Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for:

Access to Enantioenriched Dihydroquinoxalinones via Cu-Catalyzed Propargylic Substitutions

Yuxi Zhang, [&] Xiao Shu,[&] and Wusheng Guo*

Frontier Institute of Science and Technology (FIST)

Xi'an Jiaotong University, China

E-mail: wusheng.guo@mail.xjtu.edu.cn

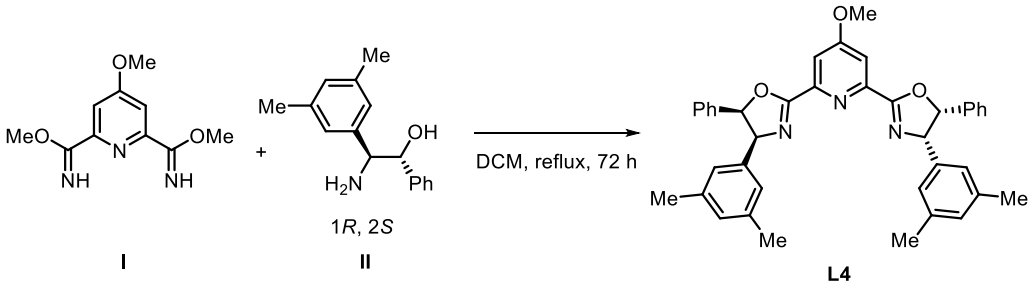
[&] *These authors contributed equally to this work*

Contents:

General comments

Commercially available reagents and solvents were purchased from Energy, *J*&K, TCI, Aladdin or Daicel, and used without further purification. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded at room temperature on a Bruker AV-400 spectrometer and referenced to the residual deuterated solvent signals. All reported NMR values are given in parts per million (ppm). FT-IR measurements were carried out on a Thermo Fisher Nicolet 6700 FT-IR spectrometer or Bruker ALPHA II. High resolution mass spectra (HRMS) were obtained on a WATERS I-Class VION IMS Qtof Spectrometer. The X-ray analysis of product **1** was collected at 100 K on a Rigaku Oxford Diffraction Supernova Dual Source, Cu at Zero equipped with an AtlasS2 CCD using Cu Kα radiation. Ligands **L1**, **L3** were synthesized according to a reported procedure.[1]

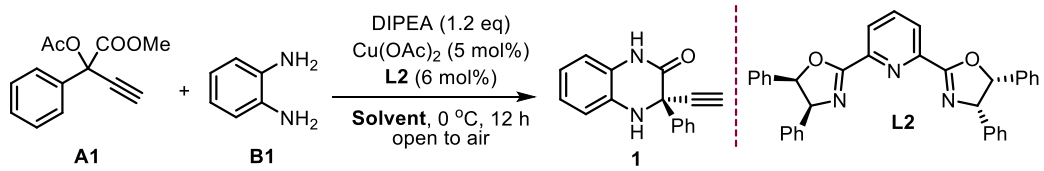
Synthesis of L4



Compound **I** (305.8mg, 1.37 mmol) was suspended in dry DCM (15 mL). Commercially available compound **II** (1*R*,2*S*)-2-amino-2-(3,5-dimethylphenyl)-1-phenylethan-1-ol (662.75 mg, 2.75 mmol)[2] was added and the mixture was refluxed for 72 h. The solvent was evaporated and the remaining solid was washed with water (15 mL) and MeOH (15 mL). Followed a recrystallization precedure in ethyl acetate to afford the desired products as a white crystalline solid (465.7 mg, 56%).

Selected screening data

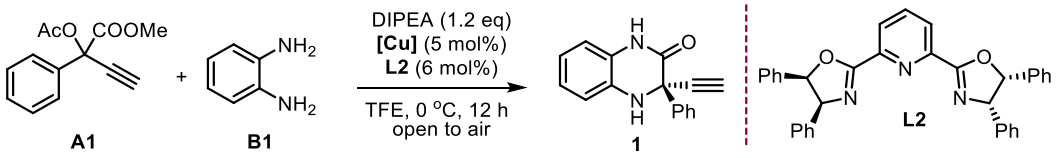
Table S1. Investigation of the solvent effect[a, b, c]



Entry	Solvent	Conv. (%)	Yield (%)	*ee* (%)
1	THF	100	0	-
2	1,4-Dioxane	100	0	-
3	2-Methoxyethanol	100	0	-
4	H_2O	100	0	-
5	ACN	100	0	-
6	DMF	100	0	-
7	DMSO	100	0	-
8	Hexane	95	70	0
9	Benzene	100	0	-
10	EtOH	100	63	40
11	MeOH	100	75	64
12	DCM	100	0	-
13	Ethyl acetate	100	0	-
14	Benzotrifluoride	100	0	-
15	TOL	100	0	-
16	TFE	100	82	80
17	**TFE/ACN=3/1**	**100**	**78**	**83**

[a] Reaction conditions until otherwise noted: the **A1** (0.1 mmol), **B1** (0.12 mmol, 1.2 eq), solvent (0.5 mL). [b] The yield was determined by ^{1}H NMR spectrum of the reaction crude in the presence of 2-methylnaphthalene as internal standard. [c] The *ee* value was determined by HPLC equipped with a chiral column.

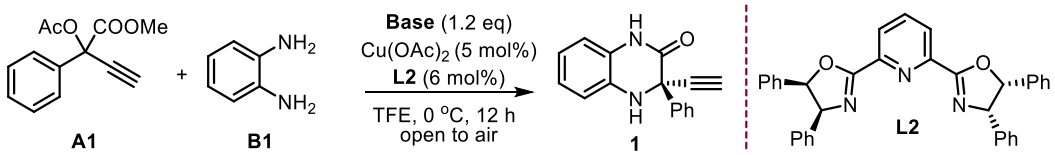
Table S2. Investigation of the effect of copper source [a, b, c]



Entry	[M]	Conv. (%)	Yield (%)	*ee* (%)
1	Cupric acetylacetonate	100	68	80
2	CuI	100	74	80
3	$Cu(OTf)_2$	100	79	80
4	$Cu(MeCN)_4PF_6$	100	55	80
5	$Cu(MeCN)_4BF_4$	100	72	80
6	CuCl	100	80	80
7	$CuBr_2$	100	51	71
8	CuBr	100	79	80
9	$CuSO_4$ $5H_2O$	100	67	80
10	CuCN	100	50	80
11	$Cu(ClO_4)_2$ $6H_2O$	100	85	75
12	**$Cu(OAc)_2$**	**100**	**82**	**80**

[a] Reaction conditions until otherwise noted: the **A1** (0.1 mmol), **B1** (0.12 mmol, 1.2 eq), solvent (0.5 mL). [b] The yield was determined by ^1H NMR spectrum of the reaction crude in the presence of 2-methylnaphthalene as internal standard. [c] The *ee* value was determined by HPLC equipped with a chiral column.

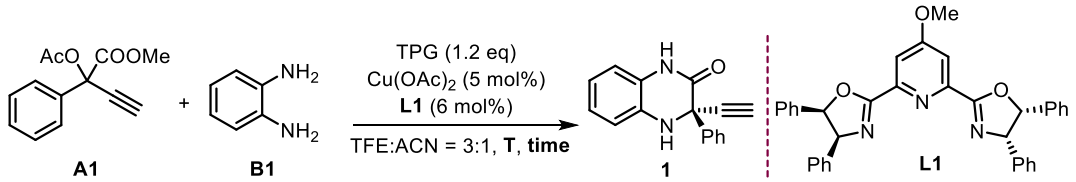
Table S3. Investigation of the base effect [a, b, c]



Entry	Base	Yield (%)	*ee* (%)
1	$CsCO_3$	17	82
2	K_2CO_3	60	82
3	$NaHCO_3$	48	40
4	NaOAc	37	42
5	Na_2CO_3	71	66
6	K_2HPO_4	68	80
7	K_3PO_4	51	80
8	NaH_2PO_4	37	25
9	Na_2HPO_4	36	26
10	Et_3N	80	80
11	DBU	63	80
12	-	51	16
13	DABCO	67	80
14	NEM	61	46
15	Cy_2NMe	19	82
16	TBD	27	81
17	Quinuclidine	66	82
18	Pyridine	53	35
19	**Triphenylguanidine**	**81**	**83**
20	Piperazine	54	81

[a] Reaction conditions until otherwise noted: the **A1** (0.1 mmol), **B1** (0.12 mmol, 1.2 eq), solvent (0.5 mL). [b] The yield was determined by ^{1}H NMR spectrum of the reaction crude in the presence of 2-methylnaphthalene as internal standard. [c] The *ee* value was determined by HPLC equipped with a chiral column.

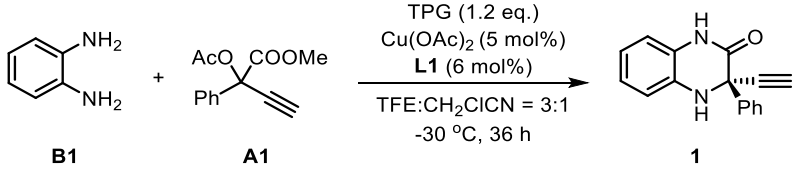
Table S4. Investigation of the effect of temperature [a, b, c]



Entry	T (^{o}C)	Time (h)	Yield (%)	*ee* (%)
1	0	12	78	84
2	-20	36	87	87
3	-30	36	**70**	**90**
4	-40	72	85	87

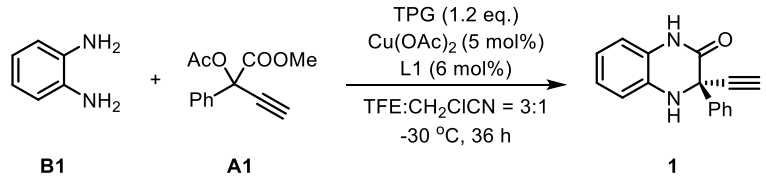
[a] Reaction conditions until otherwise noted: the **A1** (0.1 mmol), **B1** (0.12 mmol, 1.2 eq), solvent (0.5 mL). [b] The yield was determined by ^{1}H NMR spectrum of the reaction crude in the presence of 2-methylnaphthalene as internal standard. [c] The *ee* value was determined by HPLC equipped with a chiral column.

Typical procedure for the synthesis of dihydroquinoxalinones



A mixture of $Cu(OAc)_2$ (0.9 mg, 0.005 mmol, 5 mol%) and **L1** (3.3 mg, 0.006 mmol, 6 mol%) in TFE/CH_2ClCN (3/1, v/v, 0.5 mL) was stirred for 1 h at room temperature. Then, a solution of propargylic acetate **A1** (23.2 mg, 0.1 mmol, 1.0 eq.), *o*-phenylenediamine (13.0 mg, 0.12 mmol, 1.2 eq.) and TPG (1,2,3-triphenylguanidine) (34.4 mg, 0.12 mmol, 1.2 eq.) in a mixed solvent TFE/CH_2ClCN (3/1, v/v, 0.5 mL) was added dropwise. The resulting mixture was stirred at -30 ^{o}C for 36 h. After that, the reaction mixture was filtered through a silica plug and concentrated under vacuo. The resultant crude was purified by column chromatography (PE:EA = 2:1) to afford the desired product **1** as a white solid (21.3 mg, 86%, 94% *ee*).

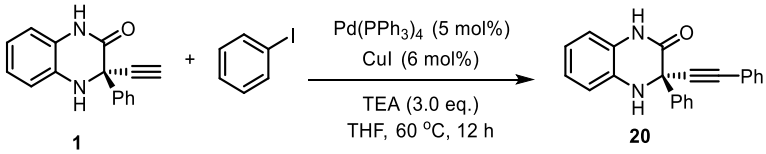
Gram-scale reactions



B1 **A1** **1**

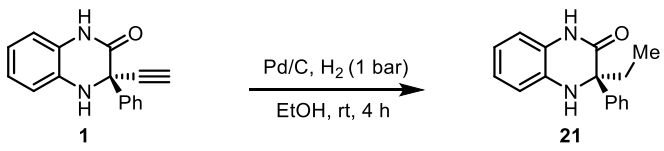
A mixture of $Cu(OAc)_2$ (45 mg, 0.25 mmol, 5 mol%) and **L1** (165 mg, 0.3 mmol, 6 mol%) in TFE/CH_2ClCN (3/1, v/v, 25 mL) was stirred for 1 h at room temperature. Then, a solution of propargylic acetate **A1** (1.16 g, 5 mmol, 1.0 eq.), *o*-phenylenediamine (650 mg, 6 mmol, 1.2 eq.) and TPG (1,2,3-triphenylguanidine) (1.72 g, 6 mmol, 1.2 eq.) in the mixed solvent TFE/CH_2ClCN (3/1, v/v, 25 mL) was added dropwise. The mixture was stirred at -30 ^oC for 36 h, and then filtered through a silica plug, concentrated in vacuo. The resultant crude was purified by column chromatography (PE:EA = 2:1) to afford the desired product **1** as a white solid (0.92 g, 74%, 92% *ee*).

Synthetic transformations of product 1



1 **20**

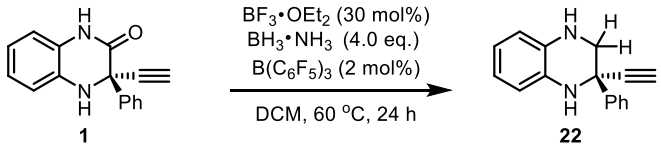
In a N_2-filled glovebox, a 2 mL of screw-capped vial was charged with **1** (0.1 mmol, 24.8 mg, 1.0 eq.), iodobenzene (24.4 mg, 0.12 mmol, 1.2 eq.), $Pd(PPh_3)_4$ (5.7 mg, 0.005 mmol, 5.0 mol%), CuI (1.0 mg, 0.006 mmol, 6.0 mol%), TEA (42 μL, 0.3 mmol, 3.0 eq.) and THF (0.5 mL). The reaction mixture was stirred at 60 ^oC for 12 h. After the completion of the reaction (monitored by TLC), the mixture was filtered through a silica plug and concentrated under reduced pressure. The resultant crude product was purified by column chromatography (PE:EA = 5:1) to afford the product **20** as a yellow solid (24.3 mg, 75%, 94% *ee*).



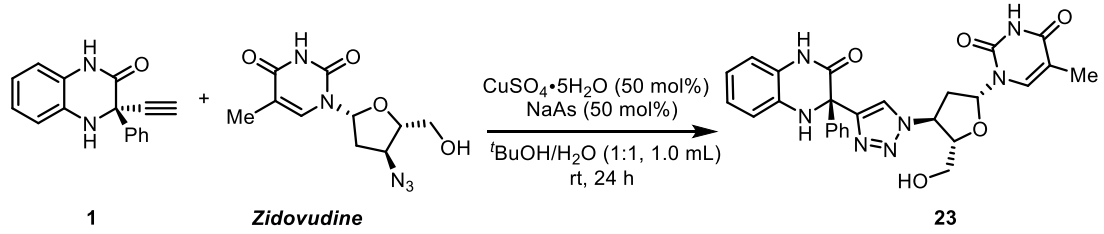
1 **21**

To a solution of **1** (24.8 mg, 0.1 mmol, 1.0 eq.) in EtOH (2 mL) was carefully added Pd/C (1.1 mg, 10 mol%) under nitrogen atmosphere. The reaction mixture was degassed and purged with hydrogen. The reaction is allowed to stir for 4 h at room

temperature. After the completion of the reaction, the mixture was filtered through a celite pad and washed with ethyl acetate. The solvents were removed and concentrated under reduced pressure. The resultant crude mixture was purified by column chromatography (PE:EA = 5:1) to afford the product **21** as a yellow solid (20.2 mg, 80%, 94% *ee*).

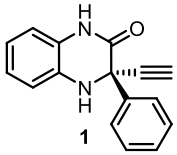


To a pressure tubing was added amide **1** (62.0 mg, 0.25 mmol), $B(C_6F_5)_3$ (2.56 mg, 2 mol %), NH_3•BH_3 (30.87 mg, 1.0 mmol, 4.0 eq.), BF_3•OEt_2 (10.64 mg, 30 mol%) and DCM (1.5 mL). Then the reaction mixture was stirred at 60 ℃ for 24 h. After cooling to ambient temperature, the mixture was diluted with ethyl acetate (5 mL). Then aqueous NaOH (5 mL, 4 M) was added to the reaction mixture, and then was extracted with ethyl acetate (5 mL). The combined organic phases were dried over Na_2SO_4, filtered and evaporated under reduced pressure. After removal of volatile materials by rotary evaporation, the resultant mixture was purified by column chromatography (PE:EA = 5:1) to afford the corresponding pure product **22** as a yellow solid (42.7 mg, 73%, 97% *ee*).



A screw-capped vial was charged with **1** (24.8 mg, 0.1 mmol), zidovudine (31 mg, 0.11 mmol) and ^{t}BuOH (0.5 mL). Afterward, a freshly prepared solution of sodium ascorbate (9.9 mg, 0.05 mmol) and $CuSO_4$ $5H_2O$ (12.5 mg, 0.05 mmol) in H_2O (0.5 mL) was added. The reaction mixture was stirred at room temperature for 24 h and then was extracted with EA (5 mL). The combined organic layer was dried over Na_2SO_4 and concentrated under vacuum. The residue was then purified by column chromatography (DCM/MeOH = 25:1) to offord the desired product **23** (48.1 mg, 93%, 95% *ee*) as a white solid.

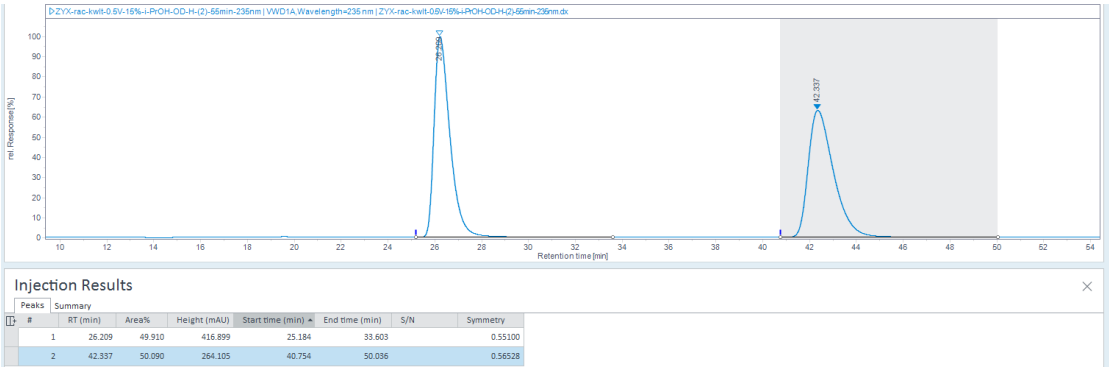
Characterization data of all the new compounds

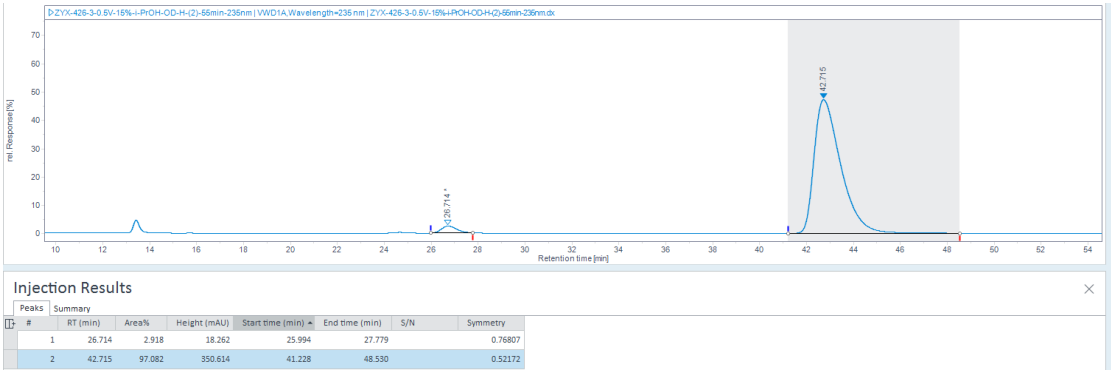


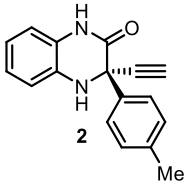
1

(*R*)-3-ethynyl-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (1): white solid; mp 154-155 ^{o}C; 21.4 mg, 86% yield; 94% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -353.94 (*c* = 1.65, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.85-7.76 (m, 2H), 7.47-7.37 (m, 3H), 6.99 (td, *J* = 7.6, 1.3 Hz, 1H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 6.79 (dd, *J* = 7.1, 4.9 Hz, 2H), 4.42 (s, 1H), 2.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 138.3, 132.2, 129.1, 128.6, 127.8, 125.5, 124.2, 120.8, 115.7, 115.0, 81.2, 76.8, 61.4; IR (neat, cm^{-1}) 3277, 1685, 1607, 1505, 1448, 1355, 1312, 749, 699; HRMS (ESI): *m/z*: calcd for $C_{16}H_{12}N_2ONa$ $[M+Na]^+$: 271.0847, found: 271.0852.

The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 26.7 min (minor) and 42.7 min (major).



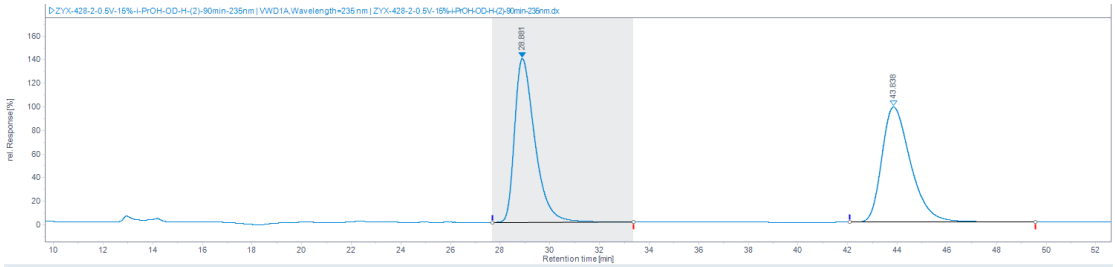




2

(*R*)-3-ethynyl-3-(p-tolyl)-3,4-dihydroquinoxalin-2(1*H*)-one (2): white solid; mp 91-93 °C; 21.2 mg, 81% yield; 92% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -112.73 (*c* = 1.10, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (s, 1H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.97 (td, *J* = 7.6, 1.3 Hz, 1H), 6.86 (td, *J* = 7.6, 1.2 Hz, 1H), 6.78 (d, *J* = 7.8 Hz, 2H), 4.40 (s, 1H), 2.66 (s, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 139.0, 135.4, 132.3, 129.3, 127.6, 125.5, 124.1, 120.7, 115.5, 115.0, 81.3, 76.6, 61.2, 21.3; IR (neat, cm^{-1}) 3279, 3057, 1684, 1607, 1505, 1447, 1353, 1311, 1227, 812, 744; HRMS (ESI): *m/z*: calcd for $C_{17}H_{14}N_2ONa$ $[M+Na]^+$: 285.1004, found: 285.1010.

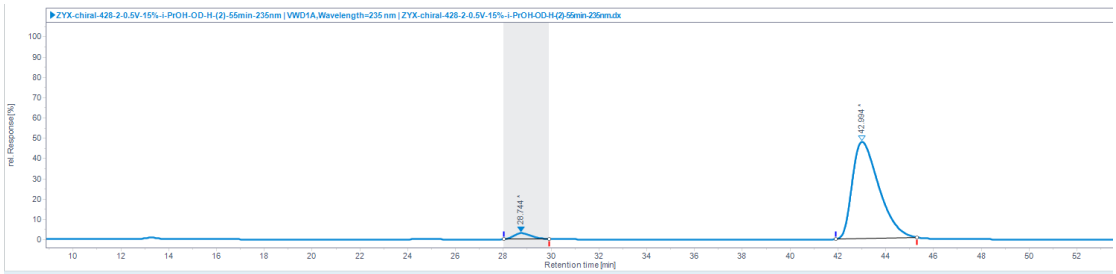
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 °C; 235 nm; retention time: 28.7 min (minor) and 43.0 min (major).



Injection Results

Peaks | Summary

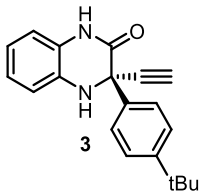
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	28.881	49.858	152.107	27.701	33.376		0.58031
2	43.838	50.142	107.035	42.074	49.559		0.64727



Injection Results

Peaks | Summary

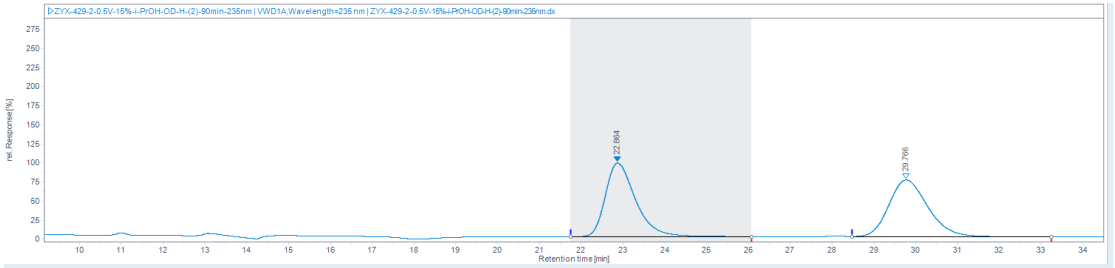
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	28.744	3.769	31.221	28.034	29.934		0.72113
2	42.994	96.231	512.662	41.894	45.288		0.55156

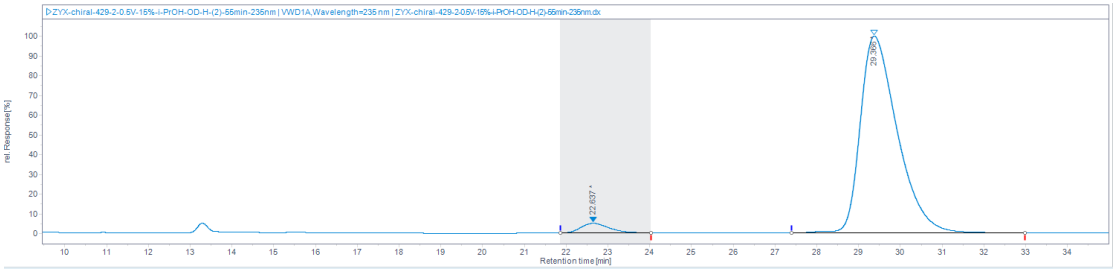


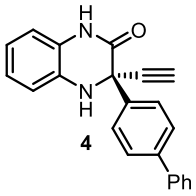
(*R*)-3-(4-(tert-butyl)phenyl)-3-ethynyl-3,4-dihydroquinoxalin-2(1*H*)-one (3): white solid; mp 82-83 °C; 21.9 mg, 72% yield; 93% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -233.68 (*c* = 0.95, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.74 (s, 1H), 7.73 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 6.96 (td, *J* = 7.6, 1.2 Hz, 1H), 6.84 (t, *J* = 7.5 Hz, 1H), 6.81-6.72 (m, 2H), 4.42 (s, 1H), 2.66 (s, 1H), 1.33 (s, 9H); ^{13}C NMR (100

MHz, $CDCl_3$) δ 165.5, 152.0, 135.4, 132.3, 127.4, 125.6, 125.5, 124.1, 120.6, 115.7, 114.9, 81.4, 76.5, 61.1, 34.7, 31.4; IR (neat, cm^{-1}) 3283, 2952, 1686, 1608, 1506, 1459, 1360, 1311, 735; HRMS (ESI): *m/z*: calcd for $C_{20}H_{20}N_2ONa$ $[M+Na]^+$: 327.1473, found: 327.1473.

The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 °C; 235 nm; retention time: 22.6 min (minor) and 29.4 min (major).



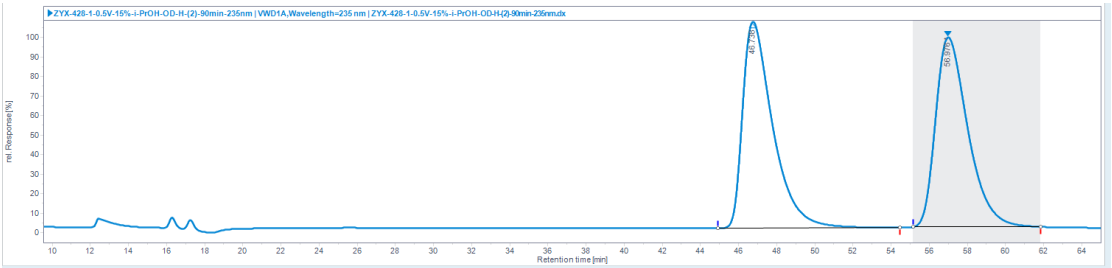




4

(*R*)-3-([1,1'-biphenyl]-4-yl)-3-ethynyl-3,4-dihydroquinoxalin-2(1*H*)-one (4): white solid; mp 59-61 °C; 24.3 mg, 75% yield; 93% *ee*; R_f = 0.3 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -128.18 (*c* = 1.10, $CHCl_3$); ^1H NMR (400 MHz, $CDCl_3$) δ 8.67 (s, 1H), 7.96-7.83 (m, 2H), 7.74-7.54 (m, 4H), 7.52-7.41 (m, 2H), 7.41-7.34 (m, 1H), 6.98 (td, *J* = 7.6, 1.5 Hz, 1H), 6.86 (td, *J* = 7.7, 1.2 Hz, 1H), 6.83-6.75 (m, 2H), 4.47 (s, 1H), 2.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 142.0, 140.7, 137.3, 132.2, 128.9, 128.2, 127.7, 127.4, 127.3, 125.5, 124.2, 120.8, 115.7, 115.0, 81.2, 76.9, 61.2; IR (neat, cm^{-1}) 3283, 3058, 2925, 1685, 1607, 1505, 1355, 1311, 909, 733, 697, 655; HRMS (ESI): *m/z*: calcd for $C_{22}H_{16}N_2ONa$ $[M+Na]^+$: 347.1160, found: 347.1161.

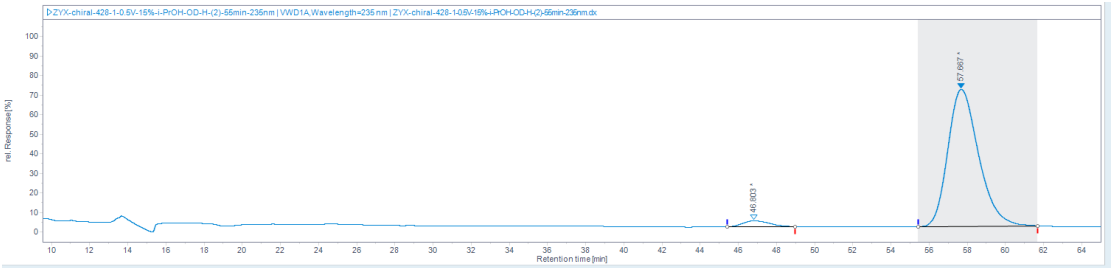
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 46.8 min (minor) and 57.7 min (major).



Injection Results

Peaks | Summary

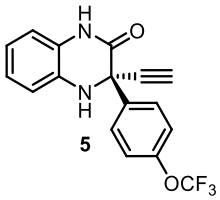
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	46.738	50.421	145.998	44.904	54.465		0.48572
2	56.976	49.579	134.094	55.158	61.834		0.60833



Injection Results

Peaks | Summary

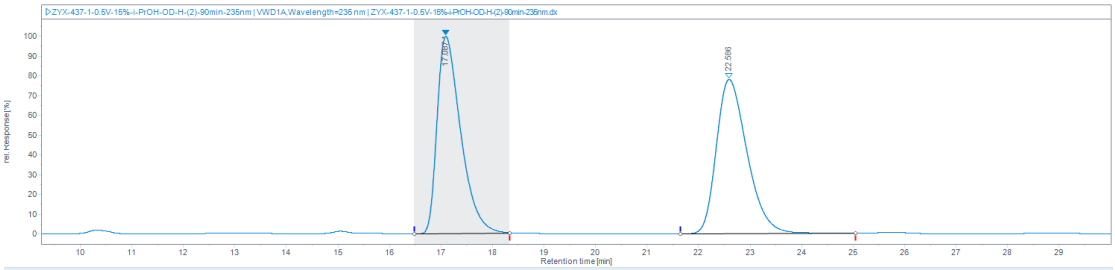
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	46.803	3.693	1.015	45.398	48.986		0.71550
2	57.667	96.307	23.245	55.422	61.687		0.74043



5

(*R*)-3-ethynyl-3-(4-(trifluoromethoxy)phenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (5): yellow solid; mp 94-95 ^{o}C; 25.2 mg, 76% yield; 89% *ee*; R_f = 0.3 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -228.57 (*c* = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H), 7.86 (d, *J* = 8.7 Hz, 2H), 7.31-7.26 (m, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.85-6.75 (m, 2H), 4.40 (s, 1H), 2.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 149.8, 136.8, 132.0, 129.6, 125.4, 124.4, 121.1, 120.84, 120.6 (q, *J* = 258.6 Hz), 115.6, 115.2, 80.7, 77.3, 61.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.72; IR (neat, cm^{-1}) 3289, 3068, 1686, 1609, 1506, 1258, 1167, 748; HRMS (ESI): *m/z*: calcd for $C_{17}H_{11}N_2O_2NaF_3$ $[M+Na]^+$: 355.0670, found: 355.0676.

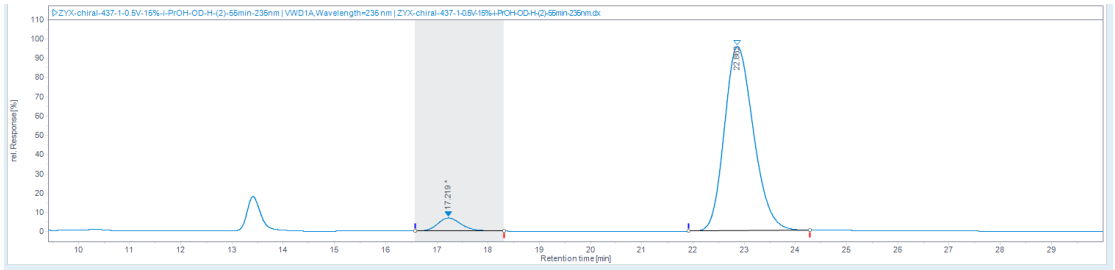
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 17.2 min (minor) and 22.9 min (major).



