Electronic Supplementary Material (ESI) for Chemical Science.

Supporting Information

Catalytic Enantioselective Synthesis of Macrodiolides and their Application in Chiral Recognition

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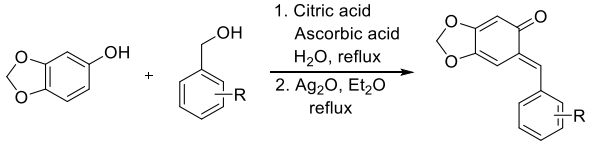
1. General Information

NMR characterization data were collected on bruker ASCEND operating at 400 MHz for ^{1}H NMR, 101 MHz for $^{13}C\{^{1}H\}$ NMR (with complete proton decoupling), and 376 MHz for $^{19}F\{^{1}H\}$ NMR (with complete proton decoupling). ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR: chemical shifts δ were recorded in ppm relative to tetramethylsilane and internally referenced to the residual solvent signal (for ^{1}H NMR: $CDCl_3$ = 7.26 ppm; for ^{13}C NMR: $CDCl_3$ = 77.16 ppm). $^{19}F\{^{1}H\}$ NMR Chemical shifts are reported in ppm with relative to $CFCl_3$ (external reference, δ $^{19}F(CFCl_3)$ = 0. Data were reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, td = triplet of doublets, dt = doublet of triplets, ddd = doublet of doublet of doublets, m = multiplet), coupling constants (Hz), integration. High performance liquid chromatography (HPLC) was performed on (Waters Alliance e2695) using the corresponding commercial chiralpak column at 25 °C with UV detector. UltraPerformance Convergence Chromatography (UPC^2) was performed on (Waters ACQUITY UPC^2) using the corresponding commercial chiralpak column at 25 °C with UV detector and enantiomeric excesses were determined in comparison with the authentic racemates. High resolution mass spectra (HRMS) were performed on Thermo Q-Exactive Focus (FTMS+c ESI) and data were reported as (m/z). Infrared spectra (IR) were recorded on Bruker Tensor II spectrometer with Plantium ATR accessory and the peaks are reported as absorption maxima (ν, cm^{-1}). Circular dichroism spectrum (CD) were recorded on Applied Photophysics Chirascan (CH_2Cl_2 as the solvent). Optical rotations were measured on Rudolph Research Analytic Automatic Polarimeter, and reported as follows: $[\alpha]_D^T$ (c = g/100 mL, λ = 589 nm, in CH_2Cl_2). Melting point ranges were determined on OptiMelt. X-ray crystallographic data were collected by a Bruker D8 Venture Photon II. UV-Vis absorption spectra were collected on HITACHI U-3900H Spectrophotometer at 25 °C and fluorescence spectra were collected on HITACHI F-7000 Spectrophotometer at 25 °C. Silica gel for Thin-layer chromatography (HG/T2354-92) made in Qingdao Haiyang Chemical Co., Ltd. All of the starting materials including the metal salts were purchased from TCI, Aladdin, Adamas, Acros, Aldrich and other companies, and used without further purification. All the solvents including toluene, tetrahydrofuran, diethyl ether, dichloromethane, chloroform, 1,2-dichloroethane, ethyl acetate, acetonitrile and so on were pre-dried over appropriate desiccants, and distilled prior to use. Reactions were monitored using thin-layer chromatography (TLC) on GF254 silica gel. Visualization of the developed plates was performed under UV light (254 nm) or using iodine, cobalt thiocyanate or $KMnO_4$. The products were purified by flash column chromatography with silicycle 300-400 mesh silica gel. The *N,N'*-dioxides were prepared according to the methods reported in the literature.[1–2]

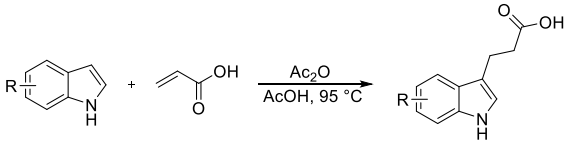
2. Substrates Synthesis

2.1 General procedure for the synthesis of *ortho*-quinone methides according to the literature procedure.[3]



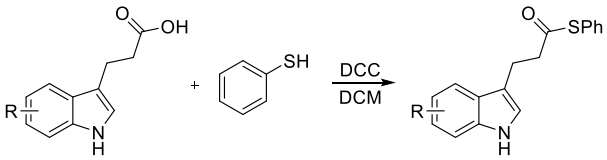
Sesamol (11.05 g, 80 mmol), benzyl alcohol (80 mmol, 1.0 equiv), citric acid (4.23 g, 22 mmol, 0.28 equiv) and ascorbic acid (1.94 g, 11 mmol, 0.14 equiv) were refluxed in water (200 mL) for 24 hours. The mixture was cooled to room temperature, extracted with DCM and concentrated in vacuo. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) then triturated in hexanes to give the intermediate phenol. The phenol (8 mmol) and Ag_2O (6.02 g, 26 mmol, 3.25 equiv) were refluxed in Et_2O (100 mL) for 4 hours. The solution was filtered, then Et_2O evaporated in vacuo, the following recrystallization (Et_2O/DCM = 10/1, v/v) was carried out to afford orange-red crystals. The product was stored at 0 °C under N_2.

2.2 General procedure for the synthesis of 3-indolepropionic acids according to the literature procedure.[4]

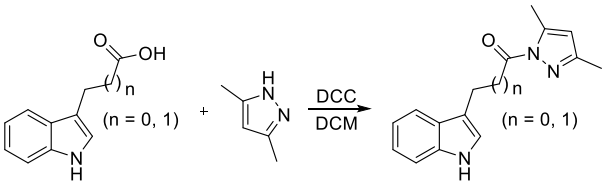


Indole (3.0 mmol) was dissolved in acetic acid (1.7 mL, 30 mmol, 10 equiv). Acrylic acid (0.5 mL, 7.2 mmol, 2.4 equiv) and acetic acid anhydride (0.6 mL, 6.3 mmol, 2.1 equiv) were added and the reaction mixture was heated to 95 °C for 24 hours. The reaction was then cooled to room temperature, which was then extracted with ethyl acetate and NaOH (4 *N*) solution. The aqueous layer was added the HCl (6 *N*) solution until the pH value was 2 and then extracted with ethyl acetate. The combined organics were dried and concentrated in vacuo. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (4/1 and 2/1, v/v) to afford corresponding product.

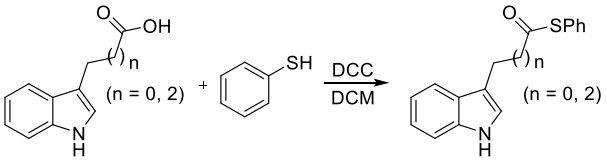
2.3 General procedure for the synthesis of C3-Substituted Indoles 2.



3-Indolepropionic acid (10 mmol) was dissolved in DCM (50 mL). Thiophenol (1.0 mL, 10 mmol, 1.0 equiv) and *N,N'*-dicyclohexylcarbodiimide (2.06 g, 10 mmol, 1.0 equiv) were added and the reaction mixture was stirred at room temperature overnight. The solution was filtered, then concentrated in vacuo. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) to afford the corresponding products **2** (10-80% yield).



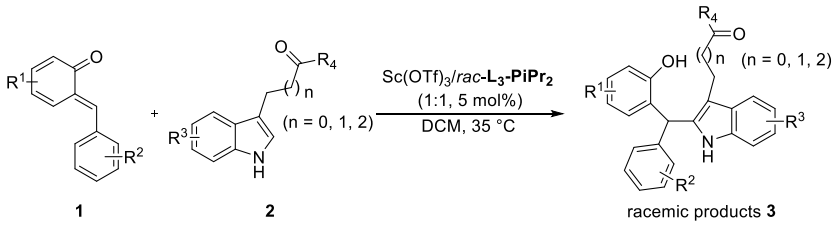
3-Indoleacetic acid/3-Indolepropionic acid (10 mmol) was dissolved in DCM (50 mL). 3,5-Dimethyl-1*H*-pyrazole (0.96 g, 10 mmol, 1.0 equiv) and *N,N'*-dicyclohexylcarbodiimide (2.06 g, 10 mmol, 1.0 equiv) were added and the reaction mixture was stirred at room temperature overnight. The solution was filtered, then concentrated in vacuo. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) to afford corresponding product.



3-Indoleacetic acid/3-Indolebutyric acid (10 mmol) was dissolved in DCM (50 mL). Thiophenol (1.0 mL, 10 mmol, 1.0 equiv) and *N,N'*-dicyclohexylcarbodiimide (2.06 g, 10 mmol, 1.0 equiv) were added and the reaction mixture was stirred at room temperature overnight. The solution was filtered, then concentrated in vacuo. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) to afford corresponding product.
Note: 3-Indoleacetic acid and 3-Indolebutyric acid obtained from commercial sources were used without further purification.

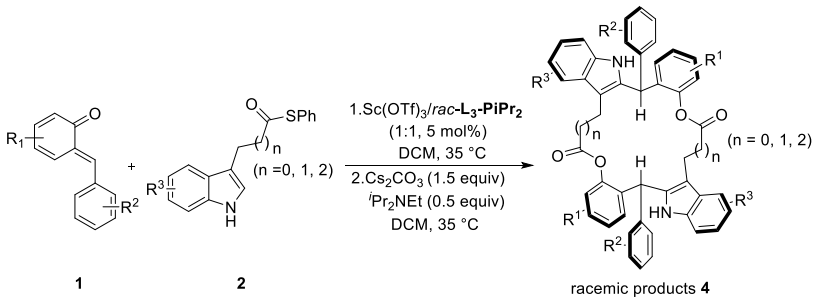
3. General Procedure for Preparation of the Racemic Products

3.1 General procedure for preparation of the racemic products 3



A dry reaction tube was charged with *ortho*-quinone methides **1** (0.10 mmol), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and the ligand *rac*-**L_3-PiPr$_2$** (3.2 mg, 0.005 mmol, 5 mol%) in anhydrous DCM (1.0 mL). The mixture was stirred at 35 °C for 30 min. Then C3-substituted indoles **2** (0.10 mmol, 1.0 equiv) was added and the reaction was stirred at 35 °C. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) to afford the desired racemic products **3**.

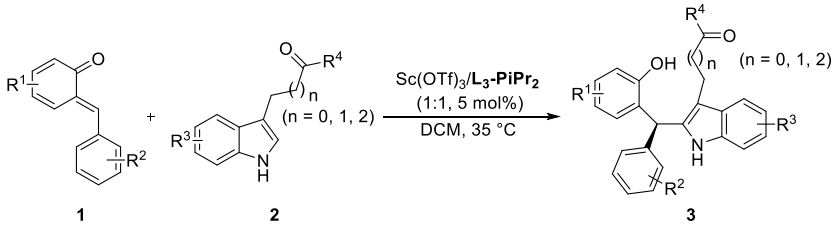
3.2 General procedure for preparation of the racemic products 4



A dry reaction tube was charged with *ortho*-quinone methides **1** (0.10 mmol), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and the ligand *rac*-**L_3-PiPr$_2$** (3.2 mg, 0.005 mmol, 5 mol%) in anhydrous DCM (1.0 mL). The mixture was stirred at 35 °C for 30 min. Then C3-substituted indoles **2** (0.10 mmol, 1.0 equiv) was added and the reaction was stirred at 35 °C. Then Cs_2CO_3 (48.9 mg, 0.15 mmol, 1.5 equiv) and $^{i}Pr_2NEt$ (8.2 μL, 0.05 mmol, 0.5 equiv) were added and the reaction was stirred at 35 °C. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) to afford the desired racemic products **4**.

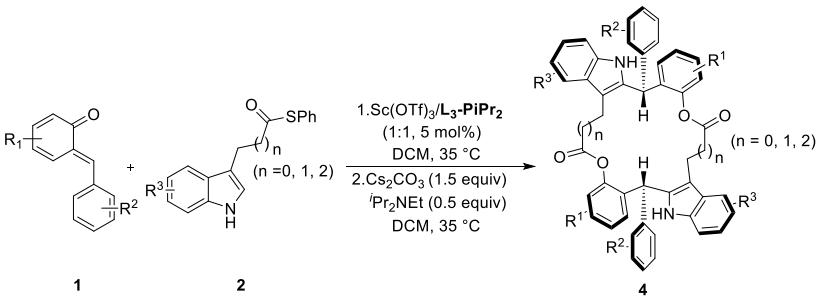
4. Representative Experimental Procedure for Reactions

4.1 Representative experimental procedure for asymmetric Friedel-Crafts alkylation reaction



A dry reaction tube was charged with *ortho*-quinone methides **1** (0.10 mmol), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and the ligand **L_3-PiPr$_2$** (3.2 mg, 0.005 mmol, 5 mol%) in anhydrous DCM (1.0 mL). The mixture was stirred at 35 °C for 30 min. Then C3-substituted indoles **2** (0.10 mmol, 1.0 equiv) was added and the reaction was stirred at 35 °C. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) to afford the corresponding products **3**.

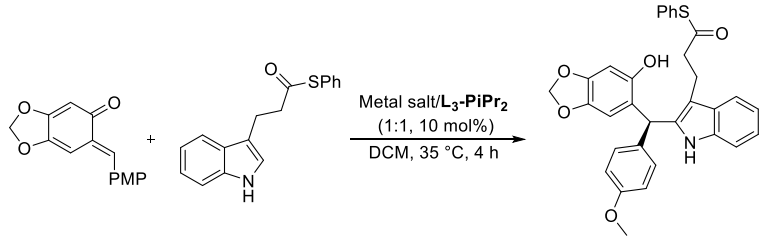
4.2 Representative experimental procedure for tandem asymmetric Friedel-Crafts alkylation/ macrolactonization reaction



A dry reaction tube was charged with *ortho*-quinone methides **1** (0.10 mmol), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and the ligand **L_3-PiPr$_2$** (3.2 mg, 0.005 mmol, 5 mol%) in anhydrous DCM (1.0 mL). The mixture was stirred at 35 °C for 30 min. Then C3-substituted indoles **2** (0.10 mmol, 1.0 equiv) was added and the reaction was stirred at 35 °C. Then Cs_2CO_3 (48.9 mg, 0.15 mmol, 1.5 equiv) and $^{i}Pr_2NEt$ (8.2 μL, 0.05 mmol, 0.5 equiv) were added and the reaction was stirred at 35 °C. The reaction mixture was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (8/1 and 4/1, v/v) to afford the corresponding products **4**.

5. Optimization of Asymmetric Friedel-Crafts Alkylation Reaction Conditions

Table S1: Optimization of the metal salt.

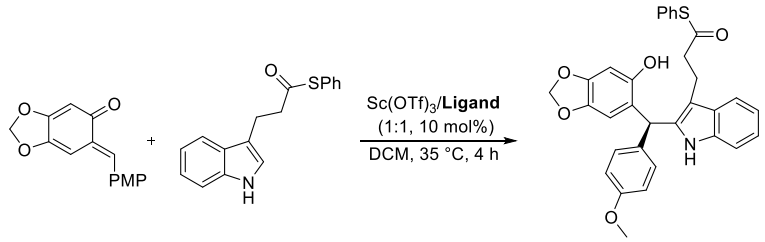


1a **2a** **3aa**

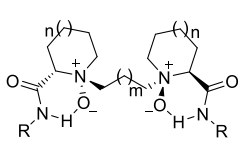
Entry[a]	Metal salt	Yield (%)[b]	ee (%)[c]
1	$Mg(OTf)_2$	n.r.	--
2	$Ni(OTf)_2$	n.r.	--
3	$Cu(OTf)_2$	n.r.	--
4	$Zn(OTf)_2$	n.r.	--
5	$La(OTf)_3$	n.r.	--
6	$Sc(OTf)_3$	96	93
7	$Y(OTf)_3$	72	71
8	$Yb(OTf)_3$	69	78
9	$Al(OTf)_3$	30	0
10	$Fe(OTf)_3$	66	86
11	$In(OTf)_3$	59	82

[a] Unless otherwise noted, *N,N'*-dioxide **L_3-PiPr$_2$** (6.5 mg, 0.01 mmol, 10 mol%), metal salt (0.01 mmol, 10 mol%) and *ortho*-quinone methide **1a** (25.6 mg, 0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred at 35 °C for further 4 hours. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase . n.r. = no reaction.

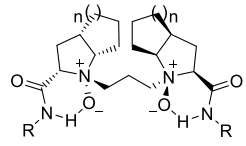
Table S2: Optimization of the ligand.



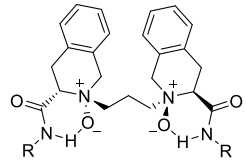
1a **2a** **3aa**



L_3-PrPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 0, m = 1
L_3-PiPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1, m = 1
L_3-PiAd: R = 1-adamantyl, n = 1, m = 1
L_3-Pi*t*Bu: R = ^{t}Bu, n = 1, m = 1
L_3-PiPh: R = C_6H_5, n = 1, m = 1
L_3-PiBn: R = $CH_2C_6H_5$, n = 1, m = 1
L_3-Pi*m*Bu$_2$: R = 3,5-^{t}Bu$_2$C$_6$H$_3$, n = 1, m = 1
L_3-PiPr$_3$: R = 2,4,6-^{i}Pr$_3$C$_6$H$_2$, n = 1, m = 1
L_3-PiEt$_2$: R = 2,6-Et$_2$C$_6$H$_3$, n = 1, m = 1
L_3-PiMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$, n = 1, m = 1
L_2-PiMe$_2$: R = 2,6-Me$_2$C$_6$H$_3$, n = 1, m = 0



L_3-RaPr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 1
L_3-PePr$_2$: R = 2,6-^{i}Pr$_2$C$_6$H$_3$, n = 2

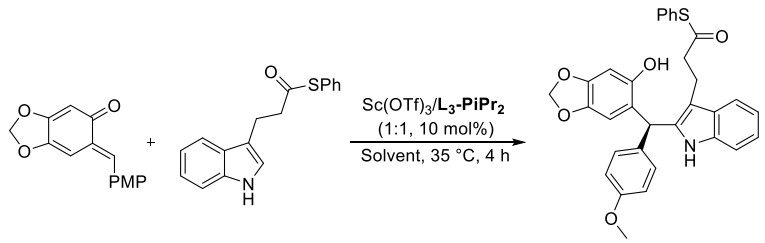


L_3-TqAd: R = 1-adamantyl

Entry[a]	**Ligand**	Yield (%)[b]	ee (%)[c]
1	**L_3-PrPr$_2$**	95	73
2	**L_3-RaPr$_2$**	83	84
3	**L_3-PePr$_2$**	84	84
4	**L_3-TqAd**	87	84
5	**L_3-PiPr$_2$**	96	93
6	**L_3-PiAd**	99	80
7	**L_3-Pi*t*Bu**	89	68
8	**L_3-PiPh**	92	66
9	**L_3-PiBn**	98	57
10	**L_3-Pi*m*Bu$_2$**	74	79
11	**L_3-PiPr$_3$**	95	86
12	**L_3-PiEt$_2$**	95	90
13	**L_3-PiMe$_2$**	99	83
14	**L_2-PiMe$_2$**	98	54

[a] Unless otherwise noted, **Ligand** (0.01 mmol, 10 mol%), Sc(OTf)$_3$ (4.9 mg, 0.01 mmol, 10 mol%) and *ortho*-quinone methide **1a** (25.6 mg, 0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred at 35 °C for further 4 hours. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S3: Optimization of solvent.

