Supporting Information

Photoinduced Deacylative Epoxidation of Ketones Derivatives with Allylic Peroxides

Jiangtao Lin,[a] Mingqian Zhou,[a] Ziyang Li,[a] Jiang Duan,[a] Xiaoyu Liu,[a] Yue Wang,[a] and Chao Shu*[a,b]

[a]State Key Laboratory of Green Pesticide, Engineering Research Center of Photoenergy Utilization for Pollution Control and Carbon Reduction, CCNU-uOttawa Joint Research Centre, College of Chemistry, Central China Normal University. 152 Luoyu Road, Wuhan, Hubei 430079 China

E-mail: chaoshu@ccnu.edu.cn

[b]Wuhan Institute of Photochemistry and Technology, 7 North Bingang Road, Wuhan, Hubei, 430083 China.

Contents

1. General Information

1.1. Solvents, reagents and starting materials

All reagents were used as received unless otherwise stated from Sigma-Aldrich, Energy Chemical, Adamas-beta®, Leyan.com and Bidepharm. Water was de-ionised and brine refers to a saturated aqueous solution of NaCl. Chlorobenzene (C_6H_5Cl) was anhydrous, purchased from Energy Chemical and Adamas-beta® and used as received. Dichloromethane (CH_2Cl_2) was anhydrous (purification using a column composed of activated alumina).

1.2. Chromatography and instrumentation

Flash column chromatography was carried out using silica gel (Aldrich, silica gel 60, 40-63 μm). Analytical thin-layer chromatography (TLC) was performed using aluminium-backed silica plates (0.25 mm, Merck, silica gel 60 F254). Compounds were visualised under UV light or by staining with aqueous basic potassium permanganate, an ethanolic solution of phosphomolybdic acid (PMA), or an ethanolic solution of ninhydrin.

^{1}H, ^{13}C and ^{19}F NMR spectra were acquired at various field strengths, as indicated, using Bruker 400 MHz, Varian VNMR 400 MHz, Varian VNMR 500 MHz, and Bruker Cryo 500 MHz spectrometers. All NMR spectra were recorded at 25 °C unless otherwise stated. Chemical shifts (δ) are given in parts per million (ppm) and referenced to $CDCl_3$ (^{1}H: 7.26 ppm) or DMSO-d_6 (^{1}H: 2.50 ppm). Coupling constants (*J*) are given in Hertz (Hz) and refer to apparent multiplicities (s = singlet, br. s = broad singlet, d = doublet, t = triplet, q = quartet, quin = quintet, sex = sextet, h = heptet, m = multiplet, dd = doublet of doublets, etc.). The ^{1}H NMR spectra are reported as follows: chemical shift (multiplicity, coupling constants, number of protons).

Gas chromatography (GC) was performed on an Agilent Technologies 6890N Network GC System using an Agilent HP-5 column (15 m × 0.25 mm × 0.25 μm).

High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF instrument using electrospray ionisation (ESI). Low-resolution mass spectra (LRMS) were recorded on an Agilent 7820A GC-MS equipped with a HP-5MS UI column (30 m x 0.25 mm x 0.25 μm) using electron ionisation (EI).

Optical rotation ($[\alpha]_D^T$) was measured on a Bellingham and Stanley Ltd. ADP220 polarimeter and is quoted in (°mL) $(g\ dm)^{-1}$.

For quantum yield experiments, commercially available potassium ferrioxalate trihydrate (Alfa Aesar) was used for actinometry, and all the absorption spectra were measured using a Perkin Elmer Lambda 25 UV/Vis Spectrophotometer.

1.3. Photochemical equipment and setup

a) The blue LEDs lamps were either 20 W 445 nm blue LEDs with a fan or 40 W Kessil PR160-450 nm LEDs Photoredox Lights were used with the intensity dial set to 100 (**Figure S1**).

During the course of the photoredox reactions, heat generated from the LEDs lamps resulted in warming of the reaction mixtures to approximately 40 ℃. For reactions performed in C_6H_5Cl, fan cooled was used to maintain a temperature of 25–30 ºC.

b) Reaction set-up:

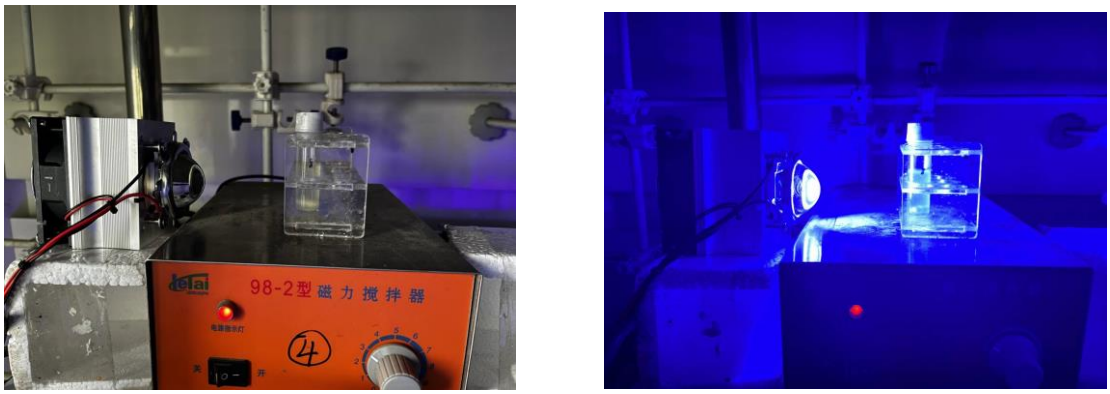
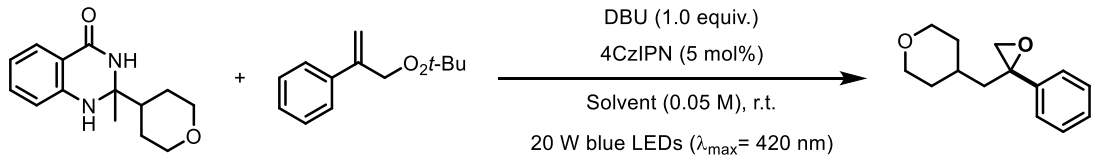


Figure S1. Photo reaction setup

2. Optimization Studies

Table S1: Opimization conditions of different solvents.[a]

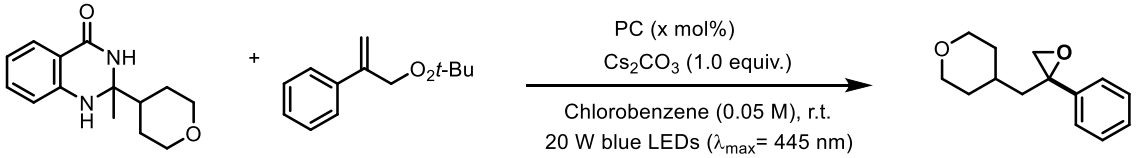


1a (1.0 equiv.) **1b** (2.0 equiv.) **1**

Entry	solvent (0.05 M)	Yield of **1** (%)[b]	Conversation of **1a** (%)[b]
1	C_6H_5Cl	38	100
2	CH_3CN	18	65
3	MTBE	5	56
4	DMF	15	45
5	THF	17	90
6	Toluene	25	85
7	1,4-dioxane	29	78
8	DMSO	12	86

[a]Reaction conditions: **1a** (0.1 mmol), **1b** (0.2 mmol), 4CzIPN (5 mol%), Solvent (2.0 mL), DBU (0.1 mmol), 25 °C, 24 h, N_2, 20 W blue LEDs, in vials; [b] Yields were determined after aqueous workup by ^{1}H NMR analysis using 1,2-diethyl phthalate as internal standard.

Table S2: Optimization the reaction conditions with different photocatalysts.[a]



1a (1.0 equiv.) **1b** (2.0 equiv.) **1**

Entry	PC (x mol%)	Yield of **1** (%)[b]	Conversation of **1a** (%)[b]
1	4CzIPN (5 mol%)	60	100
2	4CzIPN (2 mol%)	49	93
3	*fac*-Ir(ppy)$_3$ (5 mol%)	17	68
4	Eosin Y (5 mol%)	13	60
5	$Ru(bpy)_2Cl_2$ (5 mol%)	9	50
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (5 mol%)	32	95
7	TXO	4	95
8	$Ir(ppy)_2(dtbbpy)PF_6$	25	92

[a]Reaction conditions: **1a** (0.1 mmol), **1b** (0.2 mmol), PC (x mol%), Chlorobenzene (2.0 mL), Cs_2CO_3 (0.1 mmol), 25 °C, 24 h, N_2, 20 W blue LEDs, in vials; [b] Yields were determined after aqueous workup by ^1H NMR analysis using 1,2-diethyl phthalate as internal standard.

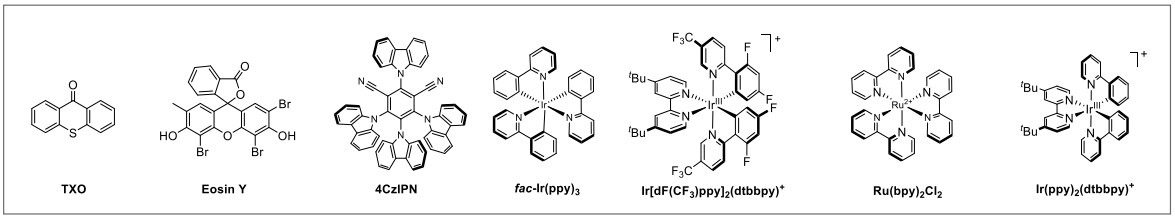
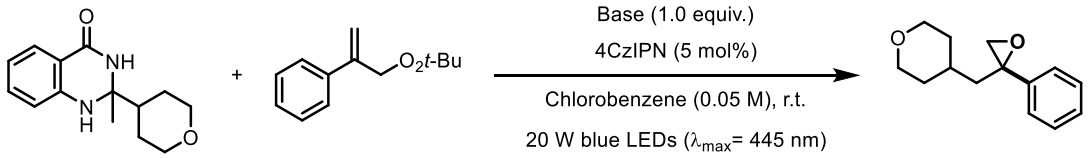


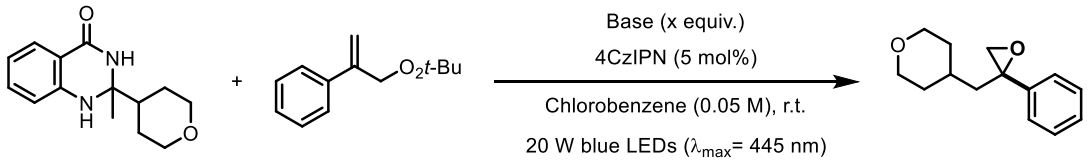
Table S3: Opimization conditions of different bases.[a]



Entry	Base (1.0 equiv.)	Yield of **1** (%)[b]	Conversation of **1a** (%)[b]
1	Cs_2CO_3	60	100
2	DMAP	32	85
3	Et_3N	8	98
4	DIPEA	8	62
5	DABCO	10	50
6	2,4,6-Collidine	14	30
7	NaOH	12	95
8	HCOOK	5	90
9	$NaHCO_3$	13	56
10	Na_2CO_3	7	54
11	DBU	38	100
12	K_3PO_4	9	56
13	LiBr	16	78

[a]Reaction conditions: **1a** (0.1 mmol), **1b** (0.2 mmol), 4CzIPN (5 mol%), Chlorobenzene (2.0 mL), base (0.1 mmol), 25 °C, 24 h, N_2, 20 W blue LEDs, in vials; [b] Yields were determined after aqueous workup by ^1H NMR analysis using 1,2-diethyl phthalate as internal standard.

Table S4: Optimize the addition ratio of bases.[a]

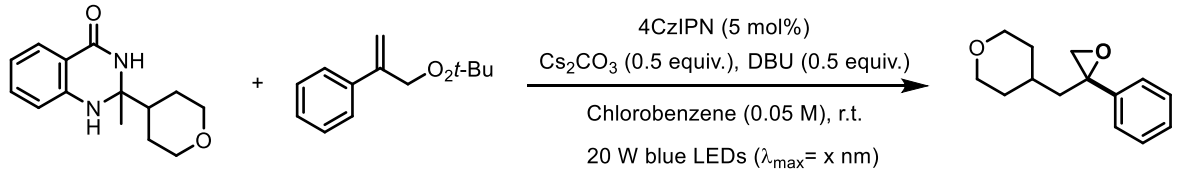


1a (1.0 equiv.) **1b** (2.0 equiv.) **1**

Entry	Bases (x equiv.)	Yield of **1** (%)[b]	Conversation of **1a** (%)[b]
1	Cs_2CO_3 (1.5 equiv.)	62	100
2	Cs_2CO_3 (0.5 equiv.), DBU (0.5 equiv.)	81	100
3	Cs_2CO_3 (1.0 equiv.), DBU (0.5 equiv.)	79	100
4	Cs_2CO_3 (1.0 equiv.), DBU (1.0 equiv.)	63	100
5	Cs_2CO_3 (0.5 equiv.), DBU (1.0 equiv.)	65	100
6	Cs_2CO_3 (1.0 equiv.), DBU (1.5 equiv.)	53	100
7	Cs_2CO_3 (1.0 equiv.), DBU (2.0 equiv.)	30	100
8	Cs_2CO_3 (0.8 equiv.), DBU (0.2 equiv.)	68	100
9	Cs_2CO_3 (1.0 equiv.), DBU (0.2 equiv.)	73	100

[a]Reaction conditions: **1a** (0.1 mmol), **1b** (0.2 mmol), 4CzIPN (5 mol%), Chlorobenzene (2.0 mL), bases (x mmol), 25 °C, 24 h, N_2, 20 W blue LEDs, in vials; [b] Yields were determined after aqueous workup by ^{1}H NMR analysis using 1,2-diethyl phthalate as internal standard.

Table S5: Opimization conditions with different light sources and control reactions. [a]

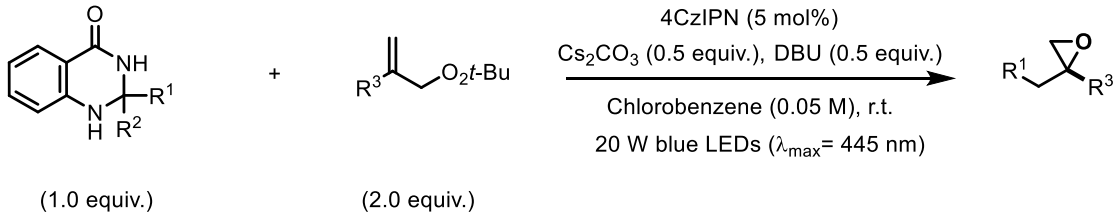


1a (1.0 equiv.) **1b** (2.0 equiv.) **1**

Entry	Variation from above	Yield of **1** (%)[b]	Conversation of **1a** (%)[b]
1	365 nm	34	40
2	390 nm	62	90
3	420 nm	76	100
4	445 nm	81	100
5[c]	Without 4CzIPN	0	0
6	Without light	0	0
7[c]	Under air	31	84

[a]Reaction conditions: **1a** (0.1 mmol), **1b** (0.2 mmol), 4CzIPN (5 mol%), Chlorobenzene (2.0 mL), Cs_2CO_3 (0.5 equiv.), DBU (0.5 equiv.), 25 °C, 24 h, N_2, 20 W blue LEDs, in vials; [b] Yields were determined after aqueous workup by ^{1}H NMR analysis using 1,2-diethyl phthalate as internal standard. [c]The reaction performed open to air under 20 W blue LEDs (λ_{max}= 445 nm).

3. General Procedure A for Photo Reaction

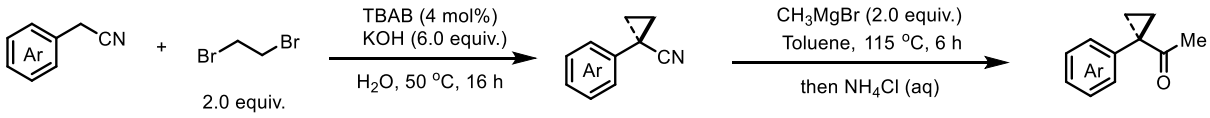


In the glove box, to a dry 7 mL vial equipped with a magnetic stir bar were added ketone derivative (0.2 mmol, 1.0 equiv.), allylic peroxide (0.4 mmol, 2.0 equiv.), 4CzIPN (0.010 mmol, 7.9 mg, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), and DBU (15.3 mg, 0.1 mmol, 0.5 equiv.). Then anhydrous chlorobenzene (4.0 mL) was added to the mixture. The vial was sealed with a septum and removed from the glove box. The reaction mixture was stirred at 800 rpm and irradiated with a 20 W blue LEDs lamp (with fan cooled) typically for 24 h, monitored by TLC. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation, and the crude product was then purified by flash Al_2O_3 (neutral) column chromatography gave the corresponding product.

4. Synthesis of Starting Materials

4.1 Synthesis of Ketone Derivatives

General procedure B for the synthesis of 1-(1-Arylcycloalkyl)ethan-1-one derivatives[1]

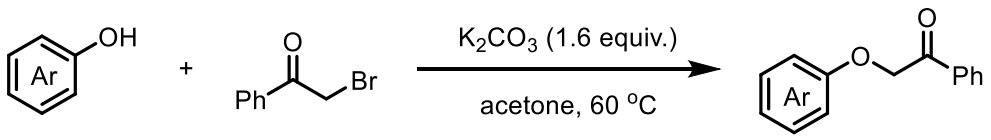


In a round bottom flask equipped with a Teflon-coated stirring bar, 2-arylacetonitrile (1.0 equiv.), KOH (6.0 equiv.) and tetrabutylammonium bromide (TBAB, 0.04 equiv.) were dissolved in water (5.0 M). The dibromoalkane (2.0 equiv.) was added dropwise to the reaction mixture. The resulting solution was heated at 50 ℃ for 16 h. After cooled down to room temperature, the reaction mixture was diluted with water and extracted with dichloromethane. The organic phase was washed with 1M HCl solution and subsequently water followed by brine solution. The solvent was dried over anhydrous sodium sulfate and removed under reduced pressure. The crude mixture was purified by flash column chromatography through silica (eluent = EtOAc/hexane) to afford 1-arylcycloalkane-1-carbonitrile, which was directly used in next step.

Under an inert atmosphere, in a separate two neck round bottom flask equipped with a condenser and Teflon-coated stirring bar, the Grignard reagent was dropwise added to the solution of 1-

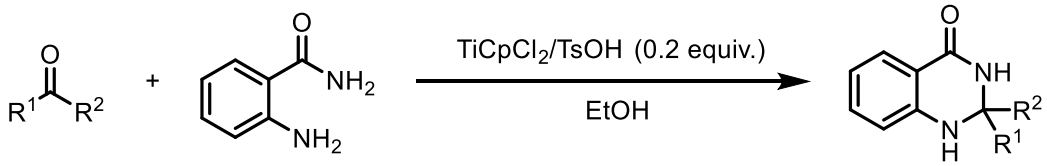
arylcycloalkane-1-carbonitrile (1.0 equiv.) in dry toluene (0.1 M) and the resulting mixture was refluxed at 115 ºC for 6 h. After cooled down to room temperature, the reaction mixture was quenched with aqueous ammonium chloride solution followed by extraction with diethyl ether. The resulting organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica (eluent = EtOAc/hexane) to afford pure 1-(1-arylcycloalkyl)ethan-1-one.

General procedure C of Ketone Derivatives[2]



To a round-bottom flask equipped with a reflux condenser, a dropping funnel, and a stir bar, phenol (1.0 equiv.), K_2CO_3 (1.6 equiv.), and acetone were added. Then, 2-bromo-1-phenylethan-1-one (1.1 equiv.) in acetone (1.0 mmol/10 mL) was added dropwise over 30 minutes at room temperature through the dropping funnel. The resulting reaction mixture was stirred at 60 ºC and monitored by TLC. Upon completion of the reaction (~ 6 h), the suspension was filtered, and the filtrate was concentrated in vacuo to afford the crude mixture, which was further purified by recrystallization from petroleum ether to give rise to product.

4.2 Synthesis of 2,3-Dihydroquinazolinone Derivatives (D)[1,3]



Anthranilamide (567.6 mg, 5.0 mmol, 1.0 equiv.), ketone (5.5 mmol, 1.1 equiv.), *p*-TsOH or $CpTiCl_2$ (0.25 mmol, 0.05 equiv.) and EtOH (10.0 mL, 0.5 M) were added to a 50 mL flame-dried single neck round flask with a stirring bar under nitrogen atmosphere. The flask was capped with a rubber septum. A needle with a nitrogen balloon was attached by piercing the septum to act as a ballast in case of gas pressure buildup. Next, the flask was placed in an oil bath with stirring at 85 ºC. The reaction mixture was stirred at that temperature for 24 h with monitoring by TLC analysis. After the ketone was totally consumed, the reaction was cooled to room temperature and the septum was removed. Water (20 mL) was added to the mixture and extracted with EtOAc (3 × 20 mL). The resulting organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica (eluent = EtOAc/hexane) to afford pure product.

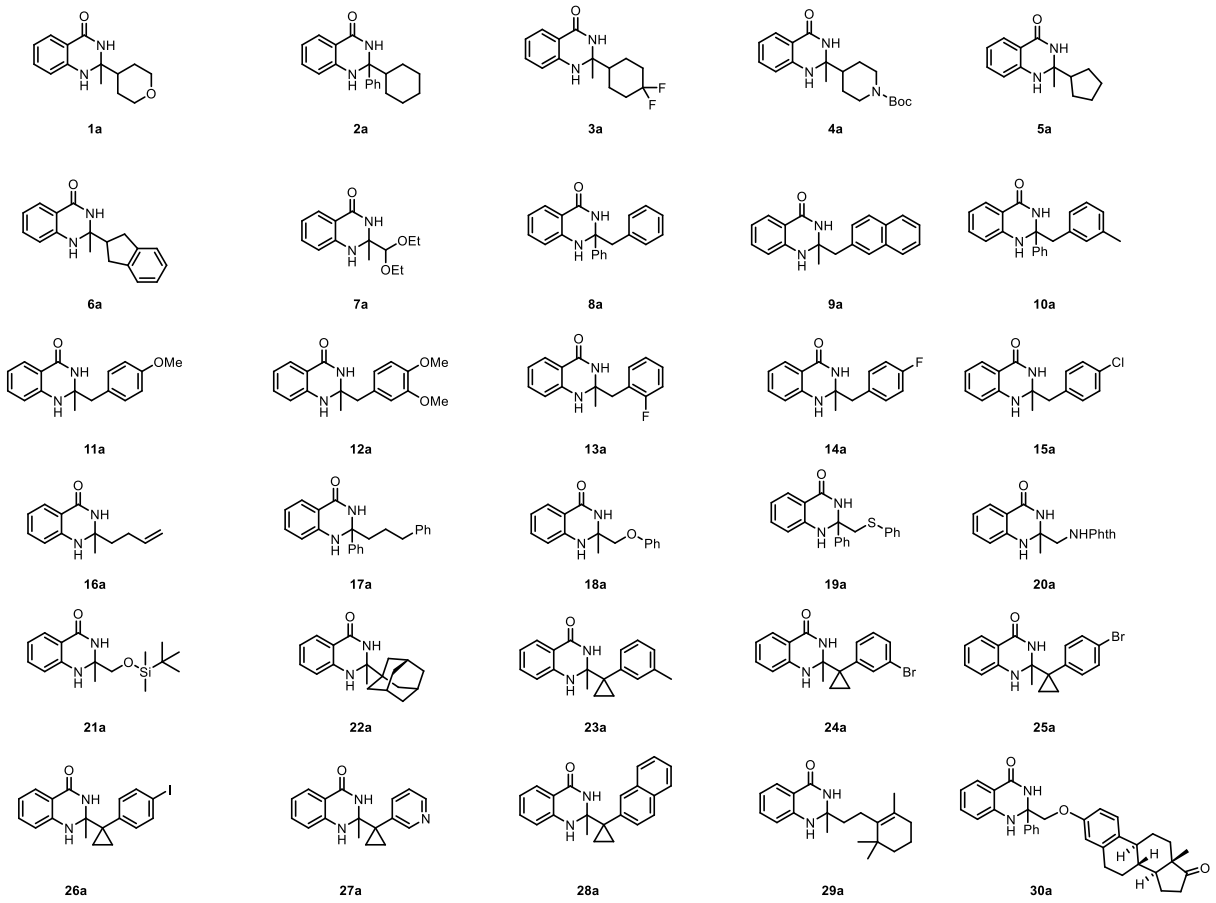
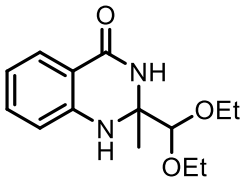


Figure S2: List of 2,3-Dihydroquinazolinone derivatives

Quinazolidinones **1a**, **2a**, **3a**, **4a**, **5a**, **6a**, **8a**, **9a**, **11a**, **12a**, **13a**, **14a**, **15a**, **17a**, **18a**, **19a**, **20a**, **21a**, **22a**, **28a**, and **29a** were prepared following the reported literatures[1,3,4,5].

2-(Diethoxymethyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (7a)



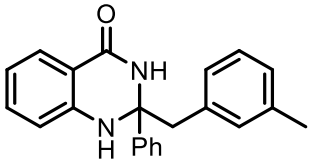
The title compound was prepared from Anthranilamide and ketone according to General Procedure D. Purification using flash silica gel column chromatography (eluent: 3:1 petroleum ether: EtOAc) gave the pure product **7a** (369.3 mg, 1.4 mmol, 70%), as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.86 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.31 – 7.27 (m, 1H), 6.84 – 6.77 (m, 1H), 6.61 (d, *J* = 8.3 Hz, 1H), 6.03 (s, 1H), 4.49 (d, *J* = 4.8 Hz, 2H), 3.88 – 3.81 (m, 2H), 3.64 – 3.55 (m, 2H), 1.44 (s, 3H), 1.27 – 1.22 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 163.6, 145.6, 134.1, 128.2, 118.6, 114.1, 105.3, 71.2, 66.8, 66.4, 21.1, 15.5, 15.4 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{21}N_2O_3$ $[M+H]^+$ 265.1547, found 265.1549.

2-(3-Methylbenzyl)-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (10a)



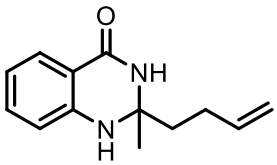
The title compound was prepared from Anthranilamide and ketone according to General Procedure D. Purification using flash silica gel column chromatography (eluent: 3:1 petroleum ether: EtOAc) gave the pure product **10a** (531.0 mg, 1.6 mmol, 81%), as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.00 (s, 1H), 7.82 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.36 – 7.32 (m, 2H), 7.26 – 7.21 (m, 4H), 7.08 – 6.99 (m, 2H), 6.78 – 6.69 (m, 2H), 6.65 – 6.62 (m, 2H), 5.03 (s, 1H), 3.49 – 3.26 (m, 2H), 2.17 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 165.2, 145.7, 143.9, 137.9, 133.9, 133.5, 131.5, 128.3, 128.2, 128.1, 127.7, 127.6, 125.9, 119.1, 116.1, 115.2, 73.1, 48.9, 21.2 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{21}N_2O$ $[M+H]^+$ 329.1648, found 329.1648.

2-(But-3-en-1-yl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (16a)



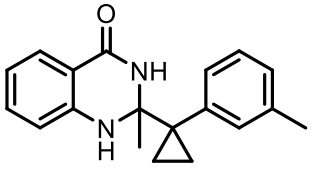
The title compound was prepared from Anthranilamide and ketone according to General Procedure D. Purification using flash silica gel column chromatography (eluent: 3:1 petroleum ether: EtOAc) gave the pure product **16a** (371.8 mg, 1.7 mmol, 86%), as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.87 (dd, J = 7.8, 1.6 Hz, 1H), 7.34 – 7.22 (m, 1H), 6.86 – 6.77 (m, 2H), 6.60 (d, J = 8.1 Hz, 1H), 5.79 (ddt, J = 16.7, 10.2, 6.5 Hz, 1H), 5.08 – 4.96 (m, 2H), 4.24 (s, 1H), 2.29 – 2.14 (m, 2H), 1.91 – 1.82 (m, 2H), 1.53 (d, J = 1.6 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 164.4, 145.9, 137.6, 133.9, 128.2, 118.5, 115.3, 114.4, 114.3, 69.8, 40.9, 28.4, 28.1 ppm.

HRMS (ESI^+) calcd. for $C_{13}H_{17}N_2O$ $[M+H]^+$ 217.1335, found 217.1334.

2-Methyl-2-(1-(m-tolyl)cyclopropyl)-2,3-dihydroquinazolin-4(1*H*)-one (23a)



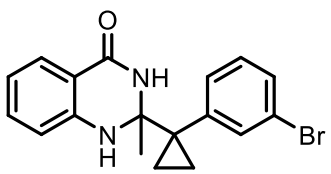
The title compound was prepared from Anthranilamide and ketone according to General Procedure D. Purification using flash silica gel column chromatography (eluent: 3:1 petroleum ether: EtOAc) gave the pure product **23a** (467.2 mg, 1.6 mmol, 80%), as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.86 (dd, J = 7.8, 1.6 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.24 – 7.14 (m, 3H), 7.08 (d, J = 7.3 Hz, 1H), 6.80 (t, J = 7.5 Hz, 1H), 6.62 (s, 1H), 6.53 (d, J = 8.0 Hz, 1H), 4.22 (s, 1H), 2.35 (s, 3H), 1.55 (s, 3H), 1.11 – 1.05 (m, 1H), 0.91 – 0.85 (m, 1H), 0.77 – 0.67 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 164.42, 146.03, 141.37, 137.87, 134.13, 132.73, 129.02, 128.13, 118.32, 114.77, 114.00, 70.47, 35.64, 28.10, 21.36, 10.64, 7.28 ppm.

HRMS (ESI^+) calcd. for $C_{19}H_{21}N_2O$ $[M+H]^+$ 293.1648, found 293.1650.

2-(1-(3-Bromophenyl)cyclopropyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (24a)



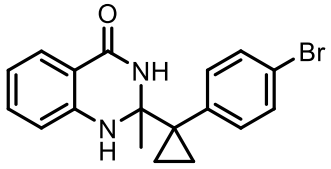
The title compound was prepared from Anthranilamide and ketone according to General Procedure D. Purification using flash silica gel column chromatography (eluent: 3:1 petroleum ether: EtOAc) gave the pure product **24a** (569.6 mg, 1.6 mmol, 83%), as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.85 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.51 (t, *J* = 1.9 Hz, 2H), 7.40 – 7.28 (m, 3H), 7.18 (t, *J* = 7.8 Hz, 1H), 6.81 (t, *J* = 7.5 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 4.23 (s, 1H), 1.56 (s, 3H), 1.15 – 1.09 (m, 1H), 0.98 – 0.92 (m, 1H), 0.76 – 0.66 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 164.9, 145.8, 144.1, 135.0, 134.2, 130.6, 130.4, 129.7, 128.1, 122.0, 118.4, 114.9, 114.0, 70.2, 35.6, 27.7, 10.9, 7.0 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{18}BrN_2O$ $[M+H]^+$ 357.0597, found 357.0599.

2-(1-(4-Bromophenyl)cyclopropyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (25a)



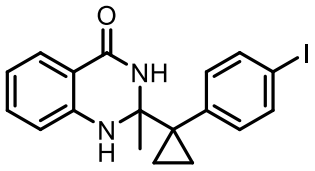
The title compound was prepared from Anthranilamide and ketone according to General Procedure D. Purification using flash silica gel column chromatography (eluent: 3:1 petroleum ether: EtOAc) gave the pure product **25a** (542.6 mg, 1.6 mmol, 81%), as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.04 (s, 1H), 7.84 (dd, J = 7.7, 1.6 Hz, 1H), 7.44 – 7.38 (m, 2H), 7.34 – 7.28 (m, 1H), 7.25 – 7.20 (m, 2H), 4.30 (s, 1H), 1.55 (s, 3H), 1.11 (dd, J = 9.1, 4.8 Hz, 1H), 0.98 (dd, J = 9.4, 4.8 Hz, 1H), 0.67 (d, J = 5.6 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 164.6, 145.8, 140.7, 134.2, 133.7, 131.3, 128.2, 121.4, 118.4, 114.8, 113.9, 70.2, 35.3, 27.8, 10.8, 7.3 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{18}N_2BrO$ $[M+H]^+$ 357.0597, found 357.0595.

2-(1-(4-Iodophenyl)cyclopropyl)-2-methyl-2,3-dihydroquinazolin-4(1*H*)-one (26a)



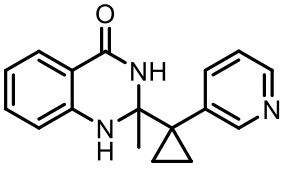
The title compound was prepared from Anthranilamide and ketone according to General Procedure D. Purification using flash silica gel column chromatography (eluent: 3:1 petroleum ether: EtOAc) gave the pure product **26a** (606.5 mg, 1.5 mmol, 75%), as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.95 (s, 1H), 7.84 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.66 – 7.59 (m, 2H), 7.36 – 7.27 (m, 1H), 7.13 – 7.05 (m, 2H), 6.83 – 6.74 (m, 1H), 6.54 (d, *J* = 8.0 Hz, 1H), 4.27 (s, 1H), 1.55 (s, 3H), 1.13 – 1.07 (m, 1H), 1.00 – 0.92 (m, 1H), 0.70 – 0.60 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 164.7, 145.8, 141.4, 137.3, 134.2, 134.0, 128.2, 118.4, 114.8, 113.9, 93.1, 70.2, 35.4, 27.7, 10.7, 7.2 ppm.

HRMS (ESI$^+$) calcd. for $C_{18}H_{18}IN_2O$ $[M+H]^+$ 405.0458, found 405.0458.

2-Methyl-2-(1-(pyridin-3-yl)cyclopropyl)-2,3-dihydroquinazolin-4(1*H*)-one (27a)



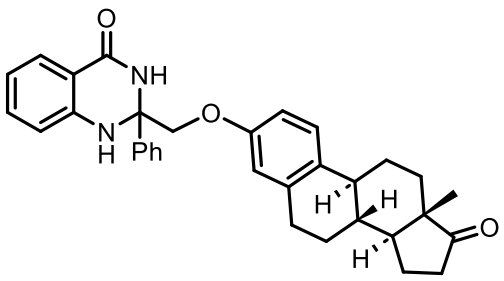
The title compound was prepared from Anthranilamide and ketone according to General Procedure D. Purification using flash silica gel column chromatography (eluent: 3:1 petroleum ether: EtOAc) gave the pure product **27a** (234.36 mg, 0.84 mmol, 42%), as a white solid.

^{1}H NMR (400 MHz, DMSO-d_6) δ_H 8.46 (d, J = 2.2 Hz, 1H), 8.38 (dd, J = 4.7, 1.6 Hz, 1H), 8.00 (d, J = 1.6 Hz, 1H), 7.68 – 7.57 (m, 1H), 7.50 (dd, J = 7.6, 1.6 Hz, 1H), 7.30 – 7.17 (m, 2H), 6.73 (d, J = 1.6 Hz, 1H), 6.63 – 6.51 (m, 2H), 1.35 (s, 3H), 1.06 – 0.89 (m, 2H), 0.58 (t, J = 2.2 Hz, 2H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6) δ_C 163.2, 152.9, 147.5, 146.8, 139.5, 137.8, 133.4, 127.0, 122.8, 115.9, 113.7, 113.3, 69.9, 33.6, 26.2, 9.4, 7.3 ppm.

HRMS (ESI$^+$) calcd. for $C_{17}H_{18}N_3O$ $[M+H]^+$ 280.1444, found 280.1445.

2-((((8*R*,9*S*,13*S*,14*S*)-13-Methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)methyl)-2-phenyl-2,3-dihydroquinazolin-4(1*H*)-one (30a）



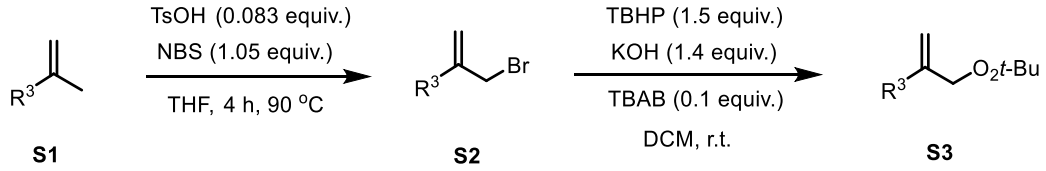
The title compound was prepared from Anthranilamide and ketone according to General Procedure D. Purification using flash silica gel column chromatography (eluent: 3:1 petroleum ether: EtOAc) gave the pure product **30a** (499.2 mg, 0.96 mmol, 48%), as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.85 (dd, J = 7.8, 1.5 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.43 (s, 1H), 7.35 – 7.27 (m, 4H), 7.13 (d, J = 8.6 Hz, 1H), 6.85 – 6.72 (m, 2H), 6.63 (dd, J = 8.6, 2.7 Hz, 1H), 6.56 (d, J = 2.7 Hz, 1H), 5.39 (s, 1H), 4.47 – 4.28 (m, 2H), 2.89 – 2.74 (m, 2H), 2.49 (dd, J = 19.0, 8.7 Hz, 1H), 2.39 – 2.25 (m, 1H), 2.24 – 2.14 (m, 2H), 2.13 – 2.04 (m, 1H), 2.02 – 1.92 (m, 2H), 1.65 – 1.51 (m, 2H), 1.47 (dd, J = 12.0, 7.8 Hz, 3H), 1.41 – 1.34 (m, 1H), 0.88 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 220.9, 164.2, 155.7, 145.5, 141.3, 137.8, 134.1, 132.9, 128.6, 128.4, 128.2, 126.5, 126.3, 119.1, 115.3, 115.1, 114.7, 112.2, 72.2, 71.2, 50.2, 47.8, 43.8, 38.1, 35.7, 31.4, 29.4, 26.3, 25.8, 21.4, 13.7 ppm.

HRMS (ESI^+) calcd. for $C_{33}H_{35}N_2O_3$ $[M+H]^+$ 507.2640, found 507.2642.

General Procedure E:



a) Synthesis of S2[6,7]:

To a solution of **S1** (5.0 mmol, 1.0 equiv.) in THF (0.5 M) was added NBS (5.3 mmol, 1.05 equiv.) and *p*-toluenesulfonic acid (0.4 mmol, 0.083 equiv.). The mixture was stirred and heated to 90 °C under reflux for 4 h. After the concentration of the reaction liquid *in vacuo*, petroleum ether was added. The formed precipitate was filtered off and then the filtrate was dried over $MgSO_4$ and evaporated. The compound **S2** was obtained as pale yellow liquid by column chromatographic purification of the crude product using hexanes as eluent.

b) Synthesis of S3[8]:

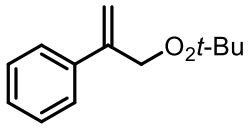
To a solution of the **S2** (1.0 equiv.), TBHP (70 wt.% in H_2O, 1.5 equiv.) and TBAB (0.1 equiv.) in DCM (0.5 M) was added powder KOH (1.4 equiv.). The resulting solution was stirred at room temperature for 6-12 h. After completion, the reaction was quenched by water. The organic layer was separated and the aqueous layer was extracted with DCM. The combined organic layer was washed with brine, dried over $MgSO_4$ and concentrated in vacuum. The residue was purified by flash silica gel chromatography (petroleum ether/EtOAc) to afford the compound **S3**.

NBS: *N*-bromosuccinimide

TBHP: *tert*-butyl hydroperoxide

TBAB: Tetrabutylammonium bromide

(3-(*tert*-Butylperoxy)prop-1-en-2-yl)benzene (1b)



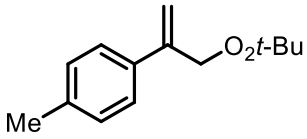
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **1b** (433.2 mg, 2.1 mmol, 42% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.49 – 7.47 (m, 2H), 7.36 – 7.28 (m, 3H), 5.58 (s, 1H), 5.39 (s, 1H), 4.83 (s, 2H), 1.23 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.7, 138.8, 128.3, 127.7, 126.1, 116.4, 80.4, 76.9, 26.4 ppm.

HRMS (ESI^+) calcd. for $C_{13}H_{19}O_2$ $[M+H]^+$ 207.1380, found 207. 1382.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-4-methylbenzene (2b)



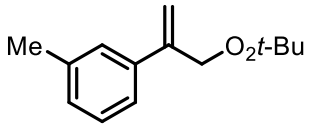
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **2b** (451.6 mg, 2.1 mmol, 41% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.37 (d, J = 8.2 Hz, 2H), 7.14 (d, J = 7.9 Hz, 2H), 5.54 (s, 1H), 5.33 (s, 1H), 4.81 (s, 2H), 2.34 (s, 3H), 1.24 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.4, 137.6, 136.0, 129.1, 126.0, 115.6, 80.4, 77.0, 26.5, 21.2 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{21}O_2$ $[M+H]^+$ 221.1536, found 221.1534.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-3-methylbenzene (3b)



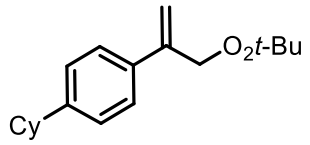
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **3b** (451.6 mg, 2.1 mmol, 41% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.35 – 7.30 (m, 2H), 7.29 – 7.24 (m, 1H), 7.16 – 7.12 (m, 1H), 5.60 (d, *J* = 1.3 Hz, 1H), 5.41 (d, *J* = 1.3 Hz, 1H), 4.86 (d, *J* = 1.2 Hz, 2H), 2.40 (s, 3H), 1.29 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.7, 138.8, 137.8, 128.5, 128.2, 126.8, 123.1, 116.1, 80.3, 76.9, 26.4, 21.5 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{21}O_2$ $[M+H]^+$ 221.1536, found 221.1535.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-4-cyclohexylbenzene (4b)



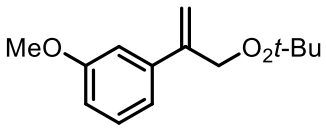
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **4b** (519.1 mg, 1.8 mmol, 36% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.44 – 7.37 (m, 2H), 7.22 – 7.14 (m, 2H), 5.56 (d, *J* = 1.3 Hz, 1H), 5.34 (d, *J* = 1.4 Hz, 1H), 4.82 (d, *J* = 0.9 Hz, 2H), 2.56 – 2.42 (m, 1H), 1.90 – 1.81 (m, 4H), 1.79 – 1.66 (m, 1H), 1.46 – 1.36 (m, 4H), 1.30 – 1.24 (m, 10H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 147.8, 142.4, 136.3, 126.8, 126.0, 115.6, 80.4, 77.1, 44.3, 34.4, 26.9, 26.5, 26.2 ppm.

HRMS (ESI^+) calcd. for $C_{19}H_{29}O_2$ $[M+H]^+$ 289.2162, found 289.2163.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-3-methoxybenzene (5b)



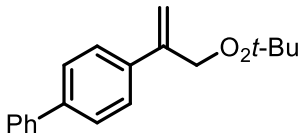
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **5b** (508.0 mg, 2.2 mmol, 43% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.25 (t, *J* = 7.9 Hz, 1H), 7.06 (d, *J* = 7.8 Hz, 1H), 7.02 (s, 1H), 6.84 (dd, *J* = 8.2, 2.4 Hz, 1H), 5.58 (s, 1H), 5.39 (s, 1H), 4.80 (s, 2H), 3.82 (s, 3H), 1.24 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 159.5, 142.6, 140.4, 129.2, 118.6, 116.7, 113.2, 111.9, 80.4, 76.7, 55.2, 26.4 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{21}O_3$ $[M+H]^+$ 237.1485, found 237.1483.

4-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-1,1'-biphenyl (6b)



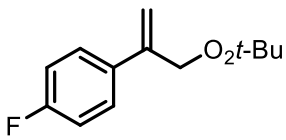
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **6b** (550.7 mg, 2.0 mmol, 39% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.60 – 7.53 (m, 6H), 7.44 – 7.40 (m, 2H), 7.35 – 7.30 (m, 1H), 5.64 (s, 1H), 5.41 (s, 1H), 4.85 (s, 2H), 1.25 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.0, 140.6, 140.4, 137.6, 128.7, 127.3, 127.0, 126.9, 126.4, 116.5, 80.4, 76.9, 26.4 ppm.

HRMS (ESI^+) calcd. for $C_{19}H_{23}O_2$ $[M+H]^+$ 283.1693, found 283.1692.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-4-fluorobenzene (7b)



Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **7b** (504.7 mg, 2.3 mmol, 45% over two steps), as a colorless oil.

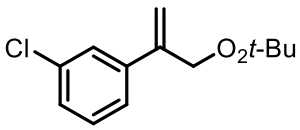
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.47 – 7.44 (m, 2H), 7.02 (t, *J* = 8.5 Hz, 2H), 5.51 (s, 1H), 5.36 (s, 1H), 4.78 (s, 2H), 1.22 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 163.7 (d, *J* = 245.0 Hz), 141.8, 134.9 (d, *J* = 3.0 Hz), 127.9 (d, *J* = 8.1 Hz), 116.5, 115.3 (d, *J* = 21.0 Hz), 80.4, 77.0, 26.4 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ_F -114.7 ppm.

HRMS (ESI^+) calcd. for $C_{13}H_{18}FO_2$ $[M+H]^+$ 225.1285, found 225.1286.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-3-chlorobenzene (8b)



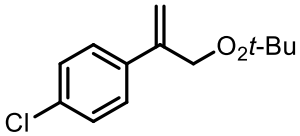
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **8b** (529.5 mg, 2.2 mmol, 44% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.47 (s, 1H), 7.36 – 7.34 (m, 1H), 7.27 – 7.25 (m, 2H), 5.59 (s, 1H), 5.42 (s, 1H), 4.78 (s, 2H), 1.23 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 141.7, 140.7, 134.2, 129.5, 127.7, 126.4, 124.3, 117.7, 80.4, 77.2, 26.4 ppm.

HRMS (ESI^+) calcd. for $C_{13}H_{18}ClO_2$ $[M+H]^+$ 241.0990, found 241.0989.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-4-chlorobenzene (9b)



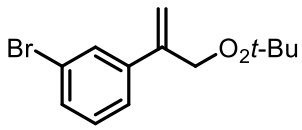
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **9b** (517.5 mg, 2.2 mmol, 43% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.42 – 7.40 (m, 2H), 7.32 – 7.29 (m, 2H), 5.56 (s, 1H), 5.39 (s, 1H), 4.78 (s, 2H), 1.22 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 141.7, 137.2, 133.6, 128.5, 127.4, 117.1, 80.4, 76.7, 26.4 ppm.

HRMS (ESI^+) calcd. for $C_{13}H_{18}ClO_2$ $[M+H]^+$ 241.0990, found 241.0988.

1-Bromo-3-(3-(*tert*-butylperoxy)prop-1-en-2-yl)benzene (10b)



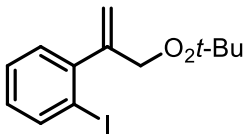
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **10b** (541.9 mg, 1.9 mmol, 38% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.62 (s, 1H), 7.41 – 7.39 (m, 2H), 7.20 (t, J = 7.9 Hz, 1H), 5.57 (s, 1H), 5.42 (s, 1H), 4.77 (s, 2H), 1.23 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 141.6, 140.9, 130.6, 129.8, 129.3, 124.7, 122.5, 117.8, 80.4, 76.7, 26.4 ppm.

HRMS (ESI^+) calcd. for $C_{13}H_{18}BrO_2$ $[M+H]^+$ 285.0485, found 285.0486.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-2-iodobenzene (11b)



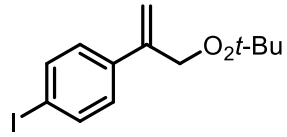
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **11b** (648.0 mg, 2.0 mmol, 39% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.86 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.03 – 6.97 (m, 1H), 5.58 (t, *J* = 1.4 Hz, 1H), 5.20 (s, 1H), 4.71 (s, 2H), 1.23 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 146.9, 145.0, 138.9, 129.9, 128.9, 127.8, 119.0, 97.7, 80.5, 77.4, 26.2 ppm.

HRMS (ESI^+) calcd. for $C_{13}H_{18}IO_2$ $[M+H]^+$ 333.0346, found 333.0343.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-4-iodobenzene (12b)



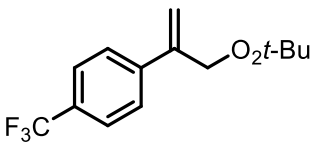
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **12b** (714.2 mg, 2.2 mmol, 43% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.67 – 7.64 (m, 2H), 7.23 – 7.20 (m, 2H), 5.57 (s, 1H), 5.39 (s, 1H), 4.77 (s, 2H), 1.22 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 141.8, 138.3, 137.4, 128.0, 117.2, 93.3, 80.4, 76.7, 26.4 ppm.

HRMS (ESI^+) calcd. for $C_{13}H_{18}IO_2$ $[M+H]^+$ 333.0346, found 333.0349.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-4-(trifluoromethyl)benzene (13b)



Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **13b** (534.9 mg, 2.0 mmol, 39% over two steps), as a colorless oil.

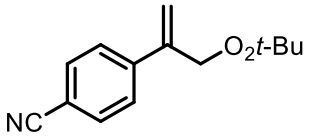
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.62 – 7.56 (m, 4H), 5.65 (s, 1H), 5.49 (s, 1H), 4.82 (s, 2H), 1.22 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 141.9, 141.9, 129.9, 128.3, 126.5, 125.4, 118.7, 80.5, 76.8, 26.4 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ_F -62.6 ppm

HRMS (ESI$^+$): calcd. for $C_{14}H_{17}F_3NaO_2$ $[M+Na]^+$ 297.1073, found 297.1071.

4-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)benzonitrile (14b)



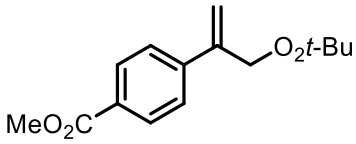
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **14b** (427.9 mg, 1.9 mmol, 37% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.67 – 7.55 (m, 4H), 5.69 (s, 1H), 5.54 (s, 1H), 4.82 (s, 2H), 1.22 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 143.3, 141.6, 132.2, 126.9, 119.7, 118.9, 111.3, 80.5, 76.5, 26.4 ppm.

HRMS (ESI$^+$): calcd. for $C_{14}H_{17}NNaO_2$ $[M+Na]^+$ 254.1151, found 254.1154.

Methyl 4-(3-(*tert*-butylperoxy)prop-1-en-2-yl)benzoate (15b)



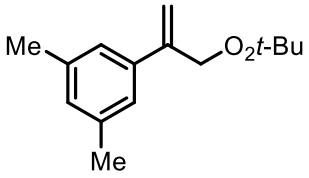
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **15b** (502.2 mg, 1.9 mmol, 38% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.06 – 8.01 (m, 2H), 7.61 – 7.54 (m, 2H), 5.70 (s, 1H), 5.52 (s, 1H), 4.86 (s, 2H), 3.94 (d, J = 1.4 Hz, 3H), 1.24 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 166.9, 143.3, 142.1, 129.7, 129.3, 126.1, 118.6, 80.5, 76.7, 52.1, 26.4 ppm.

HRMS (ESI$^+$): calcd. for $C_{15}H_{20}NaO_4$ $[M+Na]^+$ 287.1254, found 287.1253.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-3,5-dimethylbenzene (16b)



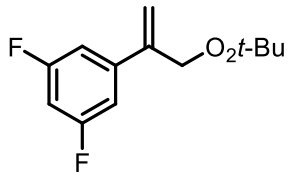
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **16b** (445.3 mg, 1.9 mmol, 38% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.09 (s, 2H), 6.93 (s, 1H), 5.54 (d, *J* = 1.2 Hz, 1H), 5.35 (d, *J* = 1.1 Hz, 1H), 4.80 (d, *J* = 0.9 Hz, 2H), 2.32 (s, 6H), 1.25 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.7, 138.8, 137.7, 129.4, 123.9, 115.9, 80.4, 77.0, 26.4, 21.4 ppm.

HRMS (ESI^+) calcd. for $C_{15}H_{23}O_2$ $[M+H]^+$ 235.1693, found 235.1692.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-3,5-difluorobenzene (17b)



Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **17b** (496.7 mg, 2.1 mmol, 41% over two steps), as a colorless oil.

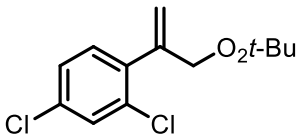
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.04 – 6.97 (m, 2H), 6.78 – 6.66 (m, 1H), 5.61 (s, 1H), 5.46 (s, 1H), 4.75 (d, *J* = 1.1 Hz, 2H), 1.23 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 164.1 (d, *J* = 14.1 Hz), 161.8 (d, *J* = 13.1 Hz), 142.1 (d, *J* = 10.1 Hz), 141.0 (d, *J* = 3.1 Hz), 118.7, 109.2 (d, *J* = 7.1 Hz), 109.0 (d, *J* = 7.1 Hz), 103.0 (d, *J* = 26.3 Hz), 80.5, 76.6, 26.4 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ_F -110.3 ppm

HRMS (ESI^+) calcd. for $C_{13}H_{17}F_2O_2$ $[M+H]^+$ 243.1191, found 243.1192.

1-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-2,4-dichlorobenzene (18b)



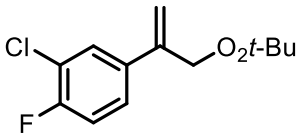
Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **18b** (701.8 mg, 2.6 mmol, 51% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.38 (s, 1H), 7.22 (d, *J* = 1.2 Hz, 2H), 5.57 (s, 1H), 5.24 (s, 1H), 4.71 (s, 2H), 1.18 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.4, 137.8, 133.7, 133.0, 131.9, 129.2, 126.8, 119.9, 80.4, 77.0, 26.2 ppm.

HRMS (ESI^+): calcd. for $C_{13}H_{16}Cl_2NaO_2$ $[M+Na]^+$ 297.0420, found 297.0421.

4-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-2-chloro-1-fluorobenzene (19b)



Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **19b** (504.5 mg, 2.0 mmol, 39% over two steps), as a colorless oil.

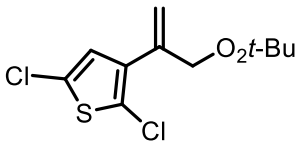
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.56 – 7.49 (m, 1H), 7.37 – 7.31 (m, 1H), 7.10 (t, *J* = 8.7 Hz, 1H), 5.54 (s, 1H), 5.40 (s, 1H), 4.76 (d, *J* = 1.2 Hz, 2H), 1.23 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 156.5, 141.0, 136.1, 128.5, 126.0, 121.0, 117.8, 116.5, 80.6, 76.9, 26.4 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ_F -117.0 ppm

HRMS (ESI^+) calcd. for $C_{13}H_{17}ClFO_2$ $[M+H]^+$ 259.0896, found 259.0897.

3-(3-(*tert*-Butylperoxy)prop-1-en-2-yl)-2,5-dichlorothiophene (20b)



Prepared following the General Procedure E. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **20b** (506.2 mg, 1.8 mmol, 36% over two steps), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.84 (s, 1H), 5.56 (d, *J* = 1.3 Hz, 2H), 4.65 (s, 2H), 1.22 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 136.3, 126.8, 125.8, 122.5, 120.5, 80.4, 77.1, 26.3 ppm.

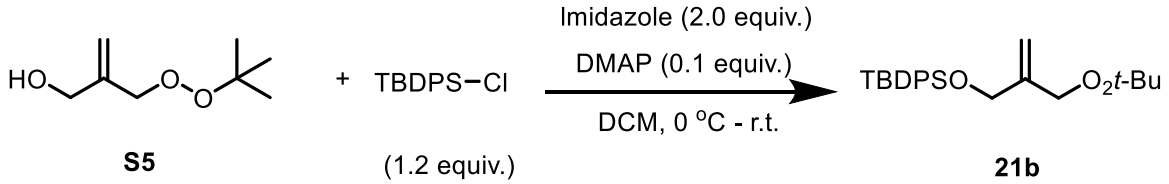
HRMS (ESI^+) calcd. for $C_{11}H_{15}Cl_2O_2S$ $[M+H]^+$ 281.0164, found 281.0160.

General Procedure F:

a) Synthesis of S4[9]:

To a solution of ethyl 2-(bromomethyl)acrylate (1.0 equiv.) in anhydrous DCM (0.1 M) was added DIBAl-H (1.0 M solution in Hexanes, 3.0 equiv.) dropwise under N_2 atmosphere at 0 °C. After 1 h, added MeOH dropwise to quench the reaction. Then the mixture was added sat. *aq*. Rochelle's salt at room temperature and stir for 1 h. After completion, the solution was filtered through a pad of celite and washed with DCM. The filtrate was washed with brine, dried over. The residue was purified by flash silica gel chromatography (10% EtOAc/Hexane) to afford the compound **S4**.

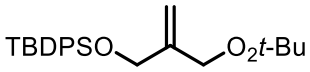
General Procedure G:



To a schlenk tube with **S5** (1.0 mmol, 1.0 equiv.), imidazole (2.0 mmol, 2.0 equiv.), DMAP (0.1 mmol, 0.1 equiv.) in DCM (0.5 M). Cool the solution at 0 °C. Add dropwise Silicon chloride (1.2 mmol, 1.2 equiv.) to the solution. The reaction was warmed to room temperature and stirred for 2 h. After the

reaction was complete, water was added and was extracted with EtOAc. The organic layers were combined and washed with brine, dried with $MgSO_4$, concentrated in vacuum, flash chromatography over silica gel afforded the product **21b**.

***tert*-Butyl((2-((*tert*-butylperoxy)methyl)allyl)oxy)diphenylsilane (21b)**



Prepared following the General Procedure G. Purification by flash column chromatography (5% EtOAc/hexane) gave the title compound **21b** (362.7 mg, 0.9 mmol, 91%), as a colorless oil.

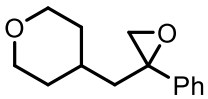
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.69 – 7.67 (m, 4H), 7.43 – 7.35 (m, 6H), 5.36 (s, 1H), 5.18 (s, 1H), 4.44 (s, 2H), 4.24 (s, 2H), 1.19 (s, 9H), 1.07 (s, 9H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 143.5, 135.5, 133.5, 129.6, 127.6, 113.6, 80.2, 75.6, 64.8, 26.8, 26.3, 19.3 ppm.

HRMS (ESI^+) calcd. for $C_{24}H_{35}O_3Si$ $[M+H]^+$ 399.2350, found 399.2352.

5. Product Characterisation

4-((2-Phenyloxiran-2-yl)methyl)tetrahydro-2*H*-pyran (1)



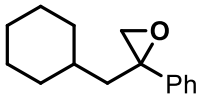
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **1** (34.0 mg, 0.15 mmol, 78%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.40 – 7.31 (m, 4H), 7.31 – 7.25 (m, 1H), 4.03 – 3.60 (m, 2H), 3.33 – 3.05 (m, 2H), 2.88 (d, J = 5.4 Hz, 1H), 2.68 (d, J = 5.5 Hz, 1H), 2.27 (dd, J = 13.8, 4.9 Hz, 1H), 1.69 – 1.50 (m, 4H), 1.40 – 1.26 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 139.9, 128.4, 127.4, 125.8, 67.8, 67.7, 59.3, 55.1, 42.6, 33.6, 33.1, 32.1 ppm.

HRMS (ESI$^+$) calcd. for $C_{14}H_{19}O_2$ $[M+H]^+$ 219.1380, found 219.1381.

3-(Cyclohexylmethyl)-2-phenyloxirane (2)



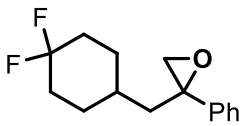
Prepared following the General Procedure A using **2a** (48.9 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **2** (29.0 mg, 0.13 mmol, 67%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.39 – 7.30 (m, 4H), 7.30 – 7.24 (m, 1H), 2.86 (d, *J* = 5.4 Hz, 1H), 2.70 (d, *J* = 5.5 Hz, 1H), 2.09 (dd, *J* = 14.3, 6.1 Hz, 1H), 1.83 – 1.75 (m, 1H), 1.67 – 1.55 (m, 5H), 1.40 – 1.28 (m, 1H), 1.19 – 1.03 (m, 3H), 1.02 – 0.86 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 140.3, 128.2, 127.2, 126.0, 59.7, 55.0, 43.3, 34.6, 33.9, 33.4, 26.3, 26.1, 26.0 ppm.

HRMS (ESI$^+$) calcd. for $C_{15}H_{21}O$ $[M+H]^+$ 217.1587, found 217.1585.

2-((4,4-Difluorocyclohexyl)methyl)-2-phenyloxirane (3)



Prepared following the General Procedure A using **3a** (56.1 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **3** (37.8 mg, 0.15 mmol, 75%) as a pale yellow liquid.

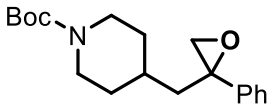
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.38 – 7.33 (m, 4H), 7.31 – 7.25 (m, 1H), 2.87 (d, *J* = 5.4 Hz, 1H), 2.68 (d, *J* = 5.5 Hz, 1H), 2.29 (dd, *J* = 14.2, 5.1 Hz, 1H), 2.05 – 1.95 (m, 2H), 1.93 – 1.87 (m, 1H), 1.74 – 1.68 (m, 1H), 1.66 – 1.56 (m, 2H), 1.53 – 1.41 (m, 2H), 1.38 – 1.27 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 139.7, 128.4 (d, *J* = 267.7 Hz), 127.5, 123.4 (d, *J* = 241.4 Hz), 59.4, 55.2, 41.4 (d, *J* = 3.0 Hz), 33.3 (m), 32.8, 29.7 (d, *J* = 9.1 Hz), 28.8 (d, *J* = 10.1 Hz). ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ_F -91.63 (d, J = 234.4 Hz), -101.93 (d, J = 236.7 Hz) ppm.

HRMS (ESI^+) calcd. for $C_{15}H_{19}F_2O$ $[M+H]^+$ 253.1398, found 253.1399.

***tert*-Butyl 4-((2-phenyloxiran-2-yl)methyl)piperidine-1-carboxylate (4)**



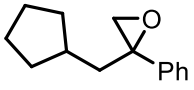
Prepared following the General Procedure A using **4a** (69.0 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **4** (50.1 mg, 0.16 mmol, 79%) as a colorless oil

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.40 – 7.32 (m, 4H), 7.31 – 7.25 (m, 1H), 4.00 (s, 2H), 2.87 (d, *J* = 5.5 Hz, 1H), 2.68 (d, *J* = 5.5 Hz, 1H), 2.64 – 2.48 (m, 2H), 2.26 (d, *J* = 9.3 Hz, 1H), 1.77 – 1.69 (m, 1H), 1.63 – 1.49 (m, 3H), 1.43 (s, 9H), 1.21 – 1.05 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 154.8, 139.8, 128.4, 127.4, 125.8, 79.2, 59.3, 55.2, 42.2, 33.0, 32.6, 32.1, 28.4 ppm.

HRMS (ESI^+) calcd. for $C_{19}H_{28}NO_3$ $[M+H]^+$ 318.2064, found 318.2064.

3-(Cyclopentylmethyl)-2-phenyloxirane (5)



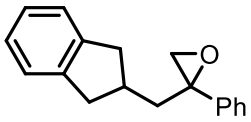
Prepared following the General Procedure A using **5a** (46.0 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **5** (25.9 mg, 0.13 mmol, 64%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.40 – 7.37 (m, 2H), 7.35 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 2.91 (d, *J* = 5.4 Hz, 1H), 2.72 (d, *J* = 5.4 Hz, 1H), 2.24 (dd, *J* = 13.7, 5.6 Hz, 1H), 1.83 – 1.66 (m, 4H), 1.61 – 1.51 (m, 2H), 1.47 – 1.37 (m, 2H), 1.26 – 1.16 (m, 1H), 1.11 – 1.02 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 140.4, 128.2, 127.3, 126.1, 60.4, 55.0, 41.7, 36.8, 33.2, 32.8, 24.9, 24.9 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{19}O$ $[M+H]^+$ 203.1430, found 203.1432.

2-((2,3-Dihydro-1*H*-inden-2-yl)methyl)-2-phenyloxirane (6)



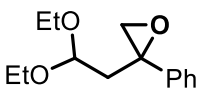
Prepared following the General Procedure A using **6a** (55.6 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **6** (38.0 mg, 0.15 mmol, 76%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.42 – 7.39 (m, 2H), 7.34 – 7.29 (m, 2H), 7.27 – 7.23 (m, 1H), 7.15 – 7.06 (m, 4H), 3.01 – 2.91 (m, 3H), 2.78 – 2.71 (m, 2H), 2.59 – 2.43 (m, 3H), 1.88 – 1.82 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 143.3, 142.9, 139.9, 128.3, 127.4, 126.1, 126.0, 125.9, 124.3, 124.1, 60.1, 54.9, 41.1, 39.7, 39.1, 37.0 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{19}O$ $[M+H]^+$ 251.1430, found 251.1432.

3-(2,2-Diethoxyethyl)-2-phenyloxirane (7)



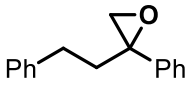
Prepared following the General Procedure A using **7a** (52.9 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **7** (27.9 mg, 0.12 mmol, 59%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.41 – 7.38 (m, 2H), 7.36 – 7.30 (m, 2H), 7.29 – 7.26 (m, 1H), 4.54 (t, *J* = 5.6 Hz, 1H), 3.65 – 3.53 (m, 2H), 3.49 – 3.33 (m, 2H), 3.04 (d, *J* = 5.4 Hz, 1H), 2.76 (d, *J* = 5.4 Hz, 1H), 2.41 (dd, *J* = 14.5, 5.4 Hz, 1H), 2.22 (dd, *J* = 14.5, 5.9 Hz, 1H), 1.17 (t, *J* = 7.0 Hz, 3H), 1.07 (t, *J* = 7.0 Hz, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 140.0, 128.2, 127.5, 126.0, 100.2, 61.5, 61.1, 58.0, 55.0, 39.8, 15.2, 15.1 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{21}O_3$ $[M+H]^+$ 237.1485, found 237.1486.

2-Phenethyl-2-phenyloxirane (8)



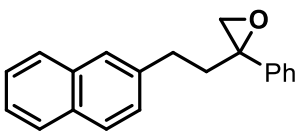
Prepared following the General Procedure A using **8a** (50.5 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **8** (27.8 mg, 0.12 mmol, 62%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.44 – 7.34 (m, 4H), 7.32 – 7.24 (m, 3H), 7.21 – 7.12 (m, 3H), 2.99 (d, J = 5.4 Hz, 1H), 2.77 (d, J = 5.3 Hz, 1H), 2.74 – 2.58 (m, 2H), 2.56 – 2.43 (m, 1H), 2.13 – 1.93 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 141.6, 139.7, 128.4, 128.4, 128.3, 127.5, 126.0, 125.9, 60.1, 55.8, 37.4, 31.1 ppm.

HRMS (ESI^+) calcd. for $C_{16}H_{17}O$ $[M+H]^+$ 225.1274, found 225.1273.

2-(2-(Naphthalen-2-yl)ethyl)-2-phenyloxirane (9)



Prepared following the General Procedure A using **9a** (60.4 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with

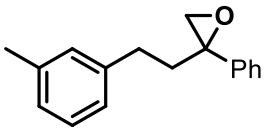
20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **9** (34.0 mg, 0.12 mmol, 62%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.77 (dd, J = 15.5, 7.7 Hz, 3H), 7.59 (s, 1H), 7.48 – 7.35 (m, 6H), 7.35 – 7.28 (m, 2H), 3.03 (d, J = 5.3 Hz, 1H), 2.94 – 2.85 (m, 1H), 2.84 – 2.75 (m, 2H), 2.66 – 2.53 (m, 1H), 2.19 – 2.06 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 139.7, 139.1, 133.6, 132.0, 128.5, 127.9, 127.6, 127.4, 127.1, 126.3, 126.0, 125.9, 125.2, 60.2, 55.8, 37.4, 31.3 ppm.

HRMS (ESI^+) calcd. for $C_{20}H_{19}O$ $[M+H]^+$ 275.1430, found 175.1430.

2-(3-Methylphenethyl)-2-phenyloxirane (10)



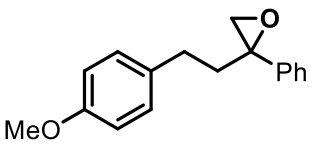
Prepared following the General Procedure A using **10a** (53.2 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **10** (35.7 mg, 0.15 mmol, 77%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.45 – 7.29 (m, 5H), 7.15 (t, J = 7.4 Hz, 1H), 7.02 – 6.93 (m, 3H), 2.99 (d, J = 5.4 Hz, 1H), 2.76 (d, J = 5.3 Hz, 1H), 2.74 – 2.45 (m, 3H), 2.10 – 1.97 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 170.6, 161.8, 134.7, 128.8, 123.9, 39.8, 29.4, 26.9 ppm.

HRMS (ESI^+) calcd. for $C_{17}H_{19}O$ $[M+H]^+$ 239.1430, found 239.1432.

2-(4-Methoxyphenethyl)-2-phenyloxirane (11)



Prepared following the General Procedure A using **11a** (56.5 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with

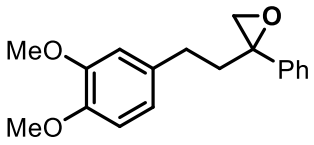
20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **11** (38.1 mg, 0.15 mmol, 73%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.47 – 7.34 (m, 4H), 7.33 – 7.28 (m, 1H), 7.11 – 7.00 (m, 2H), 6.81 (d, J = 8.6 Hz, 2H), 3.78 (s, 3H), 2.99 (d, J = 5.3 Hz, 1H), 2.76 (d, J = 5.3 Hz, 1H), 2.70 – 2.41 (m, 3H), 2.06 – 1.98 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 157.8, 139.8, 133.6, 129.2, 128.4, 127.5, 126.0, 113.8, 60.1, 55.7, 55.2, 37.7, 30.2 ppm.

HRMS (ESI^+) calcd. for $C_{17}H_{19}O_2$ $[M+H]^+$ 255.1380, found 255.1380.

2-(3,4-Dimethoxyphenethyl)-2-phenyloxirane (12)



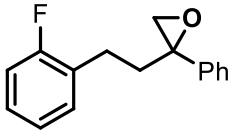
Prepared following the General Procedure A using **12a** (64.4 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **12** (39.8 mg, 0.14 mmol, 71%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.44 – 7.34 (m, 4H), 7.34 – 7.29 (m, 1H), 6.78 (d, J = 8.1 Hz, 1H), 6.72 – 6.66 (m, 2H), 3.85 (s, 6H), 3.00 (d, J = 5.3 Hz, 1H), 2.77 (d, J = 5.3 Hz, 1H), 2.73 – 2.42 (m, 3H), 2.11 – 1.90 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 148.8, 147.2, 139.7, 134.2, 128.4, 127.5, 126.0, 120.0, 111.6, 111.2, 60.1, 55.9, 55.8, 55.7, 37.6, 30.7 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{21}O_3$ $[M+H]^+$ 285.1485, found 285.1486.

(2-Fluorophenethyl)-2-phenyloxirane (13)



Prepared following the General Procedure A using **13a** (54.0 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **13** (33.9 mg, 0.14 mmol, 72%) as a pale yellow oil.

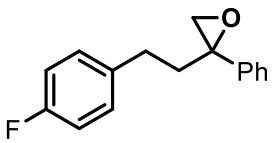
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.46 – 7.41 (m, 2H), 7.37 (dd, J = 8.5, 6.6 Hz, 2H), 7.34 – 7.27 (m, 1H), 7.19 – 7.10 (m, 2H), 7.05 – 6.95 (m, 2H), 3.00 (d, J = 5.3 Hz, 1H), 2.77 (d, J = 5.4 Hz, 1H), 2.75 – 2.63 (m, 2H), 2.60 – 2.41 (m, 1H), 2.12 – 1.72 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 162.3, 159.9, 139.5, 130.5, 130.5, 128.4, 128.4, 128.3, 127.7, 127.7, 127.5, 125.9, 124.0, 123.9, 115.3, 115.1, 59.9, 55.8, 35.8, 35.7, 24.8, 24.8 ppm.

^{19}F NMR (376 MHz, CDCl3) δ_F -118.62 ppm.

HRMS (ESI^+) calcd. for $C_{16}H_{16}FO$ $[M+H]^+$ 243.1180, found 243.1181.

2-(4-Fluorophenethyl)-2-phenyloxirane (14)



Prepared following the General Procedure A using **14a** (54.0 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **14** (34.6 mg, 0.14 mmol, 73%) as a pale yellow oil.

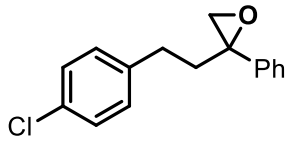
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.44 – 7.34 (m, 4H), 7.34 – 7.27 (m, 1H), 7.15 – 7.05 (m, 2H), 6.99 – 6.89 (m, 2H), 2.98 (d, J = 5.3 Hz, 1H), 2.76 (d, J = 5.3 Hz, 1H), 2.74 – 2.65 (m, 1H), 2.62 (dd, J = 11.3, 5.1 Hz, 1H), 2.54 – 2.45 (m, 1H), 2.13 – 1.84 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 162.5, 160.1, 139.6, 137.2, 137.1, 129.6, 129.6, 128.4, 127.6, 125.9, 115.2, 115.0, 60.0, 55.8, 37.6, 30.3 ppm.

^{19}F NMR (376 MHz, CDCl3) δ_F -117.55 ppm.

HRMS (ESI^+) calcd. for $C_{16}H_{16}FO$ $[M+H]^+$ 243.1180, found 243.1181.

2-(4-Chlorophenethyl)-2-phenyloxirane (15)



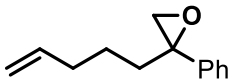
Prepared following the General Procedure A using **15a** (62.0 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **15** (37.6 mg, 0.14 mmol, 72%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.43 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 7.25 – 7.20 (m, 2H), 7.07 (d, J = 8.0 Hz, 2H), 2.99 (d, J = 5.3 Hz, 1H), 2.77 (d, J = 5.2 Hz, 1H), 2.74 – 2.45 (m, 3H), 2.05 – 1.93 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 140.0, 139.5, 131.6, 129.6, 128.5, 127.6, 125.9, 60.0, 55.8, 37.3, 30.5 ppm.

HRMS (ESI^+) calcd. for $C_{16}H_{16}ClO$ $[M+H]^+$ 259.0884, found 259.0881.

2-(Pent-4-en-1-yl)-2-phenyloxirane (16)



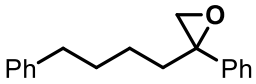
Prepared following the General Procedure A using **16a** (54.0 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **16** (28.6 mg, 0.12 mmol, 56%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.40 – 7.30 (m, 4H), 7.30 – 7.24 (m, 1H), 5.83 – 5.68 (m, 1H), 5.03 – 4.89 (m, 2H), 2.95 (d, *J* = 5.4 Hz, 1H), 2.73 (d, *J* = 5.4 Hz, 1H), 2.29 – 2.14 (m, 1H), 2.10 – 2.02 (m, 2H), 1.79 – 1.68 (m, 1H), 1.57 – 1.36 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 140.0, 138.3, 128.3, 127.4, 125.9, 114.8, 60.3, 55.5, 34.9, 33.6, 24.1 ppm.

HRMS (ESI^+) calcd. for $C_{13}H_{17}O$ $[M+H]^+$ 189.1274, found 189.1276.

2-Phenyl-2-(4-phenylbutyl)oxirane (17)



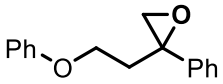
Prepared following the General Procedure A using **17a** (68.4 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **17** (30.2 mg, 0.12 mmol, 58%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.38 – 7.30 (m, 4H), 7.29 – 7.21 (m, 3H), 7.18 – 7.10 (m, 3H), 2.94 (d, *J* = 5.4 Hz, 1H), 2.72 (d, *J* = 5.4 Hz, 1H), 2.60 – 2.53 (m, 2H), 2.26 – 2.15 (m, 1H), 1.80 – 1.71 (m, 1H), 1.68 – 1.58 (m, 2H), 1.50 – 1.35 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.4, 140.0, 128.3, 128.3, 128.2, 127.3, 126.0, 125.6, 60.3, 55.5, 35.7, 35.3, 31.4, 24.6 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{21}O$ $[M+H]^+$ 253.1587, found 253.1590.

2-(2-Phenoxyethyl)-2-phenyloxirane (18)



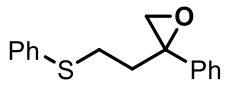
Prepared following the General Procedure A using **18a** (53.6 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **18** (40.8 mg, 0.17 mmol, 87%) as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.45 – 7.37 (m, 2H), 7.37 – 7.30 (m, 2H), 7.30 – 7.19 (m, 3H), 6.97 – 6.88 (m, 1H), 6.87 – 6.74 (m, 2H), 4.22 – 3.82 (m, 2H), 3.08 (d, J = 5.4 Hz, 1H), 2.80 (d, J = 5.3 Hz, 1H), 2.66 – 2.49 (m, 1H), 2.44 – 2.11 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 158.5, 139.5, 129.4, 128.4, 127.7, 125.9, 120.7, 114.4, 63.7, 58.3, 55.4, 35.1 ppm.

HRMS (ESI^+) calcd. for $C_{16}H_{17}O_2$ $[M+H]^+$ 241.1123, found 241.1126.

2-Phenyl-2-(2-(phenylthio)ethyl)oxirane (19)



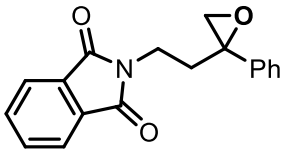
Prepared following the General Procedure A using **19a** (56.9 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **19** (37.7 mg, 0.15 mmol, 73%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.40 – 7.18 (m, 9H), 7.21 – 7.13 (m, 1H), 3.02 – 2.94 (m, 2H), 2.91 – 2.82 (m, 1H), 2.76 (d, J = 5.3 Hz, 1H), 2.58 – 2.46 (m, 1H), 2.10 – 1.97 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 138.9, 135.9, 129.0, 128.9, 128.5, 127.7, 126.0, 125.9, 59.6, 55.8, 35.4, 28.8 ppm.

HRMS (ESI^+) calcd. for $C_{16}H_{17}OS$ $[M+H]^+$ 257.0995, found 257.0996.

2-(2-(2-Phenyloxiran-2-yl)ethyl)isoindoline-1,3-dione (20)



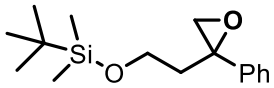
Prepared following the General Procedure A using **20a** (64.2 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **20** (35.2 mg, 0.12 mmol, 61%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.78 (dd, J = 5.4, 3.1 Hz, 2H), 7.68 (dd, J = 5.4, 3.1 Hz, 2H), 7.44 – 7.34 (m, 2H), 7.31 – 7.26 (m, 2H), 7.22 – 7.07 (m, 1H), 3.81 (t, J = 7.3 Hz, 2H), 3.01 (d, J = 5.3 Hz, 1H), 2.78 – 2.63 (m, 2H), 2.18 – 2.01 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 168.09, 138.77, 133.79, 132.04, 128.41, 127.54, 125.69, 123.09, 58.40, 55.95, 34.32, 33.28, 29.68 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{16}NO_3$ $[M+H]^+$ 294.1125, found 294.1126.

***tert*-Butyldimethyl(2-(2-phenyloxiran-2-yl)ethyl)silane (21)**



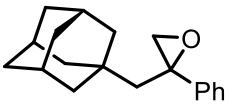
Prepared following the General Procedure A using **21a** (58.1 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **21** (31.5 mg, 0.12 mmol, 62%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.43 – 7.38 (m, 2H), 7.39 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H), 3.83 – 3.55 (m, 2H), 3.06 (d, J = 5.4 Hz, 1H), 2.79 (d, J = 5.4 Hz, 1H), 2.44 – 2.26 (m, 1H), 2.22 – 1.98 (m, 1H), 0.89 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 139.9, 128.3, 127.5, 126.0, 59.3, 58.5, 55.4, 38.6, 25.9, 18.2, -5.5 ppm.

HRMS (ESI^+) calcd. for $C_{16}H_{27}SiO_2$ $[M+H]^+$ 279.1775, found 279.1777.

2-(((3*r*,5*r*,7*r*)-Adamantan-1-yl)methyl)-2-phenyloxirane (22)



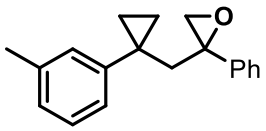
Prepared following the General Procedure A using **22a** (59.3 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **22** (45.5 mg, 0.17 mmol, 83%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.45 – 7.39 (m, 2H), 7.31 (dd, *J* = 8.3, 6.5 Hz, 2H), 7.27 – 7.24 (m, 1H), 2.82 (d, *J* = 5.5 Hz, 1H), 2.69 (d, *J* = 5.6 Hz, 1H), 2.00 (d, *J* = 14.5 Hz, 1H), 1.85 – 1.78 (m, 3H), 1.64 – 1.56 (m, 5H), 1.53 – 1.49 (m, 2H), 1.46 – 1.36 (m, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 141.5, 128.1, 127.2, 126.3, 59.0, 55.2, 50.2, 43.4, 36.8, 34.0, 28.6, 28.5 ppm.

HRMS (ESI^+) calcd. for $C_{19}H_{25}O$ $[M+H]^+$ 269.1900, found 269.1901.

2-Phenyl-2-((1-(*m*-tolyl)cyclopropyl)methyl)oxirane (23)



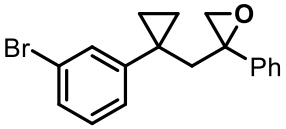
Prepared following the General Procedure A using **23a** (58.4 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **23** (37.1 mg, 0.15 mmol, 73%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.33 – 7.23 (m, 5H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.08 – 7.03 (m, 1H), 7.01 (d, *J* = 1.9 Hz, 1H), 6.98 – 6.93 (m, 1H), 2.65 – 2.58 (m, 2H), 2.39 (d, *J* = 14.6 Hz, 1H), 2.29 (s, 3H), 2.23 (d, *J* = 14.7 Hz, 1H), 0.76 – 0.64 (m, 3H), 0.50 – 0.39 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 144.8, 140.5, 137.5, 129.6, 128.0, 127.9, 127.4, 126.8, 126.7, 125.8, 60.2, 54.0, 46.2, 22.4, 21.4, 13.3, 12.5 ppm.

HRMS (ESI^+) calcd. for $C_{19}H_{21}O$ $[M+H]^+$ 265.1587, found 265.1587.

2-((1-(3-Bromophenyl)cyclopropyl)methyl)-2-phenyloxirane (24)



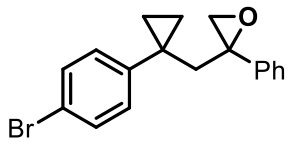
Prepared following the General Procedure A using **24a** (71.3 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **24** (47.7 mg, 0.15 mmol, 75%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.36 – 7.18 (m, 7H), 7.17 – 7.11 (m, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 2.76 – 2.58 (m, 2H), 2.45 (d, *J* = 14.8 Hz, 1H), 2.17 (d, *J* = 14.8 Hz, 1H), 0.76 – 0.63 (m, 3H), 0.61 – 0.53 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 147.4, 140.0, 132.0, 129.5, 129.0, 128.1, 127.5, 127.5, 126.6, 122.0, 60.0, 54.1, 45.9, 22.5, 13.6, 12.6 ppm.

HRMS (ESI$^+$) calcd. for $C_{18}H_{18}BrO$ $[M+H]^+$ 329.0536, found 329.0537.

3-((1-(4-Bromophenyl)cyclopropyl)methyl)-2-phenyloxirane (25)



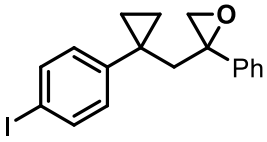
Prepared following the General Procedure A using **25a** (71.3 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **25** (48.7 mg, 0.15 mmol, 77%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.33 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.27 (s, 5H), 7.08 (dd, *J* = 8.2, 1.4 Hz, 2H), 2.70 – 2.53 (m, 2H), 2.42 (d, *J* = 14.8 Hz, 1H), 2.19 (d, *J* = 14.8 Hz, 1H), 0.73 – 0.61 (m, 3H), 0.58 – 0.50 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 144.0, 140.1, 131.0, 130.6, 128.1, 127.5, 126.7, 119.6, 60.0, 54.1, 45.9, 22.2, 13.5, 12.7 ppm.

HRMS (ESI$^+$) calcd. for $C_{18}H_{18}BrO$ $[M+H]^+$ 329.0536, found 329.0537.

2-((1-(4-Iodophenyl)cyclopropyl)methyl)-2-phenyloxirane (26)



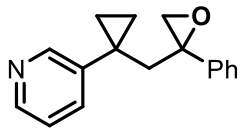
Prepared following the General Procedure A using **26a** (80.9 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **26** (52.7 mg, 0.14 mmol, 71%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.64 – 7.51 (m, 2H), 7.32 (s, 5H), 7.08 – 6.97 (m, 2H), 2.77 – 2.57 (m, 2H), 2.46 (d, *J* = 14.8 Hz, 1H), 2.24 (d, *J* = 14.8 Hz, 1H), 0.78 – 0.68 (m, 3H), 0.64 – 0.55 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 144.7, 140.1, 137.0, 130.9, 128.1, 127.5, 126.6, 91.1, 60.0, 54.1, 45.8, 22.2, 13.5, 12.7 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{18}IO$ $[M+H]^+$ 377.0397, found 377.0396.

3-(1-((2-Phenyloxiran-2-yl)methyl)cyclopropyl)pyridine (27)



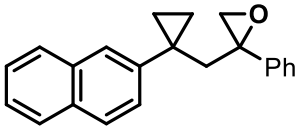
Prepared following the General Procedure A using **27a** (55.8 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (20% EtOAc/Petroleum ether) gave the title compound **27** (22.7 mg, 0.09 mmol, 42%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.45 (d, J = 2.3 Hz, 1H), 8.37 (dd, J = 4.8, 1.5 Hz, 1H), 7.49 – 7.43 (m, 1H), 7.29 – 7.23 (m, 5H), 7.11 (dd, J = 7.9, 4.8 Hz, 1H), 2.65 (dd, J = 29.0, 5.3 Hz, 2H), 2.51 (d, J = 14.8 Hz, 1H), 2.17 (d, J = 14.9 Hz, 1H), 0.80 – 0.61 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 150.6, 147.2, 140.3, 139.8, 136.4, 128.1, 127.5, 126.5, 122.8, 60.0, 54.2, 45.7, 20.6, 13.1, 12.1 ppm.

HRMS (ESI^+) calcd. for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1383, found 252.1385.

2-((1-(Naphthalen-2-yl)cyclopropyl)methyl)-2-phenyloxirane (28)



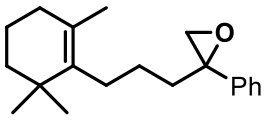
Prepared following the General Procedure A using **28a** (65.6 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **28** (44.2 mg, 0.15 mmol, 78%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.81 – 7.71 (m, 3H), 7.57 (d, *J* = 1.8 Hz, 1H), 7.48 – 7.39 (m, 3H), 7.32 – 7.17 (m, 5H), 2.66 – 2.55 (m, 2H), 2.50 (dd, *J* = 14.7, 1.0 Hz, 1H), 2.33 (dd, *J* = 14.7, 0.8 Hz, 1H), 0.88 – 0.81 (m, 1H), 0.79 – 0.74 (m, 2H), 0.61 – 0.48 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.3, 140.4, 133.3, 132.0, 128.0, 127.7, 127.5, 127.5, 127.5, 127.4, 127.0, 126.9, 125.9, 125.4, 60.2, 53.9, 46.0, 22.7, 13.5, 12.7 ppm.

HRMS (ESI^+) calcd. for $C_{22}H_{21}O$ $[M+H]^+$ 301.1587, found 301.1587.

3-Phenyl-2-(3-(2,6,6-trimethylcyclohex-1-en-1-yl)propyl)oxirane (29)



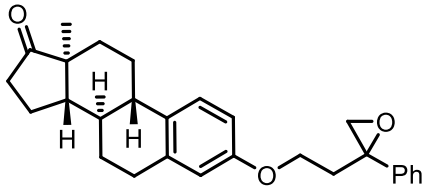
Prepared following the General Procedure A using **29a** (62.42 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **29** (47.2 mg, 0.16 mmol, 84%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.42 – 7.30 (m, 4H), 7.28 (s, 1H), 2.96 (d, J = 5.5 Hz, 1H), 2.73 (d, J = 5.4 Hz, 1H), 2.30 – 2.16 (m, 1H), 2.02 – 1.89 (m, 2H), 1.84 (t, J = 6.3 Hz, 2H), 1.79 – 1.70 (m, 1H), 1.54 – 1.49 (m, 2H), 1.47 (s, 3H), 1.45 – 1.32 (m, 4H), 0.91 (d, J = 4.7 Hz, 6H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 140.1, 137.2, 128.3, 127.3, 127.0, 125.9, 60.1, 55.6, 39.8, 35.9, 34.8, 32.7, 28.8, 28.5, 25.7, 19.8, 19.5 ppm.

HRMS (ESI^+) calcd. for $C_{20}H_{29}O$ $[M+H]^+$ 285.2213, found 285.2211.

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(2-(2-phenyloxiran-2-yl)ethoxy)-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (30)



Prepared following the General Procedure A using **30a** (104.1 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5

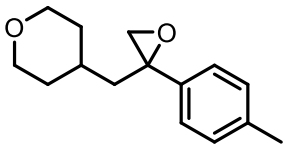
equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **30** (53.1 mg, 0.12 mmol, 64%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.44 – 7.38 (m, 2H), 7.38 – 7.26 (m, 3H), 7.17 (d, *J* = 8.6 Hz, 1H), 6.65 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.58 (d, *J* = 2.7 Hz, 1H), 4.07 – 3.90 (m, 2H), 3.09 (d, *J* = 5.3 Hz, 1H), 2.90 – 2.83 (m, 2H), 2.80 (d, *J* = 5.3 Hz, 1H), 2.64 – 2.45 (m, 2H), 2.40 – 2.29 (m, 2H), 2.28 – 2.19 (m, 1H), 2.19 – 1.91 (m, 4H), 1.67 – 1.58 (m, 2H), 1.54 – 1.46 (m, 3H), 1.45 – 1.40 (m, 1H), 0.90 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 221.0, 156.5, 139.5, 137.7, 132.1, 128.4, 127.7, 126.3, 125.9, 114.4, 112.1, 63.7, 58.3, 55.5, 50.3, 48.0, 43.9, 38.3, 35.8, 35.0, 31.5, 29.6, 26.5, 25.9, 21.5, 13.8 ppm.

HRMS (ESI^+) calcd. for $C_{28}H_{33}O_3$ $[M+H]^+$ 417.2424, found 417.2425.

4-((2-(*p*-Tolyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (31)



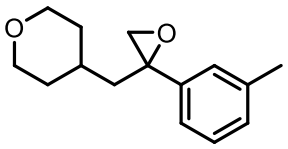
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **2b** (88.2 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **31** (38.1 mg, 0.16 mmol, 82%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.25 (d, J = 7.8 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 3.95 – 3.73 (m, 2H), 3.37 – 3.09 (m, 2H), 2.85 (d, J = 5.5 Hz, 1H), 2.67 (d, J = 5.5 Hz, 1H), 2.35 (s, 3H), 2.22 (dd, J = 13.7, 5.0 Hz, 1H), 1.71 – 1.53 (m, 4H), 1.42 – 1.28 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 137.1, 136.8, 129.1, 125.8, 67.8, 59.2, 55.1, 42.7, 33.6, 33.1, 32.1, 21.1 ppm.

HRMS (ESI^+) calcd. for $C_{15}H_{21}O_2$ $[M+H]^+$ 233.1536, found 233.1537.

4-((2-(*m*-Tolyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (32)



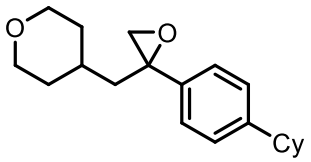
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **3b** (88.2 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **32** (30.2 mg, 0.13 mmol, 64%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.27 – 7.21 (m, 1H), 7.16 (d, J = 8.6 Hz, 2H), 7.10 (d, J = 7.5 Hz, 1H), 3.92 – 3.83 (m, 2H), 3.33 – 3.20 (m, 2H), 2.86 (d, J = 5.5 Hz, 1H), 2.67 (d, J = 5.5 Hz, 1H), 2.36 (s, 3H), 2.24 (dd, J = 13.8, 5.1 Hz, 1H), 1.71 – 1.51 (m, 4H), 1.41 – 1.26 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 139.8, 138.0, 128.2, 128.2, 126.4, 122.9, 67.8, 67.7, 59.3, 55.0, 42.6, 33.5, 33.1, 32.0, 21.5 ppm.

HRMS (ESI^+) calcd. for $C_{15}H_{21}O_2$ $[M+H]^+$ 233.1536, found 233.1537

4-((2-(4-Cyclohexylphenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (33)



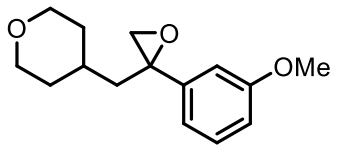
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **4b** (115.3 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **33** (44.1 mg, 0.14 mmol, 74%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.26 (d, J = 1.9 Hz, 2H), 7.20 – 7.15 (m, 2H), 3.91 – 3.83 (m, 2H), 3.35 – 3.20 (m, 2H), 2.85 (d, J = 5.5 Hz, 1H), 2.70 (d, J = 5.4 Hz, 1H), 2.56 – 2.44 (m, 1H), 2.20 (dd, J = 13.5, 4.8 Hz, 1H), 1.90 – 1.82 (m, 4H), 1.77 – 1.67 (m, 2H), 1.60 – 1.51 (m, 2H), 1.44 – 1.35 (m, 5H), 1.35 – 1.31 (m, 1H), 1.29 (dd, J = 5.5, 2.3 Hz, 1H), 1.26 (d, J = 2.4 Hz, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 147.3, 137.1, 126.8, 125.8, 67.8, 67.7, 59.2, 55.1, 44.2, 42.6, 34.4, 33.6, 33.2, 32.0, 26.8, 26.1 ppm.

HRMS (ESI^+) calcd. for $C_{20}H_{29}O_2$ $[M+H]^+$ 301.2162, found 301.2162.

4-((2-(3-Methoxyphenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (34)



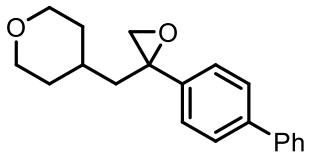
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **5b** (94.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **34** (36.8 mg, 0.14 mmol, 74%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.26 (t, J = 7.9 Hz, 1H), 6.98 – 6.90 (m, 2H), 6.86 – 6.79 (m, 1H), 3.90 – 3.84 (m, 2H), 3.81 (s, 3H), 3.35 – 3.18 (m, 2H), 2.86 (d, J = 5.5 Hz, 1H), 2.67 (d, J = 5.5 Hz, 1H), 2.27 (dd, J = 14.2, 5.3 Hz, 1H), 1.71 – 1.62 (m, 2H), 1.52 (dd, J = 14.2, 8.2 Hz, 2H), 1.39 – 1.28 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 159.7, 141.6, 129.4, 118.2, 112.7, 111.4, 67.8, 67.7, 59.2, 55.2, 55.1, 42.5, 33.6, 33.1, 32.1 ppm.

HRMS (ESI^+) calcd. for $C_{15}H_{21}O_3$ $[M+H]^+$ 249.1485, found 249.1487.

4-((2-([1,1'-Biphenyl]-4-yl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (35)



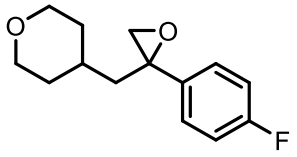
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **6b** (112.9 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **35** (44.7 mg, 0.14 mmol, 76%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.62 – 7.55 (m, 4H), 7.44 (t, J = 7.3 Hz, 4H), 7.38 – 7.30 (m, 1H), 3.89 (dd, J = 11.5, 4.4 Hz, 2H), 3.38 – 3.17 (m, 2H), 2.91 (d, J = 5.5 Hz, 1H), 2.72 (d, J = 5.4 Hz, 1H), 2.31 (dd, J = 14.1, 5.1 Hz, 1H), 1.72 – 1.57 (m, 4H), 1.41 – 1.27 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 140.6, 140.3, 138.9, 128.8, 127.4, 127.1, 127.0, 126.3, 67.8, 59.1, 55.2, 42.5, 33.6, 33.1, 32.1 ppm.

HRMS (ESI$^+$) calcd. for $C_{20}H_{23}O_2$ $[M+H]^+$ 295.1693, found 295.1691.

4-((2-(4-Fluorophenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (36)



Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **7b** (89.6 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **36** (26.4 mg, 0.11 mmol, 52%) as a pale yellow oil.

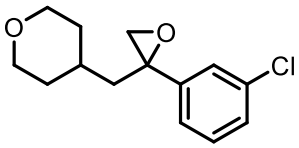
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.39 – 7.26 (m, 2H), 7.08 – 6.92 (m, 2H), 4.00 – 3.76 (m, 2H), 3.34 – 3.18 (m, 2H), 2.86 (d, J = 5.4 Hz, 1H), 2.65 (d, J = 5.4 Hz, 1H), 2.28 – 2.19 (m, 1H), 1.69 – 1.50 (m, 4H), 1.39 – 1.27 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 163.3, 160.8, 135.7, 135.7, 127.6, 127.5, 115.4, 115.2, 67.8, 67.7, 58.9, 55.1, 42.6, 33.5, 33.1, 32.1 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ_F -114.78 ppm.

HRMS (ESI$^+$) calcd. for $C_{14}H_{18}FO_2$ $[M+H]^+$ 237.1285, found 237.1287.

4-((2-(3-Chlorophenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (37)



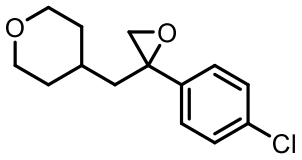
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **8b** (96.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **37** (31.7 mg, 0.13 mmol, 63%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.36 (d, J = 2.1 Hz, 1H), 7.27 (p, J = 2.8 Hz, 3H), 3.98 – 3.56 (m, 2H), 3.39 – 3.12 (m, 2H), 2.87 (d, J = 5.4 Hz, 1H), 2.63 (d, J = 5.5 Hz, 1H), 2.30 (dd, J = 14.3, 5.1 Hz, 1H), 1.71 – 1.48 (m, 4H), 1.39 – 1.26 (m, 2H). ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.1, 134.5, 129.7, 127.6, 125.9, 124.0, 67.7, 67.7, 58.7, 55.1, 42.1, 33.6, 33.0, 32.0 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{18}ClO_2$ $[M+H]^+$ 253.0990, found 253.0991.

4-((2-(4-Chlorophenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (38)



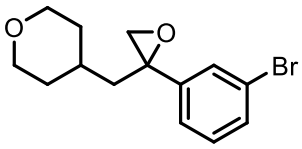
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **9b** (96.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **38** (32.7 mg, 0.13 mmol, 62%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.31 (d, J = 1.5 Hz, 4H), 3.93 – 3.82 (m, 2H), 3.36 – 3.12 (m, 2H), 2.87 (d, J = 5.4 Hz, 1H), 2.63 (d, J = 5.4 Hz, 1H), 2.28 (dd, J = 14.1, 5.1 Hz, 1H), 1.75 – 1.48 (m, 4H), 1.40 – 1.25 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 138.4, 133.2, 128.6, 127.2, 67.7, 67.7, 58.8, 55.1, 42.3, 33.5, 33.0, 32.0 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{18}ClO_2$ $[M+H]^+$ 253.0990, found 253.0991.