Injection Results

Peaks | Summary

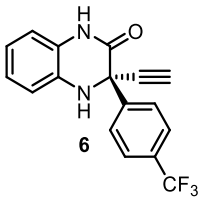
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	17.087	49.457	1059.197	16.476	18.327		0.55264
2	22.586	50.543	828.018	21.646	25.039		0.67214



Injection Results

Peaks | Summary

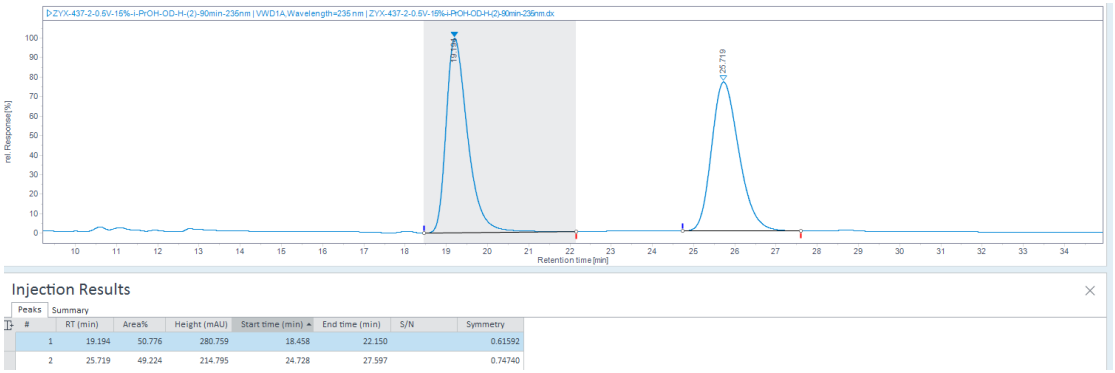
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	17.219	5.458	14.067	16.569	18.314		0.77921
2	22.862	94.542	198.205	21.916	24.276		0.78027



6

(*R*)-3-ethynyl-3-(4-(trifluoromethyl)phenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (6): yellow solid; mp 75-76 ^{o}C; 25.3 mg, 80% yield; 89% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -264.00 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.96 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.81 (t, *J* = 7.6 Hz, 2H), 4.42 (s, 1H), 2.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) one carbon signal was overlapped δ 164.4, 142.1, 131.9, 131.3 (q, *J* = 32.3 Hz), 128.4, 125.6 (q, *J* = 4.0 Hz), 125.3, 124.4, 121.2, 115.7, 115.3, 109.6 (q, *J* = 269.8 Hz), 80.5, 61.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.67; IR (neat, cm^{-1}) 3293, 1687, 1609, 1506, 1411, 1325, 1167, 1069, 749; HRMS (ESI): *m/z*: calcd for $C_{17}H_{11}N_2OF_3Na$ $[M+Na]^+$: 339.0721, found: 339.0724.

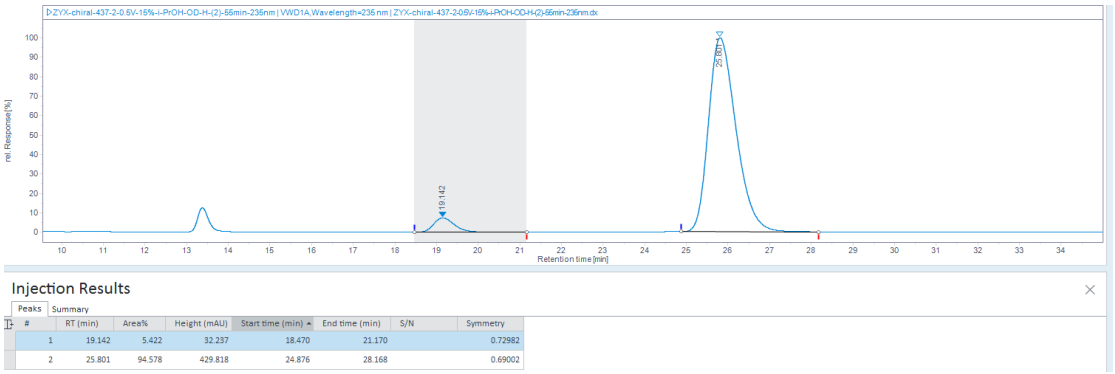
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 19.1 min (minor) and 25.8 min (major).



Injection Results

Peaks | Summary

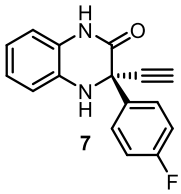
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	19.194	50.776	280.759	18.458	22.150		0.61592
2	25.719	49.224	214.795	24.728	27.597		0.74740



Injection Results

Peaks | Summary

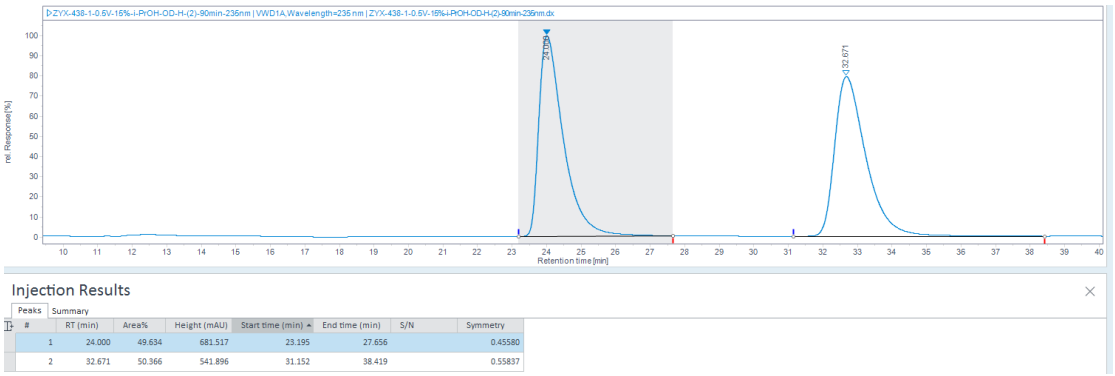
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	19.142	5.422	32.237	18.470	21.170		0.72982
2	25.801	94.578	429.818	24.876	28.168		0.69002



7

(*R*)-3-ethynyl-3-(4-fluorophenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (7): yellow solid; mp 90-92 ^{o}C; 21.5 mg, 81% yield; 90% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -159.41 (*c* = 1.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.55 (d, *J* = 8.6 Hz, 2H), 7.00 (t, *J* = 7.6 Hz, 1H), 6.89 (t, *J* = 7.6 Hz, 1H), 6.80 (t, *J* = 6.6 Hz, 2H), 4.39 (s, 1H), 2.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 163.2 (d, *J* = 247.0 Hz), 134.0 (d, *J* = 3.0 Hz), 132.1, 129.8 (d, *J* = 9.1 Hz), 125.4, 124.3, 121.0, 115.6 (d, *J* = 7.1 Hz), 115.4, 115.1, 81.0, 77.1, 60.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.08; IR (neat, cm^{-1}) 3290, 3063, 1684, 1606, 1505, 1355, 1312, 1226, 837, 746; HRMS (ESI): *m/z*: calcd for $C_{16}H_{11}N_2OFNa$ $[M+Na]^+$: 289.0753, found: 289.0756.

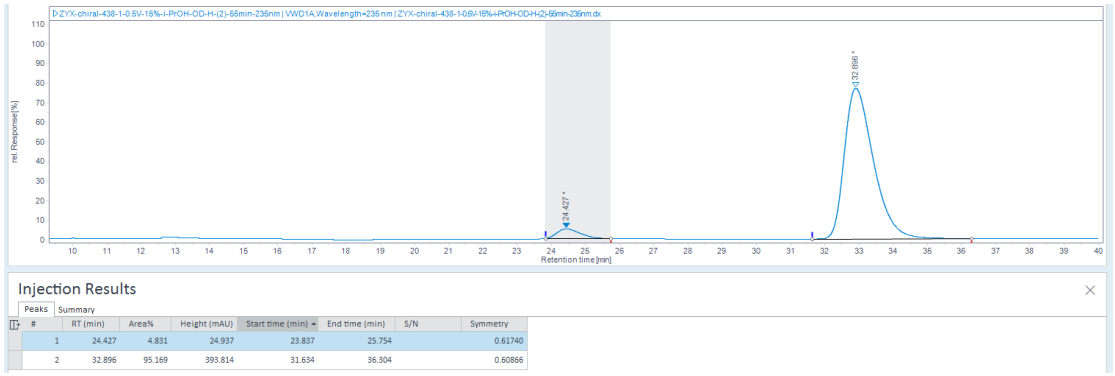
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 24.4 min (minor) and 32.9 min (major).



Injection Results

Peaks | Summary

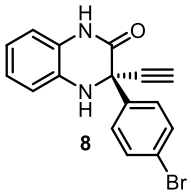
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	24.000	49.634	681.517	23.195	27.656		0.45580
2	32.671	50.366	541.896	31.152	38.419		0.55837



Injection Results

Peaks | Summary

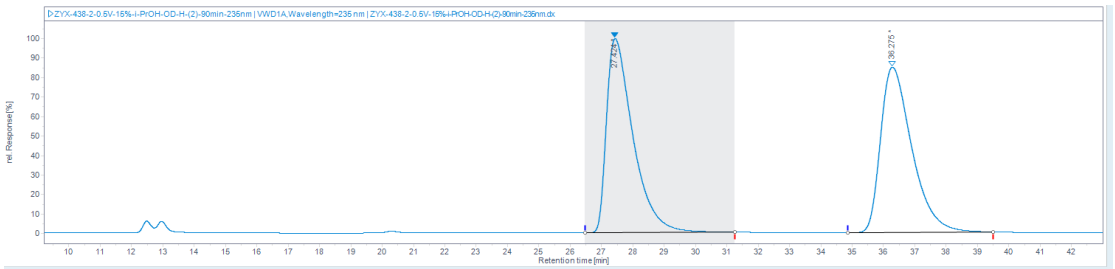
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	24.427	4.831	24.937	23.837	25.754		0.61740
2	32.896	95.169	393.814	31.634	36.304		0.60866



8

(*R*)-3-(4-bromophenyl)-3-ethynyl-3,4-dihydroquinoxalin-2(1*H*)-one (8): yellow solid; mp 113-115 ^{o}C; 25.4 mg, 78% yield; 92% *ee*; R_f = 0.3 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -231.18 (*c* = 1.70, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.69 (d, *J* = 8.7 Hz, 2H), 7.55 (d, *J* = 8.7 Hz, 2H), 6.99 (td, *J* = 7.6, 1.3 Hz, 1H), 6.89 (td, *J* = 7.6, 1.2 Hz, 1H), 6.80 (t, *J* = 6.5 Hz, 2H), 4.39 (s, 1H), 2.69 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) one carbon signal was overlapped δ 164.6, 137.3, 132.0, 131.7, 129.6, 125.4, 124.3, 123.5, 121.1, 115.6, 115.2, 80.7, 61.1; IR (neat, cm^{-1}) 3287, 1686, 1608, 1505, 1486, 1312, 1074, 1011, 748; HRMS (ESI): *m/z*: calcd for $C_{16}H_{11}N_2ONa^{79}Br$ $[M+Na]^+$: 348.9952, found: 348.9958.

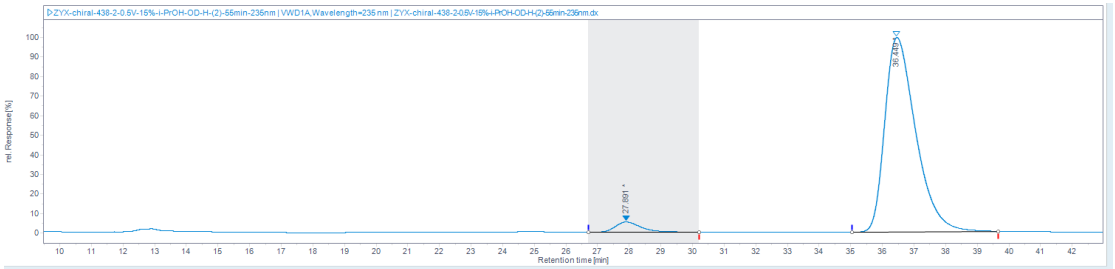
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 27.9 min (minor) and 36.4 min (major).



Injection Results

Peaks | Summary

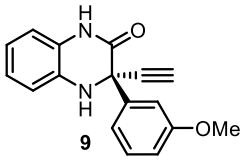
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	27.424	49.837	868.746	26.469	31.255		0.44789
2	36.275	50.163	740.401	34.853	39.500		0.57552



Injection Results

Peaks | Summary

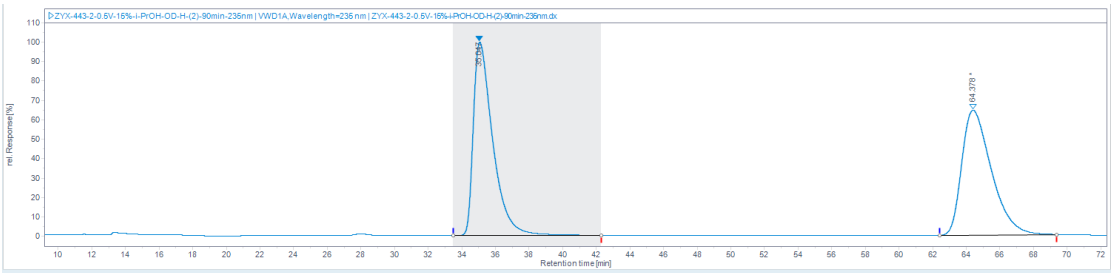
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	27.891	4.092	26.106	26.705	30.202		0.68119
2	36.449	95.908	502.120	35.041	39.668		0.60823



9

(*R*)-3-ethynyl-3-(3-methoxyphenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (9): white solid; mp 63-64 ^{o}C; 24.5 mg, 88% yield; 92% *ee*; R_f = 0.3 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -192.73 (*c* = 2.20, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.55-7.29 (m, 3H), 7.12-6.61 (m, 5H), 4.43 (s, 1H), 3.82 (s, 3H), 2.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 159.7, 139.8, 132.2, 129.6, 125.4, 124.2, 120.8, 120.1, 115.5, 115.1, 114.8, 113.4, 100.1, 81.2, 61.4, 55.5; IR (neat, cm^{-1}) 3271, 2923, 1686, 1606, 1506, 1488, 1312, 749; HRMS (ESI): *m/z*: calcd for $C_{17}H_{14}N_2O_2Na$ $[M+Na]^+$: 301.0953, found: 301.0956.

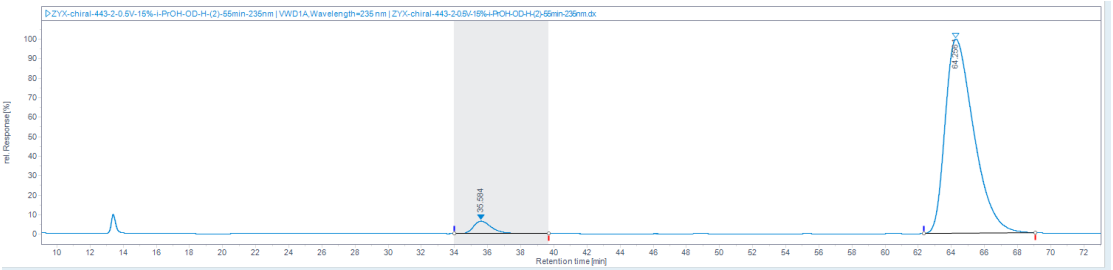
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 35.6 min (minor) and 64.3 min (major).



Injection Results

Peaks | Summary

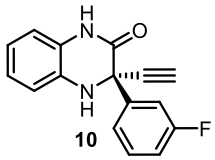
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	35.047	50.291	341.569	33.496	42.289		0.45939
2	64.378	49.709	220.794	62.406	69.359		0.58093



Injection Results

Peaks | Summary

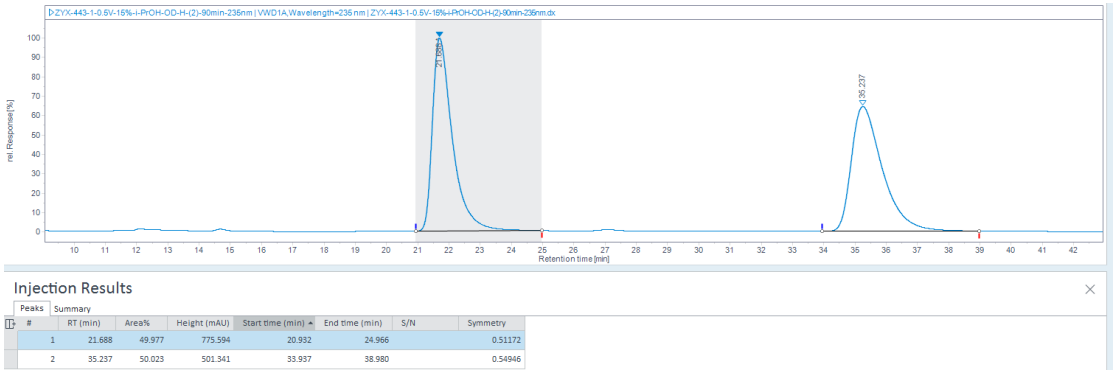
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	35.584	4.057	15.757	34.002	39.669		0.65202
2	64.256	95.943	243.115	62.342	69.069		0.57418



10

(*R*)-3-ethynyl-3-(3-fluorophenyl)-3,4-dihydroquinoxalin-2(1*H*)-one (10): yellow solid; mp 79-80 ^{o}C; 21.3 mg, 80% yield; 93% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -230.64 (*c* = 2.35, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.58-7.52 (m, 1H), 7.44-7.35 (m, 1H), 7.09 (td, *J* = 8.3, 2.1 Hz, 1H), 6.99 (td, *J* = 7.7, 1.1 Hz, 1H), 6.88 (td, *J* = 7.6, 1.0 Hz, 1H), 6.84-6.73 (m, 2H), 4.42 (s, 1H), 2.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 162.8 (d, *J* = 247.5 Hz), 140.8 (d, *J* = 7.1 Hz), 131.9, 130.1 (d, *J* = 8.1 Hz), 125.3, 124.3, 123.6 (d, *J* = 3.0 Hz), 121.0, 116.1 (d, *J* = 21.2 Hz), 115.7, 115.4, 115.1, 80.8, 77.1, 61.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.33; IR (neat, cm^{-1}) 3290, 2925, 1686, 1609, 1505, 1442, 1355, 1311, 748; HRMS (ESI): *m/z*: calcd for $C_{16}H_{11}N_2ONaF$ $[M+Na]^+$: 289.0753, found: 289.0754.

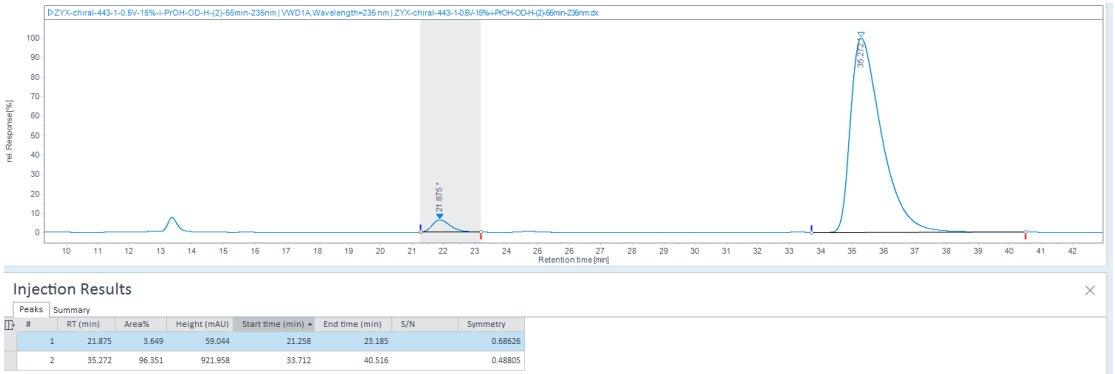
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 21.9 min (minor) and 35.3 min (major).



Injection Results

Peaks | Summary

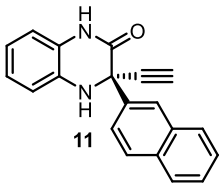
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	21.688	49.977	775.594	20.932	24.966		0.51172
2	35.237	50.023	501.341	33.937	38.980		0.54946



Injection Results

Peaks | Summary

#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	21.875	3.649	59.044	21.258	23.185		0.68626
2	35.272	96.351	921.958	33.712	40.516		0.48805



11

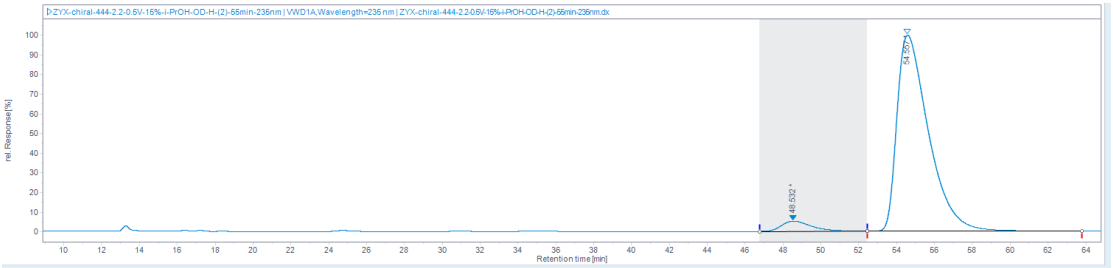
(*R*)-3-ethynyl-3-(naphthalen-2-yl)-3,4-dihydroquinoxalin-2(1*H*)-one (11): yellow solid; mp 142-143 ^{o}C; 25.3mg, 85% yield; 90% *ee*; R_f = 0.3 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -202.44 (*c* = 2.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.33 (s, 1H), 8.00-7.76 (m, 4H), 7.59-7.45 (m, 2H), 7.04-6.91 (m, 1H), 6.91-6.67 (m, 3H), 4.49 (s, 1H), 2.76 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 135.6, 133.6, 132.9, 132.2, 128.7, 128.5, 127.8, 127.2, 126.9, 126.5, 125.5, 125.4, 124.2, 120.8, 115.7, 115.0, 81.1, 77.0, 61.6; IR (neat, cm^{-1}) 3287, 3057, 1686, 1607, 1505, 1354, 1311, 749; HRMS (ESI): *m/z*: calcd for $C_{20}H_{14}N_2ONa$ $[M+Na]^+$: 321.0998, found: 321.1013.

The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 48.5 min (minor) and 54.6 min (major).

Injection Results

Peaks | Summary

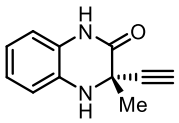
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	48.837	49.631	139.886	46.806	54.162		0.53741
2	56.208	50.369	136.893	54.162	63.816		0.59951



Injection Results

Peaks | Summary

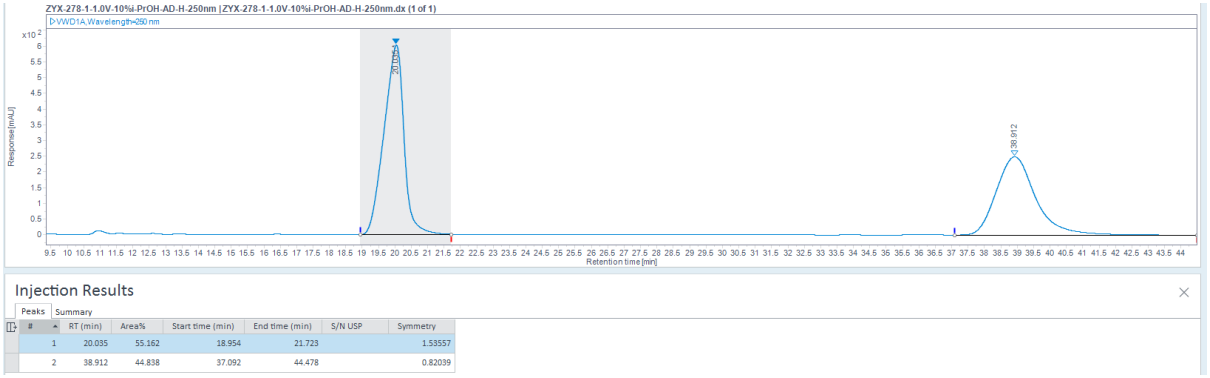
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	48.532	4.733	32.777	46.780	52.438		0.62664
2	54.557	95.267	625.649	52.438	63.803		0.47110

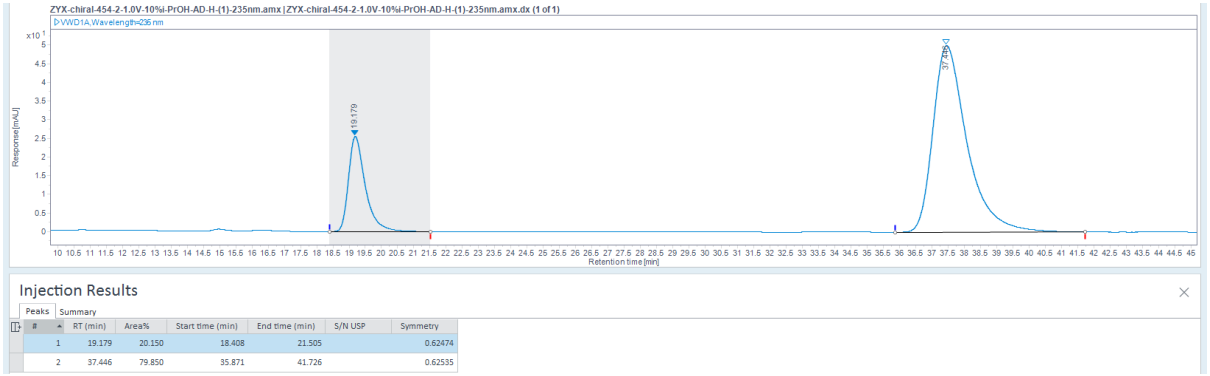


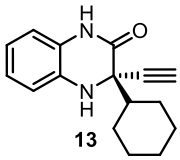
12

(*S*)-3-ethynyl-3-methyl-3,4-dihydroquinoxalin-2(1*H*)-one (12): yellow solid; mp 50-51 ^{o}C; 11.2 mg, 60% yield; 60% *ee*; R_f = 0.3 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -231.00 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (s, 1H), 6.96 (td, *J* = 7.6, 1.4 Hz, 1H), 6.87 (td, *J* = 7.6, 1.3 Hz, 1H), 6.79 (dd, *J* = 8.9, 4.4 Hz, 2H), 4.16 (s, 1H), 2.36 (s, 1H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) one carbon signal was overlapped δ 165.5, 132.5, 125.9, 124.1, 120.9, 115.4, 115.2, 73.3, 53.2, 25.1; IR (neat, cm^{-1}) 3325, 3270, 1664, 1604, 1507, 1388, 1314, 1146, 746, 663; HRMS (ESI): *m/z*: calcd for $C_{11}H_{11}N_2O$ $[M+H]^+$: 187.0871, found: 187.0874.

The *ee* was determined by HPLC analysis: CHIRALPAK ADH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 90/10; flow rate 1.0 mL/min; 35 ^{o}C; 250 nm; retention time: 19.2 min (minor) and 37.4 min (major).



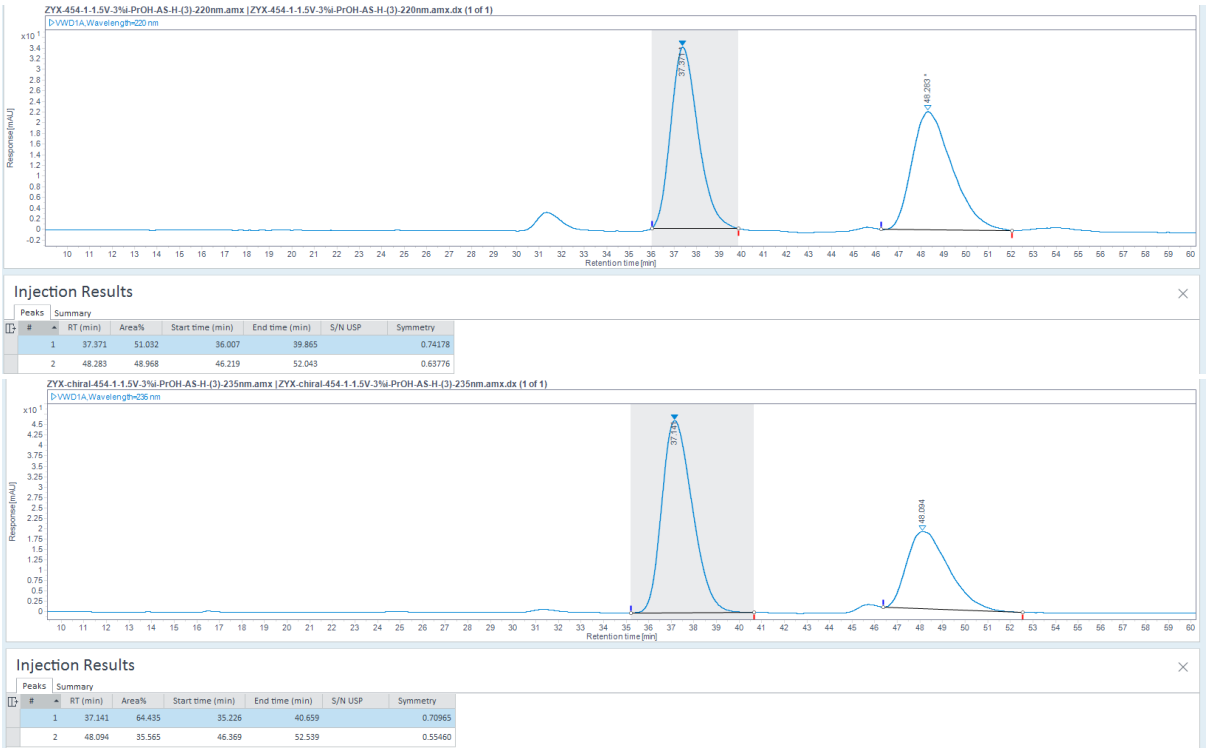


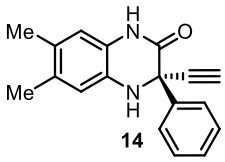


13

(*S*)-3-cyclohexyl-3-ethynyl-3,4-dihydroquinoxalin-2(1*H*)-one (13): yellow solid; mp 138-139 ^{o}C; 17.8 mg, 70% yield; 30% *ee*; R_f = 0.3 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -26.00 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62-8.42 (m, 1H), 6.97-6.86 (m, 1H), 6.86-6.66 (m, 3H), 4.10 (s, 1H), 2.47 (s, 1H), 2.22-2.03 (m, 2H), 1.89-1.66 (m, 4H), 1.34-1.15 (m, 5H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 131.9, 124.9, 124.2, 120.1, 115.2, 114.7, 81.7, 74.8, 61.3, 43.4, 27.2, 26.9, 26.5, 26.3, 26.2; IR (neat, cm^{-1}) 3279, 2929, 2853, 1681, 1607, 1505, 1449, 1362, 1313, 744; HRMS (ESI): *m/z*: calcd for $C_{16}H_{18}N_2ONa$ $[M+Na]^+$: 277.1317, found: 277.1322.

The *ee* was determined by HPLC analysis: CHIRALPAK ASH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 97/3; flow rate 1.5 mL/min; 35 ^{o}C; 235 nm; retention time: 37.1 min (major) and 48.1 min (minor).

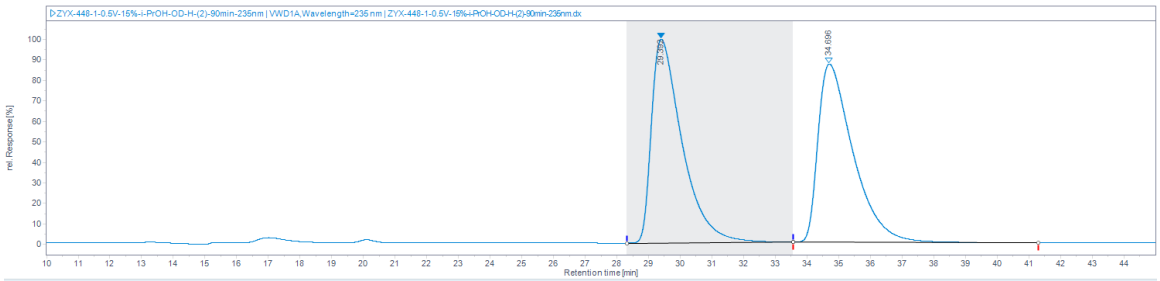




14

(*R*)-3-ethynyl-6,7-dimethyl-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (14): white solid; mp 60-61 ^{o}C; 16.6 mg, 60% yield; 74% *ee*; R_f = 0.3 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -144.76 (*c* = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 7.86-7.77 (m, 2H), 7.46-7.36 (m, 3H), 6.56 (s, 2H), 4.27 (s, 1H), 2.68 (s, 1H), 2.19 (s, 3H), 2.16 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 138.6, 132.3, 129.9, 129.0, 128.8, 128.5, 127.8, 123.2, 116.8, 116.3, 81.5, 76.5, 61.6, 19.5, 19.1; IR (neat, cm^{-1}) 3276, 2944, 1685, 1516, 1447, 1382, 1348, 1020, 871, 698; HRMS (ESI): *m/z*: calcd for $C_{18}H_{16}N_2ONa$ $[M+Na]^+$: 299.1160, found: 299.1164.

