Asymmetric Catalytic Alkynylation of Thiazolones and Azlactones for Synthesis of Quaternary α-Amino Acid Precursors

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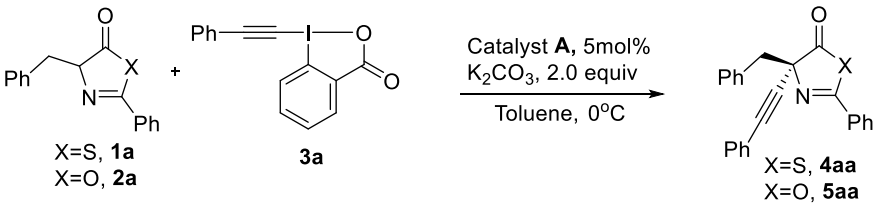
Supporting Information

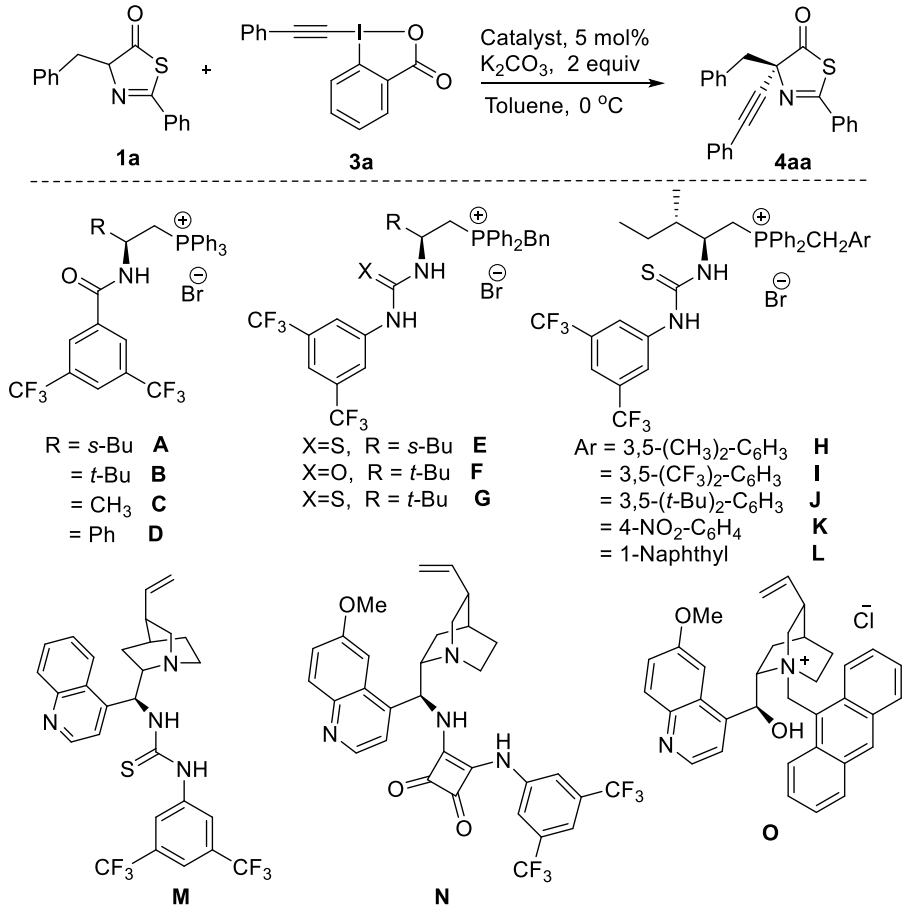
General Information: Thin-layer chromatography (TLC) carried out on 0.25 mm silica gel plates visualized with UV light and/or by staining with ethanolic phosphomolybdic acid (PMA) or iodine. Flash column chromatography was performed on silica gel (300-400 mesh). NMR spectra were recorded on Bruker Ascend^{TM} (600 MHz), JEOL (400 MHz). Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. Optical rotations were taken on JASCO P1030. High-resolution mass spectra were recorded on Agilent Technologies 6230 TOF LC/MS. Enantiomeric excesses were determined by chiral HPLC using a Shimadzu instrument.

General reaction conditions for alkynylation of thiazolones and azlactones:



Under an atmosphere of N_2, a mixture of 4-Benzyl-2-phenylthiazol-5(4H)-one **1a** (26.7 mg, 0.10 mmol) or 4-benzyl-2-phenyloxazol-5(4H)-one **2a** (25.1 mg, 0.10 mmol), 1-(phenylethynyl)-1,2-benziodoxol-3(1*H*)-one **3a** (41.8 mg, 0.12 mmol) and catalyst **A** (3.01 mg, 0.005 mmol) in toluene (1 mL) was cooled to 0 °C, and then K_2CO_3 (27.6 mg, 0.2 mmol) was added. The resulting mixture was stirred vigorously at the same temperature, and monitored by TLC. Upon the complete consumption of **1a** or **2a**, the reaction mixture was loaded directly onto a column packed with silica gel, and eluted with petroleum ether/ethyl acetate (100/1) to afford the alkynylation products **4aa** or **5aa**.

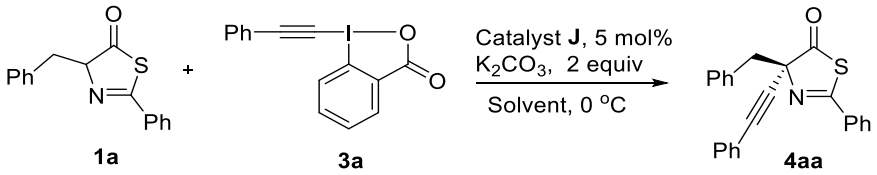
Table S1. Screening of the catalysts for the reaction between **1a** and **3a** [a]



Entry	Catalyst	Time(h)	yield[b](%)	ee[c](%)
1	**A**	12	70	31
2	**B**	12	59	31
3	**C**	14	63	21
4	**D**	18	67	21
5	**E**	12	69	65
6	**F**	15	56	62
7	**G**	12	70	65
8	**H**	12	73	73
9	**I**	18	64	73
10	**J**	12	70	80
11	**K**	24	60	65
12	**L**	18	69	69
13	**M**	18	67	22
14	**N**	15	64	26
15	**O**	18	65	5

[a] General conditions: **1a** (0.05 mmol, 1.0 equiv), **3a** (0.06 mmol, 1.2 equiv), catalyst (5 mol%), and K_2CO_3 (0.1 mmol, 2.0 equiv, 13.8 mg) in Toluene (1 mL) at 0 °C; [b] Yield referred to isolated pure **4aa**; [c] Enantiomeric excess of **4aa** was determined by chiral HPLC analysis.

Table S2. Screening of the solvents for the reaction between **1a** and **3a** [a]

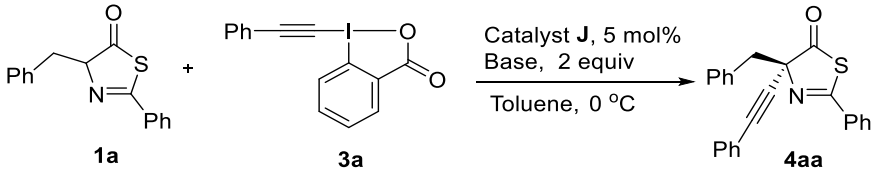


1a 3a 4aa

Entry	Solvent	Time(h)	yield[b](%)	ee[c](%)
1	DCM	6	65	45
2	PE	12	66	63
3	$CHCl_3$	10	56	70
4	Toluene	12	79	80
5	THF	18	71	10
6	MTBE	18	62	59
7	MeCN	24	50	15
8	EA	14	55	11
9	MeOH	12	--	--
10	DMF	12	--	--
11	PhCl	12	71	79
12	xylene	12	70	79

[a] General conditions: **1a** (0.05 mmol, 1.0 equiv), **3a** (0.06 mmol, 1.2 equiv), catalyst **J** (5 mol%), and K_2CO_3 (0.1 mmol, 2.0 equiv, 13.8 mg) in solvent (1 mL) at 0 °C; [b] Yield referred to isolated pure **4aa**; [c] Enantiomeric excess of **4aa** was determined by chiral HPLC analysis.

Table S3. Screening of the bases for the reaction between **1a** and **3a**[a]



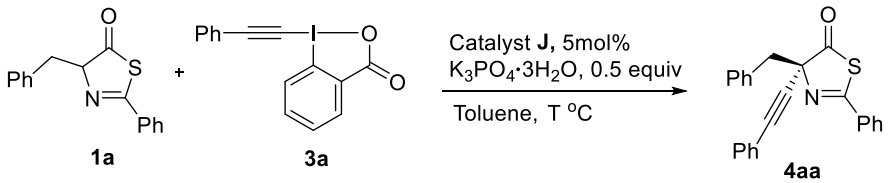
1a 3a 4aa

Entry	Base	Time(h)	yield[b](%)	ee[c](%)
1	KF	16	40	79
2	NaOH	4	45	71
3	$CsCO_3$	4	58	75
4	Na_3PO_4	12	54	79
5	K_3PO_4	12	49	75
6	CH_3COONa	12	trace	–
7	Na_2CO_3	12	60	81
8	$K_3PO_4 \cdot 3H_2O$	6	75	83
9	K_2CO_3	12	70	80
10	$K_3PO_4 \cdot 3H_2O$[d]	10	75	86
11	$K_3PO_4 \cdot 3H_2O$[e]	8	80	82
12	$K_3PO_4 \cdot 3H_2O$[f]	8	82	81

[a] General conditions: **1a** (0.05 mmol, 1.0 equiv), **3a** (0.06 mmol, 1.2 equiv), catalyst **J** (5 mol%), and base (0.1 mmol, 2.0 equiv) in Toluene (1 mL) at 0 °C; [b] Yield referred to isolated pure **4aa**; [c] Enantiomeric excess of **4aa** was determined by chiral HPLC analysis; [d] $K_3PO_4 \cdot 3H_2O$ (0.025 mmol, 0.5 equiv); [e] $K_3PO_4 \cdot 3H_2O$ (0.05 mmol,

1.0 equiv); [f] $K_3PO_4 \cdot 3H_2O$ (0.075 mmol, 1.5 equiv).

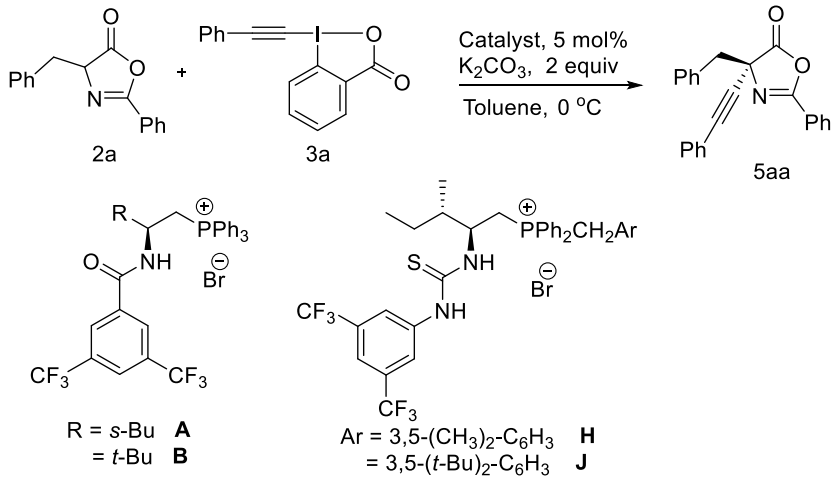
Table S4. Screening of the temperature for the reaction between **1a** and **3a**[a]



Entry	T(°C)	time	yield[b](%)	ee[c](%)
1	–10	18	75	85
3	–30	24	51	80
5	–40	24	60	79

[a] General conditions: **1a** (0.05 mmol, 1.0 equiv), **3a** (0.06 mmol, 1.2 equiv), catalyst **J** (5 mol%), and $K_3PO_4 \cdot 3H_2O$ (0.025 mmol, 0.5 equiv, 6.7 mg) in Toluene (1 mL); [b] Yield referred to isolated pure **4aa**; [c] Enantiomeric excess of **4aa** was determined by chiral HPLC analysis.

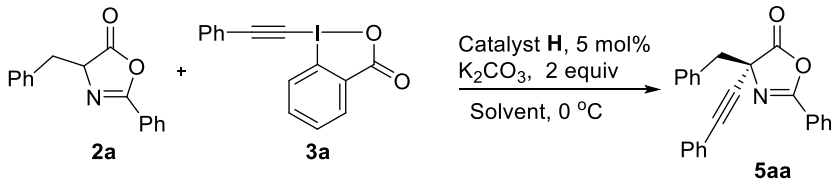
Table S5. Screening of the catalysts for the reaction between **2a** and **3a**[a]



Entry	Catalyst	Time(h)	yield[b](%)	ee[c](%)
1	**A**	36	70	23
2	**B**	36	68	23
3	**H**	48	70	73
4	**J**	48	70	51

[a] General conditions: **2a** (0.05 mmol, 1.0 equiv), **3a** (0.06 mmol, 1.2 equiv), catalyst (5 mol%), and K_2CO_3 (0.1 mmol, 2.0 equiv, 13.8 mg) in Toluene (1 mL) at 0 °C; [b] Yield referred to isolated pure **5aa**; [c] Enantiomeric excess of **5aa** was determined by chiral HPLC analysis.

Table S6. Screening of the solvents for the reaction between **2a** and **3a**[a]

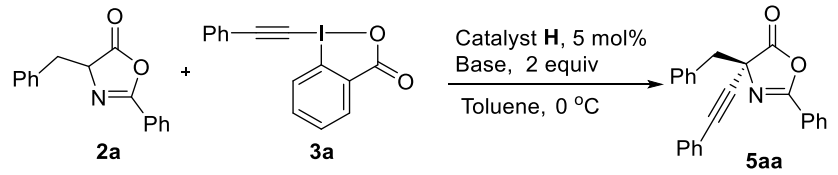


2a **3a** **5aa**

Entry	Solvent	Time(h)	yield[b](%)	ee[c](%)
1	DCM	12	82	31
2	PhCl	48	63	45
3	$CHCl_3$	18	80	31
4	Toluene	48	70	73
5	THF	12	71	11
6	MeOH	12	--	--
7	$PhCF_3$	48	70	51

[a] General conditions: **2a** (0.05 mmol, 1.0 equiv), **3a** (0.06 mmol, 1.2 equiv), catalyst **H** (5 mol%), and K_2CO_3 (0.1 mmol, 2.0 equiv, 13.8 mg) in solvent (1 mL) at 0 °C; [b] Yield referred to isolated pure **5aa**; [c] Enantiomeric excess of **5aa** was determined by chiral HPLC analysis.

Table S7. Screening of the bases for the reaction between **2a** and **3a**[a]

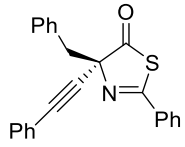


2a **3a** **5aa**

Entry	Base	Time(h)	yield[b](%)	ee[c](%)
1	KF	48	61	63
2	NaOH	1.5	85	59
3	$CsCO_3$	1.5	85	61
4	Na_3PO_4	48	70	65
5	K_3PO_4	48	76	65
6	CH_3COONa	48	--	–
7	Na_2CO_3	48	60	67
8	$K_3PO_4 \cdot 3H_2O$	18	81	60
9	DIPEA	48	--	--
10	K_2CO_3	48	70	73
11	K_2CO_3 [d]	48	62	45
12	K_2CO_3 [e]	48	59	59
13	K_2CO_3 [f]	48	63	66

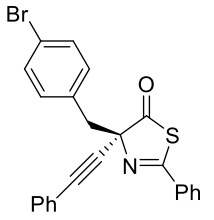
[a] General conditions: **2a** (0.05 mmol, 1.0 equiv), **3a** (0.06 mmol, 1.2 equiv), catalyst **H** (5 mol%), and base (0.1 mmol, 2.0 equiv) in Toluene (1 mL) at 0 °C; [b] Yield referred to isolated pure **5aa**; [c] Enantiomeric excess of **5aa** was determined by chiral HPLC analysis; [d] K_2CO_3 (0.025 mmol, 0.5 equiv); [e] K_2CO_3 (0.05 mmol, 1.0 equiv); [f] K_2CO_3 (0.075 mmol, 1.5 equiv).

^{1}H NMR, ^{13}C NMR, MS, HPLC and specific rotation data of 4



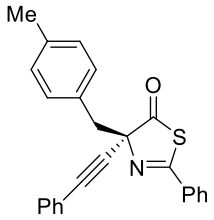
4aa

(*R*)-4-benzyl-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4aa**): following general procedure, **1a** (26.7 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4•$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE : EA = 100 : 1, light yellow solid, 27.53 mg, 75% yield, 86% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 7.4 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.49 – 7.43 (m, 4H), 7.30 (d, J = 7.3 Hz, 2H), 7.27 (dd, J = 7.4, 2.1 Hz, 3H), 7.24 – 7.18 (m, 3H), 3.66 (d, J = 13.3 Hz, 1H), 3.50 (d, J = 13.3 Hz, 1H); ^{13}CNMR (100 MHz, $CDCl_3$) δ 205.32, 165.16, 133.58, 133.11, 132.52, 132.14, 130.93, 128.99, 128.94, 128.36, 128.32, 128.10, 127.50, 121.91, 86.80, 84.91, 83.86, 46.04; HRMS (ESI) Calcd for $(C_{24}H_{18}NOS)^+$ $[M + H]^+$ 368.1104, found 368.1105; $[\alpha]_D^{20}$ +17.2 (c 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 11.31 min (minor enantiomer), t_R = 12.47 min (major enantiomer).



4ba

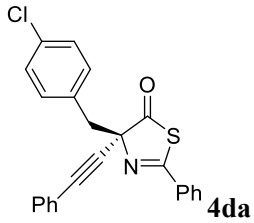
(*R*)-4-(4-bromobenzyl)-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4ba**): following general procedure, **1b** (34.5 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J**(4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4 •$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 24.5 mg, 55% yield, 67% ee; ^{1}HNMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 2H), 7.58 – 7.51 (m, 1H), 7.50 – 7.41 (m, 4H), 7.38 – 7.26 (m, 5H), 7.14 (d, J = 8.0 Hz, 2H), 3.58 (d, J = 13.3 Hz, 1H), 3.41 (d, J = 13.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.00, 165.37, 132.95, 132.74, 132.71, 132.56, 132.12, 131.25, 129.09, 129.02, 128.39, 128.36, 121.76, 87.05, 84.62, 83.49, 45.15; HRMS (ESI) calcd for $(C_{24}H_{17}BrNOS)^+$ $[M + H]^+$ 446.0209, found 446.0.208; $[\alpha]_D^{20}$ +19.8 (c 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R =12.80 min (minor enantiomer), t_R =14.20 min (major enantiomer).



4ca

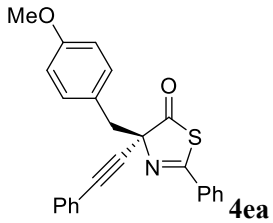
(*R*)-4-(4-methylbenzyl)-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4ca**): following general procedure: **1c** (28.1 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4 •$3H_2O$ (13.4 mg, 0.05 mmol) was

added; flash chromatography with PE : EA = 100 : 1, light yellow solid, 27.4 mg, 72% yield, 79% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, J = 7.8 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.46 (dd, J = 9.6, 5.4 Hz, 4H), 7.34 – 7.26 (m, 3H), 7.15 (d, J = 7.9 Hz, 2H), 7.03 (d, J = 7.9 Hz, 2H), 3.62 (d, J = 13.3 Hz, 1H), 3.47 (d, J = 13.3 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.27, 165.01, 137.07, 133.22, 132.46, 132.14, 130.77, 130.52, 128.92, 128.82, 128.38, 128.30, 121.99, 86.73, 85.06, 84.02, 45.67, 21.22; HRMS (ESI) calcd for $(C_{25}H_{20}NOS)^+$ $[M + H]^+$ 382.1260, found 382.1262; $[\alpha]_D^{20}$ +27.6 (c 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 11.6 min (minor enantiomer), t_R = 12.6 min (major enantiomer).



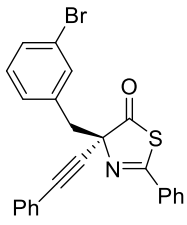
4da

(*R*)-4-(4-chlorobenzyl)-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4da**): following general procedure, **1d** (30.1 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4•$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE : EA = 100 : 1, light yellow solid, 28.5 mg, 71% yield, 69% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 2H), 7.57 – 7.51 (m, 1H), 7.50 – 7.43 (m, 4H), 7.31 (ddd, J = 9.1, 6.2, 4.5 Hz, 3H), 7.20 (s, 4H), 3.60 (d, J = 13.4 Hz, 1H), 3.44 (d, J = 13.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.03, 165.36, 133.53, 132.96, 132.70, 132.21, 132.12, 129.09, 129.02, 128.38, 128.36, 128.30, 121.75, 87.03, 84.71, 83.53, 45.12; HRMS (ESI) calcd for $(C_{24}H_{17}ClNOS)^+$ $[M + H]^+$ 402.0714, found 402.0715; $[\alpha]_D^{20}$ +24.2 (c 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 11.27 min (minor enantiomer), t_R = 12.11 min (major enantiomer).



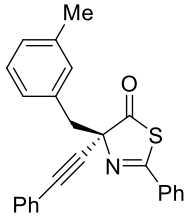
4ea

(*R*)-4-(4-methoxybenzyl)-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4ea**): following general procedure, **1e** (29.7 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4•$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE : EA = 100 : 1, light yellow solid, 24.6 mg, 62% yield, 75% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 2H), 7.52 (d, J = 7.3 Hz, 1H), 7.50 – 7.42 (m, 4H), 7.35 – 7.26 (m, 3H), 7.17 (d, J = 8.6 Hz, 2H), 6.74 (d, J = 8.6 Hz, 2H), 3.73 (s, 3H), 3.61 (d, J = 13.5 Hz, 1H), 3.46 (d, J = 13.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.47, 165.14, 158.94, 133.15, 132.49, 132.14, 131.95, 128.94, 128.37, 128.31, 125.59, 121.95, 113.50, 86.70, 85.11, 83.97, 55.23, 45.33; HRMS (ESI) calcd for $(C_{25}H_{20}NO_2S)^+$ $[M + H]^+$ 398.1209, found 398.1211; $[\alpha]_D^{20}$ +28.8 (c 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 12.46 min (minor enantiomer), t_R = 13.24 min (major enantiomer).



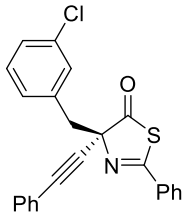
4fa

(*R*)-4-(3-bromobenzyl)-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4fa**): following general procedure: **1f** (34.5 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then $K_3PO_4 \cdot 3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 27.1 mg, 61% yield, 81% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.58 – 7.51 (m, 1H), 7.51 – 7.43 (m, 5H), 7.37 – 7.26 (m, 4H), 7.20 (d, J = 7.6 Hz, 1H), 7.10 (t, J = 7.8 Hz, 1H), 3.58 (d, J = 13.3 Hz, 1H), 3.40 (d, J = 13.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.89, 165.42, 136.01, 134.03, 132.96, 132.69, 132.17, 130.64, 129.64, 129.48, 129.10, 129.01, 128.41, 128.34, 122.01, 121.71, 87.27, 84.62, 83.35, 45.37. HRMS (ESI) calcd for $(C_{24}H_{17}BrNOS)^+$ $[M + H]^+$ 446.0209, found 446.0215; $[\alpha]_D^{20}$ +24.8 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 13.88 min (minor enantiomer), t_R = 14.78 min (major enantiomer).



4ga

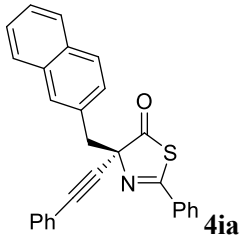
(*R*)-4-(3-methylbenzyl)-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4ga**): following general procedure: **1g** (28.1 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then $K_3PO_4 \cdot 3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 30.1 mg, 79% yield, 79% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (dd, J = 5.3, 3.3 Hz, 2H), 7.58 – 7.51 (m, 1H), 7.51 – 7.43 (m, 4H), 7.38 – 7.27 (m, 3H), 7.16 – 7.05 (m, 3H), 7.02 (d, J = 7.2 Hz, 1H), 3.64 (d, J = 13.2 Hz, 1H), 3.47 (d, J = 13.2 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.34, 165.09, 137.51, 133.41, 133.15, 132.48, 132.14, 131.83, 128.96, 128.91, 128.34, 128.31, 128.21, 127.96, 127.91, 121.95, 86.77, 84.91, 83.94, 46.11, 21.37; HRMS (ESI) calcd for $(C_{25}H_{20}NOS)^+$ $[M + H]^+$ 382.1260, found 382.1264; $[\alpha]_D^{20}$ +23.2 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R =18.34 min (minor enantiomer), t_R =19.18 min (major enantiomer).



4ha

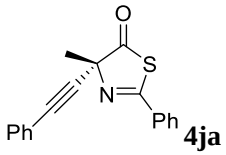
(*R*)-4-(3-chlorobenzyl)-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4ha**): following general

procedure: **1h** (30.1 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then $K_3PO_4 \cdot 3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 29.67 mg, 74% yield, 77% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.74 (m, 2H), 7.53 (d, J = 7.3 Hz, 1H), 7.46 (ddd, J = 6.9, 6.3, 4.9 Hz, 4H), 7.35 – 7.26 (m, 4H), 7.22 – 7.13 (m, 3H), 3.59 (d, J = 13.3 Hz, 1H), 3.41 (d, J = 13.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.91, 165.39, 135.72, 133.81, 132.97, 132.68, 132.15, 131.08, 129.33, 129.09, 129.05, 129.00, 128.39, 128.34, 127.73, 121.72, 87.23, 84.62, 83.37, 45.39; HRMS (ESI) calcd for $(C_{24}H_{17}ClNOS)^+$ $[M + H]^+$ 402.0714, found 402.0717; $[\alpha]_D^{20}$ +15.2 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R = 21.40 min (minor enantiomer), t_R = 22.57 min (major enantiomer).



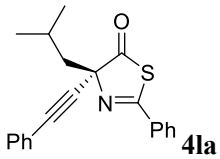
4ia

(*R*)-4-(naphthalen-2-yl)-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4ia**): following general procedure: **1i** (31.7 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then $K_3PO_4 \cdot 3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 27.11 mg, 65% yield, 67% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.72 (m, 5H), 7.70 (dd, J = 8.4, 4.8 Hz, 1H), 7.54 – 7.38 (m, 8H), 7.35 – 7.23 (m, 3H), 3.83 (dd, J = 13.3, 4.9 Hz, 1H), 3.67 (dd, J = 13.3, 5.0 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.30, 165.27, 133.21, 133.08, 132.68, 132.53, 132.16, 131.26, 129.95, 129.02, 128.93, 128.90, 128.37, 128.34, 127.94, 127.67, 127.54, 126.02, 125.93, 121.90, 86.94 , 85.10, 83.91, 46.13; HRMS (ESI) calcd for $(C_{28}H_{20}NOS)^+$ $[M + H]^+$ 418.1260, found 418.1265; $[\alpha]_D^{20}$ +35.40 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R = 29.16 min (mionr enantiomer), t_R = 31.01 min (major enantiomer).



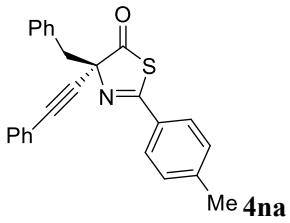
4ja

(*R*)-4-methyl-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4ja**): following general procedure: **1j** (19.1 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then $K_3PO_4 \cdot 3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 18.92 mg, 65% yield, 49% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.84 (m, 2H), 7.54 (dd, J = 5.0, 3.7 Hz, 1H), 7.51 – 7.42 (m, 4H), 7.35 – 7.25 (m, 3H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.33, 164.03, 133.25, 132.60, 132.13, 128.99, 128.93, 128.47, 128.30, 121.92, 85.66, 84.53, 80.87, 26.16; HRMS (ESI) calcd for $(C_{18}H_{14}NOS)^+$ $[M + H]^+$ 292.0791, found 292.0794; $[\alpha]_D^{20}$ -6.4 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R =9.90min (major enantiomer), t_R =10.97 min (minor enantiomer).



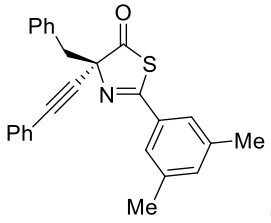
4la

(*R*)-4-isobutyl-2-phenyl-4-(phenylethynyl)thiazol-5(4H)-one (**4la**): following general procedure:**1l** (23.3 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4 •$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 18.32 mg, 55% yield, 71% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 5.3, 3.4 Hz, 2H), 7.59 – 7.41 (m, 5H), 7.34 – 7.26 (m, 3H), 2.28 (dd, J = 13.7, 5.3 Hz, 1H), 2.13 (dd, J = 12.7, 6.1 Hz, 1H), 1.93 (dd, J = 13.7, 7.0 Hz, 1H), 1.05 (dd, J = 8.8, 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.82, 163.68, 133.42, 132.48, 132.08, 128.98, 128.86, 128.46, 128.29, 126.31, 122.09, 86.10, 84.64, 84.32, 48.26, 25.66, 24.15, 23.97; HRMS (ESI) calcd for $(C_{21}H_{20}NOS)^+$ $[M + H]^+$ 334.1260, found 334.1265; $[\alpha]_D^{20}$ +23.7 (c 0.3, $CHCl_3$); HPLC (Daicel CHIRALPAK OJ-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 10.70 min (major enantiomer), t_R = 11.71 min (minor enantiomer).



4na

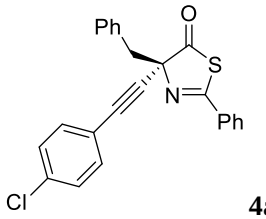
(*R*)-4-benzyl-4-(phenylethynyl)-2-(p-tolyl)thiazol-5(4H)-one (**4na**): following general procedure: **1n** (28.1 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4 •$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 28.58 mg, 75% yield, 79% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, J = 8.2 Hz, 2H), 7.46 (dd, J = 7.6, 1.8 Hz, 2H), 7.35 – 7.28 (m, 3H), 7.27 – 7.24 (m, 4H), 7.23 – 7.16 (m, 3H), 3.64 (d, J = 13.3 Hz, 1H), 3.49 (d, J = 13.3 Hz, 1H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.55, 164.94, 143.24, 133.65, 132.14, 130.94, 130.47, 129.62, 128.95, 128.33, 128.31, 128.07, 127.45, 121.97, 86.71, 84.83, 84.04, 46.09, 21.72. HRMS (ESI) calcd for $(C_{25}H_{20}NOS)^+$ $[M + H]^+$ 382.1260, found 382.1262; $[\alpha]_D^{20}$ +30.0 (c 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R =10.68 min (minor enantiomer), t_R =11.52 min (major enantiomer).



4oa

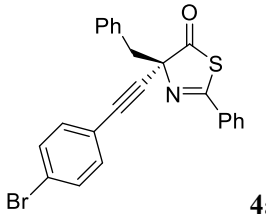
(*R*)-4-benzyl-2-(3,5-dimethylphenyl)-4-(phenylethynyl)thiazol-5(4H)-one (**4oa**): following general procedure: **1o** (29.53 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4•$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 35.16 mg, 89% yield, 75%

ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.44 (m, 2H), 7.40 (s, 2H), 7.34 – 7.18 (m, 8H), 7.16 (s, 1H), 3.66 (d, J = 13.3 Hz, 1H), 3.50 (d, J = 13.3 Hz, 1H), 2.36 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.51, 165.53, 138.69, 134.29, 133.63, 133.04, 132.15, 130.94, 128.95, 128.31, 128.11, 127.48, 126.11, 121.97, 86.75, 84.82, 83.98, 46.05, 21.22; HRMS (ESI) calcd for $(C_{26}H_{22}NOS)^+$ $[M + H]^+$ 396.1417, found 396.1422; $[\alpha]_D^{20}$ +6.4 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 97 : 3, Flow rate = 0.5 mL/min, λ = 254 nm): t_R =9.93 min (minor enantiomer), t_R =11.00 min (major enantiomer).



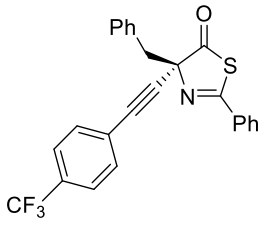
4ab

(*R*)-4-benzyl-4-((4-chlorophenyl)ethynyl)-2-phenylthiazol-5(4H)-one (**4ab**): following general procedure: **1a** (26.7 mg, 0.1 mmol, 1.0 eq.), **3b** (45.8 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4•$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 28.47 mg, 71% yield, 79% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.3 Hz, 2H), 7.52 (d, J = 7.3 Hz, 1H), 7.46 (t, J = 7.4 Hz, 2H), 7.38 (dd, J = 8.6, 1.7 Hz, 2H), 7.30 – 7.23 (m, 4H), 7.23 – 7.16 (m, 3H), 3.64 (d, J = 13.3 Hz, 1H), 3.48 (d, J = 13.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.16, 165.36, 135.12, 133.45, 133.37, 133.03, 132.60, 130.91, 128.97, 128.72, 128.36, 128.12, 127.56, 120.39, 85.68, 84.86, 46.00; HRMS (ESI) calcd for $(C_{24}H_{17}ClNOS)^+$ $[M + H]^+$ 402.0714, found 402.0716; $[\alpha]_D^{20}$ +46.6 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 10.85 min (minor enantiomer), t_R = 13.35 min (major enantiomer).



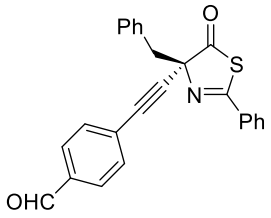
4ac

(*R*)-4-benzyl-4-((4-bromophenyl)ethynyl)-2-phenylthiazol-5(4H)-one (**4ac**): following general procedure: **1a** (26.7 mg, 0.1 mmol, 1.0 eq.), **3c** (51.1 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4•$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 22.70 mg, 51% yield, 73% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.7 Hz, 2H), 7.53 (t, J = 7.2 Hz, 1H), 7.45 (dd, J = 14.1, 8.0 Hz, 4H), 7.31 (d, J = 8.4 Hz, 2H), 7.27 – 7.17 (m, 5H), 3.63 (d, J = 13.3 Hz, 1H), 3.48 (d, J = 13.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.14, 165.38, 133.55, 133.43, 133.01, 132.61, 131.64, 130.90, 128.97, 128.36, 128.12, 127.56, 123.40, 120.85, 85.73, 85.01, 84.86, 45.98; HRMS (ESI) calcd for $(C_{24}H_{17}BrNOS)^+$ $[M + H]^+$ 446.0209, found 446.2010; $[\alpha]_D^{20}$ +10.8 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R =11.12 min (minor enantiomer), t_R =12.97 min (major enantiomer).



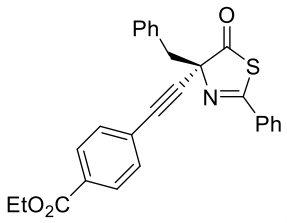
4ad

(*R*)-4-benzyl-2-phenyl-4-((4-(trifluoromethyl)phenyl)ethynyl)thiazol-5(4H)-one (**4ad**): following general procedure: **1a** (26.7 mg, 0.1 mmol, 1.0 eq.), **3d** (49.9 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4•$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 30.02 mg, 69% yield, 73% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 5.2, 3.4 Hz, 2H), 7.56 (s, 4H), 7.55 – 7.51 (m, 1H), 7.47 (t, J = 7.4 Hz, 2H), 7.27 – 7.19 (m, 5H), 3.65 (d, J = 13.3 Hz, 1H), 3.50 (d, J = 13.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.97, 165.60, 133.34, 132.97, 132.67, 132.40, 130.91, 130.72（q, $J_{C\text{-}F}$=32.6 Hz), 128.99, 128.37, 128.15, 127.63, 125.31, 125.27, 125.23, 124.83（q, $J_{C\text{-}F}$=155Hz), 86.30, 85.33, 84.79, 45.99; HRMS (ESI) calcd for $(C_{25}H_{17}F_3NOS)^+$ $[M + H]^+$ 436.0977, found 436.0983; $[\alpha]_D^{20}$ +22.00 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OJ-H, Hexane : Isopropanol = 97:3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R = 32.36 min (minor enantiomer), t_R = 39.36 min (major enantiomer).



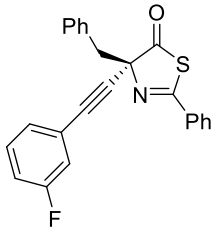
4ae

(*R*)-4-((4-benzyl-5-oxo-2-phenyl-4,5-dihydrothiazol-4-yl)ethynyl)benzaldehyde (**4ae**): following general procedure: **1a** (26.7 mg, 0.1 mmol, 1.0 eq.), **3e** (45.1 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4 •$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 28.05 mg, 71% yield, 79% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.80 (dd, J = 12.3, 7.9 Hz, 4H), 7.61 (d, J = 8.2 Hz, 2H), 7.54 (dd, J = 10.5, 4.1 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.25 (d, J = 3.2 Hz, 1H), 7.22 (dd, J = 8.0, 3.4 Hz, 4H), 3.65 (d, J = 13.3 Hz, 1H), 3.50 (d, J = 13.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.90, 191.48, 165.66, 136.02, 133.29, 132.96, 132.69, 130.90, 129.51, 129.00, 128.37, 128.16, 128.09, 127.64, 87.75, 85.73, 84.84, 45.97; HRMS (ESI) calcd for $(C_{25}H_{18}NO_2S)$ $^+[M + H]^+$ 396.1053, found 396.1055; $[\alpha]_D^{20}$ +11.80 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OJ-H, Hexane : Isopropanol = 95 : 5, Flow rate = 1.0 mL/min, λ = 254 nm): t_R = 16.88 min (major enantiomer), t_R = 20.04 min (minor enantiomer).



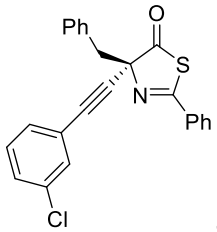
4af

(*R*)-4-((4-benzyl-5-oxo-2-phenyl-4,5-dihydrothiazol-4-yl)ethynyl)phenyl propionate (**4af**): following general procedure: **1a** (26.7 mg, 0.1 mmol, 1.0 eq.), **3f** (50.4 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then $K_3PO_4 \cdot 3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 31.61 mg, 72% yield, 79% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J = 8.2 Hz, 2H), 7.79 (d, J = 7.8 Hz, 2H), 7.52 (dd, J = 7.8, 3.2 Hz, 3H), 7.46 (t, J = 7.6 Hz, 2H), 7.29 – 7.17 (m, 5H), 4.36 (q, J = 7.1 Hz, 2H), 3.66 (d, J = 13.3 Hz, 1H), 3.50 (d, J = 13.3 Hz, 1H), 1.38 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.02, 166.02, 165.50, 133.38, 133.00, 132.63, 132.04, 130.92, 130.60, 129.44, 128.98, 128.37, 128.14, 127.59, 126.41, 86.63, 85.98, 84.86, 61.30, 45.99, 14.40; HRMS (ESI) calcd for $(C_{27}H_{22}NO_3S)^+$[M + H]$^+$ 440.1315, found 440.1315; $[\alpha]_D^{20}$ +21.40 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 12.46 min (minor enantiomer), t_R = 13.72 min (major enantiomer).



4ag

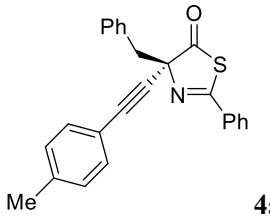
(*R*)-4-benzyl-4-((3-fluorophenyl)ethynyl)-2-phenylthiazol-5(4H)-one (**4ag**): following general procedure: **1a** (26.7 mg, 0.1 mmol, 1.0 eq.), **3g** (45.84 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then $K_3PO_4 \cdot 3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 29.26 mg, 76% yield, 79% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, J = 5.2, 3.5 Hz, 2H), 7.57 – 7.50 (m, 1H), 7.49 – 7.42 (m, 2H), 7.27 – 7.19 (m, 7H), 7.16 (d, J = 8.5 Hz, 1H), 7.10 – 6.99 (m, 1H), 3.64 (d, J = 13.3 Hz, 1H), 3.49 (d, J = 13.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.09, 165.42, 162.29（q, $J_{C\text{-}F}$=245Hz), 133.42, 133.02, 132.61, 130.91, 129.96 (q, $J_{C\text{-}F}$=8Hz), 128.97, 128.36, 128.13, 128.06, 128.03, 127.58, 123.71（q, $J_{C\text{-}F}$=10 Hz), 118.95（q, $J_{C\text{-}F}$=23 Hz), 116.43（q, $J_{C\text{-}F}$=21 Hz), 85.49, 84.80, 45.98; HRMS (ESI) calcd for $(C_{24}H_{17}FNOS)^+$ [M + H]$^+$ 386.1009, found 386.1015; $[\alpha]_D^{20}$ +35.2 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 10.67 min (minor enantiomer), t_R = 11.95 min (major enantiomer).



4ah

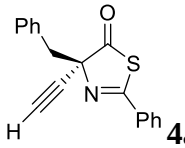
(*R*)-4-benzyl-4-((3-chlorophenyl)ethynyl)-2-phenylthiazol-5(4H)-one (**4ah**): following general procedure: **1a** (26.7 mg, 0.1 mmol, 1.0 eq.), **3h** (45.84 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then $K_3PO_4 \cdot 3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 28.07 mg, 70% yield, 73% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, J = 7.3 Hz, 2H), 7.53 (d, J = 7.2 Hz, 1H), 7.46 (dd, J = 8.4, 6.2 Hz, 3H), 7.36 – 7.28 (m, 2H), 7.28 – 7.19 (m, 6H), 3.64 (d, J = 13.3 Hz, 1H), 3.48 (d, J = 13.3 Hz,

1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.06, 165.43, 134.19, 133.41, 133.01, 132.61, 132.01, 130.91, 130.23, 129.59, 129.32, 128.97, 128.36, 128.13, 127.58, 123.59, 85.32, 85.12, 84.80, 45.97; HRMS (ESI) calcd for $(C_{24}H_{17}ClNOS)^+$ $[M + H]^+$ 402.0714, found 402.0720; $[\alpha]_D^{20}$ +3.20 (*c* 0.25, $CHCl_3$); HPLC (Daicel CHIRALPAK oD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 10.87 min (minor enantiomer), t_R = 11.96 min (major enantiomer).



4ai

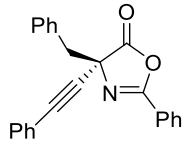
(*R*)-4-benzyl-2-phenyl-4-(p-tolylethynyl)thiazol-5(4H)-one (**4ai**): following general procedure: **1a** (26.7 mg, 0.1 mmol, 1.0 eq.), **3i** (43.4 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4•$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, light yellow solid, 28.58 mg, 75% yield, 83% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.5 Hz, 2H), 7.52 (dd, *J* = 8.3, 6.1 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.28 – 7.24 (m, 2H), 7.23 – 7.17 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 2H), 3.65 (d, *J* = 13.3 Hz, 1H), 3.49 (d, *J* = 13.3 Hz, 1H), 2.33(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.42, 165.03, 139.17, 133.65, 133.13, 132.48, 132.03, 130.93, 129.08, 128.92, 128.35, 128.08, 127.46, 118.83, 87.01, 84.96, 83.15, 46.07, 21.64; HRMS (ESI) calcd for $(C_{25}H_{20}NOS)^+$$[M + H]^+$ 382.1260, found 382.1263; $[\alpha]_D^{20}$ -2.4 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R =10.44 min (minor enantiomer), t_R =12.49 min (major enantiomer).



4ak

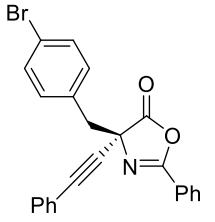
(*R*)-4-benzyl-4-ethynyl-2-phenylthiazol-5(4H)-one (**4ak**): following general procedure: **1a** (26.7 mg, 0.1 mmol, 1.0 eq.), **3k** (43.4 mg, 0.12 mmol, 1.2 eq.), catalyst **J** (4.2 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_3PO_4•$3H_2O$ (13.4 mg, 0.05 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 23.28 mg, 80% yield, 31% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.4 Hz, 2H), 7.52 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.44 (dd, *J* = 10.4, 4.6 Hz, 2H), 7.20 (d, *J* = 6.9 Hz, 5H), 3.58 (d, *J* = 13.3 Hz, 1H), 3.42 (d, *J* = 13.3 Hz, 1H), 2.64 (d, *J* = 1.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.03, 165.71, 133.15, 132.90, 132.63, 130.85, 128.95, 128.34, 128.10, 127.57, 84.13, 78.75, 75.09, 45.91; HRMS (ESI) calcd for $(C_{18}H_{14}NOS)^+$ $[M + H]^+$ 292.0791, found 292.0796; $[\alpha]_D^{20}$ +18.6 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R =20.19 min (minor enantiomer), t_R =22.77 min (major enantiomer).

^{1}H NMR, ^{13}C NMR, MS, HPLC and specific rotation data of 5



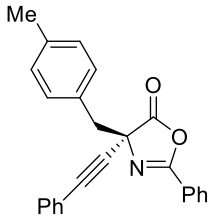
5aa

(*R*)-4-benzyl-2-phenyl-4-(phenylethynyl)oxazol-5(4H)-one (**5aa**): following general procedure: **2a** (25.1 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 24.57 mg, 70% yield, 73% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.45 (dt, J = 13.3, 4.5 Hz, 4H), 7.37 – 7.29 (m, 3H), 7.29 – 7.25 (m, 2H), 7.22 (dt, J = 12.6, 4.2 Hz, 3H), 3.58 (d, J = 13.4 Hz, 1H), 3.48 (d, J = 13.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.85, 161.69, 133.19, 133.03, 132.12, 130.70, 129.15, 128.84, 128.37, 128.31, 128.20, 127.83, 125.30, 121.61, 86.74, 82.79, 68.20, 45.19. HRMS (ESI) calcd for $(C_{24}H_{18}NO_2)^+$ $[M + H]^+$ 352.1332, found 352.1330; $[\alpha]_D^{20}$ +37.4 (*c* 0.25, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 11.31 min (minor enantiomer), t_R = 12.47 min (major enantiomer)



5ba

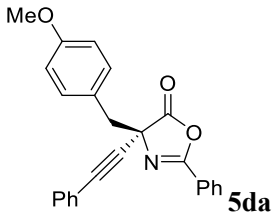
(*R*)-4-(4-bromobenzyl)-2-phenyl-4-(phenylethynyl)oxazol-5(4H)-one (**5ba**): following general procedure: **2b** (32.9 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 30.46 mg, 71% yield, 50% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.87 (m, 2H), 7.58 (t, J = 7.5 Hz, 1H), 7.50 – 7.42 (m, 4H), 7.38 – 7.27 (m, 5H), 7.15 (d, J = 8.4 Hz, 2H), 3.52 (d, J = 13.5 Hz, 1H), 3.41 (d, J = 13.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.61, 161.93, 133.40, 132.38, 132.17, 132.10, 131.48, 129.26, 128.94, 128.41, 128.26, 125.13, 122.12, 121.44, 87.02, 82.44, 67.85, 44.38; HRMS (ESI) calcd for $(C_{24}H_{17}BrNO_2)^+$$[M + H]^+$ 430.0437, found 430.0435; $[\alpha]_D^{20}$ +39.6 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R =23.61 min (major enantiomer), t_R =26.05 min (minor enantiomer).



5ca

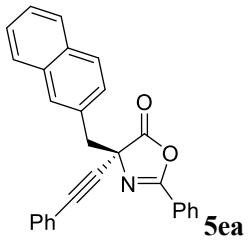
(*R*)-4-(4-methylbenzyl)-2-phenyl-4-(phenylethynyl)oxazol-5(4H)-one (**5ca**): following general procedure: **2c** (26.5 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added;

flash chromatography with PE:EA = 100:1, white solid, 27.74 mg, 76% yield, 56% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.86 (m, 2H), 7.56 (dd, J = 8.3, 6.6 Hz, 1H), 7.46 (ddd, J = 12.4, 7.6, 4.5 Hz, 4H), 7.37 – 7.26 (m, 3H), 7.14 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 7.9 Hz, 2H), 3.54 (d, J = 13.5 Hz, 1H), 3.44 (d, J = 13.5 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.00, 155.78, 131.59, 127.28, 126.25, 124.67, 124.04, 123.24, 123.15, 122.96, 122.49, 122.36, 119.52, 115.79, 80.76, 77.04, 62.42, 38.92, 23.94; HRMS (ESI) calcd for $(C_{25}H_{20}NO_2)^+$ $[M + H]^+$ 366.1489, found 366.1492; $[\alpha]_D^{20}$ +30.4 (c 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R =23.78 min (major enantiomer), t_R =25.26 min (minor enantiomer).



5da

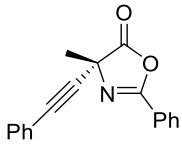
(*R*)-4-(4-methoxybenzyl)-2-phenyl-4-(phenylethynyl)oxazol-5(4H)-one (**5da**): following general procedure: **2d** (28.1 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 26.29 mg, 69% yield, 63% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 8.3, 1.1 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.51 – 7.42 (m, 4H), 7.38 – 7.28 (m, 3H), 7.22 – 7.16 (m, 2H), 6.79 – 6.71 (m, 2H), 3.72 (s, 3H), 3.54 (d, J = 13.6 Hz, 1H), 3.45 (d, J = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.92, 161.67, 159.16, 133.18, 132.12, 131.78, 129.13, 128.85, 128.37, 128.22, 125.34, 125.03, 121.65, 113.71, 86.65, 82.89, 68.38, 55.24, 44.44; HRMS (ESI) calcd for $(C_{25}H_{20}NO_3)^+$ $[M + H]^+$ 382.1438, found 382.1434; $[\alpha]_D^{20}$ +42.0 (c 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R = 27.32 min (major enantiomer), t_R = 29.68 min (minor enantiomer).



5ea

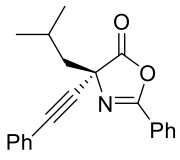
(*R*)-4-(naphthalen-2-ylmethyl)-2-phenyl-4-(phenylethynyl)oxazol-5(4H)-one (**5ea**): following general procedure: **2e** (30.1 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 30.07 mg, 75% yield, 57% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.85 (m, 2H), 7.75 (s, 3H), 7.69 (d, J = 8.4 Hz, 1H), 7.52 (t, J = 7.4 Hz, 1H), 7.47 (d, J = 6.5 Hz, 2H), 7.41 (dd, J = 8.3, 3.9 Hz, 5H), 7.36 – 7.26 (m, 3H), 3.75 (d, J = 13.4 Hz, 1H), 3.65 (d, J = 13.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.83, 161.84, 133.25, 133.20, 132.80, 132.13, 130.71, 129.83, 129.17, 128.82, 128.55, 128.38, 128.23, 127.99, 127.80, 127.65, 126.08, 126.05, 125.25, 121.60, 86.87, 82.86, 68.34, 45.25; HRMS (ESI) calcd for $(C_{28}H_{20}NO_2)^+$$[M + H]^+$ 402.1489, found 402.1486; $[\alpha]_D^{20}$ +13.40 (c 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 14.32 min (major enantiomer), t_R

= 16.22 min (minor enantiomer).



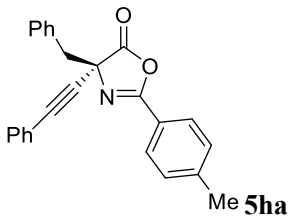
5fa

(*R*)-4-methyl-2-phenyl-4-(phenylethynyl)oxazol-5(4H)-one (**5fa**): following general procedure:**2f** (17.5 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 18.97 mg, 69% yield, 27% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.01 (m, 2H), 7.63 – 7.56 (m, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.46 (dd, J = 7.8, 1.7 Hz, 2H), 7.37 – 7.26 (m, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 175.87, 161.72, 133.33, 132.10, 129.11, 128.96, 128.35, 128.33, 125.51, 121.61, 85.57, 83.52, 63.37, 26.01. HRMS (ESI) calcd for $(C_{18}H_{14}NO_2)^+$ $[M + H]^+$ 276.1019, found 276.1021; $[\alpha]_D^{20}$ -2.4 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R = 20.92min (major enantiomer), t_R = 22.67 min (minor enantiomer).



5ga

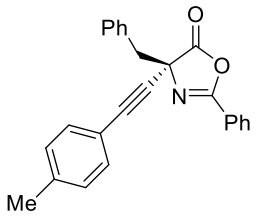
(*R*)-4-isobutyl-2-phenyl-4-(phenylethynyl)oxazol-5(4H)-one (**5ga** known compound[2l]): following general procedure: **2g** (21.7 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 17.44 mg, 55% yield, 53% ee; HRMS (ESI) calcd for $(C_{21}H_{20}NO_2)^+[M + H]^+$ 318.1489, found 318.1486; $[\alpha]_D^{20}$ +31.0 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OJ-H, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R = 18.49 min (major enantiomer), t_R = 19.77 min (minor enantiomer).



5ha

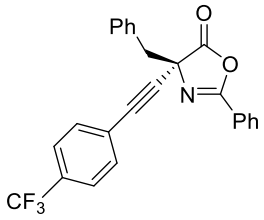
(*R*)-4-benzyl-4-(phenylethynyl)-2-(p-tolyl)oxazol-5(4H)-one (**5ha**): following general procedure: **2h** (26.5 mg, 0.1 mmol, 1.0 eq.), **3a** (41.8 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 29.20 mg, 80% yield, 59% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, J = 8.2 Hz, 2H), 7.48 – 7.44 (m, 2H), 7.31 (ddd, J = 7.3, 4.6, 2.9 Hz, 3H), 7.29 – 7.26 (m, 1H), 7.26 – 7.24 (m, 2H), 7.24 – 7.15 (m, 4H), 3.57 (d, J = 13.4 Hz, 1H), 3.47 (d, J = 13.4 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.99, 161.75, 144.01, 133.11, 132.12, 130.71, 129.58, 129.11, 128.36, 128.29, 128.18, 127.79, 122.48, 121.67, 86.64, 82.97, 68.13, 45.22, 21.86. HRMS (ESI) calcd for $(C_{25}H_{20}NO_2)^+$ $[M + H]^+$ 366.1489, found 366.1491; $[\alpha]_D^{20}$ +59.6 (*c* 0.5,

$CHCl_3$); HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R =22.61 min (major enantiomer), t_R =25.17 min (minor enantiomer).



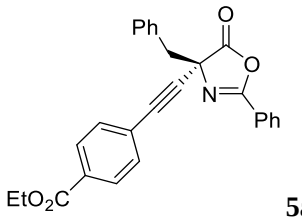
5ab

(*R*)-4-benzyl-2-phenyl-4-(p-tolylethynyl)oxazol-5(4H)-one (**5ab**): following general procedure: **2a** (25.1 mg, 0.1 mmol, 1.0 eq.), **3b** (43.4 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 27.37 mg, 75% yield, 53% ee; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.90 (d, *J* = 7.9 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.27 (s, 2H), 7.20 (d, *J* = 7.0 Hz, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 3.57 (d, *J* = 13.4 Hz, 1H), 3.47 (d, *J* = 13.5 Hz, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 174.95, 161.61, 139.37, 133.17, 133.09, 132.02, 130.70, 129.14, 128.83, 128.30, 128.19, 127.81, 125.33, 118.53, 86.95, 82.10, 68.24, 45.22, 21.66; HRMS (ESI) calcd for $(C_{25}H_{20}NO_2)^+$ [M + H]$^+$ 366.1489, found 366.1491; $[\alpha]_D^{20}$ +42.8 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R =21.85 min (major enantiomer), t_R =25.19 min (minor enantiomer).



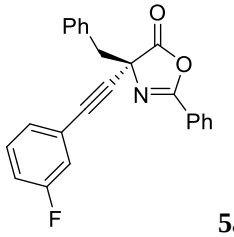
5ac

(*R*)-4-benzyl-2-phenyl-4-((4-(trifluoromethyl)phenyl)ethynyl)thiazol-5(4H)-one (**5ac**): following general procedure: **2a** (25.1 mg, 0.1 mmol, 1.0 eq.), **3c** (49.9 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 27.23 mg, 65% yield, 27% ee; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.91 (d, *J* = 8.3 Hz, 2H), 7.61 – 7.52 (m, 5H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.26 (dd, *J* = 8.7, 1.8 Hz, 2H), 7.24 – 7.17 (m, 3H), 3.58 (d, *J* = 13.4 Hz, 1H), 3.48 (d, *J* = 13.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 174.52, 161.98, 133.35, 132.79, 132.39, 130.88 (q, $J_{C\text{-}F}$=32Hz), 130.68, 128.90, 128.37, 128.22, 127.96, 125.38, 125.34, 125.29, 125.13, 123.84(q, $J_{C\text{-}F}$=273Hz), 85.28, 85.18, 68.12, 45.08; HRMS (ESI) calcd for $(C_{25}H_{17}F_3NO_2)^+$ [M + H]$^+$ 420.1206, found 420.1209; $[\alpha]_D^{20}$ +18.8 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95:5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 12.58 min (major enantiomer), t_R = 14.13 min (minor enantiomer).



5ad

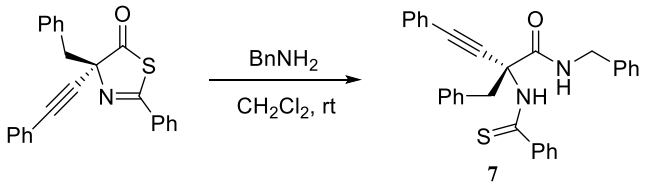
(*R*)-4-((4-benzyl-5-oxo-2-phenyl-4,5-dihydrooxazol-4-yl)ethynyl)phenyl propionate (**5ad**): following general procedure: **2a** (25.1 mg, 0.1 mmol, 1.0 eq.), **3d** (50.4 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 32.99 mg, 78% yield, 60% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.96 (m, 2H), 7.91 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.56 – 7.49 (m, 3H), 7.47 – 7.41 (m, 2H), 7.26 (dt, *J* = 9.0, 3.7 Hz, 3H), 7.21 (dd, *J* = 4.7, 2.8 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.59 (d, *J* = 13.4 Hz, 1H), 3.49(d, *J* = 13.4 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.57, 165.98, 161.91, 133.30, 132.84, 132.03, 130.78, 130.68, 129.49, 128.87, 128.35, 128.22, 127.92, 126.07, 125.18, 85.92, 85.49, 68.18, 61.33, 45.08, 14.39; HRMS (ESI) calcd for $(C_{27}H_{22}NO_4)^+$ $[M + H]^+$ 424.1543, found 424.1550; $[\alpha]_D^{20}$ +6.40 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R = 32.49 min (major enantiomer), tR = 35.80 min (minor enantiomer).



5ae

(*R*)-4-benzyl-4-((3-fluorophenyl)ethynyl)-2-phenylthiazol-5(4H)-one (**5ae**): following general procedure: **2a** (25.1 mg, 0.1 mmol, 1.0 eq.), **3e** (43.9 mg, 0.12 mmol, 1.2 eq.), catalyst **H** (3.8 mg, 0.005 mmol), was added in toluene (1.0 mL) and then K_2CO_3 (27.6 mg, 0.20 mmol) was added; flash chromatography with PE:EA = 100:1, white solid, 23.25 mg, 63% yield, 65% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (dd, *J* = 5.3, 3.3 Hz, 2H), 7.60 – 7.52 (m, 1H), 7.44 (dd, *J* = 10.7, 4.8 Hz, 2H), 7.27 – 7.24 (m, 4H), 7.24 – 7.18 (m, 3H), 7.18 – 7.13 (m, 1H), 7.08 – 7.02 (m, 1H), 3.57 (d, *J* = 13.4 Hz, 1H), 3.47 (d, *J* = 13.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.63, 162.29(d, $J_{C\text{-}F}$=245 Hz),161.86 133.28, 132.88, 130.68, 130.04(d, $J_{C\text{-}F}$=9 Hz), 128.87, 128.34, 128.21, 128.04, 127.99, 127.91, 125.20, 123.39(d, $J_{C\text{-}F}$=9 Hz), 118.94(d, $J_{C\text{-}F}$=23 Hz)，116.62 (d, $J_{C\text{-}F}$=21Hz), 85.45, 83.73, 68.11, 45.10; HRMS (ESI) calcd for $(C_{24}H_{17}FNO_2)^+$ $[M + H]^+$ 370.1238, found 370.1237; $[\alpha]_D^{20}$ +40.6 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK IA, Hexane : Isopropanol = 97 : 3, Flow rate = 0.3 mL/min, λ = 254 nm): t_R = 19.86 min (major enantiomer), tR = 22.45 min (minor enantiomer).

Ring opening of alkynylation product 4aa[1] [2]



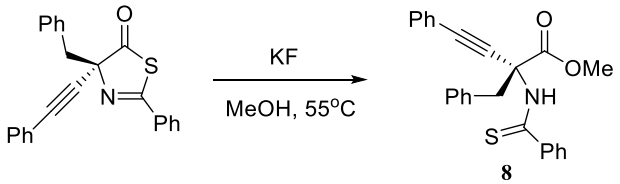
4aa 86**%** ee

7

95% yield, 86% ee

To a solution of **4aa** (36.7 mg, 0.1 mmol, 1.0 eq, 86% ee) in CH_2Cl_2 was added $BnNH_2$ (22 μL, 0.2mmol, 2.0 eq) under N_2. The reaction mixture was vigorously stirred at ambient temperature for 24 h. After consumption of the starting material **4aa** which was monitored by TLC, the reaction mixture was quenched by water, and then extracted with CH_2Cl_2 three times. The combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated after filtration. After evaporation of

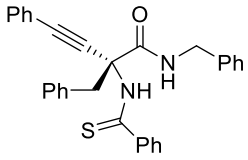
the solvent, the residue was purified by column chromatography (hexane: ethyl acetate =10:1) to give **7** (45.03 mg, 0.095 mmol, 95% yield, 86% ee).



4aa 86% ee

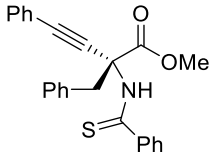
8
90% yield, 86% ee

In a sealed tube，a solution of **4aa** (36.7 mg, 0.1 mmol, 1.0 eq, 86% ee) in MeOH was added KF (0.3 mmol, 3.0 eq) under N_2. The reaction mixture was vigorously stirred at 55 °C for 0.5 h. After consumption of the starting material **4aa** which was monitored by TLC, the reaction mixture was quenched by water, and the organic phase was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated after filtration. The residue was purified by column chromatography (hexane: ethyl acetate =10:1) to give **8** (35.91 mg, 0.09 mmol, 90% yield, 86% ee).



7

(*R*)-N,2-dibenzyl-4-phenyl-2-phenylthioamidobut-3-ynamide (**7**): flash chromatography with PE:EA = 10:1, white solid, 45.03 mg, 95% yield, 86% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.81 (m, 2H), 7.61 (s, 1H), 7.55 – 7.49 (m, 1H), 7.45 (ddt, *J* = 12.7, 11.5, 4.6 Hz, 6H), 7.27 (ddt, *J* = 8.5, 3.8, 1.6 Hz, 6H), 7.22 – 7.18 (m, 3H), 7.09 (dt, *J* = 7.3, 3.7 Hz, 2H), 6.78 (t, *J* = 5.8 Hz, 1H), 4.58 (dd, *J* = 15.1, 6.7 Hz, 1H), 4.30 (dd, *J* = 15.1, 5.3 Hz, 1H), 3.61 (d, *J* = 13.2 Hz, 1H), 3.40 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.01, 168.32, 138.39, 138.07, 137.06, 135.70, 132.39, 132.20, 131.12, 128.89, 128.70, 128.66, 128.38, 127.83, 127.52, 127.38, 127.27, 126.79, 123.53, 92.27, 48.95, 43.49; HRMS (ESI) calcd for $(C_{31}H_{27}N_2OS)^+$ $[M + H]^+$ 475.1839, found 475.1855; $[\alpha]_D^{20}$ -20.0 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK OD-H, Hexane : Isopropanol = 95 : 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R = 21.01 min (minor enantiomer), t_R = 22.59 min (major enantiomer).

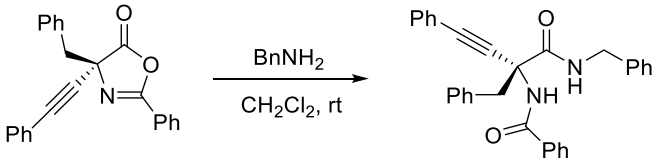


8

methyl (*R*)-2-benzyl-4-phenyl-2-phenylthioamidobut-3-ynoate (**8**): flash chromatography with PE:EA = 10:1, white solid, 35.91 mg, 90% yield, 86% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.74 (m, 2H), 7.48 (dd, *J* = 6.5, 4.3 Hz, 1H), 7.46 – 7.35 (m, 6H), 7.26 (d, *J* = 6.2 Hz, 1H), 7.18 (s, 2H), 7.12 (s, 3H), 6.95 (d, *J* = 4.8 Hz, 1H), 3.77 (d, *J* = 4.9 Hz, 3H), 3.72 (dd, *J* = 13.6, 4.7 Hz, 1H), 3.47 (dd, *J* = 13.5, 4.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.22, 167.66, 139.78, 136.36, 135.04, 132.46, 131.89, 131.11, 128.76, 128.37, 128.15, 127.74, 127.40, 126.75, 121.41, 93.16, 53.38, 46.33; HRMS (ESI) calcd for $(C_{25}H_{22}NO_2S)^+$ $[M + H]^+$ 400.1366, found 400.1372; $[\alpha]_D^{20}$ +72.6 (*c* 0.5, $CHCl_3$);

HPLC (Daicel CHIRALPAK OJ-H, Hexane : Isopropanol = 95: 5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R =35.95 min (minor enantiomer), t_R =53.01 min (major enantiomer).