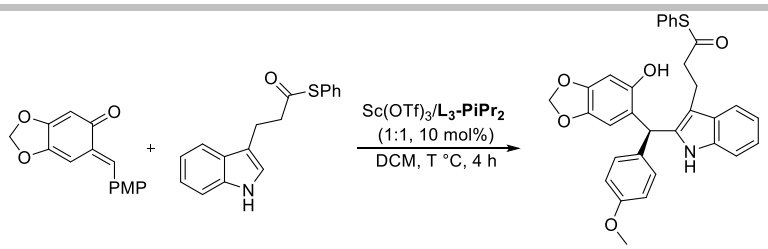


1a **2a** **3aa**

Entry[a]	Solvent	Yield (%)[b]	ee (%)[c]
1	DCM	96	93
2	DCE	92	94
3	$CHCl_3$	93	93
4	THF	56	96
5	Toluene	77	96
6	Et_2O	79	95
7	EtOAc	61	92

[a] Unless otherwise noted, *N,N'*-dioxide **L_3-PiPr$_2$** (6.5 mg, 0.01 mmol, 10 mol%), Sc(OTf)$_3$ (4.9 mg, 0.01 mmol, 10 mol%) and *ortho*-quinone methide **1a** (25.6 mg, 0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then DCM evaporated in vacuo and solvent (1.0 mL) was added. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred at 35 °C for further 4 hours. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S4: Optimization of the temperature.

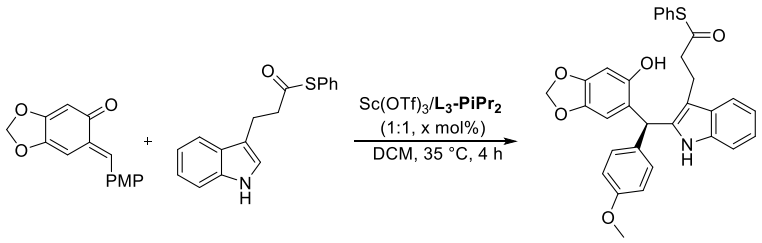


1a **2a** **3aa**

Entry[a]	T (°C)	Yield (%)[b]	ee (%)[c]
1	–10	45	96
2	0	74	96
3	10	80	95
4	20	96	93
5	35	96	93
6	50	98	91

[a] Unless otherwise noted, *N,N'*-dioxide **L_3-PiPr$_2$** (6.5 mg, 0.01 mmol, 10 mol%), $Sc(OTf)_3$ (4.9 mg, 0.01 mmol, 10 mol%) and *ortho*-quinone methide **1a** (25.6 mg, 0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred in DCM (1.0 mL) at T °C for further 4 hours. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

Table S5: Optimization of the catalyst loading.



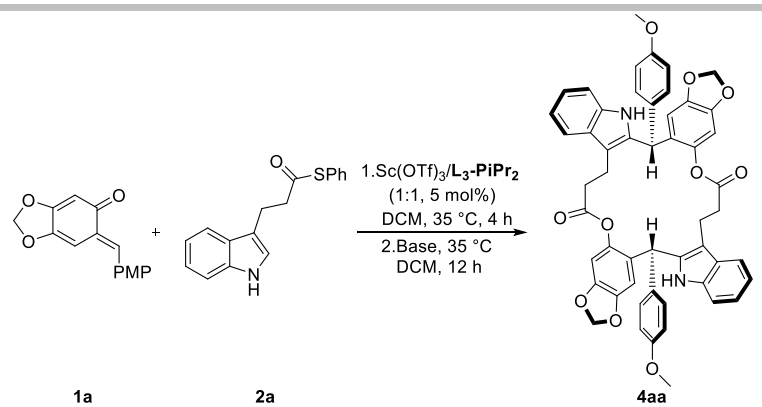
1a **2a** **3aa**

Entry[a]	x (mol%)	Yield (%)[b]	ee (%)[c]
1	10	96	93
2	5	99	93
3[d]	5	99	88
4[e]	5	94	93
5	2.5	39	56
6	1	43	36

[a] Unless otherwise noted, *N,N'*-dioxide **L_3-PiPr$_2$** (x mol%), $Sc(OTf)_3$ (x mol%) and *ortho*-quinone methide **1a** (25.6 mg, 0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred at 35 °C for further 4 hours. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase. [d] The mixture was stirred at 20 °C. [e] 4 Å M.S. (30 mg) was added.

6. Optimization of Macrolactonization Reaction Conditions

Table S6: Optimization of the base.

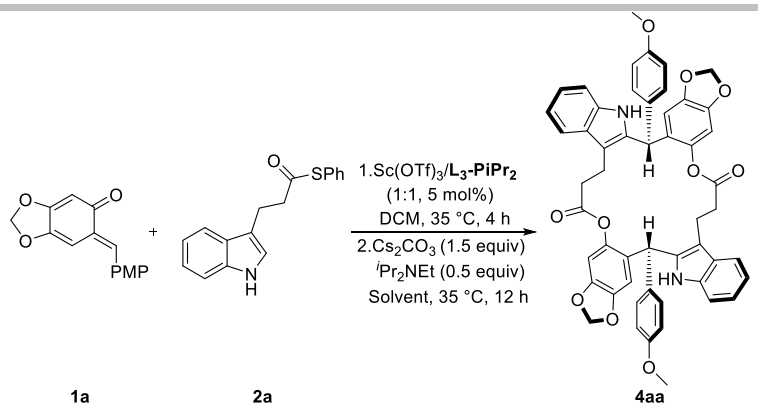


1a **2a** **4aa**

Entry[a]	Base	Yield (%)[b]	dr[c]	ee (%)[d]
1	DMAP (1.0 equiv)	47	92:8	99
2	DABCO (1.0 equiv)	trace	--	--
3	DBU (1.0 equiv)	54	92:8	99
4	DIPEA (1.0 equiv)	trace	--	--
5	NaOH (1.0 equiv)	18	92:8	99
6	NaO*t*Bu (1.0 equiv)	trace	--	--
7	CsF (1.0 equiv)	44	92:8	99
8	Cs_2CO_3 (1.0 equiv)	55	92:8	99
9	Cs_2CO_3 (2.0 equiv)	67	92:8	99
10	Cs_2CO_3 (3.0 equiv)	58	92:8	99
11	Cs_2CO_3 (1.0 equiv), CsF (1.0 equiv)	58	92:8	99
12	Cs_2CO_3 (1.0 equiv), DMAP (1.0 equiv)	52	92:8	99
13	Cs_2CO_3 (1.0 equiv), DABCO (1.0 equiv)	55	92:8	99
14	Cs_2CO_3 (1.0 equiv), DBU (1.0 equiv)	40	92:8	99
15	Cs_2CO_3 (1.0 equiv), DIPEA (1.0 equiv)	63	92:8	99
16	Cs_2CO_3 (0.5 equiv), DIPEA (1.5 equiv)	29	91:9	99
17	Cs_2CO_3 (1.5 equiv), DIPEA (0.5 equiv)	70	93:7	99
18	Cs_2CO_3 (1.5 equiv)	61	92:8	99

[a] Unless otherwise noted, *N,N'*-dioxide **L_3-PiPr$_2$** (3.2 mg, 0.005 mmol, 5 mol%), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and *ortho*-quinone methide **1a** (25.6 mg, 0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred at 35 °C for further 4 hours. Then base was added and the reaction was stirred at 35 °C for 12 hours. [b] Isolated yield. [c] Determined by ^{1}H NMR analysis. [d] Determined by UPC^2 analysis on a chiral stationary phase.

Table S7: Optimization of the solvent.

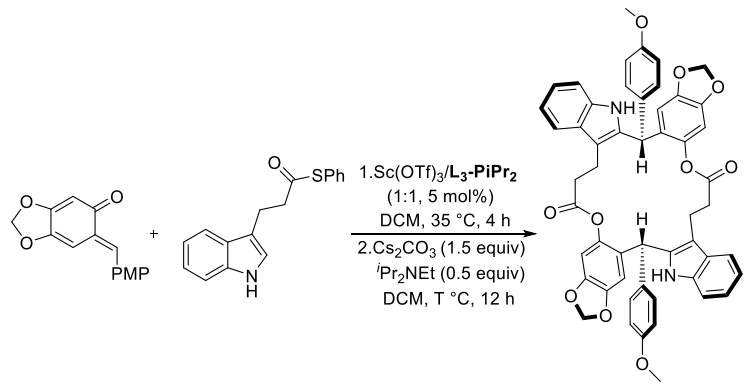


1a **2a** **4aa**

Entry[a]	Solvent	Yield (%)[b]	dr[c]	ee (%)[d]
1	DCM	70	93:7	99
2	DCE	56	93:7	99
3	$CHCl_3$	46	91:9	99
4	THF	39	92:8	99
5	Toluene	42	93:7	99
6	Et_2O	22	91:9	99
7	EtOAc	46	92:8	99

[a] Unless otherwise noted, *N,N'*-dioxide **L_3-PiPr$_2$** (3.2 mg, 0.005 mmol, 5 mol%), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and *ortho*-quinone methide **1a** (25.6 mg, 0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred at 35 °C for further 4 hours. Then DCM evaporated in vacuo and solvent (1.0 mL) was added. Then Cs_2CO_3 (48.9 mg, 0.15 mmol, 1.5 equiv) and $^iPr_2NEt$ (8.2 μL, 0.05 mmol, 0.5 equiv) were added and the reaction was stirred at 35 °C for 12 hours. [b] Isolated yield. [c] Determined by ^1H NMR analysis. [d] Determined by UPC^2 analysis on a chiral stationary phase.

Table S8: Optimization of the temperature.

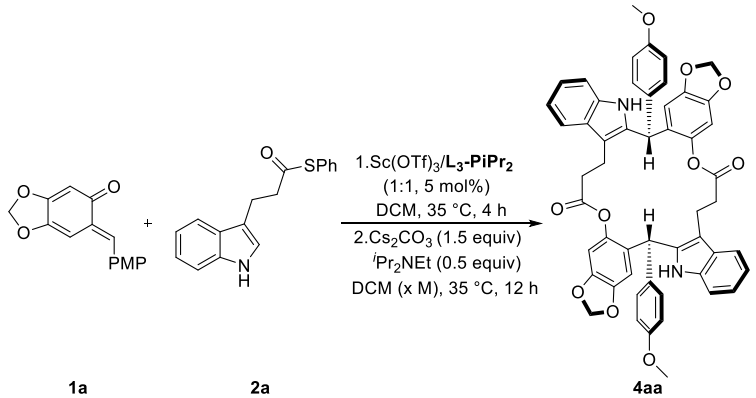


1a **2a** **4aa**

Entry[a]	T (°C)	Yield (%)[b]	dr[c]	ee (%)[d]
1	–10	27	93:7	99
2	0	43	92:8	99
3	10	53	92:8	99
4	20	61	92:8	99
5	35	70	93:7	99
6	50	57	91:9	99

[a] Unless otherwise noted, *N,N'*-dioxide **L_3-PiPr$_2$** (3.2 mg, 0.005 mmol, 5 mol%), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and *ortho*-quinone methide **1a** (25.6 mg, 0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred at 35 °C for further 4 hours. Then Cs_2CO_3 (48.9 mg, 0.15 mmol, 1.5 equiv) and $^iPr_2NEt$ (8.2 μL, 0.05 mmol, 0.5 equiv) were added and the reaction was stirred at T °C for 12 hours. [b] Isolated yield. [c] Determined by ^1H NMR analysis. [d] Determined by UPC^2 analysis on a chiral stationary phase.

Table S9: Optimization of the concentration.



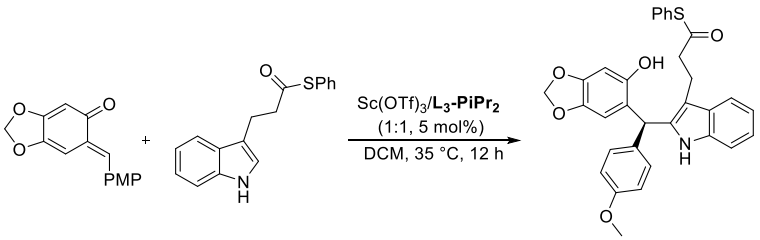
1a **2a** **4aa**

Entry[a]	x (M)	Yield (%)[b]	dr[c]	ee (%)[d]
1	0.8	56	92:8	99
2	0.4	70	92:8	99
3	0.2	66	93:7	99
4	0.1	70	93:7	99
5	0.05	70	86:14	99
6	0.025	72	92:8	99
7	0.0125	69	91:9	99

[a] Unless otherwise noted, *N,N'*-dioxide **L_3-PiPr$_2$** (3.2 mg, 0.005 mmol, 5 mol%), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and *ortho*-quinone methide **1a** (25.6 mg, 0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred at 35 °C for further 4 hours. Then DCM evaporated in vacuo. Then Cs_2CO_3 (48.9 mg, 0.15 mmol, 1.5 equiv) and $^iPr_2NEt$ (8.2 μL, 0.05 mmol, 0.5 equiv) were added and the reaction was stirred in DCM (x M) at 35 °C for 12 hours. [b] Isolated yield. [c] Determined by ^1H NMR analysis. [d] Determined by UPC^2 analysis on a chiral stationary phase.

7. Gram-Scale Synthesis of Products

7.1 Gram-scale synthesis of product 3a



1a
2.5 mmol

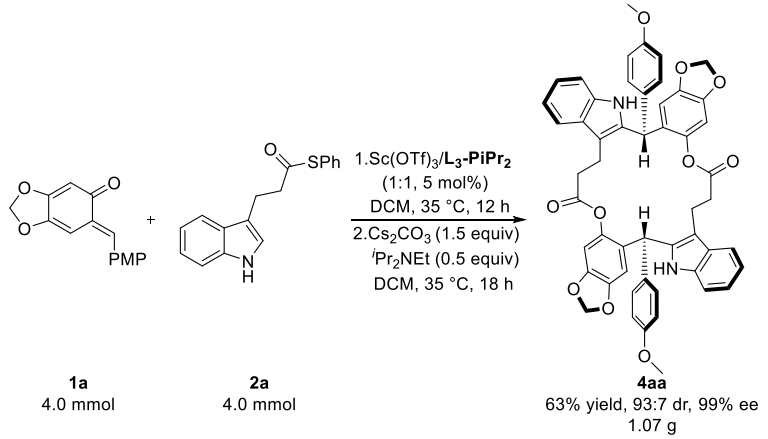
2a
2.5 mmol

3aa
97% yield, 91% ee
1.31 g

To show the synthetic utility of the methodology, a gram scale synthesis of product **3aa** was conducted. *ortho*-Quinone methide **1a** (0.64 g, 2.5 mmol) reacted with 3-indolepropanethioate **2a** (0.70 g, 2.5 mmol, 1.0 equiv) smoothly under the optimal reaction conditions, offering product **3aa** in 97% yield (1.31 g) with 91% ee.

Procedure: An oven dried round-bottom flask (100 mL) was charged with *ortho*-quinone methide **1a** (0.64 g, 2.5 mmol), $Sc(OTf)_3$ (61.5 mg, 0.125 mmol, 5 mol%) and the ligand **L_3-PiPr$_2$** (81.1 mg, 0.125 mmol, 5 mol%) in anhydrous DCM (25.0 mL). The mixture was stirred at 35 °C for 4 hours. Then 3-indolepropanethioate **2a** (0.70 g, 2.5 mmol, 1.0 equiv) was added and the reaction was stirred at 35 °C for 12 hours. After the solvent was removed in vacuo, the residue was purified by flash column chromatography on silica gel (Pet/EA = 4/1, v/v) to afford the desired product **3aa** in 97% yield (1.31 g) with 91% ee.

7.2 Gram-scale synthesis of product 3aa



1a
4.0 mmol

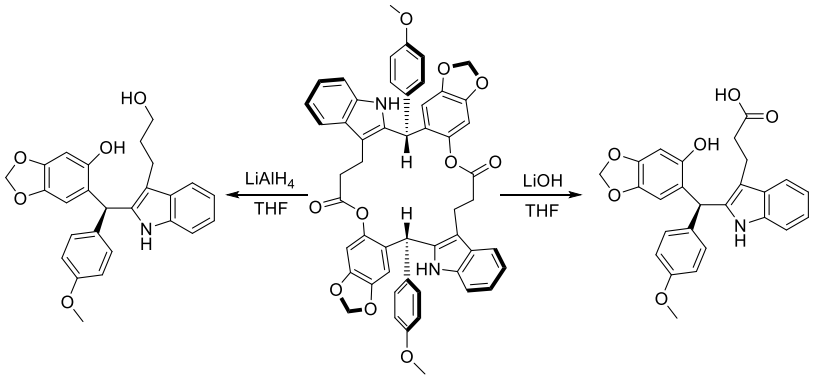
2a
4.0 mmol

4aa
63% yield, 93:7 dr, 99% ee
1.07 g

To show the synthetic utility of the methodology, a gram scale synthesis of product **4aa** was conducted. *ortho*-Quinone methide **1a** (1.03 g, 4.0 mmol) reacted with 3-indolepropanethioate **2a** (1.13 g, 4.0 mmol, 1.0 equiv) smoothly under the optimal reaction conditions, offering product **4aa** in 63% yield (1.07 g), 93:7 dr, 99% ee.