4-((2-(3-Bromophenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (39)



Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **10b** (113.6 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with

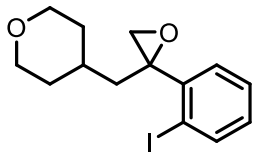
20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **39** (36.7 mg, 0.13 mmol, 62%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.52 (t, J = 1.8 Hz, 1H), 7.45 – 7.39 (m, 1H), 7.33 – 7.28 (m, 1H), 7.22 (t, J = 7.8 Hz, 1H), 3.96 – 3.77 (m, 2H), 3.42 – 3.17 (m, 2H), 2.87 (d, J = 5.4 Hz, 1H), 2.63 (d, J = 5.4 Hz, 1H), 2.29 (dd, J = 14.3, 5.2 Hz, 1H), 1.68 – 1.46 (m, 4H), 1.40 – 1.26 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.4, 130.6, 130.0, 128.8, 124.5, 122.7, 67.7, 67.7, 58.7, 55.1, 42.1, 33.6, 33.0, 32.0 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{18}BrO_2$ $[M+H]^+$ 297.0485, found 297.0485.

4-((2-(2-Iodophenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (40)



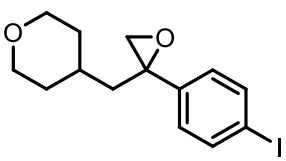
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **11b** (132.8 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **40** (28.3 mg, 0.08 mmol, 42%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.81 (dd, J = 8.0, 1.2 Hz, 1H), 7.45 – 7.30 (m, 2H), 7.07 – 6.85 (m, 1H), 3.99 – 3.77 (m, 2H), 3.38 – 3.21 (m, 2H), 3.00 (d, J = 5.0 Hz, 1H), 2.76 (d, J = 5.0 Hz, 1H), 2.37 (d, J = 12.5 Hz, 1H), 1.89 – 1.78 (m, 1H), 1.53 – 1.40 (m, 3H), 1.34 – 1.23 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 143.1, 139.1, 129.4, 128.0, 96.5, 67.8, 67.7, 63.1, 54.0, 41.8, 33.7, 31.6 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{18}IO_2$ $[M+H]^+$ 345.0346, found 345.0346.

4-((2-(4-Iodophenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (41)



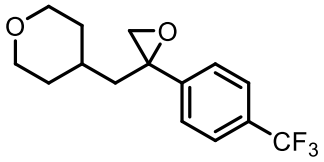
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **12b** (132.8 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **41** (47.8 mg, 0.14 mmol, 68%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.75 – 7.60 (m, 2H), 7.14 – 7.03 (m, 2H), 3.93 – 3.79 (m, 2H), 3.38 – 3.13 (m, 2H), 2.86 (d, J = 5.5 Hz, 1H), 2.61 (d, J = 5.5 Hz, 1H), 2.27 (dd, J = 14.3, 5.2 Hz, 1H), 1.67 – 1.45 (m, 4H), 1.37 – 1.25 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 139.7, 137.5, 127.8, 92.9, 67.7, 67.7, 58.9, 55.1, 42.2, 33.6, 33.0, 32.1 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{18}IO_2$ $[M+H]^+$ 345.0346, found 345.0343.

4-((2-(4-(Trifluoromethyl)phenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (42)



Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **13b** (109.6 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **42** (42.3 mg, 0.15 mmol, 74%) as a pale yellow oil.

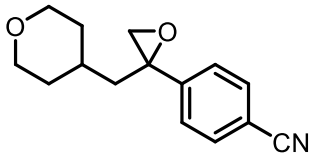
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.61 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 3.87 (dd, J = 11.8, 4.3 Hz, 2H), 3.34 – 3.18 (m, 2H), 2.91 (d, J = 5.4 Hz, 1H), 2.63 (d, J = 5.4 Hz, 1H), 2.37 (dd, J = 14.1, 4.8 Hz, 1H), 1.68 (d, J = 12.6 Hz, 1H), 1.63 – 1.55 (m, 1H), 1.55 – 1.47 (m, 2H), 1.42 – 1.28 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 144.1, 130.1, 129.8, 129.5, 126.1, 125.5, 125.4, 125.4, 125.4, 122.7, 120.0, 67.7, 67.6, 58.9, 55.2, 42.1, 33.6, 33.0, 32.0 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ_F -62.52 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{18}F_3O_2$ $[M+H]^+$ 287.1253, found 287.1255.

4-(2-((Tetrahydro-2*H*-pyran-4-yl)methyl)oxiran-2-yl)benzonitrile (43)



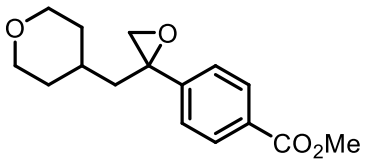
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **14b** (92.4 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **43** (34.0 mg, 0.14 mmol, 70%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.64 (d, J = 8.1 Hz, 2H), 7.48 (d, J = 8.2 Hz, 2H), 3.91 – 3.79 (m, 2H), 3.34 – 3.10 (m, 2H), 2.92 (d, J = 5.4 Hz, 1H), 2.61 (d, J = 5.4 Hz, 1H), 2.38 (dd, J = 14.1, 4.6 Hz, 1H), 1.68 – 1.63 (m, 1H), 1.60 – 1.45 (m, 3H), 1.41 – 1.28 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 145.5, 132.3, 126.4, 118.6, 111.3, 67.6, 67.6, 58.7, 55.3, 41.7, 33.5, 32.9, 32.1 ppm.

HRMS (ESI^+) calcd. for $C_{15}H_{18}NO_2$ $[M+H]^+$ 244.1332, found 244.1330.

Methyl 4-(2-((tetrahydro-2*H*-pyran-4-yl)methyl)oxiran-2-yl)benzoate (44)



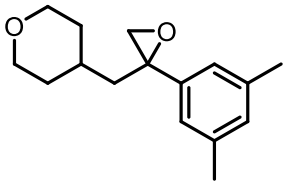
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **15b** (105.6 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **44** (38.2 mg, 0.14 mmol, 69%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.04 – 7.97 (m, 2H), 7.51 – 7.38 (m, 2H), 3.91 (s, 3H), 3.89 – 3.83 (m, 2H), 3.35 – 3.14 (m, 2H), 2.90 (d, J = 5.5 Hz, 1H), 2.64 (d, J = 5.4 Hz, 1H), 2.36 (dd, J = 14.2, 4.9 Hz, 1H), 1.71 – 1.66 (m, 1H), 1.62 – 1.53 (m, 1H), 1.53 – 1.47 (m, 2H), 1.42 – 1.29 (m, 2H) ppm..

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 166.7, 145.1, 129.8, 129.3, 125.8, 67.7, 59.1, 55.2, 52.1, 42.1, 33.6, 33.0, 32.1 ppm.

HRMS (ESI$^+$) calcd. for $C_{16}H_{21}O_4$ $[M+H]^+$ 277.1434, found 277.1436.

4-((2-(3,5-Dimethylphenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (45)



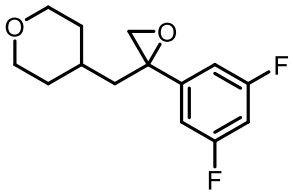
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **16b** (93.6 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **45** (30.5 mg, 0.12 mmol, 62%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.97 (s, 2H), 6.92 (s, 1H), 3.92 – 3.83 (m, 2H), 3.37 – 3.21 (m, 2H), 2.84 (d, J = 5.5 Hz, 1H), 2.66 (d, J = 5.5 Hz, 1H), 2.32 (s, 6H), 2.22 (dd, J = 13.9, 5.3 Hz, 1H), 1.71 – 1.52 (m, 4H), 1.41 – 1.28 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 139.8, 137.9, 129.1, 123.6, 67.8, 67.7, 59.3, 55.0, 42.7, 33.6, 33.2, 32.0, 21.3 ppm.

HRMS (ESI$^+$) calcd. for $C_{16}H_{23}O_2$ $[M+H]^+$ 247.1693, found 247.1695.

4-((2-(3,5-Difluorophenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (46)



Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **17b** (96.8 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **46** (35.6 mg, 0.14 mmol, 74%) as a pale yellow oil.

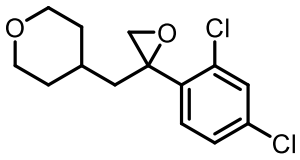
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.93 – 6.85 (m, 2H), 6.76 – 6.68 (m, 1H), 3.91 – 3.82 (m, 2H), 3.37 – 3.15 (m, 2H), 2.87 (d, J = 5.5 Hz, 1H), 2.60 (d, J = 5.4 Hz, 1H), 2.31 (dd, J = 14.5, 5.0 Hz, 1H), 1.70 – 1.56 (m, 2H), 1.53 – 1.42 (m, 2H), 1.38 – 1.23 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 164.5, 164.3, 162.0, 161.9, 144.3, 108.9, 108.8, 108.7, 108.6, 103.2, 103.0, 102.7, 67.7, 67.7, 58.5, 55.2, 41.8, 33.5, 32.9, 32.0 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ_F -109.09 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{17}F_2O_2$ $[M+H]^+$ 255.1191, found 255.1190.

4-((2-(2,4-Dichlorophenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (47)



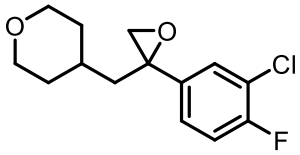
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **18b** (109.6 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **47** (26.9 mg, 0.09 mmol, 47%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.41 – 7.35 (m, 2H), 7.26 – 7.24 (m, 1H), 3.99 – 3.65 (m, 2H), 3.30 (tt, *J* = 11.6, 2.0 Hz, 2H), 2.96 (d, *J* = 5.1 Hz, 1H), 2.73 (d, *J* = 5.1 Hz, 1H), 2.32 – 2.25 (m, 1H), 1.83 – 1.73 (m, 1H), 1.55 – 1.42 (m, 3H), 1.37 – 1.26 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 136.9, 134.2, 133.1, 130.0, 129.2, 127.1, 67.7, 67.7, 59.0, 53.3, 42.1, 33.6, 33.5, 31.9 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{17}Cl_2O_2$ $[M+H]^+$ 287.0600, found 287.0601.

4-((2-(3-Chloro-4-fluorophenyl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (48)



Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **19b** (103.6 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **48** (42.1 mg, 0.16 mmol, 78%) as a pale yellow oil.

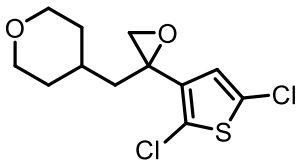
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.41 (dd, J = 7.0, 2.2 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.12 (t, J = 8.6 Hz, 1H), 3.98 – 3.78 (m, 2H), 3.36 – 3.17 (m, 2H), 2.87 (d, J = 5.4 Hz, 1H), 2.62 (d, J = 5.4 Hz, 1H), 2.27 (dd, J = 14.2, 5.0 Hz, 1H), 1.70 – 1.50 (m, 4H), 1.40 – 1.26 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 158.6, 156.1, 137.2, 137.1, 128.0, 125.6, 125.6, 121.3, 121.1, 116.7, 116.5, 67.7, 67.7, 58.4, 55.1, 42.1, 33.6, 33.0, 32.0 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ_F -116.95 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{17}ClFO_2$ $[M+H]^+$ 271.0896, found 271.0897.

4-((2-(2,5-dichlorothiophen-3-yl)oxiran-2-yl)methyl)tetrahydro-2*H*-pyran (49)



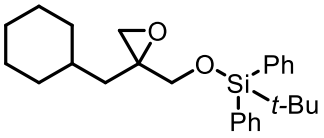
Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **20b** (112.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **49** (39.8 mg, 0.14 mmol, 68%) as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 6.77 (s, 1H), 3.95 – 3.86 (m, 2H), 3.44 – 3.26 (m, 2H), 2.86 (q, *J* = 5.2 Hz, 2H), 2.00 (dd, *J* = 13.6, 5.7 Hz, 1H), 1.68 – 1.53 (m, 4H), 1.41 – 1.26 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 137.3, 126.8, 126.1, 123.0, 67.7, 67.7, 56.1, 53.2, 42.8, 33.4, 33.4, 32.1 ppm.

HRMS (ESI^+) calcd. for $C_{12}H_{15}Cl_2SO_2$ $[M+H]^+$ 293.0164, found 293.0165.

***tert*-butyl((2-(cyclohexylmethyl)oxiran-2-yl)methoxy)diphenylsilane (50)**



Prepared following the General Procedure A using **1a** (49.3 mg, 0.20 mmol, 1.0 equiv.) and **21b** (159.2 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (5% EtOAc/Petroleum ether) gave the title compound **50** (12.5 mg, 0.03 mmol, 15%) as a pale yellow oil.

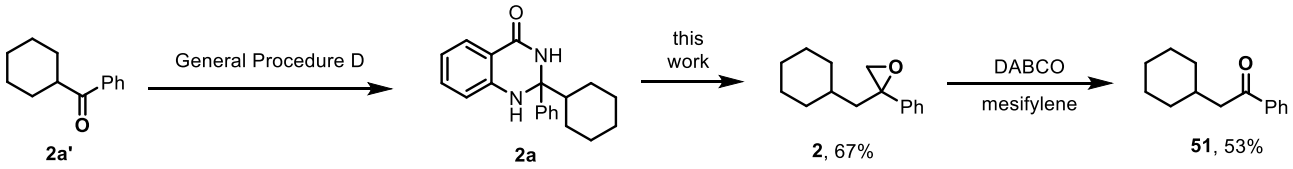
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.70 – 7.66 (m, 4H), 7.45 – 7.36 (m, 6H), 3.79 – 3.56 (m, 2H), 2.70 (dd, *J* = 5.0, 1.1 Hz, 1H), 2.56 (d, *J* = 5.0 Hz, 1H), 1.84 – 1.78 (m, 1H), 1.73 – 1.59 (m, 6H), 1.33 (d, *J* = 2.6 Hz, 1H), 1.18 – 1.10 (m, 3H), 1.06 (s, 9H), 0.95 – 0.84 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 135.7, 135.6, 133.3, 133.3, 129.7, 129.7, 127.7, 127.7, 65.4, 58.6, 50.6, 39.8, 34.4, 34.1, 33.5, 26.8, 26.4, 26.2, 26.2, 19.3 ppm.

HRMS (ESI^+) calcd. for $C_{26}H_{37}O_2Si$ $[M+H]^+$ 409.2557, found 409.2558.

6. Synthetic Application

6.1. Direct C1 homologation of ketones



a) Synthesis of 2a[3]:

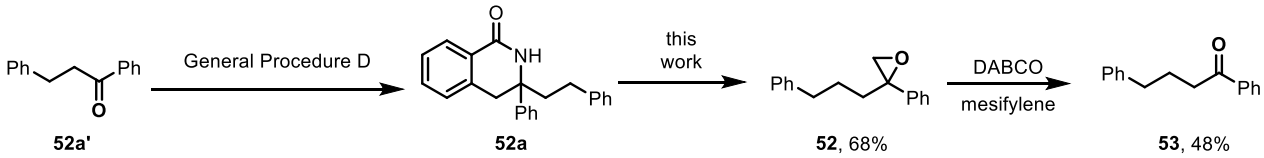
Prepared following the General Procedure using anthranilamide (567.5 mg, 5.0 mmol, 1.0 equiv.), ketone (5.5 mmol, 1.1 equiv.), $CpTiCl_2$ (0.25 mmol, 0.05 equiv.) and EtOH (10 mL, 0.5 M) were added to a 50 mL flame-dried single neck round flask with a stirring bar under nitrogen atmosphere. The flask was capped with a rubber septum. A needle with a nitrogen balloon was attached by piercing the septum to act as a ballast in case of gas pressure buildup. Next, the flask was placed in an oil bath with stirring at 85 °C. The reaction mixture was stirred at that temperature for 24 h with monitoring by TLC analysis. After the ketone was totally consumed, the reaction was cooled to room temperature and the septum was removed. Water (20 mL) was added to the mixture and extracted with EtOAc (3 × 20 mL). The resulting organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica (eluent = petroleum ether/ethyl acetate) to afford pure **2a** with 86% yield.

b) Synthesis of 2:

Prepared following the General Procedure A using **2a** (120.8 mg, 0.40 mmol, 1.0 equiv.) and **1b** (165 mg, 0.80 mmol, 2.0 equiv.), 4CzIPN (15.8 mg, 0.02 mmol, 5.0 mol%), Cs_2CO_3 (65.2 mg, 0.2 mmol, 0.5 equiv.), DBU (30.6 mg, 0.2 mmol, 0.5 equiv.), and Chlorobenzene (8.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **2** (68.0 mg, 0.24 mmol, 61%) as a colorless oil.

c) Synthesis of 51:

Epoxide **2** (21.6 mg, 0.10 mmol, 1.0 equiv.) was dissolved in 1.0 mL of mesitylene in a 7.0 mL reaction tube. After DABCO (44.9 mg, 0.40 mmol, 4.0 equiv.) was added at room temperature, the reaction mixture was heated at 165 °C for 96 h. After cooled to room temperature, the reaction mixture was directly subjected to flash column chromatography with ethyl acetate/petroleum ether (1:50, v/v) to afford product **51** (10.3 mg, 0.05 mmol, 53%), as a colorless oil.



d) Synthesis of 52a:

Prepared following the General Procedure using anthranilamide (567.5 mg, 5.0 mmol, 1.0 equiv.), ketone (5.5 mmol, 1.1 equiv.), $CpTiCl_2$ (0.25 mmol, 0.05 equiv.) and EtOH (10 mL, 0.5 M) were added to a 50 mL flame-dried single neck round flask with a stirring bar under nitrogen atmosphere. The flask was capped with a rubber septum. A needle with a nitrogen balloon was attached by piercing the septum to act as a ballast in case of gas pressure buildup. Next, the flask was placed in an oil bath with stirring at 85 °C. The reaction mixture was stirred at that temperature for 24 h with monitoring by TLC analysis. After the ketone was totally consumed, the reaction was cooled to room temperature and the septum was removed. Water (20 mL) was added to the mixture and extracted with EtOAc (3 × 20 mL). The resulting organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica (eluent = petroleum ether/ethyl acetate) to afford pure **52a** with 84% yield.

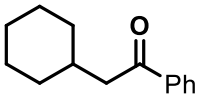
e) Synthesis of 52:

Prepared following the General Procedure A using **52a** (130.9 mg, 0.40 mmol, 1.0 equiv.) and **1b** (165 mg, 0.80 mmol, 2.0 equiv.), 4CzIPN (15.8 mg, 0.02 mmol, 5.0 mol%), Cs_2CO_3 (65.2 mg, 0.2 mmol, 0.5 equiv.), DBU (30.6 mg, 0.2 mmol, 0.5 equiv.), and Chlorobenzene (8.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **52** (64.3 mg, 0.27 mmol, 68%) as a colorless oil.

f) Synthesis of 53:

Epoxide **52** (23.8 mg, 0.10 mmol, 1.0 equiv.) was dissolved in 1.0 mL of mesitylene in a 7 mL reaction tube. After DABCO (44.9 mg, 0.40 mmol, 4.0 equiv.) was added at room temperature, the reaction mixture was heated at 165 °C for 96 h. After cooled to room temperature, the reaction mixture was directly subjected to flash column chromatography with ethyl acetate/petroleum ether (1:50, v/v) to afford product **53** (10.7 mg, 0.05 mmol, 48%), as a colorless oil.

2-Cyclohexyl-1-phenylethan-1-one (51)

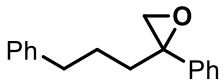


^{1}H NMR (400 MHz, $CDCl_3$) δ_H 8.03 – 7.86 (m, 2H), 7.58 – 7.50 (m, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 2.82 (d, *J* = 6.8 Hz, 2H), 2.07 – 1.89 (m, 1H), 1.78 – 1.62 (m, 5H), 1.32 – 1.15 (m, 3H), 1.08 – 0.96 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 200.3, 137.4, 132.8, 128.5, 128.1, 46.2, 34.5, 33.4, 26.2, 26.1 ppm.

HRMS (ESI^+) calcd. for $C_{14}H_{19}O$ $[M+H]^+$ 203.1430, found 203.1432.

2-Phenyl-2-(3-phenylpropyl)oxirane (52)

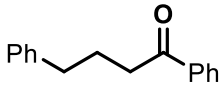


^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.34 – 7.32 (m, 3H), 7.29 – 7.21 (m, 4H), 7.19 – 7.10 (m, 3H), 2.95 (d, *J* = 5.4 Hz, 1H), 2.73 (d, *J* = 5.4 Hz, 1H), 2.70 – 2.54 (m, 2H), 2.28 – 2.17 (m, 1H), 1.80 – 1.62 (m, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 142.0, 139.9, 128.4, 128.3, 128.3, 127.4, 125.9, 125.8, 60.3, 55.5, 35.7, 35.0, 26.6 ppm.

HRMS (ESI^+) calcd. for $C_{17}H_{19}O$ $[M+H]^+$ 239.1430, found 239.1431.

1,4-Diphenylbutan-1-one (53)



^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.95 – 7.80 (m, 2H), 7.54 – 7.47 (m, 1H), 7.41 (dd, *J* = 8.4, 7.0 Hz, 2H), 7.27 (dd, *J* = 8.2, 6.9 Hz, 2H), 7.23 – 7.15 (m, 3H), 2.95 (t, *J* = 7.3 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.17 – 2.00 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 199.94, 141.57, 136.82, 132.84, 128.43, 128.40, 128.28, 127.88, 125.83, 37.54, 35.06, 25.56 ppm.

HRMS (ESI^+) calcd. for $C_{16}H_{17}O$ $[M+H]^+$ 225.1274, found 225.1274.

6.2. Scale-up reaction

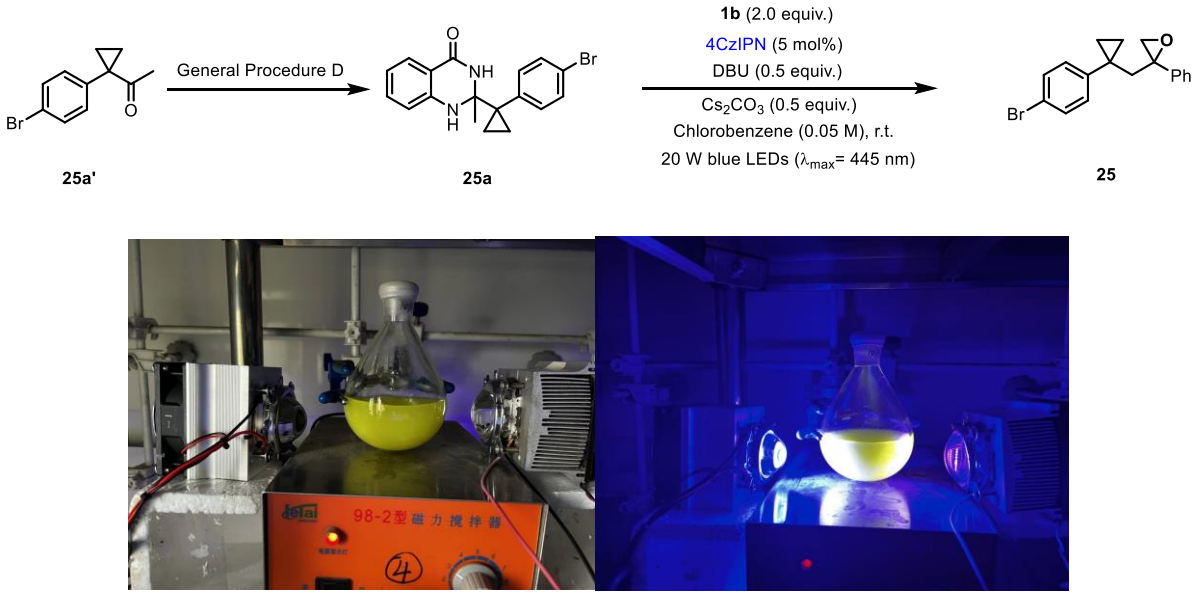


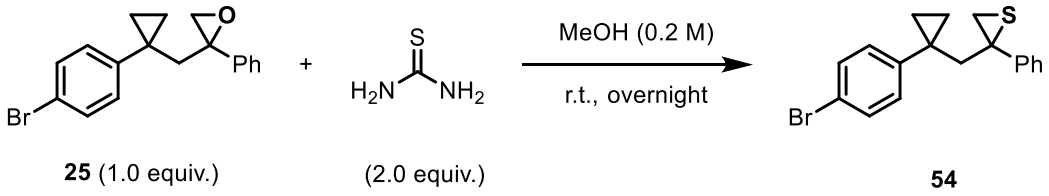
Figure S3. Reaction setup

Prepared following the General Procedure using anthranilamide (567.5 mg, 10.0 mmol, 1.0 equiv.), ketone (11.0 mmol, 1.1 equiv.), $CpTiCl_2$ (0.5 mmol, 0.05 equiv.) and EtOH (20 mL, 0.5 M) were added to a 50 mL flame-dried single neck round flask with a stirring bar under nitrogen atmosphere. The flask was capped with a rubber septum. A needle with a nitrogen balloon was attached by piercing the septum to act as a ballast in case of gas pressure buildup. Next, the flask was placed in an oil bath with stirring at 85 °C. The reaction mixture was stirred at that temperature for 24 h with monitoring by TLC analysis. After the ketone was totally consumed, the reaction was cooled to room temperature and the septum was removed. Water (20 mL) was added to the mixture and extracted with EtOAc (3 × 20 mL). The resulting organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The crude mixture was purified by flash column chromatography through silica (eluent = petroleum ether/ethyl acetate) to afford pure **25a** with 72% yield.

In the glove box, to a dry 150 mL vial equipped with a magnetic stir bar were added **25a** (5 mmol, 1.0 equiv.), **1b** (10 mmol, 2.0 equiv.), 4CzIPN (0.250 mmol, 197.2 mg, 5.0 mol%), Cs_2CO_3 (814.5 mg, 2.5 mmol, 0.5 equiv.), and DBU (380.0 mg, 2.5 mmol, 0.5 equiv.). Then anhydrous chlorobenzene (100 mL) was added to the mixture. The vial was sealed with a septum and the sealed vial was taken out of the glove box. The reaction mixture was stirred at 800 rpm and irradiated with two 20 W blue LEDs lamp (with fan cooled) typically for 24 h, monitored by TLC. After the reaction completion, the reaction was extracted with ethyl acetate, and the combined organic layer was washed with brine, dried over Na_2SO_4, filtered concentrated *in vacuum*. The crude residue was purified by flash Al_2O_3 (neutral) gave the title compound **25** (1.12 g, 3.4 mmol, 68%) as a colorless oil (**Figure S3**).

6.3. Product derivatization

(1) Synthesis of 54



25 (1.0 equiv.) (2.0 equiv.) **54**

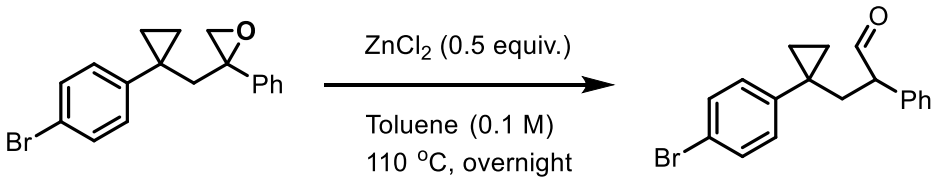
Thiourea (30.5 mg, 0.40 mmol, 2.0 equiv.) was added to a solution of **25** (65.8 mg, 0.20 mmol, 1.0 equiv.) in MeOH (1.0 mL). The mixture was stirred at r.t. for 18 h. The solvent was removed *in vacuo* after the reaction. Purification by flash column chromatography (30% EtOAc/hexane) gave the corresponding compound **54** (46.2 mg, 0.14 mmol, 67%), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.36 – 7.31 (m, 2H), 7.27 (s, 5H), 7.10 – 7.04 (m, 2H), 2.67 – 2.57 (m, 2H), 2.41 (d, *J* = 14.8 Hz, 1H), 2.18 (d, *J* = 14.8 Hz, 1H), 0.72 – 0.62 (m, 3H), 0.57 – 0.50 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 144.0, 140.1, 131.0, 130.6, 128.1, 127.5, 126.7, 119.6, 60.0, 54.0, 45.9, 22.2, 13.5, 12.6 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{18}BrS$ $[M+H]^+$ 345.0307, found 345.0309.

(2) Synthesis of 55



25 (1.0 equiv.) **55**

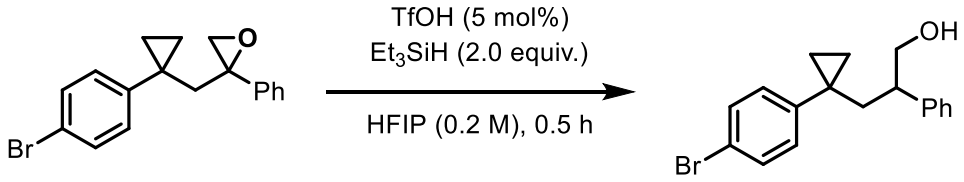
$ZnCl_2$ (13.6 mg, 0.10 mmol, 0.5 equiv.) was added to a solution of **25** (65.8 mg, 0.20 mmol, 1.0 equiv.) in Toluene (2.0 mL). The mixture was stirred at 110 °C for 12 h. The solvent was removed *in vacuo* after the reaction. Purification by flash column chromatography (hexane) gave the corresponding compound **55** (59.2 mg, 0.18 mmol, 88%), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 9.54 (t, *J* = 1.5 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.34 – 7.25 (m, 3H), 7.14 (d, *J* = 8.1 Hz, 2H), 7.10 – 7.03 (m, 2H), 3.49 – 3.40 (m, 1H), 2.58 (dd, *J* = 14.4, 6.7 Hz, 1H), 1.88 (dd, *J* = 14.4, 7.4 Hz, 1H), 0.73 – 0.62 (m, 3H), 0.45 – 0.40 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 200.3, 143.0, 136.2, 131.4, 130.9, 129.0, 127.6, 120.1, 57.3, 40.1, 23.4, 13.1, 12.9 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{18}BrO$ $[M+H]^+$ 329.0536, found 329.0537.

(3) Synthesis of 56



25 (1.0 equiv.) **56**

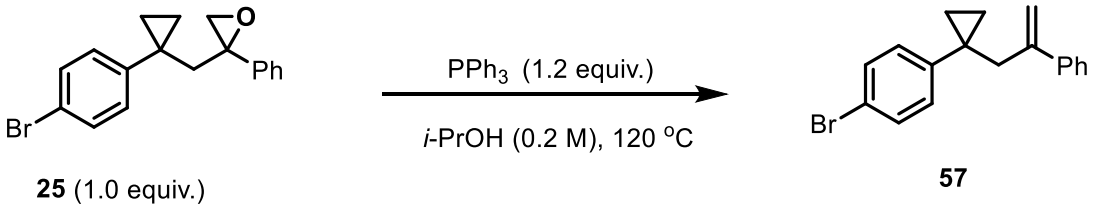
Et_3SiH (46.1 mg, 0.40 mmol, 2.0 equiv.), TfOH (1.5 mg, 0.01 mmol, 0.05 equiv.) was added to a solution of **25** (65.8 mg, 0.20 mmol, 1.0 equiv.) in HFIP (1.0 mL). The mixture was stirred at r.t. for 0.5 h. The solvent was removed *in vacuo* after the reaction. Purification by flash column chromatography (20% EtOAc/hexane) gave the corresponding compound **56** (47.6 mg, 0.15 mmol, 72%), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.40 – 7.34 (m, 2H), 7.29 – 7.19 (m, 3H), 7.14 – 7.04 (m, 4H), 3.63 (t, J = 6.3 Hz, 2H), 2.73 – 2.59 (m, 1H), 2.10 (dd, J = 14.2, 6.0 Hz, 1H), 1.78 (dd, J = 14.2, 8.3 Hz, 1H), 1.31 (s, 1H), 0.73 – 0.56 (m, 3H), 0.40 – 0.33 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 143.7, 142.3, 131.2, 130.7, 128.5, 128.1, 126.7, 119.7, 66.8, 46.5, 42.2, 23.5, 13.0, 12.8 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{20}BrO$ $[M+H]^+$ 331.0692, found 331.0692.

(4) Synthesis of 57



25 (1.0 equiv.) **57**

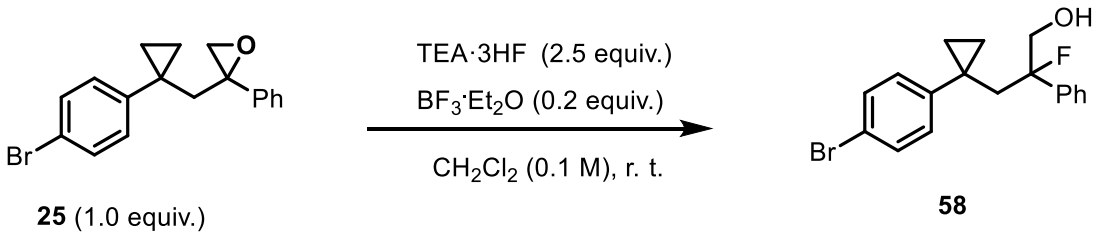
PPh_3 (63.0 mg, 0.24 mmol, 1.2 equiv.) was added to a solution of **25** (65.8 mg, 0.20 mmol, 1.0 equiv.) in *i*-PrOH (1.0 mL). The mixture was stirred at 120 °C for 36 h. The solvent was removed *in vacuo* after the reaction. Purification by flash column chromatography (hexane) gave the corresponding compound **57** (46.8 mg, 0.15 mmol, 74%), as a colorless oil.

^{1}H NMR (400 MHz, DMSO-d_6) δ_H 7.39 – 7.36 (m, 2H), 7.33 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.22 – 7.18 (m, 3H), 7.14 – 7.07 (m, 1H), 5.22 (d, *J* = 1.7 Hz, 1H), 4.95 (d, *J* = 1.7 Hz, 1H), 2.87 (s, 2H), 0.81 – 0.76 (m, 4H) ppm.

^{13}C NMR (101 MHz, DMSO-d_6) δ_C 145.4, 144.8, 141.5, 128.2, 127.9, 127.5, 127.4, 126.0, 125.4, 114.4, 42.7, 23.1, 14.0 ppm.

HRMS (ESI$^+$) calcd. for $C_{18}H_{18}Br$ $[M+H]^+$ 313.0586, found 313.0587.

(5) Synthesis of 58



25 (1.0 equiv.) **58**

TEA·3HF (6.0 μL, 0.40 mmol, 2.0 equiv.) and $BF_3{\cdot}Et_2O$ (81.0 μL, 0.04 mmol, 0.2 equiv.) was added to a solution of **25** (65.8 mg, 0.20 mmol, 1.0 equiv.) in DCM (2.0 mL). The mixture was stirred at r.t. for 12 h. The solvent was removed *in vacuo* after the reaction. Purification by flash column chromatography (hexane) gave the corresponding compound **58** (48.2 mg, 0.14 mmol, 73%), as a colorless oil.

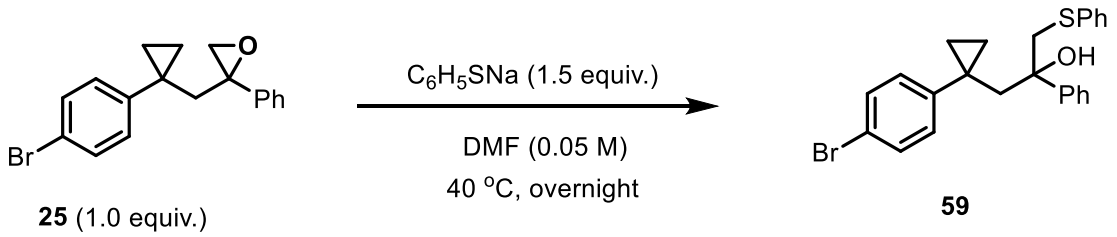
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.26 – 7.18 (m, 5H), 7.12 (dt, J = 6.8, 2.2 Hz, 2H), 7.01 – 6.93 (m, 2H), 3.80 – 3.60 (m, 2H), 2.55 – 2.22 (m, 2H), 1.70 – 1.60 (m, 1H), 0.76 – 0.69 (m, 2H), 0.65 – 0.53 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 144.2, 140.0, 139.8, 130.8, 128.1, 128.1, 127.4, 124.8, 124.7, 119.4, 101.1, 99.3, 68.7, 68.5, 46.1, 45.9, 21.2, 21.2, 13.2, 12.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) δ_F -165.59 ppm.

HRMS (ESI$^+$) calcd. for $C_{18}H_{19}BrFO$ $[M+Na]^+$ 349.0598, found 349.0598.

(6) Synthesis of 59



25 (1.0 equiv.)

59

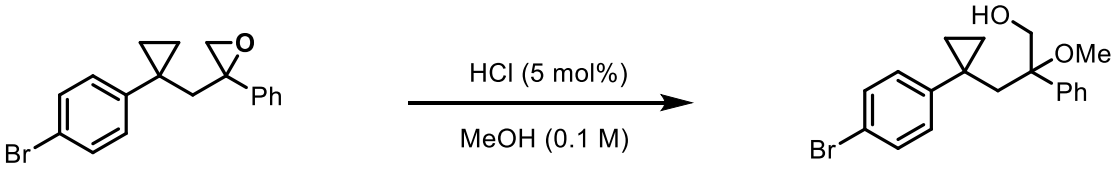
C_6H_5SNa (39.6 mg, 0.30 mmol, 1.5 equiv.) was added to a solution of **25** (65.8 mg, 0.20 mmol, 1.0 equiv.) in DMF (4.0 mL). The mixture was stirred at 40 °C for 12 h. Then partitioned between EtOAc (15 mL) and H_2O (10 mL). The phases were separated and the aqueous phase was extracted into EtOAc (2 × 15 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (5% EtOAc/hexane) gave the corresponding compound **59** (74.2 mg, 0.17 mmol, 81%), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.27 – 7.11 (m, 12H), 7.05 (d, *J* = 8.2 Hz, 2H), 3.40 (d, *J* = 13.0 Hz, 1H), 3.20 (d, *J* = 13.1 Hz, 1H), 2.61 (s, 1H), 2.43 – 2.16 (m, 2H), 0.70 – 0.58 (m, 3H), 0.57 – 0.50 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 144.8, 144.2, 136.7, 131.1, 130.9, 129.6, 128.81, 127.9, 126.8, 126.2, 125.5, 119.6, 77.0, 51.6, 48.4, 21.9, 13.1, 13.1 ppm.

HRMS (ESI^+) calcd. for $C_{24}H_{24}BrOS$ $[M+H]^+$ 439.0726, found 439.0729.

(7) Synthesis of 60



25 (1.0 equiv.)

60

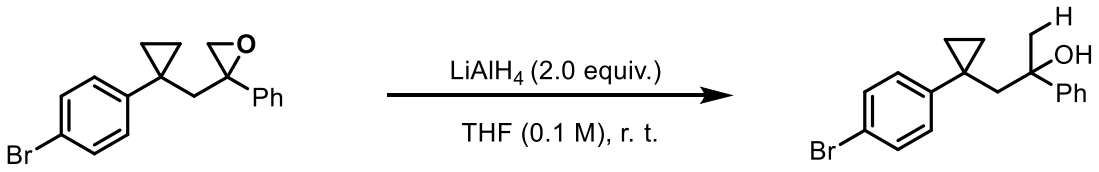
HCl (50 μL, 37% in H_2O, 0.005 equiv.) was added to a solution of **25** (65.8 mg, 0.20 mmol, 1.0 equiv.) in MeOH (2.0 mL). The mixture was stirred at r.t. for 2 h. Then partitioned between EtOAc (15 mL) and H_2O (10 mL). The phases were separated and the aqueous phase was extracted into EtOAc (2 × 15 mL). The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (5% EtOAc/hexane) gave the corresponding compound **60** (64.8 mg, 0.18 mmol, 89%), as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.24 – 7.18 (m, 5H), 7.12 – 7.06 (m, 2H), 7.01 (d, *J* = 8.2 Hz, 2H), 3.97 – 3.69 (m, 2H), 2.84 (s, 3H), 2.38 (d, *J* = 14.5 Hz, 1H), 2.08 (d, *J* = 14.6 Hz, 1H), 1.59 (dd, *J* = 8.2, 3.9 Hz, 1H), 0.74 – 0.54 (m, 3H), 0.48 – 0.37 (m, 1H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 143.9, 140.6, 130.9, 130.7, 128.1, 127.2, 126.7, 119.3, 81.6, 62.2, 49.4, 45.2, 21.5, 13.2, 13.1 ppm.

HRMS (ESI^+) calcd. for $C_{19}H_{22}BrO_2$ $[M+H]^+$ 361.0798, found 361.0799.

(8) Synthesis of 61



25 (1.0 equiv.) **61**

$LiAlH_4$ (15.2 mg, 0.40 mmol, 2.0 equiv.) was added to a solution of **25** (65.8 mg, 0.20 mmol, 1.0 equiv.) in dry THF (2.0 mL). The mixture was stirred at r.t. for 4 h. Then partitioned between EtOAc (15 mL) and H_2O. The phases were separated and the aqueous phase was extracted into EtOAc (2 × 15 mL).The combined organic phases dried ($MgSO_4$), filtered, and concentrated *in vacuo*. Purification by flash column chromatography (30% EtOAc/hexane) gave the corresponding compound **61** (47.0 mg, 0.14 mmol, 71%), as a colorless oil.

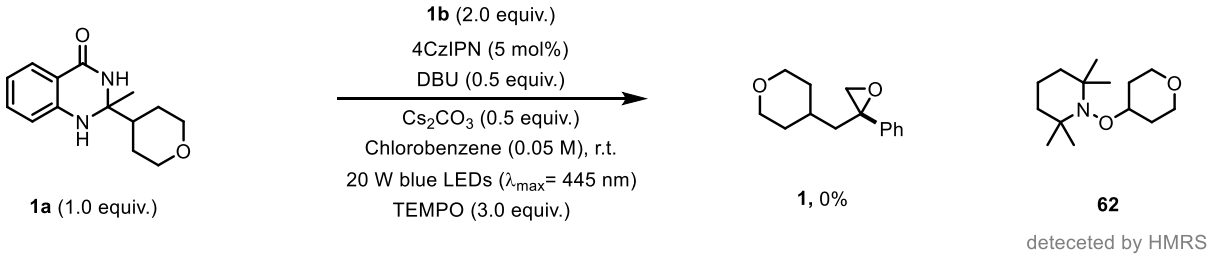
^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.33 – 7.28 (m, 2H), 7.28 – 7.21 (m, 4H), 7.21 – 7.16 (m, 1H), 7.14 – 7.07 (m, 2H), 2.32 – 2.09 (m, 2H), 1.64 (s, 1H), 1.44 (s, 3H), 0.75 – 0.47 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 147.9, 144.0, 131.3, 131.0, 127.8, 126.3, 124.8, 119.8, 75.9, 53.6, 30.6, 22.2, 13.1, 13.0 ppm.

HRMS (ESI^+) calcd. for $C_{18}H_{20}BrO$ $[M+H]^+$ 331.0692, found 331.0691.

7. Mechanistic Studies and Proposed Mechanism

7.1. Radical inhibition reactions



In the glove box, to a dry 7 mL vial equipped with a magnetic stir bar were added **1a** (0.2 mmol, 1.0 equiv.), **1b** (0.4 mmol, 2.0 equiv.), 4CzIPN (0.010 mmol, 7.9 mg, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and TEMPO (46.9 mg, 0.3 mmol, 3.0 equiv.). Then anhydrous chlorobenzene (4.0 mL) was added to the mixture. The vial was sealed with a septum and the sealed vial was taken out of the glove box. The reaction mixture was stirred at 800 rpm and irradiated with a 20 W blue LEDs lamp (with fan cooled) typically for 24 h. HRMS analysis of this reaction crude mixture showed that **62** was formed and no product **1** was observed, the reaction was completely inhibited (**Figure S4**).

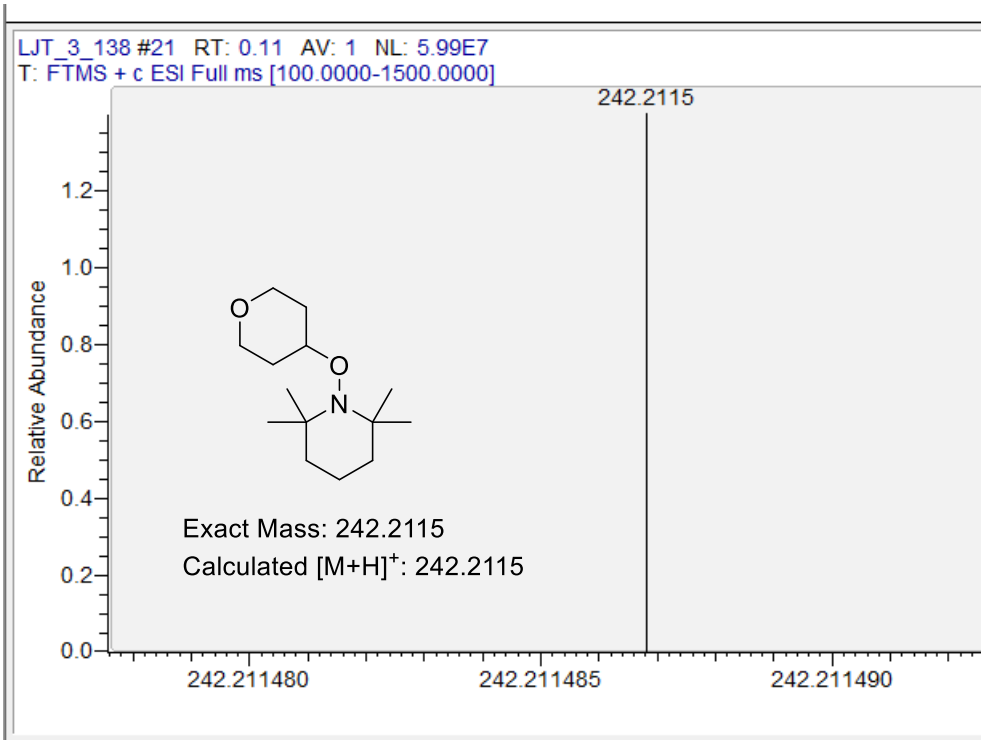
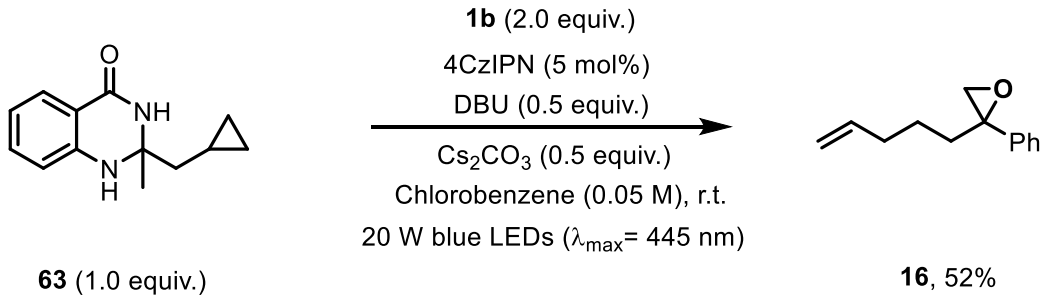


Figure S4. HRMS spectra of free radical capture experiment

These results supported the speculation that the reaction proceeded via a radical pathway and confirmed the generation radical.

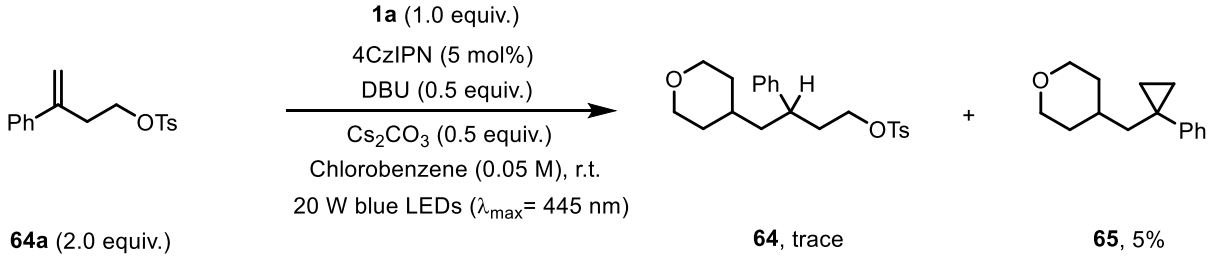
.

7.2. Radical clock reaction



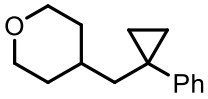
Prepared following the General Procedure A using **63**[10] (43.2 mg, 0.20 mmol, 1.0 equiv.) and **1b** (82.5 mg, 0.40 mmol, 2.0 equiv.), 4CzIPN (7.9 mg, 0.01 mmol, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), DBU (15.3 mg, 0.1 mmol, 0.5 equiv.), and Chlorobenzene (4.0 mL), which was irradiated with 20 W blue LEDs for 24 h. Purification by flash column chromatography (2% EtOAc/Petroleum ether) gave the title compound **16** (19.6 mg, 0.10 mmol, 52%) as a pale yellow oil.

7.3. Radical polar crossover reaction



In the glove box, to a dry 7 mL vial equipped with a magnetic stir bar were added **64a**[11] (0.4 mmol, 1.0 equiv.), **1a** (0.2 mmol, 1.0 equiv.), 4CzIPN (0.010 mmol, 7.9 mg, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), and DBU (15.3 mg, 0.1 mmol, 0.5 equiv.). Then anhydrous chlorobenzene (4.0 mL) was added to the mixture. The vial was sealed with a septum and the sealed vial was taken out of the glove box. The reaction mixture was stirred at 800 rpm and irradiated with a 20 W blue LEDs lamp (with fan cooled) typically for 24 h. HRMS analysis of the crude reaction mixture showed the presence of trace amounts of **64**. The crude product was purified by flash column chromatography (1% EtOAc/hexane) to afford **65** (3.2 mg, 0.03 mmol, 5%) as a colorless oil.

4-((1-Phenylcyclopropyl)methyl)tetrahydro-2*H*-pyran (65)

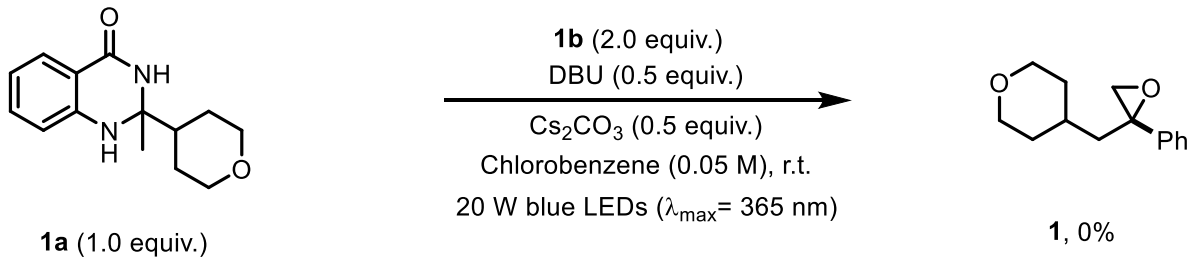


^{1}H NMR (400 MHz, $CDCl_3$) δ_H 7.33 – 7.26 (m, 4H), 7.22 – 7.16 (m, 1H), 3.89 – 3.83 (m, 2H), 3.30 – 3.20 (m, 2H), 1.66 – 1.60 (m, 2H), 1.54 (d, *J* = 6.8 Hz, 2H), 1.46 – 1.37 (m, 1H), 1.23 (dd, *J* = 12.5, 4.5 Hz, 2H), 0.83 – 0.78 (m, 2H), 0.67 – 0.61 (m, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ_C 145.1, 128.8, 128.2, 125.9, 67.9, 47.5, 33.5, 33.5, 23.3, 12.7 ppm.

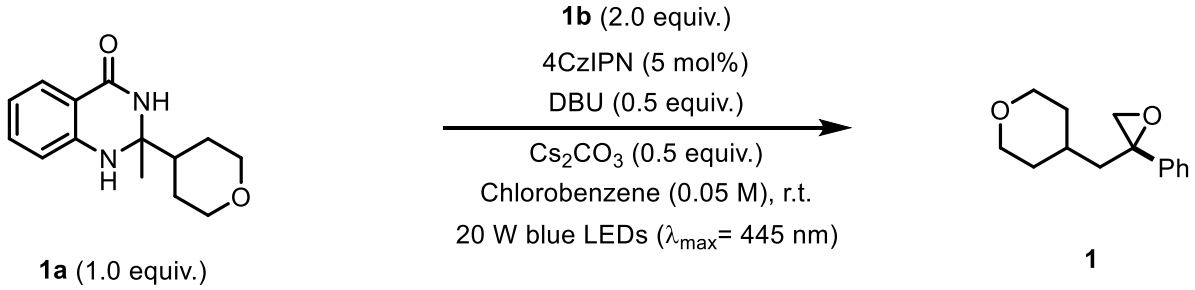
HRMS (ESI^+) calcd. for $C_{15}H_{21}O$ $[M+H]^+$ 217.1587, found 217.1587.

7.4. Direct using UV light irradiation



In the glove box, to a dry 7 mL vial equipped with a magnetic stir bar were added **1a** (0.2 mmol, 1.0 equiv.), **1b** (0.4 mmol, 2.0 equiv.), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), and DBU (15.3 mg, 0.1 mmol, 0.5 equiv.). Then anhydrous chlorobenzene (4.0 mL) was added to the mixture. The vial was sealed with a septum and the sealed vial was taken out of the glove box. The reaction mixture was stirred at 800 rpm and irradiated with a 20 W blue LEDs lamp (with fan cooled) typically for 24 h. HRMS analysis of the crude mixture of the reaction showed that no generation of **1** was observed.

7.5. Short-term photo irradiation experiments



1a (1.0 equiv.)

1

In the glove box, to a dry 7 mL vial equipped with a magnetic stir bar were added **1a** (0.2 mmol, 1.0 equiv.), **1b** (0.4 mmol, 2.0 equiv.), 4CzIPN (0.010 mmol, 7.9 mg, 5.0 mol%), Cs_2CO_3 (32.6 mg, 0.1 mmol, 0.5 equiv.), and DBU (15.3 mg, 0.1 mmol, 0.5 equiv.). Then anhydrous chlorobenzene (4.0 mL) was added to the mixture. The vial was sealed with a septum and the sealed vial was taken out of the glove box. The reaction mixture was stirred at 800 rpm and irradiated with a 20 W blue LEDs lamp (with fan cooled) with fan cooled for 30 min, from crude ^{1}H NMR with inter standard, the product **1** was observed in 20% yield. Then the system was stirred for 5 h under dark conditions. From crude ^{1}H NMR with inter standard, the product **1** was still observed in 20% yield.

7.6. Stern-Volmer fluorescence quenching experiments

Emission intensities were recorded using a VARIAN Cary Eclipse Luminescence spectrometer. All 4CzIPN solutions were excited at 445 nm, and the emission intensity at 547 nm was observed. In a typical experiment, a 1.0 $\times 10^{-4}$ M solution of 4CzIPN in DMSO was added to the appropriate amount of quencher in a screw top 1.0 cm quartz cuvette. After degassing with a stream of nitrogen for 10 minutes, the emission spectrum of the sample was collected. A fluorescence quenching phenomenon of 4CzIPN under various concentrations of **1a** was shown in **Figure S5** (Stern-Volmer plots).

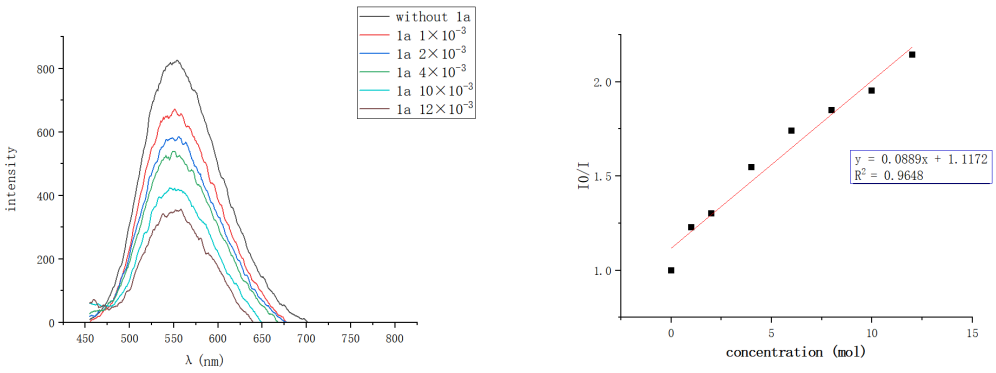


Figure S5. (left) Stern-Volmer fluorescence quenching spectra; (right) Stern-Volmer fluorescence quenching curve

7.7. Cyclic voltammetry experiments

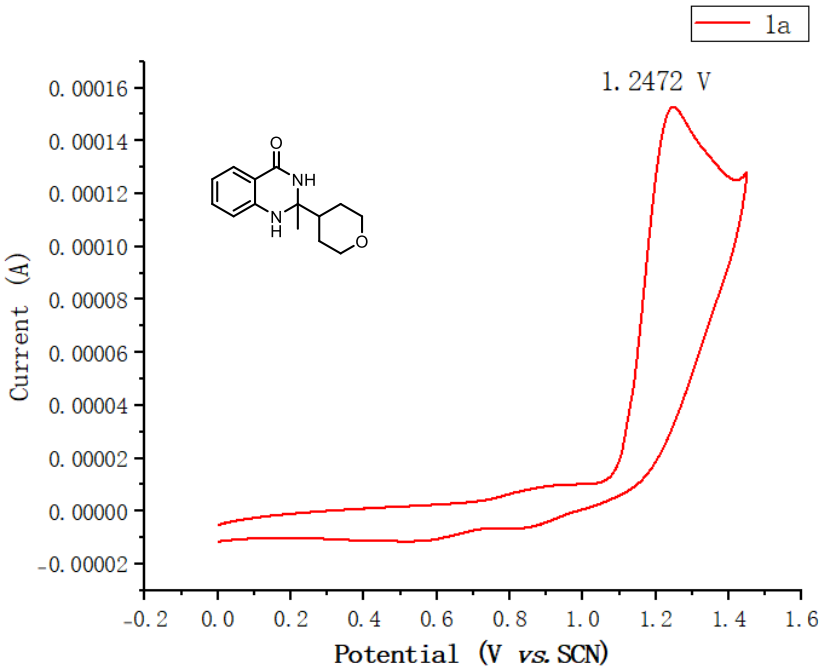


Figure S6. Cyclic voltammetry spectra

Cyclic voltammetry measurements of **1a** (0.01 M in MeCN) were taken with Pine WaveNow Potentiostat at room temperature in a 0.10 M MeCN solution of $TBANPF_6$ electrolyte. The solution was delivered to a three-electrode cell assembly and deaerated, and the solution was degassed with nitrogen for 5 min prior to voltammetric studies. Measurements were performed under room temperature (20 ^oC) with a glassy carbon working electrode (diameter, 1 mm), Pt wire as a counter electrode, and saturated calomel electrode (SCE) as reference electrode at 100 mV/s of scanning rate at room temperature (**Figure S6**).

8. References

1. P. P. Mondal, A. Pal, A. K. Prakasha and B. Sahoo, *Chem. Commun.*, 2022, **58**, 13202–13205.

2. J. Yang, Z. Li, Z. Huang and J. Zhu, *Chem. Eur. J.*, 2024, **30**, e202402475.

3. Q.-Z. Li, M.-H. He, R. Zeng, Y.-Y. Lei, Z.-Y. Yu, M. Jiang, X. Zhang and J.-L. Li, *J. Am. Chem. Soc.*, 2024, **146**, 22829–22839.

4. (a) F. Cong, R. S. Mega, J. Chen, C. S. Day and R. Martin, *Angew. Chem. Int. Ed.*, 2023, **62**, e202214633; (b) X.-Y. Lv, R. Abrams and R. Martin, *Angew. Chem. Int. Ed.*, 2023, **135**, e202217386.

5. F. Cong, R. S. Mega, J. Chen, C. S. Day and R. Martin, *Angew. Chem. Int. Ed.*, 2023, **62**, e202214633.

6. A. Cabré, G. Sciortino, G. Ujaque, X. Verdaguer, A. Lledós and A. Riera, *Org. Lett.*, 2018, **20**, 5747–5751.

7. X. Dong, L. Xu, Y. Yang, Y. Liu, X. Li, Q. Liu, L. Zheng, F. Wang and H. Liu, *Org. Chem. Front.*, 2021, **8**, 6009–6018.

8. M. Gao, Y. Zhao, C. Zhong, S. Liu, P. Liu, Q. Yin and L. Hu, *Org. Lett.*, 2019, **21**, 5679–5684.

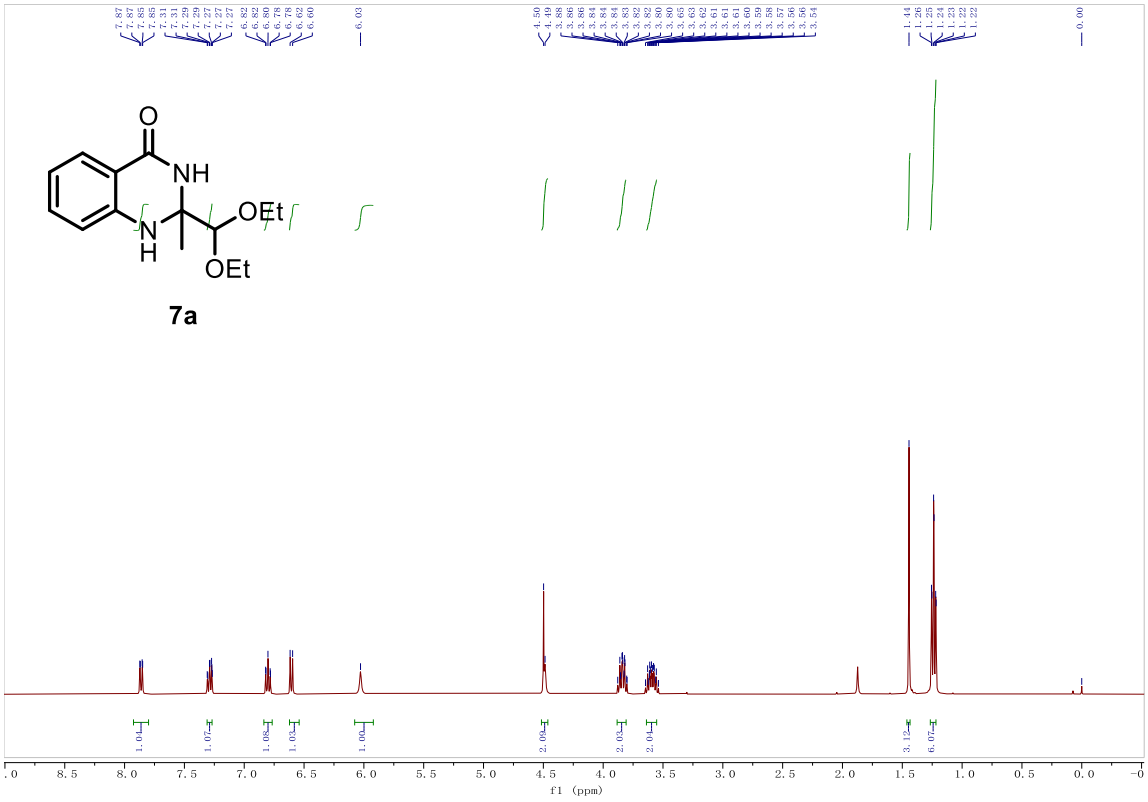
9. Y. Chen, M. G, Q. Xu, J. Zhang and L. Hu, *Org. Chem. Front.*, 2024, **11**, 2215–2219.

10. H. Wu, S. Chen, H. Wang and Y. Shang, *J. Org. Chem.*, 2025, **90**, 17768–17775.

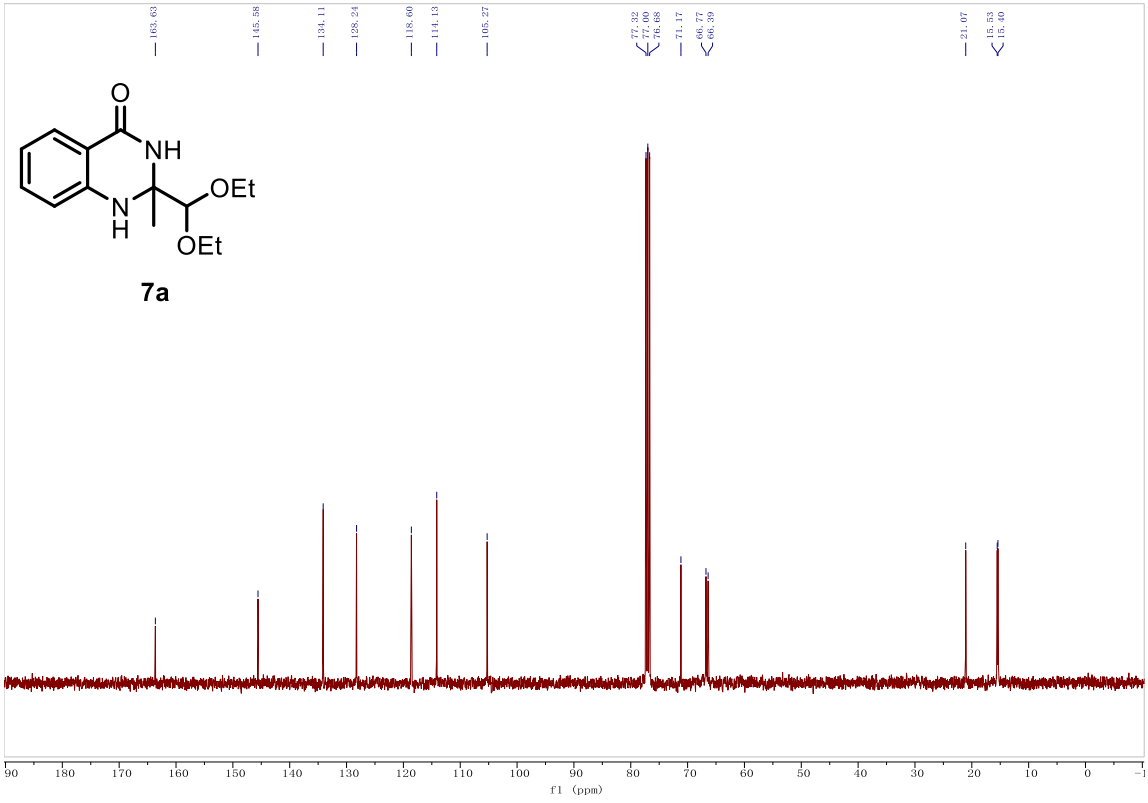
11. C.-J. Li, M.-Y. Liu, Z.-L. Wei and W.-W. Liao, *J. Org. Chem.*, 2024, **89**, 18769–18774.

9. NMR Spectra

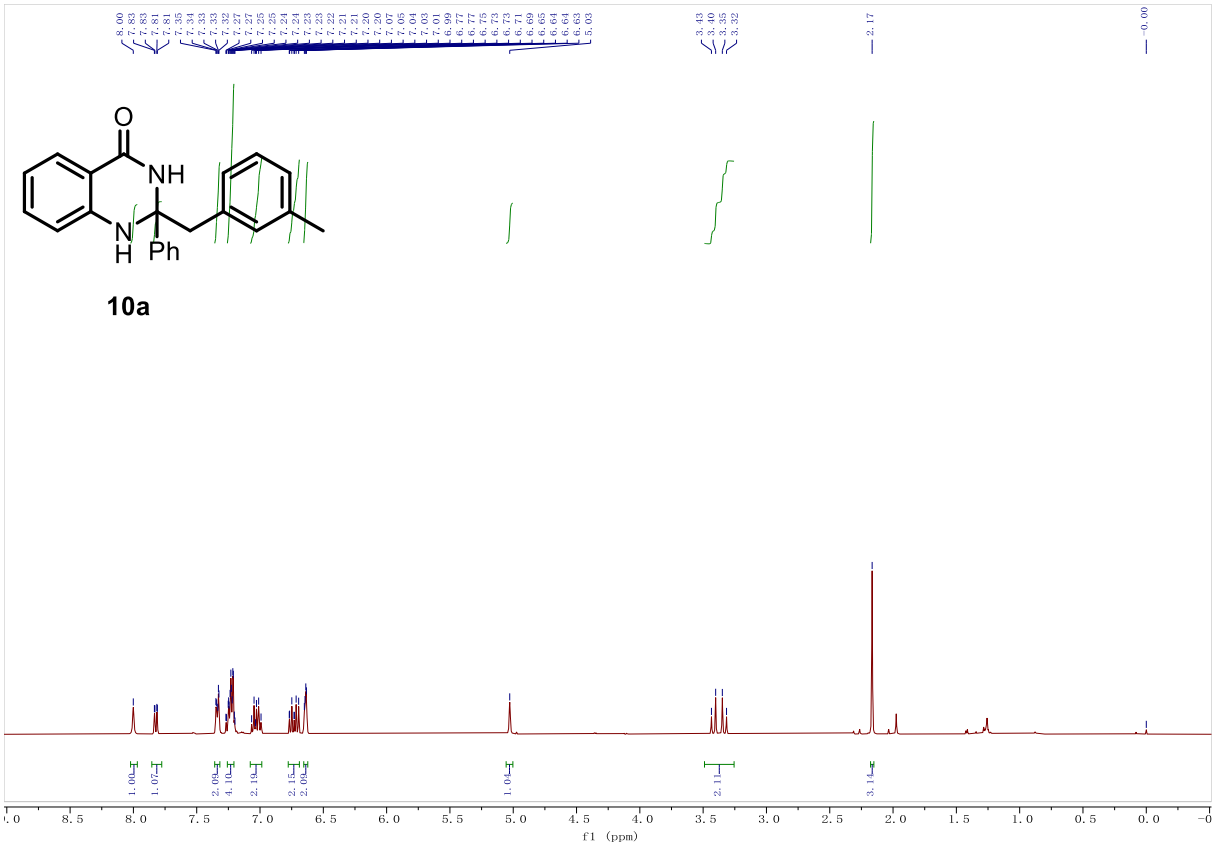
^{1}H NMR (400 MHz, $CDCl_3$)



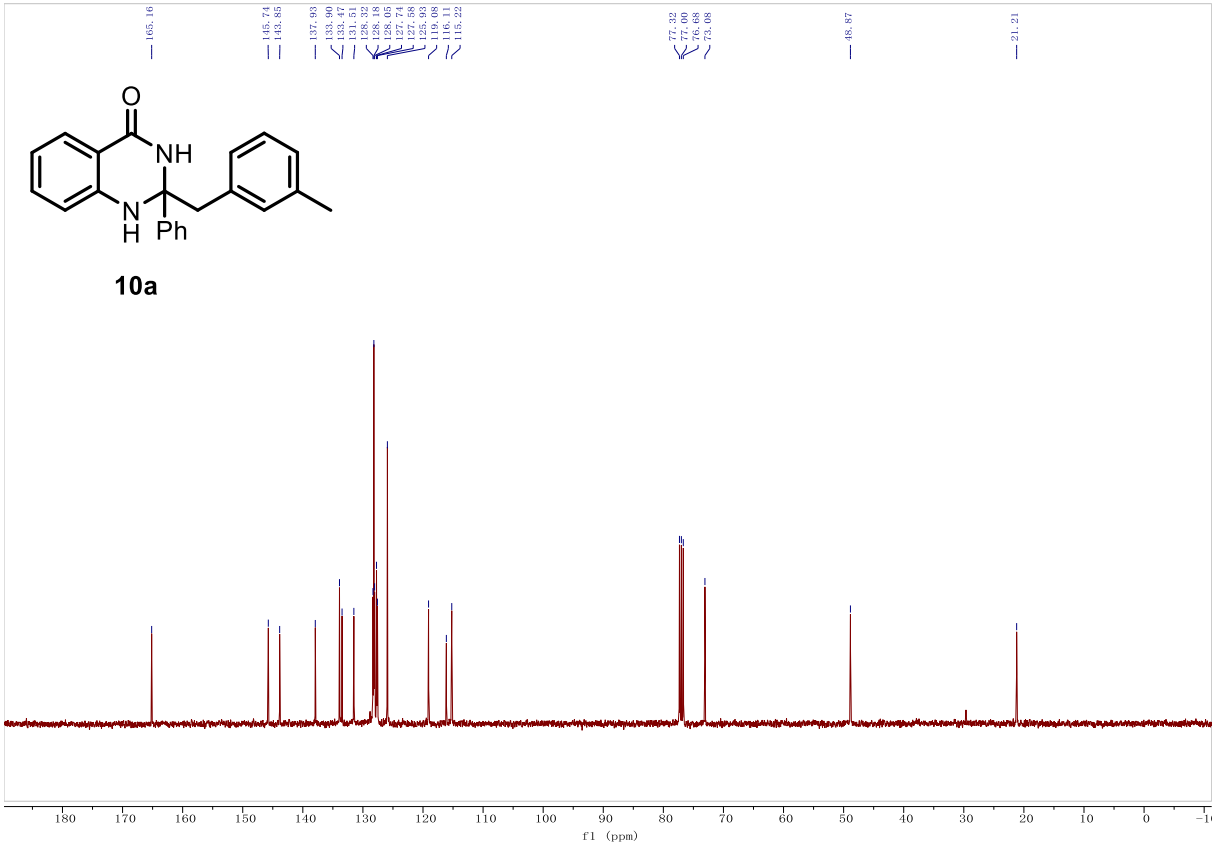
^{13}C NMR (101 MHz, $CDCl_3$)



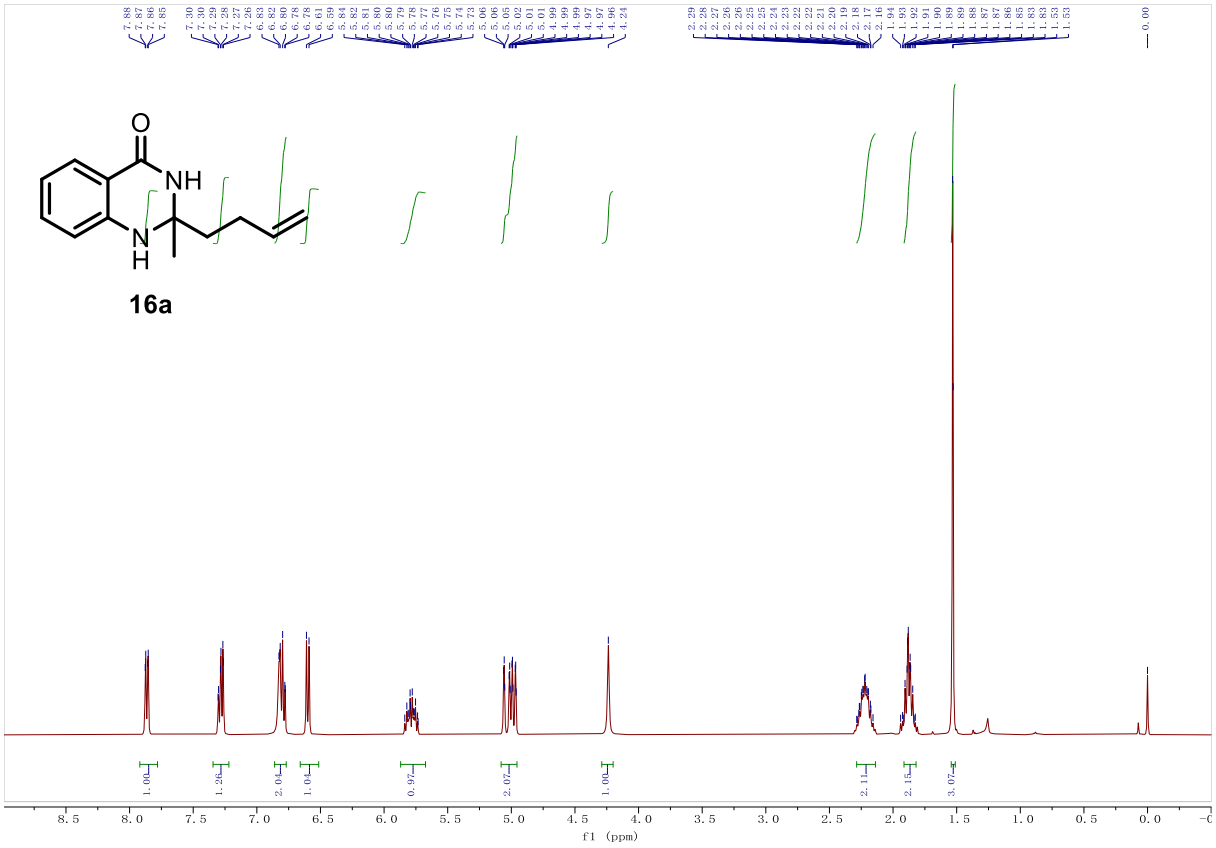
^{1}H NMR (400 MHz, $CDCl_3$)



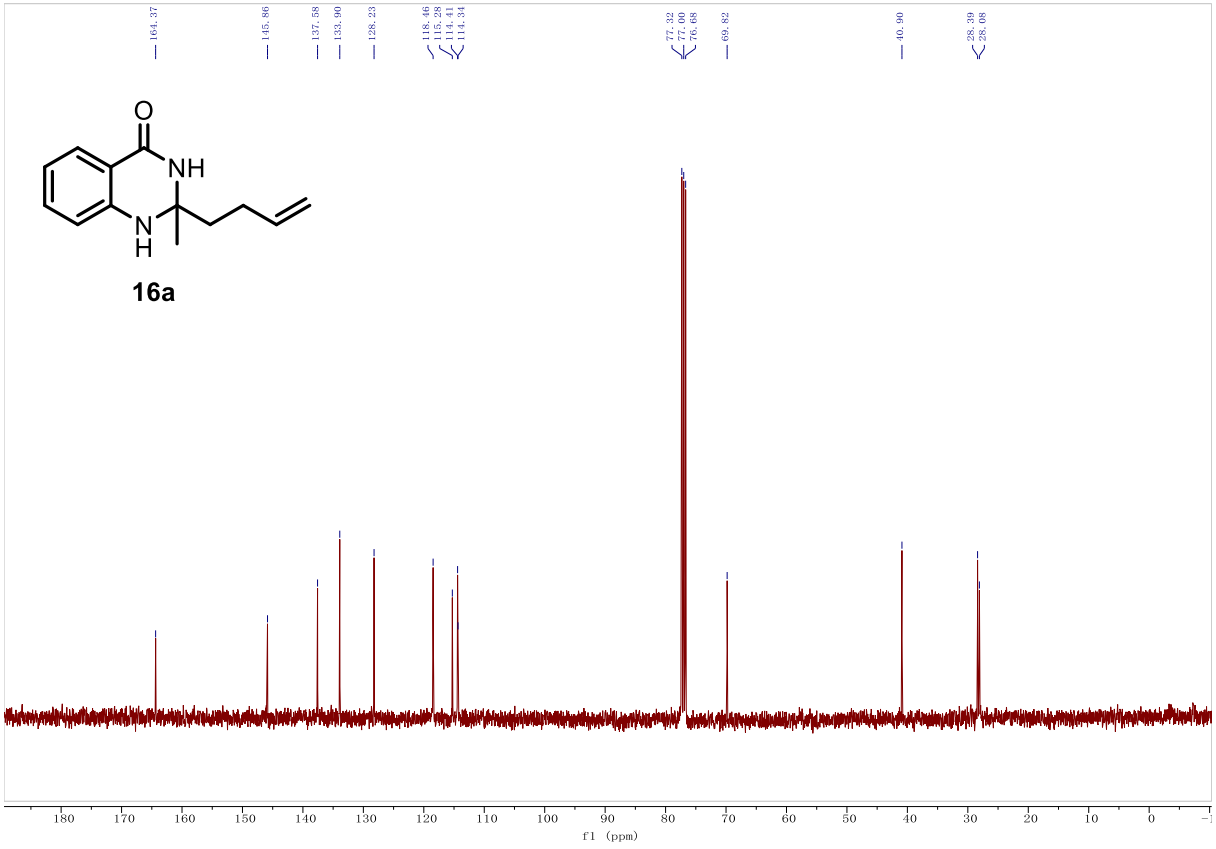
^{13}C NMR (101 MHz, $CDCl_3$)



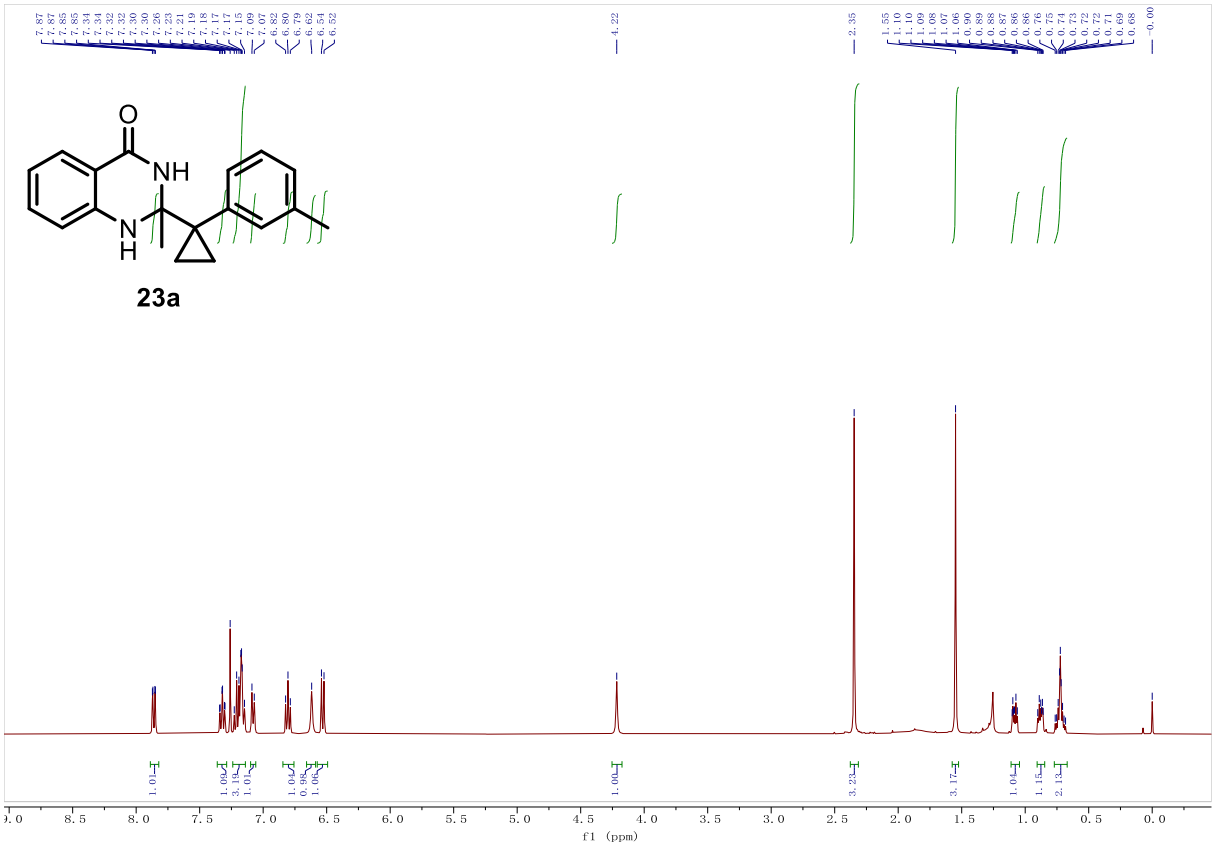
^{1}H NMR (400 MHz, $CDCl_3$)



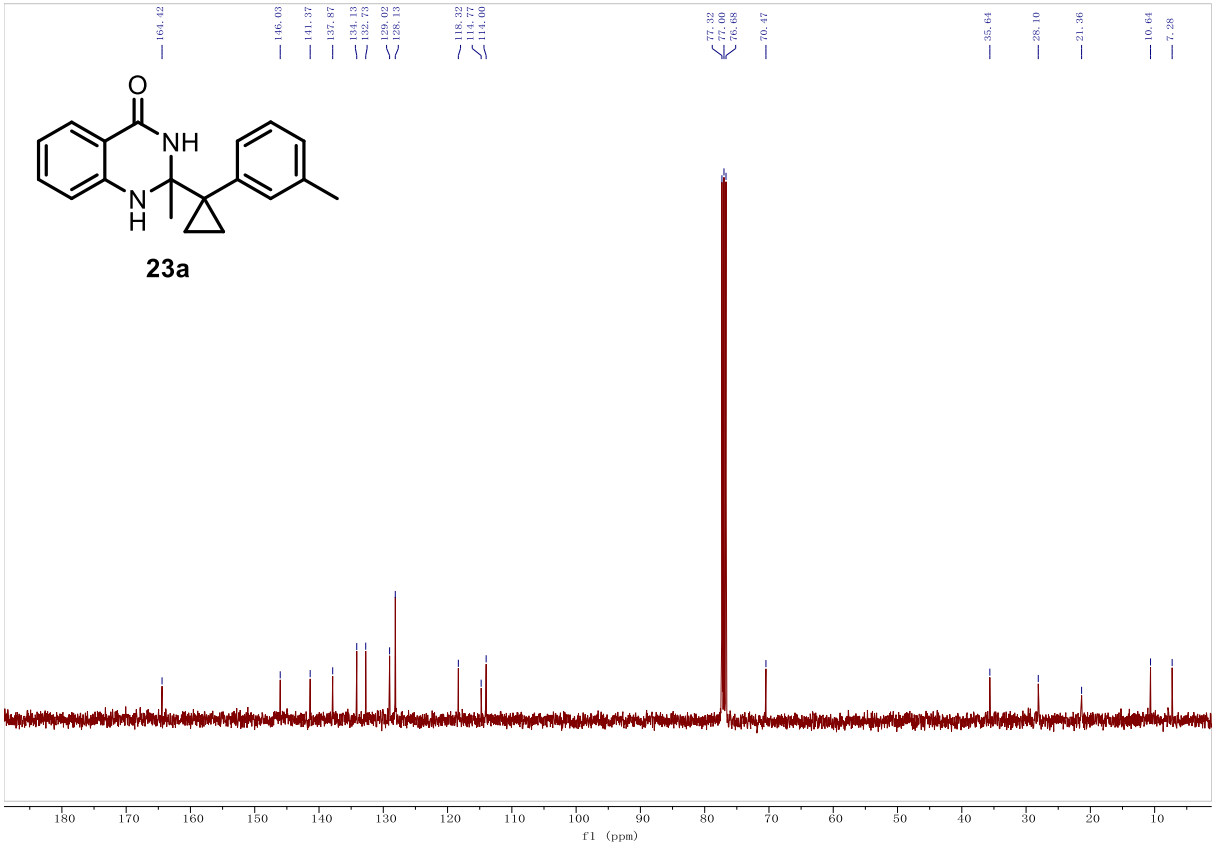
^{13}C NMR (101 MHz, $CDCl_3$)



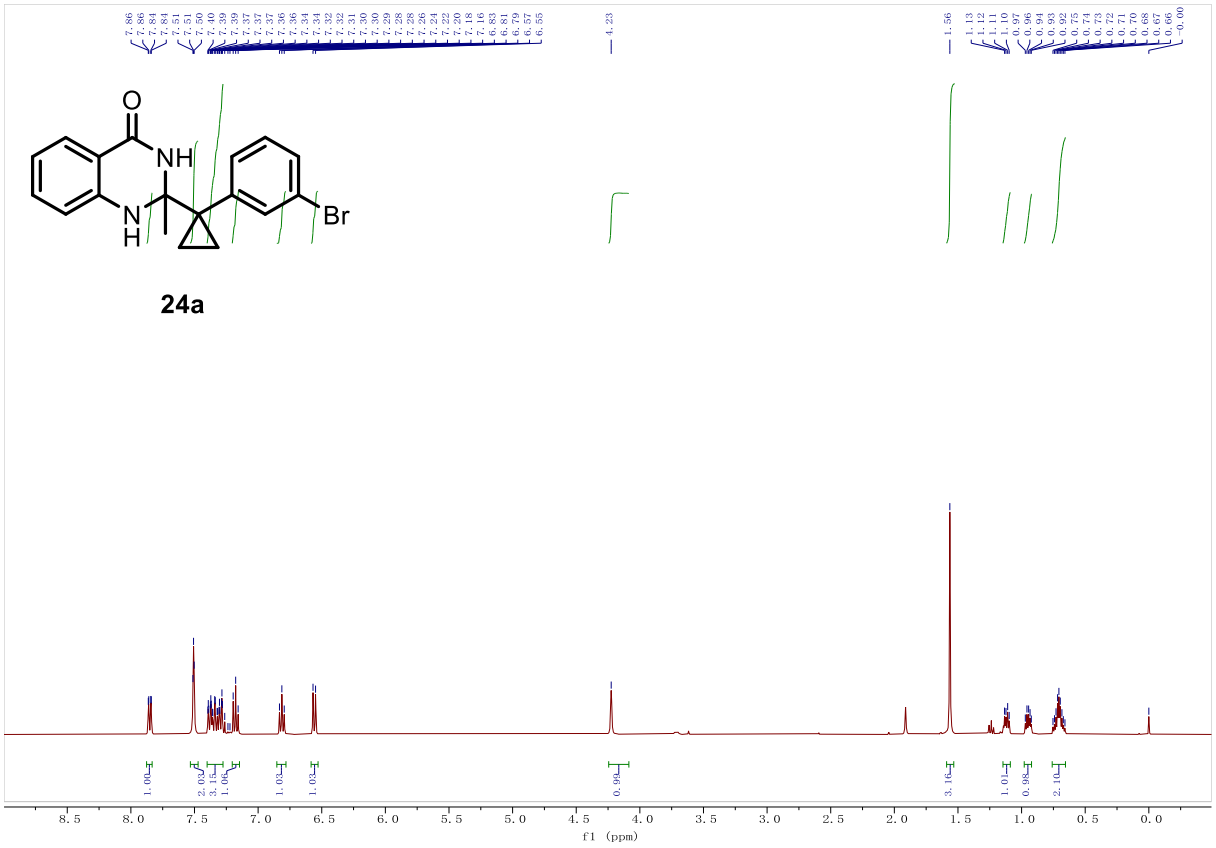
^{1}H NMR (400 MHz, $CDCl_3$)



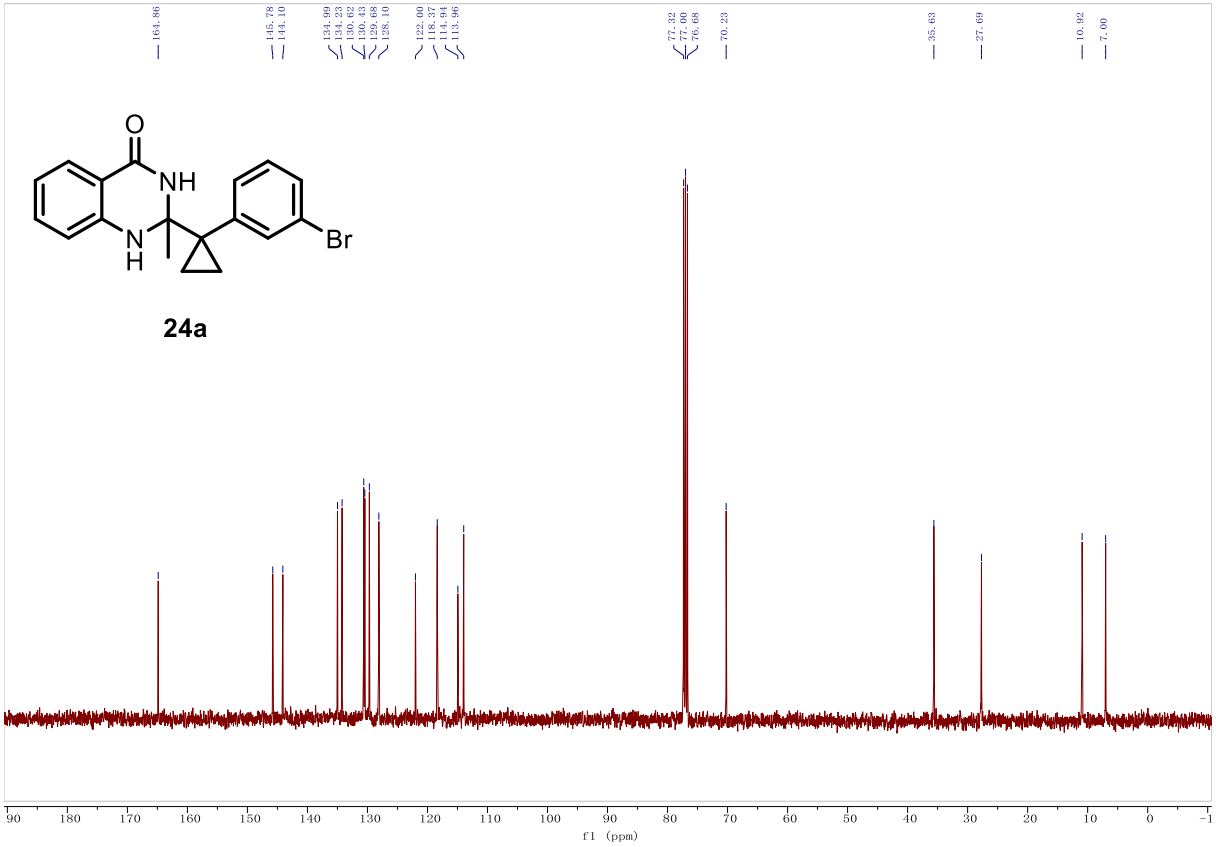
^{13}C NMR (101 MHz, $CDCl_3$)



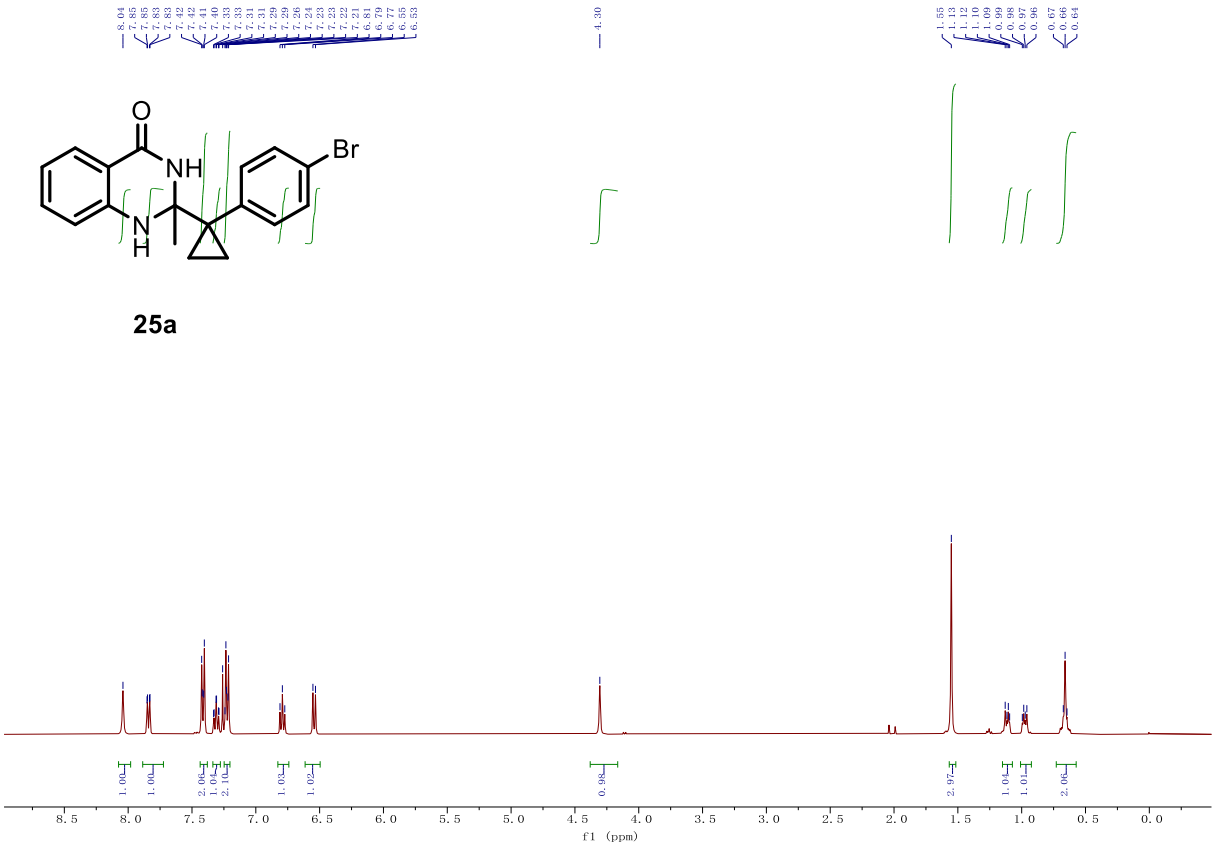
^{1}H NMR (400 MHz, $CDCl_3$)



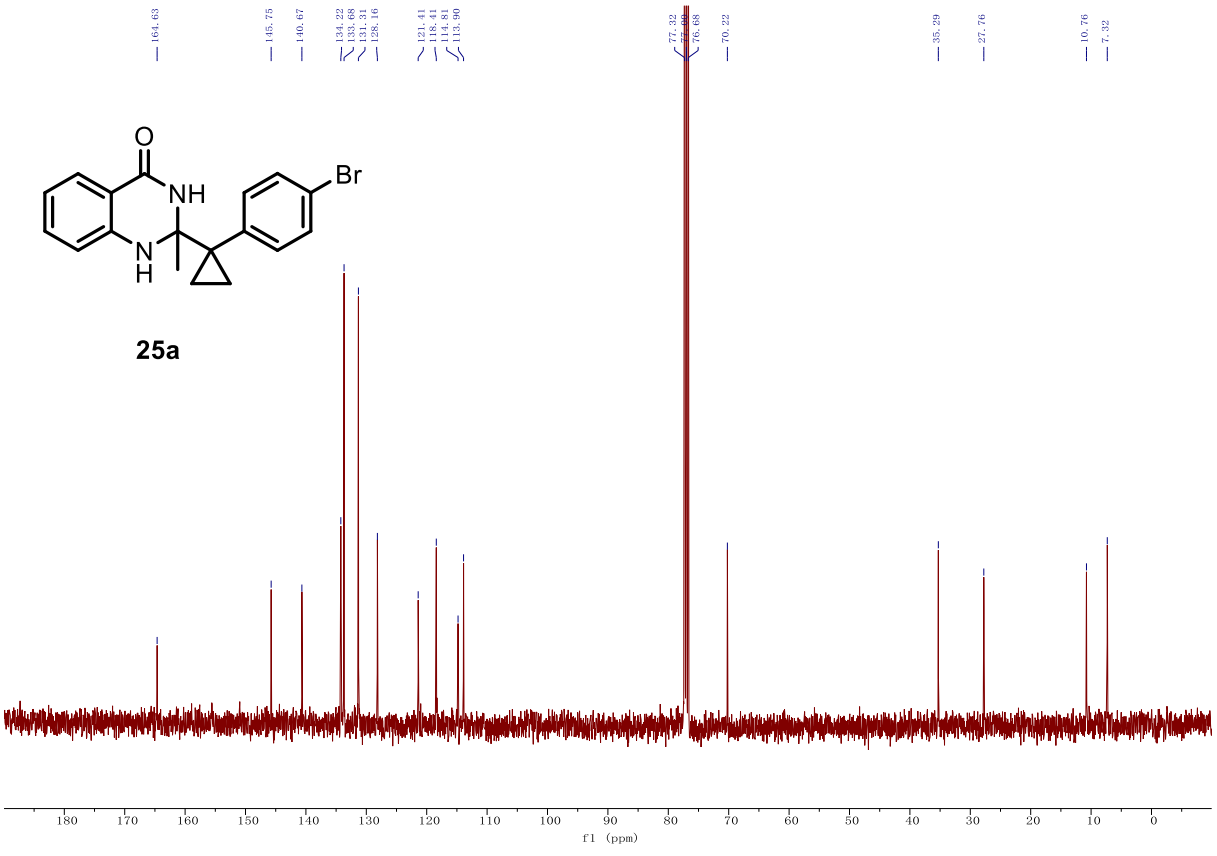
^{13}C NMR (101 MHz, $CDCl_3$)