Ring opening of alkynylation product 5aa

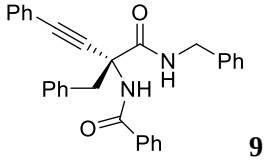


5aa 73% ee

9

90% yield, 73% ee

To a solution of **5aa** (35.1 mg, 0.1 mmol, 1.0 eq, 73% ee) in CH_2Cl_2 was added $BnNH_2$ (22 μL, 0.2 mmol, 2.0 eq) under N_2. The reaction mixture was vigorously stirred at ambient temperature for 24 h. After consumption of the starting material **5aa** which was monitored by TLC, the reaction mixture was quenched by water, and the organic phase was extracted with CH_2Cl_2 three times. The combined organic extracts were dried over anhydrous Na_2SO_4, and concentrated after filtration. After evaporation of the solvent, the residue was purified by column chromatography (hexane: ethyl acetate =10:1) to give **9** (41.22 mg, 0.090 mmol, 90% yield, 73% ee).

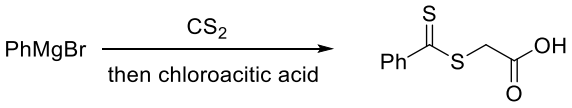


9

(R)-N-(2-benzyl-1-(benzylamino)-1-oxo-4-phenylbut-3-yn-2-yl)benzamide (**9**): flash chromatography with PE:EA = 10:1, white solid, 41.22 mg, 90% yield, 73% ee; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.76 (m, 2H), 7.50 (dd, J = 8.4, 6.3 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.40 – 7.36 (m, 2H), 7.34 – 7.25 (m, 11H), 7.23 – 7.14 (m, 3H), 6.82 (t, J = 5.6 Hz, 1H), 4.50 (dd, J = 15.0, 5.8 Hz, 1H), 4.42 (dd, J = 15.0, 5.7 Hz, 1H), 3.67 (d, J = 12.9 Hz, 1H), 3.52 (d, J = 12.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.80, 166.18, 137.44, 134.66, 134.12, 131.94, 131.90, 130.75, 129.02, 128.80, 128.65, 128.40, 128.34, 127.72, 127.66, 127.29, 121.82, 88.35, 86.23, 59.39, 44.43, 44.30; HRMS (ESI) calcd for $(C_{31}H_{27}N_2O_2)^+$ $[M + H]^+$ 459.2067, found 459.2077; $[\alpha]_D^{20}$ +3.60 (*c* 0.5, $CHCl_3$); HPLC (Daicel CHIRALPAK AS-H, Hexane : Isopropanol =95:5, Flow rate = 0.5 mL/min, λ = 254 nm): t_R =24.00 min (major enantiomer), t_R =31.55 min (minor enantiomer).

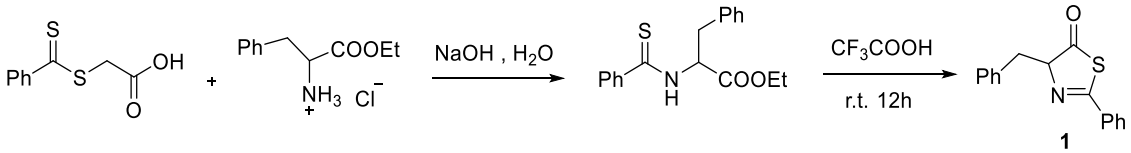
General procedure for the synthesis of 4-benzyl-2-phenylthiazol-5(4H)-one substrates 1b-1i, 1o, 1n

Known compounds **1a**[3], **1j**[3], **1k**[1] **and 1l**[4] were prepared by literature procedures. New compounds **1b**, **1c**, **1d**, **1e**, **1f**, **1g**, **1h**, **1i**, **1o** and **1m** were prepared according to literature procedures.[5] [3]



Step 1: In a round-bottom flask, following flame drying, 40 ml of 1M phenyl magnesium bromide (40 mmol) in THF was added. It was then cooled to 0 °C, and 2.42 ml of carbon disulfide (40 mmol) was slowly introduced dropwise. It was stirred at room temperature for 12 hr and then poured into 100 g of ice water and 3.78 g of chloroacetic acid (40 mmol). Anhydrous sodium carbonate 3.36 g

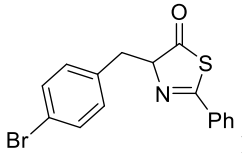
(20 mmol) was added and stirred for 24 hr at 90 °C. The liquid was adjusted to pH 2 with concentrated hydrochloric acid, and a red solid was obtained in 72% yield by recrystallization in a mixture of ethyl acetate and hexane.



1

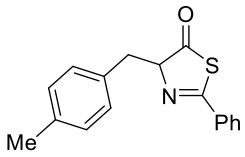
Step 2: 2-((phenylcarbonothioyl)thio)acetic acid(2 g, 9.43 mmol) was dissolved in 1 M NaOH (28.3 mL, 3 eq) solution, then 1-carboxy-2-phenylethan-1-aminium chloride was added. After consumption of the starting material, the reaction mixture was acidified to pH 7-8 with dilute HCl (aq). The aqueous layer was extracted with EtOAc (15 mL × 3). The combined organic layers were dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was loaded onto a column packed with silica gel, and eluted with petroleum ether/ethyl acetate (10:1) to afford ethyl (phenylcarbonothioyl)phenylalaninate as ligtht green solid (50% yield, 1.08 g).

Step 3: A solution of ethyl (phenylcarbonothioyl)phenylalaninate (1.08 g, 4.56 mmol) in anhydrous trifluoroacetic acid(13.5 ml) was set aside at room temp. overnight， evaporation in vacuo, followed by trituration of the residual oil with aqueous sodium hydrogen carbonate, gave pure DL-4-benzyl-2-phenyloxazole-5(4H)-thione (1.21 g, 100% yield), other products were obtained by similar treatment of the amino-acid derivative.



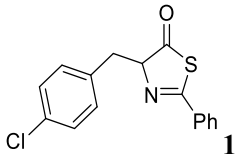
1b

4-(4-bromobenzyl)-2-phenylthiazol-5(4H)-one (**1b**): light yellow solid, 1.55 g, 99% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (s, 1H), 7.67 (d, J = 7.2 Hz, 2H), 7.43 (d, J = 8.3 Hz, 2H), 7.36 (t, J = 7.3 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.19 (d, J = 8.3 Hz, 2H), 3.87 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.23, 150.85, 140.23, 134.67, 134.42, 131.64, 131.20, 129.51, 129.39, 125.35, 119.46, 32.51; HRMS (ESI) calcd for $(C_{16}H_{13}BrNOS)^+$ $[M + H]^+$ 345.9896, found 345.9901.



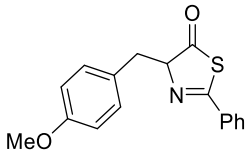
1c

4-(4-methylbenzyl)-2-phenylthiazol-5(4H)-one (**1c**): light yellow solid, 1.27 g, 99% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.97 (s, 1H), 7.67 (t, J = 6.8 Hz, 2H), 7.46 – 7.20 (m, 3H), 7.18 – 6.96 (m, 4H), 3.84 (d, J = 7.2 Hz, 2H), 2.20 (d, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.80, 150.65, 137.73, 135.63, 135.24, 134.50, 129.49, 129.33, 128.83, 125.31, 32.74, 21.14; HRMS (ESI) calcd for $(C_{17}H_{16}NOS)^+$ $[M + H]^+$ 282.0947, found 282.0955



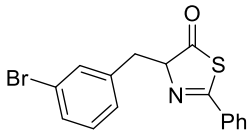
1d

4-(4-chlorobenzyl)-2-phenylthiazol-5(4H)-one (**1d**): light yellow solid, 1.36 g, 99% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (d, J = 7.4 Hz, 2H), 7.36 (t, J = 7.2 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.24 (d, J = 8.2 Hz, 2H), 3.88 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.46, 150.66, 139.83, 134.58, 134.43, 131.01, 130.78, 129.51, 129.36, 128.72, 125.32, 32.44. HRMS (ESI) calcd for $(C_{16}H_{13}ClNOS)^+$ $[M + H]^+$ 302.0401, found 302.0416.



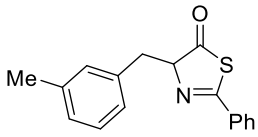
1e

4-(4-methoxybenzyl)-2-phenylthiazol-5(4H)-one (**1e**): light yellow solid, 1.34 g, 99% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.05 (s, 1H), 7.68 (d, J = 7.4 Hz, 2H), 7.33 (dt, J = 23.5, 7.1 Hz, 3H), 7.13 (t, J = 11.9 Hz, 2H), 6.80 (d, J = 8.4 Hz, 2H), 3.82 (s, 2H), 3.66 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 158.01, 152.87, 150.54, 135.77, 134.54, 132.77, 129.88, 129.48, 129.27, 125.30, 114.19, 55.48, 32.26. HRMS (ESI) calcd for $(C_{17}H_{16}NO_2S)^+$ $[M + H]^+$ 298.0896, found 298.0908.



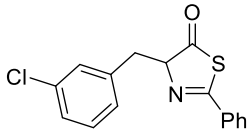
1f

4-(3-bromobenzyl)-2-phenylthiazol-5(4H)-one (**1f**): light yellow solid, 1.56 g, 99% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.67 (d, J = 7.3 Hz, 2H), 7.36 (td, J = 14.7, 7.1 Hz, 5H), 7.22 (d, J = 7.9 Hz, 2H), 3.90 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.33, 150.96, 143.62, 134.50, 134.38, 131.57, 131.03, 130.08, 129.54, 129.45, 129.32, 128.10, 125.35, 122.07, 32.66. HRMS (ESI) calcd for $(C_{16}H_{13}BrNOS)^+$ $[M + H]^+$ 345.9896, found 345.9905.



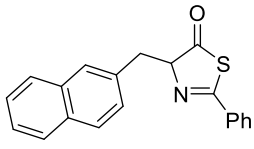
1g

4-(3-methylbenzyl)-2-phenylthiazol-5(4H)-one (**1g**): light yellow solid, 1.27 g, 99% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.15 (s, 1H), 7.68 (d, J = 7.3 Hz, 2H), 7.32 (dt, J = 24.7, 7.1 Hz, 3H), 7.11 (t, J = 7.4 Hz, 1H), 7.04 (d, J = 8.3 Hz, 2H), 6.93 (d, J = 7.3 Hz, 1H), 3.87 (s, 2H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.21, 150.48, 140.77, 137.73, 135.33, 134.55, 129.59, 129.48, 129.26, 128.67, 127.00, 126.08, 125.31, 33.14, 21.59. HRMS (ESI) calcd for $(C_{17}H_{16}NOS)^+$ $[M + H]^+$ 282.0947, found 282.0958.



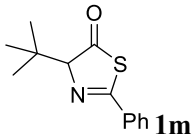
1h

methyl 2-(3-methoxyphenyl)-2-nitroacetate (**1h**): light yellow solid, 1.36 g, 99% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (s, 1H), 7.68 (d, J = 7.3 Hz, 2H), 7.40 – 7.30 (m, 3H), 7.27 (t, J = 7.6 Hz, 2H), 7.20 (d, J = 7.3 Hz, 2H), 3.92 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.38, 150.93, 143.33, 134.39, 133.39, 130.67, 129.52, 129.42, 128.69, 127.70, 126.42, 125.36, 32.72. HRMS (ESI) calcd for $(C_{16}H_{13}ClNOS)^+$ $[M + H]^+$ 302.0401, found 302.0410.



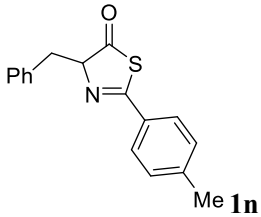
1i

4-(naphthalen-2-ylmethyl)-2-phenylthiazol-5(4H)-one (**1i**): light yellow solid, 1.43 g, 99% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.84 – 7.76 (m, 3H), 7.74 – 7.64 (m, 3H), 7.42 (dd, J = 14.6, 7.3 Hz, 3H), 7.32 (dt, J = 23.2, 7.3 Hz, 3H), 4.07 (s, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.33, 150.67, 138.51, 135.14, 134.49, 133.62, 132.12, 129.50, 129.32, 128.27, 127.97, 127.89, 126.77, 126.54, 125.82, 125.32, 33.41. HRMS (ESI) calcd for $(C_{20}H_{16}NOS)^+$ $[M + H]^+$ 318.0947, found 318.0960.



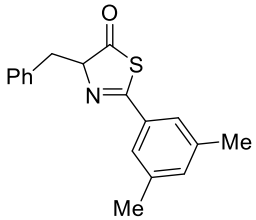
1m

4-(tert-butyl)-2-phenylthiazol-5(4H)-one (**1m**): light yellow liquid, 0.74 g, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, J = 7.7 Hz, 2H), 7.48 (ddd, J = 14.3, 10.1, 6.0 Hz, 3H), 4.49 (s, 1H), 1.15 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.46, 164.28, 133.78, 131.98, 128.88, 128.14, 91.48, 38.17, 26.99. HRMS (ESI) calcd for $(C_{13}H_{16}NOS)^+$ $[M + H]^+$ 234.0947, found 234.0942.



1n

4-benzyl-2-(p-tolyl)thiazol-5(4H)-one (**1n**): light yellow solid, 1.27 g, 99% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.60 – 7.51 (m, 2H), 7.22 (d, J = 3.3 Hz, 4H), 7.17 (d, J = 5.9 Hz, 2H), 7.14 – 7.08 (m, 1H), 3.87 (s, 2H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.41, 151.01, 140.84, 138.96, 135.12, 131.90, 130.04, 128.94, 128.78, 126.35, 125.29, 33.14, 21.36. HRMS (ESI) calcd for $(C_{17}H_{16}NOS)^+$ $[M + H]^+$ 282.0947, found 282.0951.



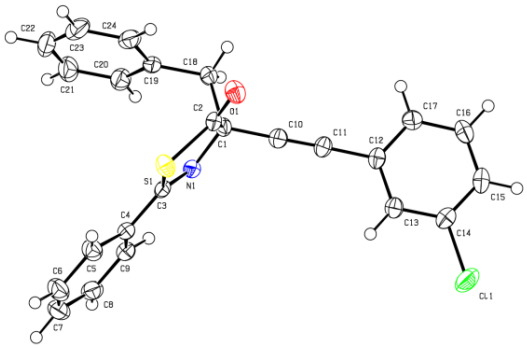
1o

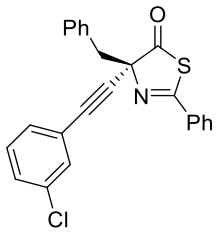
4-benzyl-2-(3,5-dimethylphenyl)thiazol-5(4H)-one (**1o**): according to general procedure: light

yellow solid, 1.33 g, 99% yield; ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.80 (d, J = 144.1 Hz, 1H), 7.29 (s, 2H), 7.25 – 7.19 (m, 4H), 7.13 (td, J = 5.9, 2.8 Hz, 1H), 6.94 (s, 1H), 3.89 (s, 2H), 2.24 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.75, 151.02, 140.86, 138.61, 135.15, 134.43, 130.87, 128.91, 128.78, 126.34, 123.07, 33.14, 21.32. HRMS (ESI) calcd for $(C_{18}H_{18}NOS)^+$ $[M + H]^+$ 296.1104, found 296.1107.

Single crystal X-Ray analysis of chiral 4ah

The crystal was developed from the solution of **4ah** in dichloromethane. CCDC 2072377 contains the supplementary crystallographic data for this paper. The absolute stereochemistry of **4ah** was determined unambiguously to be *R* with a flack parameter is 0.064(5). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

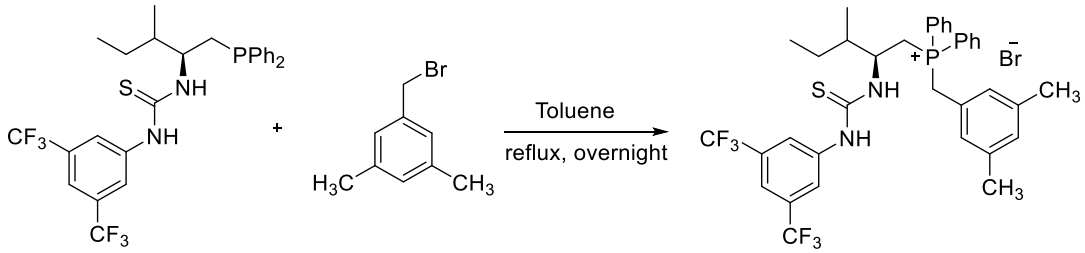




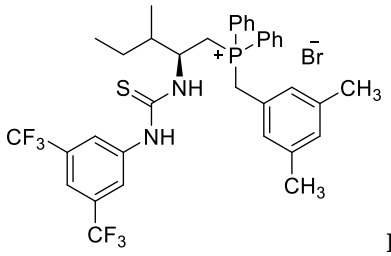
4ah

Preparation of the phase transfer catalysts:

Known catalysts **A**[6], **B**[6], **C**[7], **D**[6], **E**[13], **F**[8], **G**[13], **M**[9], **N**[10] **and O**[11] were prepared by literature procedures. The corresponding new catalysts were prepared according to literature procedures[12] [13] [14]

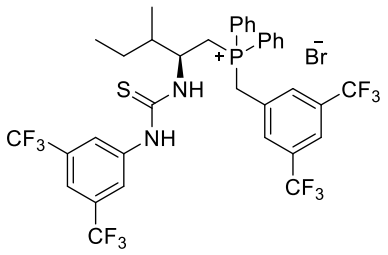


In a sealed tube , the corresponding amino acid-derived bifunctional phosphine (1.0 equiv)was dissolved in anhydrous toluene under N_2, then the corresponding benzylic halide (1.2 equiv) was added, and the resulting mixture was refluxed at 120 ^{o}C for 8 h to 12 h. After complete conversion of the starting material, which was monitored by TLC, the mixture was allowed to cool to ambient temperature and concentrated under reduced pressure. After evaporation of the solvent, the resulting mixture was purified by flash column chromatography to afford the desired phase transfer catalyst (CH_2Cl_2 : MeOH = 100:1).



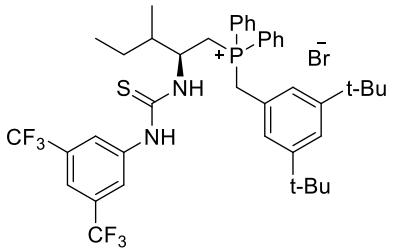
H

((2S)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-3-methylpentyl)(3,5-dimethylbenzyl)diphenylphosphonium bromide (**H**): white solid, 75% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.71 (d, J = 11.5 Hz, 2H), 8.05 (s, 2H), 7.89 – 7.70 (m, 3H), 7.67 – 7.54 (m, 5H), 7.53 – 7.44 (m, 3H), 6.90 (s, 1H), 6.44 (s, 2H), 5.41 – 5.11 (m, 1H), 4.78 (t, J = 14.6 Hz, 1H), 4.31 (t, J = 14.8 Hz, 1H), 3.43 (dd, J = 26.5, 11.5 Hz, 1H), 2.55 (t, J = 14.1 Hz, 1H), 2.12 (s, 6H), 1.76 (d, J = 29.7 Hz, 1H), 1.49 – 1.33 (m, 1H), 1.29 – 1.12 (m, 1H), 1.01 (d, J = 6.8 Hz, 3H), 0.85 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.39, 140.67, 139.12 (d, $J_{C\text{-}P}$=3.2 Hz), 135.10, 134.68, 133.60 (d, $J_{C\text{-}P}$=9.4 Hz), 133.19 (d, $J_{C\text{-}P}$=8.9 Hz), 131.18 (q, $J_{C\text{-}F}$=33.4 Hz), 130.37, 130.64, 130.16 (d, $J_{C\text{-}P}$=4.1 Hz), 130.03 (d, $J_{C\text{-}P}$=3.9 Hz), 128.23 (d, $J_{C\text{-}P}$=5.6 Hz), 125.92 (d, $J_{C\text{-}P}$=8.5 Hz), 123.33 (q, $J_{C\text{-}F}$=273 Hz), 122.65, 119.06 (d, $J_{C\text{-}P}$=83.1 Hz), 117.30, 116.48, 51.66, 41.09 (d, $J_{C\text{-}P}$=12.1Hz), 29.07 (d, $J_{C\text{-}P}$=45.1 Hz), 25.58, 24.22 (d, $J_{C\text{-}P}$=52.5 Hz), 21.15, 14.95, 11.57. HRMS (ESI) calcd for $(C_{36}H_{38}F_6N_2PS)^+$ [M - Br]$^+$ 675.2392, found 675.2200; $[\alpha]_D^{20}$ -73.4 (*c* 0.5, $CHCl_3$).



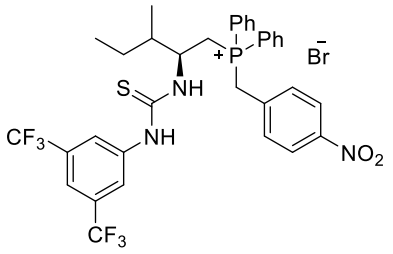
I

(3,5-bis(trifluoromethyl)benzyl)((2S)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-3-methylpentyl)diphenylphosphonium bromide (**I**): white solid, 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.82 (d, J = 9.1 Hz, 1H), 9.74 (s, 1H), 8.15 (s, 2H), 7.87 (dt, J = 7.0, 3.5 Hz, 1H), 7.82 – 7.79 (m, 1H), 7.77 – 7.69 (m, 7H), 7.61 (td, J = 7.6, 3.7 Hz, 2H), 7.55 (s, 1H), 7.25 (s, 2H), 5.32 – 5.07 (m, 2H), 4.87 (t, J = 14.6 Hz, 1H), 3.98 (dd, J = 26.5, 11.4 Hz, 1H), 2.58 – 2.43 (m, 1H), 1.84 (s, 1H), 1.23 – 1.12 (m, 2H), 1.01 (d, J = 6.8 Hz, 3H), 0.74 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.31, 140.62, 135.76 (q, $J_{C\text{-}F}$=35.3 Hz), 133.41 (d, $J_{C\text{-}P}$=9.4 Hz), 133.12, 132.71, 132.40, 132.22, 132.12, 132.04, 131.44 (q, $J_{C\text{-}F}$=33.3 Hz), 130.84, 130.72, 130.62, 130.49, 130.29 (d, $J_{C\text{-}P}$=8.7 Hz), 128.59 (d, $J_{C\text{-}P}$=12.0 Hz), 123.27 (q, $J_{C\text{-}F}$=269 Hz), 122.41 (q, $J_{C\text{-}F}$=277 Hz), 122.66, 117.63, 116.38 (d, $J_{C\text{-}P}$=28.1 Hz), 115.55 (d, $J_{C\text{-}P}$=29.6 Hz), 112.68, 51.59, 40.74 (d, $J_{C\text{-}P}$=12.0 Hz), 29.79, 28.62 (d, $J_{C\text{-}P}$=44.9 Hz), 25.74, 25.32 (d, $J_{C\text{-}P}$=50.6 Hz), 14.60, 11.37. HRMS (ESI) calcd for $(C_{36}H_{32}F_{12}N_2PS)^+$ [M - Br]$^+$ 783.1827, found 783.1821; $[\alpha]_D^{20}$ -24.4 (*c* 0.5, $CHCl_3$).



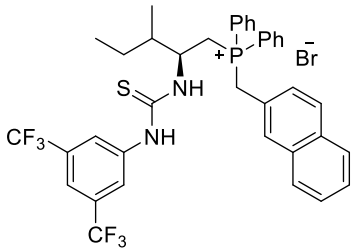
J

((2S)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-3-methylpentyl)(3,5-di-tert-butylbenzyl)diphenylphosphonium bromide (**J**): white solid, 70% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.72 (s, 1H), 9.62 (d, J = 9.3 Hz, 1H), 8.07 (s, 2H), 7.76 (dd, J = 12.3, 7.3 Hz, 3H), 7.63 – 7.49 (m, 8H), 7.30 (s, 1H), 6.74 (s, 2H), 5.24 (d, J = 12.2 Hz, 1H), 4.81 (t, J = 14.5 Hz, 1H), 4.45 (t, J = 14.8 Hz, 1H), 3.57 (dd, J = 26.5, 11.7 Hz, 1H), 2.54 (t, J = 14.3 Hz, 1H), 1.78 (s, 1H), 1.37 (dt, J = 18.1, 10.2 Hz, 2H), 1.12 (s, 18H), 0.99 (d, J = 6.7 Hz, 3H), 0.82 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.51, 152.21, 140.70, 134.83 (d, $J_{C\text{-}P}$ = 30.1 Hz), 133.34 (d, $J_{C\text{-}P}$ = 21 Hz), 133.33 (d, $J_{C\text{-}P}$ = 4 Hz), 131.19 (q, $J_{C\text{-}F}$ = 33.3Hz), 130.29 (d, $J_{C\text{-}P}$ = 3.3 Hz), 130.17 (d, $J_{C\text{-}P}$ = 3.6 Hz), 125.53 (d, $J_{C\text{-}P}$ = 8.3 Hz), 124.62 (d, $J_{C\text{-}P}$ = 5.6 Hz), 123.36 (q, $J_{C\text{-}F}$ = 271.6 Hz), 123.07, 122.69, 119.46, 118.64, 117.71, 117.30, 116.88, 51.78, 41.08 (d, $J_{C\text{-}P}$ = 12.1 Hz), 34.84, 29.64 (d, $J_{C\text{-}P}$ = 45.4Hz), 25.30, 24.54 (d, $J_{C\text{-}P}$ = 52.2Hz), 14.96, 11.69. HRMS (ESI) calcd for $(C_{42}H_{50}F_6N_2PS)^+$ $[M - Br]^+$ 759.3331, found 759.3321; $[\alpha]_D^{20}$ -48.6 (*c* 0.5, $CHCl_3$).



K

((2S)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-3-methylpentyl)(4-nitrobenzyl)diphenylphosphonium bromide (**K**): white solid, 61% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 9.60 (d, J = 9.3 Hz, 1H), 8.14 (s, 2H), 7.96 (d, J = 8.3 Hz, 2H), 7.89 – 7.79 (m, 3H), 7.74 – 7.67 (m, 5H), 7.60 – 7.54 (m, 2H), 7.52 (s, 1H), 7.13 (dd, J = 8.8, 2.3 Hz, 2H), 5.22 (t, J = 15.4 Hz, 1H), 5.11 (dd, J = 12.1, 7.1 Hz, 1H), 4.78 (t, J = 14.9 Hz, 1H), 3.88 (dt, J = 15.2, 11.3 Hz, 1H), 2.59 (t, J = 14.1 Hz, 1H), 1.86 – 1.75 (m, 1H), 1.24 – 1.13 (m, 2H), 1.00 (d, J = 6.8 Hz, 3H), 0.72 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.40, 147.86, 140.71, 135.77 (d, $J_{C\text{-}P}$=6 Hz), 135.43 (d, $J_{C\text{-}P}$=6 Hz), 135.01 (d, $J_{C\text{-}P}$=8.7 Hz), 133.62 (d, $J_{C\text{-}P}$=9.4 Hz), 133.43 (d, $J_{C\text{-}P}$=9.2 Hz), 132.19, 132.09, 131.54, 131.48, 131.38 (q, $J_{C\text{-}F}$=33 Hz), 130.69 (d, $J_{C\text{-}P}$=12.3 Hz), 130.41 (d, $J_{C\text{-}P}$=12.4 Hz), 128.62 (d, $J_{C\text{-}P}$=12.2 Hz), 124.18 (d, $J_{C\text{-}P}$=2.6 Hz), 123.26 (q, $J_{C\text{-}F}$=272 Hz), 122.63, 117.57, 116.84 (d, $J_{C\text{-}P}$=12.9 Hz), 116.01 (d, $J_{C\text{-}P}$=14.5Hz), 51.57 (d, $J_{C\text{-}P}$=4.3 Hz), 40.75 (d, $J_{C\text{-}P}$=12.0 Hz), 28.64 (d, $J_{C\text{-}P}$=44.8 Hz), 25.73, 25.40 (d, $J_{C\text{-}P}$=50.9 Hz), 14.66, 11.45 . HRMS (ESI) calcd for $(C_{34}H_{33}F_6N_3O_2PS)^+$ $[M - Br]^+$ 692.1930, found 692.1977; $[\alpha]_D^{20}$ -50.4 (*c* 0.5, $CHCl_3$).



L

((2S)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-3-methylpentyl)(naphthalen-2-ylmethyl)diphenylphosphonium bromide (**L**): white solid, 68% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (s, 1H), 9.64 (d, J = 9.4 Hz, 1H), 8.08 (s, 2H), 7.82 – 7.70 (m, 4H), 7.64 – 7.54 (m, 7H), 7.54 – 7.48 (m, 3H), 7.48 – 7.42 (m, 2H), 7.40 (s, 1H), 6.89 (d, J = 8.4 Hz, 1H), 5.40 – 5.21 (m, 1H), 4.97 (t, J = 14.7 Hz, 1H), 4.74 (t, J = 14.9 Hz, 1H), 3.58 – 3.39 (m, 1H), 2.59 (dd, J = 16.4, 12.0 Hz, 1H), 1.79 (s, 1H), 1.42 – 1.28 (m, 1H), 1.25 – 1.11 (m, 1H), 0.97 (d, J = 6.8 Hz, 3H), 0.78 (t, J = 7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 180.45, 140.76, 135.02 (d, $J_{C\text{-}P}$ = 48.0 Hz), 133.51 (d, $J_{C\text{-}P}$ = 9.3 Hz), 133.30 (d, $J_{C\text{-}P}$ = 9.1 Hz), 133.10 (d, $J_{C\text{-}P}$ = 2.9 Hz), 132.87 (d, $J_{C\text{-}P}$ = 2.0 Hz), 131.17 (q, $J_{C\text{-}F}$ = 33.3 Hz), 130.33, 130.21, 130.11, 129.24, 127.72 (d, $J_{C\text{-}P}$ = 21.4 Hz), 127.12 (d, $J_{C\text{-}P}$ = 4.3Hz), 123.35 (q, $J_{C\text{-}F}$ = 271 Hz), 123.77 (d, $J_{C\text{-}P}$ = 8.7 Hz), 122.60, 118.48 (d, $J_{C\text{-}P}$ = 83.0 Hz), 117.33, 117.25, 116.51, 51.70 (d, $J_{C\text{-}P}$ = 4.3 Hz), 41.01 (d, $J_{C\text{-}P}$ = 12.1 Hz), 29.49 (d, $J_{C\text{-}P}$ = 45.3 Hz), 25.54, 24.45 (d, $J_{C\text{-}P}$ = 52.1Hz), 14.94, 11.54. HRMS (ESI) calcd for $(C_{38}H_{36}F_6N_2PS)^+$ $[M - Br]^+$ 697.2236, found 697.2239; $[\alpha]_D^{20}$ -80.8 (*c* 0.5, $CHCl_3$).

References:

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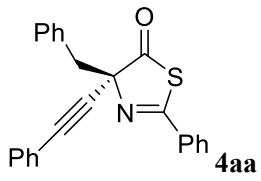
Ph
O
S
N
Ph
Ph

4aa


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7.53
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7.48
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7.21
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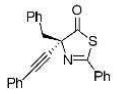
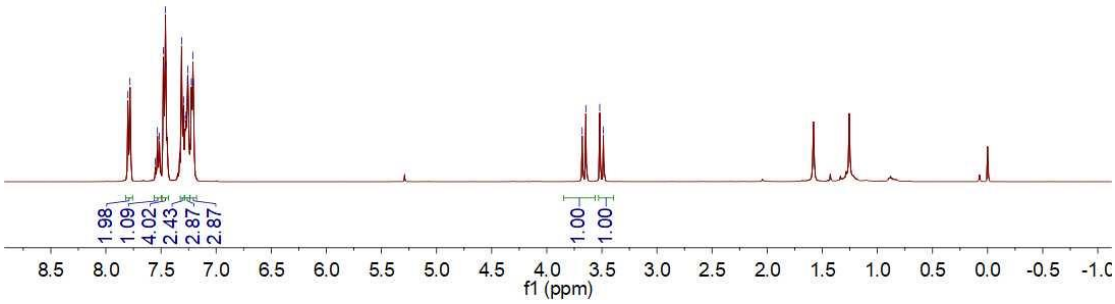
3.49

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6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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1.0
0.5
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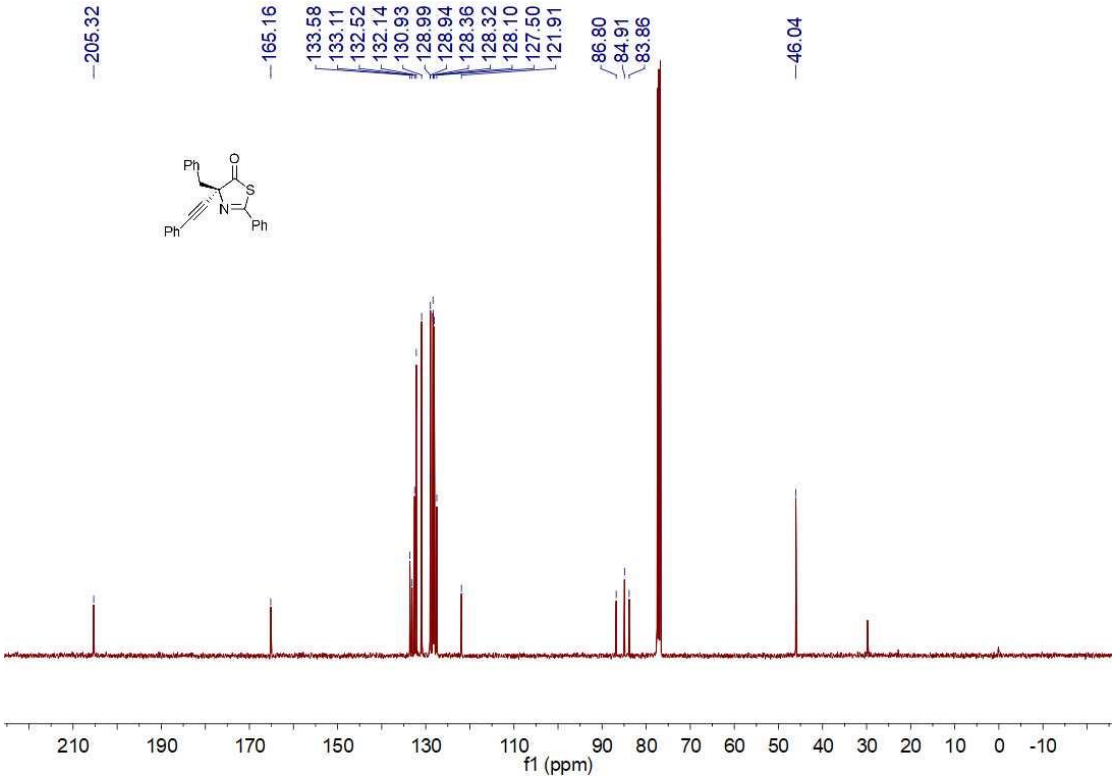
-0.5
f1 (ppm)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165.16
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128.36
128.32
128.10
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121.91
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84.91
83.86
46.04
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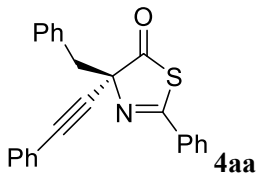
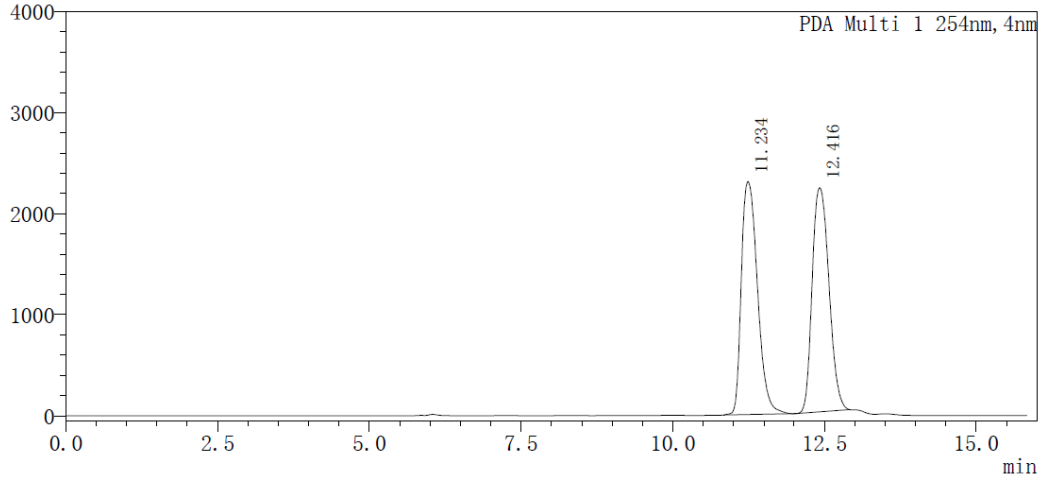
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



4aa



<Peak table>

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
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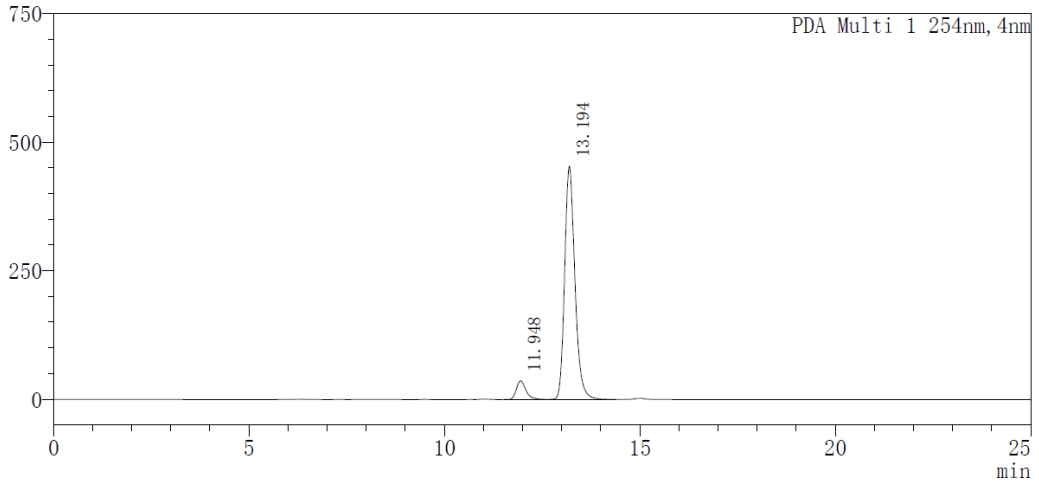
2	12.416	2218996	42761542	50.029
Total		4524401	85474134	100.000



<Peak table>

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
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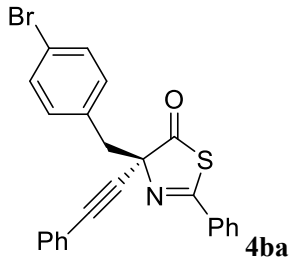
2	13.194	452991	8274161	93.063
Total		489339	8890931	100.000


Br
O
S
N
Ph
Ph

4ba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7.47
7.46
7.45
7.44
7.36
7.36
7.34
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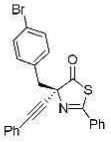
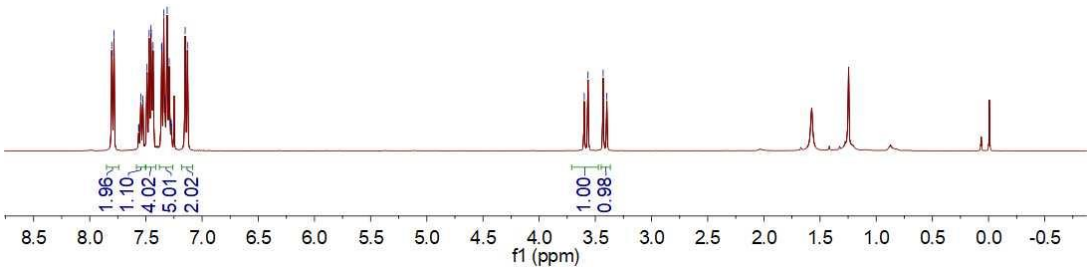
3.43
3.40

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5.5
5.0
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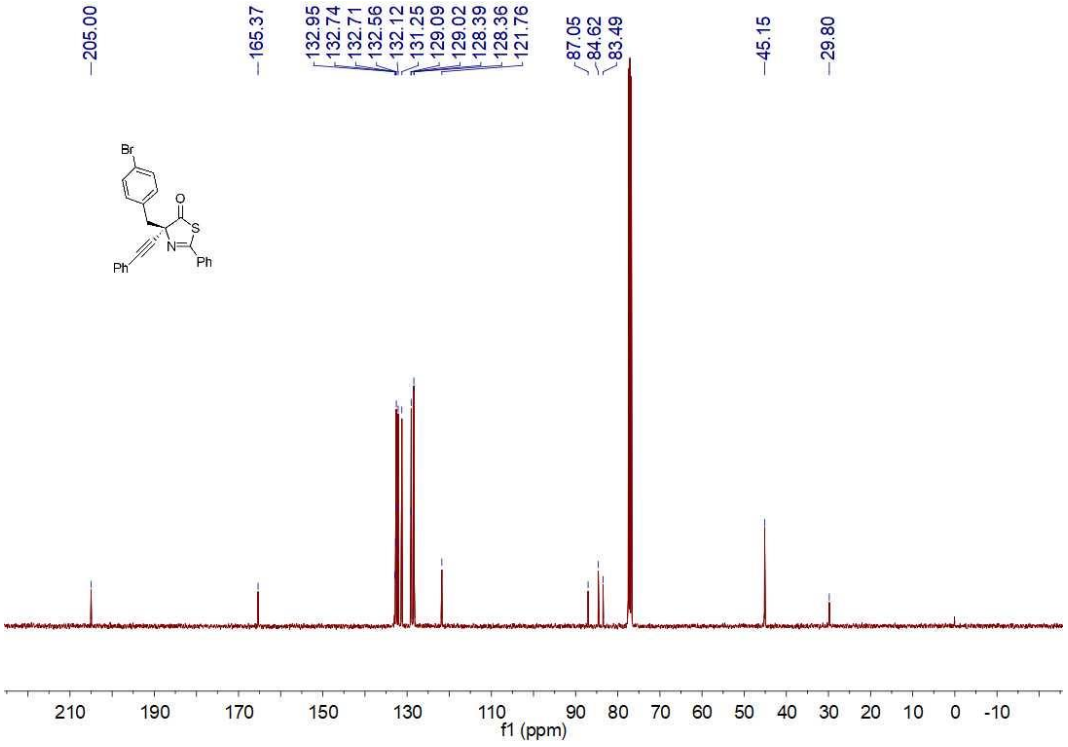
f1 (ppm)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129.02
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128.36
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83.49
45.15
29.80
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150
130
110
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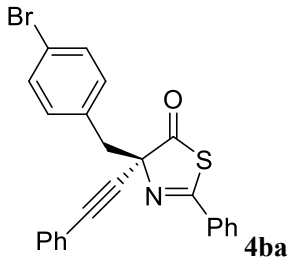
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



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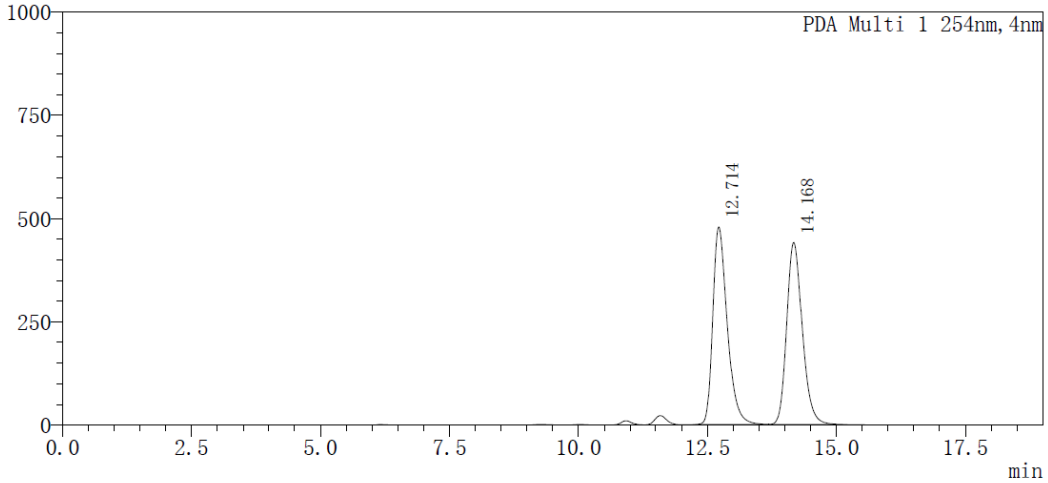

〈Peak table〉

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
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2	14.168	441162	9307623	49.818
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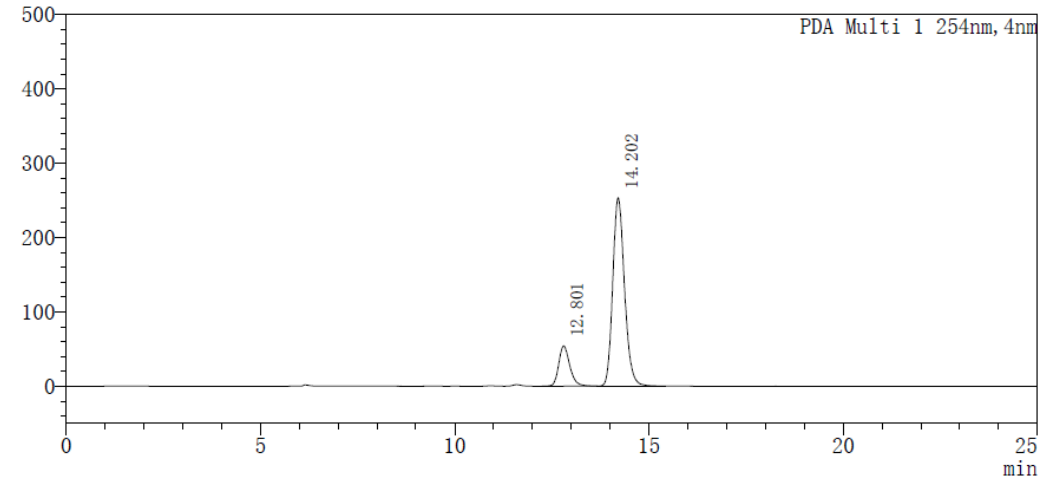

〈Peak table〉

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
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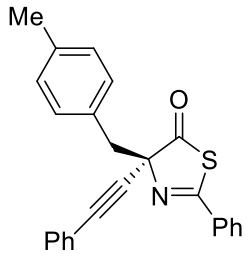
Me
O
S
N
Ph
Ph

4ca


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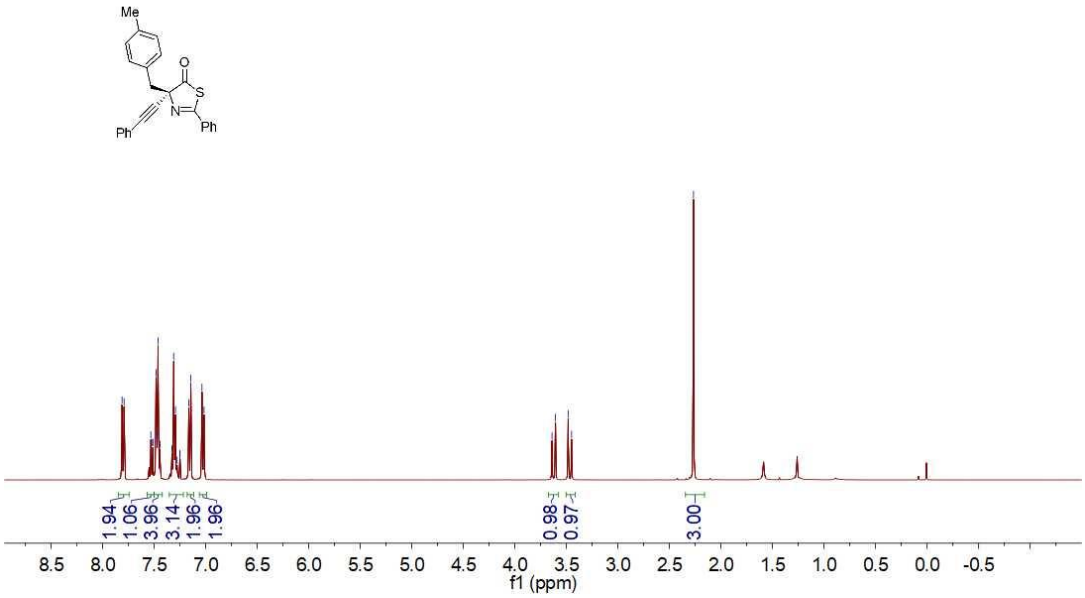
3.48
3.45
2.27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S
N
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1.96
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0.97
3.00
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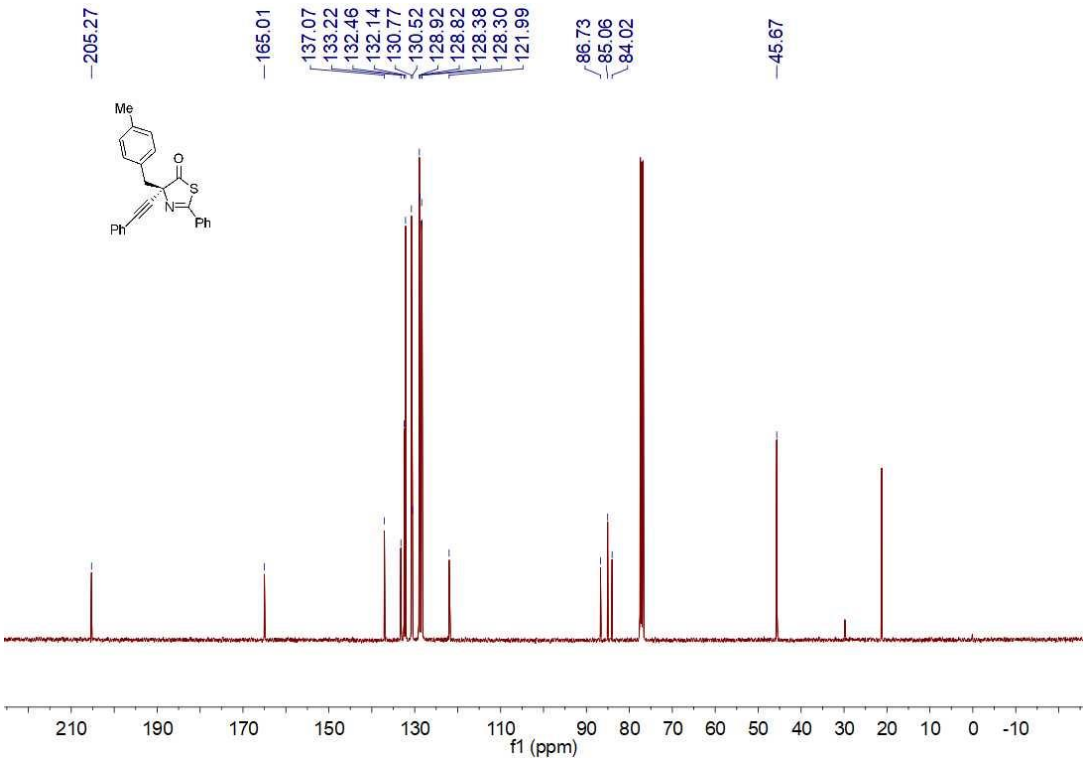
f1 (ppm)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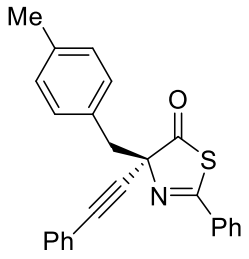
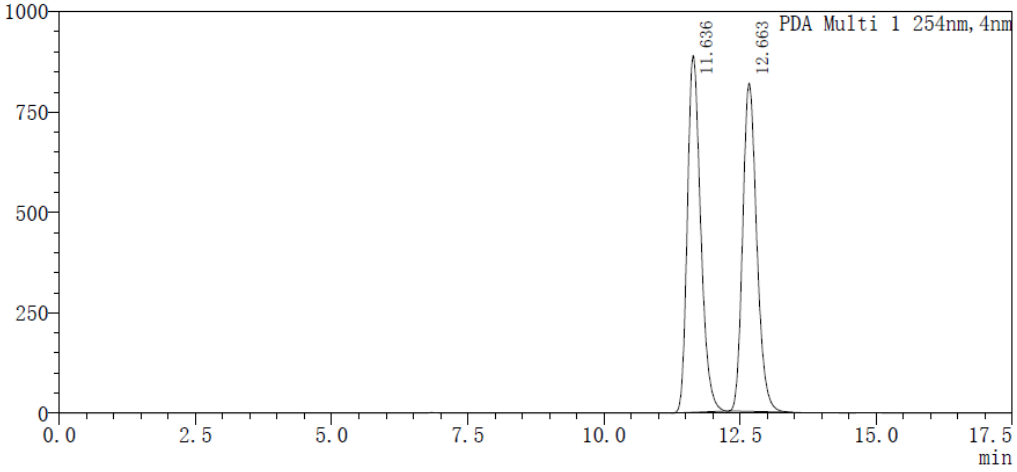
Me
O
S
N
Ph
Ph
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



4ca



<Peak table>

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
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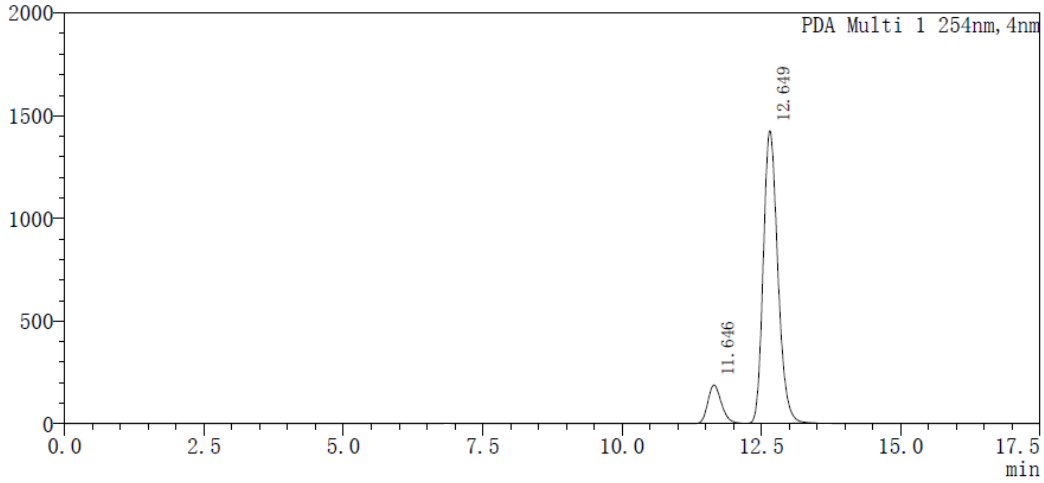
2	12.663	817213	14716928	49.319
Total		1705667	29840139	100.000



<Peak table>

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
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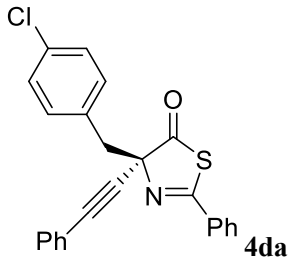
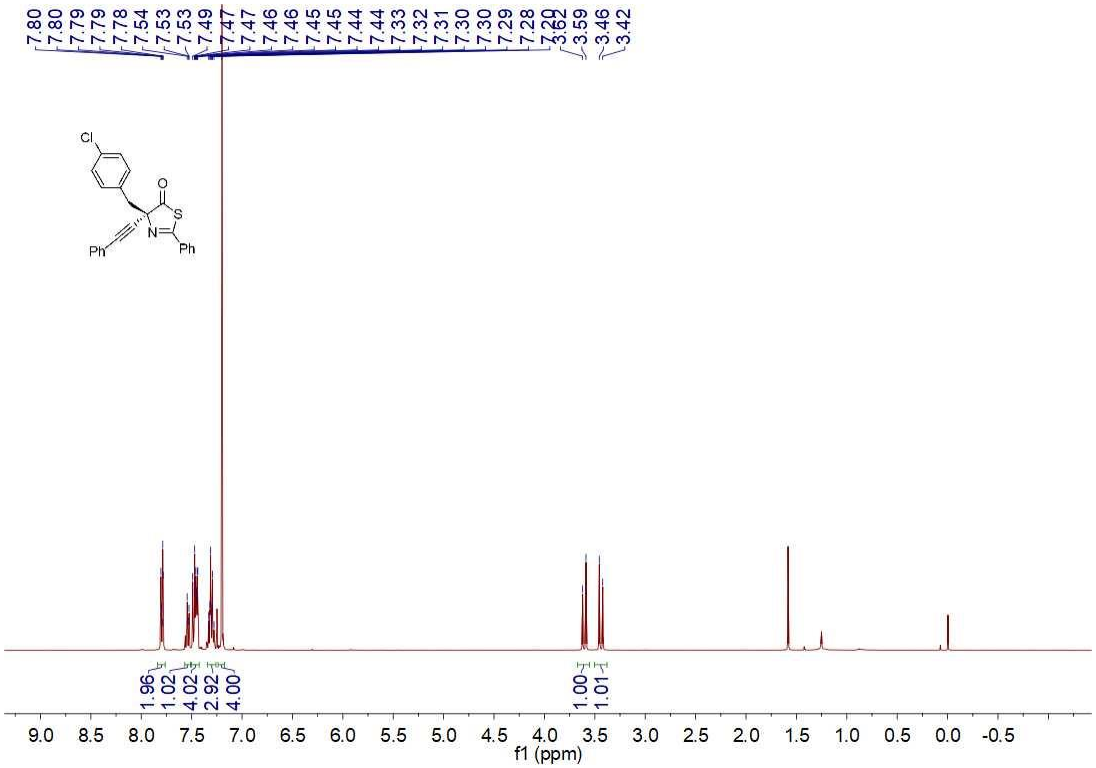

Cl
O
S
N
Ph
Ph

4da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7.29
7.28
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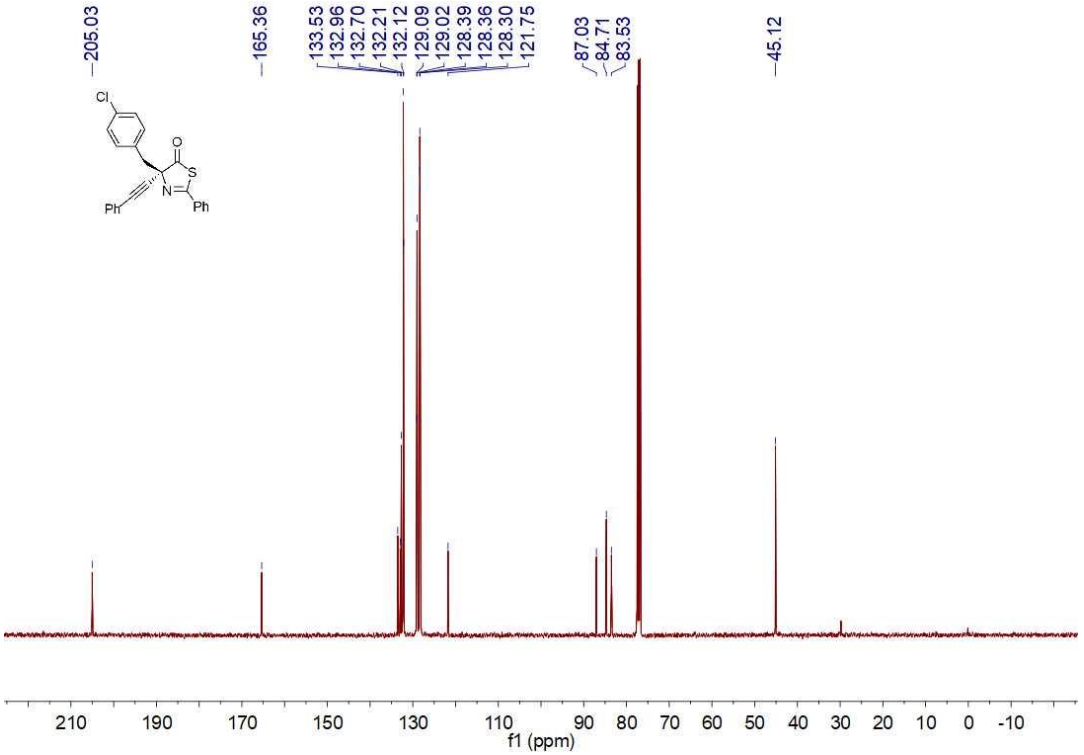
1.01
f1 (ppm)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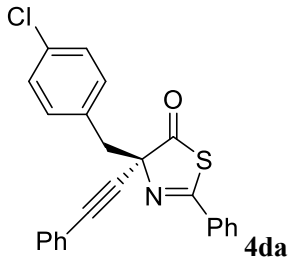
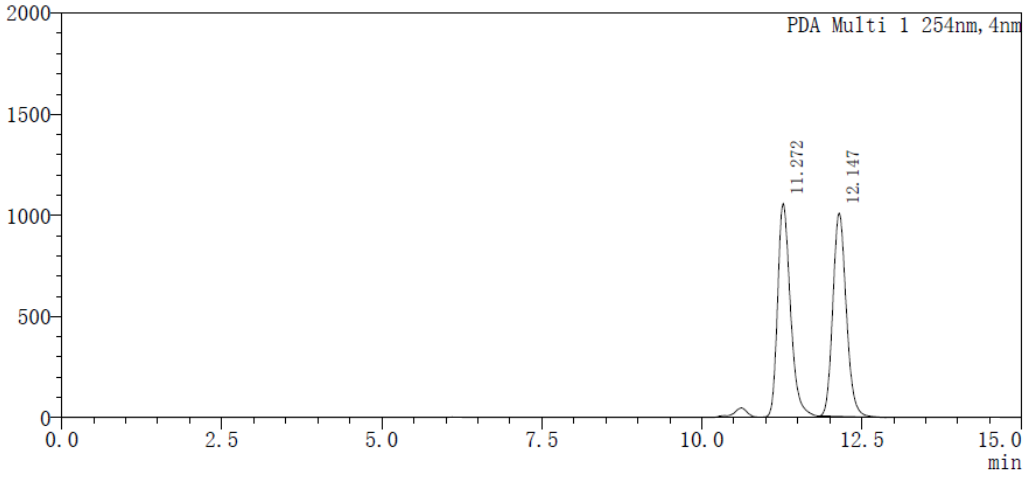
83.53
45.12
f1 (ppm)



4da



<Peak table>

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
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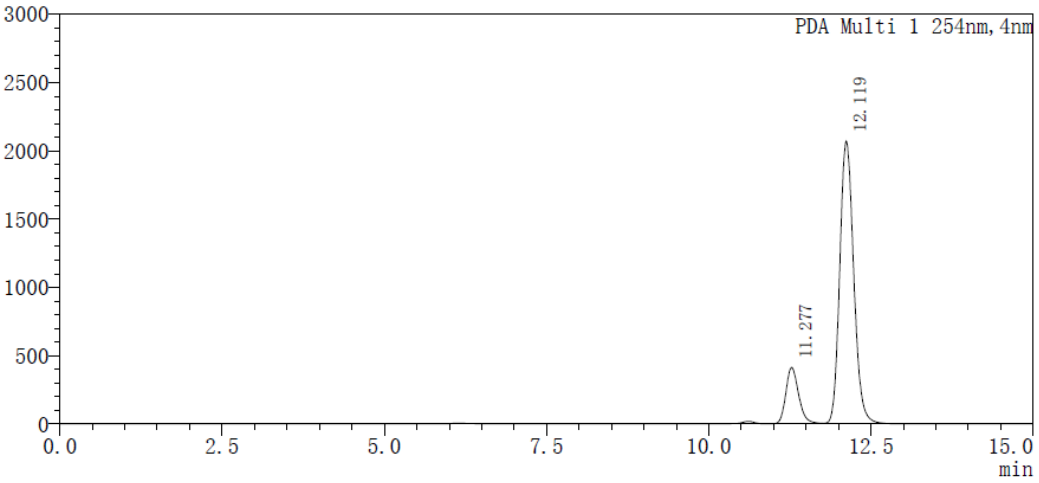