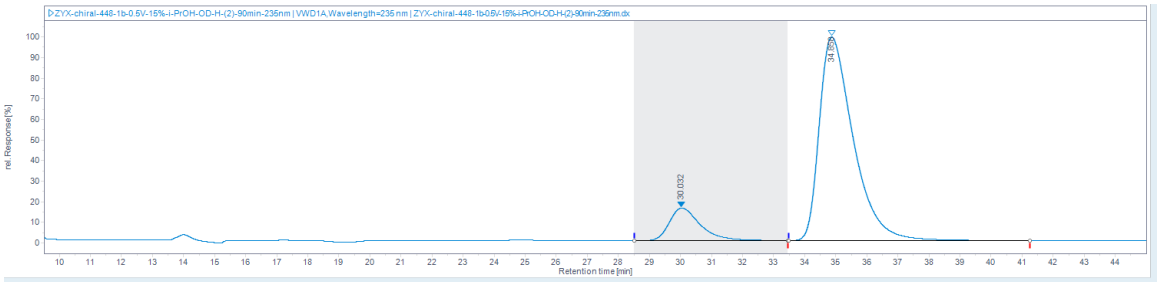
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 30.0 min (minor) and 34.9 min (major).



Injection Results

Peaks | Summary

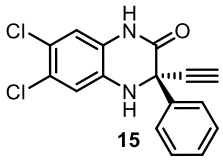
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	29.392	49.921	282.644	28.326	33.571		0.43960
2	34.696	50.079	247.814	33.573	41.303		0.44240



Injection Results

Peaks | Summary

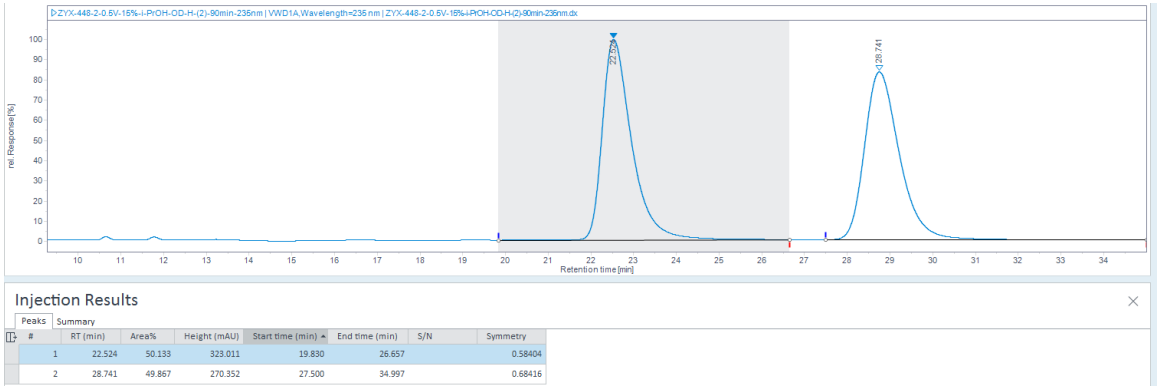
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	30.032	12.936	13.159	28.504	33.469		0.63440
2	34.858	87.064	81.897	33.471	41.248		0.53574



15

(*R*)-6,7-dichloro-3-ethynyl-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (15): yellow solid; mp 181-182 ^{o}C; 25.3 mg, 81% yield; 96% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -185.33 (*c* = 1.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (s, 1H), 7.84-7.68 (m, 2H), 7.51-7.36 (m, 3H), 6.86 (s, 2H), 4.49 (s, 1H), 2.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) one carbon signal was overlapped δ 165.0, 137.5, 131.9, 129.5, 128.8, 127.7, 127.1, 125.2, 123.5, 116.9, 116.2, 80.4, 61.1; IR (neat, cm^{-1}) 3291, 2924, 1688, 1498, 1355, 1261, 1211, 868, 697; HRMS (ESI): *m/z*: calcd for $C_{16}H_{10}N_2ONa^{35}Cl_2$ $[M+Na]^+$: 339.0068, found: 339.0071.

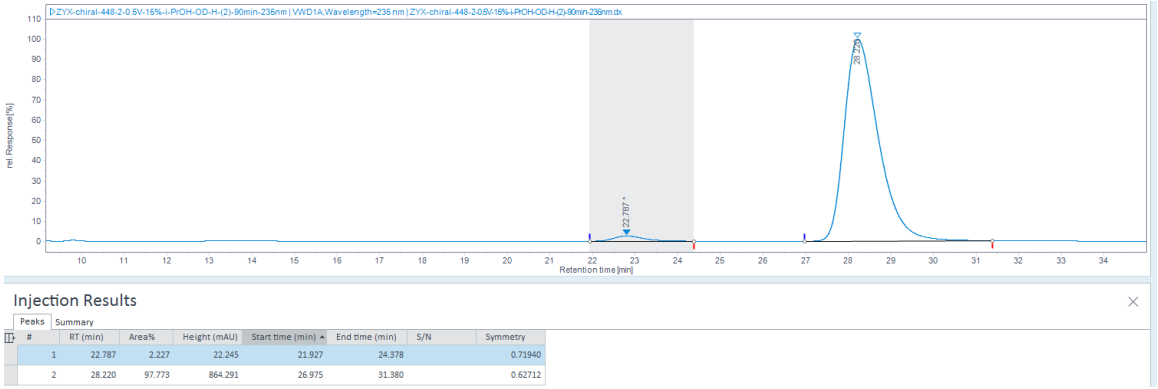
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 22.8 min (minor) and 28.2 min (major).



Injection Results

Peaks | Summary

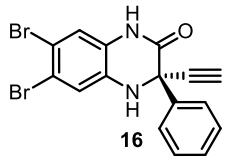
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	22.524	50.133	323.011	19.830	26.657		0.58404
2	28.741	49.867	270.352	27.500	34.997		0.68416



Injection Results

Peaks | Summary

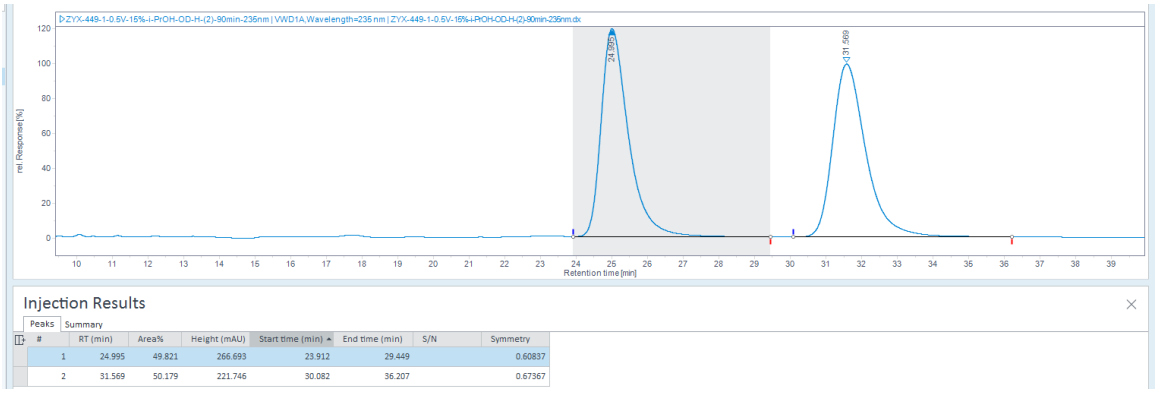
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	22.787	2.227	22.245	21.927	24.378		0.71940
2	28.220	97.773	864.291	26.975	31.380		0.62712



16

(*R*)-6,7-dibromo-3-ethynyl-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (16): yellow solid; mp 190-191 ^{o}C; 32.3 mg, 80% yield; 97% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -172.00 (*c* = 0.75, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.86-7.69 (m, 2H), 7.53-7.35 (m, 3H), 7.04 (d, *J* = 9.5 Hz, 2H), 4.49 (s, 1H), 2.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) one carbon signal was overlapped δ 164.6, 137.4, 132.6, 129.5, 128.8, 127.7, 125.9, 119.6, 119.3, 118.6, 114.6, 80.4, 61.1; IR (neat, cm^{-1}) 3293, 2924, 2853, 1689, 1605, 1494, 1351, 1287, 757; HRMS (ESI): *m/z*: calcd for $C_{16}H_{10}N_2ONa^{79}Br_2$ $[M+Na]^+$: 426.9058, found: 426.9057.

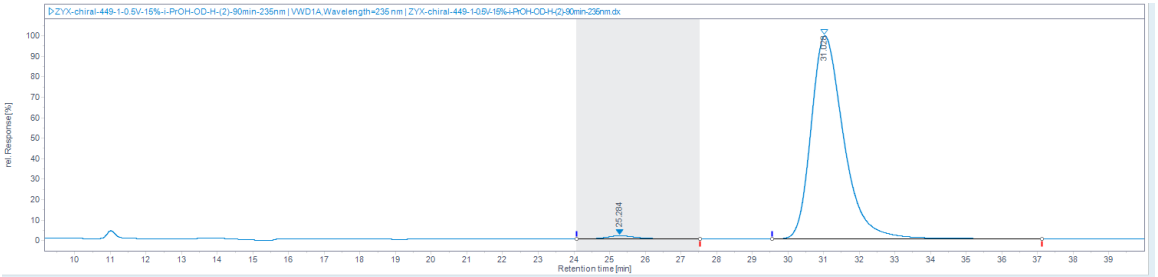
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 25.3 min (minor) and 31.0 min (major).



Injection Results

Peaks | Summary

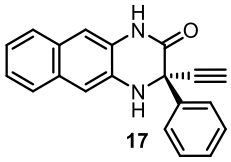
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	24.995	49.821	266.693	23.912	29.449		0.60837
2	31.569	50.179	221.746	30.082	36.207		0.67367



Injection Results

Peaks | Summary

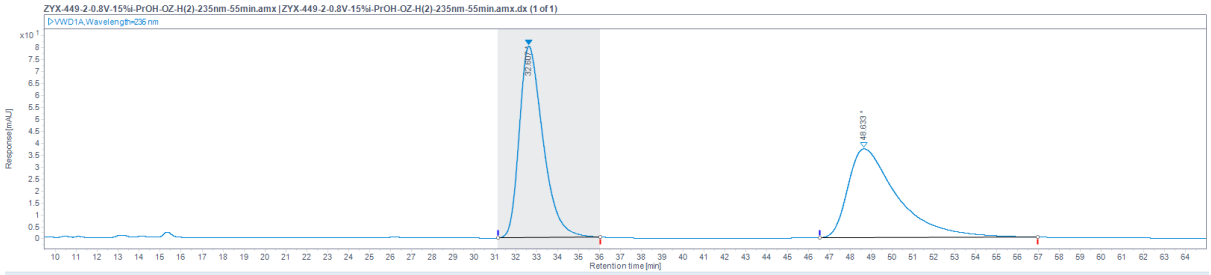
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	25.284	1.385	2.964	24.070	27.547		0.75198
2	31.028	98.615	191.667	29.560	37.137		0.68052



17

(*R*)-3-ethynyl-3-phenyl-3,4-dihydrobenzo[g]quinoxalin-2(1*H*)-one (17): yellow solid; mp 95-96 ^{o}C; 26.5 mg, 89% yield; 95% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -94.67 (*c* = 1.50, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 7.92-7.81 (m, 2H), 7.72-7.60 (m, 2H), 7.50-7.28 (m, 5H), 7.17 (d, *J* = 15.1 Hz, 2H), 4.67 (s, 1H), 2.67 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 138.1, 132.4, 131.3, 129.3, 129.1, 128.7, 127.7, 127.0, 126.7, 126.2, 125.5, 124.3, 111.8, 110.3, 81.1, 76.8, 61.6; IR (neat, cm^{-1}) 3268, 1687, 1530, 1483, 1448, 1334, 846, 745; HRMS (ESI): *m/z*: calcd for $C_{16}H_{12}N_2O_2Na$ $[M+Na]^+$: 321.0998, found: 321.0997.

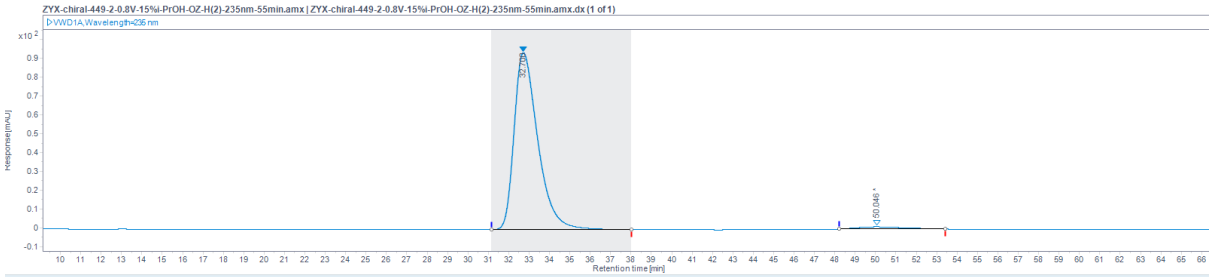
The *ee* was determined by HPLC analysis: CHIRALPAK OZH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.8 mL/min; 35 ^{o}C; 235 nm; retention time: 32.7 min (minor) and 50.0 min (major).



Injection Results

Peaks | Summary

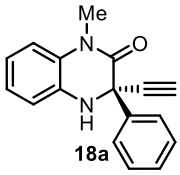
#	RT (min)	Area%	Start time (min)	End time (min)	S/N USP	Symmetry
1	32.607	50.804	31.142	36.026		0.64039
2	48.633	49.196	46.546	56.940		0.45347



Injection Results

Peaks | Summary

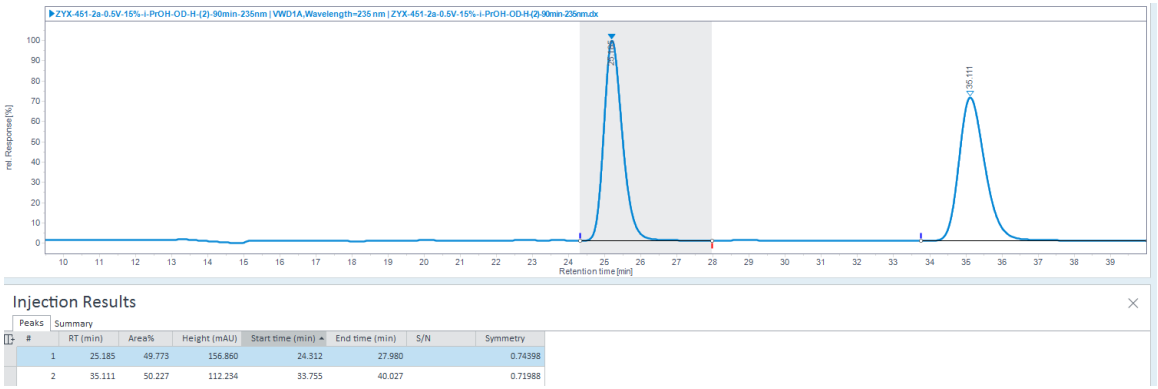
#	RT (min)	Area%	Start time (min)	End time (min)	S/N USP	Symmetry
1	32.700	97.539	31.171	38.026		0.59957
2	50.046	2.461	48.231	53.435		0.66030



18a

(*R*)-3-ethynyl-1-methyl-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (18a): white solid; mp 128-129 ^{o}C; 15.7 mg, 60% yield; 96% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -282.70 (*c* = 1.85, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 6.7 Hz, 2H), 7.49-7.33 (m, 3H), 7.12-6.92 (m, 3H), 6.91-6.72 (m, 1H), 4.45 (s, 1H), 3.44 (s, 3H), 2.61 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 138.8, 133.6, 129.0, 130.0, 128.5, 127.7, 123.9, 120.9, 115.2, 114.9, 81.4, 76.3, 61.5, 30.3; IR (neat, cm^{-1}) 3297, 1669, 1600, 1507, 1374, 1306, 1145, 748; HRMS (ESI): *m/z*: calcd for $C_{17}H_{14}N_2ONa$ $[M+Na]^+$: 285.1004, found: 285.1003.

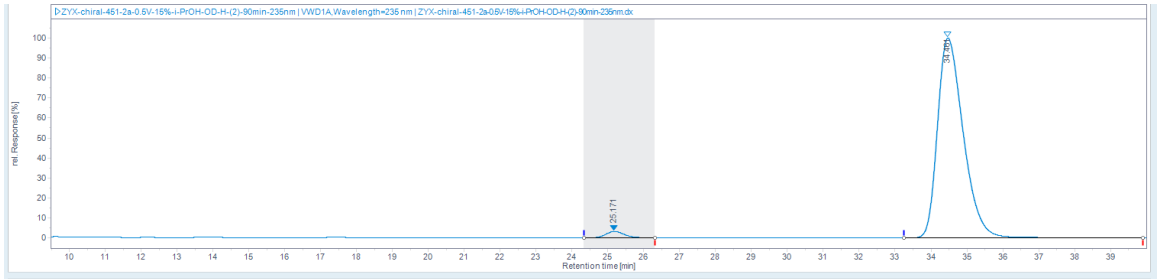
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 25.2 min (minor) and 34.5 min (major).



Injection Results

Peaks | Summary

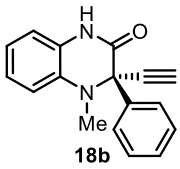
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	25.185	49.773	156.860	24.312	27.980		0.74398
2	35.111	50.227	112.234	33.755	40.027		0.71988



Injection Results

Peaks | Summary

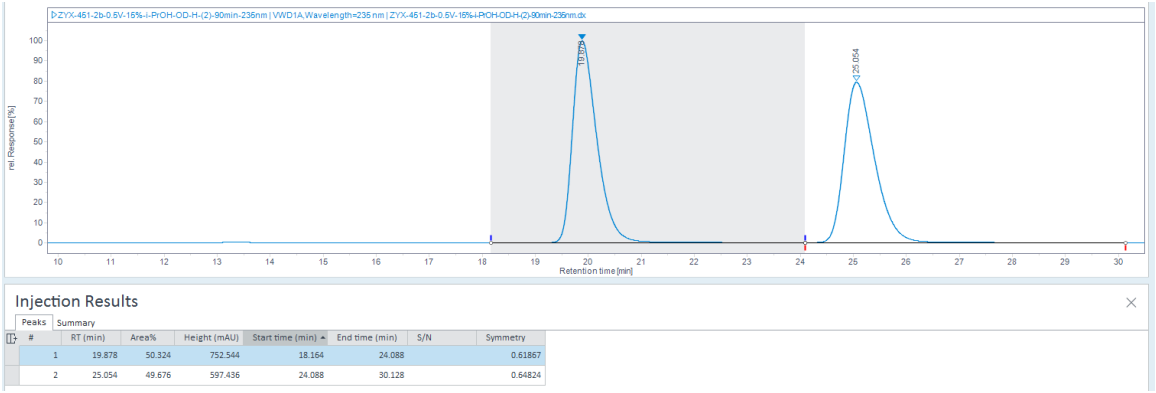
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	25.171	2.162	11.516	24.327	26.301		0.84381
2	34.461	97.838	367.342	33.244	39.897		0.63825



18b

(*R*)-3-ethynyl-4-methyl-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (18b): white solid; mp 173-174 ^{o}C; 7.9 mg, 30% yield; 37% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -96.00 (*c* = 0.25, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.77-7.67 (m, 2H), 7.46-7.35 (m, 3H), 7.10-7.02 (m, 1H), 6.90-6.72 (m, 3H), 2.72 (s, 1H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 138.4, 134.8, 128.9, 128.7, 128.0, 125.3, 124.6, 120.1, 115.2, 113.7, 78.0, 78.0, 67.7, 33.5; IR (neat, cm^{-1}) 3244, 1688, 1601, 1505, 1305, 1000, 747, 660, 588; HRMS (ESI): *m/z*: calcd for $C_{17}H_{14}N_2ONa$ $[M+Na]^+$: 285.1004, found: 285.1009.

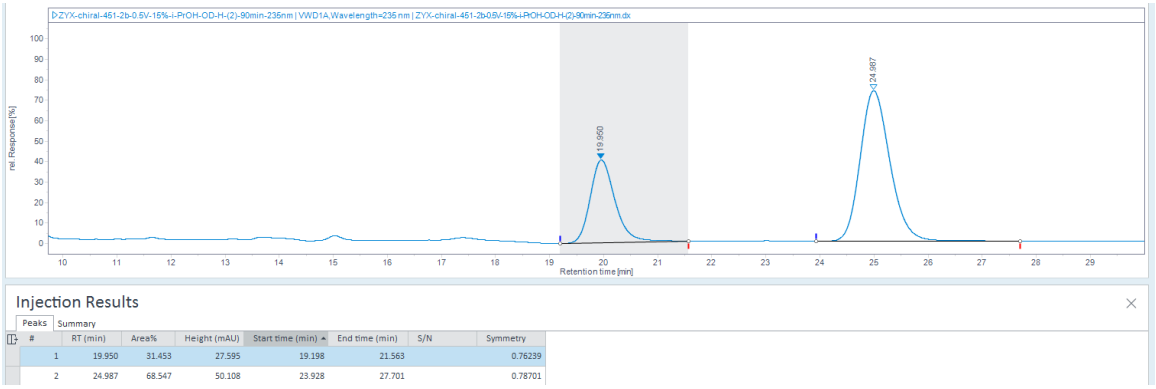
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 20.0 min (minor) and 25.0 min (major).



Injection Results

Peaks | Summary

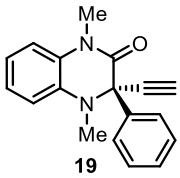
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	19.878	50.324	752.544	18.164	24.088		0.61867
2	25.054	49.676	597.436	24.088	30.128		0.64824



Injection Results

Peaks | Summary

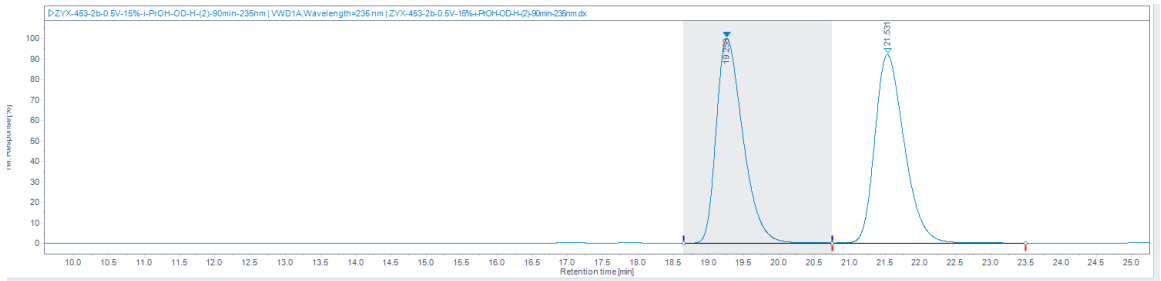
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	19.950	31.453	27.595	19.198	21.563		0.76239
2	24.987	68.547	50.108	23.928	27.701		0.78701



19

(*R*)-3-ethynyl-1,4-dimethyl-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (19): yellow solid; mp 180-181 ^{o}C; 19.9 mg, 72% yield; 40% *ee*; R_f = 0.4 (PE:EA = 2:1); $[\alpha]_D^{20}$ = -81.90 (*c* = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.68 (m, 2H), 7.45-7.34 (m, 3H), 7.16-7.10 (m, 1H), 7.07-6.96 (m, 2H), 6.90-6.84 (m, 1H), 3.46 (s, 3H), 2.64 (s, 1H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 139.0, 136.2, 129.0, 128.7, 128.6, 128.0, 124.3, 120.2, 114.3, 113.8, 78.0, 77.6, 67.8, 33.8, 30.3; IR (neat, cm^{-1}) 3276, 1675, 1506, 1376, 1302, 1158, 1134, 1049, 1008, 745; HRMS (ESI): *m/z*: calcd for $C_{18}H_{16}N_2ONa$ $[M+Na]^+$: 299.1160, found: 299.1166.

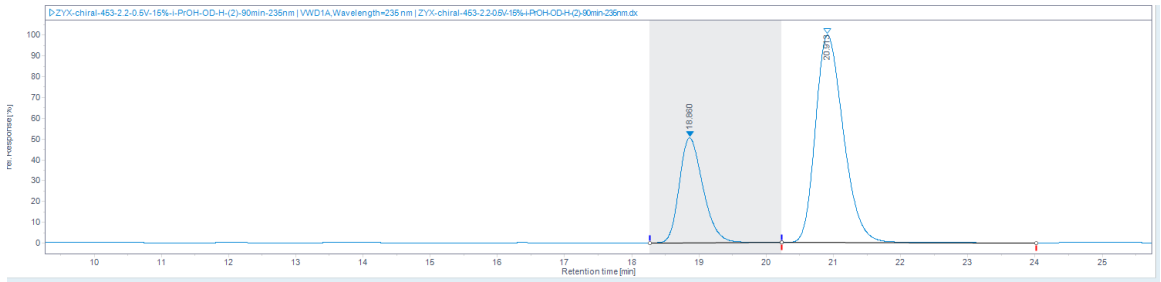
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 18.9 min (minor) and 20.9 min (major).



Injection Results

Peaks | Summary

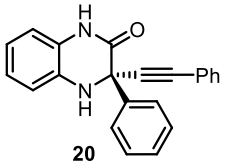
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	19.258	49.645	983.273	18.649	20.754		0.62368
2	21.531	50.355	904.068	20.756	23.493		0.69498



Injection Results

Peaks | Summary

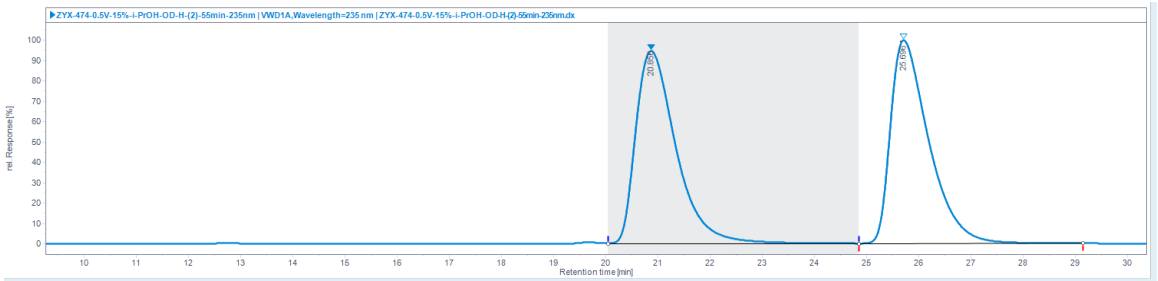
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	18.860	30.010	446.691	18.272	20.232		0.71614
2	20.913	69.990	884.676	20.232	24.022		0.71482



20

(*S*)-3-phenyl-3-(phenylethynyl)-3,4-dihydroquinoxalin-2(1*H*)-one (20): yellow solid; mp 154-155 ^{o}C; 24.3 mg, 75% yield; 94% *ee*; R_f = 0.4 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -256.33 (*c* = 3.00, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 7.99-7.81 (m, 2H), 7.47-7.21 (m, 8H), 6.99-6.89 (m, 1H), 6.87-6.71 (m, 3H), 4.49 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 139.0, 132.6, 132.0, 129.0, 128.9, 128.5, 128.3, 128.0, 125.6, 124.0, 122.0, 120.6, 115.7, 115.0, 88.7, 86.5, 62.0; IR (neat, cm^{-1}) 3241, 3078, 1685, 1607, 1505, 1447, 1350, 1310, 752, 691; HRMS (ESI): *m/z*: calcd for $C_{22}H_{16}N_2ONa$ $[M+Na]^+$: 347.1160, found: 347.1162.

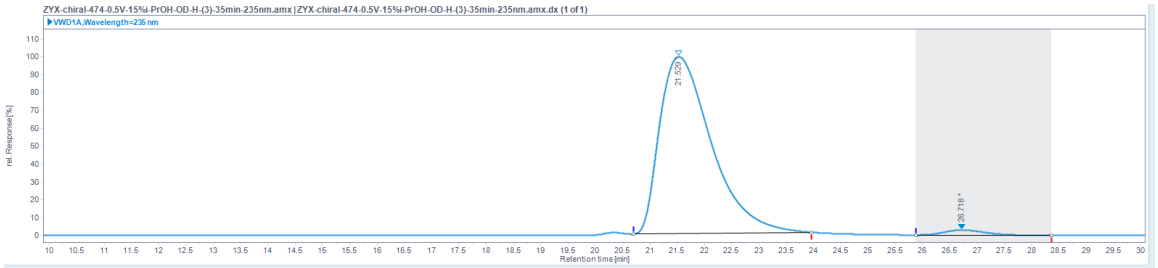
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 20.7 min (major) and 25.8 min (minor).



Injection Results

Peaks | Summary

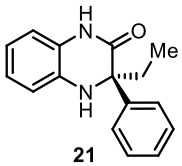
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	20.856	49.954	1812.832	20.034	24.851		0.56917
2	25.696	50.046	1914.051	24.852	29.148		0.49049



Injection Results

Peaks | Summary

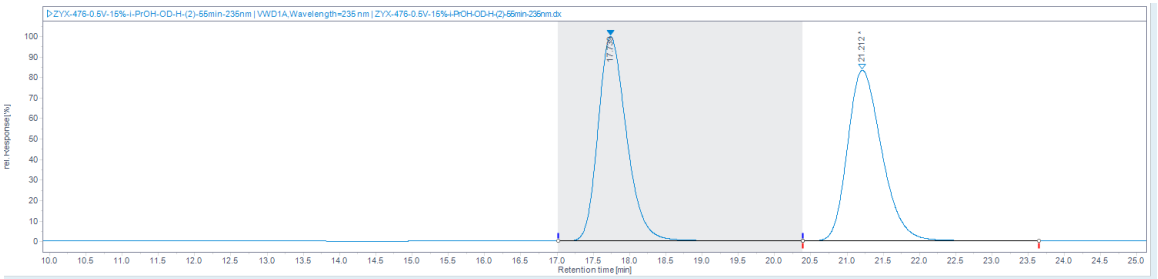
#	RT (min)	Area%	Start time (min)	End time (min)	S/N USP	Symmetry
1	21.529	97.798	20.705	23.956		0.54594
2	26.718	2.202	25.869	28.359		0.72436



21

(*R*)-3-ethyl-3-phenyl-3,4-dihydroquinoxalin-2(1*H*)-one (21): yellow solid; mp 130-131 ^{o}C; 20.2 mg, 80% yield; 94% *ee*; R_f = 0.4 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -165.71 (*c* = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (s, 1H), 7.44 (m, 2H), 7.30-7.21 (m, 3H), 6.97-6.82 (m, 2H), 6.70 (m, 1H), 6.59 (m, 1H), 4.34 (s, 1H), 2.46 (dq, *J* = 14.5, 7.3 Hz, 1H), 1.97 (dq, *J* = 14.7, 7.4 Hz, 1H), 1.01 (t, *J* = 7.4 Hz, 3H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.3, 141.9, 133.3, 128.6, 127.7, 125.8, 125.0, 124.1, 119.3, 115.1, 114.1, 64.9, 33.0, 8.6; IR (neat, cm^{-1}) 3374, 2992, 1676, 1503, 1441, 1364, 1311, 746, 702; HRMS (ESI): *m/z*: calcd for $C_{16}H_{16}N_2ONa$ $[M+Na]^+$: 275.1160, found: 275.1162.

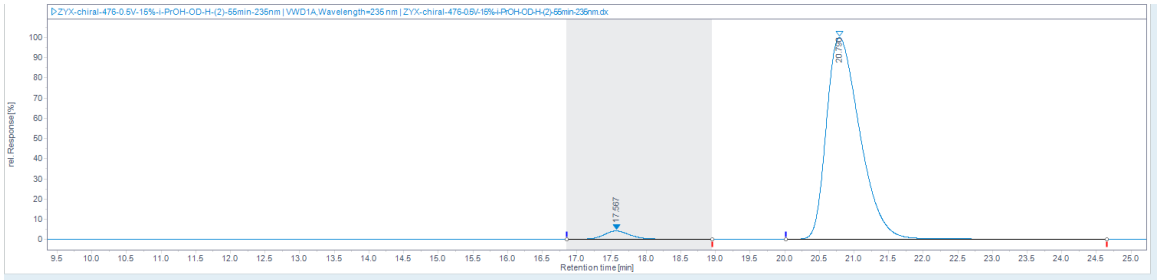
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 17.6 min (minor) and 20.8 min (major).



Injection Results

Peaks | Summary

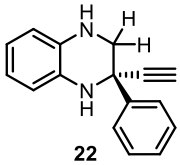
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	17.739	49.936	585.486	17.011	20.386		0.73823
2	21.212	50.064	489.043	20.388	23.643		0.72019



Injection Results

Peaks | Summary

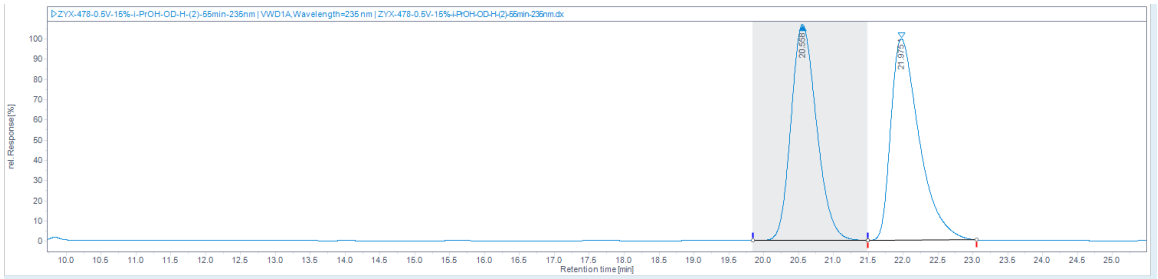
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	17.567	3.014	82.176	16.854	18.951		0.83590
2	20.790	96.986	2049.890	20.017	24.654		0.59754



22

(*R*)-2-ethynyl-2-phenyl-1,2,3,4-tetrahydroquinoxaline (22): yellow solid; mp 114-115 ^{o}C; 17.1 mg, 73% yield; 97% *ee*; R_f = 0.4 (PE:EA = 5:1); $[\alpha]_D^{20}$ = -225.00 (*c* = 0.40, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92-7.60 (m, 2H), 7.52-7.31 (m, 3H), 6.84-6.46 (m, 4H), 4.11 (s, 2H), 3.38 (dd, *J* = 30.1, 11.8 Hz, 2H), 2.54 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.3, 133.2, 131.7, 128.7, 128.4, 126.6, 119.9, 119.9, 116.6, 115.8, 84.9, 73.3, 55.2, 53.1; IR (neat, cm^{-1}) 3349, 3285, 3051, 2991, 2854, 1598, 1504, 1298, 1128, 746, 693, 651; HRMS (ESI): *m/z*: calcd for $C_{16}H_{15}N_2$ $[M+H]^+$: 234.1157, found: 234.1158.