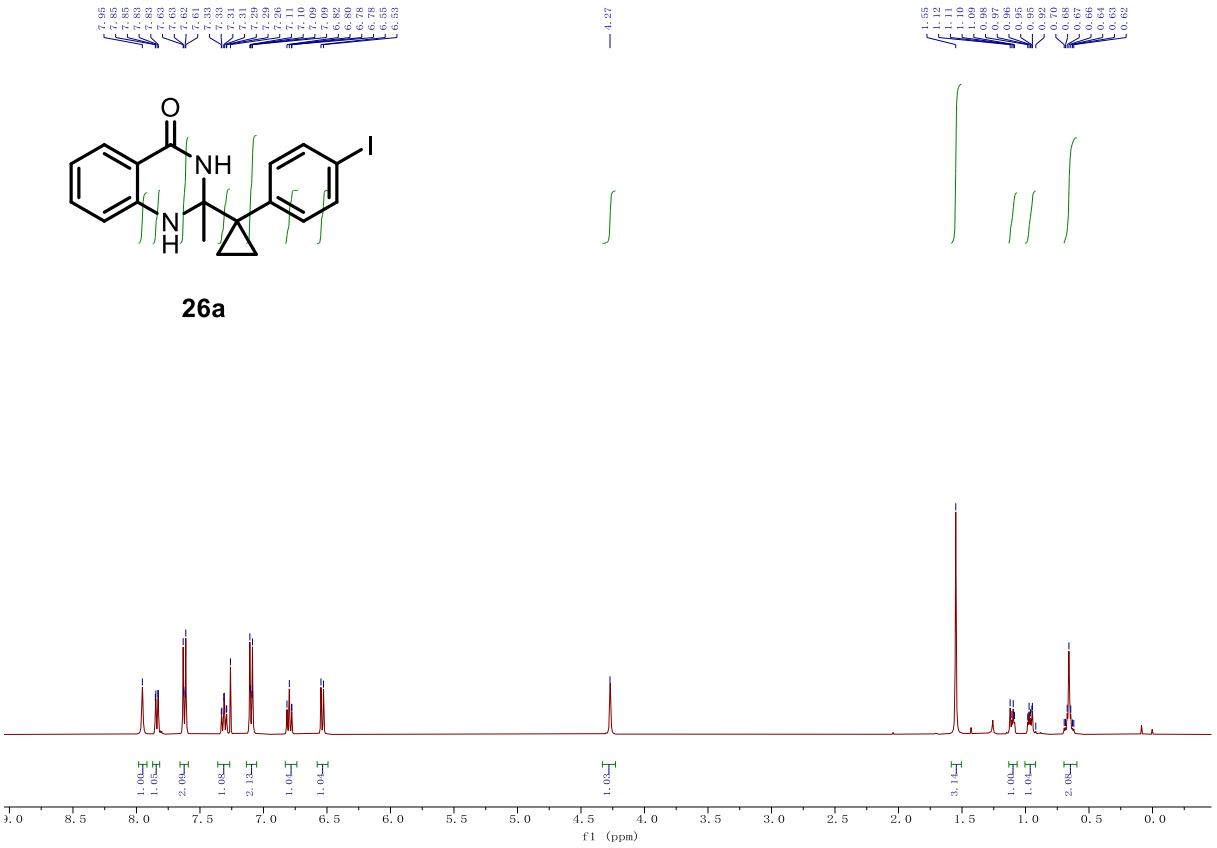
^{1}H NMR (400 MHz, $CDCl_3$)



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

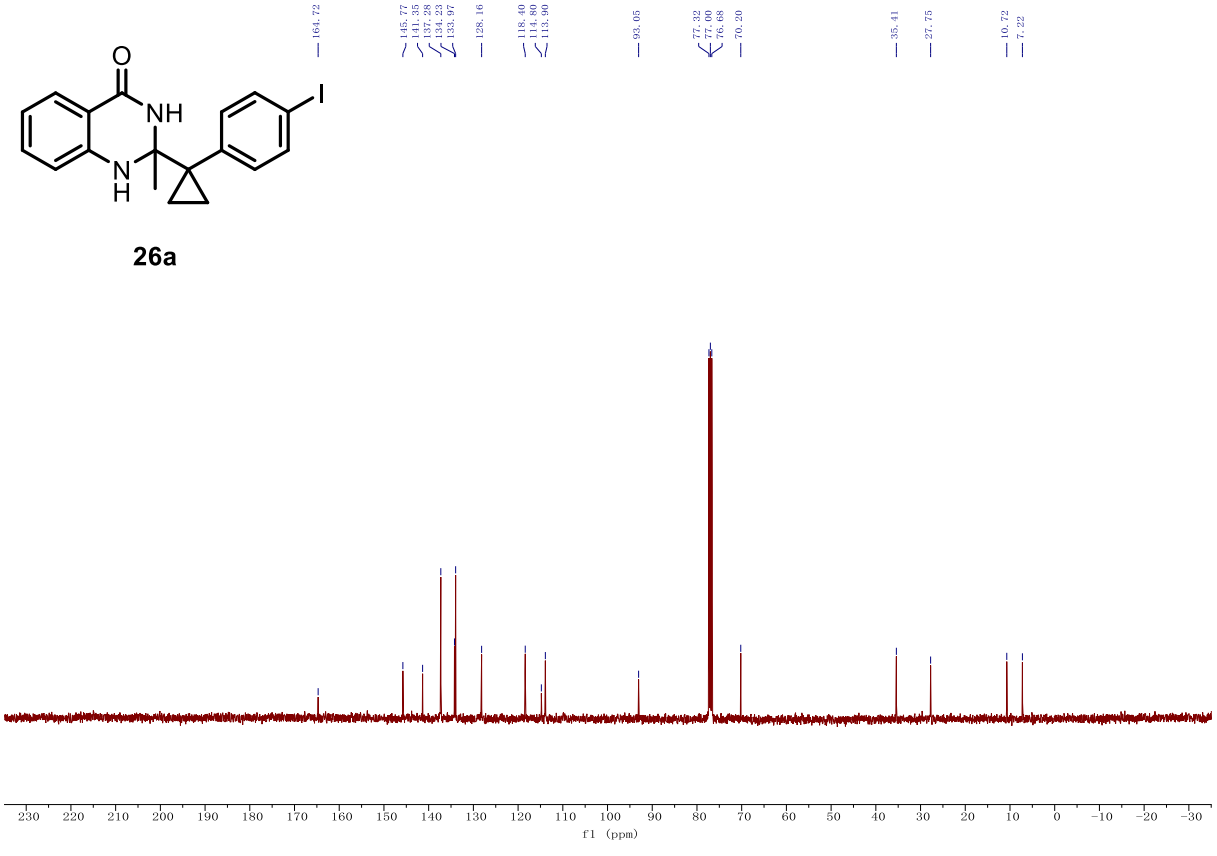


^{1}H NMR (400 MHz, $CDCl_3$)



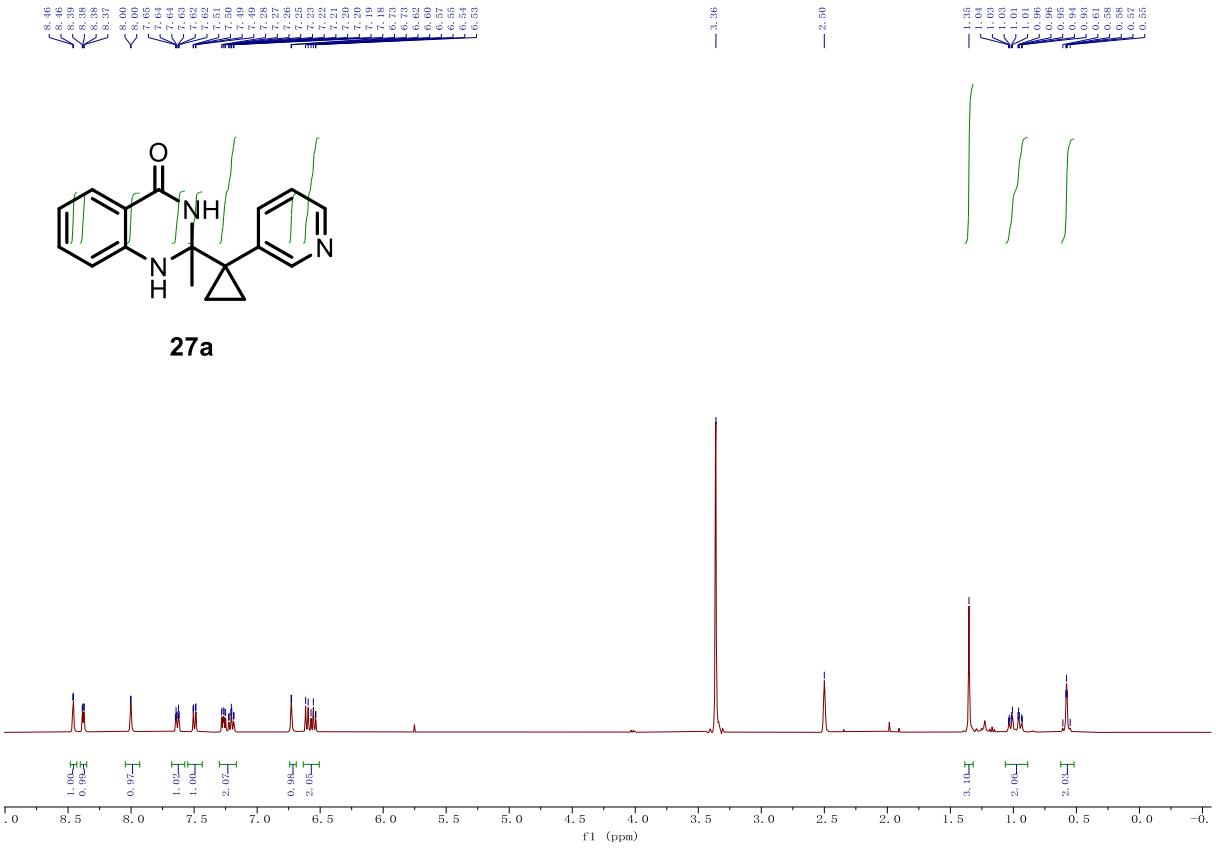
26a

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

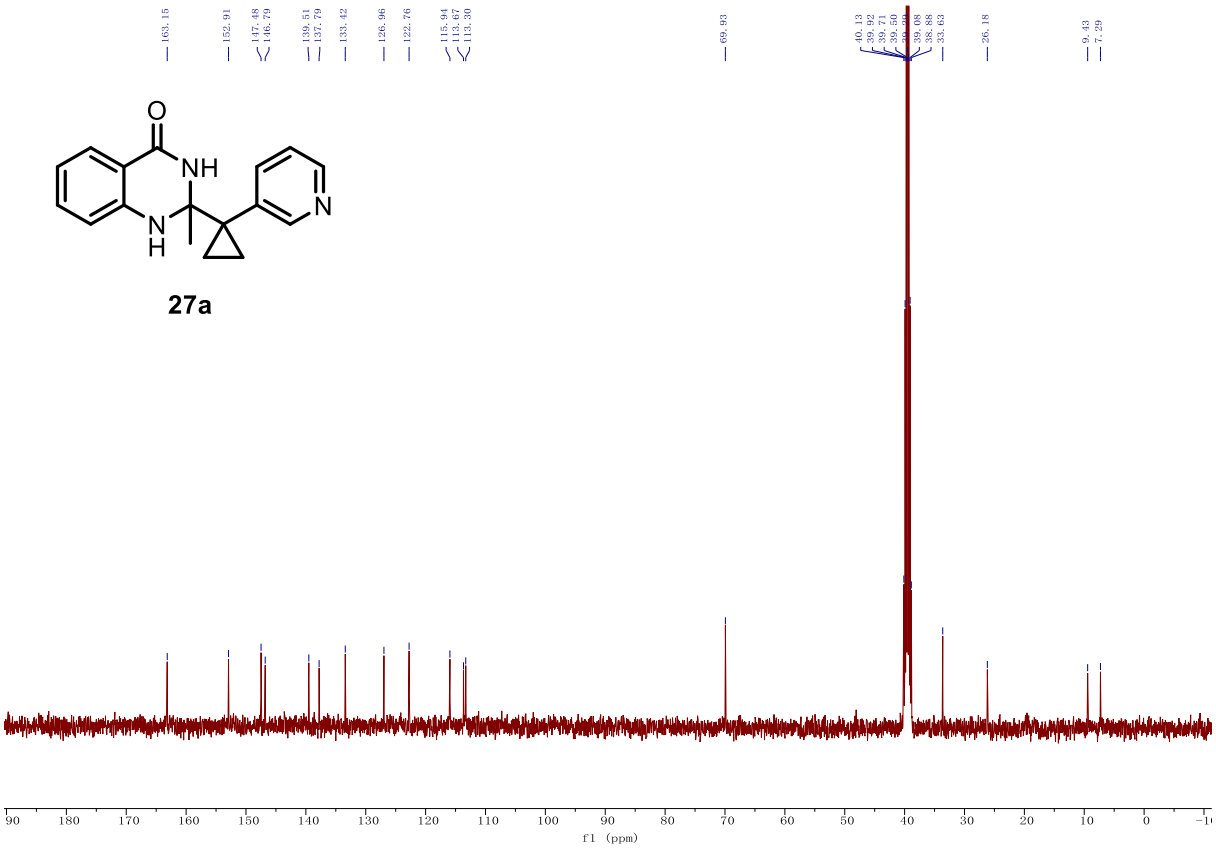


26a

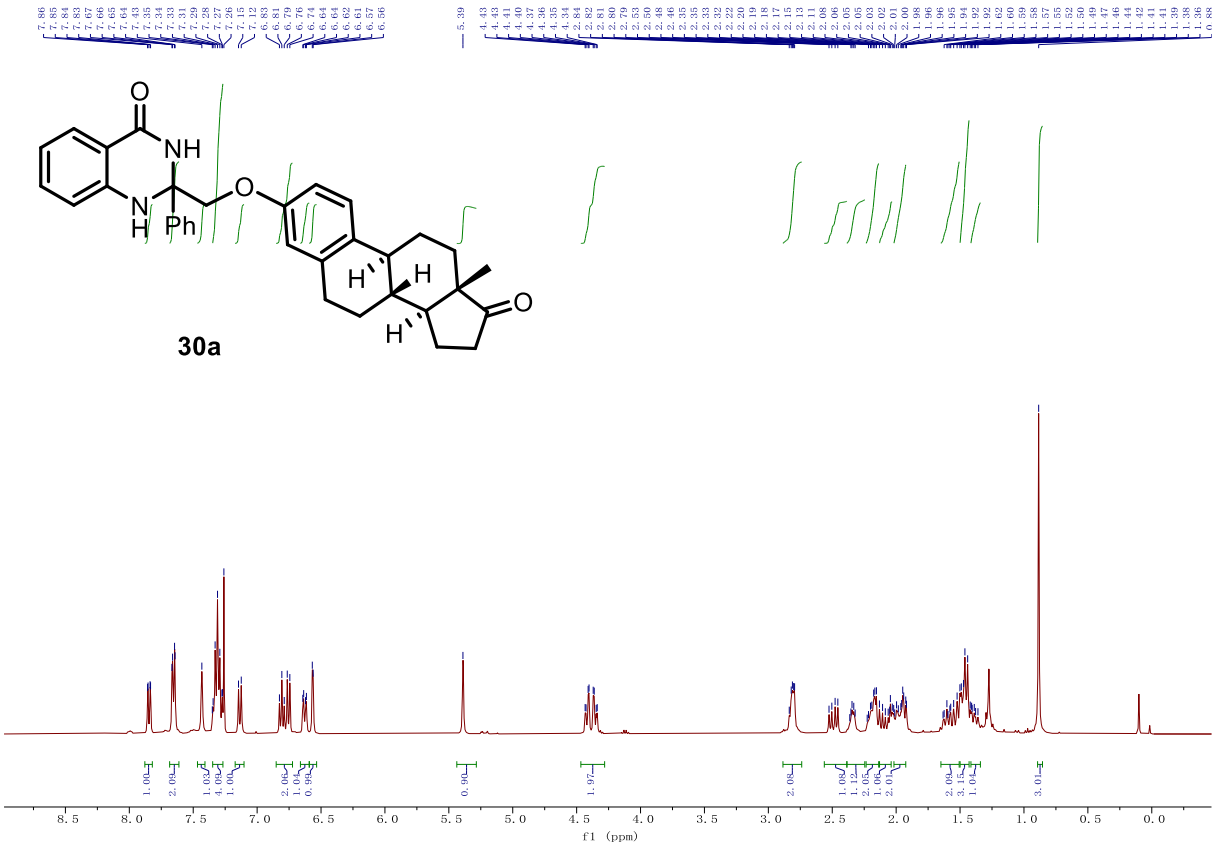
^{1}H NMR (400 MHz, DMSO-d_6)



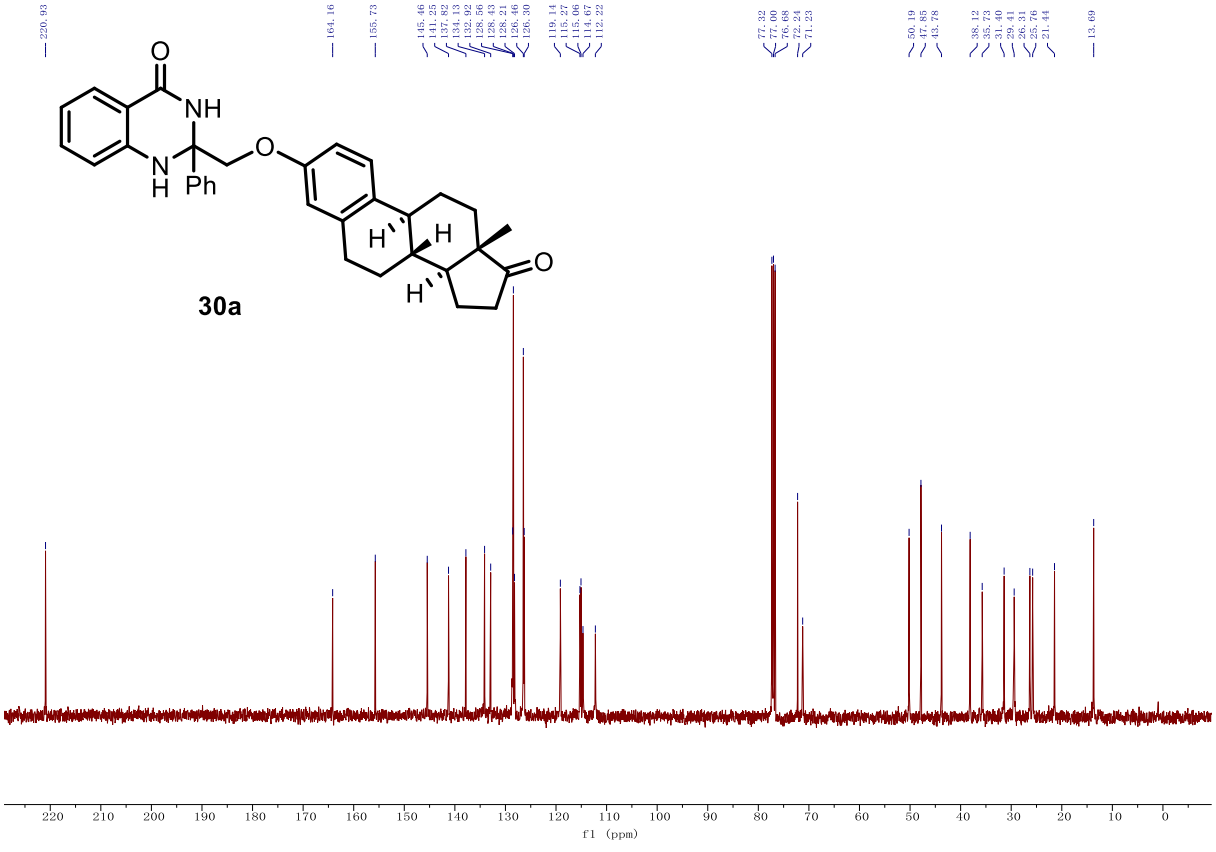
^{13}C NMR (101 MHz, DMSO-d_6)



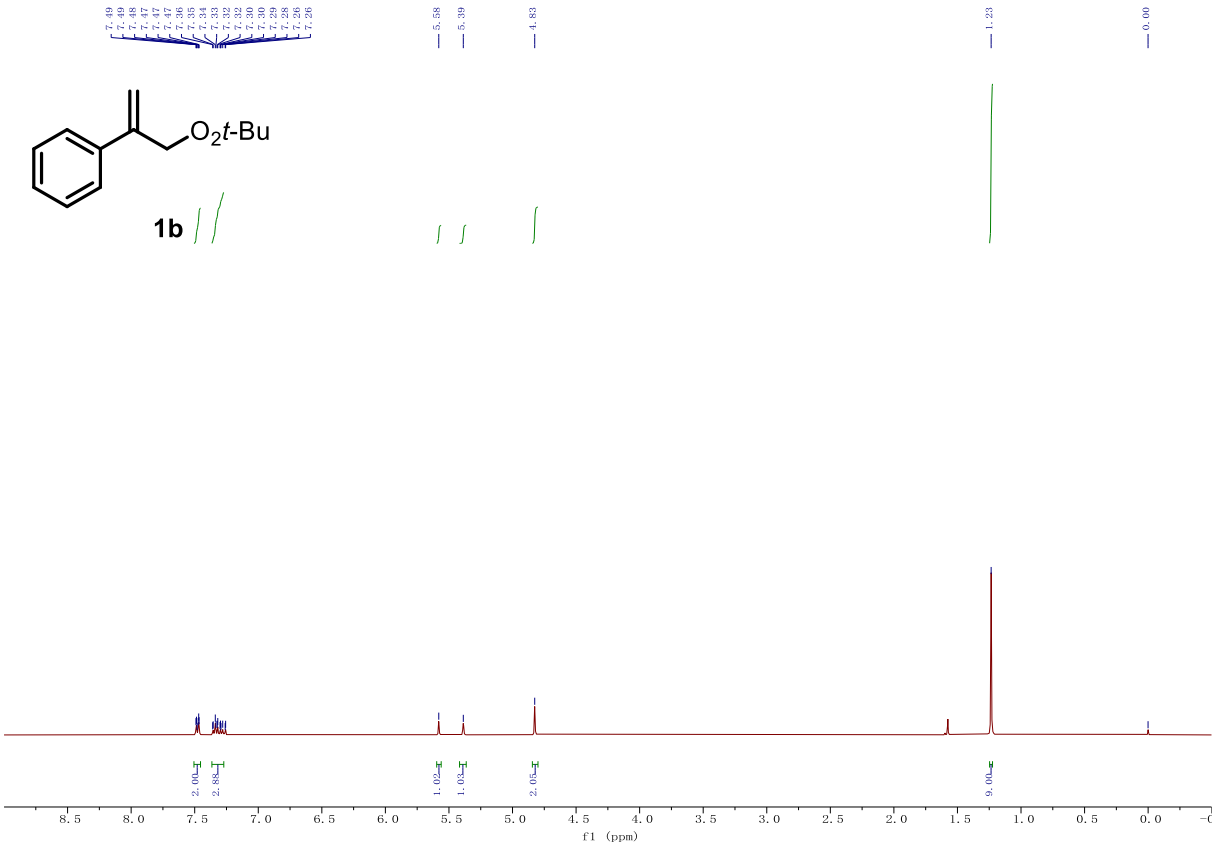
^{1}H NMR (400 MHz, $CDCl_3$)



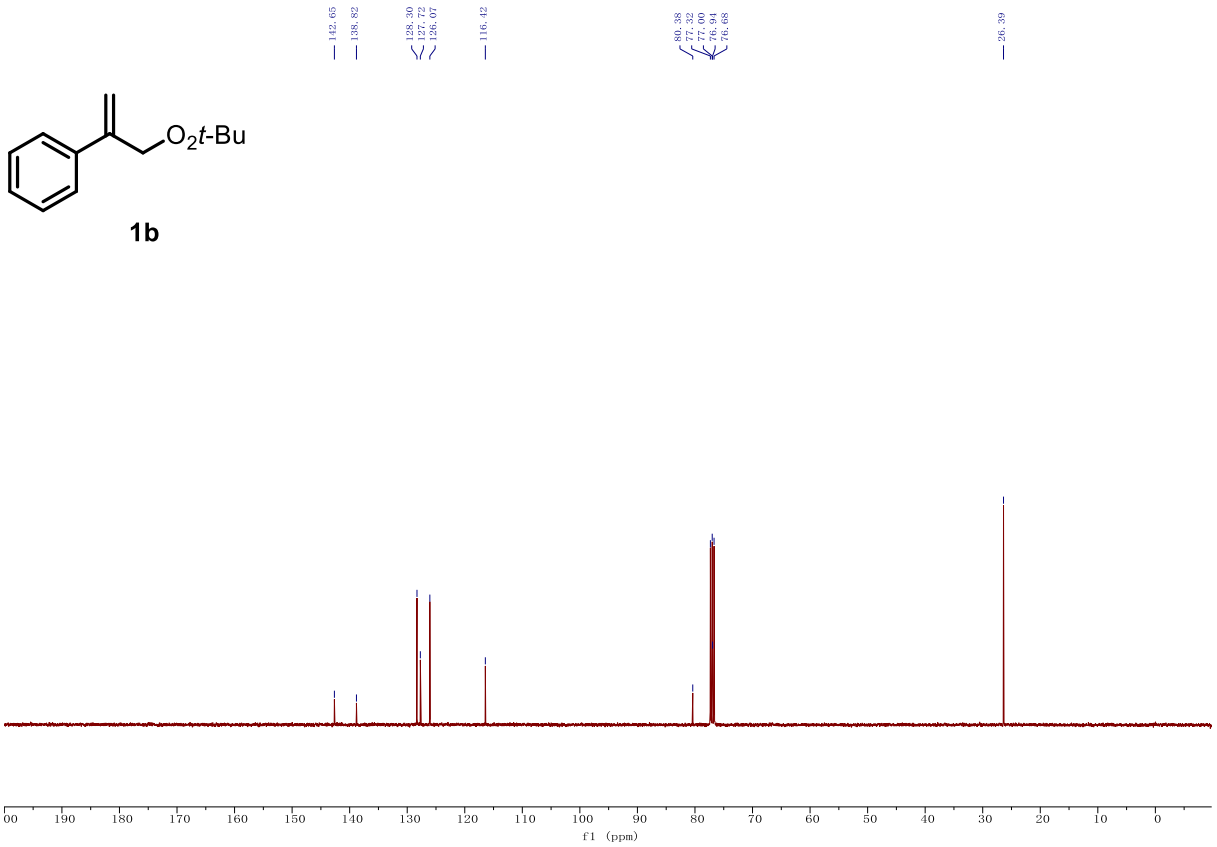
^{13}C NMR (101 MHz, $CDCl_3$)



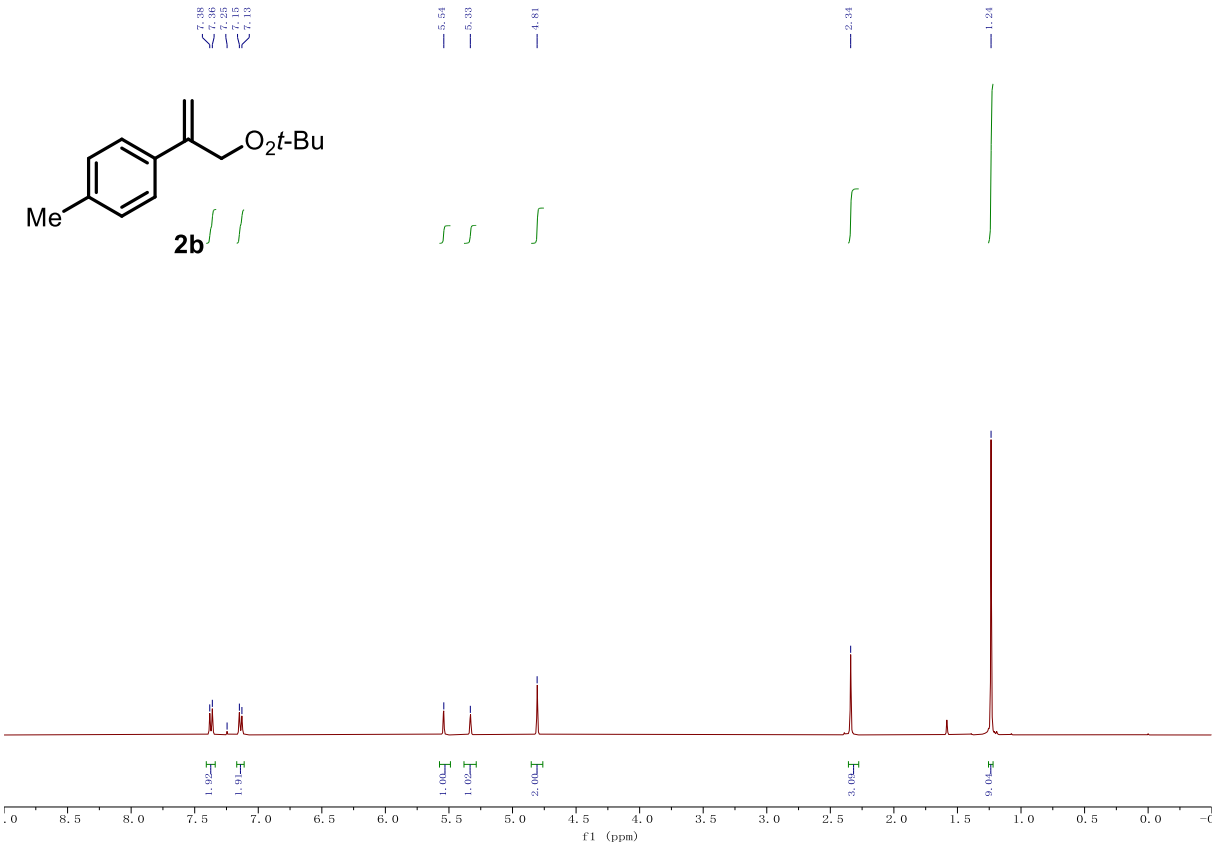
^{1}H NMR (400 MHz, $CDCl_3$)



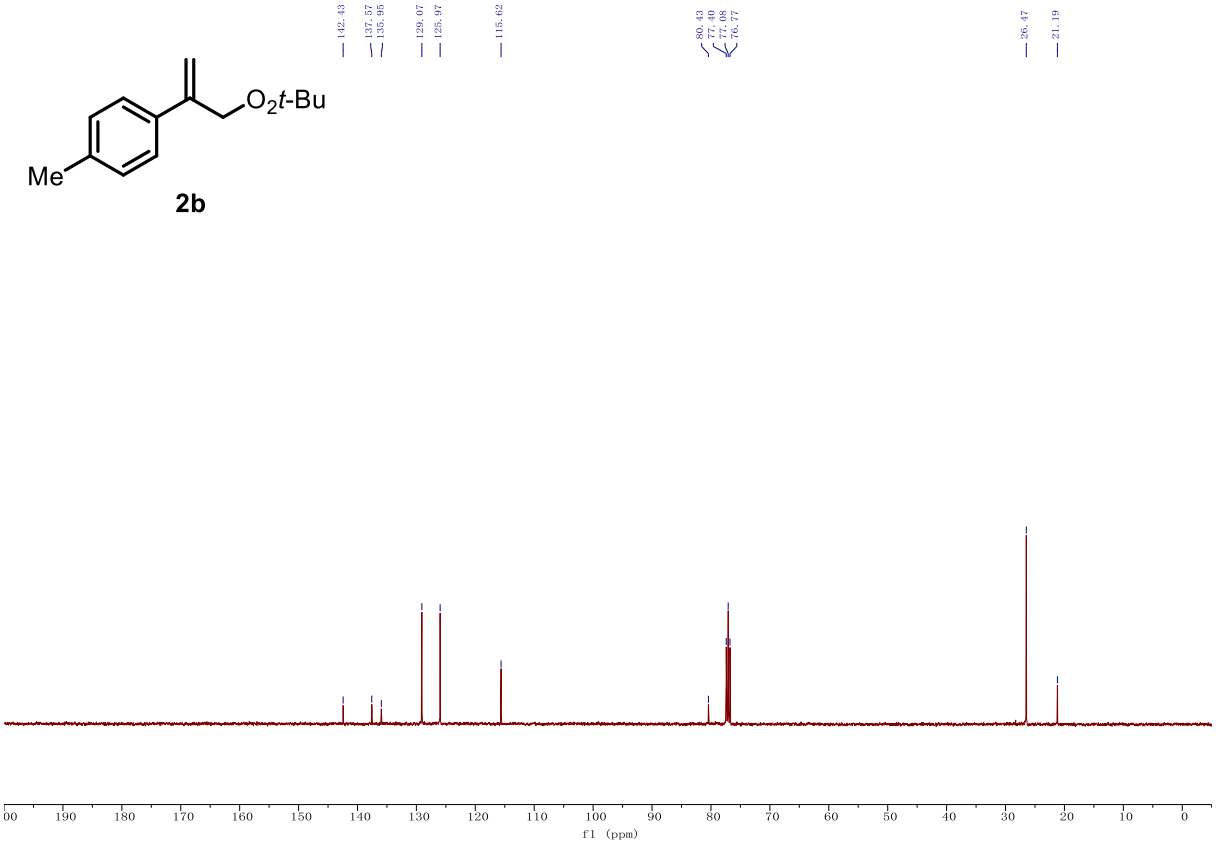
^{13}C NMR (101 MHz, $CDCl_3$)



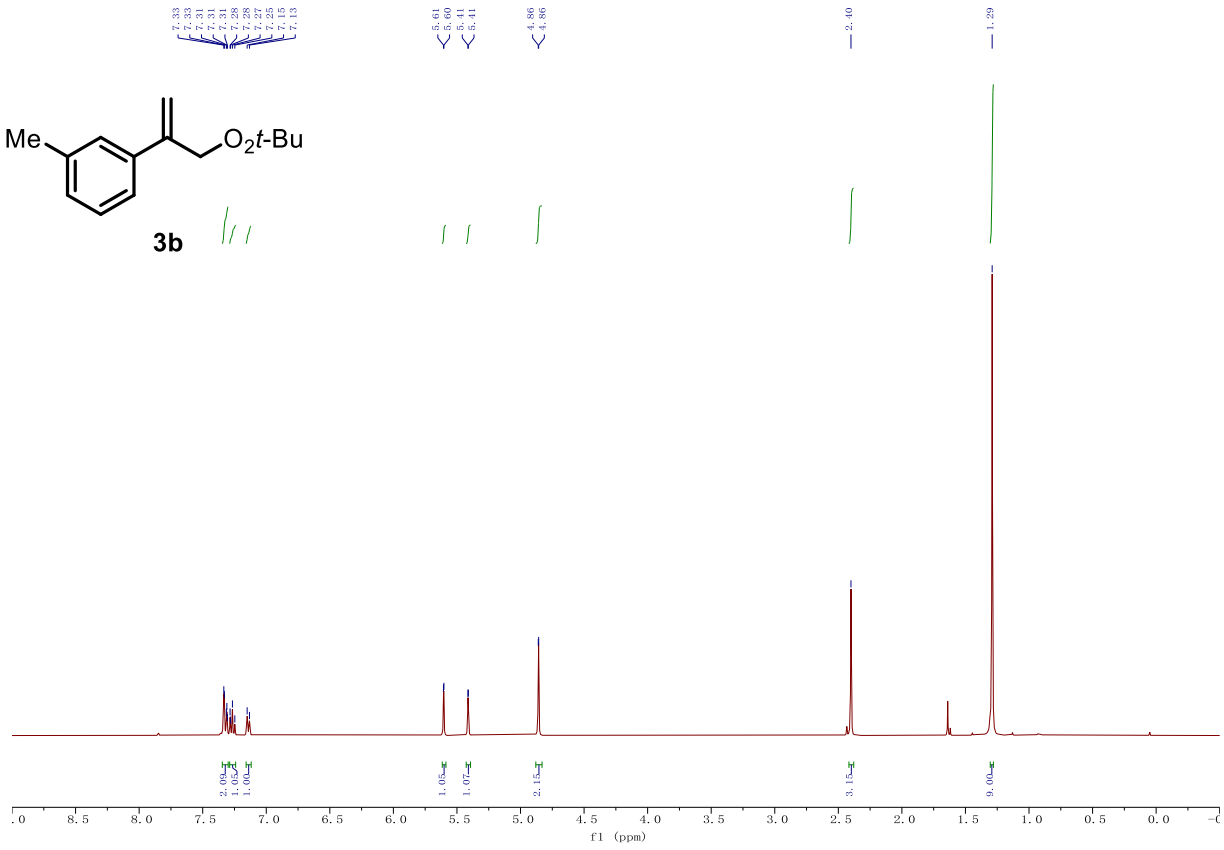
^{1}H NMR (400 MHz, $CDCl_3$)



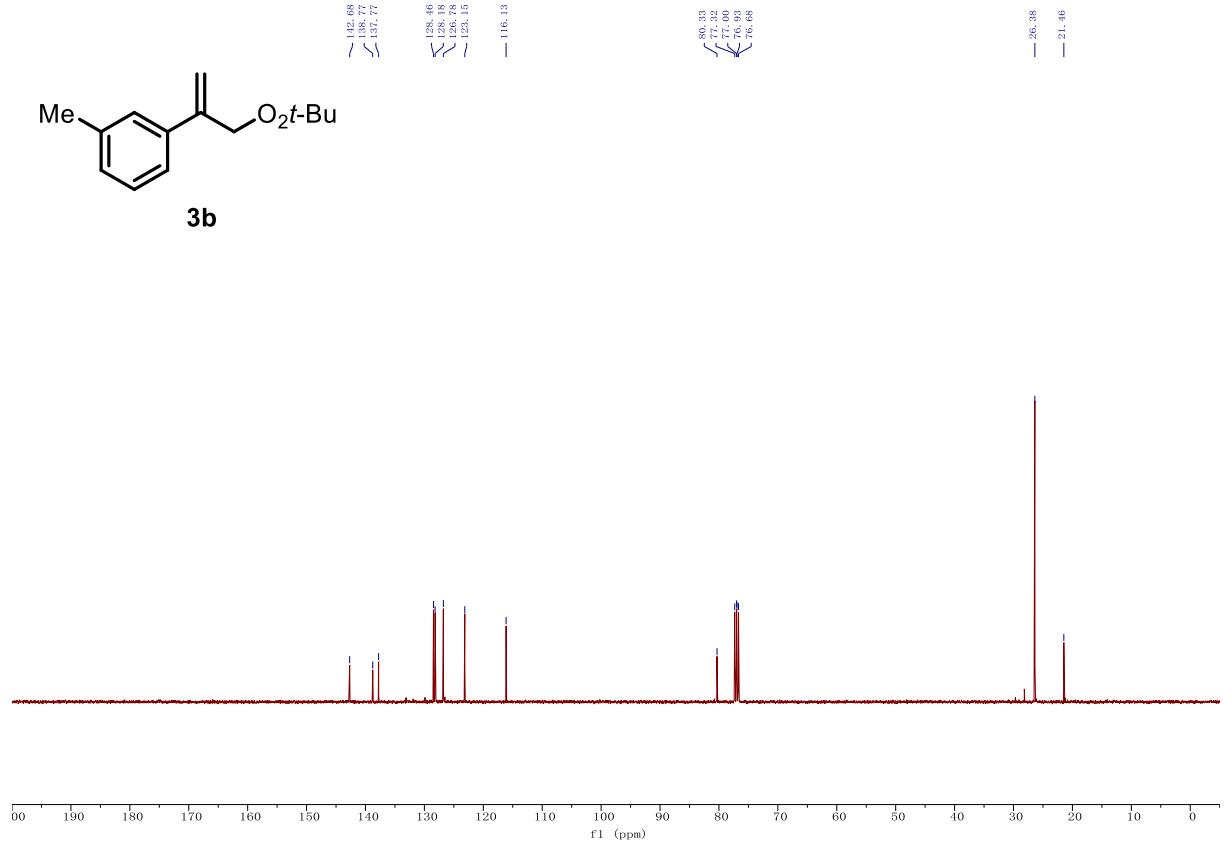
^{13}C NMR (101 MHz, $CDCl_3$)



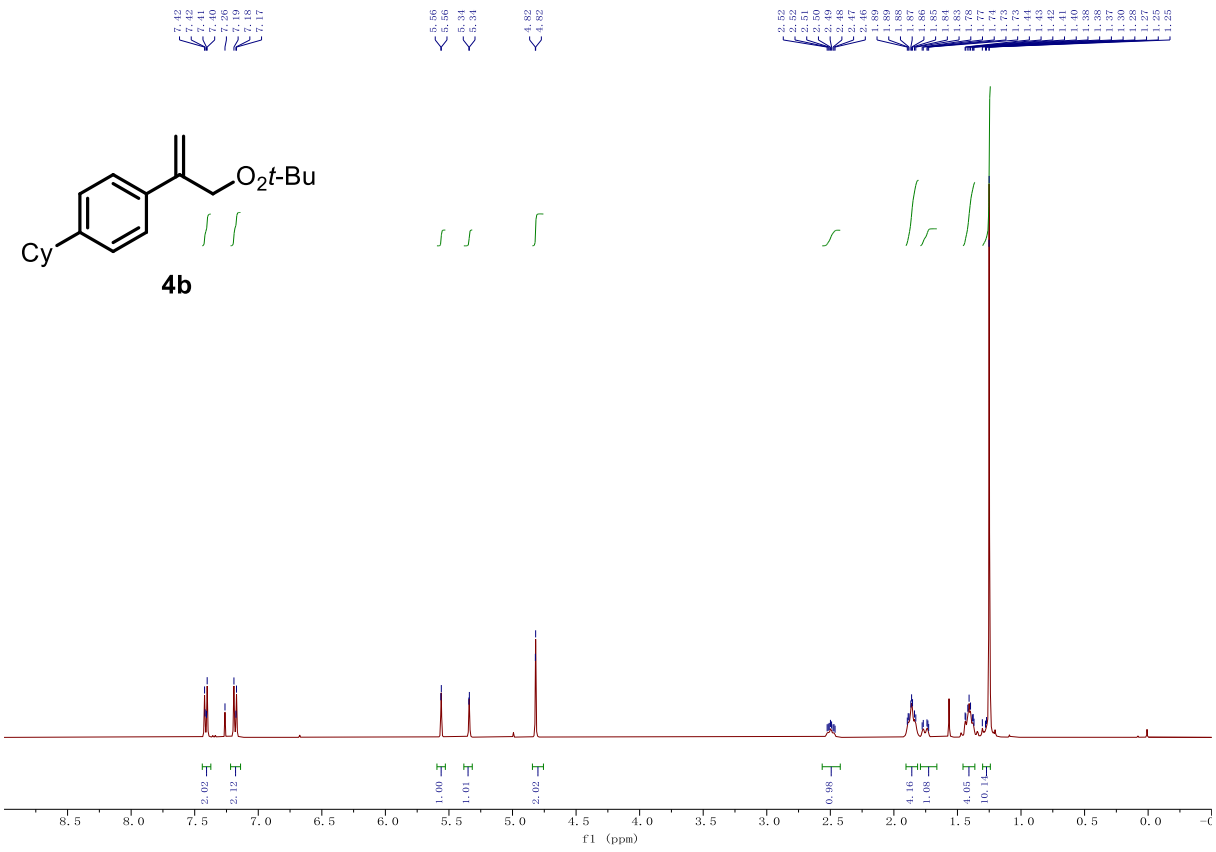
^{1}H NMR (400 MHz, $CDCl_3$)



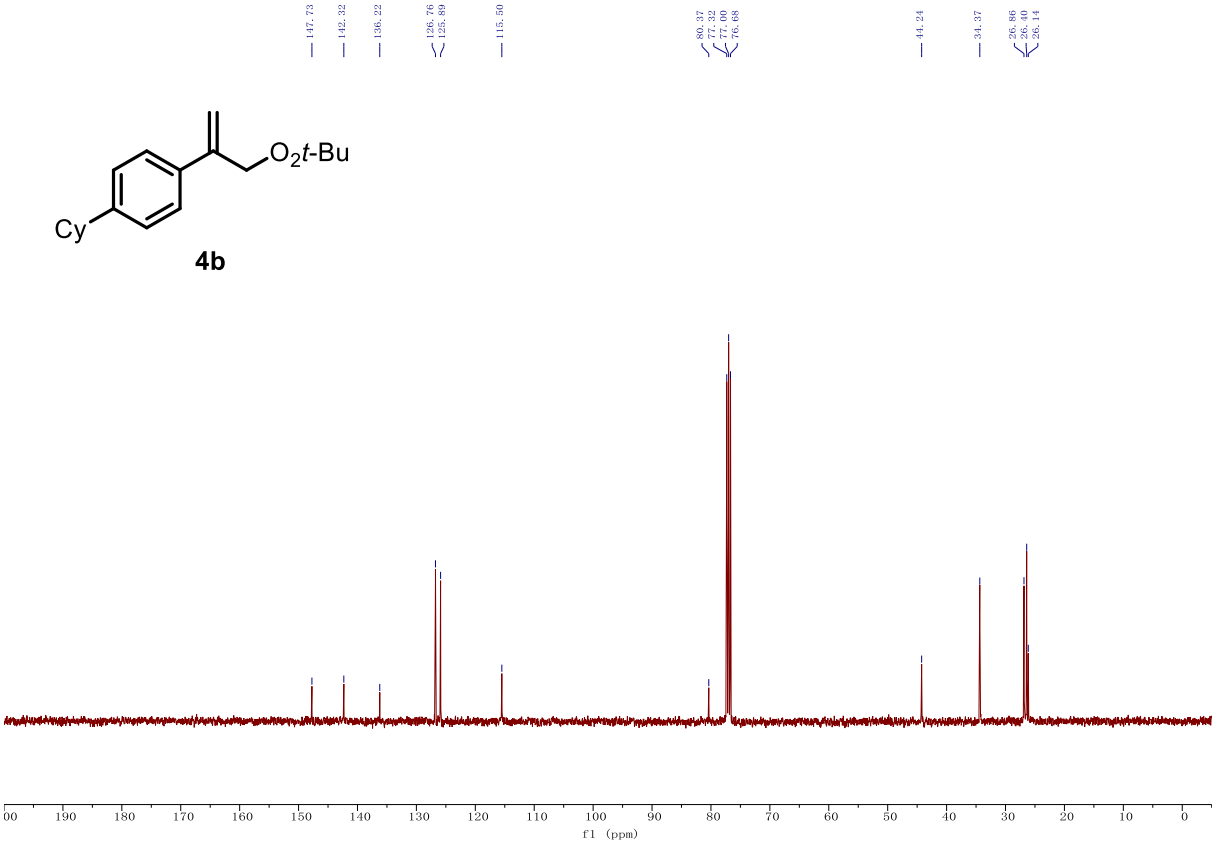
^{13}C NMR (101 MHz, $CDCl_3$)



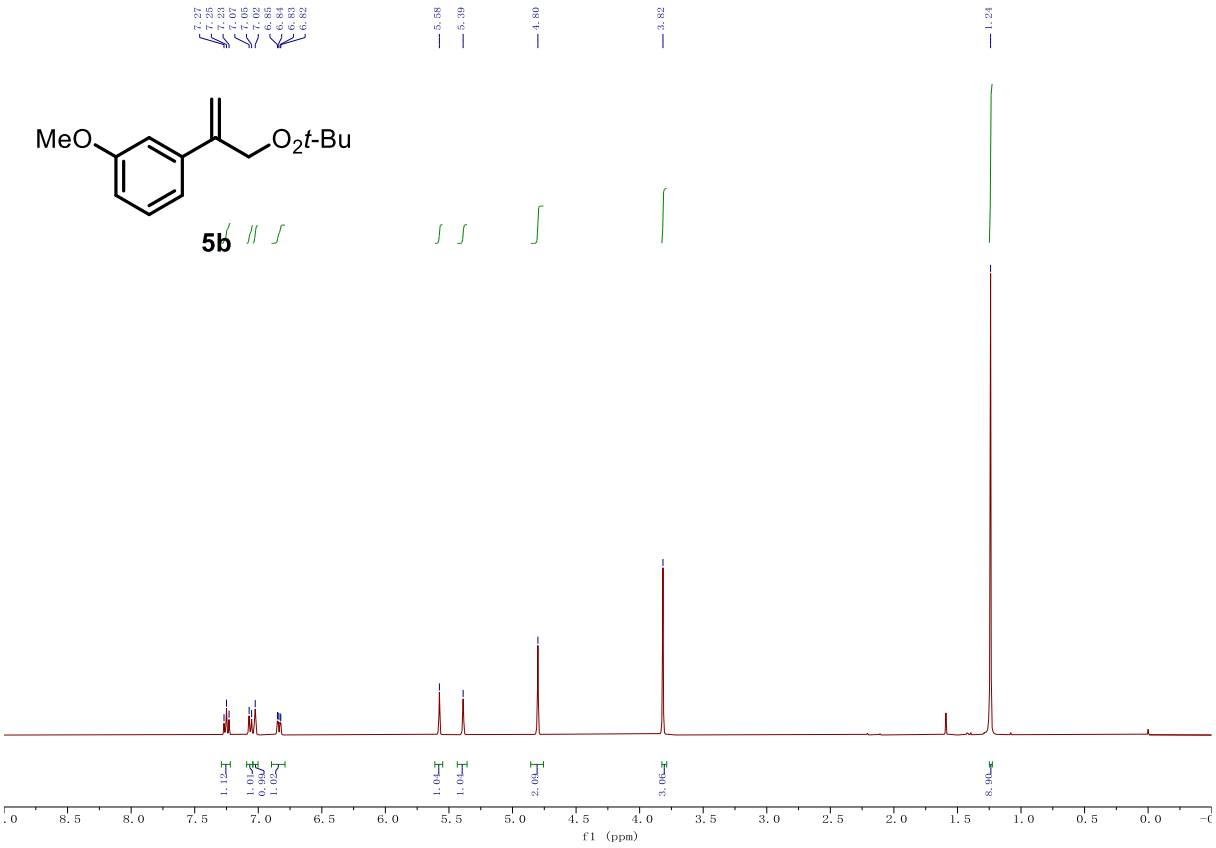
^{1}H NMR (400 MHz, $CDCl_3$)



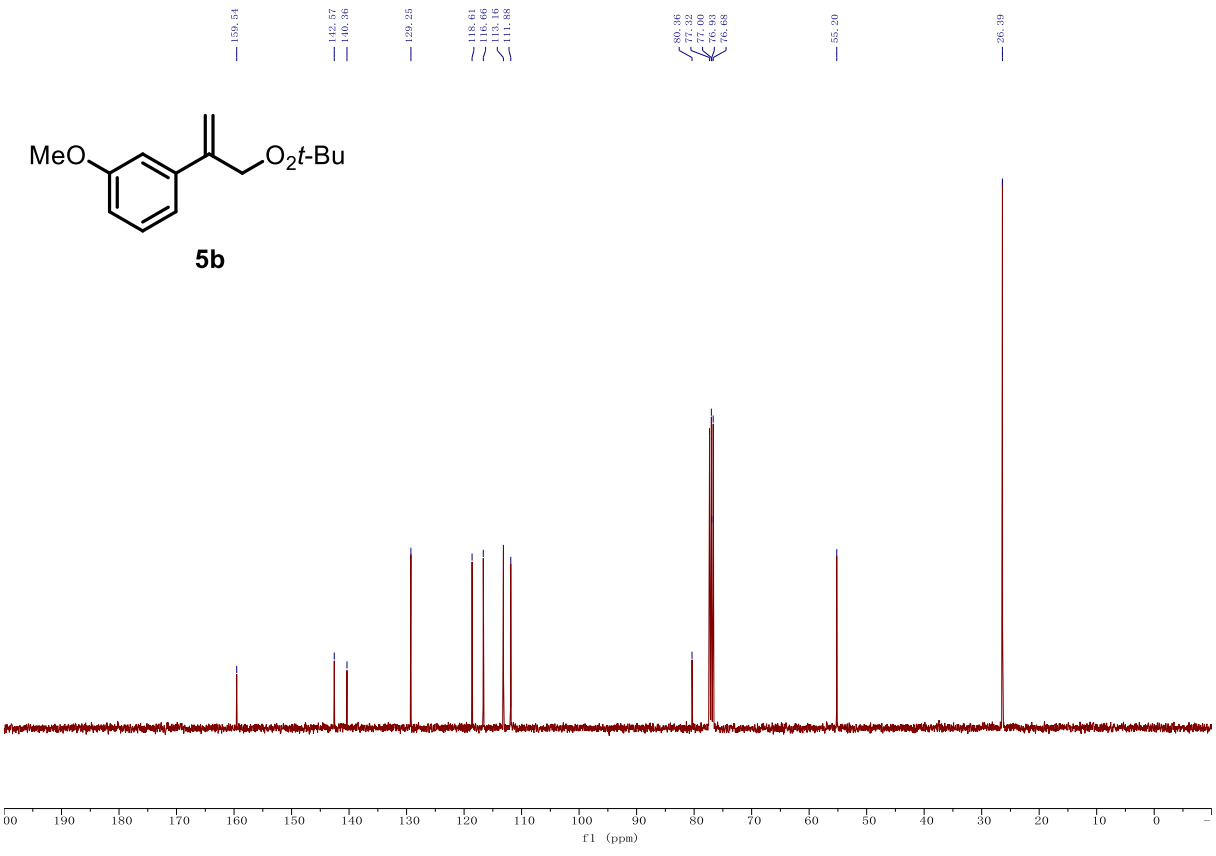
^{13}C NMR (101 MHz, $CDCl_3$)



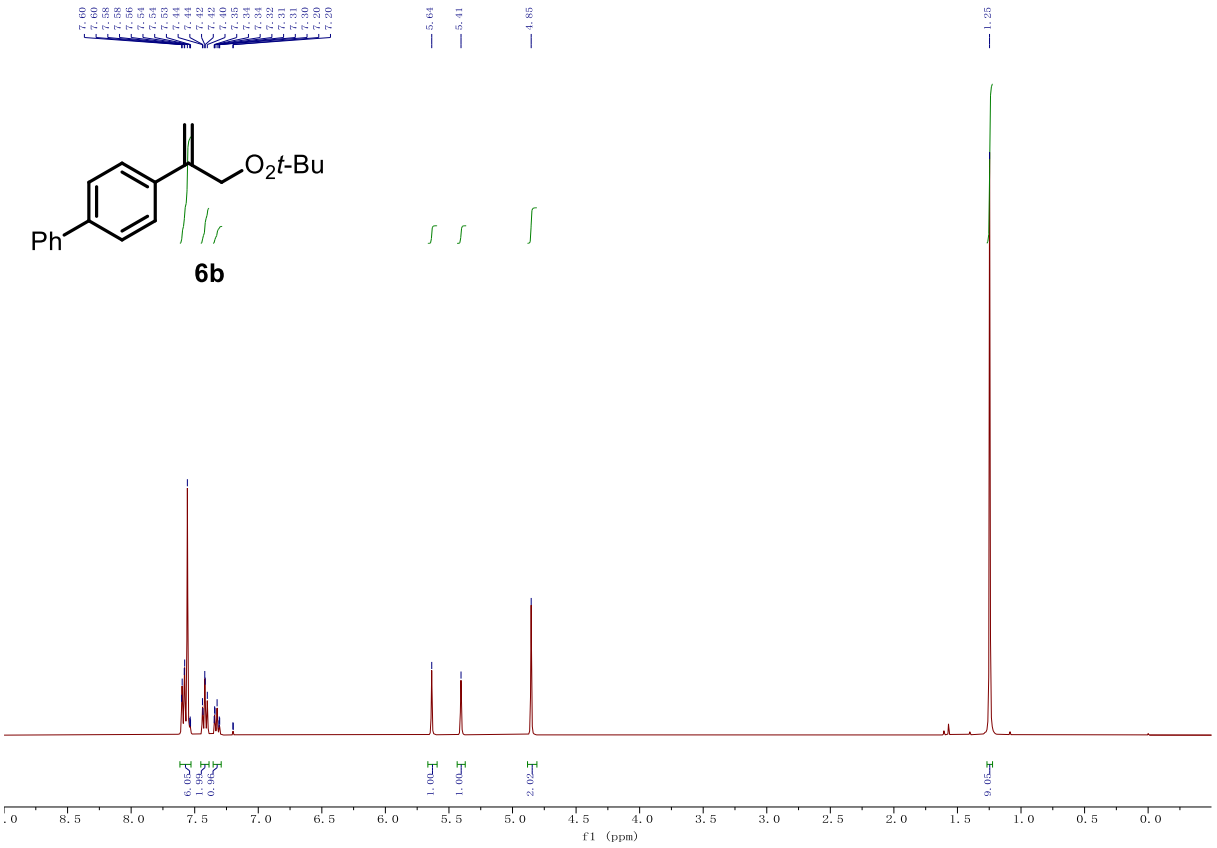
^{1}H NMR (400 MHz, $CDCl_3$)



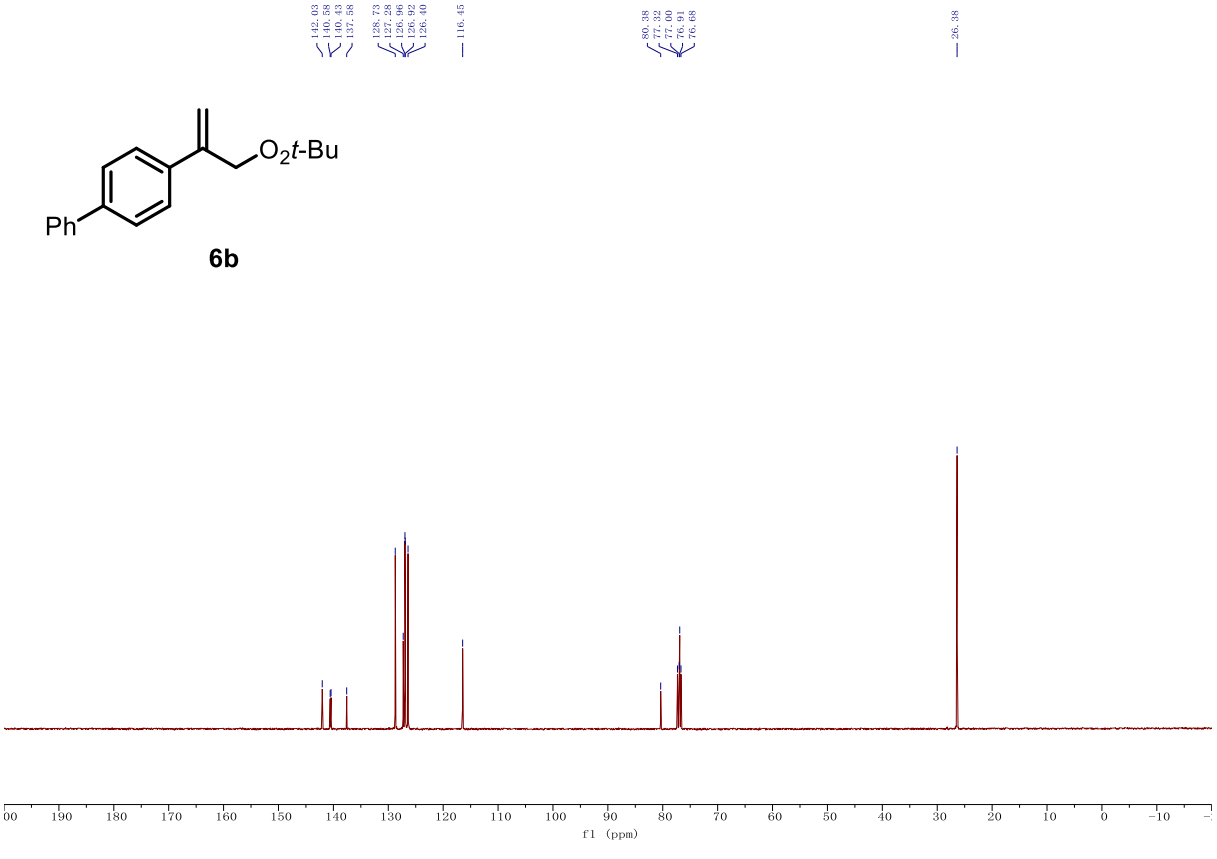
^{13}C NMR (101 MHz, $CDCl_3$)



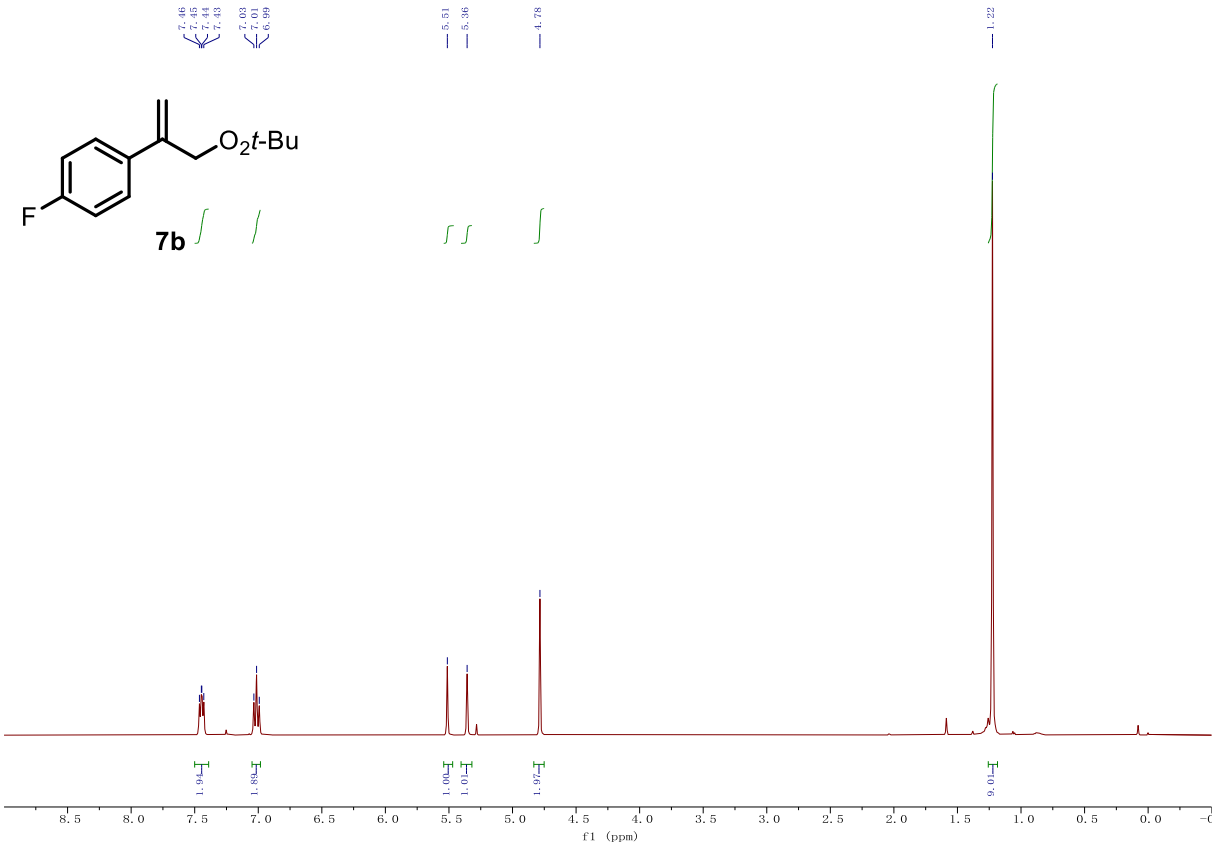
^{1}H NMR (400 MHz, $CDCl_3$)



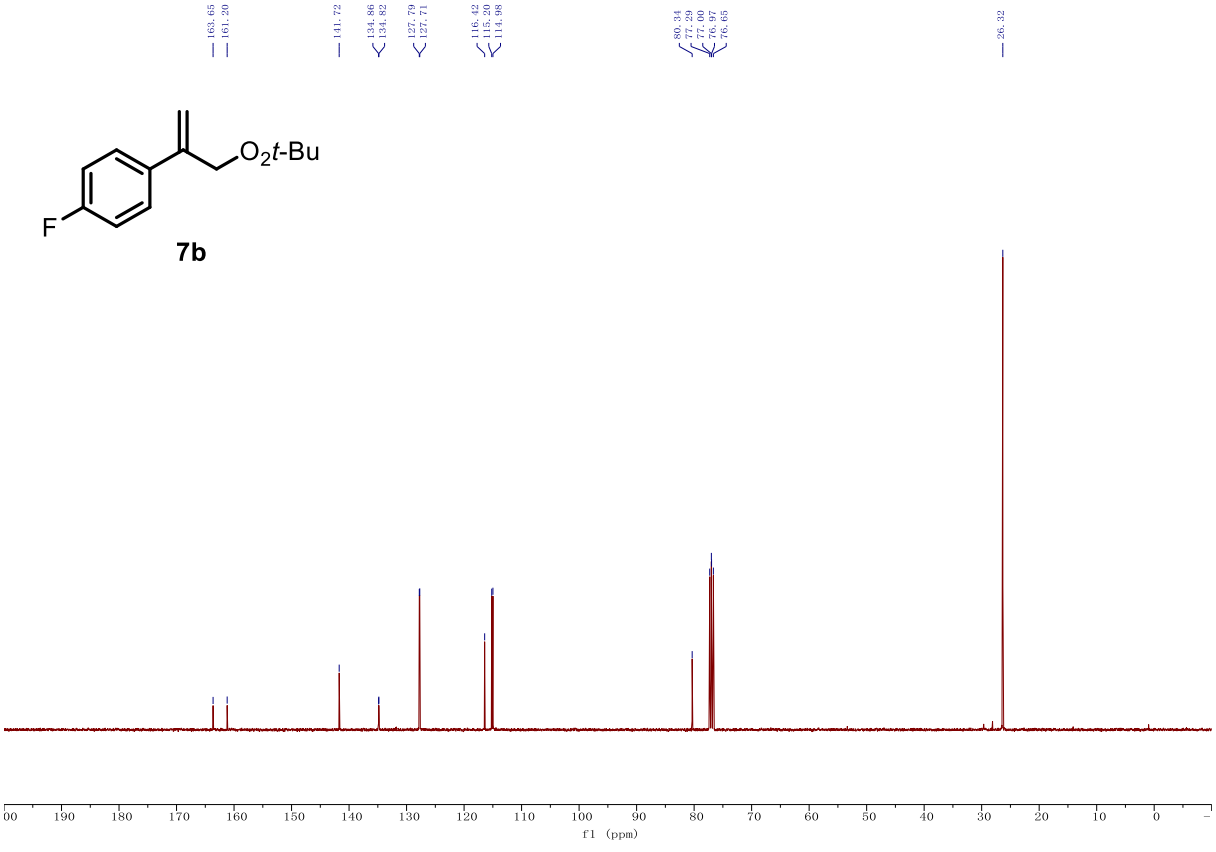
^{13}C NMR (101 MHz, $CDCl_3$)



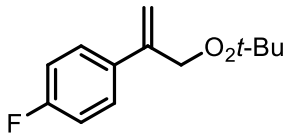
^{1}H NMR (400 MHz, $CDCl_3$)



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

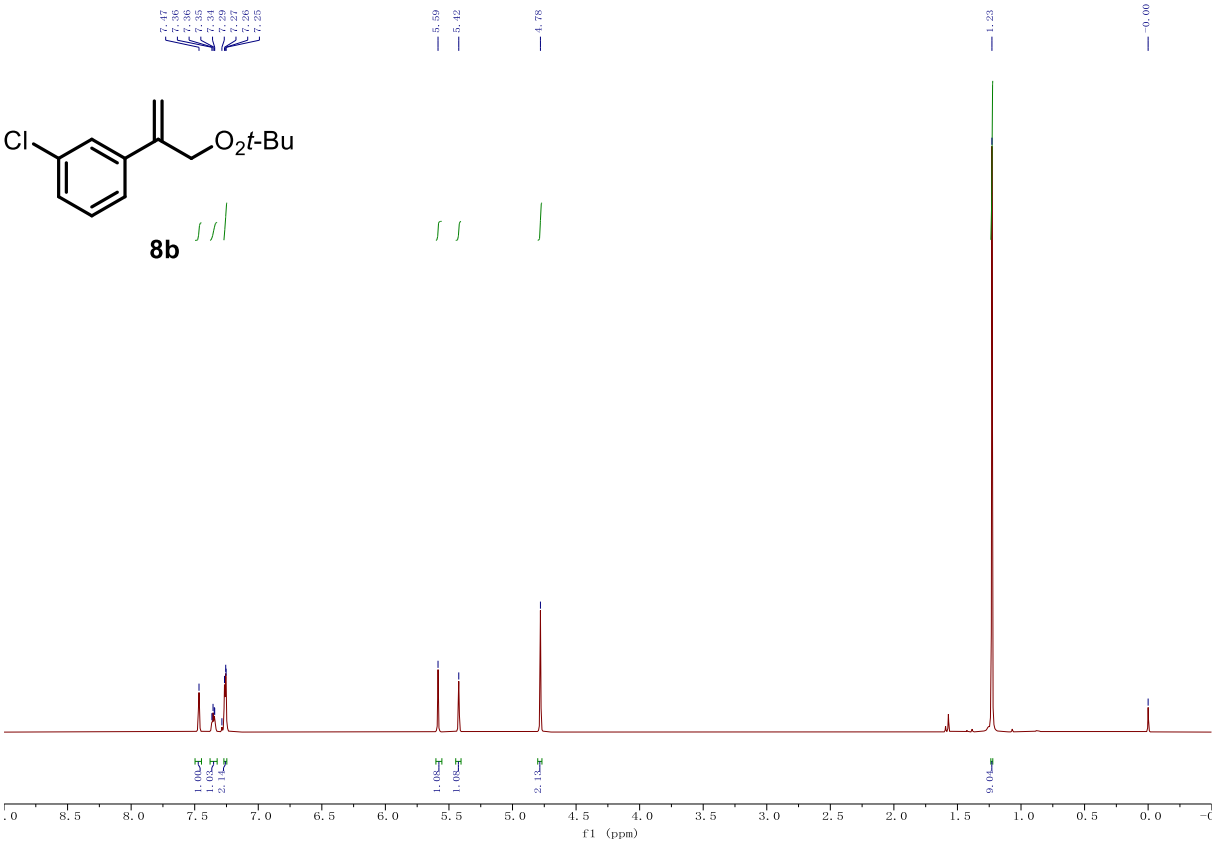


^{19}F NMR (376 MHz, $CDCl_3$)

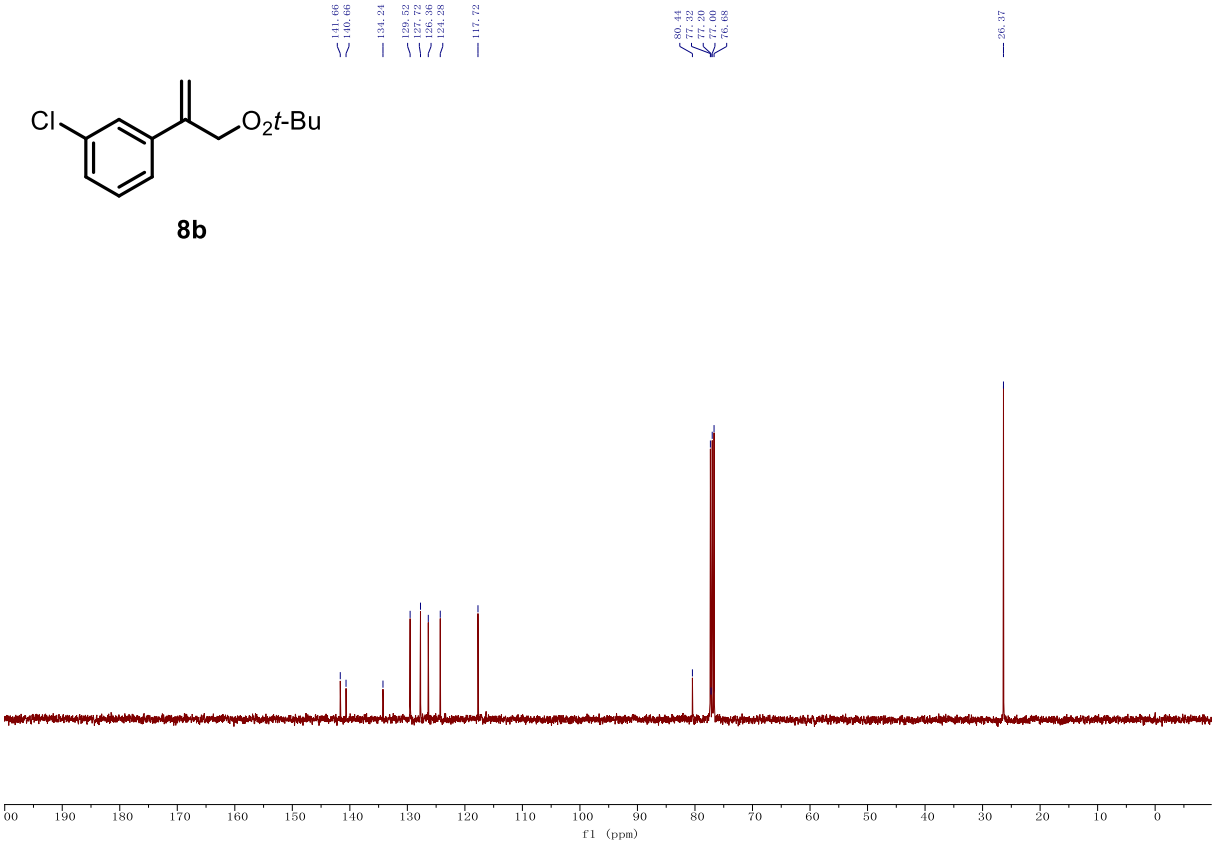


7b

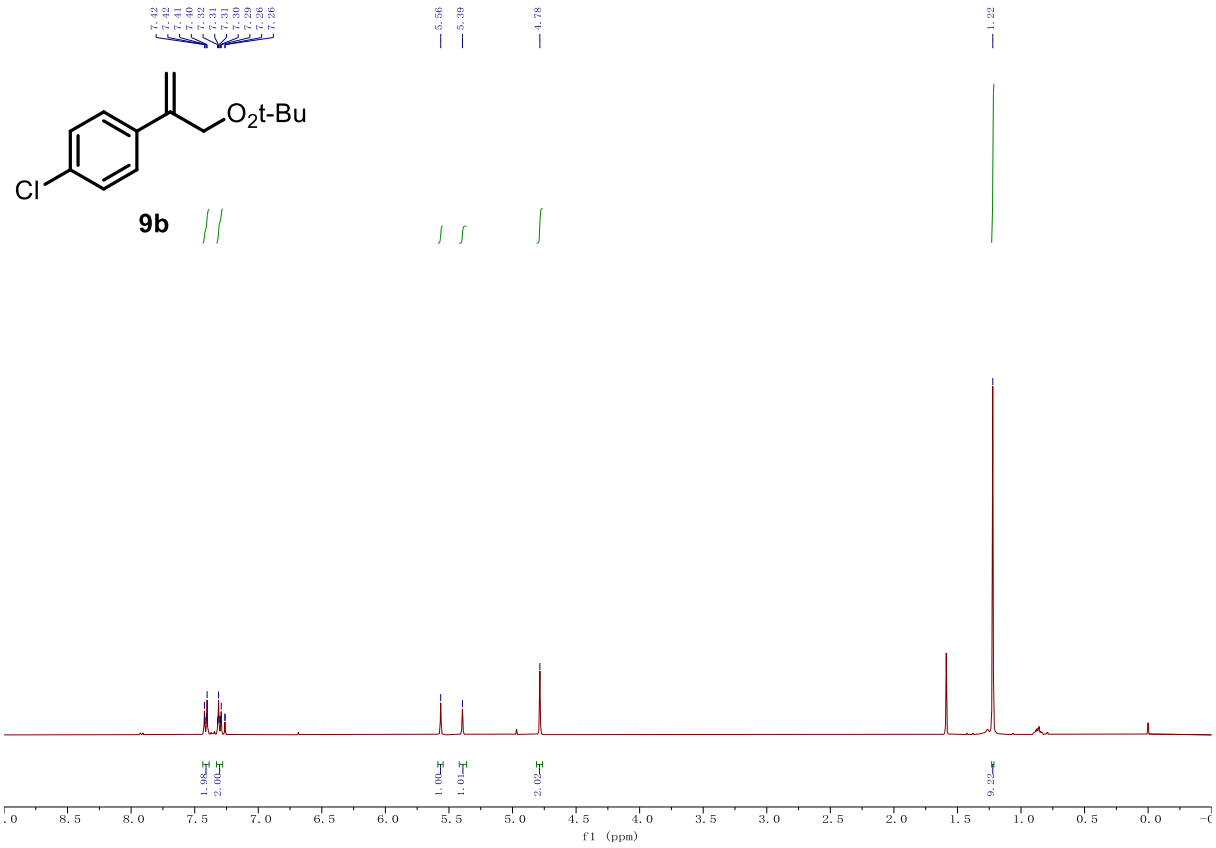
^{1}H NMR (400 MHz, $CDCl_3$)



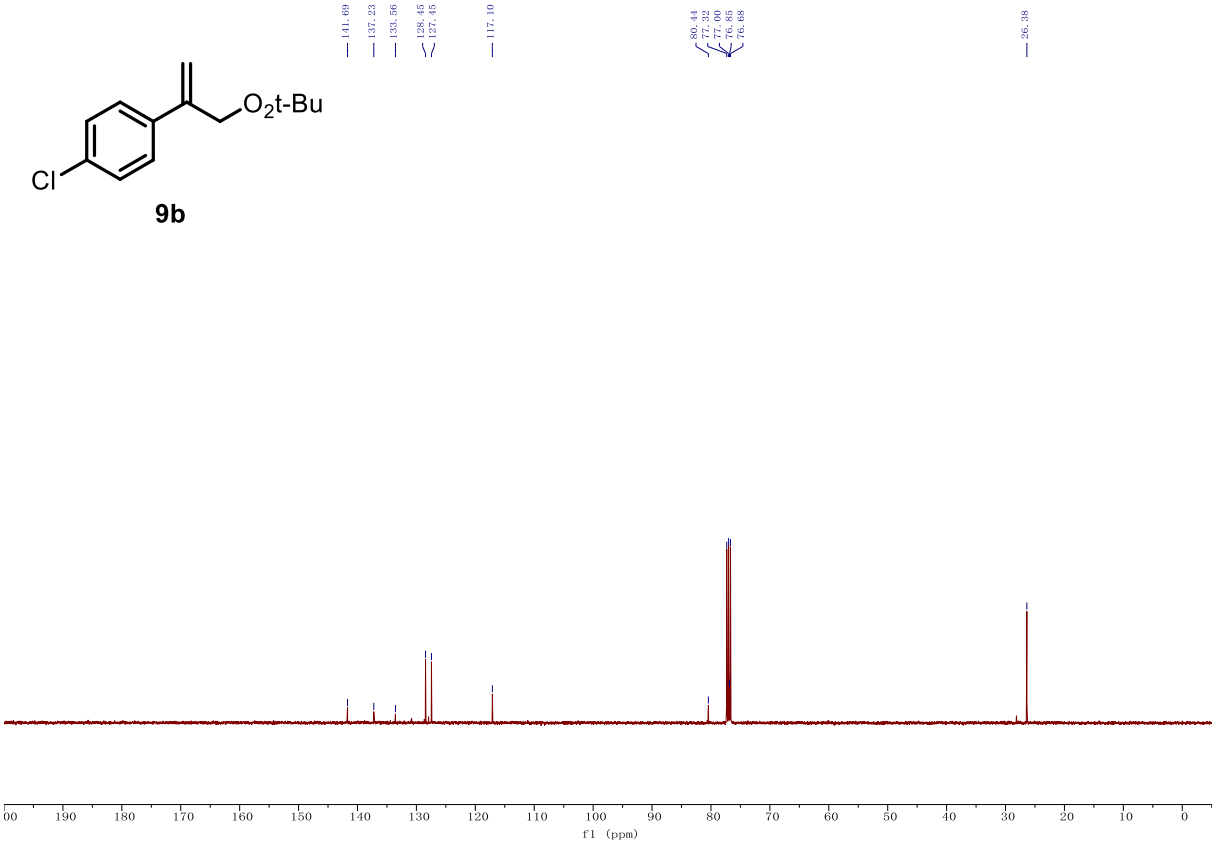
^{13}C NMR (101 MHz, $CDCl_3$)



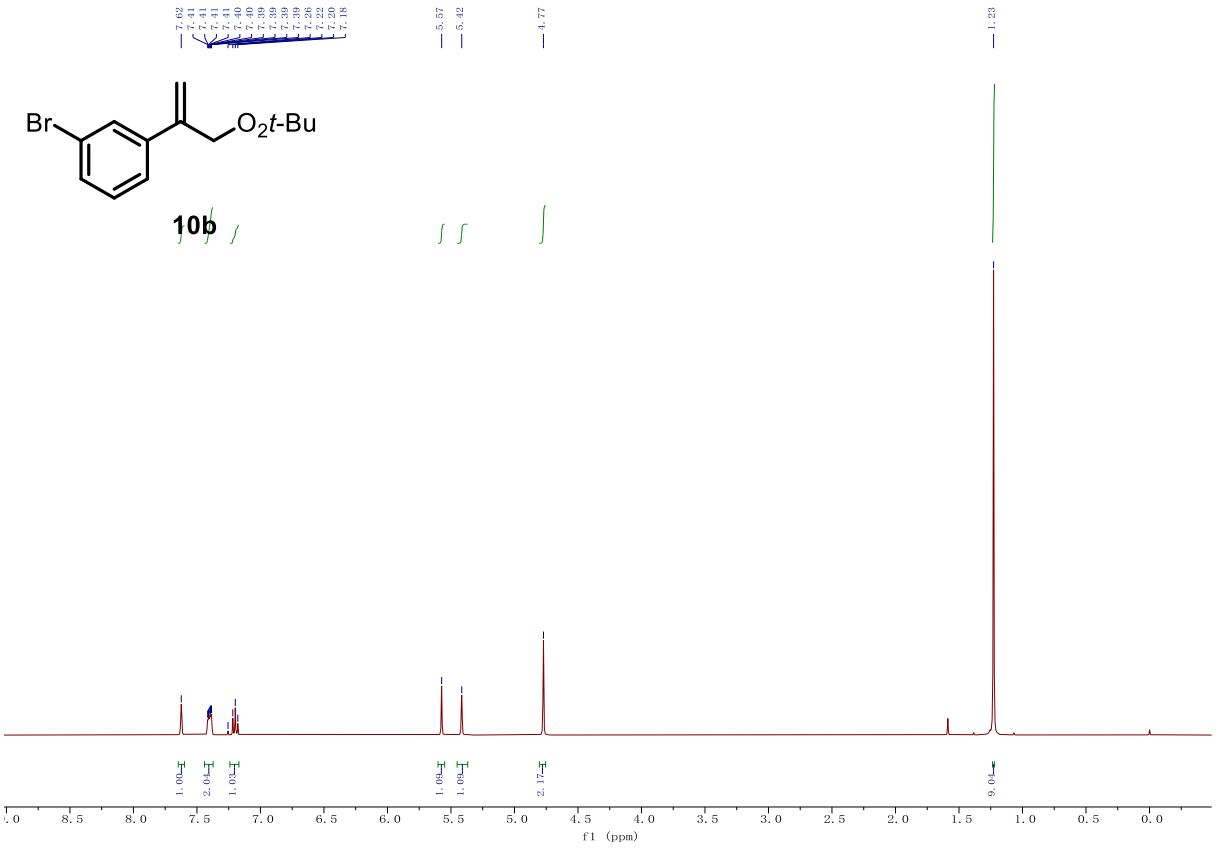
^{1}H NMR (400 MHz, $CDCl_3$)



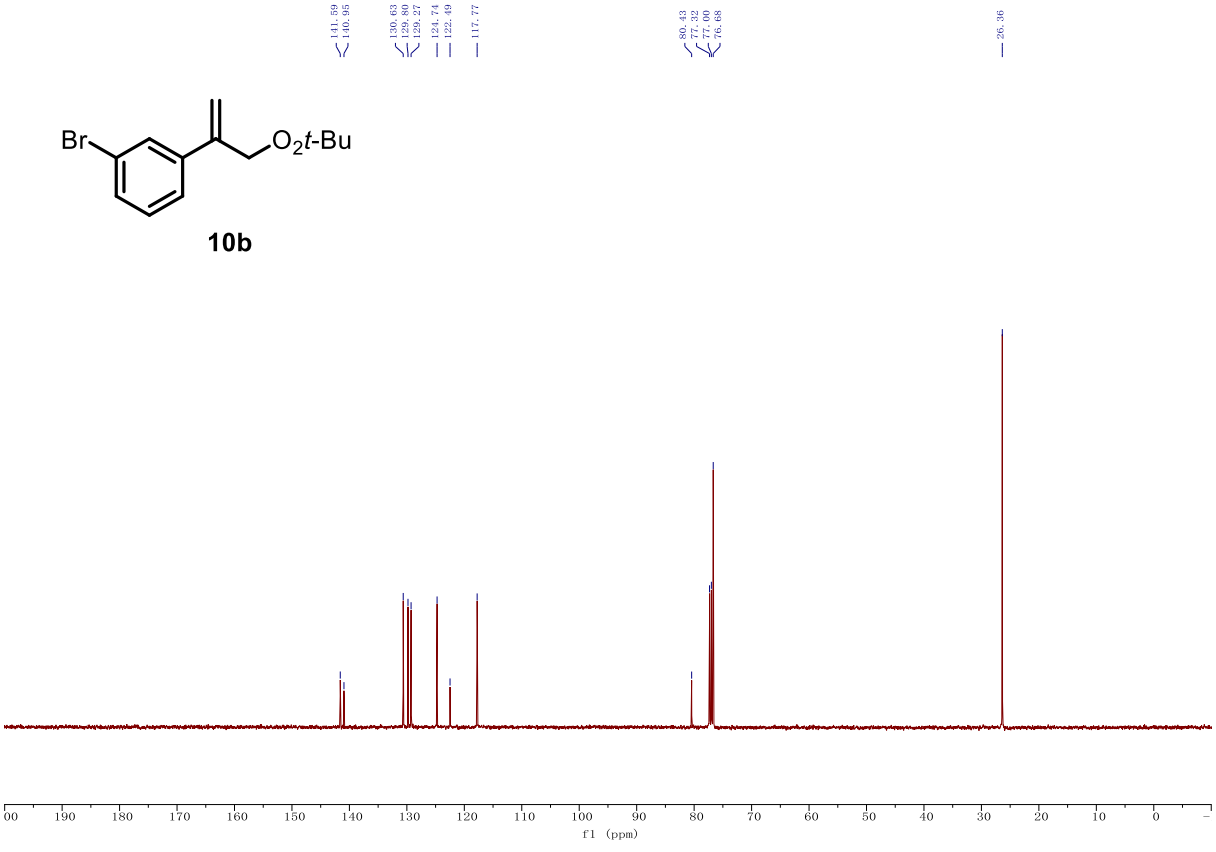
^{13}C NMR (101 MHz, $CDCl_3$)



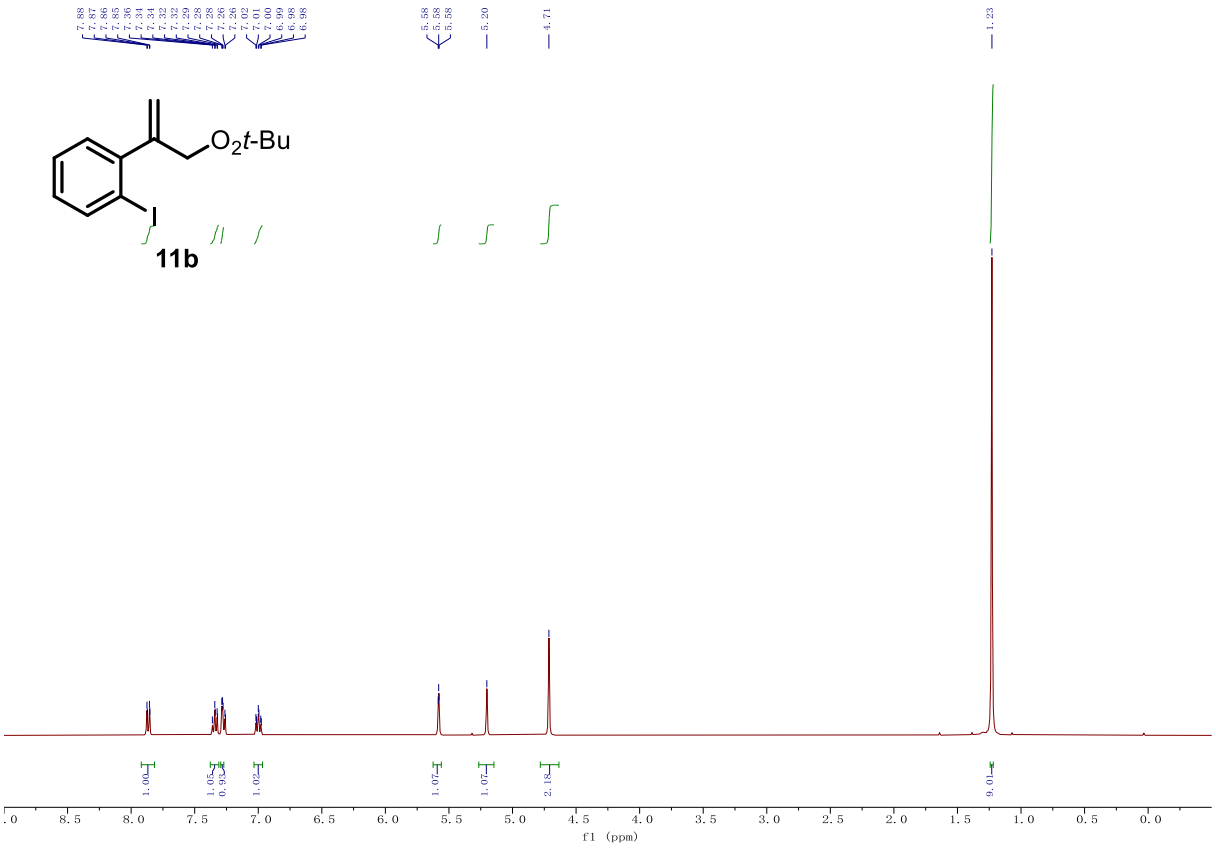
^{1}H NMR (400 MHz, $CDCl_3$)



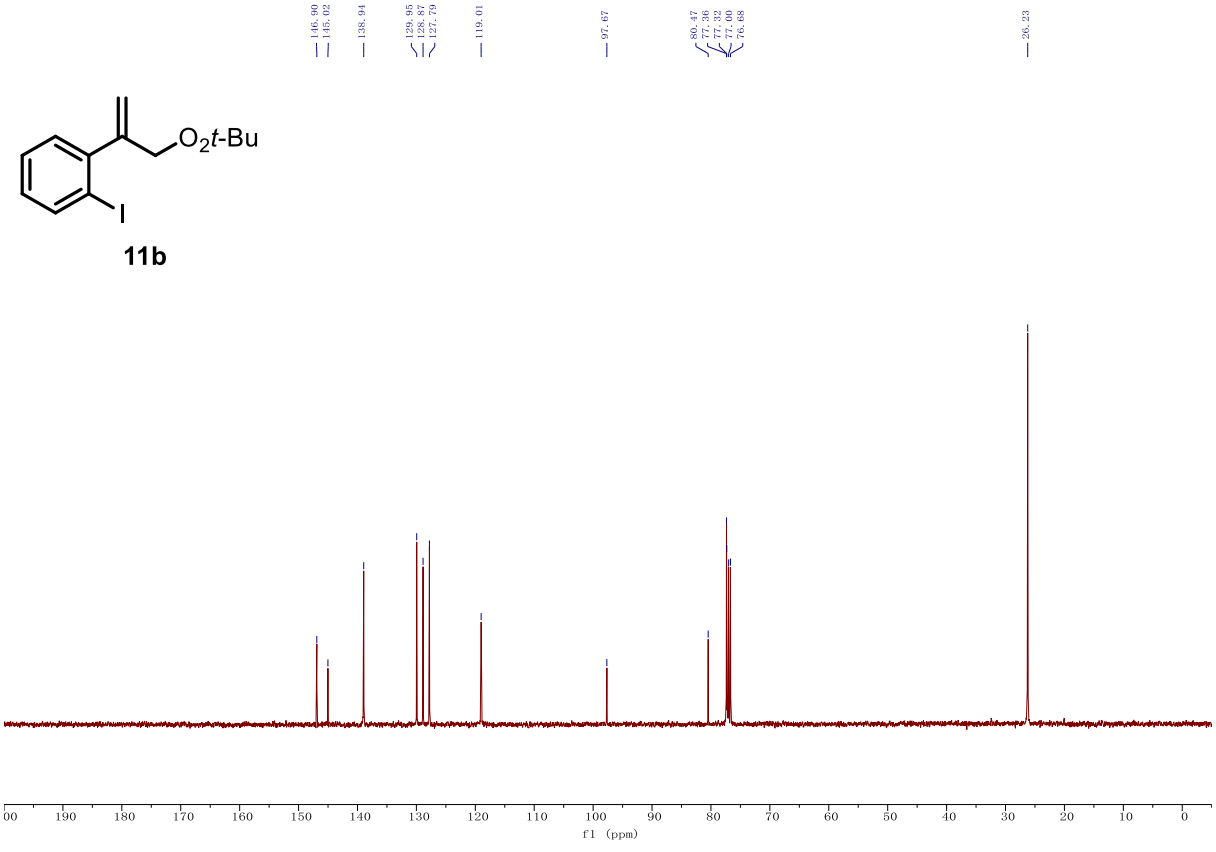
^{13}C NMR (101 MHz, $CDCl_3$)



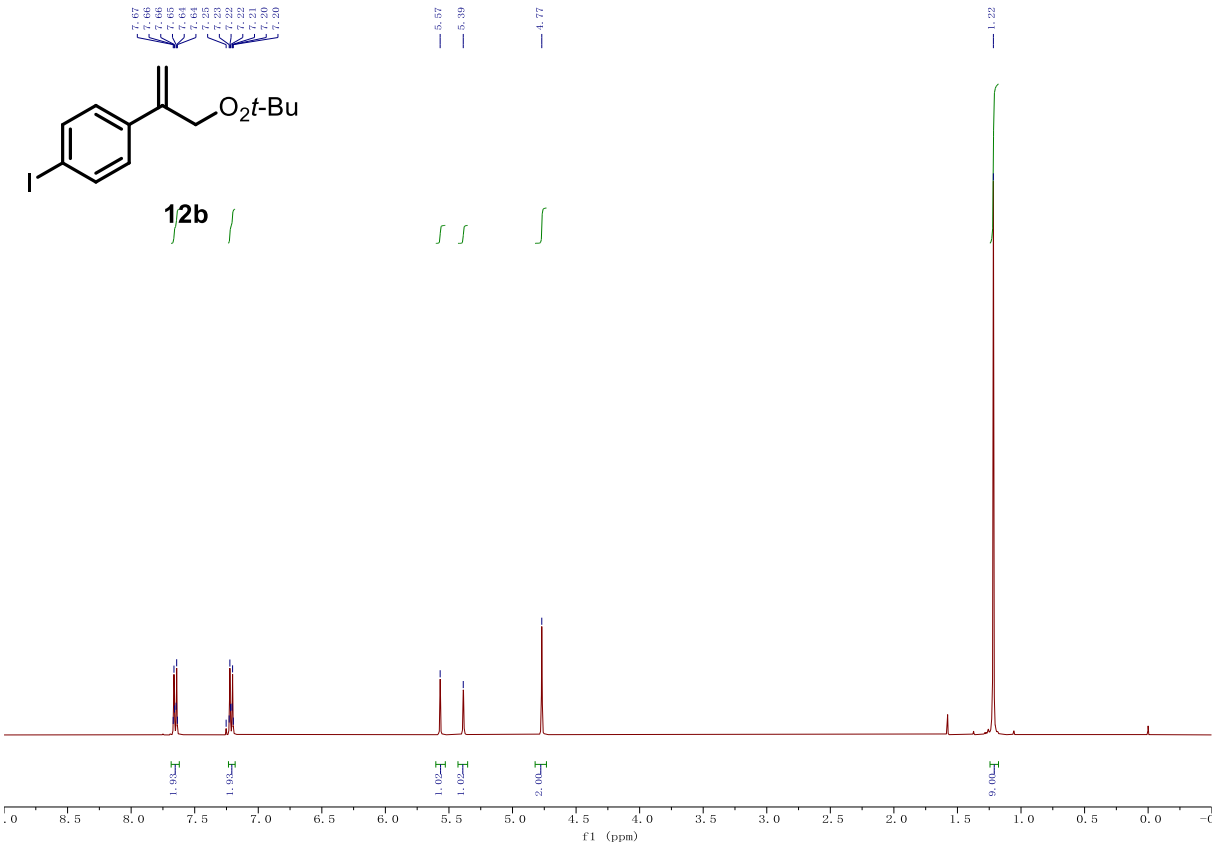
^{1}H NMR (400 MHz, $CDCl_3$)



