Supplementary Information

New conformationally flexible and recyclable aryl iodine catalysts from inexpensive chiral source for asymmetric oxidations

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1. Supplementary methods

General information. All experiments were conducted under air atmosphere unless otherwise noted. **^{1}H** and **^{13}C NMR** spectra were recorded on a Bruker Ascend^{TM} 400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: **^{1}H** ($CDCl_3$ δ 7.26; DMSO-d^6 δ 2.50), **^{13}C** ($CDCl_3$ δ 77.16; DMSO-d^6 δ 39.5). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. For thin layer chromatography (TLC), Huanghai precoated TLC plates (GF254) were used, and compounds were visualized with a UV light at 254 nm. High resolution mass spectra (HRMS) were obtained on an Agilent 1290II-6545 spectrometer. Optical rotations were recorded on a Rudolph Research Analytical Autopol I automatic polarimeter. Enantiomeric excesses (*ee*) were determined by HPLC analysis on Agilent HPLC units; column of Chiralcel OD-H, Chiralpak AD-H or AS-H was used. Melting point (MP) was obtained on Hanon MP-430.Column chromatography was performed with silica gel (200-300 mesh ASTM). Unless otherwise noted, commercially available reagents purchased from Adamas-beta, TCI, Rhawn or Energy Chemical and were used as received.

2. Synthesis of the starting materials

1) General procedure for the synthesis of 1-naphthol carboxylic acid **12a-12l** were prepared according to the literature[1].

2) General procedure for the synthesis of 2-naphthol carboxylic acid **12m-12o** were prepared according to the literature[2].

3) General procedure for the synthesis of 1-naphthol carboxylic alcohol were prepared according to the literature[3].

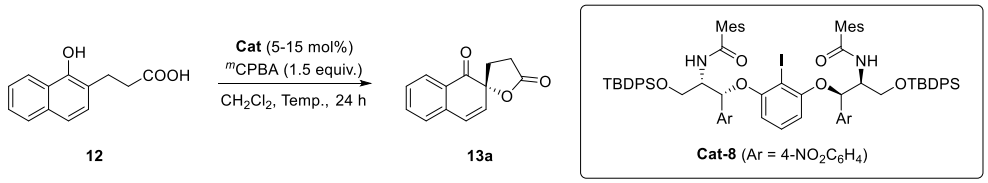
4) General procedure for the synthesis of 1-hydroxy-*N*-aryl-2-naphthamide **15a-15f** derivatives were prepared according to the literature[4].

5) General procedure for the synthesis of anilide derivatives **17a-17f** derivatives were prepared according to the literature[5].

6) General procedure for the synthesis of keto esters **19a-19k** derivatives were prepared according to the literature[6].

3. Catalysts, solvent and temperature optimization

Supplementary Table 1. Optimization of enantioselective oxidative dearomatization[a,b,c]



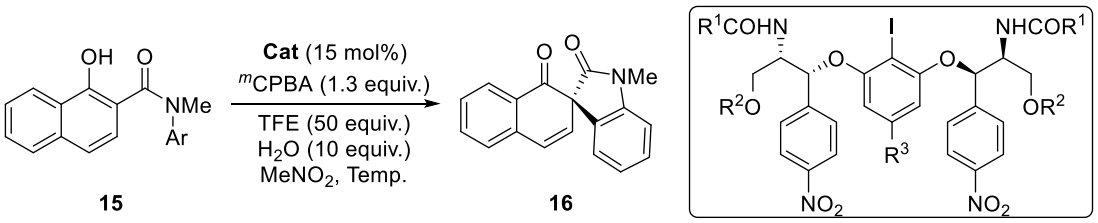
12 **13a** **Cat-8** (Ar = 4-$NO_2C_6H_4$)

Entry	Cat (mol%)	Temp. (°C)	Solvent	Yield (%)	*ee* (%)	Entry	Cat (mol%)	Temp. (°C)	Solvent	Yield (%)	*ee* (%)
1	**Cat-1** (15)	-30	CH_2Cl_2	45	85	9	**Cat-8** (15)	0	CH_2Cl_2	87	96
2	**Cat-2** (15)	-30	CH_2Cl_2	66	79	10	**Cat-33** (15)	0	CH_2Cl_2	80	92
3	**Cat-6** (15)	-30	CH_2Cl_2	56	86	11	**Cat-8** (15)	-20	toluene	77	96
4	**Cat-8** (15)	-30	CH_2Cl_2	77	98	12	**Cat-8** (15)	-20	EtOAc	44	87
5	**Cat-9** (15)	-30	CH_2Cl_2	52	90	13	**Cat-8 (15)**	-20	CH_2Cl_2 + EtOH[d]	92	98
6	**Cat-11** (15)	-30	CH_2Cl_2	47	86	14	**Cat-8** (10)[e]	-20	CH_2Cl_2 + EtOH[d]	80	98
7	**Cat-21** (15)	-30	CH_2Cl_2	35	75	15	**Cat-8** (5)[f]	-20	CH_2Cl_2 + EtOH[d]	72	98
8	**Cat-8** (15)	-20	CH_2Cl_2	82	98	16	**Cat-8** (15)	-20	CH_2Cl_2 + EtOH[g]	92	96

[a]**12** (0.2 mmol), **Cat-8** (0.03 mmol, 15 mol%), *m*CPBA (0.3 mmol, 1.5 equiv.) were stirred in CH_2Cl_2 (10 mL) at -30 to 0 °C for 24 h. [b]Isolated yield. [c]The *ee* value was determined by chiral HPLC. [d]EtOH (1 mmol, 5 equiv.) was added. [e]**Cat-8** (0.02 mmol, 10 mol%) was added. [f]**Cat-8** (0.01 mmol, 5 mol%) was added. [g]CH_2Cl_2 (5 mL), and EtOH (1 mmol, 5 equiv.) was added.

To a Schlenk tube containing **Cat-8**, *m*CPBA (0.3 mmol, 1.5 equiv.), and EtOH were added CH_2Cl_2 (10 mL) and **12** (0.2 mmol, 1.0 equiv.), the reaction mixture was stirred at 0 to -20 °C for 24 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was extracted by CH_2Cl_2 and concentrated *in vacuo*. Purification by column chromatography afforded the desired product.

Supplementary Table 2. Optimization of enantioselective oxidative spirolactonization[a,b,c]

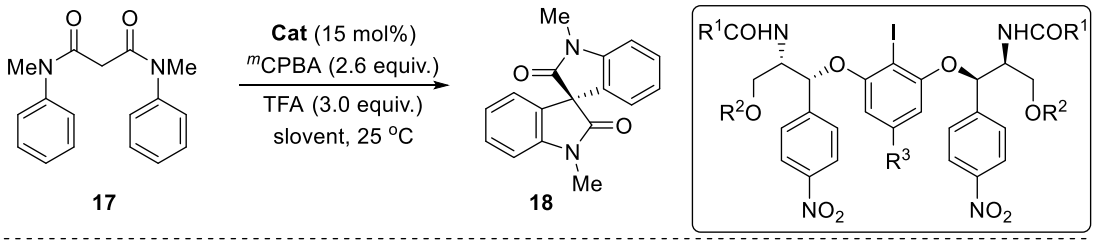


Entry	R^1	R^2	R^3	T	Yield (%)	Time	*ee* (%)
1	Mes	COMes	H	-20 °C	30	2 day	56
2	Mes	COMes	Me	-20 °C	27	2 day	53
3	Mes	COMes	COOMe	-20 °C	33	2 day	55
4	Mes	COMes	3,5-di(CF_3)C_6H_3	-20 °C	25	2 day	53
5	Mes	TBDPS	H	-20 °C	35	2 day	70
6	Ad	TBDPS	H	-20 °C	39	2 day	96
7	4-OMeC_6H_4	TBDPS	H	-20 °C	36	2 day	85
8	4-$NO_2C_6H_4$	TBDPS	H	-20 °C	42	2 day	96
9	4-MeC_6H_4	TBDPS	H	-20 °C	37	2 day	79
10	4-^{t}BuC_6H_4	TBDPS	H	-20 °C	40	2 day	87
11	4-$NO_2C_6H_4$	TBDPS	H	-20 °C	55	5 day	91
12	4-$NO_2C_6H_4$	TBDPS	H	0 °C	61	2 day	91
13	4-$NO_2C_6H_4$	TBDPS	H	-10 °C	57	3 day	94

Conditions: [a]15 (0.2 mmol), **Cat-9** (0.03 mmol, 15 mol%), ^{m}CPBA (0.26 mmol, 1.3 equiv.), TFE (10 mmol, 50 equiv.) and H_2O (2 mmol, 10 equiv.) were stirred in $MeNO_2$ (3 mL) at -10 °C. [c]Isolated yield. [d]The *ee* value was determined by chiral HPLC.

To a Schlenk tube containing **Cat-9** (0.03 mmol, 15 mol%), ^{m}CPBA (0.26 mmol, 1.3 equiv.), TFE (10 mmol, 50 equiv.), H_2O (2 mmol, 10 equiv.) and $MeNO_2$ (3 mL) were added **15** (0.2 mmol, 1.0 equiv.), the reaction mixture was stirred at -10 °C for 72 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was extracted by CH_2Cl_2 and concentrated *in vacuo*. Purification by column chromatography afforded the desired product.

Supplementary Table 3. Optimization of enantioselective direct C(sp^2)-H/C(sp^3)-H cross-coupling.[a,b,c,d]

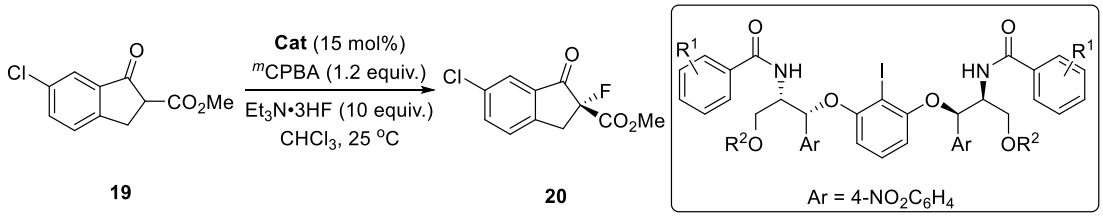


Entry	R^1	R^2	R^3	Yield (%)	Solvent	*ee* (%)
1	Mes	COMes	H	23	MeCN	4
2	Mes	COMes	Me	27	MeCN	0
3	Mes	COMes	COOMe	35	MeCN	0
4	Mes	COMes	3,5-di(CF_3)C_6H_3	20	MeCN	0
5	Mes	TBDPS	H	60	MeCN	7
6	NH(4-Me)C_6H_4	TBDPS	H	72	MeCN	74
7[b]	NH(4-Me)C_6H_4	TBDPS	H	N.R.	MeCN	00
8	NH(4-Me)C_6H_4	TBDPS	H	42	Benzonitrile	50
9	NH(4-Me)C_6H_4	TBDPS	H	37	Butyronitrile	83
10	4-MeC_6H_4	TBDPS	H	40	Butyronitrile	84
11	4-^{t}BuC_6H_4	TBDPS	H	43	Butyronitrile	77
12	^{t}Bu	TBDPS	H	52	Butyronitrile	86
13	^{t}Bu	TBDPS	H	72	MeCN	84
14[c]	^{t}Bu	TBDPS	H	72	MeCN	90

Conditions: [a]17 (0.2 mmol), **Cat-3** (0.03 mmol, 15 mol%), ^{m}CPBA (0.52 mmol, 2.6 equiv.), TFA (0.6 mmol, 3 equiv.) were stirred in MeCN (3 mL) at 25 °C for 16 h. [b]0 °C. [c]Add 3.0 equiv. H_2O. [d]Isolated yield. [e]The *ee* value was determined by chiral HPLC.

To a Schlenk tube containing **Cat-3** (0.03 mmol, 15 mol%), ^{m}CPBA (0.52 mmol, 2.6 equiv.), TFA (0.6 mmol, 3 equiv.) and H_2O and MeCN (3 mL) were added **17** (0.2 mmol, 1.0 equiv.), the reaction mixture was stirred at 25 °C for 16 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was extracted by EtOAc and concentrated *in vacuo*. Purification by column chromatography afforded the desired product.

Supplementary Table 4. Optimization of enantioselective oxidative fluorination of keto esters.[a,b,c,d]



Entry	R^1	R^2	Yield (%)	*ee* (%)
1	H	COMes	55	44
2	2,6-diMe	COMes	57	61
3	3,5-diCF_3	COMes	52	54
4	3,5-diCl	COMes	60	50
5	2,4,6-triMe	COMes	55	60
6	4-NO_2	COMes	54	33
7	2,4,6-triCl	COMes	59	65
8[b]	2,4,6-triCl	COMes	27	67
9	2,4,6-triBr	COMes	59	72
10	2,4,6-triCl	$C(C_6H_5)_3$	59	80
11	2,4,6-triBr	$C(C_6H_5)_3$	57	90

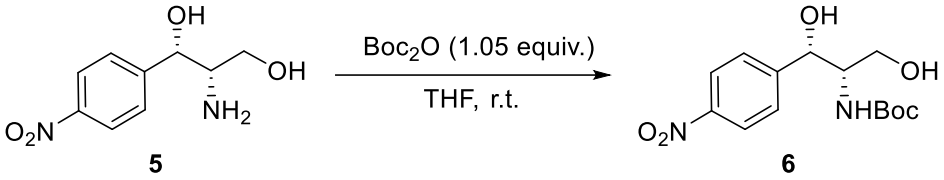
[a]19 (0.2 mmol), **Cat-38** (0.03 mmol, 15 mol%), *m*CPBA (0.3 mmol, 1.5 equiv.), and $Et_3N{\cdot}3HF$ (2 mmol, 10 equiv.) were stirred in $CHCl_3$ (8 mL) at 25 °C for 24 h. [b]DPIEA·3HF (2 mmol, 10 equiv.) was added instead of $Et_3N{\cdot}3HF$. [c]Isolated yield. [d]The *ee* value was determined by chiral HPLC.

To a Teflon tube containing *β*-ketoesters **19** (0.20 mmol, 1.0 equiv.), **Cat-38** (0.03 mmol, 15 mol%), and $CHCl_3$ (8 mL) were added amine·HF (2 mmol, 10 equiv.) and *m*CPBA (0.3 mmol, 1.5 equiv.) in turn, the reaction mixture was stirred at 25 °C for 24-72 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was extracted by CH_2Cl_2 and concentrated *in vacuo*. Purification by column chromatography afforded the desired product.

4. General procedure and spectra data of catalyst

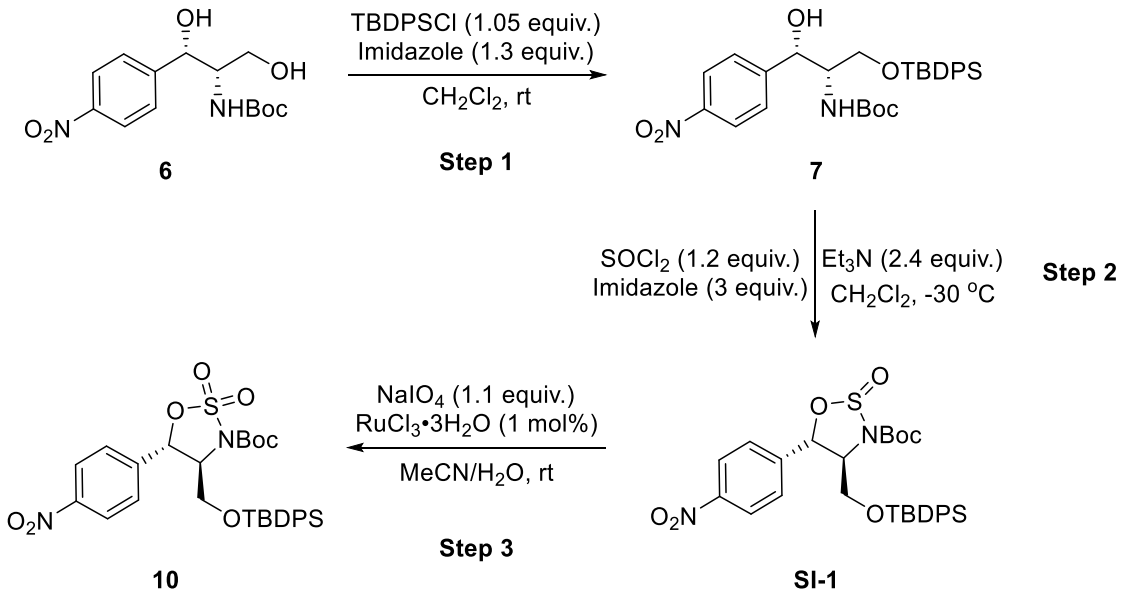
4.1 General procedure for synthesis of catalyst starting from (1*S*,2*S*)-ANP.

4.1.1 General procedure for synthesis of intermediate 11



5 6

According to a modified literature procedure,[7] to a 1-L round bottom flask containing (1*S*,2*S*)-ANP (330 mmol, 1.0 equiv.) were dissolved in THF (500 mL) at 0 °C, Boc_2O (346.5 mmol, 1.05 equiv.) was added dropwise and reaction mixture was allowed to stir at ambient temperature until full conversion of (1*S*,2*S*)-ANP, as shown by TLC. The organic layers were concentrated under vacuum. The crude product was recrystallized using ethyl acetate to afford the **6** (93.6 g, 91% yield) in a pure form.



6 7 10 SI-1

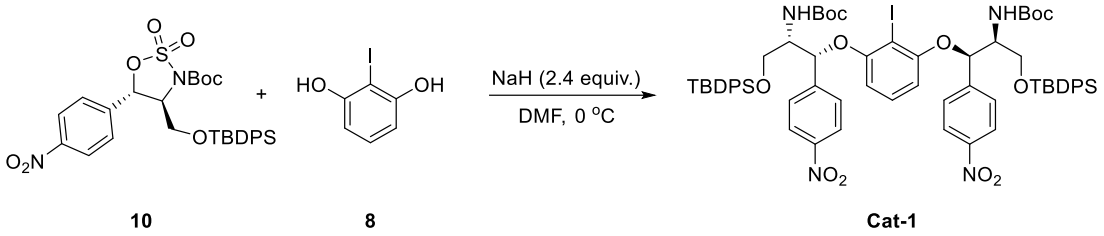
According to a modified literature procedure,[8] the cyclic sulfamidate was synthesized from the **6** by a three-step sequence: Silicon-based protection/Cyclization/$NaIO_4$ oxidation.

Step 1: the corresponding **6** (300 mmol, 1.0 equiv.) and imidazole (330 mmol, 1.3 equiv.) were dissolved in dry CH_2Cl_2 in a dry round bottom flask. TBDPSCl (315 mmol, 1.05 equiv.) dissolved in dry CH_2Cl_2 was added dropwise at 0 °C, and then the reaction mixture was allowed to stir at room temperature until TLC indicated completely consumed of the **6**. After completion of the reaction, water was added. The reaction mixture was extracted with CH_2Cl_2 (3x) and washed with brine (1x). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated under vacuum. The crude residue was directly used in the next step without further purification.

Step 2: To the dry three-necked flask, the **7** (1.0 equiv.) and imidazole (3.0 equiv.) were dissolved in dry CH_2Cl_2 under nitrogen before being cooled to −30 °C. Et_3N (2.4 equiv.) was added dropwise and the resulting mixture was stirred at −30 °C for 30 min. Then the $SOCl_2$ was added dropwise and the resulting mixture was stirred at −30 °C for 3 h until TLC indicated completely consumed of the **7**. The reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was directly used in the next step without further purification.

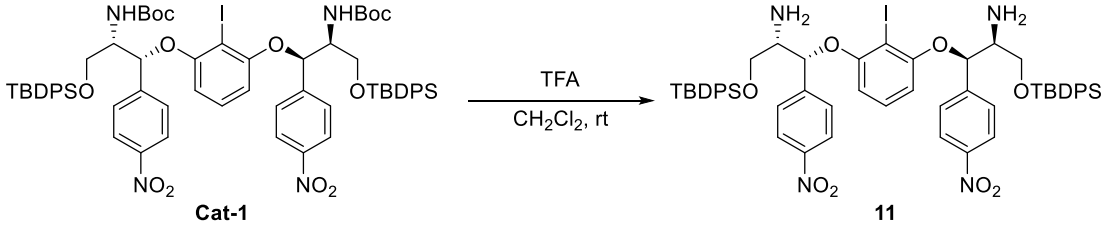
Step 3: To the three-necked flask, **SI-1** was dissolved in MeCN and water (1:1), $RuCl_3 \cdot 3H_2O$ (1 mol%) and $NaIO_4$ (1.1 equiv.) were added sequentially and the resulting mixture was stirred at room temperature for 4 h until TLC indicated completely consumed of the **SI-1**. The MeCN was concentrated under vacuum. Water was added and the reaction mixture was extracted with ethyl acetate (3x). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated under

vacuum. The crude product is recrystallized using MeOH to afford the **10** (159 g, 86% yield in three steps) in a pure form.



10 **8** **Cat-1**

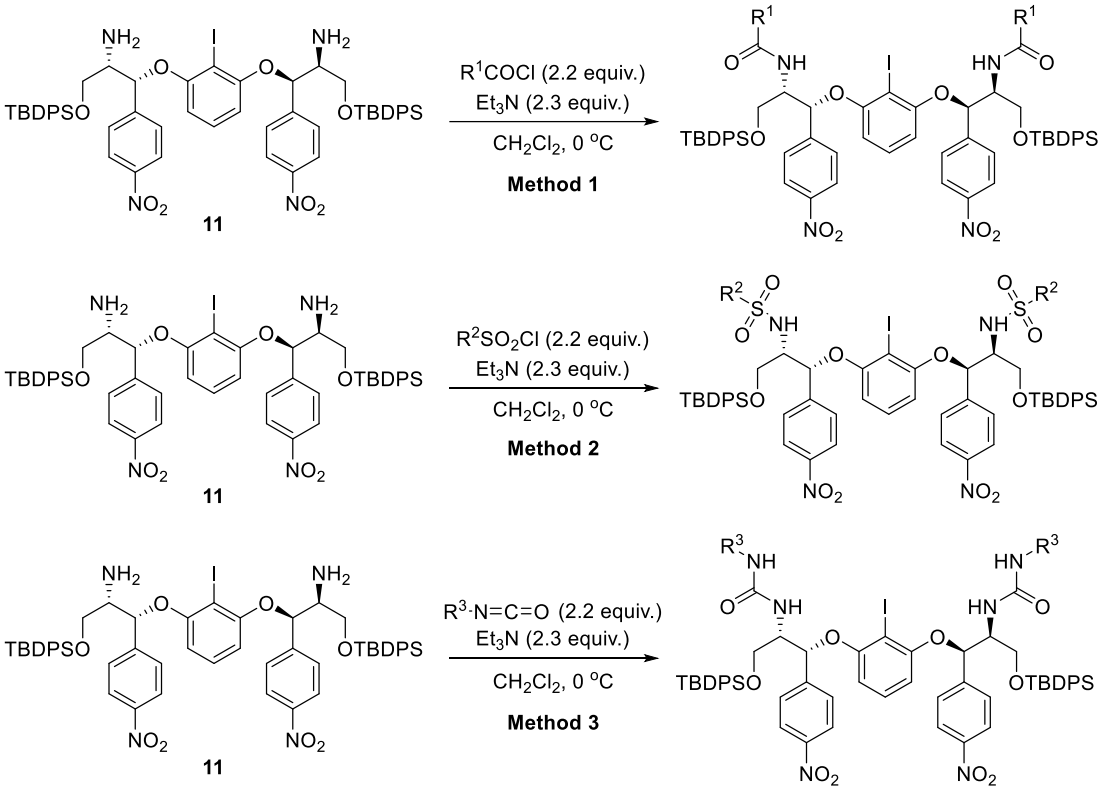
To the dry three-necked flask tube, the **8** (1.0 equiv., 130 mmol, 30.68 g) was dissolved in dry DMF (300 mL) under nitrogen before being cooled to 0 °C. NaH (2.4 equiv., 312 mmol, 12.48 g) was added and the resulting mixture was stirred at 0 °C for 30 min. Then the **10** (2.0 equiv., 260 mmol, 159 g) dissolved in dry DMF (500 mL) was added dropwise and the resulting mixture was stirred at 0 °C for 4 h until TLC indicated completely consumption of the **9**. The reaction was quenched with 1N HCl. Water is further added to the system to precipitate the solids. Crude **Cat-1** (258 g) was isolated by filtration which was directly used in the next step without further purification.



Cat-1 **11**

To the dry three-necked flask, the crude **Cat-1** (258 g) was dissolved in dry CH_2Cl_2 (120 mL). TFA (30 mL) was dropwise at 0 °C and the resulting mixture was stirred at room temperature for 2 h until TLC indicated completely consumed of the **Cat-1**. The reaction was quenched with a saturated solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude product is recrystallized using MeOH to afford the **11** (106 g, 74% yield in two steps) in a pure form.

4.1.2 General procedure for synthesis of silicon-based catalysts



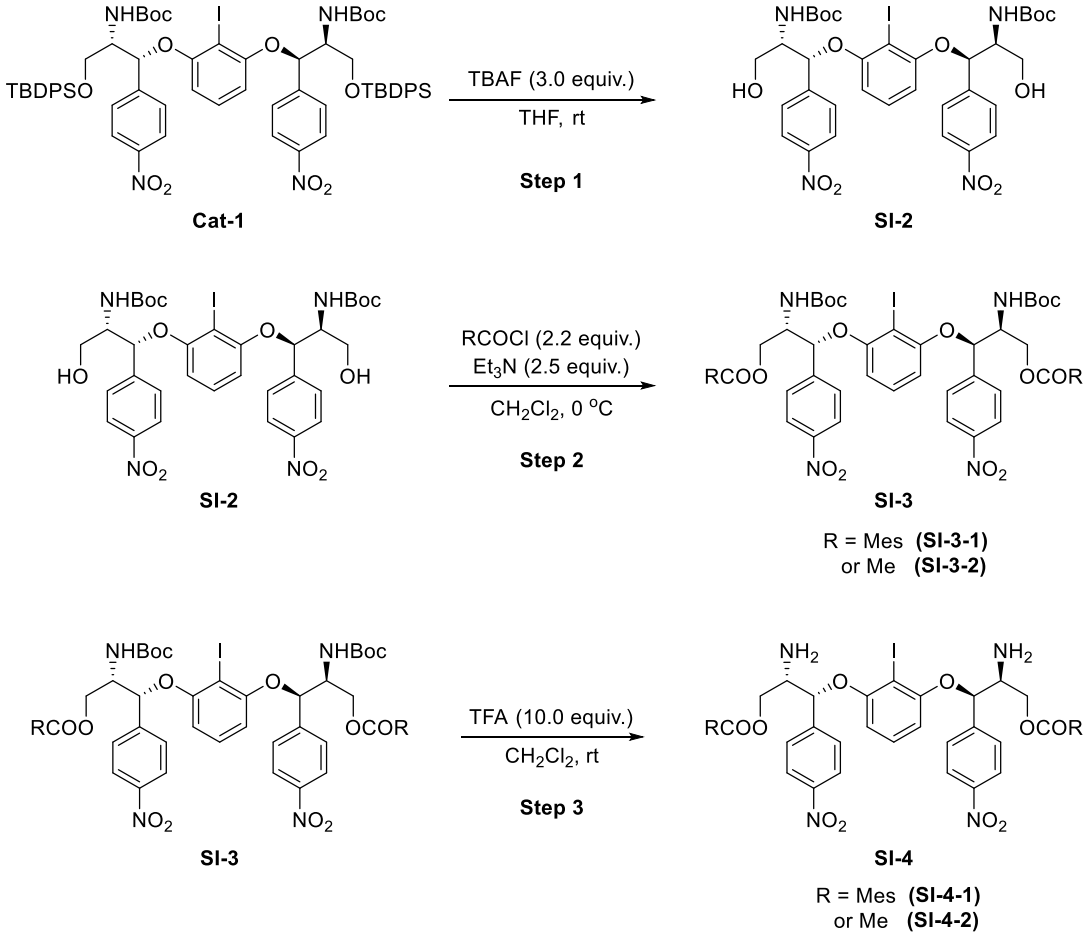
Method 1: To the dry three-necked flask, the aryl iodine intermediate **11** and Et_3N (2.3 equiv.) were dissolved in dry CH_2Cl_2 under nitrogen before being cooled to 0 °C. R^1COCl (2.2 equiv.) was added dropwise and the resulting mixture was stirred at 0 °C for 2 h until TLC indicated completely consumed of the aryl iodide. The reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was recrystallized using MeOH to afford the corresponding Chiral aryl iodine catalyst in a pure form.

Method 2: To the dry three-necked flask, the aryl iodide intermediates **11** and Et_3N (2.3 equiv.) were dissolved in dry CH_2Cl_2 under nitrogen before being cooled to 0 °C. R^2SO_2Cl (2.2 equiv.) was added dropwise and the resulting mixture was stirred at 0 °C for 2 h until TLC indicated consumption of the aryl iodide. The reaction was quenched with water. The organic layer was separated and the aqueous layer was

extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was recrystallized using MeOH to afford the corresponding Chiral aryl iodine catalyst in a pure form.

Method 3: To the dry three-necked flask, the aryl iodide intermediates **11** and Et_3N (2.3 equiv.) were dissolved in dry CH_2Cl_2 under nitrogen before being cooled to 0 °C. Isocyanates (2.2 equiv.) was added dropwise and the resulting mixture was stirred at 0 °C for 2 h until TLC indicated consumption of the aryl iodide. The reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was recrystallized using MeOH to afford the corresponding Chiral aryl iodine catalyst in a pure form.

4.1.3 General procedure for synthesis of ester catalysts



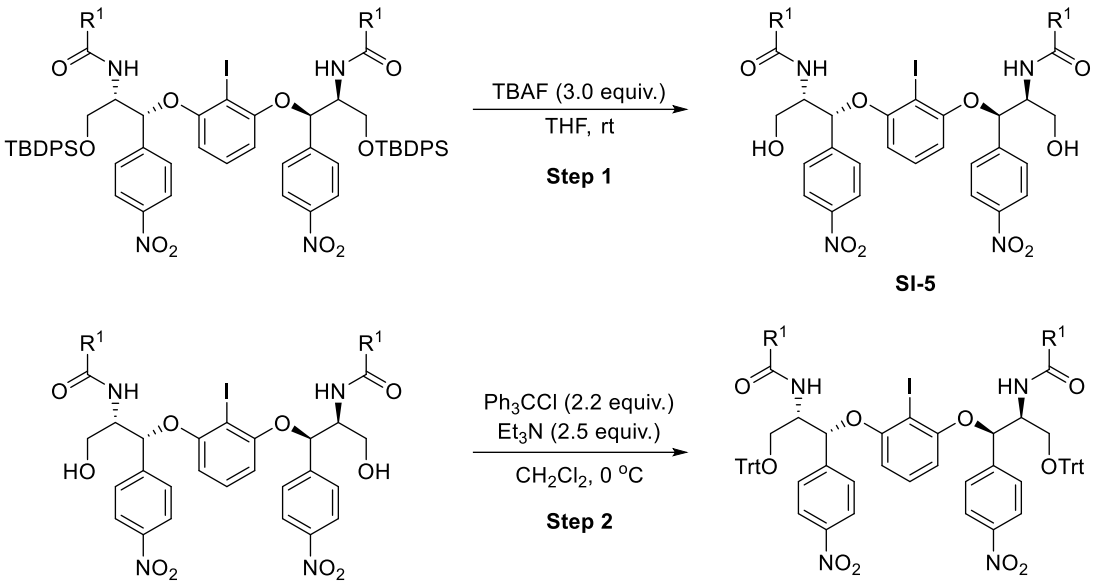
Step 1: To a round bottom flask containing the **Cat-1** (1.0 equiv.) and dry THF at room temperature was added TBAF (3.0 equiv.) dropwise. The reaction mixture was stirred for 3 h. The reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was directly used in the next step without further purification.

Step 2: To the dry three-necked flask, the **SI-2** and Et_3N (2.5 equiv.) were dissolved in dry CH_2Cl_2 under nitrogen before being cooled to 0 °C. MesCOCl (2.2 equiv.) or AcCl (2.2 equiv.) was added dropwise and the resulting mixture was stirred at 0 °C for 2 h until TLC indicated consumption of the **SI-2**. The reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was recrystallized using MeOH to afford the corresponding **SI-3** in a pure form.

Step 3: To the dry three-necked flask, the **SI-3** was dissolved in dry CH_2Cl_2. TFA was dropwise at 0 ^oC and the resulting mixture was stirred at room temperature for 2 h until TLC indicated completely consumed of the **SI-3**. The reaction was quenched with a saturated solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The residue was recrystallized using MeOH to afford the **SI-4** in a pure form.

The general procedure for synthesis of ester catalysts from **SI-4** is same to synthesis of silicon-based catalysts.

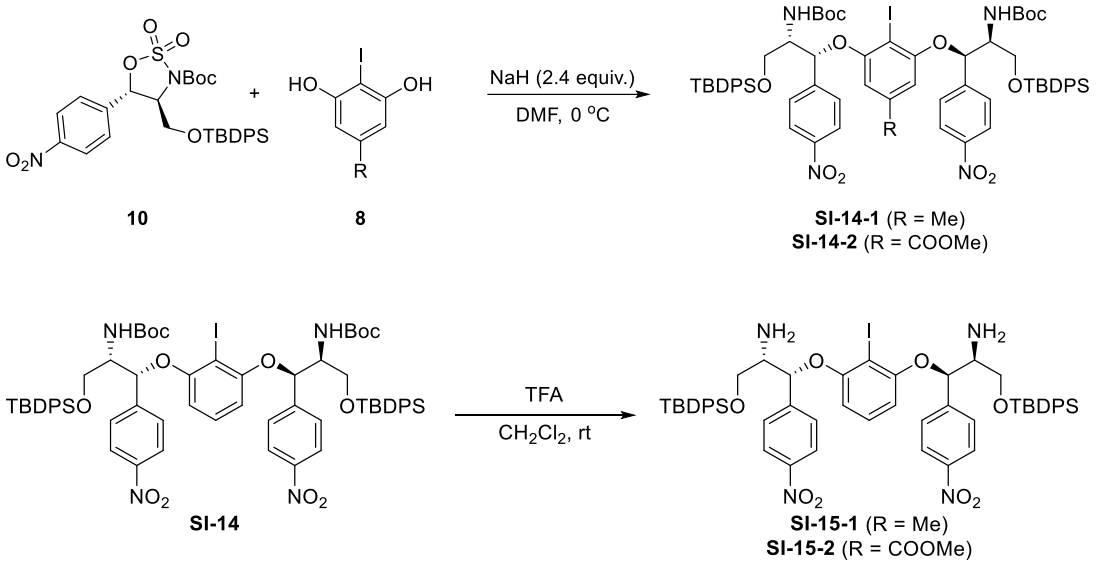
4.1.4 General procedure for synthesis of ether catalysts



Step 1: To a round bottom flask containing corresponding silicon-based catalysts (1.0 equiv.) and dry THF at room temperature was added TBAF (3.0 equiv.) dropwise. The reaction mixture was stirred for 3 h. The reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was directly used in the next step without further purification.

Step 2: To the dry three-necked flask, the **SI-5** and Et_3N (2.5 equiv.) were dissolved in dry CH_2Cl_2 under nitrogen before being cooled to 0 °C. Ph_3CCl (2.2 equiv.) was added dropwise and the resulting mixture was stirred at 0 °C for 2 h until TLC indicated consumption of the **SI-5**. The reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was recrystallized using MeOH to afford the corresponding ether catalysts in a pure form.

4.1.5 General procedure for synthesis of 2-iodo-5-substituted catalysts



10 **8**

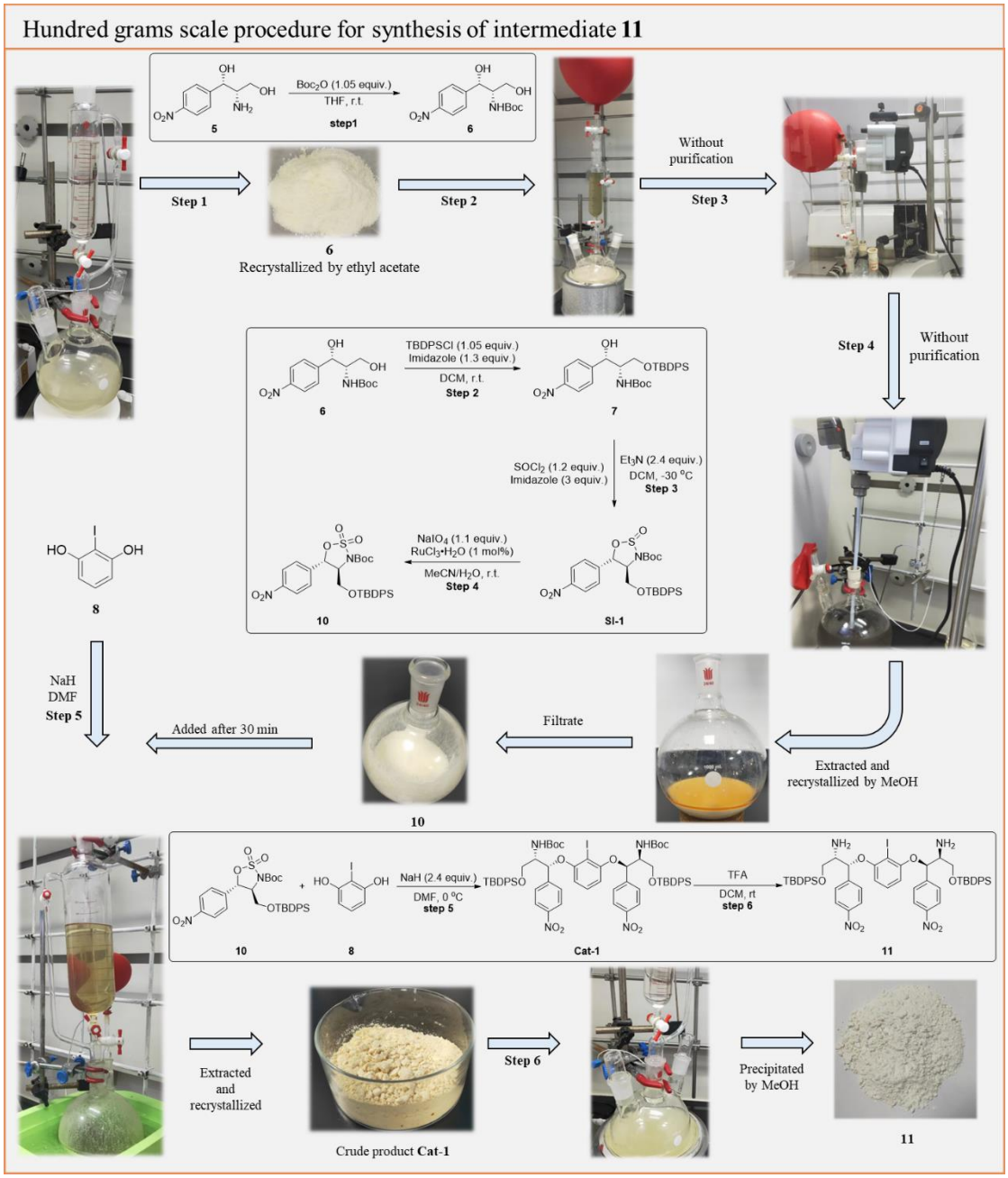
SI-14-1 (R = Me)
SI-14-2 (R = COOMe)

SI-14

SI-15-1 (R = Me)
SI-15-2 (R = COOMe)

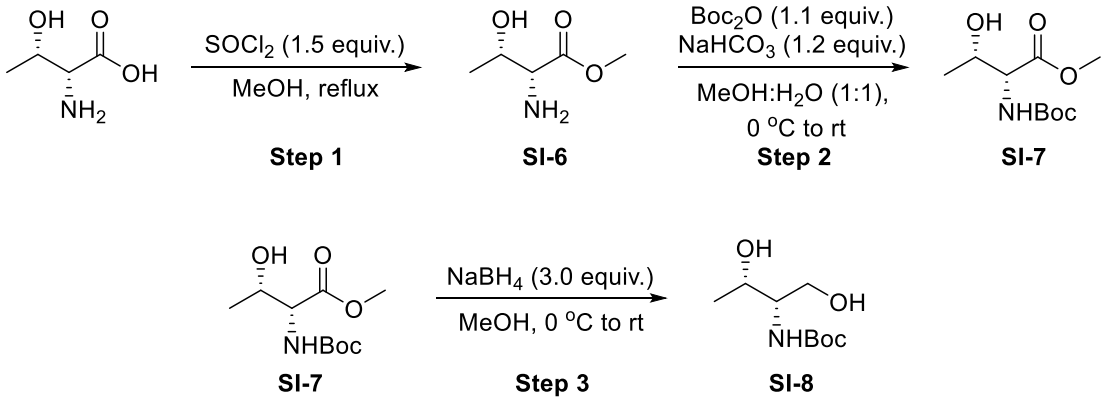
The general procedure was same to the procedure of synthesis of compound **11**.

4.2 Hundred grams scale procedure for synthesis of intermediate 11



Supplementary Figure 1. Flowchart of hundred grams scale synthesis of intermediate **11**

4.3 General procedure for synthesis of catalyst starting from *D*-threonine



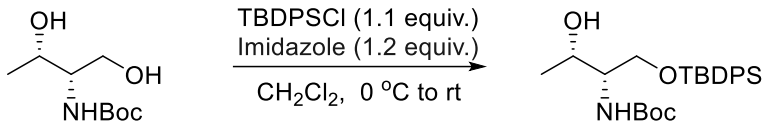
According to a modified literature procedure,[9] **SI-4** was synthesized from the *D*-threonine by a three-step sequence: Esterification/Amino protection/$NaBH_4$ reduction.

Step 1: To a 500-mL round bottom flask containing *D*-threonine (11.9 g, 100 mmol, 1.0 equiv.) and MeOH (200 mL) at 0 °C was added Thionyl chloride (150 mmol, 1.5 equiv.) dropwise. The reaction mixture was allowed to reflux overnight at 80 °C . The organic layers were concentrated under vacuum. The crude residue was directly used in the next step without further purification.

Step 2: The **SI-6** (1.0 equiv.) and $NaHCO_3$ (120 mmol, 1.2 equiv.) were dissolved in MeOH and water (1:1) before being cooled to 0 °C, Boc_2O (120 mmol, 1.2 equiv.) was added dropwise and the reaction mixture was allowed to stir at ambient temperature until full conversion of the **SI-6**, as shown by TLC. The MeOH was concentrated under vacuum. Water was added and the reaction mixture was extracted with CH_2Cl_2 (3x). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was directly used in the next step without further purification.

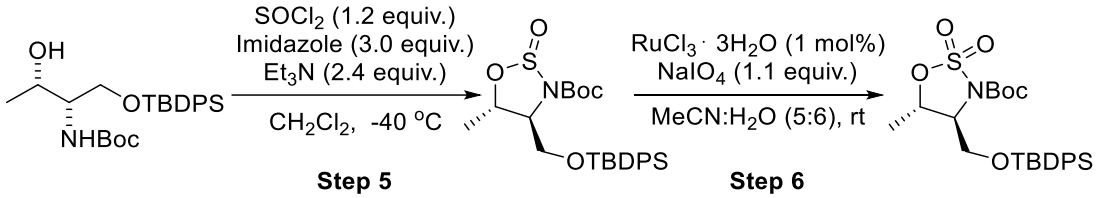
Step 3: To a 500-mL round bottom flask containing **SI-7** (1.0 equiv.) and MeOH at 0 °C was added $NaBH_4$ (300 mmol, 3.0 equiv.) portion wise. The reaction mixture was allowed to stir at 0 °C until TLC indicated full conversion of the **SI-7**. The

MeOH was concentrated under vacuum. Water was added and the reaction mixture was extracted with ethyl acetate (5x). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was subjected to column chromatography on silica gel (PE:EA 1:1) to afford the **SI-8** in a pure form. (15.4 g, 75% yield in three steps).



SI-8 **Step 4** **SI-9**

Step 4: The corresponding **SI-4** (15.4 g, 75 mmol, 1.0 equiv.) and imidaloze (6.12 g, 90 mmol, 1.2 equiv.) were dissolved in dry CH_2Cl_2 in a dry round bottom flask. TBDPSCl (21.5 mL, 82.5 mmol, 1.1 equiv.) dissolved in dry CH_2Cl_2 was added dropwise at 0 °C, and then the reaction mixture was allowed to stir at room temperature until TLC indicated full conversion of the **SI-8**. After completion of the reaction, water was added. The reaction mixture was extracted with CH_2Cl_2 (3x) and washed with brine (1x). The combined organic layers were dried over Na_2SO_4, the solvent was evaporated under vacuum. The crude residue was directly used in the next step without further purification.

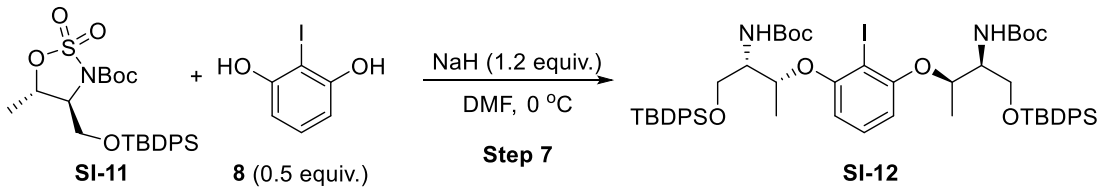


SI-9 **Step 5** **SI-10** **Step 6** **SI-11**

Step 5: According to a modified literature procedure,[] to the dry three-necked flask, the **SI-9** (1.0 equiv.) and imidazole (15.3 g, 225 mmol, 3.0 equiv.) were dissolved in dry CH_2Cl_2 under nitrogen before being cooled to −40 °C. Et_3N (25 mL, 180 mmol, 2.4 equiv.) was added dropwise and the resulting mixture was stirred at −40 °C for 30 min. Then the $SOCl_2$ (6.6 mL, 90 mmol, 1.2 equiv.) was added dropwise and the

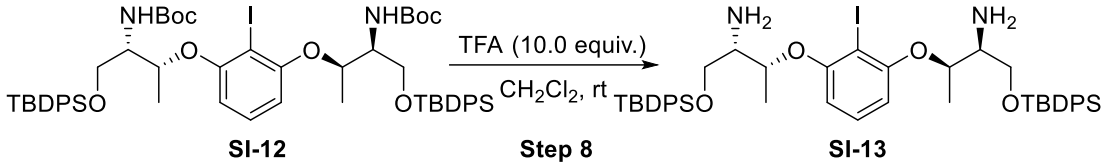
resulting mixture was stirred at −40 °C for 4 h until TLC indicated full conversion of the **SI-9**. The reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was directly used in the next step without further purification.

Step 6: To the three-necked flask, **SI-10** was dissolved in MeCN and water (1:1), $RuCl_3 \cdot 3H_2O$ (155 mg, 0.75 mmol, 1 mol%) and $NaIO_4$ (17.8 g, 82.5 mmol, 1.1 equiv.) were added sequentially and the resulting mixture was stirred at room temperature for 4 h until TLC indicated consumption of the **SI-10**. The MeCN was concentrated under vacuum. Water was added and the reaction mixture was extracted with ethyl acetate (3x). The organic layers were combined and dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was subjected to column chromatography on silica gel (PE:EA 10:1) to afford the **SI-10** in a pure form. (32.19 g, 85% yield)



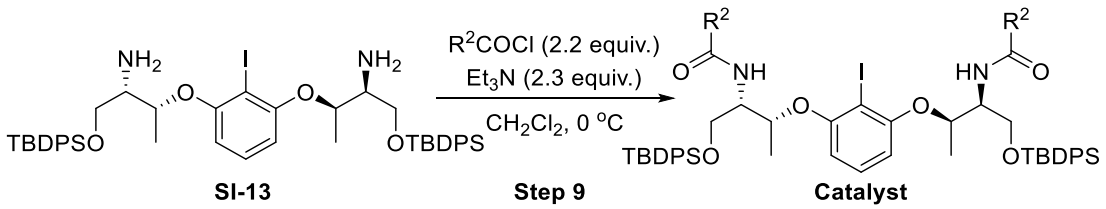
Step 7: To the dry three-necked flask, the **8** (2.36 g, 10 mmol, 0.5 equiv.) was dissolved in dry DMF under nitrogen before being cooled to 0 °C. NaH (960 mg, 24 mmol, 1.2 equiv.) was added and the resulting mixture was stirred at 0 °C for 30 min. Then the **SI-11** (10.1 g, 20 mmol, 1.0 equiv.) dissolved in dry DMF was added dropwise and the resulting mixture was stirred at 0 °C for 4 h until TLC indicated consumption of the 2-iodobenzene-1,3-diol. The reaction was quenched with 1N HCl. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was subjected to column

chromatography on silica gel (PE:EA 6:1) to afford the **SI-12 (**8.5 g, 78% yield**)** in a pure form.



SI-12 **Step 8** **SI-13**

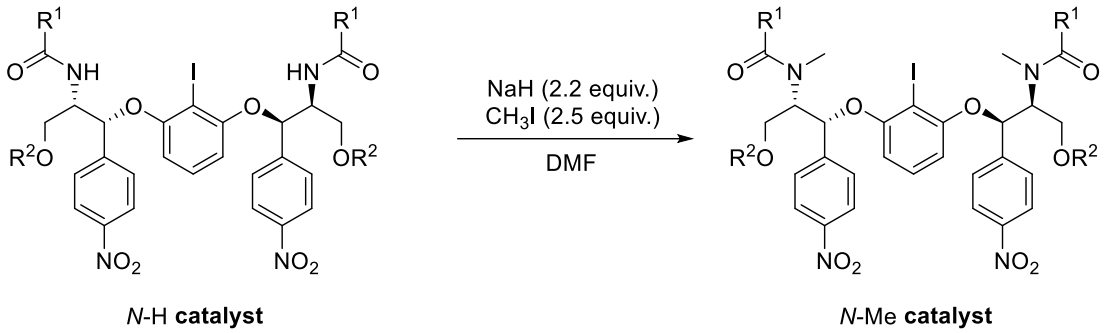
Step 8: To the dry three-necked flask, the **SI-12** (8.5 g, 7.8 mmol, 1.0 equiv.) was dissolved in dry CH_2Cl_2. TFA (10.0 equiv.) was added and the resulting mixture was stirred at room temperature for 2 h until TLC indicated consumption of the **SI-12**. The reaction was quenched with a saturated solution of $NaHCO_3$. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was subjected to column chromatography on silica gel (PE:EA 1:1) to afford the **SI-13** (6.6 g, 95% yield) in a pure form.



SI-13 **Step 9** **Catalyst**

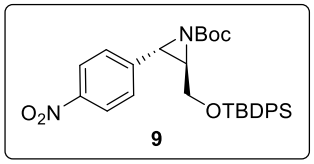
Step 9: To the dry three-necked flask, the **SI-13** and Et_3N (2.3 equiv.) were dissolved in dry CH_2Cl_2 under nitrogen before being cooled to 0 °C. R^1COCl (2.2 equiv.) was added dropwise and the resulting mixture was stirred at 0 °C for 2 h until TLC indicated consumption of the **SI-13**. The reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was recrystallized by CH_2Cl_2 and hexane to afford the corresponding the **Catalyst** a pure form.

4.4 General procedure for catalyst of the *N*-H bond of the amide moiety changed to *N*-Me bond.



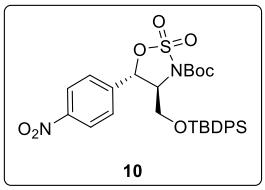
General procedure: To the dry three-necked flask tube, the corresponding *N*-H catalyst (1.0 equiv.) was dissolved in dry DMF under nitrogen before being cooled to 0°C. NaH (2.2 equiv.) was added and the resulting mixture was stirred at 0 °C for 30 min. Then the CH_3I (2.5 equiv.) was added dropwise and the resulting mixture was allowed to stirred at room temperature for 4 h until TLC indicated completely consumption of the starting material. The reaction was quenched with water. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (3x). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under vacuum. The crude residue was subjected to column chromatography on silica gel to afford the *N*-Me catalyst in a pure form.

4.5 Characterization of catalysts and intermediates.



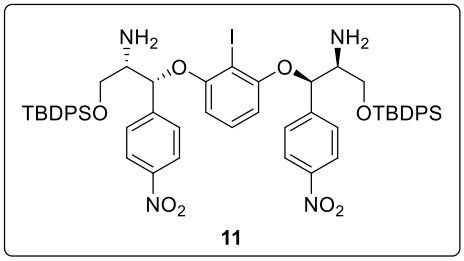
9 was isolated from mitsunobu reaction as colorless oil. DIAD (452 uL, 2.3 mmol, 2.3 equiv.) was dropwise to **8** (236 mg, 1 mmol, 1 equiv.), **7** (550 mg, 2.2 mmol, 2.2 equiv.) and PPh_3 (707 mg, 2.7 mmol, 2.7 equiv.) in THF at 0 ^oC. **9** (316 mg, 27% yield) was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 2/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) 7.97 (d, *J* = 8.9 Hz, 2H), 7.49 – 7.43 (m, 2H), 7.34 – 7.21 (m, 8H), 7.13 (dd, *J* = 8.9, 6.0 Hz, 2H), 3.69 – 3.60 (m, 2H), 3.07 (dd,

J = 11.0, 7.6 Hz, 1H), 3.03 – 2.96 (m, 1H), 1.38 (s, 9H), 0.87 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 161.6, 147.3, 142.2, 135.6, 135.3, 132.8, 132.7, 129.8, 129.8, 128.5, 127.7, 127.6, 123.3, 82.0, 60.9, 45.0, 42.4, 28.0, 27.9, 27.9, 26.7, 19.1. **HRMS** (ESI) m/z Calcd for $[C_{30}H_{36}N_2O_5Si, M+Na]^+$: 555.2286, found 555.2281.



10

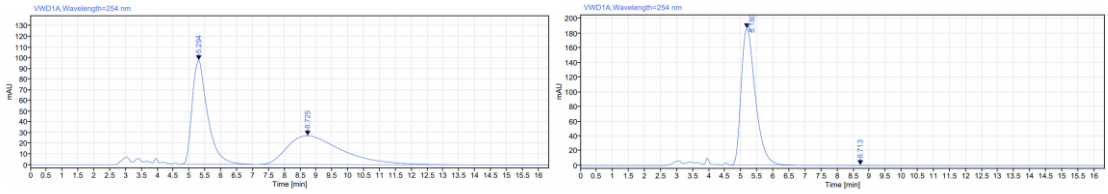
The crude product is recrystallized using MeOH to afford the **10** (159 g, 86% yield in three steps) in a pure form. **MP:** 128.7-130.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16-8.10 (m, 2H), 7.59 (m, 4H), 7.47-7.29 (m, 8H), 5.76 (d, *J* = 5.7 Hz, 1H), 4.16 (dd, *J* = 10.3, 5.0 Hz, 2H), 3.69-3.58 (m, 1H), 1.44 (s, 9H), 1.04 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 148.7, 148.2, 141.0, 135.7, 135.6, 132.4, 132.1, 130.4, 130.3, 128.2, 128.1, 128.0, 127.7, 124.3, 86.0, 79.1, 64.6, 59.6, 27.9, 26.8, 19.3. **HRMS** (ESI) m/z Calcd for $[C_{30}H_{36}N_2O_8SSi, M+H]^+$: 635.1854, found 635.1846.



11

The crude product is recrystallized using MeOH to afford the **11** (106 g, 74% in two steps) in a pure form. **MP:** 206.3-208.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.7 Hz, 4H), 7.57-7.48 (m, 8H), 7.45-7.39 (m, 4H), 7.35-7.24 (m, 8H), 7.21-7.16 (m, 4H), 6.73 (t, *J* = 8.3 Hz, 1H), 5.97 (d, *J* = 8.3 Hz, 2H), 5.31 (d, *J* = 5.8 Hz, 2H), 3.88 (dd, *J* = 10.2, 6.1 Hz, 2H), 3.61 (dd, *J* = 10.2, 5.0 Hz, 2H), 3.37-3.28 (m, 2H), 0.96 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.9, 147.8, 145.3, 135.7, 135.6, 133.1, 133.1, 130.0, 129.9, 129.7, 128.1, 128.0, 127.9, 123.9, 106.5, 80.9, 79.8, 64.9, 57.8, 27.0, 19.4. **HRMS** (ESI) m/z Calcd for $[C_{56}H_{61}IN_4O_8Si_2, M+H]^+$: 1101.3145, found 1101.3154.

Optical Rotation: $[\alpha]_D^{25}$ 8.3 (c = 1.0, $CHCl_3$). >99.9% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 5.180 min for major isomer, t_R = 8.713 min for minor isomer).

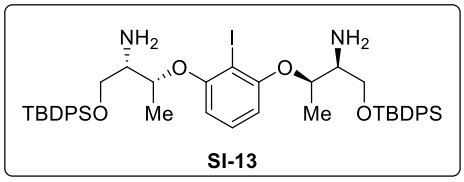


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.294	BB	2.39	3258.09	97.10	50.21	
8.725	BB	7.06	3230.29	26.87	49.79	
		Sum	6488.39			

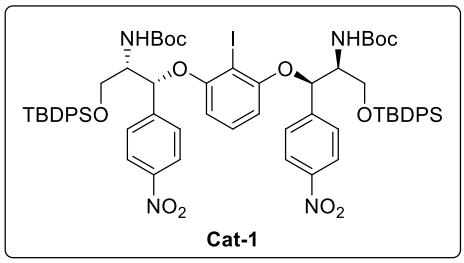
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.180	BB	2.38	5710.35	186.15	99.98	
8.713	MM m	0.18	1.40	0.11	0.02	
		Sum	5711.75			



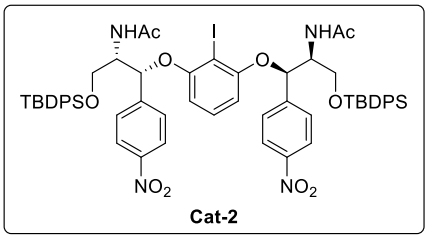
SI-13

SI-13 was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 5/1) as colorless oil. (R_f = 0.5, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70-7.60 (m, 8H), 7.46-7.29 (m, 12H), 7.15 (t, *J* = 8.3 Hz, 1H), 6.44 (d, *J* = 8.4 Hz, 2H), 4.61-4.51 (m, 2H), 3.90-3.77 (m, 4H), 3.26-3.16 (m, 2H), 1.31 (d, *J* = 6.3 Hz, 6H), 1.06 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.8, 135.7, 135.7, 133.5, 133.4, 129.9, 129.8, 129.6, 127.9, 127.9, 106.1, 81.8, 76.2, 65.5, 56.7, 27.0, 19.4, 15.2. **HRMS** (ESI) m/z Calcd for $[C_{46}H_{59}IN_2O_4Si_2, M+H]^+$: 909.2950, found 909.2971.



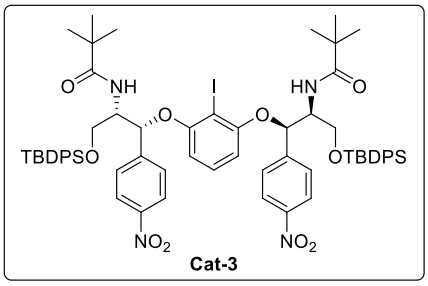
Cat-1

The crude **Cat-1** was purified by MeOH and H_2O as yellow solid. **MP:** 108.0- 111.2°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 4H), 7.61-7.47 (m, 12H), 7.36 (dd, *J* = 26.7, 7.3 Hz, 8H), 7.21 (t, *J* = 7.5 Hz, 4H), 6.84 (t, *J* = 8.2 Hz, 1H), 6.05 (d, *J* = 8.3 Hz, 2H), 5.44 (d, *J* = 6.3 Hz, 2H), 5.01 (d, *J* = 9.1 Hz, 2H), 4.30 (dd, *J* = 10.6, 5.1 Hz, 2H), 4.22-4.17 (m, 2H), 3.89-3.79 (m, 2H), 1.32 (s, 18H), 1.03 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1, 155.2, 147.7, 145.3, 135.6, 135.6, 132.9, 132.8, 130.0, 129.9, 129.7, 127.9, 127.9, 127.8, 123.8, 106.5, 79.9, 79.6, 79.5, 62.3, 57.1, 28.3, 27.0, 19.3. **HRMS** (ESI) m/z Calcd for $[C_{66}H_{77}IN_4O_{12}Si_2, M+H]^+$: 1323.4013, found 1323.4023.



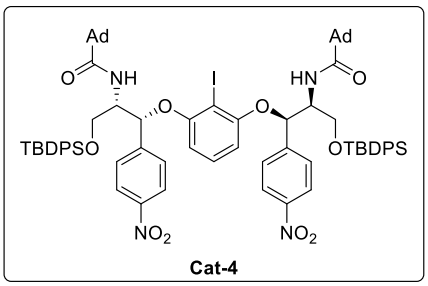
Cat-2

Cat-2 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and acetyl chloride (173.8 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.086 g, 0.9 mmol, 90%) as a white solid. **MP:** 188.0-183.2°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.6 Hz, 4H), 7.50-7.45 (m, 8H), 7.41 (d, *J* = 8.5 Hz, 4H), 7.34-7.27 (m, 4H), 7.26-7.17 (m, 8H), 6.75 (t, *J* = 8.3 Hz, 1H), 5.95 (d, *J* = 8.4 Hz, 2H), 5.80 (d, *J* = 8.7 Hz, 2H), 5.38 (d, *J* = 5.4 Hz, 2H), 4.45-4.37 (m, 2H), 4.22 (dd, *J* = 11.0, 6.2 Hz, 2H), 3.72 (dd, *J* = 10.9, 3.3 Hz, 2H), 1.76 (s, 6H), 0.94 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.9, 157.2, 147.7, 144.9, 135.6, 132.9, 132.8, 130.1, 130.0, 130.0, 128.0, 128.0, 127.5, 123.9, 106.8, 79.7, 79.5, 61.8, 56.0, 26.9, 23.3, 19.3. **HRMS** (ESI) m/z Calcd for $[C_{60}H_{65}IN_4O_{10}Si_2, M+H]^+$: 1207.3176, found 1207.3190.



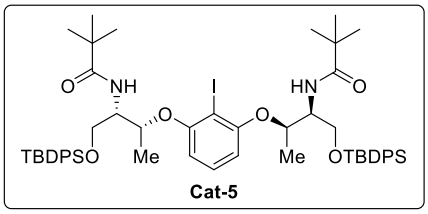
Cat-3

Cat-3 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and pivaloyl chloride (265.3 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH and water to precipitate the title compound (1.078 g, 0.85 mmol, 85%) as a white solid. **MP:** 118.1-118.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.7 Hz, 4H), 7.57-7.48 (m, 12H), 7.41-7.37 (m, 2H), 7.36-7.28 (m, 6H), 7.25-7.19 (m, 4H), 6.84 (t, *J* = 8.3 Hz, 1H), 6.23 (d, *J* = 8.3 Hz, 2H), 6.06 (d, *J* = 8.4 Hz, 2H), 5.48 (d, *J* = 6.2 Hz, 2H), 4.54-4.45 (m, 2H), 4.35 (dd, *J* = 10.8, 5.4 Hz, 2H), 3.75 (dd, *J* = 10.8, 3.3 Hz, 2H), 1.03 (s, 18H), 1.02 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.2, 157.5, 147.8, 145.2, 135.6, 135.5, 132.7, 132.6, 130.1, 130.0, 130.0, 128.0, 128.0, 127.7, 123.8, 106.8, 79.5, 61.9, 55.7, 38.8, 27.5, 26.9, 19.3. **HRMS** (ESI) m/z Calcd for $[C_{66}H_{77}IN_4O_{10}Si_2, M+H]^+$: 1269.4296, found 1269.4279.



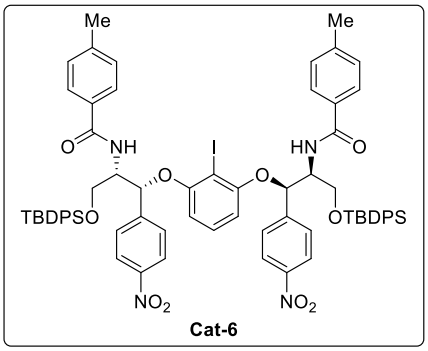
Cat-4

Cat-4 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 1-adamantanecarbonyl chloride (437.8 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.331 g, 0.92 mmol, 92%) as a white solid. **MP:** 130.5-133.2 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 4H), 7.59-7.50 (m, 12H), 7.48-7.27 (m, 8H), 7.26-7.20 (m, 4H), 6.86 (t, *J* = 8.3 Hz, 1H), 6.20 (d, *J* = 8.3 Hz, 2H), 6.07 (d, *J* = 8.4 Hz, 2H), 5.48 (d, *J* = 6.2 Hz, 2H), 4.56-4.46 (m, 2H), 4.38 (dd, *J* = 10.7, 5.4 Hz, 2H), 3.77 (dd, *J* = 10.7, 3.3 Hz, 2H), 1.98 (s, 6H), 1.75-1.57 (m, 24H), 1.03 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 177.7, 157.5, 147.7, 145.3, 135.6, 135.5, 132.7, 132.7, 130.1, 130.0, 129.9, 127.9, 127.9, 127.6, 123.7, 106.7, 79.5, 79.4, 62.0, 55.4, 40.6, 39.2, 36.4, 28.0, 26.9, 19.3. **HRMS** (ESI) m/z Calcd for $[C_{78}H_{89}IN_4O_{10}Si_2, M+Na]^+$: 1447.5054, found 1447.5073.



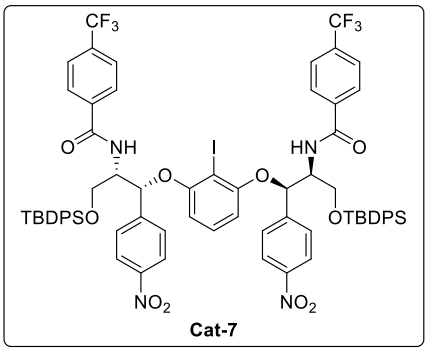
Cat-5

Cat-5 was prepared using **SI-13** (886 mg, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and pivaloyl chloride (265.3 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by DCM and hexane to precipitate the title compound (970 mg, 0.92 mmol, 92%) as a white solid. **MP:** 67.2-67.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68-7.63 (m, 4H), 7.56-7.51 (m, 4H), 7.46-7.41 (m, 2H), 7.41-7.33 (m, 6H), 7.29-7.23 (m, 4H), 7.18 (t, *J* = 8.3 Hz, 1H), 6.46 (d, *J* = 8.4 Hz, 2H), 6.21 (d, *J* = 8.6 Hz, 2H), 4.67 (p, *J* = 6.3 Hz, 2H), 4.38-4.23 (m, 4H), 3.87 (dd, *J* = 10.4, 3.4 Hz, 2H), 1.39 (d, *J* = 6.4 Hz, 6H), 1.17 (s, 18H), 1.04 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.2, 158.3, 135.6, 135.6, 133.0, 132.7, 130.0, 129.9, 127.9, 127.9, 105.9, 81.1, 74.8, 62.3, 54.6, 38.9, 27.6, 26.9, 19.3, 16.8. **HRMS** (ESI) m/z Calcd for $[C_{66}H_{77}IN_4O_{10}Si_2, M+H]^+$: 1055.4281, found 1055.4306



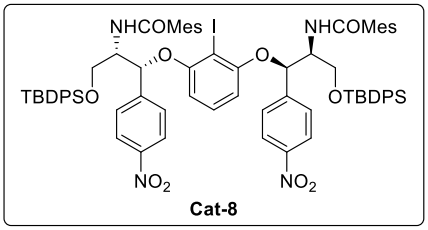
Cat-6

Cat-6 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and *p*-toluoyl chloride (339 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.096 g, 0.82 mmol, 82%) as a white solid. **MP:** 112.4-114.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.4 Hz, 4H), 7.51-7.40 (m, 16H), 7.31-7.24 (m, 4H), 7.21-7.12 (m, 12H), 6.71 (t, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 8.5 Hz, 2H), 5.94 (d, *J* = 8.4 Hz, 2H), 5.47 (d, *J* = 5.6 Hz, 2H), 4.69-4.59 (m, 2H), 4.34 (dd, *J* = 10.9, 6.1 Hz, 2H), 3.82 (dd, *J* = 10.9, 3.4 Hz, 2H), 2.30 (s, 6H), 0.91 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.0, 157.2, 147.7, 144.9, 142.5, 135.6, 135.5, 132.8, 132.7, 131.0, 130.0, 130.0, 129.4, 127.9, 127.4, 126.9, 123.9, 106.9, 80.0, 79.6, 61.9, 56.3, 26.9, 21.5, 19.2. **HRMS** (ESI) m/z Calcd for $[C_{72}H_{73}IN_4O_{10}Si_2, M+Na]^+$: 1359.3802, found 1359.3774.



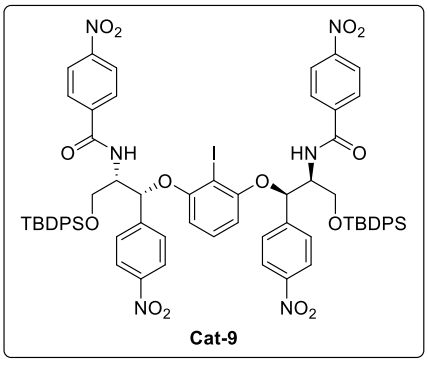
Cat-7

Cat-7 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 4-(trifluoromethyl)-benzoylchlorid (458.9 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.127 g, 0.78 mmol, 78%) as a white solid. **MP:** 120.3-121.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 4H), 7.65-7.55 (m, 8H), 7.50-7.40 (m, 12H), 7.33-7.25 (m, 4H), 7.22-7.14 (m, 8H), 6.76 (t, *J* = 8.3 Hz, 1H), 6.58 (d, *J* = 8.5 Hz, 2H), 5.97 (d, *J* = 8.4 Hz, 2H), 5.48 (d, *J* = 5.5 Hz, 2H), 4.71-4.60 (m, 2H), 4.36 (dd, *J* = 11.0, 6.2 Hz, 2H), 3.83 (dd, *J* = 11.0, 3.4 Hz, 2H), 0.93 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 157.2, 147.9, 144.6, 137.1, 135.6, 135.6, 133.6 (q, $^2J_{C-F}$ = 32.7 Hz), 132.7, 132.7, 130.2, 130.1, 128.0, 128.0, 127.4, 125.8 (q, $^3J_{C-F}$ = 3.7 Hz), 124.0, 123.7 (q, $^1J_{C-F}$ = 272.5 Hz), 107.1, 80.0, 79.5, 61.8, 56.5, 26.9, 19.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.86. **HRMS** (ESI) m/z Calcd for $[C_{72}H_{67}F_6IN_4O_{10}Si_2, M+Na]^+$: 1445.3417, found 1445.3431.



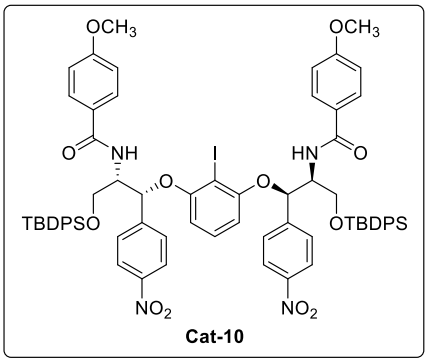
Cat-8

Cat-8 was prepared using **SI-13** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 2,4,6-trimethylbenzoyl chloride (401.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.198 g, 0.86 mmol, 86%) as a white solid. **MP:** 205.0-207.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.8 Hz, 4H), 7.53-7.40 (m, 12H), 7.30-7.24 (m, 4H), 7.18-7.11 (m, 8H), 6.78 (t, *J* = 8.3 Hz, 1H), 6.73 (s, 4H), 6.02 (dd, *J* = 8.2, 2.3 Hz, 4H), 5.69 (d, *J* = 4.9 Hz, 2H), 4.71-4.59 (m, 2H), 4.30 (dd, *J* = 11.2, 6.8 Hz, 2H), 3.81 (dd, *J* = 11.1, 3.1 Hz, 2H), 2.22 (s, 6H), 1.88 (s, 12H), 0.94 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 157.1, 147.9, 144.7, 138.9, 135.5, 134.2, 134.2, 132.7, 132.5, 130.1, 130.0, 129.9, 128.3, 127.9, 127.7, 124.0, 106.5, 79.5, 79.3, 61.7, 57.0, 26.9, 21.1, 19.2, 18.9. **HRMS** (ESI) m/z Calcd for $[C_{76}H_{81}IN_4O_{10}Si_2, M+Na]^+$: 1415.4428, found 1415.4434.



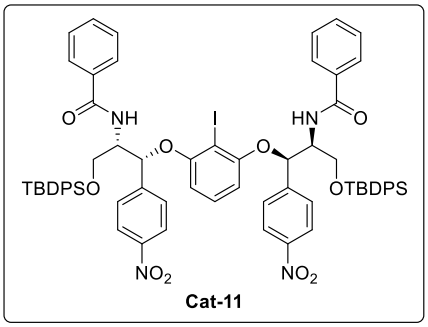
Cat-9

Cat-9 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 4-nitrobenzoyl chloride (408.2 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.3 g, 0.93 mmol, 93%) as a white solid. **MP:** 130.5-132.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.5 Hz, 4H), 8.03 (d, *J* = 8.4 Hz, 4H), 7.64 (d, *J* = 8.6 Hz, 4H), 7.50-7.41 (m, 12H), 7.34-7.27 (m, 4H), 7.23-7.15 (m, 8H), 6.77 (t, *J* = 8.3 Hz, 1H), 6.60 (d, *J* = 8.5 Hz, 2H), 5.98 (d, *J* = 8.4 Hz, 2H), 5.49 (d, *J* = 5.5 Hz, 2H), 4.65 (dtd, *J* = 9.2, 5.9, 3.4 Hz, 2H), 4.37 (dd, *J* = 11.0, 6.3 Hz, 2H), 3.84 (dd, *J* = 11.1, 3.4 Hz, 2H), 0.92 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2, 157.2, 149.8, 147.9, 144.4, 139.3, 135.6, 135.6, 132.6, 130.2, 130.1, 128.1, 128.1, 128.0, 127.4, 124.0, 123.9, 107.1, 79.9, 79.4, 61.7, 56.6, 26.9, 19.3. **HRMS** (ESI) m/z Calcd for $[C_{70}H_{67}IN_6O_{14}Si_2, M+Na]^+$: 1421.3191, found 1421.3219.



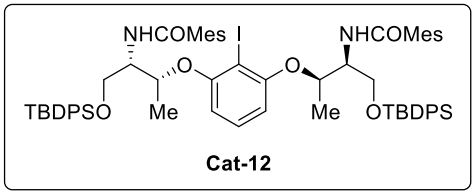
Cat-10

Cat-10 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 4-methoxybenzoyl chloride (375.3 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.232 g, 0.90 mmol, 90%) as a white solid. **MP:** 80.1-81.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 4H), 7.61 (d, *J* = 8.4 Hz, 4H), 7.58-7.50 (m, 12H), 7.42-7.35 (m, 4H), 7.31-7.24 (m, 8H), 6.93 (d, *J* = 8.3 Hz, 4H), 6.80 (t, *J* = 8.3 Hz, 1H), 6.56 (d, *J* = 8.2 Hz, 2H), 6.02 (d, *J* = 8.3 Hz, 2H), 5.55 (d, *J* = 5.2 Hz, 2H), 4.76-4.66 (m, 2H), 4.42 (dd, *J* = 10.8, 6.0 Hz, 2H), 3.93-3.88 (m, 2H), 3.88 (s, 6H), 1.01 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.7, 162.6, 157.3, 147.7, 145.0, 135.7, 135.6, 132.9, 132.8, 130.1, 130.0, 128.8, 128.0, 127.4, 126.1, 124.0, 114.0, 107.0, 80.2, 79.6, 61.9, 56.4, 55.6, 26.9, 19.3. **HRMS** (ESI) m/z Calcd for $[C_{72}H_{73}IN_4O_{12}Si_2, M+Na]^+$: 1421.3191, found 1421.3219.



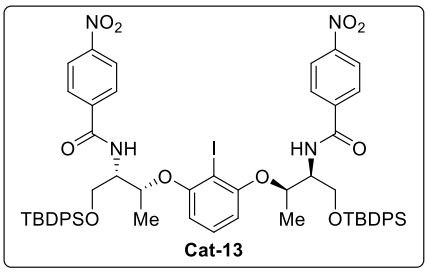
Cat-11

Cat-11 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and benzoyl chloride (309.3 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.138 g, 0.87 mmol, 87%) as a white solid. **MP:** 161.3-162.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.8 Hz, 4H), 7.56-7.52 (m, 4H), 7.49-7.41 (m, 14H), 7.38-7.33 (m, 4H), 7.32-7.25 (m, 4H), 7.22-7.14 (m, 8H), 6.73 (t, *J* = 8.3 Hz, 1H), 6.55 (d, *J* = 8.5 Hz, 2H), 5.94 (d, *J* = 8.4 Hz, 2H), 5.47 (d, *J* = 5.5 Hz, 2H), 4.68-4.60 (m, 2H), 4.34 (dd, *J* = 10.9, 6.1 Hz, 2H), 3.81 (dd, *J* = 10.9, 3.4 Hz, 2H), 0.92 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 167.2, 157.3, 147.8, 144.9, 135.7, 135.6, 133.9, 132.8, 132.8, 132.0, 130.1, 130.1, 128.8, 128.0, 127.4, 127.0, 124.0, 107.0, 80.0, 79.6, 61.9, 56.4, 26.9, 19.3. **HRMS** (ESI) m/z Calcd for $[C_{70}H_{69}IN_4O_{10}Si_2, M+H]^+$: 1309.3670, found 1309.3664.



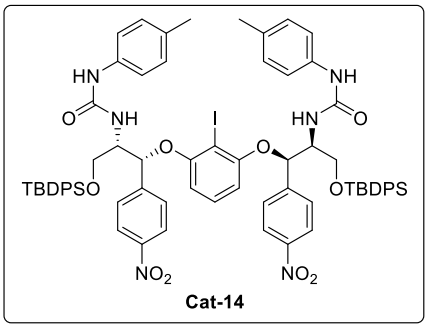
Cat-12

Cat-12 was prepared using **SI-13** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 2,4,6-trimethylbenzoyl chloride (401.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by CH_2Cl_2 and hexane to precipitate the title compound (1.138 g, 0.87 mmol, 87%) as a white solid. **MP:** 223.5-224.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.2 Hz, 4H), 7.58 (d, *J* = 7.3 Hz, 4H), 7.44 (t, *J* = 7.3 Hz, 2H), 7.36 (t, *J* = 7.4 Hz, 6H), 7.31-7.24 (m, 4H), 7.20 (t, *J* = 8.3 Hz, 1H), 6.85 (s, 4H), 6.47 (d, *J* = 8.4 Hz, 2H), 6.05 (d, *J* = 8.6 Hz, 2H), 4.84 (p, *J* = 6.1 Hz, 2H), 4.56 (m, 2H), 4.32 (dd, *J* = 10.8, 5.6 Hz, 2H), 4.06 (dd, *J* = 10.9, 3.6 Hz, 2H), 2.31 (s, 6H), 2.20 (s, 12H), 1.47 (d, *J* = 6.3 Hz, 6H), 1.06 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 157.7, 138.6, 135.7, 135.6, 134.8, 134.2, 133.1, 132.8, 130.0, 129.9, 129.9, 128.4, 127.9, 127.9, 105.7, 74.3, 62.5, 55.6, 27.0, 21.2, 19.3, 19.2, 16.7. **HRMS** (ESI) m/z Calcd for $[C_{66}H_{79}IN_2O_6Si_2, M+H]^+$: 1179.4600, found 1179.4610.



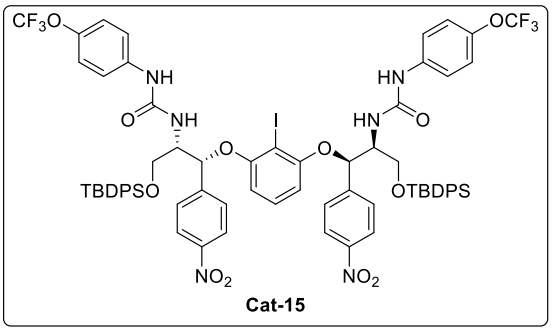
Cat-13

Cat-13 was prepared using **SI-13** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 4-nitrobenzoyl chloride (408.2 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by DCM and hexane to precipitate the title compound (1.1 g, 0.93 mmol, 93%) as a white solid. **MP:** 107.4-109.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.6 Hz, 4H), 7.78 (d, *J* = 8.8 Hz, 4H), 7.66-7.53 (m, 8H), 7.48-7.32 (m, 8H), 7.30-7.24 (m, 4H), 7.17 (t, *J* = 8.3 Hz, 1H), 6.63-6.53 (m, 2H), 6.46 (d, *J* = 8.5 Hz, 2H), 4.77-4.69 (m, 2H), 4.59-4.49 (m, 2H), 4.38-4.27 (m, 2H), 4.14-4.04 (m, 2H), 1.44 (d, *J* = 6.6 Hz, 6H), 1.03 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.2, 158.1, 149.7, 140.0, 135.7, 135.7, 133.1, 132.8, 130.2, 130.1, 128.3, 128.1, 128.0, 123.9, 106.3, 81.2, 75.4, 62.2, 55.7, 27.0, 19.4, 16.9. **HRMS** (ESI) m/z Calcd for $[C_{60}H_{65}IN_4O_{10}Si_2, M+Na]^+$: 1207.3176, found 1207.3190.



Cat-14

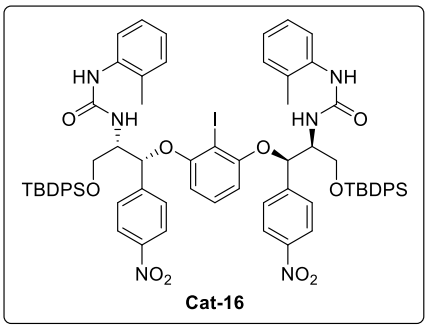
Cat-14 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and *p*-Tolyl isocyanate (292.3 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.161 g, 0.85 mmol, 85%) as a white solid. **MP:** 181.1-182.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 8.4 Hz, 4H), 7.43 – 7.37 (m, 8H), 7.34 (d, *J* = 7.4 Hz, 4H), 7.30 – 7.26 (m, 2H), 7.20 – 7.15 (m, 6H), 7.08 – 7.00 (m, 8H), 6.93 (d, 4H), 6.70 (t, *J* = 8.3 Hz, 1H), 6.52 (s, 2H), 5.92 (d, *J* = 8.4 Hz, 2H), 5.36 (d, *J* = 6.4 Hz, 2H), 5.27 (d, *J* = 8.5 Hz, 2H), 4.39 – 4.31 (m, 2H), 4.22 (dd, *J* = 10.7, 5.0 Hz, 2H), 3.68 (dd, *J* = 10.8, 3.2 Hz, 2H), 2.22 (s, 6H), 0.82 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ157.1, 155.7, 147.7, 145.4, 135.5, 135.5, 135.2, 134.9, 132.7, 132.6, 130.3, 130.0, 129.8, 127.9, 127.9, 127.8, 123.8, 123.3, 106.5, 79.3, 79.3, 62.3, 56.6, 26.8, 21.0, 19.2. **HRMS** (ESI) m/z Calcd for $[C_{72}H_{75}IN_6O_{10}Si_2, M+H]^+$: 1367.4201, found 1367.4210.



Cat-15

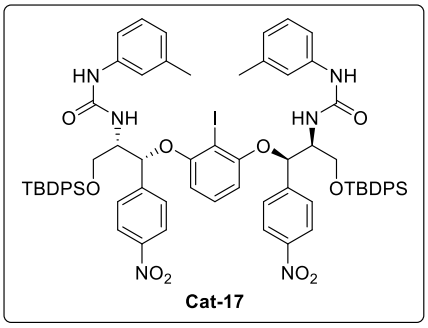
Cat-15 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 4-(trifluoromethoxy)phenyl isocyanate (446.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH and water to precipitate the title compound (1.161 g, 0.87 mmol, 87%) as a white solid. **MP:** 136.0-138.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.8 Hz, 4H), 7.58-7.53 (m, 8H), 7.48 (d, *J* = 8.9 Hz, 4H), 7.43-7.30 (m, 8H), 7.29-7.23 (m, 4H), 7.20-7.08 (m, 8H), 6.84 (t, *J* = 8.3 Hz, 1H), 6.53 (s, 2H), 6.05 (d, *J* = 8.4 Hz, 2H), 5.54 (d, *J* = 5.4 Hz, 2H), 5.19 (d, *J* = 8.0 Hz, 2H), 4.46-4.33 (m, 4H), 3.86 (dd, *J* = 10.6, 3.3 Hz, 2H), 0.99 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1, 154.9, 147.7, 145.3, 145.0, 136.8, 135.6, 135.6, 132.9, 132.9, 130.2, 130.1, 128.0, 128.0, 127.6, 123.9, 122.2, 122.0, 120.5 (d, $^1J_{C\text{-}F}$ = 257.2 Hz), 106.8, 79.9, 79.3, 62.2, 57.1, 26.9,

19.3, 19.3. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -58.09. **HRMS** (ESI) m/z Calcd for $[C_{72}H_{69}F_6IN_6O_{12}Si_2, M+H]^+$: 1529.3353, found 1529.3379.



Cat-16

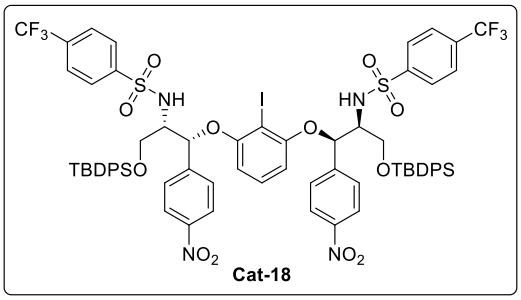
Cat-16 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and *o*-Tolyl isocyanate (292.3 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.190 g, 0.87 mmol, 87%) as a white solid. **MP:** 137.0-140.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 4H), 7.59-7.48 (m, 8H), 7.45-7.38 (m, 6H), 7.37-7.29 (m, 8H), 7.29-7.23 (m, 4H), 7.22-7.10 (m, 6H), 6.84 (t, *J* = 8.3 Hz, 1H), 6.59 (s, 2H), 6.06 (d, *J* = 8.4 Hz, 2H), 5.46 (d, *J* = 6.9 Hz, 2H), 5.26 (d, *J* = 8.6 Hz, 2H), 4.58-4.46 (m, 2H), 4.31 (dd, *J* = 10.6, 4.6 Hz, 2H), 3.79 (dd, *J* = 10.7, 3.2 Hz, 2H), 2.18 (s, 6H), 0.94 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.0, 156.0, 147.8, 145.5, 135.5, 135.4, 134.3, 132.6, 132.5, 131.5, 130.0, 129.8, 129.8, 127.9, 127.9, 127.8, 127.5, 127.2, 126.8, 123.7, 106.4, 79.3, 79.1, 62.2, 56.4, 26.8, 19.2, 18.0. **HRMS** (ESI) m/z Calcd for $[C_{72}H_{75}IN_6O_{10}Si_2, M+H]^+$: 1367.4201, found 1367.4200.



Cat-17

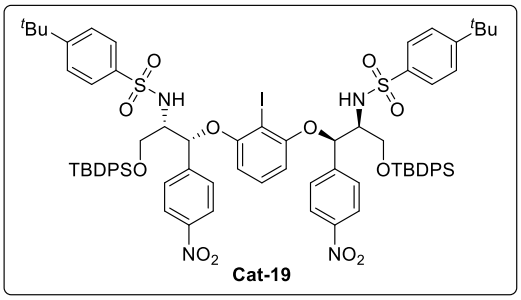
Cat-17 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and *m*-Tolyl isocyanate (292.3 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.152 g, 0.83 mmol, 83%) as a white solid. **MP:** 139.0-142.8 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 4H), 7.56-7.47 (m, 12H), 7.40-7.35 (m, 2H), 7.35-7.26 (m, 6H), 7.23-7.15 (m, 6H), 7.00 (s, 2H), 6.95 (m, 4H), 6.82 (t, *J* = 8.3 Hz, 1H), 6.78 (s, 2H), 6.05 (d, *J* = 8.5 Hz, 2H), 5.53 (d, *J* = 6.0 Hz, 2H), 5.48 (d, *J* = 8.4 Hz, 2H), 4.53-4.45 (m, 2H), 4.35 (dd, *J* = 10.8, 5.4 Hz, 2H), 3.84 (dd, *J* = 10.9, 3.3 Hz, 2H), 2.30 (s, 6H), 0.96 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 157.1, 155.5, 147.6, 145.3, 139.6, 137.7, 135.5, 135.5, 132.8, 132.7, 130.0, 129.9,

129.4, 127.9, 127.9, 127.7, 125.7, 123.8, 123.0, 119.3, 106.5, 79.5, 79.2, 62.2, 56.7, 26.8, 21.5, 19.2. **HRMS** (ESI) m/z Calcd for $[C_{72}H_{75}IN_6O_{10}Si_2, M+Na]^+$: 1389.4020, found 1389.4021.



Cat-18

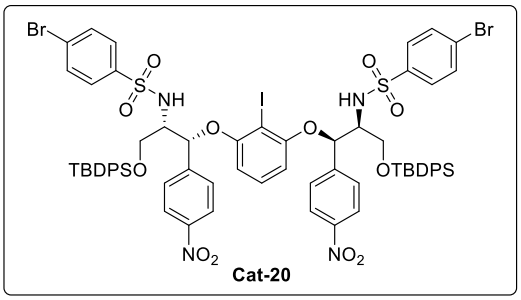
Cat-18 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and (Trifluoromethyl)benzene-1-sulfonylchloride (539 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.322 g, 0.86 mmol, 86%) as a white solid. **MP:** 116.3-119.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.3 Hz, 4H), 7.77 (d, *J* = 8.1 Hz, 4H), 7.51 (d, *J* = 8.2 Hz, 4H), 7.46-7.37 (m, 14H), 7.33-7.23 (m, 6H), 7.16 (t, *J* = 7.5 Hz, 4H), 6.81 (t, *J* = 8.3 Hz, 1H), 5.99 (d, *J* = 8.4 Hz, 2H), 5.44 (d, *J* = 6.2 Hz, 2H), 5.28 (d, *J* = 8.7 Hz, 2H), 4.24 (dd, *J* = 10.9, 4.7 Hz, 2H), 3.81-3.76 (m, 2H), 3.59 (dd, *J* = 11.0, 3.4 Hz, 2H), 0.93 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.7, 148.0, 144.1, 143.9, 135.5, 134.5 (q, $^2J_{C-F}$ = 32.7 Hz), 132.2, 132.2, 130.3, 130.1, 130.1, 128.0, 128.0, 127.8, 127.3, 126.3 (q, $^3J_{C-F}$ = 4.0 Hz), 124.0, 123.1 (q, $^1J_{C-F}$ = 273.2 Hz), 106.7, 79.2, 79.1, 61.7, 60.6, 26.9, 19.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -66.13. **HRMS** (ESI) m/z Calcd for $[C_{70}H_{67}F_6IN_4O_{12}S_2Si_2, M+Na]^+$: 1539.2577, found 1539.2573.



Cat-19

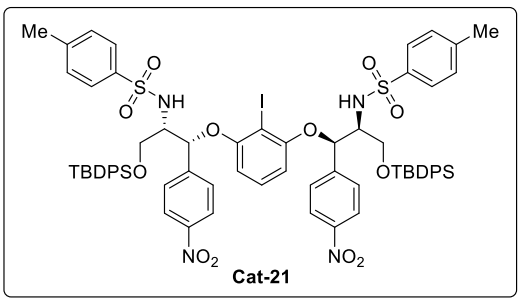
Cat-19 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 4-tert-butylbenzenesulfonyl chloride (513 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.223 g, 0.82 mmol, 82%) as a white solid. **MP:** 128.3-130.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.6 Hz, 4H), 7.57 (d, *J* = 8.5 Hz, 4H), 7.46 – 7.35 (m, 14H), 7.30 – 7.24 (m, 10H), 7.17 – 7.10

(m, 4H), 6.80 (t, *J* = 8.3 Hz, 1H), 6.01 (d, *J* = 8.4 Hz, 2H), 5.46 (d, *J* = 6.5 Hz, 2H), 5.24 (d, *J* = 8.5 Hz, 2H), 4.26 (dd, *J* = 10.7, 4.4 Hz, 2H), 3.76 – 3.68 (m, 2H), 3.65 (dd, *J* = 10.8, 3.4 Hz, 2H), 1.25 (s, 18H), 0.94 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.8, 156.7, 147.9, 144.6, 137.1, 135.5, 135.4, 132.4, 130.1, 129.9, 127.9, 127.9, 126.8, 126.1, 123.9, 106.6, 79.3, 78.8, 61.8, 60.2, 35.1, 31.1, 26.9, 19.3. **HRMS** (ESI) m/z Calcd for $[C_{76}H_{85}IN_4O_{12}S_2Si_2, M+Na]^+$: 1515.4081, found 1515.4094.



Cat-20

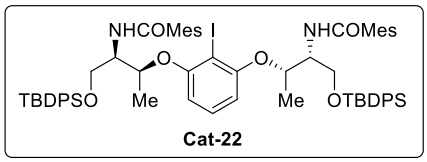
Cat-20 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 4-tert-butylbenzenesulfonyl chloride (563 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.382 g, 0.9 mmol, 90%) as a white solid. **MP:** 116.2-118.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.8 Hz, 4H), 7.51-7.34 (m, 22H), 7.34-7.26 (m, 6H), 7.14 (t, *J* = 7.6 Hz, 4H), 6.82 (t, *J* = 8.4 Hz, 1H), 6.00 (d, *J* = 8.5 Hz, 2H), 5.41 (d, *J* = 6.6 Hz, 2H), 5.24 (d, *J* = 8.8 Hz, 2H), 4.24 (dd, *J* = 10.8, 4.3 Hz, 2H), 3.80-3.70 (m, 1H), 3.61 (dd, *J* = 10.8, 3.4 Hz, 2H), 0.95 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.6, 147.9, 144.3, 139.3, 135.5, 135.4, 132.4, 132.2, 130.2, 130.1, 130.0, 128.3, 128.0, 127.9, 127.9, 124.0, 106.6, 79.3, 78.7, 61.8, 60.4, 26.9, 19.2. **HRMS** (ESI) m/z Calcd for $[C_{68}H_{67}Br_2IN_4O_{12}S_2Si_2, M+Na]^+$: 1559.1039, found 1559.1039.



Cat-21

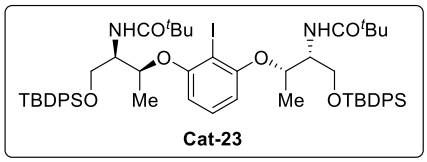
Cat-21 was prepared using **11** (1.1 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and Tosyl chloride (419.4 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.324 g, 0.94 mmol, 94%) as a white solid. **MP:** 116.0-119.6 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 4H), 7.40-7.17 (m, 18H), 7.15-7.05 (m, 6H), 7.00-6.90 (m, 4H), 6.86 (d, *J* = 8.1 Hz, 4H), 6.64 (t, *J* = 8.3

Hz, 1H), 5.88 (d, *J* = 8.5 Hz, 2H), 5.39-5.21 (m, 4H), 4.16 (dd, *J* = 10.6, 3.6 Hz, 2H), 3.73-3.51 (m, 4H), 2.12 (s, 6H), 0.80 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5, 147.6, 144.7, 143.5, 137.2, 135.4, 135.3, 132.3, 129.9, 129.7, 129.5, 127.9, 127.8, 127.7, 126.7, 123.6, 106.4, 79.2, 78.1, 62.1, 60.1, 26.8, 21.3, 19.1. **HRMS** (ESI) m/z Calcd for $[C_{70}H_{73}IN_4O_{12}S_2Si_2, M+H]^+$: 1409.3322, found 1409.3314.



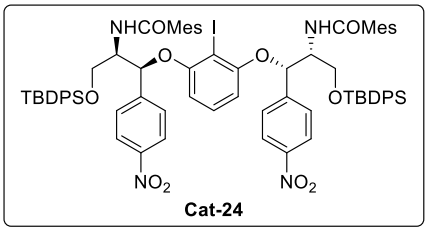
Cat-22

Cat-22 was prepared using **SI-13'** (886.3 mg, 1.0 mmol, 1.0 equiv.) starting from *L*-threonine, Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and mesitylcarbonylchloride (401.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was recrystallized by CH_2Cl_2 and hexane to yield the title compound as a white solid (1.013 g, 0.86 mmol, 86%).



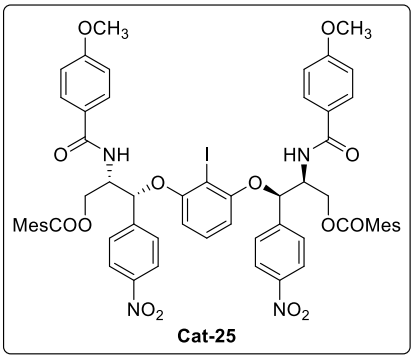
Cat-23

Cat-23 was prepared using **SI-13'** (886.3 mg, 1.0 mmol, 1.0 equiv.) starting from *L*-threonine, Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and pivaloyl chloride (265.3 mg, 2.2 mmol, 2.2 equiv.). The crude residue was recrystallized by CH_2Cl_2 and hexane to yield the title compound as a white solid (0.78 g, 0.74 mmol, 74%).



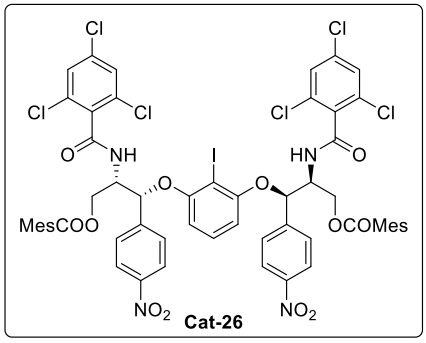
Cat-24

Cat-24 was prepared using **11'** (1.1 g, 1.0 mmol, 1.0 equiv.) starting from (1*R*,2*R*)-ANP, Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 2,4,6-trimethylbenzoyl chloride (401.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound as a white solid (1.198 g, 0.86 mmol, 86%).



Cat-25

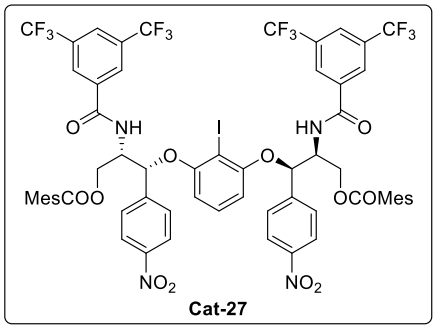
Cat-25 was prepared using **SI-4-1** (0.916 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 4-methoxybenzoyl chloride (375.3 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.1 g, 0.93 mmol, 93%) as a white solid. **MP:** 220.1-221.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 4H), 7.78 (d, *J* = 8.9 Hz, 4H), 7.63 (d, *J* = 8.6 Hz, 4H), 7.08 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 8.8 Hz, 4H), 6.85-6.81 (t, *J* = 8.3 Hz, 1H), 6.79 (s, 4H), 6.04 (d, *J* = 8.4 Hz, 2H), 5.72 (d, *J* = 3.6 Hz, 2H), 5.40-5.28 (m, 2H), 4.95-4.82 (m, 2H), 4.32 (dd, *J* = 11.9, 3.6 Hz, 2H), 3.87 (s, 6H), 2.25 (s, 6H), 2.16 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 166.8, 162.8, 157.4, 147.9, 144.1, 140.0, 135.3, 130.3, 129.9, 129.0, 128.6, 127.1, 125.4, 124.3, 114.0, 107.4, 81.2, 79.4, 61.8, 55.6, 55.6, 21.2, 19.9. **HRMS** (ESI) m/z Calcd for $[C_{60}H_{57}IN_4O_{14}, M+Na]^+$: 1207.2808, found 1207.2811.



Cat-26

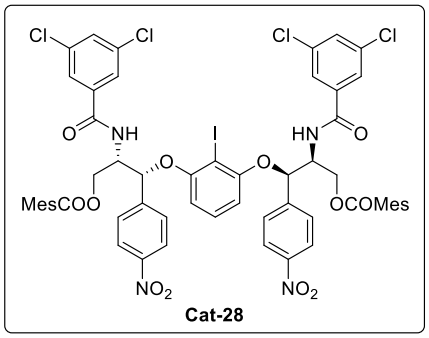
Cat-26 was prepared using **SI-4-1** (0.916 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 2,4,6-trichlorobenzoyl chloride (534.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.234 g, 0.93 mmol, 93%) as a white solid. **MP:** 170.4-173.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 4H), 7.64 (d, *J* = 8.8 Hz, 4H), 7.23 (s, 4H), 6.91 (t, *J* = 8.3 Hz, 1H), 6.79 (s, 6H), 6.15 (d, *J* = 8.4 Hz, 2H), 5.81 (d, *J* = 4.3 Hz, 2H), 5.07 (dd, *J* = 11.7, 7.3 Hz, 2H), 5.00-4.90 (m, 2H), 4.58 (dd, *J* = 11.8, 4.0 Hz, 2H), 2.26 (s, 6H), 2.17 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7, 164.0, 156.9, 147.9, 143.8, 140.1, 136.4, 135.6, 133.4, 132.8, 129.4,

128.7, 128.2, 127.5, 124.2, 107.1, 79.9, 61.8, 54.9, 21.2, 20.2. **HRMS** (ESI) m/z Calcd for $[C_{58}H_{47}Cl_6IN_4O_{12}, M+Na]^+$: 1351.0259, found 1351.0238.



Cat-27

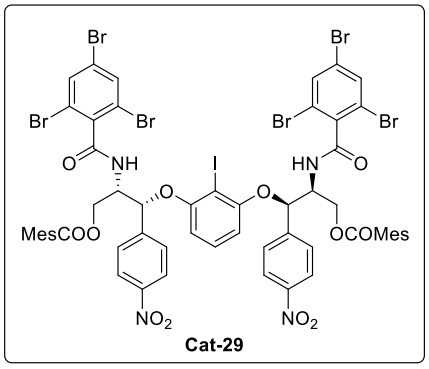
Cat-27 was prepared using **SI-4-1** (0.916 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 3,5-bis(trifluoromethyl)benzoyl chloride (609.4 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH and water to precipitate the title compound (1.234 g, 0.94 mmol, 94%) as a white solid. **MP:** 140.0-142.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 1.6 Hz, 4H), 8.19 (d, *J* = 8.8 Hz, 4H), 8.05 (s, 2H), 7.67 (d, *J* = 8.9 Hz, 4H), 7.56 (d, *J* = 8.0 Hz, 2H), 6.90 (t, *J* = 8.3 Hz, 1H), 6.81 (s, 4H), 6.12 (d, *J* = 8.5 Hz, 2H), 5.76 (d, *J* = 4.0 Hz, 2H), 5.28 (dd, *J* = 11.9, 8.6 Hz, 2H), 5.03-4.94 (m, 2H), 4.45 (dd, *J* = 12.0, 3.5 Hz, 2H), 2.25 (s, 6H), 2.18 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 164.5, 157.3, 148.1, 143.7, 140.3, 135.5, 135.5, 132.43 (q, $^2J_{C\text{-}F}$ = 34.2 Hz), 130.5, 129.5, 128.8, 127.6, 127.6, 127.2, 125.7 (q, $^3J_{C\text{-}F}$ = 2.2 Hz), 124.4, 122.9 (q, $^1J_{C\text{-}F}$ = 272.5 Hz), 107.5, 80.8, 79.0, 61.9, 55.7, 21.1, 20.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.83. **HRMS** (ESI) m/z Calcd for $[C_{62}H_{49}F_{12}IN_4O_{12}, M+Na]^+$: 1419.2092, found 1419.2098.



Cat-28

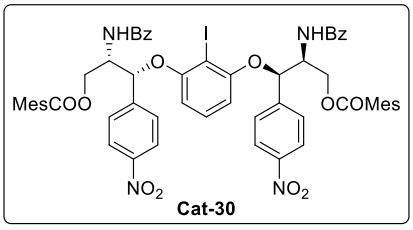
Cat-28 was prepared using **SI-4-1** (0.916 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 3,5-dichlorobenzoyl chloride (459.8 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH and water to precipitate the title compound (1.171 g, 0.93 mmol, 93%) as a white solid. **MP:** 180.0-182.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.8 Hz, 4H), 7.65 (d, *J* = 8.6 Hz, 8H), 7.53 (t, *J* = 1.9 Hz, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.87 (t, *J* = 8.3 Hz, 1H), 6.81 (s, 4H), 6.08 (d, *J* = 8.5 Hz, 2H), 5.69 (d, *J* = 3.9 Hz, 2H), 5.25 (dd, *J* = 11.9, 8.8 Hz, 2H), 4.94-4.83 (m, 2H), 4.38 (dd, *J* = 11.9, 3.5 Hz, 2H),

2.26 (s, 6H), 2.17 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 164.8, 157.4, 148.1, 143.7, 140.2, 136.2, 135.8, 135.5, 132.2, 130.5, 129.7, 128.8, 127.2, 125.8, 124.4, 107.5, 80.9, 79.3, 61.8, 55.6, 21.2, 20.1. **HRMS** (ESI) m/z Calcd for $[C_{58}H_{49}Cl_4IN_4O_{12}, M+H]^+$: 1261.1219, found 1261.1220.



Cat-29

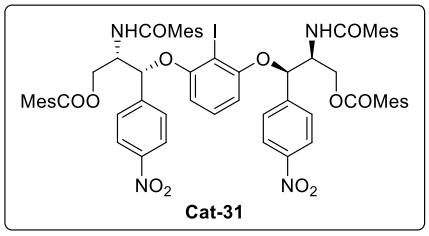
Cat-29 was prepared using **SI-4-1** (0.916 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 2,4,6-triBromobenzoyl chloride (600.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.271 g, 0.8 mmol, 80%) as a white solid. **MP:** 171.2-175.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 9.0, 2.3 Hz, 4H), 7.67-7.59 (m, 8H), 6.88 (t, *J* = 8.3 Hz, 1H), 6.80 (s, 4H), 6.57 (d, *J* = 8.0 Hz, 2H), 6.10 (d, *J* = 8.4 Hz, 2H), 5.83 (d, *J* = 3.8 Hz, 2H), 5.03-4.88 (m, 4H), 4.57 (dd, *J* = 11.3, 3.6 Hz, 2H), 2.27 (s, 6H), 2.20 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.7, 165.9, 157.0, 148.1, 143.7, 140.3, 137.7, 135.8, 134.5, 130.3, 129.5, 128.8, 127.4, 124.5, 124.4, 120.8, 107.3, 80.2, 80.1, 61.5, 54.8, 21.3, 20.5. **HRMS** (ESI) m/z Calcd for $[C_{58}H_{47}Br_6IN_4O_{12}, M+Na]^+$: 1614.7228, found 1614.7188.



Cat-30

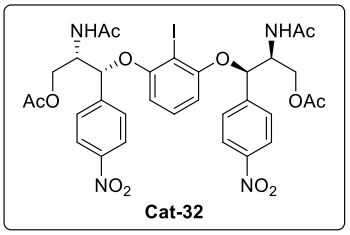
Cat-30 was prepared using **SI-4-1** (0.916 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and BzCl (310.2 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (0.9 g, 0.80 mmol, 80%) as a white solid. **MP:** 160.4-163.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.8 Hz, 4H), 7.82 (d, *J* = 7.5 Hz, 4H), 7.64 (d, *J* = 8.8 Hz, 4H), 7.57 (t, *J* = 7.4 Hz, 2H), 7.48 (t, *J* = 7.7 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 8.3 Hz, 1H), 6.79 (s, 4H), 6.04 (d, *J* = 8.4 Hz, 2H), 5.72 (d, *J* = 3.8 Hz, 2H), 5.34 (dd, *J* = 11.9, 8.9 Hz, 2H), 4.95-4.86 (m, 2H), 4.34 (dd, *J* = 11.9, 3.6 Hz, 2H), 2.25 (s, 6H), 2.16 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ

170.7, 167.3, 157.4, 148.0, 144.0, 140.1, 135.4, 133.2, 132.4, 130.4, 129.9, 129.0, 128.7, 127.2, 127.1, 124.4, 107.4, 81.1, 79.4, 61.8, 55.6, 21.2, 20.0. **HRMS** (ESI) m/z Calcd for $[C_{58}H_{53}IN_4O_{12}, M+Na]^+$: 1147.2597, found 1147.2590.



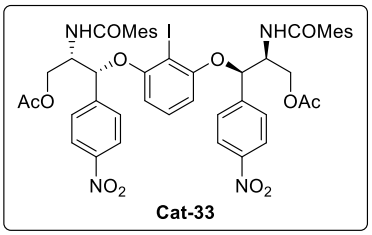
Cat-31

Cat-31 was prepared using **SI-4-1** (0.916 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 2,4,6-trimethylbenzoyl chloride (401.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.0 g, 0.83 mmol, 83%) as a white solid. **MP:** 164.0-167.0 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.5 Hz, 4H), 7.66 (d, *J* = 8.5 Hz, 4H), 6.94 (t, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 11.4 Hz, 8H), 6.45 (d, *J* = 8.6 Hz, 2H), 6.19 (d, *J* = 8.6 Hz, 2H), 5.78 (d, *J* = 4.9 Hz, 2H), 5.08-5.03 (m, 1H), 4.95 (dd, *J* = 11.7, 7.2 Hz, 2H), 4.63 (dd, *J* = 11.7, 3.2 Hz, 2H), 2.27 (s, 12H), 2.20 (s, 12H), 1.97 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 169.4, 156.9, 147.8, 143.9, 139.9, 139.0, 135.3, 133.9, 133.7, 130.1, 129.6, 128.5, 128.3, 127.5, 124.0, 106.8, 79.9, 79.5, 62.2, 53.8, 21.1, 21.0, 20.0, 18.7. **HRMS** (ESI) m/z Calcd for $[C_{64}H_{65}IN_4O_{12}, M+H]^+$: 1209.3716, found 1209.3719.