<Peak table>

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
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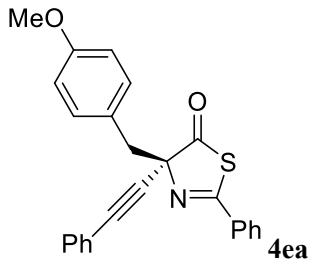
Total		2482168	36583141	100.000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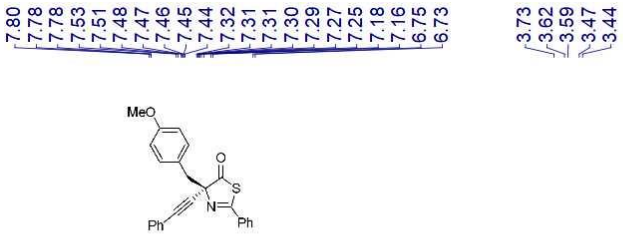
O
S
N
Ph
Ph

4ea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3.73
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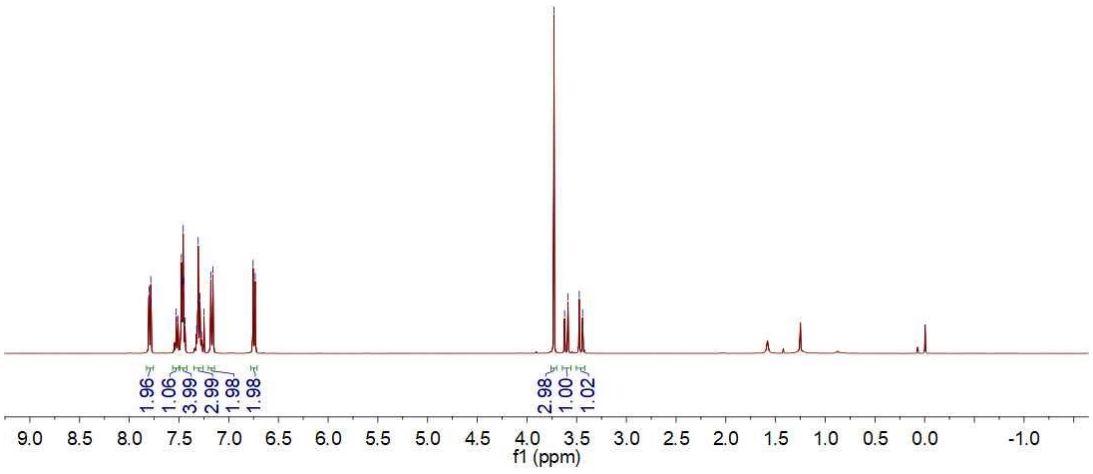
3.59
3.47
3.44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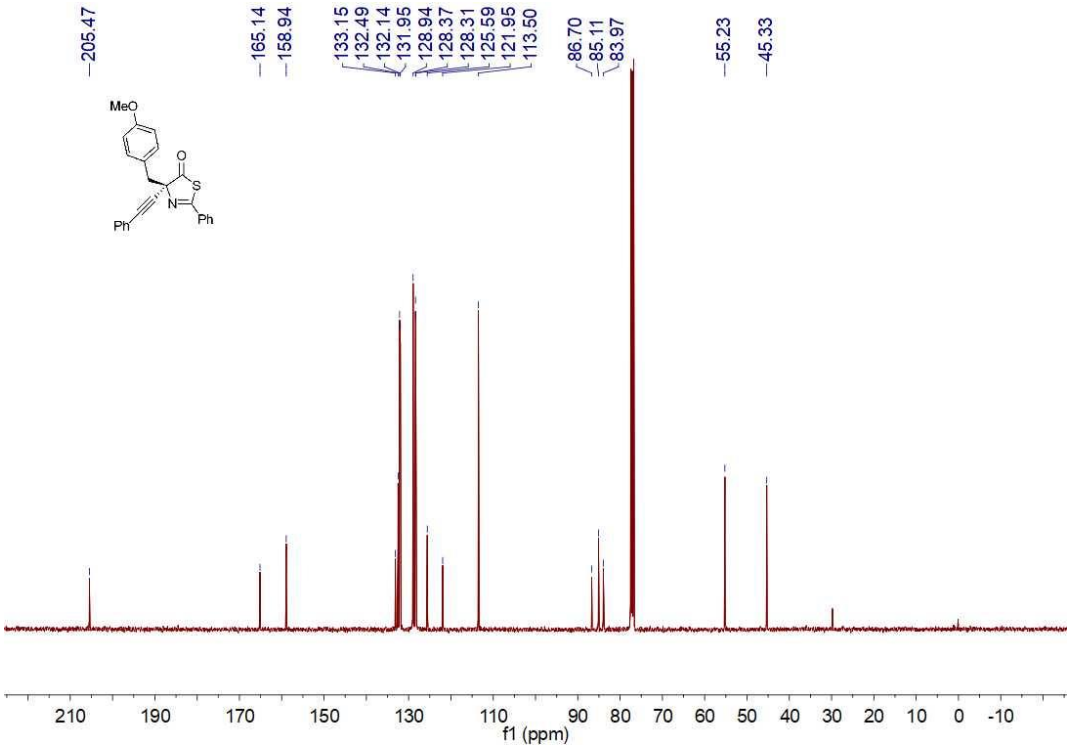
1.02
f1 (ppm)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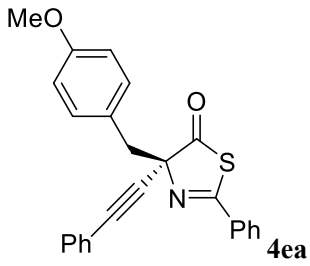
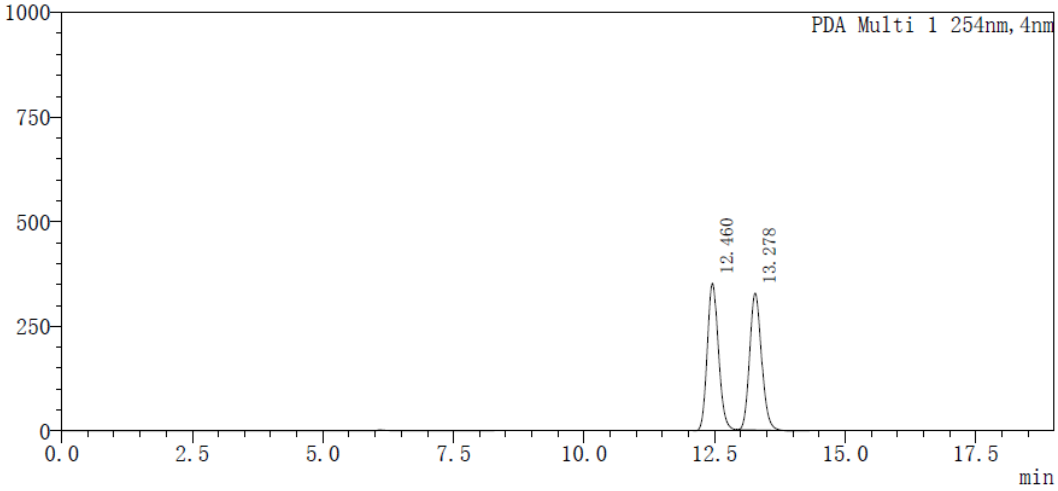
45.33
f1 (ppm)



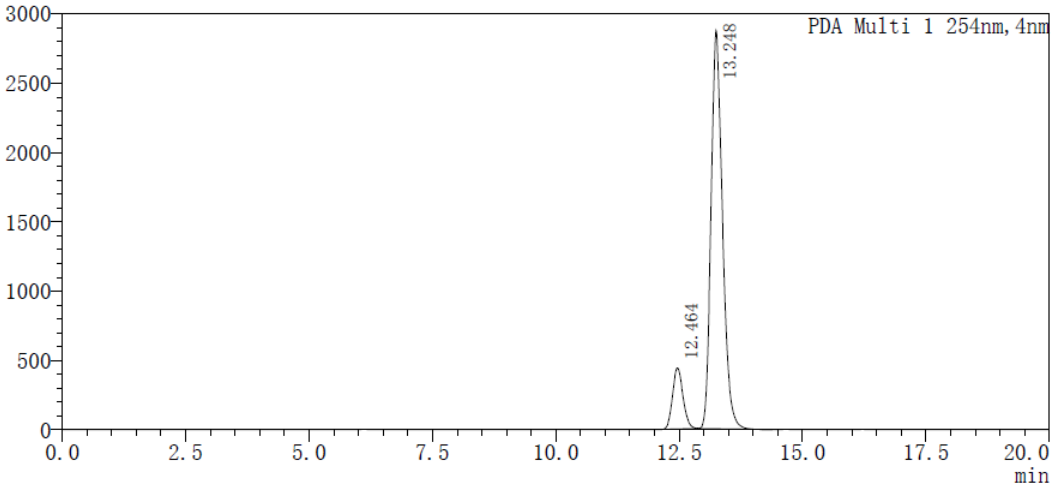
4ea



<Peak table>

PDA Ch1 254nm

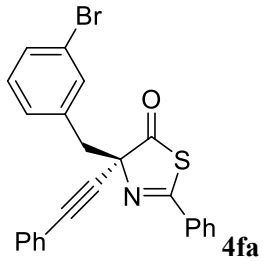
Peak#	Ret. Time	Height	Area	Area%
1	12.460	353584	5331700	50.454
2	13.278	327631	5235815	49.546
Total		681215	10567514	100.000



<Peak table>

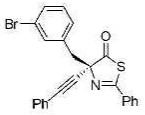
PDA Ch1 254nm

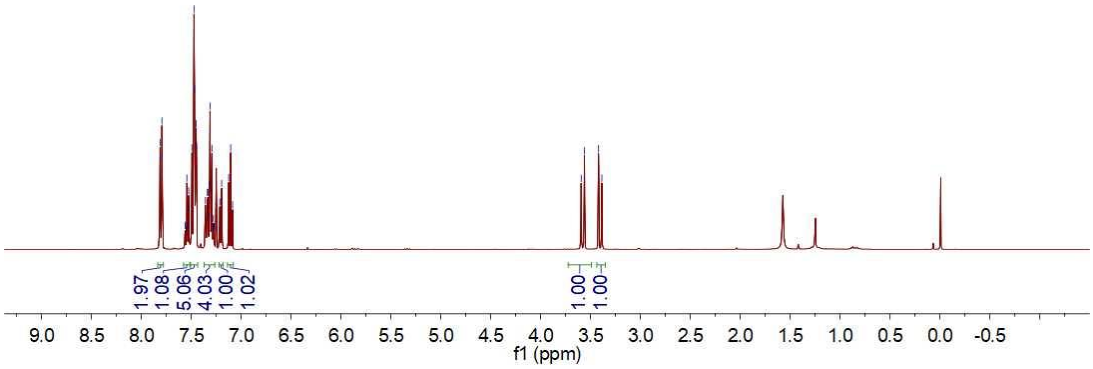
Peak#	Ret. Time	Height	Area	Area%
1	12.464	439990	6479290	12.275
2	13.248	2873977	46305283	87.725
Total		3313967	52784573	100.000

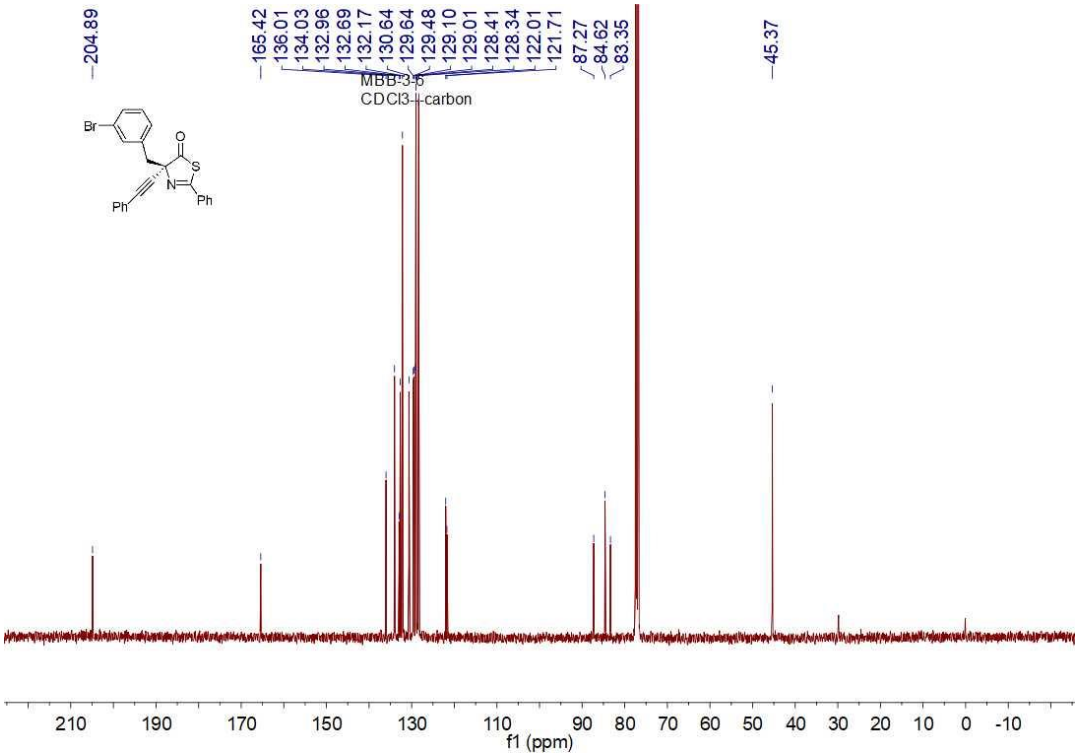

Br
O
S
N
Ph
Ph

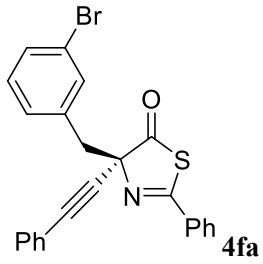
4fa


7.81
7.79
7.79
7.56
7.54
7.53
7.52
7.49
7.47
7.47
7.45
7.45
7.36
7.34
7.33
7.32
7.32
7.31
7.29
7.28
7.21
7.19
7.12
7.10
3.56
3.42
3.39

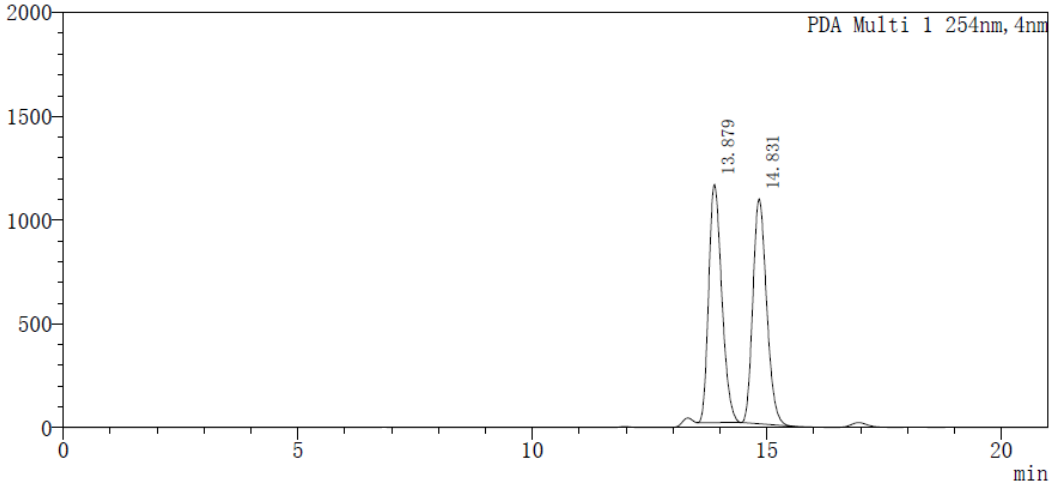

Br
O
S
N
Ph
Ph


1.97
1.08
5.06
4.03
1.00
1.02
1.00
1.00
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)


204.89
165.42
136.01
134.03
132.96
132.69
132.17
130.64
129.64
129.48
129.10
129.01
128.41
128.34
122.01
121.71
87.27
84.62
83.35
45.37
MBB-3-5
CDCl3--carbon
Br
O
S
N
Ph
Ph
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



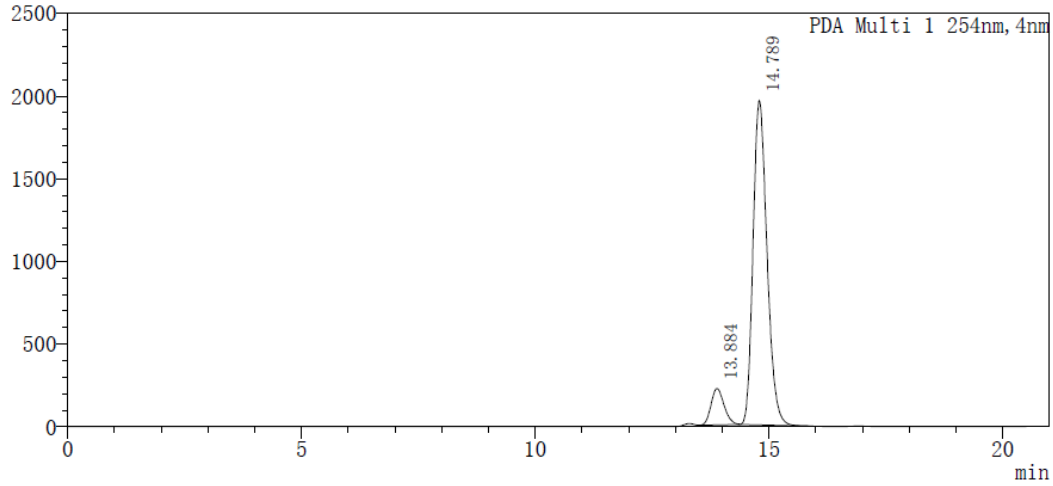
4fa



〈Peak table〉

PDA Ch1 254nm

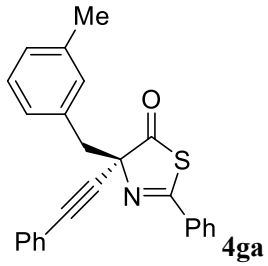
Peak#	Ret. Time	Height	Area	Area%
1	13.879	1147693	22264562	50.175
2	14.831	1083834	22109011	49.825
Total		2231527	44373573	100.000



〈Peak table〉

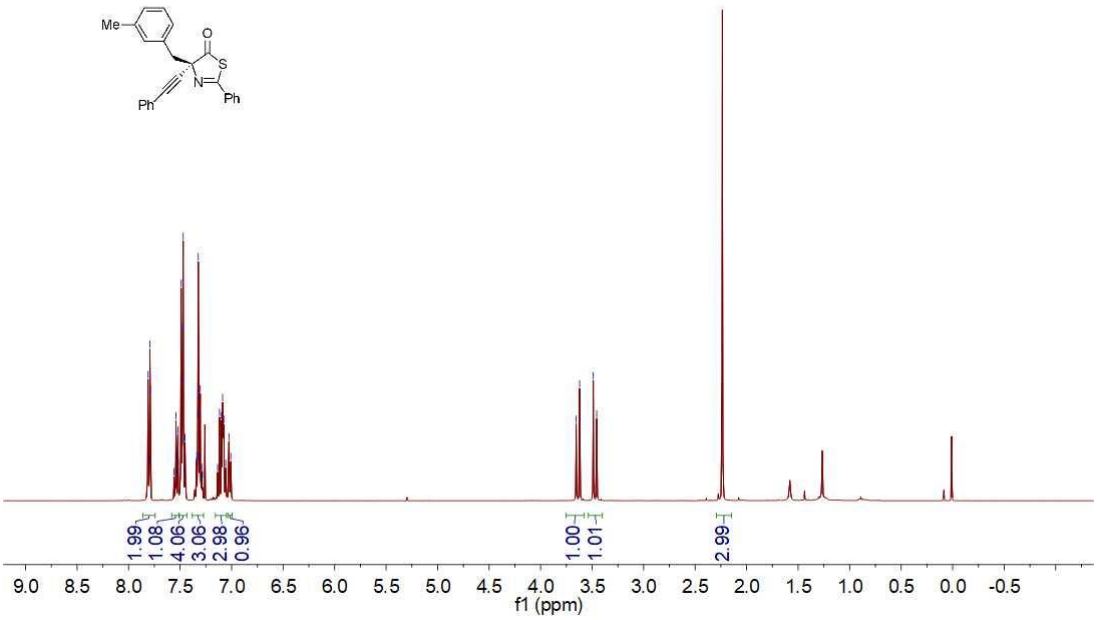
PDA Ch1 254nm

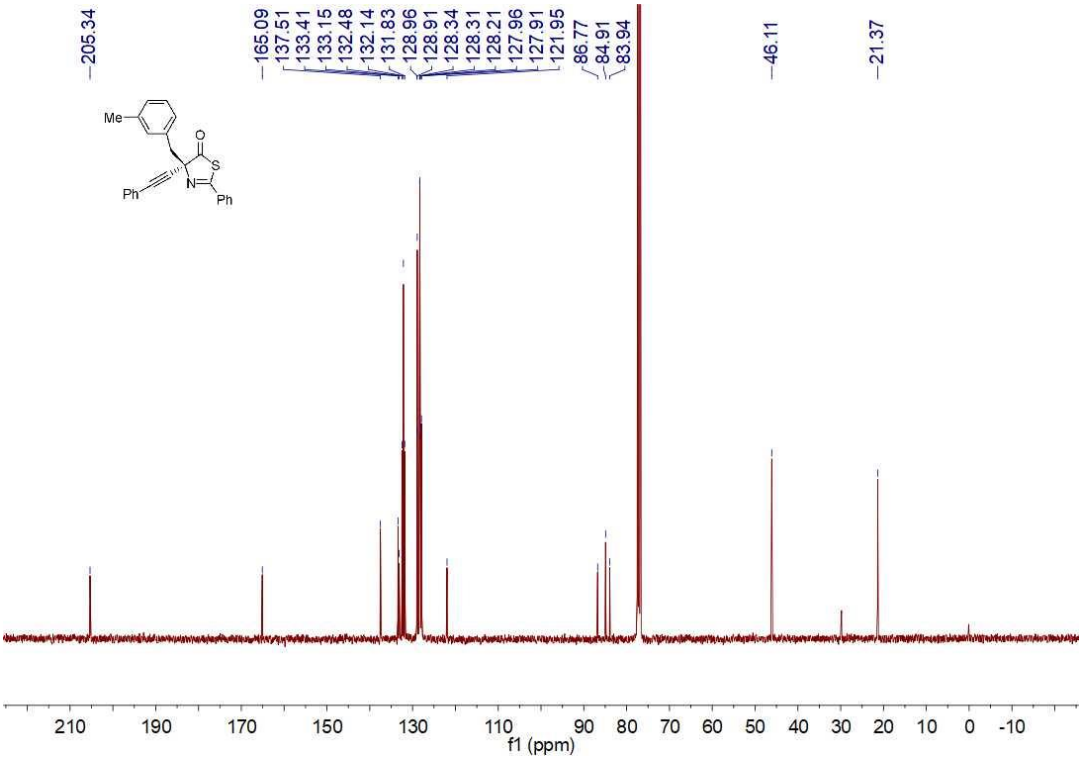
Peak#	Ret. Time	Height	Area	Area%
1	13.884	219604	4218937	9.406
2	14.789	1960565	40633022	90.594
Total		2180170	44851959	100.000

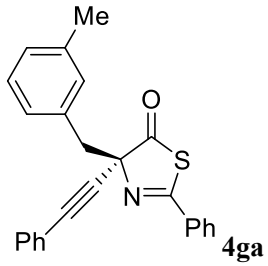

Me
O
S
N
Ph
Ph

4ga

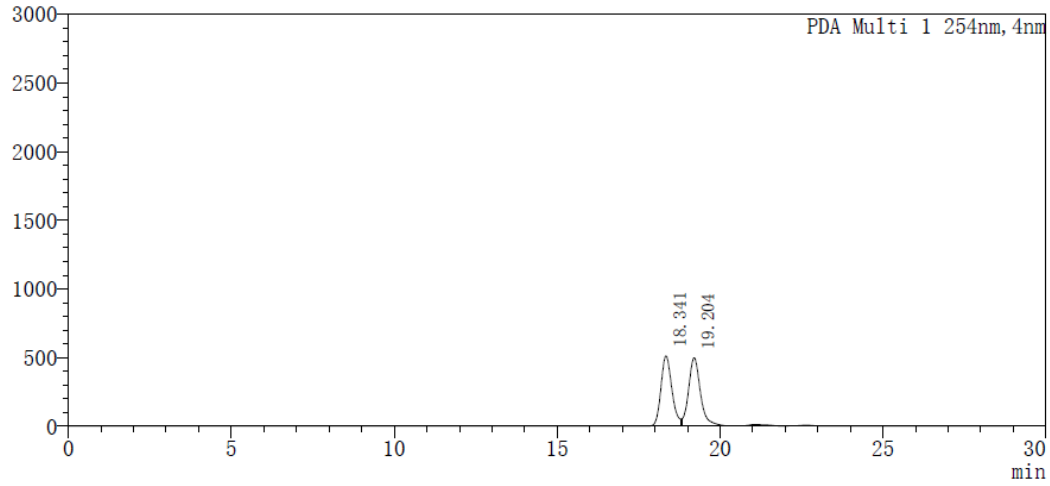

7.81
7.80
7.79
7.79
7.54
7.52
7.52
7.49
7.49
7.48
7.47
7.47
7.45
7.34
7.33
7.32
7.32
7.31
7.30
7.12
7.10
7.09
7.08
7.03
7.01
3.65
3.62
3.49
3.46


1.99
1.08
4.06
3.06
2.98
0.96
1.00
1.01
2.99
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)


205.34
165.09
137.51
133.41
133.15
132.48
132.14
131.83
128.96
128.91
128.34
128.31
128.21
127.96
127.91
121.95
86.77
84.91
83.94
46.11
21.37
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



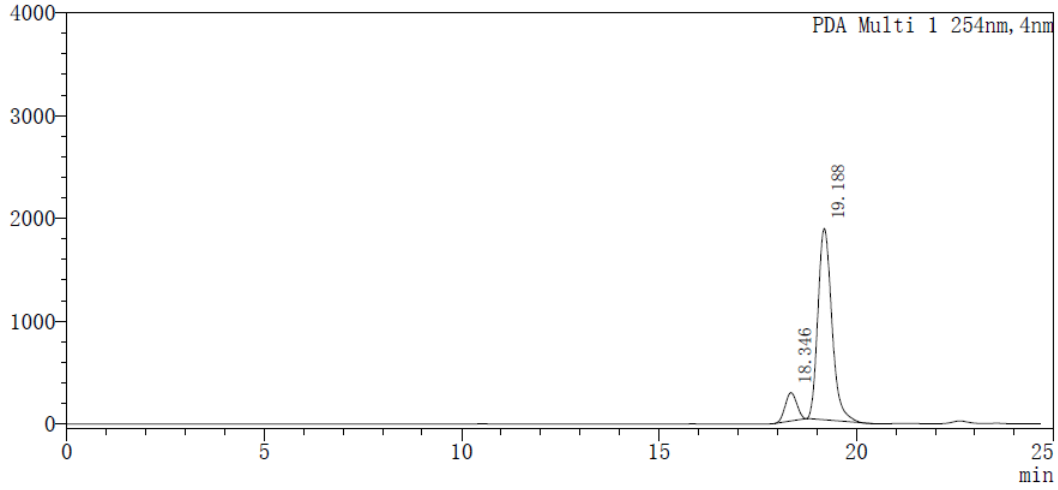
4ga



〈Peak table〉

PDA Ch1 254nm

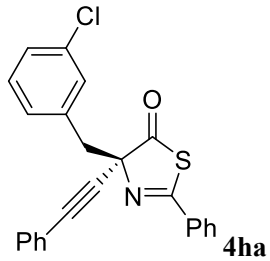
Peak#	Ret. Time	Height	Area	Area%
1	18.341	511498	11965303	48.426
2	19.204	498545	12743123	51.574
Total		1010044	24708426	100.000



〈Peak table〉

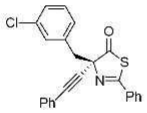
PDA Ch1 254nm

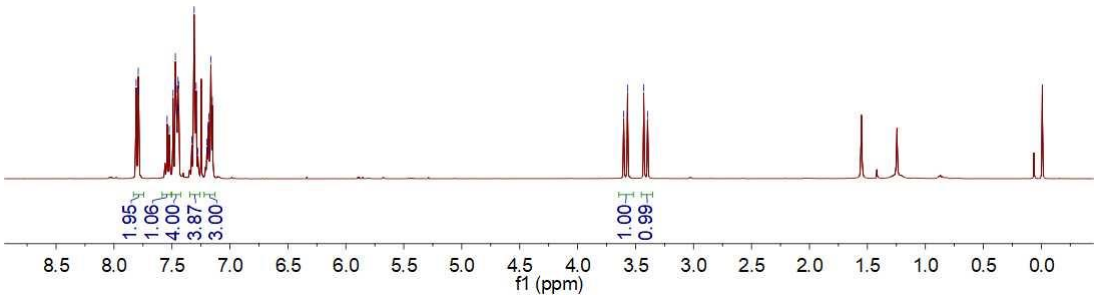
Peak#	Ret. Time	Height	Area	Area%
1	18.346	274690	5601694	10.883
2	19.188	1862131	45870741	89.117
Total		2136821	51472435	100.000

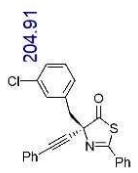

Cl
O
S
N
Ph
Ph

4ha

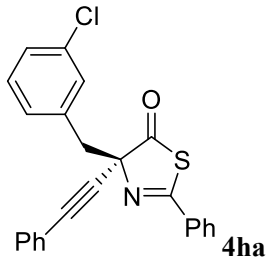

7.81
7.79
7.79
7.54
7.52
7.49
7.47
7.47
7.46
7.46
7.45
7.45
7.44
7.33
7.31
7.29
7.28
7.20
7.19
7.19
7.18
7.17
7.17
7.15
3.60
3.57
3.43
3.40



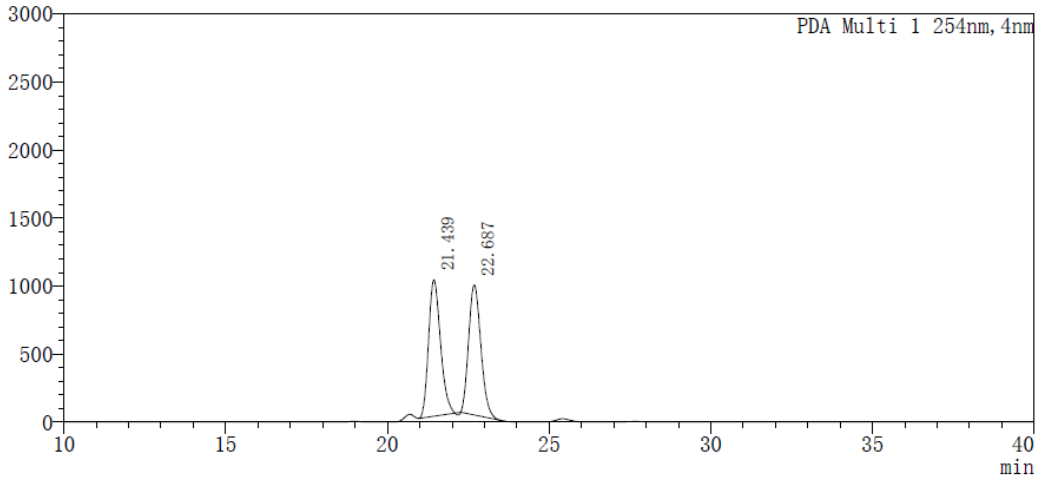

1.95
1.06
4.00
3.87
3.00
1.00
0.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)



204.91
165.39
135.72
133.81
132.97
132.68
132.15
131.08
129.33
129.09
129.05
129.00
128.39
128.34
127.73
121.72
87.23
84.62
83.37
45.39
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



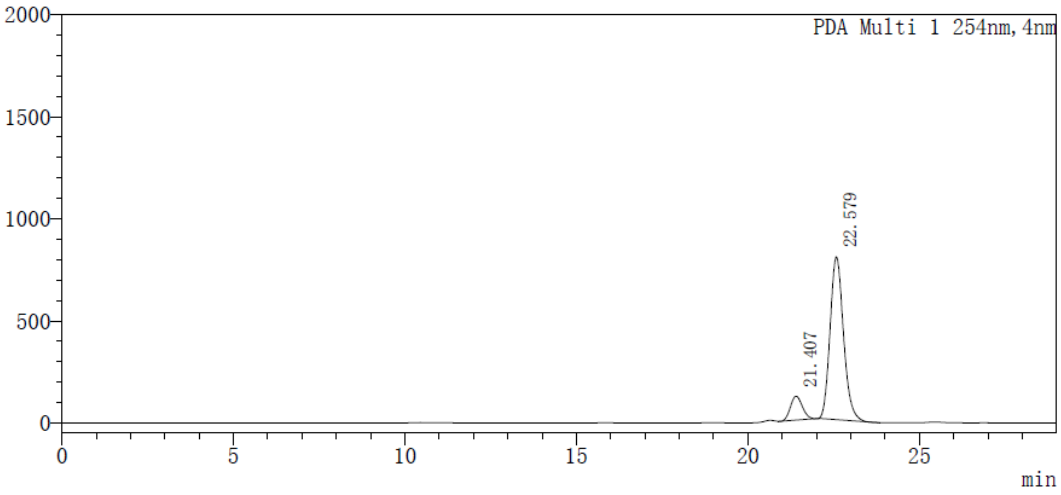
4ha



<Peak table>

PDA Ch1 254nm

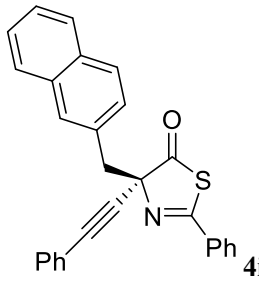
Peak#	Ret. Time	Height	Area	Area%
1	21.439	1002984	25582452	50.440
2	22.687	955725	25135657	49.560
Total		1958709	50718108	100.000



<Peak table>

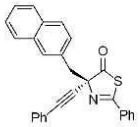
PDA Ch1 254nm

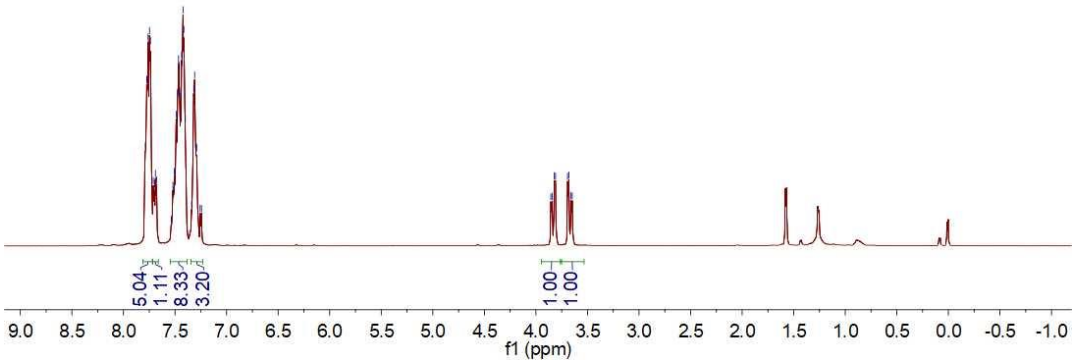
Peak#	Ret. Time	Height	Area	Area%
1	21.407	117183	2807317	11.436
2	22.579	797976	21739778	88.564
Total		915159	24547095	100.000

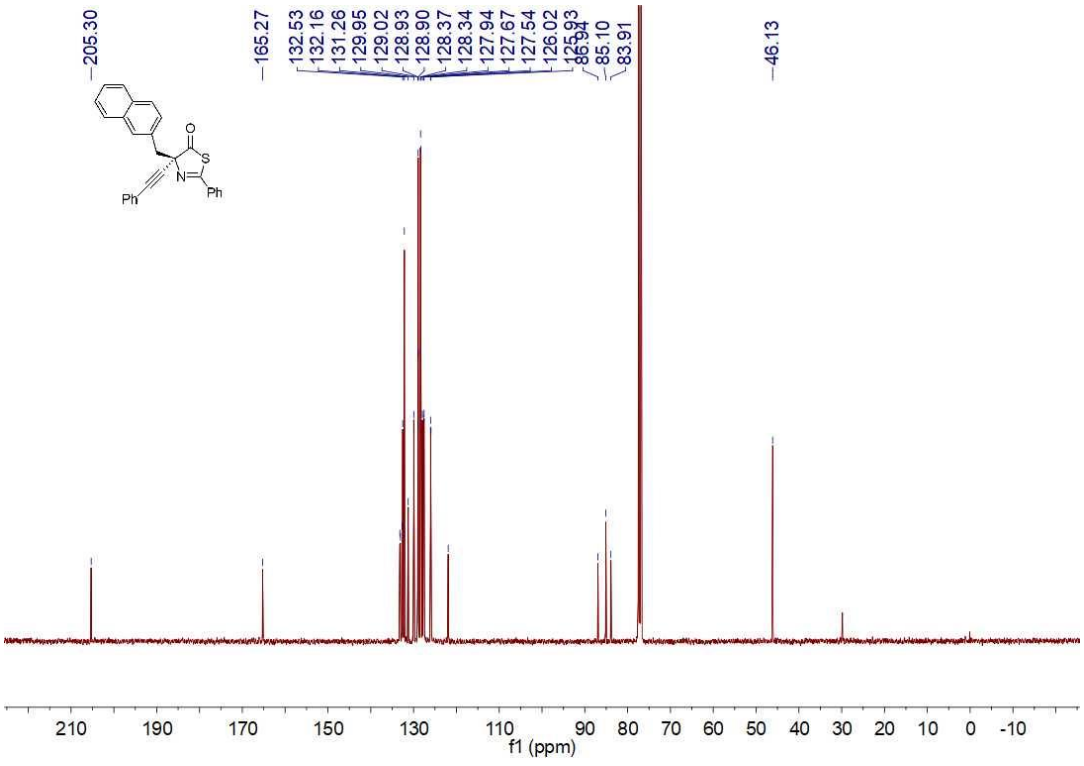

O
S
N
Ph
Ph

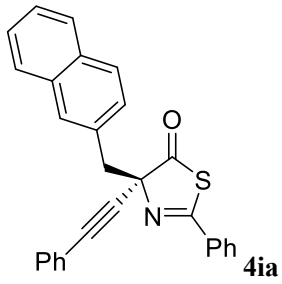
4ia


7.79
7.77
7.77
7.76
7.75
7.74
7.49
7.48
7.48
7.47
7.46
7.46
7.45
7.44
7.43
7.42
7.41
7.40
7.32
7.31
7.29
3.84
3.82
3.81
3.69
3.68
3.66
3.65

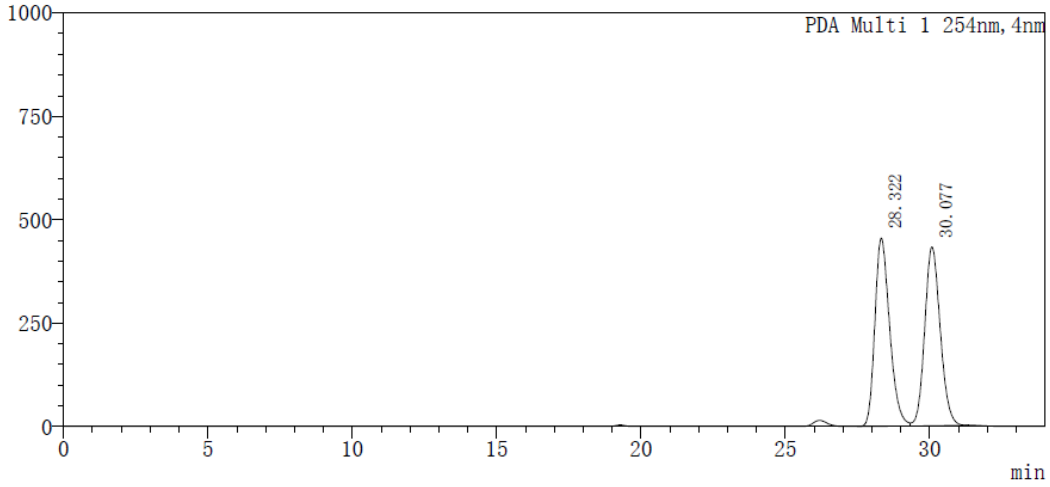



5.04
1.11
8.33
3.20
1.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


205.30
165.27
132.53
132.16
131.26
129.95
129.02
128.93
128.90
128.37
128.34
127.94
127.67
127.54
126.02
125.93
86.94
85.10
83.91
46.13
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



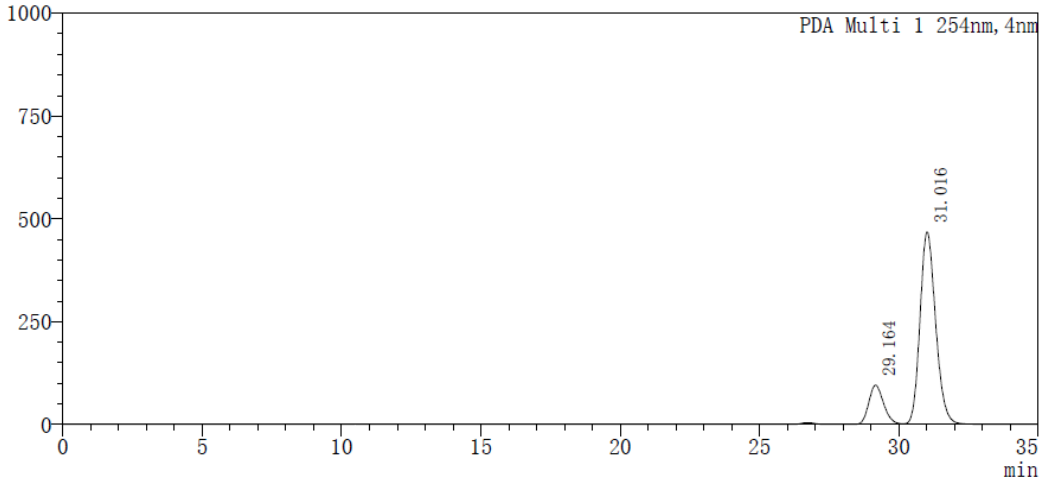
4ia



〈Peak table〉

PDA Ch1 254nm

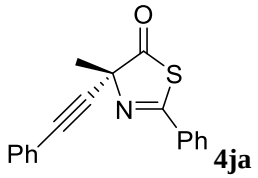
Peak#	Ret. Time	Height	Area	Area%
1	28.322	454845	16203958	50.023
2	30.077	432631	16189153	49.977
Total		887475	32393111	100.000



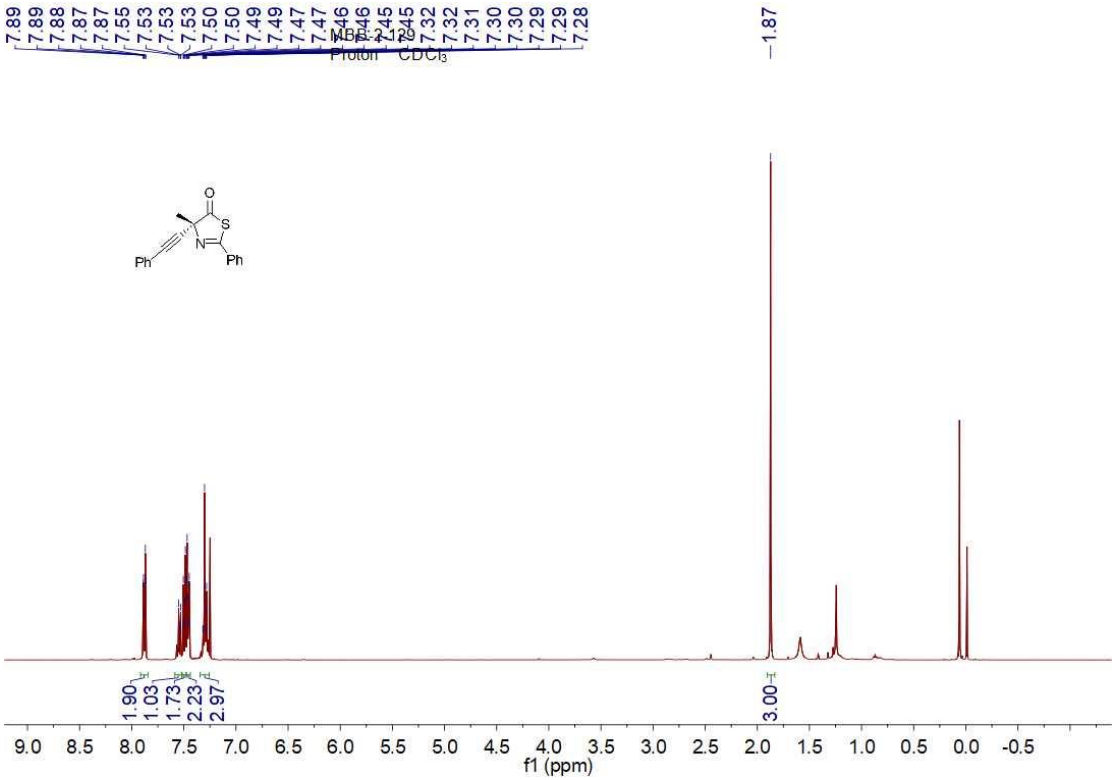
〈Peak table〉

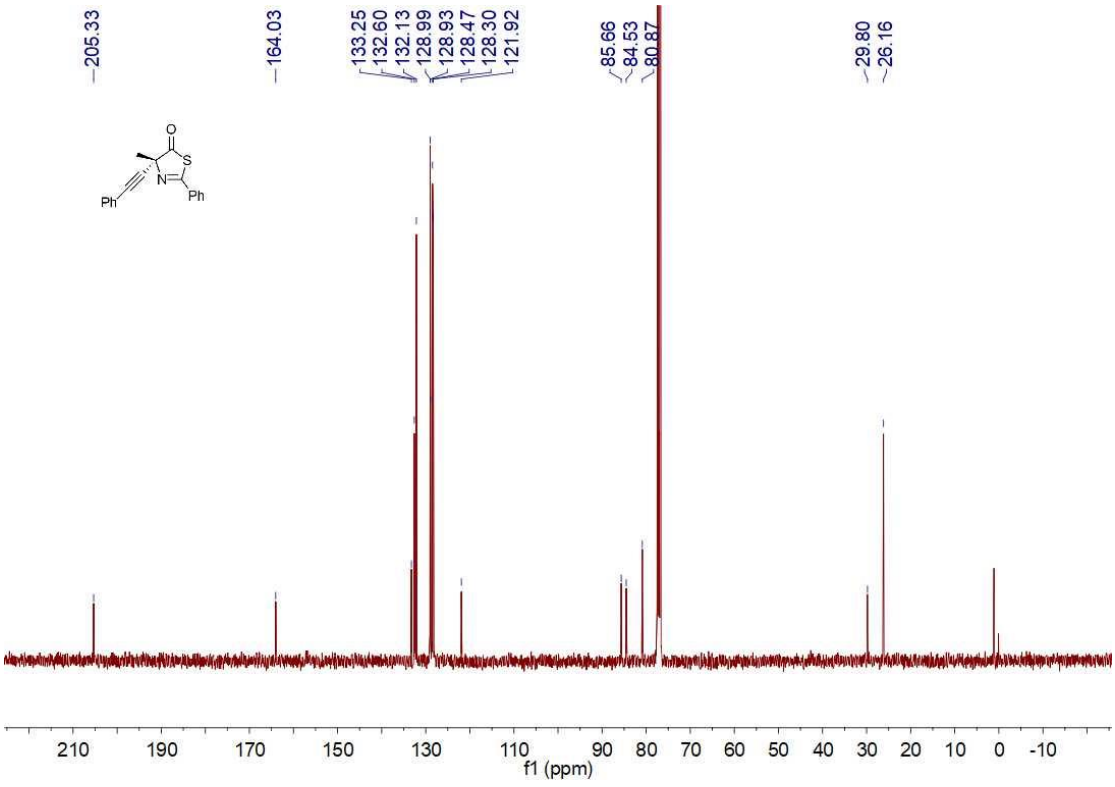
PDA Ch1 254nm

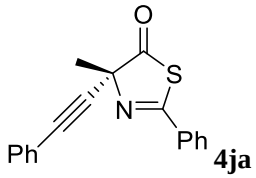
Peak#	Ret. Time	Height	Area	Area%
1	29.164	95548	3566473	16.326
2	31.016	467846	18279254	83.674
Total		563394	21845727	100.000


O
S
N
Ph
Ph

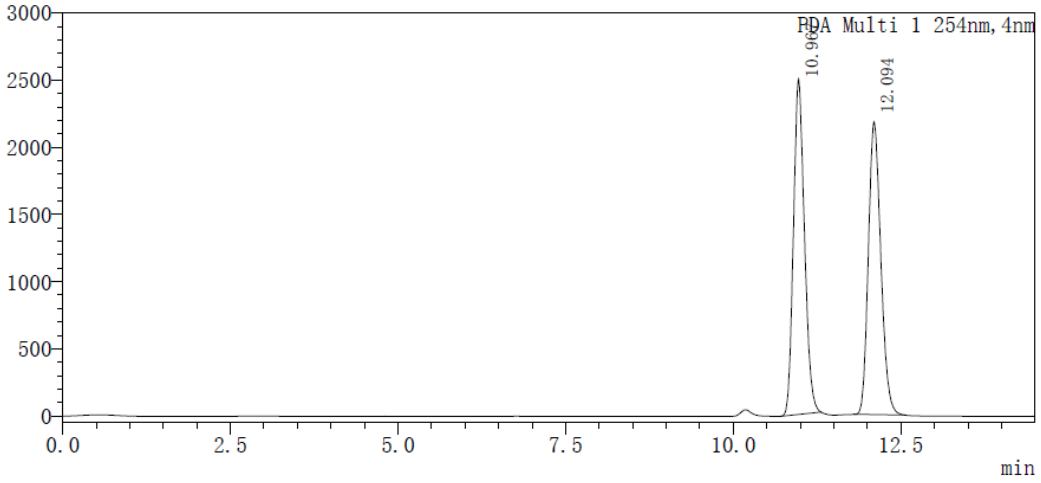
4ja


7.89
7.89
7.88
7.87
7.87
7.55
7.53
7.53
7.50
7.50
7.49
7.49
7.47
7.47
7.46
7.46
7.45
7.45
7.32
7.32
7.31
7.30
7.30
7.29
7.29
7.28
MBE-2-129
Proton CDCl3
1.87
1.90
1.03
1.73
2.23
2.97
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)


205.33
164.03
133.25
132.60
132.13
128.99
128.93
128.47
128.30
121.92
85.66
84.53
80.87
29.80
26.16
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



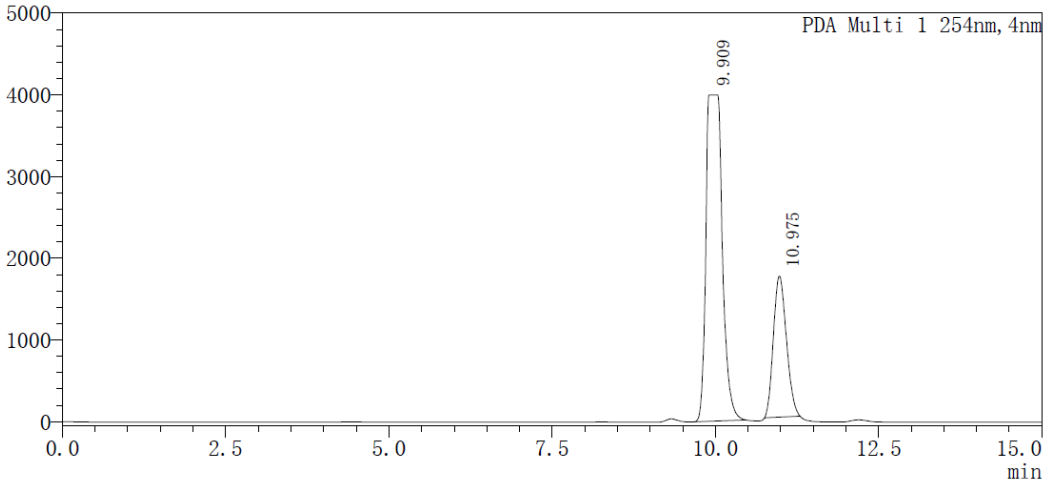
4ja



<Peak table>

PDA Ch1 254nm

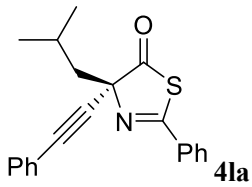
Peak#	Ret. Time	Height	Area	Area%
1	10.967	2495696	28392541	50.143
2	12.094	2179316	28230119	49.857
Total		4675012	56622659	100.000



<Peak table>

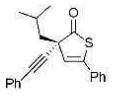
PDA Ch1 254nm

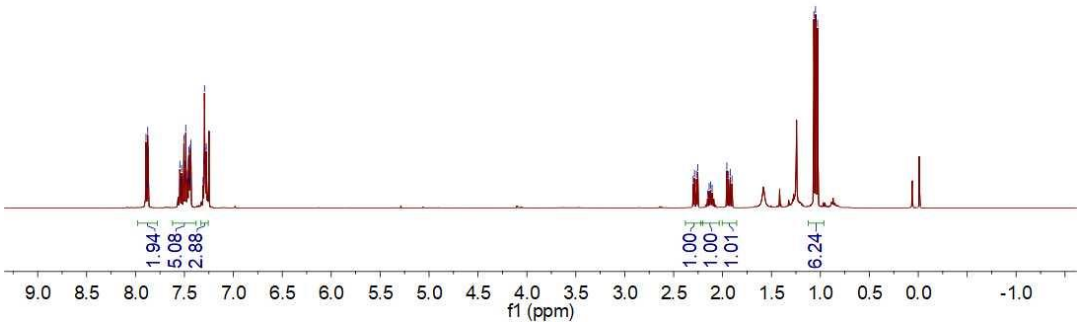
Peak#	Ret. Time	Height	Area	Area%
1	9.909	3994907	68950175	74.190
2	10.975	1726025	23987458	25.810
Total		5720932	92937633	100.000

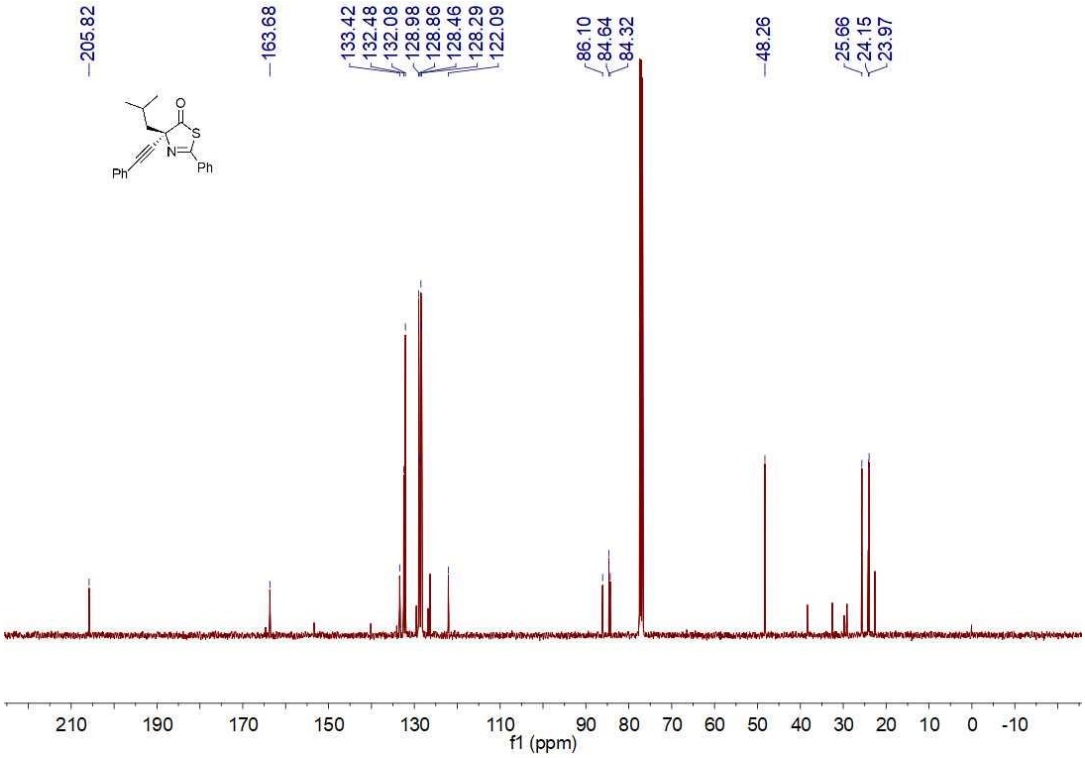

O
S
N
Ph
Ph

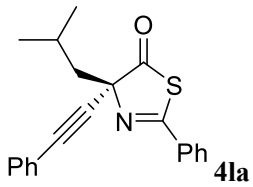
4la


7.89
7.88
7.88
7.87
7.55
7.53
7.53
7.51
7.49
7.49
7.47
7.47
7.46
7.45
7.44
7.44
7.43
7.31
7.30
7.29
7.29
7.28
2.30
2.29
2.27
2.25
2.15
2.14
2.12
2.11
1.96
1.94
1.92
1.90
1.07
1.05
1.05
1.03

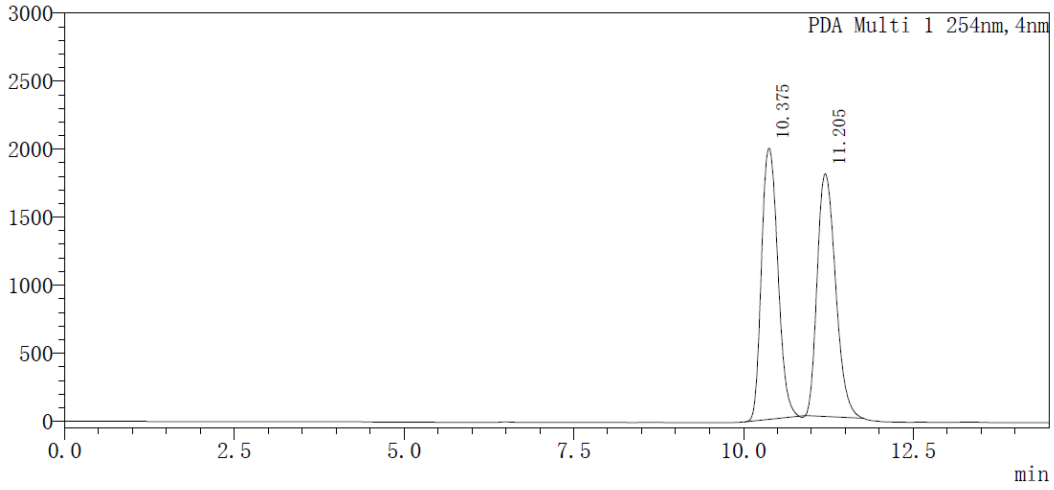

O
S
Ph
Ph


1.94
5.08
2.88
1.00
1.00
1.01
6.24
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 -1.0
f1 (ppm)


205.82
163.68
133.42
132.48
132.08
128.98
128.86
128.46
128.29
122.09
86.10
84.64
84.32
48.26
25.66
24.15
23.97
O
S
N
Ph
Ph
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



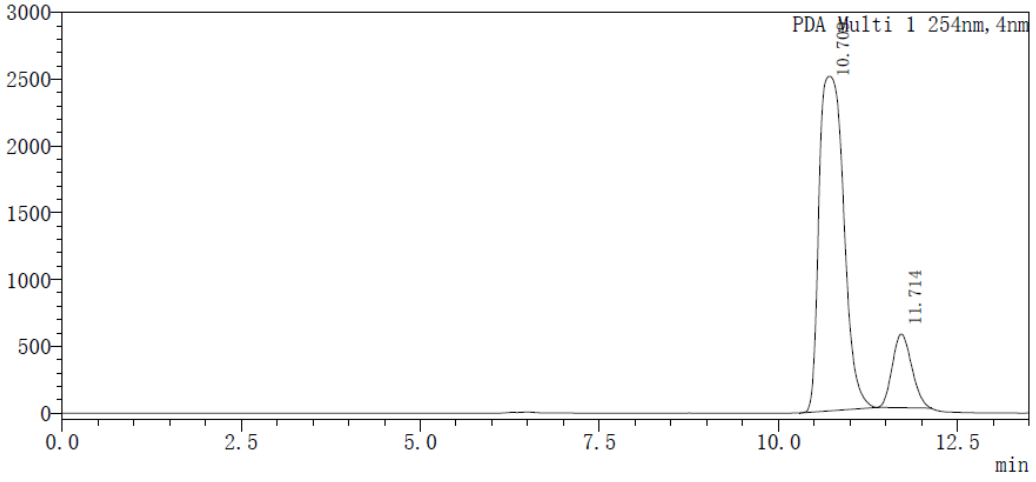
4la



<Peak table>

PDA Ch1 254nm

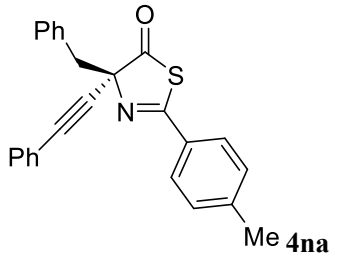
Peak#	Ret. Time	Height	Area	Area%
1	10.375	1993374	33435759	49.790
2	11.205	1784059	33717207	50.210
Total		3777433	67152967	100.000



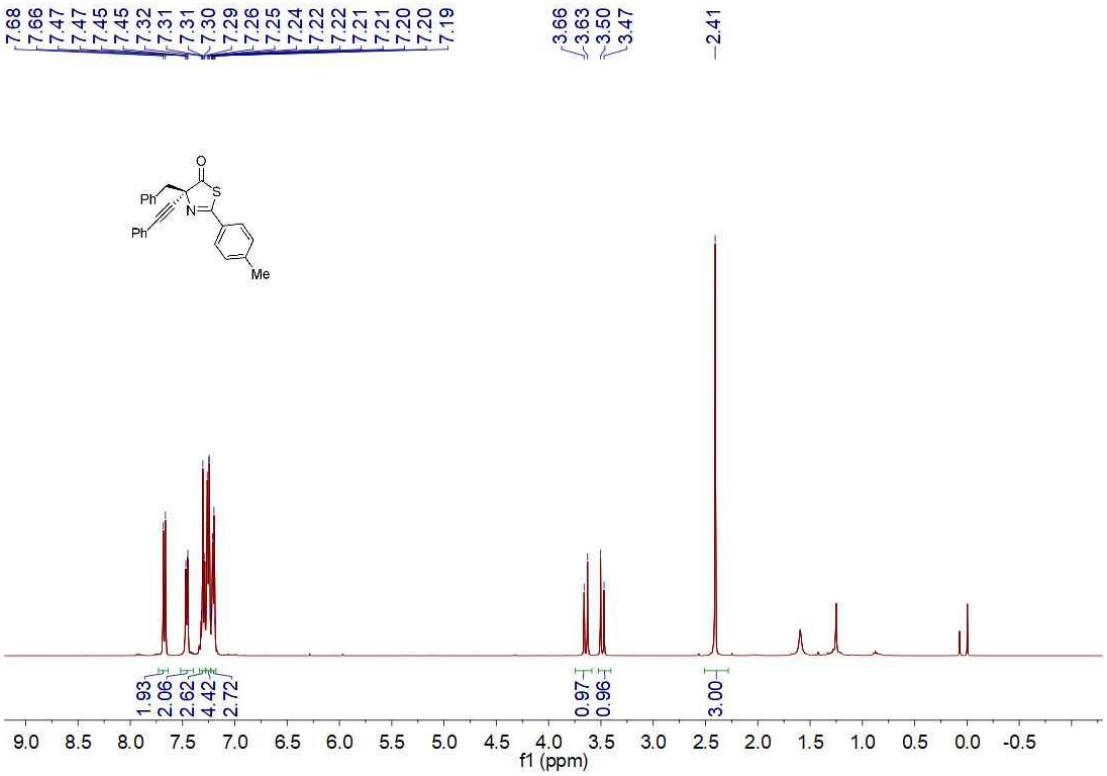
<Peak table>

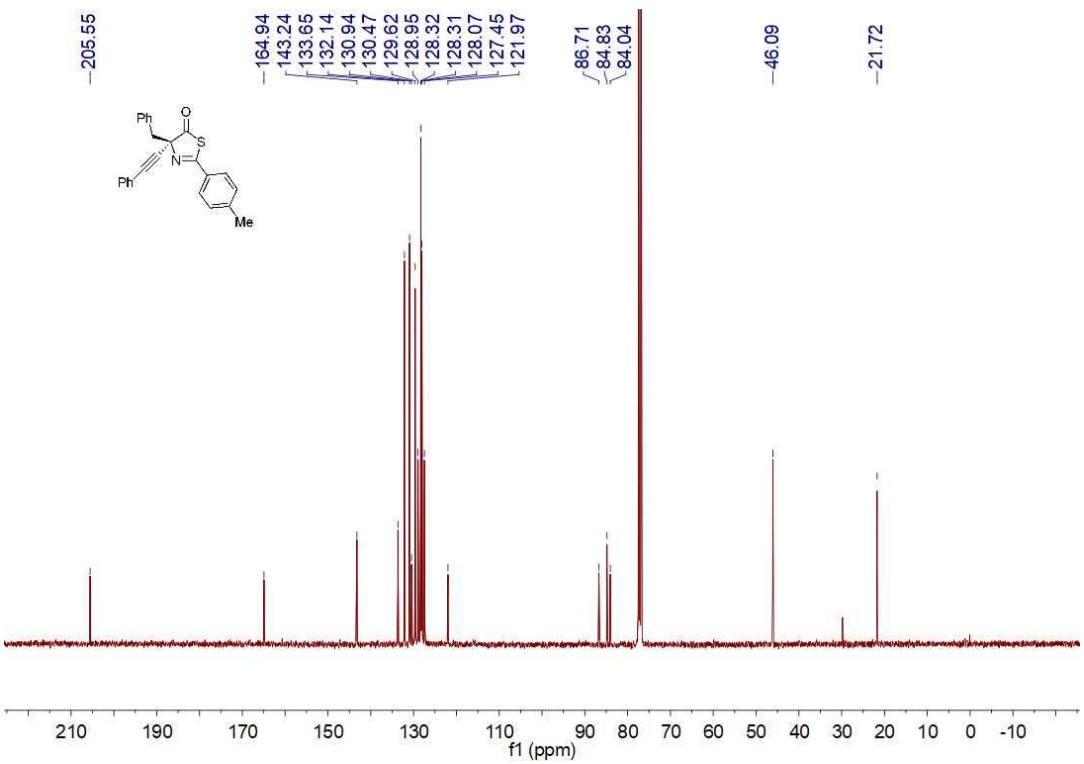
PDA Ch1 254nm

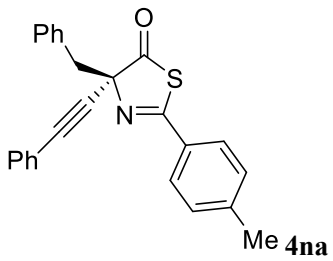
Peak#	Ret. Time	Height	Area	Area%
1	10.709	2504999	60065138	85.205
2	11.714	551869	10430108	14.795
Total		3056868	70495246	100.000