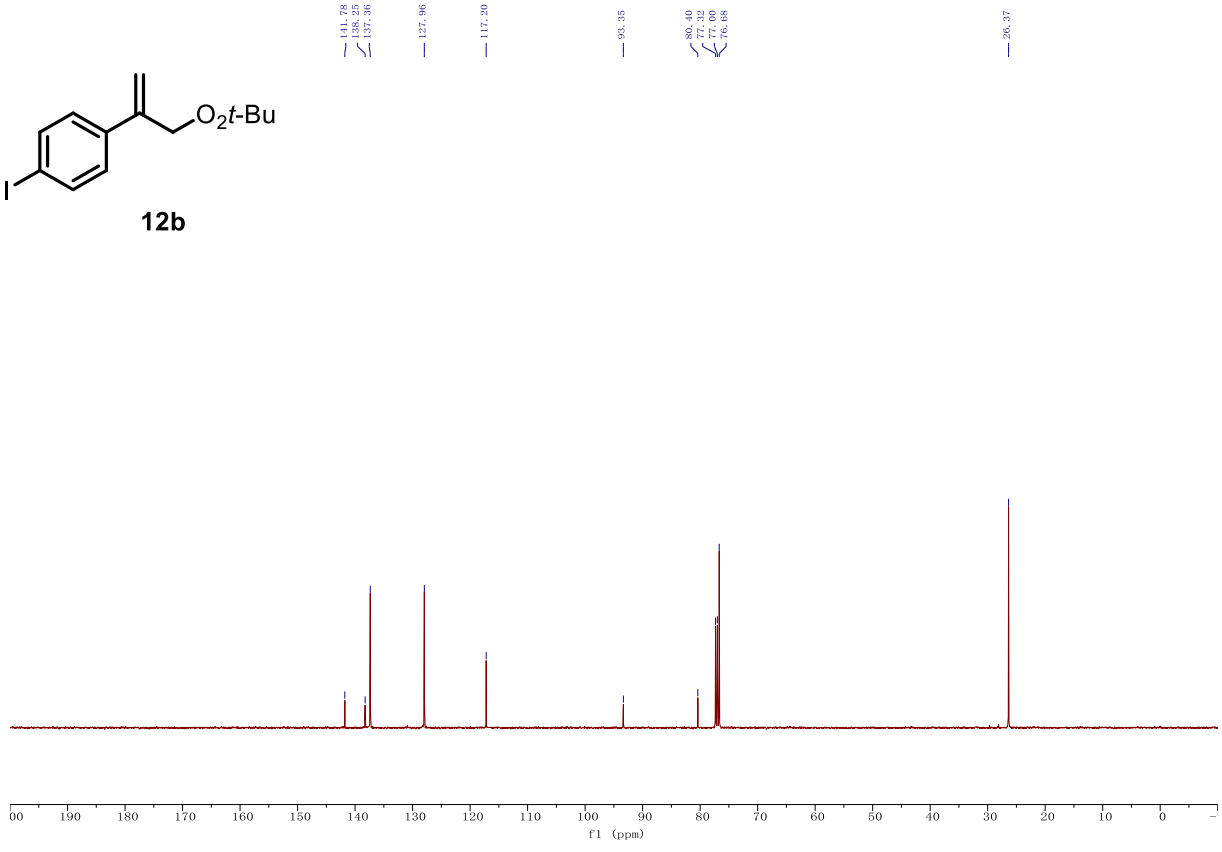
^{13}C NMR (101 MHz, $CDCl_3$)



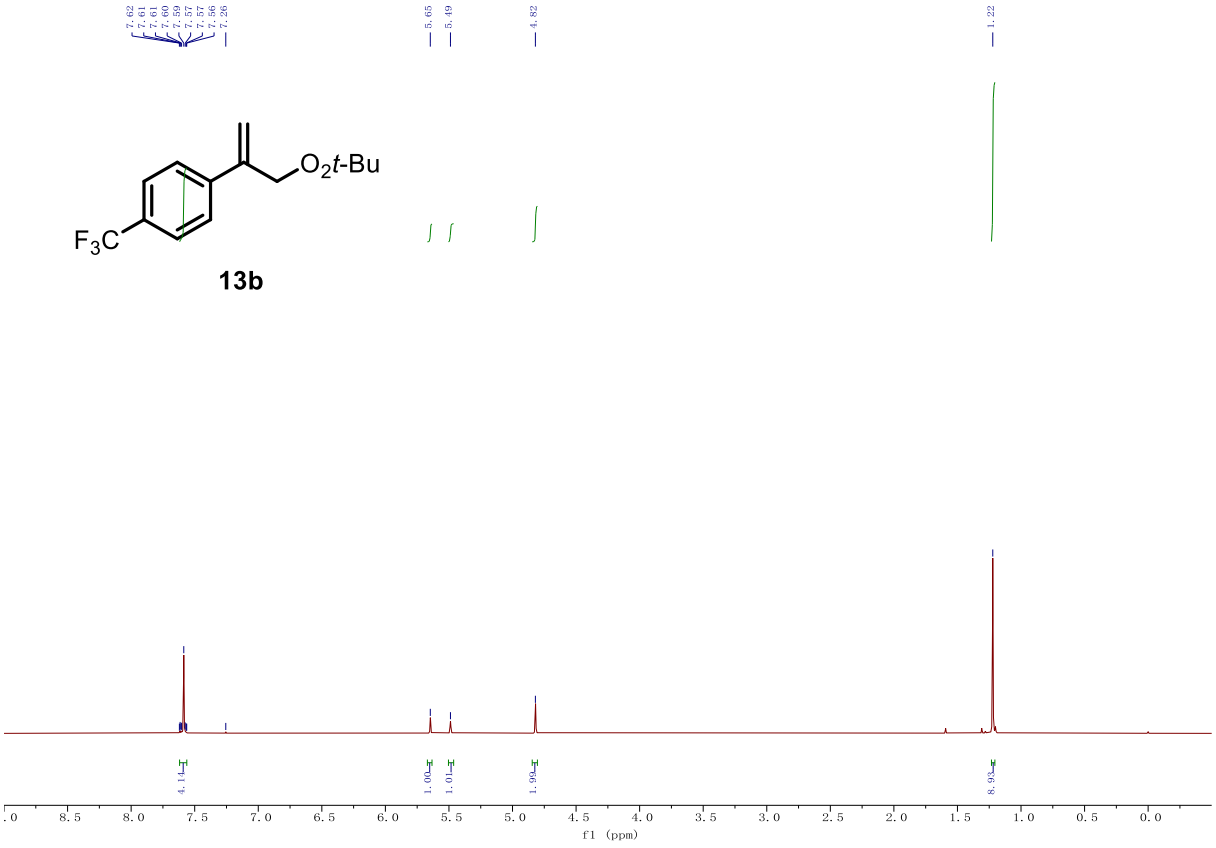
^{1}H NMR (400 MHz, $CDCl_3$)



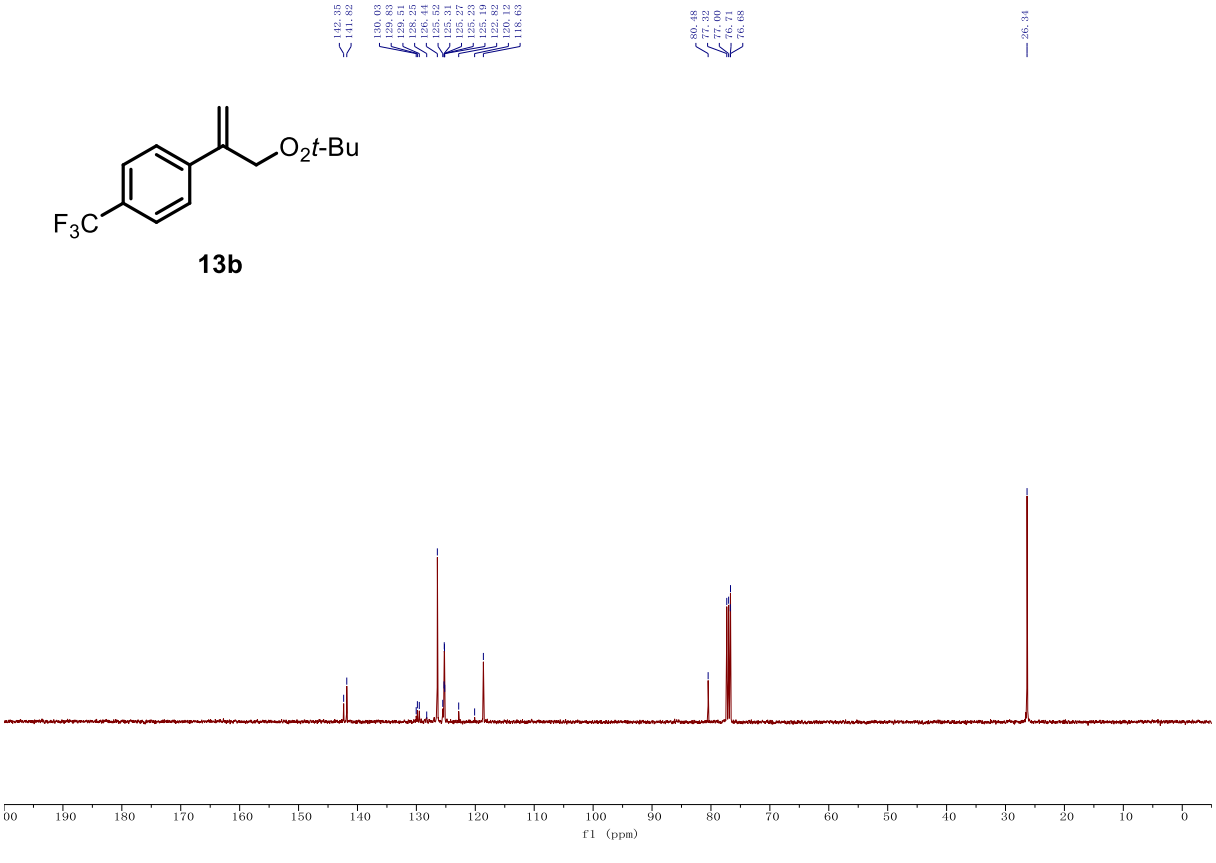
^{13}C NMR (101 MHz, $CDCl_3$)



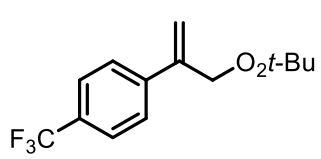
^{1}H NMR (400 MHz, $CDCl_3$)



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

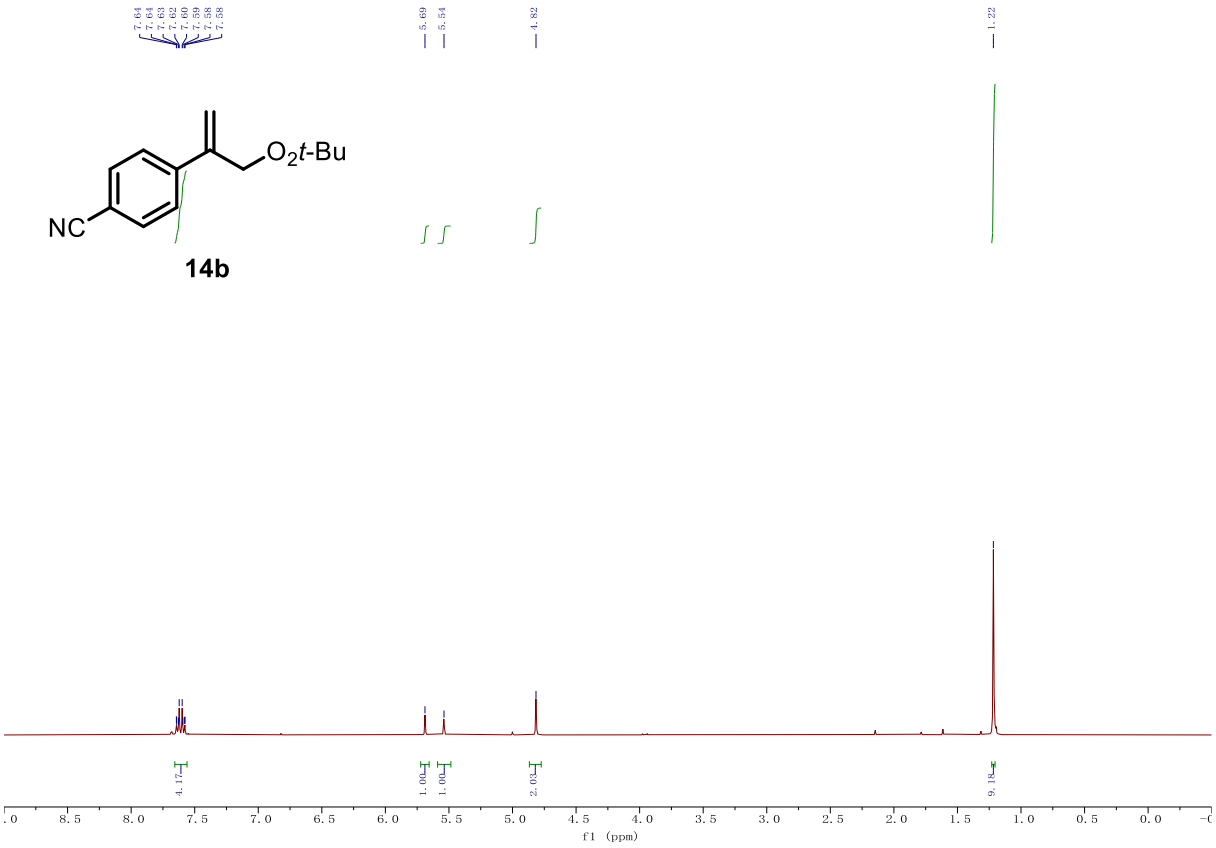


^{19}F NMR (376 MHz, $CDCl_3$)

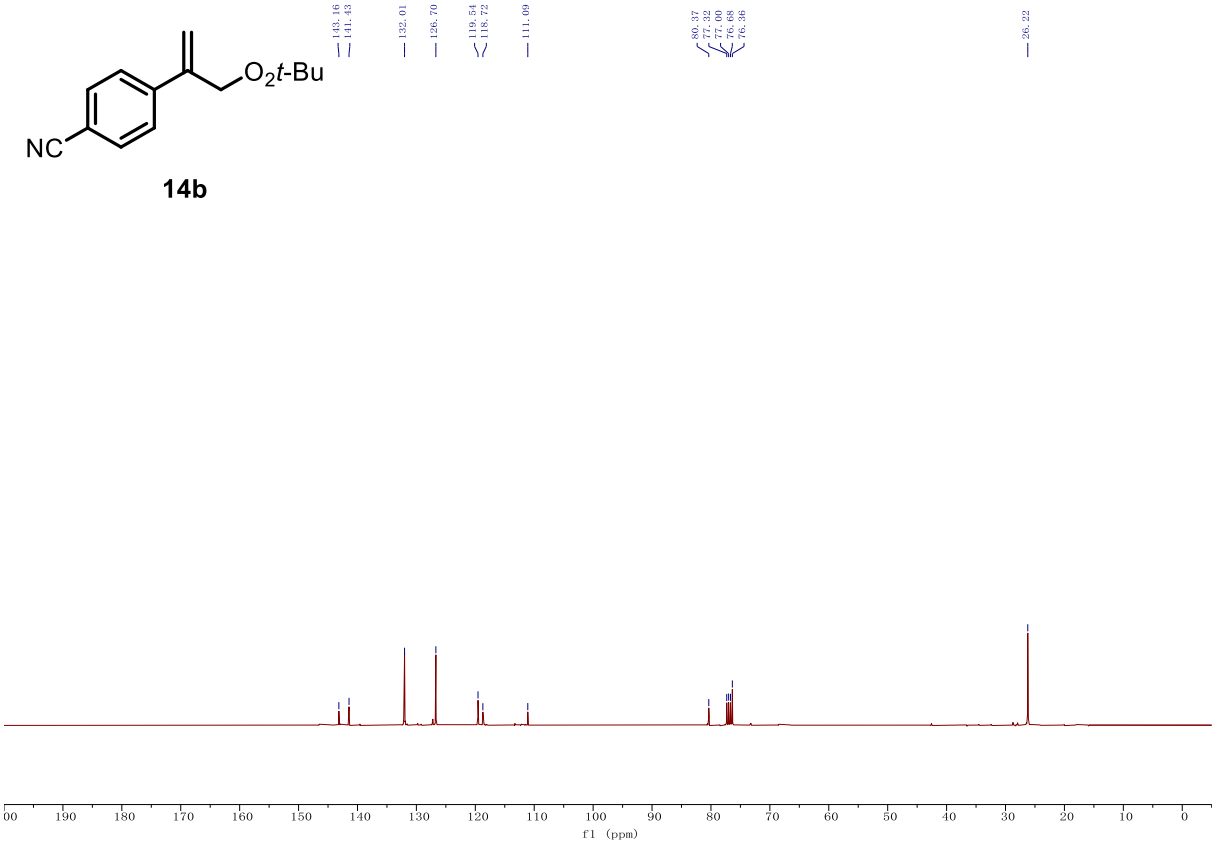


13b

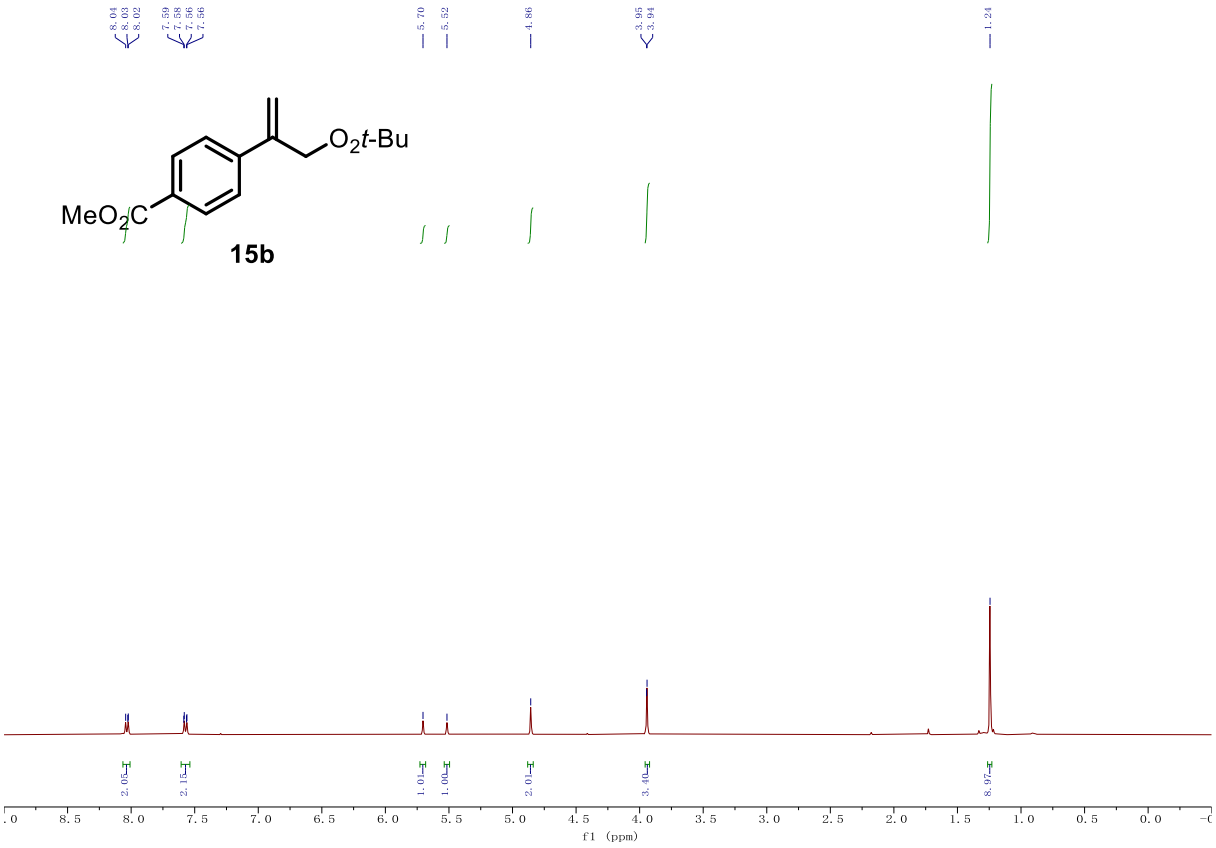
^{1}H NMR (400 MHz, $CDCl_3$)



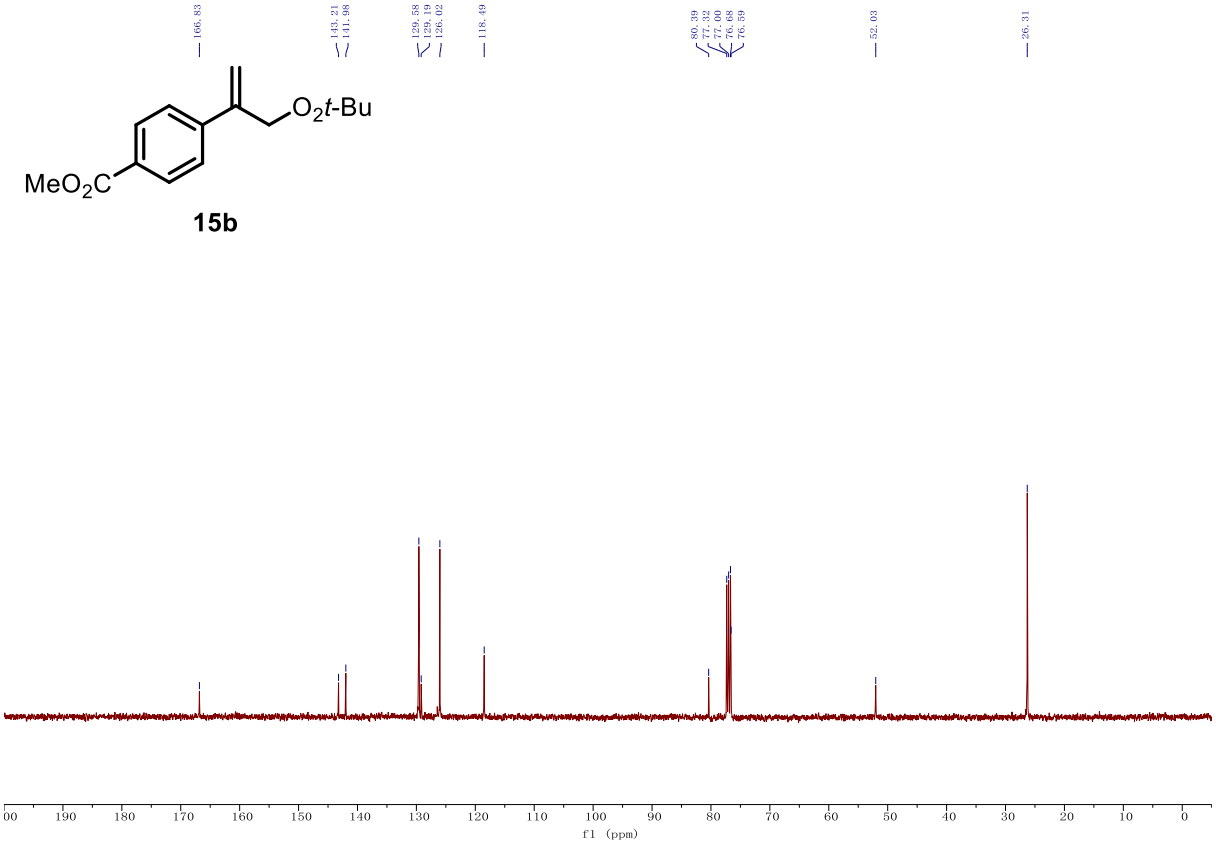
^{13}C NMR (101 MHz, $CDCl_3$)



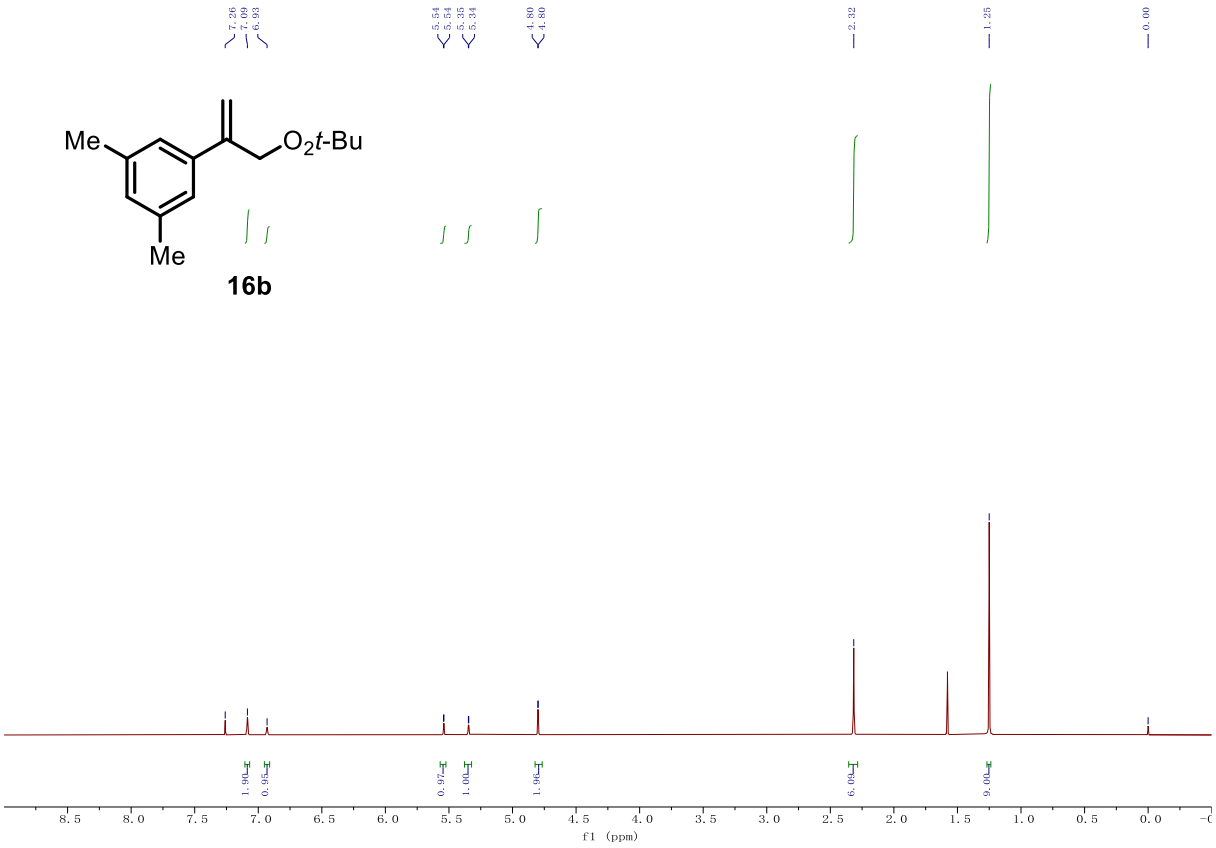
^{1}H NMR (400 MHz, $CDCl_3$)



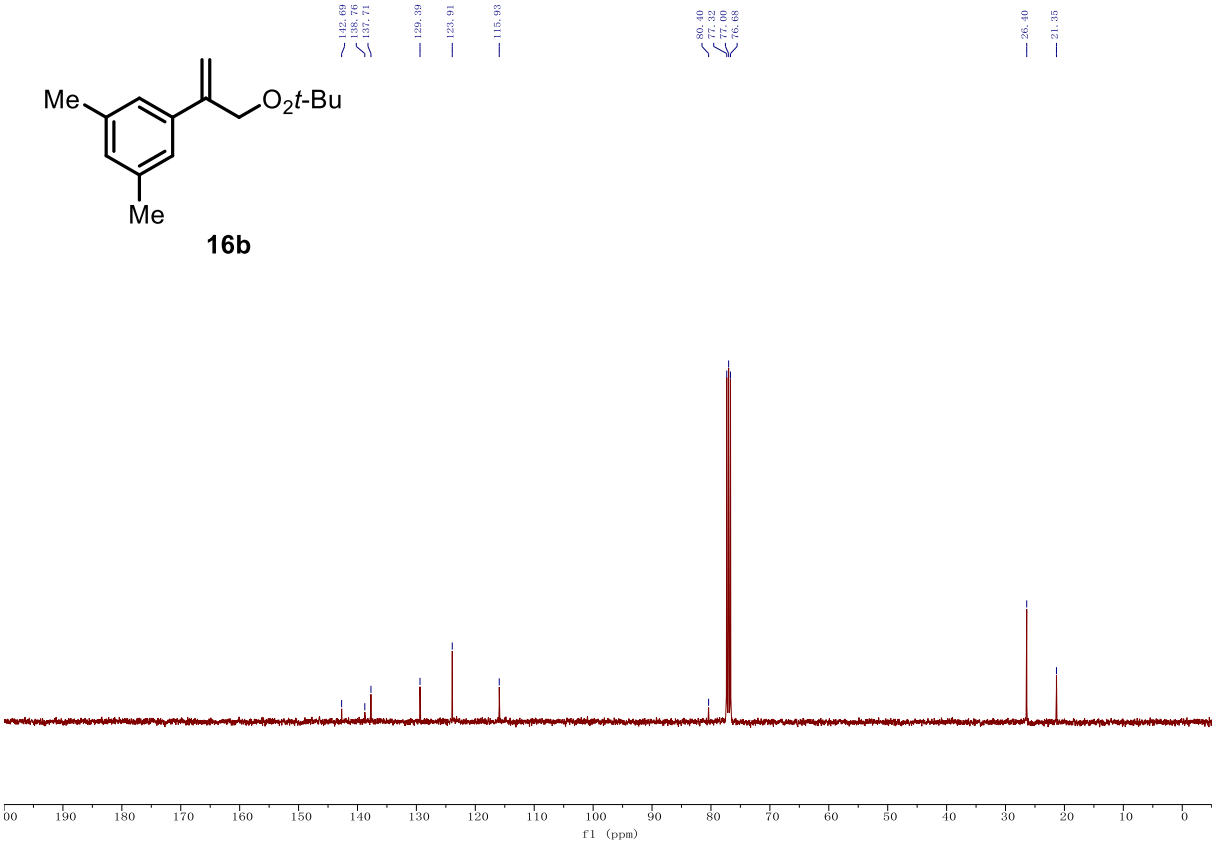
^{13}C NMR (101 MHz, $CDCl_3$)



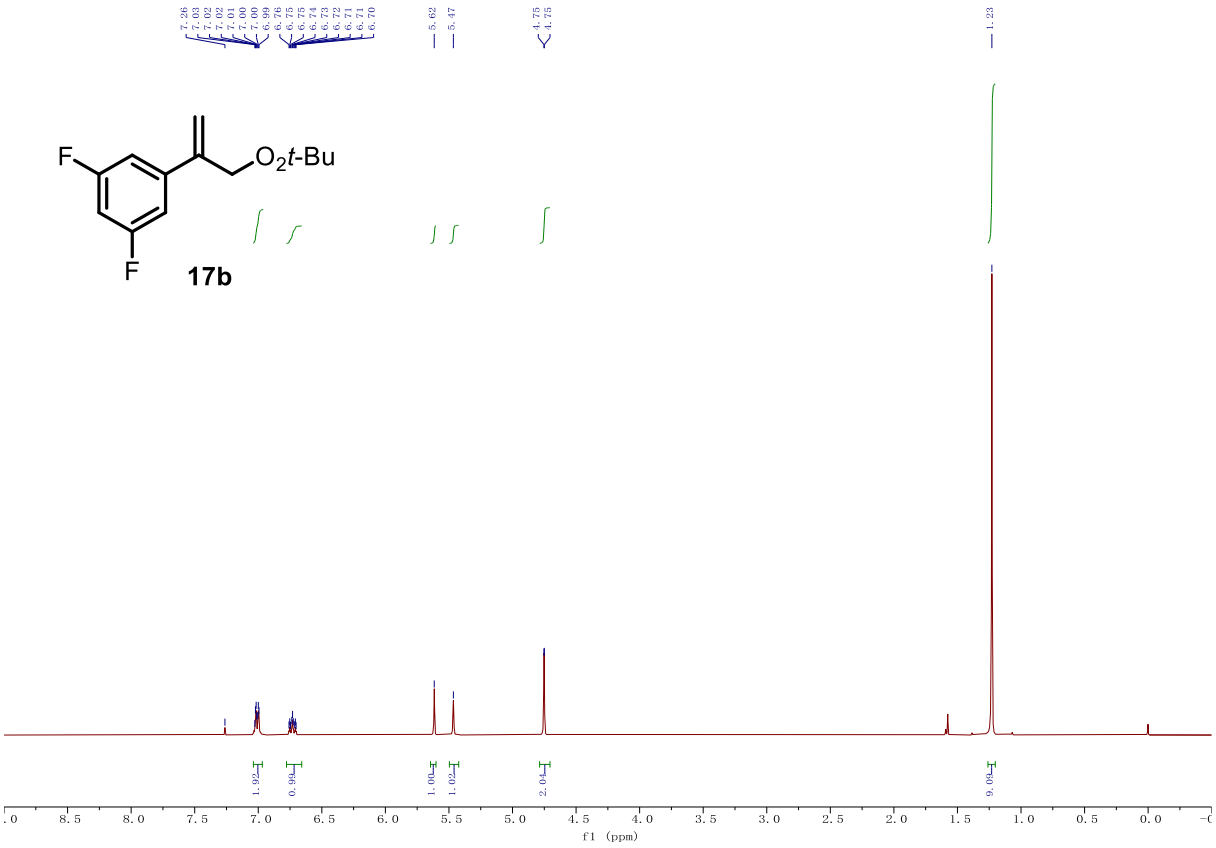
^{1}H NMR (400 MHz, $CDCl_3$)



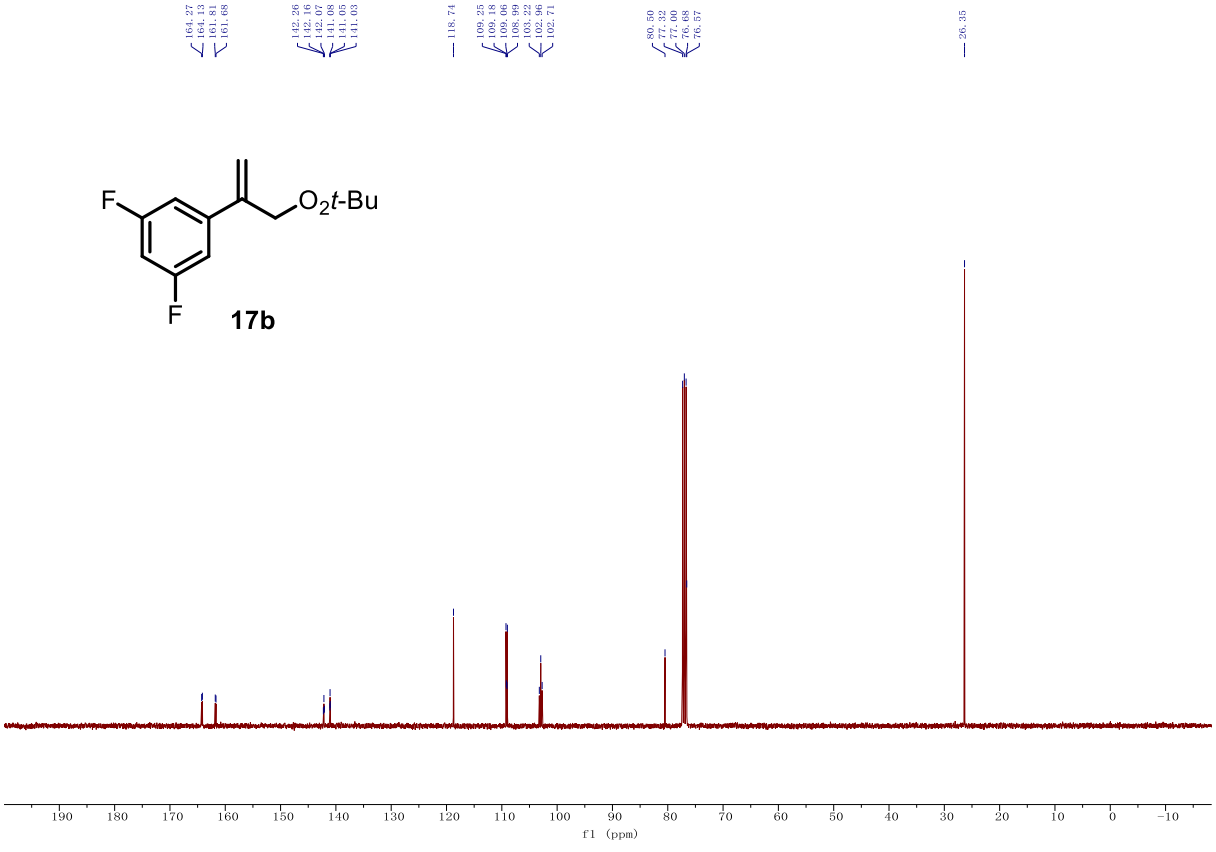
^{13}C NMR (101 MHz, $CDCl_3$)



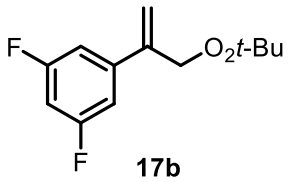
^{1}H NMR (400 MHz, $CDCl_3$)



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

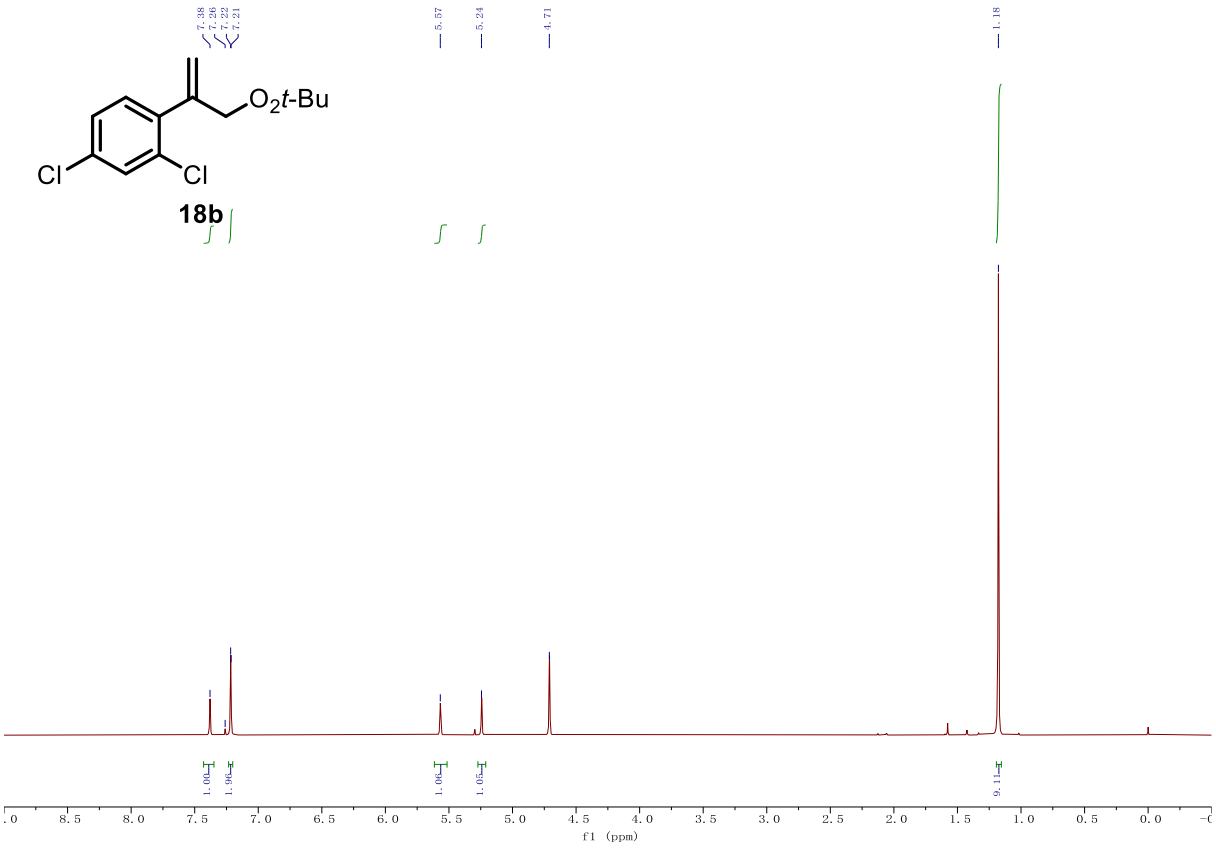


^{19}F NMR (376 MHz, $CDCl_3$)

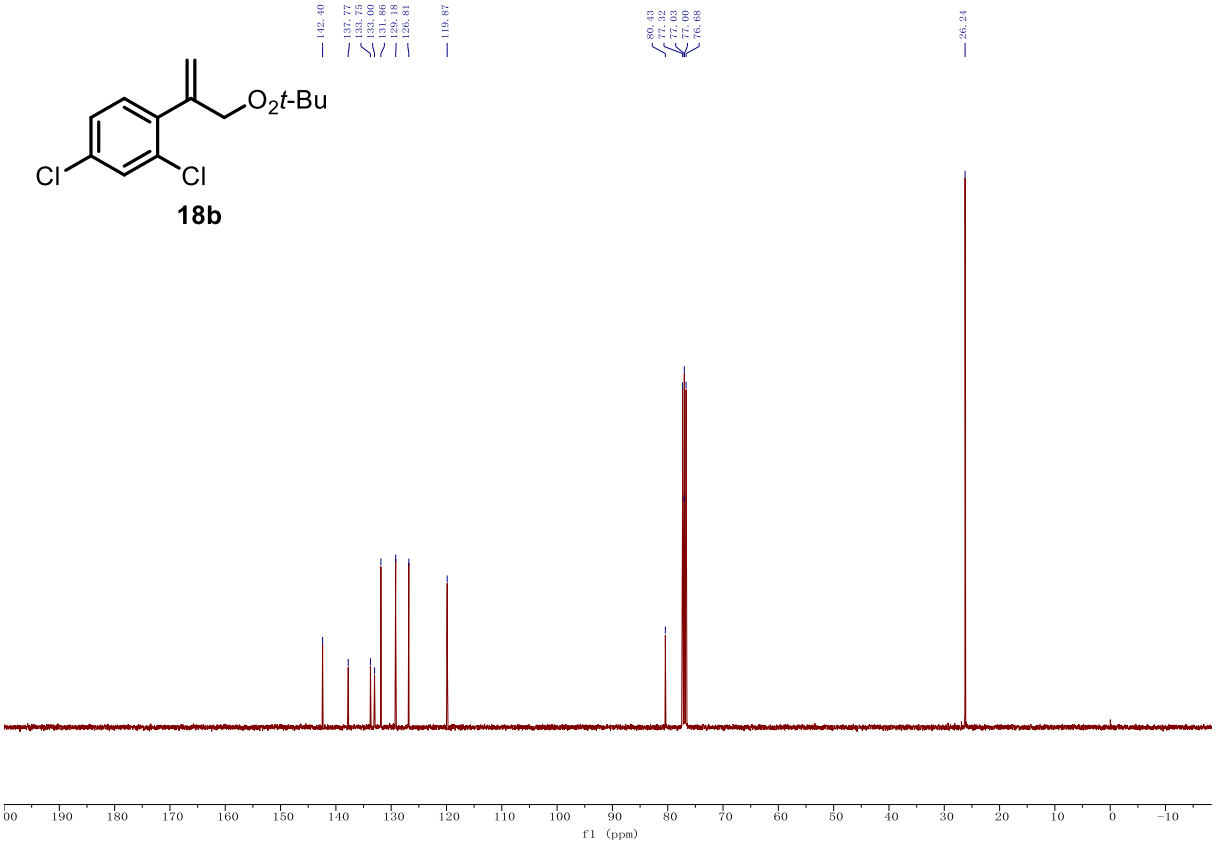


17b

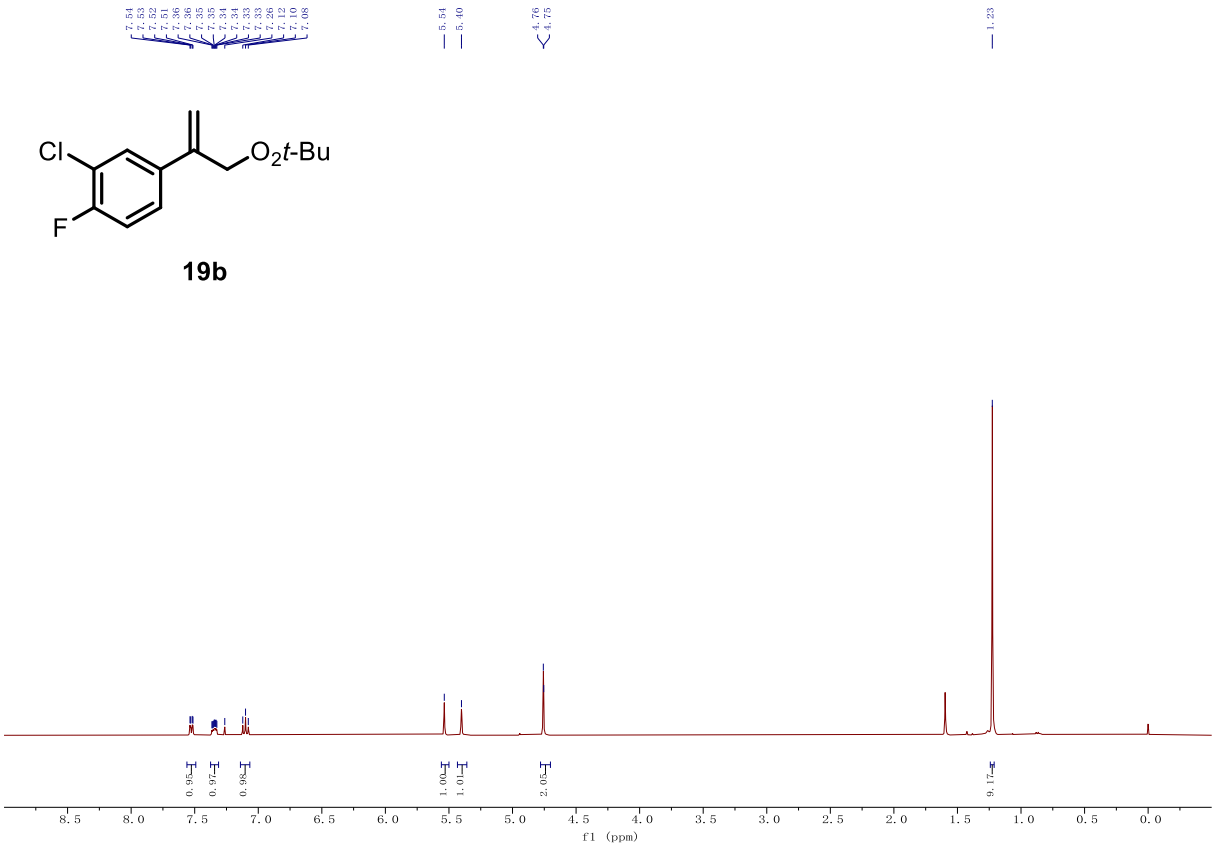
^{1}H NMR (400 MHz, $CDCl_3$)



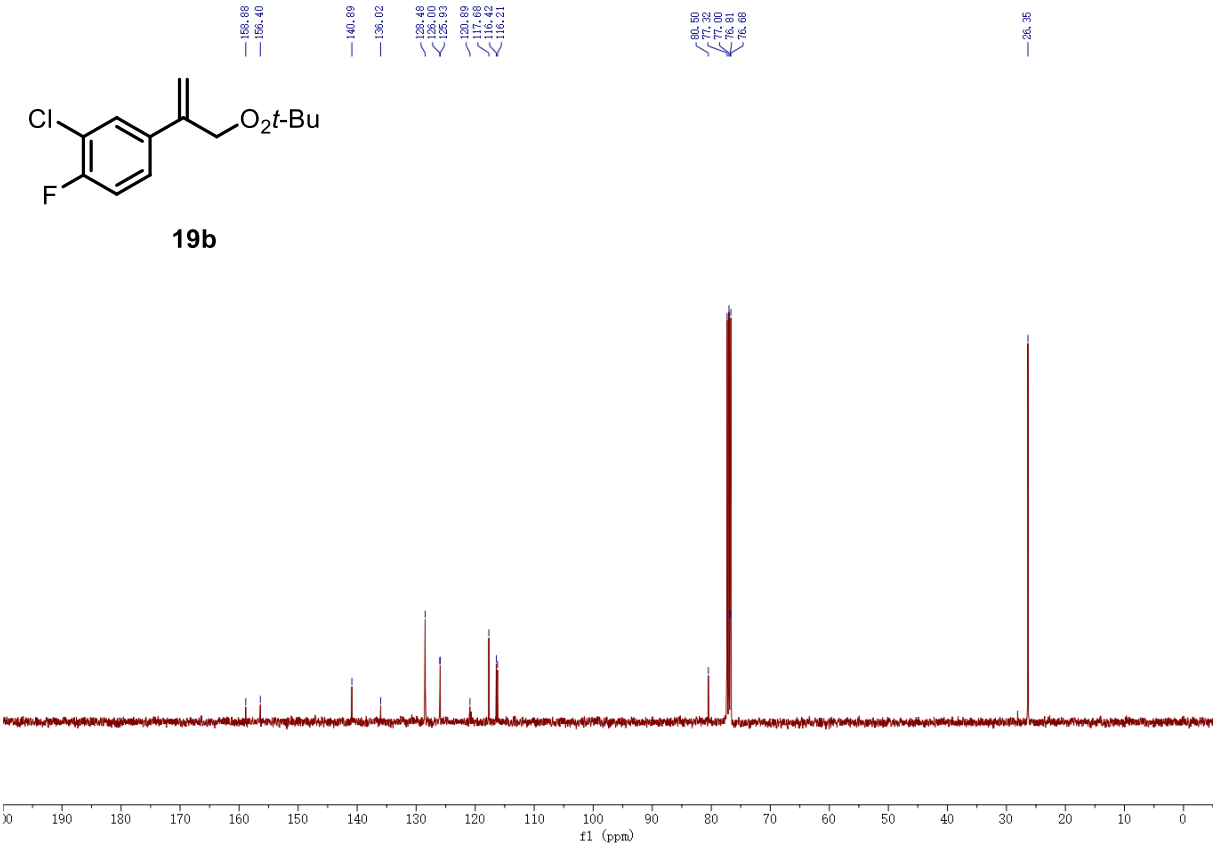
^{13}C NMR (101 MHz, $CDCl_3$)



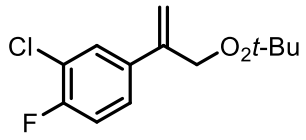
^{1}H NMR (400 MHz, $CDCl_3$)



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

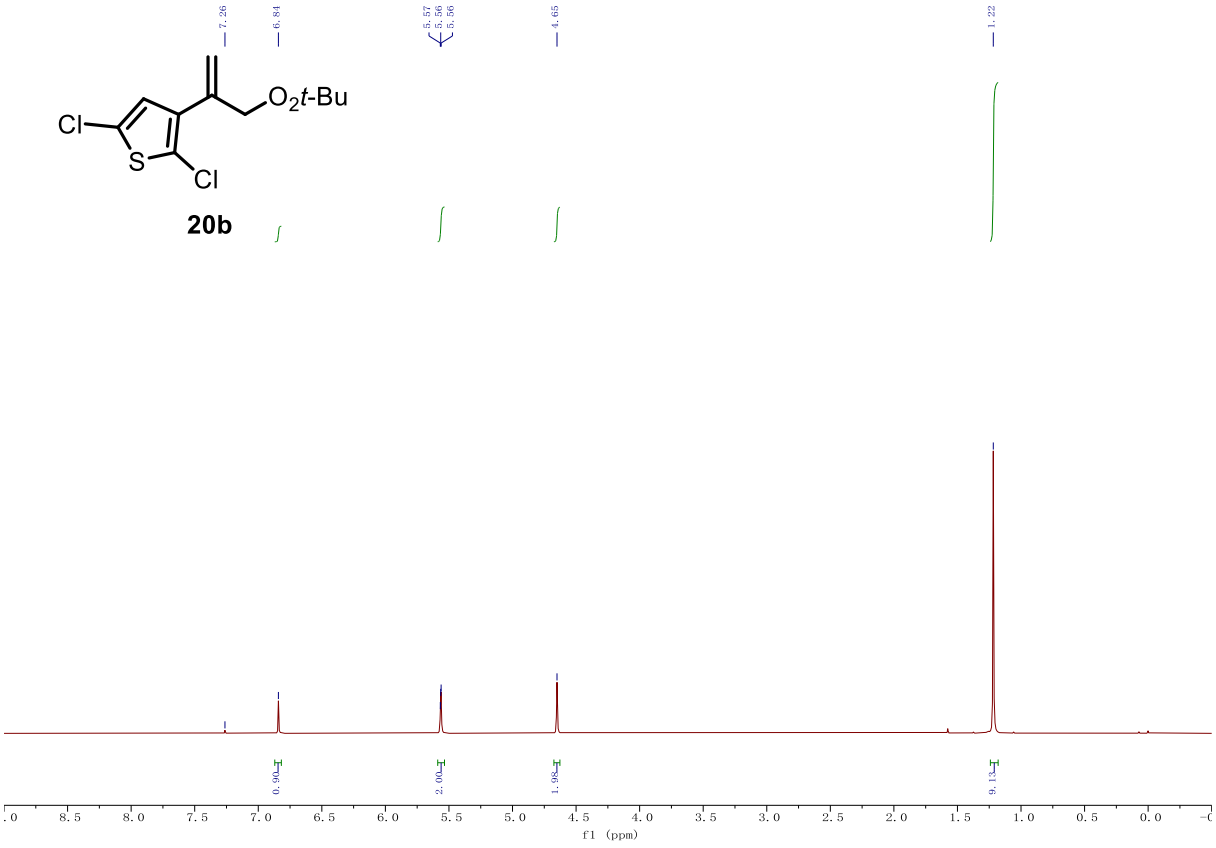


^{19}F NMR (376 MHz, $CDCl_3$)

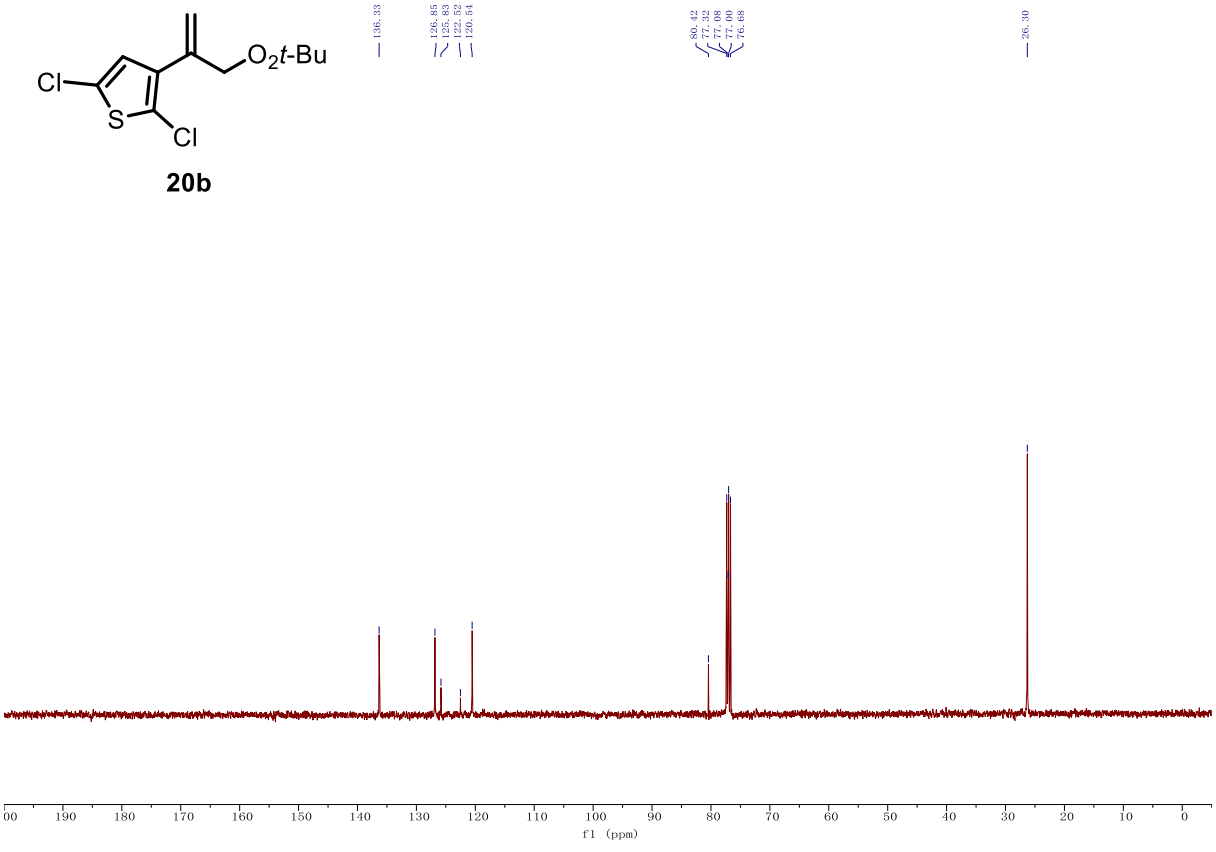


19b

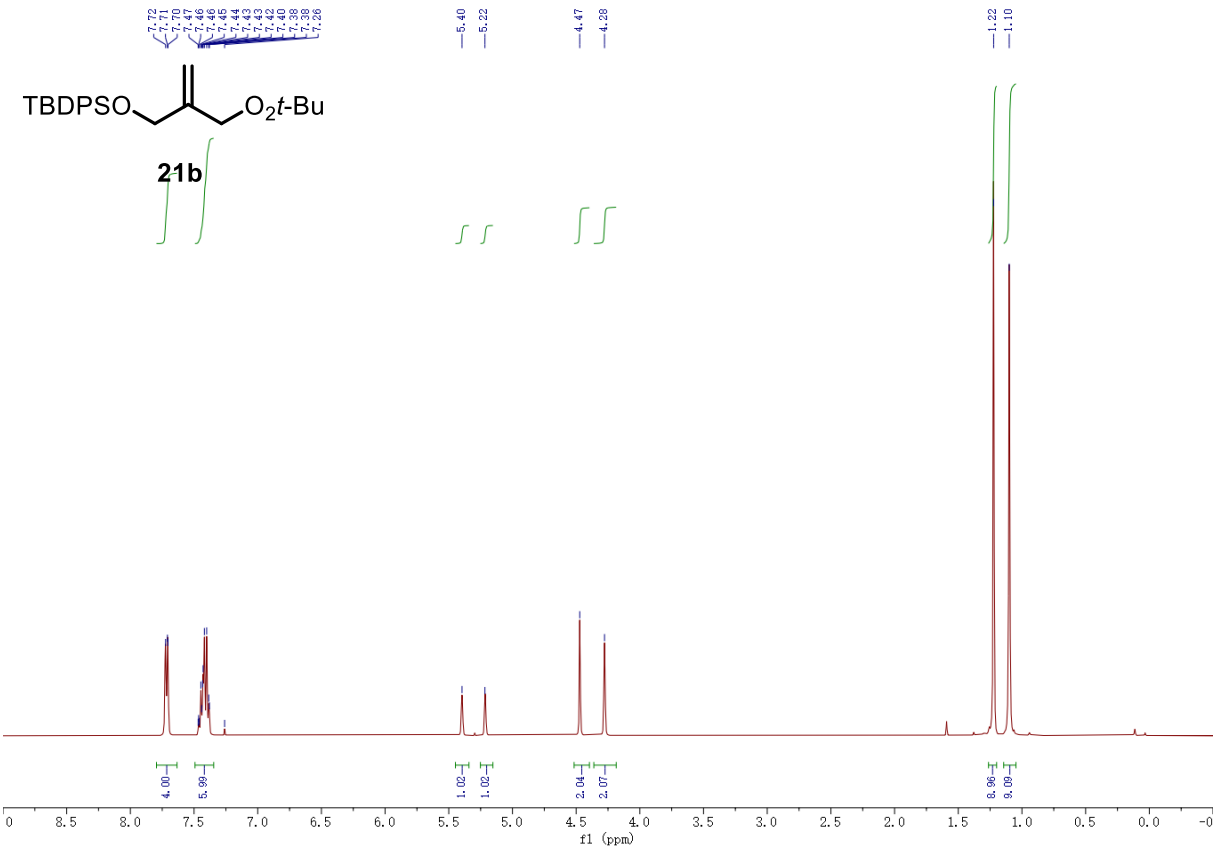
^{1}H NMR (400 MHz, $CDCl_3$)



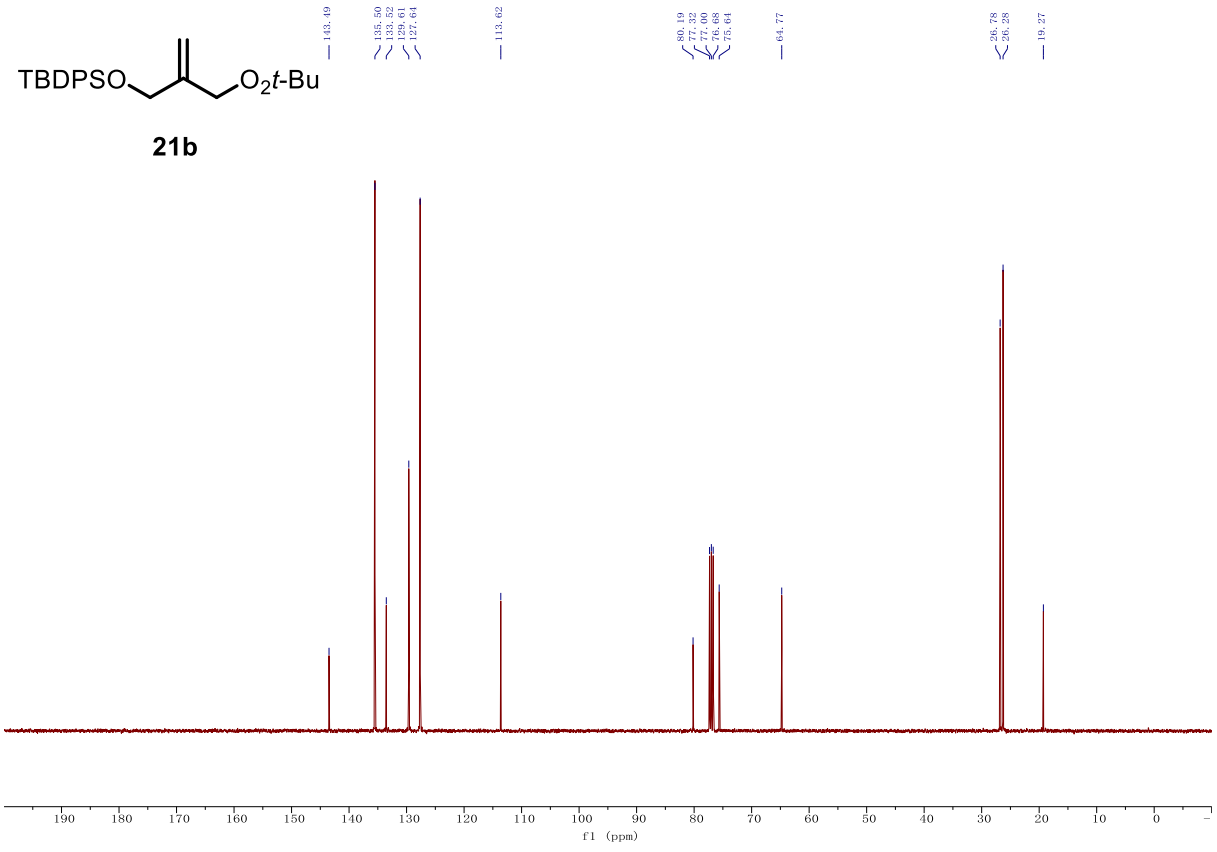
^{13}C NMR (101 MHz, $CDCl_3$)



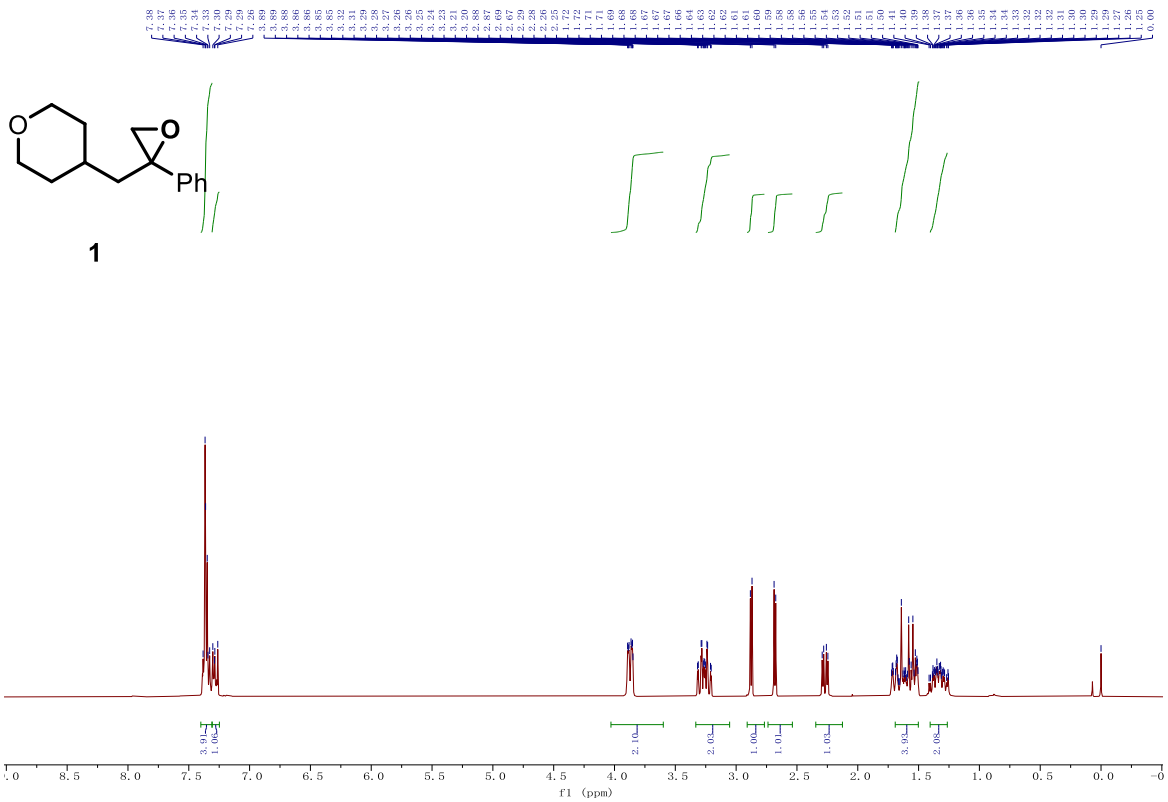
^{1}H NMR (400 MHz, $CDCl_3$)



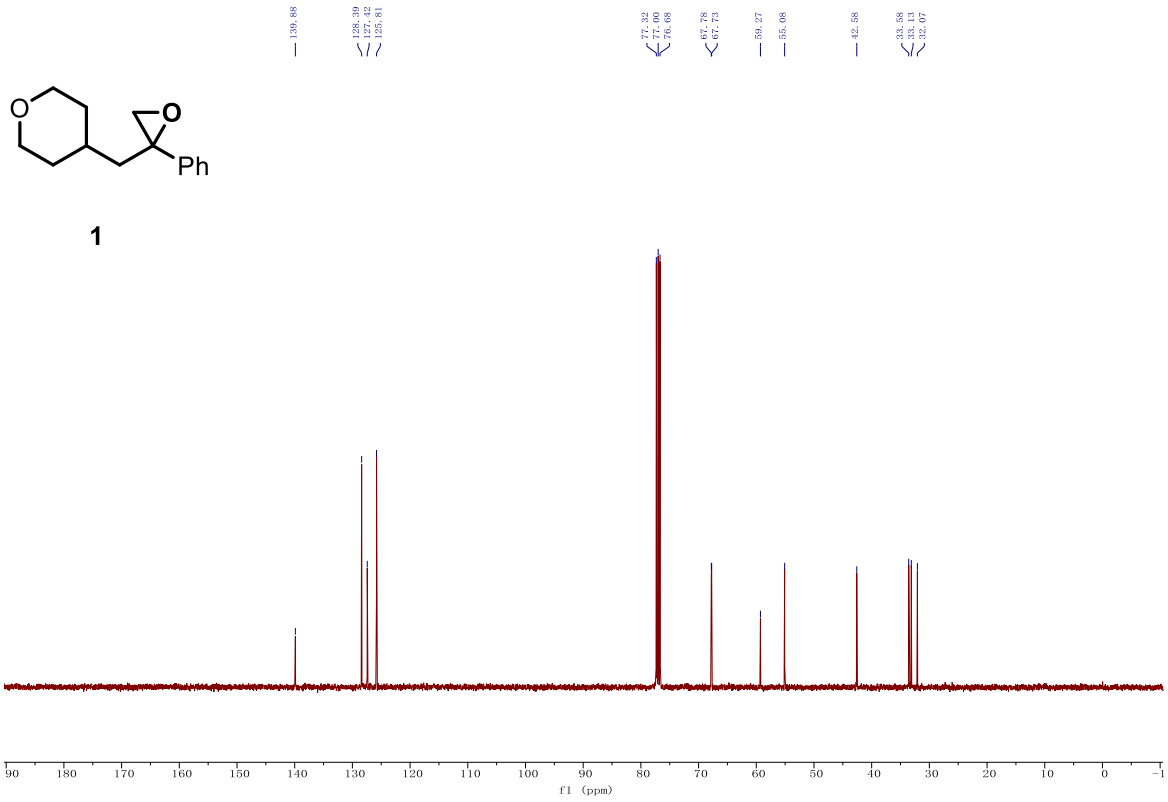
^{13}C NMR (101 MHz, $CDCl_3$)



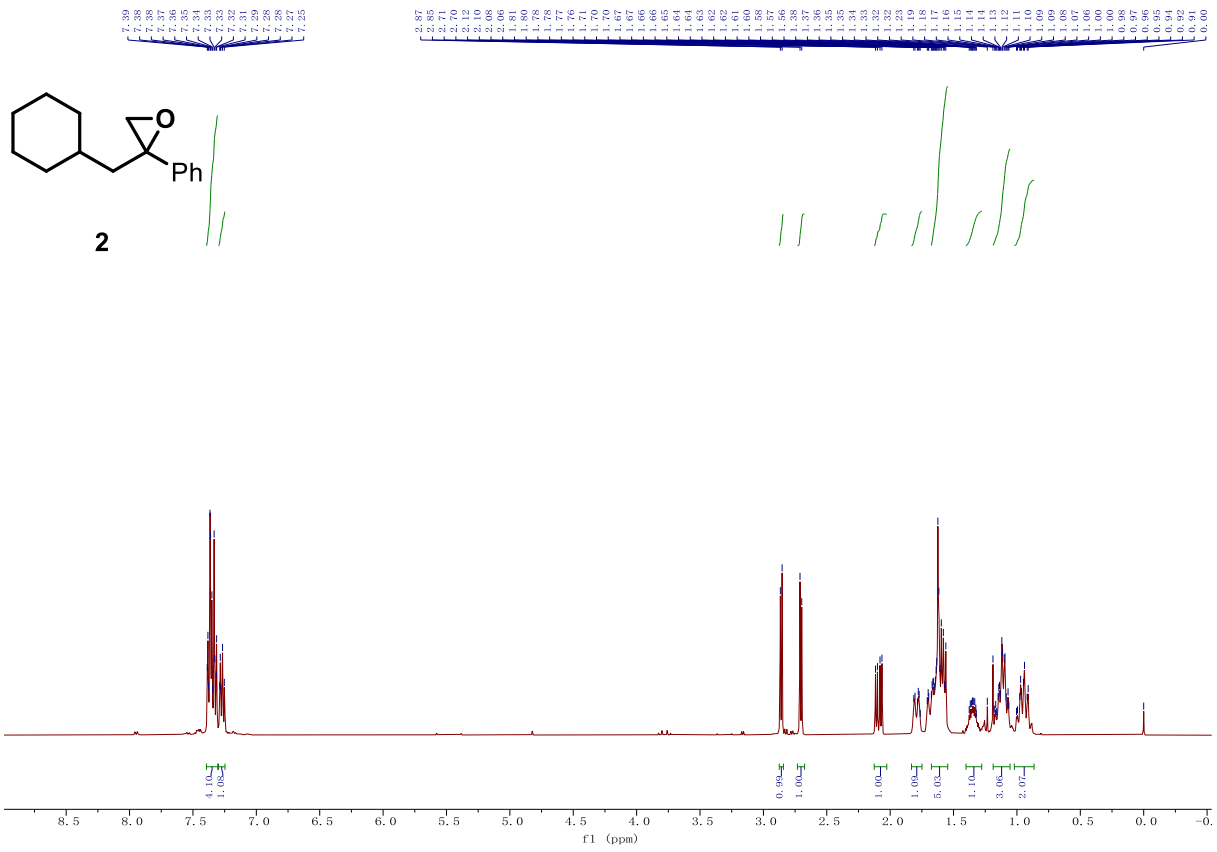
^{1}H NMR (400 MHz, $CDCl_3$)



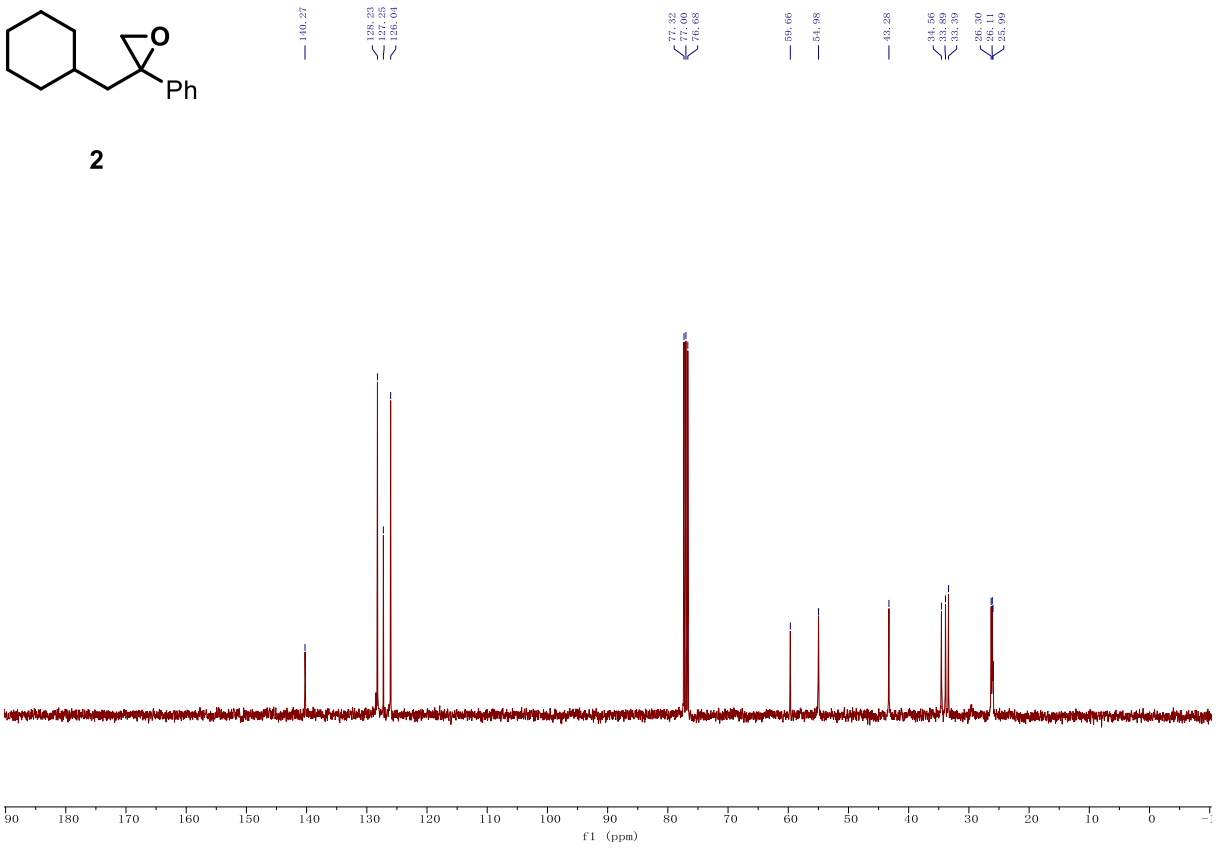
^{13}C NMR (101 MHz, $CDCl_3$)



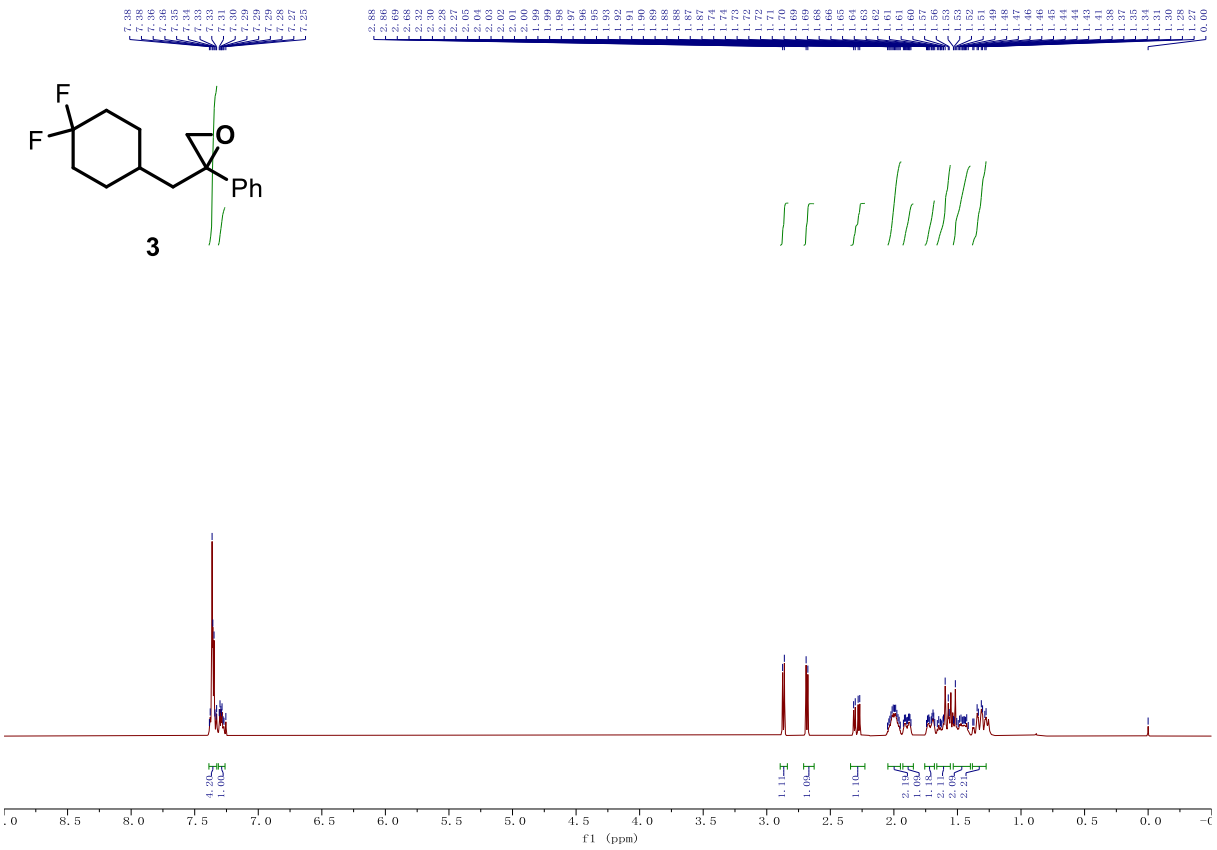
^{1}H NMR (400 MHz, $CDCl_3$)



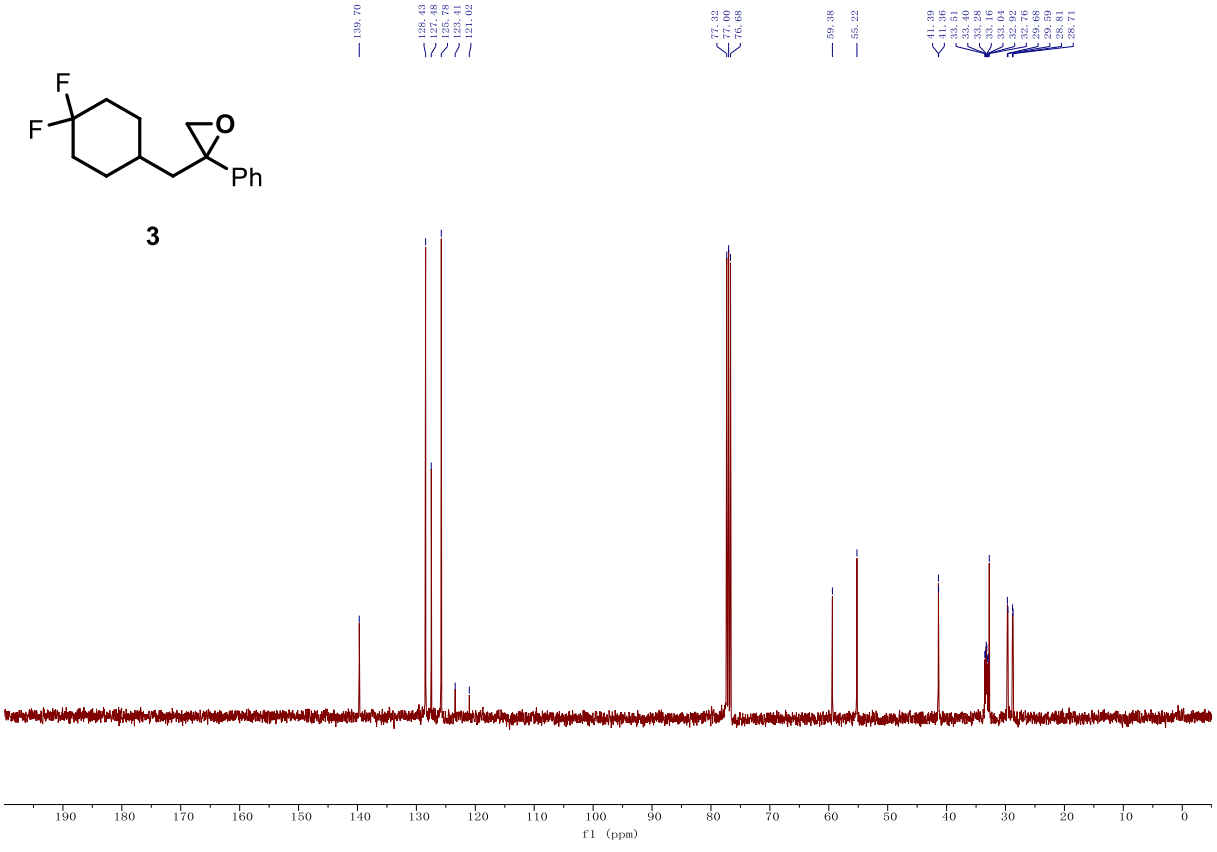
^{13}C NMR (101 MHz, $CDCl_3$)



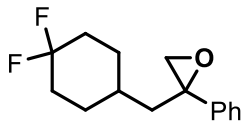
^{1}H NMR (400 MHz, $CDCl_3$)



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

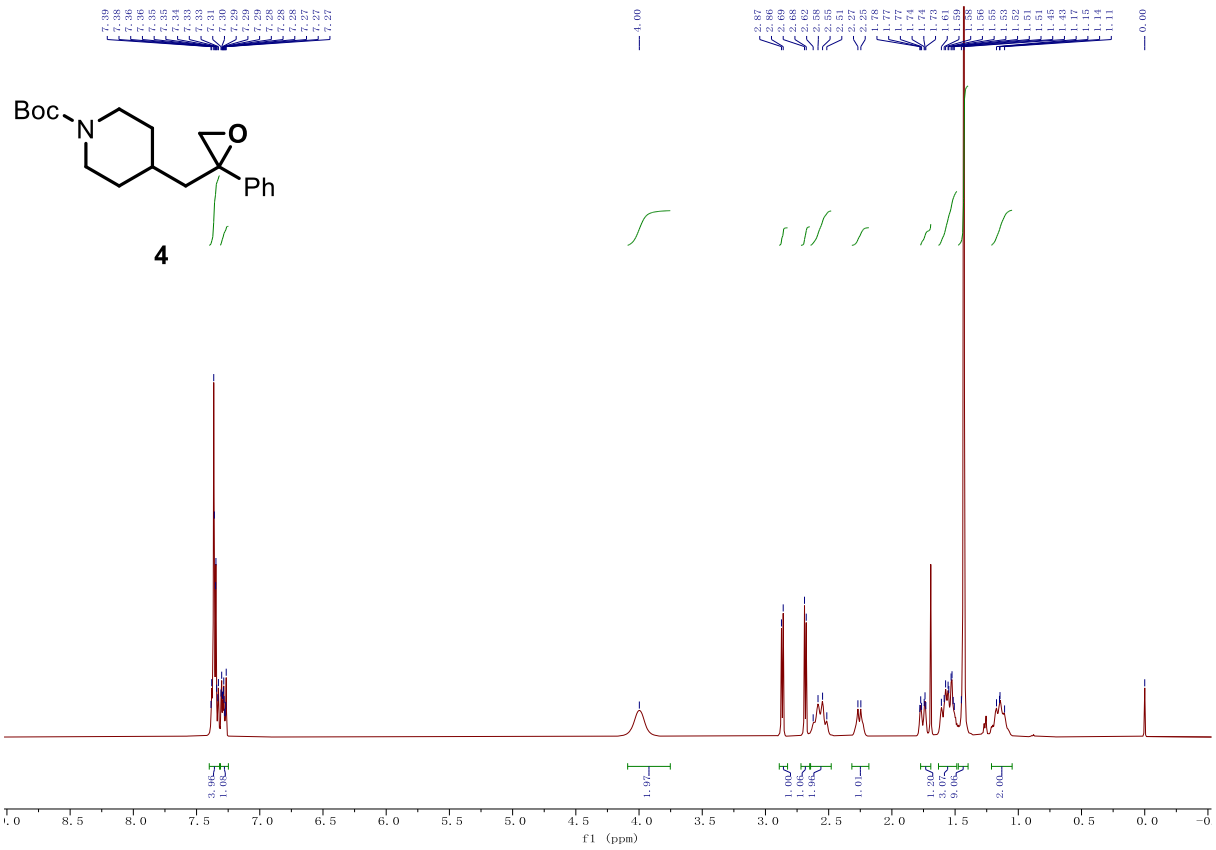


^{19}F NMR (376 MHz, $CDCl_3$)

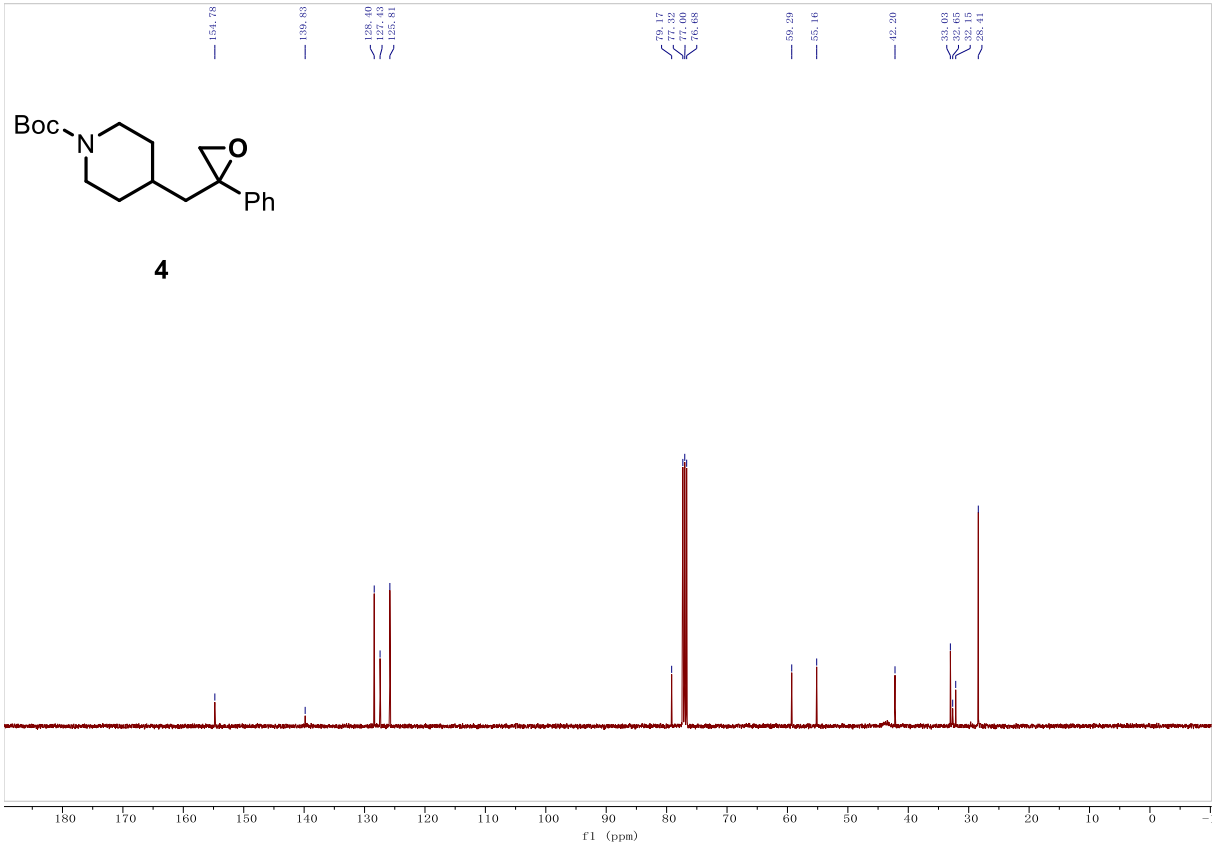


3

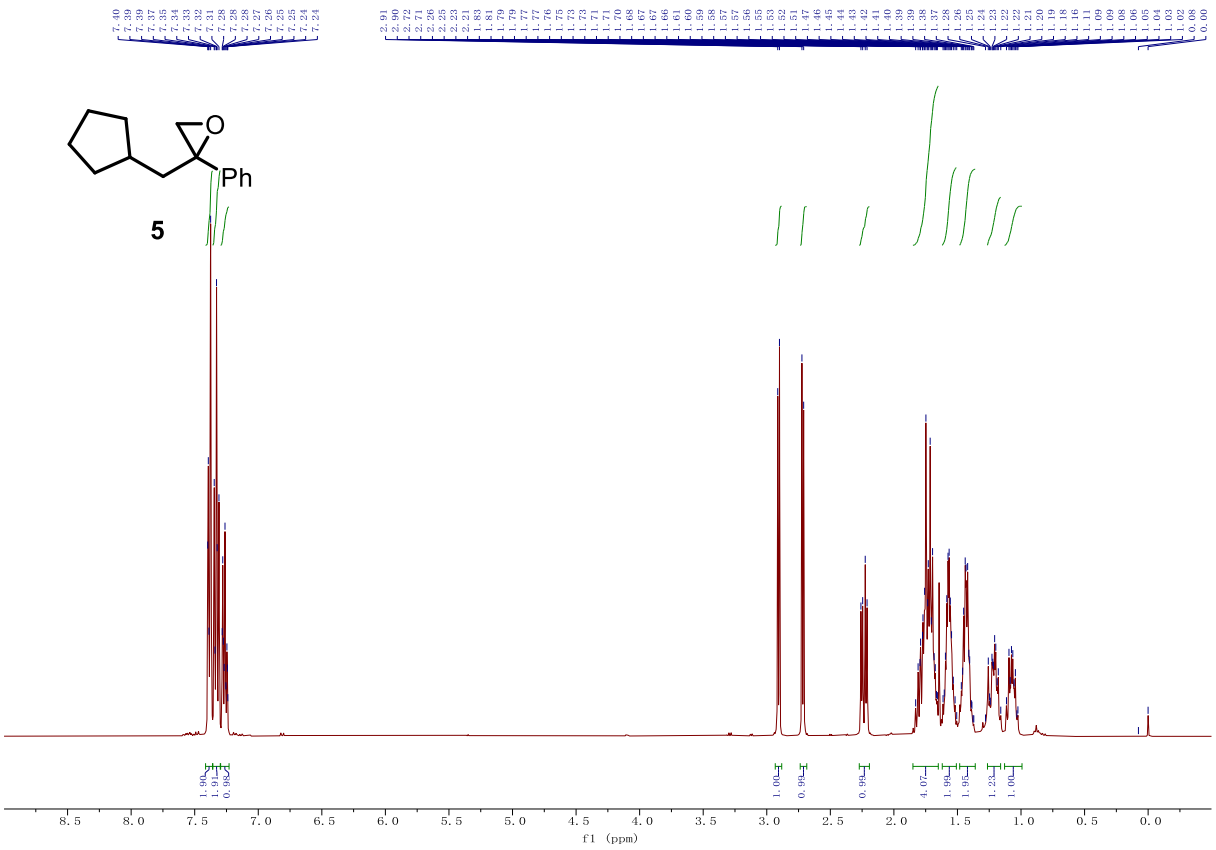
^{1}H NMR (400 MHz, $CDCl_3$)



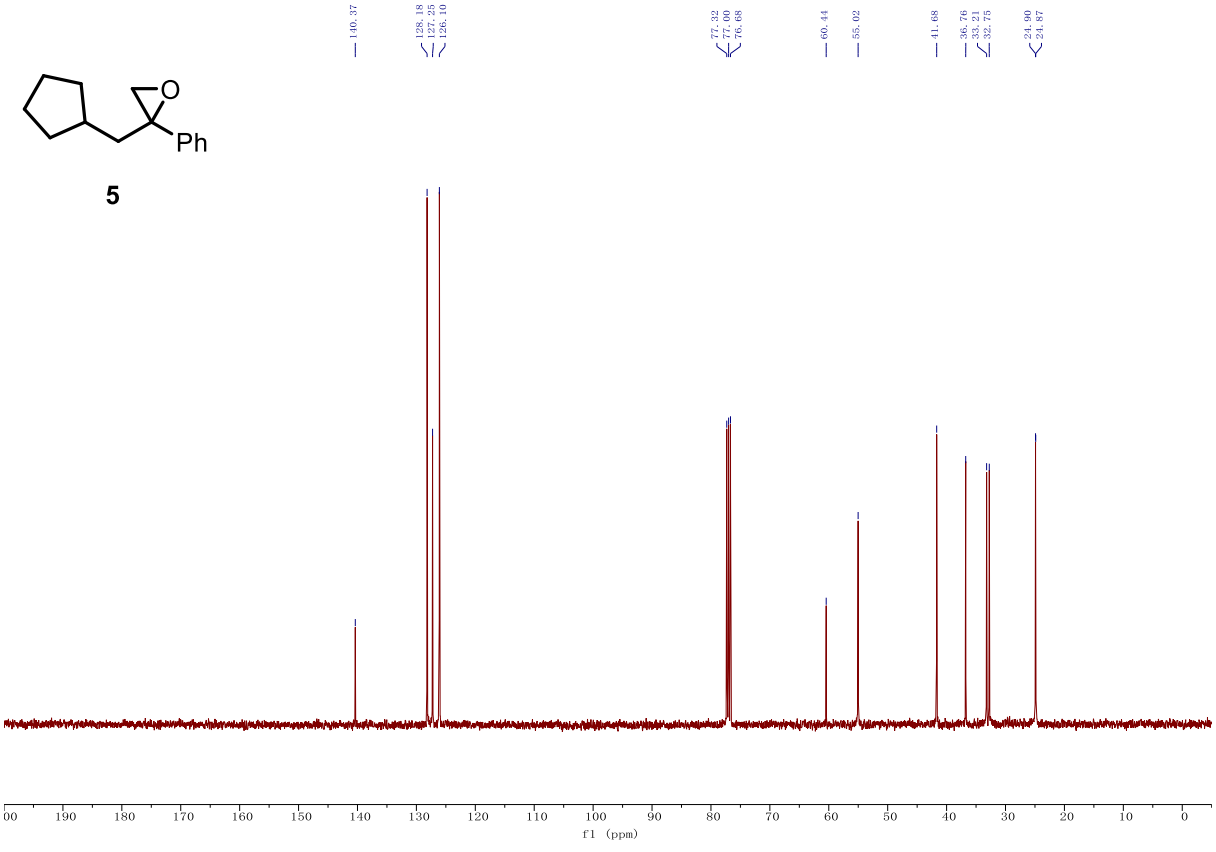
^{13}C NMR (101 MHz, $CDCl_3$)



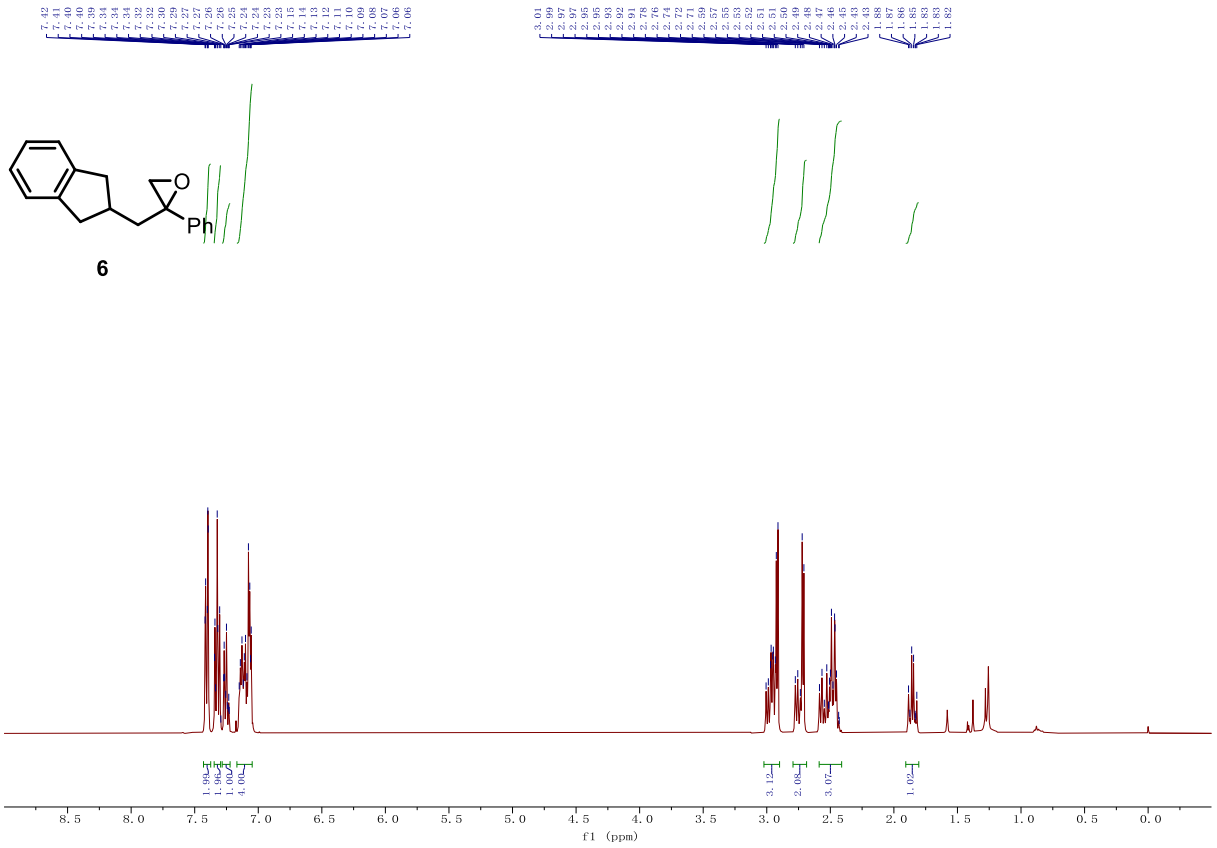
^{1}H NMR (400 MHz, $CDCl_3$)