Procedure: An oven dried round-bottom flask (100 mL) was charged with *ortho*-quinone methide **1a** (1.03 g, 4.0 mmol), $Sc(OTf)_3$ (98.4 mg, 0.2 mmol, 5 mol%) and the ligand **L_3-PiPr$_2$** (129.8 mg, 0.2 mmol, 5 mol%) in anhydrous DCM (40.0 mL). The mixture was stirred at 35 °C for 4 hours. Then 3-indolepropanethioate **2a** (1.13 g, 4.0 mmol, 1.0 equiv) was added and the reaction was stirred at 35 °C for 12 hours. Then Cs_2CO_3 (1.96 g, 6.0 mmol, 1.5 equiv) and $^{i}Pr_2NEt$ (0.331 mL, 2.0 mmol, 0.5 equiv) were added and the reaction was stirred at 35 °C for 18 hours. After the solvent was removed in vacuo, the residue was purified by flash column chromatography on silica gel (Pet/EA = 4/1, v/v) to afford the desired product **4aa** in 63% yield (1.07 g), 93:7 dr, 99% ee.

8. Transformations of the Product



6aa
92% yield, 94% ee

4aa
0.05 mmol, 93:7 dr, 99% ee

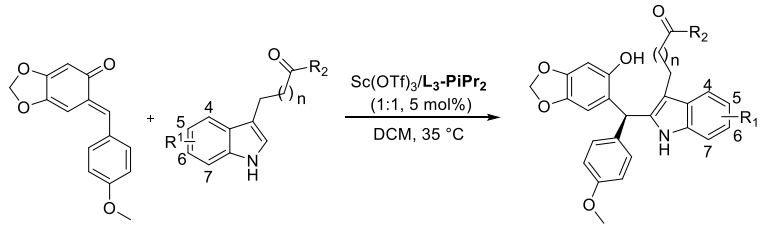
7aa
59% yield, 98% ee

Synthesis of **6aa**: A dry reaction tube was charged with **4aa** (42.7 mg, 0.05 mmol, 93:7 dr, 99% ee) in anhydrous THF (1.0 mL). The mixture was stirred at 0 °C for 10 min. Then $LiAlH_4$ (4.2 mg, 0.11 mmol, 2.2 equiv) was added at 0 °C and the reaction was stirred at 0 °C for 12 hours. After the reaction was completed, the KOH (2 *N*) solution was added. Then, the mixture was extracted with ethyl acetate, and the aqueous layer was added the HCl (1 *N*) solution until the pH value was 2 and then extracted with ethyl acetate. The combined organics were dried and concentrated in vacuo. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (4/1 and 2/1, v/v) to afford the product **6aa** (39.8 mg, 92% yield, 94% ee).

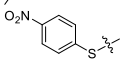
Synthesis of **7aa**: A dry reaction tube was charged with **4aa** (42.7 mg, 0.05 mmol, 93:7 dr, 99% ee) in anhydrous THF (1.0 mL). Then LiOH (9.6 mg, 0.4 mmol, 8.0 equiv) was added at 35 °C and the reaction was stirred at 35 °C for 12 hours. After the reaction was completed, the HCl (1 *N*) solution was added until the pH value was 2. Then, the mixture was extracted with ethyl acetate. The combined organics were dried and concentrated in vacuo. The residue was subjected to column chromatography on silica gel and eluted with petroleum ether/ethyl acetate (4/1 and 2/1, v/v) to afford the product **7aa** (26.2 mg, 59% yield, 98% ee).

9. Substrate Scope For the Friedel-Crafts Alkylation Reaction

Table S10: Substrate scope with C3-substituted indoles.

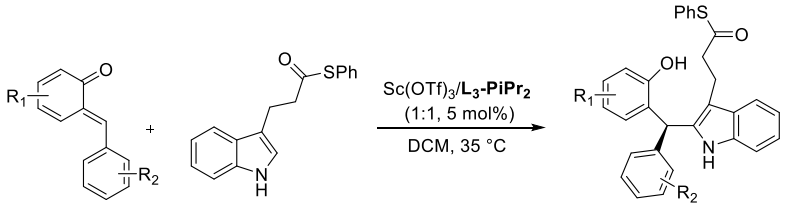


1a **2** **3**

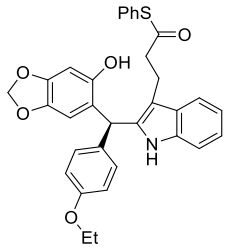
Entry[a]	R^1	n	R^2	Yield (%)[b]	ee (%)[c]	Reaction time
1	H	1	SPh	99 (**3aa**)	93	4 h
2	4-Cl	1	SPh	95 (**3ab**)	93	41 h
3	4-F	1	SPh	91 (**3ac**)	91	47 h
4	4-Me	1	SPh	99 (**3ad**)	93	16 h
5	5-Br	1	SPh	99 (**3ae**)	91	23 h
6	5-Cl	1	SPh	97 (**3af**)	92	23 h
7	5-F	1	SPh	90 (**3ag**)	91	17 h
8	5-Me	1	SPh	99 (**3ah**)	93	14 h
9	5-OMe	1	SPh	93 (**3ai**)	92	5 h
10	6-Br	1	SPh	96 (**3aj**)	91	41 h
11	6-Cl	1	SPh	99 (**3ak**)	94	14 h
12	6-F	1	SPh	98 (**3al**)	94	14 h
13	6-Me	1	SPh	95 (**3am**)	92	14 h
14	7-Cl	1	SPh	97 (**3an**)	92	64 h
15	7-Me	1	SPh	97 (**3ao**)	90	15 h
16	H	2	SPh	97 (**3ap**)	94	14 h
17	H	0	SPh	99 (**3aq**)	97	5 h
18	H	1		99 (**3ar**)	95	16 h
19	H	0		94 (**3as**)	95	4 h
20	H	1		99 (**3at**)	92	5 h

[a] Unless otherwise noted, *N,N'*-dioxide **L_3-PiPr$_2$** (3.2 mg, 0.005 mmol, 5 mol%), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and *ortho*-quinone methide **1a** (25.6 mg, 0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then indoles **2** (0.10 mmol) was added and the mixture was stirred at 35 °C. [b] Isolated yield. [c] Determined by HPLC analysis on a chiral stationary phase.

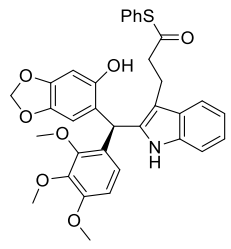
Table S11: Substrate scope with *ortho*-quinone methides.



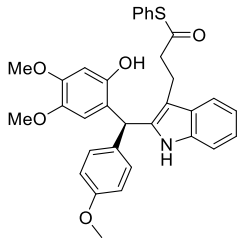
1	2a	3



3ba
99% yield, 93% ee, 4 h



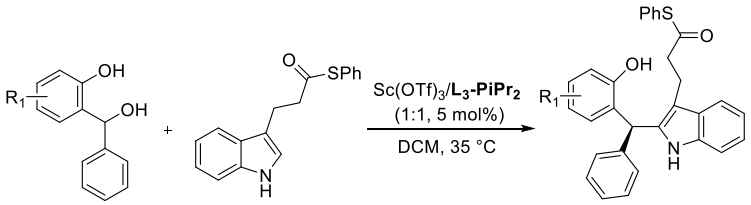
3ca
89% yield, 90% ee, 24 h



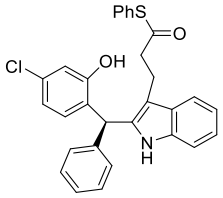
3da
99% yield, 86% ee, 9 h

Reaction conditions: Unless otherwise noted, *N,N'*-dioxide **L3-PiPr2** (3.2 mg, 0.005 mmol, 5 mol%), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and *ortho*-quinone methides **1** (0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred at 35 °C. All yields refer to isolated yield. The ee value was determined by HPLC analysis on a chiral stationary phase.

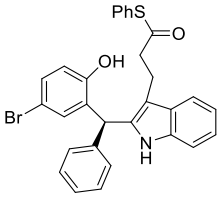
Table S12: Substrate scope with *ortho*-hydroxybenzyl alcohols.



1	2a	3



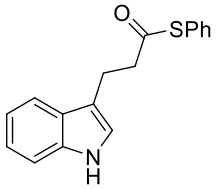
3ea
87% yield, 91% ee, 12 h



3fa
97% yield, 92% ee, 12 h

Reaction conditions: Unless otherwise noted, *N,N'*-dioxide **L3-PiPr2** (3.2 mg, 0.005 mmol, 5 mol%), $Sc(OTf)_3$ (2.5 mg, 0.005 mmol, 5 mol%) and *ortho*-hydroxybenzyl alcohols **1** (0.10 mmol) were stirred in DCM (1.0 mL) at 35 °C for 30 min. Then 3-indolepropanethioate **2a** (28.1 mg, 0.10 mmol) was added and the mixture was stirred at 35 °C. All yields refer to isolated yield. The ee value was determined by HPLC analysis on a chiral stationary phase.

10. Spectral Characterization Data for the Reaction Substrates



2a

***S*-Phenyl 3-(1*H*-indol-3-yl)propanethioate (2a)**

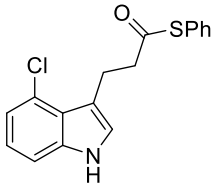
Result: white solid, m.p. 73 – 78 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.68 – 7.58 (m, 1H), 7.48 – 7.38 (m, 5H), 7.38 – 7.33 (m, 1H), 7.26 – 7.20 (m, 1H), 7.19 – 7.13 (m, 1H), 7.04 – 6.99 (m, 1H), 3.24 – 3.17 (m, 2H), 3.14 – 3.02 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.29, 136.21, 134.47, 129.33, 129.15, 127.73, 127.03, 122.08, 121.65, 119.37, 118.62, 114.28, 111.16, 44.21, 21.12;

ESI-HRMS calcd for [$C_{17}H_{15}NOS+Na^+$]: 304.0767, found 304.0765;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3410, 3055, 2928, 2854, 1695, 1582, 1479, 1449, 1342, 1227, 1177, 1040, 965, 925, 806, 744, 691, 587, 530, 481,426.



2b

***S*-Phenyl 3-(4-chloro-1*H*-indol-3-yl)propanethioate (2b)**

Result: white solid, m.p. 124 – 126 ℃;

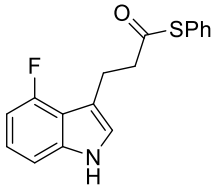
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.40 (s, 5H), 7.26 – 7.20 (m, 1H), 7.12 – 7.05 (m, 2H), 7.04 –7.00 (m, 1H), 3.43 – 3.36 (m, 2H), 3.15 – 3.09 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.30, 137.77, 134.46, 129.28, 129.13, 127.87, 126.19, 123.96, 123.51, 122.62, 120.45, 114.70, 109.96, 45.73, 22.26;

ESI-HRMS calcd for [$C_{17}H_{14}{}^{34.9689}ClNOS+Na^+$]: 338.0377, found 338.0381;

ESI-HRMS calcd for [$C_{17}H_{14}{}^{36.9659}ClNOS+Na^+$]: 340.0347, found 340.0350;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3410, 3075, 2897, 2361, 1710, 1621, 1559, 1480, 1439, 1406, 1334, 1272, 1181, 1146, 1108, 1083, 1029, 963, 938, 809, 749, 693, 634, 558.



2c

***S*-Phenyl 3-(4-fluoro-1*H*-indol-3-yl)propanethioate (2c)**

Result: white solid, m.p. 102 – 104 ℃;

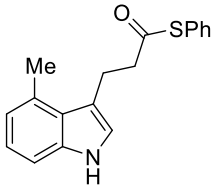
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.45 – 7.34 (m, 5H), 7.16 – 7.04 (m, 2H), 6.98 – 6.93 (m, 1H), 6.82 – 6.72 (m, 1H), 3.25 (t, *J* = 7.2 Hz, 2H), 3.09 (t, *J* = 7.2 Hz, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.24, 157.15 (*J* = 244.3 Hz), 139.10 (*J* = 11.7 Hz), 134.46, 129.27, 129.12, 127.85, 122.62 (*J* = 7.7 Hz), 122.02, 115.89 (*J* = 20.0 Hz), 113.06, 107.26 (*J* = 3.5 Hz), 104.59 (*J* = 19.4 Hz), 44.82, 22.34;

^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –123.79;

ESI-HRMS calcd for [$C_{17}H_{14}FNOS+Na^+$]: 322.0672, found 322.0674;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3375, 3060, 2926, 2362, 1884, 1694, 1632, 1580, 1550, 1503, 1478, 1440, 1352, 1247, 1224, 1174, 1032, 968, 776, 740, 692, 583, 524, 480.

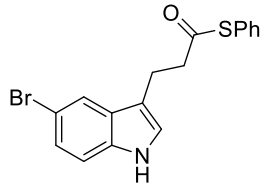


2d

***S*-Phenyl 3-(4-methyl-1*H*-indol-3-yl)propanethioate (2d)**

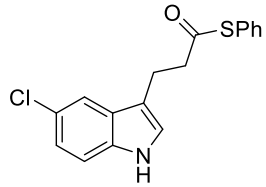
Result: white solid, m.p. 139 – 143 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.41 (s, 5H), 7.23 – 7.16 (m, 1H), 7.12 – 7.04 (m, 1H), 7.00 – 6.95 (m, 1H), 6.90 – 6.82 (m, 1H), 3.41 – 3.31 (m, 2H), 3.10 – 3.01 (m, 2H), 2.76 – 2.70 (s, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.04, 136.74, 134.47, 130.64, 129.35, 129.17, 127.74, 125.58, 122.20, 121.73, 121.15, 115.31, 109.09, 45.43, 23.07, 20.31;
ESI-HRMS calcd for [$C_{18}H_{17}NOS+Na^+$]: 318.0923, found 318.0931;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3413, 2909, 2361, 2336,1710, 1503, 1475, 1439, 1406, 1335, 1269, 1113, 1029, 966, 811, 748, 688, 530.



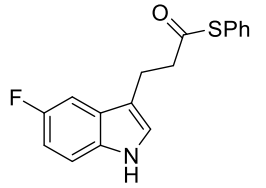
2e

***S*-Phenyl 3-(5-bromo-1*H*-indol-3-yl)propanethioate (2e)**
Result: white solid, m.p. 92 – 96 ℃;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.75 – 7.68 (m, 1H), 7.47 – 7.35 (m, 5H), 7.32 – 7.24 (m, 1H), 7.23 – 7.15 (m, 1H), 7.02 – 6.95 (m, 1H), 3.17 – 3.09 (m, 2H), 3.07 – 2.99 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.28, 134.79, 134.46, 129.40, 129.19, 128.82, 127.57, 124.88, 123.00, 121.22, 113.95, 112.66, 112.64, 44.02, 20.91;
ESI-HRMS calcd for [$C_{17}H_{14}{}^{78.9183}BrNOS+Na^+$]: 381.9872, found 381.9862;
ESI-HRMS calcd for [$C_{17}H_{14}{}^{80.9163}BrNOS+Na^+$]: 383.9851, found 383.9840;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3418, 3058, 2911, 2854, 2362, 2336, 1693, 1568, 1458, 1330, 1275, 1227, 1172, 1095, 1043, 966, 929, 880, 795, 749, 691, 589, 531, 423.



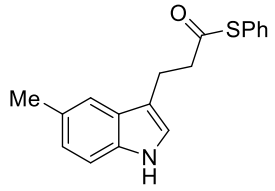
2f

***S*-Phenyl 3-(5-chloro-1*H*-indol-3-yl)propanethioate (2f)**
Result: white solid, m.p. 91 – 94 ℃;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.56 (m, 1H), 7.45 – 7.35 (m, 5H), 7.27 – 7.20 (m, 1H), 7.18 – 7.13 (m, 1H), 7.06 – 6.97 (m, 1H), 3.14 (t, *J* = 7.2 Hz, 2H), 3.03 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.17, 134.56, 134.49, 129.44, 129.22, 128.18, 127.62, 125.14, 123.19, 122.37, 118.16, 114.01, 112.23, 44.04, 20.97;
ESI-HRMS calcd for [$C_{17}H_{14}{}^{34.9689}ClNOS+Na^+$]: 338.0377, found 338.0381;
ESI-HRMS calcd for [$C_{17}H_{14}{}^{36.9659}ClNOS+Na^+$]: 340.0347, found 340.0349;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3415, 3060, 2912, 2854, 2362, 2335, 1694, 1575, 1462, 1444, 1337, 1275, 1227, 1173, 1097, 1043, 966, 930, 891, 864, 795, 749, 692, 636, 594, 531, 478, 424.



2g

***S*-Phenyl 3-(5-fluoro-1*H*-indol-3-yl)propanethioate (2g)**
Result: white solid, m.p. 75 – 78 ℃;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.45 – 7.35 (m, 5H), 7.29 – 7.21 (m, 2H), 7.08 – 7.03 (m, 1H), 6.99 – 6.91 (m, 1H), 3.18 – 3.10 (m, 2H), 3.08 – 2.98 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.21, 157.75 (*J* = 233.3 Hz), 134.46, 132.70, 129.39, 129.18, 127.66, 127.45 (*J* = 9.5 Hz), 123.50, 114.48 (*J* = 4.2 Hz), 111.78 (*J* = 9.6 Hz), 110.47 (*J* = 26.0 Hz), 103.59 (*J* = 23.3 Hz), 43.99, 21.04;
^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –124.68;
ESI-HRMS calcd for [$C_{17}H_{14}FNOS+Na^+$]: 322.0672, found 322.0677;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3407, 3059, 2914, 2854, 2361, 2336, 1693, 1629, 1582, 1483, 1449, 1351, 1286, 1234, 1164, 1094, 1029, 965, 939, 850, 795, 748, 692, 670, 601, 532, 450, 430.



2h

***S*-Phenyl 3-(5-methyl-1*H*-indol-3-yl)propanethioate (2h)**

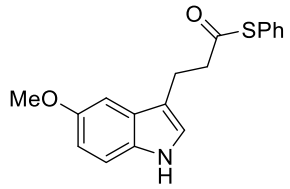
Result: white solid, m.p. 46 – 48 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.45 – 7.36 (m, 6H), 7.27 – 7.24 (m, 1H), 7.07 – 7.02 (m, 1H), 7.01 – 6.96 (m, 1H), 3.20 – 3.13 (m, 2H), 3.09 – 3.02 (m, 2H), 2.48 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.27, 134.57, 134.49, 129.32, 129.14, 128.65, 127.81, 127.29, 123.71, 121.79, 118.30, 113.86, 110.82, 44.31, 21.49, 21.18;

ESI-HRMS calcd for [$C_{18}H_{17}NOS+Na^+$]: 318.0923, found 318.0915;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3409, 3013, 2915, 2857, 2362, 2336, 1696, 1583, 1479, 1439, 1324, 1266, 1229, 1164, 1094, 1066, 1039, 965, 920, 870, 794, 749, 692, 595, 530, 426.