Ph
O
S
N
Ph
Me

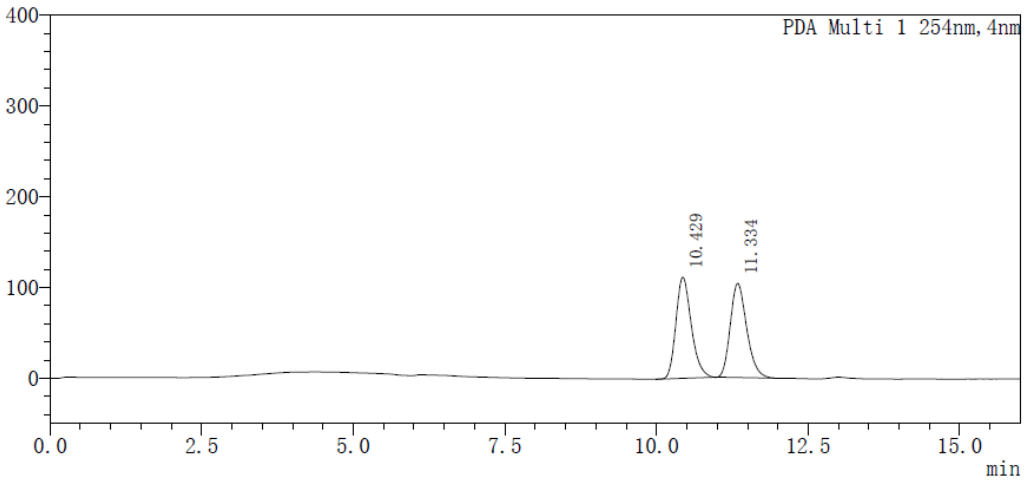
4na


7.68
7.66
7.47
7.47
7.45
7.45
7.32
7.31
7.31
7.30
7.29
7.26
7.25
7.24
7.22
7.22
7.21
7.21
7.20
7.20
7.19
3.66
3.63
3.50
3.47
2.41
1.93
2.06
2.62
4.42
2.72
0.97
0.96
3.00
f1 (ppm)


205.55
164.94
143.24
133.65
132.14
130.94
130.47
129.62
128.95
128.32
128.31
128.07
127.45
121.97
86.71
84.83
84.04
46.09
21.72
f1 (ppm)



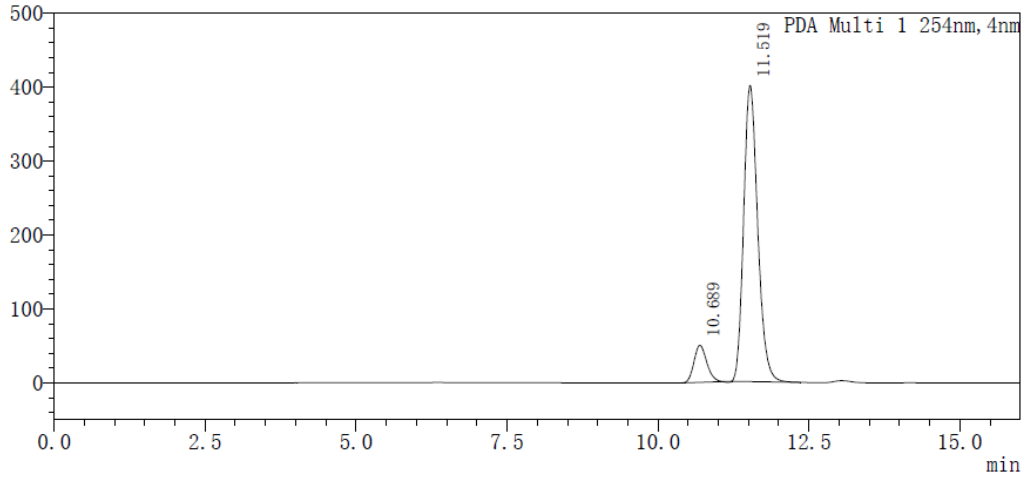
4na



<Peak table>

PDA Ch1 254nm

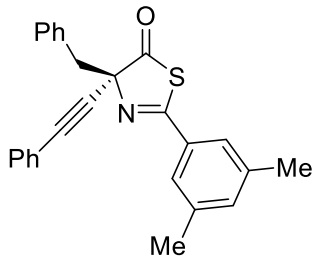
Peak#	Ret. Time	Height	Area	Area%
1	10.429	111497	1971820	50.161
2	11.334	103792	1959148	49.839
Total		215289	3930967	100.000



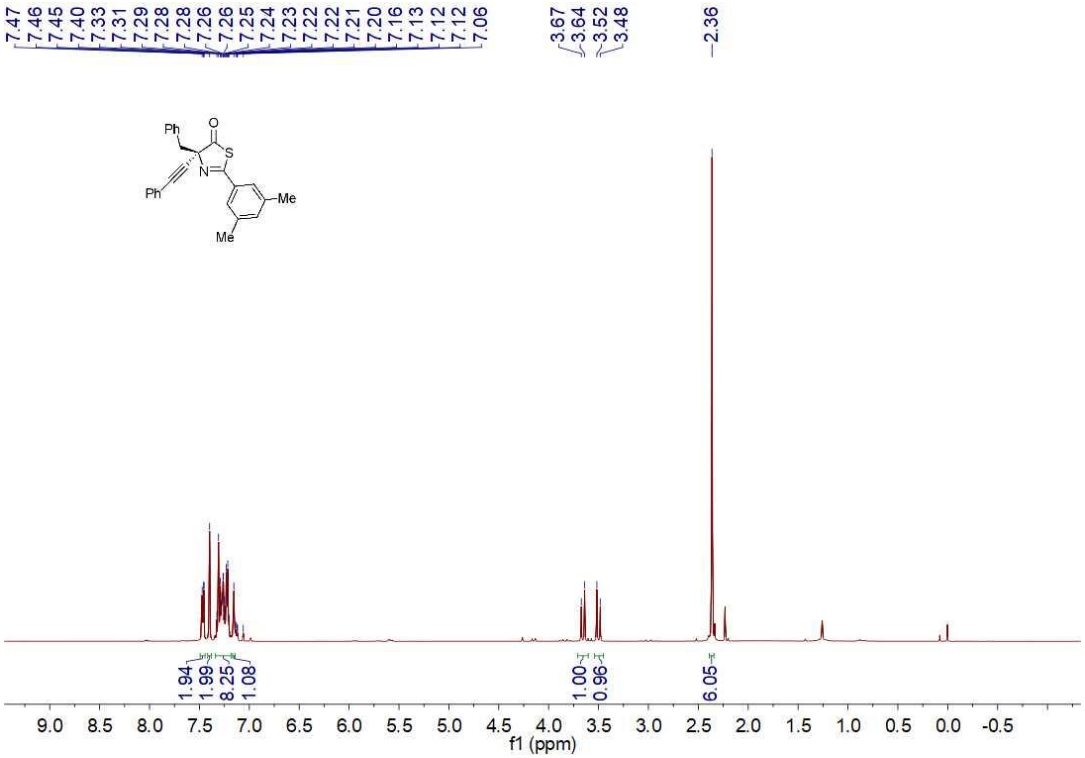
<Peak table>

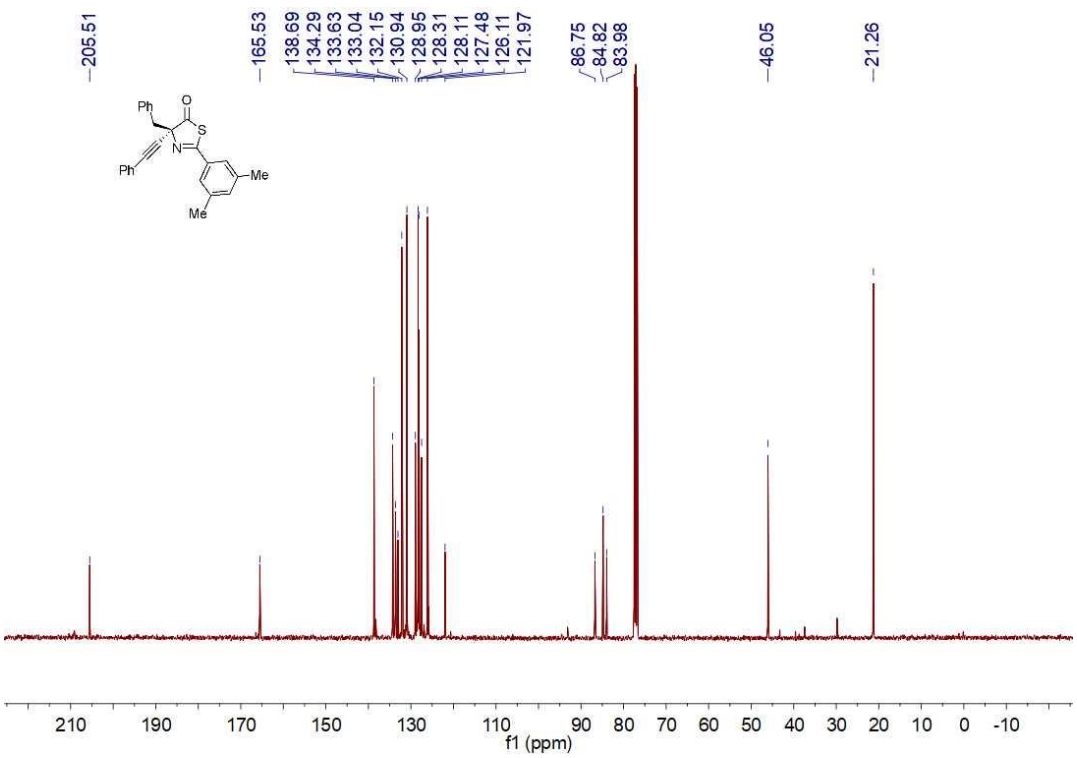
PDA Ch1 254nm

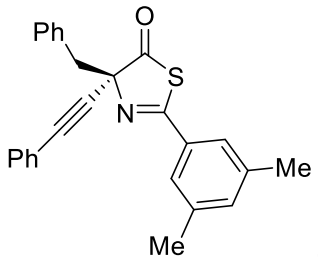
Peak#	Ret. Time	Height	Area	Area%
1	10.689	50055	730219	10.133
2	11.519	400494	6476112	89.867
Total		450549	7206331	100.000


Ph
O
S
N
Ph
Me
Me

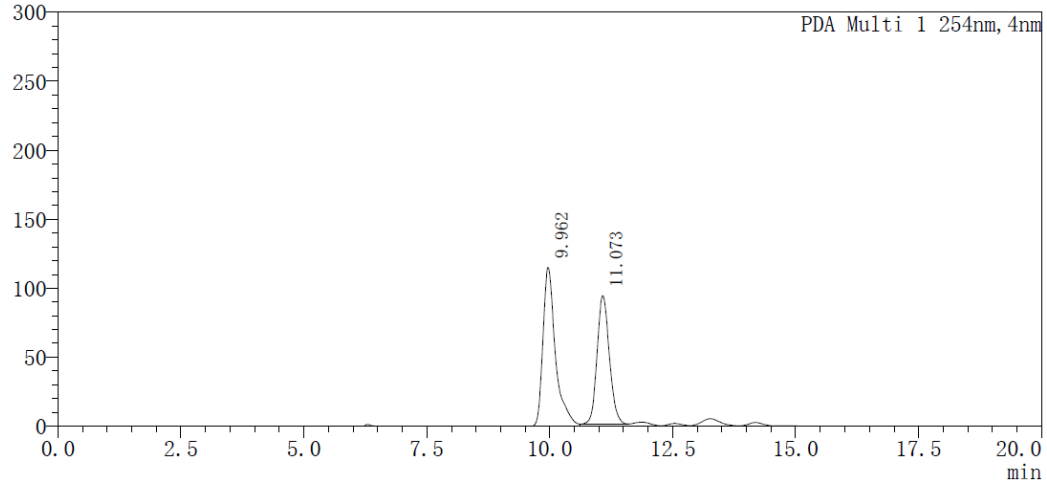
4oa


7.47
7.46
7.45
7.40
7.33
7.31
7.29
7.28
7.28
7.26
7.26
7.25
7.24
7.23
7.22
7.22
7.21
7.20
7.16
7.13
7.12
7.12
7.06
3.67
3.64
3.52
3.48
2.36
1.94
1.99
8.25
1.08
1.00
0.96
6.05
f1 (ppm)


205.51
165.53
138.69
134.29
133.63
133.04
132.15
130.94
128.95
128.31
128.11
127.48
126.11
121.97
86.75
84.82
83.98
46.05
21.26
f1 (ppm)



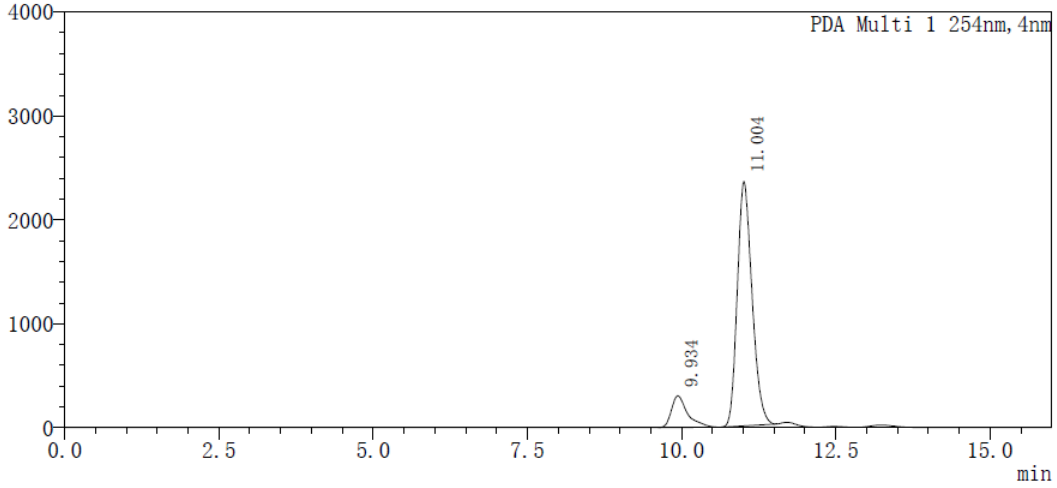
4oa



<Peak table>

PDA Ch1 254nm

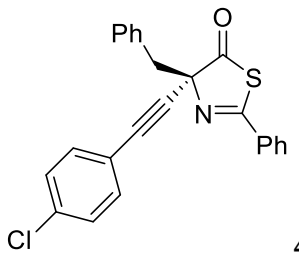
Peak#	Ret. Time	Height	Area	Area%
1	9.962	115084	2040496	55.926
2	11.073	92888	1608087	44.074
Total		207972	3648583	100.000



<Peak table>

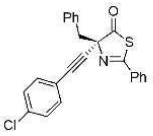
PDA Ch1 254nm

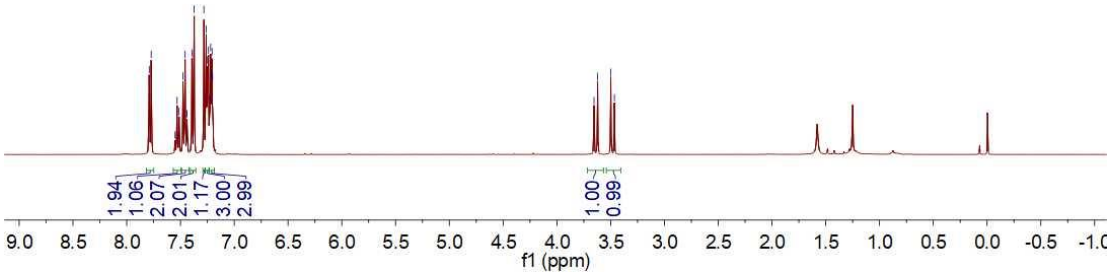
Peak#	Ret. Time	Height	Area	Area%
1	9.934	305680	5525023	12.366
2	11.004	2350526	39155562	87.634
Total		2656206	44680585	100.000

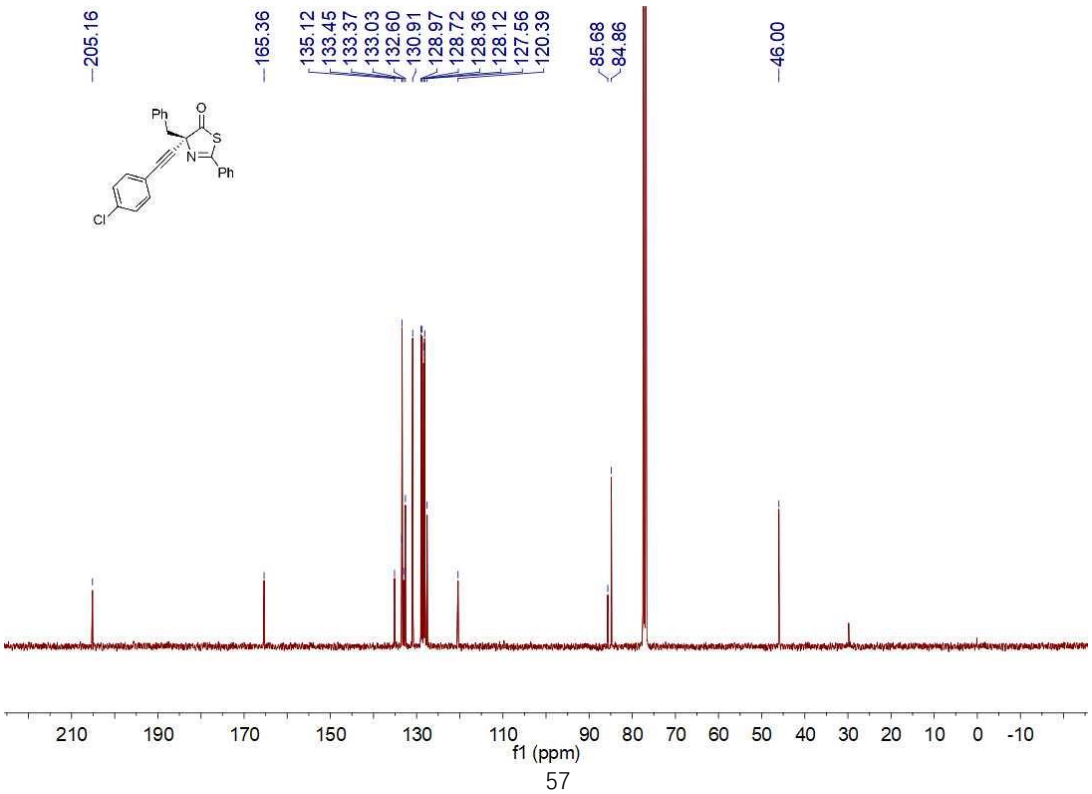

Ph
O
S
N
Ph
Cl

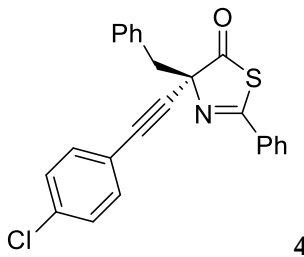
4ab


7.79
7.77
7.55
7.53
7.51
7.48
7.46
7.44
7.39
7.37
7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.21
7.20
3.65
3.62
3.50
3.47

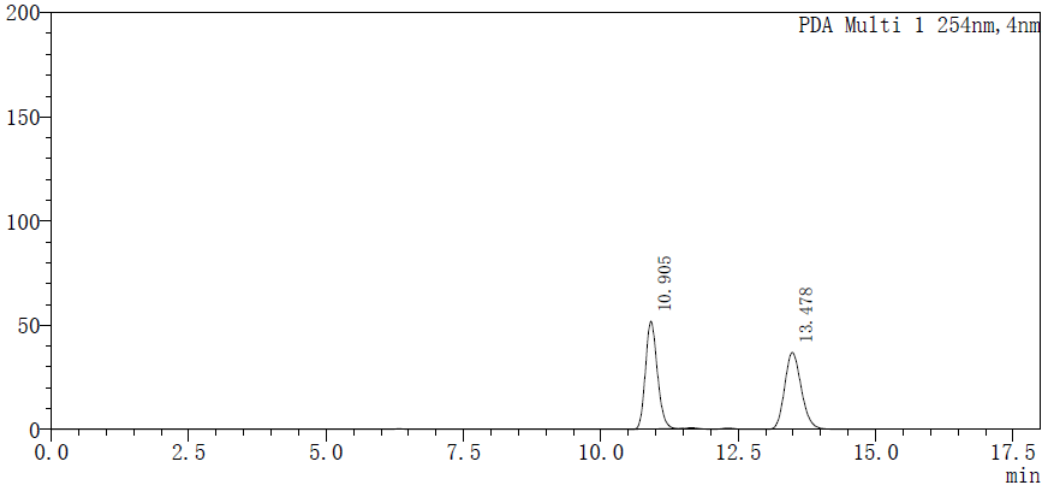

Ph
O
S
N
Ph
Cl


1.94
1.06
2.07
2.01
1.17
3.00
2.99
1.00
0.99
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)


205.16
165.36
135.12
133.45
133.37
133.03
132.60
130.91
128.97
128.72
128.36
128.12
127.56
120.39
85.68
84.86
46.00
Ph
O
S
N
Ph
Cl
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



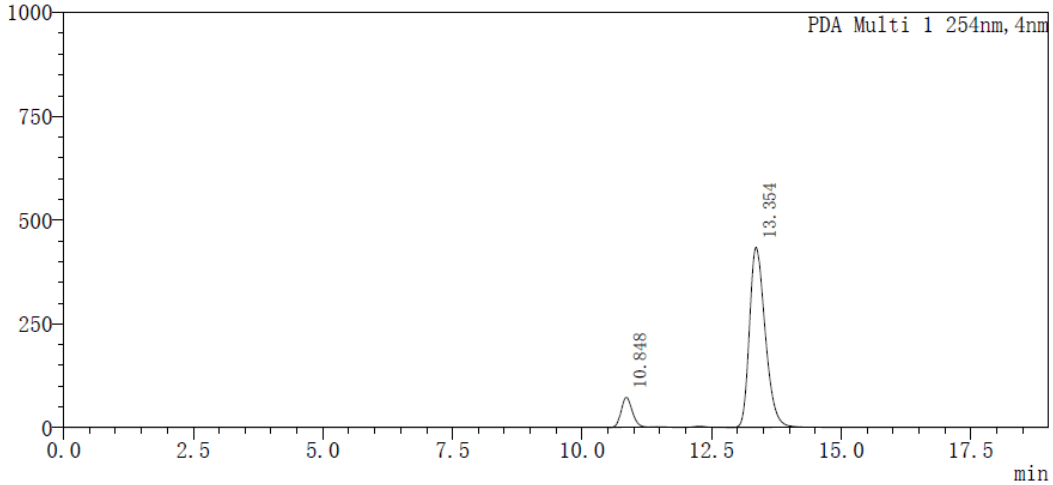
4ab



〈Peak table〉

PDA Ch1 254nm

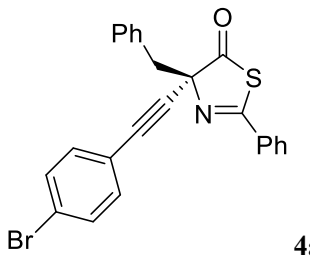
Peak#	Ret. Time	Height	Area	Area%
1	10.905	51755	779318	49.897
2	13.478	36971	782521	50.103
Total		88726	1561839	100.000



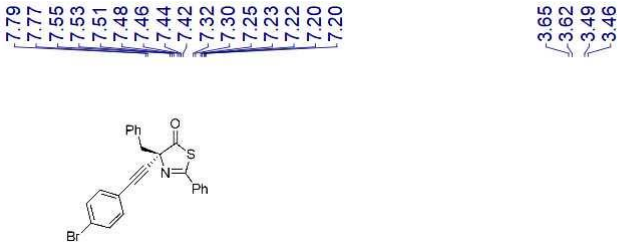
〈Peak table〉

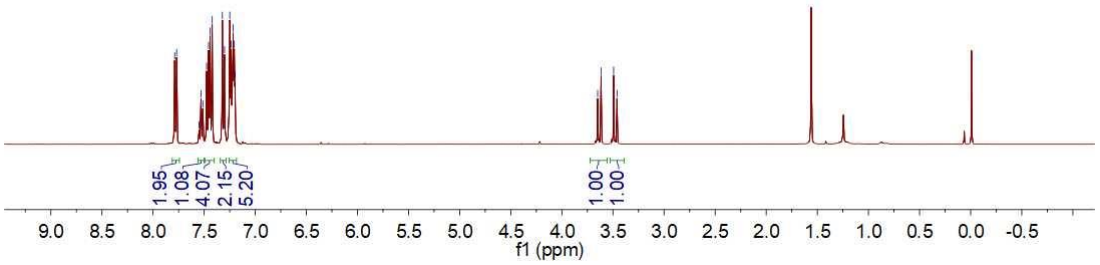
PDA Ch1 254nm

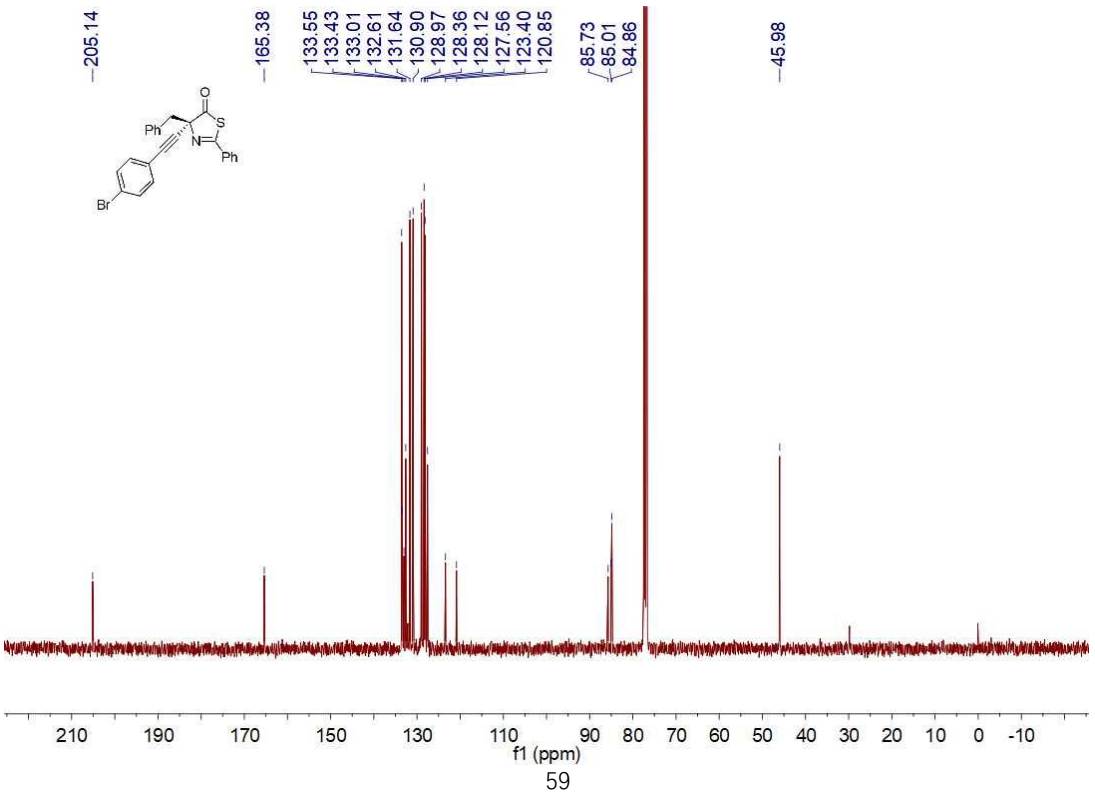
Peak#	Ret. Time	Height	Area	Area%
1	10.848	72396	1078760	10.536
2	13.354	433972	9160140	89.464
Total		506367	10238901	100.000

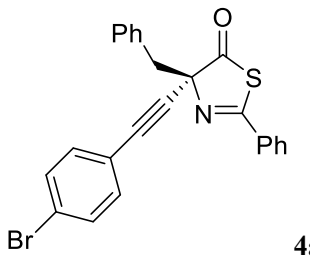

Ph
O
S
N
Ph
Br

4ac

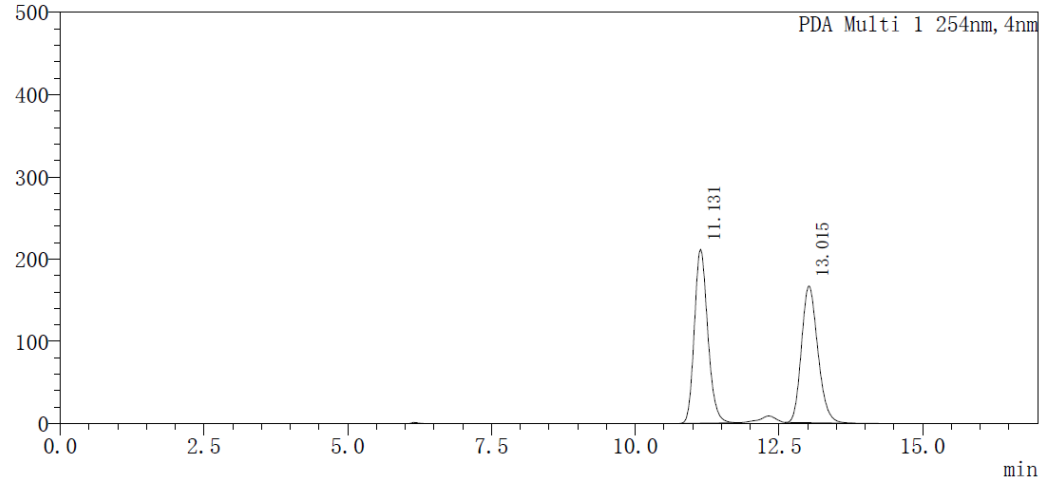

7.79
7.77
7.55
7.53
7.51
7.48
7.46
7.44
7.42
7.32
7.30
7.25
7.23
7.22
7.20
7.20
3.65
3.62
3.49
3.46


1.95
1.08
4.07
2.15
5.20
1.00
1.00
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)


205.14
165.38
133.55
133.43
133.01
132.61
131.64
130.90
128.97
128.36
128.12
127.56
123.40
120.85
85.73
85.01
84.86
45.98
210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



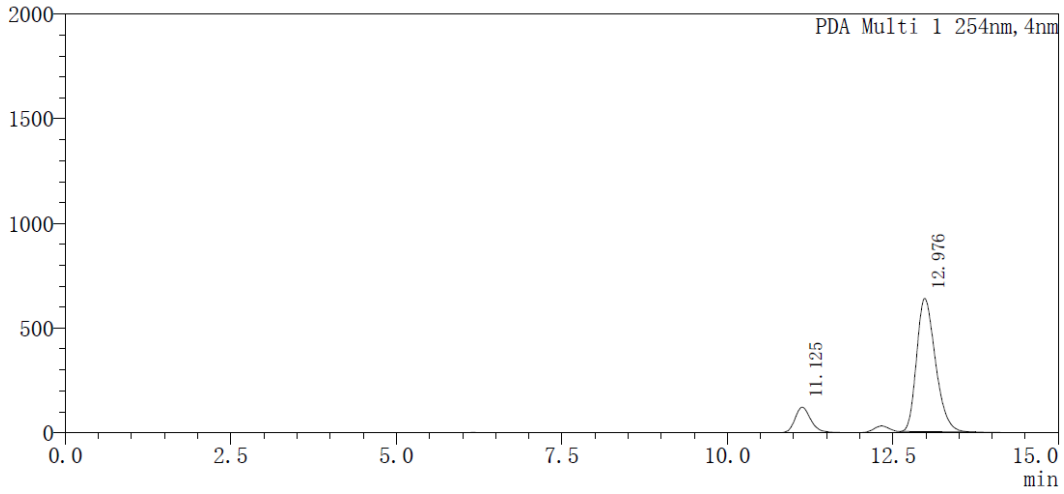
4ac



<Peak table>

PDA Ch1 254nm

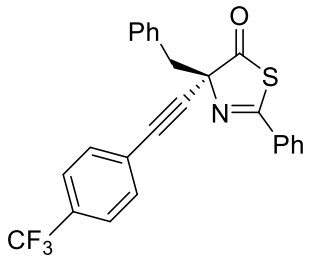
Peak#	Ret. Time	Height	Area	Area%
1	11.131	211324	3432943	51.050
2	13.015	166268	3291733	48.950
Total		377593	6724676	100.000



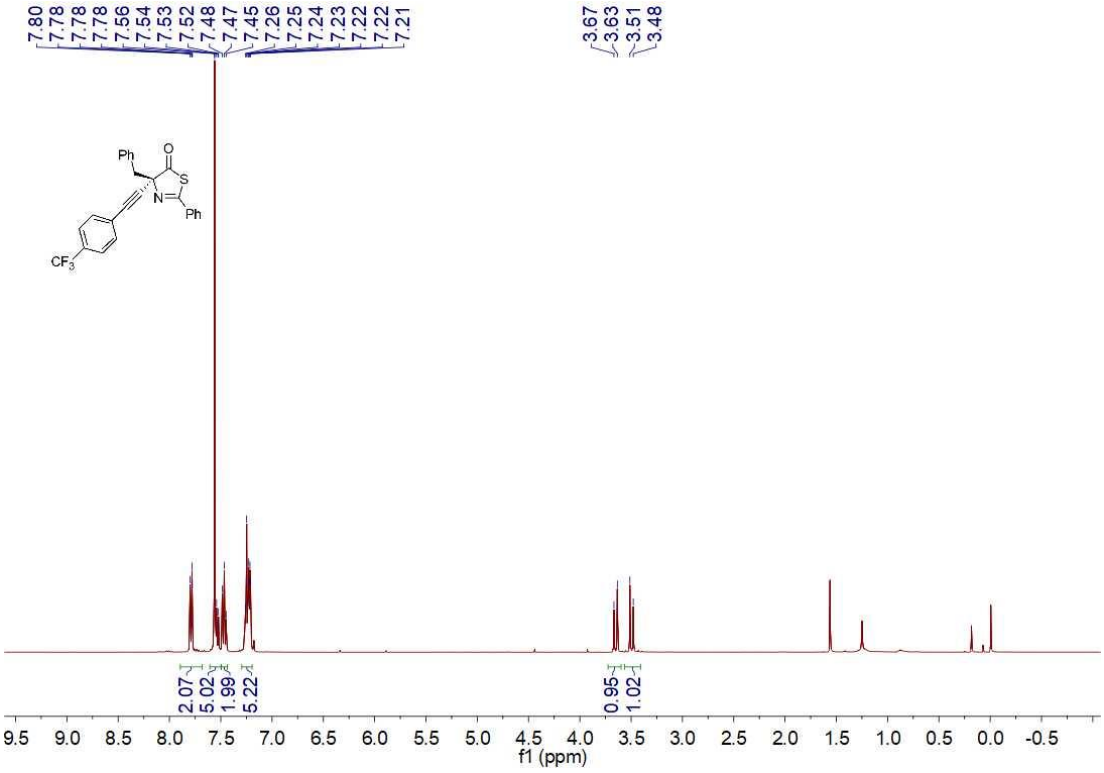
<Peak table>

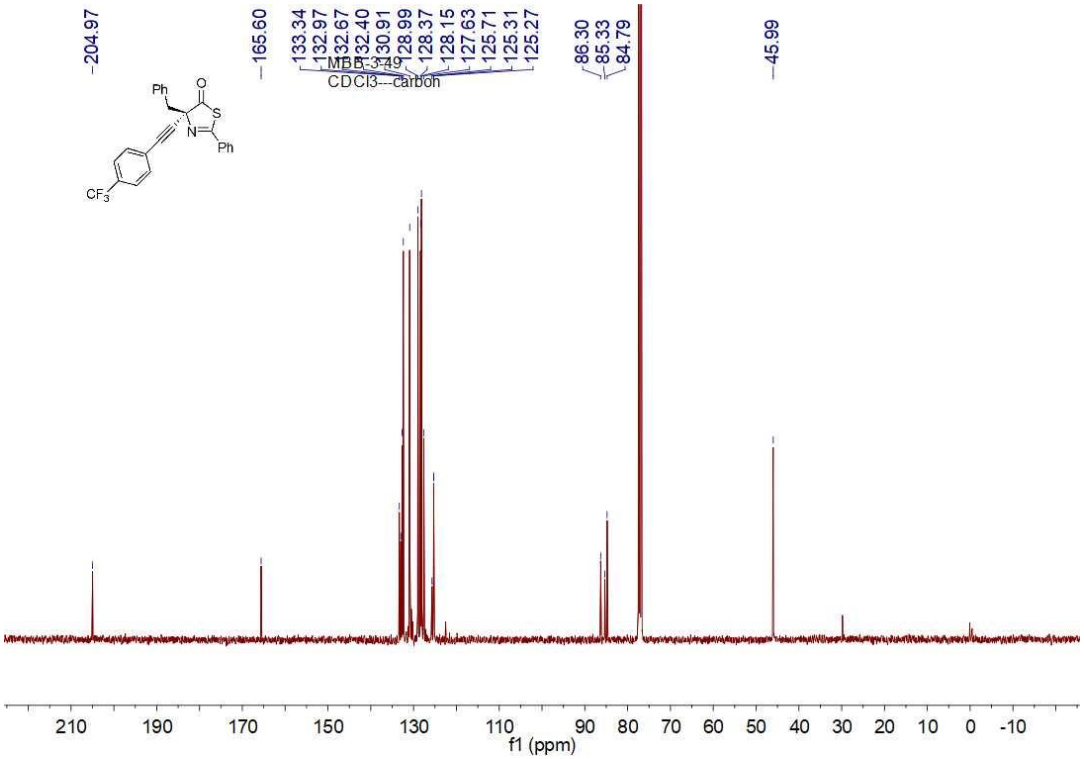
PDA Ch1 254nm

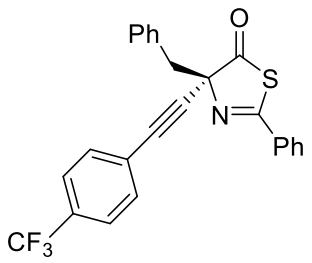
Peak#	Ret. Time	Height	Area	Area%
1	11.125	120132	1935207	13.267
2	12.976	637767	12651668	86.733
Total		757899	14586875	100.000


Ph
O
S
N
Ph
CF3

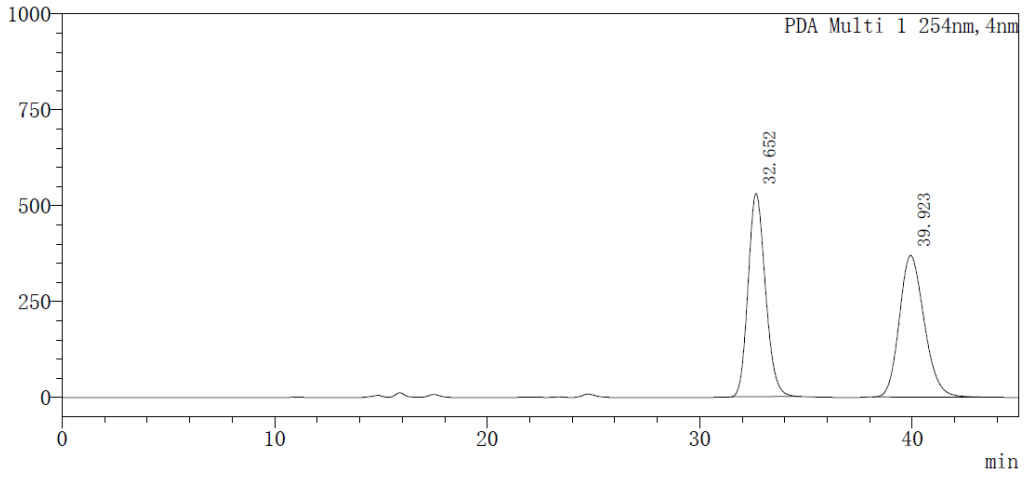
4ad


7.80
7.78
7.78
7.78
7.56
7.54
7.53
7.52
7.48
7.47
7.45
7.26
7.25
7.24
7.23
7.22
7.22
7.21
3.67
3.63
3.51
3.48
2.07
5.02
1.99
5.22
0.95
1.02
f1 (ppm)


204.97
165.60
133.34
132.97
132.67
132.40
130.91
128.99
128.37
128.15
127.63
125.71
125.31
125.27
86.30
85.33
84.79
45.99
MBB-3-49
CDCl3---carbon
f1 (ppm)



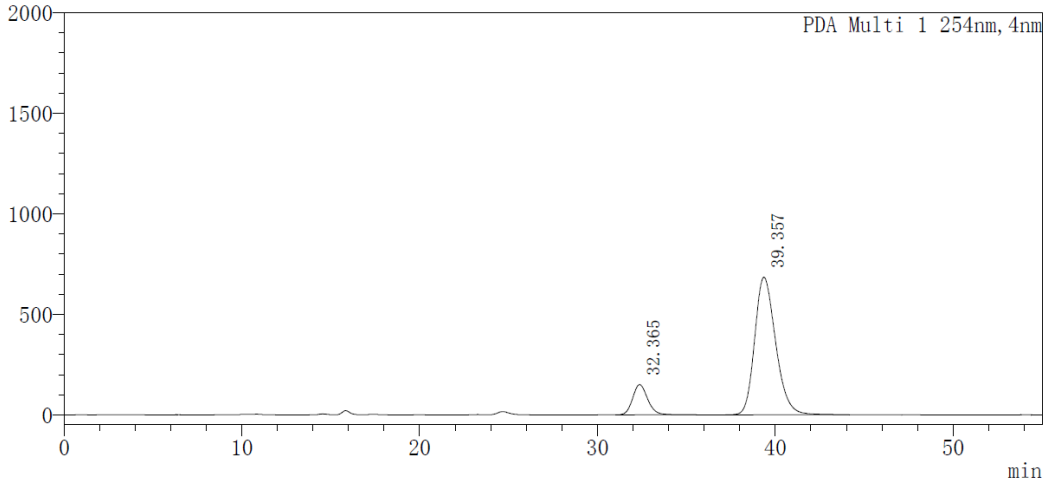
4ad



<Peak table>

PDA Ch1 254nm

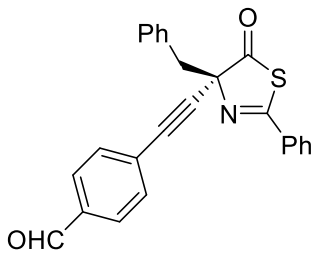
Peak#	Ret. Time	Height	Area	Area%
1	32.652	529923	30079883	50.002
2	39.923	369061	30077620	49.998
Total		898985	60157504	100.000



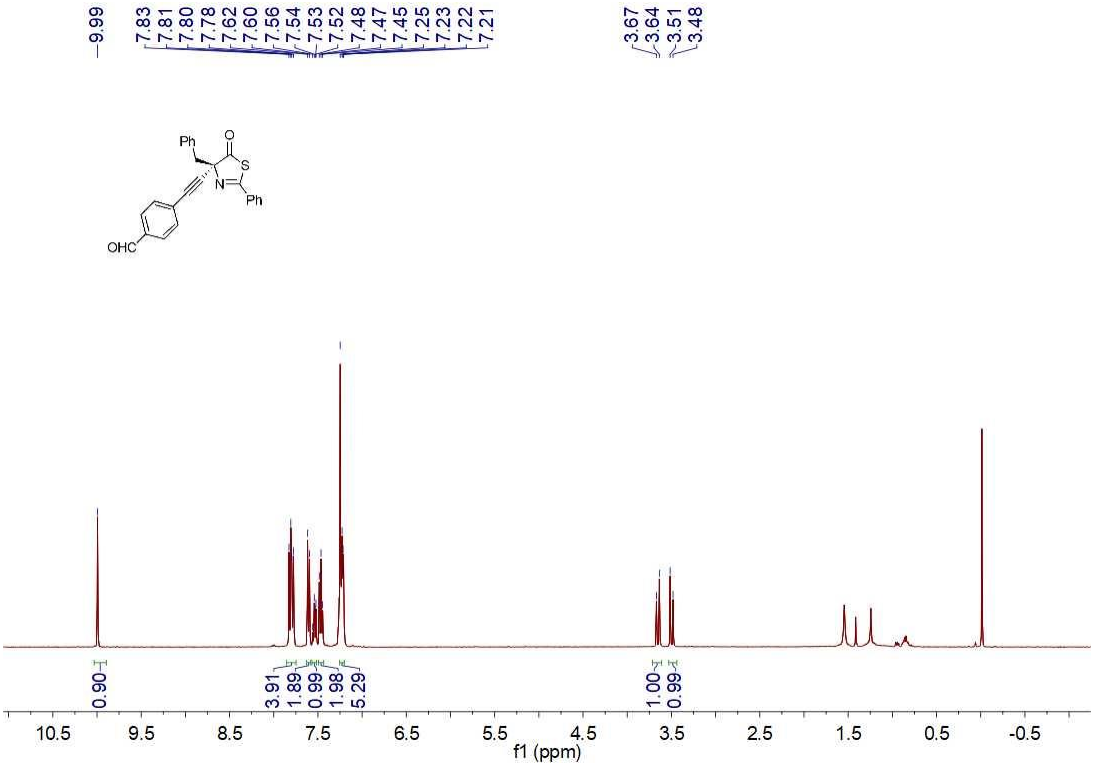
<Peak table>

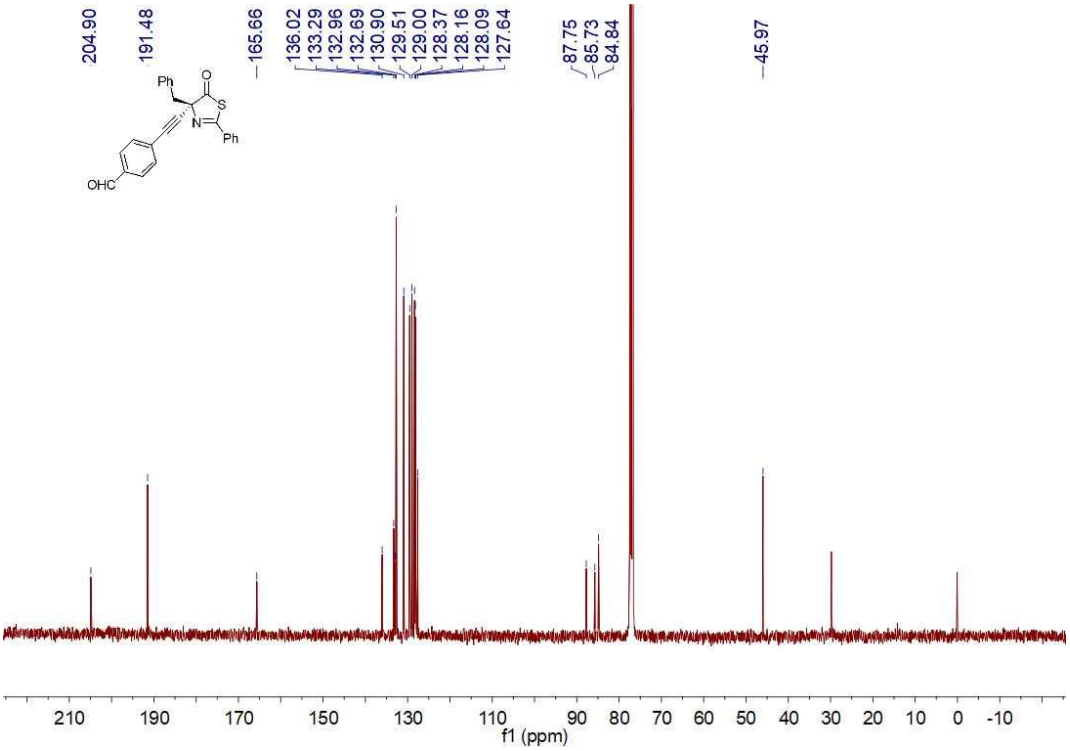
PDA Ch1 254nm

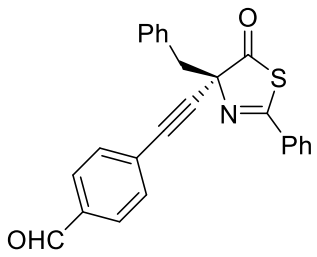
Peak#	Ret. Time	Height	Area	Area%
1	32.365	150239	8826003	13.568
2	39.357	684356	56221844	86.432
Total		834595	65047847	100.000


Ph
O
S
N
Ph
OHC

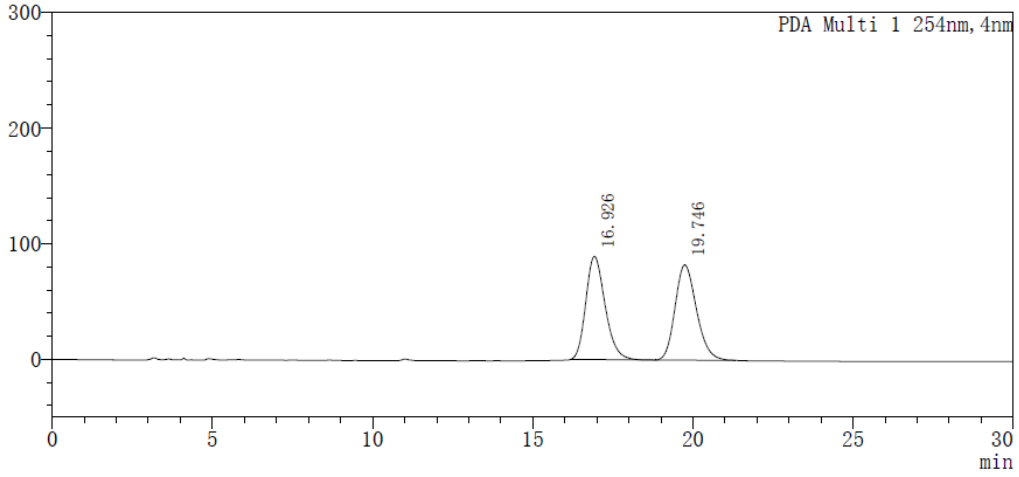
4ae


9.99
7.83
7.81
7.80
7.78
7.62
7.60
7.56
7.54
7.53
7.52
7.48
7.47
7.45
7.25
7.23
7.22
7.21
3.67
3.64
3.51
3.48
0.90
3.91
1.89
0.99
1.98
5.29
1.00
0.99
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)


204.90
191.48
165.66
136.02
133.29
132.96
132.69
130.90
129.51
129.00
128.37
128.16
128.09
127.64
87.75
85.73
84.84
45.97
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



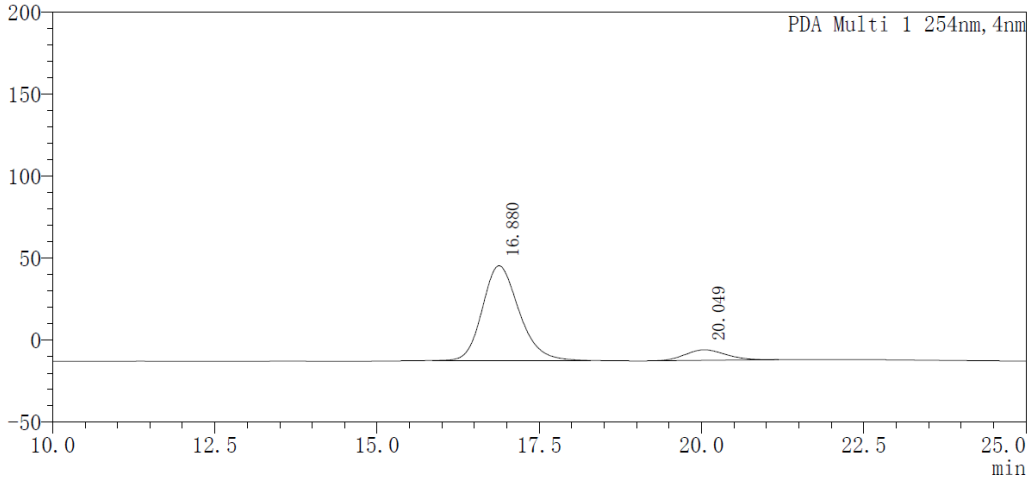
4ae



〈Peak table〉

PDA Ch1 254nm

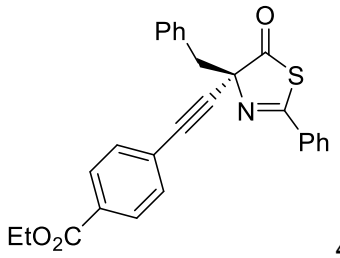
Peak#	Ret. Time	Height	Area	Area%
1	16.926	89235	3736694	49.313
2	19.746	82386	3840880	50.687
Total		171620	7577574	100.000



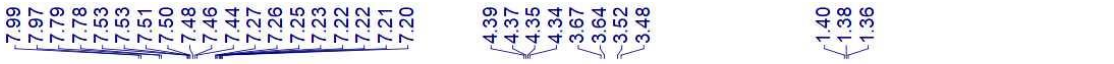
〈Peak table〉

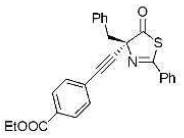
PDA Ch1 254nm

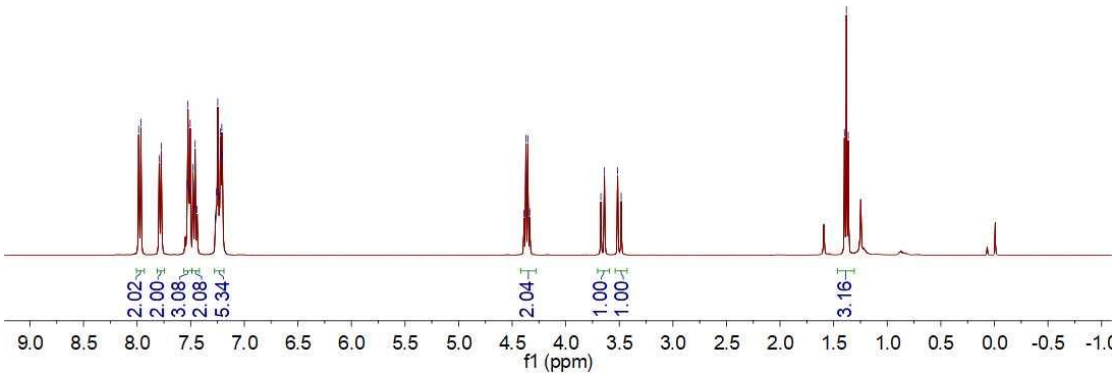
Peak#	Ret. Time	Height	Area	Area%
1	16.880	57764	2268026	89.100
2	20.049	6379	277446	10.900
Total		64142	2545472	100.000

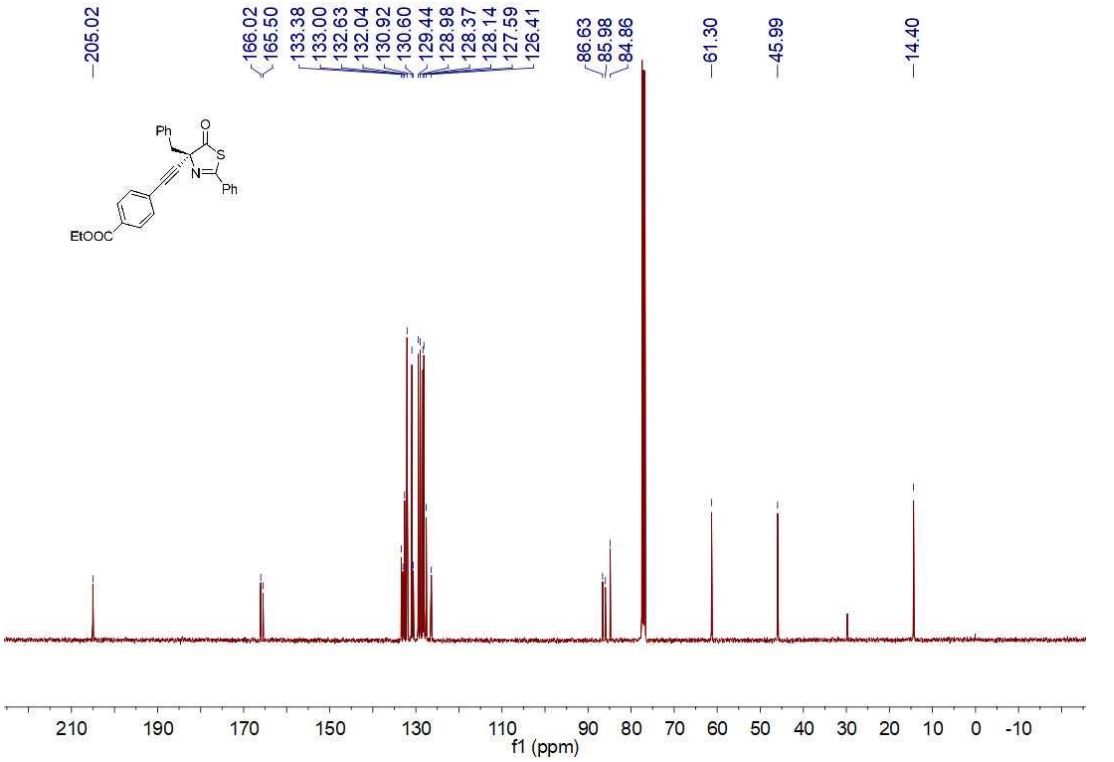

Ph
O
S
N
Ph
EtO2C

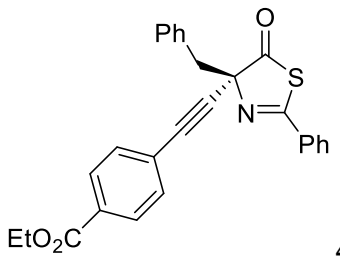
4af


7.99
7.97
7.79
7.78
7.53
7.53
7.51
7.50
7.48
7.46
7.44
7.27
7.26
7.25
7.23
7.22
7.22
7.21
7.20
4.39
4.37
4.35
4.34
3.67
3.64
3.52
3.48
1.40
1.38
1.36

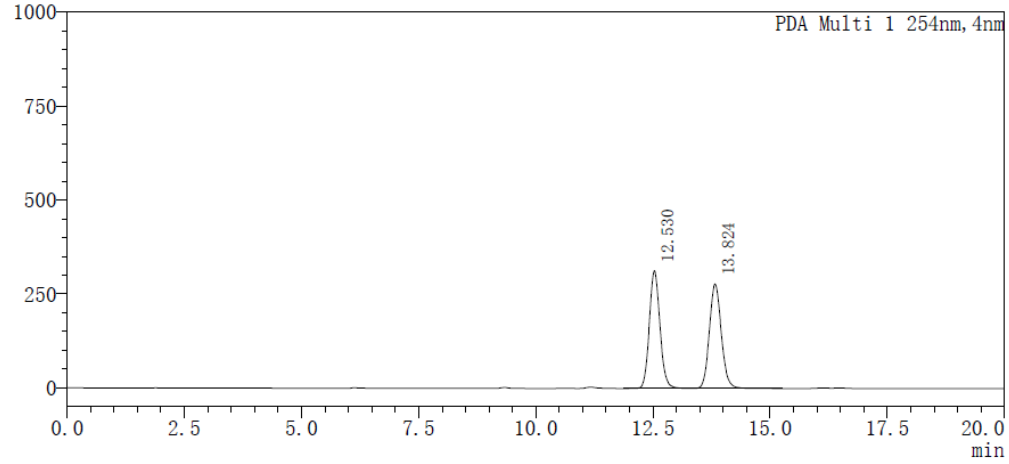

Ph
O
S
N
Ph
EtOOC


2.02
2.00
3.08
2.08
5.34
2.04
1.00
1.00
3.16
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)


205.02
166.02
165.50
133.38
133.00
132.63
132.04
130.92
130.60
129.44
128.98
128.37
128.14
127.59
126.41
86.63
85.98
84.86
61.30
45.99
14.40
Ph
O
S
N
Ph
EtOOC
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



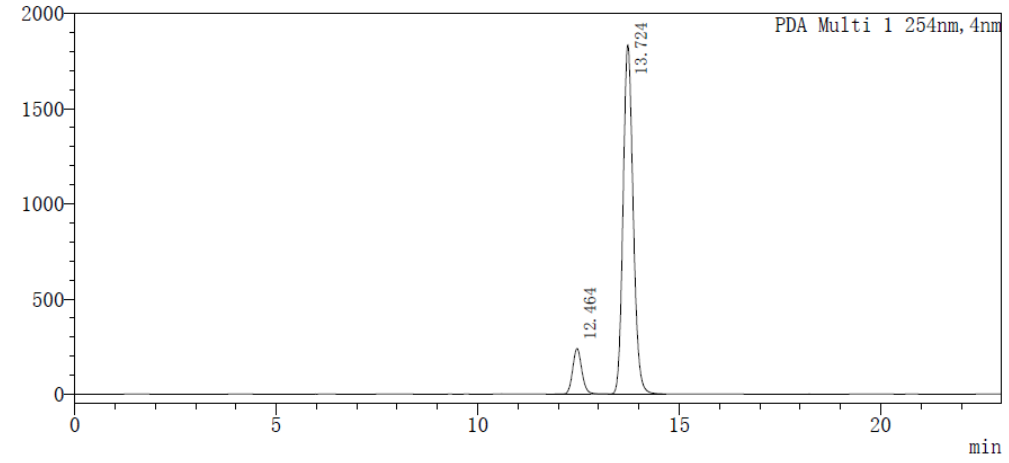
4af



〈Peak table〉

PDA Ch1 254nm

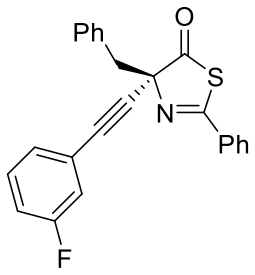
Peak#	Ret. Time	Height	Area	Area%
1	12.530	313474	4960435	49.999
2	13.824	278340	4960661	50.001
Total		591815	9921096	100.000



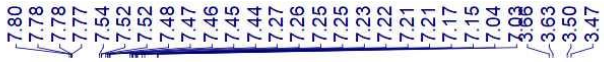
〈Peak table〉

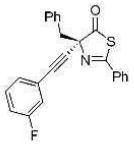
PDA Ch1 254nm

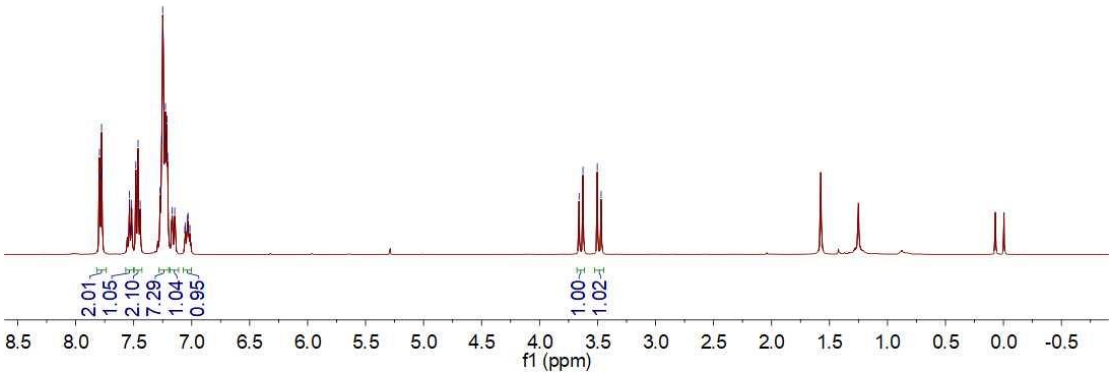
Peak#	Ret. Time	Height	Area	Area%
1	12.464	240153	3807595	10.663
2	13.724	1834956	31902134	89.337
Total		2075109	35709730	100.000

