Supplementary Information (SI) for Green Chemistry.

Supporting Information

Visible Light-Mediated Stereoselective Haloalkylation of Bicyclic Alkenes

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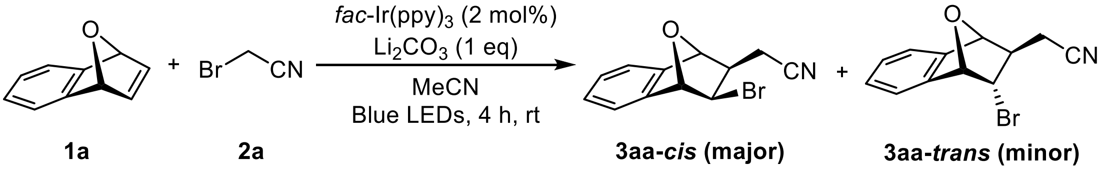
1. General information

Oxabenzonorbornadienes were synthesized according to the steps in the literature. A series of oxabenzonorbornadienes containing different substituents were synthesized according to literature method[1]. Ethyl iodiacetate and trichloromethane iodide were synthesized according to the steps in the literature[2]. Other commercially available reagents and solvents were purchased and used without further purification. All catalytic experiments were performed under an atmosphere of argon by using Glove Box. ^{1}H NMR (400 MHz/600 MHz) and ^{13}C NMR (101 MHz/151MHz) spectra were recorded on a Bruker NMR spectrometer in $CDCl_3$/CD_3OD using TMS as an internal reference with chemical shift values reported in ppm. Abbreviations used in the NMR follow-up experiments: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. High-resolution mass spectra (HRMS) were obtained by fast atom bombardment (FAB) using a double focusing magnetic sector mass spectrometer and electrospray ionization electron impact (ESI) ionization technique. The light source was 30 W blue LED (450 nm, 1 W*30, 30-50 cd/m^2, made in Everlight Electronics Ltd., China); borosilicate glass Schlenk tube (20 mL) was used as the irradiation vessel; the distance from the light source to the irradiation vessel 3 cm and no filter was used.

2. General experimental methods

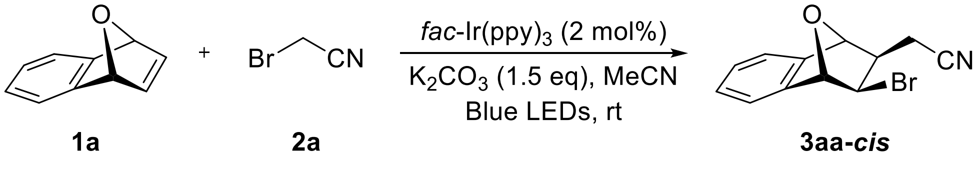


In N_2 atmosphere, a magnetic stirring rod was installed on the oven-dried Schlenk tube. *fac*-Ir(ppy)$_3$ (2 mol%, 0.02 equiv), Li_2CO_3 (0.2 mmol, 1 equiv), oxabenzonorbornadiene (0.2 mmol, 1.0 equiv), acetonitrile bromide (0.4 mmol, 2 equiv) and MeCN (2 mL) were added. The mixture is then irradiated for 4 h at room temperature with a 30 W blue LEDs (450 nm). The reaction mixture was concentrated by vacuum, combined yields and cis/trans-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using p-nitrotoluene as internal standard.

3. Investigation of the key reaction parameters

3.1. The bromoalkylation reaction of oxabenzonorbornadienes

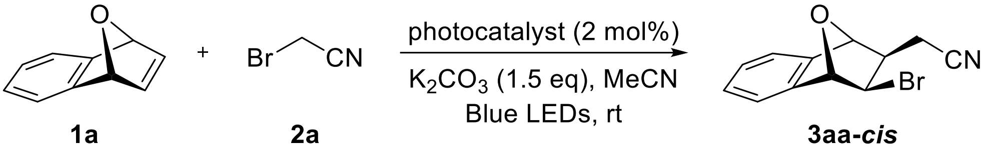
3.1.1. Controlled experiment: [a]



Entry	photocatalyst	Base	Solvent	Light source	Time (h)	Yield (%)[b]	dr[b]
1	*fac*-Ir(ppy)$_3$	K_2CO_3	MeCN	blue	9	71	73:27
2	/	K_2CO_3	MeCN	blue	9	NR[c]	--
3	*fac*-Ir(ppy)$_3$	/	MeCN	blue	10	56	55:45
4	*fac*-Ir(ppy)$_3$	K_2CO_3	MeCN	/	9	NR[c]	--

[a]General conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), photocatalyst (2 mol%) and K_2CO_3 (1.5 equiv) in MeCN (2 mL) was irradiated with 30 W blue LEDs at room temperature under argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard. [c]NR= no reaction.

3.1.2. Screening for photosensitizers and amounts: [a]

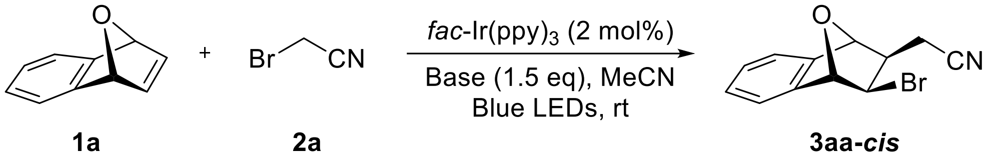


Entry	photocatalyst	Base	Solvent	Time (h)	Yield (%)[b]	dr[b]
1	*fac*-Ir(ppy)$_3$	K_2CO_3	MeCN	9	71	73:27
2	Ir[dF(CF$_3$)ppy]$_2$(dtbbpy)PF$_6$	K_2CO_3	MeCN	10	42	52:48
3	4CzIPN	K_2CO_3	MeCN	14	40	56:44
4	EosinY	K_2CO_3	MeCN	22	ND[c]	--
5	Ru(bpy)$_3$·6H$_2$O	K_2CO_3	MeCN	22	Trace[d]	--
6	Mes-ACr$^+$	K_2CO_3	MeCN	22	Trace[d]	--

[a]General conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), photocatalyst (2 mol%) and K_2CO_3 (1.5 equiv) in MeCN (2 mL) was irradiated with 30 W blue LEDs at room temperature under argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard. [c]ND= not detected. [d]trace= Raw material is declining but no product is being monitored.

Entry	***fac*-Ir(ppy)$_3$**	Base	Solvent	Time (h)	Yield (%)[b]	dr[b]
1	1%	K_2CO_3	MeCN	12	63	63:37
2	2%	K_2CO_3	MeCN	9	71	73:27
3	3%	K_2CO_3	MeCN	8	71	70:30
4	4%	K_2CO_3	MeCN	8	72	69:31
5	5%	K_2CO_3	MeCN	6	72	69:31

3.1.3. Screening for base and amounts: [a]

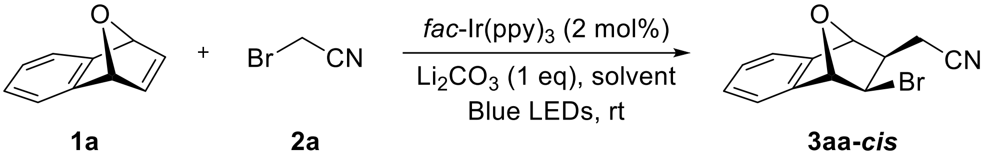


Entry	photocatalyst	Base	Solvent	Time (h)	Yield (%)[b]	dr[b]
1	*fac*-Ir(ppy)$_3$	DBU	MeCN	9	Trace[c]	--
2	*fac*-Ir(ppy)$_3$	2,6-Lutidine	MeCN	9	46	53:47
3	*fac*-Ir(ppy)$_3$	Et_3N	MeCN	9	Trace[c]	--
4	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeCN	4	86	85:15
5	*fac*-Ir(ppy)$_3$	Na_2CO_3	MeCN	9	72	72:28
6	*fac*-Ir(ppy)$_3$	$NaHCO_3$	MeCN	9	77	77:23
7	*fac*-Ir(ppy)$_3$	Cs_2CO_3	MeCN	9	39	52:48
8	*fac*-Ir(ppy)$_3$	NaOH	MeCN	9	48	50:50
9	*fac*-Ir(ppy)$_3$	K_3PO_4	MeCN	9	64	66:34
10	*fac*-Ir(ppy)$_3$	K_2HPO_4	MeCN	9	82	83:17
11	*fac*-Ir(ppy)$_3$	KH_2PO_4	MeCN	9	75	76:24

[a]General conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and base (1.5 equiv) in MeCN (2 mL) was irradiated with 30 W blue LEDs at room temperature under argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard. [c]trace= Raw material is declining but no product is being monitored.

Entry	photocatalyst	Li_2CO_3 (equiv)	solvent	Time (h)	Yield (%)[b]	dr[b]
1	*fac*-Ir(ppy)$_3$	1	MeCN	4	86	85:15
2	*fac*-Ir(ppy)$_3$	1.5	MeCN	4	86	85:15
3	*fac*-Ir(ppy)$_3$	2	MeCN	4	85	85:15
4	*fac*-Ir(ppy)$_3$	3	MeCN	4	86	85:15

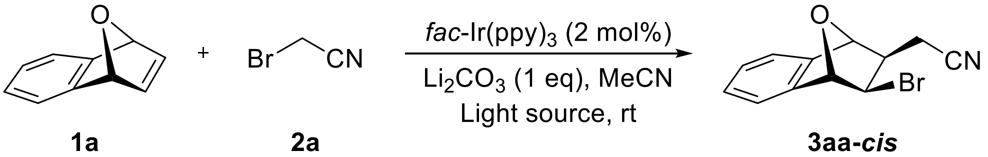
3.1.4. Solvent screening: [a]



Entry	photocatalyst	Base	Solvent	Time (h)	Yield (%)[b]	dr[b]
1	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeCN	4	86	85:15
2	*fac*-Ir(ppy)$_3$	Li_2CO_3	DCM	9	62	64:36
3	*fac*-Ir(ppy)$_3$	Li_2CO_3	Acetone	9	Trace[c]	--
4	*fac*-Ir(ppy)$_3$	Li_2CO_3	Toluene	9	40	50:50
5	*fac*-Ir(ppy)$_3$	Li_2CO_3	THF	9	42	51:49
6	*fac*-Ir(ppy)$_3$	Li_2CO_3	1,4-Dioxane	9	48	51:49
7	*fac*-Ir(ppy)$_3$	Li_2CO_3	DMF	9	47	52:48
8	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeOH	9	35	55:45
9	*fac*-Ir(ppy)$_3$	Li_2CO_3	EA	16	52	53:47
10	*fac*-Ir(ppy)$_3$	Li_2CO_3	DCE	9	65	70:30

[a]General conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and Li_2CO_3 (1 equiv) in solvent (2 mL) was irradiated with 30 W blue LEDs at room temperature under argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard. [c]trace= Raw material is declining but no product is being monitored.

3.1.5. Light source screening: [a]

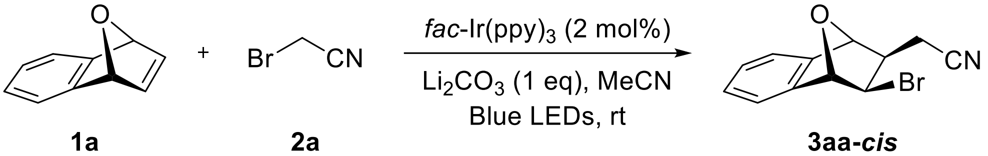


Entry	photocatalyst	Base	Solvent	Light source	Time (h)	Yield (%)[b]	dr[b]
1	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeCN	450 nm	4	86	85:15
2	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeCN	420 nm	4	82	81:19
3	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeCN	395 nm	8	84	83:17
5	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeCN	530 nm	7	71	72:28

[a]General conditions: **1a** (0.2 mmol), **2a** (0.8 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and Li_2CO_3 (1 equiv) in MeCN (2 mL) was irradiated with 30 W LEDs at room temperature under

argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard.

3.1.6. Screening of the amount of substrate: [a]

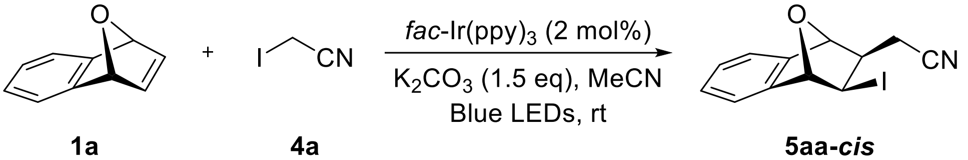


Entry	1a (mmol)	2a (mmol)	photocatalyst	Base	Solvent	Time (h)	Yield (%)[b]	dr[b]
1	0.2	0.3	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeCN	12	76	76:24
2	0.2	0.4	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeCN	4	86	85:15
3	0.2	0.6	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeCN	4	84	86:14
4	0.2	0.8	*fac*-Ir(ppy)$_3$	Li_2CO_3	MeCN	4	86	85:15

[a]General conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), *fac*-Ir(ppy)$_3$ (2 mol%) and Li_2CO_3 (1 equiv) in solvent (2 mL) was irradiated with 30 W blue LEDs at room temperature under argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard.

3.2. The iodoalkylation reaction of oxabenzonorbornadienes

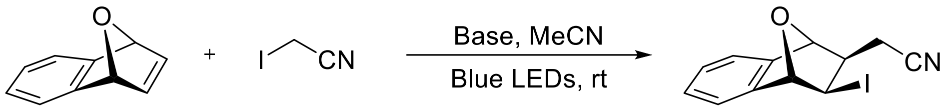
3.2.1. controlled experiment: [a]



Entry	photocatalyst	Base	Solvent	Light source	Time (h)	Yield (%)[b]	d.r.[b]
1	*fac*-Ir(ppy)$_3$	K_2CO_3	MeCN	blue	36	68	64:36
2	/	K_2CO_3	MeCN	blue	36	47	64:36
3	*fac*-Ir(ppy)$_3$	/	MeCN	blue	36	Trace[c]	--
4	*fac*-Ir(ppy)$_3$	K_2CO_3	MeCN	/	36	Trace[c]	--

[a]General conditions: **1a** (0.2 mmol), **4a** (0.6 mmol), photocatalyst (2 mol%) and K_2CO_3 (1.5 equiv) in MeCN (2 mL) was irradiated with 30 W blue LEDs at room temperature under argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard. [c]trace=Raw material is declining but no product is being monitored.

3.2.2. Screening for base and amounts: [a]



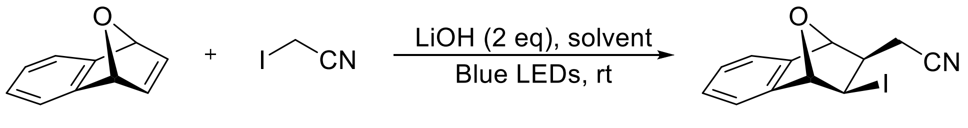
1a **4a** **5aa-*cis***

Entry	Base	Solvent	Time (h)	Yield (%)[b]	dr[b]
1	DBU	MeCN	72	39	61:39
2	2,6-Lutidine	MeCN	72	47	52:48
3	Et$_3$N	MeCN	72	52	57:43
4	K$_2$CO$_3$	MeCN	10	87	60:40
5	LiOH	MeCN	9	89	64:36
6	K$_2$HPO$_4$	MeCN	72	40	73:27
7	NaOH	MeCN	66	45	68:32
8	KOH	MeCN	66	60	66:34
9	Li$_2$CO$_3$	MeCN	66	42	82:18
10	PhCOOLi	MeCN	66	Trace[c]	--
11	Li$_2$C$_2$O$_4$	MeCN	66	49	57:43
12	LiOAc	MeCN	66	60	52:48
13	Li$_3$PO$_4$	MeCN	66	50	52:48

[a]General conditions: **1a** (0.2 mmol), **4a** (0.6 mmol) and base (1.5 equiv) in MeCN (2 mL) was irradiated with 30 W blue LEDs at room temperature under argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard. [c]trace=Raw material is declining but no product is being monitored.

Entry	LiOH (equiv)	solvent	Time (h)	Yield (%)[b]	dr[b]
1	1	MeCN	30	66	61:39
2	1.5	MeCN	9	89	64:36
3	2	MeCN	6	89	64:36
4	3	MeCN	30	58	62:38

3.2.3. Solvent screening: [a]

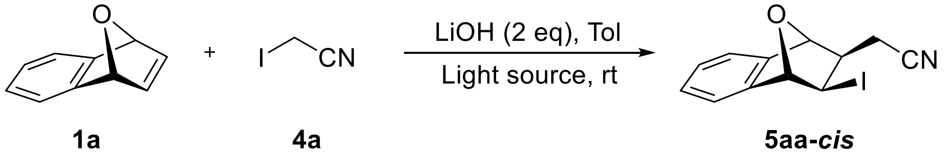


1a **4a** **5aa-*cis***

Entry	Base	Solvent	Time (h)	Yield (%)[b]	dr[b]
1	LiOH	DCM	12	95	66:34
2	LiOH	DMSO	24	Trace[c]	--
3	LiOH	Toluene	5	96	68:32
4	LiOH	THF	8	82	65:35
5	LiOH	1,4-Dioxane	24	91	64:36
6	LiOH	DMF	24	Trace[c]	--
7	LiOH	MeOH	8	81	61:39
8	LiOH	EA	24	91	66:34
9	LiOH	DCE	24	86	70:30

[a]General conditions: **1a** (0.2 mmol), **4a** (0.6 mmol) and LiOH (2 equiv) in solvent (2 mL) was irradiated with 30 W blue LEDs at room temperature under argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard. [c]trace=Raw material is declining but no product is being monitored.

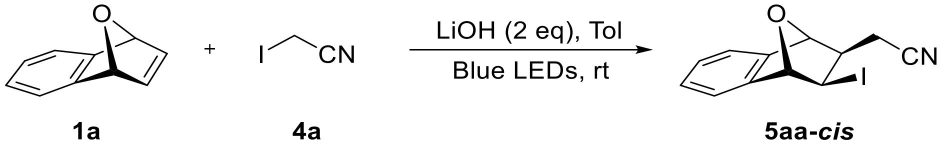
3.2.4. Light source screening: [a]



Entry	Base	Solvent	Light source	Time (h)	Yield (%)[b]	dr[b]
1	LiOH	Toluene	365 nm	16	92	57:43
2	LiOH	Toluene	390 nm	7	93	57:43
3	LiOH	Toluene	420 nm	14	87	66:34
5	LiOH	Toluene	450 nm	5	96	68:32

[a]General conditions: **1a** (0.2 mmol), **4a** (0.6 mmol) and LiOH (2 equiv) in Toluene (2 mL) was irradiated with 30 W LEDs at room temperature under argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard.

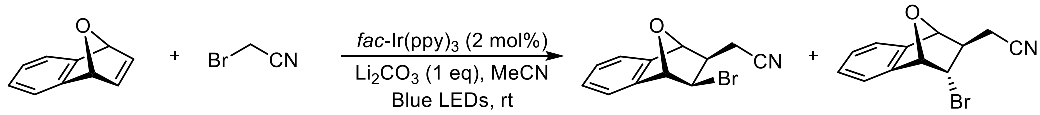
3.2.5. Screening of the amount of substrate: [a]



Entry	1a (mmol)	4a (mmol)	Base	Solvent	Time (h)	Yield (%)[b]	dr[b]
1	0.2	0.3	LiOH	Tol	9	88	65:35
2	0.2	0.4	LiOH	Tol	5	96	68:32
3	0.2	0.6	LiOH	Tol	5	96	68:32

[a]General conditions: **1a** (0.2 mmol), **4a** (0.4 mmol) and LiOH (2 equiv) in Toluene (2 mL) was irradiated with 30 W blue LEDs at room temperature under argon. [b]Combined yields and *cis*/*trans*-ratios were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard.

4. Gram-scale reaction

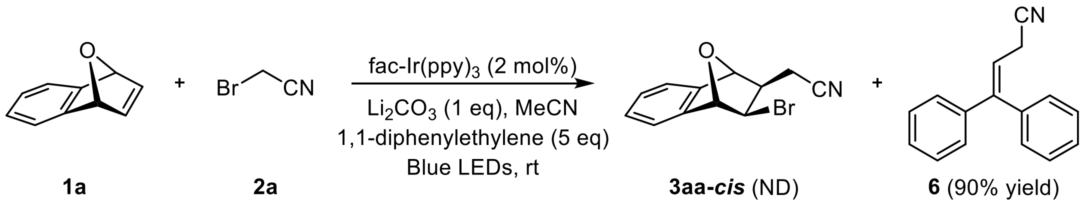


1a (1.0 g, 6.9 mmol) **2a** (1.7 g, 13.8 mmol) **3aa-*cis*** (1.18 g, 65% yield) **3aa-*trans*** (237 mg, 13% yield)

On the basis of the above experiment, in order to further confirm the practicality of the reaction system, we conducted a gram level reaction experiment on this reaction. **1a** (1.00 g, 6.9 mmol, 1 equiv), **2a** (1.70 g, 13.8 mmol, 2 equiv), *fac*-Ir(ppy)$_3$ (0.09 g, 2 mol%), Li$_2$CO$_3$ (0.50 g, 6.9 mmol, 1 equiv), MeCN (20 mL) were added to a 50 mL round-bottomed flask. After that, the reaction bottle was stirred for 16 h under a 30 W blue light and cooled by a fan to ensure a constant reaction temperature. TLC was used to monitor the reaction process, and then the reaction liquid was concentrated by vacuum and the reaction product were purified by silica gel column to give **3aa-*cis*** (1.18 g, 65% yield) and **3aa-*trans*** (237 mg, 13% yield).

5. Mechanistic studies

5.1. Free radical trapping experiment:



1a **2a** **3aa-*cis*** (ND) **6** (90% yield)

In N$_2$ atmosphere, a magnetic stirring rod was installed on the oven-dried Schlenk tube. **1a** (0.2 mmol, 1equiv), **2a** (0.4 mmol 2 equiv), *fac*-Ir(ppy)$_3$ (0.004 mmol, 0.02 equiv), Li$_2$CO$_3$ (0.2 mmol, 1 equiv), 1,1-diphenylethylene (1.0 mmol, 5 equiv) and MeCN (2 mL) were added. The mixture was then irradiated for 4 h at room temperature with a 30 W blue LED (450 nm). In this process, 1,1-diphenylethylene acts as a free radical trapping agent and completely inhibits the production of the target product **3aa-*cis***. The reaction mass was purified by flash chromatography, column eluted with petroleum ether in ethyl acetate to get 1,1-diphenylethylene adduct **6** (90%).

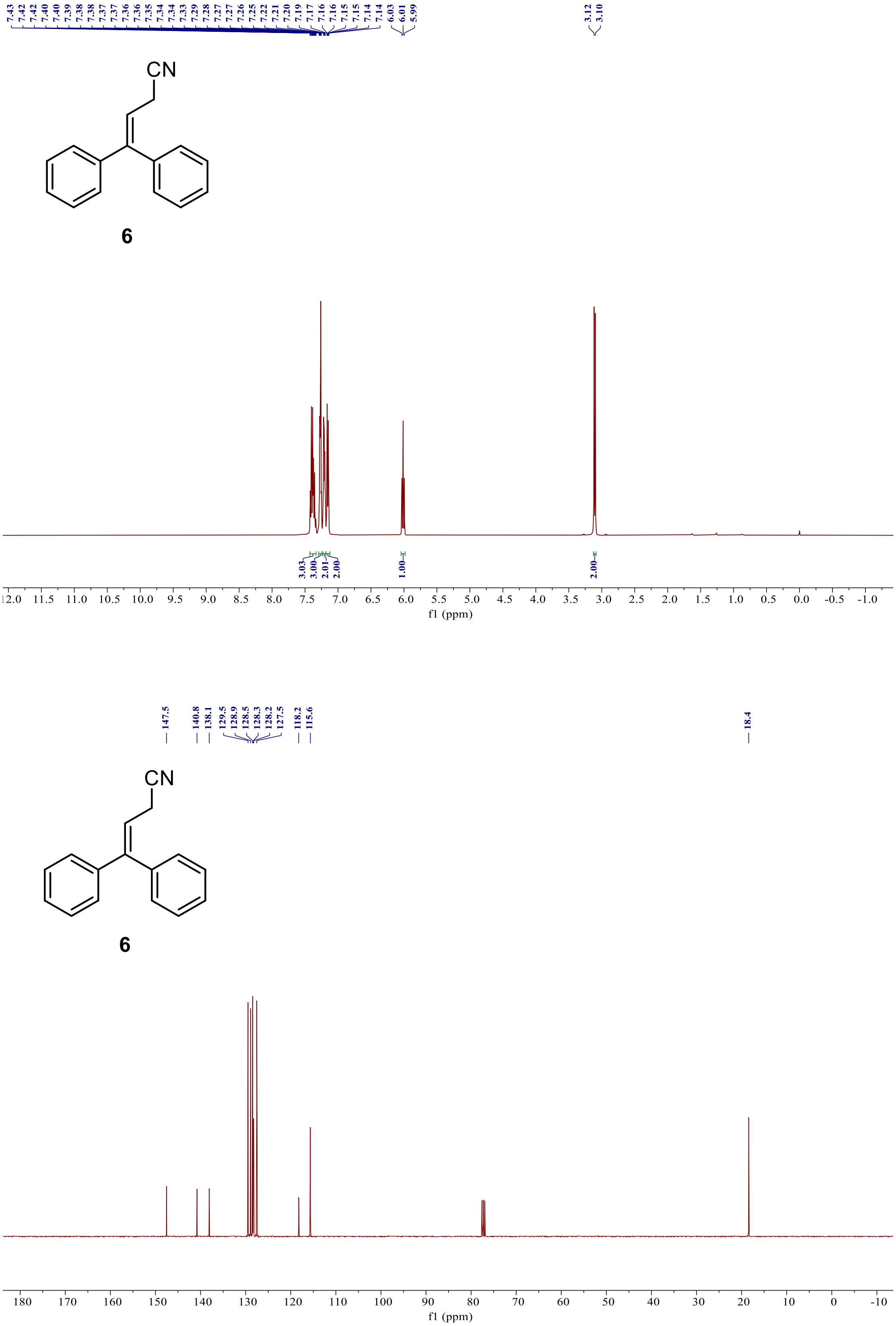
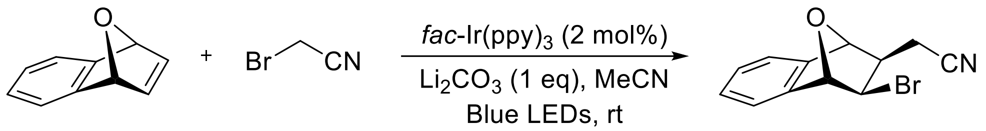


Figure 1. Free radical trapping experiment

5.2. Light/dark experiments

5.2.1. The bromoalkylation reaction of oxabenzonorbornadienes



1a **2a** **3aa-*cis***

Take eight Schlenk tubes and add the same standard reaction mixture (0.2 mmol **1a**, 0.4 mmol **2a**, 0.2 mmol Li_2CO_3, 0.004 mmol *fac*-Ir(ppy)$_3$, MeCN (2 mL) to each tube. Add a stirrer and stir the mixture. Illuminate with a blue LED at room temperature. After 1 hour, turn off the blue LED light and remove a Schlenk tube from the irradiation device for analysis. The remaining seven Schlumberger tubes were stirred for another hour without light. Then, take out a Schlenk tube for analysis, and turn on the blue LED again to illuminate the remaining six reaction tubes. After an additional hour of irradiation, turn off the blue LED light and remove a Schlenk tube for analysis, and so on until the last tube is removed and analyzed. Finally, combined yields were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard.

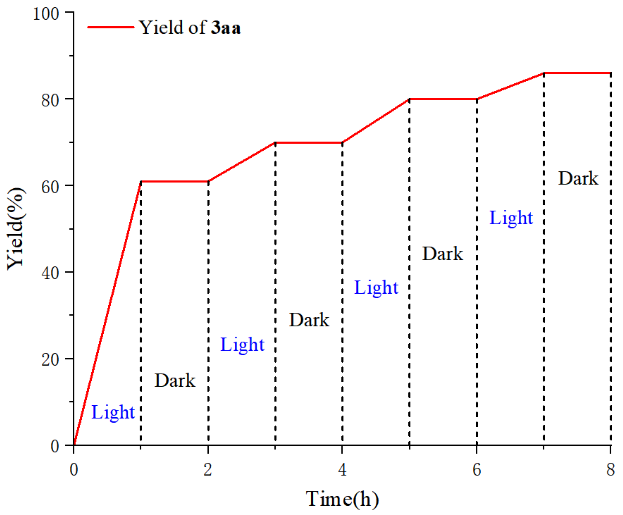
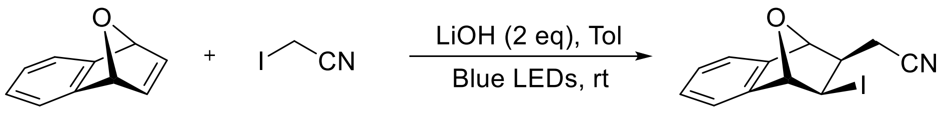


Figure 2. Light on-off experiments (a)

5.2.2. The iodoalkylation reaction of oxabenzonorbornadienes



1a **4a** **5aa-*cis***

Take ten Schlenk tubes and add the same standard reaction mixture (0.2 mmol **1a**, 0.4 mmol **4a**, 0.2 mmol LiOH, MeCN (2 mL) to each tube. Add a stirrer and stir the mixture. Illuminate with a blue LED at room temperature. After 1 hour, turn off the blue LED light and remove a Schlenk tube from the irradiation device for analysis. The remaining seven Schlumberger tubes were stirred for another hour without light. Then, take out a Schlenk tube for analysis, and turn on the blue LED again to illuminate the remaining six reaction tubes. After an additional hour of irradiation, turn off the blue

LED light and remove a Schlenk tube for analysis, and so on until the last tube is removed and analyzed. Finally, combined yields were determined by ^{1}H NMR analysis of the crude reaction mixture using P-nitrotoluene as internal standard.

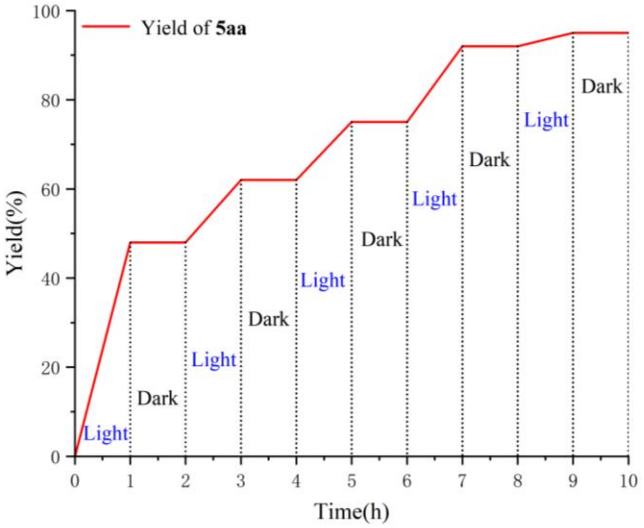


Figure 3. Light on-off experiments (b)

5.3. Stern-Volmer quenching experiments

We further monitored the effect of different concentrations of **1a** and **2a** on the steady-state luminescence emission spectra of *fac*-Ir(ppy)$_3$ solution with a concentration of 1×10^{-5} mol/L.We observed a drop of the *fac*-Ir(ppy)$_3$ luminescence signal upon increasing the **2a** concentration, with quenching of *fac*-Ir(ppy)$_3$ by **1a** with the same concentration as **2a** monitored by steady-state fluorimetry is not significant, which suggested that the **2a** acts as a quencher for the *fac*-Ir(ppy)$_3$ (Figure 3, Figure 4).

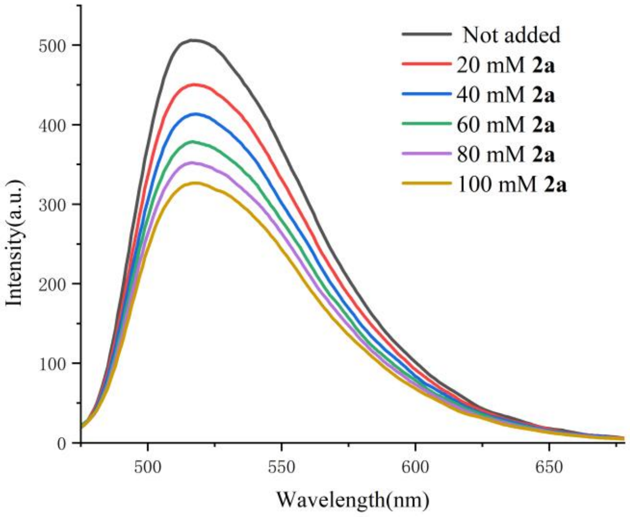


Figure 4. Fluorescence quenching experiment (a)

Quenching of *fac*-Ir(ppy)$_3$ by acetonitrile bromide **2a** monitored by steady-state fluorimetry. The luminescence spectrum of *fac*-Ir(ppy)$_3$ (0.01 mM in N$_2$-saturated acetonitrile) was measured under 450 nm illumination, in the presence of increasing amounts of acetonitrile bromide.

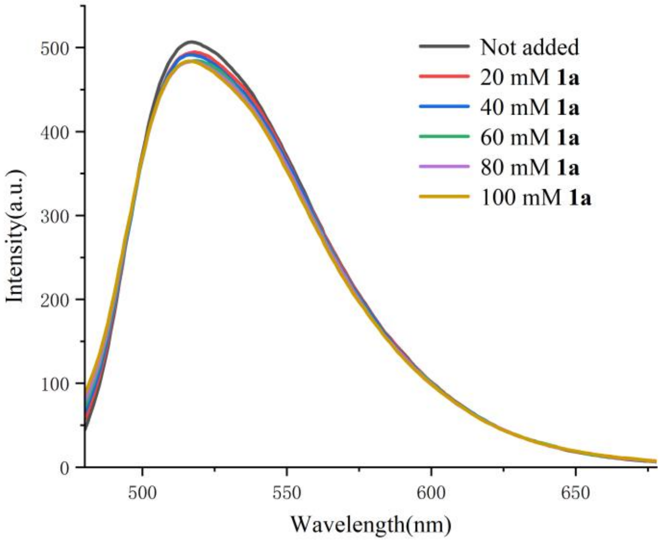


Figure 5. Fluorescence quenching experiment (b)

Quenching of *fac*-Ir(ppy)$_3$ by oxabenzonorbornadiene **1a** monitored by steady-state fluorimetry. The luminescence spectrum of *fac*-Ir(ppy)$_3$ (0.01 mM in N_2-saturated acetonitrile) was measured under 450 nm illumination, in the presence of increasing amounts of oxabenzonorbornadiene.

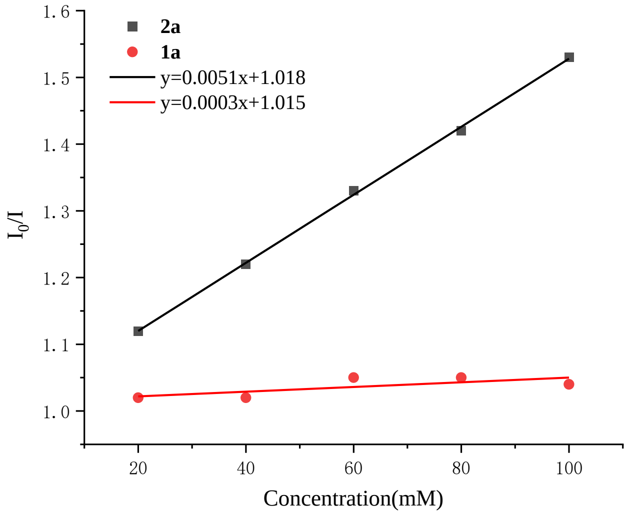


Figure 6. Fluorescence quenching experiment (c)

Stern-Volmer plots for the quenching of *fac*-Ir(ppy)$_3$ by **1a** and **2a** as monitored by steady-state fluorimetry.

5.4. UV-vis absorption spectra of different reaction component

5.4.1. The bromoalkylation reaction of oxabenzonorbornadienes

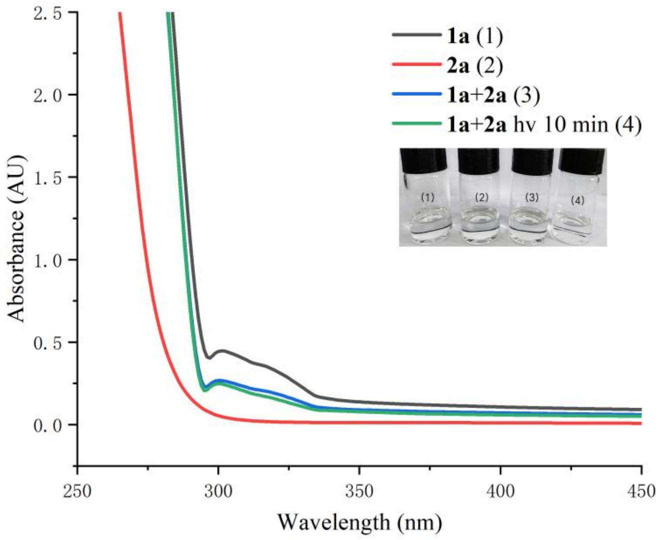


Figure 7. UV-vis absorption spectra of **1a** and **2a**

UV−vis spectrum of **1a** (0.1 M) and **2a** (0.2 M) in acetonitrile solution and their mixture, test immediately and after 10 min of irradiation (10 min, 30 W 450 nm blue LED). After **1a** and **2a** were mixed and upon blue-light irradiation for 10 minutes, there is no significant change in absorption.

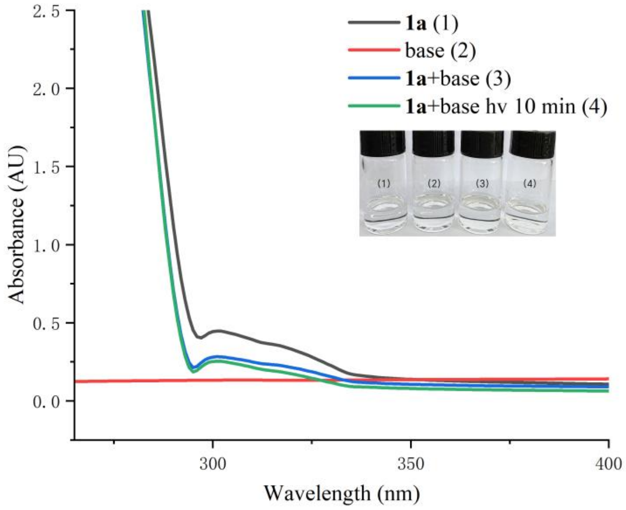


Figure 8. UV-vis absorption spectra of **1a** and base

UV−vis spectrum of **1a** (0.1 M) and base (0.1 M) in acetonitrile solution and their mixture, test immediately and after 10 min of irradiation (10 min, 30 W 450 nm blue LED). After **1a** and base were mixed and upon blue-light irradiation for 10 minutes, there is no significant change in absorption.

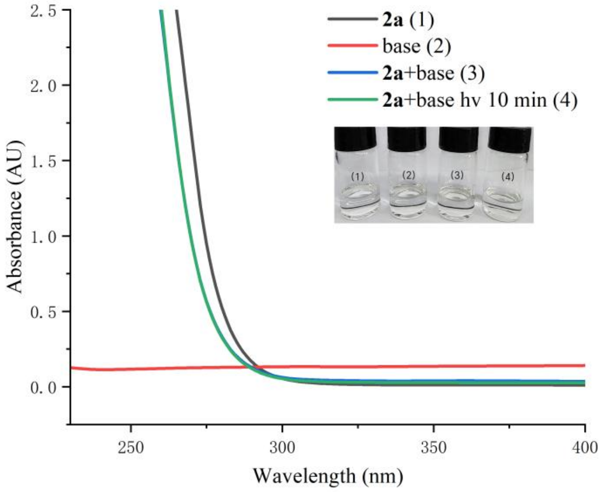


Figure 9. UV-vis absorption spectra of **2a** and base

UV−vis spectrum of **2a** (0.2 M) and base (0.1 M) in acetonitrile solution and their mixture, test immediately and after 10 min of irradiation (10 min, 30 W 450 nm blue LED). After **2a** and base were mixed and upon blue-light irradiation for 10 minutes, there is no significant change in absorption.

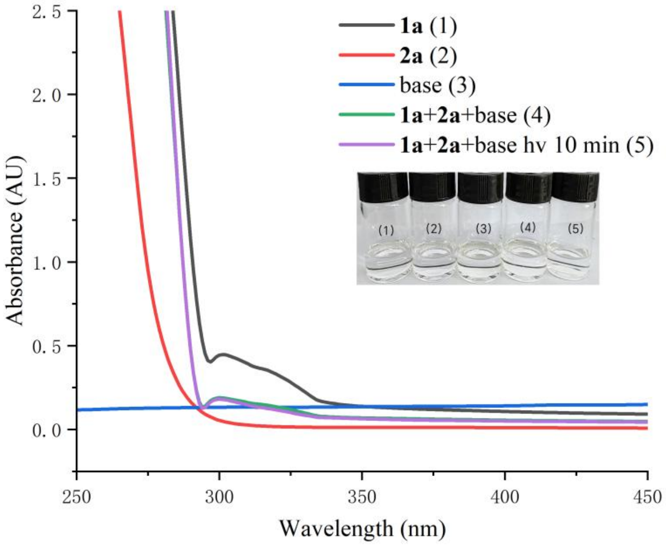


Figure 10. UV-vis absorption spectra of **1a**, **2a** and base

UV−vis spectrum of **1a** (0.1 M), **2a** (0.2 M) and base (0.1 M) in acetonitrile solution and their mixture, test immediately and after 10 min of irradiation (10 min, 30 W 450 nm blue LED). After **1a, 2a** and base were mixed and upon blue-light irradiation for 10 minutes, there were corresponding changes in absorption.

5.4.2. The iodoalkylation reaction of oxabenzonorbornadienes

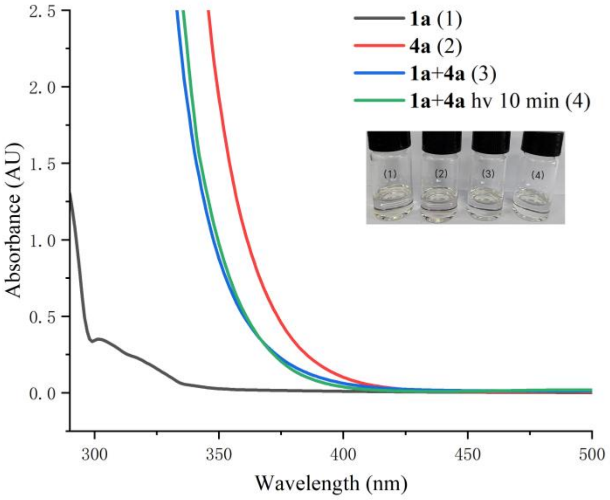


Figure 11. UV-vis absorption spectra of **1a** and **4a**

UV−vis spectrum of **1a** (0.1 M) and **4a** (0.2 M) in toluene solution and their mixture, test immediately and after 10 min of irradiation (10 min, 30 W 450 nm blue LED). After **1a** and **4a** were mixed and upon blue-light irradiation for 10 minutes, there is no significant change in absorption.

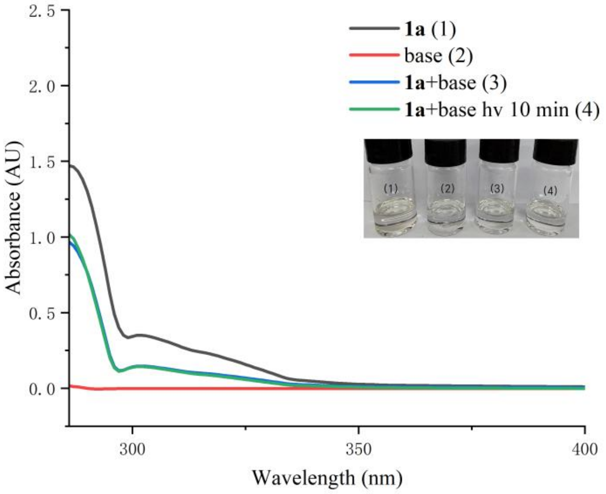


Figure 12. UV-vis absorption spectra of **1a** and base

UV−vis spectrum of **1a** (0.1 M) and base (0.2 M) in toluene solution and their mixture, test immediately and after 10 min of irradiation (10 min, 30 W 450 nm blue LED). After **1a** and base were mixed and upon blue-light irradiation for 10 minutes, there is no significant change in absorption.

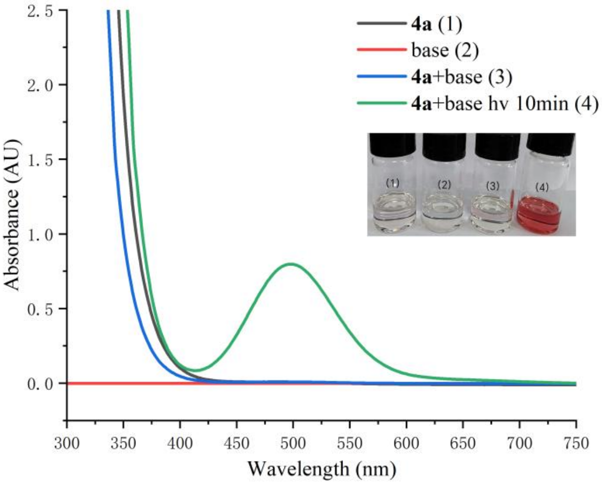


Figure 13. UV-vis absorption spectra of **4a** and base

UV−vis spectrum of **4a** (0.2 M) and base (0.2 M) in toluene solution and their mixture, test immediately and after 10 min of irradiation (10 min, 30 W 450 nm blue LED). After **4a** and base were mixed and upon blue-light irradiation for 10 minutes, the ICH_2CN/LiOH mixture turned red, accompanied by a corresponding red shift in the UV/Vis spectrum. A new absorption peak (green line) emerged in the irradiated mixture, which is attributed to charge-transfer absorption of an electron donor-acceptor (EDA) complex.

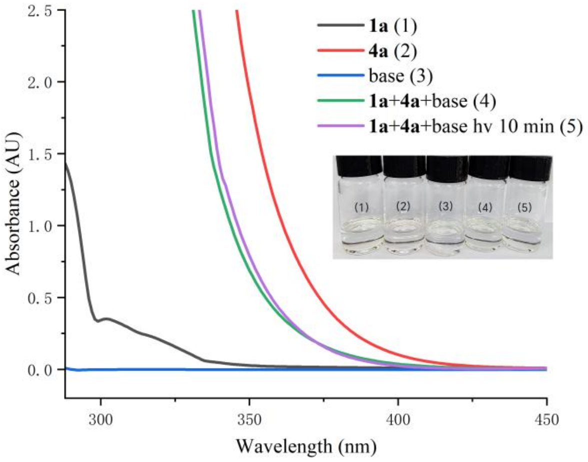


Figure 14. UV-vis absorption spectra of **1a**, **4a** and base

UV−vis spectrum of **1a** (0.1 M), **4a** (0.2 M) and base (0.2 M) in toluene solution and their mixture, test immediately and after 10 min of irradiation (10 min, 30 W 450 nm blue LED). After **1a, 4a** and base were mixed and upon blue-light irradiation for 10 minutes, there were corresponding changes in absorption.

5.5. Measurement of Quantum Yields

The photon flux of blue LED was determined by standard ferrioxalate actinometry.

0.15 mol/L solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (282 mg, 0.750 mmol) in 5.0 mL of 0.20 mol/L aqueous sulfuric acid. 0.15 mol/L buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (54.1 mg, 0.3 mmol) and sodium acetate (1.23 g, 15.0 mmol) in 20 mL of 0.20 mol/L aqueous sulfuric acid. The actinometry measurements were done as follows: To a reaction tube equipped with a stir bar was added 0.50 mL of the ferrioxalate solution. The reaction tube was sealed and placed 2 cm away from a 20 W blue LEDs. After irradiation for 20 seconds, 1.5 mL of the aqueous sulfuric acid and 2.0 mL of the buffered solution was added to the reaction tube. The solution was then allowed to rest for 1 hour to allow the resultant ferrous ions to react completely with 1,10-phenanthroline. 50 μL of the resulting solution was taken as an aliquot and diluted with 3.0 mL of 0.20 mol/L aqueous sulfuric acid. The absorbance of the resulting solution in a cuvette (l = 1.0 cm) at 510 nm was measured by UV-V is spectrometer. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

$$\text{mol Fe}^{2+} = \frac{V \times \Delta A}{l \times \varepsilon}$$

The amount of ferrous ion formed was calculated as follows:

where V is the total volume (0.024 L) of the solution that was analyzed, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples, l is the path length (1.00 cm), and ε is the molar absorptivity at 510 nm (11,100 L/(mol•cm)).

The photon flux was calculated as follows:

$$\text{photo flux} = \frac{\text{mol Fe}^{2+}}{\Phi \times t \times f}$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 0.845, which was reported for a 0.15 mol/L solution at λ = 457.9 nm) , t is the irradiation time, and f is the fraction of light absorbed at 450 nm (0.1302).

The fraction of light absorbed was determined by the following equation:

$$f = 1.0000\text{-}10^{-A}$$

where A is the measured absorbance (0.0606) of the 0.15 mol/L solution of potassium ferrioxalate at 450 nm.

The photo flux is 2.05 × 10^{-7} Einstein/s.

5.5.1. Determination of quantum yield of bromoalkylation reaction of oxabenzonorbornadienes

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a sample of oxabenzonorbornadiene **1a** (0.20 mmol), acetonitrile bromide **2a** (0.40 mmol), *fac*-Ir(ppy)$_3$ (2 mol%), Li_2CO_3 (0.20 mmol), MeCN (2 mL). The reaction mixture was stirred under the irradiation of 30 W LED at room temperature and placed 2 cm away from 30 W blue LEDs. After irradiation for 4 hours, the moles of product **3aa** formed for the model reaction were determined by determined by ^{1}H NMR spectroscopy with P-nitrotoluene as the internal standard revealed 86% yield of **3aa** (17.2×10^{-5} mol).

The quantum yield was calculated as follows:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times \text{t} \times \text{f}}$$

where flux is the photon flux determined by ferrioxalate actinometry (**2.05×10^{-7}** Einstein/s), t is the time, and f is the fraction of light absorbed by the irradiated reaction system at 450 nm, and the absorbance of the irradiated reaction system at 450 nm was 0.2079. The fraction of light absorbed at 450 nm was calculated: $f = 1.0000 - 10^{-A} = 1.0000 - 10^{-0.2079} = 0.3804$.

The quantum yield was calculated: $\Phi = 0.15$

5.5.2. Determination of quantum yield of iodoalkylation reaction of oxabenzonorbornadienes

In an oven-dried reaction tube containing a magnetic stirring bar was charged with a sample of oxabenzonorbornadiene **1a** (0.20 mmol), acetonitrile iodide **4a** (0.40 mmol), LiOH (0.40 mmol), toluene (2 mL). The reaction mixture was stirred under the irradiation of 30 W LED at room temperature and placed 2 cm away from 30 W blue LEDs. After irradiation for 5 hours, the moles of product **5aa** formed for the model reaction were determined by determined by ^{1}H NMR spectroscopy with P-nitrotoluene as the internal standard revealed 95% yield of **5aa** (1.9×10^{-4} mol).

The quantum yield was calculated as follows:

$$\Phi = \frac{\text{mol product}}{\text{flux} \times \text{t} \times \text{f}}$$

where flux is the photon flux determined by ferrioxalate actinometry (**2.05×10^{-7}** Einstein/s), t is the time, and f is the fraction of light absorbed by the irradiated reaction system at 450 nm, and the absorbance of the irradiated reaction system at 450 nm was 0.0608. The fraction of light absorbed at 450 nm was calculated: $f = 1.0000 - 10^{-A} = 1.0000 - 10^{-0.0608} = 0.1306$.

The quantum yield was calculated: $\Phi = 0.39$

6. Crystallographic Data

6.1. Crystallographic Data of Substrate 5aa-*cis*

Sample preparation: The single crystal of compound **5aa-*cis*** was cultivated in a 1.5 mL glass vial by slow evaporation technique. Compound **5aa-*cis*** (40 mg) was dissolved in the mixing solvent of dichloromethane/hexane (0.2 mL/0.8 mL) at ambient temperature. Dichloromethane and hexane spontaneously evaporate in the open air at 25 °C. After several days, the crystal of **5aa-*cis*** emerged and was collected for X-ray diffraction analysis.

Suitable single crystals of **5aa-*cis*** were mounted with nylon loops. Data was collected on an Oxford Diffraction XtalAB [Rigaku (Cu) Xray dual wavelength source, Kα, $\lambda = 1.5418$ Å] equipped with a monochromator and CCD plate detector (CrysAlisPro CCD, Oxford Diffraction Ltd) at 100 K. The structure was solved by direct methods and refined by full-matrix least-squares refinements based on F^2 Single-crystal structures of compounds **5aa-*cis*** were solved by direct methods by ShelXS in

Olex2 1.2. All nonhydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Crystal data and structure refinement parameters were summarized in following Table. CCDC Number 2443197 (**5aa-*cis***) contain the supplementary crystallographic data for this paper.

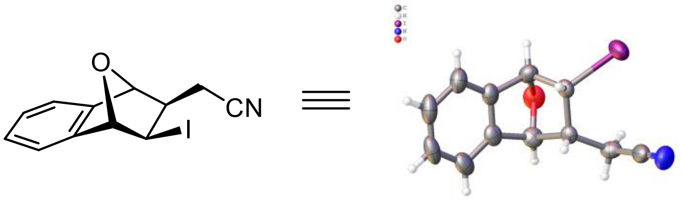


Table 1. Crystal data and structure refinement for 1120-A_auto (5aa-*cis*).

Identification code	1120-A_auto
Empirical formula	$C_{12}H_{10}INO$
Formula weight	311.11
Temperature/K	293
Crystal system	orthorhombic
Space group	Pbca
a/Å	12.7130(3)
b/Å	9.9112(3)
c/Å	17.8424(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2248.16(10)
Z	8
ρ_{calc}g/cm^3	1.838
μ/mm^{-1}	2.821
F(000)	1200.0
Crystal size/mm^3	0.06 × 0.05 × 0.04
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.93 to 58.678
Index ranges	$-16 \leq h \leq 16$, $-13 \leq k \leq 8$, $-23 \leq l \leq 23$
Reflections collected	16884
Independent reflections	2840 [R_{int} = 0.0272, R_{sigma} = 0.0200]
Data/restraints/parameters	2840/0/148
Goodness-of-fit on F^2	1.042
Final R indexes [I>=2σ (I)]	R_1 = 0.0338, wR_2 = 0.0705
Final R indexes [all data]	R_1 = 0.0568, wR_2 = 0.0811

Largest diff. peak/hole / e Å^{-3} 0.35/-0.82

Table 2. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1120-A_auto. U$_{eq}$ is defined as 1/3 of the trace of the orthogonalised U$_{IJ}$ tensor.