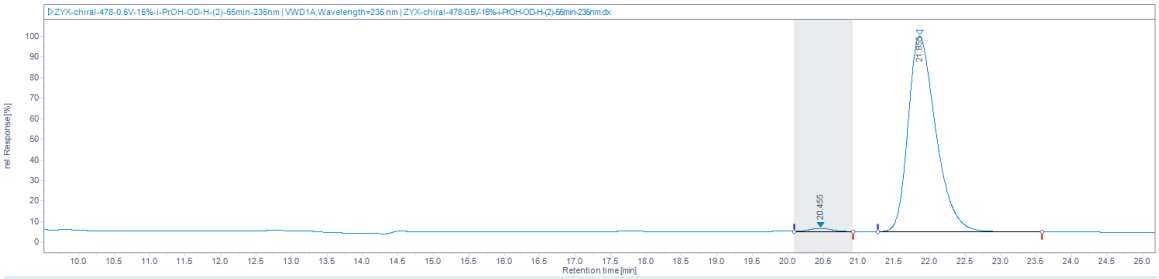
The *ee* was determined by HPLC analysis: CHIRALPAK ODH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 85/15; flow rate 0.5 mL/min; 35 ^{o}C; 235 nm; retention time: 20.5 min (minor) and 21.9 min (major).



Injection Results

Peaks | Summary

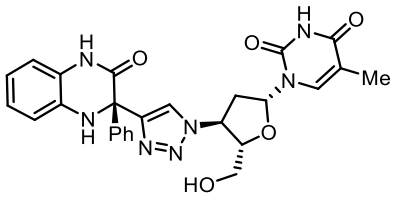
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	20.558	49.135	438.184	19.844	21.494		0.77720
2	21.975	50.865	408.260	21.494	23.056		0.54270



Injection Results

Peaks | Summary

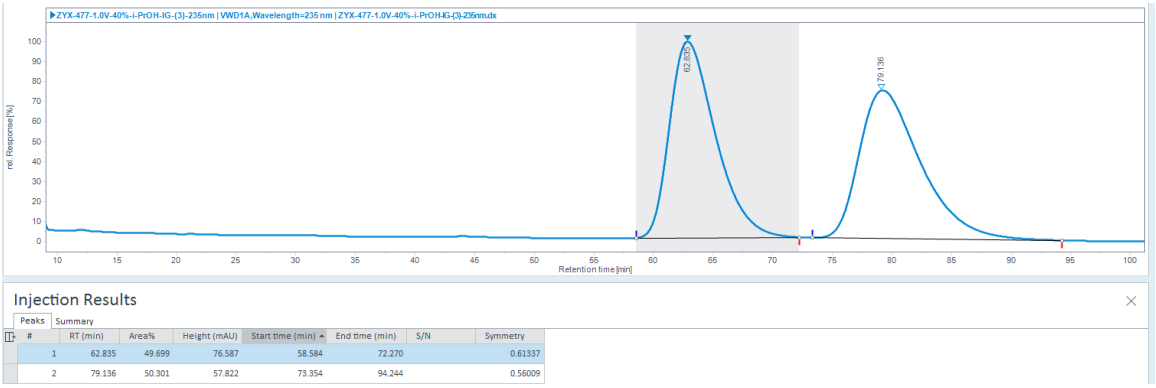
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	20.455	1.414	3.107	20.086	20.921		1.03001
2	21.855	98.586	182.759	21.264	23.578		0.65756



23

1-((2*R*,4*S*,5*S*)-5-(hydroxymethyl)-4-(4-((*S*)-3-oxo-2-phenyl-1,2,3,4-tetrahydroquinoxalin-2-yl)-1*H*-1,2,3-triazol-1-yl)tetrahydrofuran-2-yl)-5-methyldihydropyrimidine-2,4(1*H*,3*H*)-dione (23): white solid; mp 146-147 ^{o}C; 47.9 mg, 93% yield; 95% *ee*; R_f = 0.3 (DCM:MeOH = 25:1); $[\alpha]_D^{20}$ = -43.08 (*c* = 0.65, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO) δ 11.35 (s, 1H), 10.63 (s, 1H), 8.10 (d, *J* = 4.7 Hz, 1H), 7.79 (s, 1H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.40-7.11 (m, 4H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 6.58 (t, *J* = 7.5 Hz, 1H), 6.41 (t, *J* = 6.5 Hz, 1H), 5.36 (dt, *J* = 11.3, 5.6 Hz, 1H), 5.27 (q, *J* = 5.2 Hz, 1H), 4.20 (d, *J* = 4.3 Hz, 1H), 3.75-3.51 (m, 2H), 2.77-2.55 (m, 2H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, DMSO) δ 165.5, 163.8, 150.5, 149.1, 141.0, 136.3, 133.5, 128.1, 127.5, 126.8, 125.6, 123.8, 123.0, 118.2, 114.6, 114.3, 109.6, 84.4, 83.8, 62.8, 60.7, 59.1, 37.1, 12.3; IR (neat, cm^{-1}) 3244, 2106, 1675, 1505, 1445, 1312, 1269, 1100, 1056, 750, 700; HRMS (ESI): *m/z*: calcd for $C_{26}H_{25}N_7O_5Na$ $[M+Na]^+$: 538.1815, found: 538.1810.

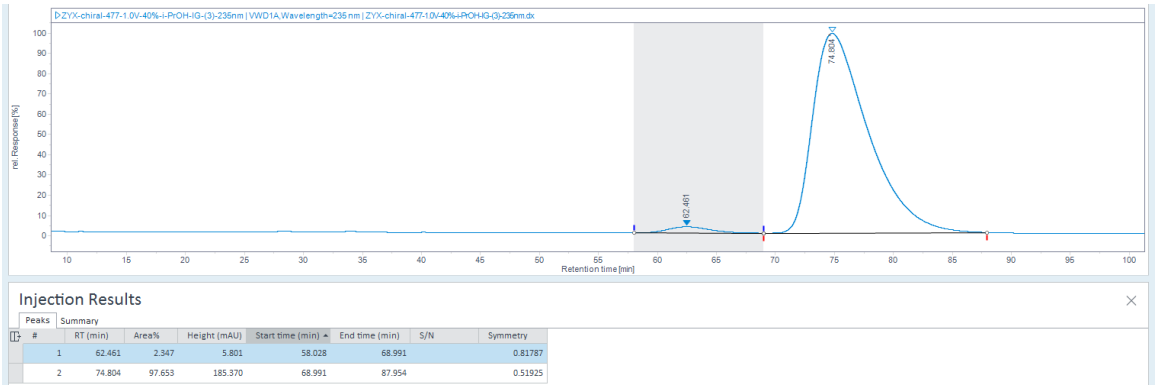
The *ee* was determined by HPLC analysis: CHIRALPAK IGH (4.6 mm i.d. × 250 mm); hexane/2-propanol = 60/40; flow rate 1.0 mL/min; 35 ^{o}C; 235 nm; retention time: 62.5 min (minor) and 74.8 min (major).



Injection Results

Peaks | Summary

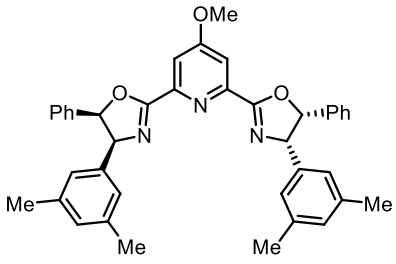
#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	62.835	49.699	76.587	58.584	72.270		0.61337
2	79.136	50.301	57.822	73.354	94.244		0.56009



Injection Results

Peaks | Summary

#	RT (min)	Area%	Height (mAU)	Start time (min)	End time (min)	S/N	Symmetry
1	62.461	2.347	5.801	58.028	68.991		0.81787
2	74.804	97.653	185.370	68.991	87.954		0.51925



L4

(4*S*,4'*S*,5*R*,5'*R*)-2,2'-(4-methoxypyridine-2,6-diyl)bis(4-(3,5-dimethylphenyl)-5-phenyl-4,5-dihydrooxazole) (L4): Purified by recrystallization to afford **L4**, white solid; mp 199-200 ^{o}C; 465.7 mg, 56% yield; $[\alpha]_D^{20}$ = -97.14 (*c* = 1.05, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 2H), 7.14-6.85 (m, 10H), 6.64 (s, 2H), 6.54 (s, 4H), 6.08 (d, *J* = 10.3 Hz, 2H), 5.70 (d, *J* = 10.3 Hz, 2H), 4.02 (s, 3H), 2.09 (s, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 164.0, 148.9, 137.1, 137.0, 136.3, 128.7, 127.5, 126.7, 126.0, 112.7, 86.4, 74.5, 56.2, 21.2; IR (neat, cm^{-1}) 2920, 1642, 1459, 1394, 1297, 1212, 1091, 1038, 970, 860, 738, 697; HRMS (ESI) *m/z*: calcd for $C_{40}H_{38}N_3O_3$ $[M+H]^+$: 608.2908; Found: 608.2908.

X-ray crystallographic information of product 1

The crystal was obtained by recrystallization in CH_2Cl_2/*n*-hexane at room temperature for four days.

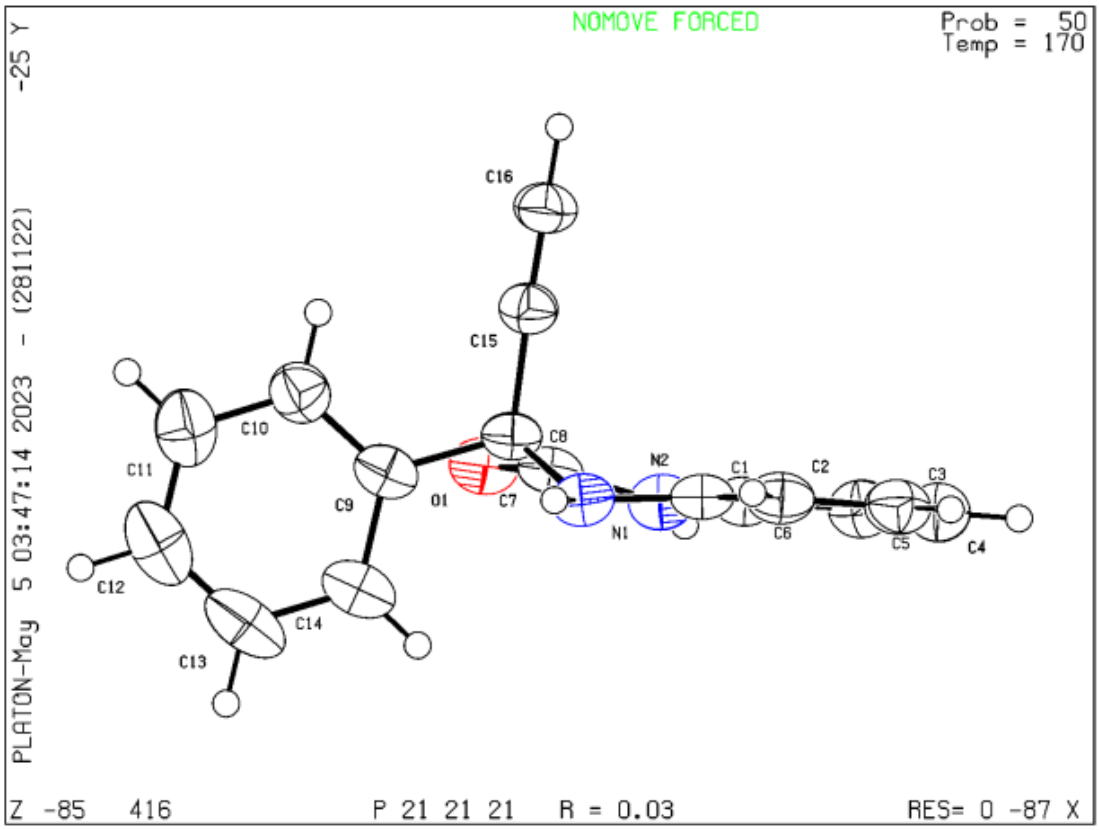


Figure 1. Molecular structure of product **1** with thermal ellipsoid of 50% probability

Table 1 Crystal data and structure refinement for 1.

Identification code	416
Empirical formula	$C_{16}H_{12}N_2O$
Formula weight	248.28
Temperature/K	169.99(10)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.96470(10)
b/Å	10.1591(2)

c/Å	15.9845(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1293.37(4)
Z	4
ρ_{calc}g/cm^3	1.275
μ/mm^{-1}	0.648
F(000)	520.0
Crystal size/mm^3	0.16 × 0.12 × 0.1
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	10.318 to 147.326
Index ranges	-9 ≤ h ≤ 9, -12 ≤ k ≤ 12, -19 ≤ l ≤ 19
Reflections collected	15891
Independent reflections	2583 [R_{int} = 0.0304, R_{sigma} = 0.0159]
Data/restraints/parameters	2583/0/177
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0291, wR_2 = 0.0789
Final R indexes [all data]	R_1 = 0.0317, wR_2 = 0.0805
Largest diff. peak/hole / e Å^{-3}	0.14/-0.12
Flack/Hooft parameter	-0.13(9)/-0.10(9)

Crystal structure determination of [1]

Crystal Data for $C_{16}H_{12}N_2O$ (*M* =248.28 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), *a* = 7.96470(10) Å, *b* = 10.1591(2) Å, *c* = 15.9845(3) Å, *V* =

1293.37(4) Å^3, Z = 4, T = 169.99(10) K, μ(Cu Kα) = 0.648 mm^{-1}, *Dcalc* = 1.275 g/cm^3, 15891 reflections measured (10.318° ≤ 2Θ ≤ 147.326°), 2583 unique (R_{int} = 0.0304, R_{sigma} = 0.0159) which were used in all calculations. The final R_1 was 0.0291 (I > 2σ(I)) and wR_2 was 0.0805 (all data).

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	7078.9(15)	1244.4(12)	2424.0(8)	48.3(3)
N1	4961.7(16)	4036.1(15)	3249.8(9)	42.1(3)
N2	6364.7(18)	1777.1(14)	3747.4(10)	45.1(3)
C1	5223.3(19)	3883.7(16)	4106.6(11)	40.4(4)
C2	4732(2)	4798.7(18)	4699.7(13)	47.0(4)
C3	4881(2)	4514(2)	5544.7(13)	51.7(5)
C4	5554(3)	3321(2)	5803.1(12)	55.7(5)
C5	6079(2)	2412(2)	5215.3(12)	51.2(4)
C6	5912(2)	2691.6(18)	4373.3(11)	42.9(4)
C7	6593.0(19)	2058.2(16)	2934.5(11)	41.0(4)
C8	6232.3(19)	3501.8(16)	2681.6(11)	39.0(4)
C9	5519(2)	3530.9(17)	1798.2(11)	43.1(4)
C10	6333(2)	4130(2)	1147.8(11)	51.2(4)
C11	5641(3)	4150(2)	346.8(13)	63.1(6)
C12	4133(3)	3543(2)	201.2(15)	69.5(7)
C13	3295(3)	2948(2)	854.9(16)	69.8(7)
C14	3967(2)	2934(2)	1655.0(14)	57.8(5)
C15	7869(2)	4201.7(17)	2747.9(11)	42.2(4)

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for 1. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C16	9173(3)	4739(2)	2826.6(12)	53.2(5)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	42.2(6)	37.2(7)	65.6(8)	-7.1(5)	1.3(5)	3.6(5)
N1	36.3(7)	33.7(7)	56.2(8)	1.4(6)	2.9(6)	4.2(6)
N2	44.2(7)	30.3(7)	60.9(9)	4.1(7)	1.2(6)	2.8(6)
C1	29.9(7)	35.0(8)	56.2(9)	0.1(7)	2.2(6)	-3.3(6)
C2	36.0(8)	38.8(9)	66.2(12)	-4.3(8)	2.9(8)	0.5(7)
C3	41.7(9)	52.7(11)	60.7(11)	-8.7(9)	3.9(8)	-2.7(8)
C4	49.0(10)	61.4(12)	56.8(10)	-0.4(9)	0.3(8)	-3.6(9)
C5	45.4(9)	46.8(10)	61.4(11)	6.2(9)	-0.9(8)	1.9(8)
C6	34.4(8)	36.9(9)	57.3(10)	-0.9(7)	1.7(7)	-1.7(6)
C7	29.2(7)	33.9(8)	59.8(10)	-2.8(8)	-1.4(7)	-1.0(6)
C8	32.7(7)	32.8(8)	51.5(9)	-1.7(7)	1.0(6)	-1.7(6)
C9	36.2(8)	35.4(8)	57.5(10)	-6.8(7)	-5.2(7)	5.1(7)
C10	45.1(9)	56.3(11)	52.1(10)	-5.6(9)	-1.7(8)	5.6(8)
C11	64.8(12)	71.3(14)	53.0(11)	-8.1(10)	-2.3(9)	23.6(12)
C12	69.6(13)	72.9(15)	66.0(13)	-25.9(12)	-22.4(12)	32.5(12)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C13	53.1(11)	61.8(14)	94.7(17)	-25.5(12)	-29.1(11)	8.9(11)
C14	45.0(10)	50.6(11)	77.7(13)	-7.6(10)	-13.4(9)	-2.2(8)
C15	39.0(8)	38.6(9)	49.1(9)	2.3(7)	-1.7(7)	-3.2(7)
C16	44.8(9)	57.1(11)	57.8(11)	7.5(9)	-6.0(8)	-15.8(9)

Table 4 Bond Lengths for 1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C7	1.224(2)	C7	C8	1.548(2)
N1	C1	1.394(2)	C8	C9	1.523(2)
N1	C8	1.464(2)	C8	C15	1.488(2)
N2	C6	1.412(2)	C9	C10	1.368(3)
N2	C7	1.343(2)	C9	C14	1.396(2)
C1	C2	1.384(2)	C10	C11	1.394(3)
C1	C6	1.396(2)	C11	C12	1.370(4)
C2	C3	1.386(3)	C12	C13	1.380(4)
C3	C4	1.388(3)	C13	C14	1.386(3)
C4	C5	1.382(3)	C15	C16	1.180(2)
C5	C6	1.382(3)			

Table 5 Bond Angles for 1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C8	117.71(13)	N1	C8	C7	108.52(14)
C7	N2	C6	125.47(15)	N1	C8	C9	108.06(13)
N1	C1	C6	117.07(15)	N1	C8	C15	112.58(13)
C2	C1	N1	123.79(16)	C9	C8	C7	109.25(13)
C2	C1	C6	118.97(17)	C15	C8	C7	105.75(13)
C1	C2	C3	120.20(17)	C15	C8	C9	112.56(14)
C2	C3	C4	120.33(18)	C10	C9	C8	122.44(15)
C5	C4	C3	119.86(19)	C10	C9	C14	119.25(18)
C6	C5	C4	119.71(18)	C14	C9	C8	118.31(17)
C1	C6	N2	117.04(16)	C9	C10	C11	121.14(19)
C5	C6	N2	122.02(16)	C12	C11	C10	119.7(2)
C5	C6	C1	120.90(16)	C11	C12	C13	119.5(2)
O1	C7	N2	122.97(16)	C12	C13	C14	121.1(2)
O1	C7	C8	121.62(16)	C13	C14	C9	119.2(2)
N2	C7	C8	115.40(14)	C16	C15	C8	177.77(19)

Table 6 Torsion Angles for 1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C7	C8	N1	152.43(15)	C4	C5	C6	C1	0.1(3)
O1	C7	C8	C9	34.8(2)	C6	N2	C7	O1	175.68(16)
O1	C7	C8	C15	-86.56(18)	C6	N2	C7	C8	-3.2(2)

Table 6 Torsion Angles for 1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
N1	C1	C2	C3	173.32(16)	C6	C1	C2	C3	-1.8(2)
N1	C1	C6	N2	3.3(2)	C7	N2	C6	C1	17.8(2)
N1	C1	C6	C5	-174.34(16)	C7	N2	C6	C5	-164.54(17)
N1	C8	C9	C10	125.68(17)	C7	C8	C9	C10	-116.43(18)
N1	C8	C9	C14	-53.6(2)	C7	C8	C9	C14	64.25(19)
N2	C7	C8	N1	-28.72(18)	C8	N1	C1	C2	146.08(15)
N2	C7	C8	C9	-146.32(14)	C8	N1	C1	C6	-38.7(2)
N2	C7	C8	C15	92.30(17)	C8	C9	C10	C11	-179.43(16)
C1	N1	C8	C7	50.22(18)	C8	C9	C14	C13	-179.93(17)
C1	N1	C8	C9	168.59(14)	C9	C10	C11	C12	-1.1(3)
C1	N1	C8	C15	-66.48(19)	C10	C9	C14	C13	0.7(3)
C1	C2	C3	C4	1.3(3)	C10	C11	C12	C13	1.7(3)
C2	C1	C6	N2	178.78(14)	C11	C12	C13	C14	-1.1(3)
C2	C1	C6	C5	1.1(2)	C12	C13	C14	C9	-0.1(3)
C2	C3	C4	C5	0.0(3)	C14	C9	C10	C11	-0.1(3)
C3	C4	C5	C6	-0.7(3)	C15	C8	C9	C10	0.7(2)
C4	C5	C6	N2	-177.39(17)	C15	C8	C9	C14	-178.59(15)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1.

Atom	*x*	*y*	*z*	U(eq)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1.

Atom	*x*	*y*	*z*	U(eq)
H1	4450(30)	4830(20)	3073(14)	55(6)
H2	6509.05	954.06	3903.16	54
H2A	4291.94	5624.36	4527.28	56
H3	4521.04	5138.72	5948.96	62
H4	5653.6	3129.43	6382.74	67
H5	6551.55	1598.07	5389.34	61
H10	7388.67	4538.22	1243.7	61
H11	6213.19	4583.39	-96.22	76
H12	3668.23	3532.56	-346.02	83
H13	2240.49	2540.41	755.05	84
H14	3377.41	2522.1	2100.69	69
H16	10223.27	5171.2	2889.98	64

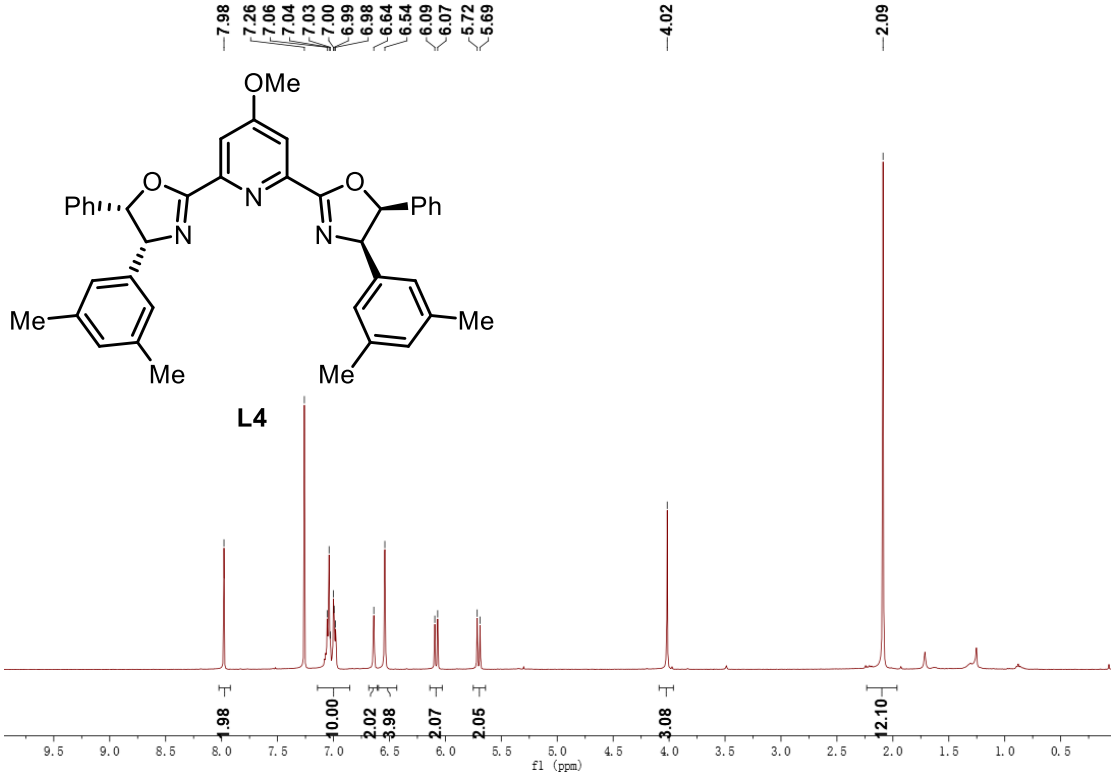
References

[1] Liu, T.; Ni, S.; Guo, W. Practical Asymmetric Amine Nucleophilic Approach for the Modular Construction of Protected *α*-Quaternary Amino Acids. *Chem. Sci*. **2022**, *13*, 6806-6812.

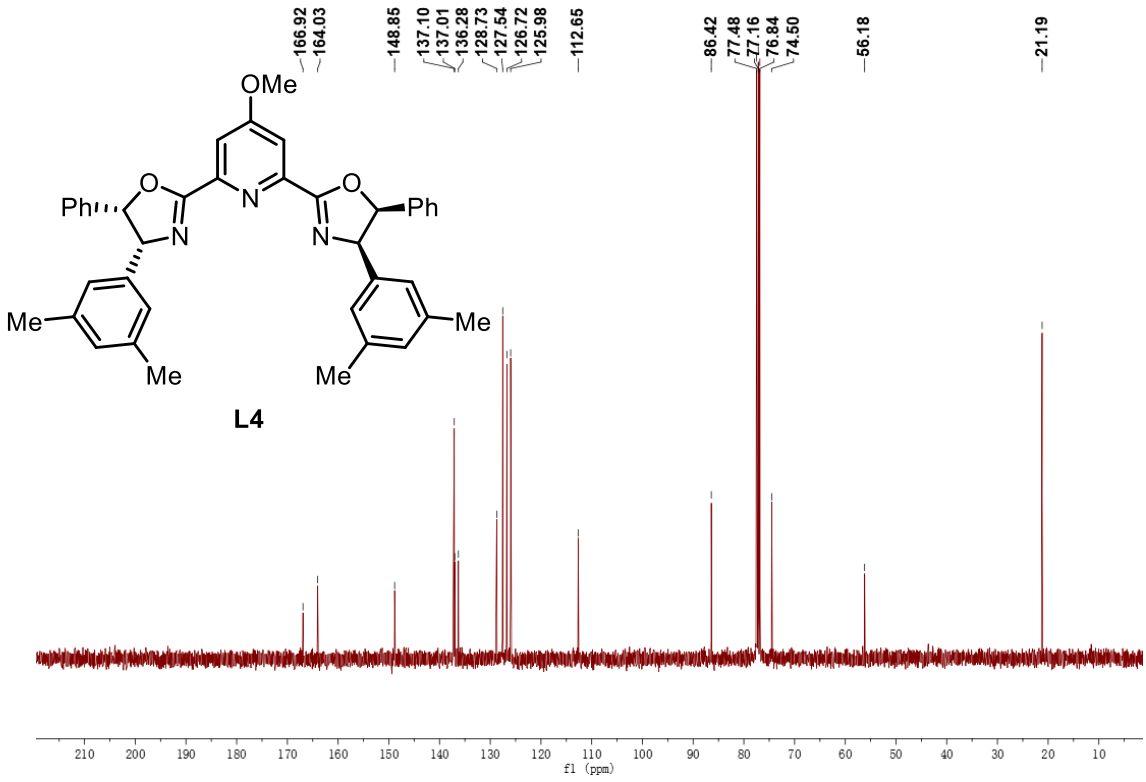
[2] Shrestha, B.; Rose, B. T.; Olen, C. L.; Roth, A.; Kwong, A. C.; Wang, Y.; Denmark, S. E. A Unified Strategy for the Asymmetric Synthesis of Highly Substituted 1, 2-Amino Alcohols Leading to Highly Substituted Bisoxazoline Ligands. *J. Org. Chem.* **2021**, *86*, 3490-3534.