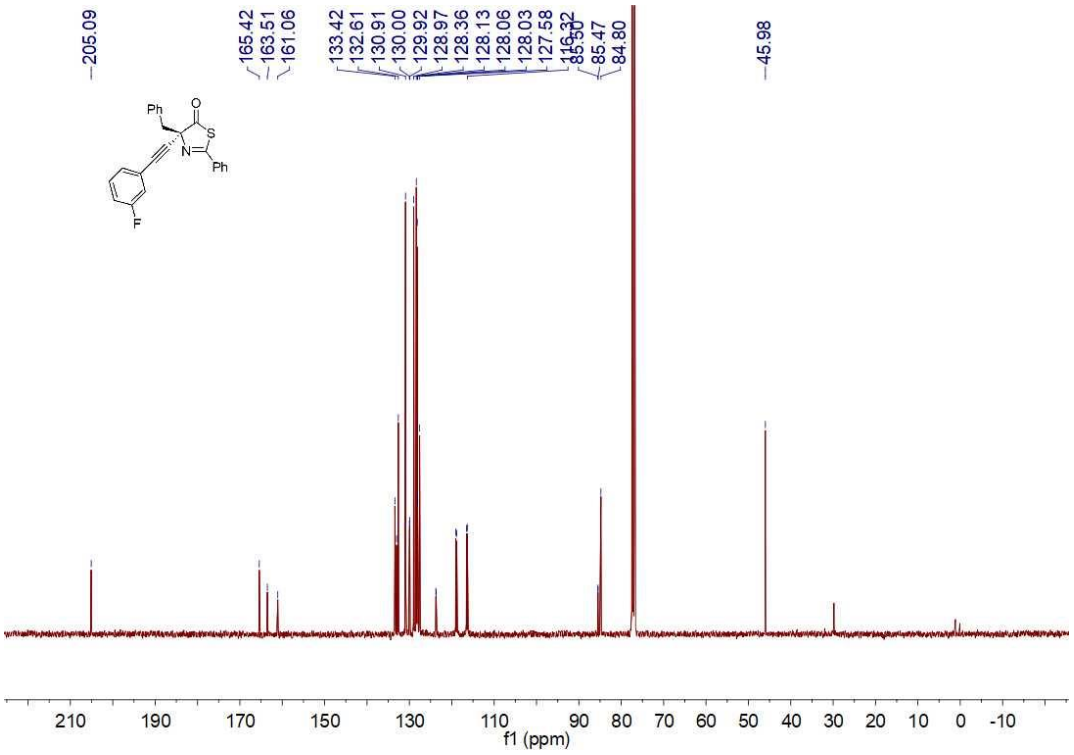

Ph
O
S
N
Ph
F

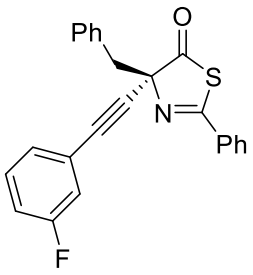
4ag


7.80
7.78
7.78
7.77
7.54
7.52
7.52
7.48
7.47
7.46
7.45
7.44
7.27
7.26
7.25
7.25
7.23
7.22
7.21
7.21
7.17
7.15
7.04
7.03
3.63
3.50
3.47

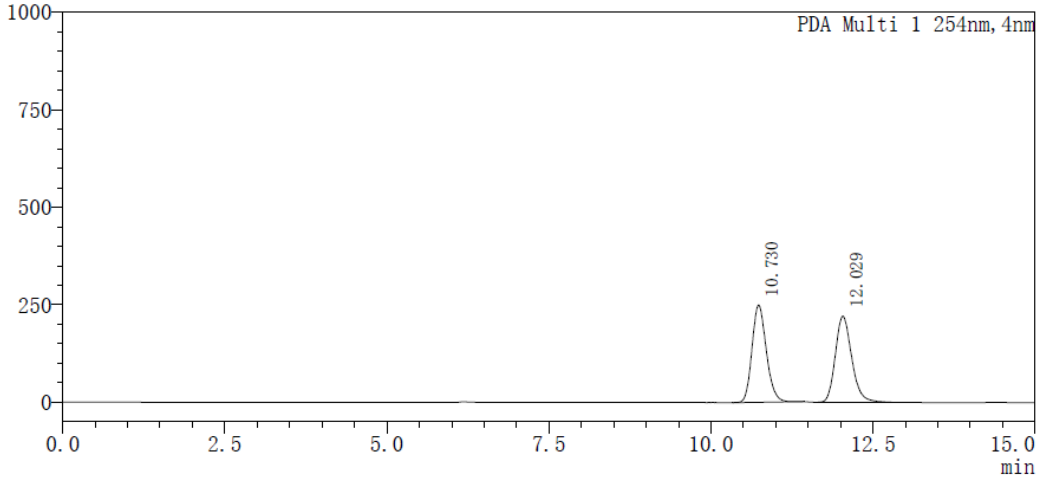

Ph
O
S
N
Ph
F


2.01
1.05
2.10
7.29
1.04
0.95
1.00
1.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


205.09
165.42
163.51
161.06
133.42
132.61
130.91
130.00
129.92
128.97
128.36
128.13
128.06
128.03
127.58
116.32
85.50
85.47
84.80
45.98
Ph
O
S
N
Ph
F
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



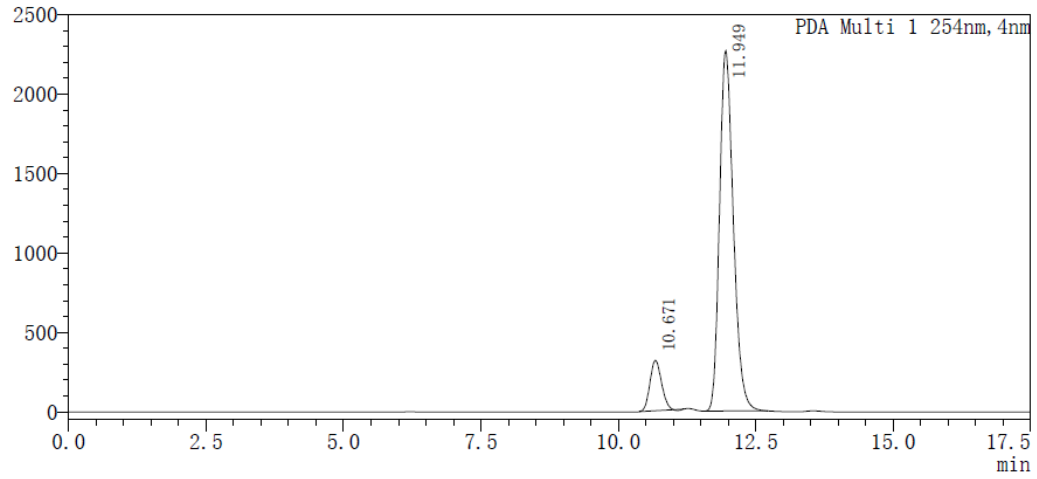
4ag



<Peak table>

PDA Ch1 254nm

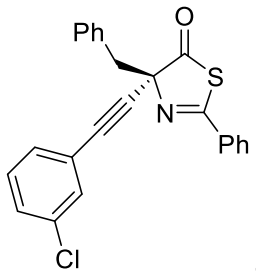
Peak#	Ret. Time	Height	Area	Area%
1	10.730	249045	3843810	49.624
2	12.029	221222	3902125	50.376
Total		470267	7745934	100.000



<Peak table>

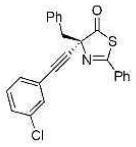
PDA Ch1 254nm

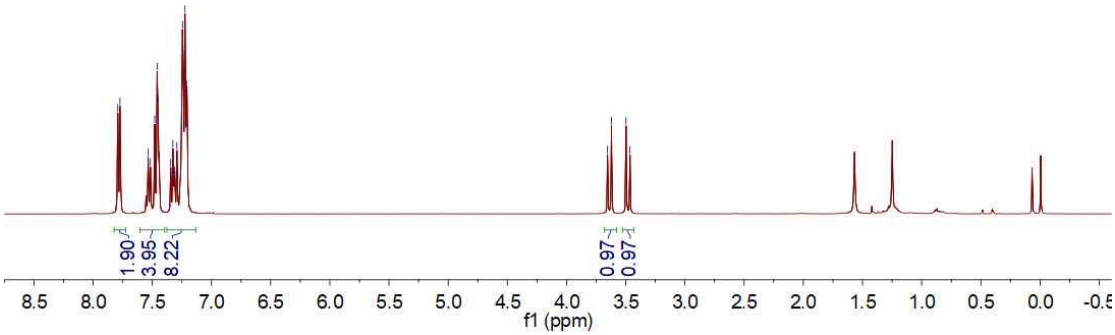
Peak#	Ret. Time	Height	Area	Area%
1	10.671	317377	4630061	10.416
2	11.949	2269576	39820404	89.584
Total		2586953	44450465	100.000

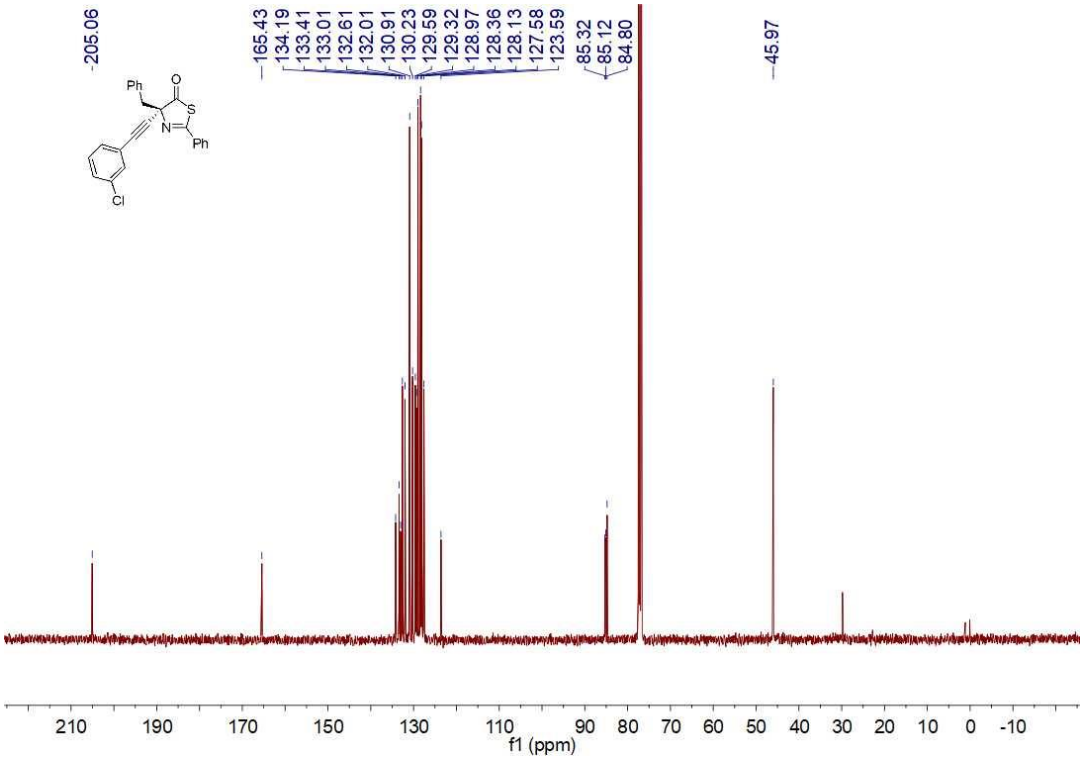

Ph
O
S
N
Ph
Cl

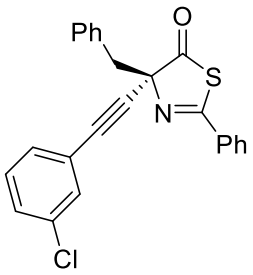
4ah


7.79
7.77
7.53
7.52
7.48
7.46
7.45
7.44
7.34
7.33
7.31
7.31
7.29
7.29
7.24
7.24
7.23
7.22
7.21
7.21
3.65
3.62
3.50
3.46

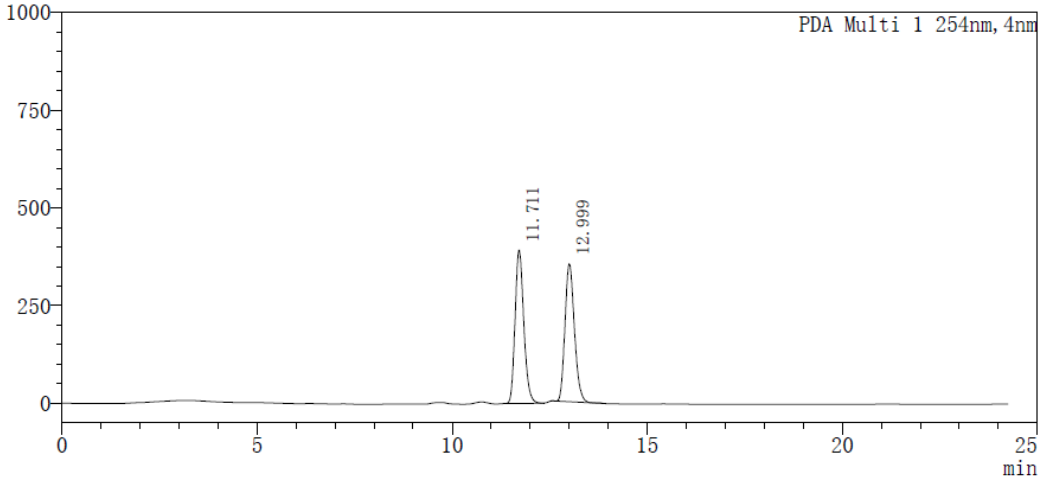



1.90
3.95
8.22
0.97
0.97
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


205.06
165.43
134.19
133.41
133.01
132.61
132.01
130.91
130.23
129.59
129.32
128.97
128.36
128.13
127.58
123.59
85.32
85.12
84.80
45.97
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



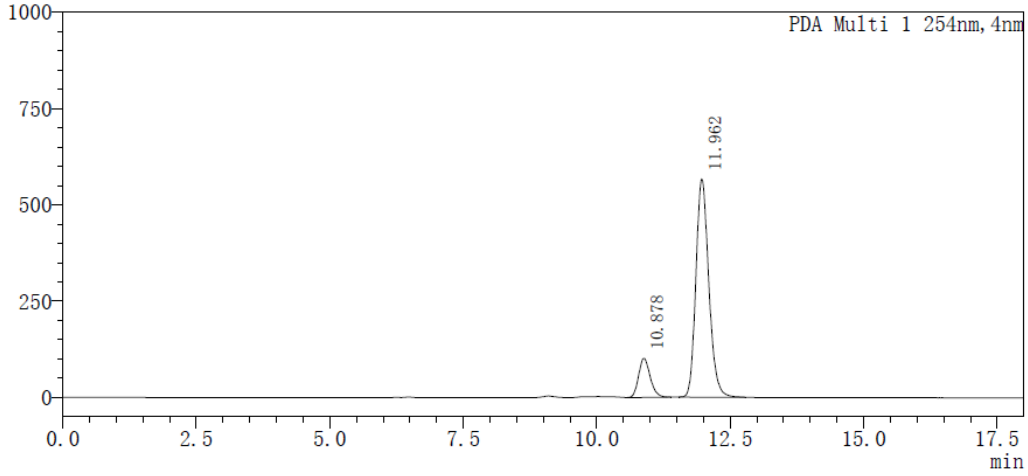
4ah



<Peak table>

PDA Ch1 254nm

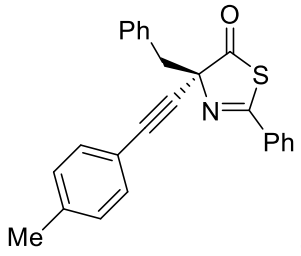
Peak#	Ret. Time	Height	Area	Area%
1	11.711	392046	6102226	50.546
2	12.999	352812	5970506	49.454
Total		744858	12072732	100.000



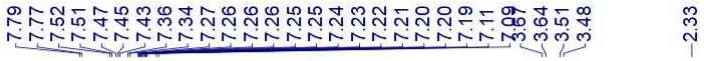
<Peak table>

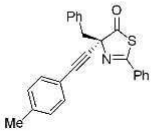
PDA Ch1 254nm

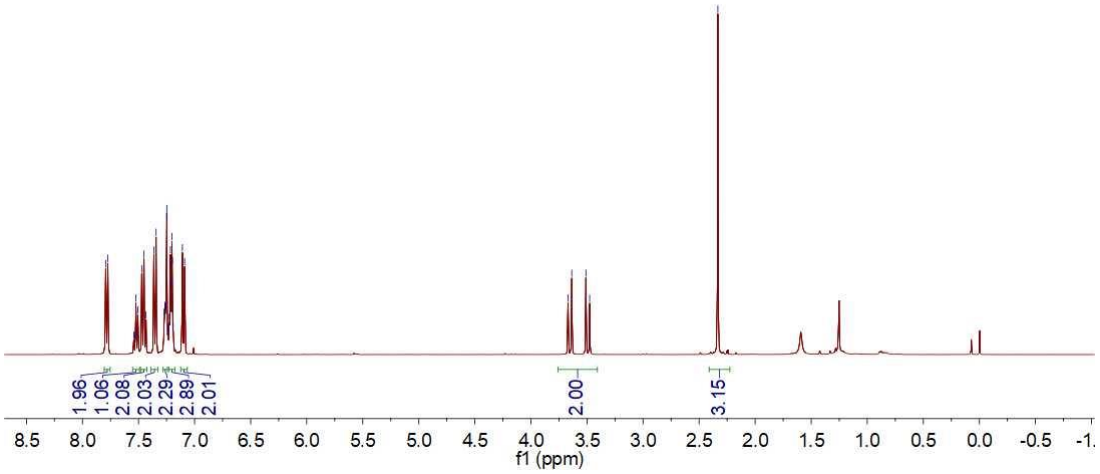
Peak#	Ret. Time	Height	Area	Area%
1	10.878	101462	1534171	13.862
2	11.962	565768	9533340	86.138
Total		667229	11067511	100.000

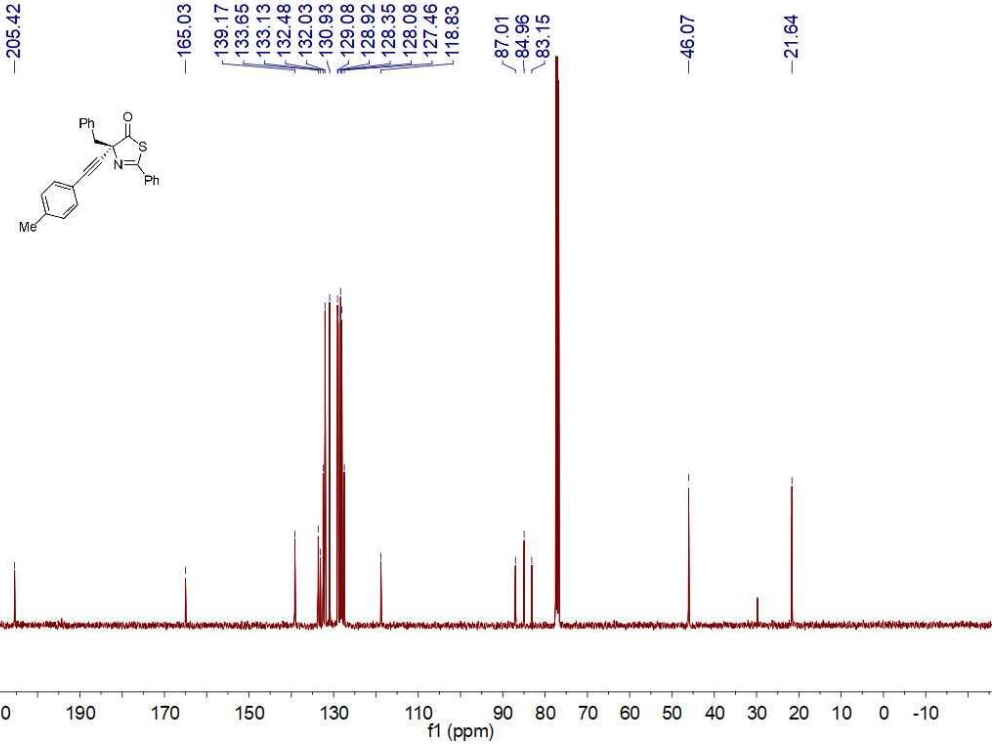

Ph
O
S
N
Ph
Me

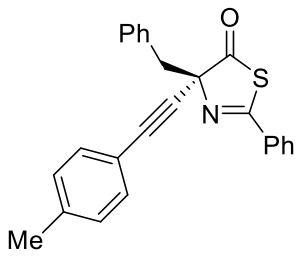
4ai


7.79
7.77
7.52
7.51
7.47
7.45
7.43
7.36
7.34
7.27
7.26
7.26
7.26
7.25
7.25
7.24
7.23
7.22
7.21
7.20
7.20
7.19
7.11
3.64
3.51
3.48
2.33

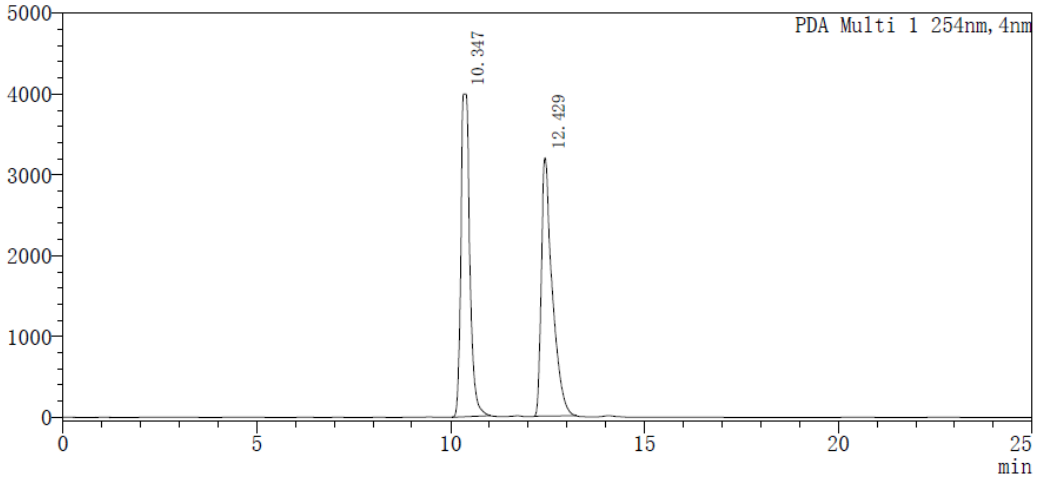

Ph
O
S
N
Ph
Me


1.96
1.06
2.08
2.03
2.29
2.89
2.01
2.00
3.15
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)


205.42
165.03
139.17
133.65
133.13
132.48
132.03
130.93
129.08
128.92
128.35
128.08
127.46
118.83
87.01
84.96
83.15
46.07
21.64
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



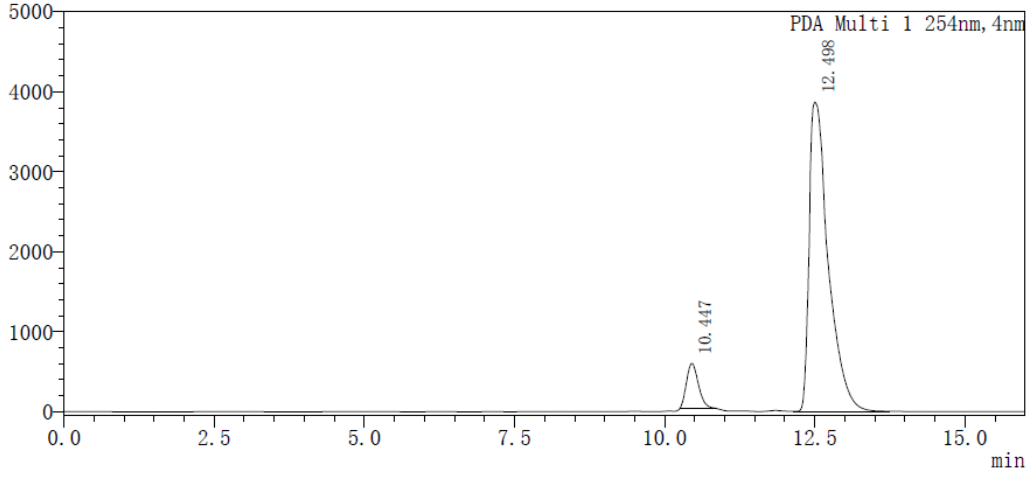
4ai



<Peak table>

PDA Ch1 254nm

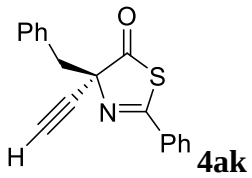
Peak#	Ret. Time	Height	Area	Area%
1	10.347	3990813	63741292	50.453
2	12.429	3193927	62597513	49.547
Total		7184740	126338804	100.000



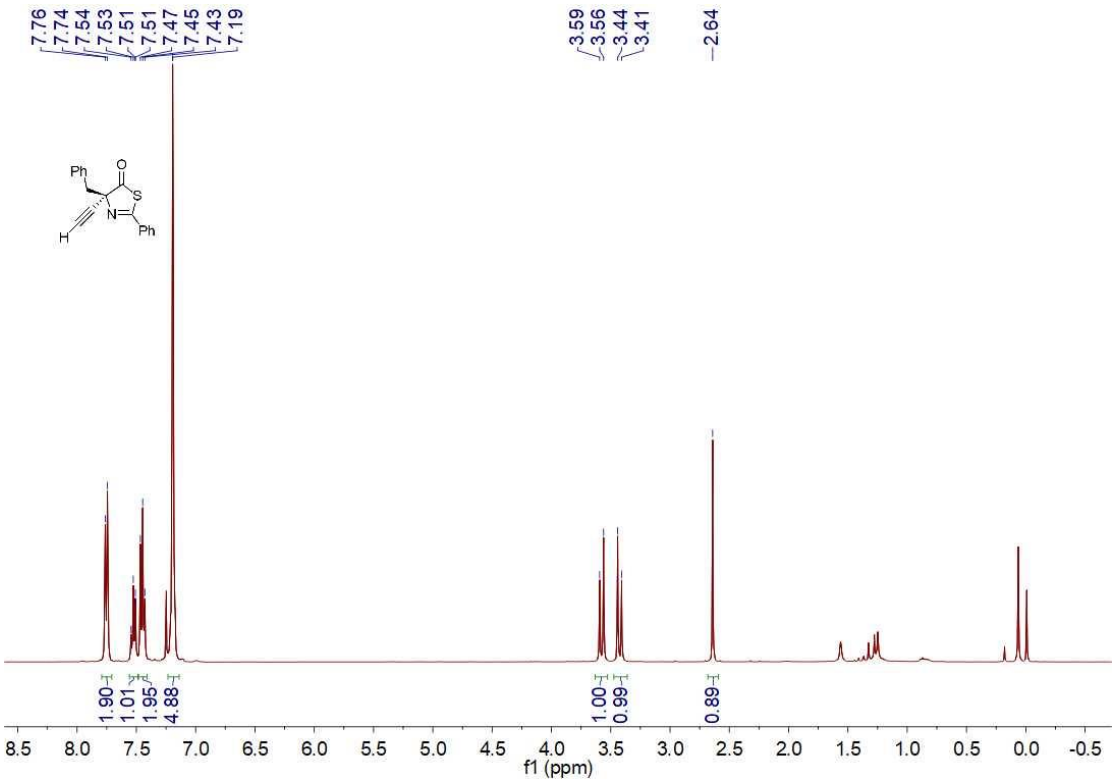
<Peak table>

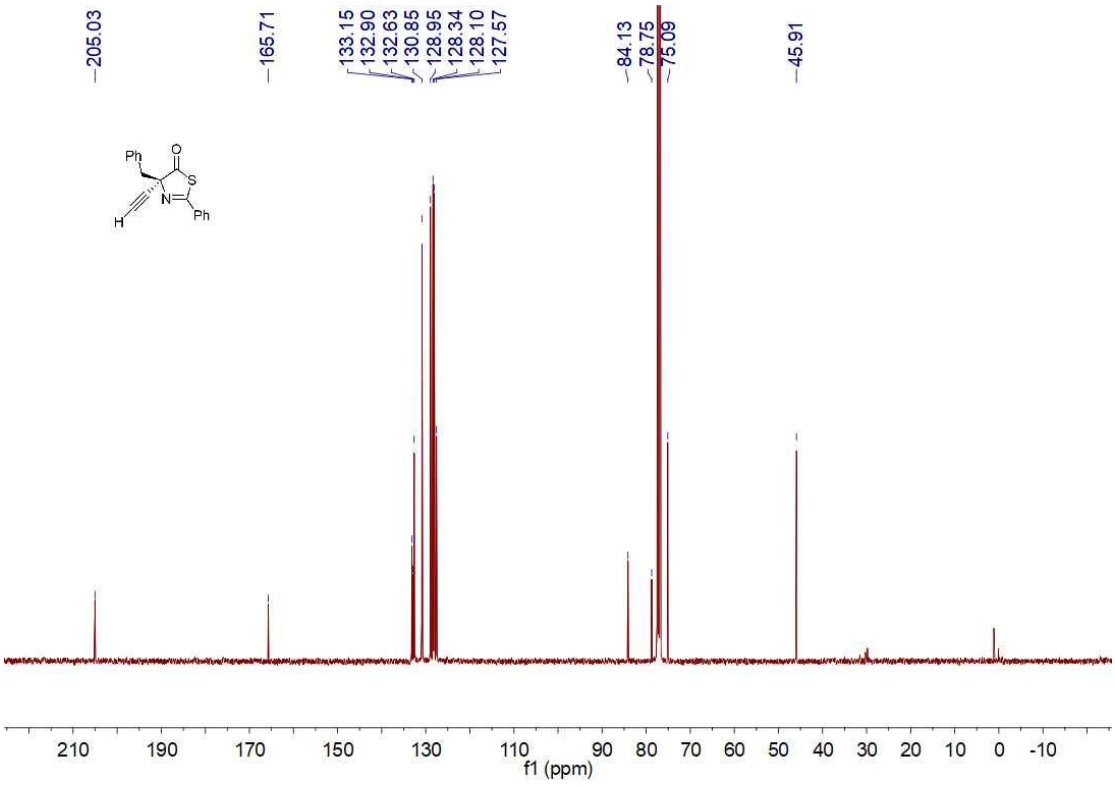
PDA Ch1 254nm

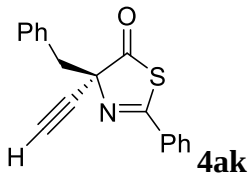
Peak#	Ret. Time	Height	Area	Area%
1	10.447	564735	7841266	8.382
2	12.498	3864440	85710931	91.618
Total		4429175	93552197	100.000


Ph
O
S
N
Ph
H

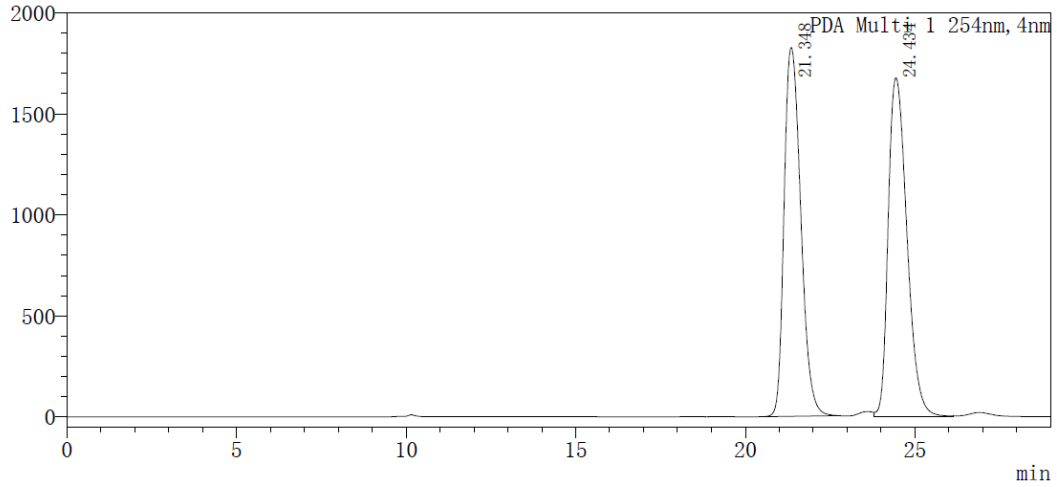
4ak


7.76
7.74
7.54
7.53
7.51
7.51
7.47
7.45
7.43
7.19
3.59
3.56
3.44
3.41
2.64
1.90
1.01
1.95
4.88
1.00
0.99
0.89
f1 (ppm)


205.03
165.71
133.15
132.90
132.63
130.85
128.95
128.34
128.10
127.57
84.13
78.75
75.09
45.91
f1 (ppm)



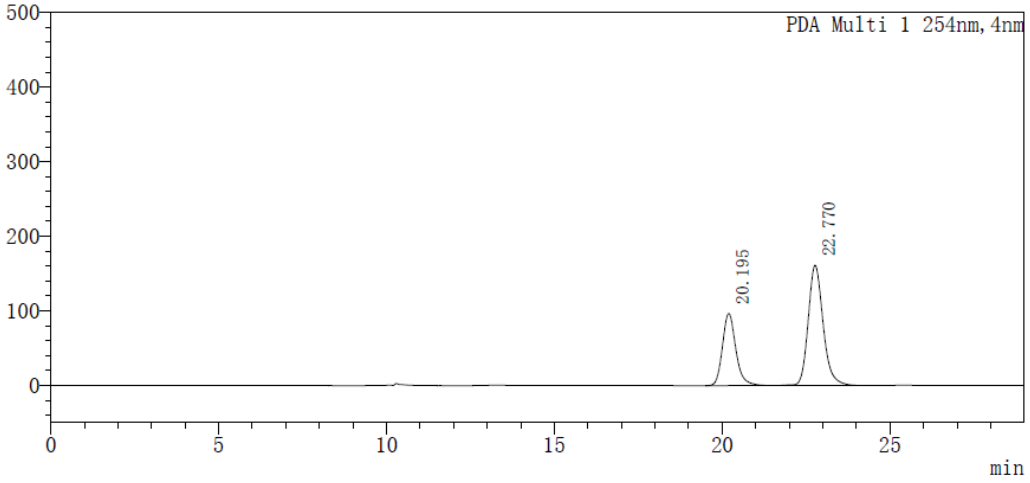
4ak



<Peak table>

PDA Ch1 254nm

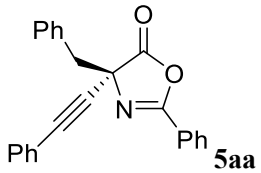
Peak#	Ret. Time	Height	Area	Area%
1	21.348	1826958	62549325	49.240
2	24.434	1678753	64480773	50.760
Total		3505711	127030097	100.000



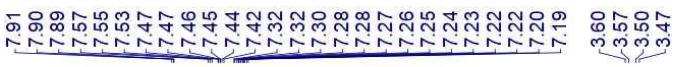
<Peak table>

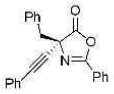
PDA Ch1 254nm

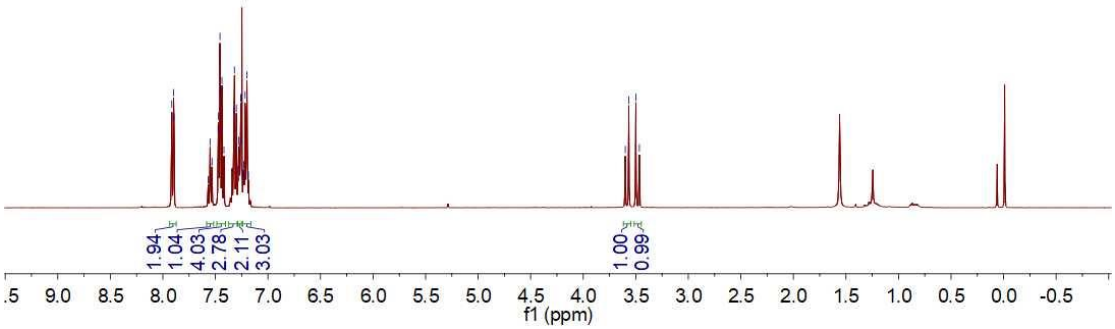
Peak#	Ret. Time	Height	Area	Area%
1	20.195	96699	2681626	34.920
2	22.770	161243	4997624	65.080
Total		257942	7679250	100.000

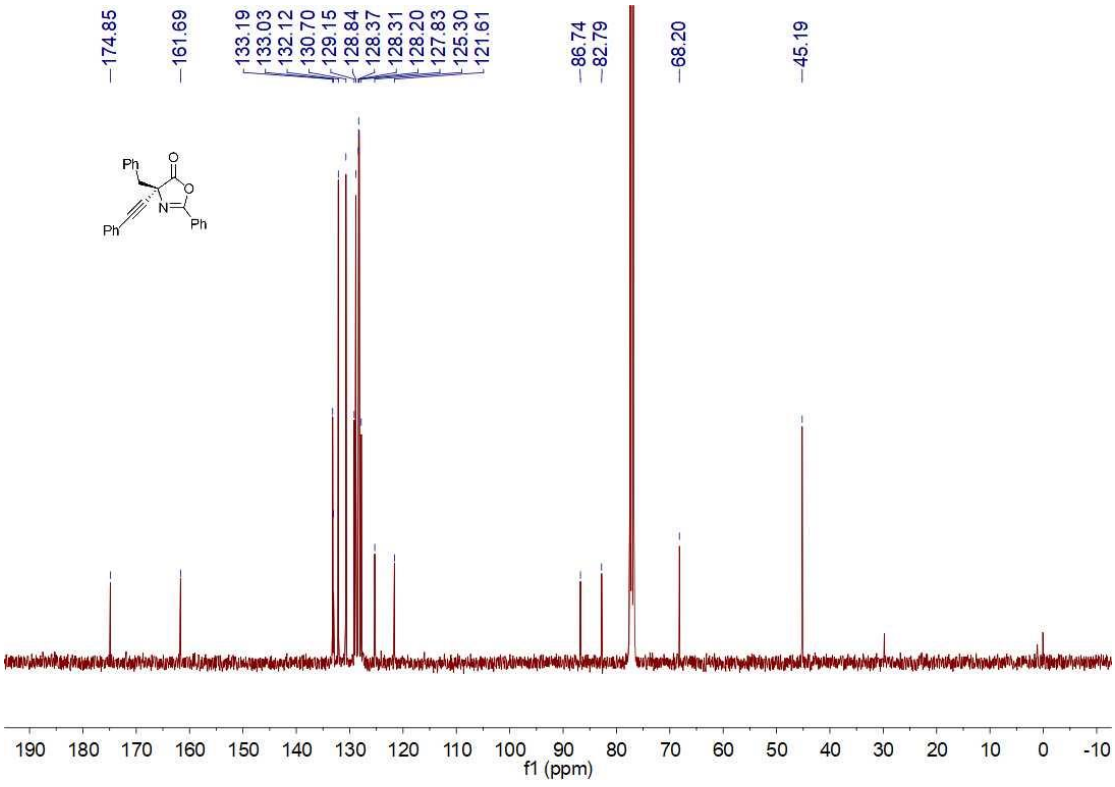

Ph
O
O
N
Ph
Ph

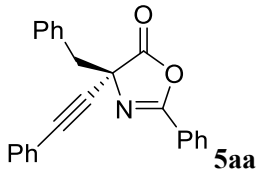
5aa


7.91
7.90
7.89
7.57
7.55
7.53
7.47
7.47
7.46
7.45
7.44
7.42
7.32
7.30
7.28
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.22
7.20
7.19
3.60
3.57
3.50
3.47

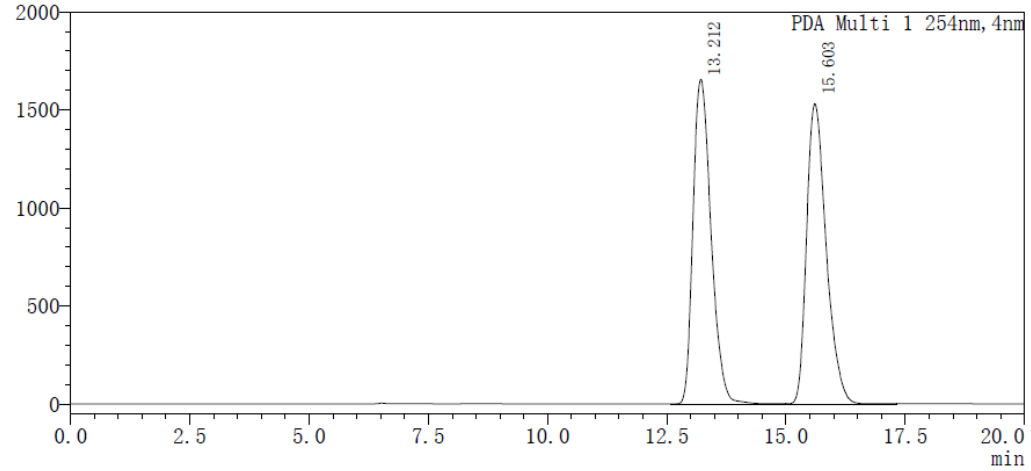



1.94
1.04
4.03
2.78
2.11
3.03
1.00
0.99
f1 (ppm)


174.85
161.69
133.19
133.03
132.12
130.70
129.15
128.84
128.37
128.31
128.20
127.83
125.30
121.61
86.74
82.79
68.20
45.19
f1 (ppm)



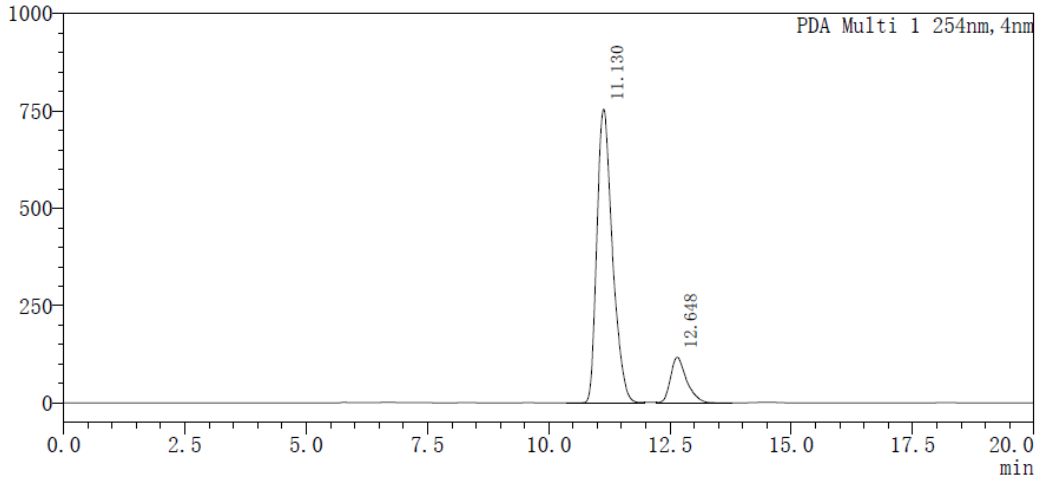
5aa



<Peak table>

PDA Ch1 254nm

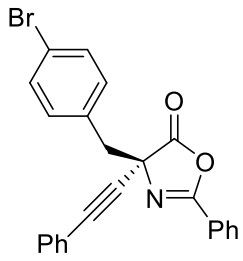
Peak#	Ret. Time	Height	Area	Area%
1	13.212	1656447	43691817	49.856
2	15.603	1532736	43944773	50.144
Total		3189183	87636590	100.000



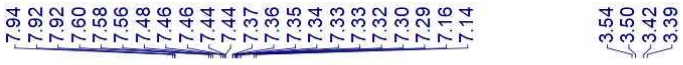
<Peak table>

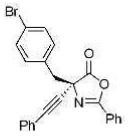
PDA Ch1 254nm

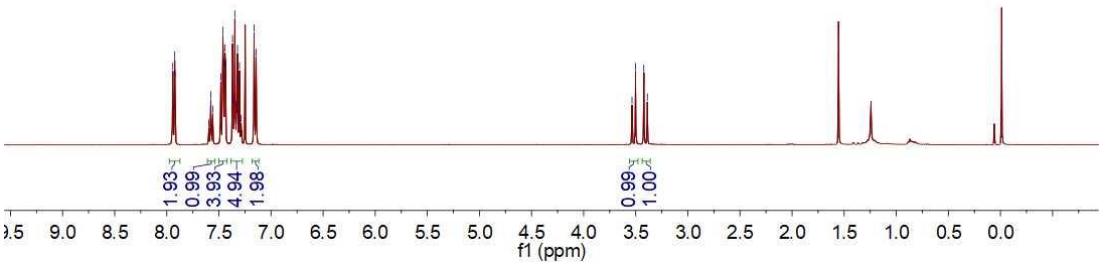
Peak#	Ret. Time	Height	Area	Area%
1	11.130	754435	16820558	86.154
2	12.648	117168	2703311	13.846
Total		871602	19523868	100.000

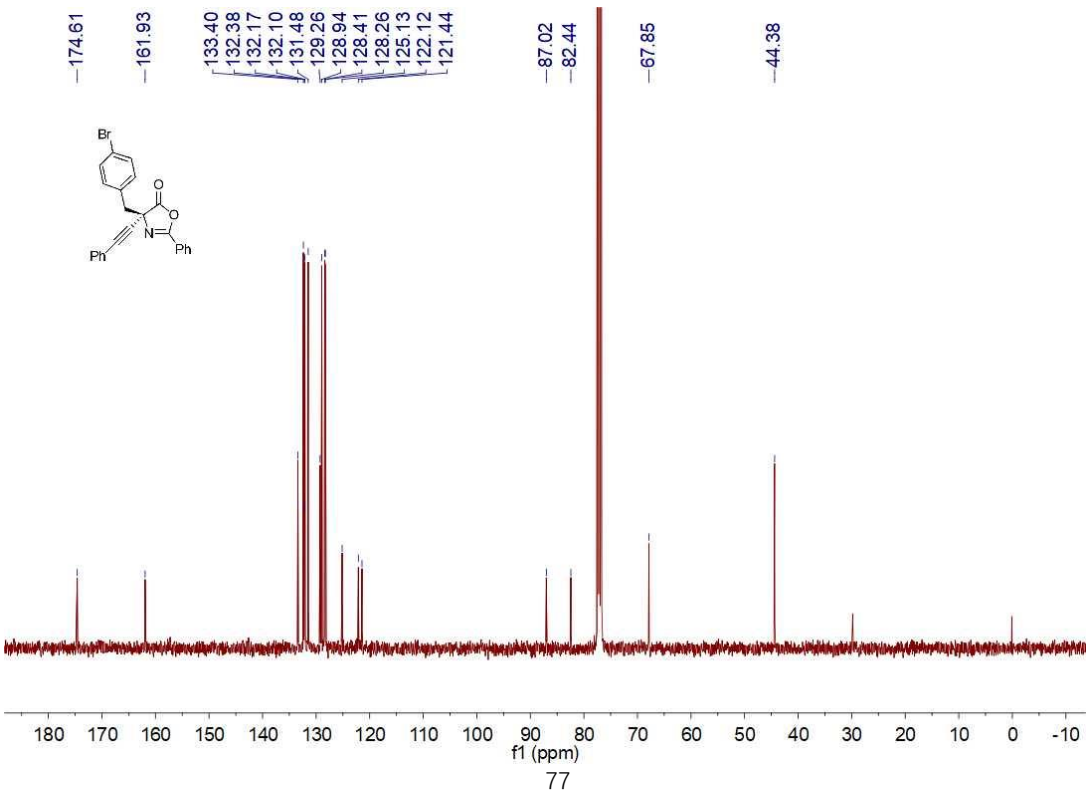

Br
O
O
N
Ph
Ph

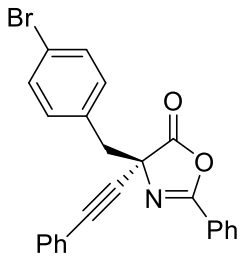
5ba


7.94
7.92
7.92
7.60
7.58
7.56
7.48
7.46
7.46
7.44
7.44
7.37
7.36
7.35
7.34
7.33
7.33
7.32
7.30
7.29
7.16
7.14
3.54
3.50
3.42
3.39

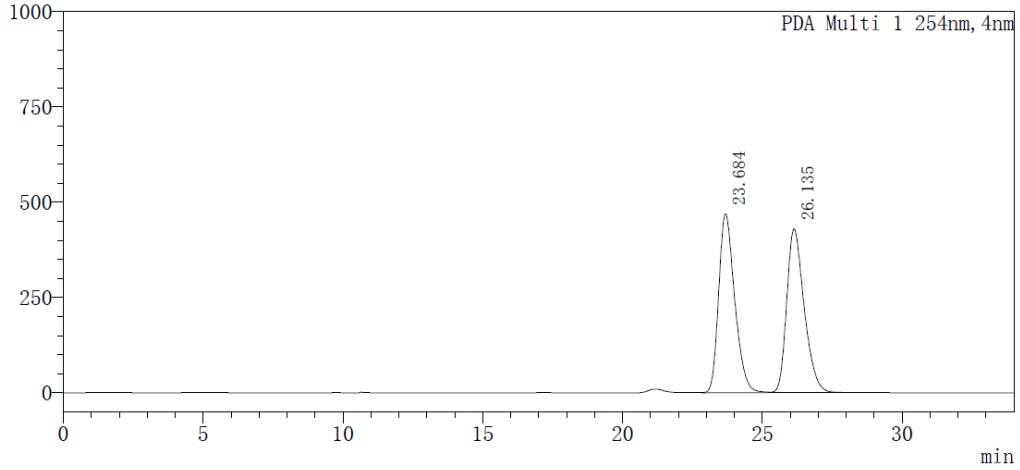



1.93
0.99
3.93
4.94
1.98
0.99
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


174.61
161.93
133.40
132.38
132.17
132.10
131.48
129.26
128.94
128.41
128.26
125.13
122.12
121.44
87.02
82.44
67.85
44.38
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



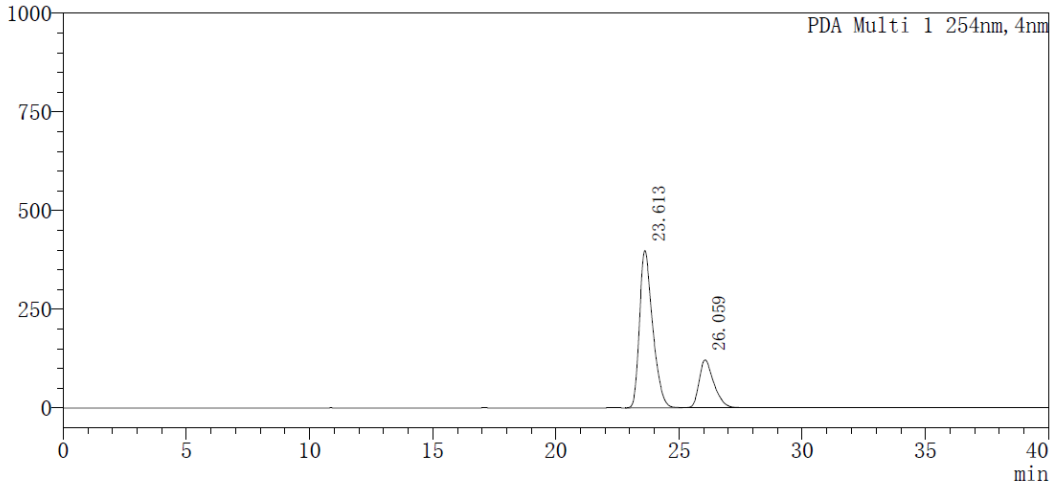
5ba



<Peak table>

PDA Ch1 254nm

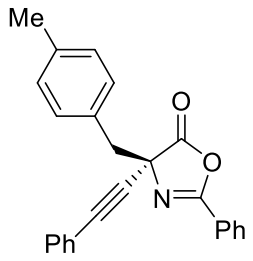
Peak#	Ret. Time	Height	Area	Area%
1	23.684	469365	18736941	50.098
2	26.135	429459	18663418	49.902
Total		898825	37400359	100.000



<Peak table>

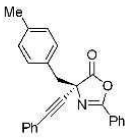
PDA Ch1 254nm

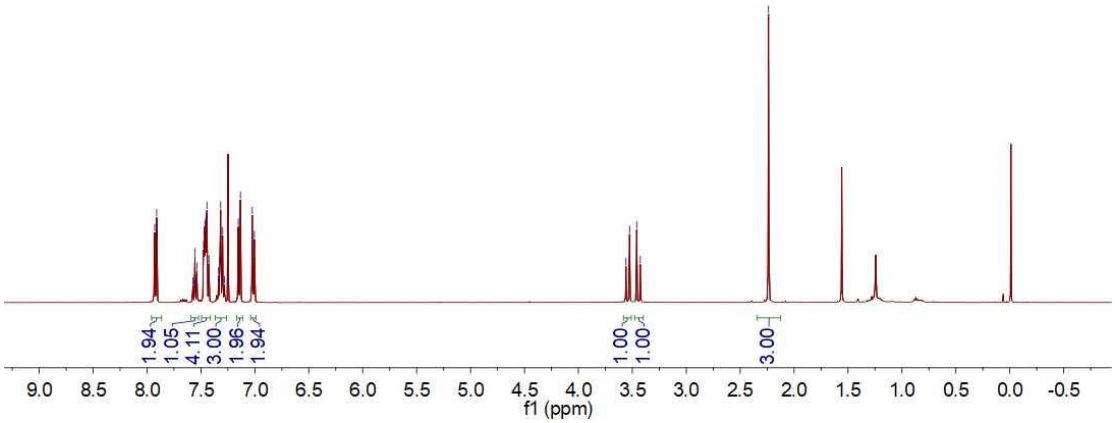
Peak#	Ret. Time	Height	Area	Area%
1	23.613	398383	14821830	74.664
2	26.059	121287	5029604	25.336
Total		519669	19851433	100.000

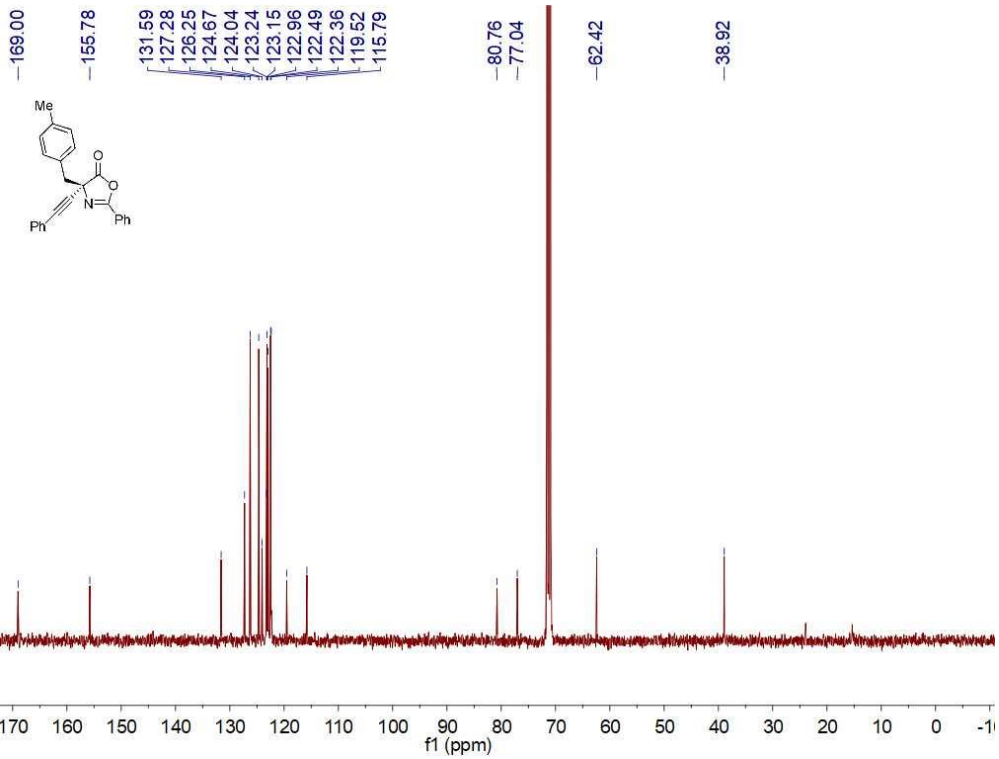

Me
O
O
N
Ph
Ph

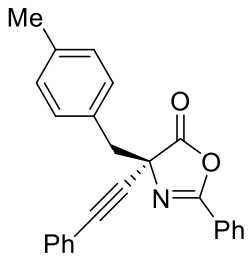
5ca


7.93
7.91
7.91
7.57
7.56
7.56
7.54
7.48
7.47
7.46
7.46
7.45
7.44
7.43
7.34
7.33
7.32
7.31
7.30
7.28
7.15
7.13
7.02
7.00
3.56
3.53
3.46
3.43
2.24

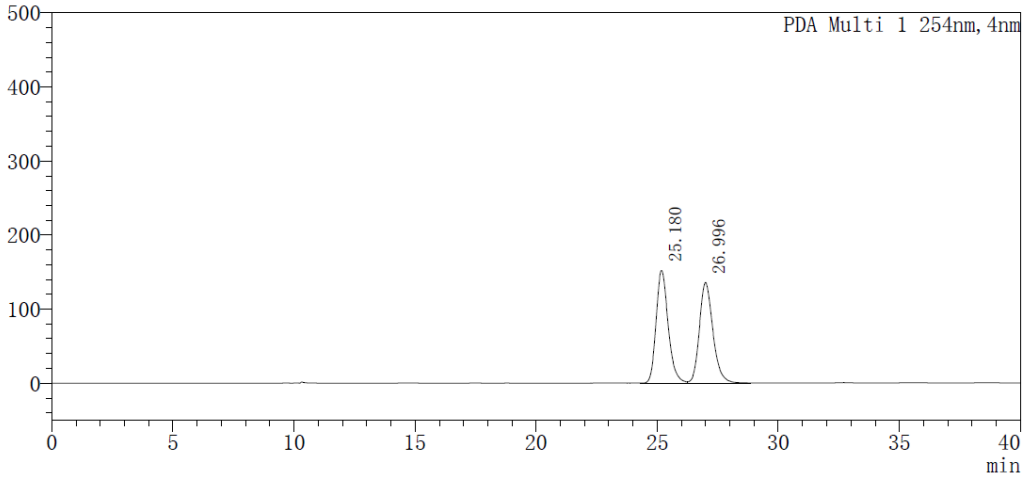

Me
O
O
N
Ph
Ph


1.94
1.05
4.11
3.00
1.96
1.94
1.00
1.00
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)


169.00
155.78
131.59
127.28
126.25
124.67
124.04
123.24
123.15
122.96
122.49
122.36
119.52
115.79
80.76
77.04
62.42
38.92
Me
O
O
N
Ph
Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



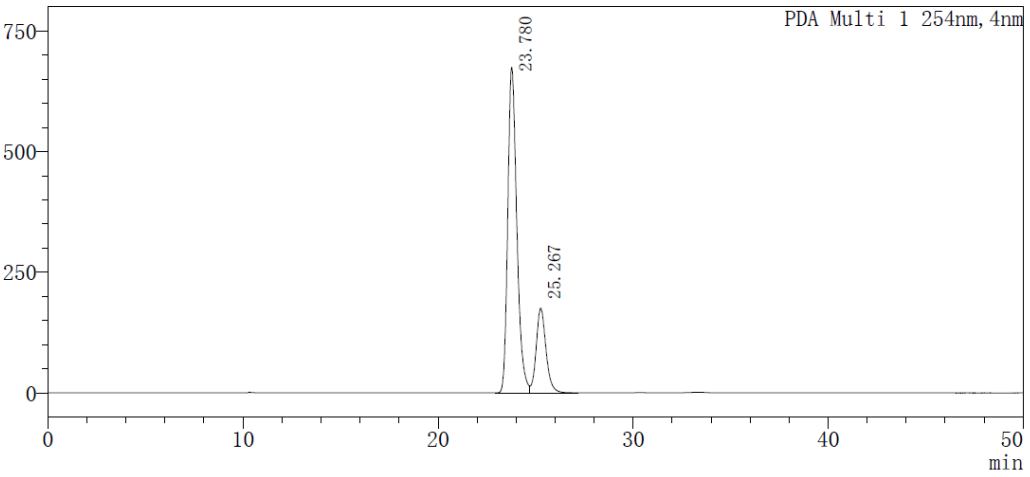
5ca



<Peak table>

PDA Ch1 254nm

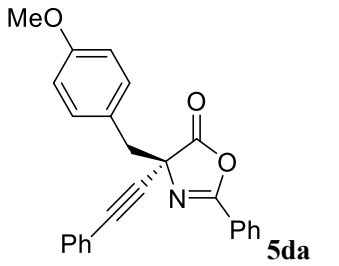
Peak#	Ret. Time	Height	Area	Area%
1	25.180	152232	5284214	50.075
2	26.996	135697	5268333	49.925
Total		287929	10552547	100.000



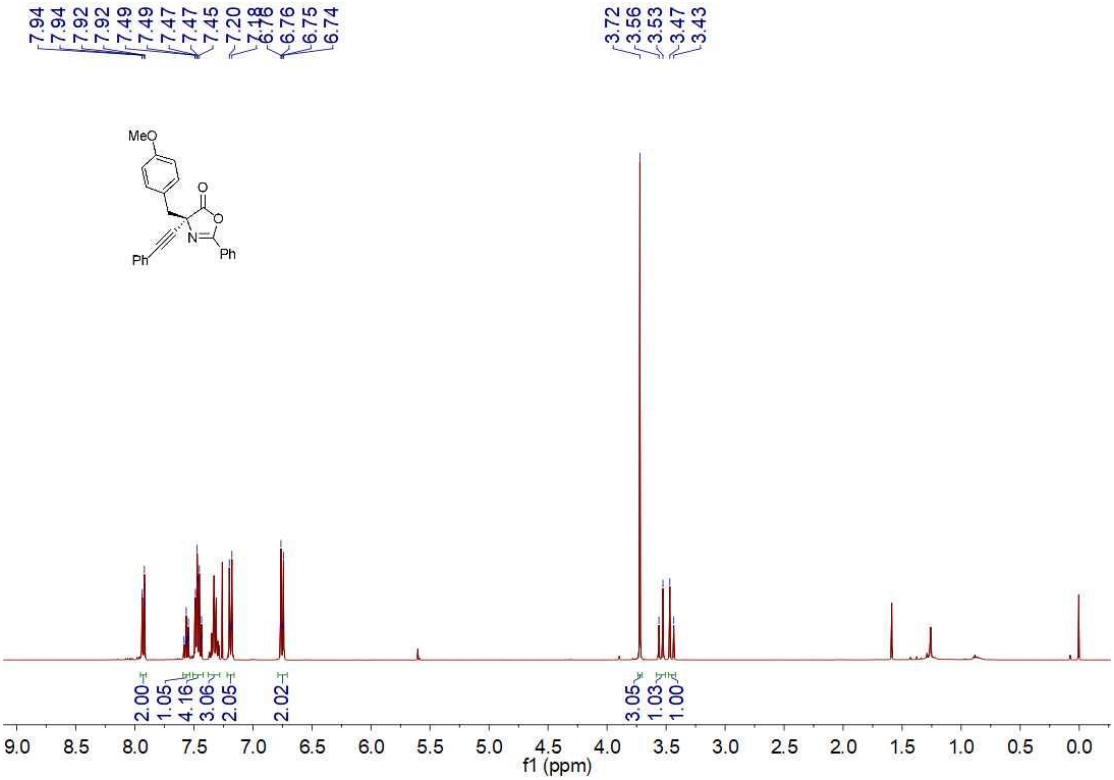
<Peak table>

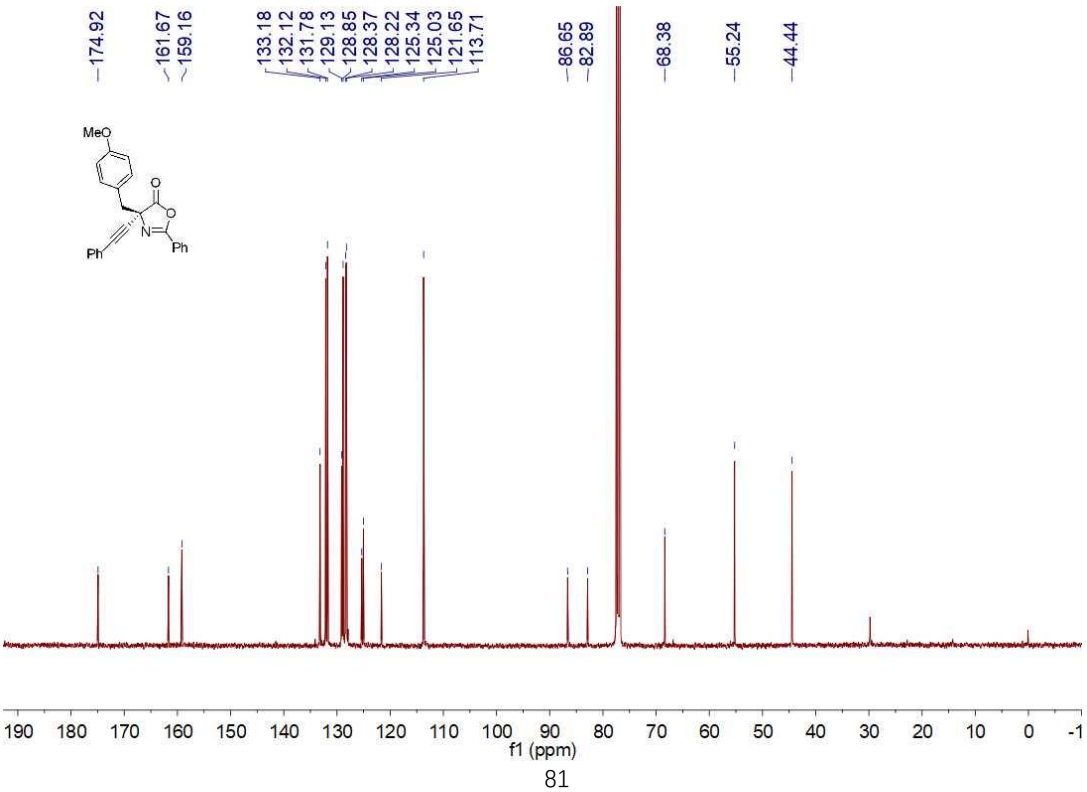
PDA Ch1 254nm

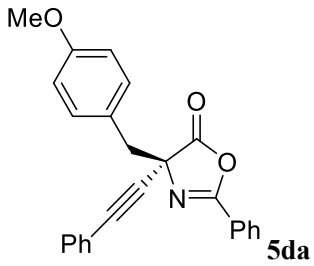
Peak#	Ret. Time	Height	Area	Area%
1	23.780	674450	21806539	78.051
2	25.267	175395	6132331	21.949
Total		849844	27938870	100.000