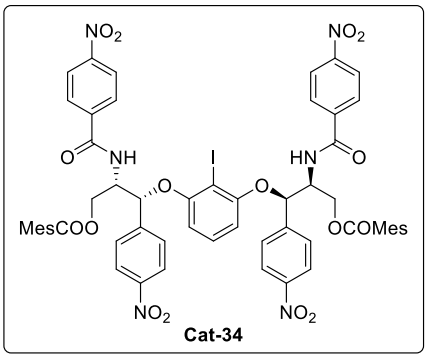
Cat-32

Cat-32 was prepared using **SI-4-2** (0.708 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and acetyl chloride (173.8 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (0.665 g, 0.84 mmol, 84%) as a white solid. **MP:** 161.3-164.1 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 4H), 7.57 (d, *J* = 8.6 Hz, 4H), 6.87 (t, *J* = 8.4 Hz, 1H), 6.30 (d, *J* = 8.0 Hz, 2H), 6.05 (d, *J* = 8.5 Hz, 2H), 5.54 (d, *J* = 3.3 Hz, 2H), 4.72-4.53 (m, 4H), 4.21-4.09 (m, 2H), 1.99 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.2, 170.4, 157.1, 147.9, 144.0, 130.3, 127.2, 124.3, 107.3, 80.8, 79.2, 61.6, 54.0, 23.5, 20.9. **HRMS** (ESI) m/z Calcd for $[C_{32}H_{33}IN_4O_{12}, M+H]^+$: 793.1212, found 793.1217.



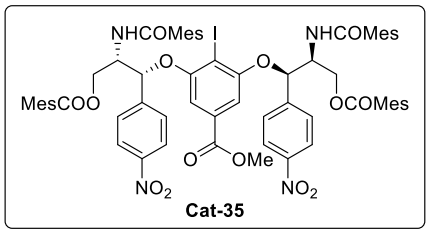
Cat-33

Cat-33 was prepared using **SI-4-2** (0.708 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 2,4,6-trimethylbenzoyl chloride (401.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (0.920 g, 0.92 mmol, 92%) as a white solid. **MP:** 298.5-301.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.8 Hz, 4H), 7.64 (d, *J* = 8.8 Hz, 4H), 6.93 (t, *J* = 8.3 Hz, 1H), 6.83 (s, 4H), 6.35 (d, *J* = 8.3 Hz, 2H), 6.14 (d, *J* = 8.5 Hz, 2H), 5.78 (d, *J* = 3.8 Hz, 2H), 4.92-4.83 (m, 2H), 4.68 (dd, *J* = 11.9, 8.9 Hz, 2H), 4.24 (dd, *J* = 11.8, 3.6 Hz, 2H), 2.29 (s, 6H), 2.06 (s, 12H), 2.01 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.9, 157.1, 148.1, 143.7, 139.2, 134.1, 133.9, 130.5, 128.4, 127.4, 124.3, 106.9, 80.6, 79.4, 61.4, 54.2, 21.2, 20.8, 18.9. **HRMS** (ESI) m/z Calcd for $[C_{48}H_{49}IN_4O_{12}, M+Na]^+$: 1023.2284, found 1043.2294.



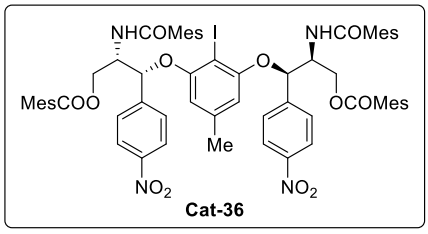
Cat-34

Cat-34 was prepared using **SI-4-1** (0.916 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 4-nitrobenzoyl chloride (408.2 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH to precipitate the title compound (1.130 g, 0.93 mmol, 93%) as a white solid. **MP:** 168.0-171.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.30-8.24 (m, 4H), 8.20 (d, *J* = 8.9 Hz, 4H), 7.97 (d, *J* = 8.8 Hz, 4H), 7.65 (d, *J* = 8.8 Hz, 4H), 7.43 (dd, *J* = 8.0, 3.6 Hz, 2H), 6.88 (t, *J* = 8.3 Hz, 1H), 6.79 (s, 4H), 6.08 (dd, *J* = 8.4, 1.9 Hz, 2H), 5.73 (d, *J* = 3.9 Hz, 2H), 5.40 (dd, *J* = 12.0, 9.1 Hz, 2H), 4.95-4.86 (m, 1H), 4.41-4.33 (m, 2H), 2.24 (s, 6H), 2.14 (s, 12H).**^{13}C NMR** (100 MHz, $CDCl_3$) δ171.0, 165.2, 157.3, 150.0, 148.1, 143.6, 140.3, 138.6, 135.3, 130.5, 129.5, 128.8, 128.4, 127.1, 124.5, 124.1, 107.6, 81.0, 79.4, 61.8, 56.0, 21.2, 20.0. **HRMS** (ESI) m/z Calcd for $[C_{58}H_{47}Br_6IN_4O_{12}, M+H]^+$: 1209.3716, found 1209.3719.



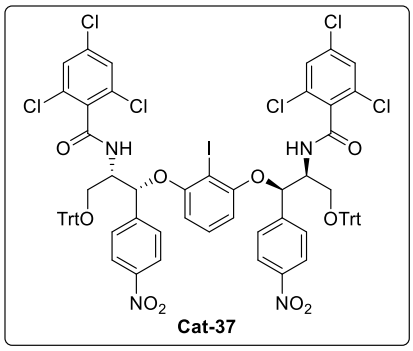
Cat-35

Cat-35 was prepared using **SI-15-2** (0.974 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 2,4,6-trimethylbenzoyl chloride (401.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH and water to precipitate the title compound (1.126 g, 0.89 mmol, 89%) as a white solid. **MP:** 134.0-137.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.8 Hz, 4H), 7.67 (d, *J* = 8.8 Hz, 4H), 6.79 (d, *J* = 16.0 Hz, 10H), 6.22 (d, *J* = 8.6 Hz, 2H), 5.81 (d, *J* = 5.1 Hz, 2H), 5.06 (m, 2H), 4.94 (dd, *J* = 11.7, 6.6 Hz, 2H), 4.57 (dd, *J* = 11.8, 3.9 Hz, 2H), 3.73 (s, 3H), 2.26 (s, 6H), 2.26 (s, 6H), 2.17 (s, 12H), 1.94 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 169.6, 165.2, 157.0, 148.2, 143.4, 140.2, 139.3, 135.4, 134.1, 133.7, 132.4, 129.7, 128.7, 128.5, 127.7, 124.4, 107.3, 86.1, 79.9, 62.3, 53.8, 52.8, 21.2, 21.2, 20.1, 18.9. **HRMS** (ESI) m/z Calcd for $[C_{66}H_{67}IN_4O_{14}, M+Na]^+$: 1289.3591, found 1289.3595.

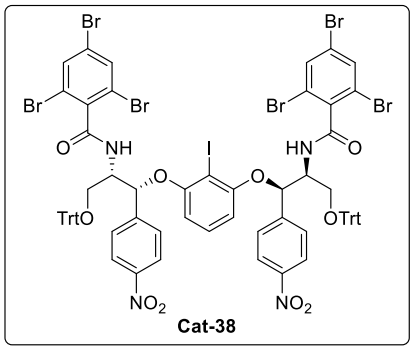


Cat-36

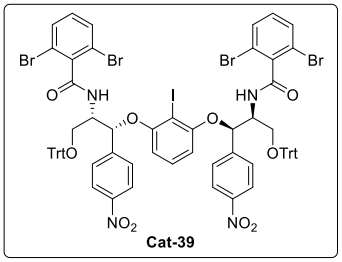
Cat-36 was prepared using **SI-15-1** (0.930 g, 1.0 mmol, 1.0 equiv.), Et_3N (232.3 mg, 2.3 mmol, 2.3 equiv.) and 2,4,6-trimethylbenzoyl chloride (401.6 mg, 2.2 mmol, 2.2 equiv.). The crude residue was purified by MeOH and water to precipitate the title compound (1.038 g, 0.85 mmol, 85%) as a white solid. **MP:** 147.3-149.7 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.9 Hz, 4H), 7.66 (d, *J* = 8.8 Hz, 4H), 6.79 (d, *J* = 4.6 Hz, 8H), 6.29 (d, *J* = 8.4 Hz, 2H), 5.96 (s, 2H), 5.78 (d, *J* = 4.4 Hz, 2H), 4.98 (m, 2H), 4.89 (dd, *J* = 11.6, 7.5 Hz, 2H), 4.55 (dd, *J* = 11.6, 4.0 Hz, 2H), 2.28 (s, 6H), 2.26 (s, 6H), 2.18 (s, 12H), 2.00 (s, 3H), 1.97 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 169.6, 156.8, 148.0, 144.1, 141.2, 140.1, 139.2, 135.5, 134.2, 133.8, 129.7, 128.6, 128.5, 128.5, 127.5, 124.3, 107.9, 79.9, 75.6, 62.1, 54.2, 21.9, 21.2, 21.2, 20.2, 18.9. **HRMS** (ESI) m/z Calcd for $[C_{65}H_{67}IN_4O_{12}, M+Na]^+$: 1245.3692, found 1245.3704.



Cat-37 was prepared following the procedure of synthesis of ether catalyst. The crude residue was purified by MeOH to precipitate the title compound (1.411 g, 0.92 mmol, 92%) as a white solid. **MP:** 159.3-162.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 4H), 7.53 (d, *J* = 8.8 Hz, 4H), 7.38-7.29 (m, 16H), 7.19 (dd, *J* = 5.1, 1.9 Hz, 18H), 6.86 (t, *J* = 8.3 Hz, 1H), 6.11 (t, *J* = 8.6 Hz, 4H), 5.76 (d, *J* = 4.6 Hz, 2H), 4.86-4.76 (m, 2H), 3.84 (dd, *J* = 10.4, 6.9 Hz, 2H), 3.48 (dd, *J* = 10.4, 3.5 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 163.9, 157.0, 147.9, 144.3, 143.4, 136.3, 133.9, 133.0, 130.2, 128.7, 128.3, 128.0, 127.7, 127.3, 124.1, 106.8, 87.4, 80.1, 79.8, 60.9, 55.8. **HRMS** (ESI) m/z Calcd for $[C_{76}H_{57}Cl_6IN_4O_{10}, M+Na]^+$: 1543.0986, found 1543.0985.

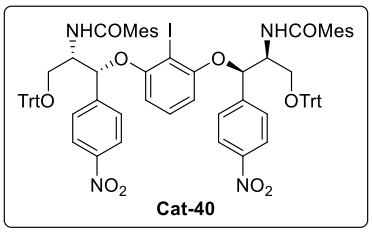


Cat-38 was prepared following the procedure of synthesis of ether catalyst. The crude residue was purified by MeOH to precipitate the title compound (1.462 g, 0.82 mmol, 82%) as a white solid. **MP:** 187.2-189.4 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.5 Hz, 4H), 7.66 (s, 4H), 7.52 (d, *J* = 8.8 Hz, 4H), 7.38-7.31 (m, 12H), 7.24-7.17 (m, 18H), 6.84 (t, *J* = 8.3 Hz, 1H), 6.18-6.02 (m, 3H), 5.82 (d, *J* = 3.8 Hz, 2H), 4.81-4.71 (m, 2H), 3.89-3.80 (m, 2H), 3.53 (dd, *J* = 10.4, 3.7 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.9, 157.0, 147.8, 144.2, 143.4, 138.1, 134.3, 130.1, 128.7, 128.0, 127.5, 127.3, 124.2, 124.1, 120.9, 106.8, 87.4, 80.3, 79.8, 60.7, 56.2. **HRMS** (ESI) m/z Calcd for $[C_{76}H_{55}Br_6IN_4O_{10}, M+Na]^+$: 1806.7955, found 1806.7957.



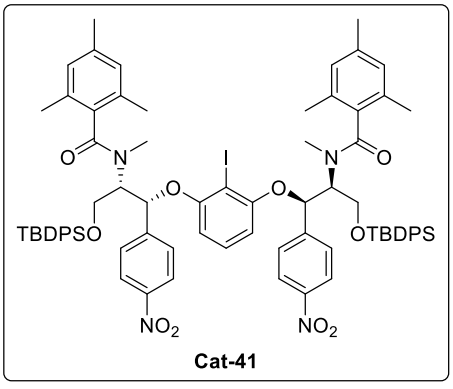
Cat-39 was prepared following the procedure of synthesis of ether catalyst. The crude residue was purified by MeOH to precipitate the title compound (1.462 g, 0.82 mmol, 82%) as a white solid. **MP:** 185.1-

187.3 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.5 Hz, 4H), 7.42 (dd, *J* = 16.3, 8.3 Hz, 8H), 7.31-7.24 (m, 12H), 7.17-6.98 (m, 20H), 6.73 (t, *J* = 8.3 Hz, 1H), 6.01 (dd, *J* = 24.5, 8.2 Hz, 4H), 5.77 (d, *J* = 3.9 Hz, 2H), 4.77-4.65 (m, 2H), 3.79-3.71 (m, 2H), 3.46 (dd, *J* = 10.5, 3.9 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.6, 156.9, 147.7, 144.4, 143.4, 139.1, 131.8, 131.7, 130.0, 128.7, 127.9, 127.4, 127.2, 124.0, 120.4, 106.8, 87.3, 80.4, 79.8, 60.7, 56.1. **HRMS** (ESI) m/z Calcd for $[C_{76}H_{57}Br_4IN_4O_{10}, M+Na]^+$: 1650.9745, found 1650.9754.



Cat-40

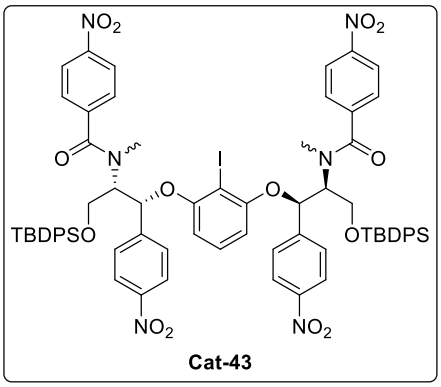
Cat-40 was prepared following the procedure of synthesis of ether catalyst. The crude residue was purified by MeOH to precipitate the title compound (1.148 g, 0.82 mmol, 82%) as a white solid. **MP:** 192.0-194.5 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 8.8 Hz, 4H), 7.51 (d, *J* = 8.8 Hz, 4H), 7.29-7.22 (m, 12H), 7.18-7.01 (m, 18H), 6.82 (t, *J* = 8.3 Hz, 1H), 6.73 (s, 4H), 6.09 (d, *J* = 8.5 Hz, 2H), 6.01 (d, *J* = 8.4 Hz, 2H), 5.75 (d, *J* = 4.9 Hz, 2H), 4.86-4.80 (m, 2H), 3.76 (dd, *J* = 10.2, 6.8 Hz, 2H), 3.41 (dd, *J* = 10.2, 3.4 Hz, 2H), 2.21 (s, 6H), 1.88 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 156.9, 147.8, 144.6, 143.3, 138.9, 134.2, 134.1, 130.1, 128.5, 128.3, 127.9, 127.7, 127.2, 123.9, 106.4, 87.2, 79.7, 79.7, 61.3, 55.3, 21.1, 18.9. **HRMS** (ESI) m/z Calcd for $[C_{82}H_{73}IN_4O_{10}, M+Na]^+$: 1423.4264, found 1423.4256.



Cat-41

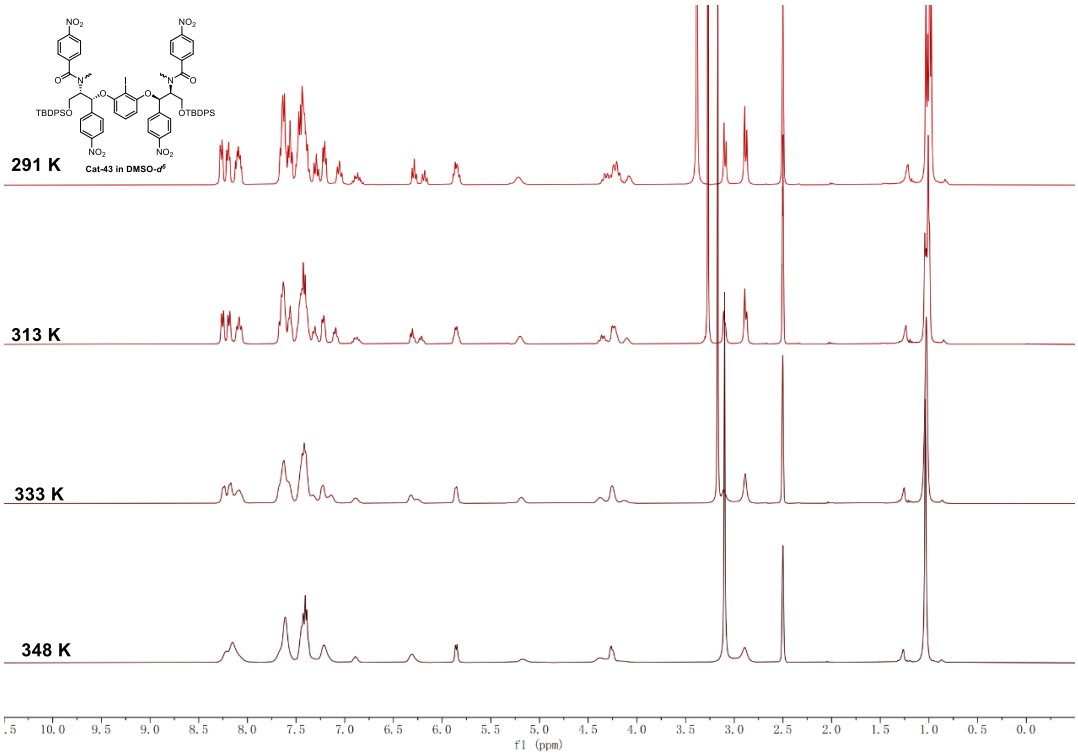
Cat-41 was prepared following the procedure of synthesis of catalyst with N-Me amide moiety. CH_3I (156 uL, 2.5 mmol, 2.5 equiv.) was dropwise to **Cat-8** (1.39 g, 1.0 mmol, 1.0 equiv.) and NaH (88 mg, 2.2 mmol, 2.2 equiv.). The crude residue was isolated through silica gel eluting with petroleum ether/ethyl acetate (5/1 to 2/1) to get **cat-41** (1.20 g, 83% yield) as a white solid. **MP:** 222.0- 125.4°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.6 Hz, 4H), 7.58 (d, *J* = 7.0 Hz, 4H), 7.48 (dd, *J* = 12.7, 7.9 Hz, 8H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.37-7.29 (m, 6H), 7.22 (t, *J* = 7.5 Hz, 4H),

6.86 (s, 2H), 6.82 (t, *J* = 8.4 Hz, 1H), 6.74 (s, 2H), 6.06 (d, *J* = 8.4 Hz, 2H), 5.90 (d, *J* = 4.1 Hz, 2H), 5.15-4.97 (m, 2H), 4.70-4.54 (m, 2H), 3.80 (dd, *J* = 11.8, 3.3 Hz, 2H), 3.09 (s, 6H), 2.27 (s, 6H), 2.20 (s, 6H), 1.69 (s, 6H), 0.99 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 173.0, 156.9, 147.7, 144.7, 138.3, 135.6, 135.5, 133.9, 133.3, 133.2, 132.9, 132.4, 130.2, 129.9, 128.4, 128.3, 127.9, 127.8, 127.4, 124.0, 106.1, 80.0, 78.4, 60.9, 59.5, 33.4, 26.8, 21.2, 19.1, 19.0, 18.3. **HRMS** (ESI) m/z Calcd for $[C_{78}H_{85}IN_4O_{10}Si_2, M+Na]^+$: 1443.4741, found 1443.4813.

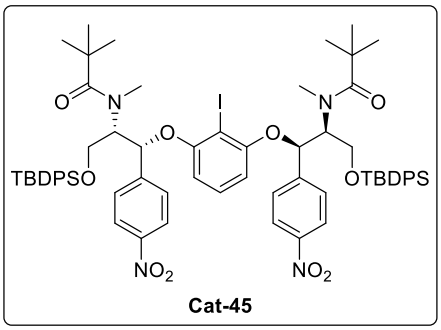


Cat-43

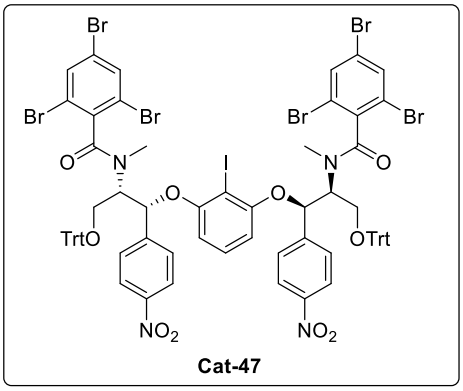
Cat-43 was prepared following the procedure of synthesis of catalyst with N-Me amide moiety. CH_3I (156 uL, 2.5 mmol, 2.5 equiv.) was dropwise to **Cat-9** (1.42 g, 1.0 mmol, 1.0 equiv.) and NaH (88 mg, 2.2 mmol, 2.2 equiv.). The crude residue was isolated through silica gel eluting with petroleum ether/ethyl acetate (5/1 to 2/1) to get **Cat-43** [1.22 g, 86% yield. (The atropisomer ratio of **Cat-43** = 4:1 was detected by ^{1}H NMR in $CDCl_3$)] as a white solid. **MP:** 164.4- 167.3°C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.6 Hz, 4H), 8.10 (d, *J* = 8.5 Hz, 4H), 7.66–7.54 (m, 8H), 7.51–7.38 (m, 16H), 7.30 (t, *J* = 7.4 Hz, 4H), 6.80 (t, *J* = 8.4 Hz, 1H), 5.98 (d, *J* = 8.4 Hz, 2H), 5.74 (d, *J* = 5.0 Hz, 2H), 4.84–4.58 (m, 4H), 4.04 (d, *J* = 8.9 Hz, 2H), 3.08 (s, 6H), 1.06 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 156.6, 148.5, 147.9, 144.7, 142.4, 135.7, 135.6, 133.0, 132.5, 130.1, 128.0, 128.0, 127.9, 127.2, 124.1, 106.6, 79.7, 78.7, 64.8, 59.3, 36.7, 26.9, 19.3. **HRMS** (ESI) m/z Calcd for $[C_{72}H_{71}IN_6O_{14}Si_2, M+H]^+$: 1449.3504, found 1449.3537.



Supplementary Figure 2. Variable temperature NMR experiments of atropisomers **Cat-43** in DMSO-d^6

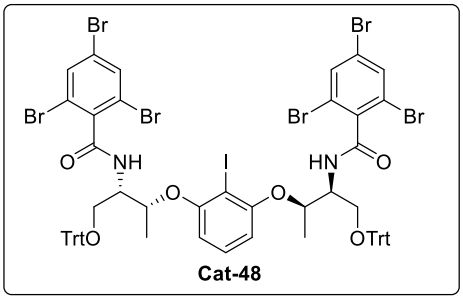


Cat-45 was prepared following the procedure of synthesis of catalyst with N-Me amide moiety. CH_3I (156 uL, 2.5 mmol, 2.5 equiv.) was dropwise to **Cat-3** (1.27 g, 1.0 mmol, 1.0 equiv.) and NaH (88 mg, 2.2 mmol, 2.2 equiv.). The crude residue was isolated through silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1) to get **Cat-43** (583 mg, 45% yield) as a white solid. **MP:** 116.0-116.9 °C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 4H), 7.74 – 7.22 (m, 24H), 6.71 (t, *J* = 8.3 Hz, 1H), 5.92 (d, *J* = 8.5 Hz, 2H), 5.66 (br s, 2H), 4.77 (br s, 2H), 4.57 (t, *J* = 10.6 Hz, 2H), 3.90 (br s, 2H), 3.26 (br s, 6H), 1.25 (s, 18H), 1.01 (s, 18H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 178.7, 156.7, 147.5, 145.4, 135.5, 135.5, 133.1, 132.8, 129.8, 129.7, 129.6, 127.8, 127.2, 123.6, 106.2, 80.0, 78.6, 61.9, 59.2, 39.1, 28.0, 26.7, 19.1. **HRMS** (ESI) m/z Calcd for $[C_{68}H_{81}IN_4O_{10}Si_2, M+K]^+$: 1335.4167, found 1335.4230.



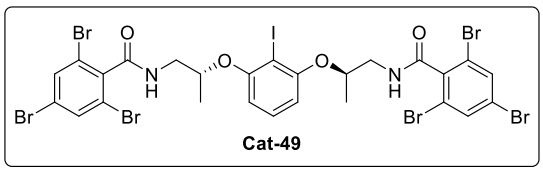
Cat-47

Cat-47 was prepared following the procedure of synthesis of catalyst with N-Me amide moiety. CH_3I (156 uL, 2.5 mmol, 2.5 equiv.) was dropwise to **Cat-38** (1.78 g, 1.0 mmol, 1.0 equiv.) and NaH (88 mg, 2.2 mmol, 2.2 equiv.). The crude residue was isolated through silica gel eluting with petroleum ether/ethyl acetate (5/1 to 2/1) to get **Cat-47** (1.59 g, 86% yield) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 4H), 7.74 (d, *J* = 1.9 Hz, 2H), 7.62 (d, *J* = 1.9 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 4H), 7.34 (dd, *J* = 6.8, 3.1 Hz, 12H), 7.25-7.16 (m, 18H), 6.75 (t, *J* = 8.3 Hz, 1H), 5.95 (d, *J* = 8.5 Hz, 2H), 5.91 (s, 2H), 5.20-5.06 (m, 2H), 3.94 (t, *J* = 10.5 Hz, 2H), 3.51 (dd, *J* = 11.0, 3.5 Hz, 2H), 2.91 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 168.0, 156.6, 147.7, 144.4, 143.4, 138.2, 134.6, 134.2, 130.1, 128.6, 128.0, 127.3, 127.1, 124.1, 123.6, 120.6, 120.4, 106.1, 87.3, 80.3, 78.5, 60.1, 57.7, 33.1. **HRMS** (ESI) m/z Calcd for $[C_{78}H_{59}Br_6IN_4O_{10}, M+Na]^+$: 1834.8268, found 1834.8277.



Cat-48

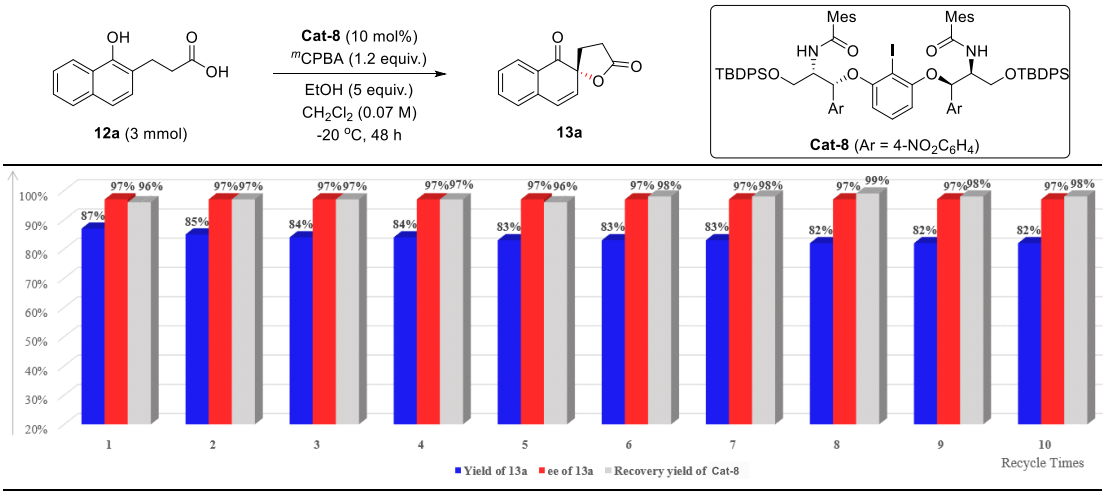
Cat-48 was prepared following the procedure of synthesis of ether catalyst. The crude residue was purified by DCM and hexane to precipitate the title compound as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (s, 4H), 7.41 (d, *J* = 6.8 Hz, 12H), 7.25 – 7.13 (m, 19H), 6.44 (d, *J* = 8.4 Hz, 2H), 5.98 (d, *J* = 8.6 Hz, 2H), 4.94 – 4.81 (m, 2H), 4.64 – 4.49 (m, 2H), 3.82 (dd, *J* = 10.1, 6.3 Hz, 2H), 3.62 (dd, *J* = 10.0, 3.4 Hz, 2H), 1.44 (d, *J* = 6.4 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 165.7, 157.7, 143.7, 138.6, 134.3, 129.9, 128.9, 128.0, 127.2, 123.8, 121.1, 105.9, 87.1, 82.1, 74.9, 61.5, 54.8, 16.9. **HRMS** (ESI) m/z Calcd for $[C_{66}H_{77}Br_6IN_2O_6, M+Na]^+$: 1592.7941, found 1592.7988.



Cat-49

Cat-49 were prepared according to the literature[2]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (s, 4H), 7.21 (t, *J* = 8.3 Hz, 1H), 6.54 (d, *J* = 8.3 Hz, 2H), 6.36 (t, *J* = 6.3 Hz, 2H), 4.70 (td, *J* = 6.9, 3.3 Hz, 2H), 3.94 (ddd, *J* = 14.0, 7.1, 3.3 Hz, 2H), 3.63–3.48 (m, 2H), 1.44 (d, *J* = 6.3 Hz, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 166.0, 157.7, 138.7, 134.4, 130.3, 123.9, 121.0, 107.6, 82.9, 75.2, 44.9, 17.7. **HRMS** (ESI) m/z Calcd for $[C_{26}H_{21}Br_6IN_2O_4, M+Na]^+$: 1048.5538, found 1048.5578.

5. General procedure of recycle experiments in oxidative dearomatization

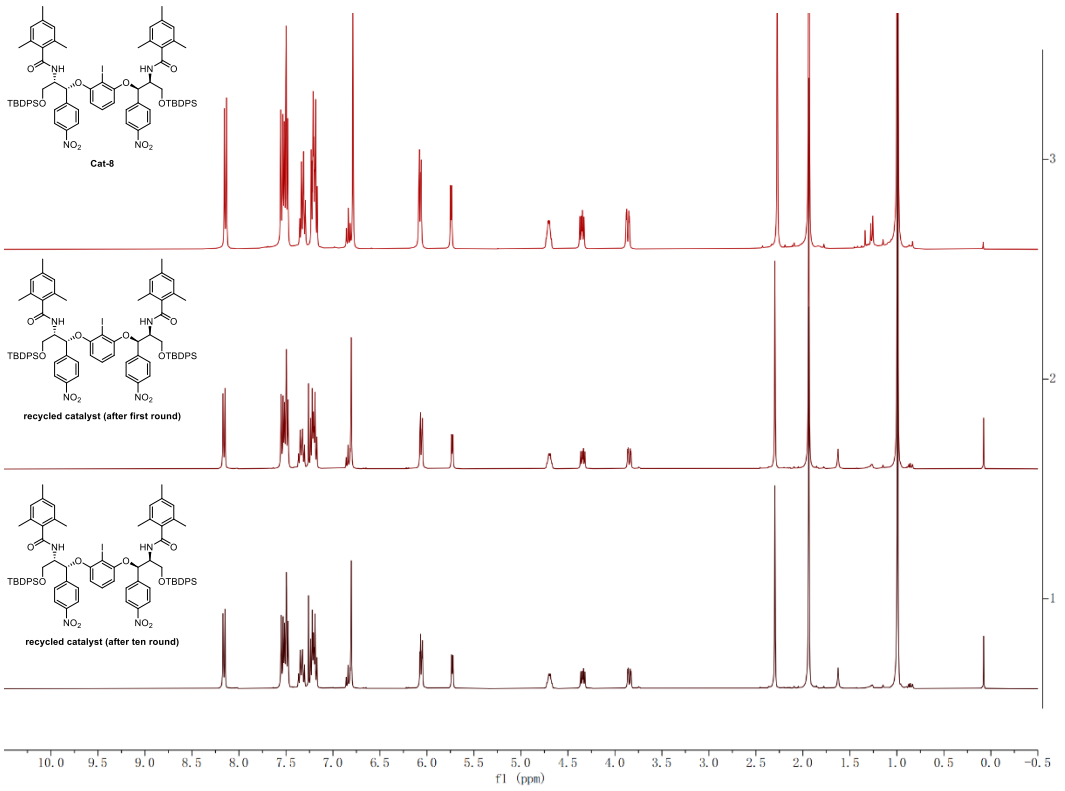


Supplementary Figure 3. Catalyst recovery and recycle experiments in oxidative dearomatization.

General procedure: To a Schlenk tube containing **Cat-8** (417.2 mg, 0.3 mmol, 10 mol%), ^{m}CPBA (732.7 mg, 3.6 mmol, 1.2 equiv.) and EtOH (0.873 ml, 5 equiv.) were added CH_2Cl_2 (10 mL) and **12a** (648 mg, 3 mmol, 1.0 equiv.). At the end of each reaction of the cycle, the reaction mixture was quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na_2SO_4. The mixture was concentrated in vacuo, the residue was subsequently dissolved by 30 mL of MeOH, H_2O (10 mL) was finally added to precipitate the catalyst which could enter the next cycle. The filtrate was concentrated in vacuo to get the crude product which could be further recrystallized by the mixture (10 mL, 1:300 volume ratio) of ethyl acetate and petroleum ether. After ten catalytic reactions, 320 mg of catalyst was obtained with a total recovery of 76.4%.

Supplementary Table 5. Data of recycle experiment.

yield of **13a**	recovery yield of **Cat-8**	*ee* of **13a**
87% (559 mg)	96% (402 mg)	97%
85% (545 mg)	97% (389 mg)	97%
84% (540 mg)	97% (377 mg)	97%
84% (539 mg)	97% (363 mg)	97%
83% (532 mg)	96% (350 mg)	97%
83% (532 mg)	98% (342 mg)	97%
83% (530 mg)	98% (335 mg)	97%
82% (527 mg)	99% (330 mg)	97%
82% (526 mg)	98% (325 mg)	97%
82% (526 mg)	98% (320 mg)	97%

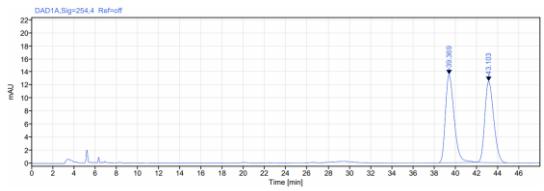


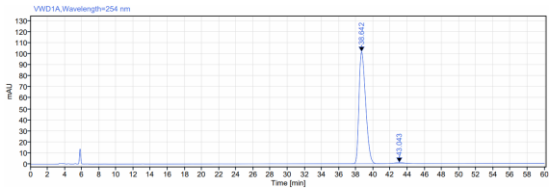
Supplementary Figure 4. Comparison of recovered catalyst

6. Gram scale operation

To a Schlenk tube containing **Cat-8** (487.2 mg, 0.35 mmol, 5 mol%), ^{m}CPBA (1.718 g, 8.3 mmol, 1.2 equiv.) and EtOH (2.0 mL, 5 equiv.) were added CH_2Cl_2 (10 mL) and **12a** (1.512 g, 7 mmol, 1.0 equiv.). And the reaction was stirred at -20 ^{o}C for 48 h. The reaction mixture was quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was then extracted with dichloromethane, washed with brine, dried over anhydrous Na_2SO_4. The mixture was concentrated in vacuo, the residue was subsequently dissolved by 70 mL of MeOH, H_2O (15 mL) was finally added to precipitate the catalyst (467 mg, 96% recovery yield). The product **13a** was obtained in 1.19g with 80% yield and 99% *ee* via recrystallization.

HPLC conditions: Chiralpak AS-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 38.642 min for major isomer, t_R = 43.043 min for minor isomer





Signal: DAD1A,Sig=254,4 Ref=off

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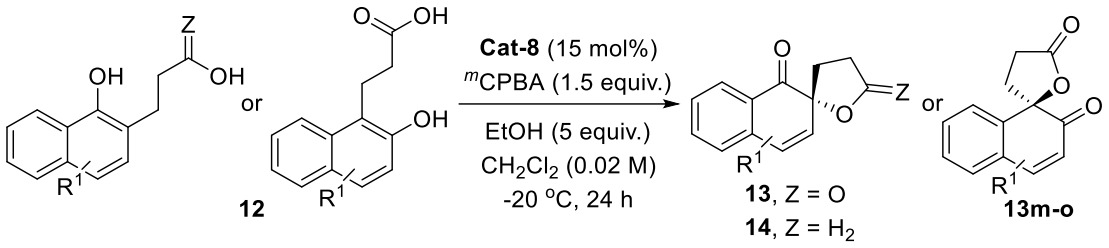
39.369	BM m	0.84	766.14	13.51	51.38	
43.103	MB m	0.87	725.03	12.44	48.62	
		Sum	1491.17			

Signal: VWD1A,Wavelength=254 nm

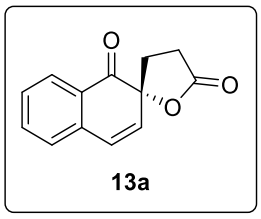
RT [min]	Type	Width [min]	Area	Height	Area%	Name
38.642	BB	3.27	5470.42	101.38	99.48	
43.043	MM m	0.76	28.54	0.44	0.52	
		Sum	5498.95			

7. Spectra data of substrate.

7.1 Characterization of enantioselective oxidative dearomatization



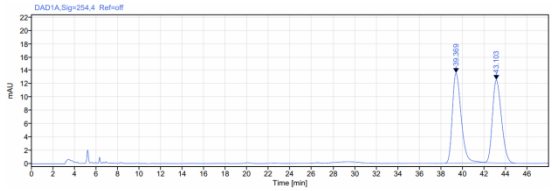
General procedure: To a Schlenk tube containing **Cat-8** (0.03 mmol, 15 mol%), ^{m}CPBA (0.3 mmol, 1.5 equiv.), and EtOH (1 mmol, 5 equiv.) were added CH_2Cl_2 (10 mL) and **12** (0.2 mmol, 1.0 equiv.), the reaction mixture was stirred at 0 to -20 °C for 24 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was subsequently extracted with dichloromethane, washed with brine, dried over anhydrous Na_2SO_4. Finally, the mixture was concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to afford the product **13**.

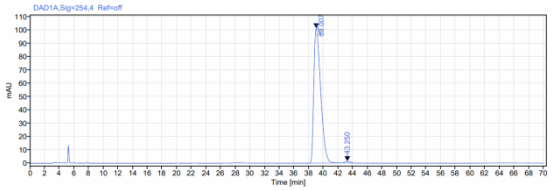


The reaction of 1-naphthol derivative **12a** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 24 h afforded compound **13a** (39.4 mg) in 92% yield as a white solid. The title compound **13a** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 6.68 (d, *J* = 9.9 Hz, 1H), 6.23 (d, *J* = 9.9 Hz, 1H), 2.92 (ddd, *J* = 9.7, 11.2,17.6 Hz, 1H), 2.62 (ddd, *J* = 2.0, 9.6, 17.6 Hz, 1H), 2.44 (ddd, *J* = 2.0, 9.6, 13.2Hz, 1H), 2.22 (ddd, *J* = 9.8, 11.2, 13.2 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7, 176.7, 136.9, 135.8, 132.3,

129.0, 128.1, 128.0, 127.8, 127.4, 83.6, 31.3, 26.6. **HRMS** (ESI) m/z Calcd for $[C_{13}H_{10}O_3, M + H]^+$: 215.0703; Found: 215.0701.

Optical Rotation: $[\alpha]_D^{25}$ 186.2 (c = 1.0, $CHCl_3$). 98% *ee* (HPLC conditions: Chiralpak AS-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 39.007 min for major isomer, t_R = 43.250 min for minor isomer)



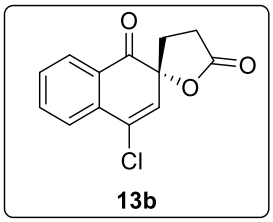


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
39.369	BM m	0.84	766.14	13.51	51.38	
43.103	MB m	0.87	725.03	12.44	48.62	
		Sum	1491.17			

Signal: DAD1A,Sig=254,4 Ref=off

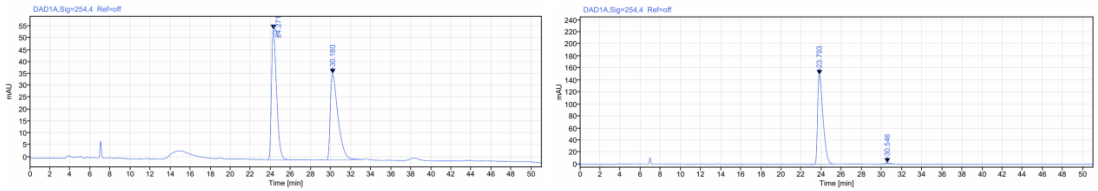
RT [min]	Type	Width [min]	Area	Height	Area%	Name
39.007	BM m	1.00	6587.57	101.13	99.00	
43.250	MM m	0.63	66.61	1.26	1.00	
		Sum	6654.18			



13b

The reaction of 1-naphthol derivative **12b** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 °C for 24 h afforded compound **13a** (45.6 mg) in 92% yield as a white solid. The title compound **13b** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.5, petroleum ether/ethyl acetate = 3/1).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 1H), 7.79-7.70 (m, 2H), 7.50 (m, 1H), 6.39 (s, 1H), 2.88 (ddd, *J* = 17.6, 11.2, 9.5 Hz, 1H), 2.61 (ddd, *J* = 17.7, 9.6, 2.3 Hz, 1H), 2.44 (ddd, *J* = 13.5, 9.6, 2.3 Hz, 1H), 2.24 (ddd, *J* = 13.4, 11.1, 9.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.9, 176.0, 135.9, 134.6, 131.8, 130.2, 129.2, 128.1, 127.3, 126.2, 83.6, 31.5, 26.6. **HRMS** (ESI) m/z Calcd for $[C_{13}H_9ClO_3, M + H]^+$: 249.0313, 251.0289; Found: 249.0313, 251.0287.

Optical Rotation: $[\alpha]_D^{25}$ 101.1 (c = 1.0, $CHCl_3$). 98% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 23.793 min for major isomer, t_R = 30.546 min for major isomer)



Signal: DAD1A,Sig=254,4 Ref=off

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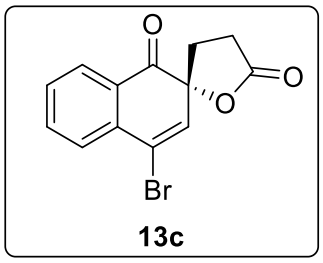
30.180	BB	3.46	1928.54	36.19	50.03	
		Sum	3855.04			

Signal: DAD1A,Sig=254,4 Ref=off

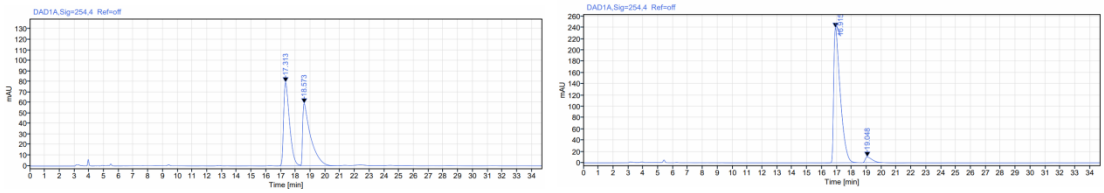
RT [min]	Type	Width [min]	Area	Height	Area%	Name
23.793	MB m	0.57	5568.53	148.58	98.78	
30.546	MM m	0.51	68.88	1.67	1.22	
		Sum	5637.41			



13c

The reaction of 1-naphthol derivative **12c** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at 0 ^{o}C for 24 h afforded compound **13c** (49.5 mg) in 85% yield as a white solid. The title compound **13c** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 4.0 Hz, 2H), 7.59-7.41 (m, 1H), 6.66 (s, 1H), 2.87 (ddd, *J* = 17.6, 11.1, 9.6 Hz, 1H), 2.61 (ddd, *J* = 17.6, 9.6, 2.4 Hz, 1H), 2.45 (ddd, *J* = 13.3, 9.5, 2.4 Hz, 1H), 2.36-2.11 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 194.9, 175.9, 136.0, 135.2, 133.5, 130.2, 128.9, 128.0, 127.4, 122.6, 84.4, 31.2, 26.5. **HRMS** (ESI) m/z Calcd for [$C_{13}H_9O_3Br$, M + H] $^{+}$: 292.9808, 294.9793; Found: 292.9804, 294.9786.

Optical Rotation: $[\alpha]_D^{25}$ 95.7 (c = 1.0, $CHCl_3$). 92% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 16.915 min for major isomer, t_R = 19.048 min for minor isomer).



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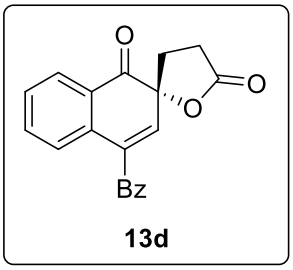
18.573	VB	2.46	2231.69	59.26	50.08	
		Sum	4456.21			

Signal: DAD1A,Sig=254,4 Ref=off

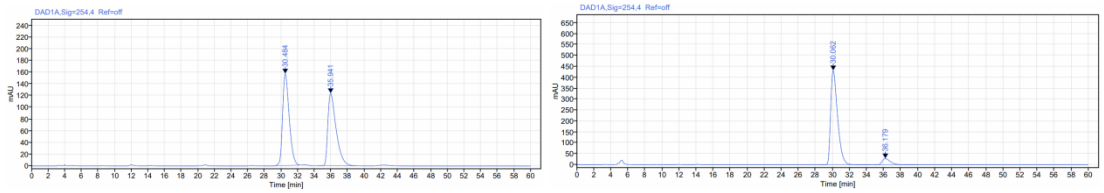
RT [min]	Type	Width [min]	Area	Height	Area%	Name
16.915	BM m	0.45	7372.19	239.15	95.82	
19.048	MM m	0.46	321.89	10.02	4.18	
		Sum	7694.09			



13d

The reaction of 1-naphthol derivative **12d** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 24 h afforded compound **13a** (58.7 mg) in 92% yield as a white solid. The title compound **13d** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 2/1). (R_f = 0.5, petroleum ether/ethyl acetate = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.8, 1.5 Hz, 1H), 8.02-7.88 (m, 2H), 7.66-7.56 (m, 2H), 7.53-7.42 (m, 3H), 7.39 (d, *J* = 7.8 Hz, 1H), 6.38 (s, 1H), 2.89 (ddd, *J* = 17.6, 11.3, 9.6 Hz, 1H), 2.60 (ddd, *J* = 17.6, 9.6, 2.2 Hz, 1H), 2.51 (ddd, *J* = 13.5, 9.5, 2.2 Hz, 1H), 2.28 (ddd, *J* = 13.4, 11.3, 9.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.4, 194.6, 176.0, 137.5, 136.1, 135.8, 134.4, 134.3, 134.2, 130.1, 129.9, 129.0, 128.5, 127.4, 127.0, 82.8, 31.2, 26.3. **HRMS** (ESI) m/z Calcd for [$C_{20}H_{14}O_4$, M + H] $^{+}$: 319.0965; Found: 319.0964.

Optical Rotation: $[\alpha]_D^{25}$ -36.8 (c = 1.0, $CHCl_3$). 85% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 30.062 min for major isomer, t_R = 36.179 min for minor isomer).

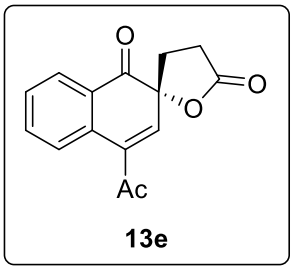


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
30.484	BB	3.38	8663.84	156.94	50.36	
35.941	BB	5.31	8540.48	123.52	49.64	
		Sum	17204.32			

Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
30.062	BB	5.84	24247.44	431.38	92.75	
36.179	BB	5.11	1894.43	27.98	7.25	
		Sum	26141.87			

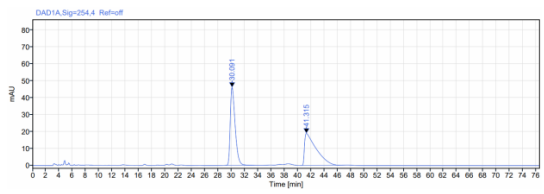


13e

The reaction of 1-naphthol derivative **12e** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at 0 ^{o}C for 80 h afforded compound **13e** (36.2 mg) in 71% yield as a white solid. The title compound **13e** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl

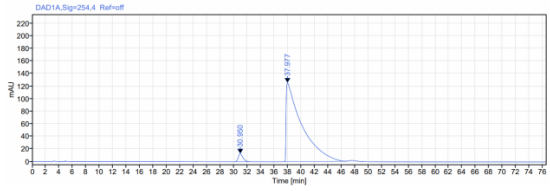
acetate (10/1 to 3/1). (R_f = 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.65 (td, *J* = 7.7, 1.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 6.82 (s, 1H), 2.83 (ddd, *J* = 17.7, 11.4, 9.4 Hz, 1H), 2.65-2.58 (m, 1H), 2.54 (s, 3H), 2.44 (ddd, *J* = 13.7, 9.3, 2.1 Hz, 1H), 2.28 (ddd, *J* = 13.4, 11.5, 9.5 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.1, 195.2, 175.8, 137.3, 137.0, 135.7, 133.2, 129.7, 128.4, 127.7, 127.5, 83.3, 31.1, 29.0, 26.2. **HRMS** (ESI) m/z Calcd for $[C_{15}H_{12}O_4, M + H]^+$: 257.0807; Found: 257.0808.

Optical Rotation: $[\alpha]_D^{25}$ 180.1 (c = 1.0, $CHCl_3$). 94% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 30.95 min for minor isomer, t_R = 37.977 min for major isomer).



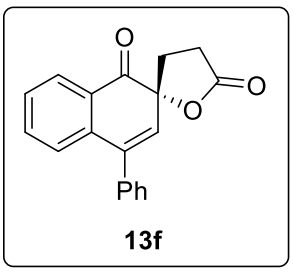
Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
30.091	BB	4.38	2348.86	46.05	50.36	
41.315	BB	5.86	2315.63	18.91	49.64	
		Sum	4664.49			



Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
30.950	BB	3.26	620.65	12.49	2.96	
37.977	BM m	2.04	20313.98	124.95	97.04	
		Sum	20934.64			

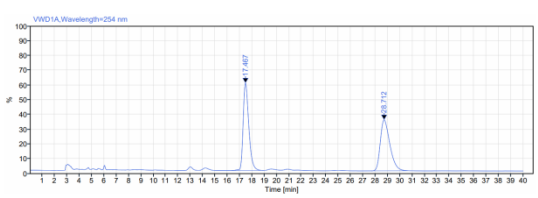


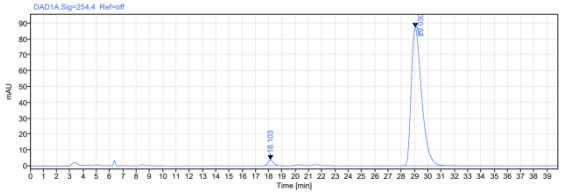
13f

The reaction of 1-naphthol derivative **12f** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 °C for 24 h afforded compound **13f** (34.8 mg) in 60% yield as a white solid. The title compound **13f** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.56 (td, *J* = 7.7, 1.5 Hz, 1H), 7.48-7.41 (m, 4H), 7.35 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.16 (d, *J* = 7.8 Hz, 1H), 6.12 (s, 1H), 2.92 (ddd, *J* = 17.6, 11.3, 9.6 Hz, 1H), 2.63 (ddd, *J* = 17.6, 9.6, 2.2 Hz, 1H), 2.53 (ddd, *J* = 13.4, 9.5, 2.2 Hz, 1H), 2.28 (ddd, *J* = 13.4, 11.3, 9.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.6, 176.6, 140.0, 137.7, 137.5, 135.5, 130.7, 129.1, 128.9, 128.8,

128.6, 128.3, 127.7, 127.5, 83.9, 31.6, 26.9. **HRMS** (ESI) m/z Calcd for [$C_{19}H_{14}O_3$, M + H] $^+$: 291.1016; Found: 291.1015.

Optical Rotation: $[\alpha]_D^{25}$ 76 (c = 0.2, $CHCl_3$). 96% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 18.103 min for minor isomer, t_R = 29.030 min for major isomer).



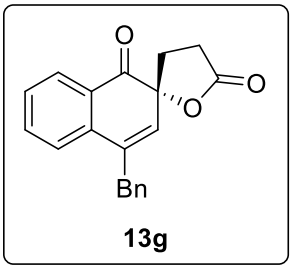


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
17.467	BB	2.61	843.00	26.56	50.33	
28.712	BB	3.21	831.87	15.49	49.67	
		Sum	1674.86			

Signal: DAD1A,Sig=254,4 Ref=off

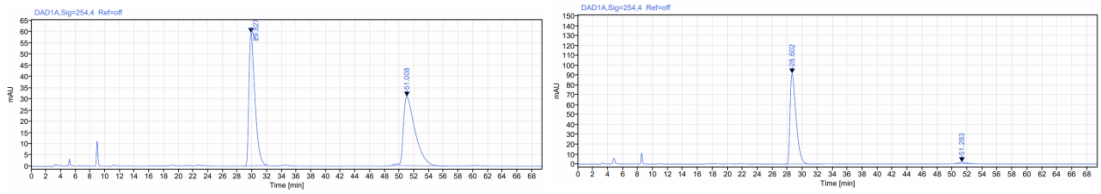
RT [min]	Type	Width [min]	Area	Height	Area%	Name
18.103	MM m	0.45	99.74	3.33	2.06	
29.030	BB	4.10	4736.84	86.75	97.94	
		Sum	4836.57			



13g

The reaction of 1-naphthol derivative **12g** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 °C for 24 h afforded compound **13g** (48.6 mg) in 80% yield as a white solid. The title compound **13g** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.4, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.31 (dd, *J* = 12.9, 7.2 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.17 (d, *J* = 7.5 Hz, 3H), 5.82 (s, 1H), 3.81 (s, 2H), 2.79 (m, 1H), 2.48 (m, 1H), 2.36 (m, 1H), 2.18-2.03 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.7, 176.6, 137.5, 137.2, 135.9, 135.6, 130.9, 128.9, 128.9, 128.8, 128.1, 127.7, 126.9, 125.2, 83.8, 38.8, 31.6, 26.8. **HRMS** (ESI) m/z Calcd for [$C_{20}H_{16}O_3$, M + H] $^+$: 305.1172; Found: 305.1176.

Optical Rotation: $[\alpha]_D^{25}$ 104.2 (c = 1, $CHCl_3$). 96% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 28.602 min for major isomer, t_R = 51.283 min for minor isomer).

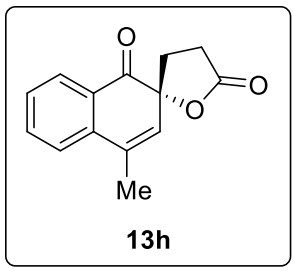


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
29.827	BM m	0.86	3374.85	59.27	50.02	
51.008	MM m	1.47	3372.33	30.70	49.98	
		Sum	6747.17			

Signal: DAD1A,Sig=254,4 Ref=off

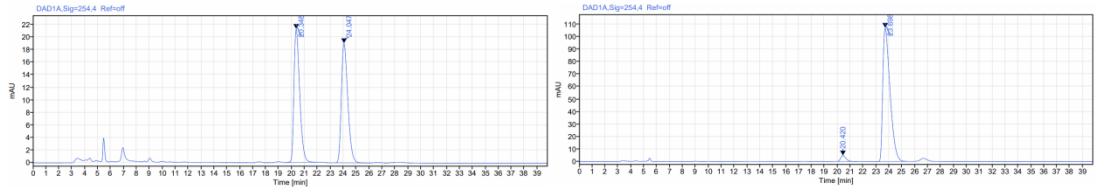
RT [min]	Type	Width [min]	Area	Height	Area%	Name
28.602	BB	4.55	5089.27	91.66	97.79	
51.283	MM m	0.96	114.80	1.41	2.21	
		Sum	5204.08			



13h

The reaction of 1-naphthol derivative **12h** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and *m*CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^oC for 24 h afforded compound **13h** (28.8 mg) in 63% yield as a white solid. The title compound **13h** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.6 Hz, 1H), 7.67 (td, *J* = 7.6, 1.6 Hz, 1H), 7.47-7.37 (m, 2H), 6.01 (s, 1H), 2.87 (ddd, *J* = 17.6, 11.2, 9.7 Hz, 1H), 2.57 (ddd, *J* = 17.6, 9.5, 1.9 Hz, 1H), 2.39 (ddd, *J* = 13.5, 9.6, 2.3 Hz, 1H), 2.18 (s, 3H), 2.22-2.08 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.9, 176.8, 138.0, 135.7, 133.2, 129.0, 128.8, 127.9, 127.4, 125.0, 83.7, 31.6, 26.9, 19.4. **HRMS** (ESI) m/z Calcd for [$C_{14}H_{12}O_3$, M + H] $^+$: 229.0859; Found: 229.0861.

Optical Rotation: $[\alpha]_D^{25}$ 104.2 (c = 1, $CHCl_3$). 93% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^oC, wavelength = 254 nm, t_R = 20.420 min for minor isomer, t_R = 23.698 min for major isomer).

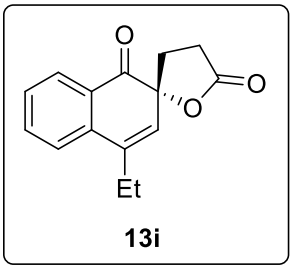


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
20.348	BB	2.31	655.59	21.23	49.81	
24.047	BB	2.26	660.64	19.01	50.19	
		Sum	1316.22			

Signal: DAD1A,Sig=254,4 Ref=off

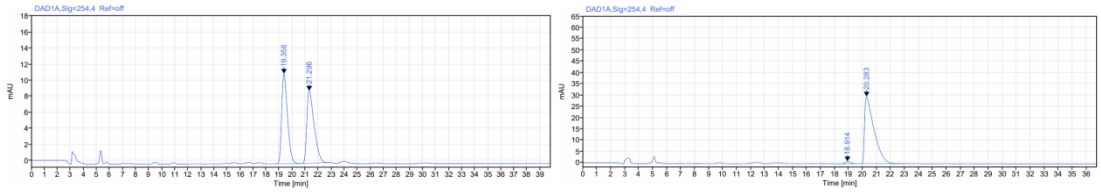
RT [min]	Type	Width [min]	Area	Height	Area%	Name
20.420	BB	1.65	138.44	4.72	3.21	
23.698	BB	2.64	4171.41	106.94	96.79	
		Sum	4309.85			



13i

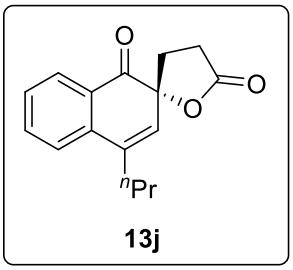
The reaction of 1-naphthol derivative **12i** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 24 h afforded compound **13i** (32.4 mg) in 92% yield as a white solid. The title compound **13i** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.66 (td, *J* = 7.8, 1.2 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 5.98 (s, 1H), 2.86 (ddd, *J* = 17.6, 11.3, 9.6 Hz, 1H), 2.62-2.52 (m, 3H), 2.39 (ddd, *J* = 13.2, 9.5, 1.9 Hz, 1H), 2.16 (ddd, *J* = 13.4, 11.4, 9.6 Hz, 1H), 1.23 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ = 197.0, 176.7, 138.3, 137.5, 135.6, 128.6, 128.1, 127.6, 127.2, 124.4, 83.9, 31.6, 26.9, 25.1, 12.4. **HRMS** (ESI) m/z Calcd for [$C_{15}H_{14}O_3$, M + H] $^{+}$: 243.1016; Found: 243.1016.

Optical Rotation: $[\alpha]_D^{25}$ 176.6 (c = 1, $CHCl_3$). 96% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 18.914 min for minor isomer, t_R = 20.283 min for major isomer).



Signal:	DAD1A,Sig=254,4 Ref=off					
RT [min]	Type	Width [min]	Area	Height	Area%	Name
19.356	BB	1.81	346.11	11.20	49.63	
21.296	BB	2.01	351.25	9.02	50.37	
		Sum	697.36			

Signal:	DAD1A,Sig=254,4 Ref=off					
RT [min]	Type	Width [min]	Area	Height	Area%	Name
18.914	MM m	0.37	30.26	1.05	2.11	
20.283	BB	3.28	1400.29	29.79	97.89	
		Sum	1430.55			

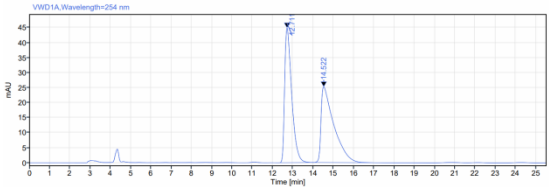


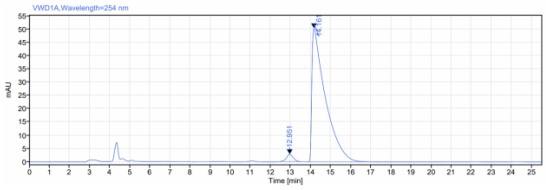
13j

The reaction of 1-naphthol derivative **12j** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 24 h afforded compound **13j** (32.2 mg) in 63% yield as a white solid. The title compound **13j** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.4, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.65 (td, *J* = 7.6, 1.5 Hz, 1H), 7.46-

7.34 (m, 2H), 5.97 (s 1H), 2.85 (ddd, *J* = 17.6, 11.4, 9.5 Hz, 1H), 2.63-2.53 (m, 1H), 2.55-2.45 (m, 2H), 2.39 (ddd, *J* = 13.5, 9.5, 2.1 Hz, 1H), 2.15 (ddd, *J* = 13.5, 11.4, 9.5 Hz, 1H), 1.69-1.55 (m, 2H), 1.00 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.0, 176.7, 137.4, 136.8, 135.6, 128.6, 128.3, 128.1, 127.7, 124.7, 83.9, 34.3, 31.6, 26.8, 21.2, 14.0. **HRMS** (ESI) m/z Calcd for $[C_{16}H_{16}O_3, M + H]^+$: 257.1172; Found: 257.1175.

Optical Rotation: $[\alpha]_D^{25}$ 169.8 (c = 1.0, $CHCl_3$). 94% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 12.951 min for minor isomer, t_R = 14.161 min for major isomer).



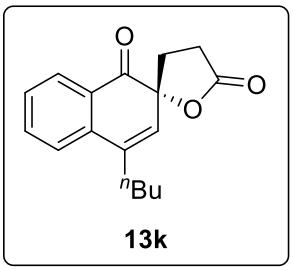


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.711	BB	1.72	1083.18	44.86	49.50	
14.522	BB	3.13	1105.21	25.18	50.50	
		Sum	2188.39			

Signal: VWD1A,Wavelength=254 nm

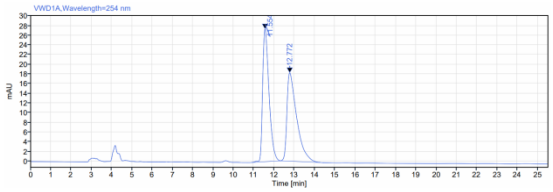
RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.951	MM m	0.36	64.39	2.72	2.67	
14.161	BB	3.57	2345.06	50.31	97.33	
		Sum	2409.45			

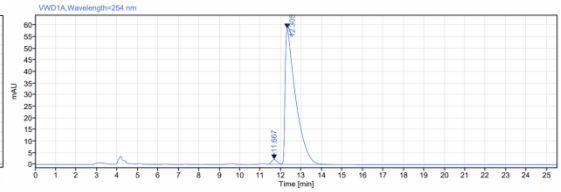


13k

The reaction of 1-naphthol derivative **12k** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 °C for 24 h afforded compound **13k** (32.9 mg) in 61% yield and as a white solid. The title compound **13k** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.4, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.65 (td, *J* = 7.6, 1.5 Hz, 1H), 7.47-7.34 (m, 2H), 5.98 (s, 1H), 2.85 (ddd, *J* = 17.6, 11.4, 9.5 Hz, 1H), 2.58 (td, *J* = 8.8, 8.0, 2.1 Hz, 1H), 2.52 (ddd, *J* = 9.1, 5.3, 2.0 Hz, 2H), 2.38 (ddd, *J* = 13.4, 9.5, 2.1 Hz, 1H), 2.15 (ddd, *J* = 13.4, 11.4, 9.5 Hz, 1H), 1.63-1.51 (m, 2H), 1.49-1.35 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.0, 176.7, 137.4, 137.1, 135.6, 128.6, 128.1, 128.1, 127.7, 124.7, 83.9, 32.0, 31.6, 30.2, 26.9, 22.6, 14.0. HRMS (ESI) m/z Calcd for $[C_{17}H_{18}O_3, M + H]^+$: 271.1328; Found: 271.1325.

Optical Rotation: $[\alpha]_D^{25}$ 160.6 (c = 1.0, $CHCl_3$). 96% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 11.667 min for minor isomer, t_R = 12.305 min for major isomer).



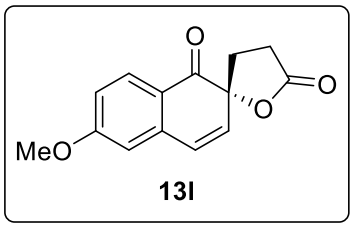


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.554	BB	1.44	595.85	27.39	49.41	
12.772	BB	2.14	610.03	18.24	50.59	
		Sum	1205.88			

Signal: VWD1A,Wavelength=254 nm

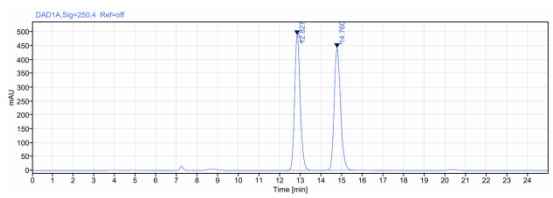
RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.667	BV	0.70	40.99	2.07	1.93	
12.305	VB	2.86	2087.15	58.45	98.07	
		Sum	2128.14			

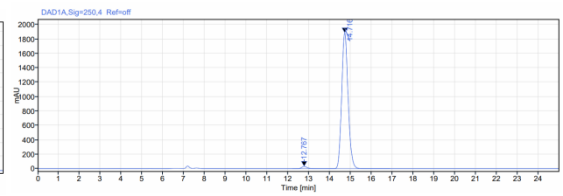


13l

The reaction of 1-naphthol derivative **12l** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 °C for 24 h afforded compound **13l** (46.3 mg) in 95% yield as a white solid. The title compound **13l** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.5, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 8.6 Hz, 1H), 6.88 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.70 (d, *J* = 2.5 Hz, 1H), 6.59 (d, *J* = 9.9 Hz, 1H), 6.20 (d, *J* = 9.9 Hz, 1H), 3.89 (s, 3H), 2.93 (m, 1H), 2.58 (ddd, *J* = 17.6, 9.6, 2.1 Hz, 1H), 2.39 (ddd, *J* = 12.2, 9.6, 2.2 Hz, 1H), 2.16 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.0, 176.9, 165.7, 139.2, 133.4, 130.6, 128.0, 120.7, 114.5, 113.0, 83.1, 55.9, 31.7, 26.9. **HRMS** (ESI) m/z Calcd for $[C_{14}H_{12}O_4, M + H]^+$: 245.0808; Found: 245.0809.

Optical Rotation: $[\alpha]_D^{25}$ 138.3 (c = 1, $CHCl_3$). 97% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 75:25, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 12.767 min for minor isomer, t_R = 14.716 min for major isomer).



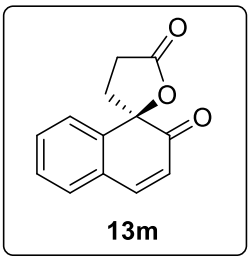


Signal: DAD1A,Sig=250,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.827	BB	1.50	9219.17	487.57	49.38	
14.760	BB	1.80	9451.28	440.60	50.62	
		Sum	18670.45			

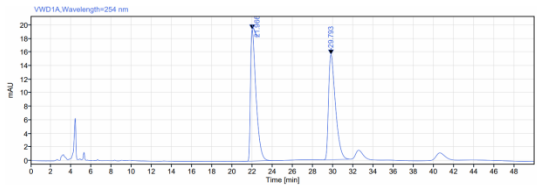
Signal: DAD1A,Sig=250,4 Ref=off

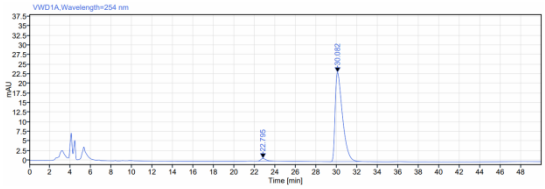
RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.767	BB	1.63	605.27	31.80	1.48	
14.716	BB	3.05	40424.58	1886.82	98.52	
		Sum	41029.85			



The reaction of 2-naphthol derivative **12m** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), HFIP (10 mmol, 50 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 24 h afforded compound **13m** (31.1 mg) in 73% yield as a white solid. The title compound **13m** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (3/1 to 1/1). (R_f = 0.5, petroleum ether/ethyl acetate = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.47 (dd, *J* = 9.3, 6.7 Hz, 2H), 7.43-7.33 (m, 2H), 6.17 (d, *J* = 9.9 Hz, 1H), 2.84 (ddd, *J* = 17.1, 11.6, 9.3 Hz, 1H), 2.71-2.60 (m, 2H), 2.15 (ddd, *J* = 14.0, 11.6, 9.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.7, 176.6, 146.2, 140.7, 131.2, 129.9, 129.3, 129.3, 125.9, 122.7, 86.0, 35.9, 26.7. **HRMS** (ESI) m/z Calcd for $[C_{13}H_{10}O_3, M + H]^+$: 215.0698; Found: 215.0703.

Optical Rotation: $[\alpha]_D^{25}$ 264.2 (c = 1.0, $CHCl_3$). 96% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 11.667 min for minor isomer, t_R = 12.305 min for major isomer).



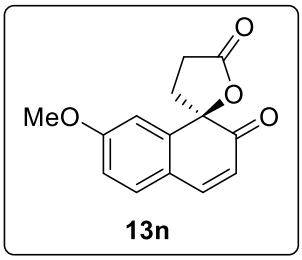


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
21.966	BB	2.37	744.76	19.39	50.16	
29.793	BB	2.66	739.99	15.48	49.84	
		Sum	1484.75			

Signal: VWD1A,Wavelength=254 nm

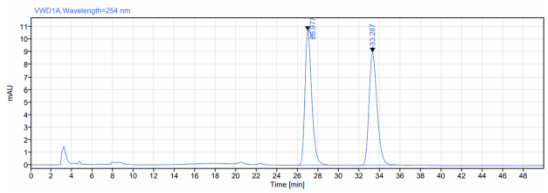
RT [min]	Type	Width [min]	Area	Height	Area%	Name
22.795	MM m	0.46	24.42	0.68	2.06	
30.082	BB	3.40	1163.71	23.26	97.94	
		Sum	1188.13			

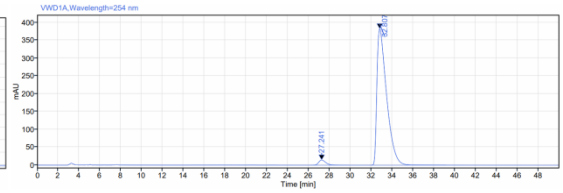


The reaction of 2-naphthol derivative **12n** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), HFIP (10 mmol, 50 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 24 h afforded compound **13n** (39.0 mg) in 80% yield as a white solid. The title compound **13n** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (3/1 to 1/1). (R_f = 0.5, petroleum ether/ethyl acetate = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.9 Hz, 1H), 7.24 (d, *J* = 2.7 Hz, 1H), 7.05 (d, *J* = 2.6 Hz, 1H), 6.85 (dd, *J* = 8.4, 2.6 Hz, 1H), 5.99 (d, *J* = 9.9 Hz, 1H), 3.83 (s, 3H), 2.80 (ddd, *J*

= 17.4, 11.7, 9.4 Hz, 1H), 2.66-2.57 (m, 2H), 2.11 (ddd, *J* = 13.8, 11.7, 9.6 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 197.6, 176.7, 162.3, 146.2, 143.1, 131.7, 122.3, 119.9, 114.5, 111.7, 86.1, 55.8, 36.2, 26.7. **HRMS** (ESI) m/z calcd for $[C_{14}H_{12}O_4 + H]^+$: 245.0814, found: 245.0808.

Optical Rotation: $[\alpha]_D^{25}$ 232.2 (c = 1.0, $CHCl_3$). 95% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 28.241 min for minor isomer, t_R = 32.807 min for major isomer).



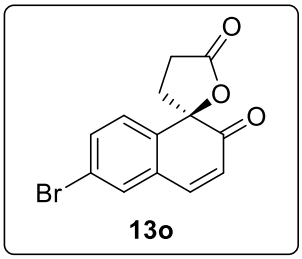


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
26.977	BB	3.16	489.85	10.65	50.03	
33.287	BB	3.57	489.32	8.95	49.97	
		Sum	979.17			

Signal: VWD1A,Wavelength=254 nm

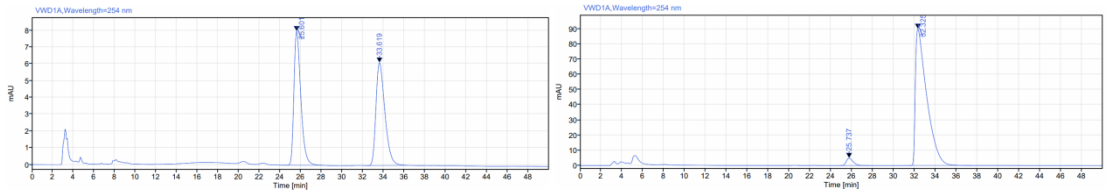
RT [min]	Type	Width [min]	Area	Height	Area%	Name
27.241	BB	3.76	696.44	14.63	2.75	
32.807	BB	7.27	24643.61	382.70	97.25	
		Sum	25340.06			



13o

The reaction of 2-naphthol derivative **12o** (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), HFIP (10 mmol, 50 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 °C for 24 h afforded compound **13o** (39.0 mg) in 61% yield as a white solid. The title compound **13o** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (3/1 to 1/1). (R_f = 0.5, petroleum ether/ethyl acetate = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.49 (d, *J* = 2.0 Hz, 1H), 7.45-7.37 (m, 2H), 6.20 (d, *J* = 10.0 Hz, 1H), 2.82 (ddd, *J* = 16.9, 11.6, 9.0 Hz, 1H), 2.68-2.59 (m, 2H), 2.11 (ddd, *J* = 14.3, 11.6, 9.7 Hz, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.9, 176.2, 144.5, 139.4, 133.8, 132.4, 131.1, 127.6, 123.9, 123.2, 85.5, 35.7, 26.6. **HRMS** (ESI) m/z calcd for $[C_{13}H_9BrO_3 + H]^+$: 292.9808, 294.9788; Found: 292.9803, 294.9784.

Optical Rotation: $[\alpha]_D^{25}$ 172.5 (c = 0.5, $CHCl_3$). 93% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 25.737 min for minor isomer, t_R = 32.325 min for major isomer).

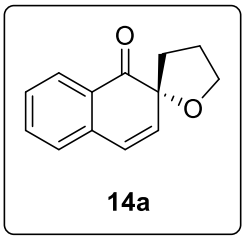


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
25.601	BB	3.35	369.12	7.98	50.05	
33.619	BB	3.64	368.43	6.12	49.95	
	Sum		737.54			

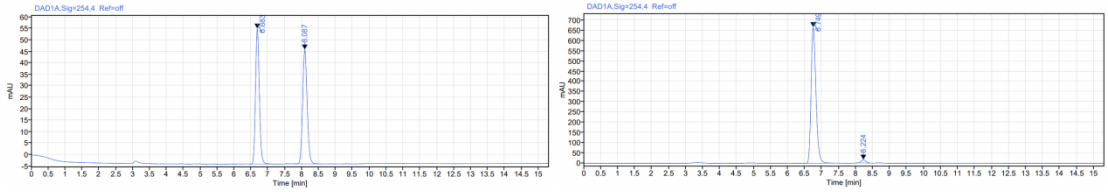
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
25.737	BB	2.96	228.30	4.91	3.26	
32.325	BB	5.95	6777.37	89.98	96.74	
	Sum		7005.67			



The reaction of 1-naphthol derivative (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and *m*CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 °C for 16 h afforded compound **14a** (30.0 mg) in 76% yield as a white solid. The title compound **14a** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.6, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.95 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.32 (td, *J* = 7.6, 1.2 Hz, 1H), 7.17 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.49 (d, *J* = 9.9 Hz, 1H), 6.16 (d, *J* = 9.9 Hz, 1H), 4.36-4.26 (m, 1H), 4.19-4.09 (m, 1H), 2.27-2.16 (m, 2H), 2.08-1.99 (m, 1H), 1.96-1.85 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.0, 137.5, 136.7, 134.8, 129.0, 128.1, 127.4, 127.2, 125.7, 84.3, 70.7, 36.6, 25.3. **HRMS** (ESI) m/z Calcd for [$C_{13}H_{12}O_2$, M + H] $^+$: 201.0910; Found: 201.0907.

Optical Rotation: $[\alpha]_D^{25}$ 247.2 (c = 0.5, $CHCl_3$). 96% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 6.749 min for major isomer, t_R = 8.22 min for minor isomer).

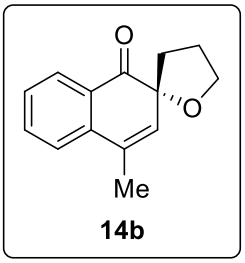


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.683	VB	0.84	464.30	59.02	49.98	
8.087	BB	0.88	464.61	49.79	50.02	
	Sum		928.92			

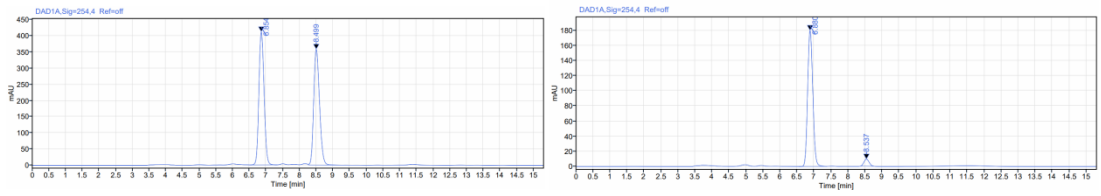
Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.749	BM m	0.15	6578.97	664.72	97.85	
8.224	MM m	0.15	144.85	15.03	2.15	
	Sum		6723.82			



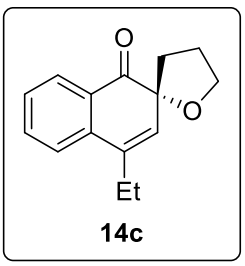
14b

The reaction of 1-naphthol derivative (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 16 h afforded compound **14b** (22.1 mg) in 52% yield as a solid. The title compound **14b** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.6, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.59 (td, *J* = 7.6, 1.5 Hz, 1H), 7.34 (td, *J* = 7.7, 6.3 Hz, 2H), 5.97 (s, 1H), 4.30-4.21 (m, 1H), 4.17-4.06 (m, 1H), 2.19 (ddd, *J* = 11.8, 7.7, 3.9 Hz, 2H), 2.12 (s, 3H), 2.07-1.99 (m, 1H), 1.92-1.82 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.1, 138.5, 134.7, 133.2, 130.6, 129.0, 127.9, 127.4, 124.4, 84.1, 70.4, 36.4, 25.4, 19.4. **HRMS** (ESI) m/z Calcd for [$C_{14}H_{14}O_2$, M + H] $^{+}$: 215.1067; Found: 215.1070. **Optical Rotation:** $[\alpha]_D^{25}$ 216.2 (c = 0.5, $CHCl_3$). 90% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 6.880 min for major isomer, t_R = 8.537 min for minor isomer).



Signal: DAD1A,Sig=254,4 Ref=off						
RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.854	VB	0.80	4433.64	411.96	50.60	
8.499	VB	0.96	4328.19	358.30	49.40	
		Sum	8761.83			

Signal: DAD1A,Sig=254,4 Ref=off						
RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.880	BV	0.83	1902.30	180.02	95.10	
8.537	MM m	0.17	98.02	9.30	4.90	
		Sum	2000.33			

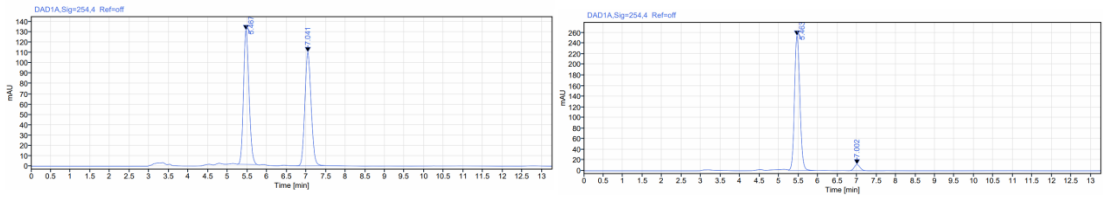


14c

The reaction of 1-naphthol derivative (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 16 h afforded compound **14c** (28.7 mg) in 63% yield as oil. The title compound **14c** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.6, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.58 (td, *J* = 7.6, 1.5 Hz, 1H), 7.39-7.31 (m, 2H), 5.96 (s,

1H), 4.32-4.25 (m, 1H), 4.17-4.11 (m, 1H), 2.55-2.47 (m, 2H), 2.24-2.16 (m, 2H), 2.07-1.99 (m, 1H), 1.91-1.83 (m, 1H), 1.21 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 138.0, 135.9, 134.6, 131.3, 129.3, 127.8, 127.5, 123.9, 84.4, 70.5, 36.5, 25.3, 25.1, 12.6. **HRMS** (ESI) m/z Calcd for [$C_{15}H_{16}O_2$, M + H] $^+$: 229.1223; Found: 229.1225.

Optical Rotation: $[\alpha]_D^{25}$ 176.6 (c = 1, $CHCl_3$). 91% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 5.463 min for major isomer, t_R = 7.002 min for minor isomer).

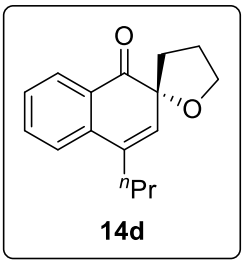


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.467	MM m	0.15	1273.85	129.95	50.87	
7.041	VM m	0.17	1230.05	110.00	49.13	
		Sum	2503.90			

Signal: DAD1A,Sig=254,4 Ref=off

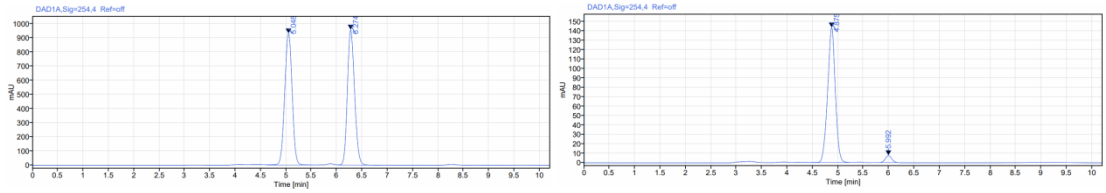
RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.463	VB	0.77	2439.64	253.93	95.32	
7.002	BM m	0.16	119.82	11.61	4.68	
		Sum	2559.47			



14d

The reaction of 1-naphthol derivative (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 16 h afforded compound **14c** (30.1 mg) in 64% yield as oil. The title compound **14c** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.6, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.57 (td, *J* = 7.6, 1.5 Hz, 1H), 7.38-7.28 (m, 2H), 5.95 (s, 1H), 4.31-4.24 (m, 1H), 4.17-4.08 (m, 1H), 2.50-2.41 (m, 2H), 2.24-2.14 (m, 2H), 2.06-1.97 (m, 1H), 1.93-1.83 (m, 1H), 1.66-1.56 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 137.9, 134.6, 134.3, 132.5, 129.3, 127.7, 127.5, 124.1, 84.4, 70.4, 36.6, 34.5, 25.3, 21.3, 14.1. **HRMS** (ESI) m/z Calcd for [$C_{16}H_{18}O_2$, M + H] $^+$: 243.1380; Found: 243.1381.

Optical Rotation: $[\alpha]_D^{25}$ 169.8 (c = 1.0, $CHCl_3$). 92% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 4.875 min for major isomer, t_R = 5.992 min for minor isomer).

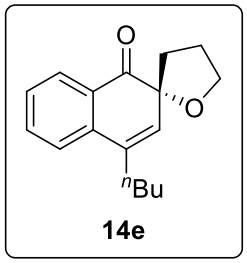


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.048	VB	0.93	9516.75	927.05	50.34	
6.274	VV	0.83	9390.06	953.72	49.66	
		Sum	18906.81			

Signal: DAD1A,Sig=254,4 Ref=off

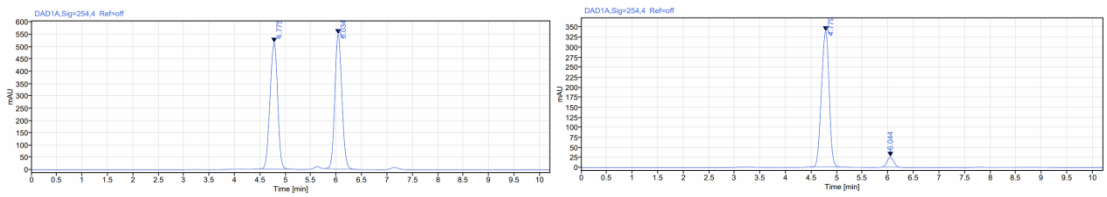
RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.875	BV	0.75	1514.77	143.74	95.83	
5.992	MM m	0.14	65.92	7.56	4.17	
		Sum	1580.69			



14e

The reaction of 1-naphthol derivative (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 °C for 16 h afforded compound **14e** (31.2 mg) in 61% yield as oil. The title compound **14e** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.6, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.57 (td, *J* = 7.6, 1.5 Hz, 1H), 7.39-7.30 (m, 2H), 5.95 (s, 1H), 4.31-4.25 (m, 1H), 4.17-4.10 (m, 1H), 2.51-2.43 (m, 2H), 2.24-2.15 (m, 2H), 2.06-1.98 (m, 1H), 1.92-1.83 (m, 1H), 1.60-1.52 (m, 2H), 1.46-1.36 (m, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.3, 137.9, 134.6, 134.6, 132.4, 129.4, 127.7, 127.5, 124.1, 84.4, 70.4, 36.6, 32.1, 30.4, 25.3, 22.7, 14.1. **HRMS** (ESI) m/z Calcd for [$C_{15}H_{12}O_4$, M + H] $^+$: 257.0807; Found: 257.0808.

Optical Rotation: $[\alpha]_D^{25}$ 176.4 (c = 0.5, $CHCl_3$). 88% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 4.779 min for major isomer, t_R = 6.044 min for minor isomer).

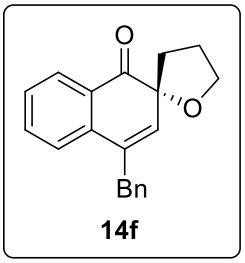


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.775	MM m	0.17	5337.01	512.43	50.22	
6.034	MM m	0.15	5290.33	547.47	49.78	
		Sum	10627.35			

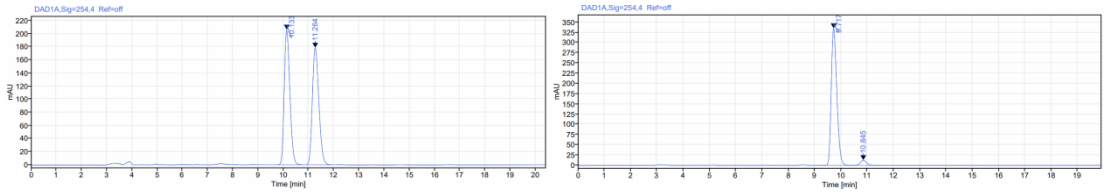
Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.779	MM m	0.17	3540.01	338.04	94.02	
6.044	MM m	0.14	225.33	25.29	5.98	
		Sum	3765.34			



14f

The reaction of 1-naphthol derivative (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 16 h afforded compound **14f** (41.1 mg) in 71% yield as a solid. The title compound **14f** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.6, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99-7.87 (m, 1H), 7.43 (td, *J* = 7.6, 1.3 Hz, 1H), 7.28-7.14 (m, 7H), 5.91 (s, 1H), 4.25 (td, *J* = 7.7, 5.3 Hz, 1H), 4.12-4.03 (m, 1H), 3.79 (s, 2H), 2.25-2.10 (m, 2H), 2.04-1.94 (m, 1H), 1.92-1.81 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 202.0, 138.4, 137.6, 135.4, 134.6, 133.1, 129.3, 128.7, 128.7, 127.9, 127.5, 126.6, 124.8, 84.5, 70.6, 38.9, 36.7, 25.2. **HRMS** (ESI) m/z Calcd for [$C_{20}H_{18}O_2$, M + H] $^{+}$: 291.1380; Found: 291.1382. **Optical Rotation:** $[\alpha]_D^{25}$ 136.0 (c = 1, $CHCl_3$). 92% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 9.717 min for major isomer, t_R = 10.845 min for minor isomer).

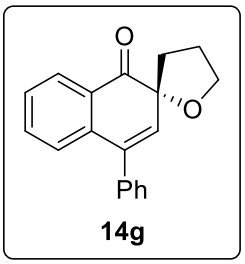


Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.133	BB	1.31	3202.88	205.56	50.08	
11.264	BB	1.15	3192.97	178.05	49.92	
		Sum	6395.85			

Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.717	BV	1.20	4937.78	334.51	95.94	
10.845	VB	0.98	208.98	12.41	4.06	
		Sum	5146.76			

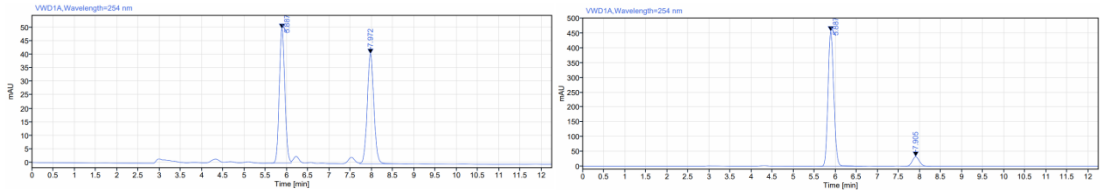


14g

The reaction of 1-naphthol derivative (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 16 h afforded compound **14g** (38.6 mg) in 70% yield as oil. The title compound **14g** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.6, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.51-7.33 (m, 7H), 7.09 (d, *J* = 7.8 Hz, 1H), 6.11 (s, 1H), 4.36-4.29 (m, 1H), 4.22-4.10 (m, 1H), 2.37-2.30 (m, 1H), 2.28-2.19 (m, 1H), 2.12-

1.97 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 201.8, 138.7, 137.9, 137.6, 135.2, 134.4, 129.3, 129.0, 128.6, 128.2, 128.0, 127.6, 126.8, 84.5, 70.6, 36.8, 25.5. **HRMS** (ESI) m/z Calcd for [$C_{19}H_{16}O_2$, M + H] $^+$: 277.1223; Found: 277.1223.

Optical Rotation: $[\alpha]_D^{25}$ 98.0 (c = 0.5, $CHCl_3$). 84% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 5.887 min for major isomer, t_R = 7.905 min for minor isomer).

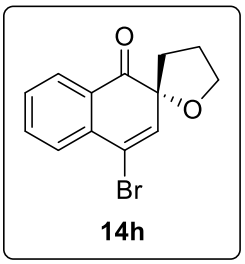


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.887	BV	0.47	455.40	49.83	50.50	
7.972	VB	1.13	446.32	40.78	49.50	
		Sum	901.72			

Signal: VWD1A,Wavelength=254 nm

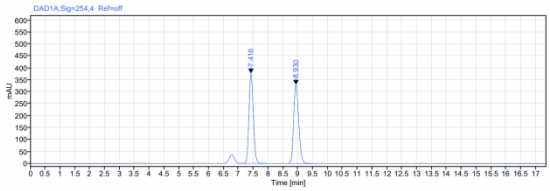
RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.887	VV	0.99	4371.99	456.68	92.07	
7.905	MM m	0.18	376.36	32.03	7.93	
		Sum	4748.35			



14h

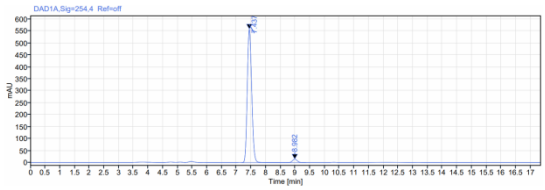
The reaction of 1-naphthol derivative (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 °C for 16 h afforded compound **14h** (40.1 mg) in 74% yield as oil. The title compound **14h** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.6, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.3 Hz, 1H), 7.71-7.61 (m, 2H), 7.48-7.36 (m, 1H), 6.62 (s, 1H), 4.32-4.22 (m, 1H), 4.19-4.08 (m, 1H), 2.31-2.13 (m, 2H), 2.13-1.91 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.8, 137.9, 135.7, 135.0, 129.4, 129.0, 128.2, 127.5, 119.8, 85.6, 70.8, 36.5, 25.4. **HRMS** (ESI) m/z Calcd for [$C_{13}H_{11}O_2Br$, M + Na] $^+$: 300.9840; Found: 300.9848.

Optical Rotation: $[\alpha]_D^{25}$ 137 (c = 0.5, $CHCl_3$). 94% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 7.437 min for major isomer, t_R = 8.982 min for minor isomer).



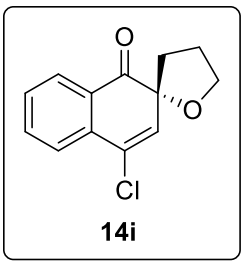
Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.416	BB	0.99	3882.04	375.12	49.91	
8.930	BV	1.04	3896.06	328.80	50.09	
		Sum	7778.10			



Signal: DAD1A,Sig=254,4 Ref=off

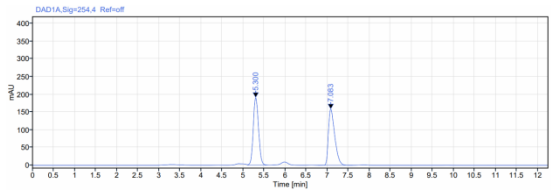
RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.437	VB	1.47	5839.77	558.39	97.16	
8.982	BB	0.69	170.46	14.53	2.84	
		Sum	6010.23			



14i

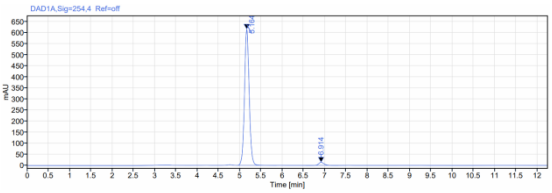
The reaction of 1-naphthol derivative (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 16 h afforded compound **14i** (34.8 mg) in 74% yield as oil. The title compound **14i** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.6, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.66-7.55 (m, 2H), 7.37 (td, *J* = 7.3, 1.7 Hz, 1H), 6.28 (s, 1H), 4.20 (m, 1H), 4.12-4.03 (m, 1H), 2.16 (m, 2H), 2.00 (ddd, *J* = 16.0, 8.9, 3.6 Hz, 1H), 1.94-1.82 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 199.7, 135.0, 134.9, 133.4, 129.4, 129.1, 128.9, 127.5, 125.5, 84.7, 70.7, 36.6, 25.4. **HRMS** (ESI) m/z Calcd for [$C_{13}H_{11}O_2Cl$, M + H]$^{+}$: 235.0520; Found: 235.0508.

Optical Rotation: $[\alpha]_D^{25}$ 110.5 (c = 0.5, $CHCl_3$). 95% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 5.164 min for major isomer, t_R = 6.914 min for minor isomer)



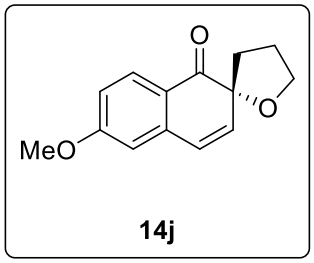
Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.300	VB	0.53	1646.67	190.16	49.94	
7.083	VV	0.81	1650.74	158.17	50.06	
		Sum	3297.41			



Signal: DAD1A,Sig=254,4 Ref=off

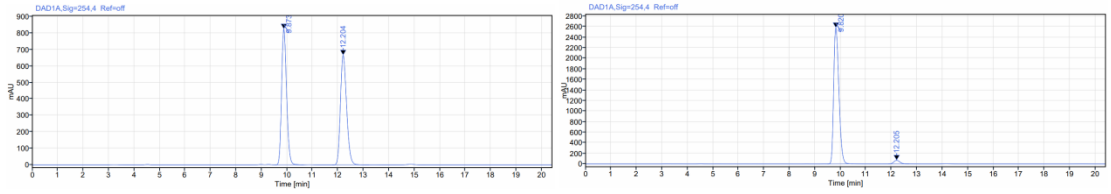
RT [min]	Type	Width [min]	Area	Height	Area%	Name
5.164	VV	0.93	4716.05	613.83	97.39	
6.914	BB	0.76	126.55	13.95	2.61	
		Sum	4842.60			



14j

The reaction of 1-naphthol derivative (0.2 mmol, 1 equiv.), **Cat-8** (0.03 mmol, 15 mol%), EtOH (1 mmol, 5 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) were added to dry CH_2Cl_2 at -20 ^{o}C for 16 h afforded compound **14j** (33.6 mg) in 73% yield as a whtie solid. The title compound **14j** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 3/1). (R_f = 0.6, petroleum ether/ethyl acetate = 3/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.6 Hz, 1H), 7.25 (dd, *J* = 8.6, 2.5 Hz, 1H), 7.06 (d, *J* = 2.5 Hz, 1H), 6.87 (d, *J* = 9.8 Hz, 1H), 6.60 (d, *J* = 9.8 Hz, 1H), 4.78-4.67 (m, 1H), 4.62-4.51 (m, 1H), 4.29 (s, 3H), 2.73-2.59 (m, 2H), 2.51-2.41 (m, 1H), 2.39-2.25 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 200.4, 164.9, 139.7, 137.7, 129.9, 125.6, 122.4, 113.7, 112.1, 83.6, 70.8, 55.7, 37.0, 25.5. **HRMS** (ESI) m/z Calcd for [$C_{14}H_{14}O_3$, M + H] $^{+}$: 231.1016; Found: 231.1016.

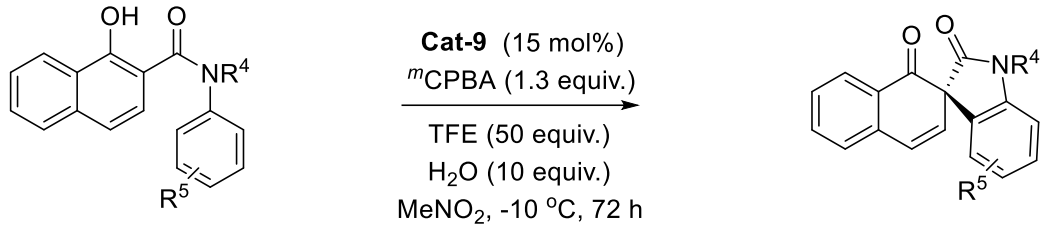
Optical Rotation: $[\alpha]_D^{25}$ 172.5 (c = 0.5, $CHCl_3$). 94% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 9.820 min for major isomer, t_R = 12.205 min for minor isomer).



Signal:	DAD1A,Sig=254,4 Ref=off					
RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.873	BV	1.12	11242.08	824.39	50.10	
12.204	BB	1.45	11197.44	665.54	49.90	
		Sum	22439.52			

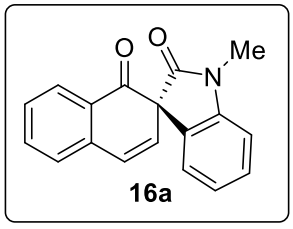
Signal:	DAD1A,Sig=254,4 Ref=off					
RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.820	VM m	0.22	36558.27	2579.62	97.01	
12.205	MM m	0.26	1127.41	68.82	2.99	
		Sum	37685.68			

7.2 Characterization of oxidative spirolactonization



15 **16**

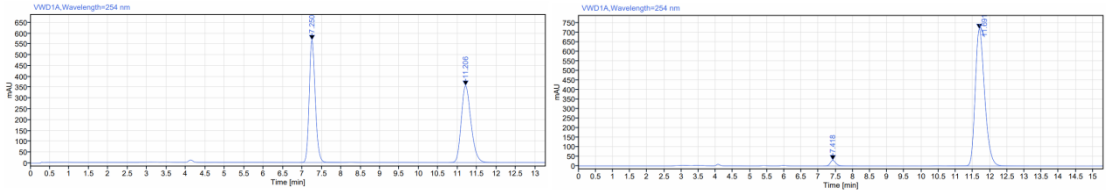
General procedure: To a Schlenk tube containing **Cat-9** (0.03 mmol, 15 mol%), ^{m}CPBA (0.26 mmol, 1.3 equiv.), TFE (10 mmol, 50 equiv.), H_2O (2 mmol, 10 equiv.) and $MeNO_2$ (3 mL) were added **15** (0.2 mmol, 1.0 equiv.), the reaction mixture was stirred at -10 °C for 72 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. Finally, the organic layer was subsequently extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4. The mixture was concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to afford the product **16**.



16a

The reaction of the **15a** (55.4 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (52.9 mg, 0.26 mmol, 1.3 equiv.), **Cat-9** (42 mg, 0.03 mmol, 15 mol%), H_2O (36.0 mg, 2.0 mmol, 10.0 equiv.), TFE (1.0g, 10 mmol, 50.0 equiv.) in $MeNO_2$ (dried, 3.0 mL) at -10 °C for 72 h afforded compound **16a** (29.7 mg) in 54% yield as a white solid. The title compound **16a** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 2/1). (R_f = 0.5, petroleum ether/ethyl acetate = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.68-7.59 (m, 2H), 7.44-7.28 (m, 7H), 7.02-6.96 (m, 2H), 6.96-6.89 (m, 7H), 6.03 (d, *J* = 9.6 Hz, 2H), 3.28 (s, 7H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.2, 172.9, 145.0, 138.4, 135.5, 129.5, 129.3, 128.8, 128.7, 128.5, 128.2, 128.2, 127.8, 123.5, 123.2, 109.1, 64.5, 27.0., **HRMS** (ESI) m/z Calcd for $[C_{18}H_{13}NO_2, M + H]^+$:276.1019; Found: 276.1017.

Optical Rotation: $[\alpha]_D^{25}$ -4.2 (c = 1.0, $CHCl_3$). 95% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 7.418 min for minor isomer, t_R = 11.691 min for major isomer).

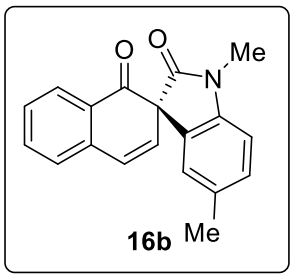


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.250	BB	1.03	6138.37	564.86	49.96	
11.206	BB	1.29	6147.29	354.09	50.04	
		Sum	12285.66			

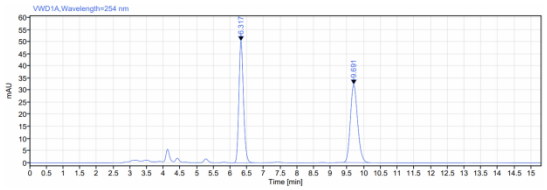
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.418	BB	0.99	344.21	29.72	2.45	
11.691	BB	2.40	13699.25	716.13	97.55	
		Sum	14043.46			



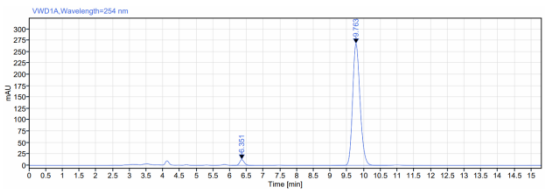
The reaction of the **15b** (58.2 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (52.9 mg, 0.26 mmol, 1.3 equiv.), **Cat-9** (42.0 mg, 0.03 mmol, 15 mol%), H_2O (36.0 mg, 2.0 mmol, 10.0 equiv.), TFE (1.0g, 10 mmol, 50.0 equiv.) in $MeNO_2$ (dried, 3.0 mL) at -10 °C for 72 h afforded compound **16b** (34.68 mg) in 60% yield as a white solid. The title compound **16b** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 2/1). (R_f = 0.5, petroleum ether/ethyl acetate = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.68-7.60 (m, 1H), 7.44-7.33 (m, 2H), 7.16-7.09 (m, 1H), 6.91 (d, *J* = 9.6 Hz, 1H), 6.81 (d, *J* = 8.0 Hz, 1H), 6.75 (s, 1H), 6.02 (d, *J* = 9.6 Hz, 1H), 3.26 (s, 3H), 2.24 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.4, 172.8, 142.6, 138.5, 135.4, 132.9, 129.8, 129.5, 128.8, 128.8, 128.5, 128.2, 128.0, 127.8, 124.3, 108.9, 64.6, 27.1, 21.1., **HRMS** (ESI) m/z Calcd for $[C_{19}H_{15}NO_2, M+H]^+$: 290.1176, found 290.1175.

Optical Rotation: $[\alpha]_D^{25}$ 54.9 (c = 1.0, $CHCl_3$). 94% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 6.351 min for minor isomer, t_R = 9.763 min for major isomer).



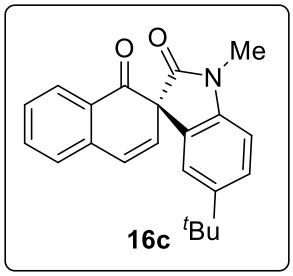
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.317	BB	0.83	480.28	50.23	49.87	
9.691	BB	0.92	482.75	32.17	50.13	
		Sum	963.04			



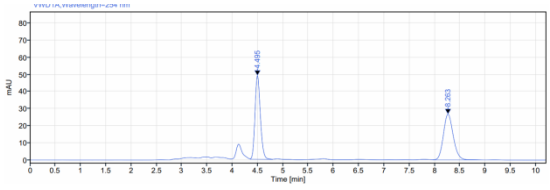
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.351	BB	0.66	122.95	12.72	2.89	
9.763	BB	1.66	4126.41	268.08	97.11	
		Sum	4249.36			



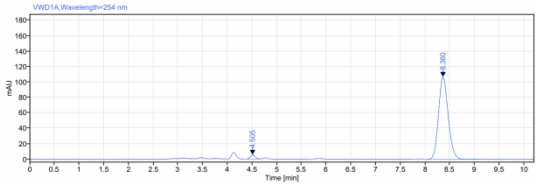
The reaction of the **15c** (66.6 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (52.9 mg, 0.26 mmol, 1.3 equiv.), **Cat-9** (42.0 mg, 0.03 mmol, 15 mol%), H_2O (36.0 mg, 2.0 mmol, 10.0 equiv.), TFE (1.0g, 10 mmol, 50.0 equiv.) in $MeNO_2$ (dried, 3.0 mL) at -10 °C for 72 h afforded compound **16c** (42.3 mg) in 64% yield as a white solid. The title compound **16c** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 2/1). (R_f = 0.5, petroleum ether/ethyl acetate = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 1H), 7.69-7.61 (m, 1H), 7.41-7.33 (m, 3H), 6.97-6.89 (m, 2H), 6.85 (d, *J* = 8.3 Hz, 1H), 6.03 (d, *J* = 9.6 Hz, 1H), 3.26 (s, 3H), 1.22 (s, 9H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.4, 172.8, 146.6, 142.6, 138.5, 135.5, 129.7, 128.8, 128.8, 128.6, 128.2, 128.2, 127.9, 126.2, 120.7, 108.6, 64.9, 34.7, 31.6, 27.1., **HRMS** (ESI) m/z Calcd for $[C_{22}H_{21}NO_2, M+H]^+$: 332.1646, found 332.1648.

Optical Rotation: $[\alpha]_D^{25}$ 88.6 (c = 0.5, $CHCl_3$). 94% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 4.505 min for minor isomer, t_R = 8.360 min for major isomer).



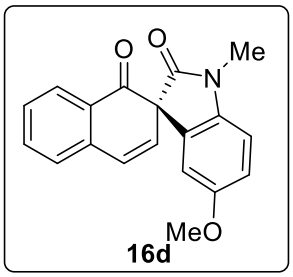
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.495	VV	0.45	359.85	49.03	49.80	
8.263	VB	1.02	362.74	26.81	50.20	
		Sum	722.59			



Signal: VWD1A,Wavelength=254 nm

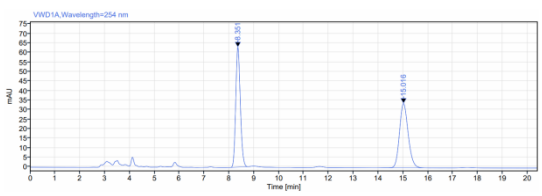
RT [min]	Type	Width [min]	Area	Height	Area%	Name
4.505	BV	0.29	40.39	5.51	2.71	
8.360	VB	0.99	1451.51	106.85	97.29	
		Sum	1491.90			



16d

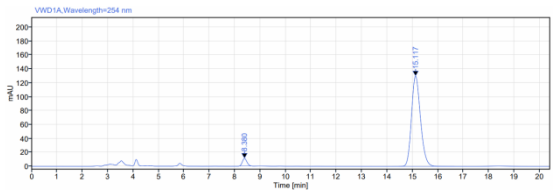
The reaction of the **15d** (61.4 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (52.9 mg, 0.26 mmol, 1.3 equiv.), **Cat-9** (42.0 mg, 0.03 mmol, 15 mol%), H_2O (36.0 mg, 2.0 mmol, 10.0 equiv.), TFE (1.0g, 10 mmol, 50.0 equiv.) in $MeNO_2$ (dried, 3.0 mL) at -10 °C for 72 h afforded compound **16d** (45.14 mg) in 74% yield as a white solid. The title compound **16d** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 2/1). (R_f = 0.5, petroleum ether/ethyl acetate = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.66-7.62 (m, 1H), 7.44-7.32 (m, 2H), 6.91 (d, *J* = 9.6 Hz, 1H), 6.88-6.77 (m, 2H), 6.56 (d, *J* = 2.3 Hz, 1H), 6.02 (d, *J* = 9.6 Hz, 1H), 3.69 (s, 3H), 3.25 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.2, 172.5, 156.3, 138.4, 138.4, 135.5, 130.0, 129.4, 128.9, 128.5, 128.2, 128.2, 127.9, 113.7, 111.0, 109.4, 64.9, 55.9, 27.2., **HRMS** (ESI) m/z Calcd for $[C_{19}H_{15}NO_3, M+H]^+$:306.1125, found 306.1125.