2i

***S*-Phenyl 3-(5-methoxy-1*H*-indol-3-yl)propanethioate (2i)**

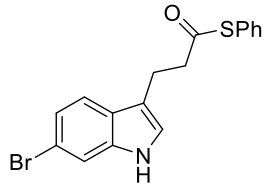
Result: white solid, m.p. 61 – 66 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.92 (s, 1H), 7.41 (m, 5H), 7.27 – 7.21 (m, 1H), 7.07 – 6.95 (m, 2H), 6.97 – 6.85 (m, 1H), 3.91 – 3.85 (m, 3H), 3.21 – 3.12 (m, 2H), 3.11 – 3.03 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.33, 153.98, 134.47, 131.37, 129.35, 129.16, 127.75, 127.44, 122.46, 113.99, 112.27, 111.92, 100.48, 55.91, 44.14, 21.16;

ESI-HRMS calcd for [$C_{18}H_{17}NO_2S+Na^+$]: 334.0872, found 334.0881;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3408, 3057, 2995, 2939, 2907, 2831, 2362, 2336, 1696, 1624, 1583, 1483, 1444, 1294, 1256, 1214, 1170, 1032, 965, 923, 832, 796, 749, 693, 669, 620, 531, 431.



2j

***S*-Phenyl 3-(6-bromo-1*H*-indol-3-yl)propanethioate (2j)**

Result: white solid, m.p. 95 – 98 ℃;

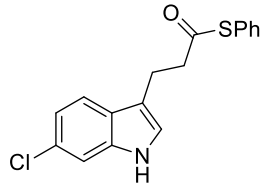
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.10 (s, 1H), 7.50 – 7.32 (m, 7H), 7.28 – 7.20 (m, 1H), 6.96 (s, 1H), 3.15 (t, J = 7.2 Hz, 2H), 3.09 – 2.98 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.31, 136.98, 134.43, 129.40, 129.17, 127.58, 125.97, 122.62, 122.31, 119.86, 115.59, 114.41, 114.10, 44.04, 20.93;

ESI-HRMS calcd for [$C_{17}H_{14}{}^{78.9183}BrNOS+Na^+$]: 381.9872, found 381.9880;

ESI-HRMS calcd for [$C_{17}H_{14}{}^{80.9163}BrNOS+Na^+$]: 383.9851, found 383.9858;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3417, 3059, 2911, 2361, 2335, 1694, 1614, 1547, 1475, 1448, 1405, 1333, 1268, 1231, 1176, 1096, 1041, 966, 894, 849, 803, 750, 691, 577, 530, 488, 426.



2k

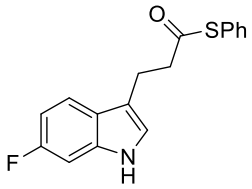
***S*-Phenyl 3-(6-chloro-1*H*-indol-3-yl)propanethioate (2k)**

Result: white solid, m.p. 94 – 97 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.49 (d, J = 8.4 Hz, 1H), 7.45 – 7.35 (m, 5H), 7.35 – 7.29 (m, 1H), 7.15 – 7.08 (m, 1H), 7.03 – 6.91 (m, 1H), 3.20 – 3.11 (m, 2H), 3.09 – 3.00 (m, 2H);

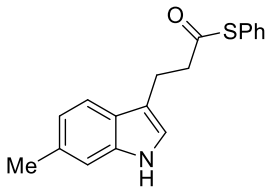
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.15, 136.55, 134.48, 129.46, 129.22, 127.98, 127.61, 125.70, 122.37, 120.12, 119.52, 114.37, 111.14, 44.07, 20.99;

ESI-HRMS calcd for [$C_{17}H_{14}{}^{34.9689}ClNOS+Na^+$]: 338.0377, found 338.0369;
ESI-HRMS calcd for [$C_{17}H_{14}{}^{36.9659}ClNOS+Na^+$]: 340.0347, found 340.0337;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3399, 3061, 2912, 2855, 2361, 2335, 1692, 1618, 1579, 1549, 1476, 1447, 1405, 1334, 1265, 1231, 1176, 1097, 1064, 1038, 966, 906, 848, 804, 748, 691, 584, 533, 487, 474, 429.



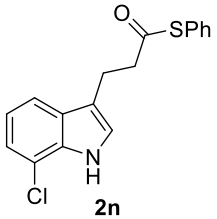
2l

***S*-Phenyl 3-(6-fluoro-1*H*-indol-3-yl)propanethioate (2l)**
Result: white solid, m.p. 100 – 102 ℃;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.53 – 7.46 (m, 1H), 7.44 – 7.40 (m, 5H), 7.07 – 7.01 (m, 1H), 7.01 – 6.96 (m, 1H), 6.65 – 6.86 (m, 1H), 3.16 (t, J=7.6, 2H), 3.09 – 3.00 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.16, 160.05 (*J* = 236.3 Hz), 136.14 (*J* = 12.4 Hz), 134.46, 129.39, 129.18, 127.66, 123.70, 121.84 (*J* = 3.1 Hz), 119.38 (*J* = 10.1 Hz), 114.50, 108.18 (*J* = 24.3 Hz), 97.46 (*J* = 25.9 Hz), 44.10, 21.05;
^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –121.16;
ESI-HRMS calcd for [$C_{17}H_{14}FNOS+Na^+$]: 322.0672, found 322.0671;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3731, 3412, 3009, 2362, 2336, 1695, 1628, 1557, 1498, 1454, 1410, 1340, 1308, 1267, 1139, 1040, 955, 837, 803, 752, 690, 597, 482.



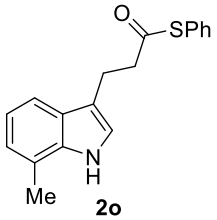
2m

***S*-Phenyl 3-(6-methyl-1*H*-indol-3-yl)propanethioate (2m)**
Result: white solid, m.p. 74 – 77 ℃;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.45 – 7.37 (m, 5H), 7.18 – 7.14 (s, 1H), 7.01 – 6.96 (m, 1H), 6.96 – 6.92 (m, 1H), 3.21 – 3.13 (m, 2H), 3.09 – 3.02 (m, 2H), 2.48 (s, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.25, 136.71, 134.47, 131.92, 129.31, 129.14, 127.80, 124.92, 121.16, 120.96, 118.29, 114.19, 111.11, 44.27, 21.69, 21.22;
ESI-HRMS calcd for [$C_{18}H_{17}NOS+Na^+$]: 318.0923, found 318.0922;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3407, 3012, 2916, 2858, 2362, 2336, 1696, 1628, 1551, 1447, 1403, 1339, 1267, 1178, 1157, 1069, 1037, 966, 926, 800, 750, 691, 662, 653, 591, 530, 478, 430.



2n

***S*-Phenyl 3-(7-chloro-1*H*-indol-3-yl)propanethioate (2n)**
Result: white solid, m.p. 153 – 155 ℃;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.35 (m, 5H), 7.21 (d, *J* = 7.6 Hz, 1H), 7.12 – 7.03 (m, 2H), 3.21 – 3.13 (m, 2H), 3.09 – 3.01 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.05, 134.46, 133.49, 129.39, 129.17, 128.55, 127.62, 122.33, 121.47, 120.21, 117.33, 116.67, 115.50, 44.07, 21.13;
ESI-HRMS calcd for [$C_{17}H_{14}{}^{34.9689}ClNOS+Na^+$]: 338.0377, found 338.0374;
ESI-HRMS calcd for [$C_{17}H_{14}{}^{36.9659}ClNOS+Na^+$]: 340.0347, found 340.0344;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3387, 3067, 2912, 2362, 2336, 1718, 1625, 1559, 1483, 1441, 1408, 1330, 1268, 1194, 1139, 1105, 1086, 1045, 964, 898, 855, 809, 753, 695, 633, 587, 548.



2o

***S*-Phenyl 3-(7-methyl-1*H*-indol-3-yl)propanethioate (2o)**

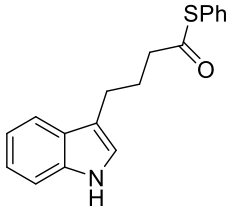
Result: yellow solid, m.p. 161 – 166 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.44 – 7.38 (m, 5H), 7.08 (t, *J* = 7.6 Hz, 1H), 7.05 – 7.00 (m, 2H), 3.23 – 3.16 (m, 2H), 3.11 – 3.03 (m, 2H), 2.49 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.21, 135.83, 134.48, 129.31, 129.14, 127.79, 126.59, 122.64, 121.36, 120.34, 119.65, 116.37, 114.87, 44.28, 21.27, 16.55;

ESI-HRMS calcd for [$C_{18}H_{17}NOS+Na^+$]: 318.0923, found 318.0930;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3407, 3053, 2971, 2911, 2850, 2362, 2336, 1709, 1613, 1475, 1444, 1405, 1375, 1333, 1263, 1228, 1165, 1122, 1097, 1055, 1027, 1000, 963, 911, 862, 808, 749, 696, 635, 591, 542, 495, 448.



2p

***S*-Phenyl 4-(1*H*-indol-3-yl)butanethioate (2p)**

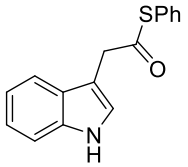
Result: white solid, m.p. 88 – 92 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.43 (s, 5H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.13 (m, 1H), 7.01 – 6.97 (m, 1H), 2.88 (t, *J* = 7.2 Hz, 2H), 2.76 (t, *J* = 7.2 Hz, 2H), 2.22 – 2.12 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.64, 136.29, 134.46, 129.29, 129.13, 127.80, 127.29, 121.91, 121.59, 119.18, 118.81, 115.16, 111.09, 43.15, 25.87, 24.25;

ESI-HRMS calcd for [$C_{18}H_{17}NOS+Na^+$]: 318.0923, found 318.0916;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3410, 3055, 2931, 2850, 2360, 2334, 1695, 1620, 1582, 1479, 1450, 1343, 1229, 1167, 1087, 987, 744, 690, 586, 527, 481, 456, 425.



2q

***S*-Phenyl 2-(1*H*-indol-3-yl)ethanethioate (2q)**

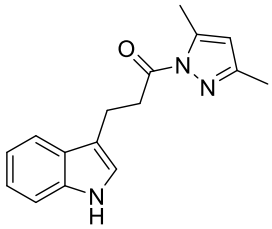
Result: white solid, m.p. 83 – 85 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.34 (m, 6H), 7.25 – 7.15 (m, 3H), 4.09 (d, *J* = 0.8 Hz, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 196.44, 136.07, 134.44, 129.22, 129.07, 128.11, 127.23, 123.98, 122.40, 119.95, 118.88, 111.28, 107.78, 40.23;

ESI-HRMS calcd for [$C_{16}H_{13}NOS+Na^+$]: 290.0610, found 290.0602;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3407, 3056, 2899, 2361, 1689, 1479, 1457, 1346, 1229, 1185, 1095, 1066, 1003, 744, 712, 690, 612, 501,425.



2r

1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-(1*H*-indol-3-yl)propan-1-one (2r)

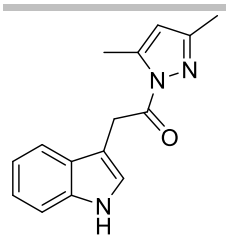
Result: white solid, m.p. 98 – 103 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (s, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.23 – 7.10 (m, 2H), 7.09 – 7.01 (m, 1H), 5.96 (s, 1H), 3.53 (t, *J* = 7.6 Hz, 2H), 3.23 (t, *J* = 7.6 Hz, 2H), 2.56 (s, 3H), 2.24 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 173.63, 151.83, 143.98, 136.25, 127.31, 121.94, 121.56, 119.23, 118.84, 115.11, 111.02, 35.95, 19.98, 14.55, 13.77;

ESI-HRMS calcd for [$C_{16}H_{17}N_3O+Na^+$]: 290.1264, found 290.1259;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3409, 3054, 2925, 2858, 2361, 1722, 1583, 1454, 1412, 1381, 1329, 1226, 1172, 1142, 1096, 1032, 965, 809, 743, 701, 585, 480, 425.



2s

1-(3,5-Dimethyl-1H-pyrazol-1-yl)-2-(1H-indol-3-yl)ethan-1-one (2s)

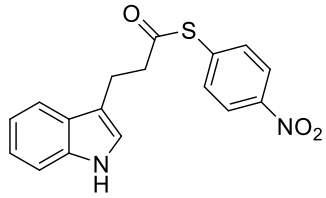
Result: white solid, m.p. 123 – 126 ℃;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.12 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.17 – 7.11 (m, 1H), 5.99 (s, 1H), 4.61 (s, 2H), 2.54 (s, 3H), 2.31 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.94, 151.87, 144.34, 136.01, 127.58, 123.70, 122.06, 119.62, 119.09, 111.21, 111.10, 108.36, 31.84, 14.55, 13.85;

ESI-HRMS calcd for [$C_{15}H_{15}N_3O$+Na^+]: 276.1107, found 276.1104;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3404, 3055, 2984, 2927, 2362, 1720, 1620, 1584, 1456, 1410, 1379, 1341, 1251, 1226, 1171, 1095, 964, 805, 743, 636, 591, 511, 424.



2t

***S*-(4-Nitrophenyl) 3-(1*H*-indol-3-yl)propanethioate (2t)**

Result: yellow solid, m.p. 95 – 98 ℃;

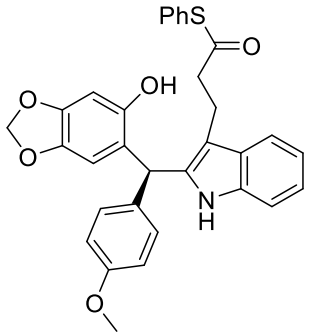
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 – 8.18 (m, 2H), 8.03 (s, 1H), 7.61 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.41 – 7.35 (m, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.13 (m, 1H), 7.06 – 7.01 (m, 1H), 3.22 (t, *J* = 7.2 Hz, 2H), 3.17 – 3.08 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 194.94, 148.00, 136.27, 136.23, 134.64, 126.94, 123.86, 122.23, 121.71, 119.50, 118.54, 113.88, 111.24, 44.74, 21.09;

ESI-HRMS calcd for [$C_{17}H_{14}N_2O_3S$+Na^+]: 349.0617, found 349.0622;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3413, 3098, 3059, 2913, 2852, 2362, 1706, 1598, 1517, 1455, 1422, 1342, 1276, 1178, 1099, 1035, 962, 850, 811, 743, 688, 587, 502, 426.

11. Spectral Characterization Data for the Reaction Products



3aa

***S*-Phenyl (*S*)-3-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3aa)**

0.1 mmol (**2a**) scale reaction:

Result: white solid, 53.2 mg, 99% yield, 93% ee, m.p. 69 – 71 ℃; $[\alpha]_D^{21}$ = –45.8 (*c* = 0.88 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 10.92 min, $t_r(_{major})$ = 13.77 min;

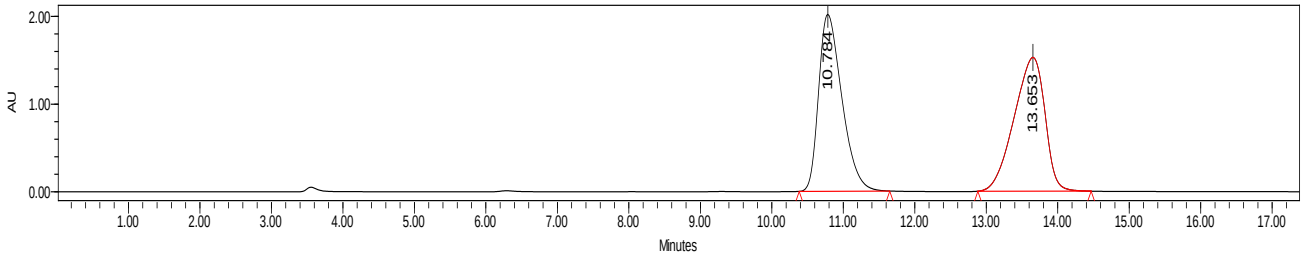
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.60 – 7.53 (m, 1H), 7.43 – 7.36 (m, 3H), 7.35 – 7.29 (m, 2H), 7.28 – 7.24 (m, 1H), 7.21 – 7.10 (m, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.43 – 6.38 (m, 2H), 5.93 – 5.85 (m, 3H), 5.15 (s, 1H), 3.80 (s, 3H), 3.15 – 3.01 (m, 2H), 2.97 – 2.81 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.45, 158.52, 148.15, 147.03, 141.67, 135.58, 135.20, 134.43, 132.96, 129.50, 129.35, 129.11, 128.20, 127.53, 121.57, 120.60, 119.51, 118.25, 114.19, 110.96, 110.53, 109.13, 101.14, 99.28, 55.24, 43.70, 41.71, 20.06;

ESI-HRMS calcd for [$C_{32}H_{27}NO_5S$+Na^+]: 560.1502, found 560.1511;

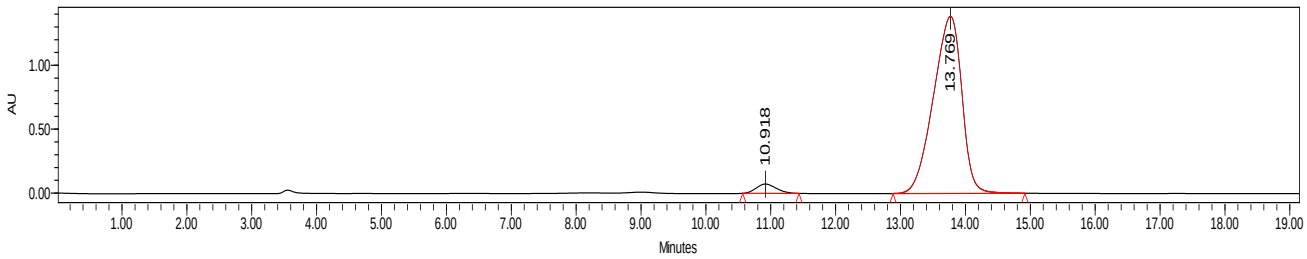
IR (film): $\tilde{\nu}$ (cm^{-1}) 3784, 3401, 3055, 2901, 2836, 2770, 2393, 2284, 1686, 1610, 1584, 1506, 1483, 1437, 1300, 1242, 1170, 1035, 934, 874, 846, 792, 740, 695, 596, 520, 435.