Atom	***x***	***y***	***z***	**U(eq)**
I1	2502.7(2)	5244.2(3)	5448.8(2)	59.39(12)
O1	3187(2)	4498(2)	3578.1(14)	49.4(6)
C9	2891(2)	6247(3)	4405.7(16)	34.5(6)
C5	3427(3)	6371(3)	2847.3(18)	41.7(7)
C4	4198(3)	6382(3)	3397.0(18)	41.2(7)
C10	2014(2)	6253(3)	3791.4(17)	32.8(6)
C11	921(3)	5643(4)	3998(2)	42.4(8)
N1	-82(3)	7282(4)	4847(2)	71.2(10)
C8	2578(3)	5466(3)	3158(2)	43.0(7)
C12	366(3)	6511(4)	4476(2)	50.4(9)
C7	3778(3)	5466(3)	4009(2)	43.0(8)
C6	3518(3)	7171(4)	2217.7(19)	53.0(9)
C3	5086(3)	7170(4)	3328(2)	54.0(9)
C1	4415(4)	7952(4)	2146(2)	62.4(11)
C2	5185(3)	7946(4)	2687(2)	63.4(11)

Table 3. Anisotropic Displacement Parameters (Å^2×10^3) for 1120-A_auto. The Anisotropic displacement factor exponent takes the form: -2π^2[h^{2}a*^{2}U$_{11}$+2hka*b*U$_{12}$+…].

Atom	**U$_{11}$**	**U$_{22}$**	**U$_{33}$**	**U$_{23}$**	**U$_{13}$**	**U$_{12}$**
I1	59.69(17)	76.5(2)	41.98(16)	18.75(12)	-0.45(12)	-7.67(13)
O1	61.6(15)	24.0(11)	62.7(16)	-1.8(11)	9.0(12)	5.6(10)
C9	40.7(15)	28.6(15)	34.2(16)	3.8(13)	2.1(13)	-6.2(13)
C5	50.4(19)	34.5(17)	40.4(18)	-7.5(14)	10.8(15)	6.2(14)
C4	45.6(18)	35.3(16)	42.8(18)	-2.5(15)	13.4(15)	4.4(14)
C10	38.0(16)	24.2(14)	36.2(17)	2.7(13)	3.4(13)	-1.3(12)
C11	45.4(19)	34.0(19)	48(2)	2.4(17)	-13.4(16)	-4.9(15)
N1	51(2)	102(3)	60(2)	1(2)	13.5(18)	12(2)
C8	51.9(19)	35.1(16)	41.8(18)	-10.1(14)	-0.6(15)	-1.2(15)
C12	36.4(17)	69(3)	46(2)	15.6(19)	-0.2(15)	-10.0(17)
C7	38.8(17)	39.9(18)	50(2)	6.8(16)	-0.6(15)	5.0(14)
C6	69(2)	54(2)	35.6(18)	-2.0(16)	13.1(17)	11.6(19)
C3	49(2)	56(2)	57(2)	-3.7(19)	16.9(18)	-4.5(17)
C1	83(3)	54(2)	51(2)	7.0(19)	35(2)	5(2)

C2	67(3)	54(2)	70(3)	-4(2)	37(2)	-11(2)

Table 4. Bond Lengths for 1120-A_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I1	C9	2.167(3)	C4	C3	1.379(5)
O1	C8	1.443(4)	C10	C11	1.559(5)
O1	C7	1.442(4)	C10	C8	1.549(4)
C9	C10	1.564(4)	C11	C12	1.402(5)
C9	C7	1.539(4)	N1	C12	1.160(5)
C5	C4	1.387(5)	C6	C1	1.384(6)
C5	C8	1.509(5)	C3	C2	1.385(6)
C5	C6	1.380(5)	C1	C2	1.374(6)
C4	C7	1.517(4)			

Table 5. Bond Angles for 1120-A_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C7	O1	C8	96.5(2)	C12	C11	C10	110.7(3)
C10	C9	I1	116.2(2)	O1	C8	C5	101.7(3)
C7	C9	I1	109.3(2)	O1	C8	C10	101.8(3)
C7	C9	C10	101.7(2)	C5	C8	C10	107.5(2)
C4	C5	C8	104.5(3)	N1	C12	C11	176.6(4)
C6	C5	C4	120.8(3)	O1	C7	C9	101.4(2)
C6	C5	C8	134.5(3)	O1	C7	C4	101.4(3)
C5	C4	C7	104.8(3)	C4	C7	C9	106.8(2)
C3	C4	C5	121.4(3)	C5	C6	C1	117.7(4)
C3	C4	C7	133.8(3)	C4	C3	C2	117.6(4)
C11	C10	C9	117.9(3)	C2	C1	C6	121.4(4)
C8	C10	C9	100.3(2)	C1	C2	C3	121.2(4)
C8	C10	C11	112.9(3)				

Table 6. Torsion Angles for 1120-A_auto.

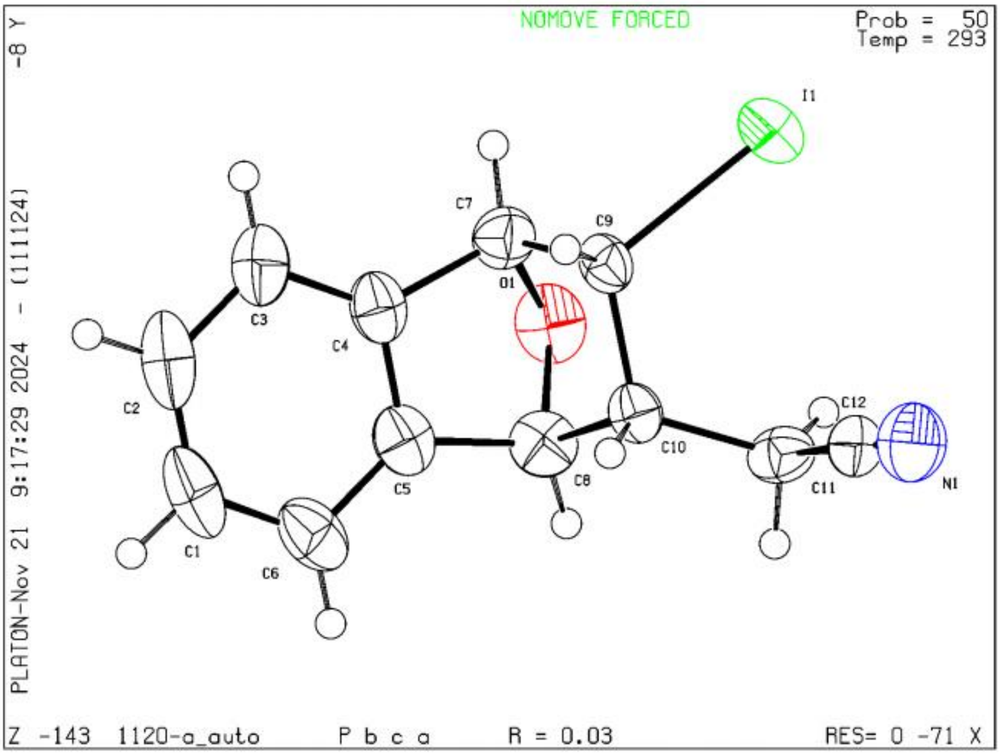
A	B	C	D	Angle/°	A	B	C	D	Angle/°
I1	C9	C10	C11	4.5(4)	C8	O1	C7	C9	58.3(3)
I1	C9	C10	C8	-118.6(2)	C8	O1	C7	C4	-51.6(3)
I1	C9	C7	O1	88.1(2)	C8	C5	C4	C7	0.6(3)
I1	C9	C7	C4	-166.2(2)	C8	C5	C4	C3	-176.5(3)
C9	C10	C11	C12	73.8(4)	C8	C5	C6	C1	175.4(3)
C9	C10	C8	O1	35.3(3)	C8	C10	C11	C12	-169.8(3)
C9	C10	C8	C5	-71.1(3)	C7	O1	C8	C5	52.3(3)
C5	C4	C7	O1	32.3(3)	C7	O1	C8	C10	-58.6(3)

C5	C4	C7	C9	-73.5(3)	C7	C9	C10	C11	123.0(3)
C5	C4	C3	C2	-0.4(5)	C7	C9	C10	C8	0.0(3)
C5	C6	C1	C2	-0.7(5)	C7	C4	C3	C2	-176.5(3)
C4	C5	C8	O1	-33.3(3)	C6	C5	C4	C7	176.0(3)
C4	C5	C8	C10	73.2(3)	C6	C5	C4	C3	-1.1(5)
C4	C5	C6	C1	1.6(5)	C6	C5	C8	O1	152.2(3)
C4	C3	C2	C1	1.4(6)	C6	C5	C8	C10	-101.3(4)
C10	C9	C7	O1	-35.3(3)	C6	C1	C2	C3	-0.8(6)
C10	C9	C7	C4	70.4(3)	C3	C4	C7	O1	-151.1(4)
C11	C10	C8	O1	-91.1(3)	C3	C4	C7	C9	103.1(4)
C11	C10	C8	C5	162.5(3)					

Table 7. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1120-A_auto.

Atom	***x***	***y***	***z***	**U(eq)**
H9	3120	7173.13	4507.34	41
H8	2108.38	5073.17	2781	52
H7	4311.92	5081.08	4342.44	52
H6	2994.41	7184.8	1853.63	64
H3	5600.55	7180.3	3698.71	65
H1	4497.45	8492.07	1724.31	75
H2	5783.36	8473	2620.12	76
H10	1900(20)	7100(30)	3656(16)	25(7)
H11A	900(20)	4940(30)	4153(16)	16(8)
H11B	630(20)	5570(30)	3611(18)	28(8)

Datablock 1120-a_auto - ellipsoid plot



6.2. Crystallographic Data of Substrate 5aa-*trans*

Sample preparation: The single crystal of compound **5aa-*trans*** was cultivated in a 1.5 mL glass vial by slow evaporation technique. Compound **5aa-*trans*** (40 mg) was dissolved in the mixing solvent of Dichloromethane/hexane (0.2 mL/0.8 mL) at ambient temperature. Dichloromethane and hexane spontaneously evaporate in the open air at 25 °C. After several days, the crystal of **5aa-*trans*** emerged and was collected for X-ray diffraction analysis.

Suitable single crystals of **5aa-*trans*** were mounted with nylon loops. Data was collected on an Oxford Diffraction XtalAB [Rigaku (Cu) Xray dual wavelength source, Kα, λ = 1.5418 Å] equipped with a monochromator and CCD plate detector (CrysAlisPro CCD, Oxford Diffraction Ltd) at 100 K. The structure was solved by direct methods and refined by full-matrix least-squares refinements based on F^2 Single-crystal structures of compounds **5aa-*trans*** were solved by direct methods by ShelXS in Olex2 1.2. All nonhydrogen atoms were refined with anisotropic thermal parameters, and all hydrogen atoms were included in calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Crystal data and structure refinement parameters were summarized in following Table. CCDC Number 2443198 (**5aa-*trans***) contain the supplementary crystallographic data for this paper.

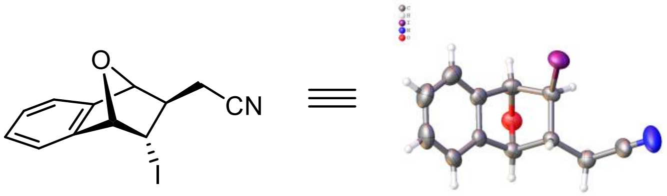


Table 8. Crystal data and structure refinement for 1120-B_auto (5aa-*trans*).

Identification code	1120-B_auto
Empirical formula	$C_{12}H_{10}INO$
Formula weight	311.11
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	13.9738(8)
b/Å	8.8365(4)
c/Å	9.5185(5)
α/°	90
β/°	101.071(6)
γ/°	90
Volume/Å^3	1153.47(11)
Z	4
ρ_{calc}g/cm^3	1.792
μ/mm^{-1}	2.749
F(000)	600.0
Crystal size/mm^3	0.07 × 0.06 × 0.05
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	6.644 to 58.608
Index ranges	$-18 \leq h \leq 19, -12 \leq k \leq 11, -11 \leq l \leq 12$
Reflections collected	9557
Independent reflections	2795 [R_{int} = 0.0395, R_{sigma} = 0.0392]
Data/restraints/parameters	2795/0/136
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0356, wR_2 = 0.0774
Final R indexes [all data]	R_1 = 0.0471, wR_2 = 0.0844
Largest diff. peak/hole / e Å^{-3}	0.38/-1.09

Table 9. Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for 1120-B_auto. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	***x***	***y***	***z***	**U(eq)**
I001	6722.0(2)	3322.6(3)	2656.2(2)	52.62(12)

O002	8796.4(16)	6053(3)	5426(2)	42.8(5)
C003	8022(2)	4429(3)	3725(3)	35.1(6)
C004	8330(2)	5843(3)	2952(3)	31.6(6)
C005	7469(2)	7457(4)	4410(3)	33.8(6)
C006	7125(2)	6204(4)	5054(3)	36.6(7)
C007	9287(2)	5609(4)	2409(3)	40.1(7)
N008	9145(3)	3555(4)	436(5)	76.1(12)
C009	7946(2)	5068(4)	5204(3)	39.7(7)
C00A	9211(2)	4451(4)	1311(4)	45.6(8)
C00B	8461(2)	7017(3)	4186(3)	36.3(7)
C00C	6894(3)	8731(4)	4059(3)	43.8(8)
C00D	6207(3)	6194(5)	5370(4)	51.4(9)
C00E	5976(3)	8724(5)	4391(4)	57.3(10)
C00F	5628(3)	7492(5)	5029(4)	57.5(10)

Table 10. Anisotropic Displacement Parameters (Å^2×10^3) for 1120-B_auto. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\dots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
I001	54.24(18)	43.74(17)	58.30(18)	-7.06(10)	6.81(12)	-15.88(10)
O002	38.6(12)	48.2(13)	35.9(11)	3.3(10)	-7.0(9)	0.7(10)
C003	33.1(15)	29.1(15)	40.5(15)	4.6(13)	0.6(12)	1.8(12)
C004	30.5(15)	28.7(15)	33.8(14)	1.7(12)	2.3(11)	1.2(11)
C005	39.4(17)	33.1(17)	27.8(13)	-5.8(12)	3.7(12)	1.7(13)
C006	41.4(18)	42.2(18)	24.6(13)	-1.2(13)	2.4(12)	-0.2(14)
C007	31.8(16)	44.3(19)	43.0(16)	0.8(14)	3.6(13)	0.3(14)
N008	61(2)	68(3)	104(3)	-39(2)	27(2)	-5.8(18)
C009	43.9(18)	39.0(18)	34.1(14)	9.1(13)	2.2(13)	-1.1(14)
C00A	33.9(17)	41.4(19)	63(2)	-4.5(17)	14.0(15)	4.1(14)
C00B	40.0(17)	32.1(16)	34.0(15)	1.7(13)	0.4(13)	-2.4(13)
C00C	57(2)	33.3(17)	41.0(17)	-3.4(14)	8.2(15)	5.7(15)
C00D	54(2)	63(2)	39.3(17)	-3.9(17)	13.1(16)	-8.7(19)
C00E	54(2)	63(2)	54(2)	-10.0(19)	7.8(18)	23(2)
C00F	44(2)	76(3)	56(2)	-8(2)	17.8(17)	9(2)

Table 11. Bond Lengths for 1120-B_auto.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
I001	C003	2.140(3)	C005	C00C	1.386(4)
O002	C009	1.455(4)	C006	C009	1.510(4)
O002	C00B	1.458(3)	C006	C00D	1.373(5)
C003	C004	1.553(4)	C007	C00A	1.453(5)

C003	C009	1.539(4)	N008	C00A	1.139(4)
C004	C007	1.536(4)	C00C	C00E	1.379(5)
C004	C00B	1.552(4)	C00D	C00F	1.406(6)
C005	C006	1.394(4)	C00E	C00F	1.379(6)
C005	C00B	1.494(4)			

Table 12. Bond Angles for 1120-B_auto.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C009	O002	C00B	96.1(2)	C00A	C007	C004	112.9(3)
C004	C003	I001	115.46(18)	O002	C009	C003	98.9(2)
C009	C003	I001	113.7(2)	O002	C009	C006	101.6(2)
C009	C003	C004	102.3(2)	C006	C009	C003	110.0(2)
C007	C004	C003	112.9(2)	N008	C00A	C007	179.0(4)
C007	C004	C00B	111.2(2)	O002	C00B	C004	101.2(2)
C00B	C004	C003	100.5(2)	O002	C00B	C005	101.5(2)
C006	C005	C00B	105.3(3)	C005	C00B	C004	107.7(2)
C00C	C005	C006	121.2(3)	C00E	C00C	C005	117.5(3)
C00C	C005	C00B	133.4(3)	C006	C00D	C00F	117.7(4)
C005	C006	C009	104.5(3)	C00C	C00E	C00F	121.8(4)
C00D	C006	C005	121.1(3)	C00E	C00F	C00D	120.6(4)
C00D	C006	C009	134.4(3)				

Table 13. Torsion Angles for 1120-B_auto.

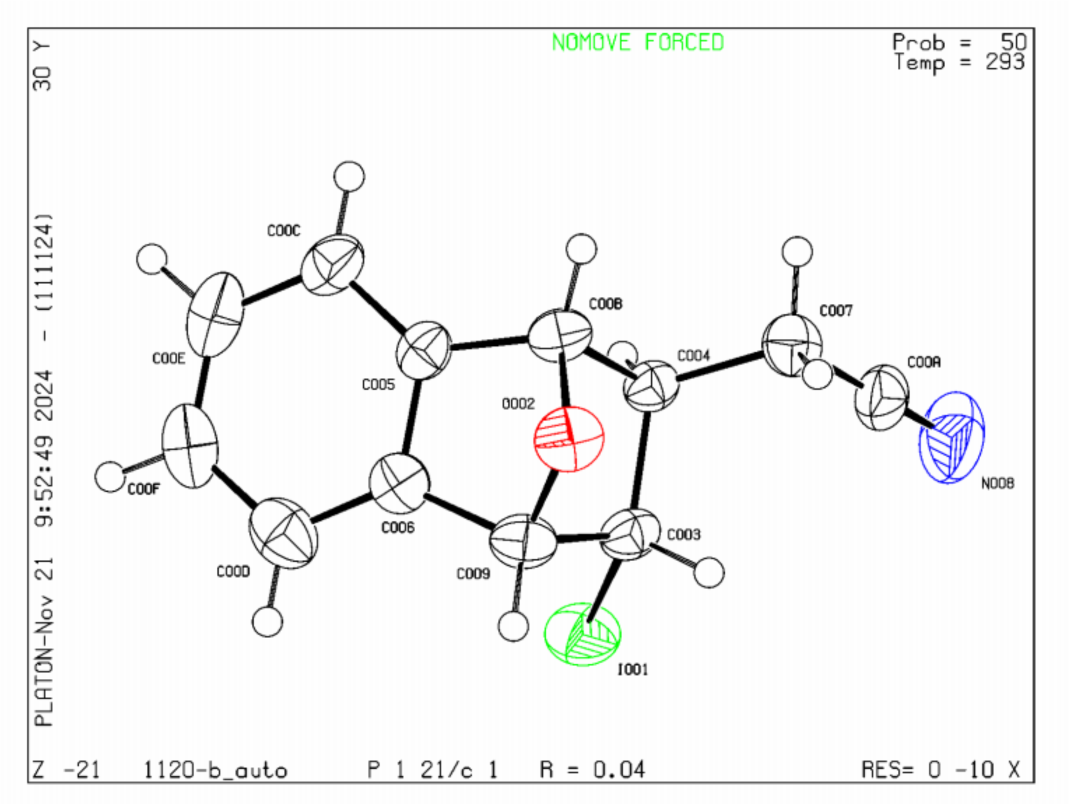
A	B	C	D	Angle/°	A	B	C	D	Angle/°
I001	C003	C004	C007	-113.0(2)	C009	O002	C00B	C004	-58.8(3)
I001	C003	C004	C00B	128.5(2)	C009	O002	C00B	C005	52.1(3)
I001	C003	C009	O002	-165.24(17)	C009	C003	C004	C007	123.0(3)
I001	C003	C009	C006	-59.4(3)	C009	C003	C004	C00B	4.6(3)
C003	C004	C007	C00A	64.4(3)	C009	C006	C00D	C00F	-178.2(3)
C003	C004	C00B	O002	32.4(3)	C00B	O002	C009	C003	61.1(2)
C003	C004	C00B	C005	-73.7(3)	C00B	O002	C009	C006	-51.5(2)
C004	C003	C009	O002	-40.1(3)	C00B	C004	C007	C00A	176.5(3)
C004	C003	C009	C006	65.7(3)	C00B	C005	C006	C009	0.8(3)
C005	C006	C009	O002	32.3(3)	C00B	C005	C006	C00D	-177.7(3)
C005	C006	C009	C003	-71.7(3)	C00B	C005	C00C	C00E	177.5(3)
C005	C006	C00D	C00F	-0.3(5)	C00C	C005	C006	C009	178.0(3)
C005	C00C	C00E	C00F	-1.1(5)	C00C	C005	C006	C00D	-0.4(4)
C006	C005	C00B	O002	-33.5(3)	C00C	C005	C00B	O002	149.7(3)
C006	C005	C00B	C004	72.3(3)	C00C	C005	C00B	C004	-104.4(4)
C006	C005	C00C	C00E	1.1(4)	C00C	C00E	C00F	C00D	0.4(6)

C006	C00D	C00F	C00E	0.3(5)	C00D	C006	C009	O002	-149.5(3)
C007	C004	C00B	O002	-87.4(3)	C00D	C006	C009	C003	106.5(4)
C007	C004	C00B	C005	166.6(2)					

Table 14. Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 1120-B_auto.

Atom	*x*	*y*	*z*	U(eq)
H003	8557.44	3696.07	3851.52	42
H004	7806.07	6154.22	2166.39	38
H00A	9474.24	6557.59	2025.65	48
H00B	9796.46	5328.46	3209.16	48
H009	7945.95	4304.42	5950.44	48
H00C	8892.93	7867.11	4082.47	44
H00D	7118.92	9559.7	3614.58	53
H00E	5976.68	5356.88	5794.97	62
H00F	5581.04	9572.63	4180.55	69
H00G	5003.58	7520.83	5234.23	69

Datablock 1120-b_auto - ellipsoid plot



7. DFT calculation

Computational methods

All density functional theory (DFT) calculations were performed to understand the origin of the enantioselectivity. B3LYP-D3[3] method combined with a Def2-SVP basis set[4] for all atoms were used to fully optimize all structures in the gas-phase. Then, vibrational frequency calculations on these optimized geometries were carried out at the same level of theory to confirm no imaginary frequency for all local minimum, and one appropriate imaginary frequency for each transition state. To obtain higher accurate energies, the Def2-TZVP basis set was also used for the single-point energy calculations in PCM solvent model[5] using CH_3CN solution. The single-point energy calculations are also performed using basis sets (Def2-TZVP) for all atoms to obtain more accurate electronic energies. To examine the effect of DFT functional, a few other common and reliable M06-2X, PBE0-D3, and B97X-D methods[6] were also used for the single-point energy calculations on the key intermediates and transition states in CH_3CN solution. All DFT calculations were carried out by Gaussian16 program.[7] All 3D images of the optimized structures were shown by CYLview.[8] All free energies are corrected with Grimme's quasi-harmonic approximation for vibrational entropy correction at all frequencies below than 100 cm^{-1} by GoodVibes using default settings.[9] The steric maps were generated by SambVca 2.0 program.[10] The distance of the coordination point from the center of the sphere is defined as 2.2 Angstrom, and the value of mesh spacing for numbering integration is defined as 0.050. Other default parameters are used.

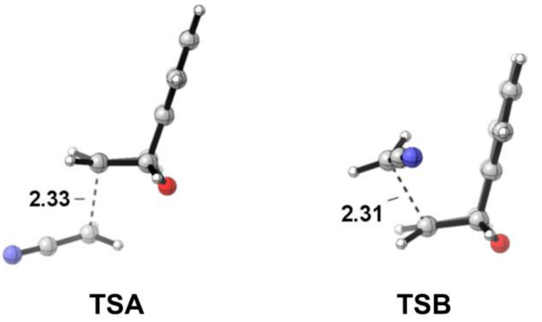
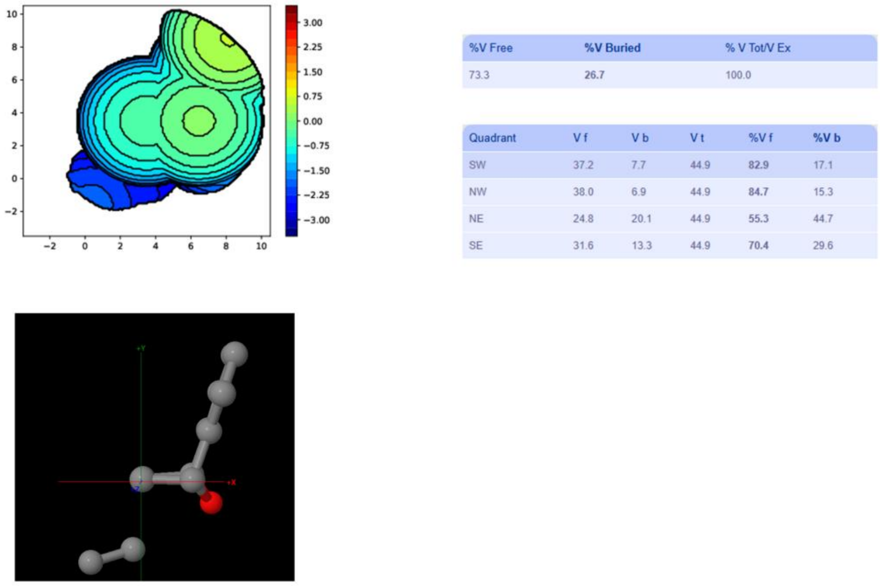


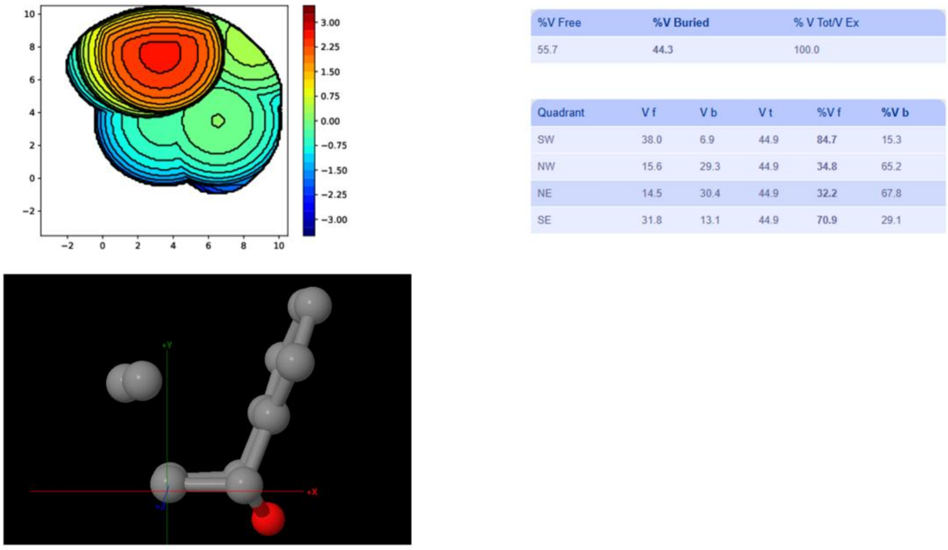
Figure 15. 3D geometrical structures for TSA and TSB with bond distances (Å).



%V Free	%V Buried	% V Tot/V Ex
73.3	26.7	100.0

Quadrant	V f	V b	V t	%V f	%V b
SW	37.2	7.7	44.9	82.9	17.1
NW	38.0	6.9	44.9	84.7	15.3
NE	24.8	20.1	44.9	55.3	44.7
SE	31.6	13.3	44.9	70.4	29.6

Figure 16. Steric map of Mn-ligand part and substrate for **TSA** with the computed buried volumes (in %).



%V Free	%V Buried	% V Tot/V Ex
55.7	44.3	100.0

Quadrant	V f	V b	V t	%V f	%V b
SW	38.0	6.9	44.9	84.7	15.3
NW	15.6	29.3	44.9	34.8	65.2
NE	14.5	30.4	44.9	32.2	67.8
SE	31.8	13.1	44.9	70.9	29.1

Figure 17. Steric map of Mn-ligand part and substrate for **TSB** with the computed buried volumes (in %).

Table 15. The relative corrected free energies (in kcal/mol) of transition states (**TSA** and **TSB**) in CH_3CN solution evaluated by the other PCM DFTs/Def2-TZVP methods based on the B3LYP-D3/Def2-SVP-optimized structures in gas-phase.

	DG$_{soln}$ (B3LYP-D3)	**DG$_{soln}$ (M06-2X)**	**DG$_{soln}$ (PBE0-D3)**	**DG$_{soln}$ (wB97X-D)**
Sub	0.0	0.0	0.0	0.0
TSA	14.5	16.8	13.7	16.2
TSB	17.4	19.2	16.6	18.8
DDG	2.9	2.5	2.9	2.6

Table 16. The absolute electronic and corrected free energies (in Hartree) of the optimized structures of intermediates and transition states by the B3LYP-D3 method in gas-phase. The free energies (G-qh) are corrected with the quasi-harmonic entropy correction.

	E$_{gas}$	**G$_{gas}$-qh**
CH_2CN	-131.99585	-131.98929
Sub	-460.71165	-460.59169
TSA	-592.70894	-592.56146
TSB	-592.70579	-592.55748

Table 17. The absolute electronic energies (in Hartree) for transition states (**TSA** and **TSB**) evaluated by the other PCM(CH_3CN) DFTs/def2-TZVP methods based on the B3LYP-D3/def2-SVP-optimized structures in gas-phase.

	E$_{soln}$ (B3LYP-D3)	**E$_{soln}$ (M06-2X)**	**E$_{soln}$ (PBE0-D3)**	**E$_{soln}$ (wB97X-D)**
Sub	-132.15616	-132.09032	-131.98954	-132.09847
Mn6-fac	-461.22161	-461.02134	-460.67880	-461.04950
6TS-R	-593.37562	-593.10593	-592.66740	-593.14307
6TS-S	-593.37190	-593.10281	-592.66363	-593.13976

Cartesian coordinates XYZs

CH_2CN.xyz

C	0.000712	1.197239	0.000000
H	0.000557	1.746584	0.944438
H	0.000557	1.746584	-0.944438
C	0.000000	-0.188913	0.000000
N	-0.000770	-1.363303	0.000000

Sub.xyz

C	-1.267419	1.069643	0.352384
C	-1.267460	-1.069509	0.352592
C	-1.986973	0.668471	-0.954444
H	-2.326403	1.356125	-1.728835
C	-1.987079	-0.668696	-0.954245
H	-2.326708	-1.356415	-1.728487
H	-1.494009	2.054161	0.779455
H	-1.493975	-2.053925	0.779937
C	0.215630	-0.703878	0.161519
C	1.385174	-1.421850	-0.003126
C	0.215690	0.703988	0.161511
C	2.586618	-0.697421	-0.164134
H	1.391674	-2.515181	-0.002617
C	1.385309	1.421827	-0.003156

C	2.586682	0.697268	-0.164141
H	3.529044	-1.237706	-0.285708
H	1.391926	2.515157	-0.002702
H	3.529159	1.237461	-0.285720
O	-1.674718	0.000159	1.220764

TSA.xyz

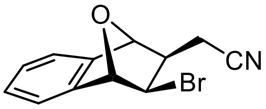
C	-0.024506	-1.220371	0.684974
C	0.201289	0.912527	0.571173
C	0.898944	-0.987083	-0.517837
H	1.236374	-1.744432	-1.224268
C	1.098266	0.366592	-0.565778
H	1.420517	0.940164	-1.434548
H	0.028462	-2.187138	1.199603
H	0.452490	1.896646	0.984251
C	-1.255013	0.671582	0.152321
C	-2.296115	1.486327	-0.253489
C	-1.408183	-0.725643	0.232979
C	-3.523263	0.871642	-0.581361
H	-2.184015	2.571943	-0.315603
C	-2.603749	-1.338049	-0.097493
C	-3.673804	-0.513741	-0.504847
H	-4.367787	1.489798	-0.896178
H	-2.727652	-2.422574	-0.040090
H	-4.635109	-0.966881	-0.759947
O	0.364623	-0.131502	1.545123
C	3.147482	0.775802	0.460299
H	2.814073	0.309483	1.388583
H	3.099769	1.865948	0.396037
C	4.101847	0.113502	-0.330518
N	4.852389	-0.454209	-1.023051

TSB.xyz

C	0.498370	1.000334	1.088669
C	-1.037287	1.902419	-0.107234
C	1.240442	1.500828	-0.189799
H	2.305574	1.723389	-0.220199
C	0.249056	2.102770	-0.922594
H	0.328113	2.617689	-1.879785
H	1.103533	0.890416	1.994994
H	-1.854499	2.610257	-0.290977
C	-1.379971	0.408842	-0.128871
C	-2.353548	-0.359175	-0.746263
C	-0.388728	-0.178182	0.677686
C	-2.334741	-1.750139	-0.517797
H	-3.122727	0.090503	-1.379766
C	-0.357248	-1.544095	0.901565
C	-1.357184	-2.330567	0.294390
H	-3.100347	-2.381407	-0.976059
H	0.424129	-2.002841	1.510701
H	-1.365744	-3.410635	0.460885
O	-0.502765	2.026938	1.225784
C	1.890356	-0.379285	-1.372141
H	0.898603	-0.748809	-1.636578
H	2.458189	0.135681	-2.150350
C	2.610865	-1.092810	-0.397736
N	3.180716	-1.632197	0.468802

8. Characterization data of products

2-((1*S*,2*R*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetonitrile (3aa-*cis*)



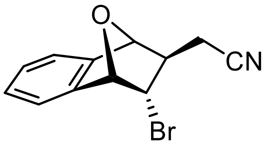
72% yield, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.31 (m, 2H), 7.25 – 7.21 (m, 2H), 5.45 (s, 1H), 5.29 (s, 1H), 4.13 (d, *J* = 7.1 Hz, 1H), 2.76 – 2.73 (m, 2H), 2.34 (dt, *J* = 9.0, 7.0 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 144.0, 142.0, 128.4, 127.9, 120.4, 119.9, 119.1, 88.0, 83.1, 51.6, 41.3, 22.9.

MP: 132°C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{10}BrNO$ 264.0019; Found 264.0013.

2-((1*S*,2*R*,3*S*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetonitrile (3aa-*trans*)



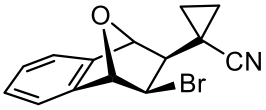
9% yield, white solid, ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.42 – 7.40 (m, 1H), 7.36 – 7.33 (m, 1H), 7.29 (dd, *J* = 5.4, 3.1 Hz, 2H), 5.41 (d, *J* = 4.6 Hz, 1H), 5.19 (s, 1H), 3.91 (dd, *J* = 4.6, 3.3 Hz, 1H), 2.76 (dd, *J* = 16.6, 6.7 Hz, 1H), 2.68 (dd, *J* = 16.7, 8.9 Hz, 1H), 2.17 (ddd, *J* = 8.9, 6.5, 3.3 Hz, 1H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 143.2, 141.1, 128.1, 127.1, 123.1, 119.2, 117.6, 82.9, 82.8, 48.3, 46.3, 20.8.

MP: 95°C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{10}BrNO$ 264.0019; Found 264.0018.

1-((1*S*,2*R*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)cyclopropane-1-carbonitrile (3ab-*cis*)



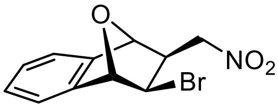
29% yield, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.40 (m, 1H), 7.29 – 7.26 (m, 3H), 5.45 (d, *J* = 4.6 Hz, 1H), 5.31 (s, 1H), 4.29 (t, *J* = 4.3 Hz, 1H), 1.49 (d, *J* = 3.9 Hz, 1H), 1.46 – 1.37 (m, 2H), 1.22 – 1.15 (m, 1H), 1.08 – 1.00 (m, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 144.1, 141.5, 127.9, 127.1, 123.3, 121.7, 118.7, 82.9, 82.3, 56.4, 45.2, 13.6, 13.1, 11.9.

MP: 102°C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{14}H_{12}BrNO$ 290.0175; Found 290.0184.

(1*S*,2*R*,3*R*,4*S*)-2-bromo-3-(nitromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3ac-*cis*)



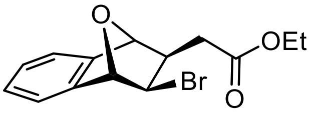
62% yield, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.34 (m, 1H), 7.33 – 7.31 (m, 1H), 7.27 (d, *J* = 2.4 Hz, 1H), 7.26 – 7.24 (m, 1H), 5.50 (s, 1H), 5.29 (s, 1H), 4.82 (dd, *J* = 14.3, 5.5 Hz, 1H), 4.68 (dd, *J* = 14.3, 9.6 Hz, 1H), 4.21 (d, *J* = 7.3 Hz, 1H), 2.84 (ddd, *J* = 9.7, 7.3, 5.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.0, 141.7, 128.5, 127.9, 120.5, 119.8, 87.7, 81.9, 78.4, 50.0, 42.0.

MP: 132^{o}C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{11}H_{10}BrNO_3$ 283.9917; Found 283.9921.

ethyl 2-((1*S*,2*R*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetate (3ad-*cis*)

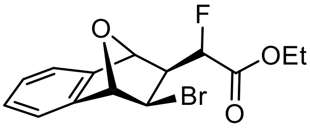


43% yield, light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.28 (m, 2H), 7.24 – 7.18 (m, 2H), 5.45 (s, 1H), 5.16 (s, 1H), 4.21 – 4.16 (m, 3H), 2.86 (dd, *J* = 17.3, 6.6 Hz, 1H), 2.74 (dd, *J* = 17.2, 9.0 Hz, 1H), 2.46 (dt, *J* = 8.9, 6.9 Hz, 1H), 1.29 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.6, 145.6, 142.0, 128.0, 127.3, 120.4, 119.4, 87.8, 83.8, 60.8, 53.4, 40.6, 38.9, 14.3.

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{14}H_{15}BrO_3$ 311.0277; Found 311.0284.

ethyl (*S*)-2-((1*S*,2*S*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)-2-fluoroacetate (3ae-*cis*)



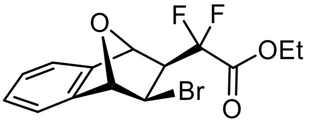
33% yield, white oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 6.9, 1.5 Hz, 1H), 7.24 – 7.15 (m, 3H), 5.49 (s, 1H), 5.45 (d, *J* = 2.1 Hz, 1H), 5.06 (dd, *J* = 46.9, 9.0 Hz, 1H), 4.22 (tdq, *J* = 10.4, 6.5, 3.7 Hz, 2H), 4.08 (d, *J* = 7.3 Hz, 1H), 2.61 (ddd, *J* = 12.7, 9.0, 7.3 Hz, 1H), 1.27 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.0 (d, *J* = 22.0 Hz), 144.9, 142.0, 128.3, 127.6, 120.6, 119.5, 91.3 (d, *J* = 177.1 Hz), 87.5, 80.2 (d, *J* = 5.7 Hz), 62.1, 49.0 (d, *J* = 6.1 Hz), 45.8 (d, *J* = 23.2 Hz), 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -186.72.

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{14}H_{14}BrFO_3$ 329.0183; Found 329.0175.

ethyl 2-((1*S*,2*S*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)-2,2-difluoroacetate (3af-*cis*)

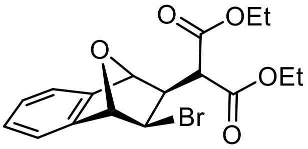


44% yield, white oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (dd, *J* = 5.7, 2.8 Hz, 1H), 7.37 – 7.28 (m, 3H), 5.56 (s, 1H), 5.40 (d, *J* = 4.6 Hz, 1H), 4.48 (t, *J* = 4.4 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 2.49 (ddd, *J* = 16.4, 9.9, 4.1 Hz, 1H), 1.38 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (t, *J* = 32.0 Hz), 143.2, 141.8, 128.2, 127.3, 123.3, 119.0, 115.1 (dd, *J* = 255.6, 253.3 Hz), 82.0, 79.5 (dd, *J* = 5.1, 2.3 Hz), 63.6, 56.2 (t, *J* = 24.0 Hz), 40.2 (t, *J* = 3.0 Hz), 14.0.

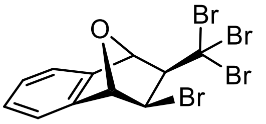
^{19}F NMR (376 MHz, CDCl$_3$) δ -107.49 (d, J = 256.0 Hz), -109.47 (d, J = 255.7 Hz).
HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{14}H_{13}BrF_2O_3$ 347.0089; Found 347.0090.

diethyl 2-((1*S*,2*R*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)malonate (3ag-*cis*)



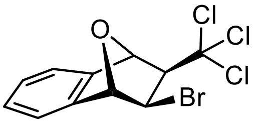
66% yield, white oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 – 7.27 (m, 1H), 7.21 – 7.15 (m, 3H), 5.43 (s, 1H), 5.11 (s, 1H), 4.30 – 4.21 (m, 3H), 4.15 (qd, J = 7.2, 1.5 Hz, 2H), 3.88 (d, J = 12.1 Hz, 1H), 2.74 (dd, J = 12.1, 6.9 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 168.8, 168.2, 145.8, 141.5, 128.2, 127.5, 120.7, 119.2, 87.8, 81.8, 62.1, 61.9, 56.2, 53.0, 45.0, 14.2, 14.0.
HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{17}H_{19}BrO_5$ 383.0489; Found 383.0480.

(1*S*,2*R*,3*R*,4*S*)-2-bromo-3-(tribromomethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3ah-*cis*)



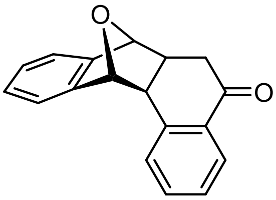
65% yield, yellow oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.44 (m, 1H), 7.41 (dd, J = 6.0, 2.5 Hz, 1H), 7.33 – 7.30 (m, 2H), 5.56 (d, J = 4.6 Hz, 1H), 5.49 (s, 1H), 4.31 (t, J = 4.5 Hz, 1H), 3.23 (d, J = 4.3 Hz, 1H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 143.5, 142.4, 128.1, 127.2, 123.6, 118.8, 84.0, 83.5, 73.3, 46.4, 40.0.
HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{11}H_8Br_4O$ 472.7381; Found 472.7376.

(1*S*,2*R*,3*S*,4*S*)-2-bromo-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3ai-*cis*)



88% yield, light yellow oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.48 – 7.44 (m, 1H), 7.39 (dd, J = 6.0, 2.5 Hz, 1H), 7.33 – 7.30 (m, 2H), 5.54 (s, 1H), 5.49 (d, J = 4.6 Hz, 1H), 4.45 (t, J = 4.5 Hz, 1H), 3.02 (d, J = 4.3 Hz, 1H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 143.7, 142.3, 128.2, 127.3, 123.6, 118.9, 99.2, 83.1, 82.5, 71.2, 44.5.
HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{11}H_8BrCl_3O$ 340.8897; Found 340.8888.

6a,7,12,12a-tetrahydro-7,12-epoxytetraphen-5(6H)-one (3aj')



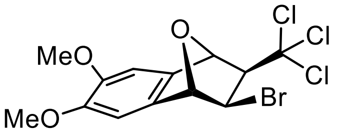
75% yield, yellow solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.60 (td, *J* = 7.5, 1.5 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.41 – 7.31 (m, 3H), 7.25 – 7.20 (m, 2H), 5.19 (s, 1H), 5.00 (s, 1H), 3.26 (d, *J* = 7.8 Hz, 1H), 2.94 (dd, *J* = 15.3, 2.9 Hz, 1H), 2.83 (dd, *J* = 15.3, 8.3 Hz, 1H), 2.54 (td, *J* = 8.1, 2.9 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 198.2, 145.1, 144.4, 143.0, 134.7, 133.6, 129.1, 127.3, 127.3, 126.9, 125.8, 119.4, 119.4, 87.8, 86.4, 43.9, 42.2, 37.7.

MP: 61°C

HRMS (ESI$^+$) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{14}O_2$ 285.0886; Found 4285.0894.

(1*S*,2*R*,3*S*,4*S*)-2-bromo-6,7-dimethoxy-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3bi-*cis*)



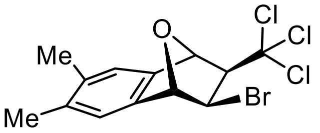
87% yield, yellow solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.02 (s, 1H), 6.94 (s, 1H), 5.45 – 5.41 (m, 2H), 4.41 (t, *J* = 4.3 Hz, 1H), 3.91 (s, 6H), 2.96 (d, *J* = 4.2 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 149.1, 148.3, 136.0, 134.6, 107.7, 102.9, 99.3, 83.3, 82.7, 71.5, 56.4, 56.3, 45.4.

MP: 118°C

HRMS (ESI$^+$) m/z: [M + Na]$^+$ Calcd for $C_{13}H_{12}BrCl_3O_3$ 422.8928; Found 422.8920.

(1*S*,2*R*,3*S*,4*S*)-2-bromo-6,7-dimethyl-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3ci-*cis*)



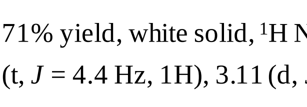
86% yield, yellow solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.22 (s, 1H), 7.16 (s, 1H), 5.46 (s, 1H), 5.42 (d, *J* = 4.5 Hz, 1H), 4.42 (t, *J* = 4.4 Hz, 1H), 2.99 (d, *J* = 4.3 Hz, 1H), 2.30 (s, 6H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 141.5, 139.9, 136.5, 135.6, 124.7, 120.1, 99.4, 83.0, 82.4, 71.5, 45.1, 20.2.

MP: 114°C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{13}H_{12}BrCl_3O$ 368.9210; Found 368.9217.

(1*S*,2*R*,3*S*,4*S*)-2-bromo-6,7-difluoro-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3di-*cis*)



71% yield, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.00 – 6.97 (m, 2H), 5.77 – 5.74 (m, 2H), 4.45 (t, *J* = 4.4 Hz, 1H), 3.11 (d, *J* = 4.3 Hz, 1H).

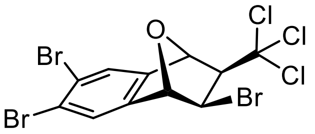
^{13}C NMR (101 MHz, CDCl$_3$) δ 153.6 (dd, *J* = 246.9, 2.5 Hz), 150.4 (dd, *J* = 245.6, 2.5 Hz), 131.6 (dd, *J* = 22.3, 4.2 Hz), 131.0 (dd, *J* = 22.3, 4.1 Hz), 117.8 (dd, *J* = 23.6, 7.0 Hz), 117.3 (dd, *J* = 24.1, 6.9 Hz), 98.3, 81.3 (d, *J* = 2.8 Hz), 79.9 (d, *J* = 1.7 Hz), 70.7, 43.4.

^{19}F NMR (376 MHz, CDCl$_3$) δ -122.95 (d, *J* = 23.9 Hz), -124.63 (d, *J* = 23.6 Hz).

MP: 74^{o}C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{11}H_6BrCl_3F_2O$ 376.8708; Found 376.8715.

(1*S*,2*R*,3*S*,4*S*)-2,6,7-tribromo-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3ei-*cis*)



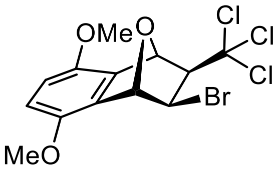
83% yield, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.67 (d, *J* = 16.6 Hz, 2H), 5.48 (s, 1H), 5.44 (d, *J* = 4.6 Hz, 1H), 4.41 (t, *J* = 4.5 Hz, 1H), 3.01 (d, *J* = 4.4 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 144.4, 143.3, 128.7, 124.4, 124.4, 123.7, 98.6, 82.6, 81.8, 70.8, 43.5.

MP: 109^{o}C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{11}H_6Br_3Cl_3O$ 496.7107; Found 496.7117.

(1*S*,2*R*,3*S*,4*S*)-2-bromo-5,8-dimethoxy-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3fi-*cis*)



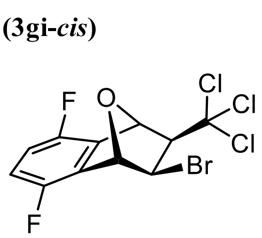
84% yield, yellow solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.77 (d, *J* = 1.6 Hz, 2H), 5.71 (d, *J* = 4.5 Hz, 1H), 5.67 (s, 1H), 4.41 (t, *J* = 4.3 Hz, 1H), 3.85 (d, *J* = 6.7 Hz, 6H), 3.07 (d, *J* = 4.3 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 149.3, 146.1, 132.5, 131.9, 112.5, 112.2, 99.2, 81.3, 80.5, 70.9, 56.3, 56.1, 44.6.

MP: 103^{o}C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{13}H_{12}BrCl_3O_3$ 400.9108; Found 400.9109.

(1*S*,2*R*,3*S*,4*S*)-2-bromo-5,8-difluoro-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3gi-*cis*)



74% yield, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 6.98 (m, *J* = 4.5 Hz, 2H), 5.77 – 5.74 (m, 2H), 4.44 (t, *J* = 4.4 Hz, 1H), 3.11 (d, *J* = 4.3 Hz, 1H).

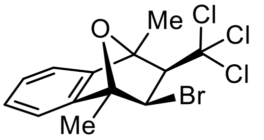
^{13}C NMR (101 MHz, CDCl$_3$) δ 153.6 (dd, *J* = 247.0, 2.5 Hz), 150.4 (dd, *J* = 245.6, 2.5 Hz), 131.6 (dd, *J* = 22.3, 4.2 Hz), 131.1 (dd, *J* = 22.3, 4.0 Hz), 117.8 (dd, *J* = 23.6, 7.1 Hz), 117.3 (dd, *J* = 24.2, 6.9 Hz), 98.3, 81.3 (d, *J* = 2.8 Hz), 79.9 (d, *J* = 1.6 Hz), 70.7, 43.4.

^{19}F NMR (376 MHz, CDCl$_3$) δ -122.94 (d, *J* = 23.4 Hz), -124.61 (d, *J* = 23.8 Hz).

MP: 83°C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{11}H_6BrCl_3F_2O$ 376.8708; Found 376.8706.

(1*S*,2*R*,3*S*,4*S*)-2-bromo-1,4-dimethyl-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (3hi-*cis*)



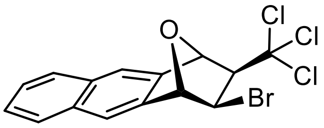
50% yield, yellow solid, ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.33 – 7.29 (m, 3H), 7.25 – 7.23 (m, 1H), 4.25 (d, *J* = 4.5 Hz, 1H), 3.07 (d, *J* = 4.5 Hz, 1H), 2.05 (s, 3H), 1.88 (s, 3H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 147.9, 145.5, 128.0, 127.2, 121.9, 117.9, 99.1, 87.3, 87.0, 72.7, 54.6, 16.4, 15.1.

MP: 119°C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{13}H_{12}BrCl_3O$ 368.9210; Found 368.9217.

(1*S*,2*R*,3*S*,4*S*)-2-bromo-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxyanthracene (3ii-*cis*)



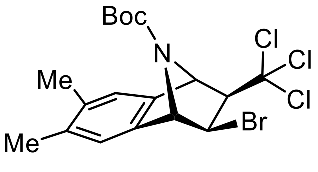
61% yield, yellow solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.92 – 7.85 (m, 3H), 7.78 (s, 1H), 7.56 – 7.53 (m, 2H), 5.67 (s, 1H), 5.60 (d, *J* = 4.7 Hz, 1H), 4.53 (t, *J* = 4.6 Hz, 1H), 3.15 (d, *J* = 4.6 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 140.9, 139.1, 133.1, 132.7, 128.6, 128.4, 126.7, 126.6, 122.5, 117.6, 99.2, 83.2, 82.4, 71.7, 45.0.

MP: 117°C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{15}H_{10}BrCl_3O$ 390.9053; Found 390.9051.

tert-butyl (1*S*,2*R*,3*S*,4*S*)-2-bromo-6,7-dimethyl-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3ji-*cis*)



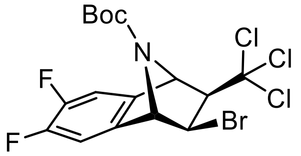
80% yield, white solid, ^{1}H NMR (600 MHz, CDCl$_3$) δ 7.21 (s, 1H), 7.15 (s, 1H), 5.32 – 5.15 (m, 2H), 4.50 (t, *J* = 4.2 Hz, 1H), 2.87 (d, *J* = 4.4 Hz, 1H), 2.28 (s, 6H), 1.35 (s, 9H).

^{13}C NMR (151 MHz, CDCl$_3$) δ 152.9 (d, *J* = 50.8 Hz), 141.6 (d, *J* = 91.1 Hz), 139.9 (d, *J* = 86.7 Hz), 136.1, 135.1, 125.4 (d, *J* = 77.3 Hz), 120.9 (d, *J* = 87.8 Hz), 99.2, 81.0, 71.6 (d, *J* = 118.6 Hz), 65.7 (d, *J* = 170.5 Hz), 64.1 (d, *J* = 81.4 Hz), 45.9 (d, *J* = 33.5 Hz), 28.2, 20.1 (d, *J* = 1.8 Hz).

MP: 140°C

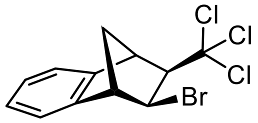
HRMS (ESI$^+$) m/z: [M + Na]$^+$ Calcd for $C_{18}H_{21}BrCl_3NO_2$ 489.9713; Found 489.9721.

tert-butyl (1*S*,2*R*,3*S*,4*S*)-2-bromo-6,7-difluoro-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epiminonaphthalene-9-carboxylate (3ki-*cis*)



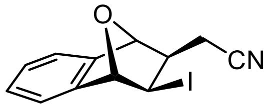
75% yield, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.28 (dd, *J* = 8.8, 6.9 Hz, 1H), 7.22 (dd, *J* = 8.7, 6.8 Hz, 1H), 5.32 – 5.20 (m, 2H), 4.50 (t, *J* = 4.4 Hz, 1H), 2.85 (d, *J* = 4.4 Hz, 1H), 1.35 (s, 9H).
^{13}C NMR (151 MHz, CDCl$_3$) δ 153.0, 150.5 (dd, *J* = 76.6, 13.6 Hz), 148.8 (dd, *J* = 76.0, 13.5 Hz), 139.9 (d, *J* = 98.0 Hz), 138.7 (d, *J* = 76.3 Hz), 114.1, 110.0, 98.5, 81.8, 71.0 (d, *J* = 96.8 Hz), 65.8 (d, *J* = 123.9 Hz), 64.0, 44.8, 28.1.
^{19}F NMR (376 MHz, CDCl$_3$) δ -136.71 (d, *J* = 19.2 Hz), -137.94 (d, *J* = 19.1 Hz).
MP: 131^{o}C
HRMS (ESI$^+$) m/z: [M + Na]$^+$ Calcd for $C_{16}H_{15}BrCl_3F_2NO_2$ 497.9212; Found 497.9203.