Optical Rotation: $[\alpha]_D^{25}$ 57 (c = 1, $CHCl_3$). 92% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 8.380 min for minor isomer, t_R = 15.117 min for major isomer).



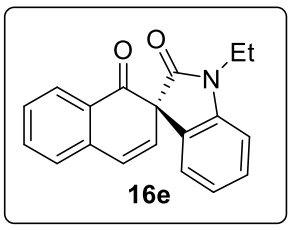
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.351	BB	0.71	809.64	62.98	49.79	
15.016	BB	1.67	816.47	33.78	50.21	
		Sum	1626.11			



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.380	MM m	0.19	136.41	11.00	4.09	
15.117	BB	2.19	3201.27	129.86	95.91	
		Sum	3337.68			

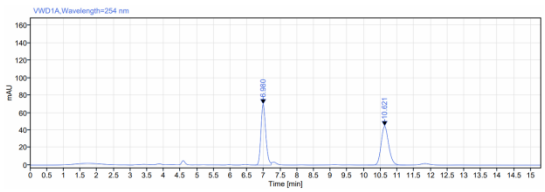


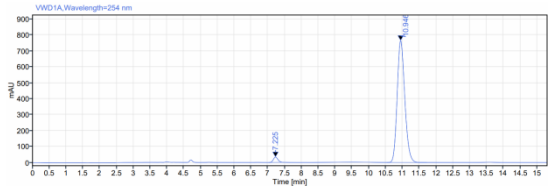
16e

The reaction of the **15e** (58.2 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (52.9 mg, 0.26 mmol, 1.3 equiv.), **Cat-9** (42.0 mg, 0.03 mmol, 15 mol%), H_2O (36.0 mg, 2.0 mmol, 10.0 equiv.), TFE (1.0g, 10 mmol, 50.0 equiv.) in $MeNO_2$ (dry, 3.0 ml) at -10 °C for 72 h afforded compound **16e** (31.2 mg) in 54% yield as oil. The title compound **16e** was isolated through chromatography on silica gel eluting with

petroleum ether/ethyl acetate (5/1 to 2/1). (R_f = 0.5, petroleum ether/ethyl acetate = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 9.2 Hz, 1H), 7.68-7.60 (m, 1H), 7.42-7.29 (m, 3H), 7.02-6.87 (m, 4H), 6.04 (d, *J* = 9.6 Hz, 1H), 3.91-3.74 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.2, 172.6, 144.1, 138.4, 135.4, 129.5, 129.4, 129.0, 128.8, 128.8, 128.5, 128.2, 127.8, 123.7, 123.0, 109.3, 64.5, 35.6, 12.7., **HRMS** (ESI) m/z Calcd for [$C_{19}H_{15}NO_2$, M+H]$^+$: 290.1176, found 290.1178.

Optical Rotation: $[\alpha]_D^{25}$ -14.7 (c = 0.5, $CHCl_3$). 95% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 7.225 min for minor isomer, t_R = 10.946 min for major isomer).



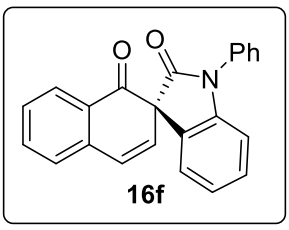


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
6.980	VM m	0.15	699.49	69.66	50.17	
10.621	BB	1.13	694.64	44.44	49.83	
		Sum	1394.14			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.225	MM m	0.15	318.58	33.66	2.58	
10.946	VB	1.18	12014.78	764.32	97.42	
		Sum	12333.36			

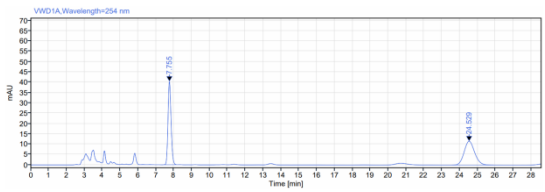


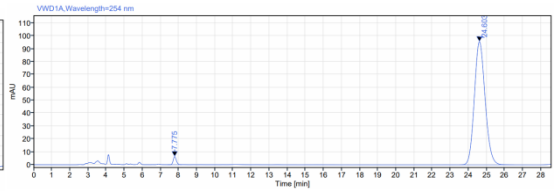
16f

The reaction of the **15f** (67.4 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (52.9 mg, 0.26 mmol, 1.3 equiv.), **Cat-9** (42.0 mg, 0.03 mmol, 15 mol%), H_2O (36.0 mg, 2.0 mmol, 10.0 equiv.), TFE (1.0g, 10 mmol, 50.0 equiv.) in $MeNO_2$ (dry., 3.0 mL) at -10 °C for 24 h afforded compound **16f** (27.1 mg) in 40% yield as oil. The title compound **16f** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 2/1). (R_f = 0.5, petroleum ether/ethyl acetate = 2/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.7 Hz, 1H), 7.68-7.60 (m, 1H), 7.57-7.46 (m, 4H), 7.45-7.34 (m, 3H), 7.28-7.20 (m, 1H), 7.03-6.93 (m, 3H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.19 (d, *J* = 9.6 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1, 172.4, 145.1, 138.4, 135.5, 134.3, 129.8, 129.4, 129.3, 128.9, 128.9, 128.5, 128.4,

128.4, 128.2, 127.9, 126.8, 123.8, 123.6, 110.4, 64.6., **HRMS** (ESI) m/z Calcd for $[C_{23}H_{15}NO_2, M+Na]^+$: 338.1176, found 338.1178.

Optical Rotation: $[\alpha]_D^{25}$ -128.2 (c = 1, $CHCl_3$). 96% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 ºC, wavelength = 254 nm, t_R = 7.775 min for minor isomer, t_R = 24.603 min for major isomer).





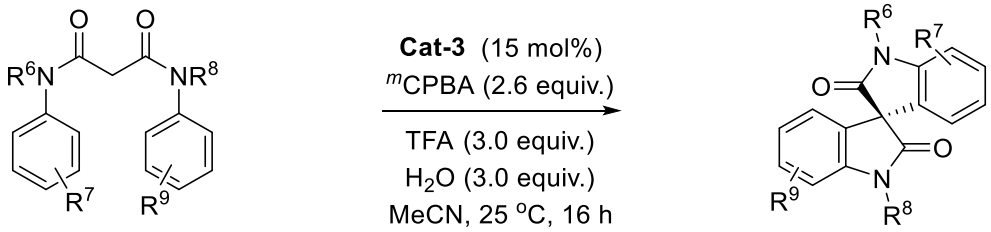
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.755	BB	0.88	478.07	40.39	50.40	
24.529	BB	2.30	470.51	11.55	49.60	
		Sum	948.58			

Signal: VWD1A,Wavelength=254 nm

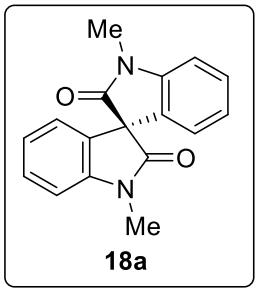
RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.775	BB	0.76	75.42	6.33	1.87	
24.603	BB	3.00	3947.10	95.76	98.13	
		Sum	4022.51			

7.3 Characterization of direct C(sp^2)-H/C(sp^3)-H cross-coupling



17 **18**

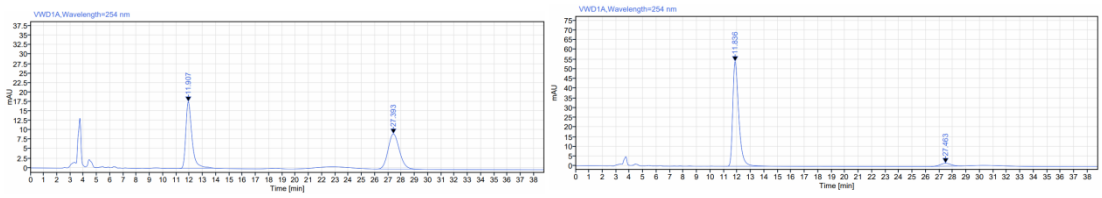
General procedure: To a Schlenk tube containing **Cat-3** (0.03 mmol, 15 mol%), ^{m}CPBA (0.52 mmol, 2.6 equiv.), TFA (0.6 mmol, 3 equiv.) and H_2O (0.6 mmol, 3 equiv.) and MeCN (3 mL) were added **17** (0.2 mmol, 1.0 equiv.), the reaction mixture was stirred at 25 °C for 16 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was subsequently extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4. Finally, the mixture was concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to afford the product **18**.



18a

The reaction of the **17a** (56.4 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (105.6 mg, 0.52 mmol, 2.6 equiv.), **Cat-3** (38.0 mg, 0.03 mmol, 15 mol%), H_2O (10.8 mg, 0.6 mmol, 3.0 equiv.), TFE (60.0g, 0.6 mmol, 3.0 equiv.) in MeCN (dry, 3.0 mL) at room temperature for 16 h afforded compound **18a** (40.0 mg) in 72% yield as a white solid. The title compound **18a** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 1/1). (R_f = 0.5, petroleum ether/ethyl acetate = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ7.36 (t, *J* = 8.4 Hz, 1H), 7.02 (t, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.88 (d, *J* = 6.2 Hz, 1H), 3.31 (s, 2H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ172.3, 145.4, 129.7, 127.9, 124.0, 123.4, 109.0, 62.4, 27.2. **HRMS** (ESI) m/z Calcd for $[C_{17}H_{14}N_2O_2, M+H]^+$: 279.1128, found 279.1129.

Optical Rotation: $[\alpha]_D^{25}$ -71 (c = 0.5, $CHCl_3$). 90% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 11.836 min for major isomer, t_R = 27.463 min for minor isomer).

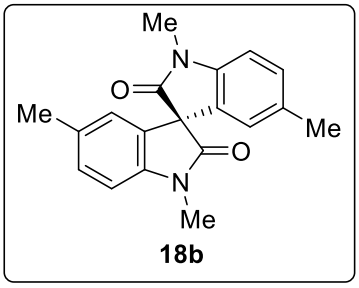


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.907	BM m	0.49	573.32	17.62	50.93	
27.393	BB	3.40	552.33	9.31	49.07	
		Sum	1125.65			

Signal: VWD1A,Wavelength=254 nm

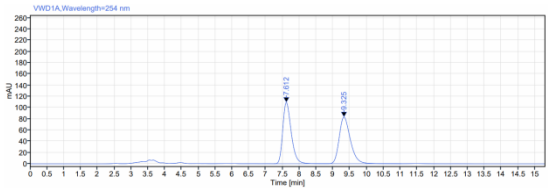
RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.836	BB	3.73	1681.58	54.02	95.25	
27.463	MM m	0.67	83.79	1.50	4.75	
		Sum	1765.37			



18b

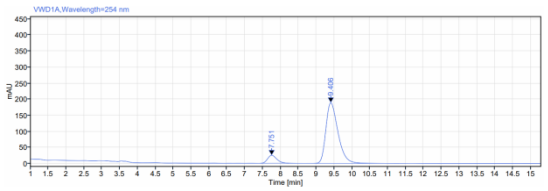
The reaction of the **17b** (62.0 mg, 0.2 mmol, 1.0 equiv.), *m*CPBA (105.6 mg, 0.52 mmol, 2.6 equiv.), **Cat-3** (38.0 mg, 0.03 mmol, 15 mol%), H_2O (10.8 mg, 0.6 mmol, 3.0 equiv.), TFE (60.0g, 0.6 mmol, 3.0 equiv.) in MeCN (dry, 3.0 mL) at room temperature for 16 h afforded compound **18b** (48.9 mg) in 80% yield as a white solid. The title compound **18b** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 1/1). (R_f = 0.5, petroleum ether/ethyl acetate = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 8.0, 1.7 Hz, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 6.71 (s, 1H), 3.29 (s, 3H), 2.25 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.4, 143.0, 133.1, 129.9, 128.0, 124.7, 108.6, 62.5, 27.1, 21.1., **HRMS** (ESI) m/z Calcd for [$C_{19}H_{18}N_2O_2$, M+H]$^+$: 307.1441, found 307.1441.

Optical Rotation: $[\alpha]_D^{25}$ -111.2 (c = 0.5, $CHCl_3$). 82% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 7.751 min for minor isomer, t_R = 9.406 min for major isomer).



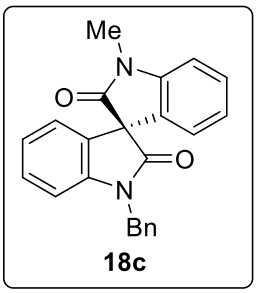
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.612	BB	1.55	1909.96	109.10	49.86	
9.325	BB	2.24	1920.78	82.96	50.14	
		Sum	3830.74			



Signal: VWD1A,Wavelength=254 nm

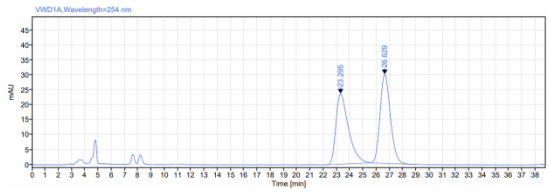
RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.751	MM m	0.27	439.31	24.84	9.01	
9.406	MB m	0.36	4436.61	188.62	90.99	
		Sum	4875.92			



18c

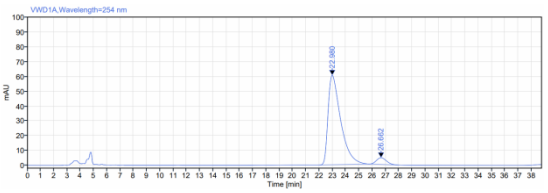
The reaction of the **17c** (71.6 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (105.6 mg, 0.52 mmol, 2.6 equiv.), **Cat-3** (38.0 mg, 0.03 mmol, 15 mol%), H_2O (10.8 mg, 0.6 mmol, 3.0 equiv.), TFE (60.0g, 0.6 mmol, 3.0 equiv.) in MeCN (dry, 3.0 mL) at room temperature for 16 h afforded compound **18c** (33.3 mg) in 47% yield as a white solid. The title compound **18c** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 1/1). (R_f = 0.5, petroleum ether/ethyl acetate = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.21 (m, 7H), 7.15-6.89 (m, 5H), 6.84 (d, *J* = 7.9 Hz, 1H), 5.06 (t, *J* = 11.1 Hz, 2H), 3.36 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 172.3, 145.5, 144.4, 135.3, 129.8, 129.6, 129.0, 127.9, 127.9, 127.8, 127.2, 124.0, 123.9, 123.5, 123.4, 110.0, 109.0, 62.4, 44.3, 27.1., **HRMS** (ESI) m/z Calcd for $[C_{23}H_{18}N_2O_2, M+H]^+$:355.1441, found 355.1440.

Optical Rotation: $[\alpha]_D^{25}$ -29.2 (c = 0.5, $CHCl_3$). 89% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 22.980 min for major isomer, t_R = 26.662 min for minor isomer).



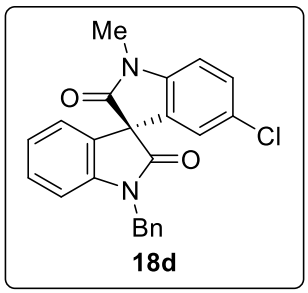
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
23.295	BB	3.36	1552.02	23.52	49.08	
26.629	BB	3.28	1610.11	29.74	50.92	
		Sum	3162.13			



Signal: VWD1A,Wavelength=254 nm

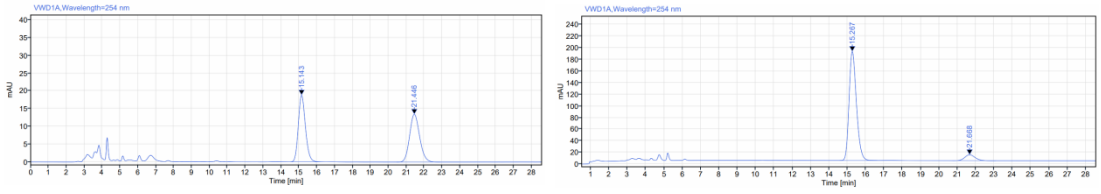
RT [min]	Type	Width [min]	Area	Height	Area%	Name
22.980	BB	3.78	3985.52	60.55	94.43	
26.662	BB	2.25	235.20	4.53	5.57	
		Sum	4220.72			



18d

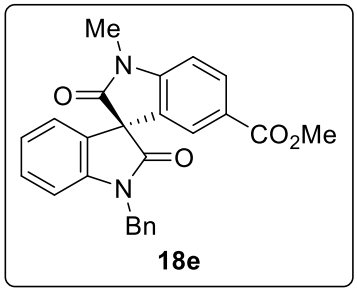
The reaction of the **17d** (78.4 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (105.6 mg, 0.52 mmol, 2.6 equiv.), **Cat-3** (38.0 mg, 0.03 mmol, 15 mol%), H_2O (10.8 mg, 0.6 mmol, 3.0 equiv.), TFE (60.0g, 0.6 mmol, 3.0 equiv.) in MeCN (dry, 3.0 mL) at room temperature for 16 h afforded compound **18d** (31.8 mg) in 41% yield as a white solid. The title compound **18d** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 1/1). (R_f = 0.5, petroleum ether/ethyl acetate = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.33 (m, 5H), 7.32-7.27 (m, 1H), 7.25-7.22 (m, 1H), 7.00 (td, *J* = 7.6, 1.0 Hz, 1H), 6.96-6.84 (m, 3H), 6.81 (d, *J* = 7.9 Hz, 1H), 5.11-4.89 (m, 2H), 3.32 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.9, 171.8, 144.4, 144.1, 135.1, 129.9, 129.8, 129.3, 129.1, 128.8, 127.9, 127.2, 127.2, 124.5, 124.1, 123.6, 110.2, 109.9, 62.3, 44.5, 27.3., **HRMS** (ESI) m/z Calcd for $[C_{23}H_{17}ClN_2O_2, M+H]^+$: 389.1051, 391.1022, found 389.1057, 391.1039

Optical Rotation: $[\alpha]_D^{25}$ -74.8 (c = 0.5, $CHCl_3$). 86% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 15.267 min for major isomer, t_R = 21.668 min for minor isomer).



Signal:	VWD1A,Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%	Name
15.143	BB	1.99	518.42	18.82	49.70	
21.446	BB	2.43	524.78	13.47	50.30	
		Sum	1043.20			

Signal:	VWD1A,Wavelength=254 nm					
RT [min]	Type	Width [min]	Area	Height	Area%	Name
15.267	BB	2.05	5215.84	187.25	92.95	
21.668	BB	2.34	395.74	10.13	7.05	
		Sum	5611.58			

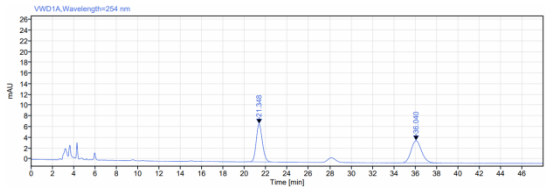


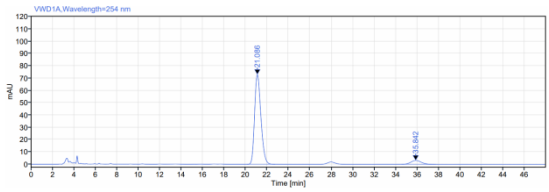
18e

The reaction of the **17e** (83.2 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (105.6 mg, 0.52 mmol, 2.6 equiv.), **Cat-3** (38.0 mg, 0.03 mmol, 15 mol%), H_2O (10.8 mg, 0.6 mmol, 3.0 equiv.), TFE (60.0g, 0.6 mmol, 3.0 equiv.) in MeCN (dry, 3.0 mL) at room temperature for 16 h afforded

compound **18e** (51.0 mg) in 62% yield as a white solid. The title compound **18e** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 1/1). (R_f = 0.5, petroleum ether/ethyl acetate = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (dt, *J* = 8.3, 1.4 Hz, 1H), 7.61 (d, *J* = 1.6 Hz, 1H), 7.40-7.34 (m, 4H), 7.30 (p, *J* = 2.9 Hz, 1H), 7.24 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.05-6.97 (m, 2H), 6.84 (dd, *J* = 23.5, 7.7 Hz, 2H), 5.13-4.89 (m, 2H), 3.85 (s, 3H), 3.37 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 172.0, 166.5, 149.5, 144.5, 135.1, 132.4, 129.9, 129.1, 127.9, 127.2, 127.2, 125.5, 125.4, 124.1, 123.7, 110.2, 108.6, 62.1, 52.3, 44.5, 27.4. **HRMS** (ESI) m/z Calcd for $[C_{25}H_{20}N_2O_4, M+H]^+$: 413.1496, found 413.1496.

Optical Rotation: $[\alpha]_D^{25}$ -176.6 (c = 0.5, $CHCl_3$). 87% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 15.267 min for major isomer, t_R = 21.668 min for minor isomer).



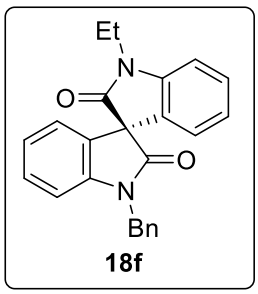


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
21.348	BB	2.16	280.12	7.05	49.87	
36.040	BB	3.53	281.59	4.14	50.13	
		Sum	561.71			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
21.086	BB	2.61	2988.03	73.04	93.38	
35.842	BB	3.20	211.95	3.14	6.62	
		Sum	3199.98			

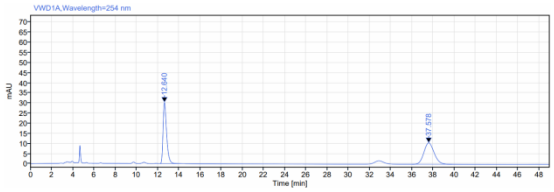


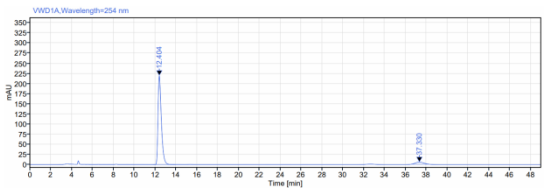
18f

The reaction of the **17f** (74.4 mg, 0.2 mmol, 1.0 equiv.), ^{m}CPBA (105.6 mg, 0.52 mmol, 2.6 equiv.), **Cat-3** (38.0 mg, 0.03 mmol, 15 mol%), H_2O (10.8 mg, 0.6 mmol, 3.0 equiv.), TFE (60.0g, 0.6 mmol, 3.0 equiv.) in MeCN (dry, 3.0 mL) at room temperature for 16 h afforded compound **18f** (38.3 mg) in 52% yield as a white solid. The title compound **18f** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (5/1 to 1/1). (R_f = 0.5, petroleum ether/ethyl acetate = 1/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57-7.33 (m, 5H), 7.29 (d, *J* = 6.9 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 7.01 (dq, *J* = 14.2, 7.5 Hz, 3H), 6.90 (dd, *J* = 17.3, 7.4 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 1H), 5.11-4.88 (m, 2H),

4.02-3.75 (m, 2H), 1.37 (t, *J* = 7.2 Hz, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.5, 171.9, 144.6, 144.4, 135.3, 129.7, 129.5, 129.0, 128.2, 128.1, 127.8, 127.2, 124.1, 123.8, 123.4, 123.3, 110.0, 109.1, 62.4, 44.3, 35.6, 12.8., **HRMS** (ESI) m/z Calcd for $[C_{24}H_{20}N_2O_2$， $M+H]^+$: 368.1598, found 369.1604.

Optical Rotation: $[\alpha]_D^{25}$ -11.6 (c = 0.5, $CHCl_3$). 89% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 12.404 min for major isomer, t_R = 37.330 min for minor isomer).





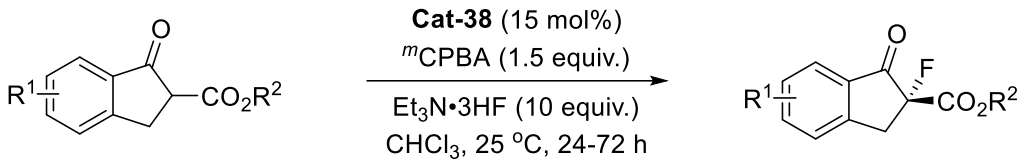
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.640	BB	2.23	707.44	30.30	49.92	
37.578	BB	3.76	709.57	10.56	50.08	
		Sum	1417.01			

Signal: VWD1A,Wavelength=254 nm

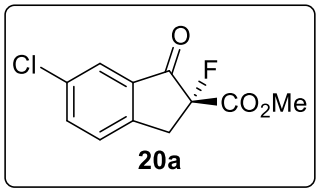
RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.404	MB m	0.34	4910.84	220.04	94.47	
37.330	MM m	0.84	287.62	5.28	5.53	
		Sum	5198.46			

7.4 Characterization of oxidative fluorination of keto esters.



19 **20**

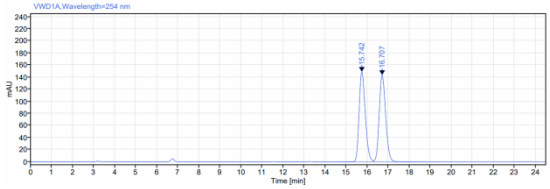
General procedure: To a Teflon tube containing *β*-ketoesters **19** (0.20 mmol, 1.0 equiv.), **Cat-38** (0.03 mmol, 15 mol%), and $CHCl_3$ (8 mL) were added NEt_3·3HF (2 mmol, 10 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) in turn, the reaction mixture was stirred at 25 °C for 24-72 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was subsequently extracted with dichloromethane, washed with brine, dried over anhydrous Na_2SO_4. Finally, the mixture was concentrated *in vacuo*, and then the residue was purified by silica gel column chromatography to afford the desired product **20**.

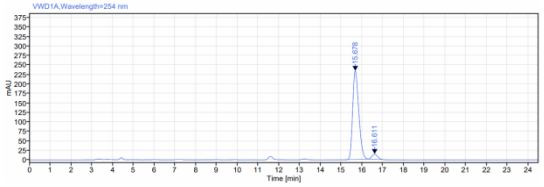


20a

The reaction of the *β*-keto ester **19a** (44.8 mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), NEt_3·3HF (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 24 h afforded compound **20a** (27.6 mg) in 57% yield as a white solid. The title compound **20a** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 5/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 2.1 Hz, 1H), 7.66 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.46 (d, *J* = 8.2 Hz, 1H), 3.81 (s, 3H), 3.77 (dd, *J* = 17.7, 10.8 Hz, 1H), 3.41 (dd, *J* = 22.9, 17.7 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1 (d, $^2J_{C\text{-}F}$ = 18.3 Hz), 167.4 (d, $^2J_{C\text{-}F}$ = 27.7 Hz), 149.0 (d, $^3J_{C\text{-}F}$ = 3.7 Hz), 136.9, 135.3, 134.8(d, $^3J_{C\text{-}F}$ = 1.4 Hz), 128.0, 125.5, 94.9 (d,$^1J_{C\text{-}F}$ = 202.8 Hz), 53.6, 38.0 (d, $^2J_{C\text{-}F}$ = 24.0 Hz)., **^{19}F NMR** (376 MHz, $CDCl_3$) δ -164.16. **GC-MS (EI)** m/z Calcd for $[C_{11}H_8ClFO]^+$: 242.0, 244.0; found 242.0, 244.0

Optical Rotation: $[\alpha]_D^{25}$ 4.2 (c = 0.5, $CHCl_3$). 90% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, 30 ºC, wavelength = 254 nm, t_R = 15.678 min for major isomer, t_R = 16.611 min for minor isomer).



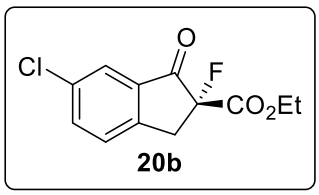


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
15.742	BV	1.49	3043.52	148.70	49.80	
16.707	VB	2.38	3067.44	143.30	50.20	
		Sum	6110.96			

Signal: VWD1A,Wavelength=254 nm

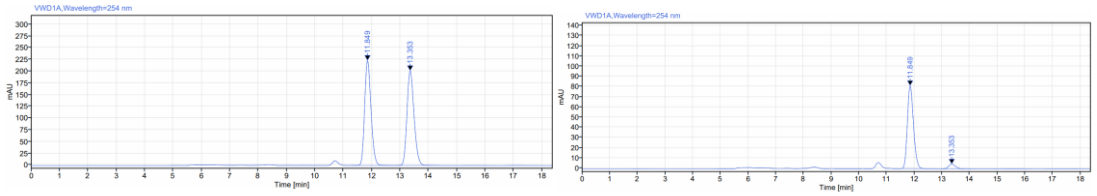
RT [min]	Type	Width [min]	Area	Height	Area%	Name
15.678	MM m	0.32	4781.89	233.46	94.93	
16.611	MM m	0.30	255.55	13.51	5.07	
		Sum	5037.44			



20b

The reaction of the *β*-keto ester **19b** (47.6mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), $NEt_3{\cdot}3HF$ (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 24 h afforded compound **20b** (26.6 mg) in 52% yield as oil. The title compound **20b** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 5/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 2.4 Hz, 1H), 7.66 (dd, *J* = 8.1, 2.4 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 4.27 (q, *J* = 7.1 Hz, 2H), 3.75 (dd, *J* = 17.8, 11.0 Hz, 1H), 3.39 (dd, *J* = 23.0, 17.7 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.3 (d, $^2J_{C\text{-}F}$ = 18.2 Hz), 167.0 (d, $^2J_{C\text{-}F}$ = 27.6 Hz), 149.1 (d, $^3J_{C\text{-}F}$ = 4.4 Hz), 136.8, 135.2, 134.8, 127.9, 125.4, 94.8 (d, $^1J_{C\text{-}F}$ = 202.7 Hz), 62.9, 38.0 (d, $^2J_{C\text{-}F}$ = 24.0 Hz), 14.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -164.04. **GC-MS (EI)** m/z Calcd for $[C_{12}H_{10}ClFO_3]^+$: 256.0, found 256.0.

Optical Rotation: $[\alpha]_D^{25}$ 2.7 (c = 1.0, $CHCl_3$). 88% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 0.5 mL/min, 30 ºC, wavelength = 254 nm, t_R = 11.849 min for major isomer, t_R = 13.353 min for minor isomer).

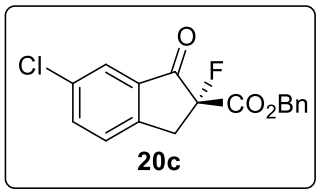


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.849	BB	1.54	3482.50	223.91	50.03	
13.353	BB	1.27	3478.97	201.94	49.97	
		Sum	6961.47			

Signal: VWD1A,Wavelength=254 nm

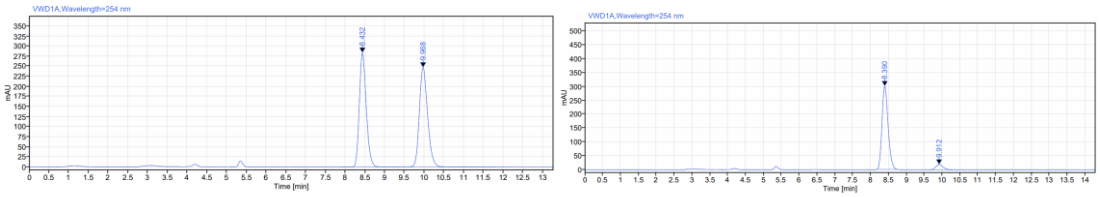
RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.849	MM m	0.24	1235.88	81.32	94.18	
13.353	BB	0.83	76.42	4.57	5.82	
		Sum	1312.30			



20c

The reaction of the *β*-keto ester **19c** (60.0 mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), $NEt_3 \cdot 3HF$ (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 24 h afforded compound **20c** (31.8 mg) in 50% yield as oil. The title compound **20c** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 5/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 2.1 Hz, 1H), 7.65 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 7.37-7.30 (m, 3H), 7.30-7.24 (m, 2H), 5.30-5.19 (m, 2H), 3.73 (dd, *J* = 17.7, 11.1 Hz, 1H), 3.39 (dd, *J* = 22.8, 17.7 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.1(d, $^{2}J_{C-F}$ = 18.7 Hz), 166.9 (d, $^{2}J_{C-F}$ = 28.3 Hz), 149.0 (d, $^{3}J_{C-F}$ = 3.7 Hz), 136.9, 135.3, 134.8, 134.6, 128.8, 128.3, 127.9, 125.4, 94.8 (d, $^{1}J_{C-F}$ = 203.0 Hz), 68.2, 37.9 (d, $^{2}J_{C-F}$ = 24.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -164.02. **HRMS** (ESI) m/z Calcd for $[C_{17}H_{12}ClFO_3, M+Na]^+$:341.0369, found 341.0353.

Optical Rotation: $[\alpha]_D^{25}$ -1.6 (c = 0.25, $CHCl_3$). 85% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 8.390 min for major isomer, t_R = 9.912 min for minor isomer).

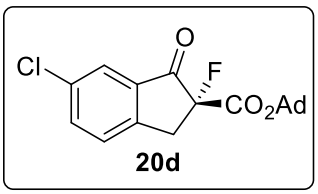


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.432	BB	1.26	3454.08	283.39	48.99	
9.968	BB	2.72	3596.54	246.69	51.01	
		Sum	7050.62			

Signal: VWD1A,Wavelength=254 nm

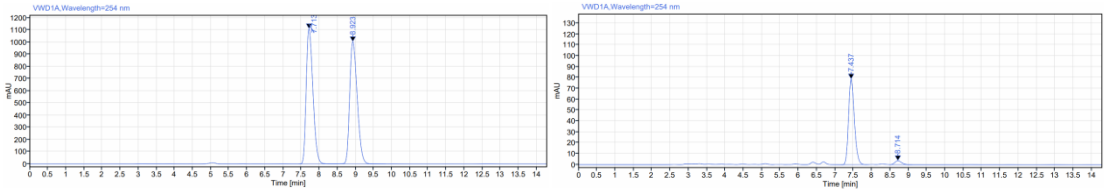
RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.390	MM m	0.18	3549.33	299.85	92.77	
9.912	MM m	0.22	276.46	19.08	7.23	
		Sum	3825.79			



20d

The reaction of the *β*-keto ester **19d** (68.8 mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), $NEt_3{\cdot}3HF$ (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 24 h afforded compound **20d** (29.7 mg) in 41% yield as white solid. The title compound **20d** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 5/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.65-7.60 (m, 1H), 7.44 (d, *J* = 8.1 Hz, 1H), 3.69 (dd, *J* = 17.6, 10.0 Hz, 1H), 3.35 (dd, *J* = 22.5, 17.6 Hz, 1H), 2.13 (s, 3H), 2.02 (d, *J* = 3.5 Hz, 6H), 1.60 (t, *J* = 3.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.8 (d, $^{2}J_{C\text{-}F}$ = 18.9 Hz), 165.4 (d, $^{2}J_{C\text{-}F}$ = 27.6 Hz), 149.2 ($^{3}J_{C\text{-}F}$, *J* = 3.6 Hz), 136.5, 135.1, 134.9, 127.8, 125.1, 94.5 (d, $^{1}J_{C\text{-}F}$ = 202.7 Hz), 84.6, 41.1, 38.1 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 35.9, 30.9. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -163.60. **HRMS** (ESI) m/z Calcd for $[C_{20}H_{20}ClFO_3, M+Na]^+$: 385.0977, found 385.0973.

Optical Rotation: $[\alpha]_D^{25}$ 10.8 (c = 0.5, $CHCl_3$). 90% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 7.437 min for major isomer, t_R = 8.714 min for minor isomer).

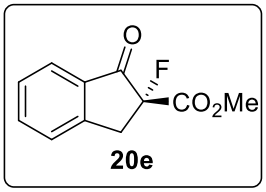


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.713	BB	0.97	14307.65	1109.24	49.64	
8.923	BB	1.44	14515.52	1002.67	50.36	
		Sum	28823.17			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.437	BB	0.70	865.33	78.65	94.89	
8.714	VB	0.61	46.60	3.57	5.11	
		Sum	911.93			

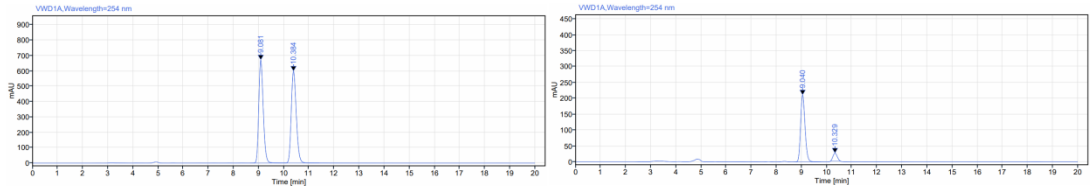


20e

The reaction of the *β*-keto ester **19e** (38 mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), $NEt_3{\cdot}3HF$ (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 48 h afforded compound **20e** (20.8 mg) in 50% yield as oil. The title compound **20e** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 5/1).

(R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.68 (m, 1H), 7.49 (m, 1H), 7.46-7.39 (m, 1H), 3.84-3.72 (m, 1H), 3.76 (s, 3H), 3.41 (dd, *J* = 23.5, 17.7 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.3 (d, $^2J_{C\text{-}F}$ = 18.2 Hz), 167.7 (d, $^2J_{C\text{-}F}$ = 28.3 Hz), 150.9 (d, $^3J_{C\text{-}F}$ = 3.6 Hz), 136.9, 133.1, 128.7, 126.7 (d, $^3J_{C\text{-}F}$ = 1.04 Hz), 125.6, 94.6 (d, $^1J_{C\text{-}F}$ = 201.3 Hz), 53.3, 38.2 (d, $^2J_{C\text{-}F}$ = 24.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -164.53. **HRMS** (ESI) m/z Calcd for $[C_{11}H_9FO_3, M+Na]^+$:231.0428, found 231.0422.

Optical Rotation: $[\alpha]_D^{25}$ -17.0 (c = 1.0, $CHCl_3$). 80% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 8.124 min for major isomer, t_R = 9.052 min for minor isomer).

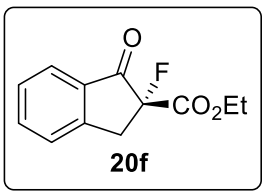


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.081	BB	1.28	8295.28	671.45	49.99	
10.384	BB	1.46	8297.97	598.02	50.01	
		Sum	16593.25			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.040	BM m	0.19	2585.25	210.86	89.78	
10.329	MM m	0.19	294.41	24.77	10.22	
		Sum	2879.67			

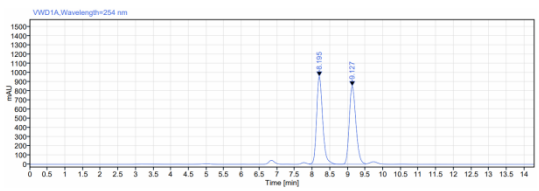


20f

The reaction of the *β*-keto ester **19f** (72.4mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), $NEt_3{\cdot}3HF$ (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 24 h afforded compound **20f** (25.8 mg) in 58% yield as oil. The title compound **20f** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 5/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.71 (td, *J* = 7.5, 1.2 Hz, 1H), 7.54-7.43 (m, 2H), 4.28 (q, *J* = 7.1 Hz, 2H), 3.79 (dd, *J* = 17.6, 11.5 Hz, 1H), 3.44 (dd, *J* = 23.3, 17.6 Hz, 1H), 1.26 (t, *J* = 7.1 Hz, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 195.5 (d, $^2J_{C\text{-}F}$ = 18.8 Hz), 167.5 (d, $^2J_{C\text{-}F}$ = 27.6 Hz), 151.1 (d, $^3J_{C\text{-}F}$ = 3.6 Hz), 136.9, 133.4, 128.8, 126.7, 125.8, 94.6 (d, $^1J_{C\text{-}F}$ = 201.3

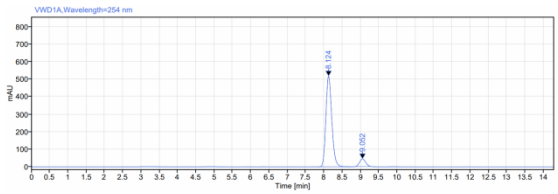
Hz), 62.8, 38.4 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz), 14.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -164.44. **HRMS** (ESI) m/z Calcd for $[C_{12}H_{11}FO_3, M+Na]^+$:245.0584, found 245.0578.

Optical Rotation: $[\alpha]_D^{25}$ -3.5 (c = 0.5, $CHCl_3$). 84% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 30 ºC, wavelength = 254 nm, t_R = 8.124 min for major isomer, t_R = 9.052 min for minor isomer).



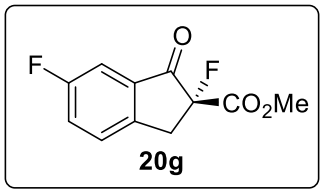
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.195	VB	0.91	11398.84	956.64	50.64	
9.127	BM m	0.20	11111.23	850.81	49.36	
		Sum	22510.07			



Signal: VWD1A,Wavelength=254 nm

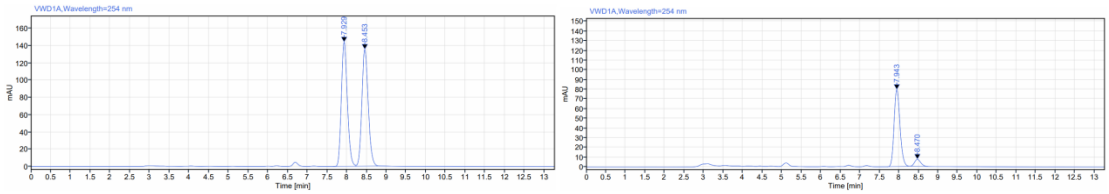
RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.124	MM m	0.17	5827.57	518.95	91.94	
9.052	MM m	0.18	510.98	44.01	8.06	
		Sum	6338.54			



20g

The reaction of the *β*-keto ester **19g** (40.8 mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), $NEt_3{\cdot}3HF$ (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 24 h afforded compound **20g** (23.9 mg) in 53% yield as a white solid. The title compound **20g** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 5/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53-7.38 (m, 3H), 3.81 (s, 3H), 3.76 (dd, *J* = 17.3, 10.6 Hz, 1H), 3.40 (dd, *J* = 23.0, 18.6 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.5 (dd, $^{2}J_{C\text{-}F}$ = 18.8, 3.5 Hz), 167.5 (d, $^{2}J_{C\text{-}F}$ = 27.7 Hz), 162.9 (d, $^{1}J_{C\text{-}F}$ = 250.6 Hz), 146.5 (dd, $^{3}J_{C\text{-}F}$ = 3.5, 2.3 Hz), 135.0 (d, $^{3}J_{C\text{-}F}$ = 7.9 Hz), 128.3 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 124.8 (d, $^{2}J_{C\text{-}F}$ = 23.6 Hz), 111.5 (d, $^{2}J_{C\text{-}F}$ = 22.5 Hz), 95.1 (d, $^{1}J_{C\text{-}F}$ = 202.4 Hz), 53.5, 37.8 (d, $^{2}J_{C\text{-}F}$ = 24.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -163.95, δ -111.89. **HRMS** (ESI) m/z Calcd for $[C_{11}H_8FO_3, M+H]^+$: 227.0514, found 227.0508.

Optical Rotation: $[\alpha]_D^{25}$ 3.2 (c = 0.5, $CHCl_3$). 83% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 30 ºC, wavelength = 254 nm, t_R = 7.943 min for major isomer, t_R = 8.470 min for minor isomer).

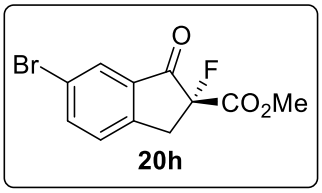


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.929	MM m	0.16	1526.52	144.16	50.01	
8.453	MM m	0.17	1525.94	135.50	49.99	
		Sum	3052.46			

Signal: VWD1A,Wavelength=254 nm

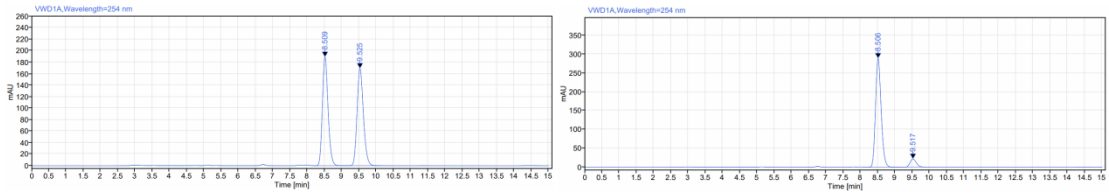
RT [min]	Type	Width [min]	Area	Height	Area%	Name
7.943	MM m	0.16	835.04	79.30	91.48	
8.470	MM m	0.17	77.75	7.18	8.52	
		Sum	912.79			



20h

The reaction of the *β*-keto ester **19h** (53.6 mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), $NEt_3{\cdot}3HF$ (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 24 h afforded compound **20h** (36.4 mg) in 64% yield as a white solid. The title compound **20h** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 5/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 2.0 Hz, 1H), 7.80 (dd, *J* = 8.2, 2.0 Hz, 1H), 7.40 (d, *J* = 8.2 Hz, 1H), 3.80 (s, 3H), 3.74 (dd, *J* = 17.8, 10.7 Hz, 1H), 3.37 (dd, *J* = 22.9, 17.8 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.0 (d, $^{2}J_{C\text{-}F}$ = 18.3 Hz), 167.4 (d, $^{2}J_{C\text{-}F}$ = 27.7 Hz), 149.4 (d, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 139.7, 135.0, 128.5, 128.3, 122.9, 94.7 (d, $^{1}J_{C\text{-}F}$ = 202.8 Hz), 53.5, 38.0 (d, $^{2}J_{C\text{-}F}$ = 24.2 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -164.2. **GC-MS** (EI) m/z Calcd for $[C_{11}H_8BrFO_3]^+$: 286.0, 288.0; found 286.0, 288.0.

Optical Rotation: $[\alpha]_D^{25}$ 4.8 (c = 0.5, $CHCl_3$). 85% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 8.506 min for major isomer, t_R = 9.517 min for minor isomer).

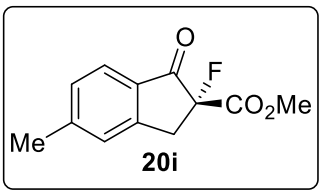


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.509	VB	0.92	2176.28	189.83	50.02	
9.525	BM m	0.20	2174.20	169.75	49.98	
		Sum	4350.48			

Signal: VWD1A,Wavelength=254 nm

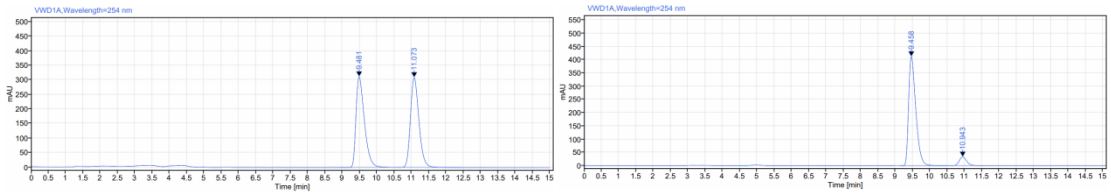
RT [min]	Type	Width [min]	Area	Height	Area%	Name
8.506	VB	1.00	3302.53	290.06	92.42	
9.517	MM m	0.19	270.94	21.84	7.58	
		Sum	3573.47			



20i

The reaction of the *β*-keto ester **19i** (40.8 mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), $NEt_3{\cdot}3HF$ (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 48 h afforded compound **20i** (21.3 mg) in 48% yield as white solid. The title compound **20i** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 5/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.28-7.21 (m, 2H), 3.75 (s, 3H), 3.70 (dd, *J* = 17.8, 11.2 Hz, 1H), 3.33 (dd, *J* = 23.4, 17.7 Hz, 1H), 2.43 (s, 3H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 194.6 (d, $^{2}J_{C\text{-}F}$ = 18.2 Hz), 167.9 (d, $^{2}J_{C\text{-}F}$ = 27.9 Hz), 151.4 (d, $^{3}J_{C\text{-}F}$ = 3.8 Hz), 148.8, 130.9, 130.1, 127.0, 125.5, 95.0 (d, $^{1}J_{C\text{-}F}$ = 201.2 Hz), 53.3, 38.1 (d, $^{2}J_{C\text{-}F}$ = 23.9 Hz), 22.4. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -164.30. **HRMS** (ESI) m/z Calcd for $[C_{12}H_{11}FO_3, M+Na]^+$:245.0584, found 245.0576.

Optical Rotation: $[\alpha]_D^{25}$ -3.5 (c = 0.5, $CHCl_3$). 85% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 9.458 min for major isomer, t_R = 10.943 min for minor isomer).

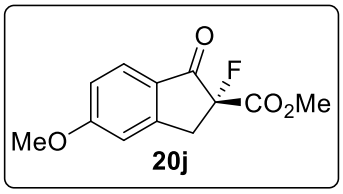


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.481	BB	1.76	5264.97	312.56	49.98	
11.073	BB	1.77	5269.13	309.53	50.02	
		Sum	10534.10			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
9.458	VM m	0.22	5949.18	412.50	92.48	
10.943	MM m	0.23	484.01	32.98	7.52	
		Sum	6433.19			

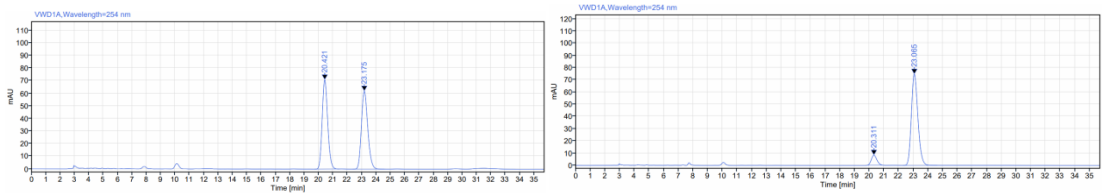


20j

The reaction of the *β*-keto ester **19j** (44.0 mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), $NEt_3{\cdot}3HF$ (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 72 h afforded compound **20j** (21.3 mg) in 50% yield as a white solid. The title compound **20j** was isolated through chromatography on silica gel eluting with petroleum

ether/ethyl acetate (20/1 to 5/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.6 Hz, 1H), 6.98 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.91 (d, *J* = 2.2 Hz, 1H), 3.92 (s, 3H), 3.81 (s, 3H), 3.75 (dd, *J* = 17.7, 11.0 Hz, 1H), 3.38 (dd, *J* = 23.0, 17.7 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.1 (d, $^2J_{C\text{-}F}$ = 18.2 Hz), 168.1 (d, $^2J_{C\text{-}F}$ = 28.3 Hz), 167.0, 154.2 (d, $^3J_{C\text{-}F}$ = 3.7 Hz), 127.7, 126.4, 116.9, 109.9, 95.2 (d, $^1J_{C\text{-}F}$ = 201.3 Hz), 56.1, 53.4, 38.4 (d, $^2J_{C\text{-}F}$ = 24.0 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -163.60. **HRMS** (ESI) m/z Calcd for [$C_{12}H_{11}FO_4$, M+Na]$^+$:261.0534, found 261.0528

Optical Rotation: $[\alpha]_D^{25}$ 37 (c = 1, $CHCl_3$). 83% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 20.311 min for minor isomer, t_R = 23.065 min for major isomer).

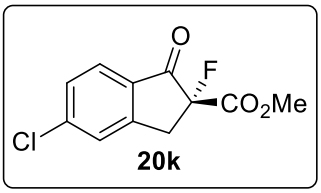


Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
20.421	BB	1.71	1899.28	70.93	49.87	
23.175	BB	2.22	1909.20	61.98	50.13	
		Sum	3808.48			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
20.311	MM m	0.41	216.25	8.25	8.55	
23.065	BB	2.33	2313.19	74.70	91.45	
		Sum	2529.44			

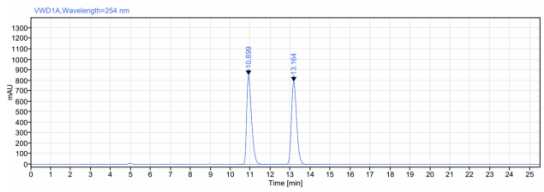


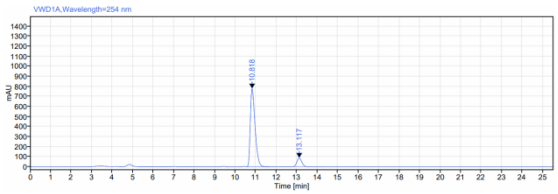
20k

The reaction of the *β*-keto ester **19k** (44.8 mg, 0.20 mmol, 1.0 equiv.), ^{m}CPBA (61.8mg, 0.3 mmol, 1.5 equiv.), **Cat-38** (0.03 mmol, 15 mol%), NEt_3·3HF (334 uL, 2 mmol, 10 equiv.) in $CHCl_3$ (8 mL) at 25 °C for 48 h afforded compound **20k** (22.3 mg) in 46% yield as a white solid. The title compound **20k** was isolated through chromatography on silica gel eluting with petroleum ether/ethyl acetate (20/1 to 5/1). (R_f = 0.6, petroleum ether/ethyl acetate = 5/1). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.49 (s, 1H), 7.43 (d, *J* = 10.0 Hz, 1H), 3.79 (s, 3H), 3.77 (dd, *J* = 17.9, 11.1 Hz, 1H), 3.40 (dd, *J* = 23.0, 17.8 Hz, 1H).; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 193.8 (d, $^2J_{C\text{-}F}$ = 18.2 Hz), 167.4 (d, $^2J_{C\text{-}F}$ = 28.2 Hz), 152.3 (d, $^3J_{C\text{-}F}$ = 4.2 Hz), 143.6, 131.7, 129.7, 127.0, 126.8, 94.6 (d, $^1J_{C\text{-}F}$ = 202.4 Hz), 53.5,

38.0 ($^{2}J_{C\text{-}F}$, J = 24.1 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -164.07. **GC-MS (EI)** m/z Calcd for $[C_{11}H_8ClFO]^+$: 242.0, 244.0; found 242.0, 244.0

Optical Rotation: $[\alpha]_D^{25}$ 33 (c = 1, $CHCl_3$). 80% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 90:10, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 10.818 min for major isomer, t_R = 13.117 min for minor isomer).





Signal: VWD1A,Wavelength=254 nm

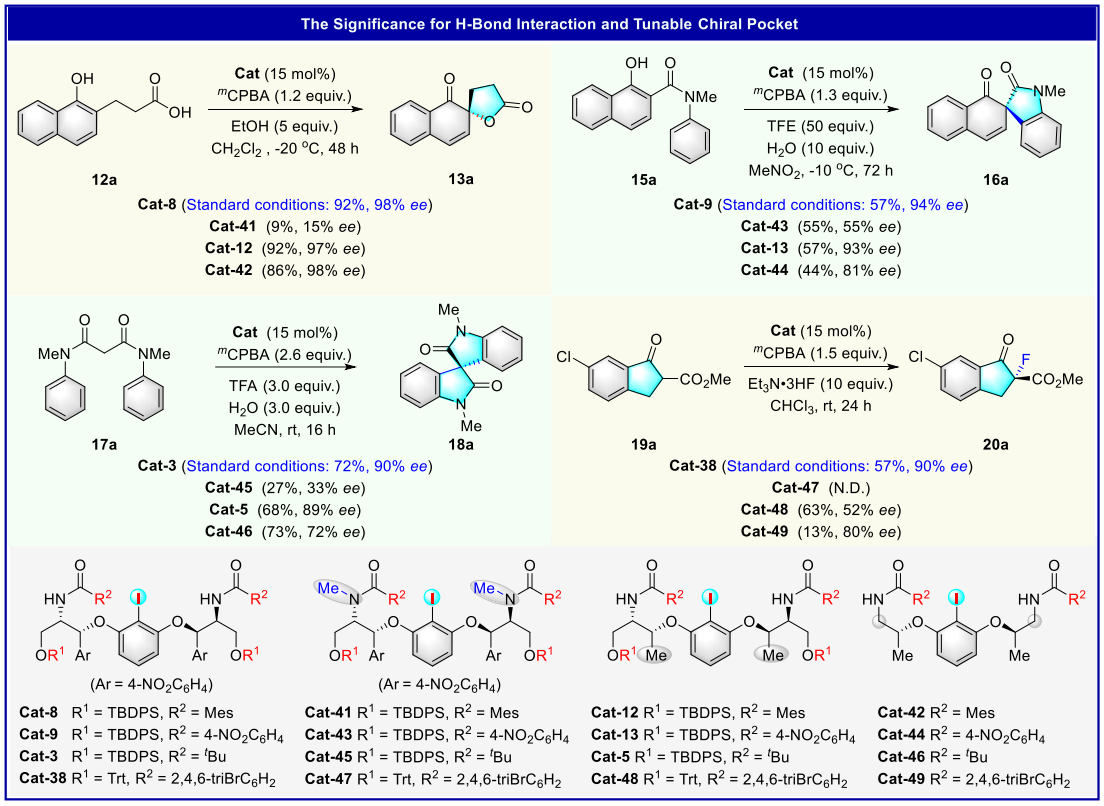
RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.899	BB	2.06	14425.53	848.00	50.25	
13.164	BB	2.45	14282.49	786.17	49.75	
		Sum	28708.02			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
10.818	MM m	0.25	12529.78	776.38	89.92	
13.117	MM m	0.26	1404.63	84.53	10.08	
		Sum	13934.41			

8. Investigation of the significance for H-bond interactions and tunable chiral pocket

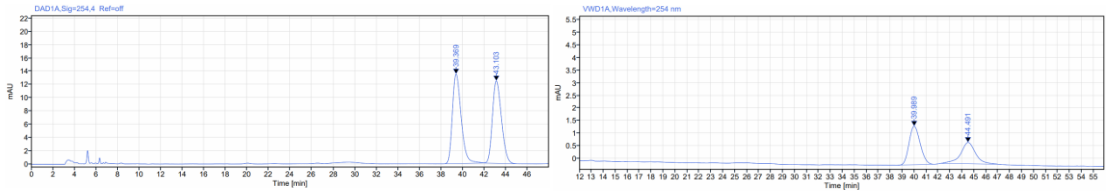
Supplementary Table 5. Investigation of the significance for H-bond interactions and tunable chiral pocket.



General procedure for the control experiment of oxidative dearomatization: To a Schlenk tube containing **Cat** (0.03 mmol, 15 mol%), ^{m}CPBA (0.3 mmol, 1.5 equiv.) and EtOH (1 mmol, 5 equiv.) were added CH_2Cl_2 (10 mL) and **12a** (0.2 mmol). The reaction mixture was stirred at -20 °C for 24 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was subsequently extracted with dichloromethane, washed with brine, dried over anhydrous Na_2SO_4. Finally, the mixture was concentrated in vacuo and then the residue was purified by silica gel column chromatography to afford the product **13a**.

Experiment of oxidative dearomatization using **Cat-41:** 15% *ee* (HPLC conditions: Chiralpak AS-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C,

wavelength = 254 nm, t_R = 39.989 min for major isomer, t_R = 44.491 min for minor isomer)



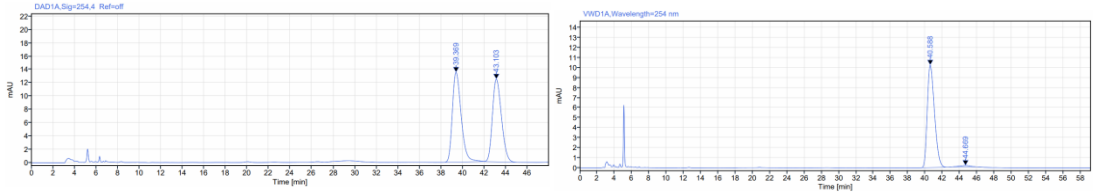
Signal: DAD1A,Sig=254,4 Ref=off

RT [min]	Type	Width [min]	Area	Height	Area%	Name
39.369	BM m	0.84	766.14	13.51	51.38	
43.103	MB m	0.87	725.03	12.44	48.62	
		Sum	1491.17			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
39.989	MM m	0.76	98.84	1.53	57.25	
44.491	MM m	1.02	73.80	0.84	42.75	
		Sum	172.64			

Experiment of oxidative dearomatization using **Cat-12:** 97% *ee* (HPLC conditions: Chiralpak AS-H column, *n*-Hexane/*i*-PrOH = 85:15, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 40.588 min for major isomer, t_R = 44.669 min for minor isomer)



Signal: DAD1A,Sig=254,4 Ref=off

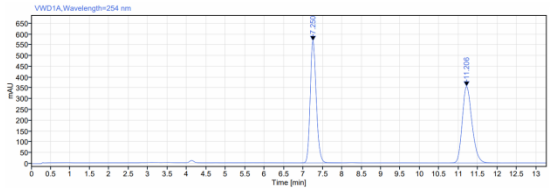
RT [min]	Type	Width [min]	Area	Height	Area%	Name
39.369	BM m	0.84	766.14	13.51	51.38	
43.103	MB m	0.87	725.03	12.44	48.62	
		Sum	1491.17			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
40.588	BB	2.91	592.84	10.26	98.28	
44.669	MM m	0.90	10.36	0.14	1.72	
		Sum	603.20			

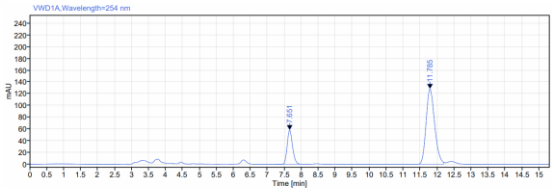
General procedure for the control experiment of oxidative spirolactonization. To a Schlenk tube containing **Cat** (0.03 mmol, 15 mol%), ^{m}CPBA (0.26 mmol, 1.3 equiv.), TFE (10 mmol, 50 equiv.), H_2O (2 mmol, 10 equiv.) and $MeNO_2$ (3 mL) were added **15a** (0.2 mmol). The reaction mixture was stirred at -10 °C for 72 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. Finally, the organic layer was subsequently extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4. The mixture was concentrated *in vacuo* and then the residue was purified by silica gel column chromatography to afford the product **16a**.

Experiment of oxidative spirolactonization using **Cat-43:** 55% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 7.651 min for minor isomer, t_R = 11.785 min for major isomer).



Signal: VWD1A,Wavelength=254 nm

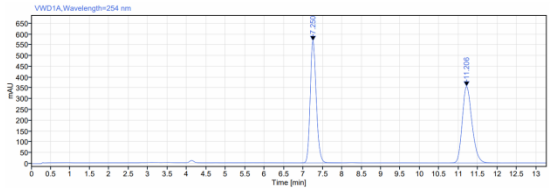
RT [min]	Type	Width [min]	Area	Height	Area%
7.250	BB	1.03	6138.37	564.86	49.96
11.206	BB	1.29	6147.29	354.09	50.04
		Sum	12285.66		



Signal: VWD1A,Wavelength=254 nm

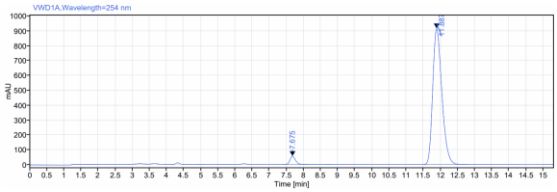
RT [min]	Type	Width [min]	Area	Height	Area%
7.651	BB	1.01	642.11	58.07	22.28
11.785	MM m	0.27	2240.04	128.17	77.72
		Sum	2882.14		

Experiment of oxidative spirolactonization using **Cat-13:** 93% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 7.675 min for minor isomer, t_R = 11.887 min for major isomer).



Signal: VWD1A,Wavelength=254 nm

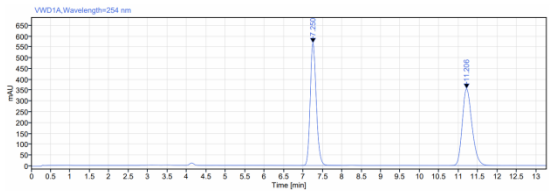
RT [min]	Type	Width [min]	Area	Height	Area%
7.250	BB	1.03	6138.37	564.86	49.96
11.206	BB	1.29	6147.29	354.09	50.04
		Sum	12285.66		



Signal: VWD1A,Wavelength=254 nm

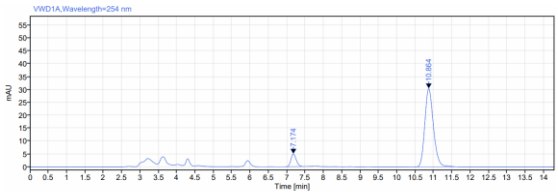
RT [min]	Type	Width [min]	Area	Height	Area%
7.675	MM m	0.17	625.35	55.02	3.56
11.887	MM m	0.29	16953.90	913.48	96.44
		Sum	17579.24		

Experiment of oxidative spirolactonization using **Cat-44:** 81% *ee* (HPLC conditions: Chiralpak AD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 7.174 min for minor isomer, t_R = 10.864 min for major isomer).



Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%
7.250	BB	1.03	6138.37	564.86	49.96
11.206	BB	1.29	6147.29	354.09	50.04
		Sum	12285.66		

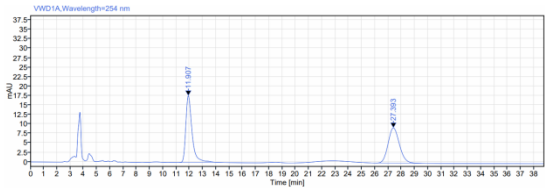


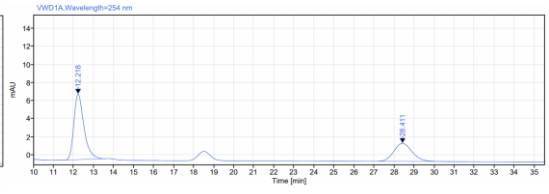
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%
7.174	BB	0.56	50.03	4.90	9.17
10.864	BM m	0.25	495.79	30.36	90.83
		Sum	545.81		

General procedure for the control experiment of direct C(sp^2)-H/C(sp^3)-H cross-coupling. To a Schlenk tube containing **Cat** (0.03 mmol, 15 mol%), ^{m}CPBA (0.52 mmol, 2.6 equiv.), TFA (0.6 mmol, 3 equiv.) and H_2O (0.6 mmol, 3 equiv.) and MeCN (3 mL) were added **17a** (0.2 mmol). The reaction mixture was stirred at 25 °C for 16 hours. which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was subsequently extracted with ethyl acetate, washed with brine, dried over anhydrous Na_2SO_4. Finally, the mixture was concentrated *in vacuo* and then the residue was purified by silica gel column chromatography to afford the product **18a**.

Experiment of direct C(sp^2)-H/C(sp^3)-H cross-coupling using **Cat-45:** 33% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 11.907 min for major isomer, t_R = 27.393 min for minor isomer).





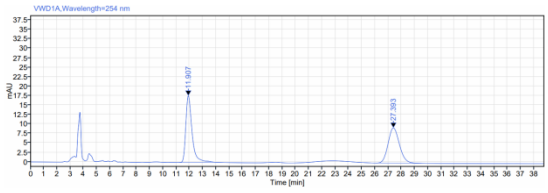
Signal: VWD1A,Wavelength=254 nm

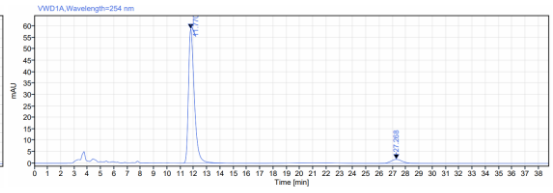
RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.907	BM m	0.49	573.32	17.62	50.93	
27.393	BB	3.40	552.33	9.31	49.07	
		Sum	1125.65			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
12.218	BB	1.99	254.65	7.27	66.70	
28.411	BB	3.11	127.11	2.00	33.30	
		Sum	381.76			

Experiment of direct C(sp^2)-H/C(sp^3)-H cross-coupling using **Cat-5:** 89% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 11.770 min for major isomer, t_R = 27.268 min for minor isomer).





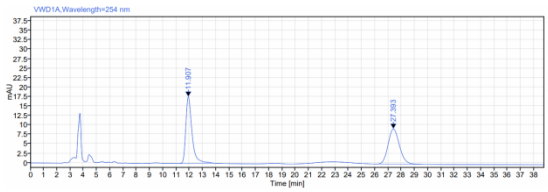
Signal: VWD1A,Wavelength=254 nm

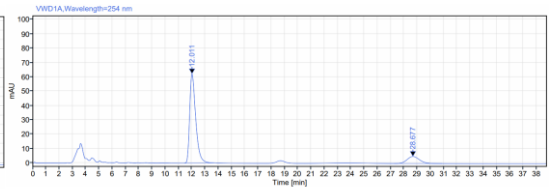
RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.907	BM m	0.49	573.32	17.62	50.93	
27.393	BB	3.40	552.33	9.31	49.07	
		Sum	1125.65			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
11.770	BB	3.87	1804.97	58.70	94.59	
27.268	BB	2.93	103.22	1.74	5.41	
		Sum	1908.19			

Experiment of direct C(sp^2)-H/C(sp^3)-H cross-coupling using **Cat-46:** 72% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 70:30, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 12.011 min for major isomer, t_R = 28.677min for minor isomer).





Signal: VWD1A,Wavelength=254 nm

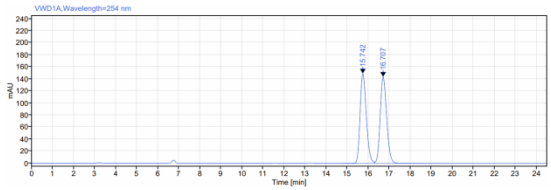
RT [min]	Type	Width [min]	Area	Height	Area%
11.907	BM m	0.49	573.32	17.62	50.93
27.393	BB	3.40	552.33	9.31	49.07
		Sum	1125.65		

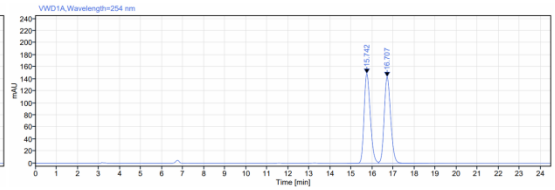
Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%
12.011	MM m	0.48	1964.89	62.23	85.96
28.677	BB	3.59	320.91	4.93	14.04
		Sum	2285.79		

General procedure for the control experiment of fluorinated keto esters. To 25 mL Teflon tube containing *β*-ketoesters **19a** (0.20 mmol), **Cat** (0.03 mmol, 15 mol%), and $CHCl_3$ (8 mL) were added. Subsequently, $NEt_3{\cdot}3HF$ (2 mmol, 10 equiv.) and ^{m}CPBA (0.3 mmol, 1.5 equiv.) was loaded in turn. The reaction mixture was stirred at 25 °C for 24 hours, which was then quenched in the sequence of saturated $Na_2S_2O_3$ and $NaHCO_3$ aqueous solution. The organic layer was subsequently extracted with dichloromethane, washed with brine, dried over anhydrous Na_2SO_4. Finally, the mixture was concentrated *in vacuo* and then the residue was purified by silica gel column chromatography to afford desired products **20a**.

Experiment of fluorinated keto esters using **Cat-48**: 80% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, 30 °C, wavelength = 254 nm, t_R = 15.839 min for major isomer, t_R = 16.792 min for minor isomer).





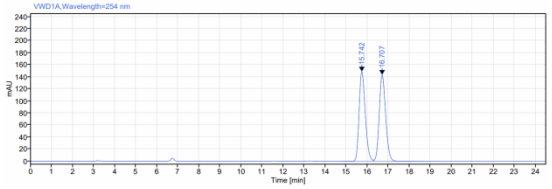
Signal: VWD1A,Wavelength=254 nm

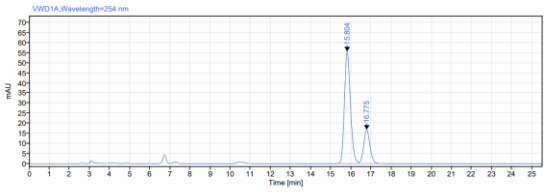
RT [min]	Type	Width [min]	Area	Height	Area%
15.742	BV	1.49	3043.52	148.70	49.80
16.707	VB	2.38	3067.44	143.30	50.20
		Sum	6110.96		

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%
15.742	BV	1.49	3043.52	148.70	49.80
16.707	VB	2.38	3067.44	143.30	50.20
		Sum	6110.96		

Experiment of fluorinated keto esters using **Cat-49**: 52% *ee* (HPLC conditions: Chiralpak OD-H column, *n*-Hexane/*i*-PrOH = 95:5, flow rate = 1.0 mL/min, 30 ^{o}C, wavelength = 254 nm, t_R = 15.804 min for major isomer, t_R = 16.775 min for minor isomer).





Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
15.742	BV	1.49	3043.52	148.70	49.80	
16.707	VB	2.38	3067.44	143.30	50.20	
		Sum	6110.96			

Signal: VWD1A,Wavelength=254 nm

RT [min]	Type	Width [min]	Area	Height	Area%	Name
15.804	BM m	0.32	1151.15	55.41	76.13	
16.775	MM m	0.34	360.97	16.59	23.87	
		Sum	1512.12			

9. Reference

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[5] Wu, H., He, Y.-P., Xu, L., Zhang, D.-Y. & Gong, L.-Z. Asymmetric organocatalytic direct $C(sp^2)$−H/$C(sp^3)$−H oxidative cross-coupling by chiral iodine reagent. *Angew. Chem. Int. Ed.* **53**, 3466−3469 (2014).

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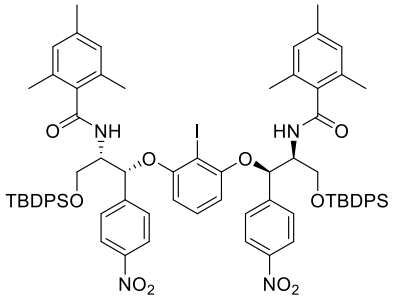
[8] Bower, J.F., Szeto, P. & Gallagher, T. Enantiopure 1,4-benzoxazines via 1,2-cyclic sulfamidates. Synthesis of levofloxacin. *Org. Lett.* **9**, 3283−3286 (2007).

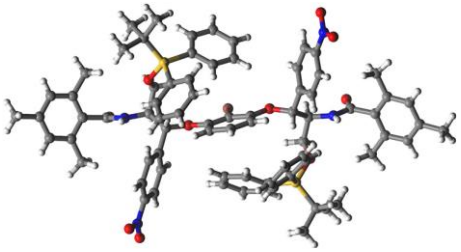
[9] Butler, E., Florentino, L., Cornut, D., Gomez-Campillos, G., Liu, H., Regan, A. C. & Thomas, E. J. Enantiopure 1,4-benzoxazines via 1,2-cyclic sulfamidates. Synthesis of macrocyclic precursors of the vioprolides. *Org. Biomol. Chem*. **16**, 6935−6960 (2018).

10. X-ray crystallography analysis

Cat-8 (CCDC 2236217)



Cat-8



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_230104_zhj_mes

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_230104_zhj_mes

```
Bond precision:   C-C = 0.0042 A          Wavelength=0.71073

Cell:              a=13.3936(3)      b=27.4740(6)      c=9.5840(2)
                   alpha=90          beta=90           gamma=90
Temperature:       170 K

                  Calculated                Reported
Volume            3526.68(13)               3526.68(13)
Space group       P 21 21 2                 P 21 21 2
Hall group        P 2 2ab                   P 2 2ab
Moiety formula    C76 H81 I N4 O10 Si2      C76 H81 I N4 O10 Si2
Sum formula       C76 H81 I N4 O10 Si2      C76 H81 I N4 O10 Si2
Mr                1393.53                   1393.52
Dx,g cm-3         1.312                     1.312
Z                 2                         2
Mu (mm-1)         0.549                     0.549
F000              1452.0                    1452.0
F000'             1451.95
h,k,lmax          17,35,12                  17,35,12
Nref              8135[ 4559]               8123
Tmin,Tmax         0.810,0.848               0.679,0.746
Tmin'             0.768

Correction method= # Reported T Limits: Tmin=0.679 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.78/1.00        Theta(max)= 27.495

R(reflections)= 0.0245( 7539)                    wR2(reflections)=
                                                 0.0584( 8123)
S = 1.046                  Npar= 470
```

```
The following ALERTS were generated. Each ALERT has the format
       test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.
```

Alert level C

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PLAT220_ALERT_2_C NonSolvent    Resd 1   C    Ueq(max)/Ueq(min) Range        4.3 Ratio
PLAT222_ALERT_3_C NonSolvent Resd 1   H    Uiso(max)/Uiso(min) Range        4.1 Ratio
PLAT911_ALERT_3_C Missing FCF Refl Between Thmin & STh/L=     0.600           3 Report
```

Alert level G

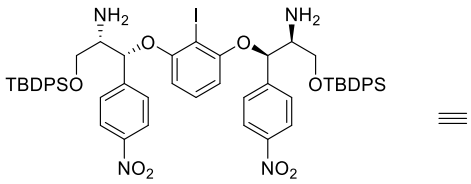
```
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite          13 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...           9 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms .............            1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records          15 Report
PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records           1 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used      0.0200 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used      0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used      0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used      0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used      0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used      0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used      0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used      0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used      0.0400 Report
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )          13% Note
PLAT791_ALERT_4_G Model has Chirality at C5           (Sohnke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C12          (Sohnke SpGr)          S Verify
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............          111 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).           2 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600           1 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File           3 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.           9 Info
```

```
  0 ALERT level A = Most likely a serious problem - resolve or explain
  0 ALERT level B = A potentially serious problem, consider carefully
  3 ALERT level C = Check. Ensure it is not caused by an omission or oversight
 22 ALERT level G = General information/check it is not something unexpected

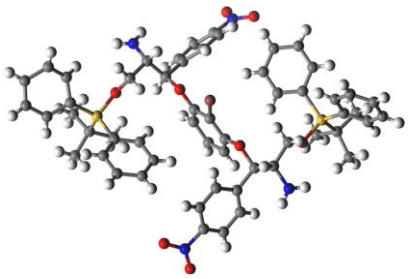
  0 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
  5 ALERT type 2 Indicator that the structure model may be wrong or deficient
 14 ALERT type 3 Indicator that the structure quality may be low
  5 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```

Supplementary Figure 5. Single-crystal X-ray crystallography of **Cat-8**

11 (CCDC 2236218)



11



checkCIF/PLATON report

Structure factors have been supplied for datablock(s) mo_230103_zhj_nh2_0m

THIS REPORT IS FOR GUIDANCE ONLY. IF USED AS PART OF A REVIEW PROCEDURE FOR PUBLICATION, IT SHOULD NOT REPLACE THE EXPERTISE OF AN EXPERIENCED CRYSTALLOGRAPHIC REFEREE.

No syntax errors found. CIF dictionary Interpreting this report

Datablock: mo_230103_zhj_nh2_0m

```
Bond precision:   C-C = 0.0087 A          Wavelength=0.71073

Cell:               a=28.216(9)      b=13.252(2)      c=14.528(3)
                    alpha=90         beta=90          gamma=90
Temperature:        170 K

                 Calculated                Reported
Volume           5432(2)                   5432(2)
Space group      P 21 21 2                 P 21 21 2
Hall group       P 2 2ab                   P 2 2ab
Moiety formula   C56 H60 I N4 O8 Si2       C56 H60 I N4 O8 Si2
Sum formula      C56 H60 I N4 O8 Si2       C56 H61 I N4 O8 Si2
Mr               1100.16                   1101.16
Dx,g cm-3        1.345                     1.346
Z                4                         4
Mu (mm-1)        0.690                     0.690
F000             2276.0                    2280.0
F000'            2275.63
h,k,lmax         39,18,20                  38,18,20
Nref             16096[ 8799]              15884
Tmin,Tmax        0.767,0.813               0.663,0.746
Tmin'            0.718

Correction method= # Reported T Limits: Tmin=0.663 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.81/0.99        Theta(max)= 30.159

R(reflections)= 0.0439( 11790)                wR2(reflections)=
                                              0.1185( 15884)
S = 1.035                  Npar= 811
```

The following ALERTS were generated. Each ALERT has the format
test-name_ALERT_alert-type_alert-level.
Click on the hyperlinks for more details of the test.

Alert level C

```
PLAT041_ALERT_1_C Calc. and Reported SumFormula    Strings  Differ     Please Check
PLAT068_ALERT_1_C Reported F000 Differs from Calcd (or Missing)...     Please Check
PLAT220_ALERT_2_C NonSolvent   Resd 1  C   Ueq(max)/Ueq(min) Range       3.5 Ratio
PLAT234_ALERT_4_C Large Hirshfeld Difference C17      --C18      .      0.17 Ang.
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of       C16 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of       C18 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of       C24 Check
PLAT241_ALERT_2_C High   'MainMol' Ueq as Compared to Neighbors of       C47 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C10 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C14 Check
PLAT242_ALERT_2_C Low    'MainMol' Ueq as Compared to Neighbors of       C35 Check
PLAT342_ALERT_3_C Low Bond Precision on  C-C Bonds ..............   0.00868 Ang.
PLAT415_ALERT_2_C Short Inter D-H..H-X       H1B      ..H36C     .      2.05 Ang.
                                                 x,y,1+z  =     1_556 Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N1       --H1A      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N1       --H1B      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N3       --H3A      .     Please Check
PLAT420_ALERT_2_C D-H Bond Without Acceptor  N3       --H3B      .     Please Check
PLAT934_ALERT_3_C Number of (Iobs-Icalc)/Sigma(W) > 10 Outliers ..          1 Check
PLAT975_ALERT_2_C Check Calcd Resid. Dens.  1.08Ang From C7      .      0.52 eA-3
```

Alert level G

```
FORMU01_ALERT_1_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and _chemical_formula_moiety. This is
           usually due to the moiety formula being in the wrong format.
           Atom count from _chemical_formula_sum:   C56 H61 I1 N4 O8 Si2
           Atom count from _chemical_formula_moiety:C56 H60 I1 N4 O8 Si2
FORMU01_ALERT_2_G  There is a discrepancy between the atom counts in the
           _chemical_formula_sum and the formula from the _atom_site* data.
           Atom count from _chemical_formula_sum:C56 H61 I1 N4 O8 Si2
           Atom count from the _atom_site data:  C56 H60 I1 N4 O8 Si2
CELLZ01_ALERT_1_G Difference between formula and atom_site contents detected.
CELLZ01_ALERT_1_G WARNING: H atoms missing from atom site list. Is this intentional?
          From the CIF: _cell_formula_units_Z    4
          From the CIF: _chemical_formula_sum  C56 H61 I N4 O8 Si2
          TEST: Compare cell contents of formula and atom_site data

          atom    Z*formula  cif sites diff
          C         224.00    224.00    0.00
          H         244.00    240.00    4.00
          I           4.00      4.00    0.00
          N          16.00     16.00    0.00
          O          32.00     32.00    0.00
          Si          8.00      8.00    0.00
PLAT002_ALERT_2_G Number of Distance or Angle Restraints on AtSite         40 Note
PLAT003_ALERT_2_G Number of Uiso or Uij Restrained non-H Atoms ...         39 Report
PLAT007_ALERT_5_G Number of Unrefined Donor-H Atoms ..............          4 Report
PLAT172_ALERT_4_G The CIF-Embedded .res File Contains DFIX Records          1 Report
PLAT176_ALERT_4_G The CIF-Embedded .res File Contains SADI Records         44 Report
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PLAT178_ALERT_4_G The CIF-Embedded .res File Contains SIMU Records          3 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used     0.0200 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used     0.0100 Report
PLAT188_ALERT_3_G A Non-default SIMU Restraint Value has been used     0.0100 Report
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PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
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PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
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PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT191_ALERT_3_G A Non-default SADI Restraint Value has been used     0.0400 Report
PLAT301_ALERT_3_G Main Residue  Disorder .............(Resd  1  )         25% Note
PLAT367_ALERT_2_G Long?  C(sp?)-C(sp?) Bond  C7       - C8       .       1.55 Ang.
PLAT410_ALERT_2_G Short Intra H...H Contact  H28      ..H48      .       2.08 Ang.
                                                      x,y,z  =     1_555 Check
PLAT410_ALERT_2_G Short Intra H...H Contact  H34B     ..H40A     .       2.03 Ang.
                                                      x,y,z  =     1_555 Check
PLAT410_ALERT_2_G Short Intra H...H Contact  H44A     ..H46      .       1.93 Ang.
                                                      x,y,z  =     1_555 Check
PLAT412_ALERT_2_G Short Intra XH3 .. XHn     H37C     ..H44      .       2.12 Ang.
                                                      x,y,z  =     1_555 Check
PLAT789_ALERT_4_G Atoms with Negative _atom_site_disorder_group  #        26 Check
PLAT791_ALERT_4_G Model has Chirality at C8          (Sohnke SpGr)          S Verify
PLAT791_ALERT_4_G Model has Chirality at C32         (Sohnke SpGr)          R Verify
PLAT791_ALERT_4_G Model has Chirality at C33         (Sohnke SpGr)          S Verify
PLAT811_ALERT_5_G No ADDSYM Analysis: Too Many Excluded Atoms ....          ! Info
PLAT860_ALERT_3_G Number of Least-Squares Restraints ............         585 Note
PLAT910_ALERT_3_G Missing # of FCF Reflection(s) Below Theta(Min).          4 Note
PLAT912_ALERT_4_G Missing # of FCF Reflections Above STh/L=  0.600         20 Note
PLAT933_ALERT_2_G Number of HKL-OMIT Records in Embedded .res File          1 Note
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.          1 Info
```

---

 0 **ALERT level A** = Most likely a serious problem - resolve or explain
 0 **ALERT level B** = A potentially serious problem, consider carefully
19 **ALERT level C** = Check. Ensure it is not caused by an omission or oversight
53 **ALERT level G** = General information/check it is not something unexpected

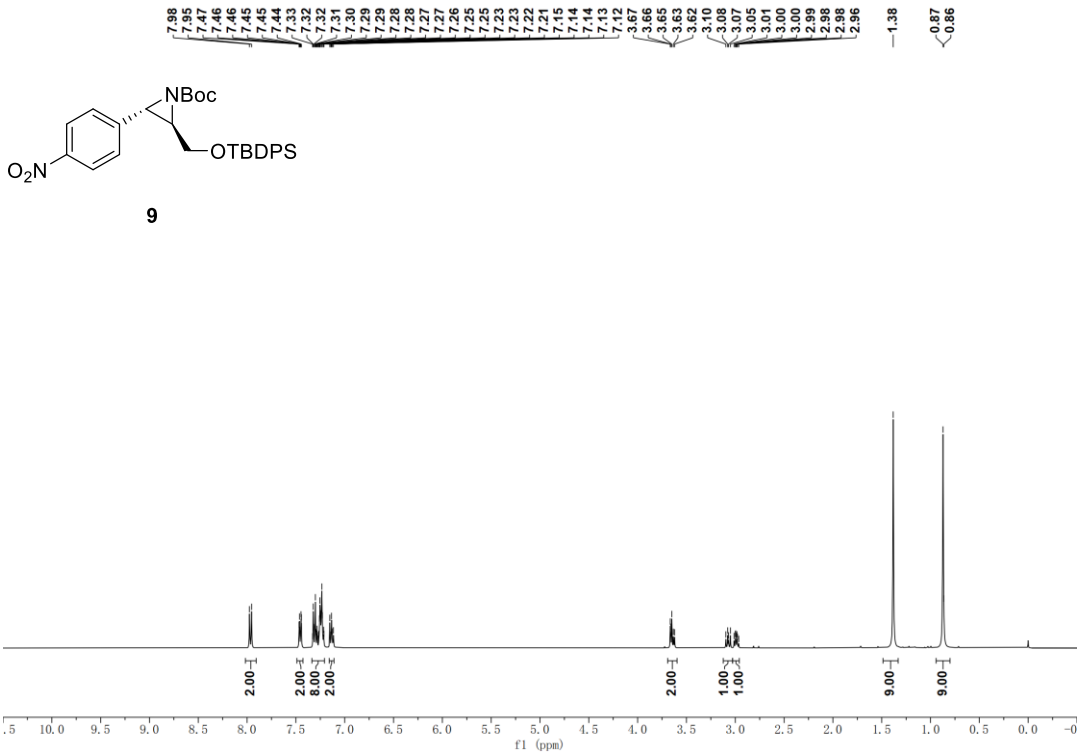
 5 ALERT type 1 CIF construction/syntax error, inconsistent or missing data

24 ALERT type 2 Indicator that the structure model may be wrong or deficient
32 ALERT type 3 Indicator that the structure quality may be low
 9 ALERT type 4 Improvement, methodology, query or suggestion
 2 ALERT type 5 Informative message, check

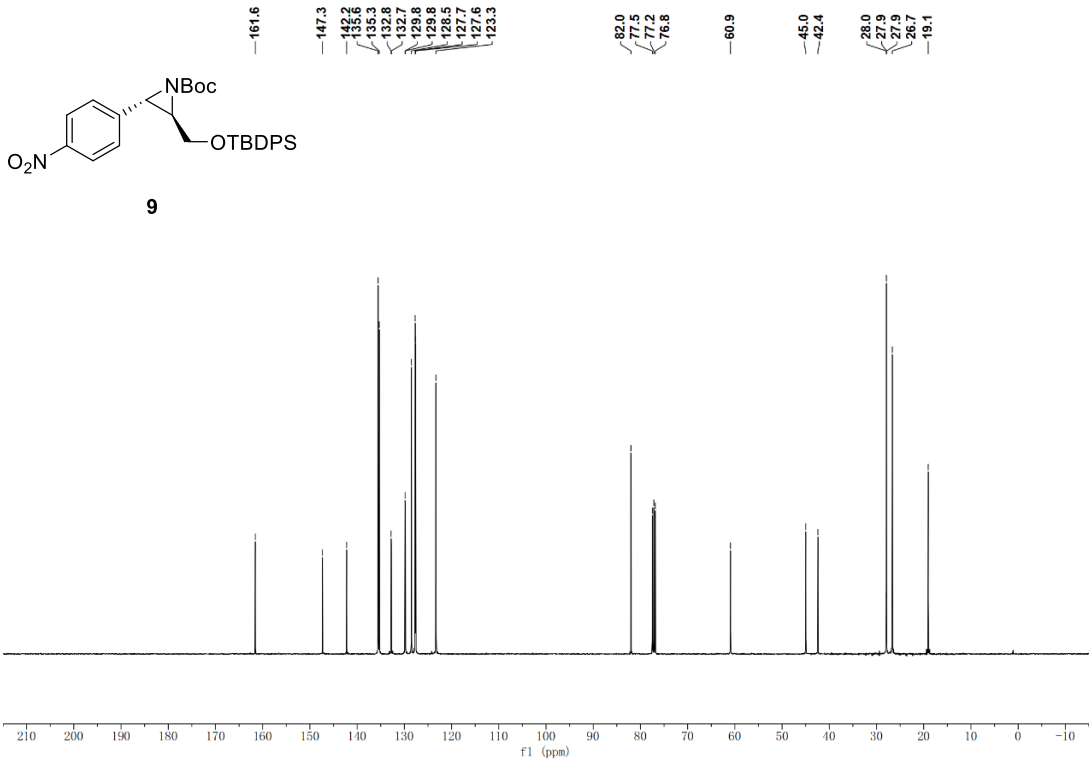
Supplementary Figure 6. Single-crystal X-ray crystallography of **11**

11. ^{1}H, ^{13}C, ^{19}F spectrum of compounds

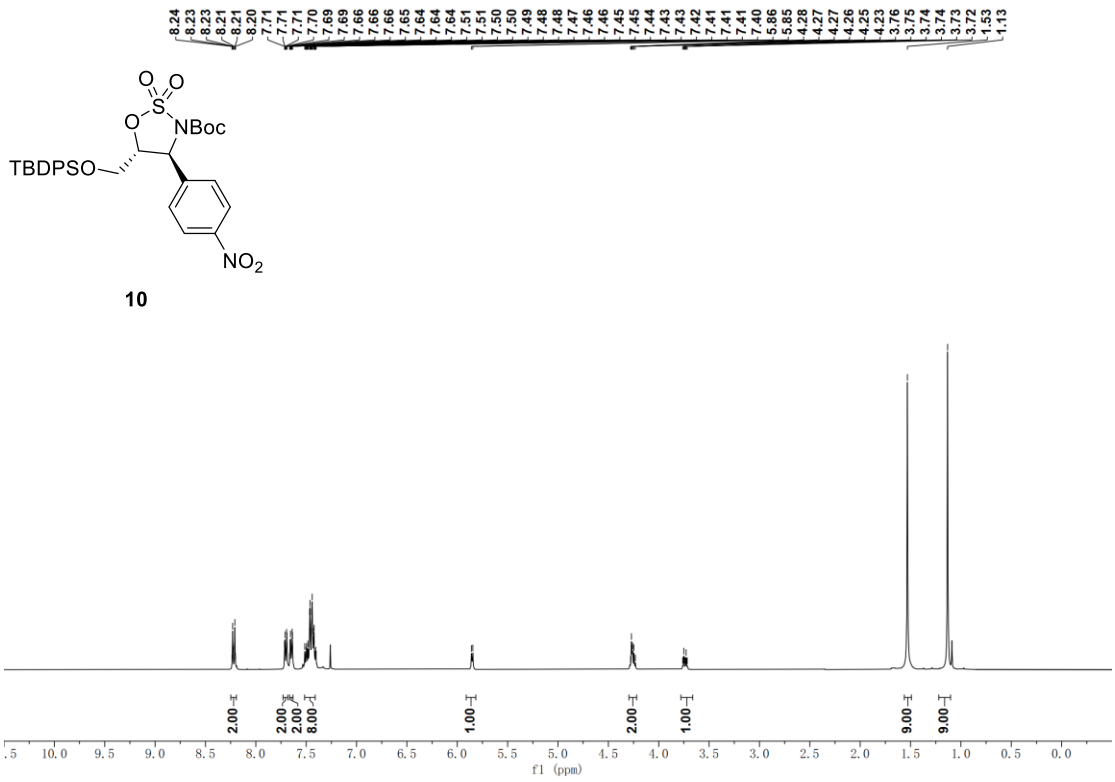
11.1 NMR spectra of intermediates and catalyst



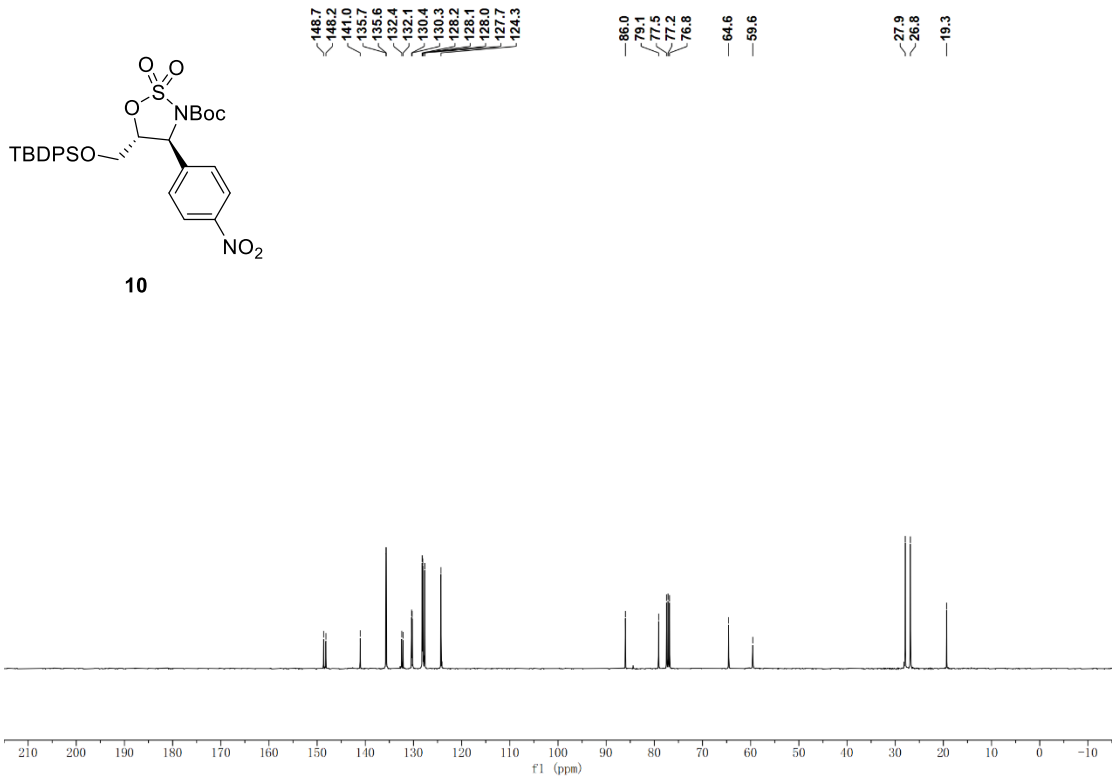
Supplementary Figure 7. ^{1}H NMR Spectrum of **9** (**400** MHz, $CDCl_3$)



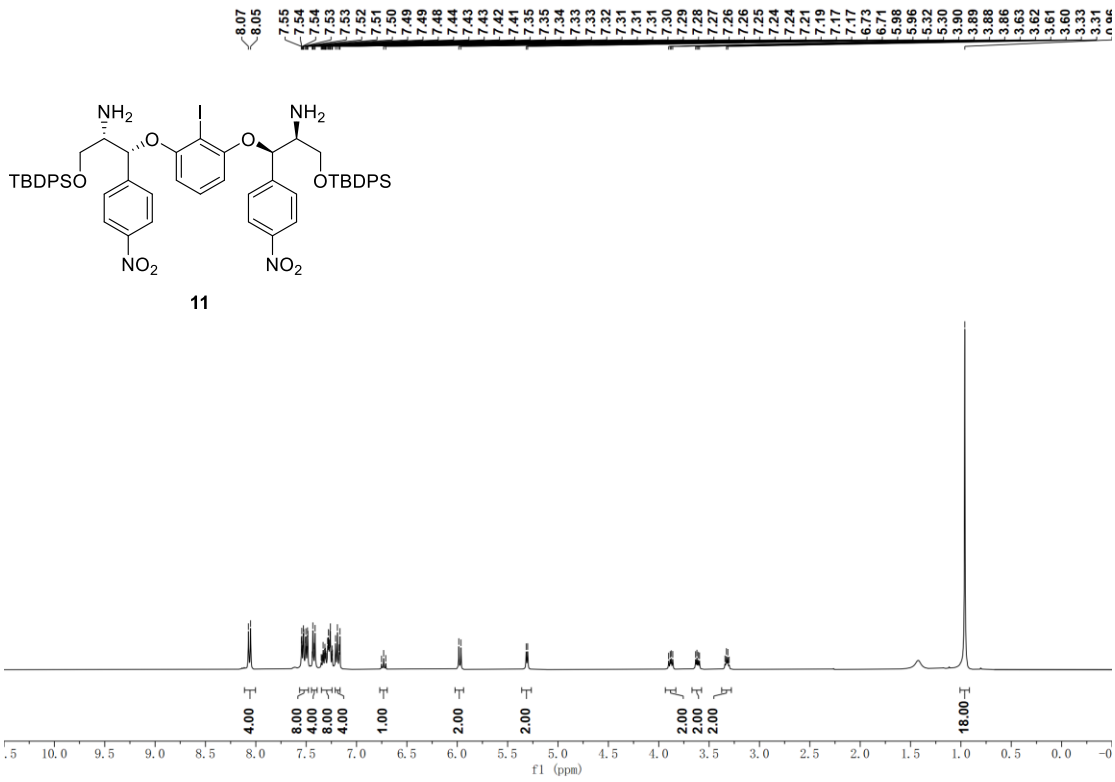
Supplementary Figure 8. ^{13}C NMR Spectrum of **9** (**100** MHz, $CDCl_3$)



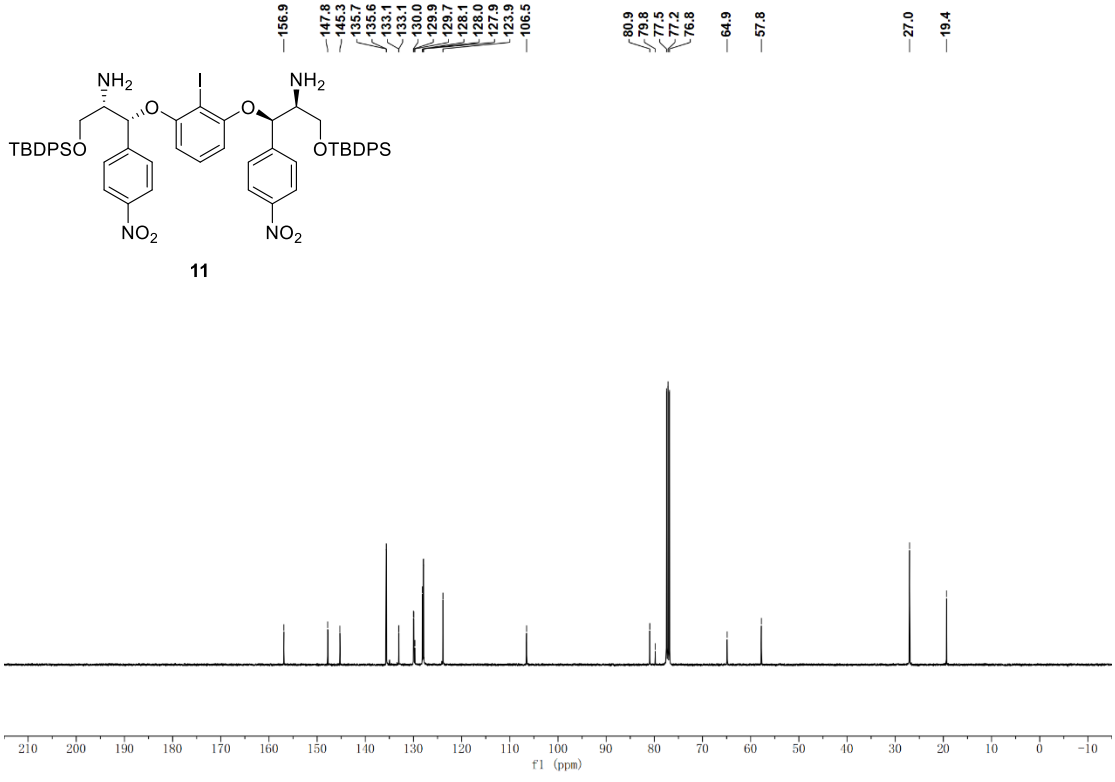
Supplementary Figure 9. ^{1}H NMR Spectrum of **10** (**400** MHz, $CDCl_3$)



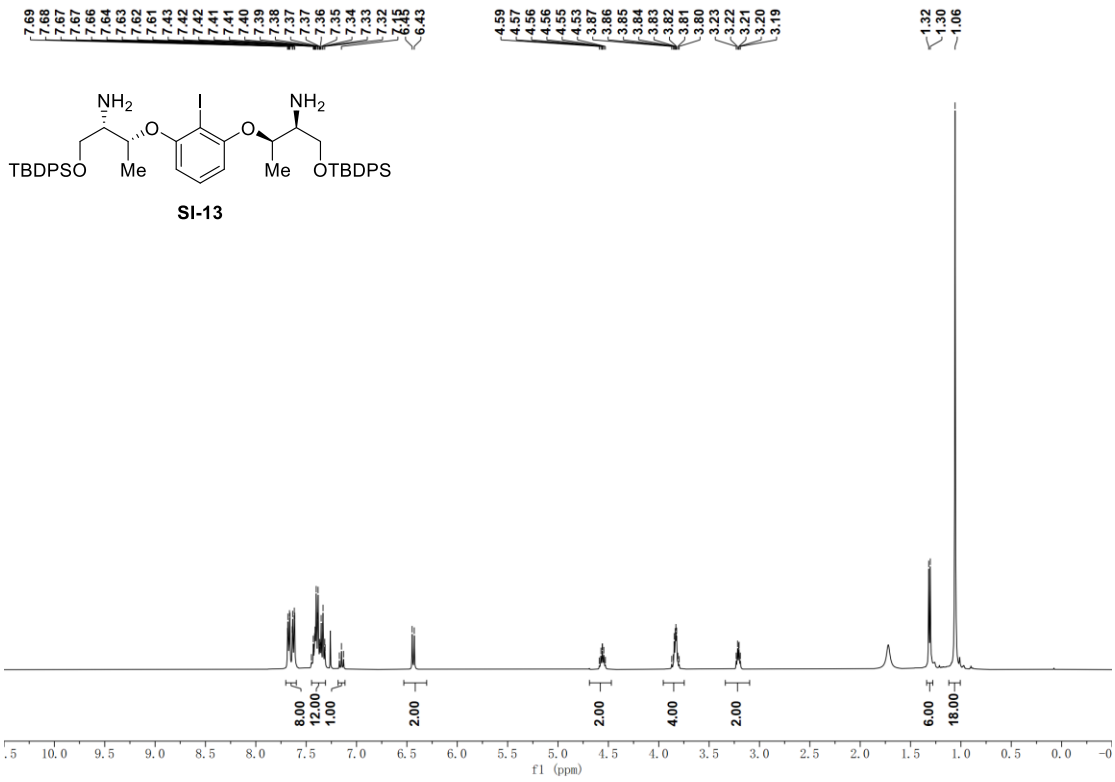
Supplementary Figure 10. ^{13}C NMR Spectrum of **10** (**100** MHz, $CDCl_3$)



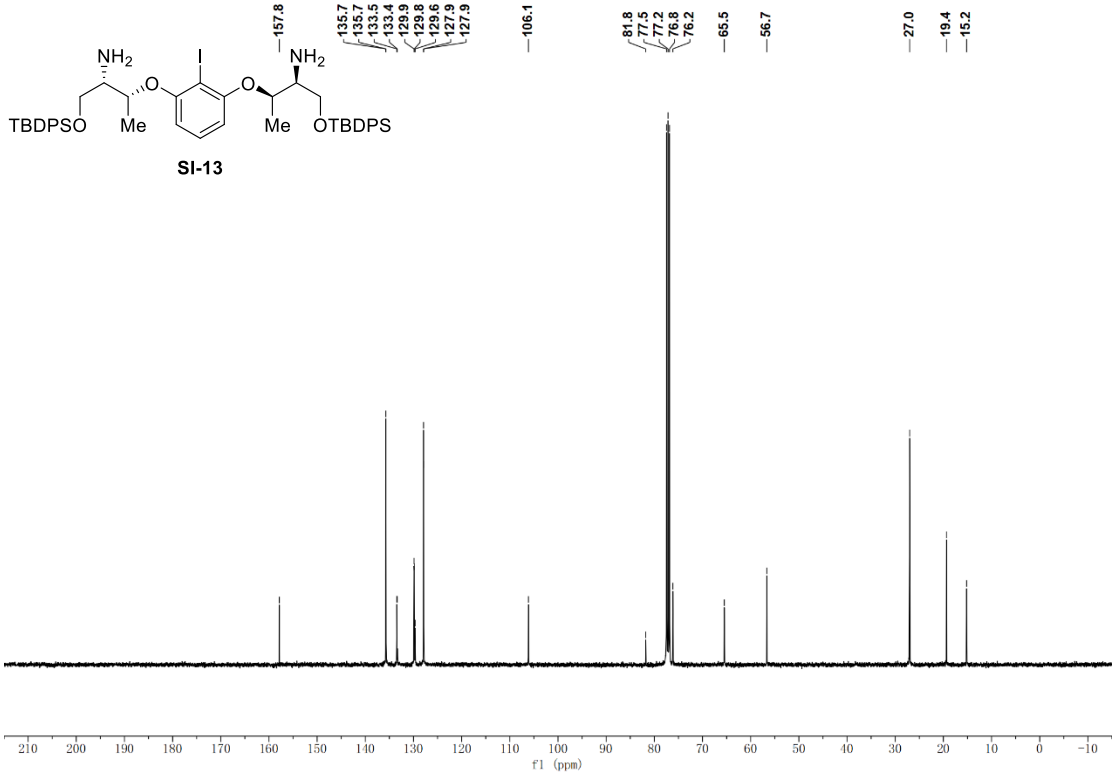
Supplementary Figure 11. ^{1}H NMR Spectrum of **11** (**400** MHz, $CDCl_3$)



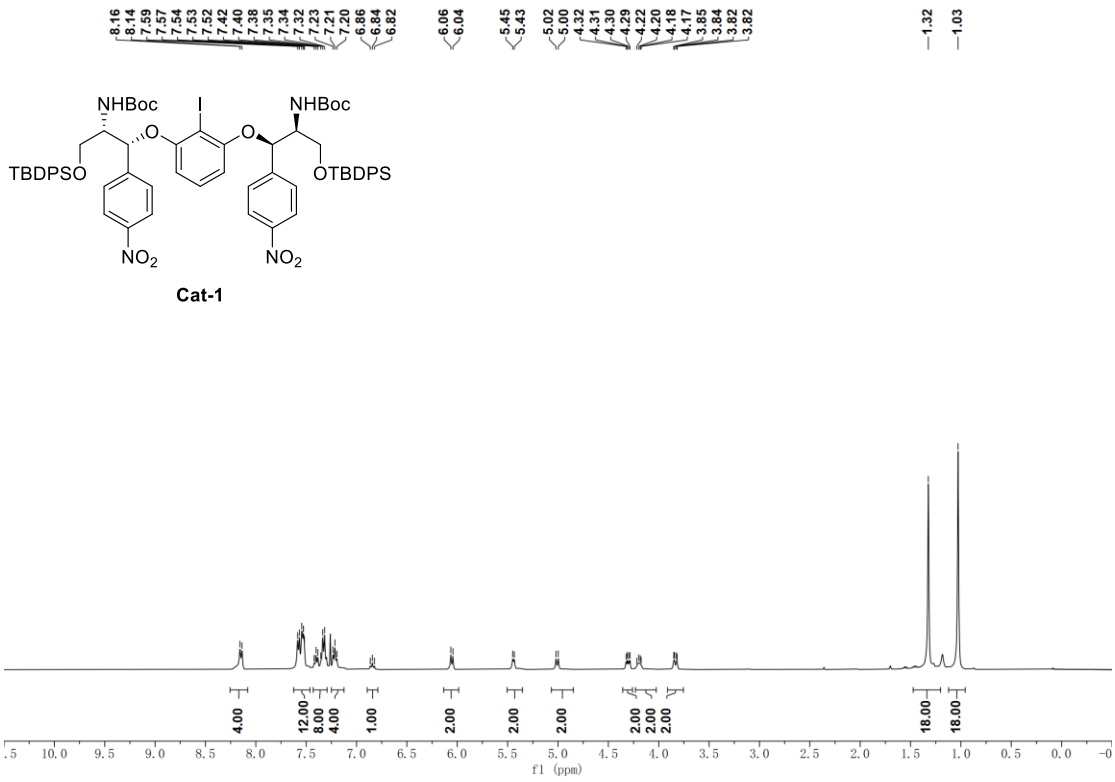
Supplementary Figure 12. ^{13}C NMR Spectrum of **11** (**100** MHz, $CDCl_3$)



