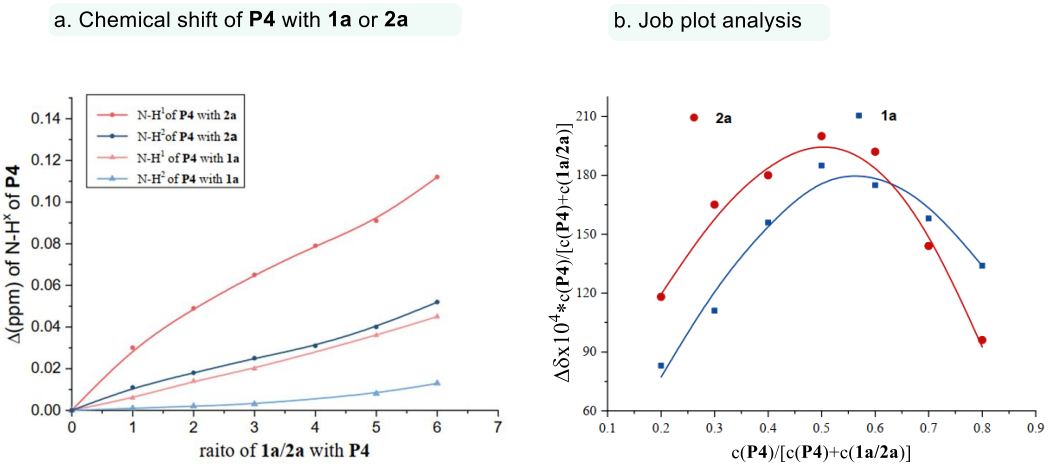


Figure S12. ^{1}H NMR titration of substrate **1a** or **2a** with **P4**

B. Proposed reaction catalytic cycle

It was plausible to propose a reaction catalytic cycle presented as Figure S13. At first the diphenylphosphine oxide **2a** was deprotonated by iodide ion and converted into diphenylphosphinite anion, which was stabilized and simultaneously activated by the catalyst **P4** via H-bonding and ion-pair interaction. Subsequently, the nucleophilic addition of the anionic **P**-specie towaeds cyclic imine substrate **1a** preferentially occurred via the transition state **TS-1**, which quickly was protonated experiencing the transition state **TS-2** to produce product (*R*)-**5a** and release catalyst **P4** that would enter the next reaction cycle.

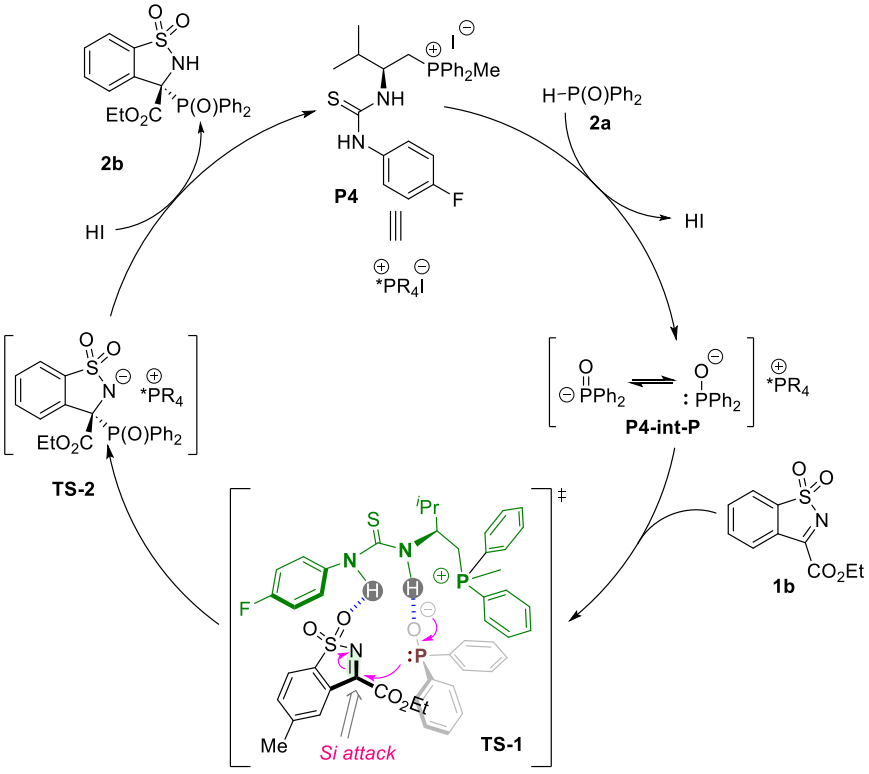


Figure S13. Proposed reaction mechanism

C. Structure characteristics of bifunctional phosphonium salt catalyst P4 by-DFT calculation

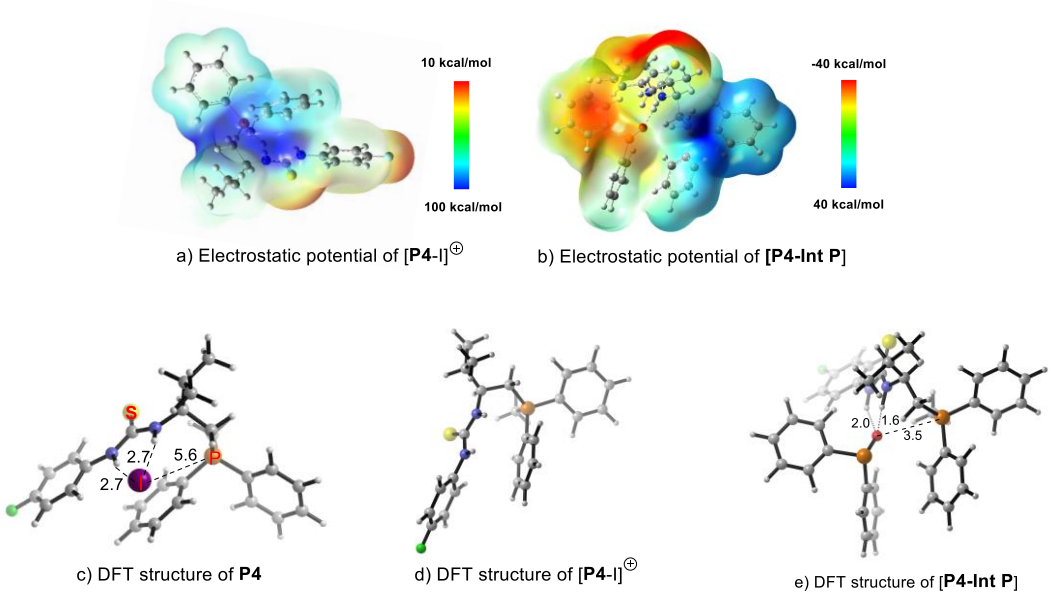


Figure S14. The electrostatic potential and DFT structure of catalysts, catalyst cations, and catalyst complexes. (The optimized structures were calculated at the M062X-D3/6-311+G(d,p)-SMD(CH_2Cl_2)//M062X-D3/6-31G(d,p)-SMD(CH_2Cl_2) level of theory).

D. Cartesian coordinates of DFT-computed structures

P4

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P	-2.35508800	-1.02153100	0.62610700
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N	0.00763600	1.12046800	1.27936200
C	-1.26298100	1.21988000	1.96772600
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C	-0.87182300	-1.49290100	-0.28645000
C	3.95910400	-0.09725800	-0.64318100
N	2.02838800	0.32201800	0.68458100

C	3.24196500	-0.36773000	0.54082400
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C	3.76563800	-1.30237600	1.44959400
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[**P4-I**]$^{+}$

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[**P4-Int-P**]

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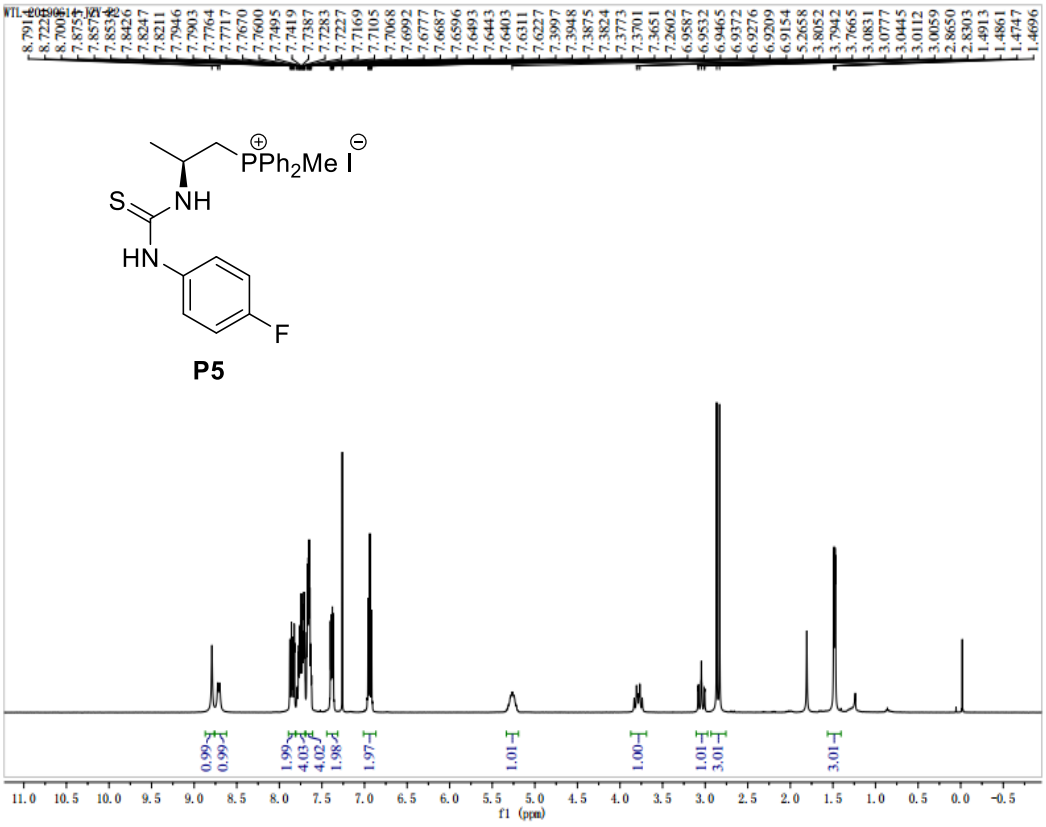
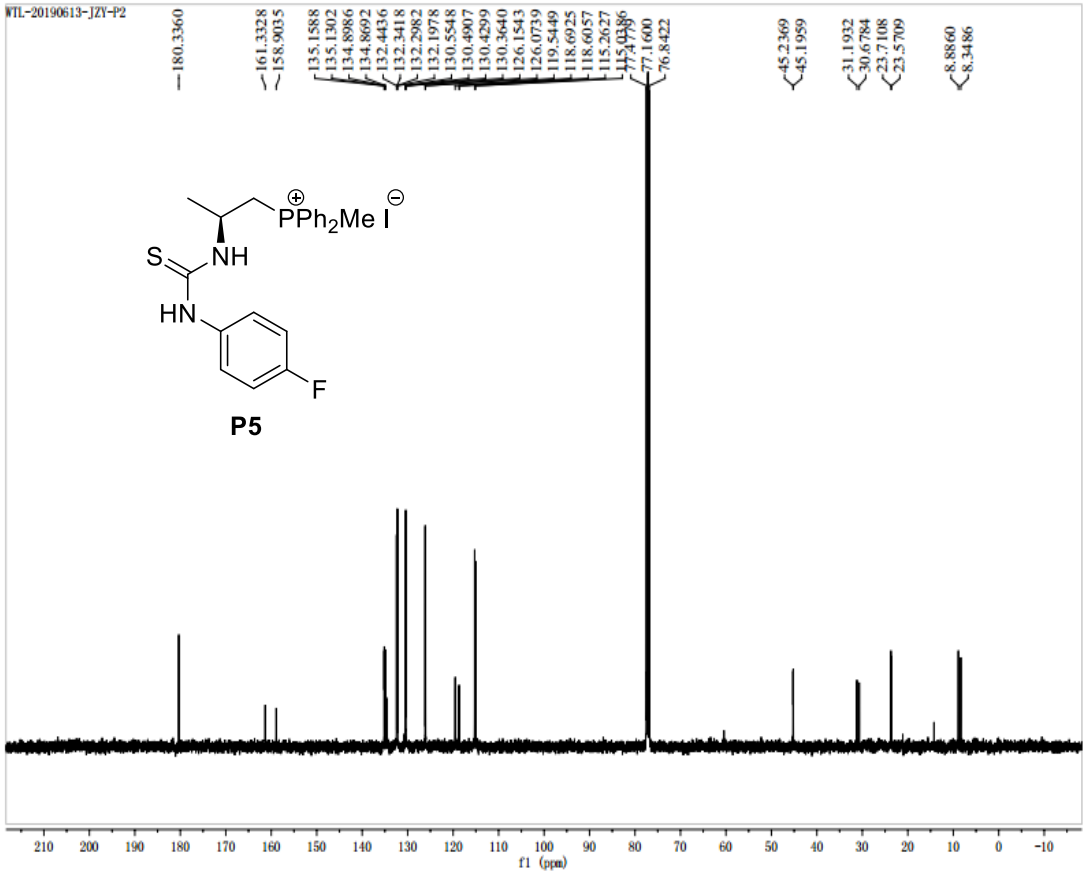
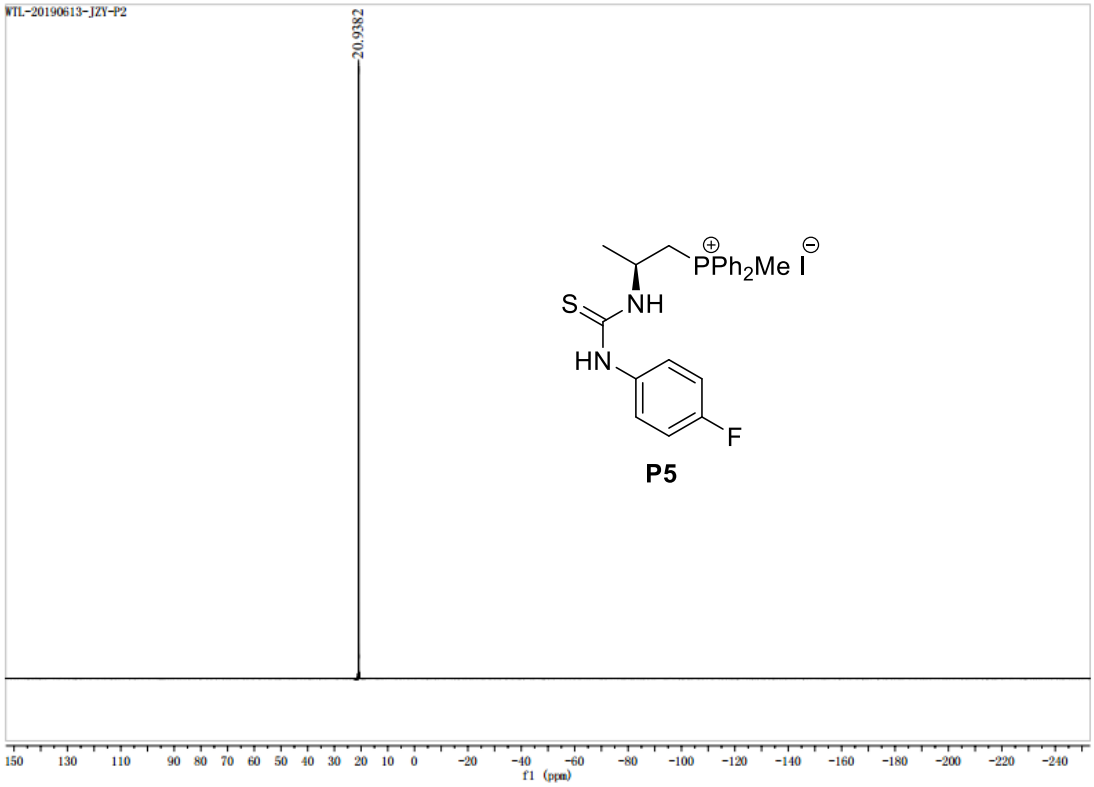
10. NMR spectra



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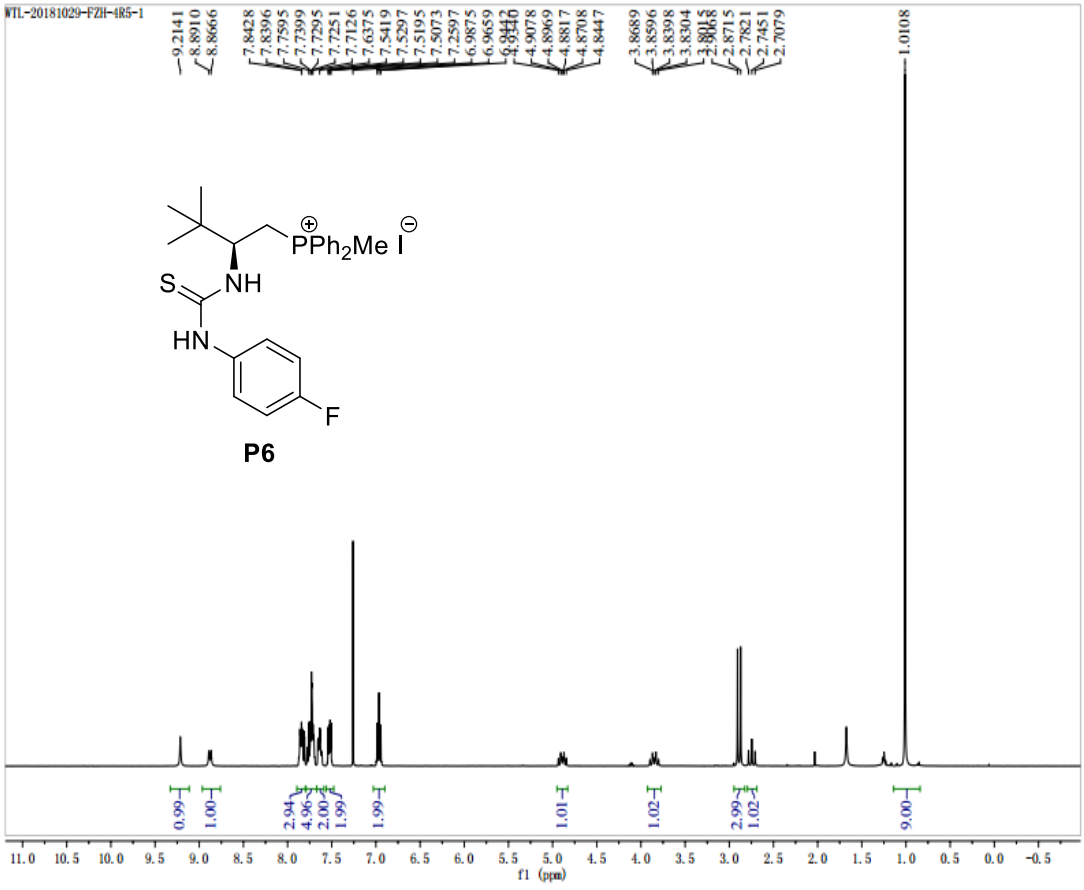
f1 (ppm)

P5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S
NH
HN
F
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1.00
2.94
4.96
2.00
1.99
1.99
1.01
1.02
2.99
1.02
9.00
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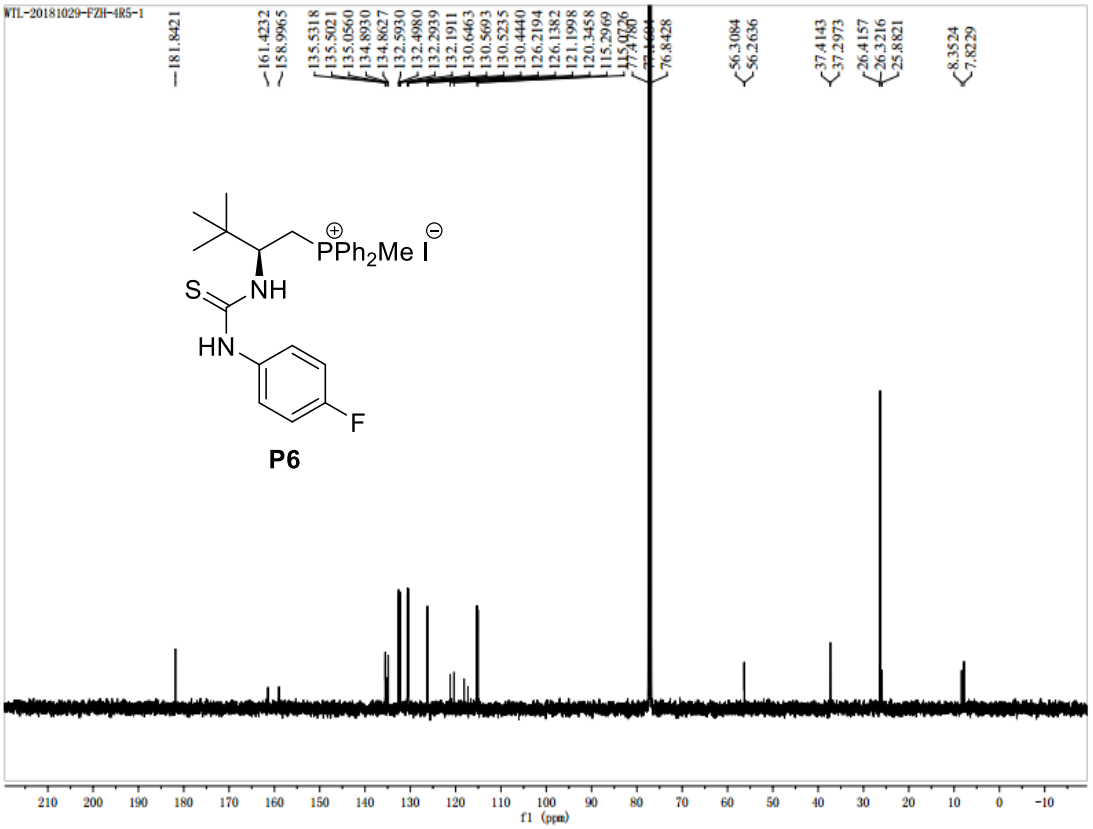
f1 (ppm)

P6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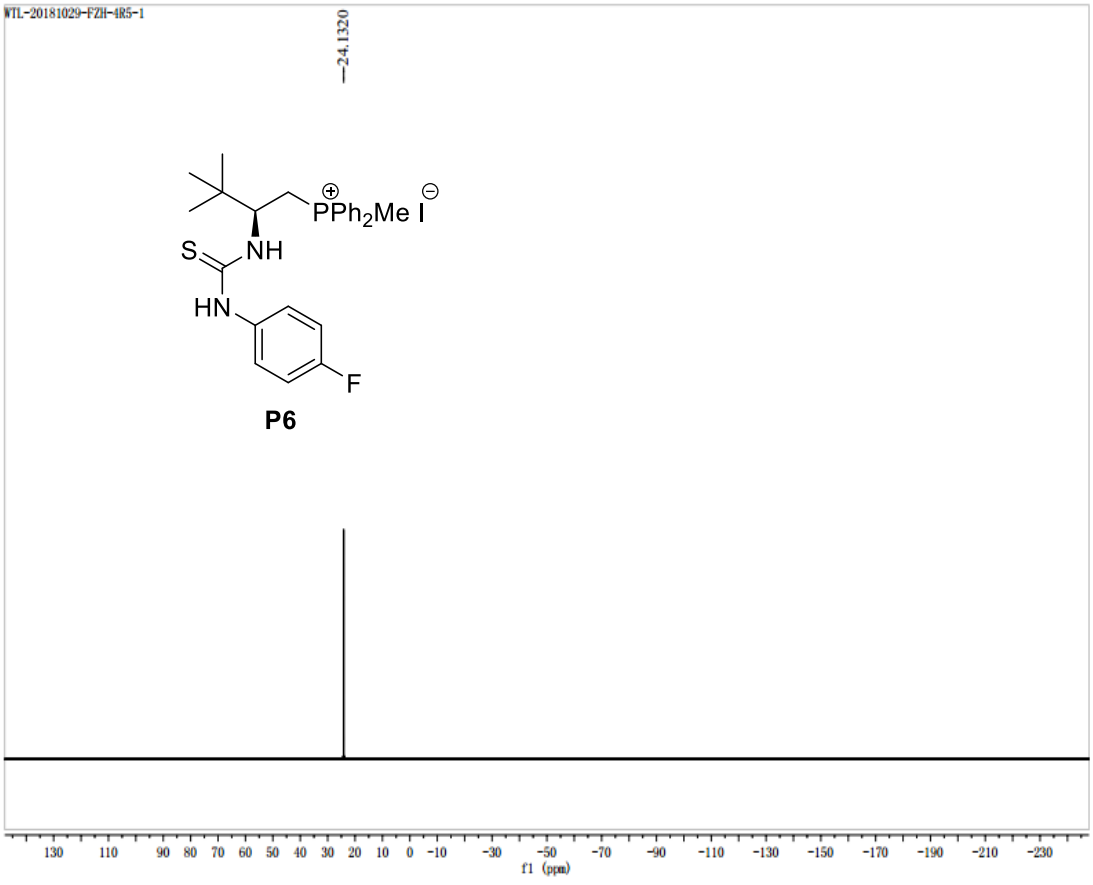
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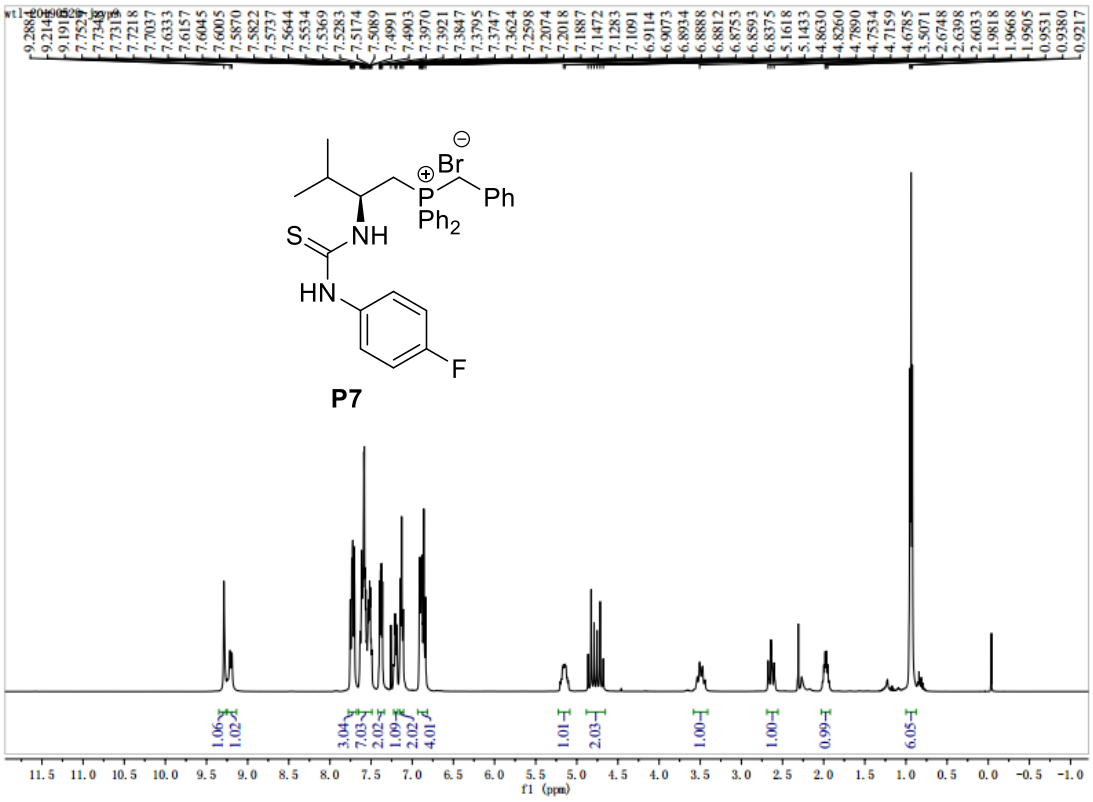
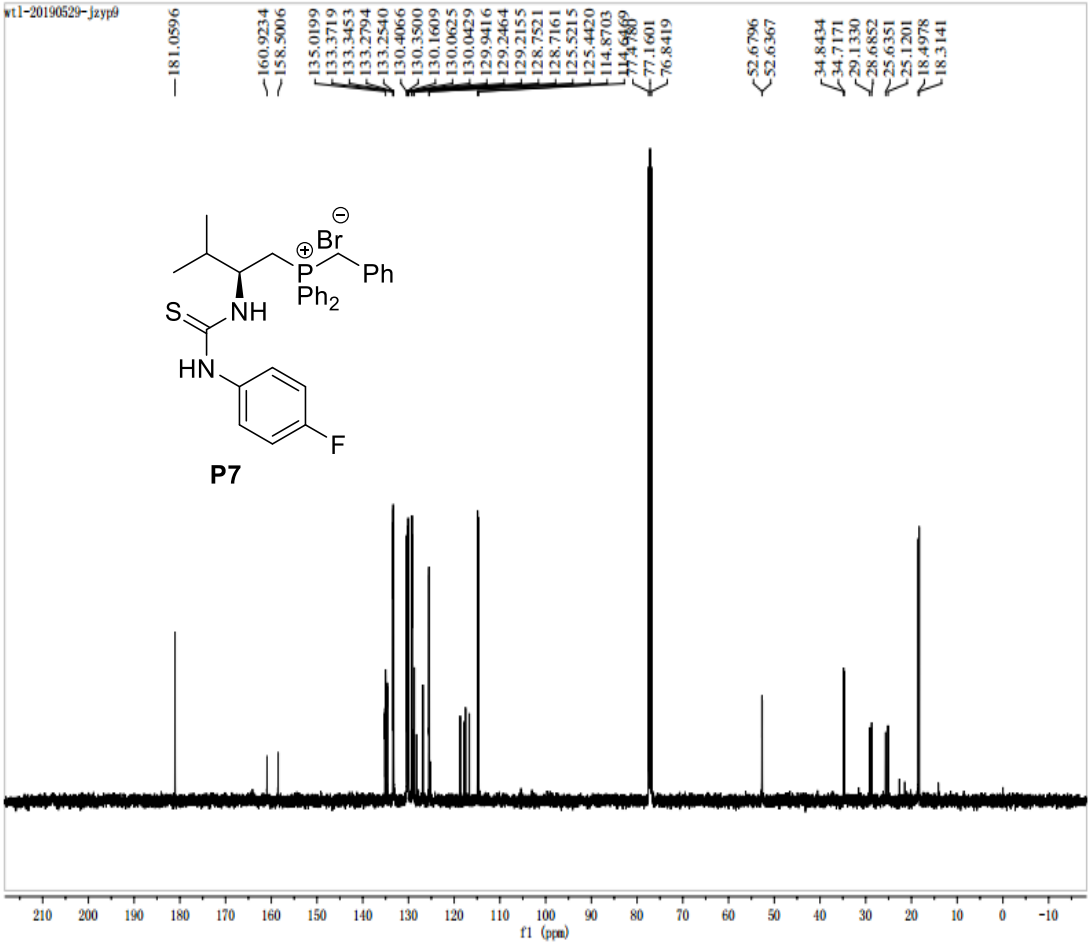
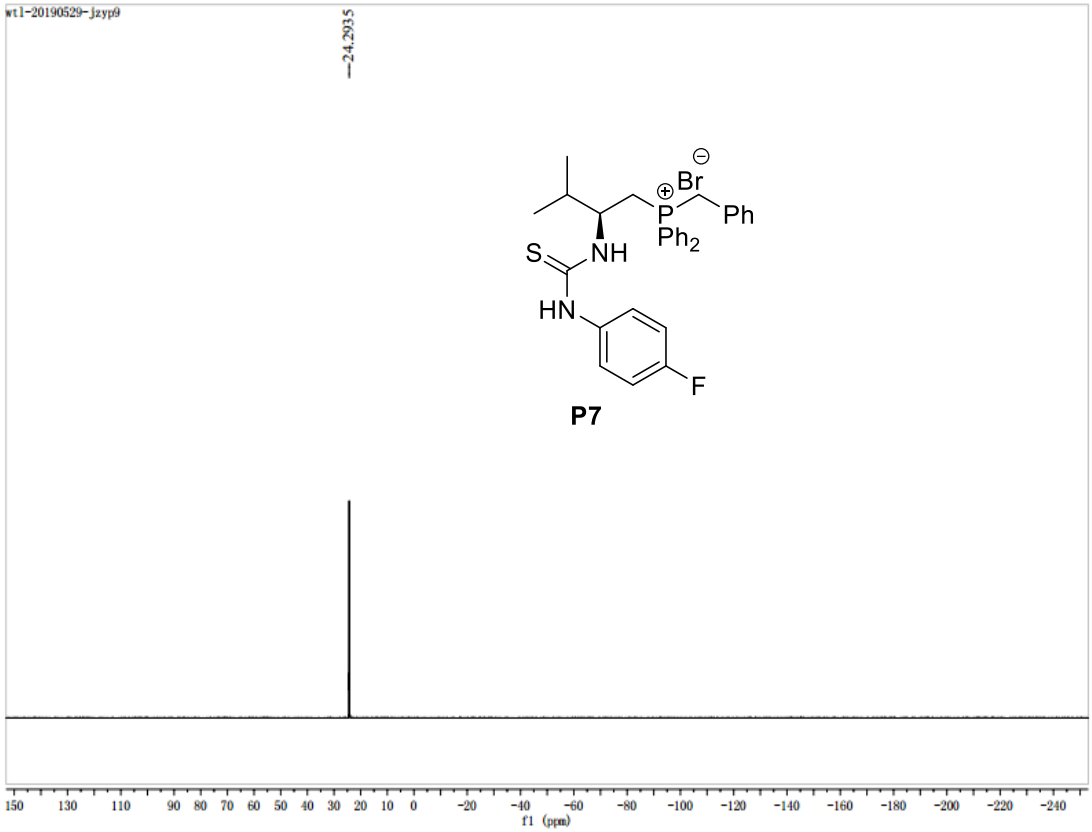
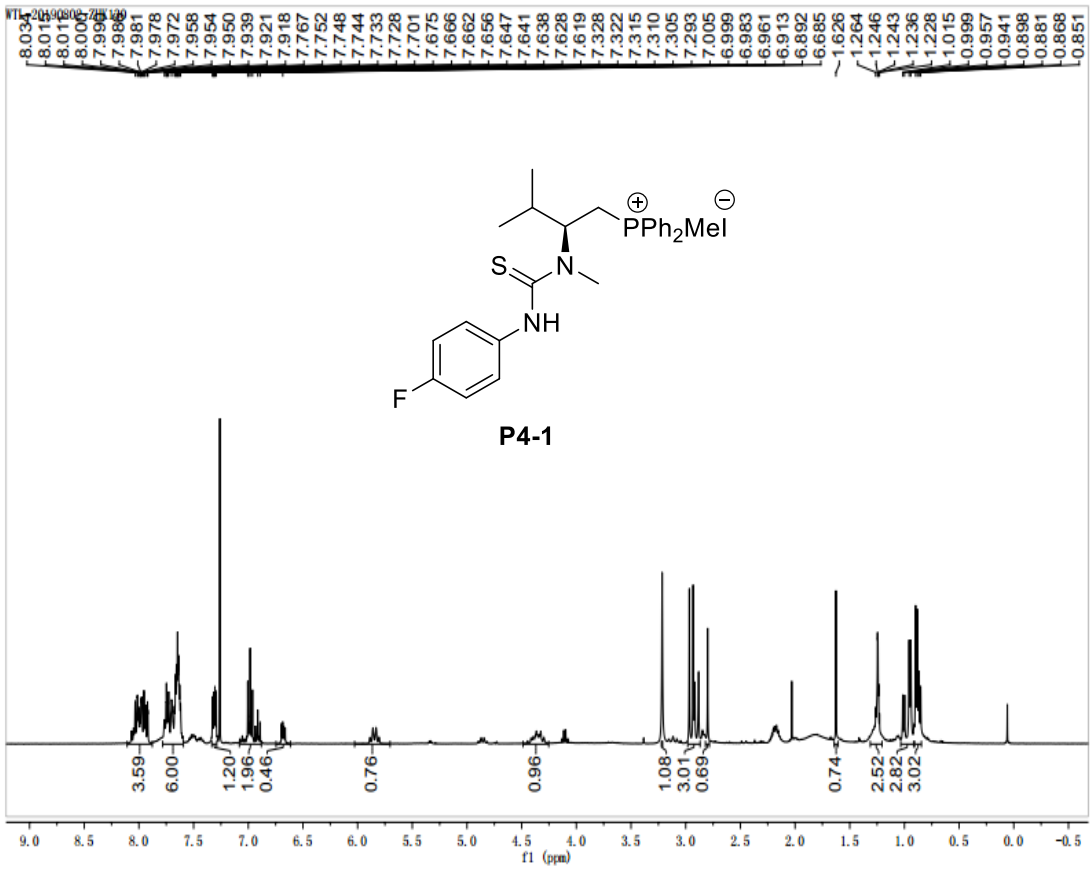
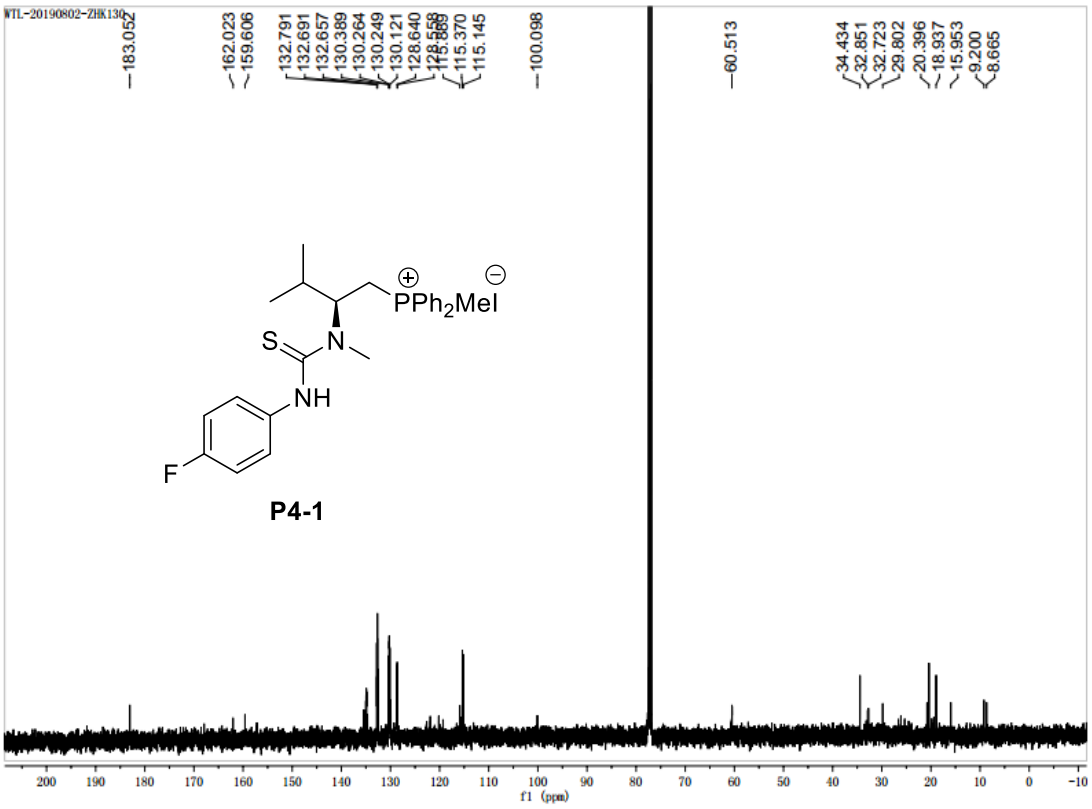
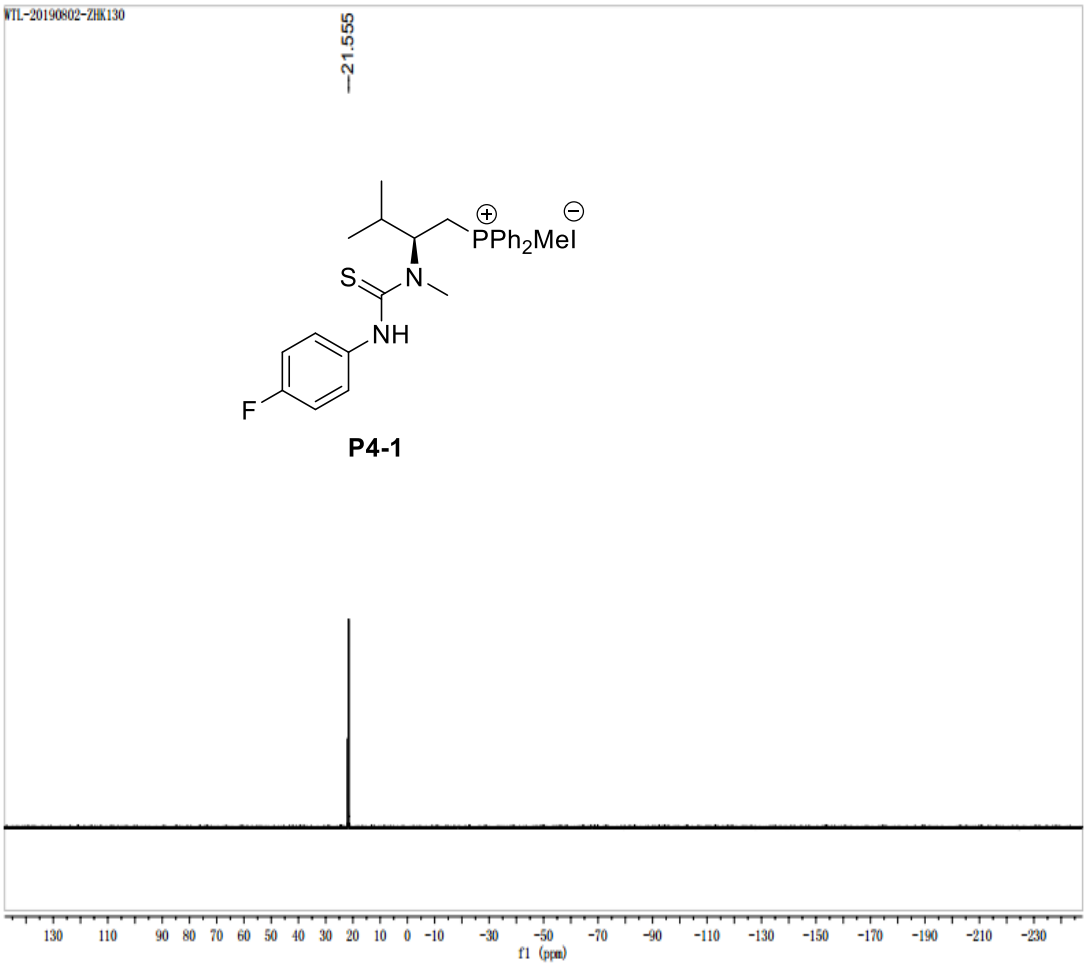

Br
Ph
P
Ph2
S
NH
HN
F
P7
f1 (ppm)

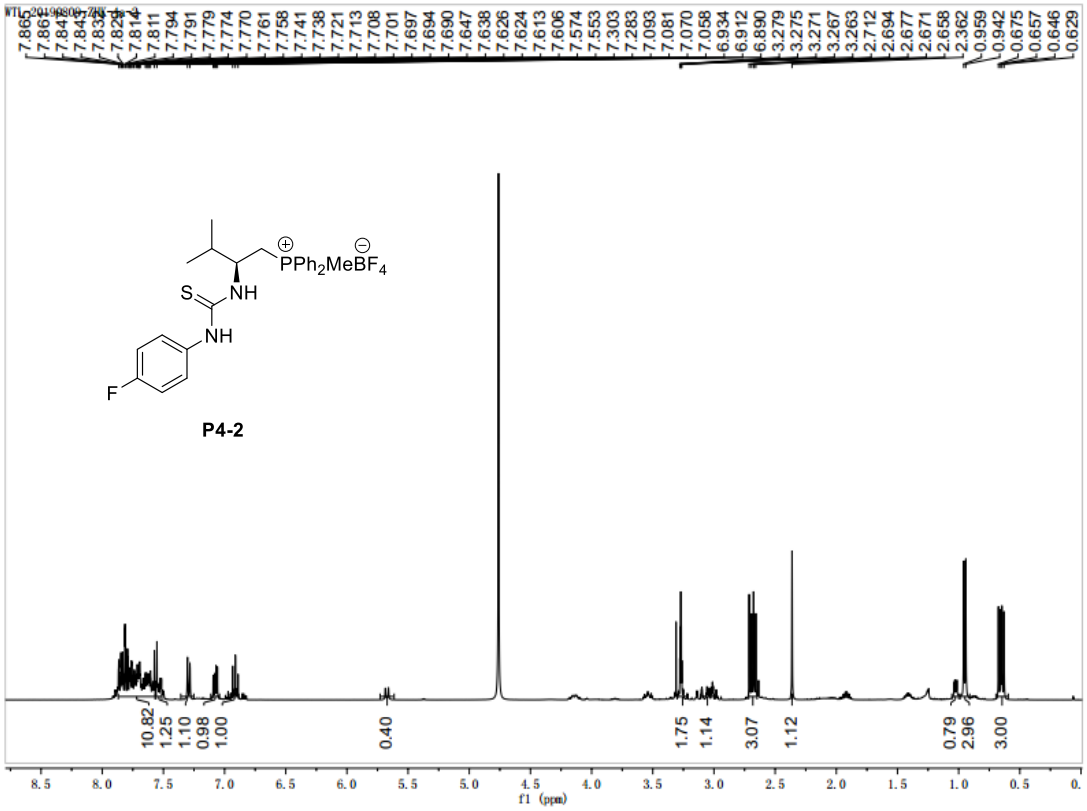

wt1-20190529-jzyp9
Br
Ph
P
Ph2
S
NH
HN
F
P7
f1 (ppm)

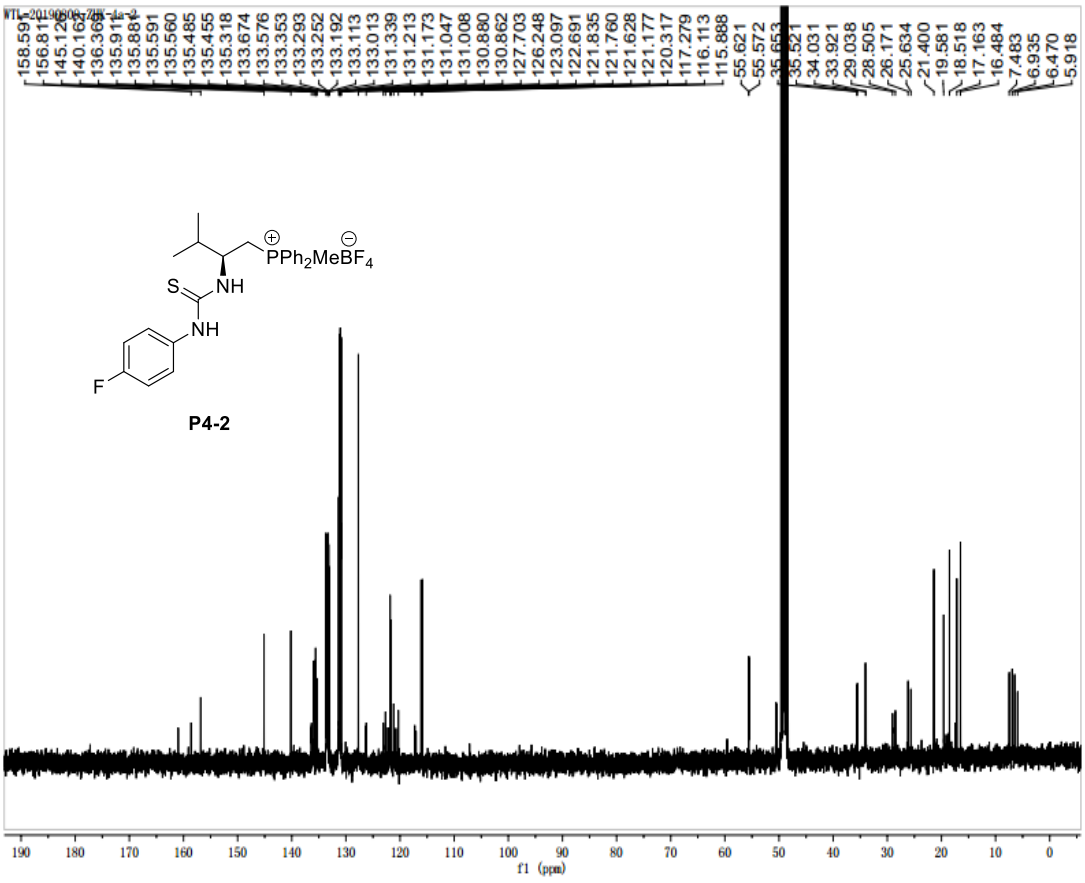

wtl-20190529-jzyp9
-24.2935
Br
P
Ph
Ph2
S
NH
HN
F
P7
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

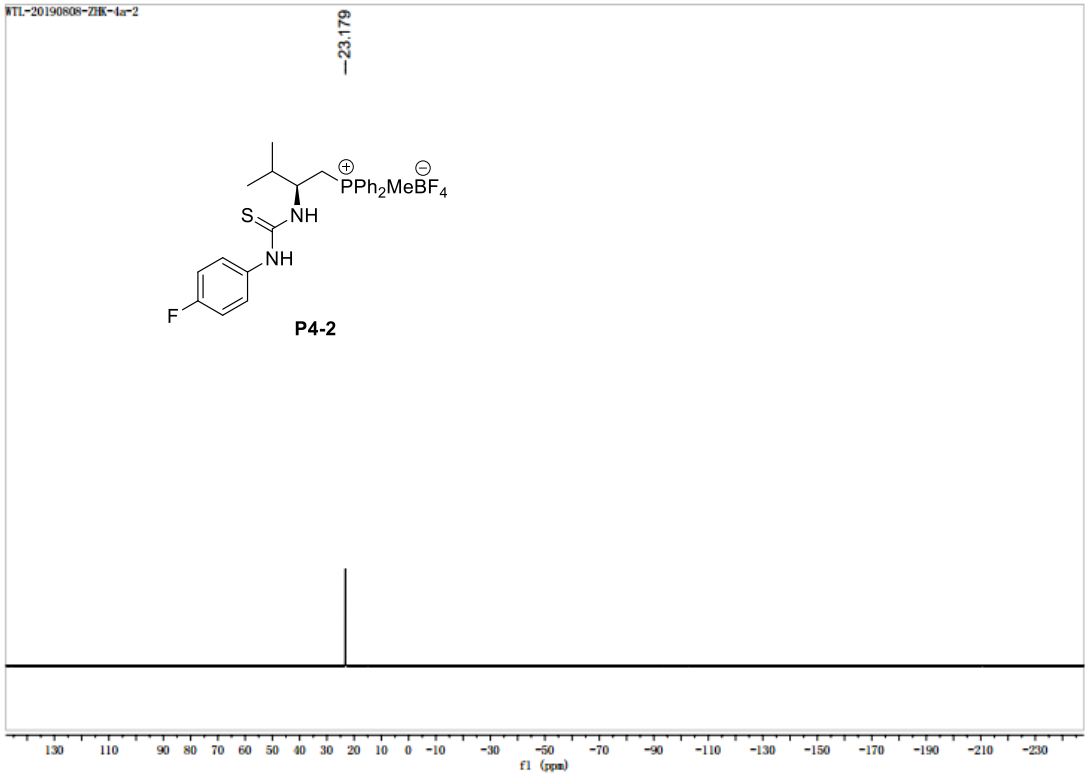

PPh2MeI
S
N
NH
F
P4-1
3.59 6.00 1.20 1.96 0.46 0.76 0.96 1.08 3.01 0.69 0.74 2.52 2.82 3.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

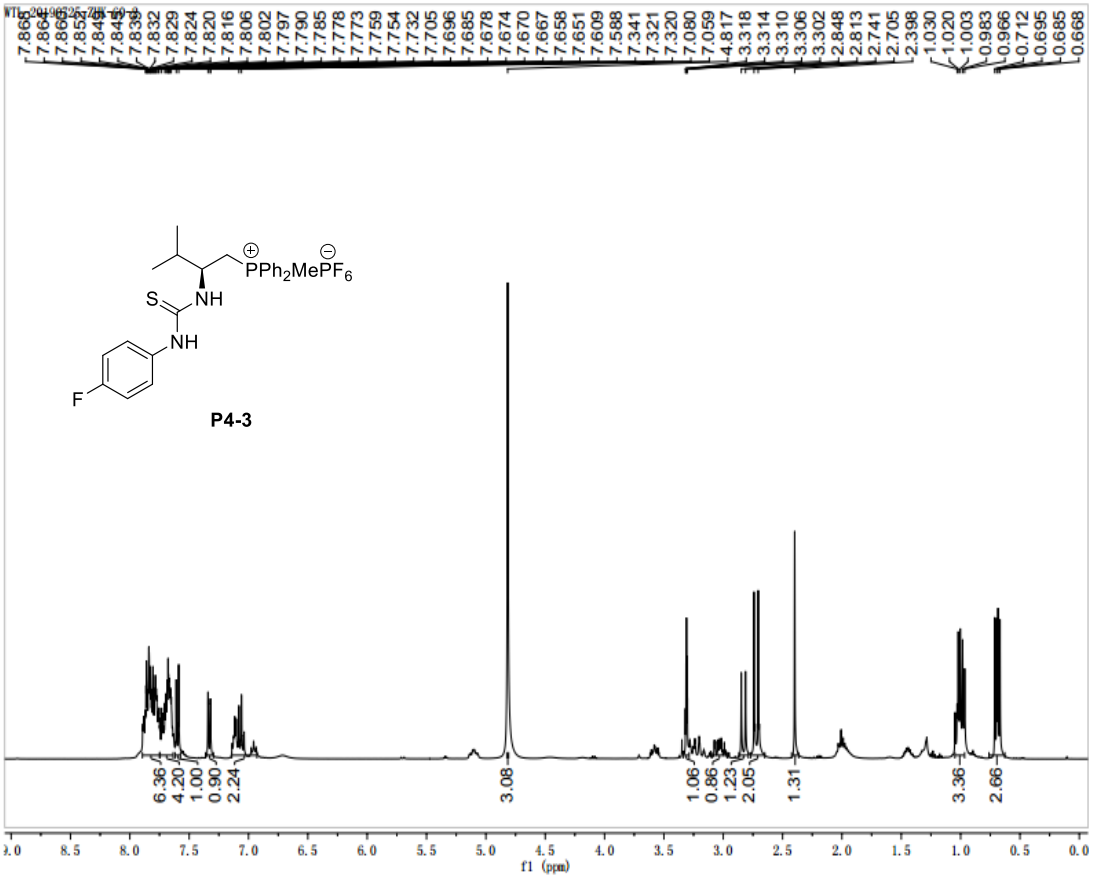

WTL-20190802-ZHK130
183.052
162.023
159.606
132.791
132.691
132.657
130.389
130.264
130.249
130.121
128.640
128.558
115.889
115.370
115.145
100.098
60.513
34.434
32.851
32.723
29.802
20.396
18.937
15.953
9.200
8.665
PPh2MeI
S
N
NH
F
P4-1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

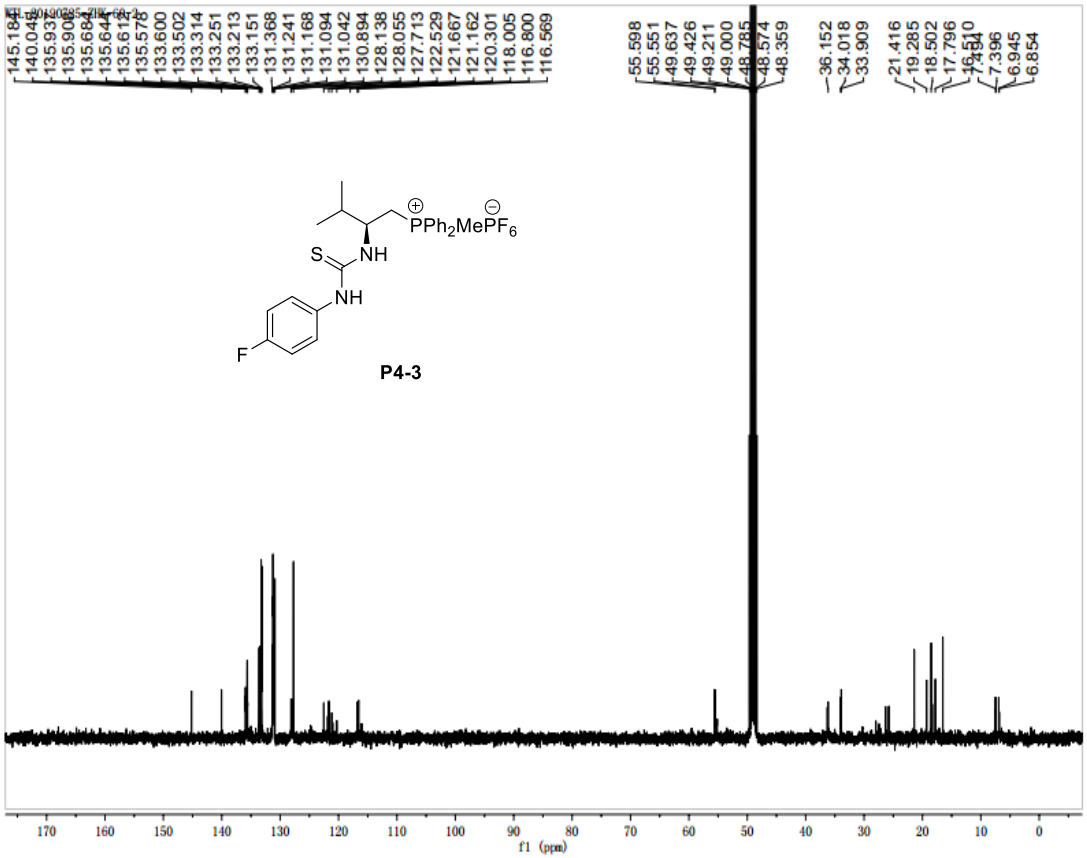

WTL-20190802-ZHK130
21.555
PPh2MeI
S
N
NH
F
P4-1
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

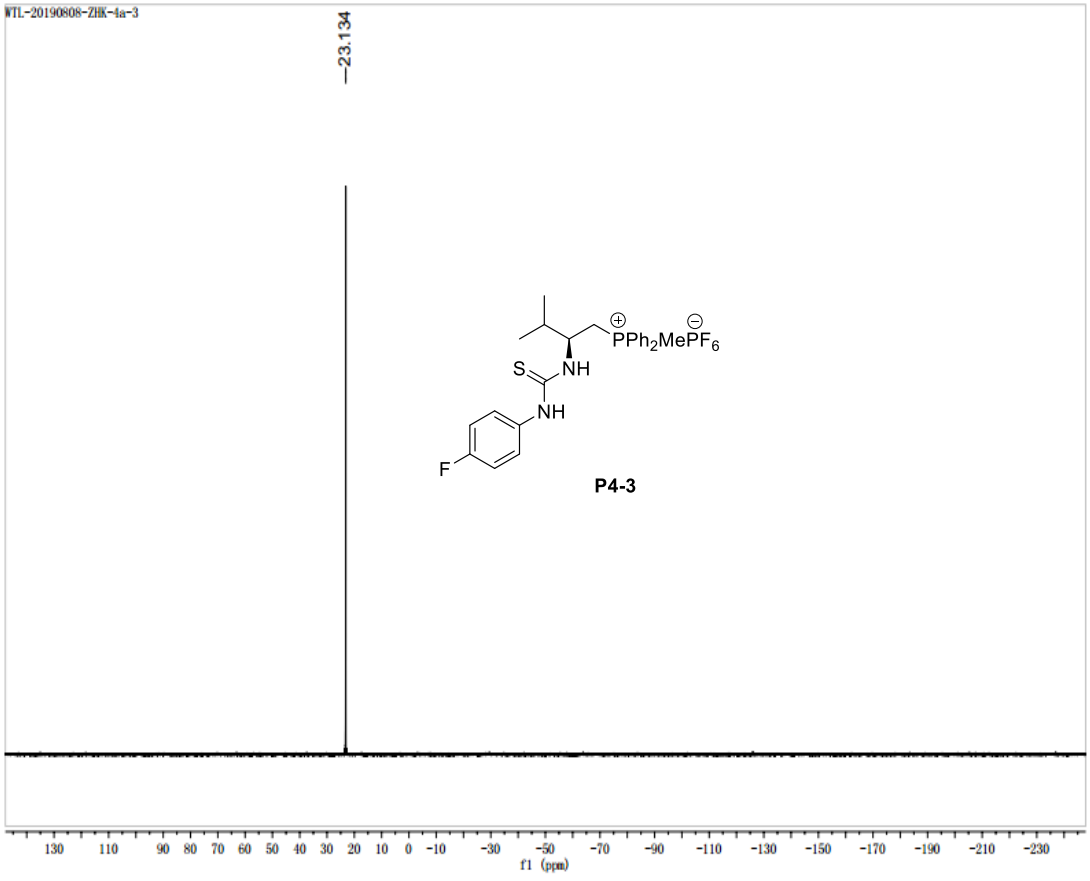

PPh2MeBF4
S
NH
NH
F
P4-2
10.82
1.25
1.10
0.98
1.00
0.40
1.75
1.14
3.07
1.12
0.79
2.96
3.00
f1 (ppm)

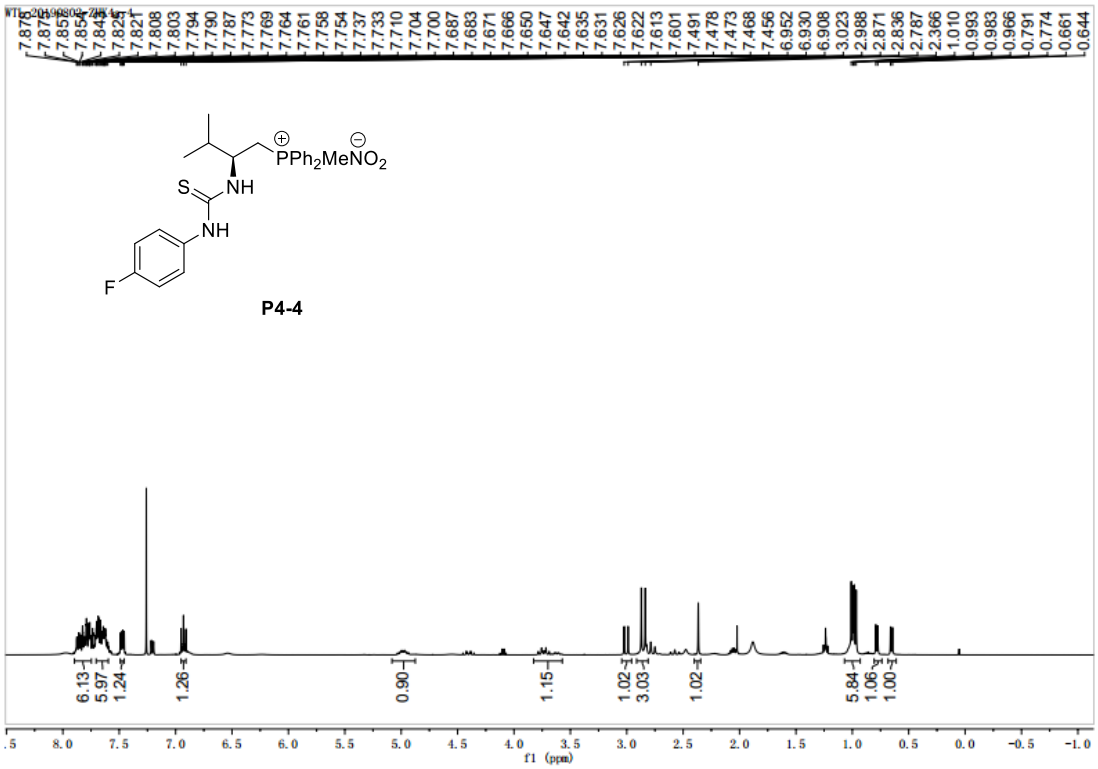

PPh2MeBF4
S
NH
NH
F
P4-2
f1 (ppm)

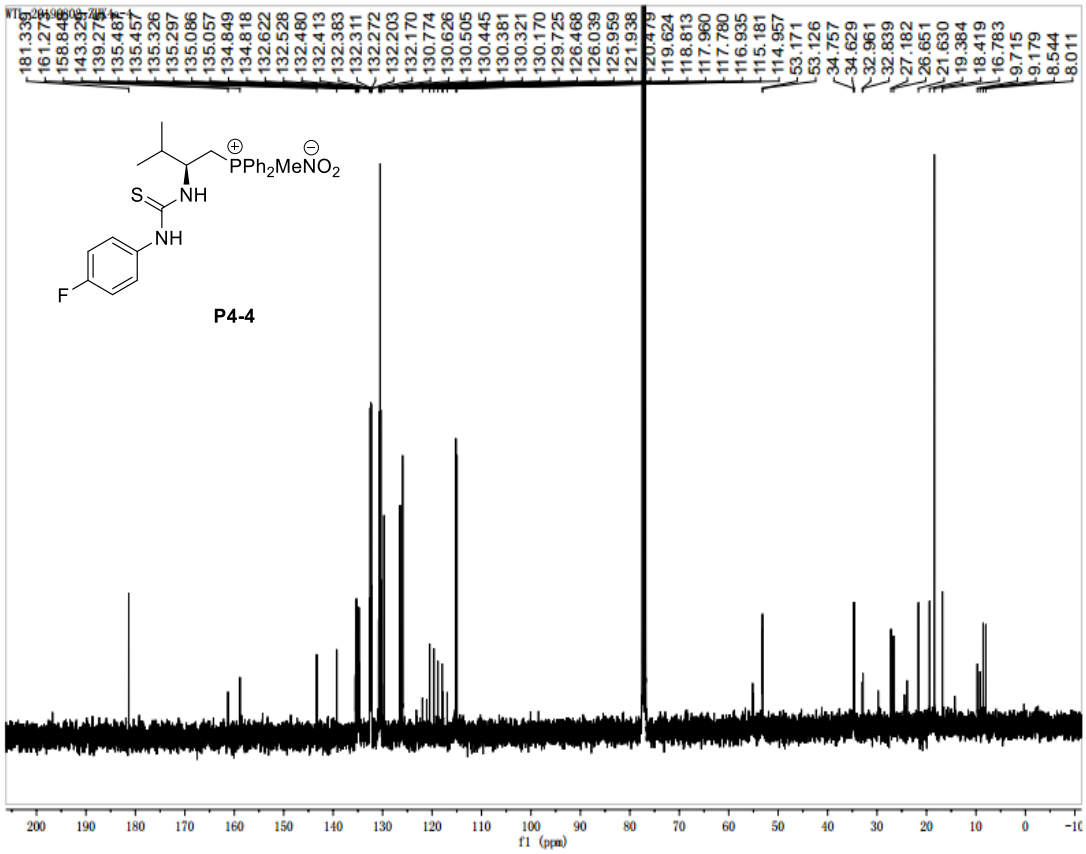

WTL-20190808-ZHK-4a-2
-23.179
PPh2MeBF4
S
NH
NH
F
P4-2
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

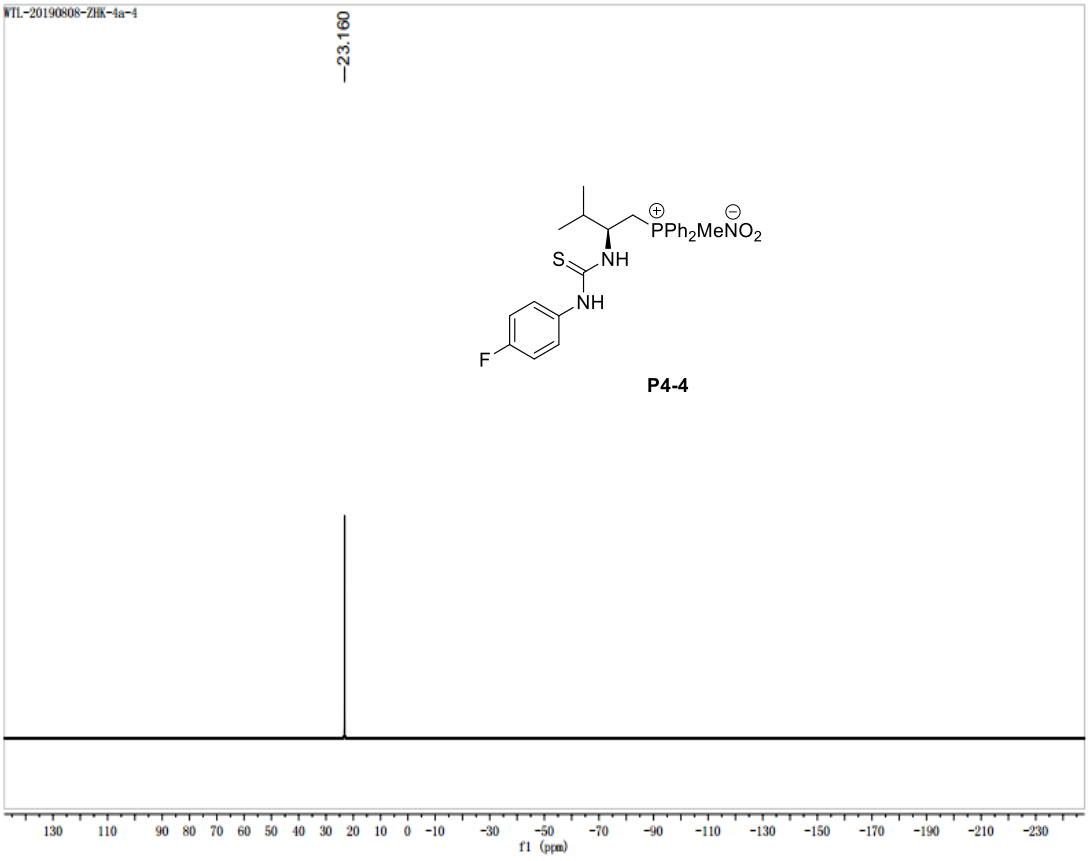

PPh2MePF6
S
NH
NH
F
P4-3
6.36
4.20
1.00
0.90
2.24
3.08
1.06
0.86
1.23
2.05
1.31
3.36
2.66
f1 (ppm)

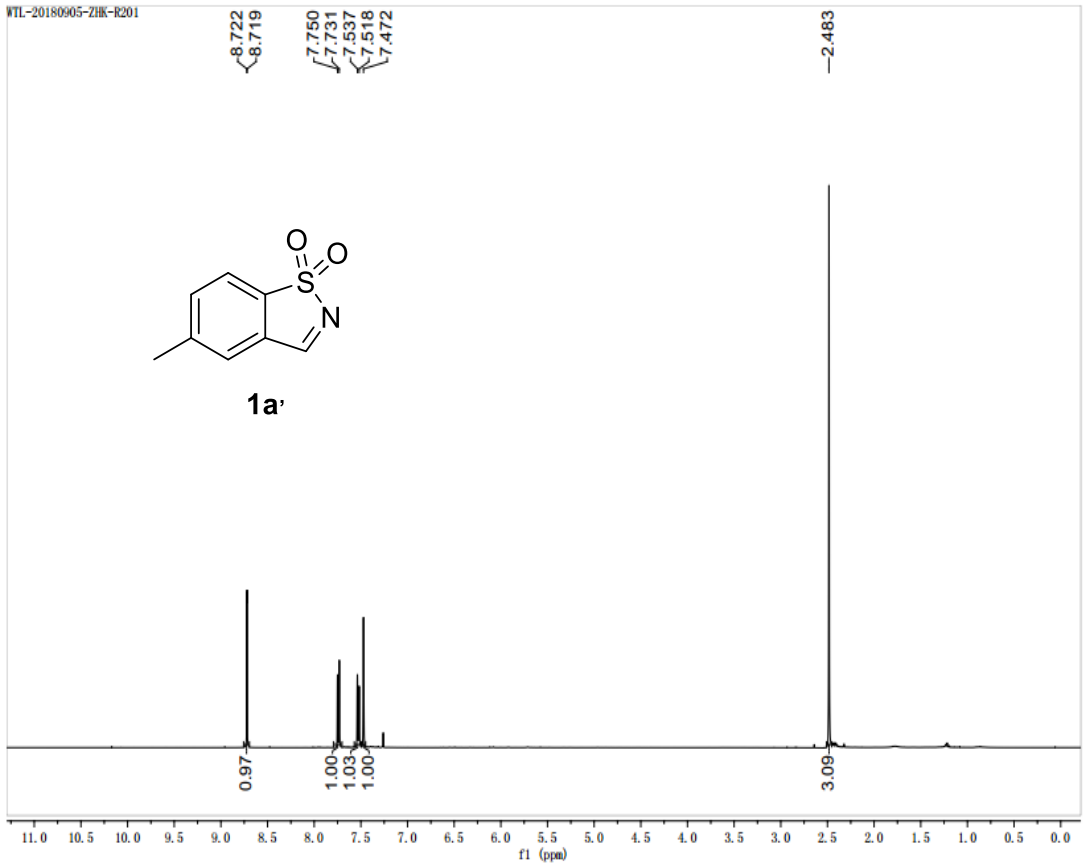

145.184
140.045
135.931
135.906
135.684
135.644
135.617
135.578
133.600
133.502
133.314
133.251
133.213
133.151
131.368
131.241
131.168
131.094
131.042
130.894
128.138
128.055
127.713
122.529
121.667
121.162
120.301
118.005
116.800
116.569
55.598
55.551
49.637
49.426
49.211
49.000
48.785
48.574
48.359
36.152
34.018
33.909
21.416
19.285
18.502
17.796
16.510
16.154
7.396
6.945
6.854
PPh2MePF6
S
NH
NH
F
P4-3
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

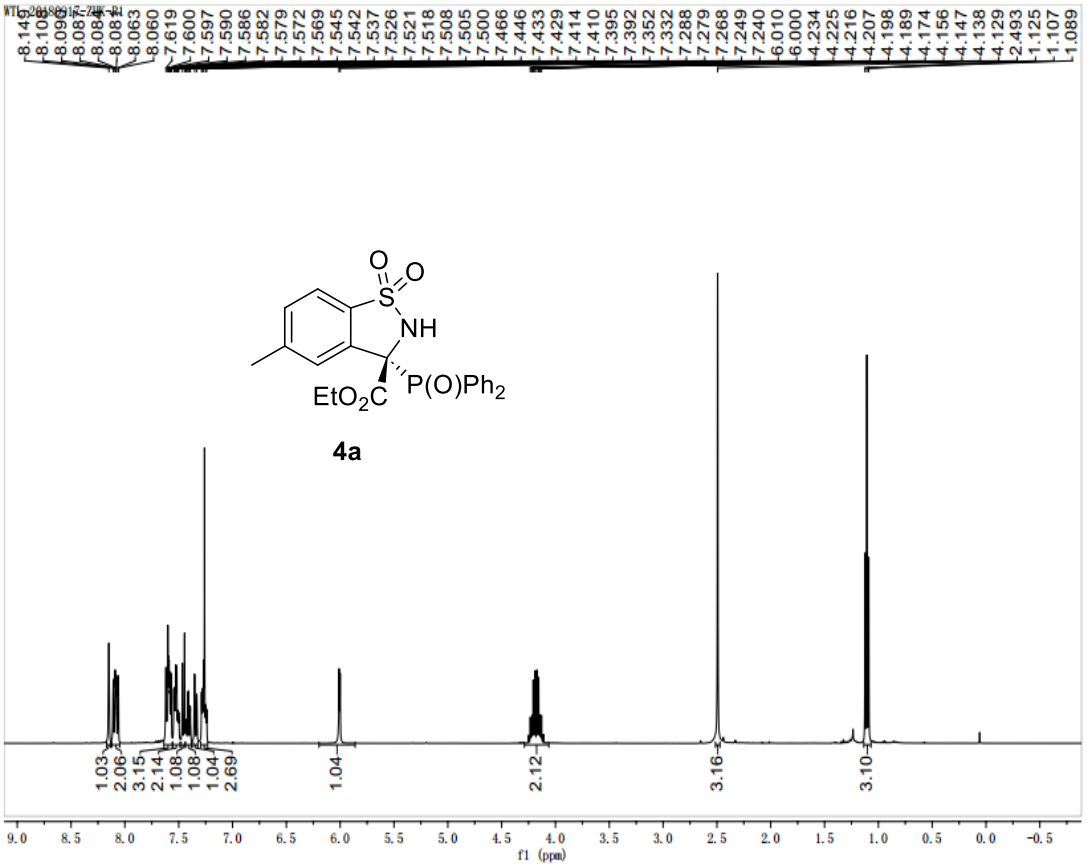

WTL-20190808-ZHK-4a-3
23.134
PPh2MePF6
S
NH
NH
F
P4-3
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


PPh2MeNO2
S
NH
NH
F
P4-4
f1 (ppm)

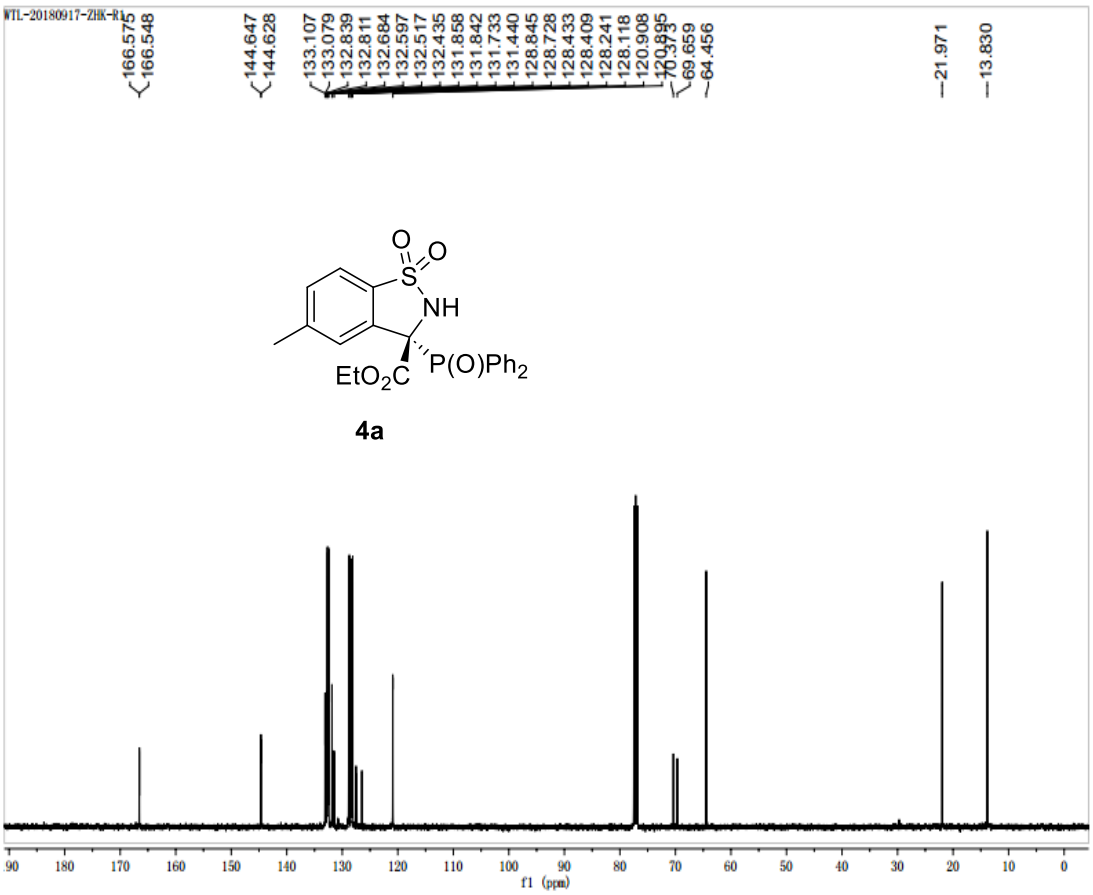

PPh2MeNO2
S
NH
NH
F
P4-4
f1 (ppm)