Racemic **3aa**:

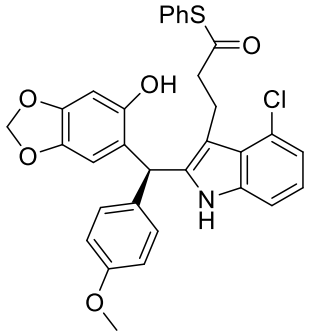


	Retention Time	Area	% Area
1	10.784	45562245	49.94
2	13.653	45670037	50.06

Chiral **3aa:**

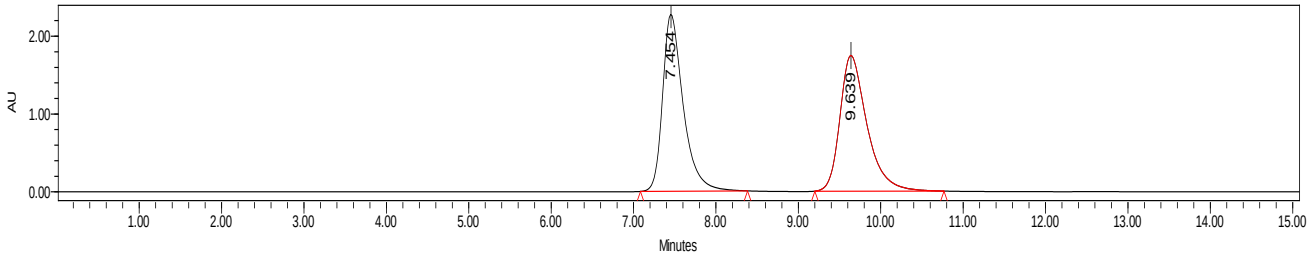


	Retention Time	Area	% Area
1	10.918	1558440	3.57
2	13.769	42137290	96.43



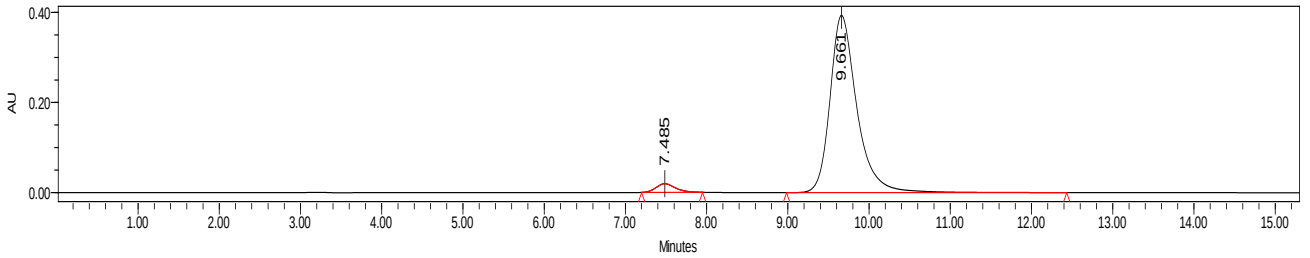
3ab

***S*-Phenyl (*S*)-3-{4-chloro-2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3ab)**
0.1 mmol (**2ab**) scale reaction:
Result: yellow oil, 54.3 mg, 95% yield, 93% ee; $[\alpha]_D^{20}$ = –38.3 (*c* = 0.95 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 7.49 min, $t_r(_{major})$ = 9.66 min;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.47 – 7.32 (m, 5H), 7.16 – 7.11 (m, 1H), 7.10 – 7.06 (m, 1H), 7.05 – 7.01 (m, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.40 (s, 1H), 6.37 (s, 1H), 5.94 (s, 1H), 5.89 (d, *J* = 6.0 Hz, 2H), 5.30 (s, 1H), 3.79 (s, 3H), 3.35 – 3.15 (m, 2H), 3.05 – 2.95 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 199.00, 158.57, 148.18, 147.14, 141.70, 137.41, 136.50, 134.44, 132.74, 129.48, 129.33, 129.12, 127.64, 125.36, 125.09, 121.94, 120.62, 120.18, 114.23, 110.64, 109.70, 109.12, 101.19, 99.35, 55.26, 45.52, 41.35, 20.52;
ESI-HRMS calcd for $[C_{32}H_{26}{}^{34.9689}ClNO_5S+Na^+]$: 594.1112, found 594.1108;
ESI-HRMS calcd for $[C_{32}H_{26}{}^{36.9659}ClNO_5S+Na^+]$: 596.1083, found 596.1089;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3390, 3059, 3001, 2933, 2900, 2837, 1681, 1611, 1582, 1506, 1482, 1436, 1300, 1242, 1170, 1111, 1034, 937, 909, 874, 854, 834, 773, 733, 696, 602, 574, 531, 455.
Racemic **3ab**:

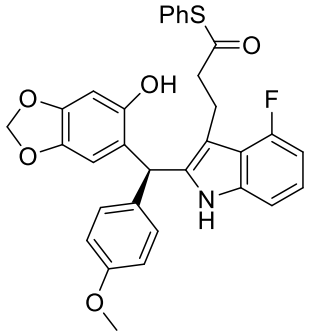


	Retention Time	Area	% Area
1	7.454	39452462	49.86
2	9.639	39667962	50.14

Chiral **3ab:**



	Retention Time	Area	% Area
1	7.485	319510	3.41
2	9.661	9043741	96.59



3ac

***S*-Phenyl (*S*)-3-{4-fluoro-2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3ac)**

0.1 mmol (**2c**) scale reaction:

Result: yellow oil, 50.6 mg, 91% yield, 91% ee; $[\alpha]_D^{19}$ = –54.7 (*c* = 0.65 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 7.49 min, $t_r(_{major})$ = 10.36 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 1H), 7.43 – 7.36 (m, 3H), 7.36 – 7.31 (m, 2H), 7.08 – 7.01 (m, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.80 – 6.74 (m, 1H), 6.41 (s, 1H), 6.37 (s, 1H), 5.91 – 5.89 (m, 2H), 5.88 – 5.86 (m, 1H), 5.25 (s, 1H), 3.79 (s, 3H), 3.13 – 3.06 (m, 2H), 3.05 – 2.94 (m, 2H);

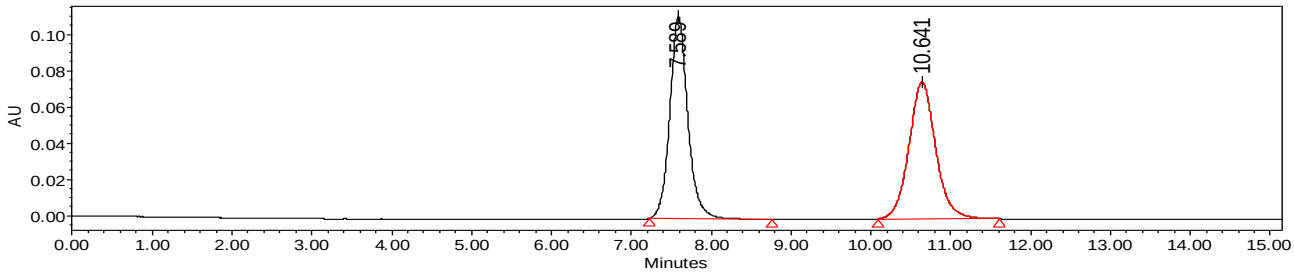
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 199.03, 158.57, 156.61 (*J* = 243.6 Hz), 148.29, 147.17, 141.70, 137.86 (*J* = 12.0 Hz), 135.84, 134.44, 132.88, 129.42, 129.33, 129.11, 127.59, 121.94 (*J* = 7.8 Hz), 120.21, 116.93 (*J* = 19.8 Hz), 114.22, 109.15 (*J* = 2.8 Hz), 109.06, 107.09 (*J* = 3.6 Hz), 104.73 (*J* = 19.6 Hz), 101.18, 99.40, 55.25, 44.42, 41.35, 20.75;

^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –124.30;

ESI-HRMS calcd for $[C_{32}H_{26}FNO_5S+Na^+]$: 578.1408, found 578.1413;

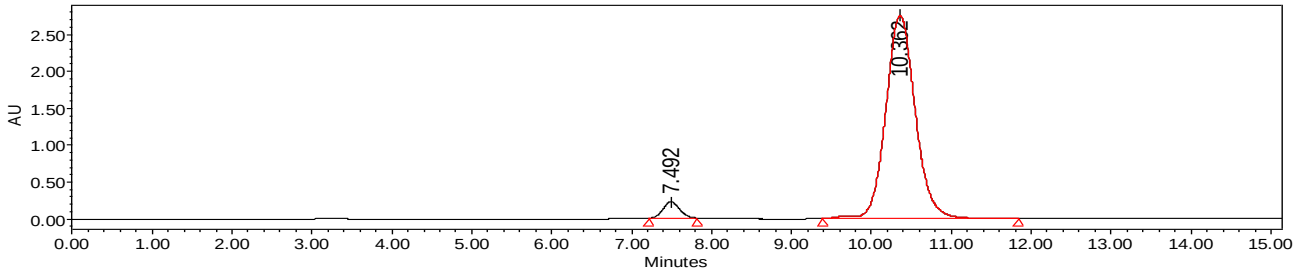
IR (film): $\tilde{\nu}$ (cm^{-1}) 3396, 3060, 3002, 2901, 2837, 1686, 1630, 1611, 1583, 1505, 1483, 1439, 1406, 1336, 1299, 1230, 1172, 1037, 936, 910, 857, 775, 735, 696, 604, 563, 530, 485.

Racemic **3ac**:

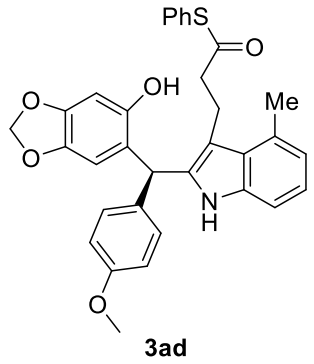


	Retention Time	Area	% Area
1	7.589	1751396	49.92
2	10.641	1756855	50.08

Chiral **3ac:**

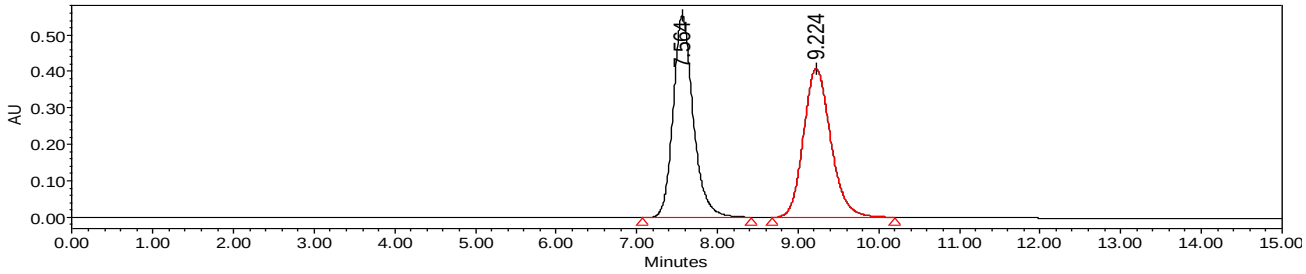


	Retention Time	Area	% Area
1	7.492	3216540	4.35
2	10.362	70754103	95.65



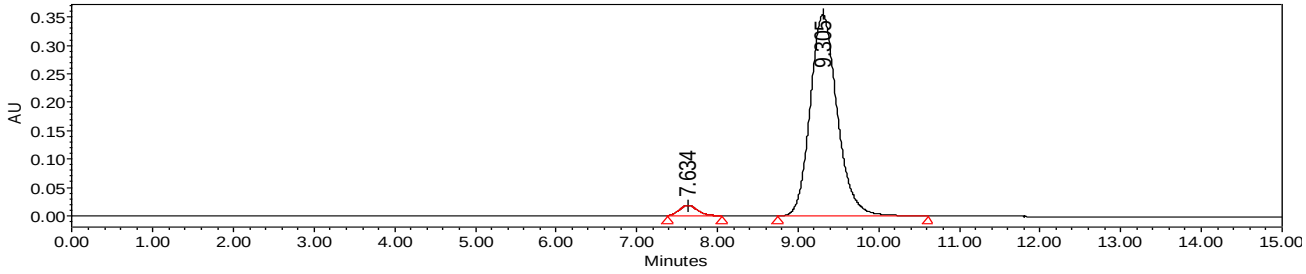
3ad

***S*-Phenyl (*S*)-3-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-4-methyl-1*H*-indol-3-yl}propanethioate (3ad)**
0.1 mmol (**2d**) scale reaction:
Result: yellow oil, 54.6 mg, 99% yield, 93% ee; $[\alpha]_D^{20}$ = –37.9 (*c* = 0.69 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_{r(minor)}$ = 7.63 min, $t_{r(major)}$ = 9.31 min;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.43 – 7.35 (m, 5H), 7.13 – 7.08 (m, 1H), 7.07 – 7.01 (m, 3H), 6.89 – 6.81 (m, 3H), 6.40 (d, *J* = 4.8 Hz, 2H), 5.91 – 5.89 (m, 2H), 5.89 – 5.87 (m, 1H), 5.10 (s, 1H), 3.80 (s, 3H), 3.27 – 3.18 (m, 2H), 2.84 – 2.77 (m, 2H), 2.73 (s, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.05, 158.56, 148.07, 147.02, 141.71, 135.79, 135.47, 134.42, 132.96, 129.90, 129.56, 129.38, 129.15, 127.56, 126.61, 121.53, 121.50, 120.69, 114.22, 111.19, 109.17, 108.91, 101.16, 99.26, 55.26, 45.76, 41.46, 21.49, 20.13;
ESI-HRMS calcd for [$C_{33}H_{29}NO_5S$+Na^+]: 574.1659, found 574.1651;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3402, 3053, 2953, 2902, 2837, 1689, 1611, 1582, 1505, 1484, 1438, 1331, 1298, 1241, 1169, 1035, 993, 935, 855, 740, 696, 597, 535, 458.
Racemic **3ad**:

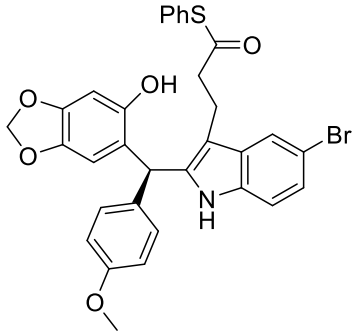


	Retention Time	Area	% Area
1	7.564	9569609	50.07
2	9.224	9543602	49.93

Chiral **3ad:**

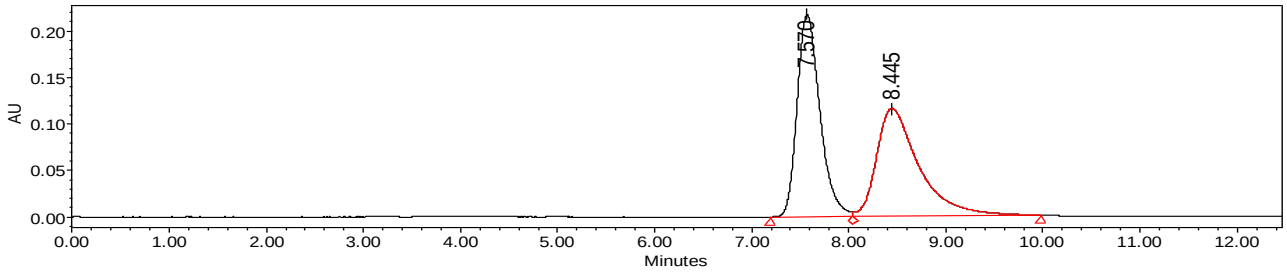


	Retention Time	Area	% Area
1	7.634	292136	3.40
2	9.305	8299774	96.60



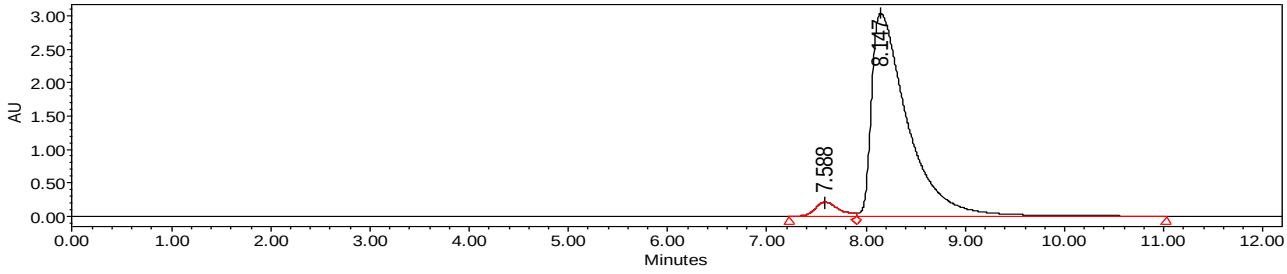
3ae

***S*-Phenyl (*S*)-3-{5-bromo-2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3ae)**
0.1 mmol (**2e**) scale reaction:
Result: white solid, 61.0 mg, 99% yield, 91% ee, m.p. 78 – 82 ℃; $[\alpha]_D^{20}$ = –55.7 (*c* = 0.63 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 7.59 min, $t_r(_{major})$ = 8.15 min;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.65 (s, 1H), 7.43 – 7.35 (m, 3H), 7.35 – 7.28 (m, 2H), 7.24 – 7.18 (m, 1H), 7.13 – 7.06 (m, 1H), 6.99 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.39 (d, J=8.2, 2H), 5.93 – 5.87 (m, 2H), 5.86 (s, 1H), 5.12 (s, 1H), 3.79 (s, 3H), 3.07 – 2.95 (m, 2H), 2.91 – 2.79 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.48, 158.62, 148.08, 147.17, 141.80, 137.23, 134.45, 133.73, 132.67, 130.03, 129.43, 129.18, 127.43, 124.33, 120.79, 120.32, 114.27, 112.82, 112.40, 110.21, 109.06, 101.22, 99.37, 55.27, 43.49, 41.69, 19.92;
ESI-HRMS calcd for $[C_{32}H_{26}{}^{78.9183}BrNO_5S+Na^+]$: 638.0607, found 638.0613;
ESI-HRMS calcd for $[C_{32}H_{26}{}^{80.9163}BrNO_5S+Na^+]$: 640.0587, found 640.0576;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3403, 3059, 3001, 2903, 2837, 1687, 1611, 1580, 1507, 1482, 1464, 1439, 1301, 1244, 1173, 1038, 934, 878, 796, 745, 695, 595, 529.
Racemic **3ae**:

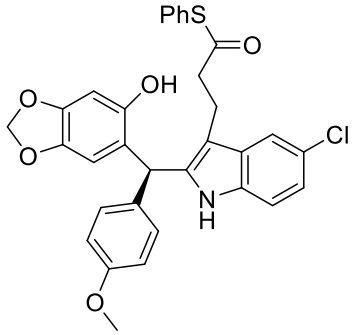


	Retention Time	Area	% Area
1	7.570	3547235	50.24
2	8.445	3513457	49.76

Chiral **3ae:**



	Retention Time	Area	% Area
1	7.588	3461052	4.34
2	8.147	76339566	95.66



3af

***S*-Phenyl (*S*)-3-{5-chloro-2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3af)**

0.1 mmol (**2f**) scale reaction:

Result: white solid, 55.4 mg, 97% yield, 92% ee, m.p. 162 – 166 °C; $[\alpha]_D^{20}$ = –60.0 (*c* = 0.59 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 7.48 min, $t_r(_{major})$ = 8.28 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.51 – 7.47 (m, 1H), 7.44 – 7.35 (m, 3H), 7.35 – 7.28 (m, 2H), 7.17 – 7.12 (m, 1H), 7.11 – 7.06 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.39 (d, *J* = 6.4 Hz, 2H), 5.91 – 5.87 (m, 2H), 5.86 (s, 1H), 5.13 (s, 1H), 3.79 (s, 3H), 3.06 – 2.95 (m, 2H), 2.92 – 2.78 (m, 2H);

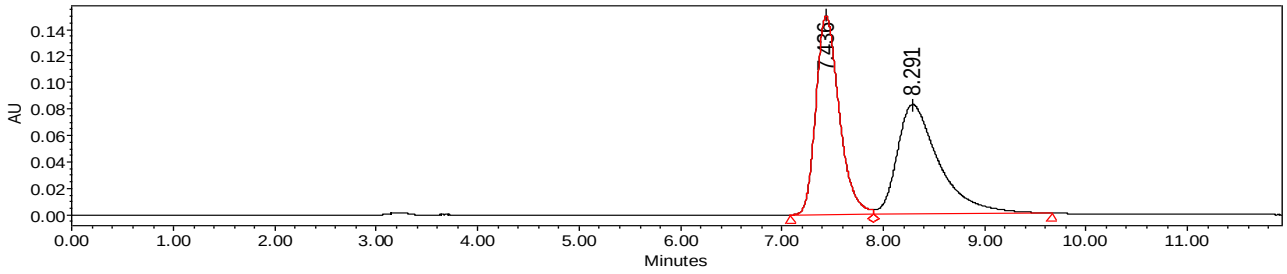
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.48, 158.61, 148.09, 147.16, 141.79, 137.39, 134.44, 133.46, 132.69, 129.43, 129.37, 129.17, 127.44, 125.26, 121.76, 120.34, 117.73, 114.26, 111.95, 110.29, 109.07, 101.21, 99.36, 55.26, 43.49, 41.72, 19.94;

ESI-HRMS calcd for $[C_{32}H_{26}{}^{34.9689}ClNO_5S+Na^+]$: 594.1112, found 594.1121;

ESI-HRMS calcd for $[C_{32}H_{26}{}^{36.9659}ClNO_5S+Na^+]$: 596.1083, found 596.1089;

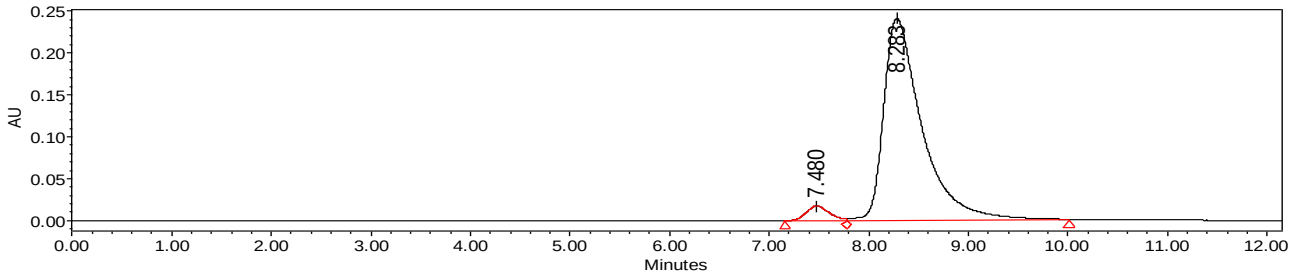
IR (film): $\tilde{\nu}$ (cm^{-1}) 3401, 3059, 3001, 2903, 2837, 1684, 1611, 1580, 1507, 1481, 1439, 1301, 1244, 1172, 1037, 934, 879, 857, 797, 743, 695, 601, 532, 457, 433.

Racemic **3af**:

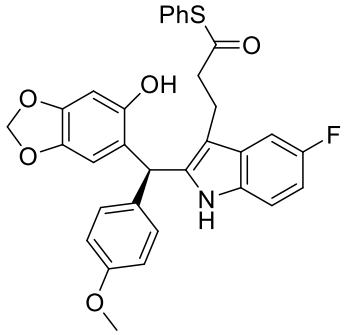


	Retention Time	Area	% Area
1	7.436	2405701	50.27
2	8.291	2379459	49.73

Chiral **3af:**



	Retention Time	Area	% Area
1	7.480	270446	4.05
2	8.283	6409325	95.95



3ag

***S*-Phenyl (*S*)-3-{5-fluoro-2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3ag)**

0.1 mmol (**2g**) scale reaction:

Result: white solid, 50.0 mg, 90% yield, 91% ee, m.p. 77 – 79 ℃; $[\alpha]_D^{20}$ = –40.8 (*c* = 0.78 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IB, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 9.42 min, $t_r(_{major})$ = 10.31 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.42 – 7.35 (m, 3H), 7.35 – 7.29 (m, 2H), 7.21 – 7.11 (m, 2H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.93 – 6.86 (m, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 4.0 Hz, 2H), 5.91 – 5.87 (m, 2H), 5.87 (s, 1H), 5.14 (s, 1H), 3.79 (s, 3H), 3.08 – 2.95 (m, 2H), 2.90 – 2.79 (m, 2H);

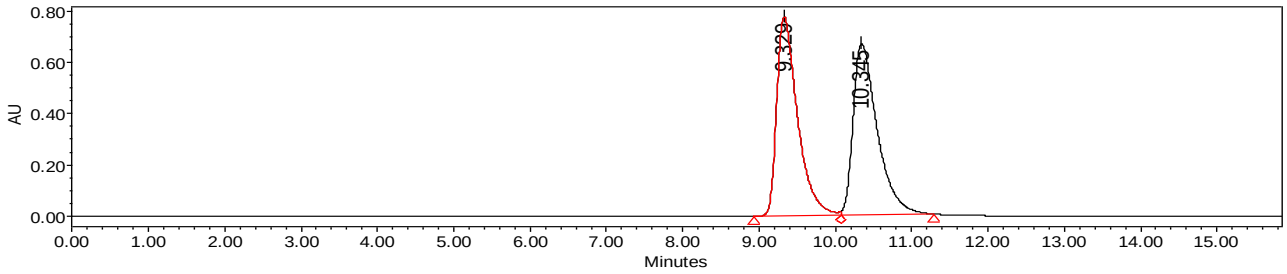
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.44, 158.59, 157.82 (*J* = 233.3 Hz), 148.10, 147.12, 141.75, 137.72, 134.42, 132.76, 131.62, 129.46, 129.42, 129.15, 128.65 (*J* = 9.5 Hz), 127.47, 120.41, 114.25, 111.55 (*J* = 9.6 Hz), 110.70 (*J* = 4.6 Hz), 109.70 (*J* = 26.0 Hz), 109.08, 103.25 (*J* = 23.4 Hz), 101.19, 99.32, 55.26, 43.43, 41.78, 20.04;

^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –124.28;

ESI-HRMS calcd for [$C_{32}H_{26}FNO_5S$+Na^+]: 578.1408, found 578.1407;

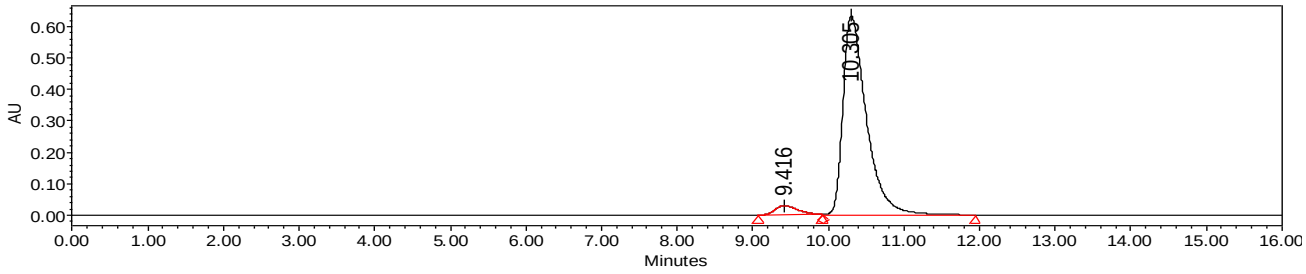
IR (film): $\tilde{\nu}$ (cm^{-1}) 3400, 3059, 3001, 2903, 2838, 1687, 1611, 1583, 1506, 1483, 1441, 1298, 1241, 1171, 1093, 1036, 934, 848, 795, 741, 696, 612, 537, 474.

Racemic **3ag**:

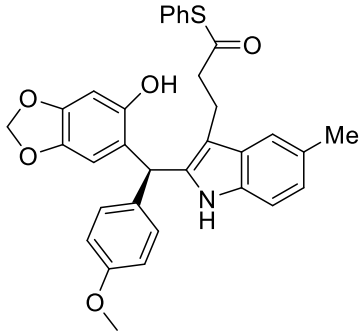


	Retention Time	Area	% Area
1	9.329	14724304	50.15
2	10.345	14638743	49.85

Chiral **3ag:**

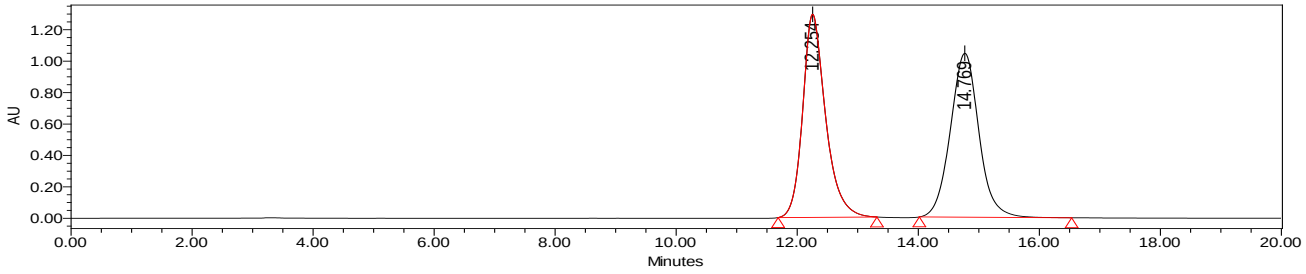


	Retention Time	Area	% Area
1	9.416	623978	4.36
2	10.305	13674067	95.64



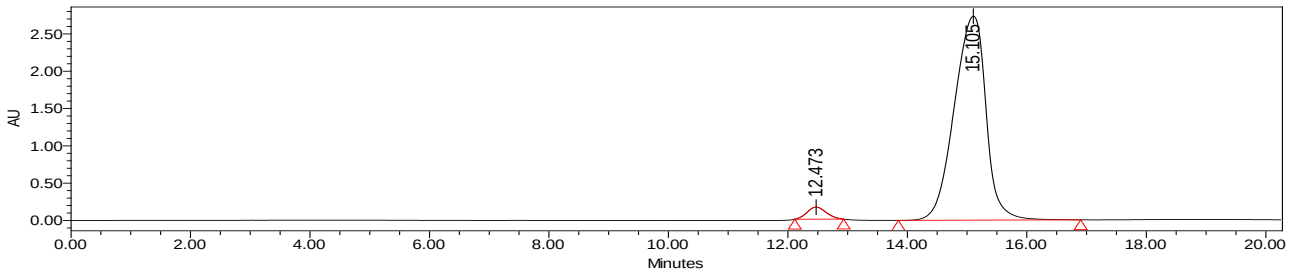
3ah

***S*-Phenyl (*S*)-3-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-5-methyl-1*H*-indol-3-yl}propanethioate (3ah)**
0.1 mmol (**2h**) scale reaction:
Result: yellow oil, 54.6 mg, 99% yield, 93% ee; $[\alpha]_D^{20}$ = –51.0 (*c* = 0.78 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, $t_{r(minor)}$ = 12.47 min, $t_{r(major)}$ = 15.11 min;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.42 – 7.37 (m, 3H), 7.36 – 7.30 (m, 3H), 7.18 – 7.13 (m, 1H), 7.06 – 7.01 (m, 2H), 7.01 – 6.97 (m, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.40 (d, *J* = 5.2 Hz, 2H), 5.91 – 5.87 (m, 2H), 5.86 (s, 1H), 5.09 (s, 1H), 3.80 (s, 3H), 3.10 – 3.00 (m, 2H), 2.95 – 2.80 (m, 2H), 2.48 (s, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.43, 158.54, 148.20, 147.04, 141.68, 135.62, 134.44, 133.52, 132.98, 129.51, 129.34, 129.11, 128.81, 128.45, 127.61, 123.14, 120.64, 117.94, 114.19, 110.67, 110.15, 109.12, 101.13, 99.30, 55.25, 43.72, 41.78, 21.51, 20.09;
ESI-HRMS calcd for [$C_{33}H_{29}NO_5S$+Na^+]: 574.1659, found 574.1656;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3406, 3007, 2909, 2362, 1690, 1611, 1583, 1506, 1482, 1439, 1304, 1244, 1171, 1037, 936, 909, 874, 796, 734, 693, 606, 534, 436.
Racemic **3ah**:

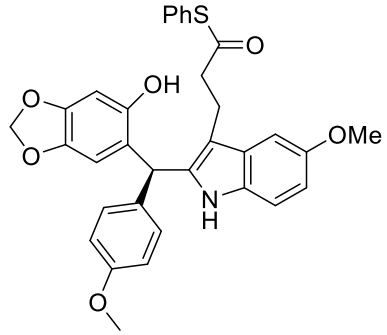


	Retention Time	Area	% Area
1	12.254	33989555	49.95
2	14.769	34063508	50.05

Chiral **3ah:**

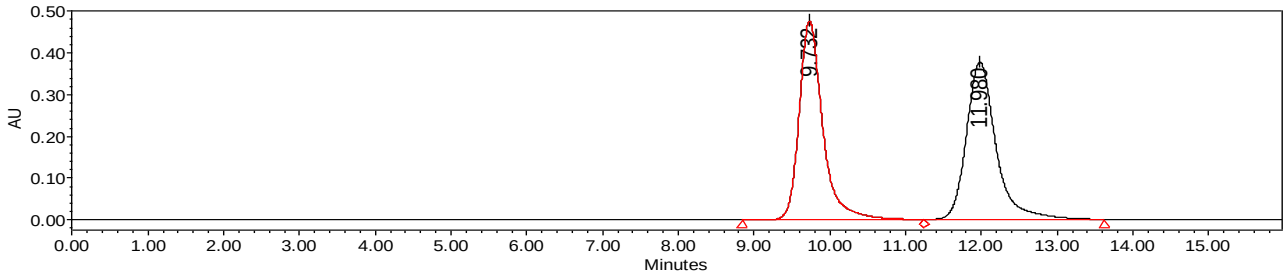


	Retention Time	Area	% Area
1	12.473	3613298	3.46
2	15.105	100906263	96.54



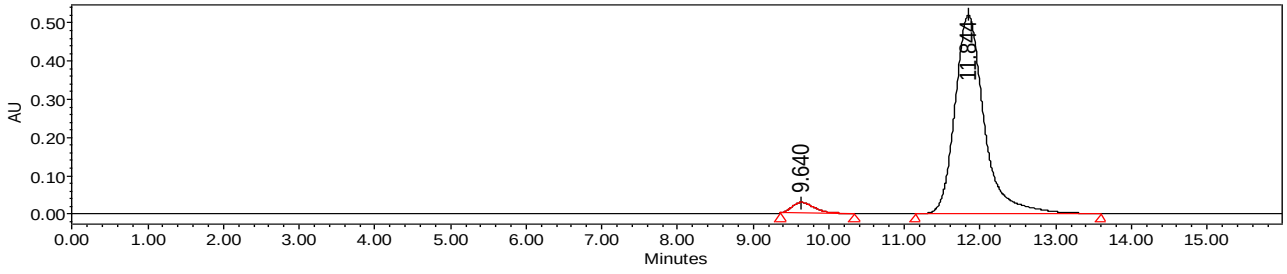
3ai

***S*-Phenyl (*S*)-3-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-5-methoxy-1*H*-indol-3-yl}propanethioate(3ai)**
0.1 mmol (**2i**) scale reaction:
Result: white solid, 52.8 mg, 93% yield, 92% ee, m.p. 77 – 79 ℃; $[\alpha]_D^{21}$ = –57.1 (*c* = 0.62 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 9.64 min, $t_r(_{major})$ = 11.84 min;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (s, 1H), 7.42 – 7.35 (m, 3H), 7.33 – 7.28 (m, 2H), 7.17 – 7.12 (m, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 7.00 – 6.95 (m, 1H), 6.87 – 6.79 (m, 3H), 6.40 (d, *J* = 4.4 Hz, 2H), 5.90 – 5.87 (m, 2H), 5.85 (s, 1H), 5.12 (s, 1H), 3.85 (s, 3H), 3.79 (s, 3H), 3.09 – 2.99 (m, 2H), 2.91 – 2.79 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.43, 158.56, 154.05, 148.16, 147.05, 141.69, 136.46, 134.43, 132.94, 130.32, 129.52, 129.35, 129.10,128.68, 127.59, 120.62, 114.21, 111.68, 111.42, 110.40, 109.13, 101.15, 100.46, 99.28, 55.98, 55.25, 43.56, 41.84, 20.14;
ESI-HRMS calcd for [$C_{33}H_{29}NO_6S$+Na^+]: 590.1608, found 590.1604;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3398, 3057, 2997, 2902, 2834, 1694, 1615, 1584, 1506, 1482, 1439, 1300, 1243, 1215, 1171, 1101, 1034, 936, 833, 795, 739, 696, 625, 587, 533, 441.
Racemic **3ai**:

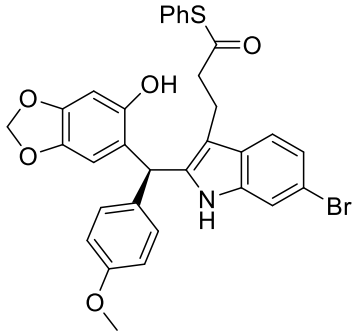


	Retention Time	Area	% Area
1	9.732	10278316	50.11
2	11.980	10234026	49.89

Chiral **3ai:**



	Retention Time	Area	% Area
1	9.640	578134	3.99
2	11.844	13920859	96.01



3aj

***S*-Phenyl (*S*)-3-{6-bromo-2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3aj)**

0.1 mmol (**2j**) scale reaction:

Result: white solid, 59.2 mg, 96% yield, 91% ee, m.p. 74 – 78 ℃; $[\alpha]_D^{21}$ = –40.0 (*c* = 0.81 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 15.74 min, $t_r(_{major})$ = 18.34 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.42 – 7.34 (m, 5H), 7.32 – 7.27 (m, 2H), 7.23 – 7.17 (m, 1H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.39 (s, 2H), 5.90 – 5.87 (m, 2H), 5.84 (s, 1H), 5.12 (s, 1H), 3.79 (s, 3H), 3.08 – 2.98 (m, 2H), 2.89 – 2.79 (m, 2H);

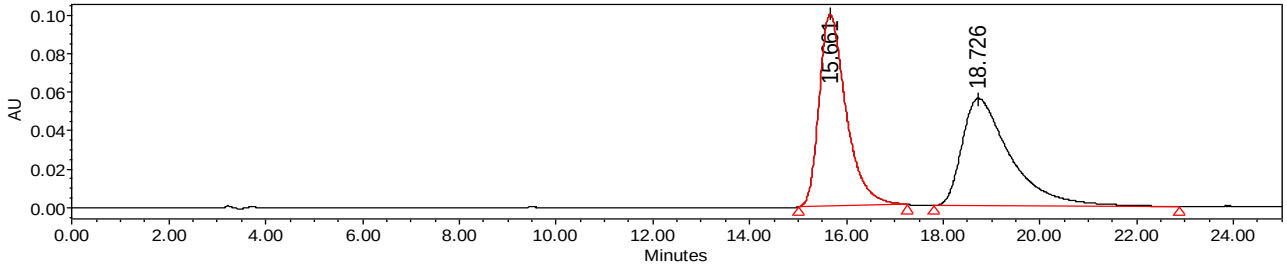
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.36, 158.59, 148.04, 147.14, 141.78, 136.48, 135.90, 134.40, 132.68, 129.41, 129.15, 127.42, 127.11, 122.73, 120.35, 119.50, 114.98, 114.26, 113.89, 110.65, 109.08, 101.21, 99.33, 55.27, 43.58, 41.73, 19.95;

ESI-HRMS calcd for $[C_{32}H_{26}{}^{78.9183}BrNO_5S+Na^+]$: 638.0607, found 638.0611;

ESI-HRMS calcd for $[C_{32}H_{26}{}^{80.9163}BrNO_5S+Na^+]$: 640.0587, found 640.0584;

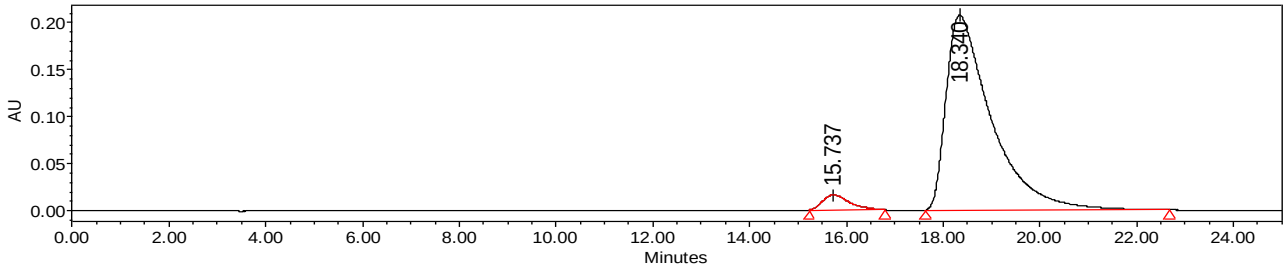
IR (film): $\tilde{\nu}$ (cm^{-1}) 3398, 3057, 3001, 2900, 1683, 1611, 1583, 1506, 1482, 1438, 1331, 1295, 1242, 1170, 1035, 934, 848, 799, 738, 695, 618, 523, 432.

Racemic **3aj**:

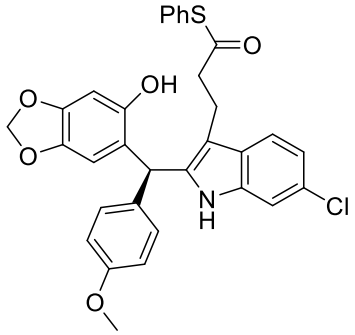


	Retention Time	Area	% Area
1	15.661	3867058	49.94
2	18.726	3876338	50.06

Chiral **3aj:**

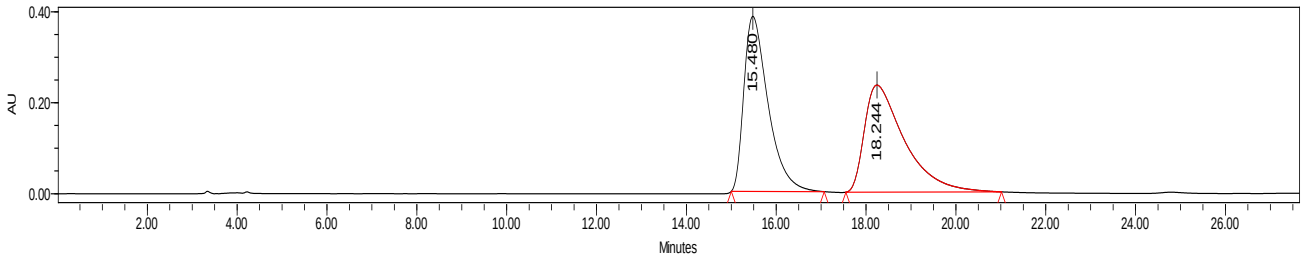


	Retention Time	Area	% Area
1	15.737	617660	4.37
2	18.340	13505363	95.63



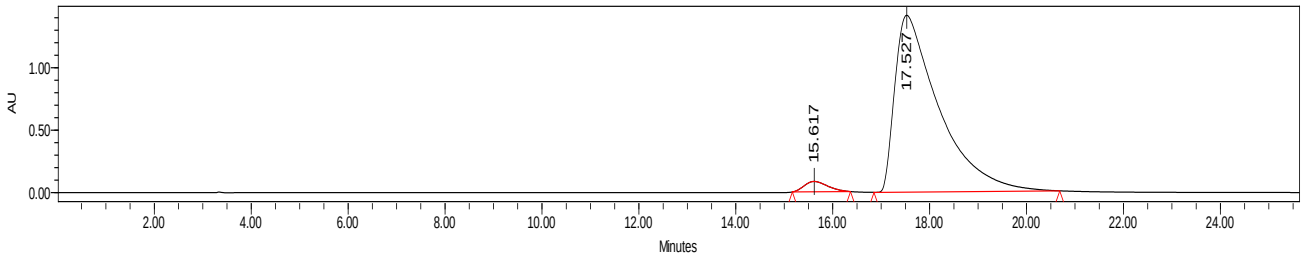
3ak

***S*-Phenyl (*S*)-3-{6-chloro-2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3ak)**
0.1 mmol (**2k**) scale reaction:
Result: white solid, 56.6 mg, 99% yield, 94% ee, m.p. 68 – 70 °C; $[\alpha]_D^{20}$ = –47.7 (*c* = 0.80 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 15.62 min, $t_r(_{major})$ = 17.53 min;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.45 – 7.41 (m, 1H), 7.40 – 7.34 (m, 3H), 7.32 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 7.10 – 7.05 (m, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.39 (d, *J* = 4.0 Hz, 2H), 5.90 – 5.86 (m, 2H), 5.85 (s, 1H), 5.15 (s, 1H), 3.79 (s, 3H), 3.08 – 2.98 (m, 2H), 2.88 – 2.80 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.38, 158.58, 148.04, 147.11, 141.76, 136.51, 135.47, 134.40, 132.73, 129.41, 129.14, 127.42, 127.39, 126.80, 120.39, 120.15, 119.11, 114.25, 110.92, 110.59, 109.09, 101.20, 99.31, 55.26, 43.60, 41.74, 19.98;
ESI-HRMS calcd for $[C_{32}H_{26}{}^{34.9689}ClNO_5S+Na^+]$: 594.1112, found 594.1102;
ESI-HRMS calcd for $[C_{32}H_{26}{}^{36.9659}ClNO_5S+Na^+]$: 596.1083, found 596.1074;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3394, 3057, 3002, 2900, 2837, 2770, 1681, 1611, 1583, 1505, 1482, 1458, 1437, 1333, 1295, 1241, 1169, 1034, 931, 847, 800, 733, 694, 630, 522, 454, 433.
Racemic **3ak**:

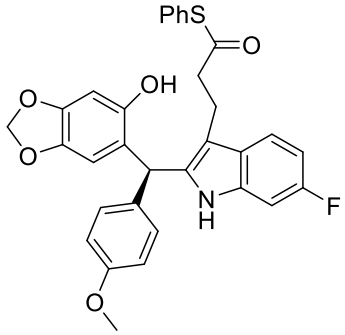


	Retention Time	Area	% Area
1	15.480	14402944	49.74
2	18.244	14553879	50.26

Chiral **3ak:**

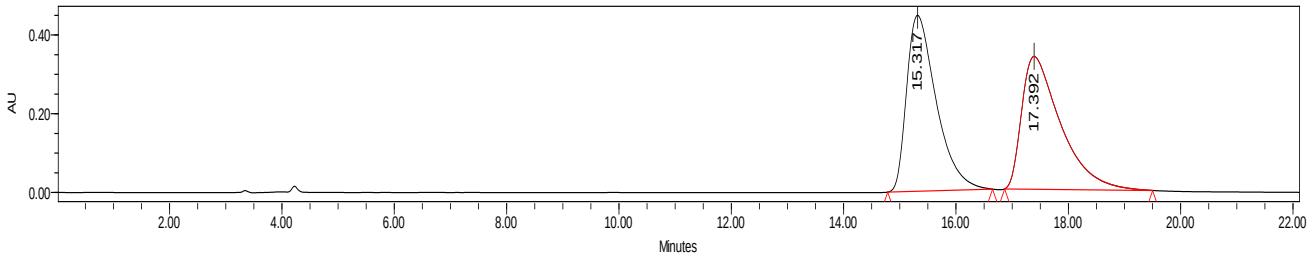


	Retention Time	Area	% Area
1	15.617	2790389	3.02
2	17.527	89481467	96.98



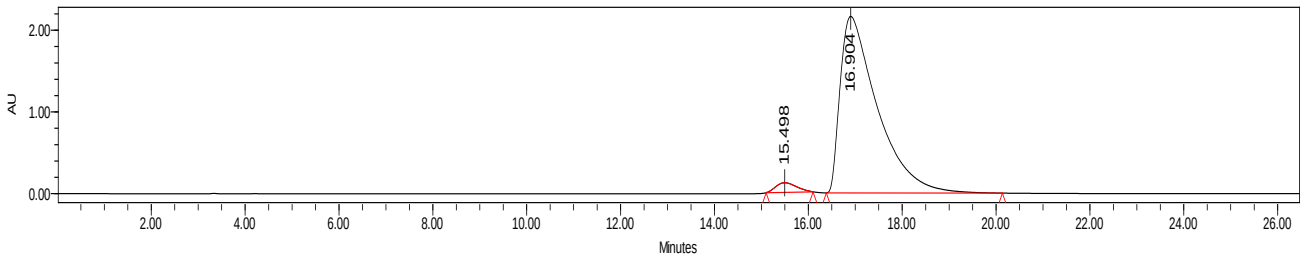
3al

***S*-Phenyl (*S*)-3-{6-fluoro-2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3al)**
0.1 mmol (**2l**) scale reaction:
Result: white solid, 54.5 mg, 98% yield, 94% ee, m.p. 74 – 76 ℃; $[\alpha]_D^{20}$ = –46.9 (*c* = 0.65 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 15.50 min, $t_r(_{major})$ = 16.90 min;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (s, 1H), 7.47 – 7.41 (m, 1H), 7.40 – 7.35 (m, 3H), 7.33 – 7.28 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.96 – 6.91 (m, 1H), 6.91 – 6.86 (m, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.41 – 6.39 (m, 2H), 5.92 – 5.86 (m, 2H), 5.83 (s, 1H), 5.11 (s, 1H), 3.79 (s, 3H), 3.11 – 3.00 (m, 2H), 2.91 – 2.80 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.32, 159.66 (*J* = 235.8 Hz), 158.57, 148.07, 147.10, 141.77, 135.84 (*J* = 3.5 Hz), 135.08 (*J* = 12.4 Hz), 134.41, 132.84, 129.41, 129.14, 127.47, 124.76, 120.54, 118.92 (*J* = 10.0 Hz), 114.25, 110.52, 109.11, 108.07 (*J* = 24.2 Hz), 101.19, 99.35, 97.43 (*J* = 25.9 Hz), 55.26, 43.67, 41.81, 20.03;
^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –121.48;
ESI-HRMS calcd for $[C_{32}H_{26}FNO_5S+Na^+]$: 578.1408, found 578.1404;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3399, 3061, 2903, 2837, 1687, 1625, 1585, 1506, 1485, 1460, 1439, 1345, 1296, 1238, 1172, 1131, 1037, 960, 935, 910, 875, 836, 799, 738, 693, 654, 608, 528, 482, 440.
Racemic **3al**:

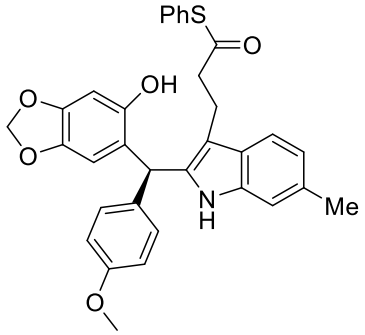


	Retention Time	Area	% Area
1	15.317	16383386	50.21
2	17.392	16243775	49.79

Chiral **3al:**



	Retention Time	Area	% Area
1	15.498	3621377	2.96
2	16.904	118876919	97.04



3am

***S*-Phenyl (*S*)-3-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-6-methyl-1*H*-indol-3-yl}propanethioate (3am)**

0.1 mmol (**2m**) scale reaction:

Result: yellow oil, 52.4 mg, 95% yield, 92% ee; $[\alpha]_D^{20}$ = –55.3 (*c* = 0.75 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, $t_{r(minor)}$ = 16.71 min, $t_{r(major)}$ = 22.08 min;

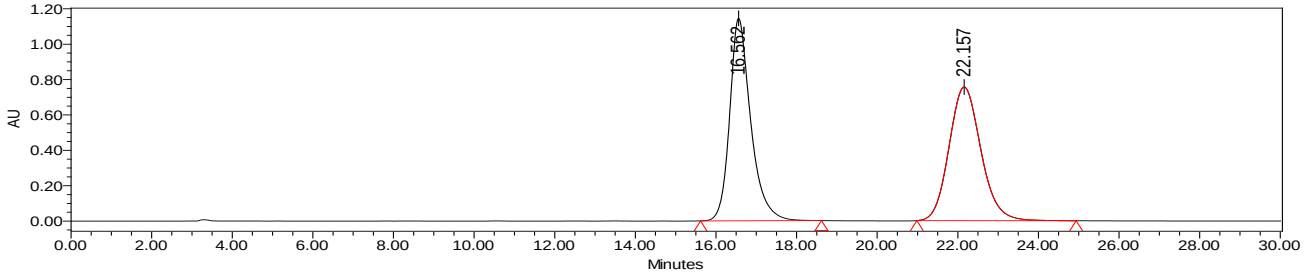
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.36 (m, 3H), 7.36 – 7.31 (m, 2H), 7.07 (s, 1H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.98 (d, *J* = 8.0 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.41 (s, 2H), 5.91 – 5.87 (m, 2H), 5.85 (s, 1H), 5.09 (s, 1H), 3.80 (s, 3H), 3.12 – 2.99 (m, 2H), 2.95 – 2.82 (m, 2H), 2.46 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.35, 158.52, 148.20, 147.02, 141.67, 135.68, 134.70, 134.43, 133.03, 131.45, 129.49, 129.33, 129.10, 127.60, 126.02, 121.20, 120.69, 117.97, 114.18, 110.99, 110.46, 109.11, 101.13, 99.29, 55.25, 43.74, 41.76, 21.65, 20.11;

ESI-HRMS calcd for [$C_{33}H_{29}NO_5S$+Na^+]: 574.1659, found 574.1659;

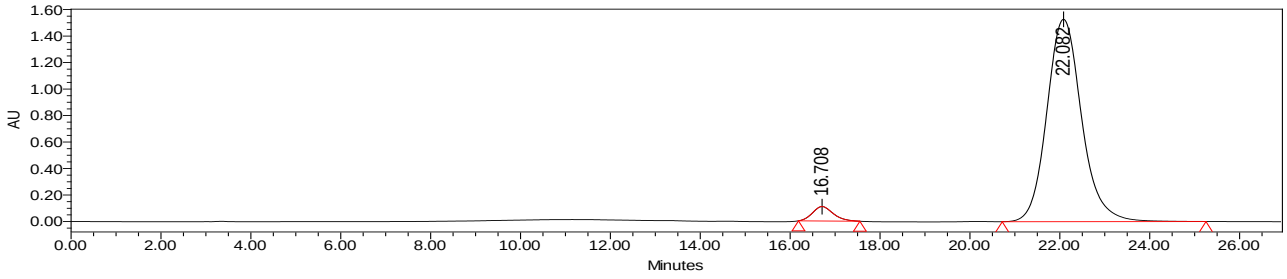
IR (film): $\tilde{\nu}$ (cm^{-1}) 3403, 3058, 3008, 2911, 1688, 1612, 1583, 1506, 1482, 1438, 1335, 1300, 1242, 1170, 1036, 936, 909, 874, 853, 800, 733, 692, 652, 609, 528, 483, 437.