(1*S*,2*S*,3*S*,4*S*)-2-bromo-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-methanonaphthalene (3li-*cis*)



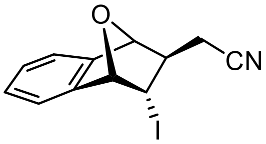
81% yield, white oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.34 (m, 1H), 7.30 – 7.28 (m, 1H), 7.20 (dd, *J* = 5.3, 3.2 Hz, 2H), 4.55 (t, *J* = 4.4 Hz, 1H), 3.65 (d, *J* = 15.9 Hz, 2H), 2.86 (d, *J* = 5.1 Hz, 1H), 2.61 (d, *J* = 10.2 Hz, 1H), 1.99 (d, *J* = 10.3 Hz, 1H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 147.1, 144.4, 127.2, 126.3, 124.7, 120.4, 100.6, 71.5, 52.4, 50.3, 48.5, 45.9.
HRMS (ESI$^+$) m/z: [M + Na]$^+$ Calcd for $C_{12}H_{10}BrCl_3$ 360.8924; Found 360.8931.

2-((1*S*,2*R*,3*R*,4*S*)-3-iodo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetonitrile (5aa-*cis*)



62% yield, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.32 – 7.28 (m, 2H), 7.21 (td, *J* = 6.9, 1.2 Hz, 2H), 5.55 (s, 1H), 5.24 (s, 1H), 4.06 (d, *J* = 7.3 Hz, 1H), 2.72 – 2.69 (m, 2H), 2.05 (dt, *J* = 8.9, 7.2 Hz, 1H).
^{13}C NMR (101 MHz, CDCl$_3$) δ 143.5, 142.9, 128.2, 127.9, 119.9, 119.9, 119.4, 89.7, 82.9, 40.3, 29.0, 28.4.
MP: 153^{o}C
HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{10}INO$ 311.9880; Found 311.9873.

2-((1*S*,2*R*,3*S*,4*S*)-3-iodo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetonitrile (5aa-*trans*)



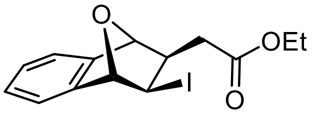
29% yield, white solid, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.34 – 7.31 (m, 1H), 7.28 (dd, *J* = 7.1, 1.5 Hz, 1H), 7.24 – 7.19 (m, 2H), 5.30 (d, *J* = 4.5 Hz, 1H), 5.14 (s, 1H), 3.68 (t, *J* = 4.1 Hz, 1H), 2.60 (qd, *J* = 16.8, 7.7 Hz, 2H), 2.14 (ddd, *J* = 8.7, 6.6, 3.7 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 143.1, 142.4, 128.1, 126.9, 123.2, 119.3, 117.7, 83.9, 82.5, 49.1, 21.2, 20.6.

MP: 127^{o}C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{10}INO$ 311.9880; Found 311.9890.

ethyl 2-((1*S*,2*R*,3*R*,4*S*)-3-iodo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetate (5ab-*cis*)

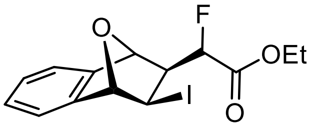


57% yield, yellow oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.30 (d, *J* = 7.0 Hz, 2H), 7.20 (m, *J* = 7.3 Hz, 2H), 5.58 (s, 1H), 5.12 (s, 1H), 4.19 (dt, *J* = 12.9, 7.1 Hz, 3H), 2.87 – 2.70 (m, 2H), 2.16 (q, *J* = 7.5 Hz, 1H), 1.30 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 172.7, 145.1, 142.8, 127.8, 127.4, 119.9, 119.5, 89.4, 83.8, 60.8, 44.4, 39.5, 31.0, 14.3.

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{14}H_{15}IO_3$ 359.0139; Found 359.0140.

ethyl (*S*)-2-fluoro-2-((1*S*,2*S*,3*R*,4*S*)-3-iodo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetate (5ac-*cis*)



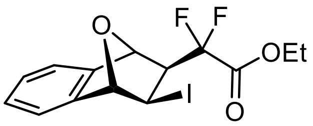
30% yield, yellow oil, ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.40 – 7.37 (m, 1H), 7.34 – 7.26 (m, 3H), 5.45 (s, 1H), 5.36 (dd, *J* = 4.7, 2.3 Hz, 1H), 4.86 (dd, *J* = 48.7, 9.7 Hz, 1H), 4.42 – 4.22 (m, 2H), 4.13 (t, *J* = 4.3 Hz, 1H), 2.33 (td, *J* = 9.9, 4.1 Hz, 1H), 1.37 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 168.2 (d, *J* = 24.1 Hz), 143.0, 142.9, 128.1, 126.8, 123.0, 119.2, 88.6 (d, *J* = 187.4 Hz), 83.6, 80.3 (d, *J* = 3.7 Hz), 62.4, 54.6 (d, *J* = 23.1 Hz), 16.3 (d, *J* = 6.3 Hz), 14.2.

^{19}F NMR (376 MHz, CDCl$_3$) δ -185.74.

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{14}H_{14}FIO_3$ 377.0044; Found 377.0047.

ethyl 2,2-difluoro-2-((1*S*,2*S*,3*R*,4*S*)-3-iodo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetate (5ad-*cis*)

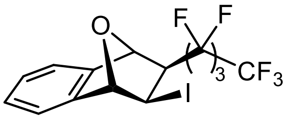


69% yield, yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.39 (m, 1H), 7.35 – 7.26 (m, 3H), 5.55 (s, 1H), 5.34 (d, *J* = 4.5 Hz, 1H), 4.41 – 4.31 (m, 3H), 2.51 (ddd, *J* = 16.4, 9.6, 4.6 Hz, 1H), 1.39 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 163.2 (t, *J* = 32.0 Hz), 143.0, 143.0, 128.1, 126.9, 123.3, 119.0, 118.0 – 112.3 (m), 83.2, 79.1 (dd, *J* = 5.0, 2.2 Hz), 63.6, 56.8 (t, *J* = 24.1 Hz), 14.2 – 14.0 (m), 14.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -107.37 (d, *J* = 254.8 Hz), -109.57 (d, *J* = 254.8 Hz).

(1*S*,2*R*,3*S*,4*S*)-2-iodo-3-(perfluorobutyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (5ae-*cis*)



77% yield, light yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.17 (m, 3H), 5.53 (s, 1H), 5.33 (d, *J* = 4.5 Hz, 1H), 4.24 (t, *J* = 4.7 Hz, 1H), 2.44 (td, *J* = 15.4, 4.8 Hz, 1H).

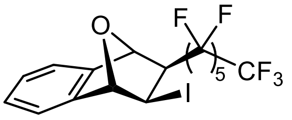
^{13}C NMR (151 MHz, $CDCl_3$) δ 142.9, 142.8, 128.3, 127.2, 123.5, 119.7 (dt, *J* = 158.7, 33.0 Hz), 118.8, 118.6 – 114.1 (m), 113.2 – 110.0 (m), 109.7 – 106.5 (m), 83.2, 79.2 (t, *J* = 4.5 Hz), 54.1 (dd, *J* = 22.7, 19.0 Hz), 13.5 (d, *J* = 2.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.91 (tt, *J* = 9.7, 3.3 Hz), -114.45 (ddp, *J* = 18.8, 10.4, 3.4 Hz), -115.19 (tdd, *J* = 15.3, 6.4, 3.4 Hz), -116.26 (dddq, *J* = 16.7, 12.5, 6.9, 3.5 Hz), -117.00 (dddq, *J* = 16.1, 12.7, 6.5, 3.3 Hz), -121.82 (pt, *J* = 9.8, 5.3 Hz), -125.89 (dddd, *J* = 29.1, 16.5, 12.2, 4.4 Hz).

MP: 45^{o}C

HRMS (ESI^+) m/z: $[M + Na]^+$ Calcd for $C_{14}H_8F_9IO$ 512.9368; Found 512.9363.

(1*S*,2*R*,3*S*,4*S*)-2-iodo-3-(perfluorohexyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (5af-*cis*)



90% yield, light yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 1H), 7.25 – 7.16 (m, 3H), 5.52 (s, 1H), 5.32 (d, *J* = 4.5 Hz, 1H), 4.23 (t, *J* = 4.7 Hz, 1H), 2.50 – 2.37 (m, 1H).

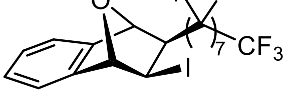
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 142.9, 128.3, 127.2, 123.6, 119.7 (dt, *J* = 112.1, 32.5 Hz), 118.8, 119.1 – 118.5 (m), 117.9 (dt, *J* = 83.1, 32.6 Hz), 116.6 – 114.1 (m), 113.6 – 108.0 (m), 107.2 – 106.3 (m), 83.3, 79.2 (t, *J* = 3.9 Hz), 54.2 (dd, *J* = 22.7, 19.0 Hz), 13.6 (d, *J* = 2.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -80.85 (td, *J* = 10.1, 3.0 Hz), -114.21 (ddq, *J* = 21.4, 13.0, 4.4 Hz), -114.95 (ddp, *J* = 18.0, 12.9, 4.3 Hz), -116.12 (ddt, *J* = 18.4, 14.3, 4.0 Hz), -116.86 (ddt, *J* = 18.6, 14.3, 4.1 Hz), -120.86 (ddq, *J* = 18.8, 10.9, 3.5 Hz), -121.77 (tq, *J* = 22.6, 11.9, 11.1 Hz), -122.79 (dddd, *J* = 27.2, 18.0, 13.3, 9.0 Hz), -126.04 – -126.24 (m).

MP: 69^{o}C

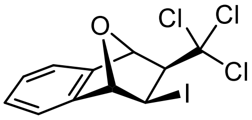
HRMS (ESI^+) m/z: $[M + Na]^+$ Calcd for $C_{16}H_8F_{13}IO$ 612.9304; Found 612.9311.

(1*S*,2*R*,3*S*,4*S*)-2-iodo-3-(perfluorooctyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (5ag-*cis*)



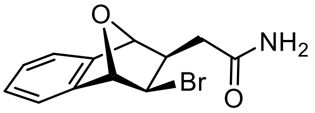
83% yield, light yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.44 (m, 1H), 7.36 – 7.27 (m, 3H), 5.62 (s, 1H), 5.41 (d, *J* = 4.5 Hz, 1H), 4.32 (t, *J* = 4.6 Hz, 1H), 2.53 (ddd, *J* = 16.4, 14.2, 4.8 Hz, 1H).
^{13}C NMR (151 MHz, $CDCl_3$) δ 143.0, 142.9, 128.3, 127.2, 123.6, 120.5 – 118.5 (m), 118.8, 117.9 (dt, *J* = 72.7, 32.6 Hz), 116.8 – 113.9 (m), 113.0 (dt, *J* = 80.6, 34.1 Hz), 112.4 – 111.0 (m), 111.0 – 109.6 (m), 109.6 – 108.0 (m), 107.3 – 106.2 (m), 83.3, 79.3 (t, *J* = 3.6 Hz), 54.3 (dd, *J* = 22.7, 18.9 Hz), 13.6 (d, *J* = 2.5 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -80.92 (t, *J* = 10.0 Hz), -114.16 – -114.31 (m), -114.98 (tt, *J* = 15.1, 4.1 Hz), -116.15 (t, *J* = 15.7 Hz), -116.82 – -116.97 (m), -120.83 (t, *J* = 15.7 Hz), -121.62 (dt, *J* = 28.7, 11.9 Hz), -121.76 – -122.10 (m), -122.81 (dt, *J* = 19.9, 10.2 Hz), -126.24 (ddt, *J* = 18.7, 13.3, 6.4 Hz).
MP: 78°C
HRMS (ESI$^+$) m/z: [M + Na]$^+$ Calcd for $C_{18}H_8F_{17}IO$ 712.9241; Found 712.9241.

(1*S*,2*R*,3*S*,4*S*)-2-iodo-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene (5ah-*cis*)



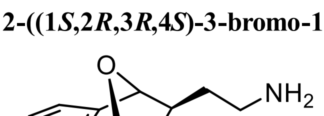
59% yield, light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.42 (m, 1H), 7.39 – 7.36 (m, 1H), 7.30 (ddd, *J* = 8.5, 6.8, 1.3 Hz, 2H), 5.53 (s, 1H), 5.43 (d, *J* = 4.5 Hz, 1H), 4.33 (t, *J* = 4.6 Hz, 1H), 3.03 (d, *J* = 4.8 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 143.5, 128.1, 127.0, 123.6, 118.9, 99.6, 84.4, 81.9, 71.3, 19.1.
HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{11}H_8Cl_3IO$ 388.8758; Found 388.8753.

2-((1*S*,2*R*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetamide (7)



92% yield, white solid, ^{1}H NMR (600 MHz, MeOD) δ 7.39 – 7.35 (m, 1H), 7.32 – 7.28 (m, 1H), 7.21 (m, *J* = 7.6, 1.4 Hz, 2H), 5.44 (s, 1H), 5.15 (s, 1H), 4.28 (d, *J* = 7.1 Hz, 1H), 2.73 (dd, *J* = 15.7, 6.3 Hz, 1H), 2.63 (dd, *J* = 15.7, 9.2 Hz, 1H), 2.42 (dt, *J* = 9.1, 6.7 Hz, 1H).
^{13}C NMR (151 MHz, MeOD) δ 175.9, 145.8, 142.2, 127.6, 126.9, 120.1, 118.9, 87.9, 83.6, 53.8, 40.9, 39.4.
MP: 189°C
HRMS (ESI$^+$) m/z: [M + Na]$^+$ Calcd for $C_{12}H_{12}BrNO_2$ 303.9944; Found 303.9948.

2-((1*S*,2*R*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)ethan-1-amine (8)

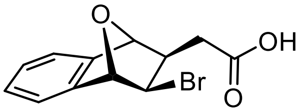


75% yield, yellow solid, ^{1}H NMR (400 MHz, CD_3OD_SPE) δ 7.41 – 7.36 (m, 1H), 7.34 – 7.30 (m, 1H), 7.24 – 7.20 (m, 2H), 5.47 (s, 1H), 5.19 (s, 1H), 4.29 (d, *J* = 6.4 Hz, 1H), 3.12 – 3.01 (m, 2H), 2.16 – 2.08 (m, 1H), 2.03 – 1.95 (m, 2H).
^{13}C NMR (151 MHz, MeOD) δ 145.7, 142.2, 127.6, 127.0, 120.2, 119.0, 87.9, 83.2, 54.1, 41.6, 38.6, 32.0.

MP: 206°C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{14}BrNO$ 268.0332; Found 268.0331.

2-((1*S*,2*R*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetic acid (9)



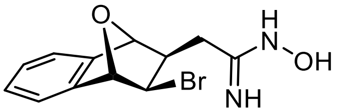
96% yield, light yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.29 (m, 2H), 7.25 – 7.20 (m, 2H), 5.48 (s, 1H), 5.19 (s, 1H), 4.22 (d, *J* = 7.1 Hz, 1H), 2.97 (dd, *J* = 17.7, 6.7 Hz, 1H), 2.83 (dd, *J* = 17.7, 8.7 Hz, 1H), 2.46 (q, *J* = 7.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.6, 145.4, 141.9, 128.1, 127.4, 120.4, 119.5, 87.8, 83.8, 53.2, 40.4, 38.7.

MP: 140°C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{11}BrO_3$ 282.9964; Found 282.9973.

2-((1*S*,2*R*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)-N-hydroxyacetimidamide (10)



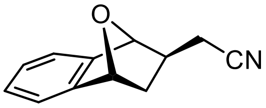
70% yield, white solid, ^{1}H NMR (400 MHz, CD_3OD_SPE) δ 7.40 – 7.33 (m, 1H), 7.30 – 7.24 (m, 1H), 7.25 – 7.16 (m, 2H), 5.44 (s, 1H), 5.25 (s, 1H), 4.28 (d, *J* = 5.8 Hz, 1H), 2.94 – 2.83 (m, 1H), 2.48 – 2.38 (m, 2H).

^{13}C NMR (101 MHz, CD_3OD_SPE) δ 158.5, 145.8, 142.5, 127.5, 126.9, 120.0, 118.9, 87.9, 82.6, 54.0, 40.8, 32.5.

MP: 153°C

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{13}BrN_2O_2$ 297.0233; Found 297.0240.

2-((1*S*,2*S*,4*R*)-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)acetonitrile (11)

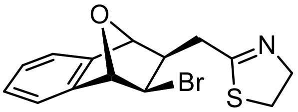


83% yield, light yellow oil, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dt, *J* = 7.7, 3.9 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.19 (dd, *J* = 5.4, 3.0 Hz, 2H), 5.43 (d, *J* = 4.8 Hz, 1H), 5.17 (s, 1H), 2.63 (dd, *J* = 16.7, 8.4 Hz, 1H), 2.54 (dd, *J* = 16.7, 7.2 Hz, 1H), 2.14 (qd, *J* = 7.9, 3.6 Hz, 1H), 1.78 (dd, *J* = 12.0, 7.8 Hz, 1H), 1.68 (ddd, *J* = 12.0, 4.9, 3.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 143.8, 127.2, 127.0, 119.5, 119.0, 119.0, 82.2, 79.5, 37.5, 34.8, 22.6.

HRMS (ESI$^+$) m/z: [M + H]$^+$ Calcd for $C_{12}H_{11}NO$ 186.0913; Found 186.0919.

2-(((1*S*,2*R*,3*R*,4*S*)-3-bromo-1,2,3,4-tetrahydro-1,4-epoxynaphthalen-2-yl)methyl)-4,5-dihydrothiazole (12)



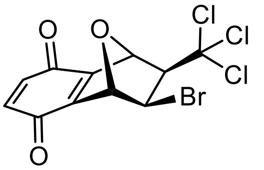
90% yield, white solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 2H), 7.25 – 7.19 (m, 2H), 5.50 (s, 1H), 5.25 (s, 1H), 4.33 – 4.23 (m, 3H), 3.37 (t, *J* = 8.4 Hz, 2H), 3.03 – 2.90 (m, 2H), 2.57 (dt, *J* = 9.3, 6.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.0, 145.8, 142.1, 127.9, 127.2, 120.3, 119.4, 87.8, 83.6, 64.7, 53.8, 42.4, 38.5, 33.9.

MP: 82°C

HRMS (ESI$^+$) m/z: $[M + H]^+$ Calcd for $C_{14}H_{14}BrNOS$ 324.0052; Found 324.0060.

(1*S*,2*R*,3*S*,4*S*)-2-bromo-3-(trichloromethyl)-1,2,3,4-tetrahydro-1,4-epoxynaphthalene-5,8-dione (13)



64% yield, yellow solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 2H), 5.67 (d, *J* = 4.6 Hz, 1H), 5.59 (s, 1H), 4.36 (t, *J* = 4.2 Hz, 1H), 3.12 (d, *J* = 3.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 181.8, 181.7, 151.4, 150.0, 136.5, 136.2, 97.7, 81.2, 80.7, 68.6, 41.5.

MP: 107°C

HRMS (ESI$^+$) m/z: $[M + H]^+$ Calcd for $C_{11}H_6BrCl_3O_3$ 370.8639; Found 370.8643.

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[7] Gaussian 16, Revision A.03, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.;

Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2016**.

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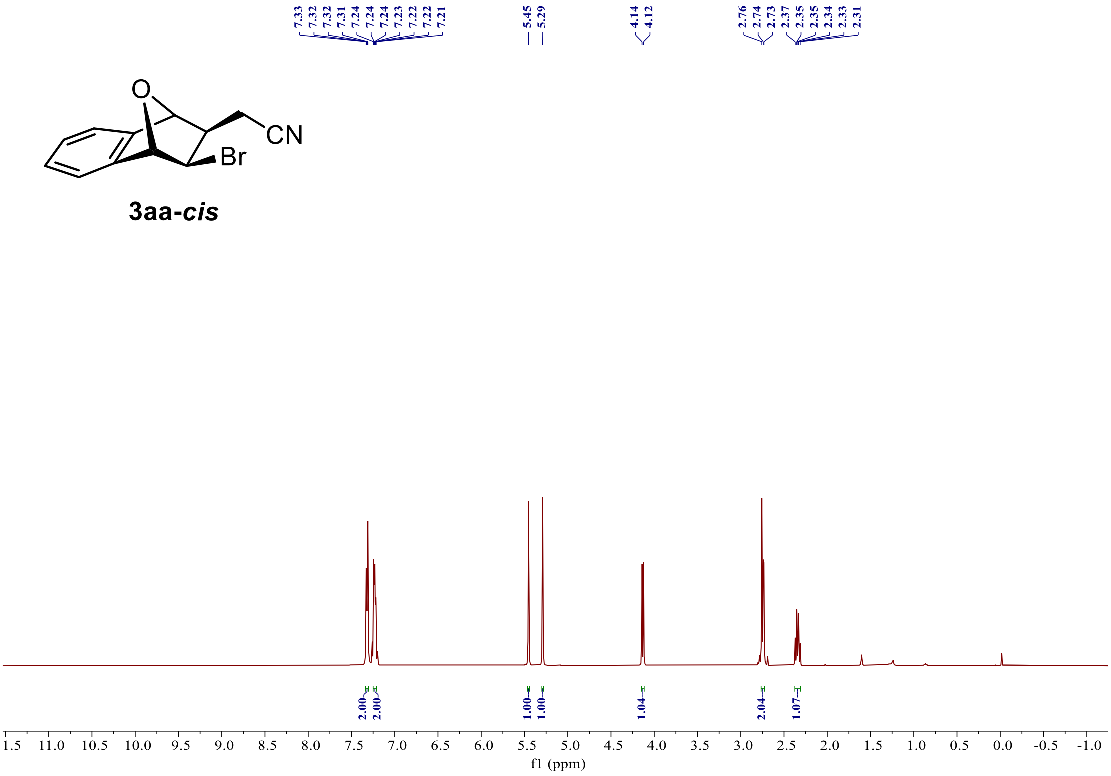
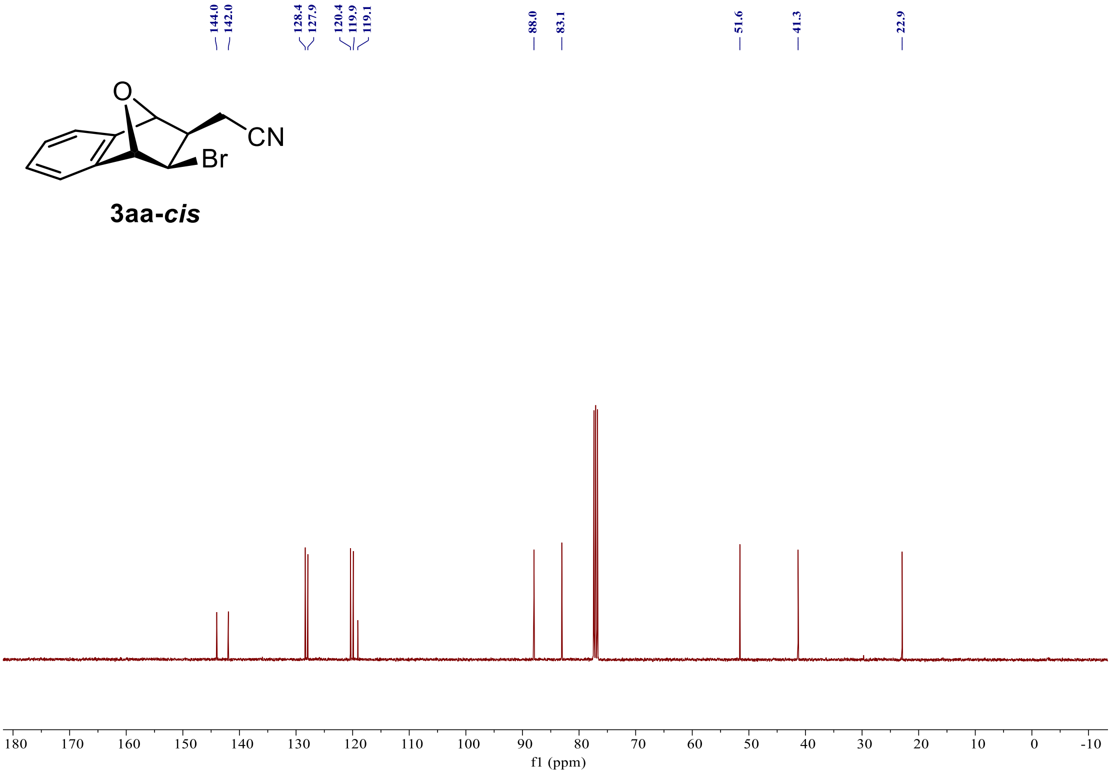
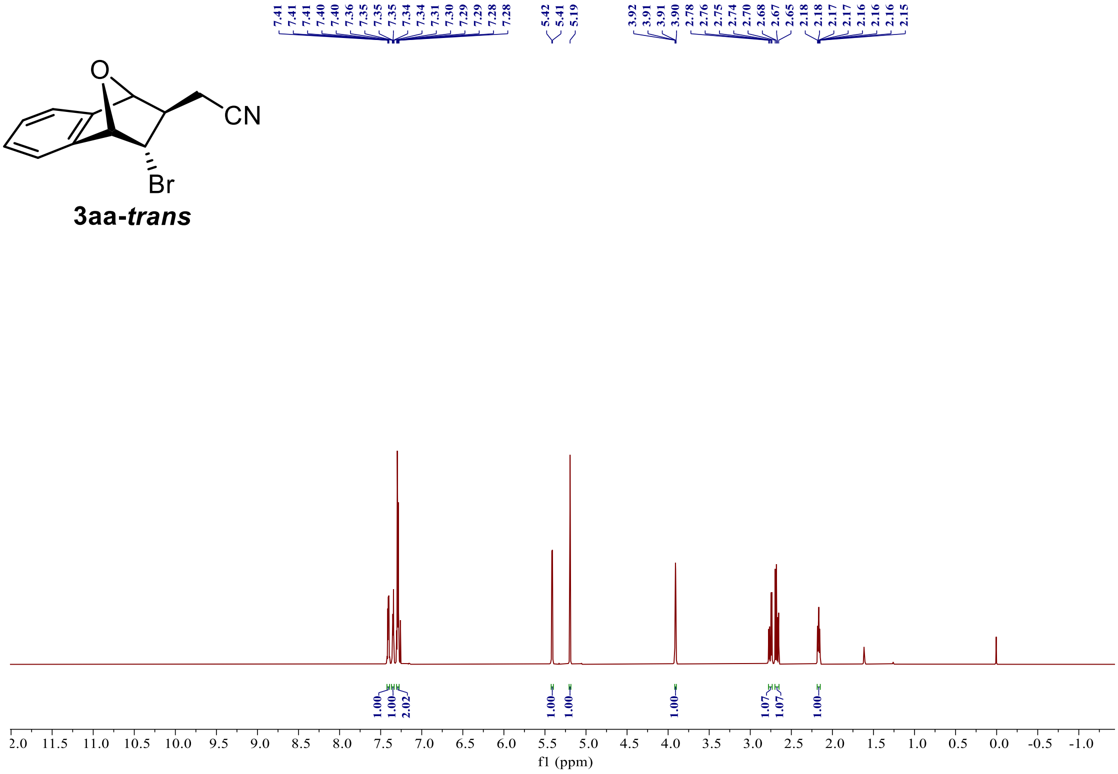
10. NMR Spectra of Products







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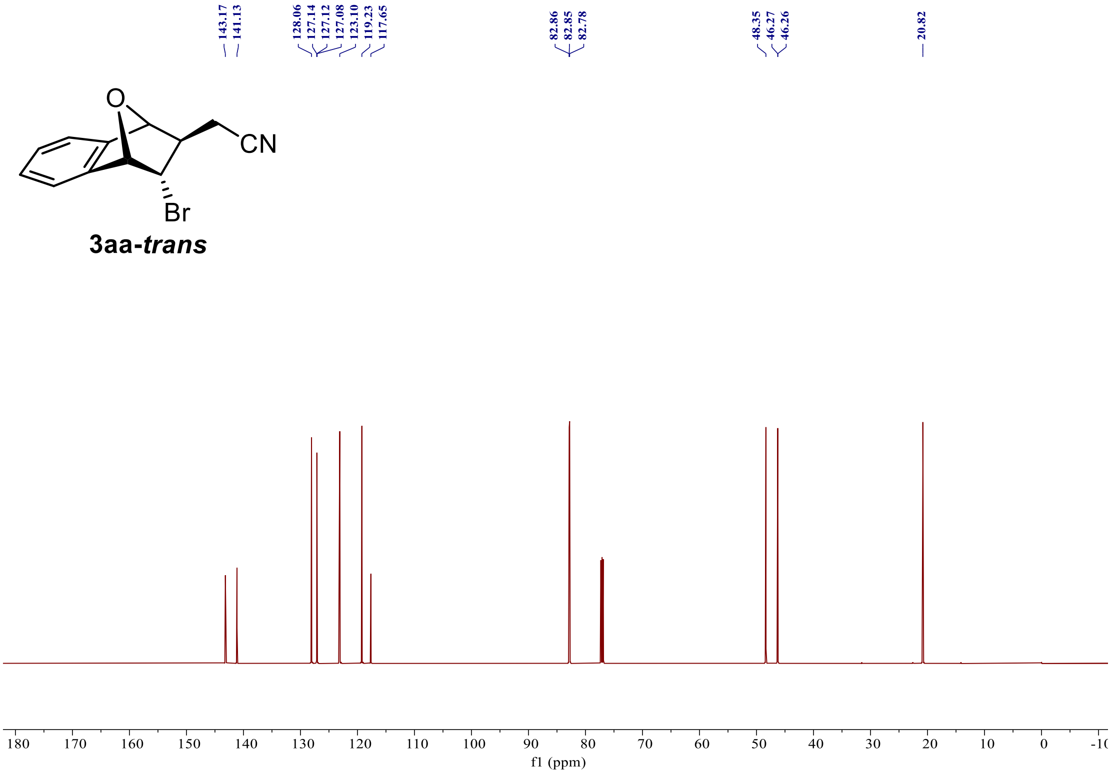

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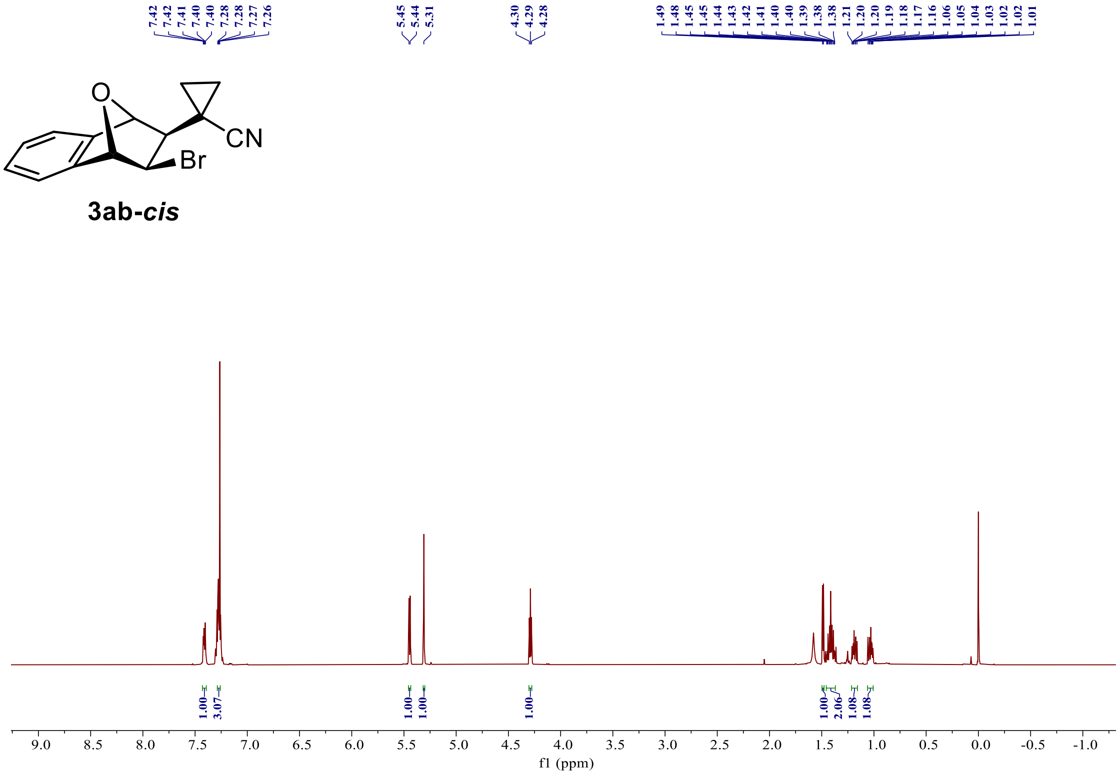

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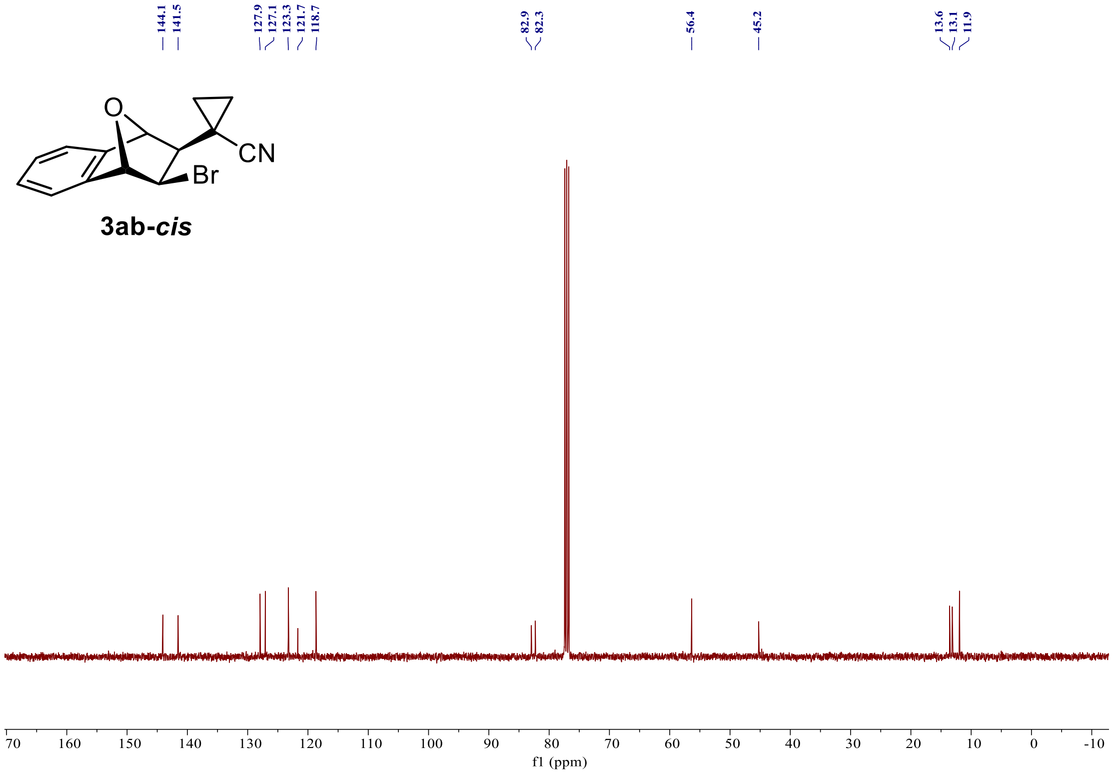

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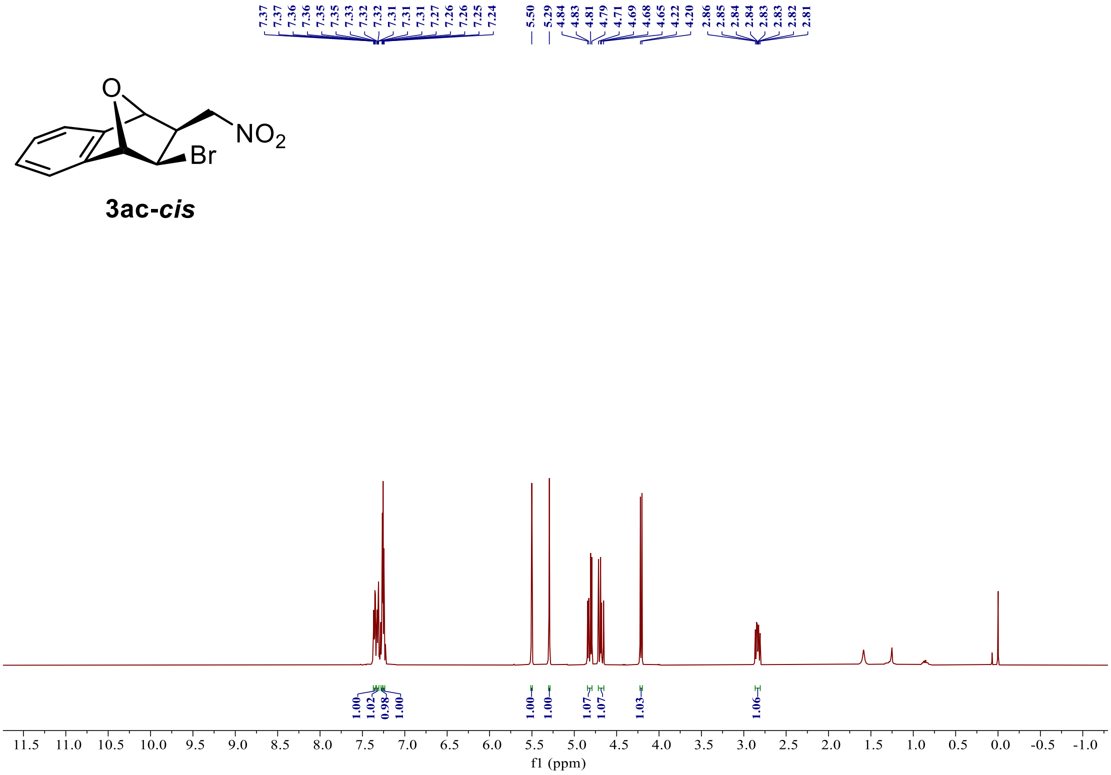

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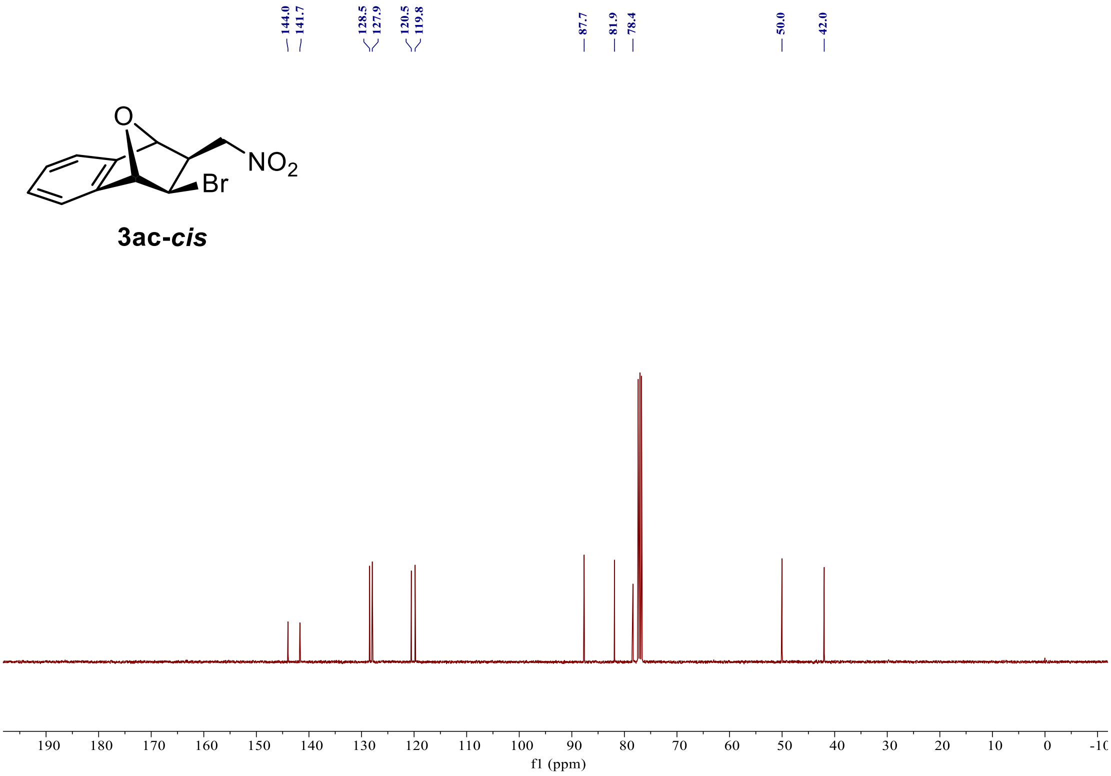

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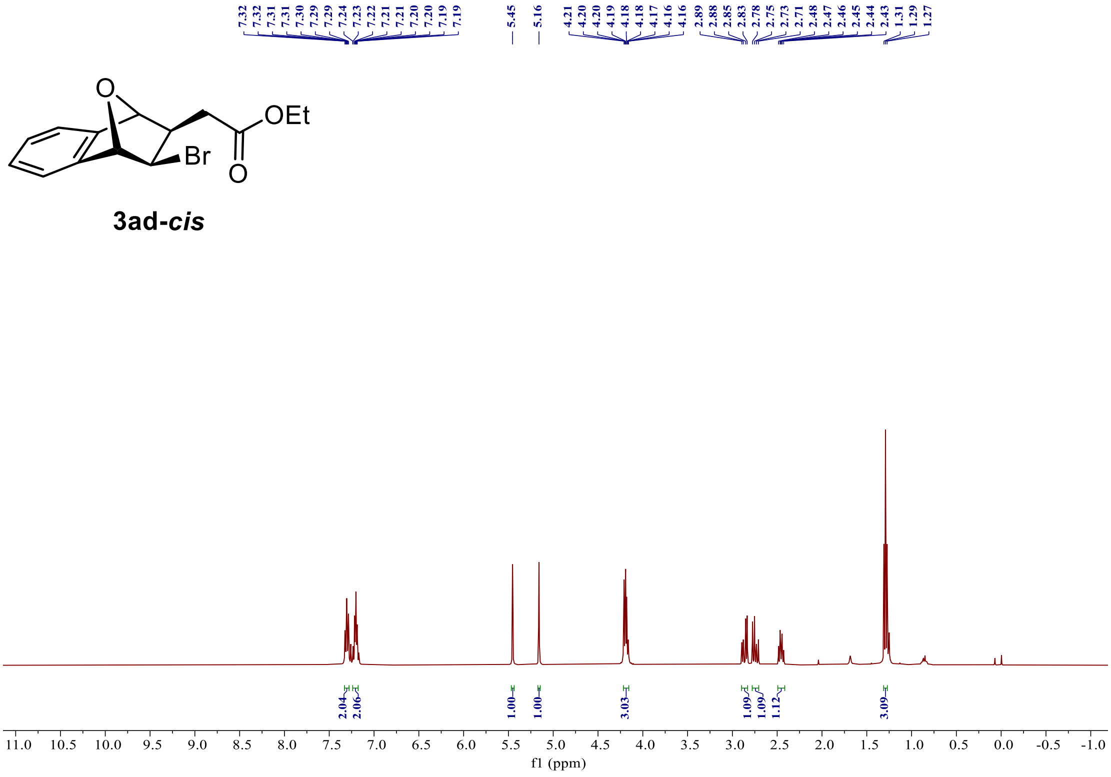

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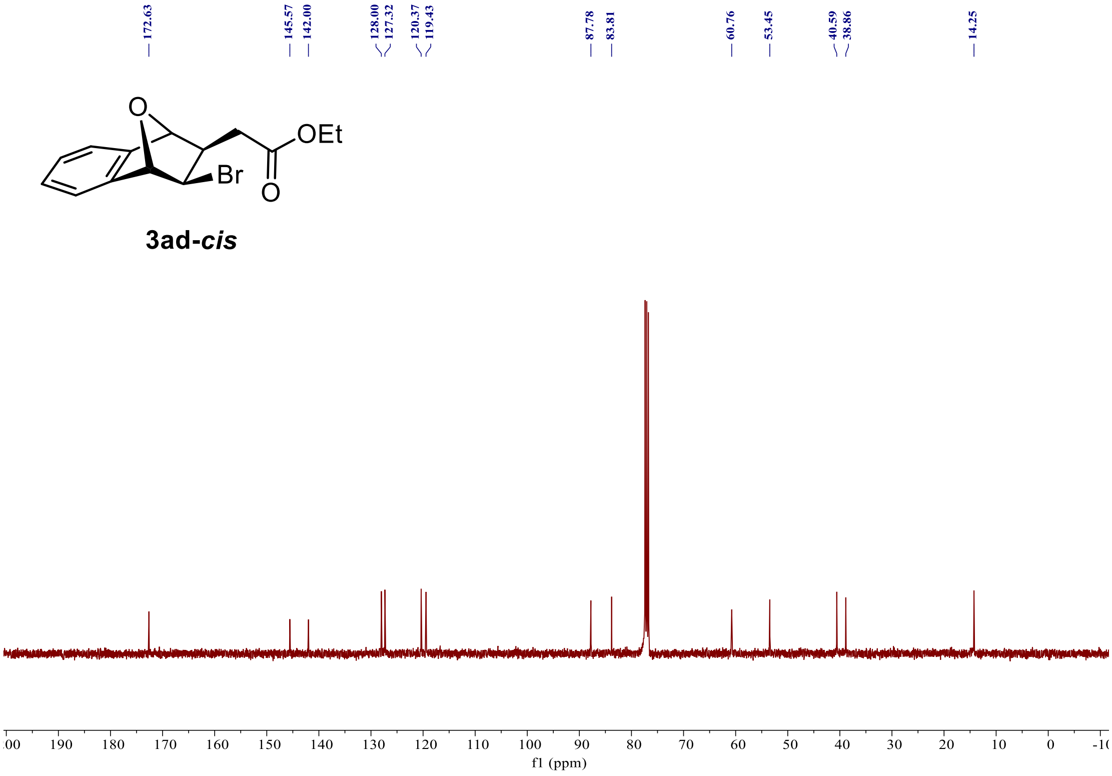

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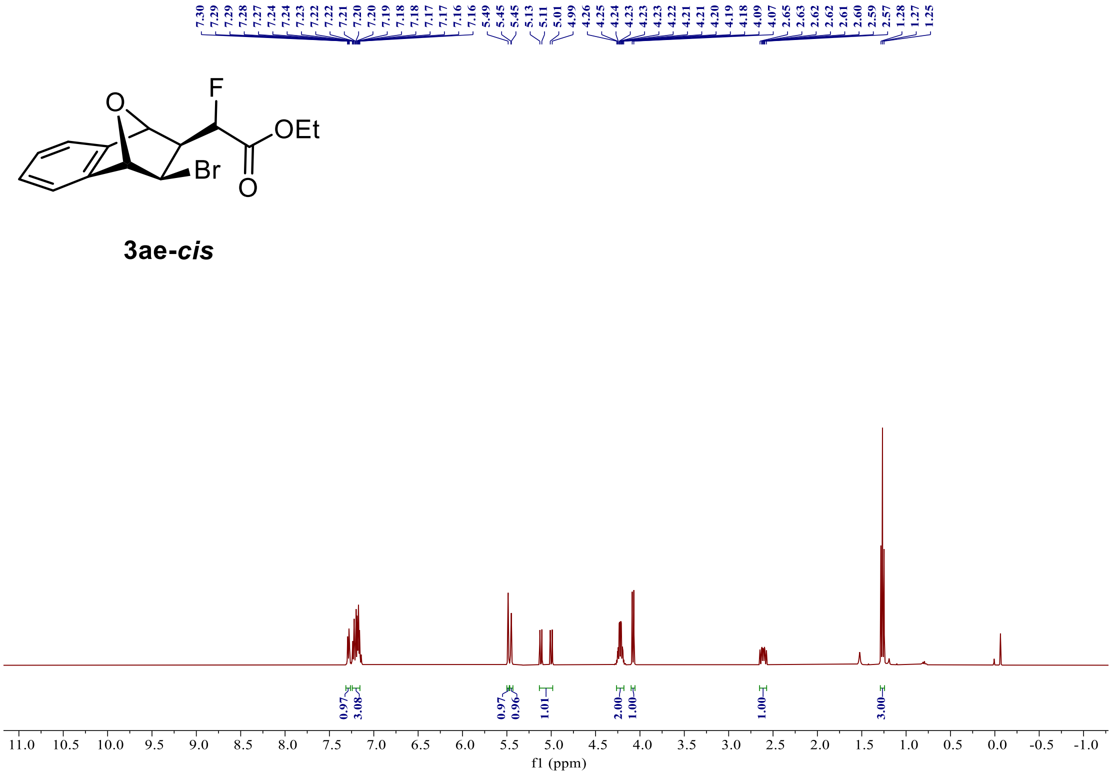

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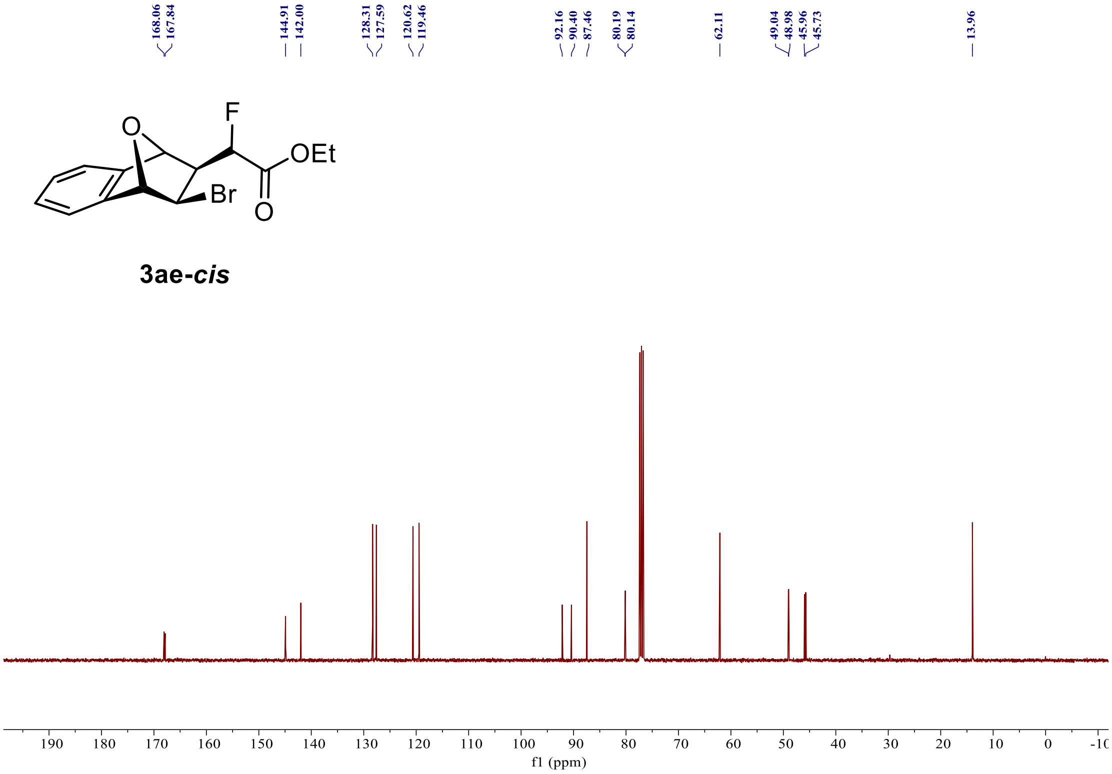

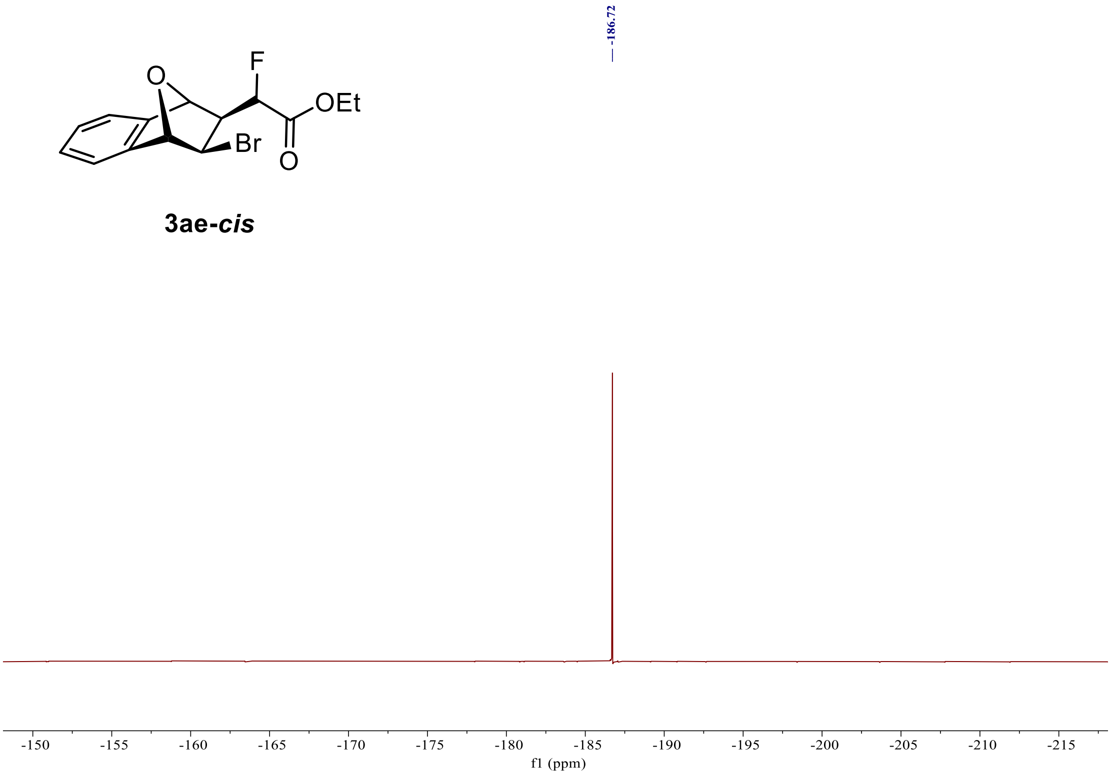

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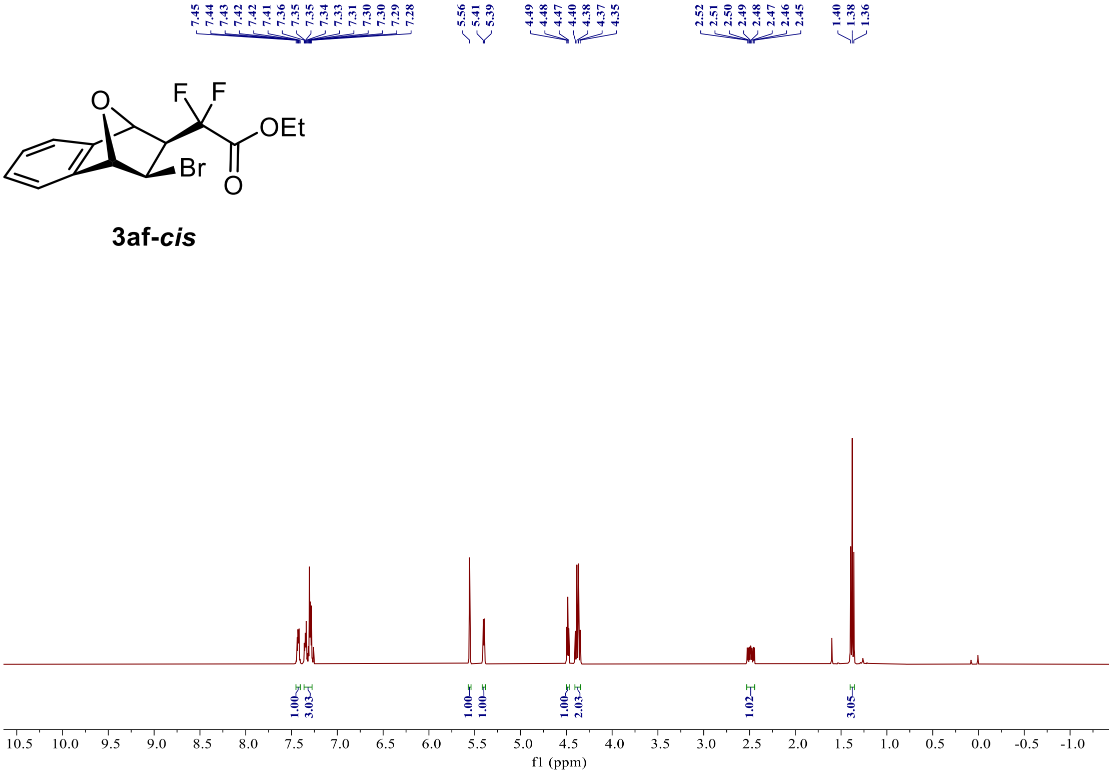