WTL-20190808-ZHK-4a-4
23.160
PPh2MeNO2
S
NH
NH
F
P4-4
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

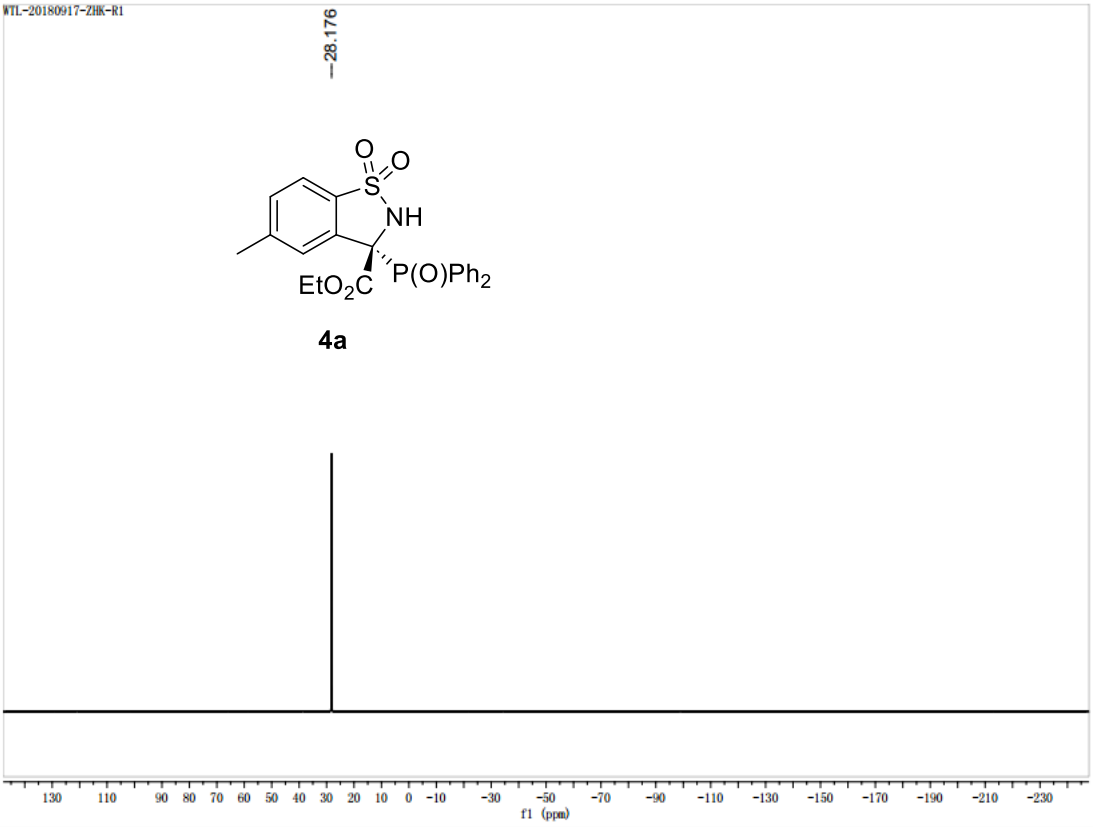

WTL-20180905-ZHK-R201
8.722
8.719
7.750
7.731
7.537
7.518
7.472
2.483
O
O
S
N
1a'
0.97
1.00
1.03
1.00
3.09
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


8.145
8.106
8.090
8.087
8.084
8.081
8.063
8.060
7.619
7.600
7.597
7.590
7.586
7.582
7.579
7.572
7.569
7.545
7.542
7.537
7.526
7.521
7.518
7.508
7.505
7.500
7.466
7.446
7.433
7.429
7.414
7.410
7.395
7.392
7.352
7.332
7.288
7.279
7.268
7.249
7.240
6.010
6.000
4.234
4.225
4.216
4.207
4.198
4.189
4.174
4.156
4.147
4.138
4.129
2.493
1.125
1.107
1.089
O
O
S
NH
EtO2C
P(O)Ph2
1.03
2.06
3.15
2.14
1.08
1.08
1.04
2.69
1.04
2.12
3.16
3.10
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

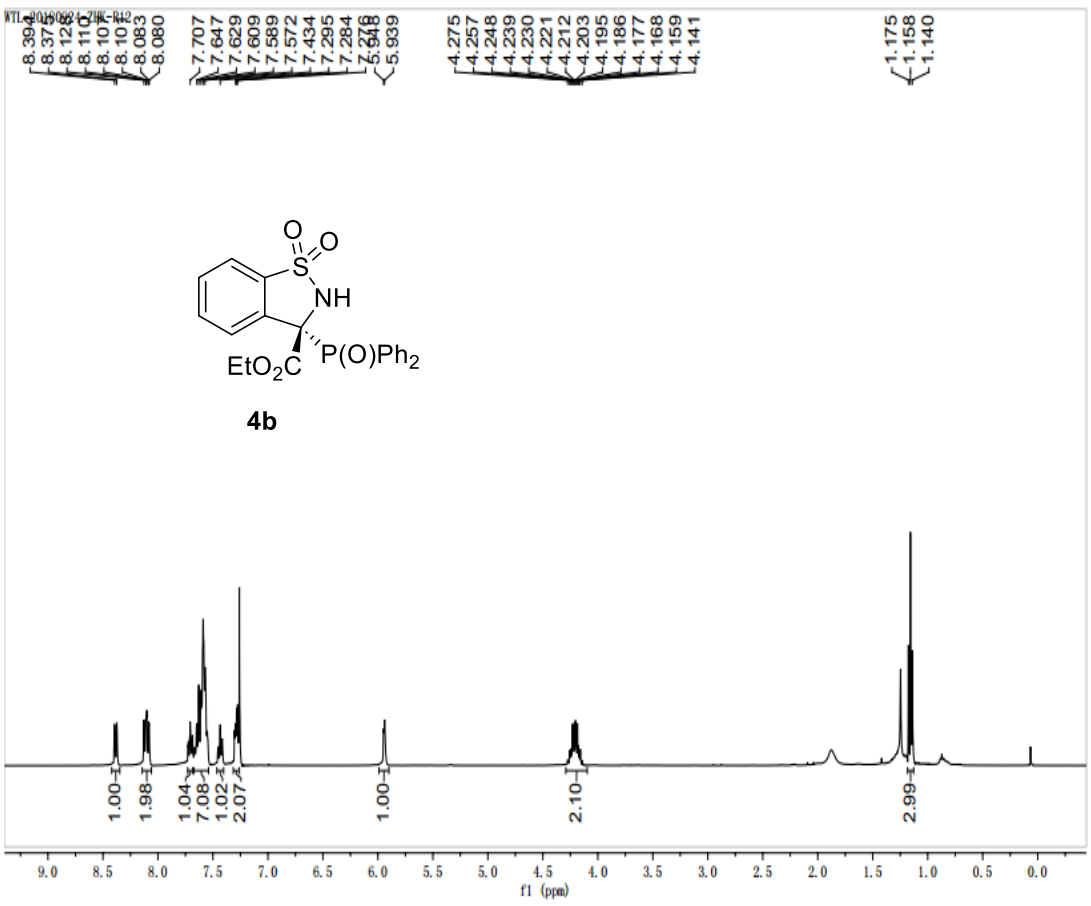
4a


WTL-20180917-ZHK-R1
166.575
166.548
144.647
144.628
133.107
133.079
132.839
132.811
132.684
132.597
132.517
132.435
131.858
131.842
131.733
131.440
128.845
128.728
128.433
128.409
128.241
128.118
120.908
120.895
70.373
69.659
64.456
21.971
13.830
O
O
S
NH
EtO2C
P(O)Ph2
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

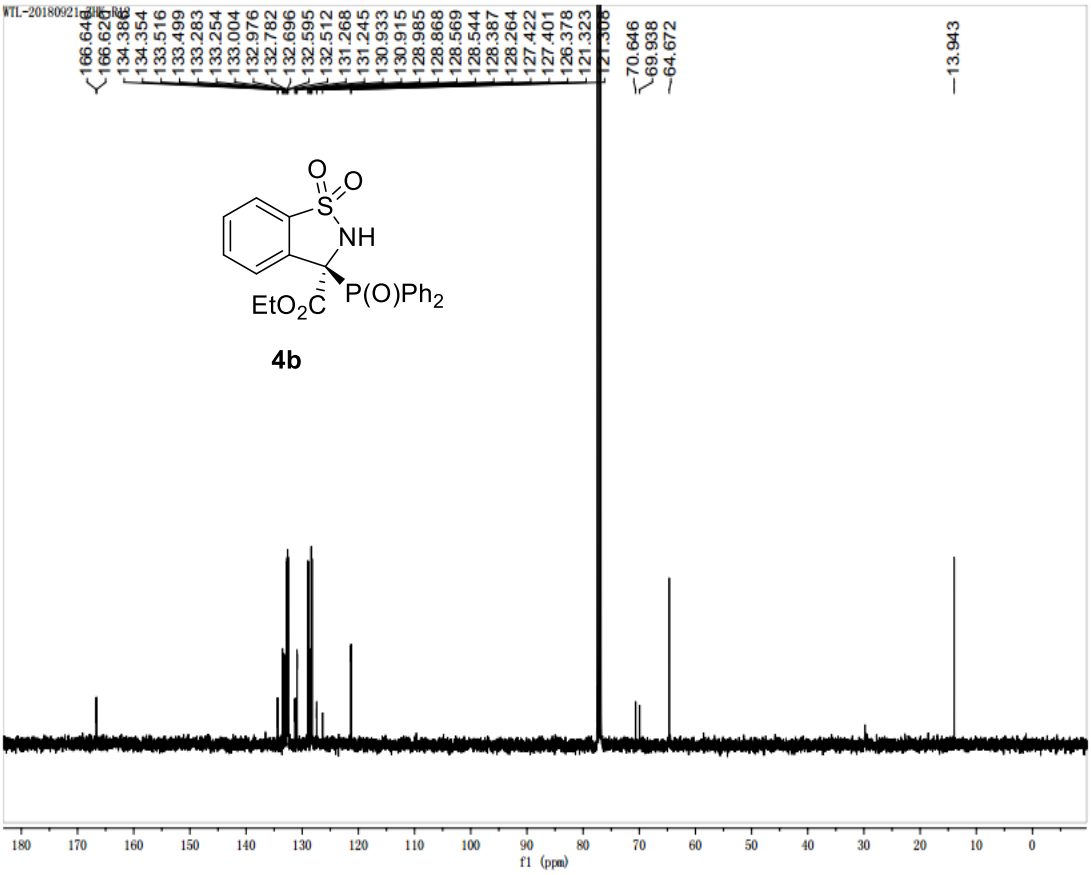
4a

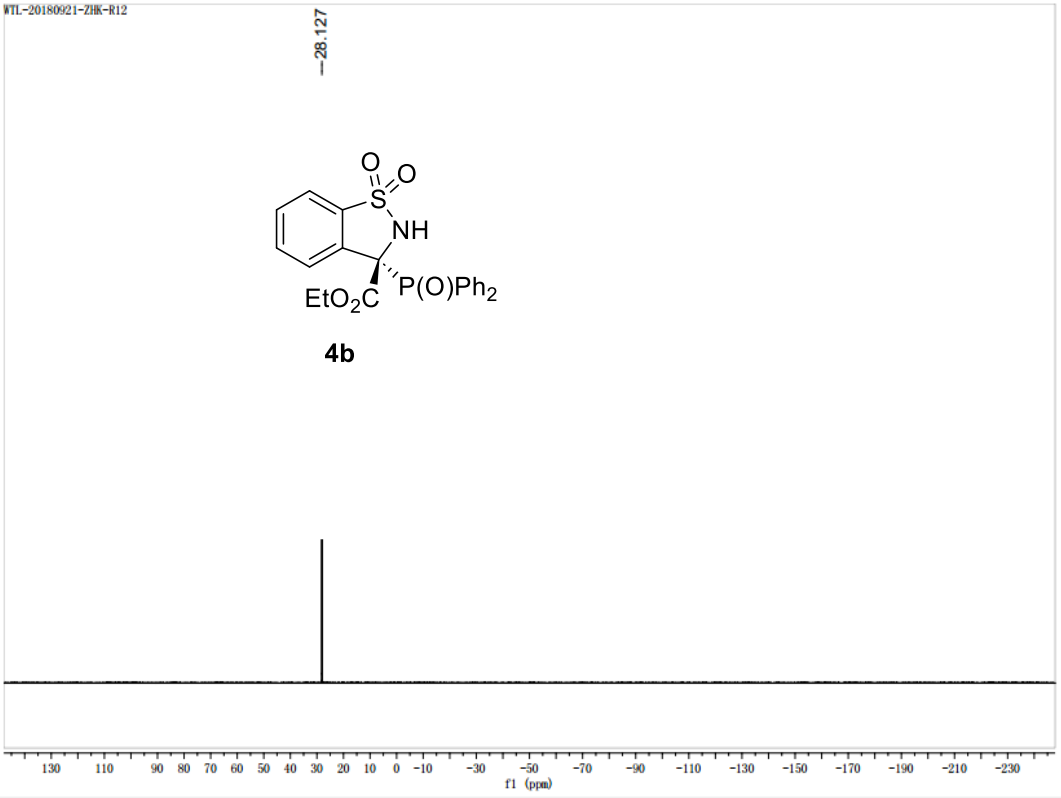

WTL-20180917-ZHK-R1
28.176
O
O
S
NH
EtO2C
P(O)Ph2
f1 (ppm)

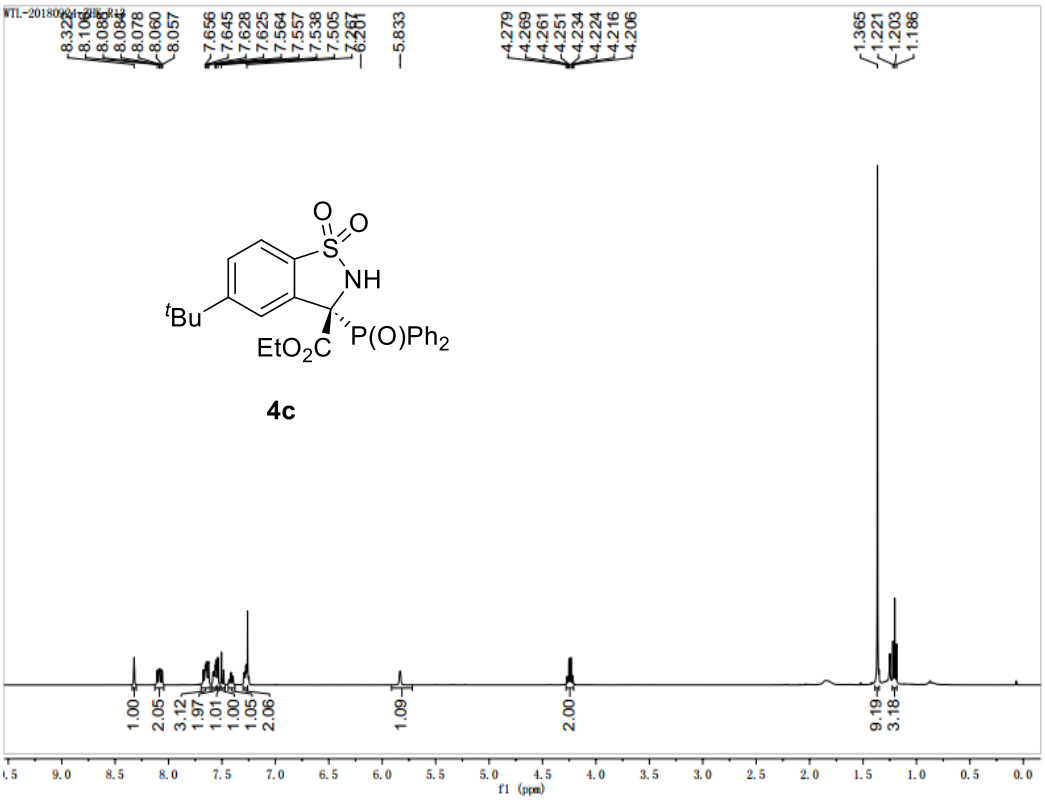
4a


8.394
8.375
8.128
8.110
8.101
8.083
8.080
7.707
7.647
7.629
7.609
7.589
7.572
7.434
7.295
7.284
7.276
5.948
5.939
4.275
4.257
4.248
4.239
4.230
4.221
4.212
4.203
4.195
4.186
4.177
4.168
4.159
4.141
1.175
1.158
1.140
O
O
S
NH
EtO2C
P(O)Ph2
1.00
1.98
1.04
7.08
1.02
2.07
1.00
2.10
2.99
f1 (ppm)

4b

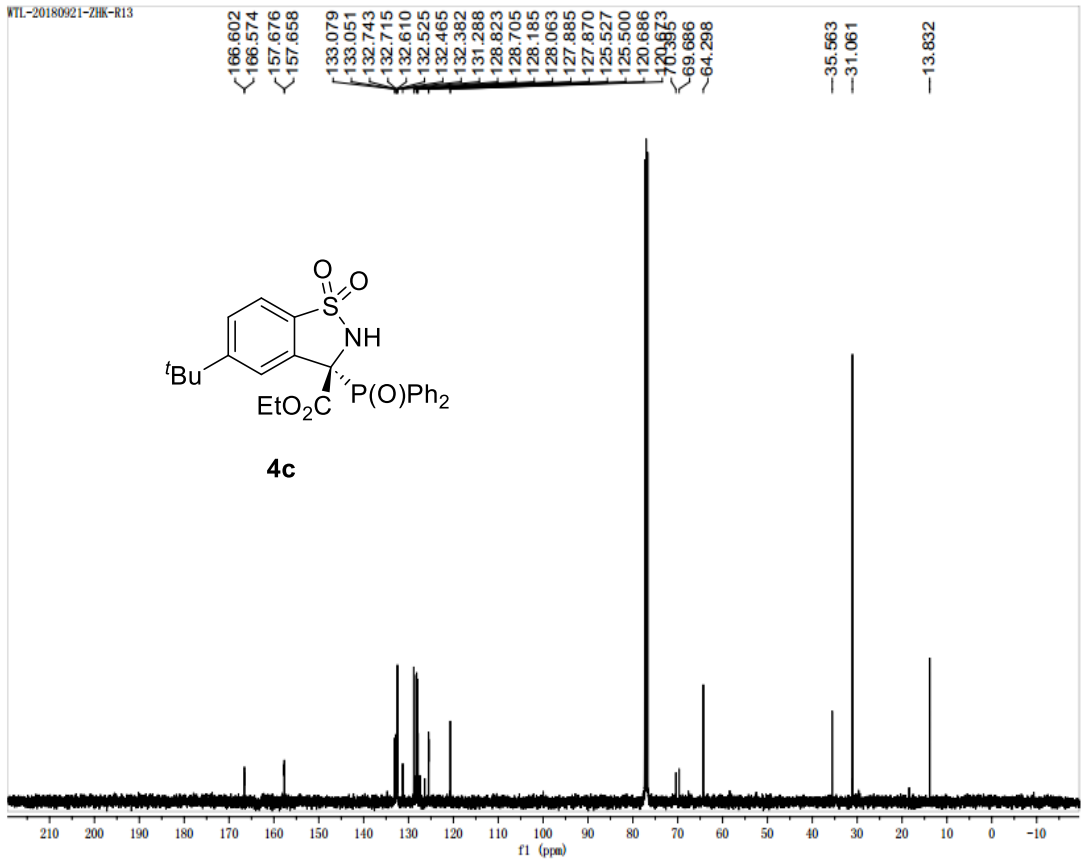

166.646
166.626
134.386
134.354
133.516
133.499
133.283
133.254
133.004
132.976
132.782
132.696
132.595
132.512
131.268
131.245
130.933
130.915
128.985
128.868
128.569
128.544
128.387
128.264
127.422
127.401
126.378
121.323
121.308
70.646
69.938
64.672
13.943
O
O
S
NH
EtO2C
P(O)Ph2
4b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


WTL-20180921-ZHK-R12
28.127
O
O
S
NH
EtO2C
P(O)Ph2
4b
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)


8.322
8.106
8.088
8.084
8.078
8.060
8.057
7.656
7.645
7.628
7.625
7.564
7.557
7.538
7.505
7.267
7.261
5.833
4.279
4.269
4.261
4.251
4.234
4.224
4.216
4.206
1.365
1.221
1.203
1.186
1.00
2.05
3.12
1.97
1.01
1.00
1.05
2.06
1.09
2.00
9.19
3.18
f1 (ppm)

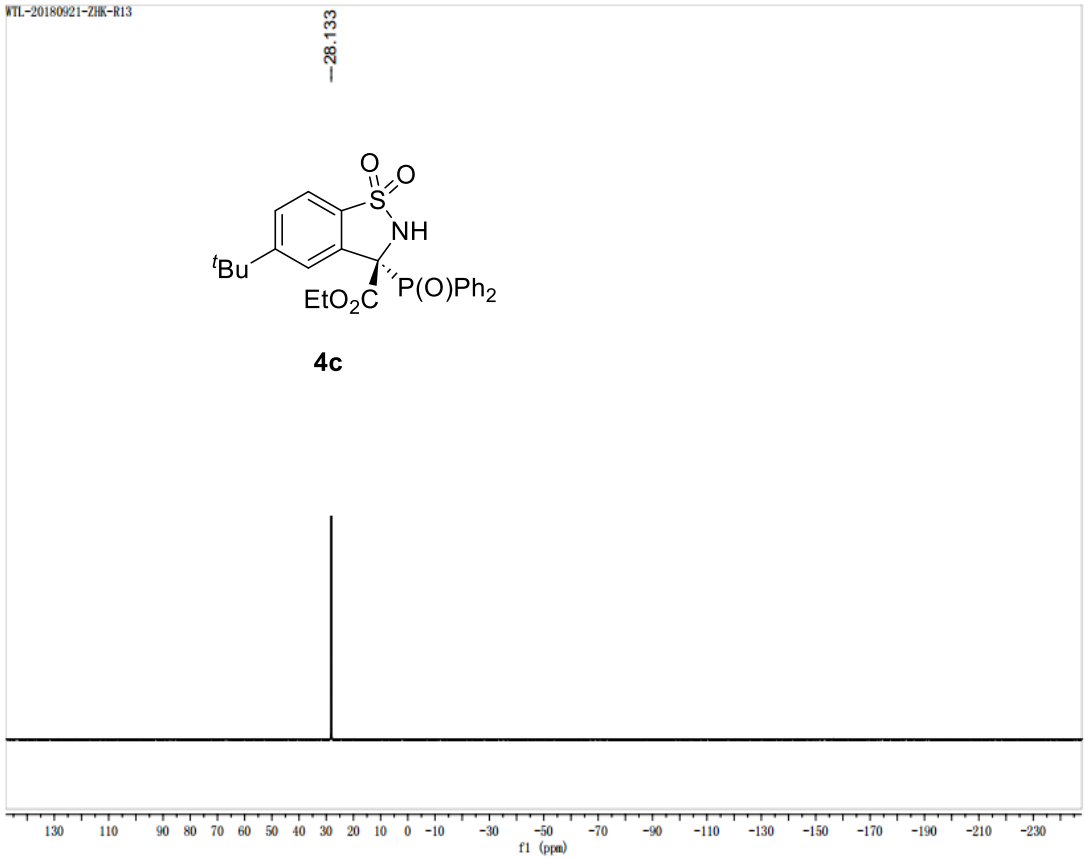
O
O
S
NH
tBu
EtO2C
P(O)Ph2

4c

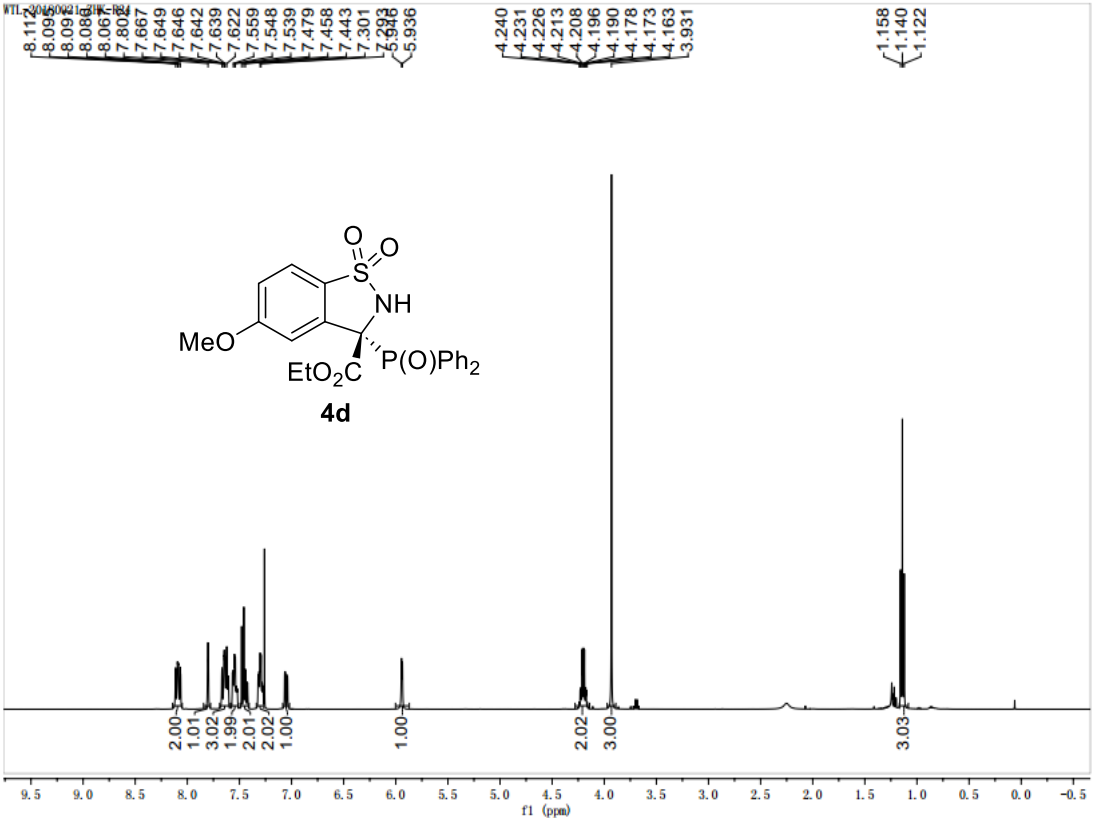

WTL-20180921-ZHK-R13
166.602
166.574
157.676
157.658
133.079
133.051
132.743
132.715
132.610
132.525
132.465
132.382
131.288
128.823
128.705
128.185
128.063
127.885
127.870
125.527
125.500
120.686
120.673
69.686
64.298
35.563
31.061
13.832
f1 (ppm)

O
O
S
NH
tBu
EtO2C
P(O)Ph2

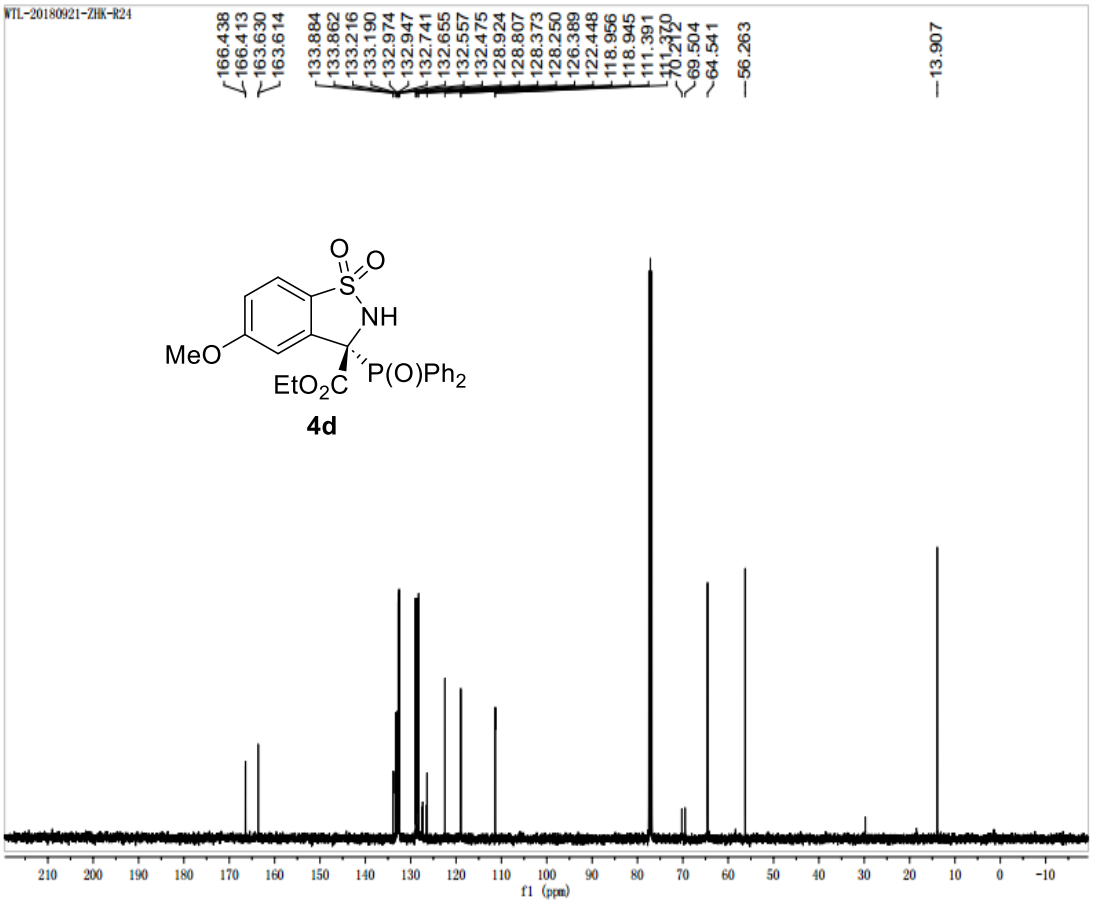
4c

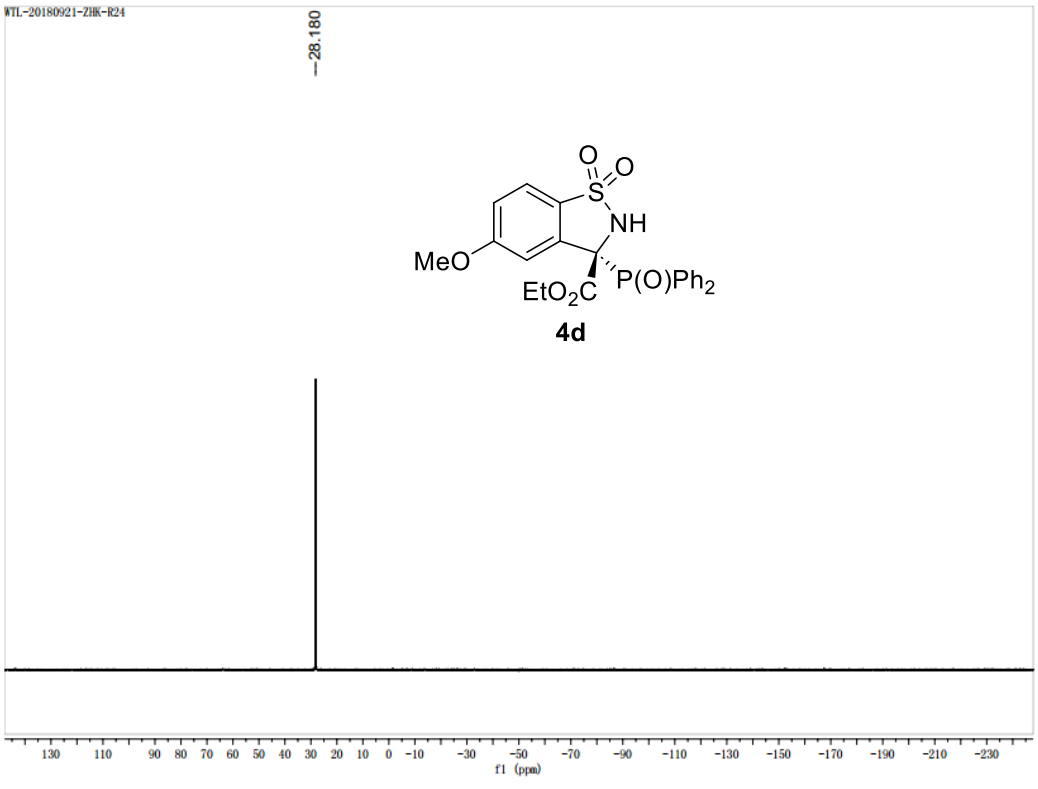

WTL-20180921-ZHK-R13
28.133
O
O
S
NH
tBu
EtO2C
P(O)Ph2
f1 (ppm)

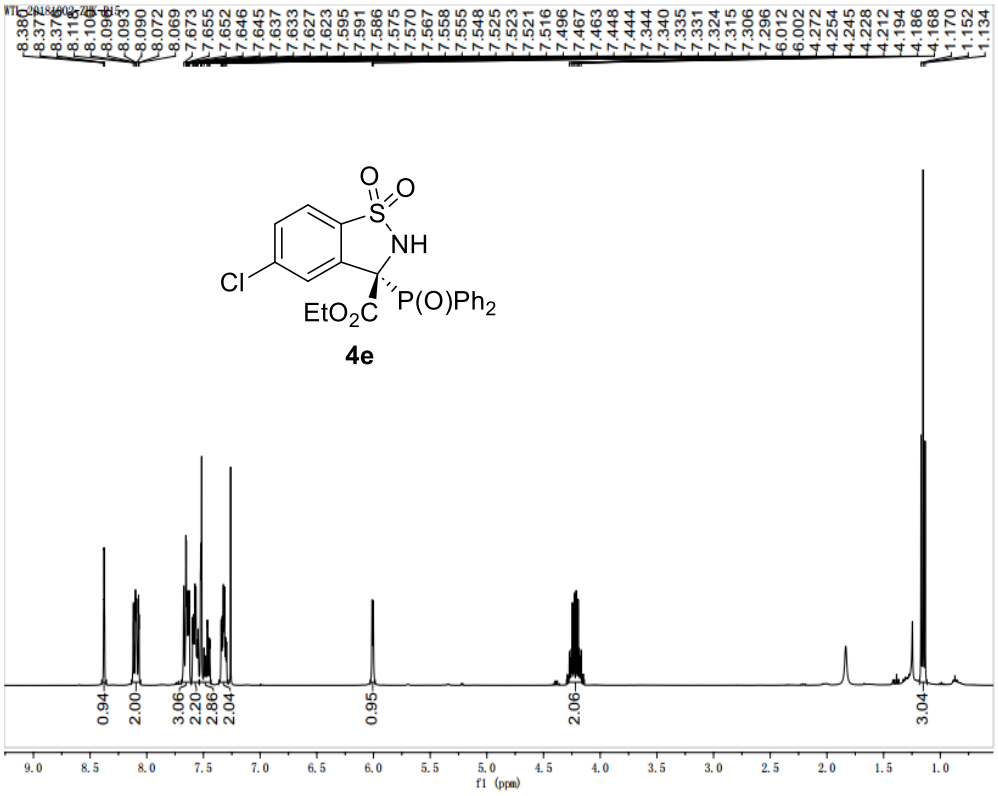
4c

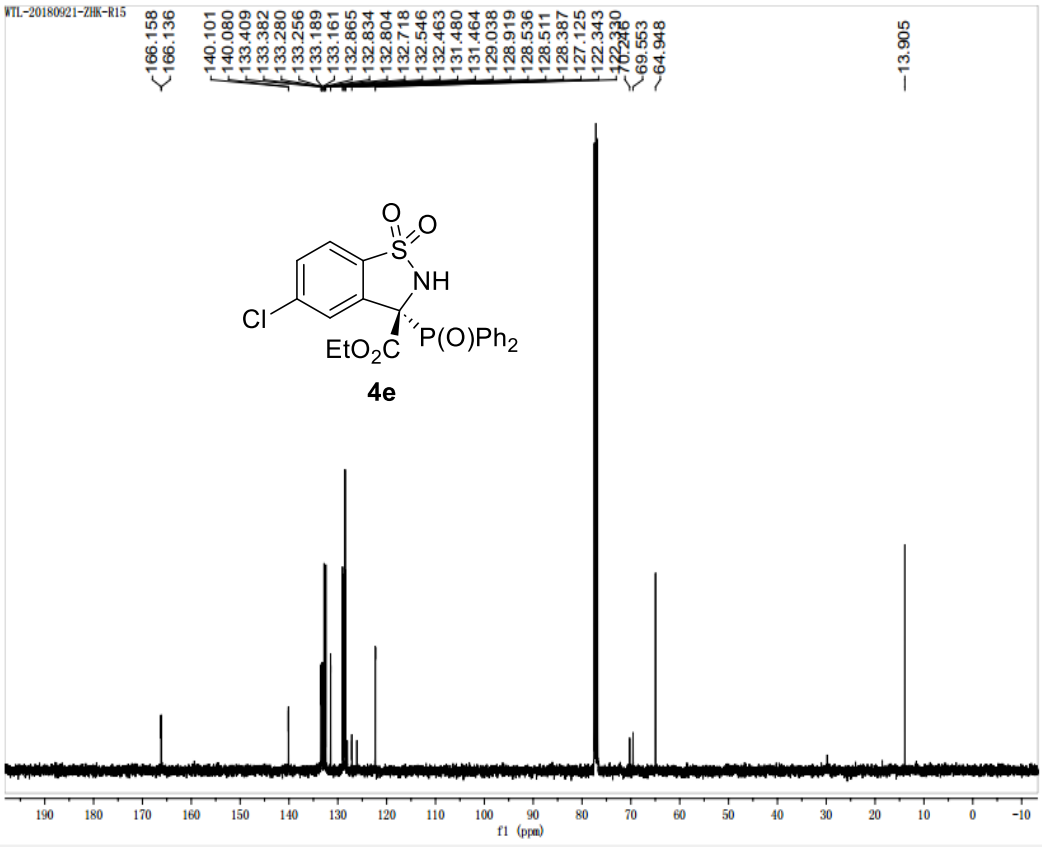

8.112
8.095
8.091
8.086
8.067
7.802
7.667
7.649
7.646
7.642
7.639
7.622
7.559
7.548
7.539
7.479
7.458
7.443
7.301
7.293
5.948
5.936
4.240
4.231
4.226
4.213
4.208
4.196
4.190
4.178
4.173
4.163
3.931
1.158
1.140
1.122
O
O
S
NH
MeO
EtO2C
P(O)Ph2
2.00
1.01
3.02
1.99
2.01
2.02
1.00
1.00
2.02
3.00
3.03
f1 (ppm)

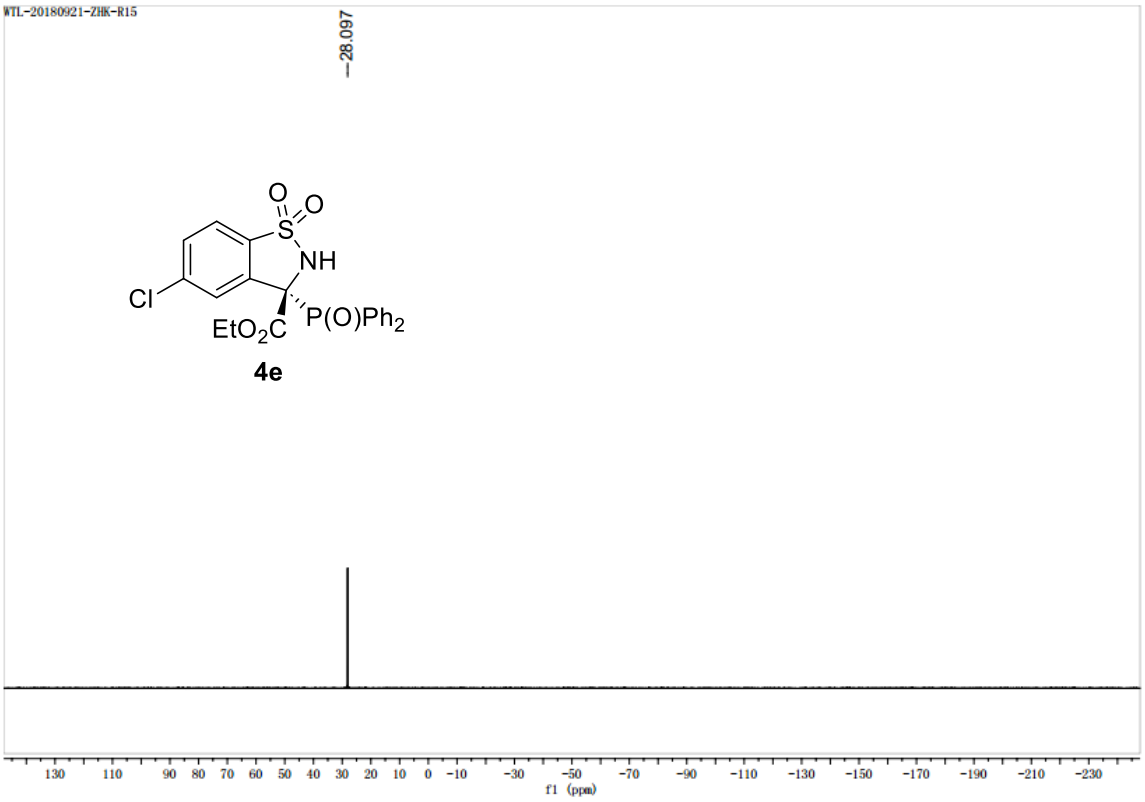
4d

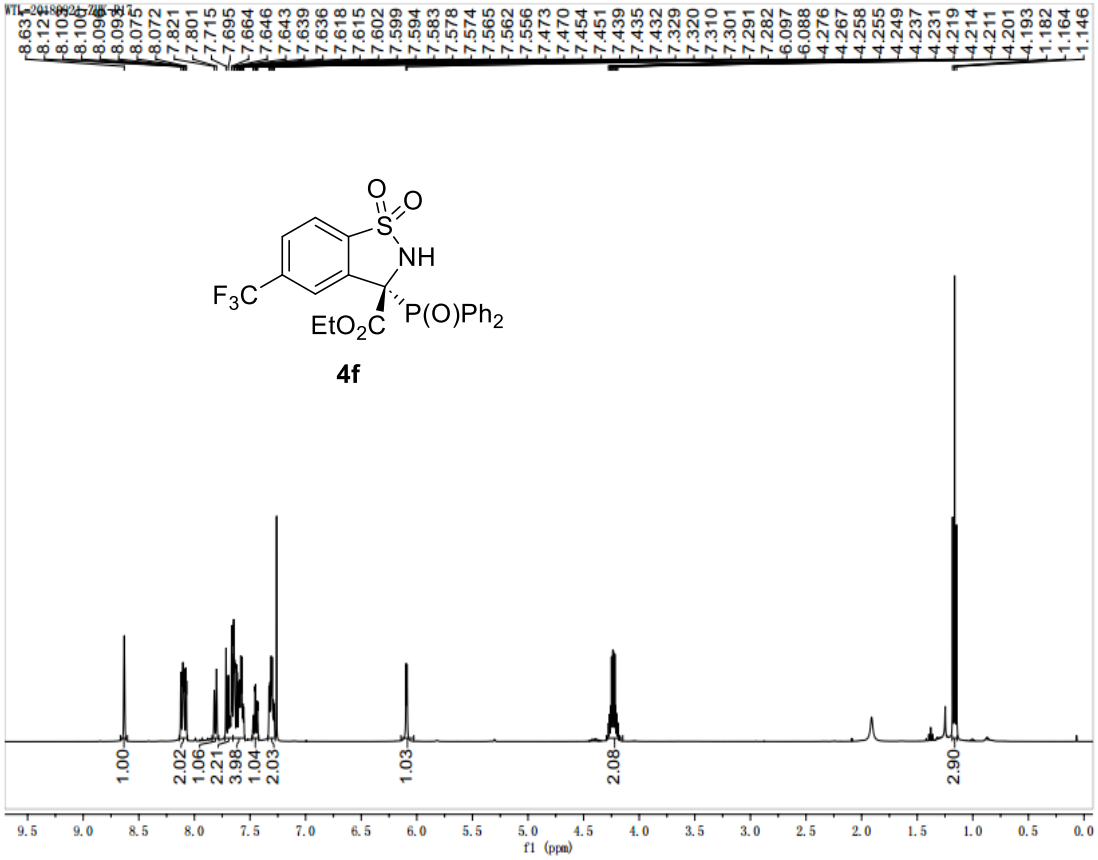

WTL-20180921-ZHK-R24
166.438
166.413
163.630
163.614
133.884
133.862
133.216
133.190
132.974
132.947
132.741
132.655
132.557
132.475
128.924
128.807
128.373
128.250
126.389
122.448
118.956
118.945
111.391
111.370
70.212
69.504
64.541
56.263
13.907
MeO
EtO2C
P(O)Ph2
4d
f1 (ppm)

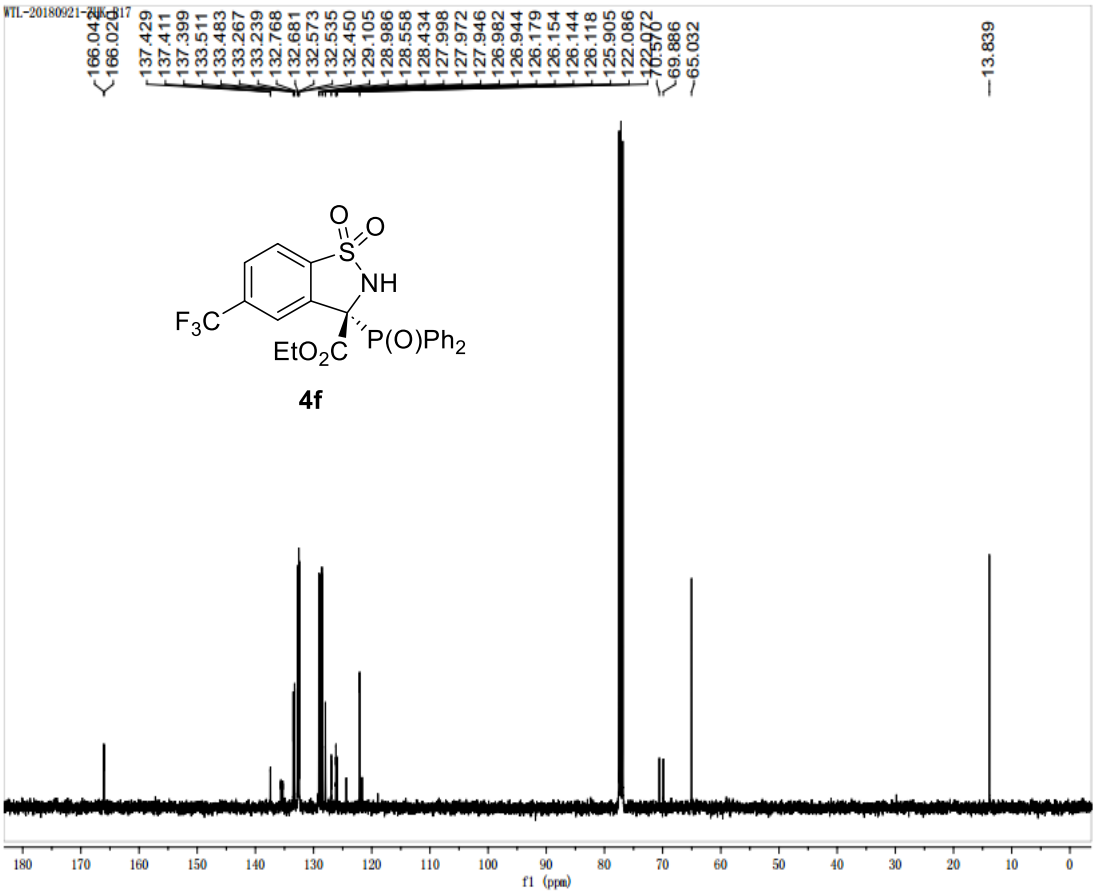

WTL-20180921-ZHK-R24
28.180
MeO
EtO2C
P(O)Ph2
4d
f1 (ppm)


8.380
8.377
8.375
8.115
8.106
8.096
8.093
8.090
8.072
8.069
7.673
7.655
7.652
7.646
7.645
7.637
7.633
7.627
7.623
7.595
7.591
7.586
7.575
7.570
7.567
7.558
7.555
7.548
7.525
7.523
7.521
7.516
7.496
7.467
7.463
7.448
7.444
7.344
7.340
7.335
7.331
7.324
7.315
7.306
7.296
6.012
6.002
4.272
4.254
4.245
4.228
4.212
4.194
4.186
4.168
1.170
1.152
1.134
O
O
S
NH
Cl
EtO2C
P(O)Ph2
4e
0.94
2.00
3.06
2.20
2.86
2.04
0.95
2.06
3.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

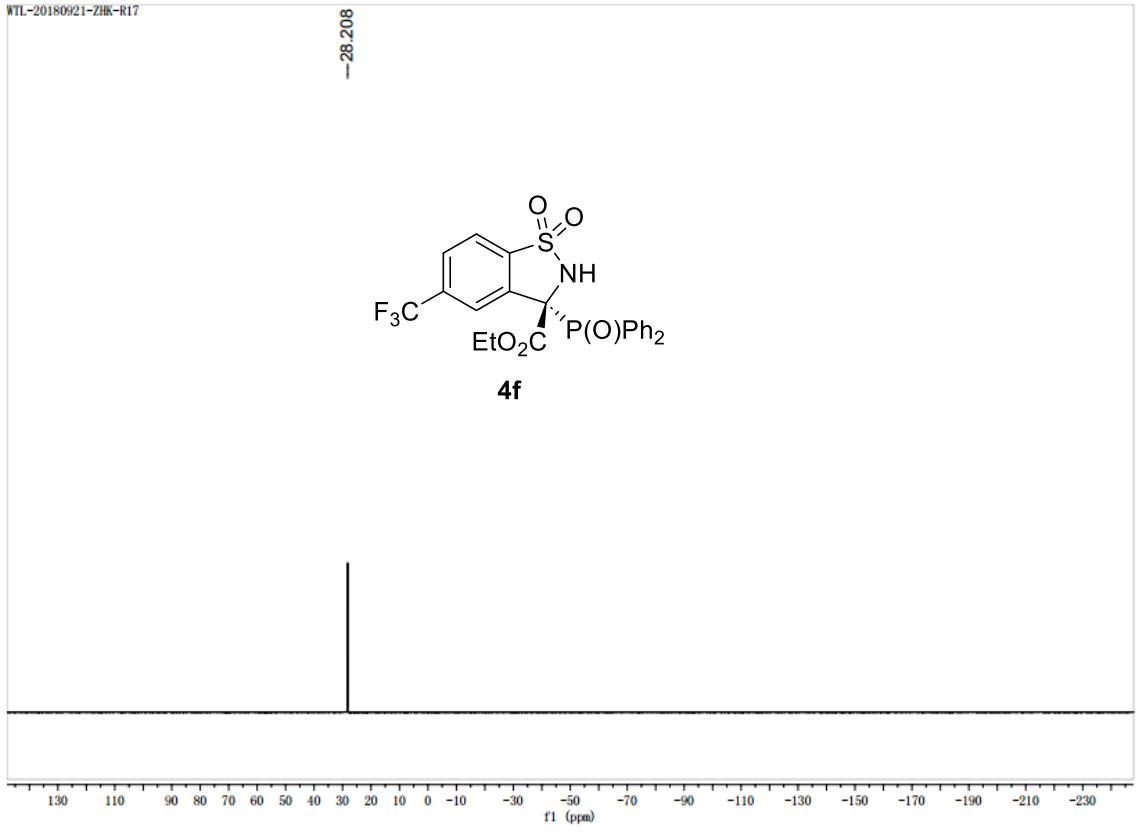

WTL-20180921-ZHK-R15
166.158
166.136
140.101
140.080
133.409
133.382
133.280
133.256
133.189
133.161
132.865
132.834
132.804
132.718
132.546
132.463
131.480
131.464
129.038
128.919
128.536
128.511
128.387
127.125
122.343
122.330
70.248
69.553
64.948
13.905
O
O
S
NH
Cl
EtO2C
P(O)Ph2
4e
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


WTL-20180921-ZHK-R15
28.097
O
O
S
NH
Cl
EtO2C
P(O)Ph2
4e
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

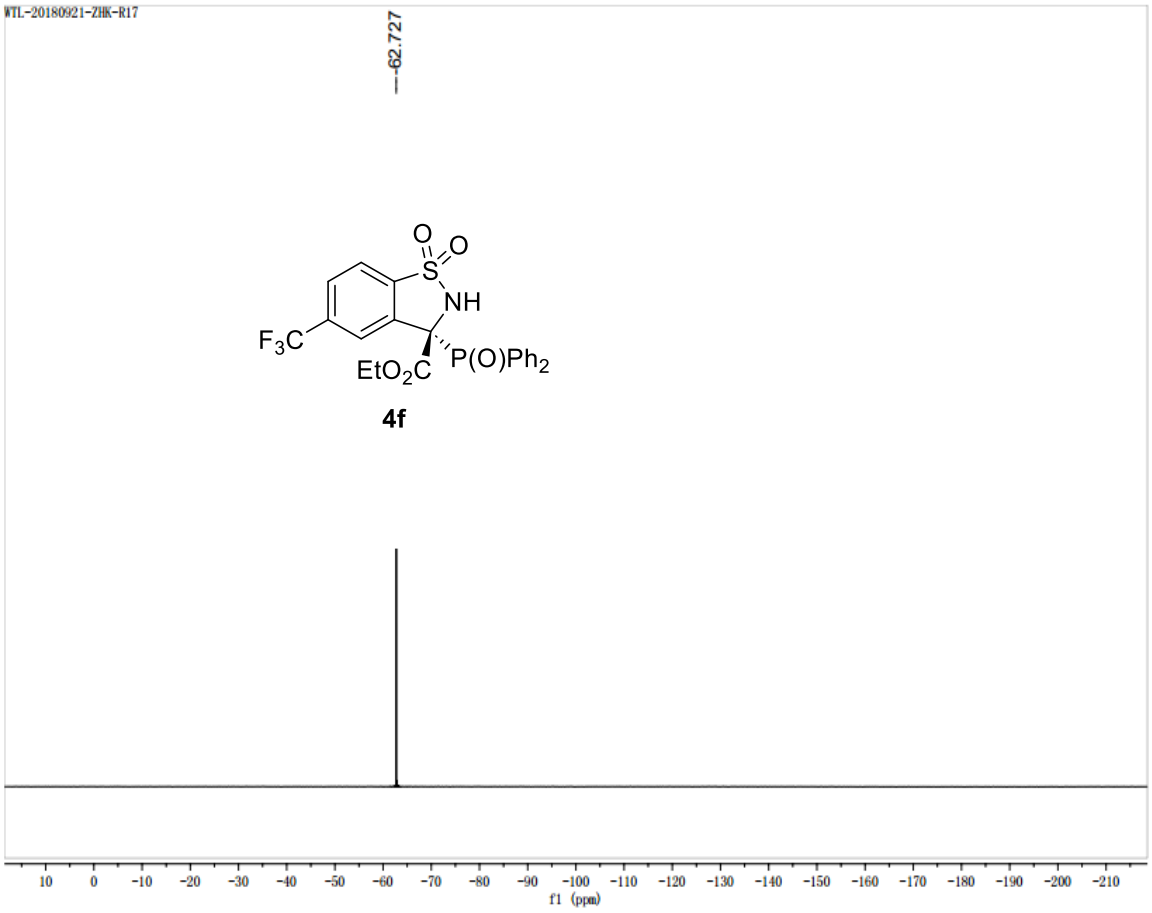

8.631 8.121 8.103 8.100 8.096 8.093 8.075 8.072 7.821 7.801 7.715 7.695 7.664 7.646 7.643 7.639 7.636 7.618 7.615 7.602 7.599 7.594 7.583 7.578 7.574 7.565 7.562 7.556 7.473 7.470 7.454 7.451 7.439 7.435 7.432 7.329 7.320 7.310 7.301 7.291 7.282 6.097 6.088 4.276 4.267 4.258 4.255 4.249 4.237 4.231 4.219 4.214 4.211 4.201 4.193 1.182 1.164 1.146
O
O
S
NH
F3C
EtO2C
P(O)Ph2
4f
1.00 2.02 1.06 2.21 3.98 1.04 2.03 1.03 2.08 2.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


WTL-20180921-ZHK-R17
166.042
166.026
137.429
137.411
137.399
133.511
133.483
133.267
133.239
132.768
132.681
132.573
132.535
132.450
129.105
128.986
128.558
128.434
127.998
127.972
127.946
126.982
126.944
126.179
126.154
126.144
126.118
125.905
122.086
122.072
70.570
69.886
65.032
13.839
O
O
S
NH
F3C
EtO2C
P(O)Ph2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

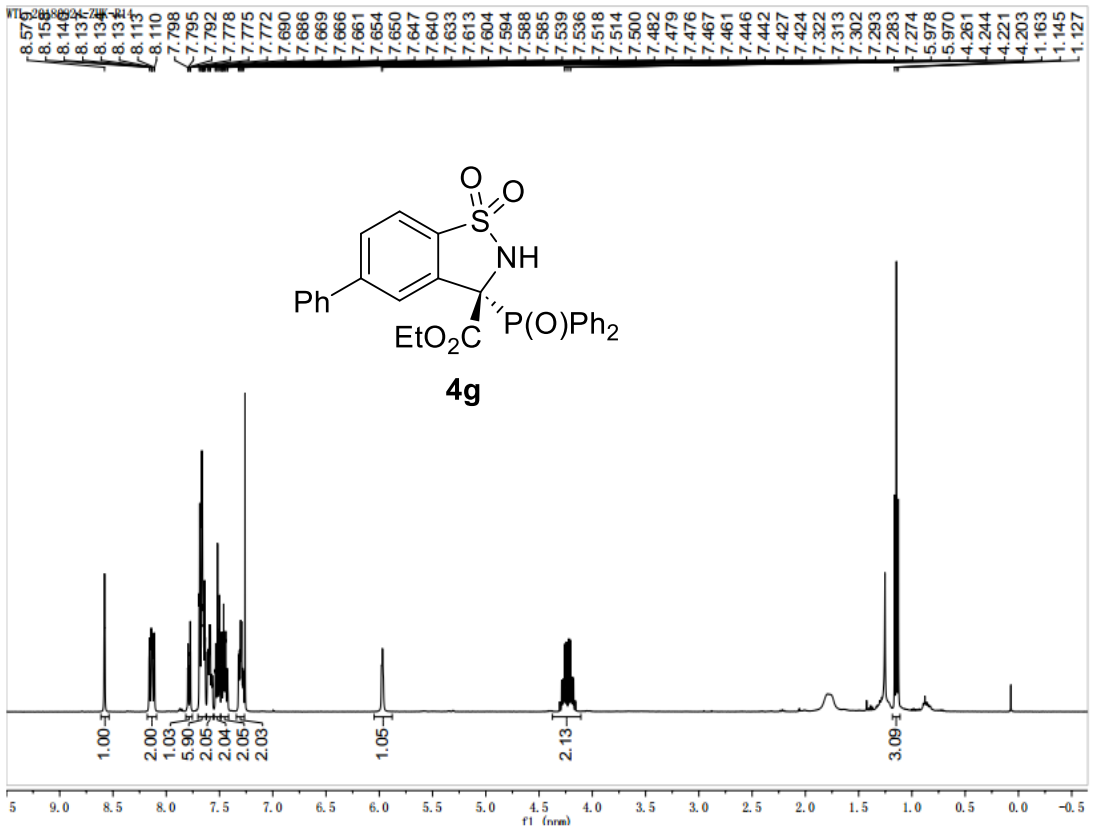
4f


WTL-20180921-ZHK-R17
28.208
O
O
S
NH
F3C
EtO2C
P(O)Ph2
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

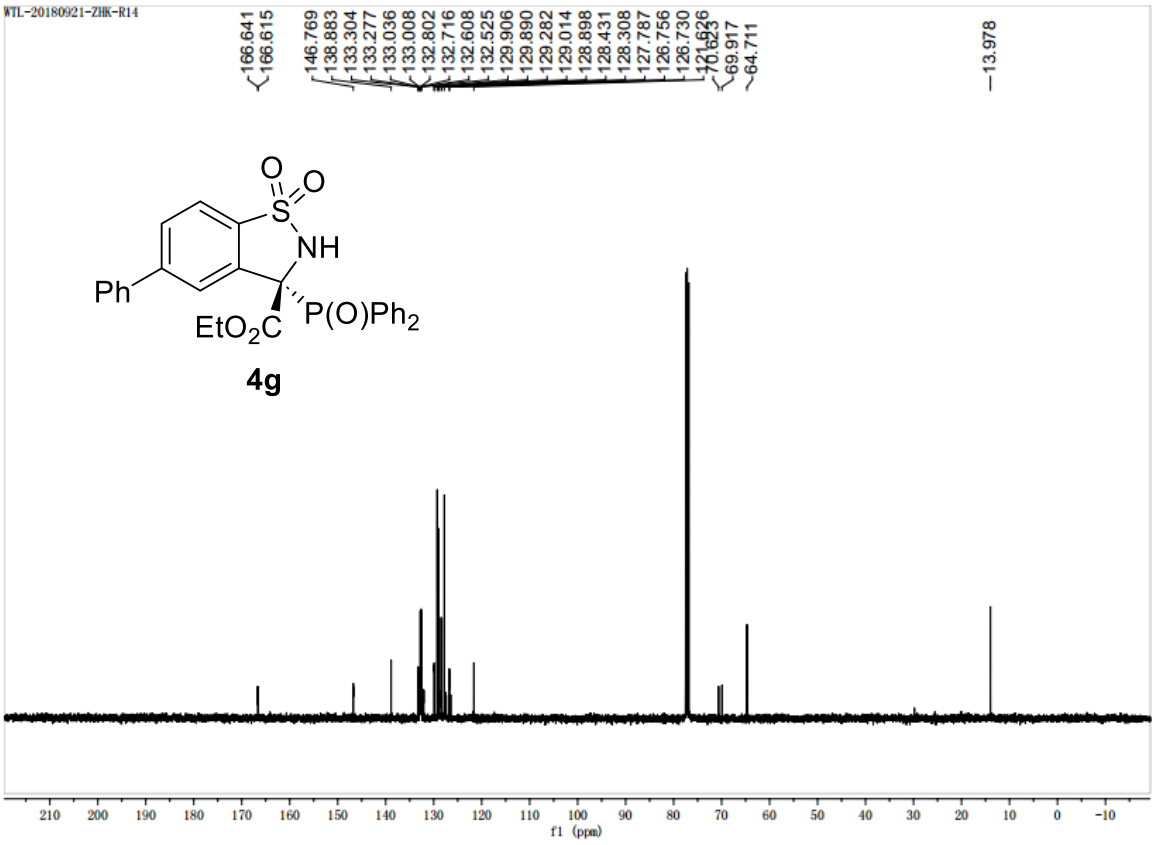
4f

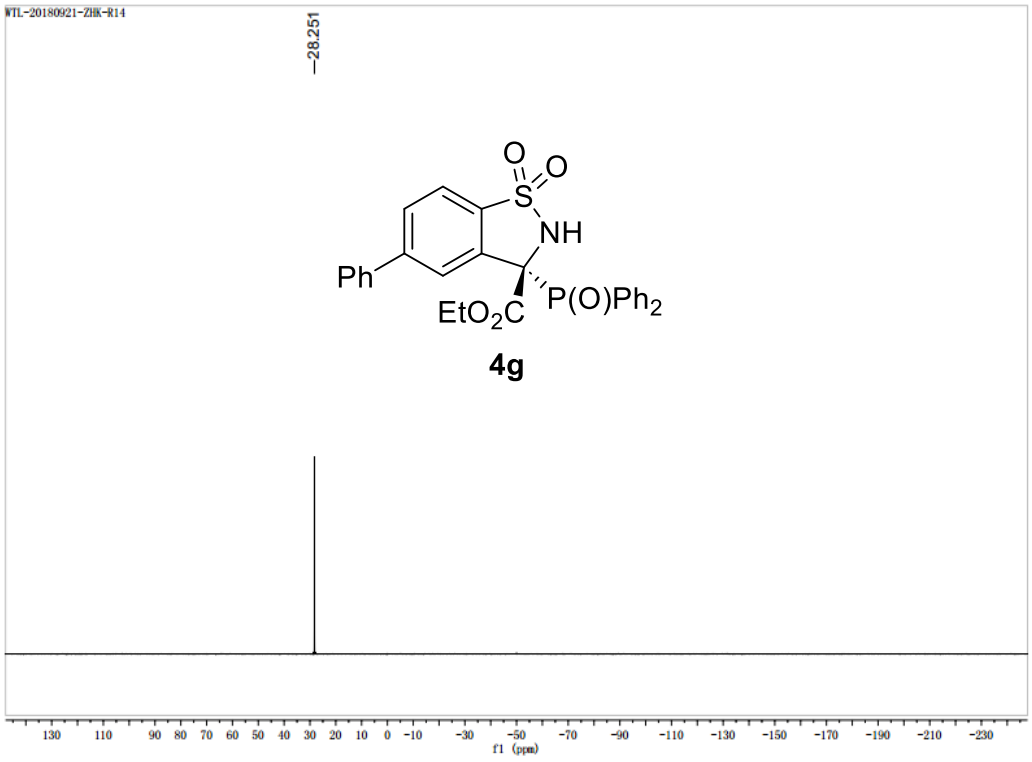

WTL-20180921-ZHK-R17
62.727
O
O
S
NH
F3C
EtO2C
P(O)Ph2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

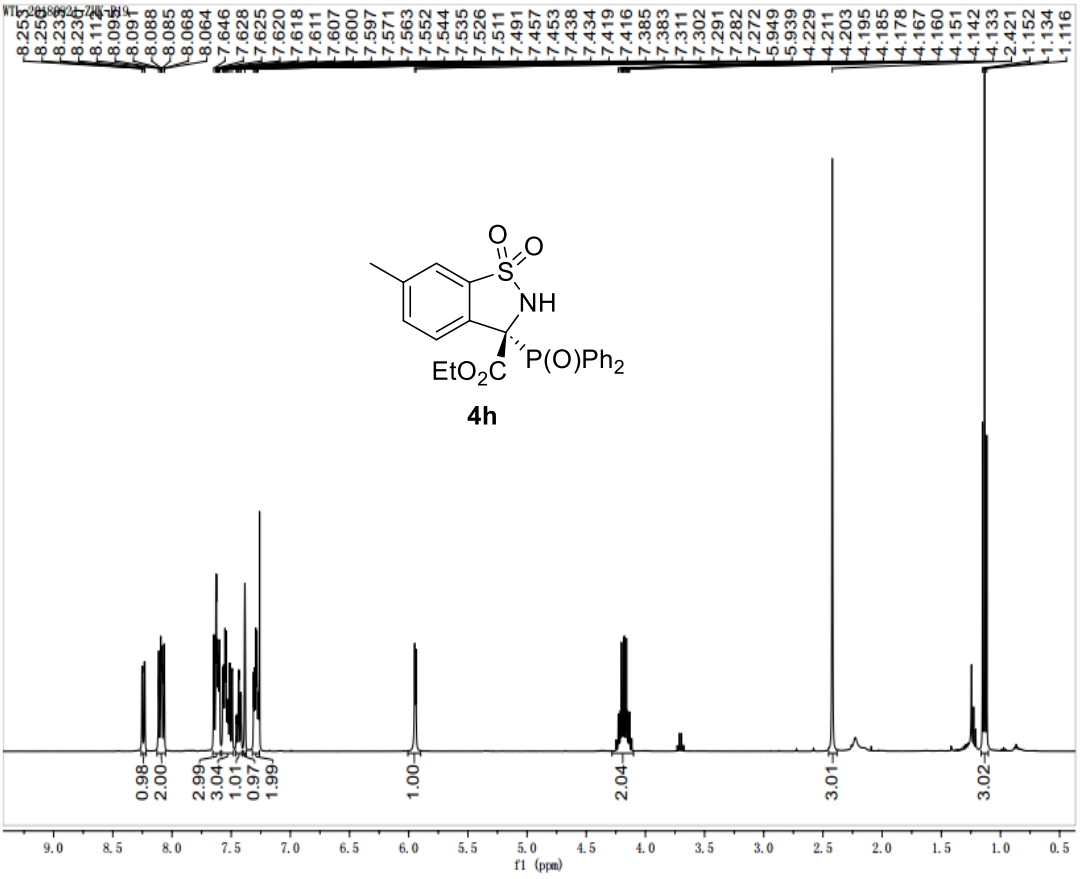
4f


8.579 8.158 8.145 8.137 8.134 8.113 8.110 7.798 7.795 7.792 7.778 7.775 7.772 7.690 7.686 7.669 7.666 7.661 7.654 7.650 7.647 7.640 7.633 7.613 7.604 7.594 7.588 7.585 7.539 7.536 7.518 7.514 7.500 7.482 7.479 7.476 7.467 7.461 7.446 7.442 7.427 7.424 7.322 7.313 7.302 7.293 7.283 7.274 5.978 5.970 4.261 4.244 4.221 4.203 1.163 1.145 1.127
O
O
S
NH
Ph
EtO2C
P(O)Ph2
1.00 2.00 1.03 5.90 2.05 2.04 2.05 2.03 1.05 2.13 3.09
5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

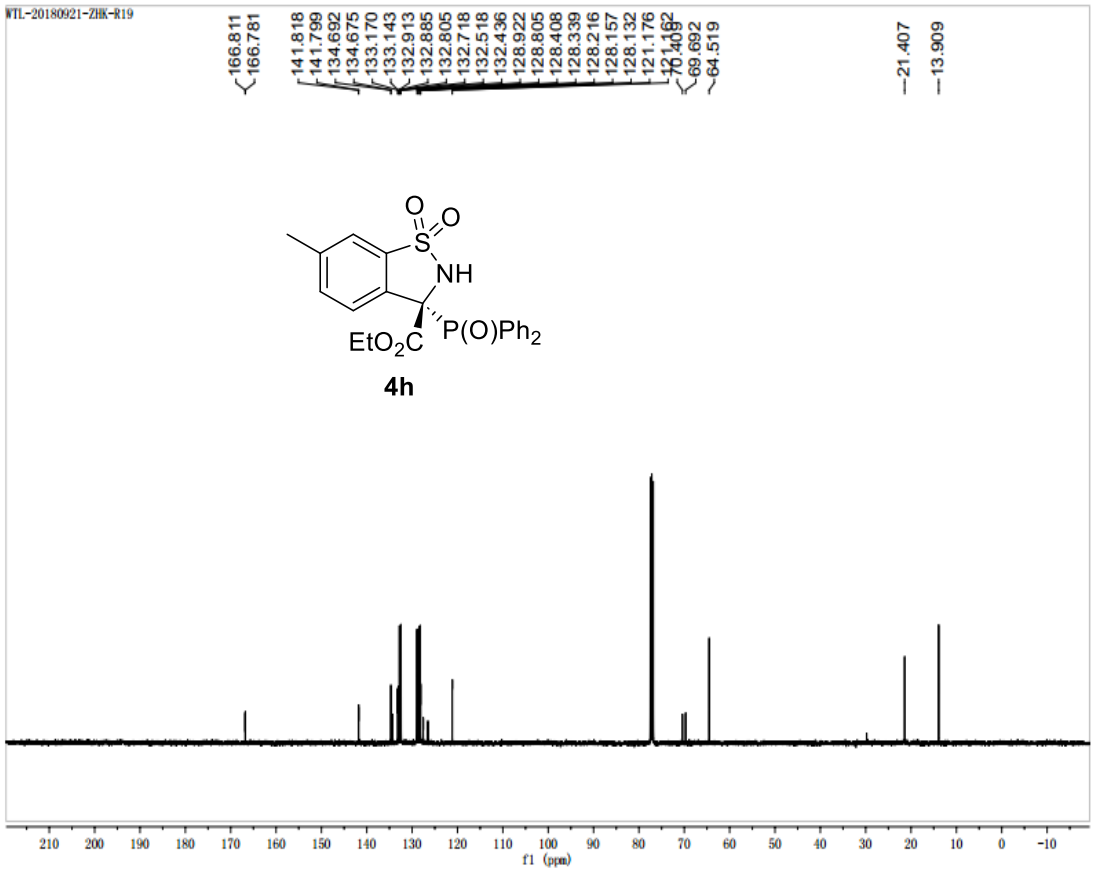
4g


WTL-20180921-ZHK-R14
166.641
166.615
146.769
138.883
133.304
133.277
133.036
133.008
132.802
132.716
132.608
132.525
129.906
129.890
129.282
129.014
128.898
128.431
128.308
127.787
126.756
126.730
121.626
70.623
69.917
64.711
13.978
O
O
S
NH
Ph
EtO2C
P(O)Ph2
4g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

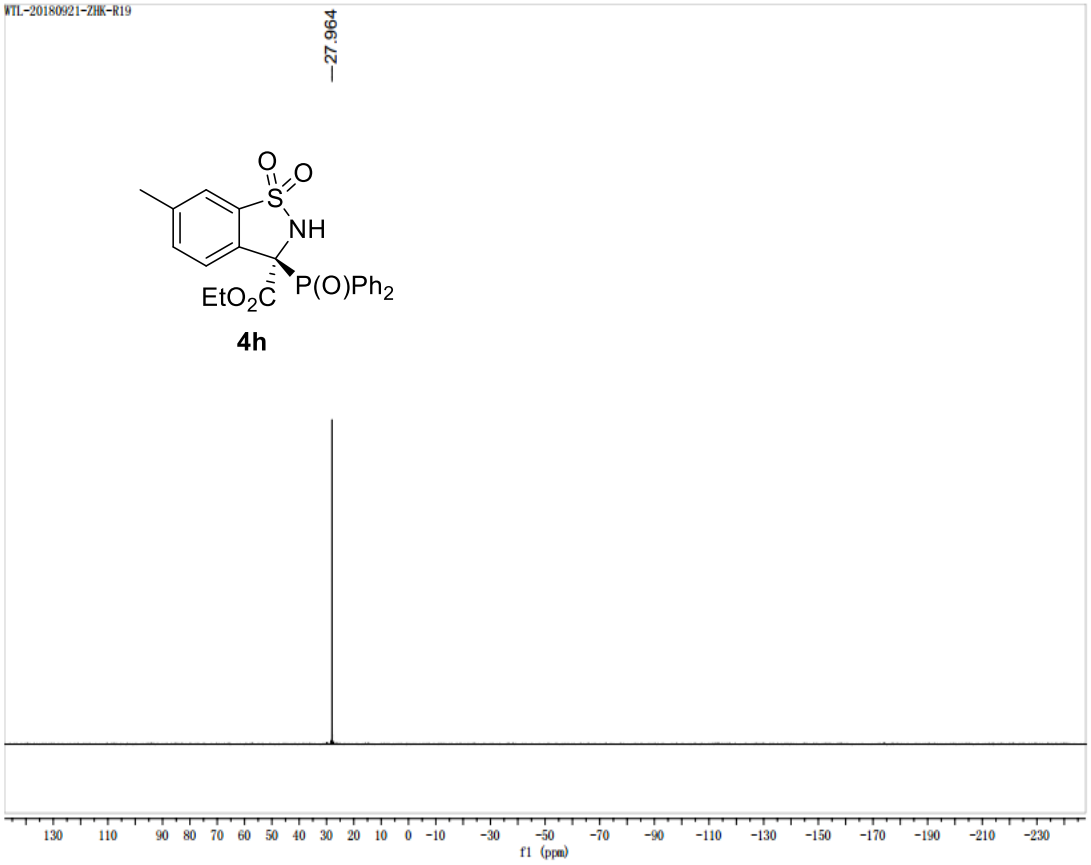

WTL-20180921-ZHK-R14
28.251
O
O
S
NH
Ph
EtO2C
P(O)Ph2
4g
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