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

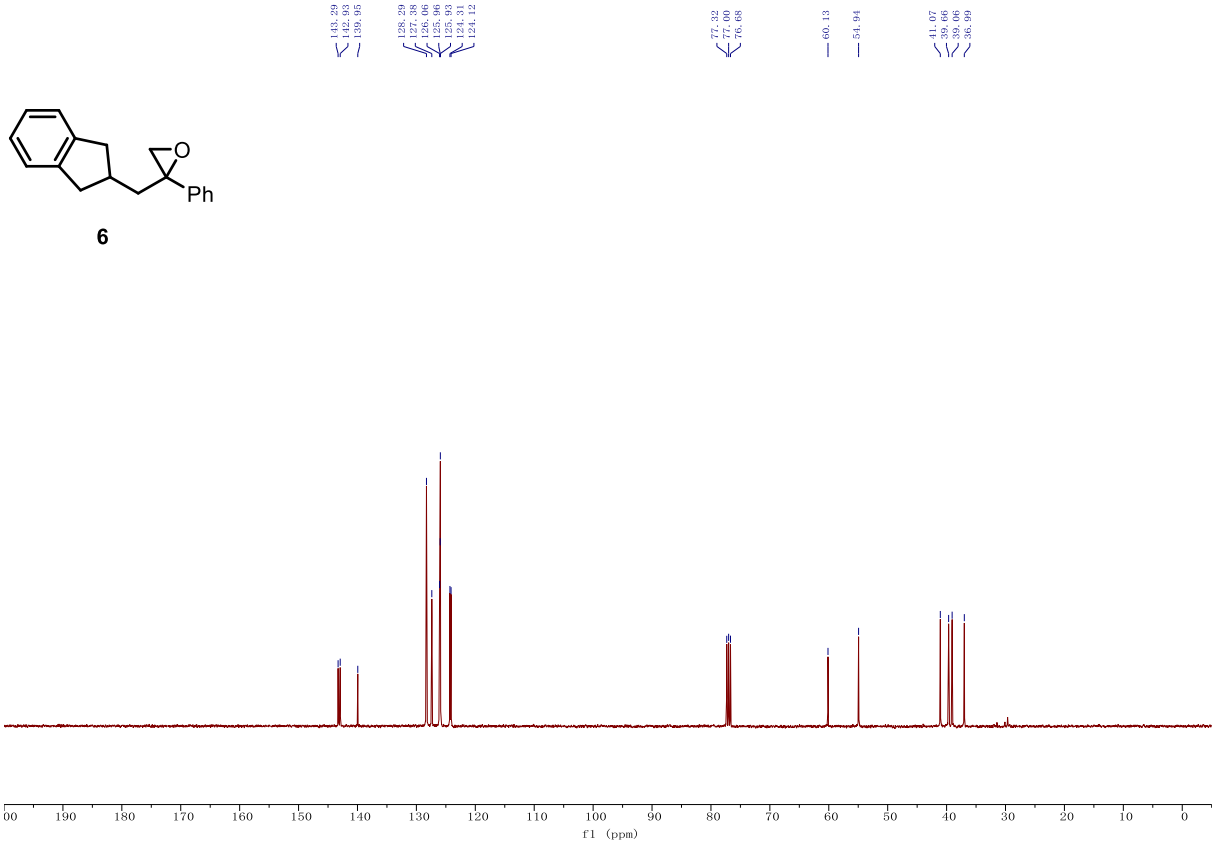


^{1}H NMR (400 MHz, $CDCl_3$)



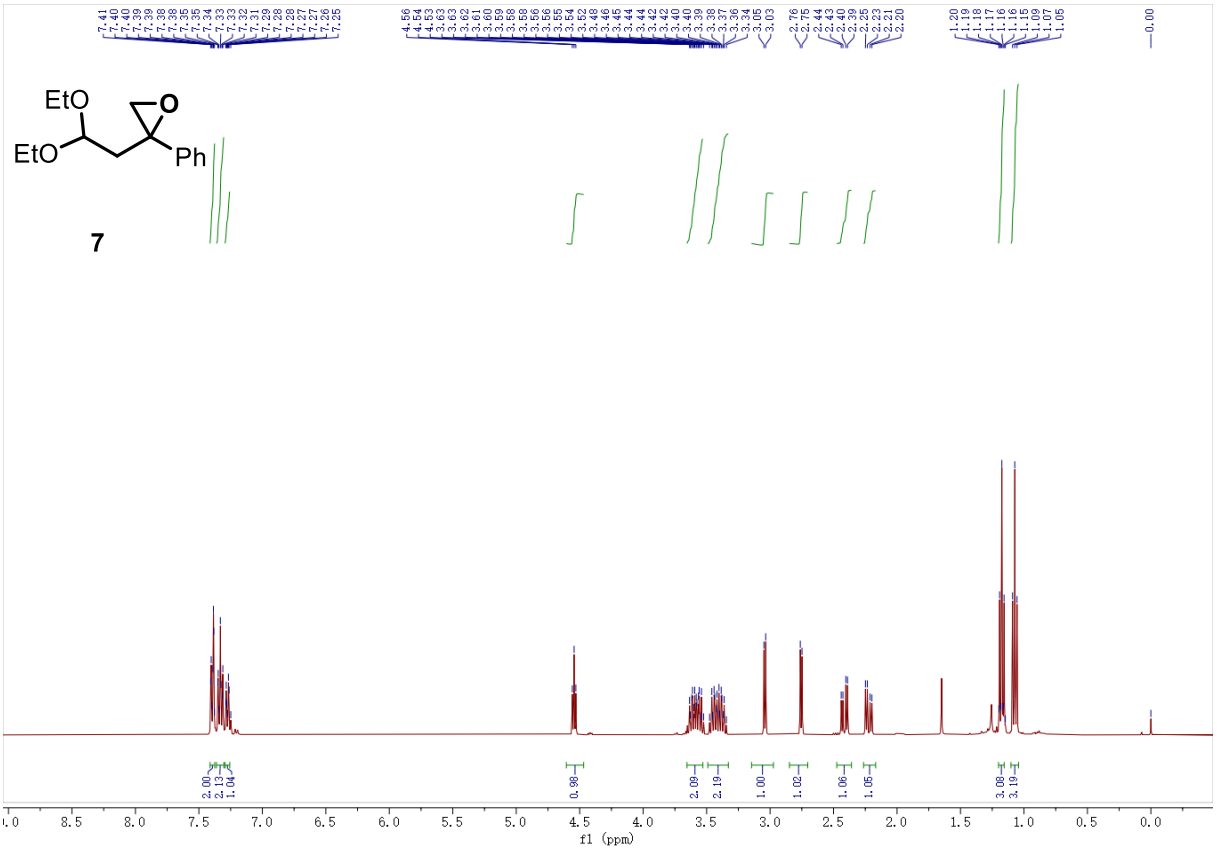
6

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

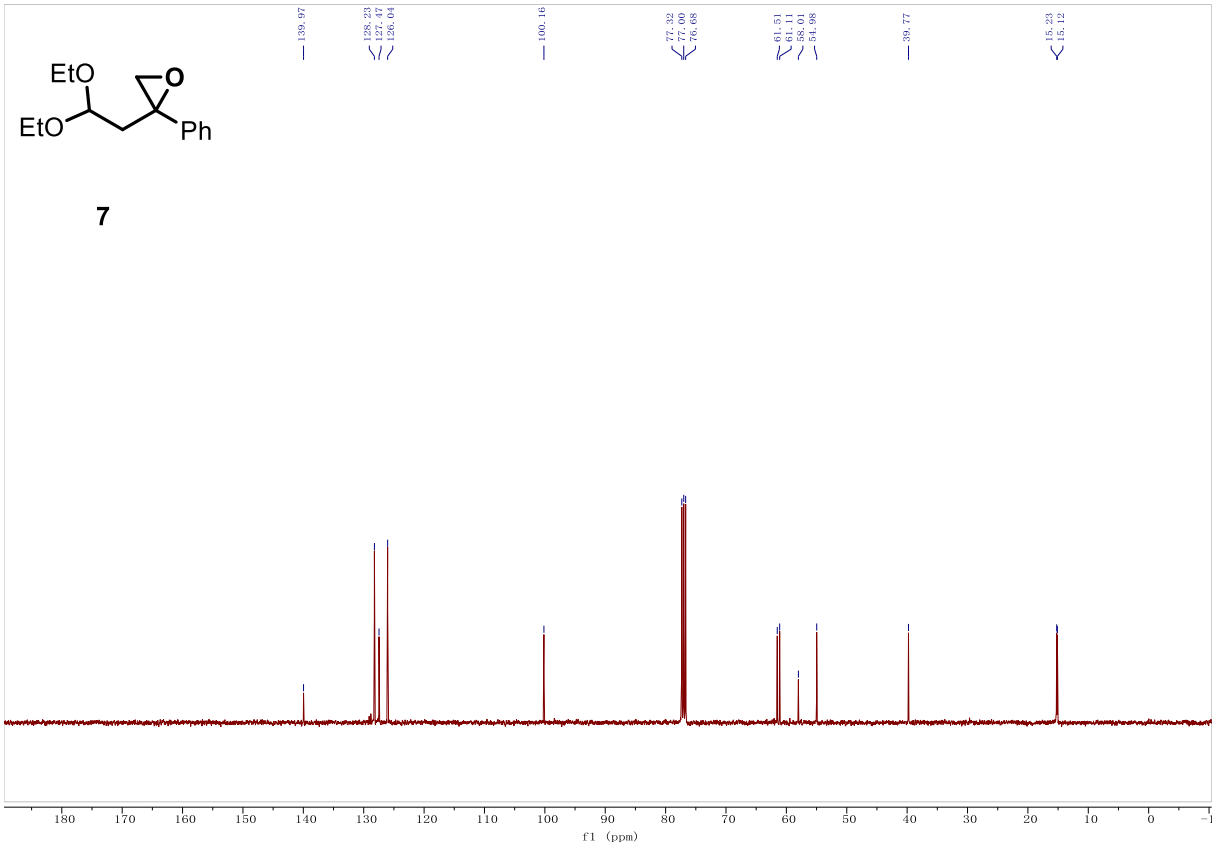


6

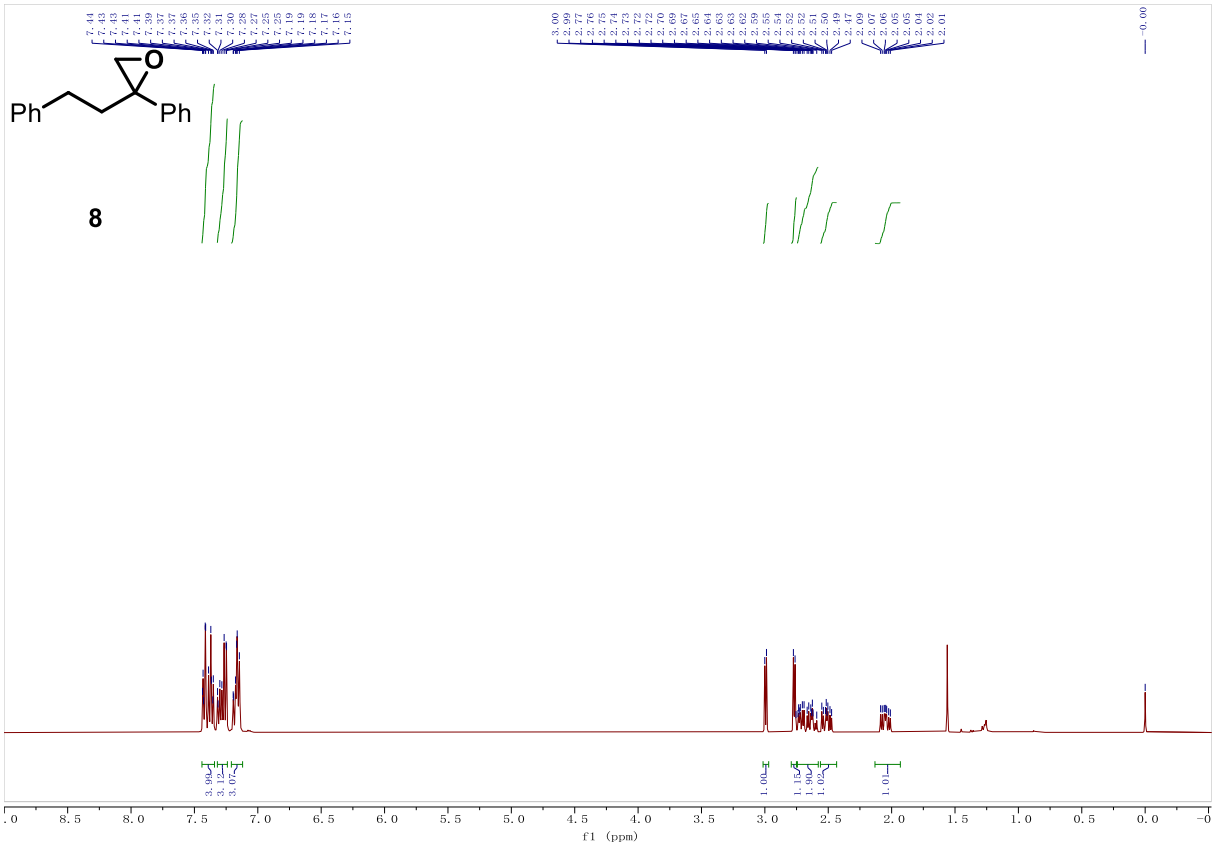
^{1}H NMR (400 MHz, $CDCl_3$)



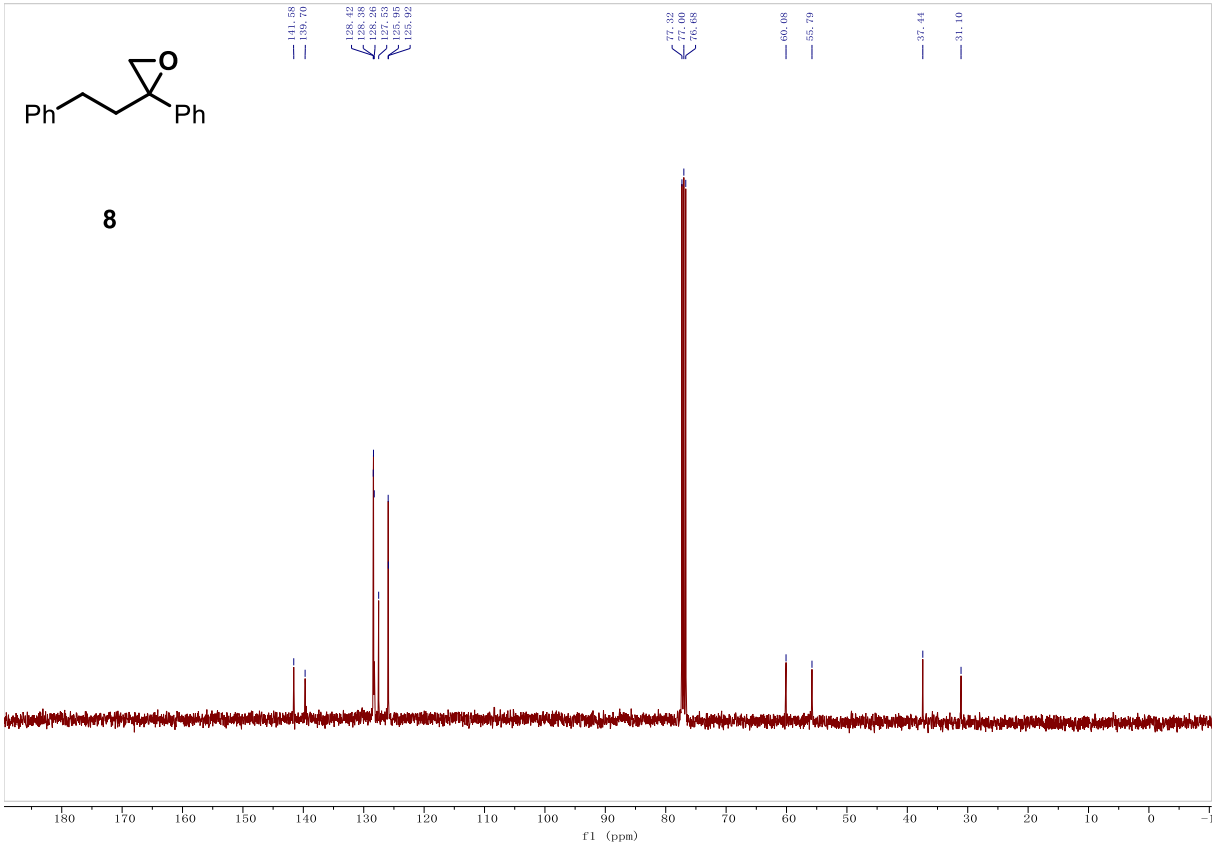
^{13}C NMR (101 MHz, $CDCl_3$)



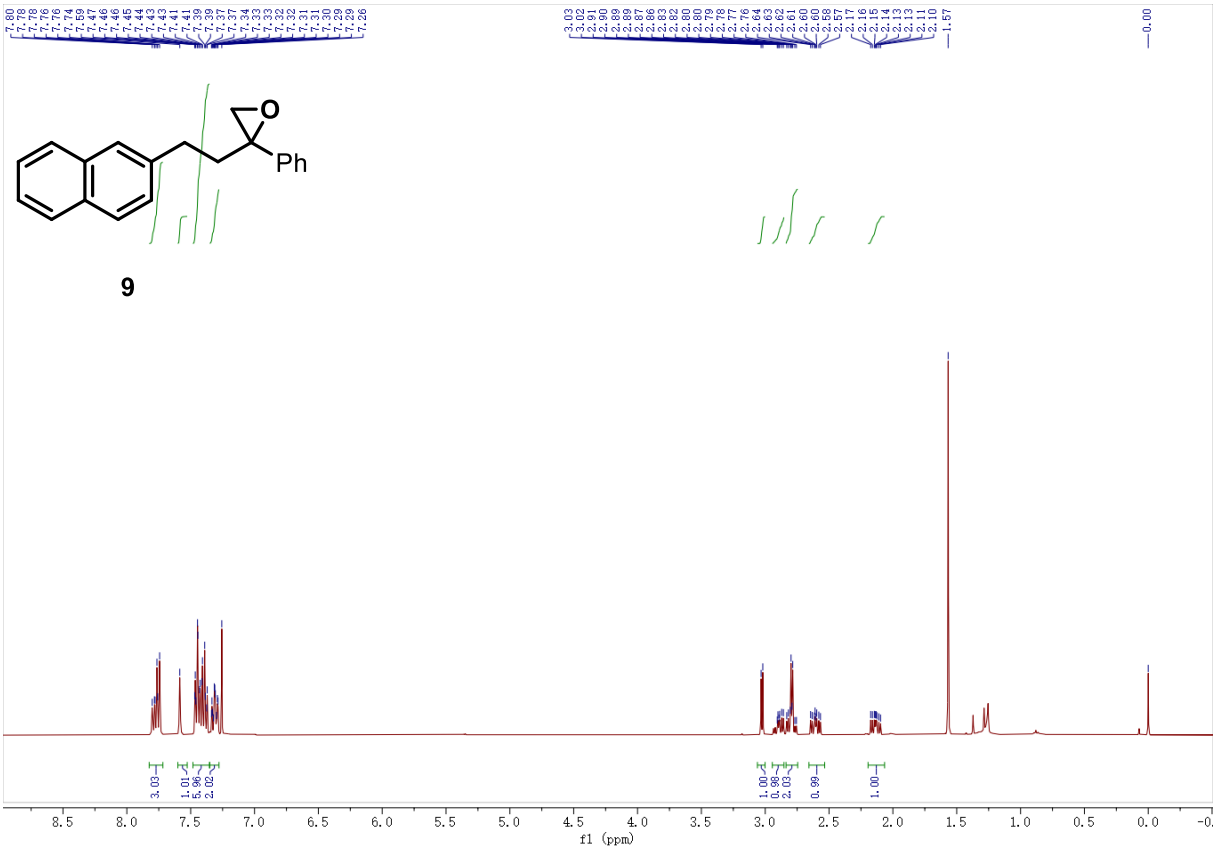
^{1}H NMR (400 MHz, $CDCl_3$)



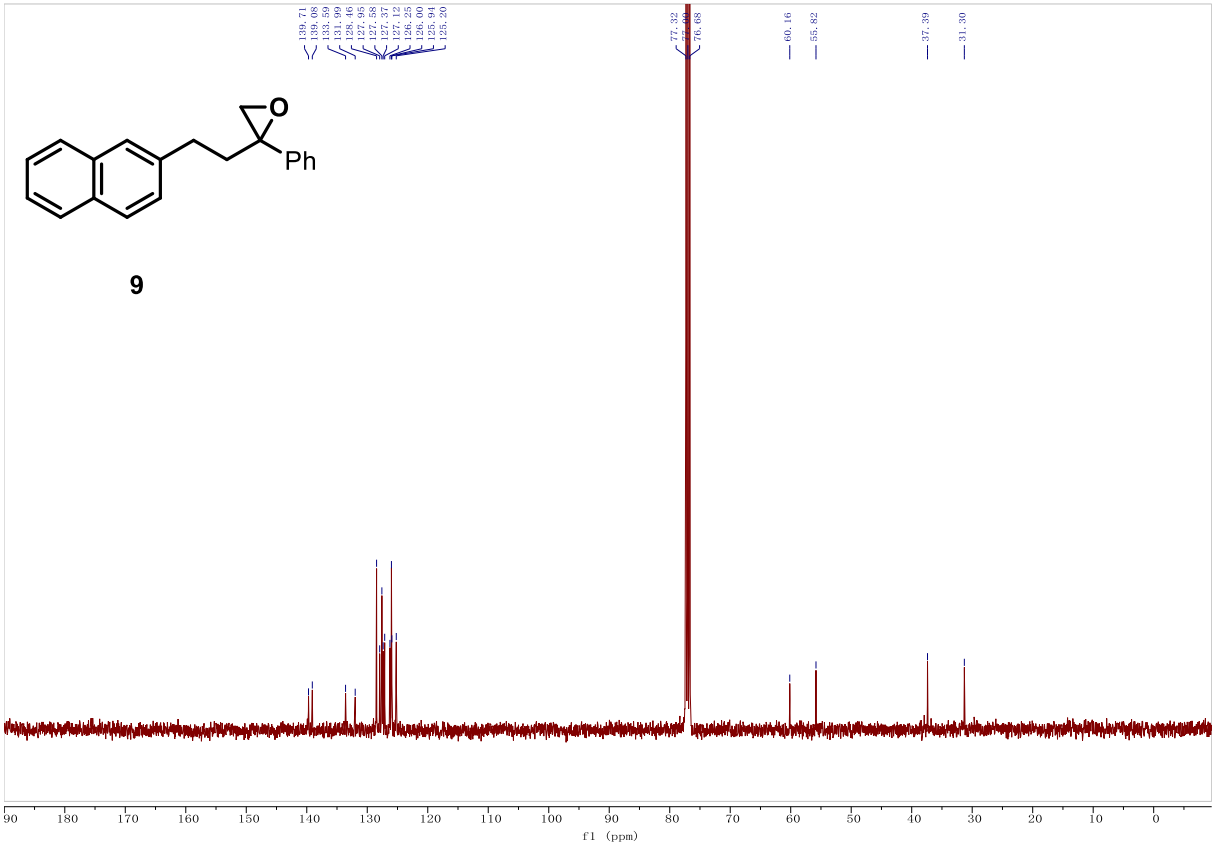
^{13}C NMR (101 MHz, $CDCl_3$)



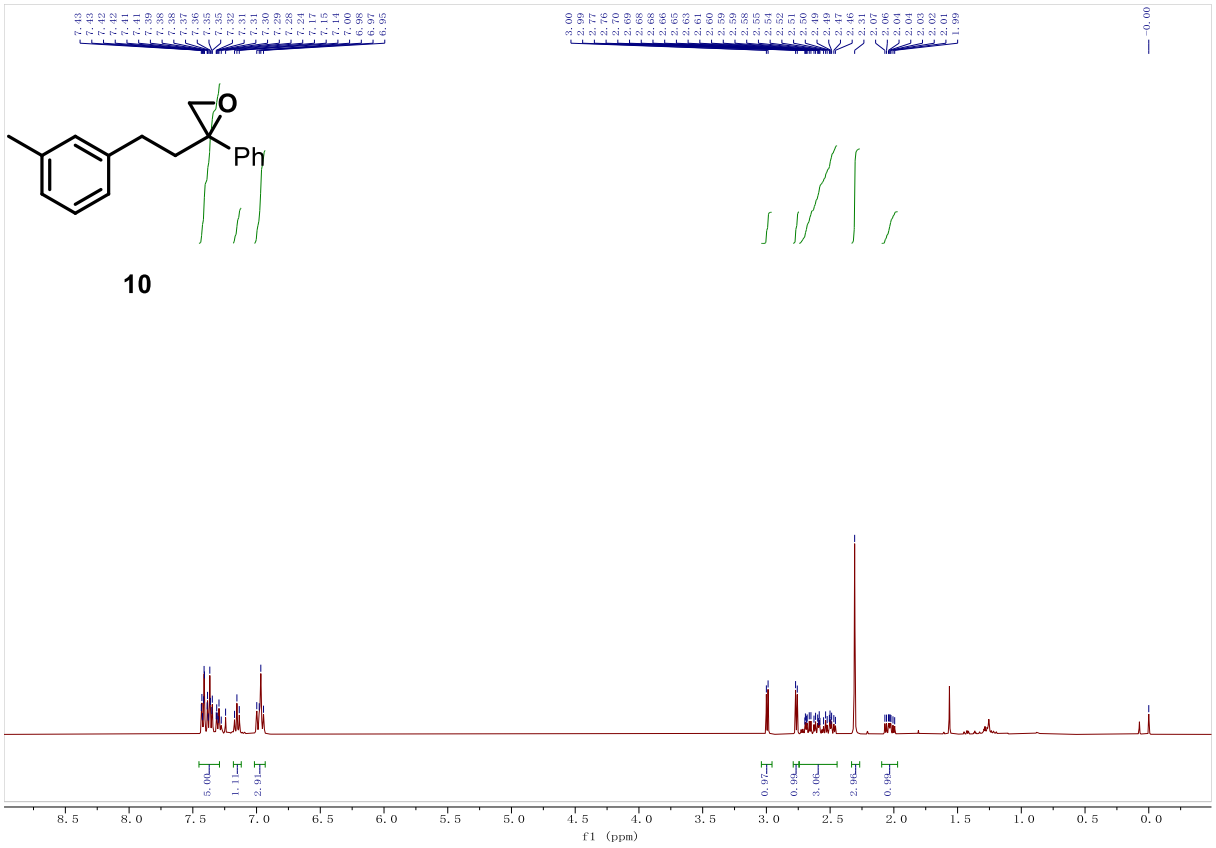
^{1}H NMR (400 MHz, $CDCl_3$)



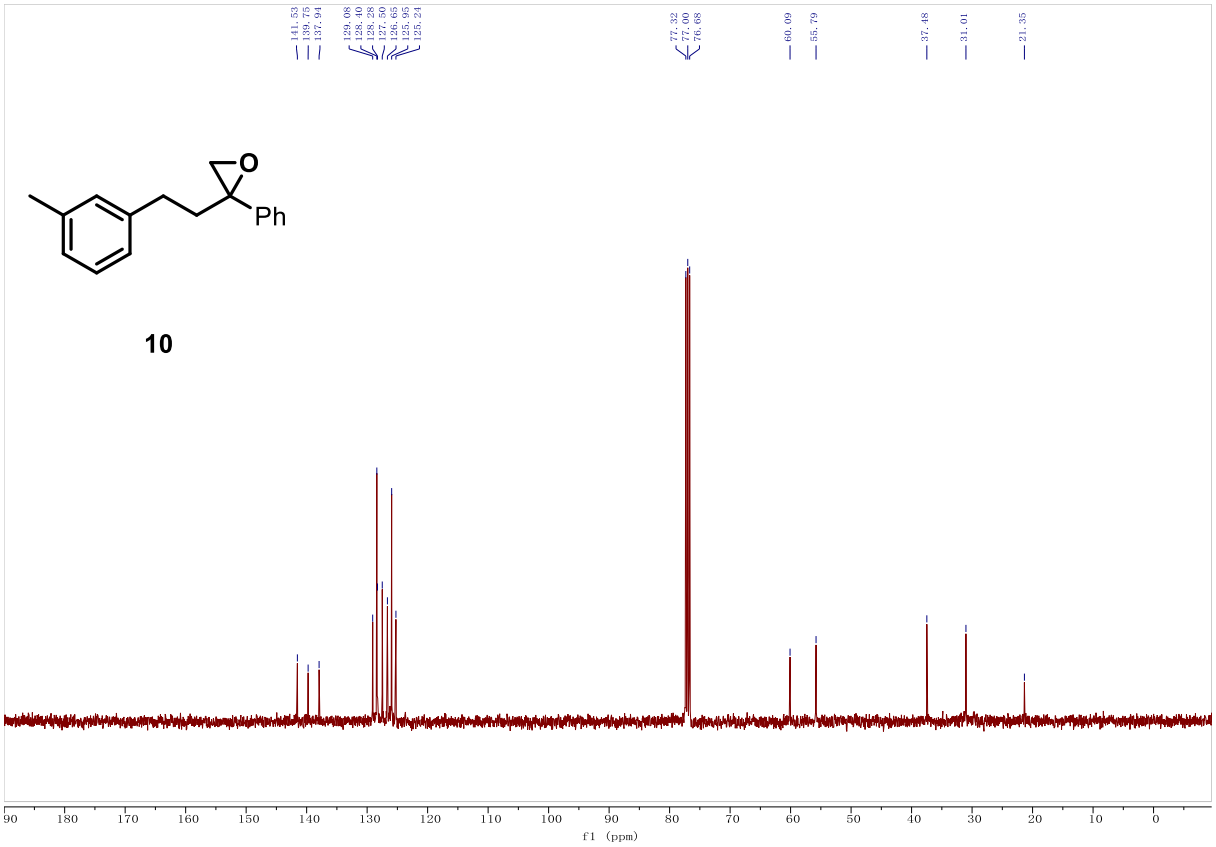
^{13}C NMR (101 MHz, $CDCl_3$)



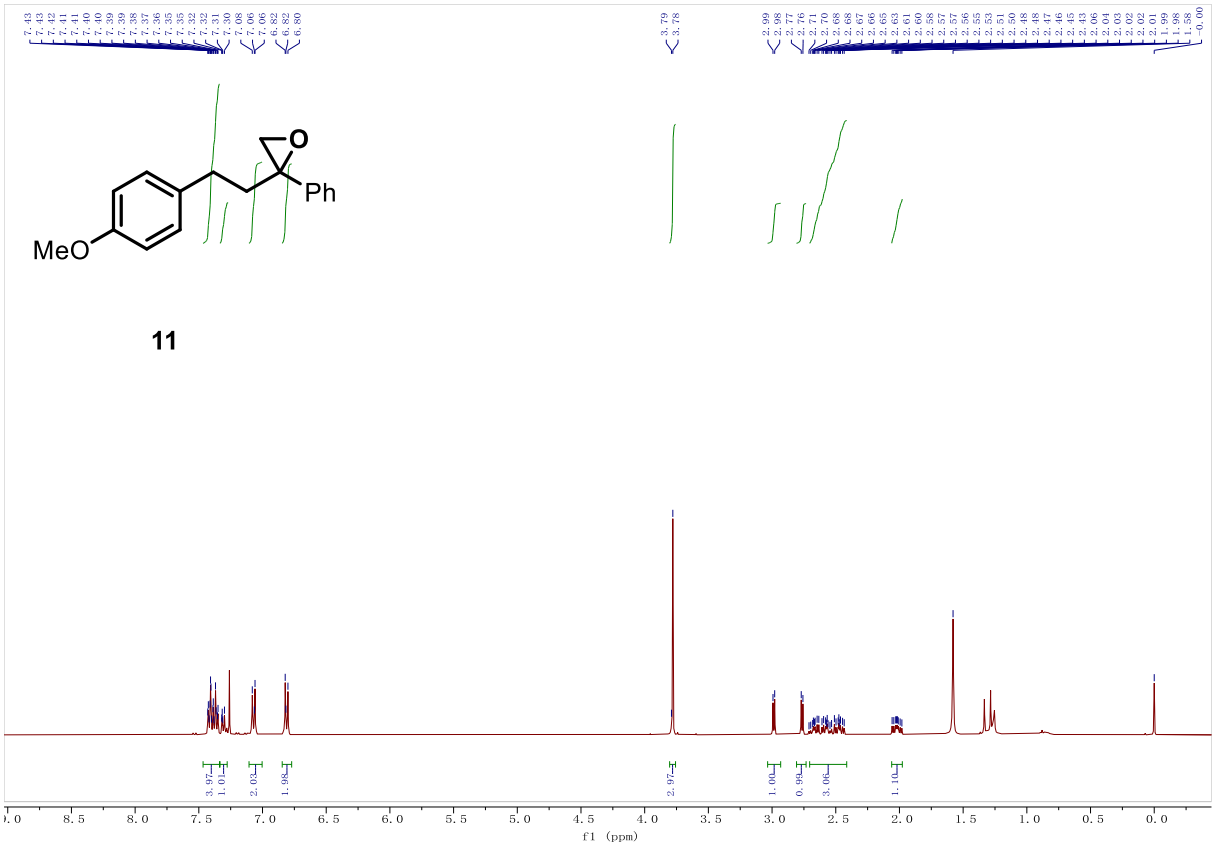
^{1}H NMR (400 MHz, $CDCl_3$)



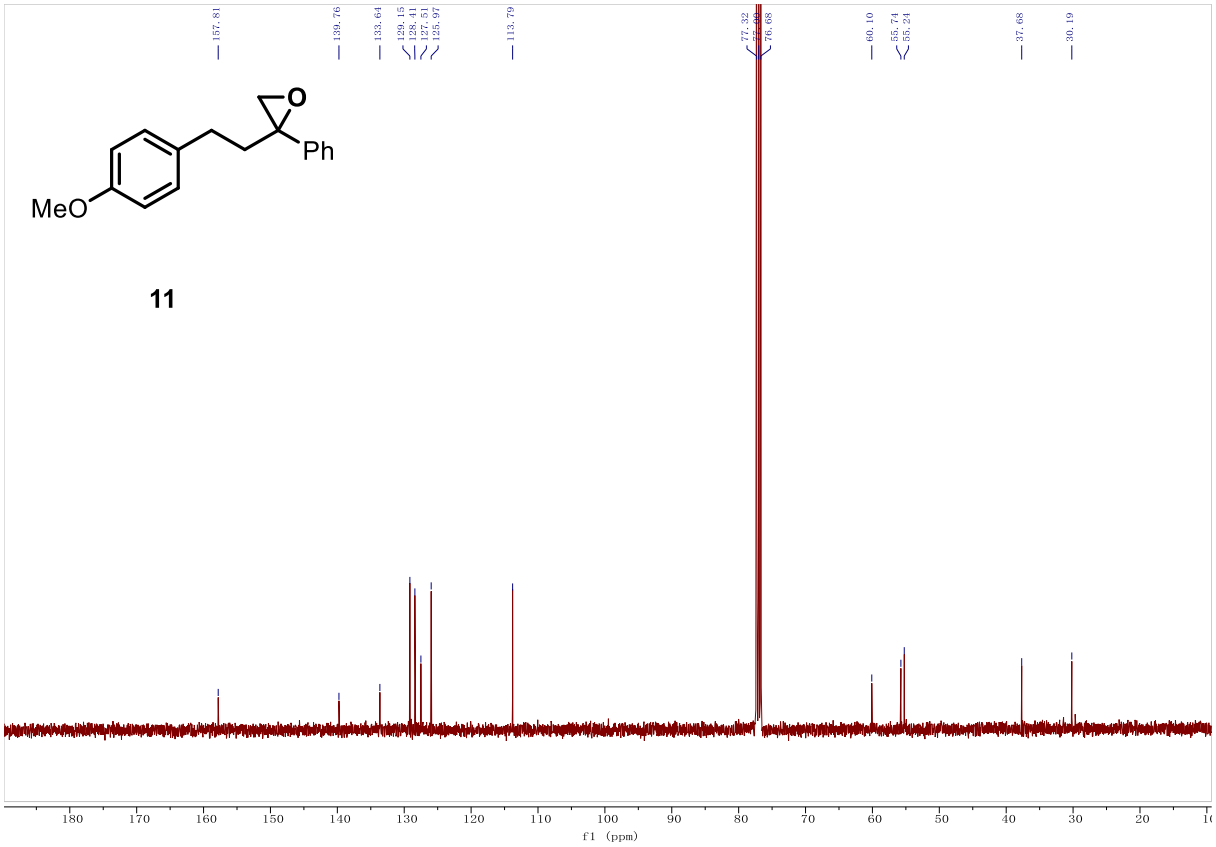
^{13}C NMR (101 MHz, $CDCl_3$)



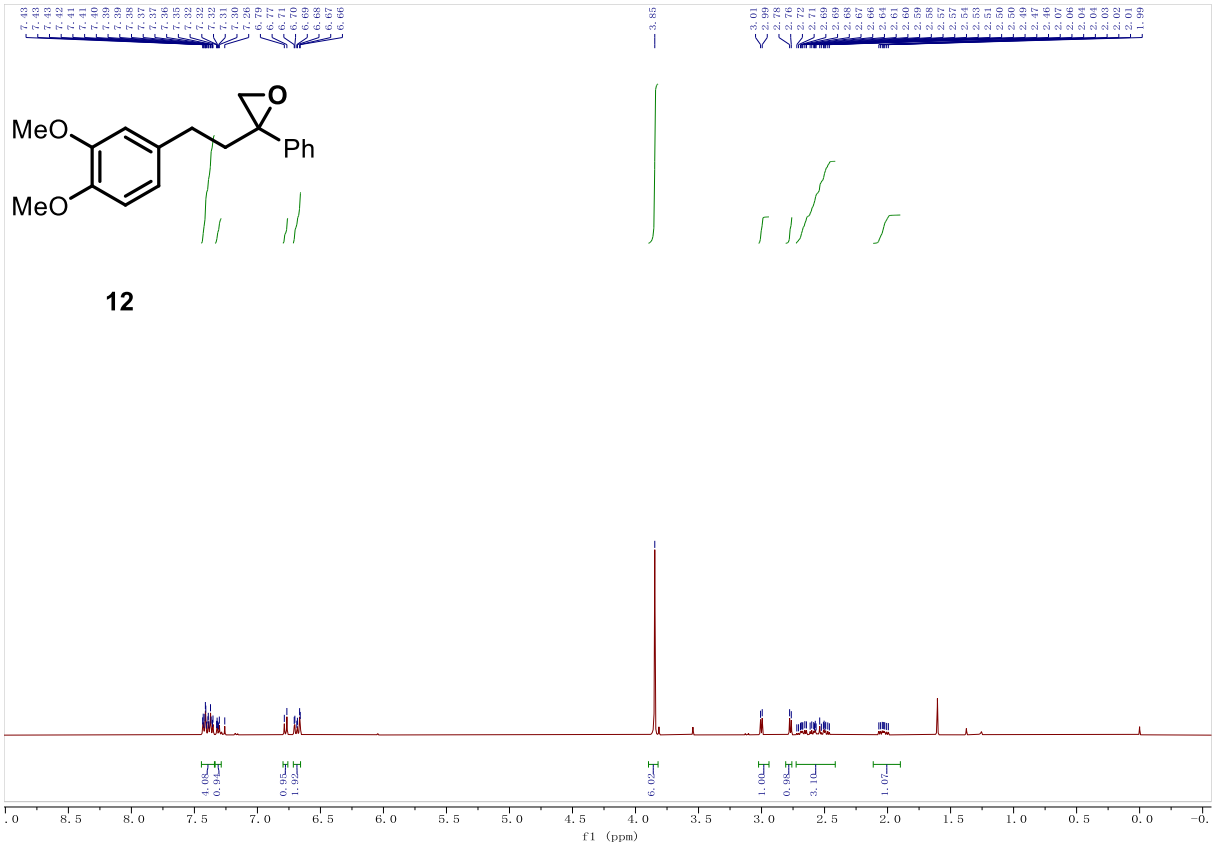
^{1}H NMR (400 MHz, $CDCl_3$)



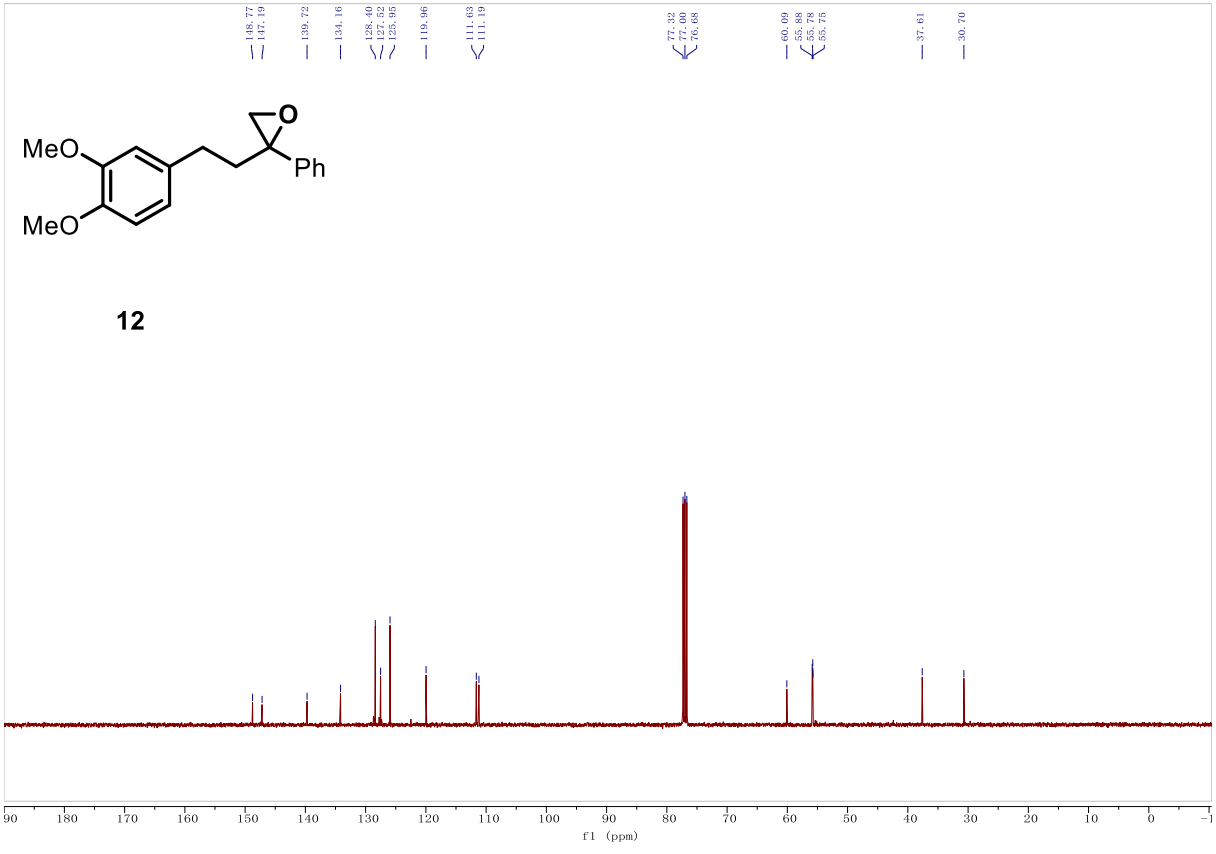
^{13}C NMR (101 MHz, $CDCl_3$)



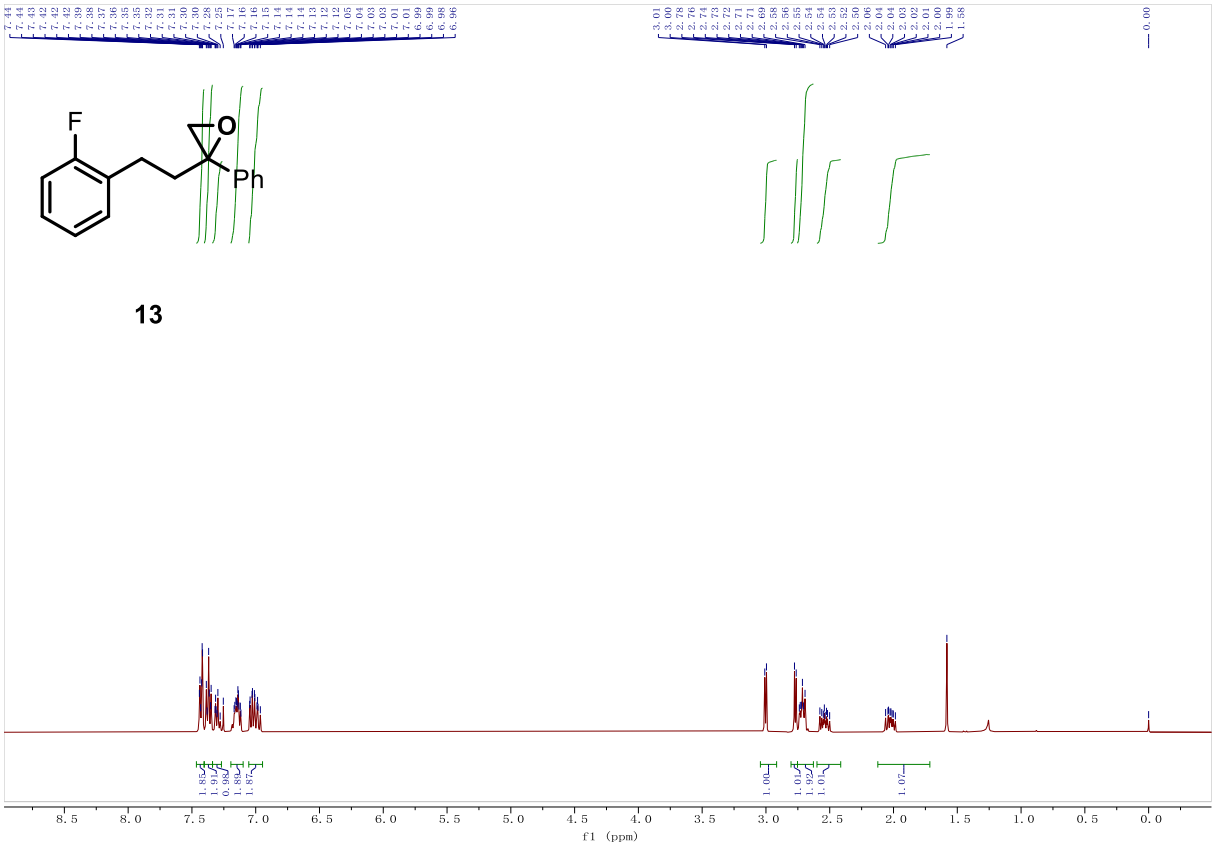
^{1}H NMR (400 MHz, $CDCl_3$)



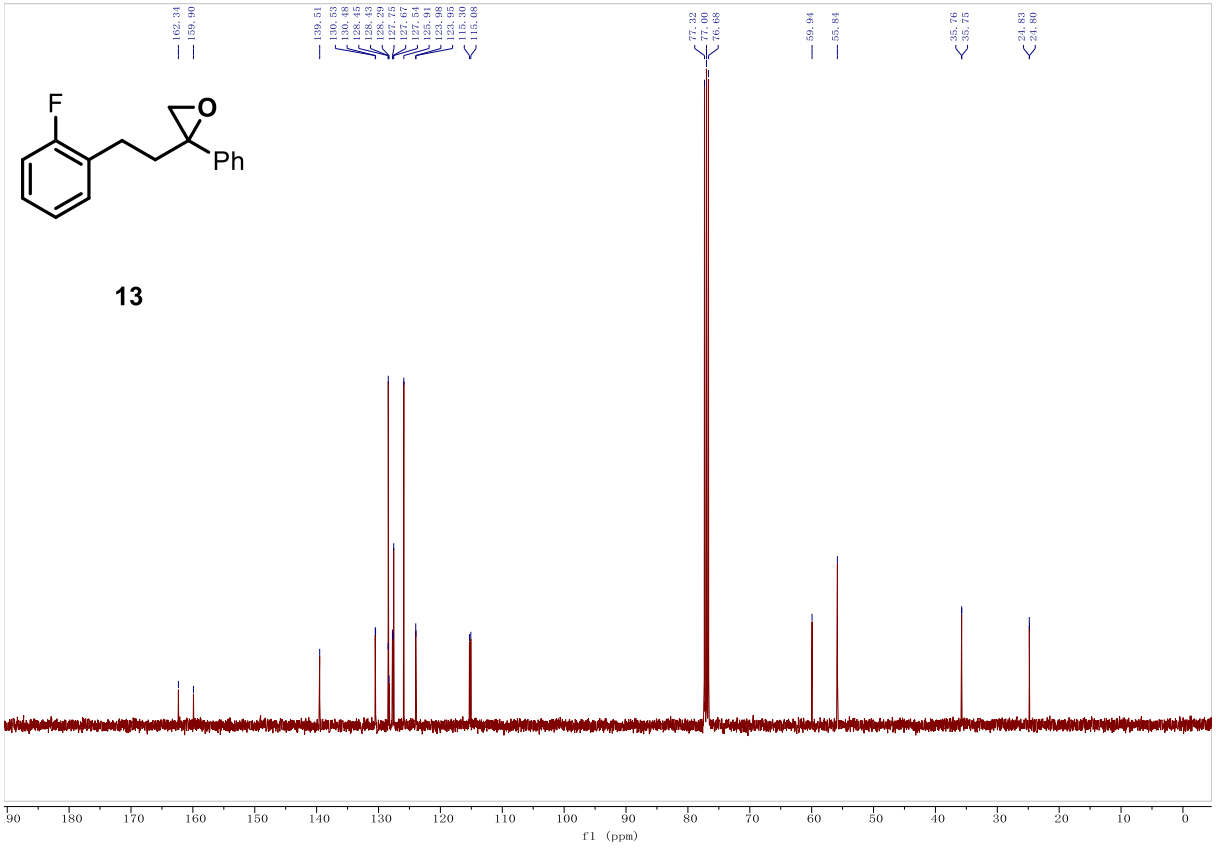
^{13}C NMR (101 MHz, $CDCl_3$)



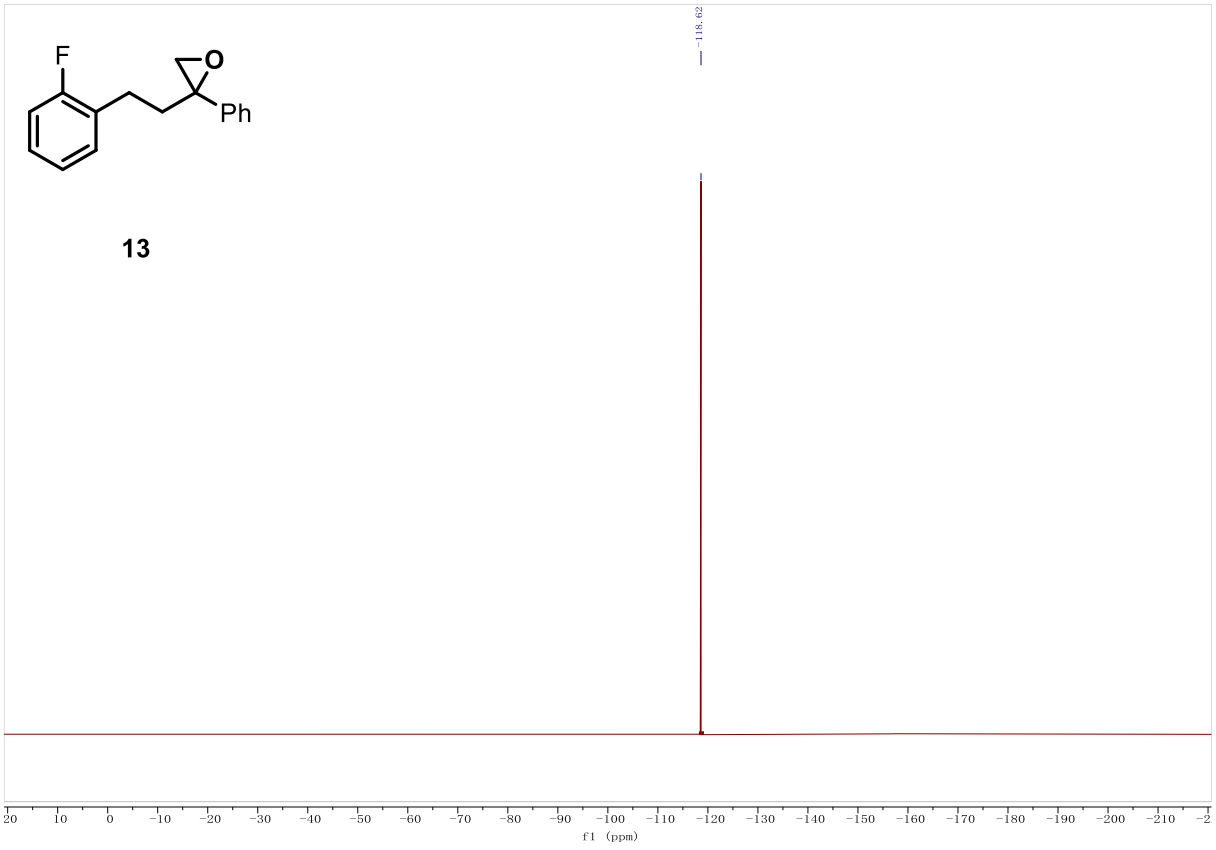
^{1}H NMR (400 MHz, $CDCl_3$)



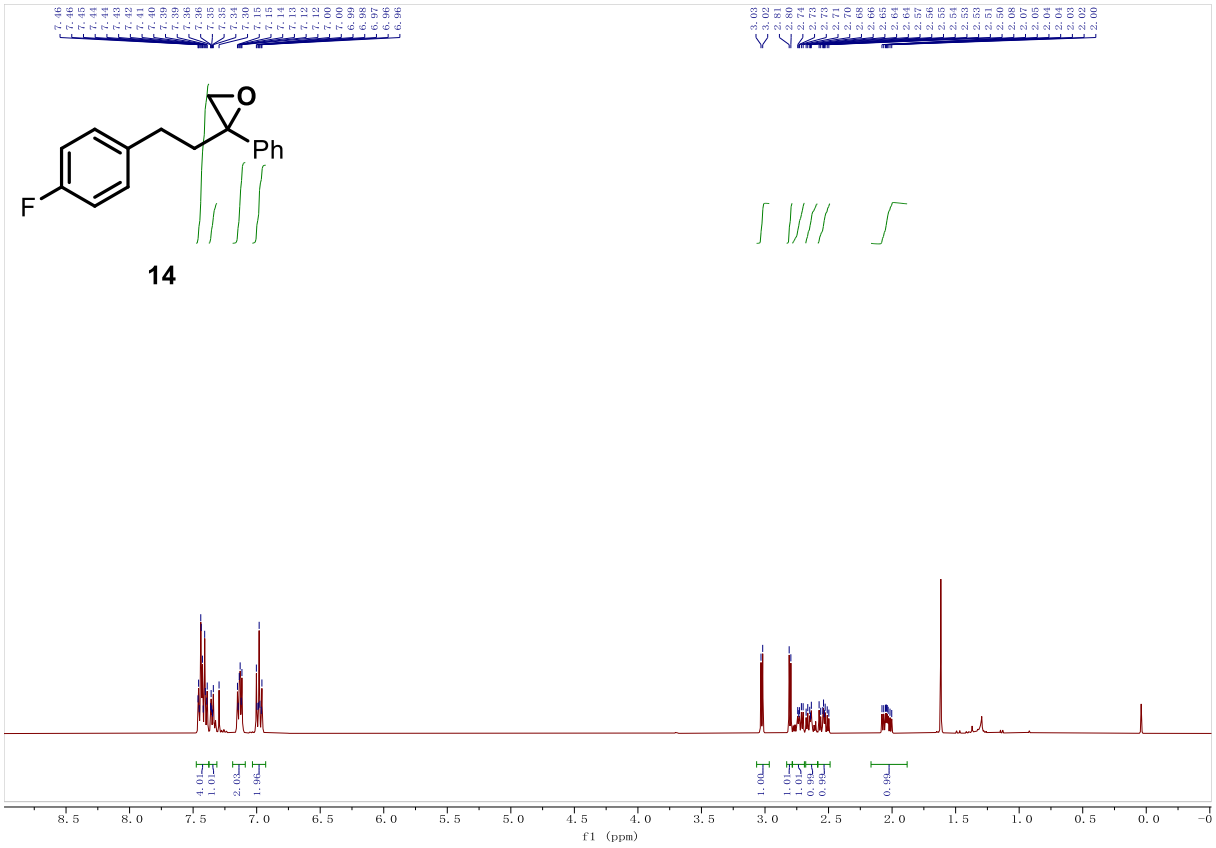
^{13}C NMR (101 MHz, $CDCl_3$)



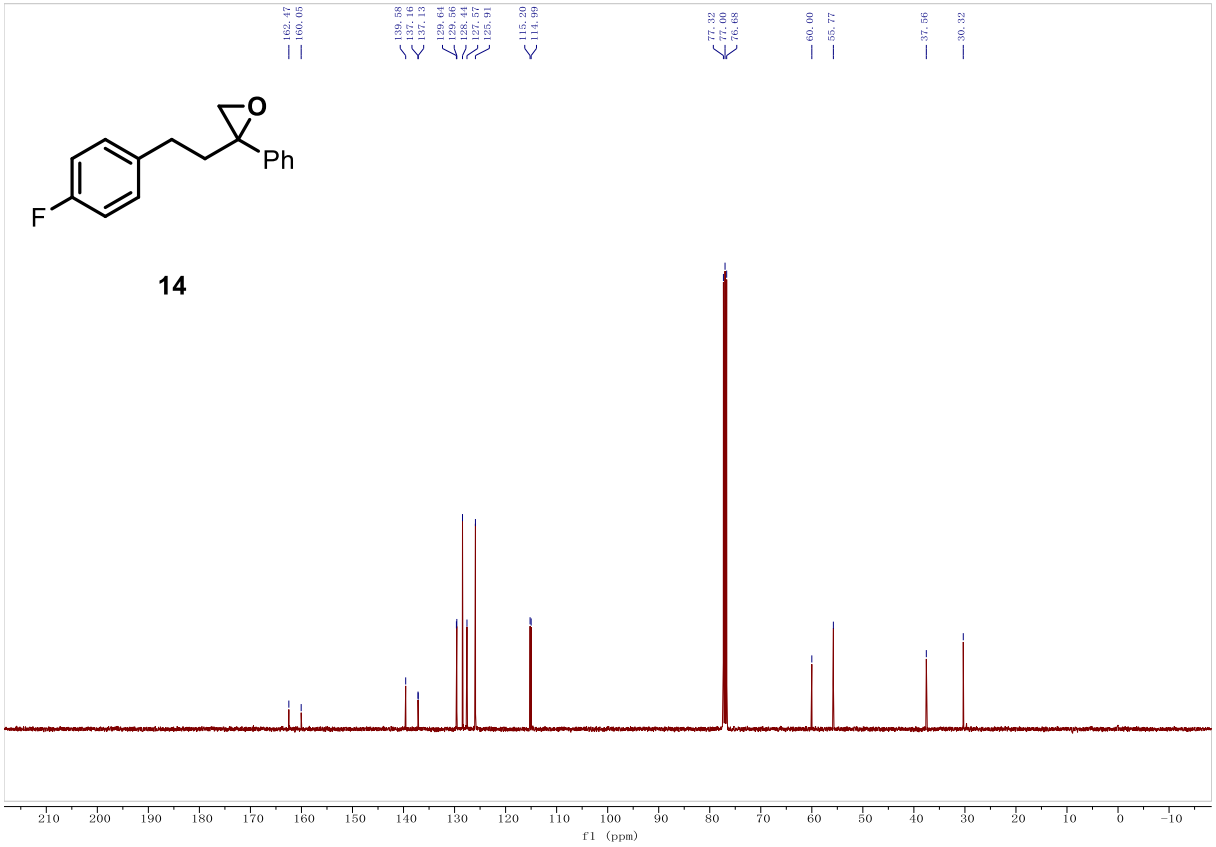
^{19}F NMR (376 MHz, $CDCl_3$)



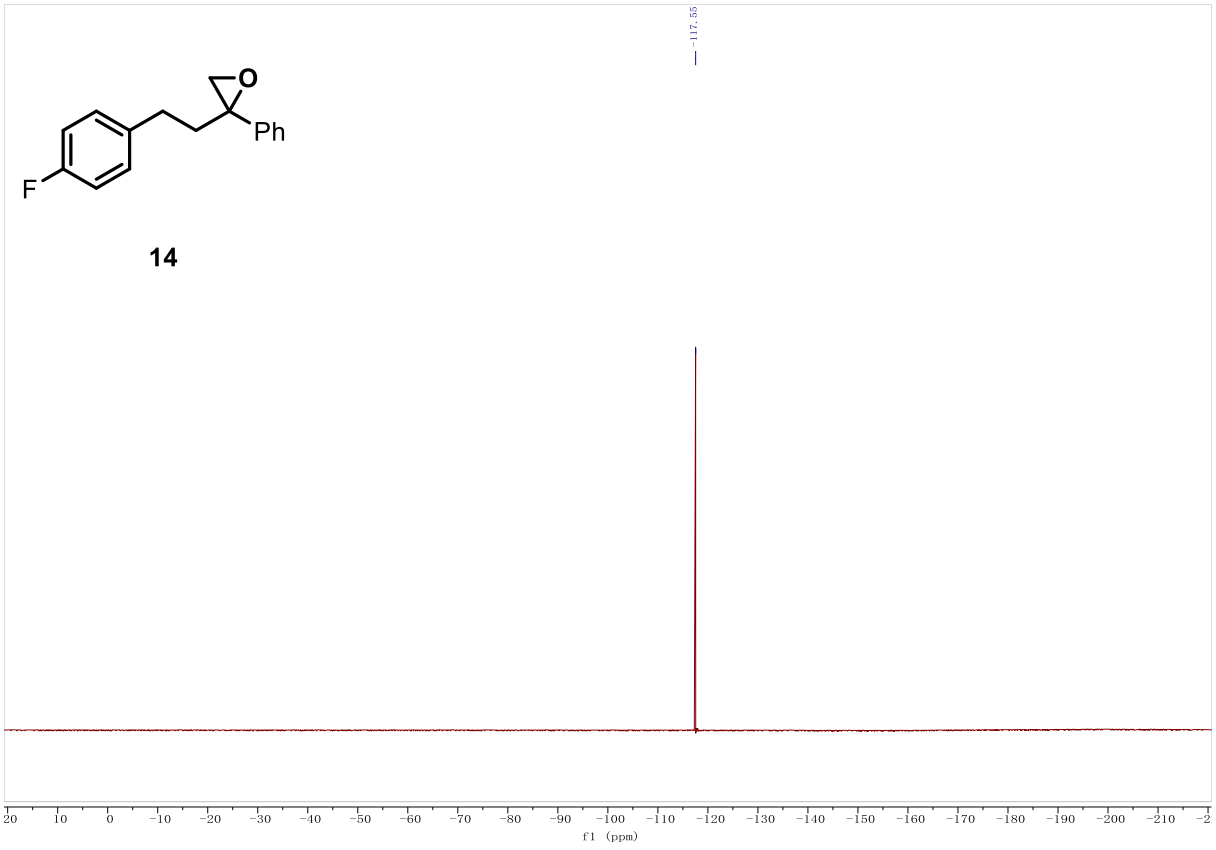
^{1}H NMR (400 MHz, $CDCl_3$)



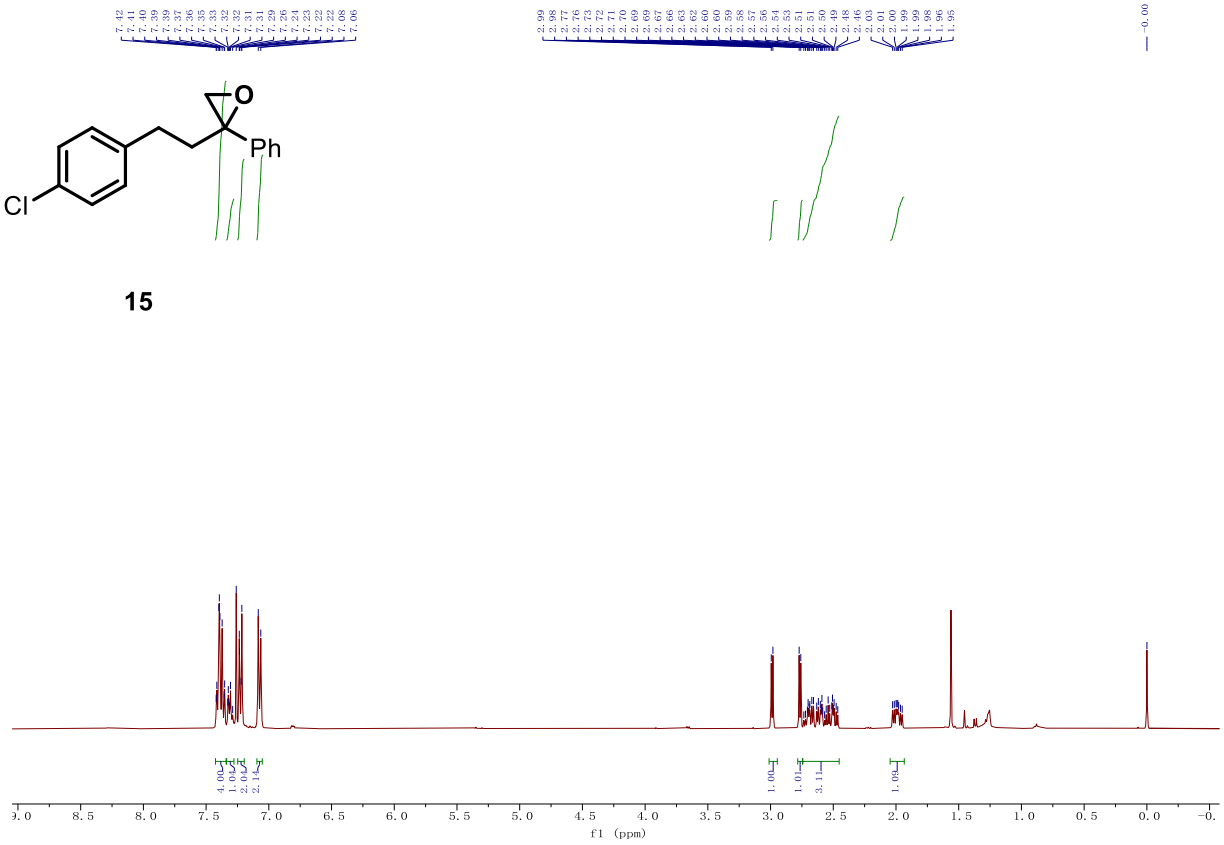
^{13}C NMR (101 MHz, $CDCl_3$)



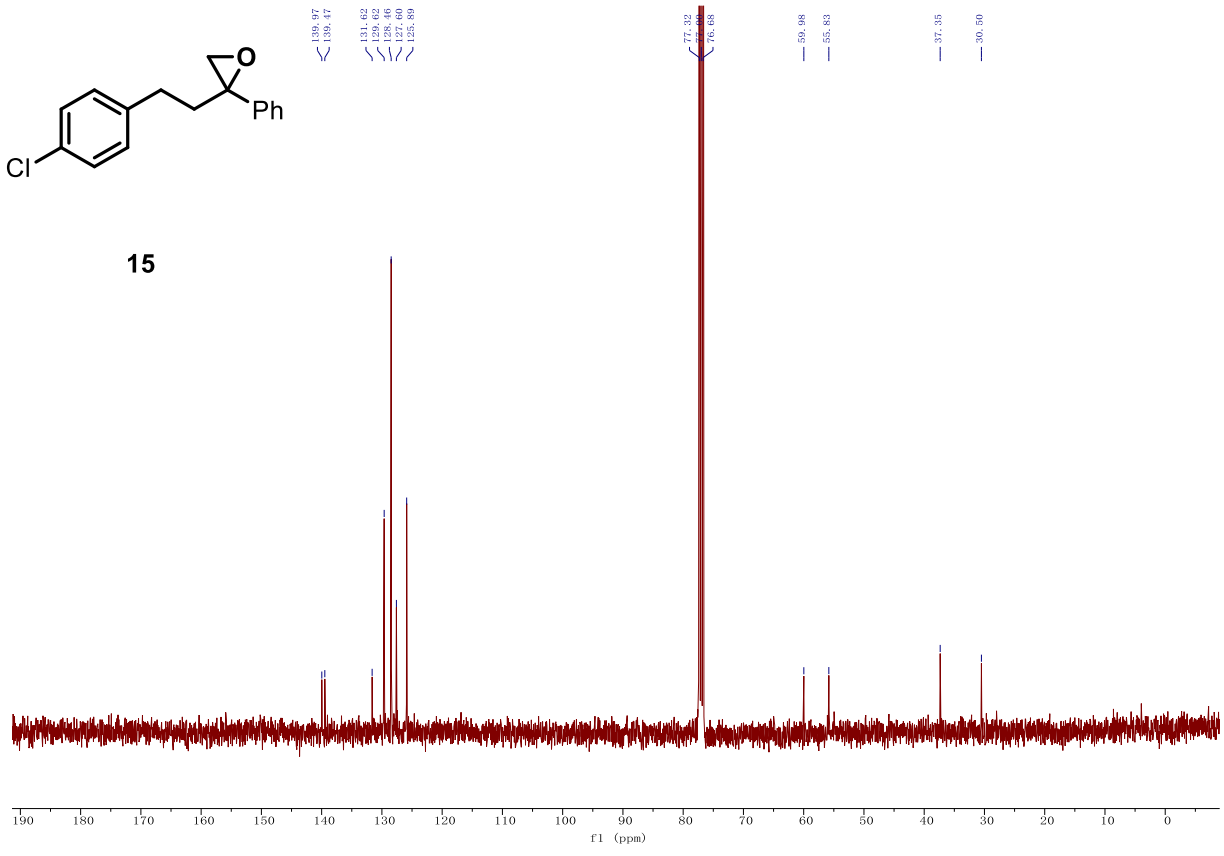
^{19}F NMR (376 MHz, $CDCl_3$)



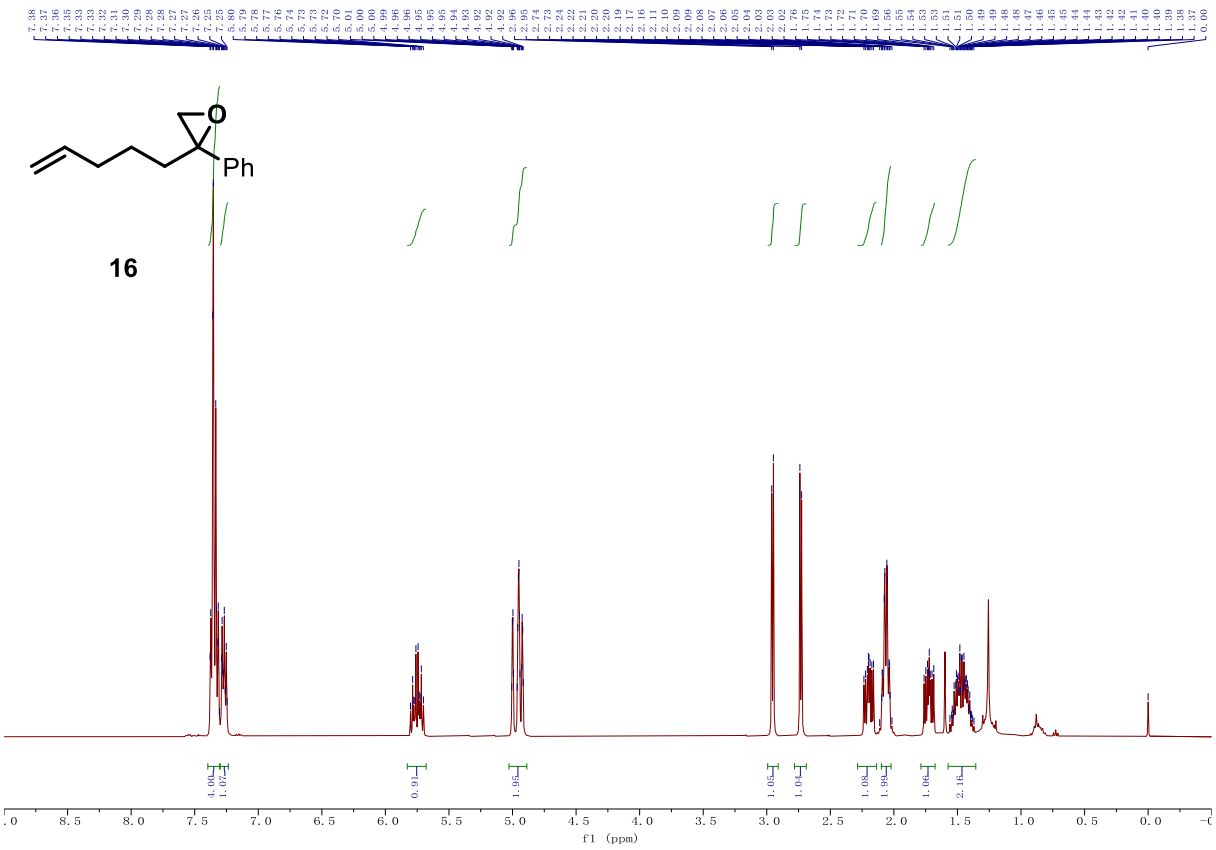
^{1}H NMR (400 MHz, $CDCl_3$)



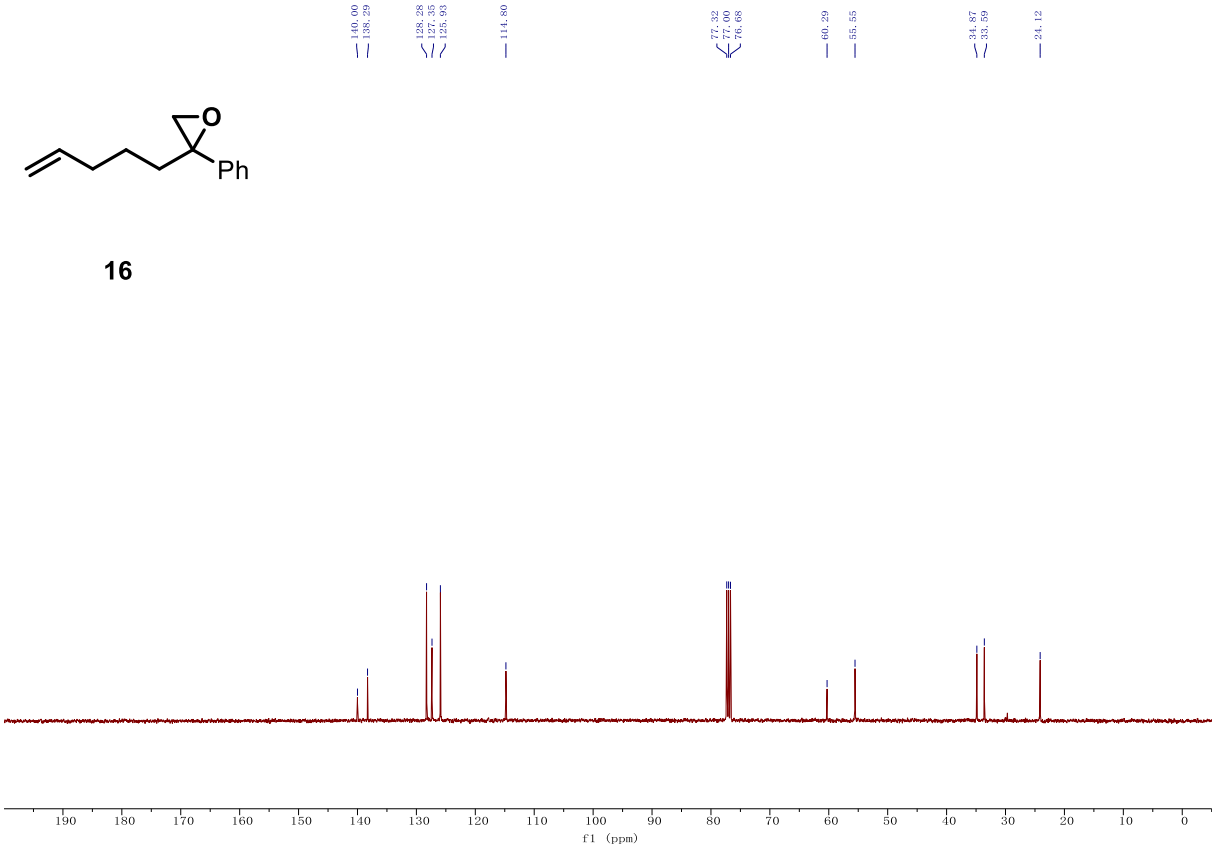
^{13}C NMR (101 MHz, $CDCl_3$)



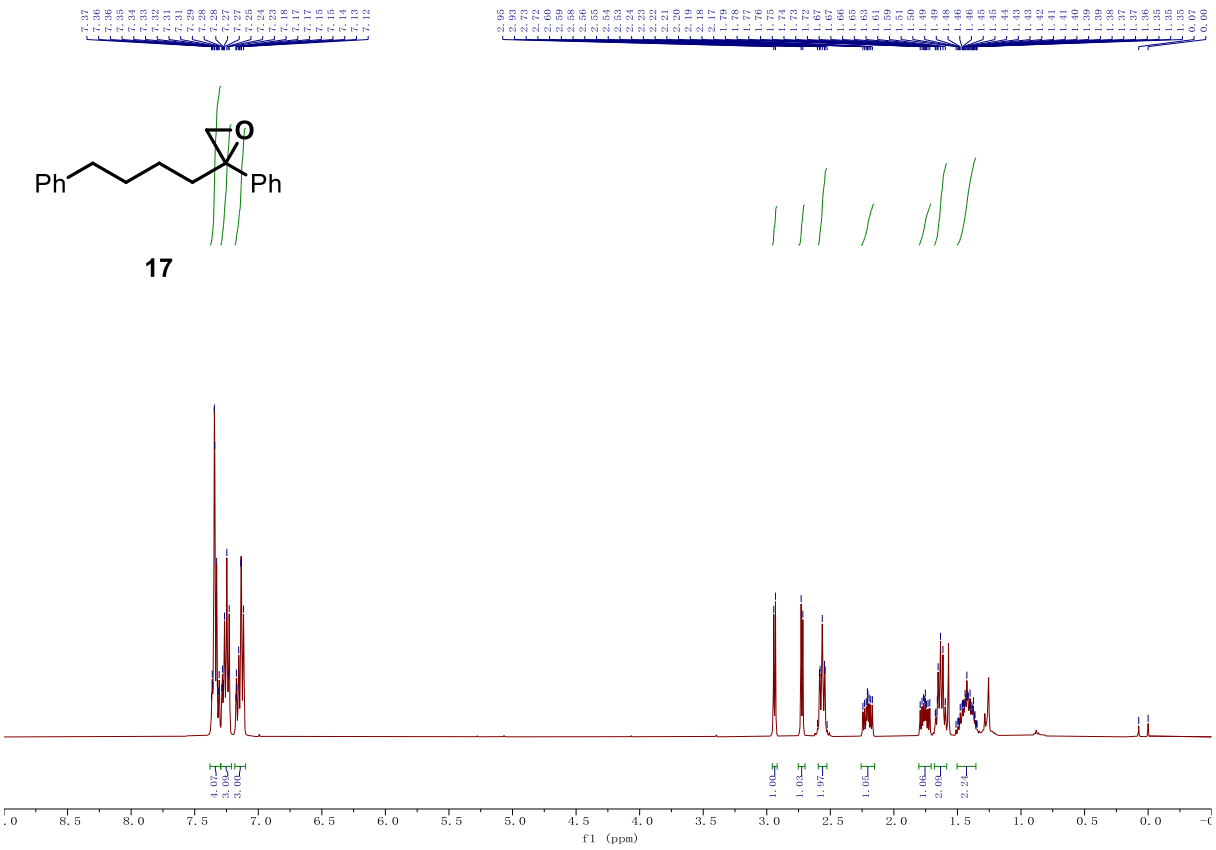
^{1}H NMR (400 MHz, $CDCl_3$)



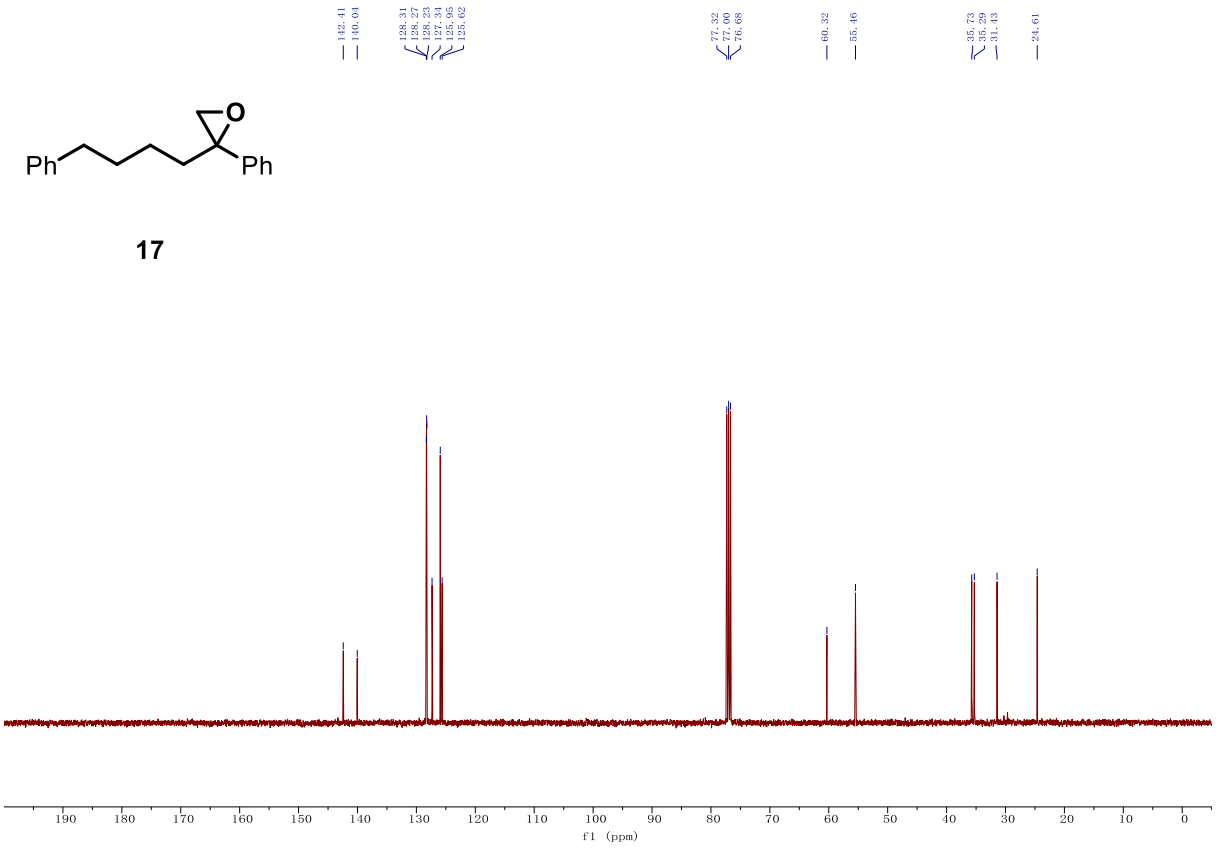
^{13}C NMR (101 MHz, $CDCl_3$)



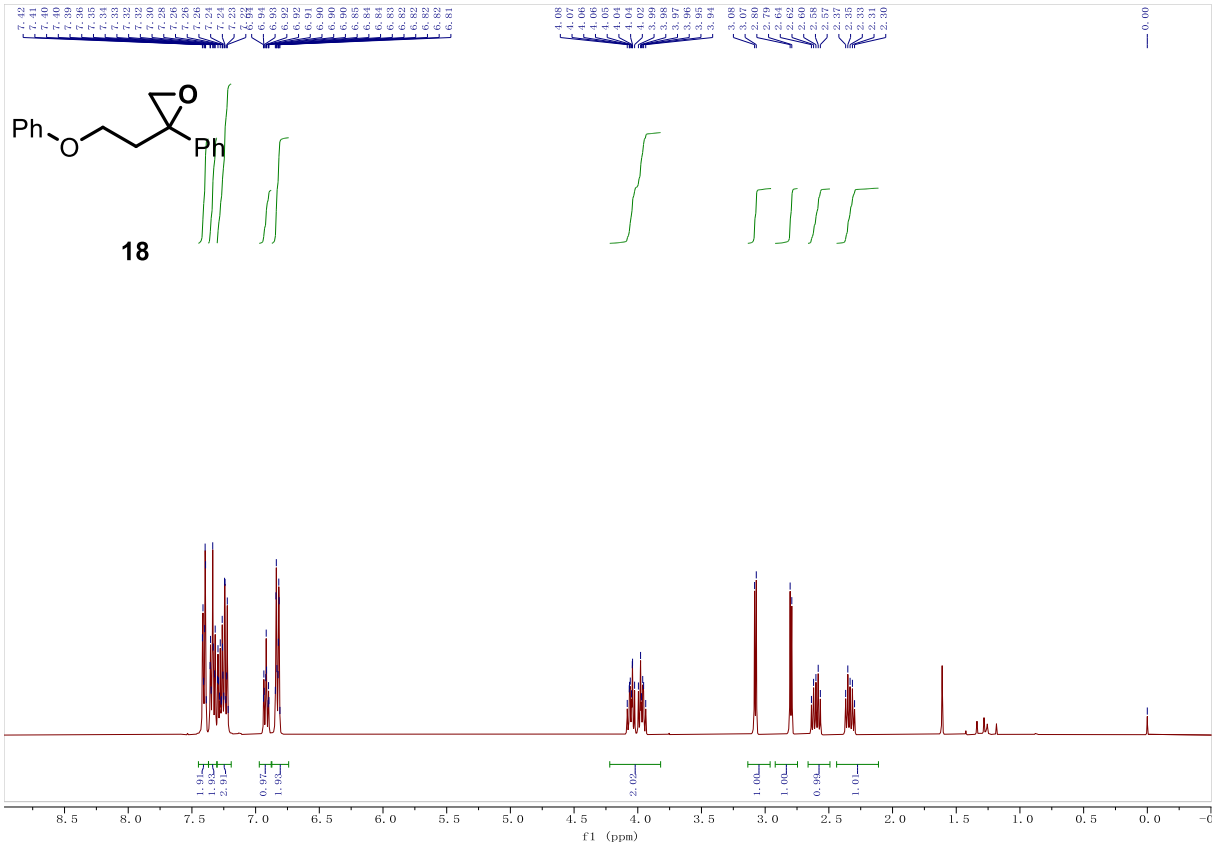
^{1}H NMR (400 MHz, $CDCl_3$)



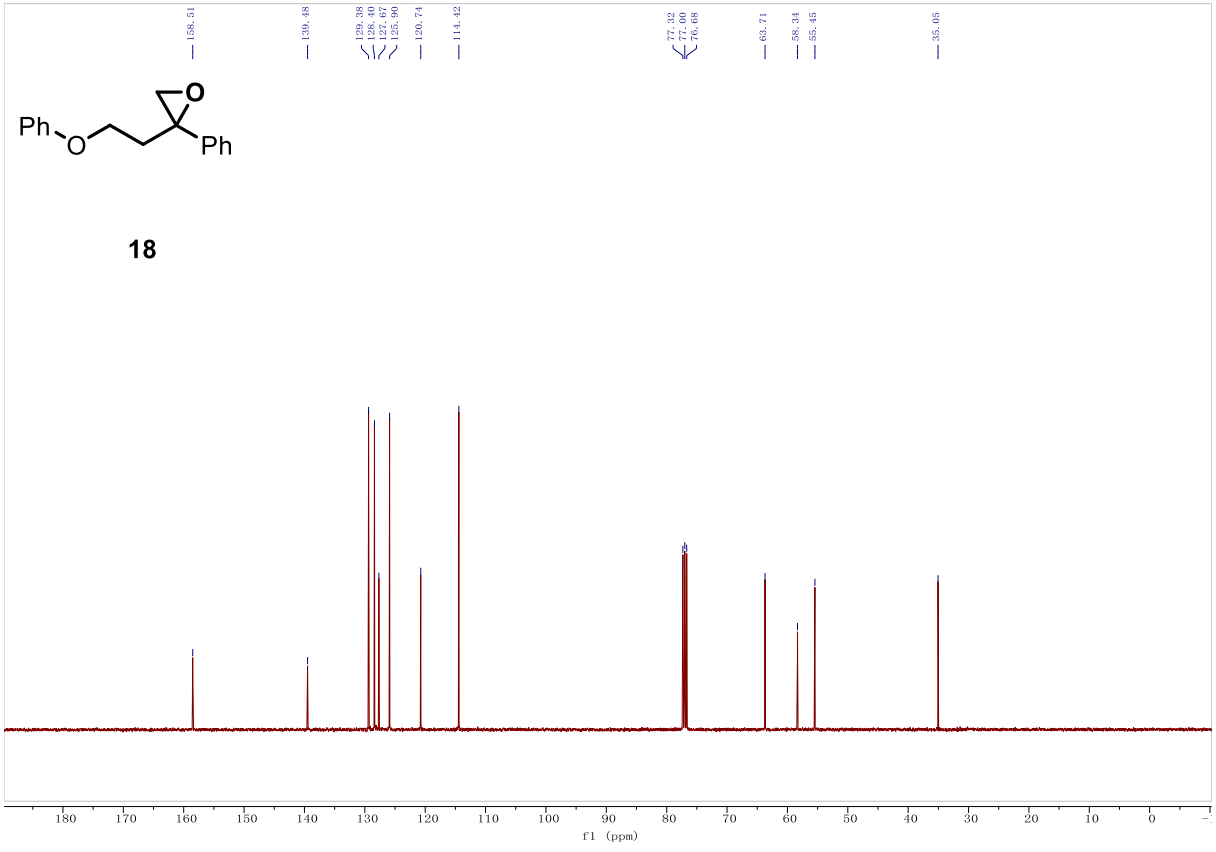
^{13}C NMR (101 MHz, $CDCl_3$)



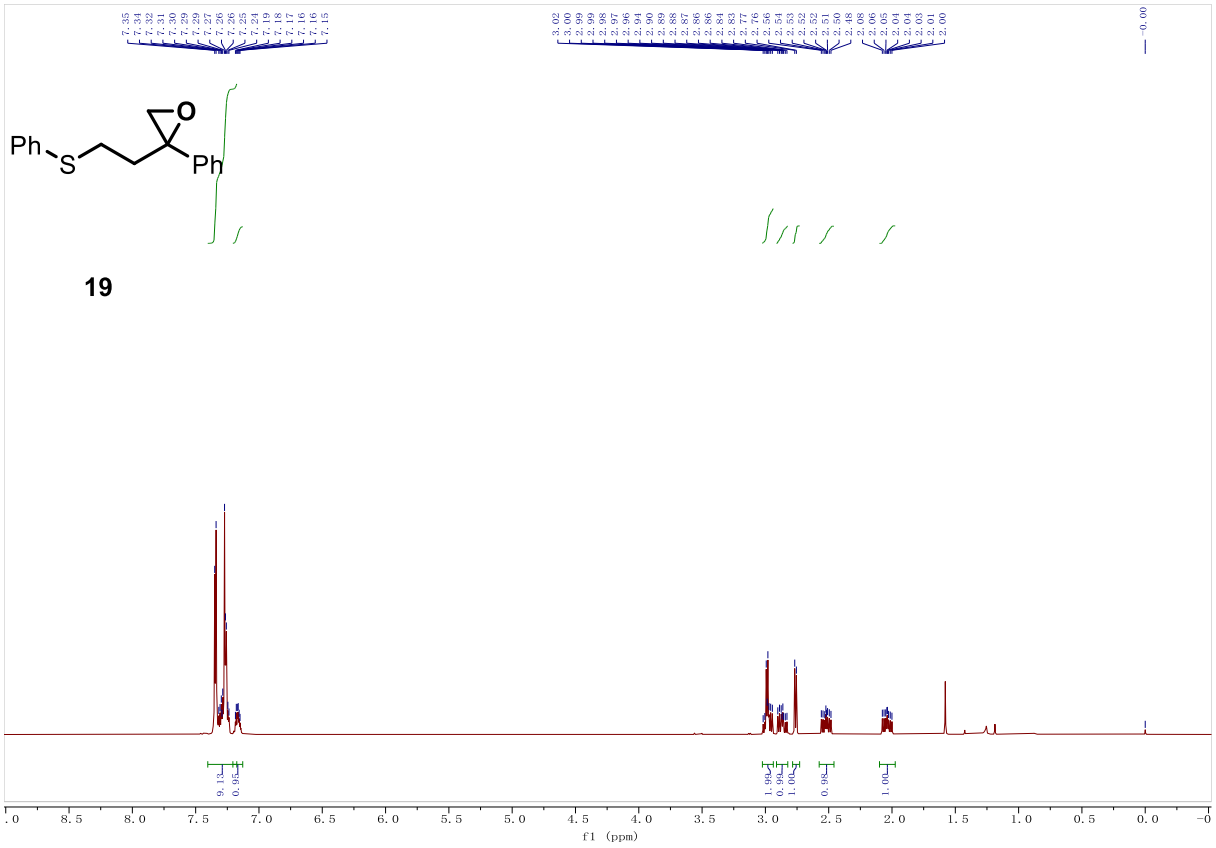
^{1}H NMR (400 MHz, $CDCl_3$)



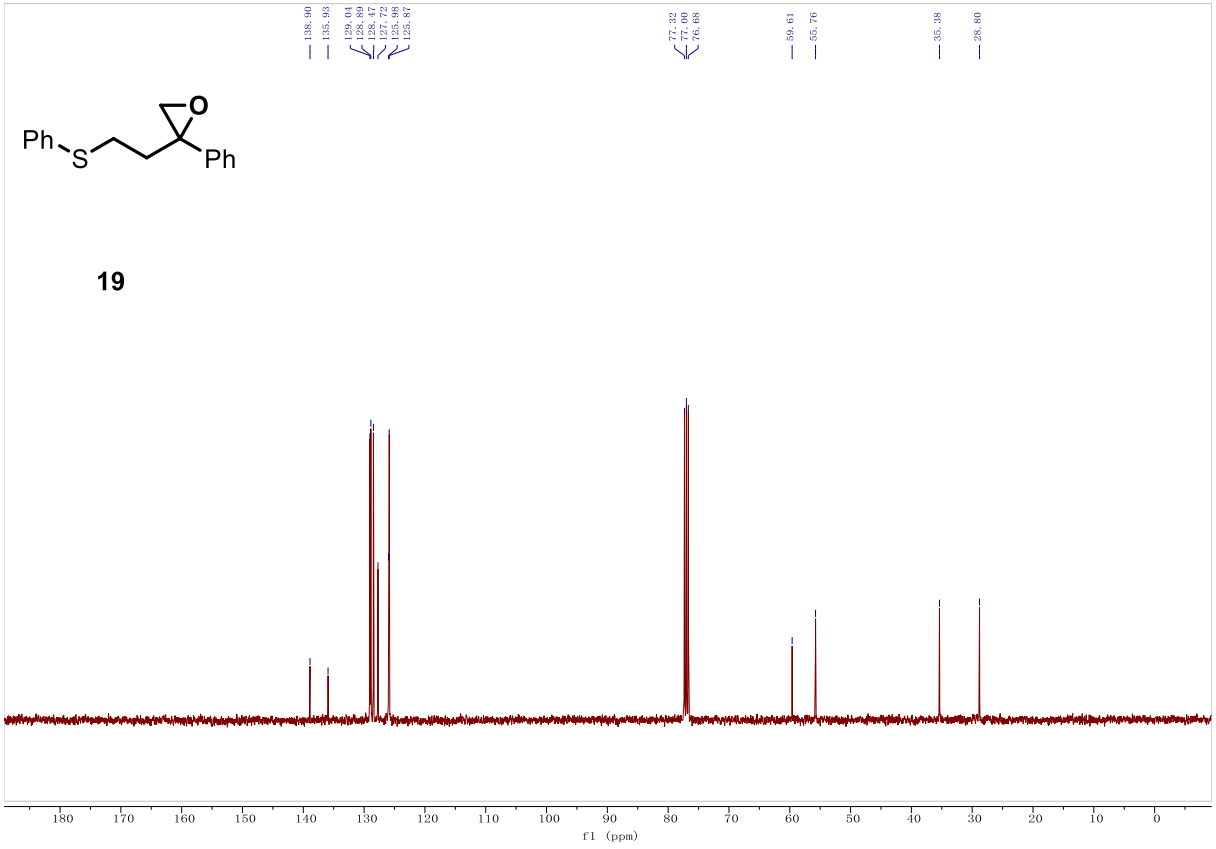
^{13}C NMR (101 MHz, $CDCl_3$)



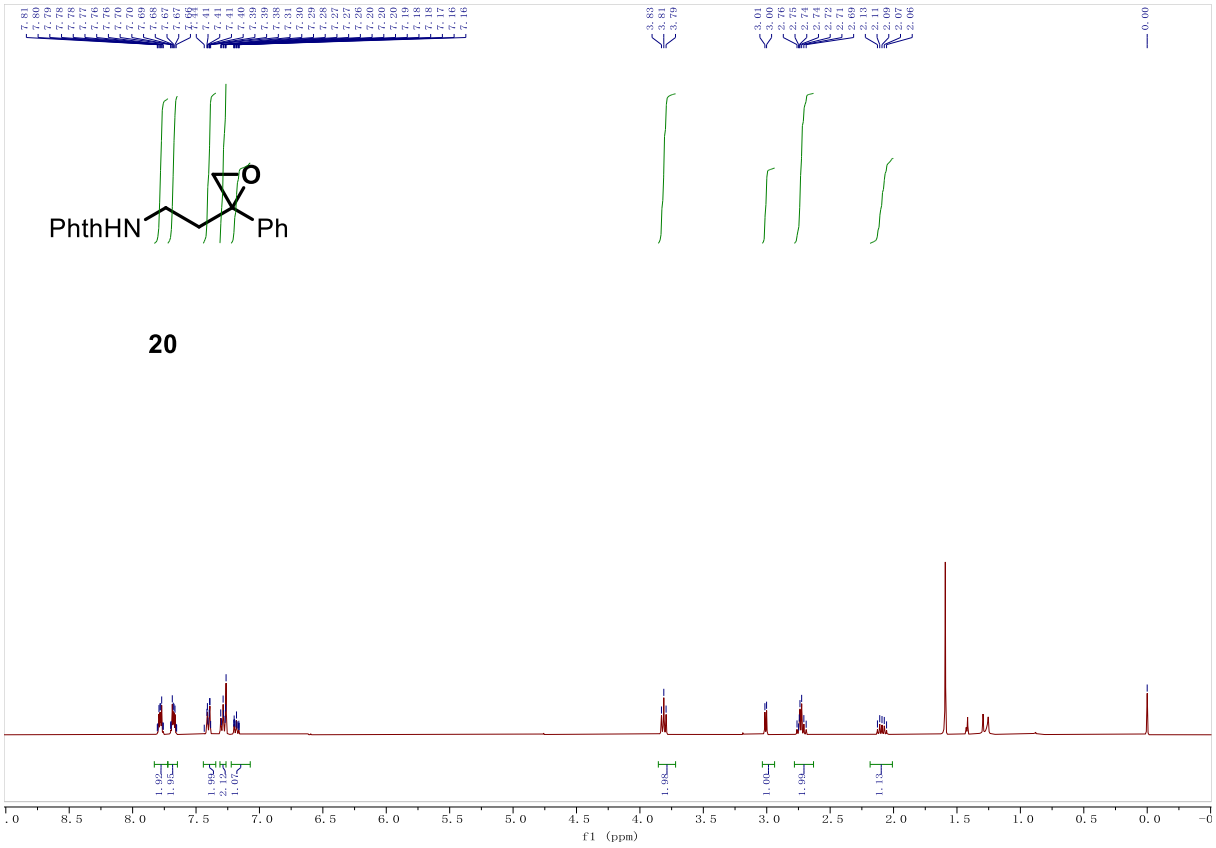
^{1}H NMR (400 MHz, $CDCl_3$)