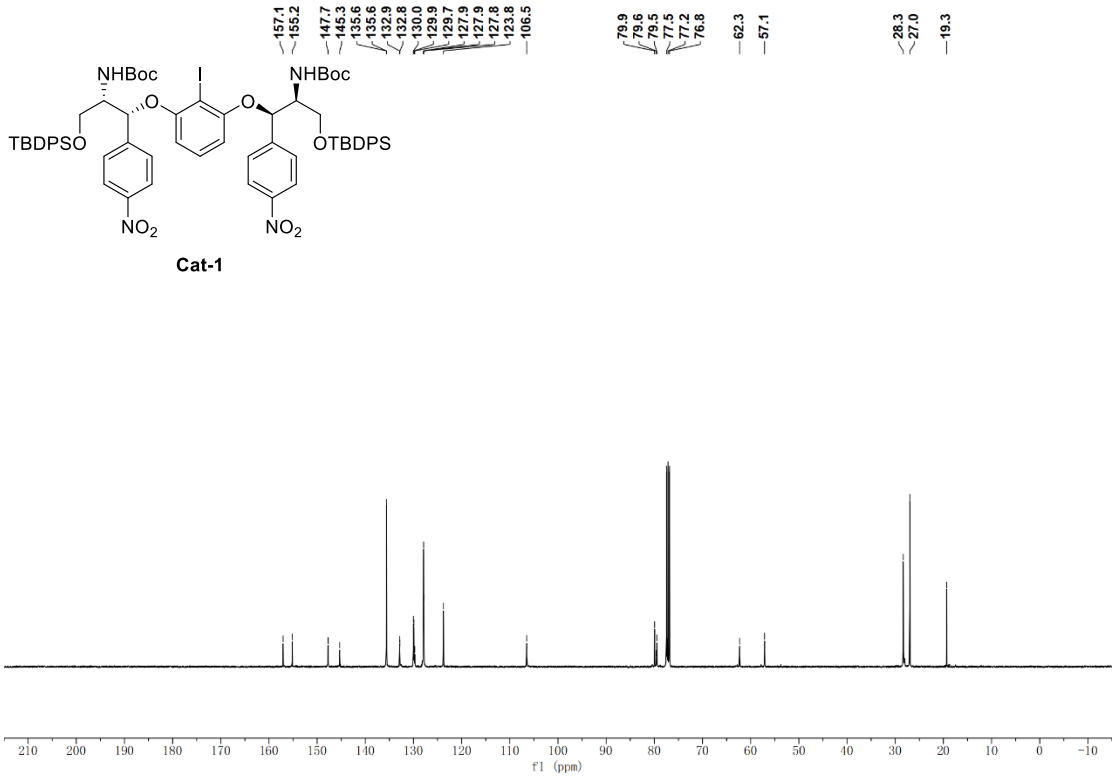
Supplementary Figure 13. ^{1}H NMR Spectrum of **SI-13** (**400** MHz, $CDCl_3$)



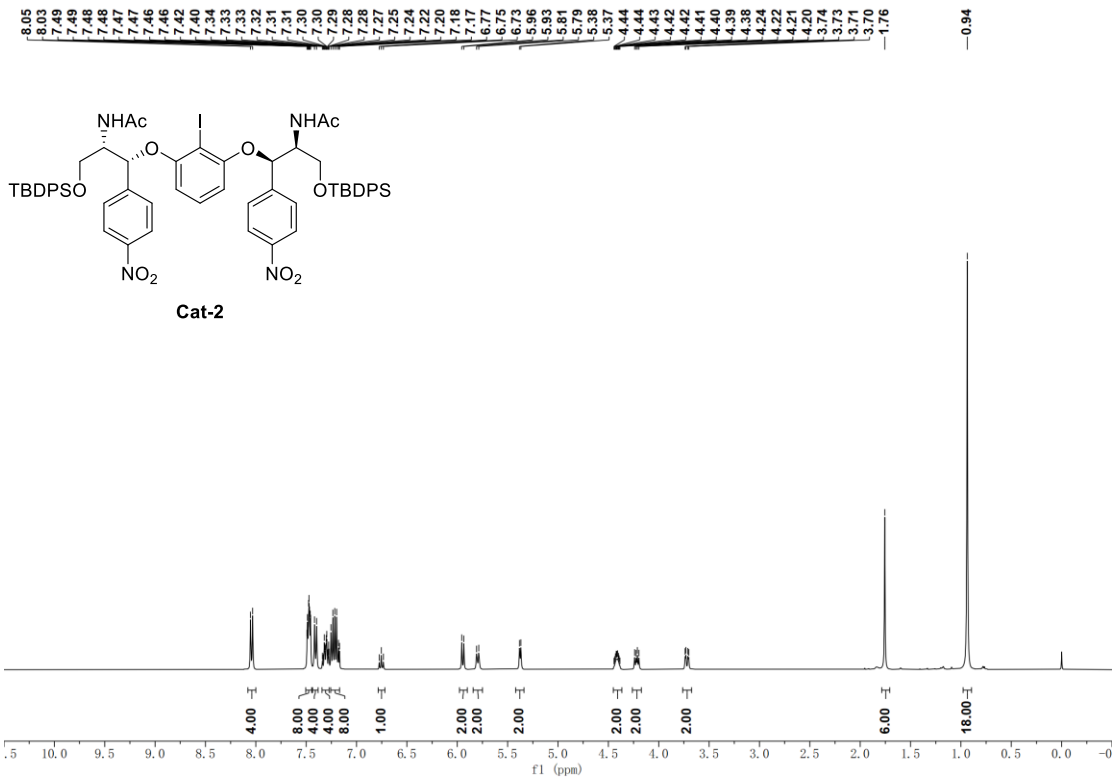
Supplementary Figure 14. ^{13}C NMR Spectrum of **SI-13** (**100** MHz, $CDCl_3$)



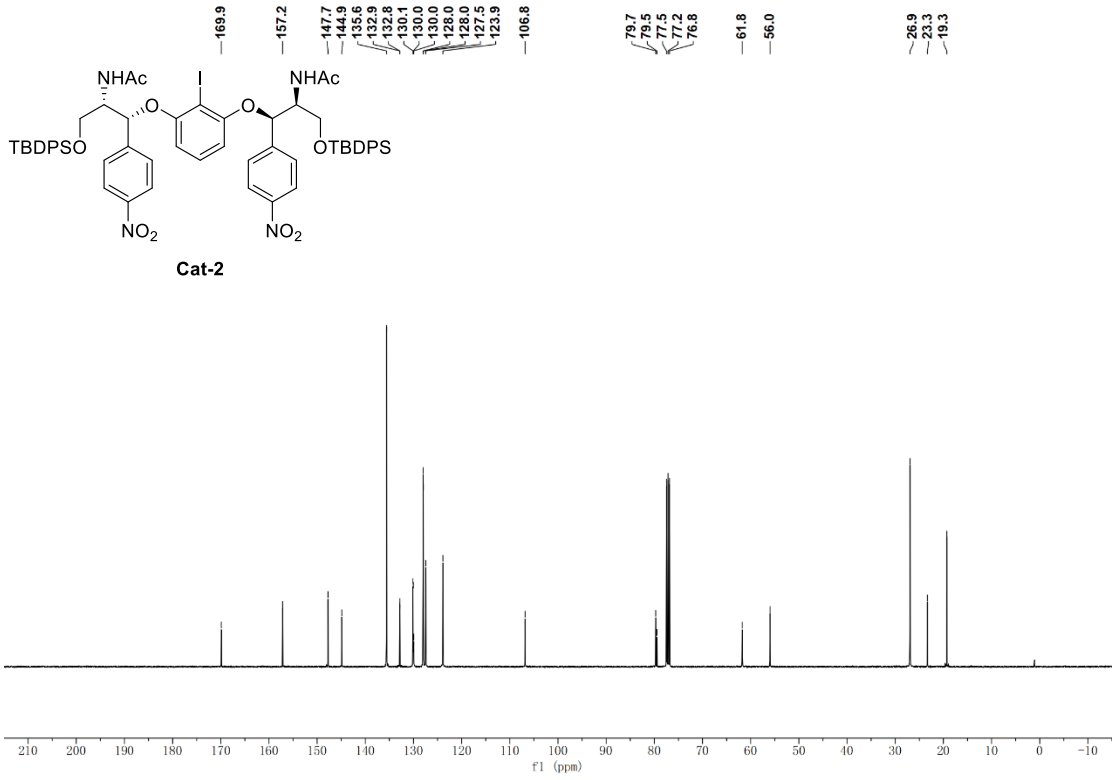
Supplementary Figure 15. ^{1}H NMR Spectrum of **Cat-1** (**400** MHz, $CDCl_3$)



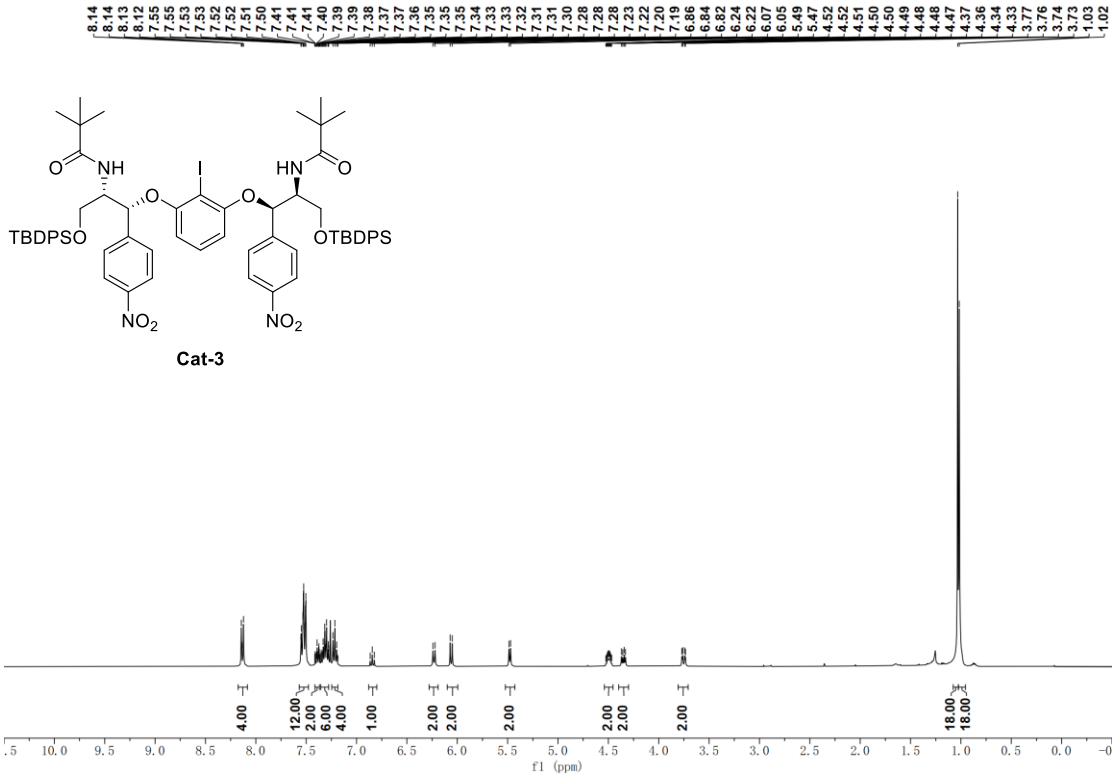
Supplementary Figure 16. ^{13}C NMR Spectrum of **Cat-1** (**100** MHz, $CDCl_3$)



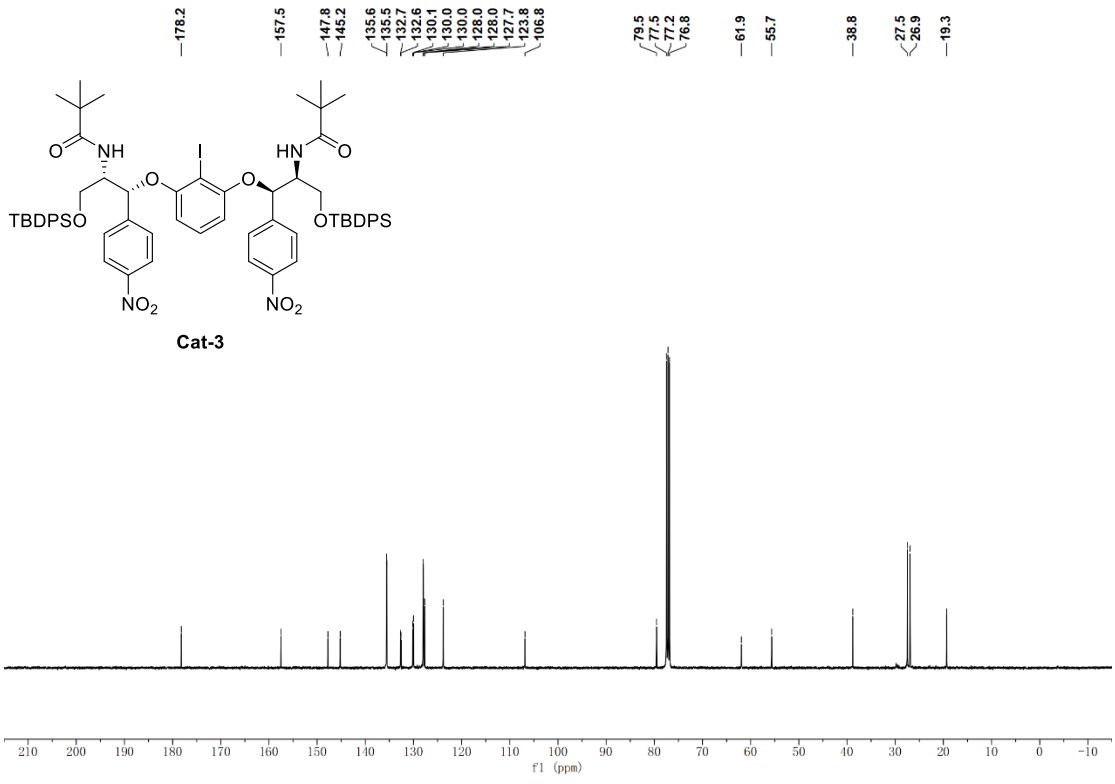
Supplementary Figure 17. ^{1}H NMR Spectrum of **Cat-2** (**400** MHz, $CDCl_3$)



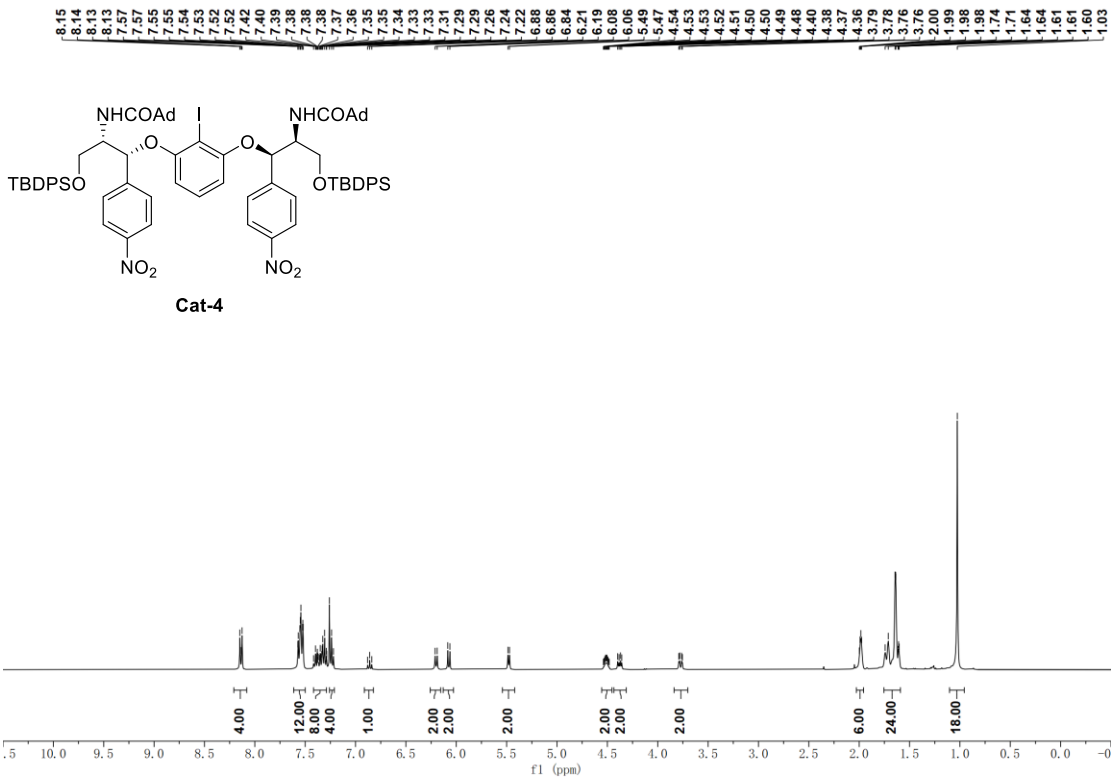
Supplementary Figure 18. ^{13}C NMR Spectrum of **Cat-2** (**100** MHz, $CDCl_3$)



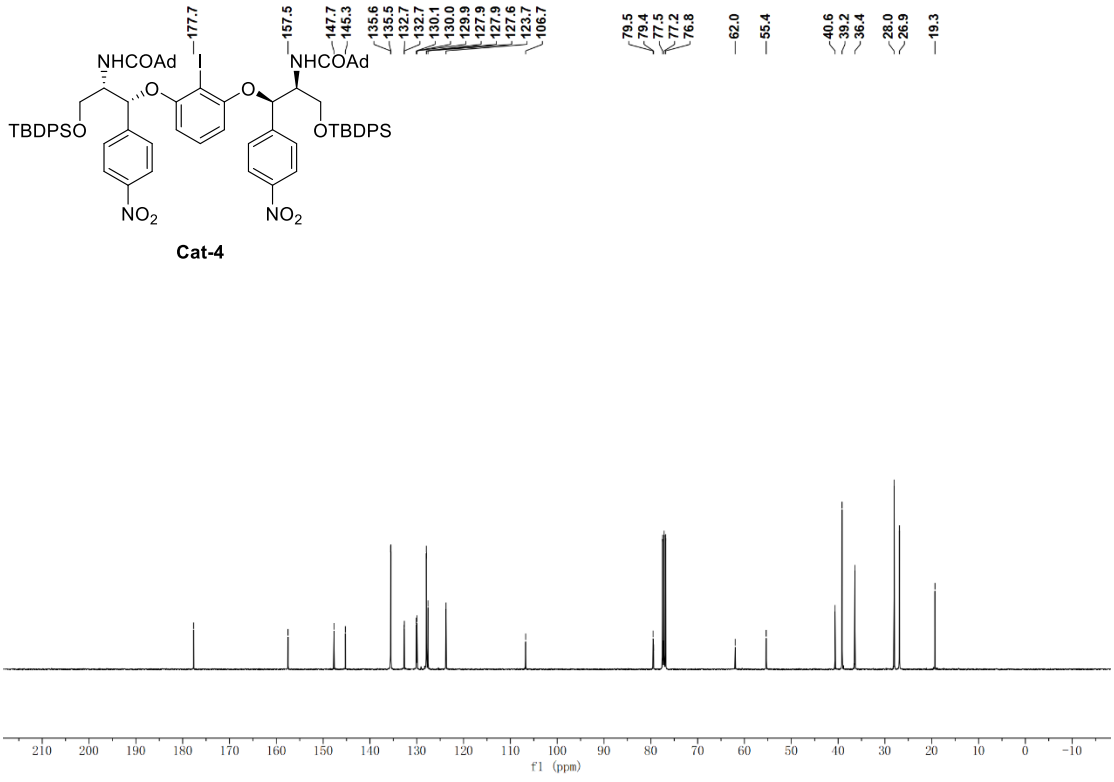
Supplementary Figure 19. ^{1}H NMR Spectrum of **Cat-3** (**400** MHz, $CDCl_3$)



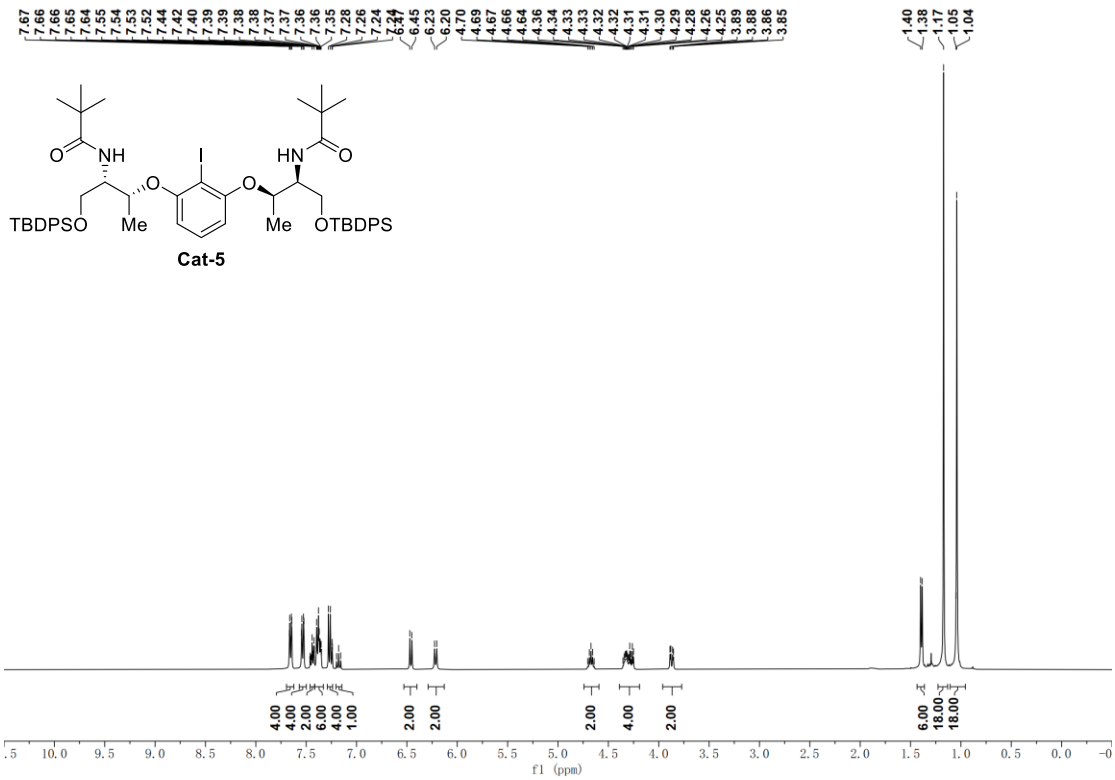
Supplementary Figure 20. ^{13}C NMR Spectrum of **Cat-3** (**100** MHz, $CDCl_3$)



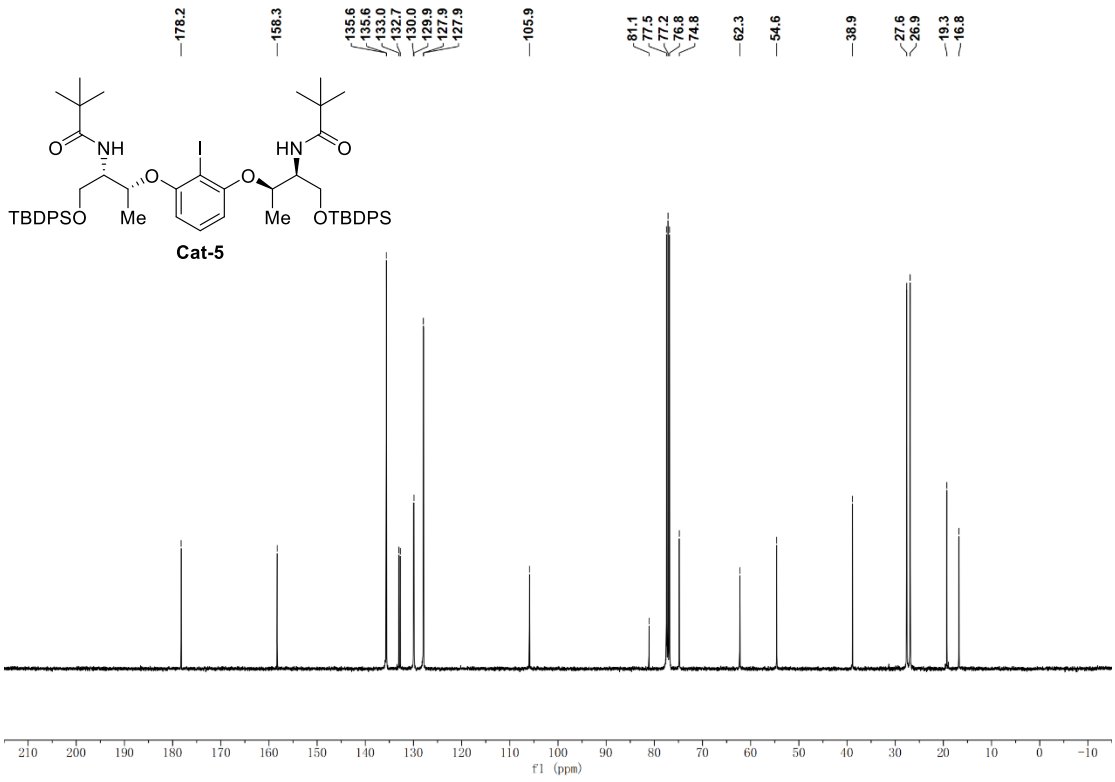
Supplementary Figure 21. ^{1}H NMR Spectrum of **Cat-4** (**400** MHz, $CDCl_3$)



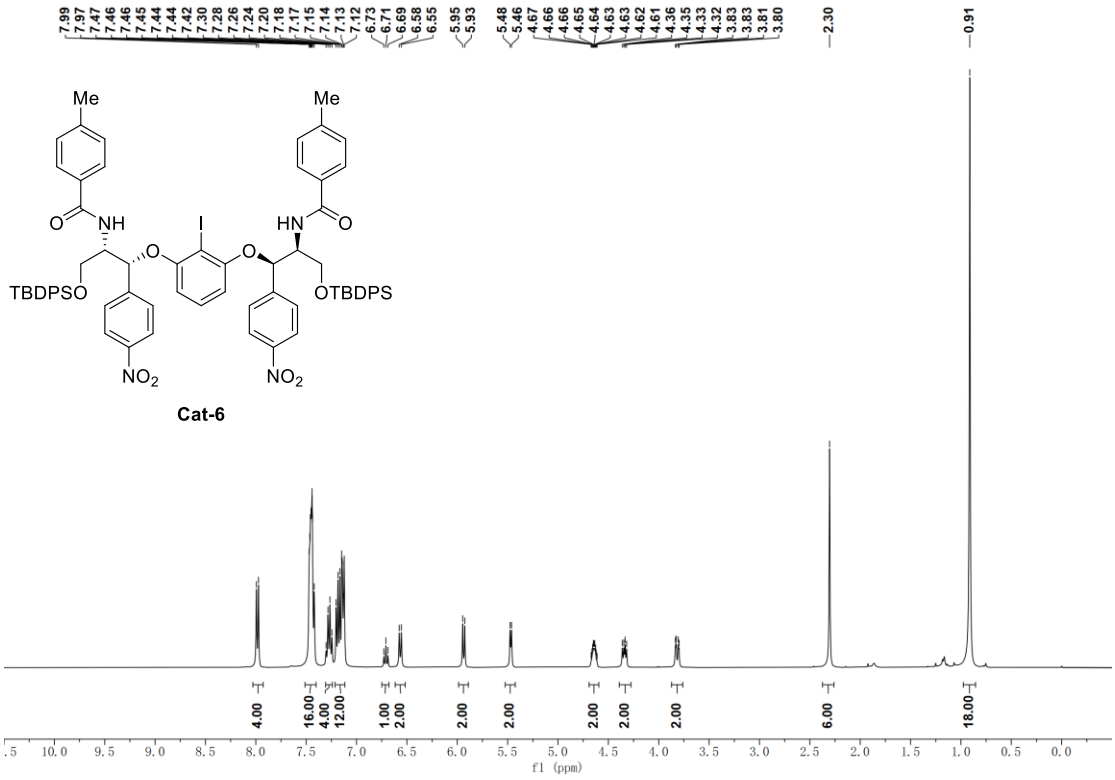
Supplementary Figure 22. ^{13}C NMR Spectrum of **Cat-4** (**100** MHz, $CDCl_3$)



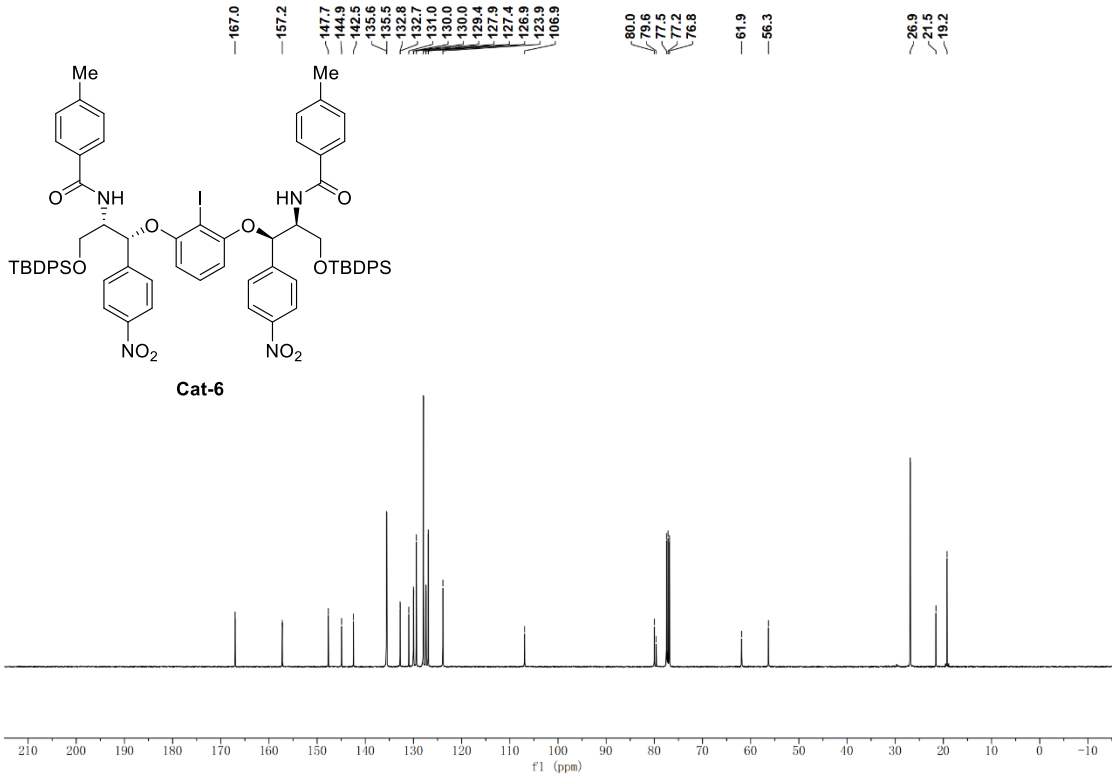
Supplementary Figure 23. ^{1}H NMR Spectrum of **Cat-5** (**400** MHz, $CDCl_3$)



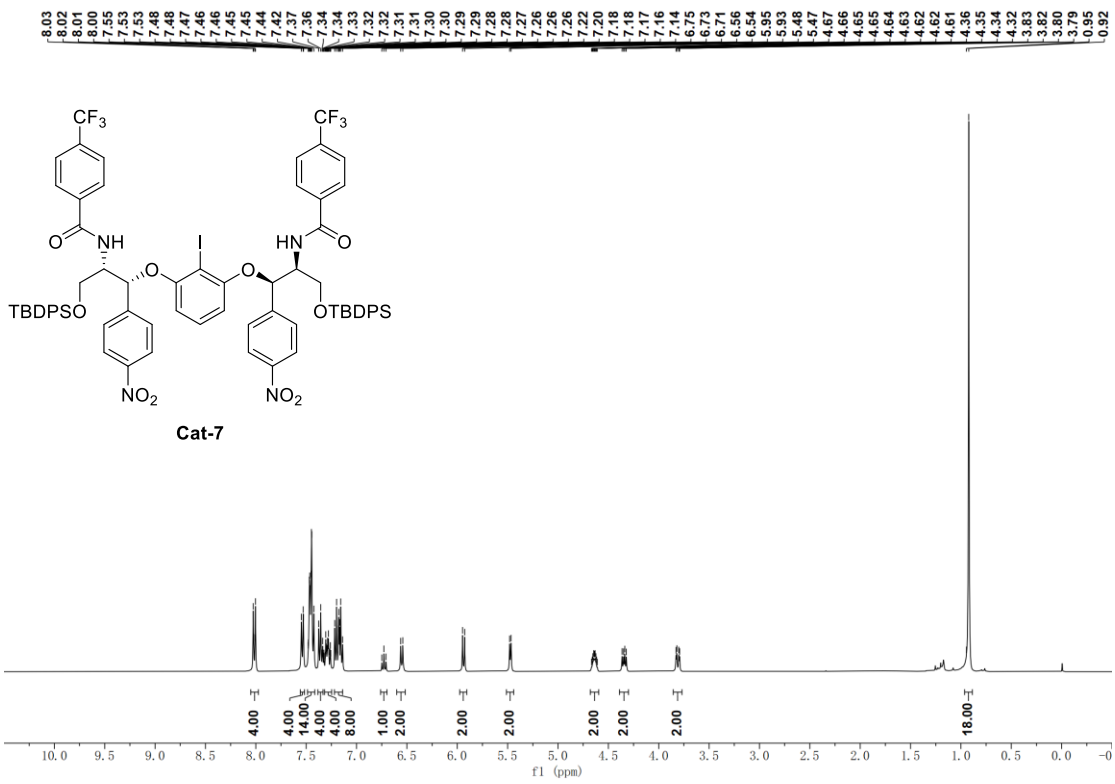
Supplementary Figure 24. ^{13}C NMR Spectrum of **Cat-5** (**100** MHz, $CDCl_3$)



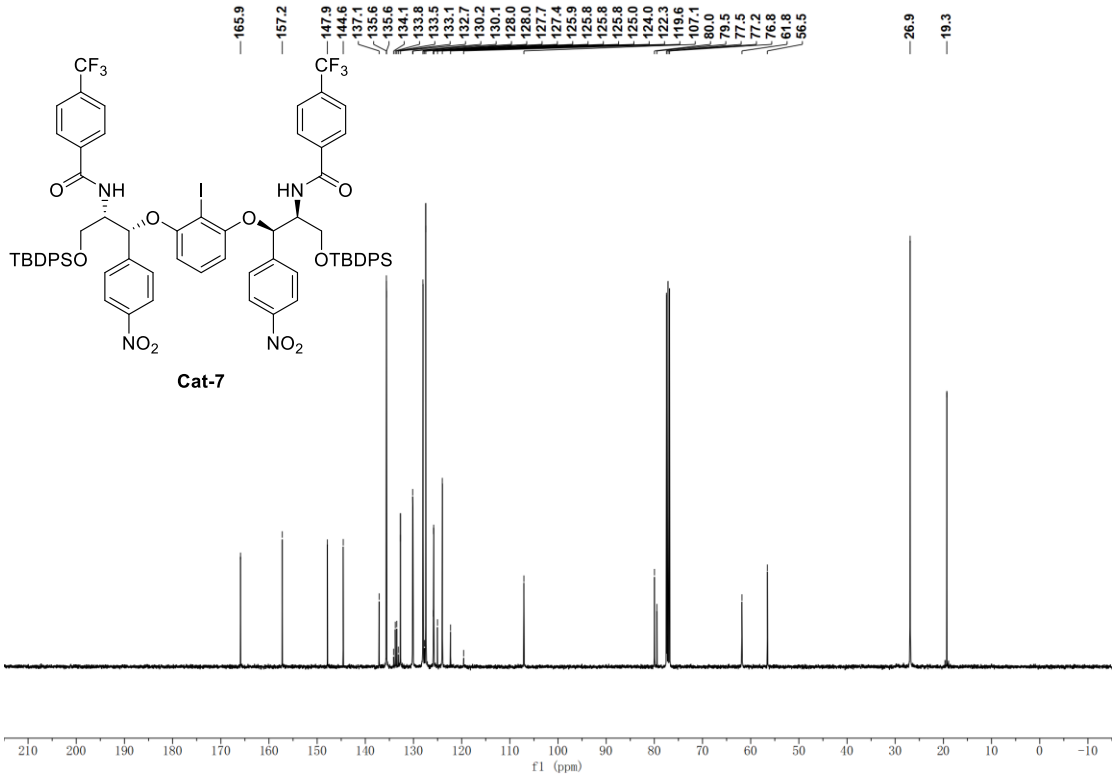
Supplementary Figure 25. ^{1}H NMR Spectrum of **Cat-6** (**400** MHz, $CDCl_3$)



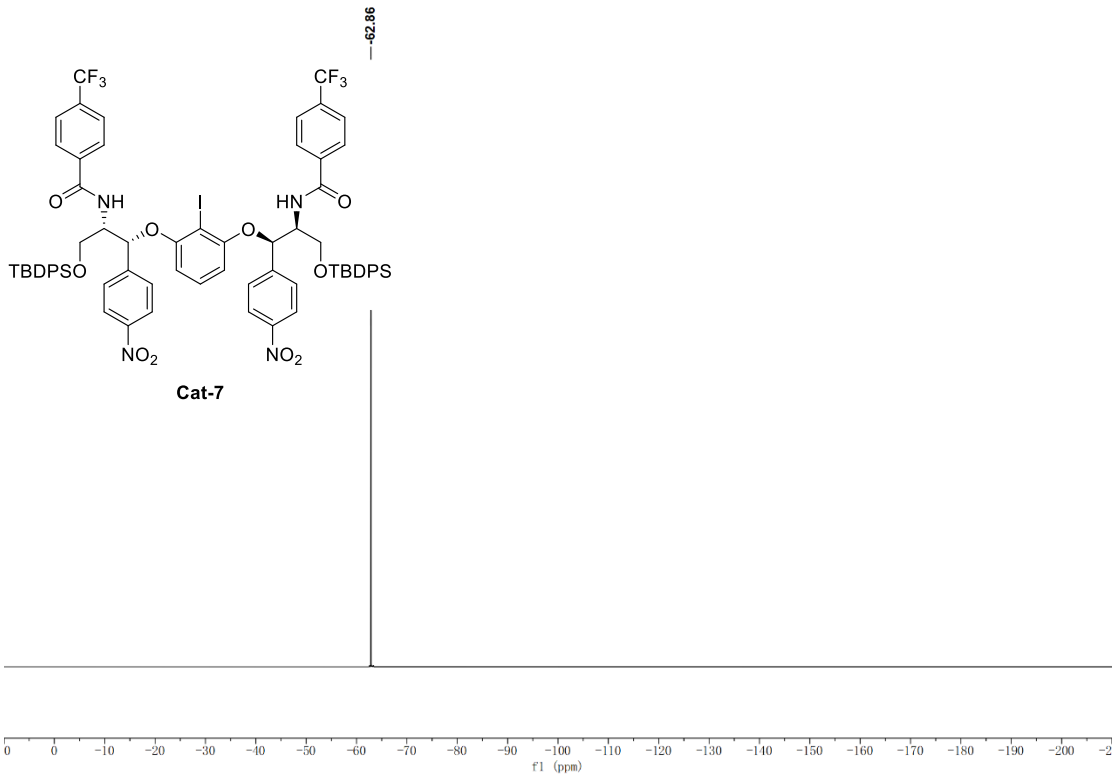
Supplementary Figure 26. ^{13}C NMR Spectrum of **Cat-6** (**100** MHz, $CDCl_3$)



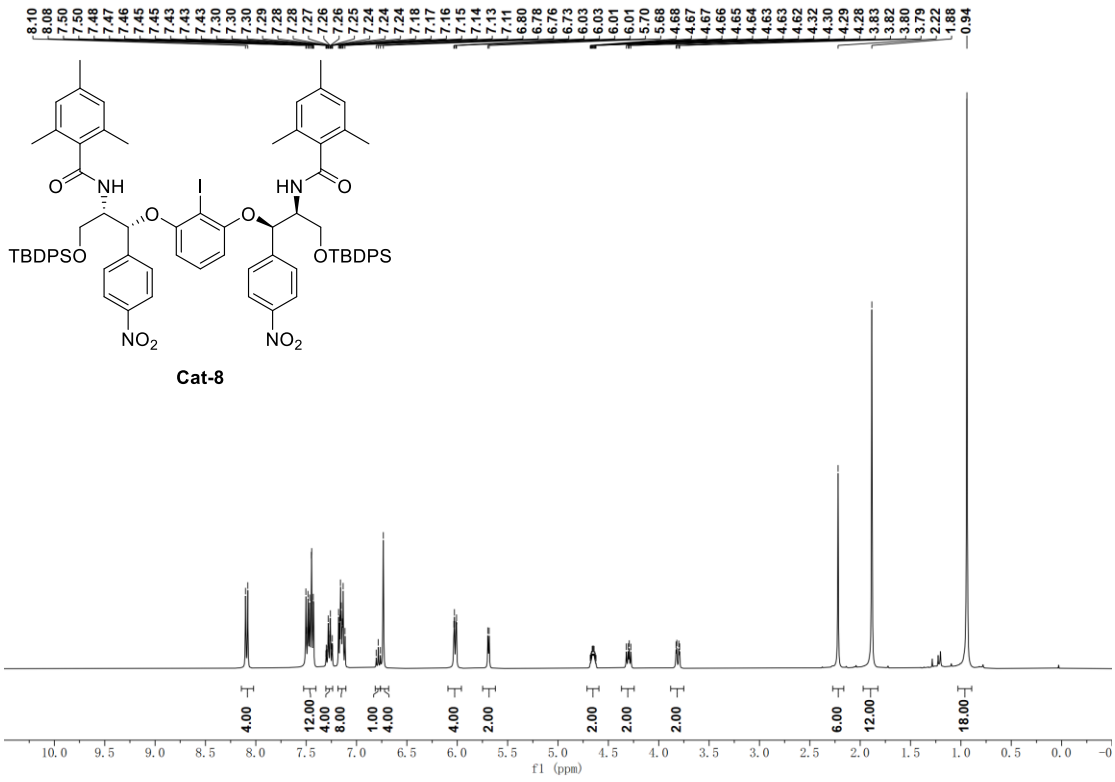
Supplementary Figure 27. ^{1}H NMR Spectrum of **Cat-7** (**400** MHz, $CDCl_3$)



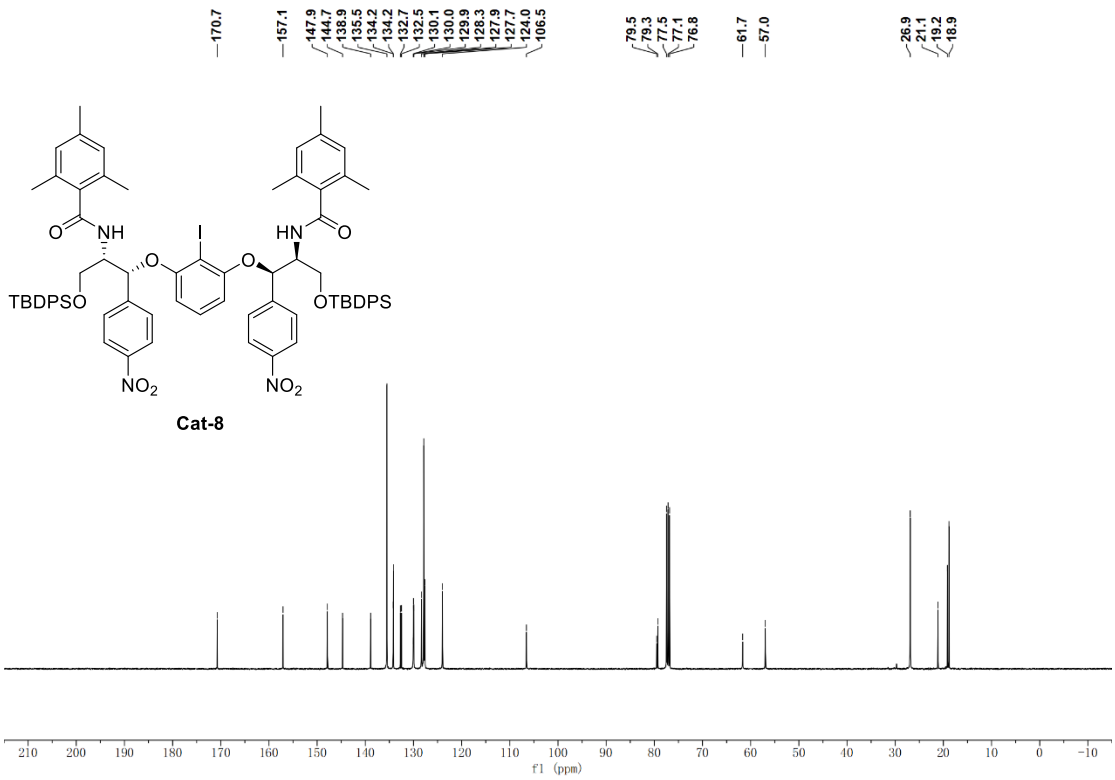
Supplementary Figure 28. ^{13}C NMR Spectrum of **Cat-7** (**100** MHz, $CDCl_3$)



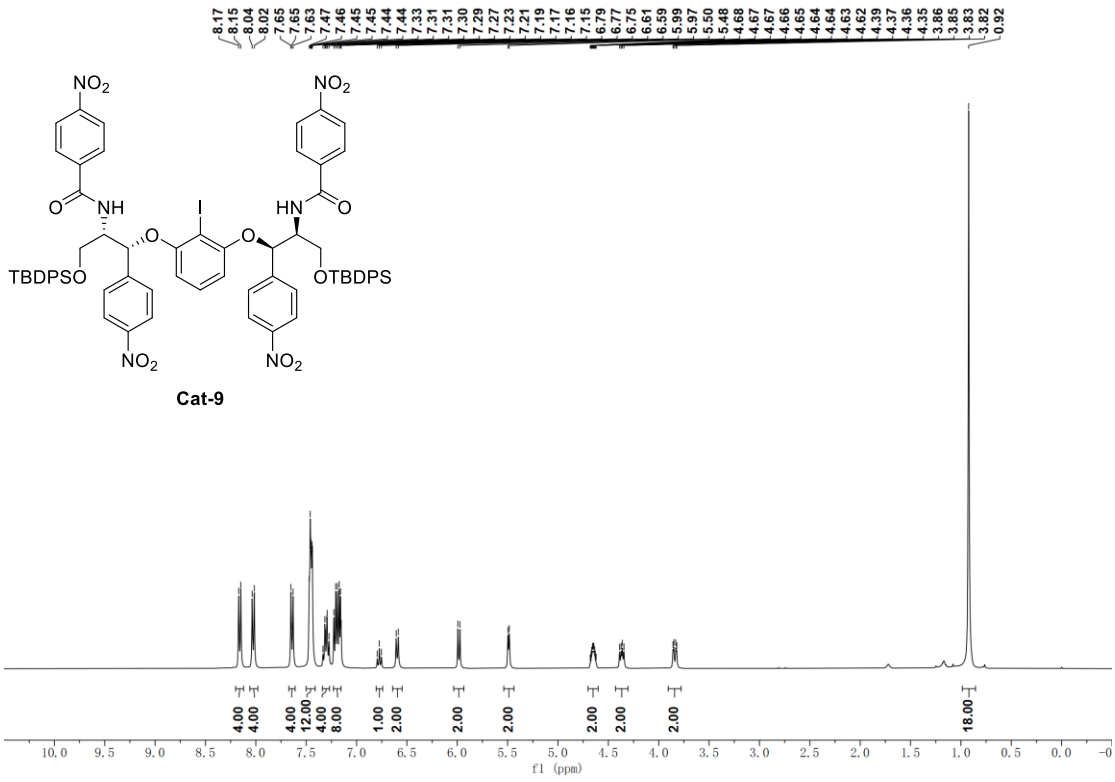
Supplementary Figure 29. ^{19}F NMR Spectrum of **Cat-7** (**376** MHz, $CDCl_3$)



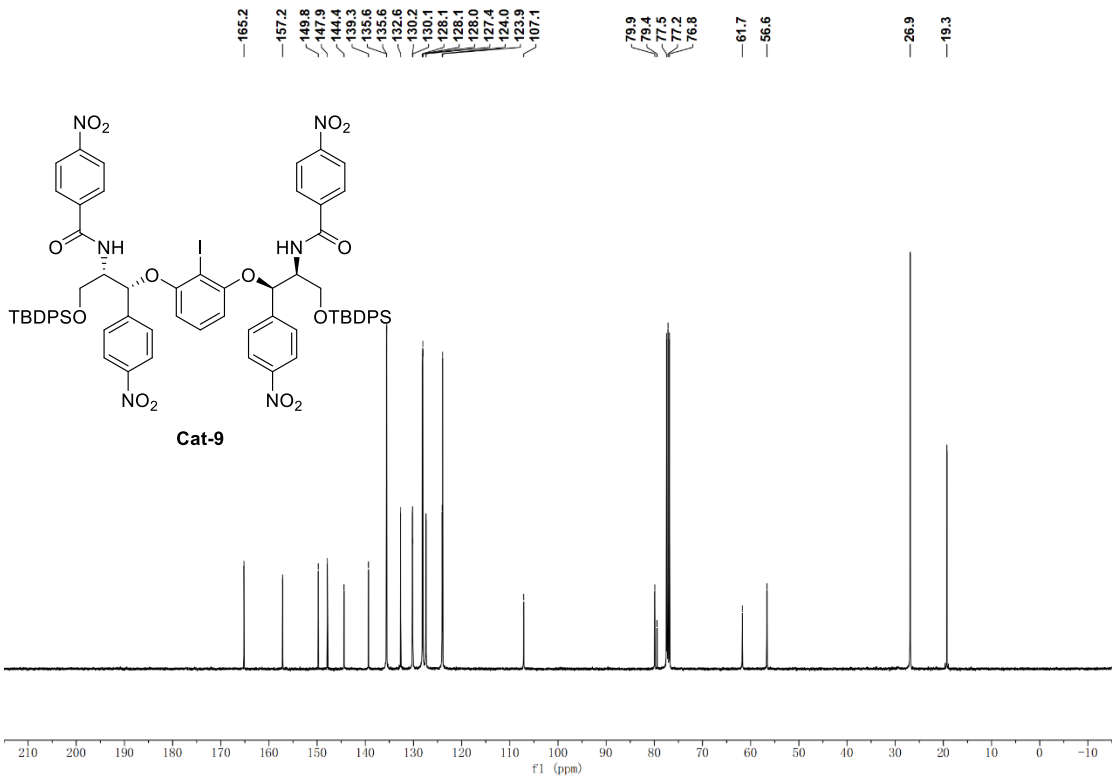
Supplementary Figure 30. ^{11}H NMR Spectrum of **Cat-8** (**400** MHz, $CDCl_3$)



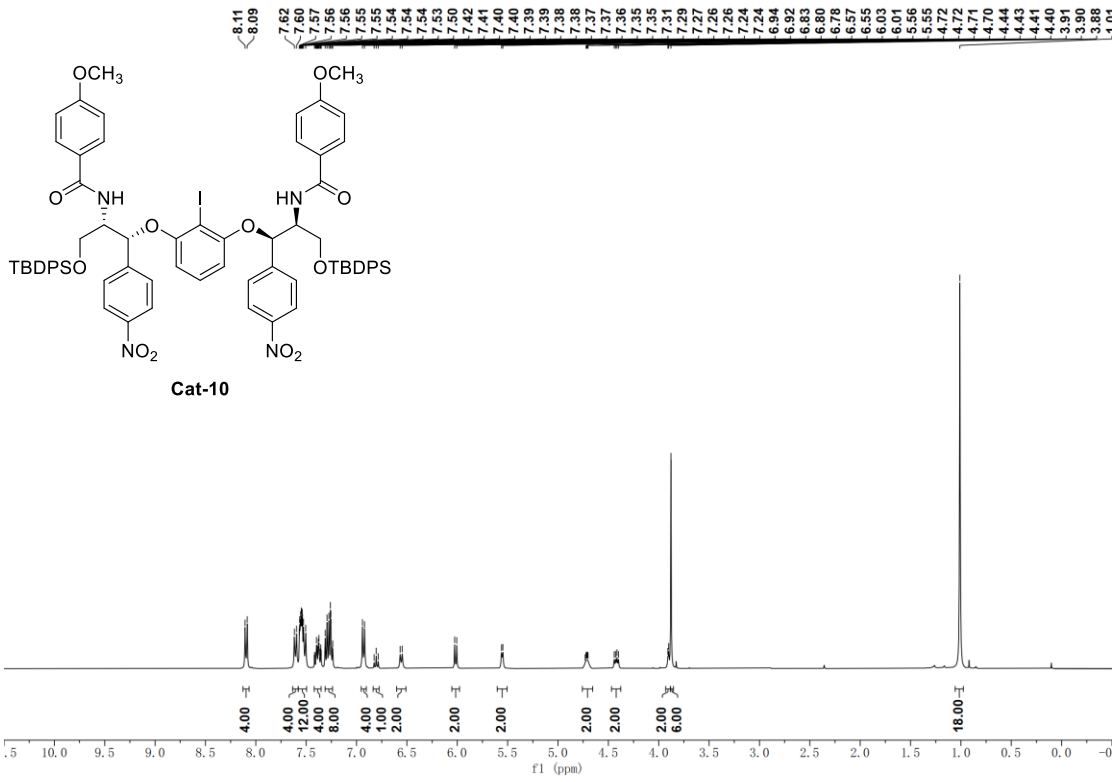
Supplementary Figure 31. ^{13}C NMR Spectrum of **Cat-8** (**100** MHz, $CDCl_3$)



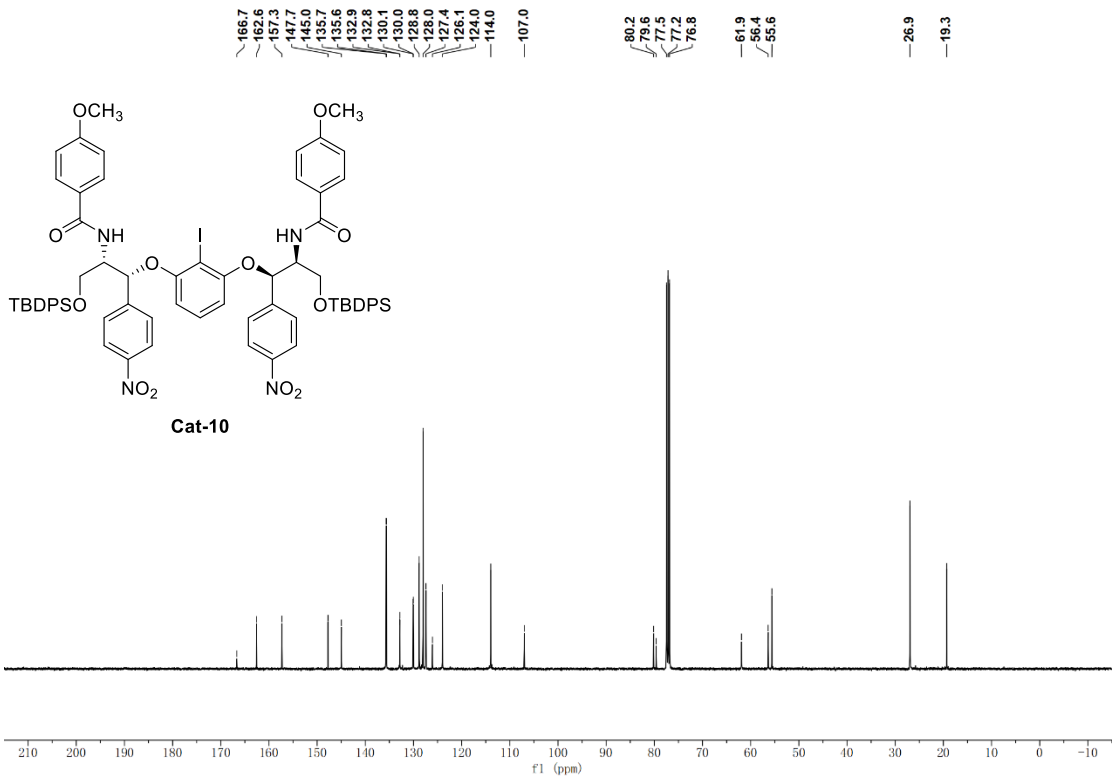
Supplementary Figure 32. ^{1}H NMR Spectrum of **Cat-9** (**400** MHz, $CDCl_3$)



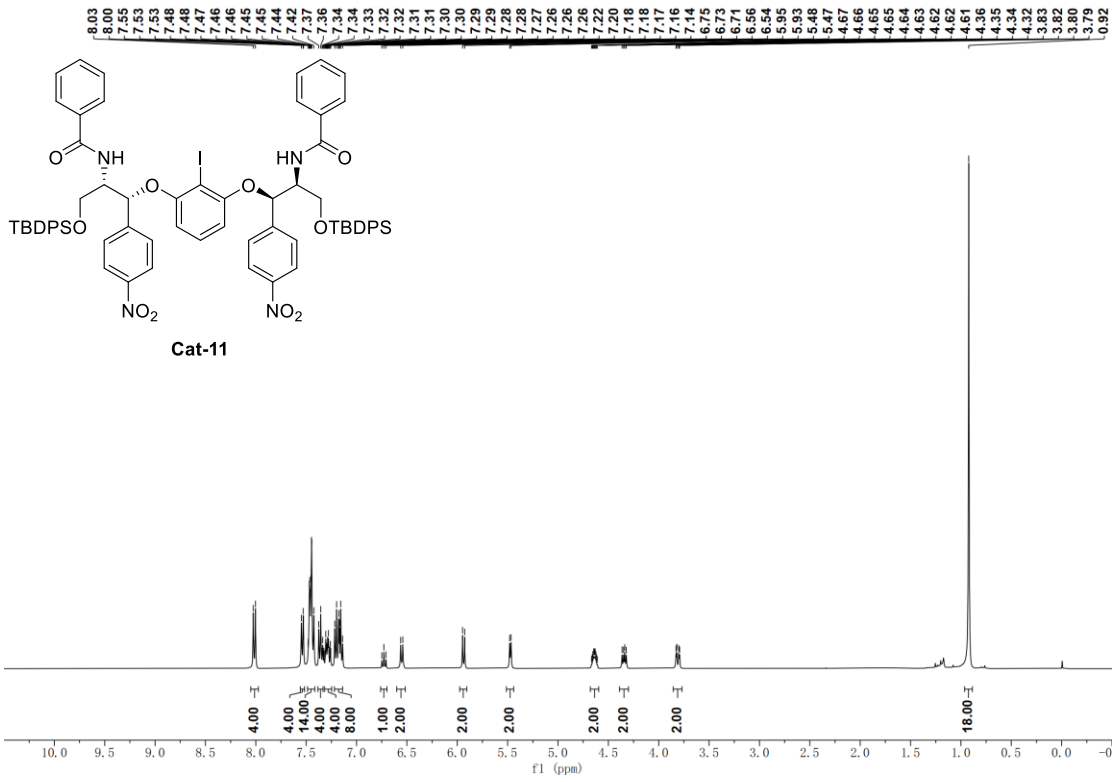
Supplementary Figure 33. ^{13}C NMR Spectrum of **Cat-9** (**100** MHz, $CDCl_3$)



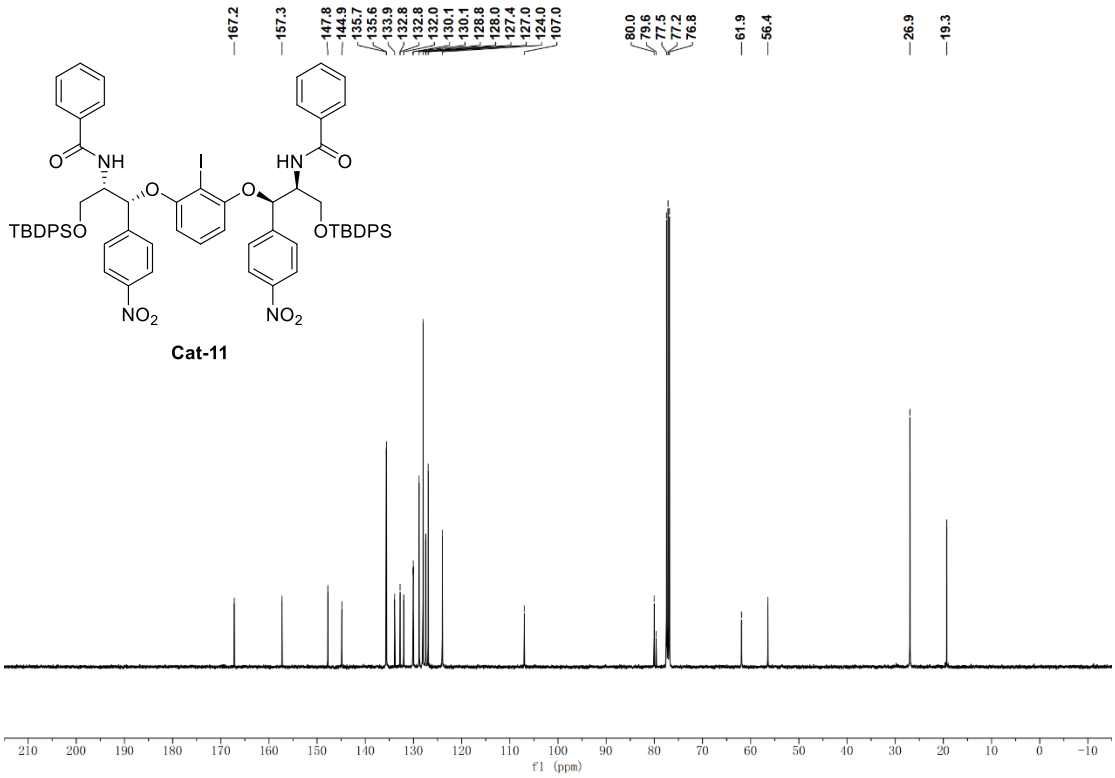
Supplementary Figure 34. ^{1}H NMR Spectrum of **Cat-10** (**400** MHz, $CDCl_3$)



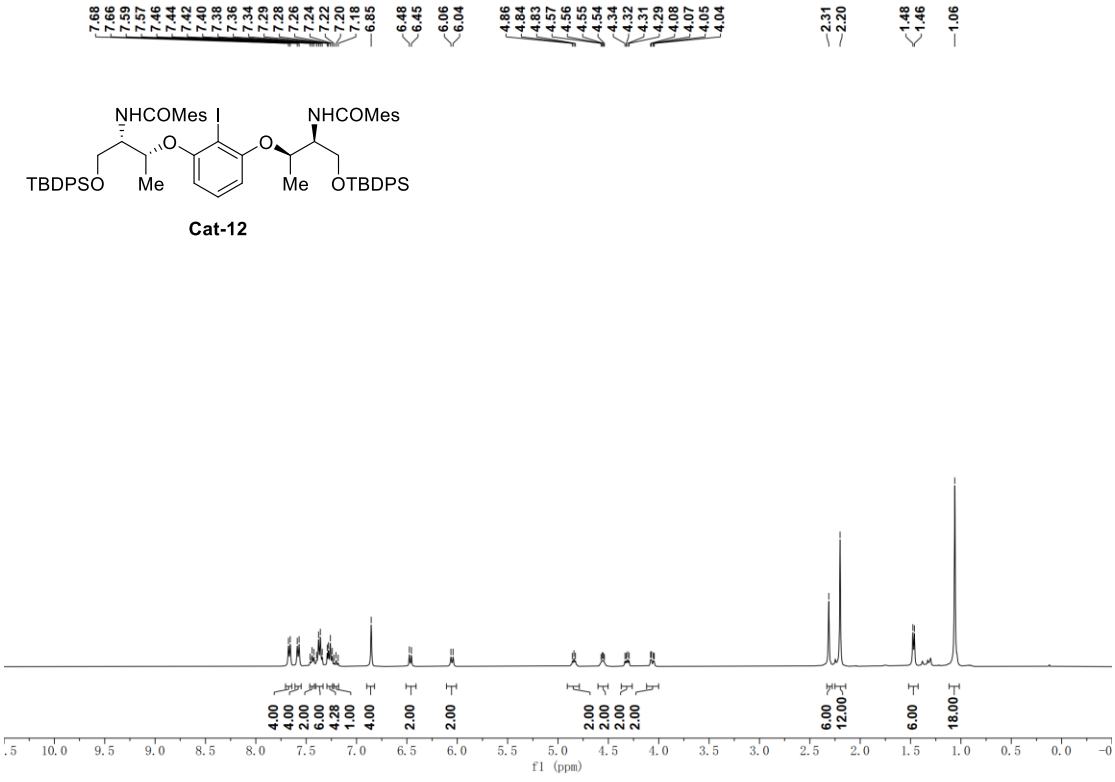
Supplementary Figure 35. ^{13}C NMR Spectrum of **Cat-10** (**100** MHz, $CDCl_3$)



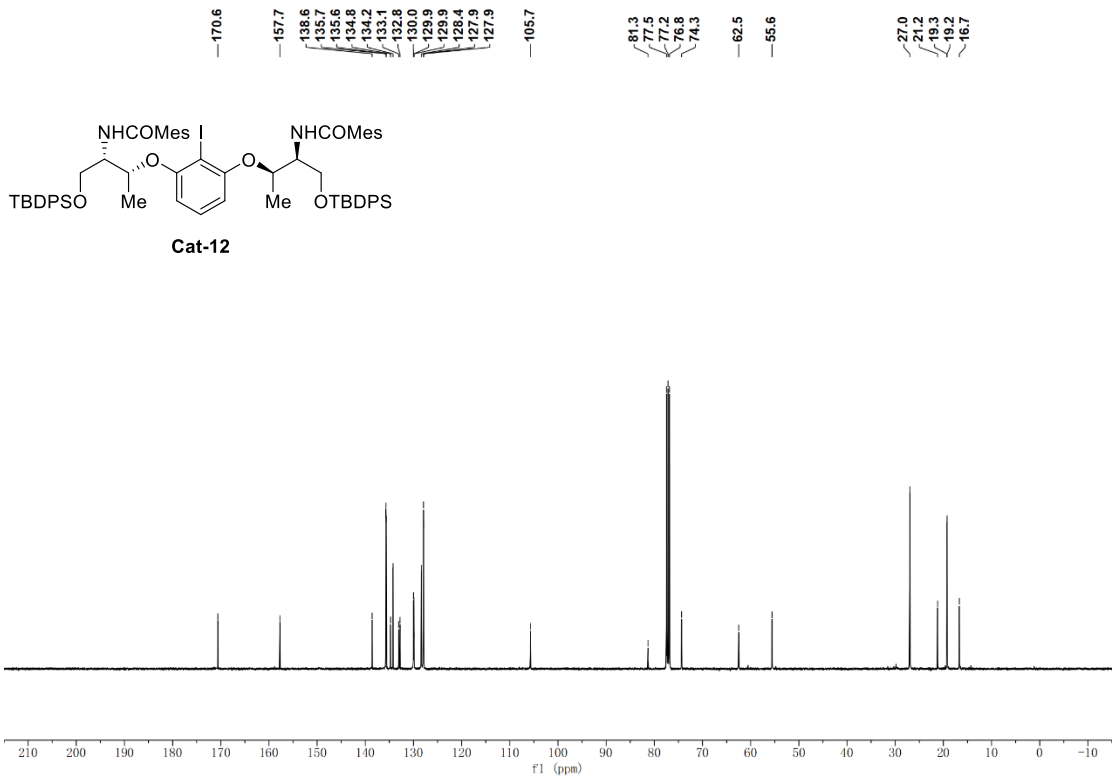
Supplementary Figure 36. ^{1}H NMR Spectrum of **Cat-11** (**400** MHz, $CDCl_3$)



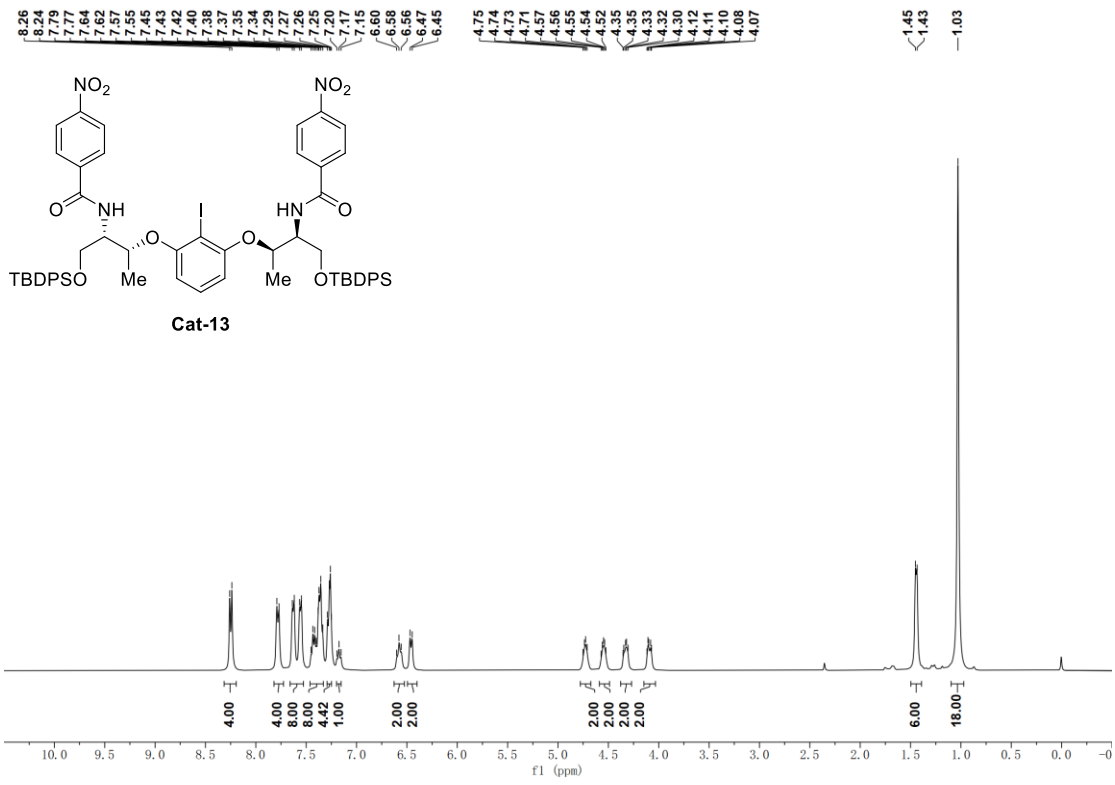
Supplementary Figure 37. ^{13}C NMR Spectrum of **Cat-11** (**100** MHz, $CDCl_3$)



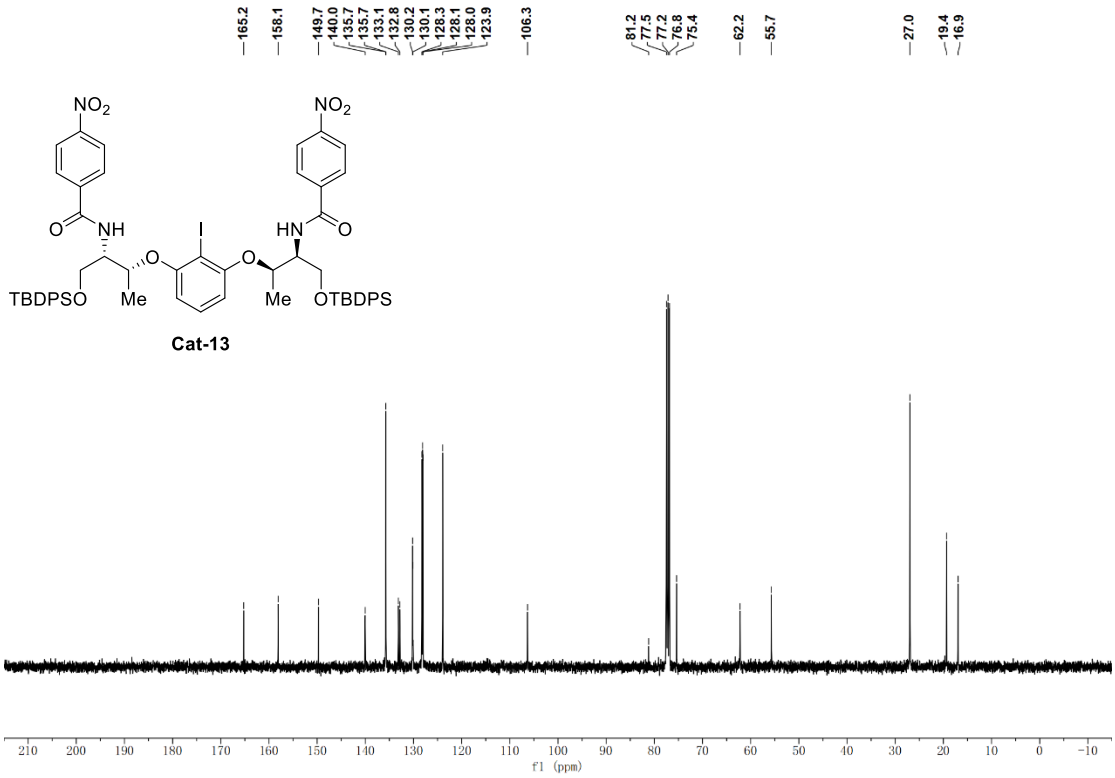
Supplementary Figure 38. ^{1}H NMR Spectrum of **Cat-12** (**400** MHz, $CDCl_3$)



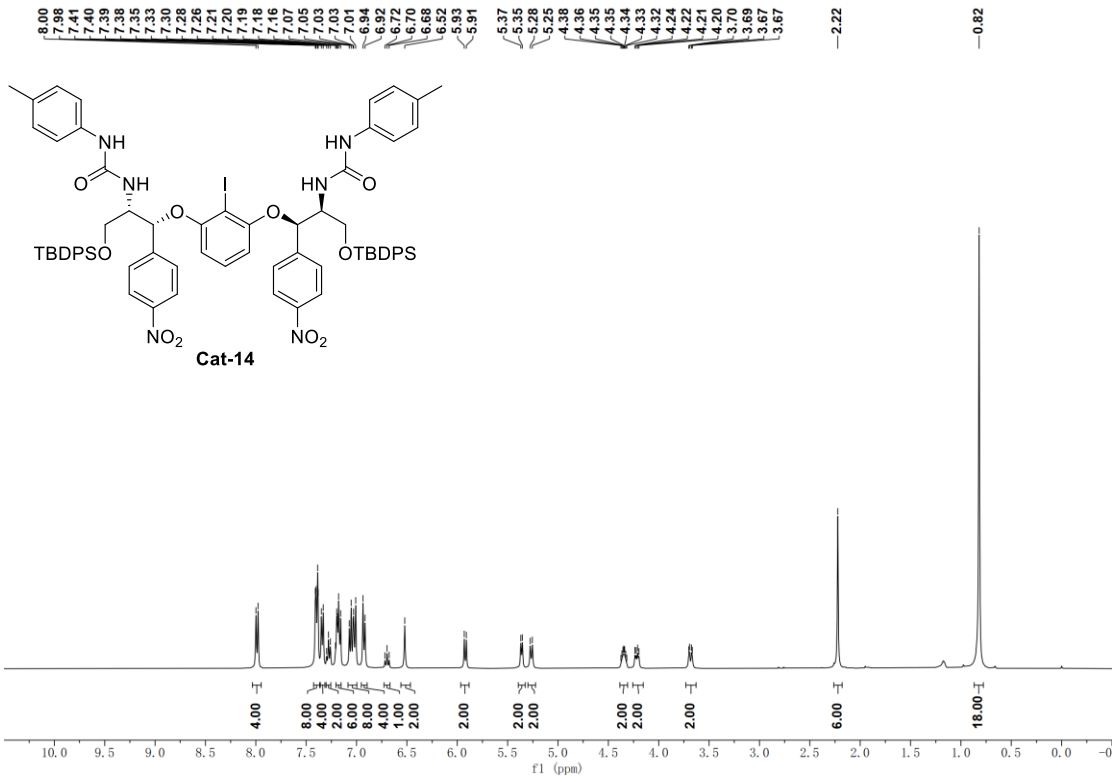
Supplementary Figure 39. ^{13}C NMR Spectrum of **Cat-12** (**100** MHz, $CDCl_3$)



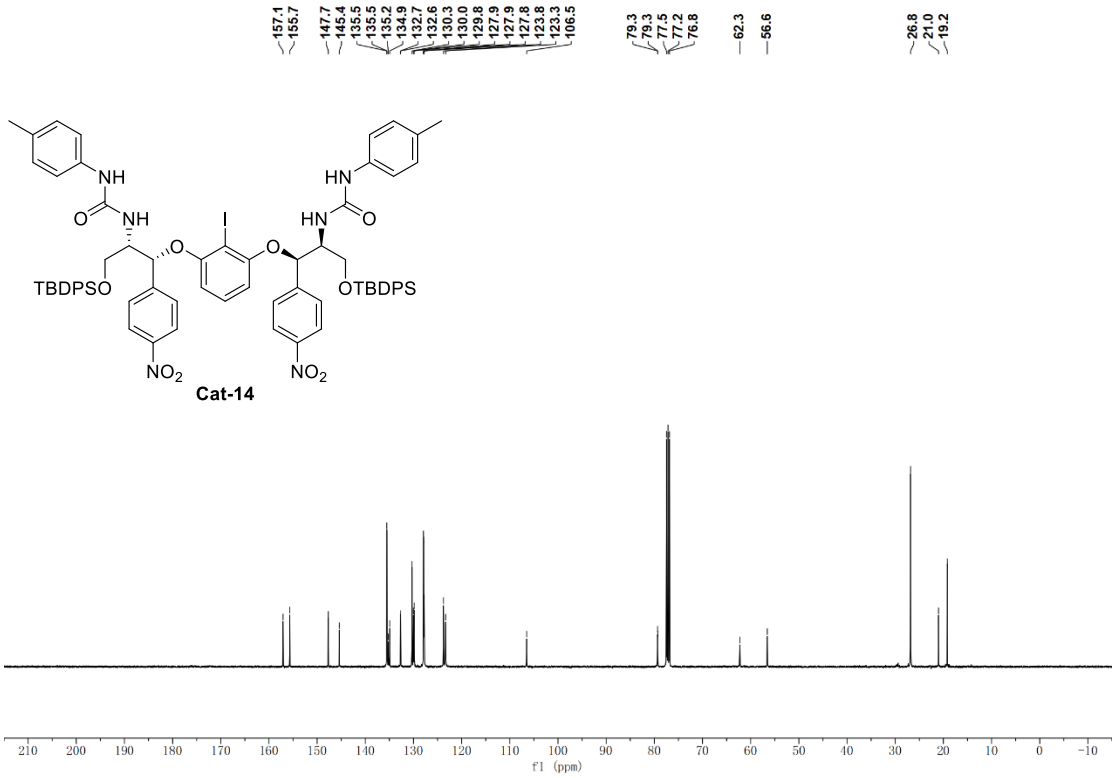
Supplementary Figure 40. ^{1}H NMR Spectrum of **Cat-13** (**400** MHz, $CDCl_3$)



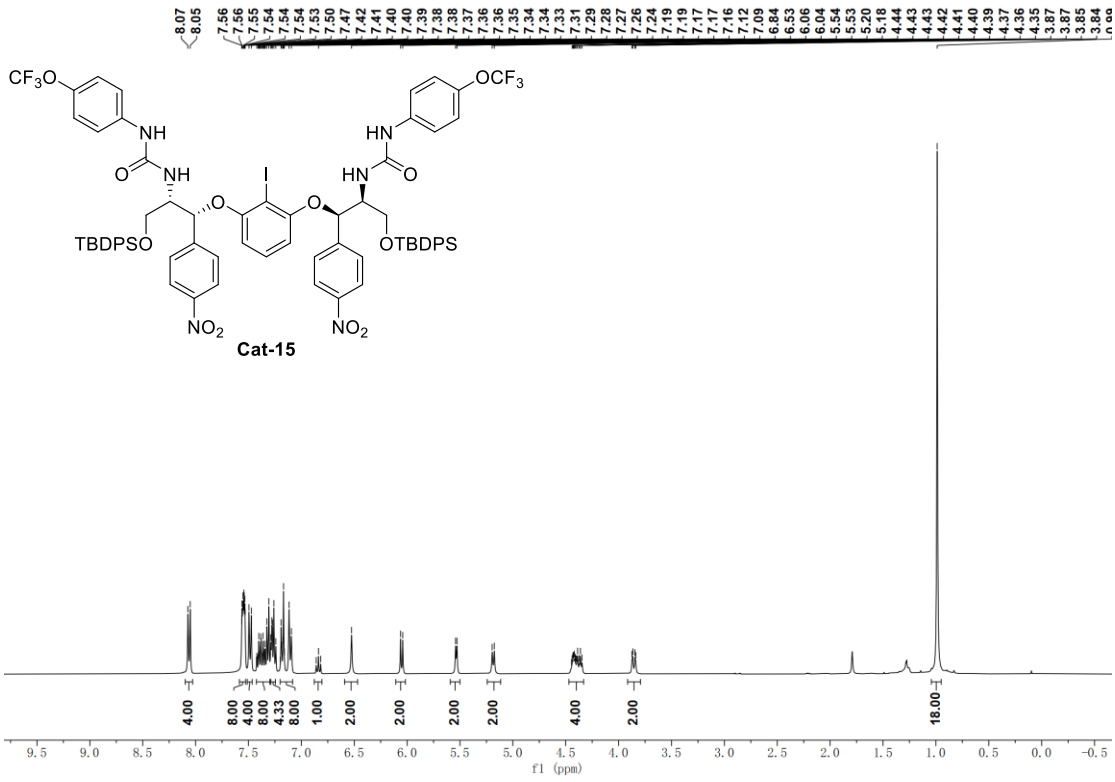
Supplementary Figure 41. ^{13}C NMR Spectrum of **Cat-13** (**100** MHz, $CDCl_3$)



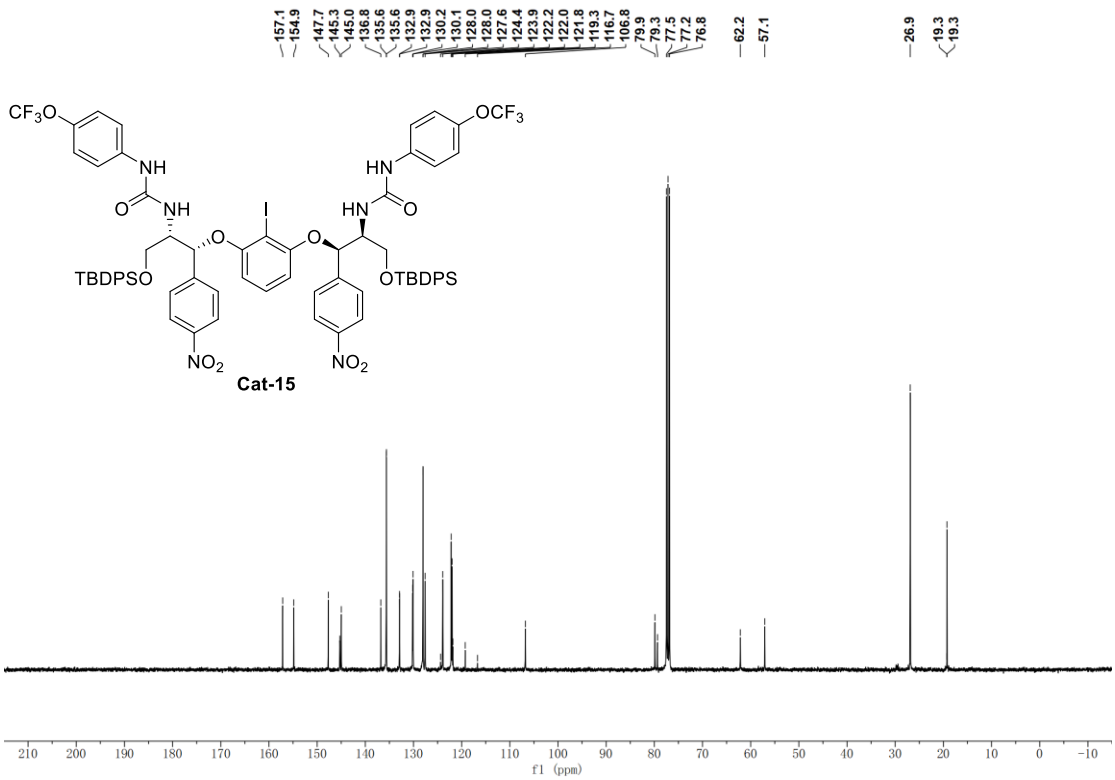
Supplementary Figure 42. ^{1}H NMR Spectrum of **Cat-14** (**400** MHz, $CDCl_3$)



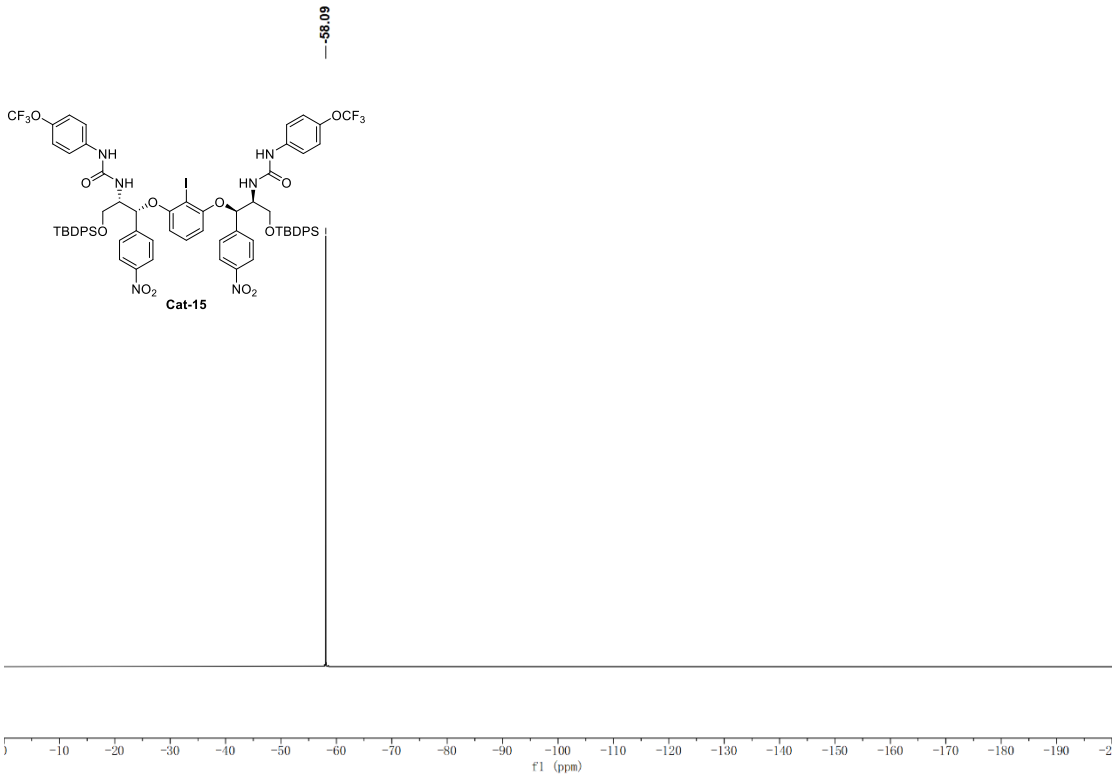
Supplementary Figure 43. ^{13}C NMR Spectrum of **Cat-14** (**100** MHz, $CDCl_3$)



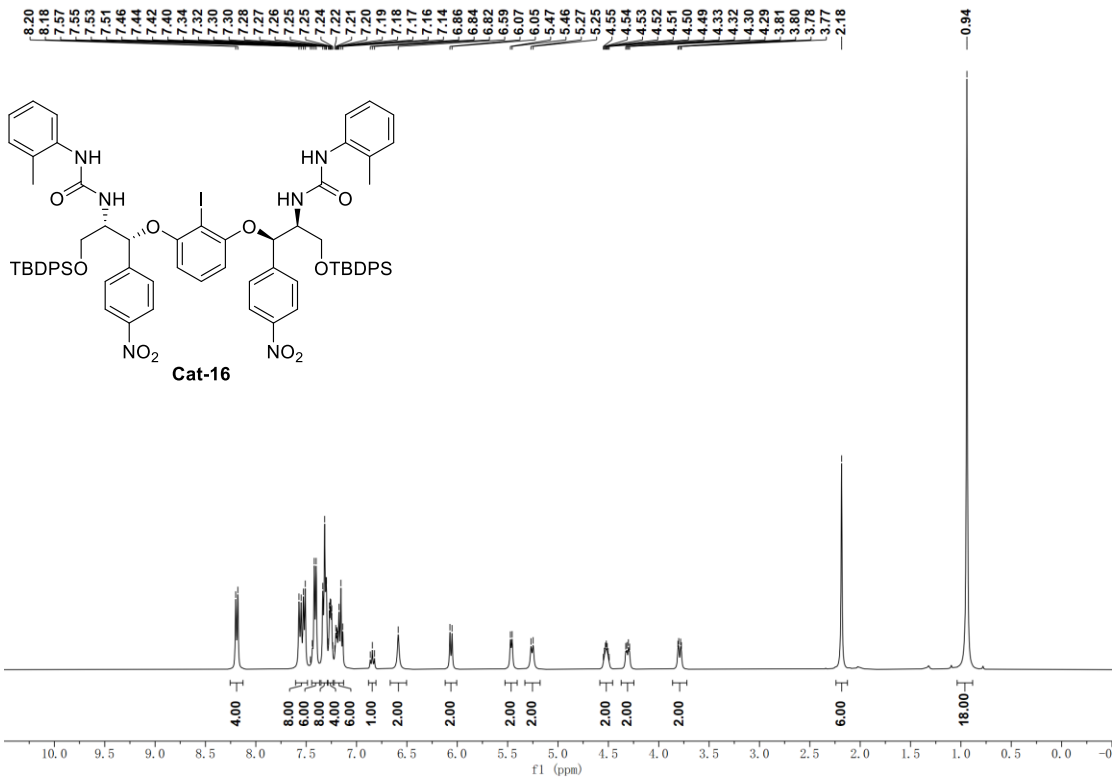
Supplementary Figure 44. ^{1}H NMR Spectrum of **Cat-15** (**400** MHz, $CDCl_3$)



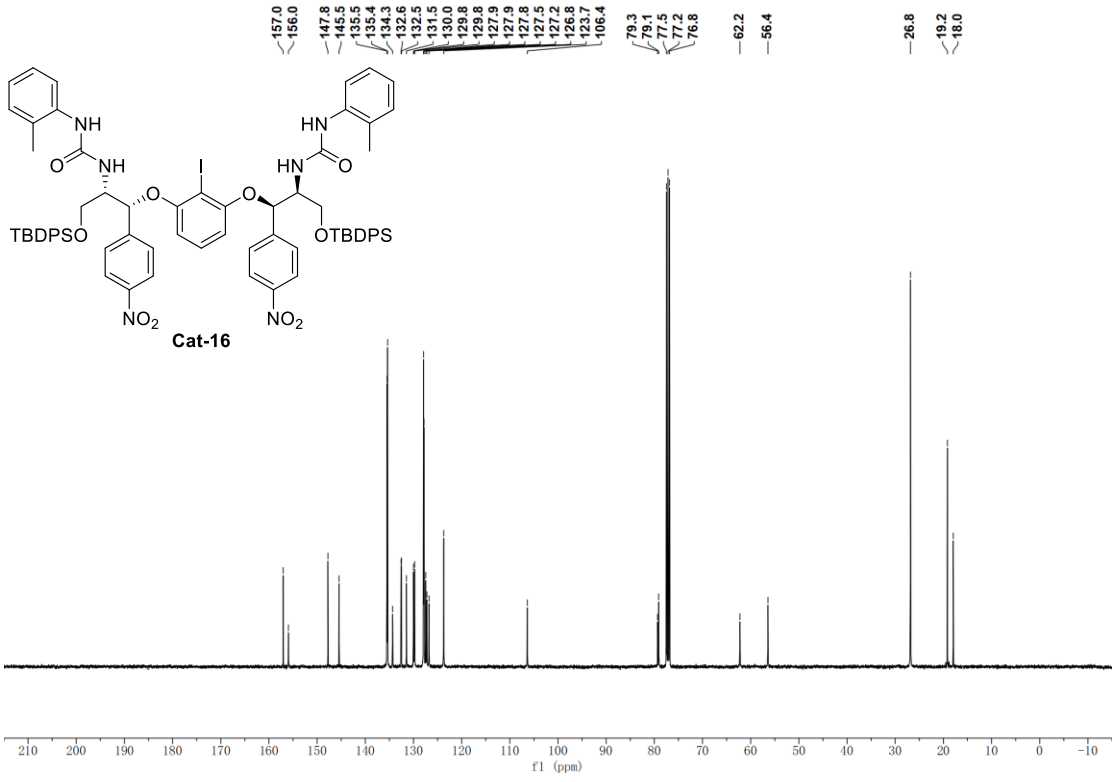
Supplementary Figure 45. ^{13}C NMR Spectrum of **Cat-15** (**100** MHz, $CDCl_3$)



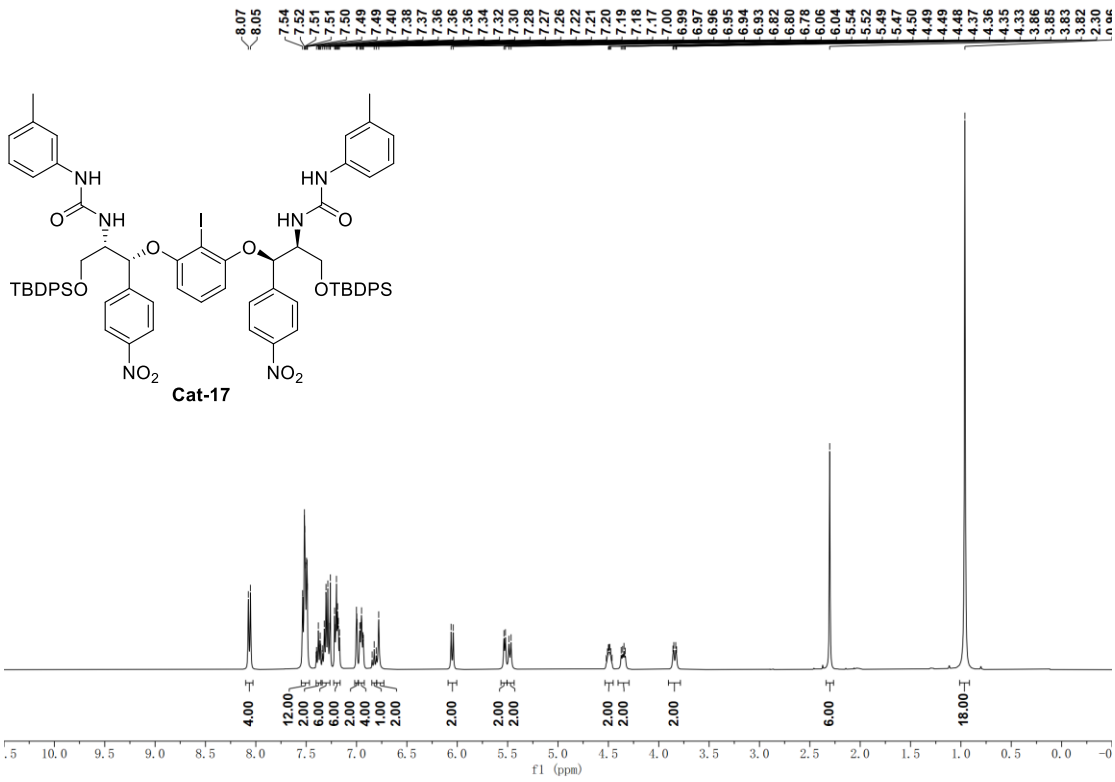
Supplementary Figure 46. ^{19}F NMR Spectrum of **Cat-15** (376 MHz, $CDCl_3$)



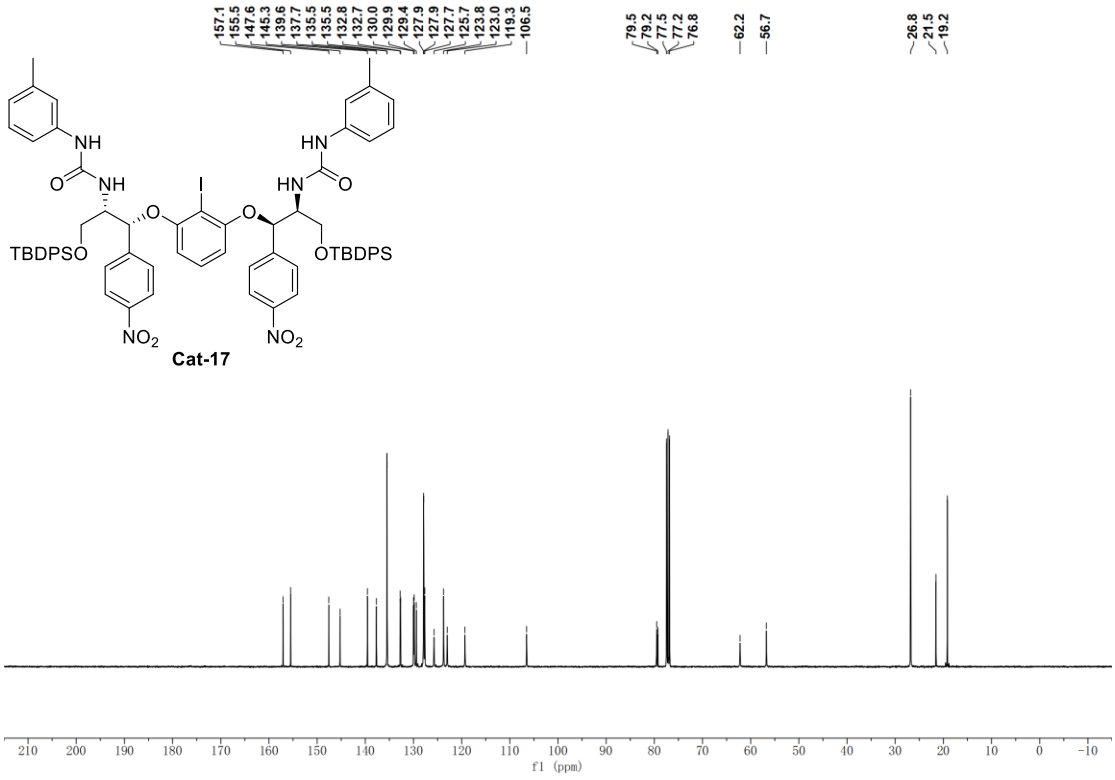
Supplementary Figure 47. ^{1}H NMR Spectrum of **Cat-16** (**400** MHz, $CDCl_3$)



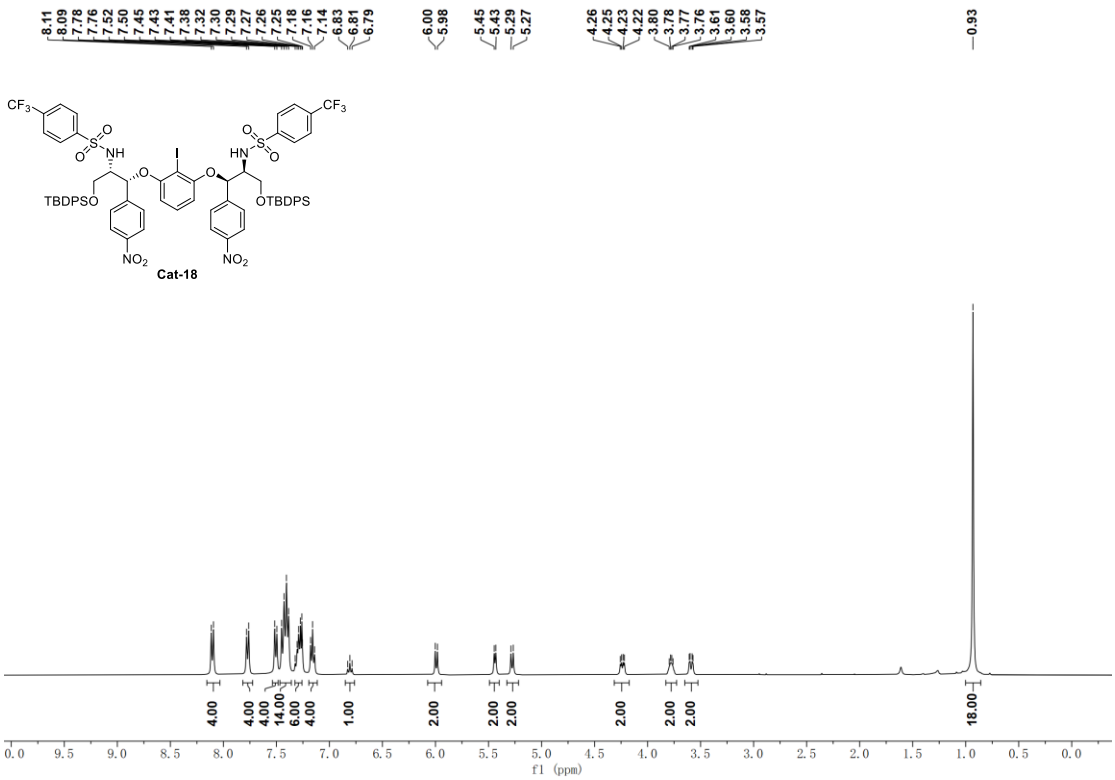
Supplementary Figure 48. ^{13}C NMR Spectrum of **Cat-16** (**100** MHz, $CDCl_3$)



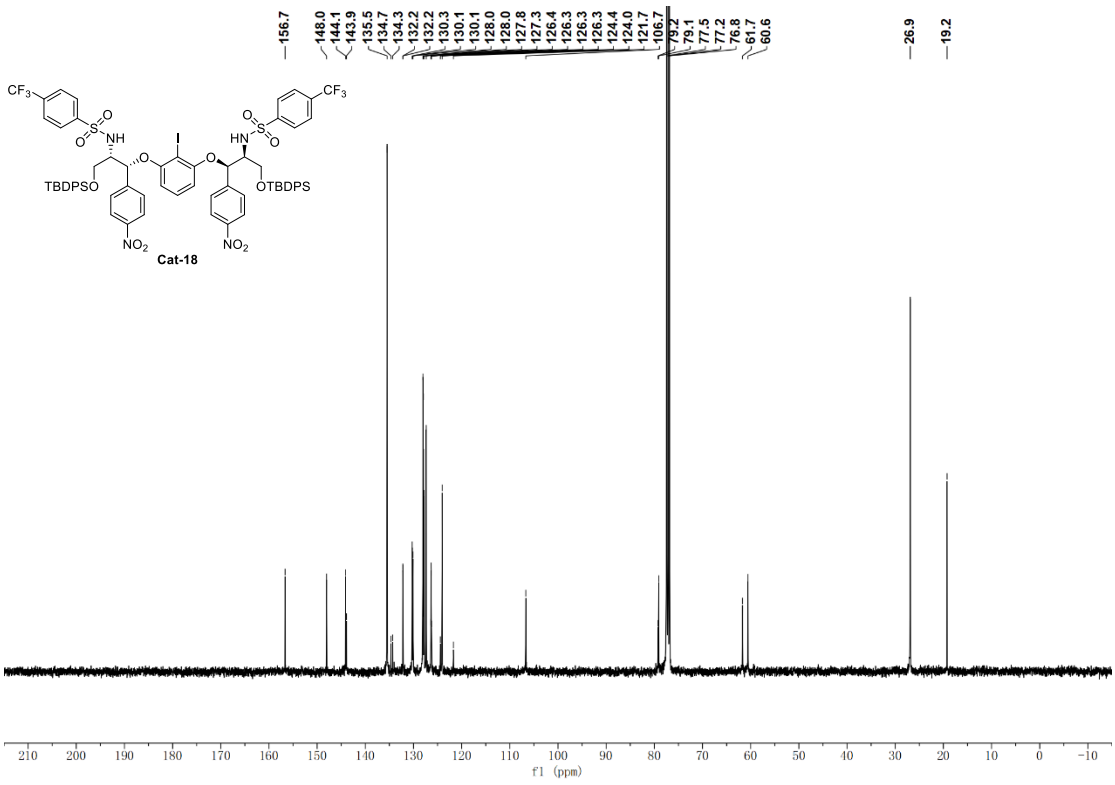
Supplementary Figure 49. ^{1}H NMR Spectrum of **Cat-17** (**400** MHz, $CDCl_3$)



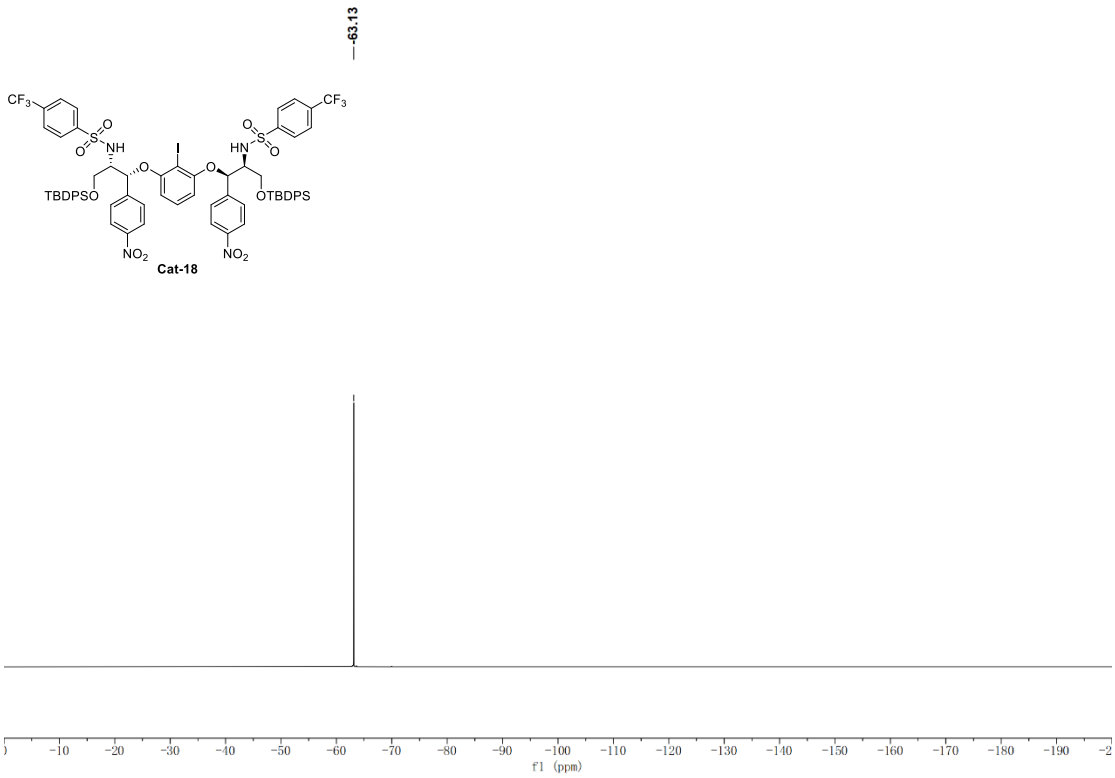
Supplementary Figure 50. ^{13}C NMR Spectrum of **Cat-17** (**100** MHz, $CDCl_3$)



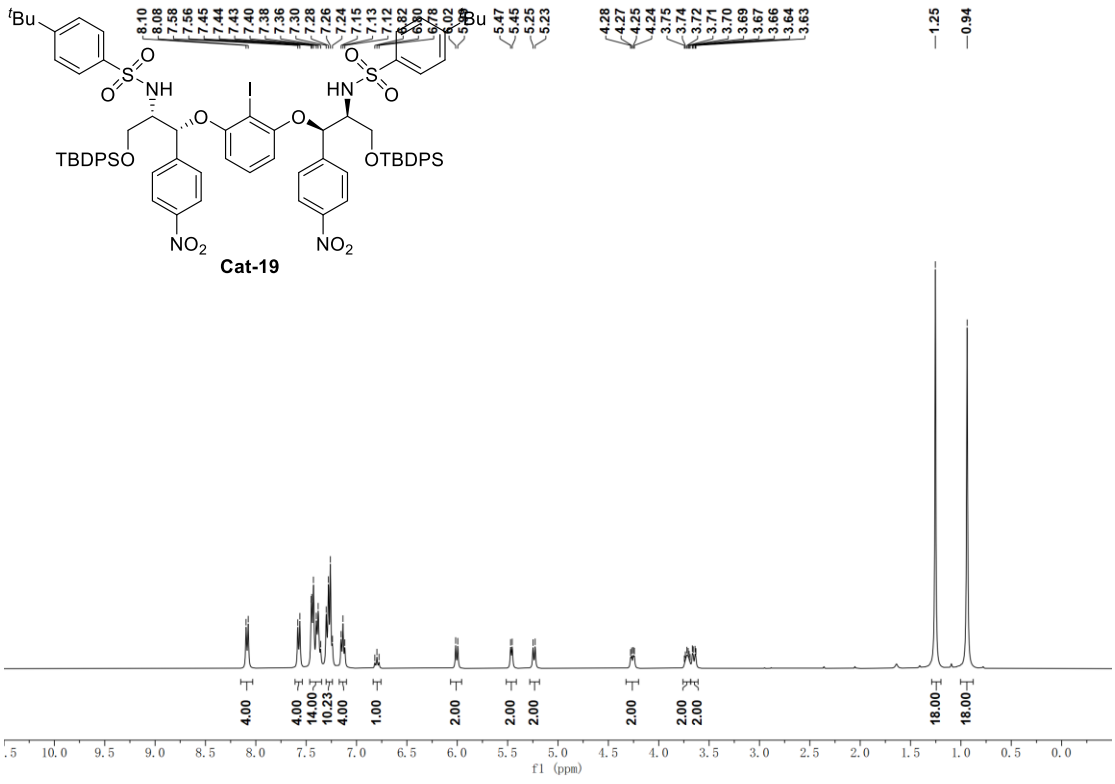
Supplementary Figure 51. ^{1}H NMR Spectrum of **Cat-18** (**400** MHz, $CDCl_3$)