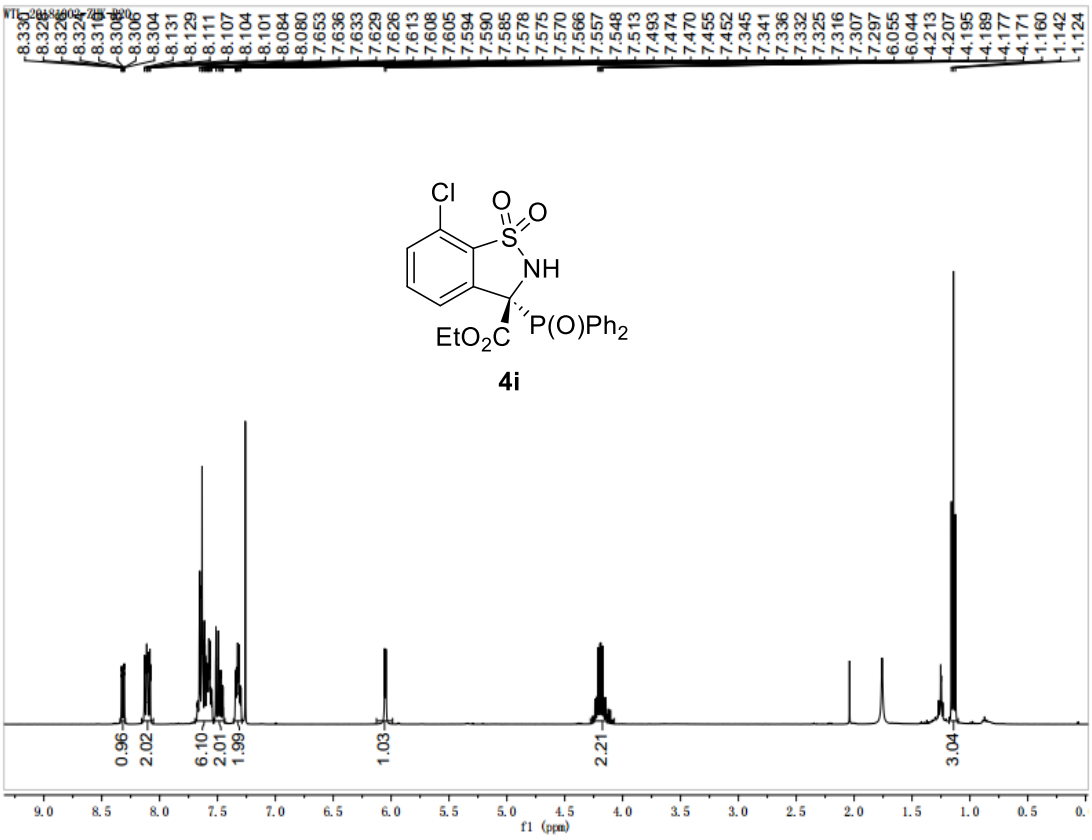

8.251
8.250
8.232
8.230
8.112
8.091
8.088
8.085
8.068
8.064
7.646
7.628
7.625
7.620
7.618
7.611
7.607
7.600
7.597
7.571
7.563
7.552
7.544
7.535
7.526
7.511
7.491
7.457
7.453
7.438
7.434
7.419
7.416
7.385
7.383
7.311
7.302
7.291
7.282
7.272
5.949
5.939
4.229
4.211
4.203
4.195
4.185
4.178
4.167
4.160
4.151
4.142
4.133
2.421
1.152
1.134
1.116
O
O
S
NH
EtO2C
P(O)Ph2
0.98
2.00
2.99
3.04
1.01
0.97
1.99
1.00
2.04
3.01
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

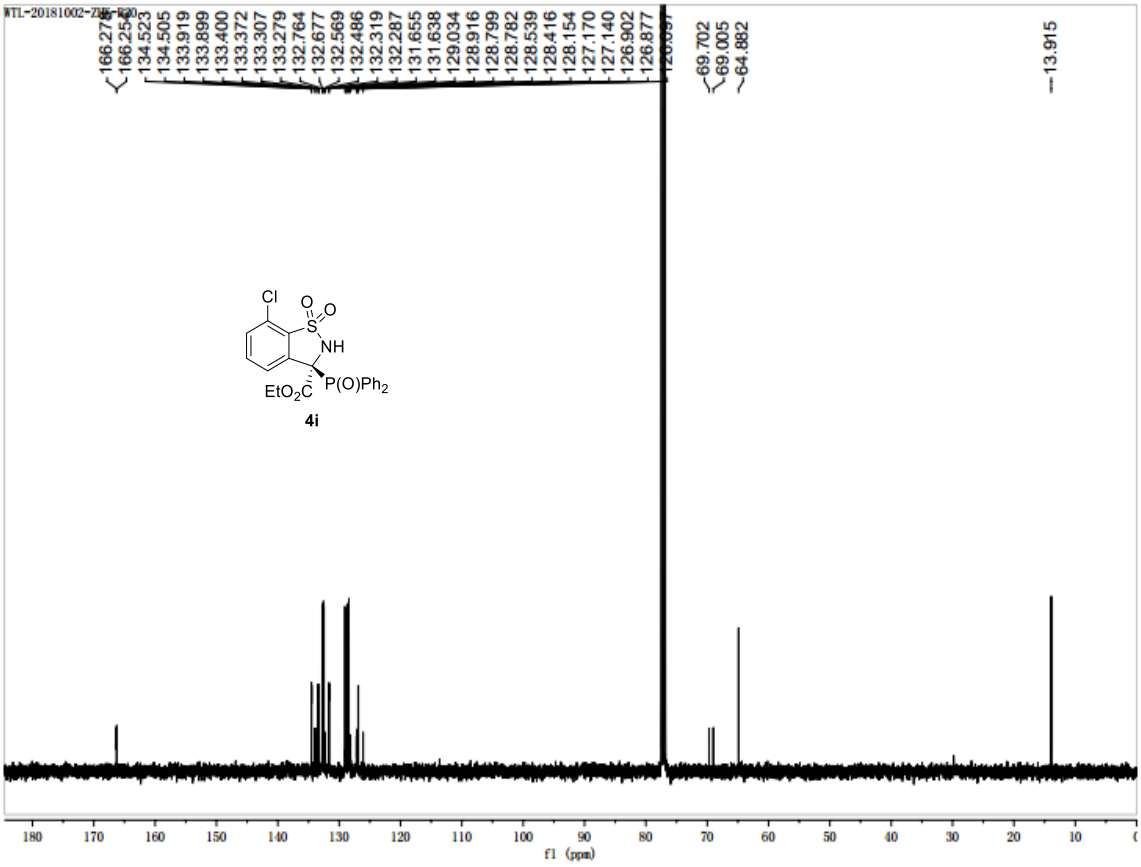
4h

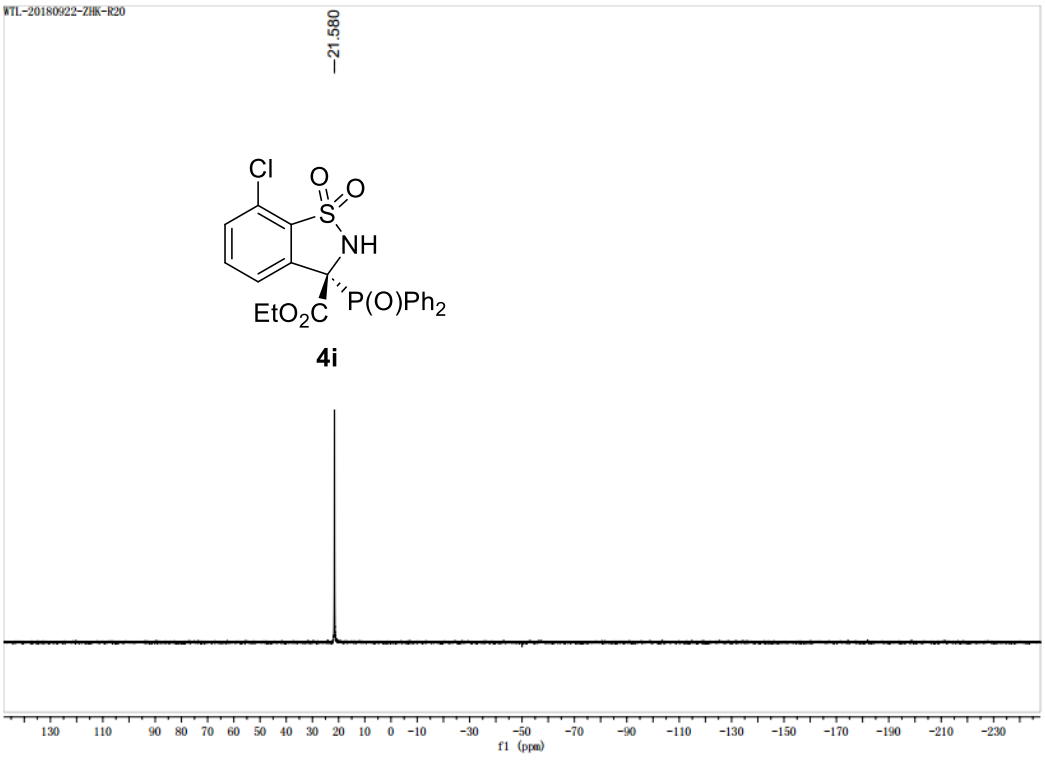

WTL-20180921-ZHK-R19
166.811
166.781
141.818
141.799
134.692
134.675
133.170
133.143
132.913
132.885
132.805
132.718
132.518
132.436
128.922
128.805
128.408
128.339
128.216
128.157
128.132
121.176
121.162
70.409
69.692
64.519
21.407
13.909
O
O
S
NH
EtO2C
P(O)Ph2
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

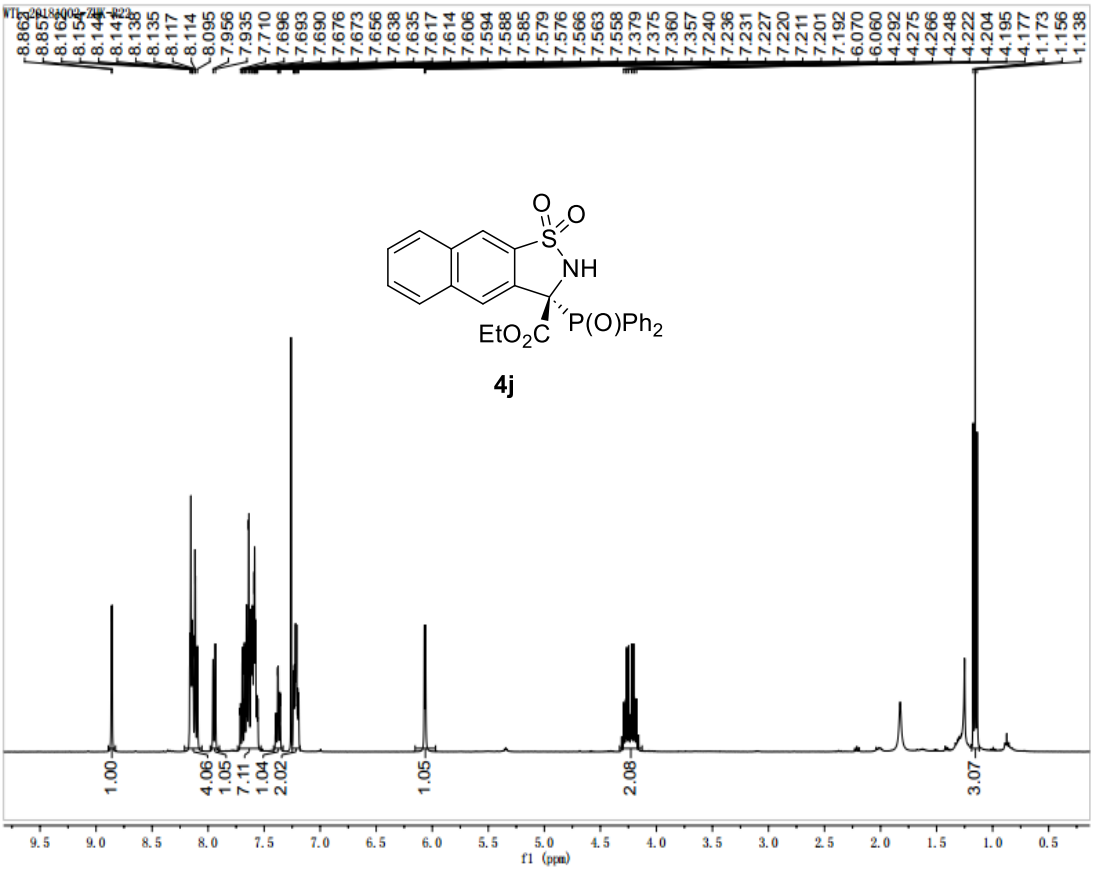
4h


WTL-20180921-ZHK-R19
27.964
O
O
S
NH
EtO2C
P(O)Ph2
4h
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

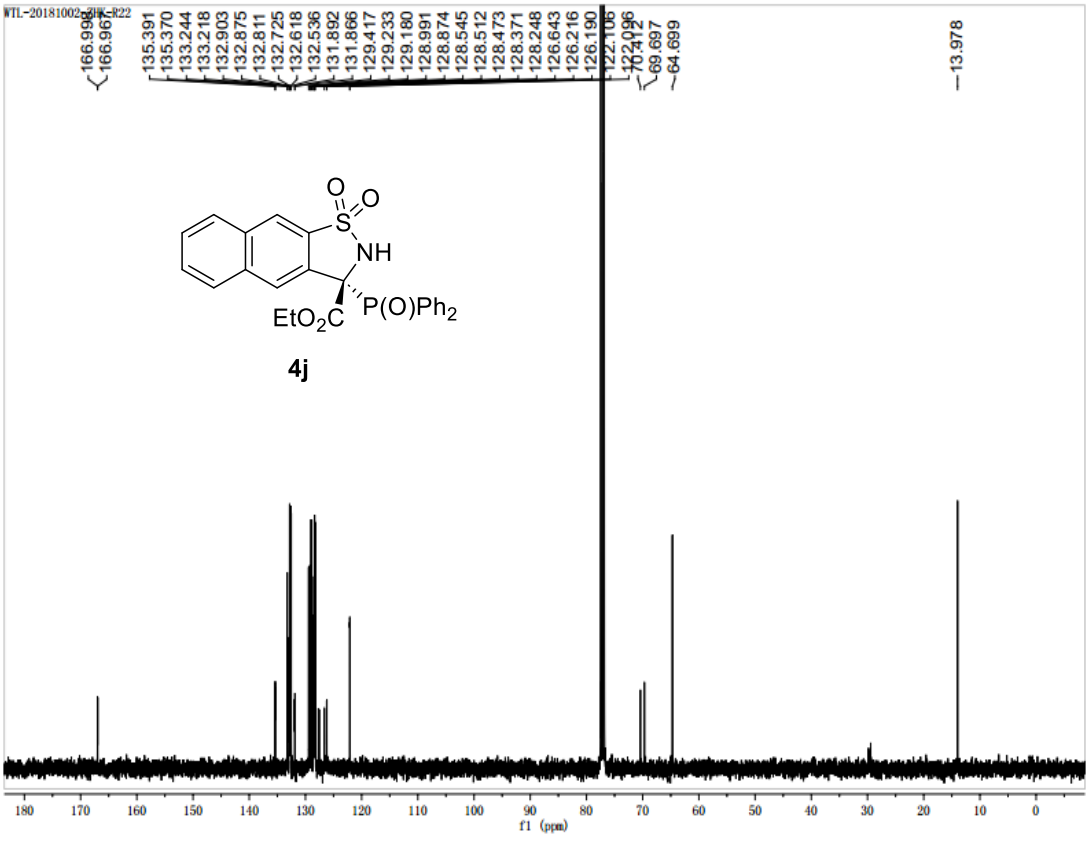

8.336 8.328 8.324 8.316 8.306 8.304 8.131 8.129 8.111 8.107 8.104 8.101 8.084 8.080 7.653 7.636 7.633 7.629 7.626 7.613 7.608 7.605 7.594 7.590 7.585 7.578 7.575 7.570 7.566 7.557 7.548 7.513 7.493 7.474 7.470 7.455 7.452 7.345 7.341 7.336 7.332 7.325 7.316 7.307 7.297 6.055 6.044 4.213 4.207 4.195 4.189 4.177 4.171 1.160 1.142 1.124
Cl
O
O
S
NH
EtO2C
P(O)Ph2
4i
0.96 2.02 6.10 2.01 1.99 1.03 2.21 3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)


WTL-20181002-ZHK-R20
166.276
166.254
134.523
134.505
133.919
133.899
133.400
133.372
133.307
133.279
132.764
132.677
132.569
132.486
132.319
132.287
131.655
131.638
129.034
128.916
128.799
128.782
128.539
128.416
128.154
127.170
127.140
126.902
126.877
120.097
69.702
69.005
64.882
13.915
Cl
O
O
S
NH
EtO2C
P(O)Ph2
4i
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

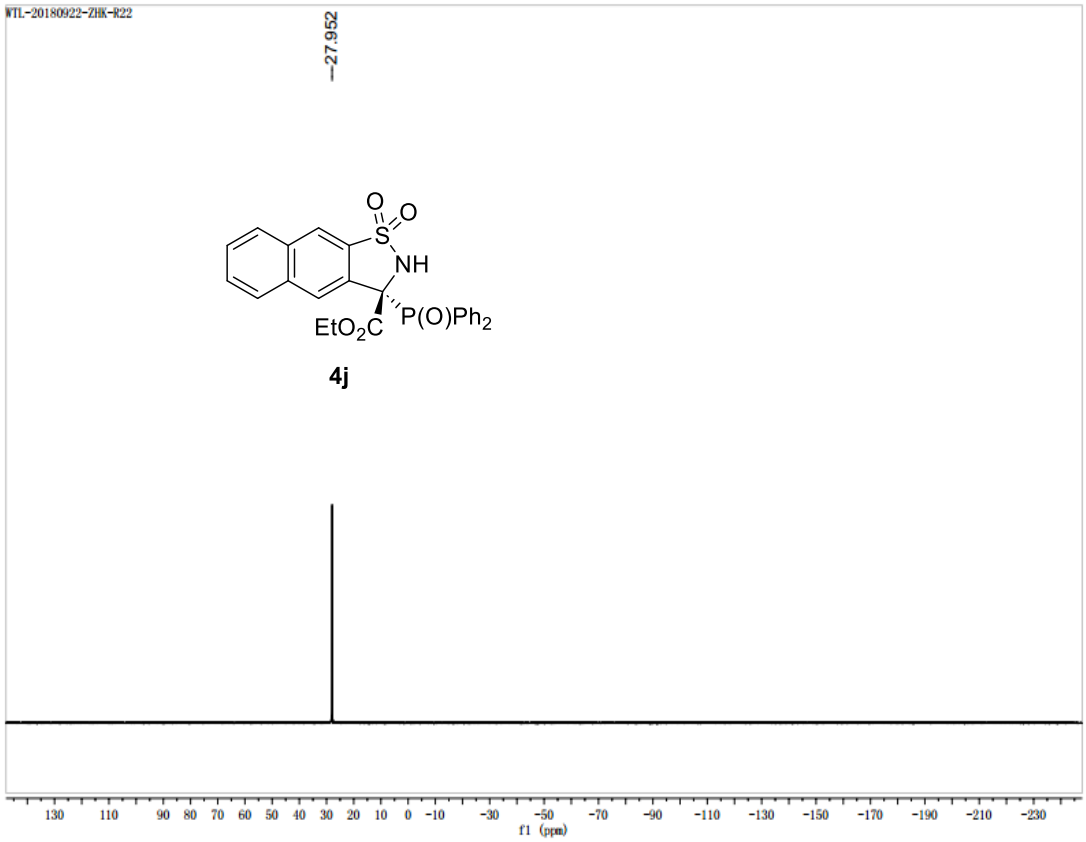

WTL-20180922-ZHK-R20
21.580
Cl
O
O
S
NH
EtO2C
P(O)Ph2
4i
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

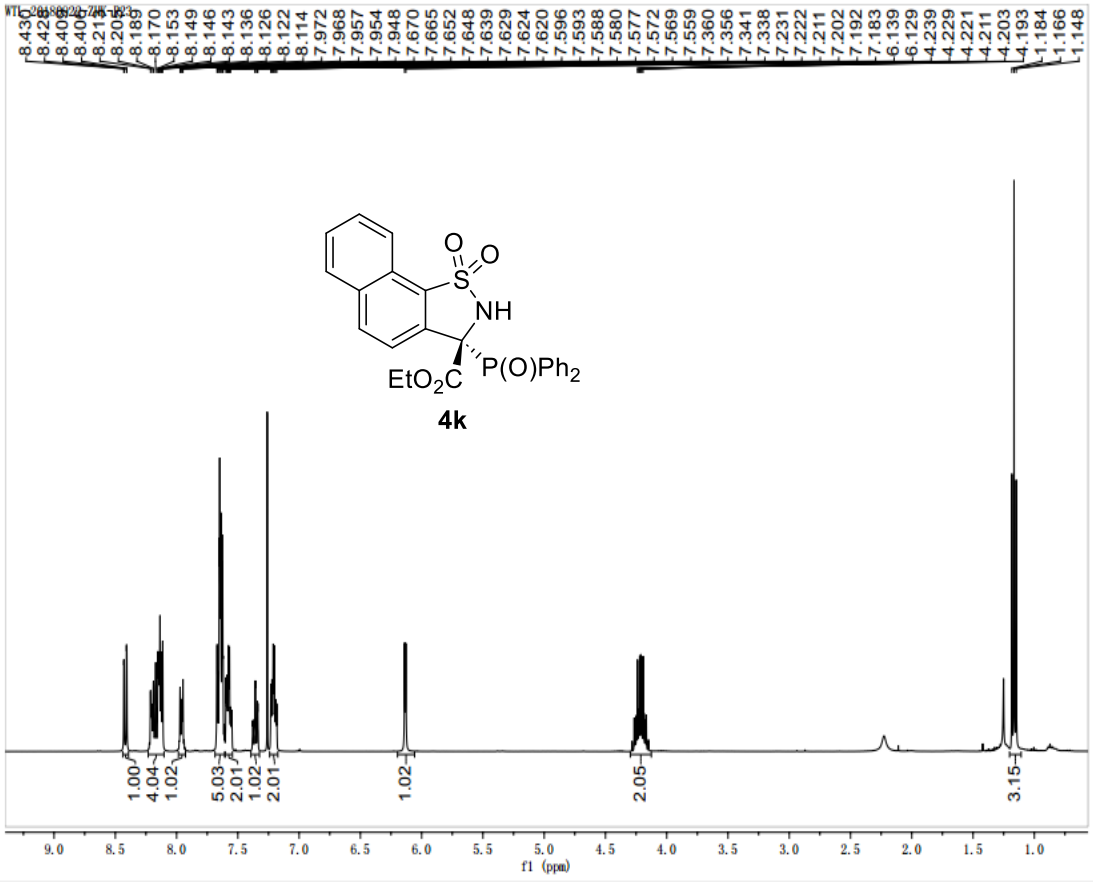

8.862
8.851
8.162
8.154
8.147
8.138
8.135
8.117
8.114
8.095
7.956
7.935
7.710
7.696
7.693
7.690
7.676
7.673
7.656
7.638
7.635
7.617
7.614
7.606
7.594
7.588
7.585
7.579
7.576
7.566
7.563
7.558
7.379
7.375
7.360
7.357
7.240
7.236
7.231
7.227
7.220
7.211
7.201
7.192
6.070
6.060
4.292
4.275
4.266
4.248
4.222
4.204
4.195
4.177
1.173
1.156
1.138
O
O
S
NH
EtO2C
P(O)Ph2
1.00
4.06
1.05
7.11
1.04
2.02
1.05
2.08
3.07
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

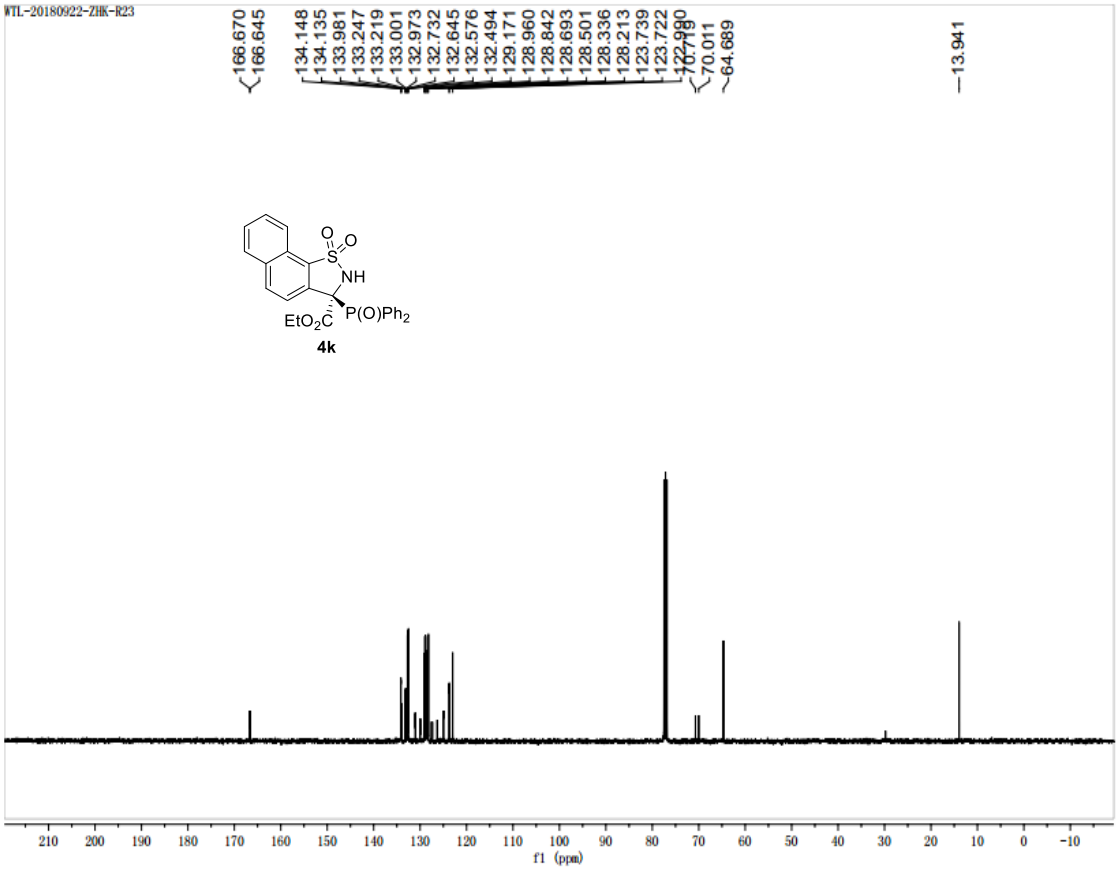
4j

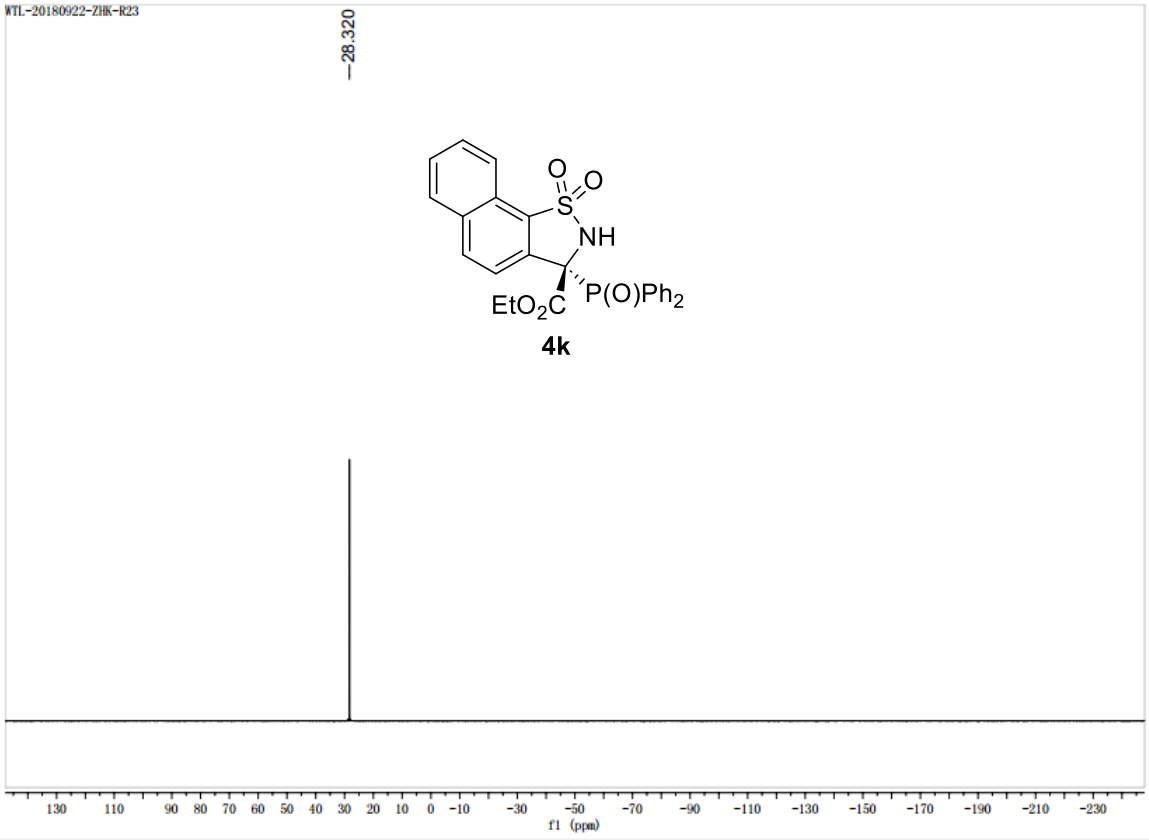

166.996
166.967
135.391
135.370
133.244
133.218
132.903
132.875
132.811
132.725
132.618
132.536
131.892
131.866
129.417
129.233
129.180
128.991
128.874
128.545
128.512
128.473
128.371
128.248
126.643
126.216
126.190
122.106
122.096
70.412
69.697
64.699
13.978
O
O
S
NH
EtO2C
P(O)Ph2
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

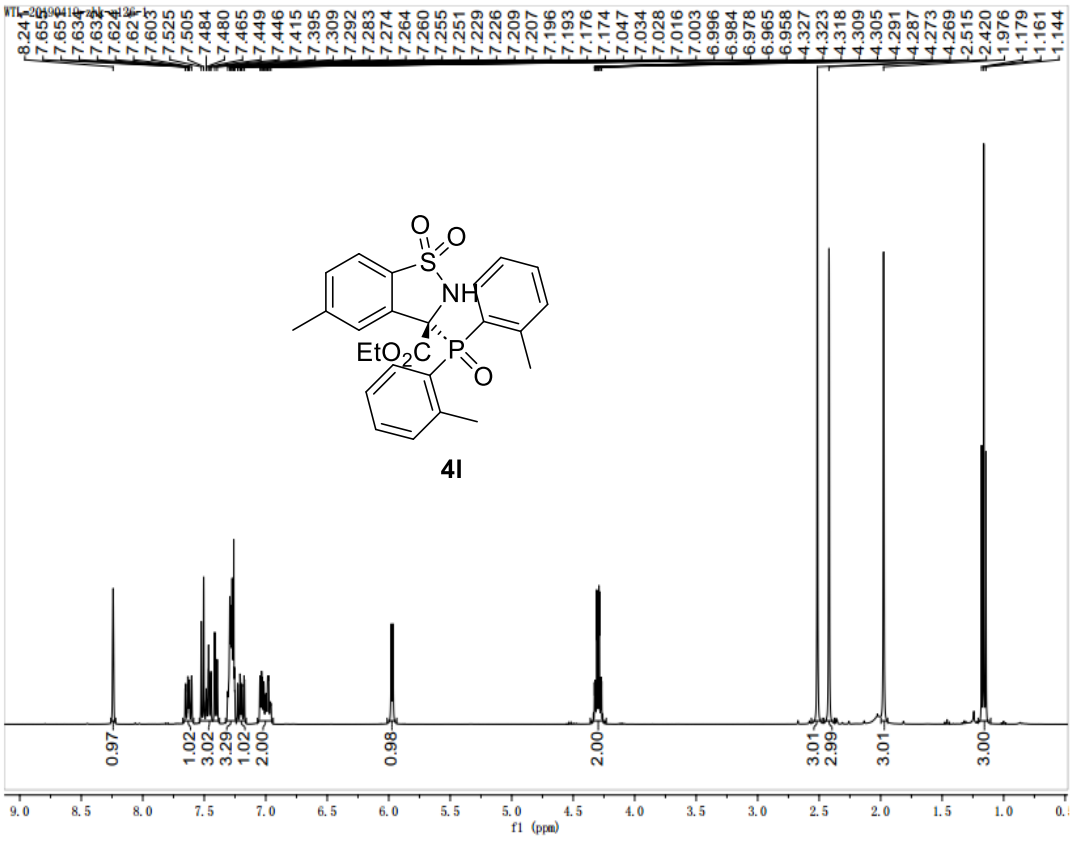
4j

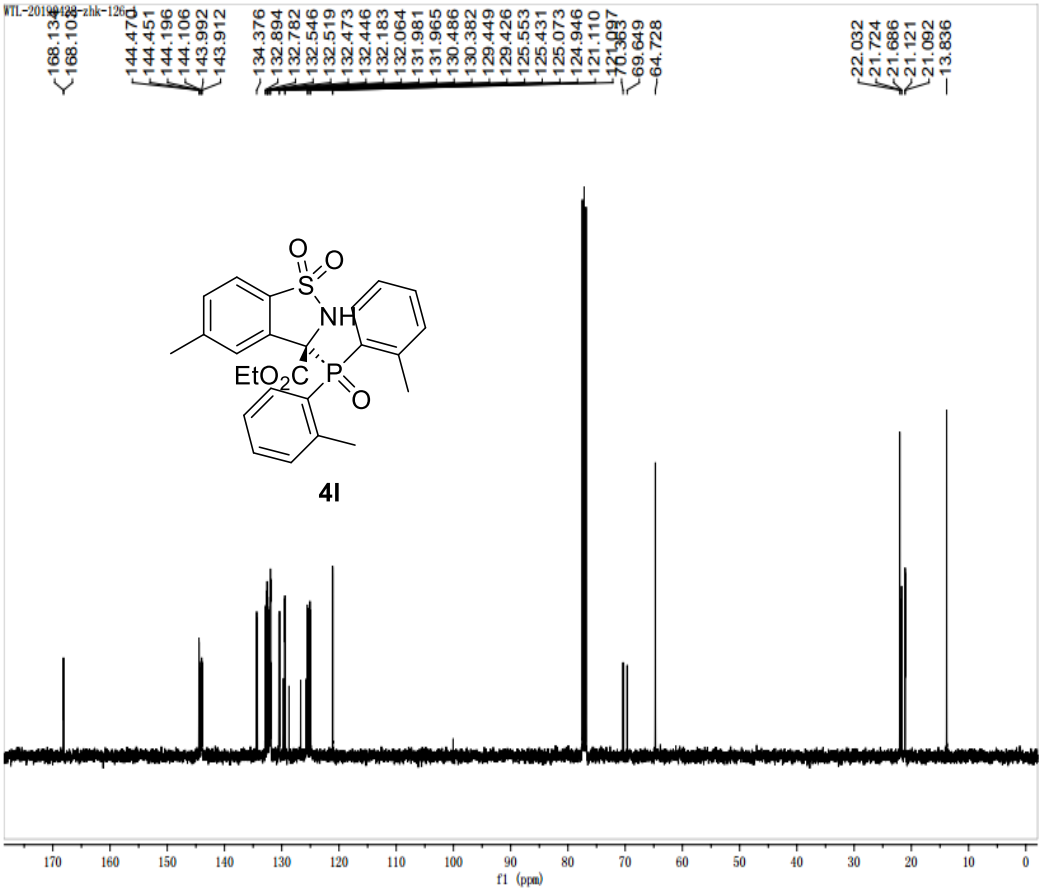

WTL-20180922-ZHK-R22
27.952
O
O
S
NH
EtO2C
P(O)Ph2
4j
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

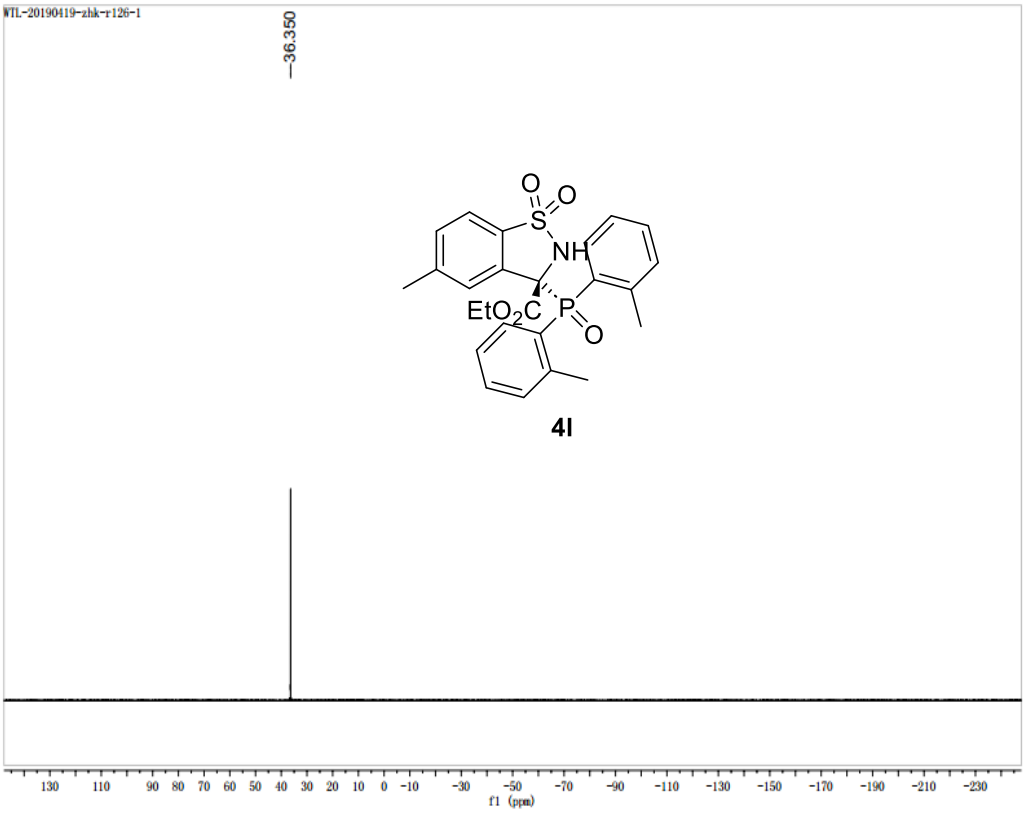

8.430 8.428 8.409 8.405 8.402 8.215 8.209 8.189 8.170 8.153 8.149 8.146 8.143 8.136 8.126 8.122 8.114 7.972 7.968 7.957 7.954 7.948 7.670 7.665 7.652 7.648 7.639 7.629 7.624 7.620 7.596 7.593 7.588 7.580 7.577 7.572 7.569 7.559 7.360 7.356 7.341 7.338 7.231 7.222 7.211 7.202 7.192 7.183 6.139 6.129 4.239 4.229 4.221 4.211 4.203 4.193 1.184 1.166 1.148
O
O
S
NH
EtO2C
P(O)Ph2
4k
1.00 4.04 1.02 5.03 2.01 1.02 2.01 1.02 2.05 3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)

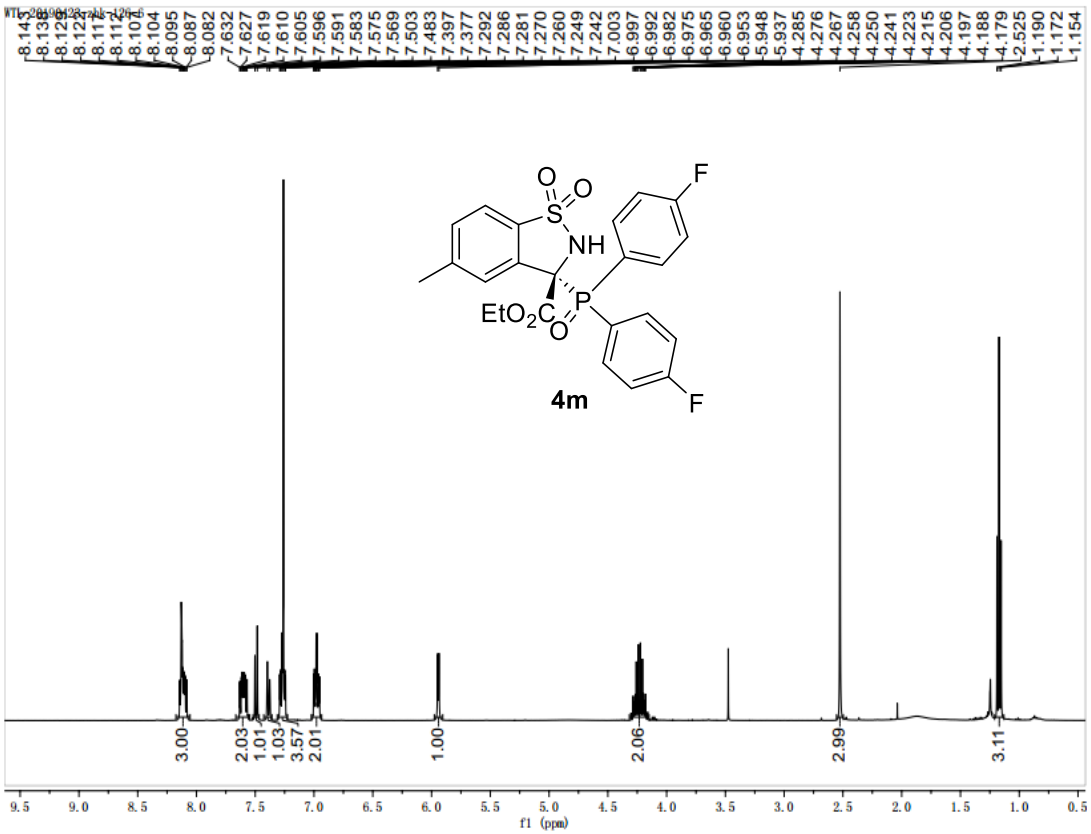

WTL-20180922-ZHK-R23
166.670
166.645
134.148
134.135
133.981
133.247
133.219
133.001
132.973
132.732
132.645
132.576
132.494
129.171
128.960
128.842
128.693
128.501
128.336
128.213
123.739
123.722
122.980
70.011
64.689
13.941
O
O
S
NH
EtO2C
P(O)Ph2
4k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

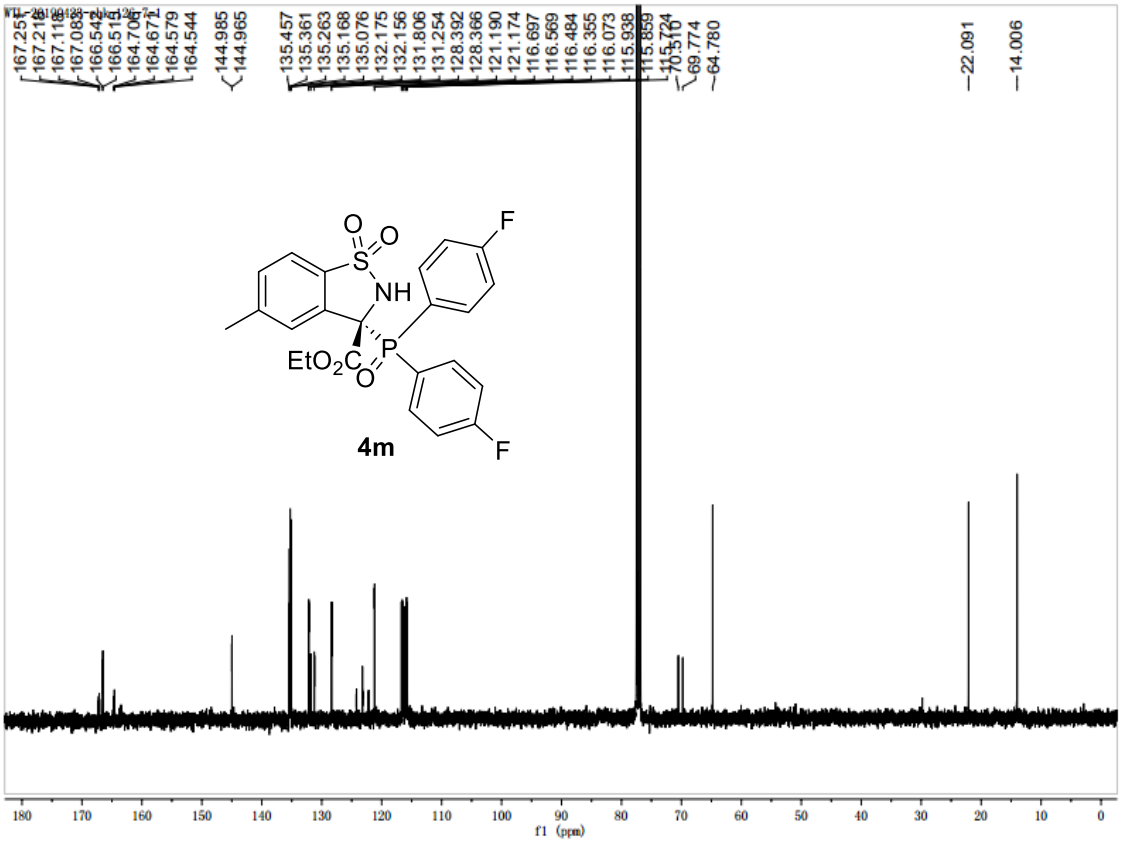

WTL-20180922-ZHK-R23
28.320
O
O
S
NH
EtO2C
P(O)Ph2
4k
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

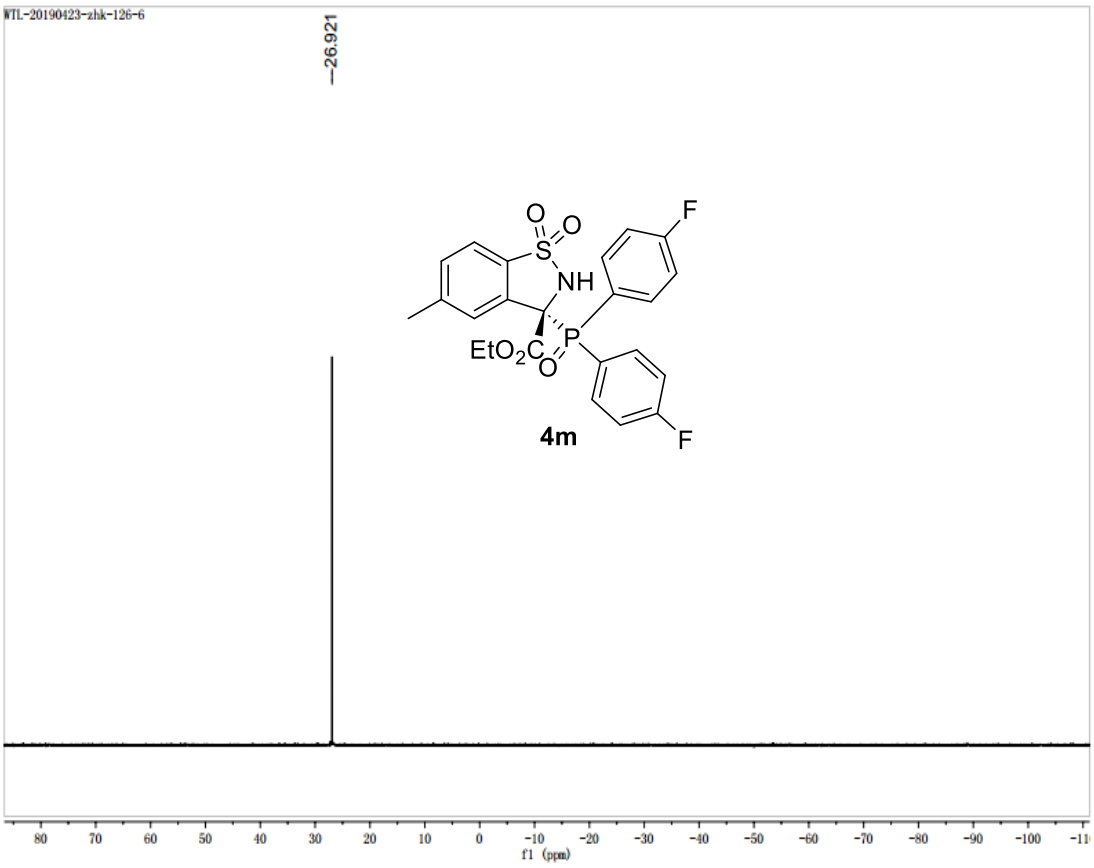

4l
f1 (ppm)

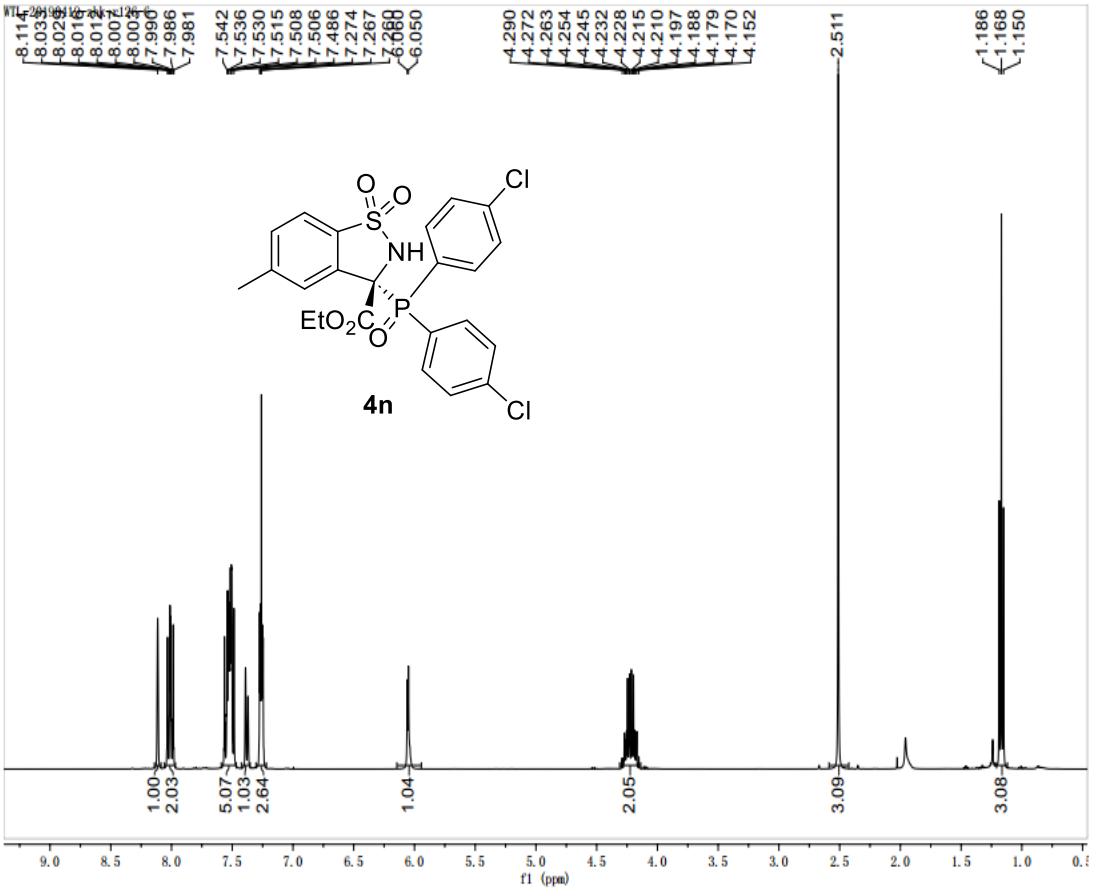

4l
f1 (ppm)

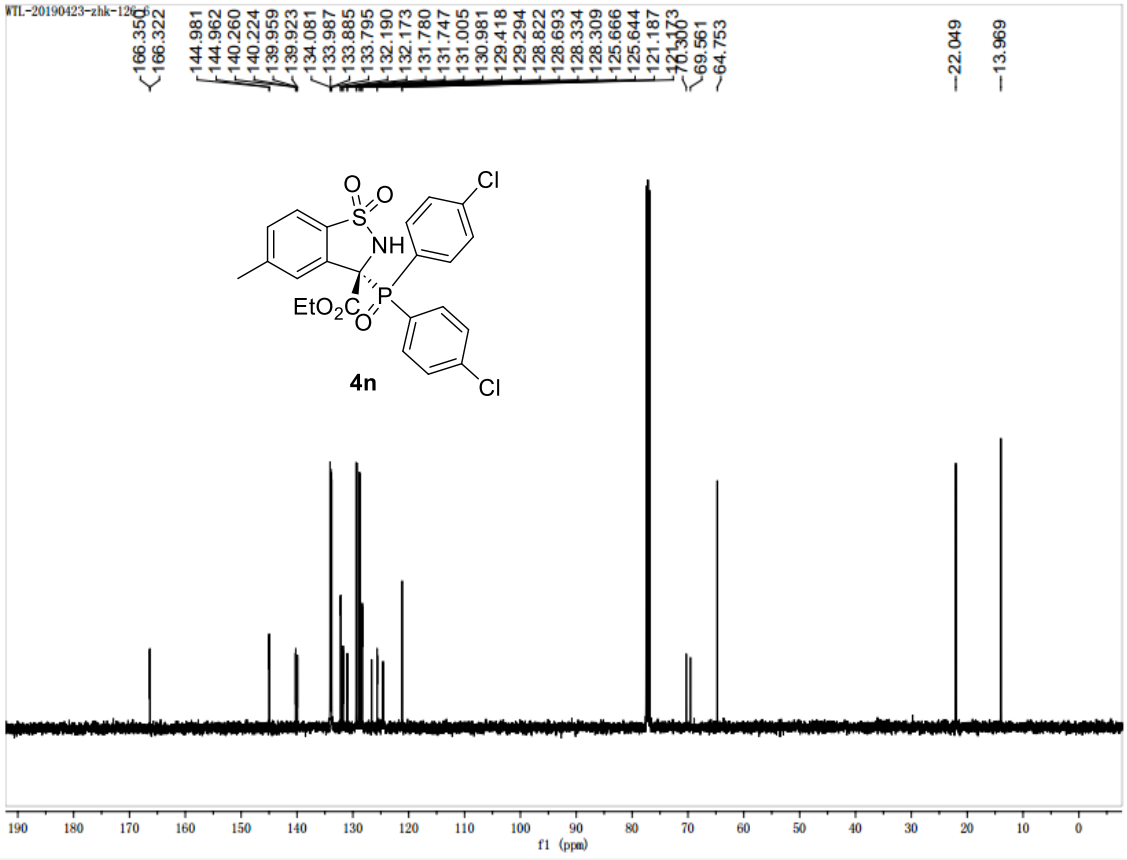

WTL-20190419-zhk-r126-1
36.350
O
O
S
NH
EtO2C
P
O
4l
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

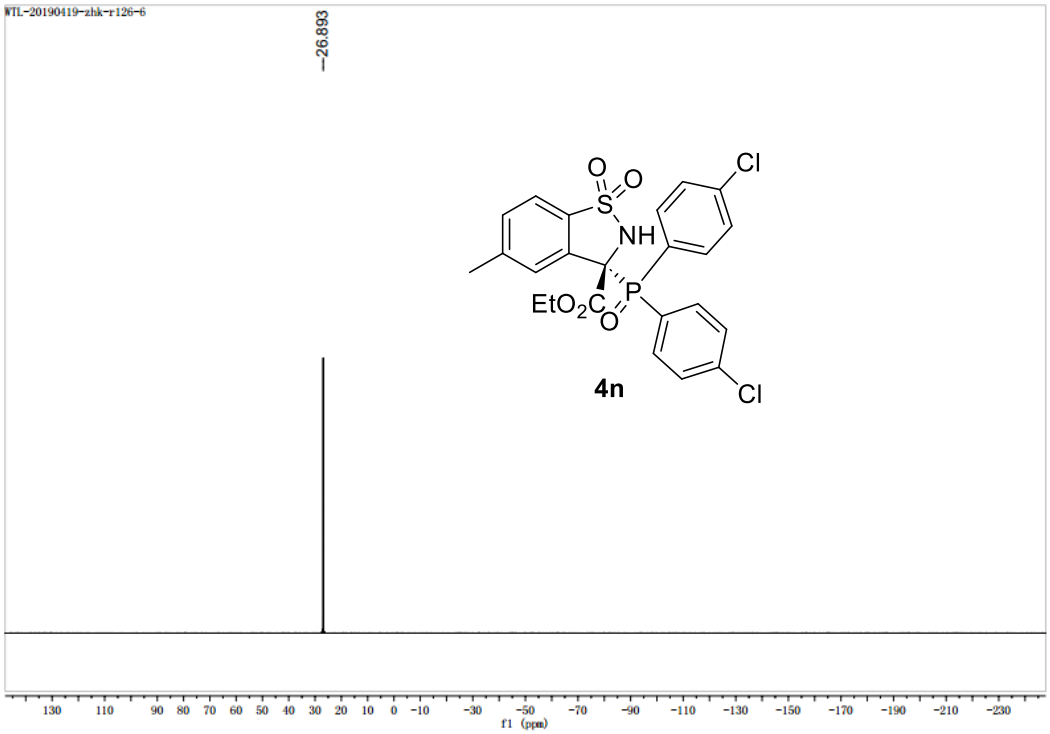

8.145 8.138 8.129 8.123 8.117 8.112 8.107 8.104 8.095 8.087 8.082 7.632 7.627 7.619 7.610 7.605 7.596 7.591 7.583 7.575 7.569 7.503 7.483 7.397 7.377 7.292 7.286 7.281 7.270 7.260 7.249 7.242 7.003 6.997 6.992 6.982 6.975 6.965 6.960 6.953 5.948 5.937 4.285 4.276 4.267 4.258 4.250 4.241 4.223 4.215 4.206 4.197 4.188 4.179 2.525 1.190 1.172 1.154
O
O
S
NH
EtO2C
P
O
F
F
4m
3.00 2.03 1.01 1.03 3.57 2.01 1.00 2.06 2.99 3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

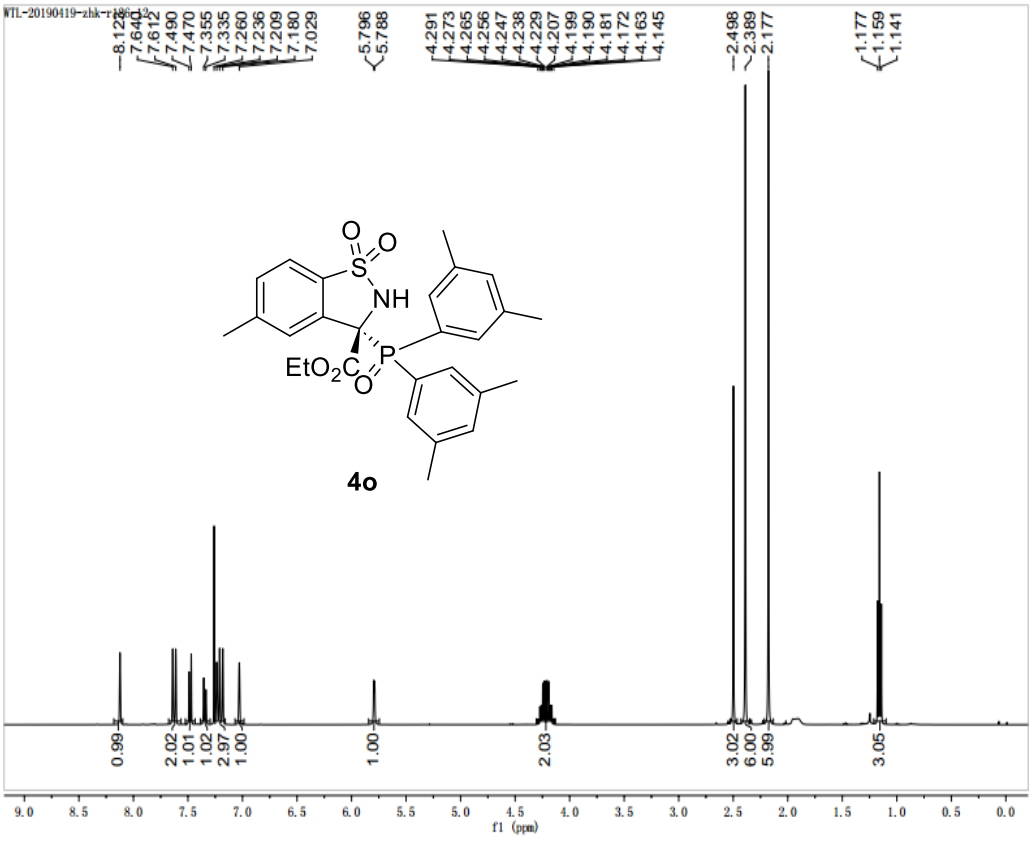

167.251
167.216
167.118
167.083
166.542
166.515
164.706
164.671
164.579
164.544
144.985
144.965
135.457
135.361
135.263
135.168
135.076
132.175
132.156
131.806
131.254
128.392
128.366
121.190
121.174
116.697
116.569
116.484
116.355
116.073
115.938
115.859
70.516
69.774
64.780
22.091
14.006
O
O
S
NH
P
EtO2C
O
F
F
4m
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

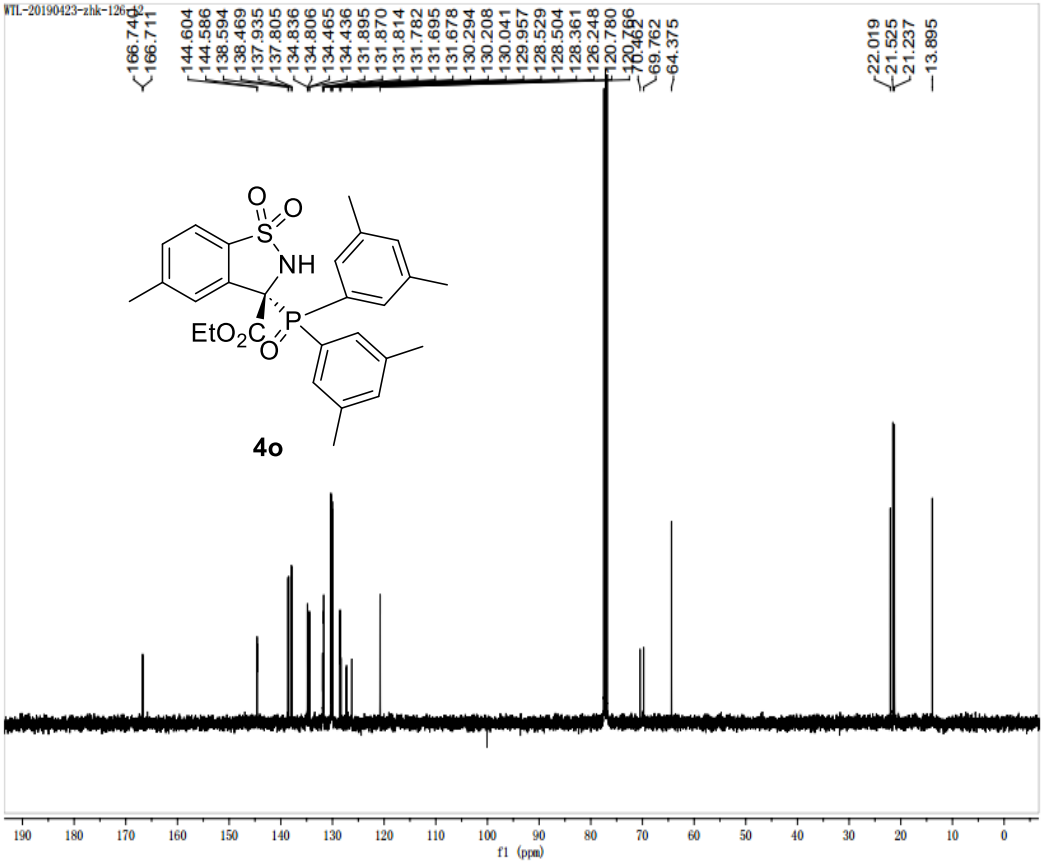

WTL-20190423-zhk-126-6
26.921
O
O
S
NH
P
EtO2C
O
F
F
4m
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
f1 (ppm)

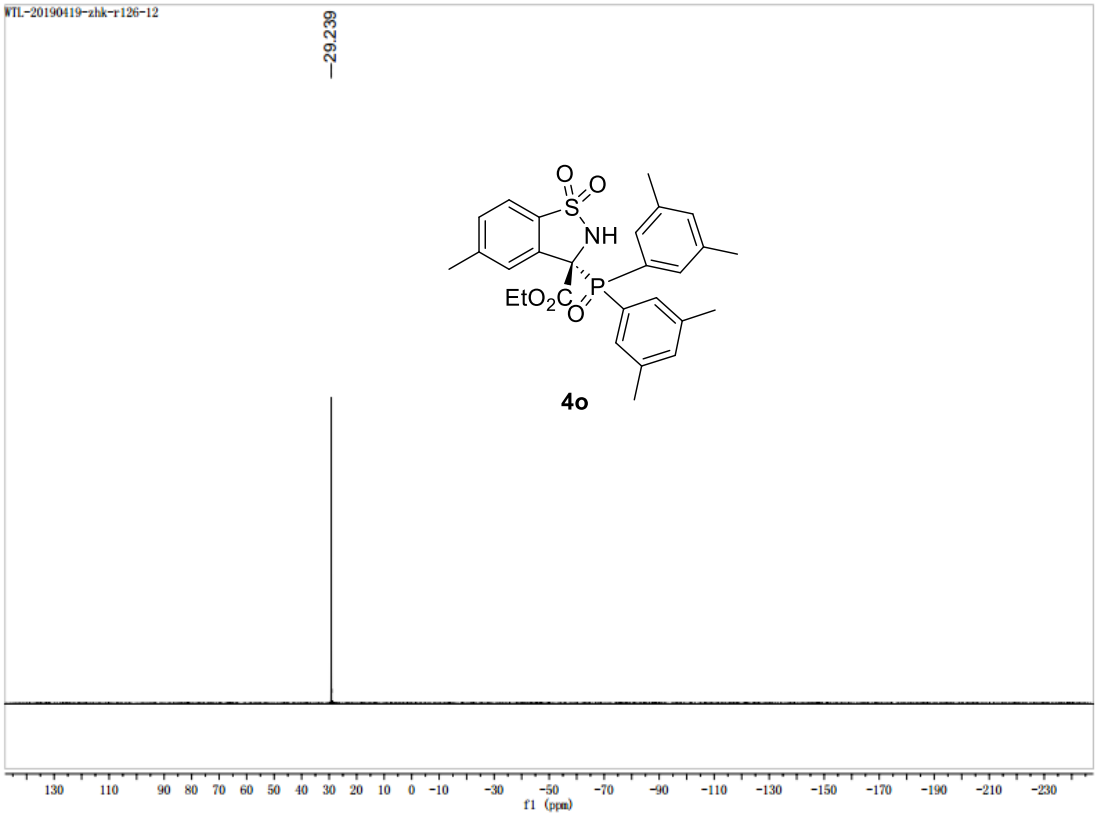

8.114
8.035
8.026
8.016
8.012
8.007
8.003
7.990
7.986
7.981
7.542
7.536
7.530
7.515
7.508
7.506
7.486
7.274
7.267
7.260
6.050
4.290
4.272
4.263
4.254
4.245
4.232
4.228
4.215
4.210
4.197
4.188
4.179
4.170
4.152
2.511
1.186
1.168
1.150
Cl
O
O
S
NH
P
EtO2C
O
Cl
4n
1.00
2.03
5.07
1.03
2.64
1.04
2.05
3.09
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

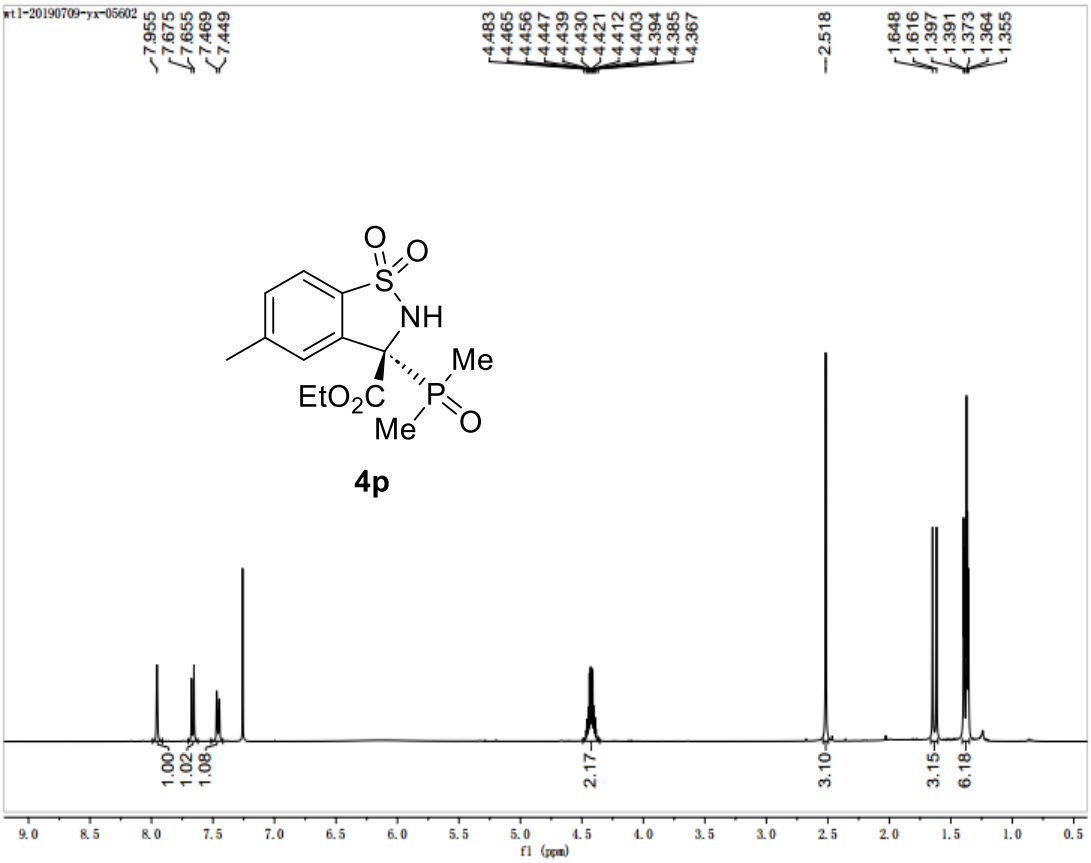

166.350
166.322
144.981
144.962
140.260
140.224
139.959
139.923
134.081
133.987
133.885
133.795
132.190
132.173
131.780
131.747
131.005
130.981
129.418
129.294
128.822
128.693
128.334
128.309
125.666
125.644
121.187
121.173
70.300
69.561
64.753
22.049
13.969
Cl
O
O
S
NH
P
EtO2C
O
Cl
4n
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

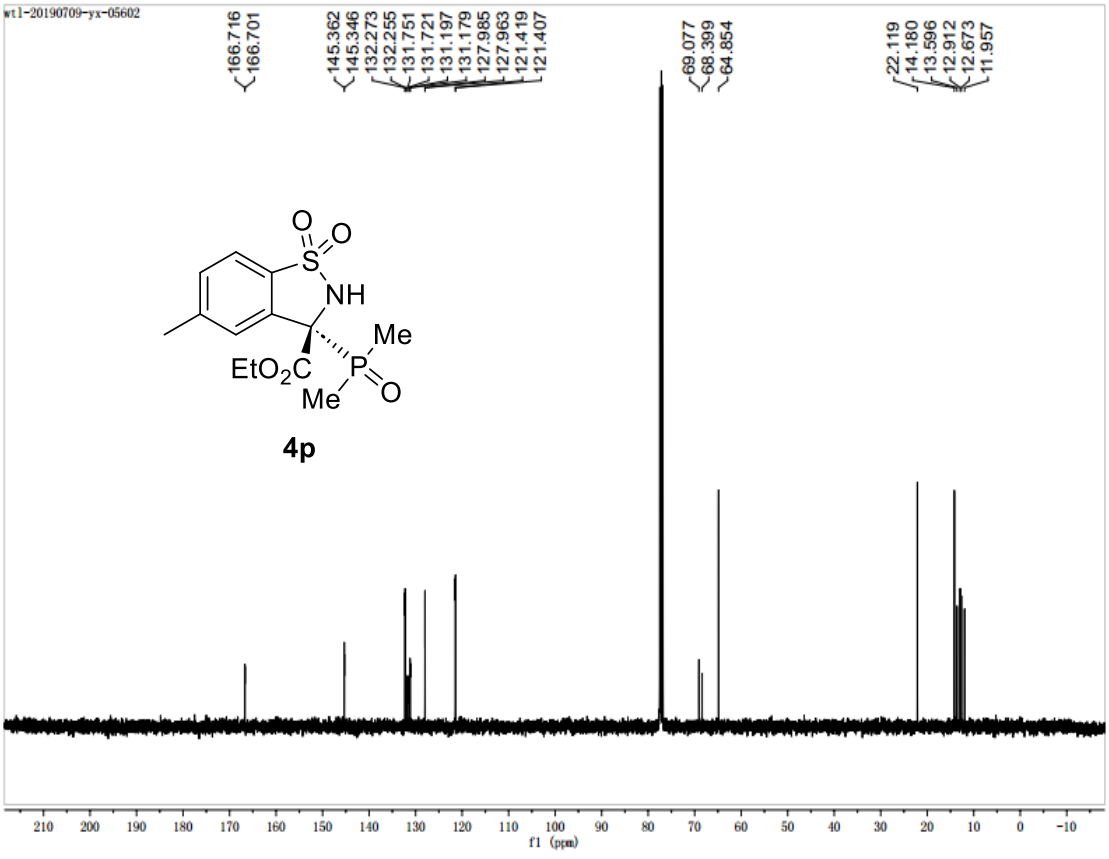

WTL-20190419-zhk-r126-6
26.893
Cl
O
O
S
NH
EtO2C
P
O
Cl
4n
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

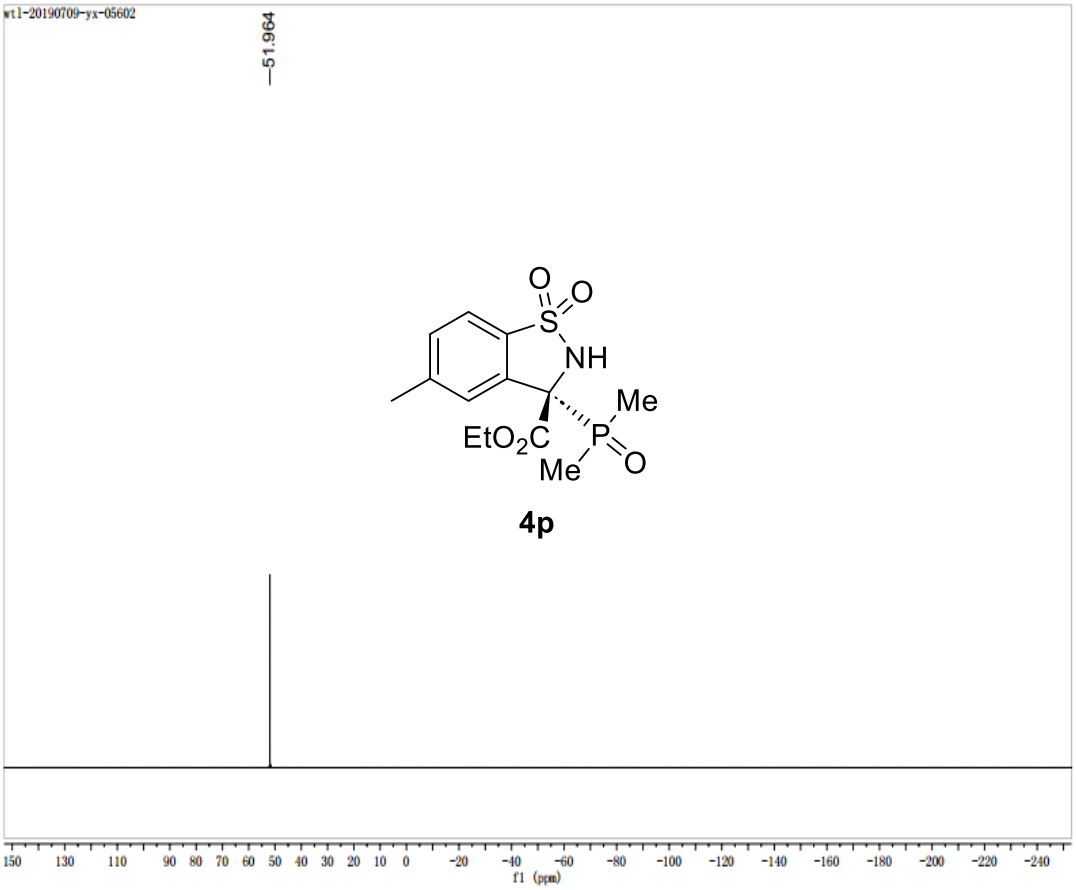

8.122
7.642
7.612
7.490
7.470
7.355
7.335
7.260
7.236
7.209
7.180
7.029
5.796
5.788
4.291
4.273
4.265
4.256
4.247
4.238
4.229
4.207
4.199
4.190
4.181
4.172
4.163
4.145
2.498
2.389
2.177
1.177
1.159
1.141
O
O
S
NH
EtO2C
P
O
4o
0.99
2.02
1.01
1.02
2.97
1.00
1.00
2.03
3.02
6.00
5.99
3.05
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

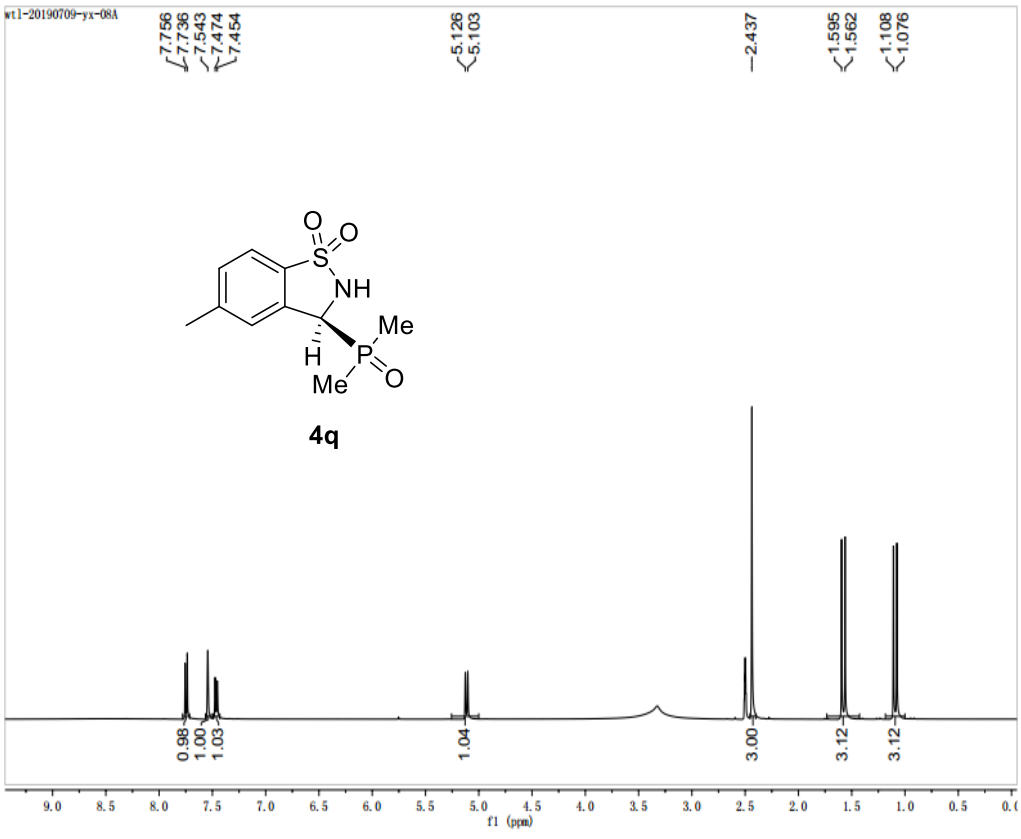

WTL-20190423-zhk-126-13
166.742
166.711
144.604
144.586
138.594
138.469
137.935
137.805
134.836
134.806
134.465
134.436
131.895
131.870
131.814
131.782
131.695
131.678
130.294
130.208
130.041
129.957
128.529
128.504
128.361
126.248
120.780
120.766
70.462
69.762
64.375
22.019
21.525
21.237
13.895
O
O
S
NH
EtO2C
P
O
4o
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