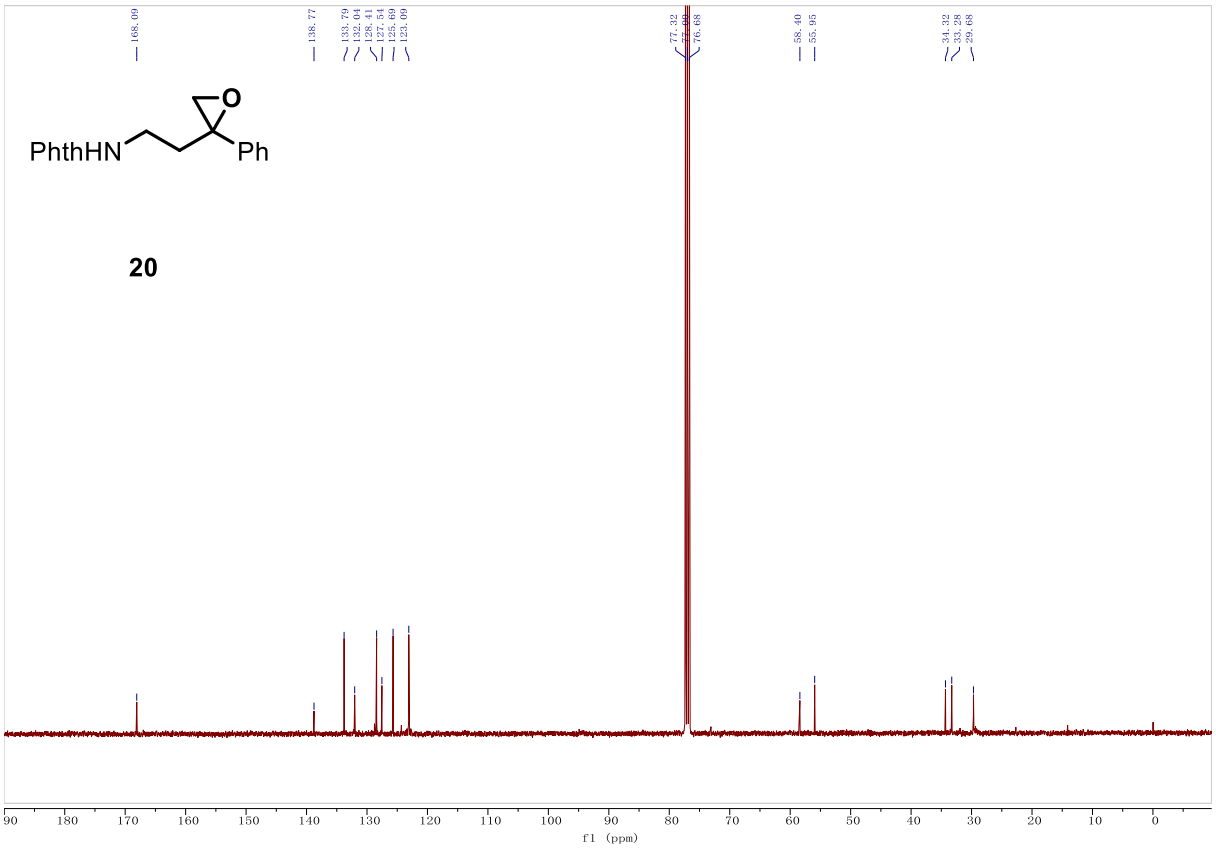
^{13}C NMR (101 MHz, $CDCl_3$)



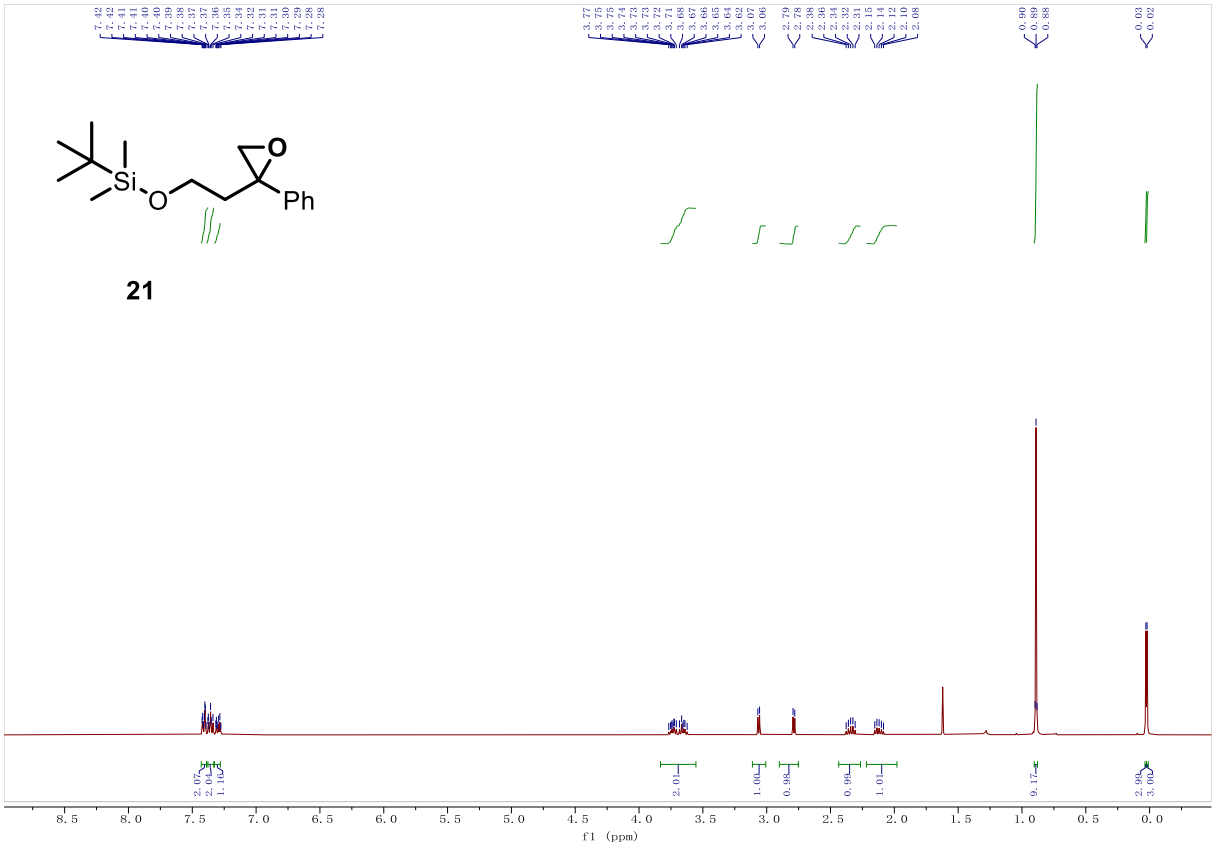
^{1}H NMR (400 MHz, $CDCl_3$)



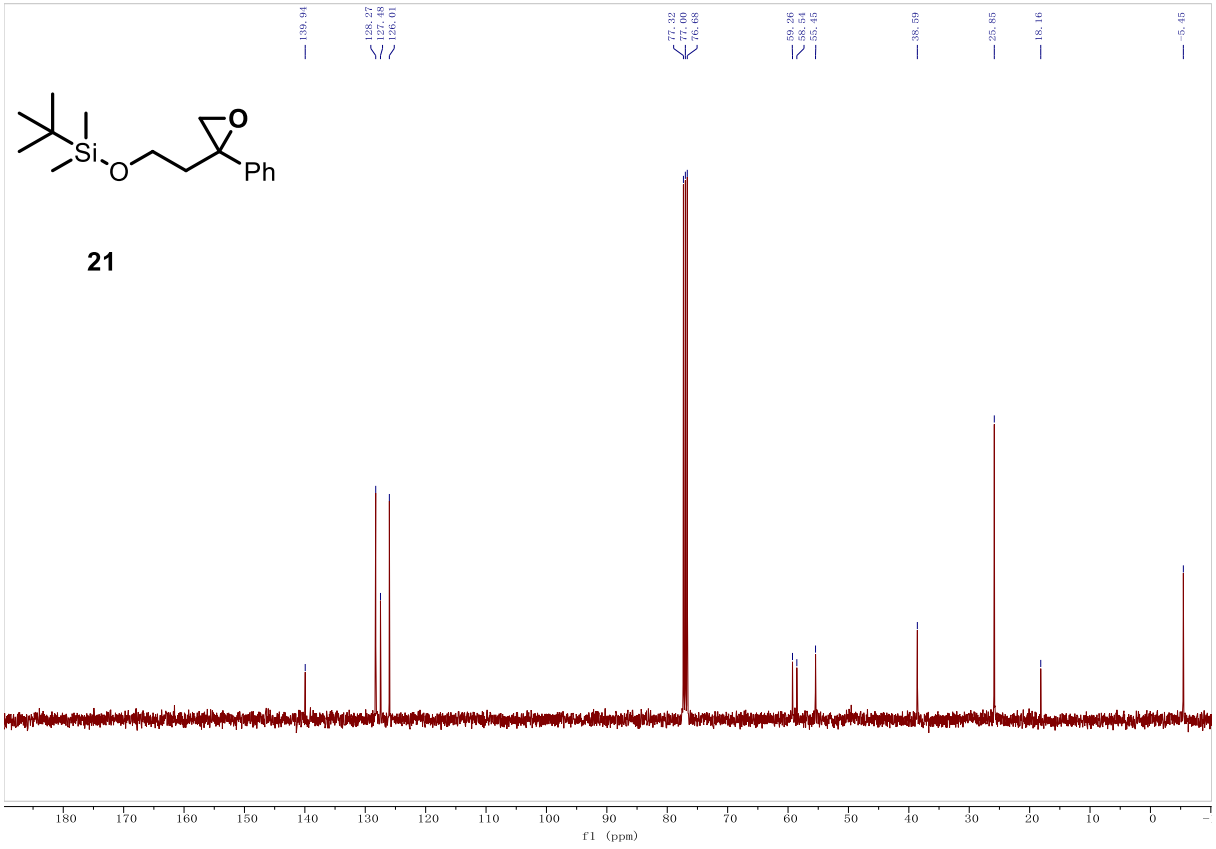
^{13}C NMR (101 MHz, $CDCl_3$)



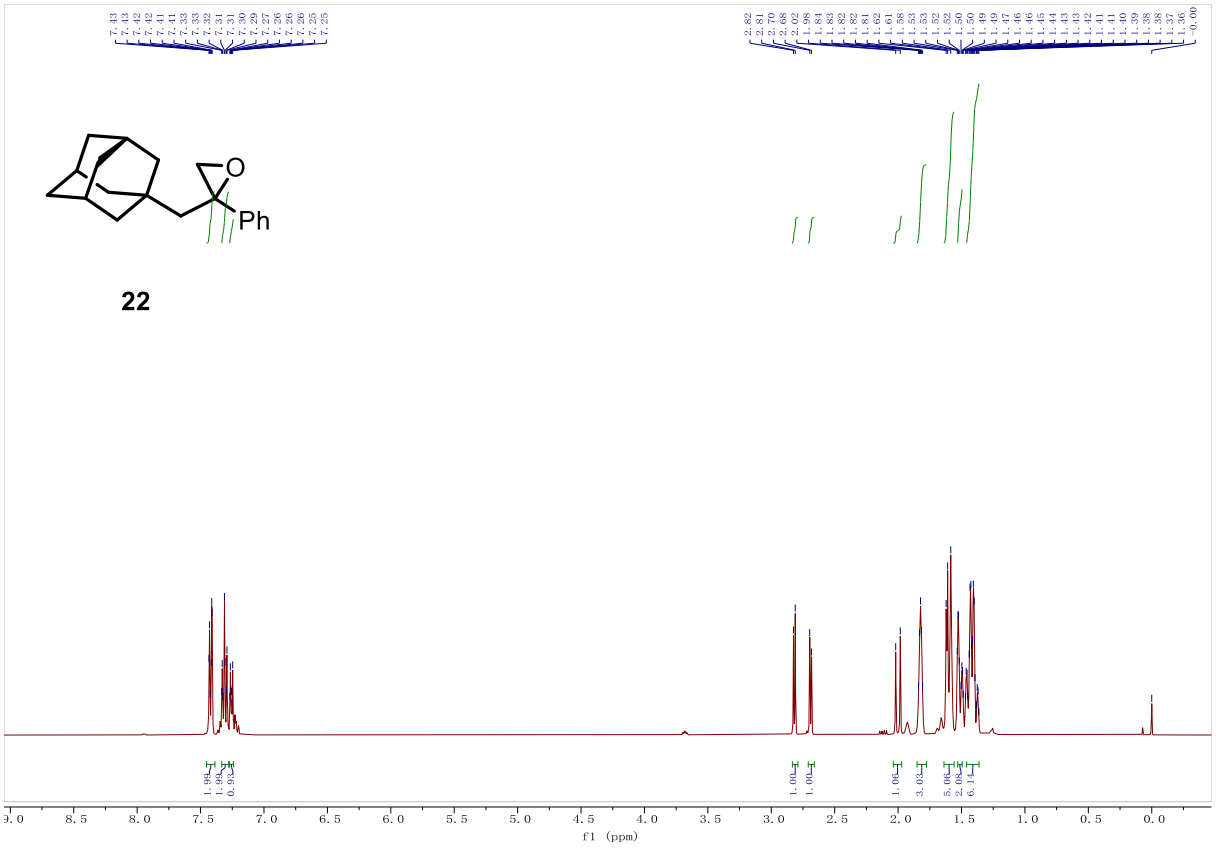
^{1}H NMR (400 MHz, $CDCl_3$)



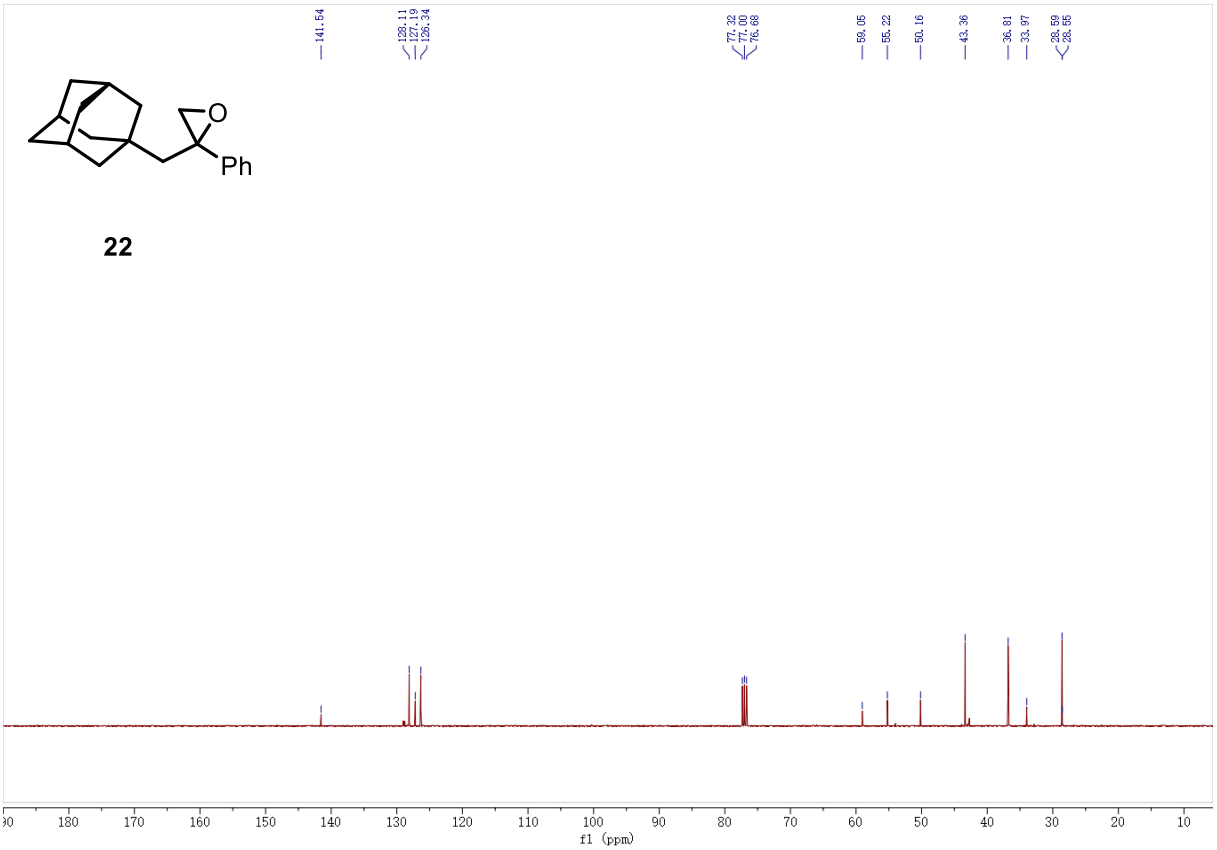
^{13}C NMR (101 MHz, $CDCl_3$)



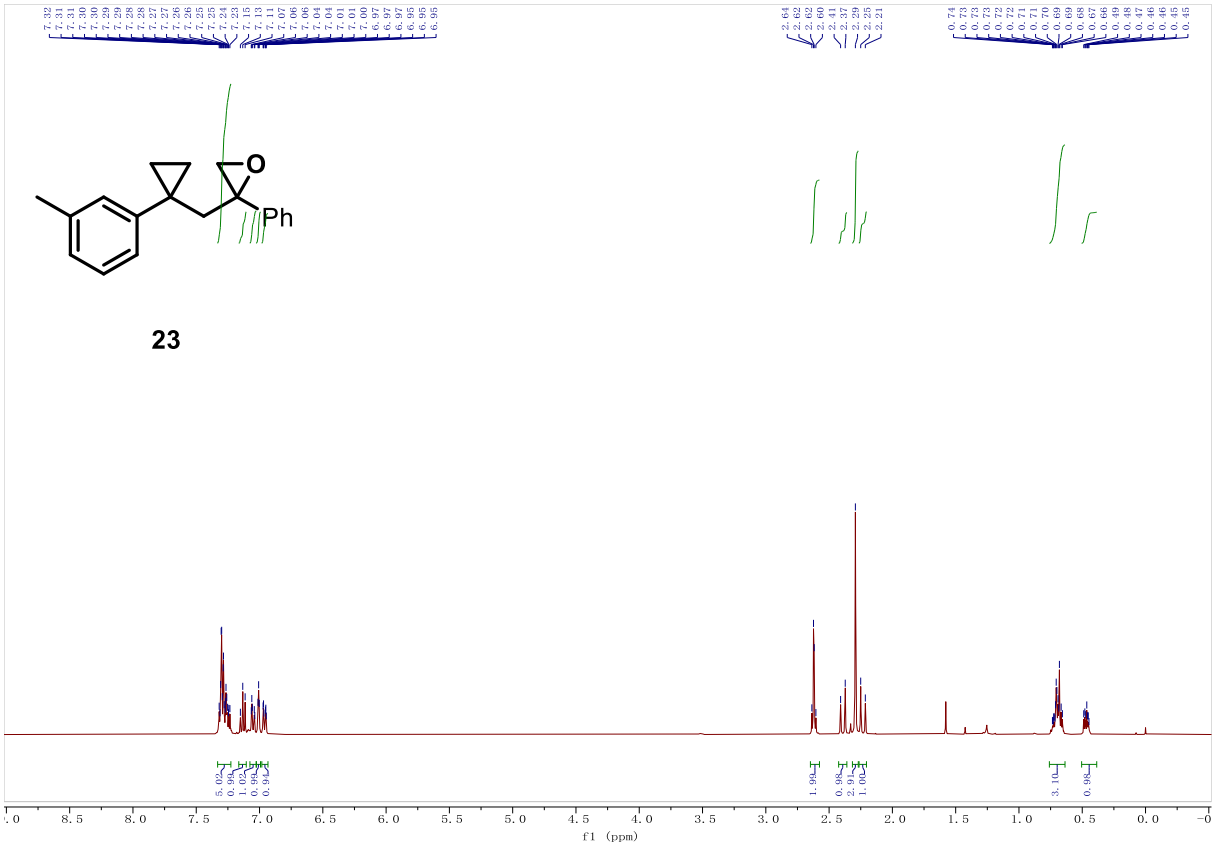
^{1}H NMR (400 MHz, $CDCl_3$)



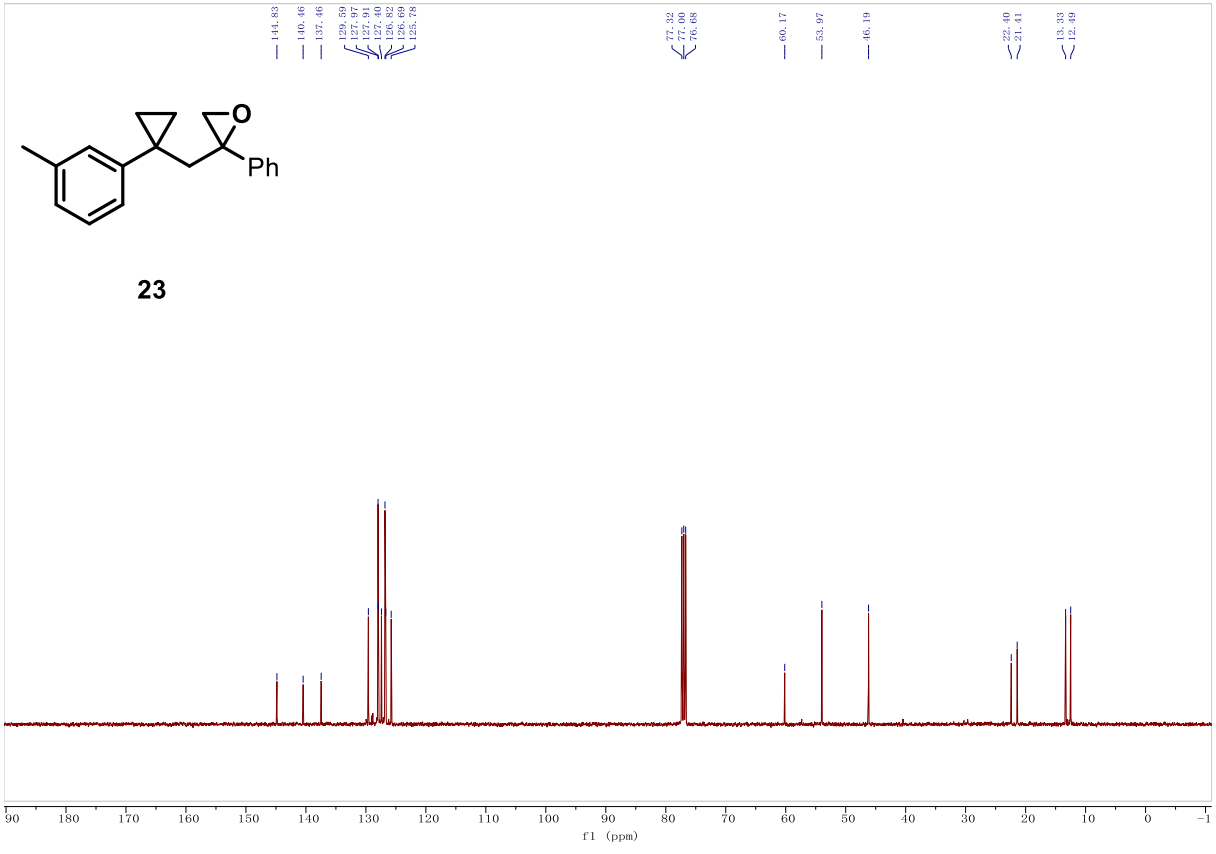
^{13}C NMR (101 MHz, $CDCl_3$)



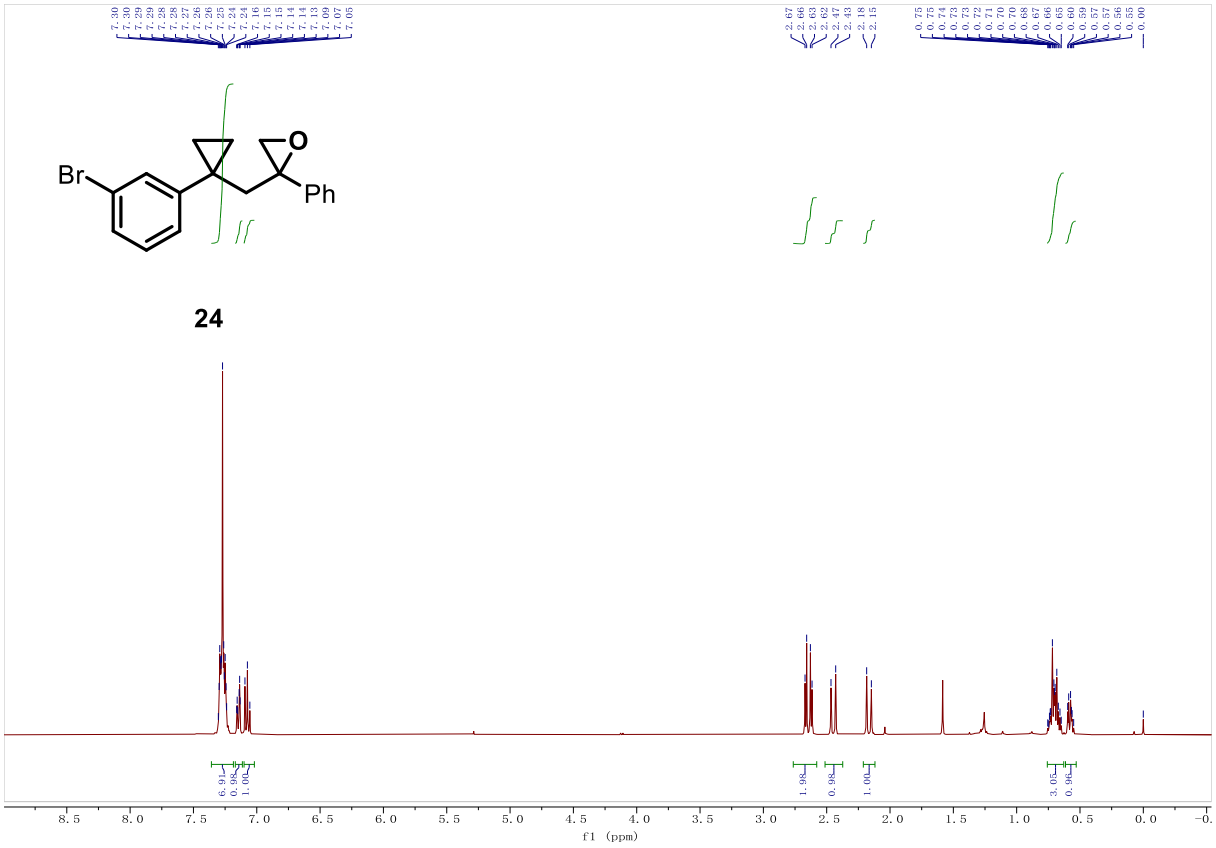
^{1}H NMR (400 MHz, $CDCl_3$)



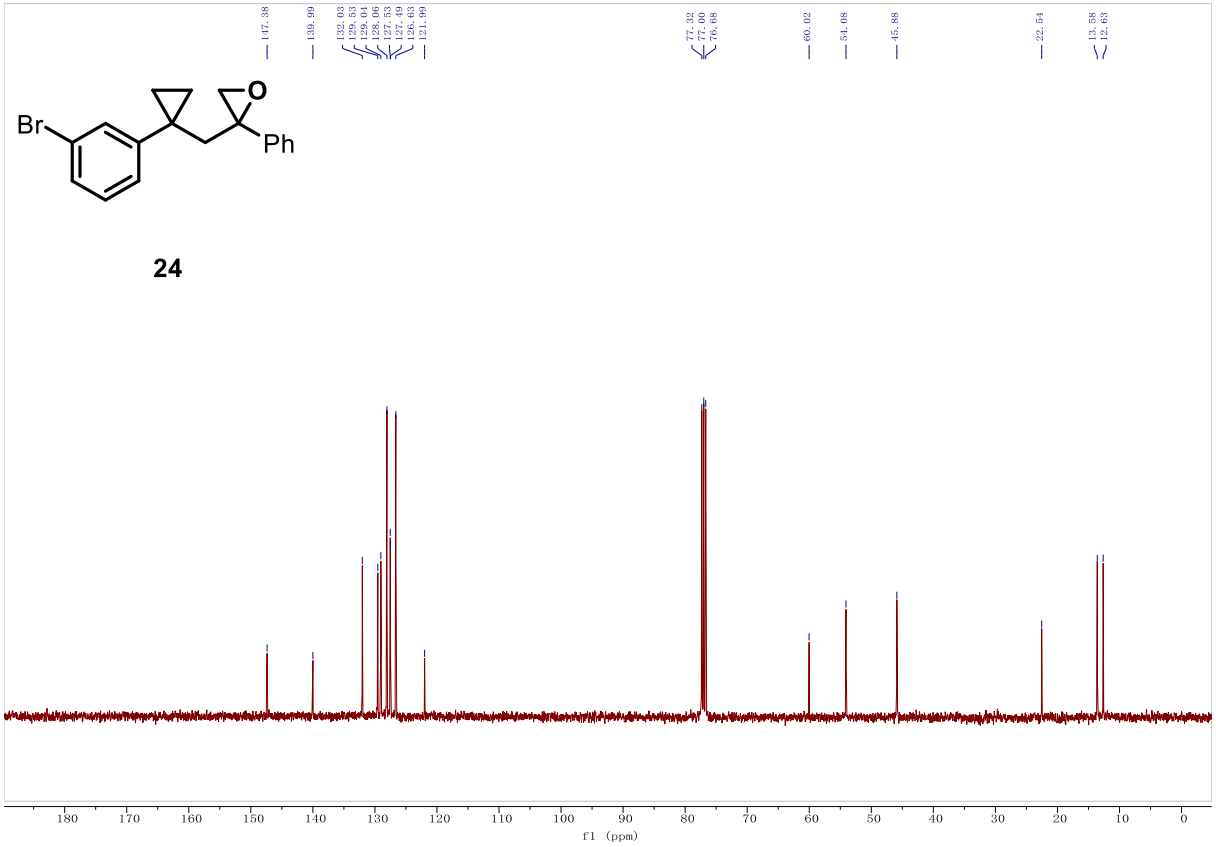
^{13}C NMR (101 MHz, $CDCl_3$)



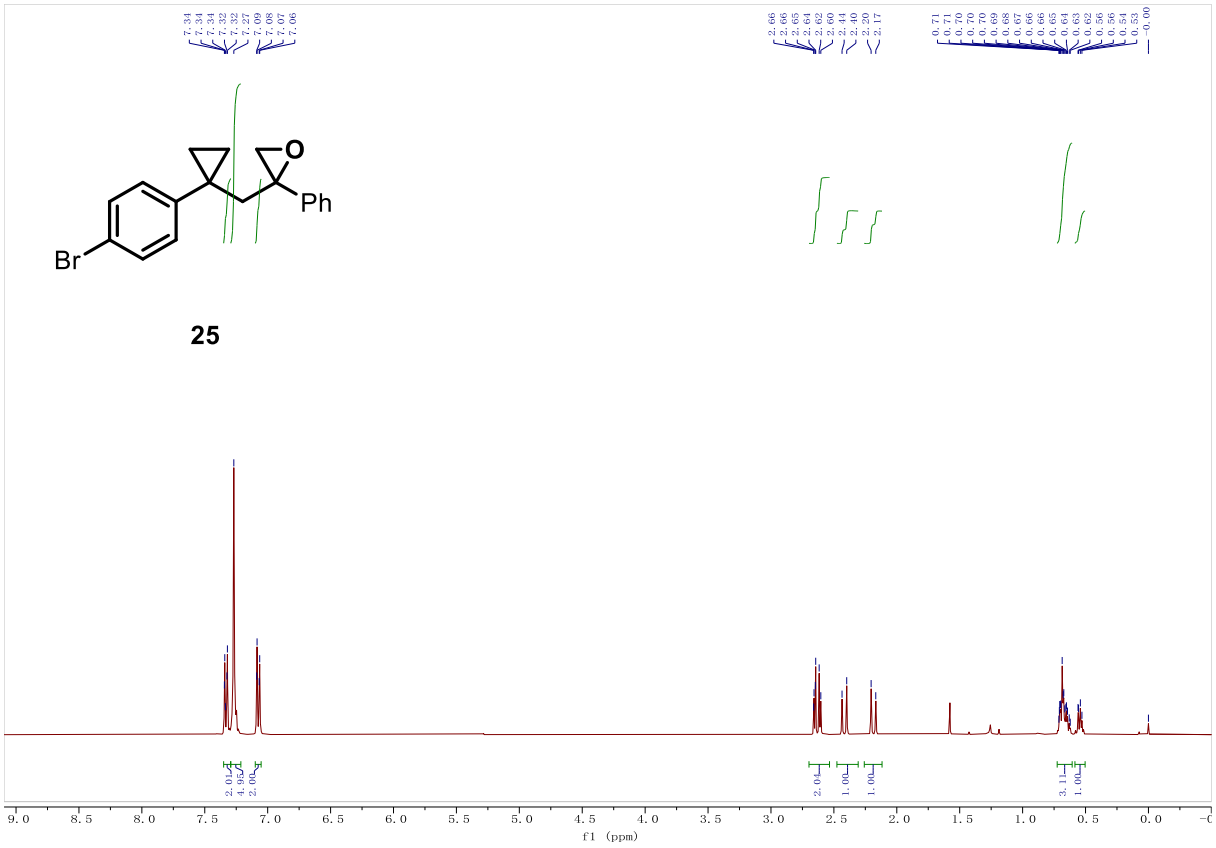
^{1}H NMR (400 MHz, $CDCl_3$)



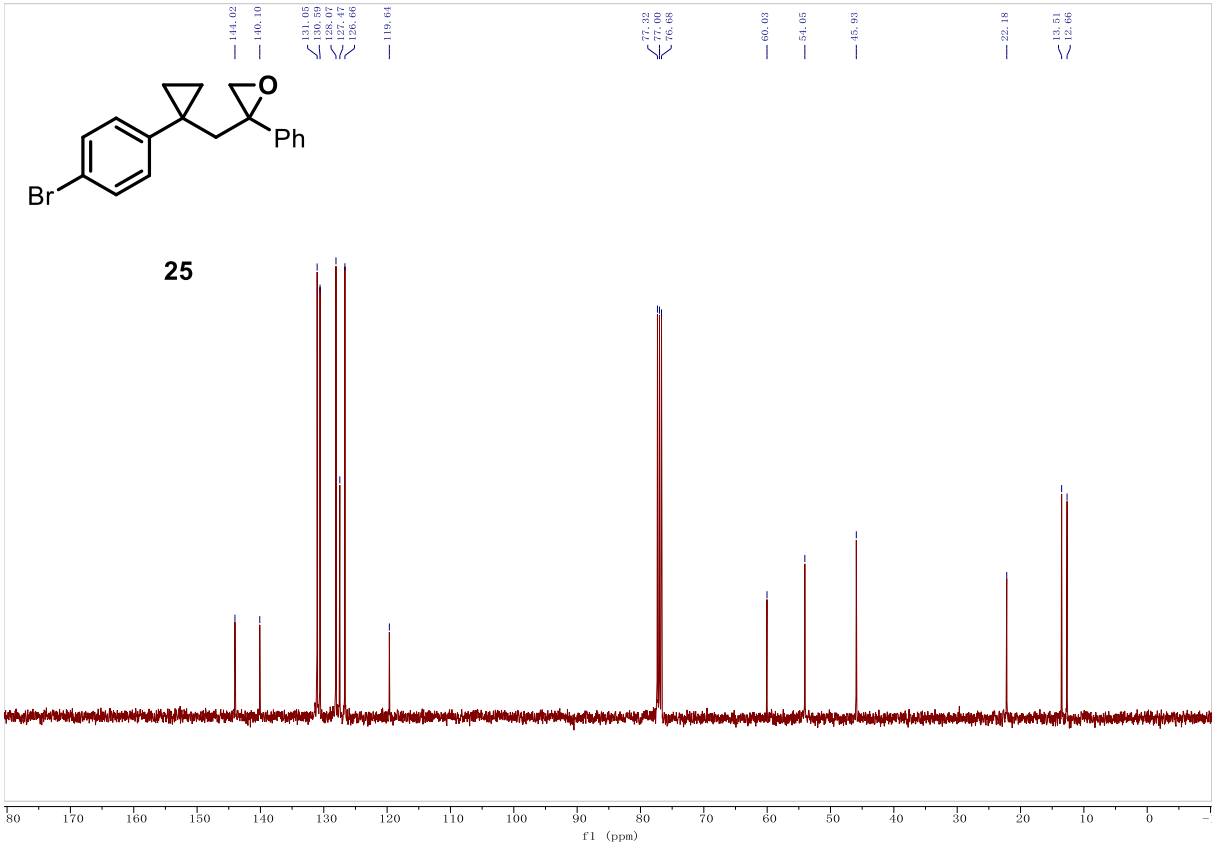
^{13}C NMR (101 MHz, $CDCl_3$)



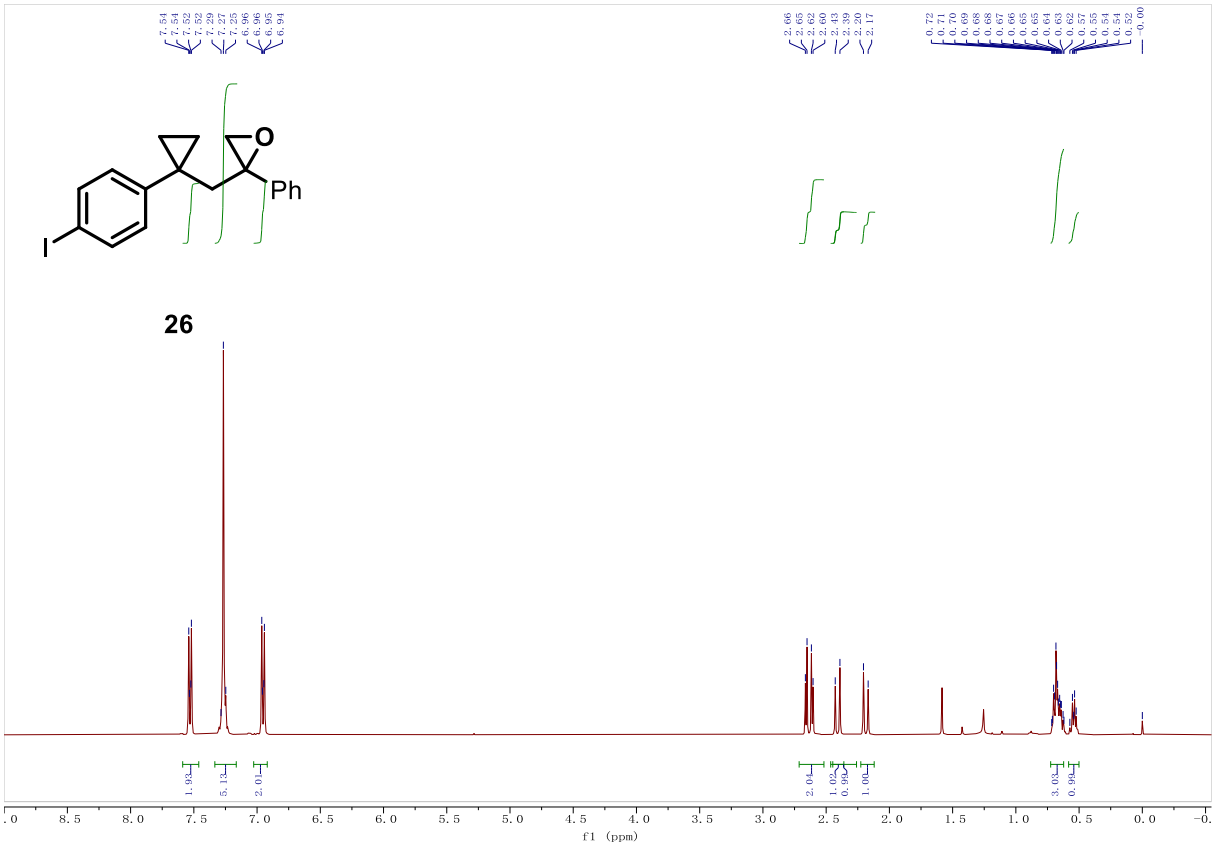
^{1}H NMR (400 MHz, $CDCl_3$)



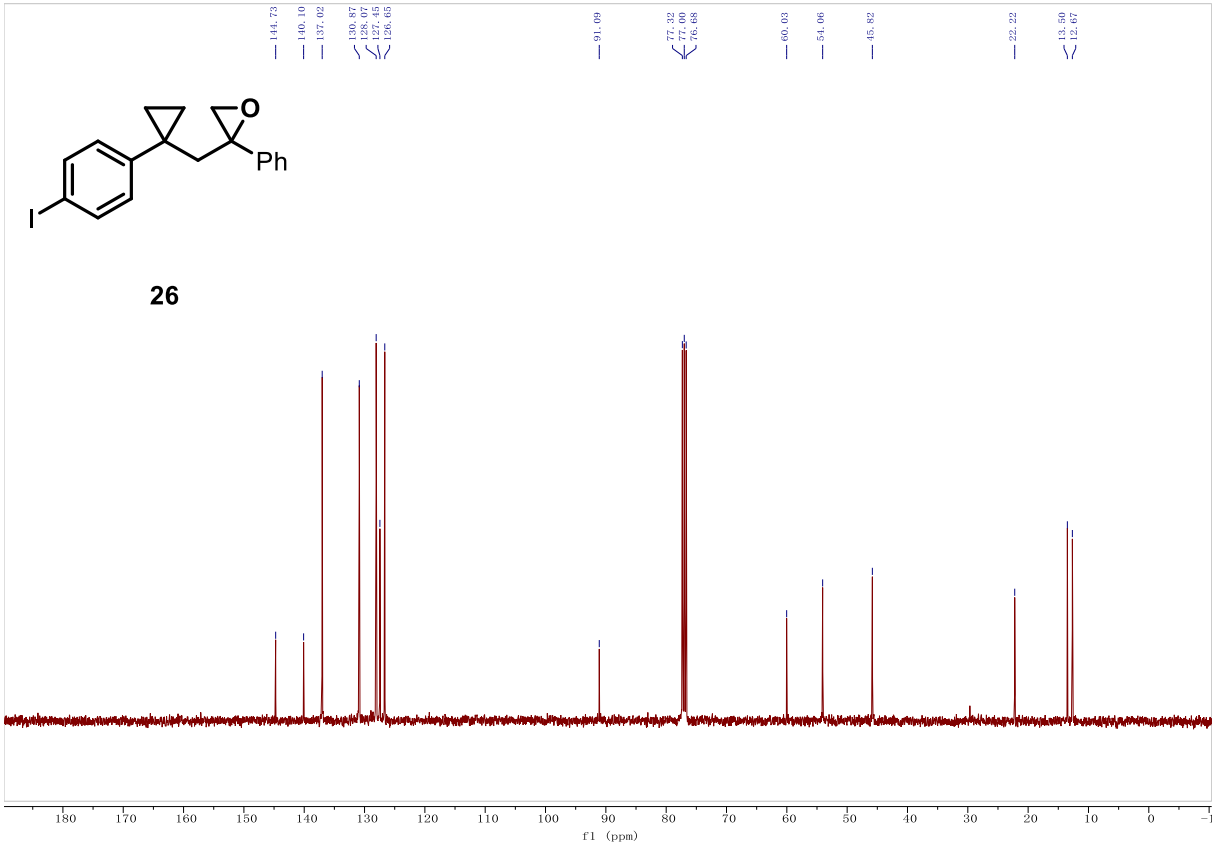
^{13}C NMR (101 MHz, $CDCl_3$)



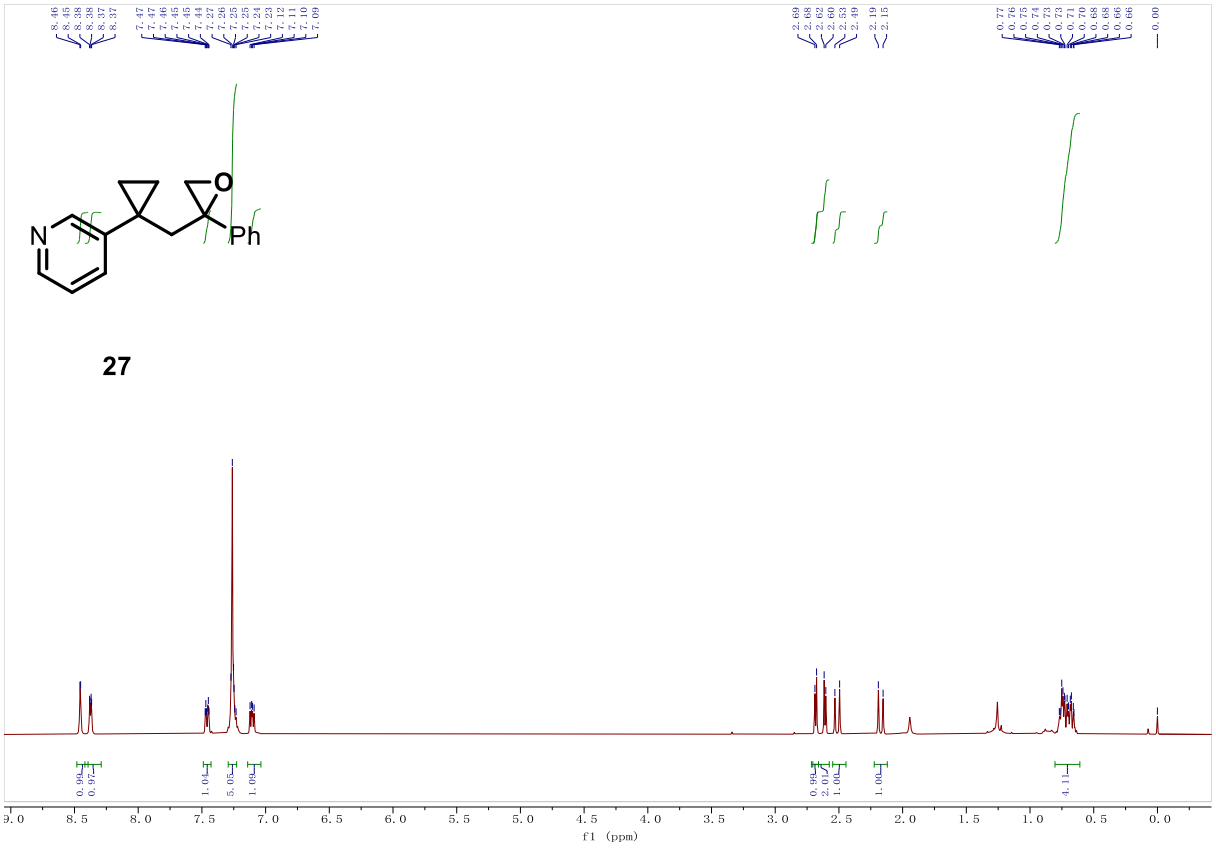
^{1}H NMR (400 MHz, $CDCl_3$)



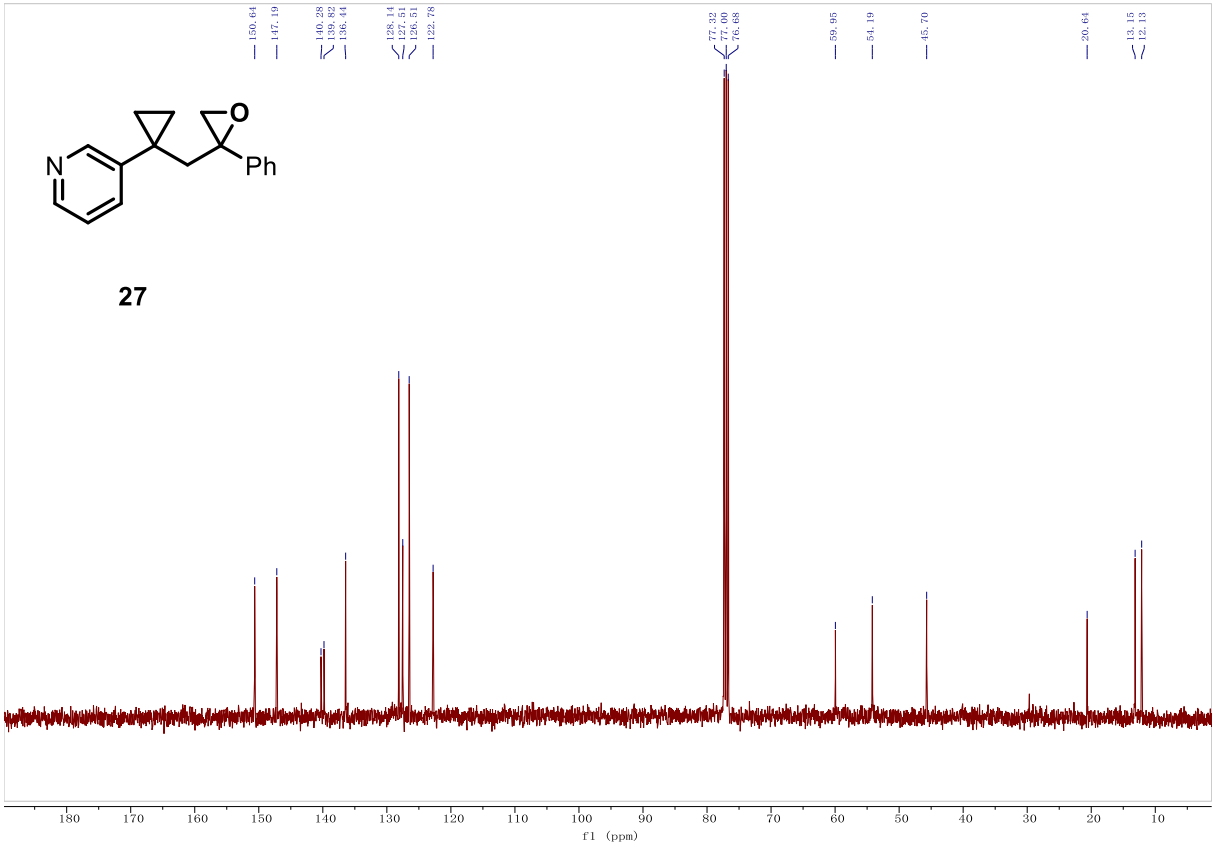
^{13}C NMR (101 MHz, $CDCl_3$)



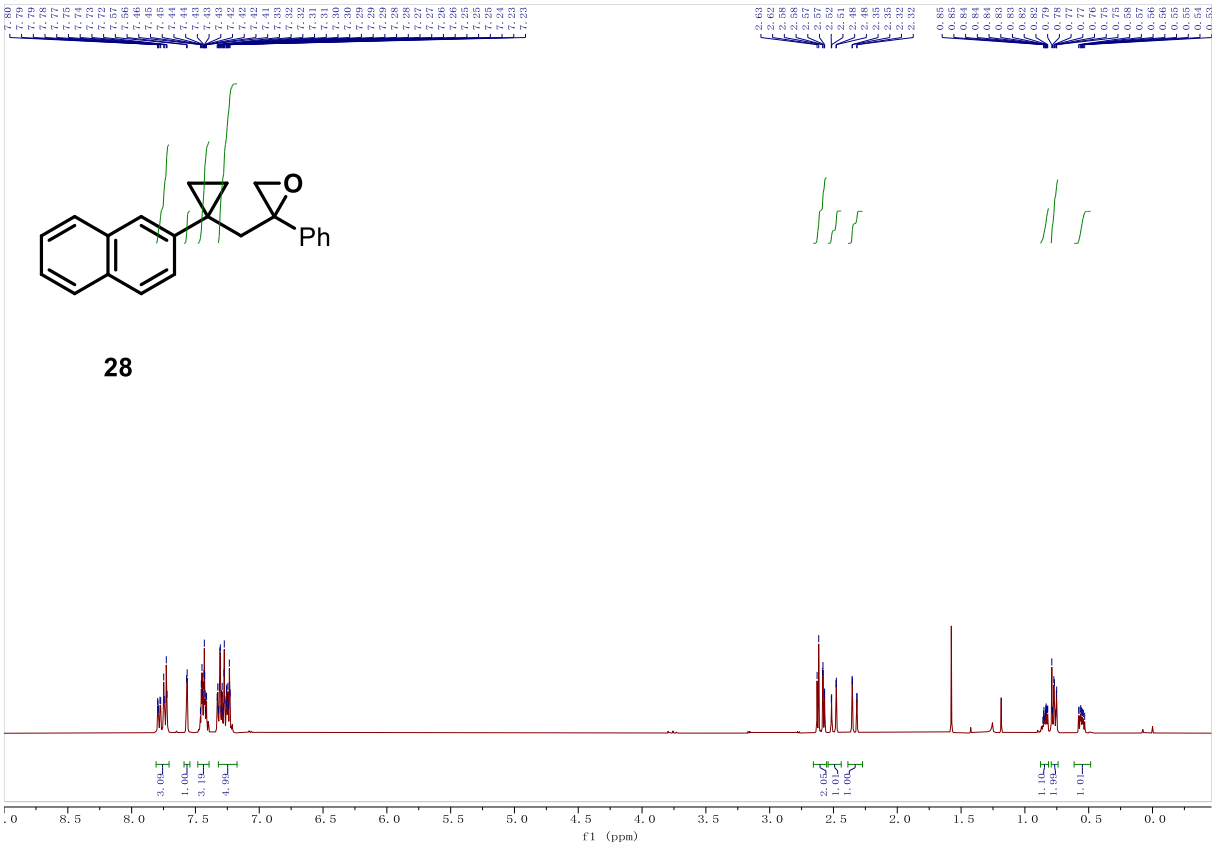
^{1}H NMR (400 MHz, $CDCl_3$)



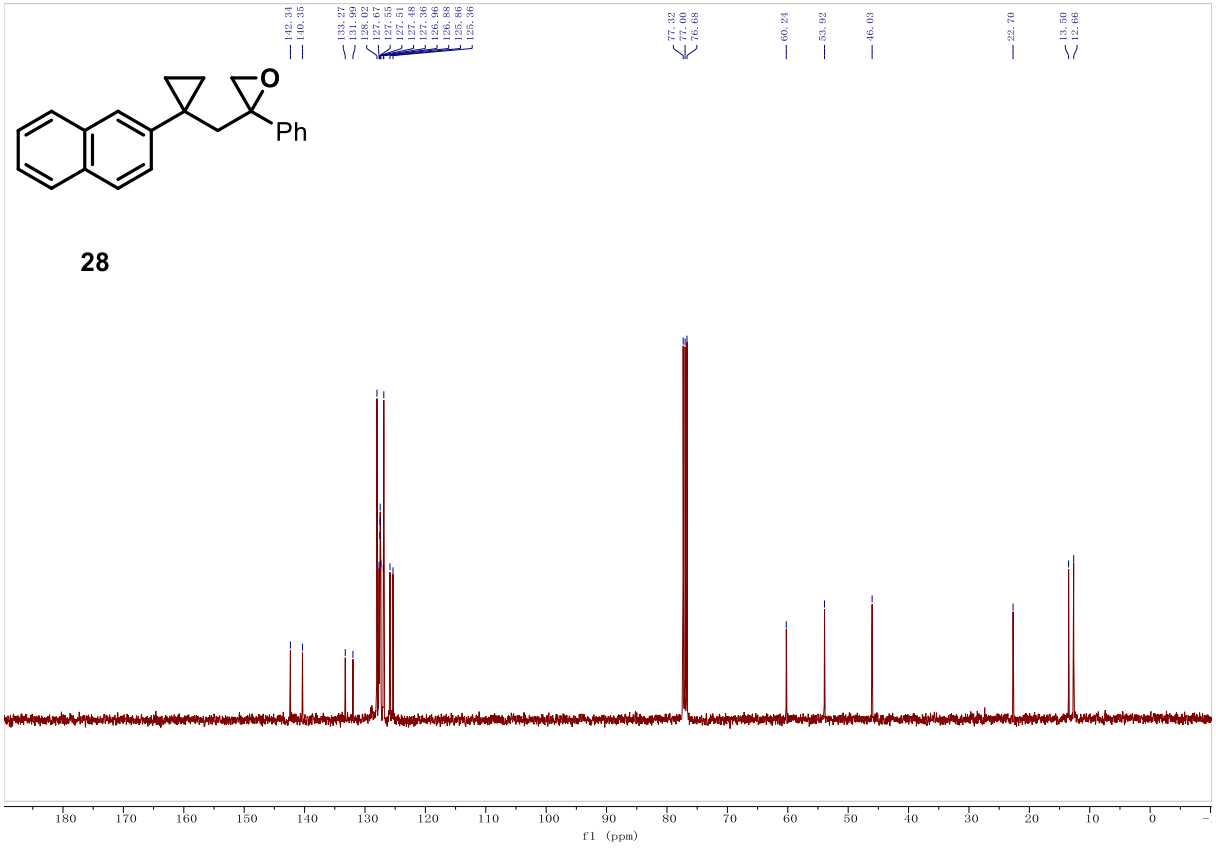
^{13}C NMR (101 MHz, $CDCl_3$)



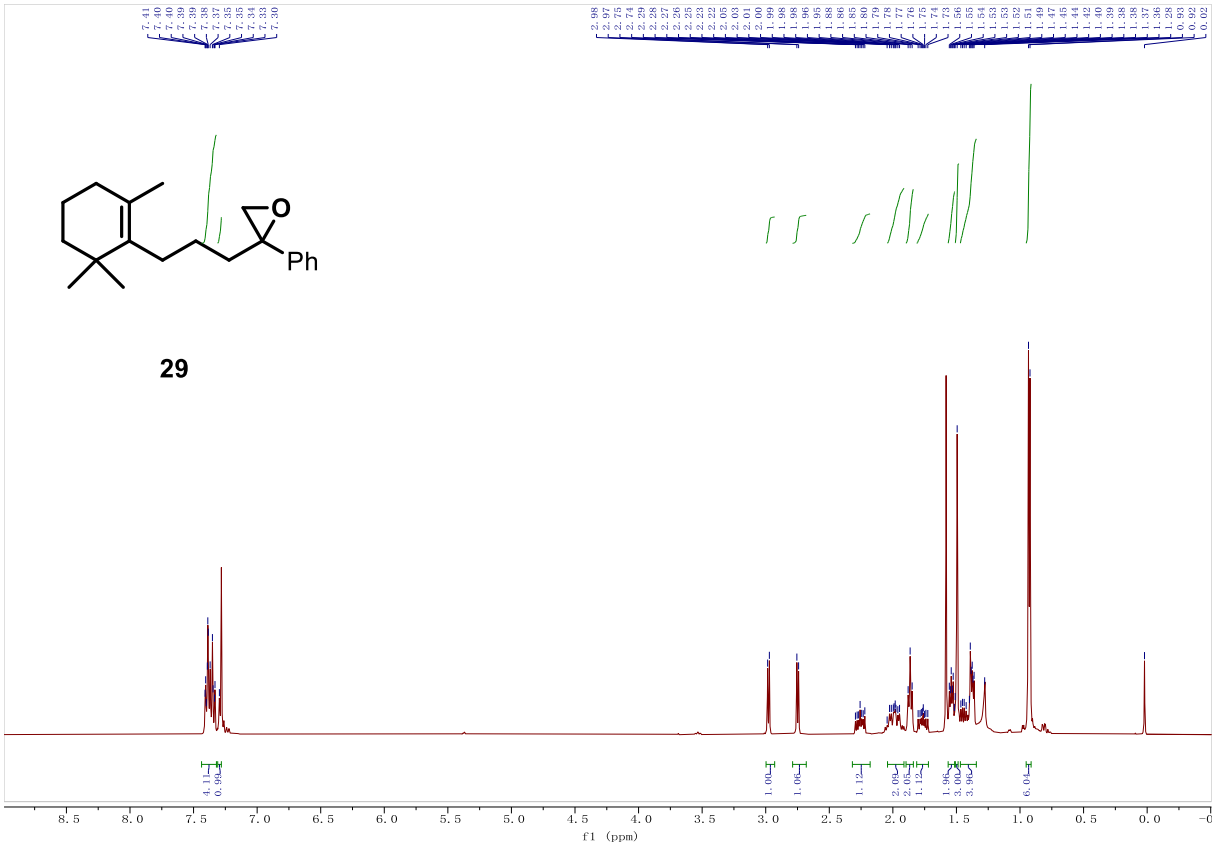
^{1}H NMR (400 MHz, $CDCl_3$)



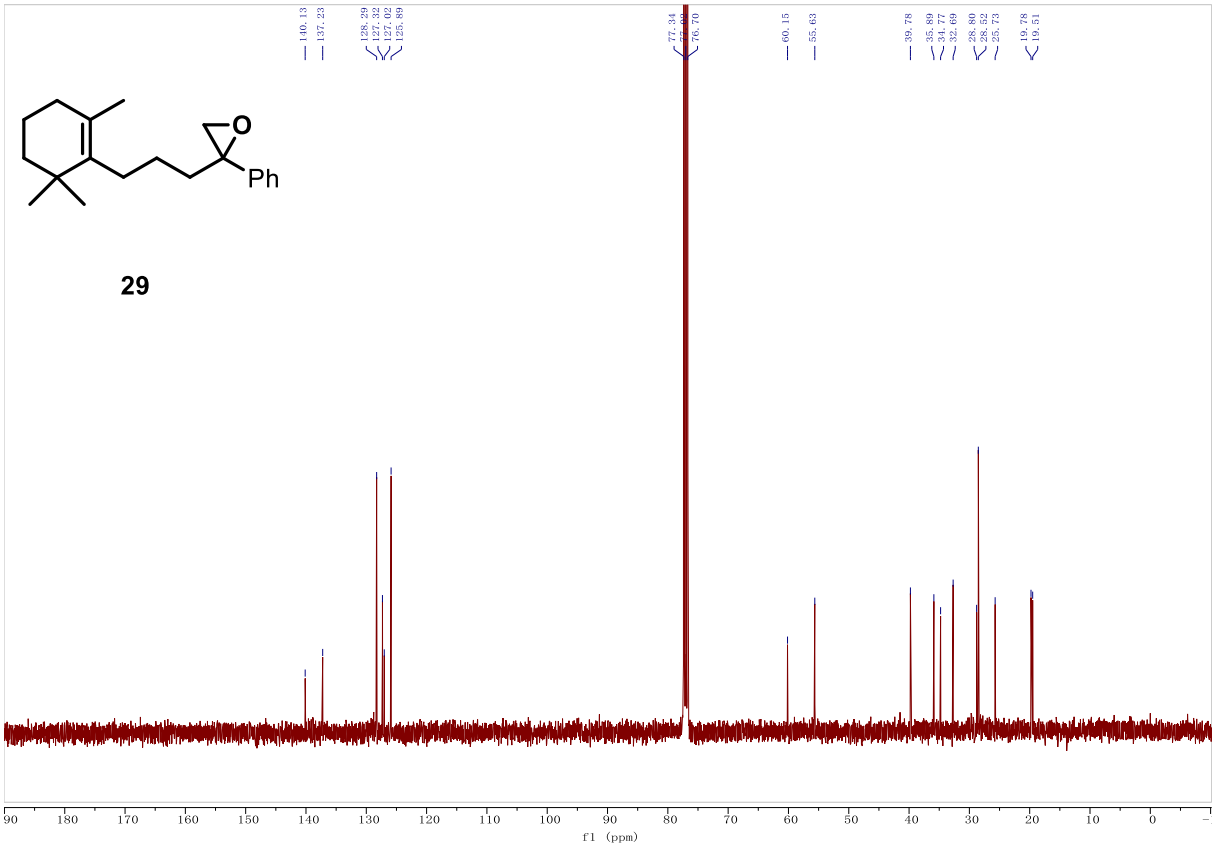
^{13}C NMR (101 MHz, $CDCl_3$)



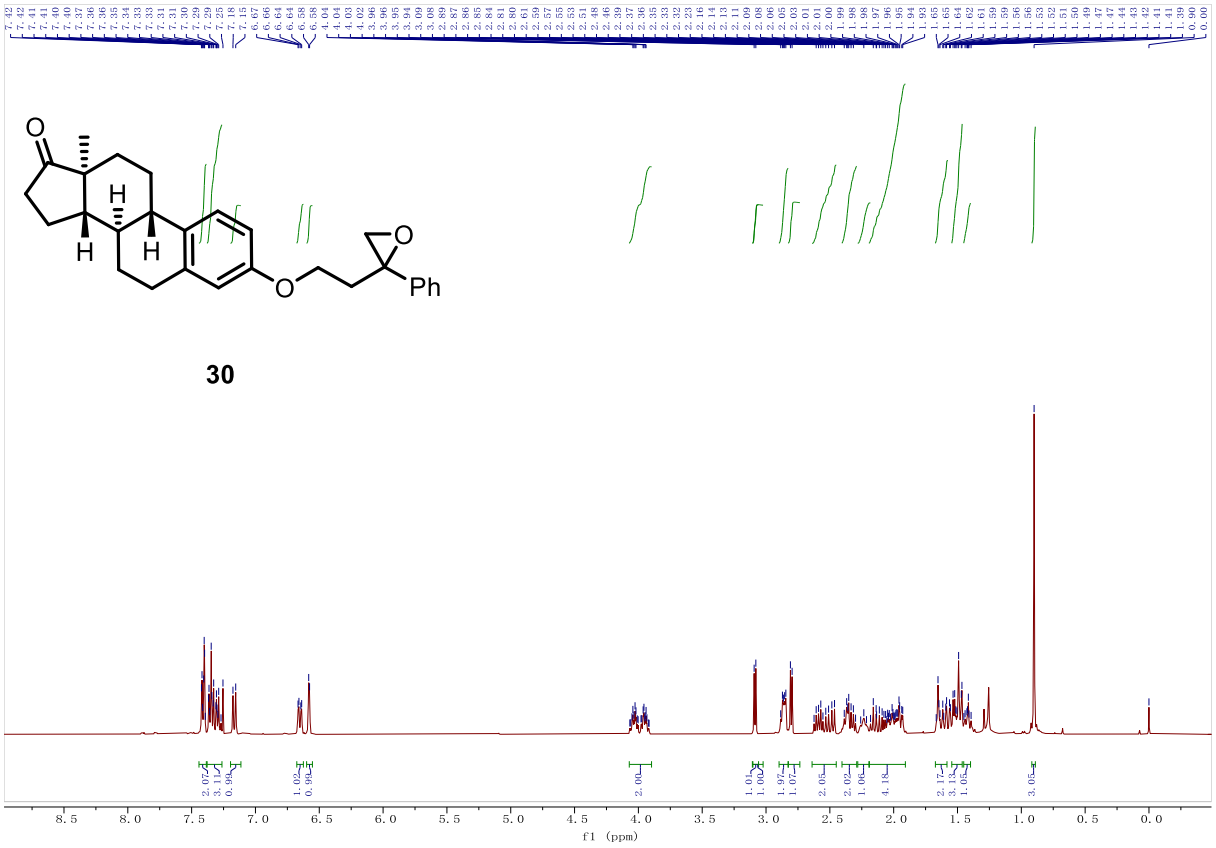
^{1}H NMR (400 MHz, $CDCl_3$)



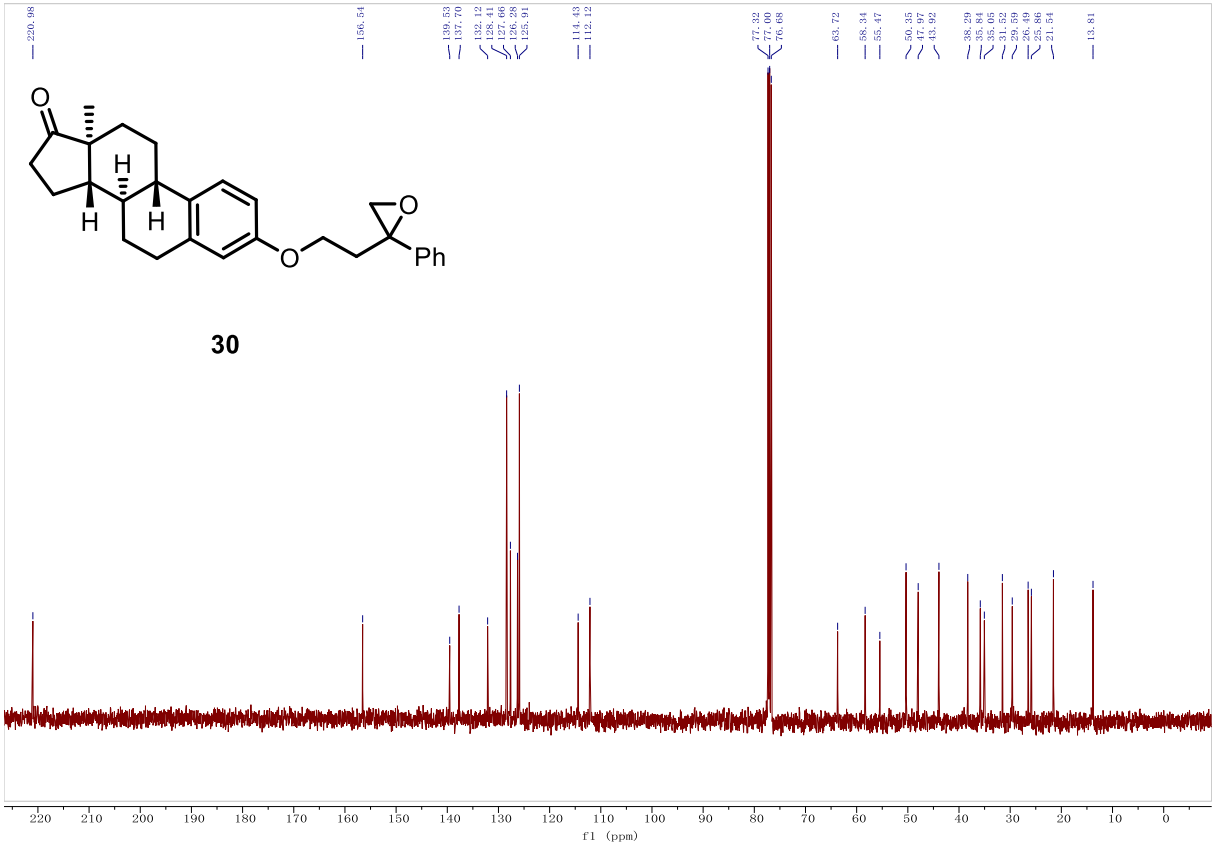
^{13}C NMR (101 MHz, $CDCl_3$)



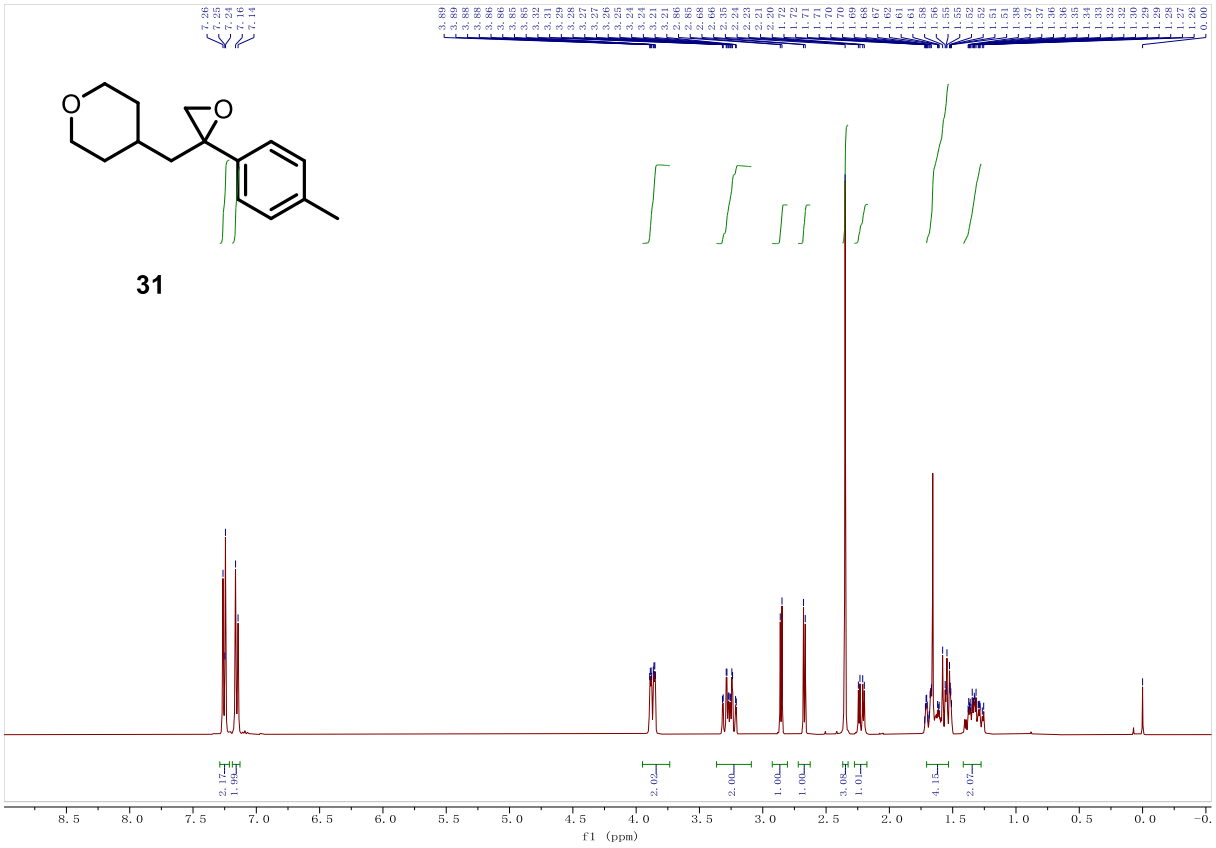
^{1}H NMR (400 MHz, $CDCl_3$)



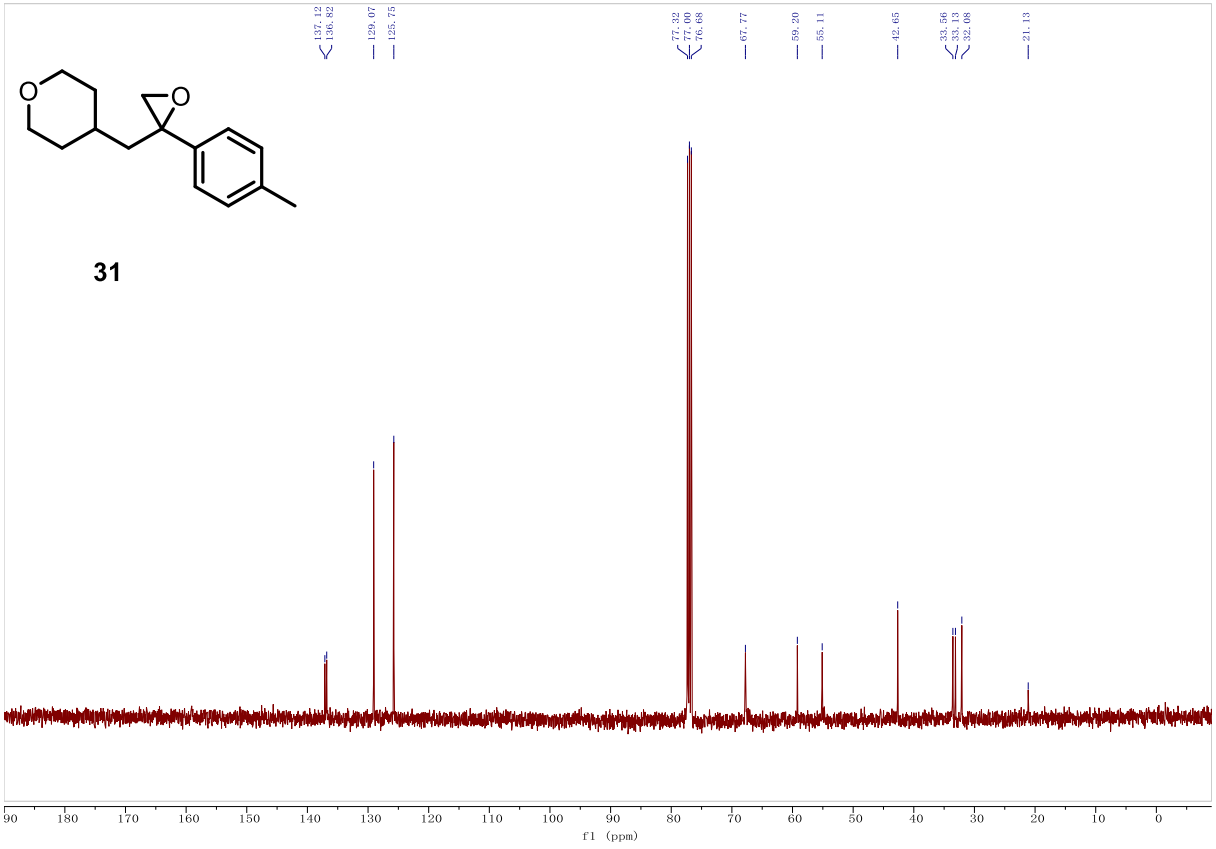
^{13}C NMR (101 MHz, $CDCl_3$)



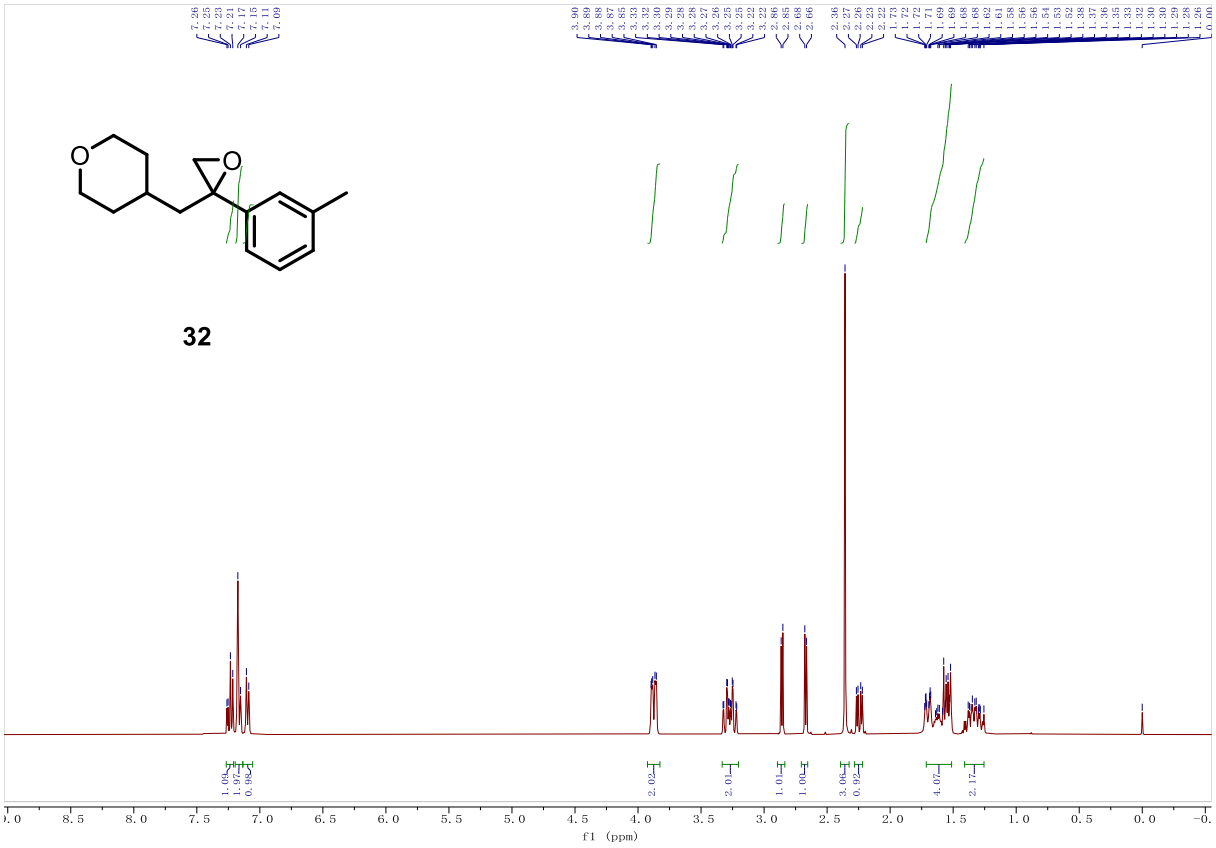
^{1}H NMR (400 MHz, $CDCl_3$)



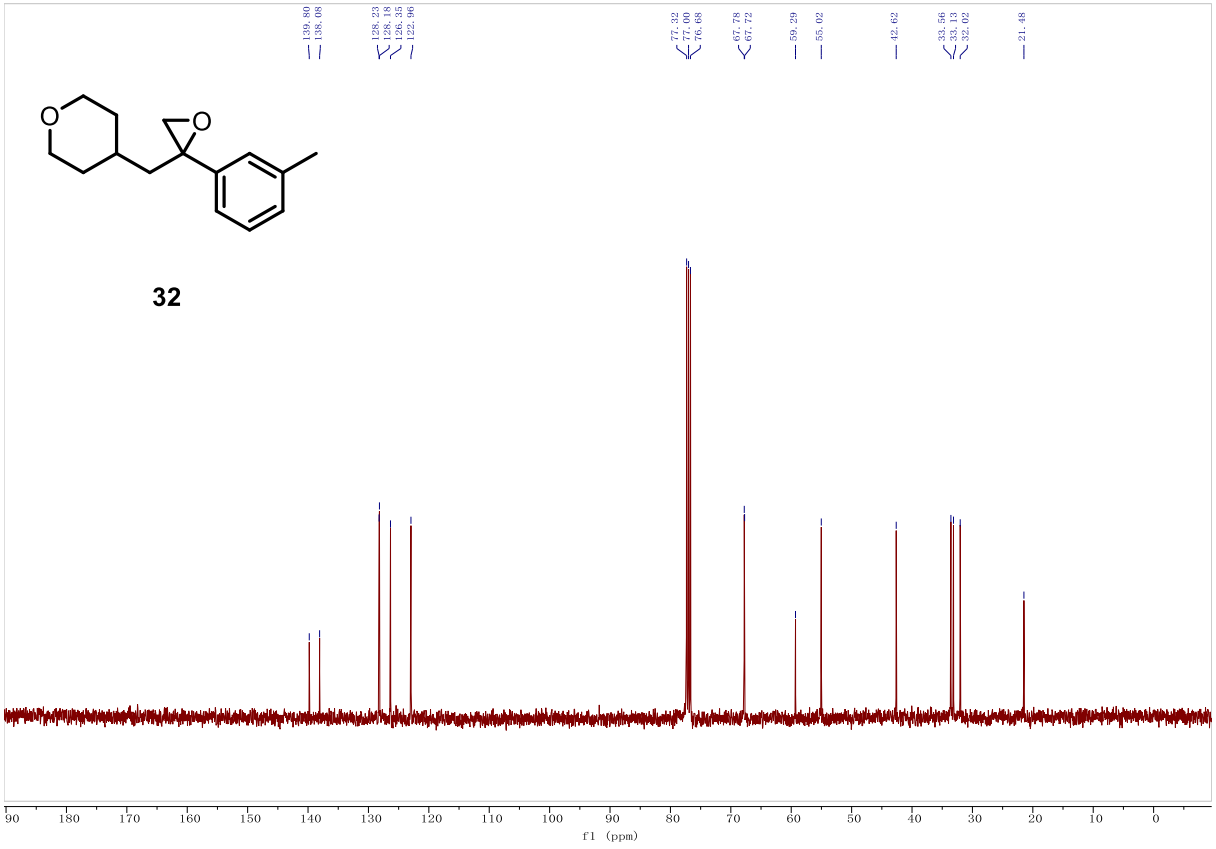
^{13}C NMR (101 MHz, $CDCl_3$)



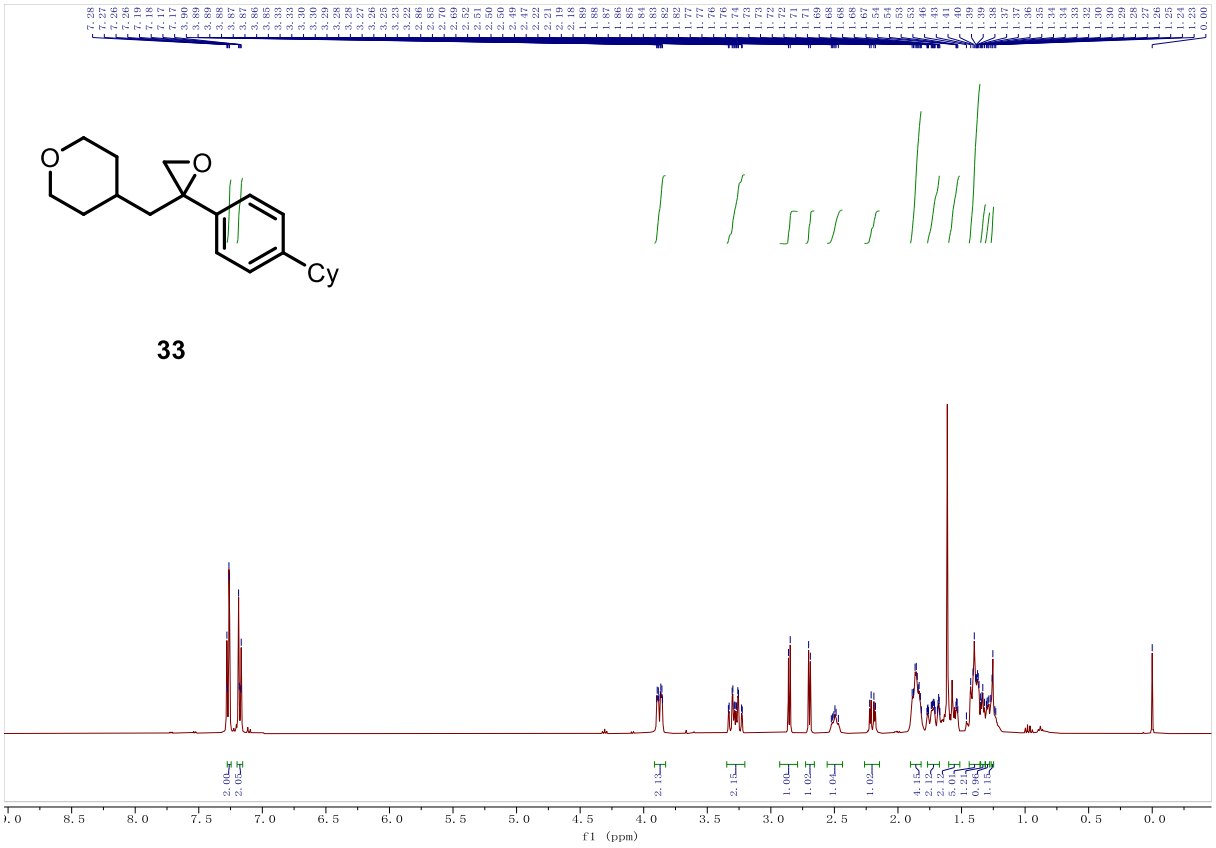
^{1}H NMR (400 MHz, $CDCl_3$)



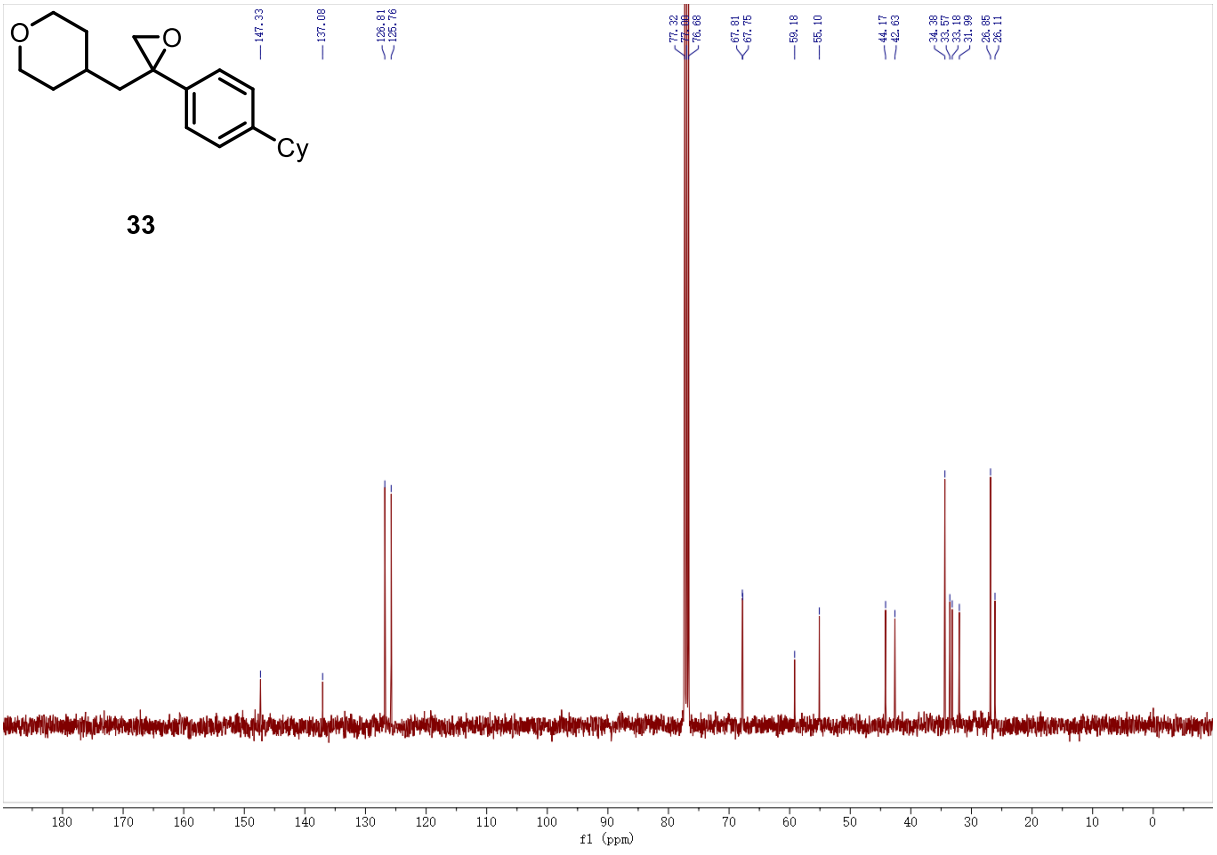
^{13}C NMR (101 MHz, $CDCl_3$)



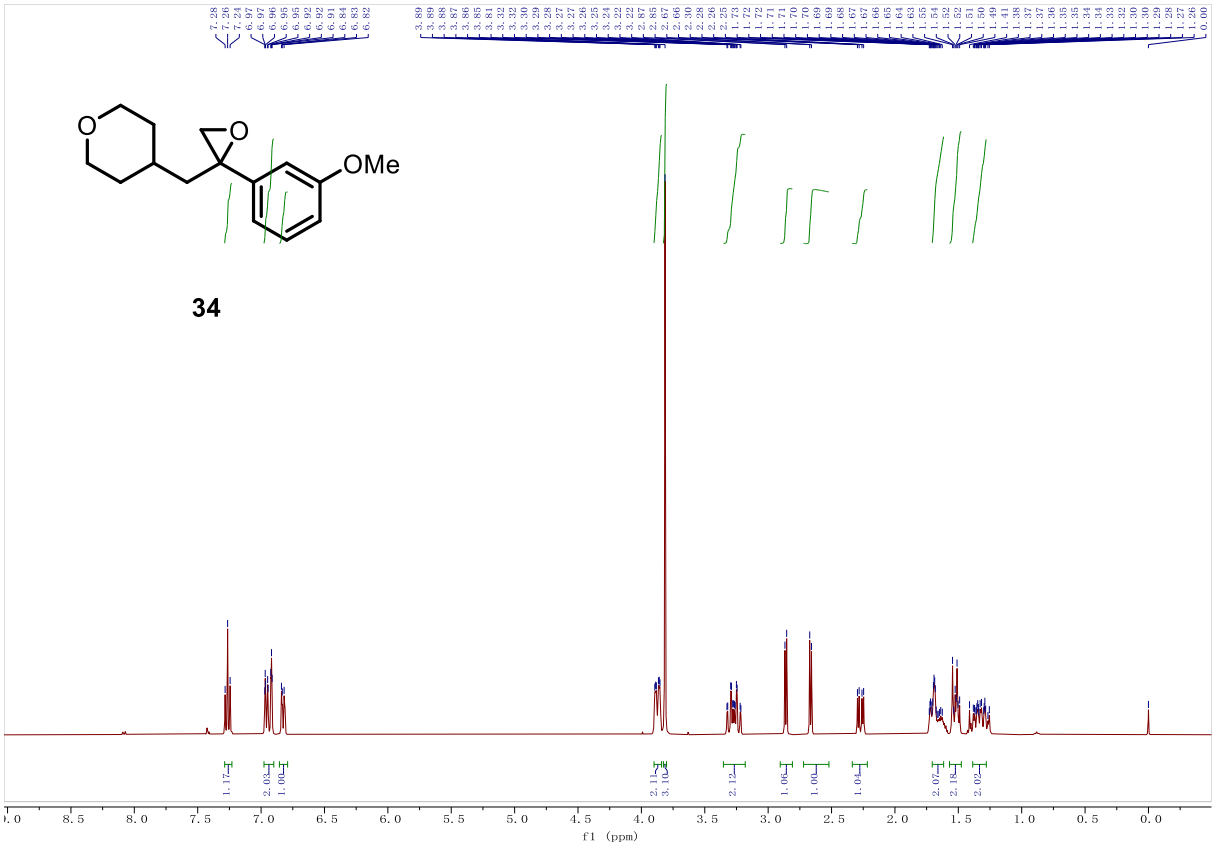
^{1}H NMR (400 MHz, $CDCl_3$)



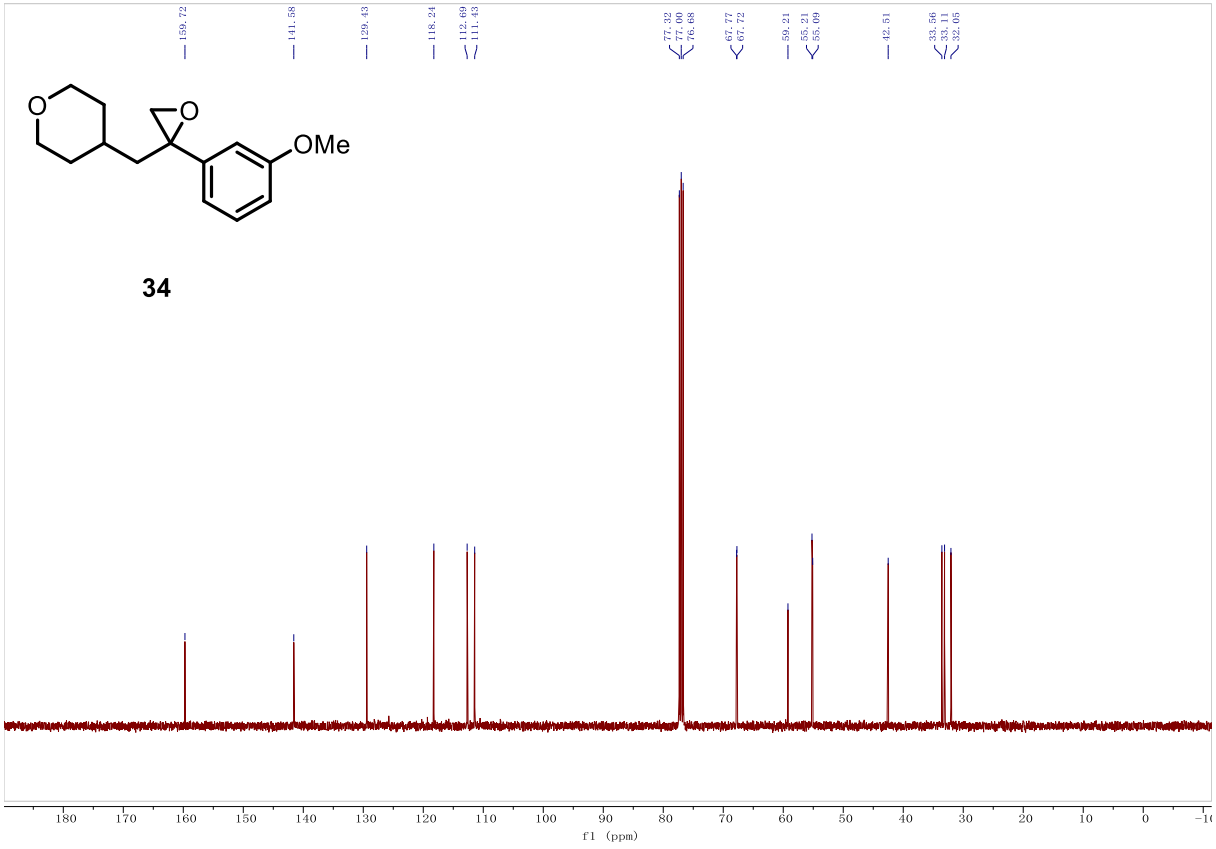
^{13}C NMR (101 MHz, $CDCl_3$)



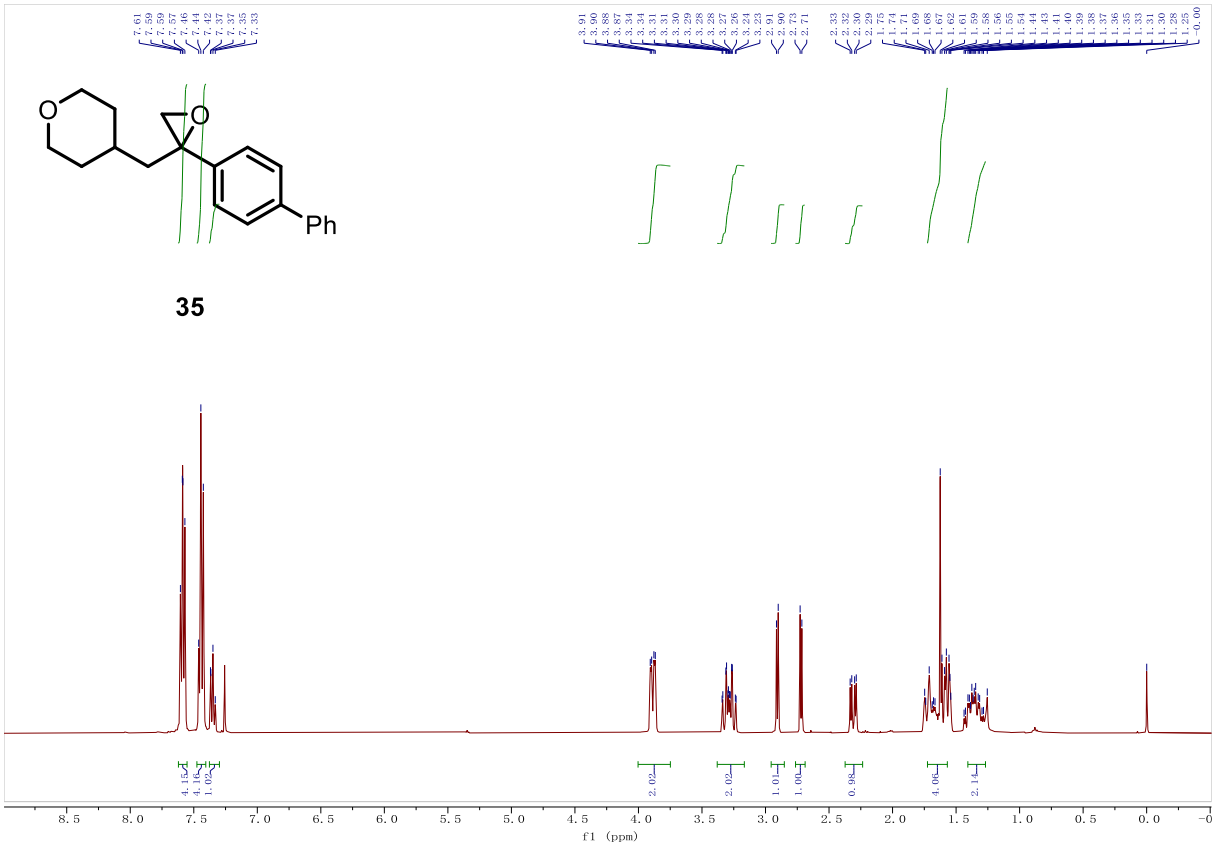
^{1}H NMR (400 MHz, $CDCl_3$)