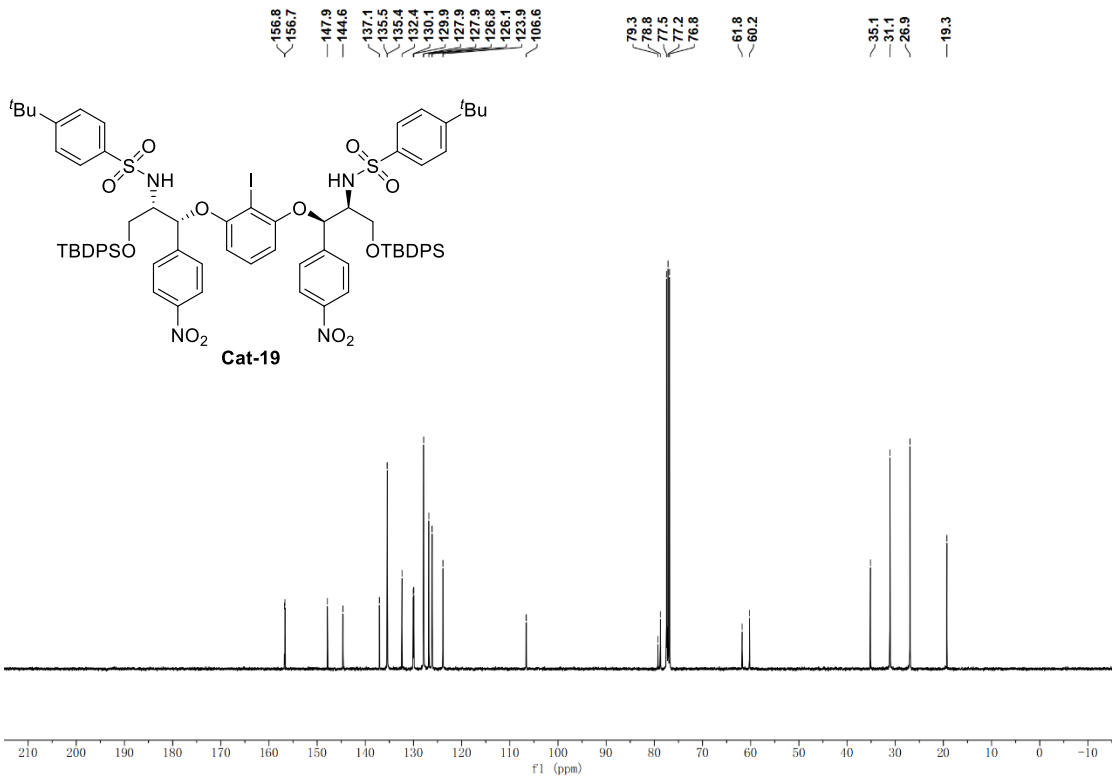
Supplementary Figure 52. ^{13}C NMR Spectrum of **Cat-18** (**100** MHz, $CDCl_3$)



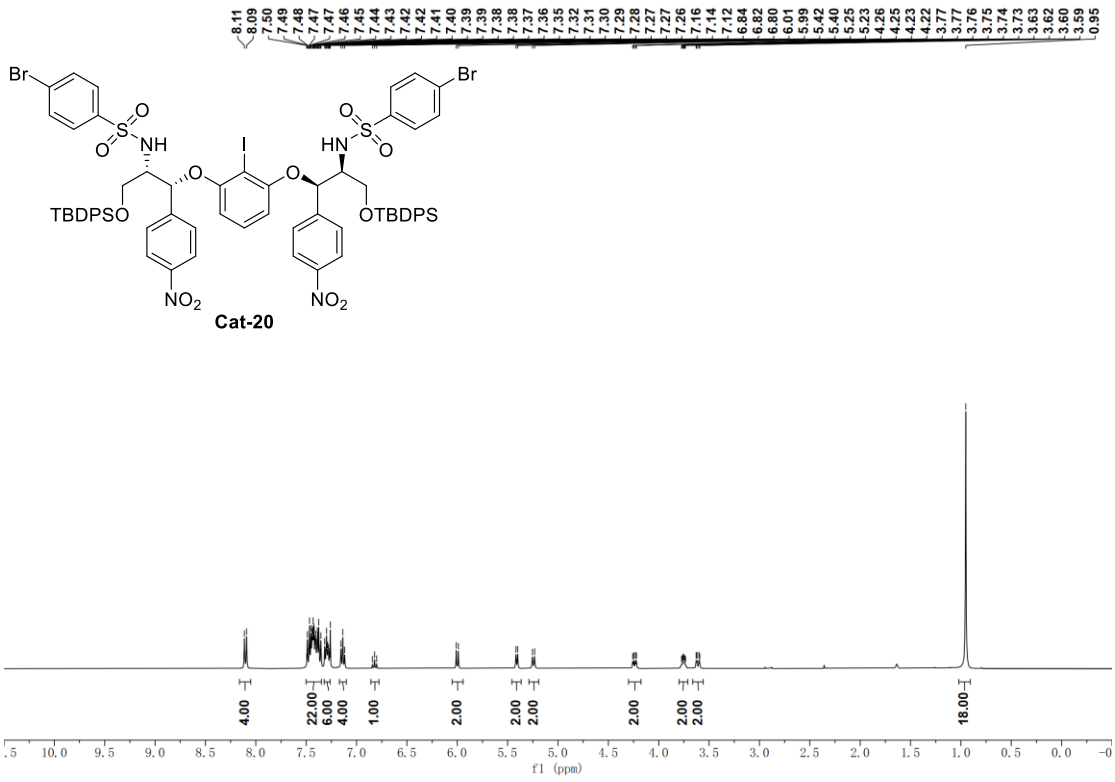
Supplementary Figure 53. ^{19}F NMR Spectrum of **Cat-18** (376 MHz, $CDCl_3$)



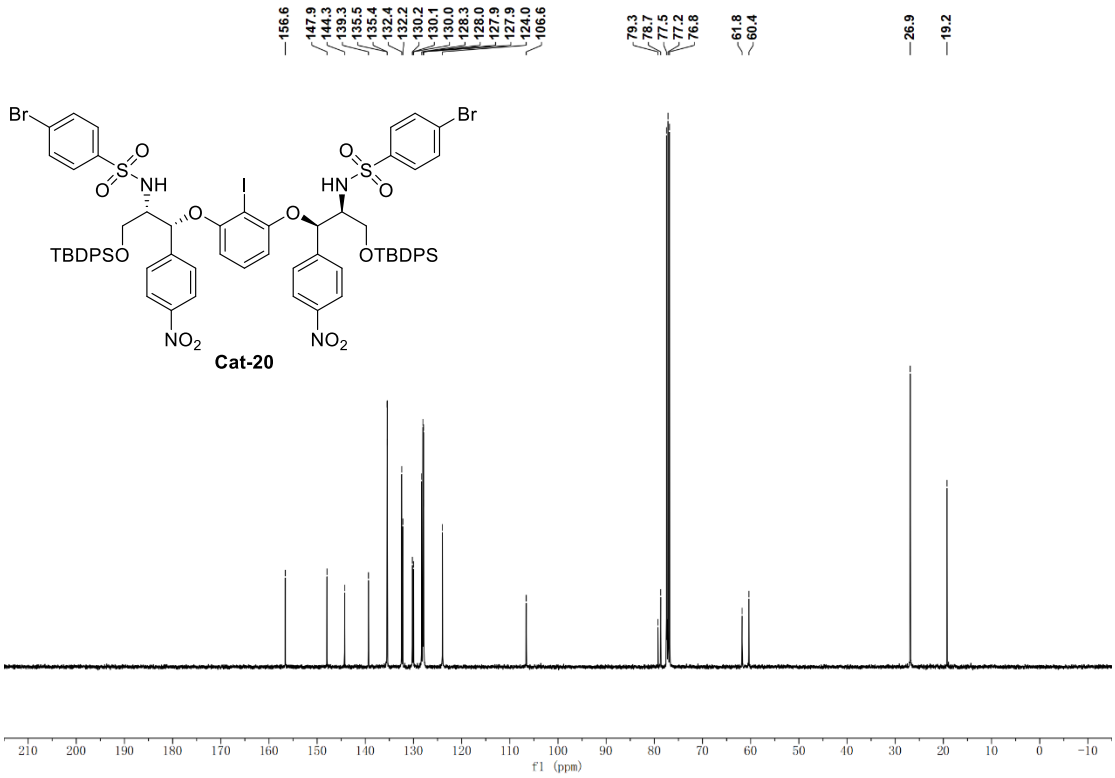
Supplementary Figure 54. ^{1}H NMR Spectrum of **Cat-19** (**400** MHz, $CDCl_3$)



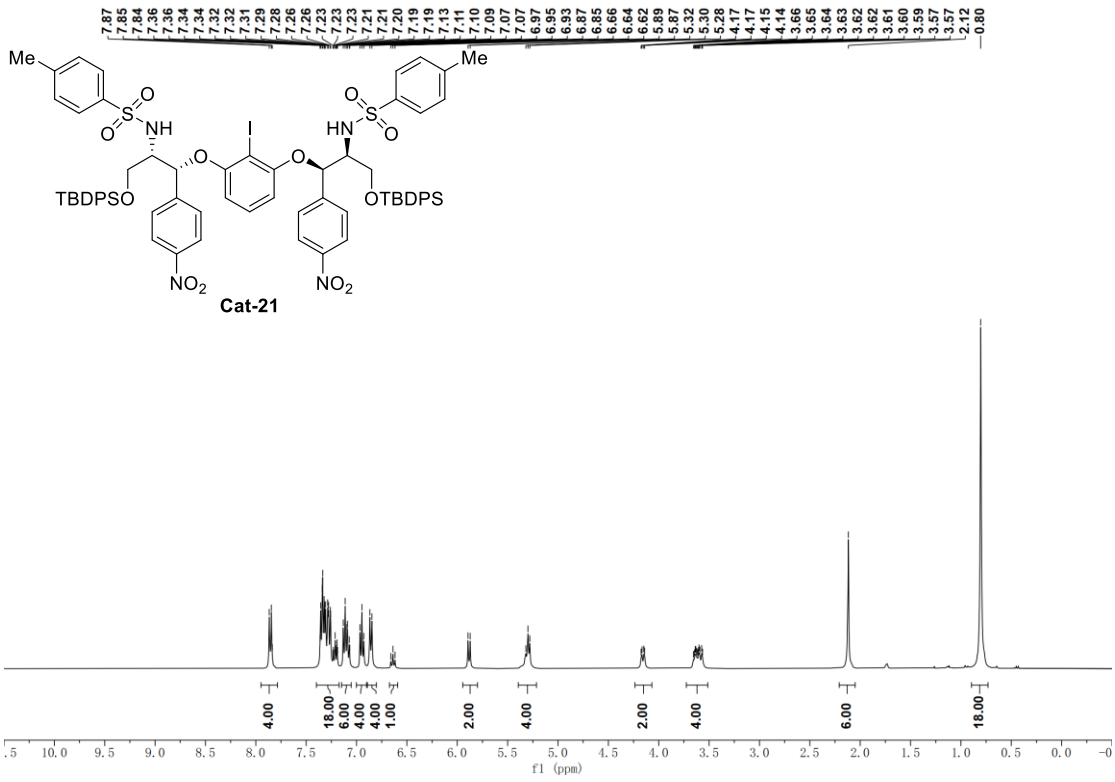
Supplementary Figure 55. ^{13}C NMR Spectrum of **Cat-19** (**100** MHz, $CDCl_3$)



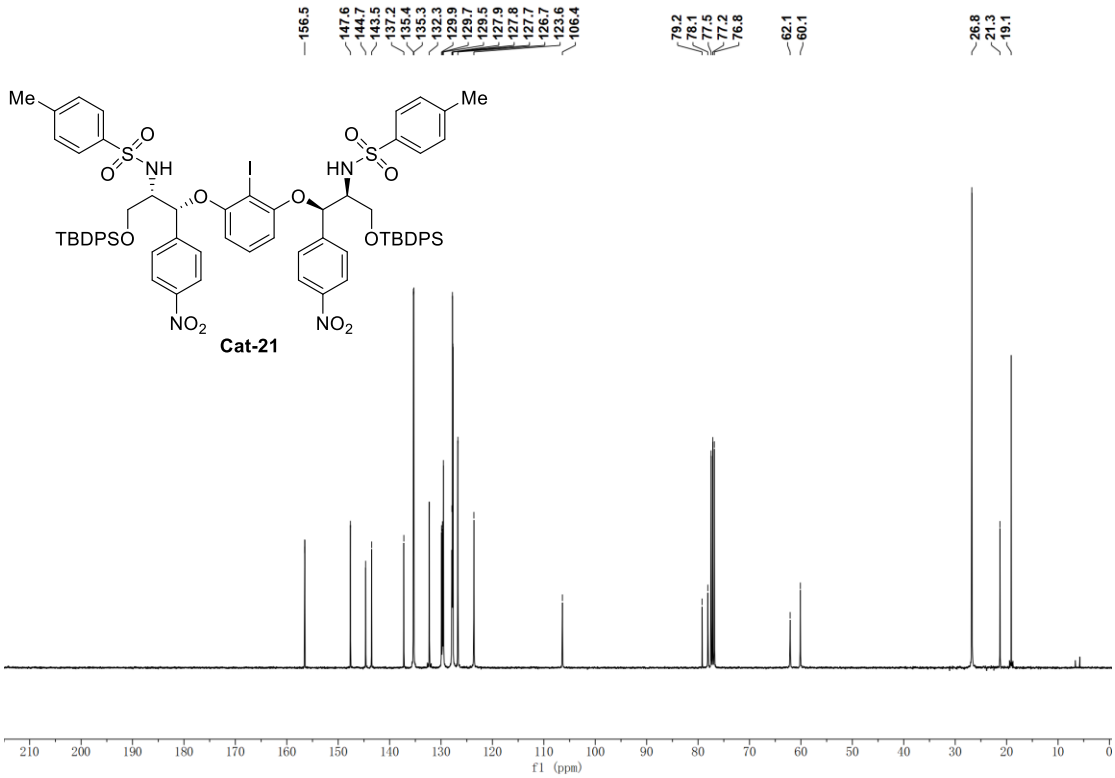
Supplementary Figure 56. ^{1}H NMR Spectrum of **Cat-20** (**400** MHz, $CDCl_3$)



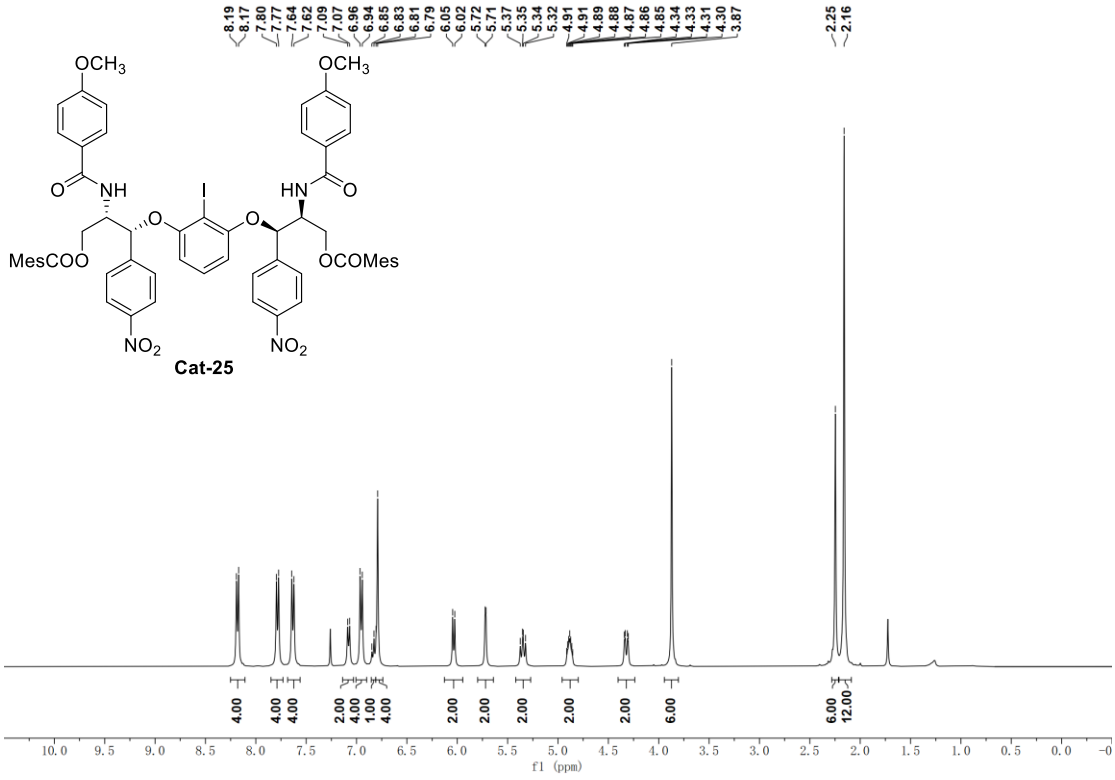
Supplementary Figure 57. ^{13}C NMR Spectrum of **Cat-20** (**100** MHz, $CDCl_3$)



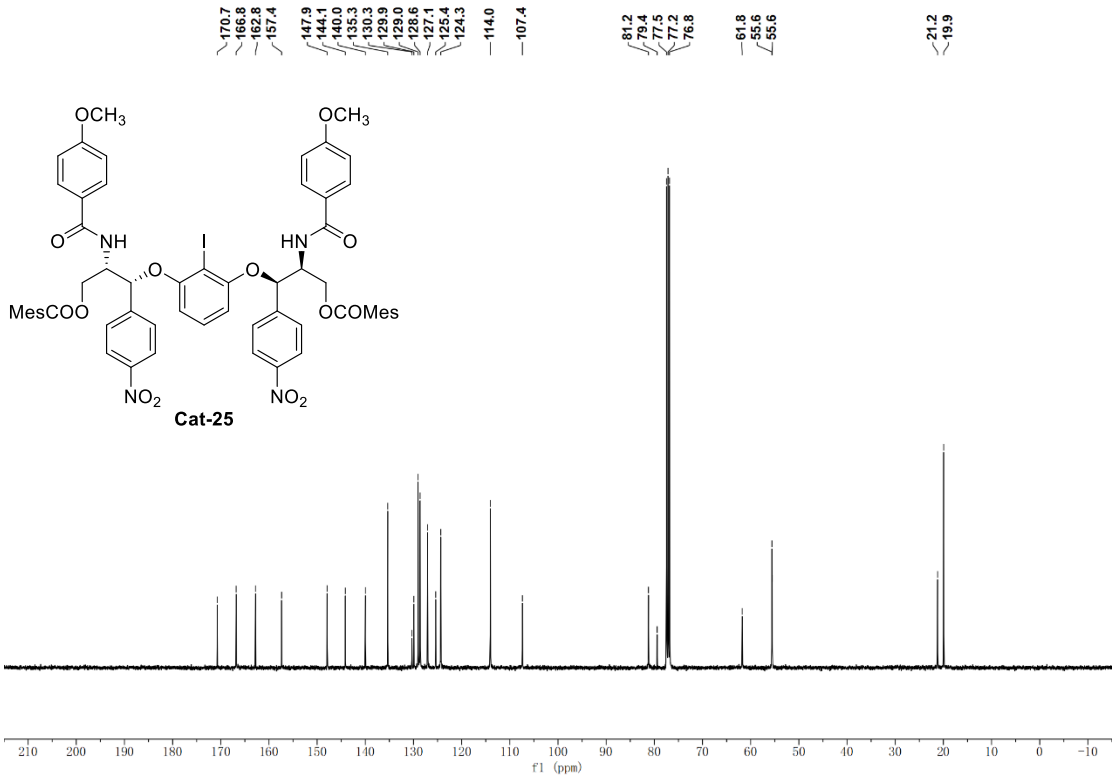
Supplementary Figure 58. ^{1}H NMR Spectrum of **Cat-21** (**400** MHz, $CDCl_3$)



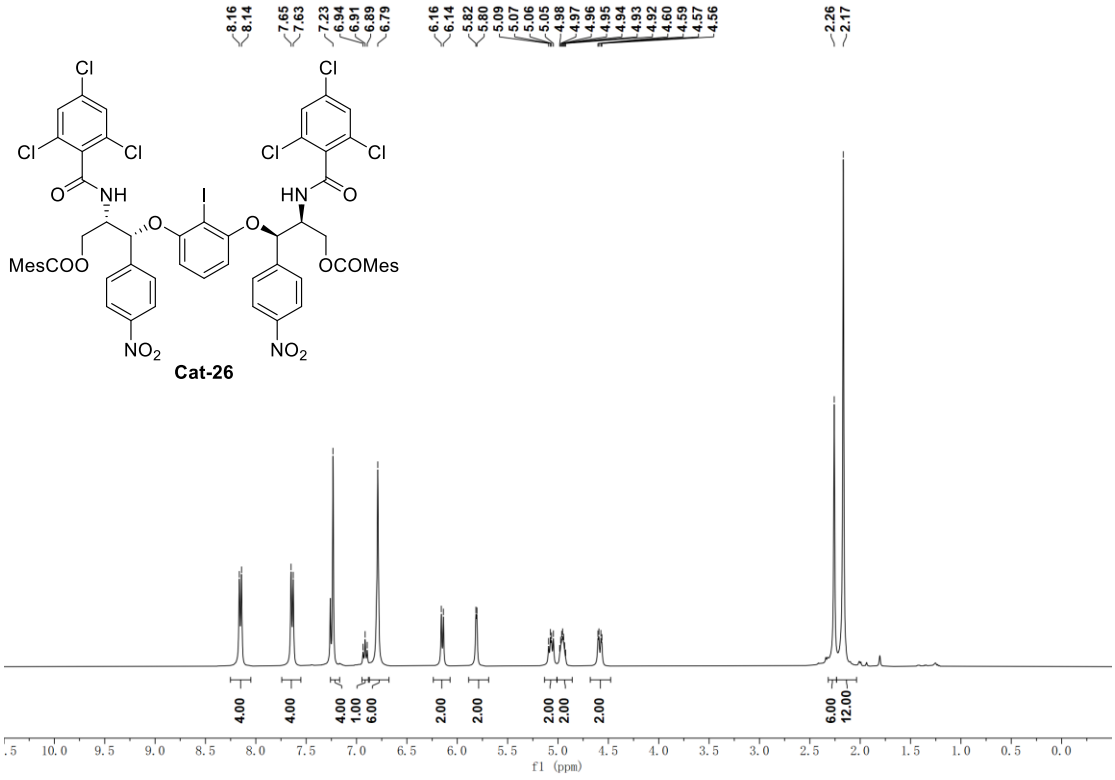
Supplementary Figure 59. ^{13}C NMR Spectrum of **Cat-21** (**100** MHz, $CDCl_3$)



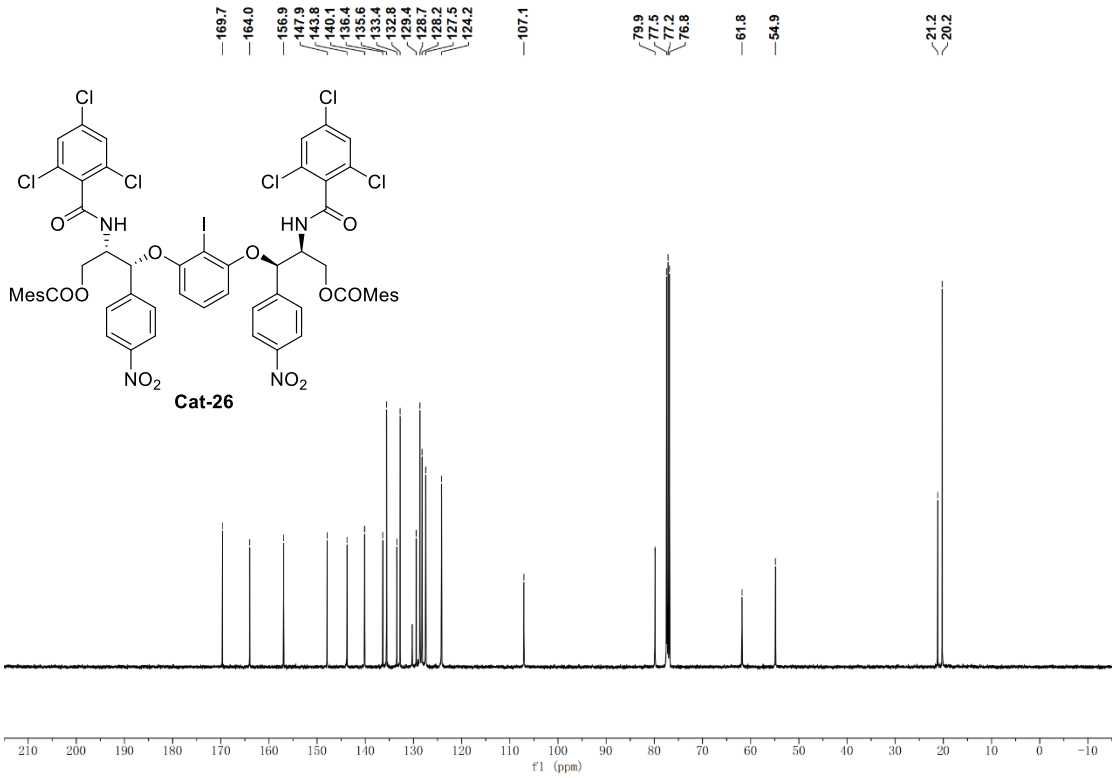
Supplementary Figure 60. ^{1}H NMR Spectrum of **Cat-25** (**400** MHz, $CDCl_3$)



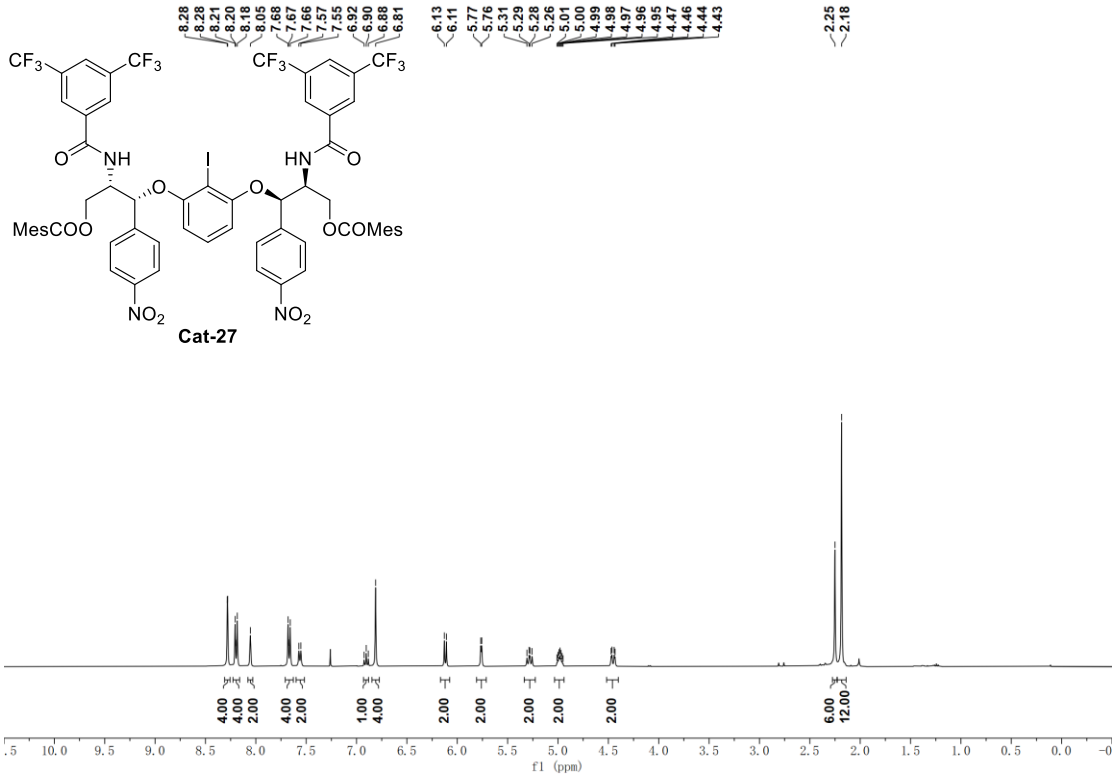
Supplementary Figure 61. ^{13}C NMR Spectrum of **Cat-25** (**100** MHz, $CDCl_3$)



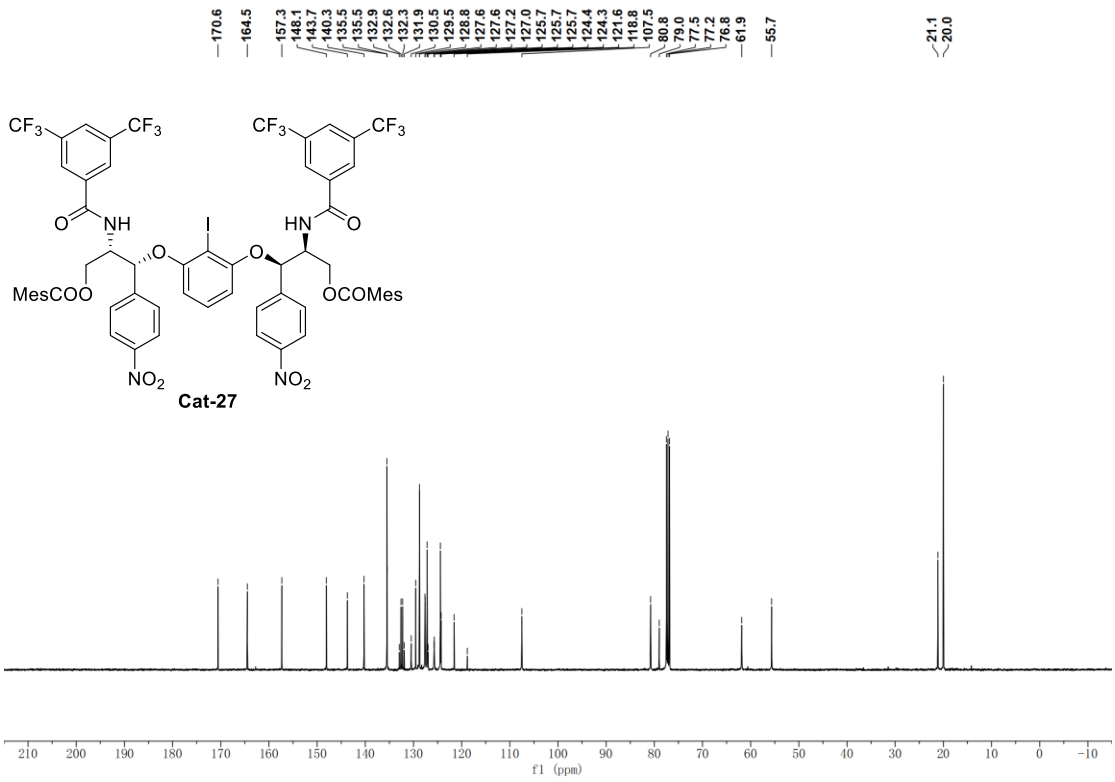
Supplementary Figure 62. ^{11}H NMR Spectrum of **Cat-26** (**400** MHz, $CDCl_3$)



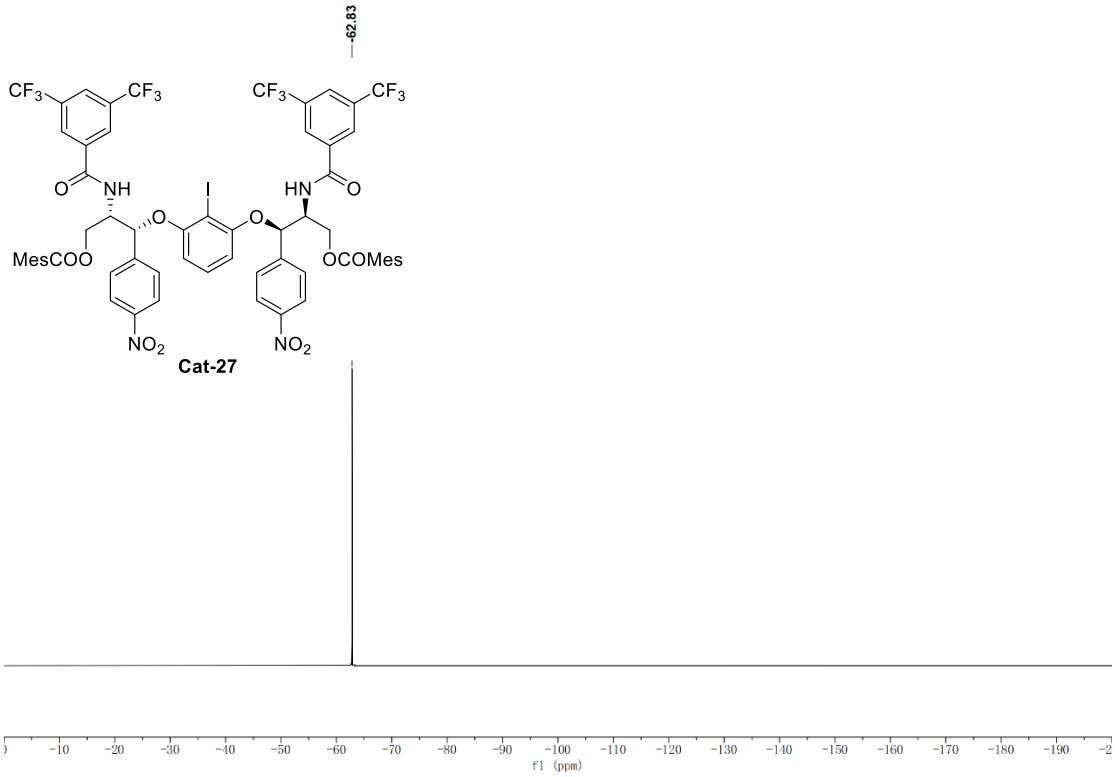
Supplementary Figure 63. ^{13}C NMR Spectrum of **Cat-26** (**100** MHz, $CDCl_3$)



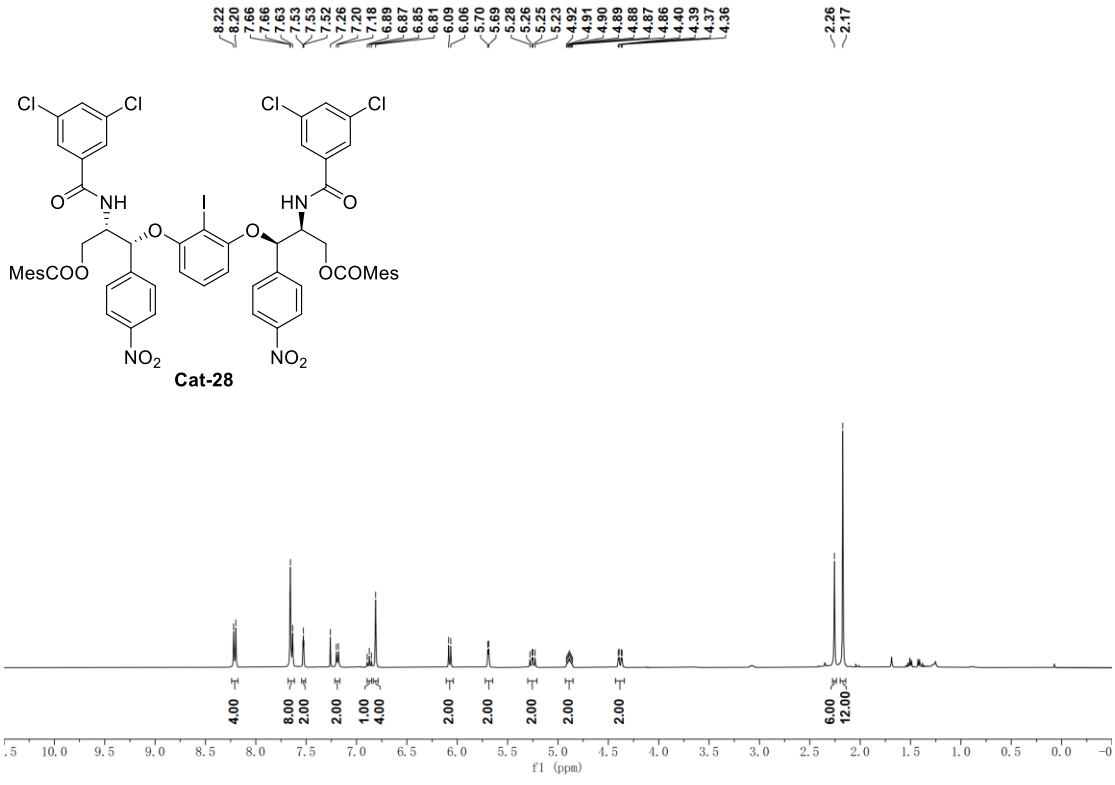
Supplementary Figure 64. ^{1}H NMR Spectrum of **Cat-27** (**400** MHz, $CDCl_3$)



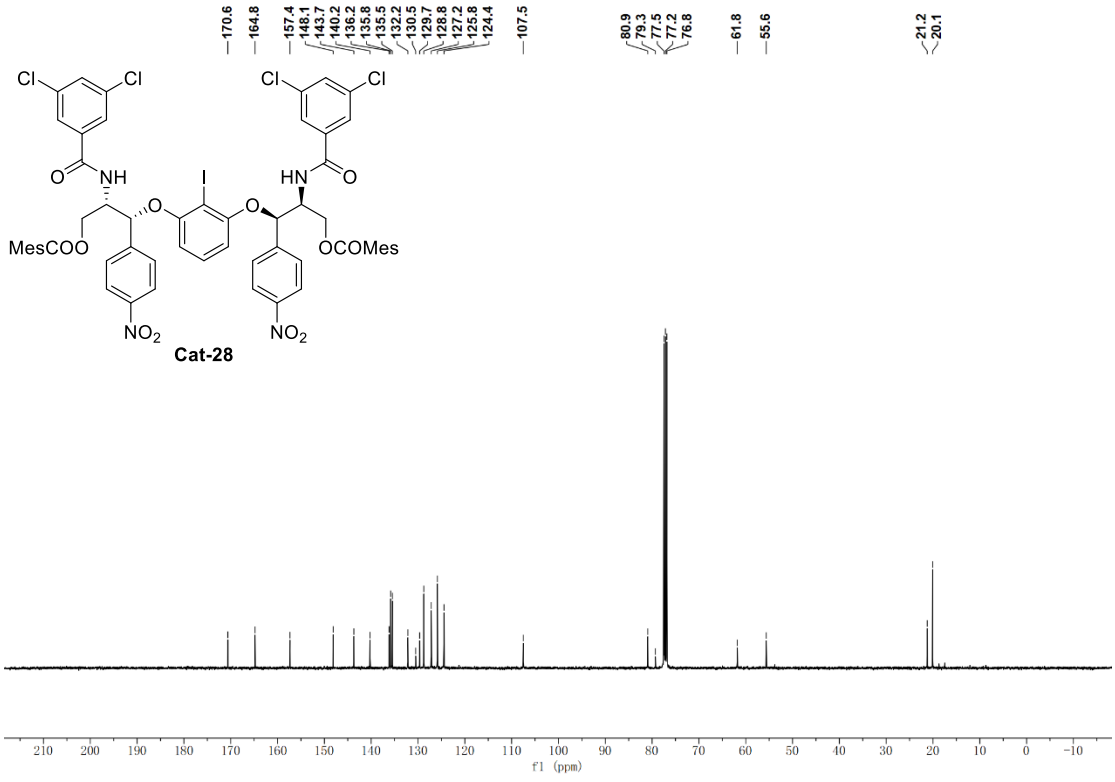
Supplementary Figure 65. ^{13}C NMR Spectrum of **Cat-27** (**100** MHz, $CDCl_3$)



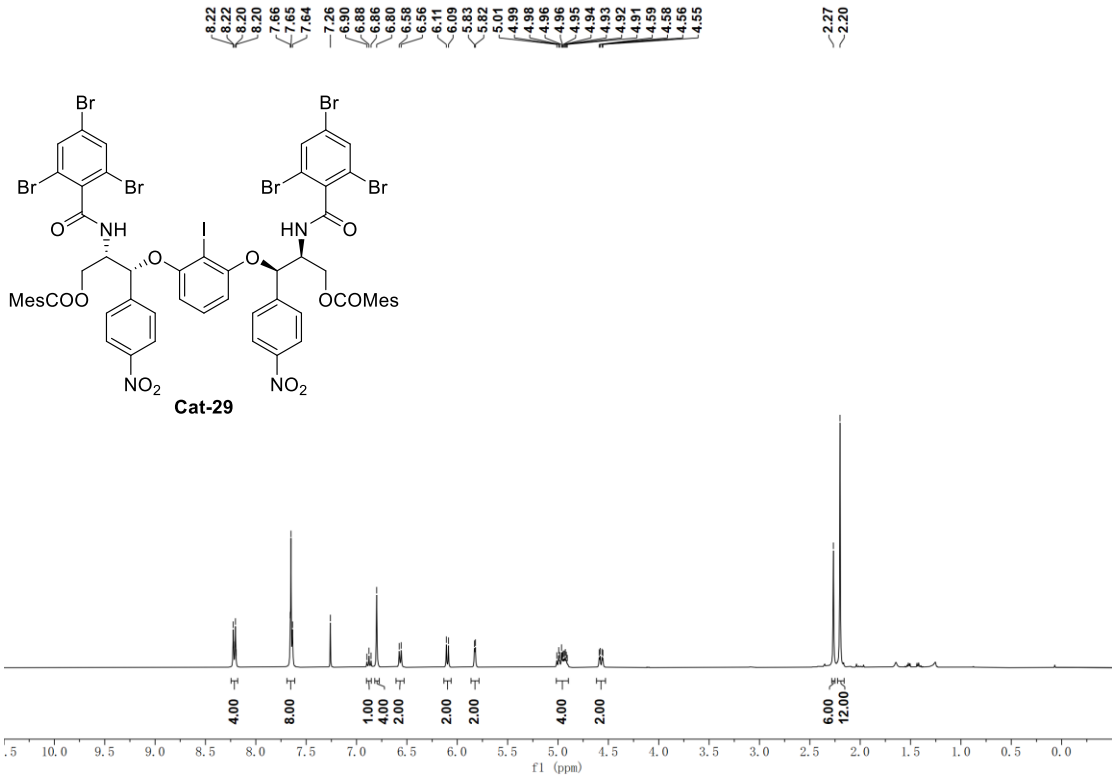
Supplementary Figure 66. ^{19}F NMR Spectrum of **Cat-27** (**376** MHz, $CDCl_3$)



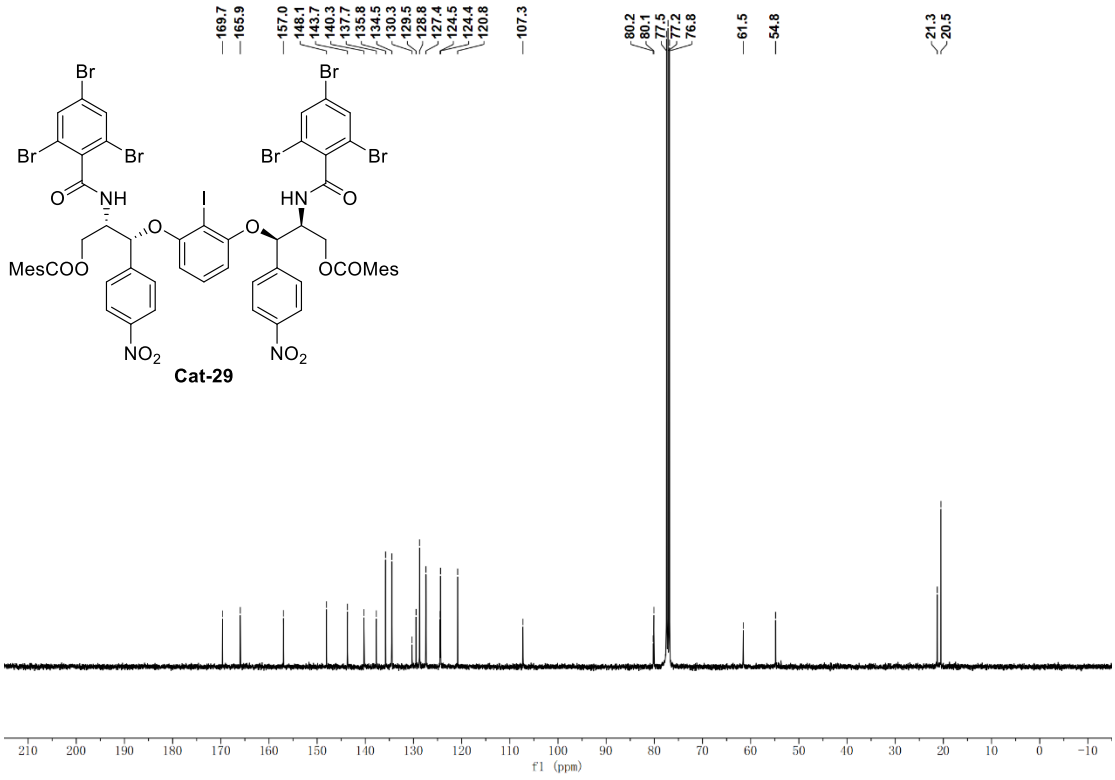
Supplementary Figure 67. ^{1}H NMR Spectrum of **Cat-28** (**400** MHz, $CDCl_3$)



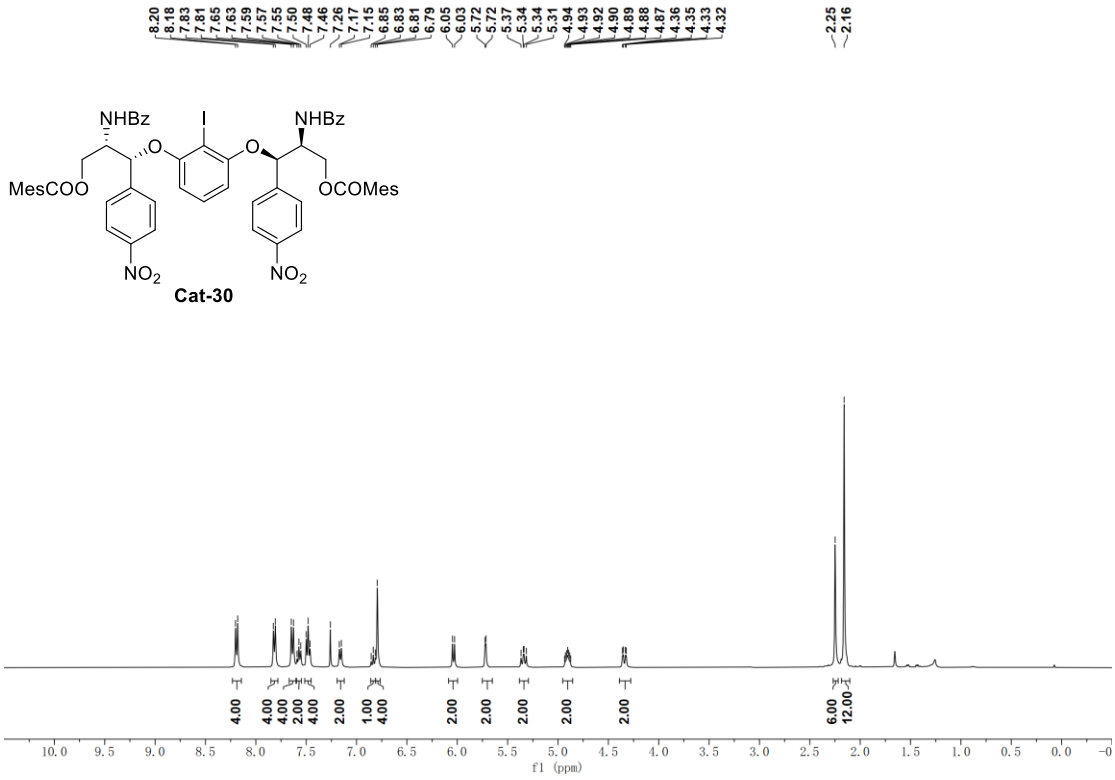
Supplementary Figure 68. ^{13}C NMR Spectrum of **Cat-28** (**100** MHz, $CDCl_3$)



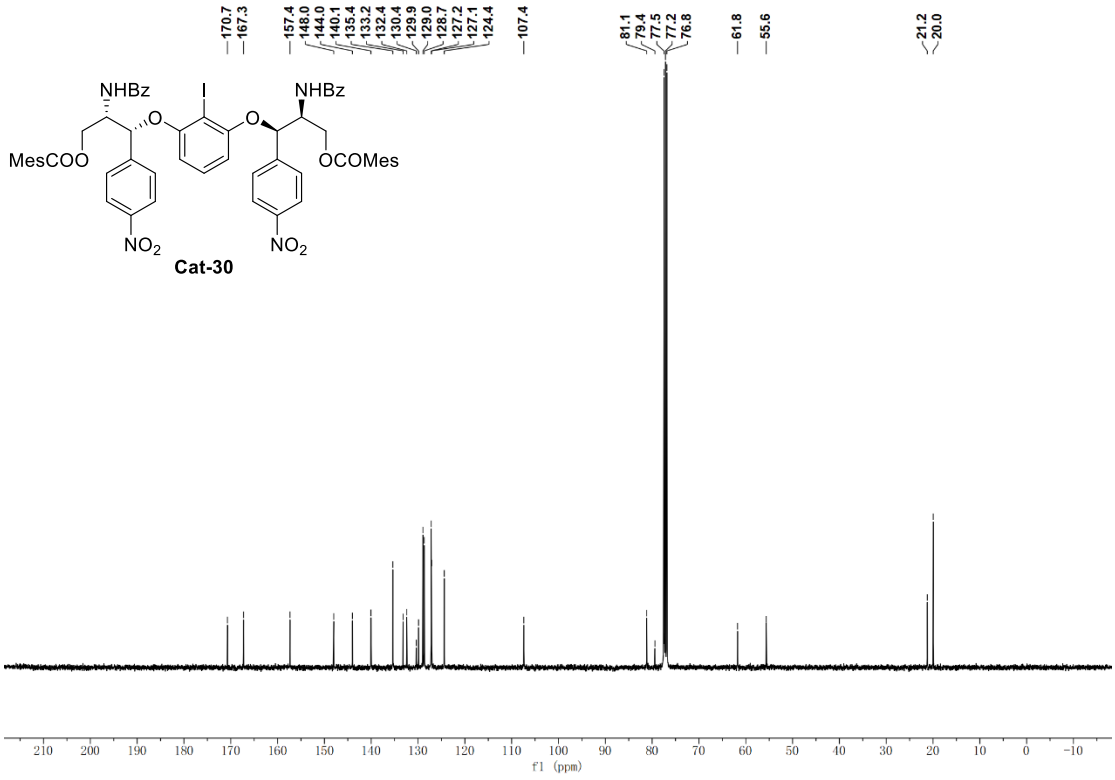
Supplementary Figure 69. ^{1}H NMR Spectrum of **Cat-29** (**400** MHz, $CDCl_3$)



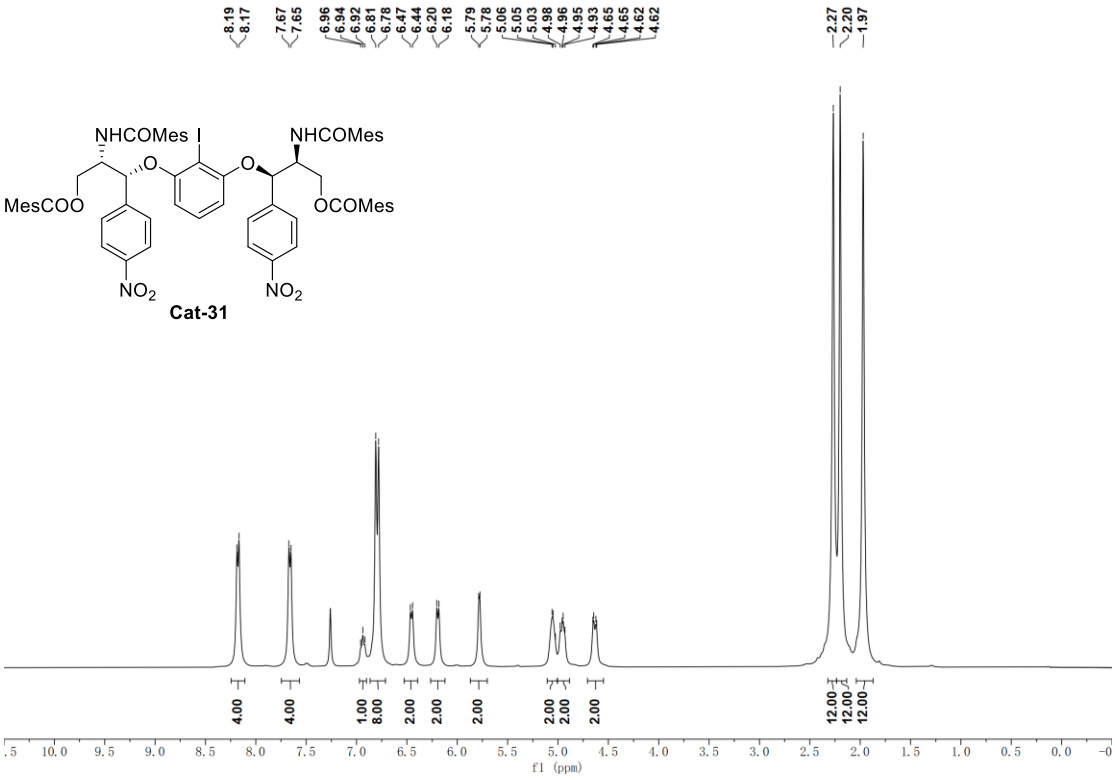
Supplementary Figure 70. ^{13}C NMR Spectrum of **Cat-29** (**100** MHz, $CDCl_3$)



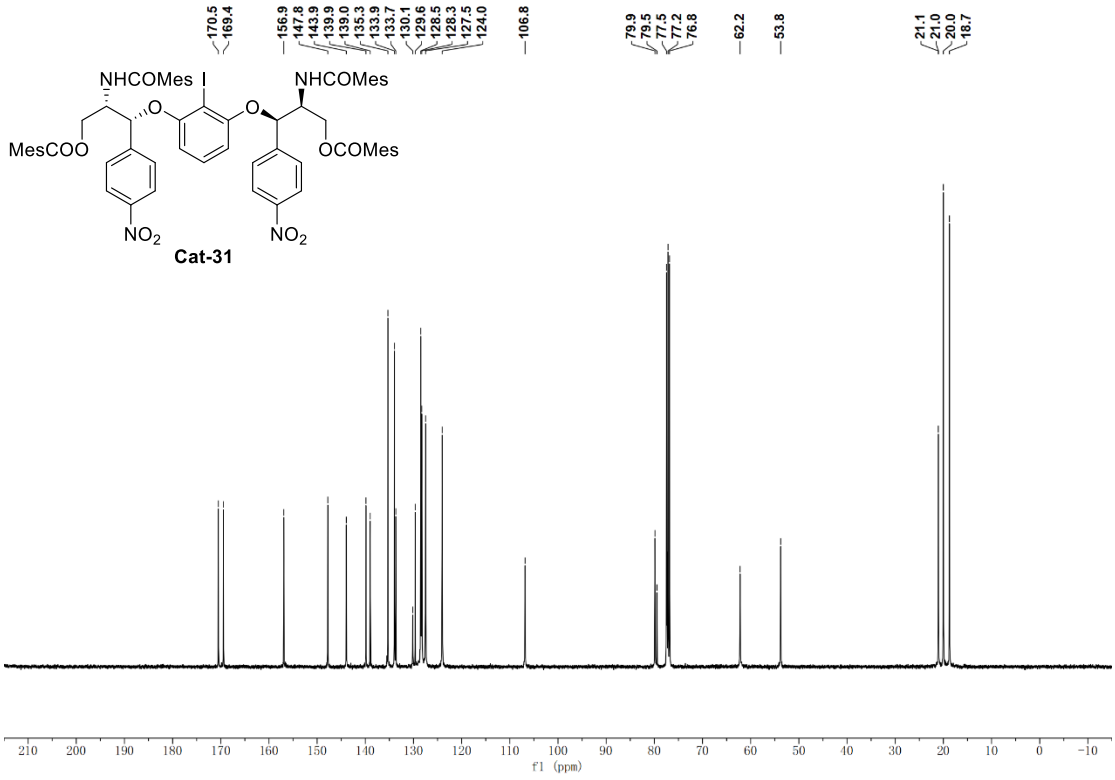
Supplementary Figure 71. ^{1}H NMR Spectrum of **Cat-30** (**400** MHz, $CDCl_3$)



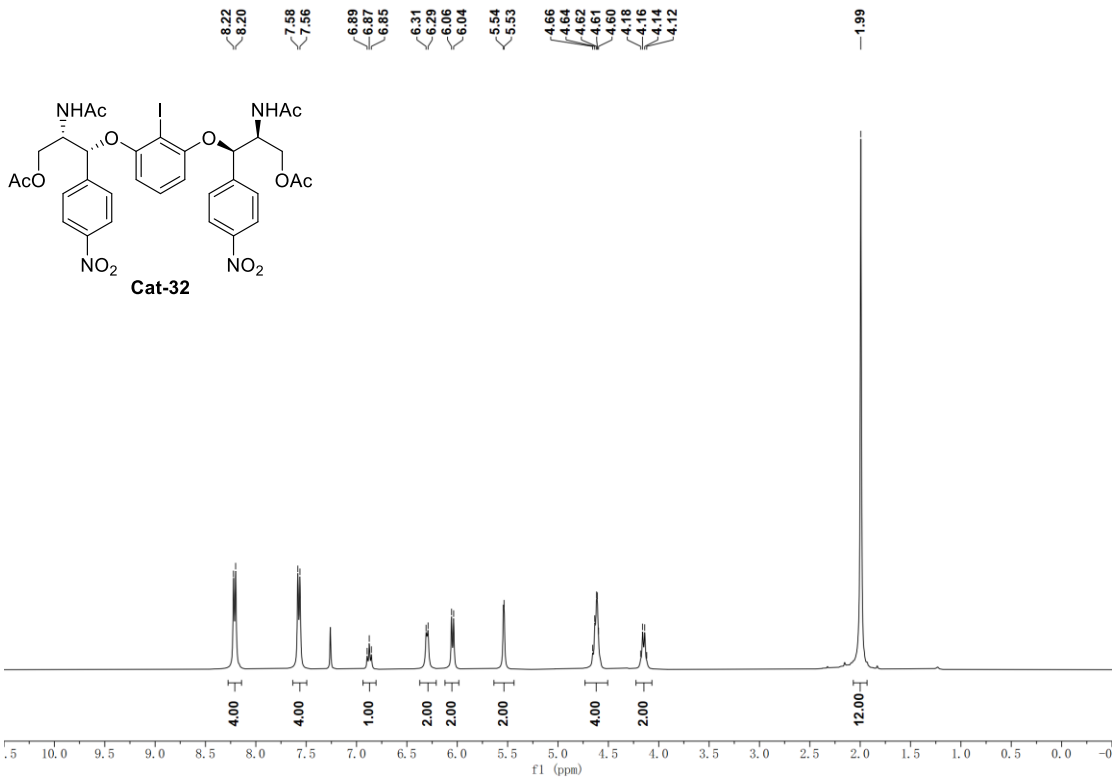
Supplementary Figure 72. ^{13}C NMR Spectrum of **Cat-30** (**100** MHz, $CDCl_3$)



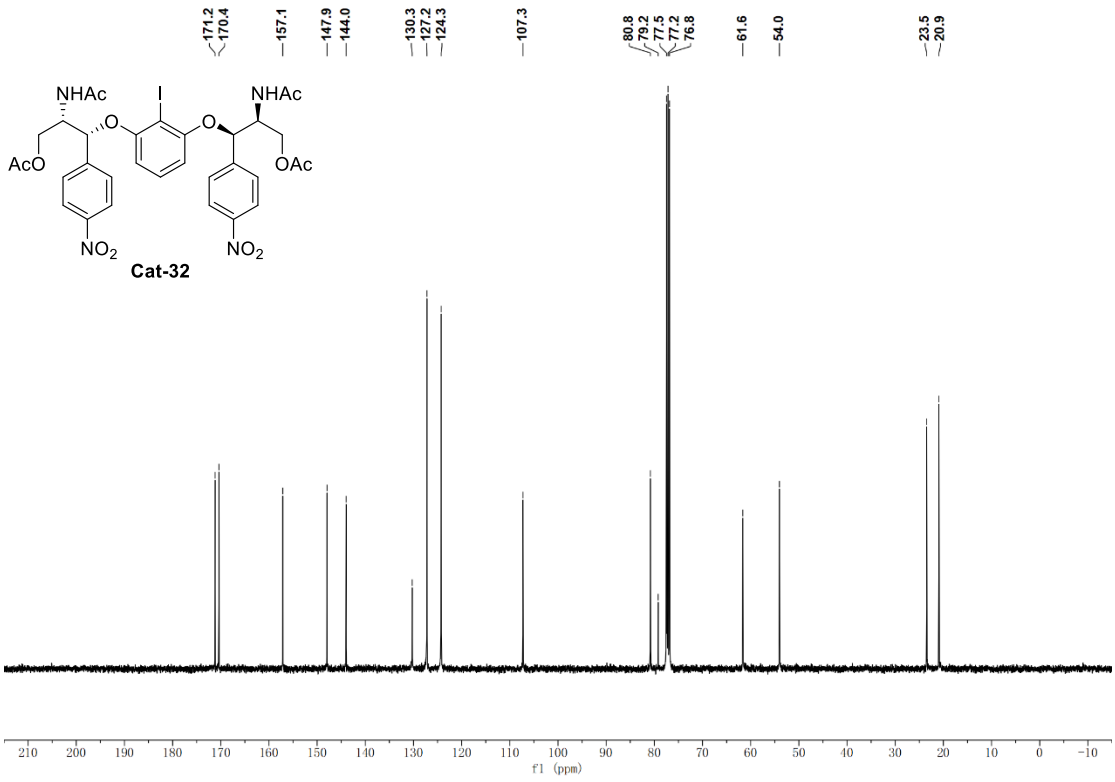
Supplementary Figure 73. ^{1}H NMR Spectrum of **Cat-31** (**400** MHz, $CDCl_3$)



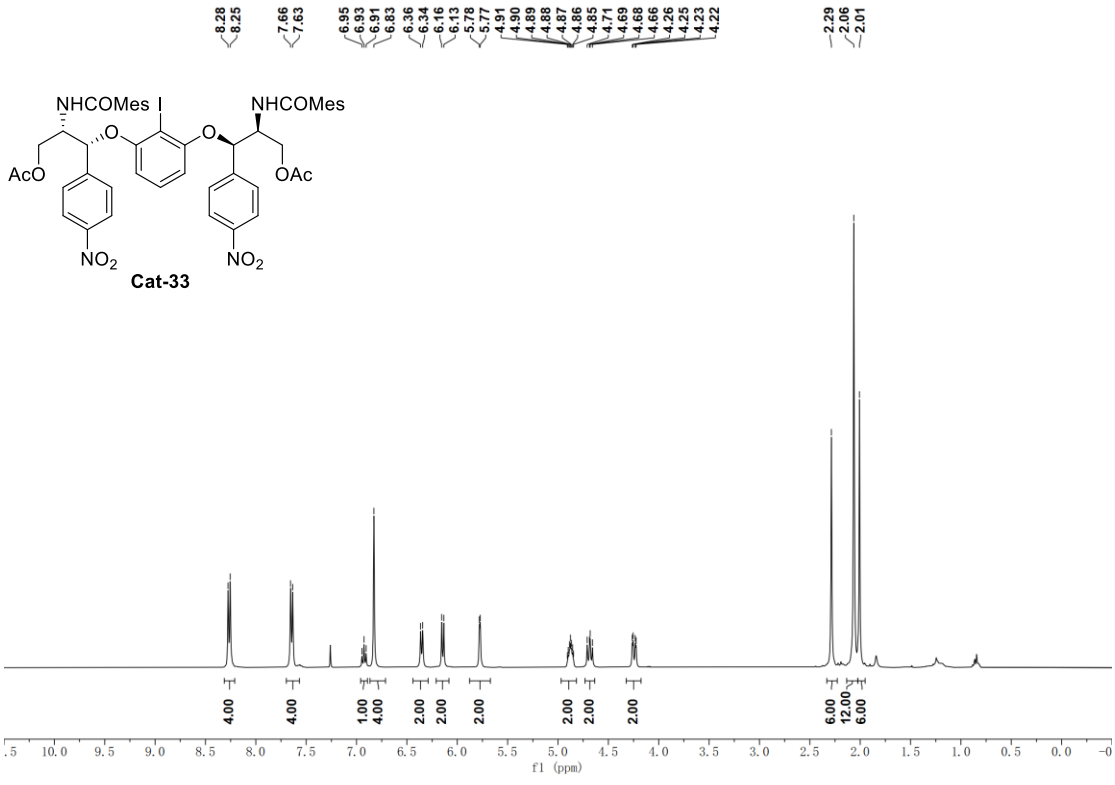
Supplementary Figure 74. ^{13}C NMR Spectrum of **Cat-31** (**100** MHz, $CDCl_3$)



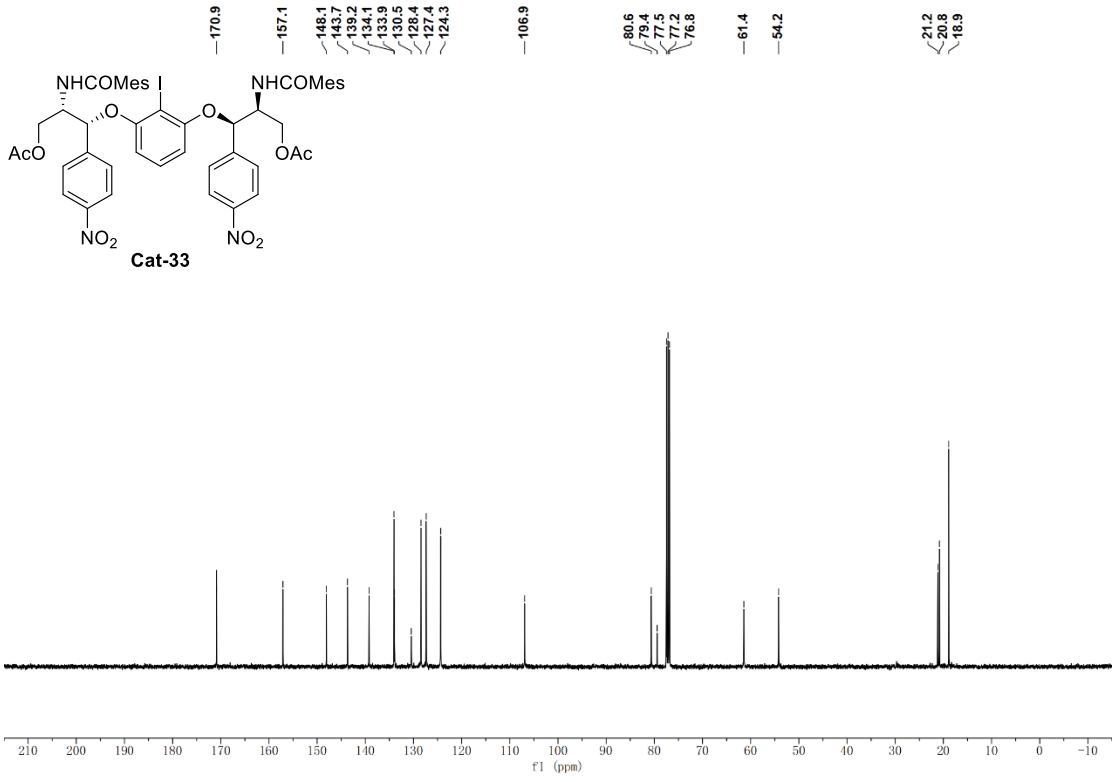
Supplementary Figure 75. ^{1}H NMR Spectrum of **Cat-32** (**400** MHz, $CDCl_3$)



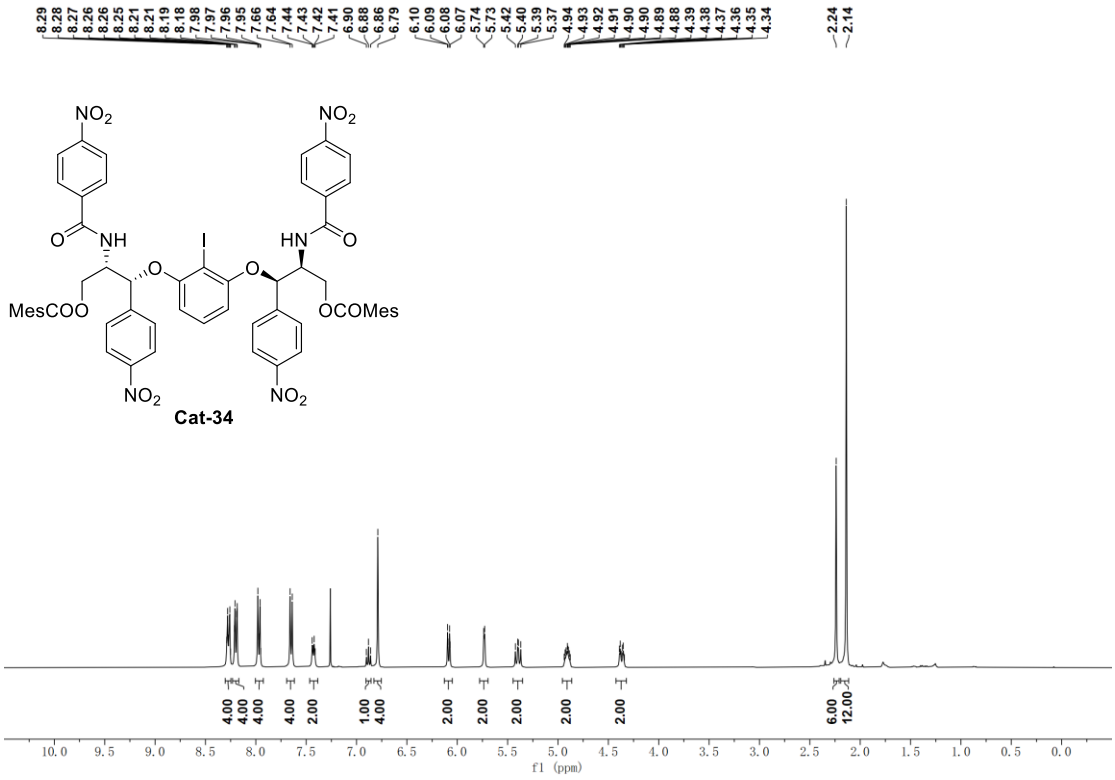
Supplementary Figure 76. ^{13}C NMR Spectrum of **Cat-32** (**100** MHz, $CDCl_3$)



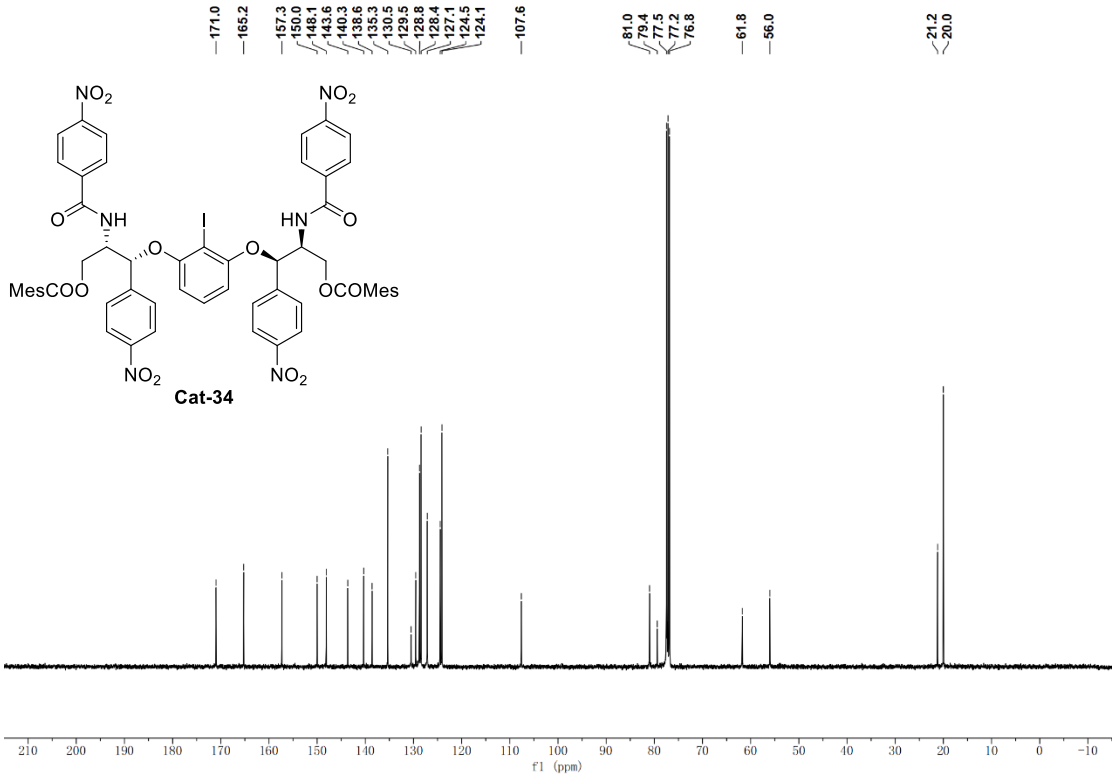
Supplementary Figure 77. ^{1}H NMR Spectrum of **Cat-33** (**400** MHz, $CDCl_3$)



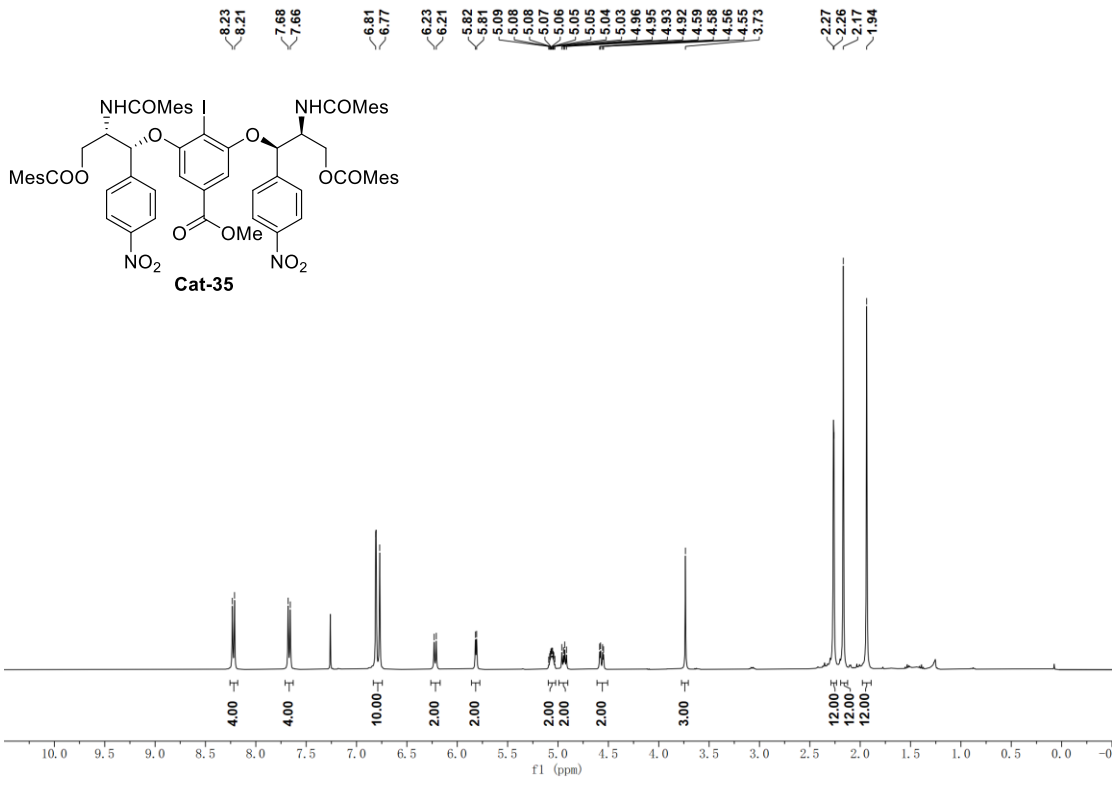
Supplementary Figure 78. ^{13}C NMR Spectrum of **Cat-33** (**100** MHz, $CDCl_3$)



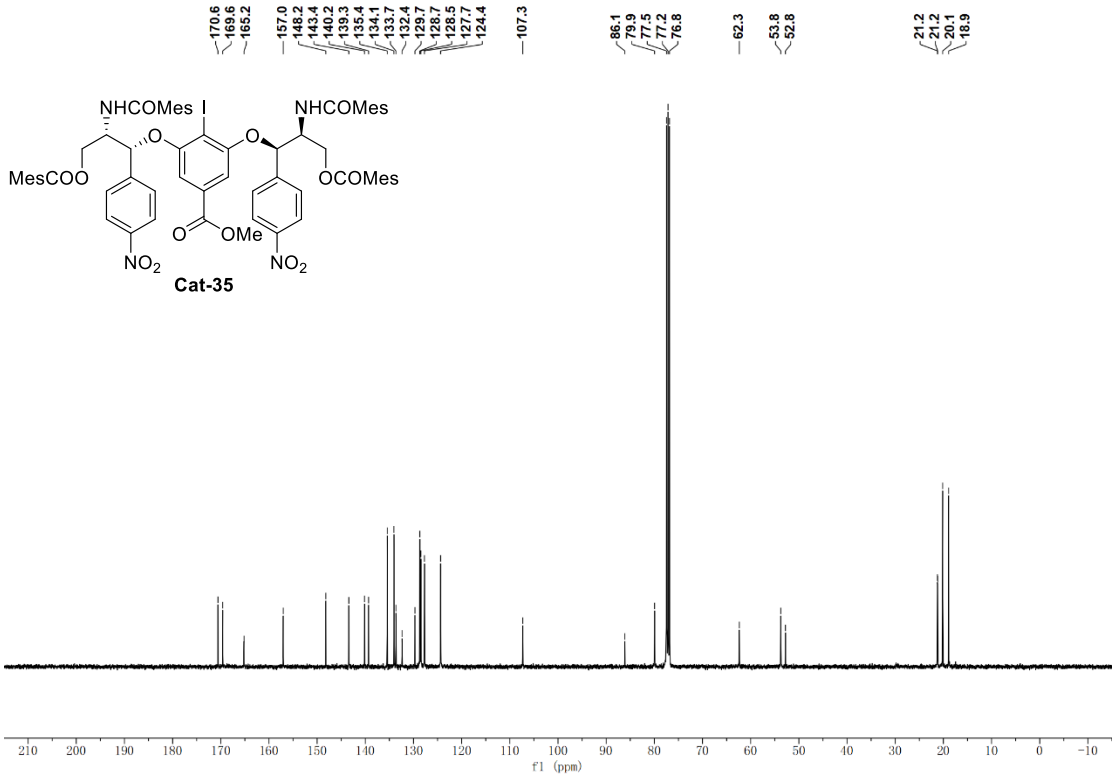
Supplementary Figure 79. ^{1}H NMR Spectrum of **Cat-34** (**400** MHz, $CDCl_3$)



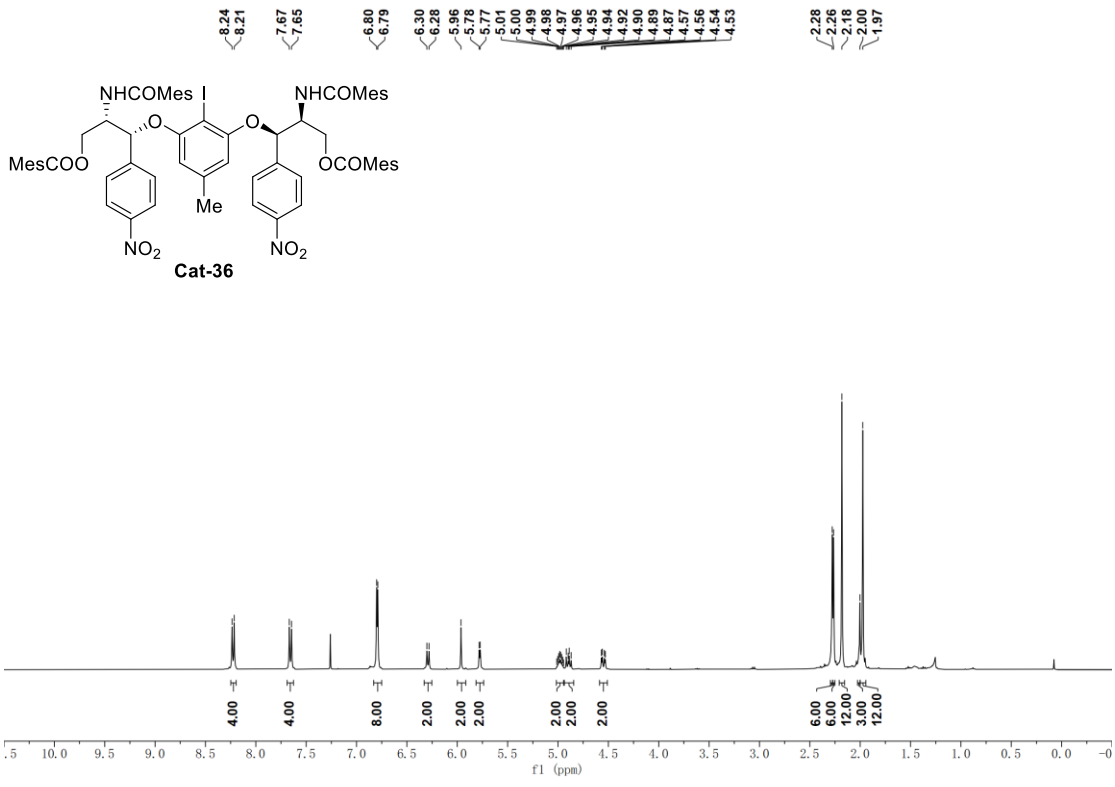
Supplementary Figure 80. ^{13}C NMR Spectrum of **Cat-34** (**100** MHz, $CDCl_3$)



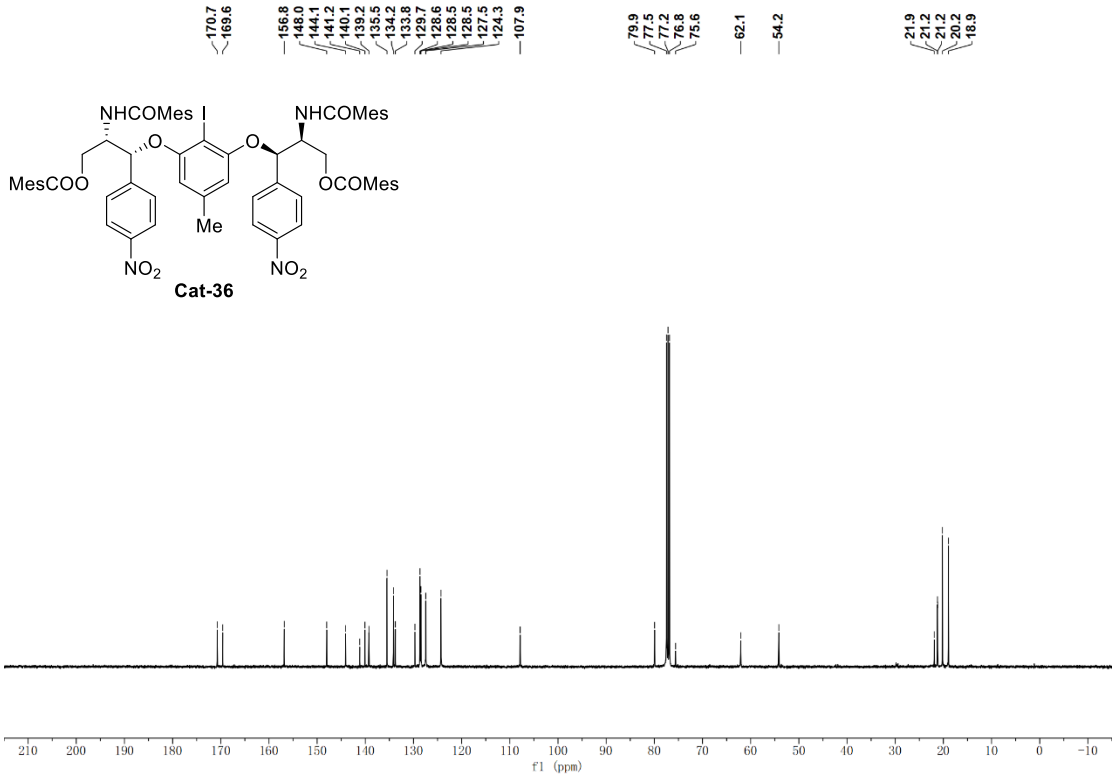
Supplementary Figure 81. ^{1}H NMR Spectrum of **Cat-35** (**400** MHz, $CDCl_3$)



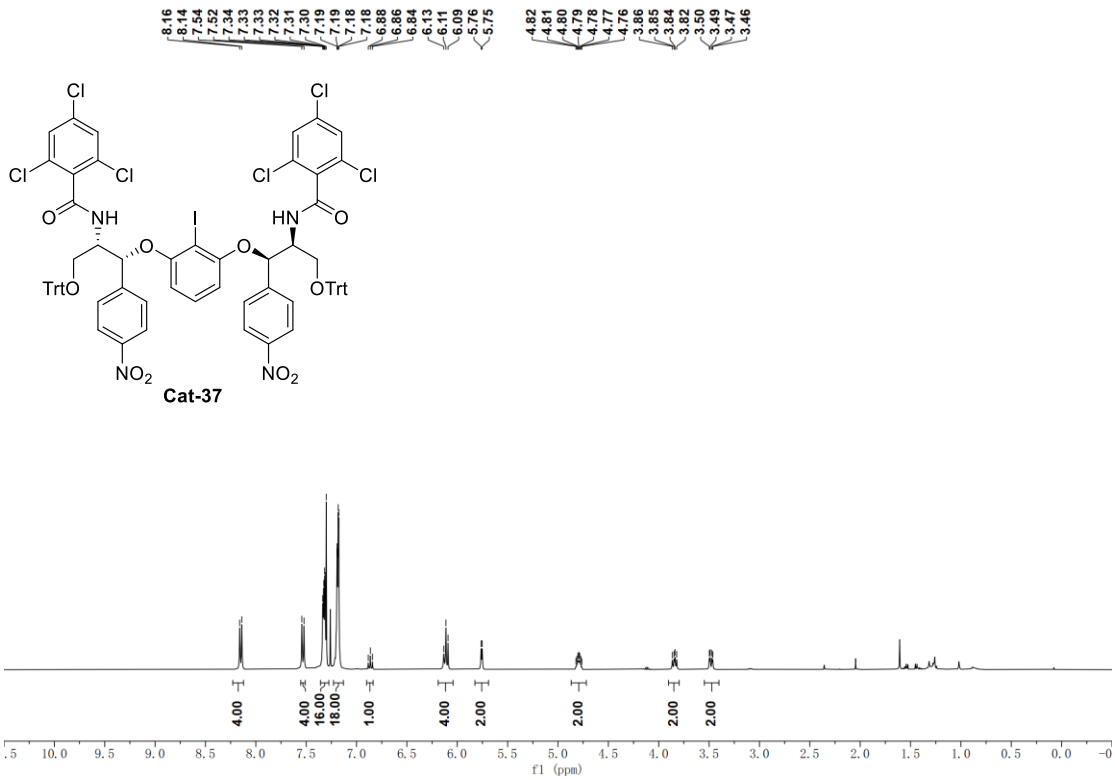
Supplementary Figure 82. ^{13}C NMR Spectrum of **Cat-35** (**100** MHz, $CDCl_3$)



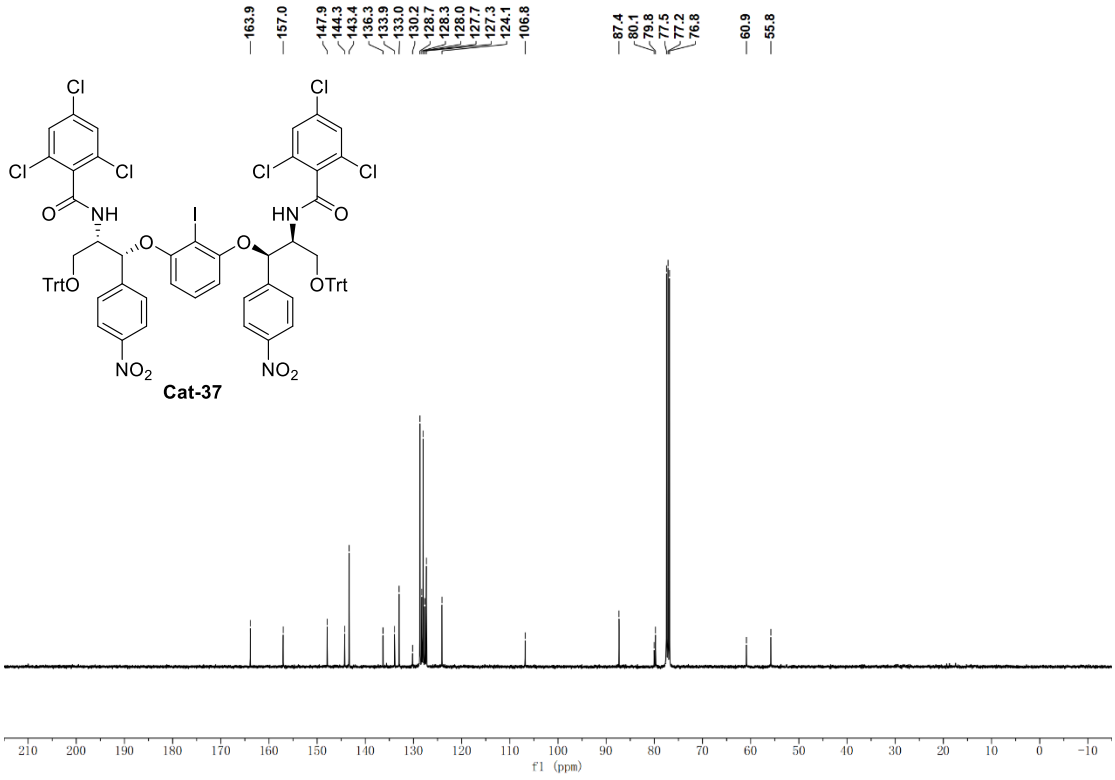
Supplementary Figure 83. ^{1}H NMR Spectrum of **Cat-36** (**400** MHz, $CDCl_3$)



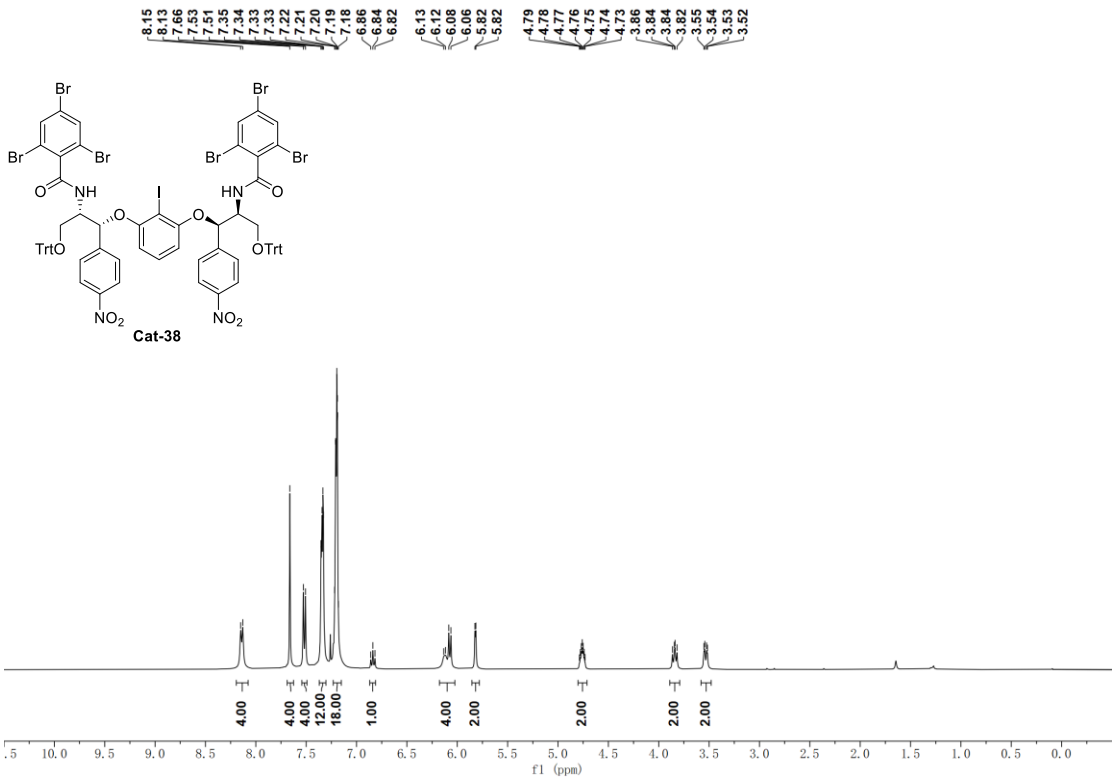
Supplementary Figure 84. ^{13}C NMR Spectrum of **Cat-36** (**100** MHz, $CDCl_3$)



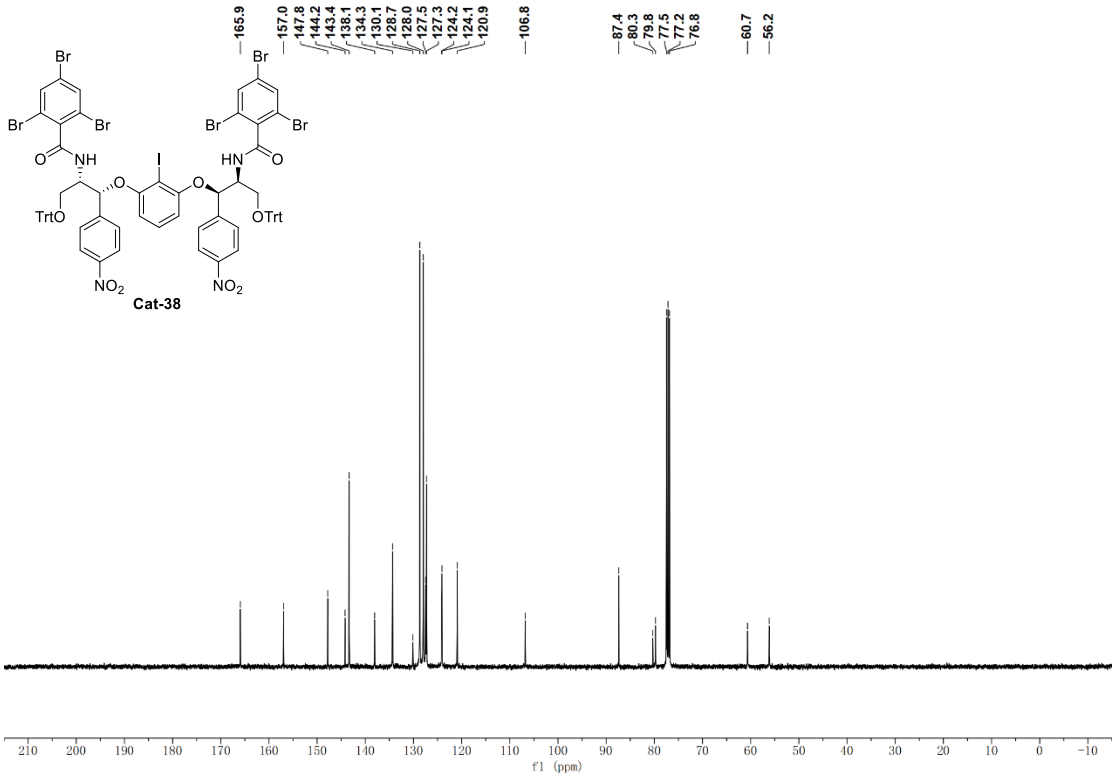
Supplementary Figure 85. ^{1}H NMR Spectrum of **Cat-37** (**400** MHz, $CDCl_3$)



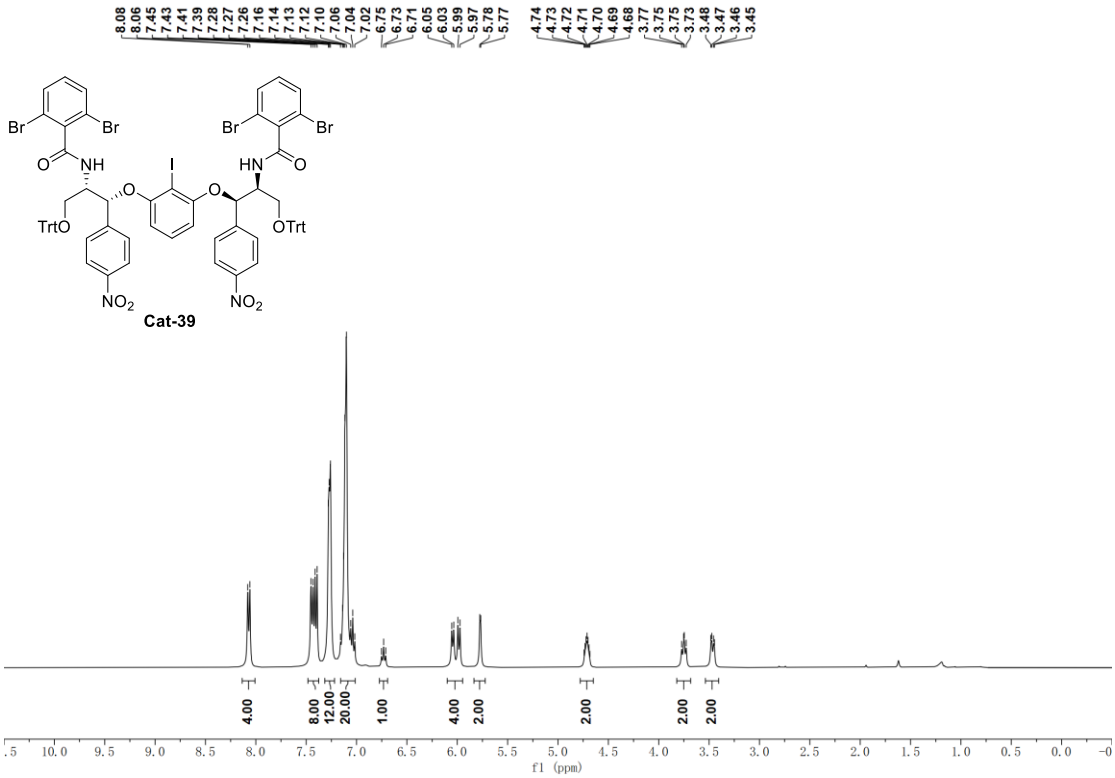
Supplementary Figure 86. ^{13}C NMR Spectrum of **Cat-37** (**100** MHz, $CDCl_3$)



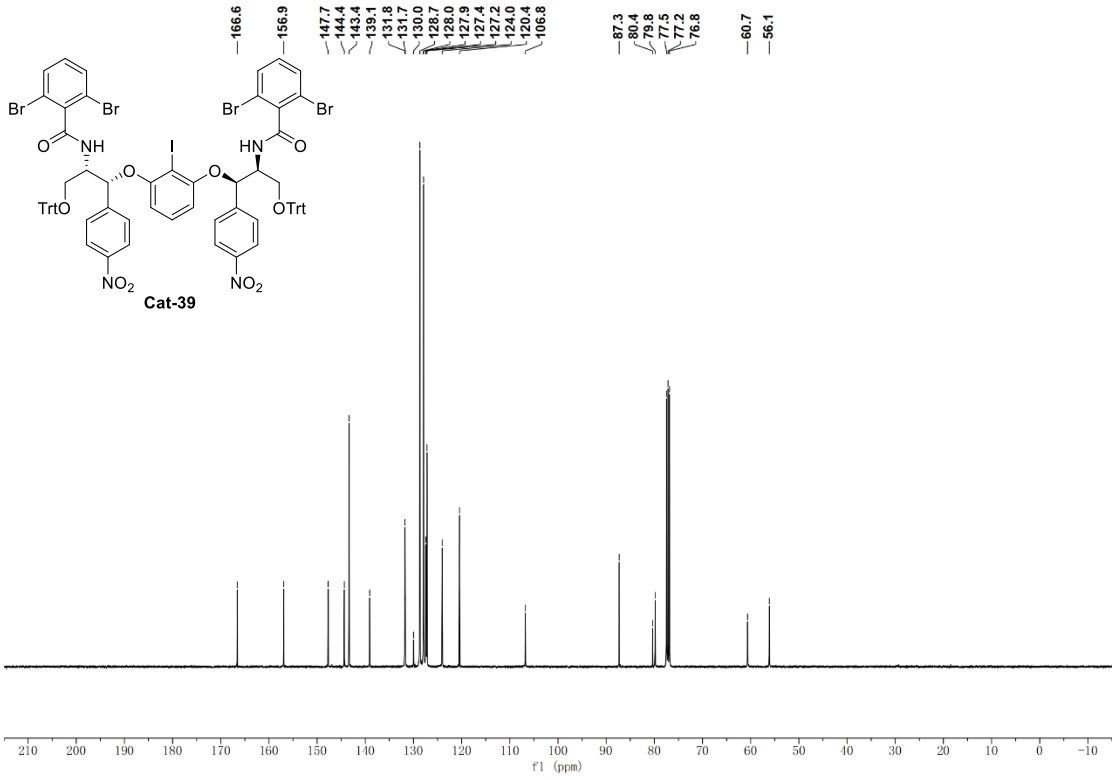
Supplementary Figure 87. ^{1}H NMR Spectrum of **Cat-38** (**400** MHz, $CDCl_3$)



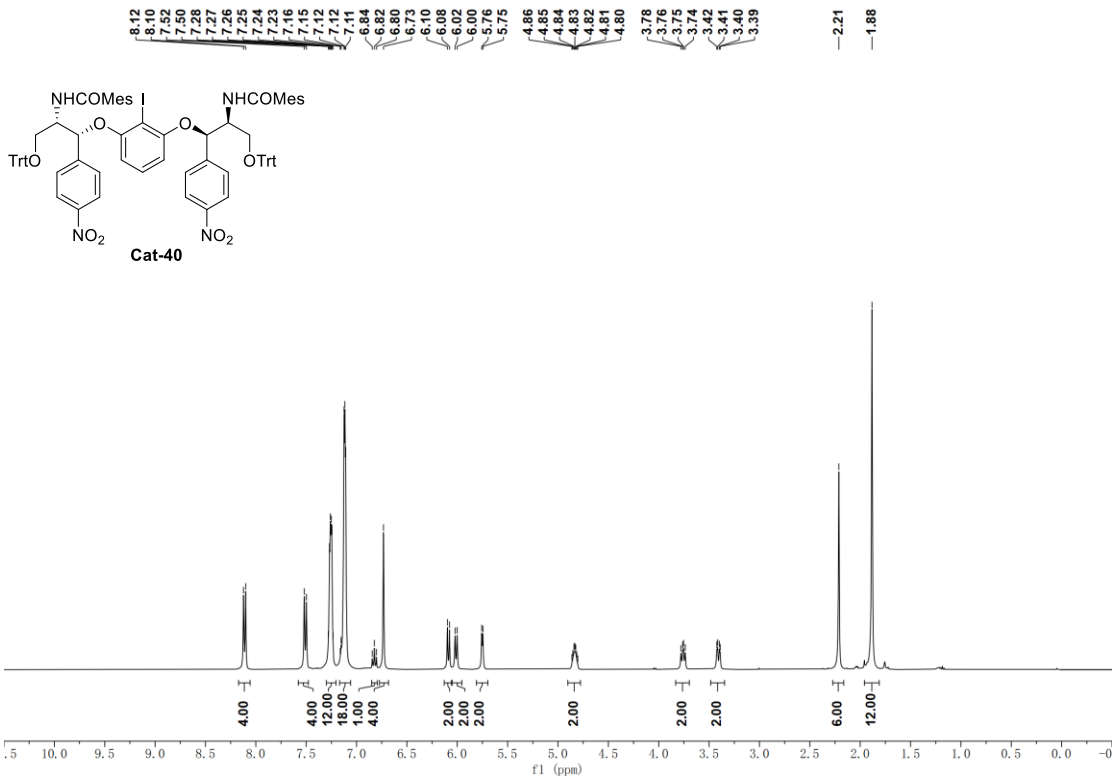
Supplementary Figure 88. ^{13}C NMR Spectrum of **Cat-38** (**100** MHz, $CDCl_3$)



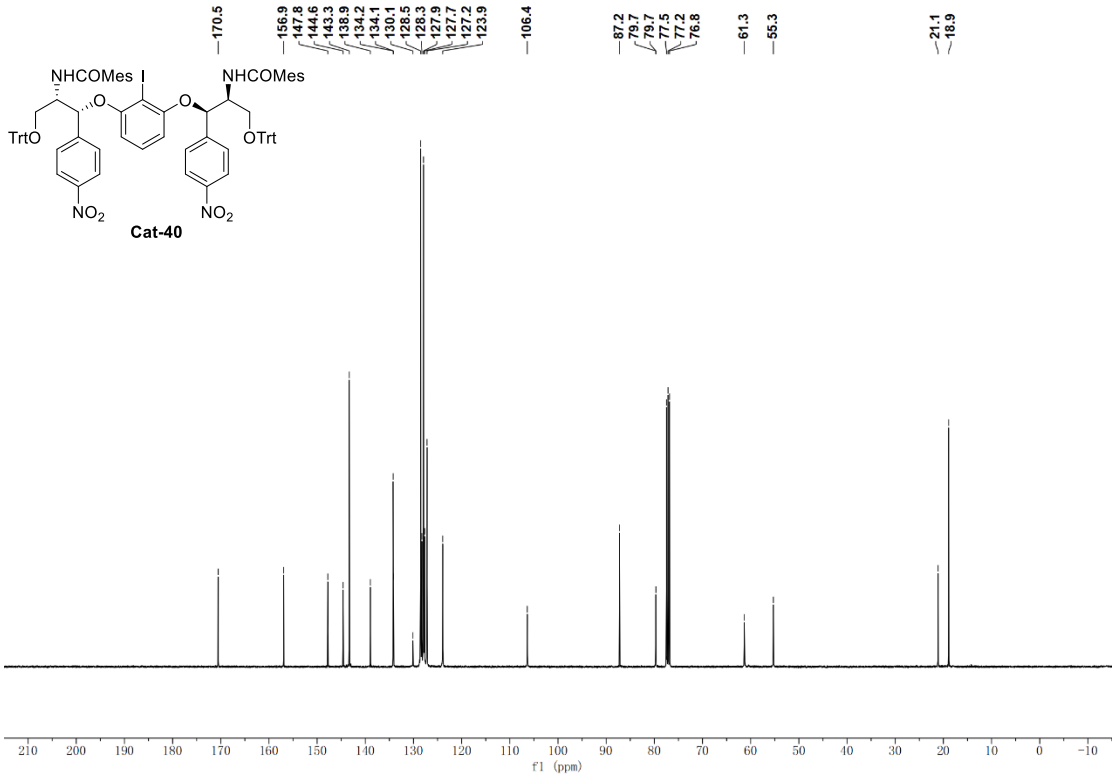
Supplementary Figure 89. ^{1}H NMR Spectrum of **Cat-39** (**400** MHz, $CDCl_3$)



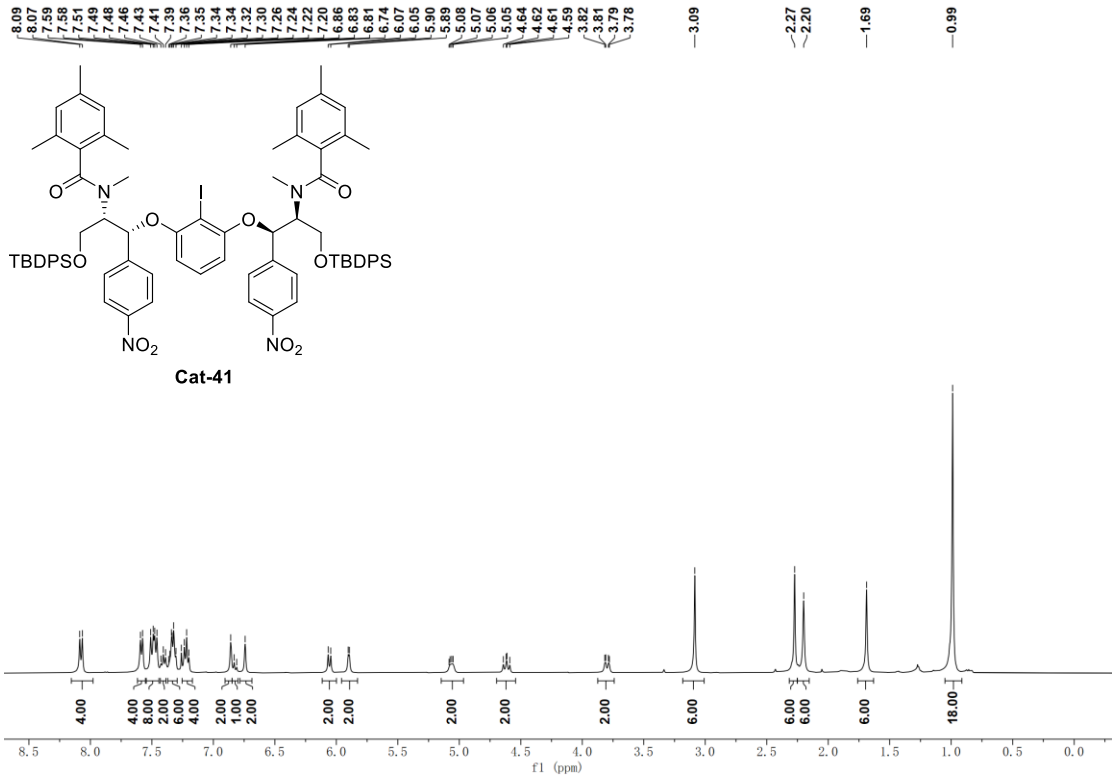
Supplementary Figure 90. ^{13}C NMR Spectrum of **Cat-39** (**100** MHz, $CDCl_3$)