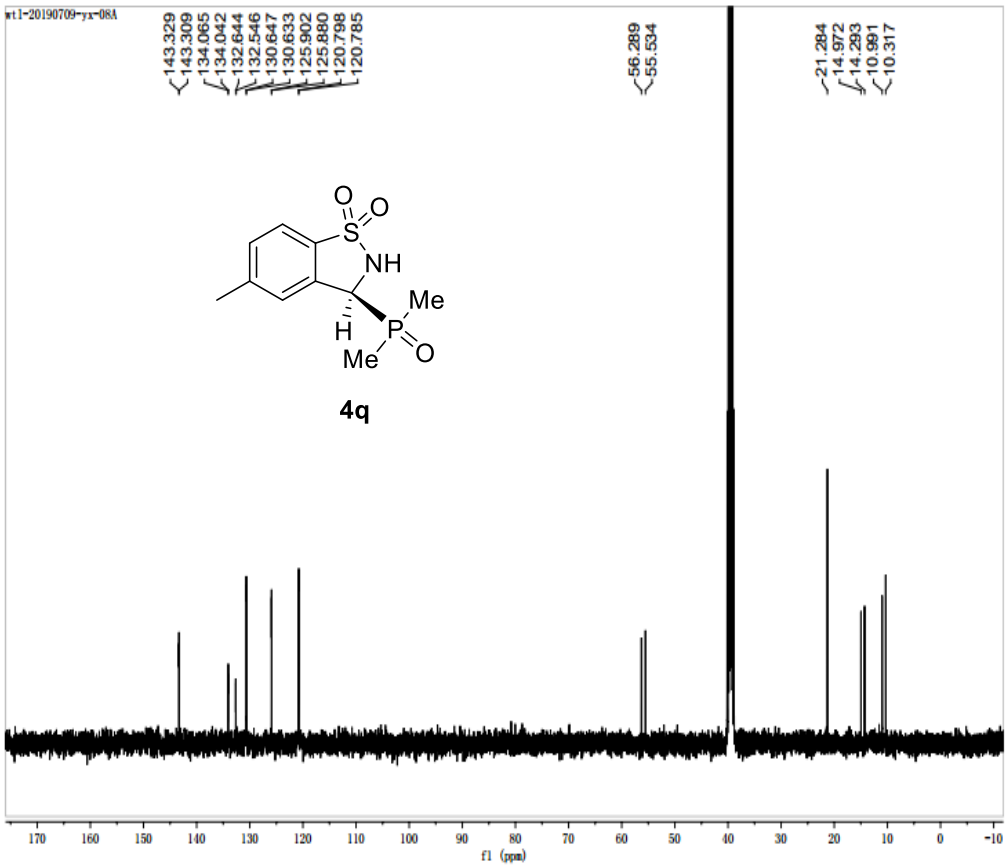

WTL-20190419-zhk-r126-12
29.239
O
O
S
NH
EtO2C
P
O
4o
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

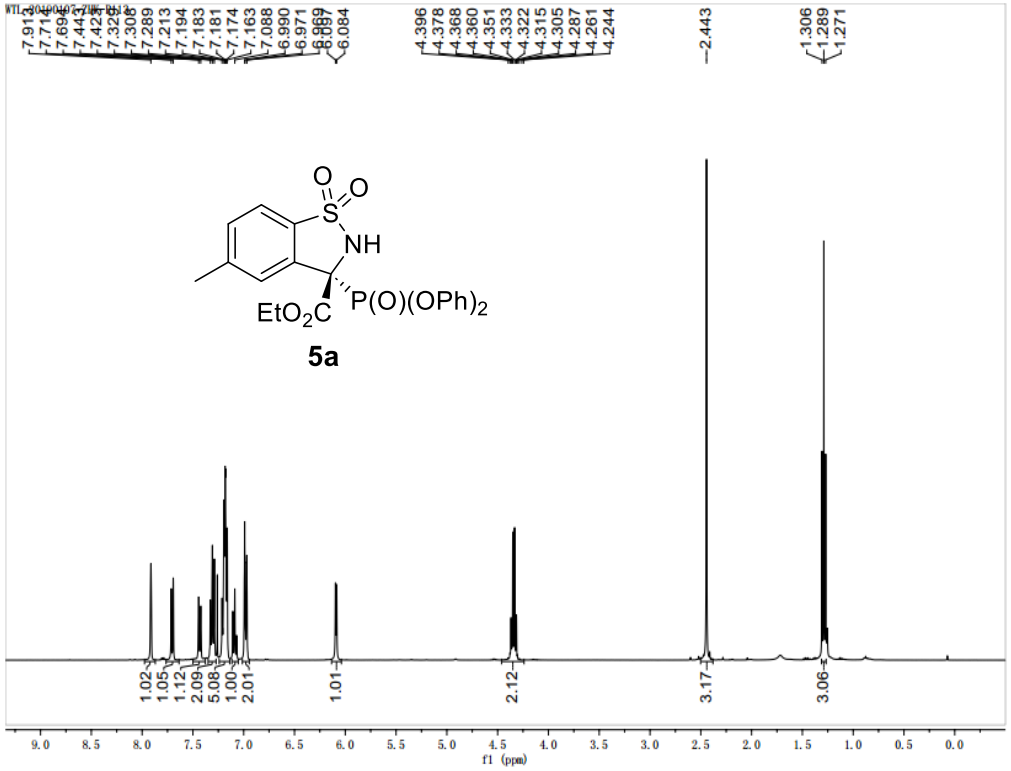

wtl-20190709-yx-05602
7.955
7.675
7.655
7.469
7.449
4.483
4.465
4.456
4.447
4.439
4.430
4.421
4.412
4.403
4.394
4.385
4.367
2.518
1.648
1.616
1.397
1.391
1.373
1.364
1.355
O
O
S
NH
Me
EtO2C
P
O
Me
4p
1.00
1.02
1.08
2.17
3.10
3.15
6.18
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

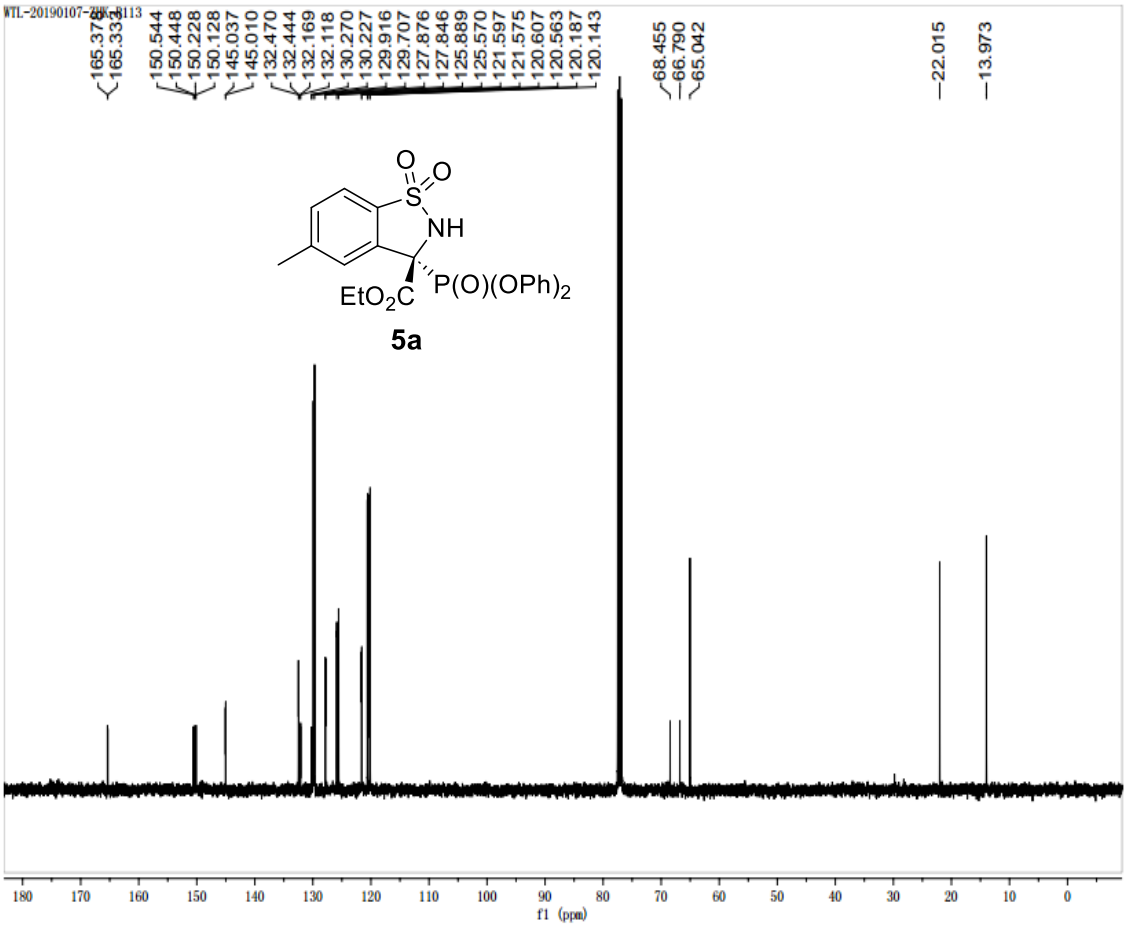

wtl-20190709-yx-05602
166.716
166.701
145.362
145.346
132.273
132.255
131.751
131.721
131.197
131.179
127.985
127.963
121.419
121.407
69.077
68.399
64.854
22.119
14.180
13.596
12.912
12.673
11.957
O
O
S
NH
Me
EtO2C
P
O
Me
4p
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

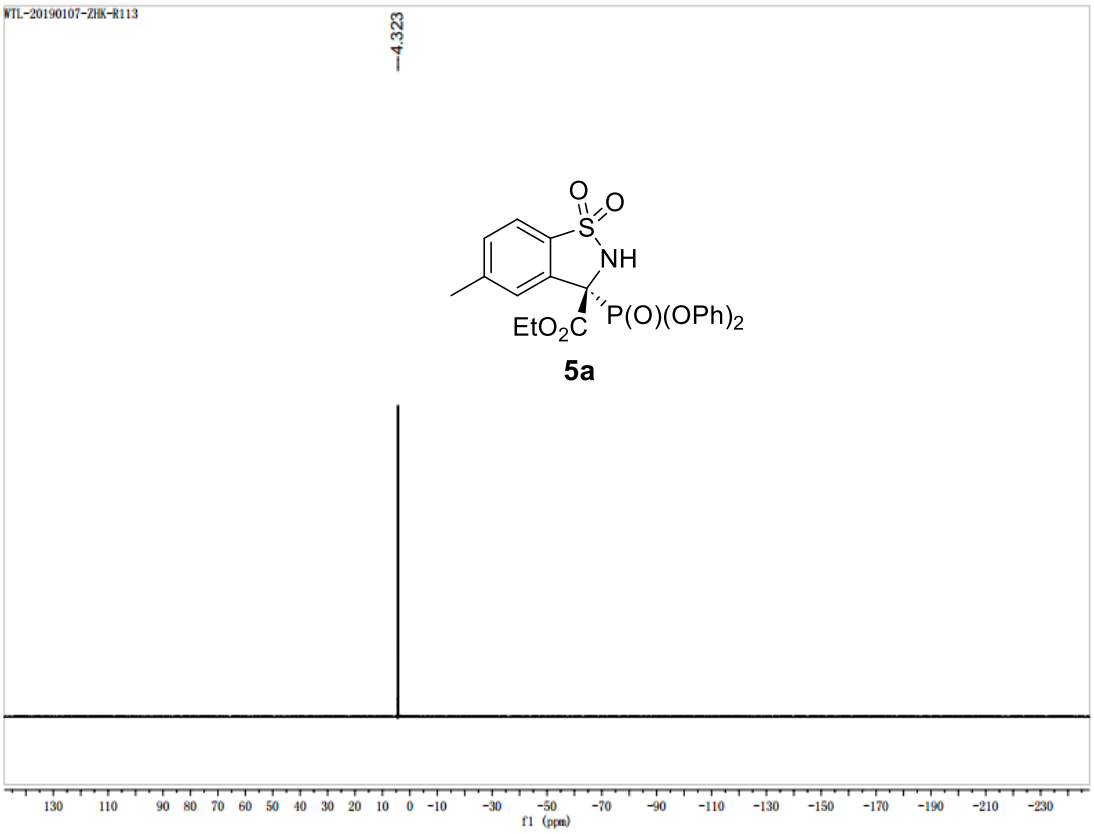

wt1-20190709-yx-05602
51.964
O
O
S
NH
Me
EtO2C
P
O
Me
4p
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

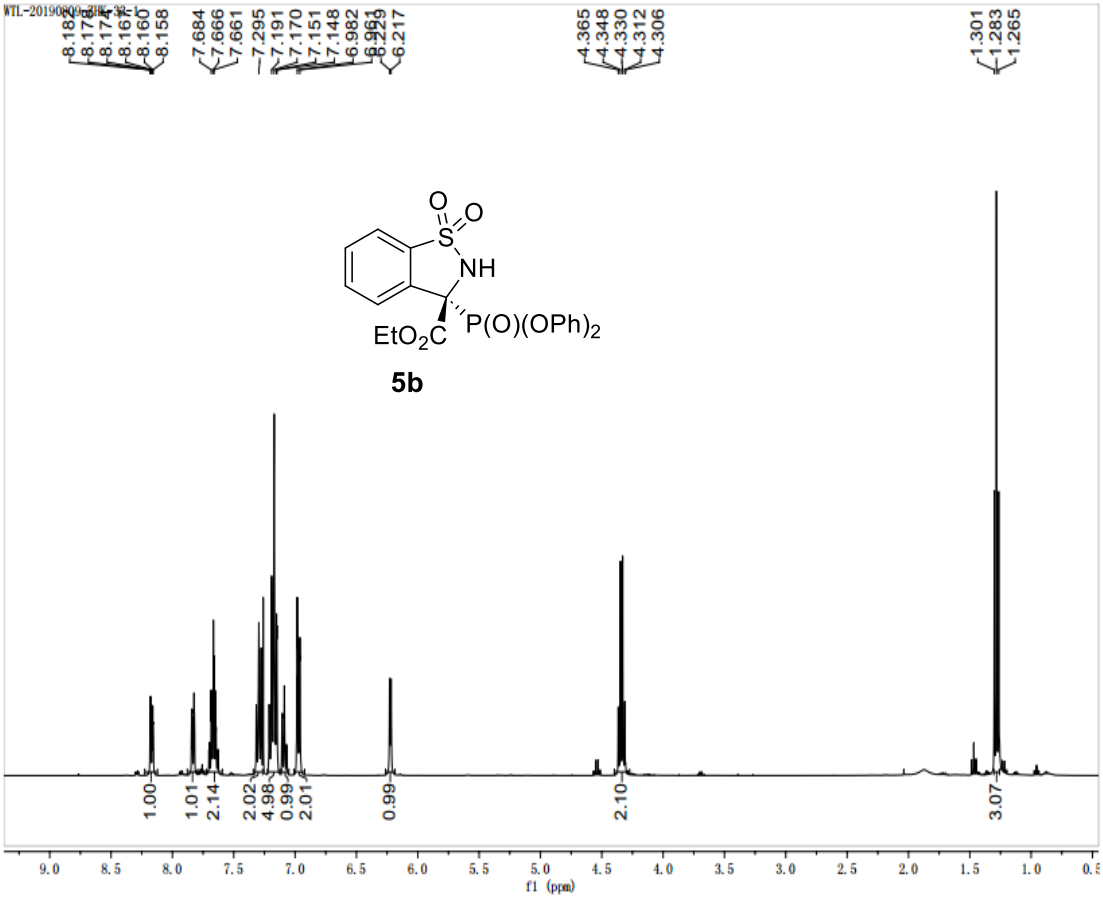

wt1-20190709-yx-08A
7.756
7.736
7.543
7.474
7.454
5.126
5.103
2.437
1.595
1.562
1.108
1.076
O
O
S
NH
Me
H
P
O
Me
4q
0.98
1.00
1.03
1.04
3.00
3.12
3.12
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

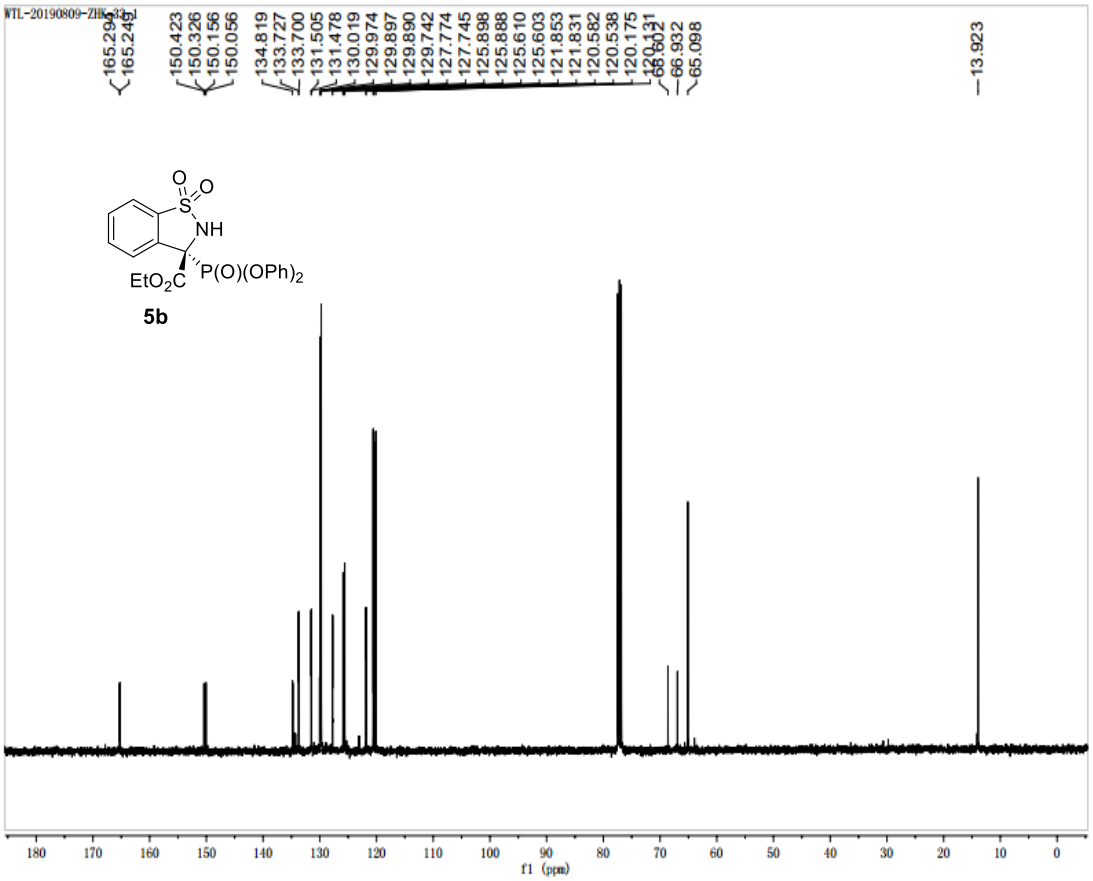

wtl-20190709-yx-08A
143.329
143.309
134.065
134.042
132.644
132.546
130.647
130.633
125.902
125.880
120.798
120.785
56.289
55.534
21.284
14.972
14.293
10.991
10.317
O
O
S
NH
Me
H
P
O
Me
4q
f1 (ppm)

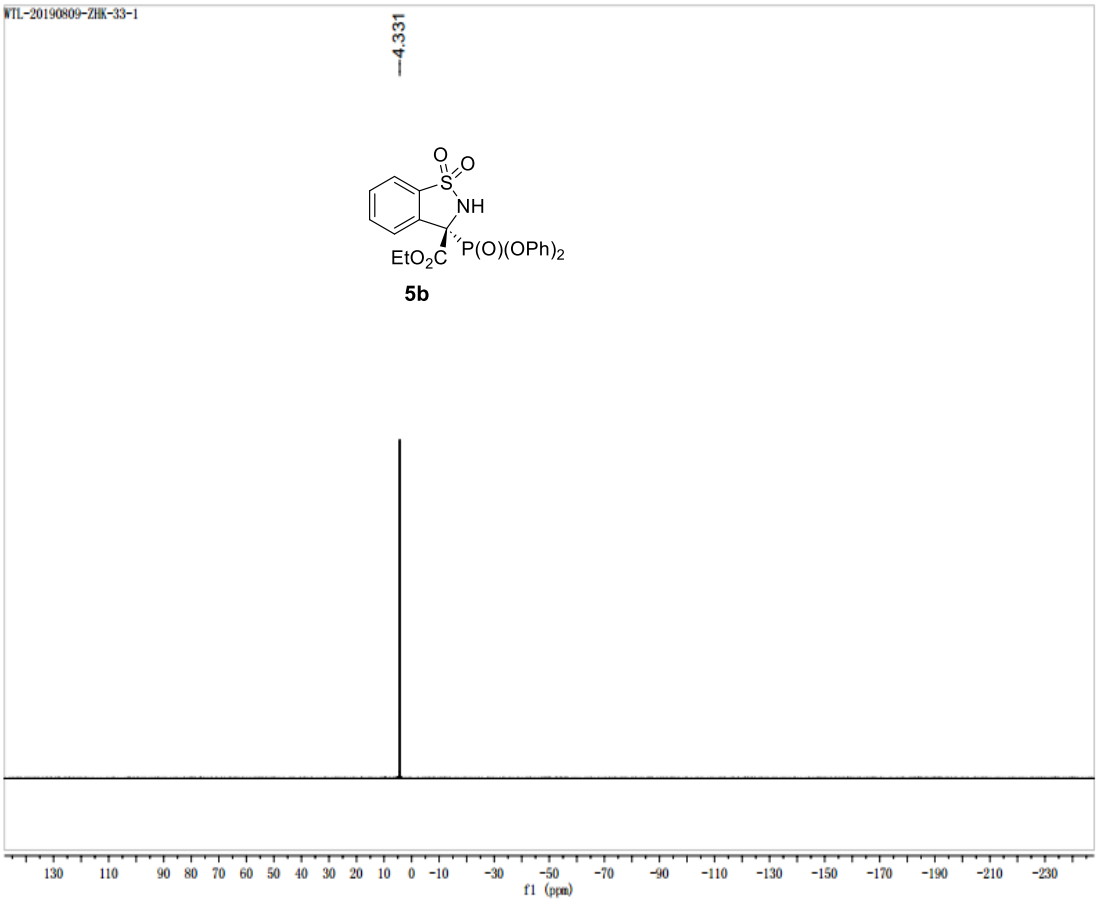

7.912
7.714
7.694
7.443
7.423
7.326
7.308
7.289
7.213
7.194
7.183
7.181
7.174
7.163
7.088
6.990
6.971
6.097
6.084
4.396
4.378
4.368
4.360
4.351
4.333
4.322
4.315
4.305
4.287
4.261
4.244
2.443
1.306
1.289
1.271
O
O
S
NH
EtO2C
P(O)(OPh)2
5a
1.02
1.05
1.12
2.09
5.08
1.00
2.01
1.01
2.12
3.17
3.06
f1 (ppm)


WTL-20190107-ZHK-R113
165.376
165.331
150.544
150.448
150.228
150.128
145.037
145.010
132.470
132.444
132.169
132.118
130.270
130.227
129.916
129.707
127.876
127.846
125.889
125.570
121.597
121.575
120.607
120.563
120.187
120.143
68.455
66.790
65.042
22.015
13.973
O
O
S
NH
EtO2C
P(O)(OPh)2
5a
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

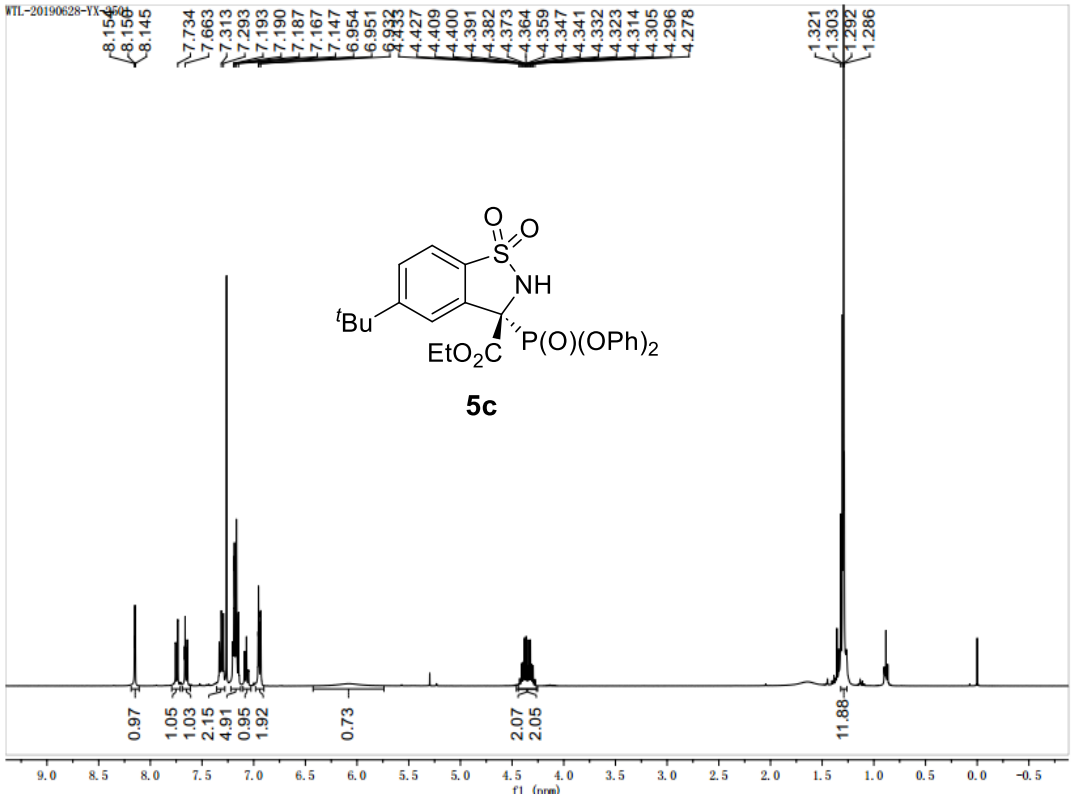

WTL-20190107-ZHK-R113
4.323
O
O
S
NH
EtO2C
P(O)(OPh)2
5a
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


8.182
8.174
8.167
8.160
8.158
7.684
7.666
7.661
7.295
7.191
7.170
7.151
7.148
6.982
6.961
6.217
4.365
4.348
4.330
4.312
4.306
1.301
1.283
1.265
O
O
S
NH
EtO2C
P(O)(OPh)2
5b
1.00
1.01
2.14
2.02
4.98
0.99
2.01
0.99
2.10
3.07
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

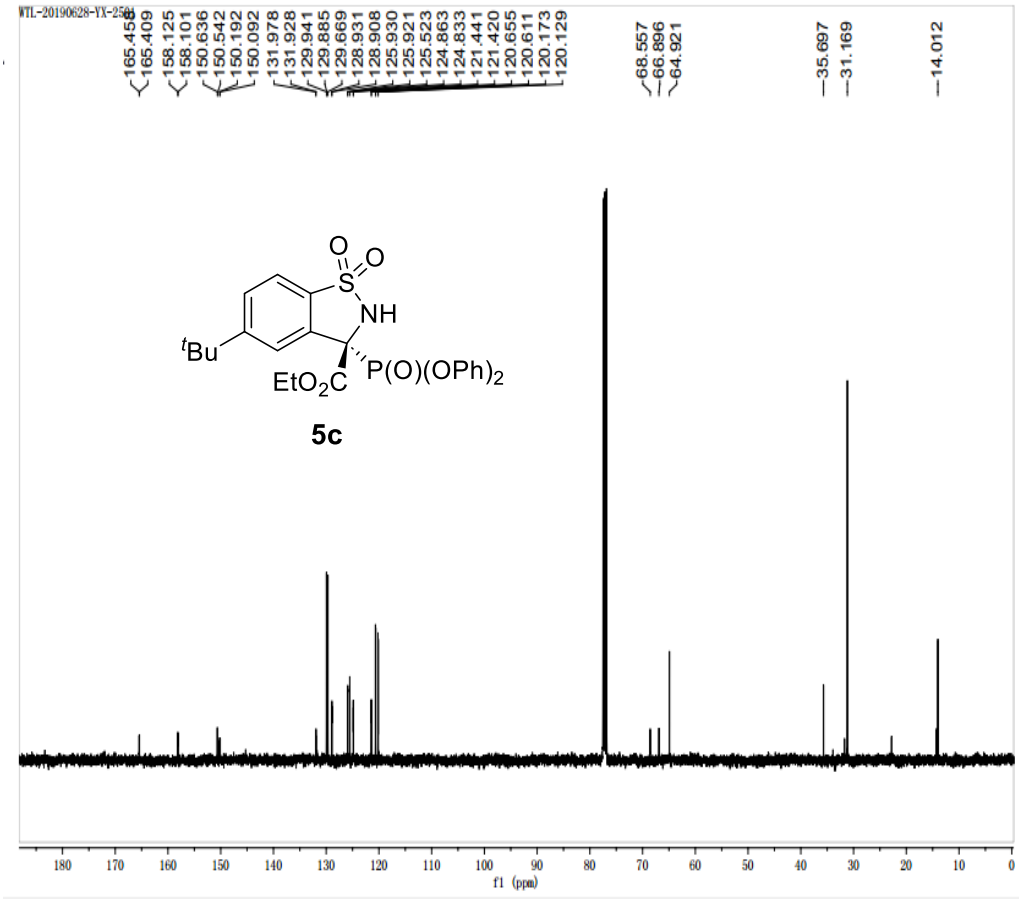

165.296
165.240
150.423
150.326
150.156
150.056
134.819
133.727
133.700
131.505
131.478
130.019
129.974
129.897
129.890
129.742
127.774
127.745
125.898
125.888
125.610
125.603
121.853
121.831
120.582
120.538
120.175
120.131
66.932
65.098
13.923
O
O
S
NH
EtO2C
P(O)(OPh)2
5b
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

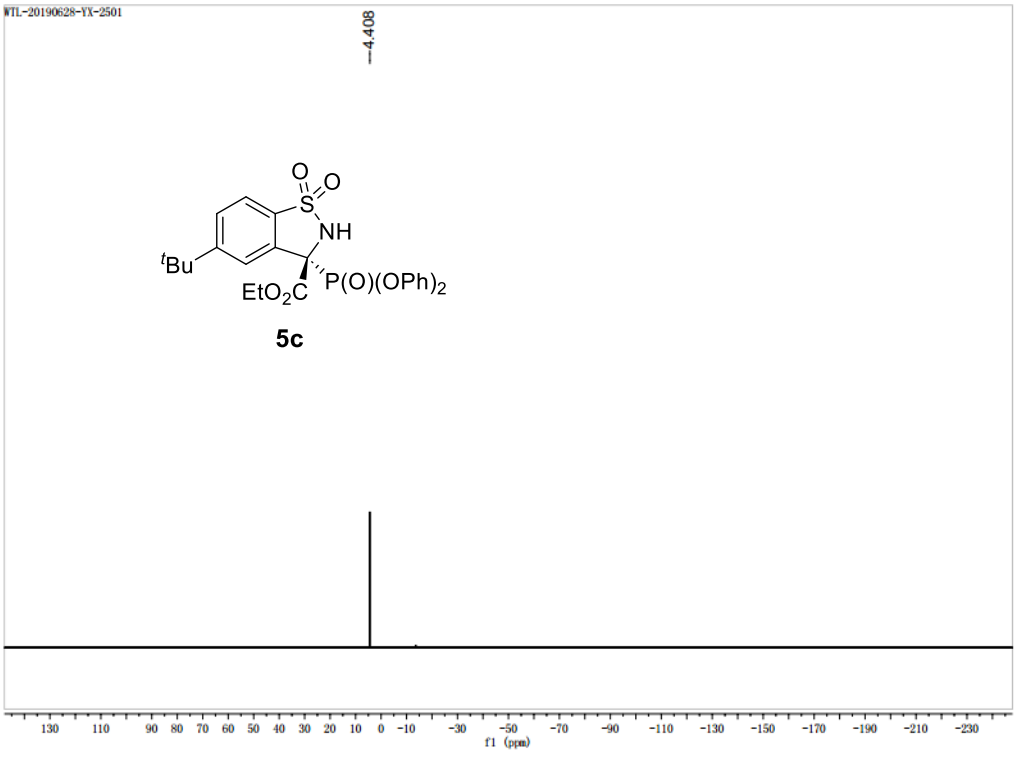

WTL-20190809-ZHK-33-1
4.331
NH
EtO2C
P(O)(OPh)2
f1 (ppm)

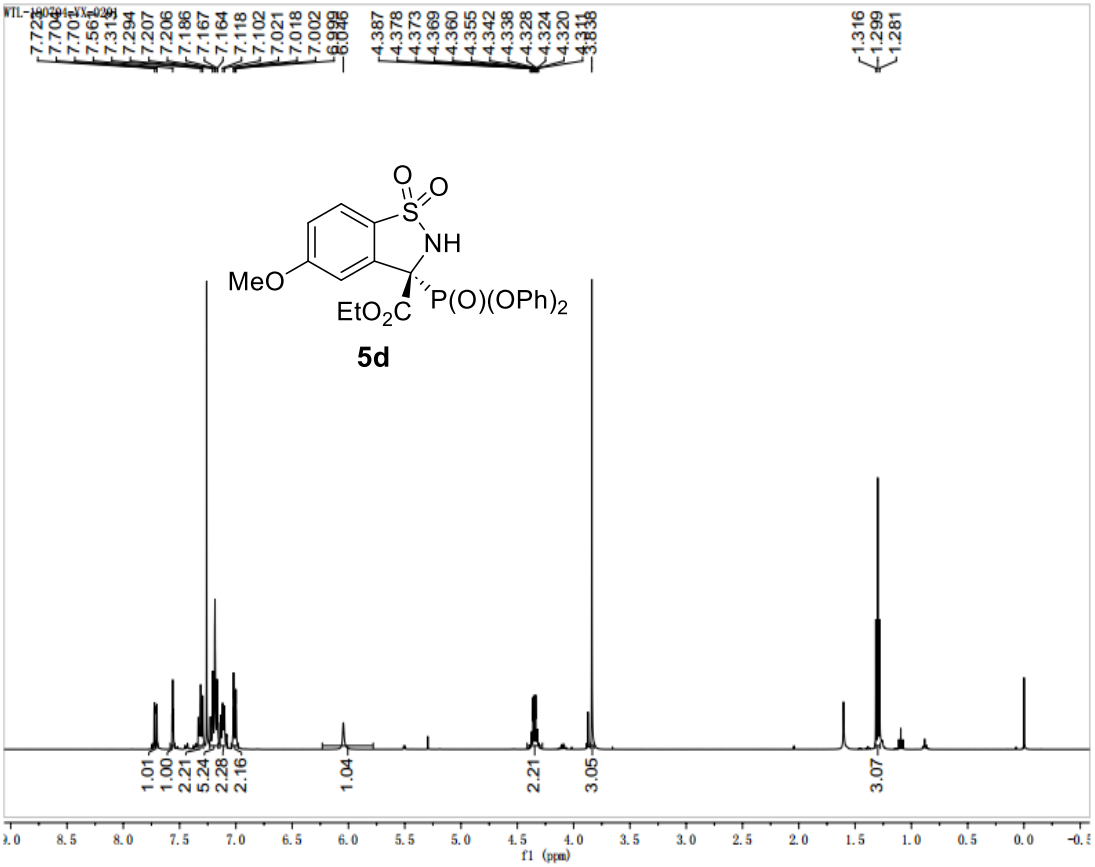
5b

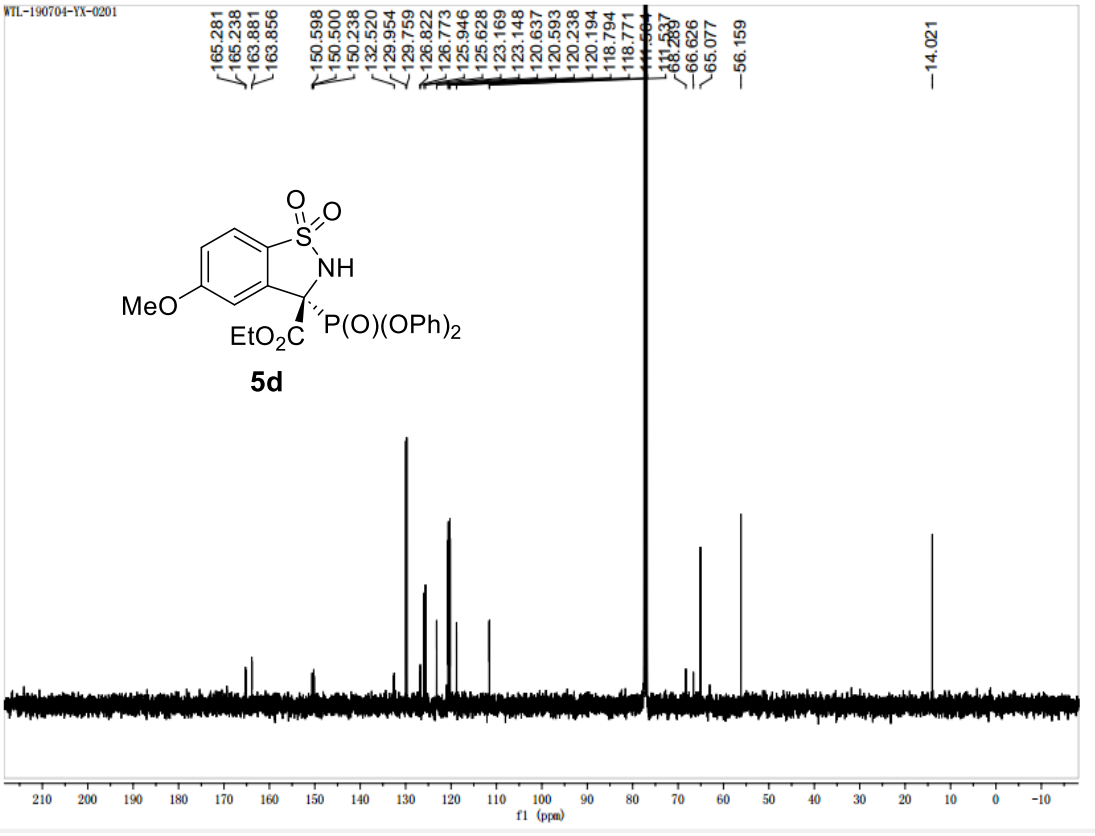

8.154
8.145
7.734
7.663
7.313
7.293
7.193
7.190
7.187
7.167
7.147
6.954
6.951
6.933
4.433
4.427
4.409
4.400
4.391
4.382
4.373
4.364
4.359
4.347
4.341
4.332
4.323
4.314
4.305
4.296
4.278
1.321
1.303
1.292
1.286
NH
tBu
EtO2C
P(O)(OPh)2
0.97
1.05
1.03
2.15
4.91
0.95
1.92
0.73
2.07
2.05
11.88
f1 (ppm)

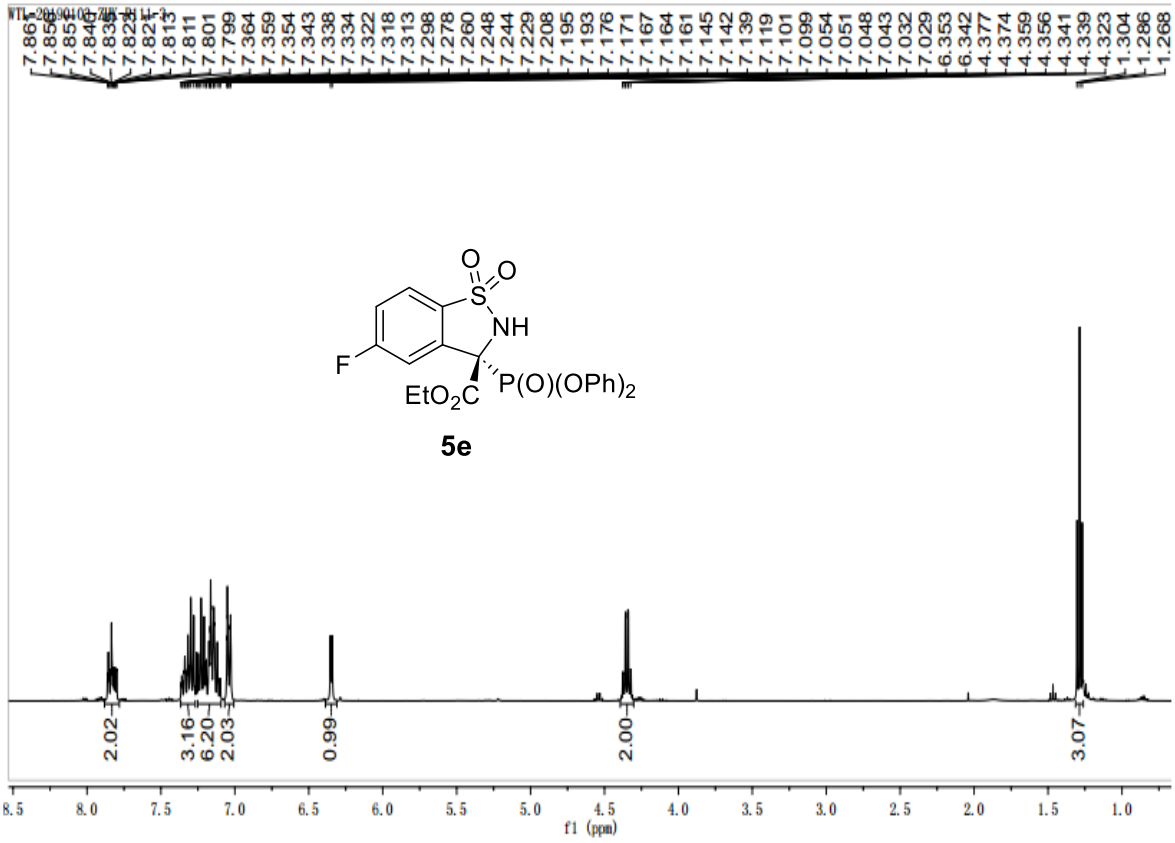
5c


WTL-20190628-YX-2501
165.458
165.409
158.125
158.101
150.636
150.542
150.192
150.092
131.978
131.928
129.941
129.885
129.669
128.931
128.908
125.930
125.921
125.523
124.863
124.833
121.441
121.420
120.655
120.611
120.173
120.129
68.557
66.896
64.921
35.697
31.169
14.012
O
O
S
NH
tBu
EtO2C
P(O)(OPh)2
5c
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

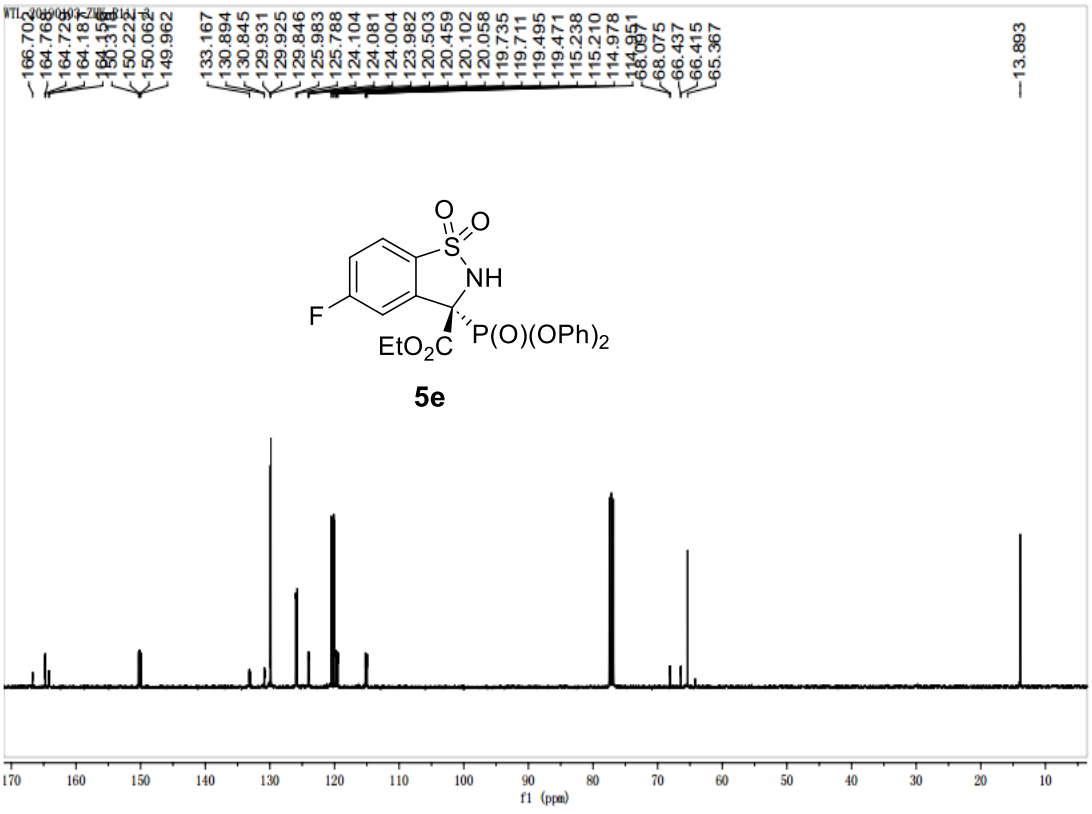

WTL-20190628-YX-2501
4.408
O
O
S
NH
tBu
EtO2C
P(O)(OPh)2
5c
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)


MeO
NH
EtO2C
P(O)(OPh)2
5d
f1 (ppm)

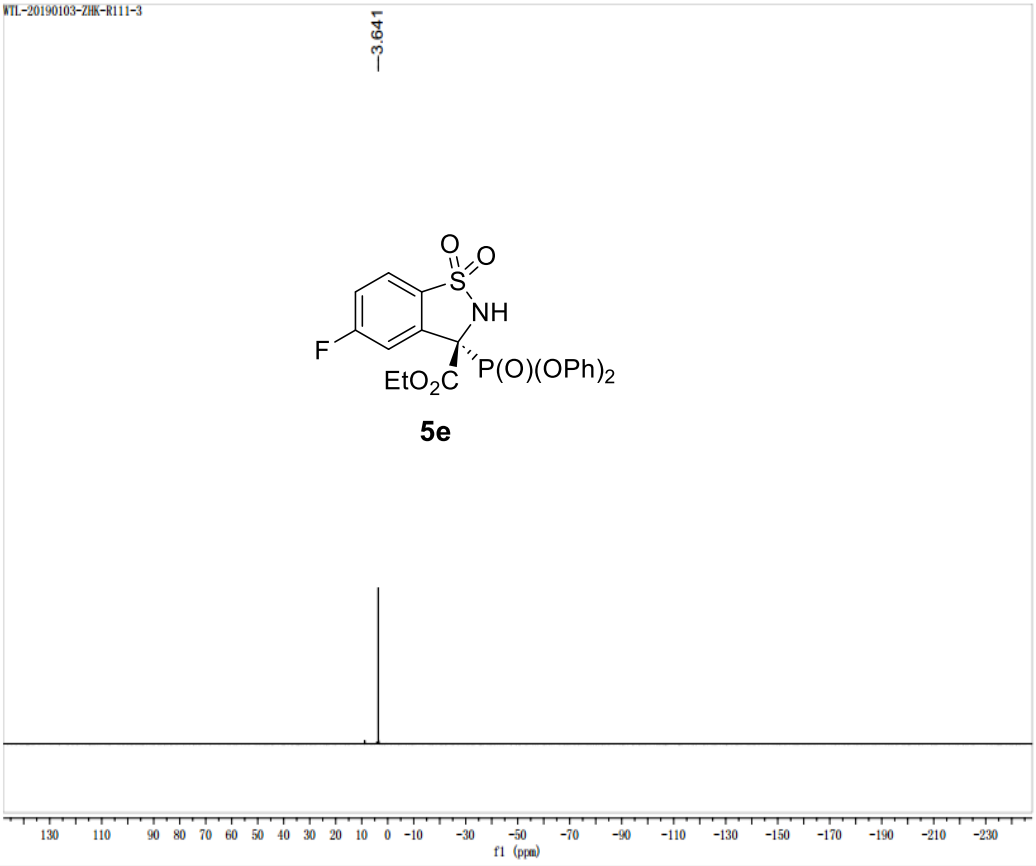

MeO
NH
EtO2C
P(O)(OPh)2
5d
f1 (ppm)


7.861
7.856
7.851
7.840
7.835
7.824
7.813
7.811
7.801
7.799
7.364
7.359
7.354
7.343
7.338
7.334
7.322
7.318
7.313
7.298
7.278
7.260
7.248
7.244
7.229
7.208
7.195
7.193
7.176
7.171
7.167
7.164
7.161
7.145
7.142
7.139
7.119
7.101
7.099
7.054
7.051
7.048
7.043
7.032
7.029
6.353
6.342
4.377
4.374
4.359
4.356
4.341
4.339
4.323
1.304
1.286
1.268
O
O
S
NH
F
EtO2C
P(O)(OPh)2
2.02
3.16
6.20
2.03
0.99
2.00
3.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
f1 (ppm)

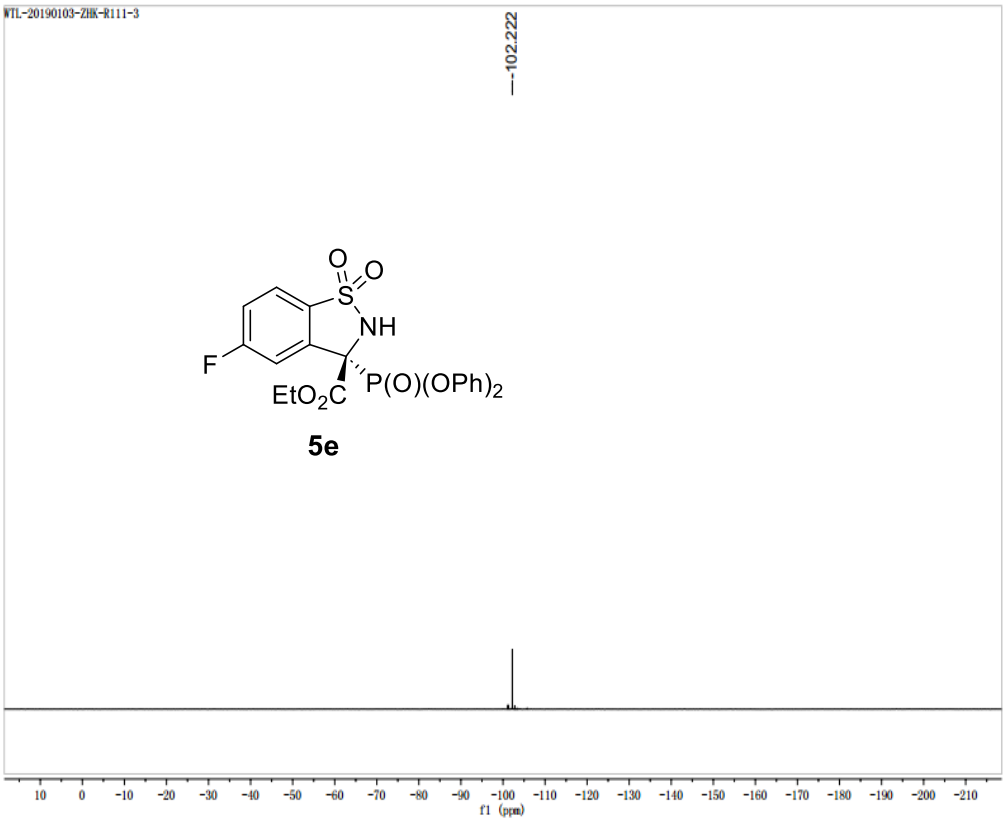
5e


166.702
164.765
164.729
164.187
150.224
150.062
149.962
133.167
130.894
130.845
129.931
129.925
129.846
125.983
125.788
124.104
124.081
124.004
123.982
120.503
120.459
120.102
120.058
119.735
119.711
119.495
119.471
115.238
115.210
114.978
114.951
68.097
68.075
66.437
66.415
65.367
13.893
O
O
S
NH
F
EtO2C
P(O)(OPh)2
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

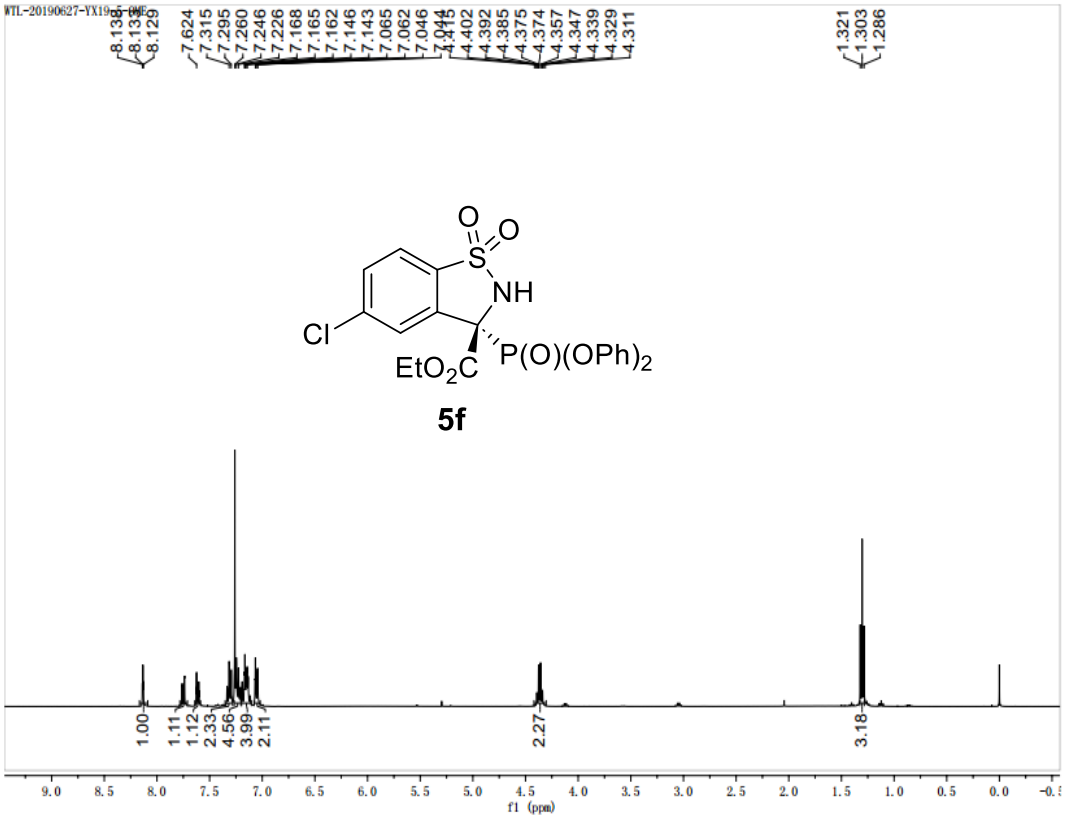
5e

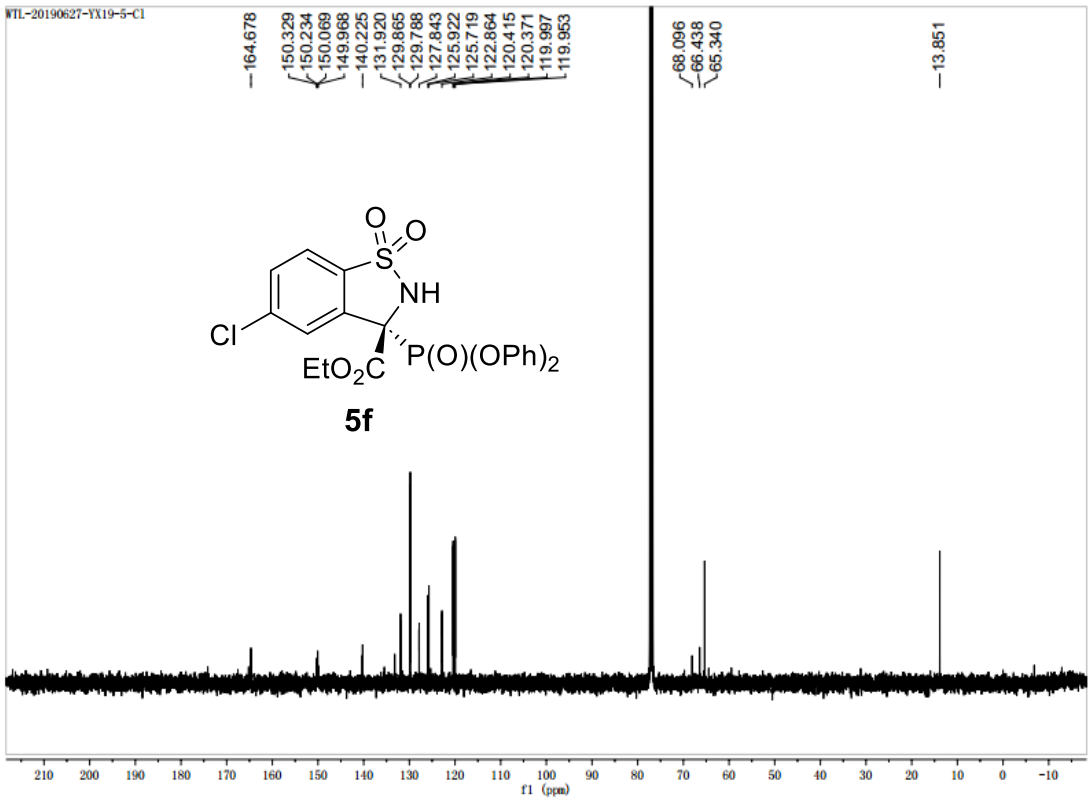

WTL-20190103-ZHK-R111-3
-3.641
O
O
S
NH
F
EtO2C
P(O)(OPh)2
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

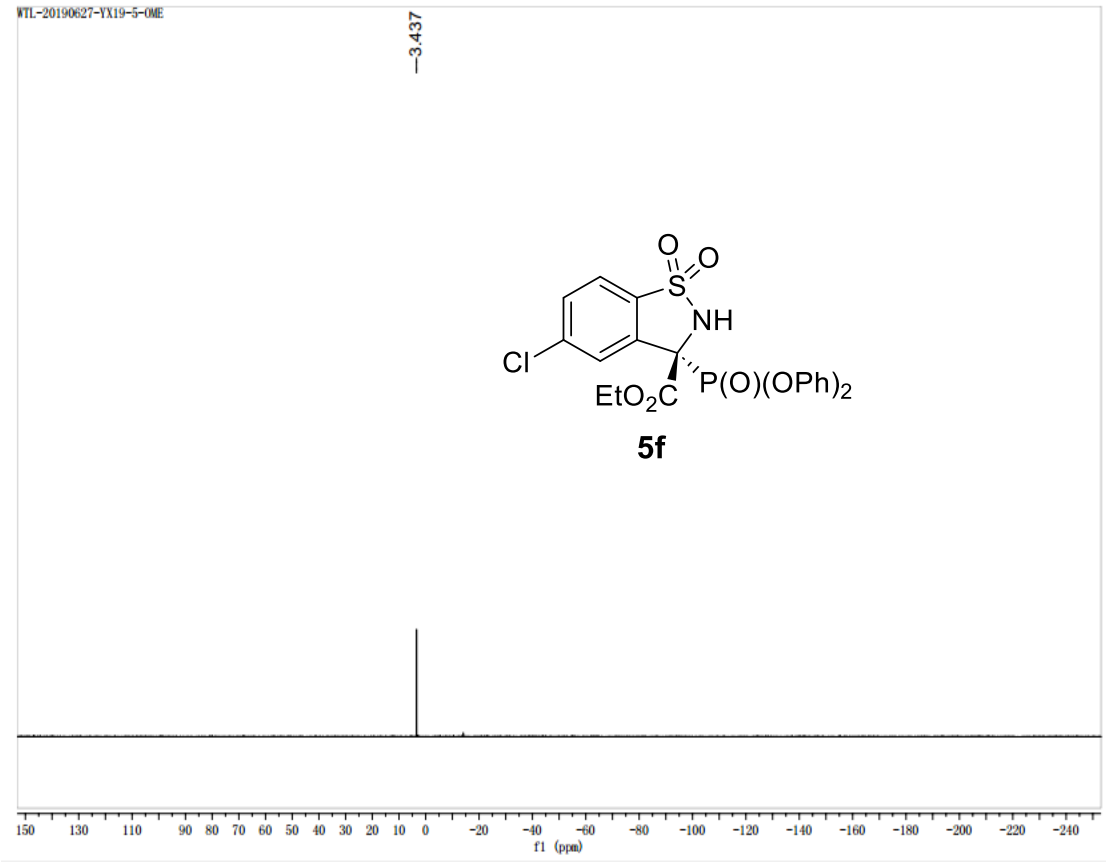
5e

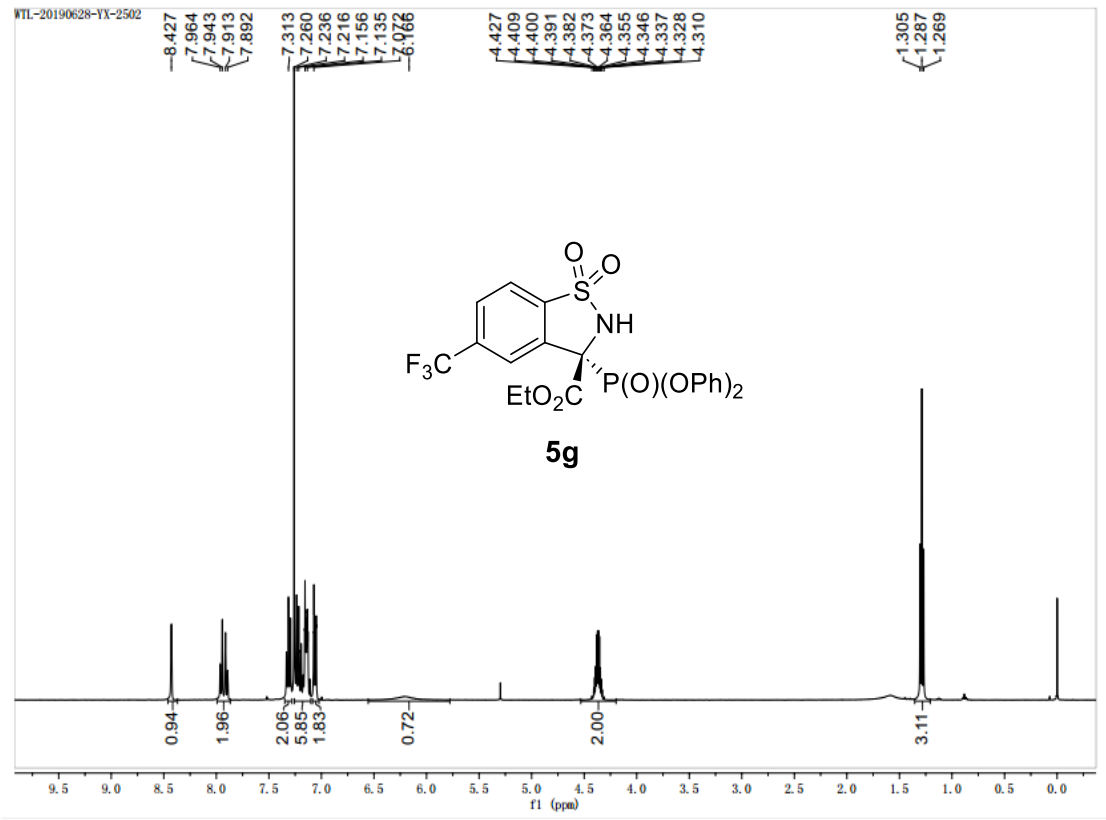

WTL-20190103-ZHK-R111-3
-102.222
O
O
S
NH
F
EtO2C
P(O)(OPh)2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

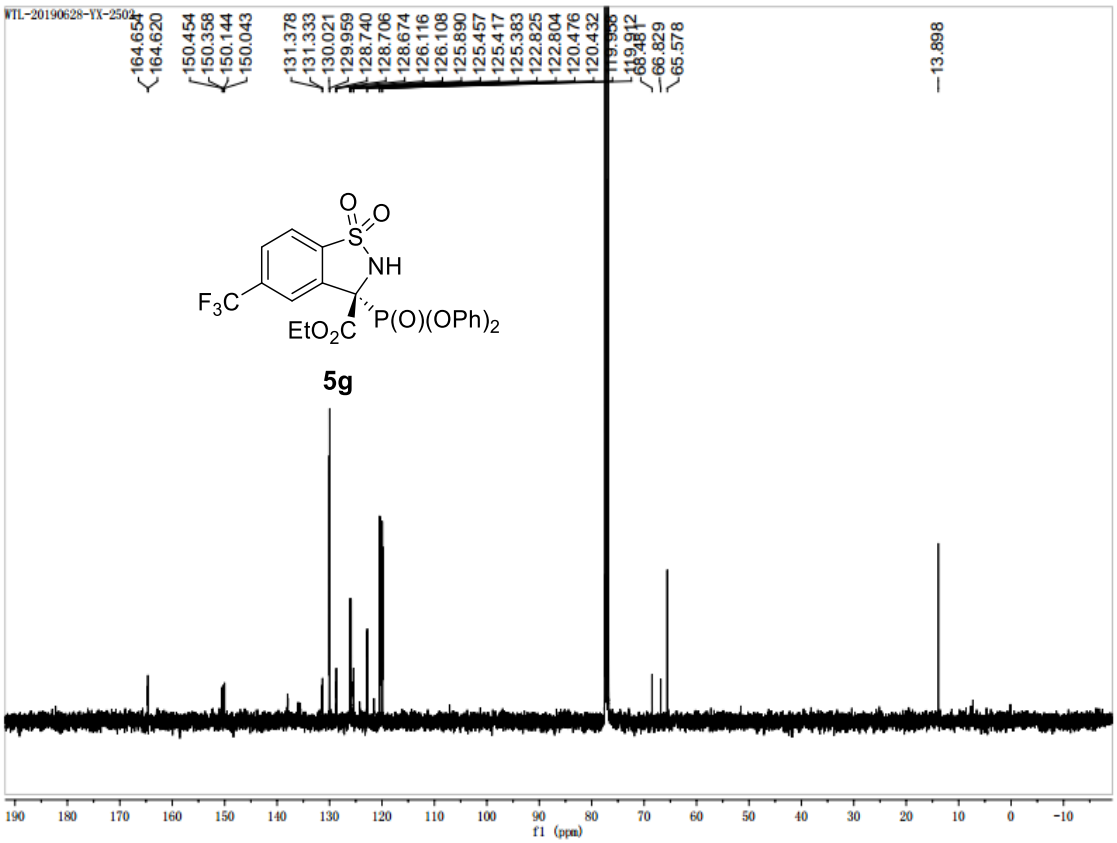
5e

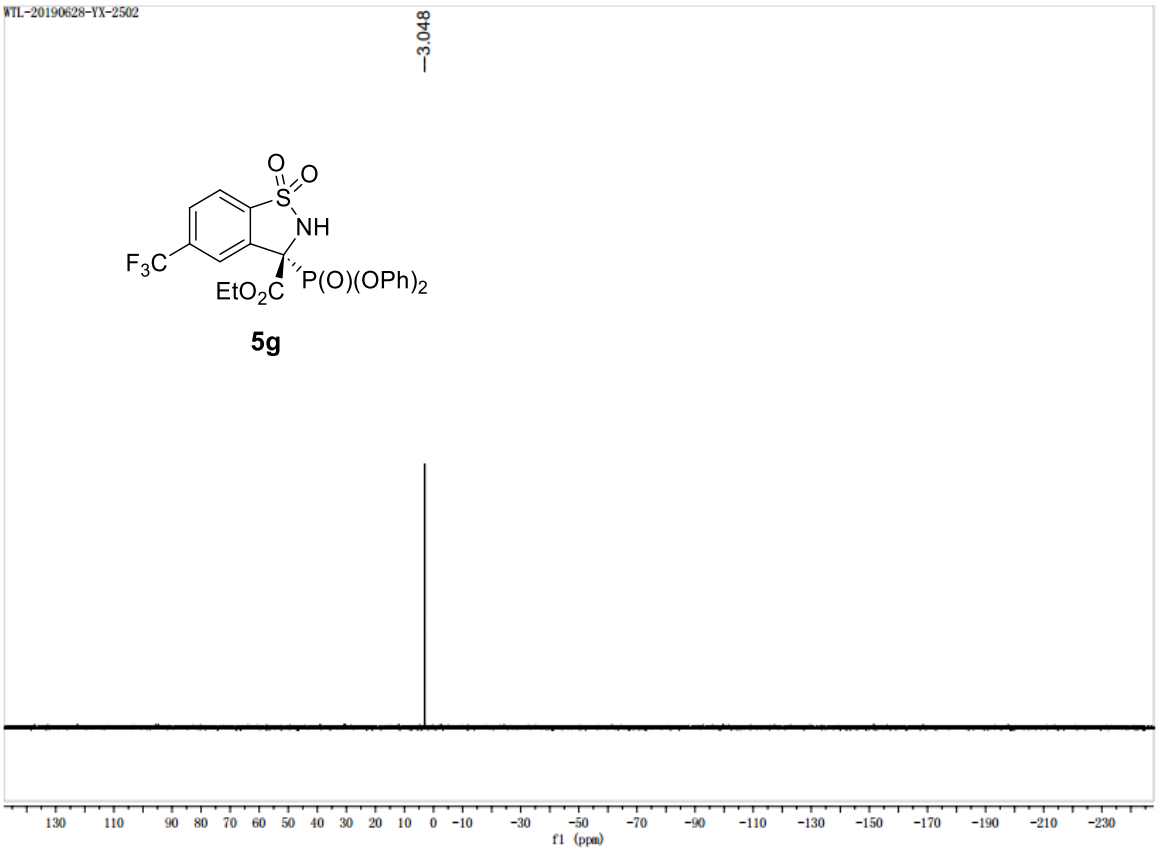

8.138
8.133
8.129
7.624
7.315
7.295
7.260
7.246
7.226
7.168
7.165
7.162
7.146
7.143
7.065
7.062
7.046
4.402
4.392
4.385
4.375
4.374
4.357
4.347
4.339
4.329
4.311
1.321
1.303
1.286
O
O
S
NH
Cl
EtO2C
P(O)(OPh)2
5f
1.00
1.11
1.12
2.33
4.56
3.99
2.11
2.27
3.18
f1 (ppm)

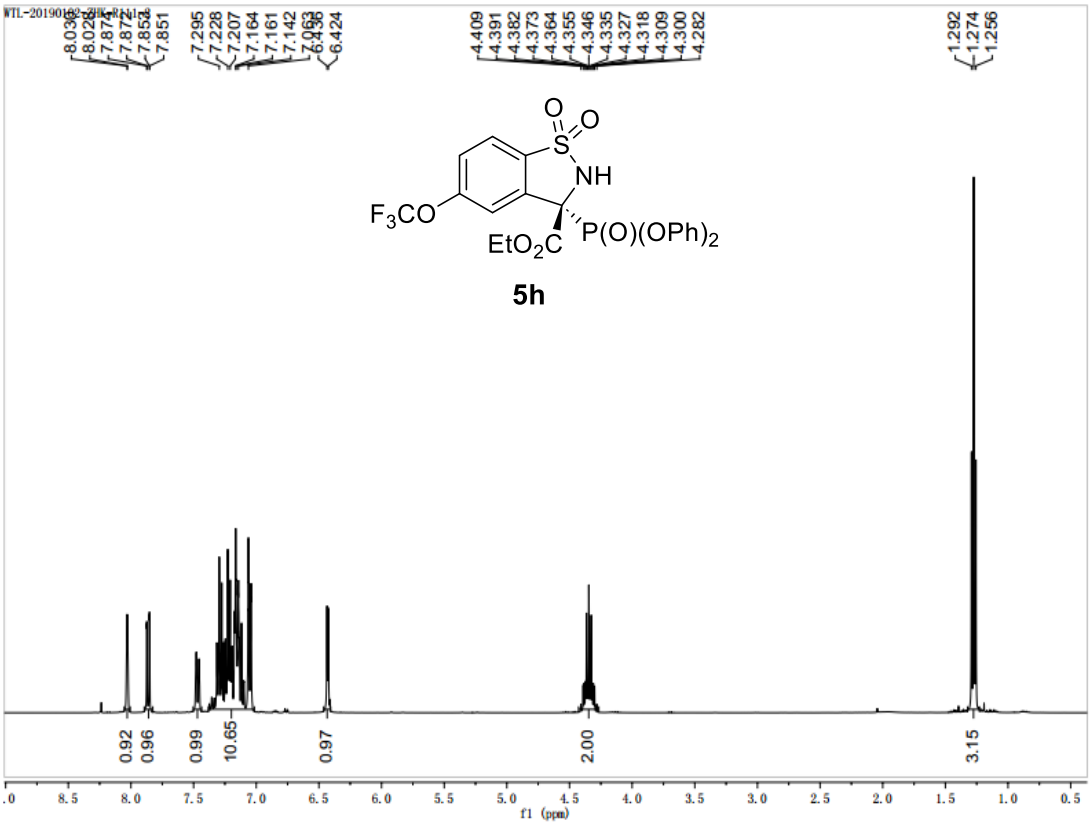

WTL-20190627-YX19-5-C1
164.678
150.329
150.234
150.069
149.968
140.225
131.920
129.865
129.788
127.843
125.922
125.719
122.864
120.415
120.371
119.997
119.953
68.096
66.438
65.340
13.851
O
O
S
NH
Cl
EtO2C
P(O)(OPh)2
5f
f1 (ppm)

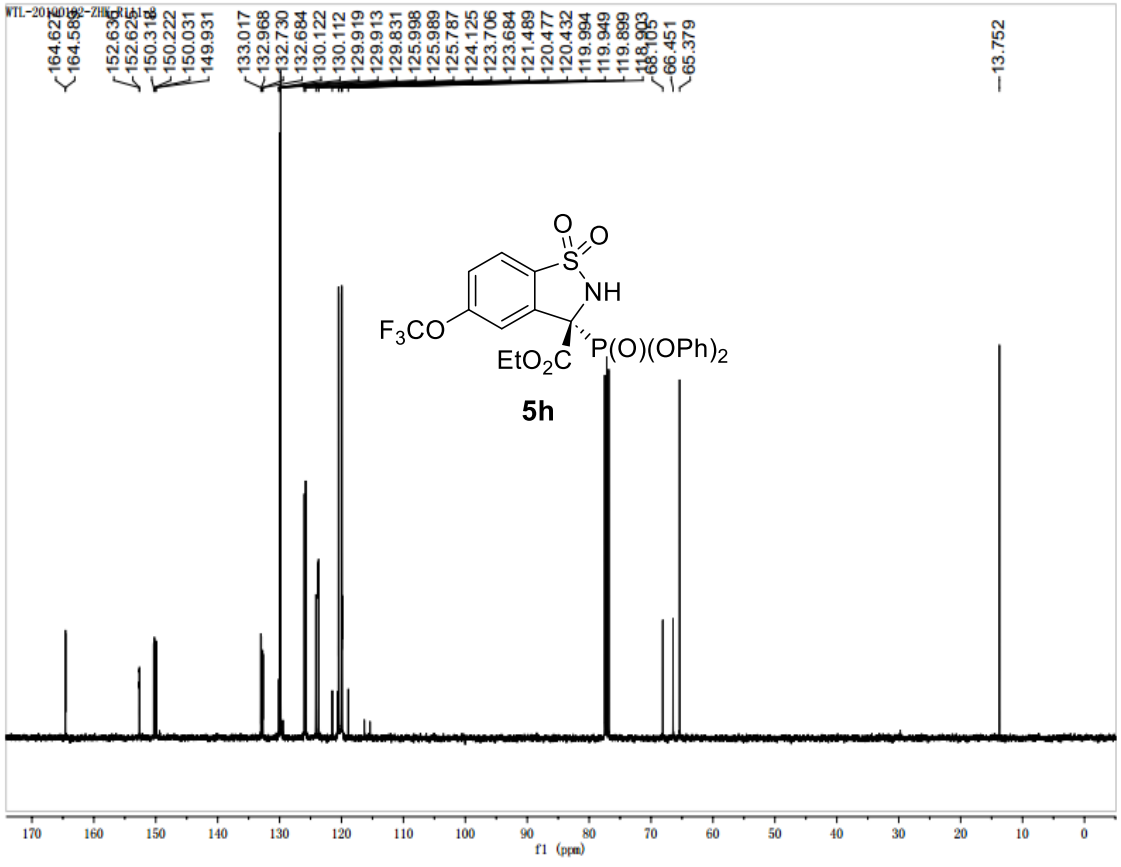

WTL-20190627-YX19-5-OME
-3.437
O
O
S
NH
Cl
EtO2C
P(O)(OPh)2
5f
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