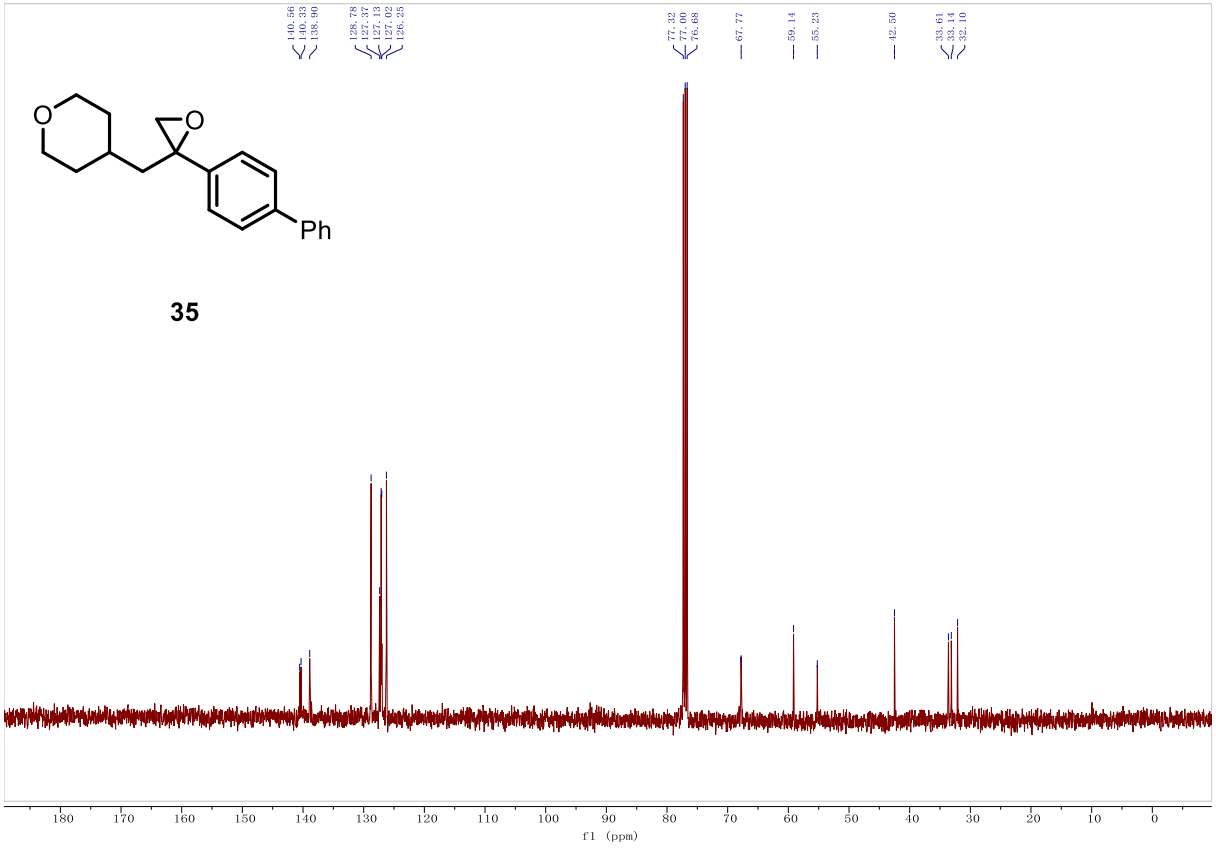
^{13}C NMR (101 MHz, $CDCl_3$)



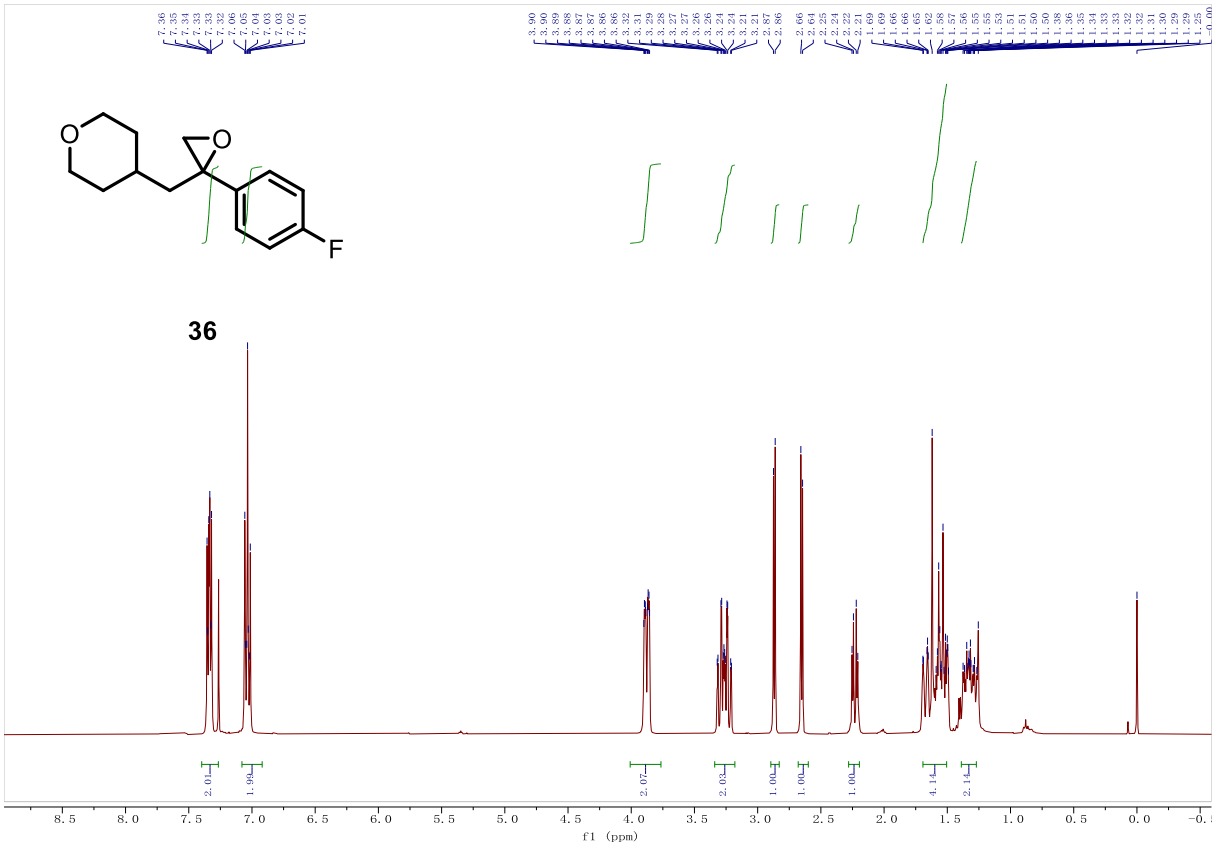
^{1}H NMR (400 MHz, $CDCl_3$)



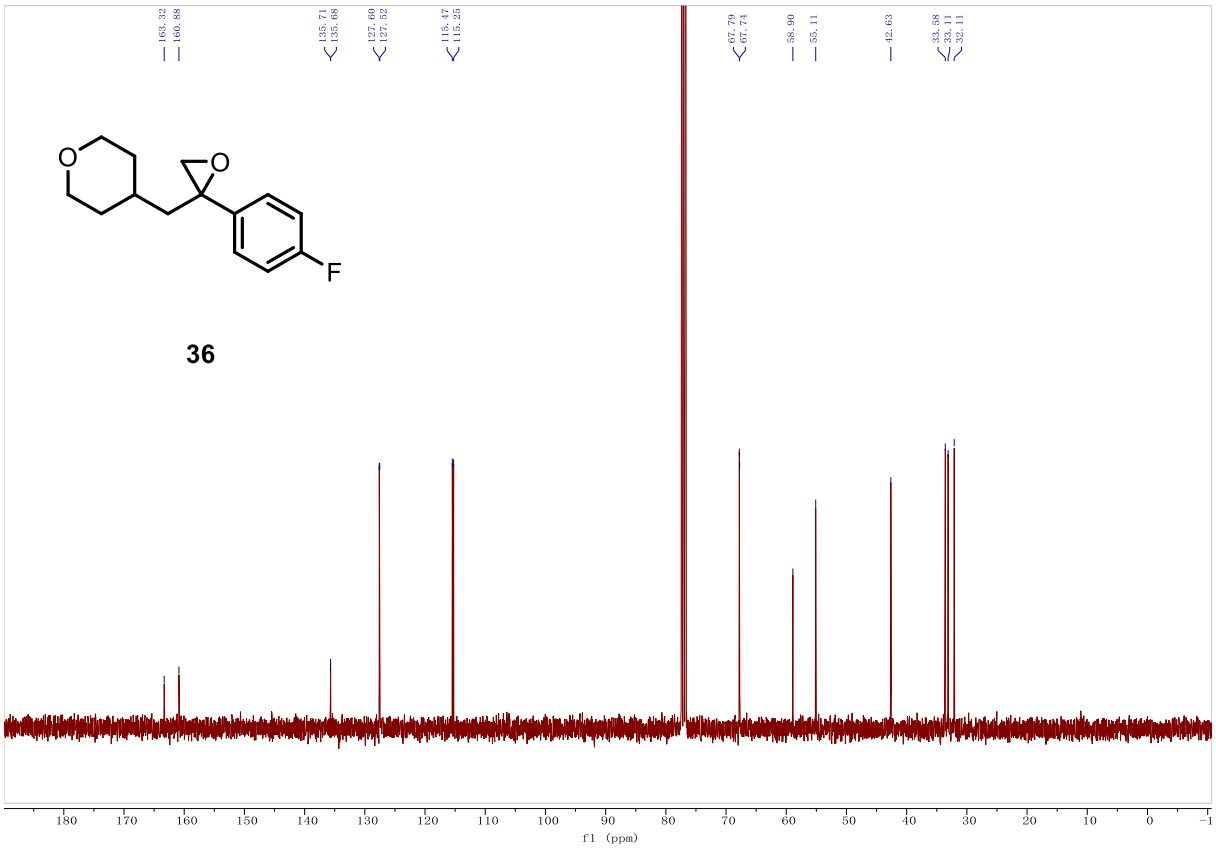
^{13}C NMR (101 MHz, $CDCl_3$)



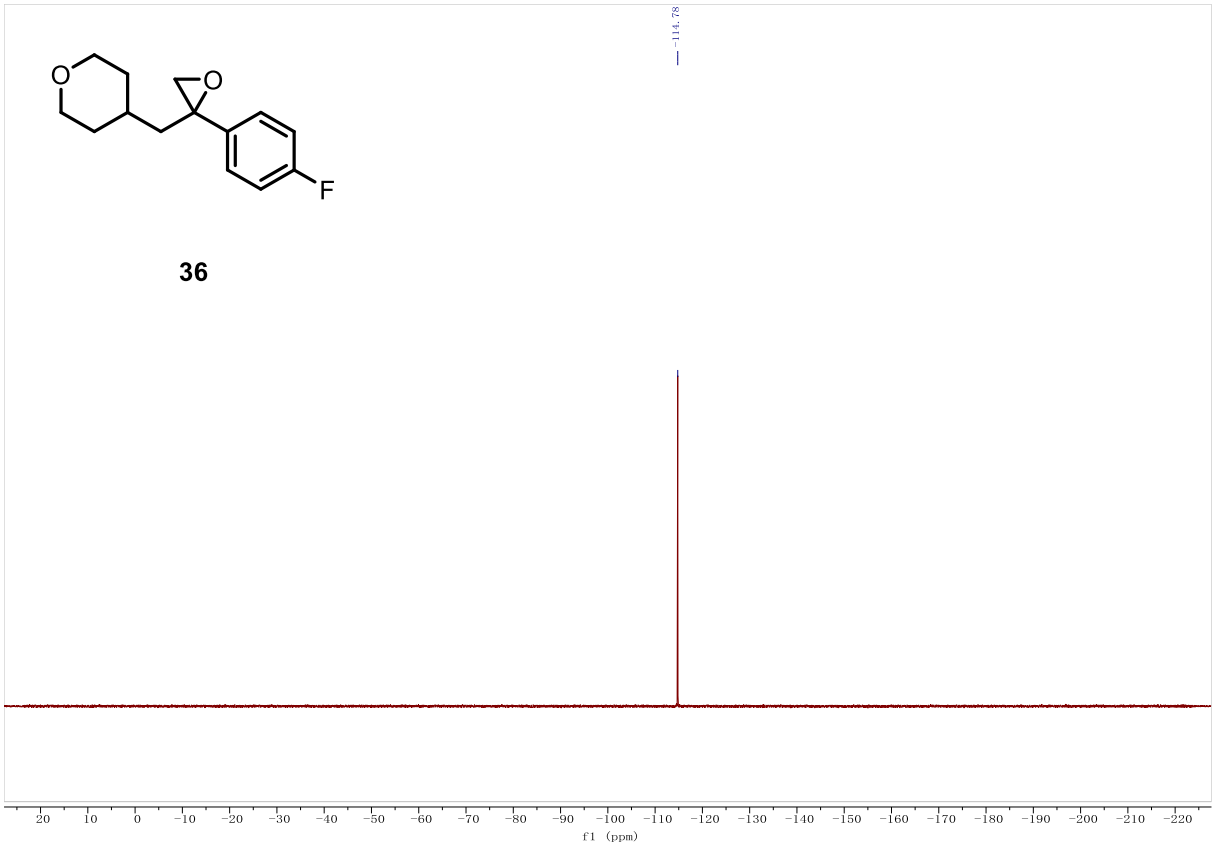
^{1}H NMR (400 MHz, $CDCl_3$)



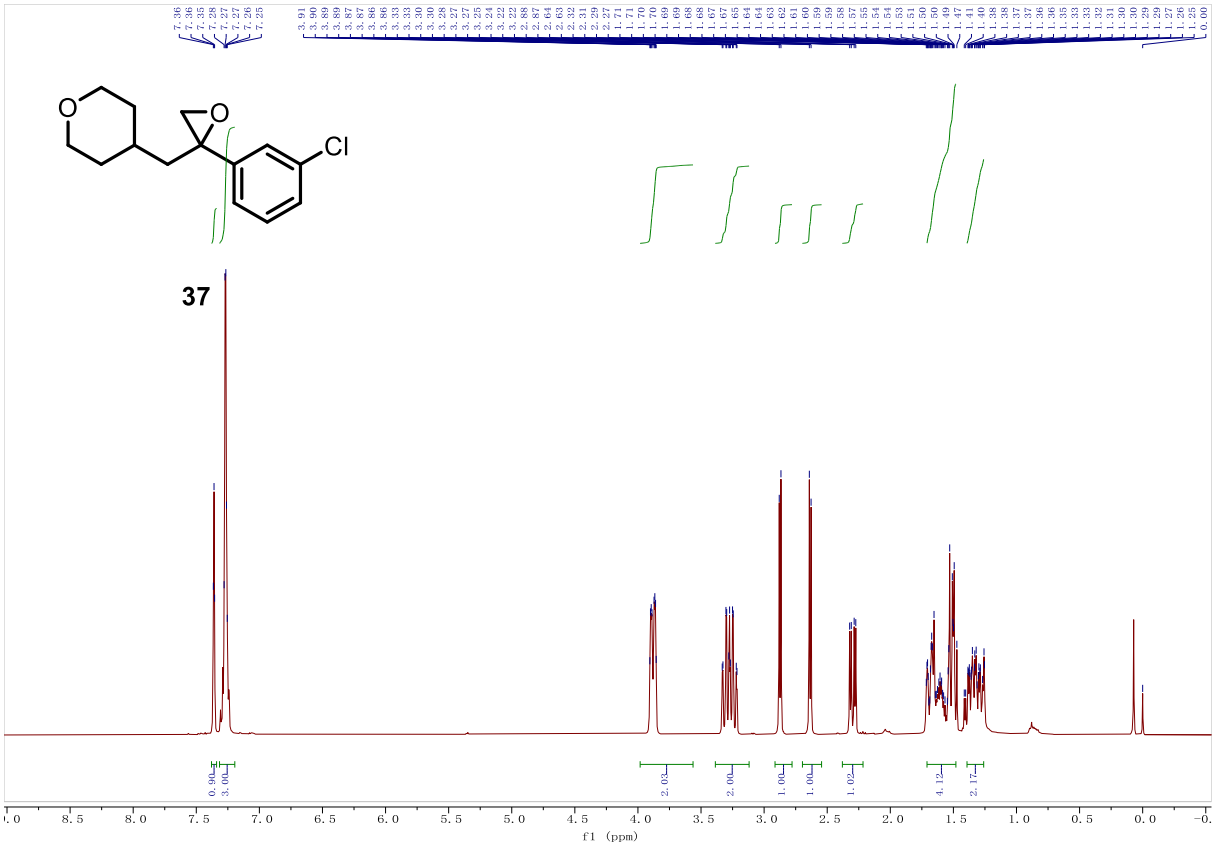
^{13}C NMR (101 MHz, $CDCl_3$)



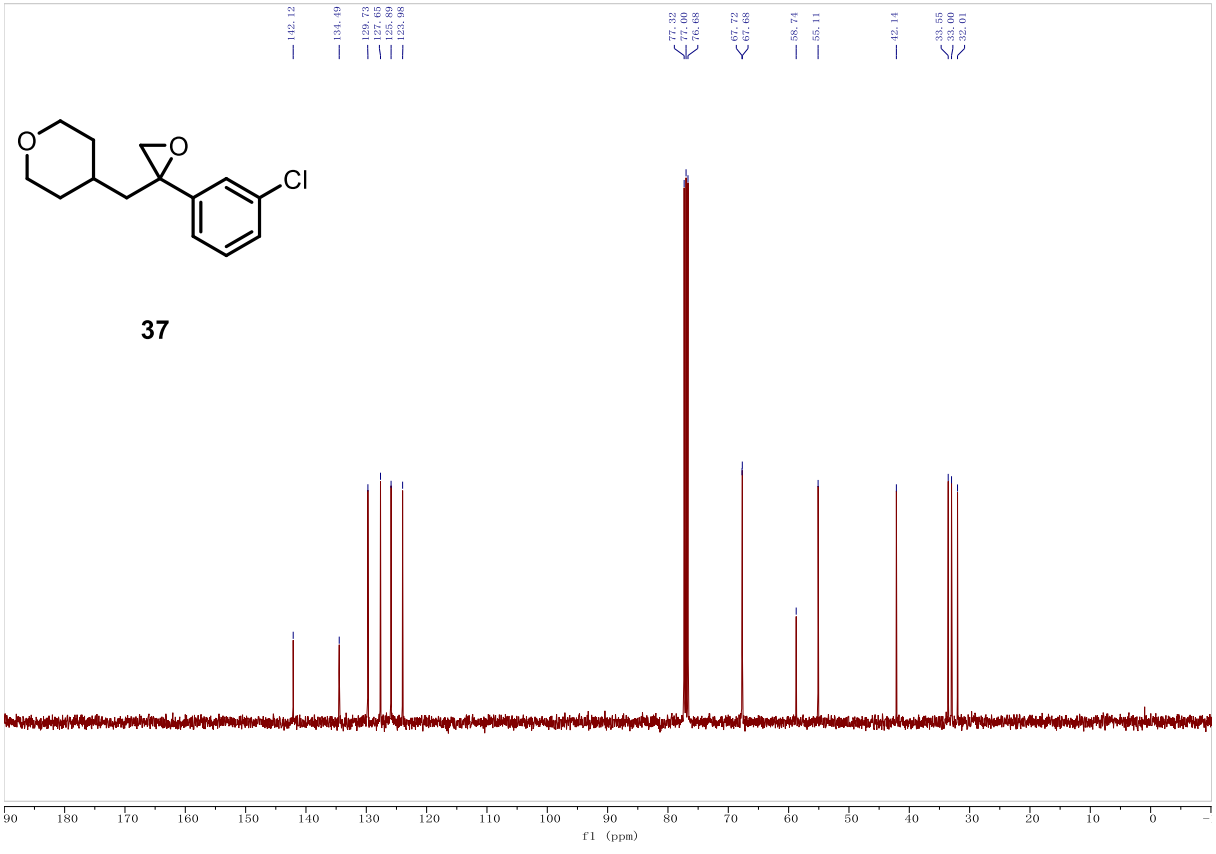
^{13}C NMR (101 MHz, $CDCl_3$)



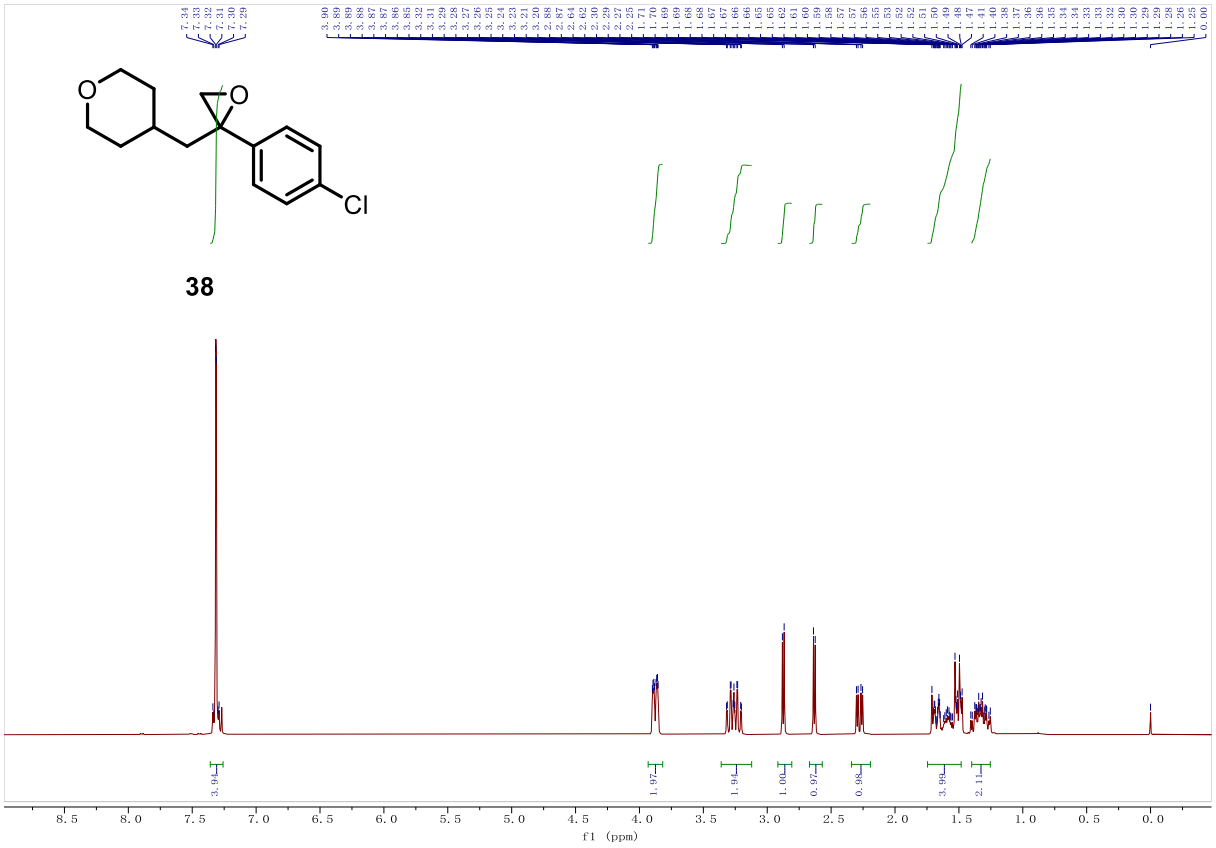
^{1}H NMR (400 MHz, $CDCl_3$)



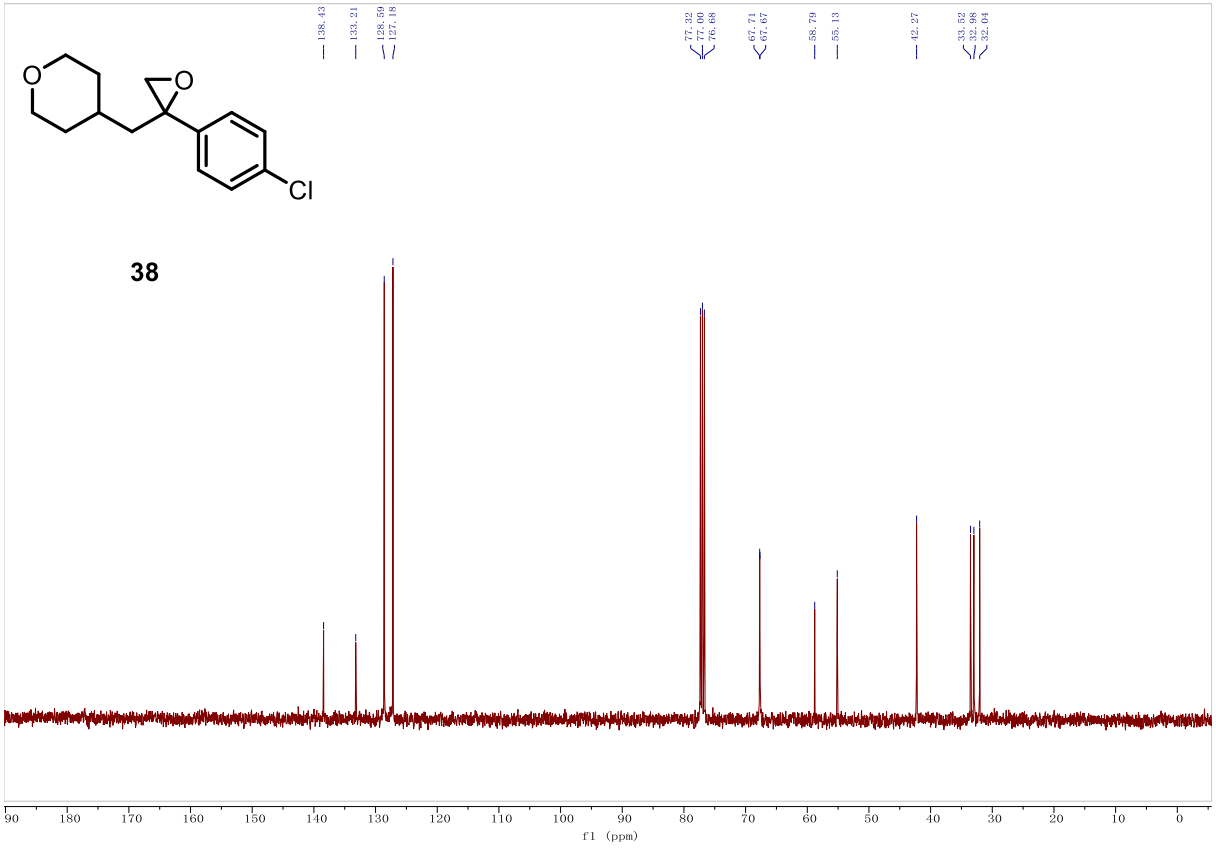
^{13}C NMR (101 MHz, $CDCl_3$)



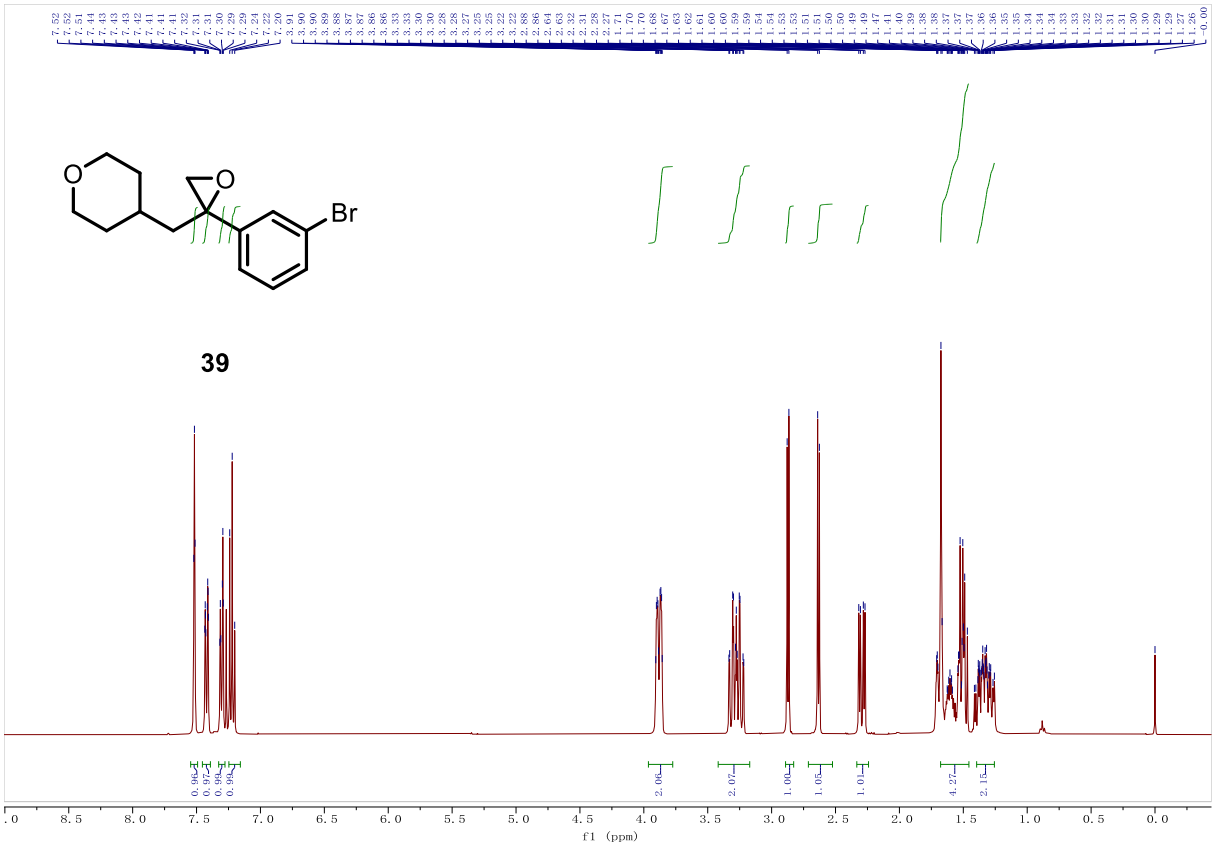
^{1}H NMR (400 MHz, $CDCl_3$)



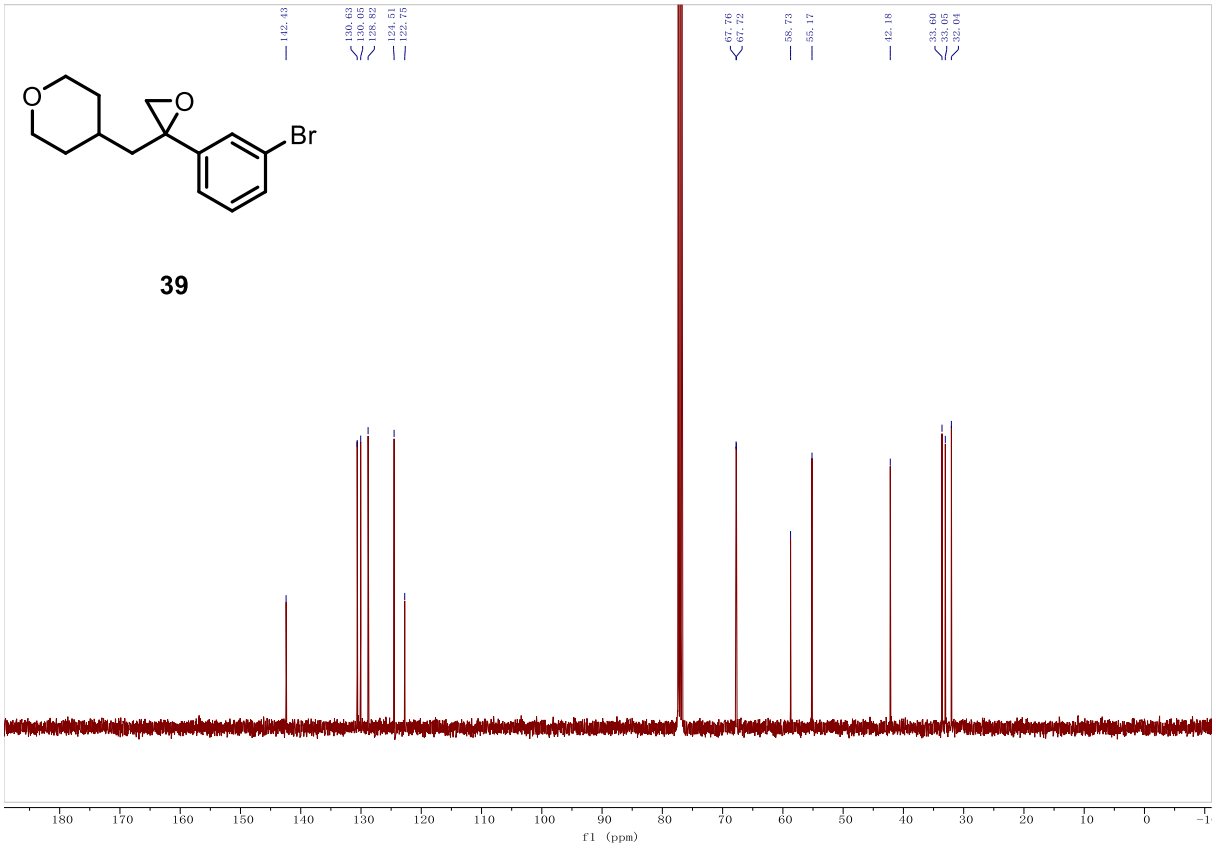
^{13}C NMR (101 MHz, $CDCl_3$)



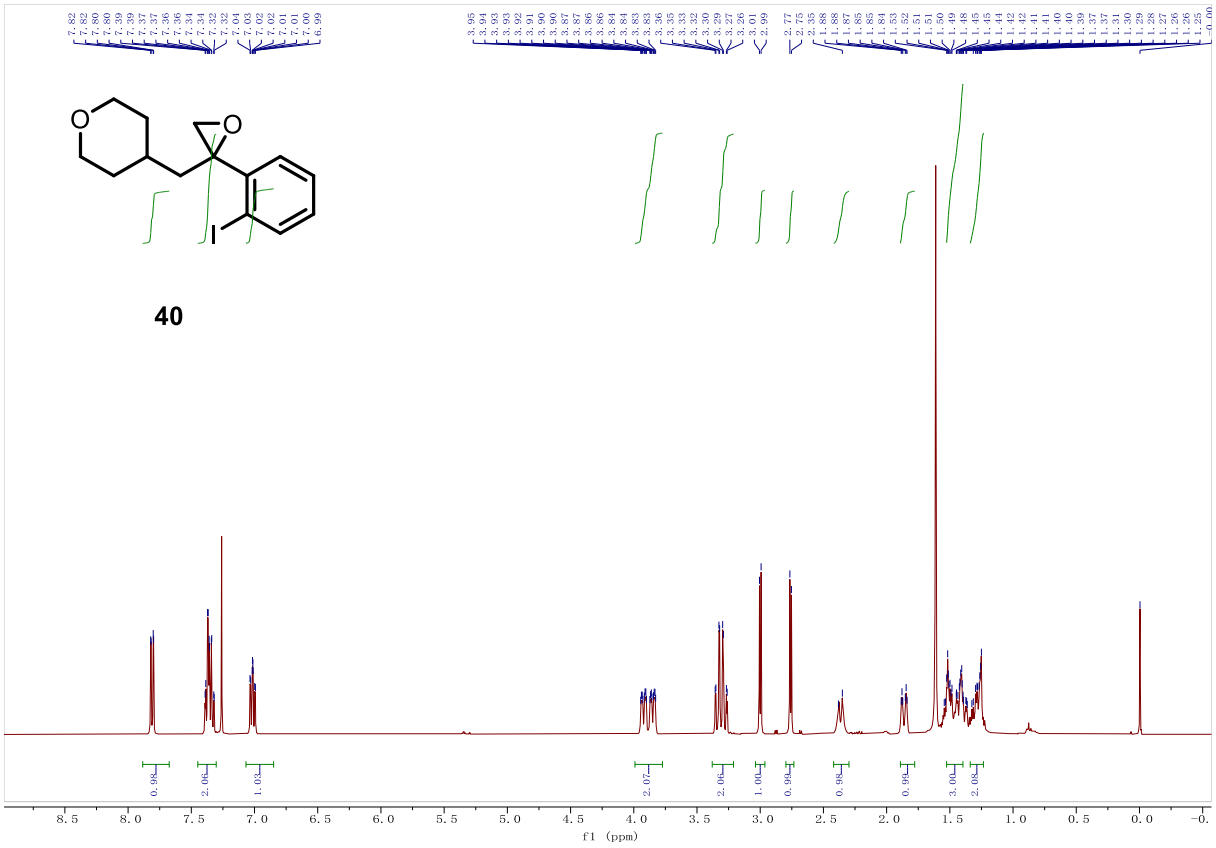
^{1}H NMR (400 MHz, $CDCl_3$)



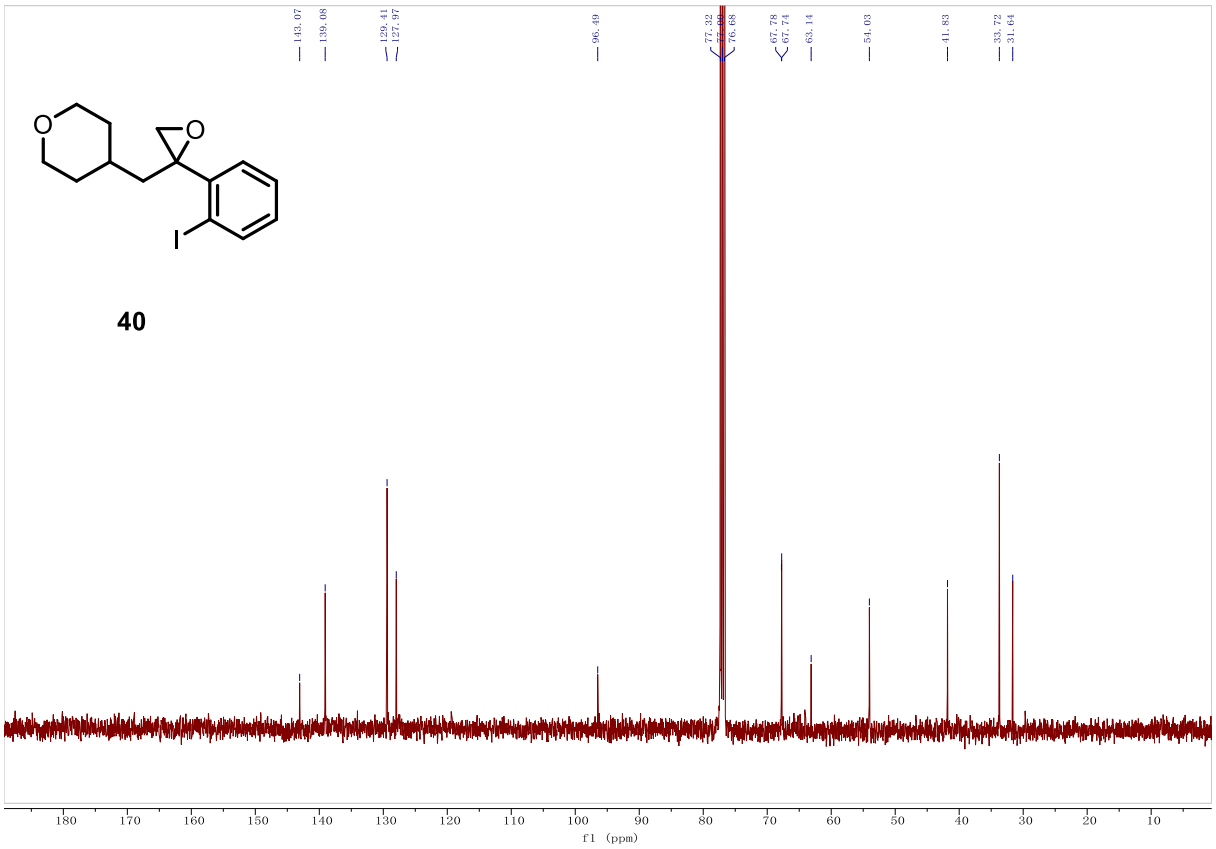
^{13}C NMR (101 MHz, $CDCl_3$)



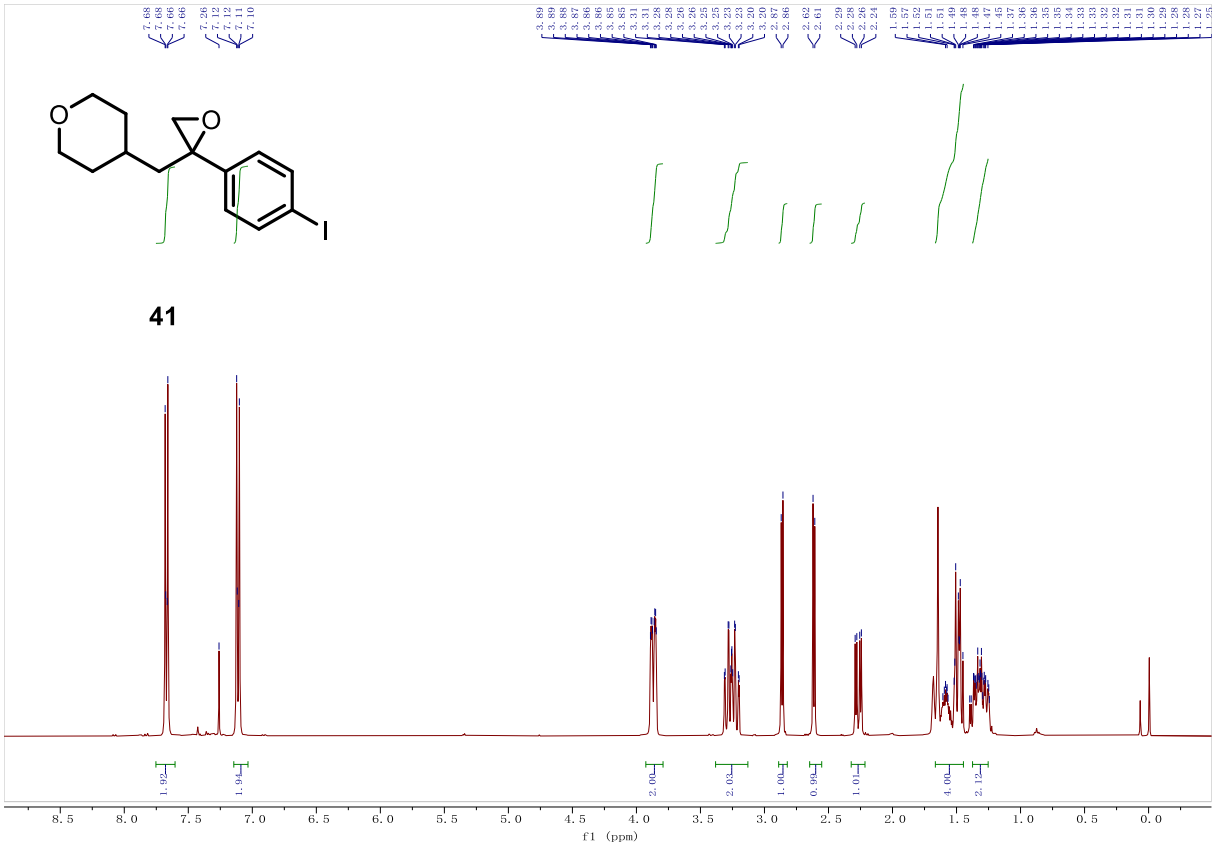
^{1}H NMR (400 MHz, $CDCl_3$)



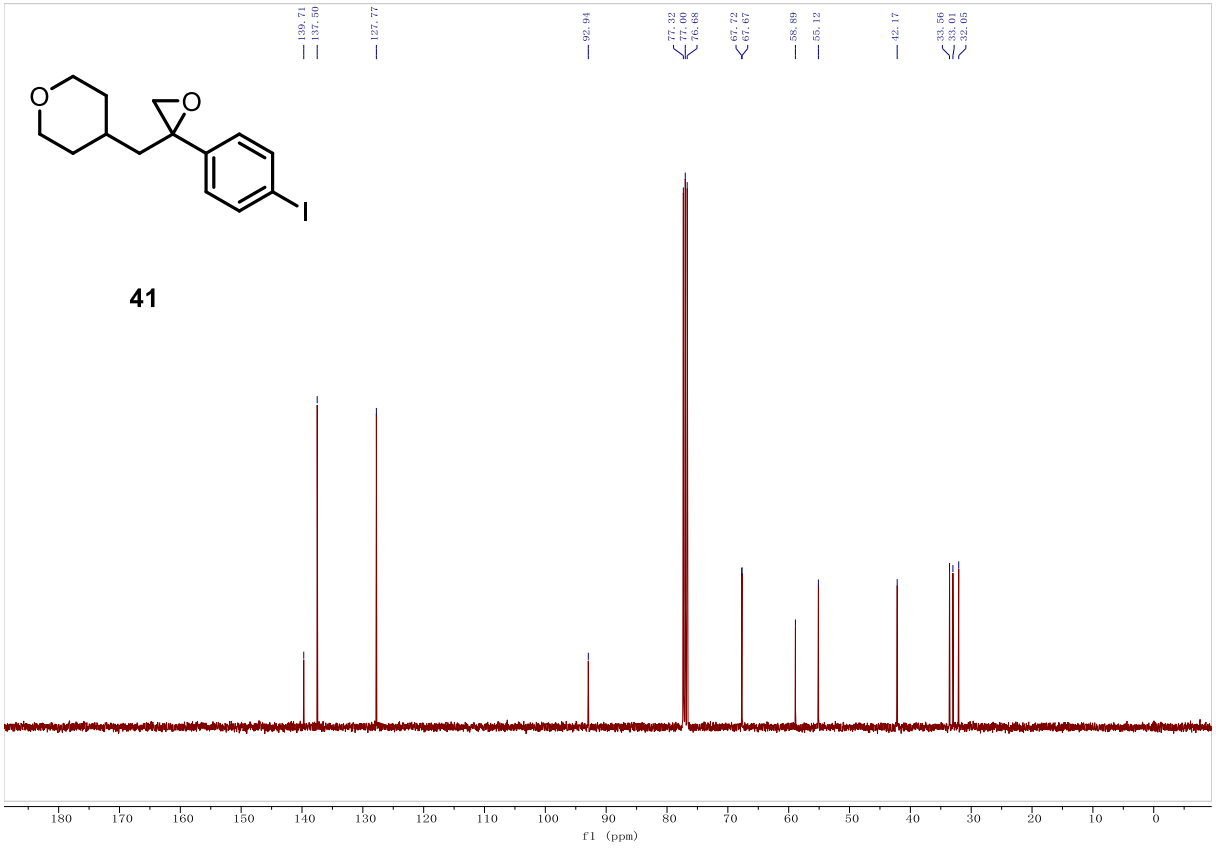
^{13}C NMR (101 MHz, $CDCl_3$)



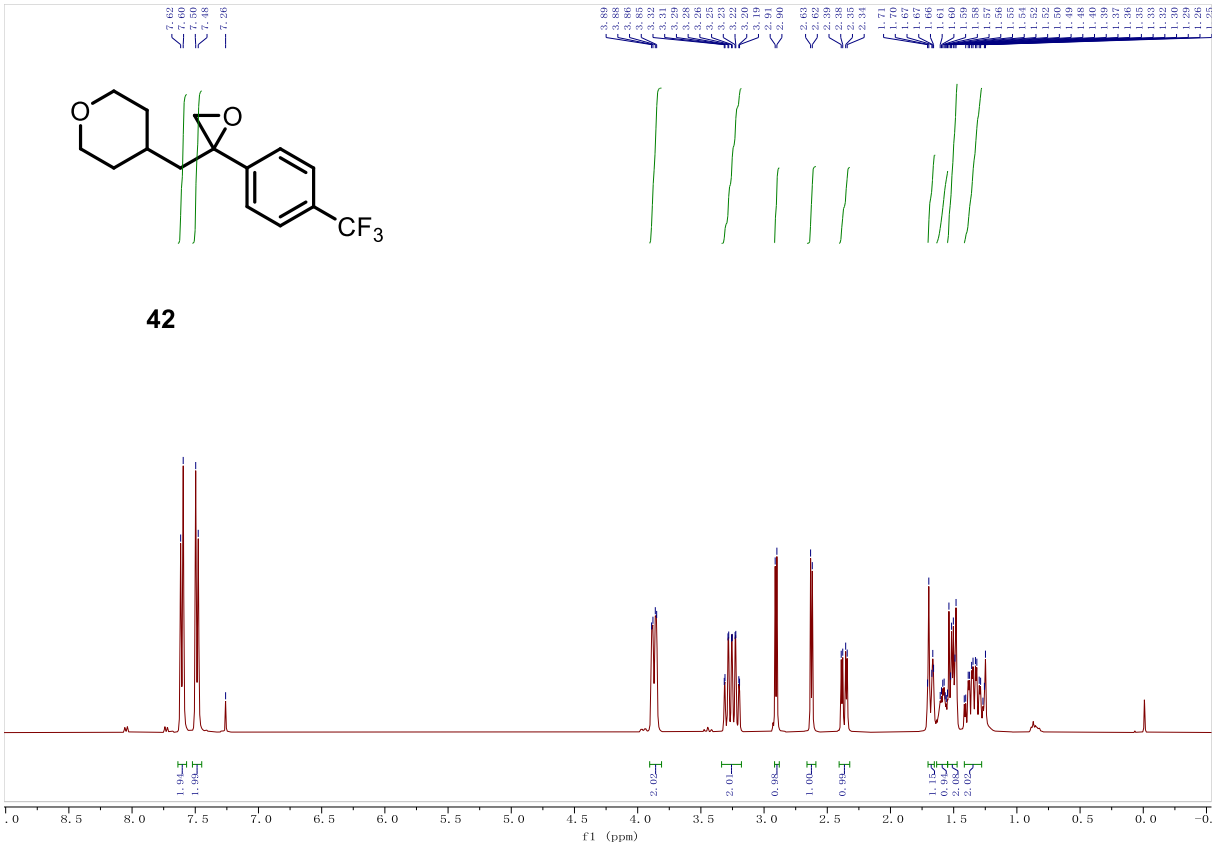
^{1}H NMR (400 MHz, $CDCl_3$)



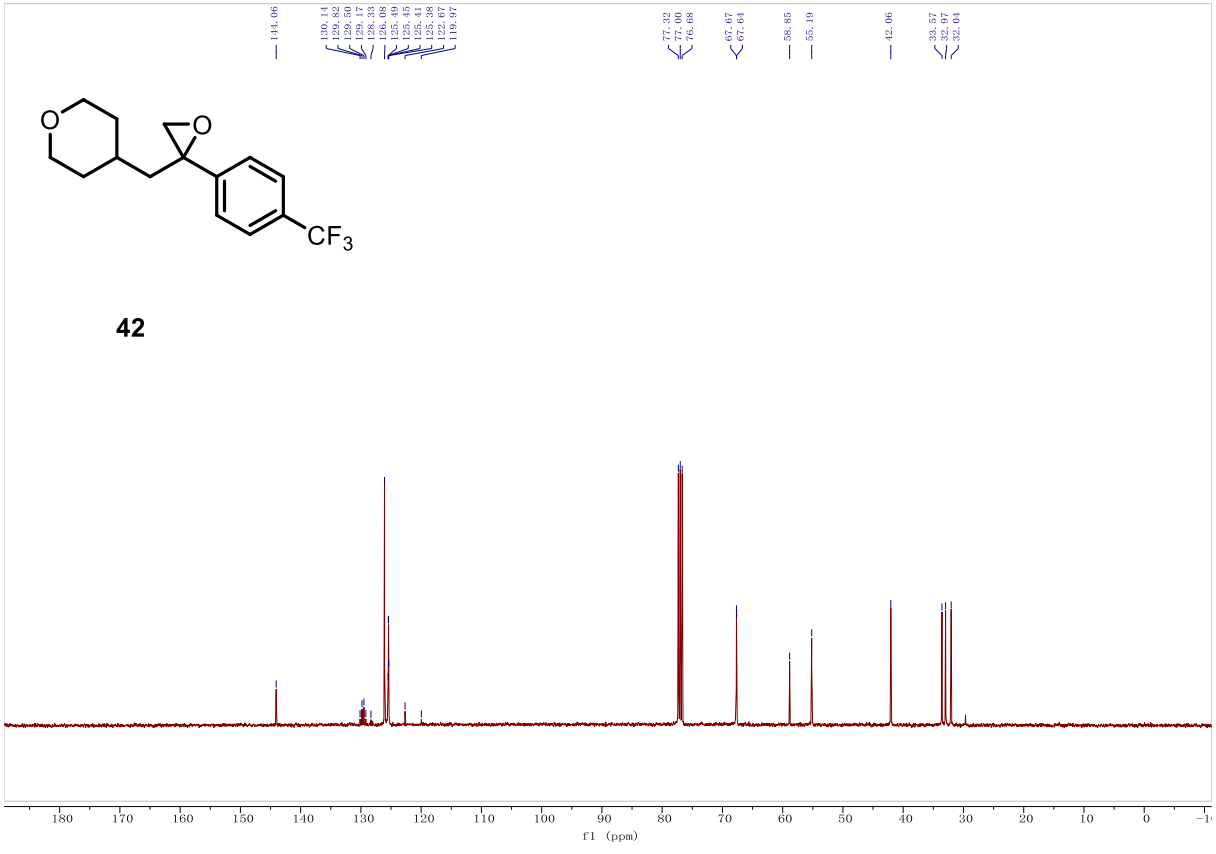
^{13}C NMR (101 MHz, $CDCl_3$)



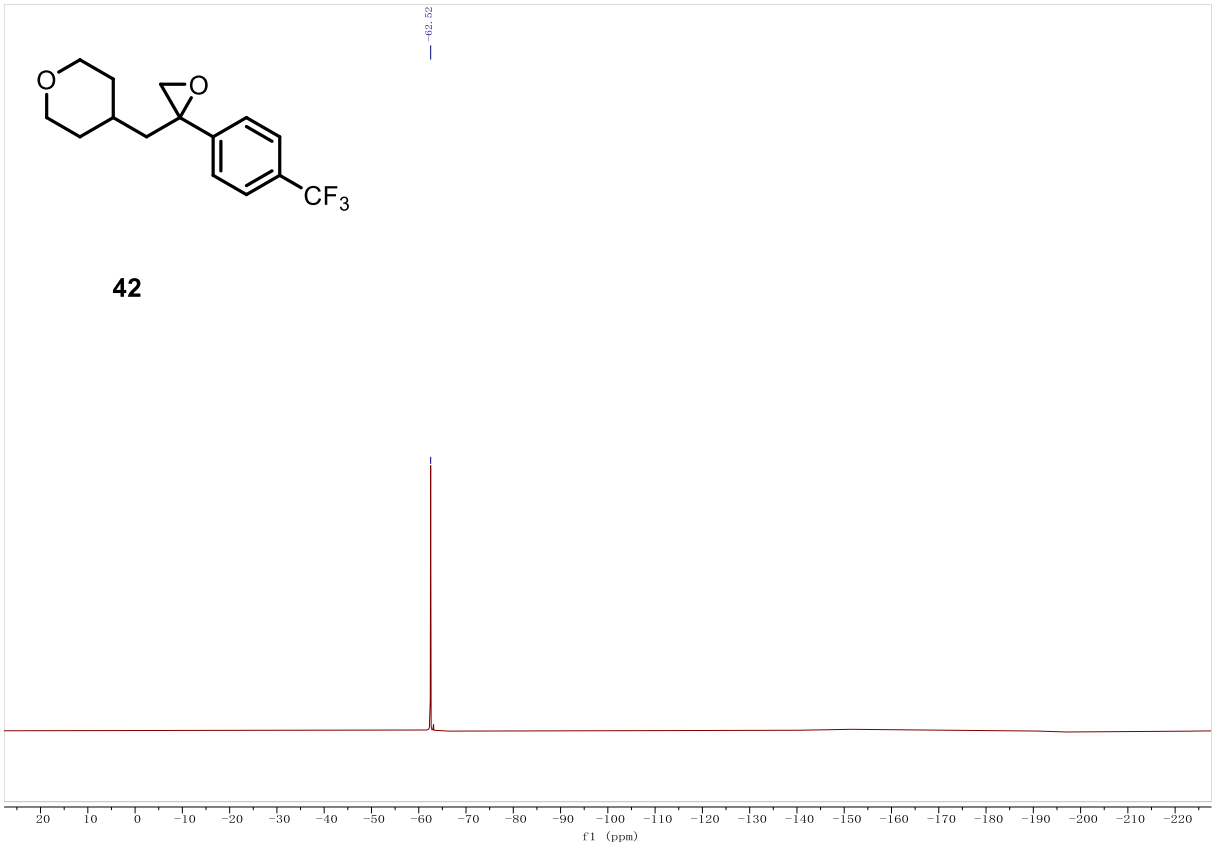
^{1}H NMR (400 MHz, $CDCl_3$)



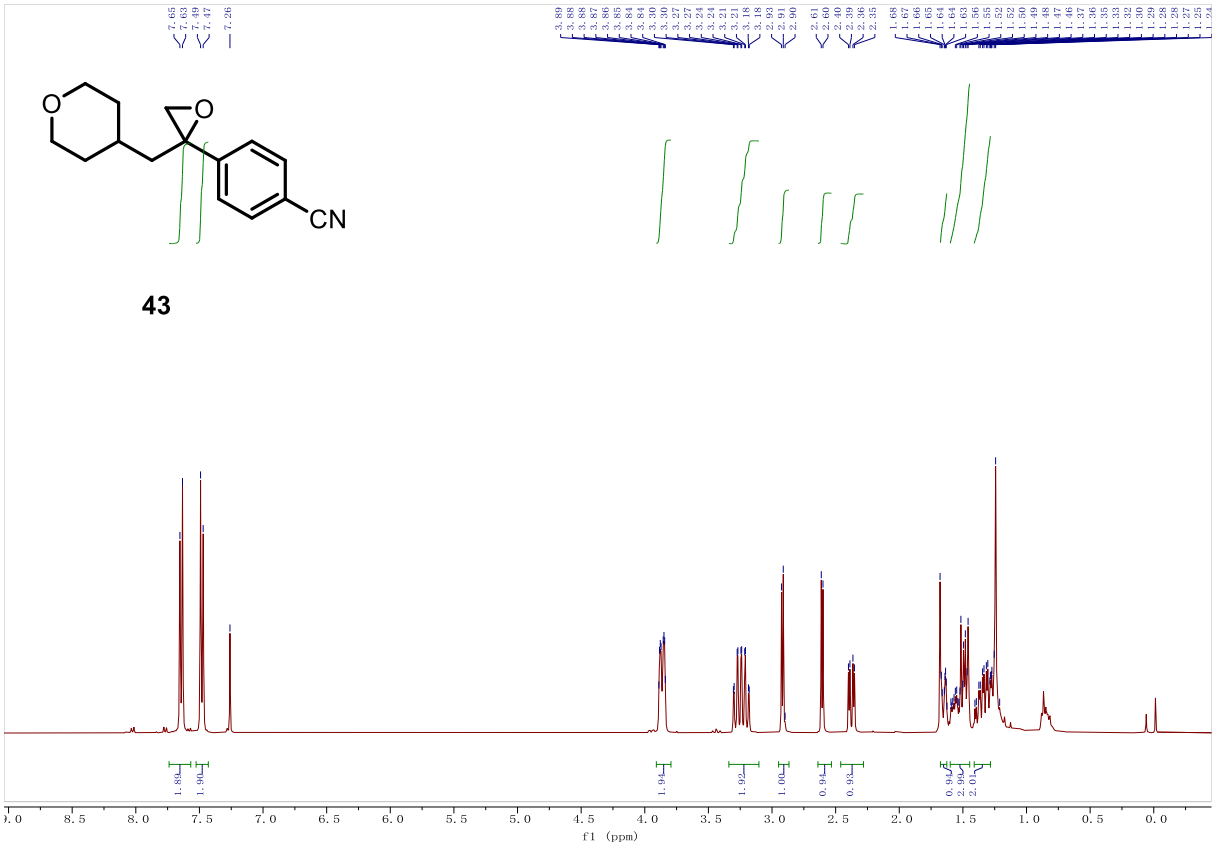
^{13}C NMR (101 MHz, $CDCl_3$)



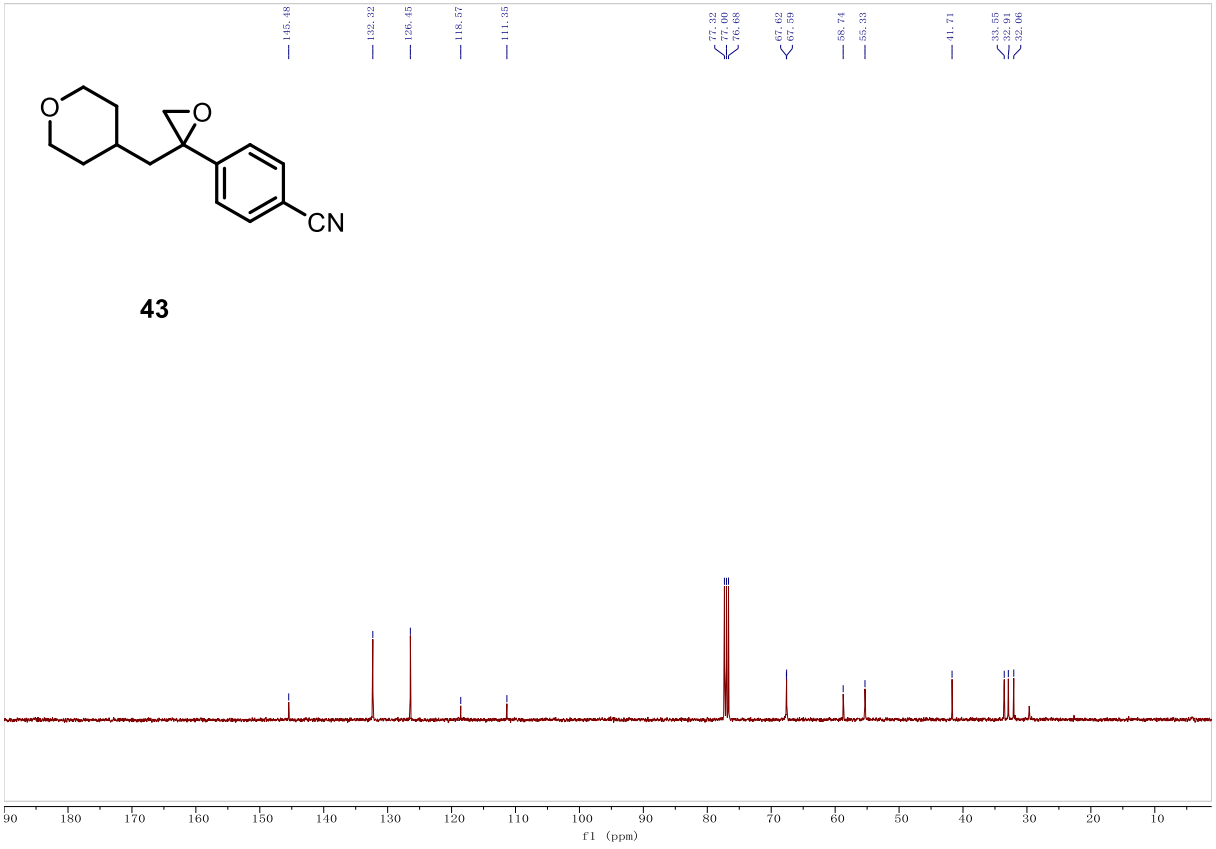
^{19}F NMR (376 MHz, $CDCl_3$)



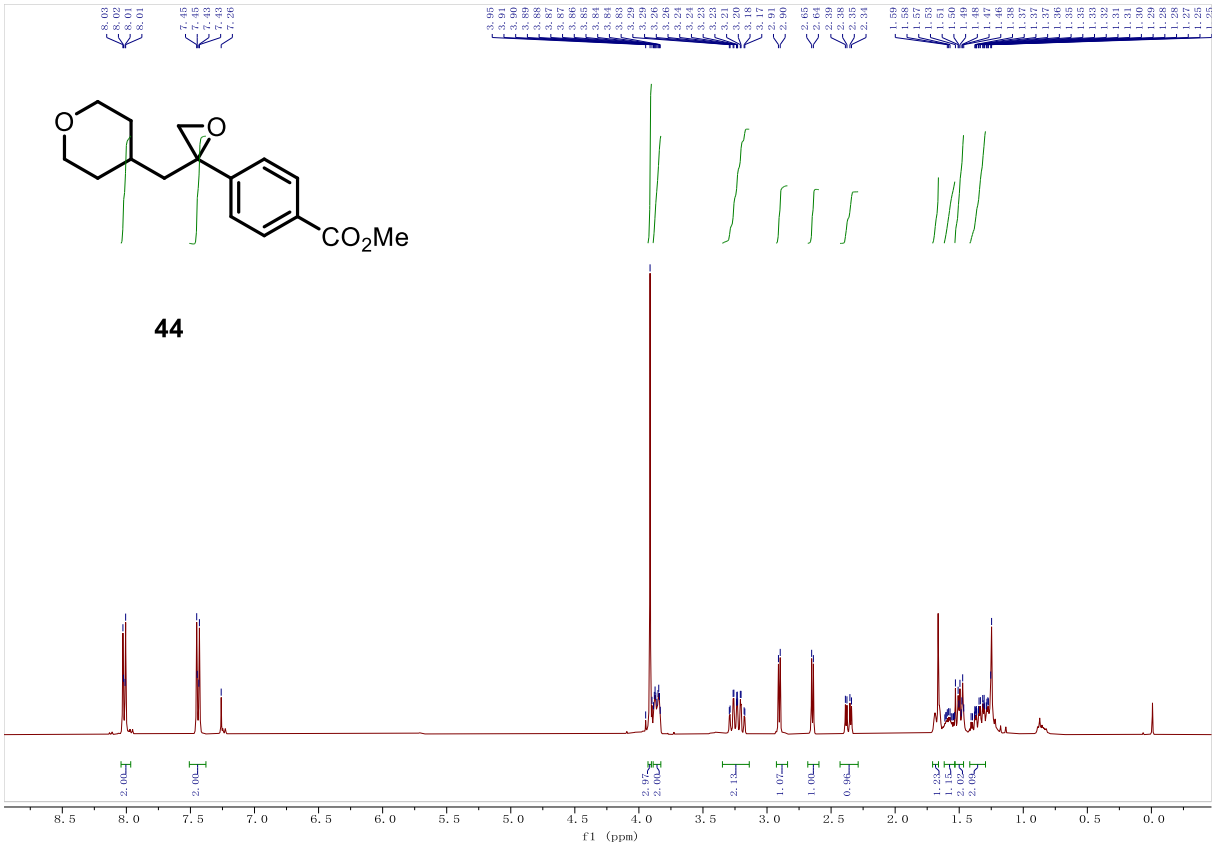
^{1}H NMR (400 MHz, $CDCl_3$)



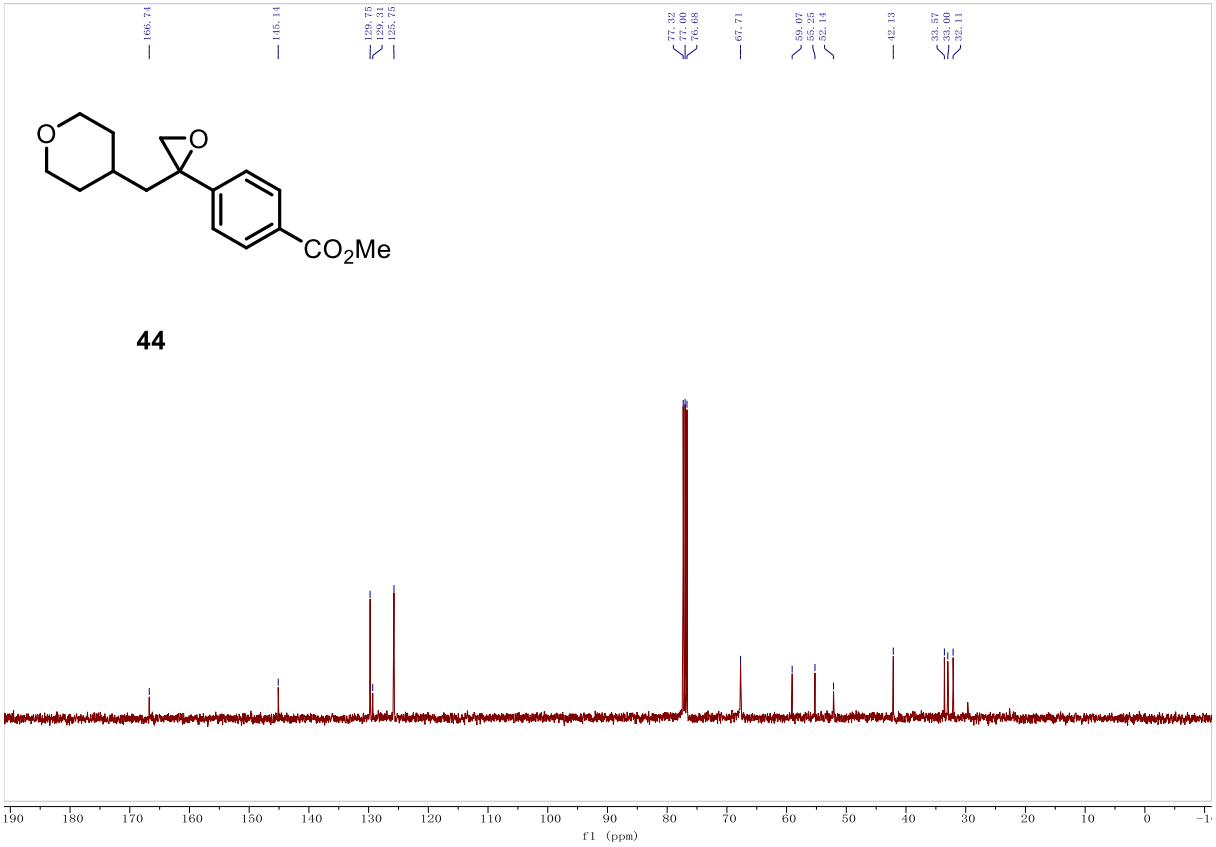
^{13}C NMR (101 MHz, $CDCl_3$)



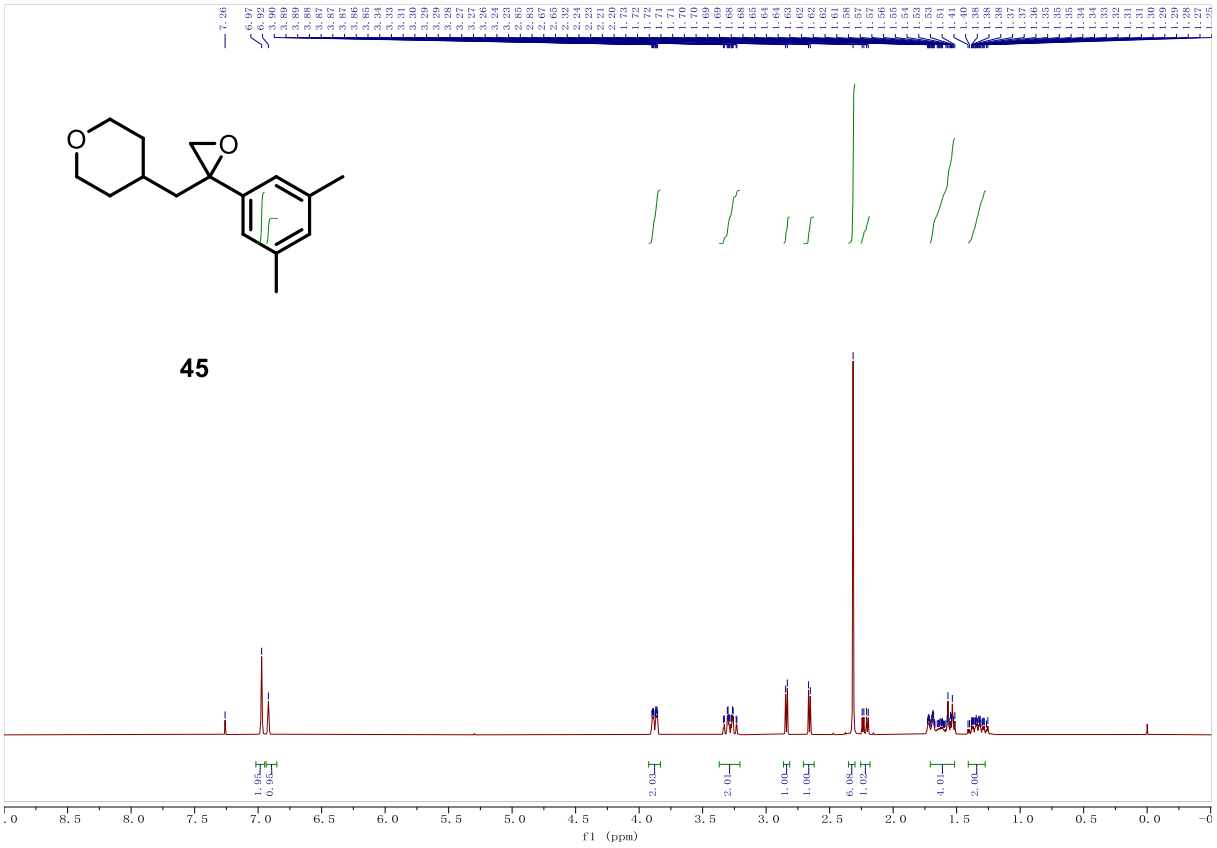
^{1}H NMR (400 MHz, $CDCl_3$)



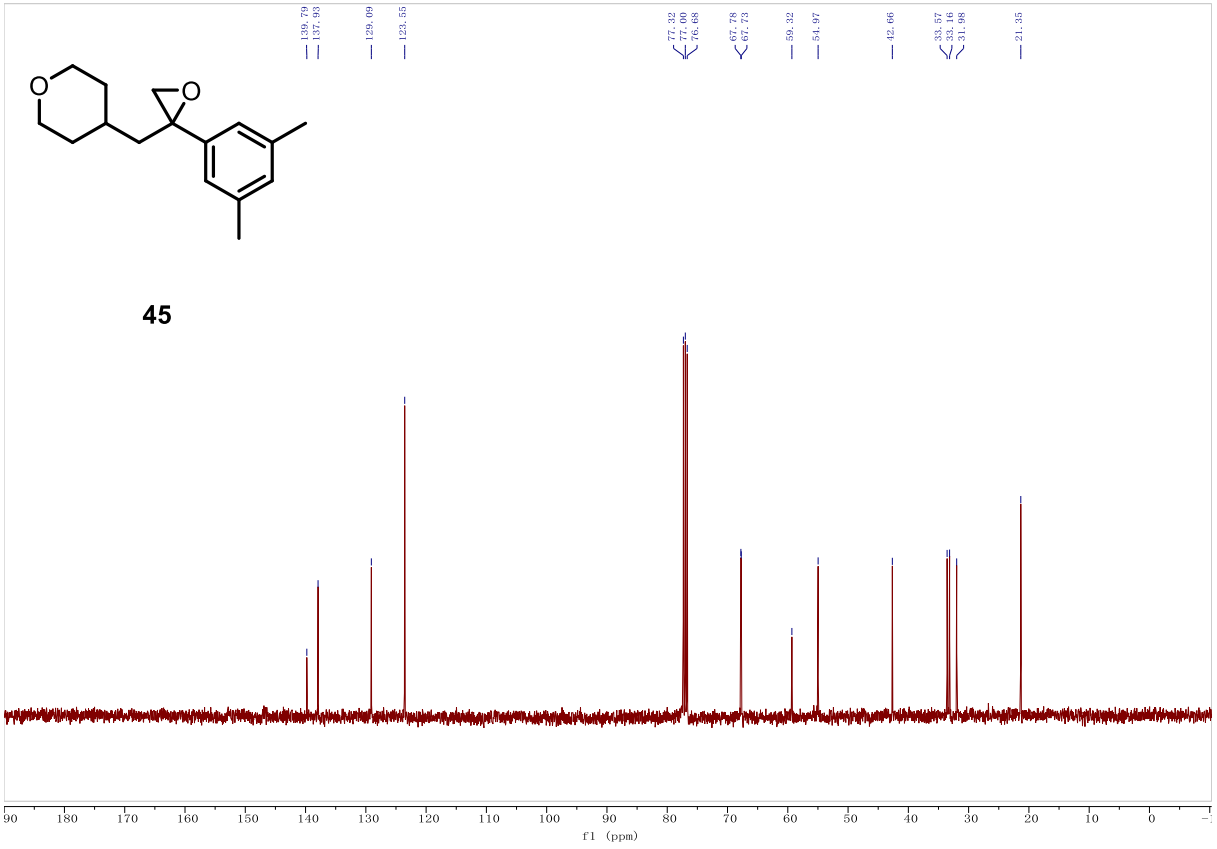
^{13}C NMR (101 MHz, $CDCl_3$)



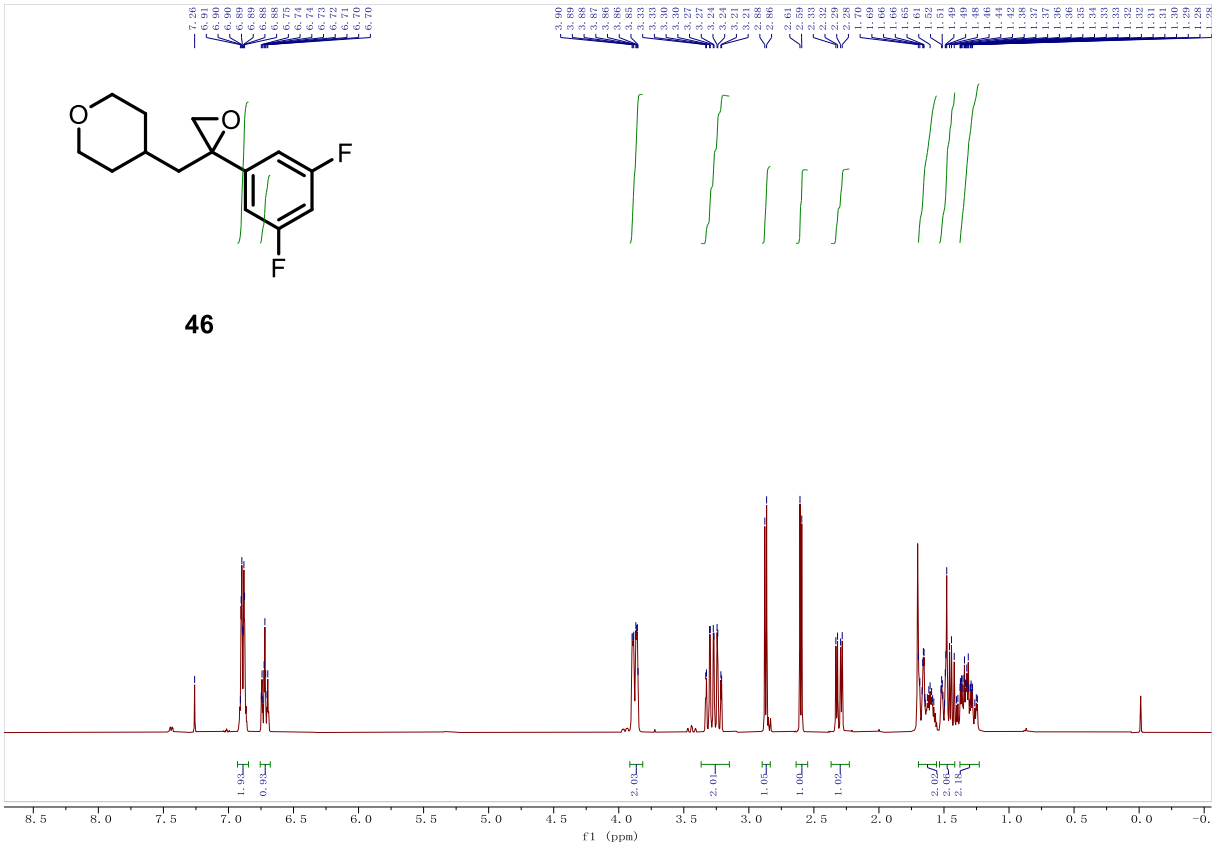
^{1}H NMR (400 MHz, $CDCl_3$)



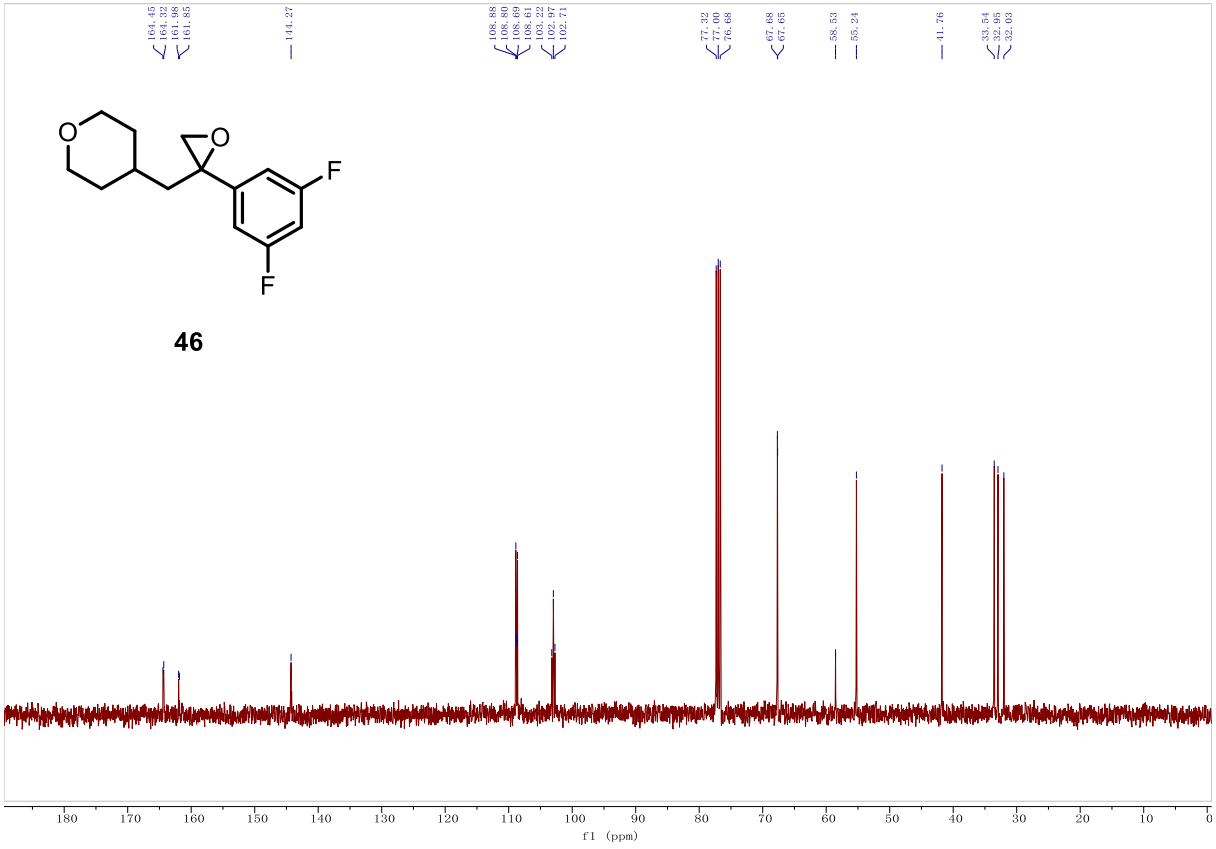
^{13}C NMR (101 MHz, $CDCl_3$)



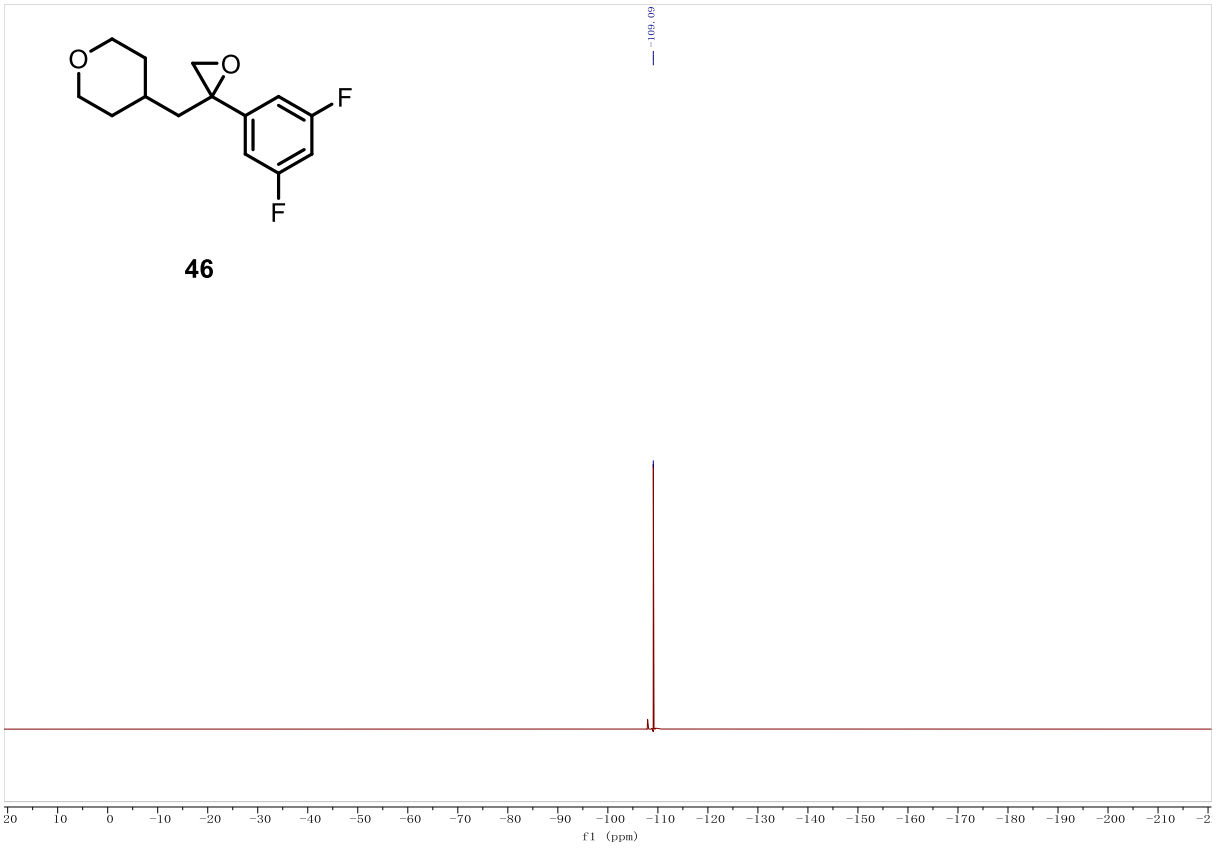
^{1}H NMR (400 MHz, $CDCl_3$)



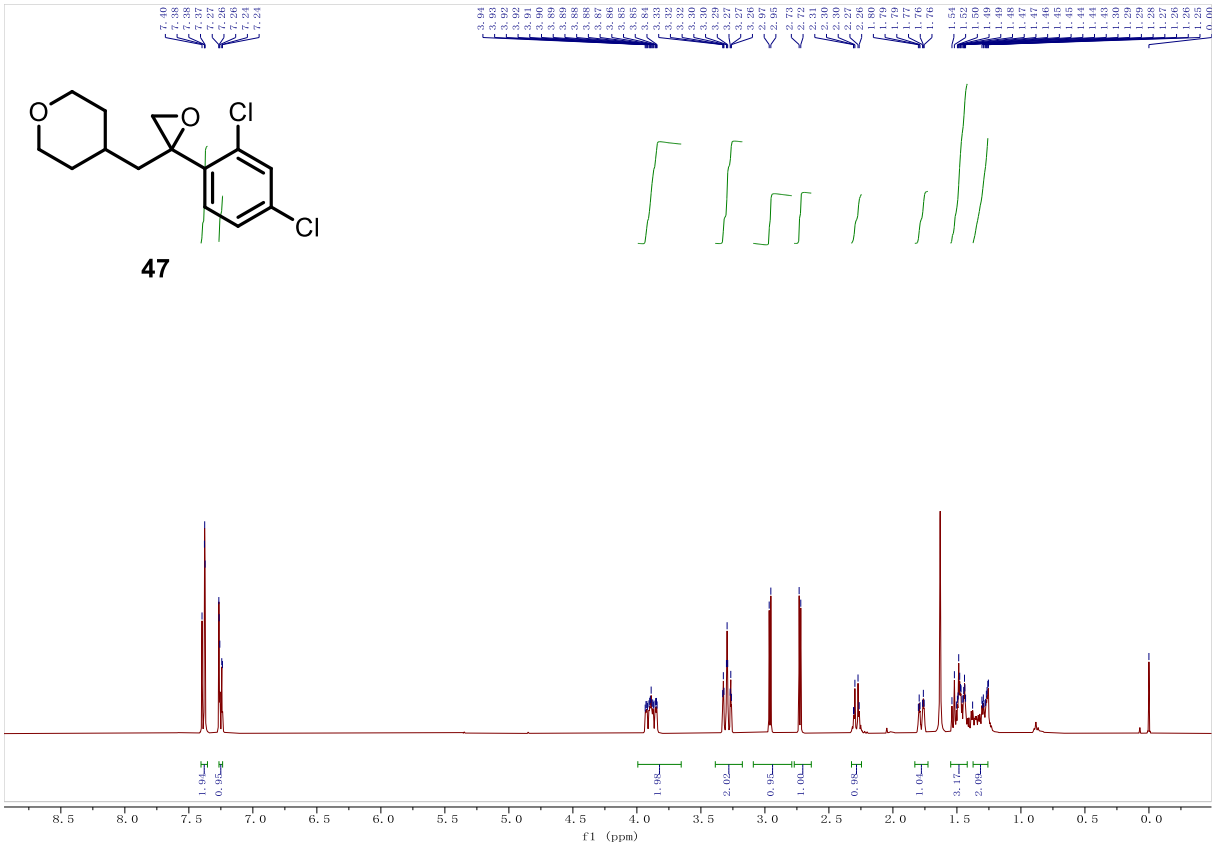
^{13}C NMR (101 MHz, $CDCl_3$)



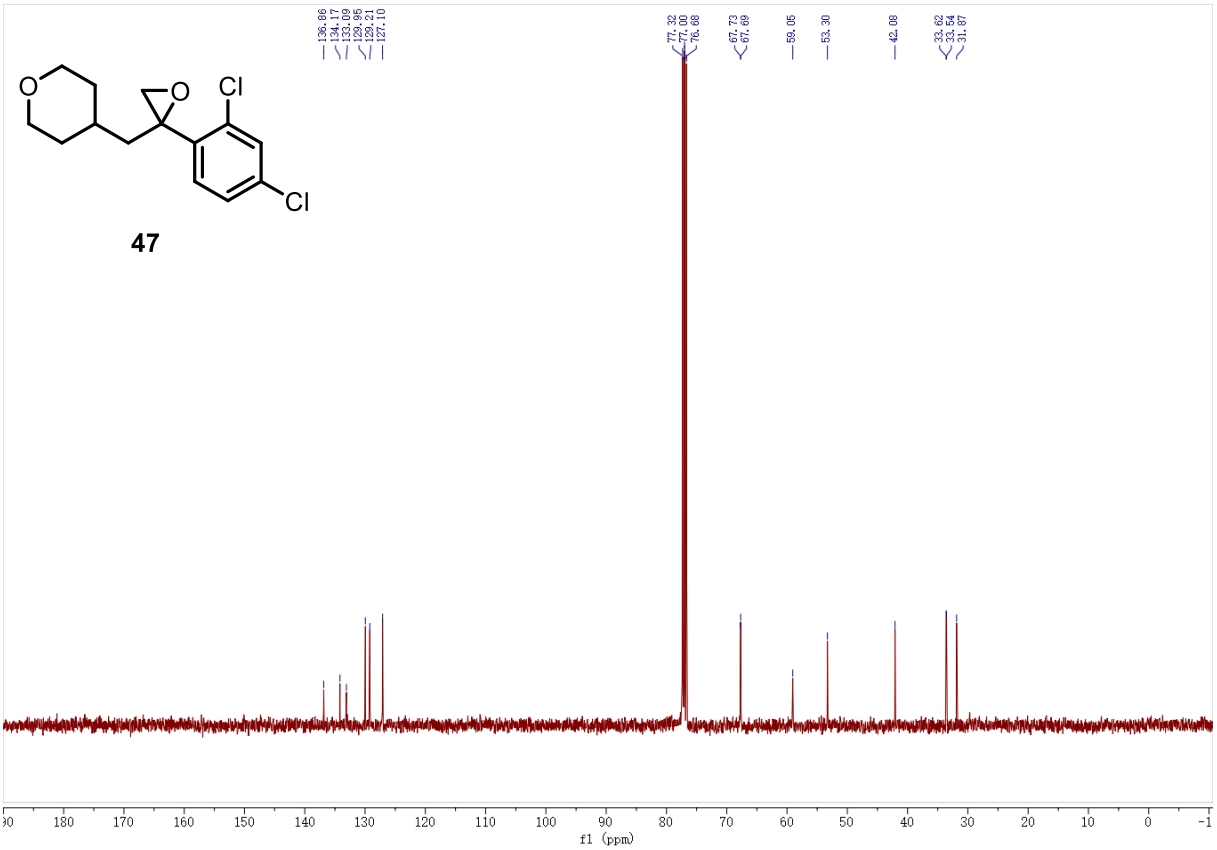
^{19}F NMR (376 MHz, $CDCl_3$)



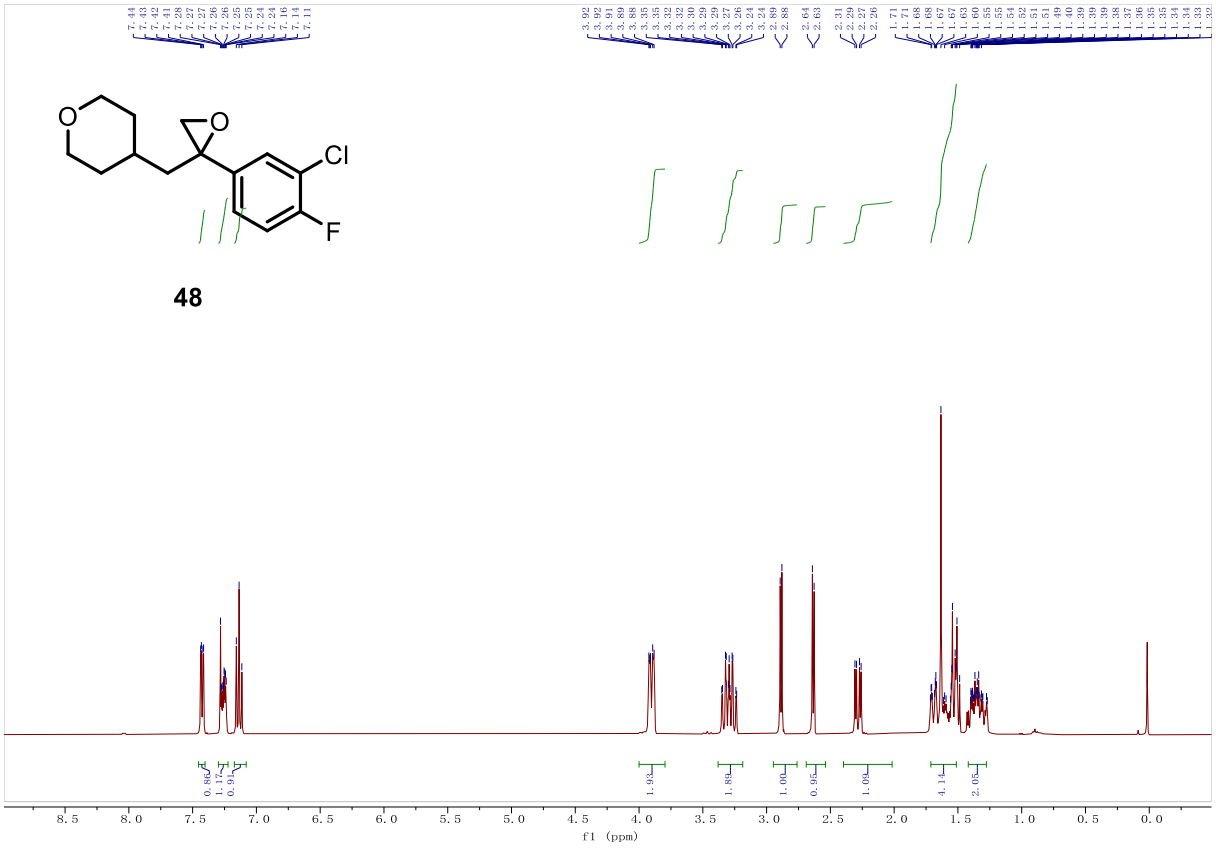
^{1}H NMR (400 MHz, $CDCl_3$)