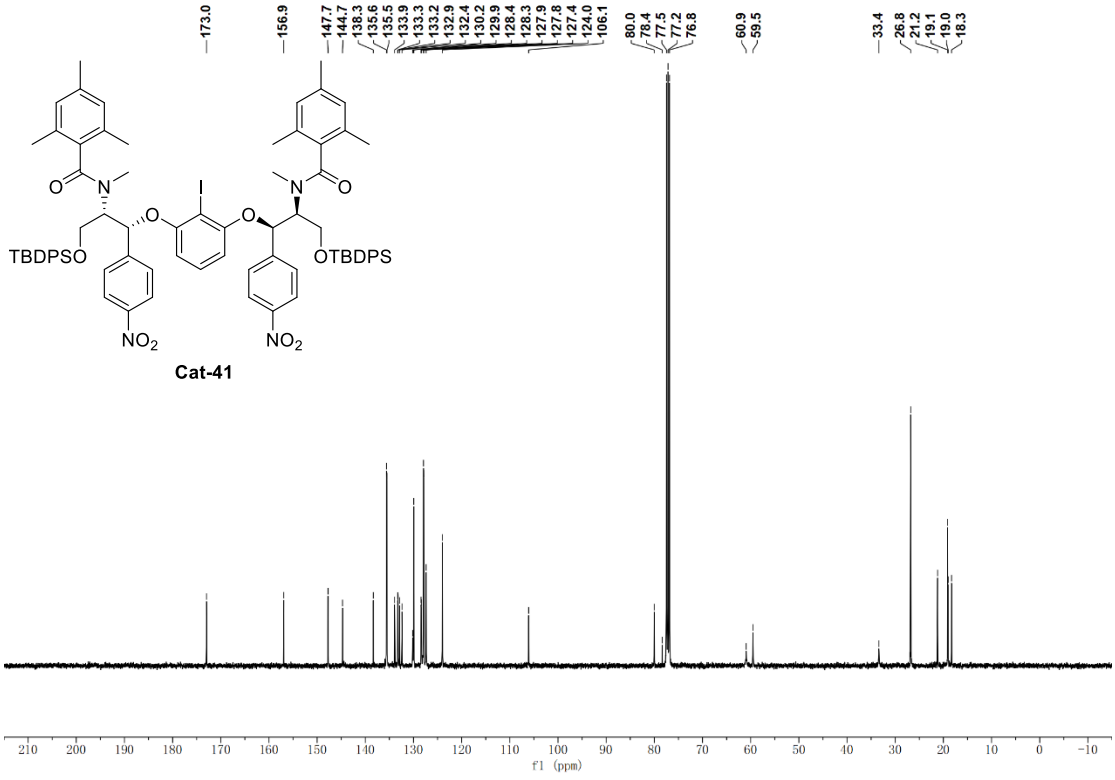
Supplementary Figure 91. ^{1}H NMR Spectrum of **Cat-40** (**400** MHz, $CDCl_3$)



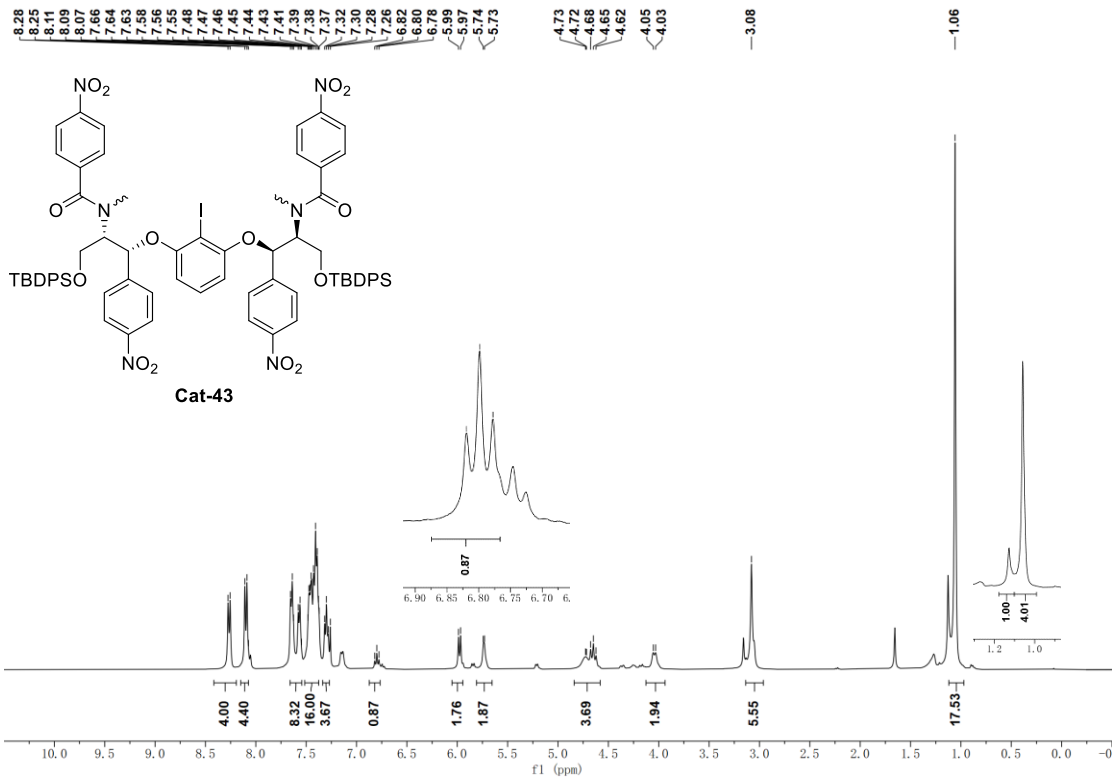
Supplementary Figure 92. ^{13}C NMR Spectrum of **Cat-40** (**100** MHz, $CDCl_3$)



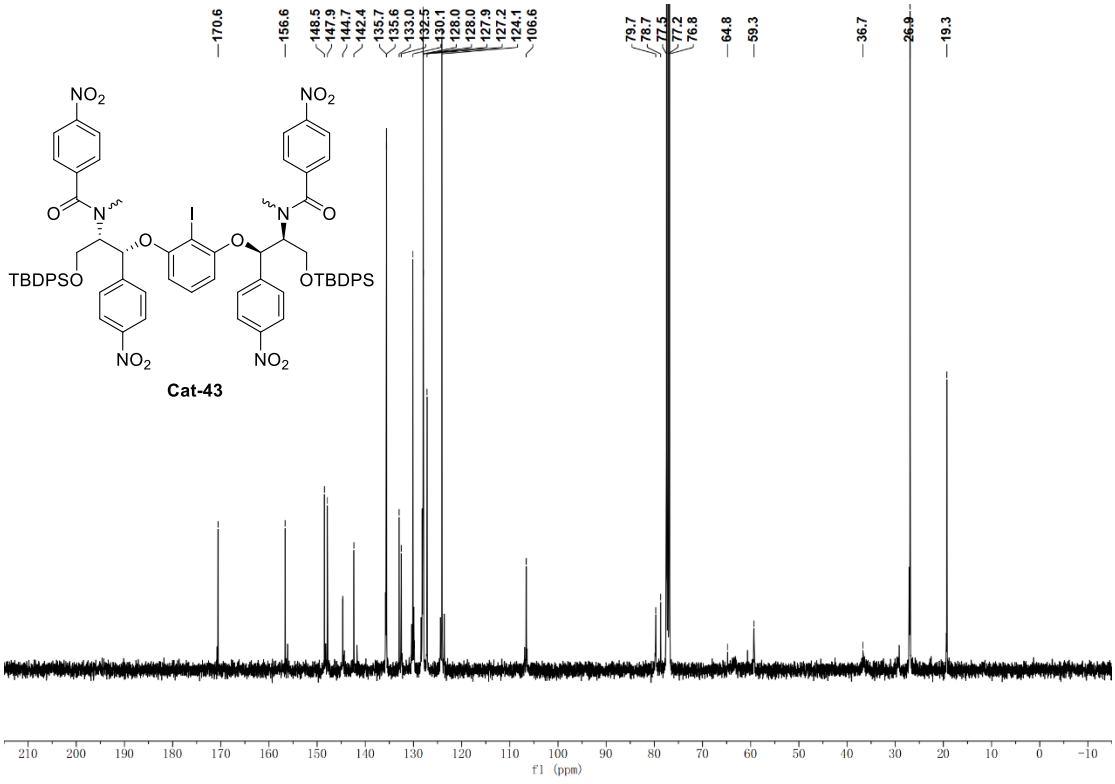
Supplementary Figure 93. ^{1}H NMR Spectrum of **Cat-41** (**400** MHz, $CDCl_3$)



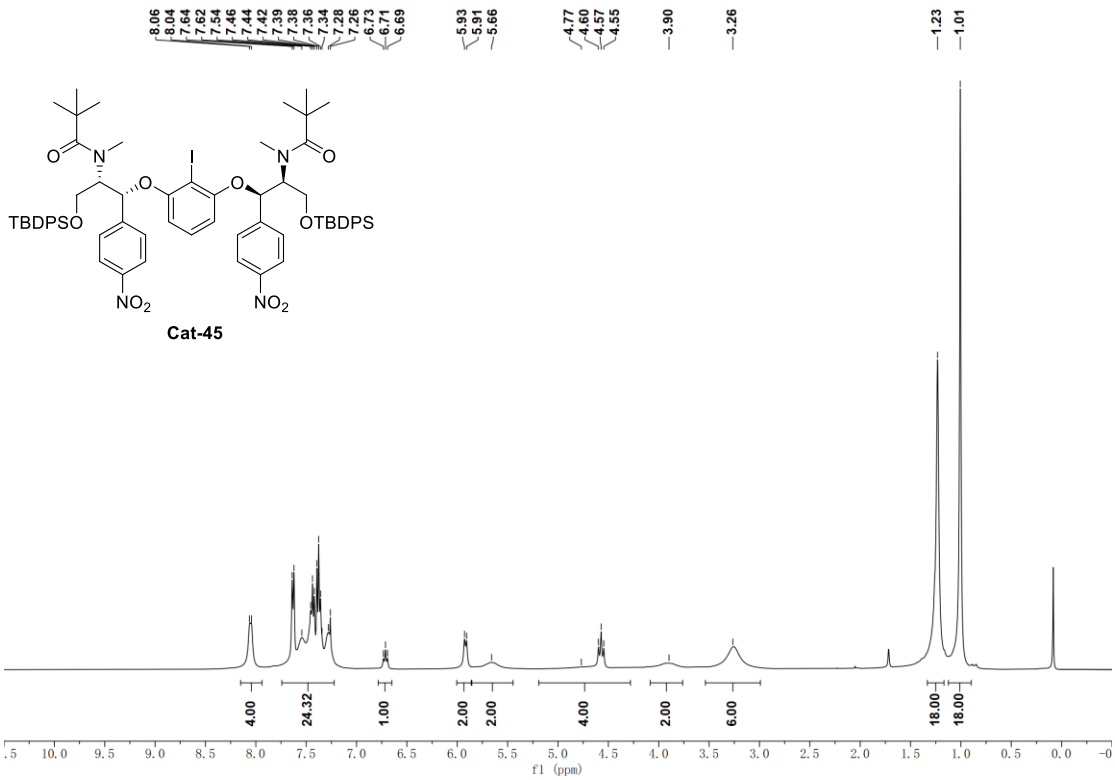
Supplementary Figure 94. ^{13}C NMR Spectrum of **Cat-41** (**100** MHz, $CDCl_3$)



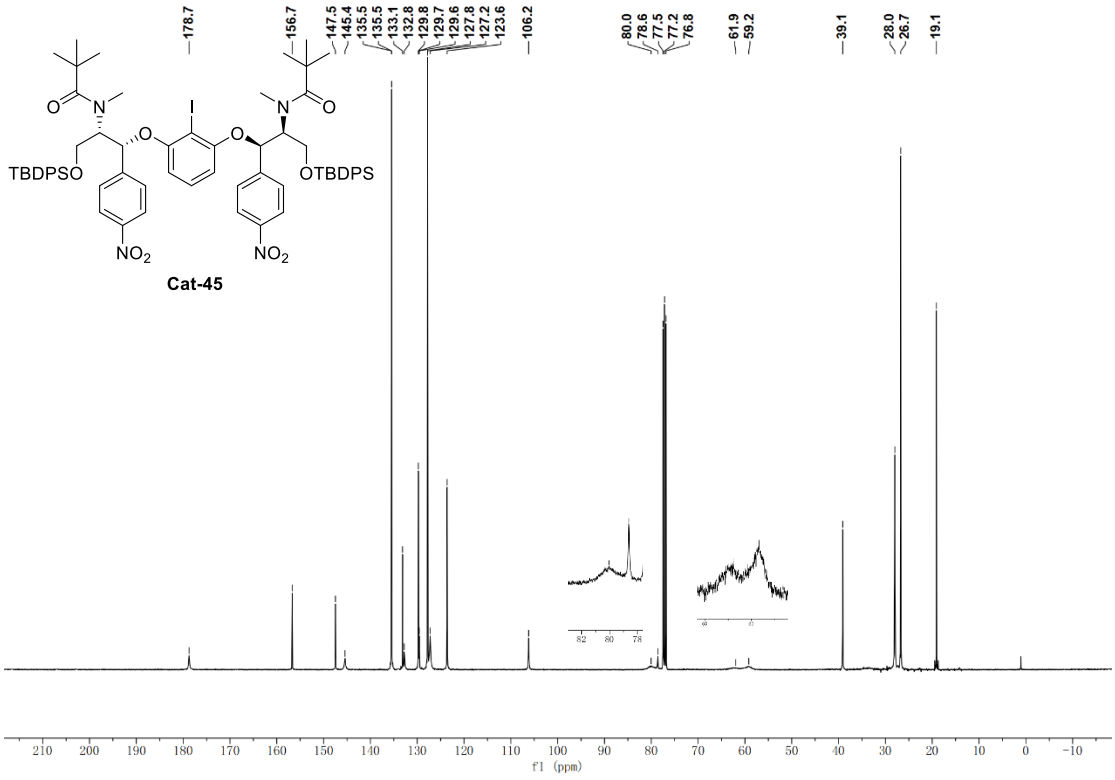
Supplementary Figure 95. ^{1}H NMR Spectrum of **Cat-43** (**400** MHz, $CDCl_3$)



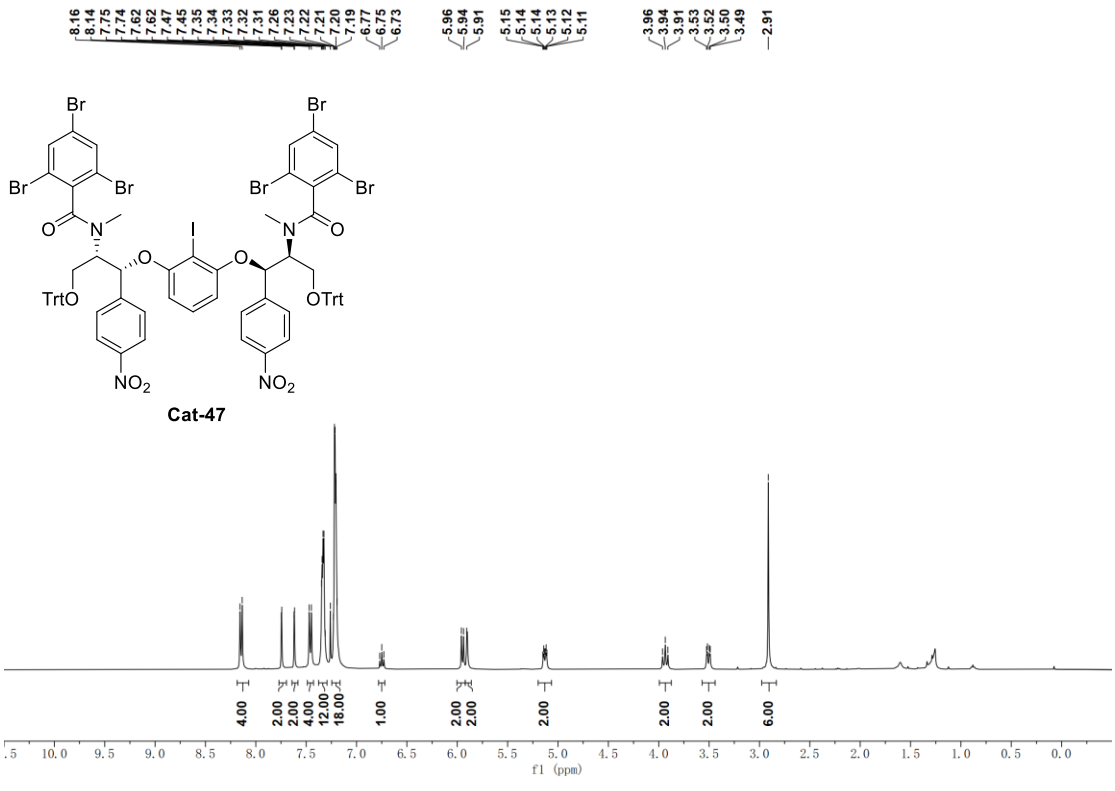
Supplementary Figure 96. ^{13}C NMR Spectrum of **Cat-43** (**100** MHz, $CDCl_3$)



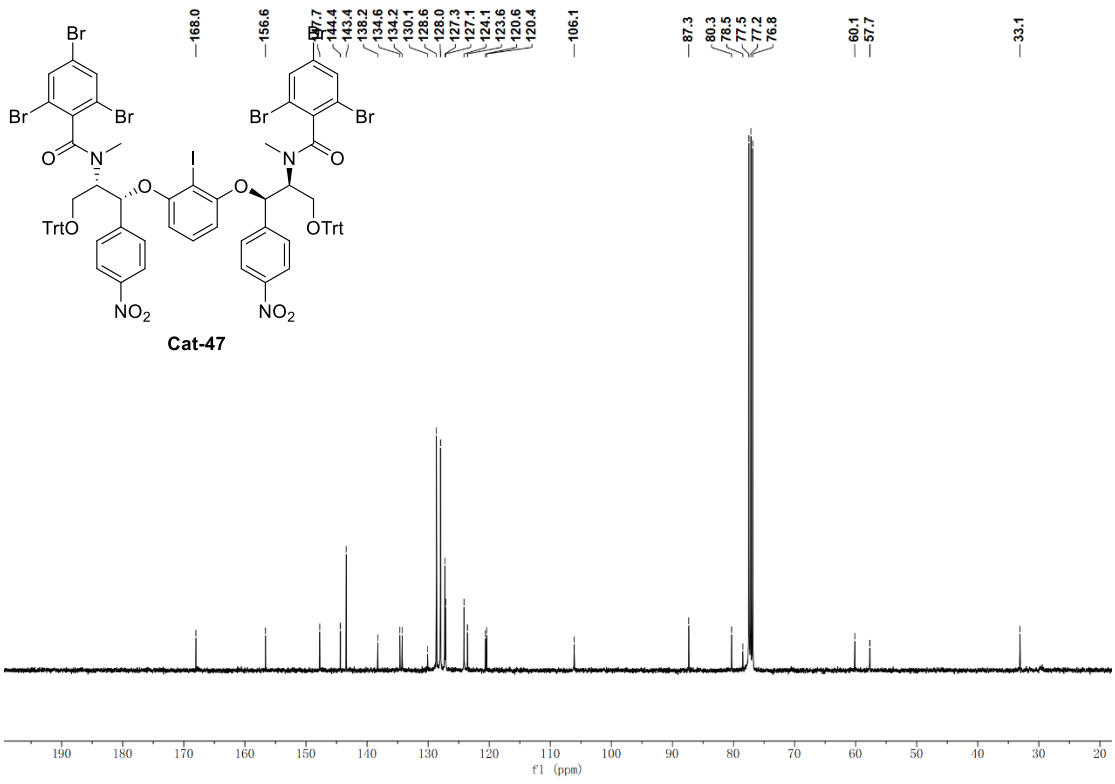
Supplementary Figure 97. ^{1}H NMR Spectrum of **Cat-45** (**400** MHz, $CDCl_3$)



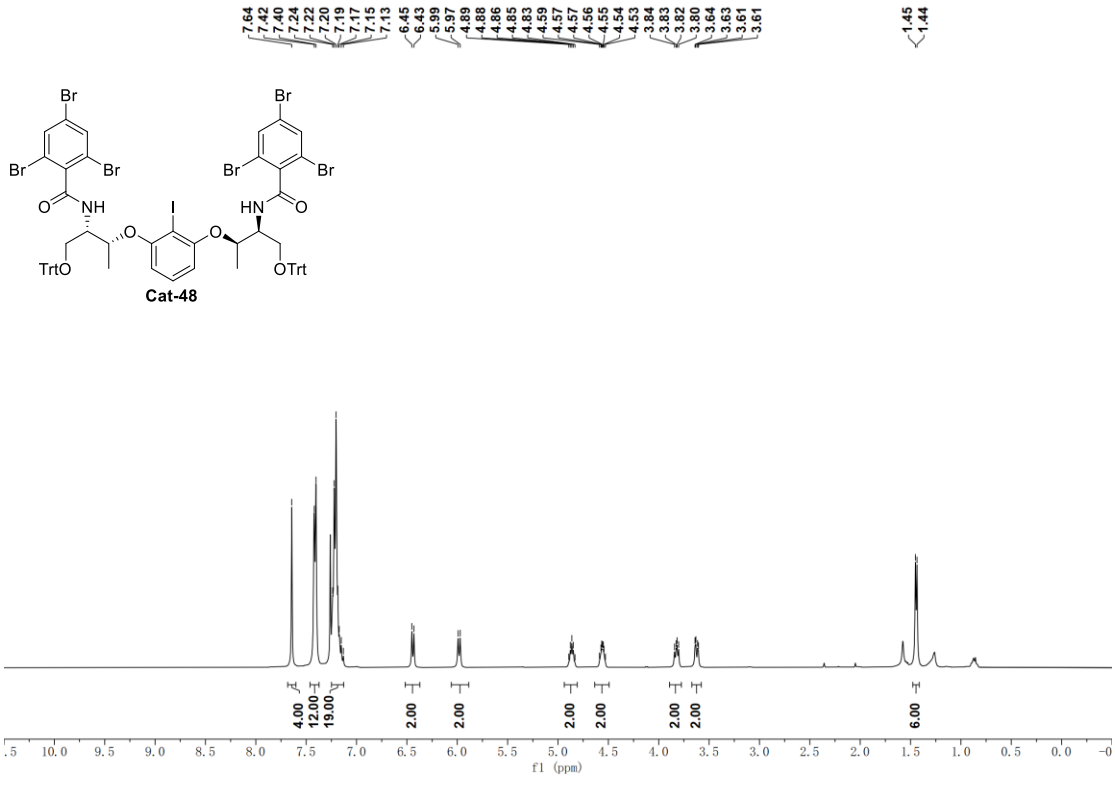
Supplementary Figure 98. ^{13}C NMR Spectrum of **Cat-45** (**100** MHz, $CDCl_3$)



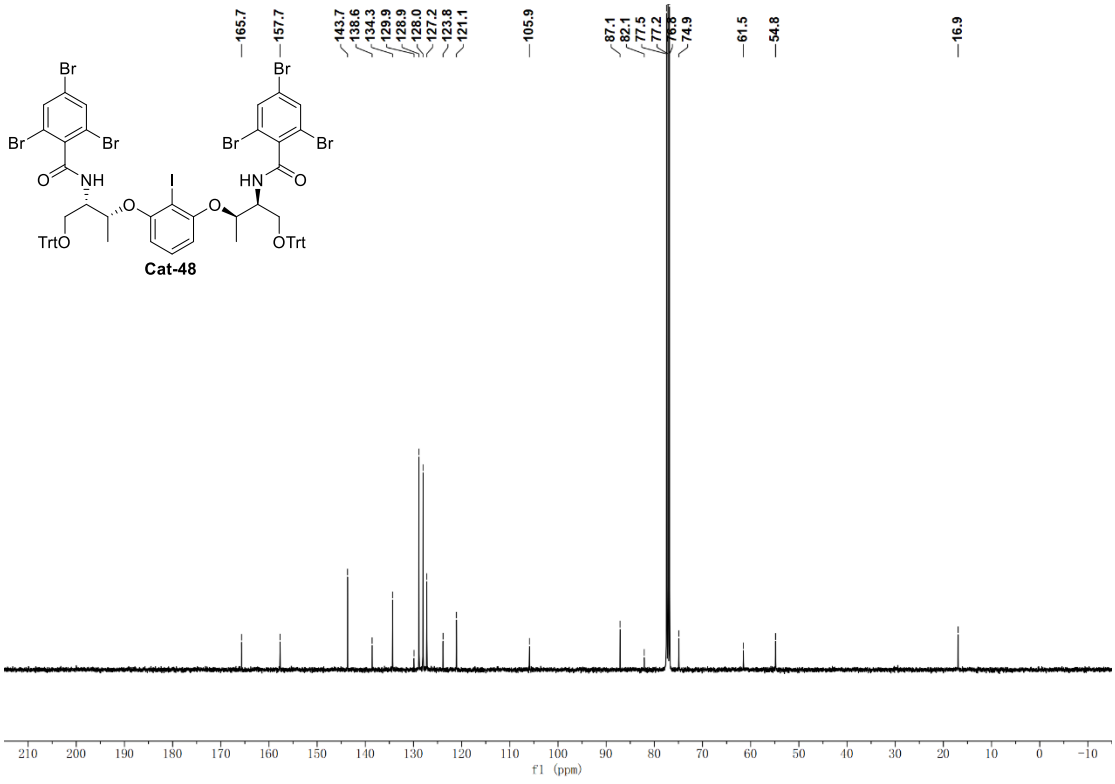
Supplementary Figure 99. ^{1}H NMR Spectrum of **Cat-47** (**400** MHz, $CDCl_3$)



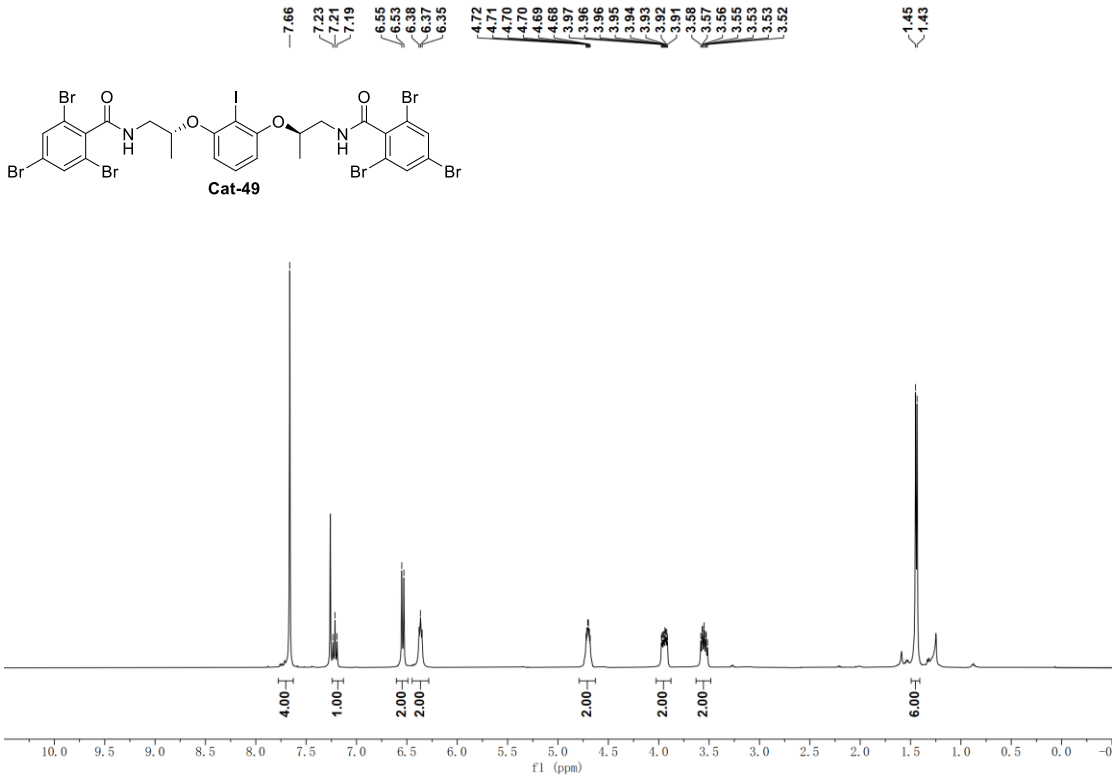
Supplementary Figure 100. ^{13}C NMR Spectrum of **Cat-47** (**100** MHz, $CDCl_3$)



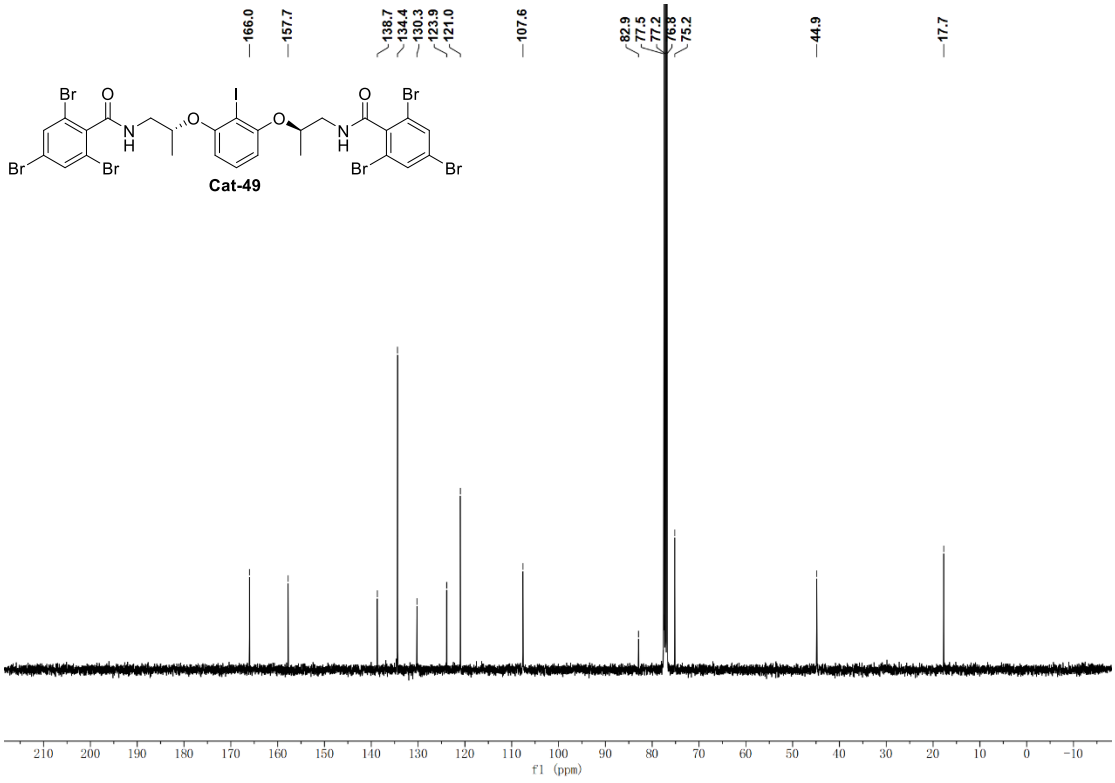
Supplementary Figure 101. ^{1}H NMR Spectrum of **Cat-48** (**400** MHz, $CDCl_3$)



Supplementary Figure 102. ^{13}C NMR Spectrum of **Cat-48** (**100** MHz, $CDCl_3$)



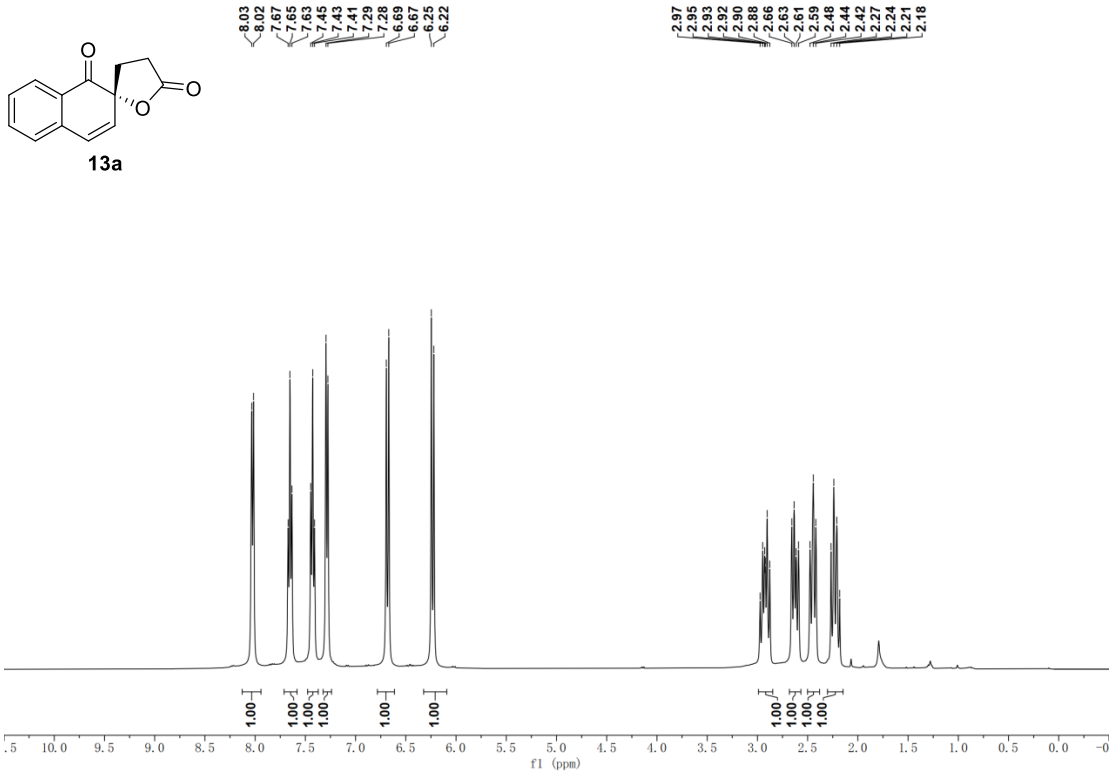
Supplementary Figure 103. ^{1}H NMR Spectrum of **Cat-49** (**400** MHz, $CDCl_3$)



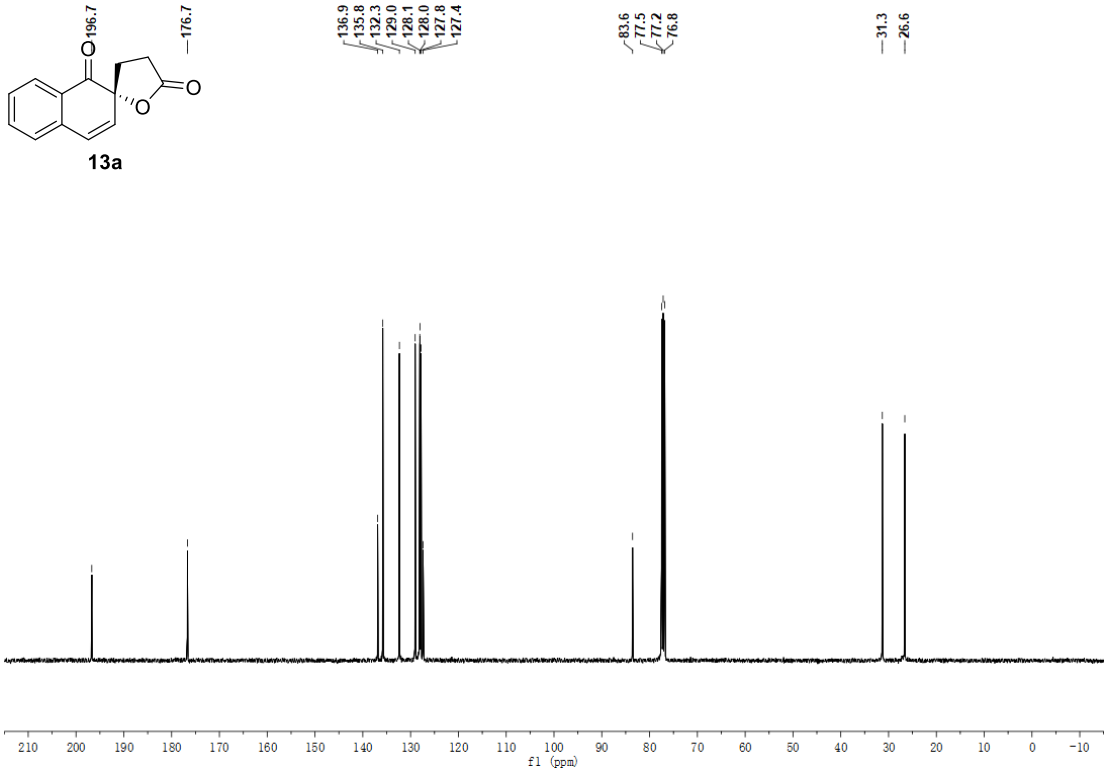
Supplementary Figure 104. ^{13}C NMR Spectrum of **Cat-49** (**100** MHz, $CDCl_3$)

11.2 NMR spectra of product

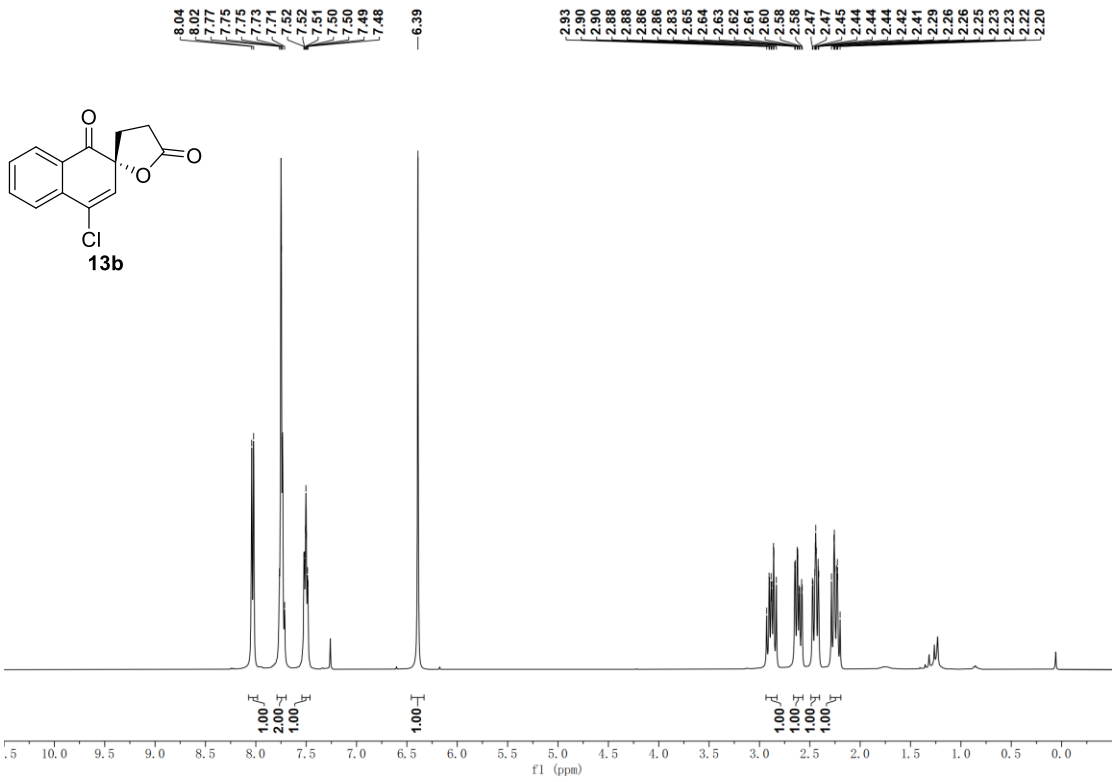
11.2.1 Spectrum of enantioselective oxidative dearomatization



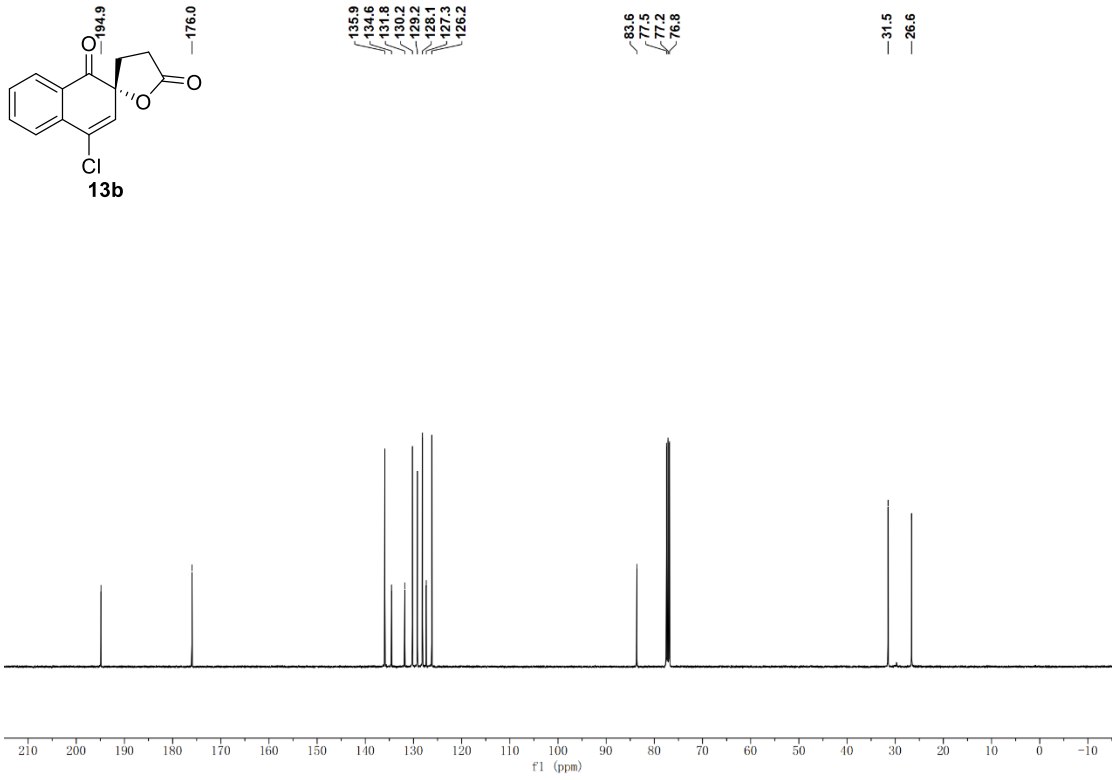
Supplementary Figure 105. ^{1}H NMR Spectrum of **13a** (**400** MHz, $CDCl_3$)



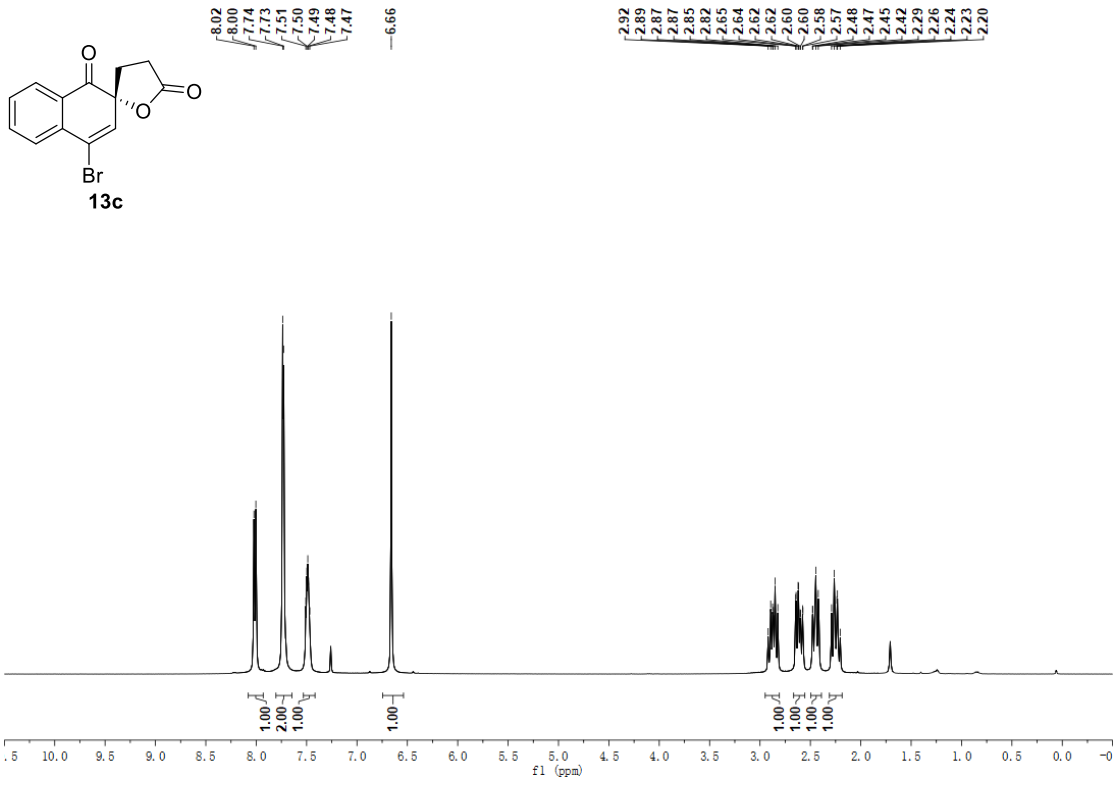
Supplementary Figure 106. ^{13}C NMR Spectrum of **13a** (**100** MHz, $CDCl_3$)



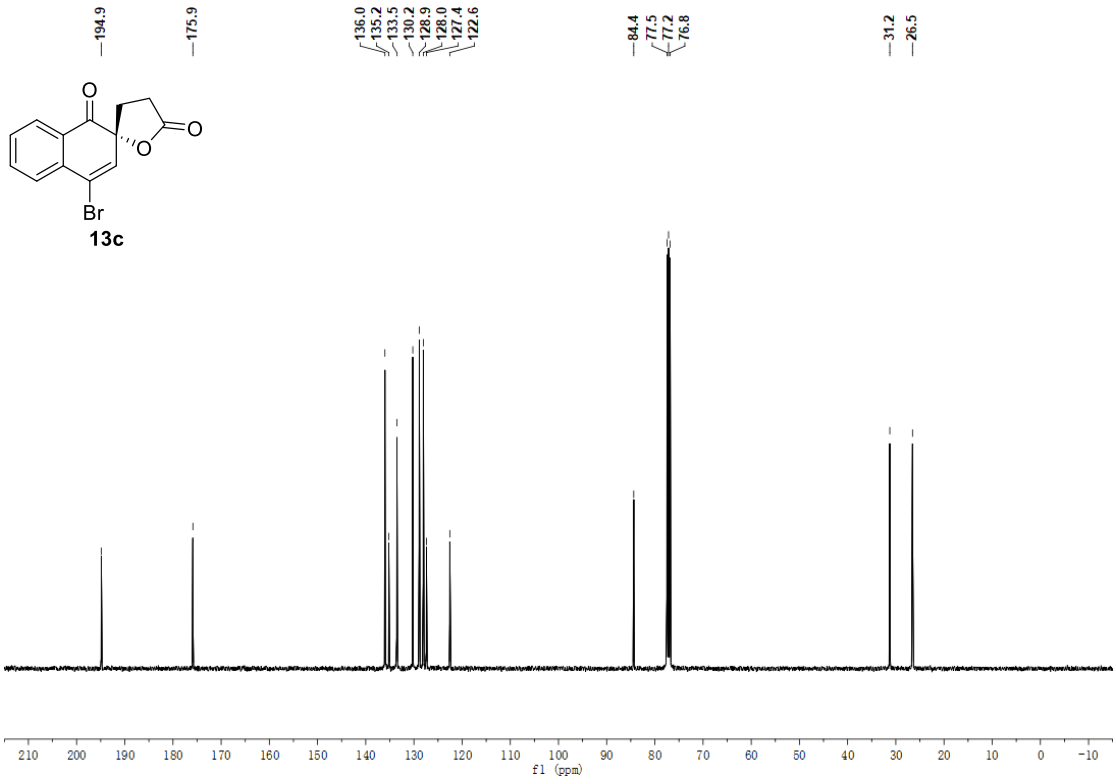
Supplementary Figure 107. ^{1}H NMR Spectrum of **13b** (**400** MHz, $CDCl_3$)



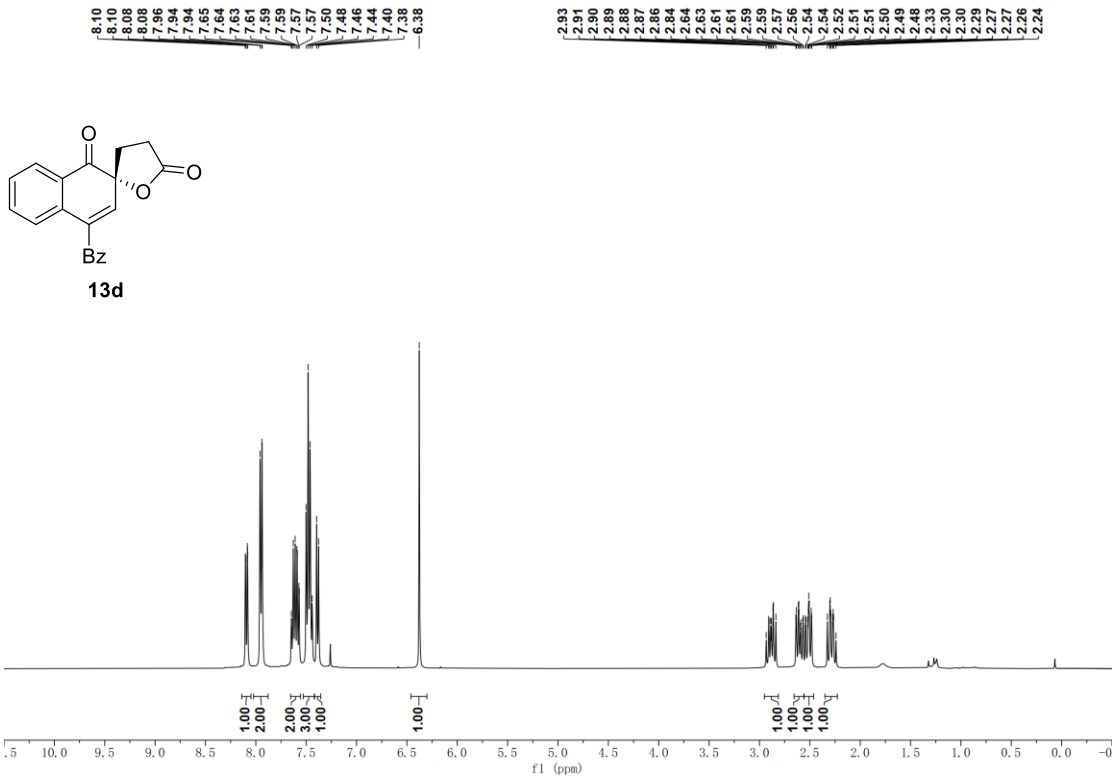
Supplementary Figure 108. ^{13}C NMR Spectrum of **13b** (**100** MHz, $CDCl_3$)



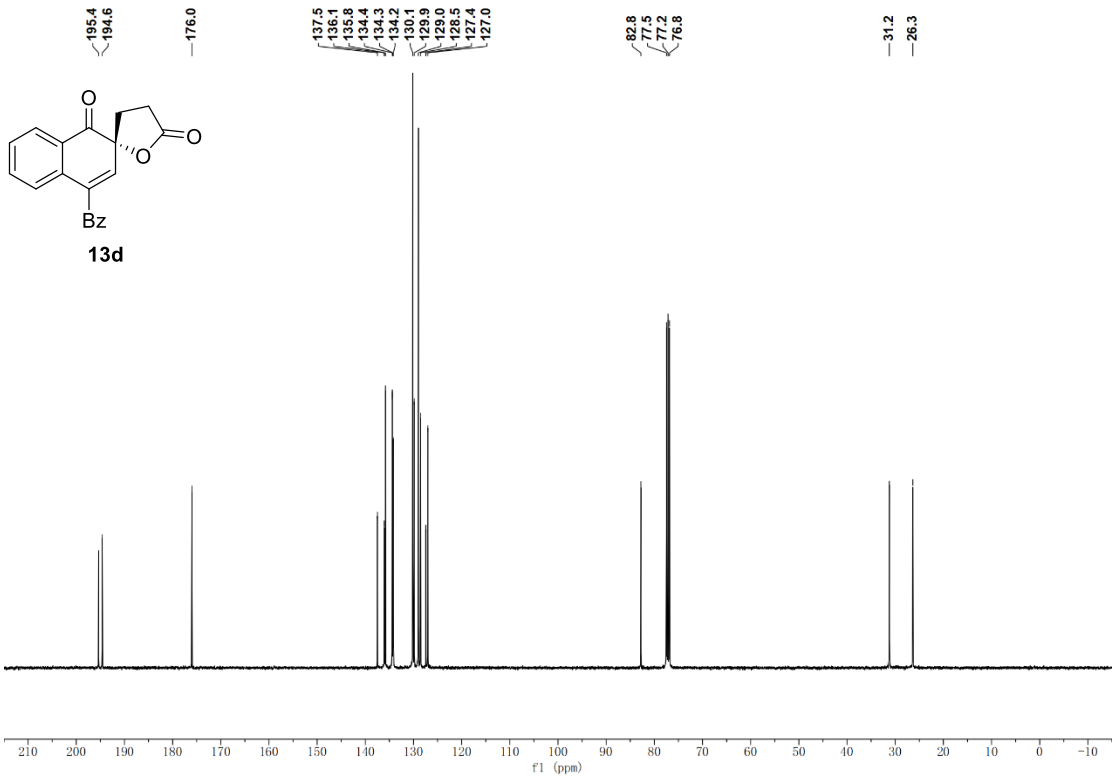
Supplementary Figure 109. ^{1}H NMR Spectrum of **13c** (**400** MHz, $CDCl_3$)



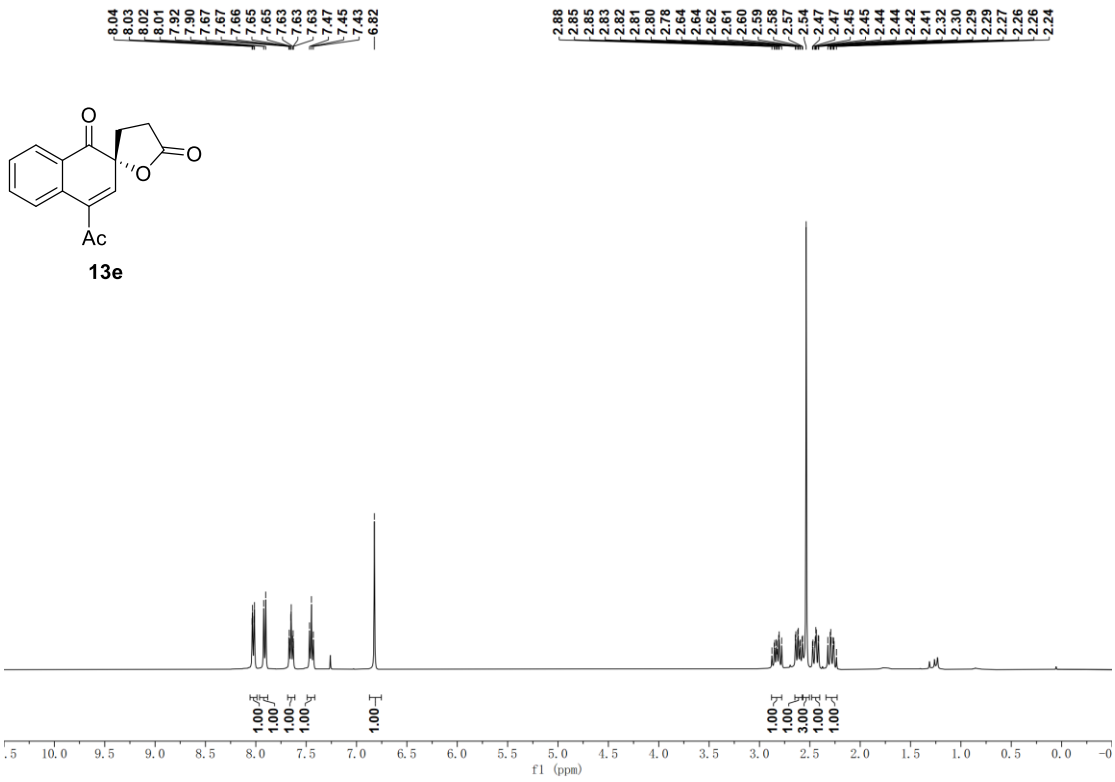
Supplementary Figure 110. ^{13}C NMR Spectrum of **13c** (**100** MHz, $CDCl_3$)



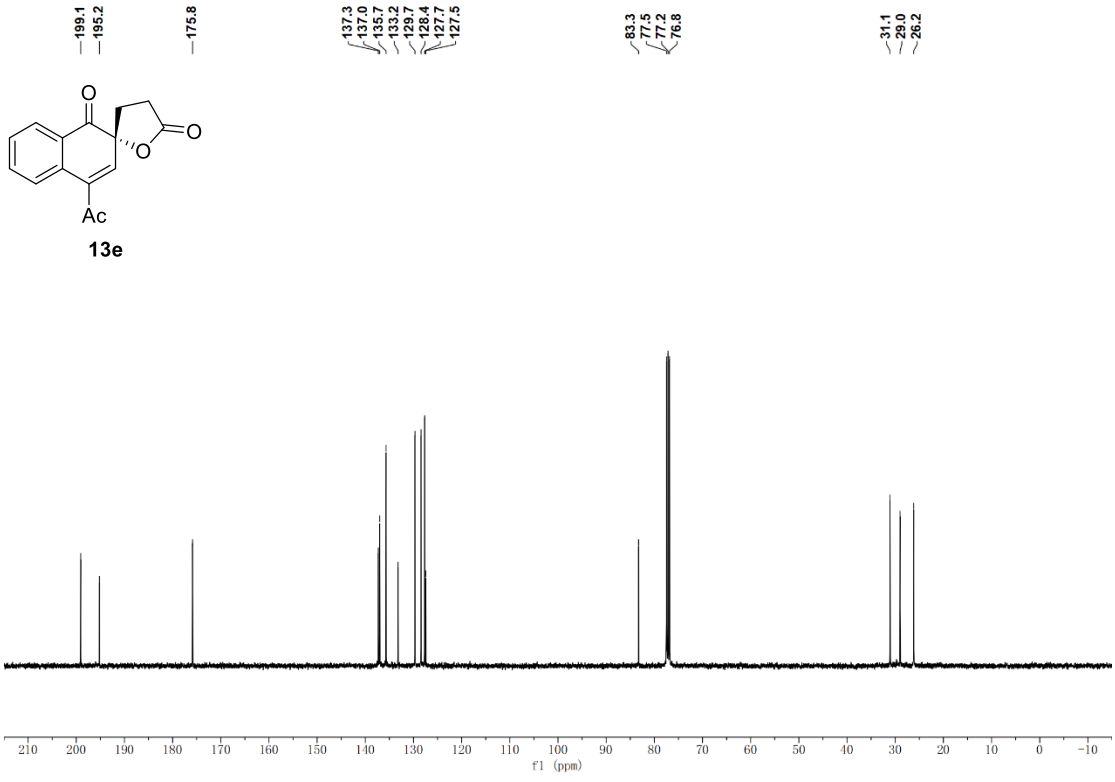
Supplementary Figure 111. ^{1}H NMR Spectrum of **13d** (**400** MHz, $CDCl_3$)



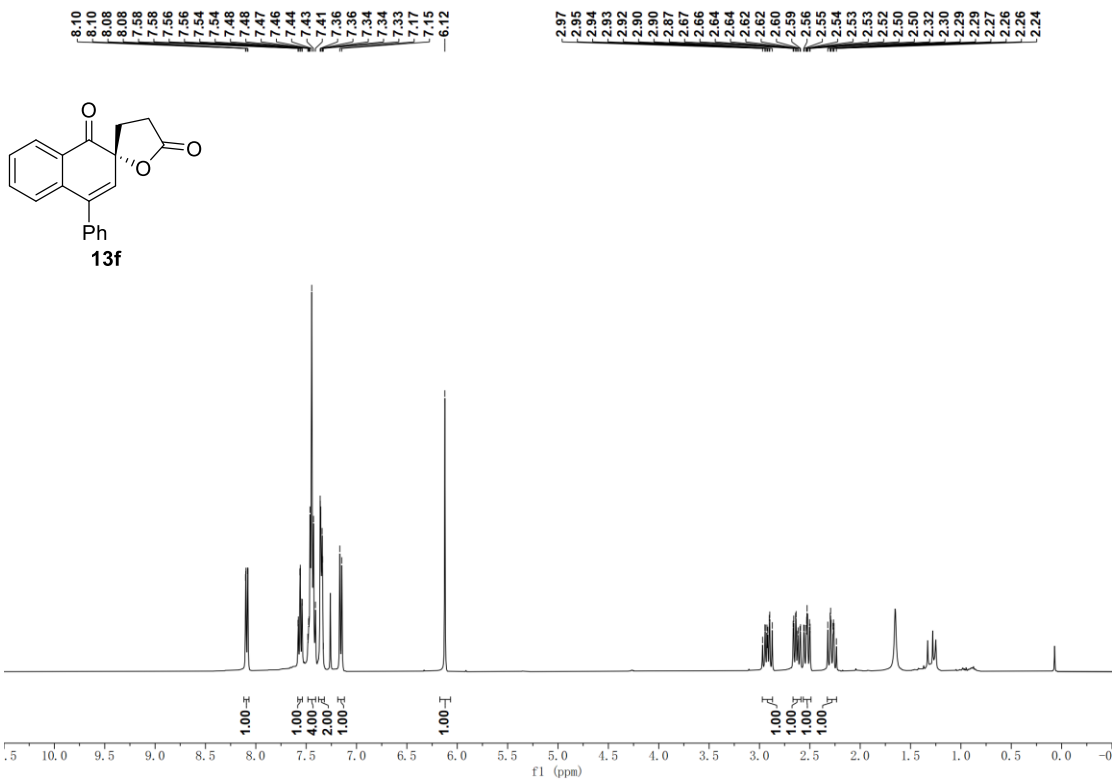
Supplementary Figure 112. ^{13}C NMR Spectrum of **13d** (**100** MHz, $CDCl_3$)



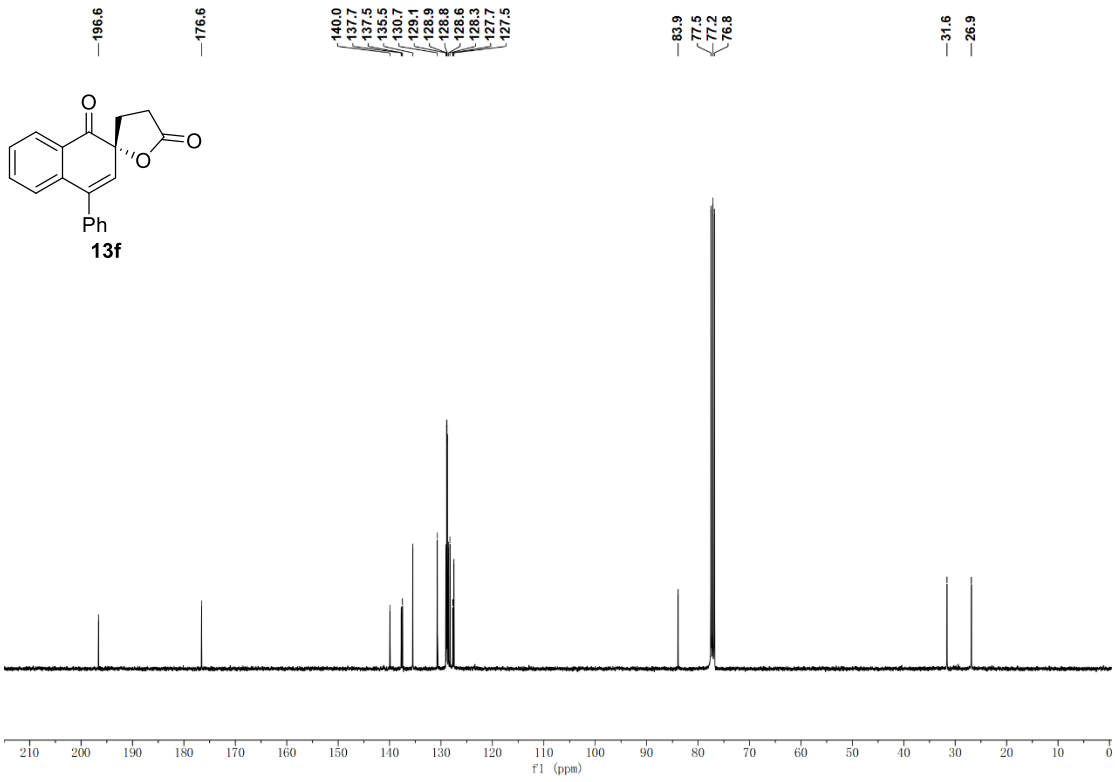
Supplementary Figure 113. ^{1}H NMR Spectrum of **13e** (**400** MHz, $CDCl_3$)



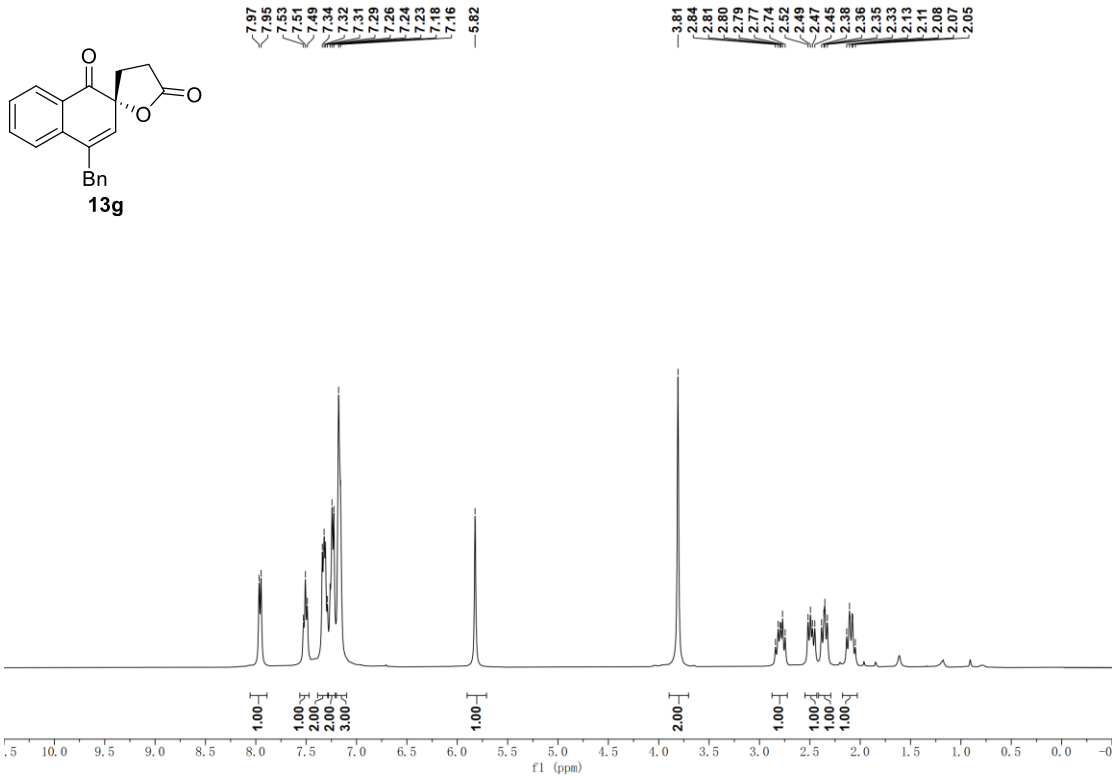
Supplementary Figure 114. ^{13}C NMR Spectrum of **13e** (**100** MHz, $CDCl_3$)



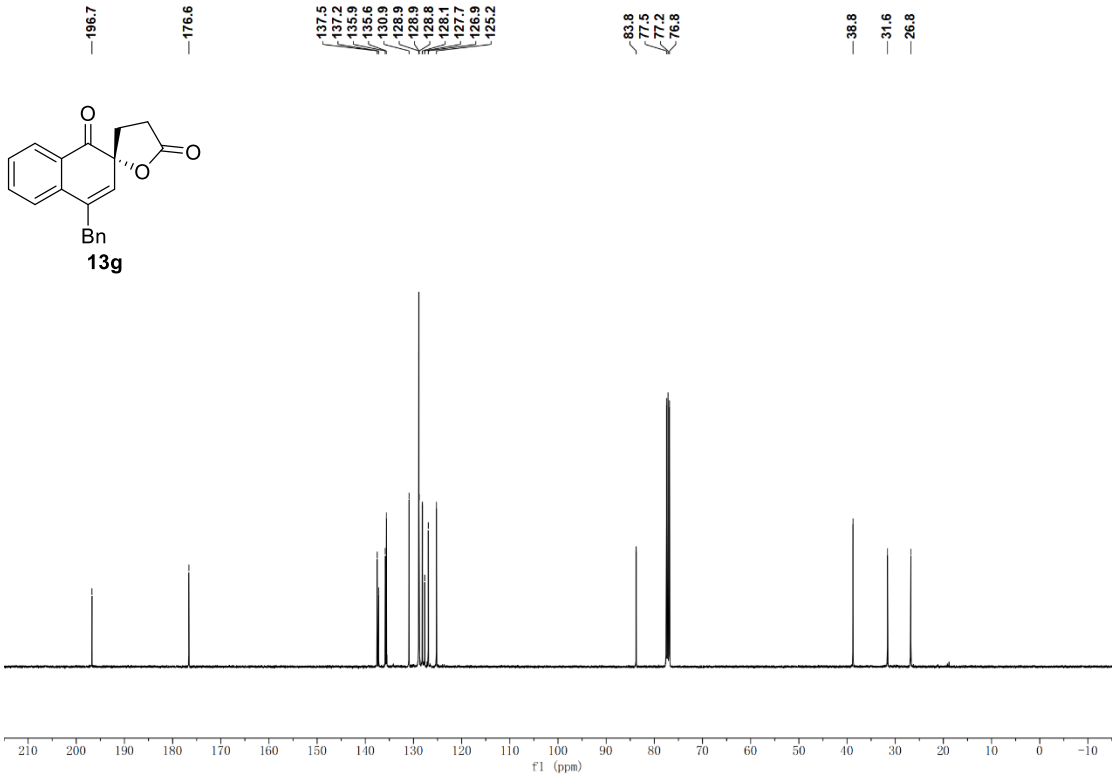
Supplementary Figure 115. ^{1}H NMR Spectrum of **13f** (**400** MHz, $CDCl_3$)



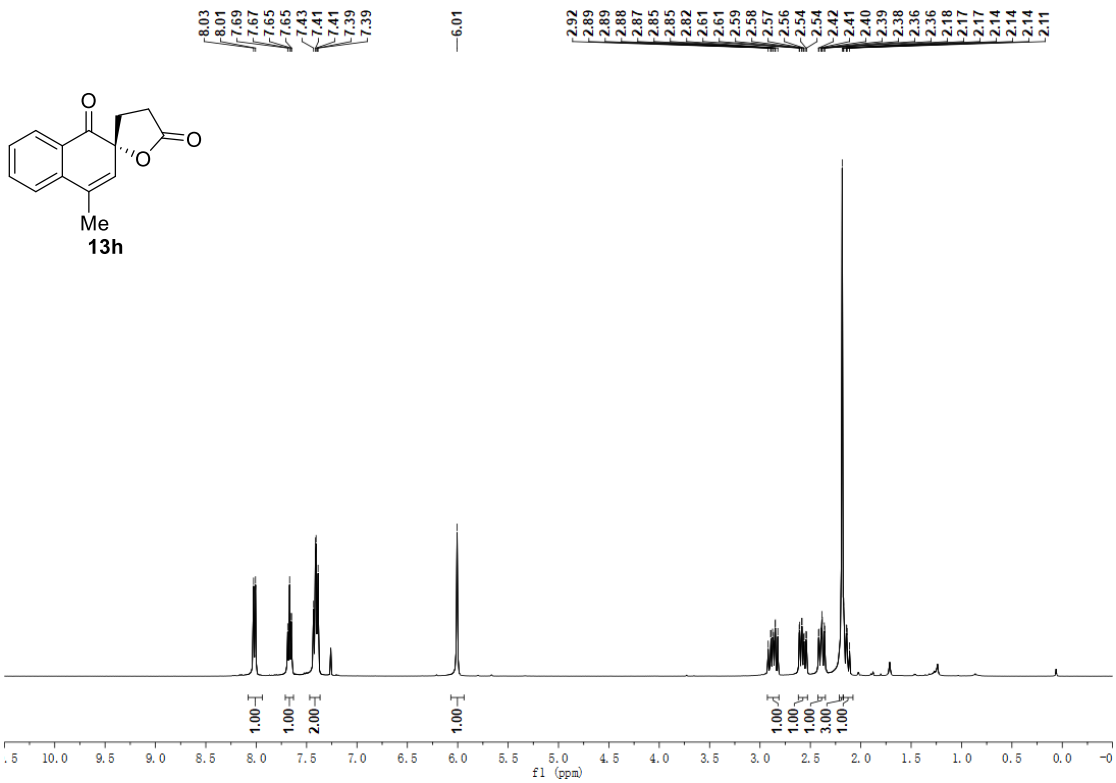
Supplementary Figure 116. ^{13}C NMR Spectrum of **13f** (**100** MHz, $CDCl_3$)



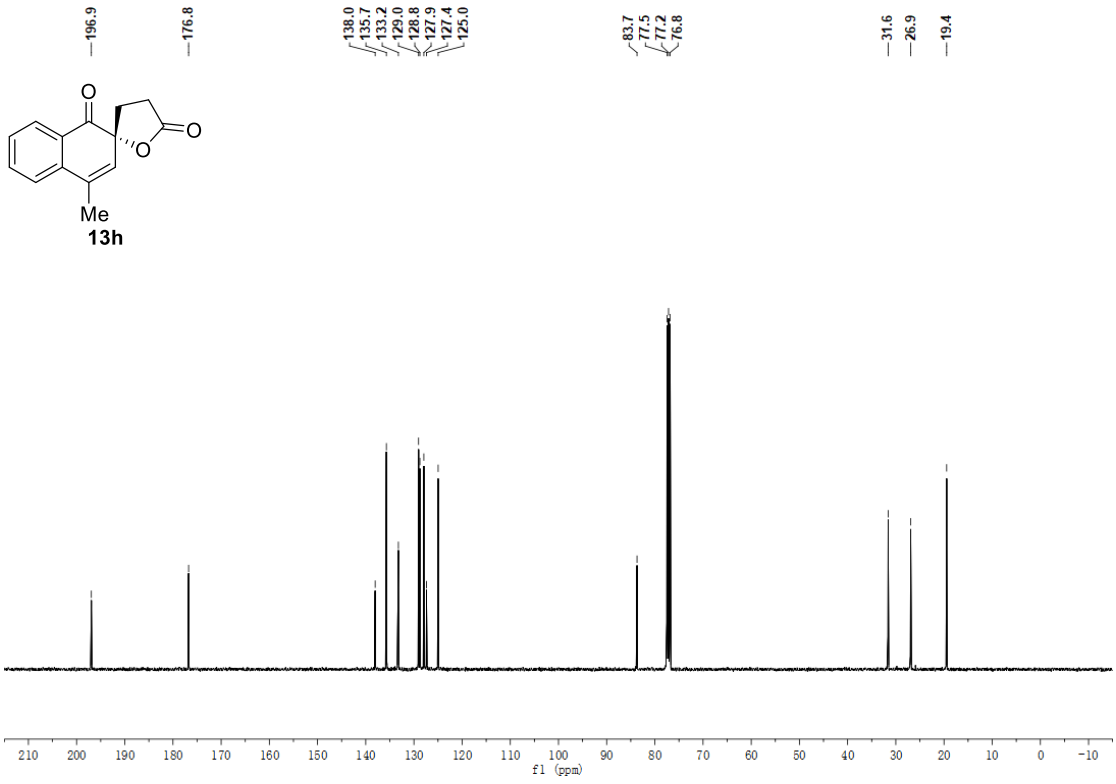
Supplementary Figure 117. ^{1}H NMR Spectrum of **13g** (**400** MHz, $CDCl_3$)



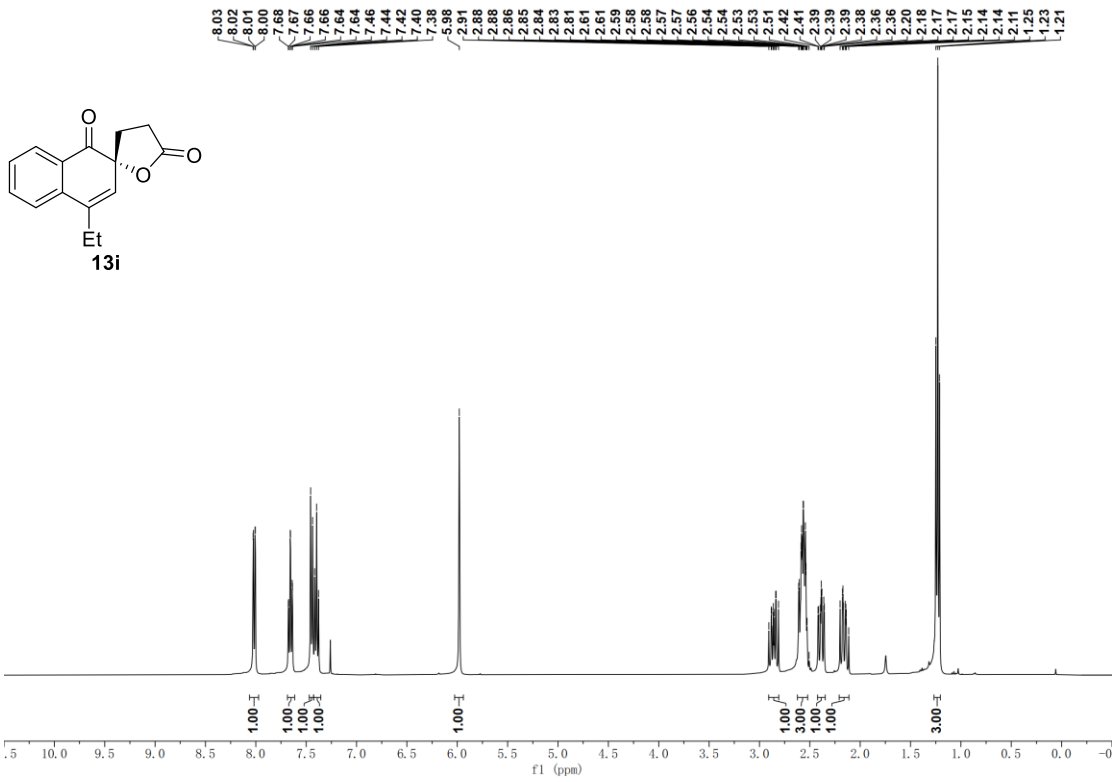
Supplementary Figure 118. ^{13}C NMR Spectrum of **13g** (**100** MHz, CDCl)



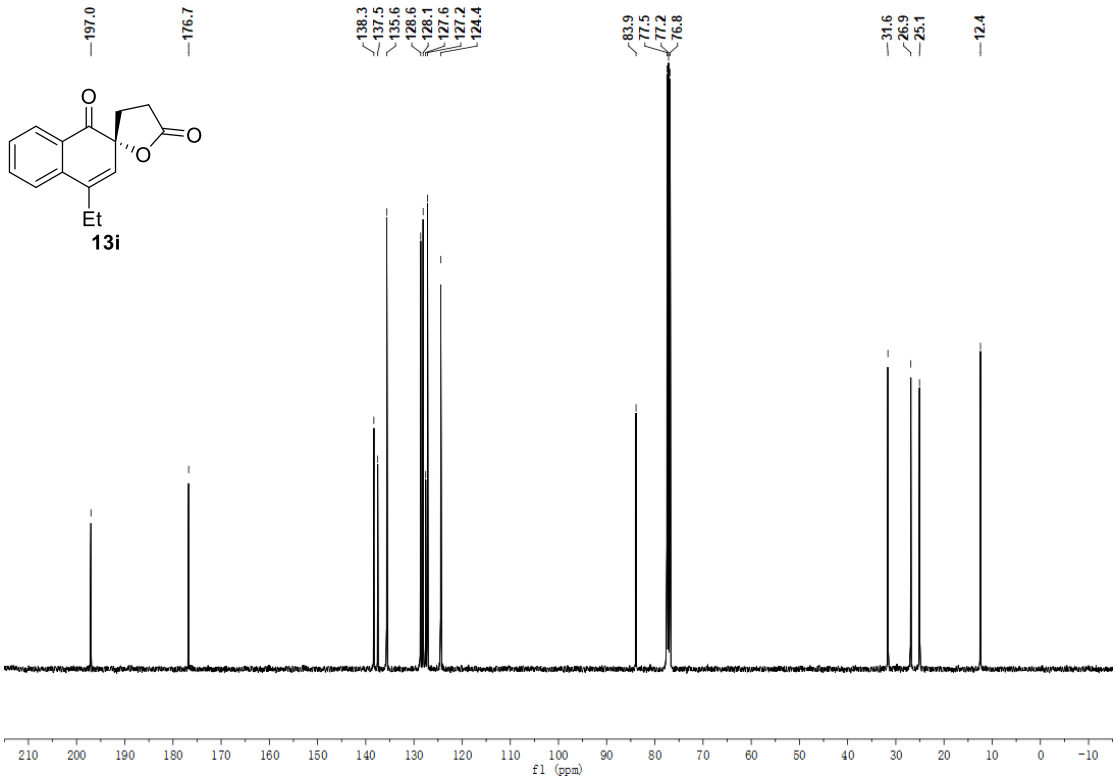
Supplementary Figure 119. ^{1}H NMR Spectrum of **13h** (**400** MHz, $CDCl_3$)



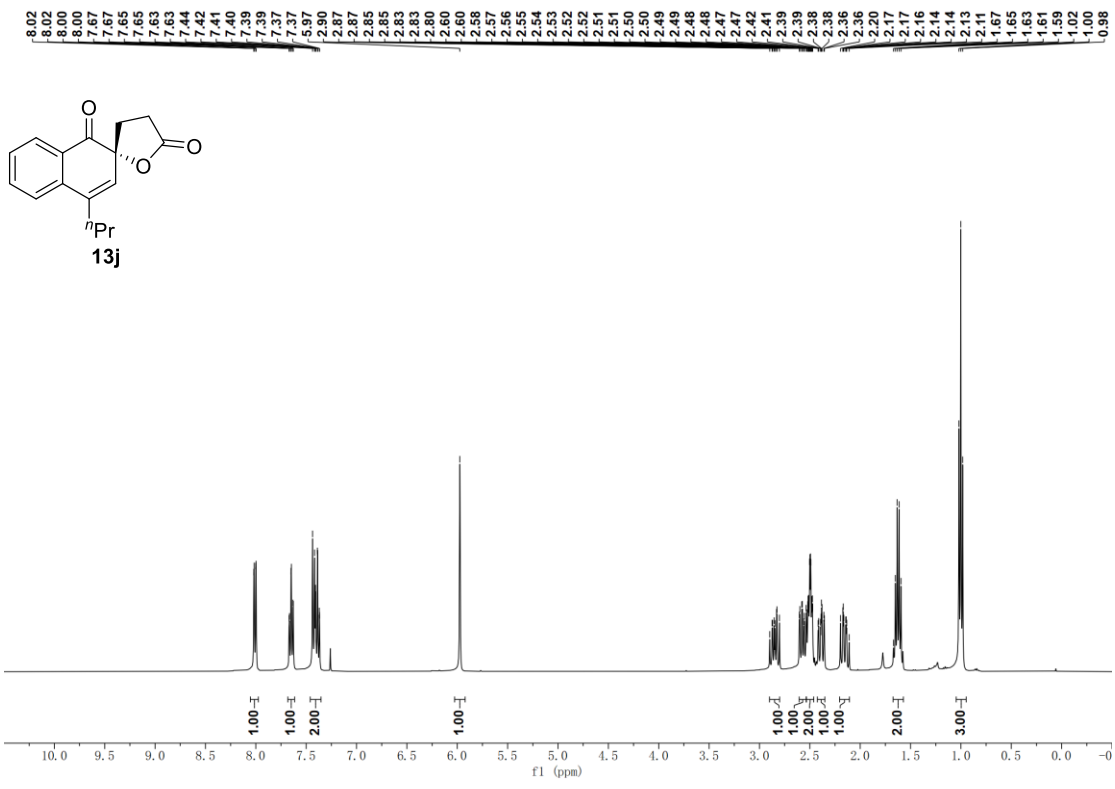
Supplementary Figure 120. ^{13}C NMR Spectrum of **13h** (**100** MHz, $CDCl_3$)



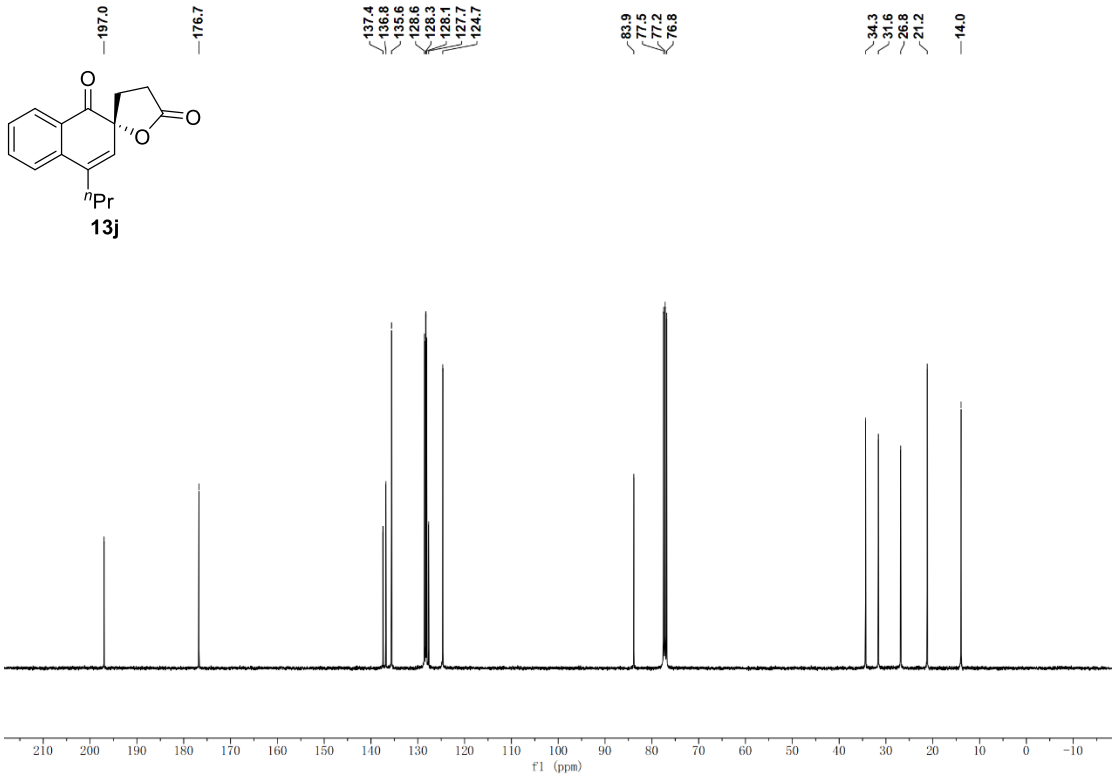
Supplementary Figure 121. ^{1}H NMR Spectrum of **13i** (**400** MHz, $CDCl_3$)



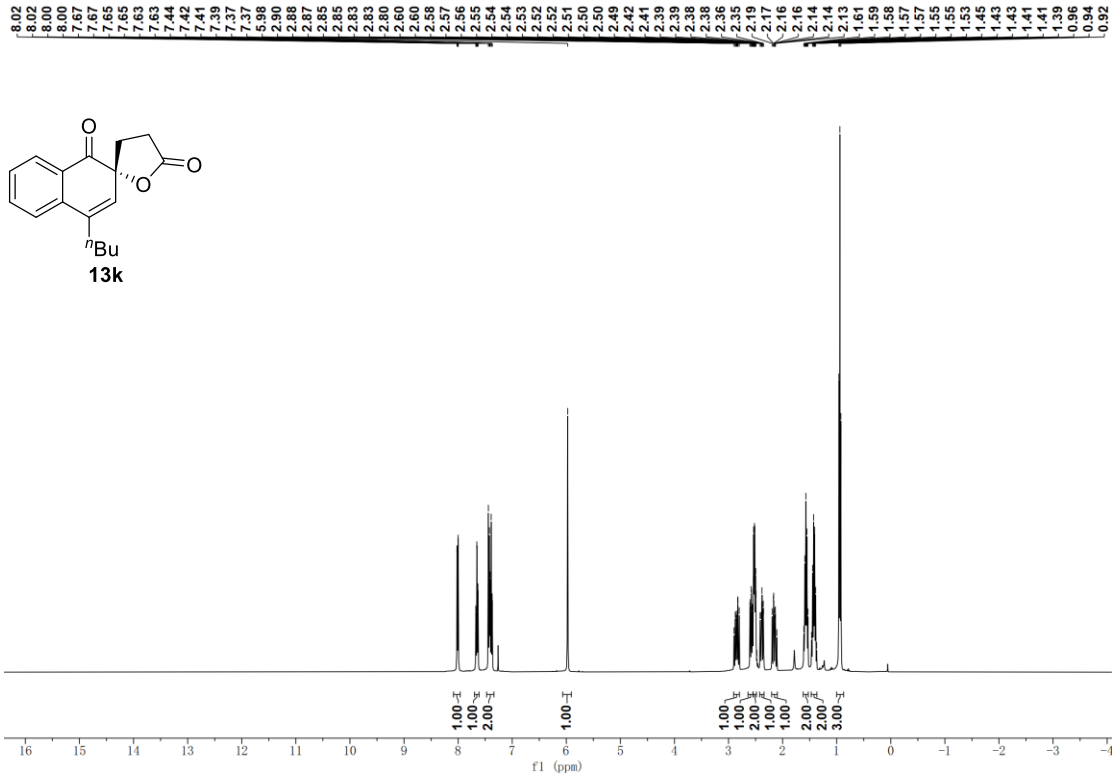
Supplementary Figure 122. ^{13}C NMR Spectrum of **13i** (**100** MHz, $CDCl_3$)



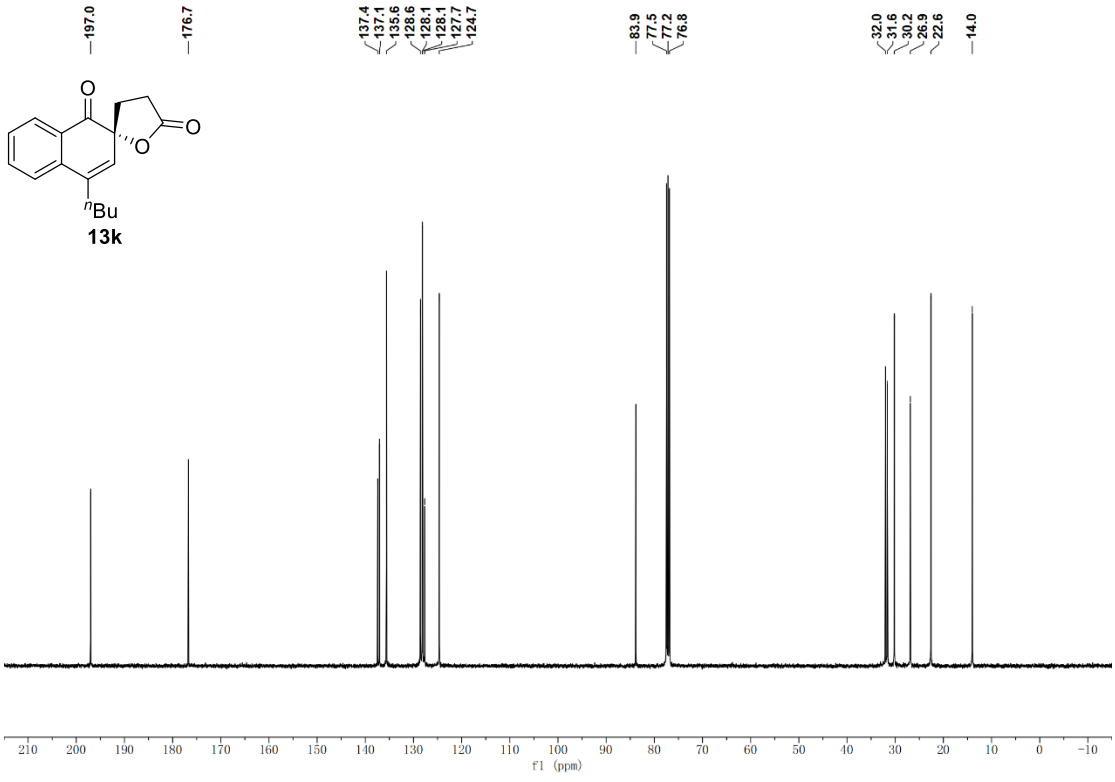
Supplementary Figure 123. ^{11}H NMR Spectrum of **13j** (**400** MHz, $CDCl_3$)



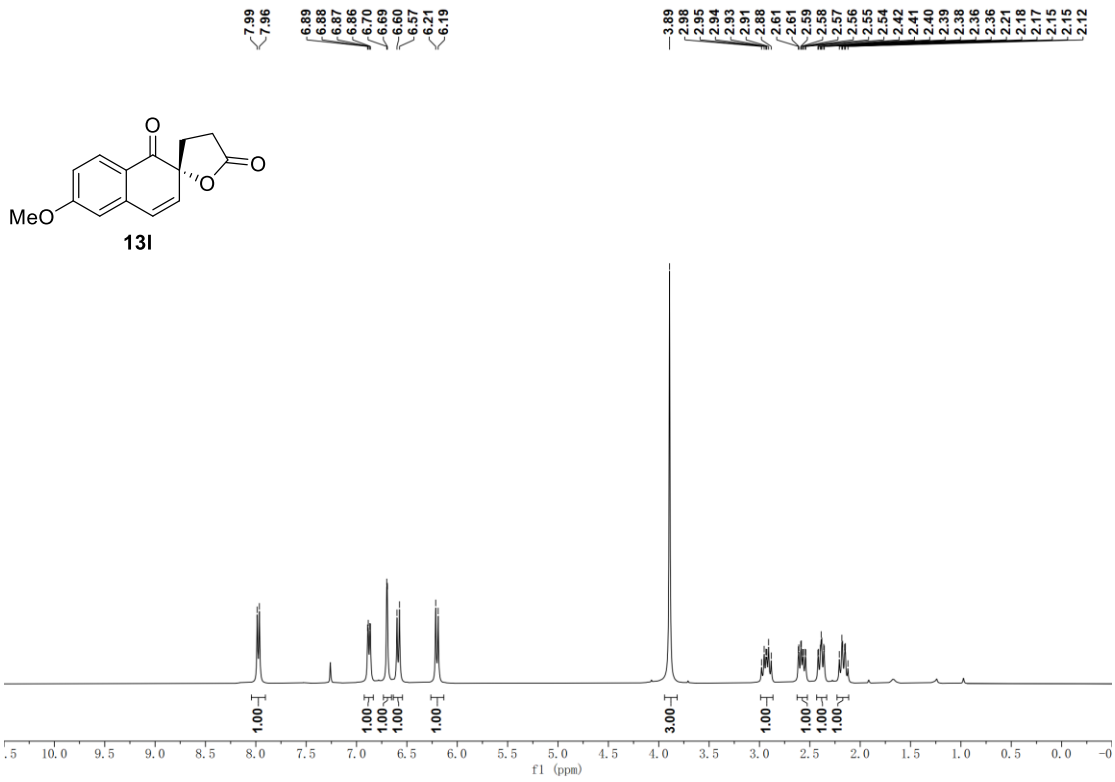
Supplementary Figure 124. ^{13}C NMR Spectrum of **13j** (**100** MHz, $CDCl_3$)



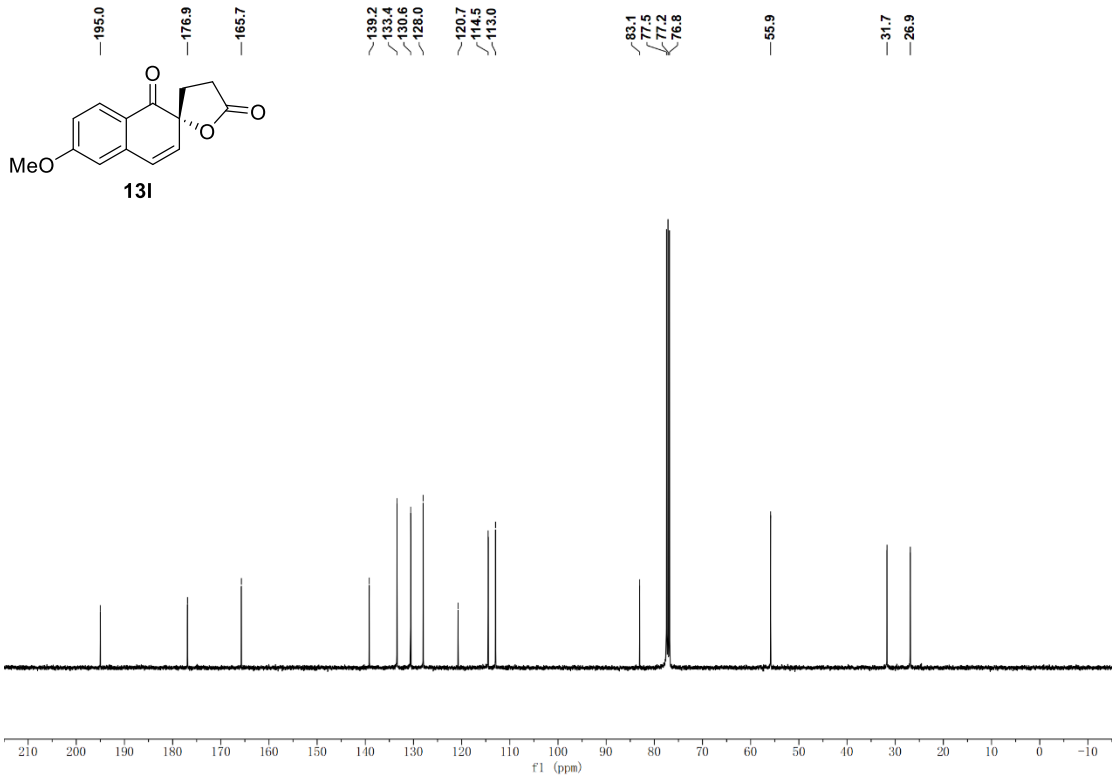
Supplementary Figure 125. ^{1}H NMR Spectrum of **13k** (**400** MHz, $CDCl_3$)



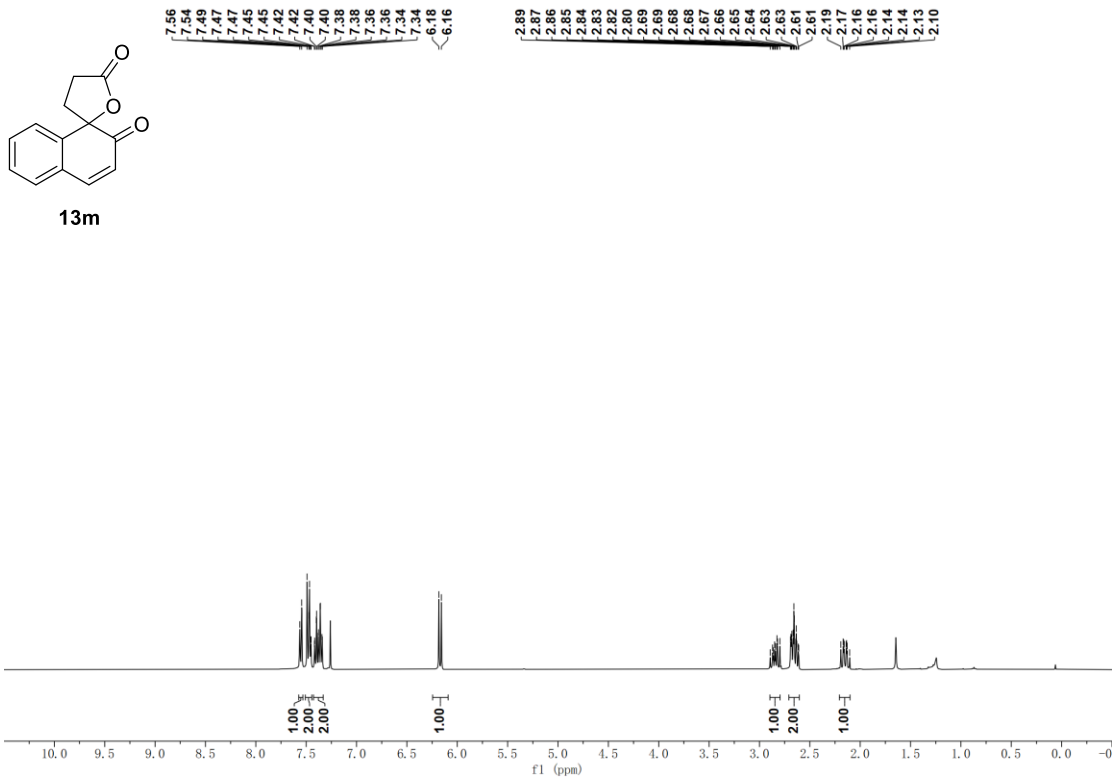
Supplementary Figure 126. ^{13}C NMR Spectrum of **13k** (**100** MHz, $CDCl_3$)



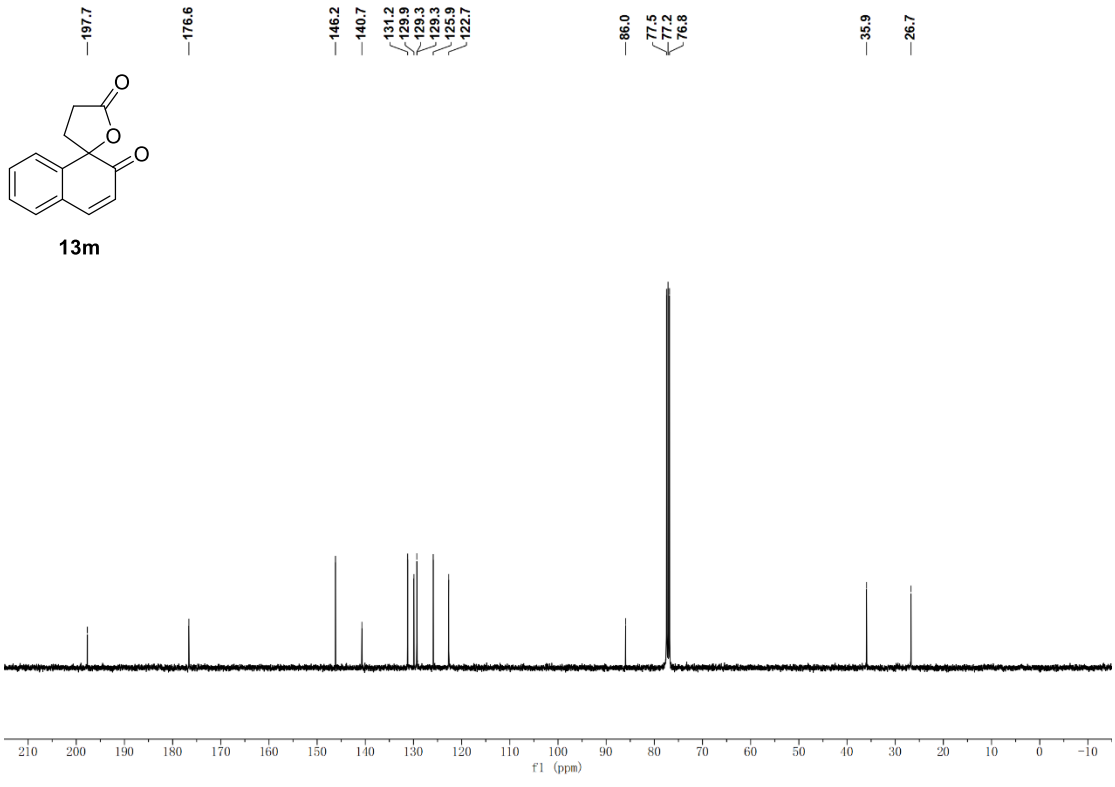
Supplementary Figure 127. ^{1}H NMR Spectrum of **13l** (**400** MHz, $CDCl_3$)



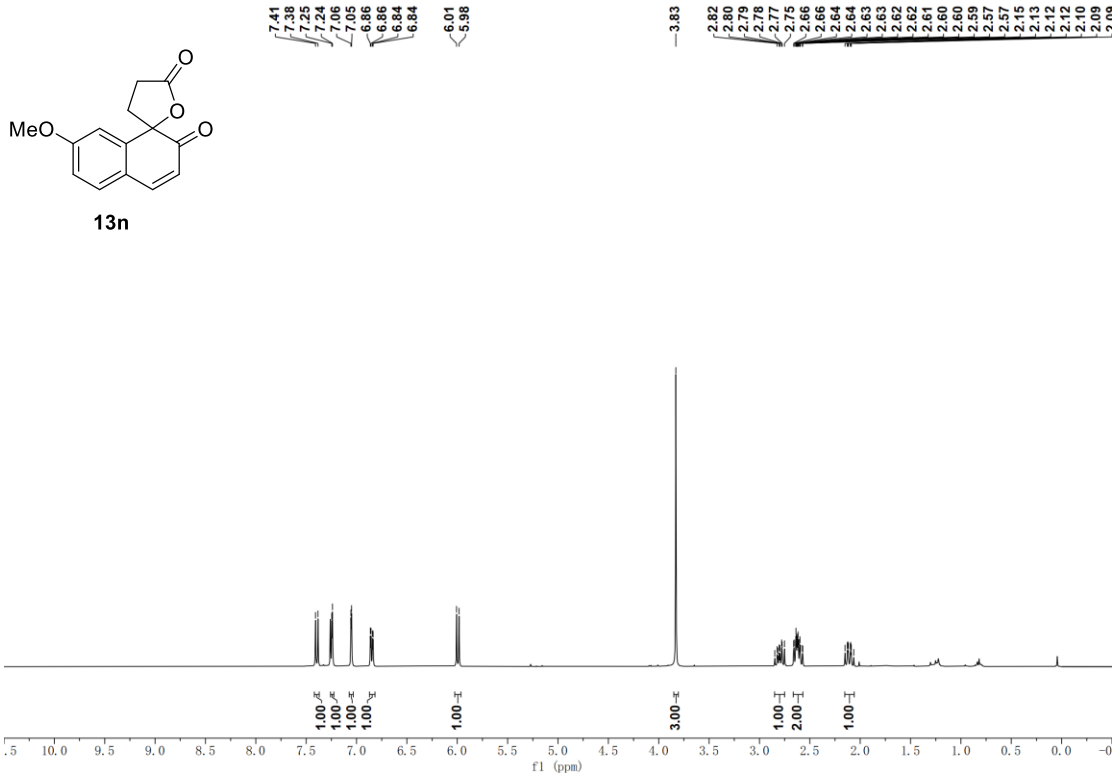
Supplementary Figure 128. ^{13}C NMR Spectrum of **13l** (**100** MHz, $CDCl_3$)



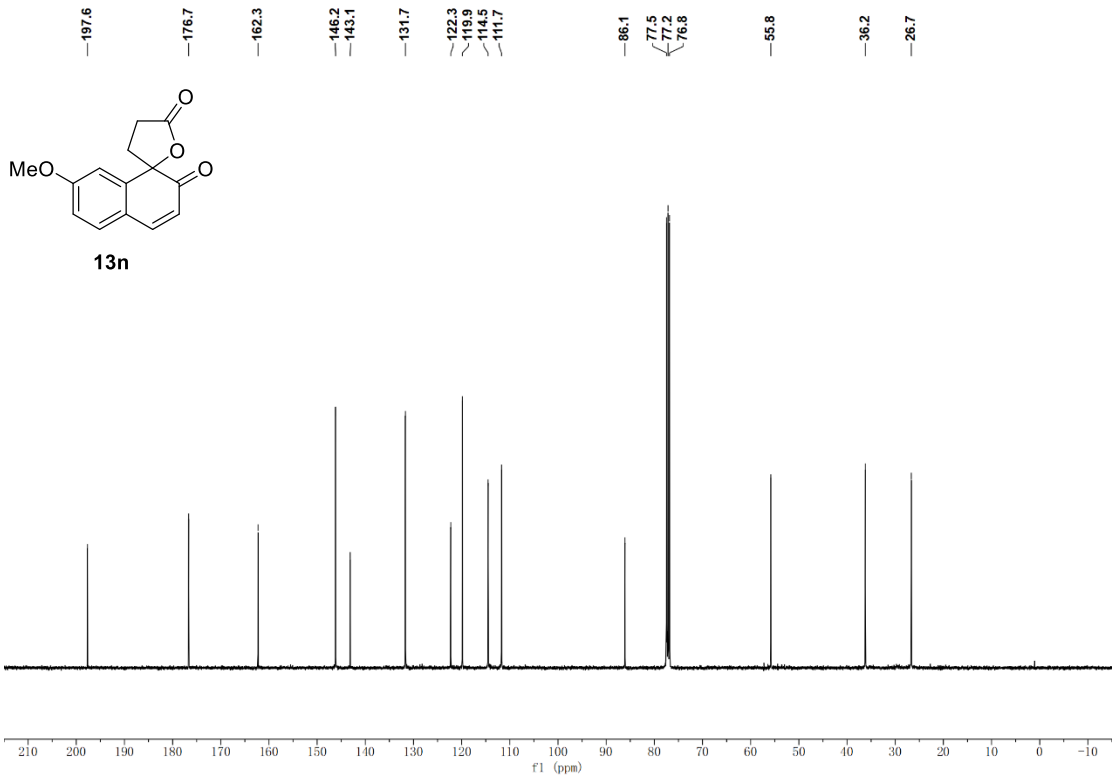
Supplementary Figure 129. ^{1}H NMR Spectrum of **13m** (**400** MHz, $CDCl_3$)