MeO
O
O
N
Ph
Ph

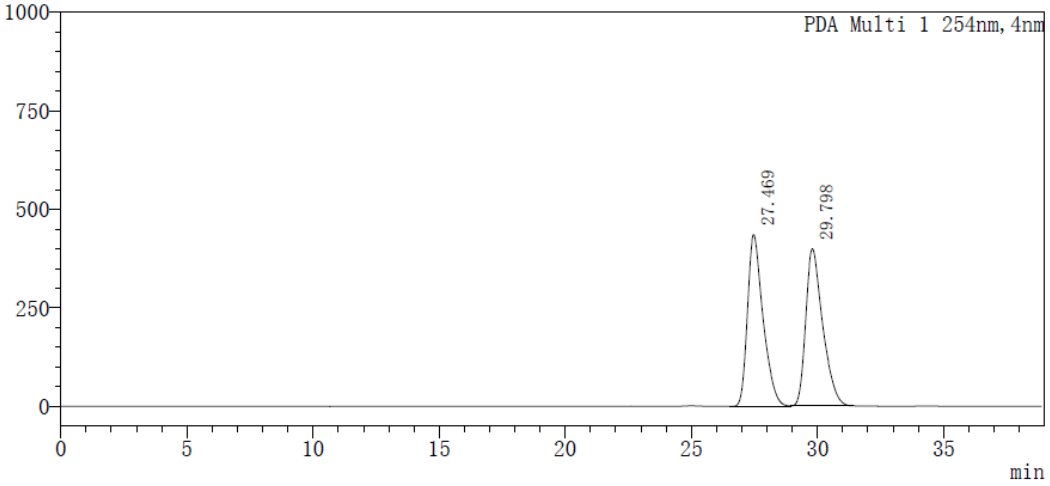
5da


7.94
7.94
7.92
7.92
7.49
7.49
7.47
7.47
7.45
7.20
7.18
6.76
6.75
6.74
3.72
3.56
3.53
3.47
3.43
MeO
Ph
Ph
2.00
1.05
4.16
3.06
2.05
2.02
3.05
1.03
1.00
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
f1 (ppm)


174.92
161.67
159.16
133.18
132.12
131.78
129.13
128.85
128.37
128.22
125.34
125.03
121.65
113.71
86.65
82.89
68.38
55.24
44.44
MeO
Ph
Ph
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)



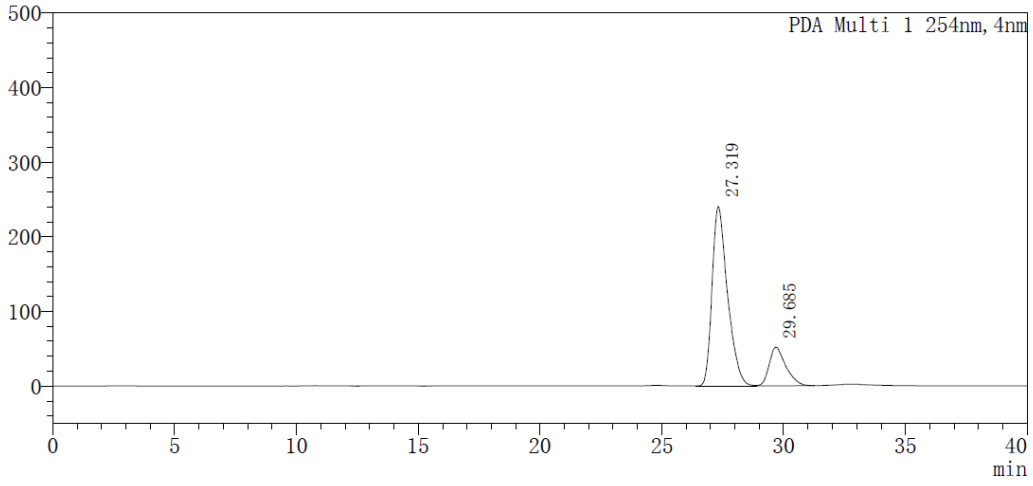
5da



<Peak table>

PDA Ch1 254nm

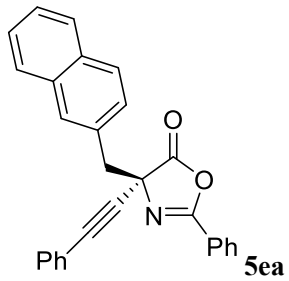
Peak#	Ret. Time	Height	Area	Area%
1	27.469	436101	18791482	50.190
2	29.798	398389	18649292	49.810
Total		834491	37440774	100.000



<Peak table>

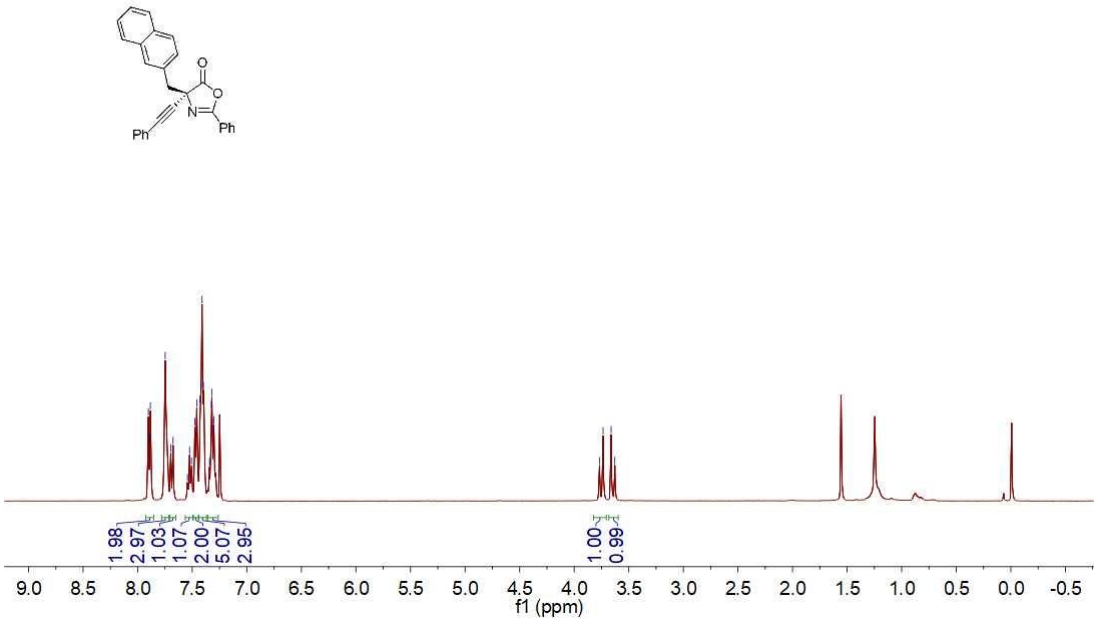
PDA Ch1 254nm

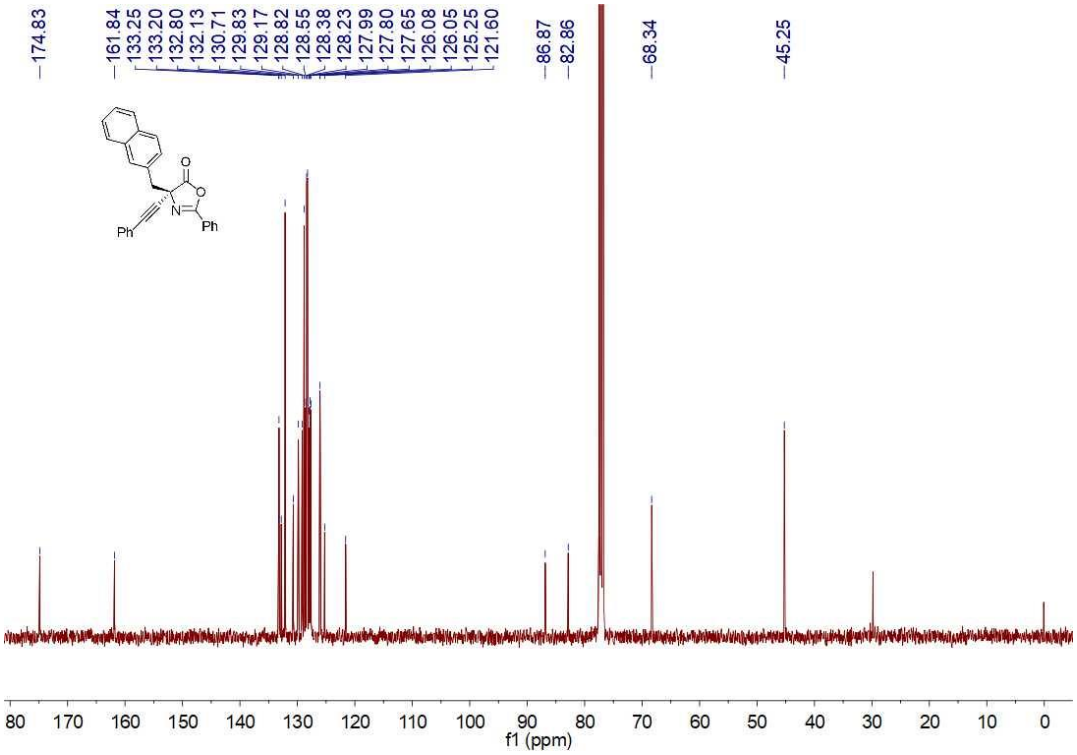
Peak#	Ret. Time	Height	Area	Area%
1	27.319	240371	10583808	81.270
2	29.685	51481	2439208	18.730
Total		291853	13023016	100.000

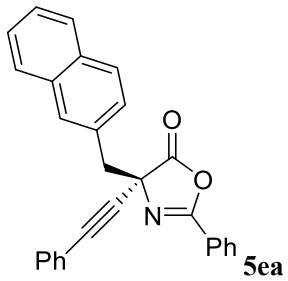

O
O
N
Ph
Ph

5ea

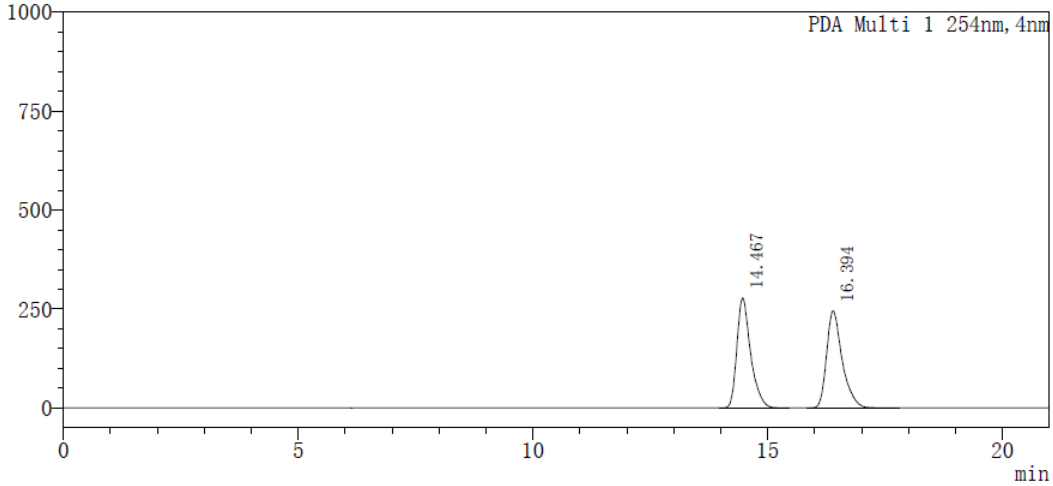

7.90
7.89
7.88
7.75
7.70
7.68
7.54
7.52
7.51
7.47
7.46
7.43
7.42
7.41
7.40
7.34
7.32
7.31
7.30
3.77
3.74
3.66
3.63


1.98
2.97
1.03
1.07
2.00
5.07
2.95
1.00
0.99
f1 (ppm)


174.83
161.84
133.25
133.20
132.80
132.13
130.71
129.83
129.17
128.82
128.55
128.38
128.23
127.99
127.80
127.65
126.08
126.05
125.25
121.60
86.87
82.86
68.34
45.25
f1 (ppm)



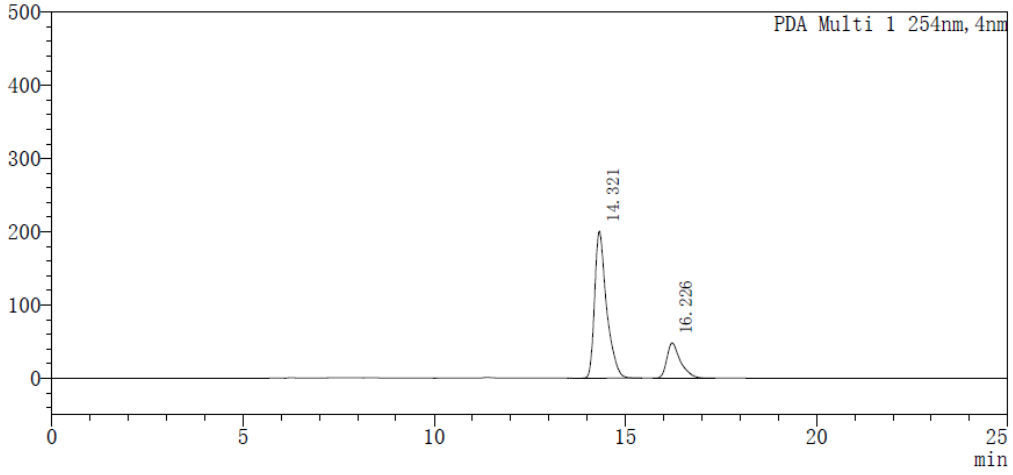
5ea



〈Peak table〉

PDA Ch1 254nm

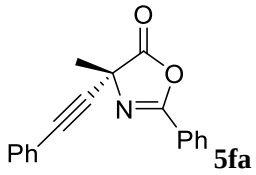
Peak#	Ret. Time	Height	Area	Area%
1	14.467	277933	5673058	49.999
2	16.394	245132	5673182	50.001
Total		523066	11346240	100.000



〈Peak table〉

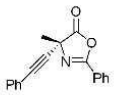
PDA Ch1 254nm

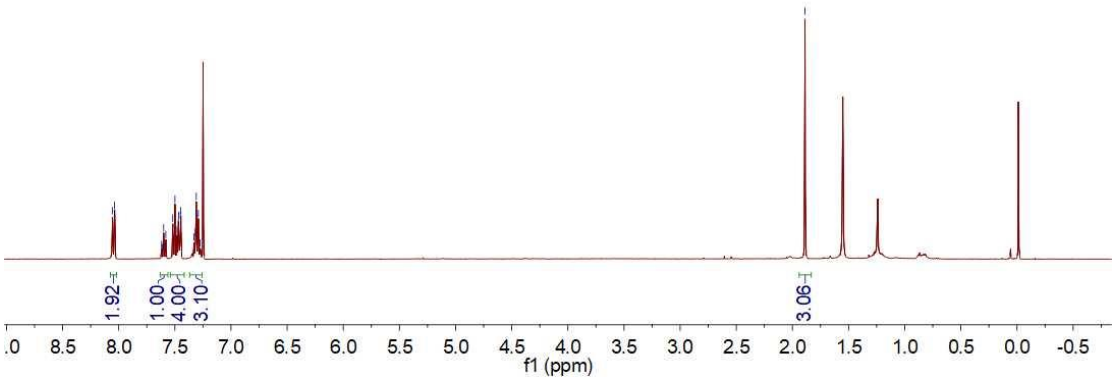
Peak#	Ret. Time	Height	Area	Area%
1	14.321	200625	4345834	78.633
2	16.226	48078	1180919	21.367
Total		248703	5526753	100.000

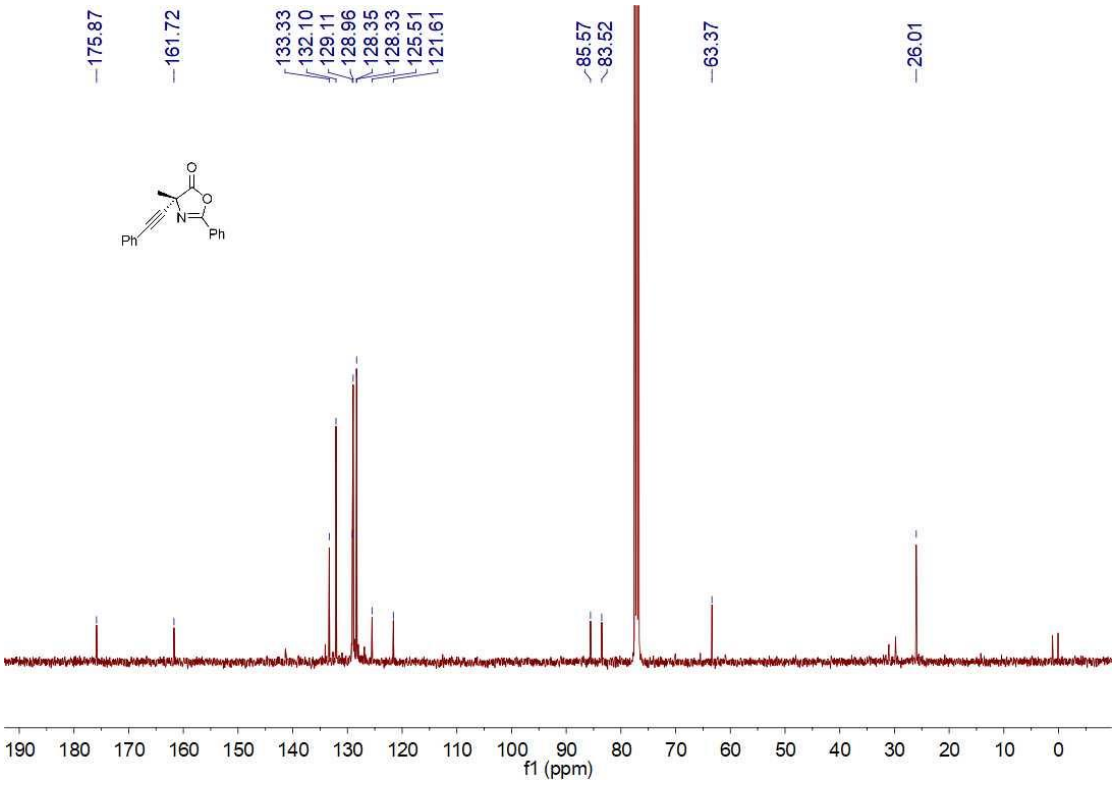

O
O
N
Ph
Ph

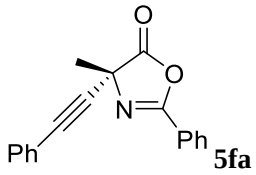
5fa


8.06
8.04
8.03
7.62
7.61
7.60
7.60
7.58
7.52
7.50
7.48
7.47
7.47
7.45
7.45
7.33
7.32
7.31
7.31
7.29
7.28
1.89

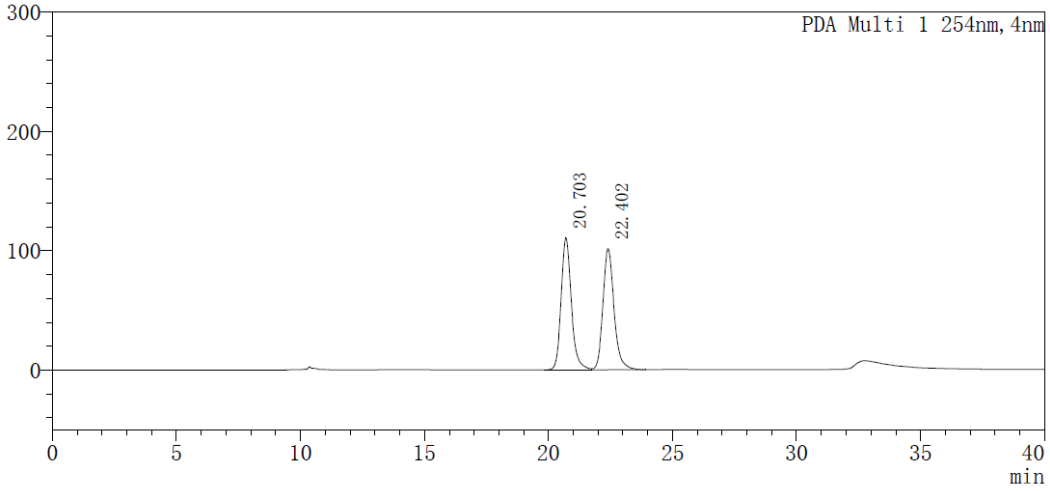



1.92
1.00
4.00
3.10
3.06
f1 (ppm)


175.87
161.72
133.33
132.10
129.11
128.96
128.35
128.33
125.51
121.61
85.57
83.52
63.37
26.01
f1 (ppm)



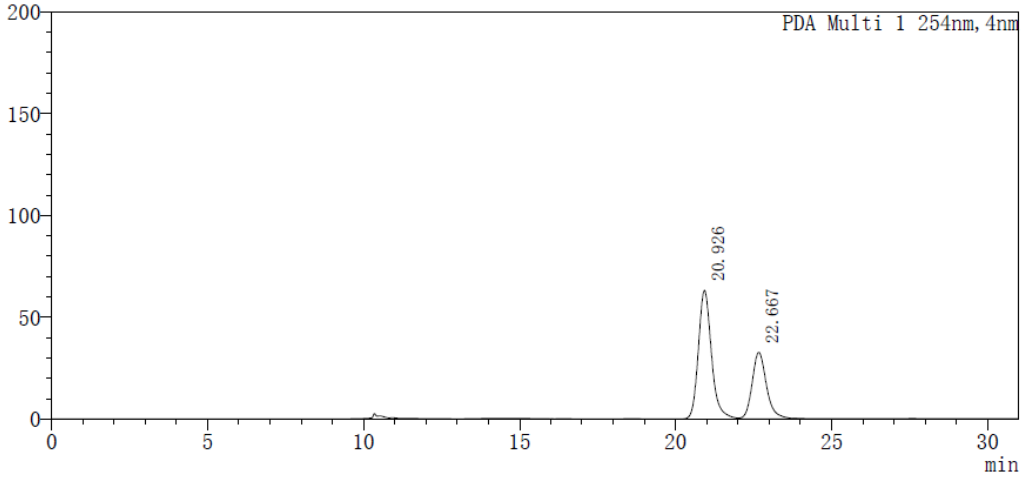
5fa



<Peak table>

PDA Ch1 254nm

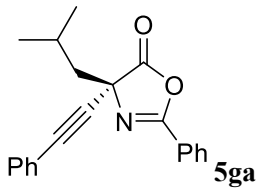
Peak#	Ret. Time	Height	Area	Area%
1	20.703	110672	3185423	50.227
2	22.402	101460	3156611	49.773
Total		212132	6342033	100.000



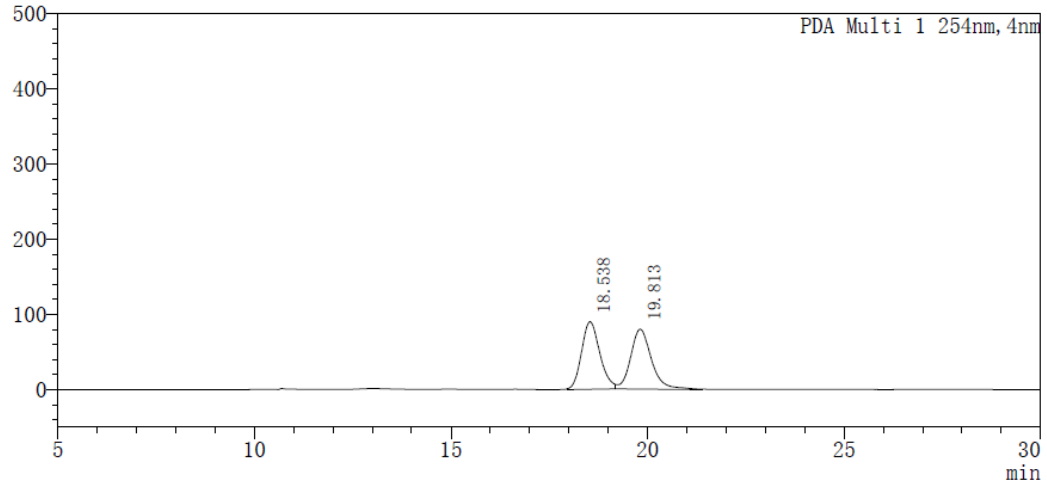
<Peak table>

PDA Ch1 254nm

Peak#	Ret. Time	Height	Area	Area%
1	20.926	63147	1846162	63.863
2	22.667	32635	1044655	36.137
Total		95782	2890817	100.000



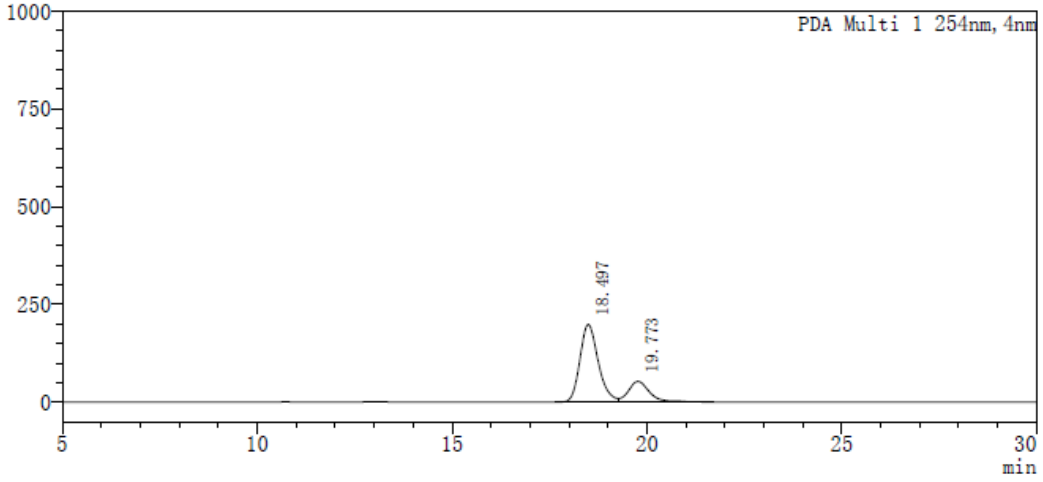
5ga



〈Peak table〉

PDA Ch1 254nm

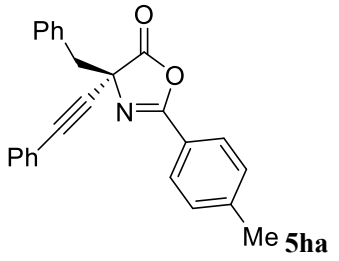
Peak#	Ret. Time	Height	Area	Area%
1	18.538	89872	2905571	49.615
2	19.813	79756	2950628	50.385
Total		169628	5856199	100.000



〈Peak table〉

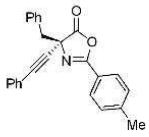
PDA Ch1 254nm

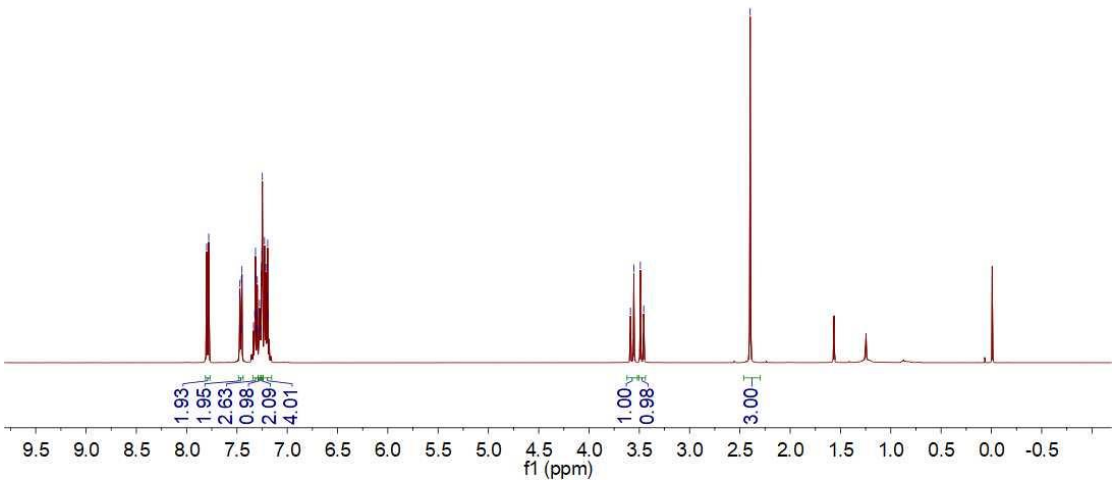
Peak#	Ret. Time	Height	Area	Area%
1	18.497	198607	6507368	76.271
2	19.773	53031	2024583	23.729
Total		251638	8531952	100.000

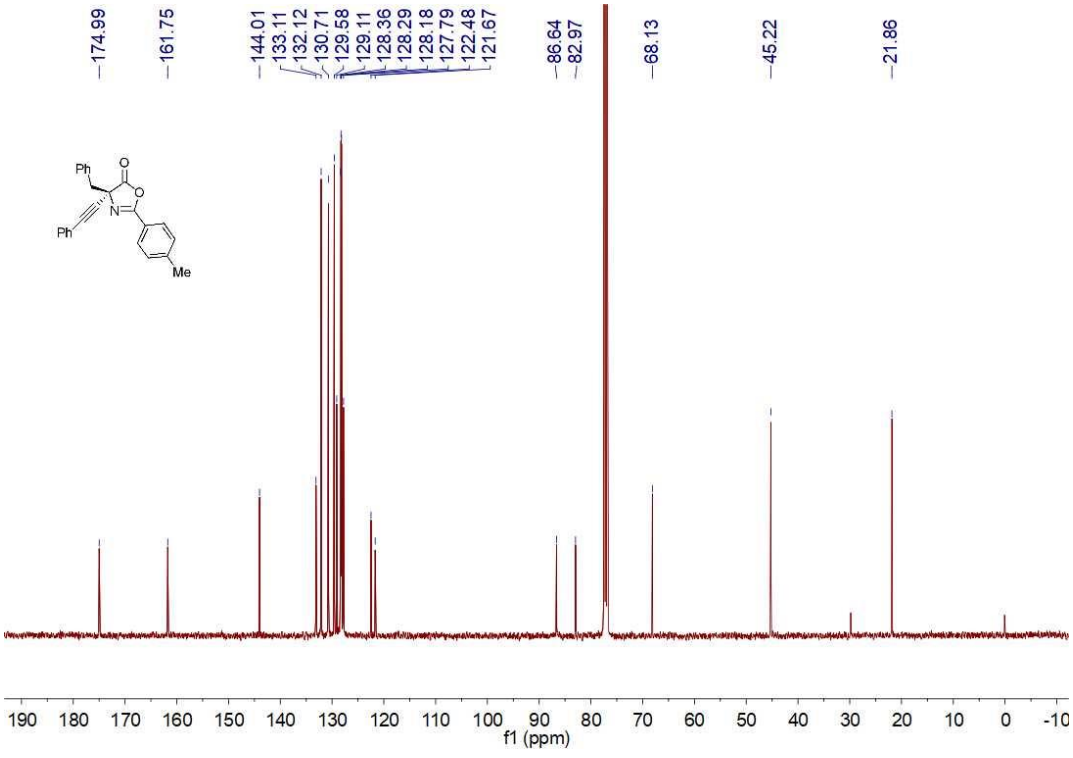

Ph
O
O
N
Ph
Me

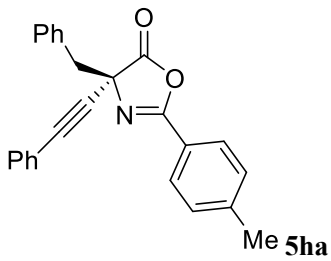
5ha


7.80
7.78
7.47
7.47
7.46
7.45
7.45
7.33
7.32
7.32
7.30
7.30
7.30
7.28
7.28
7.27
7.26
7.25
7.25
7.23
7.21
7.20
7.19
7.19
3.59
3.55
3.49
3.46
2.40

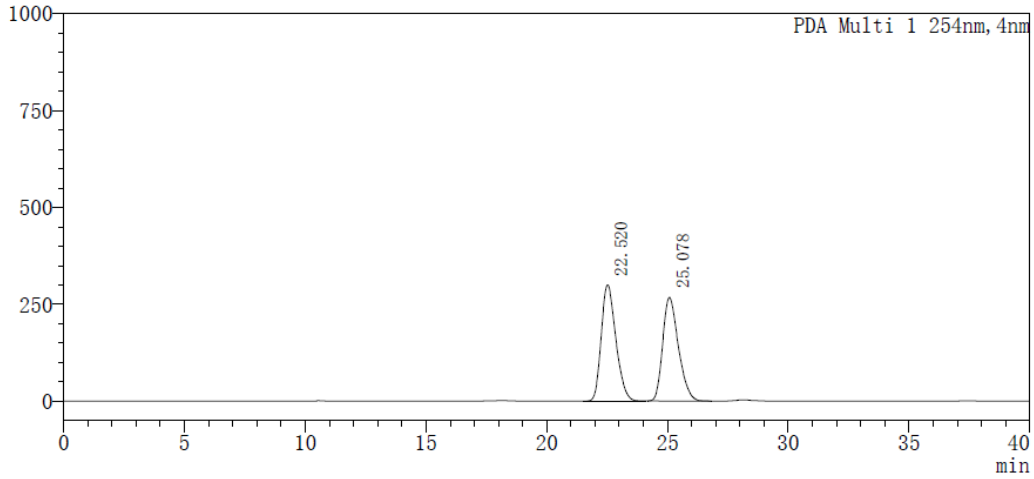

Ph
O
O
N
Ph
Me


1.93
1.95
2.63
0.98
2.09
4.01
1.00
0.98
3.00
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)


174.99
161.75
144.01
133.11
132.12
130.71
129.58
129.11
128.36
128.29
128.18
127.79
122.48
121.67
86.64
82.97
68.13
45.22
21.86
Ph
O
O
N
Ph
Me
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



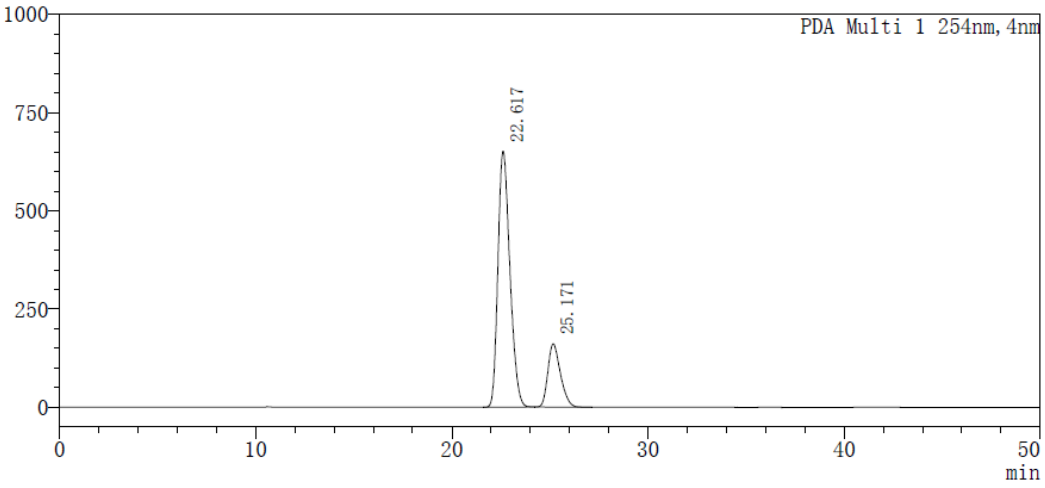
5ha



<Peak table>

PDA Ch1 254nm

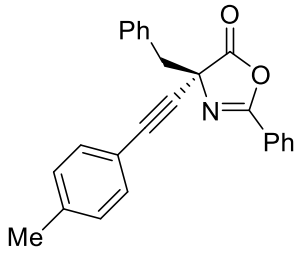
Peak#	Ret. Time	Height	Area	Area%
1	22.520	299991	12671237	51.163
2	25.078	267687	12095348	48.837
Total		567678	24766585	100.000



<Peak table>

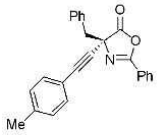
PDA Ch1 254nm

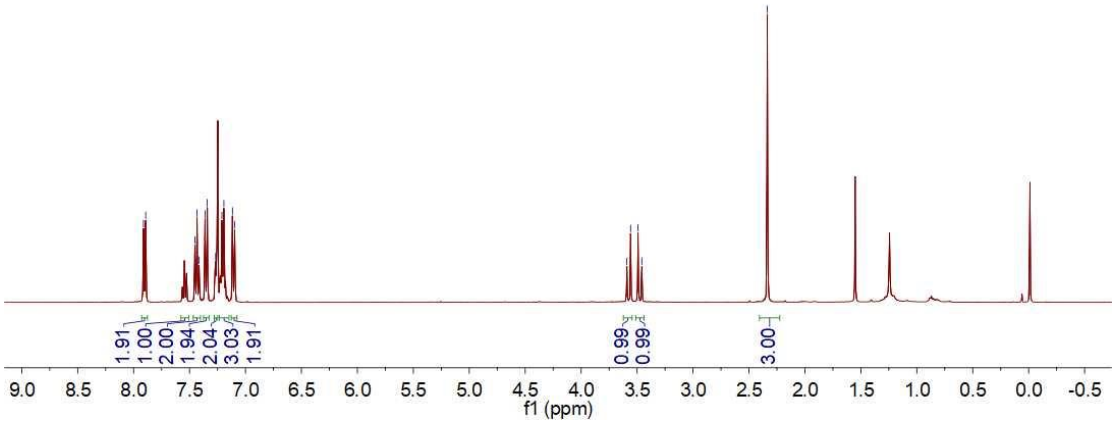
Peak#	Ret. Time	Height	Area	Area%
1	22.617	651847	27642840	79.317
2	25.171	160983	7208187	20.683
Total		812830	34851027	100.000

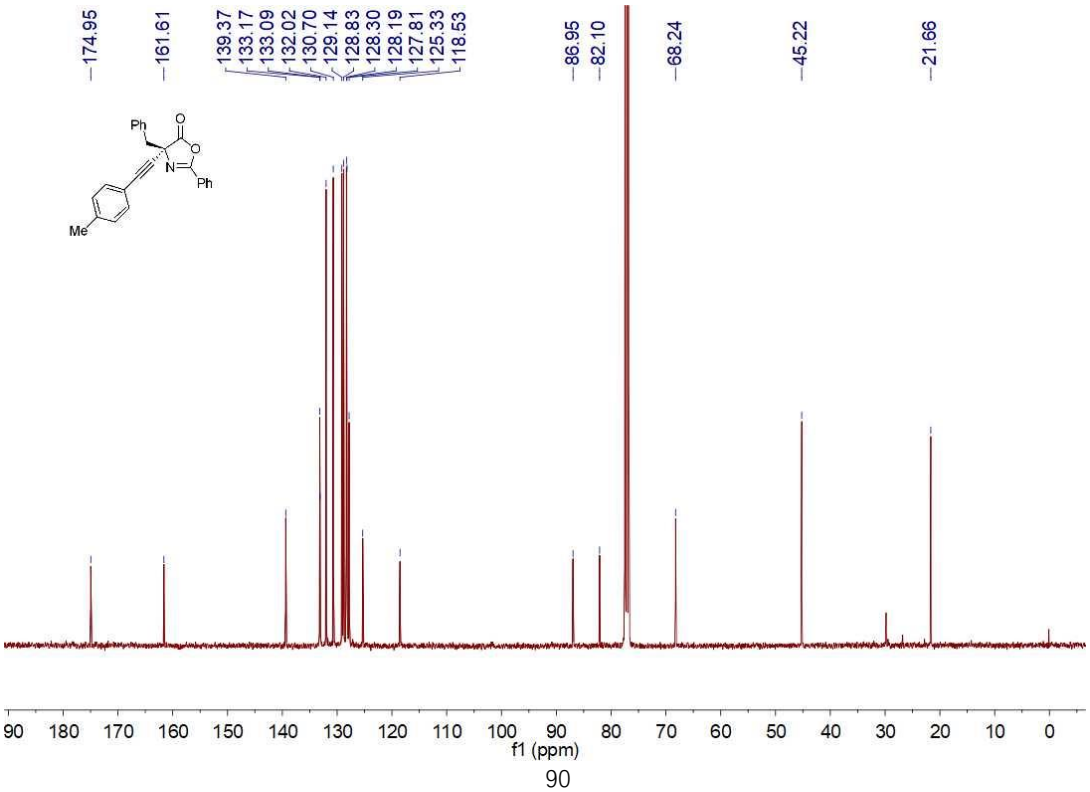

Ph
O
O
N
Ph
Me

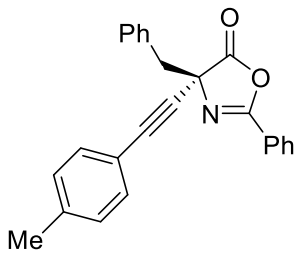
5ab


7.91
7.89
7.45
7.43
7.41
7.36
7.34
7.27
7.21
7.19
7.12
7.10
3.59
3.56
3.49
3.46
2.34

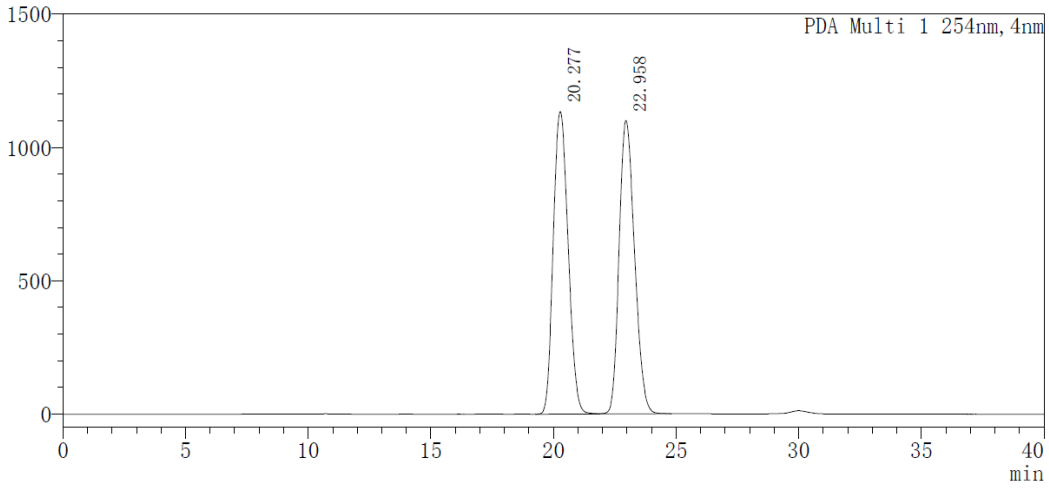



1.91
1.00
2.00
1.94
2.04
3.03
1.91
0.99
0.99
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


174.95
161.61
139.37
133.17
133.09
132.02
130.70
129.14
128.83
128.30
128.19
127.81
125.33
118.53
86.95
82.10
68.24
45.22
21.66
90 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



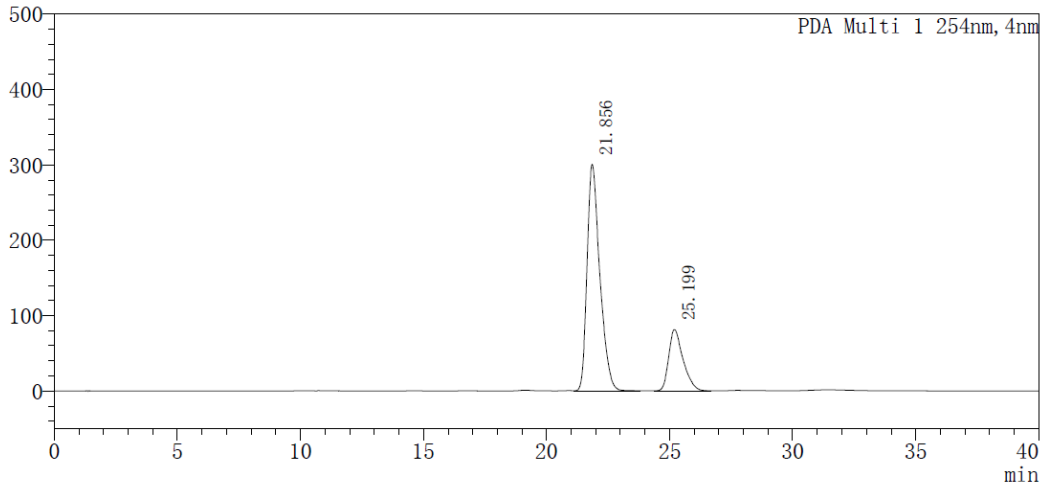
5ab



<Peak table>

PDA Ch1 254nm

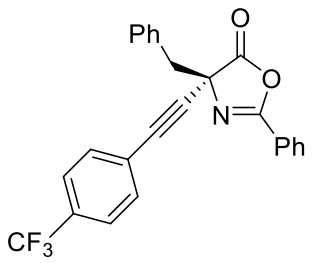
Peak#	Ret. Time	Height	Area	Area%
1	20.277	1133681	47852577	49.890
2	22.958	1099850	48062933	50.110
Total		2233531	95915510	100.000



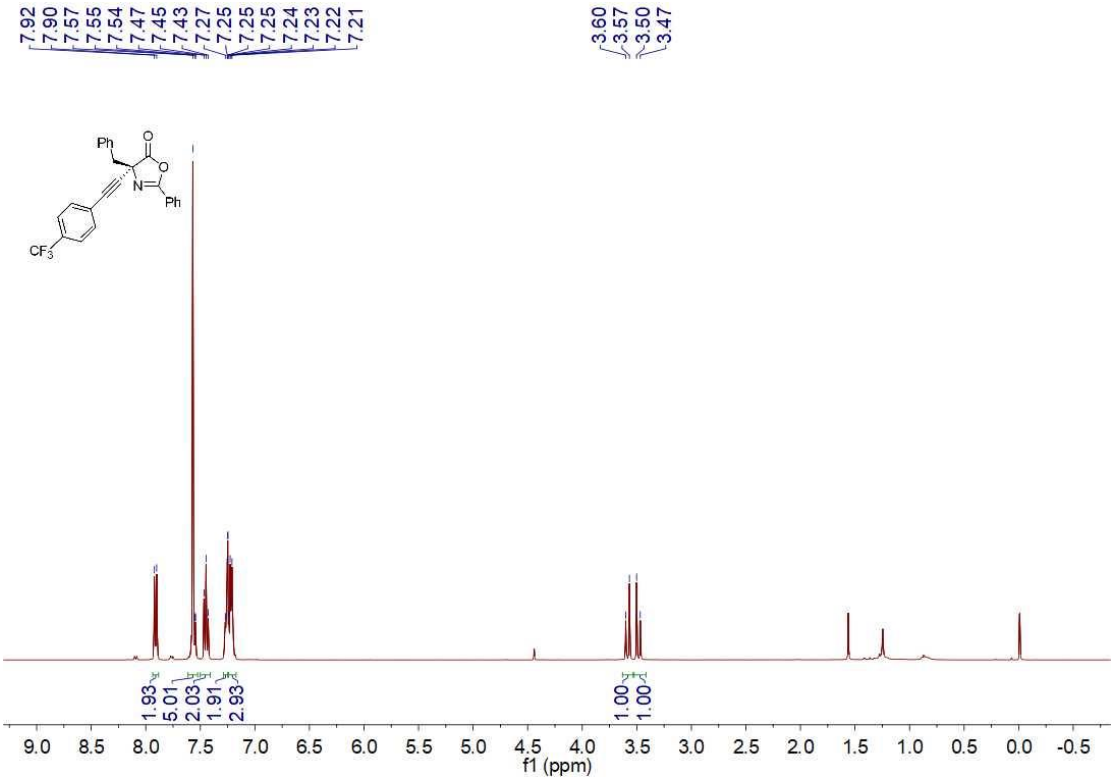
<Peak table>

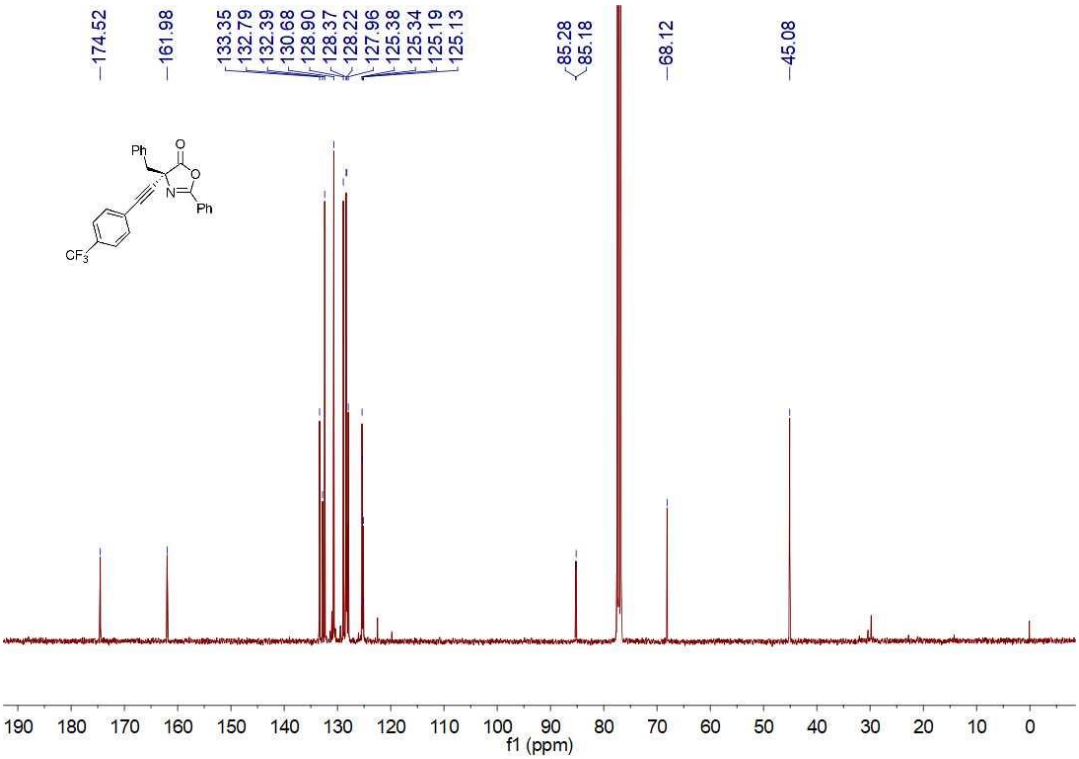
PDA Ch1 254nm

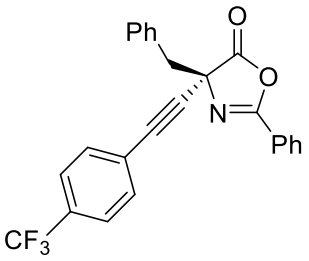
Peak#	Ret. Time	Height	Area	Area%
1	21.856	300634	10835624	76.761
2	25.199	81198	3280455	23.239
Total		381832	14116079	100.000


Ph
O
O
N
Ph
CF3

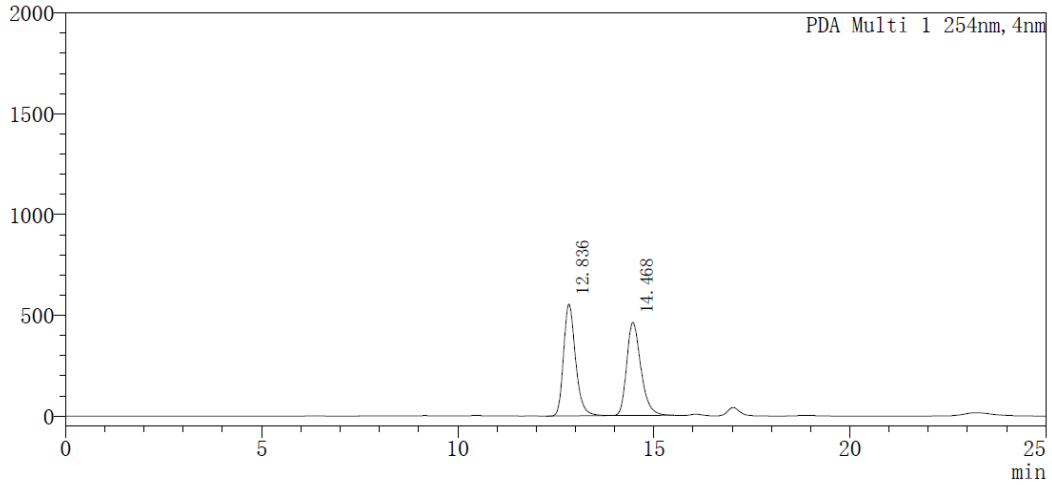
5ac


7.92
7.90
7.57
7.55
7.54
7.47
7.45
7.43
7.27
7.25
7.25
7.25
7.24
7.23
7.22
7.21
3.60
3.57
3.50
3.47
1.93
5.01
2.03
1.91
2.93
1.00
1.00
f1 (ppm)


174.52
161.98
133.35
132.79
132.39
130.68
128.90
128.37
128.22
127.96
125.38
125.34
125.19
125.13
85.28
85.18
68.12
45.08
f1 (ppm)



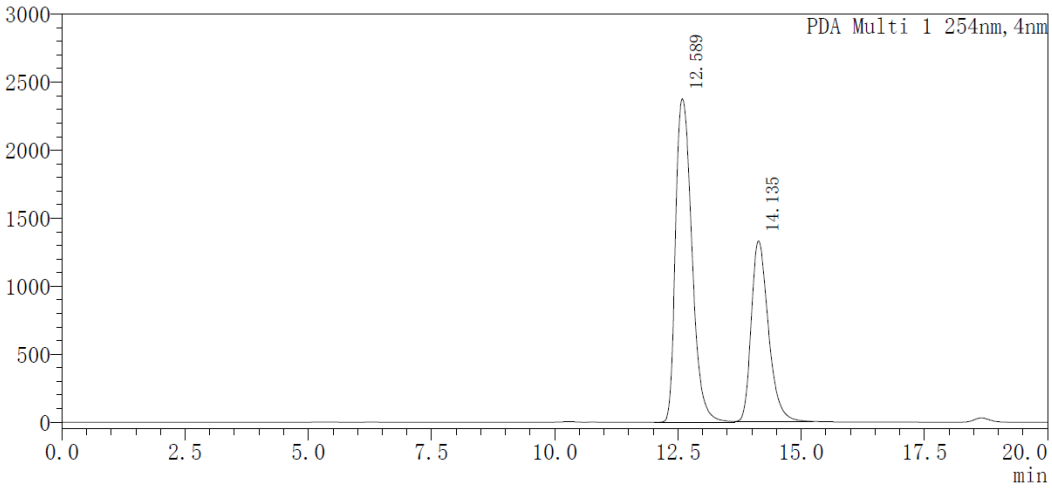
5ac



<Peak table>

PDA Ch1 254nm

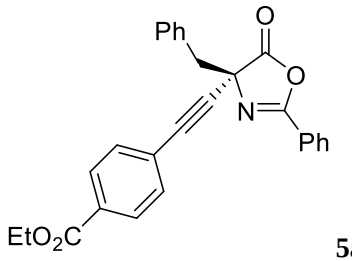
Peak#	Ret. Time	Height	Area	Area%
1	12.836	554411	11772947	50.206
2	14.468	462647	11676176	49.794
Total		1017058	23449123	100.000



<Peak table>

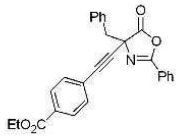
PDA Ch1 254nm

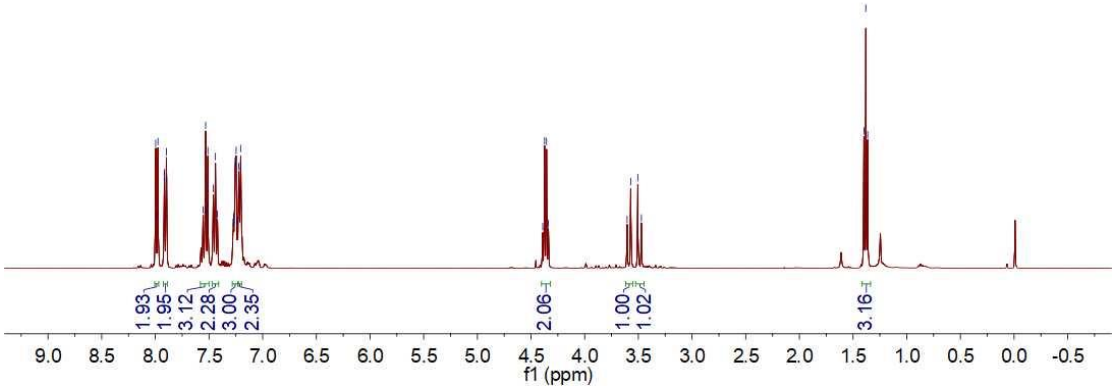
Peak#	Ret. Time	Height	Area	Area%
1	12.589	2379241	54994714	63.134
2	14.135	1327265	32112891	36.866
Total		3706506	87107605	100.000

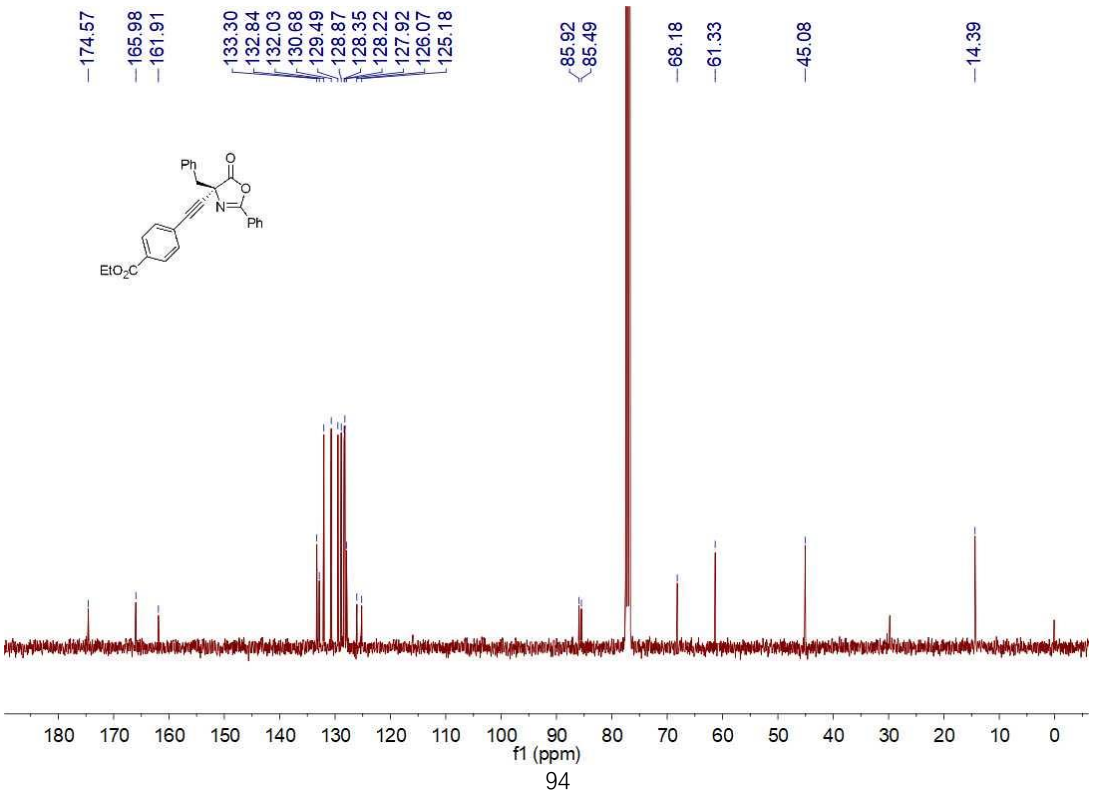

Ph
O
O
N
Ph
EtO2C

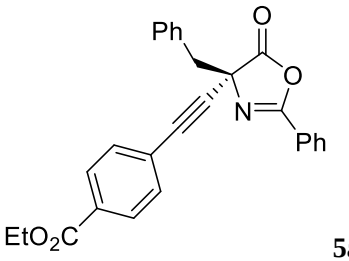
5ad


8.00
7.99
7.98
7.92
7.92
7.90
7.89
7.56
7.53
7.53
7.51
7.46
7.44
7.42
7.27
7.26
7.25
7.22
7.21
7.21
4.39
4.37
4.36
4.34
3.60
3.57
3.51
3.47
1.40
1.38
1.36

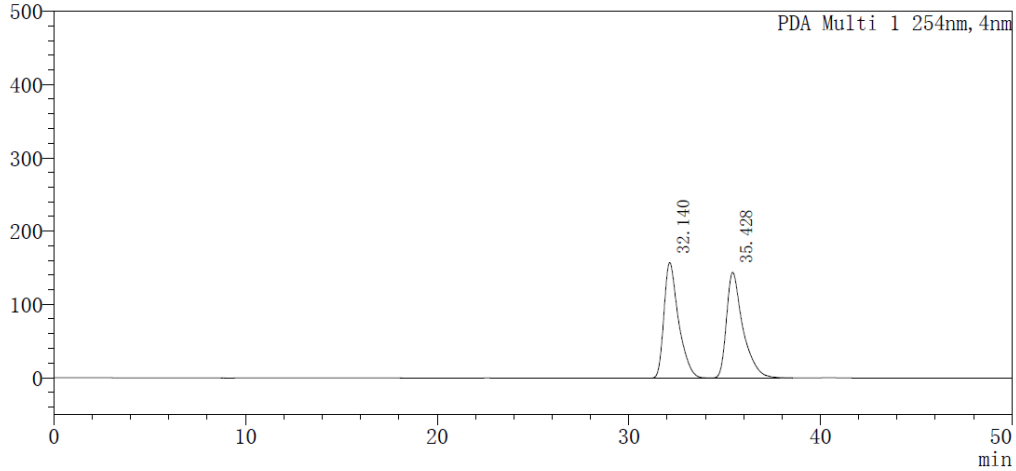



1.93
1.95
3.12
2.28
3.00
2.35
2.06
1.00
1.02
3.16
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


174.57
165.98
161.91
133.30
132.84
132.03
130.68
129.49
128.87
128.35
128.22
127.92
126.07
125.18
85.92
85.49
68.18
61.33
45.08
14.39
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