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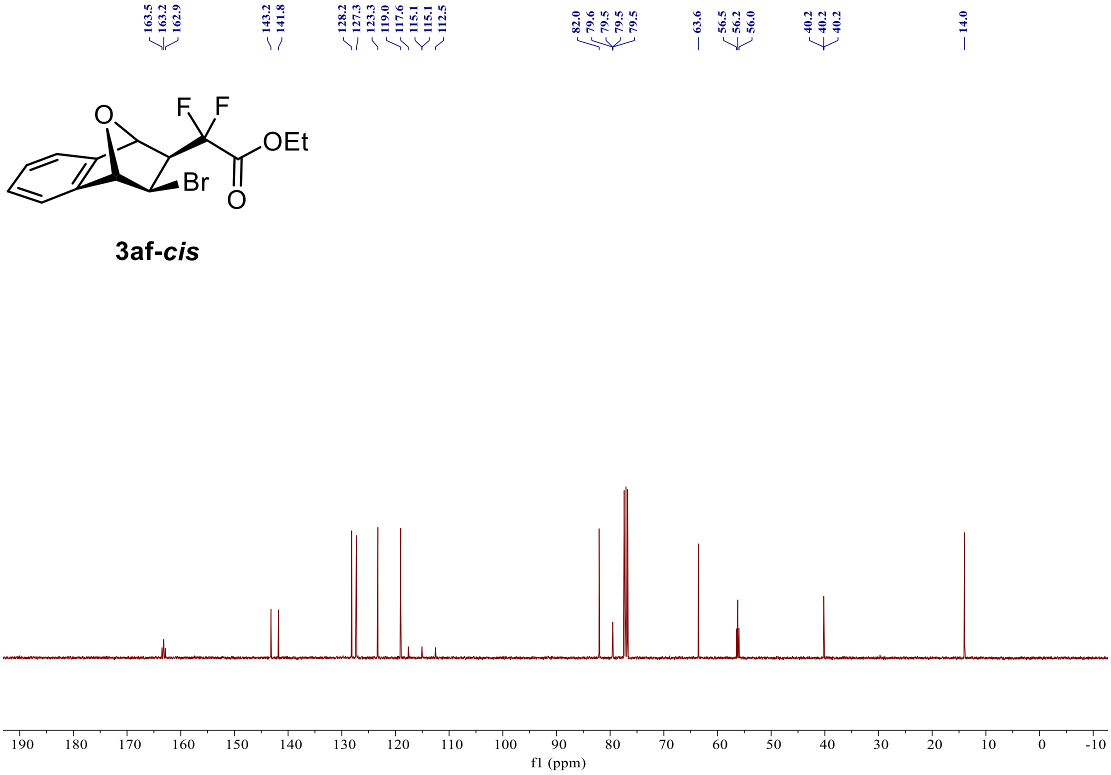

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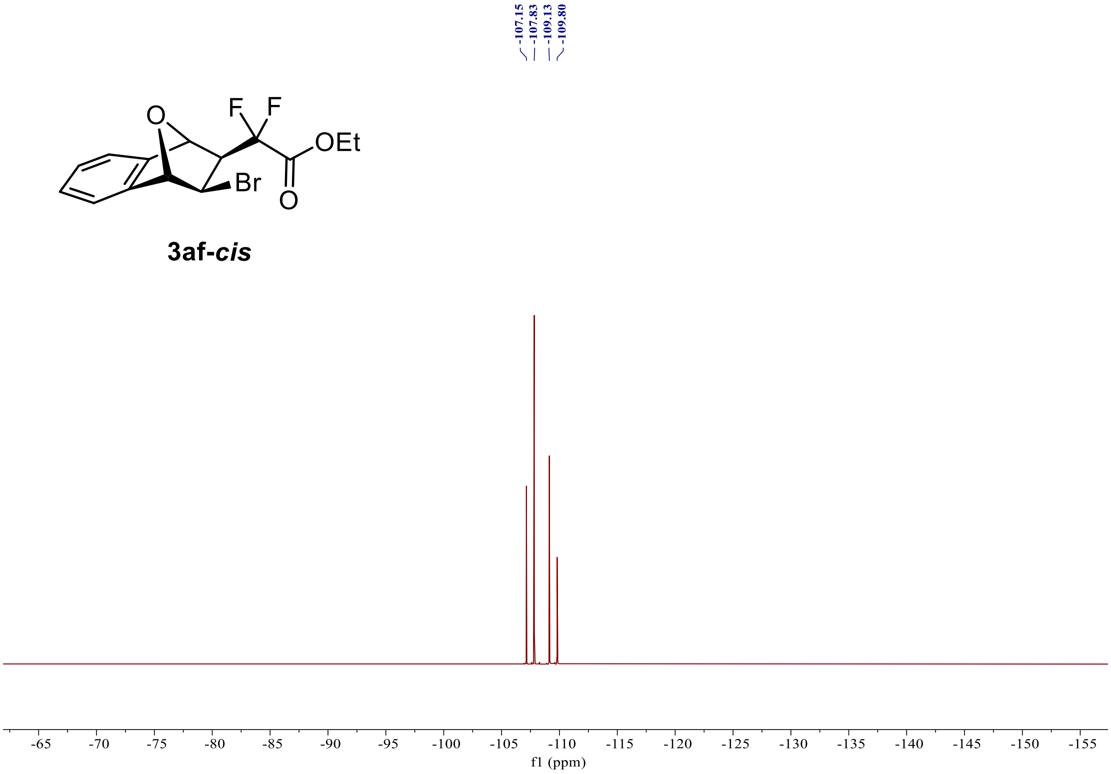

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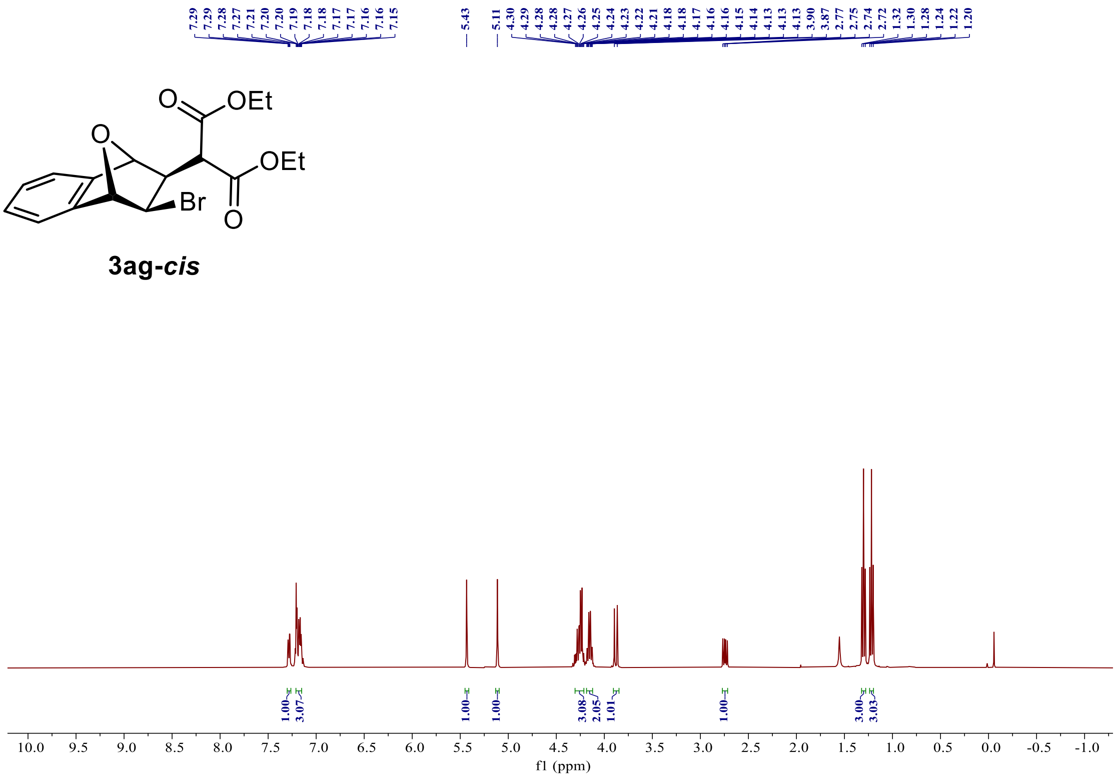

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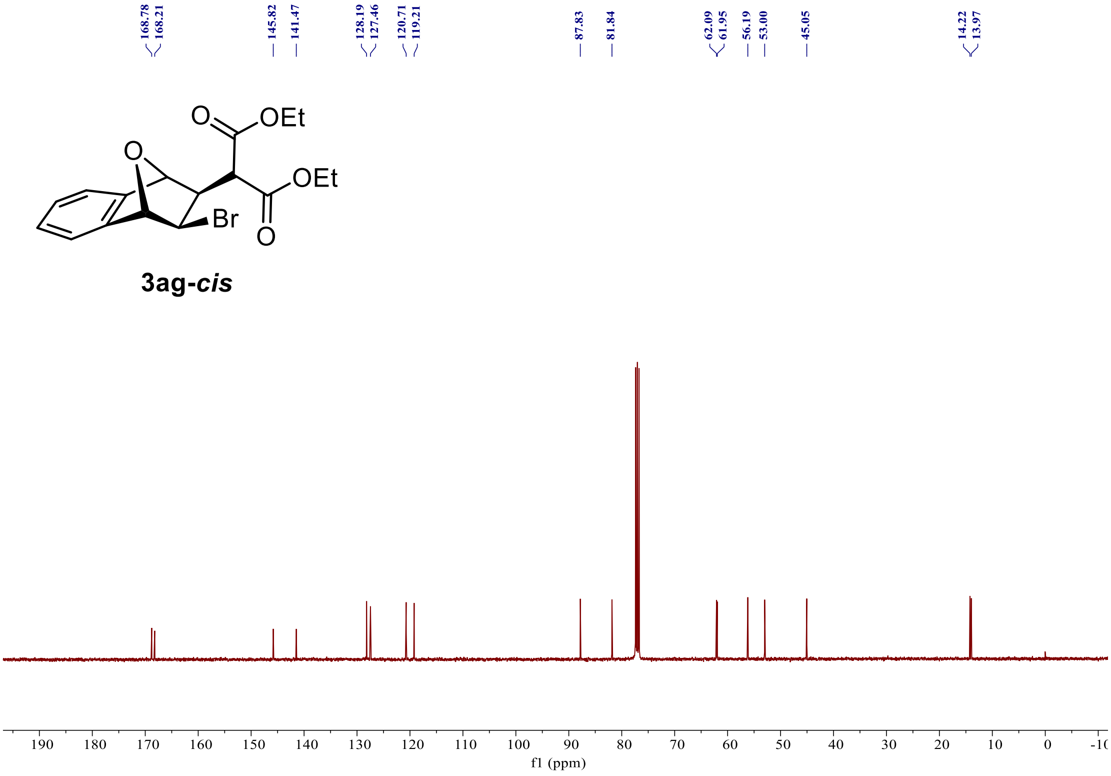

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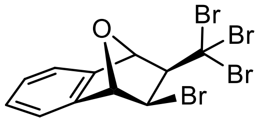

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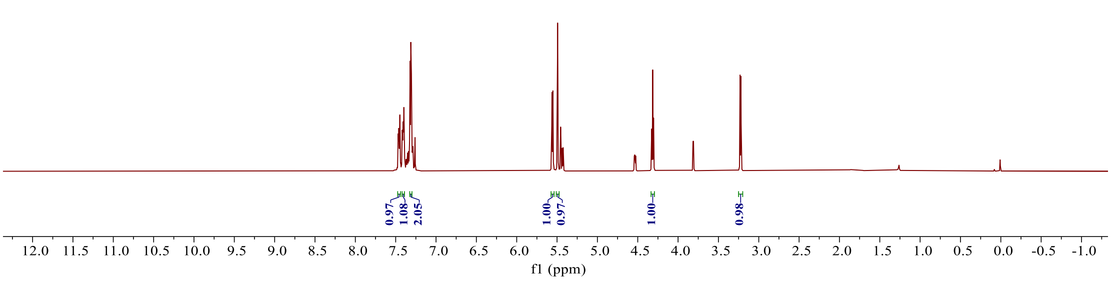

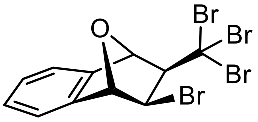

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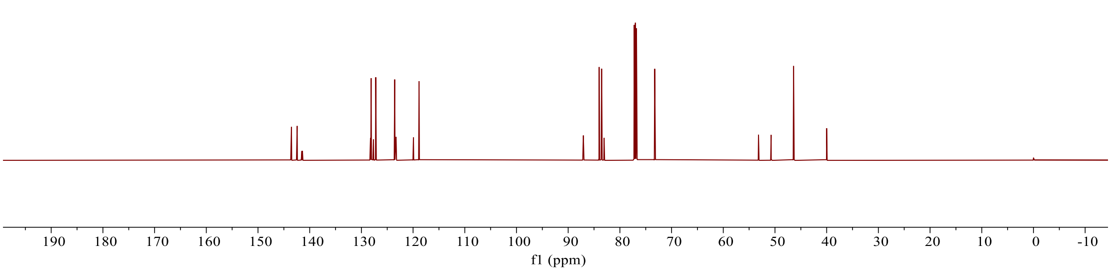

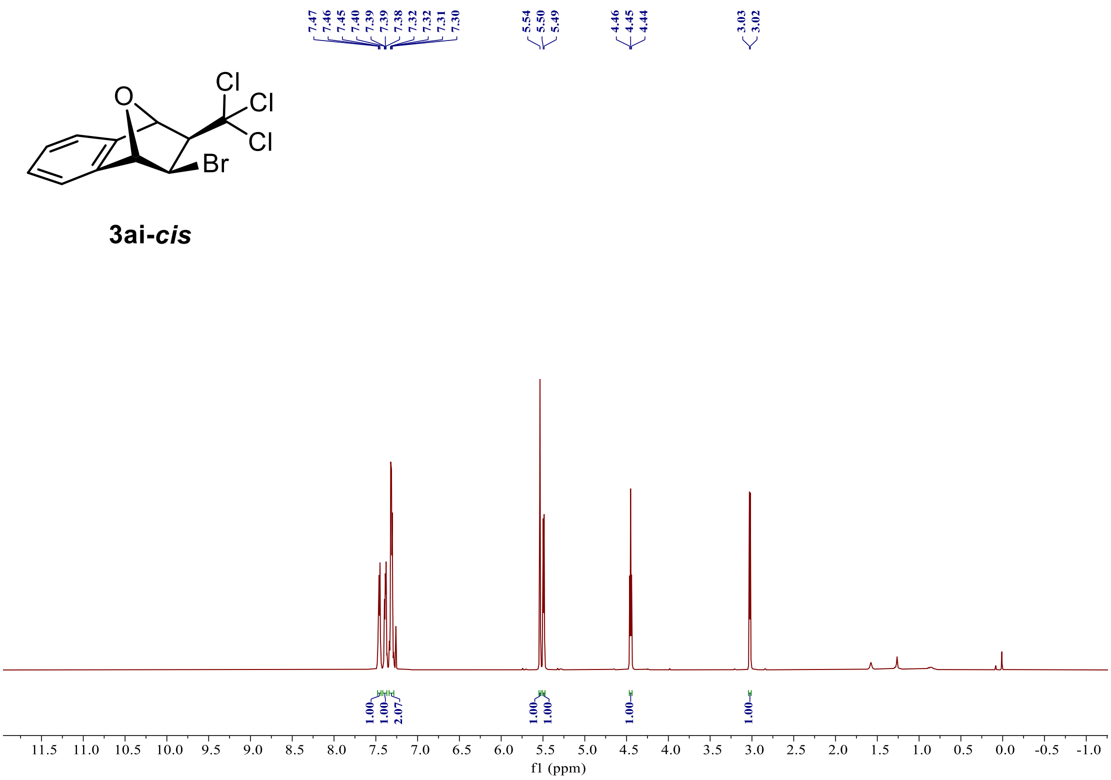

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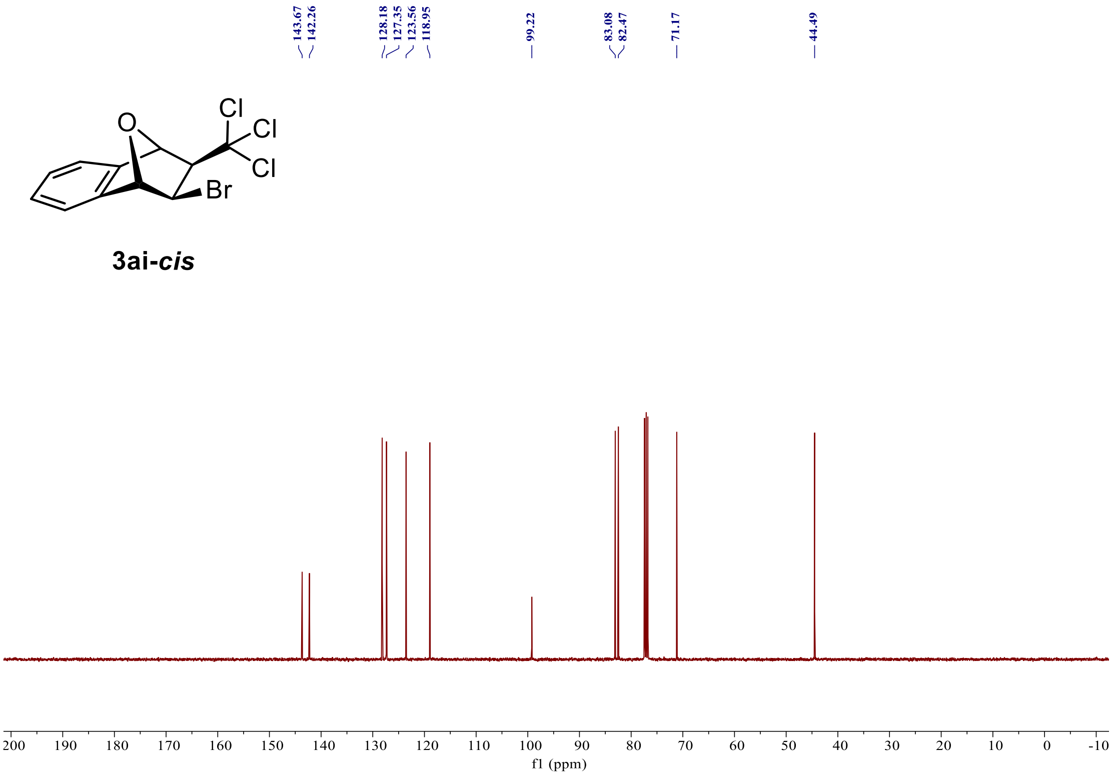

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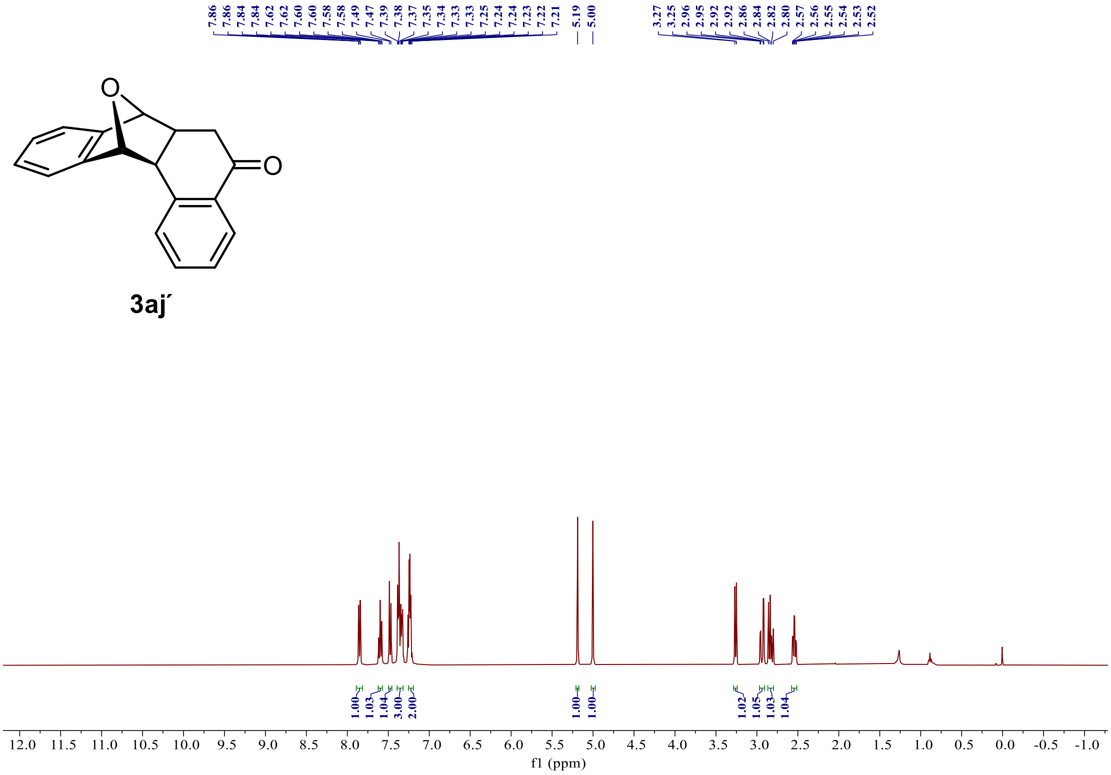
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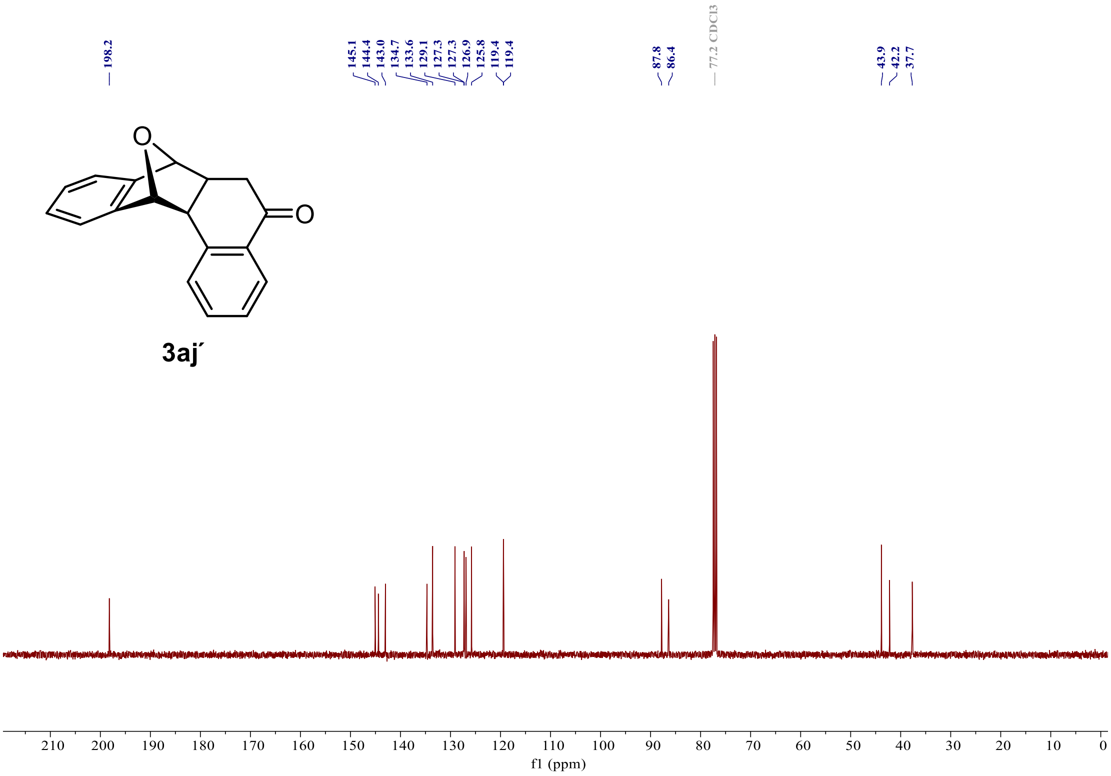
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43.9
42.2
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O
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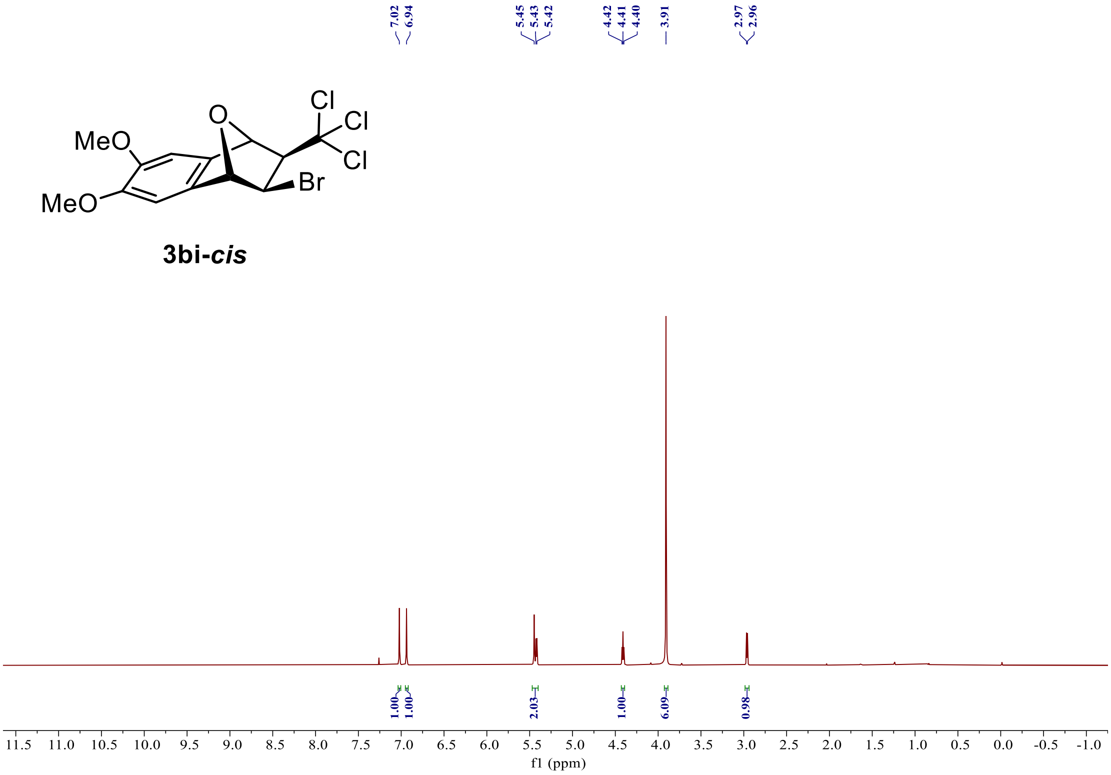

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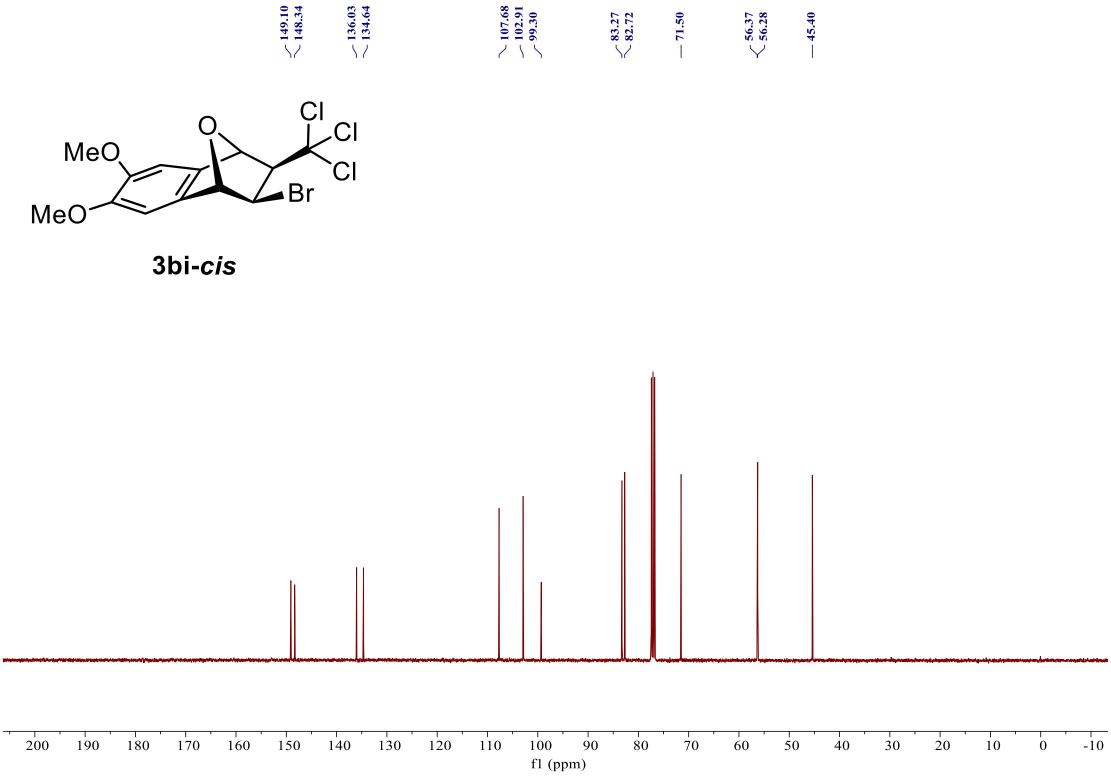

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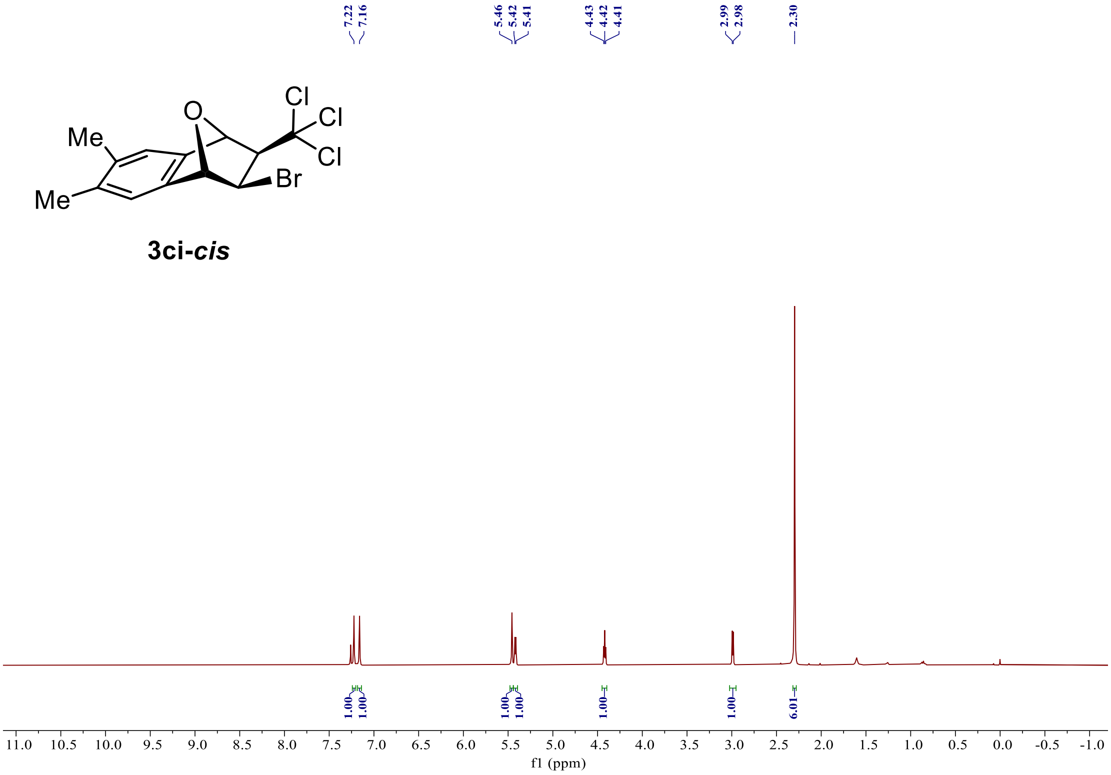

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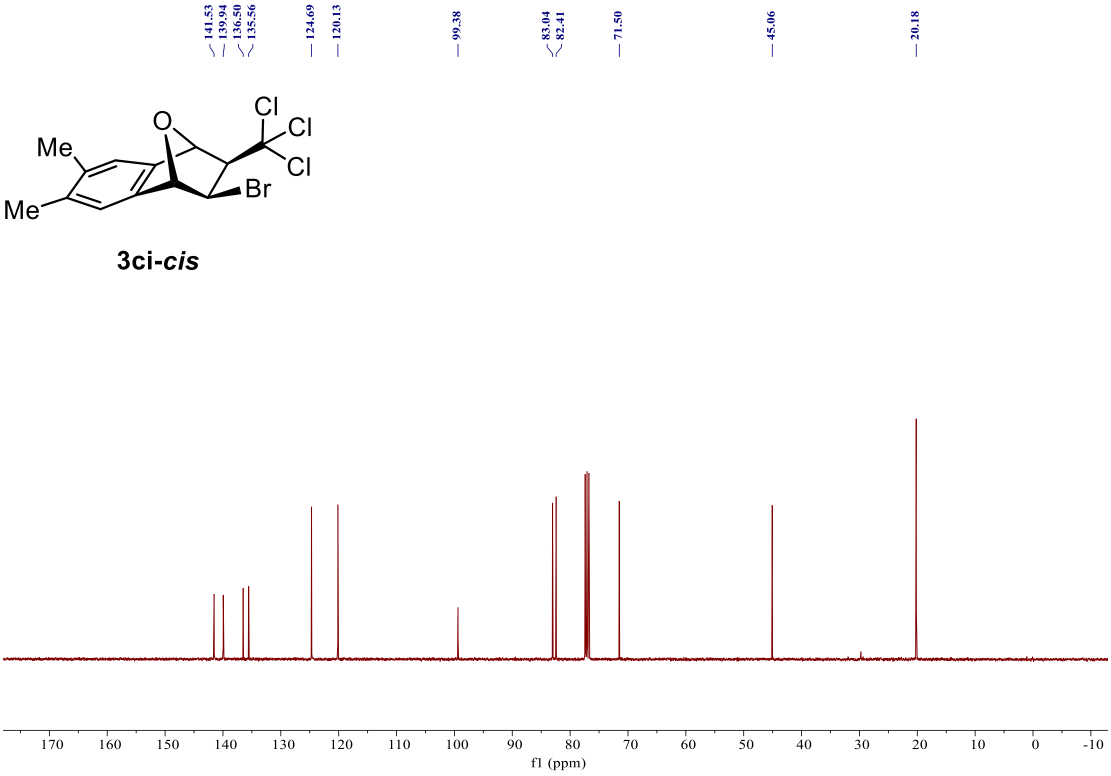

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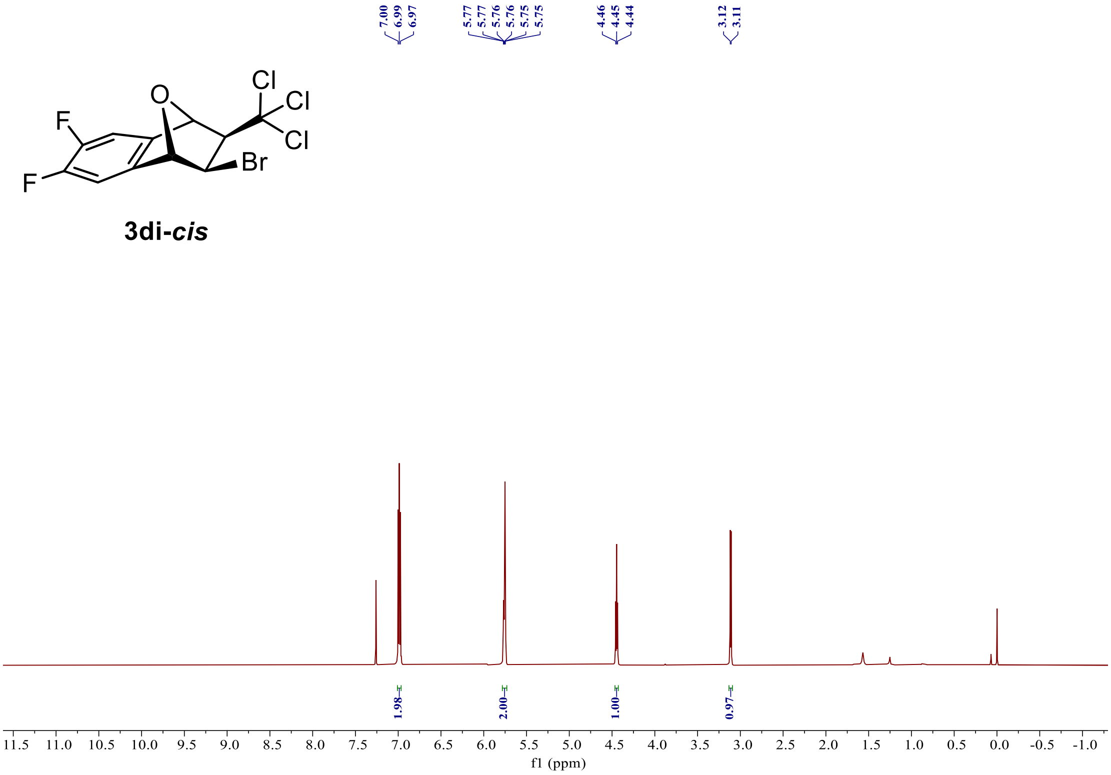
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Cl
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0.97
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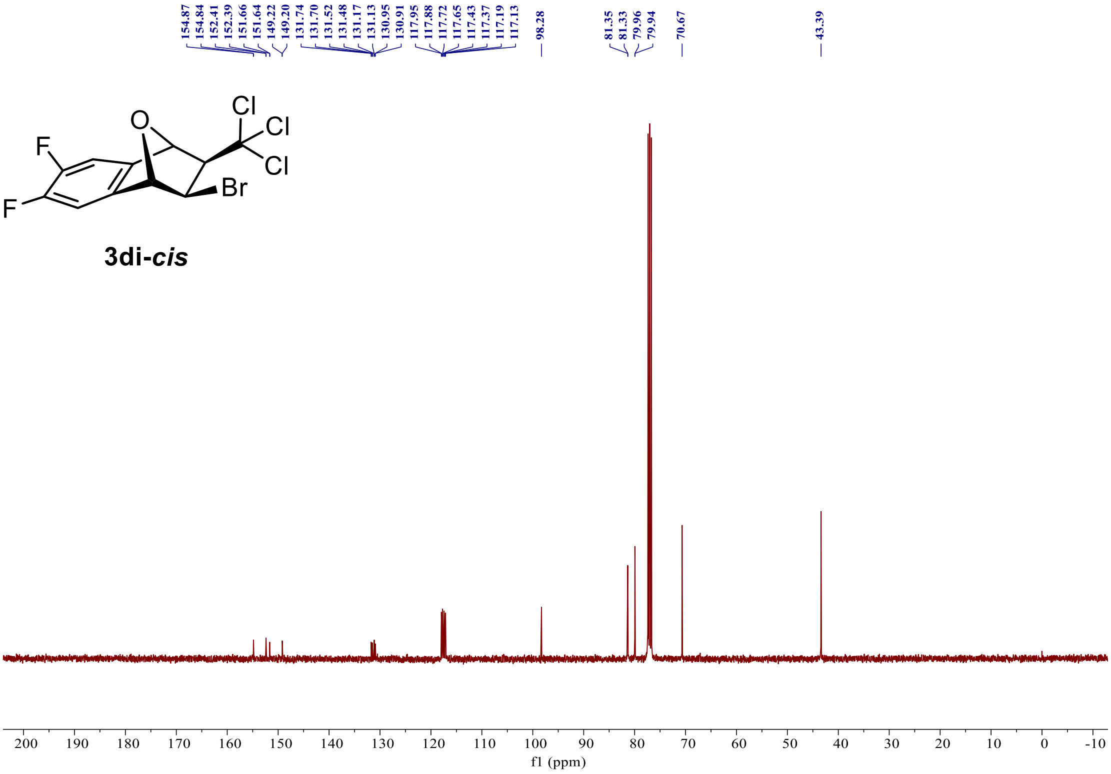
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Cl
Cl
Br
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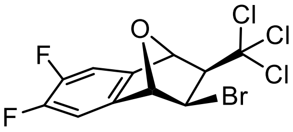

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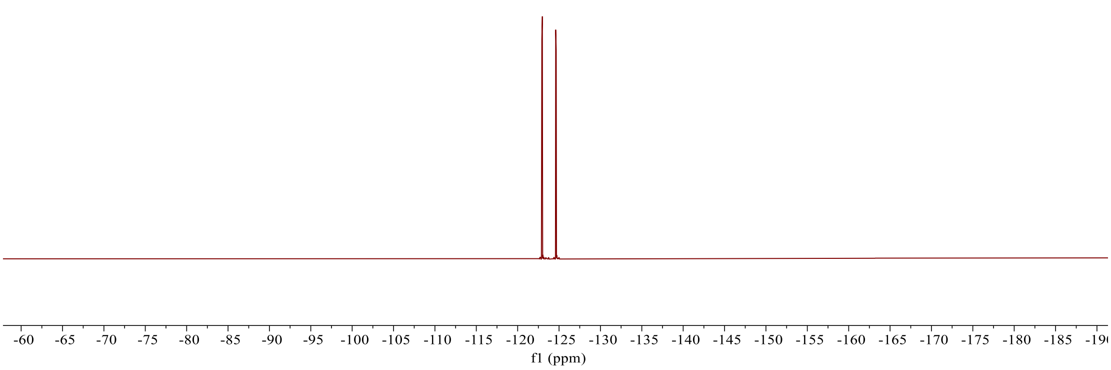

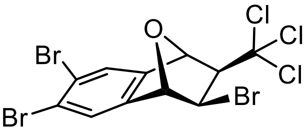

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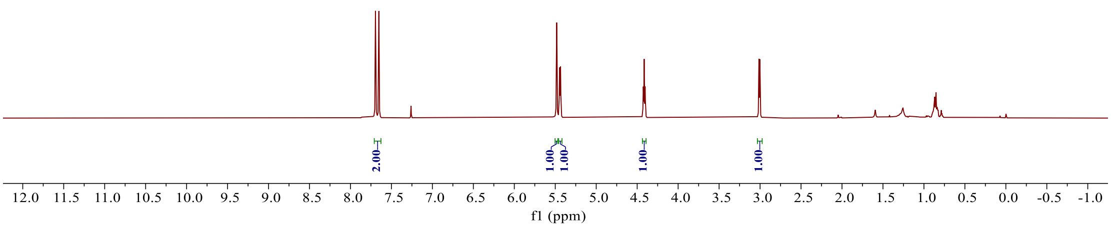

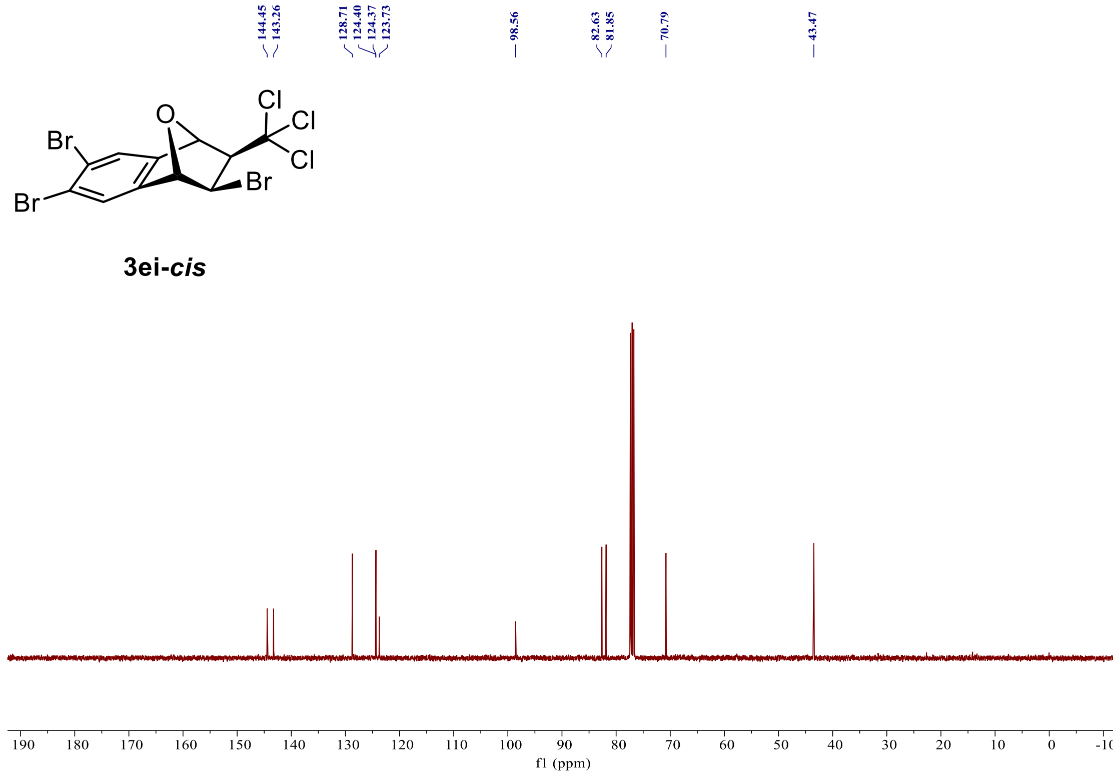

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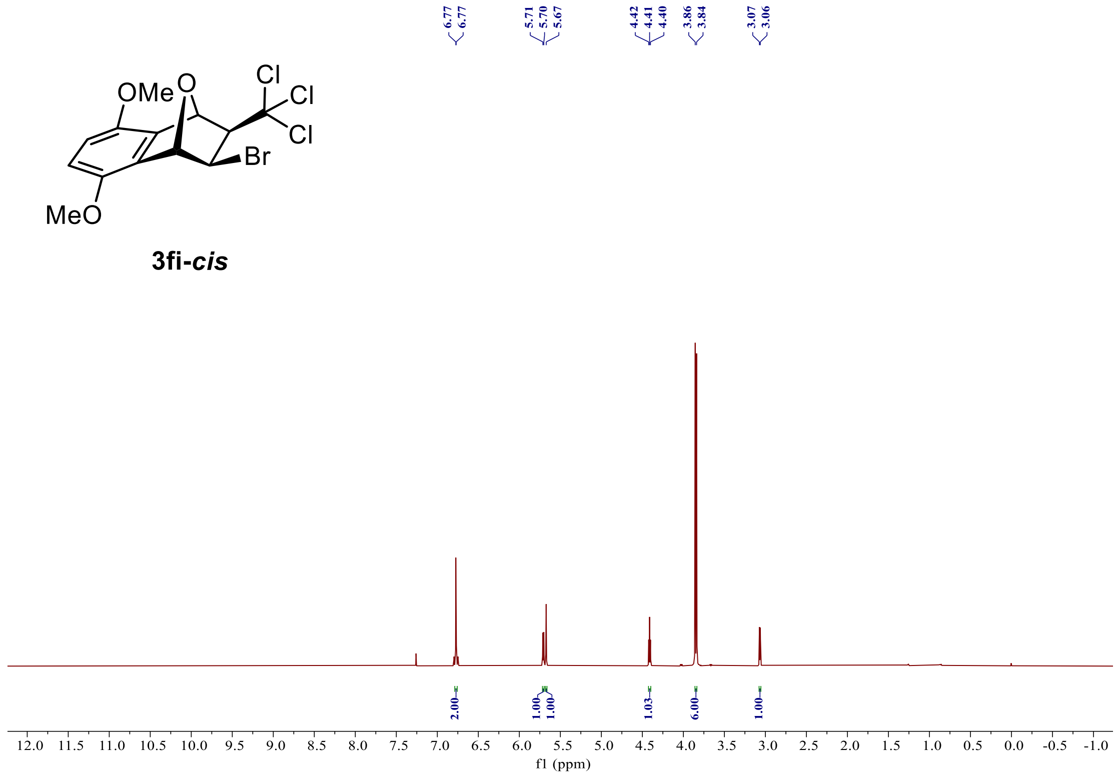
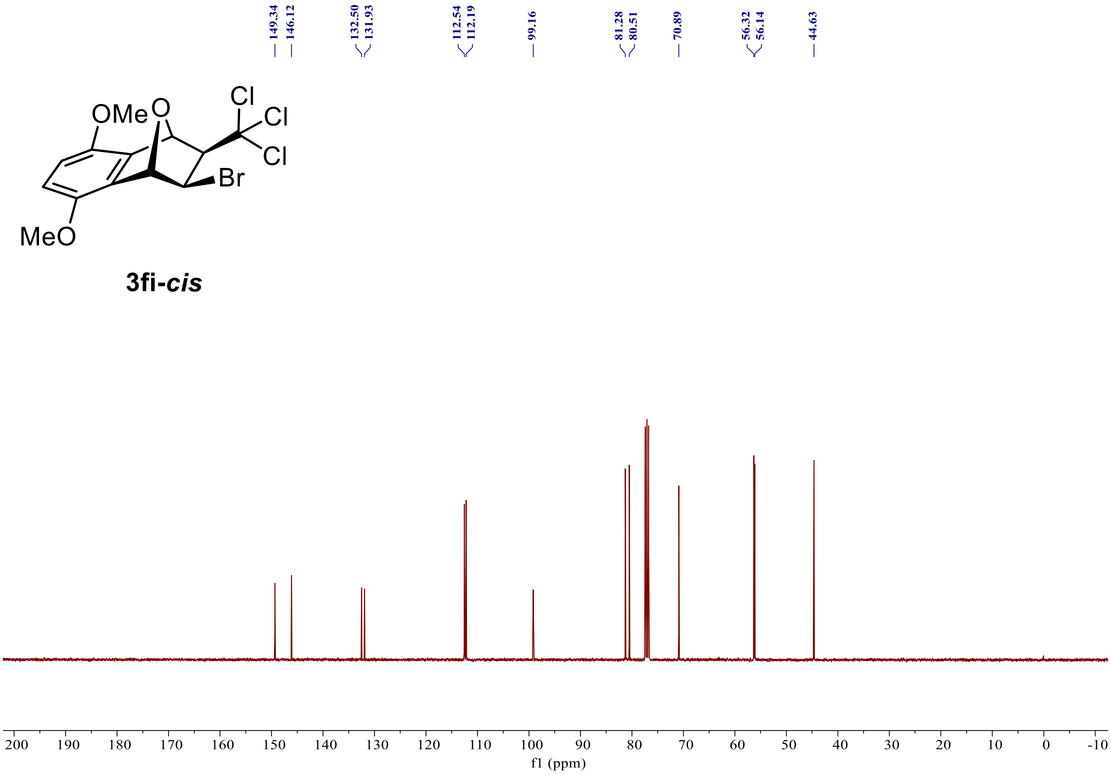
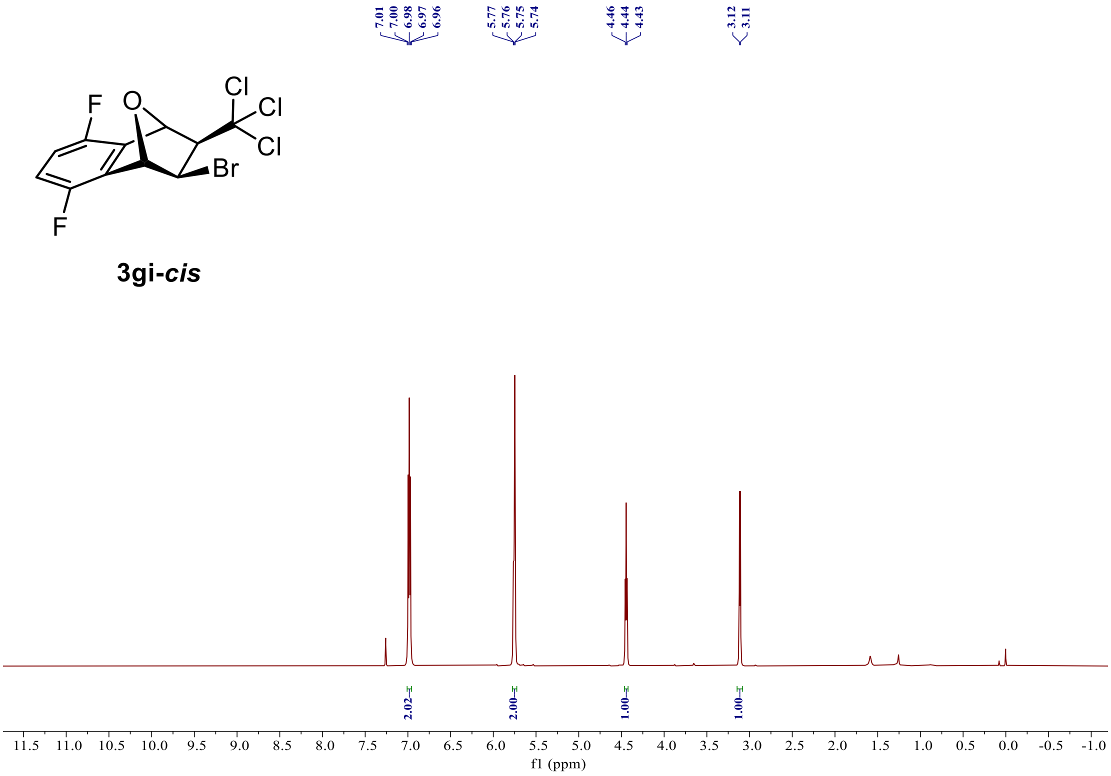