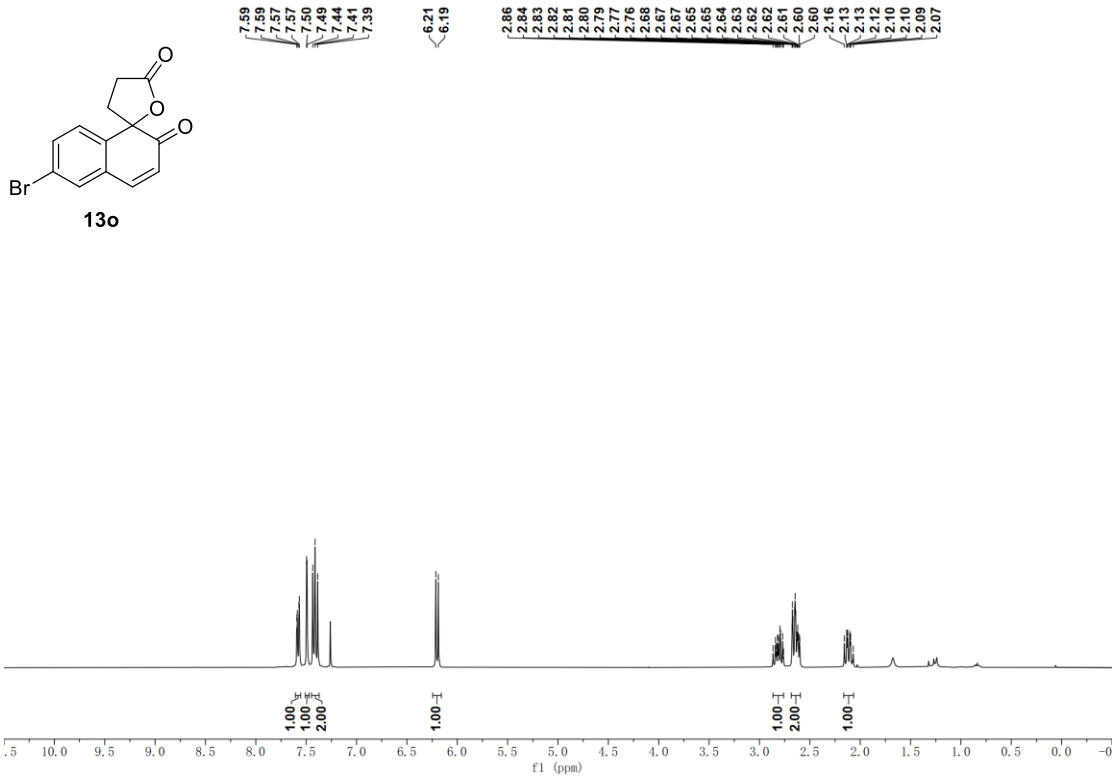
Supplementary Figure 130. ^{13}C NMR Spectrum of **13m** (**100** MHz, $CDCl_3$)



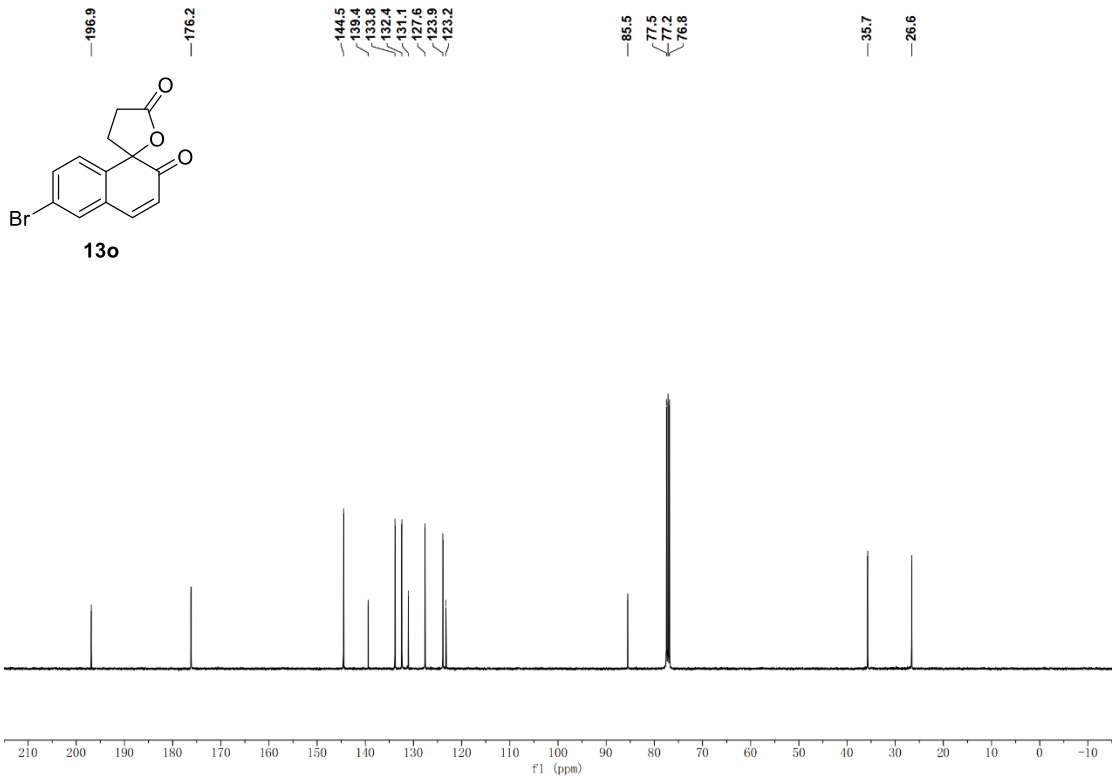
Supplementary Figure 131. ^{1}H NMR Spectrum of **13n** (**400** MHz, $CDCl_3$)



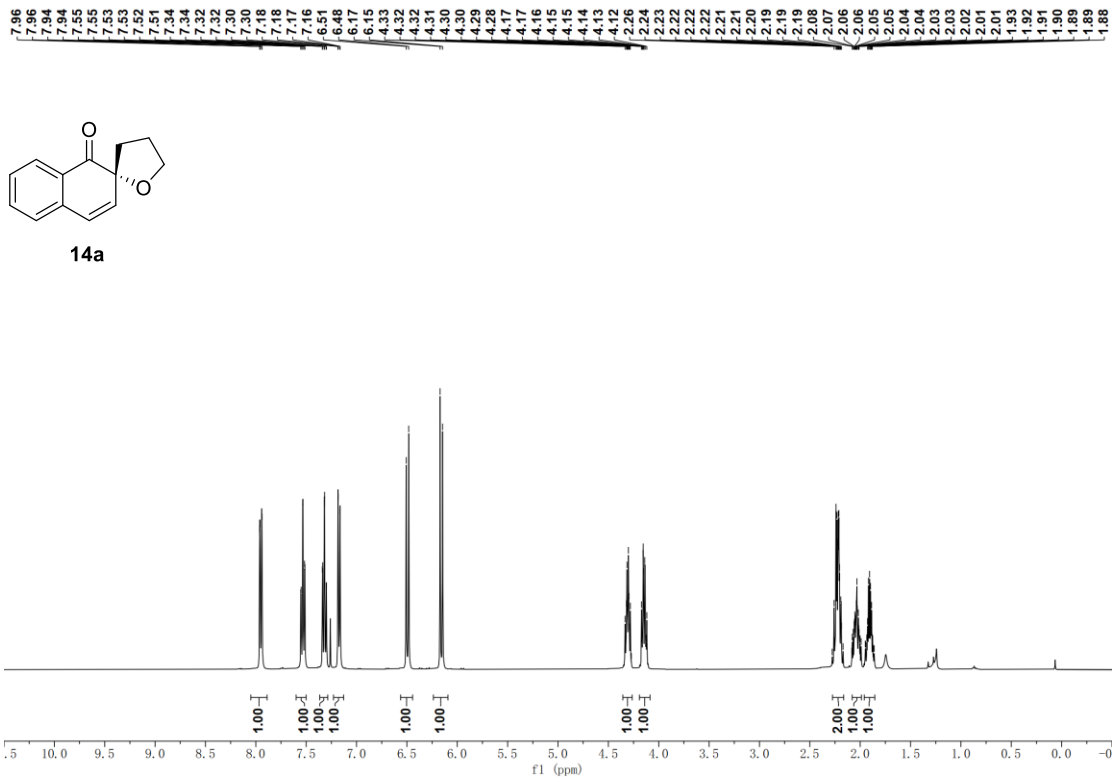
Supplementary Figure 132. ^{13}C NMR Spectrum of **13n** (**100** MHz, $CDCl_3$)



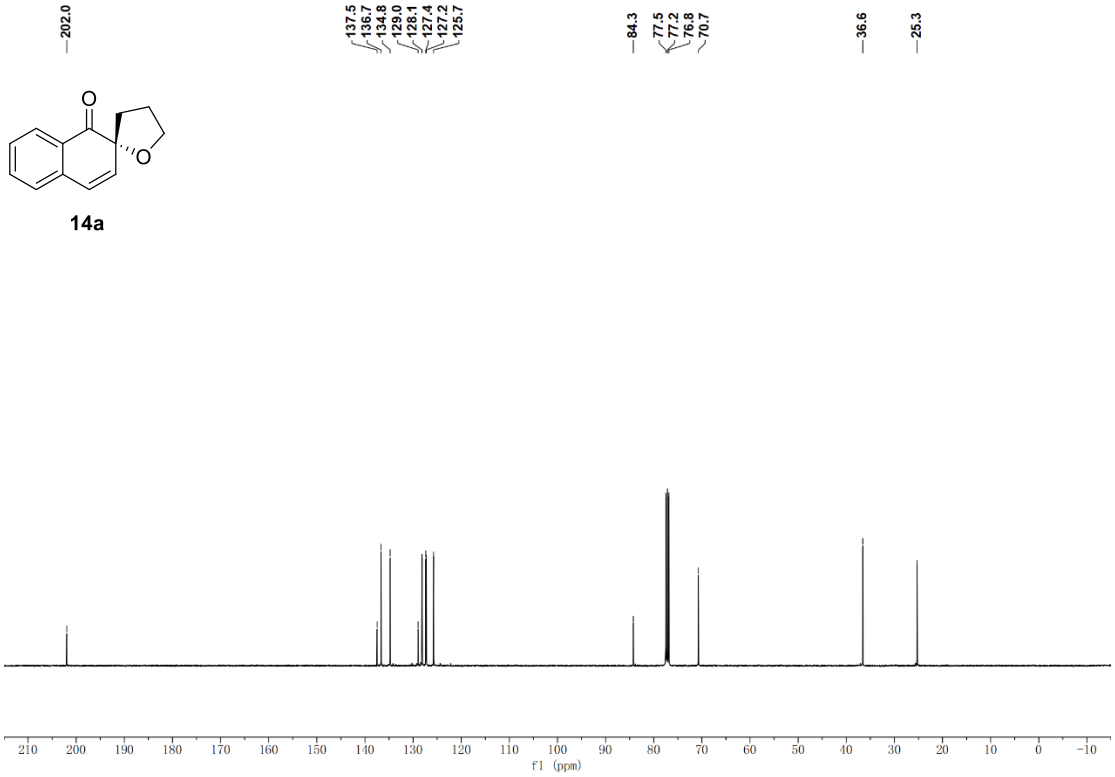
Supplementary Figure 133. ^{1}H NMR Spectrum of **13o** (**400** MHz, $CDCl_3$)



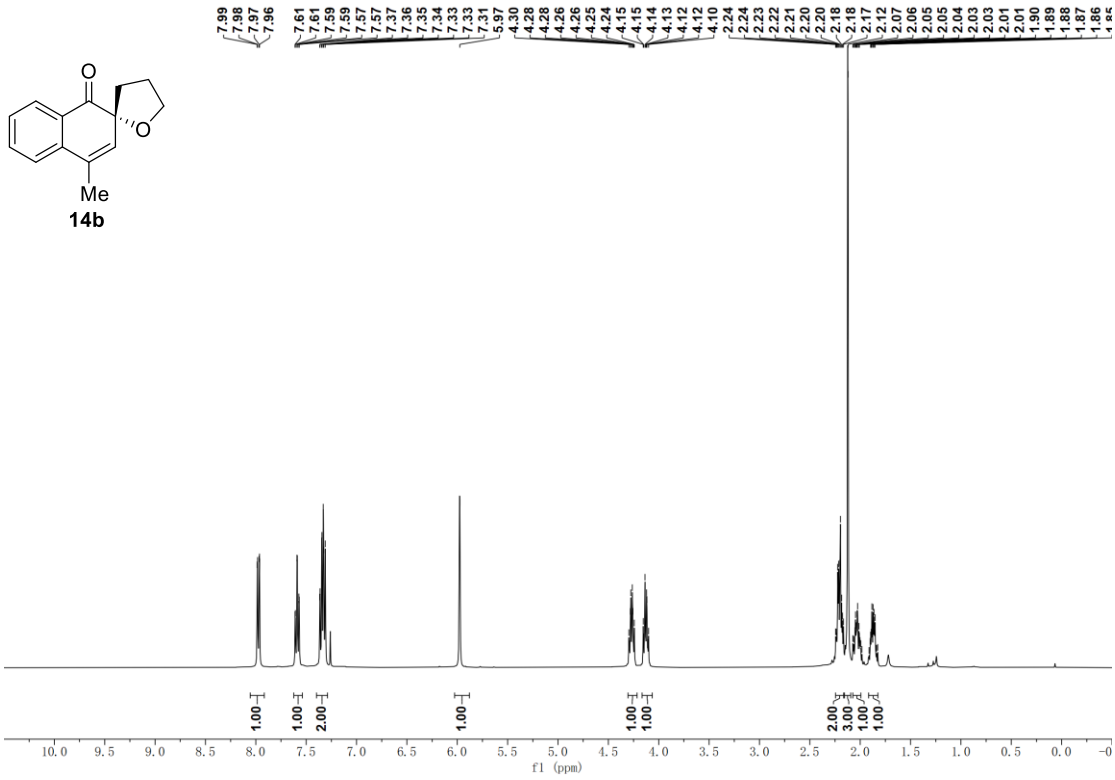
Supplementary Figure 134. ^{13}C NMR Spectrum of **13o** (**100** MHz, $CDCl_3$)



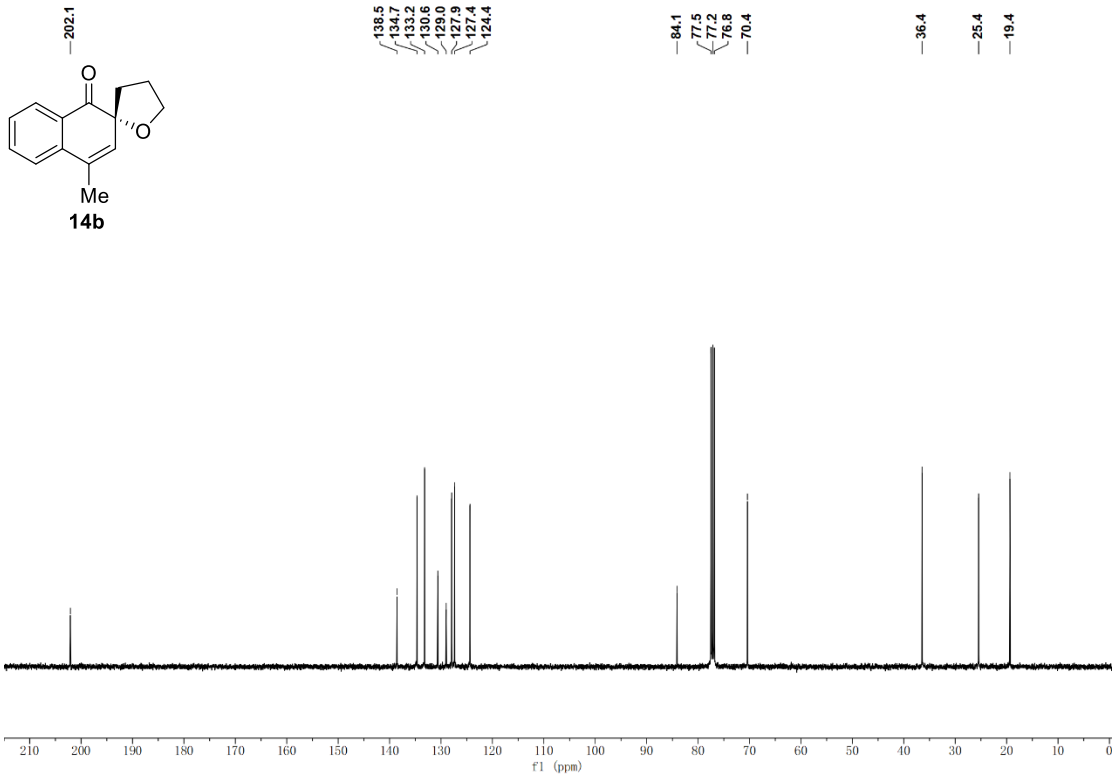
Supplementary Figure 135. ^{1}H NMR Spectrum of **14a** (**400** MHz, $CDCl_3$)



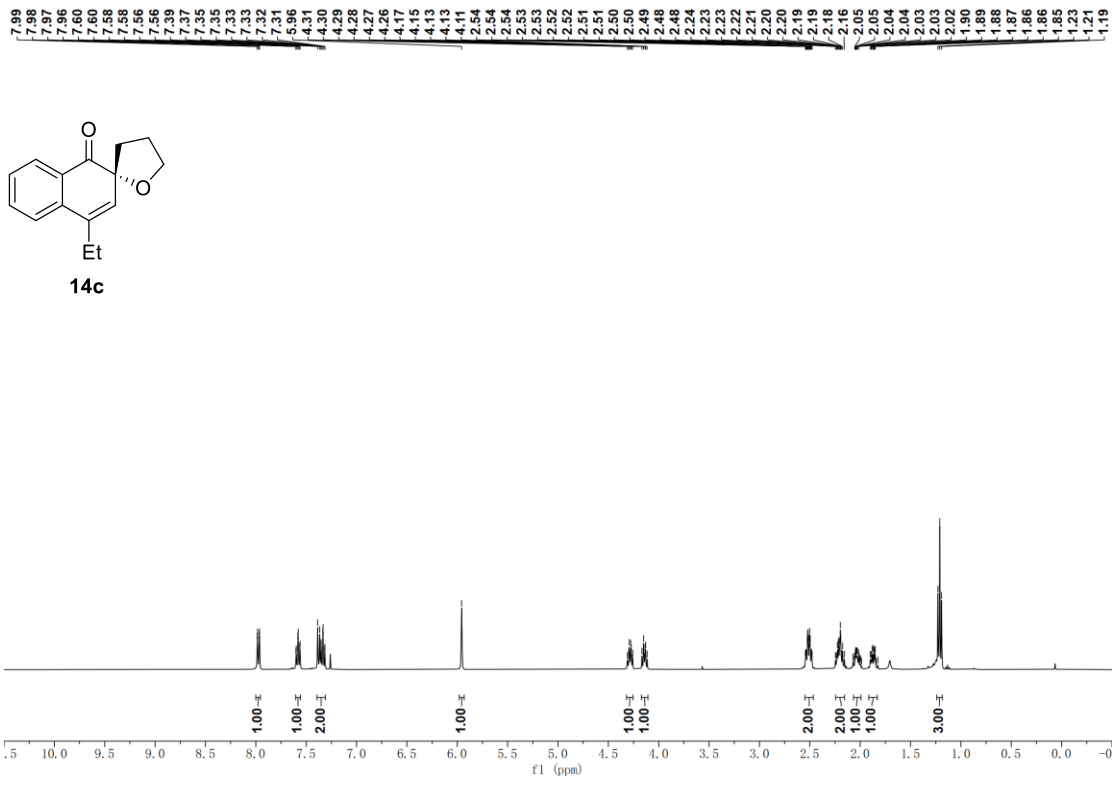
Supplementary Figure 136. ^{13}C NMR Spectrum of **14a** (**100** MHz, $CDCl_3$)



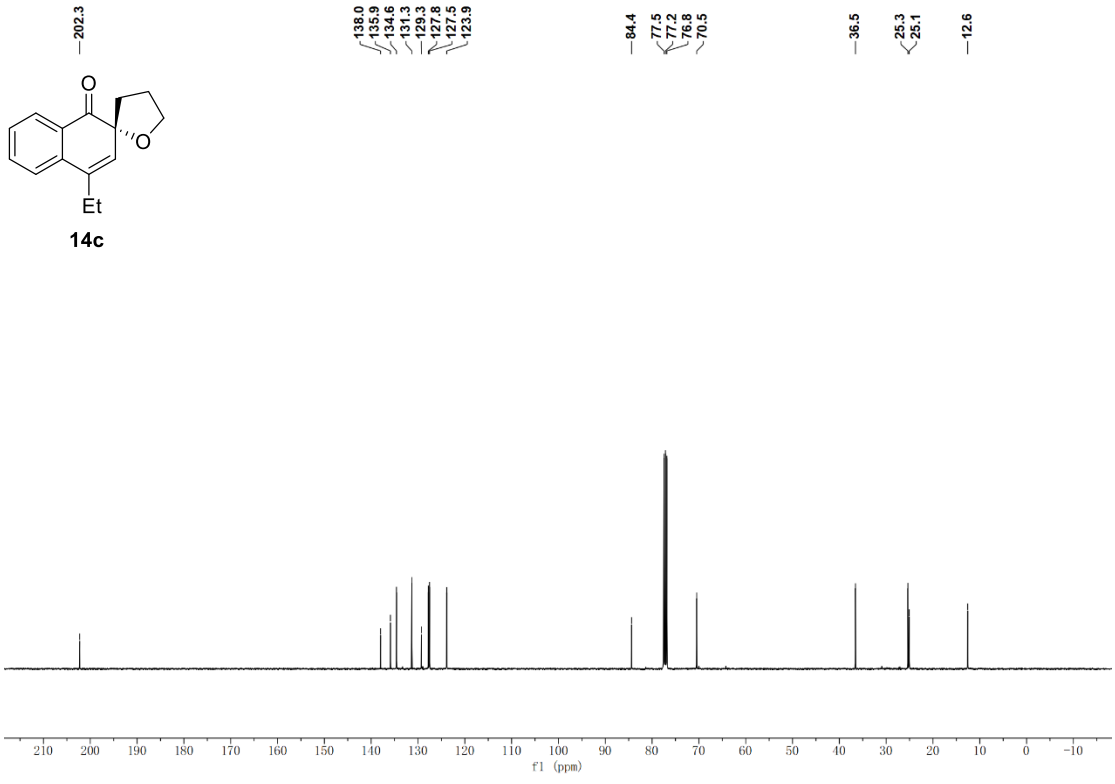
Supplementary Figure 137. ^{1}H NMR Spectrum of **14b** (**400** MHz, $CDCl_3$)



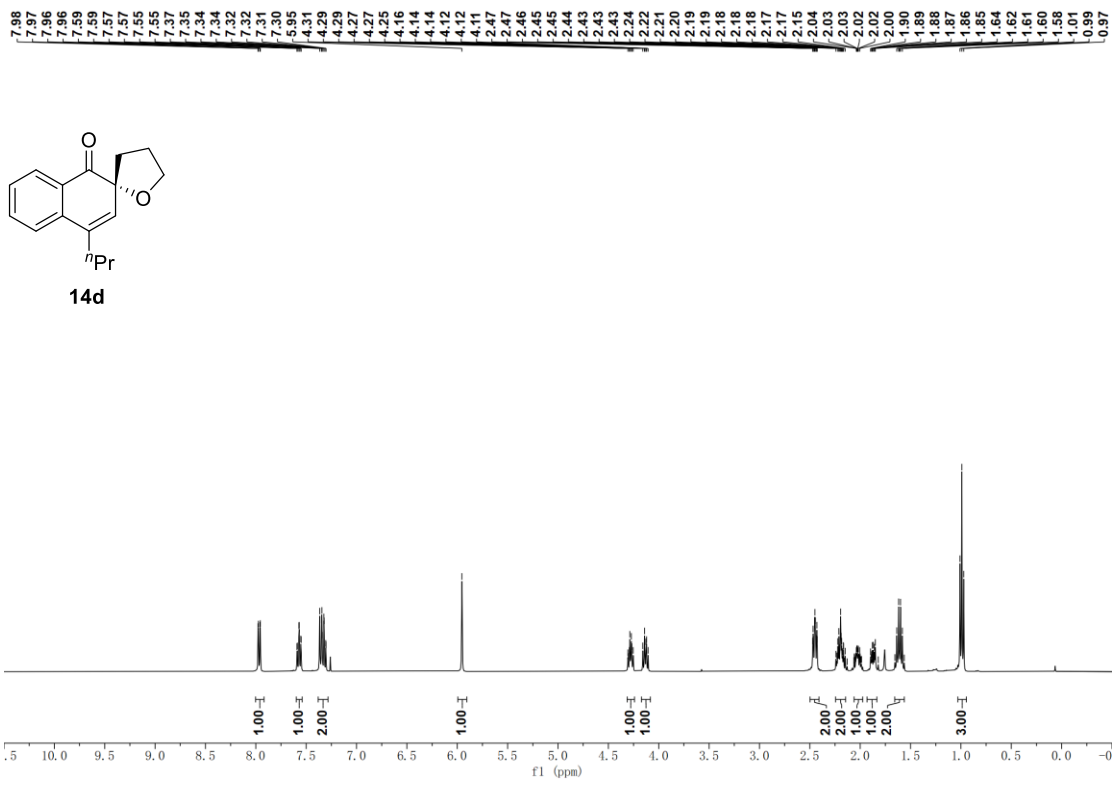
Supplementary Figure 138. ^{13}C NMR Spectrum of **14b** (**100** MHz, $CDCl_3$)



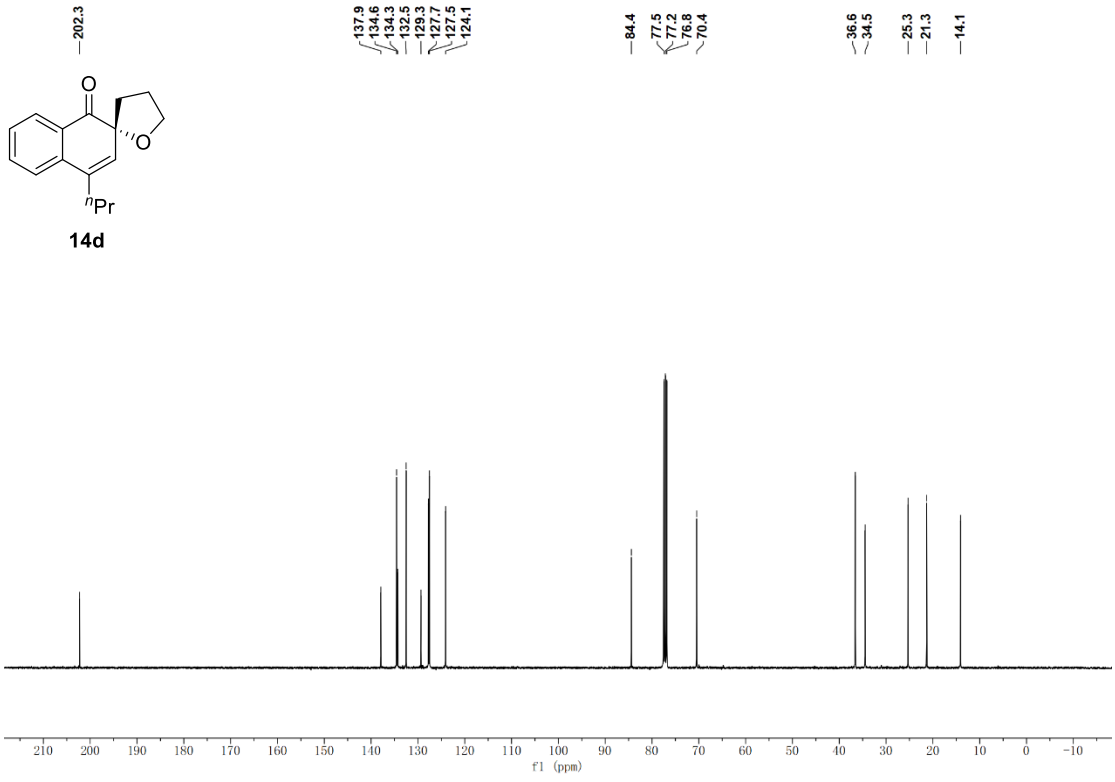
Supplementary Figure 139. ^{1}H NMR Spectrum of **14c** (**400** MHz, $CDCl_3$)



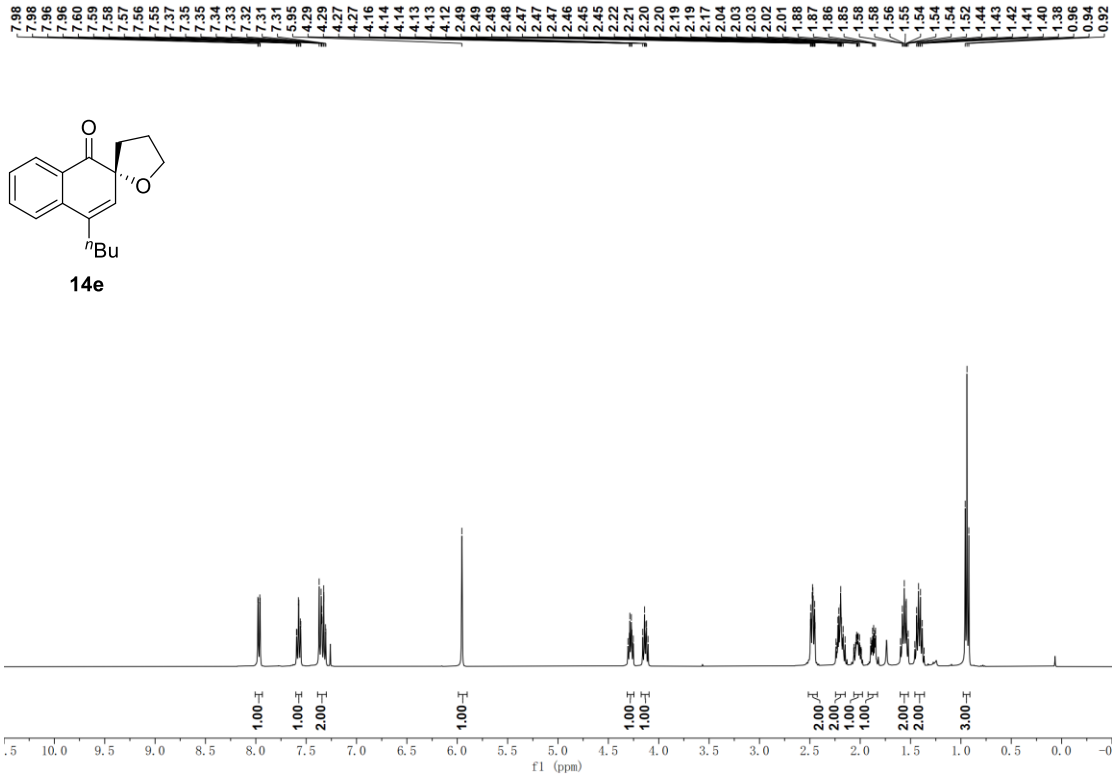
Supplementary Figure 140. ^{13}C NMR Spectrum of **14c** (**100** MHz, $CDCl_3$)



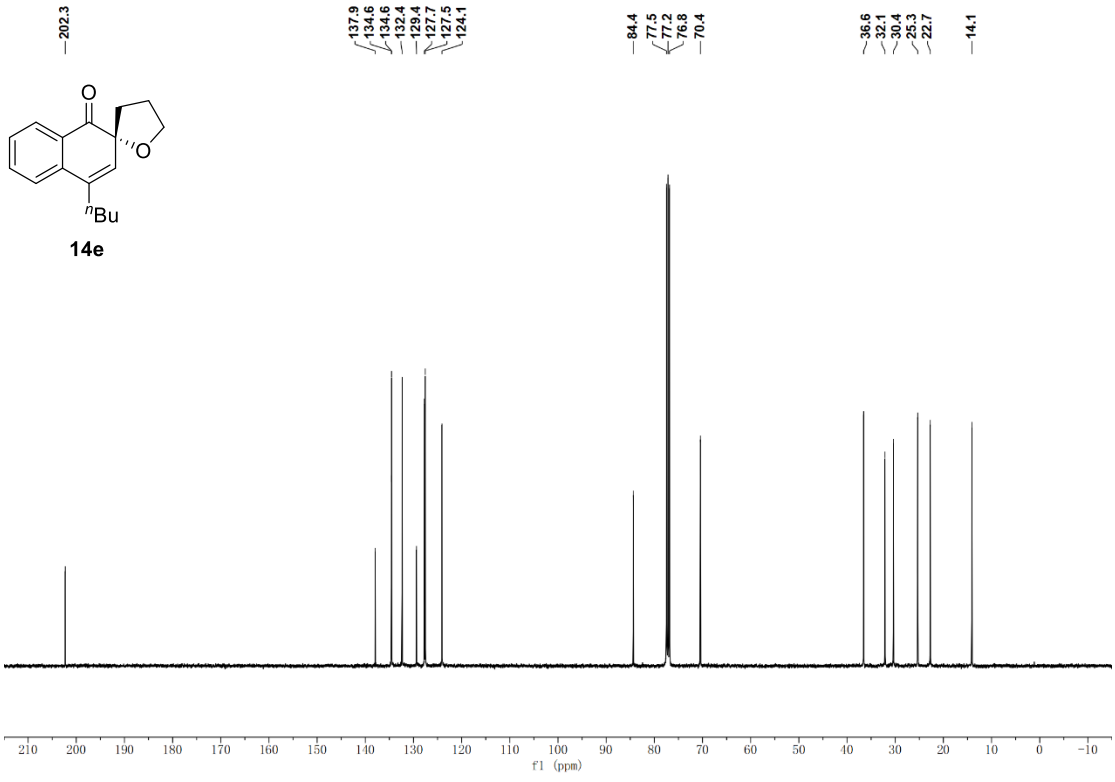
Supplementary Figure 141. ^{1}H NMR Spectrum of **14d** (**400** MHz, $CDCl_3$)



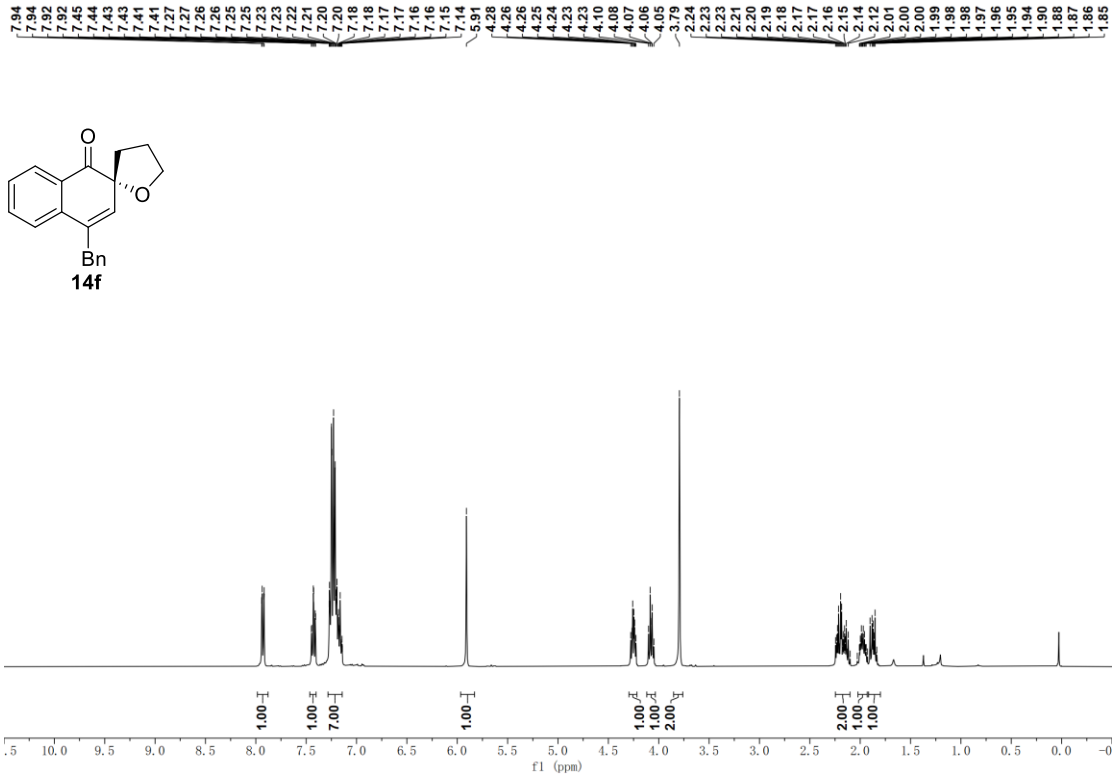
Supplementary Figure 142. ^{13}C NMR Spectrum of **14d** (**100** MHz, $CDCl_3$)



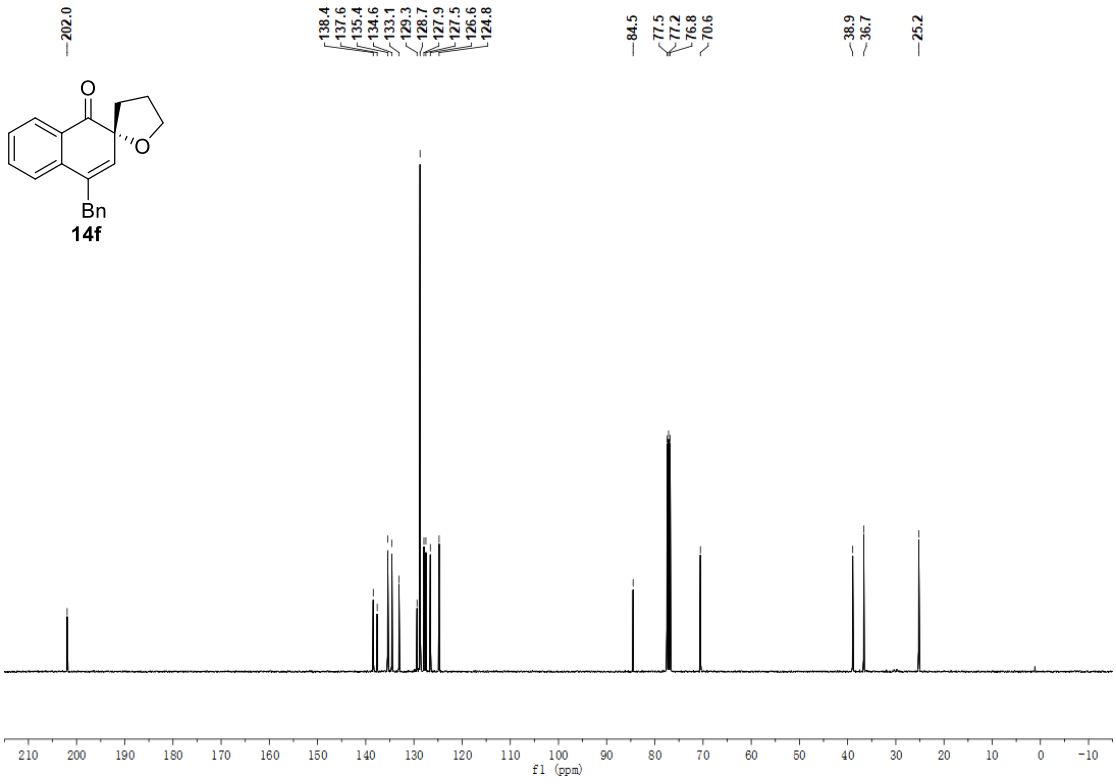
Supplementary Figure 143. ^{1}H NMR Spectrum of **14e** (**400** MHz, $CDCl_3$)



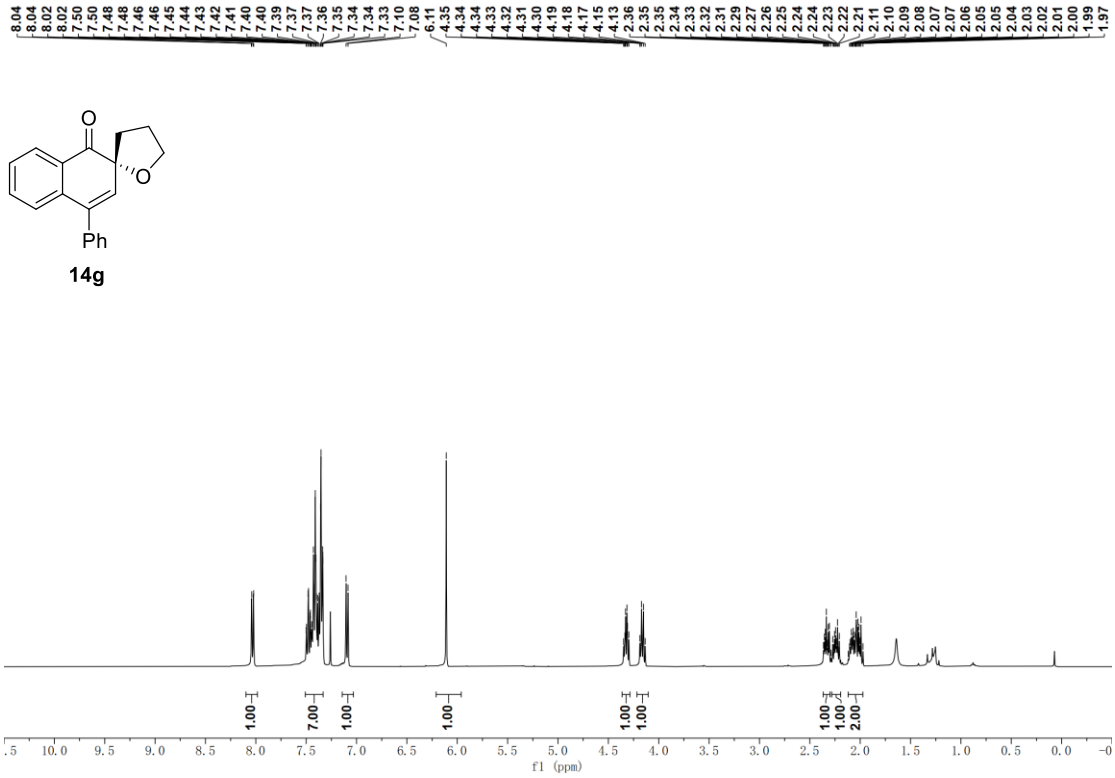
Supplementary Figure 144. ^{13}C NMR Spectrum of **14e** (**100** MHz, $CDCl_3$)



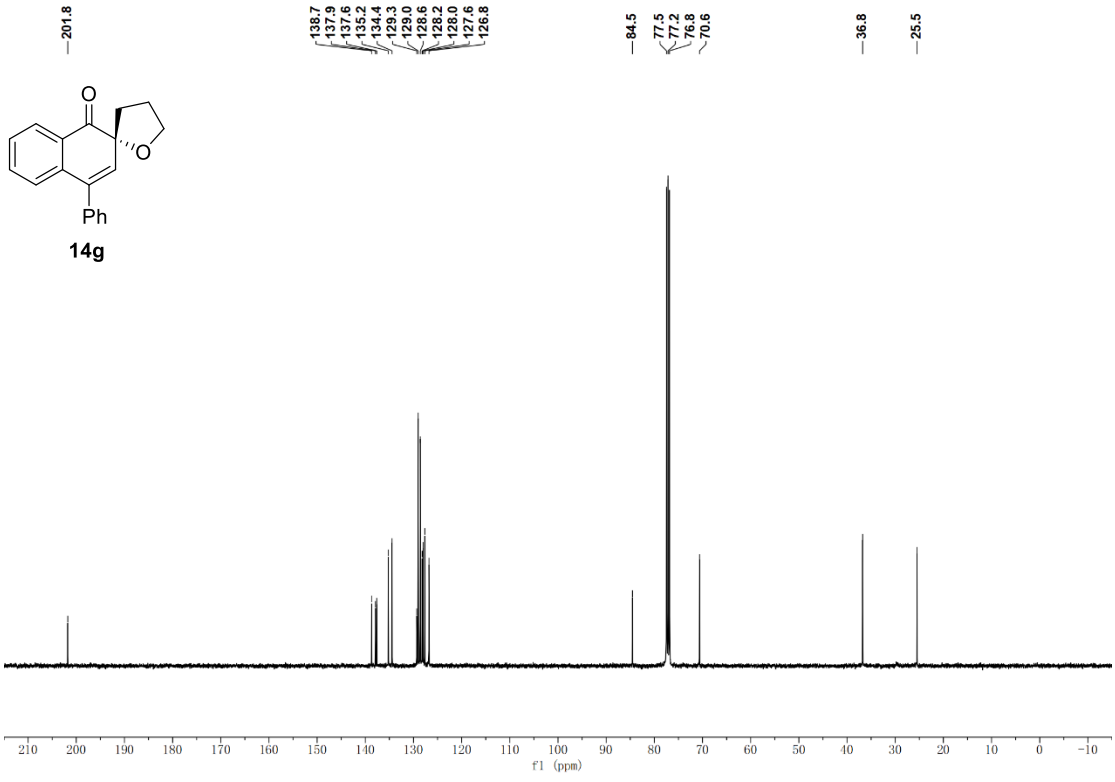
Supplementary Figure 145. ^{1}H NMR Spectrum of **14f** (**400** MHz, $CDCl_3$)



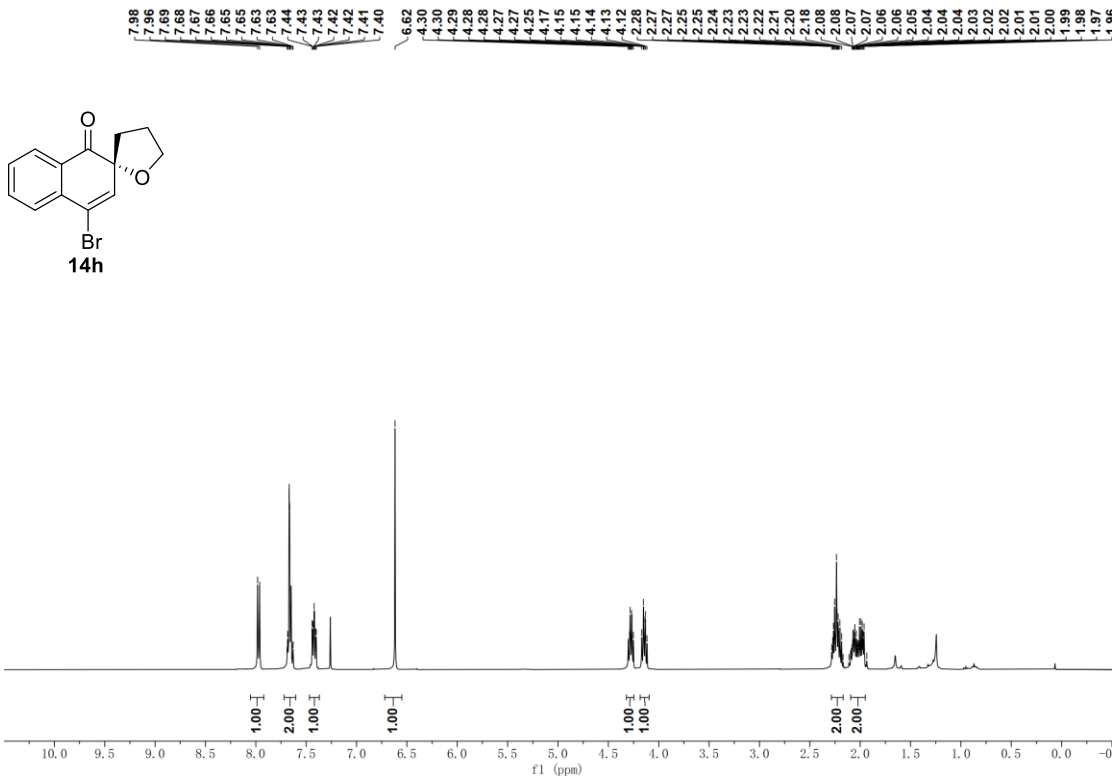
Supplementary Figure 146. ^{13}C NMR Spectrum of **14f** (**100** MHz, $CDCl_3$)



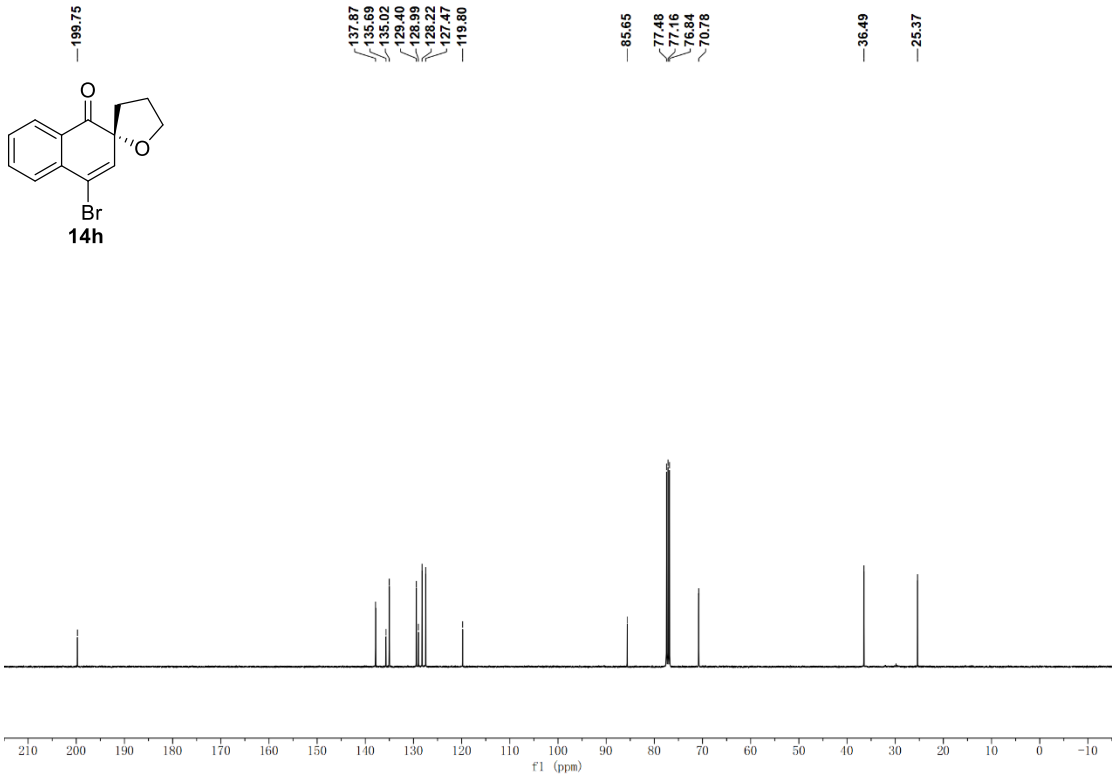
Supplementary Figure 147. ^{1}H NMR Spectrum of **14g** (**400** MHz, $CDCl_3$)



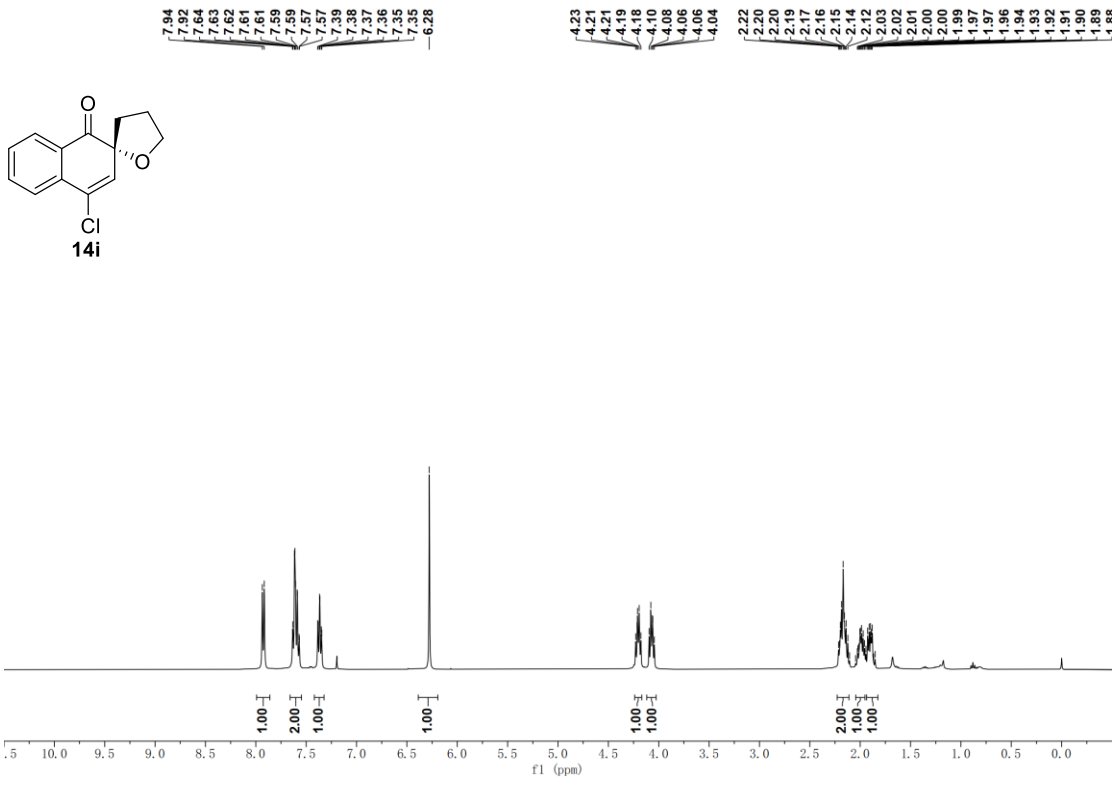
Supplementary Figure 148. ^{13}C NMR Spectrum of **14g** (**100** MHz, $CDCl_3$)



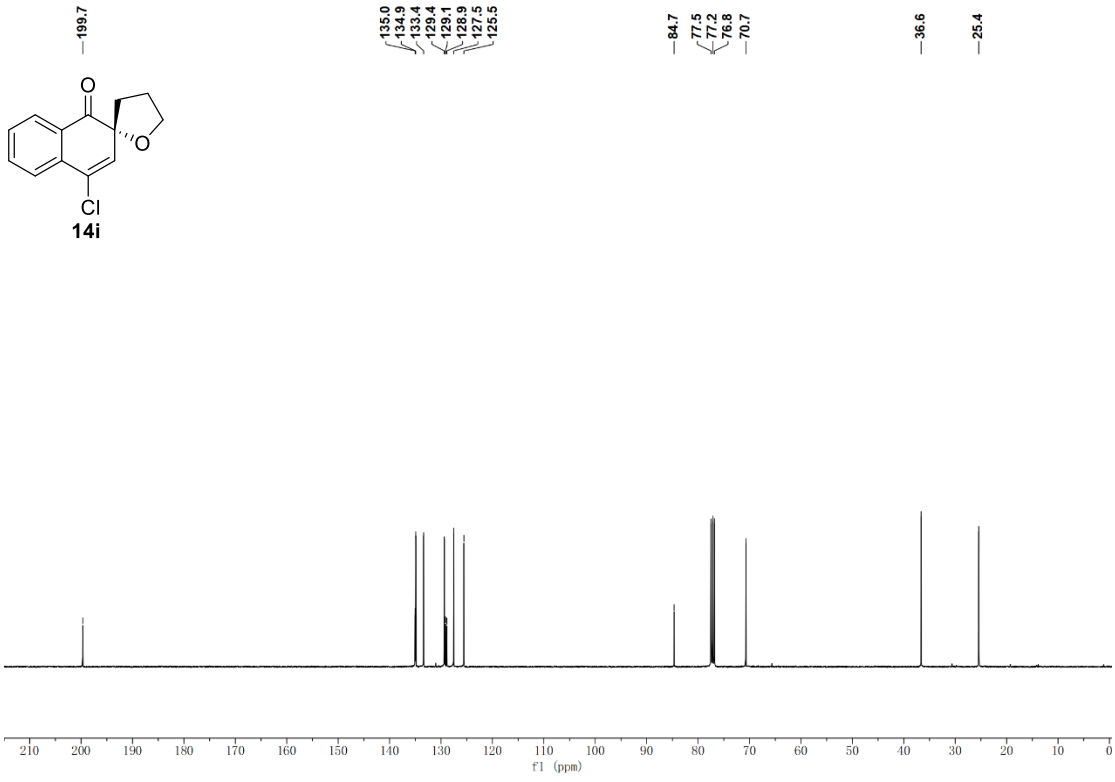
Supplementary Figure 149. ^{1}H NMR Spectrum of **14h** (**400** MHz, $CDCl_3$)



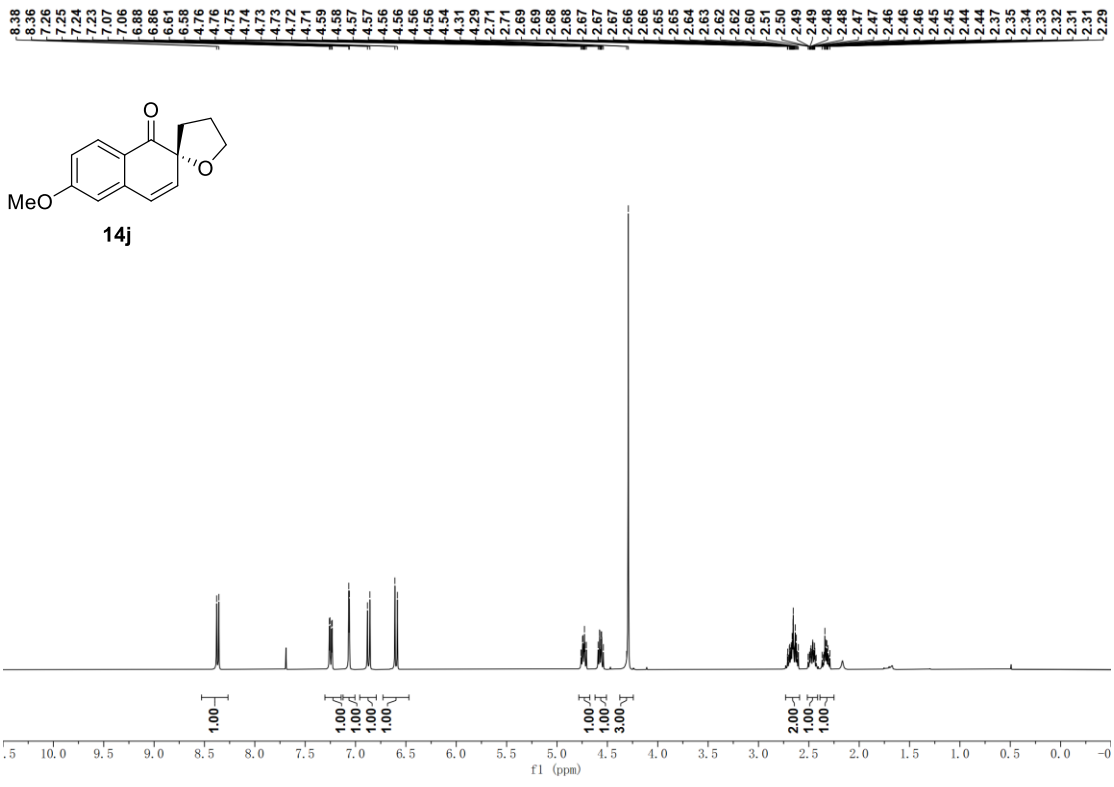
Supplementary Figure 150. ^{13}C NMR Spectrum of **14h** (**100** MHz, $CDCl_3$)



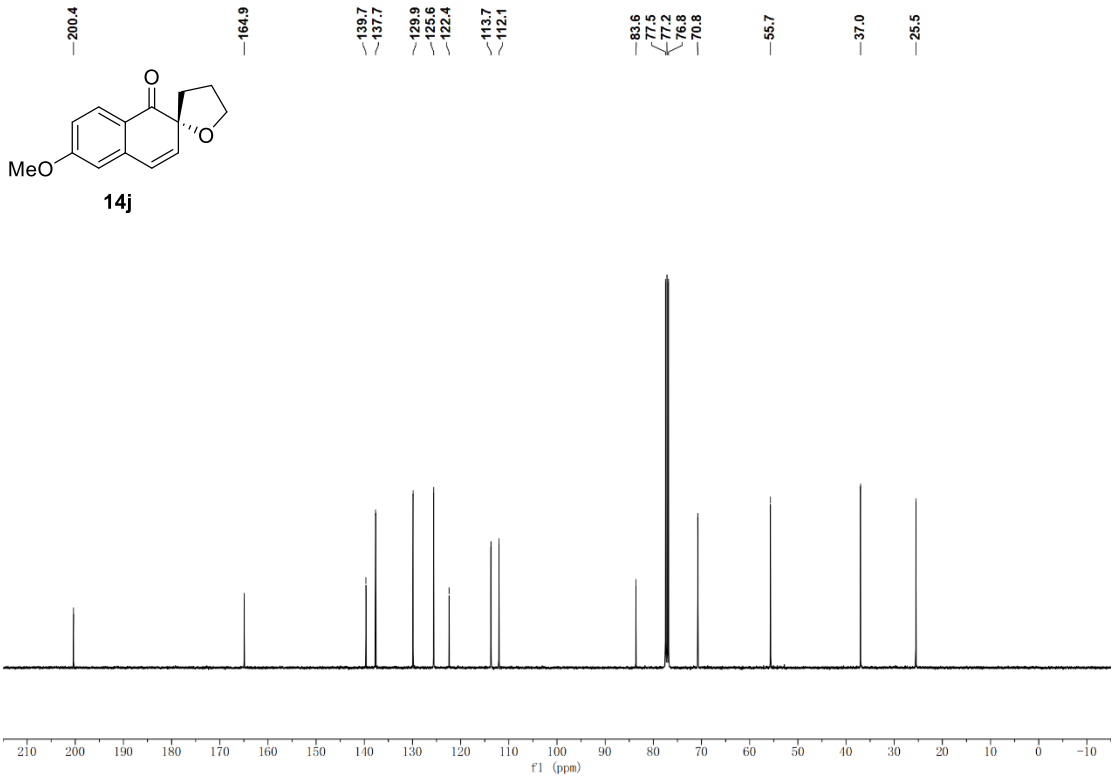
Supplementary Figure 151. ^{1}H NMR Spectrum of **14i** (**400** MHz, $CDCl_3$)



Supplementary Figure 152. ^{13}C NMR Spectrum of **14i** (**100** MHz, $CDCl_3$)

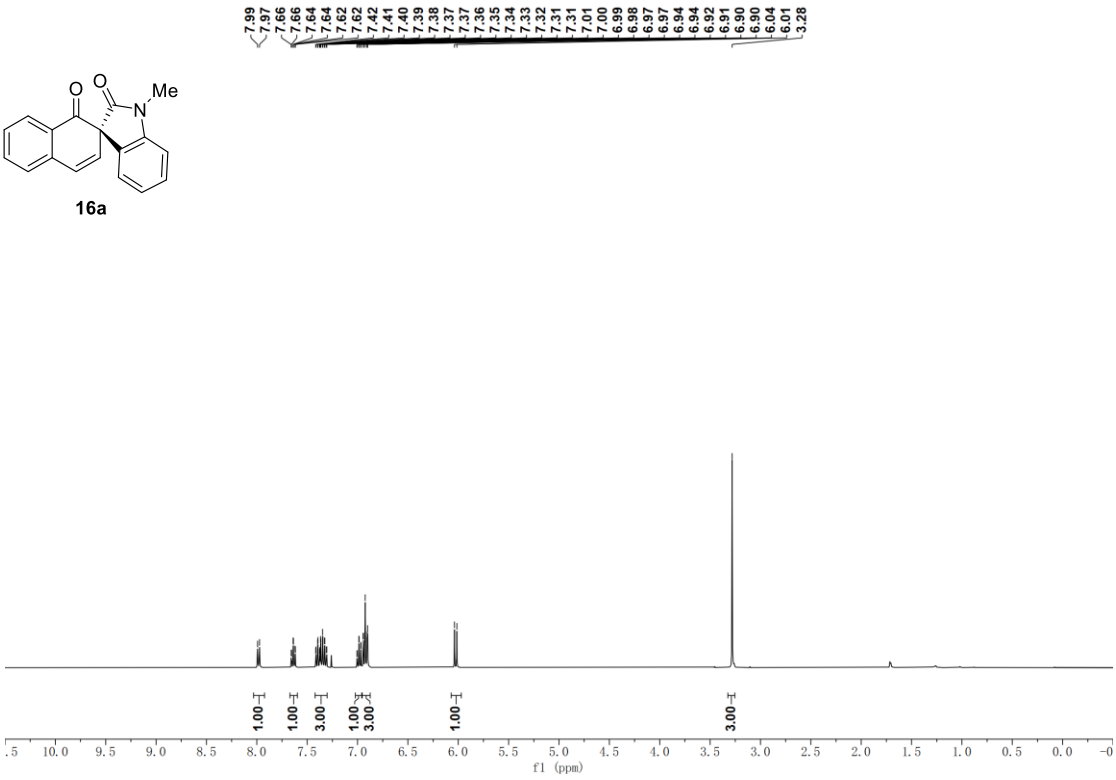


Supplementary Figure 153. ^{1}H NMR Spectrum of **14j** (**400** MHz, $CDCl_3$)

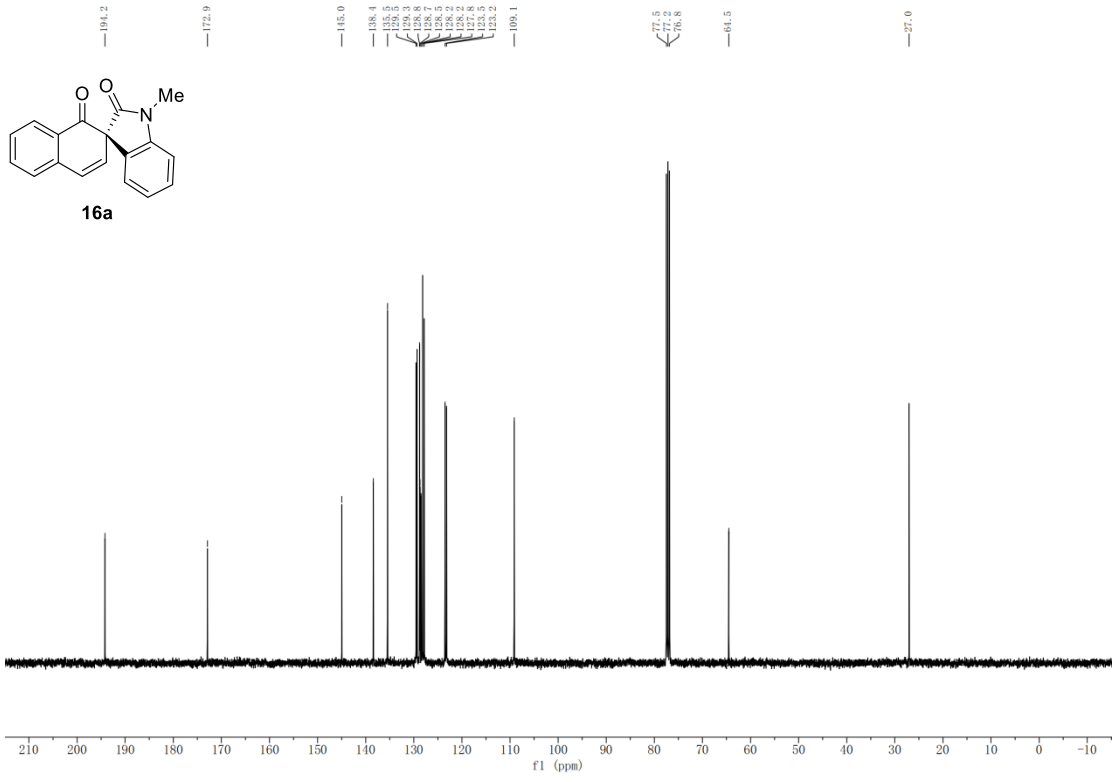


Supplementary Figure 154. ^{13}C NMR Spectrum of **14j** (**100** MHz, $CDCl_3$)

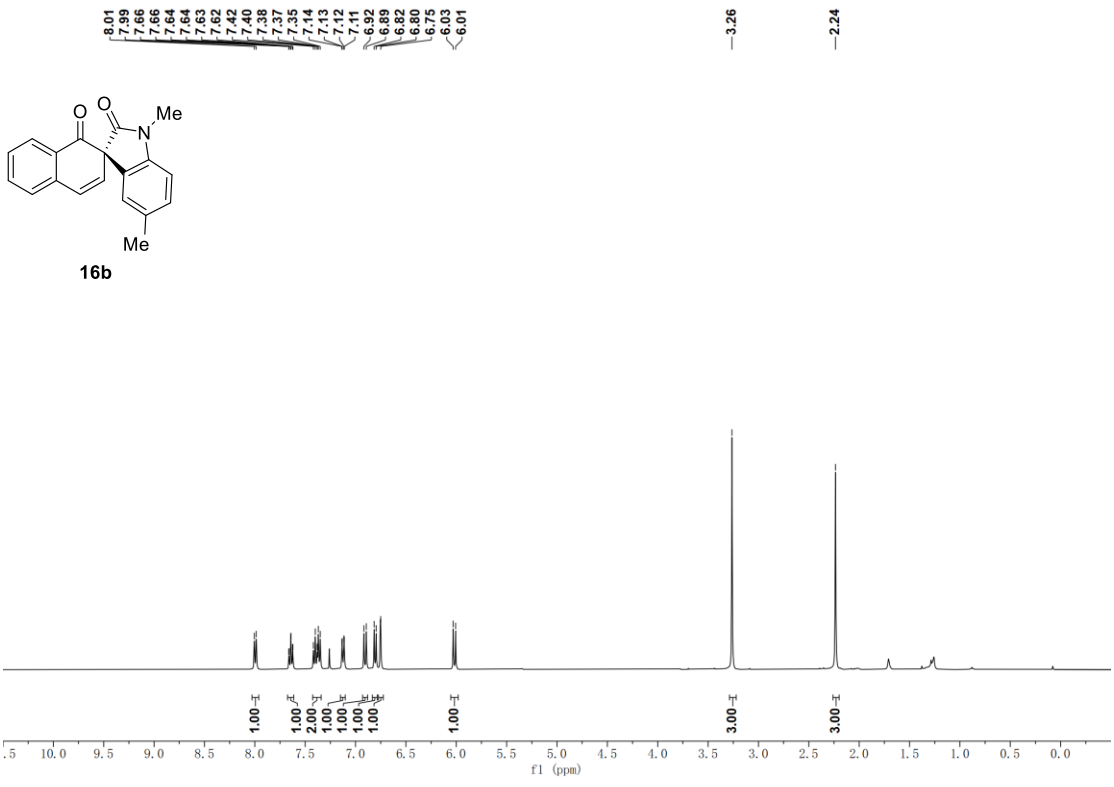
11.2.2 Spectrum of oxidative spirolactonization



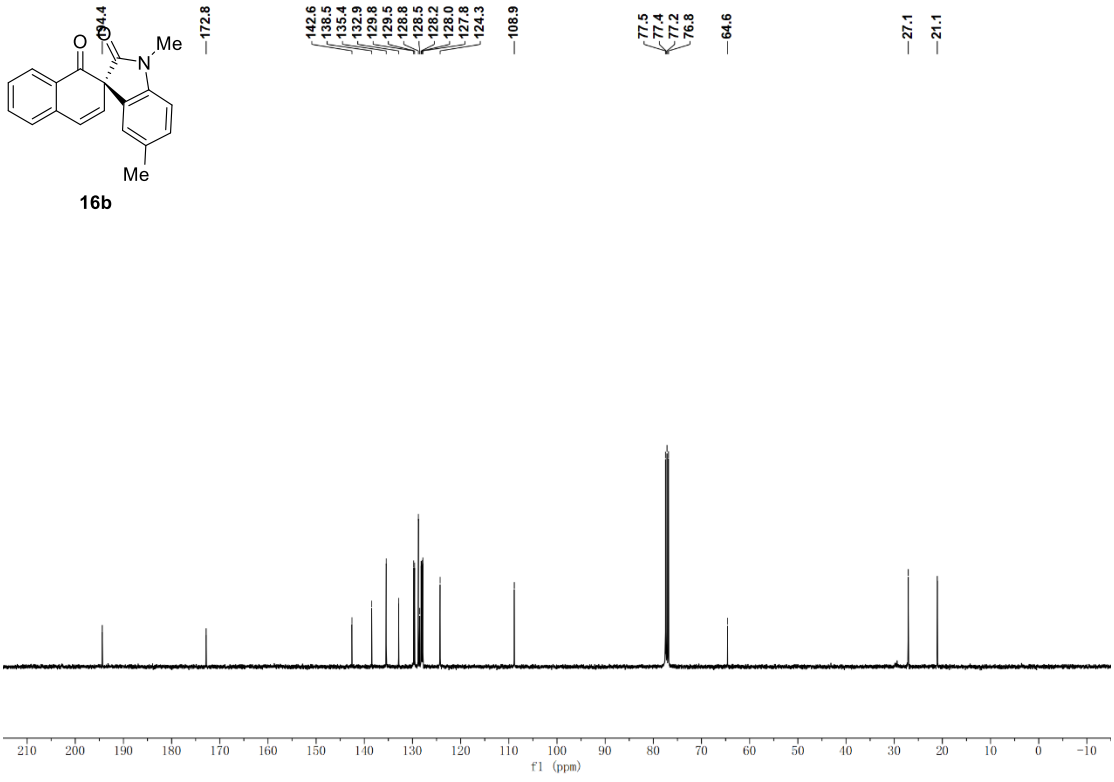
Supplementary Figure 155. ^{1}H NMR Spectrum of **16a** (**400** MHz, $CDCl_3$)



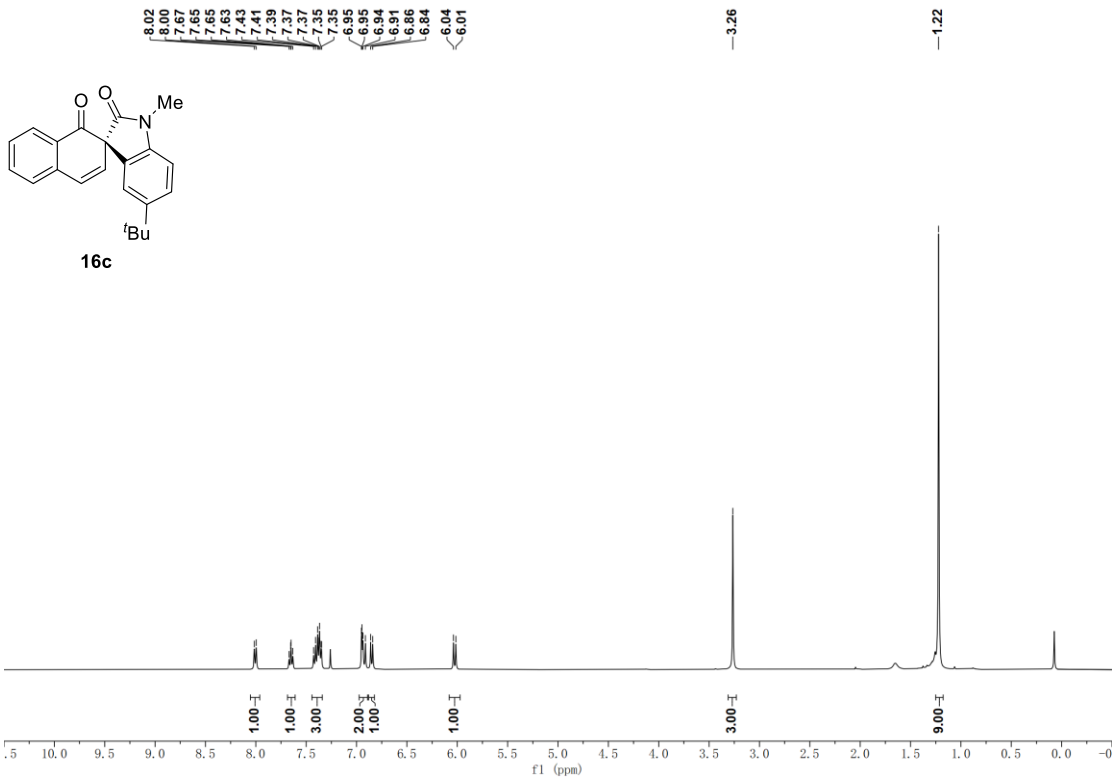
Supplementary Figure 156. ^{13}C NMR Spectrum of **16a** (**100** MHz, $CDCl_3$)



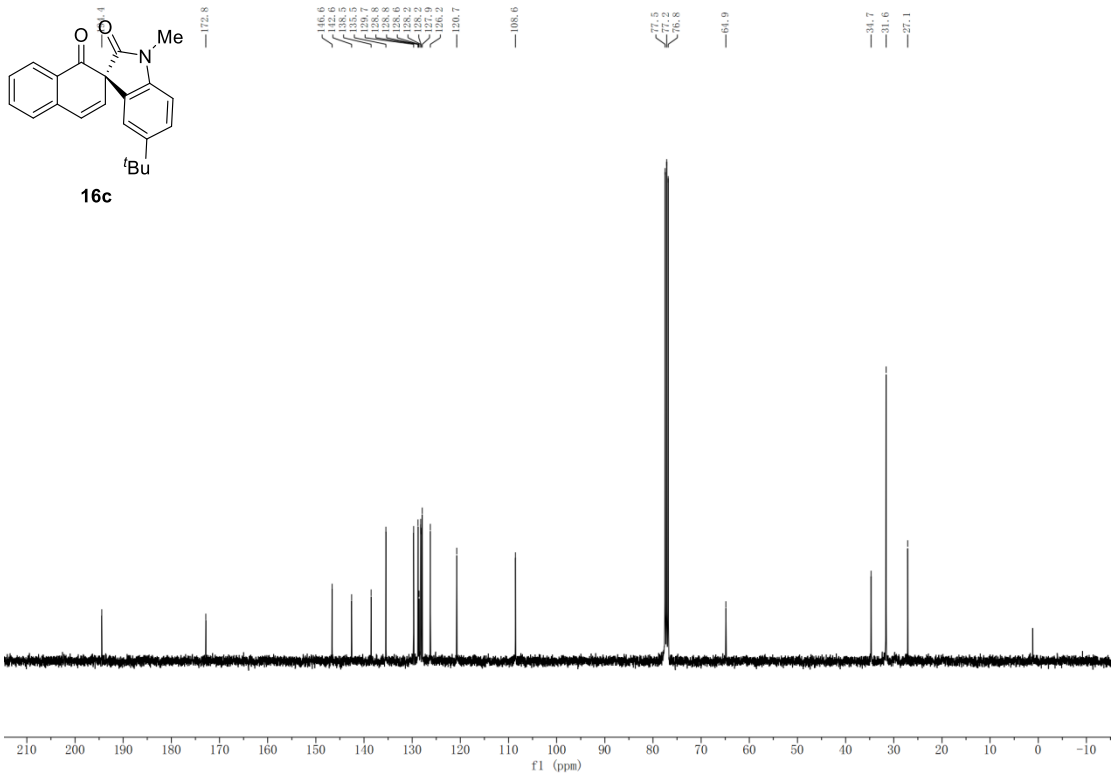
Supplementary Figure 157. ^{1}H NMR Spectrum of **16b** (**400** MHz, $CDCl_3$)



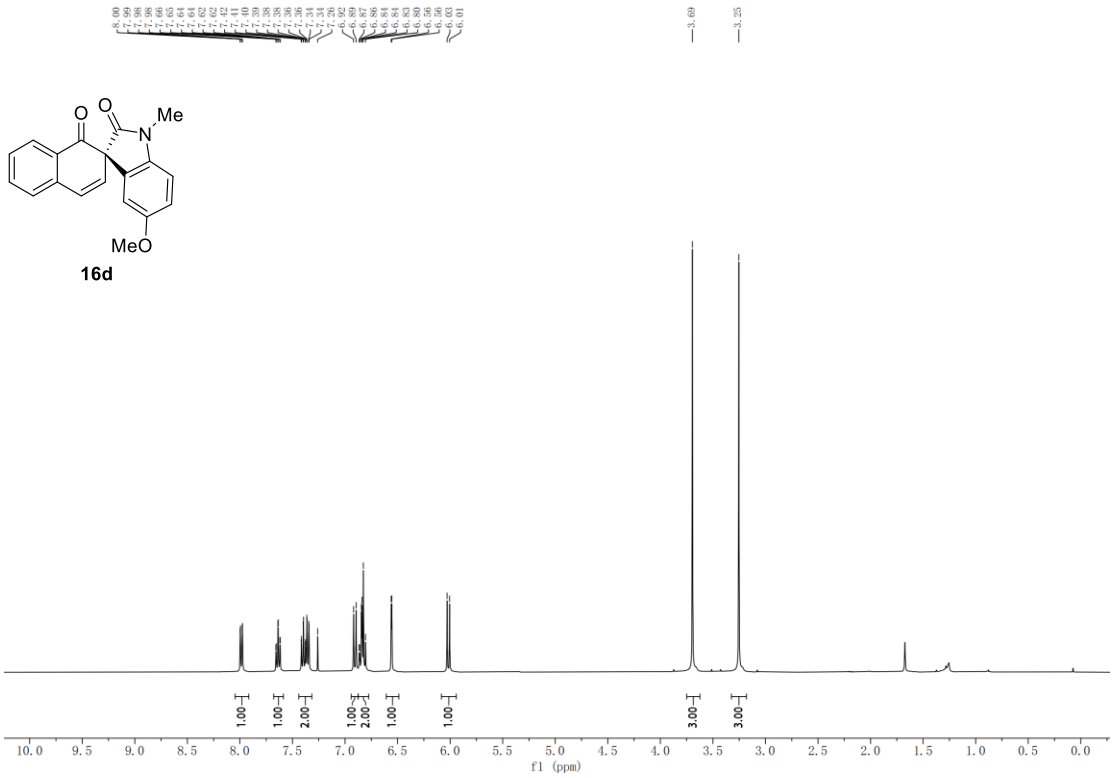
Supplementary Figure 158. ^{13}C NMR Spectrum of **16b** (**100** MHz, $CDCl_3$)



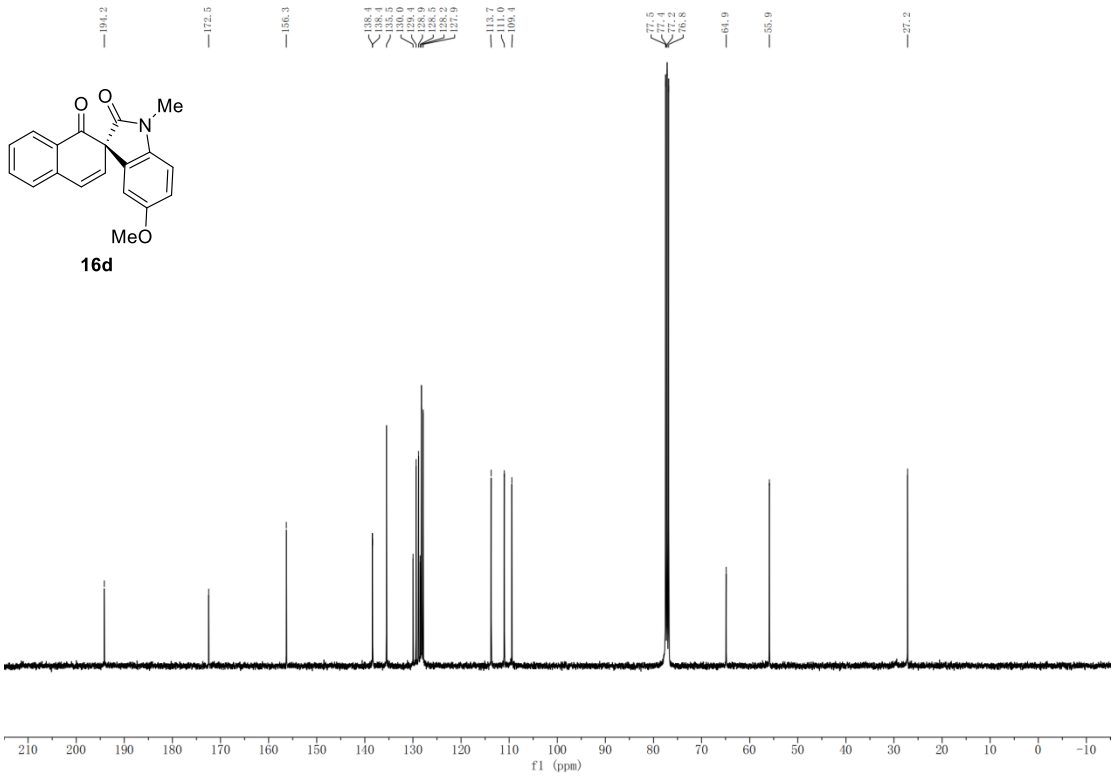
Supplementary Figure 159. ^{1}H NMR Spectrum of **16c** (**400** MHz, $CDCl_3$)



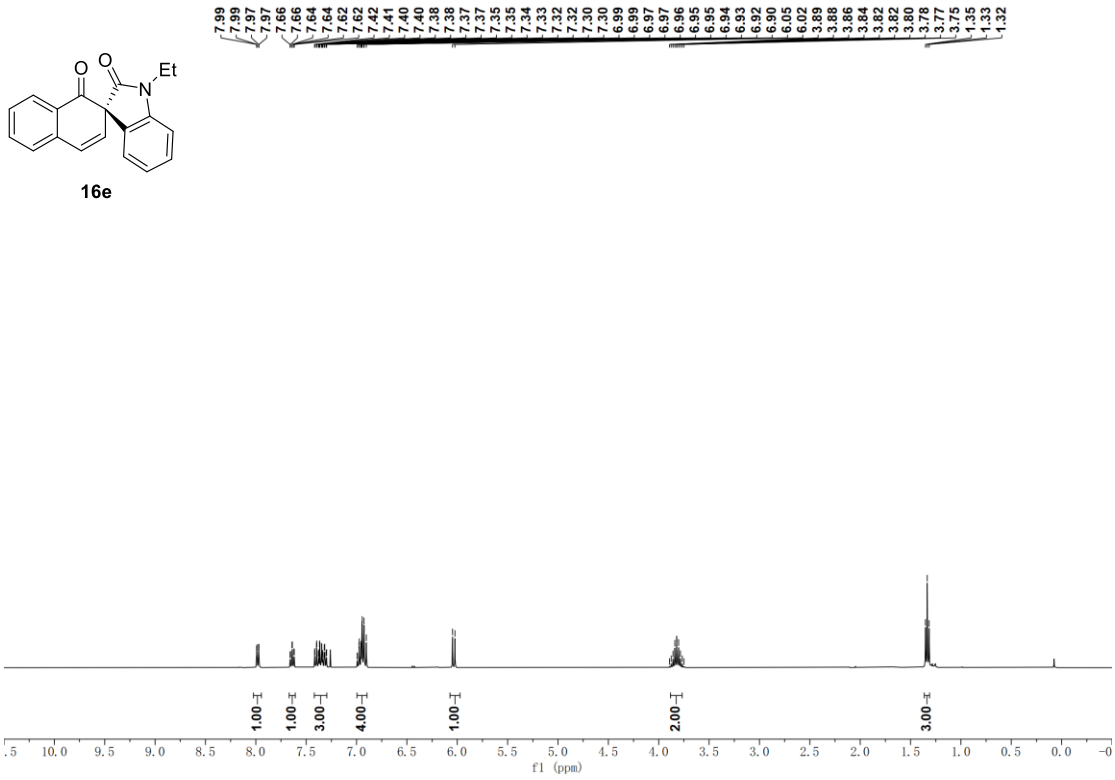
Supplementary Figure 160. ^{13}C NMR Spectrum of **16c** (**100** MHz, $CDCl_3$)



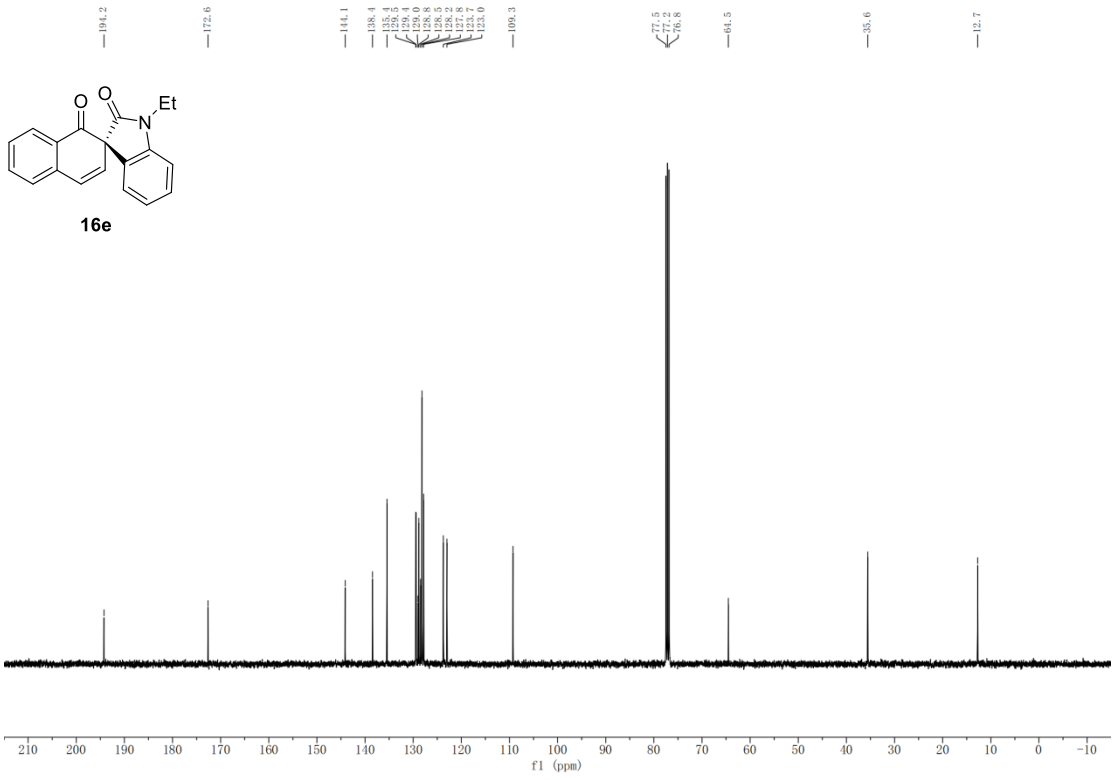
Supplementary Figure 161. ^{1}H NMR Spectrum of **16d** (**400** MHz, $CDCl_3$)



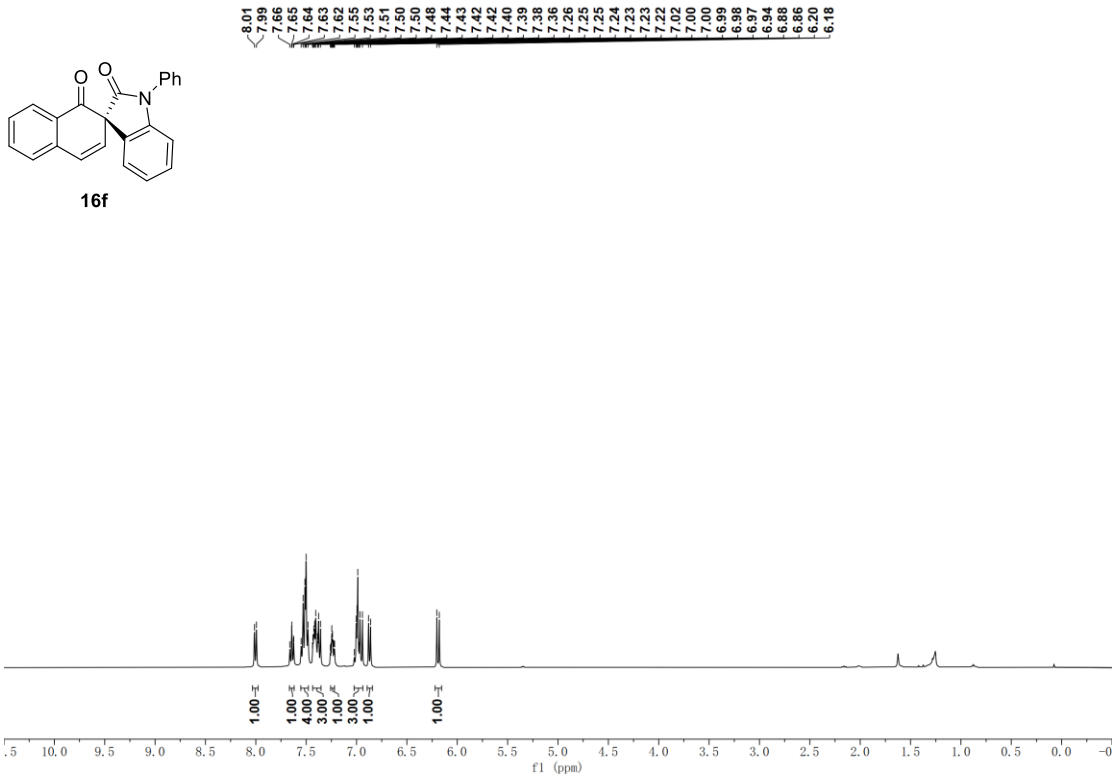
Supplementary Figure 162. ^{13}C NMR Spectrum of **16d** (**100** MHz, $CDCl_3$)



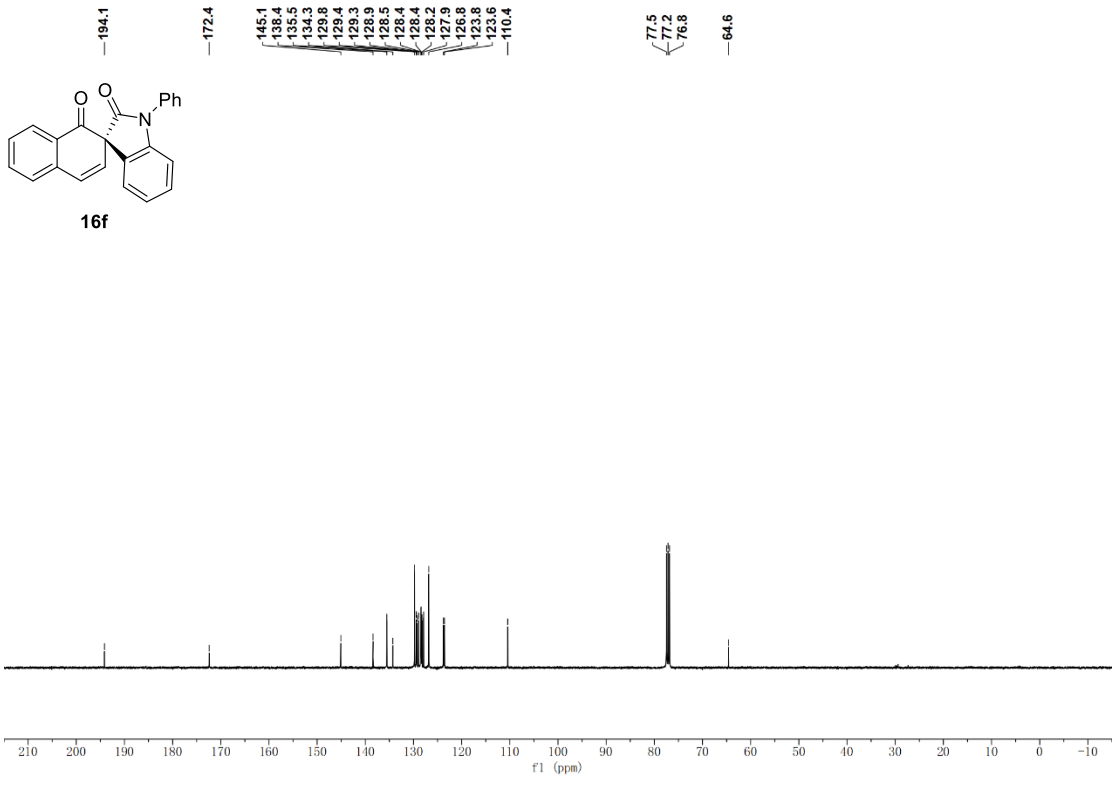
Supplementary Figure 163. ^{1}H NMR Spectrum of **16e** (**400** MHz, $CDCl_3$)



Supplementary Figure 164. ^{13}C NMR Spectrum of **16e** (**100** MHz, $CDCl_3$)

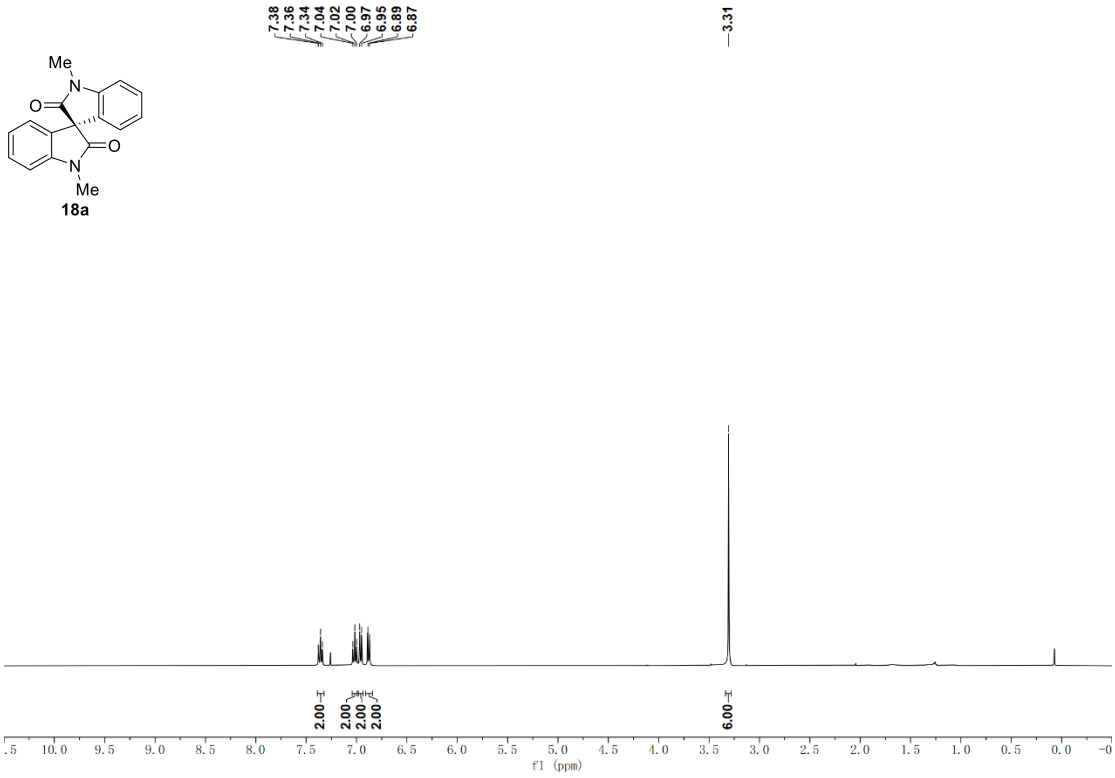


Supplementary Figure 165. ^{1}H NMR Spectrum of **16f** (**400** MHz, $CDCl_3$)

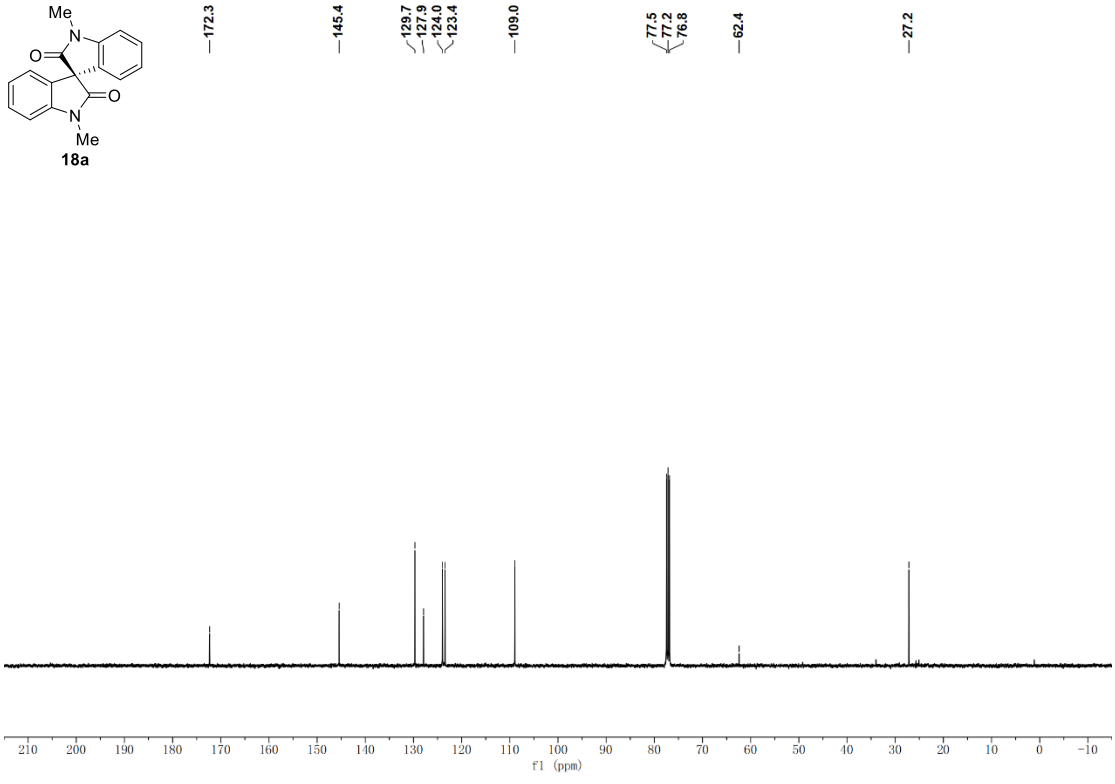


Supplementary Figure 166. ^{13}C NMR Spectrum of **16f** (**100** MHz, $CDCl_3$)

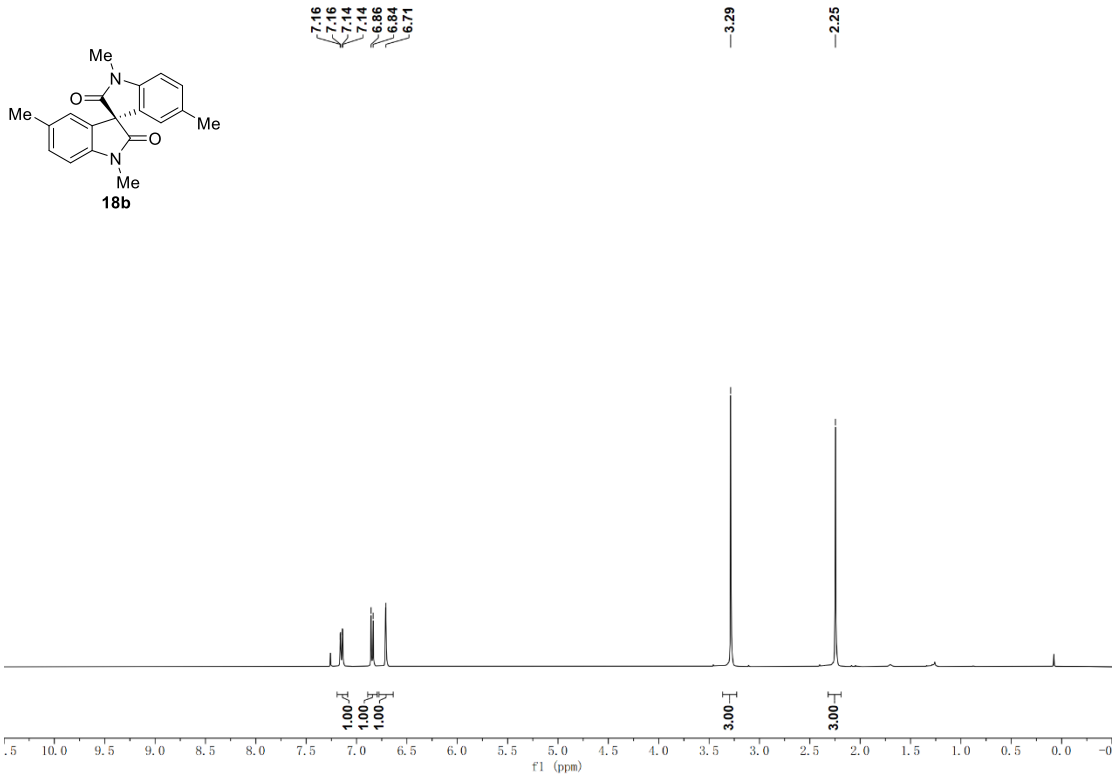
11.2.3 Spectrum of direct C(sp^2)-H/C(sp^3)-H cross-coupling



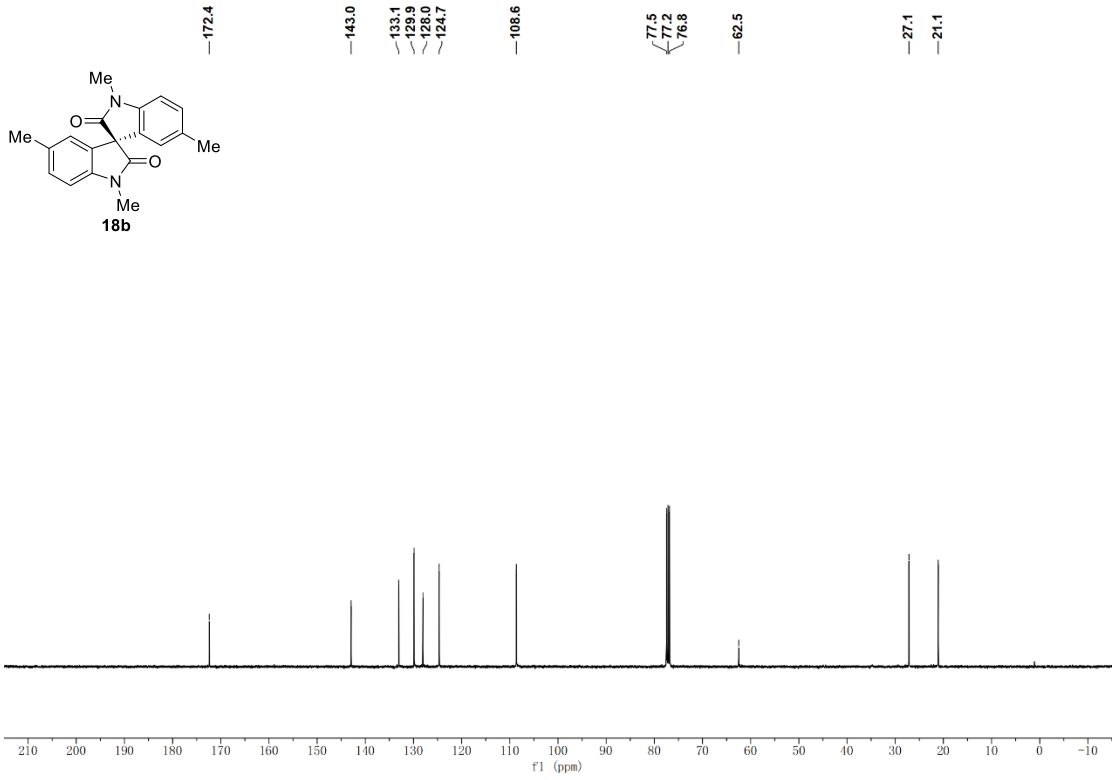
Supplementary Figure 167. ^{1}H NMR Spectrum of **18a** (**400** MHz, $CDCl_3$)