NMR spectra

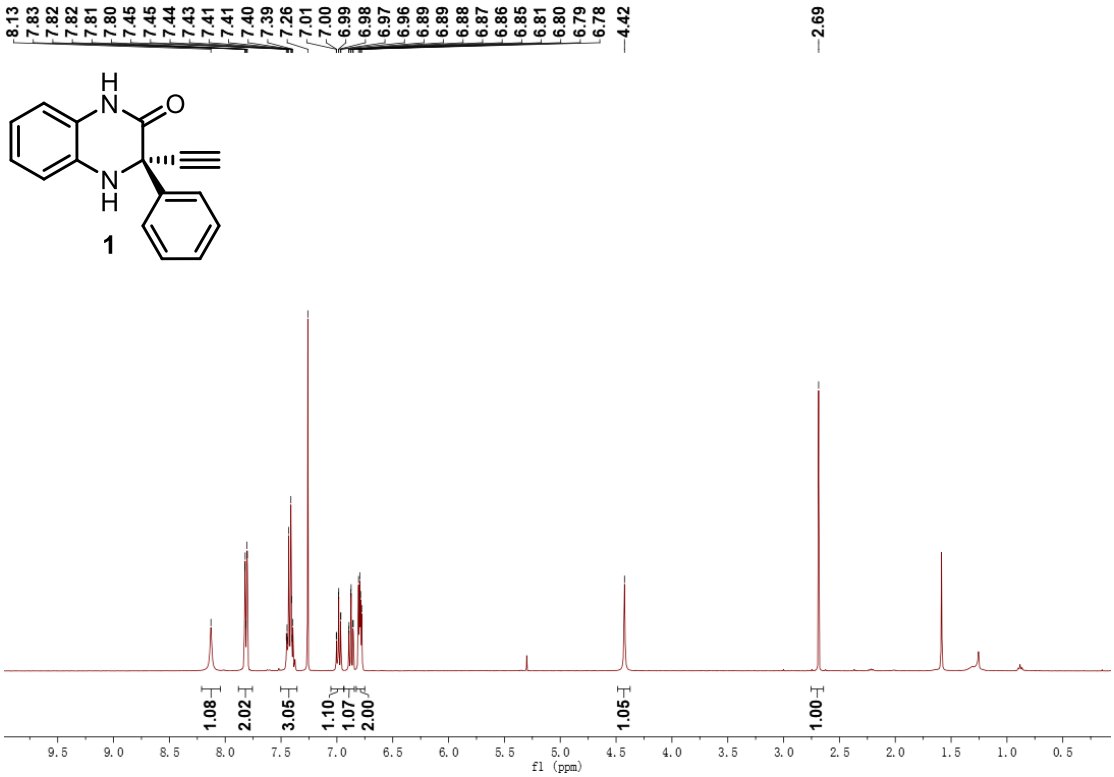
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



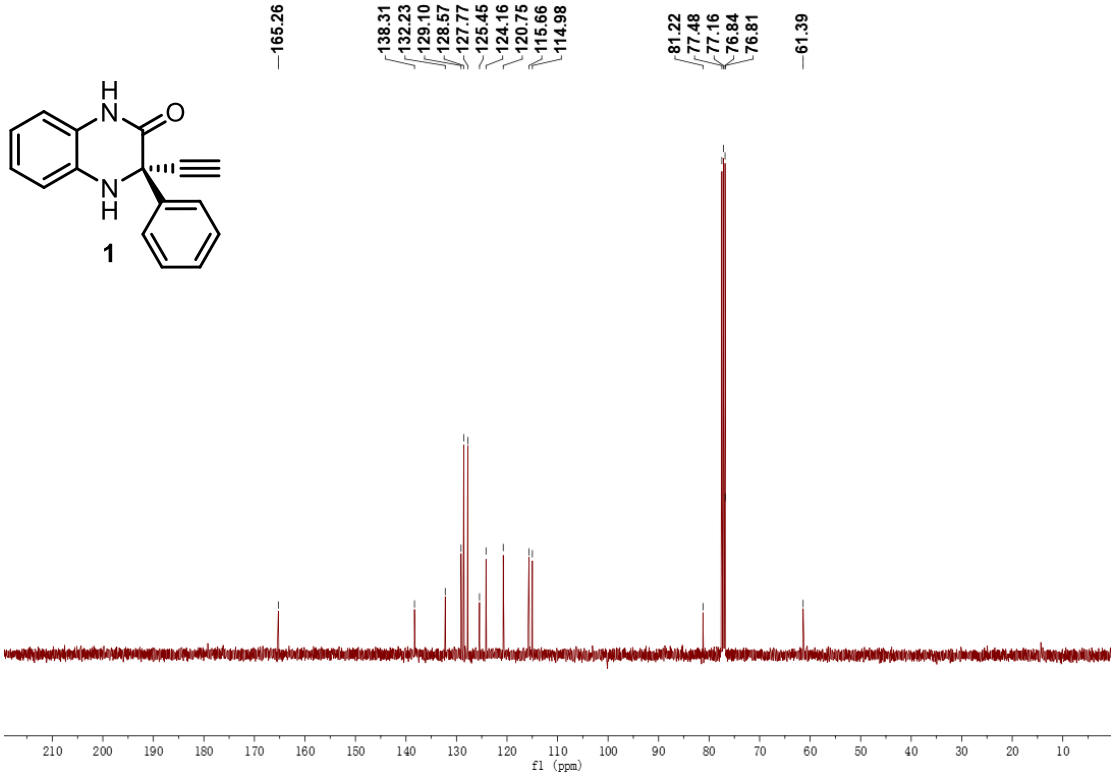
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



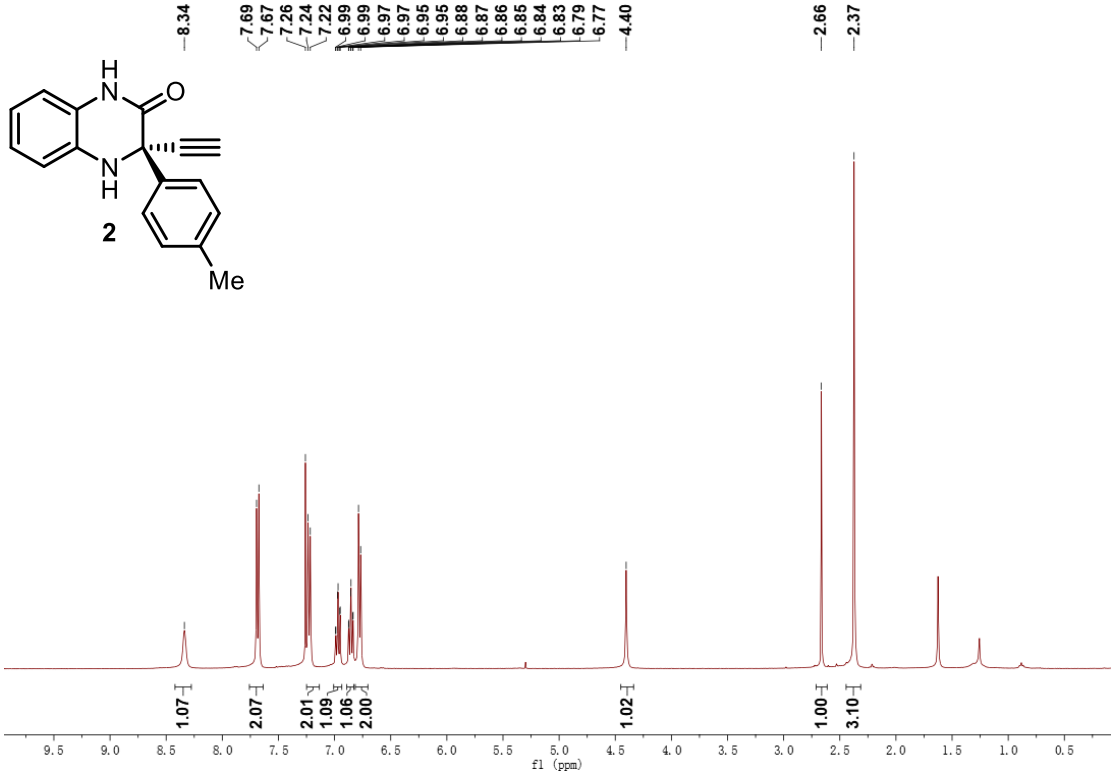
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



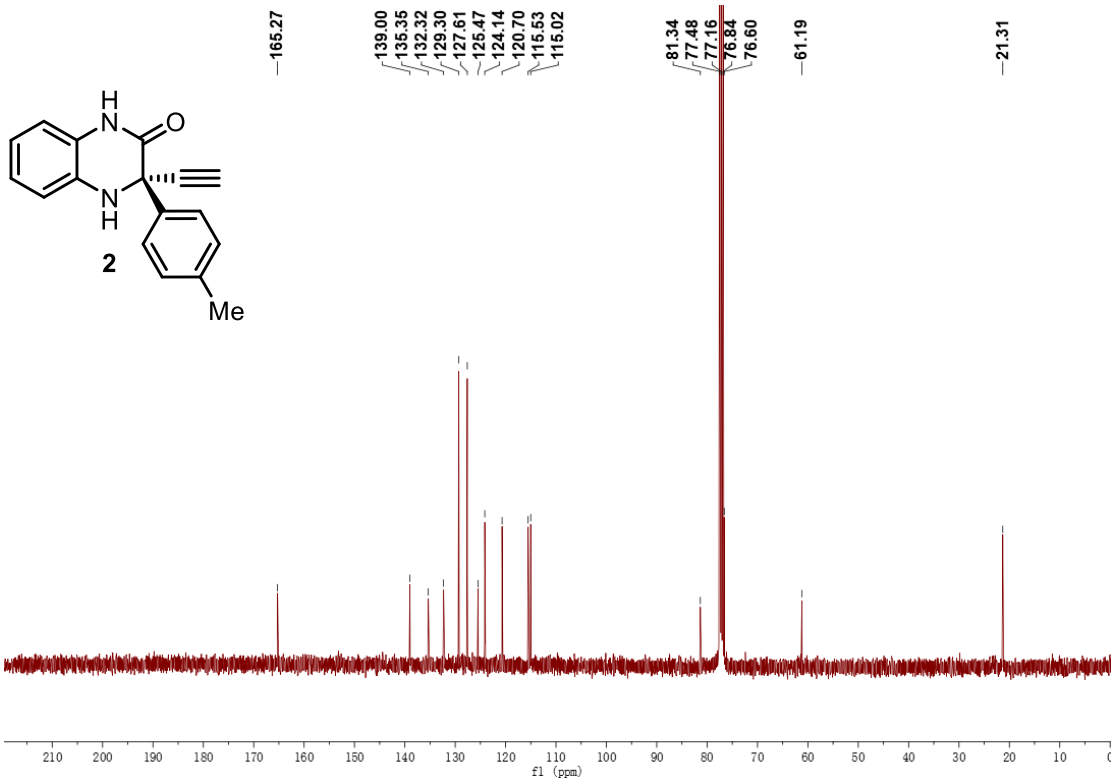
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



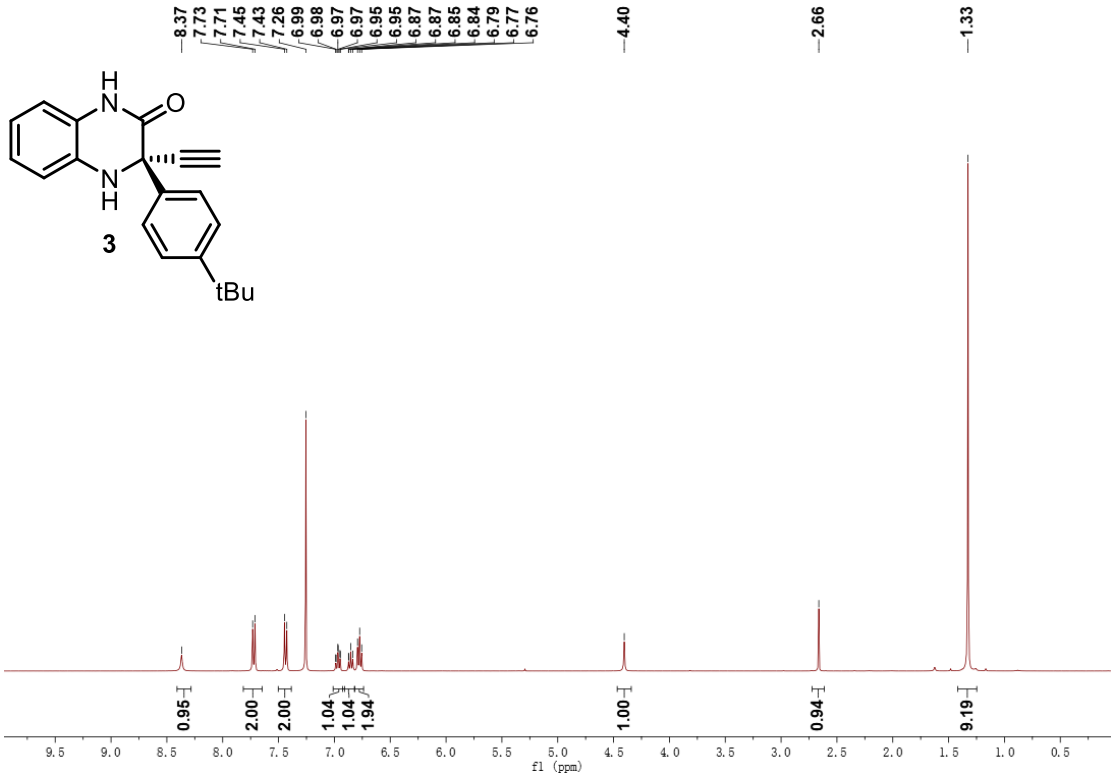
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



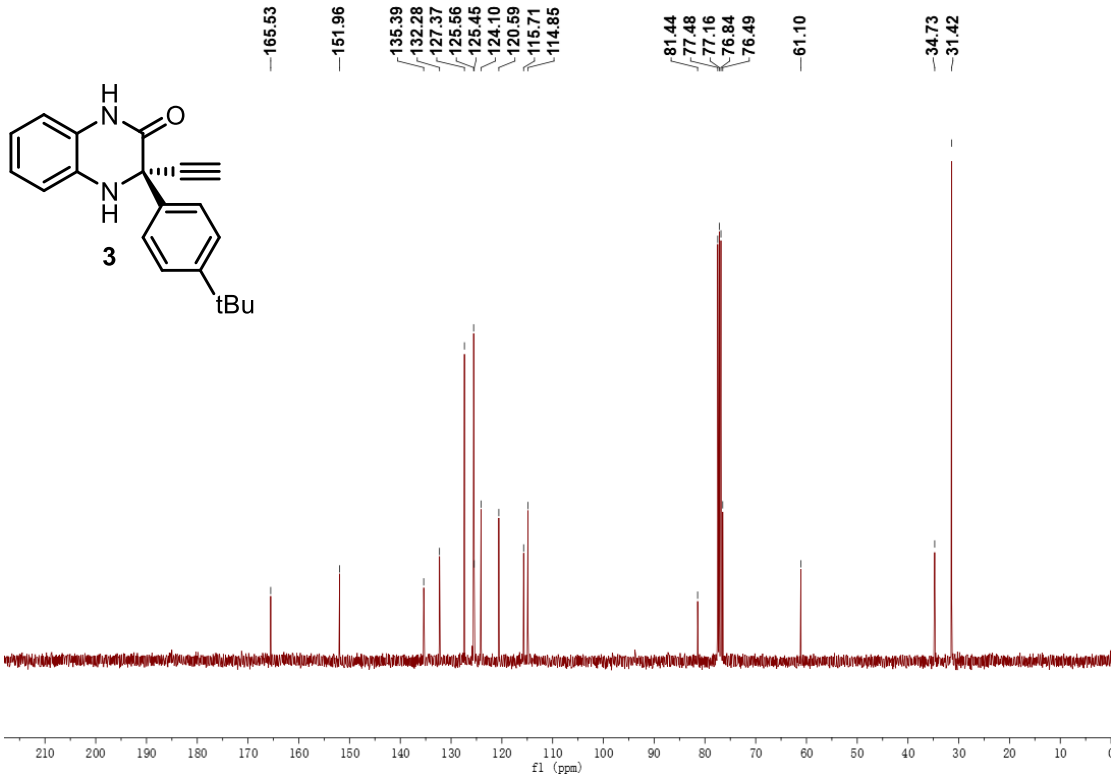
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



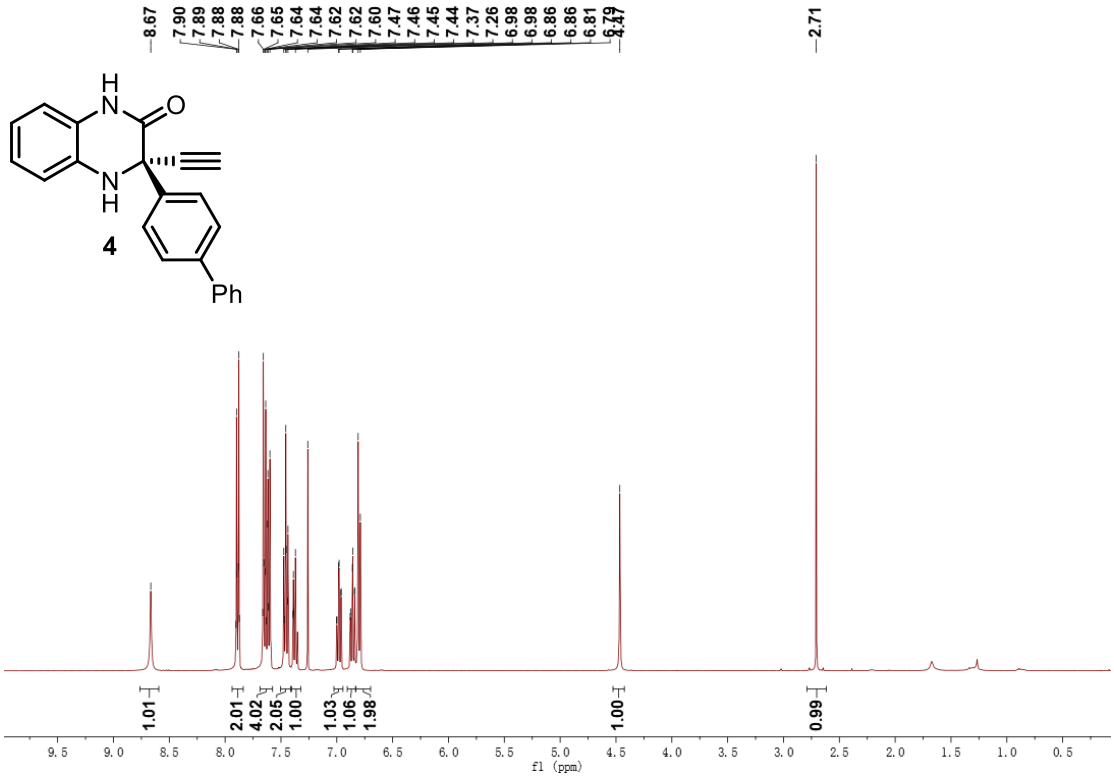
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



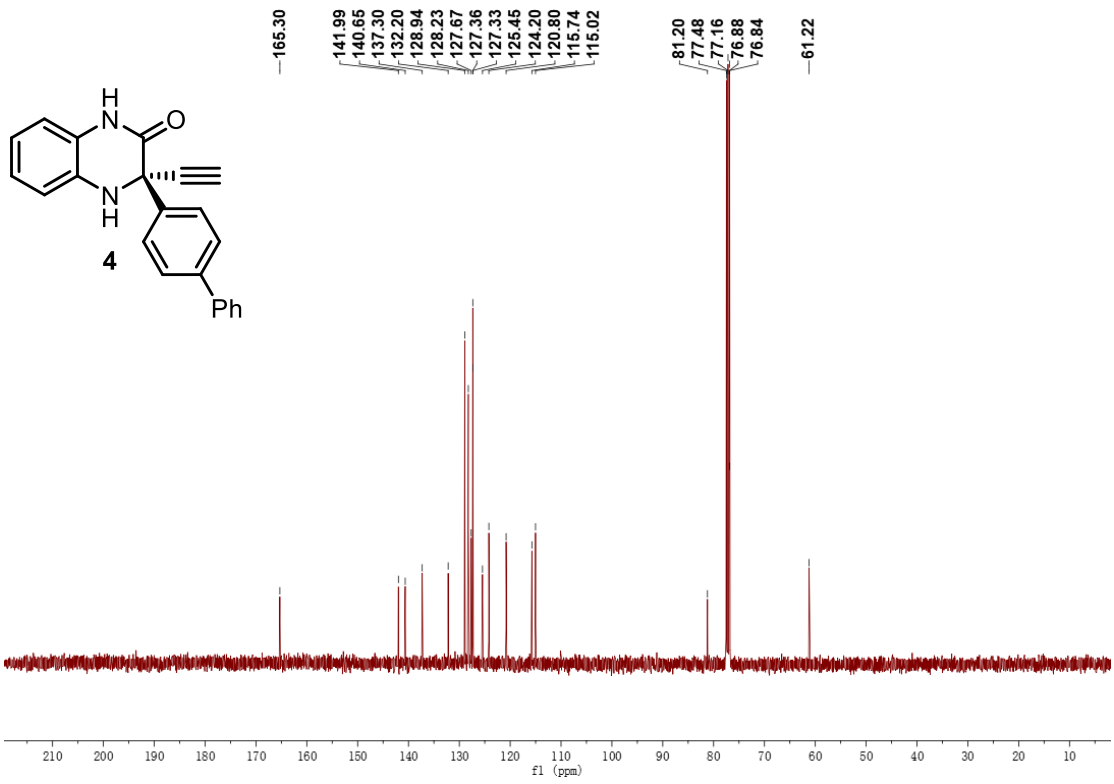
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



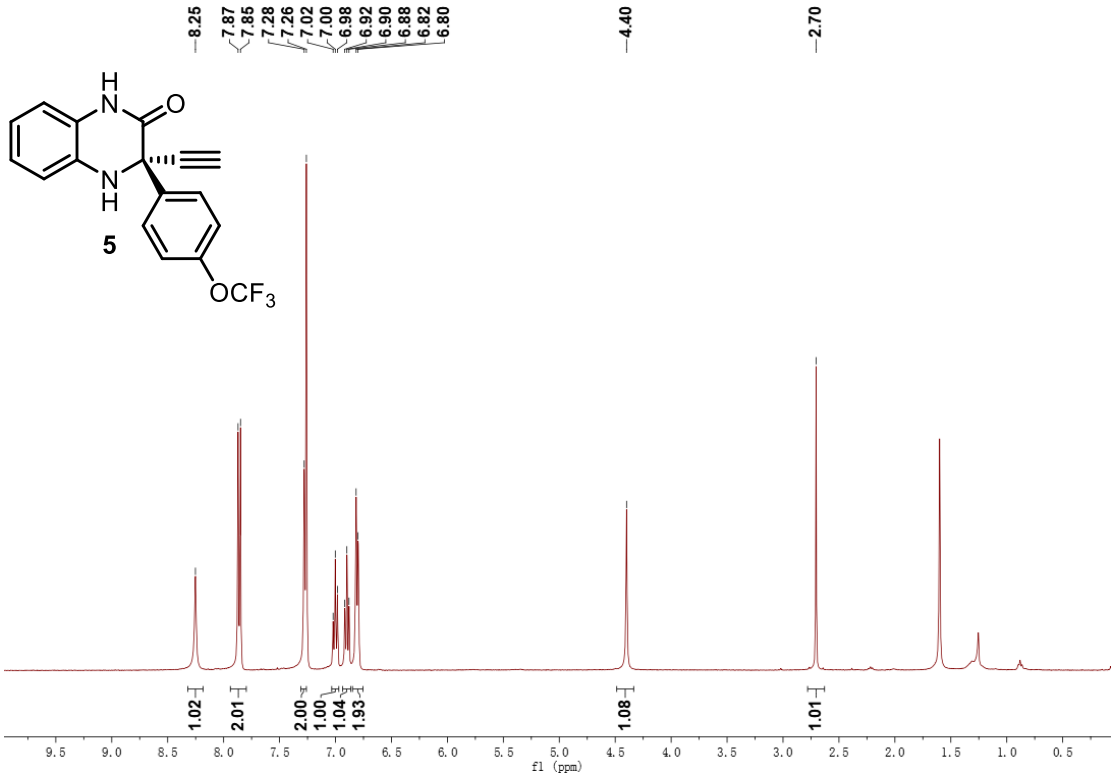
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



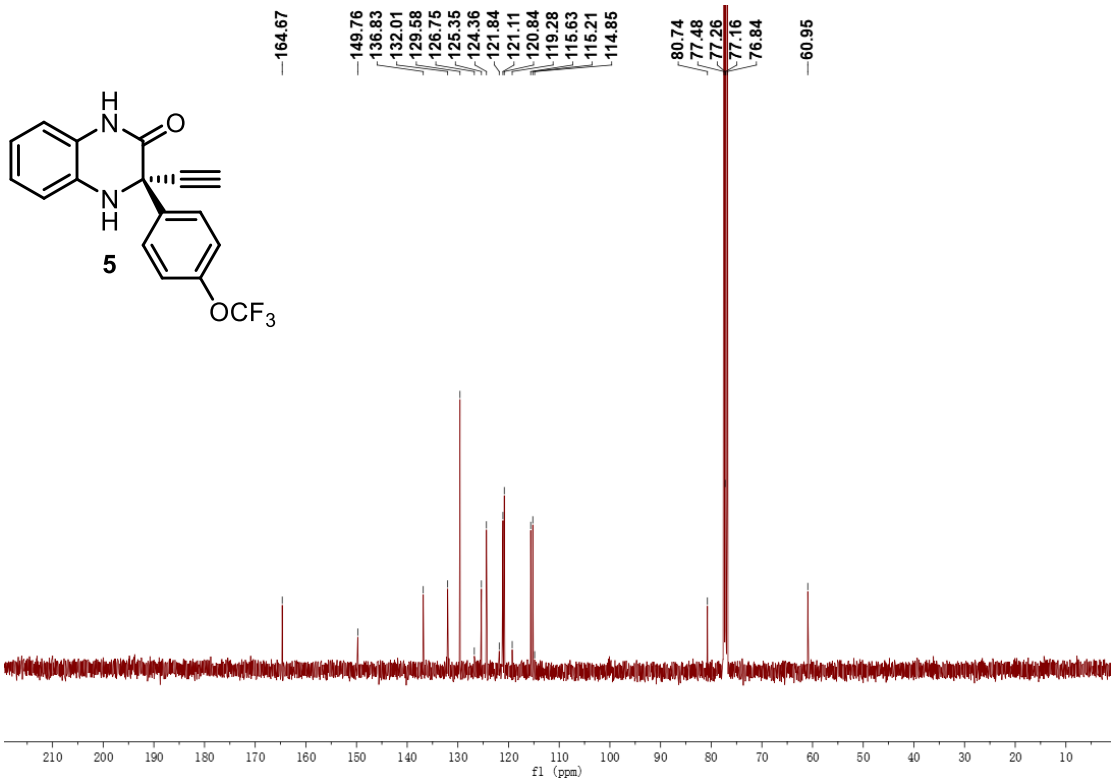
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



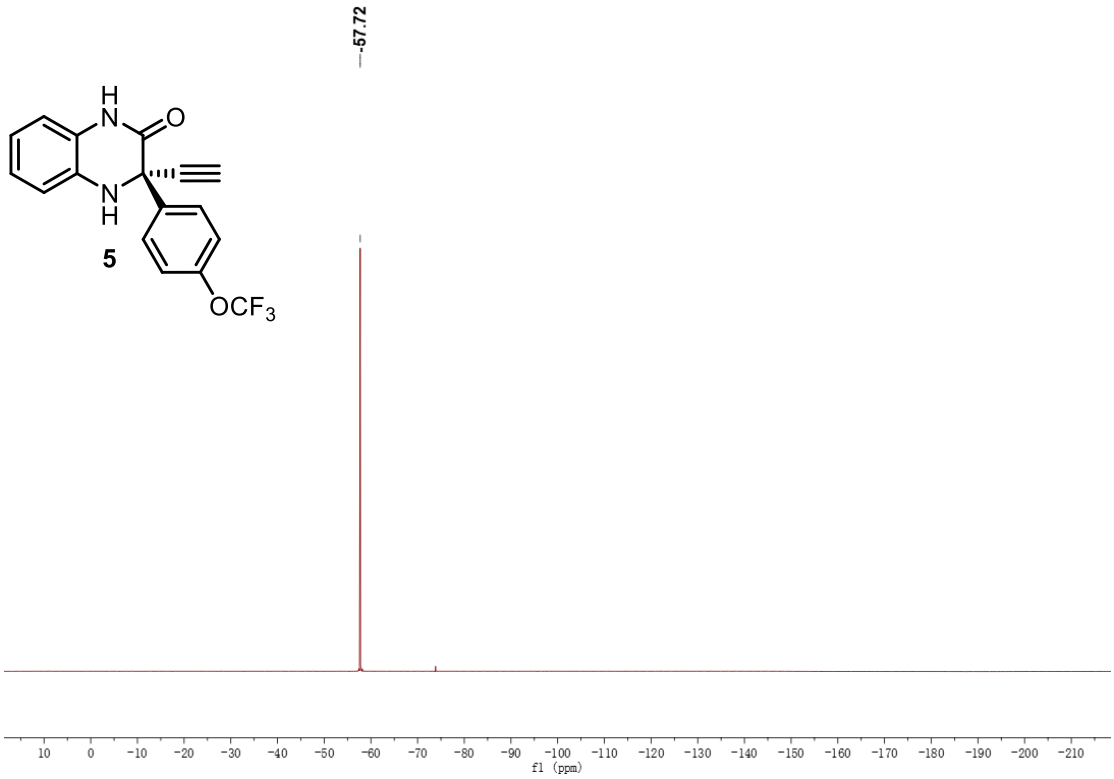
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



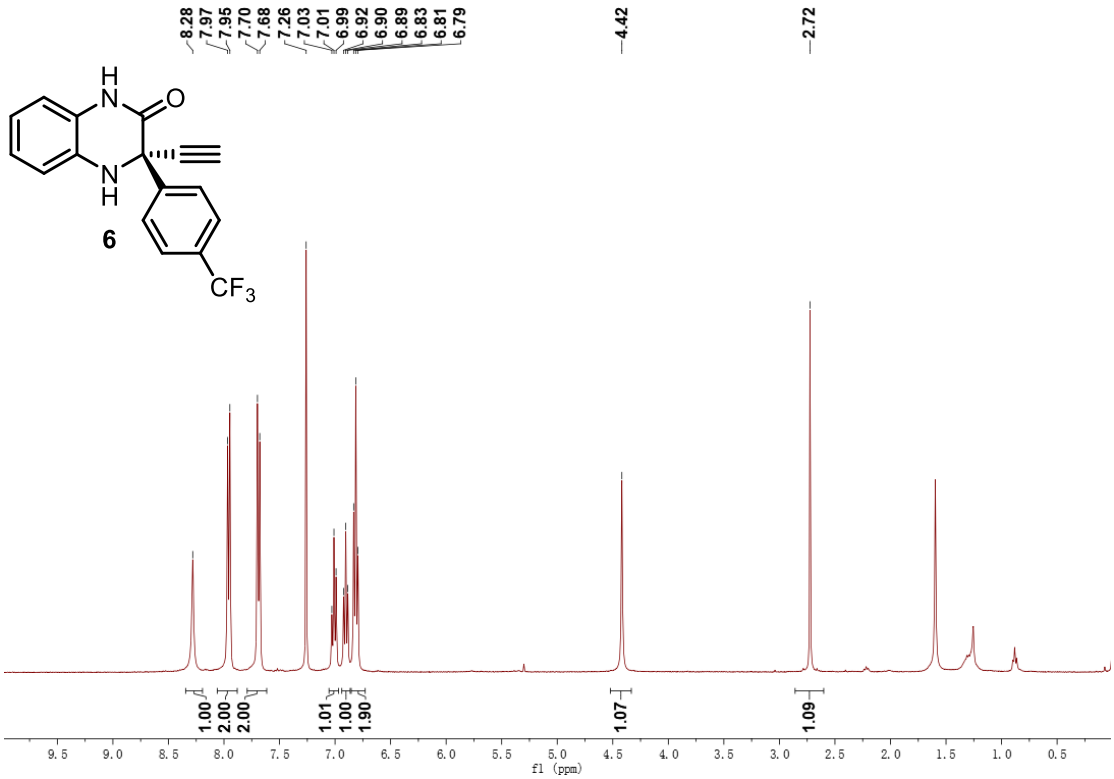
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



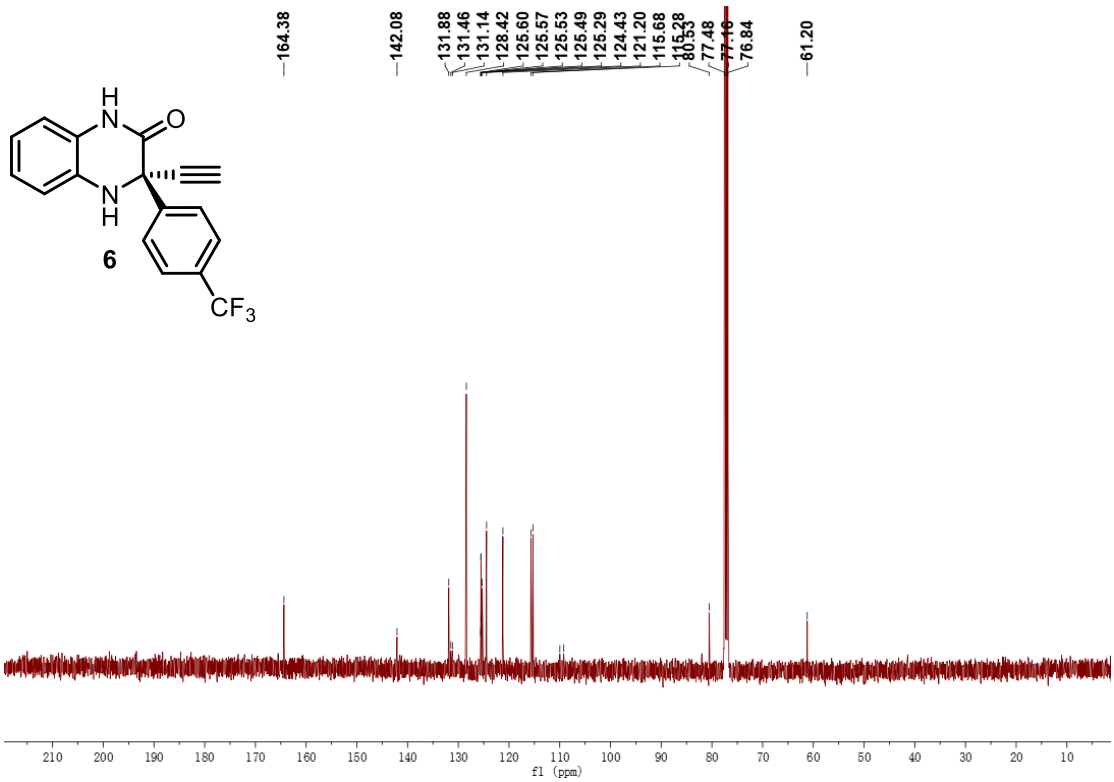
^{19}F NMR spectrum (376 MHz, CDCl3)



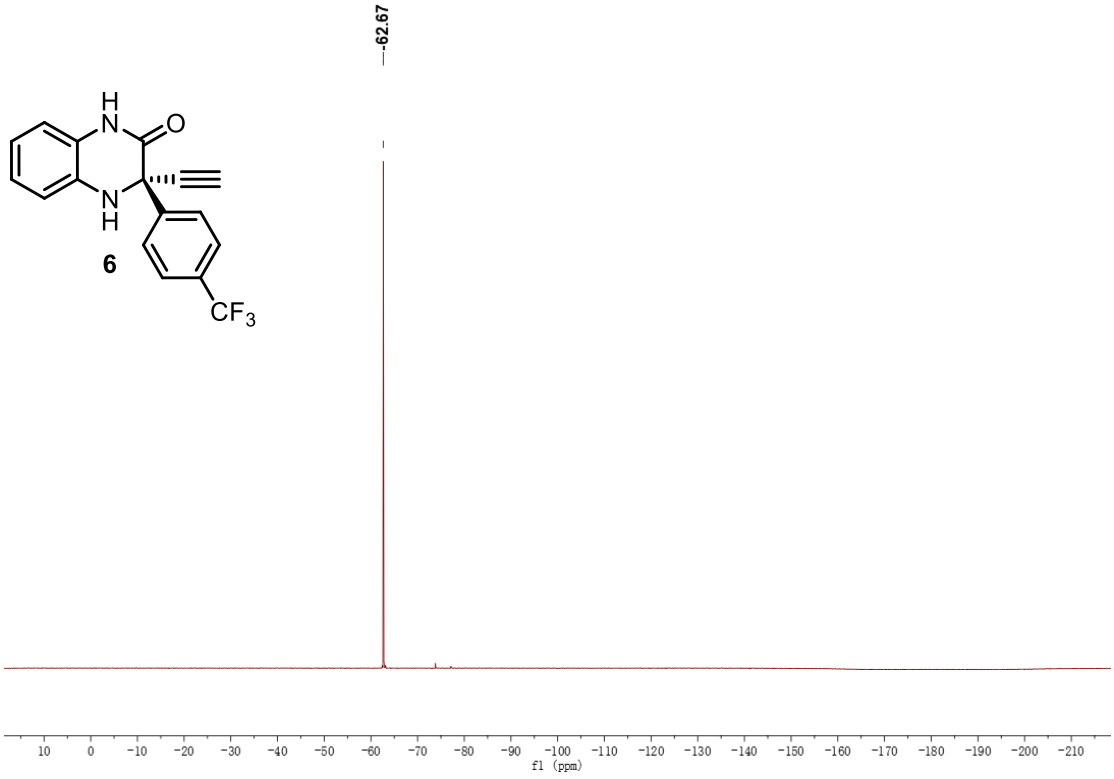
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