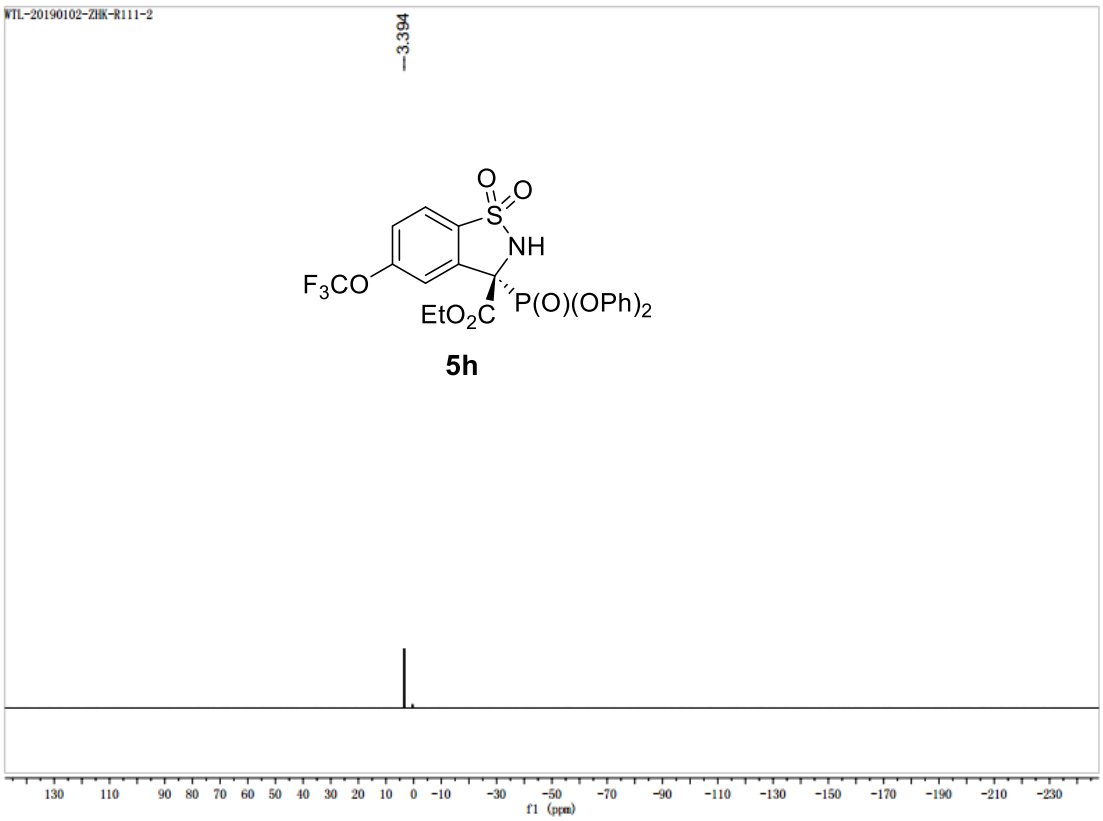

WTL-20190628-YX-2502
8.427
7.964
7.943
7.913
7.892
7.313
7.260
7.236
7.216
7.156
7.135
7.072
6.166
4.427
4.409
4.400
4.391
4.382
4.373
4.364
4.355
4.346
4.337
4.328
4.310
1.305
1.287
1.269
O
O
S
NH
F3C
EtO2C
P(O)(OPh)2
5g
0.94
1.96
2.06
5.85
1.83
0.72
2.00
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


WTL-20190628-YX-2502
164.654
164.620
150.454
150.358
150.144
150.043
131.378
131.333
130.021
129.959
128.740
128.706
128.674
126.116
126.108
125.890
125.457
125.417
125.383
122.825
122.804
120.476
120.432
119.966
119.912
68.481
66.829
65.578
13.898
O
O
S
NH
F3C
EtO2C
P(O)(OPh)2
5g
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

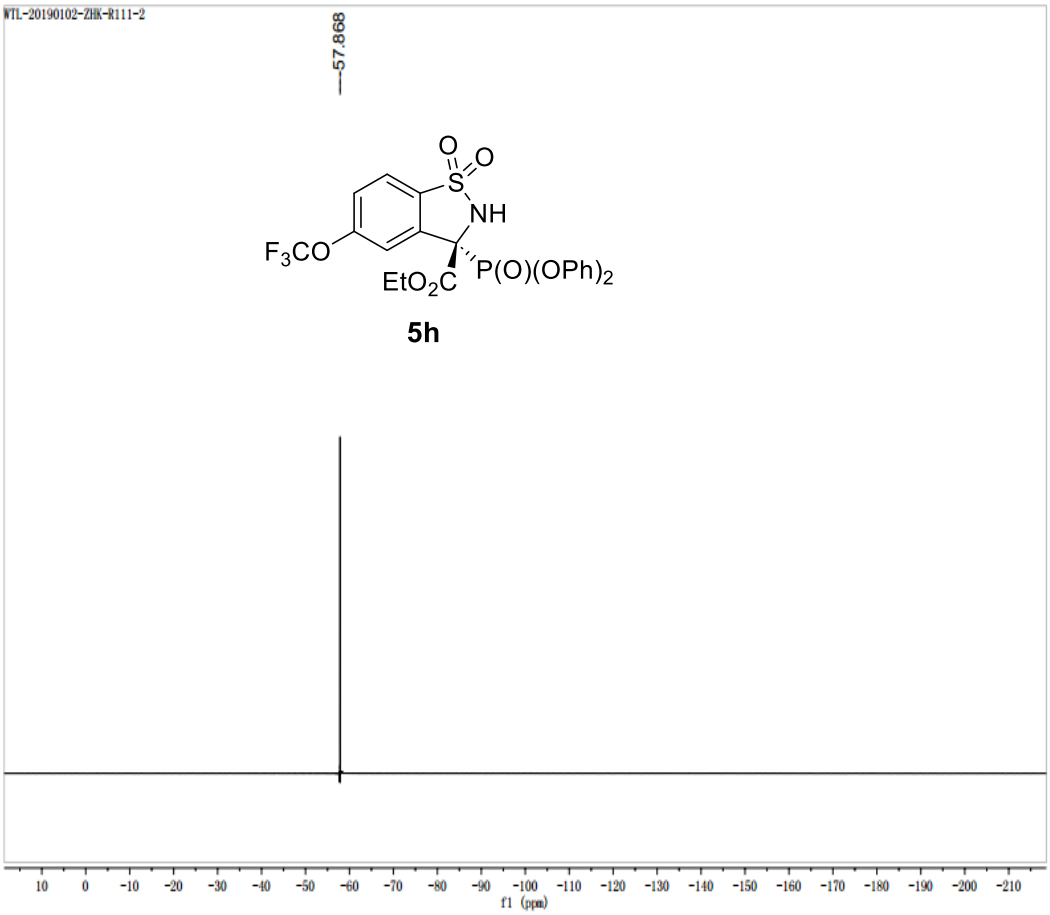

WTL-20190628-YX-2502
-3.048
O
O
S
NH
F3C
EtO2C
P(O)(OPh)2
5g
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


8.036
8.026
7.874
7.872
7.853
7.851
7.295
7.228
7.207
7.164
7.161
7.142
7.063
6.436
6.424
4.409
4.391
4.382
4.373
4.364
4.355
4.346
4.335
4.327
4.318
4.309
4.300
4.282
1.292
1.274
1.256
O
O
S
NH
F3CO
EtO2C
P(O)(OPh)2
5h
0.92
0.96
0.99
10.65
0.97
2.00
3.15
f1 (ppm)

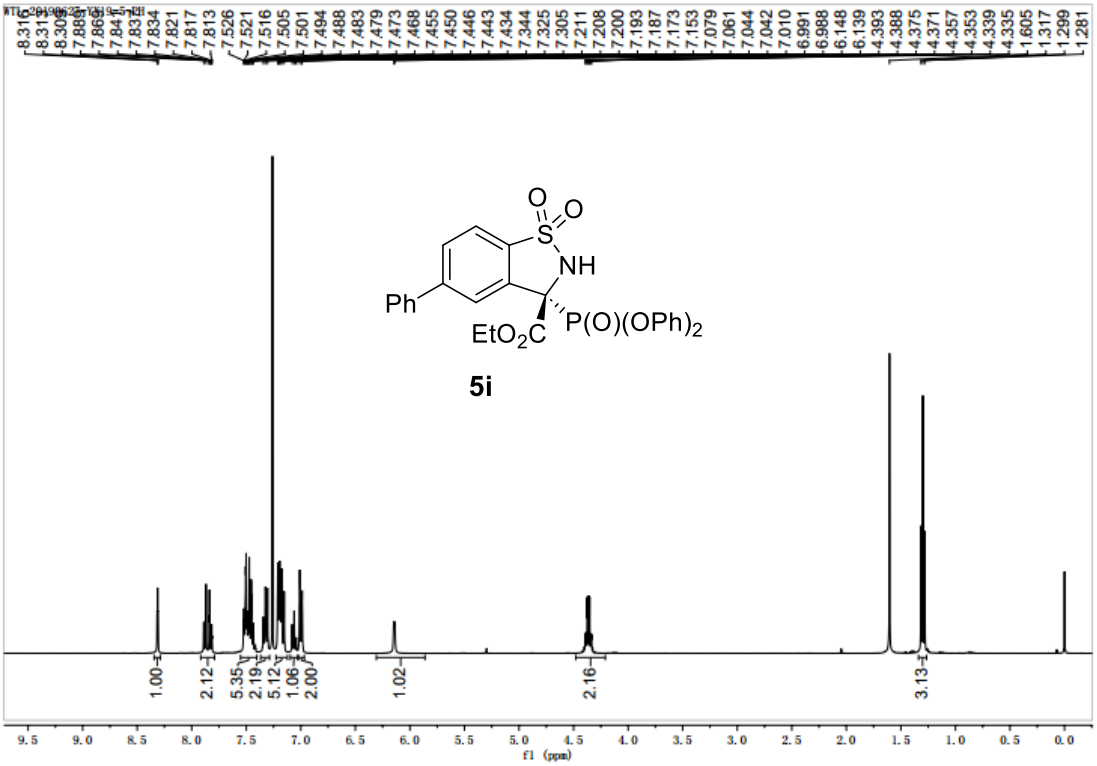

164.621
164.582
152.637
152.625
150.318
150.222
150.031
149.931
133.017
132.968
132.730
132.684
130.122
130.112
129.919
129.913
129.831
125.998
125.989
125.787
124.125
123.706
123.684
121.489
120.477
120.432
119.994
119.949
119.899
68.105
66.451
65.379
13.752
O
O
S
NH
F3CO
EtO2C
P(O)(OPh)2
5h
f1 (ppm)

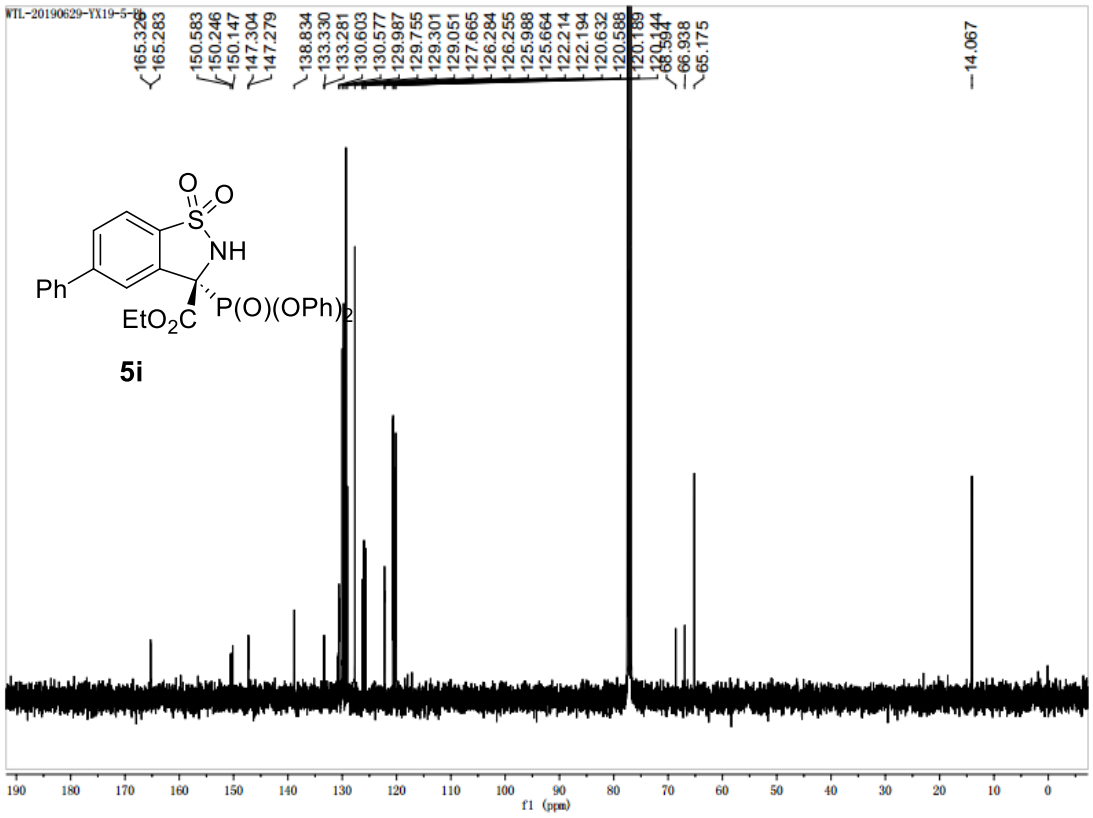

WTL-20190102-ZHK-R111-2
3.394
O
O
S
NH
F3CO
EtO2C
P(O)(OPh)2
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

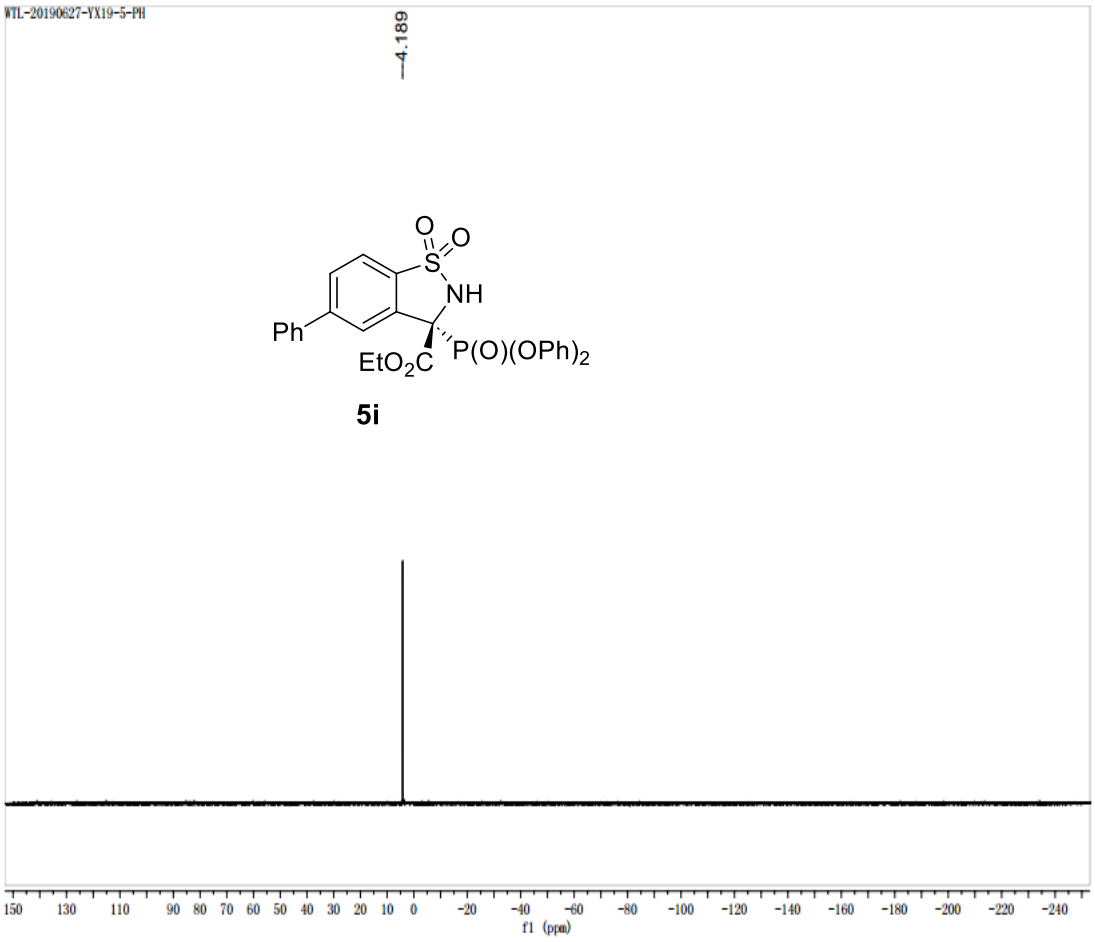
5h

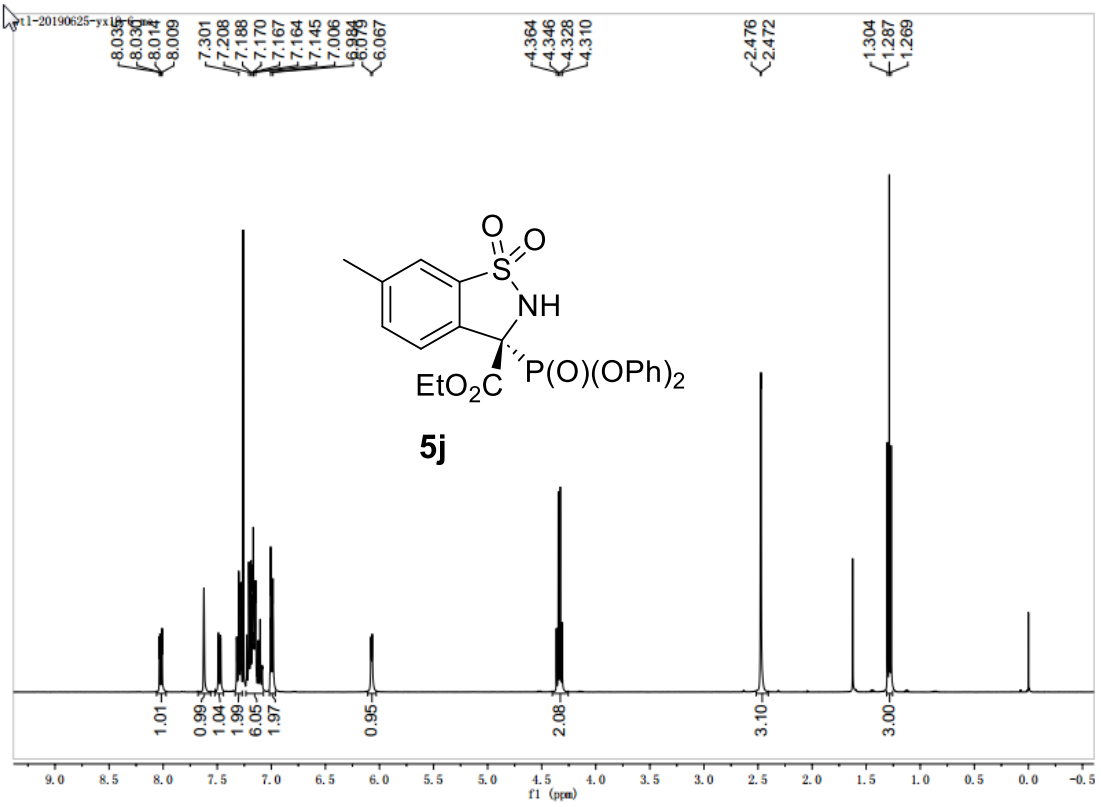

WTL-20190102-ZHK-R111-2
57.868
O
O
S
NH
F3CO
EtO2C
P(O)(OPh)2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

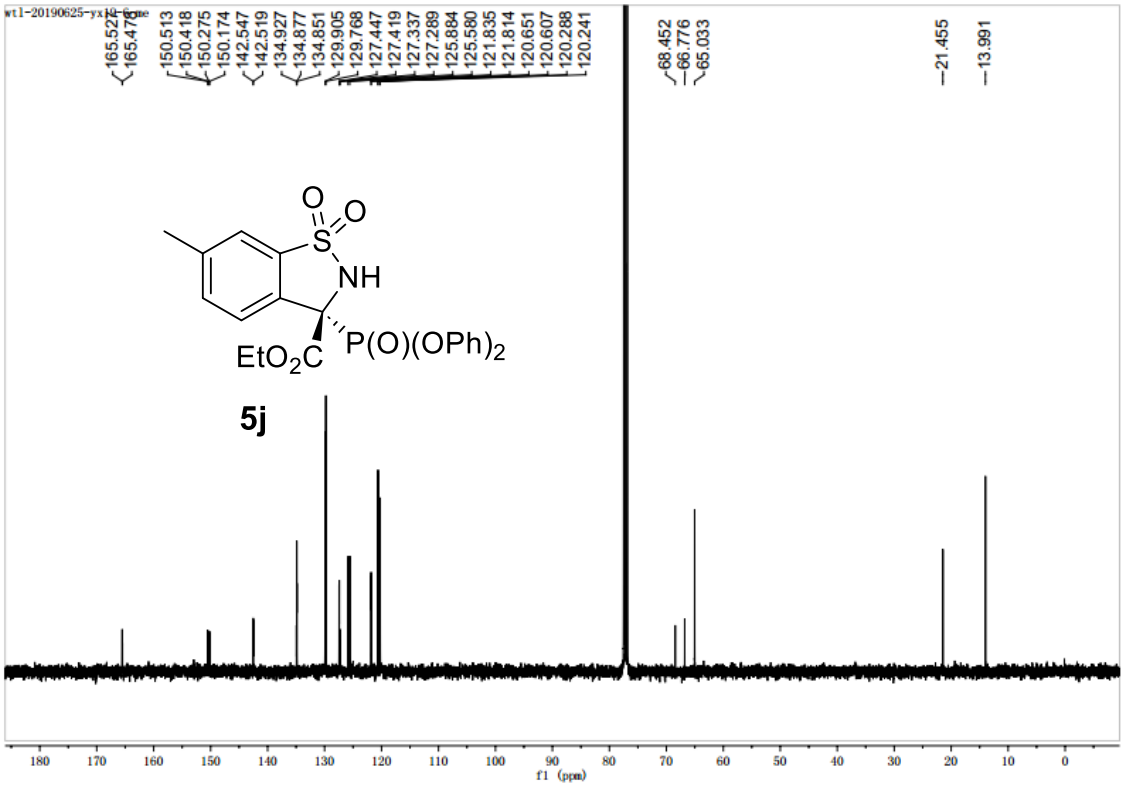
5h


8.316
8.311
8.306
7.886
7.865
7.841
7.834
7.821
7.817
7.813
7.526
7.521
7.516
7.505
7.501
7.494
7.488
7.483
7.479
7.473
7.468
7.455
7.450
7.446
7.443
7.434
7.344
7.325
7.305
7.211
7.208
7.200
7.193
7.187
7.173
7.153
7.079
7.061
7.044
7.042
7.010
6.991
6.988
6.148
6.139
4.393
4.388
4.375
4.371
4.357
4.353
4.339
4.335
1.605
1.317
1.299
1.281
O
O
S
NH
Ph
EtO2C
P(O)(OPh)2
5i
1.00
2.12
5.35
2.19
5.12
1.06
2.00
1.02
2.16
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

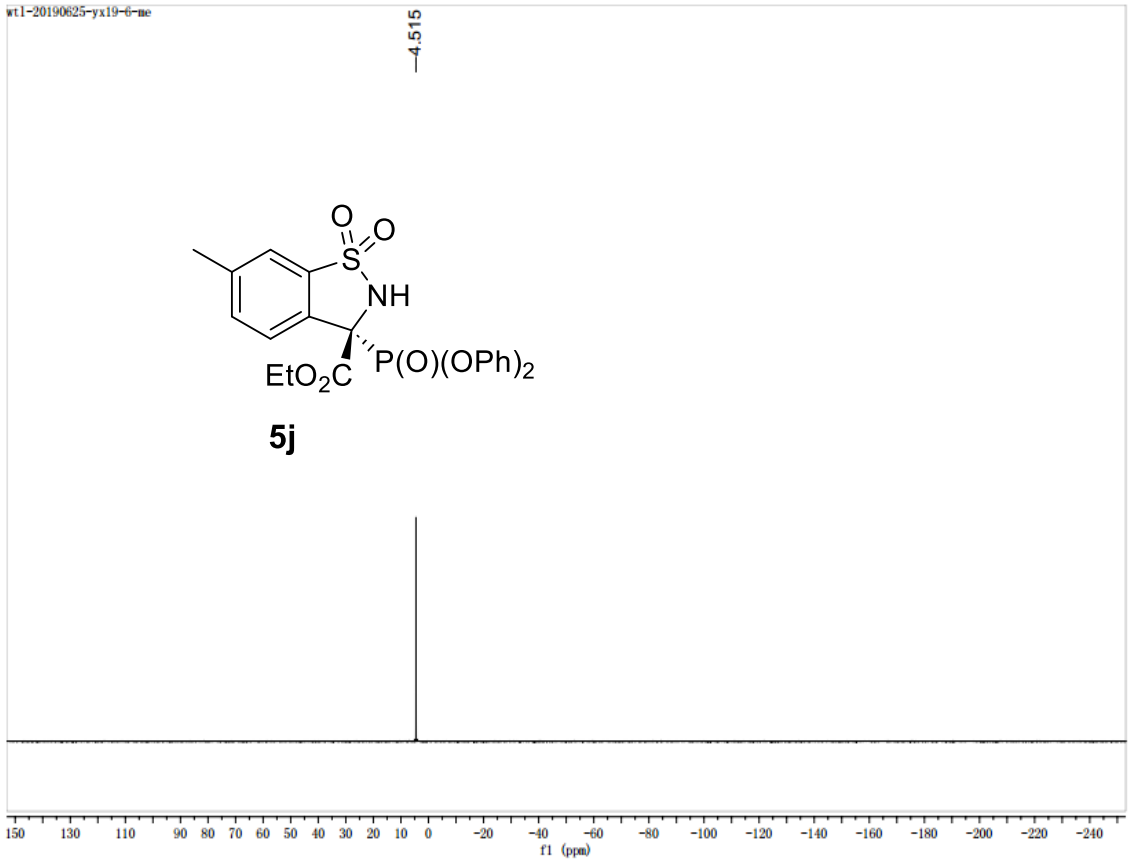

165.326
165.283
150.583
150.246
150.147
147.304
147.279
138.834
133.330
133.281
130.603
130.577
129.987
129.755
129.301
129.051
127.665
126.284
126.255
125.988
125.664
122.214
122.194
120.632
120.588
120.189
120.144
68.594
66.938
65.175
14.067
O
O
S
NH
Ph
EtO2C
P(O)(OPh)2
5i
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


WTL-20190627-YX19-5-PH
4.189
O
O
S
NH
Ph
EtO2C
P(O)(OPh)2
5i
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

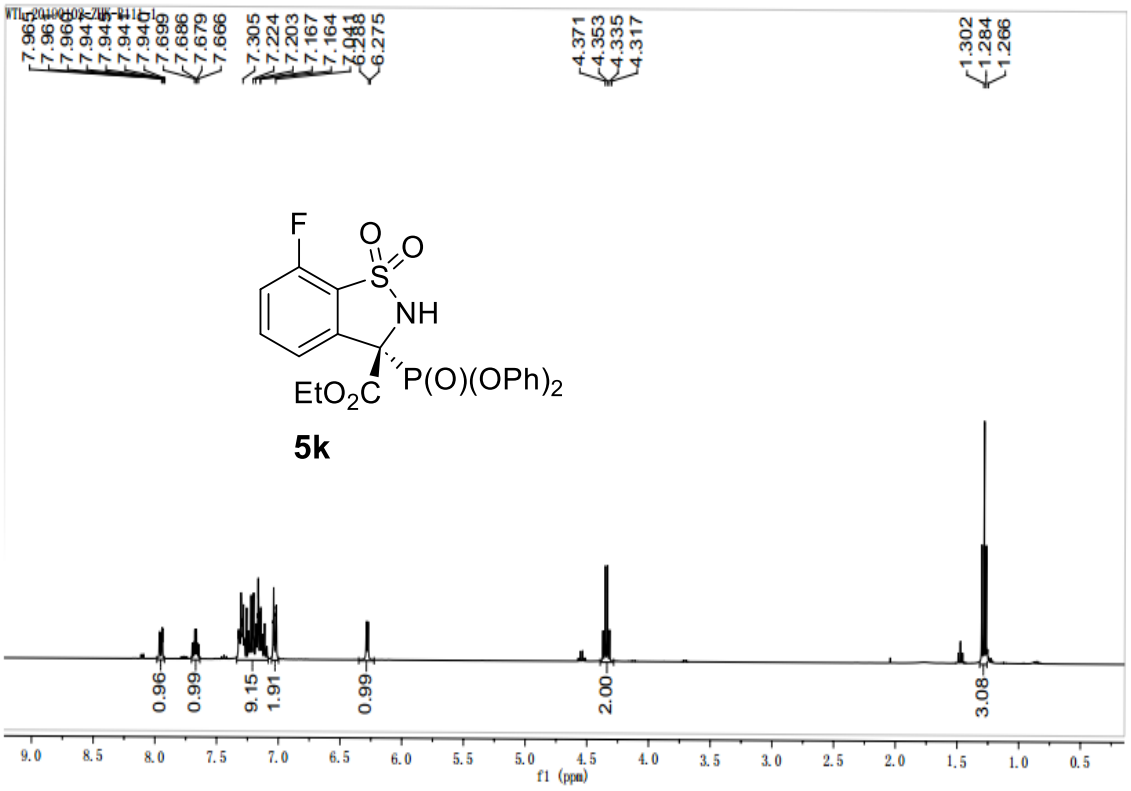

8.035
8.030
8.014
8.009
7.301
7.208
7.188
7.170
7.167
7.164
7.145
7.006
6.084
6.079
6.067
4.364
4.346
4.328
4.310
2.476
2.472
1.304
1.287
1.269
O
O
S
NH
EtO2C
P(O)(OPh)2
5j
1.01
0.99
1.04
1.99
6.05
1.97
0.95
2.08
3.10
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

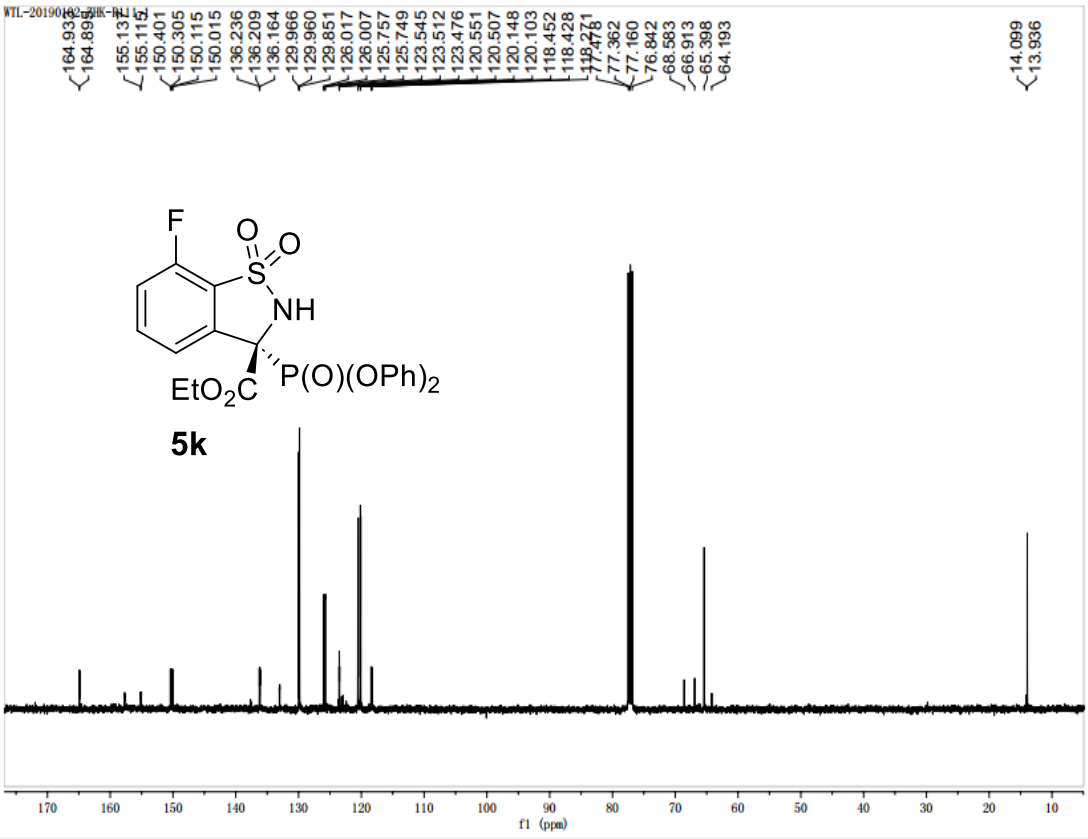

wt1-20190625-yx19-6-me
165.527
165.478
150.513
150.418
150.275
150.174
142.547
142.519
134.927
134.877
134.851
129.905
129.768
127.447
127.419
127.337
127.289
125.884
125.580
121.835
121.814
120.651
120.607
120.288
120.241
68.452
66.776
65.033
21.455
13.991
O
O
S
NH
EtO2C
P(O)(OPh)2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

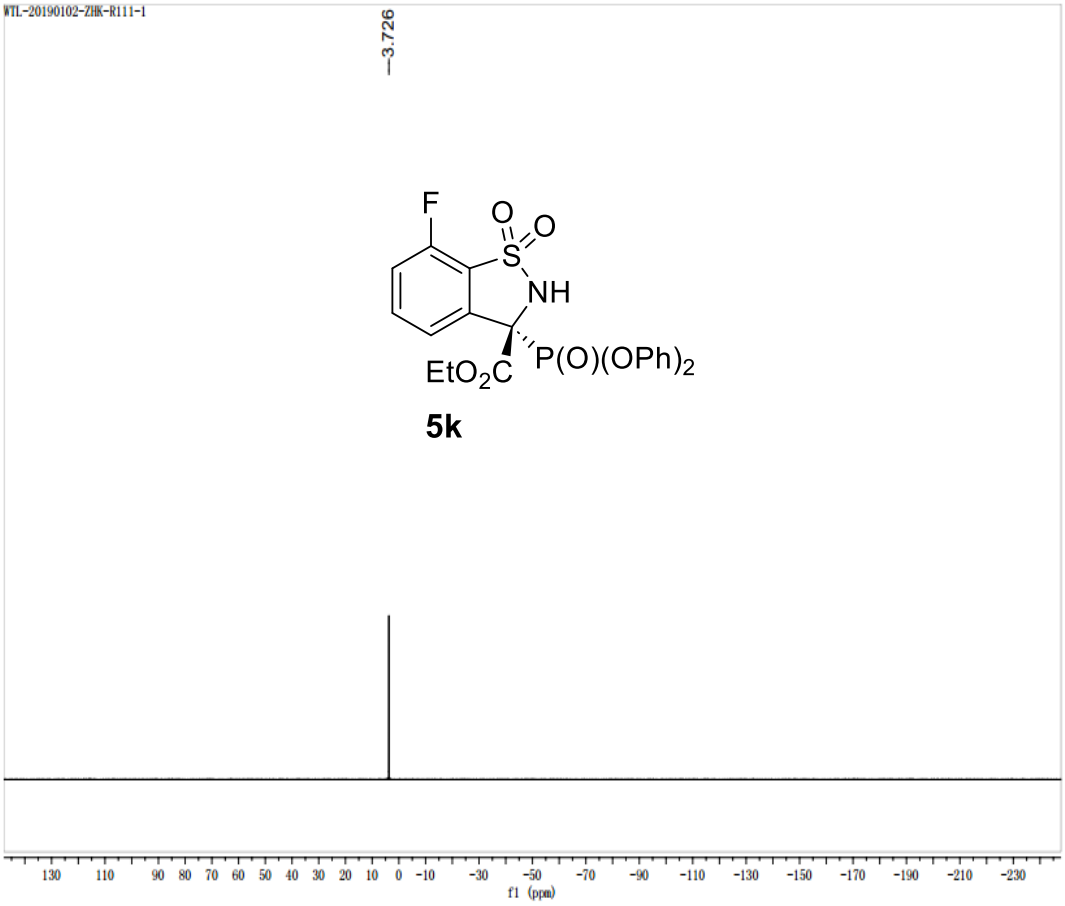
5j

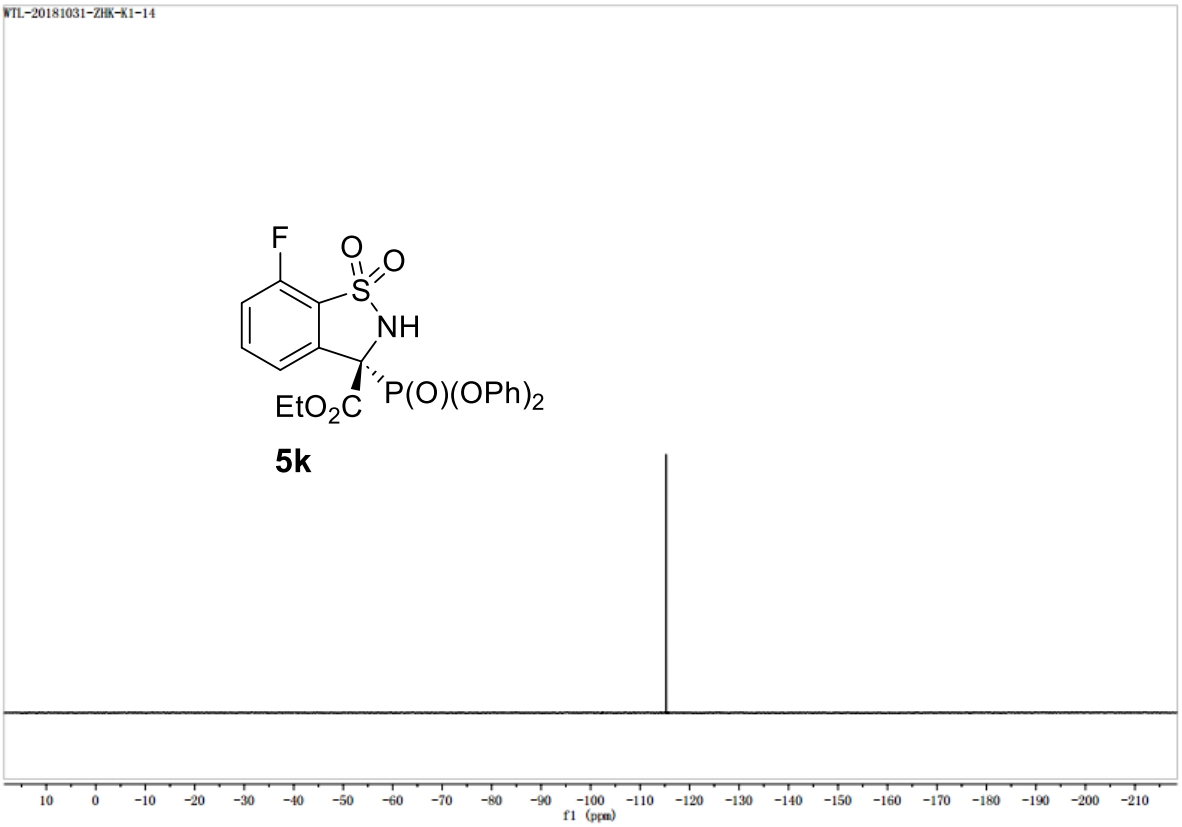

wt1-20190625-yx19-6-me
4.515
O
O
S
NH
EtO2C
P(O)(OPh)2
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

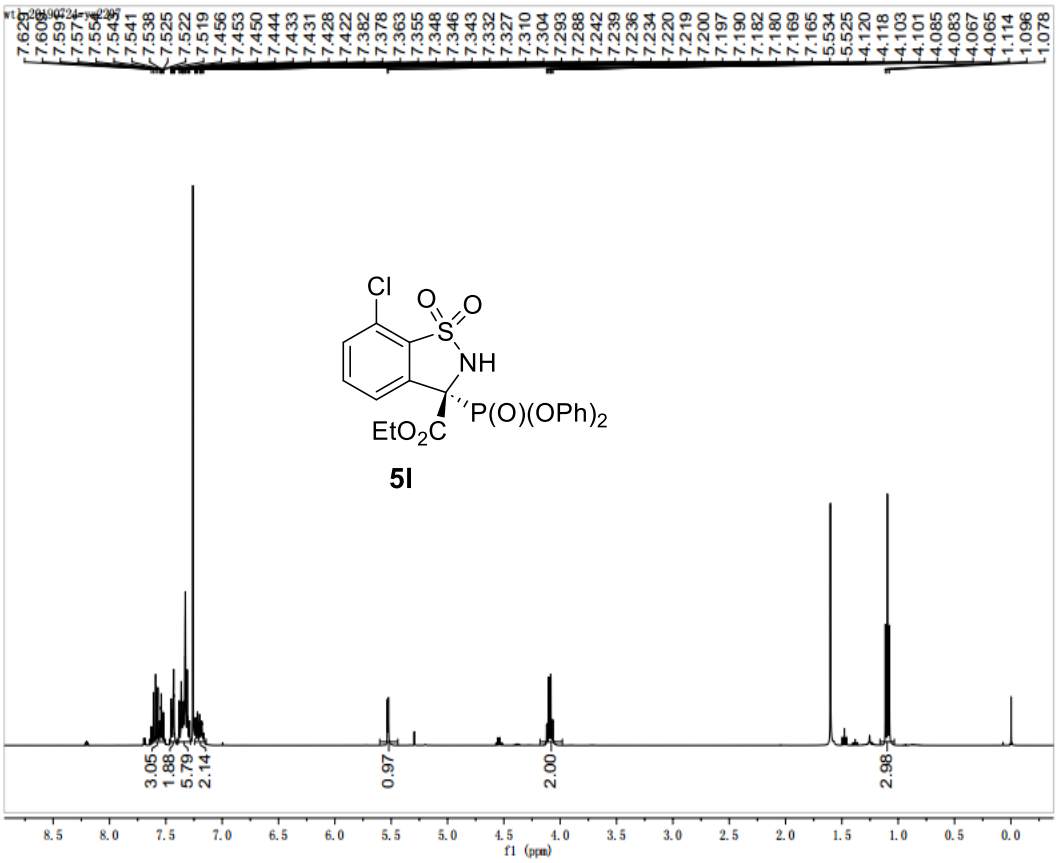
5j

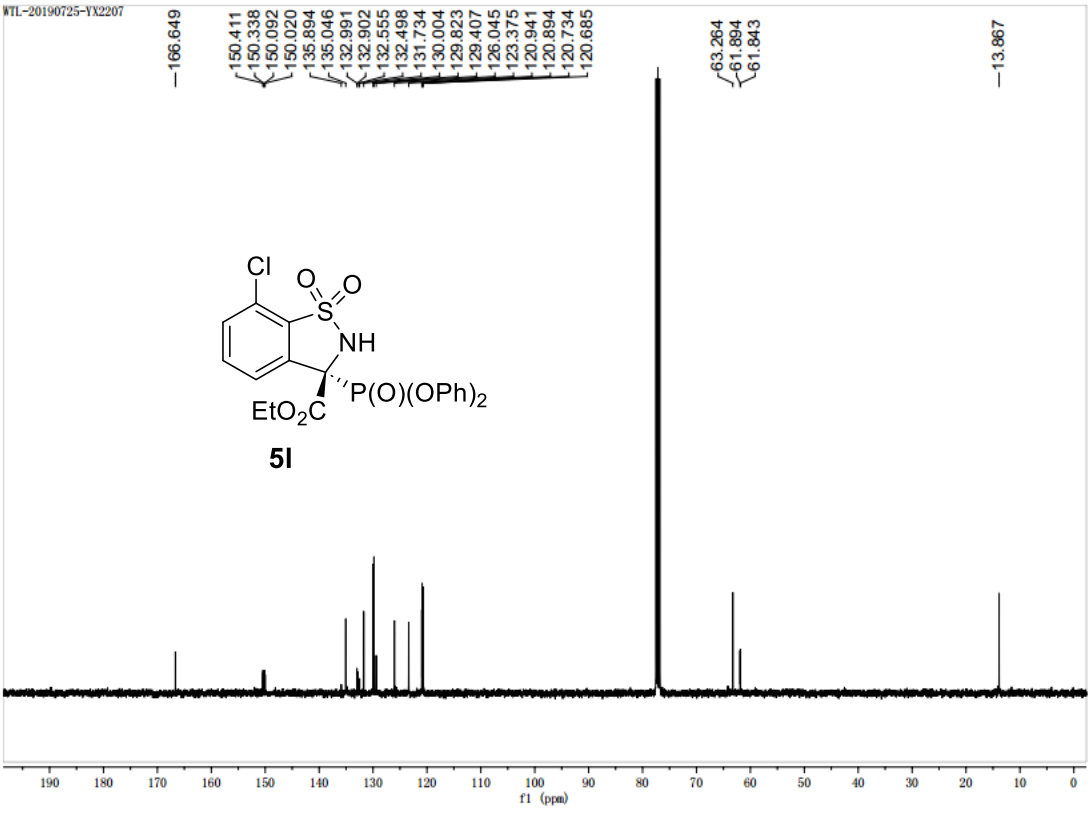

F
O
O
S
NH
EtO2C
P(O)(OPh)2
5k
f1 (ppm)

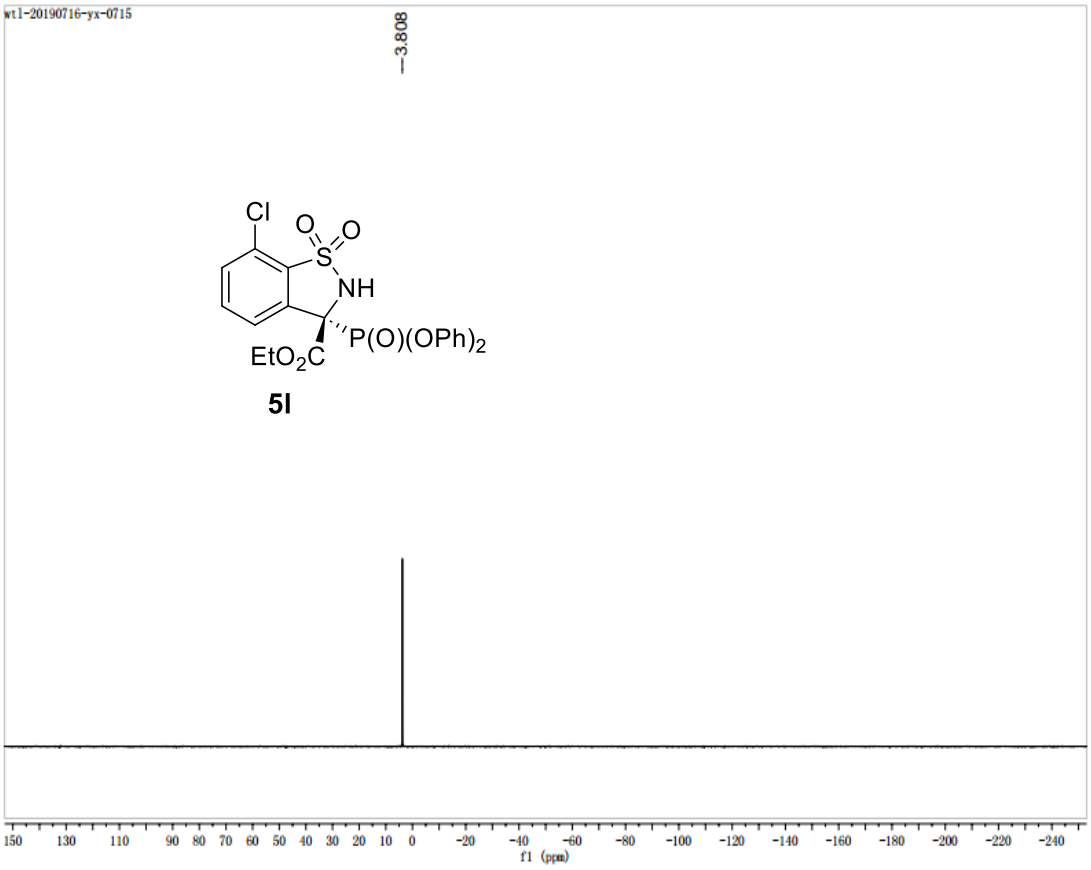

F
O
O
S
NH
EtO2C
P(O)(OPh)2
5k
f1 (ppm)

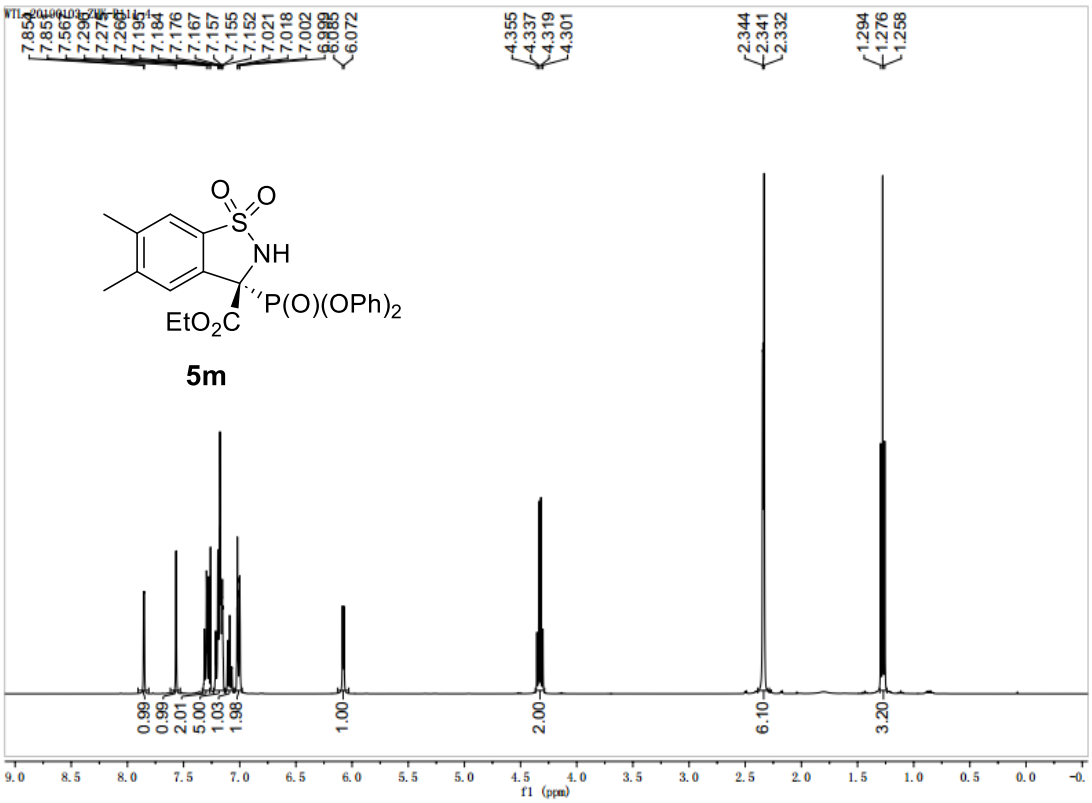

WTL-20190102-ZHK-R111-1
-3.726
F
O
O
S
NH
EtO2C
P(O)(OPh)2
5k
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

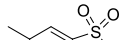

WTL-20181031-ZHK-K1-14
F
O
O
S
NH
EtO2C
P(O)(OPh)2
5k
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

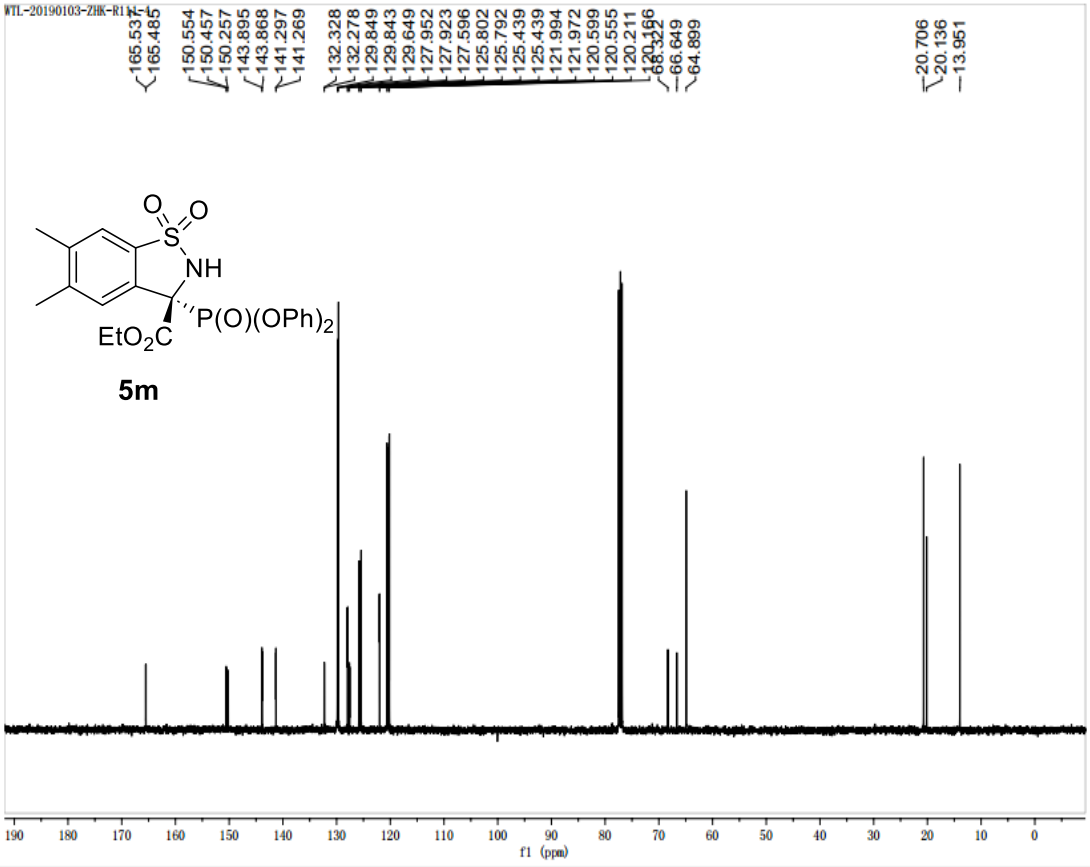

Cl
O
O
S
NH
P(O)(OPh)2
EtO2C
5l
3.05
1.88
5.79
2.14
0.97
2.00
2.98
f1 (ppm)

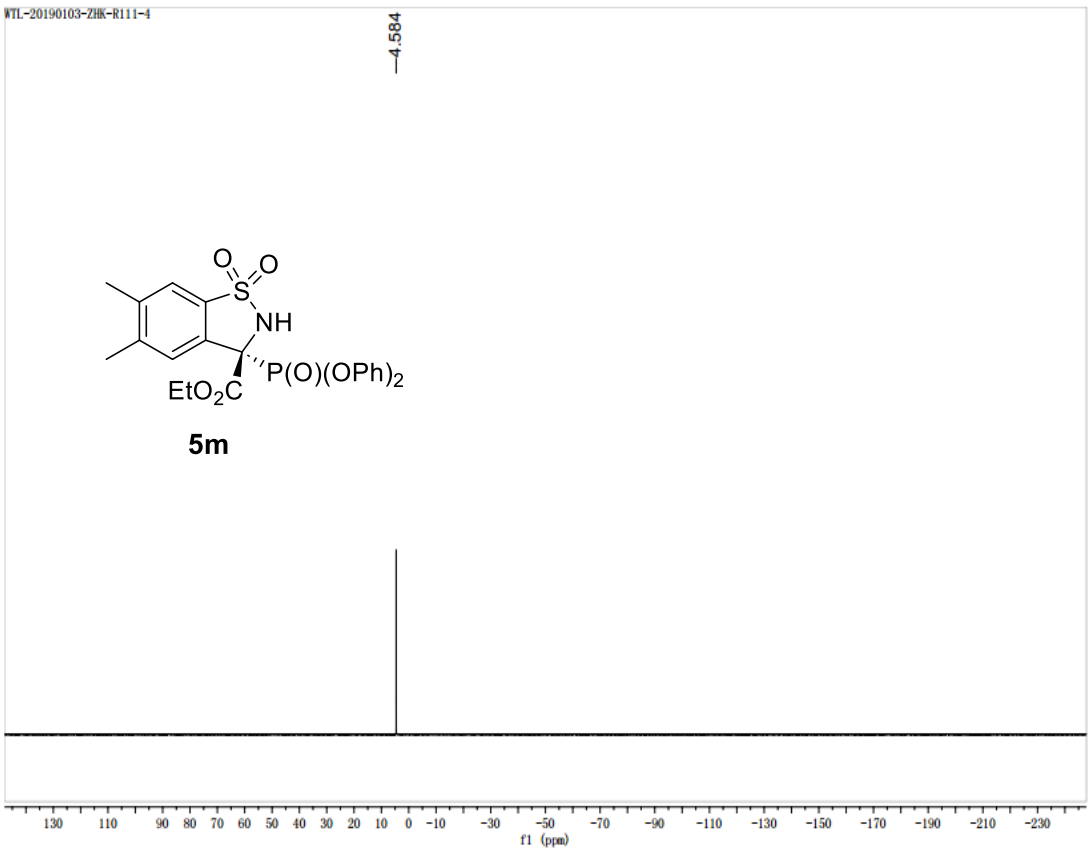

WTL-20190725-YX2207
166.649
150.411
150.338
150.092
150.020
135.894
135.046
132.991
132.902
132.555
132.498
131.734
130.004
129.823
129.407
126.045
123.375
120.941
120.894
120.734
120.685
63.264
61.894
61.843
13.867
Cl
O
O
S
NH
P(O)(OPh)2
EtO2C
5l
f1 (ppm)

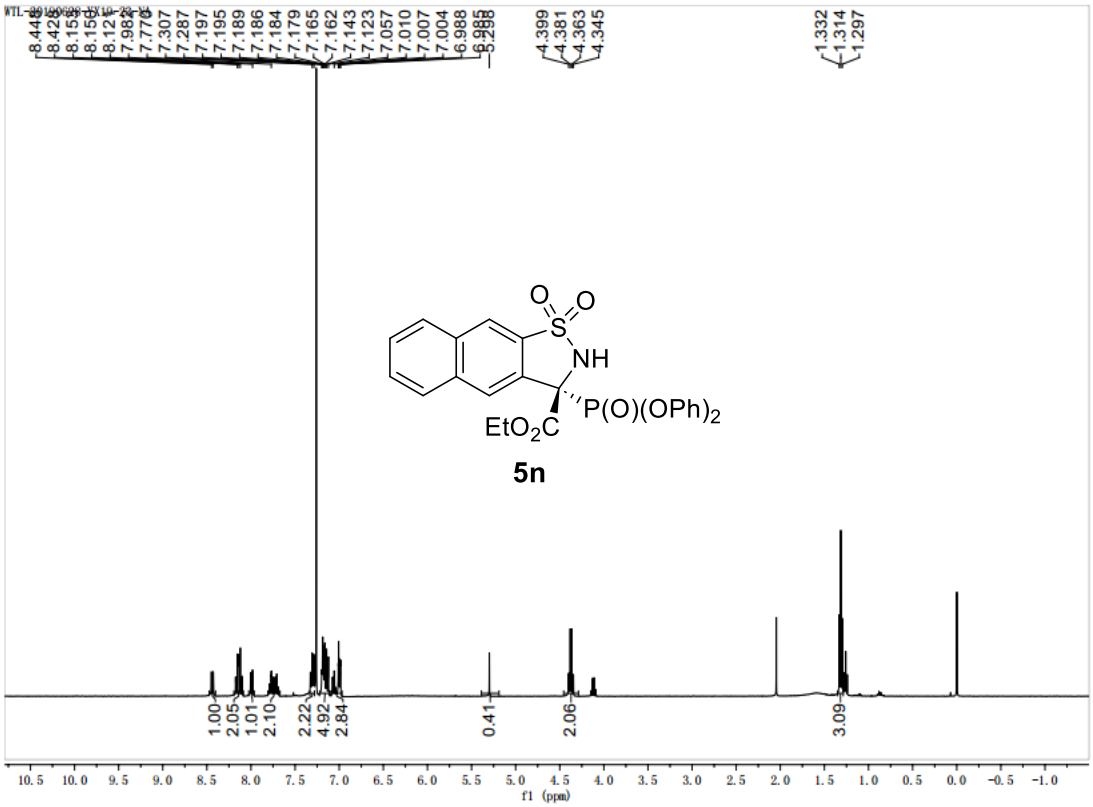

wtl-20190716-yx-0715
3.808
Cl
O
O
S
NH
P(O)(OPh)2
EtO2C
5l
f1 (ppm)

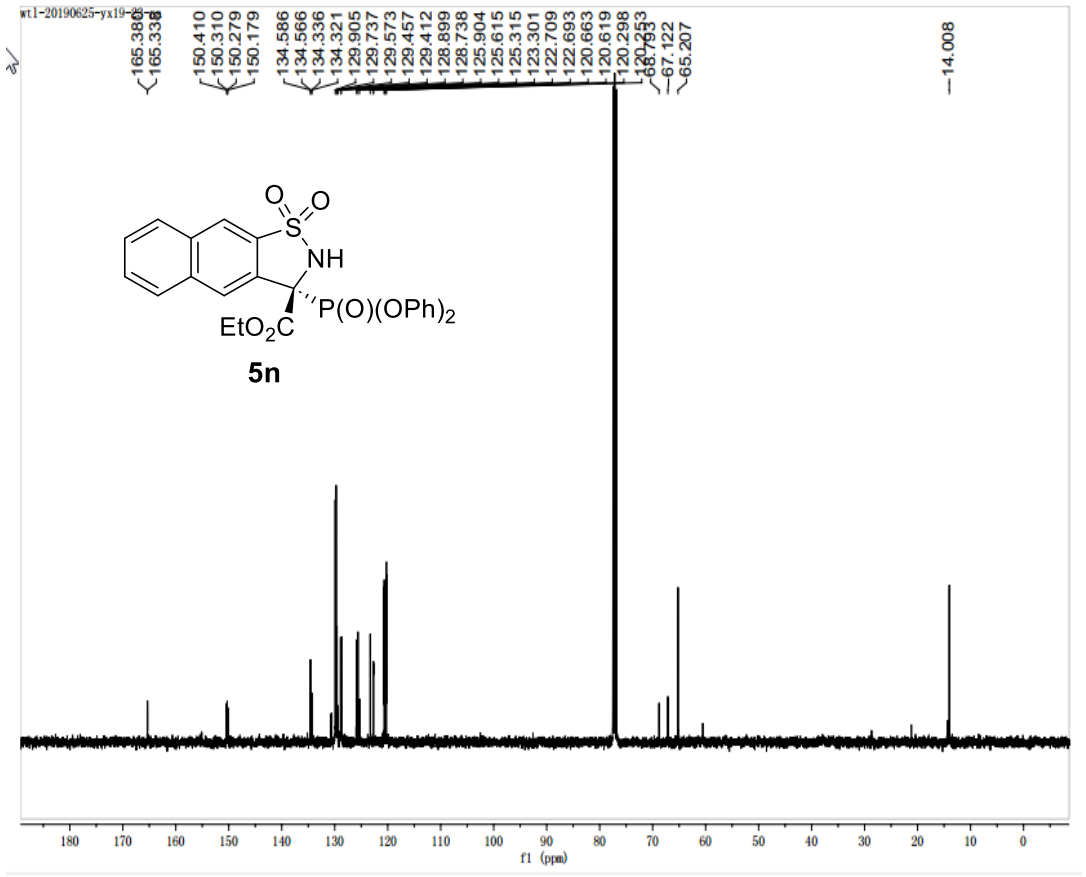

7.852
7.851
7.567
7.296
7.274
7.266
7.195
7.184
7.176
7.167
7.157
7.155
7.152
7.021
7.018
7.002
6.999
6.085
6.072
4.355
4.337
4.319
4.301
2.344
2.341
2.332
1.294
1.276
1.258
O
O
S
NH
P(O)(OPh)2
EtO2C
5m
0.99
0.99
2.01
5.00
1.03
1.98
1.00
2.00
6.10
3.20
f1 (ppm)

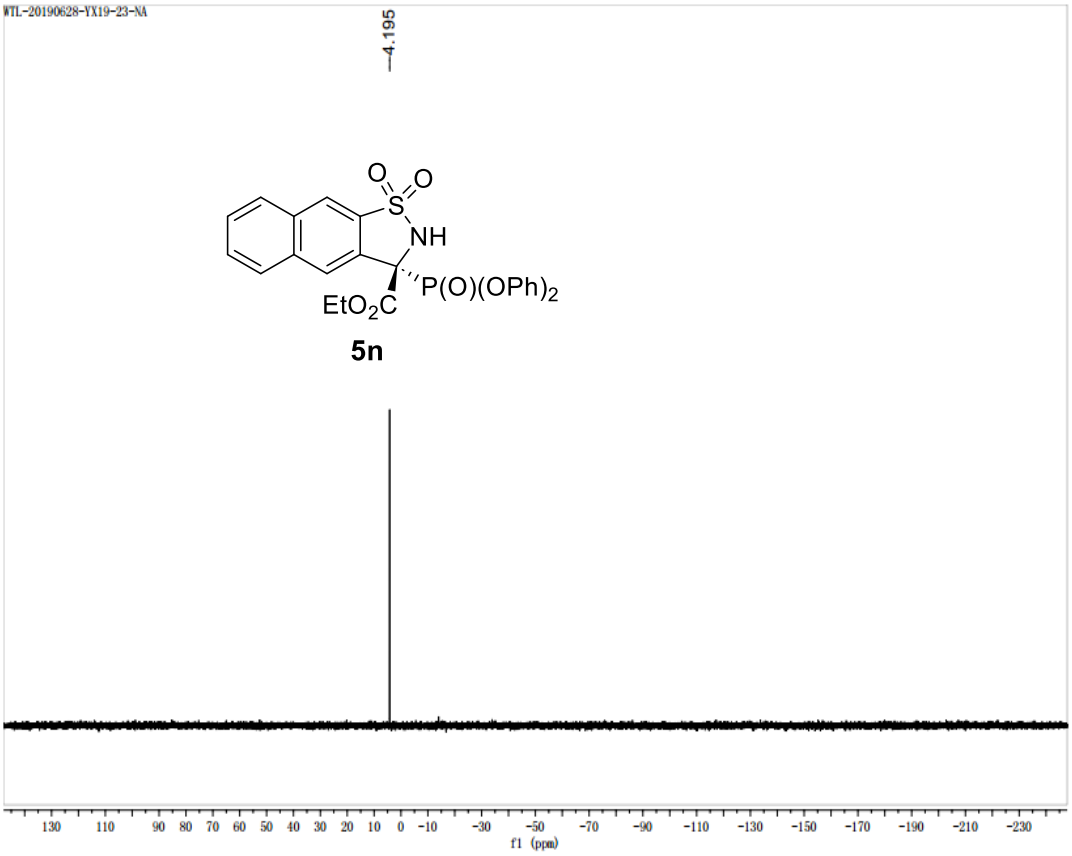

O
O
S

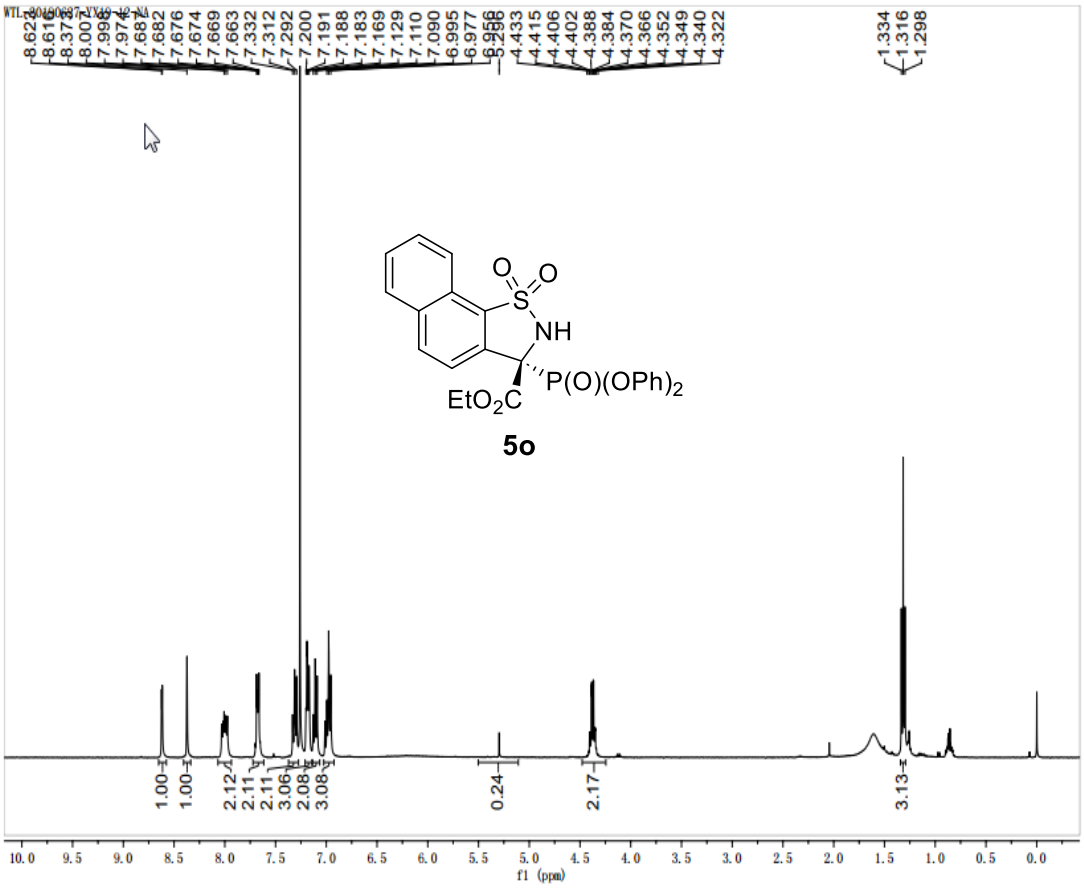

WTL-20190103-ZHK-R111-5
165.537
165.485
150.554
150.457
150.257
143.895
143.868
141.297
141.269
132.328
132.278
129.849
129.843
129.649
127.952
127.923
127.596
125.802
125.792
125.439
125.439
121.994
121.972
120.599
120.555
120.211
120.166
66.649
64.899
20.706
20.136
13.951
O
O
S
NH
P(O)(OPh)2
EtO2C
5m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

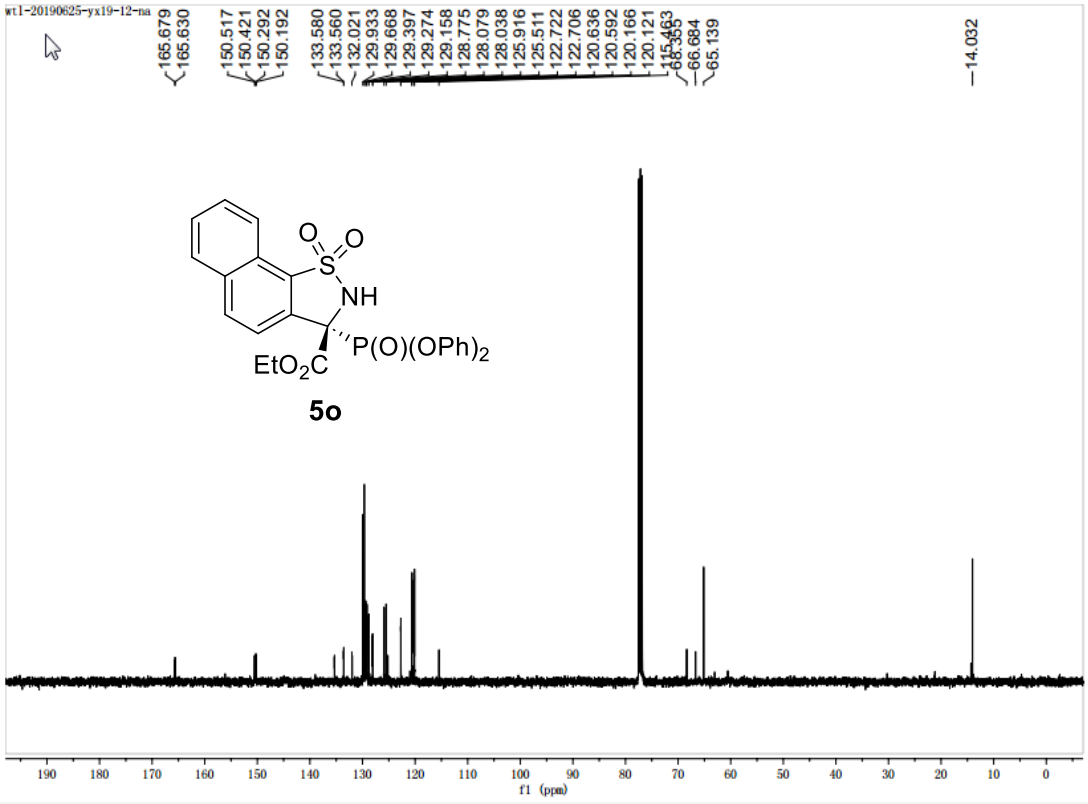

WTL-20190103-ZHK-R111-4
4.584
O
O
S
NH
P(O)(OPh)2
EtO2C
5m
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

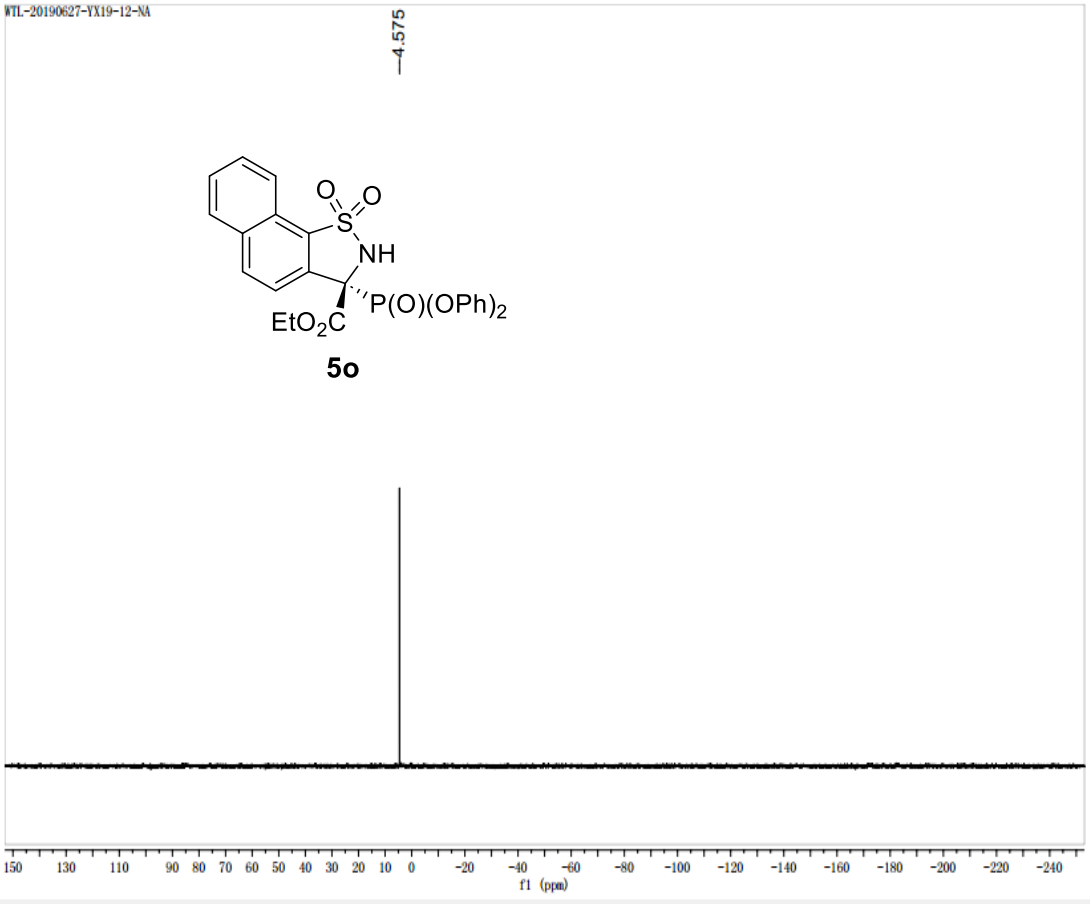

8.448
8.426
8.158
8.121
7.982
7.776
7.307
7.287
7.197
7.195
7.189
7.186
7.184
7.179
7.165
7.162
7.143
7.123
7.057
7.010
7.007
7.004
6.988
6.985
5.298
4.399
4.381
4.363
4.345
1.332
1.314
1.297
O
O
S
NH
P(O)(OPh)2
EtO2C
5n
1.00
2.05
1.01
2.10
2.22
4.92
2.84
0.41
2.06
3.09
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

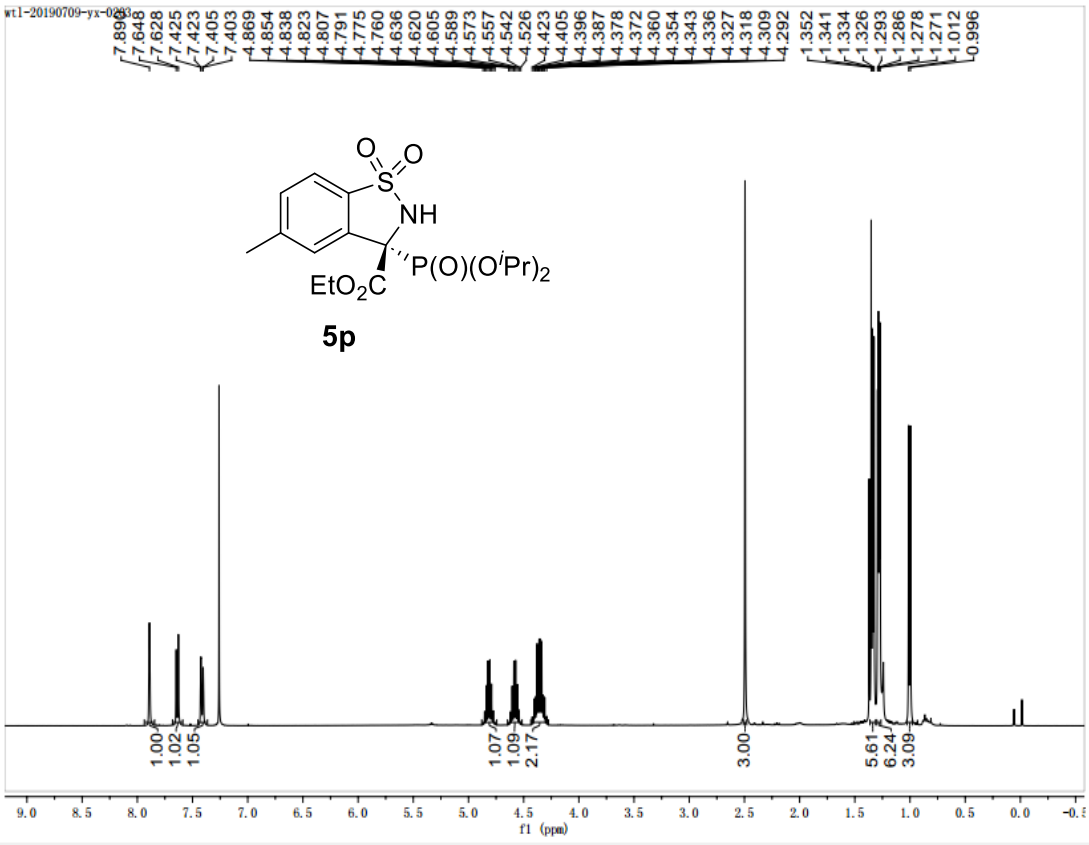

wtl-20190625-yx19-2
165.386
165.338
150.410
150.310
150.279
150.179
134.586
134.566
134.336
134.321
129.905
129.737
129.573
129.457
129.412
128.899
128.738
125.904
125.615
125.315
123.301
122.709
122.693
120.663
120.619
120.298
120.253
68.793
67.122
65.207
14.008
O
O
S
NH
P(O)(OPh)2
EtO2C
5n
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