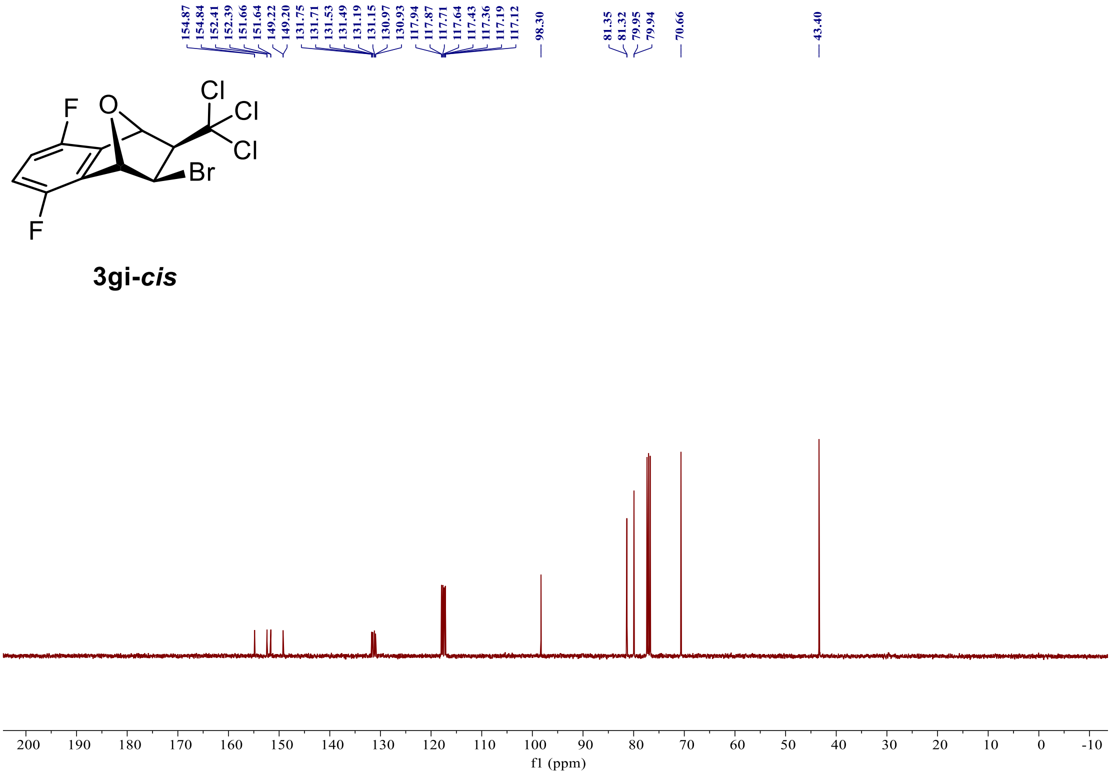
3fi-*cis*

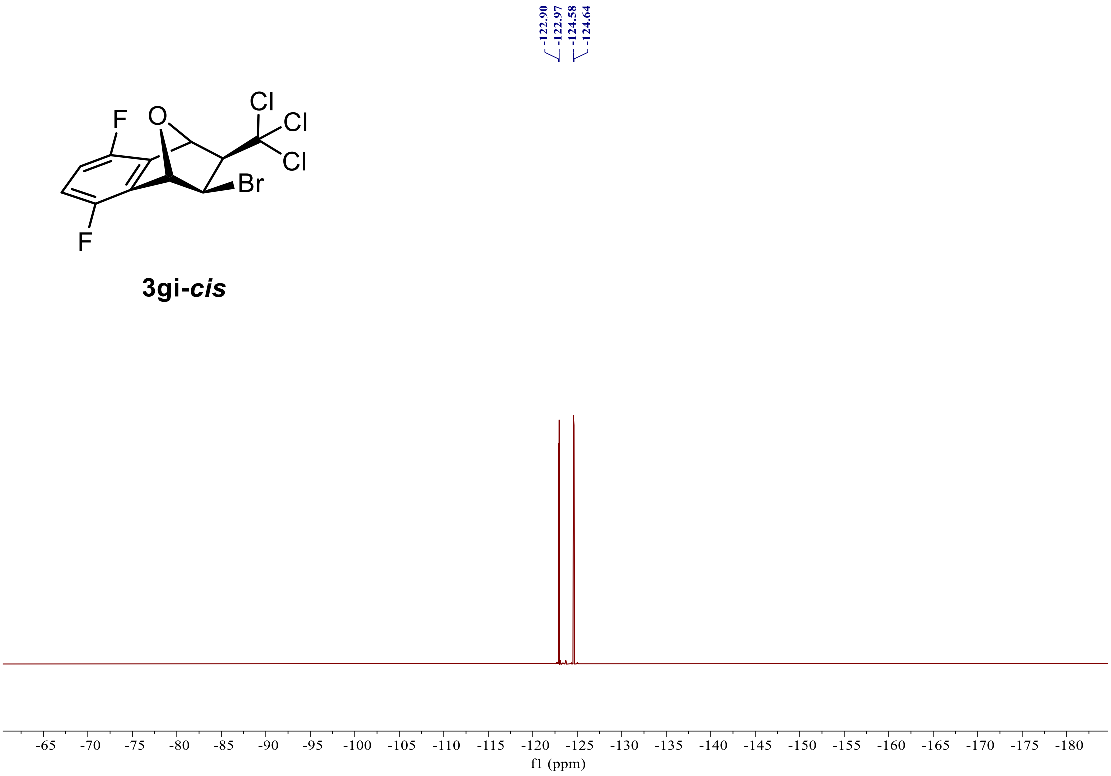


3fi-*cis*



3gi-*cis*


154.87
154.84
152.41
152.39
151.66
151.64
149.22
149.20
131.75
131.71
131.53
131.49
131.19
131.15
130.97
130.93
117.94
117.87
117.71
117.64
117.43
117.36
117.19
117.12
98.30
81.35
81.32
79.95
79.94
70.66
43.40
F
O
Cl
Cl
Cl
Br
F
3gi-*cis*
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-122.90
-122.97
-124.58
-124.64
F
O
Cl
Cl
Cl
Br
F
3gi-*cis*
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
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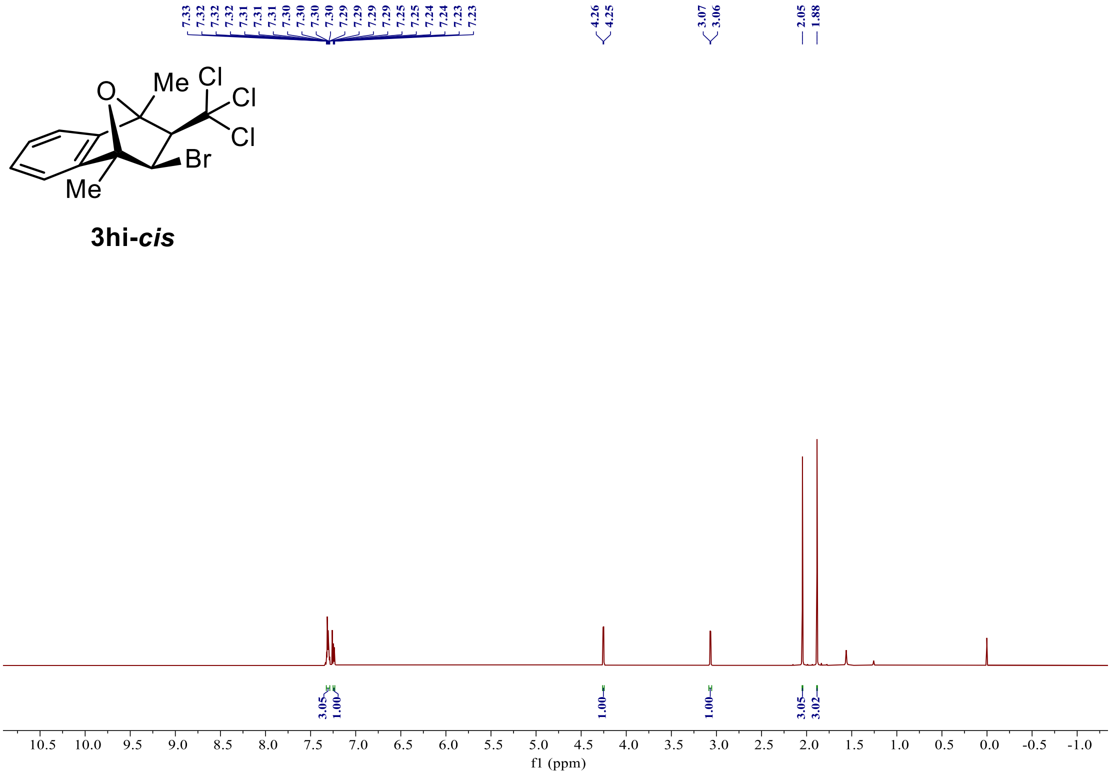
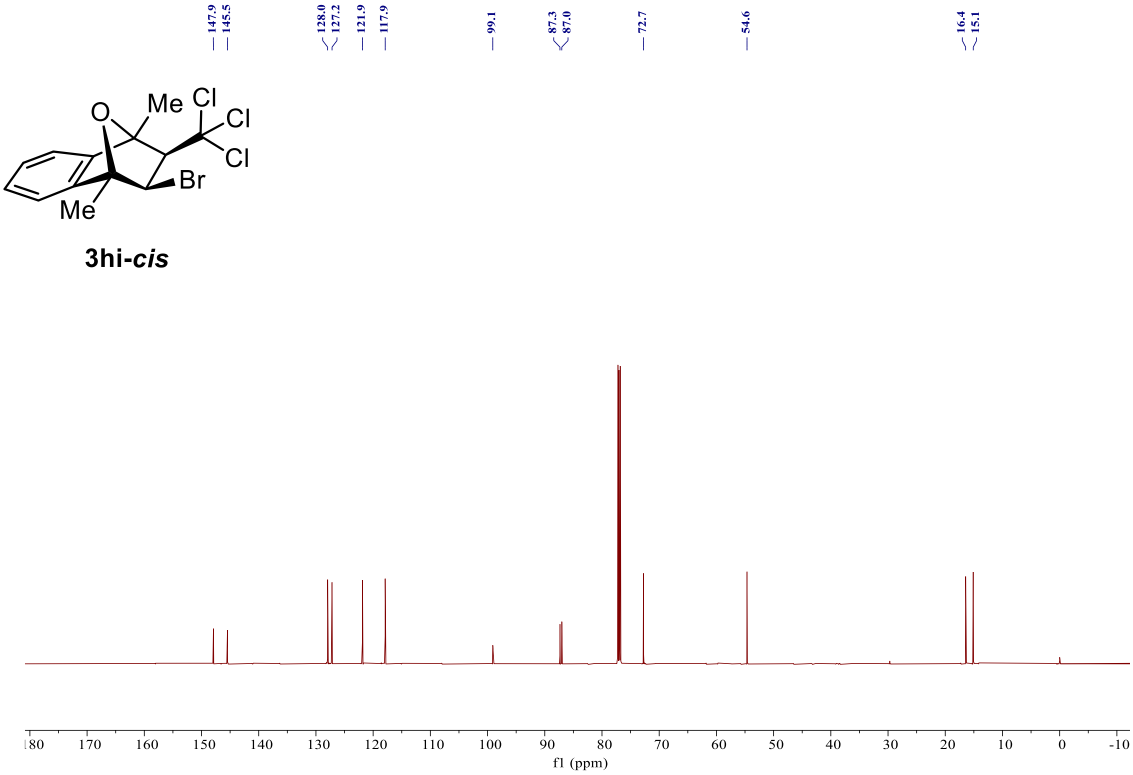
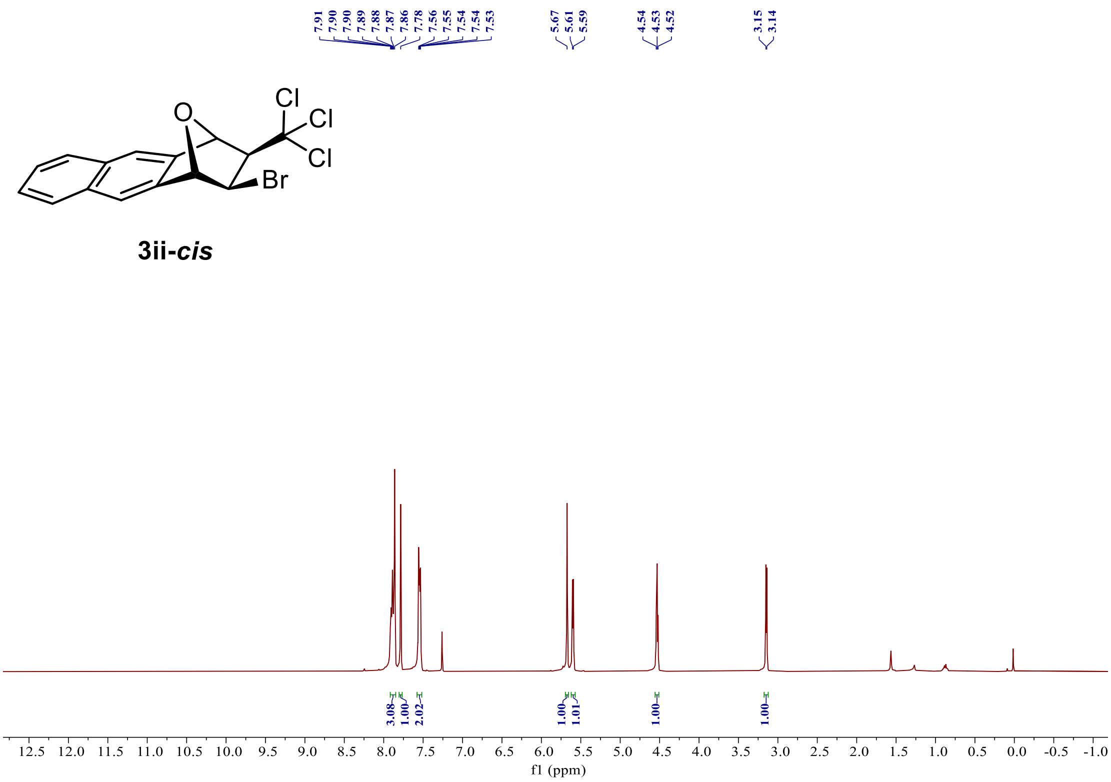
-170
-175
-180
f1 (ppm)

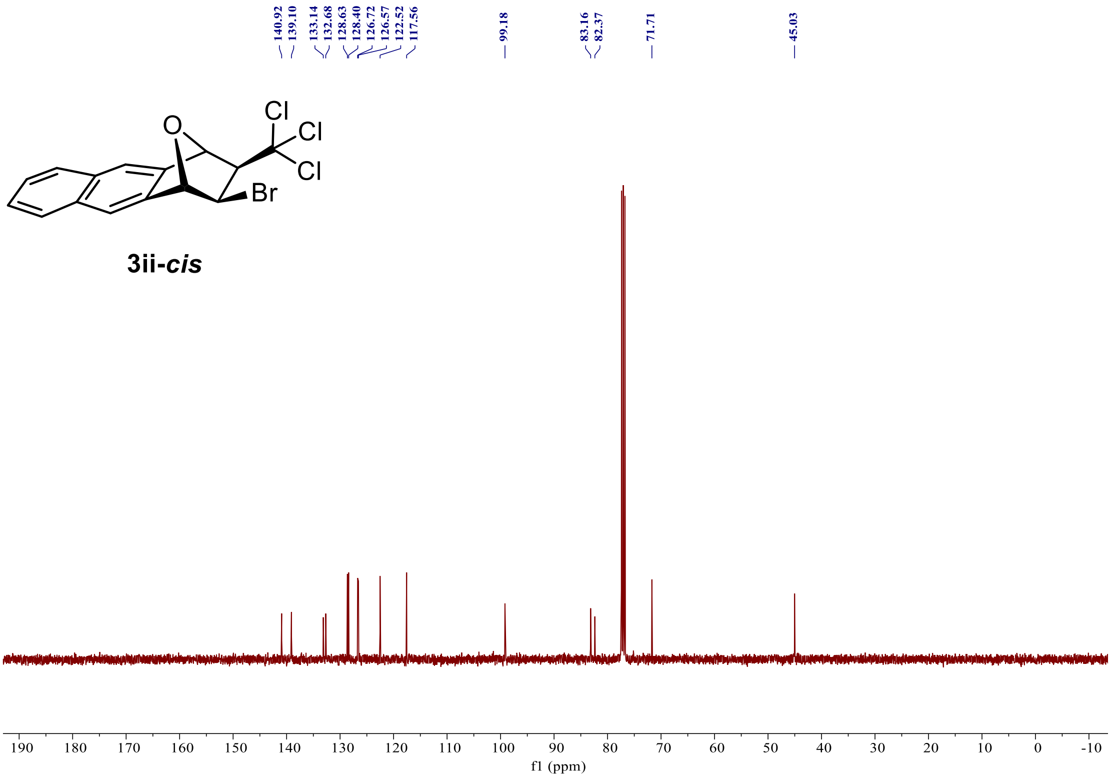


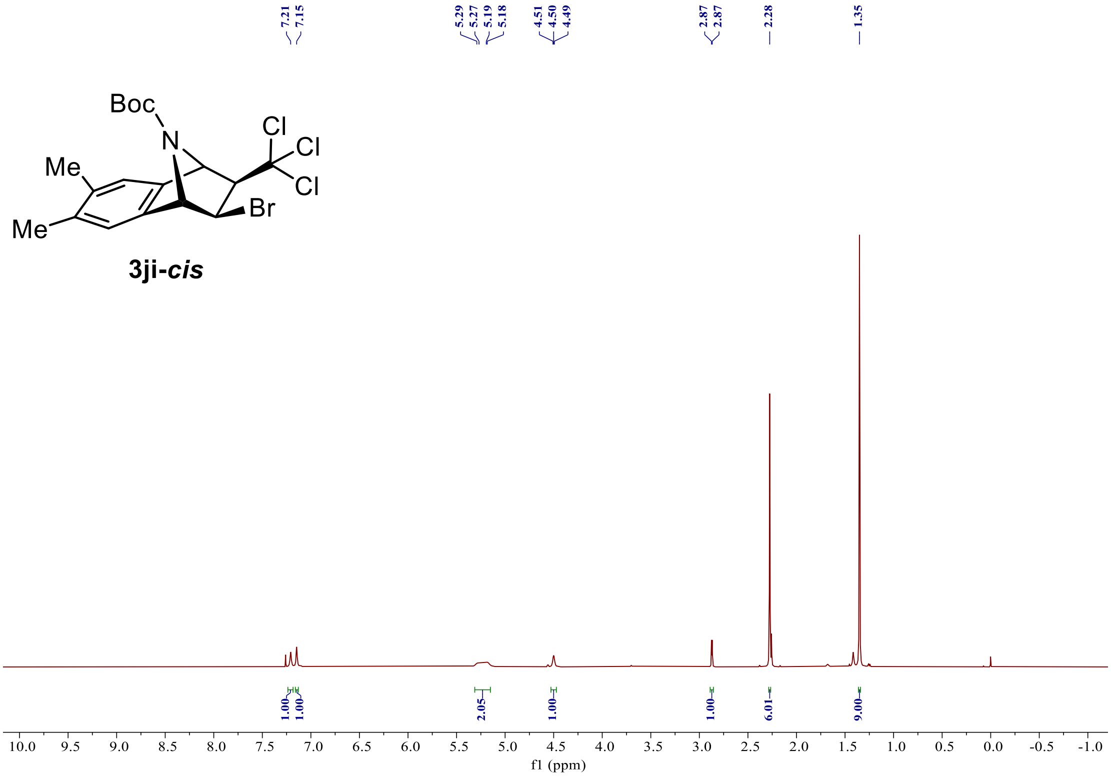
3hi-*cis*

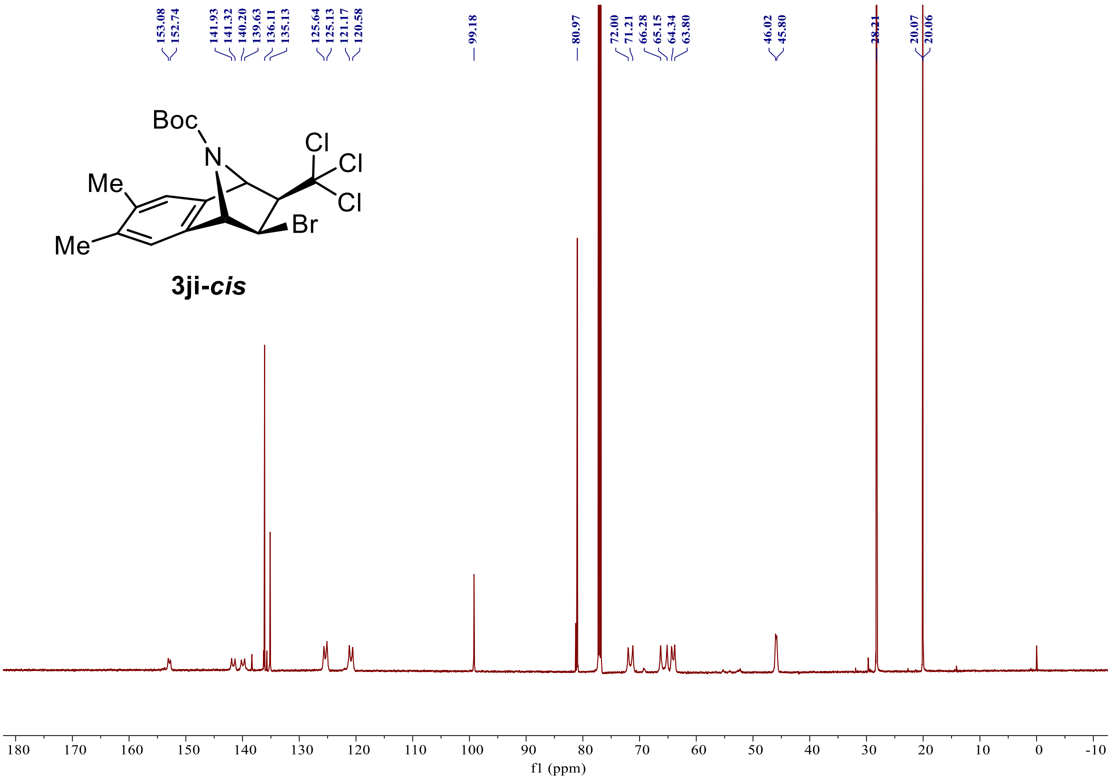


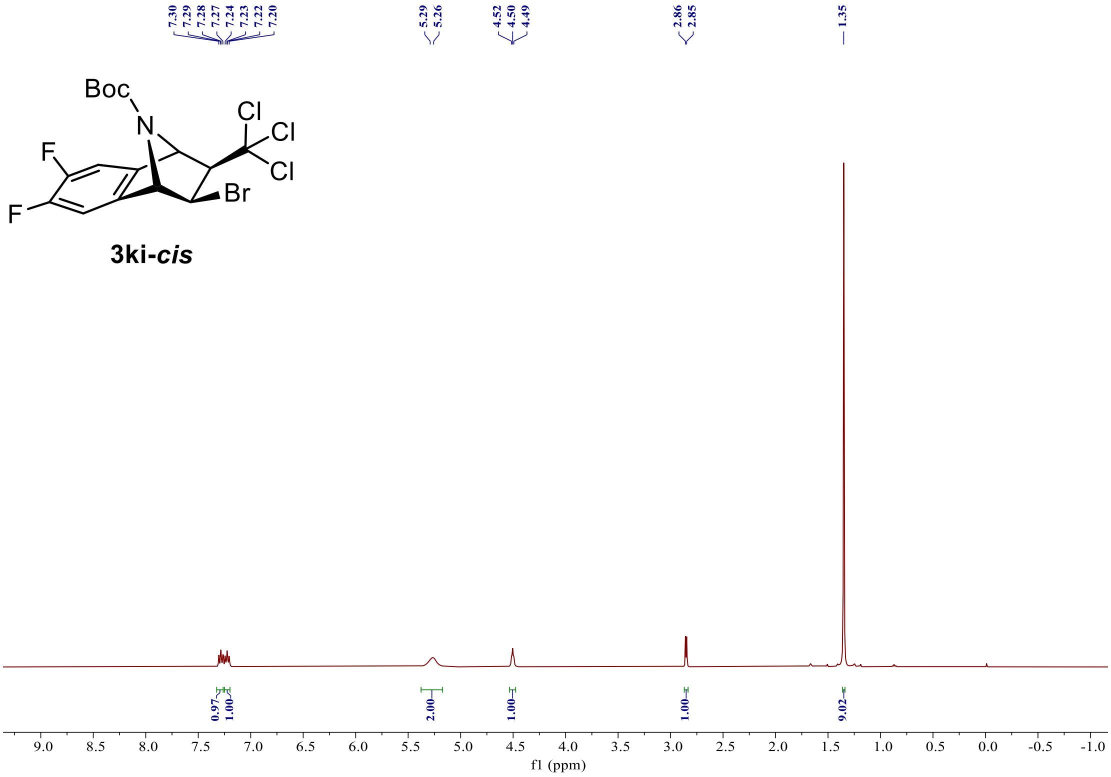
3hi-*cis*


3ii-*cis*

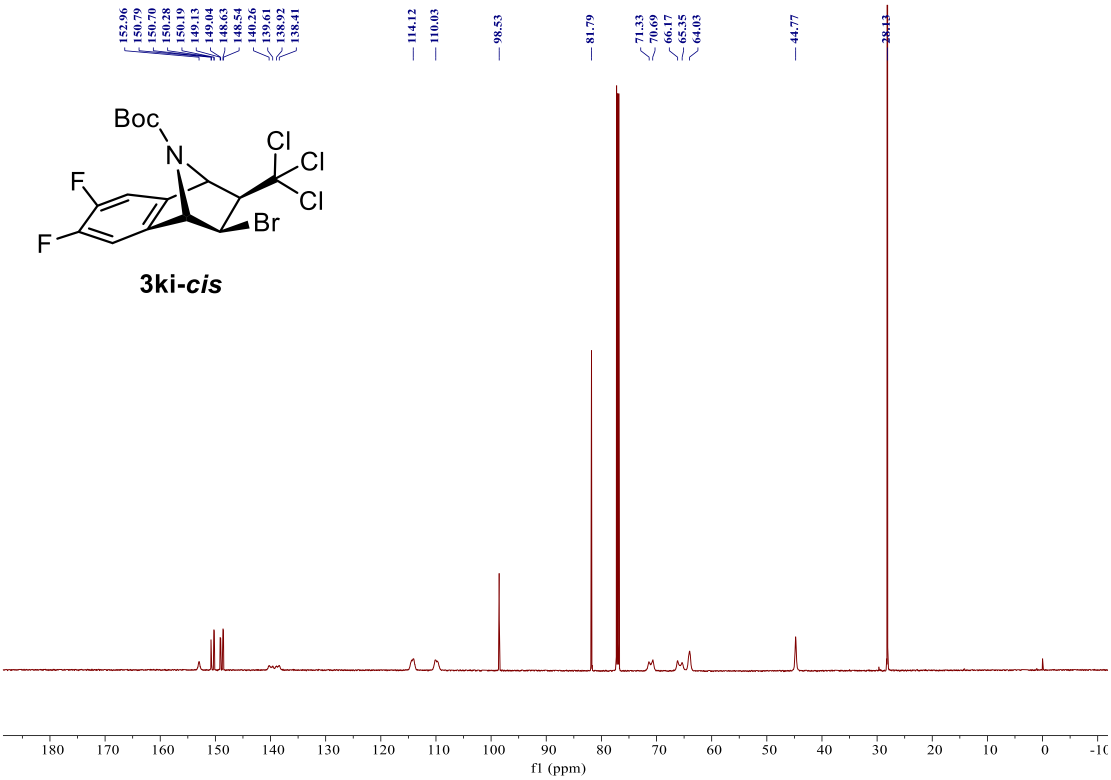

3ii-*cis*


7.21
7.15
5.29
5.27
5.19
5.18
4.51
4.50
4.49
2.87
2.87
2.28
1.35
Boc
N
Cl
Cl
Cl
Me
Me
Br
3ji-cis
1.00
1.00
2.05
1.00
1.00
6.01
9.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

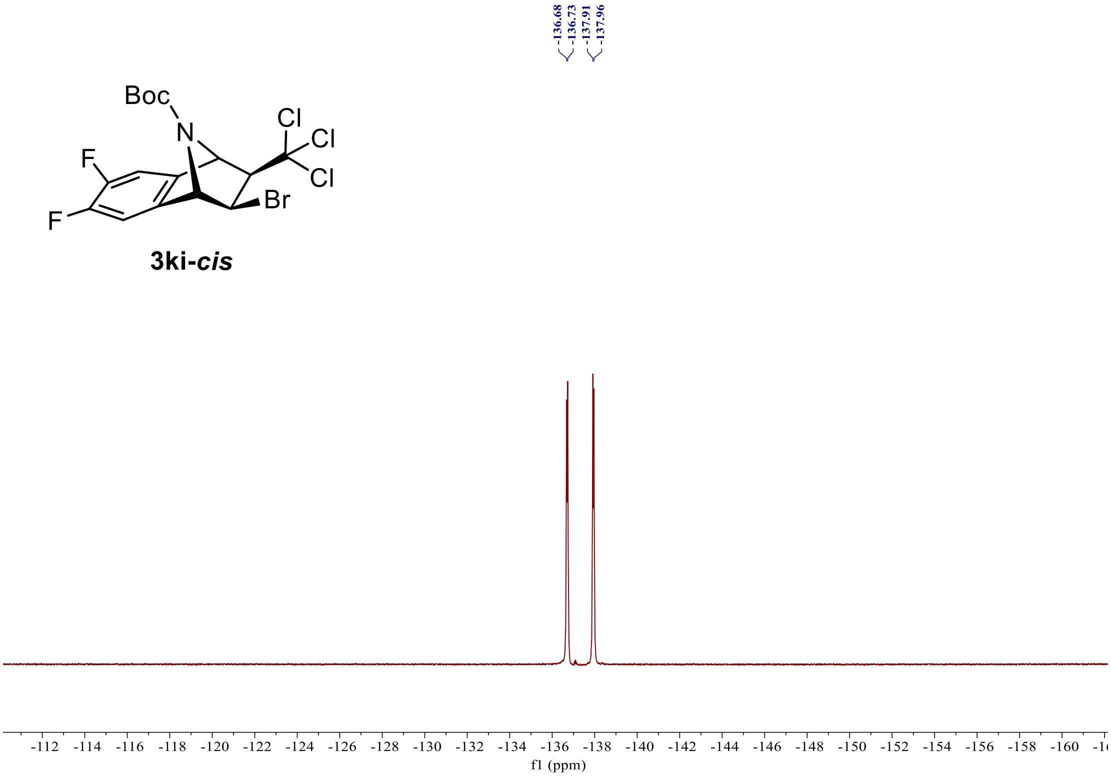

153.08
152.74
141.93
141.32
140.20
139.63
136.11
135.13
125.64
125.13
121.17
120.58
99.18
80.97
72.00
71.21
66.28
65.15
64.34
63.80
46.02
45.80
28.21
20.07
20.06
Boc
N
Cl
Cl
Cl
Me
Me
Br
3ji-cis
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