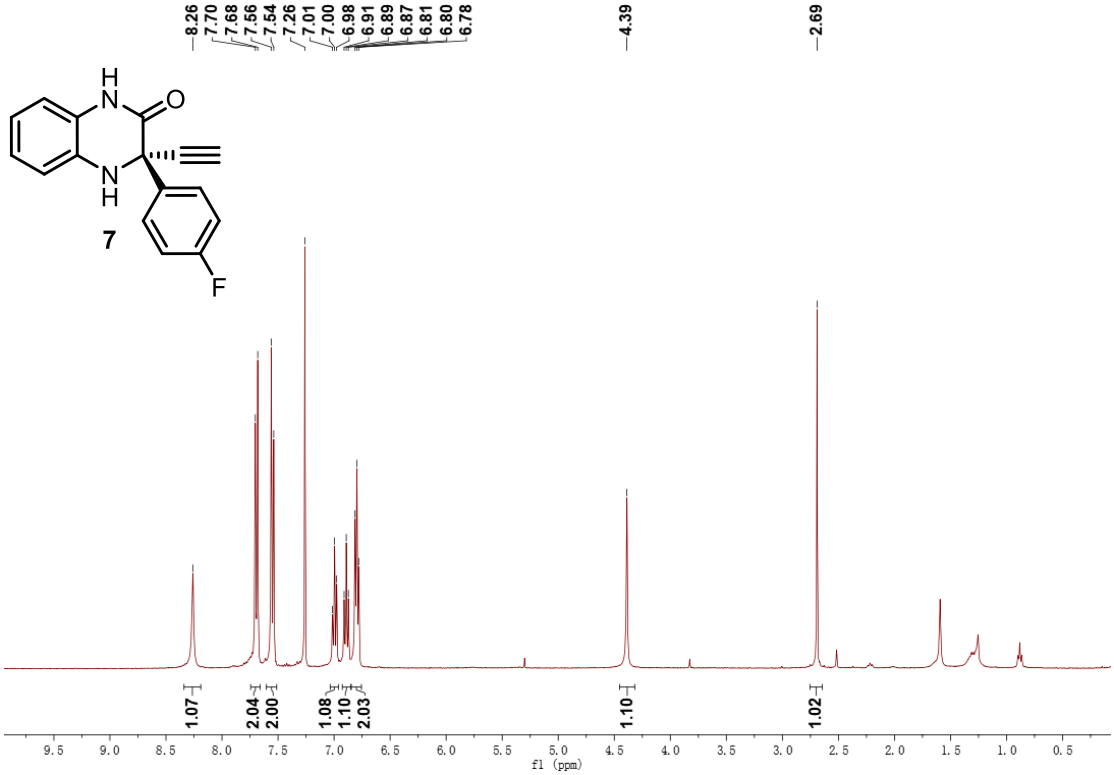
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



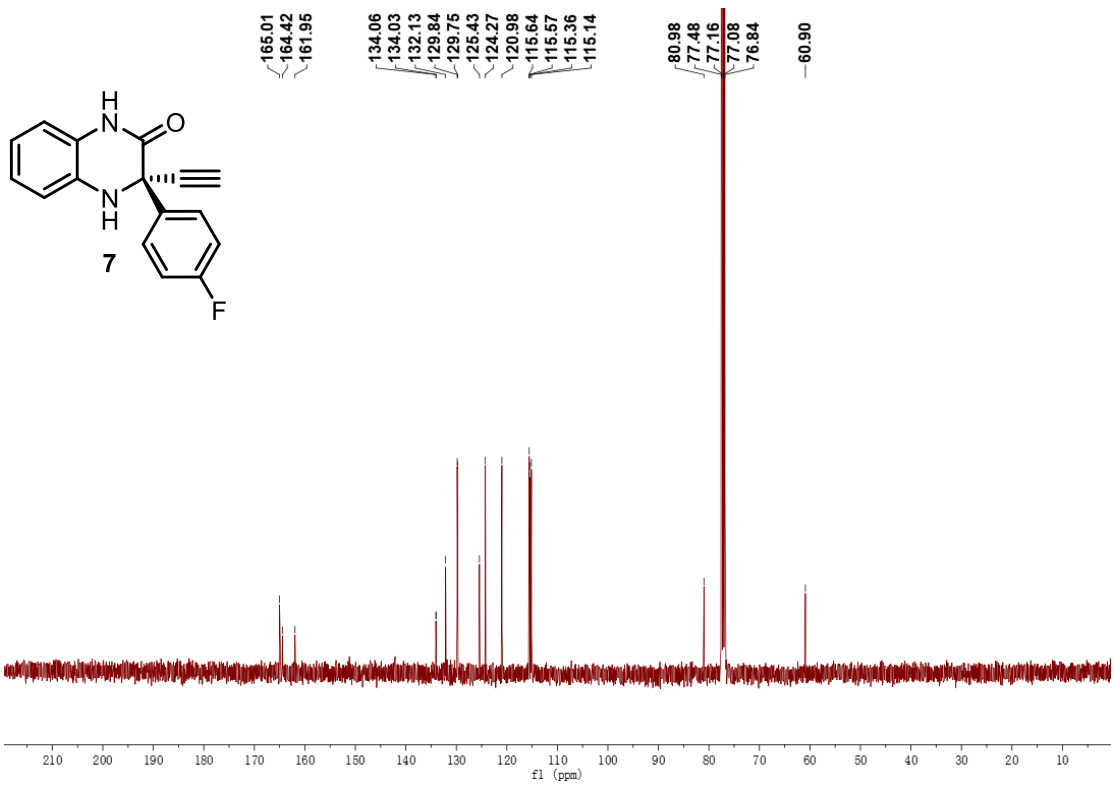
^{19}F NMR spectrum (376 MHz, CDCl3)



^{1}H NMR spectrum (400 MHz, $CDCl_3$)

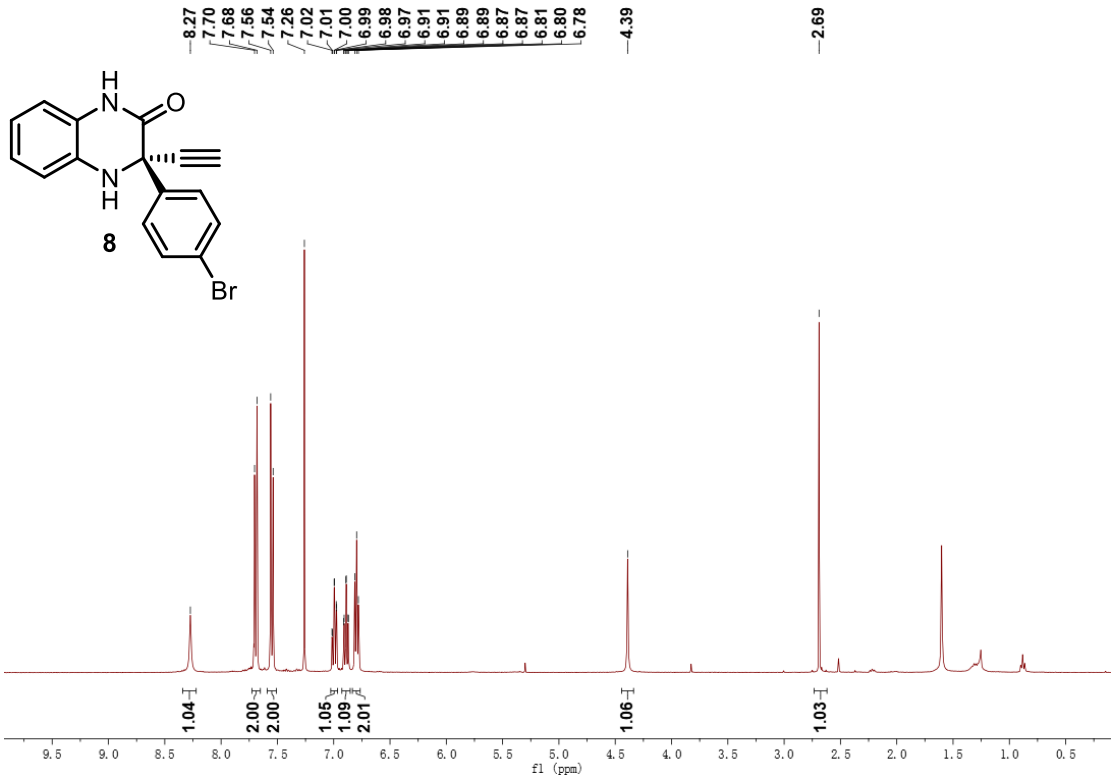


^{13}C NMR spectrum (100 MHz, $CDCl_3$)

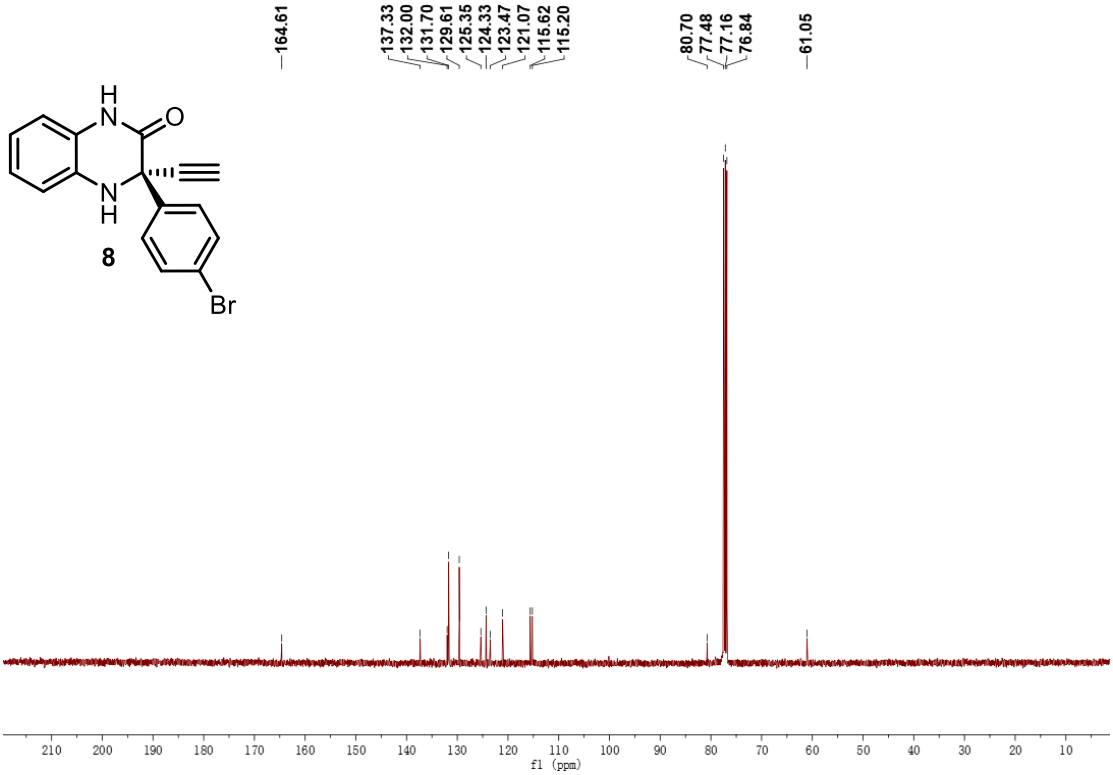


^{19}F NMR spectrum (376 MHz, CDCl3)

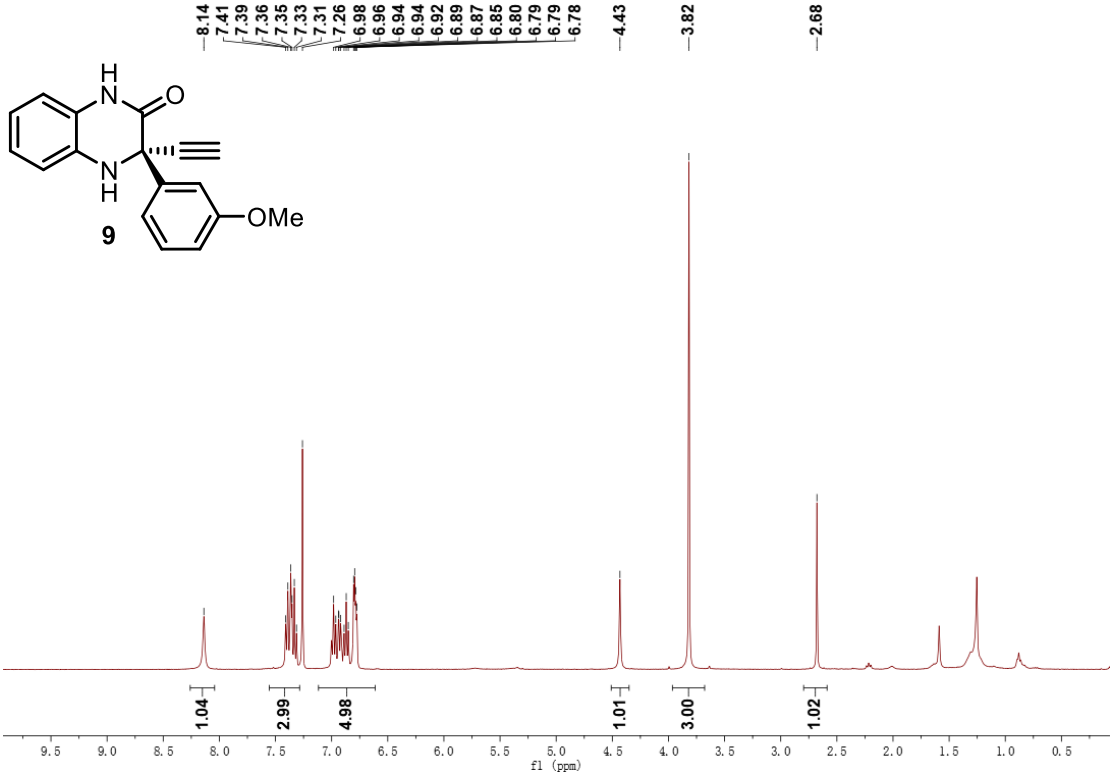
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



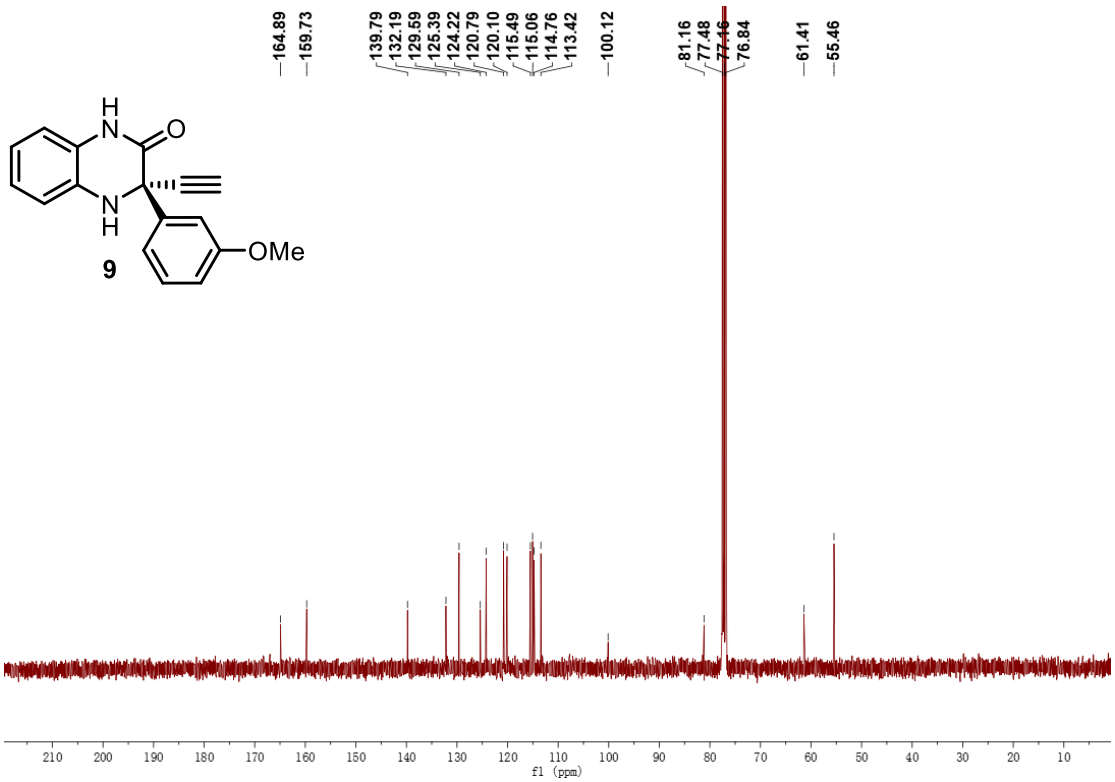
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



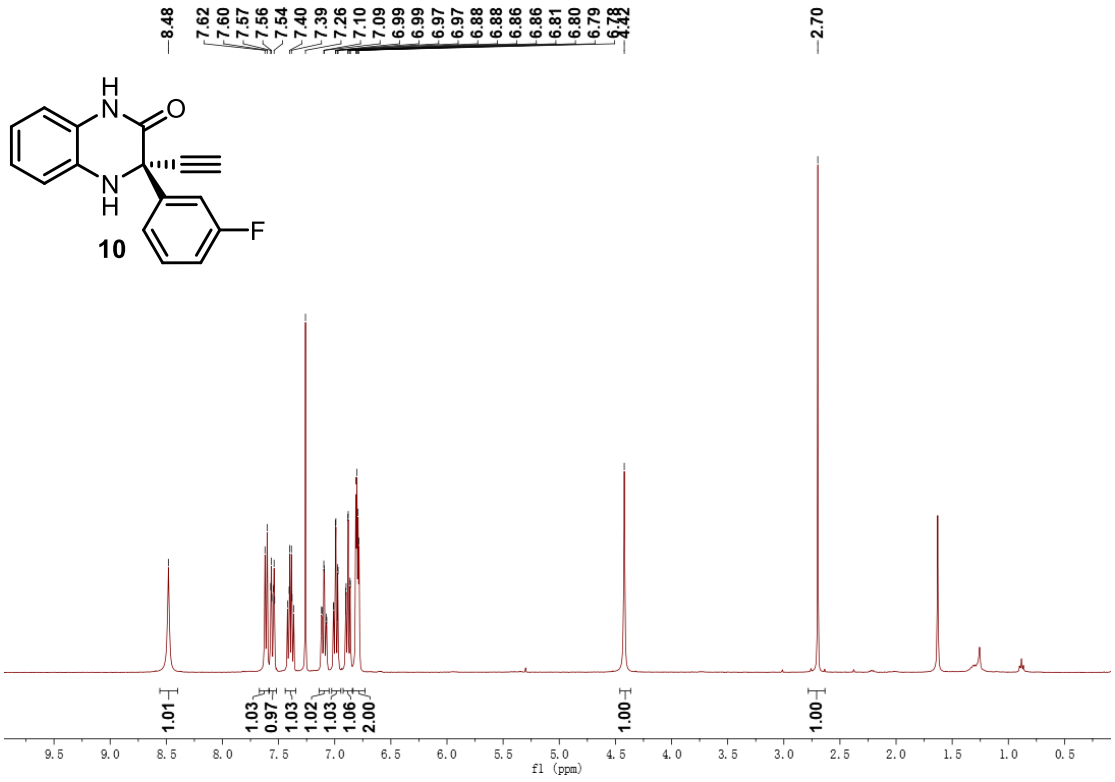
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



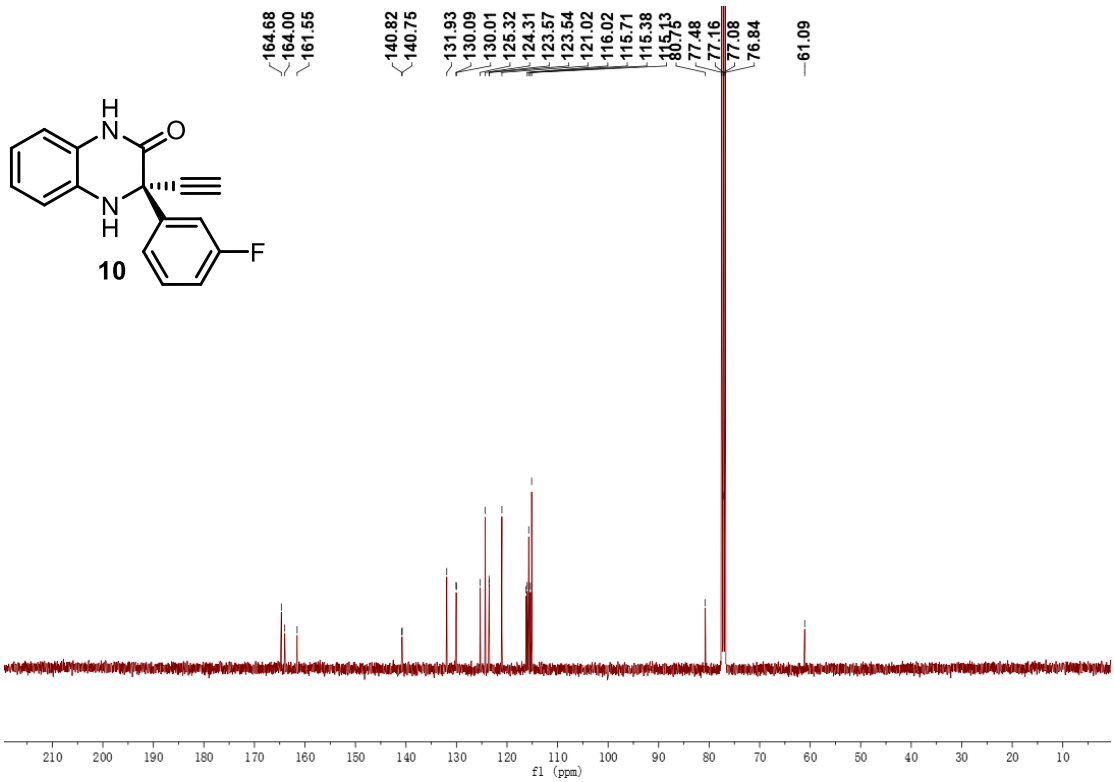
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



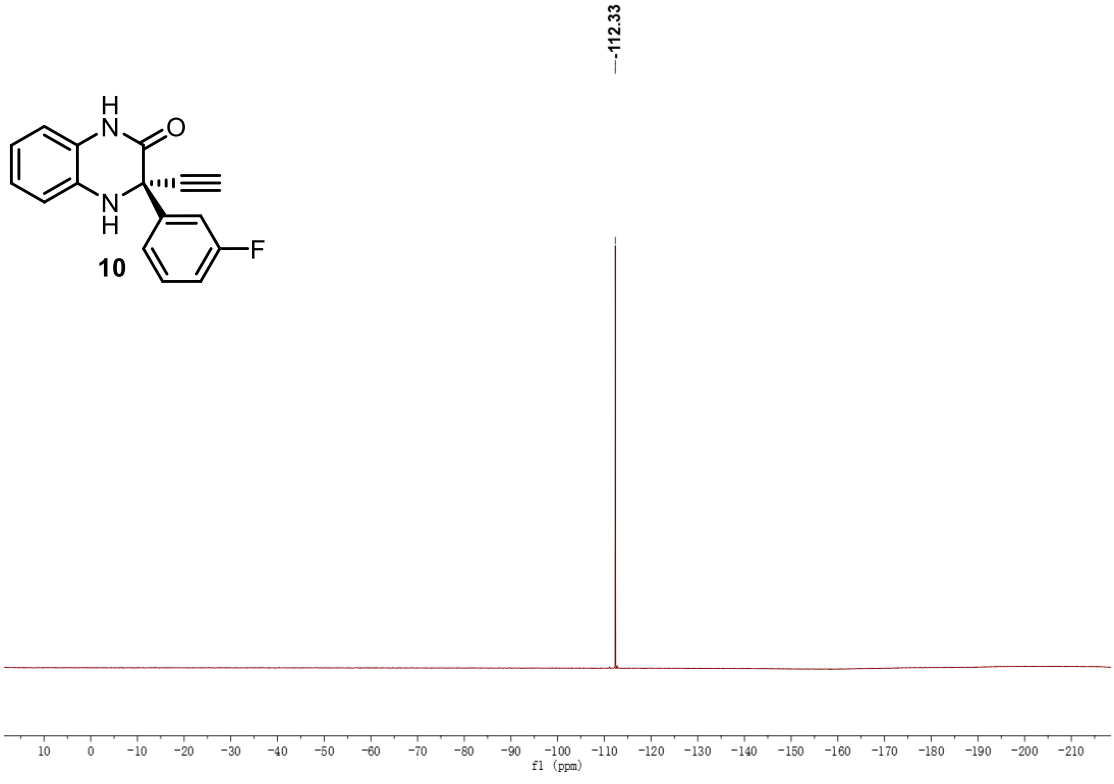
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



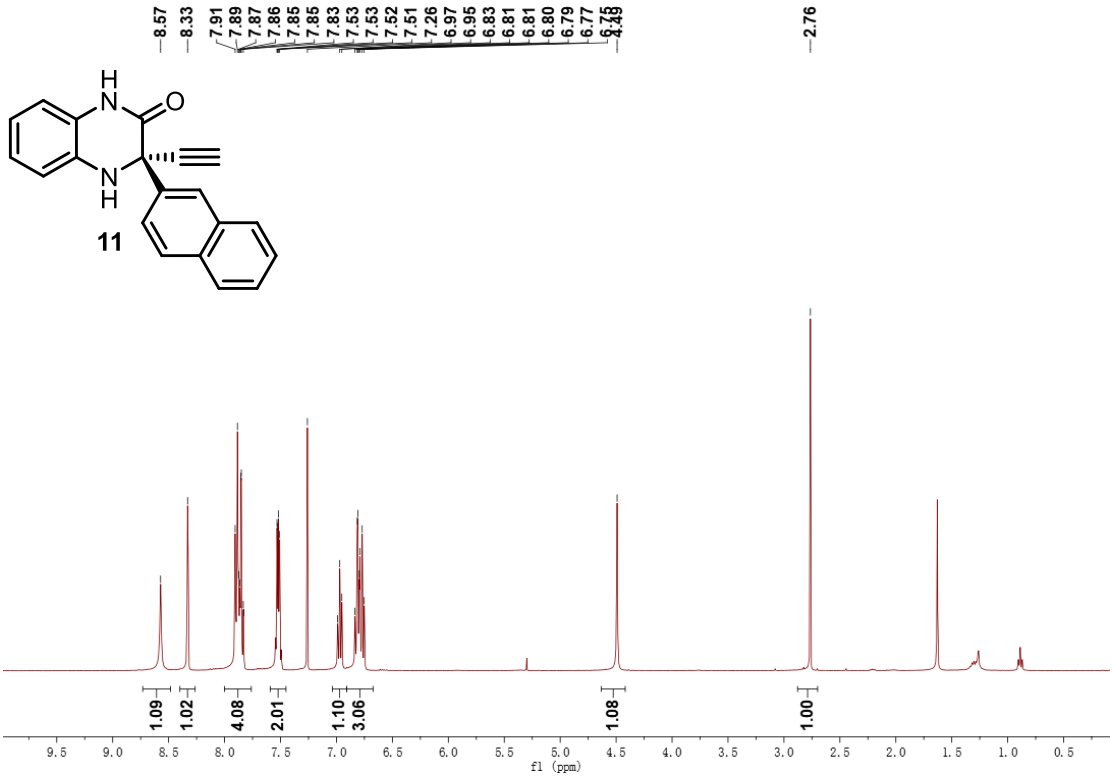
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



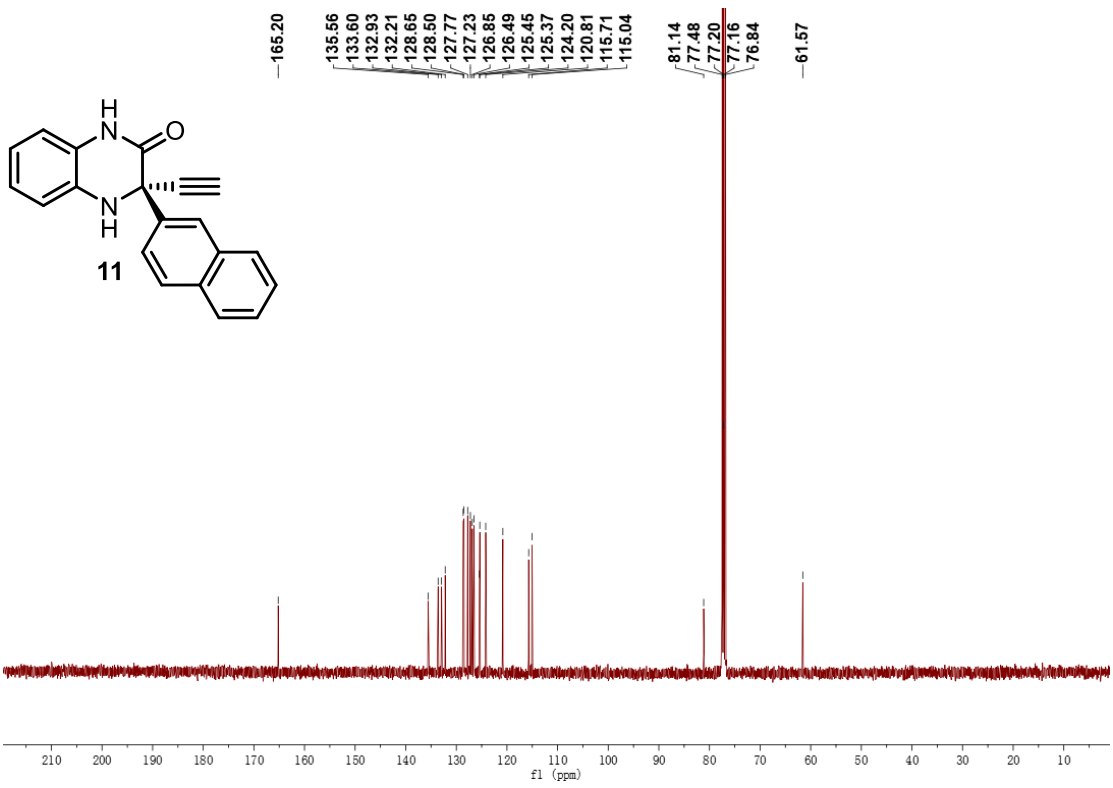
^{19}F NMR spectrum (376 MHz, CDCl3)



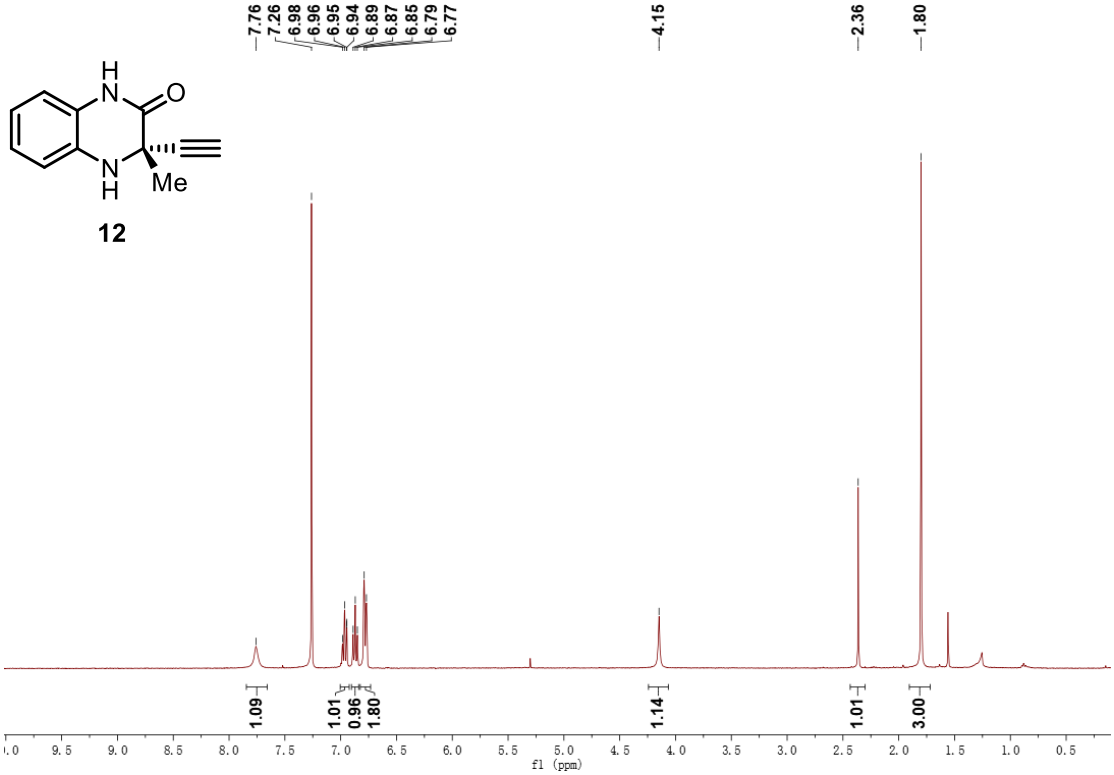
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



^{13}C NMR spectrum (100 MHz, $CDCl_3$)