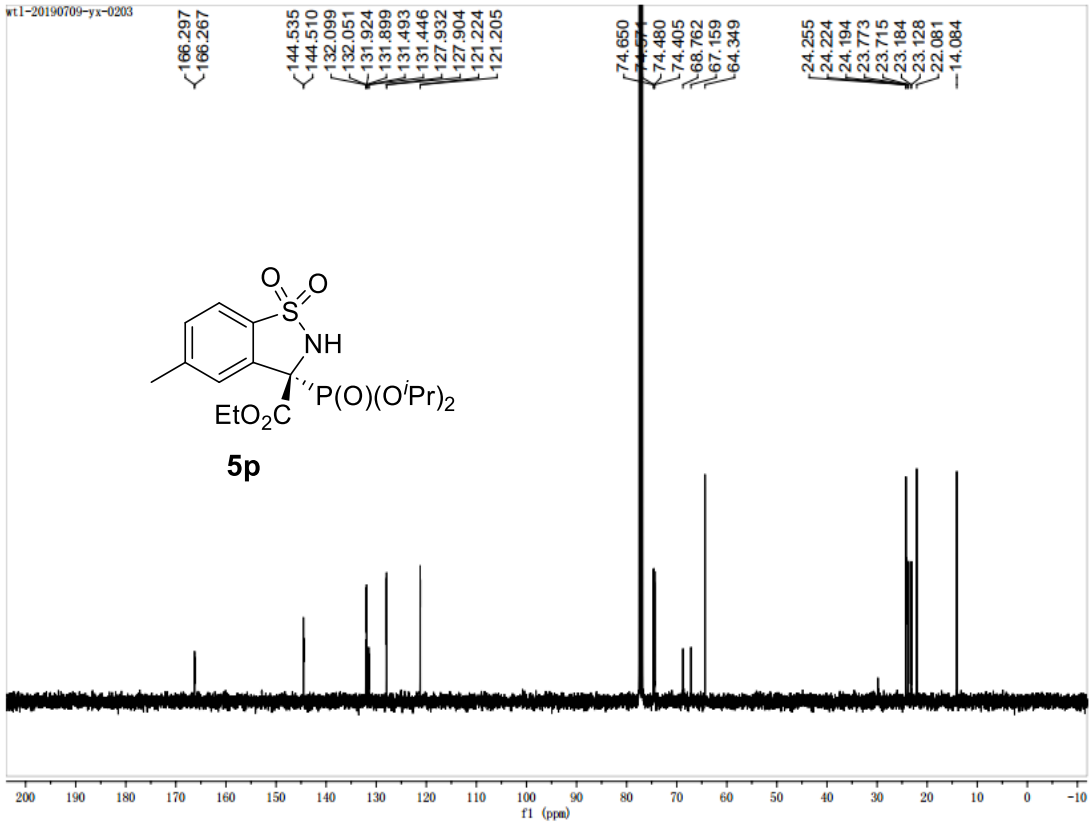

WTL-20190628-YX19-23-NA
-4.195
O
O
S
NH
P(O)(OPh)2
EtO2C
5n
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

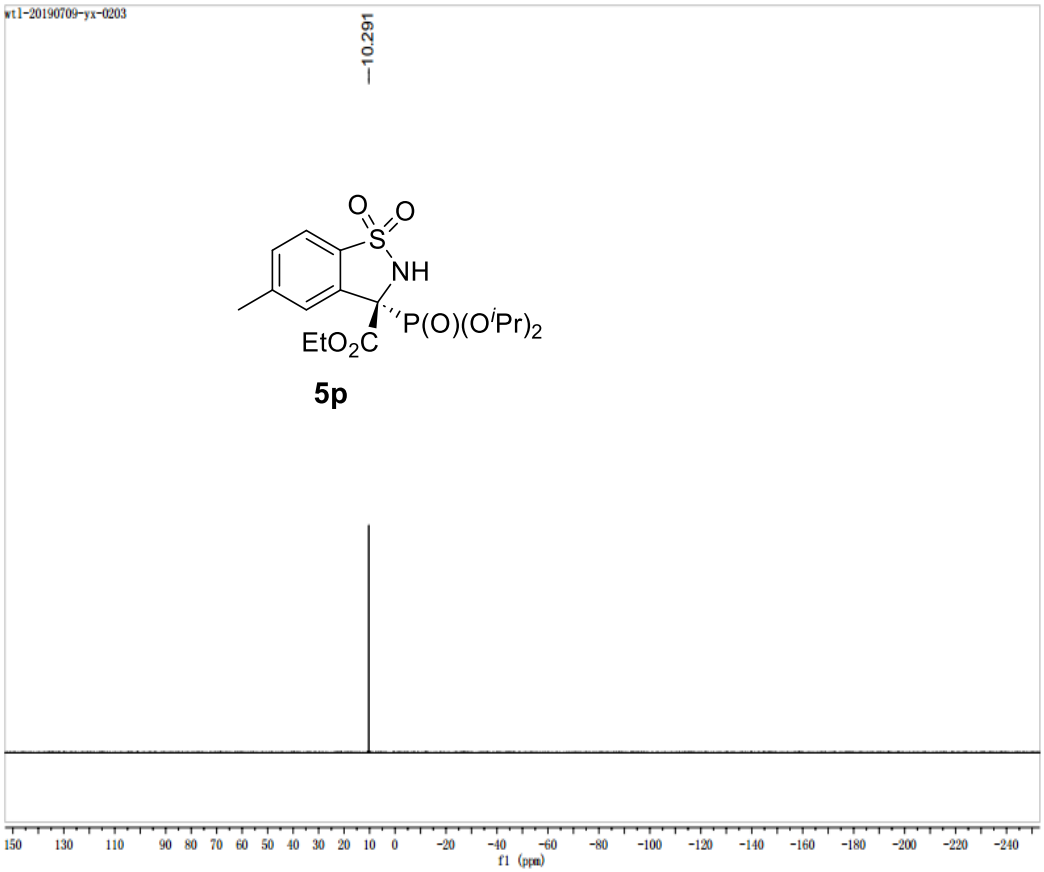

8.625
8.618
8.378
8.001
7.998
7.974
7.681
7.682
7.676
7.674
7.669
7.663
7.332
7.312
7.292
7.200
7.191
7.188
7.183
7.169
7.129
7.110
7.090
6.995
6.977
6.956
5.298
4.433
4.415
4.406
4.402
4.388
4.384
4.370
4.366
4.352
4.349
4.340
4.322
1.334
1.316
1.298
O
O
S
NH
P(O)(OPh)2
EtO2C
5o
1.00
1.00
2.12
2.11
2.11
3.06
2.08
3.08
0.24
2.17
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

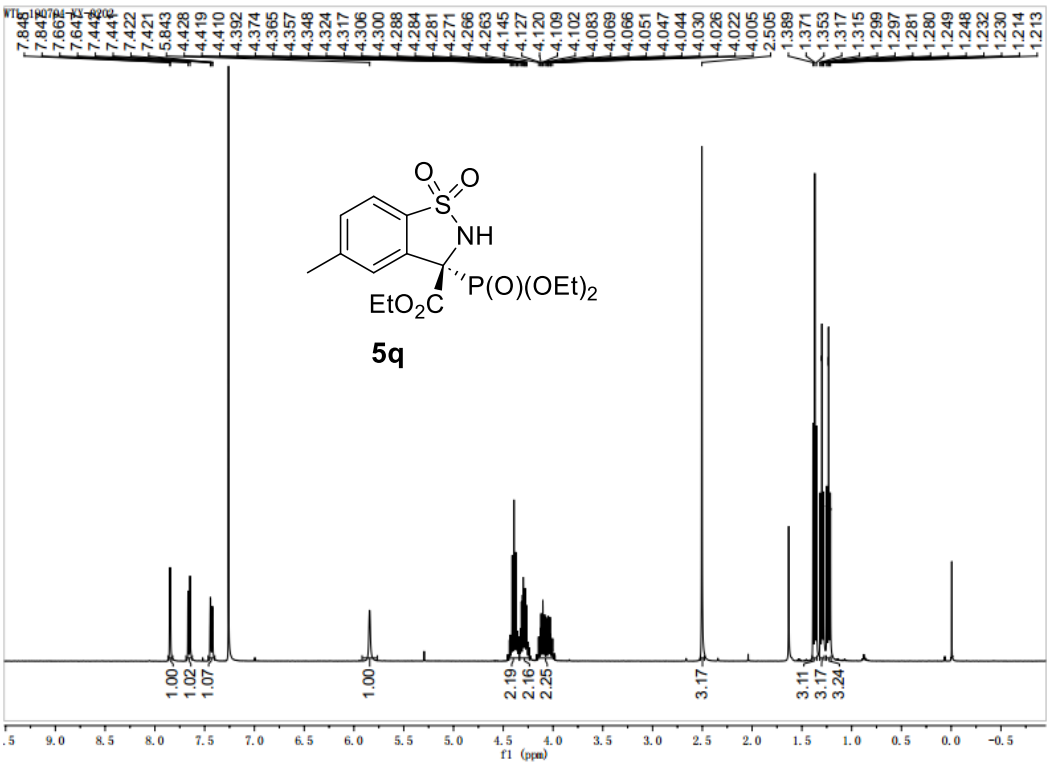

wt1-20190625-yx19-12-na
165.679
165.630
150.517
150.421
150.292
150.192
133.580
133.560
132.021
129.933
129.668
129.397
129.274
129.158
128.775
128.079
128.038
125.916
125.511
122.722
122.706
120.636
120.592
120.166
120.121
115.463
68.355
66.684
65.139
14.032
O
O
S
NH
P(O)(OPh)2
EtO2C
5o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

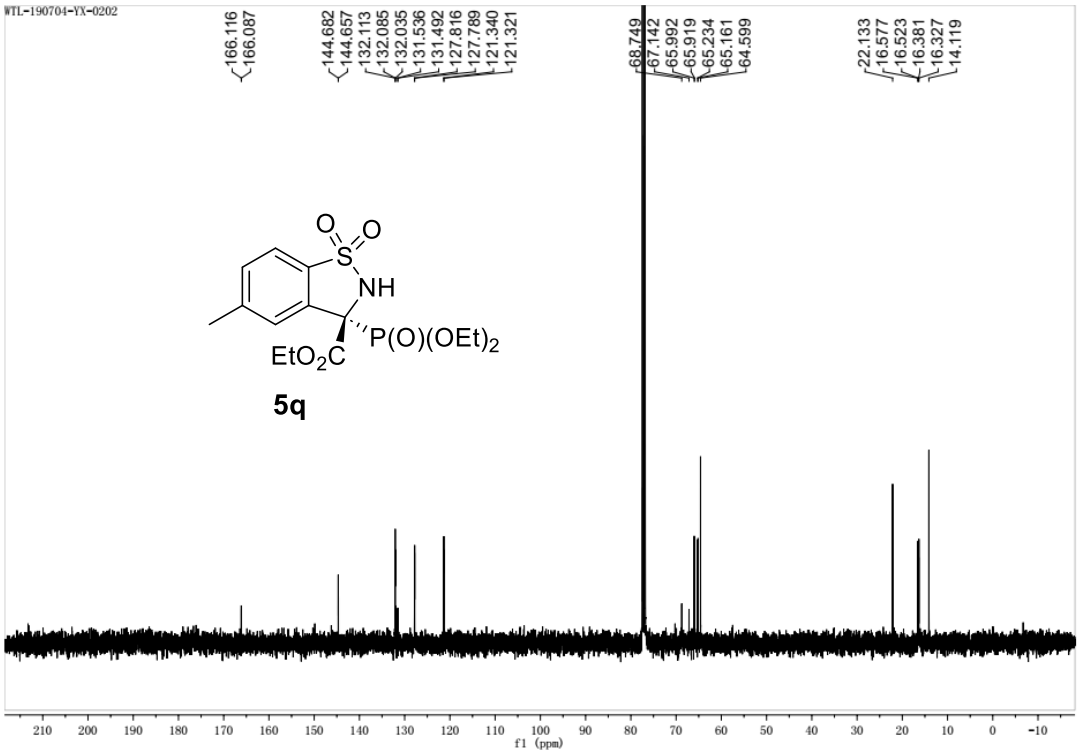

WTL-20190627-YX19-12-NA
4.575
O
O
S
NH
P(O)(OPh)2
EtO2C
5o
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

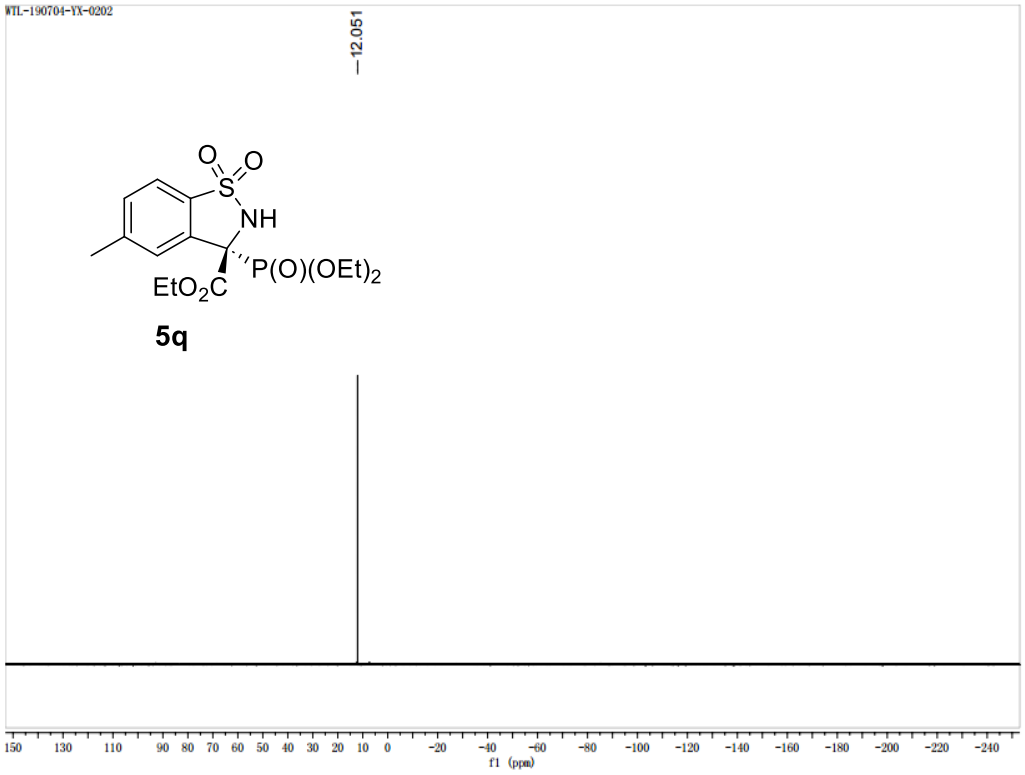

wt1-20190709-yx-0203
7.896
7.648
7.628
7.425
7.423
7.405
7.403
4.869
4.854
4.838
4.823
4.807
4.791
4.775
4.760
4.636
4.620
4.605
4.589
4.573
4.557
4.542
4.526
4.423
4.405
4.396
4.387
4.378
4.372
4.360
4.354
4.343
4.336
4.327
4.318
4.309
4.292
1.352
1.341
1.334
1.326
1.293
1.286
1.278
1.271
1.012
0.996
O
O
S
NH
P(O)(O^{i}Pr)$_2$
EtO$_2$C
5p
1.00
1.02
1.05
1.07
1.09
2.17
3.00
5.61
6.24
3.09
f1 (ppm)

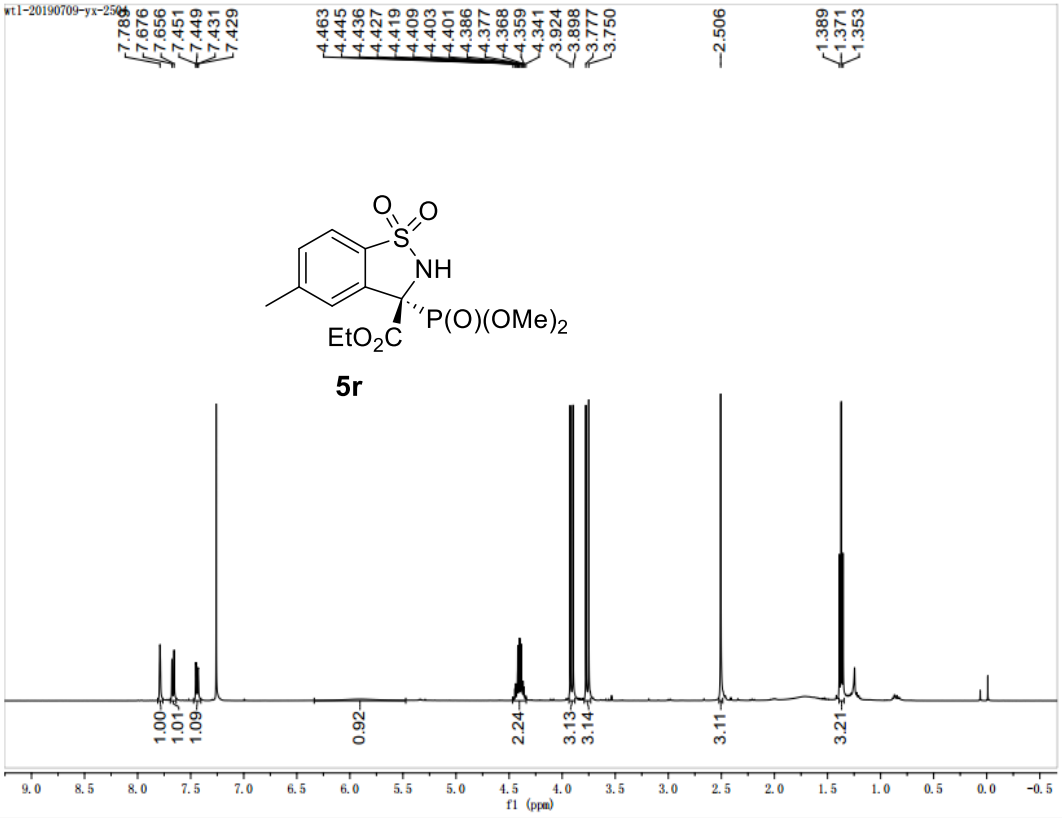

wt1-20190709-yx-0203
166.297
166.267
144.535
144.510
132.099
132.051
131.924
131.899
131.493
131.446
127.932
127.904
121.224
121.205
74.650
74.574
74.480
74.405
68.762
67.159
64.349
24.255
24.224
24.194
23.773
23.715
23.184
23.128
22.081
14.084
O
O
S
NH
P(O)(O^{i}Pr)$_2$
EtO$_2$C
5p
f1 (ppm)

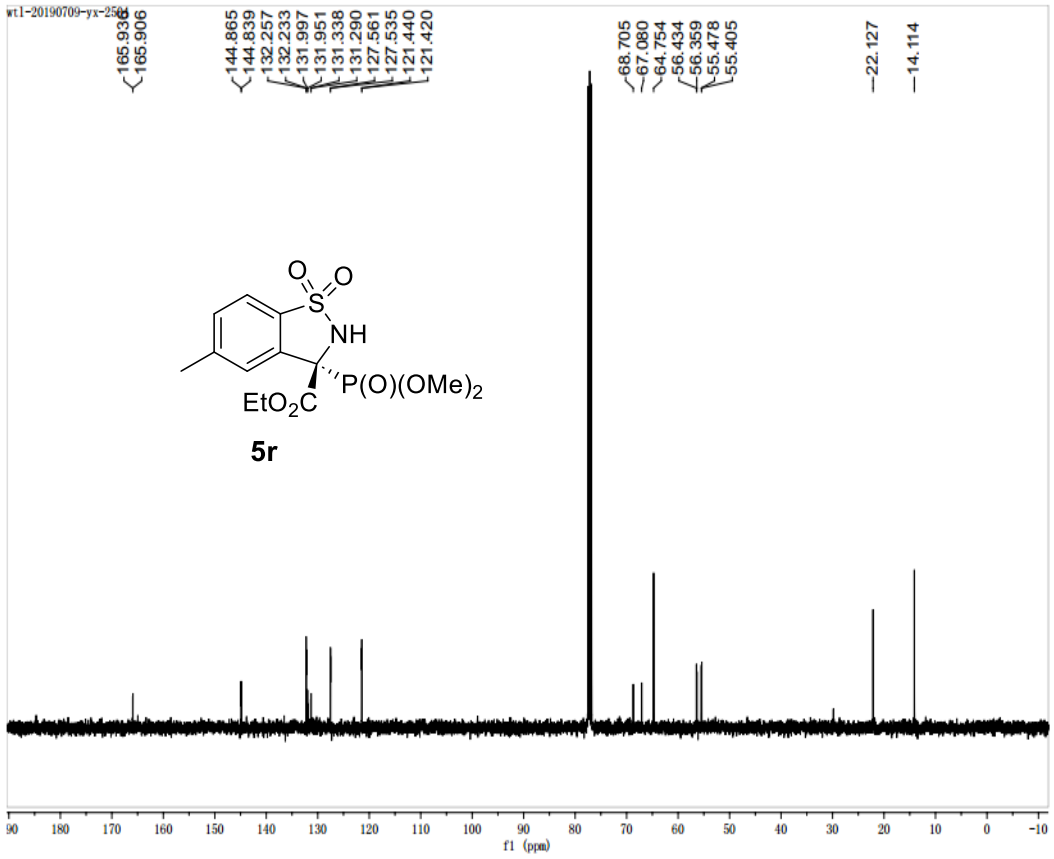

wt1-20190709-yx-0203
10.291
NH
P(O)(OiPr)2
EtO2C
5p
f1 (ppm)

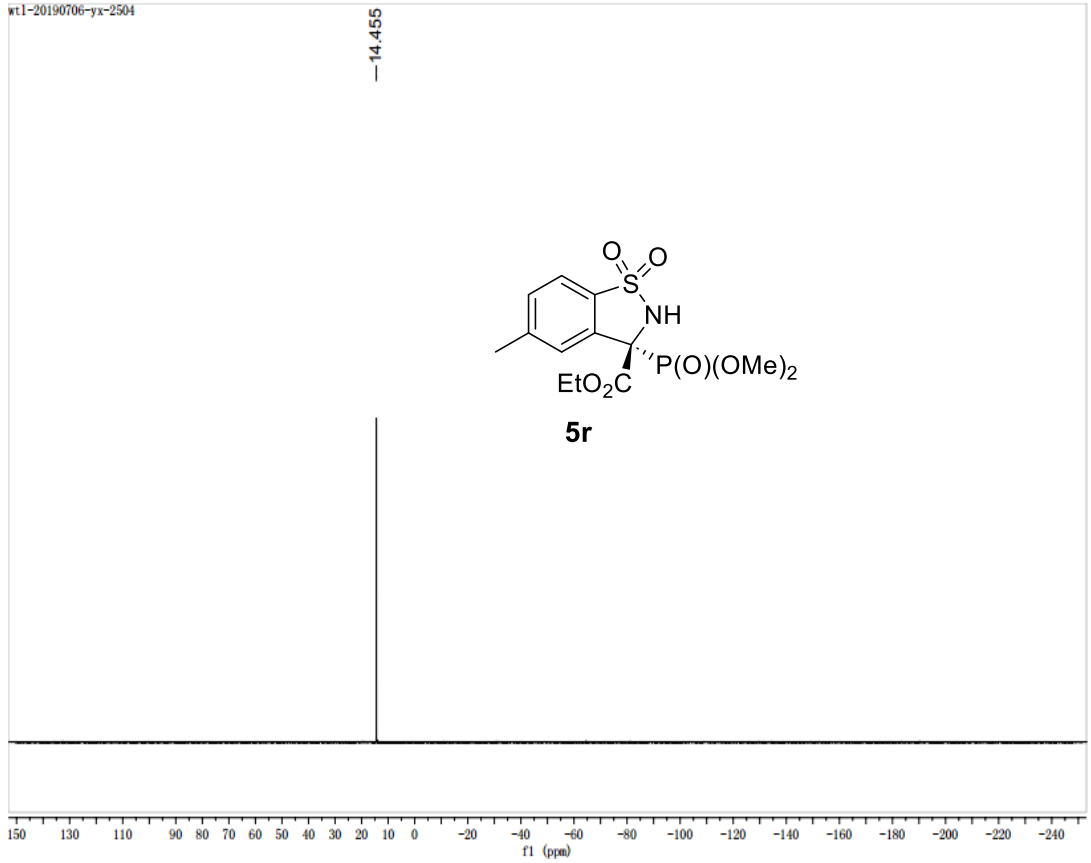

NH
P(O)(OEt)2
EtO2C
5q
1.00
1.02
1.07
1.00
2.19
2.16
2.25
3.17
3.11
3.17
3.24
f1 (ppm)

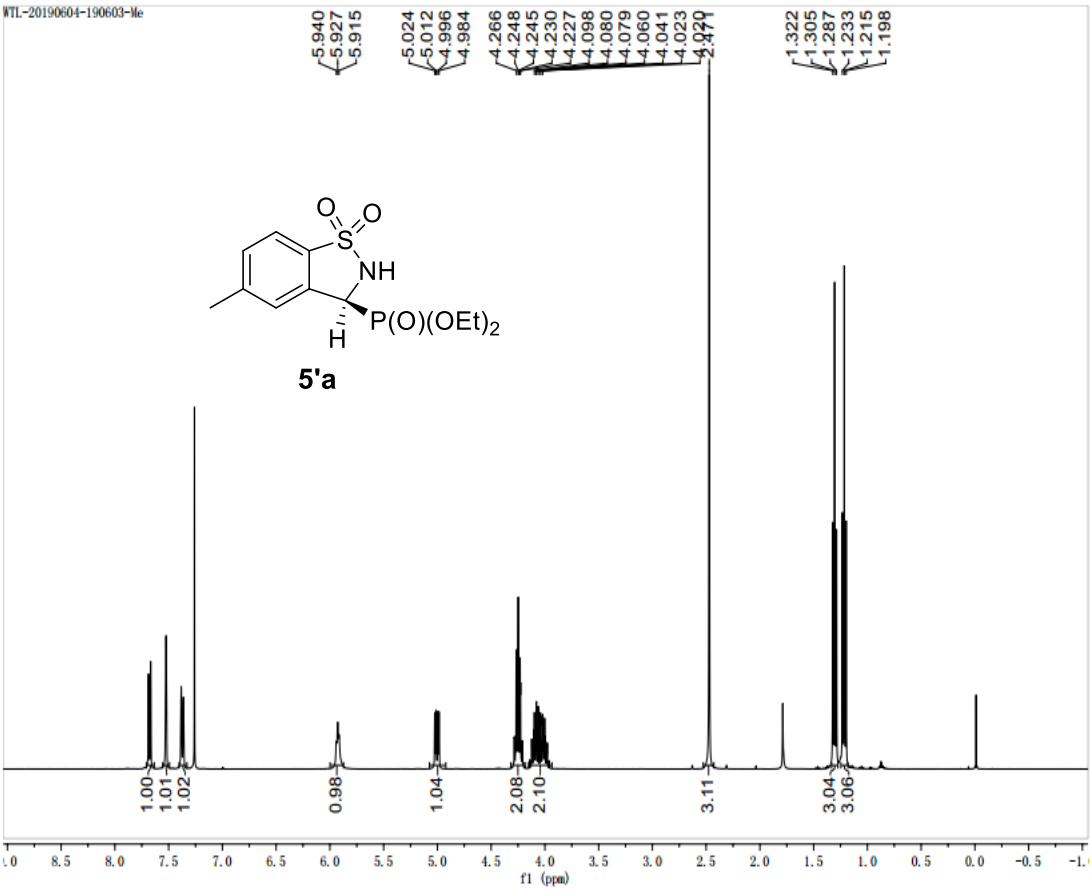

WTL-190704-YX-0202
166.116
166.087
144.682
144.657
132.113
132.085
132.035
131.536
131.492
127.816
127.789
121.340
121.321
68.749
67.142
65.992
65.919
65.234
65.161
64.599
22.133
16.577
16.523
16.381
16.327
14.119
O
O
S
NH
P(O)(OEt)2
EtO2C
5q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

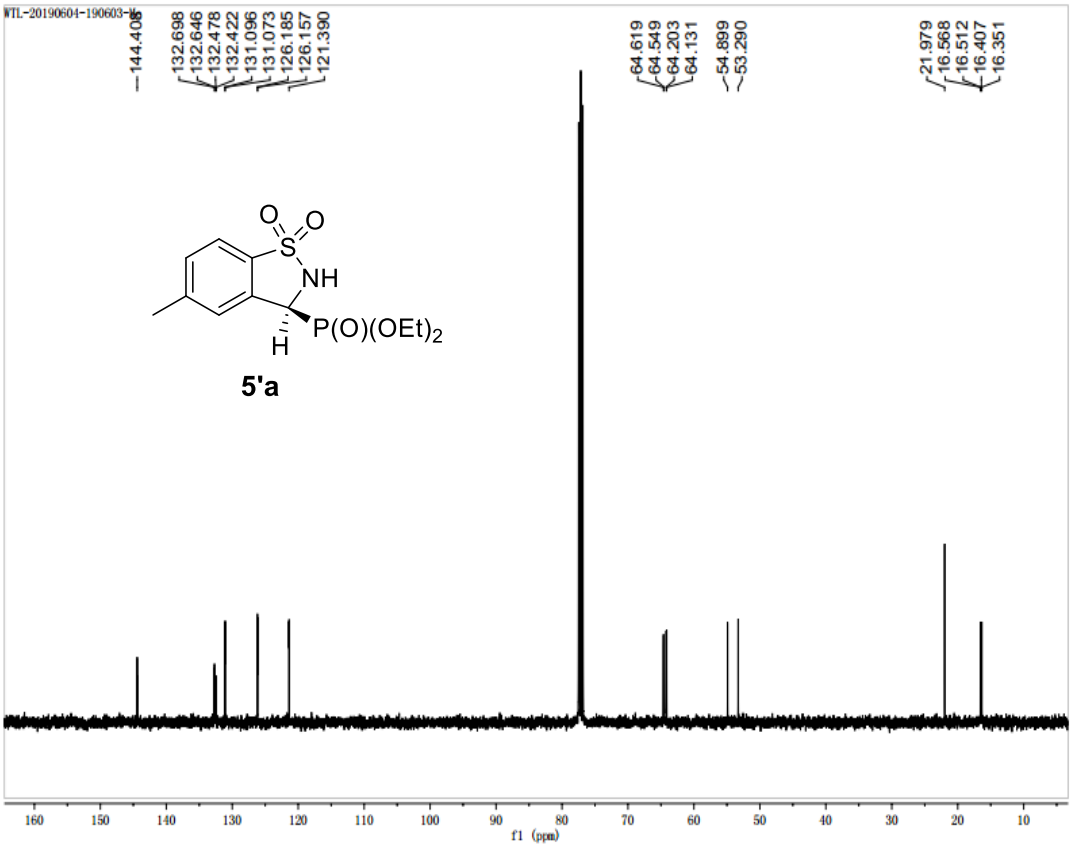

WTL-190704-YX-0202
12.051
O
O
S
NH
P(O)(OEt)2
EtO2C
5q
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)


7.789
7.676
7.656
7.451
7.449
7.431
7.429
4.463
4.445
4.436
4.427
4.419
4.409
4.403
4.401
4.386
4.377
4.368
4.359
4.341
3.924
3.898
3.777
3.750
2.506
1.389
1.371
1.353
O
O
S
NH
P(O)(OMe)2
EtO2C
5r
1.00
1.01
1.09
0.92
2.24
3.13
3.14
3.11
3.21
f1 (ppm)

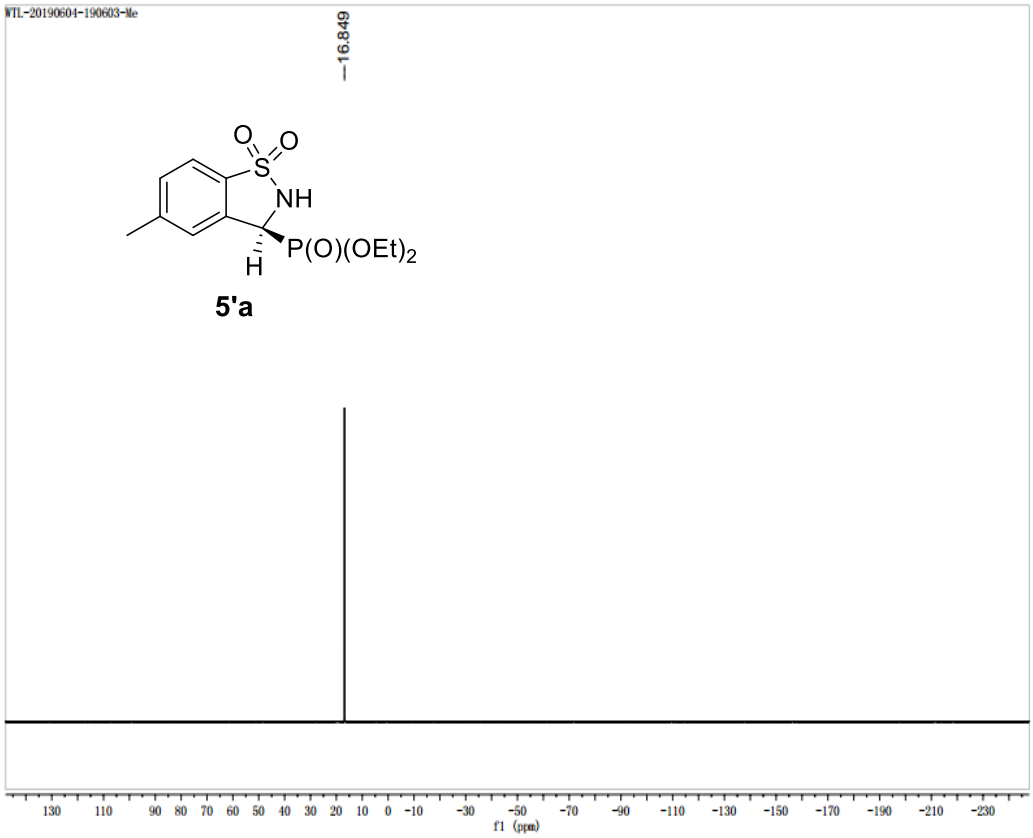

165.936
165.906
144.865
144.839
132.257
132.233
131.997
131.951
131.338
131.290
127.561
127.535
121.440
121.420
68.705
67.080
64.754
56.434
56.359
55.478
55.405
22.127
14.114
O
O
S
NH
P(O)(OMe)2
EtO2C
5r
f1 (ppm)


wt1-20190706-yx-2504
14.455
O
O
S
NH
P(O)(OMe)2
EtO2C
5r
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

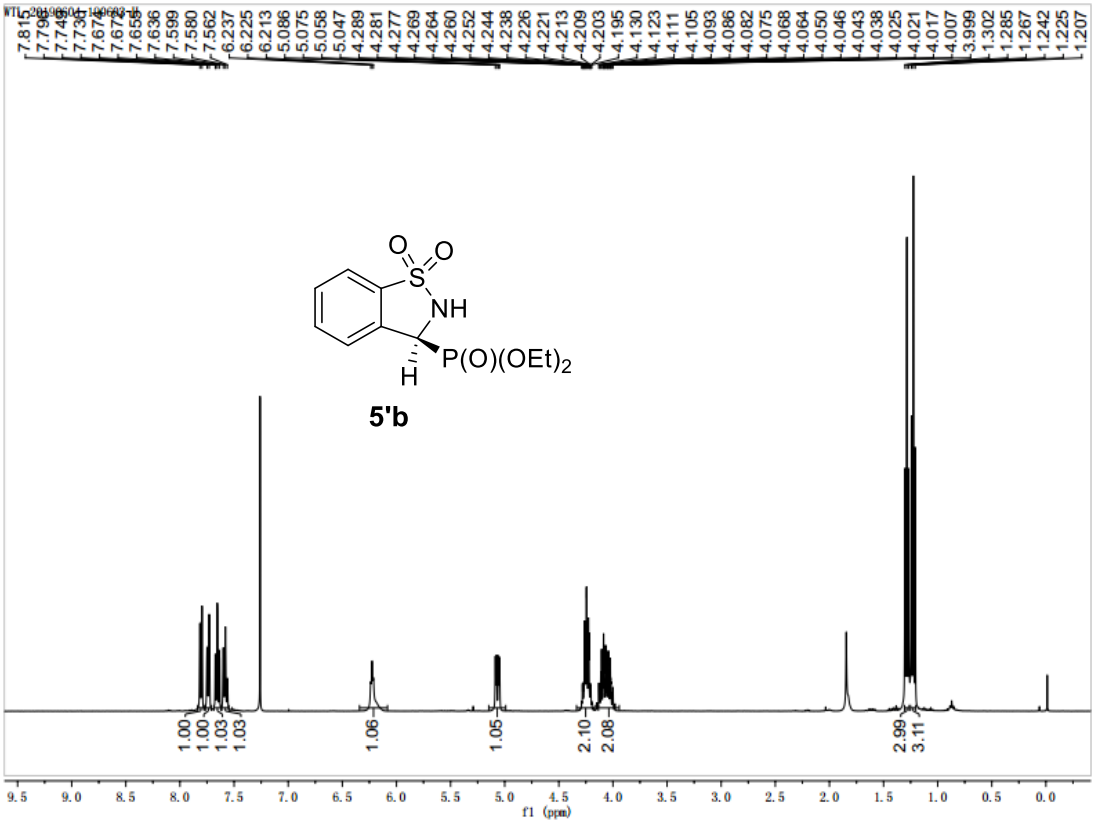

WTL-20190604-190603-Me
5.940
5.927
5.915
5.024
5.012
4.996
4.984
4.266
4.248
4.245
4.230
4.227
4.098
4.080
4.079
4.060
4.041
4.023
4.020
2.471
1.322
1.305
1.287
1.233
1.215
1.198
O
O
S
NH
P(O)(OEt)2
H
5'a
1.00
1.01
1.02
0.98
1.04
2.08
2.10
3.11
3.04
3.06
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

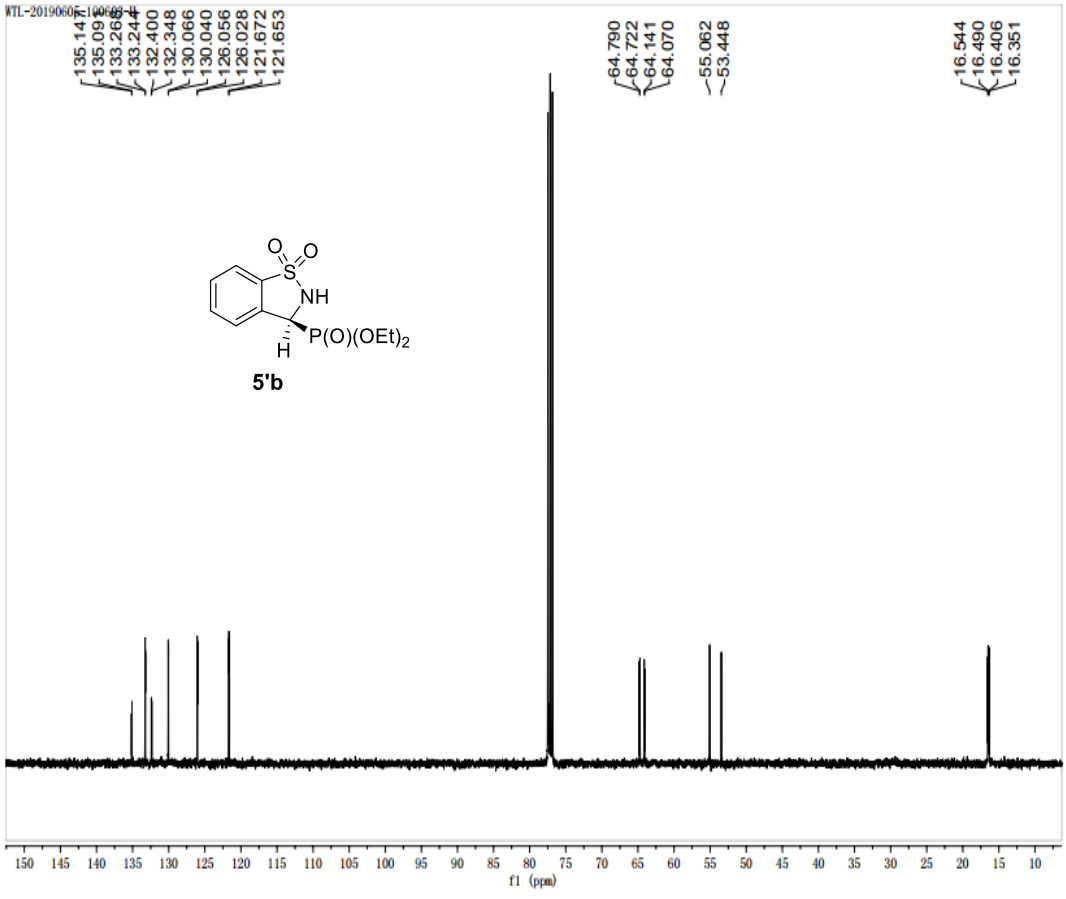

WTL-20190604-190603-Me
144.408
132.698
132.646
132.478
132.422
131.096
131.073
126.185
126.157
121.390
64.619
64.549
64.203
64.131
54.899
53.290
21.979
16.568
16.512
16.407
16.351
O
O
S
NH
H
P(O)(OEt)2
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

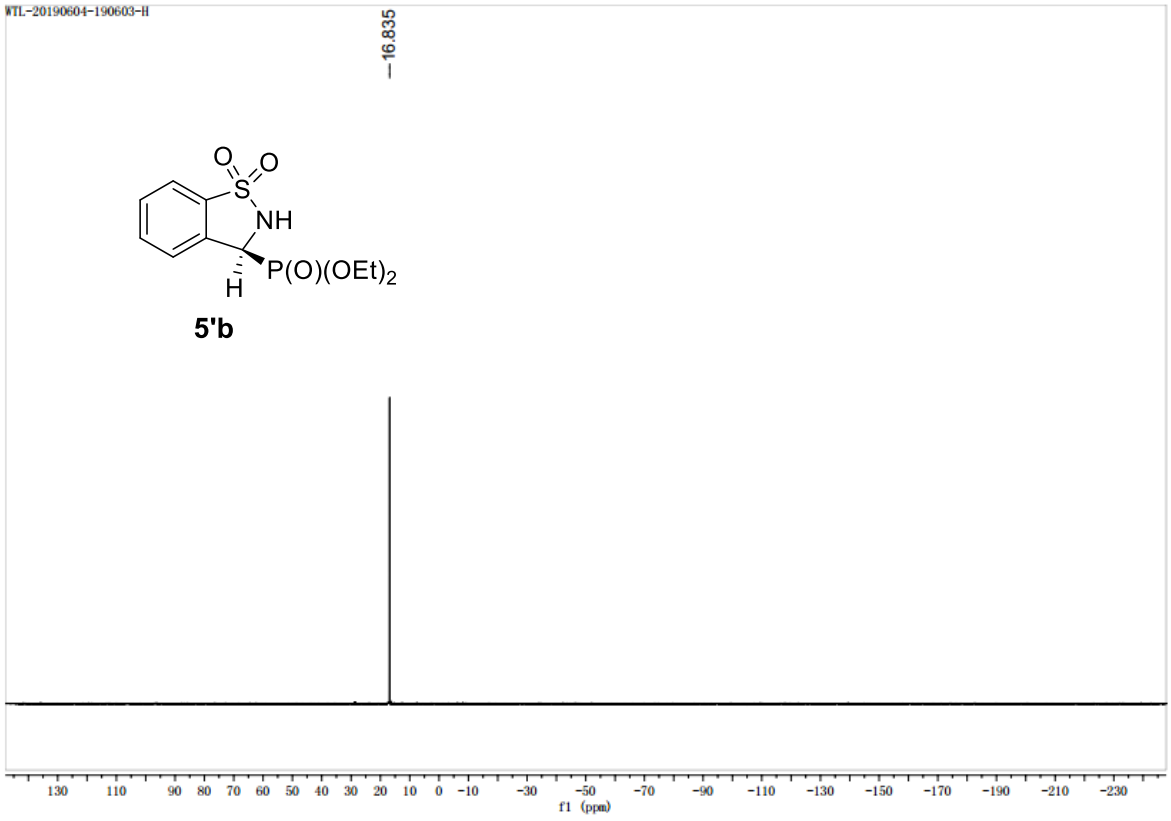
5'a

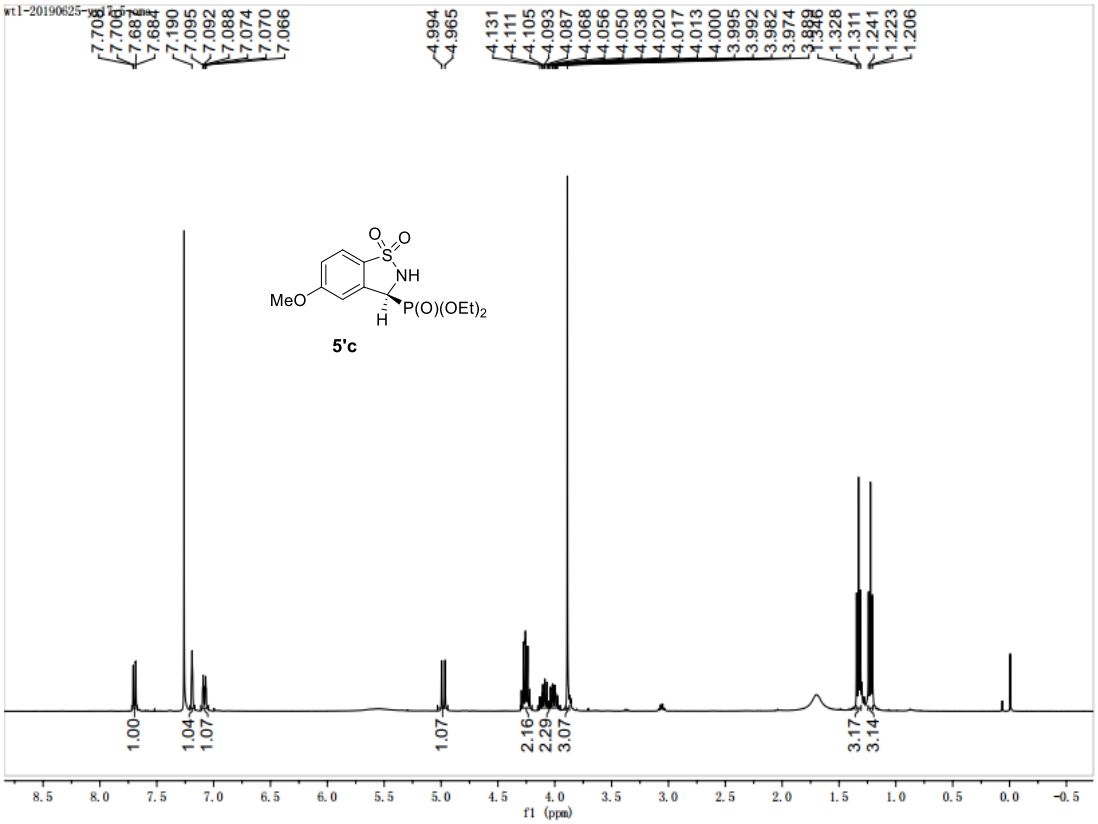

WTL-20190604-190603-Me
16.849
O
O
S
NH
H
P(O)(OEt)2
130
110
90
80
70
60
50
40
30
20
10
0
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
f1 (ppm)

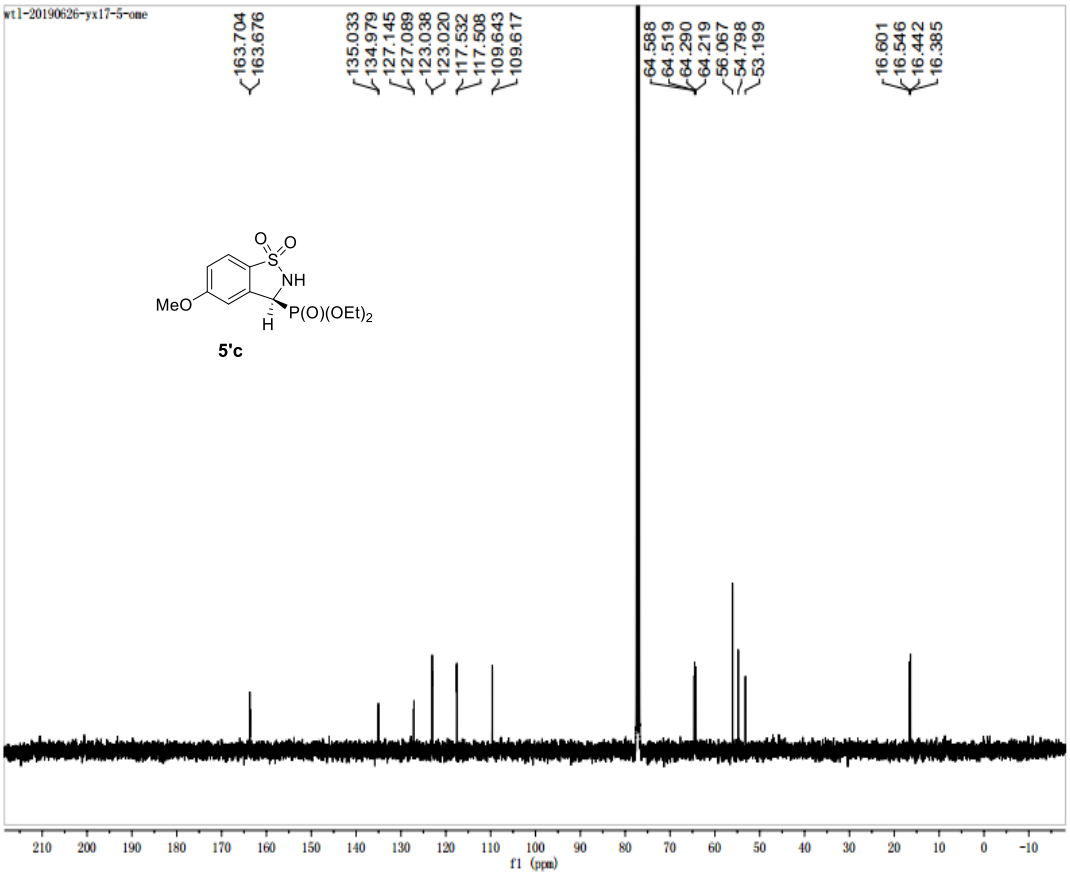
5'a

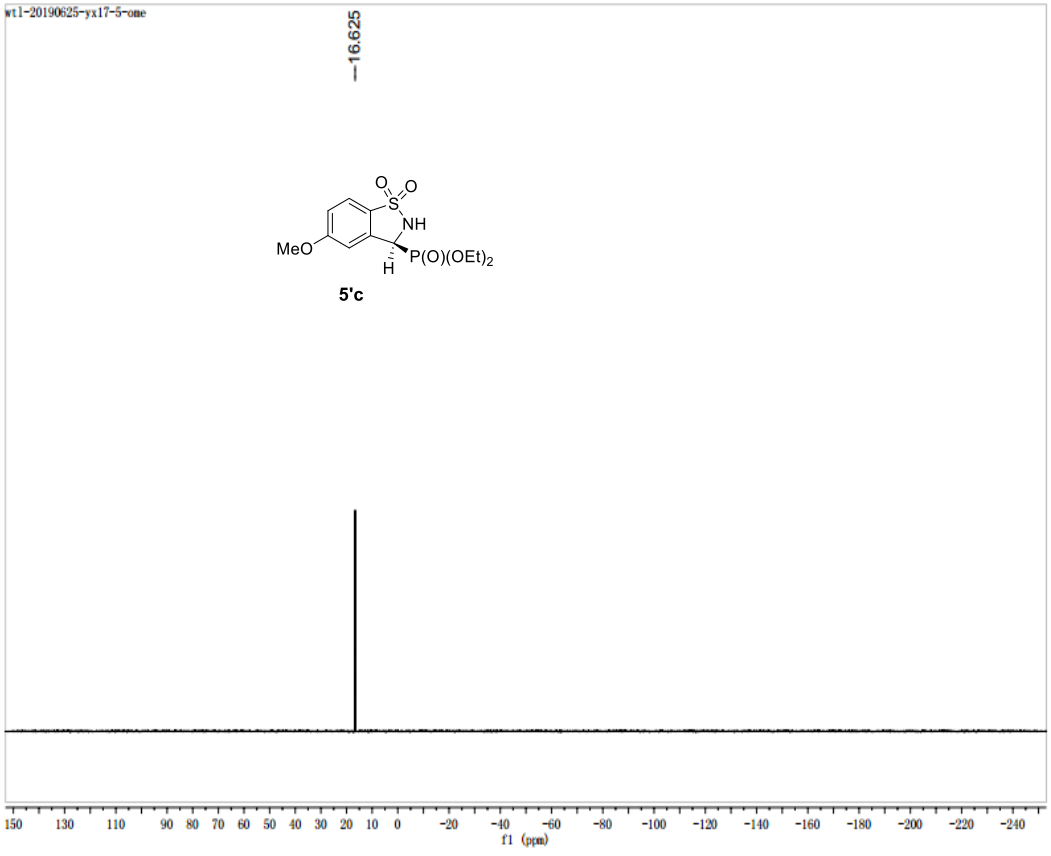

7.815
7.796
7.743
7.734
7.674
7.672
7.658
7.636
7.599
7.580
7.562
6.237
6.225
6.213
5.086
5.075
5.058
5.047
4.289
4.281
4.277
4.269
4.264
4.260
4.252
4.244
4.238
4.226
4.221
4.213
4.209
4.203
4.195
4.130
4.123
4.111
4.105
4.093
4.086
4.082
4.075
4.068
4.064
4.050
4.046
4.043
4.038
4.025
4.021
4.017
4.007
3.999
1.302
1.285
1.267
1.242
1.225
1.207
O
O
S
NH
P(O)(OEt)2
H
5'b
1.00
1.00
1.03
1.03
1.06
1.05
2.10
2.08
2.99
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

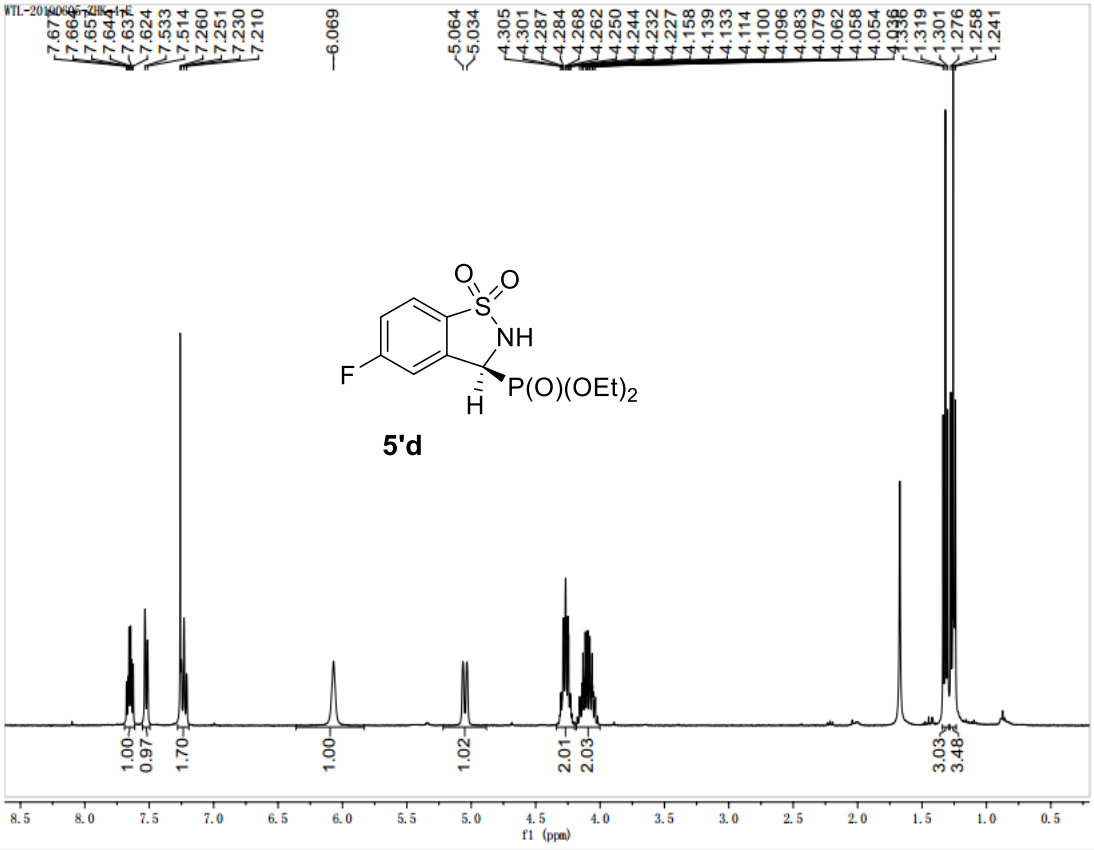

135.141
135.091
133.266
133.244
132.400
132.348
130.066
130.040
126.056
126.028
121.672
121.653
64.790
64.722
64.141
64.070
55.062
53.448
16.544
16.490
16.406
16.351
O
O
S
NH
P(O)(OEt)2
H
5'b
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

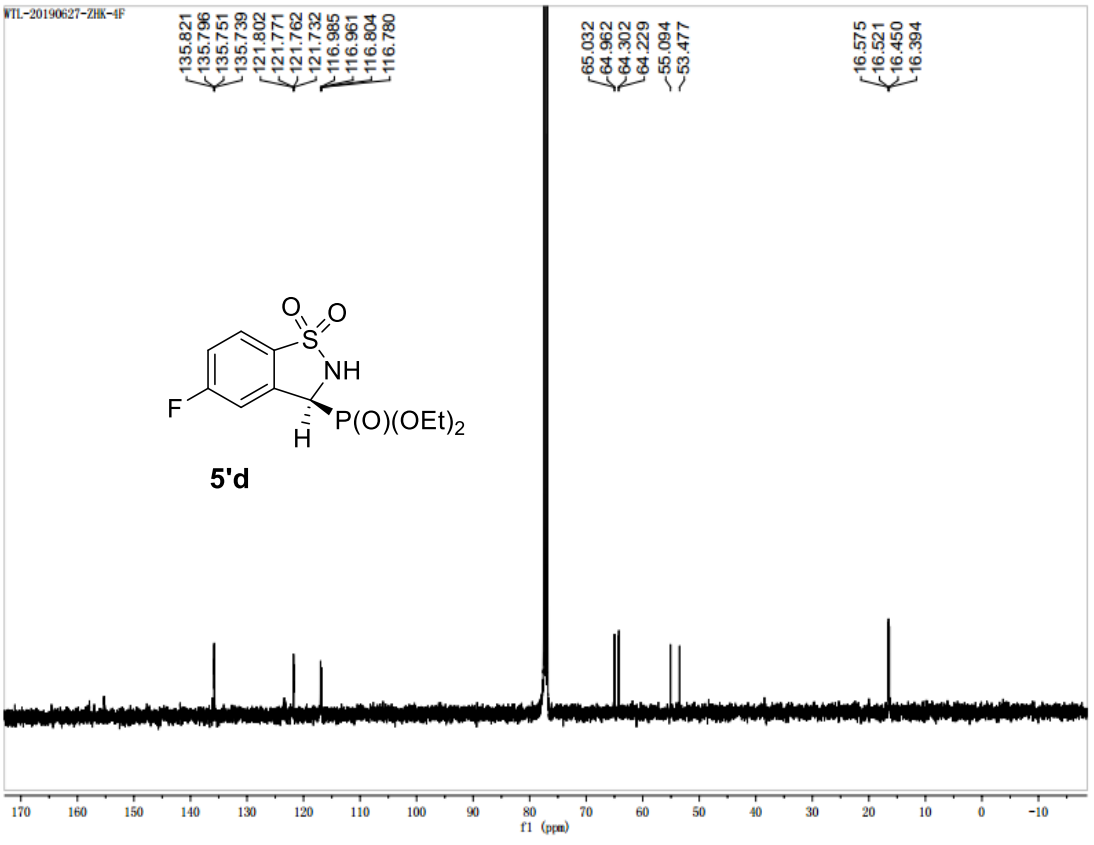

WTL-20190604-190603-H
16.835
O
O
S
NH
P(O)(OEt)2
H
5'b
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

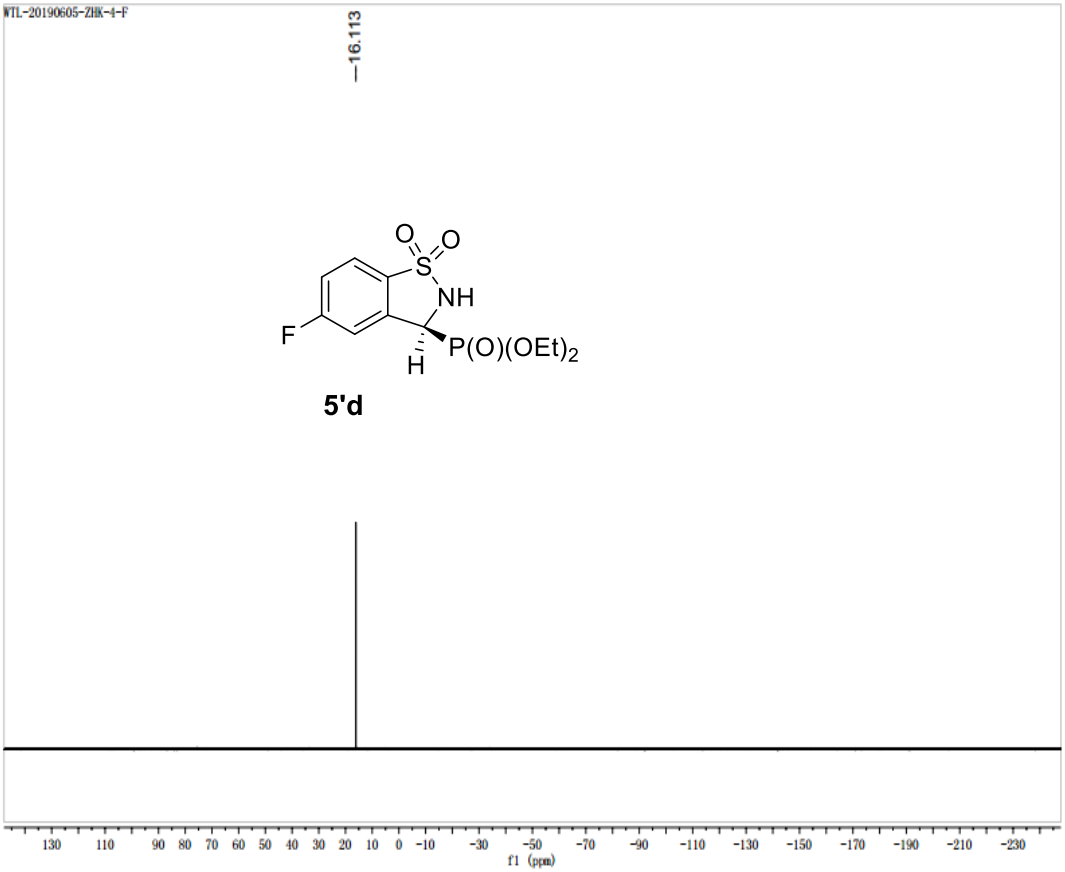

wtl-20190625-
7.708
7.706
7.684
7.190
7.095
7.092
7.088
7.074
7.070
7.066
4.994
4.965
4.131
4.111
4.105
4.093
4.087
4.068
4.056
4.050
4.038
4.020
4.017
4.013
4.000
3.995
3.992
3.982
3.974
1.328
1.311
1.241
1.223
1.206
O
O
S
NH
MeO
P(O)(OEt)2
H
5'c
1.00
1.04
1.07
1.07
2.16
2.29
3.07
3.17
3.14
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


wt1-20190626-yx17-5-one
163.704
163.676
135.033
134.979
127.145
127.089
123.038
123.020
117.532
117.508
109.643
109.617
64.588
64.519
64.290
64.219
56.067
54.798
53.199
16.601
16.546
16.442
16.385
MeO
NH
P(O)(OEt)2
H
5'c
f1 (ppm)

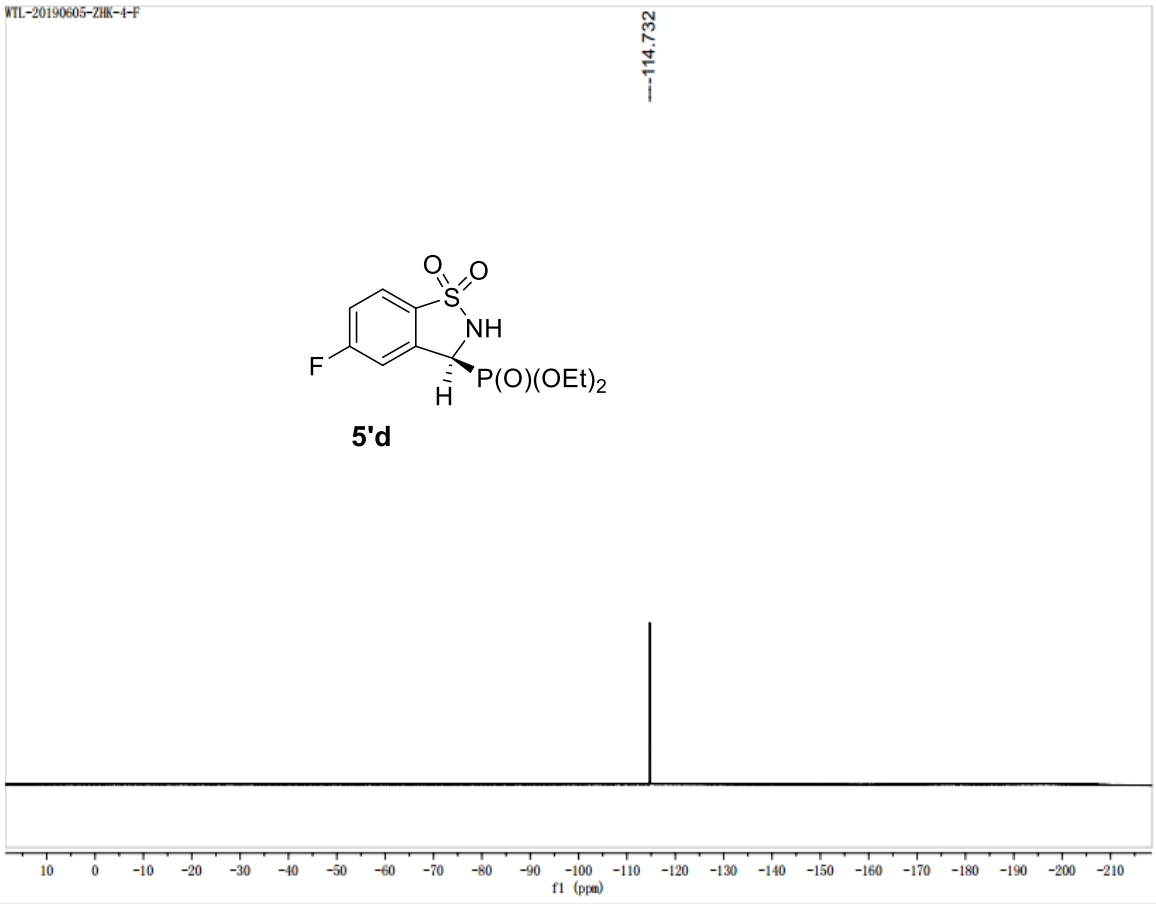

wt1-20190625-yx17-5-one
16.625
MeO
NH
P(O)(OEt)2
H
5'c
f1 (ppm)


7.678
7.664
7.651
7.644
7.637
7.624
7.533
7.514
7.260
7.251
7.230
7.210
6.069
5.064
5.034
4.305
4.301
4.287
4.284
4.268
4.262
4.250
4.244
4.232
4.227
4.158
4.139
4.133
4.114
4.100
4.096
4.083
4.079
4.062
4.058
4.054
1.319
1.301
1.276
1.258
1.241
O
O
S
NH
F
P(O)(OEt)2
H
5'd
1.00
0.97
1.70
1.00
1.02
2.01
2.03
3.03
3.48
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

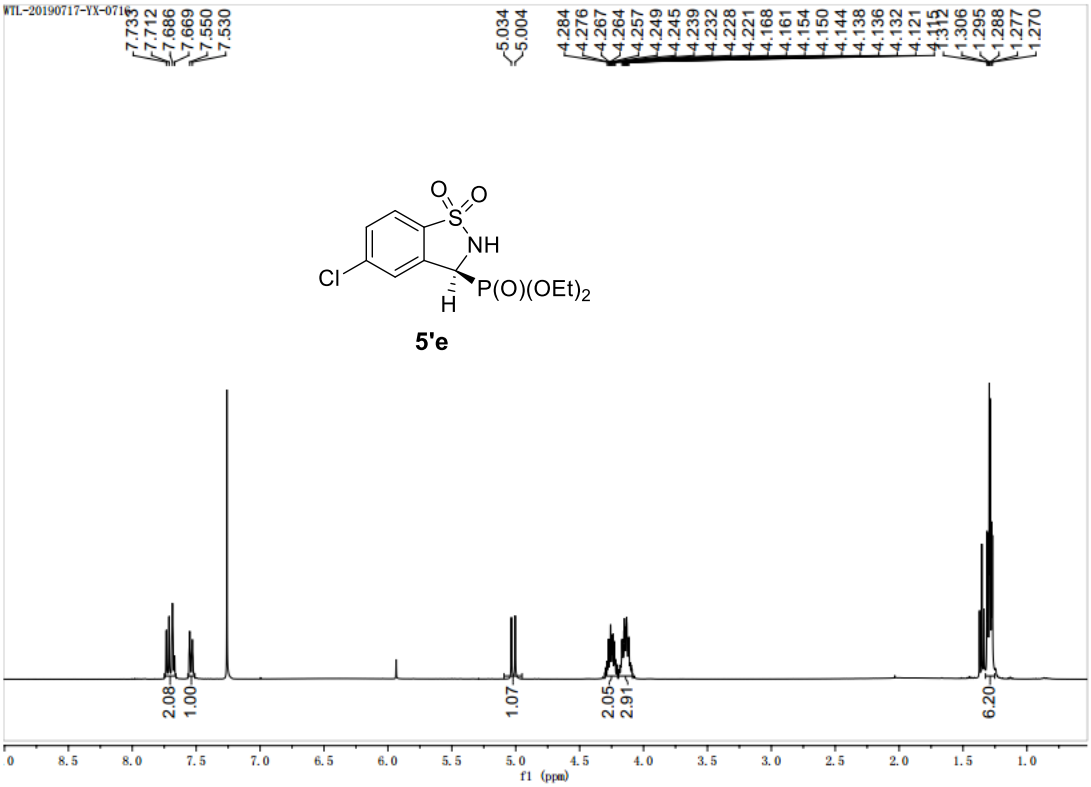

WTL-20190627-ZHK-4F
135.821
135.796
135.751
135.739
121.802
121.771
121.762
121.732
116.985
116.961
116.804
116.780
65.032
64.962
64.302
64.229
55.094
53.477
16.575
16.521
16.450
16.394
O
O
S
NH
F
P(O)(OEt)2
H
5'd
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

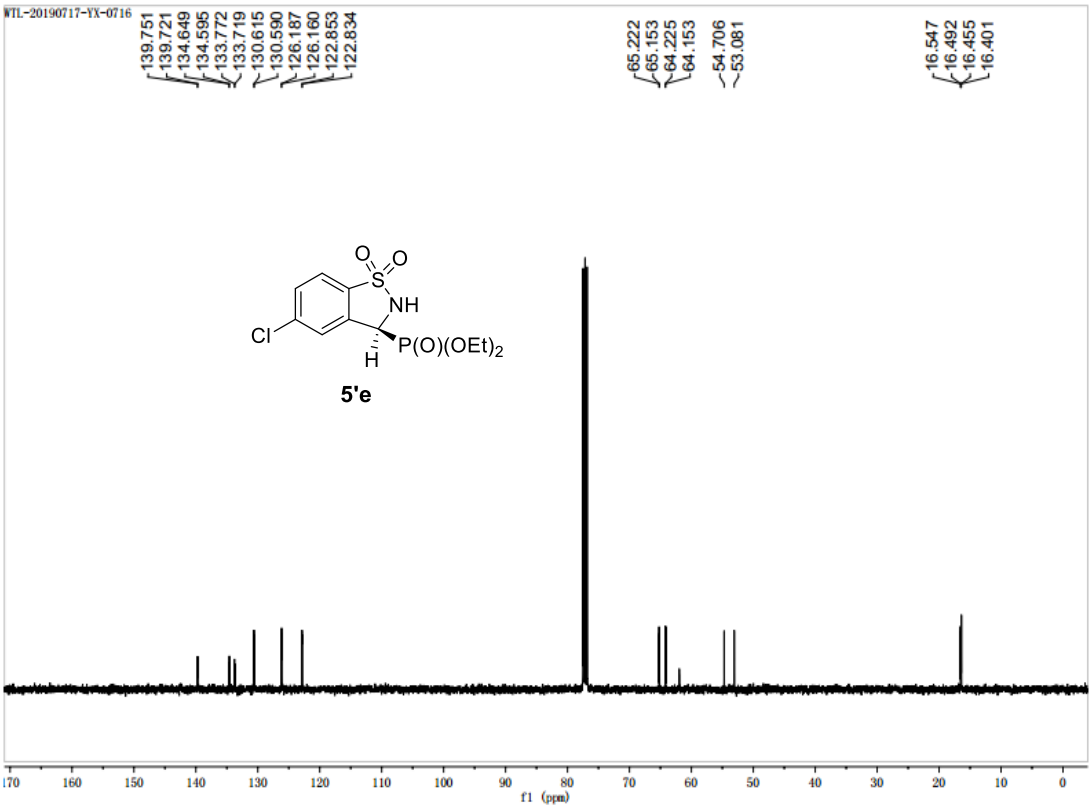

WTL-20190605-ZHK-4-F
-16.113
O
O
S
NH
F
H
P(O)(OEt)2
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

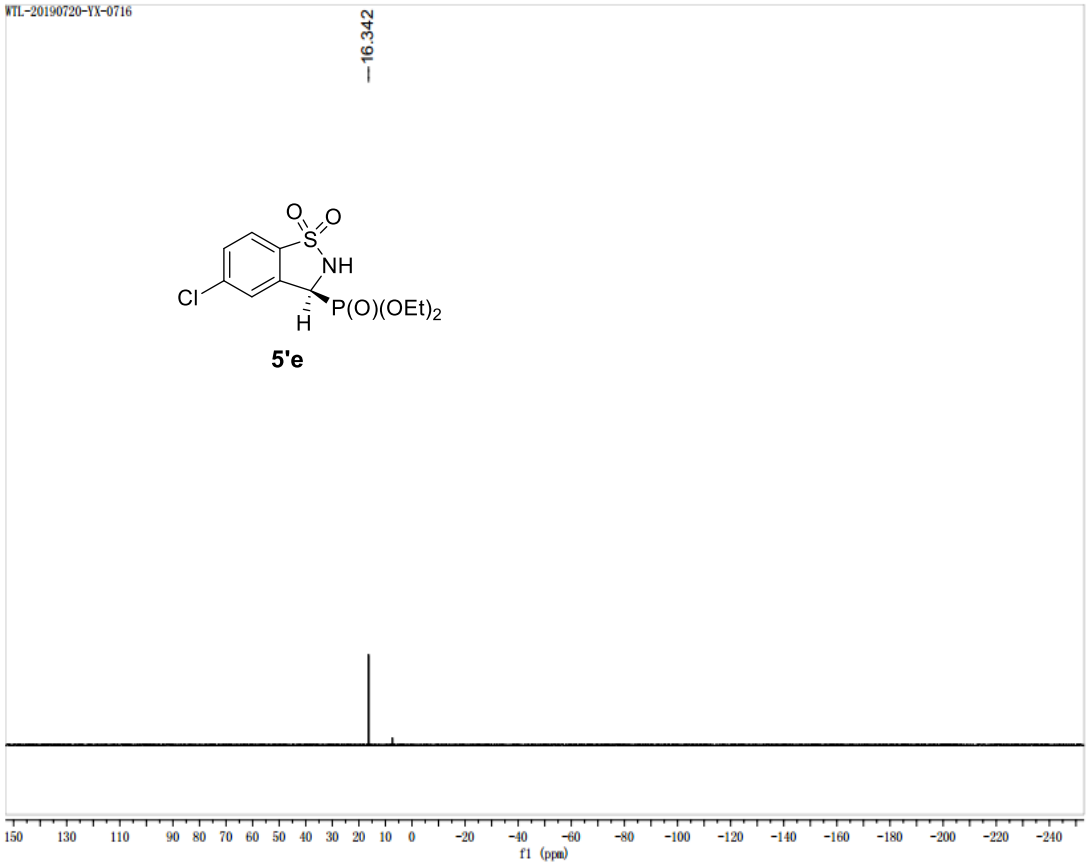
5'd

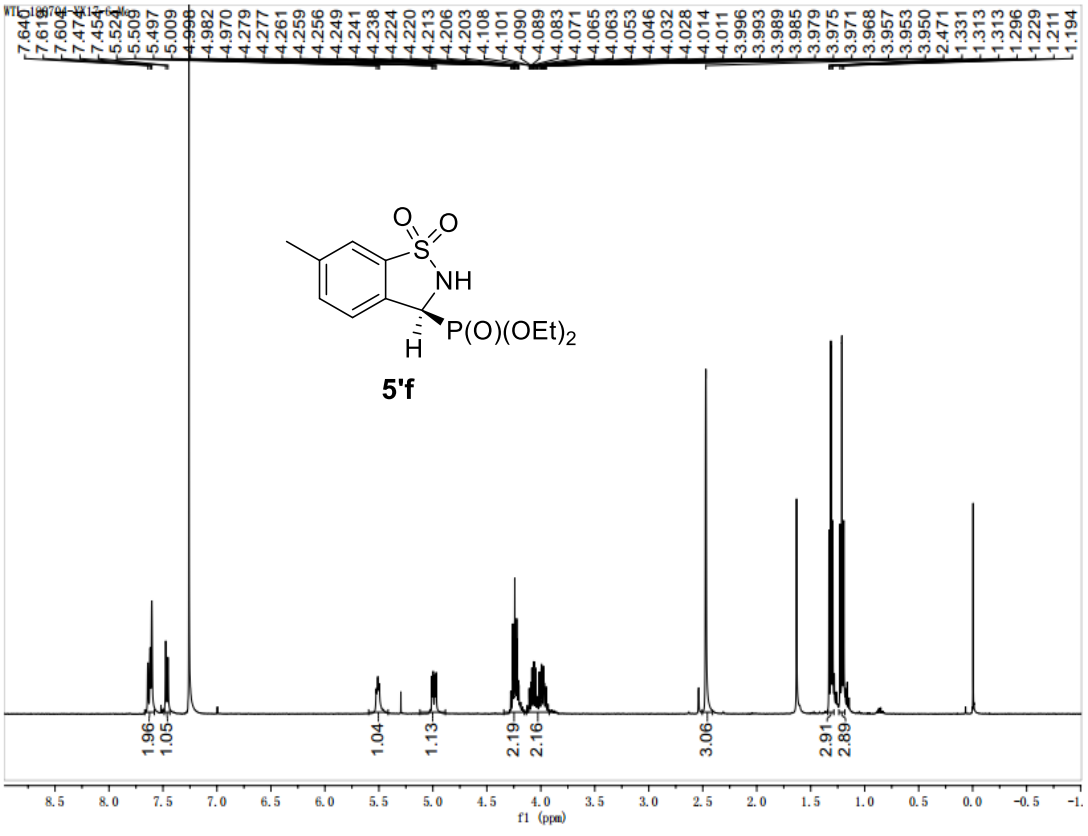

WTL-20190605-ZHK-4-F
-114.732
O
O
S
NH
F
H
P(O)(OEt)2
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