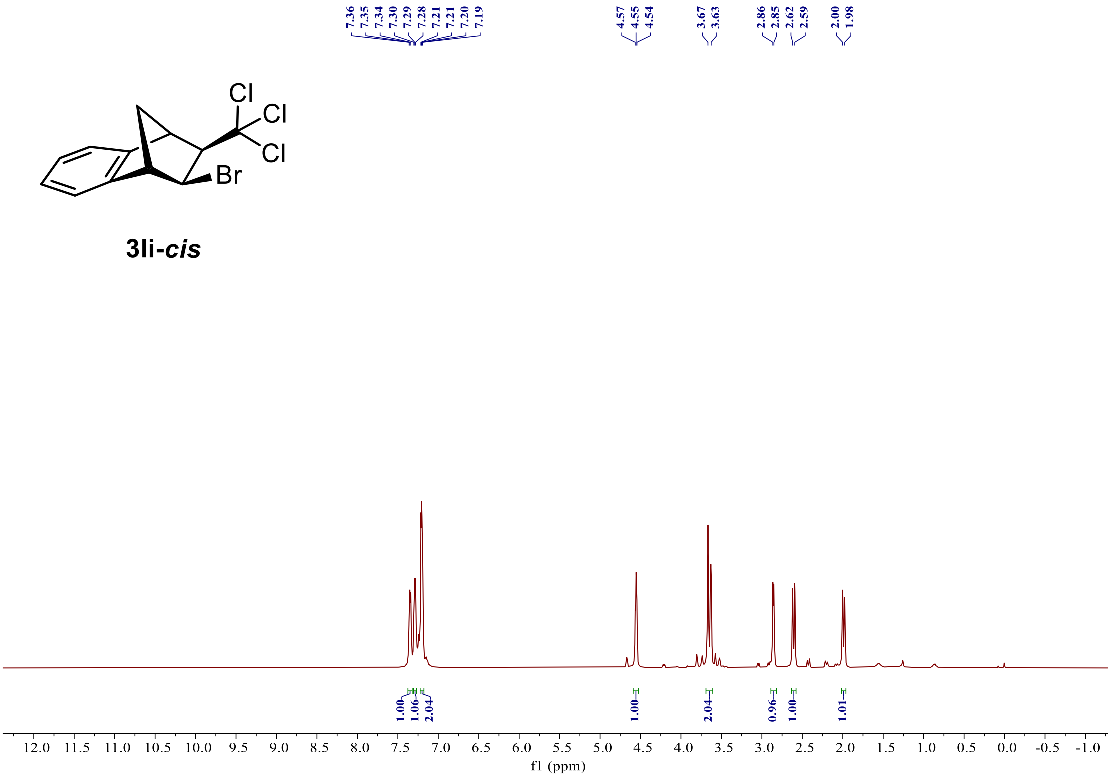
3ki-*cis*



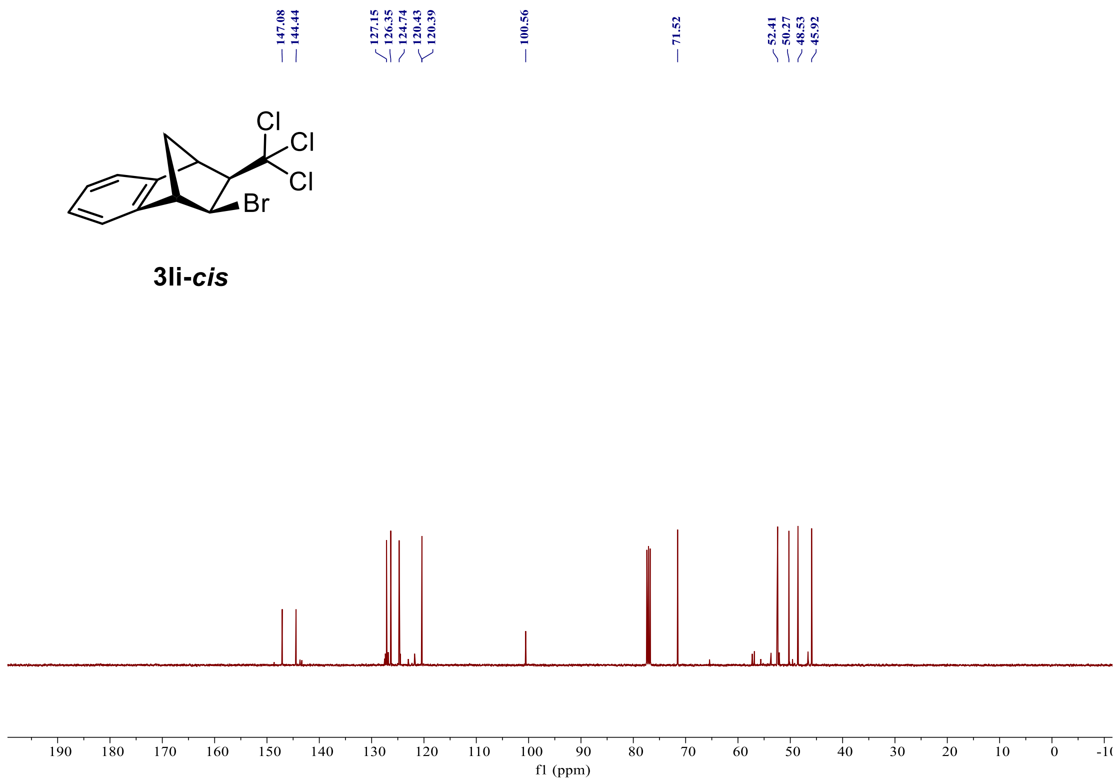
3ki-*cis*



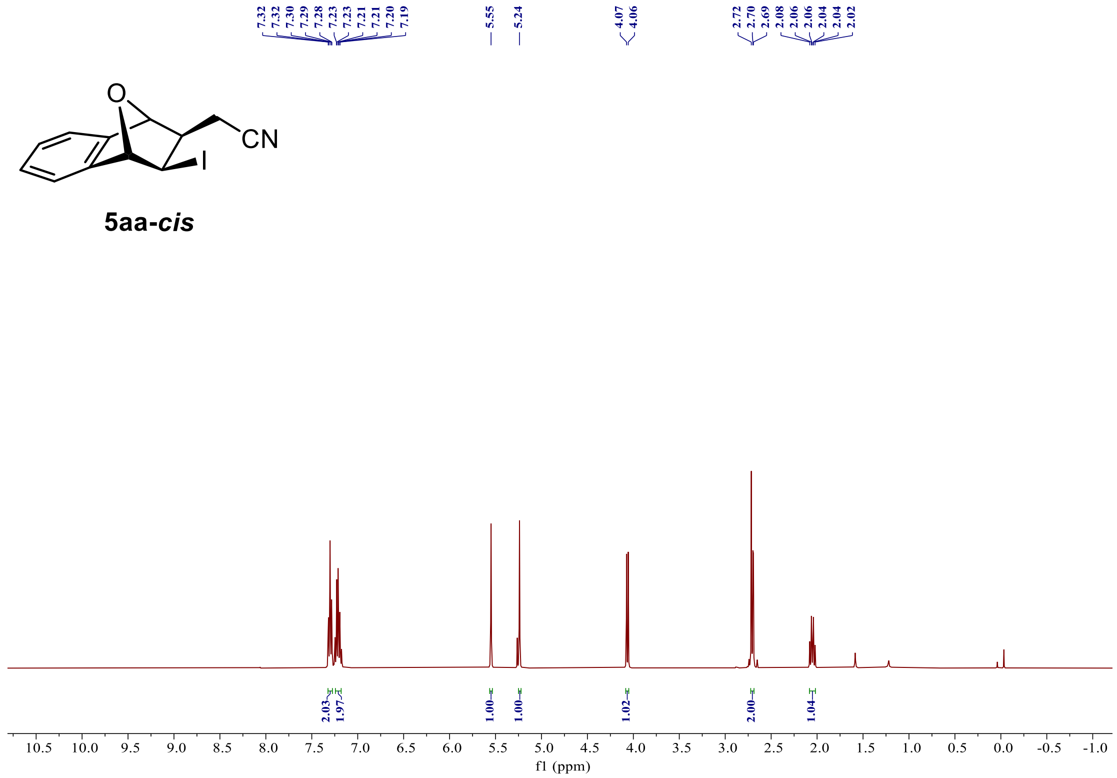
3ki-*cis*



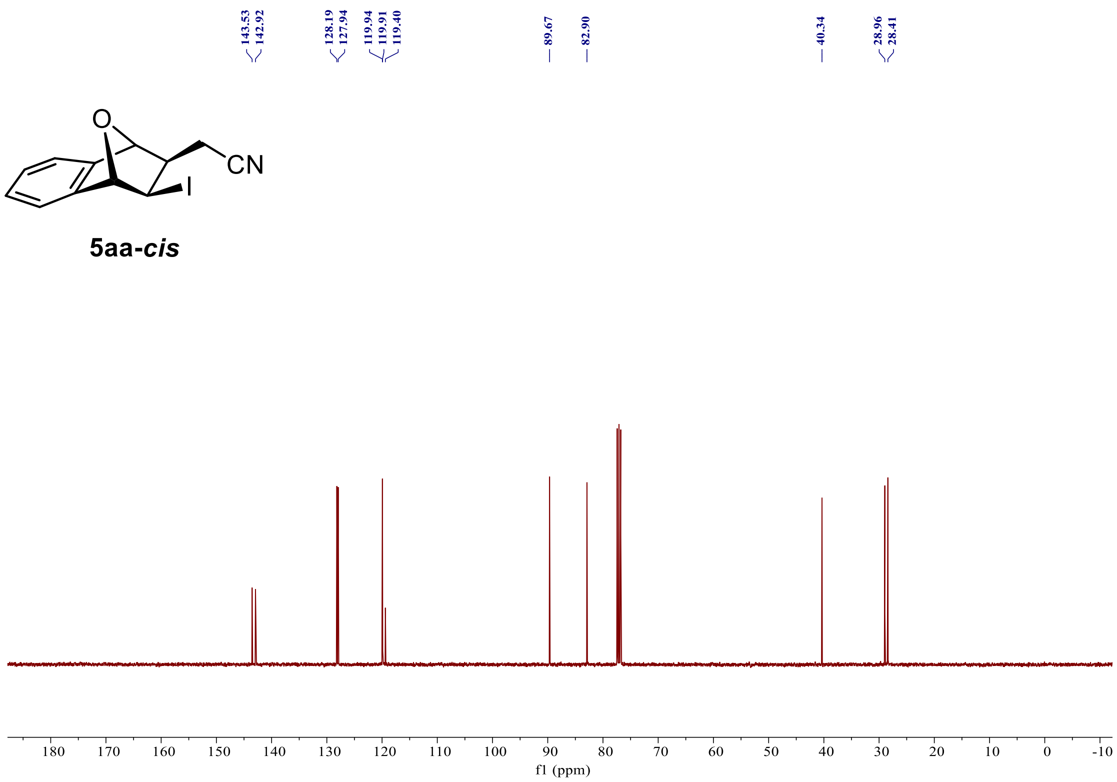
3li-*cis*

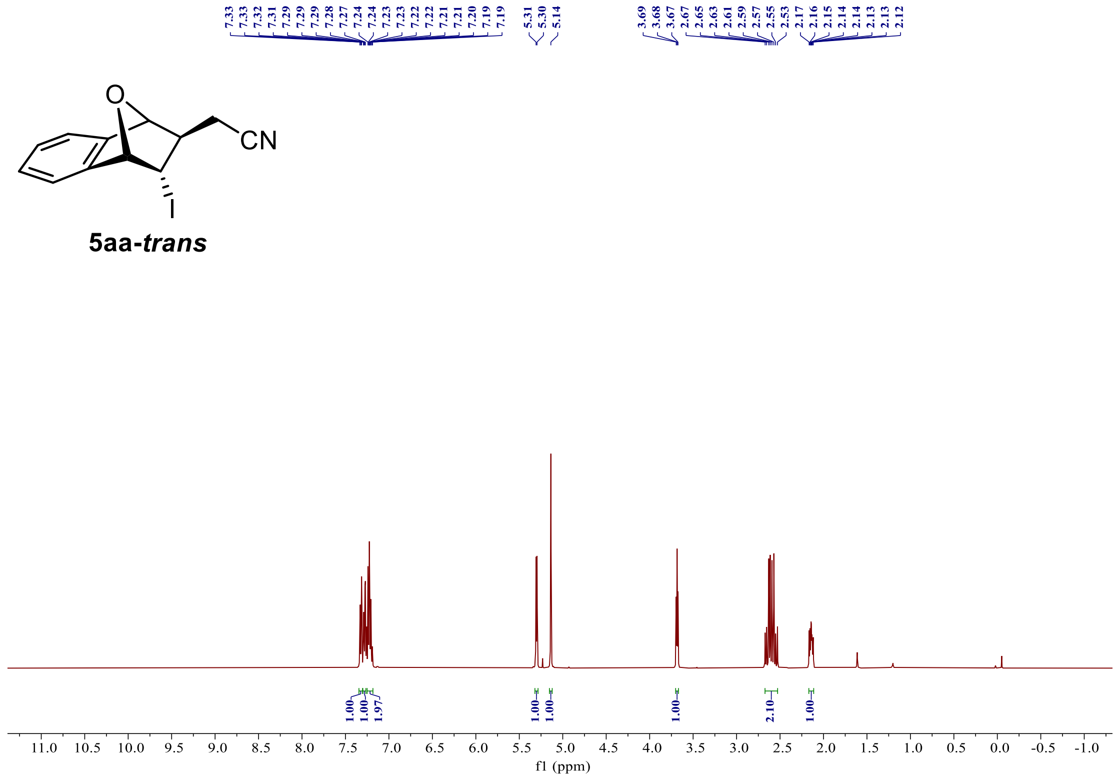


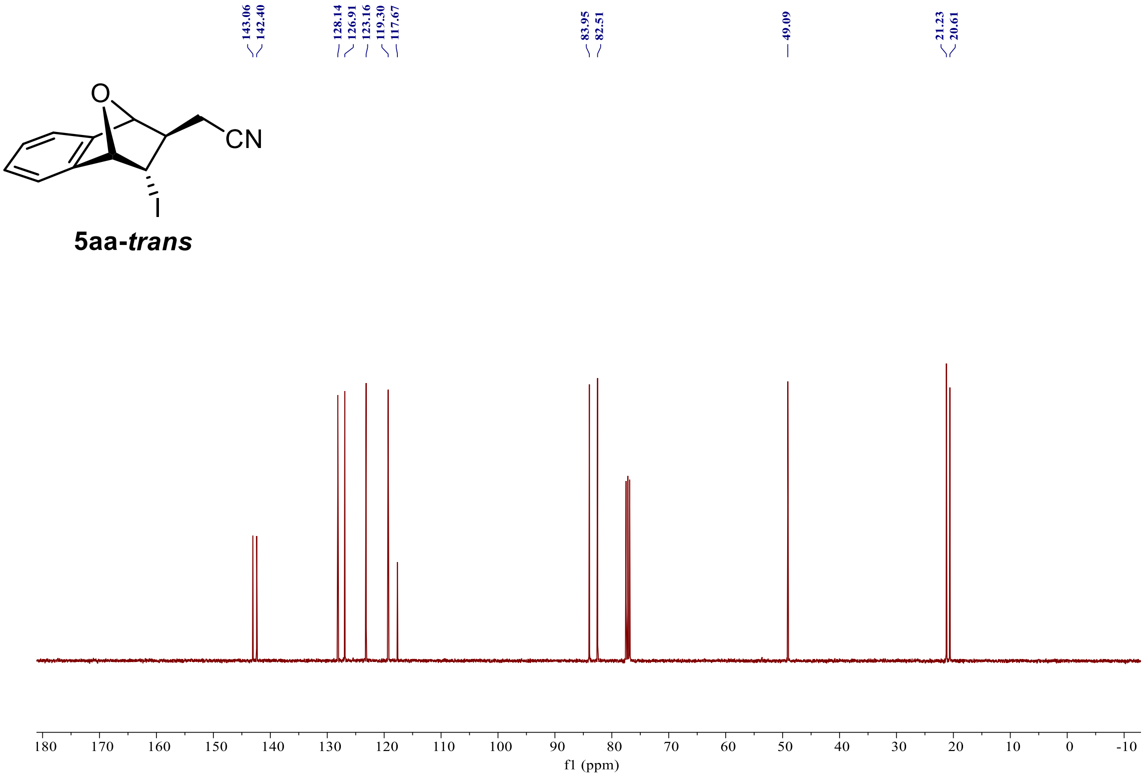
3li-*cis*



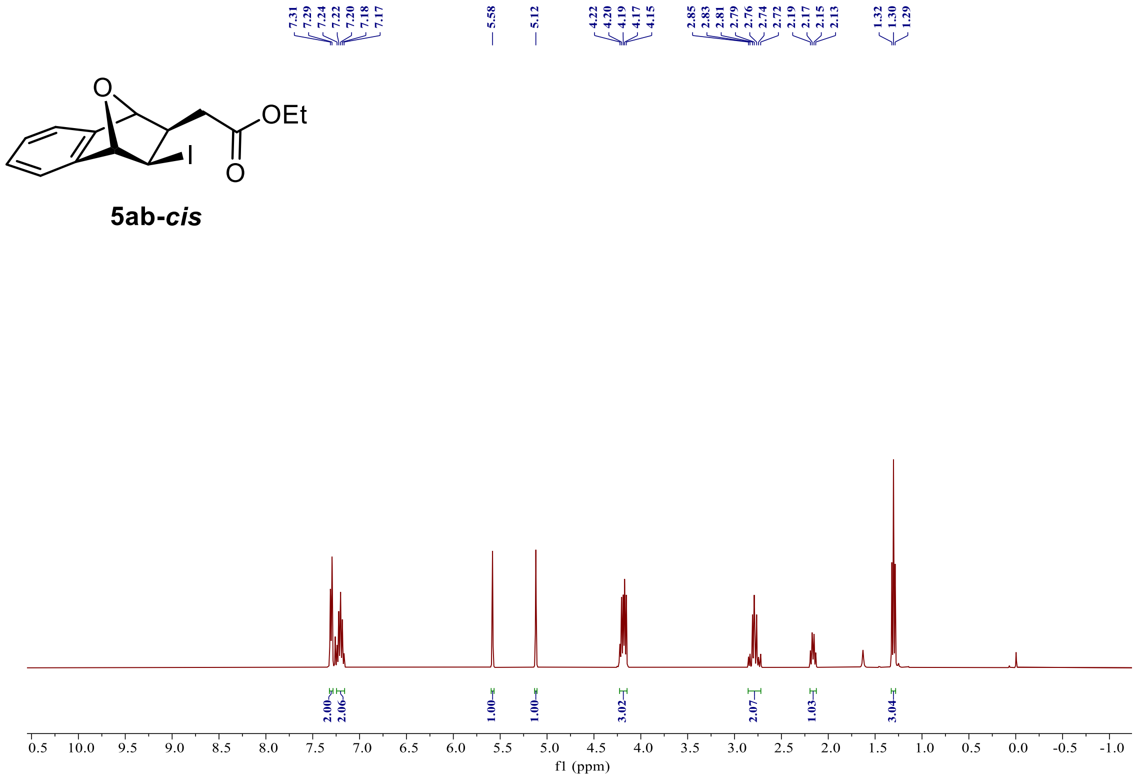
5aa-*cis*


5aa-*cis*

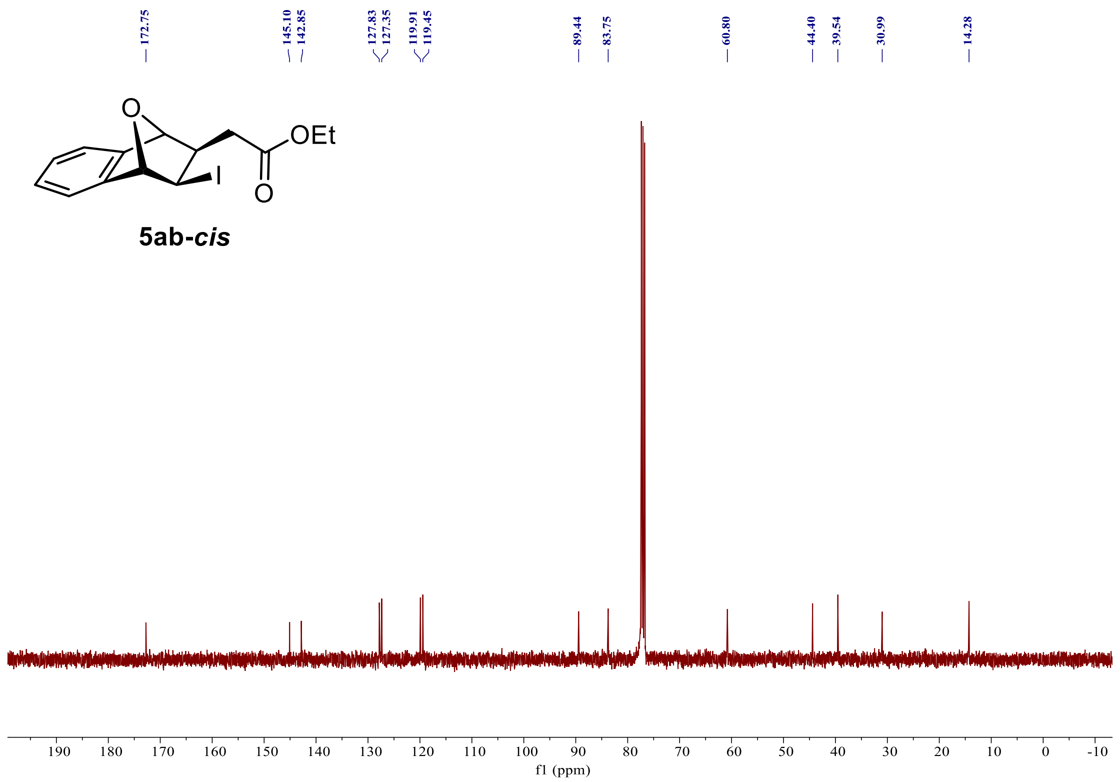

5aa-*trans*



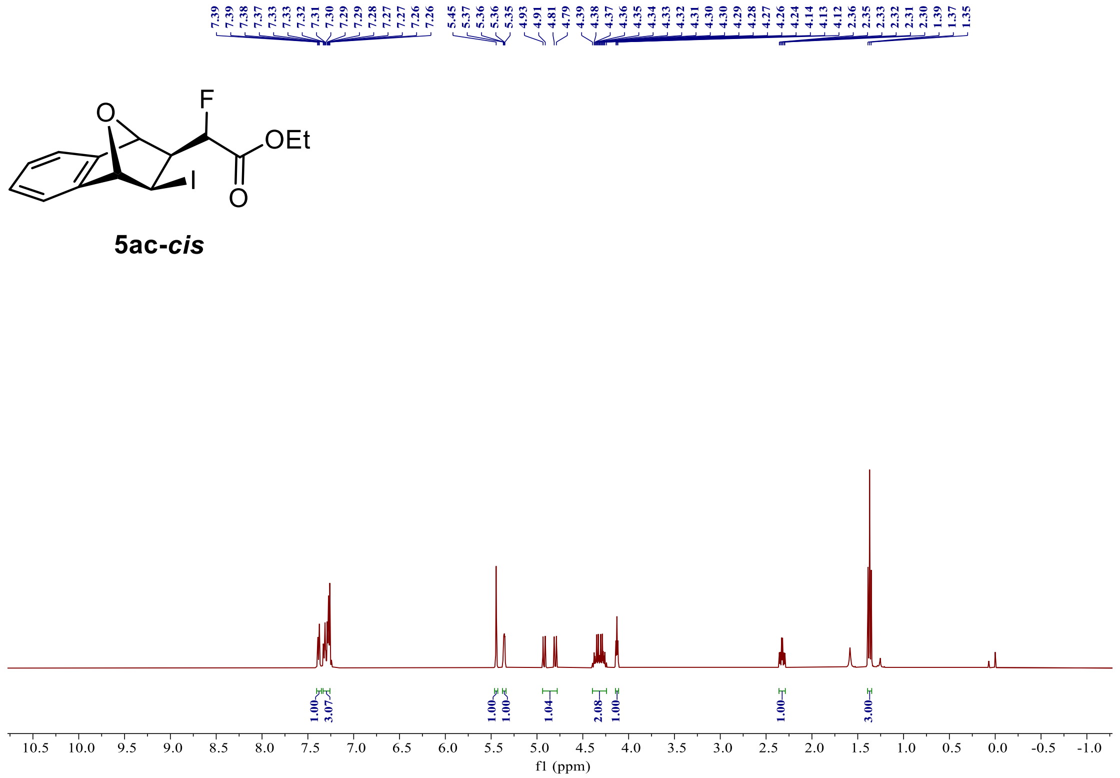
5aa-*trans*



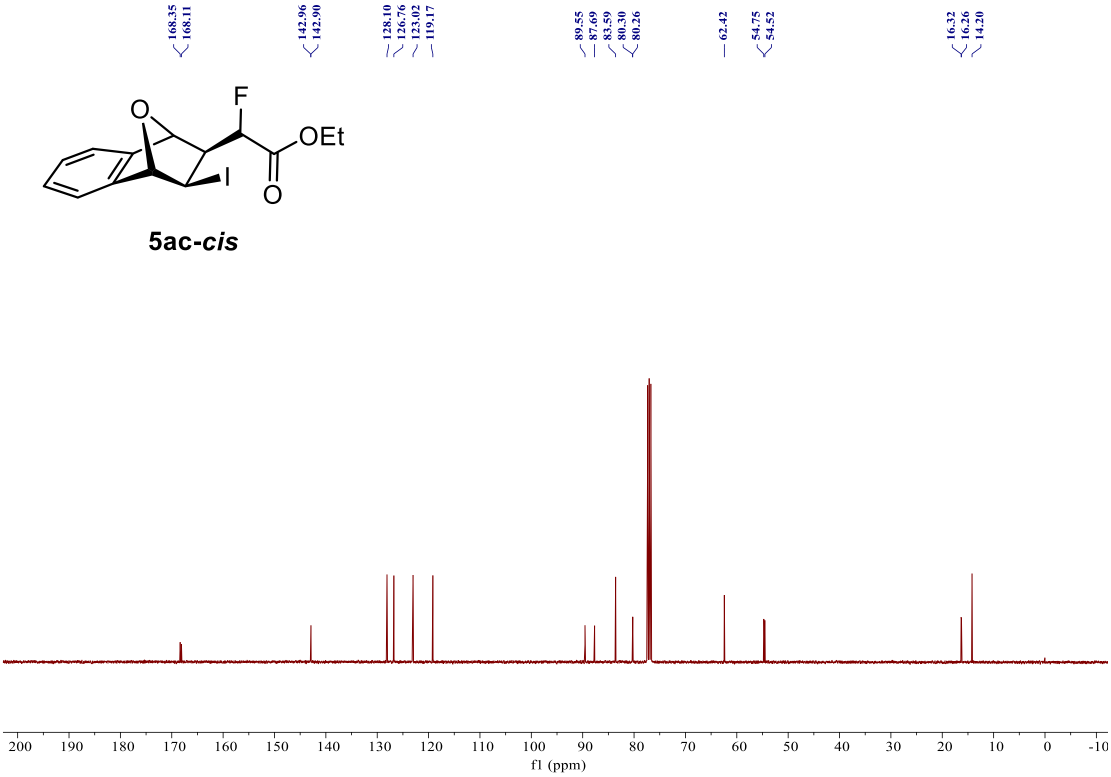
5ab-*cis*



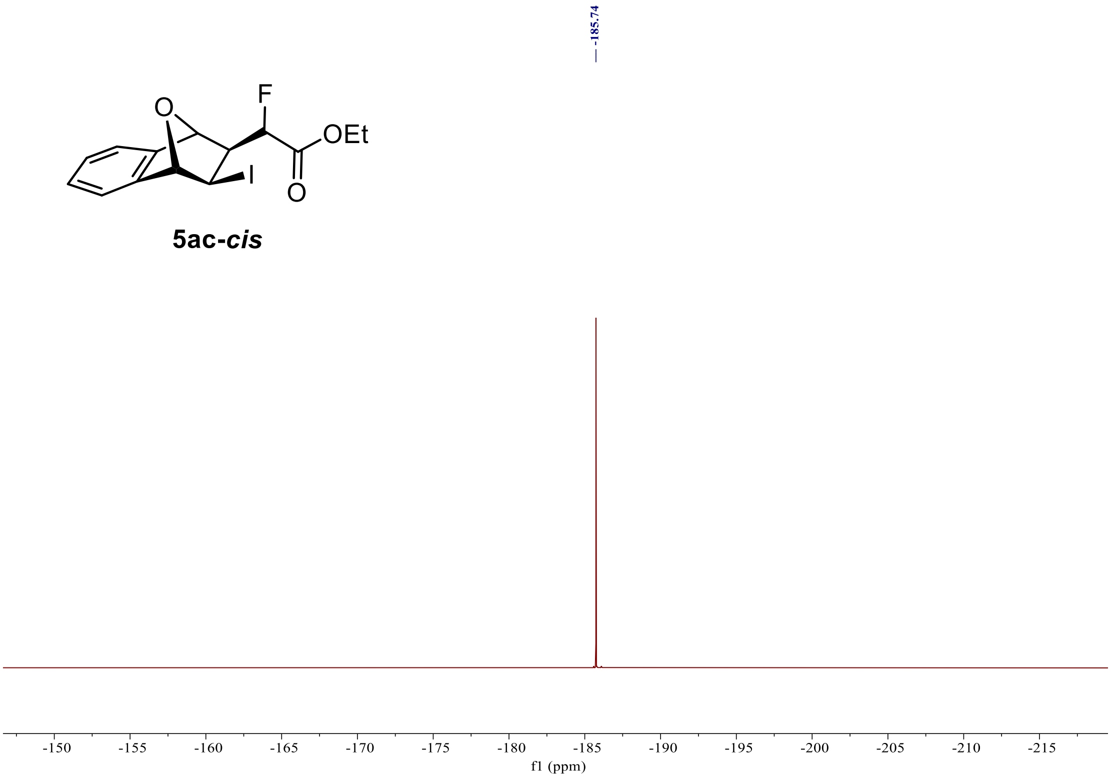
5ab-*cis*



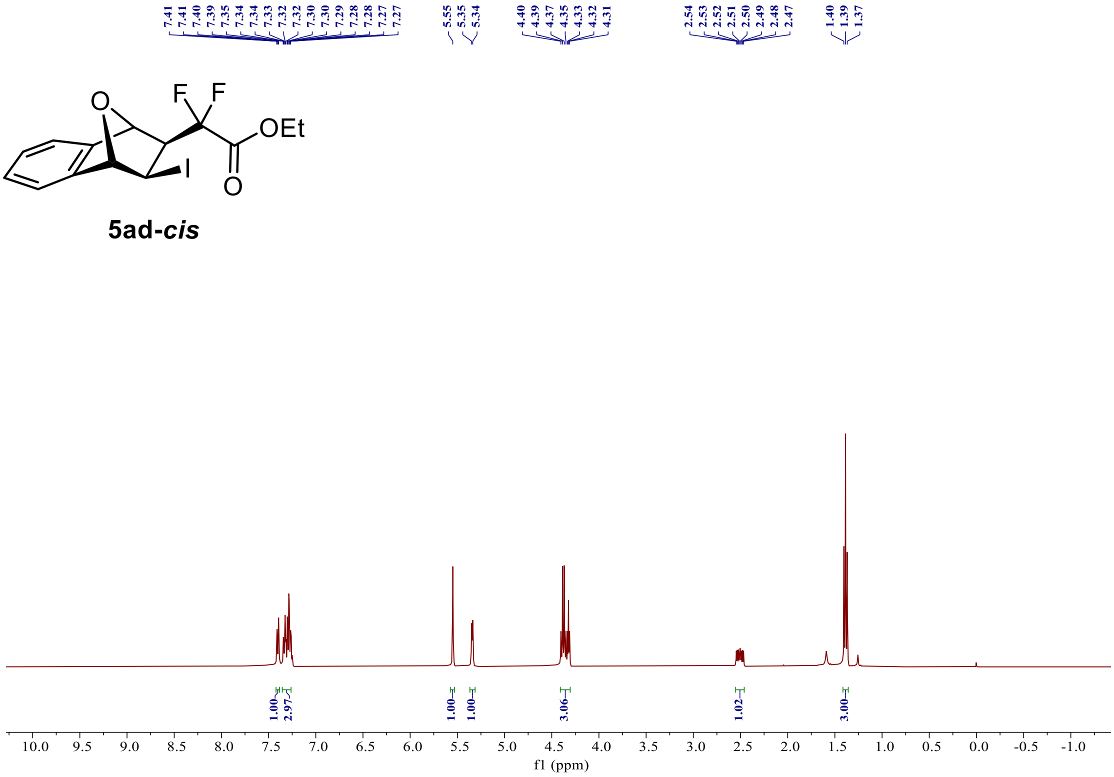
5ac-*cis*

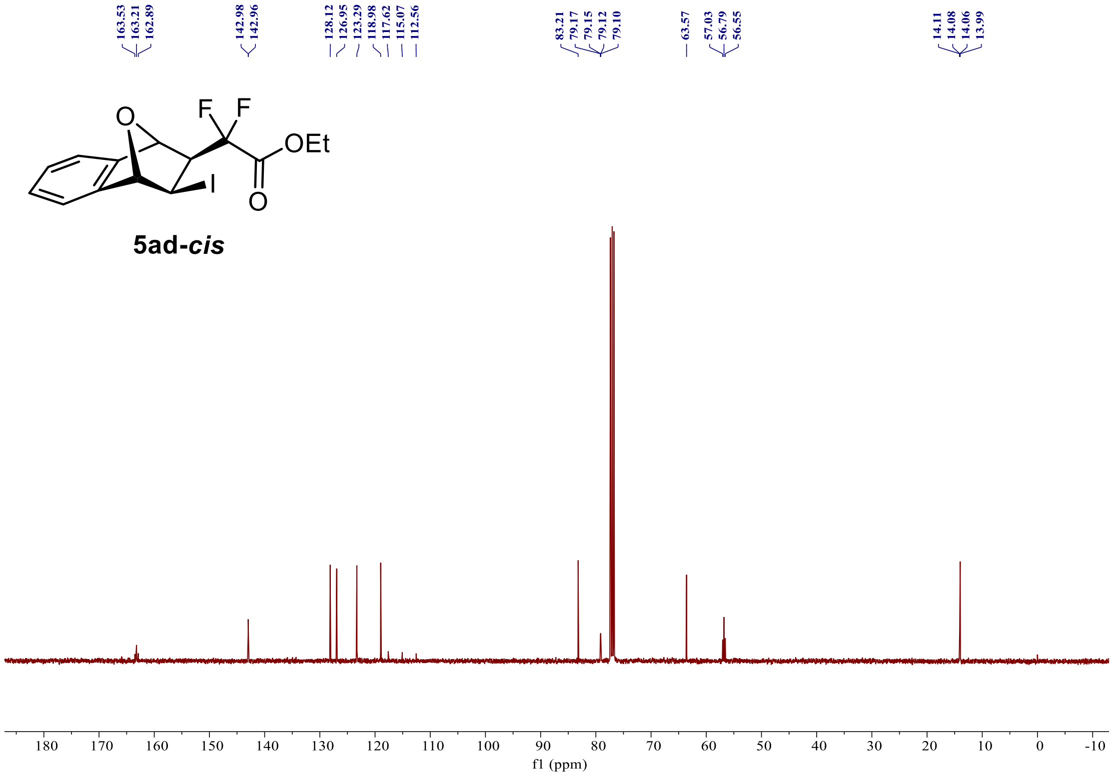


5ac-*cis*



5ac-*cis*


7.41
7.41
7.40
7.39
7.35
7.34
7.34
7.33
7.32
7.32
7.30
7.30
7.29
7.28
7.28
7.27
5.55
5.35
5.34
4.40
4.39
4.37
4.35
4.33
4.32
4.31
2.54
2.53
2.52
2.51
2.50
2.49
2.48
2.47
1.40
1.39
1.37
F
F
O
OEt
I
O
5ad-cis
1.00
2.97
1.00
1.00
3.06
1.02
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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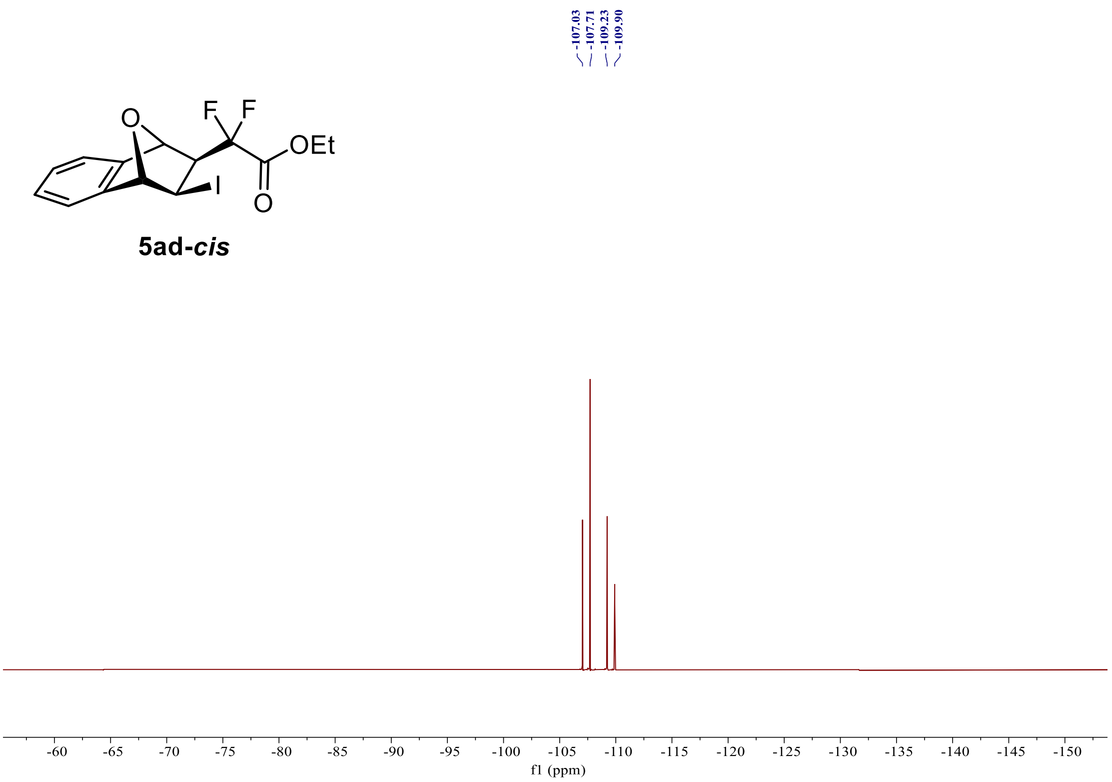
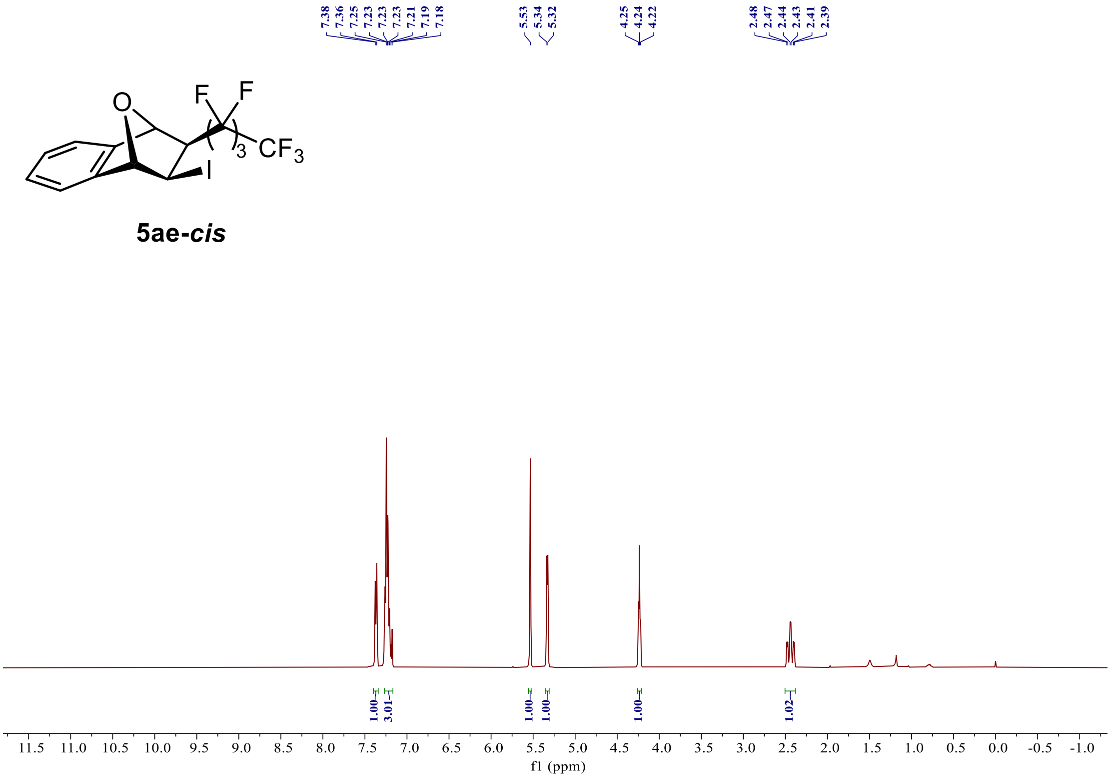
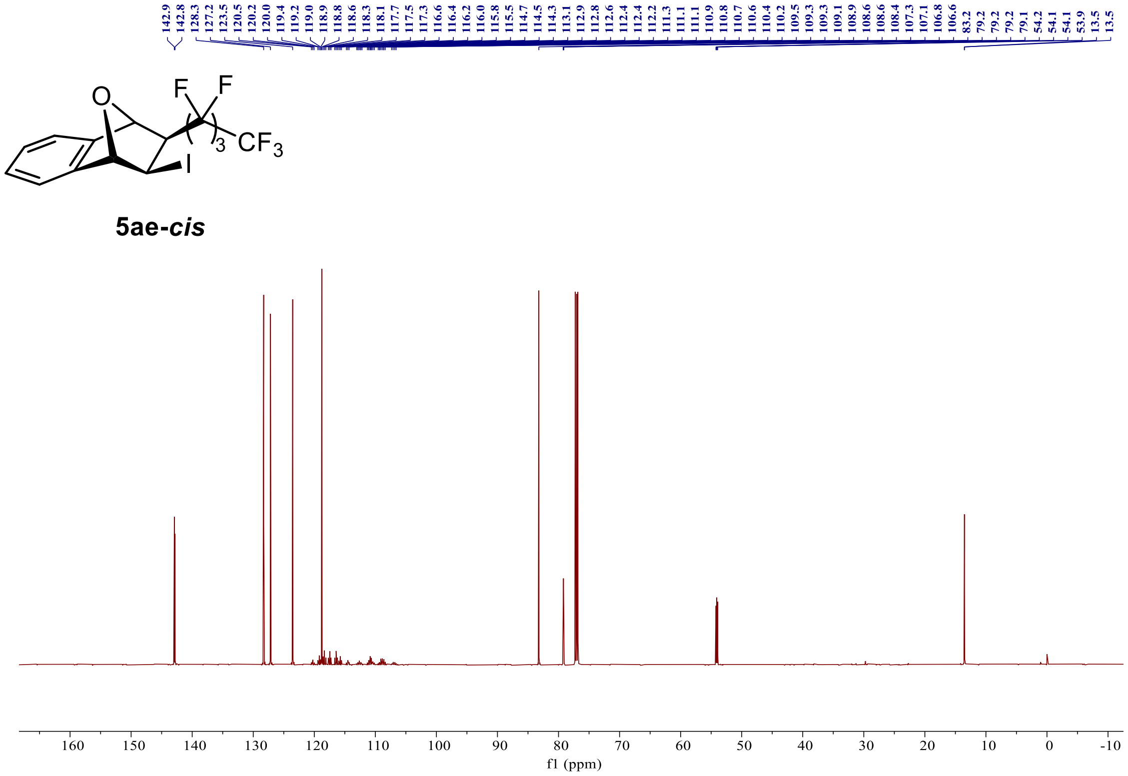
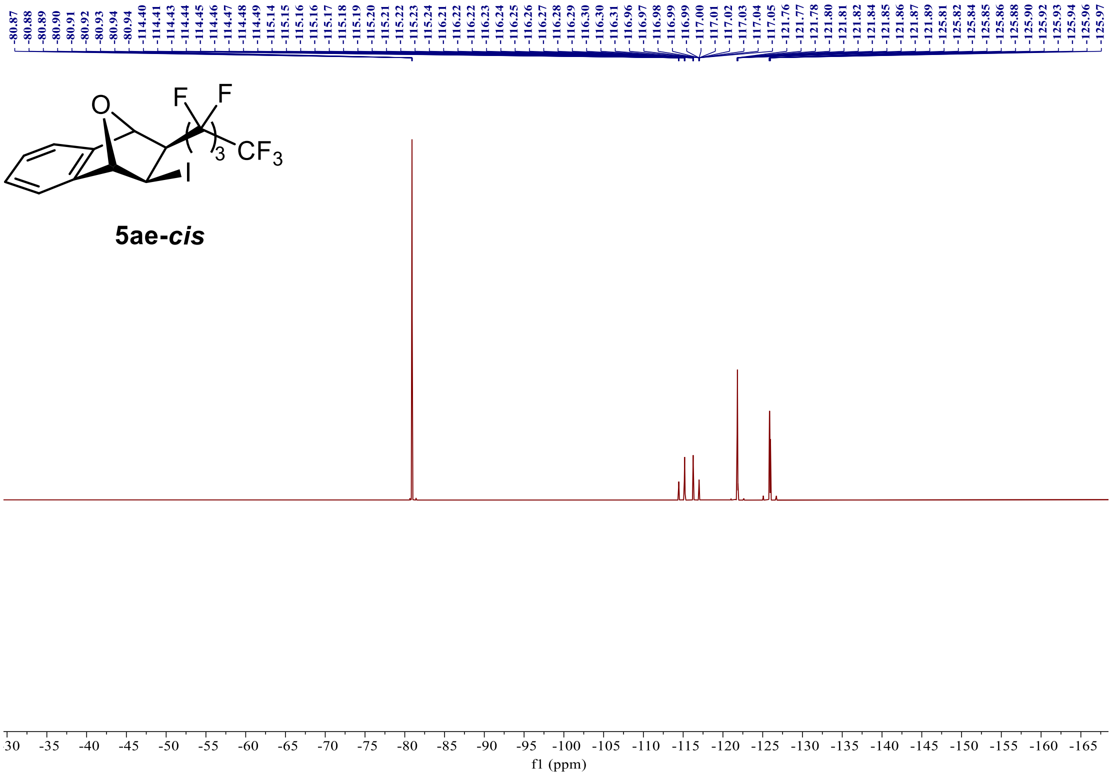
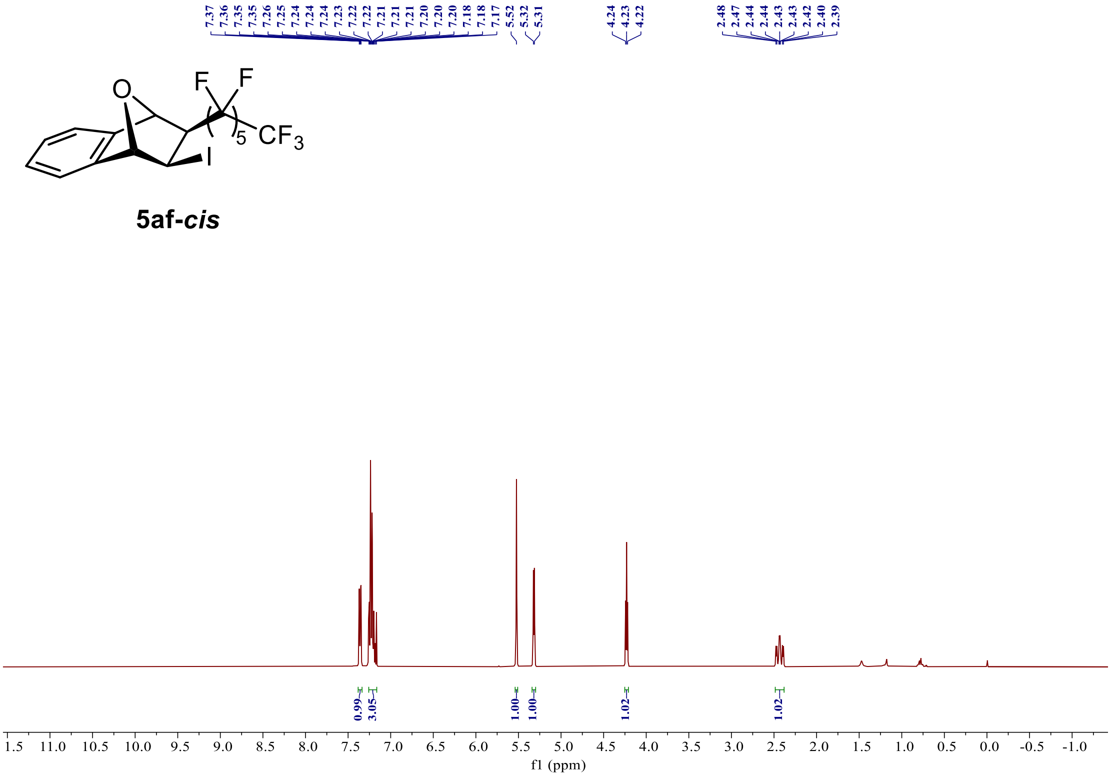
163.21
162.89
142.98
142.96
128.12
126.95
123.29
118.98
117.62
115.07
112.56
83.21
79.17
79.15
79.12
79.10
63.57
57.03
56.79
56.55
14.11
14.08
14.06
13.99
F
F
O
OEt
I
O
5ad-cis
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


5ad-*cis*

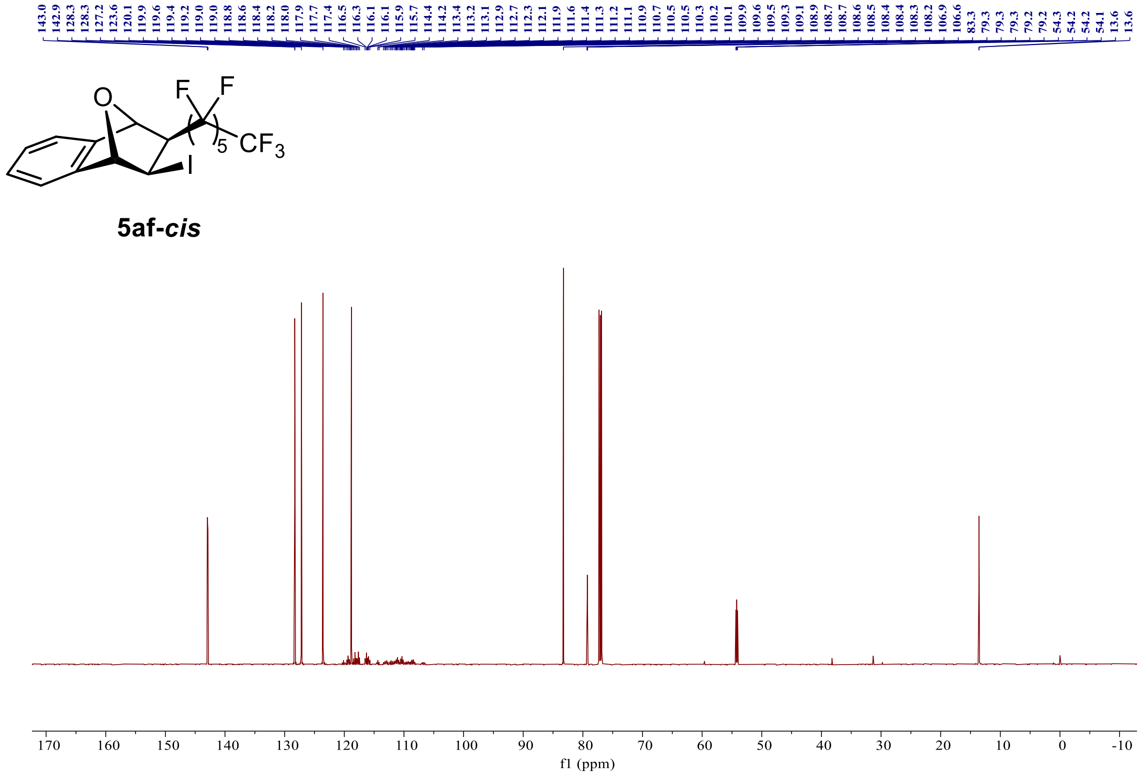

5ae-*cis*


5ae-*cis*

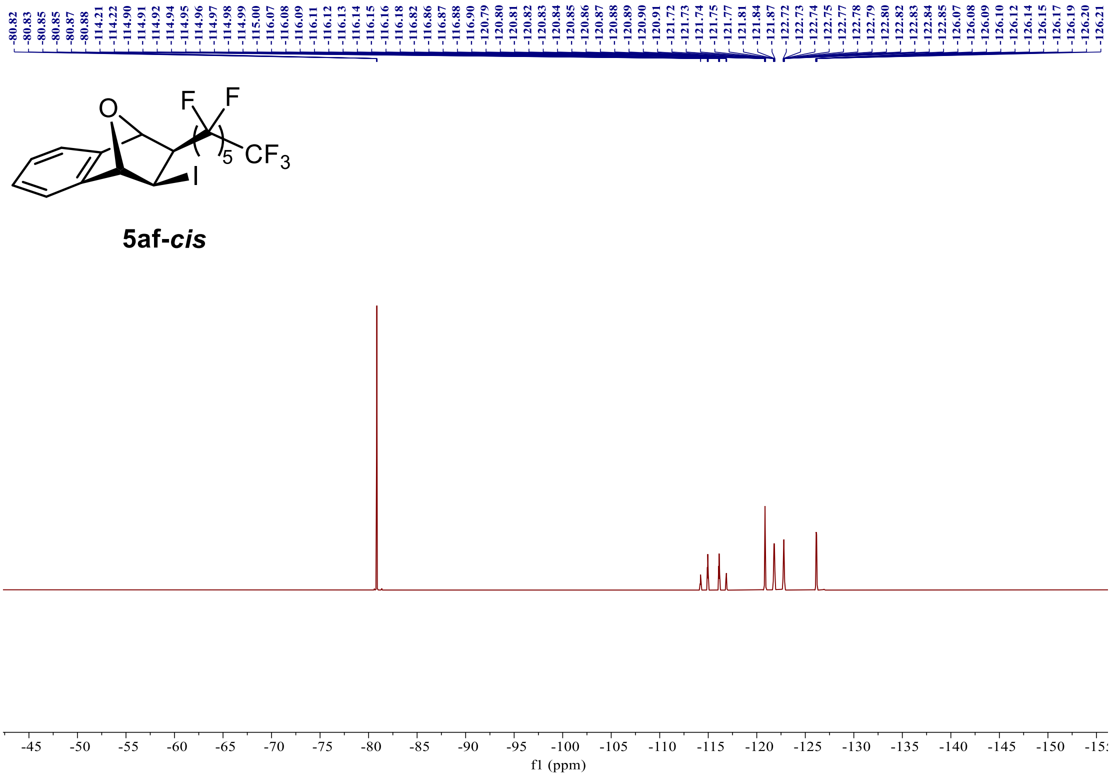

5ae-*cis*



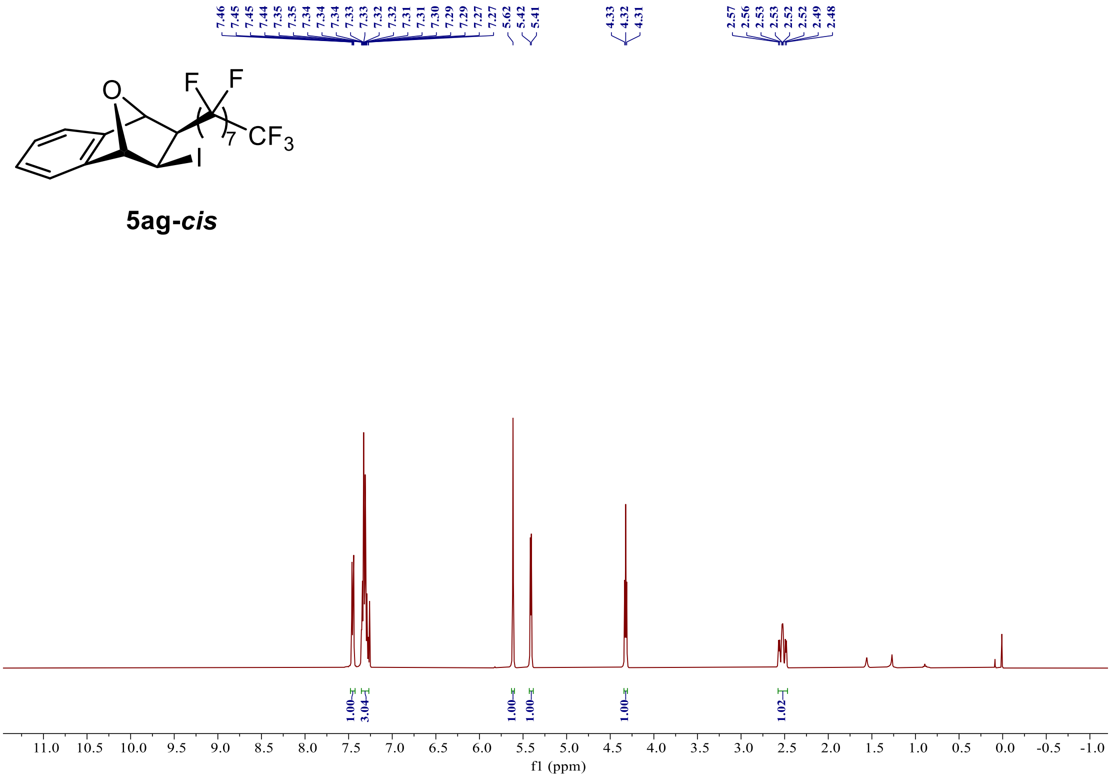
5af-*cis*



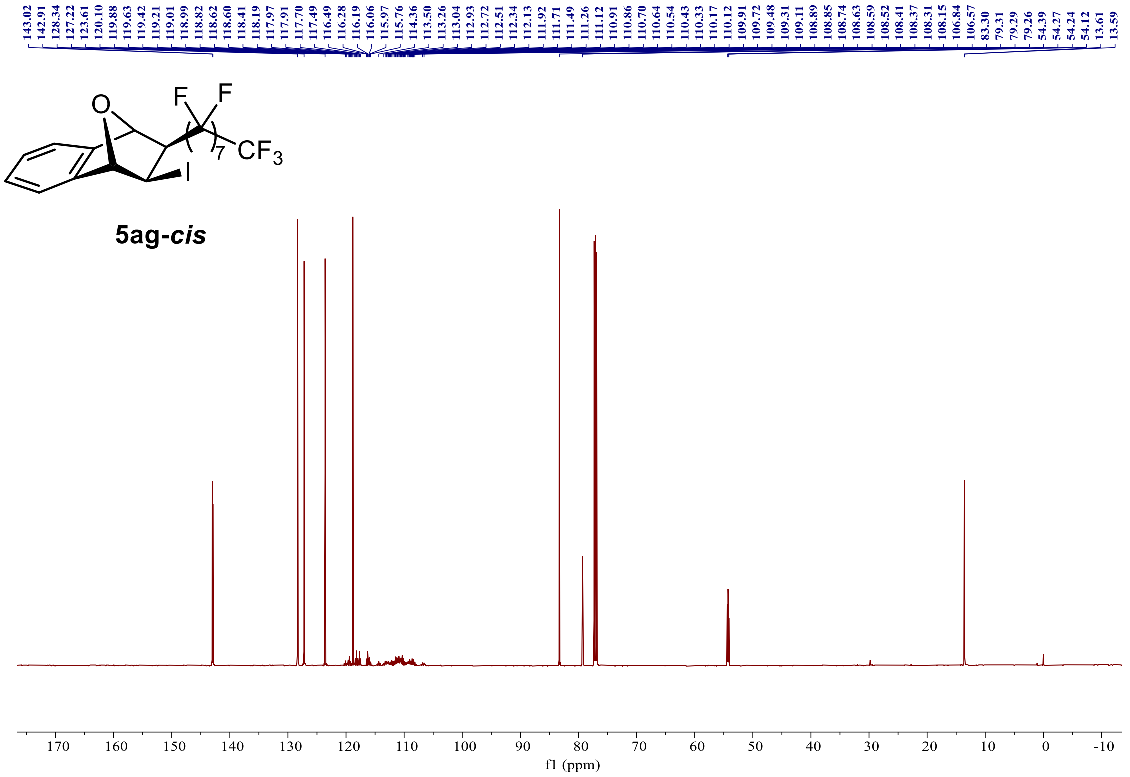
5af-*cis*

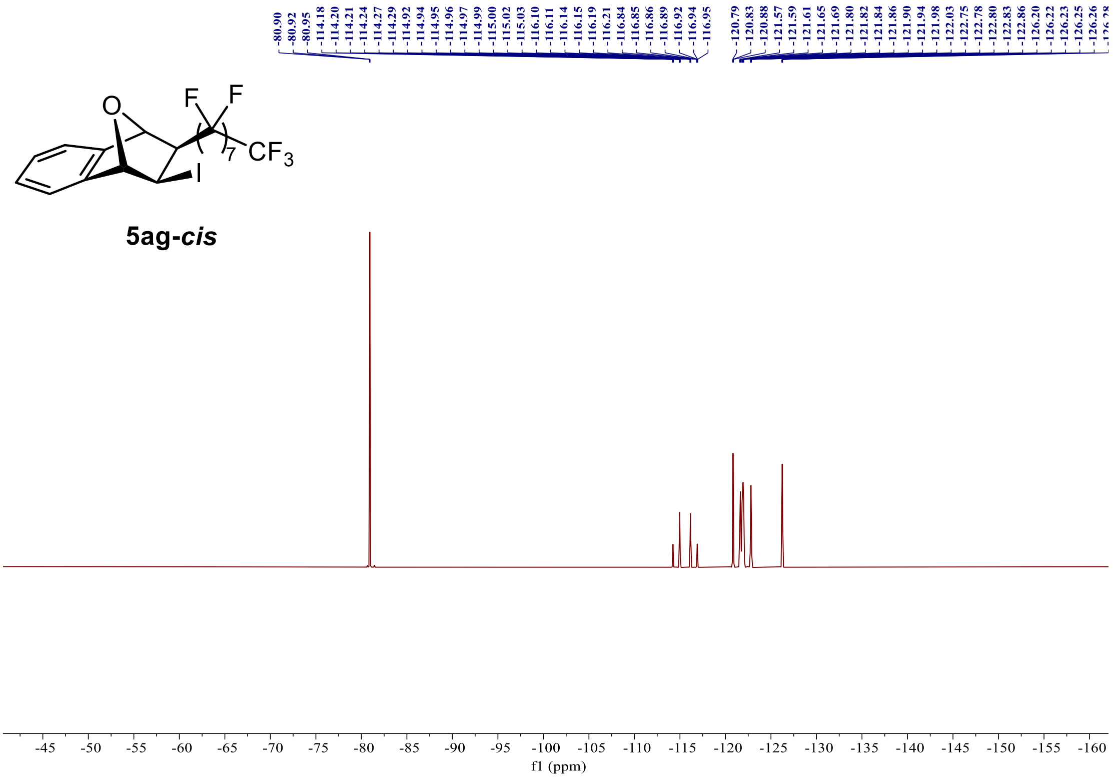


5af-*cis*



5ag-*cis*


143.02
142.91
128.34
127.22
123.61
120.10
119.88
119.63
119.42
119.21
119.01
118.99
118.82
118.62
118.60
118.41
118.19
117.97
117.91
117.70
117.49
116.49
116.28
116.19
116.06
115.97
115.76
114.36
113.50
113.26
113.04
112.93
112.72
112.51
112.34
112.13
111.92
111.71
111.49
111.26
111.12
110.91
110.86
110.70
110.64
110.54
110.43
110.33
110.17
110.12
109.91
109.72
109.48
109.31
109.11
108.89
108.85
108.74
108.63
108.59
108.52
108.41
108.37
108.31
108.15
106.84
106.57
83.30
79.31
79.29
79.26
54.39
54.27
54.24
54.12
13.61
13.59
O
F
F
7
CF3
I
5ag-cis
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


-80.90
-80.92
-80.95
-114.18
-114.20
-114.21
-114.24
-114.27
-114.29
-114.92
-114.94
-114.95
-114.96
-114.97
-114.99
-115.00
-115.02
-115.03
-116.10
-116.11
-116.14
-116.15
-116.19
-116.21
-116.84
-116.85
-116.86
-116.89
-116.92
-116.94
-116.95
-120.79
-120.83
-120.88
-121.57
-121.59
-121.61
-121.65
-121.69
-121.80
-121.82
-121.84
-121.86
-121.90
-121.94
-121.98
-122.03
-122.75
-122.78
-122.80
-122.83
-122.86
-126.20
-126.22
-126.23
-126.25
-126.26
O
F
F
7
CF3
I
5ag-cis
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
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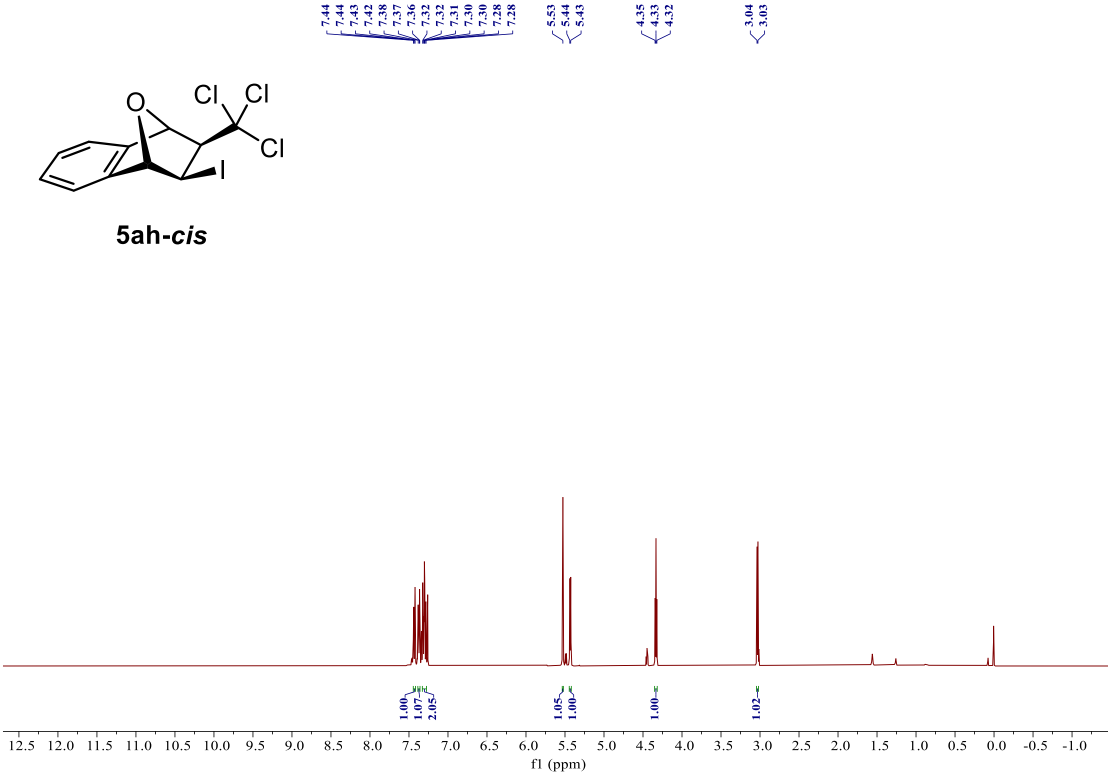
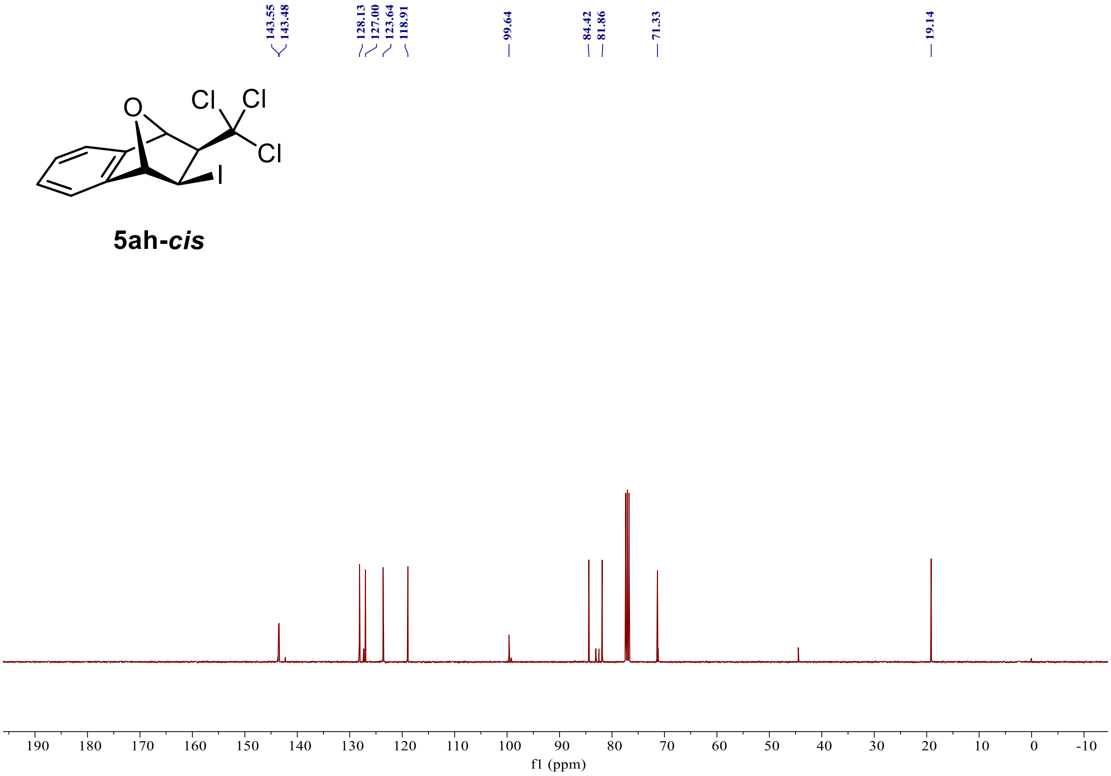
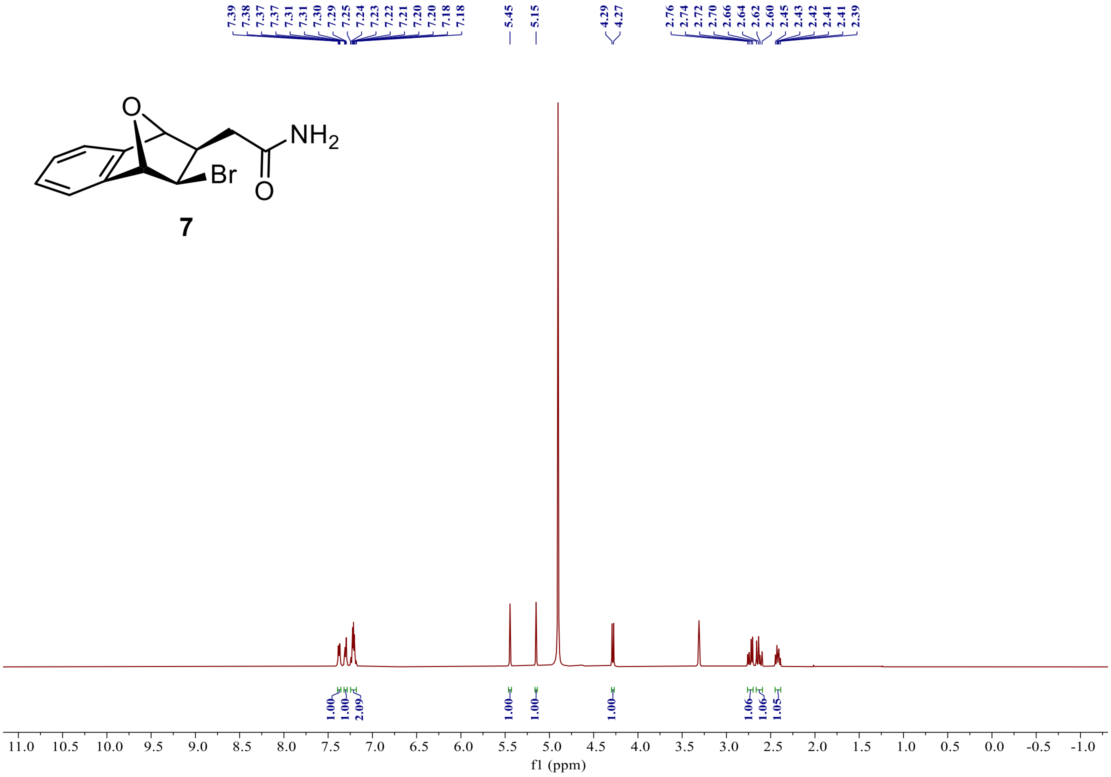
-150
-155
-160
f1 (ppm)