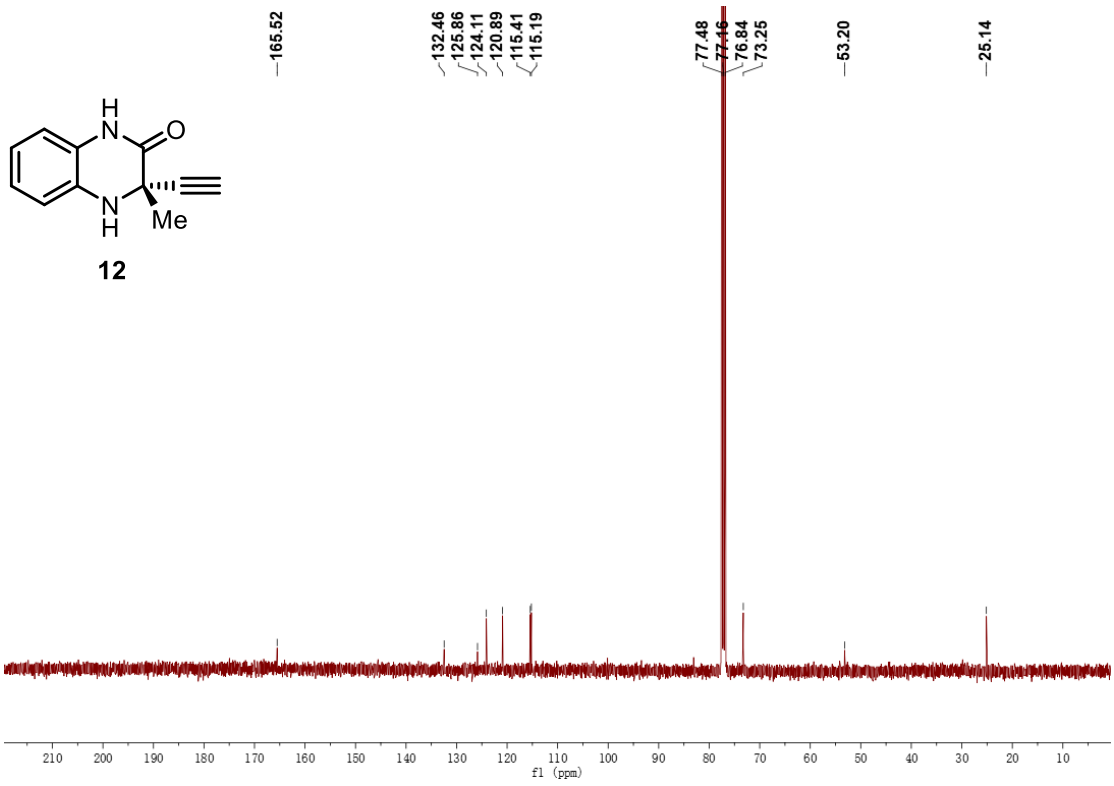


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



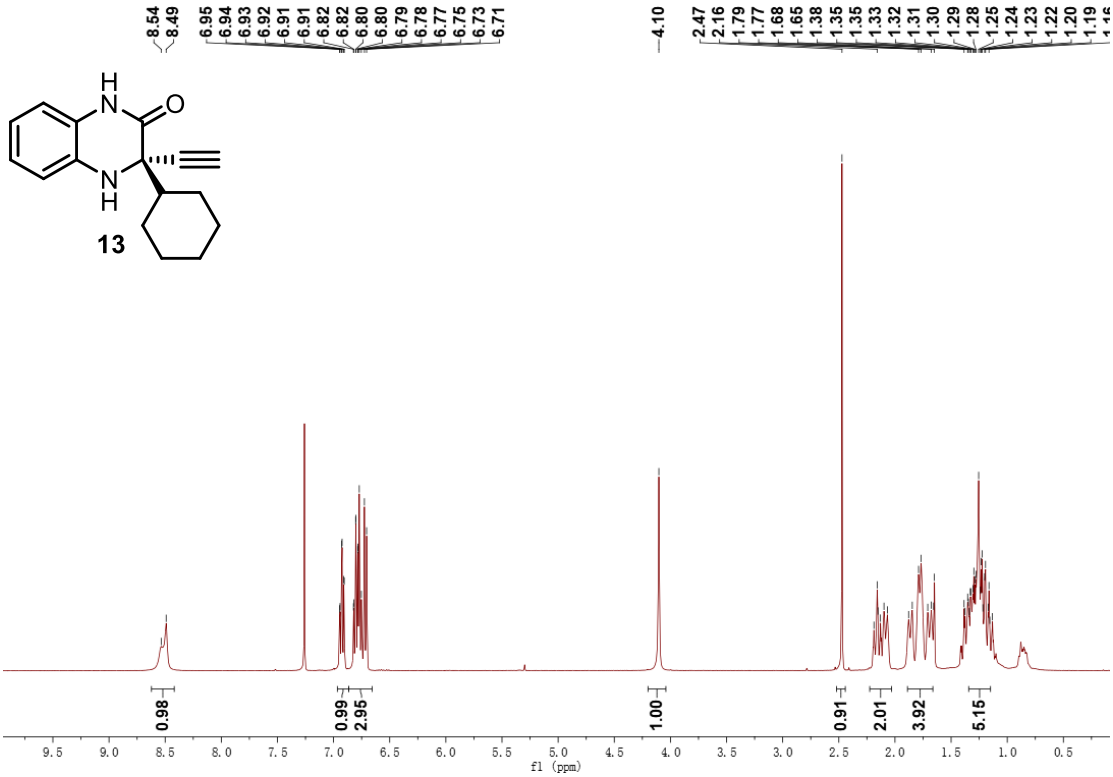
12

^{13}C NMR spectrum (100 MHz, $CDCl_3$)

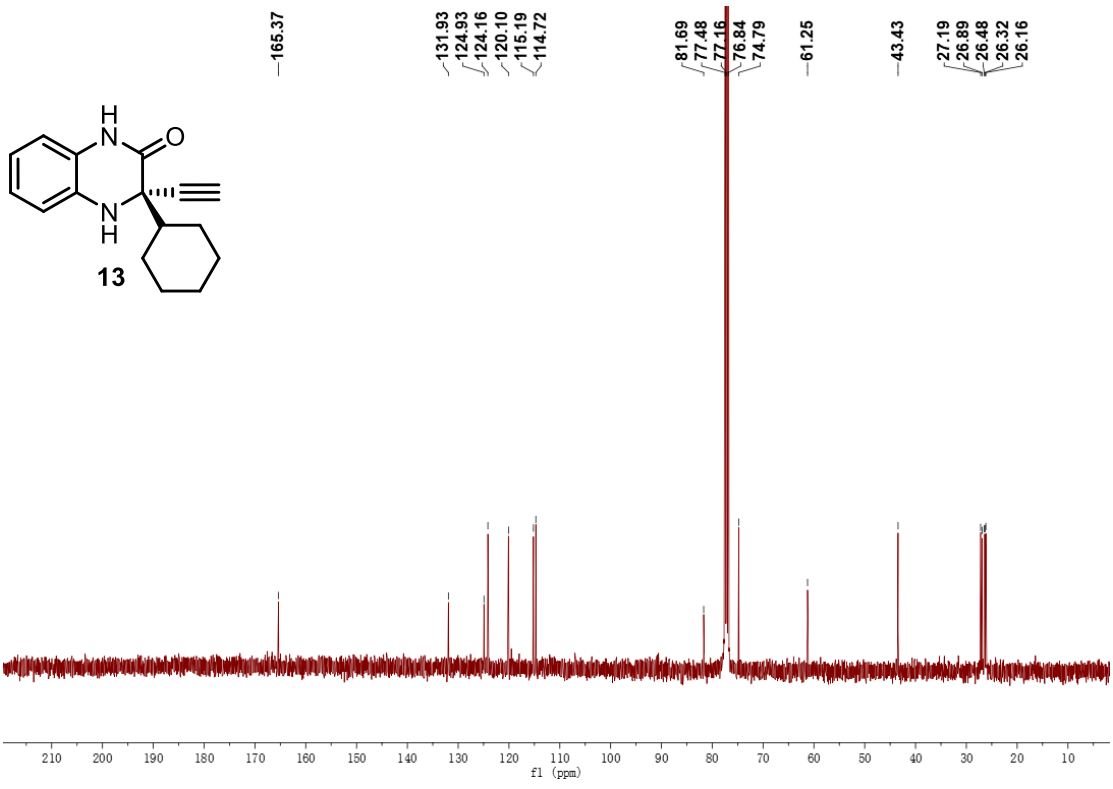


12

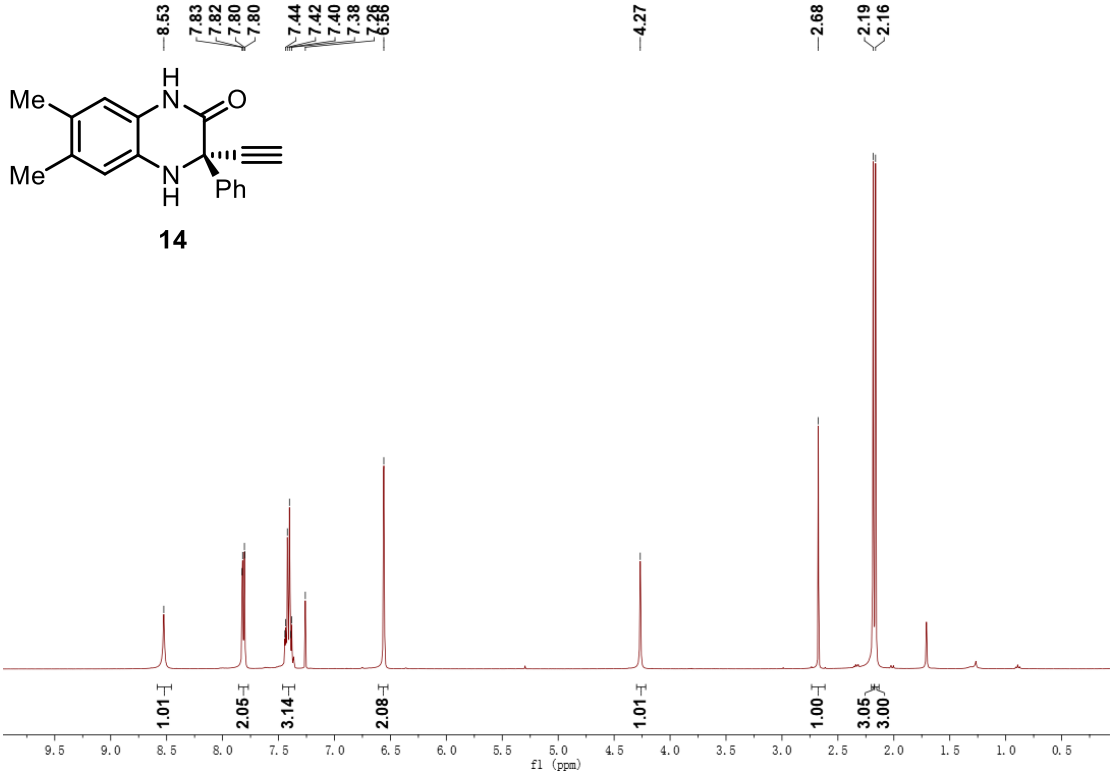
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



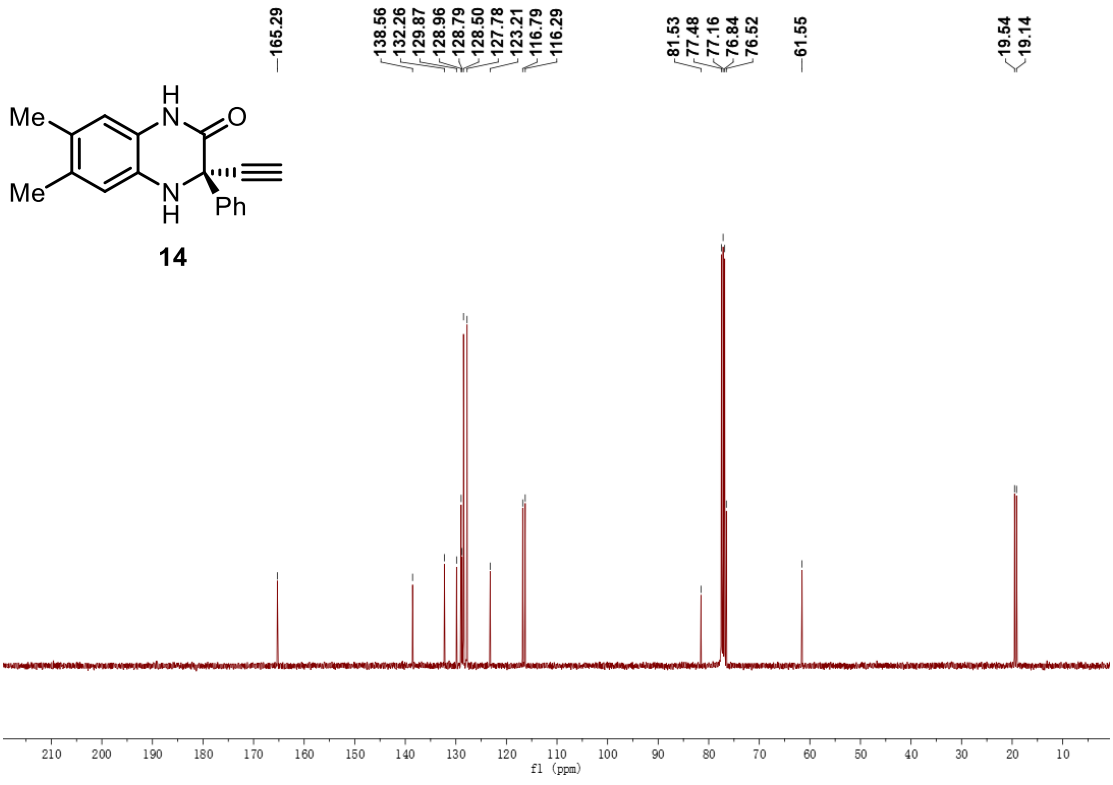
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



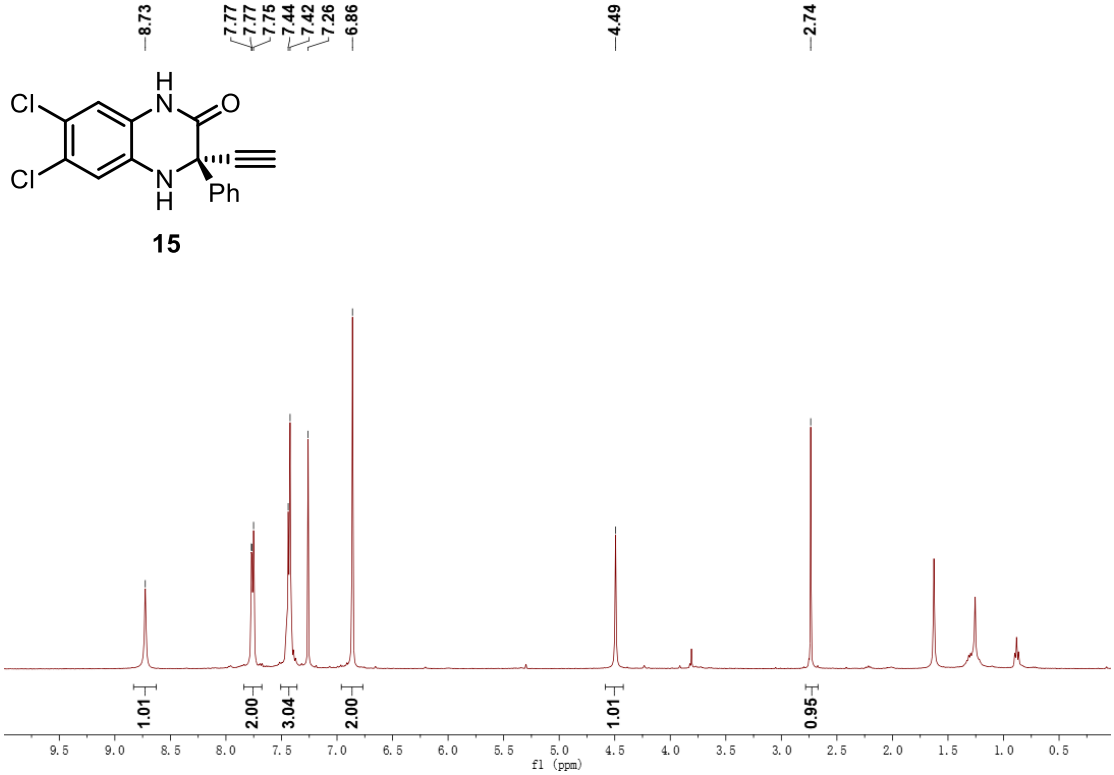
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



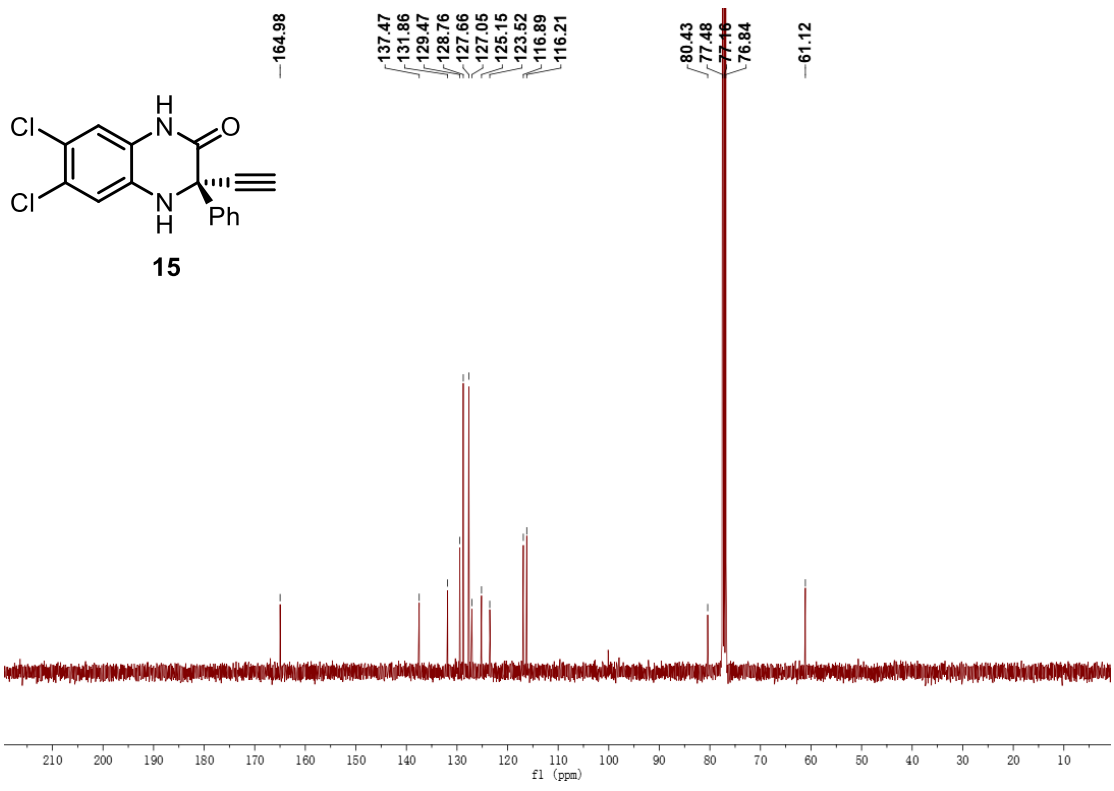
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



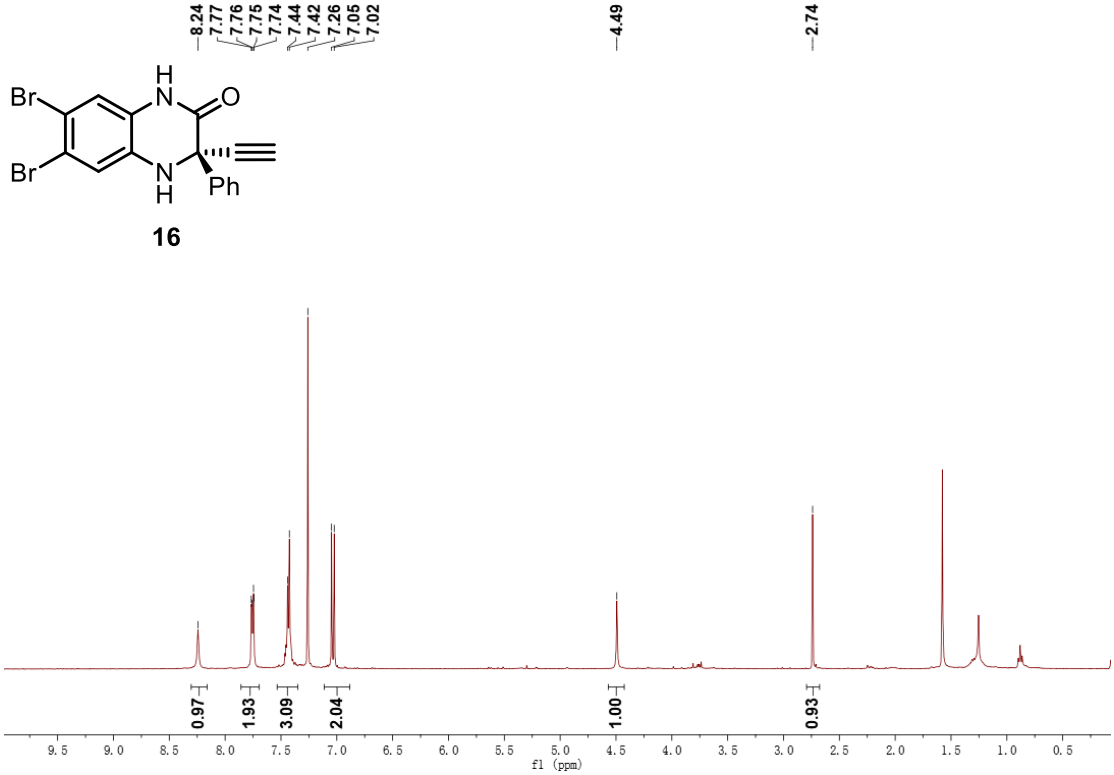
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



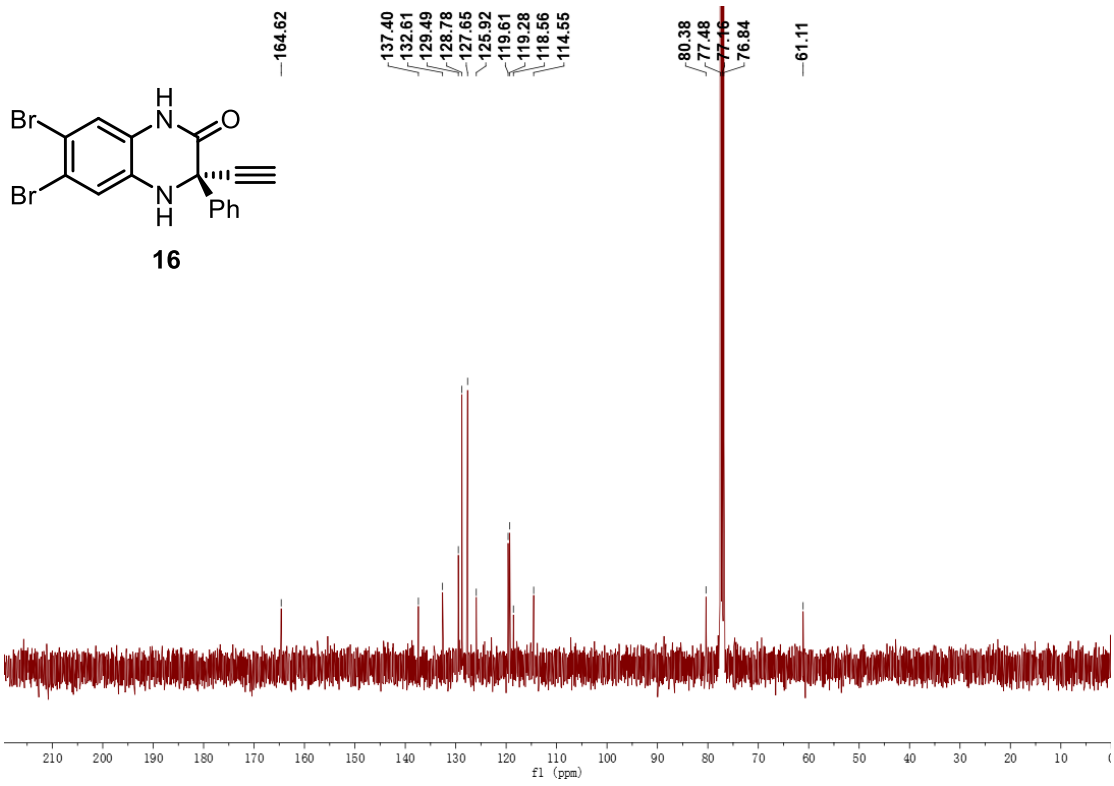
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



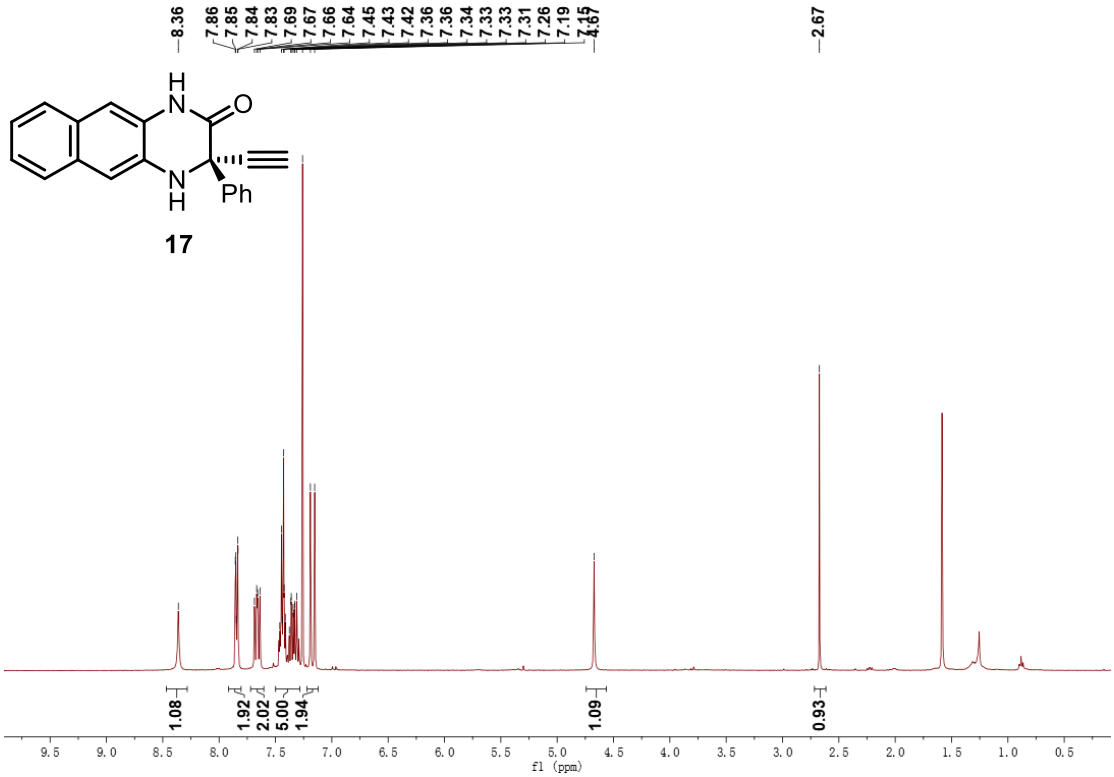
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



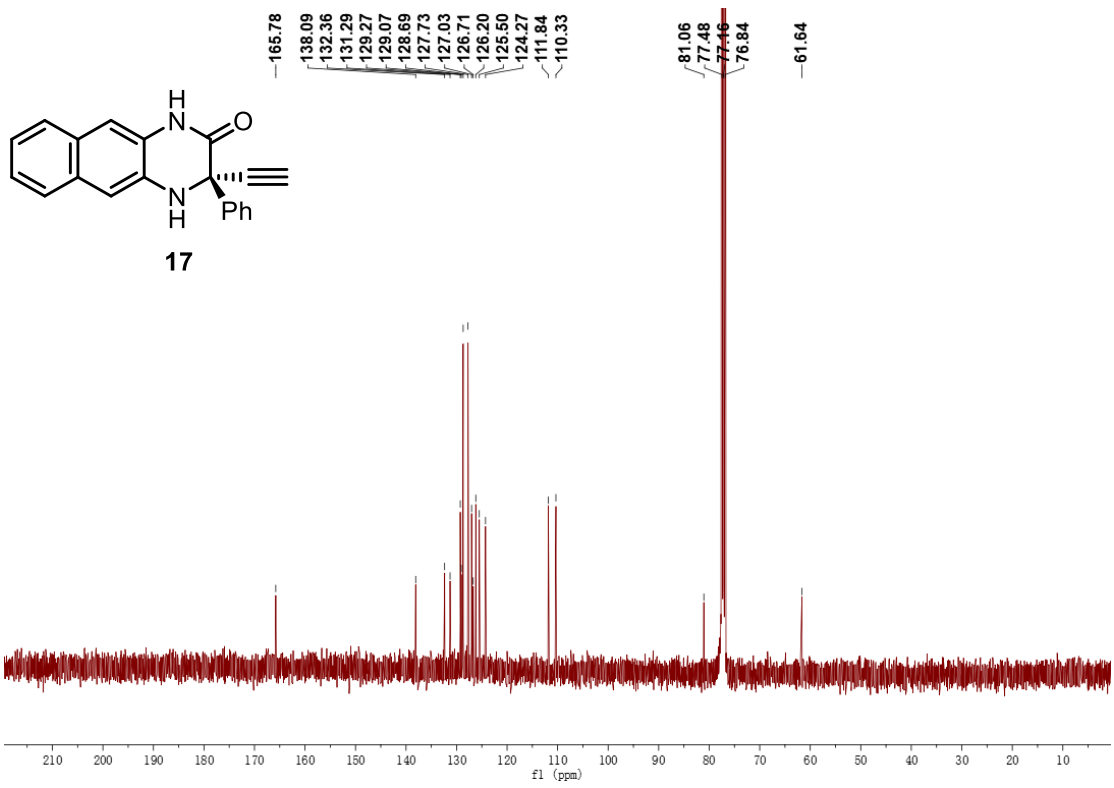
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



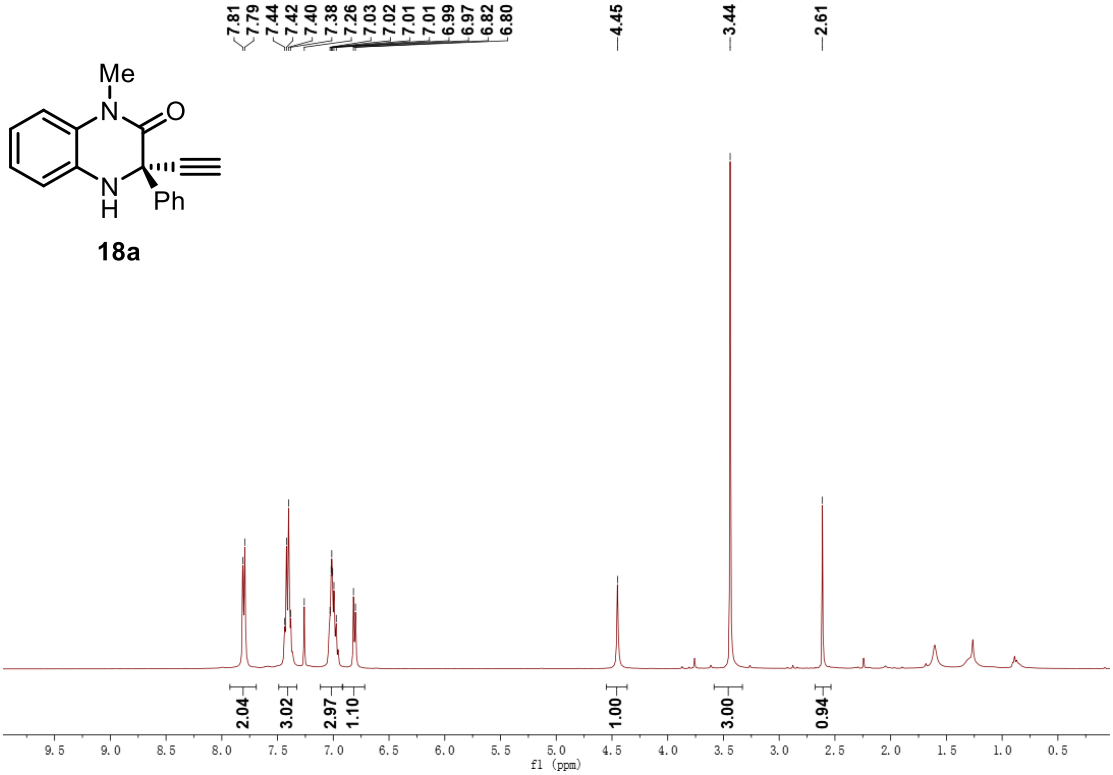
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



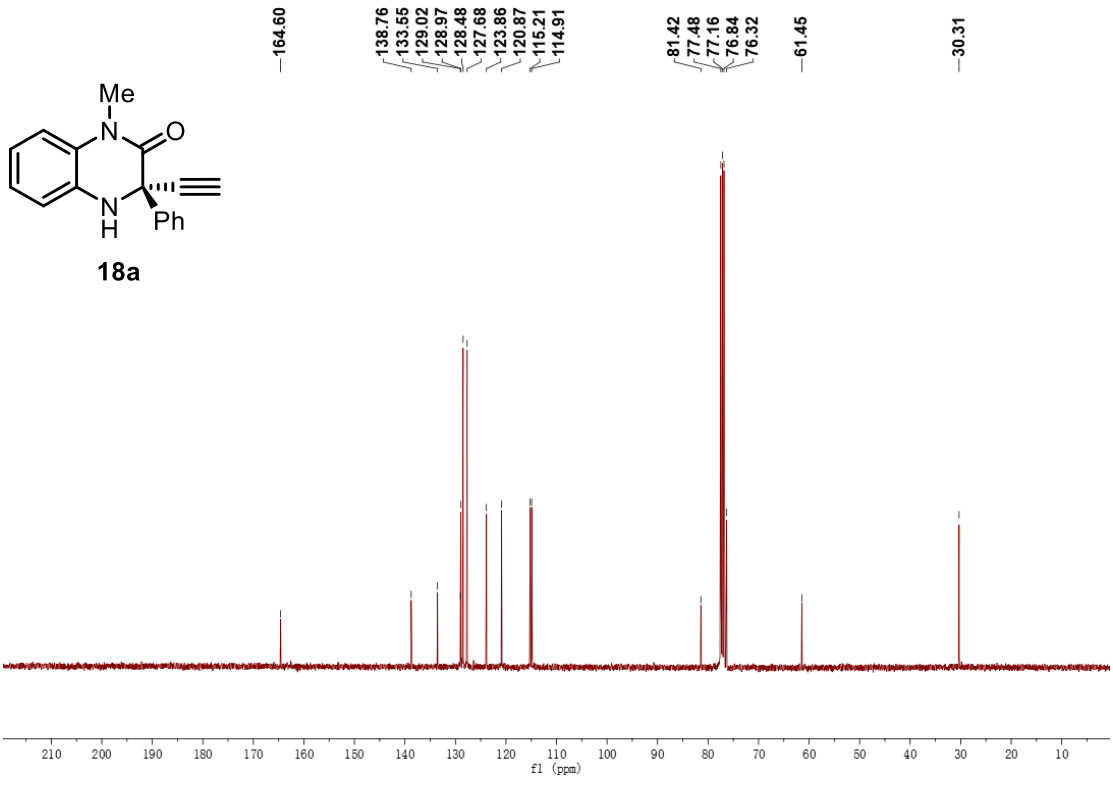
^{13}C NMR spectrum (100 MHz, $CDCl_3$)