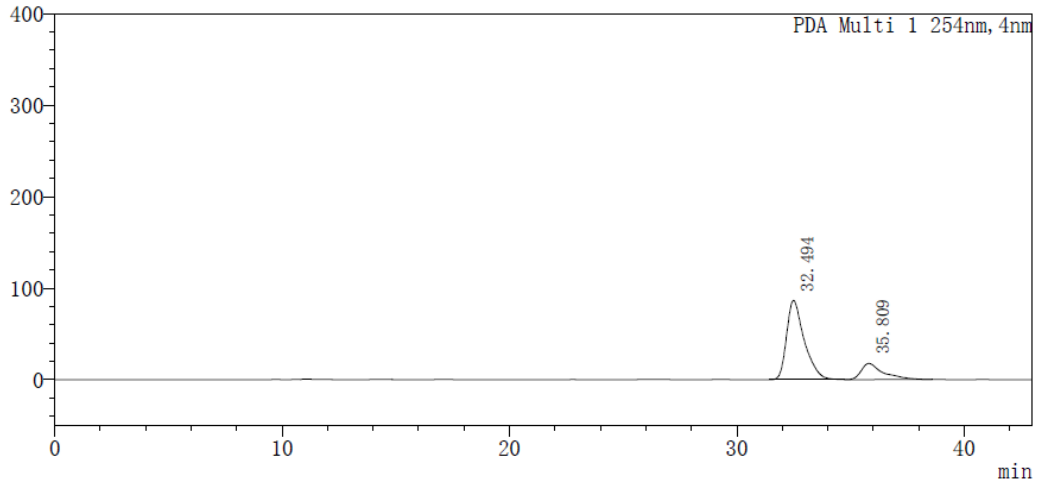
5ad



<Peak table>

PDA Ch1 254nm

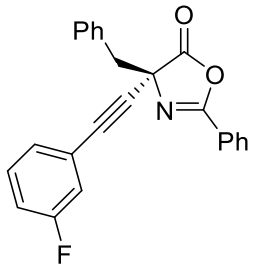
Peak#	Ret. Time	Height	Area	Area%
1	32.140	157930	8371501	49.220
2	35.428	144445	8636968	50.780
Total		302375	17008469	100.000



<Peak table>

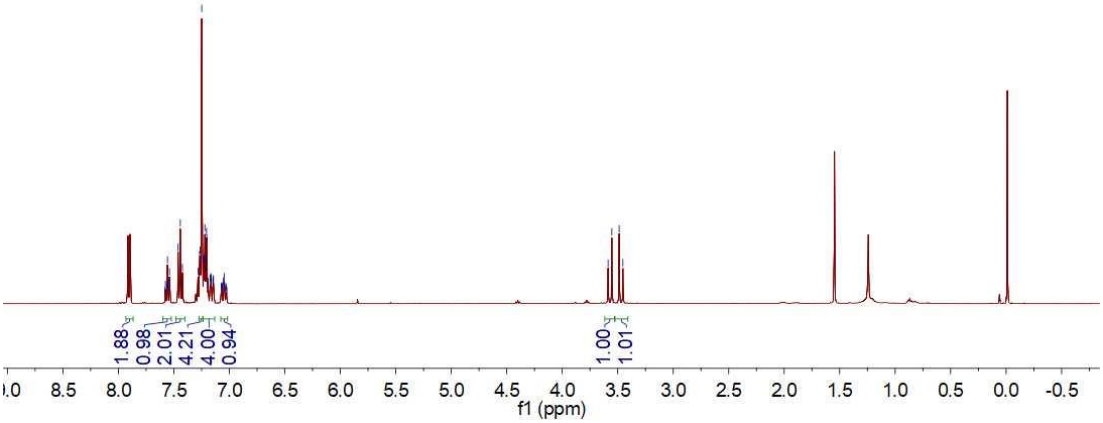
PDA Ch1 254nm

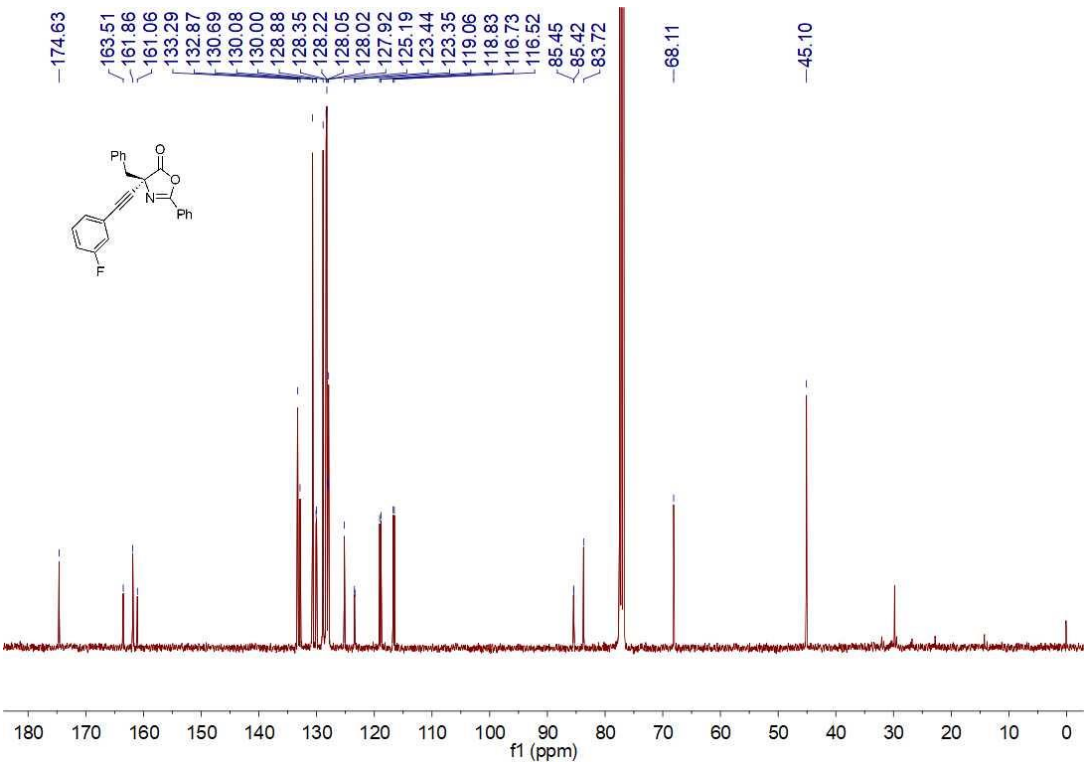
Peak#	Ret. Time	Height	Area	Area%
1	32.494	86613	4665730	79.845
2	35.809	17645	1177760	20.155
Total		104258	5843490	100.000

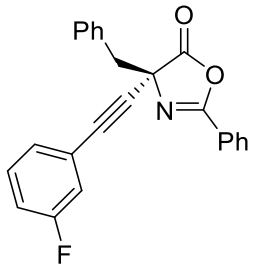

Ph
O
O
N
Ph
F

5ae

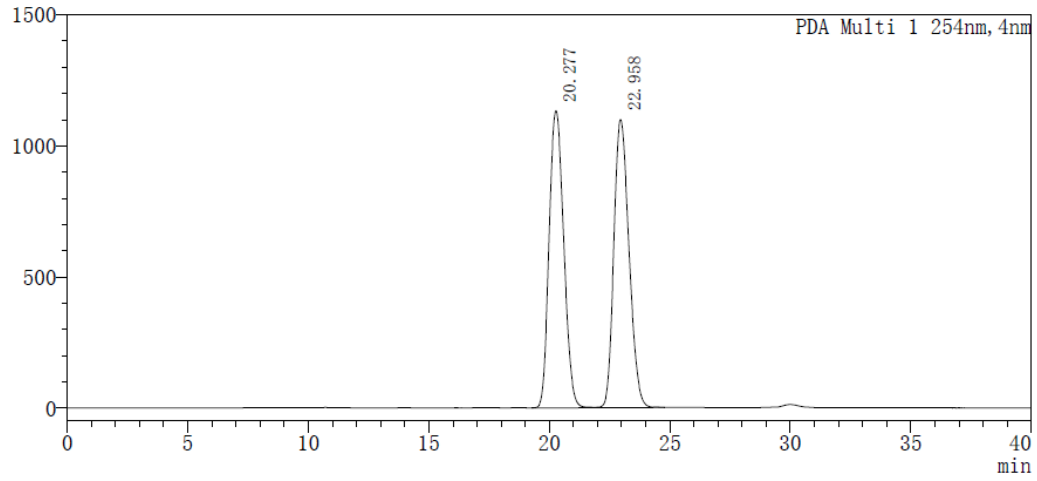

7.56
7.54
7.46
7.44
7.42
7.28
7.27
7.26
7.25
7.23
7.23
7.22
7.22
7.21
7.21
7.20
7.19
7.17
7.17
7.17
7.16
7.15
7.15
7.14
7.05
3.55
3.49
3.45


1.88
0.98
2.01
4.21
4.00
0.94
1.00
1.01
f1 (ppm)


174.63
163.51
161.86
161.06
133.29
132.87
130.69
130.08
130.00
128.88
128.35
128.22
128.05
128.02
127.92
125.19
123.44
123.35
119.06
118.83
116.73
116.52
85.45
85.42
83.72
68.11
45.10
f1 (ppm)



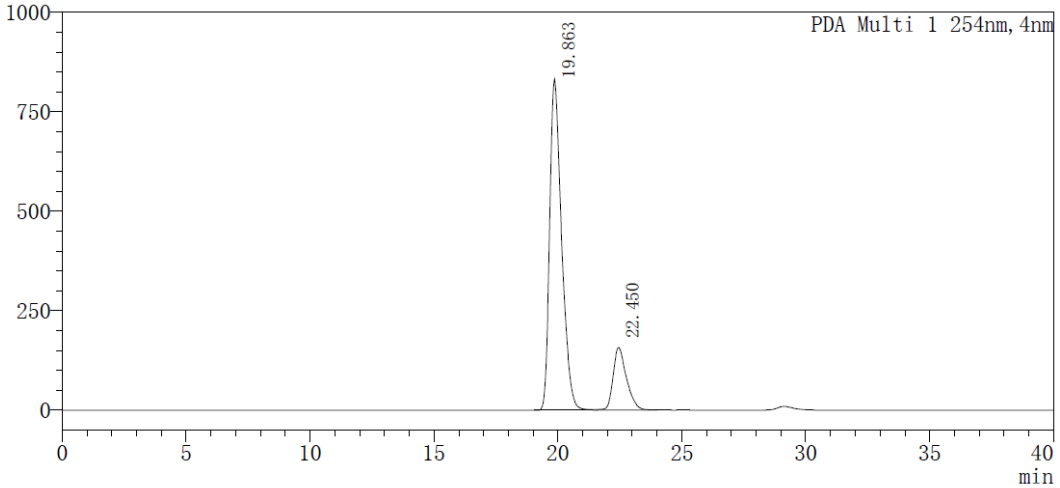
5ae



<Peak table>

PDA Ch1 254nm

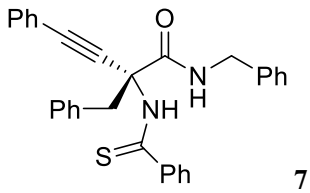
Peak#	Ret. Time	Height	Area	Area%
1	20.277	1133681	47852577	49.890
2	22.958	1099850	48062933	50.110
Total		2233531	95915510	100.000



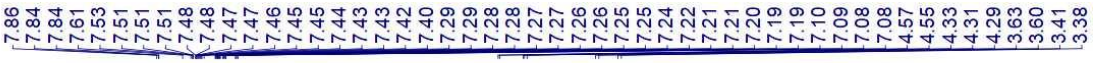
<Peak table>

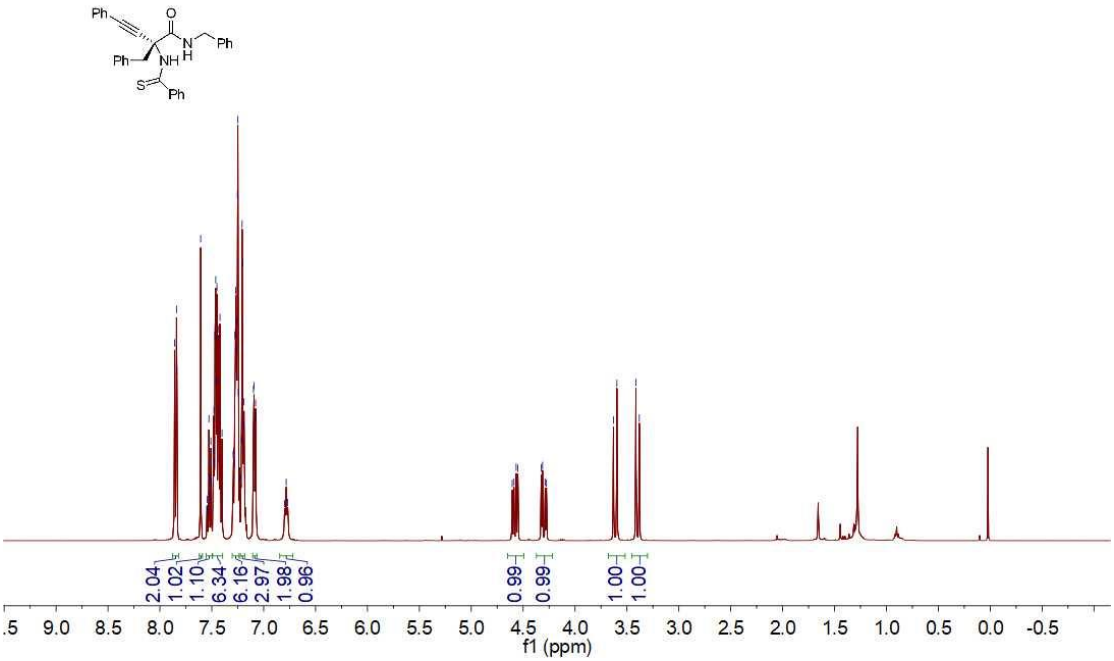
PDA Ch1 254nm

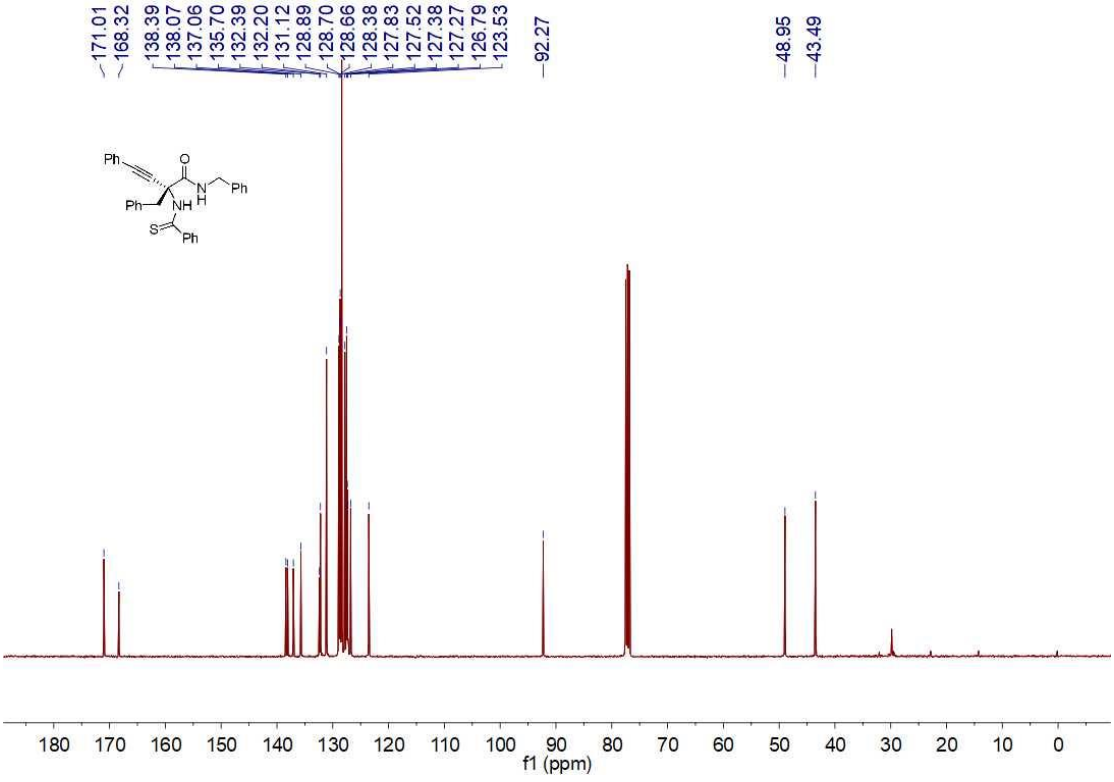
Peak#	Ret. Time	Height	Area	Area%
1	19.863	830996	27894061	82.524
2	22.450	157190	5907002	17.476
Total		988185	33801063	100.000

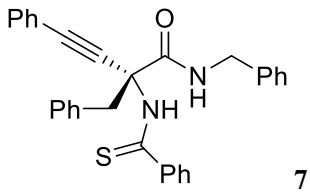

Ph
O
N
H
Ph
Ph
NH
S
Ph

7

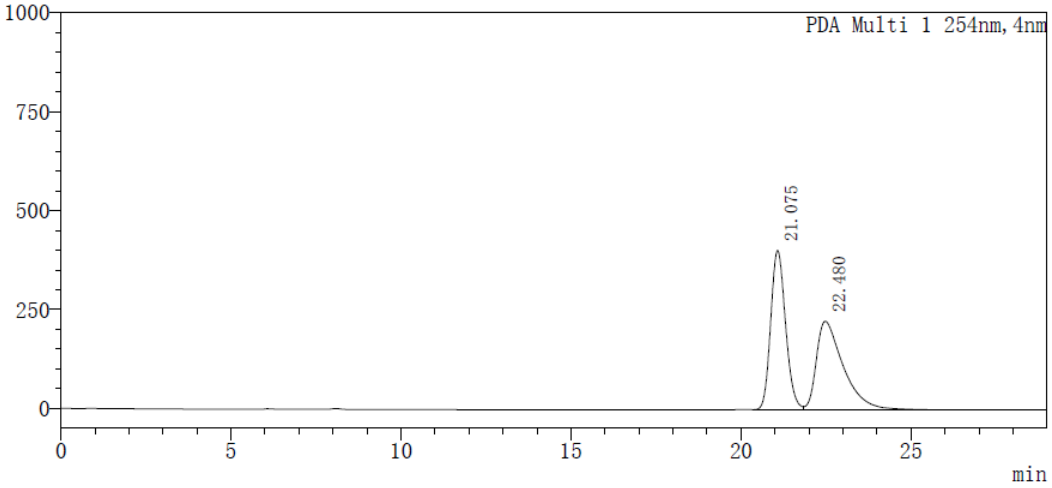

7.86
7.84
7.84
7.61
7.53
7.51
7.51
7.51
7.48
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.43
7.43
7.42
7.40
7.29
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.25
7.25
7.24
7.22
7.21
7.21
7.20
7.19
7.19
7.10
7.09
7.08
7.08
4.57
4.55
4.33
4.31
4.29
3.63
3.60
3.41
3.38


2.04
1.02
1.10
6.34
6.16
2.97
1.98
0.96
0.99
0.99
1.00
1.00
f1 (ppm)


171.01
168.32
138.39
138.07
137.06
135.70
132.39
132.20
131.12
128.89
128.70
128.66
128.38
127.83
127.52
127.38
127.27
126.79
123.53
92.27
48.95
43.49
f1 (ppm)



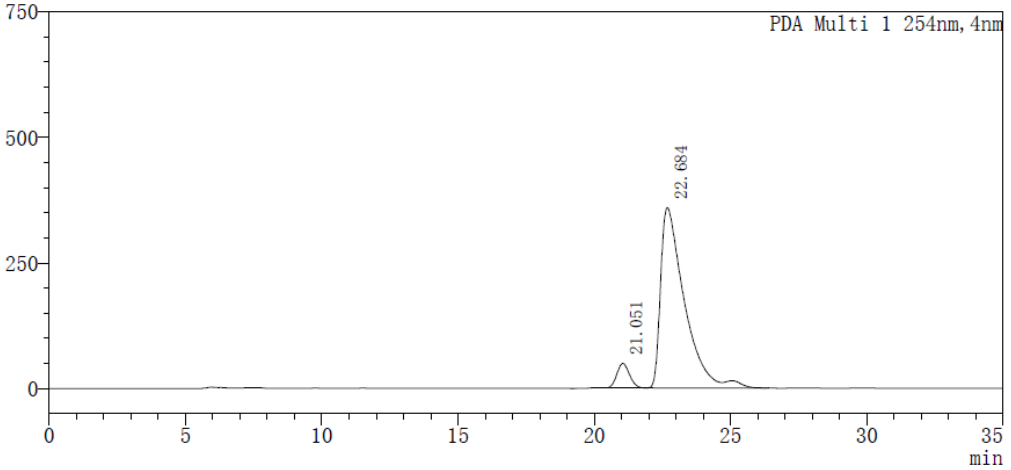
7



〈Peak table〉

PDA Ch1 254nm

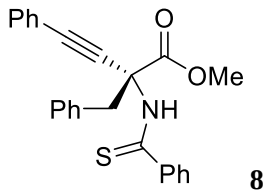
Peak#	Ret. Time	Height	Area	Area%
1	21.075	402630	12267256	49.893
2	22.480	223605	12319857	50.107
Total		626235	24587113	100.000



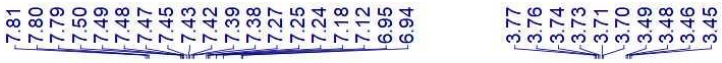
〈Peak table〉

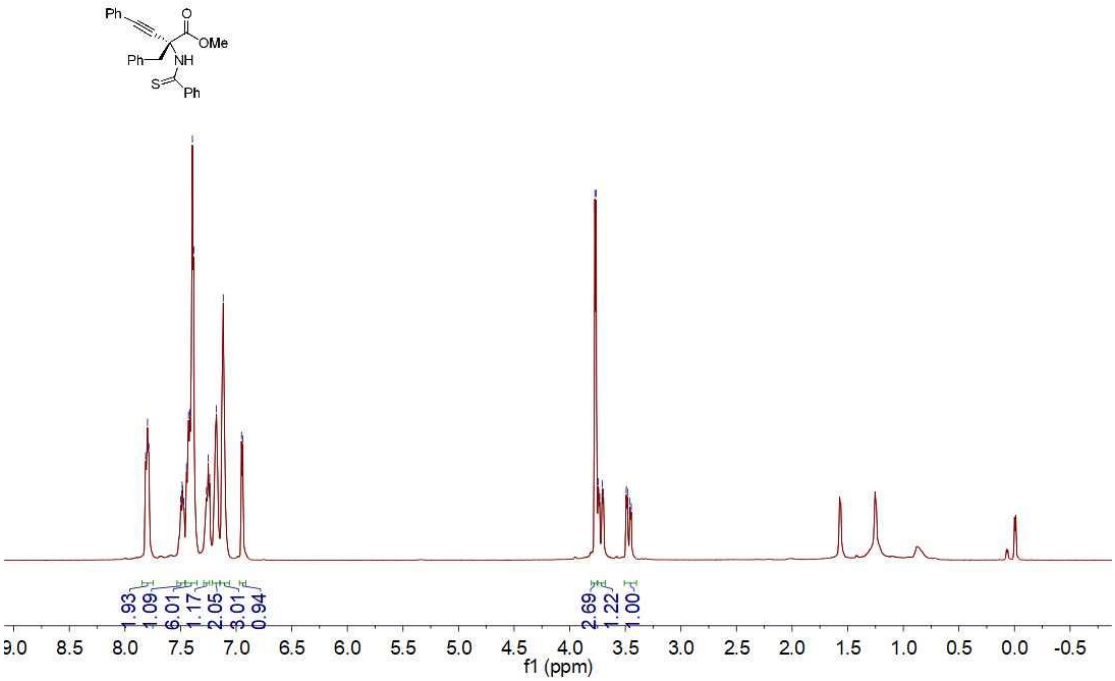
PDA Ch1 254nm

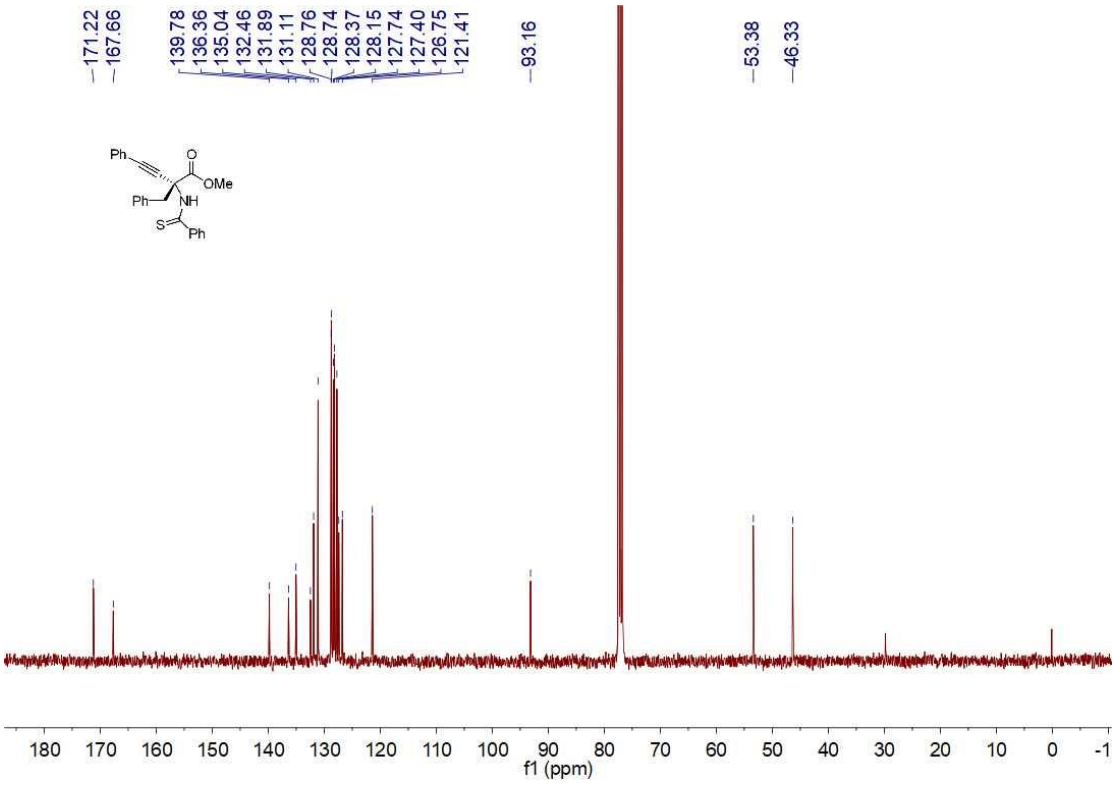
Peak#	Ret. Time	Height	Area	Area%
1	21.051	48607	1560838	6.661
2	22.684	358808	21872027	93.339
Total		407415	23432864	100.000

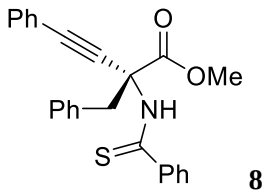

Ph
O
OMe
Ph
NH
S
Ph

8

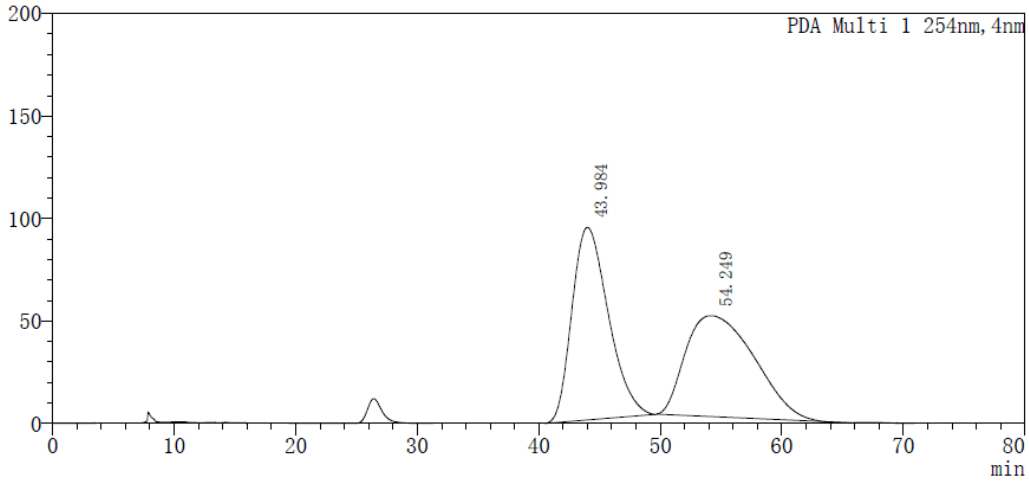

7.81
7.80
7.79
7.50
7.49
7.48
7.47
7.45
7.43
7.42
7.39
7.38
7.27
7.25
7.24
7.18
7.12
6.95
6.94
3.77
3.76
3.74
3.73
3.71
3.70
3.49
3.48
3.46
3.45


1.93
1.09
6.01
1.17
2.05
3.01
0.94
2.69
1.22
1.00
f1 (ppm)


171.22
167.66
139.78
136.36
135.04
132.46
131.89
131.11
128.76
128.74
128.37
128.15
127.74
127.40
126.75
121.41
93.16
53.38
46.33
f1 (ppm)



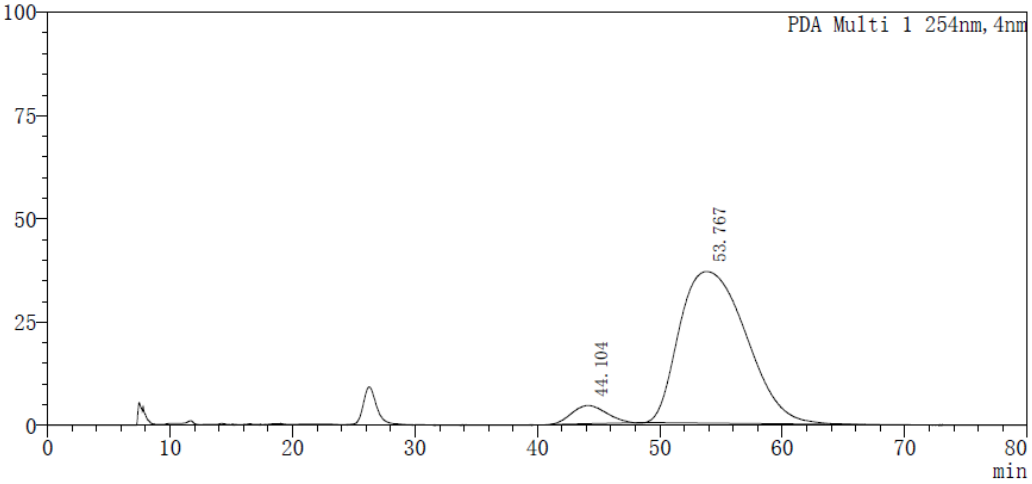
8



〈Peak table〉

PDA Ch1 254nm

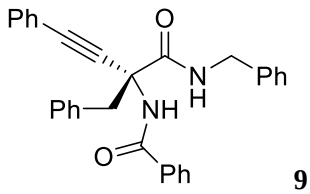
Peak#	Ret. Time	Height	Area	Area%
1	43.984	94053	19608822	50.249
2	54.249	49254	19414188	49.751
Total		143306	39023010	100.000



〈Peak table〉

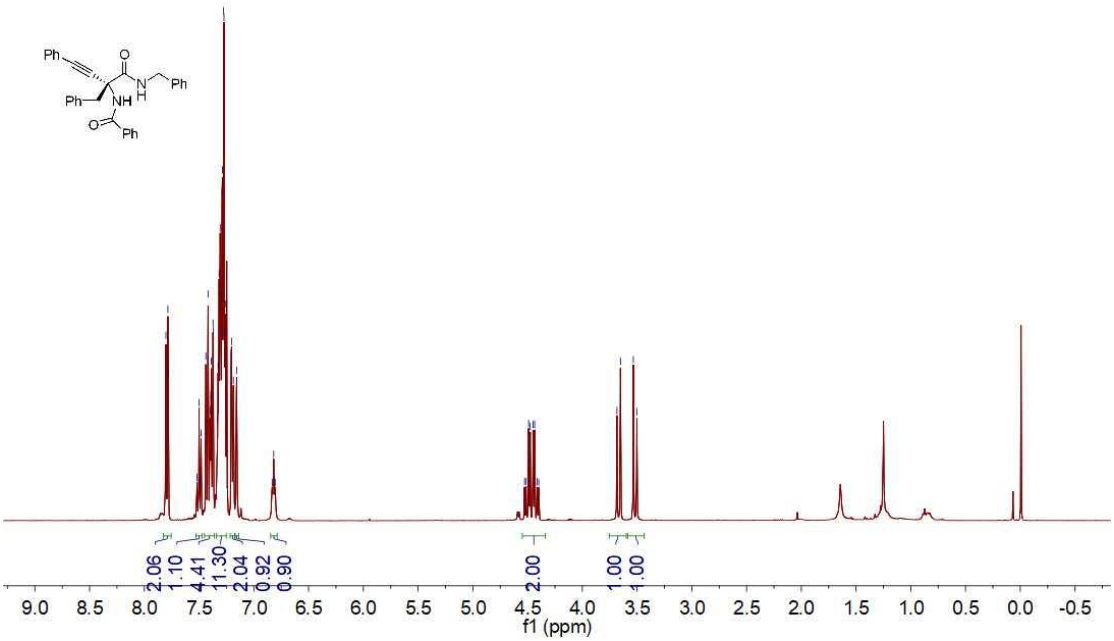
PDA Ch1 254nm

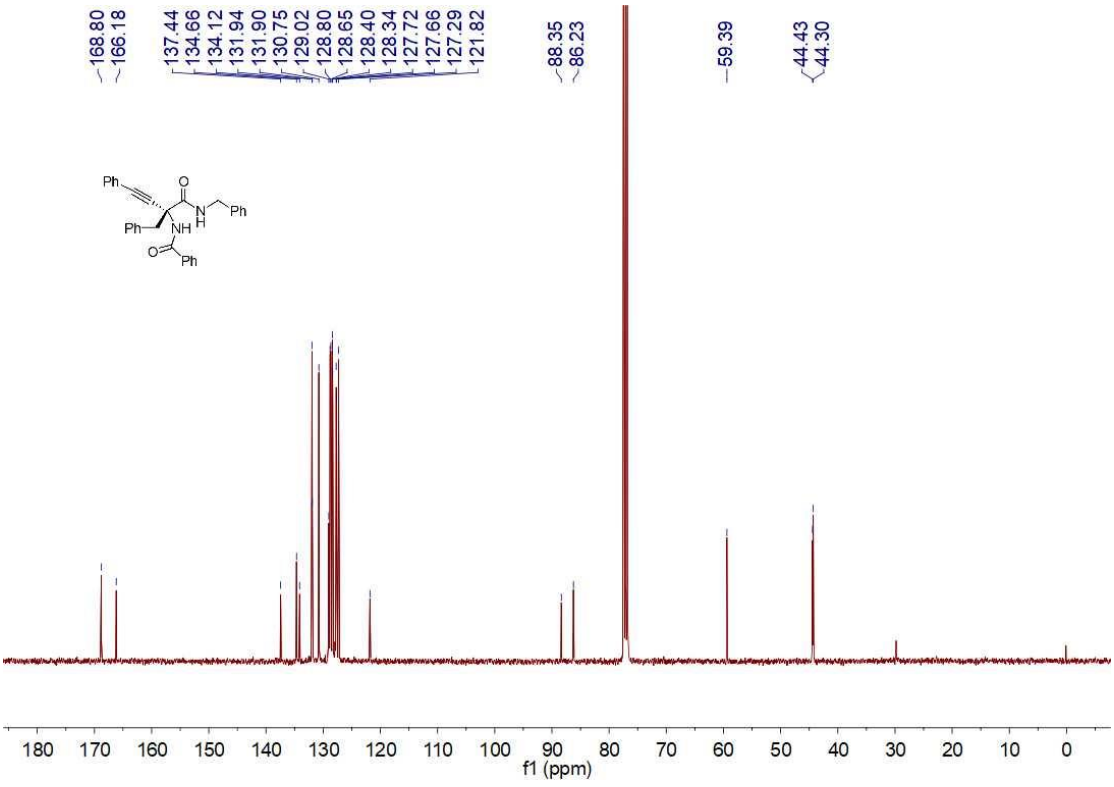
Peak#	Ret. Time	Height	Area	Area%
1	44.104	4372	856072	5.783
2	53.767	36691	13947603	94.217
Total		41063	14803675	100.000

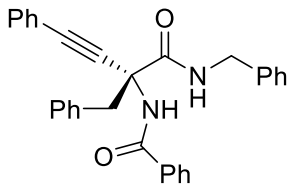


9

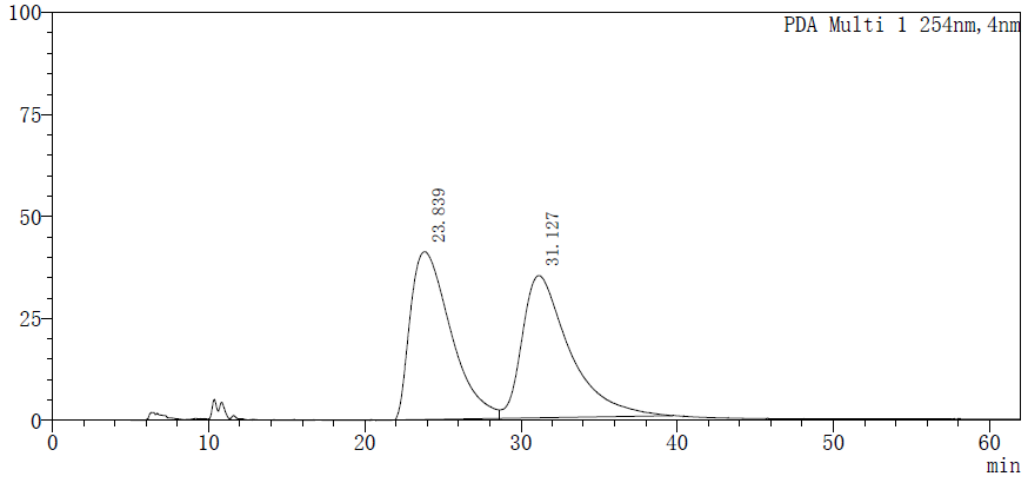

7.80
7.78
7.44
7.42
7.39
7.37
7.37
7.32
7.31
7.30
7.29
7.29
7.28
7.27
7.27
7.26
7.21
4.53
4.51
4.49
4.48
4.45
4.44
4.41
4.40
3.68
3.65
3.53
3.50


2.06
1.10
4.41
11.30
2.04
0.92
0.90
2.00
1.00
1.00
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)


168.80
166.18
137.44
134.66
134.12
131.94
131.90
130.75
129.02
128.80
128.65
128.40
128.34
127.72
127.66
127.29
121.82
88.35
86.23
59.39
44.43
44.30
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



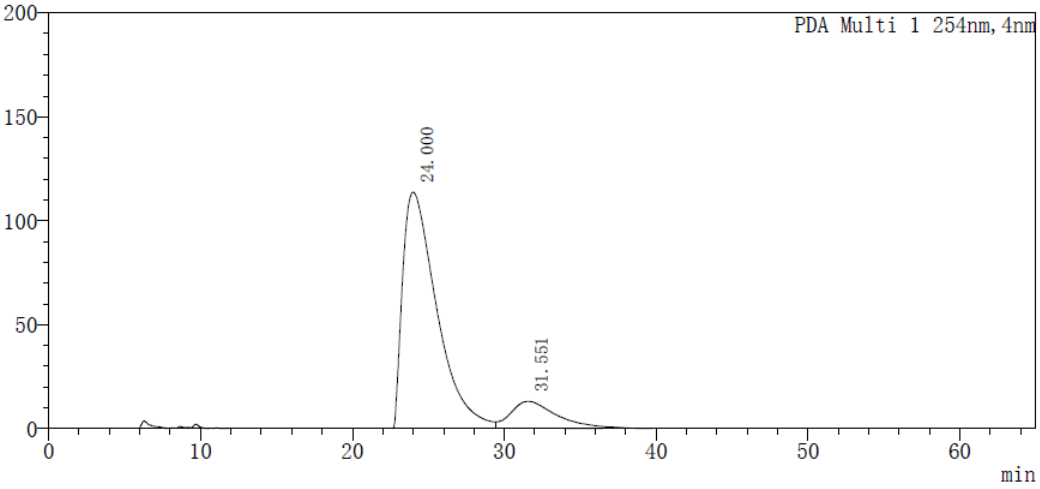
9



<Peak table>

PDA Ch1 254nm

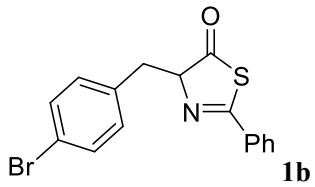
Peak#	Ret. Time	Height	Area	Area%
1	23.839	41133	7425499	50.174
2	31.127	34872	7374009	49.826
Total		76005	14799509	100.000



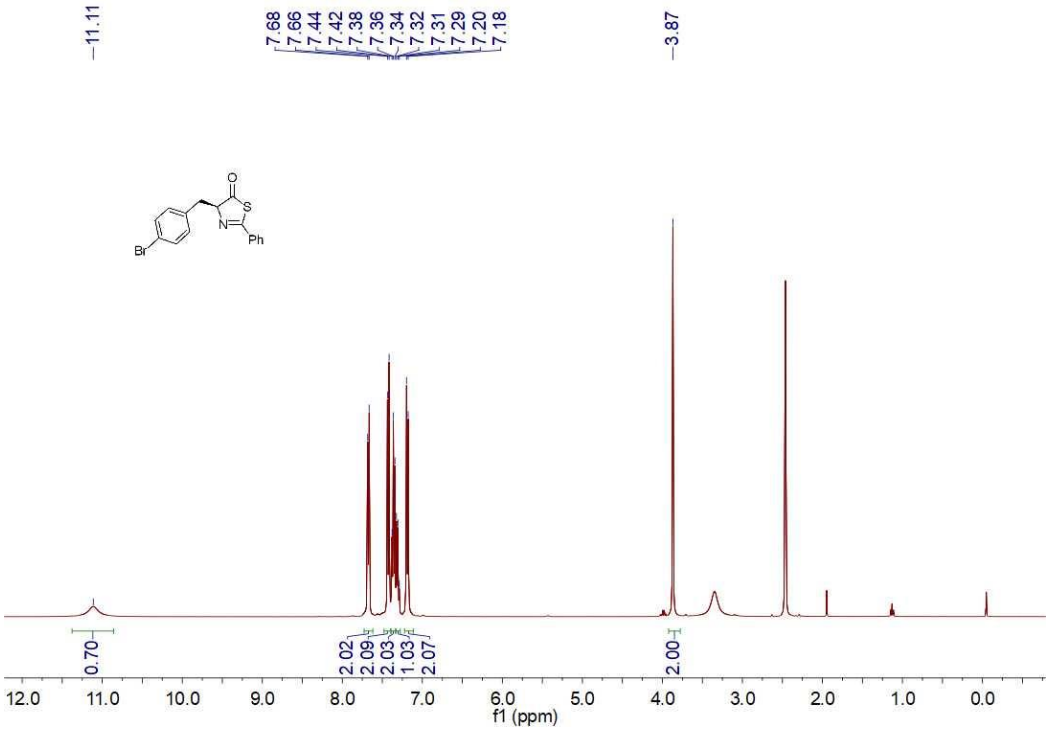
<Peak table>

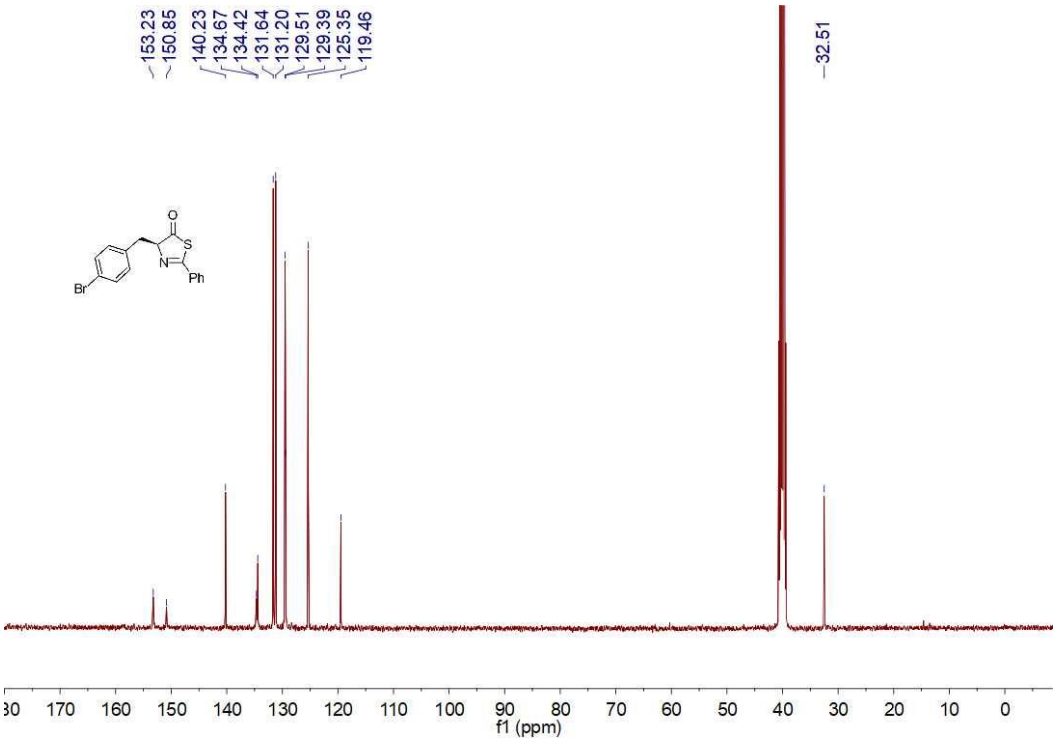
PDA Ch1 254nm

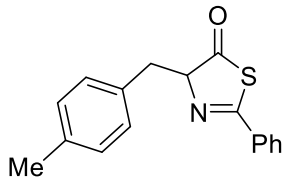
Peak#	Ret. Time	Height	Area	Area%
1	24.000	114180	17938560	86.381
2	31.551	13259	2828168	13.619
Total		127439	20766728	100.000


O
S
N
Ph
Br

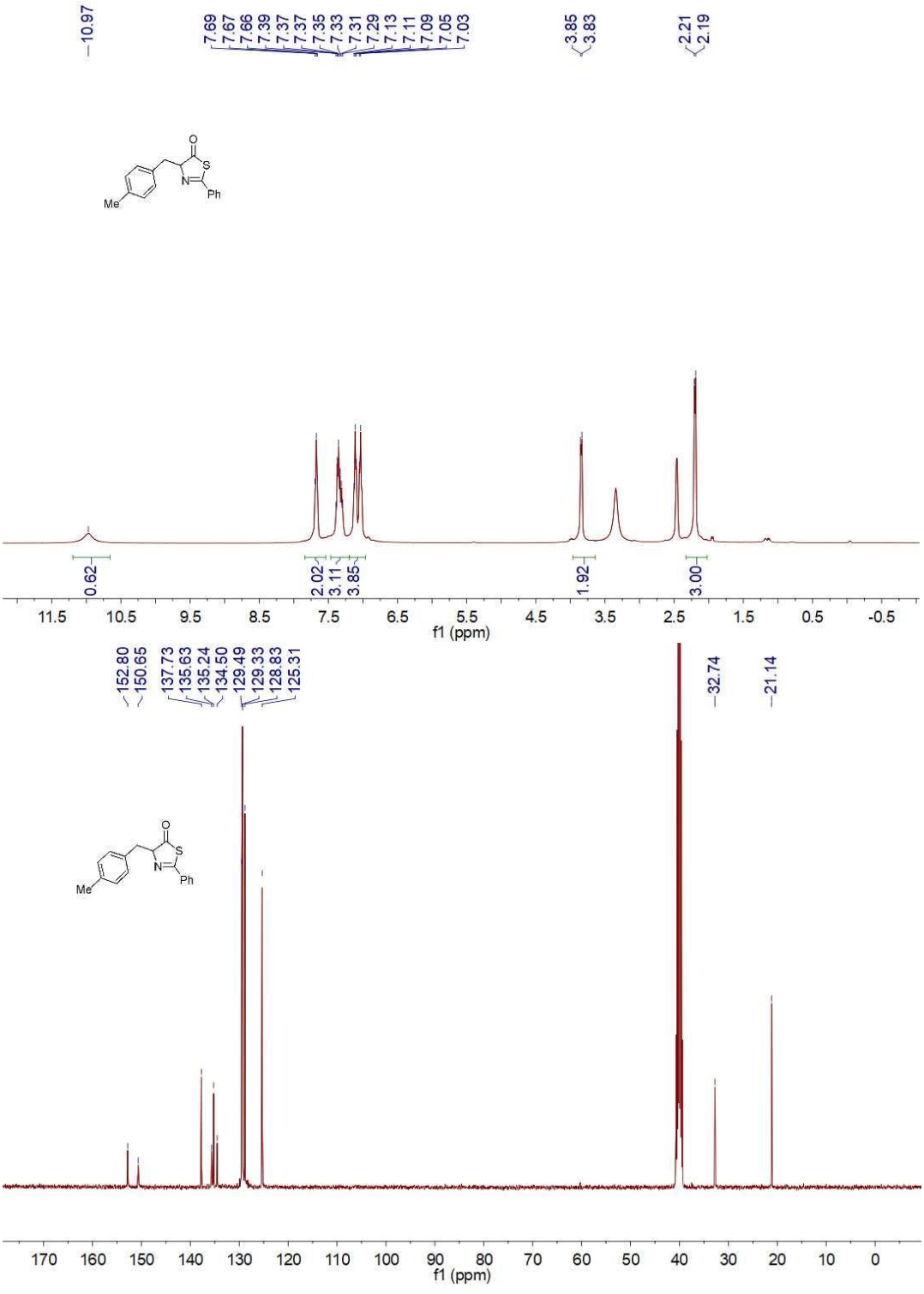
1b

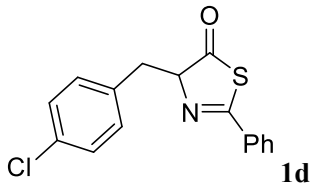

11.11
7.68
7.66
7.44
7.42
7.38
7.36
7.34
7.32
7.31
7.29
7.20
7.18
3.87
0.70
2.02
2.09
2.03
1.03
2.07
2.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)


153.23
150.85
140.23
134.67
134.42
131.64
131.20
129.51
129.39
125.35
119.46
32.51
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

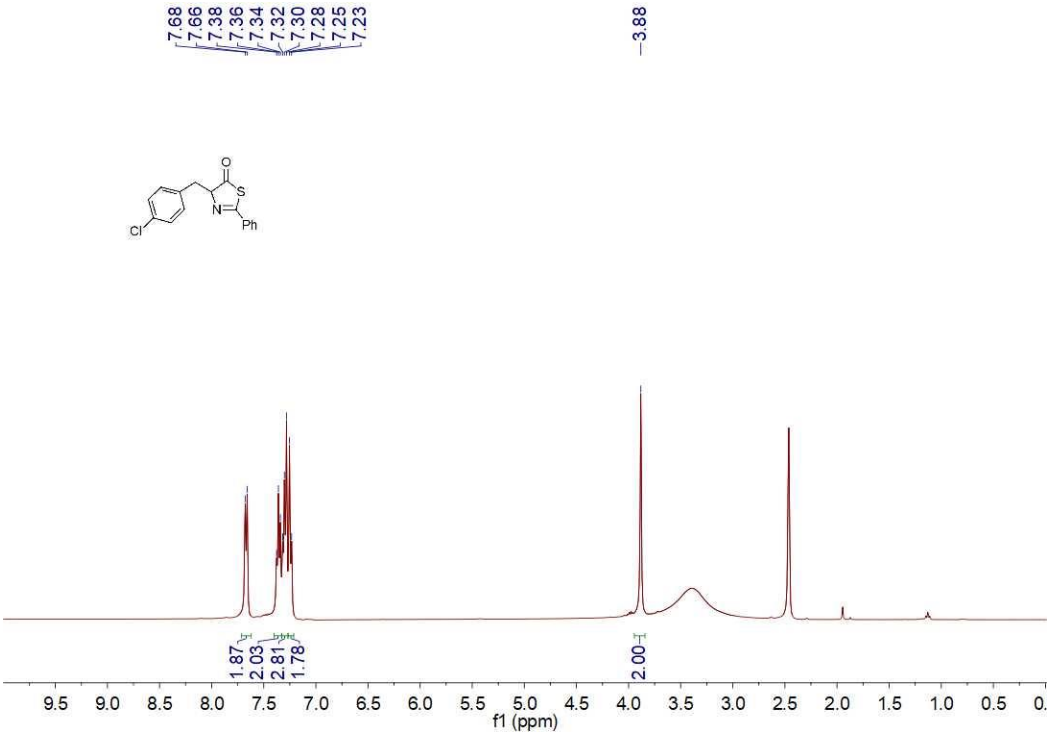

O
S
N
Ph
Me

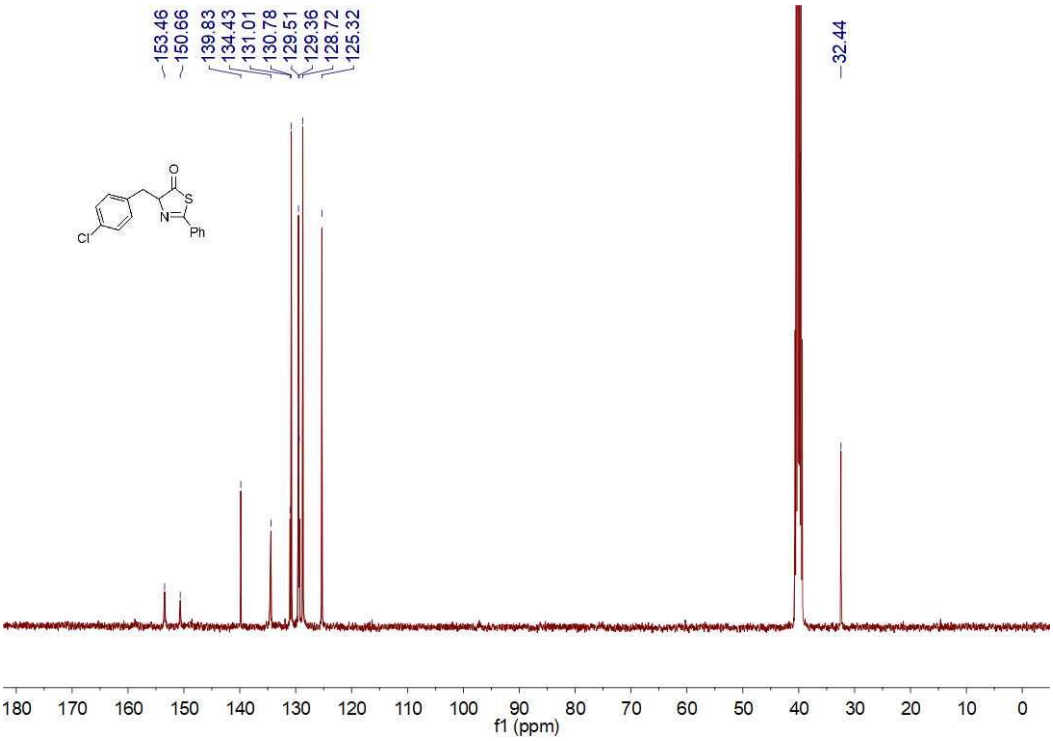
1c

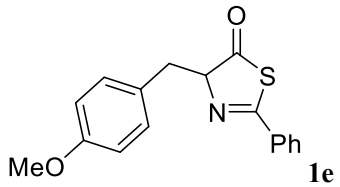

10.97
7.69
7.67
7.66
7.39
7.37
7.37
7.35
7.33
7.31
7.29
7.13
7.11
7.09
7.05
7.03
3.85
3.83
2.21
2.19
0.62
2.02
3.11
3.85
1.92
3.00
f1 (ppm)
152.80
150.65
137.73
135.63
135.24
134.50
129.49
129.33
128.83
125.31
32.74
21.14
f1 (ppm)


O
S
N
Ph
Cl

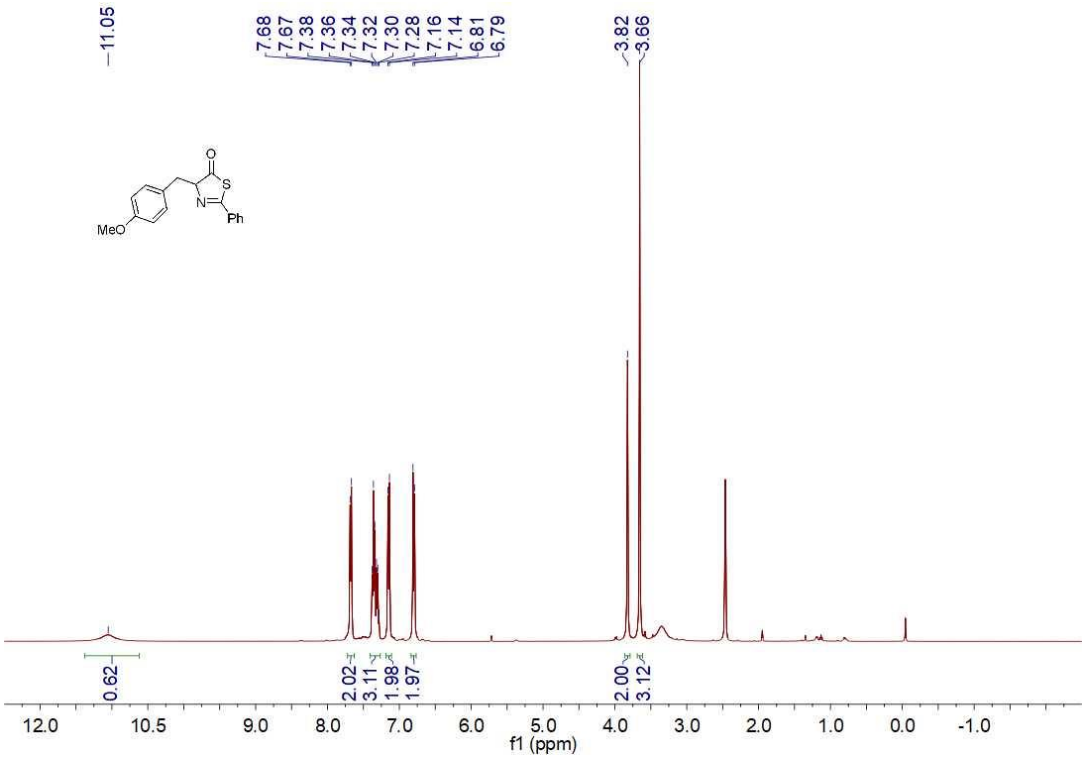
1d

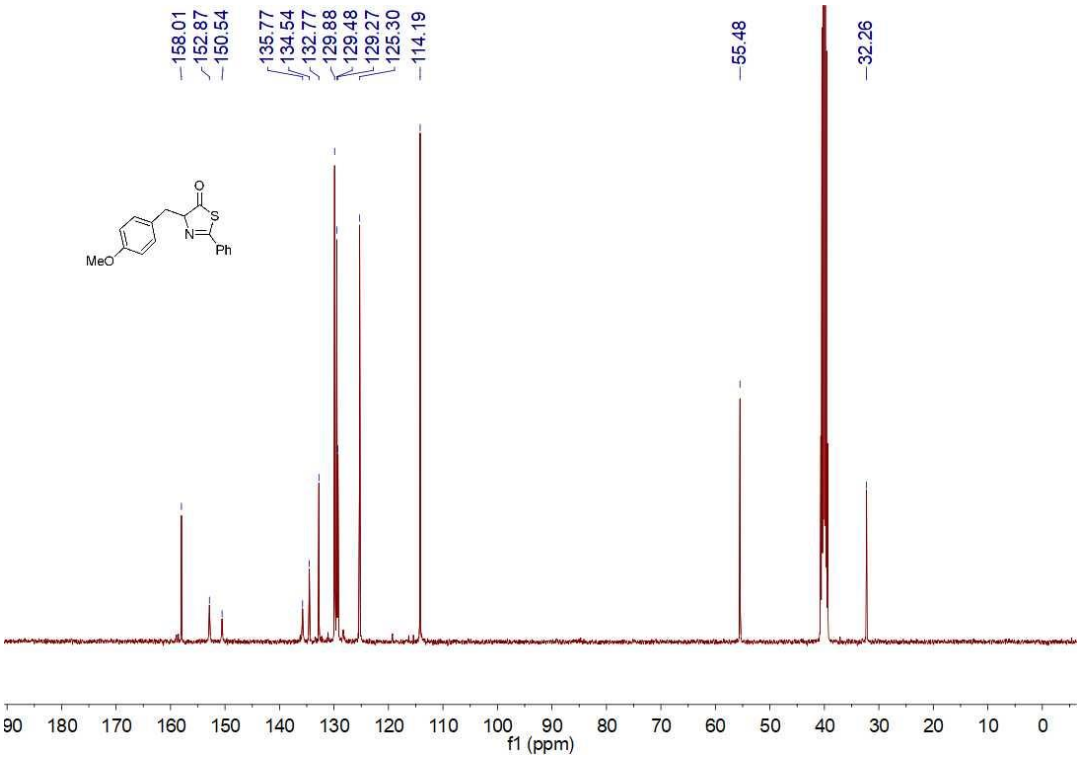

7.68
7.66
7.38
7.36
7.34
7.32
7.30
7.28
7.25
7.23
3.88
1.87
2.03
2.81
1.78
2.00
f1 (ppm)

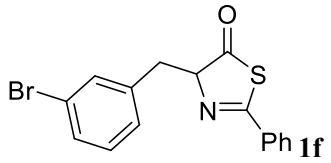

153.46
150.66
139.83
134.43
131.01
130.78
129.51
129.36
128.72
125.32
32.44
f1 (ppm)


O
S
N
Ph
MeO

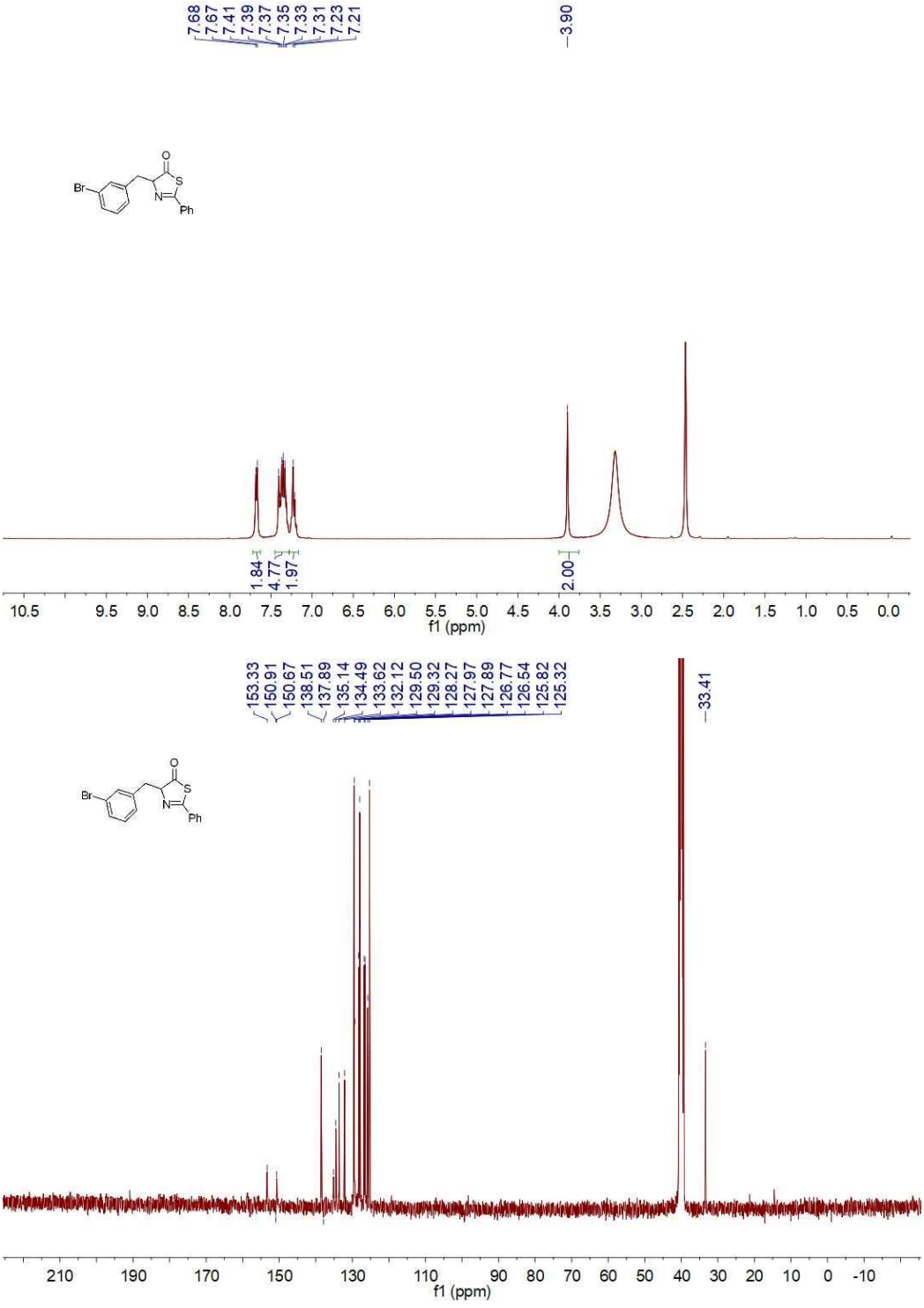
1e

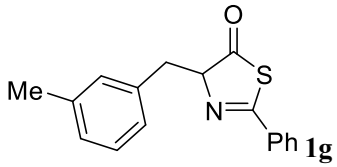

11.05
7.68
7.67
7.38
7.36
7.34
7.32
7.30
7.28
7.16
7.14
6.81
6.79
3.82
3.66
0.62
2.02
3.11
1.98
1.97
2.00
3.12
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