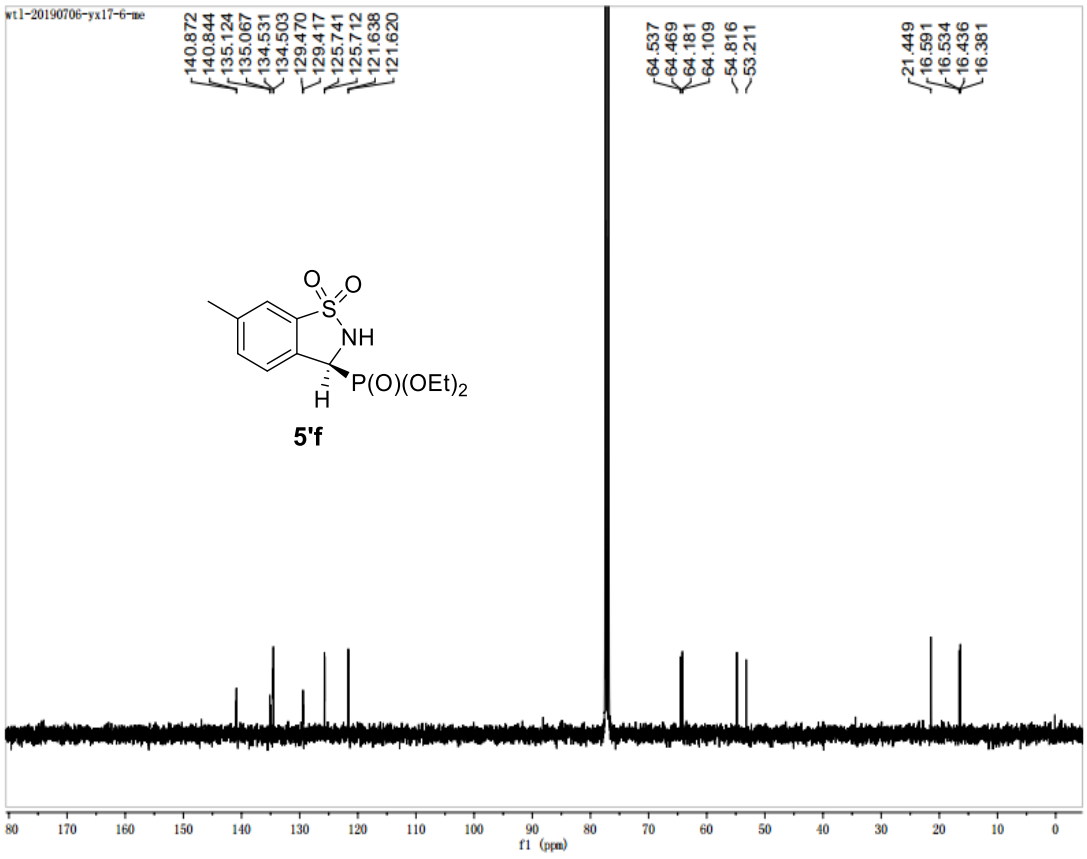
5'd


WTL-20190717-YX-0716
7.733
7.712
7.686
7.669
7.550
7.530
5.034
5.004
4.284
4.276
4.267
4.264
4.257
4.249
4.245
4.239
4.232
4.228
4.221
4.168
4.161
4.154
4.150
4.144
4.138
4.136
4.132
4.121
1.312
1.306
1.295
1.288
1.277
1.270
O
O
S
NH
Cl
P(O)(OEt)2
H
5'e
2.08
1.00
1.07
2.05
2.91
6.20
f1 (ppm)

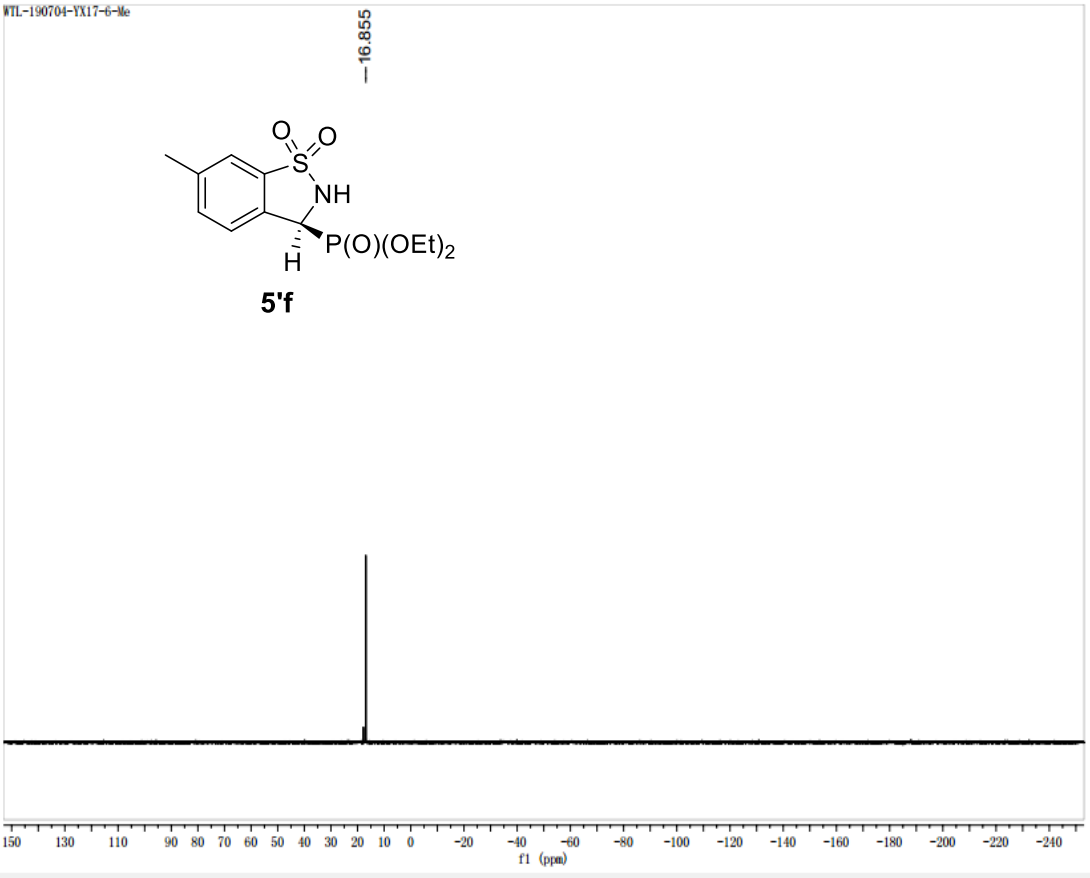

WTL-20190717-YX-0716
139.751
139.721
134.649
134.595
133.772
133.719
130.615
130.590
126.187
126.160
122.853
122.834
65.222
65.153
64.225
64.153
54.706
53.081
16.547
16.492
16.455
16.401
O
O
S
NH
Cl
P(O)(OEt)2
H
5'e
f1 (ppm)


WTL-20190720-YX-0716
16.342
O
O
S
NH
Cl
H
P(O)(OEt)2
5'e
f1 (ppm)

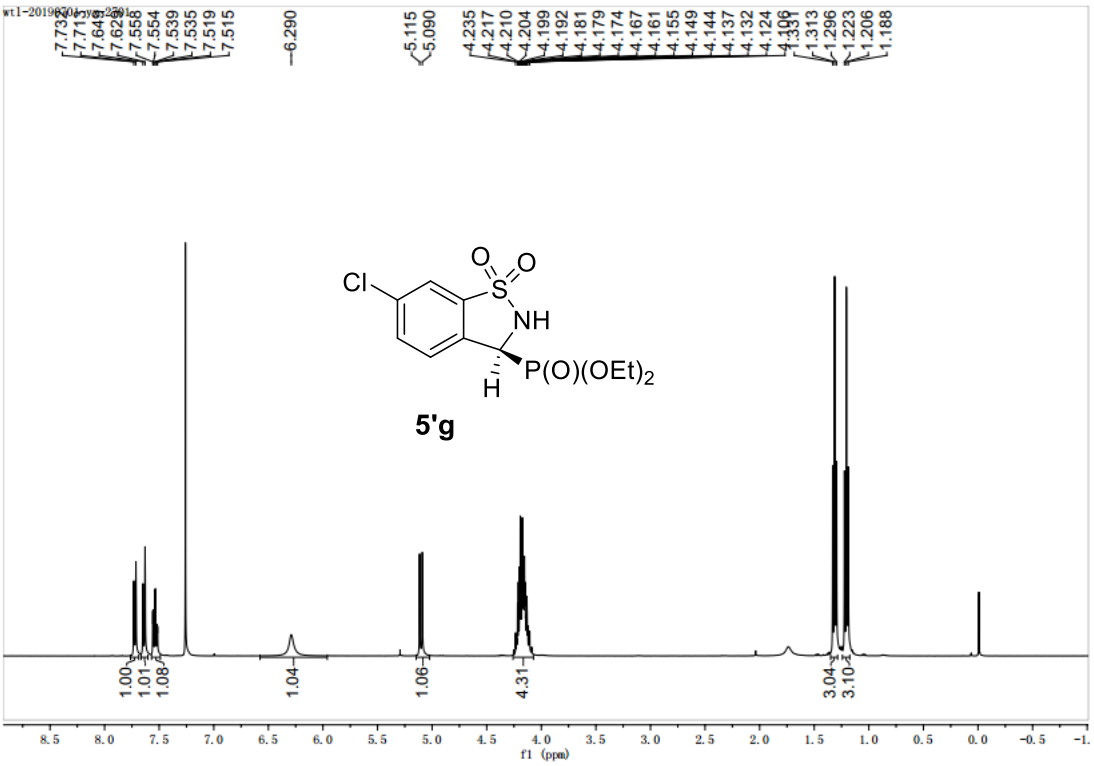

O
O
S
NH
H
P(O)(OEt)2
5'f
1.96
1.05
1.04
1.13
2.19
2.16
3.06
2.91
2.89
f1 (ppm)

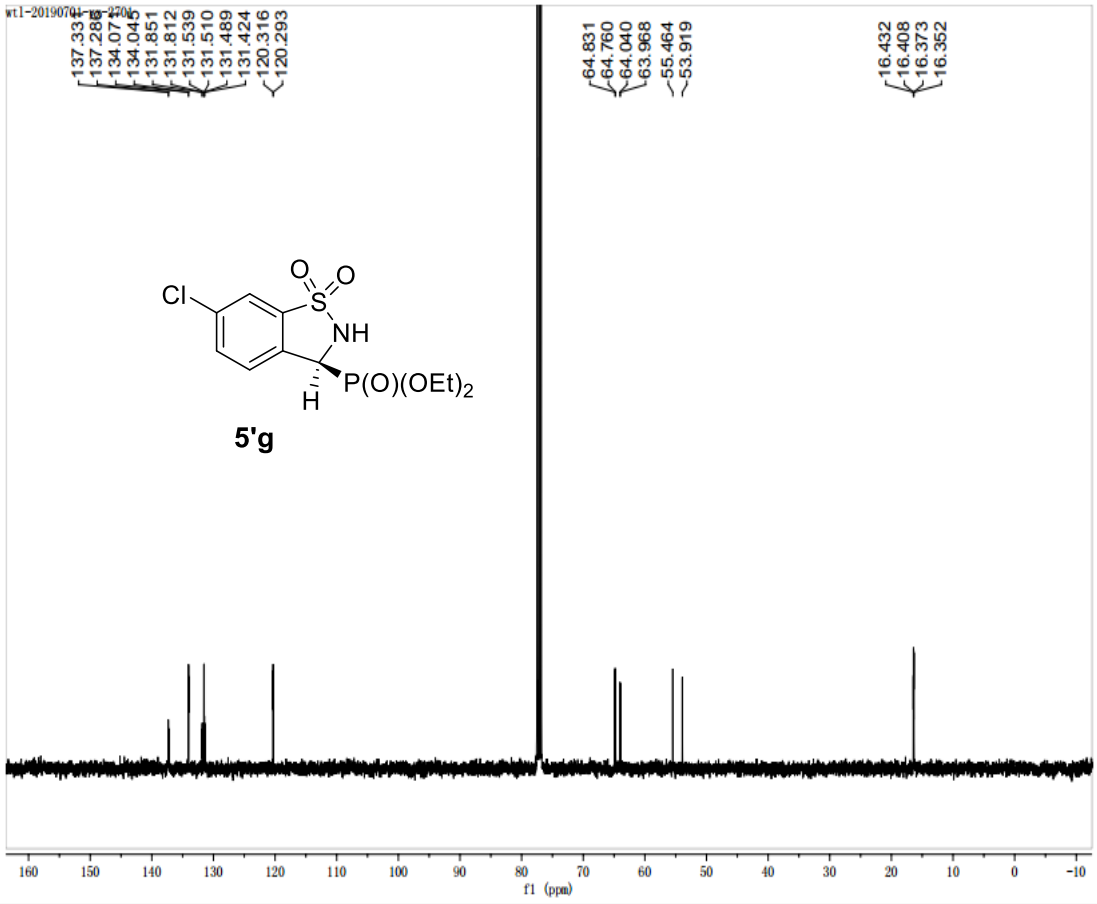

wtl-20190706-yx17-6-me
140.872
140.844
135.124
135.067
134.531
134.503
129.470
129.417
125.741
125.712
121.638
121.620
64.537
64.469
64.181
64.109
54.816
53.211
21.449
16.591
16.534
16.436
16.381
O
O
S
NH
P(O)(OEt)2
H
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

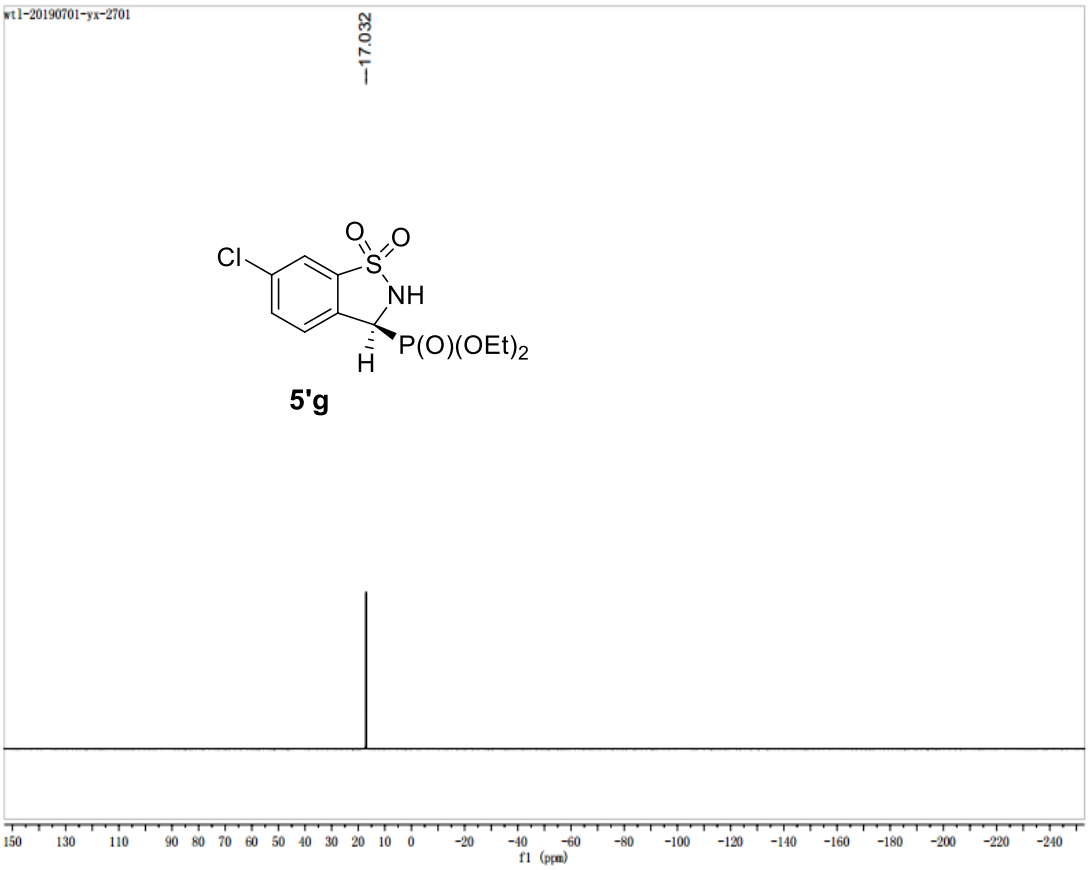
5'f


WTL-190704-YX17-6-Me
16.855
O
O
S
NH
P(O)(OEt)2
H
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)

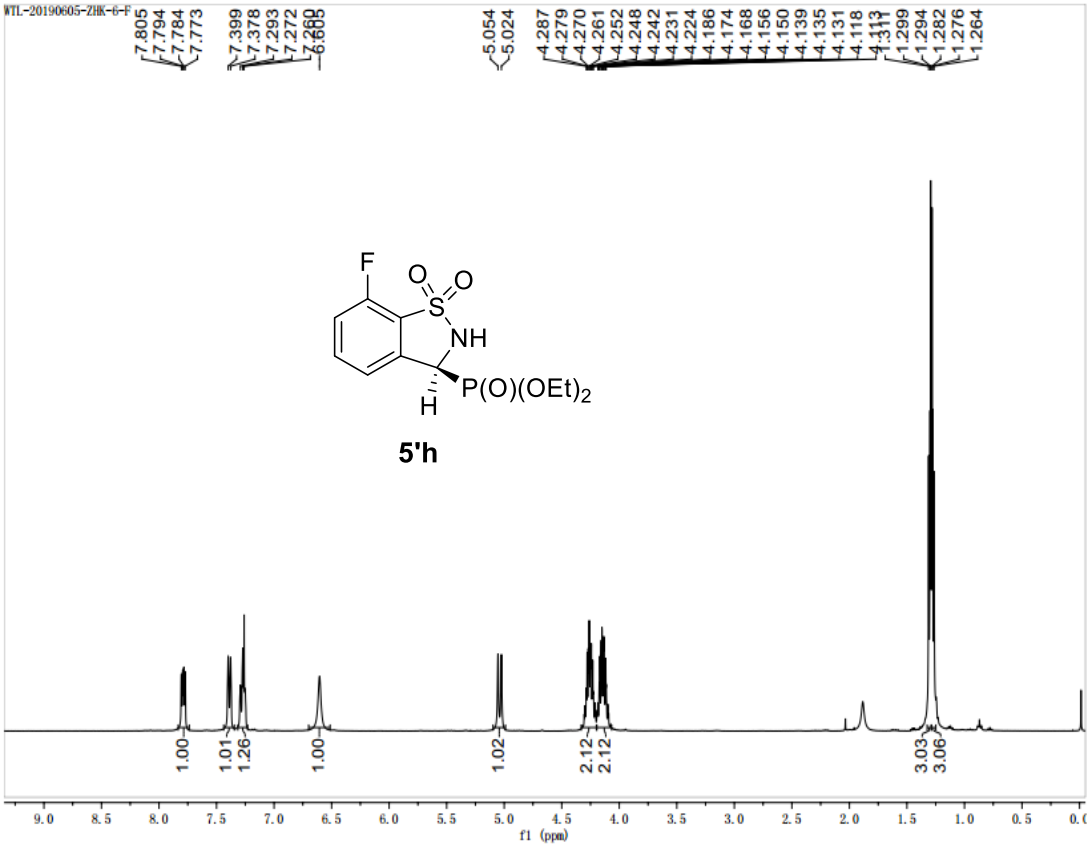
5'f


7.734
7.711
7.643
7.623
7.558
7.554
7.539
7.535
7.519
7.515
6.290
5.115
5.090
4.235
4.217
4.210
4.204
4.199
4.192
4.181
4.179
4.174
4.167
4.161
4.155
4.149
4.144
4.137
4.132
4.124
4.106
1.331
1.313
1.296
1.223
1.206
1.188
Cl
O
O
S
NH
P(O)(OEt)2
H
5'g
1.00
1.01
1.08
1.04
1.06
4.31
3.04
3.10
f1 (ppm)

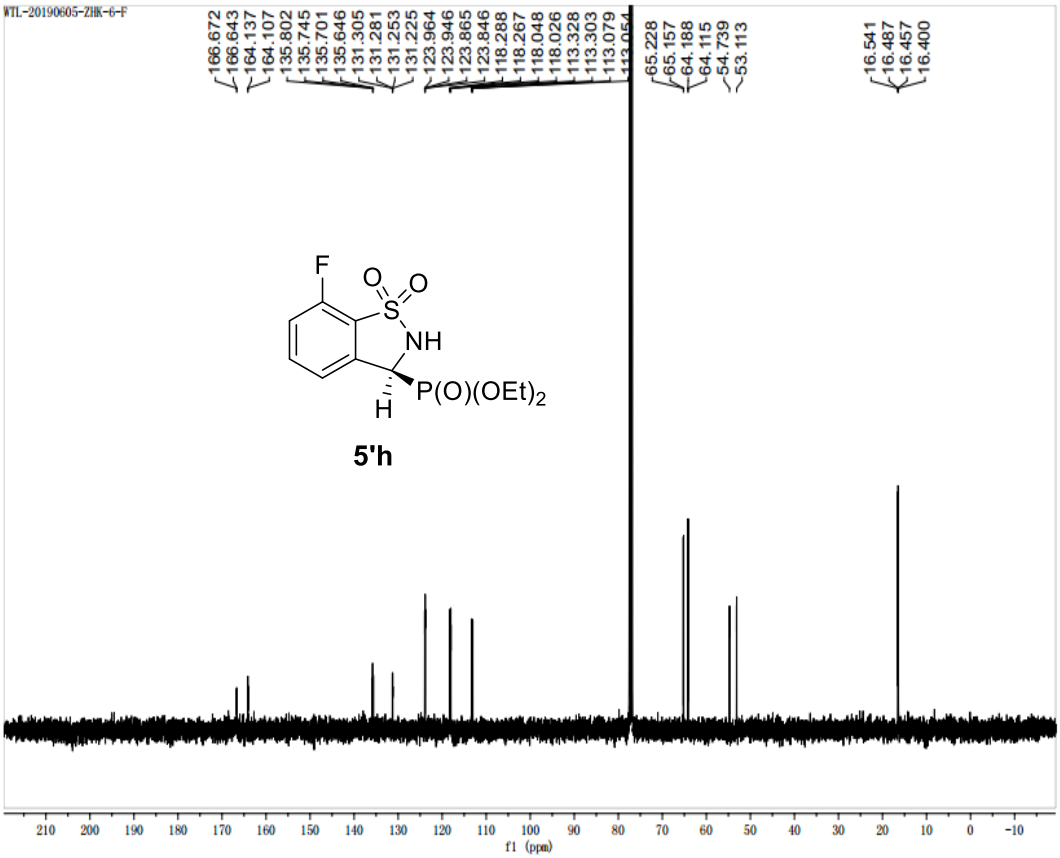

137.331
137.280
134.071
134.045
131.851
131.812
131.539
131.510
131.489
131.424
120.316
120.293
64.831
64.760
64.040
63.968
55.464
53.919
16.432
16.408
16.373
16.352
Cl
O
O
S
NH
P(O)(OEt)2
H
5'g
f1 (ppm)


wt1-20190701-yx-2701
17.032
Cl
O
O
S
NH
H
P(O)(OEt)2
f1 (ppm)

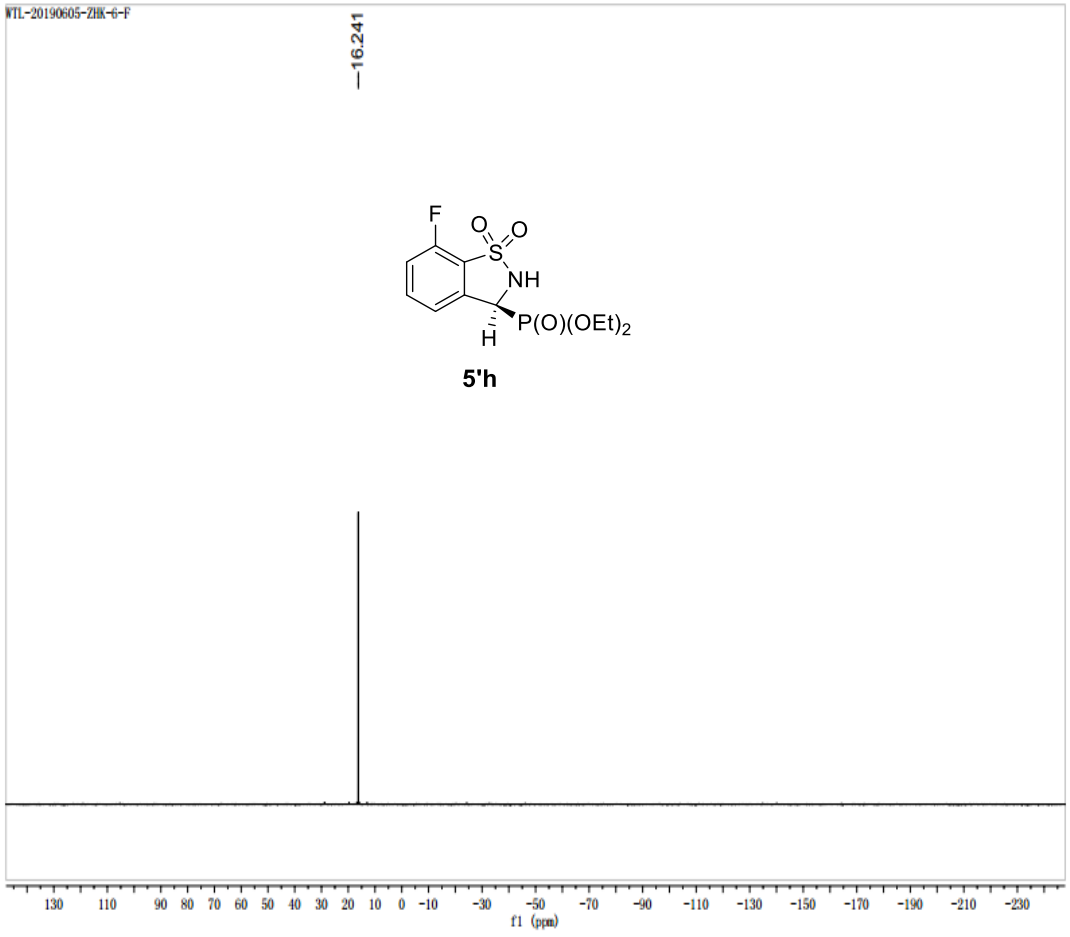
5'g


WTL-20190605-ZHK-6-F
7.805
7.794
7.784
7.773
7.399
7.378
7.293
7.272
6.669
5.054
5.024
4.287
4.279
4.270
4.261
4.252
4.248
4.242
4.231
4.224
4.186
4.174
4.168
4.156
4.150
4.139
4.135
4.131
4.118
4.113
1.299
1.294
1.282
1.276
1.264
F
O
O
S
NH
H
P(O)(OEt)2
1.00
1.01
1.26
1.00
1.02
2.12
2.12
3.03
3.06
f1 (ppm)

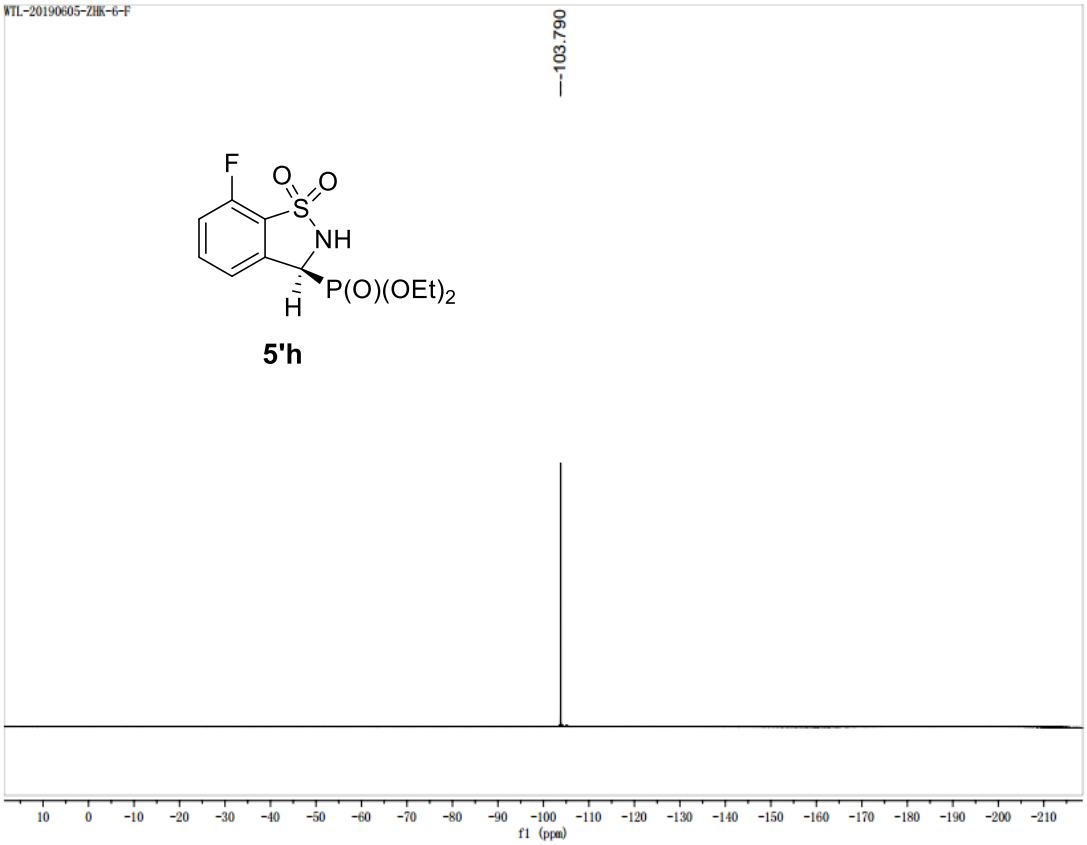
5'h


WTL-20190605-ZHK-6-F
166.672
166.643
164.137
164.107
135.802
135.745
135.701
135.646
131.305
131.281
131.253
131.225
123.964
123.946
123.865
123.846
118.288
118.267
118.048
118.026
113.328
113.303
113.079
113.054
65.228
65.157
64.188
64.115
54.739
53.113
16.541
16.487
16.457
16.400
F
O
O
S
NH
H
P(O)(OEt)2
f1 (ppm)

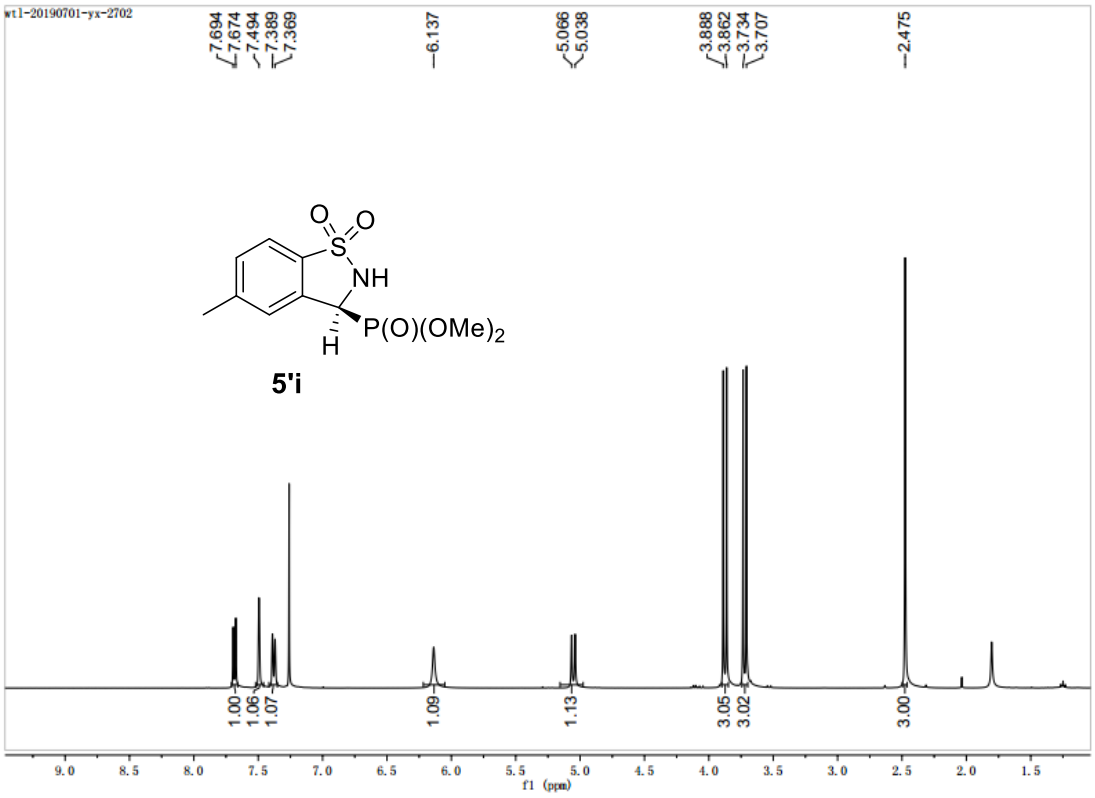
5'h


WTL-20190605-ZHK-6-F
16.241
F
O
O
S
NH
H
P(O)(OEt)2
f1 (ppm)

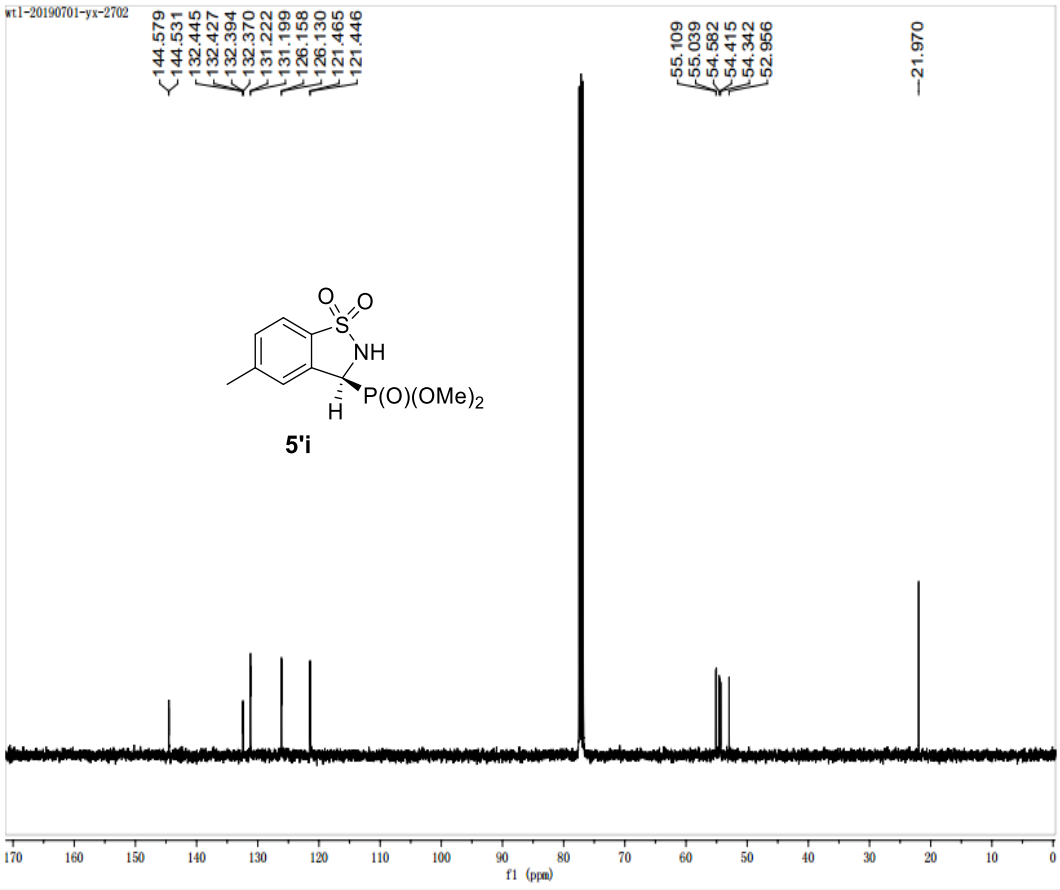
5'h

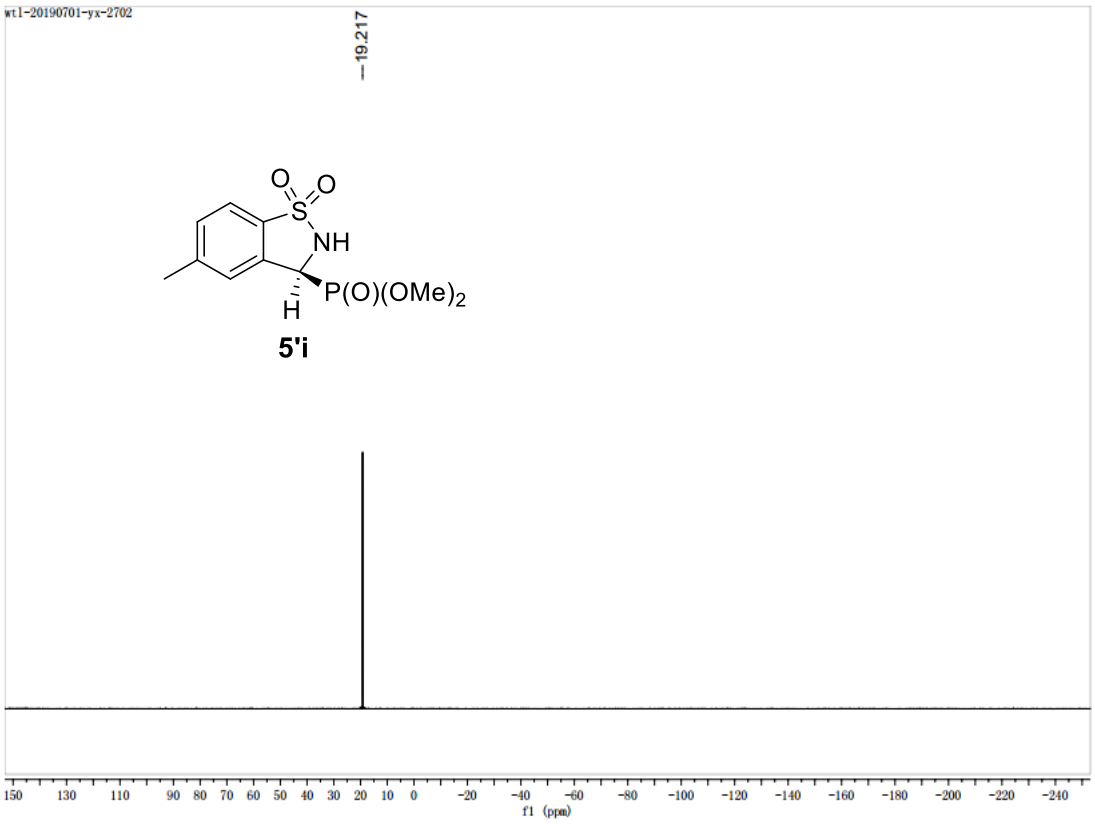

WTL-20190605-ZHK-6-F
-103.790
F
O
O
S
NH
P(O)(OEt)2
H
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

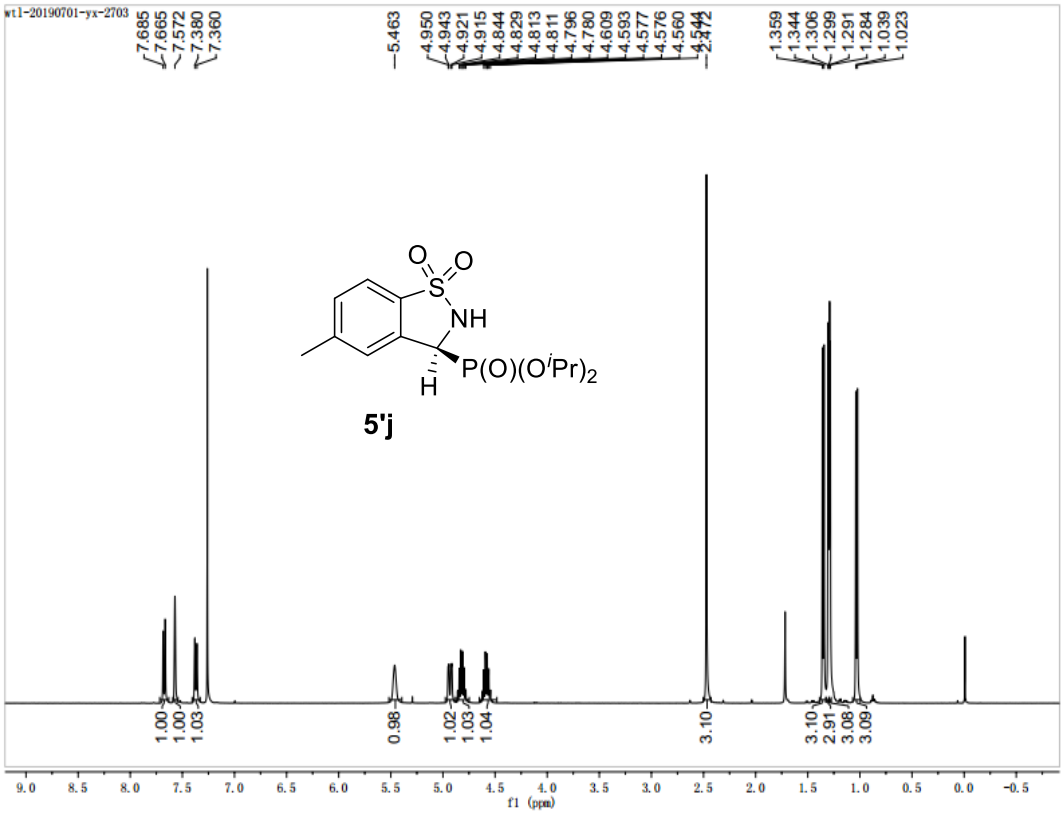
5'h

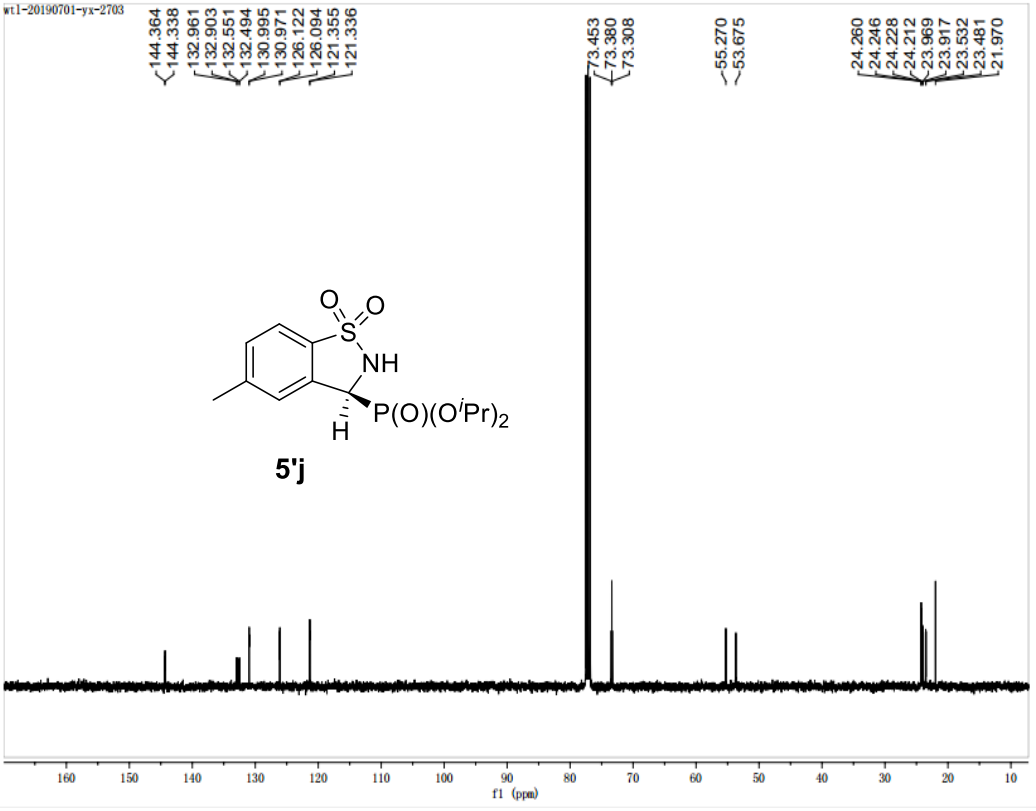

wtl-20190701-yx-2702
7.694
7.674
7.494
7.389
7.369
6.137
5.066
5.038
3.888
3.862
3.734
3.707
2.475
O
O
S
NH
P(O)(OMe)2
H
1.00
1.06
1.07
1.09
1.13
3.05
3.02
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

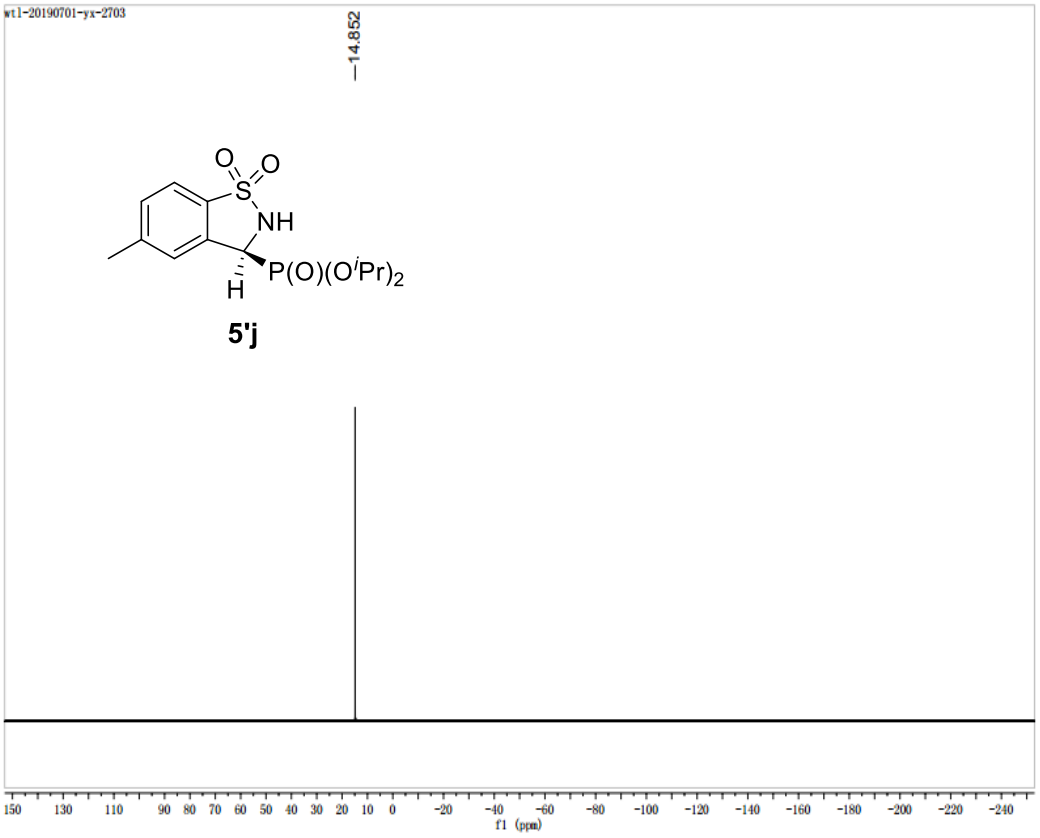
5'i


wt1-20190701-yx-2702
144.579
144.531
132.445
132.427
132.394
132.370
131.222
131.199
126.158
126.130
121.465
121.446
55.109
55.039
54.582
54.415
54.342
52.956
21.970
O
O
S
NH
H
P(O)(OMe)2
5'i
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

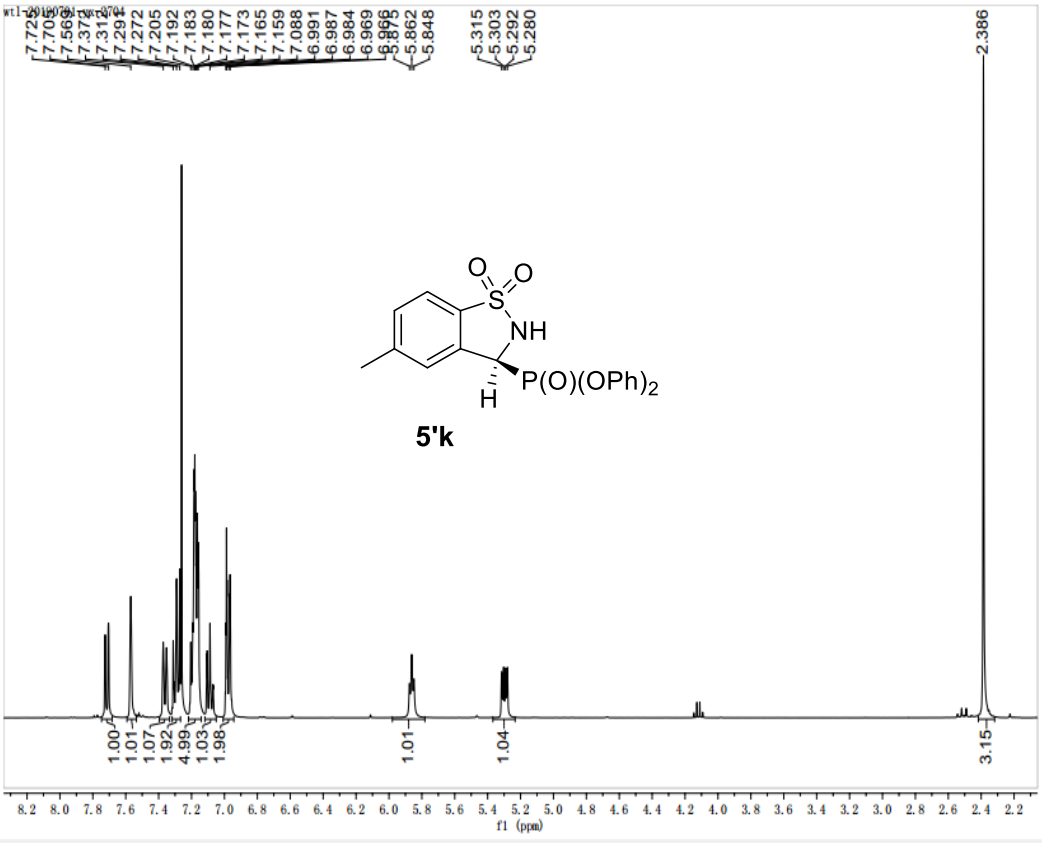

wt1-20190701-yx-2702
19.217
O
O
S
NH
H
P(O)(OMe)2
5'i
150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40 -60 -80 -100 -120 -140 -160 -180 -200 -220 -240
f1 (ppm)


wt1-20190701-yx-2703
7.685
7.665
7.572
7.380
7.360
5.463
4.950
4.943
4.921
4.915
4.844
4.829
4.813
4.811
4.796
4.780
4.609
4.593
4.577
4.576
4.560
4.544
2.472
1.359
1.344
1.306
1.299
1.291
1.284
1.039
1.023
O
O
S
NH
H
P(O)(O^{i}Pr)$_2$
5'j
1.00
1.00
1.03
0.98
1.02
1.03
1.04
3.10
3.10
2.91
3.08
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

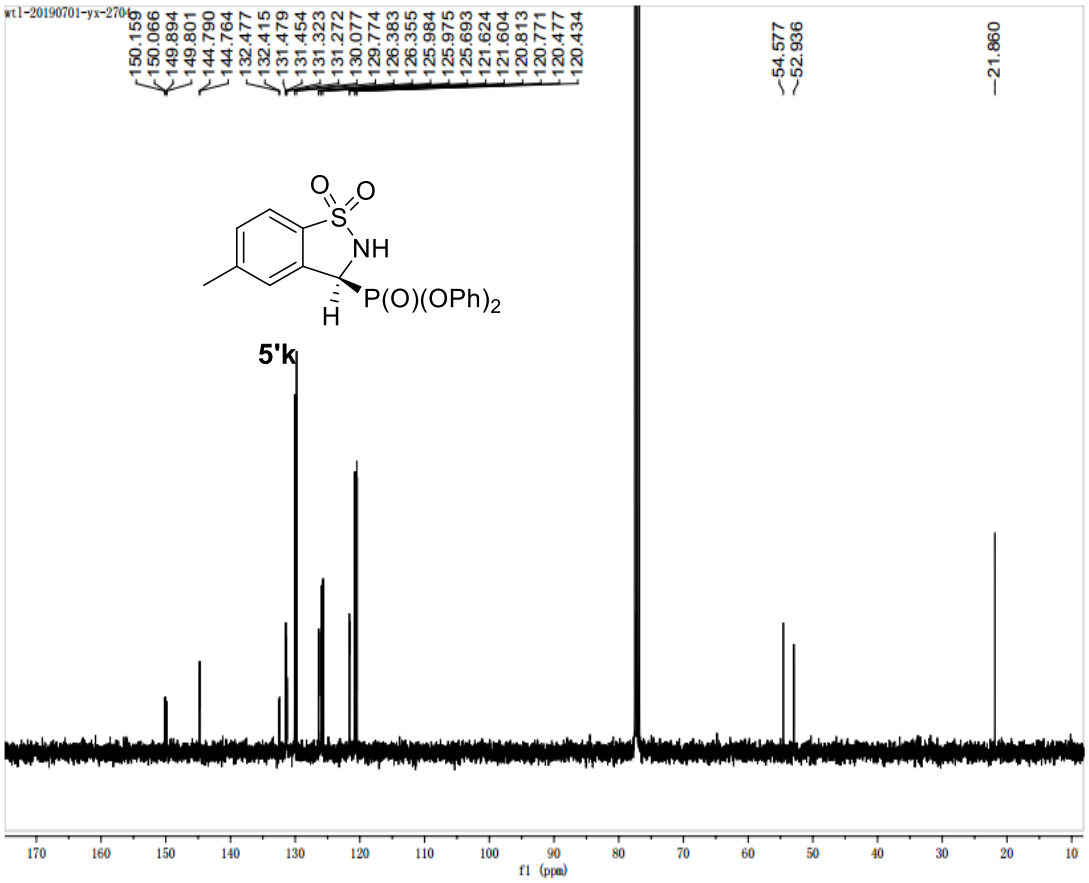

wt1-20190701-yx-2703
144.364
144.338
132.961
132.903
132.551
132.494
130.995
130.971
126.122
126.094
121.355
121.336
73.453
73.380
73.308
55.270
53.675
24.260
24.246
24.228
24.212
23.969
23.917
23.532
23.481
21.970
O
O
S
NH
H
P(O)(O^{i}Pr)$_2$
5'j
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

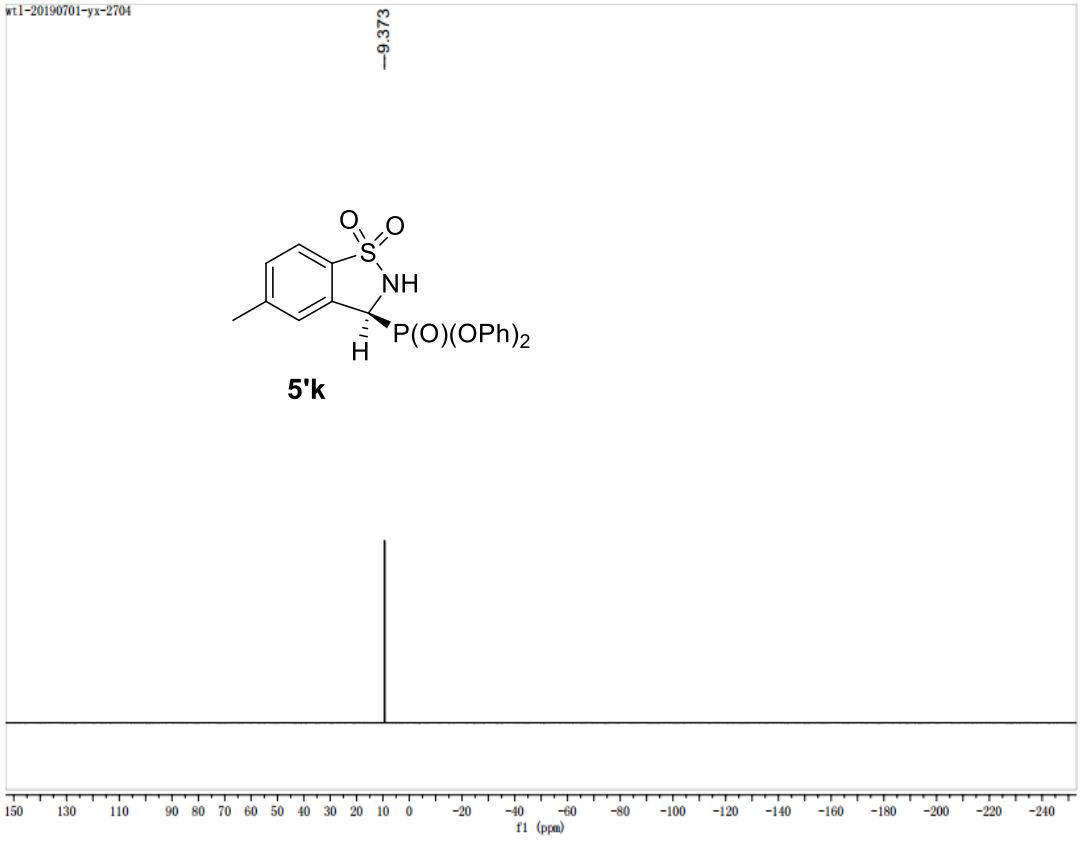

wtl-20190701-yx-2703
14.852
O
O
S
NH
P(O)(O^{i}Pr)$_2$
H
f1 (ppm)

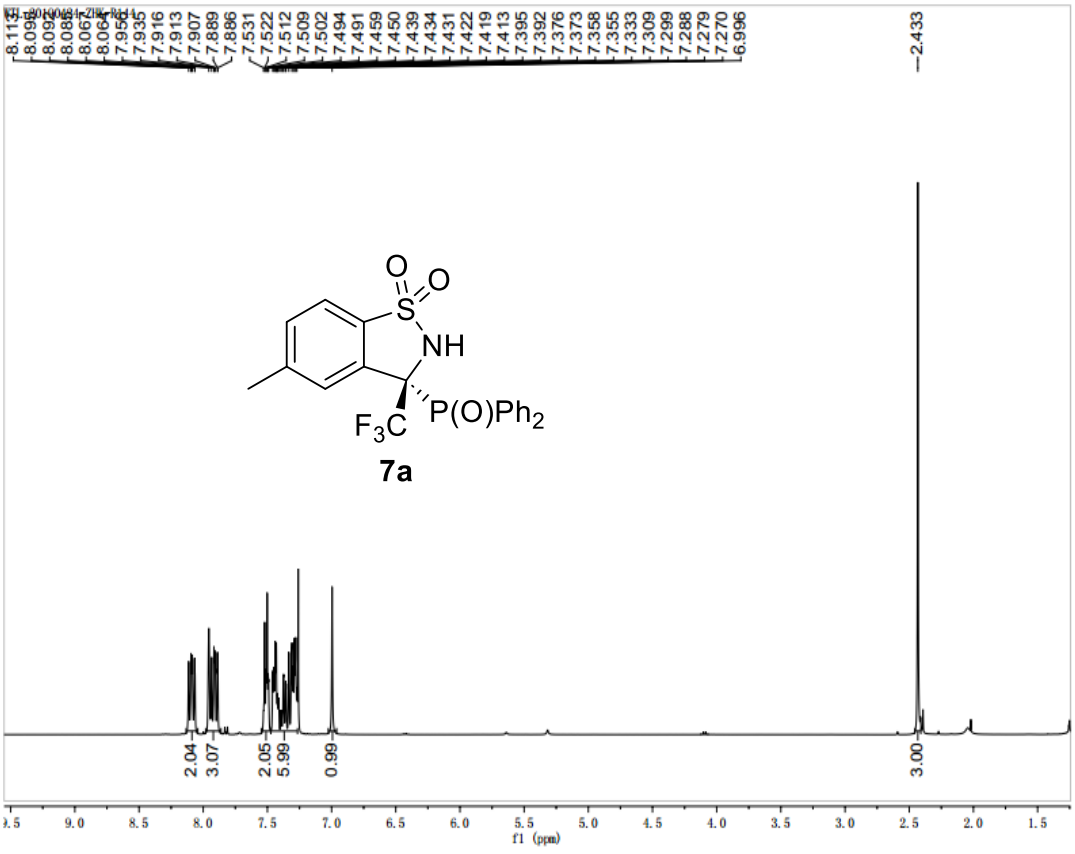
5'j

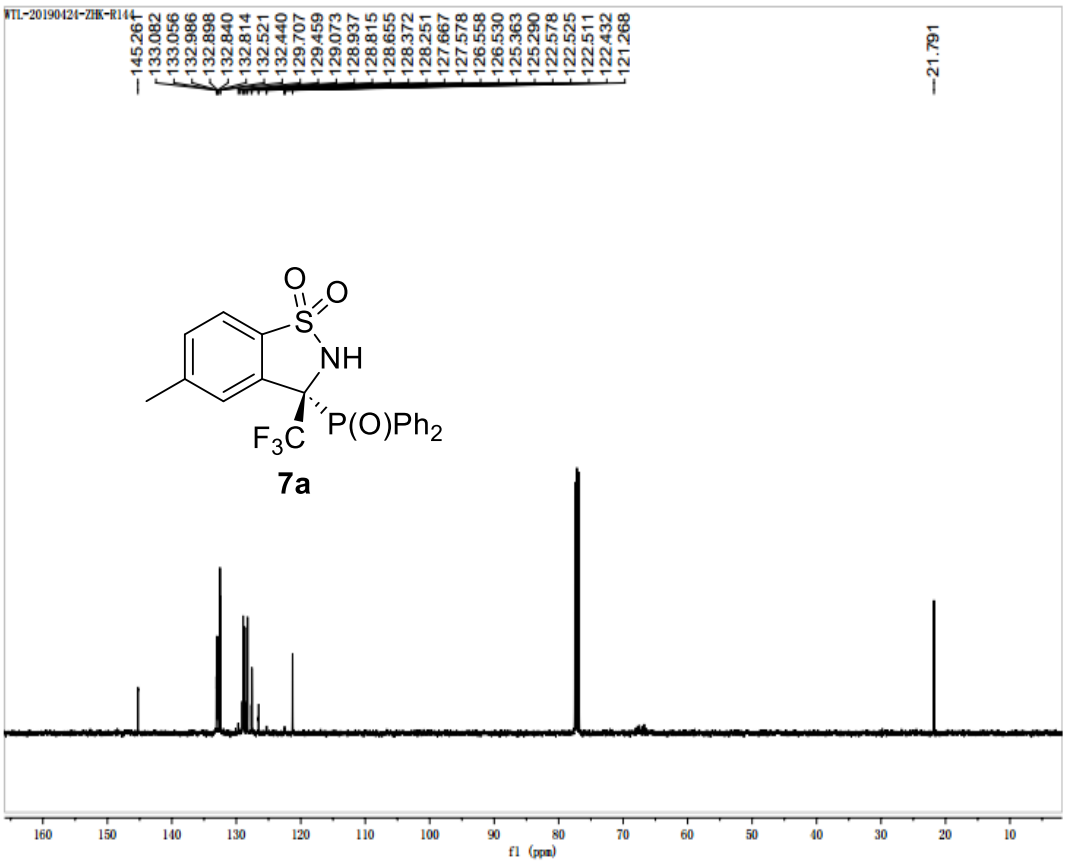

7.722
7.706
7.569
7.374
7.314
7.291
7.272
7.205
7.192
7.183
7.180
7.177
7.173
7.165
7.159
7.088
6.991
6.987
6.984
6.969
6.966
5.875
5.862
5.848
5.315
5.303
5.292
5.280
2.386
O
O
S
NH
P(O)(OPh)$_2$
H
1.00
1.01
1.07
1.92
4.99
1.03
1.98
1.01
1.04
3.15
f1 (ppm)

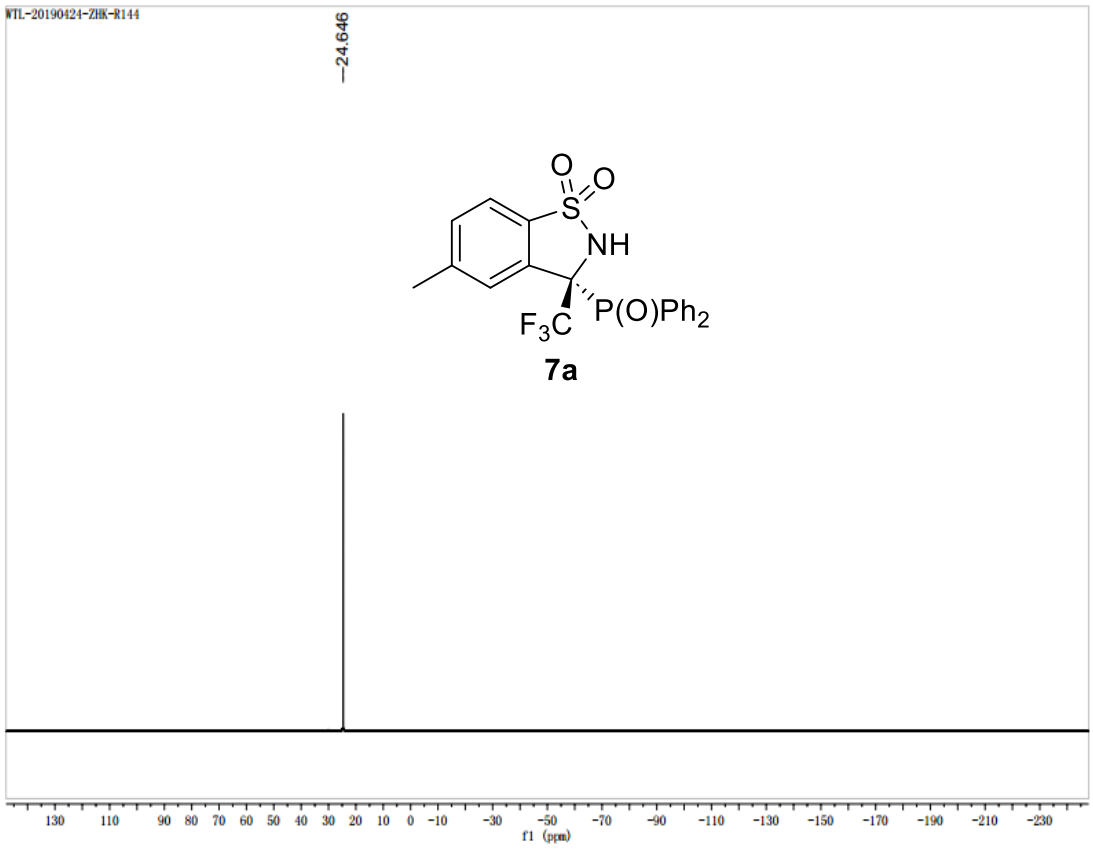
5'k

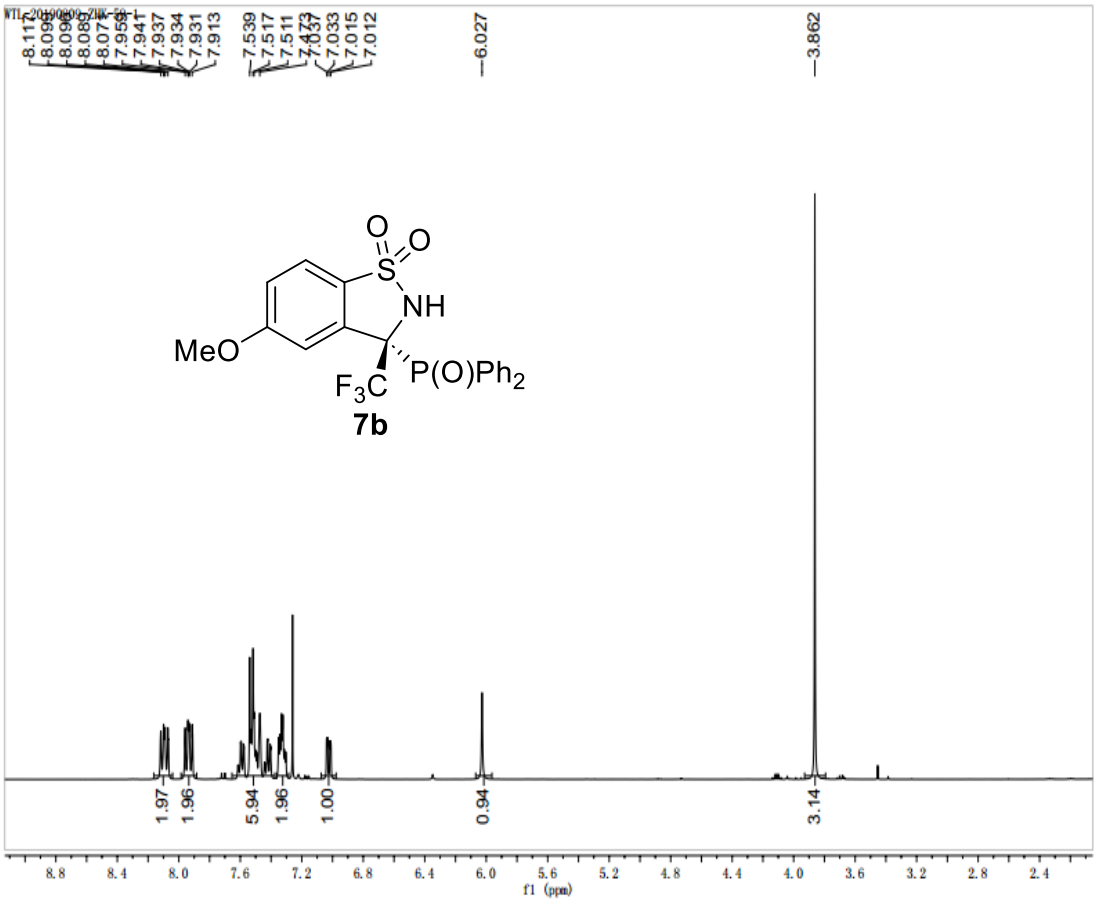

wt1-20190701-yx-2704
150.159
150.066
149.894
149.801
144.790
144.764
132.477
132.415
131.479
131.454
131.323
131.272
130.077
129.774
126.383
126.355
125.984
125.975
125.693
121.624
121.604
120.813
120.771
120.477
120.434
54.577
52.936
21.860
O
O
S
NH
P(O)(OPh)2
H
5'k
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

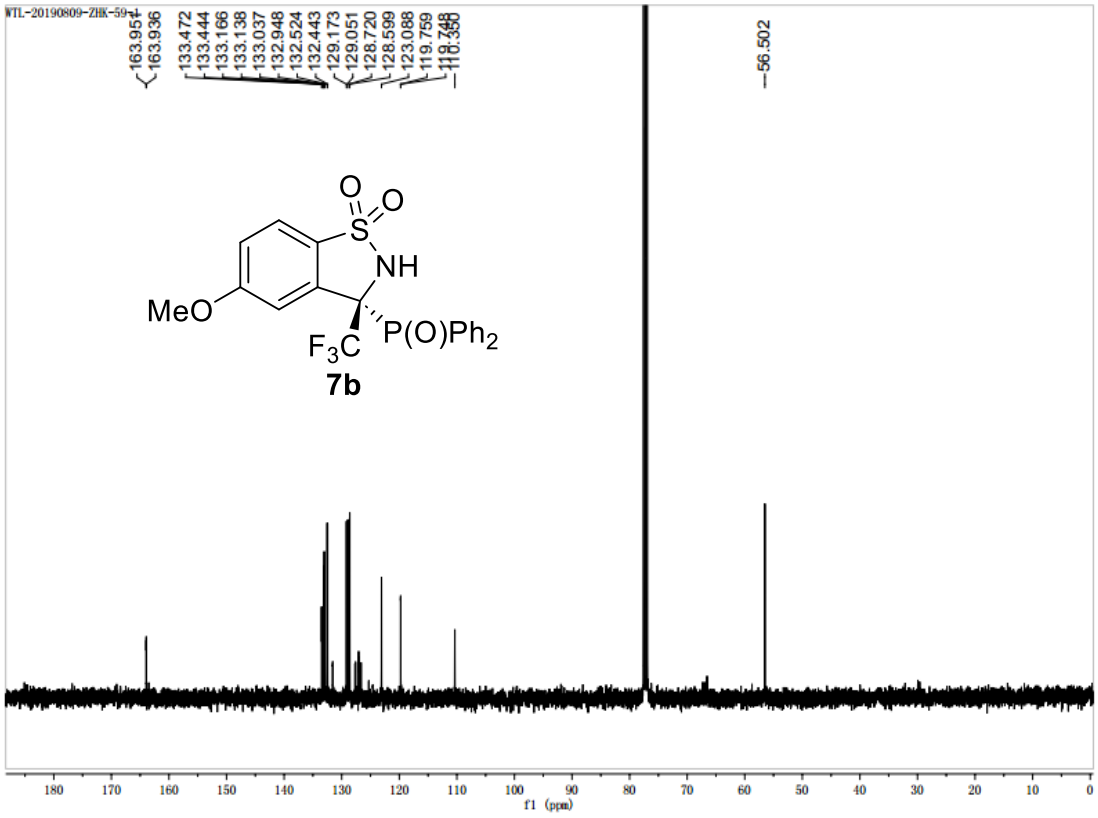

wt1-20190701-yx-2704
9.373
O
O
S
NH
P(O)(OPh)2
H
5'k
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
-220
-240
f1 (ppm)

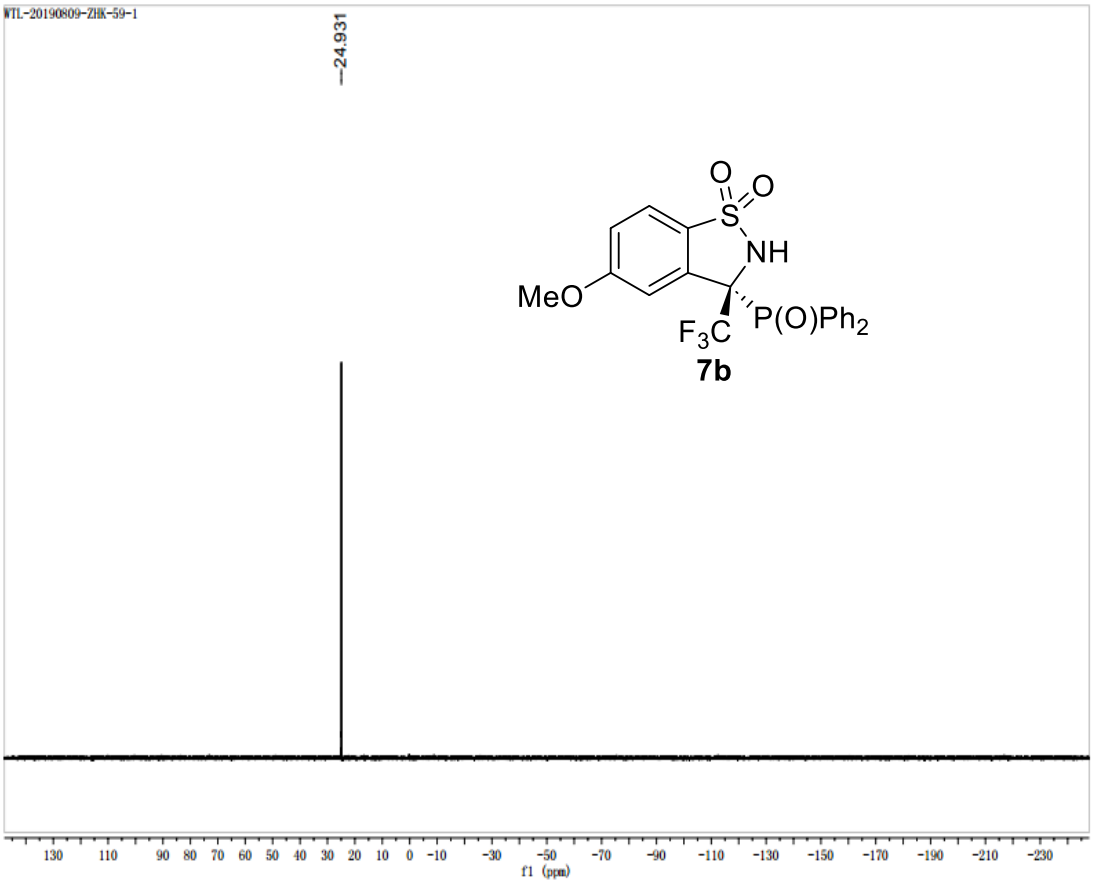

8.113
8.095
8.092
8.088
8.067
8.064
7.956
7.936
7.916
7.913
7.907
7.889
7.886
7.531
7.522
7.512
7.509
7.502
7.494
7.491
7.459
7.450
7.439
7.434
7.431
7.422
7.419
7.413
7.395
7.392
7.376
7.373
7.358
7.355
7.333
7.309
7.299
7.288
7.279
7.270
6.996
2.433
O
O
S
NH
F3C
P(O)Ph2
7a
2.04
3.07
2.05
5.99
0.99
3.00
f1 (ppm)