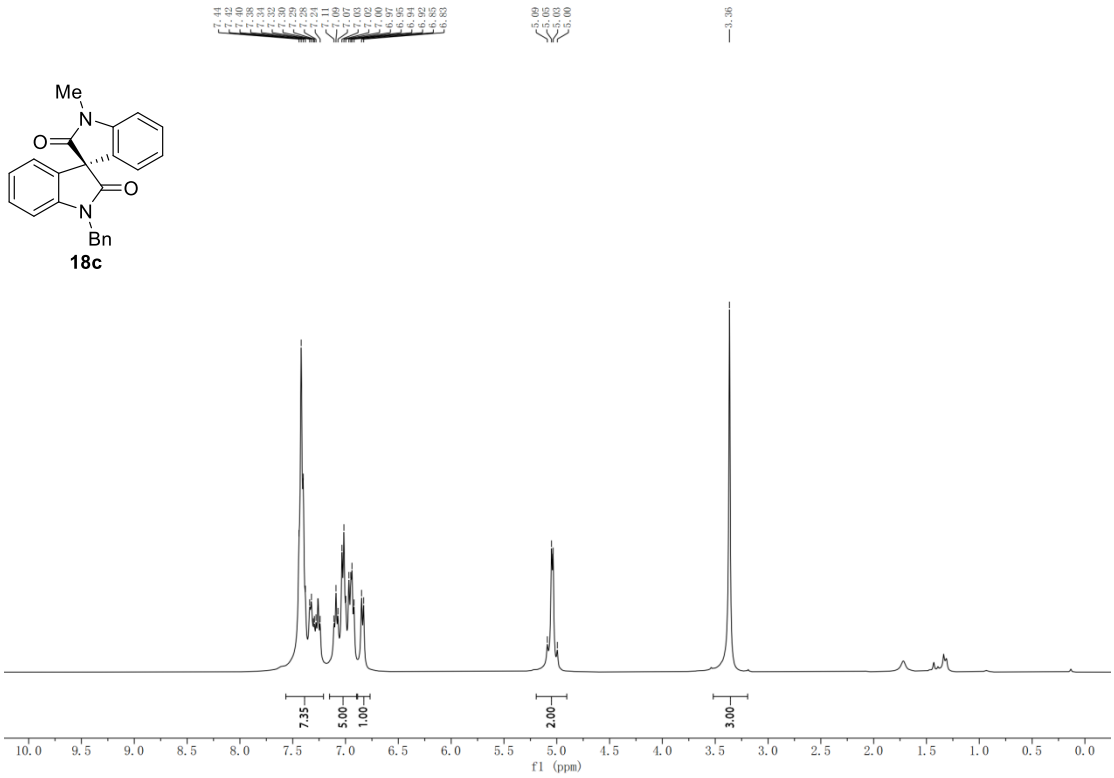
Supplementary Figure 168. ^{13}C NMR Spectrum of **18a** (**100** MHz, $CDCl_3$)



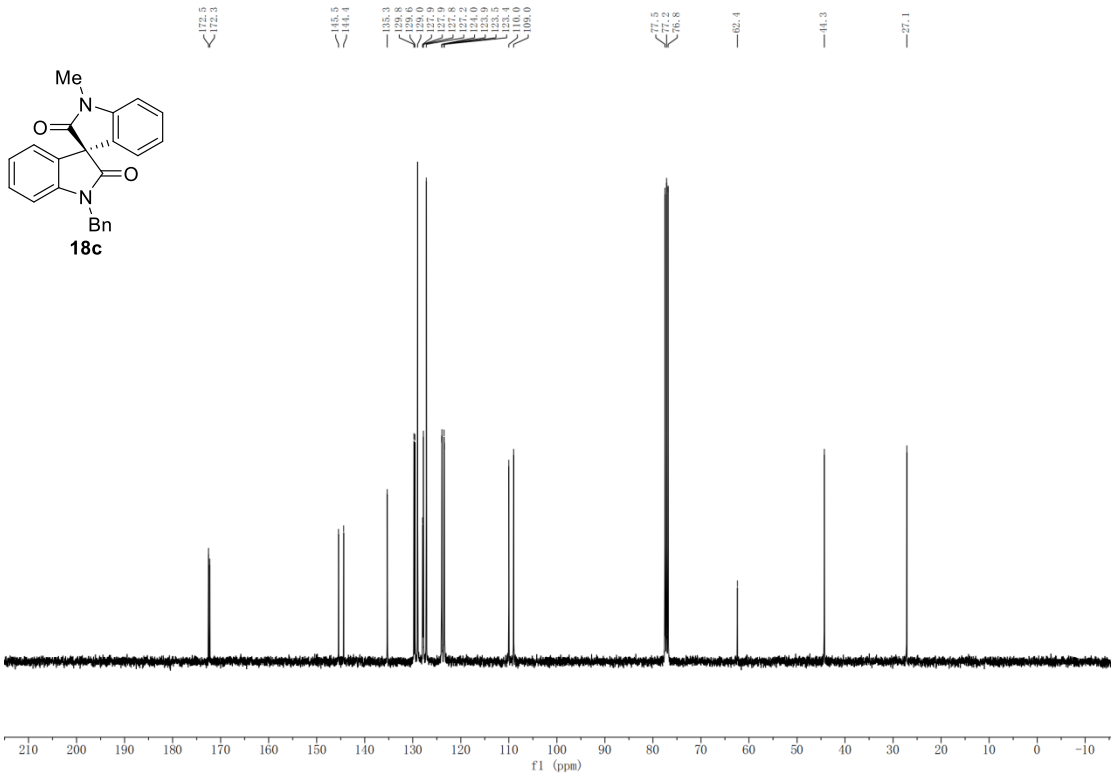
Supplementary Figure 169. ^{1}H NMR Spectrum of **18b** (**400** MHz, $CDCl_3$)



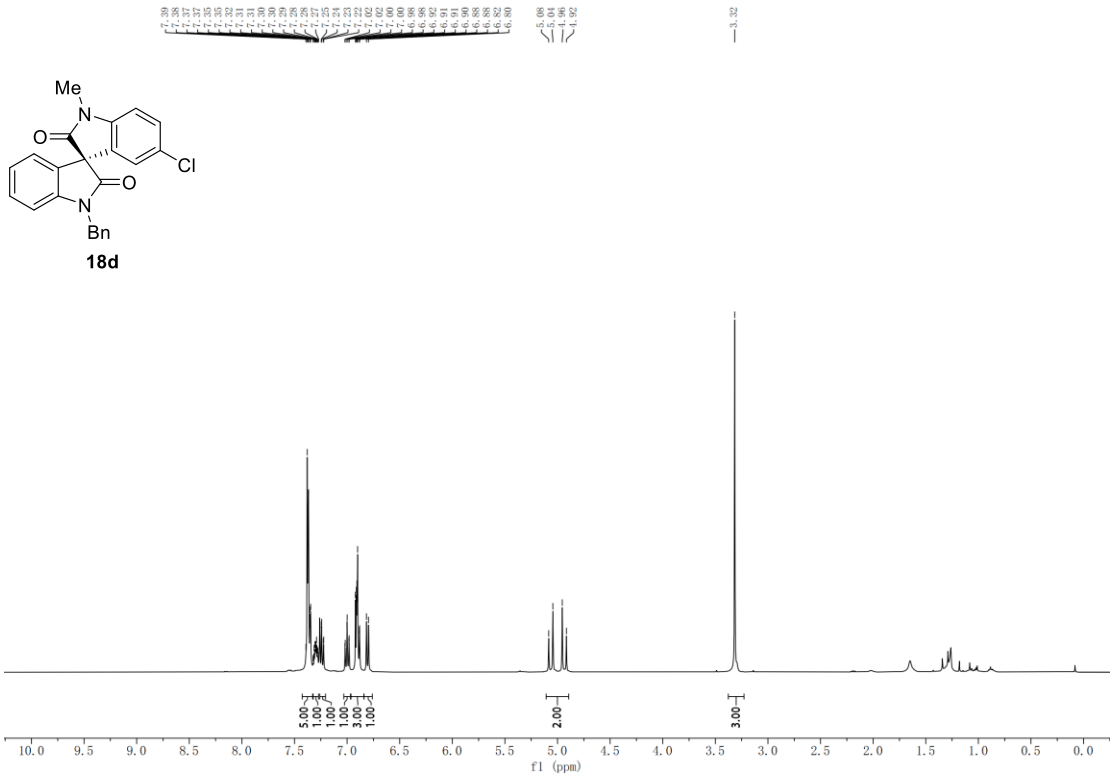
Supplementary Figure 170. ^{13}C NMR Spectrum of **18b** (**100** MHz, $CDCl_3$)



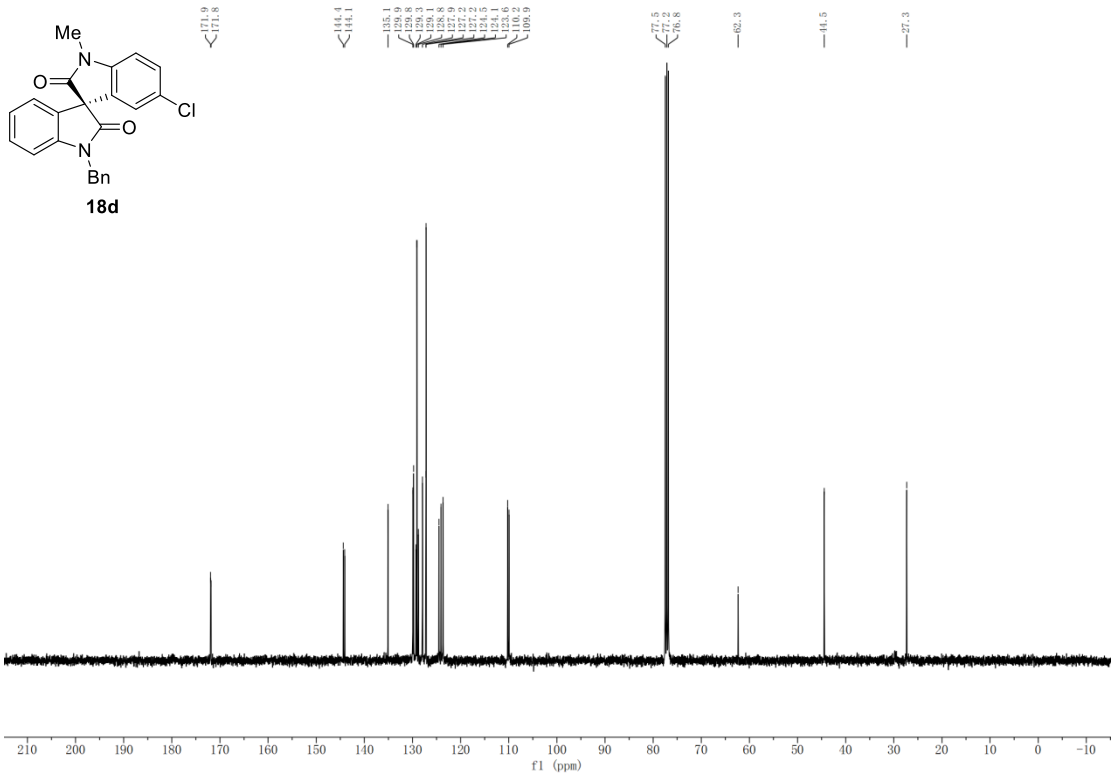
Supplementary Figure 171. ^{1}H NMR Spectrum of **18c** (**400** MHz, $CDCl_3$)



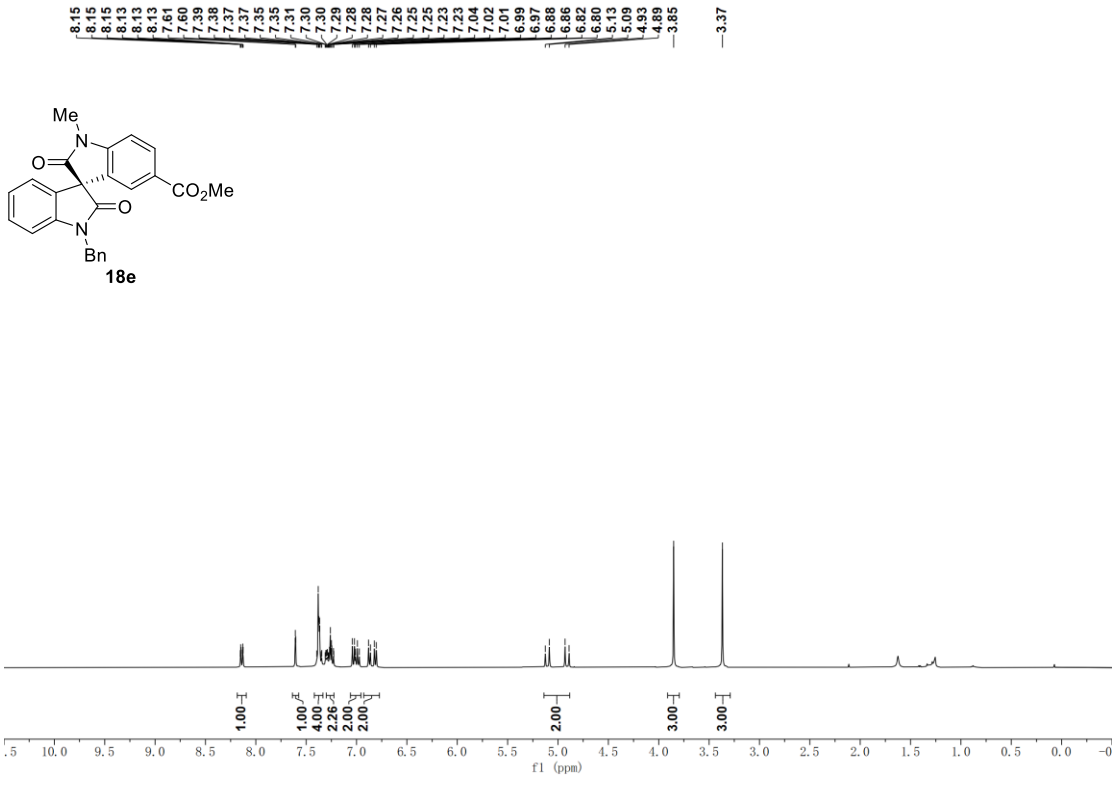
Supplementary Figure 172. ^{13}C NMR Spectrum of **18c** (**100** MHz, $CDCl_3$)



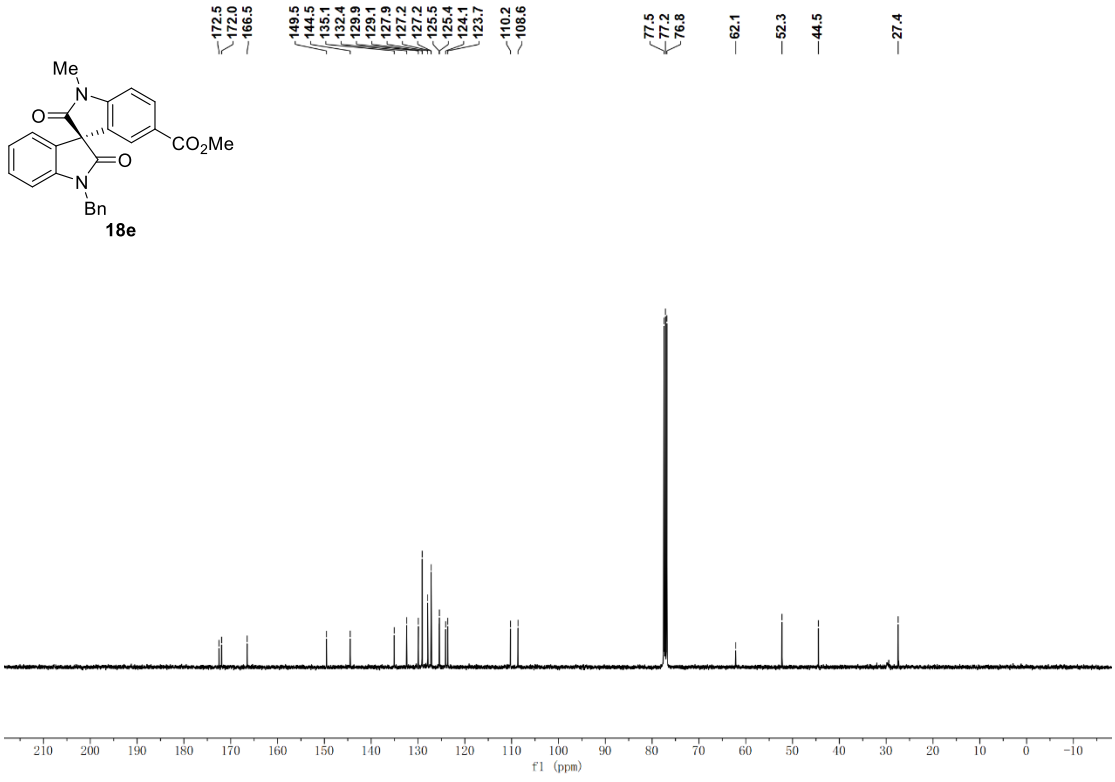
Supplementary Figure 173. ^{1}H NMR Spectrum of **18d** (**400** MHz, $CDCl_3$)



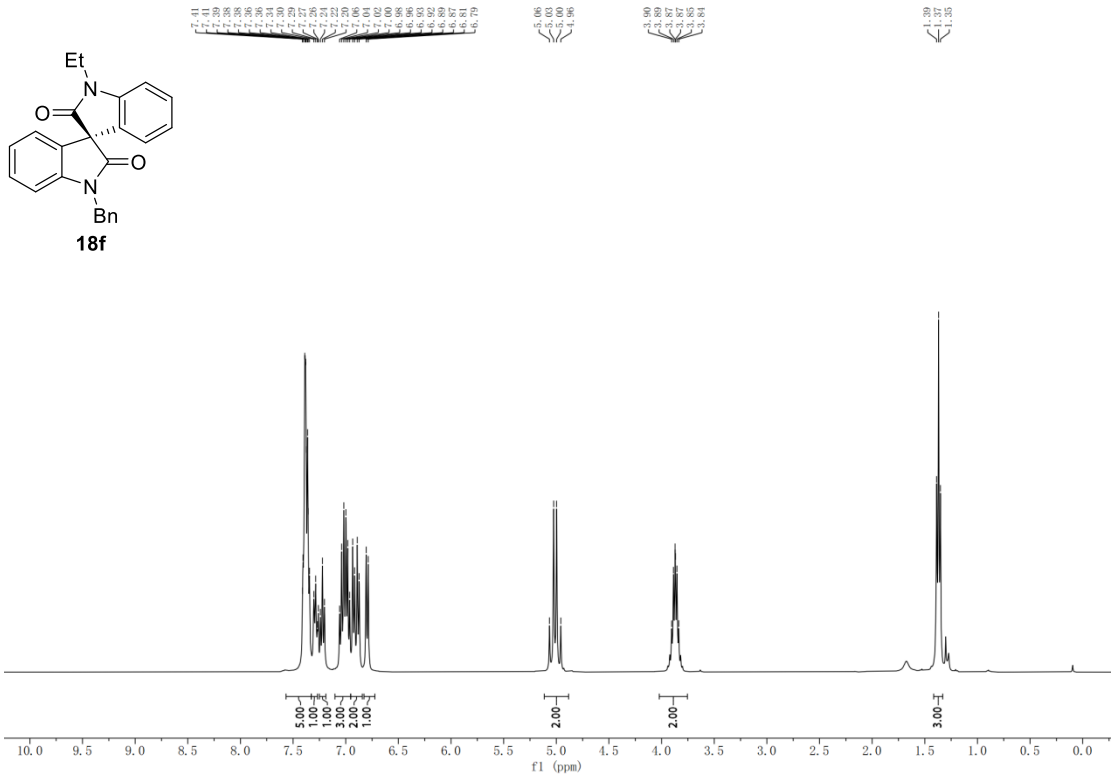
Supplementary Figure 174. ^{13}C NMR Spectrum of **18d** (**100** MHz, $CDCl_3$)



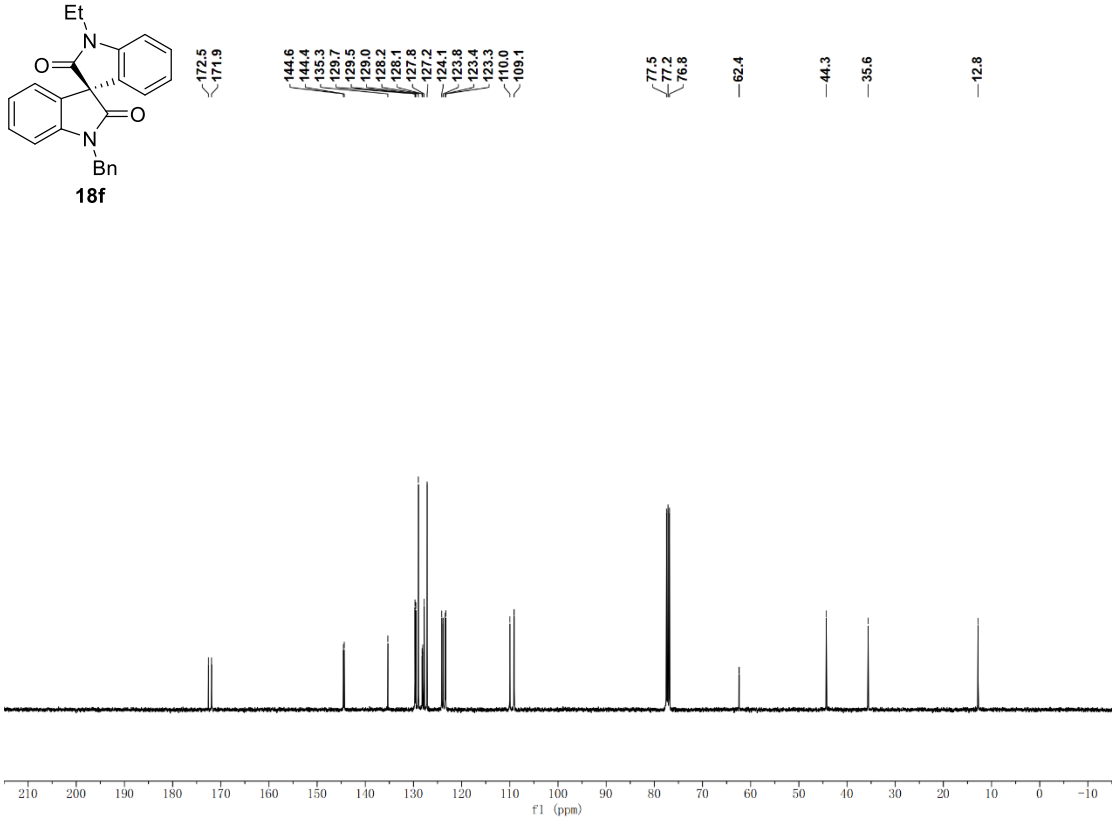
Supplementary Figure 175. ^{1}H NMR Spectrum of **18e** (**400** MHz, $CDCl_3$)



Supplementary Figure 176. ^{13}C NMR Spectrum of **18e** (**100** MHz, $CDCl_3$)

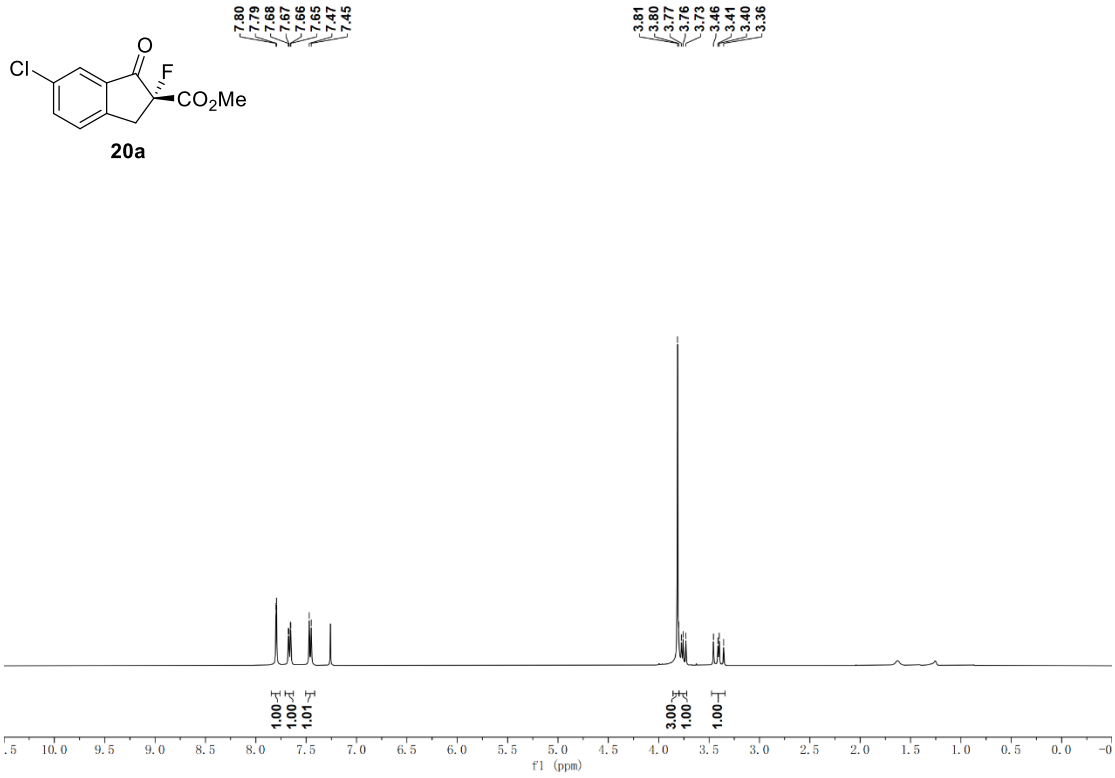


Supplementary Figure 177. ^{1}H NMR Spectrum of **18f** (**400** MHz, $CDCl_3$)

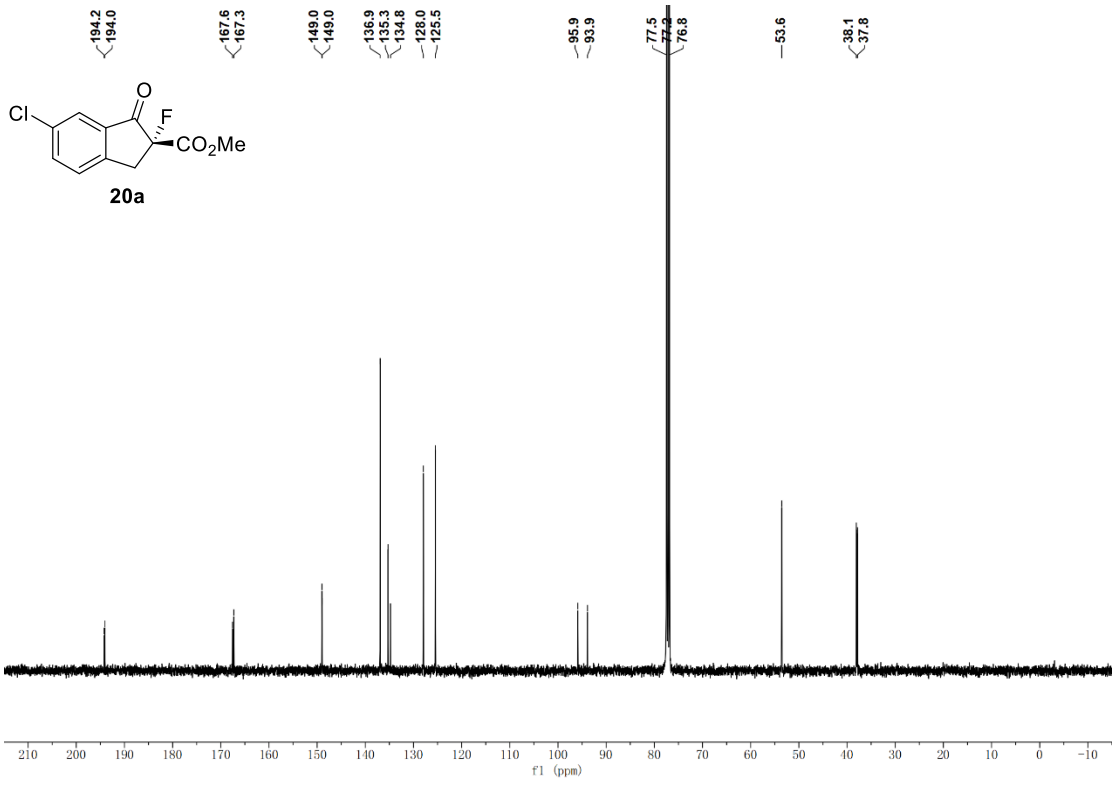


Supplementary Figure 178. ^{13}C NMR Spectrum of **18f** (**100** MHz, $CDCl_3$)

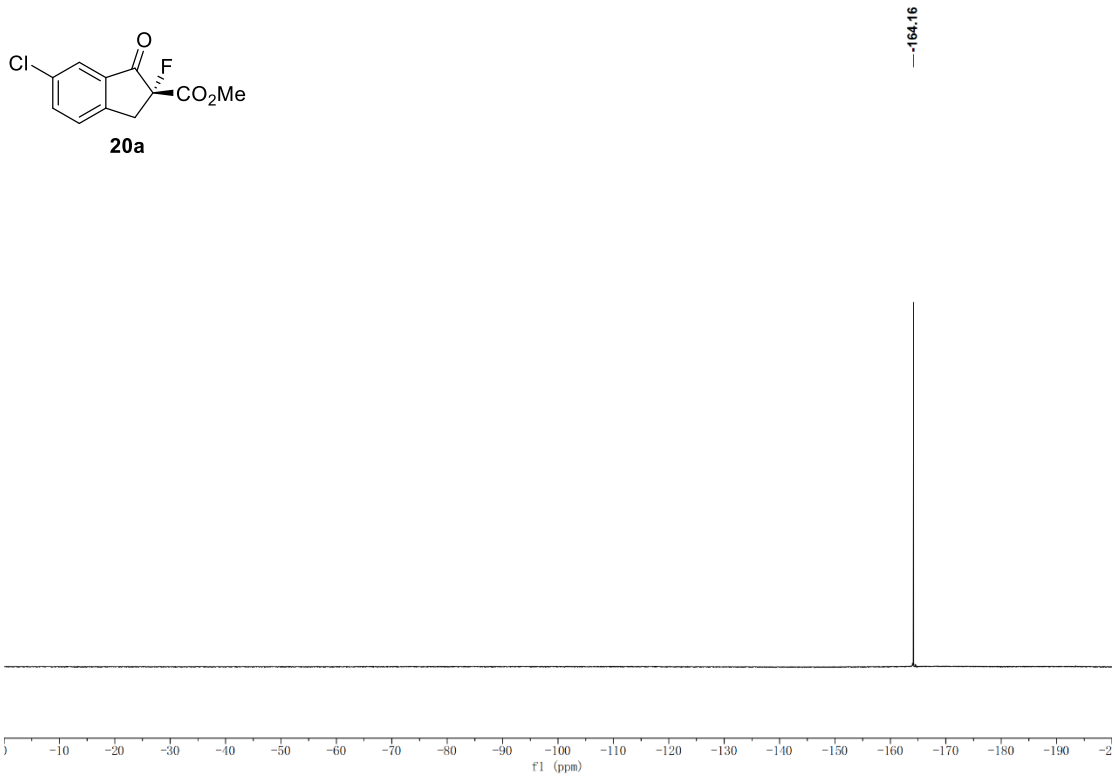
11.2.4 Spectrum of oxidative fluorination of keto esters



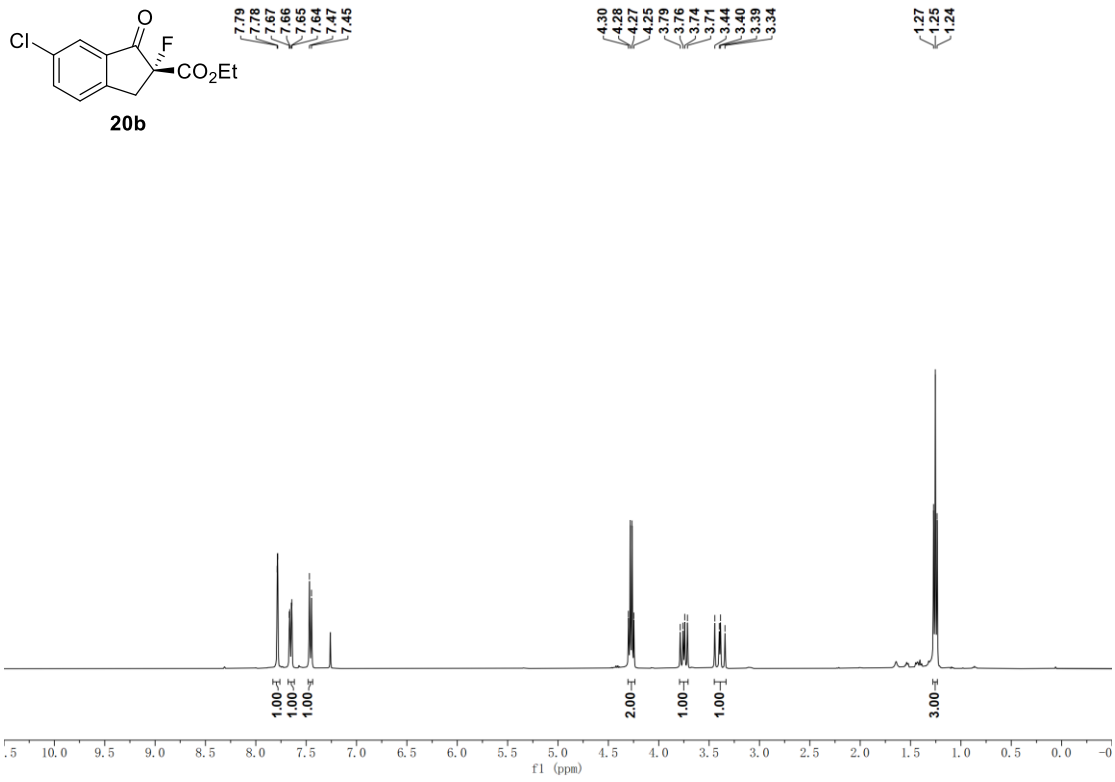
Supplementary Figure 179. ^{1}H NMR Spectrum of **20a** (400 MHz, $CDCl_3$)



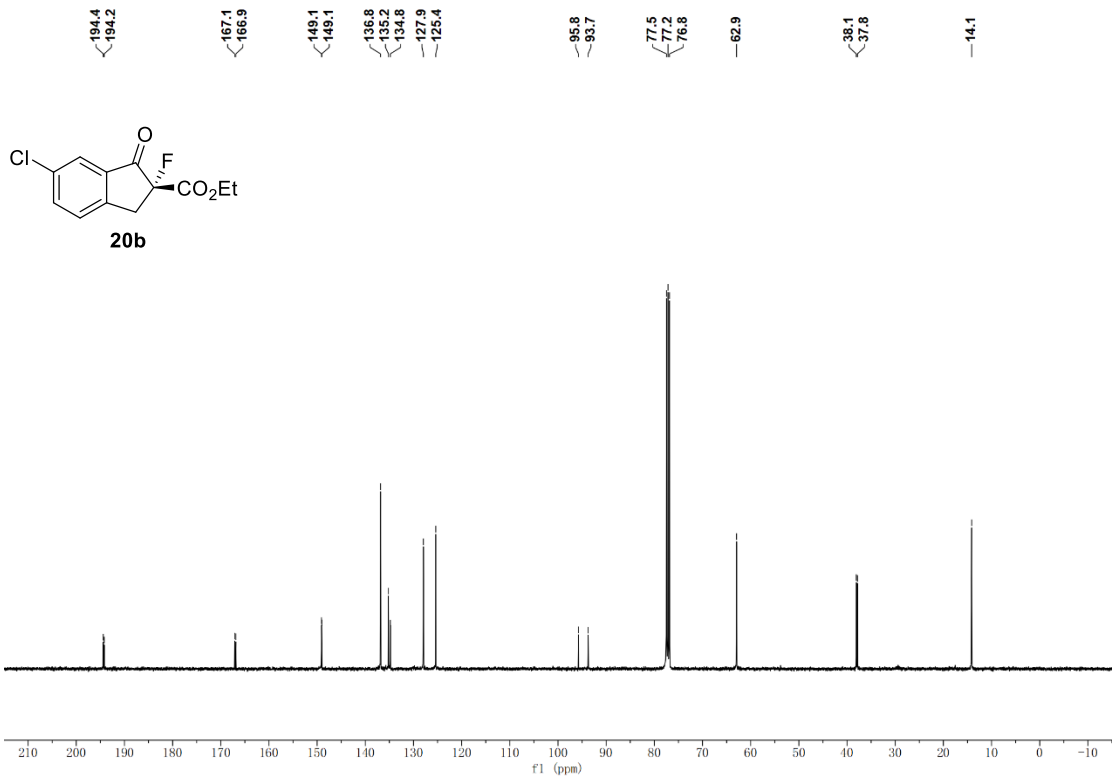
Supplementary Figure 180. ^{13}C NMR Spectrum of **20a** (100 MHz, $CDCl_3$)



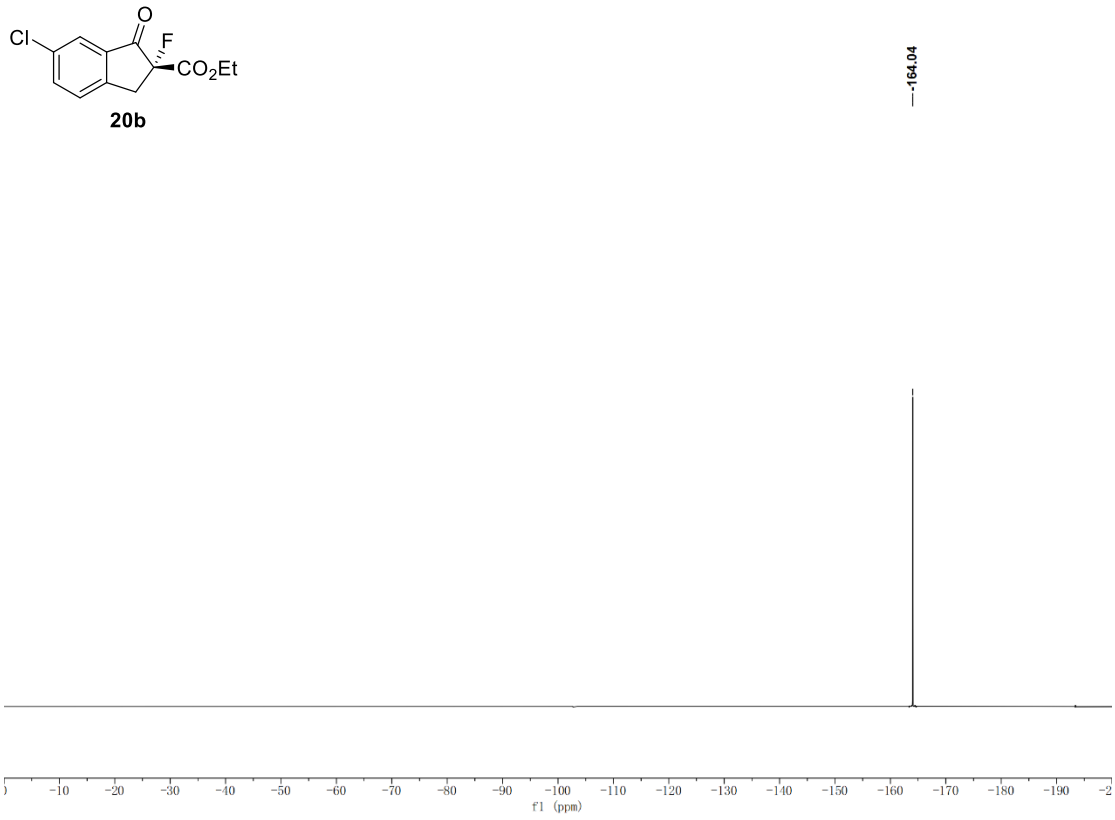
Supplementary Figure 181. ^{19}F NMR Spectrum of **20a** (376 MHz, $CDCl_3$)



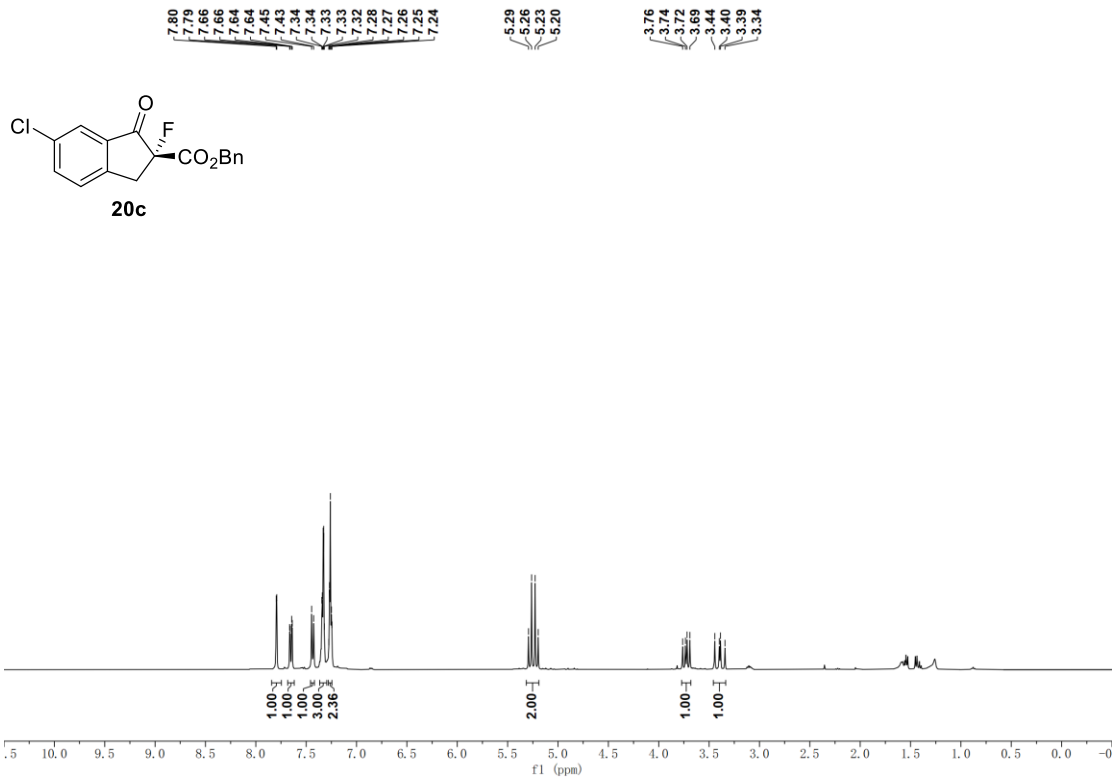
Supplementary Figure 182. ^{1}H NMR Spectrum of **20b** (400 MHz, $CDCl_3$)



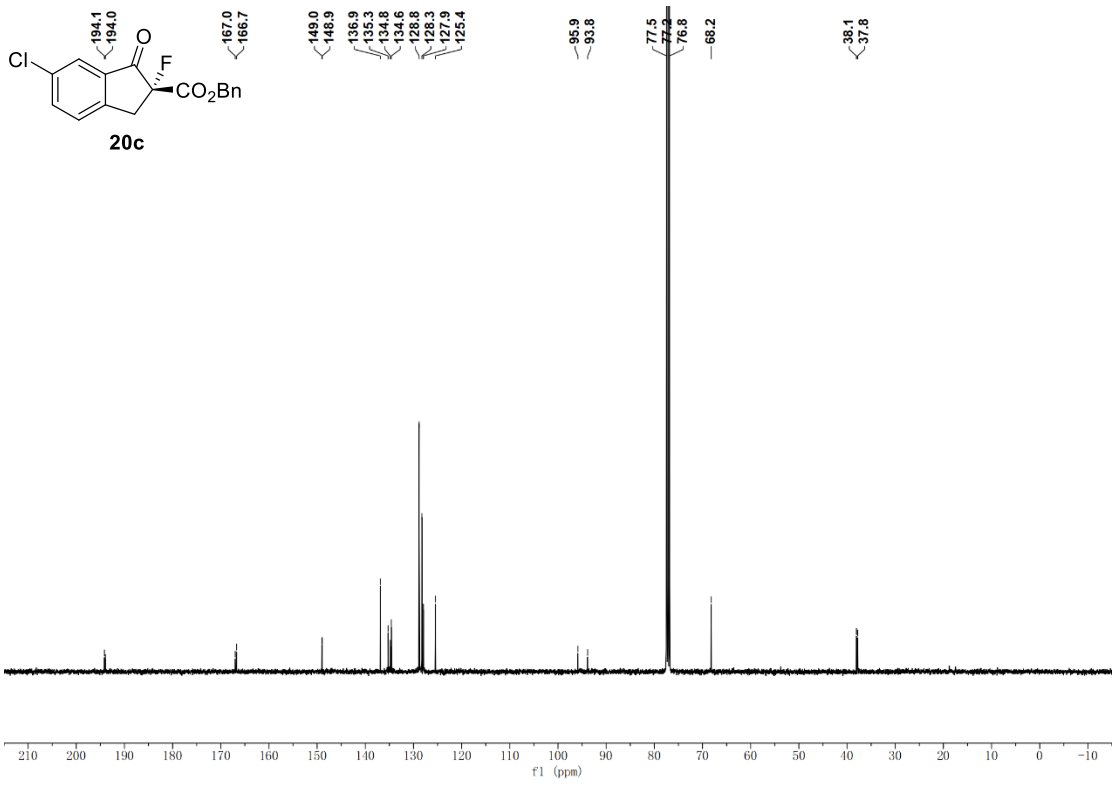
Supplementary Figure 183. ^{13}C NMR Spectrum of **20b** (100 MHz, $CDCl_3$)



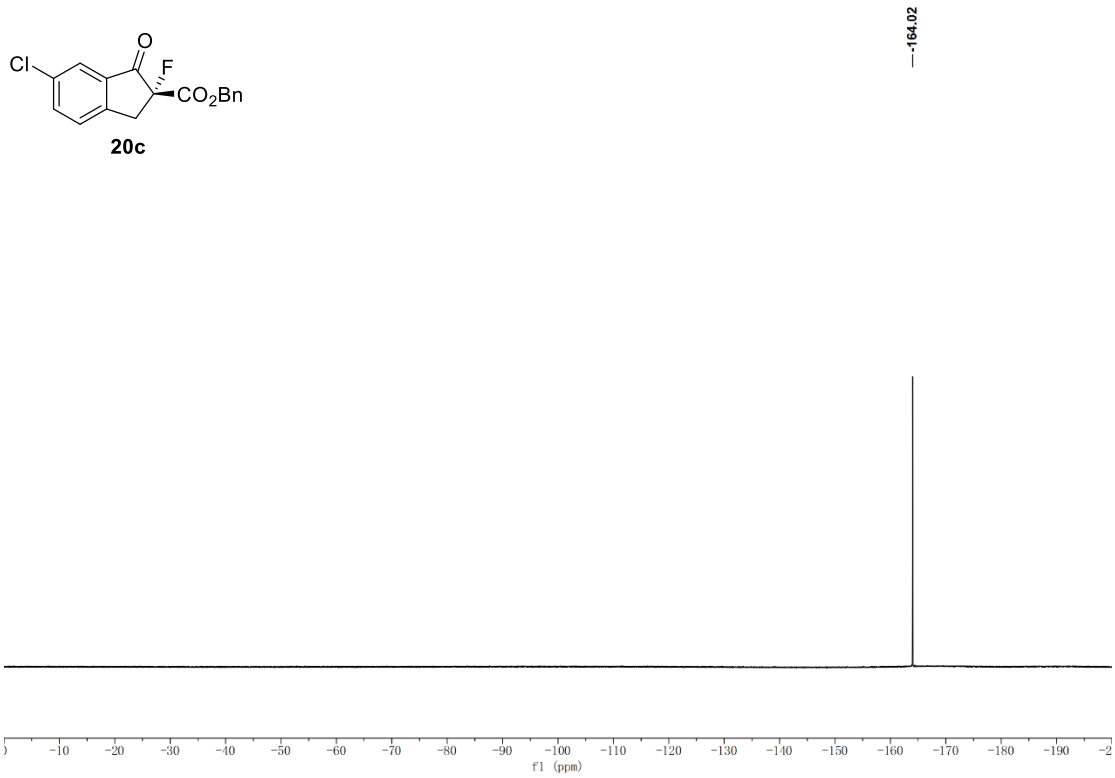
Supplementary Figure 184. ^{19}F NMR Spectrum of **20b** (376 MHz, $CDCl_3$)



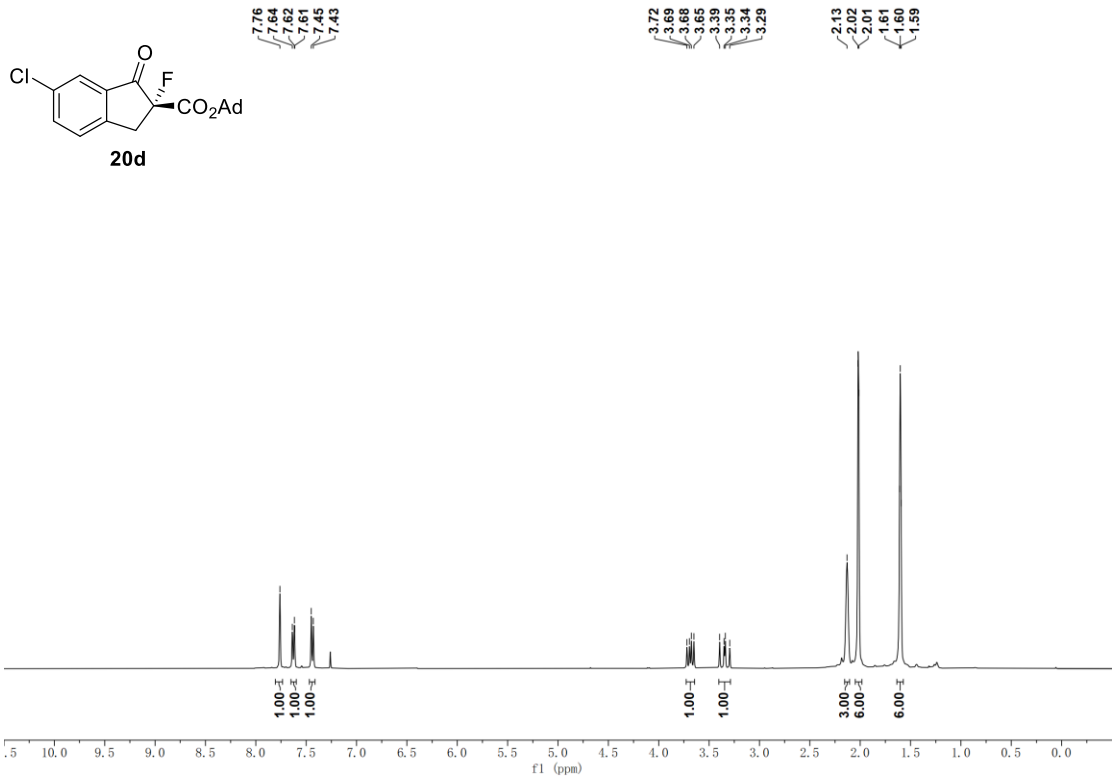
Supplementary Figure 185. ^{1}H NMR Spectrum of **20c** (400 MHz, $CDCl_3$)



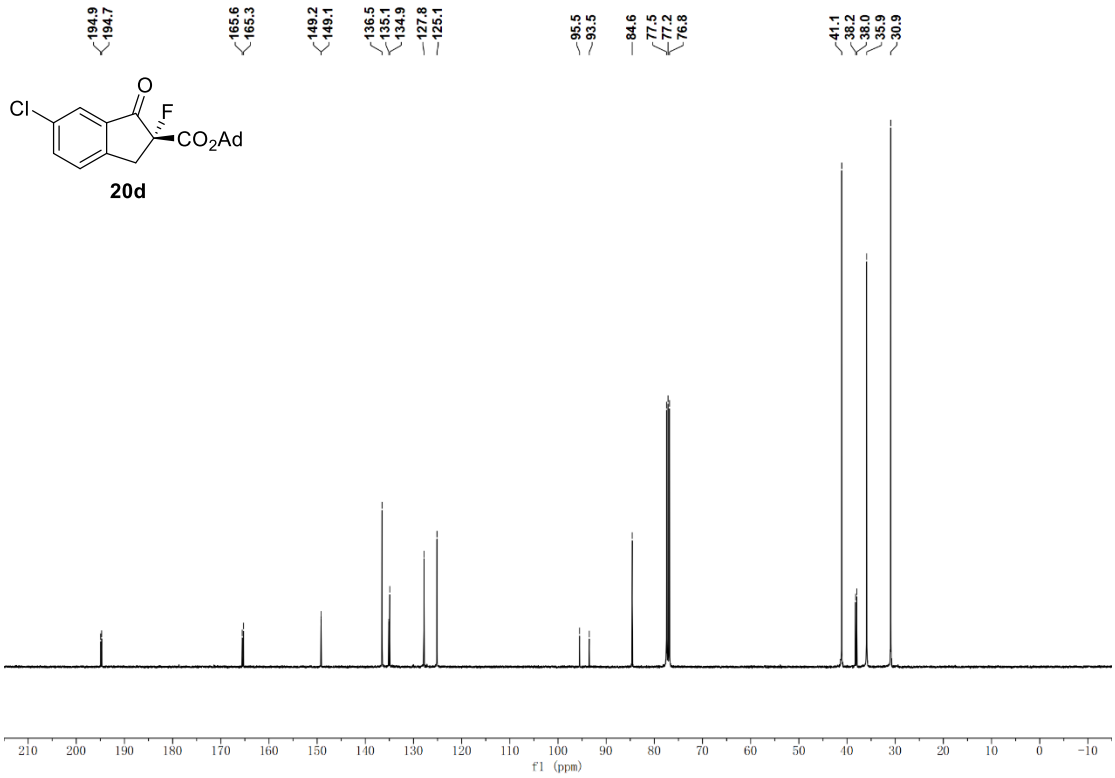
Supplementary Figure 186. ^{13}C NMR Spectrum of **20c** (100 MHz, $CDCl_3$)



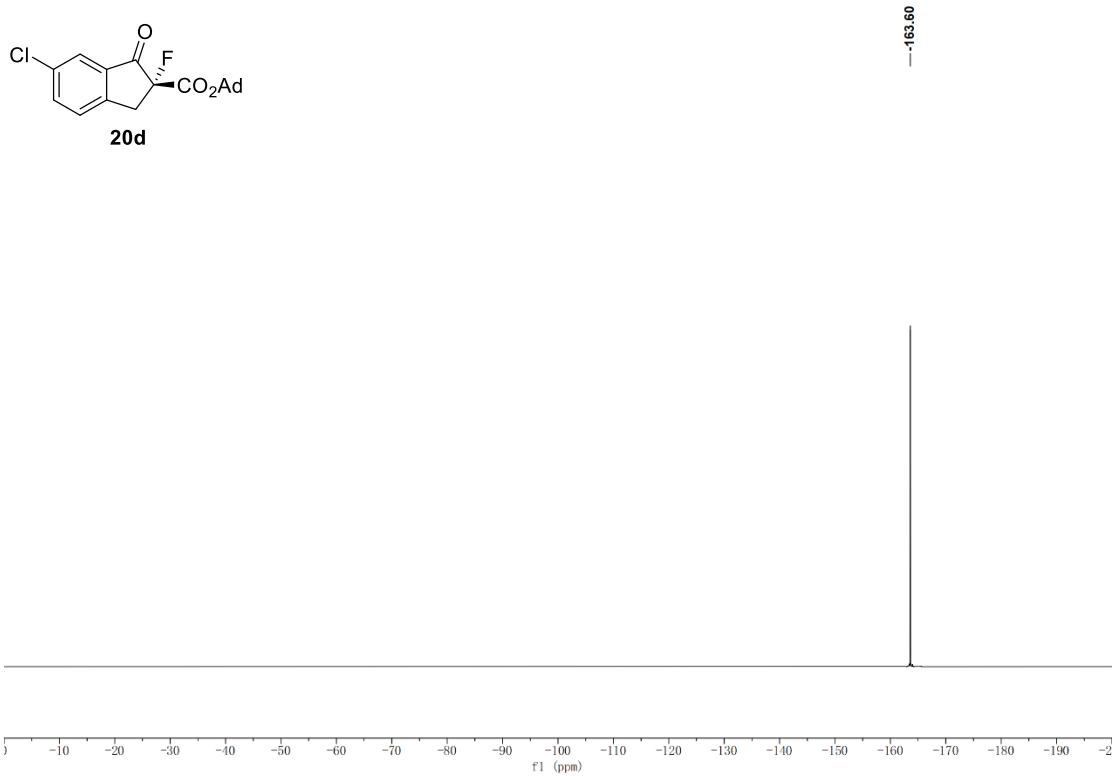
Supplementary Figure 187. ^{19}F NMR Spectrum of **20c** (376 MHz, $CDCl_3$)



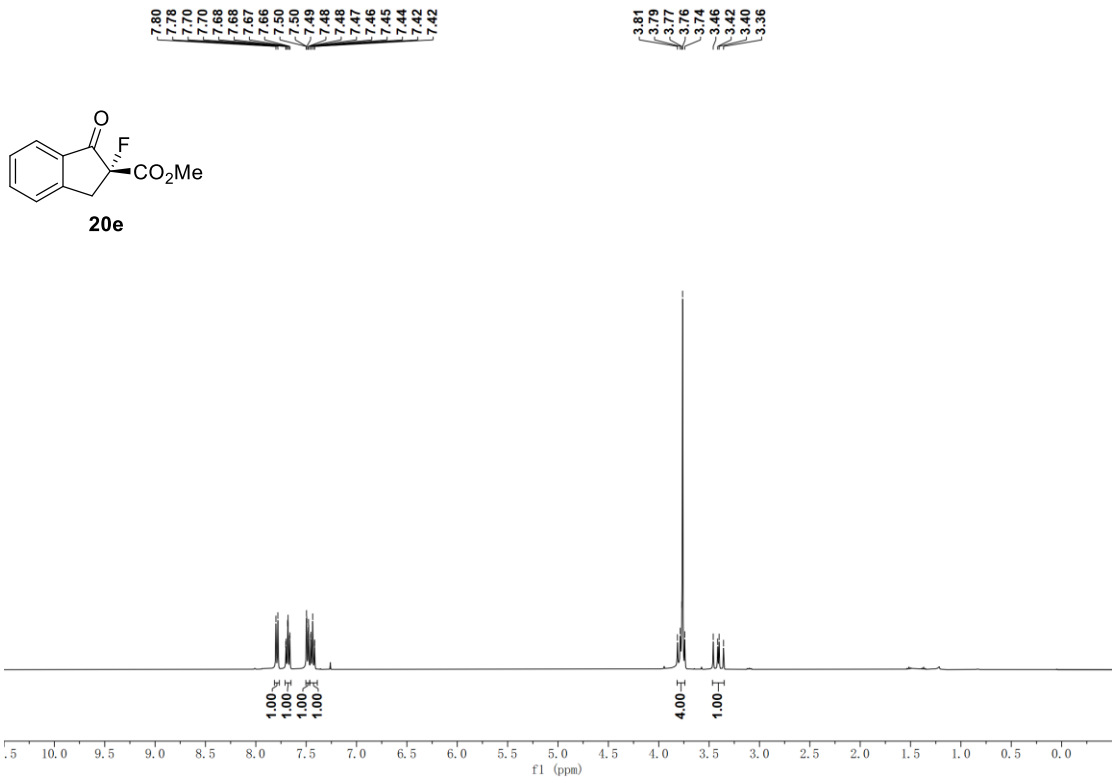
Supplementary Figure 188. ^{1}H NMR Spectrum of **20d** (400 MHz, $CDCl_3$)



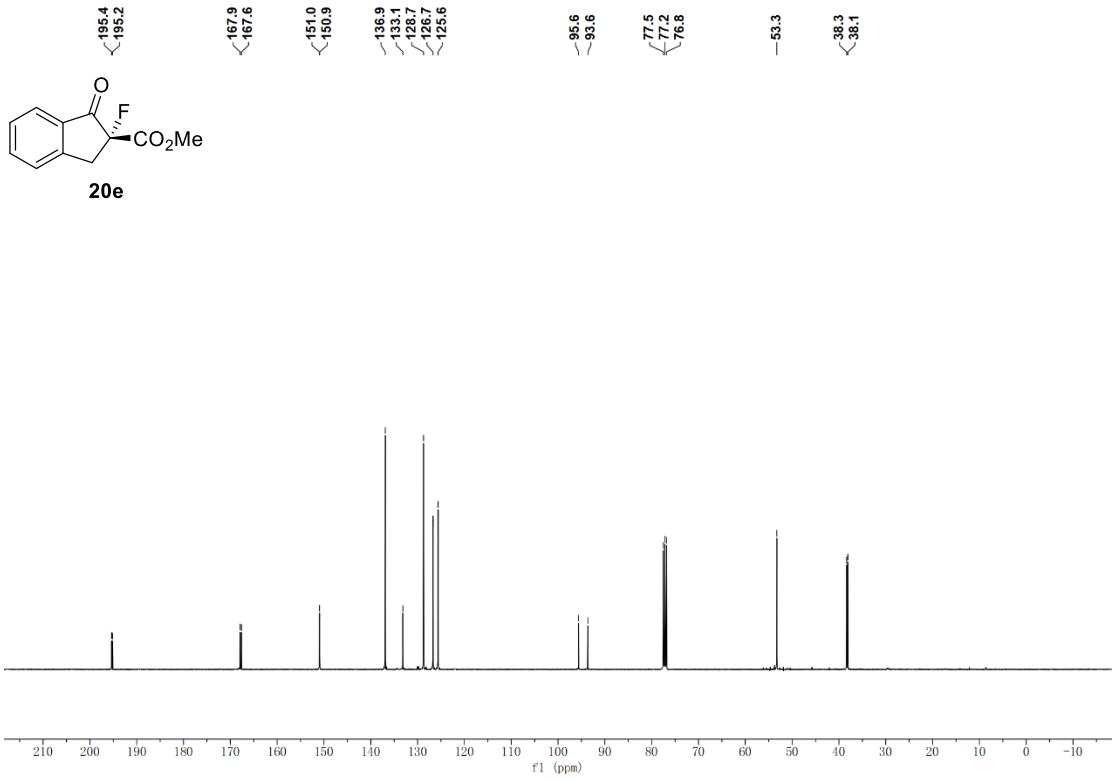
Supplementary Figure 189. ^{13}C NMR Spectrum of **20d** (100 MHz, $CDCl_3$)



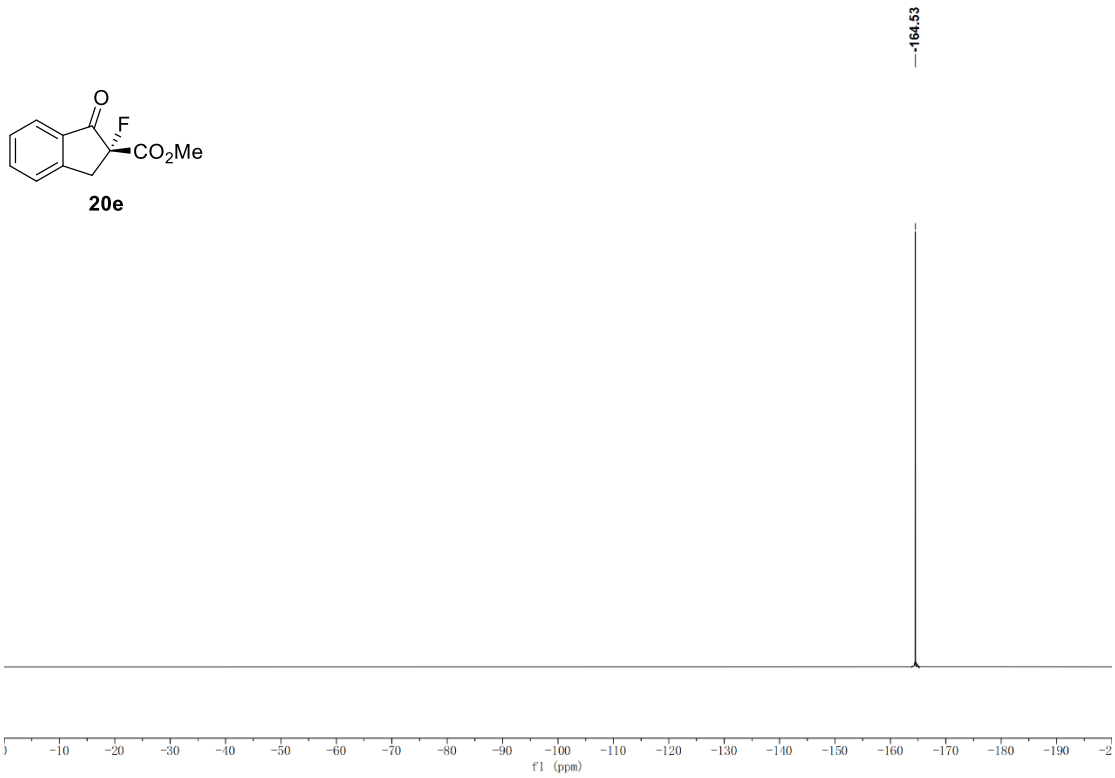
Supplementary Figure 190. ^{19}F NMR Spectrum of **20d** (376 MHz, $CDCl_3$)



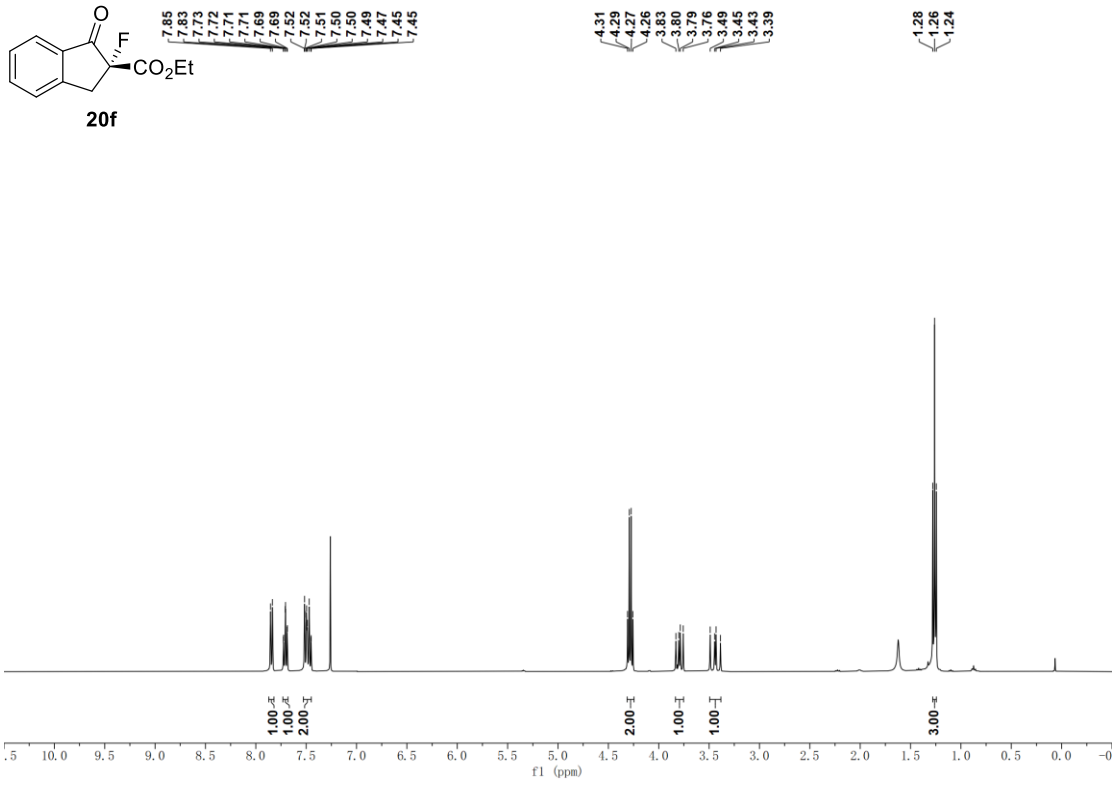
Supplementary Figure 191. ^{1}H NMR Spectrum of **20e** (400 MHz, $CDCl_3$)



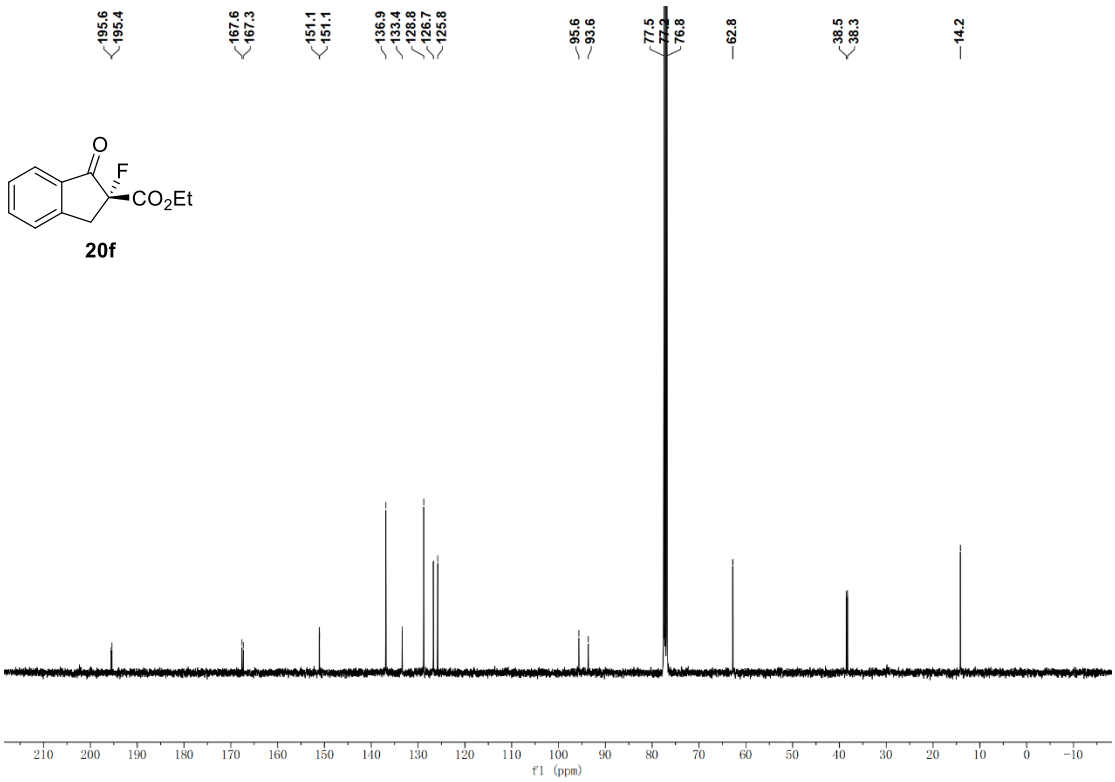
Supplementary Figure 192. ^{13}C NMR Spectrum of **20e** (100 MHz, $CDCl_3$)



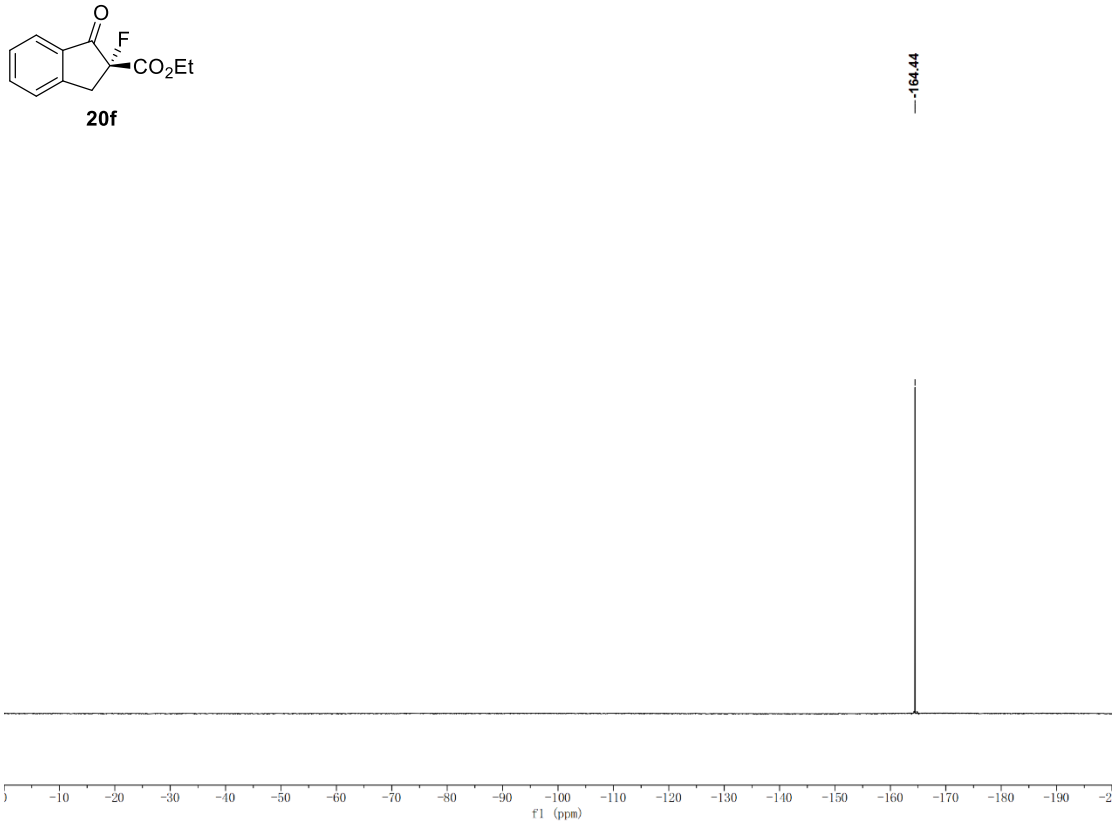
Supplementary Figure 193. ^{19}F NMR Spectrum of **20e** (376 MHz, $CDCl_3$)



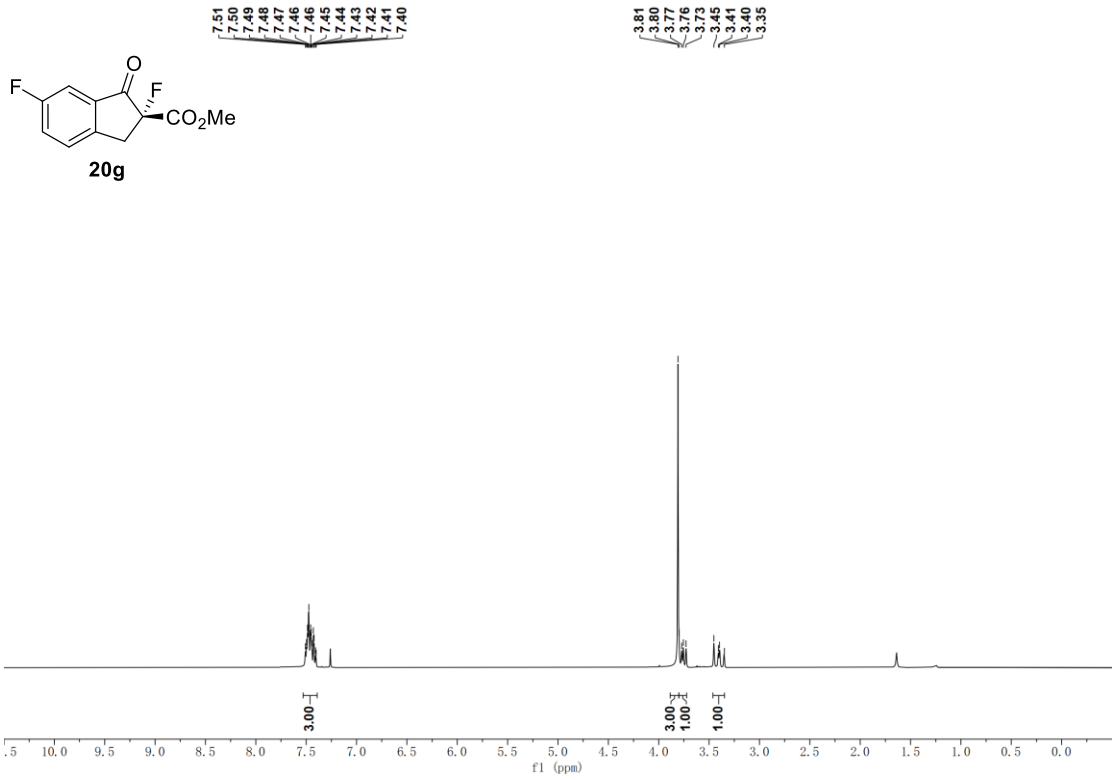
Supplementary Figure 194. ^{1}H NMR Spectrum of **20f** (400 MHz, $CDCl_3$)



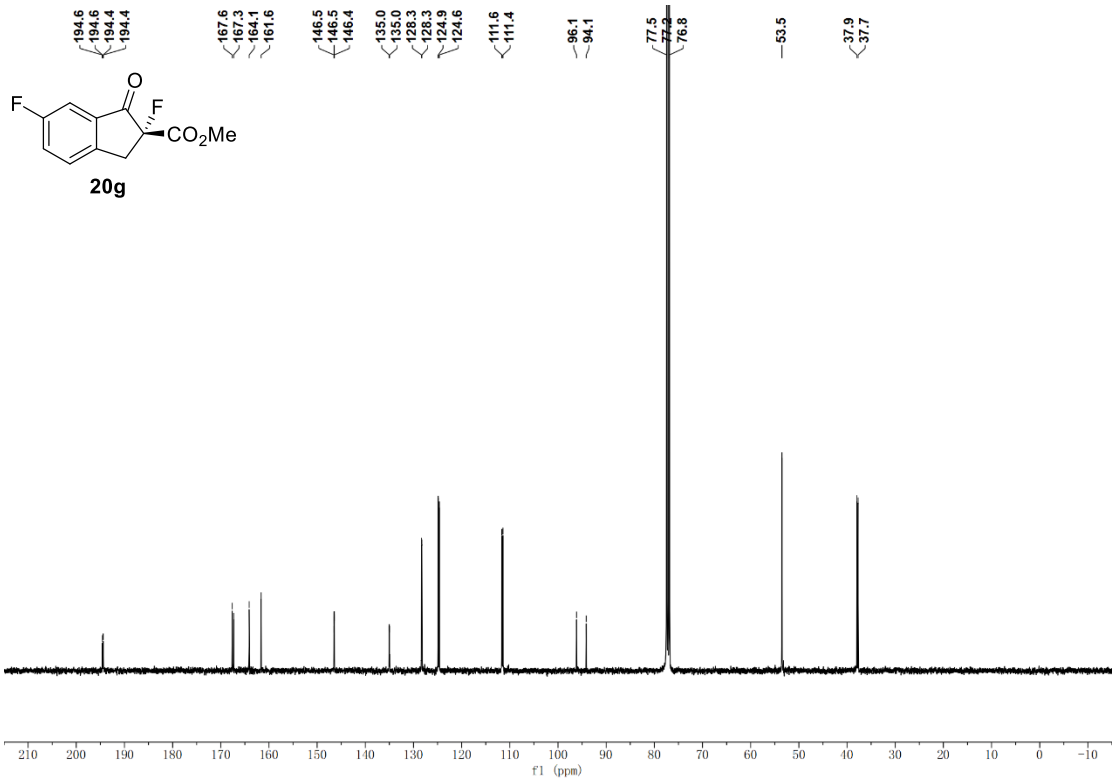
Supplementary Figure 195. ^{13}C NMR Spectrum of **20f** (100 MHz, $CDCl_3$)



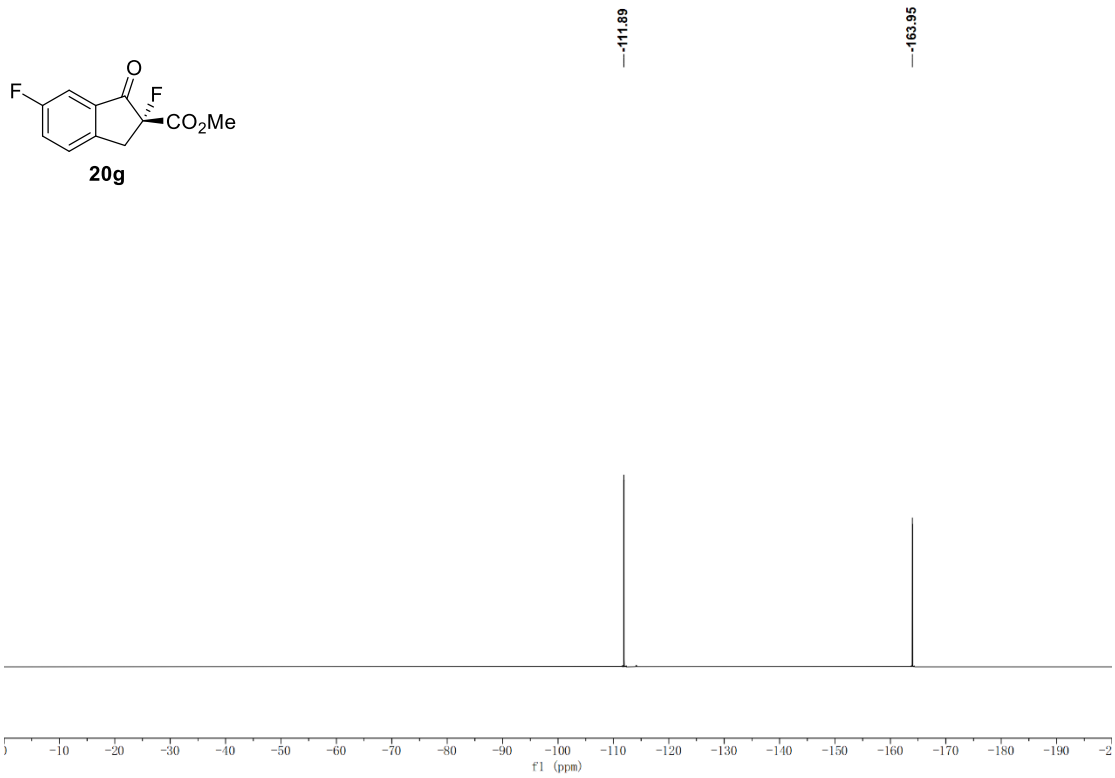
Supplementary Figure 196. ^{19}F NMR Spectrum of **20f** (376 MHz, $CDCl_3$)



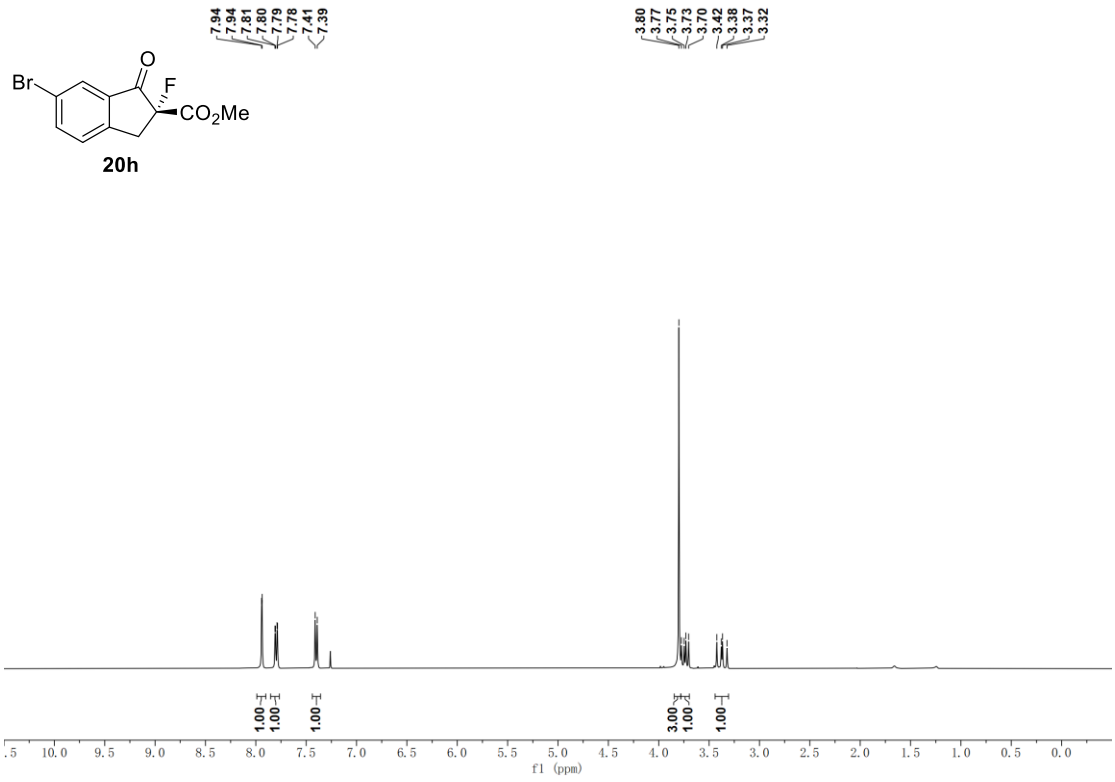
Supplementary Figure 197. ^{1}H NMR Spectrum of **20g** (400 MHz, $CDCl_3$)



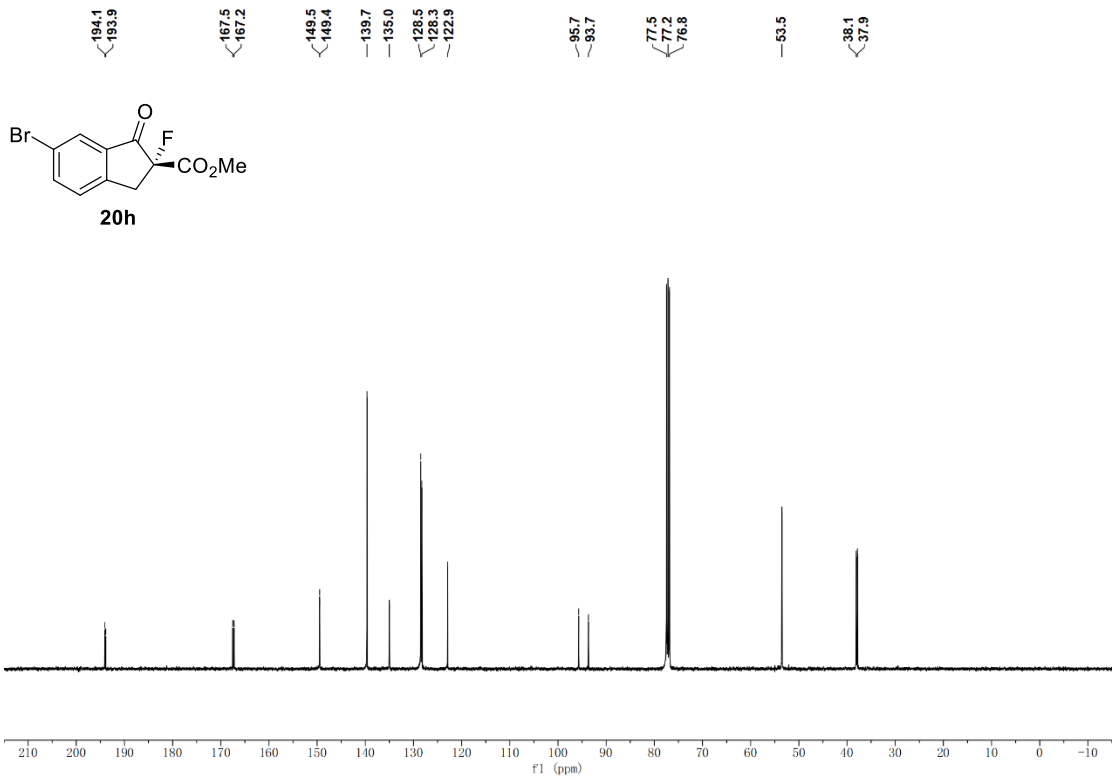
Supplementary Figure 198. ^{13}C NMR Spectrum of **20g** (100 MHz, $CDCl_3$)



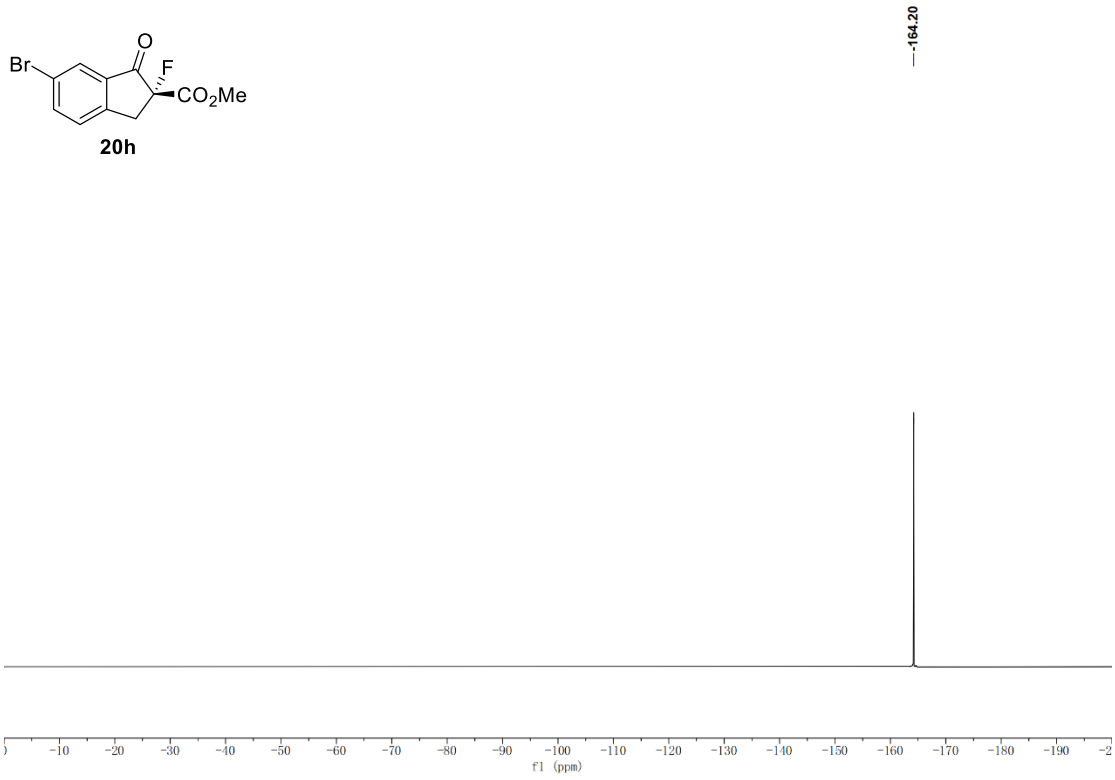
Supplementary Figure 199. ^{19}F NMR Spectrum of **20g** (376 MHz, $CDCl_3$)



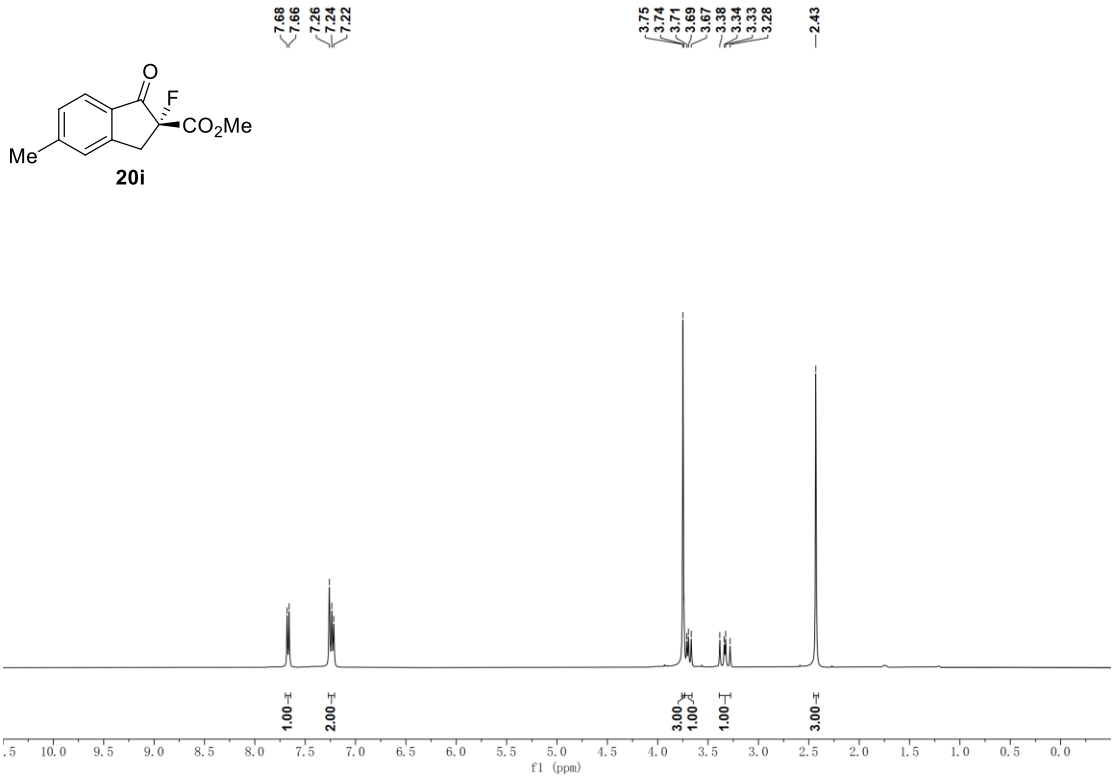
Supplementary Figure 200. ^{1}H NMR Spectrum of **20h** (400 MHz, $CDCl_3$)



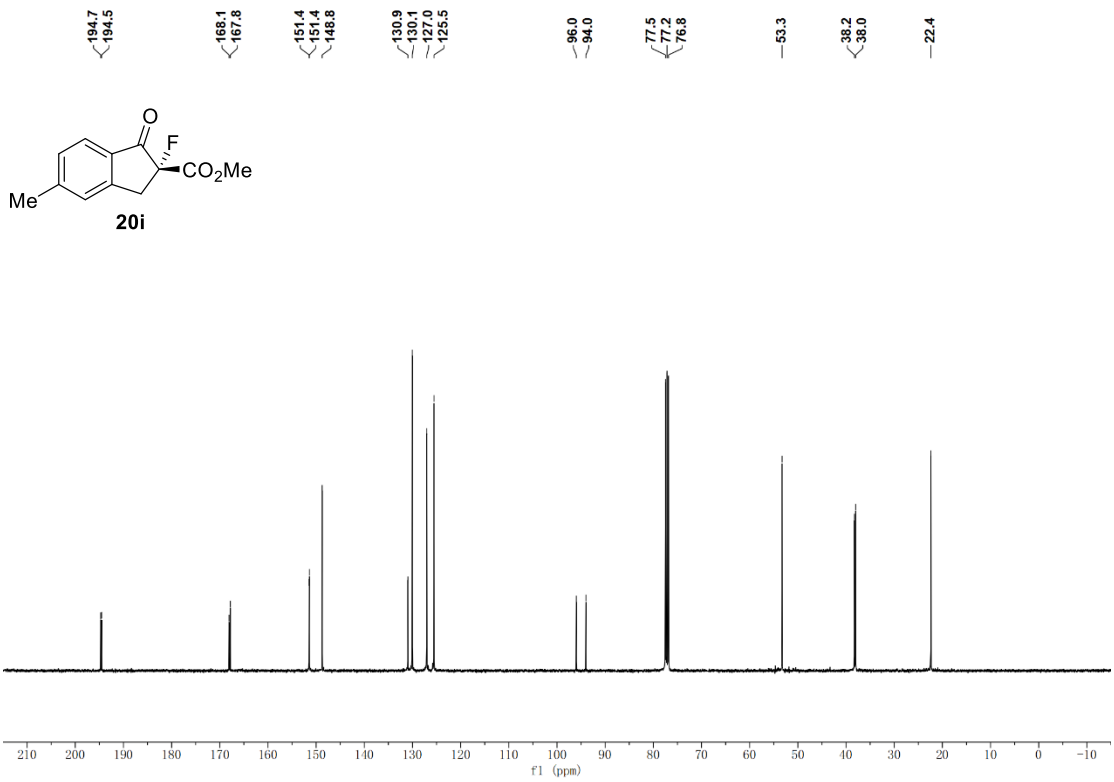
Supplementary Figure 201. ^{13}C NMR Spectrum of **20h** (100 MHz, $CDCl_3$)



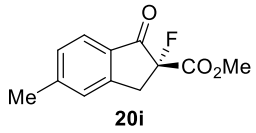
Supplementary Figure 202. ^{19}F NMR Spectrum of **20h** (376 MHz, $CDCl_3$)



Supplementary Figure 203. ^{1}H NMR Spectrum of **20i** (400 MHz, $CDCl_3$)

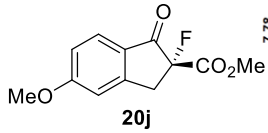


Supplementary Figure 204. ^{13}C NMR Spectrum of **20i** (100 MHz, $CDCl_3$)



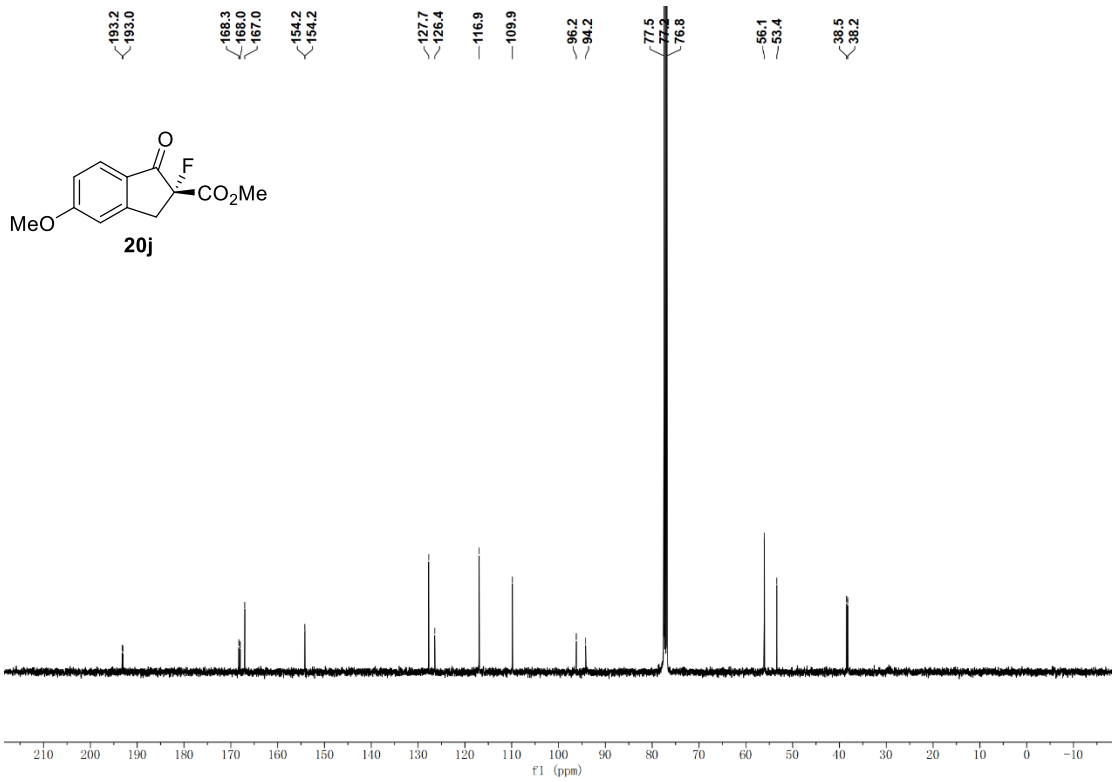
20i

Supplementary Figure 205. ^{19}F NMR Spectrum of **20i** (376 MHz, $CDCl_3$)

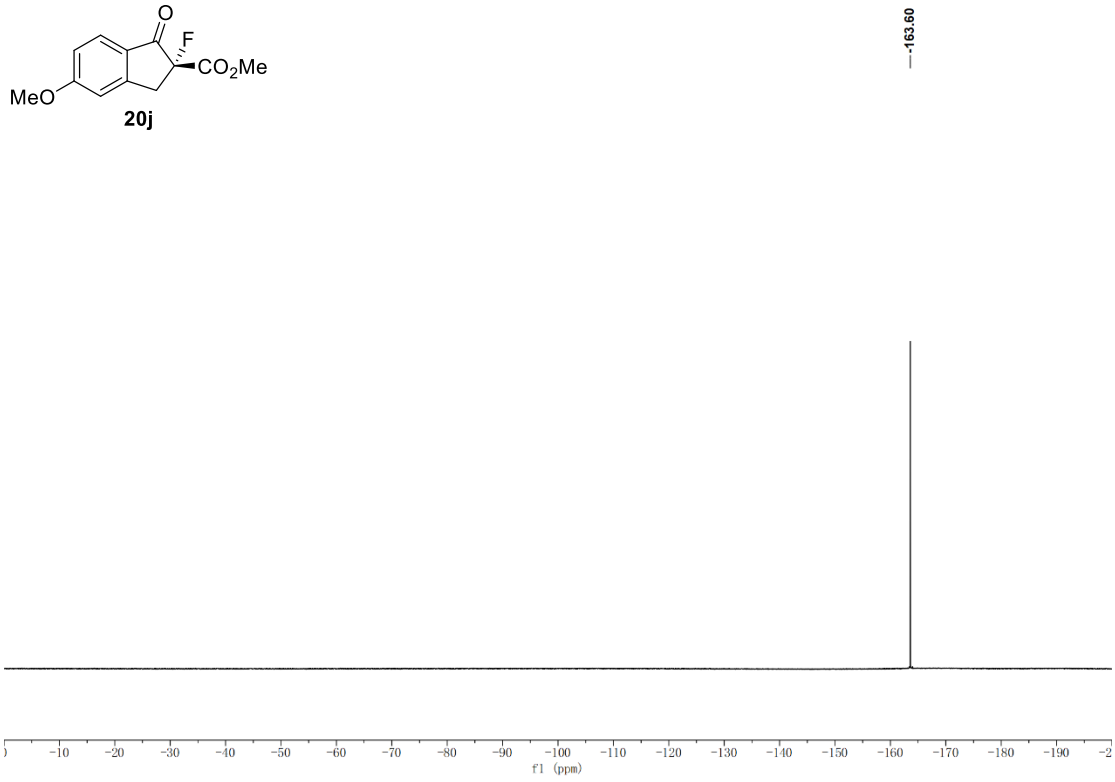


20j

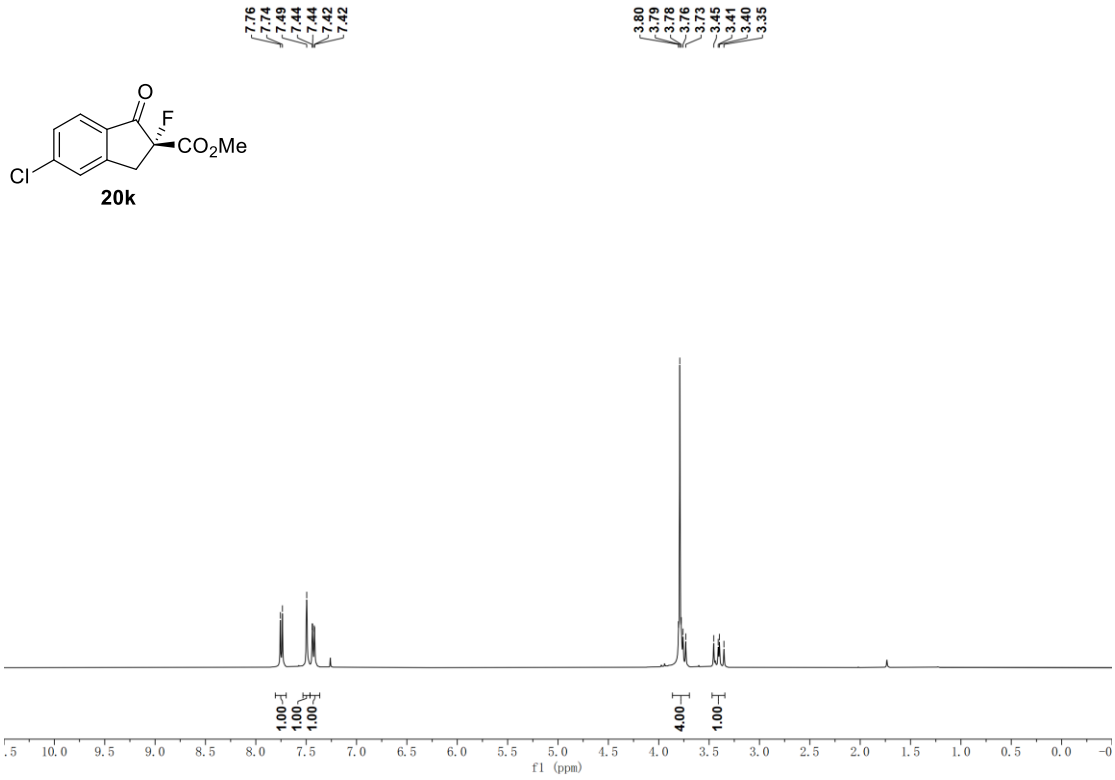
Supplementary Figure 206. ^{1}H NMR Spectrum of **20j** (400 MHz, $CDCl_3$)



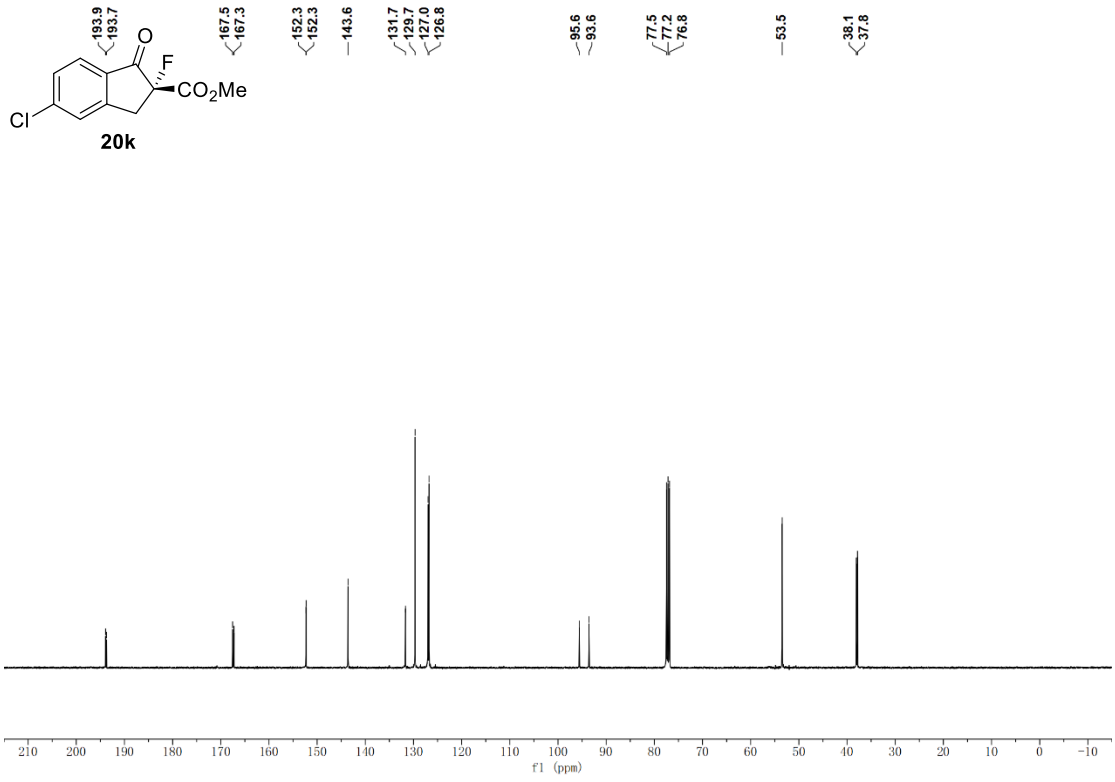
Supplementary Figure 207. ^{13}C NMR Spectrum of **20j** (100 MHz, $CDCl_3$)



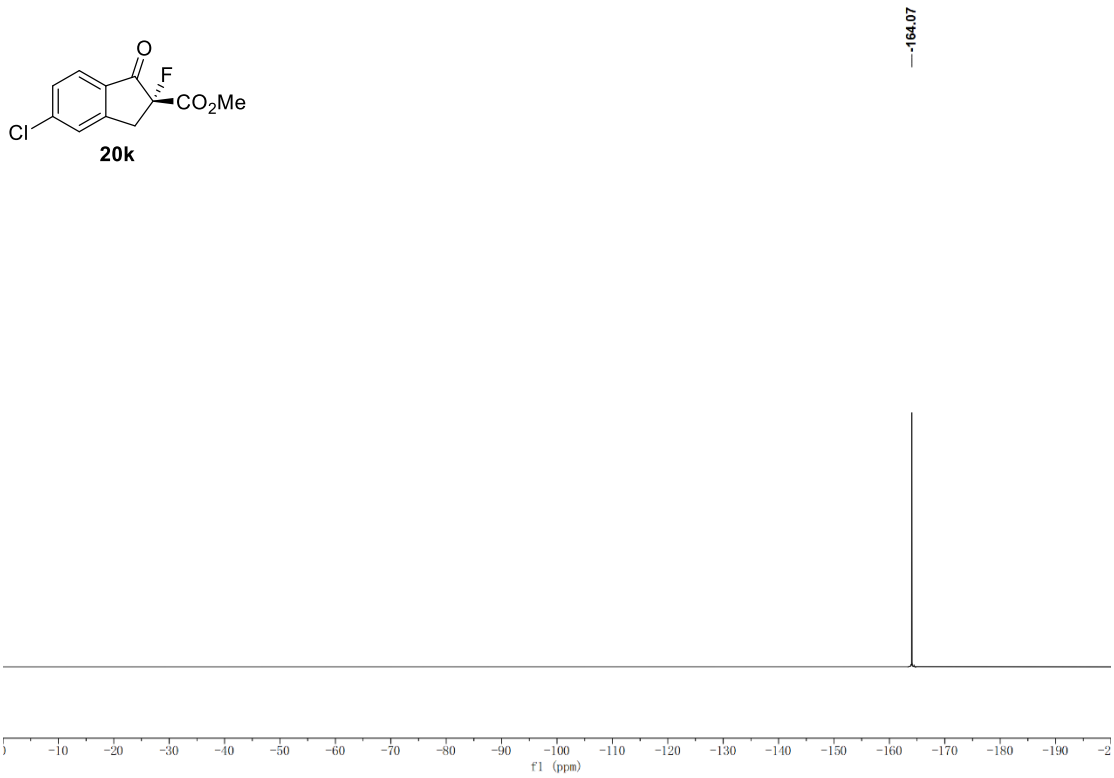
Supplementary Figure 208. ^{19}F NMR Spectrum of **20j** (376 MHz, $CDCl_3$)



Supplementary Figure 209. ^{1}H NMR Spectrum of **20k** (400 MHz, $CDCl_3$)



Supplementary Figure 210. ^{13}C NMR Spectrum of **20k** (100 MHz, $CDCl_3$)



Supplementary Figure 211. ^{19}F NMR Spectrum of **20i** (376 MHz, $CDCl_3$)