5ah-*cis*



5ah-*cis*


7.39
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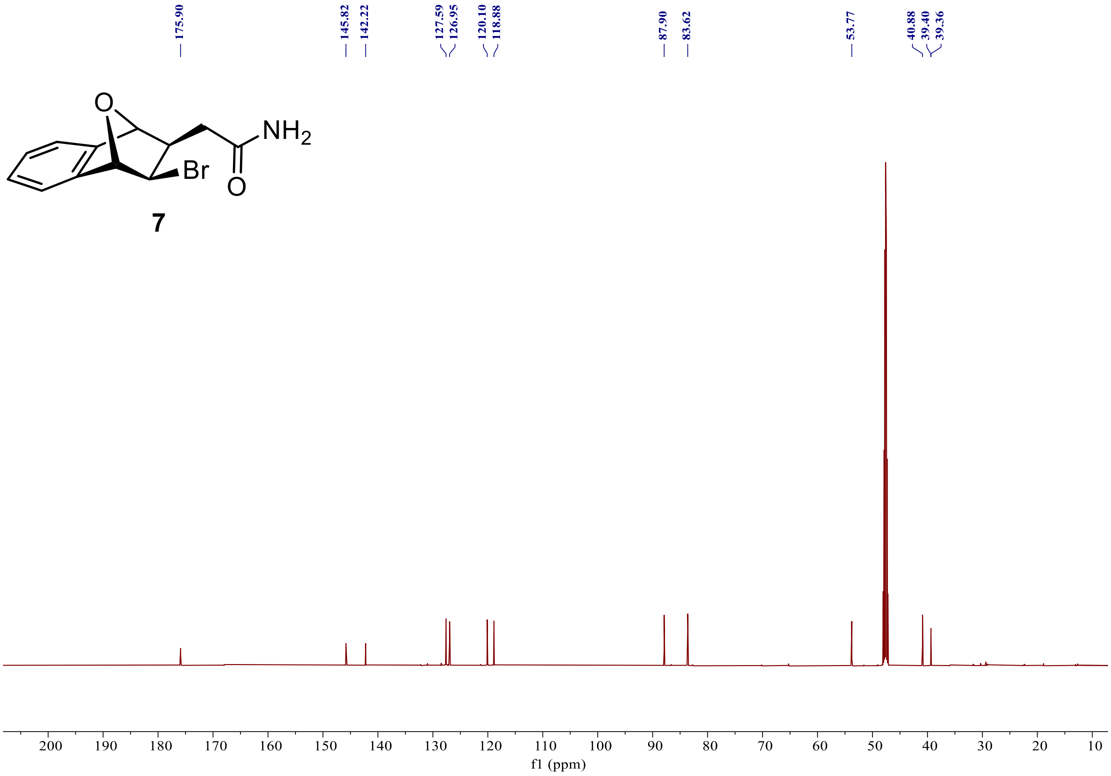
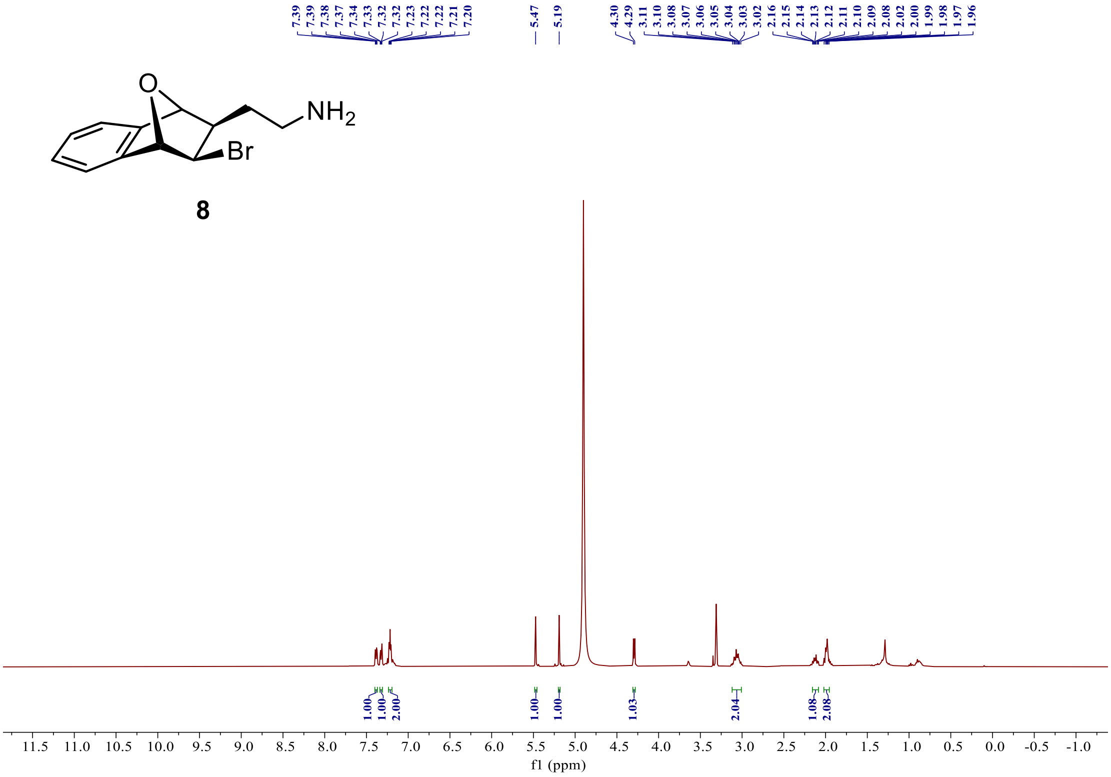
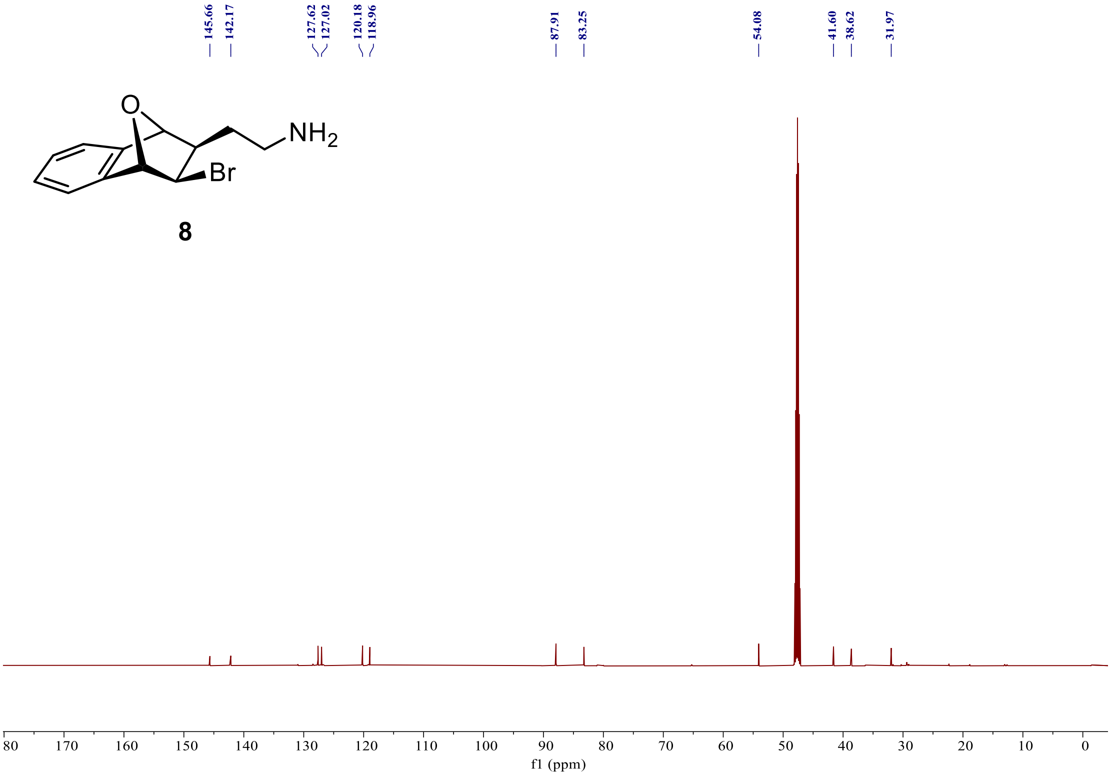
7.37
7.31
7.30
7.29
7.25
7.24
7.23
7.22
7.21
7.20
7.20
7.18
7.18
5.45
5.15
4.29
4.27
2.76
2.74
2.72
2.70
2.66
2.64
2.62
2.60
2.45
2.43
2.42
2.41
2.41
2.39
O
NH2
Br
O
7
1.00
1.00
2.09
1.00
1.00
1.00
1.06
1.06
1.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

ff

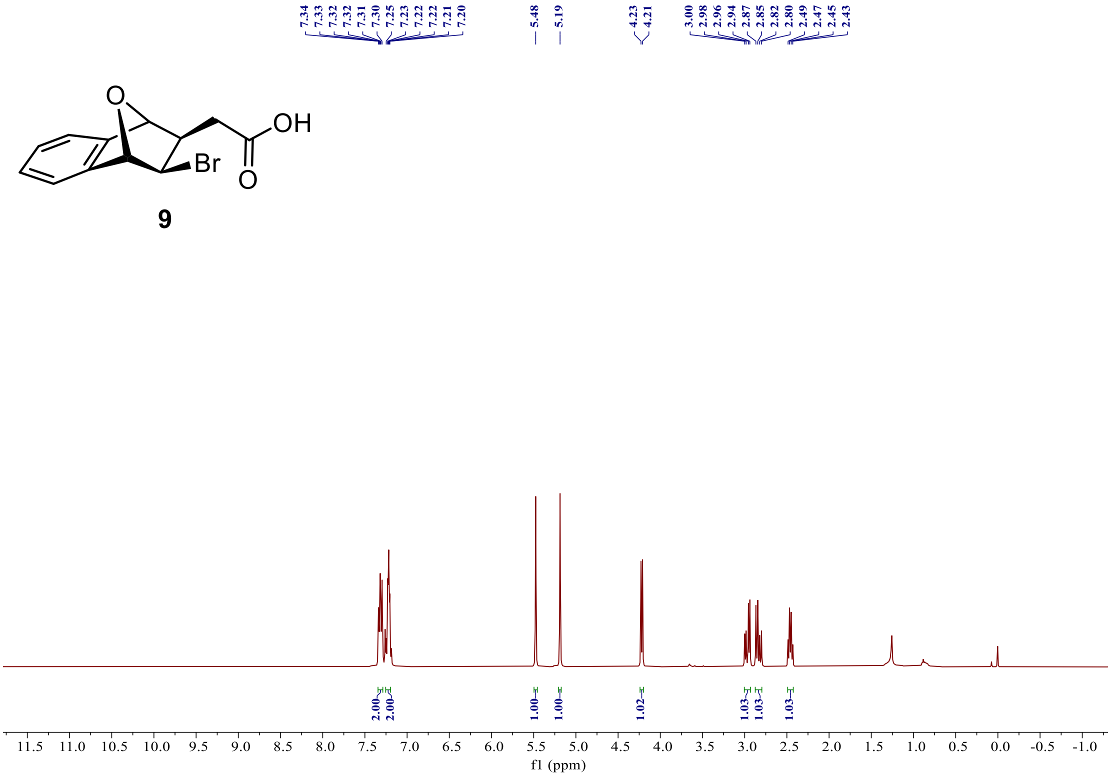

175.90
145.82
142.22
127.59
126.95
120.10
118.88
87.90
83.62
53.77
40.88
39.40
39.36
O
NH2
Br
O
7
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.39
7.39
7.38
7.37
7.34
7.33
7.32
7.32
7.23
7.22
7.22
7.21
7.20
5.47
5.19
4.30
4.29
3.11
3.10
3.08
3.07
3.06
3.05
3.04
3.03
3.02
2.16
2.15
2.14
2.13
2.12
2.11
2.10
2.09
2.08
2.02
2.00
1.99
1.98
1.97
1.96
O
NH2
Br
1.00
1.00
2.00
1.00
1.00
1.03
2.04
1.08
2.08
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

8


145.66
142.17
127.62
127.02
120.18
118.96
87.91
83.25
54.08
41.60
38.62
31.97
O
NH2
Br
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

8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7.32
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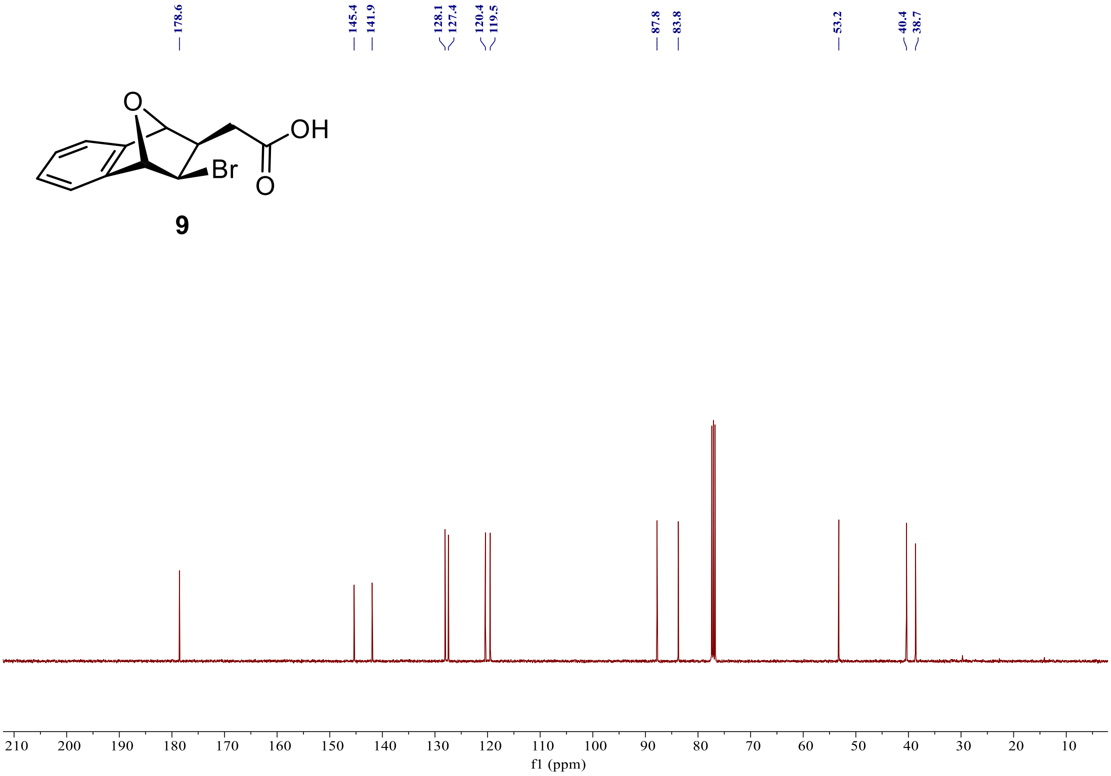
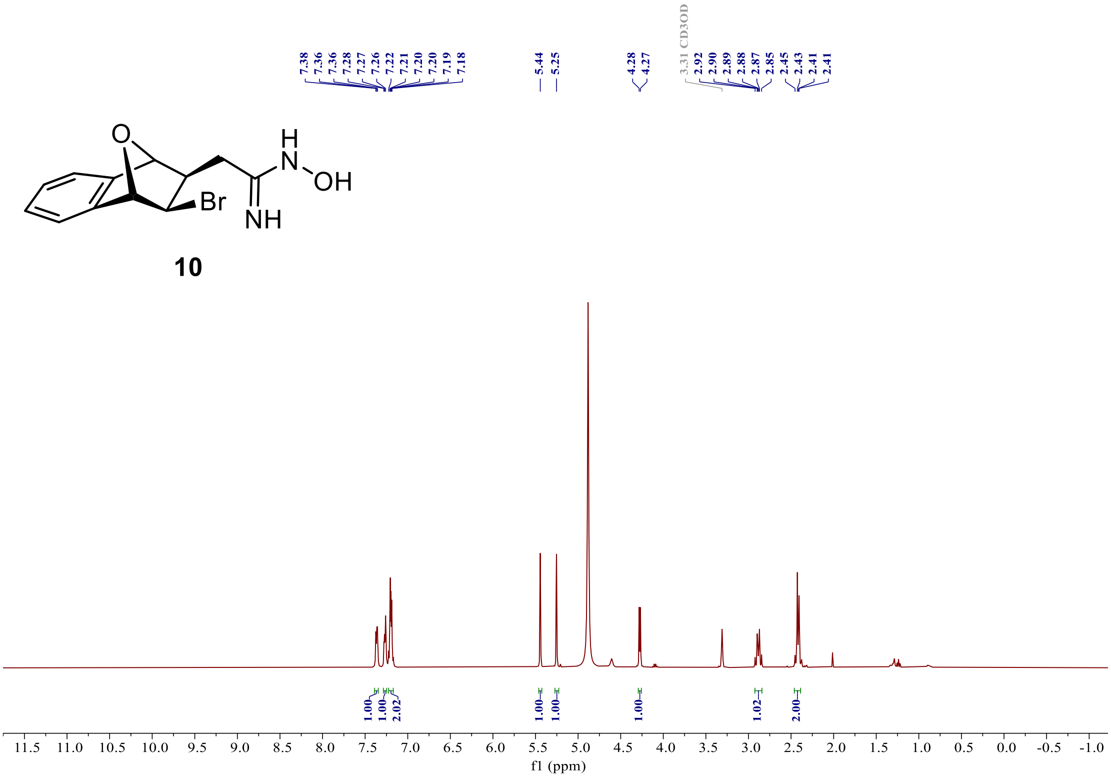
7.31
7.30
7.25
7.23
7.22
7.22
7.21
7.20
5.48
5.19
4.23
4.21
3.00
2.98
2.96
2.94
2.87
2.85
2.82
2.80
2.49
2.47
2.45
2.43
O
OH
Br
O
2.00
2.00
1.00
1.00
1.02
1.03
1.03
1.03
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

9

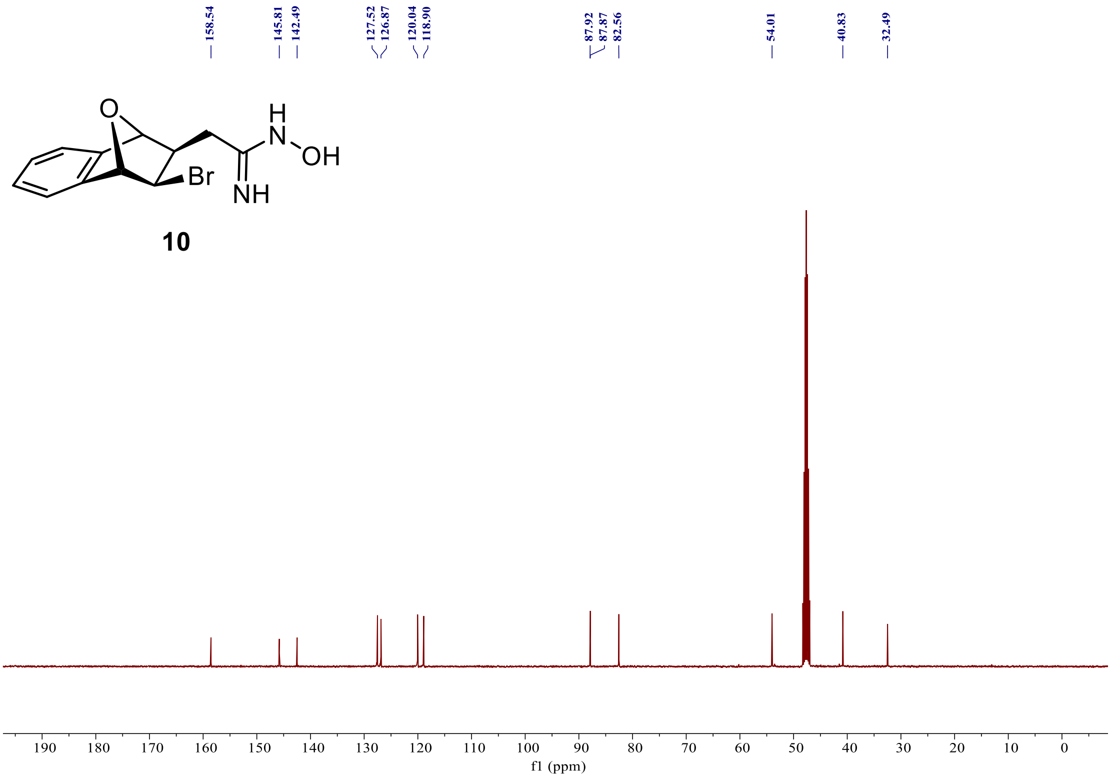

178.6
145.4
141.9
128.1
127.4
120.4
119.5
87.8
83.8
53.2
40.4
38.7
O
OH
Br
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

9



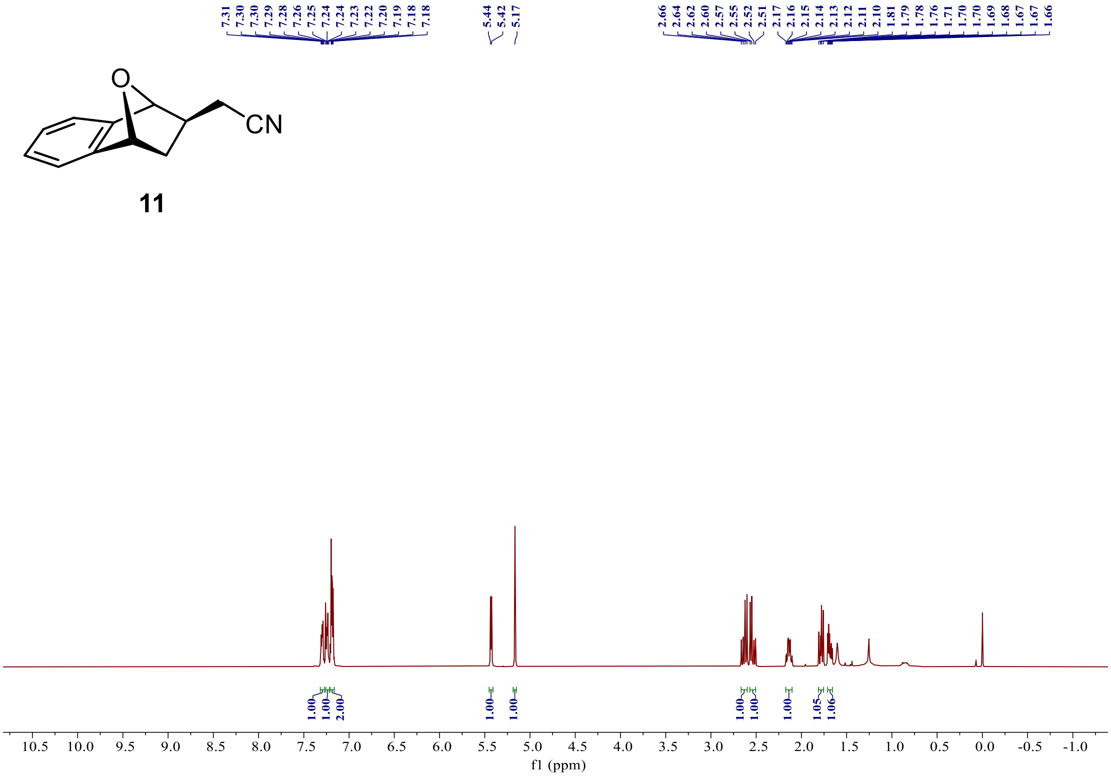
10

7.38
7.36
7.36
7.28
7.27
7.26
7.22
7.21
7.20
7.20
7.19
7.18
5.44
5.25
4.28
4.27
3.31 CD3OD
2.92
2.90
2.89
2.88
2.87
2.85
2.45
2.43
2.41
2.41
O
H
N
OH
Br
NH
1.00
1.00
2.02
1.00
1.00
1.00
1.02
2.00
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)



10

158.54
145.81
142.49
127.52
126.87
120.04
118.90
87.92
87.87
82.56
54.01
40.83
32.49
O
H
N
OH
Br
NH
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.24
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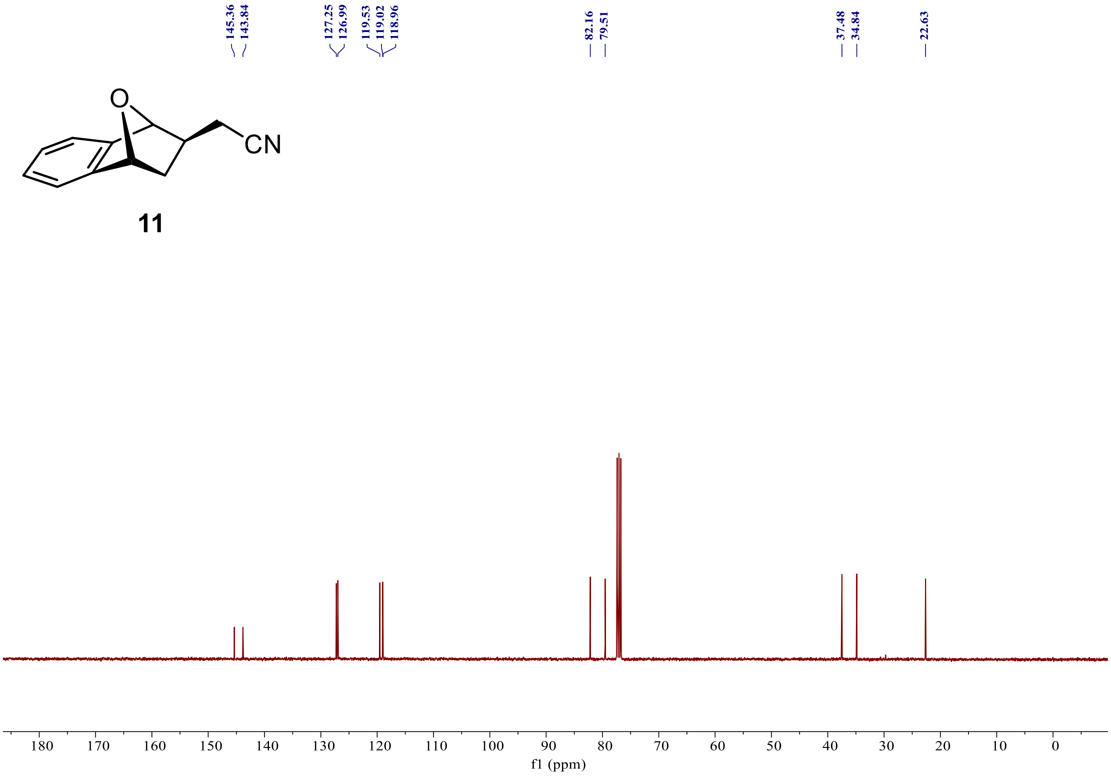
7.22
7.20
7.19
7.18
7.18
5.44
5.42
5.17
2.66
2.64
2.62
2.60
2.57
2.55
2.52
2.51
2.17
2.16
2.15
2.14
2.13
2.12
2.11
2.10
1.81
1.79
1.78
1.76
1.71
1.70
1.69
1.68
1.67
1.67
1.66
O
CN
11
1.00
1.00
2.00
1.00
1.00
1.00
1.00
1.00
1.05
1.06
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)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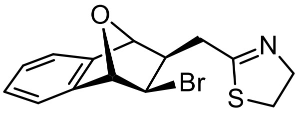
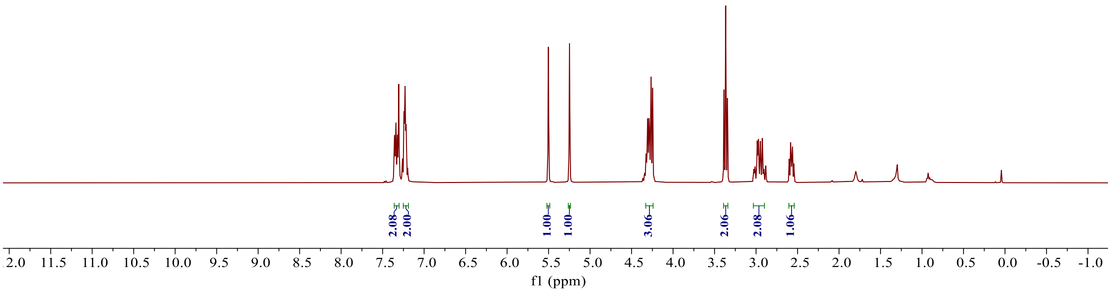
143.84
127.25
126.99
119.53
119.02
118.96
82.16
79.51
37.48
34.84
22.63
O
CN
11
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



12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7.35
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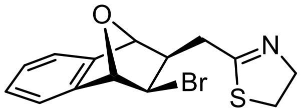
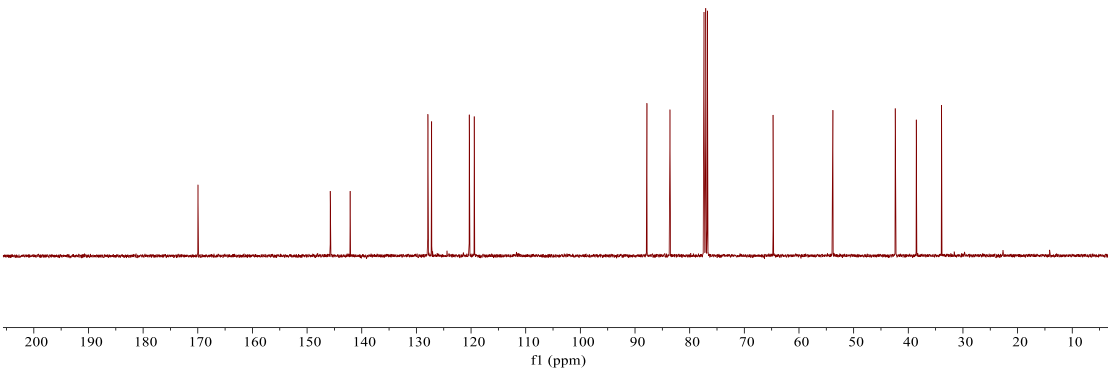
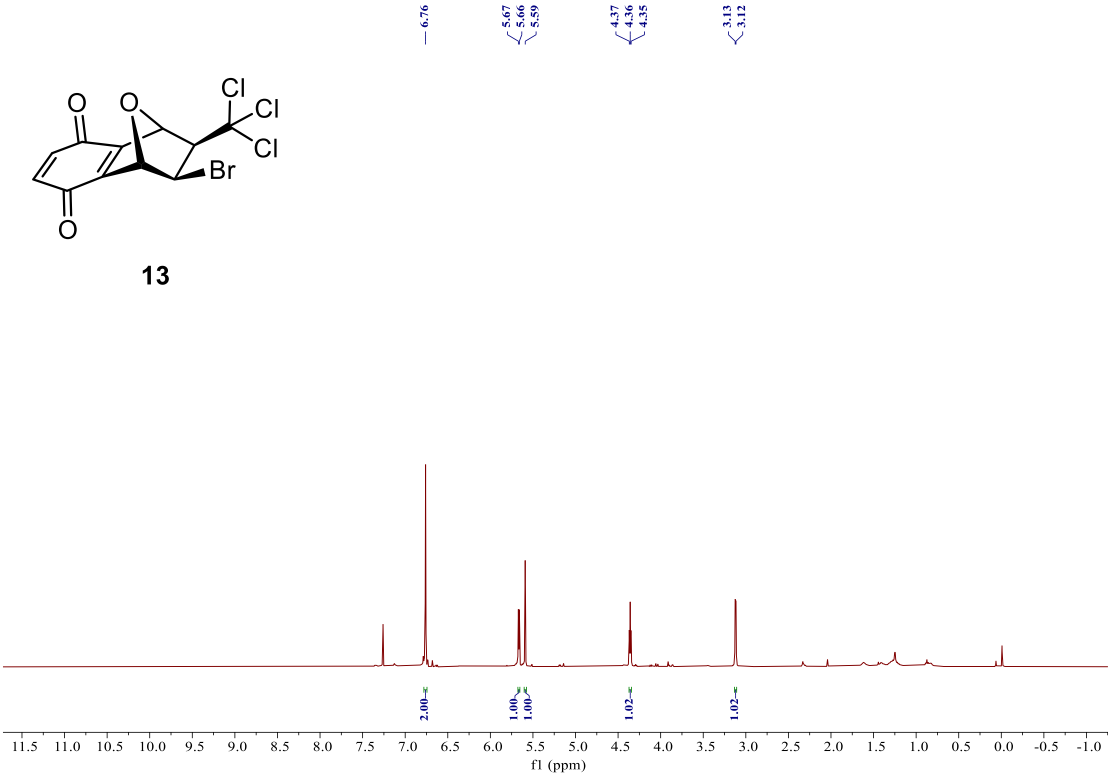
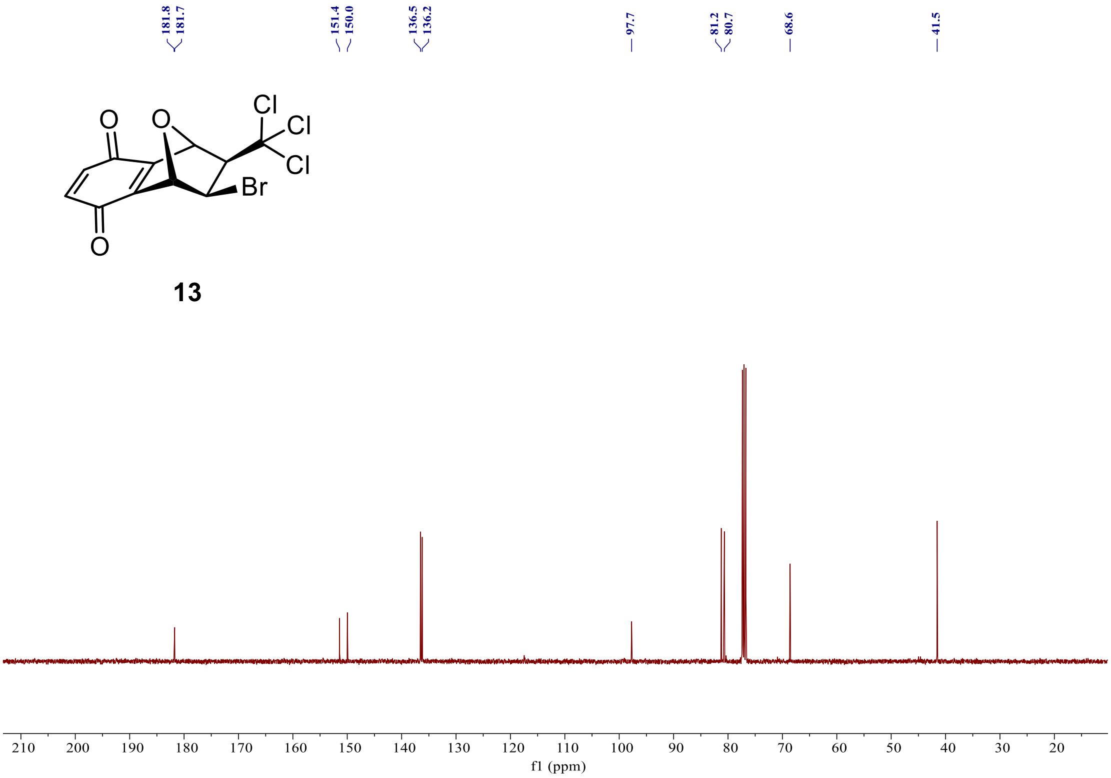
7.32
7.31
7.31
7.24
7.24
7.23
7.22
7.22
7.20
7.20
5.50
5.25
4.33
4.33
4.32
4.31
4.31
4.29
4.29
4.26
4.25
3.39
3.37
3.35
3.03
3.03
3.02
3.02
3.01
3.01
2.99
2.99
2.98
2.98
2.97
2.97
2.95
2.95
2.94
2.92
2.91
2.90
2.60
2.58
2.58
2.57
2.56
2.54
2.08
2.00
1.00
1.00
3.06
2.06
2.08
1.06
2.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)



12

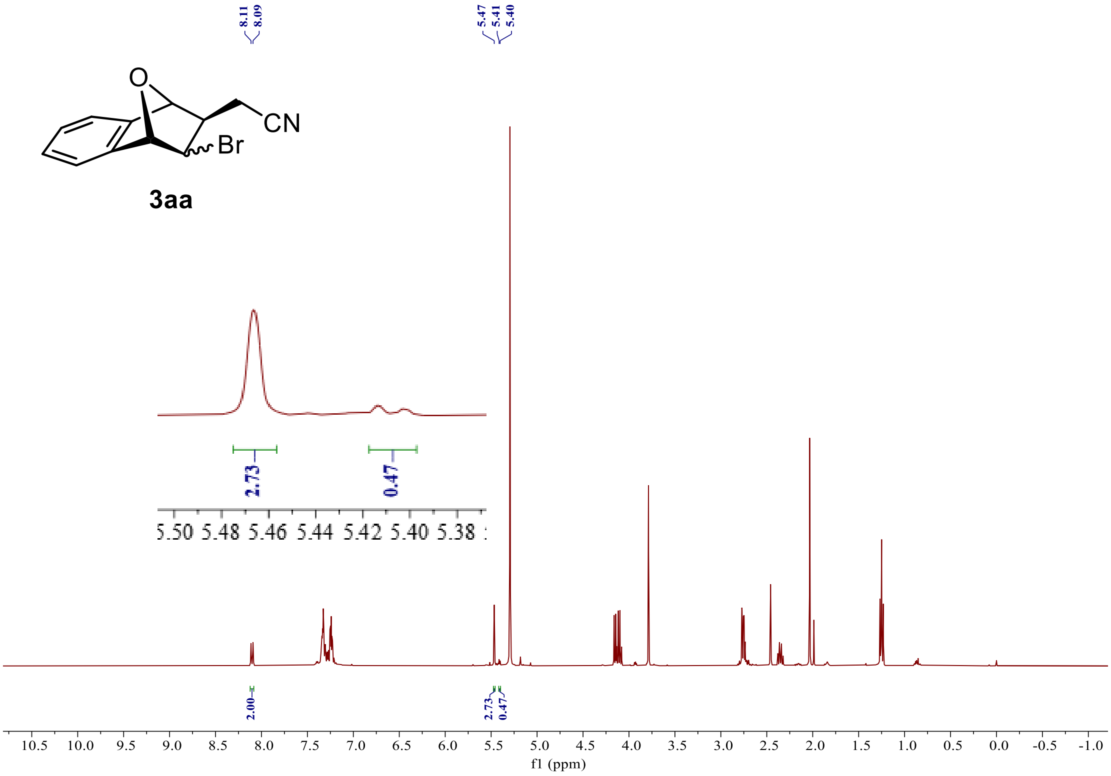

170.0
145.8
142.1
127.9
127.2
120.3
119.4
87.8
83.6
64.7
53.8
42.4
38.5
33.9
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


6.76
5.67
5.66
5.59
4.37
4.36
4.35
3.13
3.12
O
O
O
Cl
Cl
Cl
Br
13
2.00
1.00
1.00
1.02
1.02
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

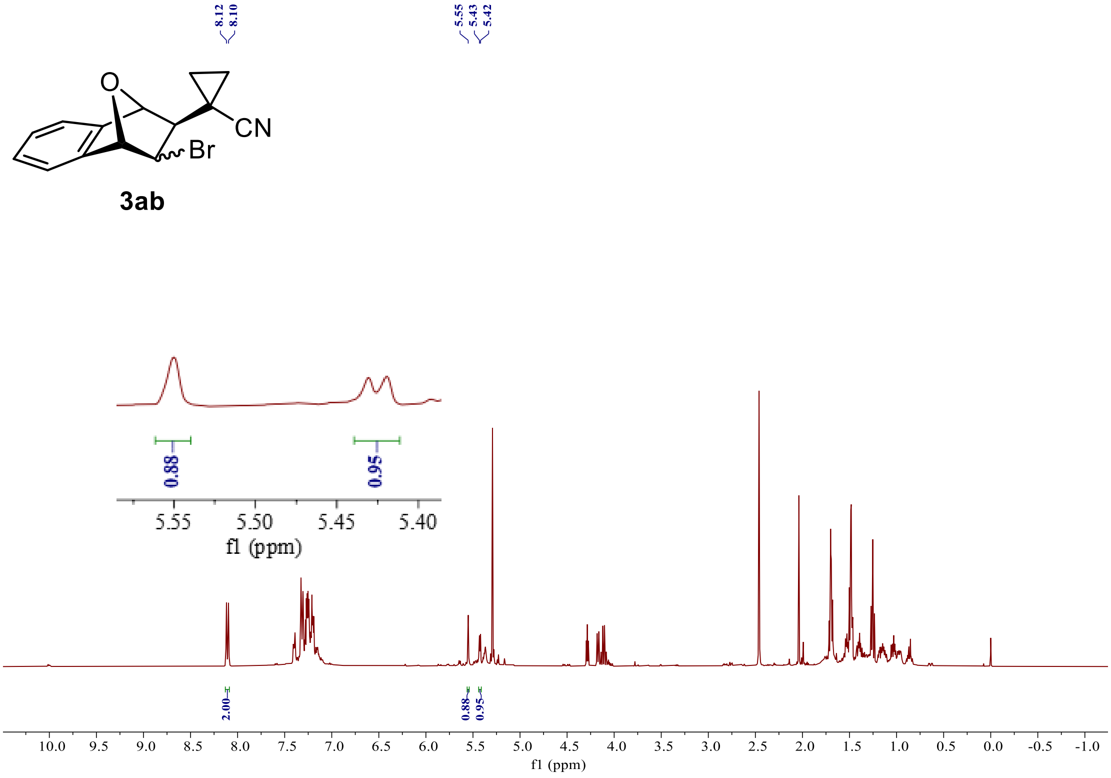

181.8
181.7
151.4
150.0
136.5
136.2
97.7
81.2
80.7
68.6
41.5
O
O
O
Cl
Cl
Cl
Br
13
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

11. NMR evaluation of *cis-trans* diastereomer of crude mixture

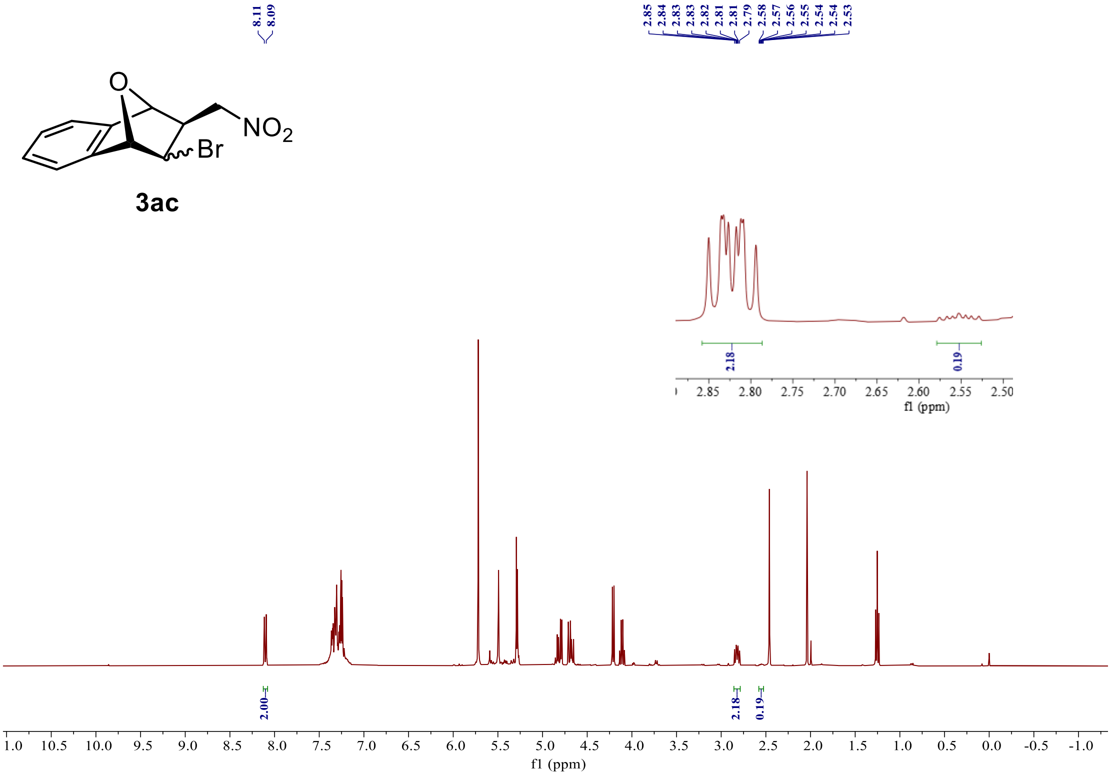
The crude mixture of **3aa** with 0.05 mmol p-nitrotoluene as the internal standard.



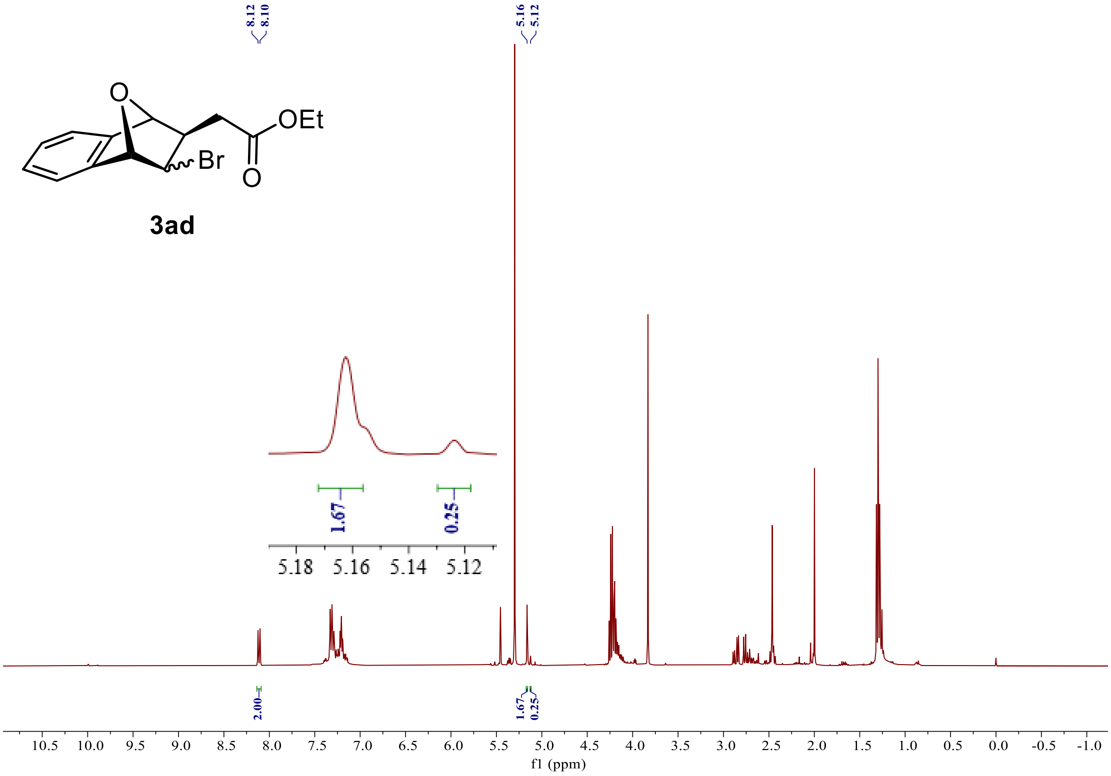
The crude mixture of **3ab** with 0.06 mmol p-nitrotoluene as the internal standard.



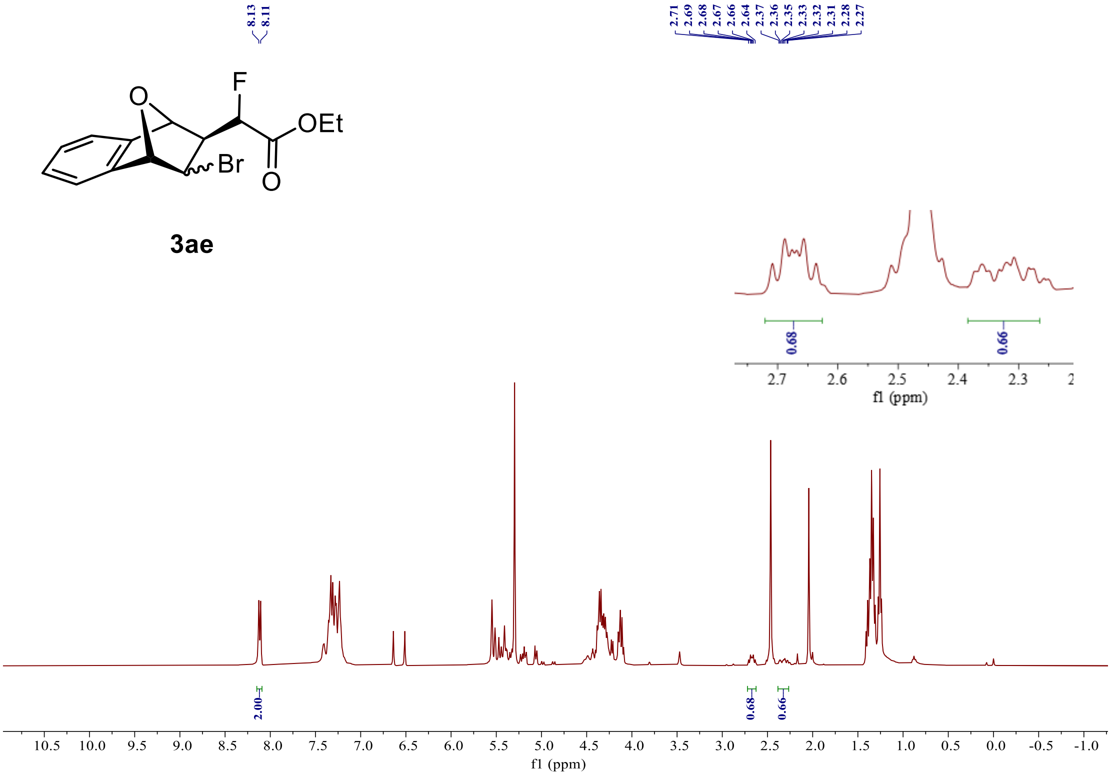
The crude mixture of **3ac** with 0.06 mmol p-nitrotoluene as the internal standard.



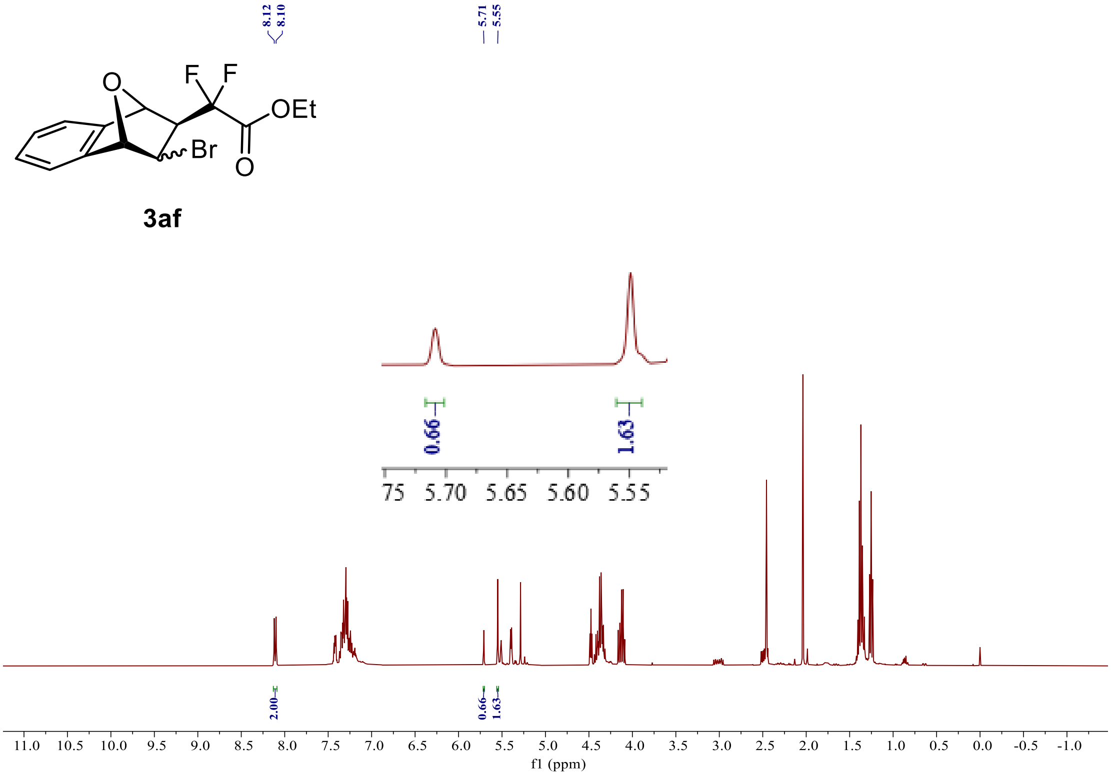
The crude mixture of **3ad** with 0.05 mmol p-nitrotoluene as the internal standard.



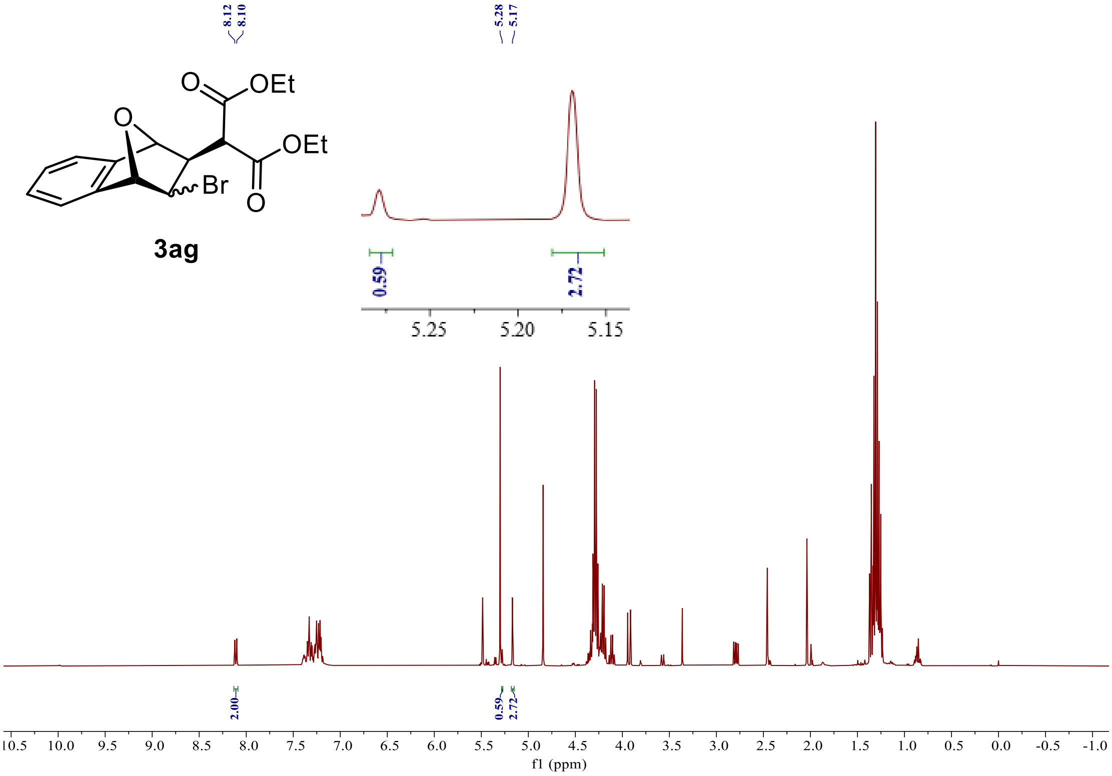
The crude mixture of **3ae** with 0.05 mmol p-nitrotoluene as the internal standard.



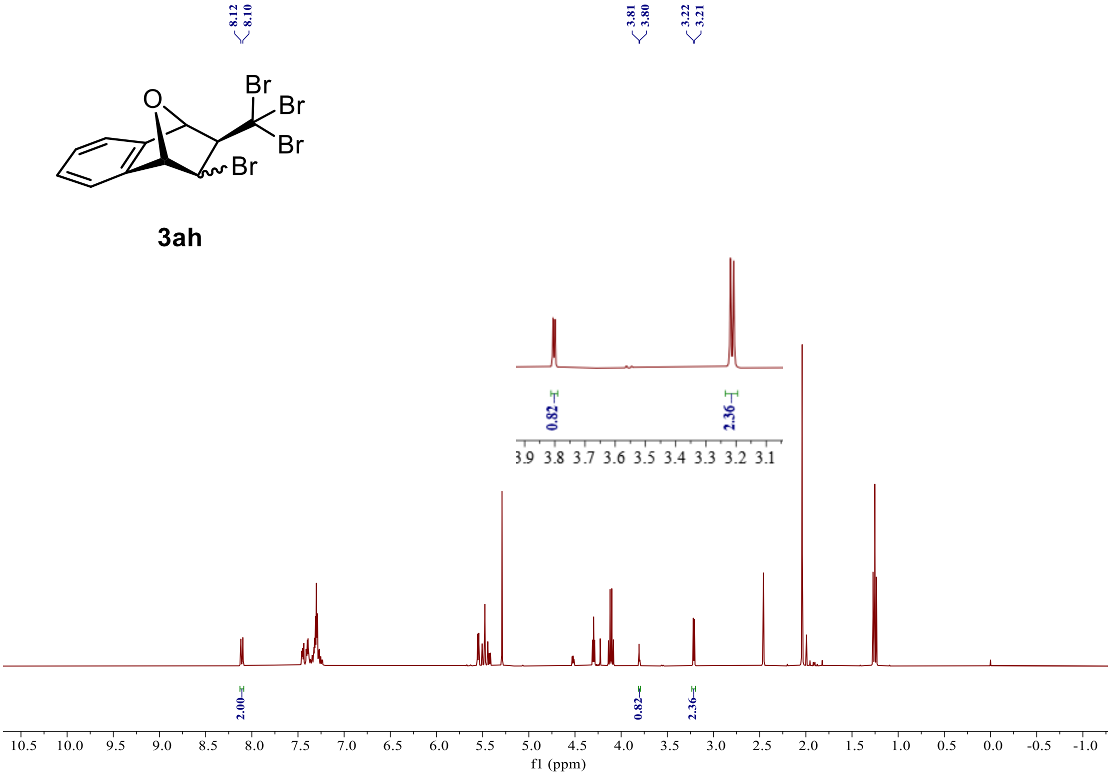
The crude mixture of **3af** with 0.06 mmol p-nitrotoluene as the internal standard.