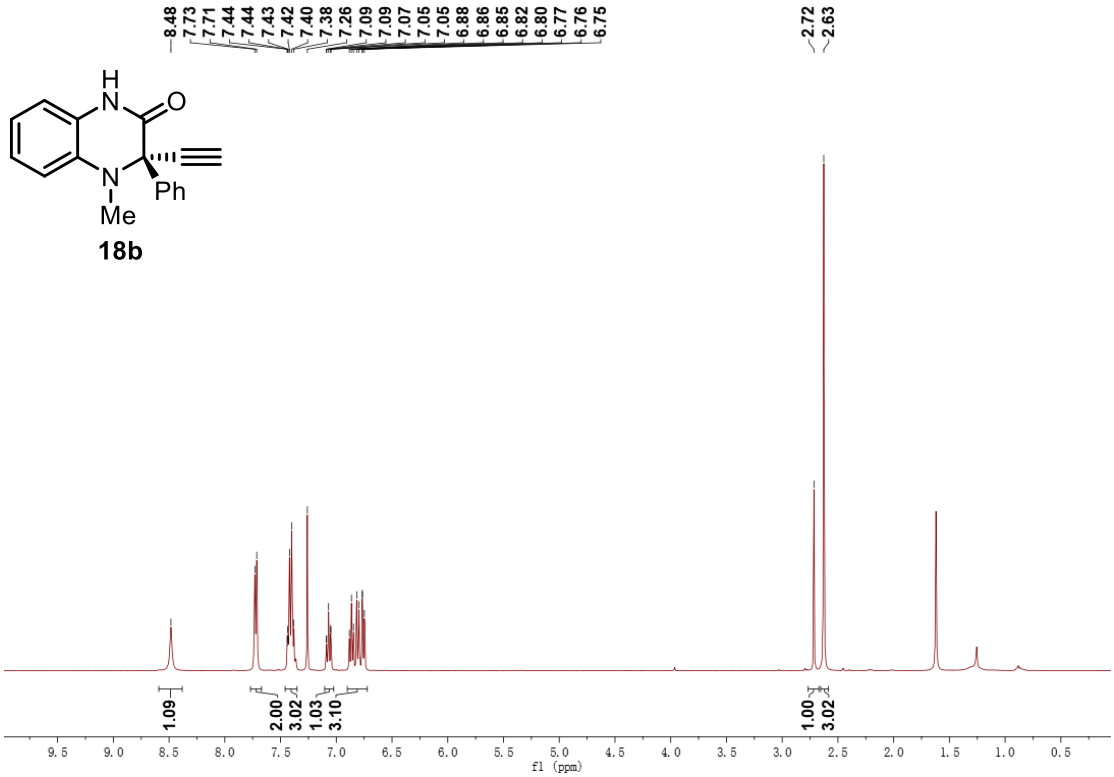
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



^{13}C NMR spectrum (100 MHz, $CDCl_3$)

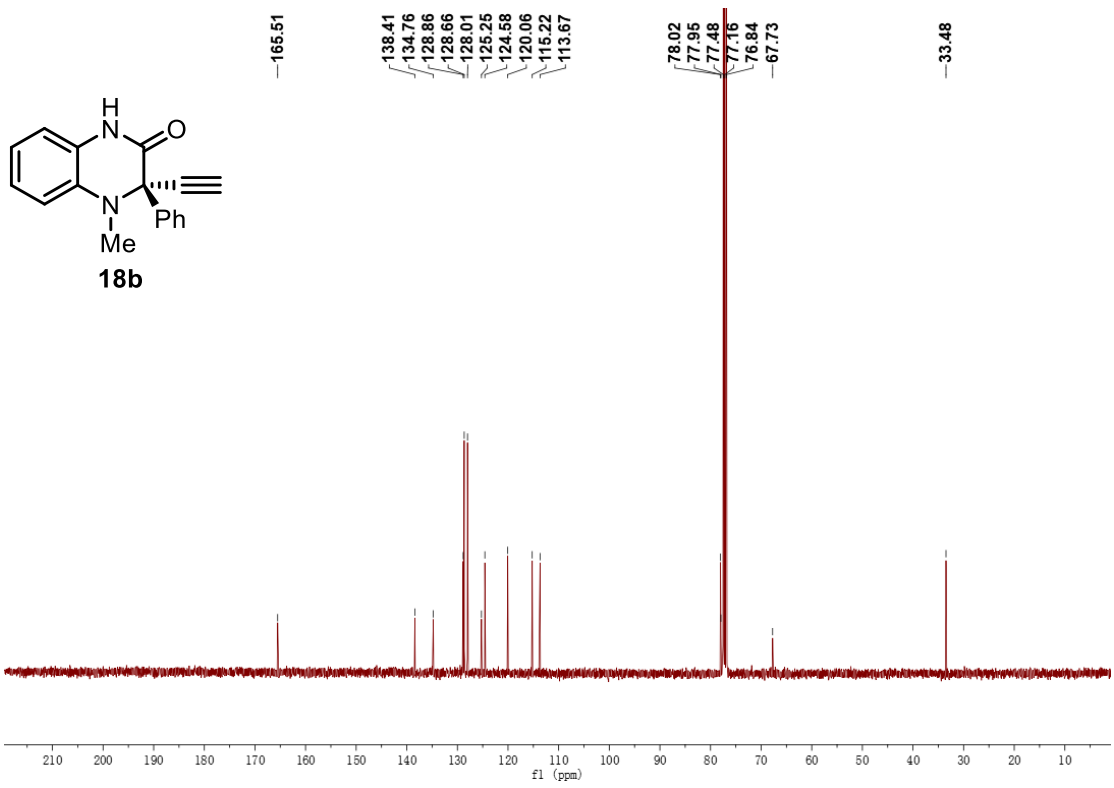


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



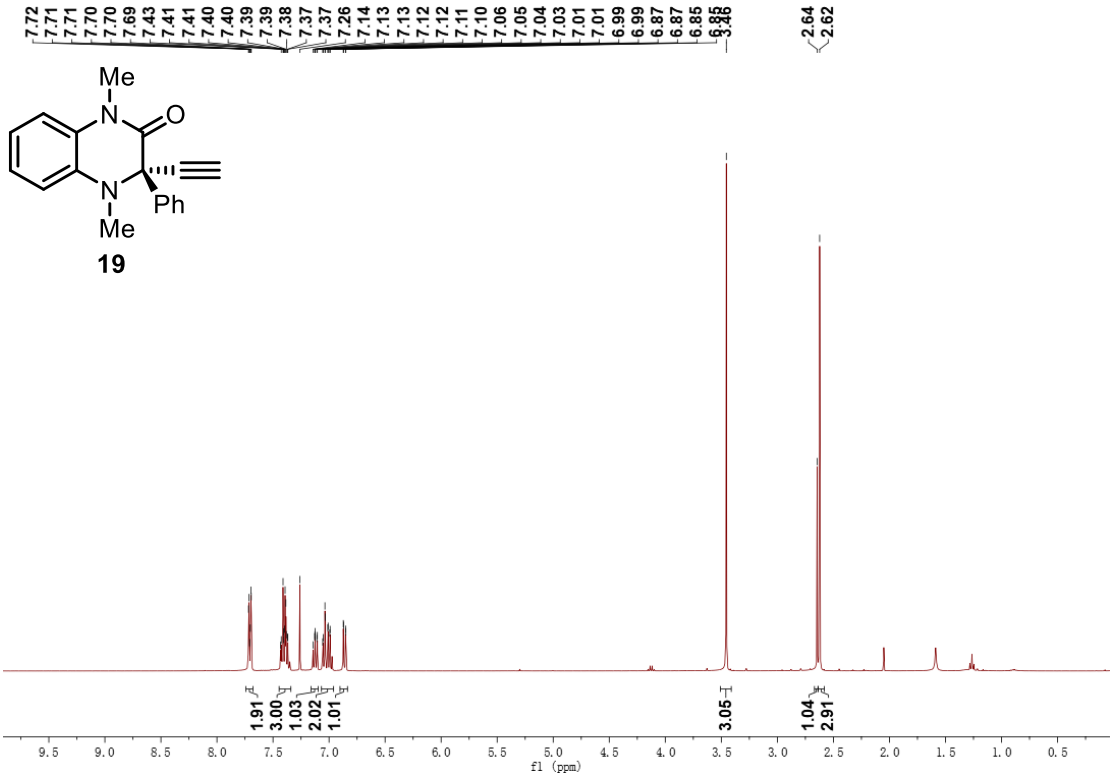
18b

^{13}C NMR spectrum (100 MHz, $CDCl_3$)

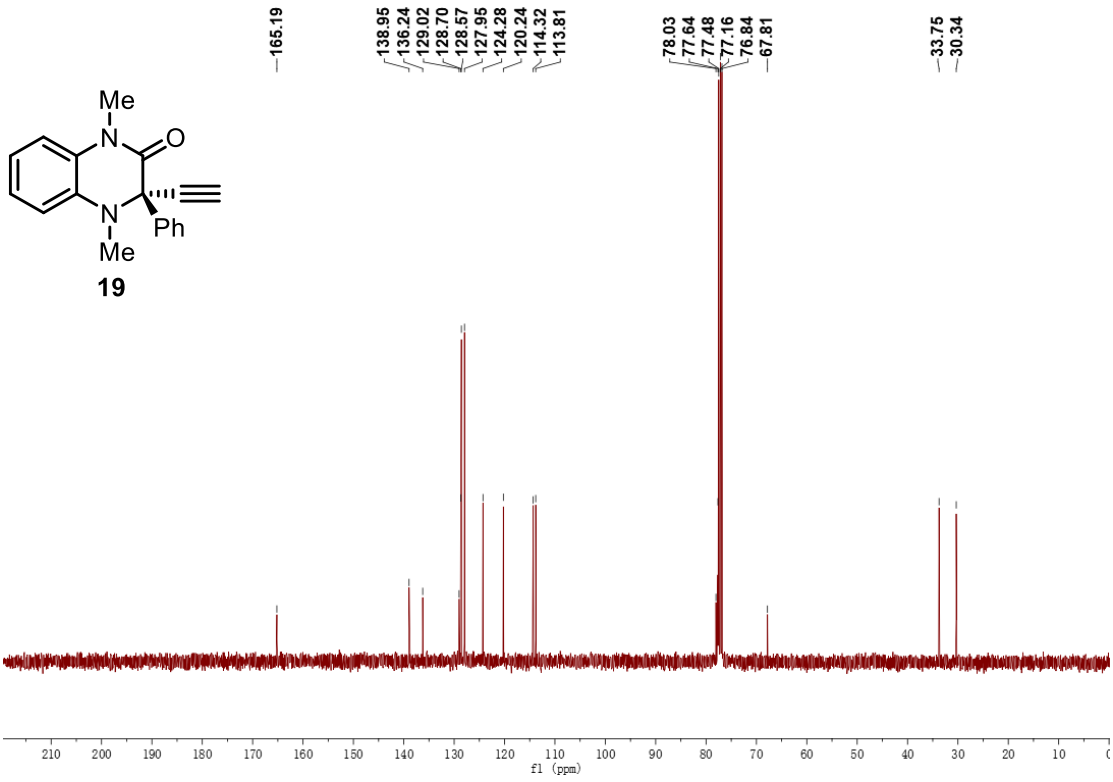


18b

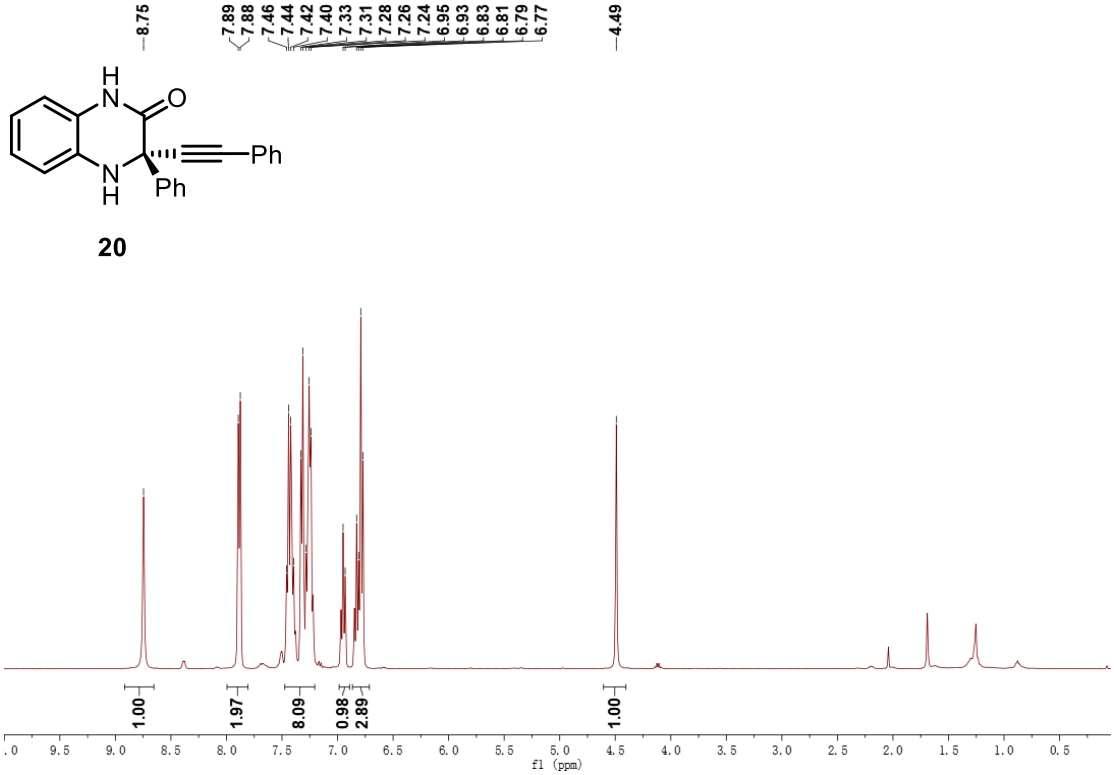
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



^{13}C NMR spectrum (100 MHz, $CDCl_3$)

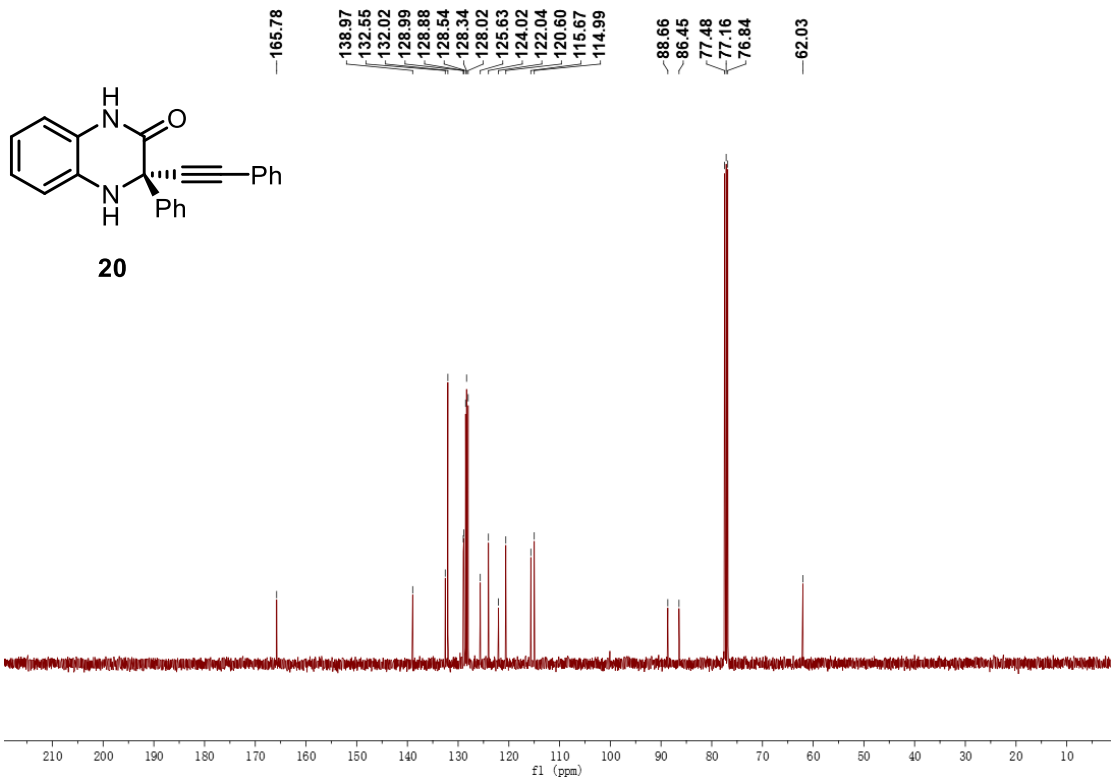


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



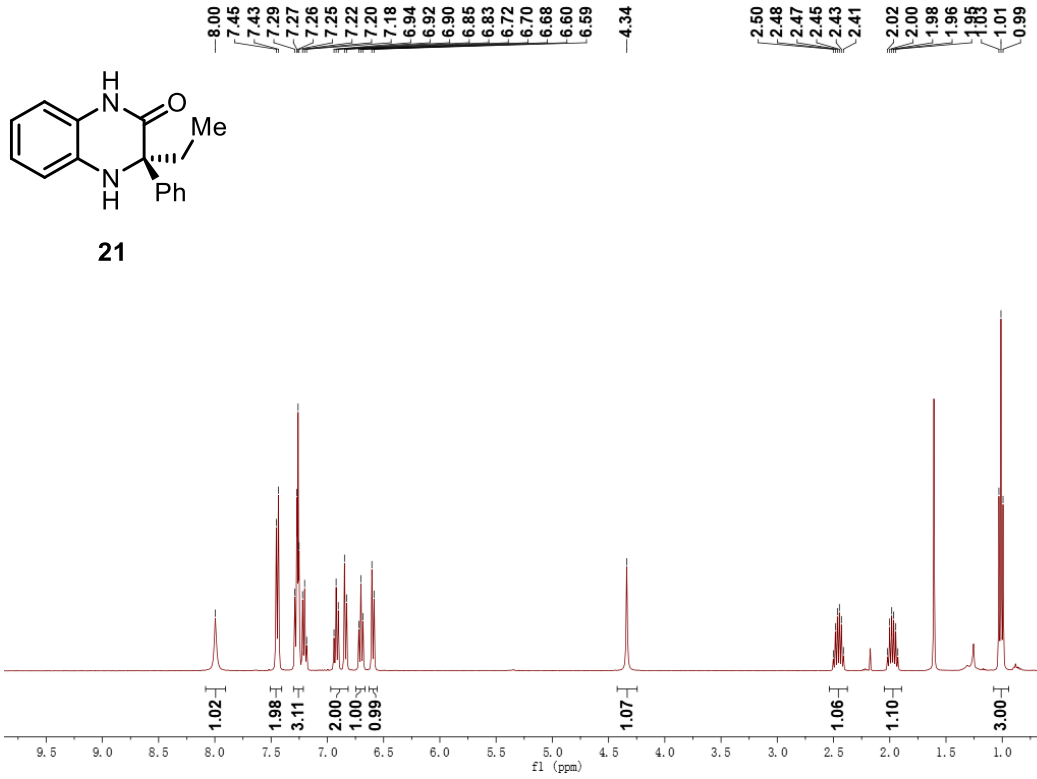
20

^{13}C NMR spectrum (100 MHz, $CDCl_3$)

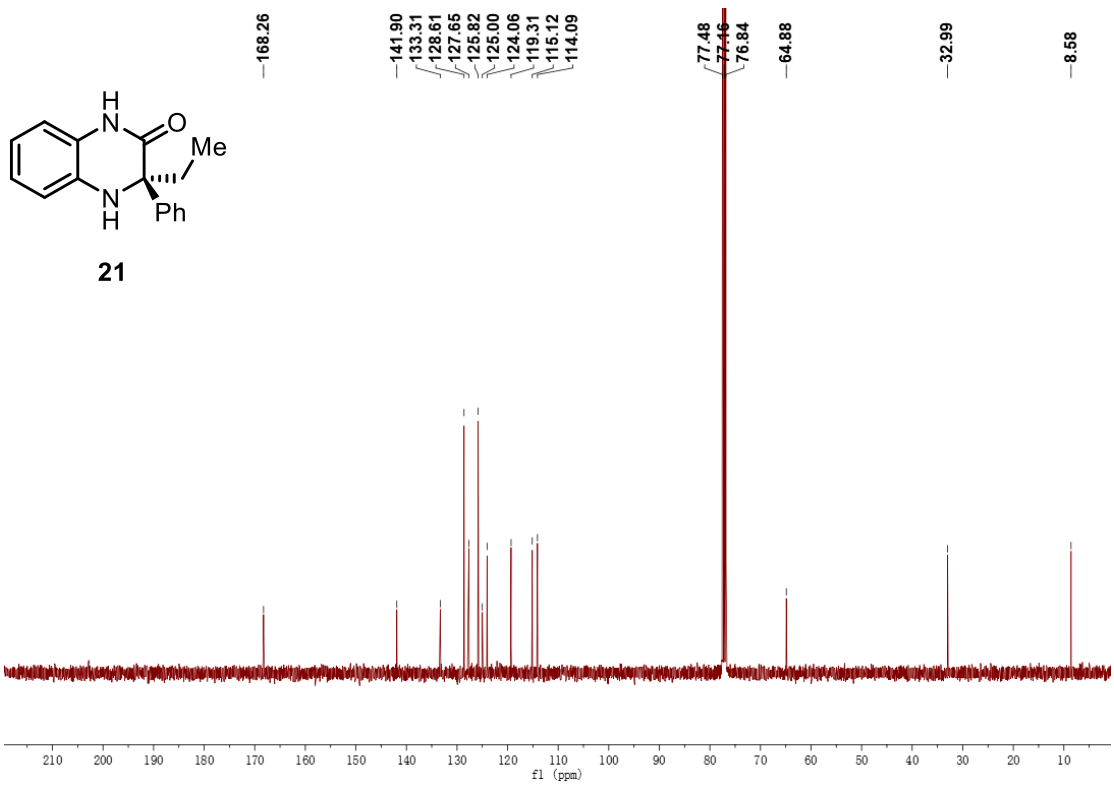


20

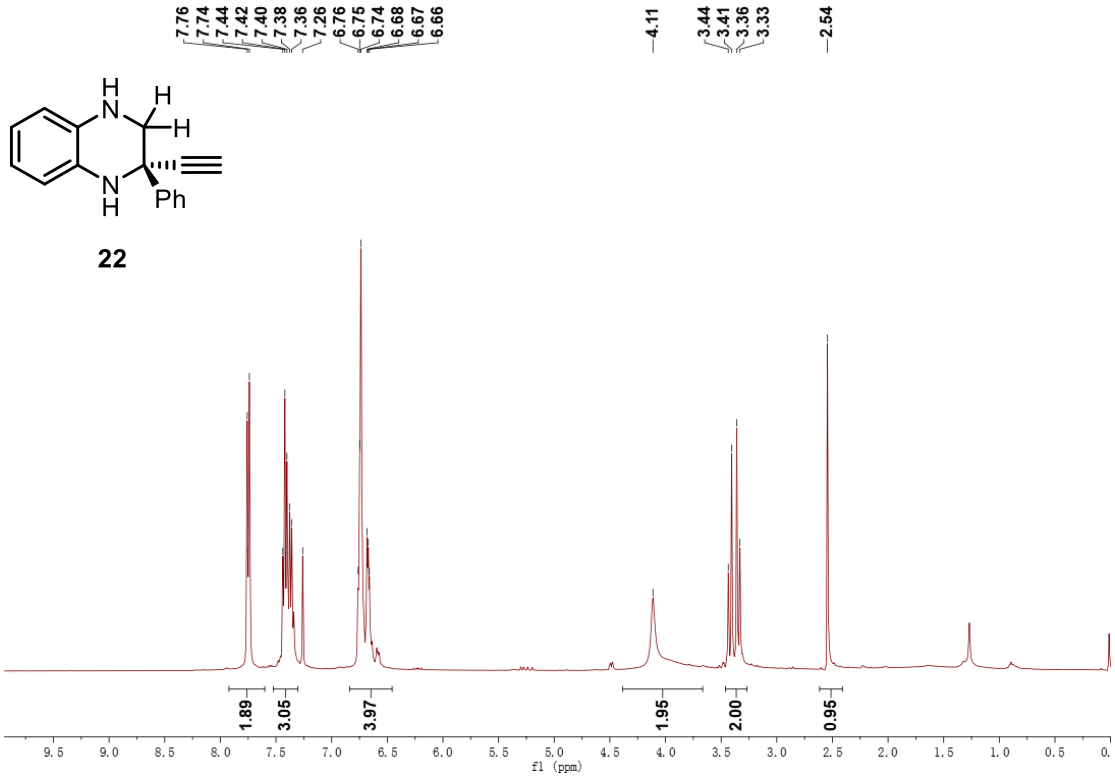
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



^{13}C NMR spectrum (100 MHz, $CDCl_3$)

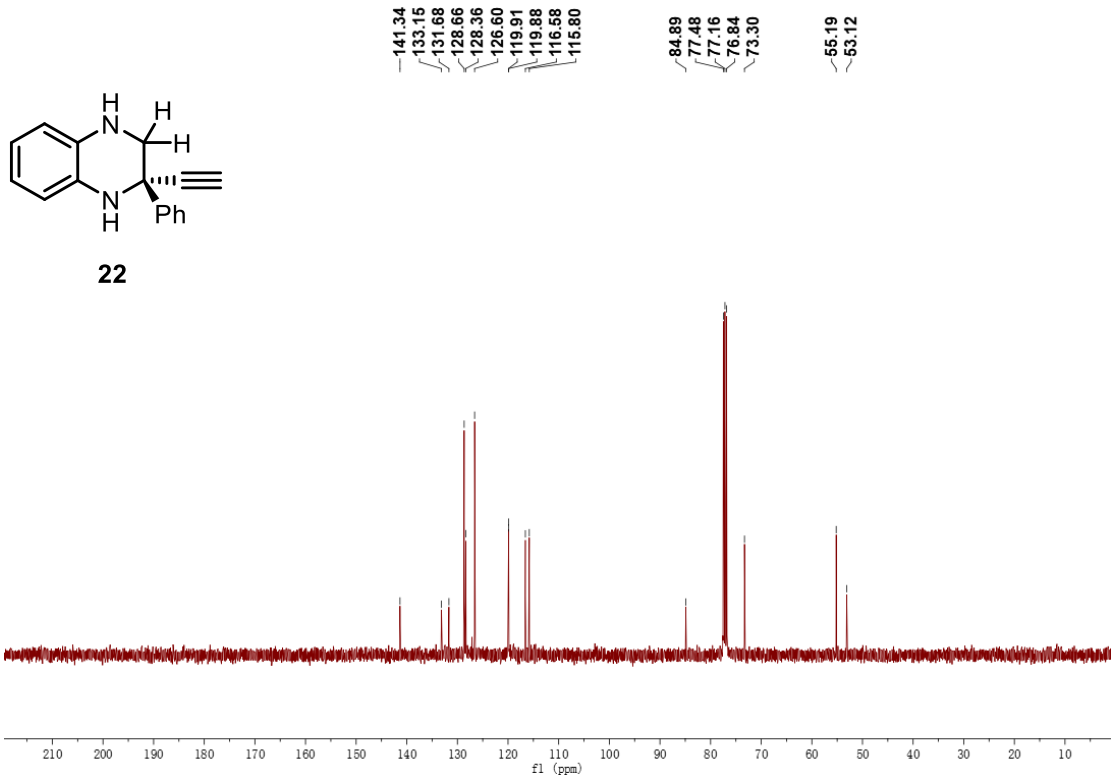


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



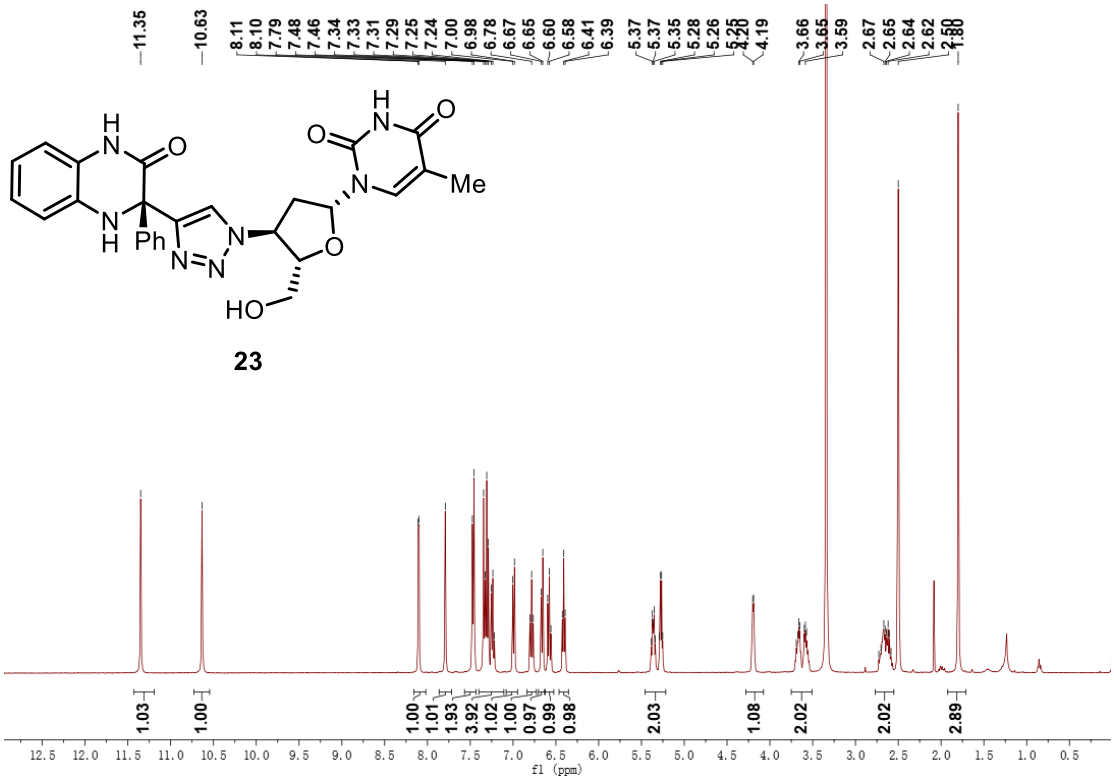
22

^{13}C NMR spectrum (100 MHz, $CDCl_3$)



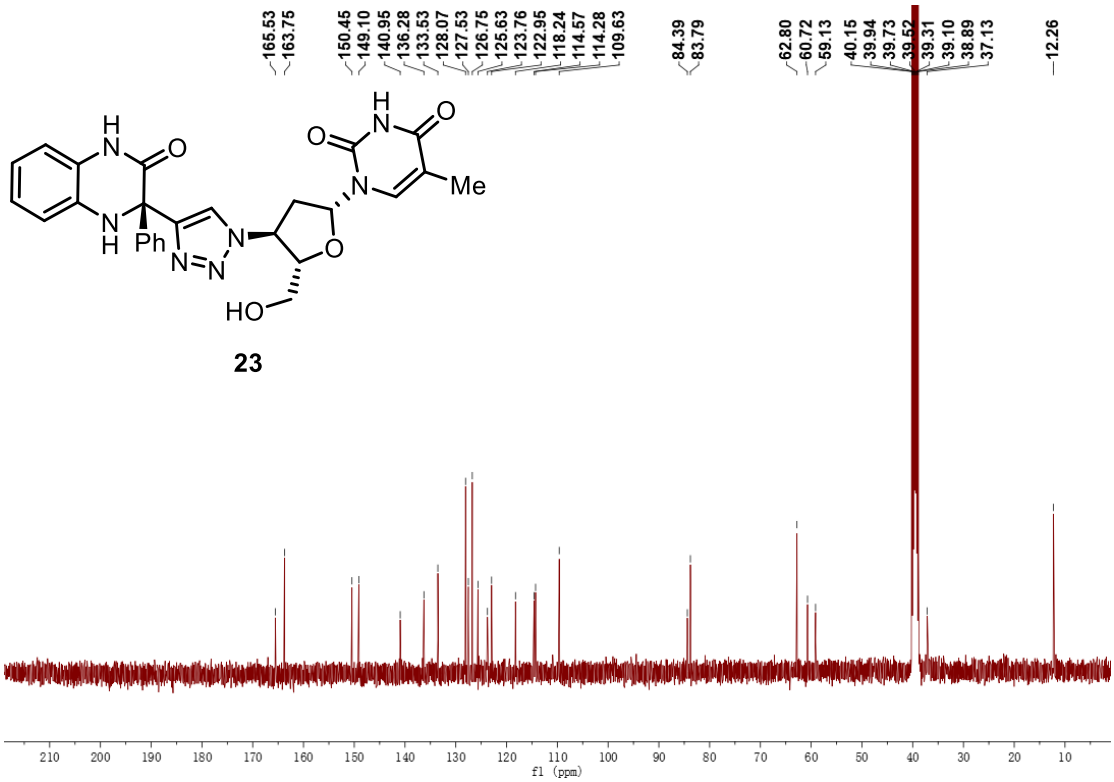
22

^{1}H NMR spectrum (400 MHz, DMSO)



23

^{13}C NMR spectrum (100 MHz, DMSO)



23