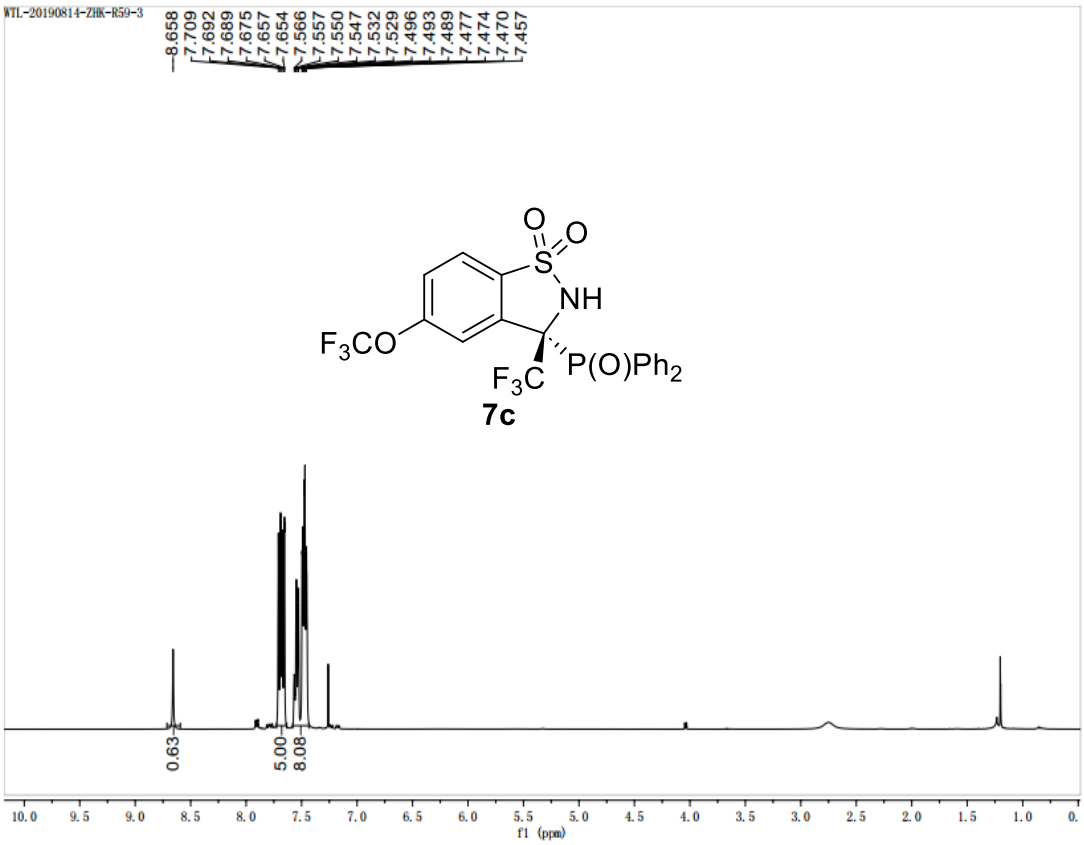

WTL-20190424-ZHK-R144
145.261
133.082
133.056
132.986
132.898
132.840
132.814
132.521
132.440
129.707
129.459
129.073
128.937
128.815
128.655
128.372
128.251
127.667
127.578
126.558
126.530
125.363
125.290
122.578
122.525
122.511
122.432
121.268
21.791
O
O
S
NH
F3C
P(O)Ph2
7a
f1 (ppm)


WTL-20190424-ZHK-R144
-24.646
O
O
S
NH
F3C
P(O)Ph2
7a
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

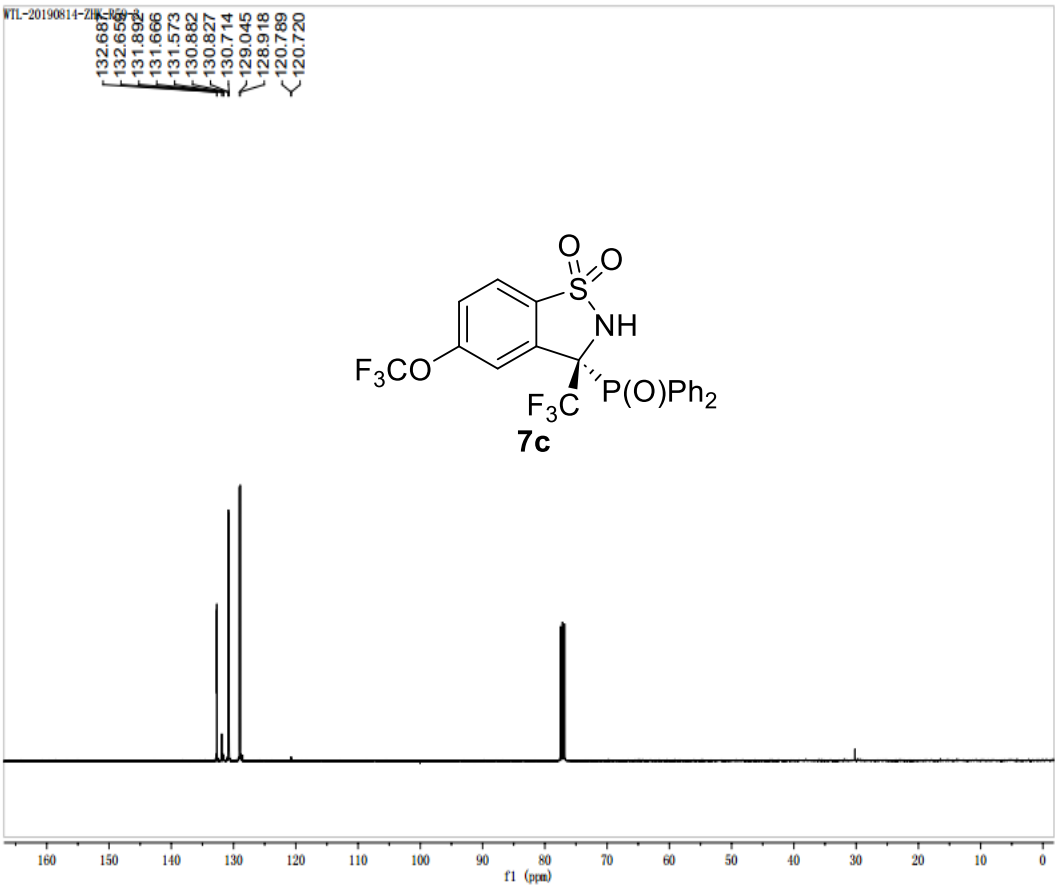

8.117
8.095
8.080
8.077
7.959
7.941
7.937
7.934
7.931
7.913
7.539
7.517
7.511
7.473
7.037
7.033
7.015
7.012
-6.027
-3.862
O
O
S
NH
MeO
F3C
P(O)Ph2
7b
1.97
1.96
5.94
1.96
1.00
0.94
3.14
8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4
f1 (ppm)


WTL-20190809-ZHK-59-1
163.951
163.936
133.472
133.444
133.166
133.138
133.037
132.948
132.524
132.443
129.173
129.051
128.720
128.599
123.088
119.759
56.502
O
O
S
NH
MeO
F3C
P(O)Ph2
7b
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

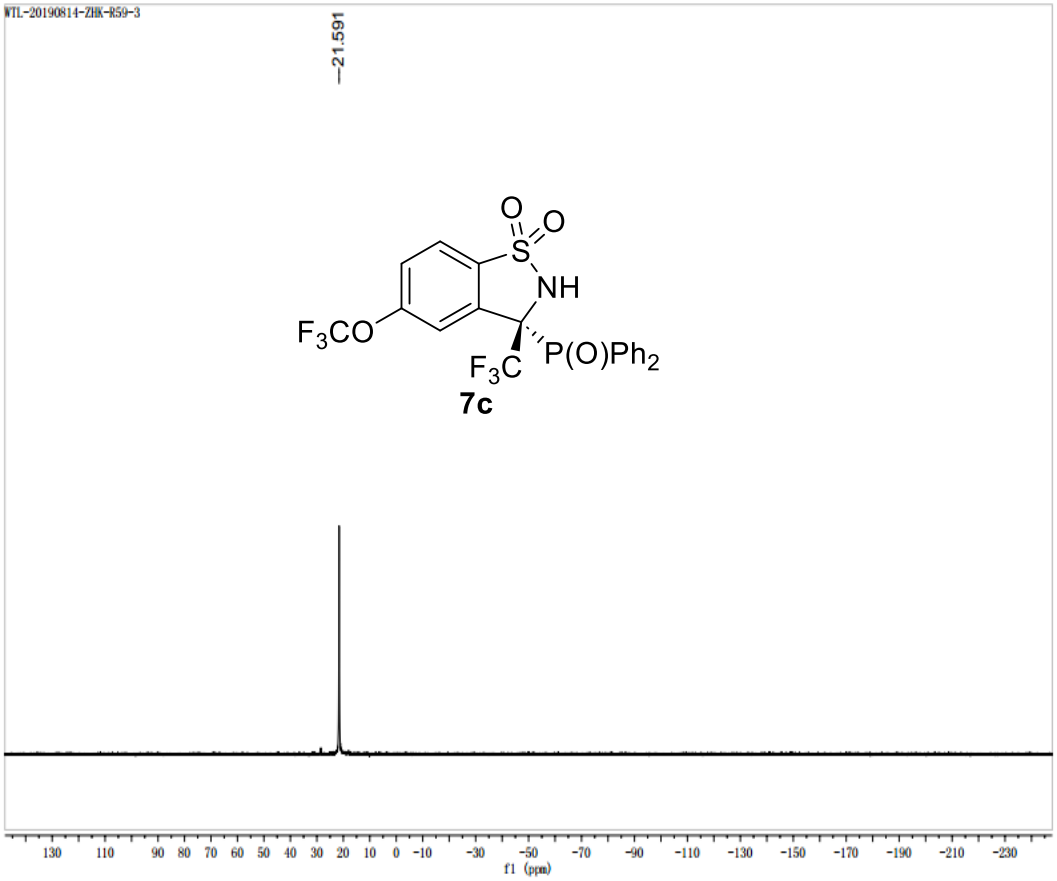

WTL-20190809-ZHK-59-1
24.931
O
O
S
NH
MeO
F3C
P(O)Ph2
7b
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

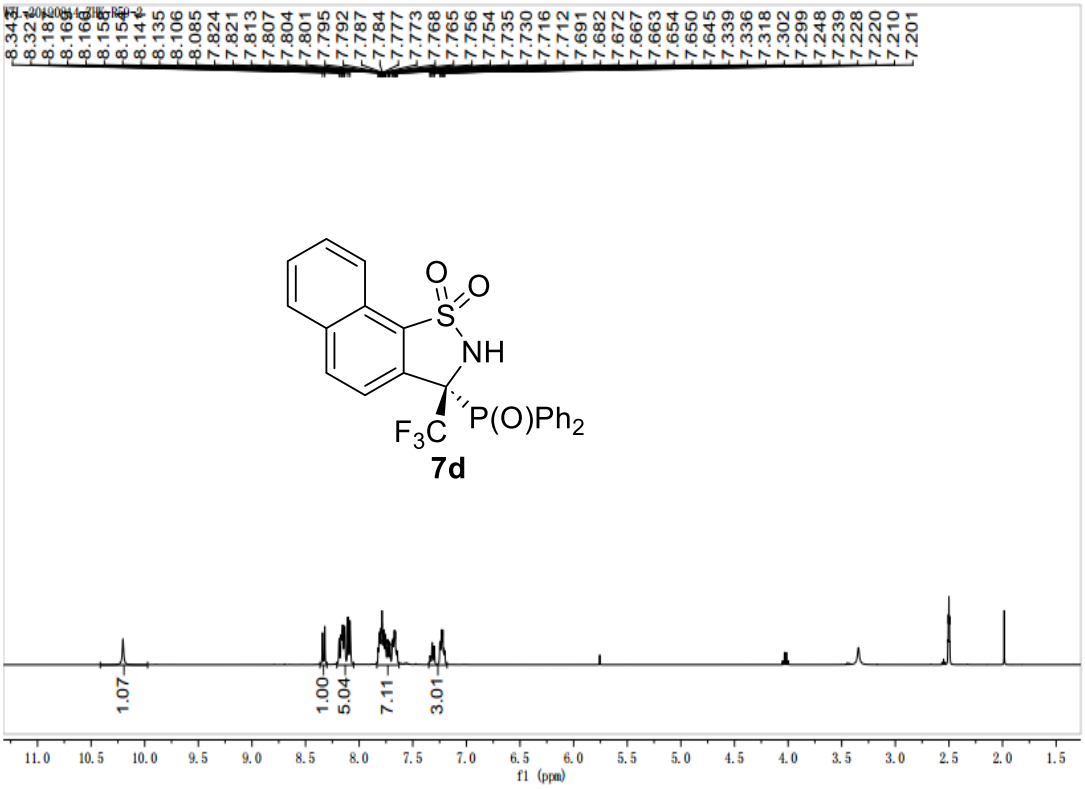

WTL-20190814-ZHK-R59-3
8.658
7.709
7.692
7.689
7.675
7.657
7.654
7.566
7.557
7.550
7.547
7.532
7.529
7.496
7.493
7.489
7.477
7.474
7.470
7.457
O
O
S
NH
F3CO
F3C
P(O)Ph2
0.63
5.00
8.08
f1 (ppm)

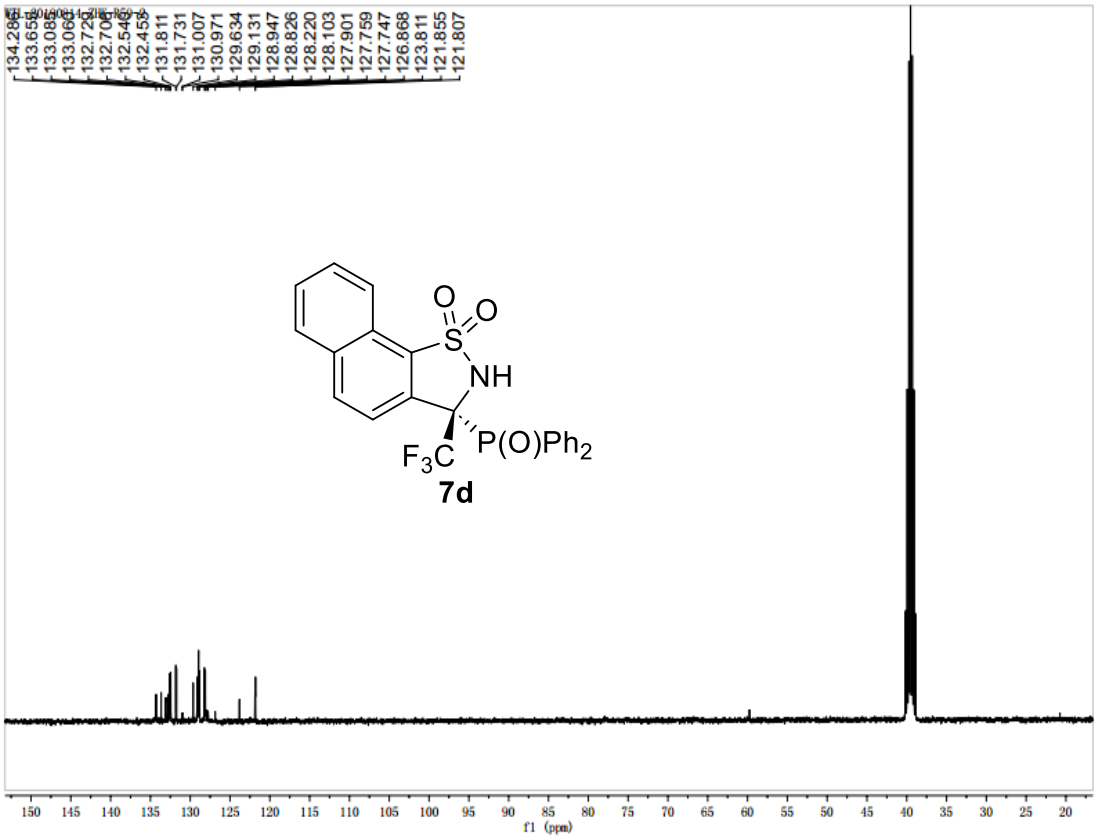
7c

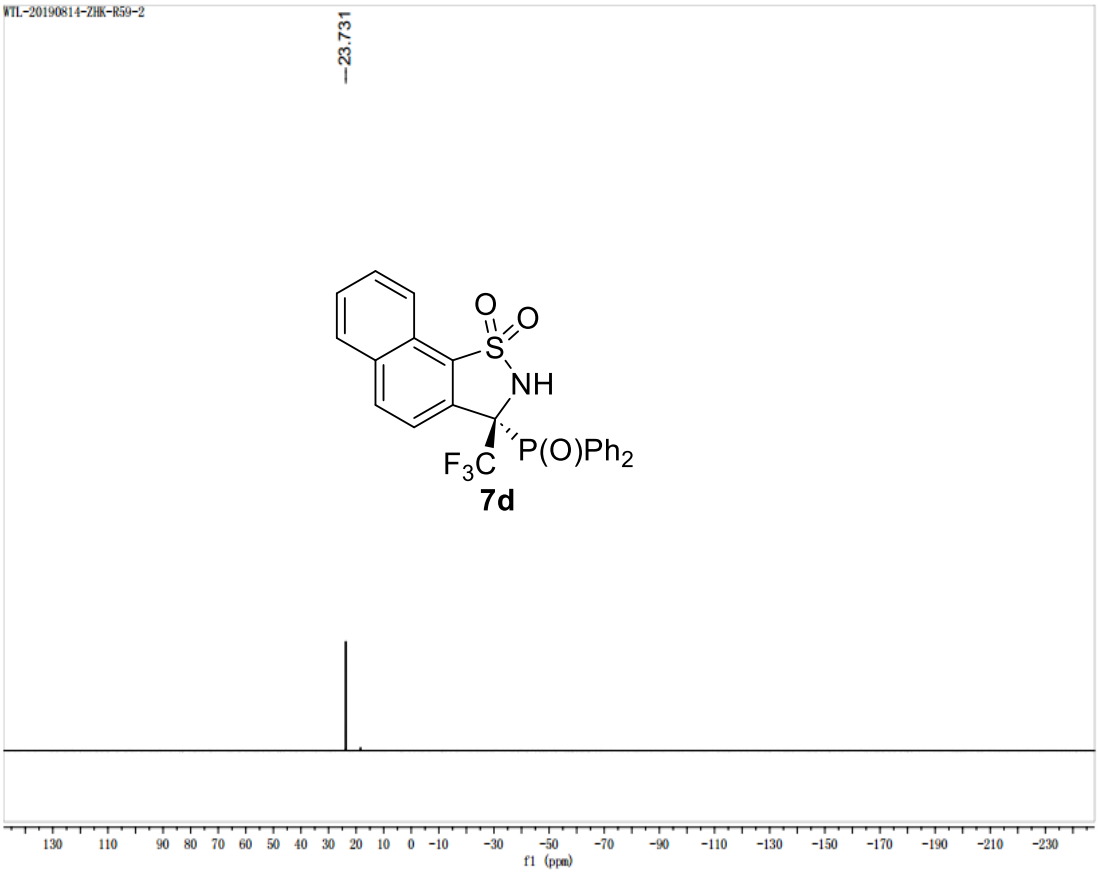

WTL-20190814-ZHK-R59-2
132.681
132.659
131.892
131.666
131.573
130.882
130.827
130.714
129.045
128.918
120.789
120.720
O
O
S
NH
F3CO
F3C
P(O)Ph2
f1 (ppm)

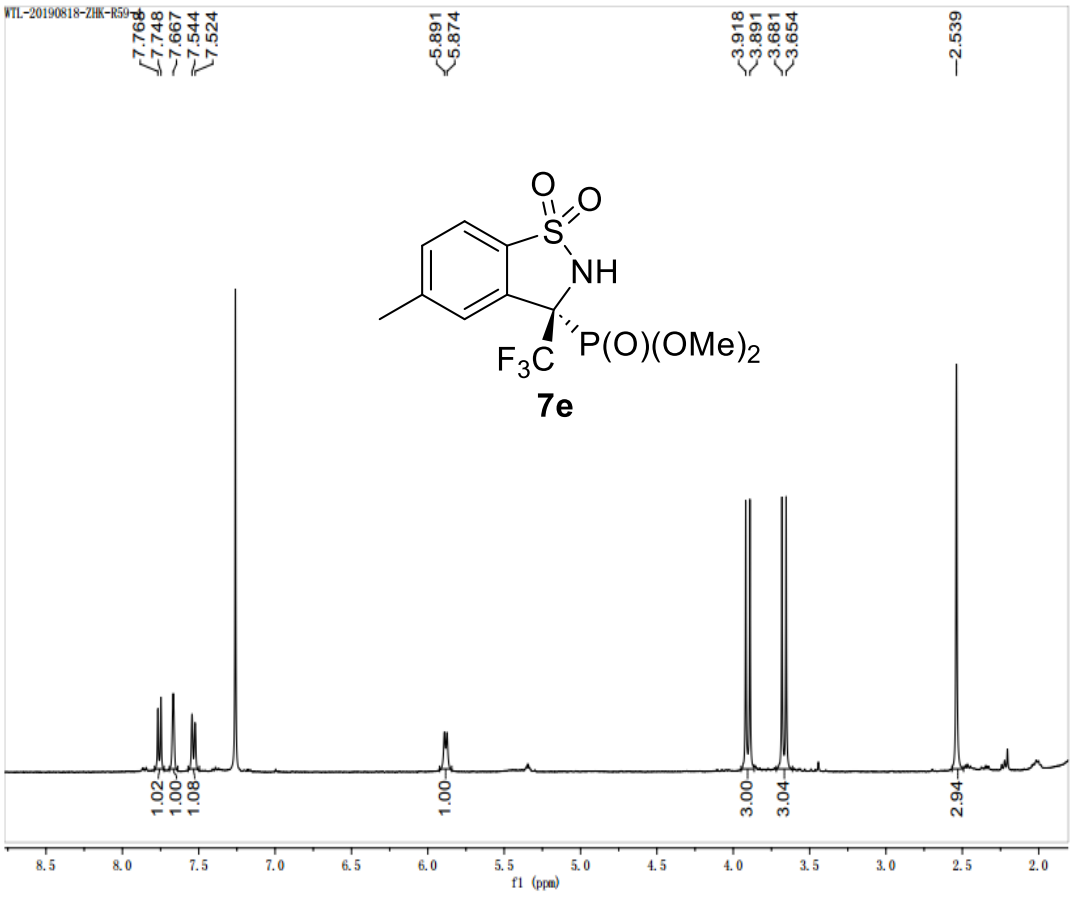
7c

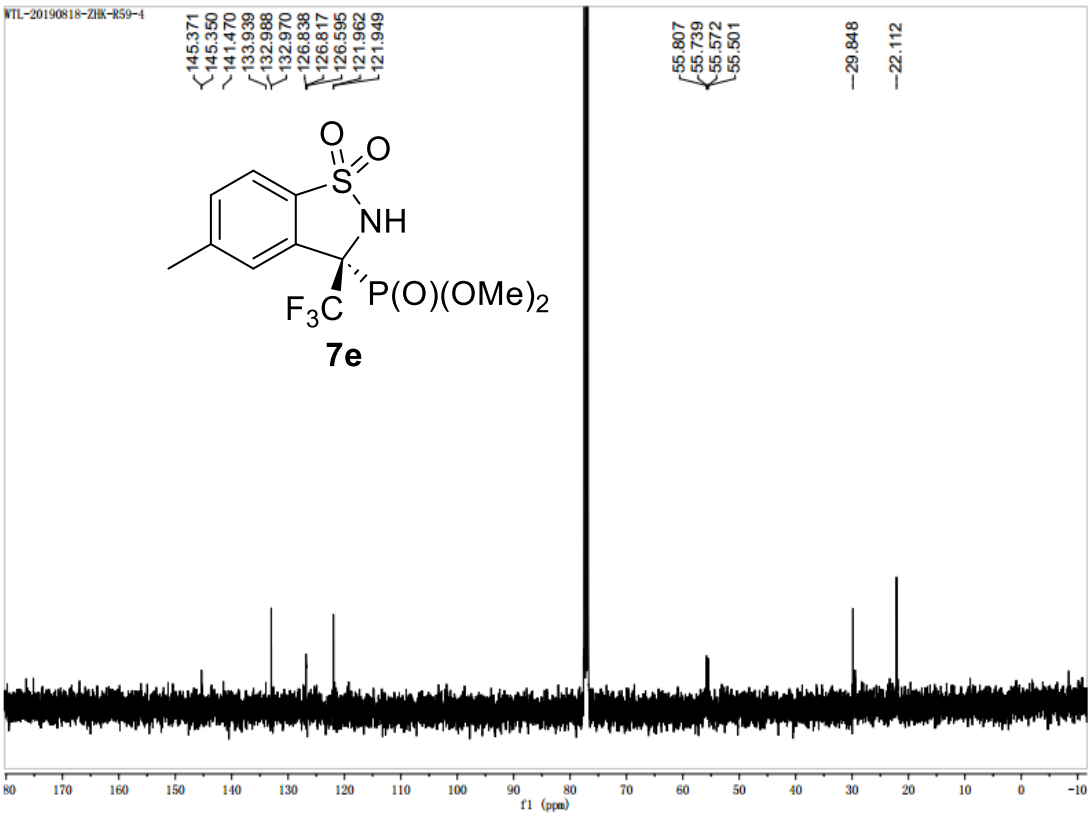

WTL-20190814-ZHK-R59-3
21.591
O
O
S
NH
F3CO
F3C
P(O)Ph2
7c
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

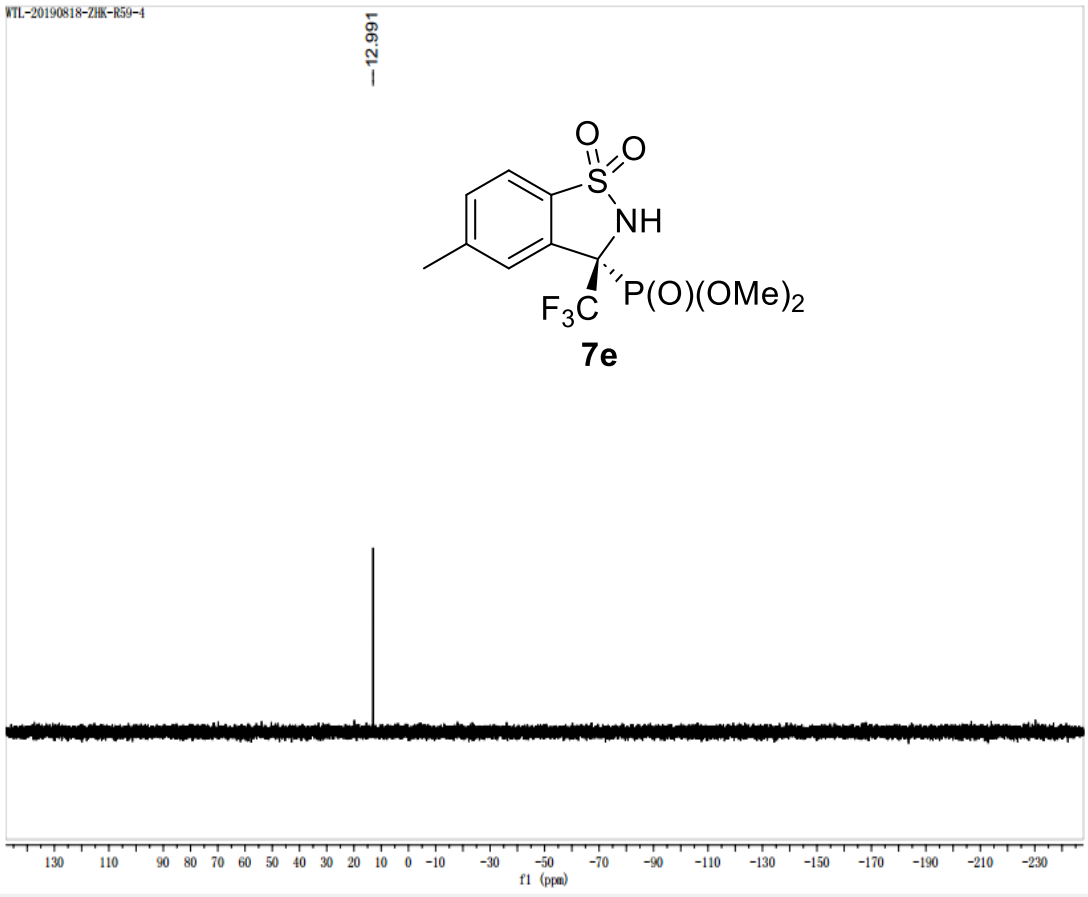

8.345 8.327 8.181 8.163 8.158 8.154 8.141 8.135 8.106 8.085 7.824 7.821 7.813 7.807 7.804 7.801 7.795 7.792 7.787 7.784 7.777 7.773 7.768 7.765 7.756 7.754 7.735 7.730 7.716 7.712 7.691 7.682 7.672 7.667 7.663 7.654 7.650 7.645 7.339 7.336 7.318 7.302 7.299 7.248 7.239 7.228 7.220 7.210 7.201
O
O
S
NH
F3C
P(O)Ph2
7d
1.07
1.00
5.04
7.11
3.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5
f1 (ppm)

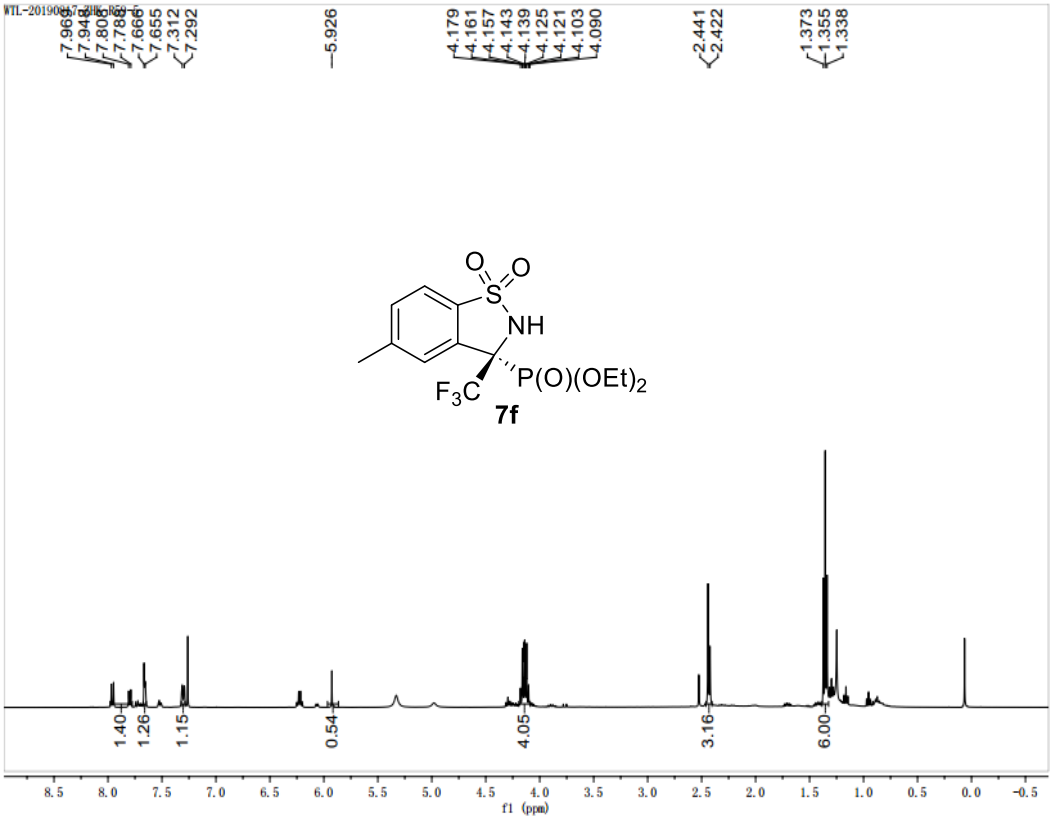

134.286
133.655
133.085
133.066
132.729
132.706
132.546
132.458
131.811
131.731
131.007
130.971
129.634
129.131
128.947
128.826
128.220
128.103
127.901
127.759
127.747
126.868
123.811
121.855
121.807
O
O
S
NH
F3C
P(O)Ph2
7d
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

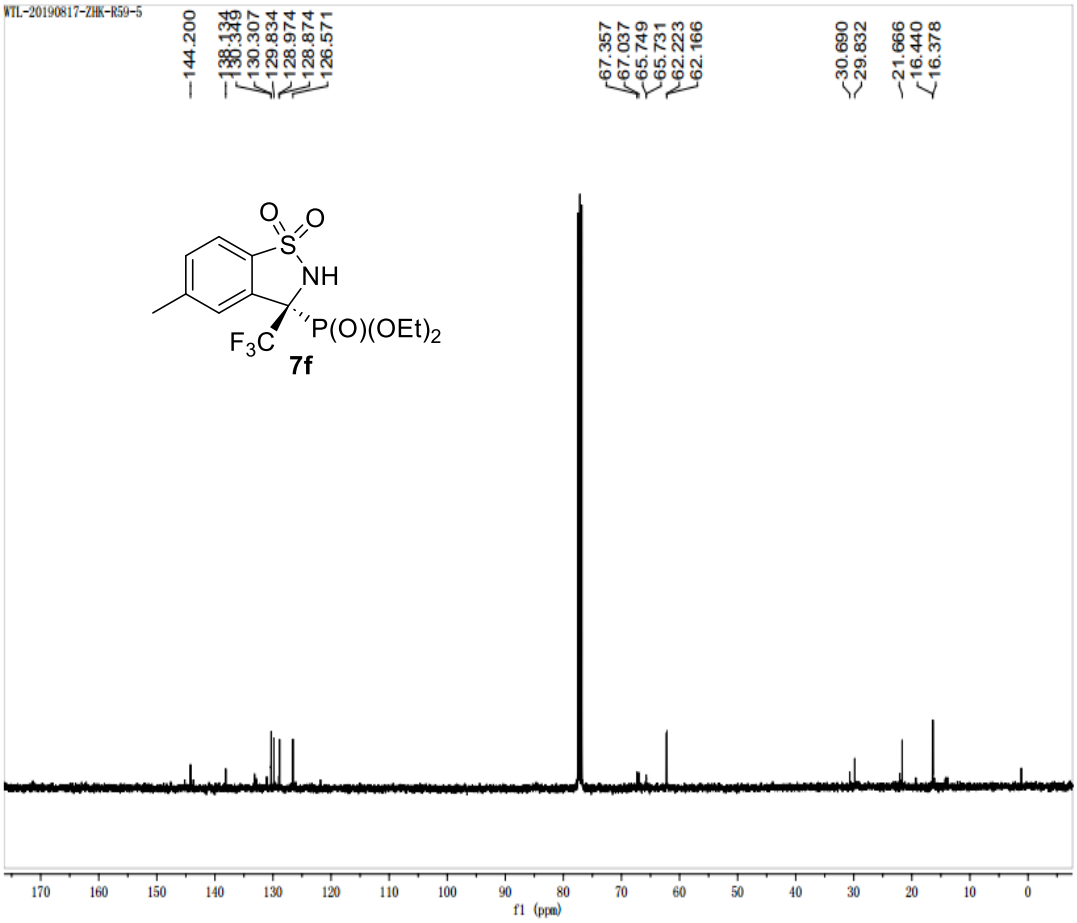

WTL-20190814-ZHK-R59-2
-23.731
O
O
S
NH
F3C
P(O)Ph2
7d
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

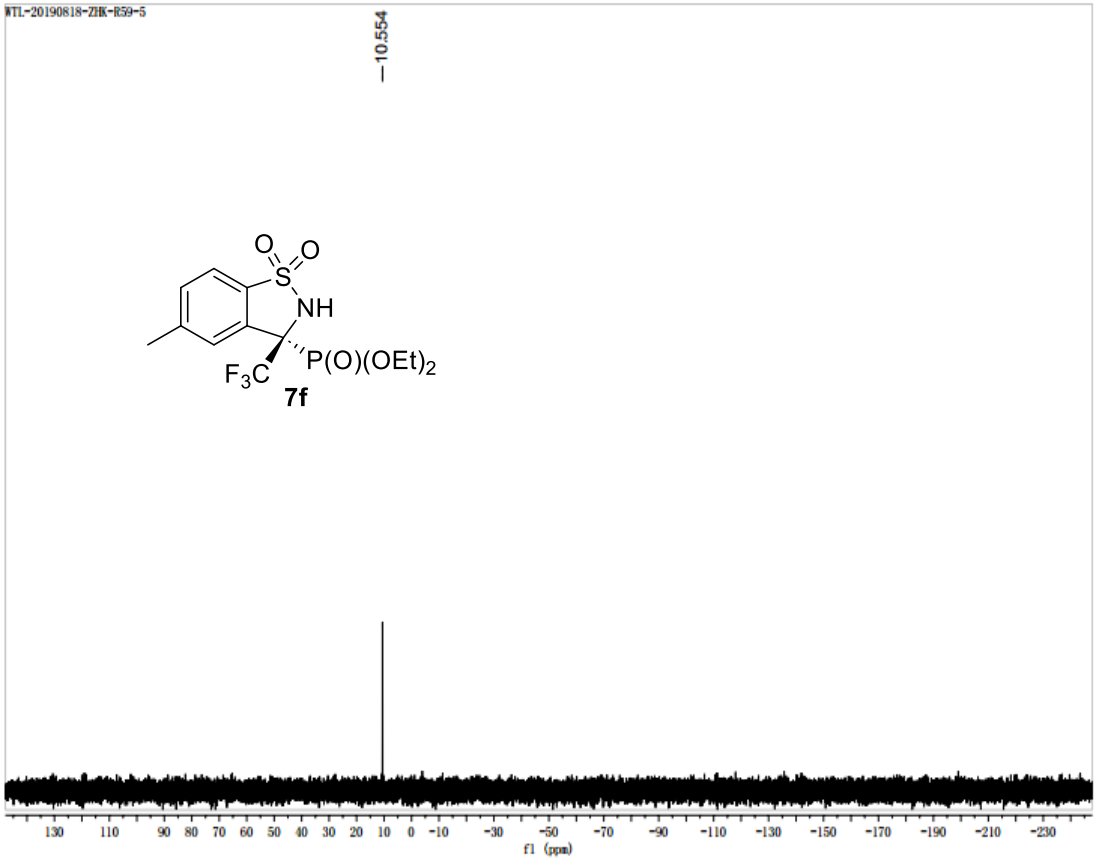

WTL-20190818-ZHK-R59-4
7.768
7.748
7.667
7.544
7.524
5.891
5.874
3.918
3.891
3.681
3.654
2.539
O
O
S
NH
F3C
P(O)(OMe)2
7e
1.02
1.00
1.08
1.00
3.00
3.04
2.94
f1 (ppm)

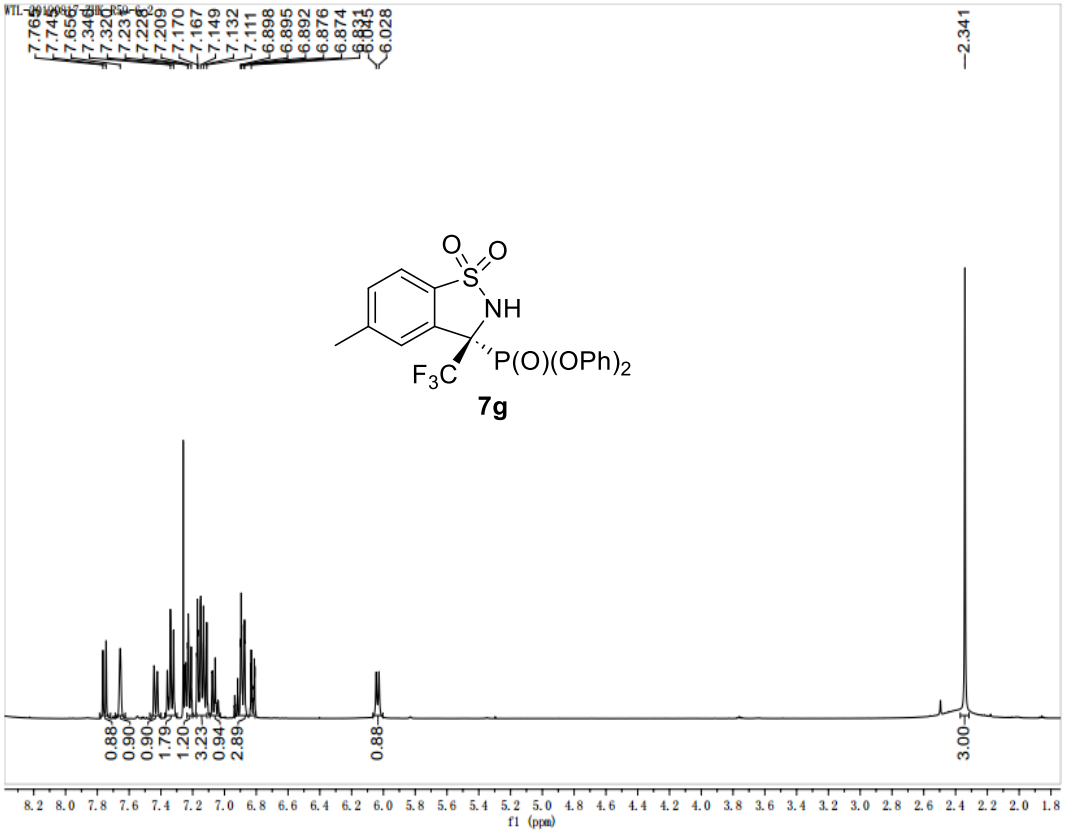

WTL-20190818-ZHK-R59-4
145.371
145.350
141.470
133.939
132.988
132.970
126.838
126.817
126.595
121.962
121.949
55.807
55.739
55.572
55.501
29.848
22.112
O
O
S
NH
F3C
P(O)(OMe)2
7e
f1 (ppm)

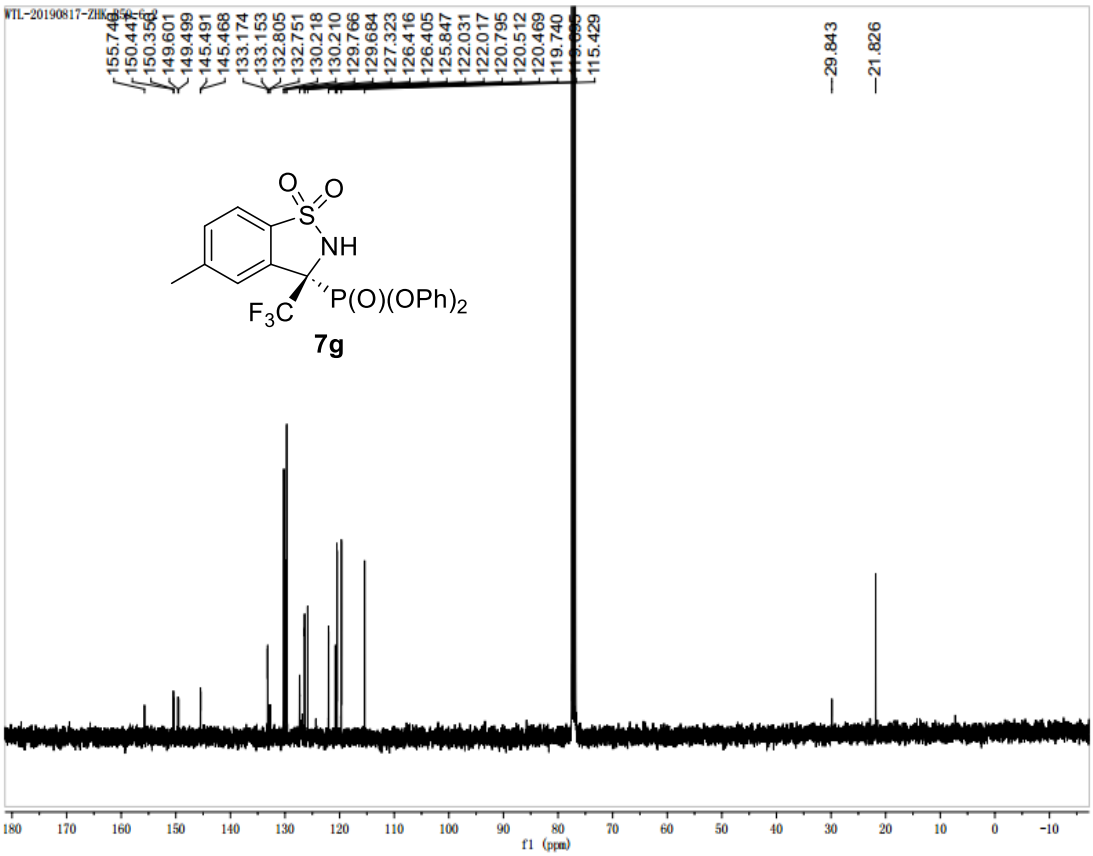

WTL-20190818-ZHK-R59-4
12.991
O
O
S
NH
F3C
P(O)(OMe)2
7e
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

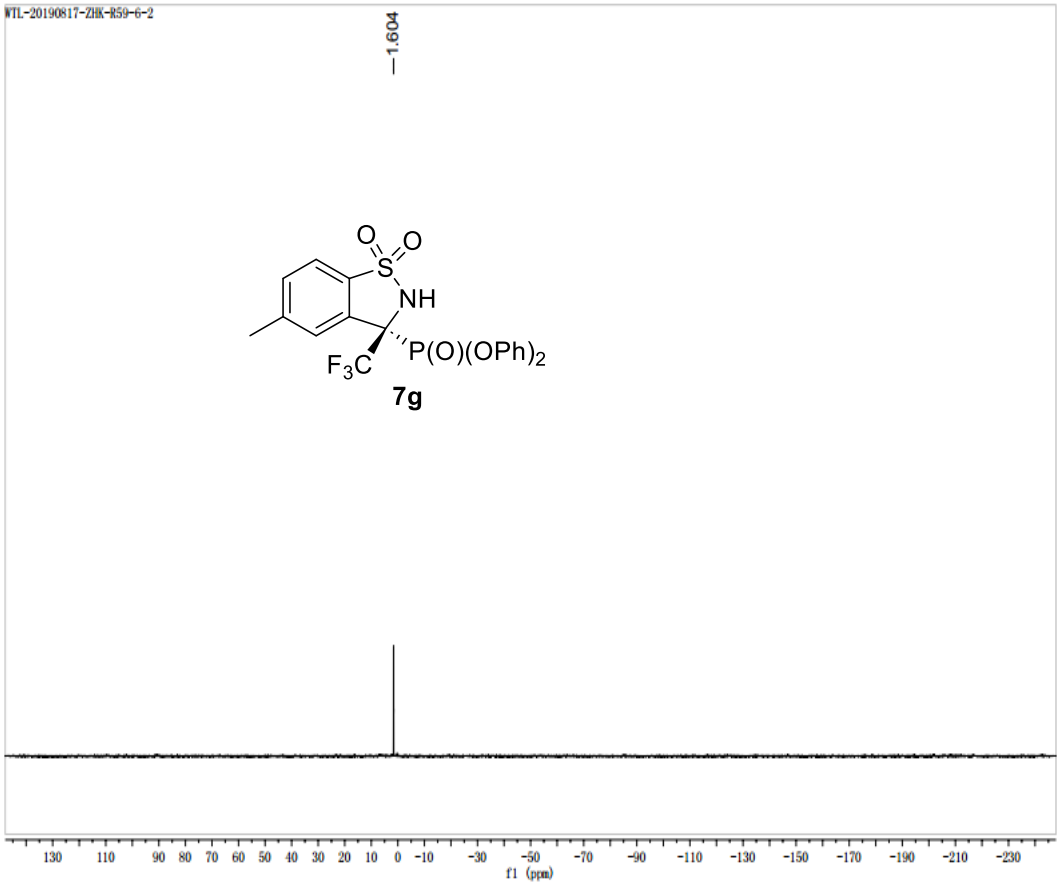

7.969
7.948
7.809
7.788
7.666
7.655
7.312
7.292
5.926
4.179
4.161
4.157
4.143
4.139
4.125
4.121
4.103
4.090
2.441
2.422
1.373
1.355
1.338
O
O
S
NH
F3C
P(O)(OEt)2
7f
1.40
1.26
1.15
0.54
4.05
3.16
6.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

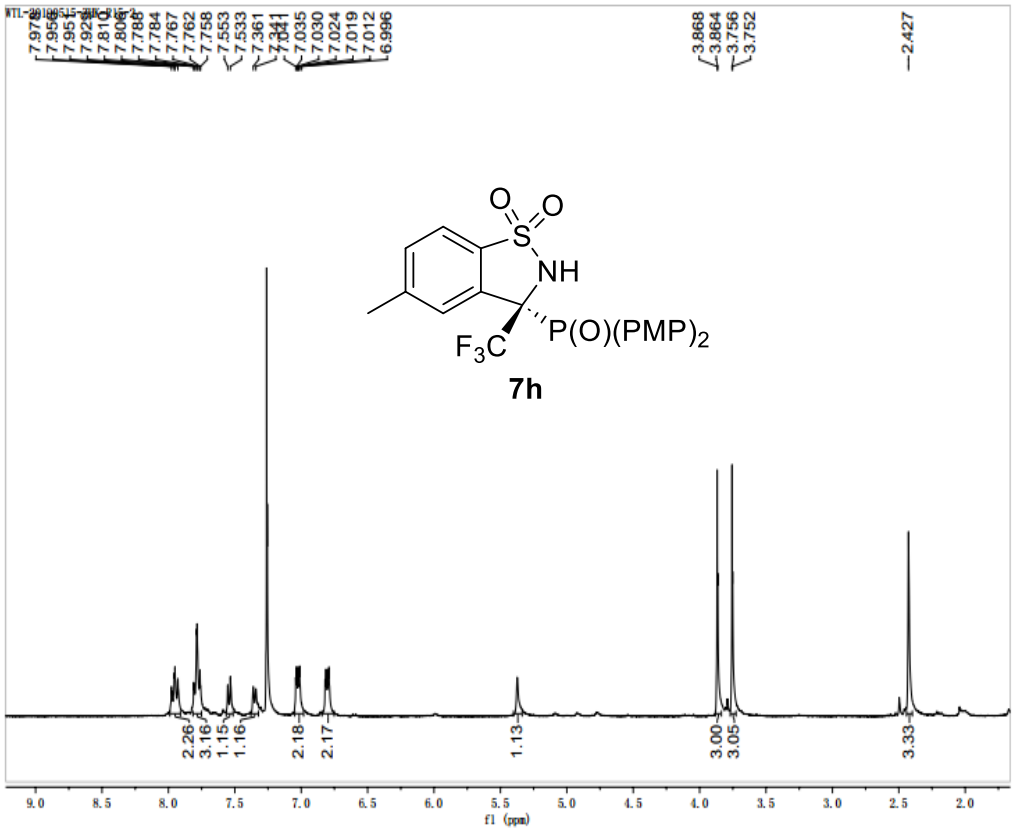

WTL-20190817-ZHK-R59-5
144.200
138.134
130.349
130.307
129.834
128.974
128.874
126.571
67.357
67.037
65.749
65.731
62.223
62.166
30.690
29.832
21.666
16.440
16.378
O
O
S
NH
F3C
P(O)(OEt)2
7f
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

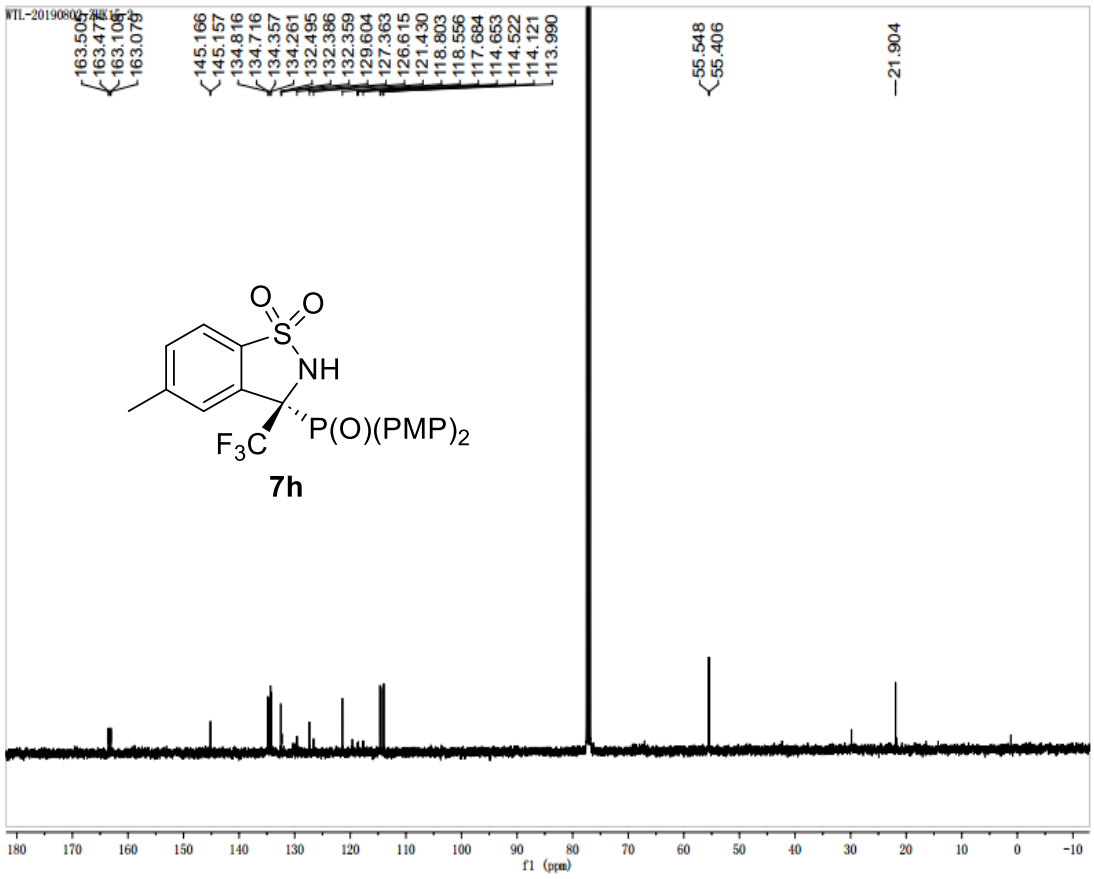

WTL-20190818-ZHK-R59-5
10.554
O
O
S
NH
F3C
P(O)(OEt)2
7f
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

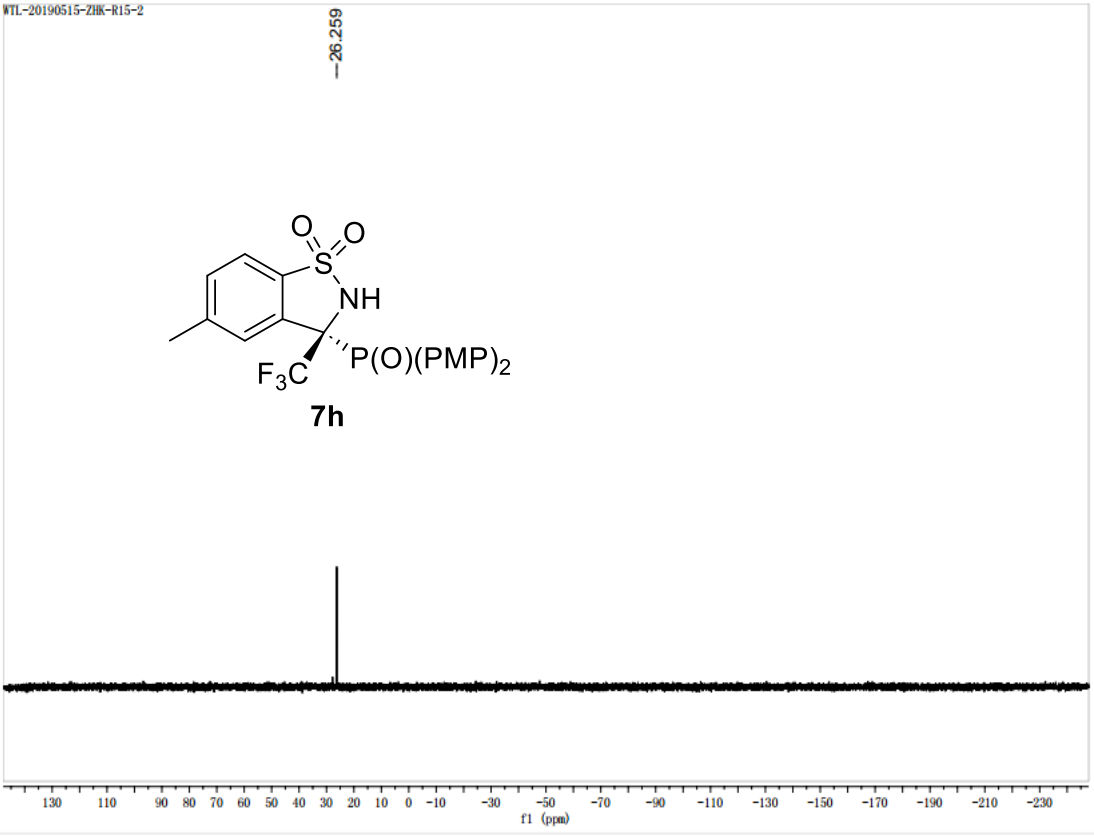

7.765
7.744
7.655
7.344
7.320
7.231
7.226
7.209
7.170
7.167
7.149
7.132
7.111
6.898
6.895
6.892
6.876
6.874
6.831
6.045
6.028
2.341
O
O
S
NH
F3C
P(O)(OPh)2
7g
0.88
0.90
0.90
1.79
1.20
3.23
0.94
2.89
0.88
3.00
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 4.8 4.6 4.4 4.2 4.0 3.8 3.6 3.4 3.2 3.0 2.8 2.6 2.4 2.2 2.0 1.8
f1 (ppm)

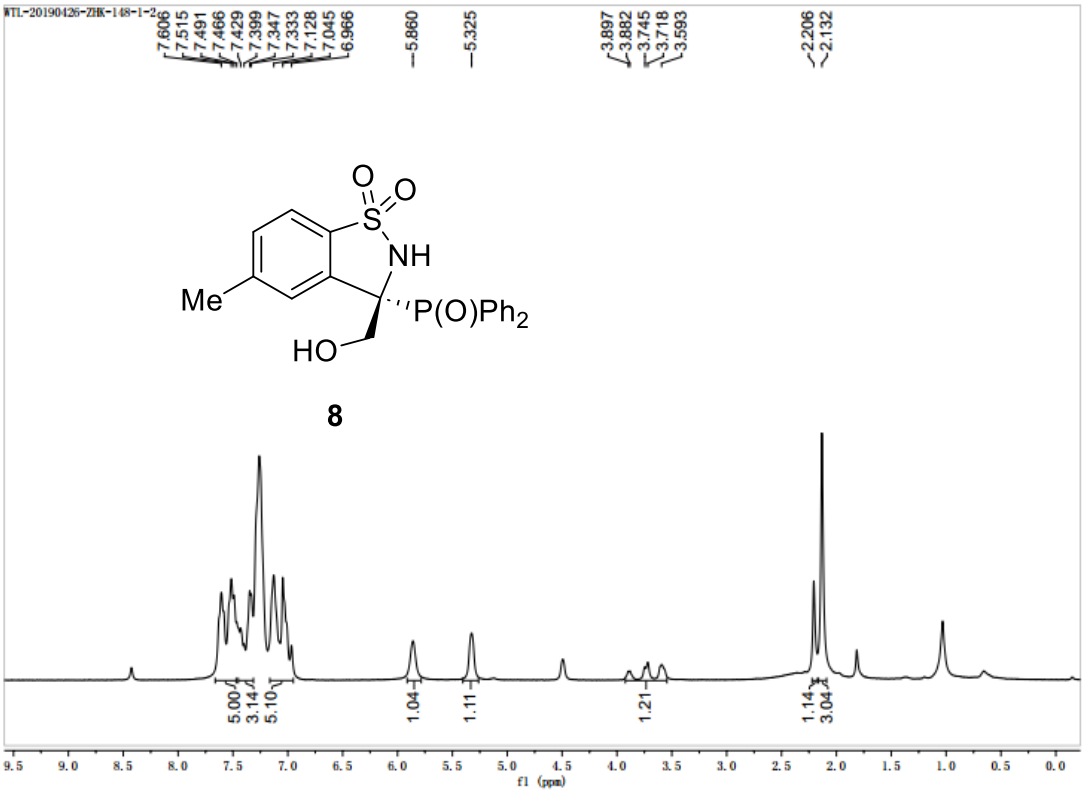

155.746
150.441
150.356
149.601
149.499
145.491
145.468
133.174
133.153
132.805
132.751
130.218
130.210
129.766
129.684
127.323
126.416
126.405
125.847
122.031
122.017
120.795
120.512
120.469
119.740
115.429
29.843
21.826
O
O
S
NH
F3C
P(O)(OPh)2
7g
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


WTL-20190817-ZHK-R59-6-2
-1.604
O
O
S
NH
F3C
P(O)(OPh)2
7g
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

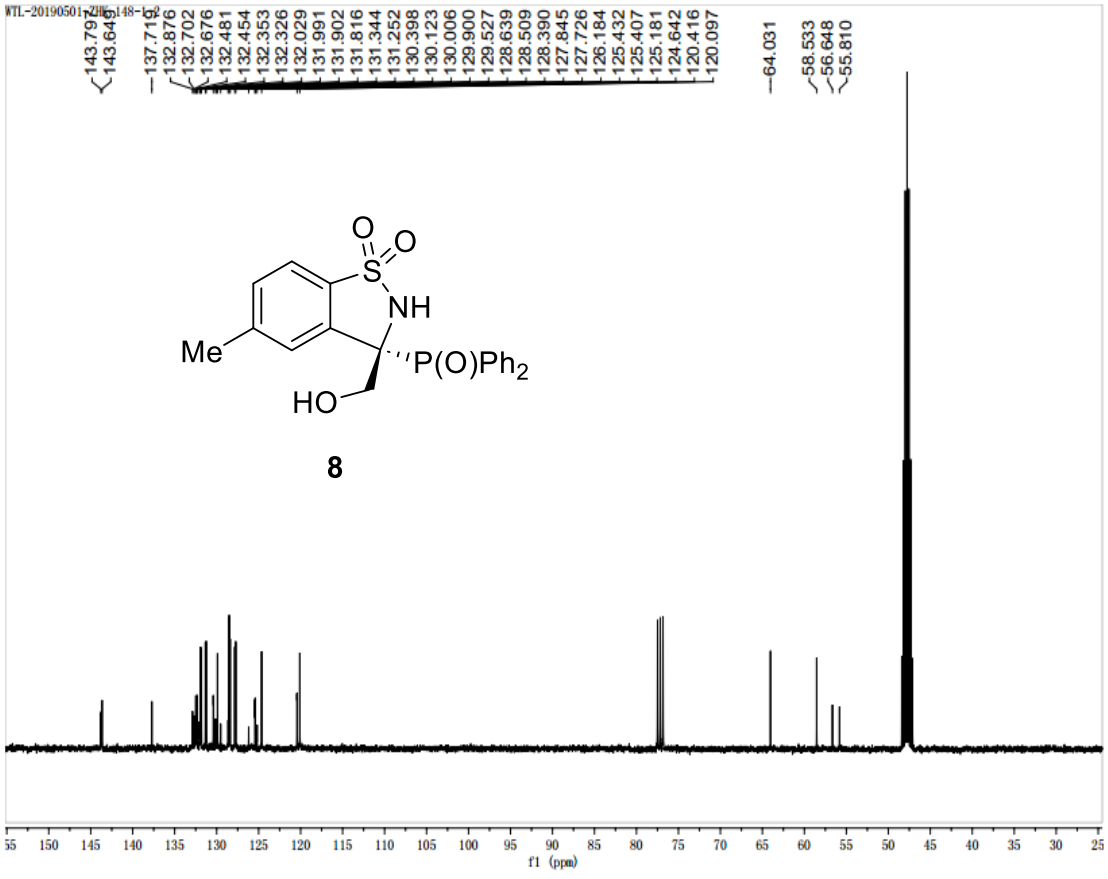

7.976
7.956
7.951
7.923
7.810
7.808
7.785
7.784
7.767
7.762
7.758
7.553
7.533
7.361
7.341
7.035
7.030
7.024
7.019
7.012
6.996
3.868
3.864
3.756
3.752
2.427
O
O
S
NH
F3C
P(O)(PMP)2
7h
2.26
3.16
1.15
1.16
2.18
2.17
1.13
3.00
3.05
3.33
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0
f1 (ppm)


163.505
163.477
163.106
163.079
145.166
145.157
134.816
134.716
134.357
134.261
132.495
132.386
132.359
129.604
127.363
126.615
121.430
118.803
118.556
117.684
114.653
114.522
114.121
113.990
55.548
55.406
21.904
O
O
S
NH
P(O)(PMP)2
F3C
7h
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

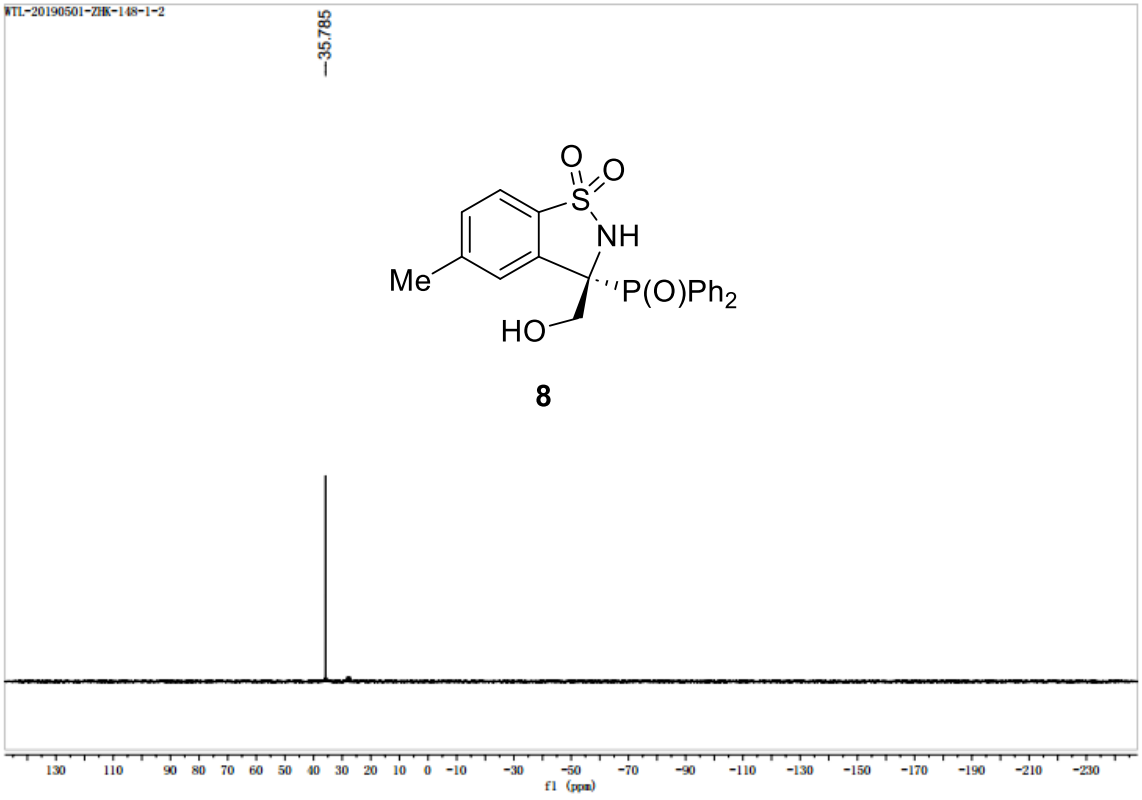

WTL-20190515-ZHK-R15-2
26.259
O
O
S
NH
P(O)(PMP)2
F3C
7h
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)


7.606
7.515
7.491
7.466
7.429
7.399
7.347
7.333
7.128
7.045
6.966
5.860
5.325
3.897
3.882
3.745
3.718
3.593
2.206
2.132
O
O
S
NH
Me
P(O)Ph2
HO
5.00
3.14
5.10
1.04
1.11
1.21
1.14
3.04
f1 (ppm)

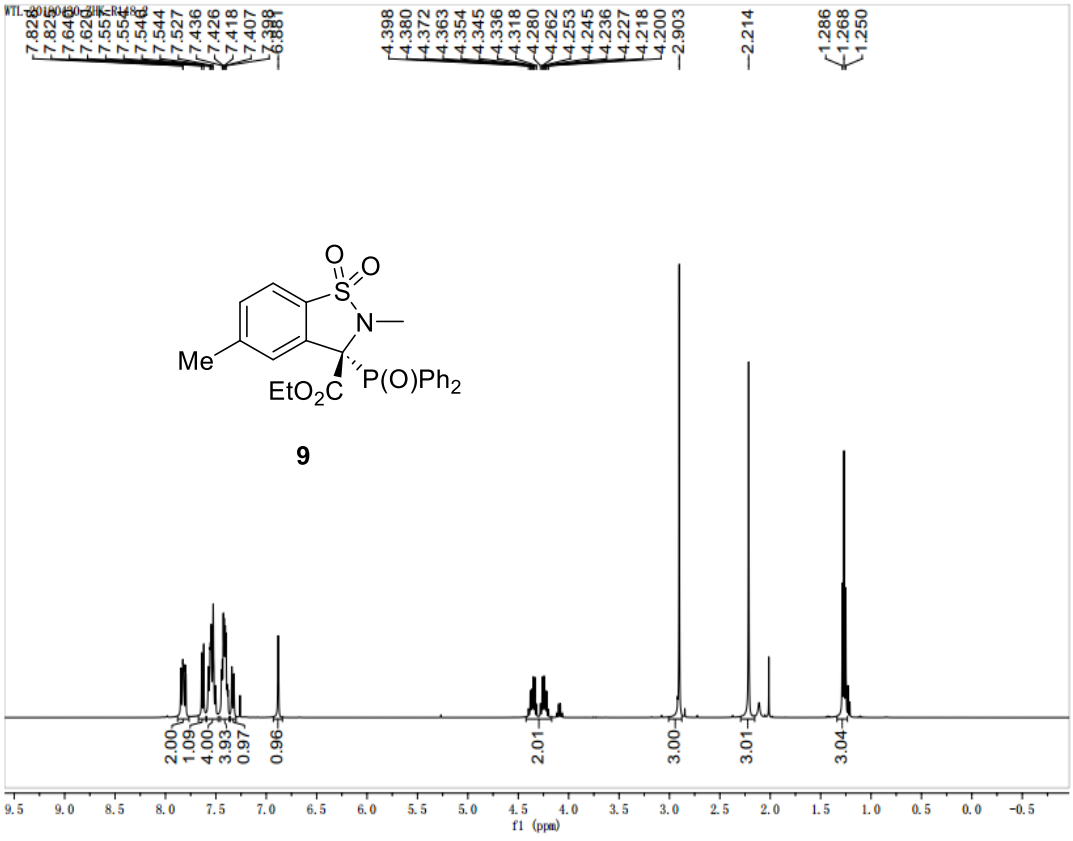
8


143.791
143.643
137.715
132.876
132.702
132.676
132.481
132.454
132.353
132.326
132.029
131.991
131.902
131.816
131.344
131.252
130.398
130.123
130.006
129.900
129.527
128.639
128.509
128.390
127.845
127.726
126.184
125.432
125.407
125.181
124.642
120.416
120.097
64.031
58.533
56.648
55.810
O
O
S
NH
Me
P(O)Ph2
HO
f1 (ppm)

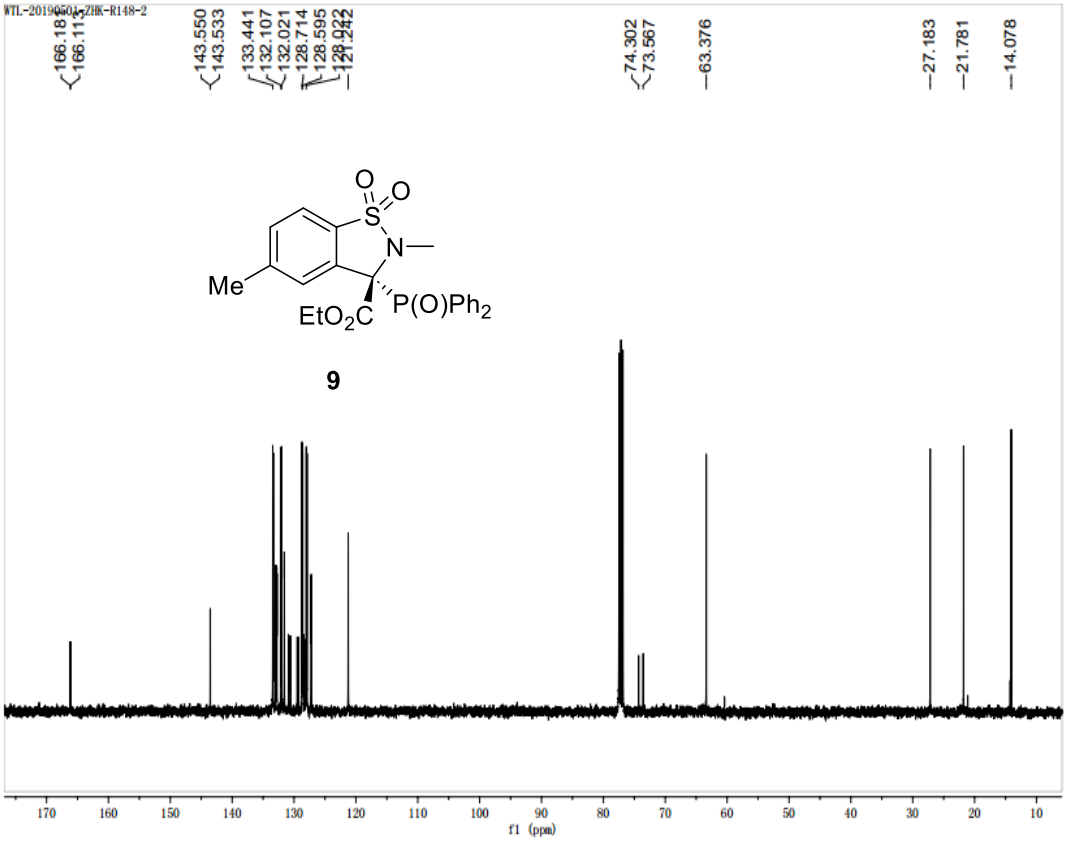
8

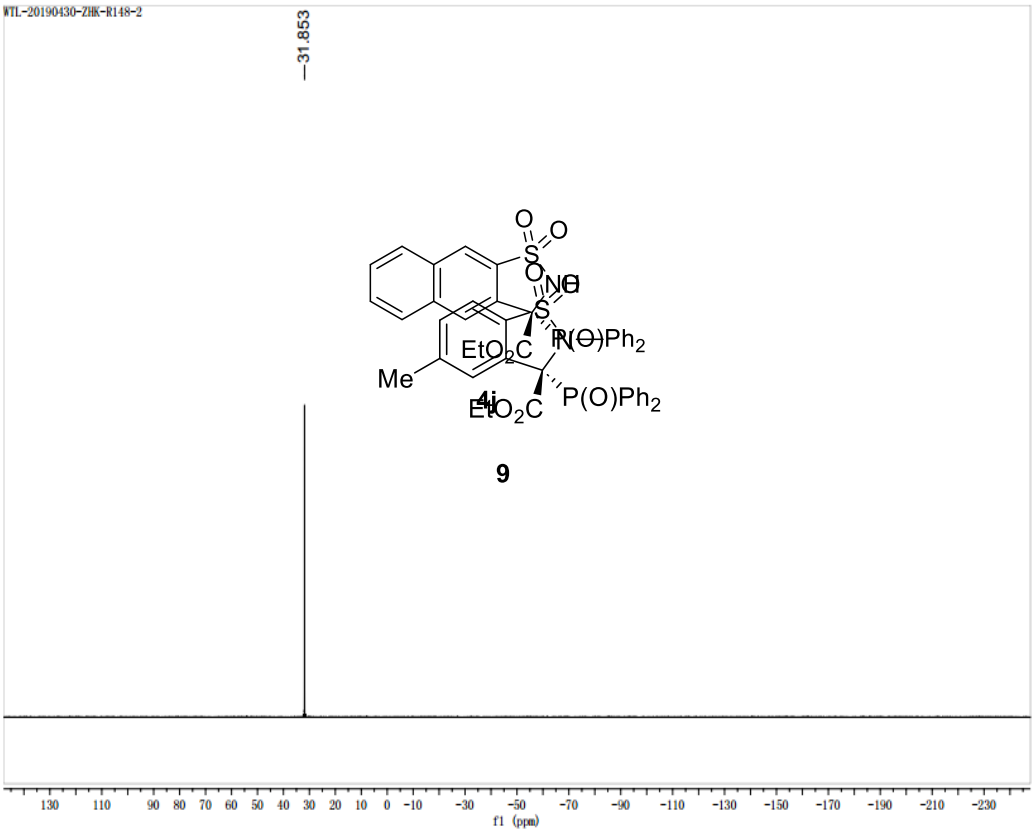

WTL-20190501-ZHK-148-1-2
35.785
O
O
S
NH
Me
P(O)Ph2
HO
130 110 90 80 70 60 50 40 30 20 10 0 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230
f1 (ppm)

8


7.826
7.825
7.646
7.626
7.551
7.544
7.544
7.527
7.436
7.426
7.418
7.407
7.398
6.881
4.398
4.380
4.372
4.363
4.354
4.345
4.336
4.318
4.280
4.262
4.253
4.245
4.236
4.227
4.218
4.200
2.903
2.214
1.286
1.268
1.250
O
O
S
N
Me
EtO2C
P(O)Ph2
2.00
1.09
4.00
3.93
0.97
0.96
2.01
3.00
3.01
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

9


WTL-20190501-ZHK-R148-2
166.181
166.113
143.550
143.533
133.441
132.107
132.021
128.714
128.595
74.302
73.567
63.376
27.183
21.781
14.078
Me
EtO2C
P(O)Ph2
9
f1 (ppm)


WTL-20190430-ZHK-R148-2
31.853
Me
EtO2C
P(O)Ph2
9
f1 (ppm)