158.01
152.87
150.54
135.77
134.54
132.77
129.88
129.48
129.27
125.30
114.19
55.48
32.26
90
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

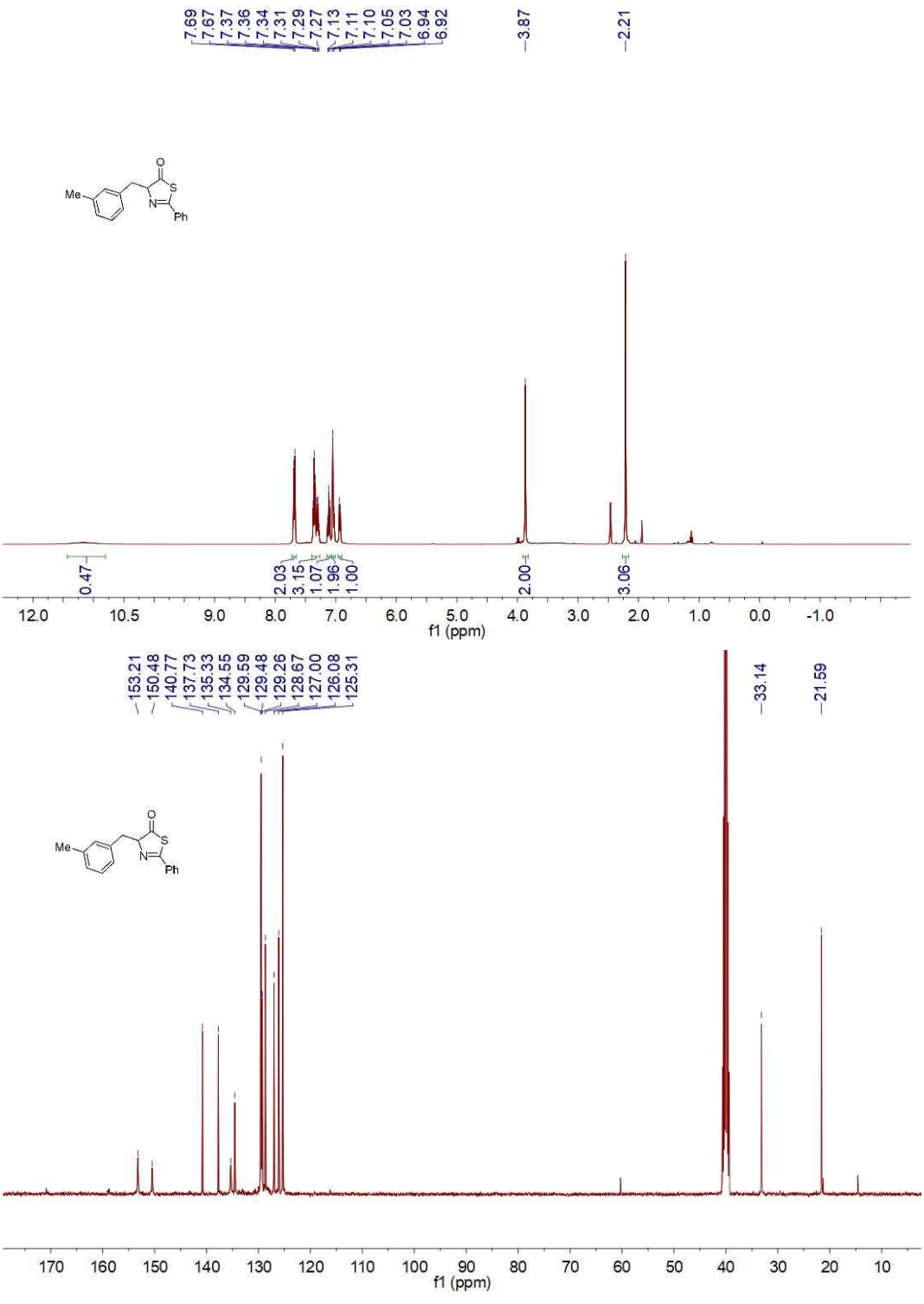

O
S
Br
N
Ph

1f


7.68
7.67
7.41
7.39
7.37
7.35
7.33
7.31
7.23
7.21
3.90
1.84
4.77
1.97
2.00
f1 (ppm)
153.33
150.91
150.67
138.51
137.89
135.14
134.49
133.62
132.12
129.50
129.32
128.27
127.97
127.89
126.77
126.54
125.82
125.32
33.41
f1 (ppm)


O
S
N
Me
Ph

1g


7.69
7.67
7.37
7.36
7.34
7.31
7.29
7.27
7.13
7.11
7.10
7.05
7.03
6.94
6.92
3.87
2.21
0.47
2.03
3.15
1.07
1.96
1.00
2.00
3.06
f1 (ppm)
153.21
150.48
140.77
137.73
135.33
134.55
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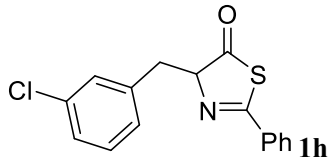
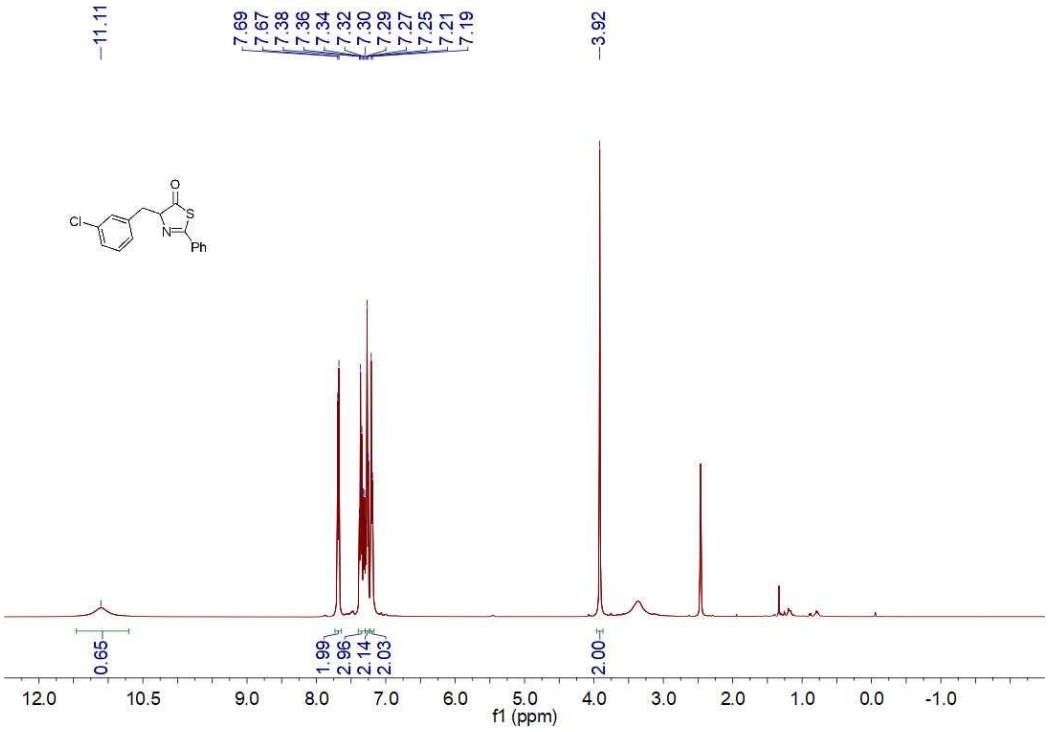
129.48
129.26
128.67
127.00
126.08
125.31
33.14
21.59
f1 (ppm)


O
S
Cl
N
Ph

1h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7.67
7.38
7.36
7.34
7.32
7.30
7.29
7.27
7.25
7.21
7.19
3.92
0.65
1.99
2.96
2.14
2.03
2.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
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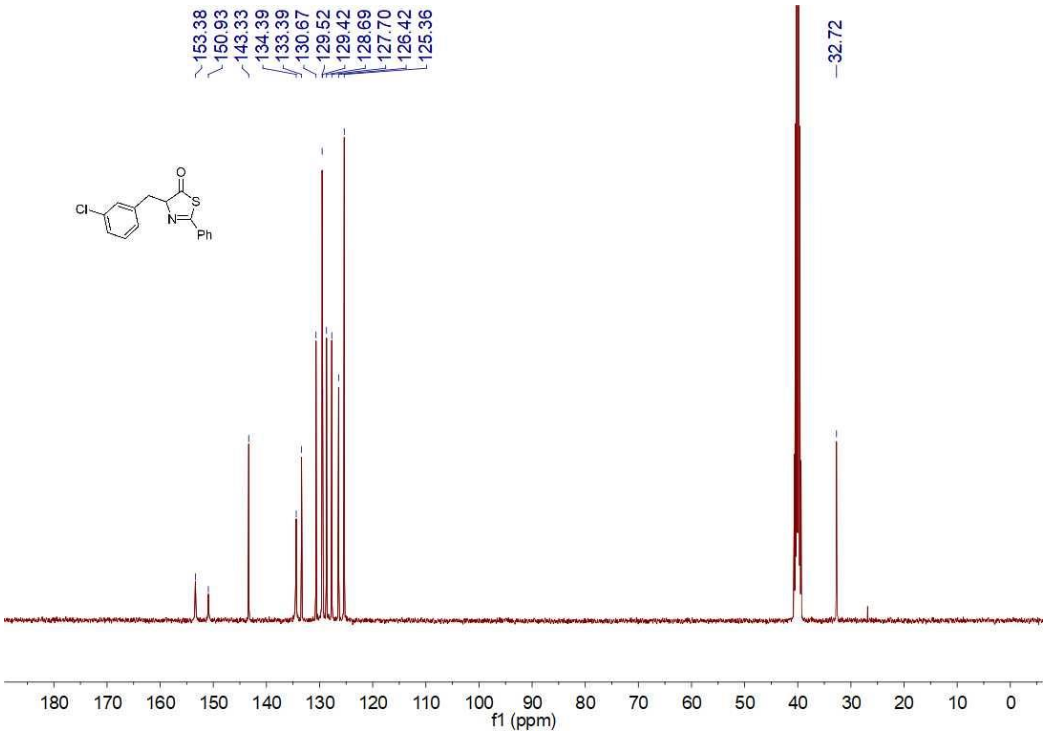
-1.0
f1 (ppm)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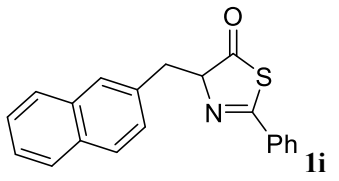
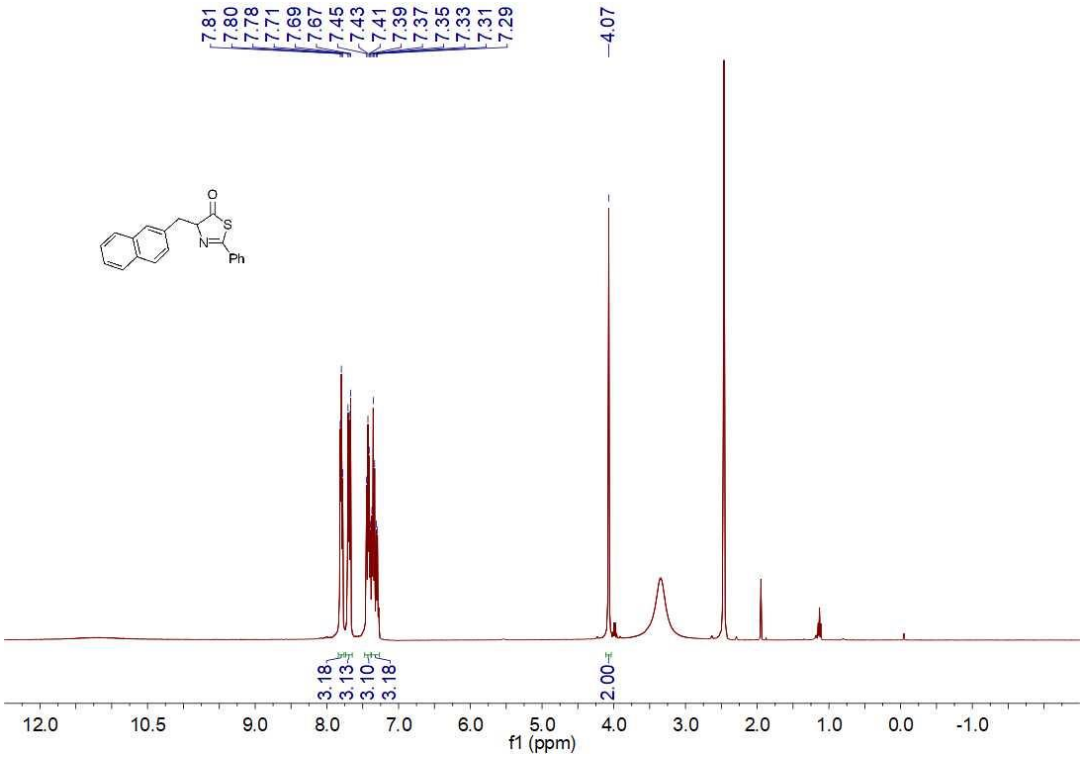
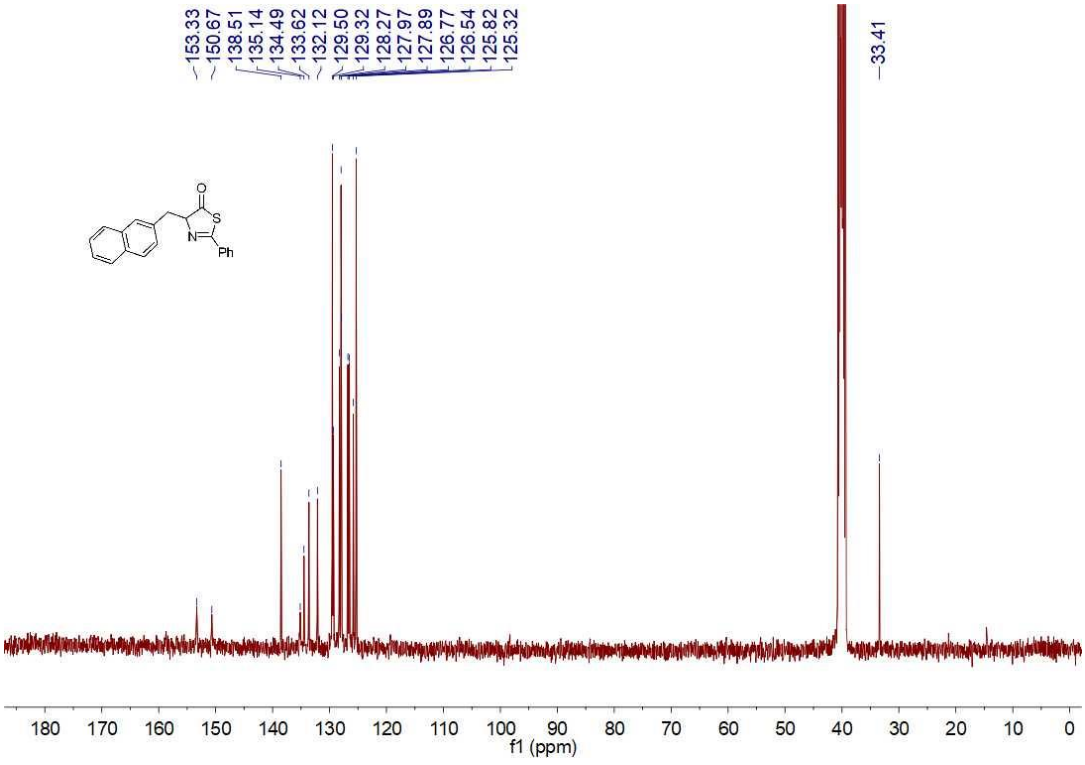
150.93
143.33
134.39
133.39
130.67
129.52
129.42
128.69
127.70
126.42
125.36
32.72
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
S
N
Ph

1i


7.81
7.80
7.78
7.71
7.69
7.67
7.45
7.43
7.41
7.39
7.37
7.35
7.33
7.31
7.29
4.07
3.18
3.13
3.10
3.18
2.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)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133.62
132.12
129.50
129.32
128.27
127.97
127.89
126.77
126.54
125.82
125.32
33.41
180
170
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150
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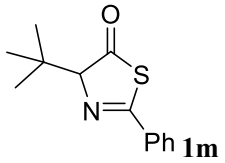
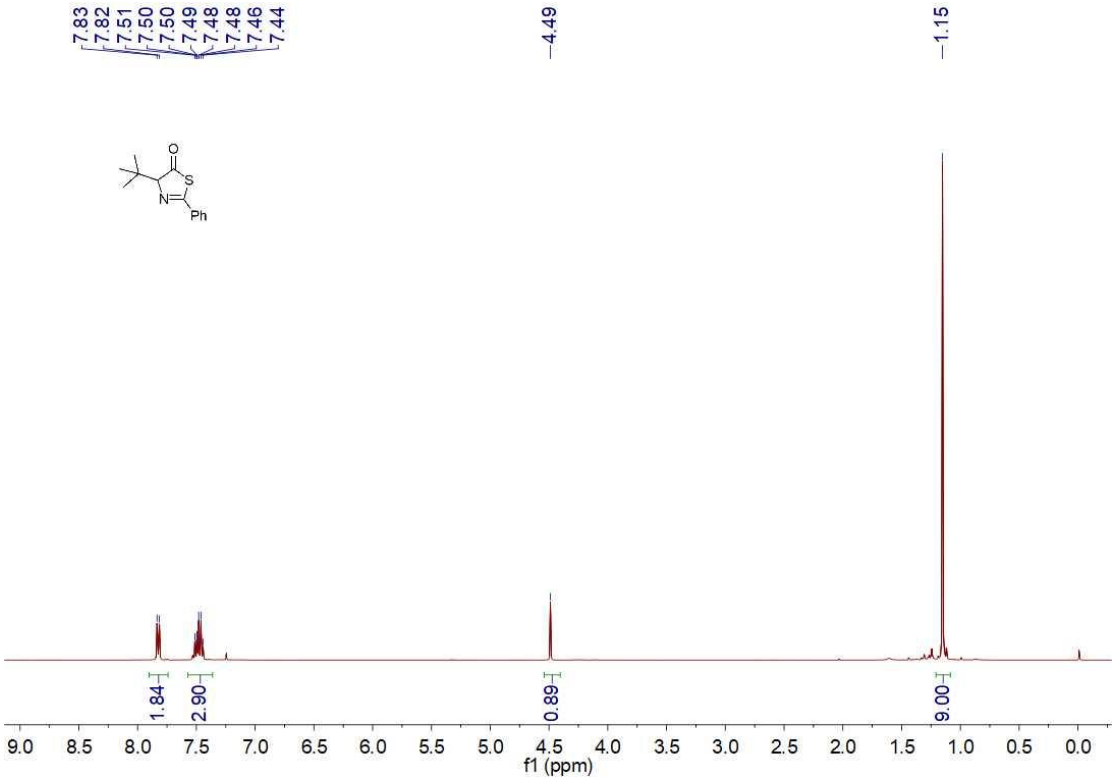
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
S
N
Ph

1m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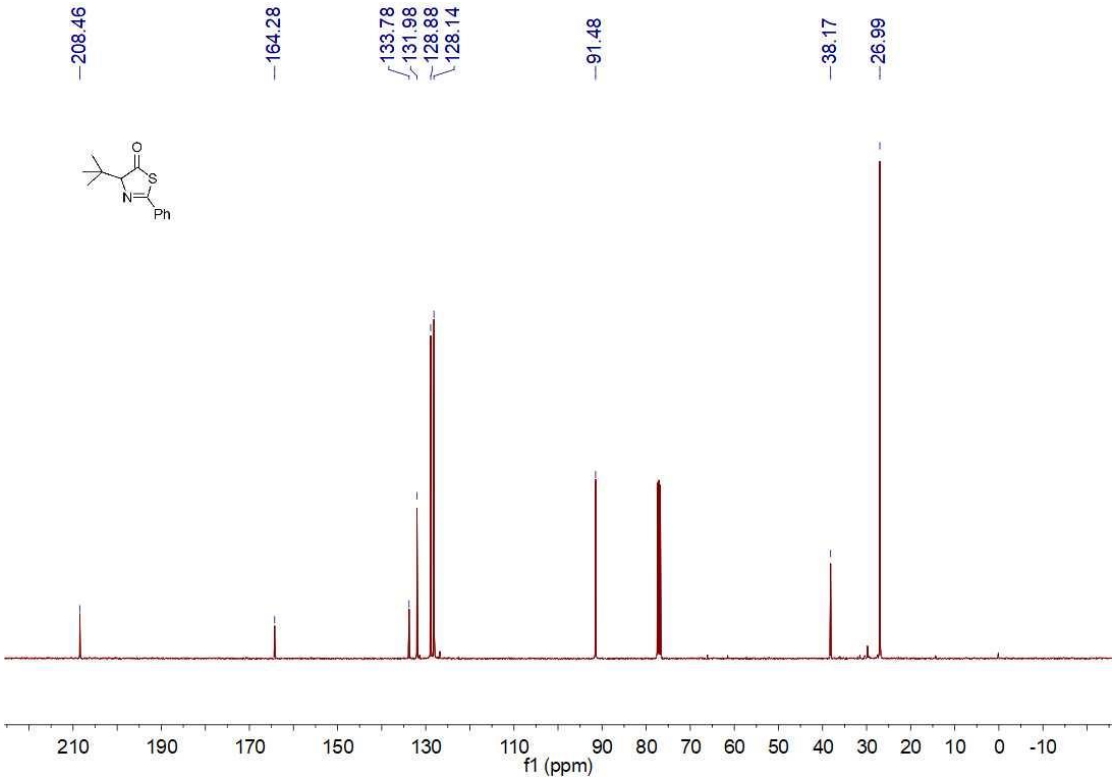
7.82
7.51
7.50
7.50
7.49
7.48
7.48
7.46
7.44
4.49
1.15
1.84
2.90
0.89
9.00
f1 (ppm)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164.28
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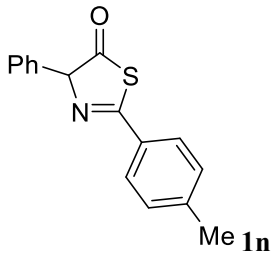
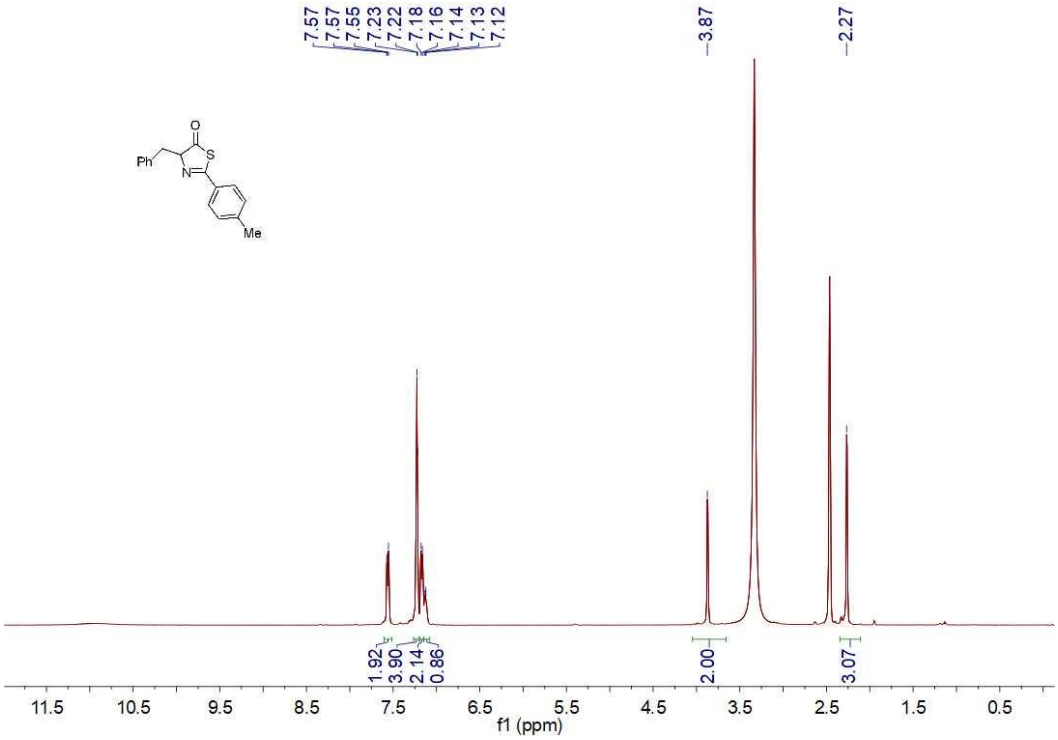
131.98
128.88
128.14
91.48
38.17
26.99
f1 (ppm)


O
Ph
S
N
Me

1n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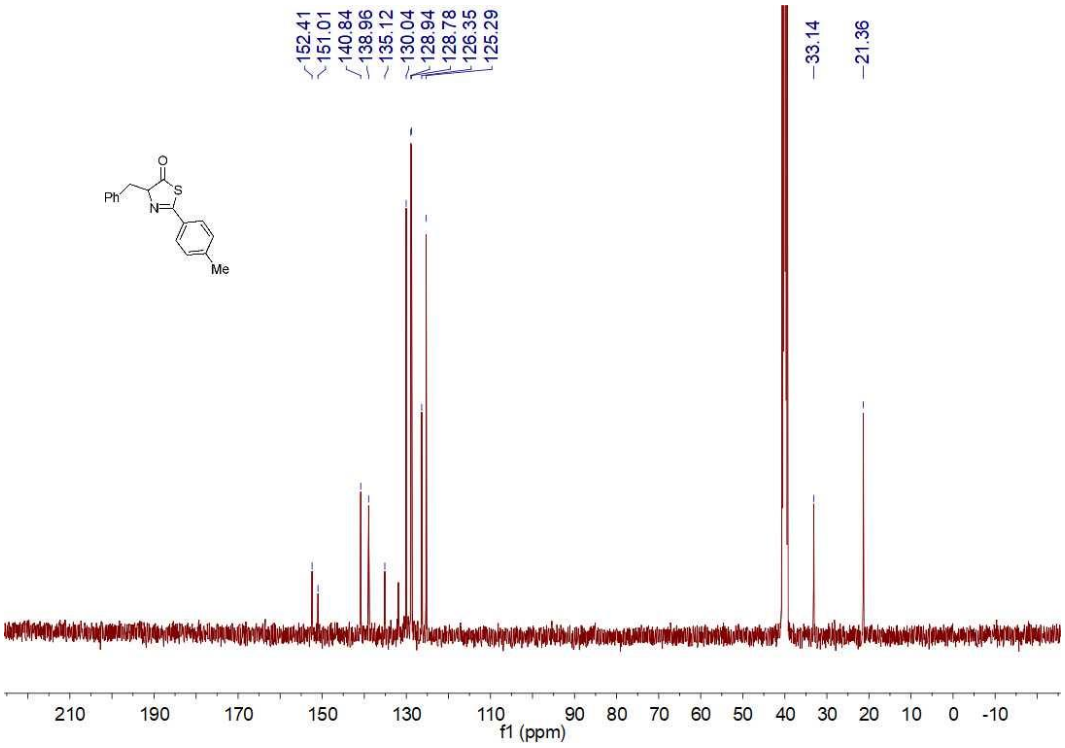
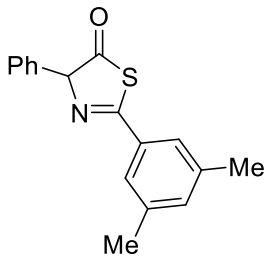
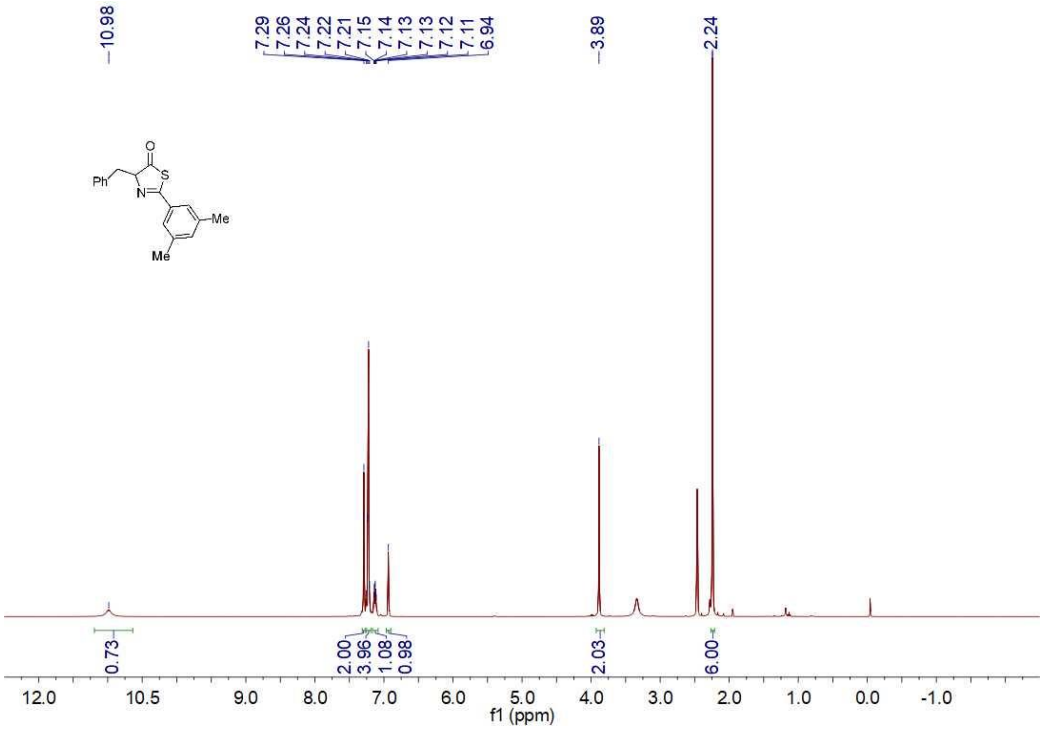
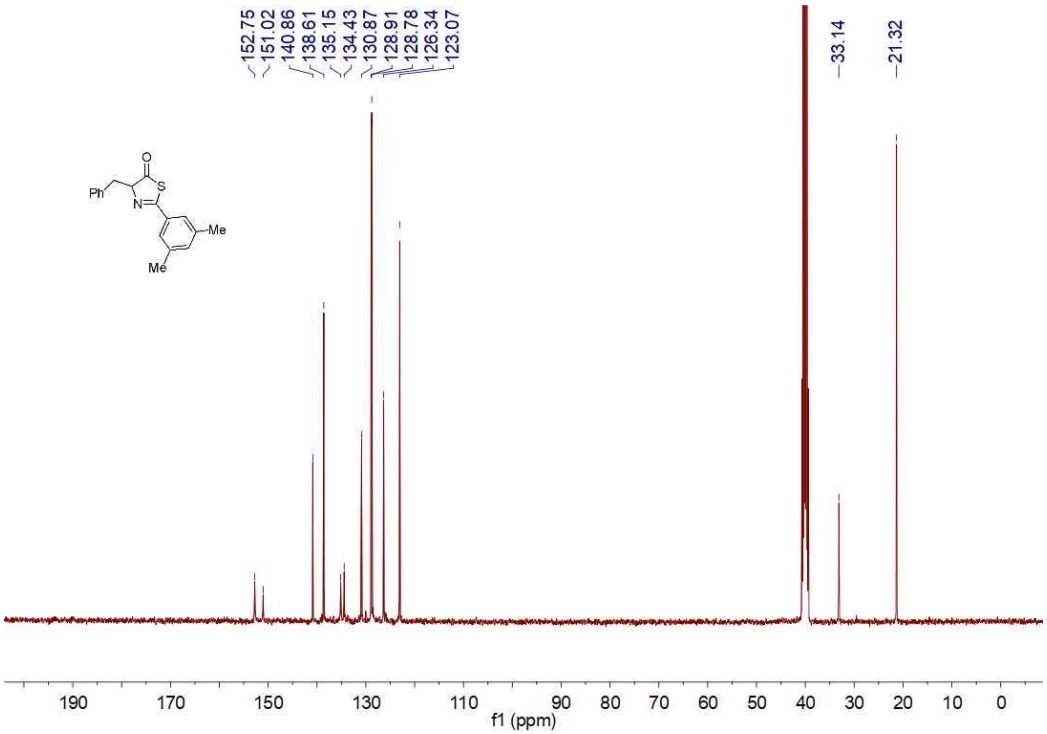
7.57
7.55
7.23
7.22
7.18
7.16
7.14
7.13
7.12
3.87
2.27
1.92
3.90
2.14
0.86
2.00
3.07
11.5
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

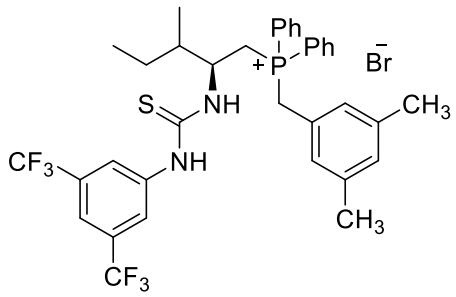

152.41
151.01
140.84
138.96
135.12
130.04
128.94
128.78
126.35
125.29
33.14
21.36
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


O
Ph
S
N
Me
Me

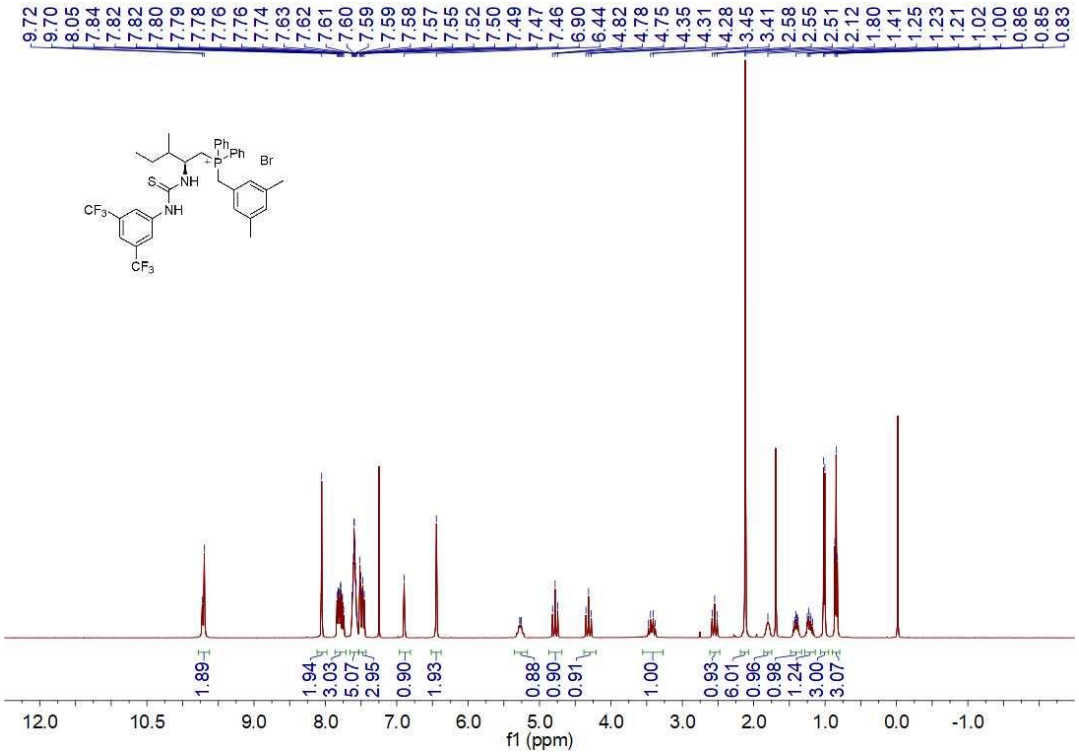
1o

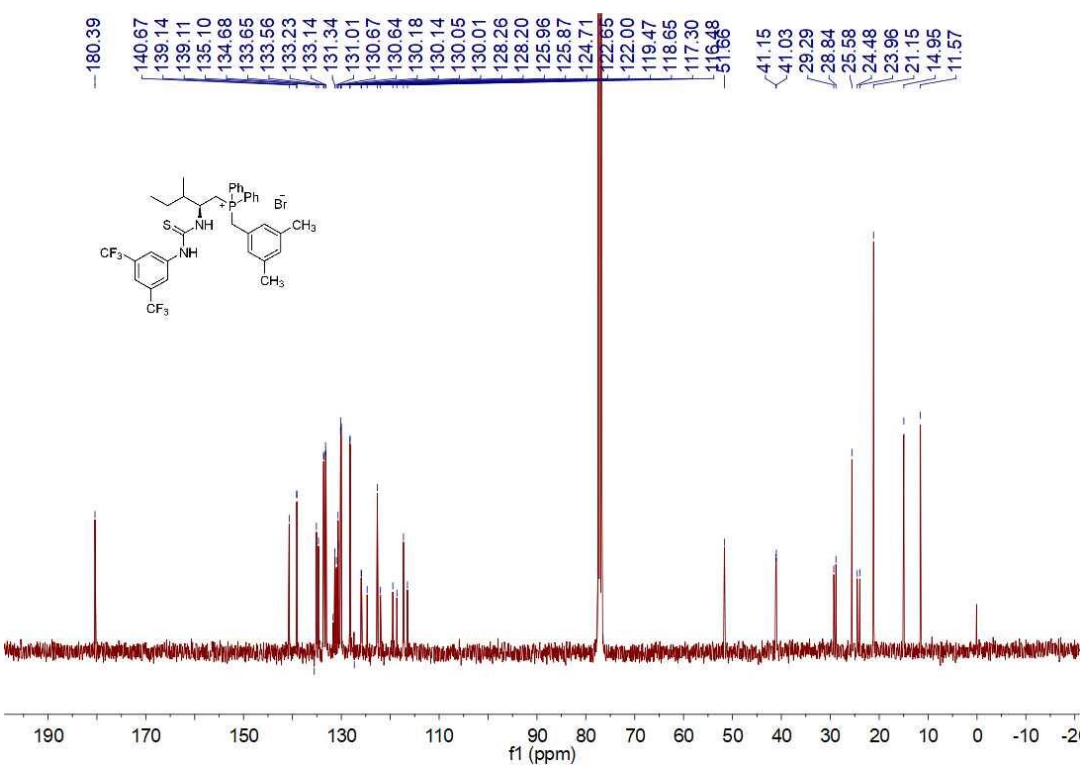

10.98
7.29
7.26
7.24
7.22
7.21
7.15
7.14
7.13
7.13
7.12
7.11
6.94
3.89
2.24
0.73
2.00
3.96
1.08
0.98
2.03
6.00
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

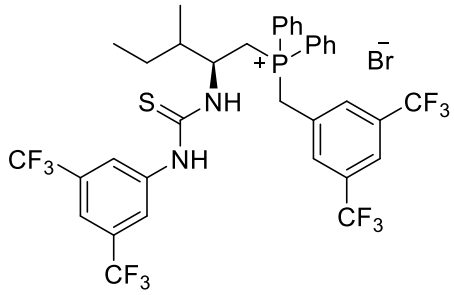

152.75
151.02
140.86
138.61
135.15
134.43
130.87
128.91
128.78
126.34
123.07
33.14
21.32
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



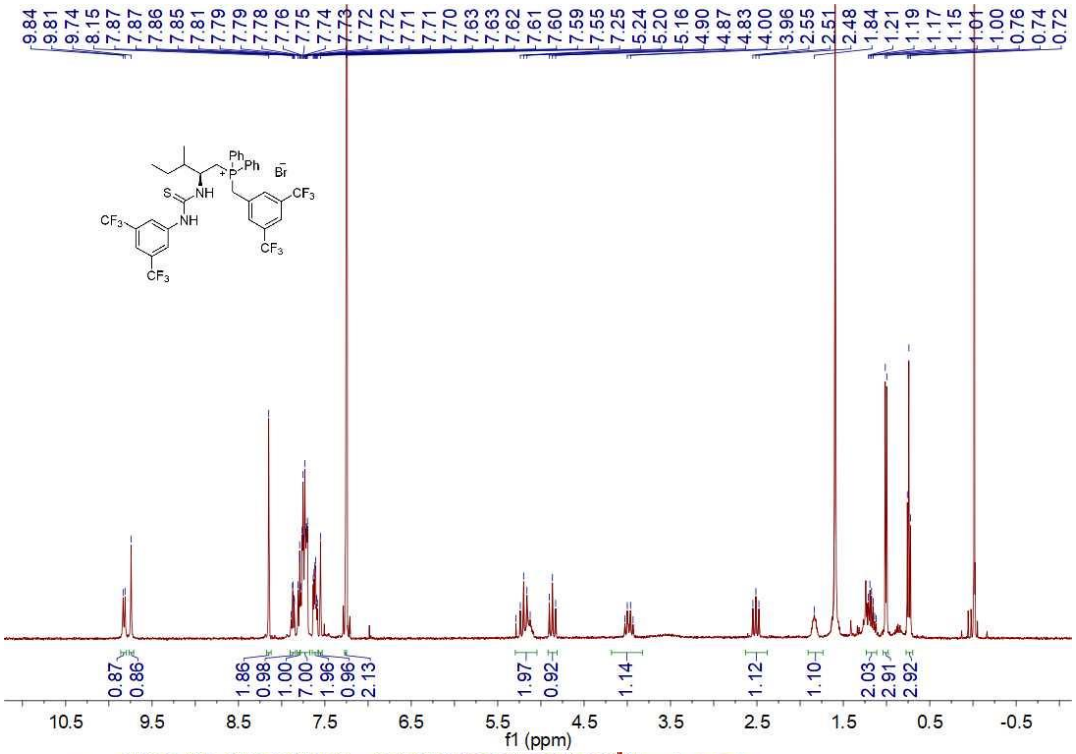
H

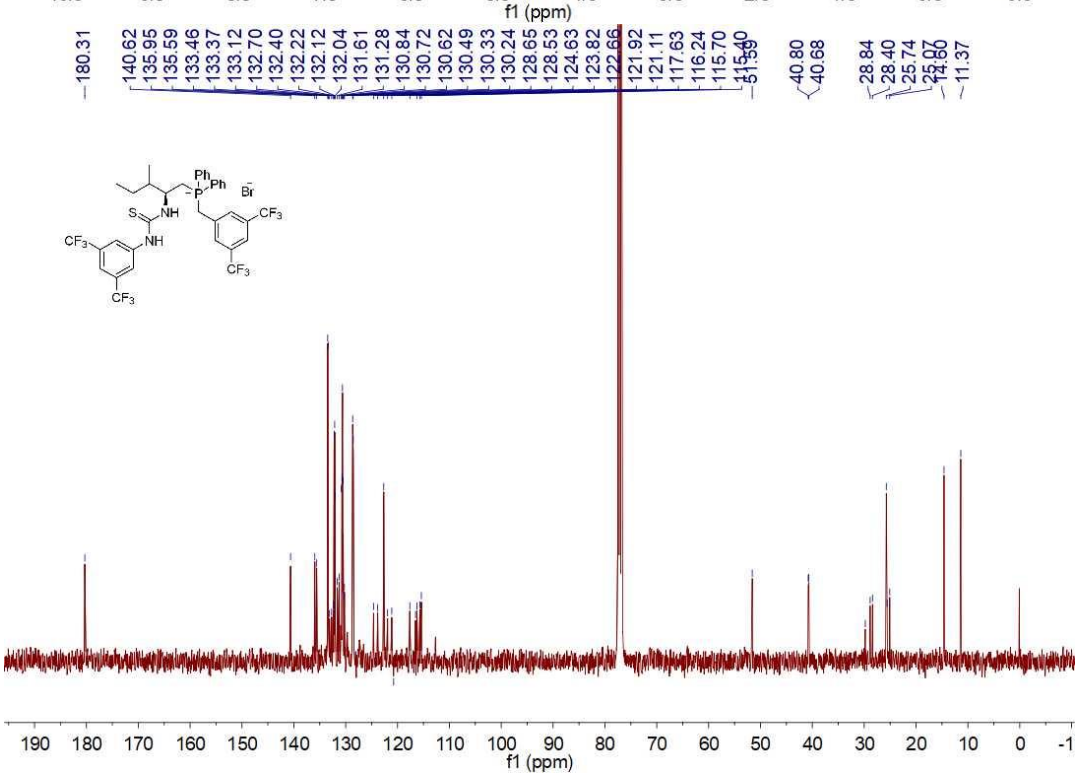

9.72 9.70 8.05 7.84 7.82 7.82 7.80 7.79 7.78 7.76 7.76 7.74 7.63 7.62 7.61 7.60 7.59 7.59 7.58 7.57 7.55 7.52 7.50 7.49 7.47 7.46 6.90 6.44 4.82 4.78 4.75 4.35 4.31 4.28 3.45 3.41 2.58 2.55 2.51 2.12 1.80 1.41 1.25 1.23 1.21 1.02 1.00 0.86 0.85 0.83
1.89 1.94 3.03 5.07 2.95 0.90 1.93 0.88 0.90 0.91 1.00 0.93 6.01 0.96 0.98 1.24 3.00 3.07
12.0 10.5 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

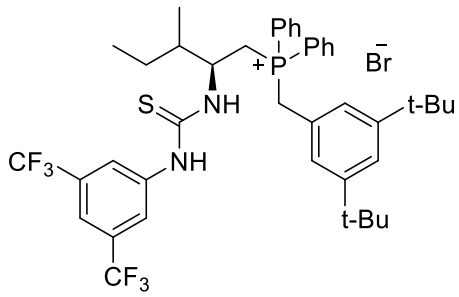

180.39 140.67 139.14 139.11 135.10 134.68 133.65 133.56 133.23 133.14 131.34 131.01 130.67 130.64 130.18 130.14 130.05 130.01 128.26 128.20 125.96 125.87 124.71 122.65 122.00 119.47 118.65 117.30 116.48 51.66 41.15 41.03 29.29 28.84 25.58 24.48 23.96 21.15 14.95 11.57
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



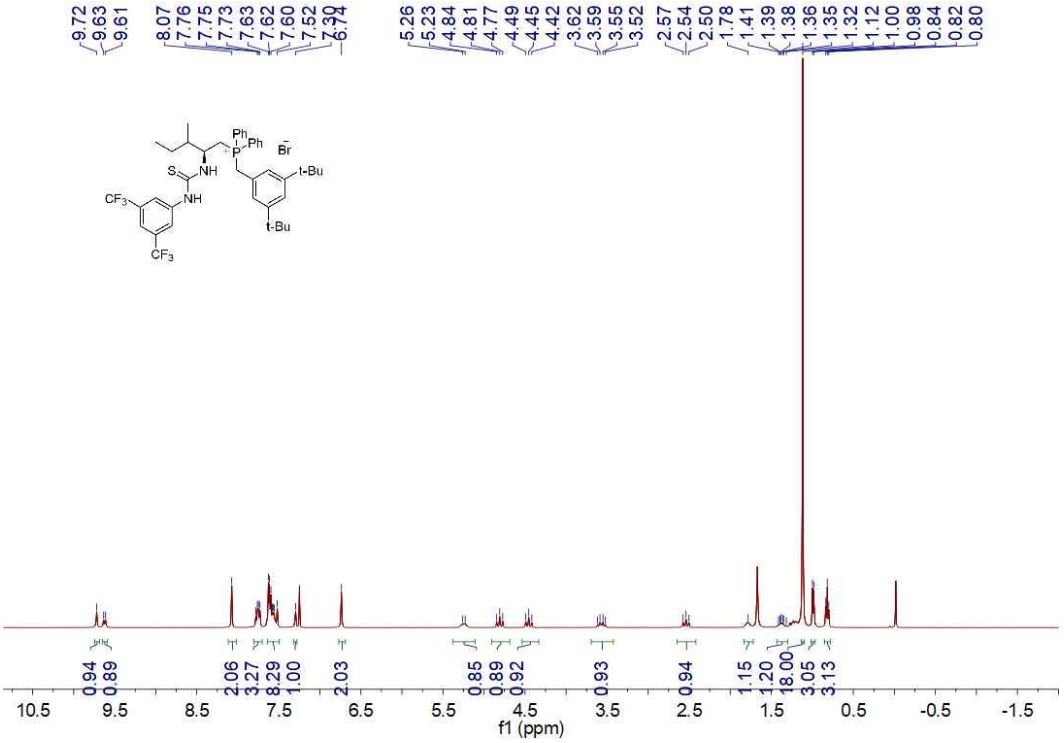
I

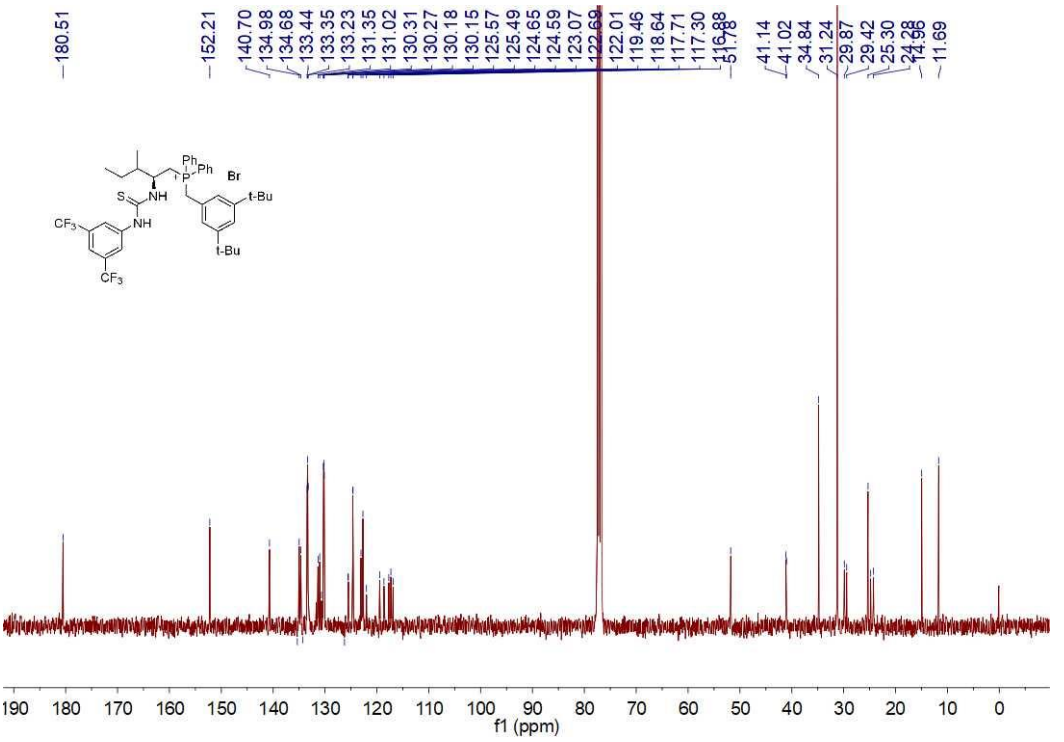

9.84 9.81 9.74 8.15 7.87 7.87 7.86 7.85 7.81 7.79 7.79 7.78 7.76 7.75 7.74 7.73 7.72 7.72 7.71 7.71 7.70 7.63 7.62 7.61 7.60 7.59 7.55 7.25 5.24 5.20 5.16 4.90 4.87 4.83 4.00 3.96 2.55 2.51 2.48 1.84 1.21 1.19 1.17 1.15 1.01 1.00 0.76 0.74 0.72
0.87 0.86 1.86 0.98 1.00 7.00 1.96 0.96 2.13 1.97 0.92 1.14 1.12 1.10 2.03 2.91 2.92
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)


180.31 140.62 135.95 135.59 133.46 133.37 133.12 132.70 132.40 132.22 132.12 132.04 131.61 131.28 130.84 130.72 130.62 130.49 130.33 130.24 128.65 128.53 124.63 123.82 122.66 121.92 121.11 117.63 116.24 115.70 40.80 40.68 28.84 28.40 25.74 14.80 11.37
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -1
f1 (ppm)


Ph
Ph
P
+
Br
S
NH
t-Bu
NH
CF3
t-Bu
CF3

J


9.72
9.63
9.61
8.07
7.76
7.75
7.73
7.63
7.62
7.60
7.52
7.30
6.74
5.26
5.23
4.84
4.81
4.77
4.49
4.45
4.42
3.62
3.59
3.55
3.52
2.57
2.54
2.50
1.78
1.41
1.39
1.38
1.36
1.35
1.32
1.12
1.00
0.98
0.84
0.82
0.80
0.94
0.89
2.06
3.27
8.29
1.00
2.03
0.85
0.89
0.92
0.93
0.94
1.15
1.20
18.00
3.05
3.13
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
-1.5
f1 (ppm)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152.21
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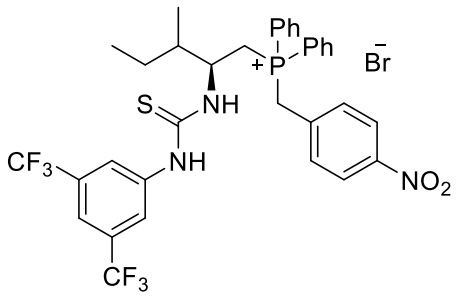
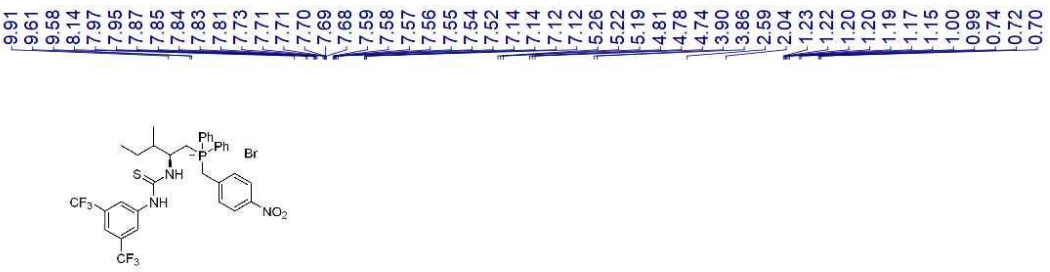
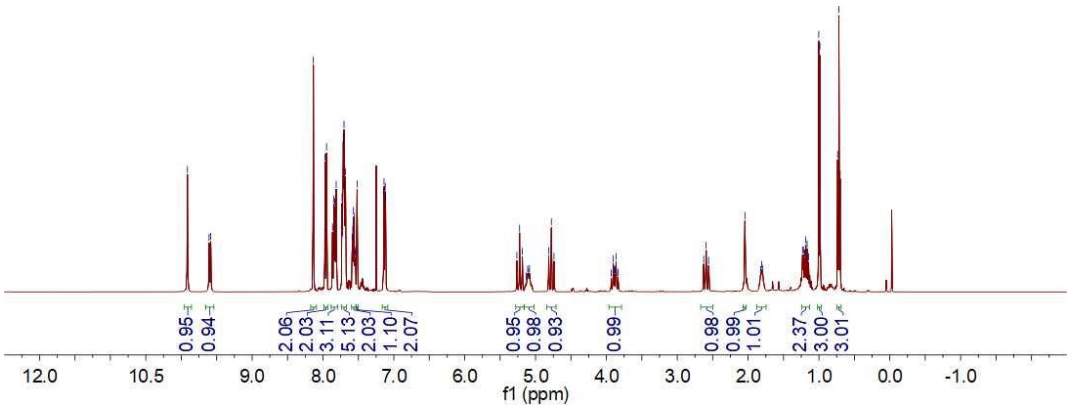
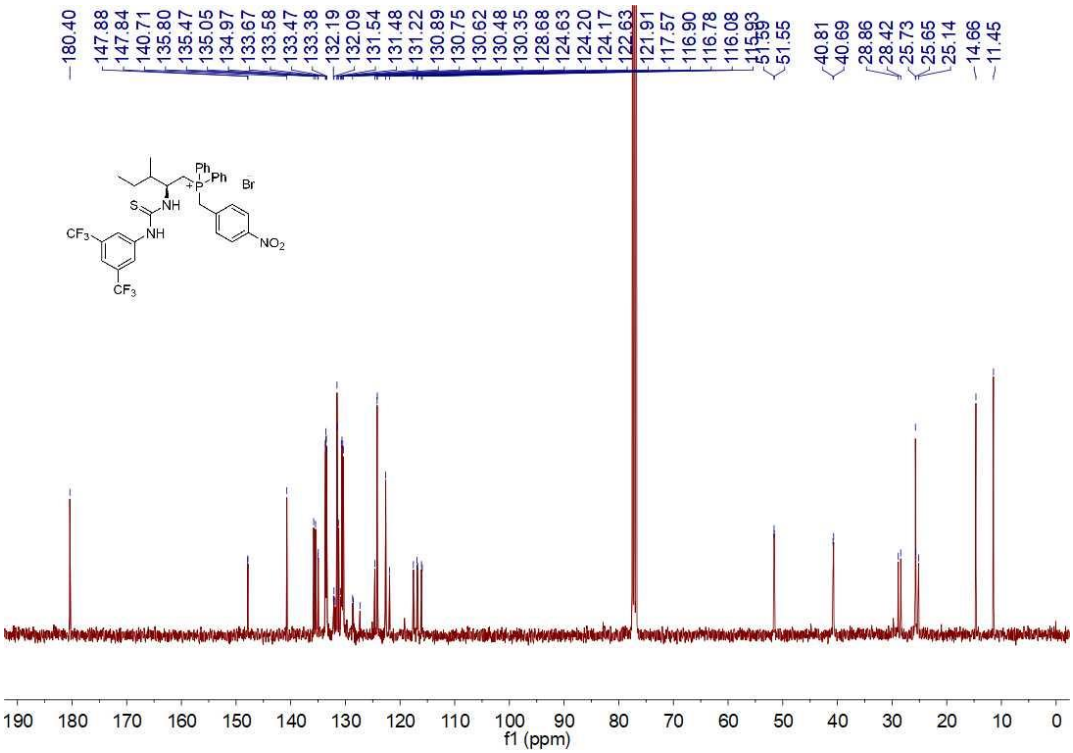
134.68
133.44
133.35
133.23
131.35
131.02
130.31
130.27
130.18
130.15
125.57
125.49
124.65
124.59
123.07
122.69
122.01
119.46
118.64
117.71
117.30
116.88
51.78
41.14
41.02
34.84
31.24
29.87
29.42
25.30
24.28
14.98
11.69
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

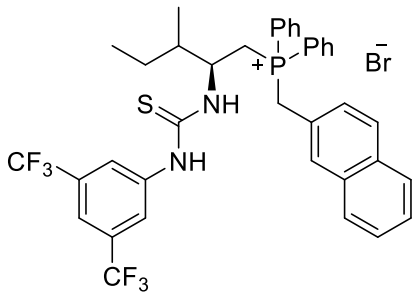


K








Ph
Ph
P
Br
S
NH
NH
CF3
CF3

L


9.85
9.65
9.63
8.08
7.80
7.78
7.77
7.76
7.75
7.75
7.74
7.73
7.73
7.63
7.61
7.60
7.59
7.57
7.55
7.54
7.53
7.52
7.51
7.49
7.47
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7.46
7.44
7.44
7.40
6.90
6.88
5.01
4.97
4.94
4.77
4.74
4.70
3.52
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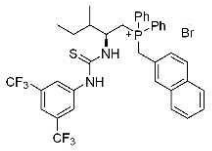
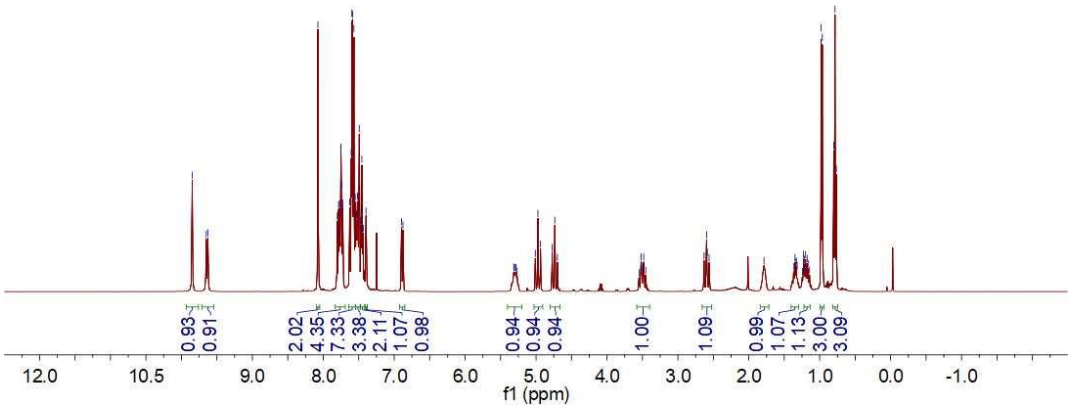
2.63
2.60
2.58
1.23
1.20
0.98
0.96
0.80
0.78
0.77




0.93
0.91
2.02
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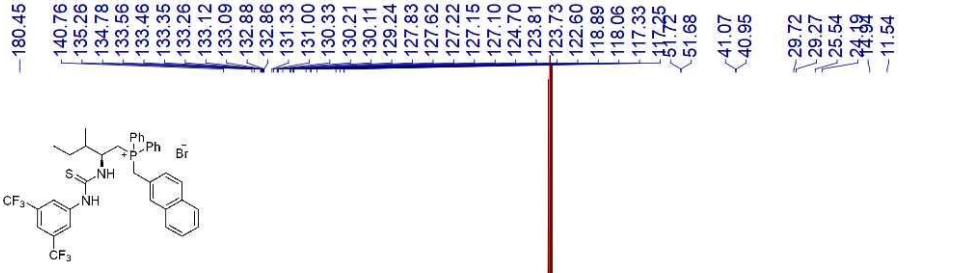
7.33
3.38
2.11
1.07
0.98
0.94
0.94
0.94
1.00
1.09
0.99
1.07
1.13
3.00
3.09
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)


180.45
140.76
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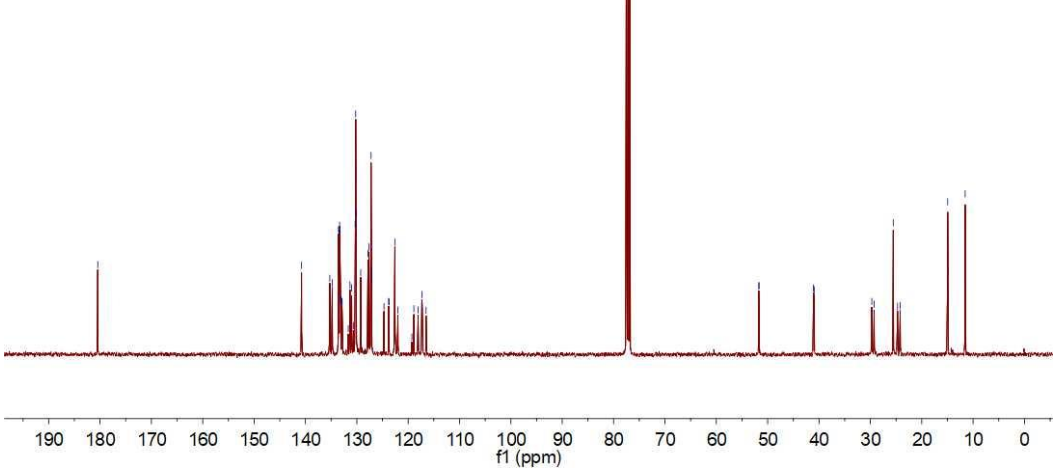
133.46
133.35
133.26
133.12
133.09
132.88
132.86
131.33
131.00
130.33
130.21
130.11
129.24
127.83
127.62
127.22
127.15
127.10
124.70
123.81
123.73
122.60
118.89
118.06
117.33
51.72
51.68
41.07
40.95
29.72
29.27
25.54
24.19
24.04
11.54


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)