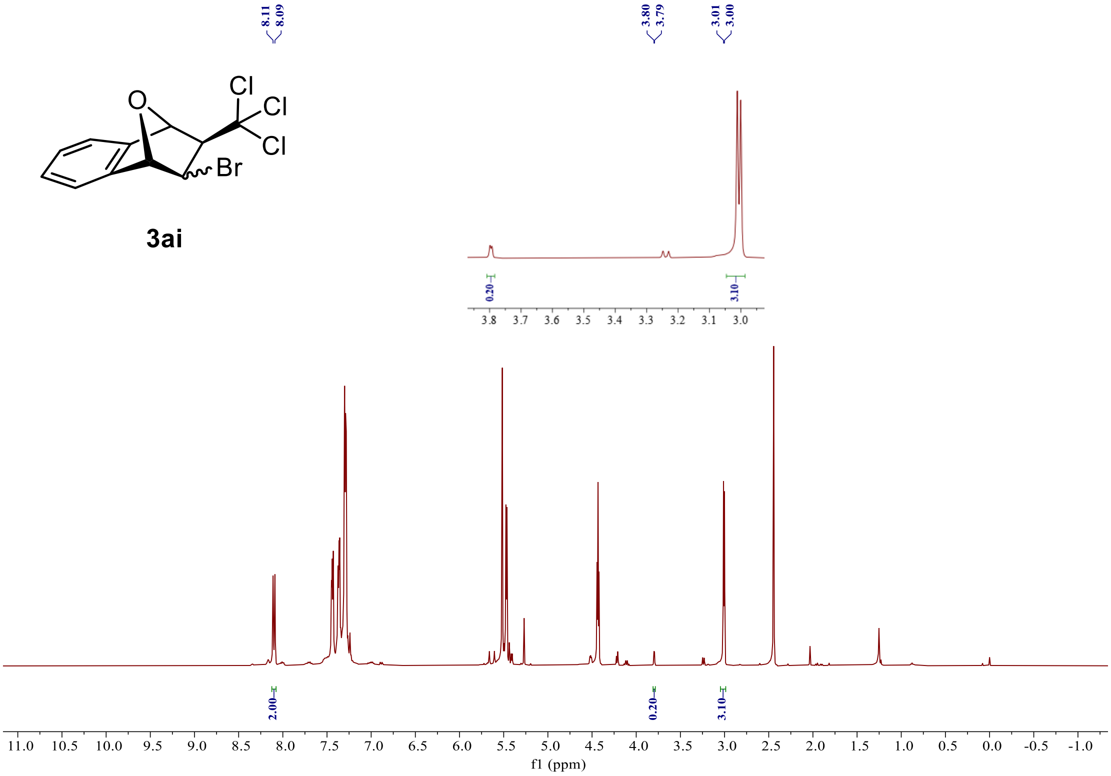
The crude mixture of **3ag** with 0.05 mmol p-nitrotoluene as the internal standard.


3ag

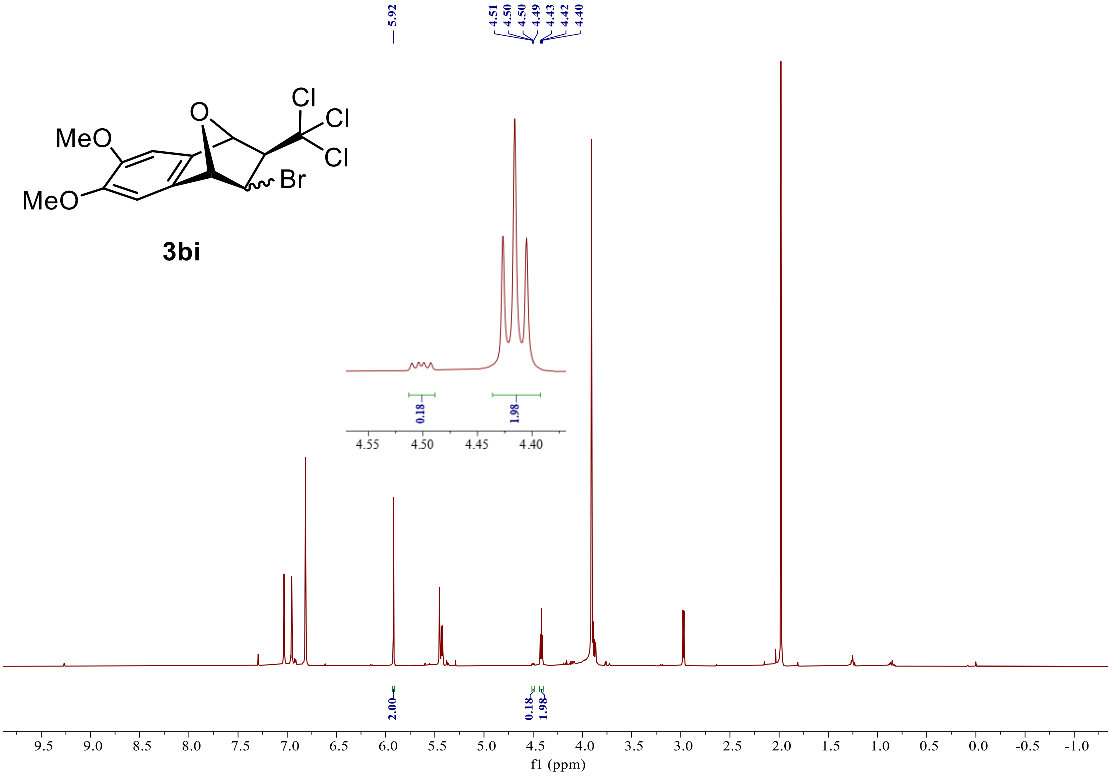
The crude mixture of **3ah** with 0.06 mmol p-nitrotoluene as the internal standard.


3ah

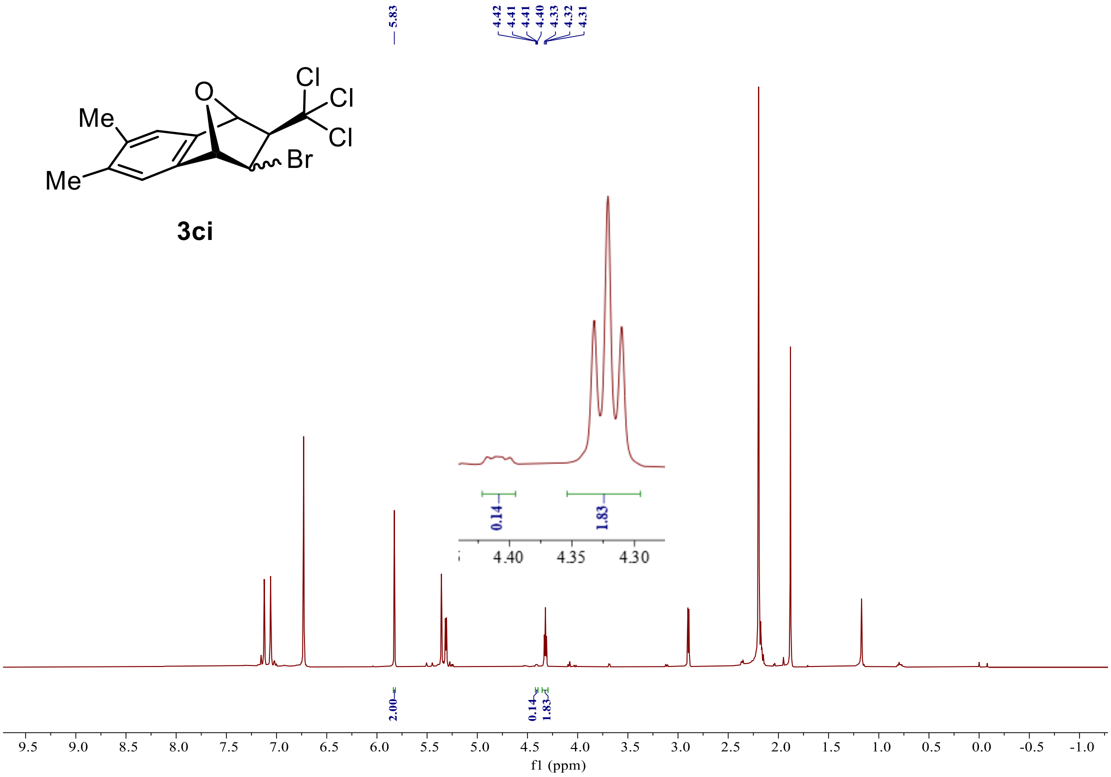
The crude mixture of **3ai** with 0.06 mmol p-nitrotoluene as the internal standard.



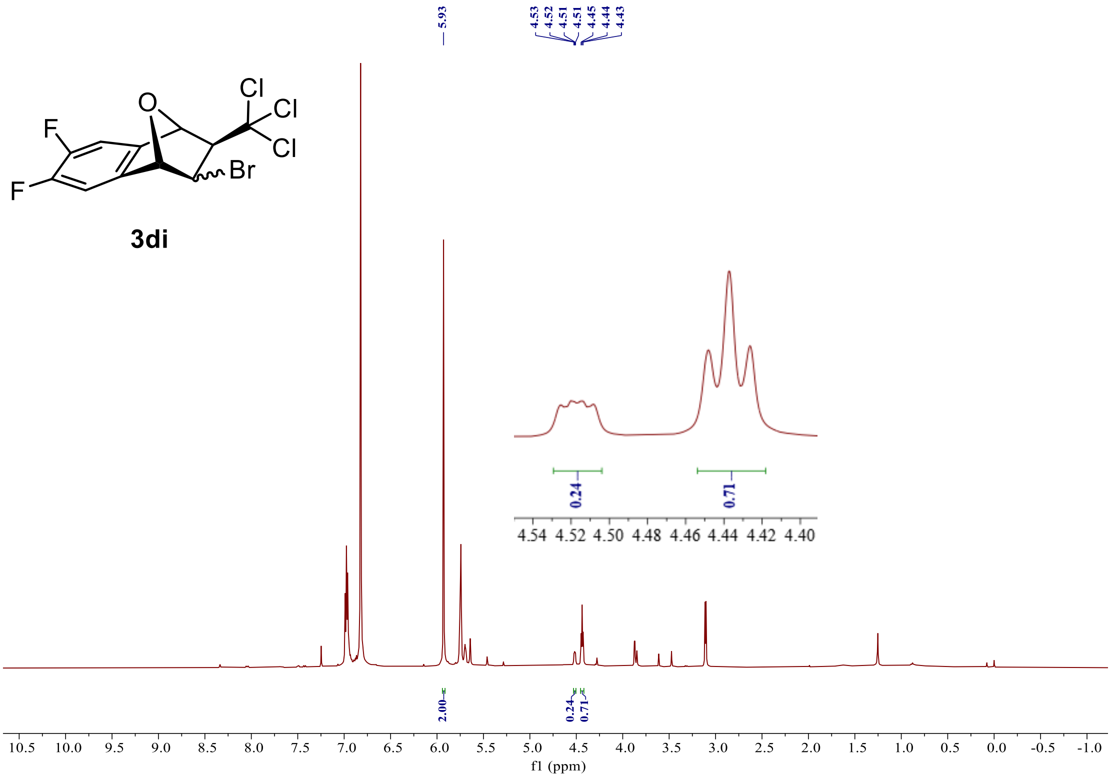
The crude mixture of **3bi** with 0.09 mmol 1,3-Benzodioxole as the internal standard.



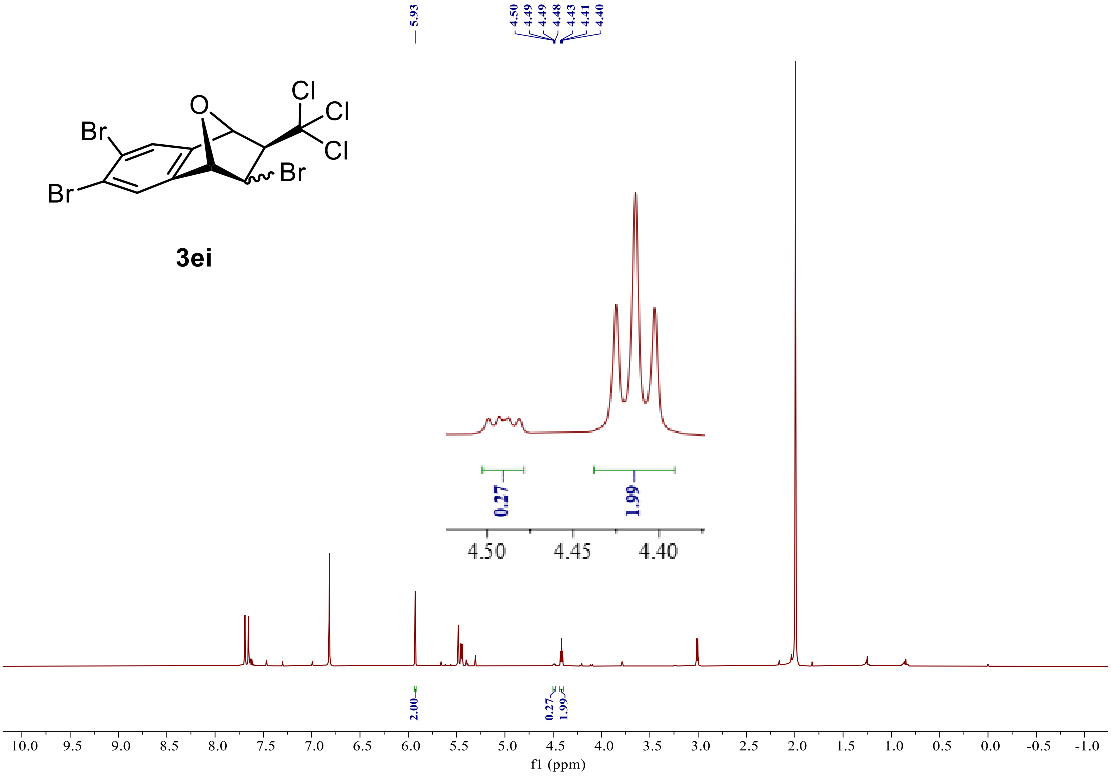
The crude mixture of **3ci** with 0.09 mmol 1,3-Benzodioxole as the internal standard.



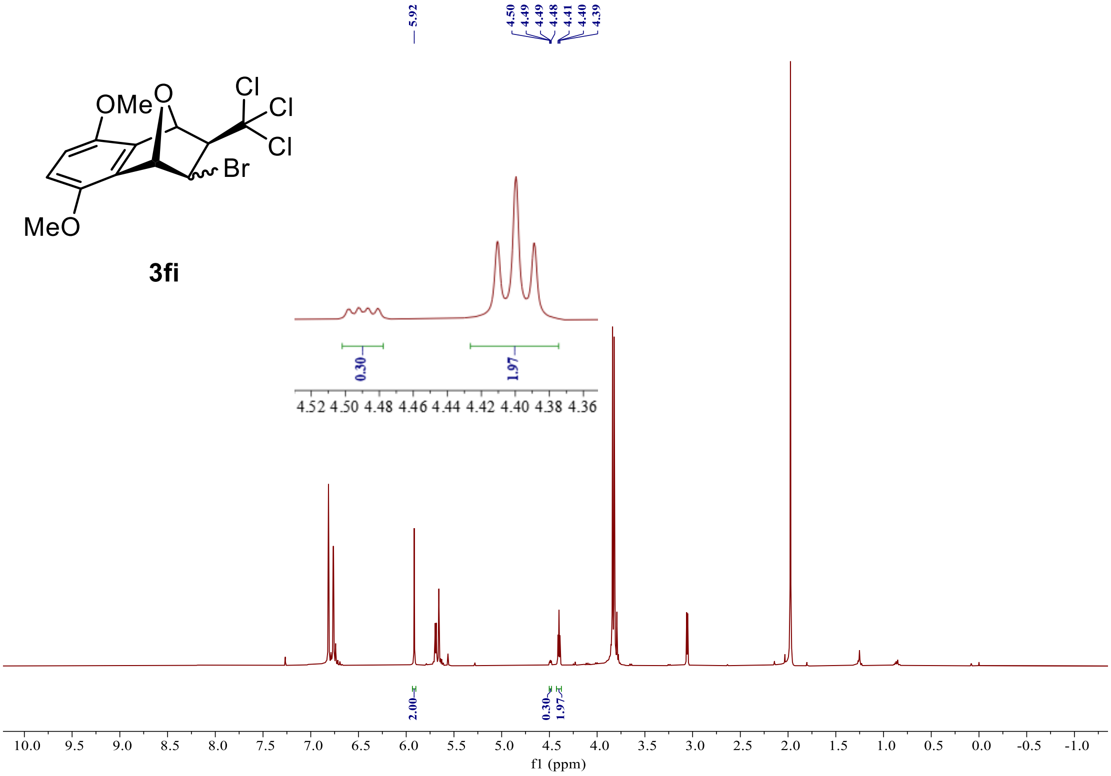
The crude mixture of **3di** with 0.10 mmol 1,3-Benzodioxole as the internal standard.



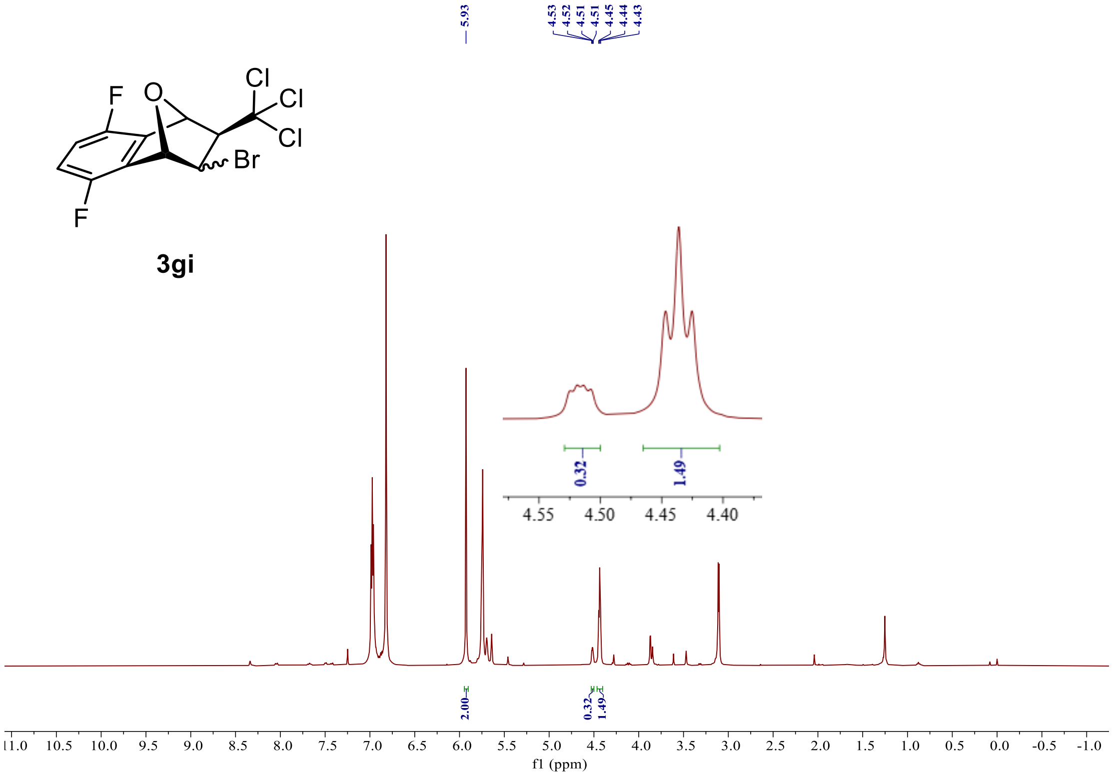
The crude mixture of **3ei** with 0.08 mmol 1,3-Benzodioxole as the internal standard.



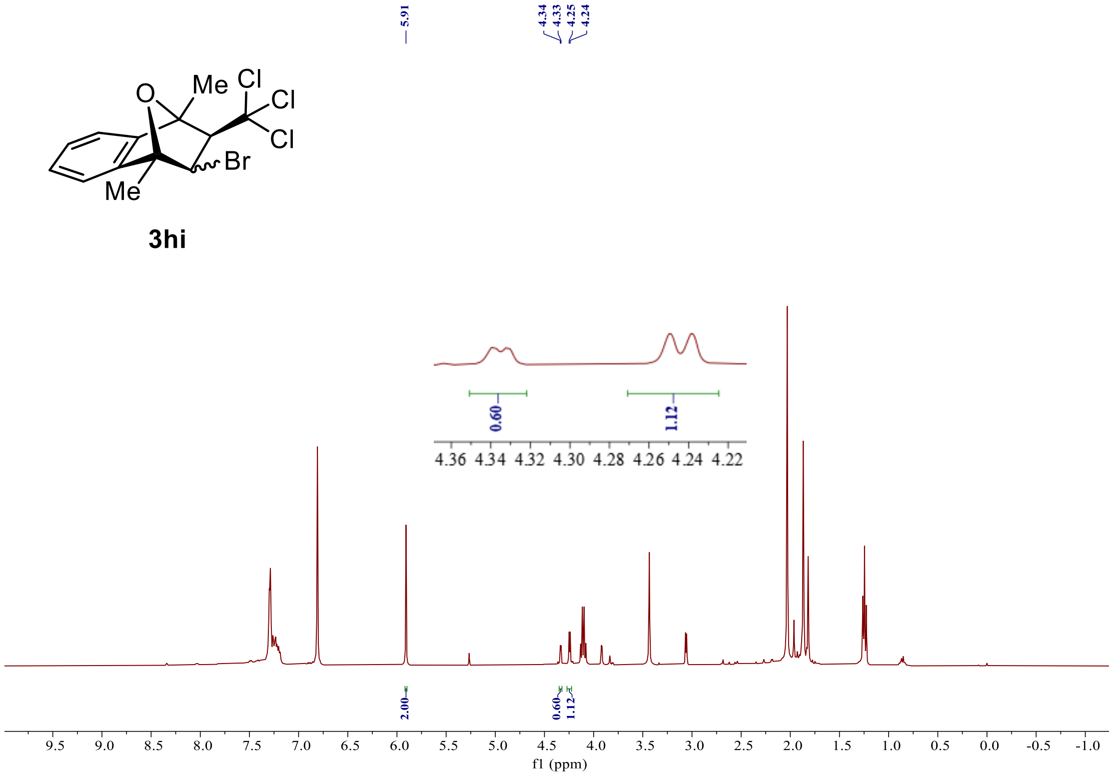
The crude mixture of **3fi** with 0.09 mmol 1,3-Benzodioxole as the internal standard.



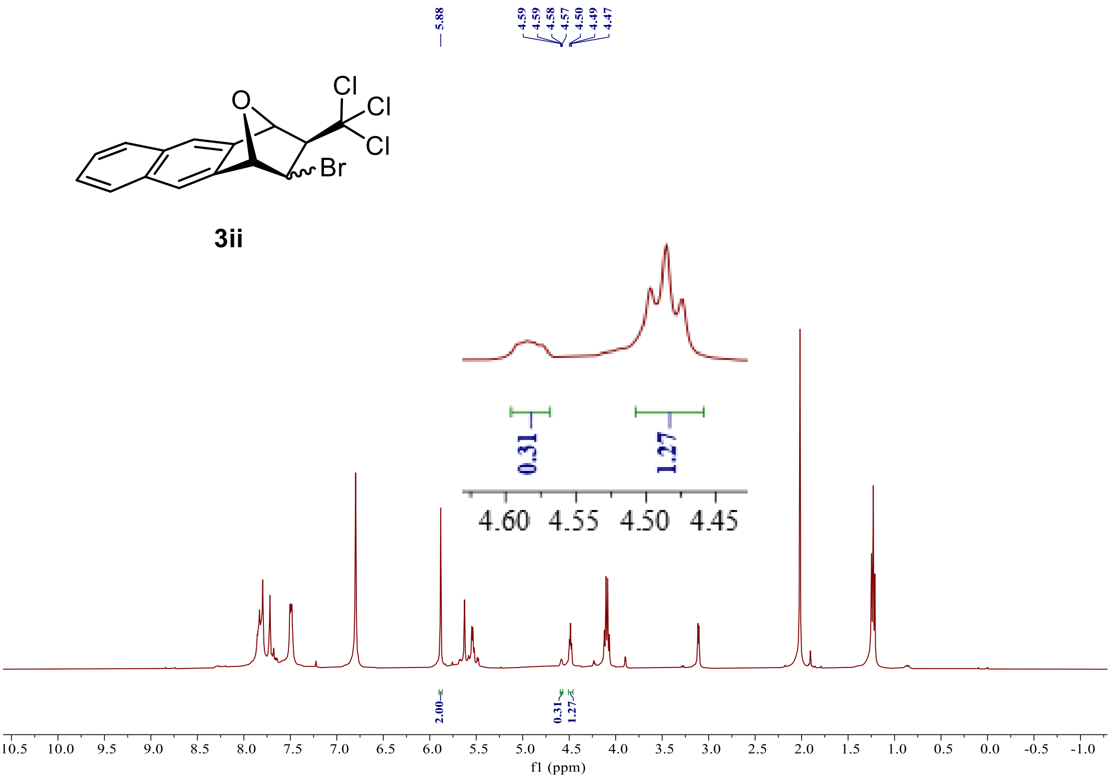
The crude mixture of **3gi** with 0.10 mmol 1,3-Benzodioxole as the internal standard.



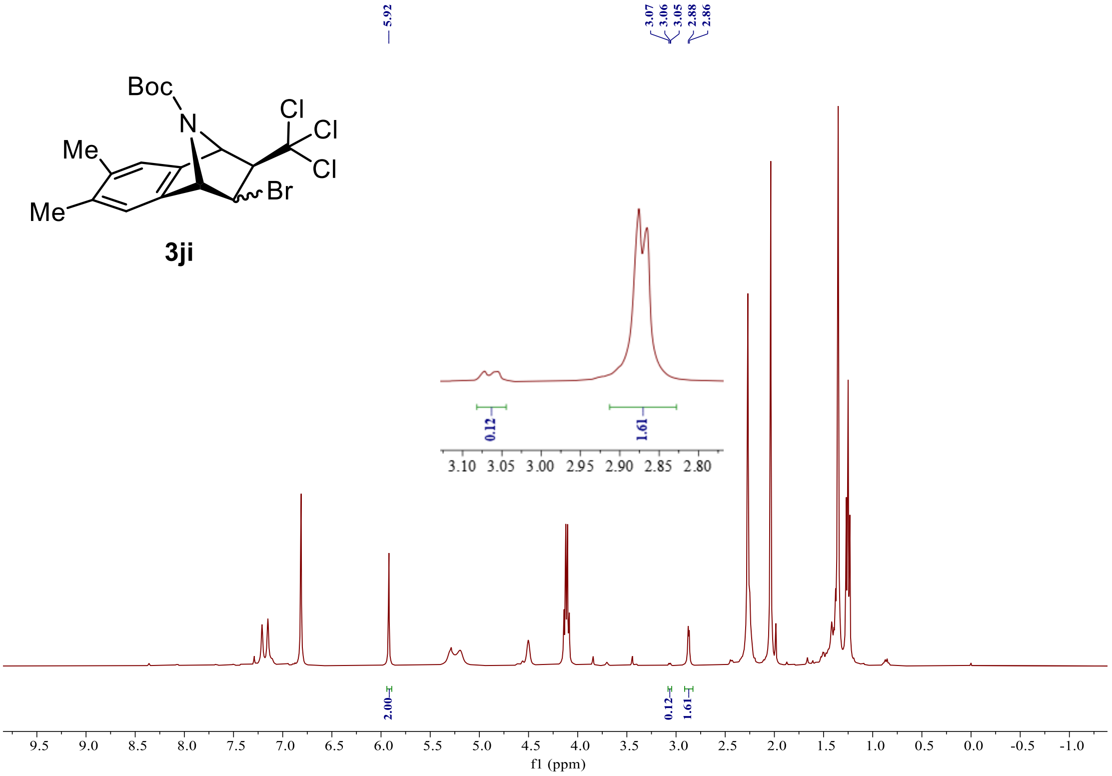
The crude mixture of **3hi** with 0.09 mmol 1,3-Benzodioxole as the internal standard.



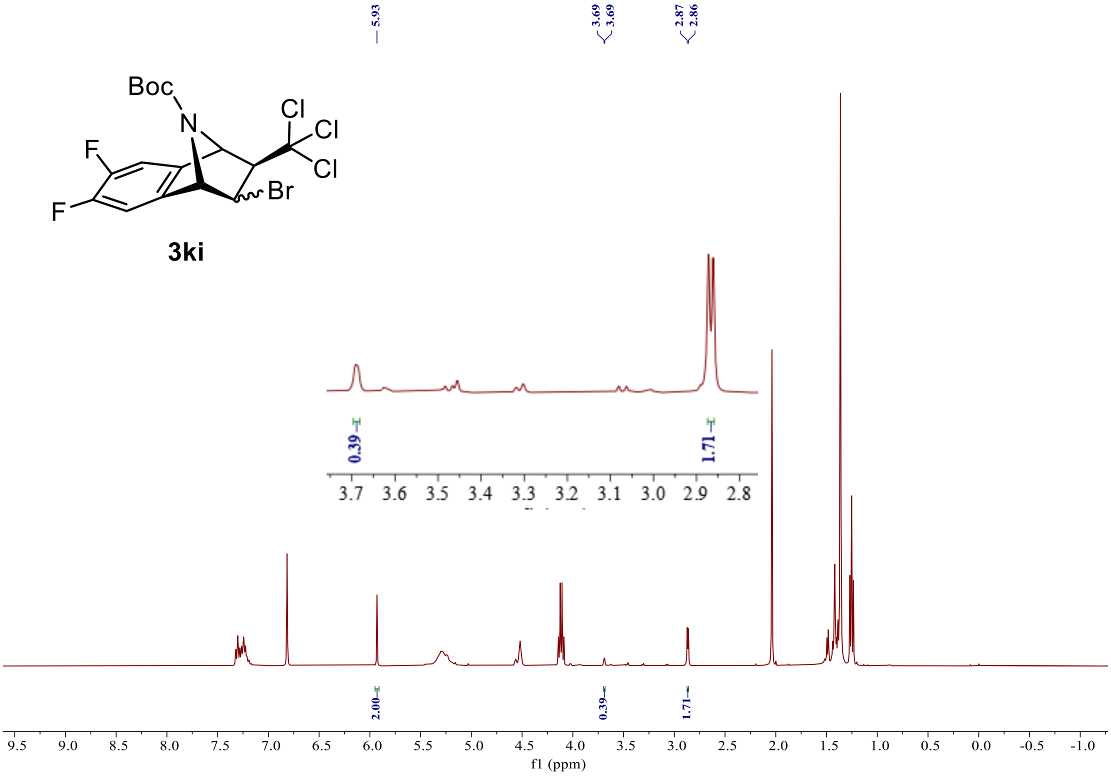
The crude mixture of **3ii** with 0.10 mmol 1,3-Benzodioxole as the internal standard.



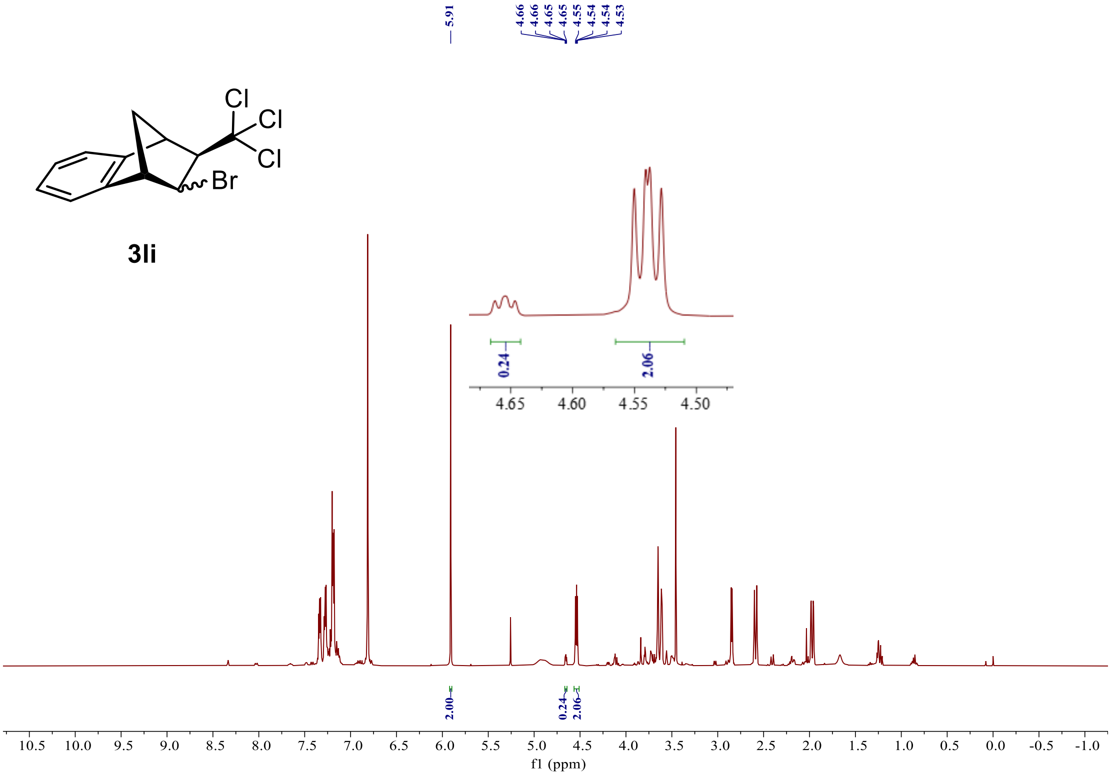
The crude mixture of **3ji** with 0.10 mmol 1,3-Benzodioxole as the internal standard.



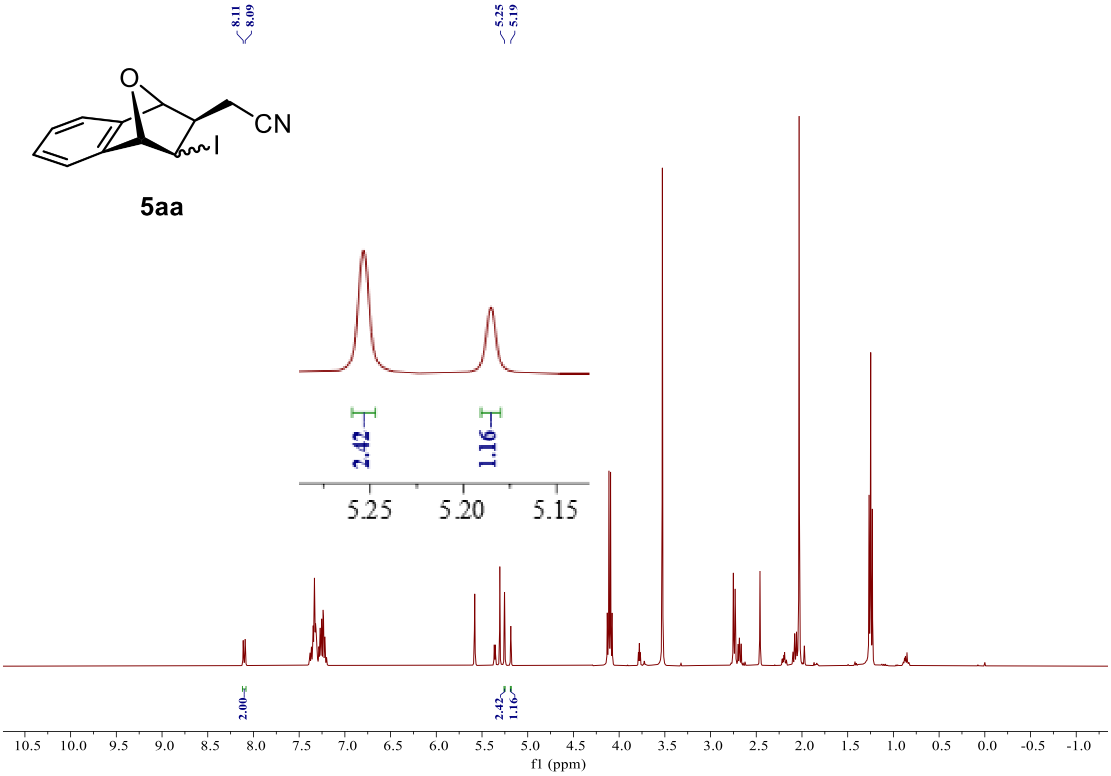
The crude mixture of **3ki** with 0.09 mmol 1,3-Benzodioxole as the internal standard.



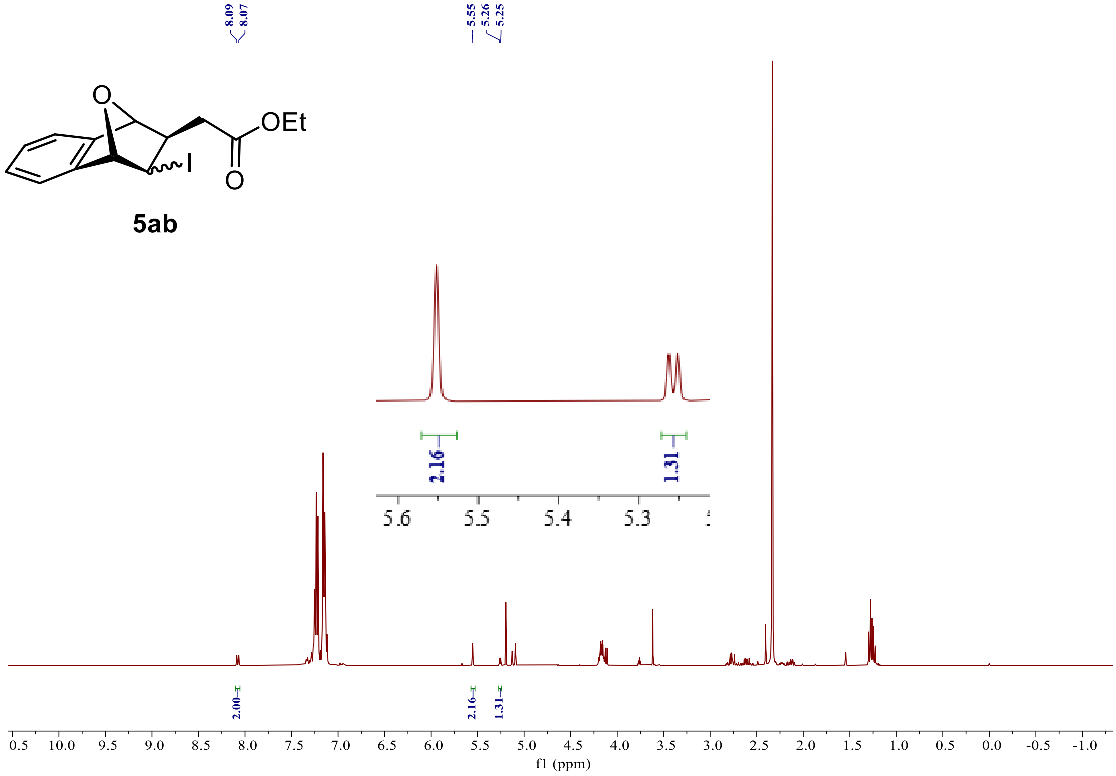
The crude mixture of **3li** with 0.08 mmol 1,3-Benzodioxole as the internal standard.



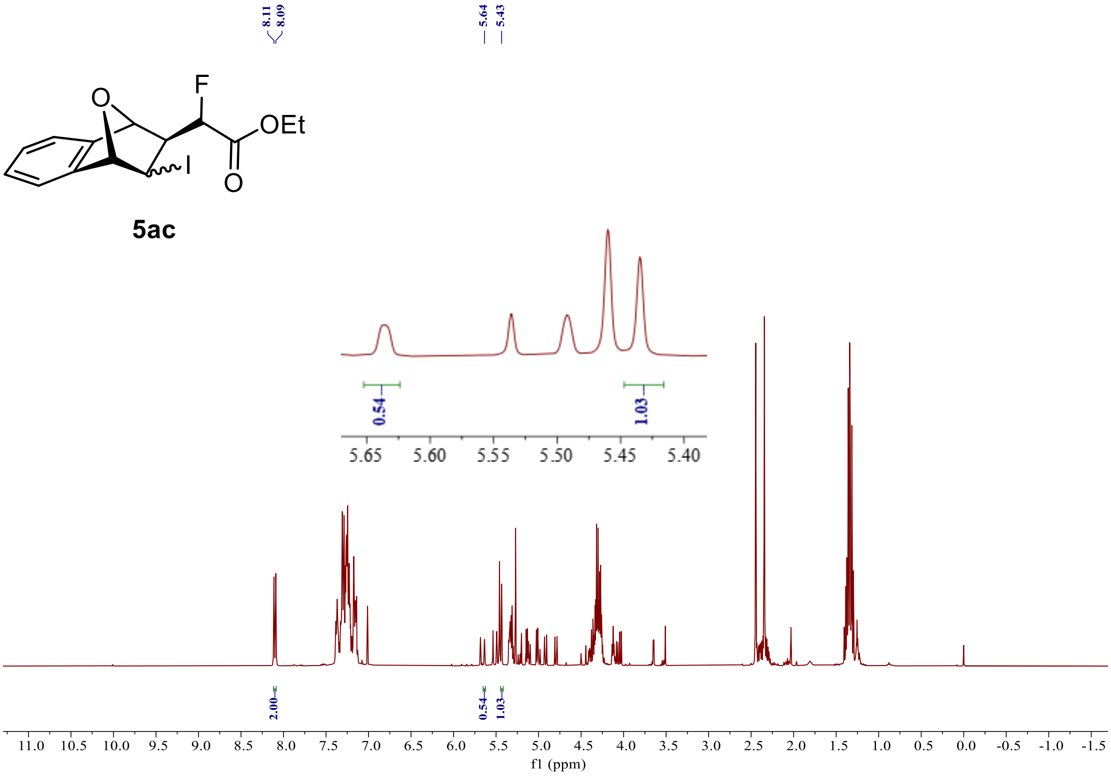
The crude mixture of **5aa** with 0.05 mmol p-nitrotoluene as the internal standard.



The crude mixture of **5ab** with 0.05 mmol p-nitrotoluene as the internal standard.

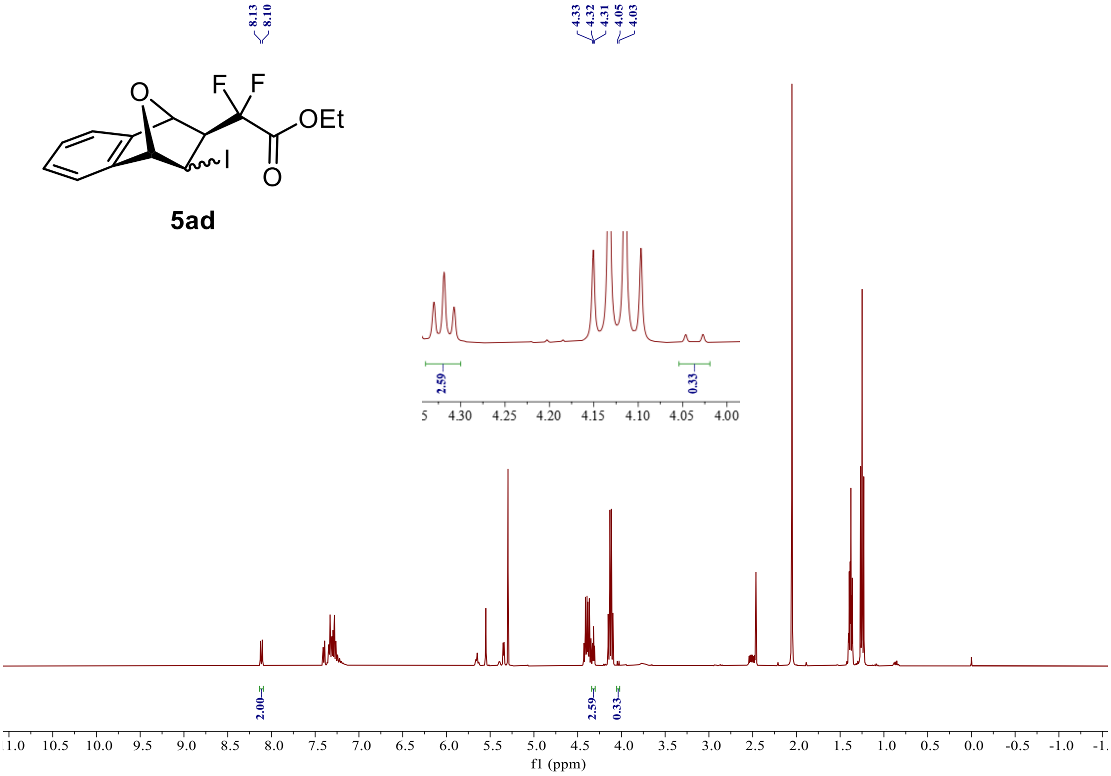


The crude mixture of **5ac** with 0.06 mmol p-nitrotoluene as the internal standard.



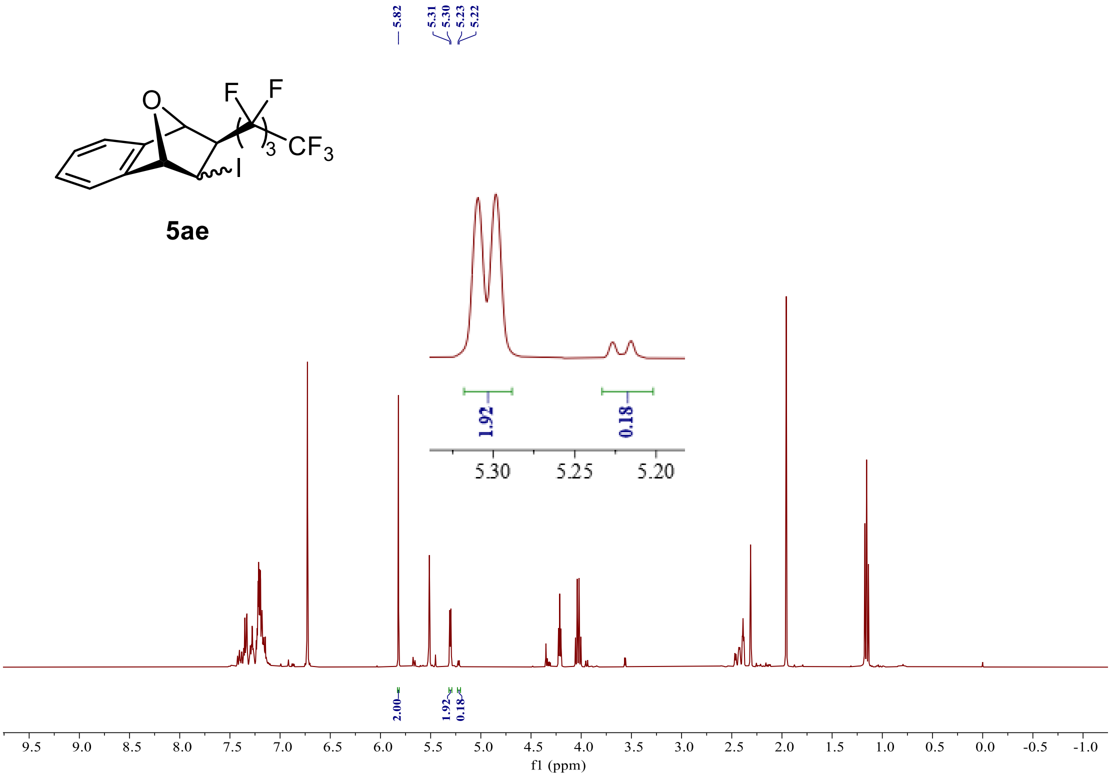
5ac

The crude mixture of **5ad** with 0.05 mmol p-nitrotoluene as the internal standard.

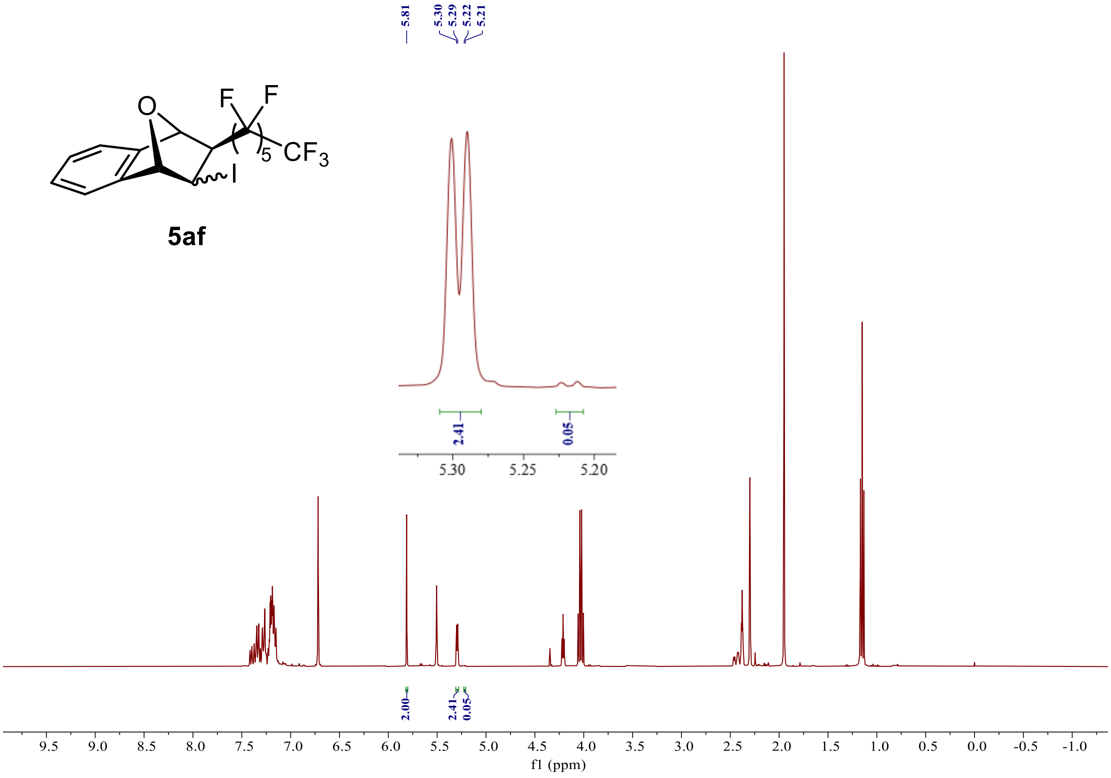


5ad

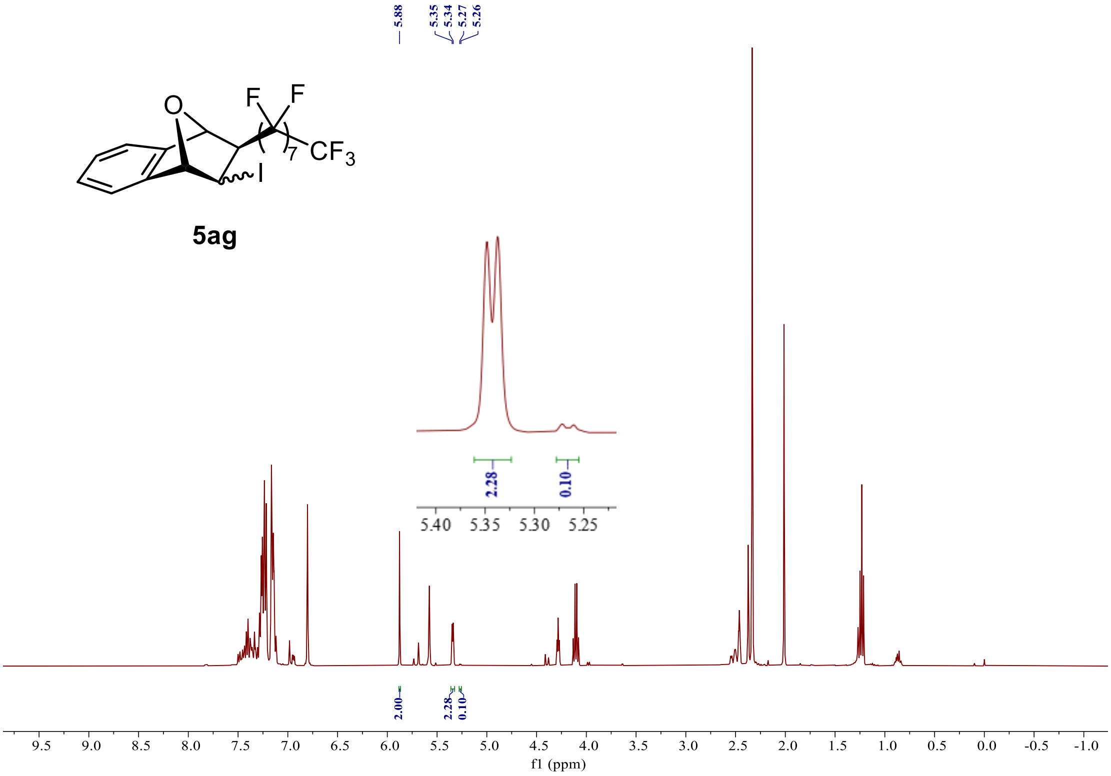
The crude mixture of **5ae** with 0.08 mmol 1,3-Benzodioxole as the internal standard.



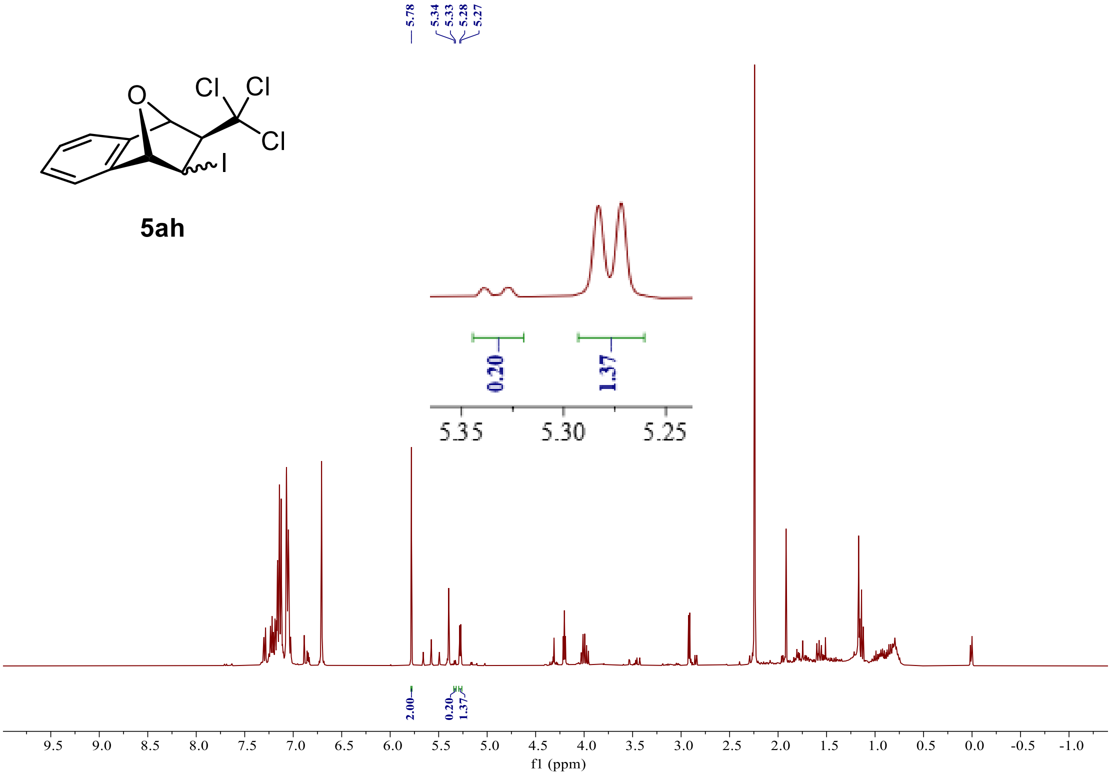
The crude mixture of **5af** with 0.08 mmol 1,3-Benzodioxole as the internal standard.



The crude mixture of **5ag** with 0.08 mmol 1,3-Benzodioxole as the internal standard.


5ag

The crude mixture of **5ah** with 0.09 mmol 1,3-Benzodioxole as the internal standard.


5ah