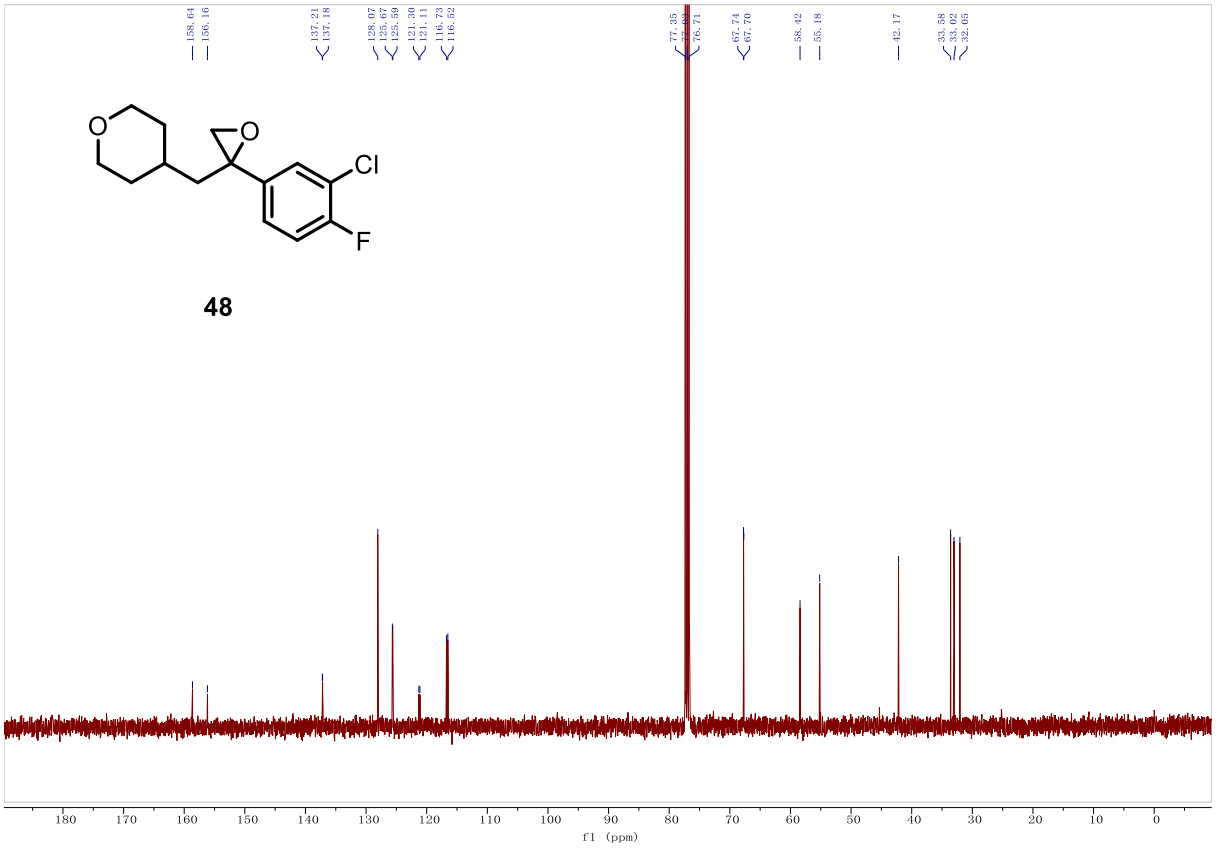
^{13}C NMR (101 MHz, $CDCl_3$)



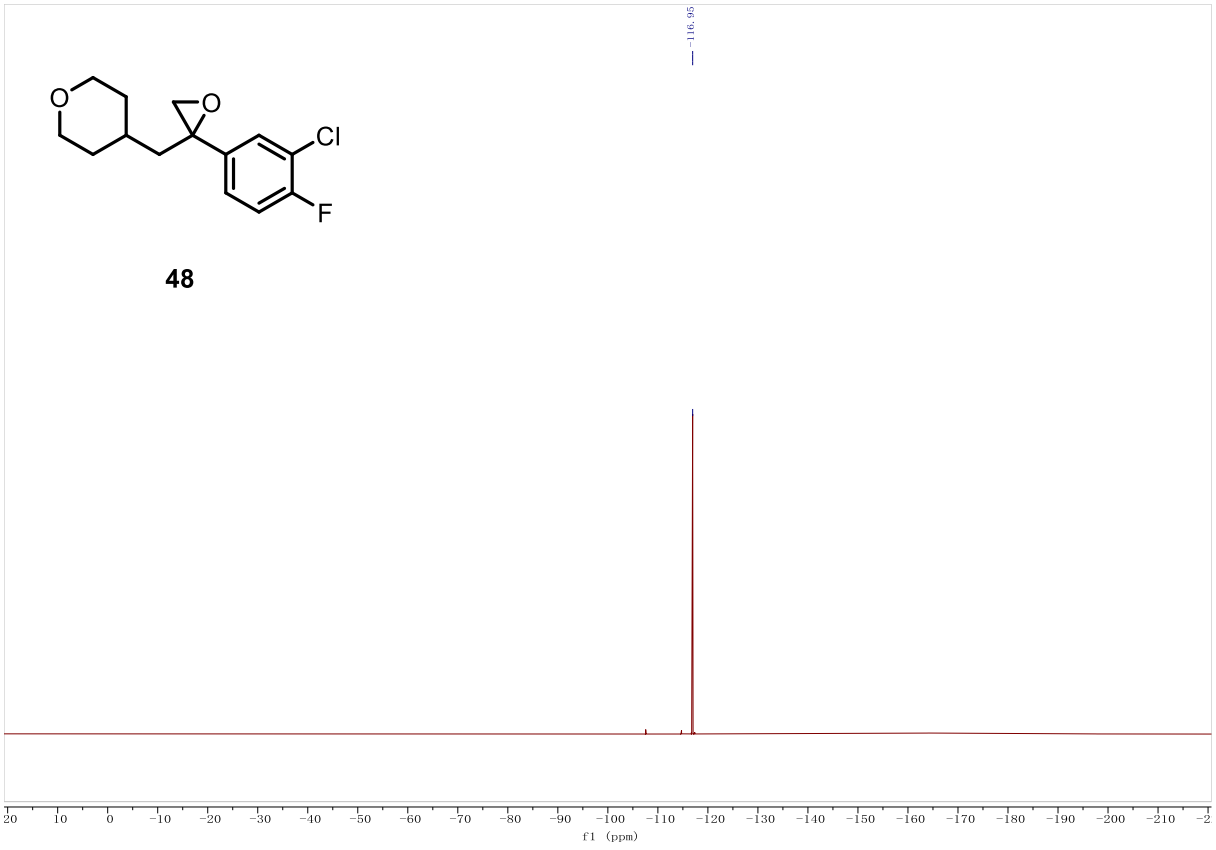
^{1}H NMR (400 MHz, $CDCl_3$)



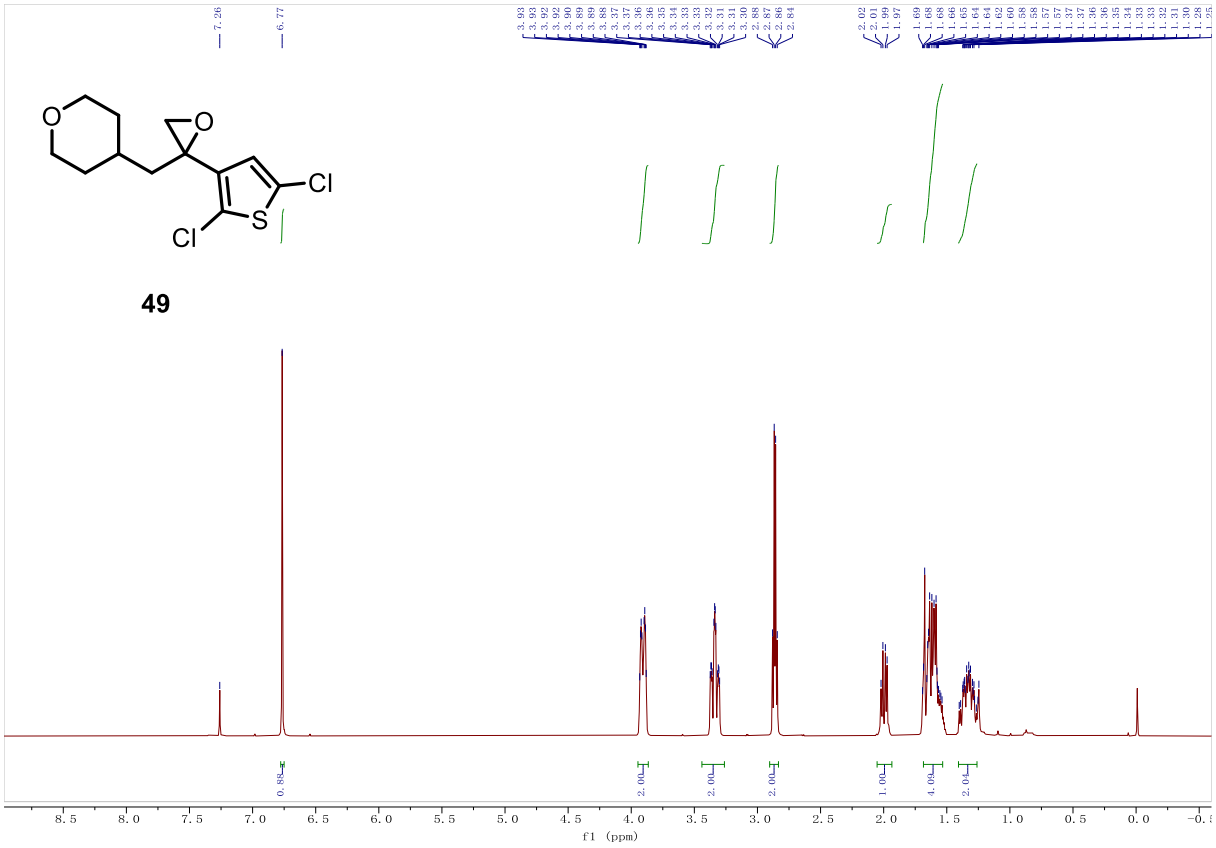
^{13}C NMR (101 MHz, $CDCl_3$)



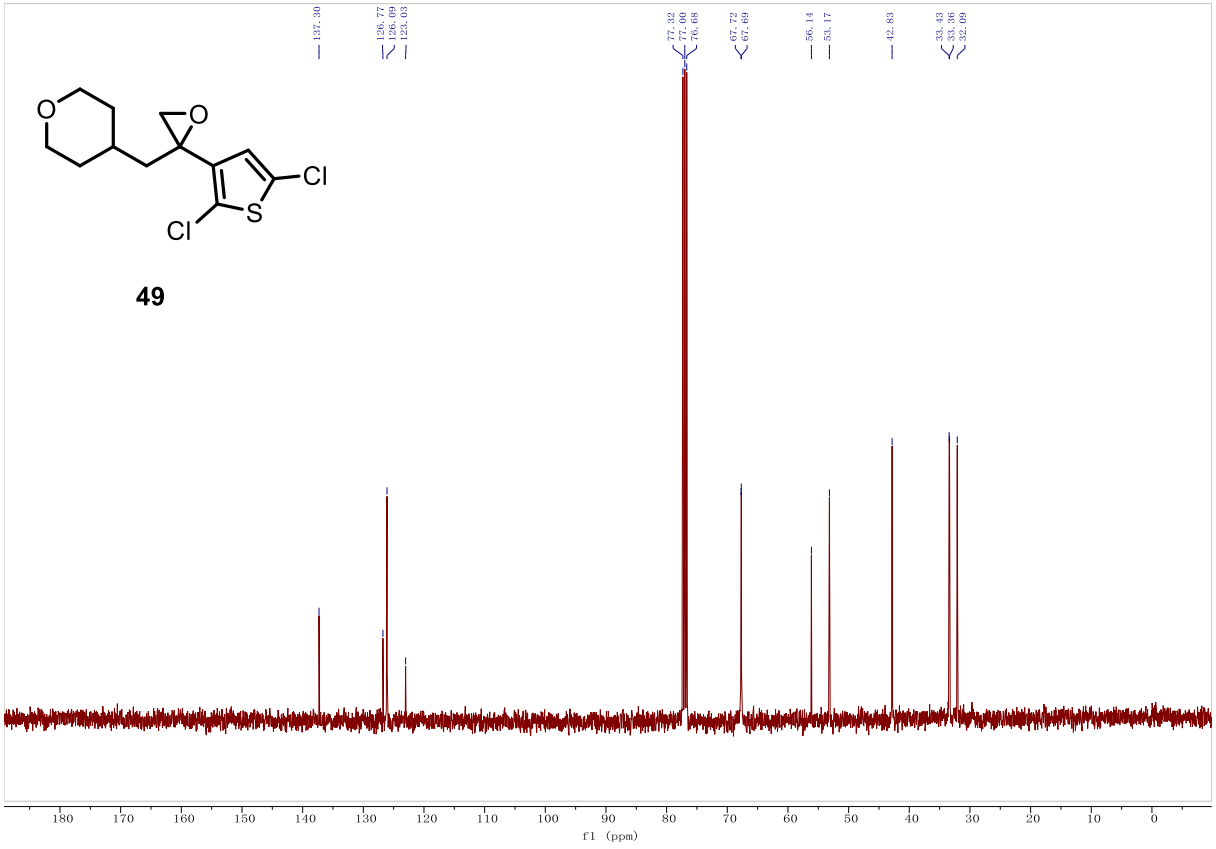
^{19}F NMR (376 MHz, $CDCl_3$)



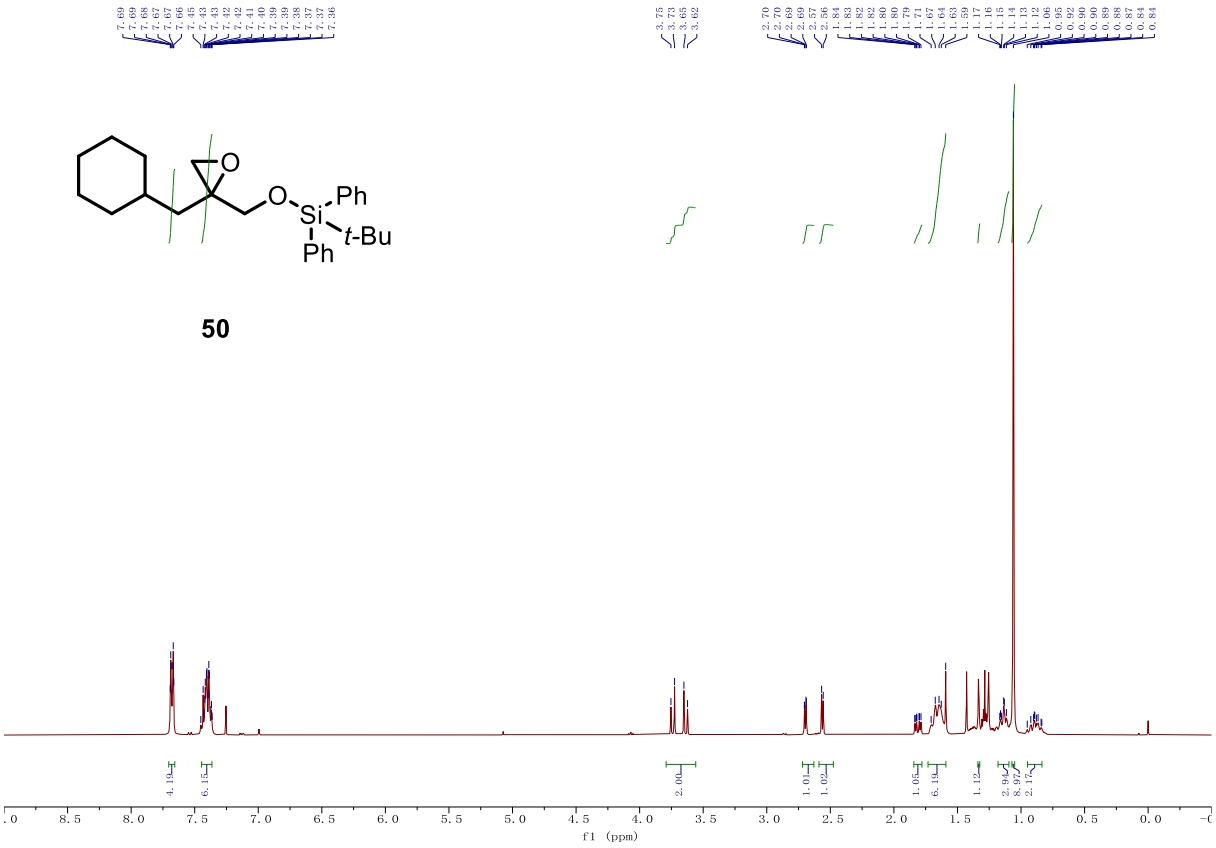
^{1}H NMR (400 MHz, $CDCl_3$)



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

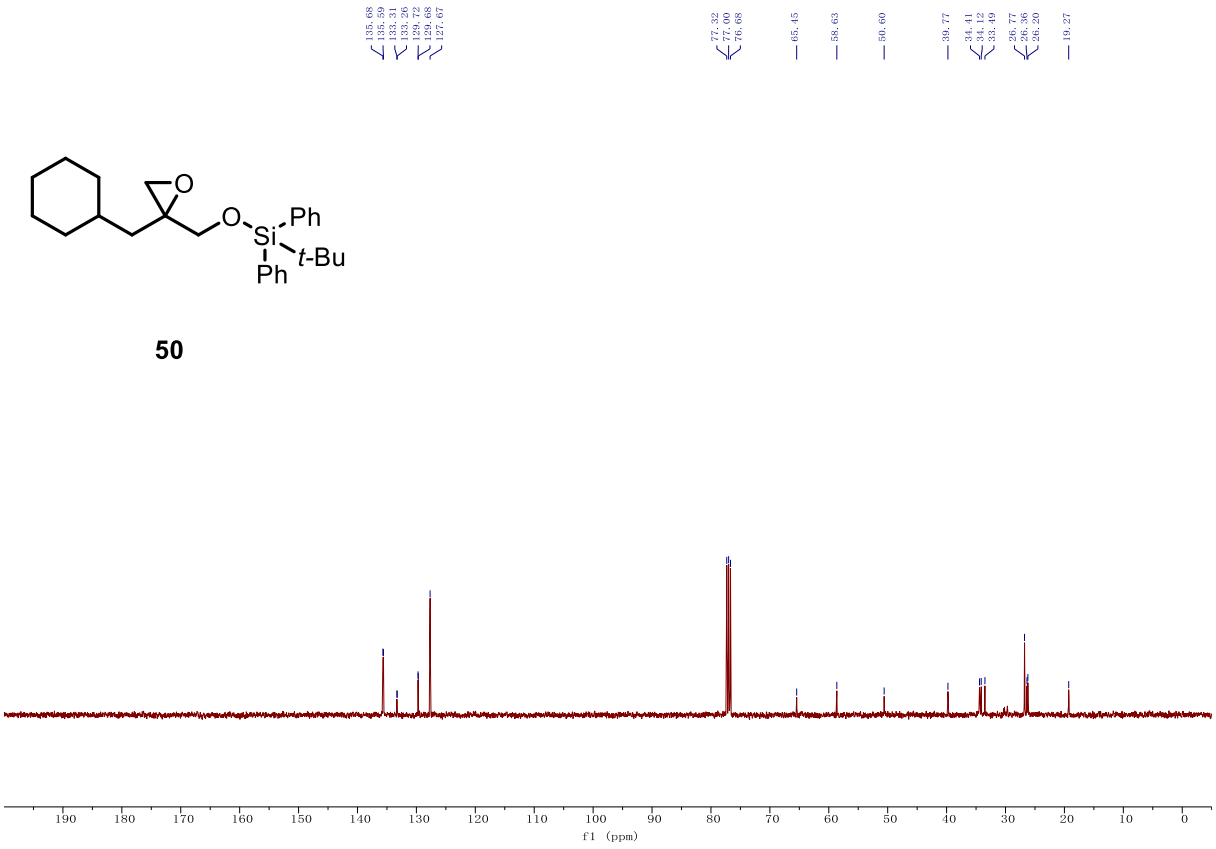


^{1}H NMR (400 MHz, $CDCl_3$)



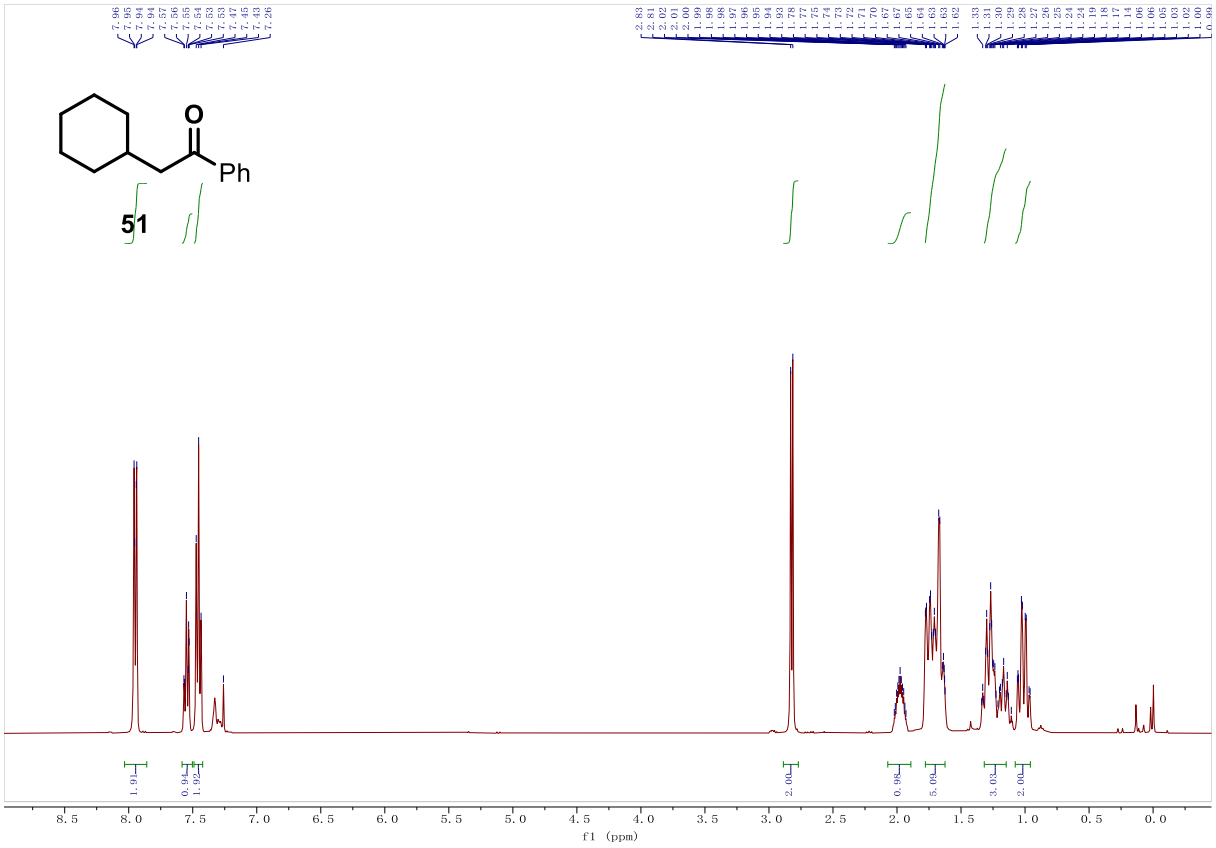
50

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

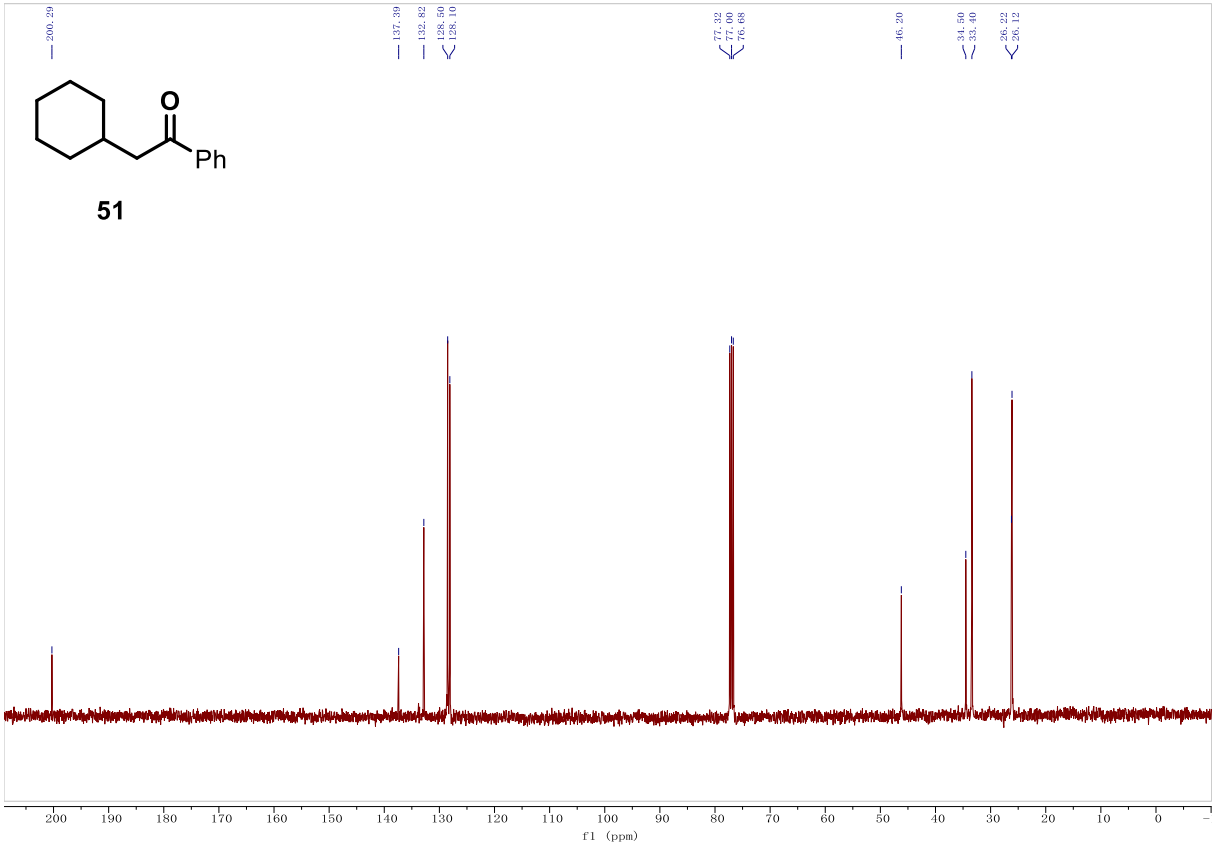


50

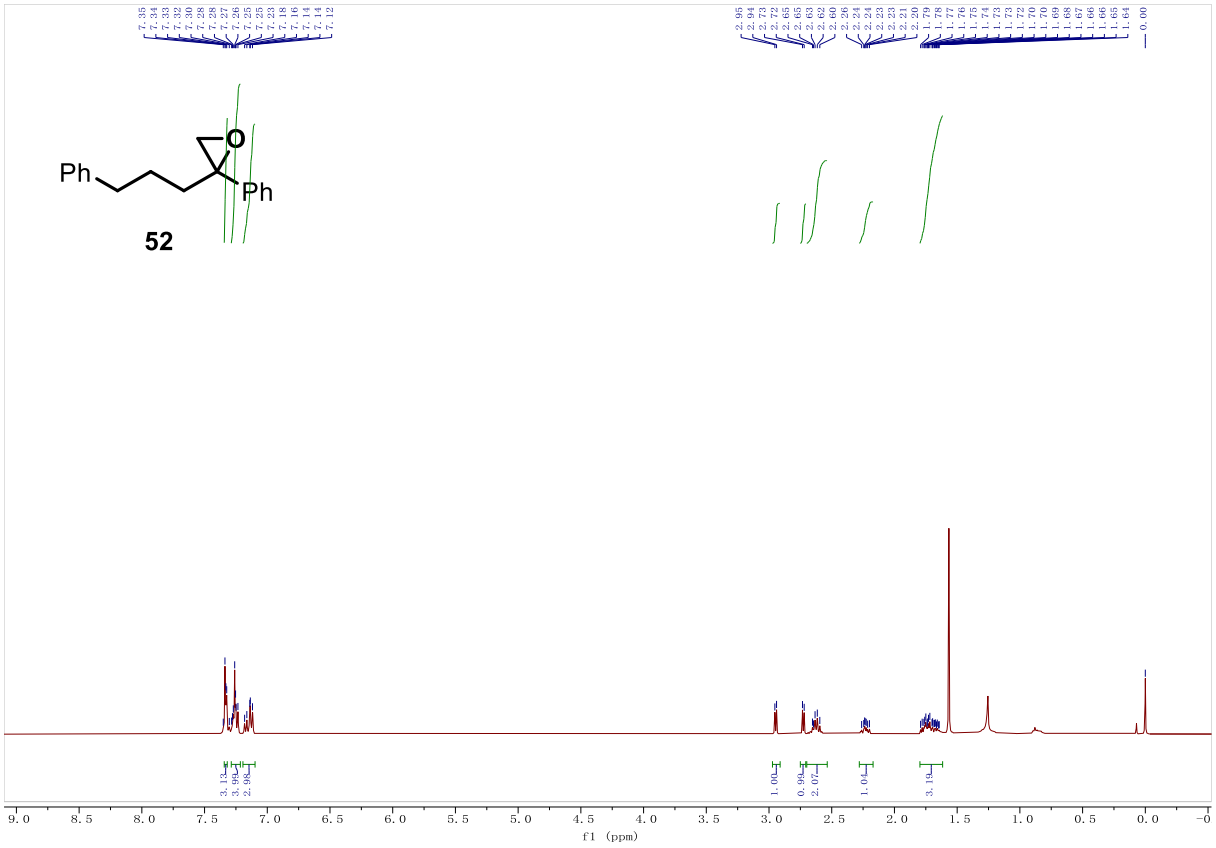
^{1}H NMR (400 MHz, $CDCl_3$)



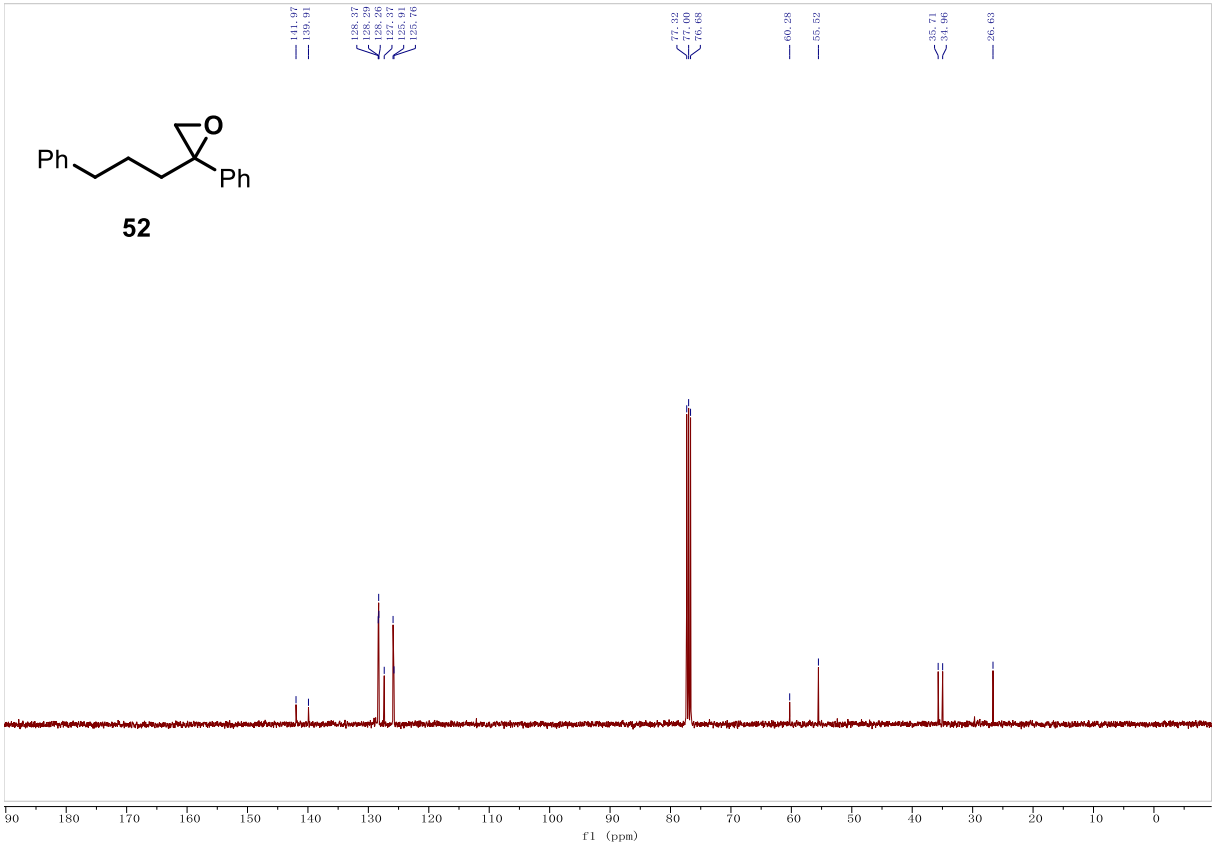
^{13}C NMR (101 MHz, $CDCl_3$)



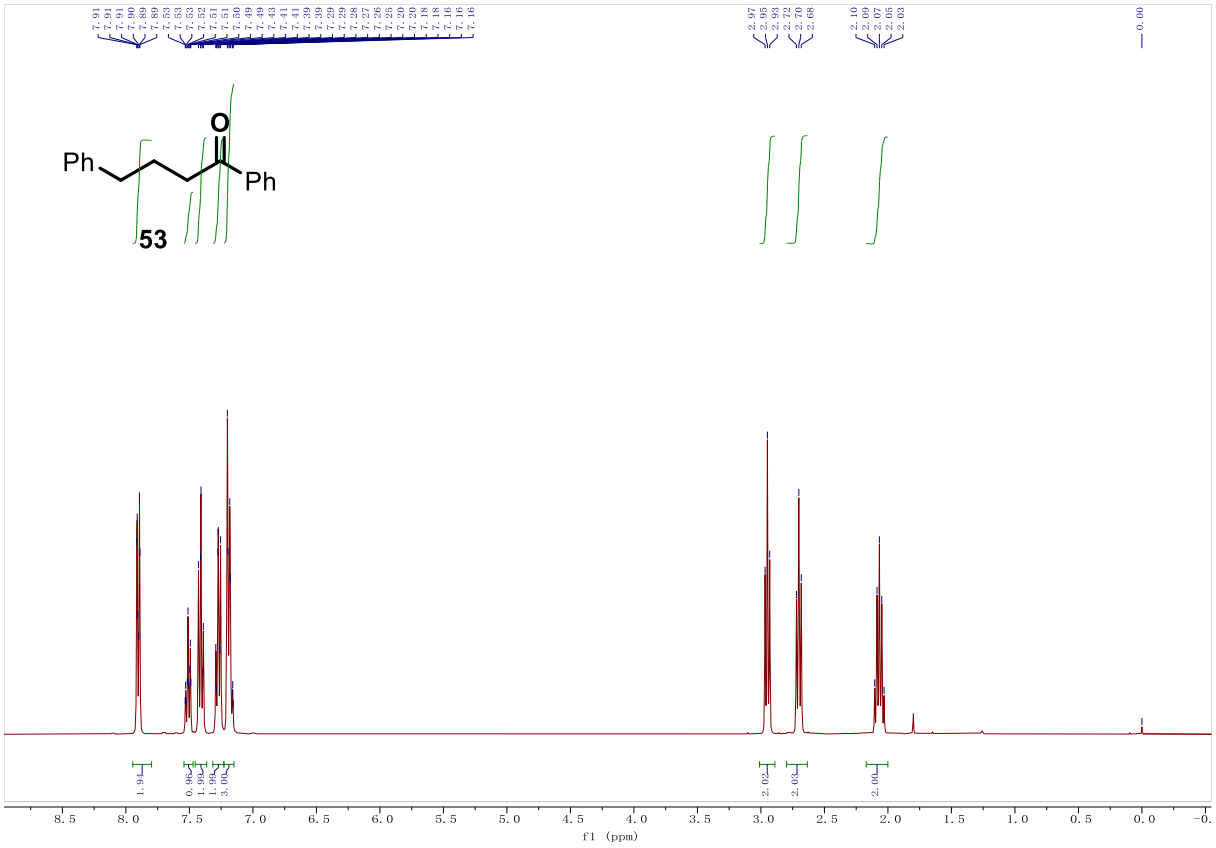
^{1}H NMR (400 MHz, $CDCl_3$)



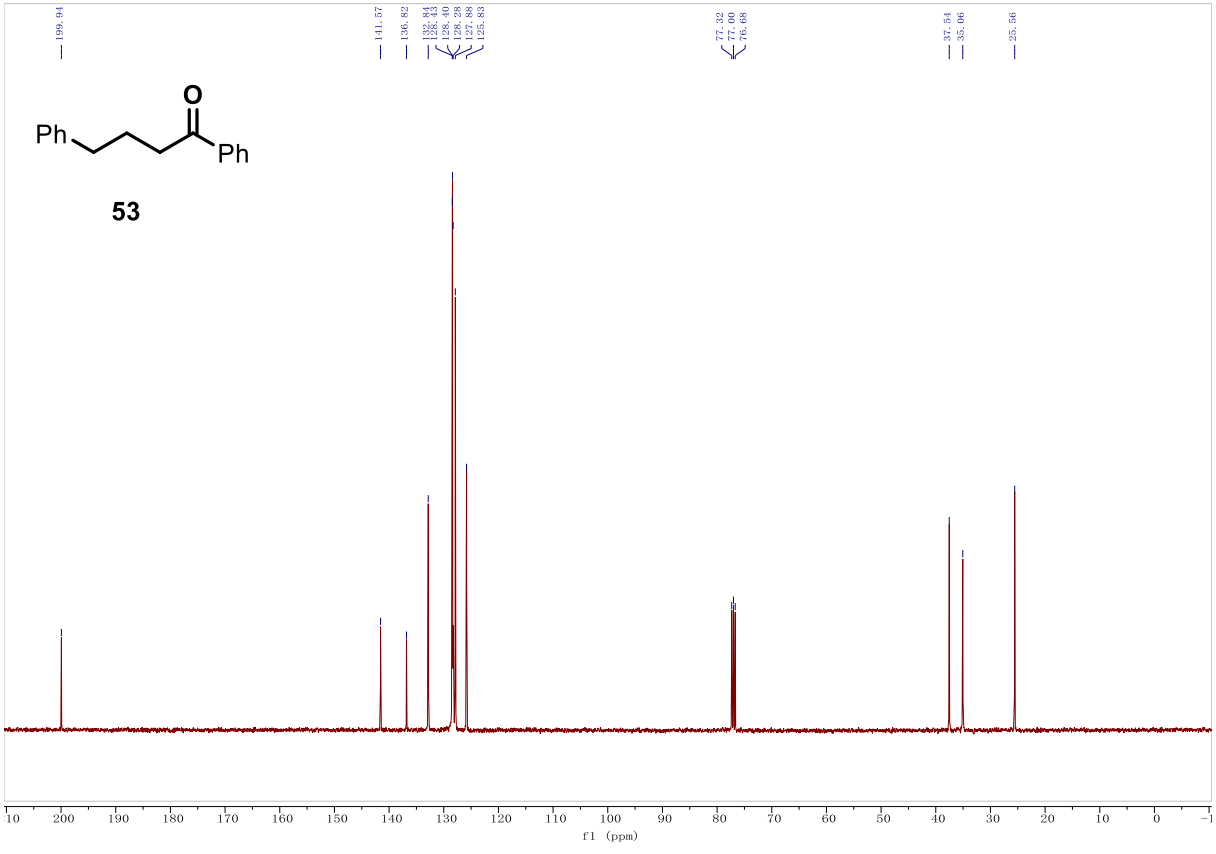
^{13}C NMR (101 MHz, $CDCl_3$)



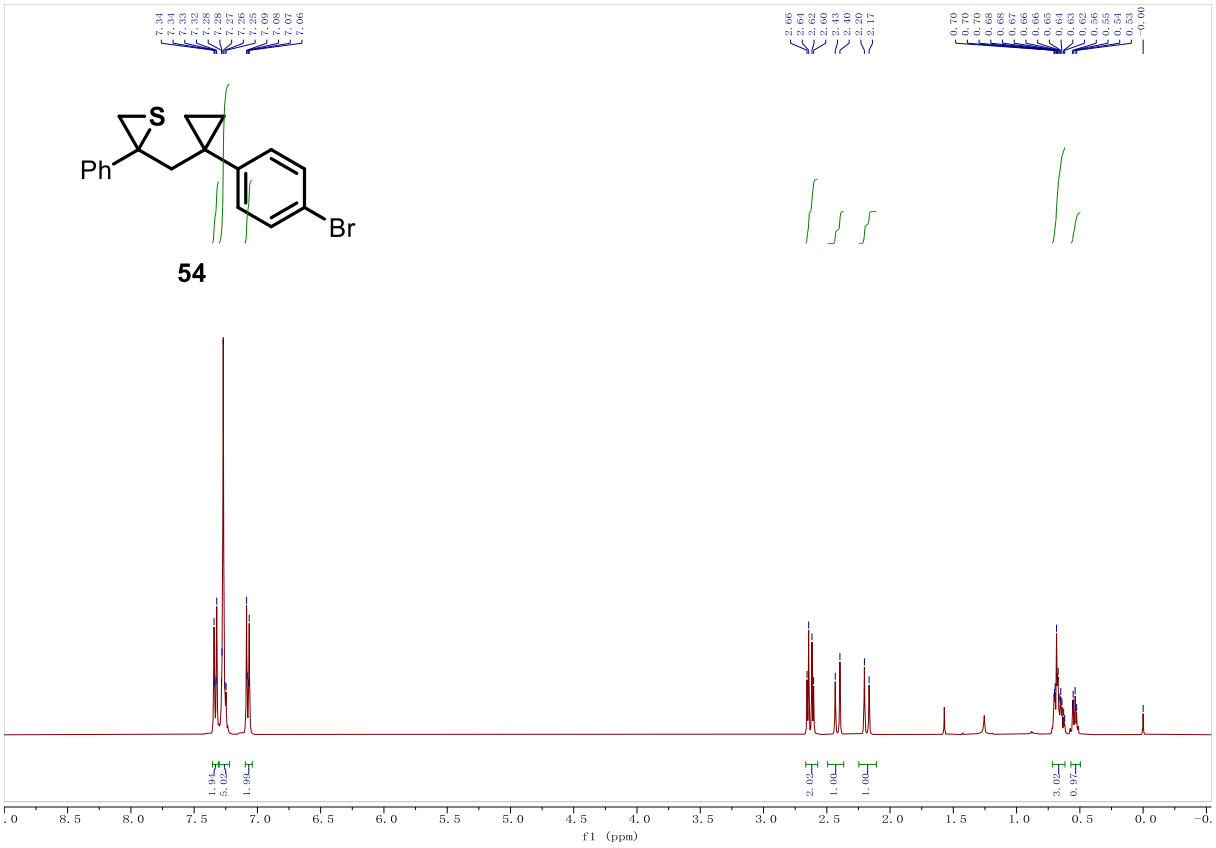
^{1}H NMR (400 MHz, $CDCl_3$)



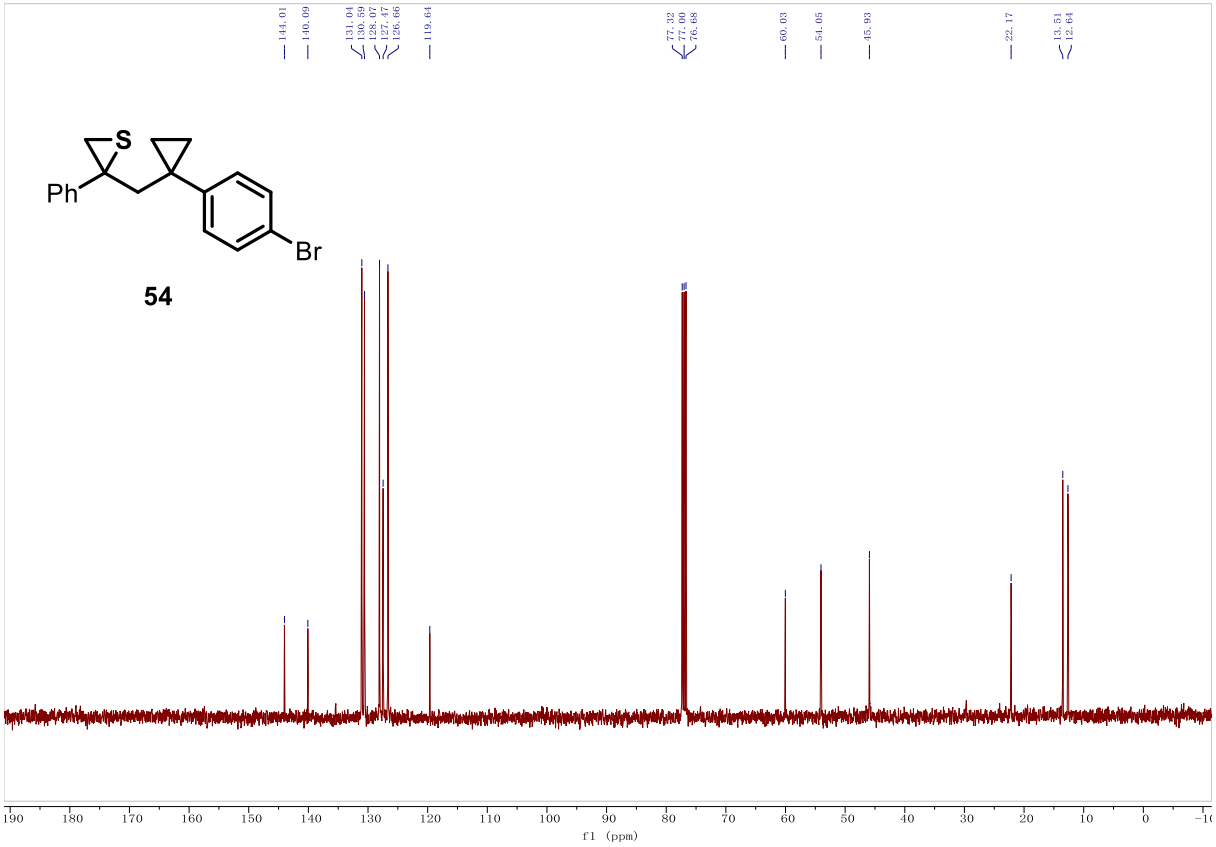
^{13}C NMR (101 MHz, $CDCl_3$)



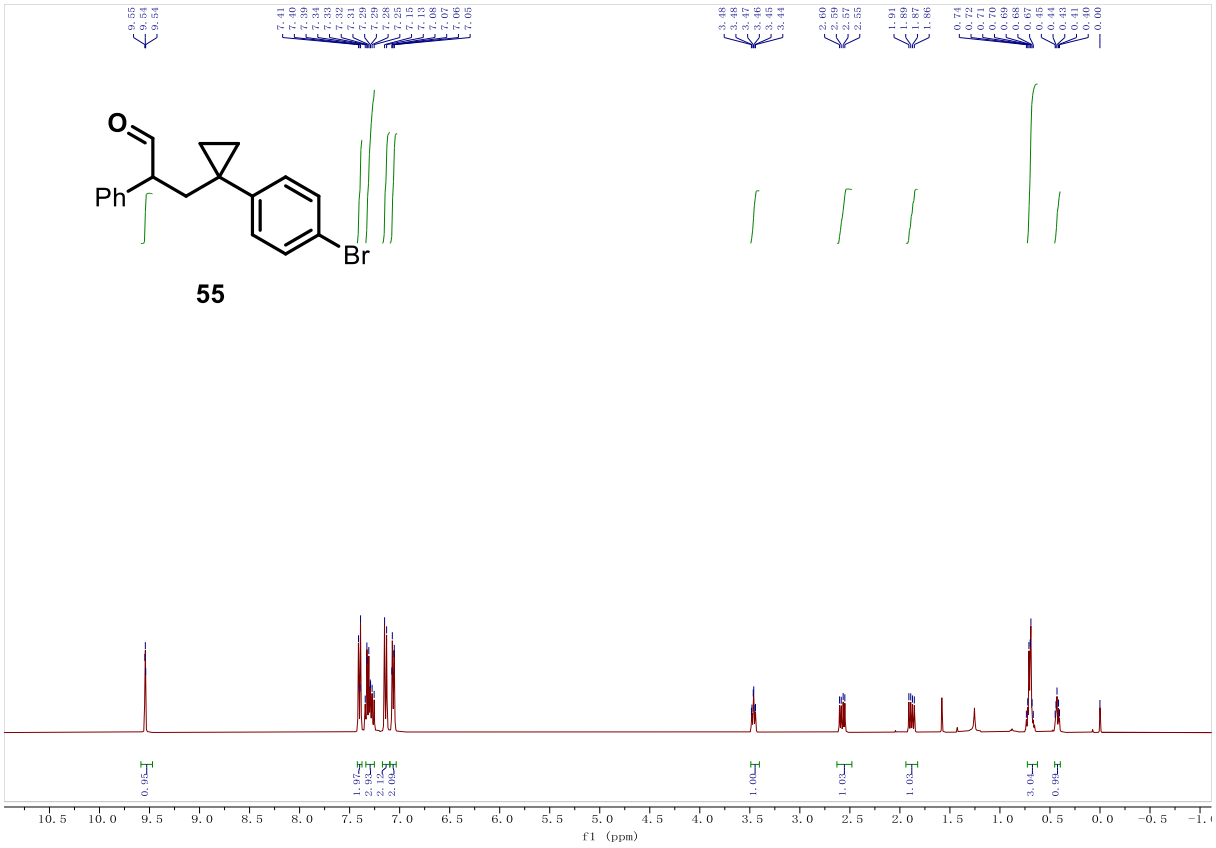
^{1}H NMR (400 MHz, $CDCl_3$)



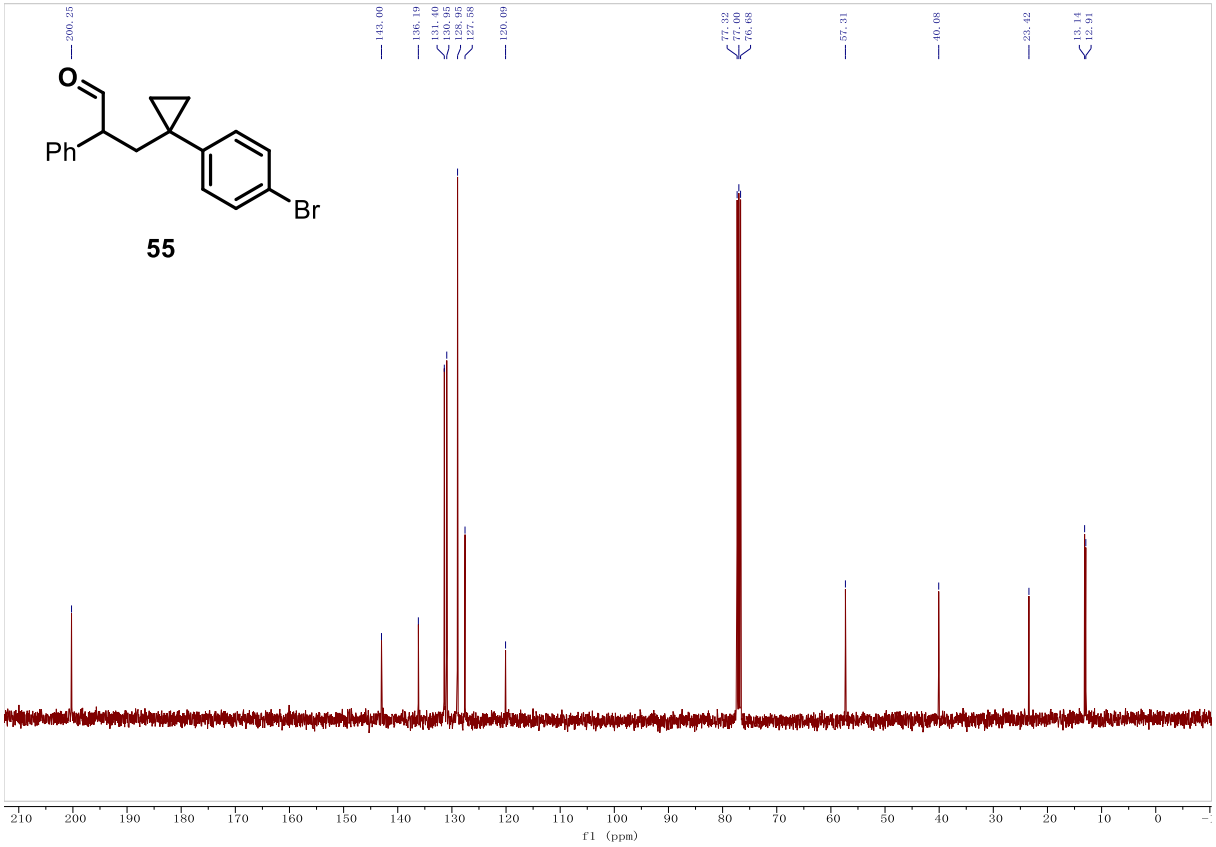
^{13}C NMR (101 MHz, $CDCl_3$)



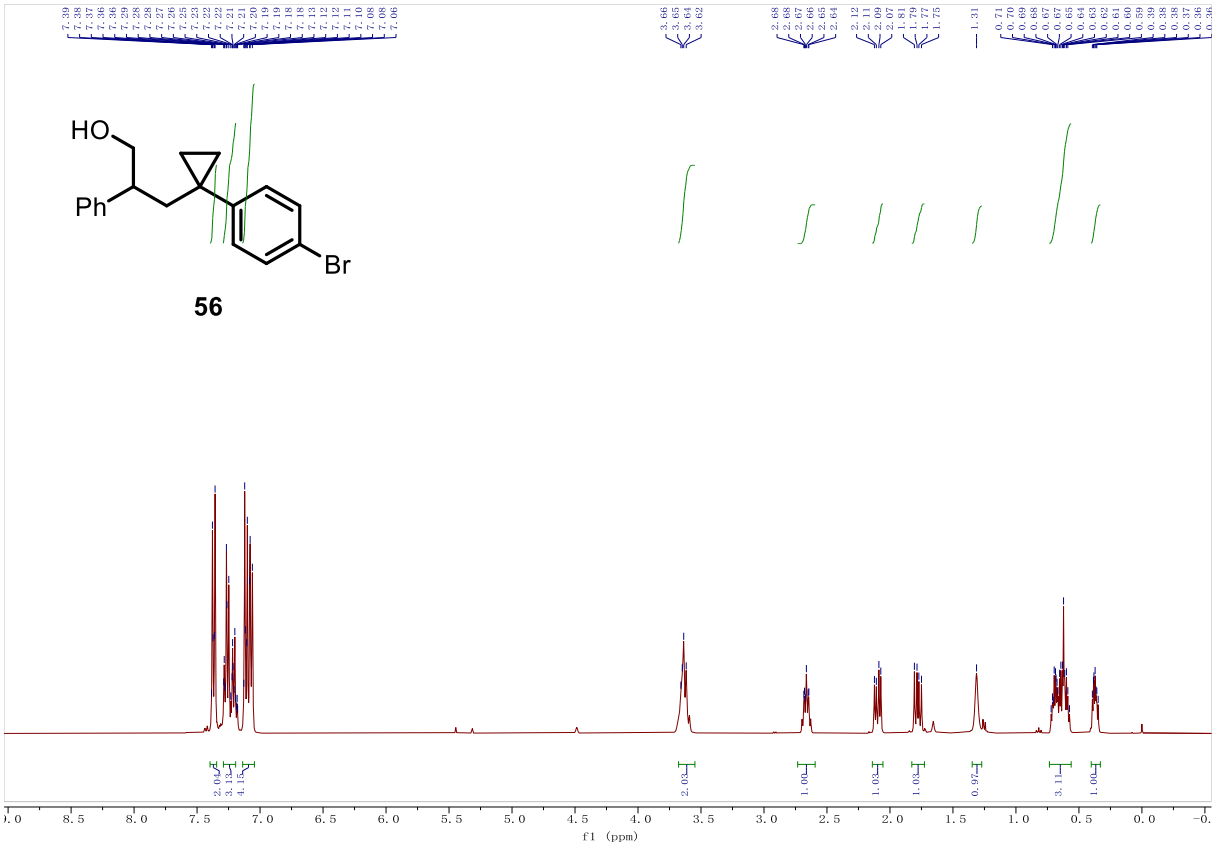
^{1}H NMR (400 MHz, $CDCl_3$)



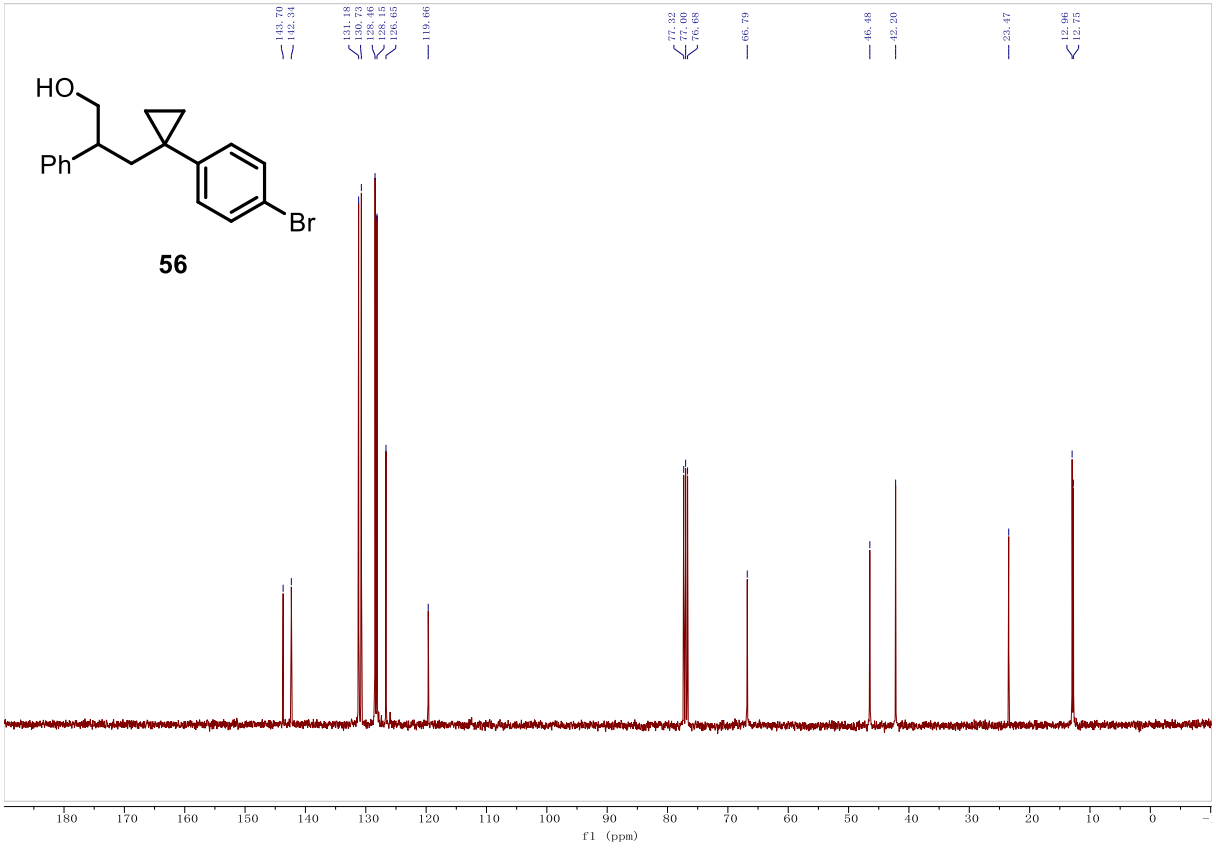
^{13}C NMR (101 MHz, $CDCl_3$)



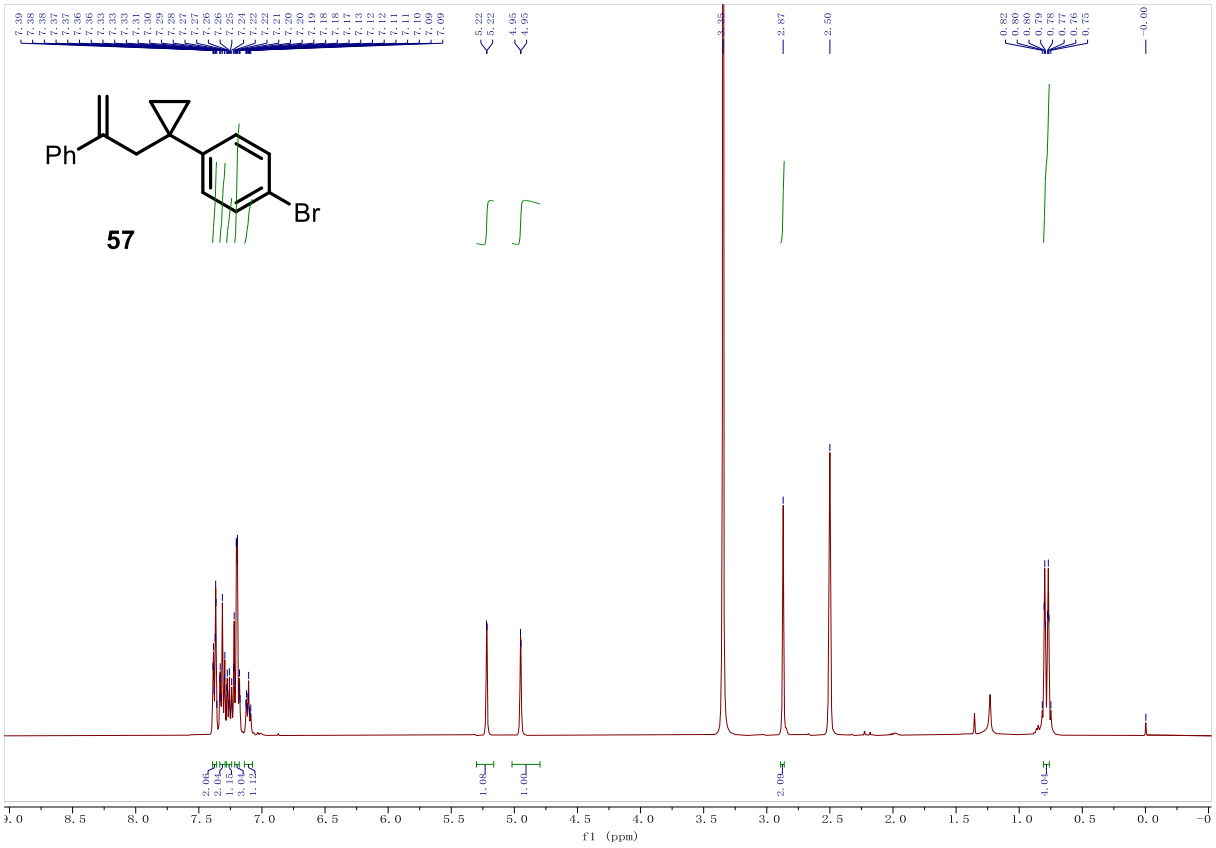
^{1}H NMR (400 MHz, $CDCl_3$)



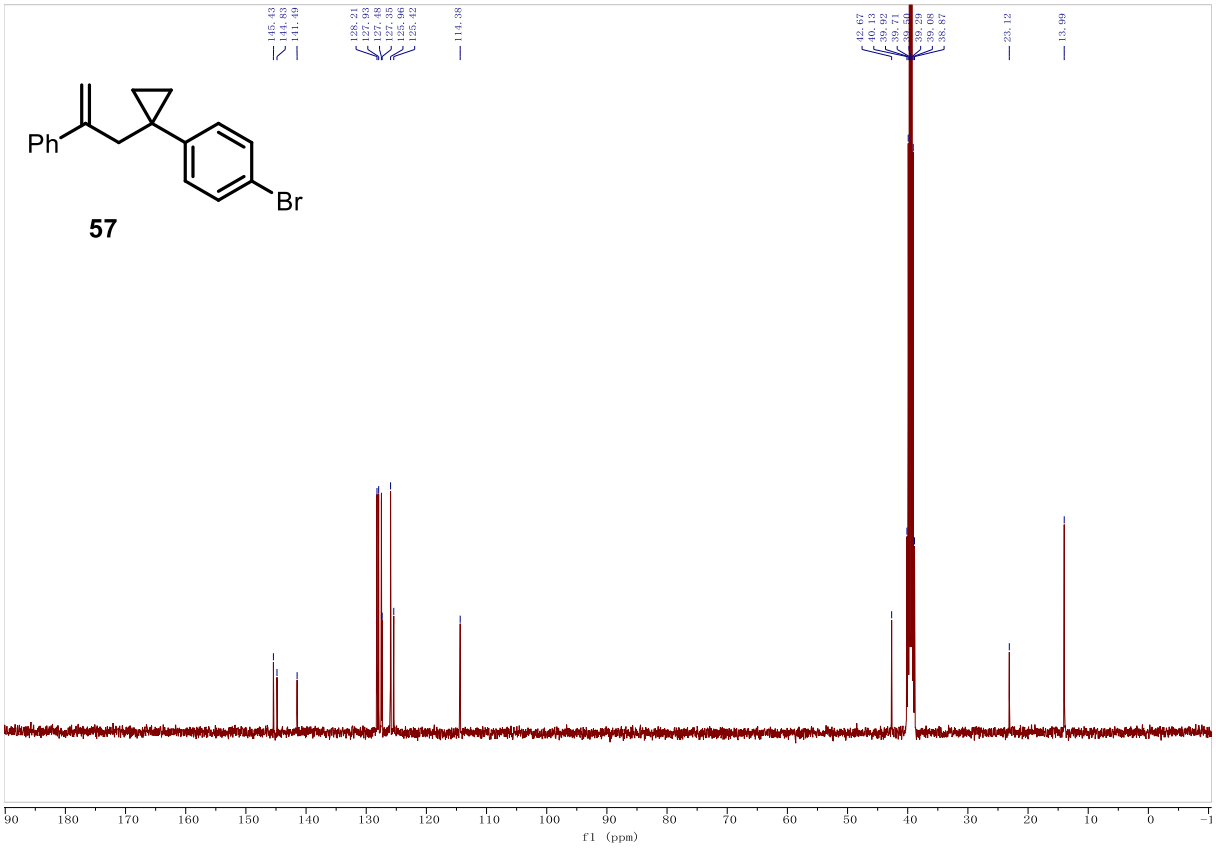
^{13}C NMR (101 MHz, $CDCl_3$)



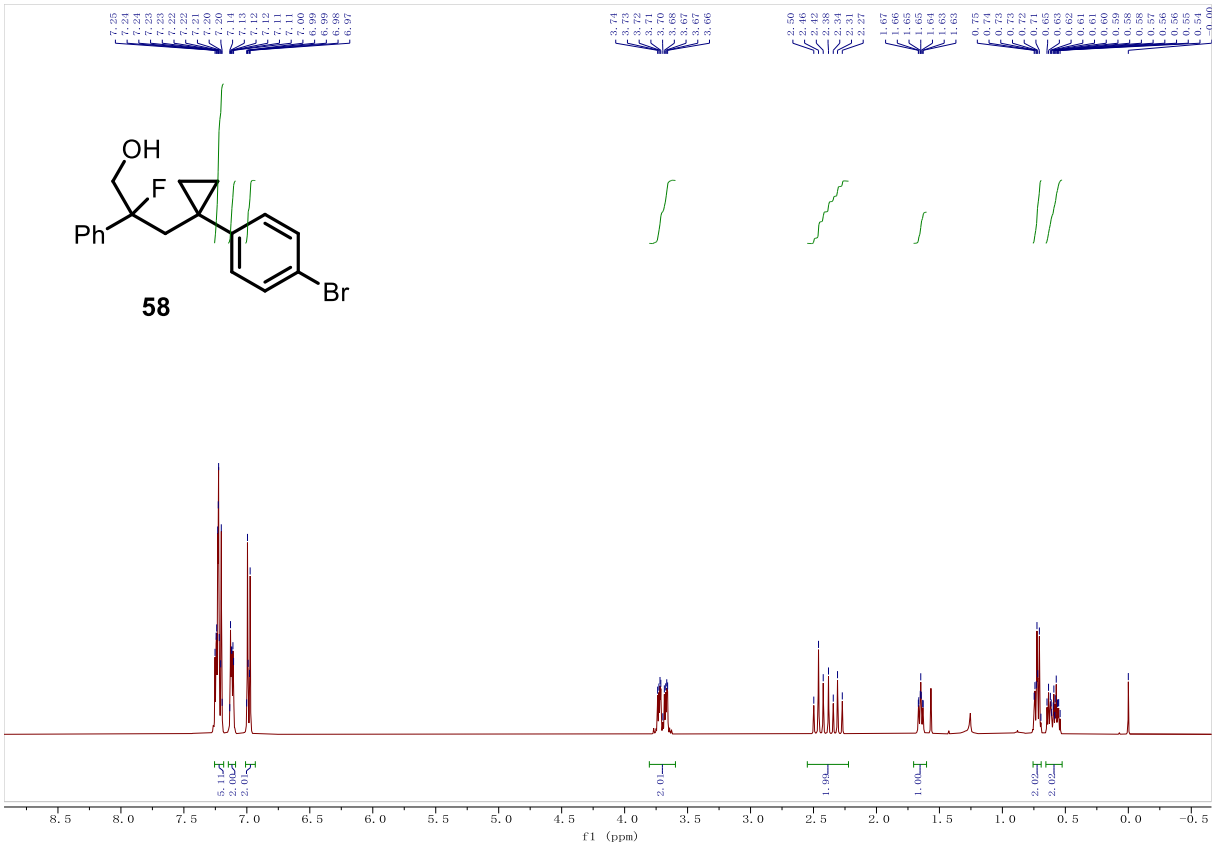
^{1}H NMR (400 MHz, DMSO-d_6)



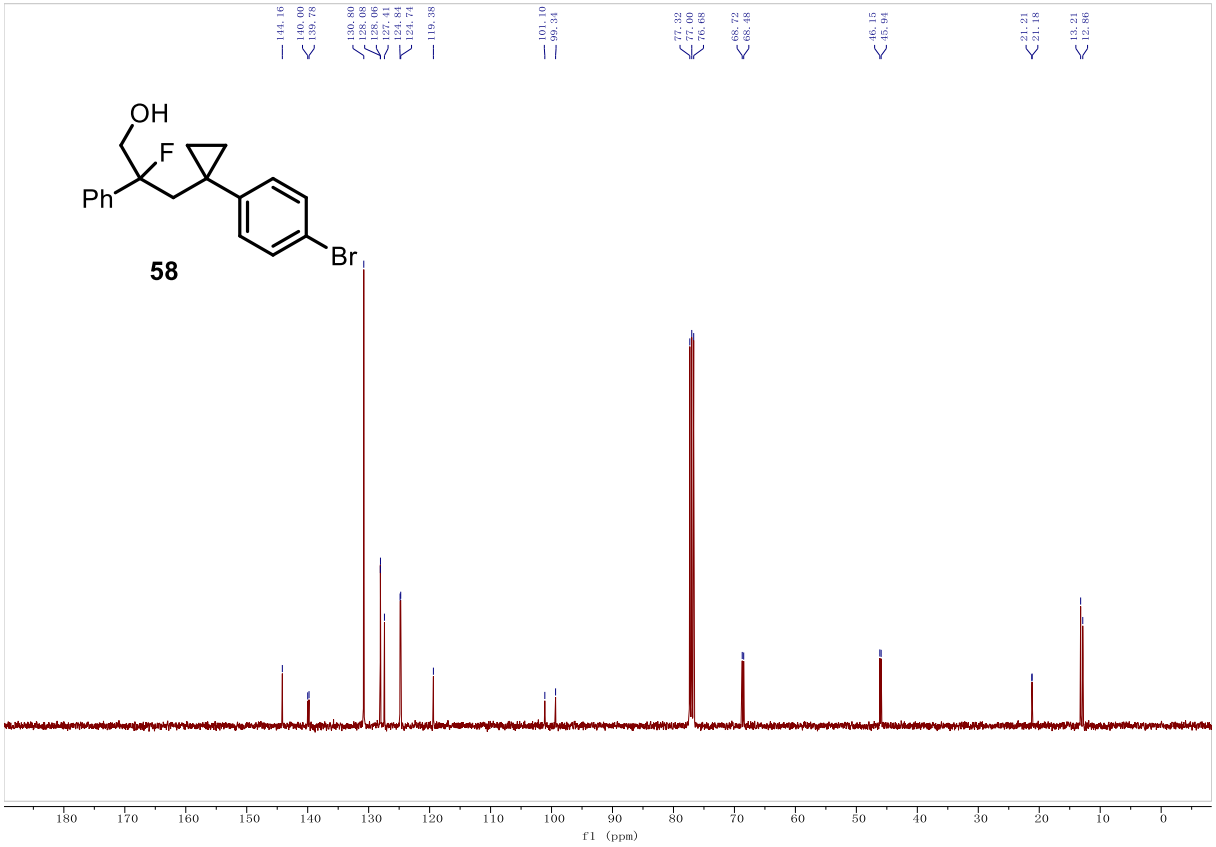
^{13}C NMR (101 MHz, DMSO-d_6)



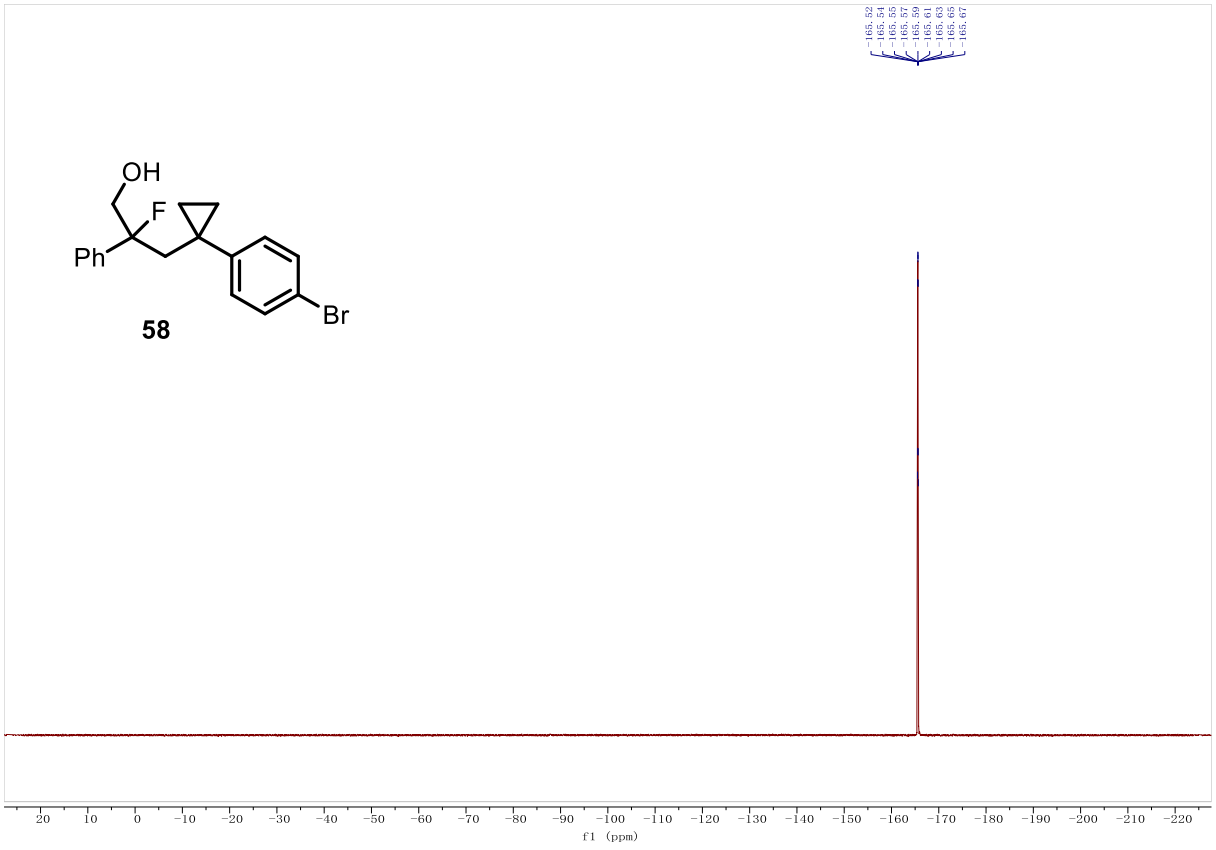
^{1}H NMR (400 MHz, $CDCl_3$)



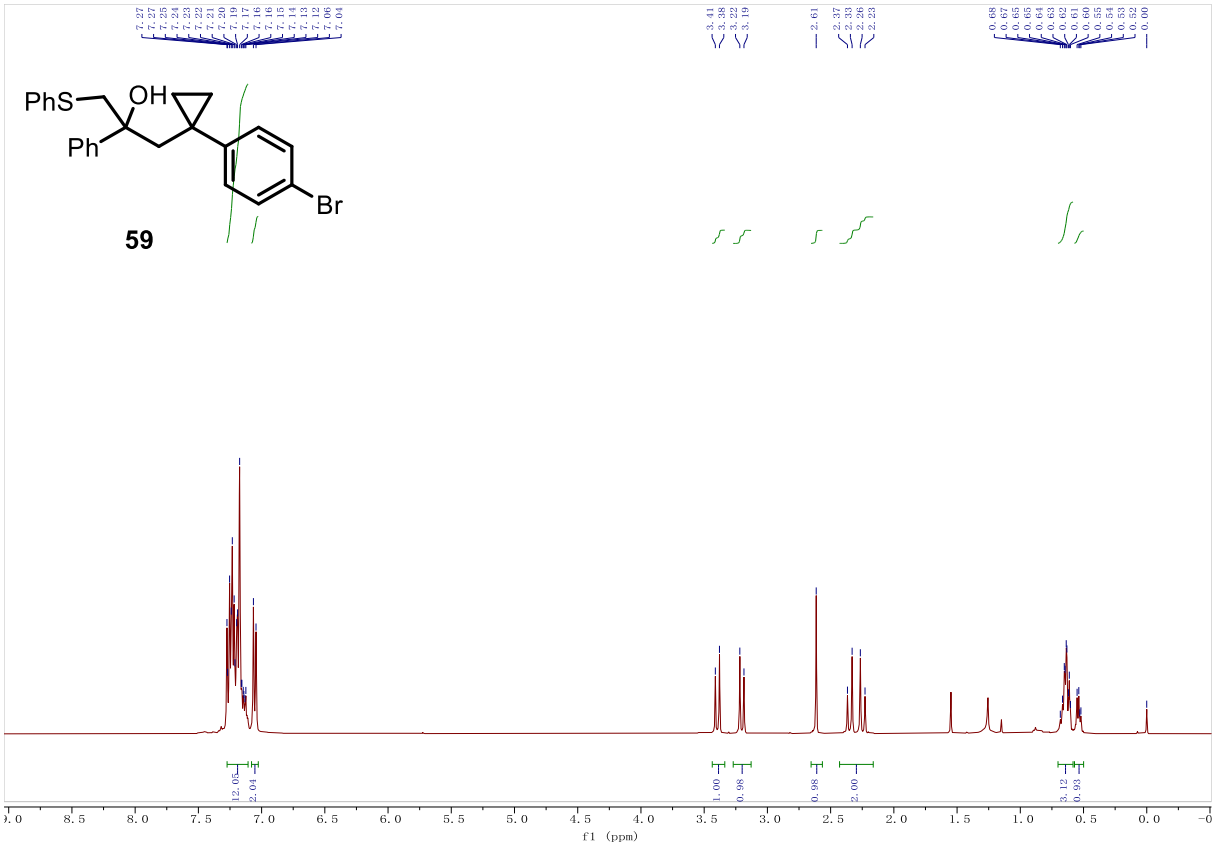
^{13}C NMR (101 MHz, $CDCl_3$)



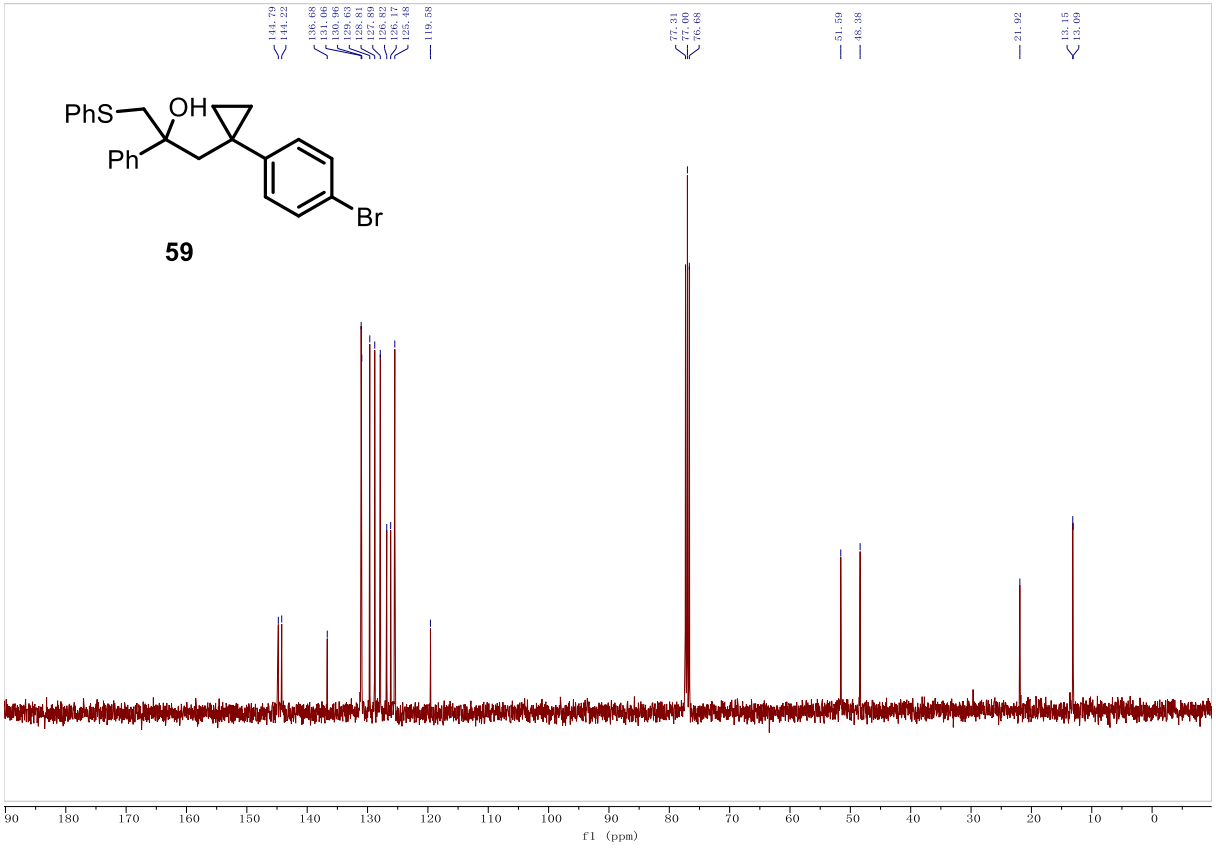
^{19}F NMR (376 MHz, $CDCl_3$)



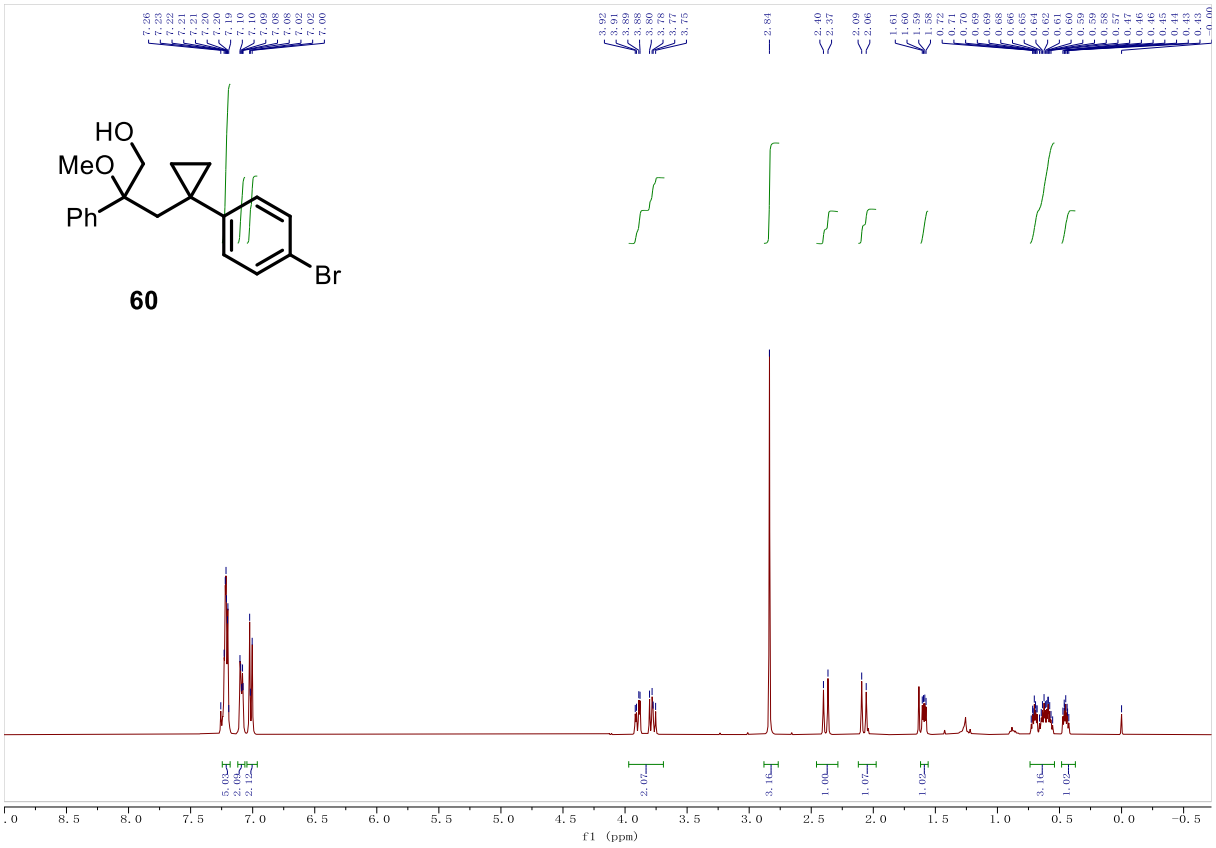
^{1}H NMR (400 MHz, $CDCl_3$)



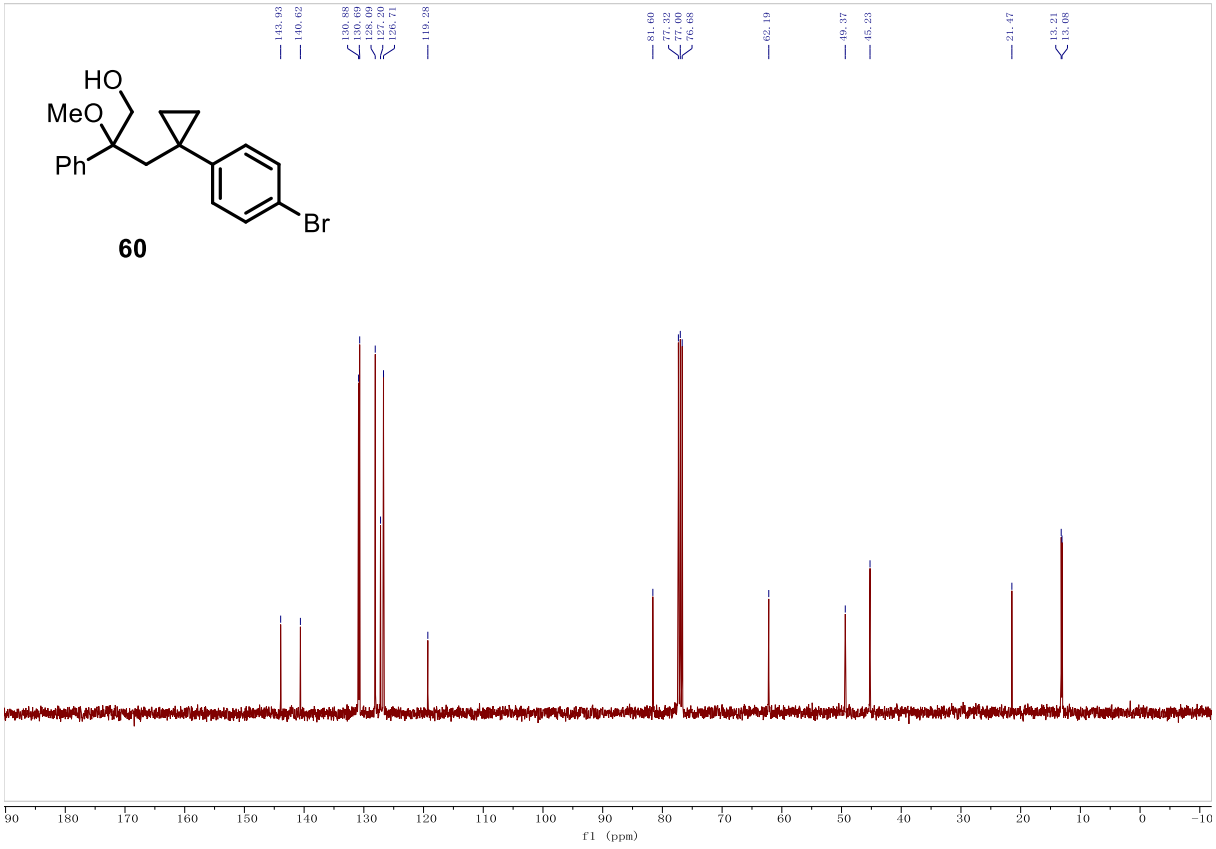
^{13}C NMR (101 MHz, $CDCl_3$)



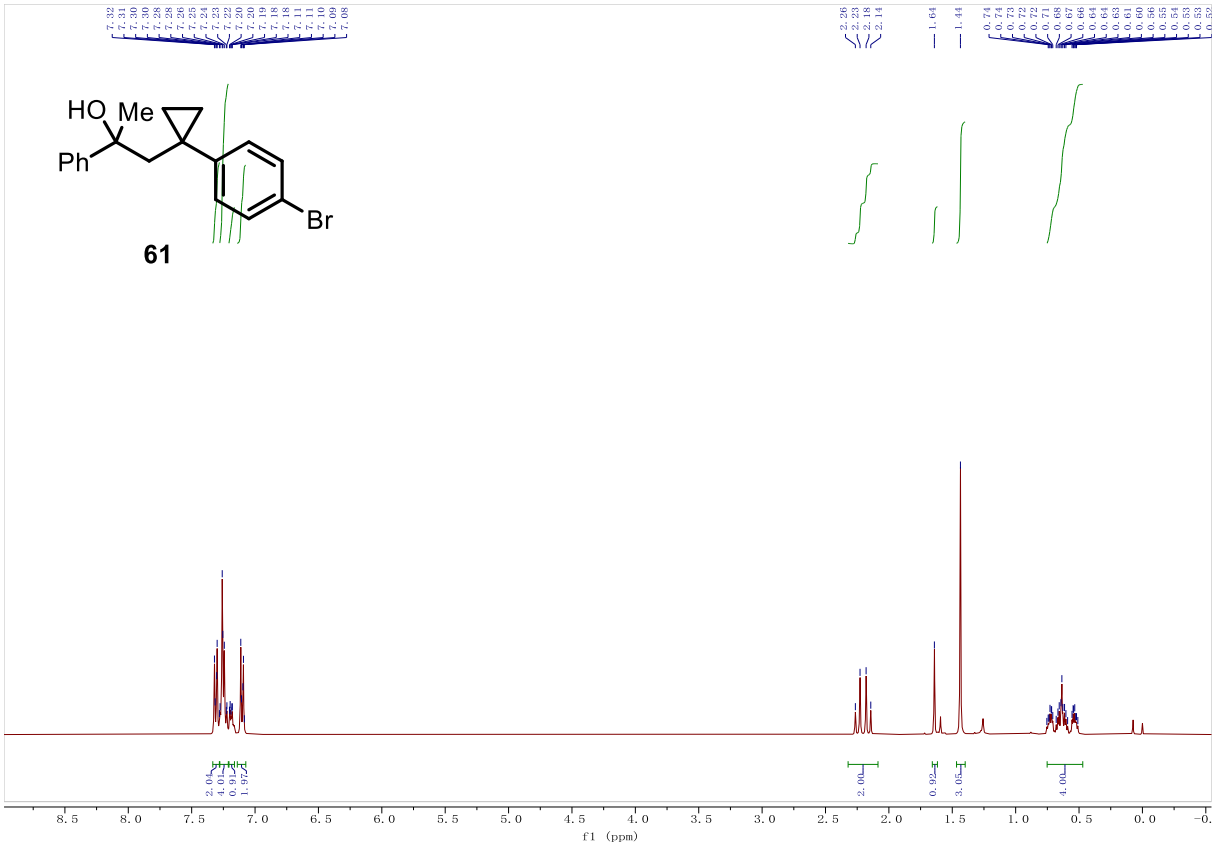
^{1}H NMR (400 MHz, $CDCl_3$)



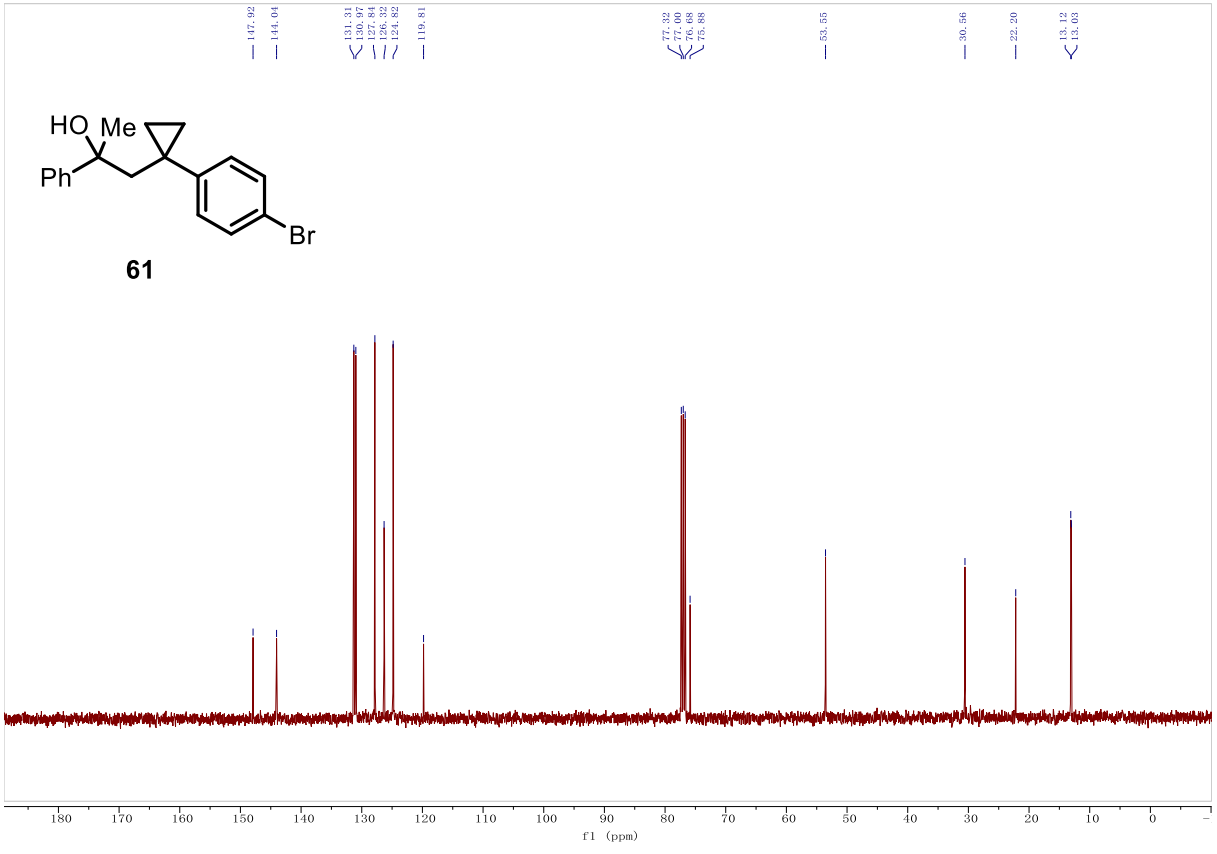
^{13}C NMR (101 MHz, $CDCl_3$)



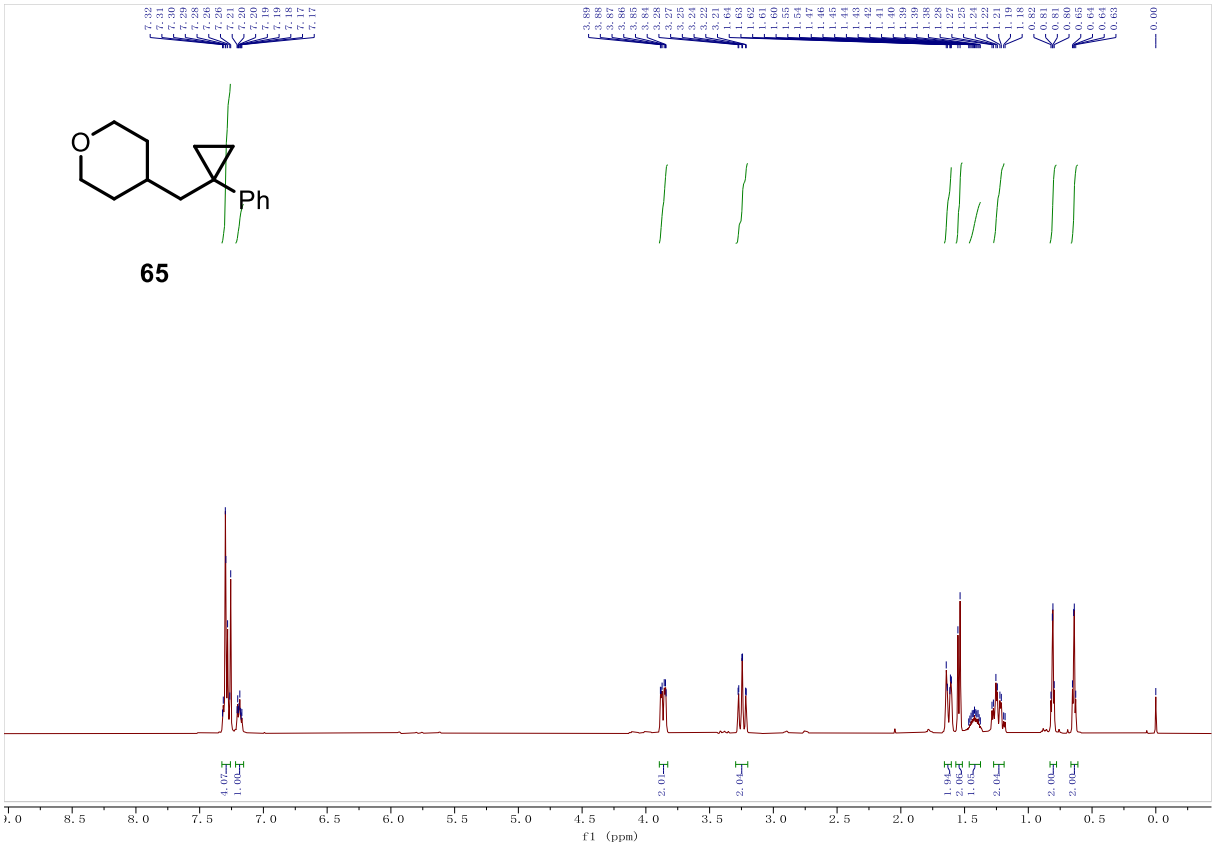
^{1}H NMR (400 MHz, $CDCl_3$)



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



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



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