Racemic **3am**:

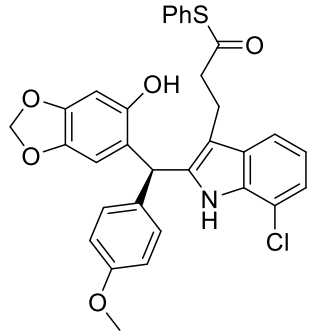


	Retention Time	Area	% Area
1	16.562	41479934	50.01
2	22.157	41464042	49.99

Chiral **3am**:

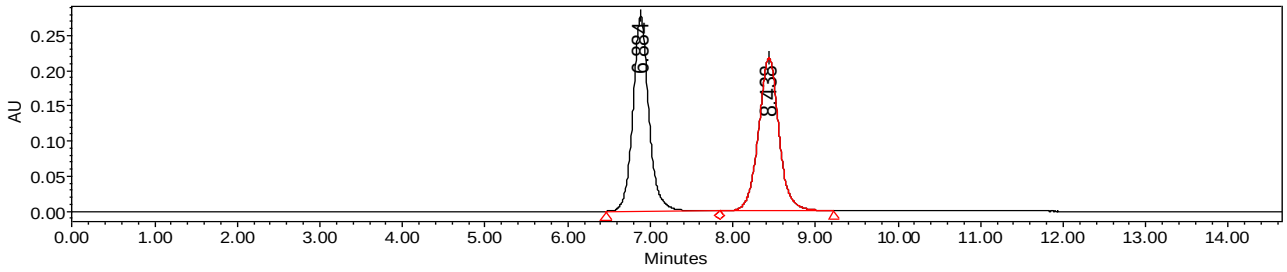


	Retention Time	Area	% Area
1	16.708	3477769	4.07
2	22.082	82024856	95.93



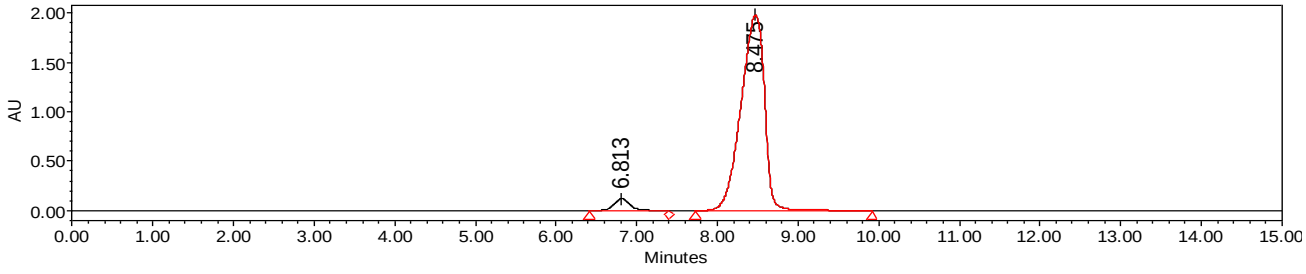
3an

***S*-Phenyl (*S*)-3-{7-chloro-2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3an)**
0.1 mmol (**2n**) scale reaction:
Result: yellow oil, 55.5 mg, 97% yield, 92% ee; $[\alpha]_D^{20}$ = –34.4 (*c* = 0.67 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 6.81 min, $t_r(_{major})$ = 8.48 min;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.45 (d, *J* = 8.0 Hz, 1H), 7.41 – 7.35 (m, 3H), 7.34 – 7.29 (m, 2H), 7.18 – 7.13 (m, 1H), 7.08 – 7.01 (m, 3H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.43 (d, *J* = 8.0 Hz, 2H), 5.93 – 5.88 (m, 2H), 5.88 (s, 1H), 5.10 (s, 1H), 3.80 (s, 3H), 3.10 – 3.02 (m, 2H), 2.89 – 2.81 (m, 2H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.15, 158.62, 148.01, 147.18, 141.84, 136.68, 134.42, 132.60, 132.45, 129.65, 129.40, 129.14, 127.46, 121.02, 120.34, 120.32, 116.91, 116.37, 114.28, 111.70, 109.17, 101.23, 99.36, 55.26, 43.65, 41.90, 20.19;
ESI-HRMS calcd for $[C_{32}H_{26}{}^{34.9689}ClNO_5S+Na^+]$: 594.1112, found 594.1114;
ESI-HRMS calcd for $[C_{32}H_{26}{}^{36.9659}ClNO_5S+Na^+]$: 596.1083, found 596.1093;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3446, 3386, 3060, 3002, 2901, 2836, 1683, 1612, 1580, 1506, 1485, 1440, 1333, 1296, 1244, 1172, 1037, 936, 909, 878, 841, 784, 736, 695, 611, 584, 535, 474.
Racemic **3an**:

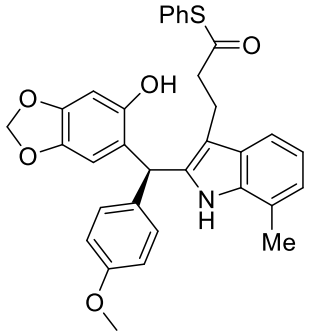


	Retention Time	Area	% Area
1	6.884	3739126	50.13
2	8.438	3719887	49.87

Chiral **3an:**

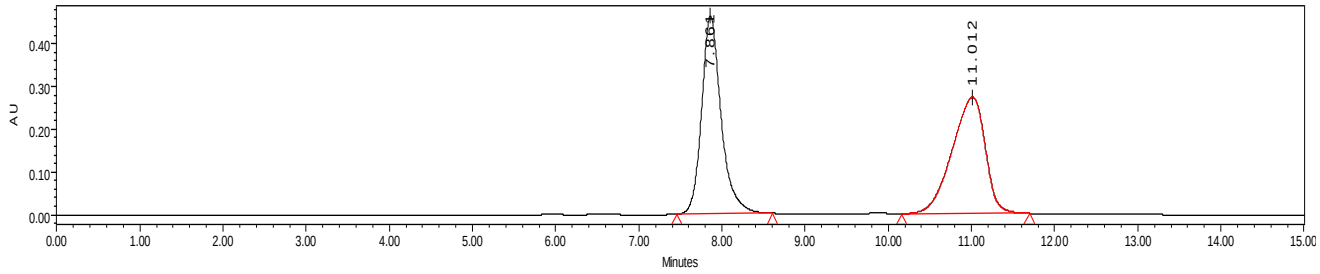


	Retention Time	Area	% Area
1	6.813	1619211	3.91
2	8.475	39797959	96.09



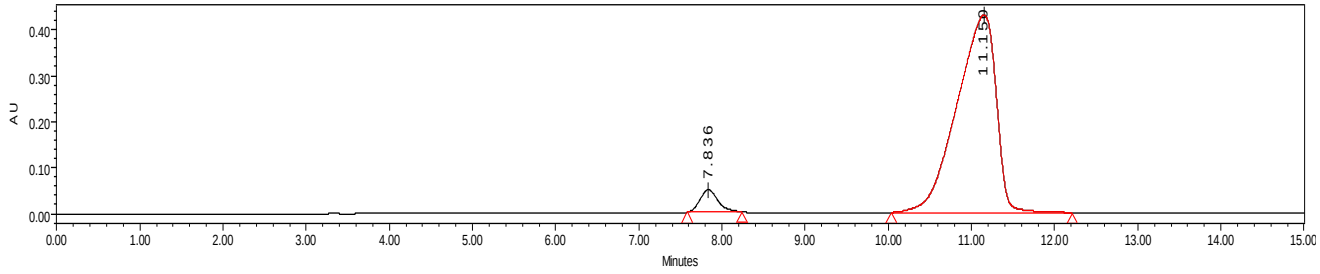
3ao

***S*-Phenyl (*S*)-3-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-7-methyl-1*H*-indol-3-yl}propanethioate (3ao)**
0.1 mmol (**2o**) scale reaction:
Result: white solid, 53.5 mg, 97% yield, 90% ee, m.p. 64 – 66 ℃; $[\alpha]_D^{21}$ = –50.2 (*c* = 0.54 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 7.84 min, $t_r(_{major})$ = 11.15 min;
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (s, 1H), 7.45 – 7.41 (m, 1H), 7.41 – 7.37 (m, 3H), 7.37 – 7.31 (m, 2H), 7.11 – 7.02 (m, 3H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 6.0 Hz, 2H), 5.93 – 5.88 (m, 2H), 5.88 (s, 1H), 5.05 (s, 1H), 3.80 (s, 3H), 3.12 – 3.04 (m, 2H), 2.95 – 2.82 (m, 2H), 2.39 (s, 3H);
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.25, 158.57, 148.17, 147.09, 141.76, 135.11, 134.84, 134.44, 132.90, 129.46, 129.33, 129.11, 127.74, 127.61, 122.33, 120.70, 120.12, 119.80, 115.99, 114.21, 111.30, 109.21, 101.17, 99.39, 55.25, 43.79, 42.00, 20.18, 16.56;
ESI-HRMS calcd for [$C_{33}H_{29}NO_5S$+Na^+]: 574.1659, found 574.1649;
IR (film): $\tilde{\nu}$ (cm^{-1}) 3452, 3397, 3053, 2901, 2837, 1686, 1611, 1583, 1505, 1483, 1438, 1336, 1297, 1243, 1169, 1033, 994, 934, 880, 844, 786, 740, 696, 589, 534, 453.
Racemic **3ao**:

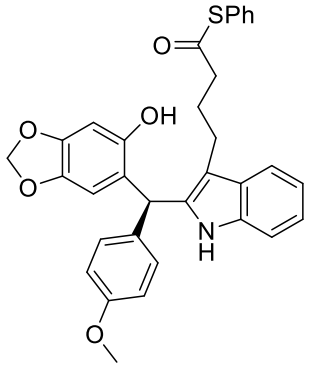


	Retention Time	Area	% Area
1	7.861	7587121	50.13
2	11.012	7547084	49.87

Chiral **3ao:**



	Retention Time	Area	% Area
1	7.836	732786	4.95
2	11.150	14070617	95.05



3ap

***S*-Phenyl (*S*)-4-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}butanethioate (3ap)**

0.1 mmol (**2p**) scale reaction:

Result: yellow oil, 53.5 mg, 97% yield, 94% ee; $[\alpha]_D^{21}$ = –20.4 (*c* = 0.57 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_{r(minor)}$ = 10.93 min, $t_{r(major)}$ = 15.80 min;

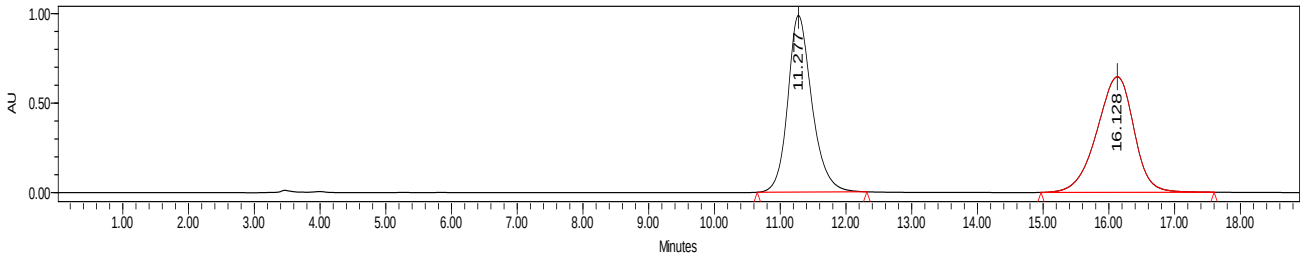
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.59 (d, *J* = 7.2 Hz, 1H), 7.44 – 7.32 (m, 5H), 7.28 – 7.23 (m, 1H), 7.20 – 7.10 (m, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.86 (d, *J* = 8.8 Hz, 2H), 6.44 (s, 1H), 6.39 (s, 1H), 5.90 – 5.87 (m, 2H), 5.82 (s, 1H), 4.99 (s, 1H), 3.80 (s, 3H), 2.79 (t, *J* = 7.6 Hz, 2H), 2.61 (t, *J* = 7.2 Hz, 2H), 2.06 – 1.94 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.25, 158.56, 147.92,146.97, 141.81, 135.35, 135.30, 134.48, 132.98, 129.49, 129.29, 129.12, 128.60, 127.72, 121.49, 121.15, 119.39, 118.61, 114.23, 111.72, 110.83, 109.19, 101.16, 99.37, 55.25, 43.16, 41.90, 25.96, 23.26;

ESI-HRMS calcd for [$C_{33}H_{29}NO_5S$+Na^+]: 574.1659, found 574.1666;

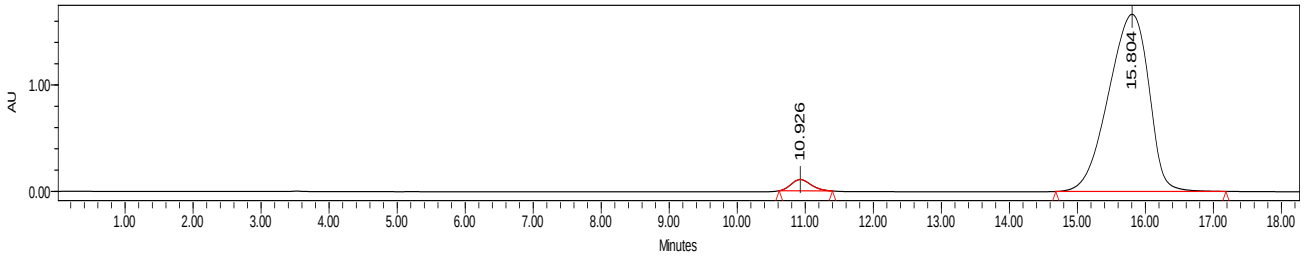
IR (film): $\tilde{\nu}$ (cm^{-1}) 3406, 3056, 2930, 2902, 2840, 2362, 1687, 1611, 1583, 1506, 1483, 1437, 1300, 1242, 1170, 1035, 934, 910, 875, 847, 792, 743, 692, 614, 522, 435.

Racemic **3ap**:

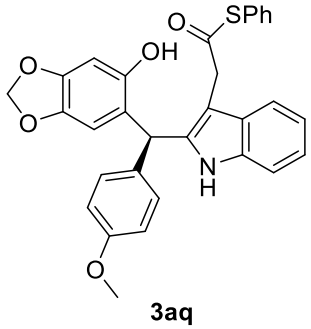


	Retention Time	Area	% Area
1	11.277	25110903	49.88
2	16.128	25230995	50.12

Chiral **3ap:**



	Retention Time	Area	% Area
1	10.926	2173943	3.08
2	15.804	68501747	96.92



3aq

***S*-Phenyl (*S*)-2-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}ethanethioate (3aq)**

0.1 mmol (**2q**) scale reaction:

Result: yellow solid, 51.8 mg, 99% yield, 97% ee, m.p. 66 – 68 ℃; $[\alpha]_D^{19}$ = –64.7 (*c* = 0.78 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IE, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 9.73 min, $t_r(_{major})$ = 10.89 min;

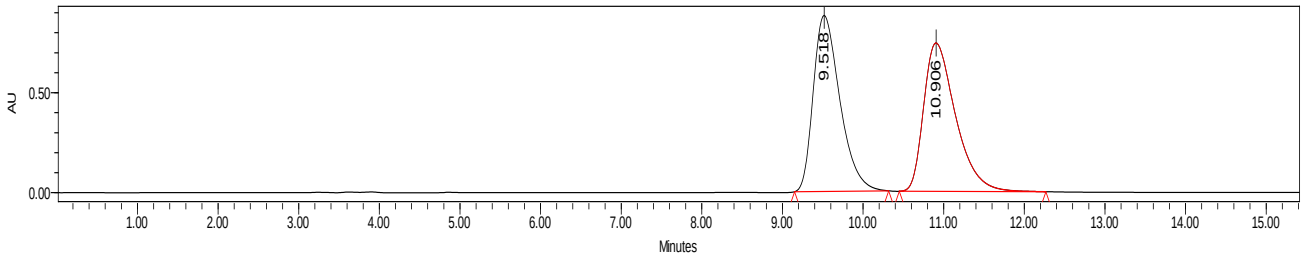
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.69 – 7.60 (m, 1H), 7.39 – 7.32 (m, 5H), 7.31 – 7.27 (m, 1H), 7.22 – 7.15 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.44 (s, 1H), 6.39 (s, 1H), 5.91 (s, 1H), 5.89 – 5.85 (m, 2H), 5.70 (s, 1H), 4.07 (d, *J* = 16.4 Hz, 1H), 3.88 (d, *J* = 16.4 Hz, 1H), 3.80 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.67, 158.66, 148.69, 147.26, 141.60, 137.35, 135.10, 134.32, 132.27, 129.63, 129.36, 129.10, 128.36, 127.60, 122.04, 120.09, 119.79, 118.24, 114.20, 111.08, 108.81, 104.90, 101.15, 99.45, 55.26, 41.85, 38.75;

ESI-HRMS calcd for [$C_{31}H_{25}NO_5S$+Na$^+$]: 546.1346, found 546.1346;

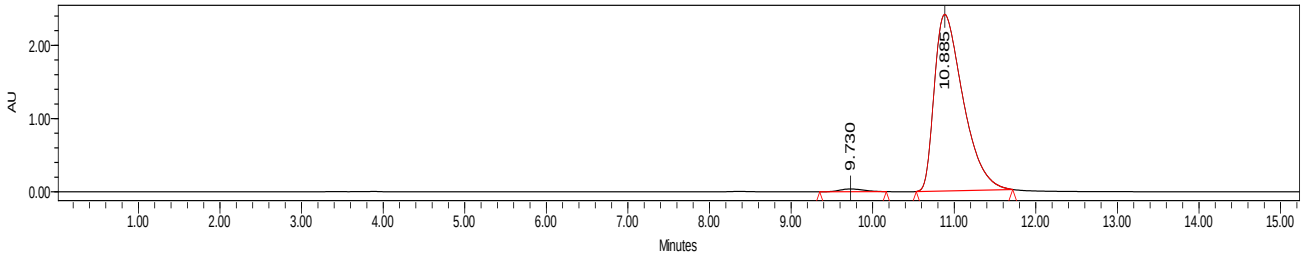
IR (film): $\tilde{\nu}$ (cm^{-1}) 3398, 3057, 2898, 2836, 1685, 1612, 1583, 1507, 1483, 1439, 1406, 1298, 1244, 1172, 1036, 963, 934, 875, 843, 794, 743, 693, 609, 555, 520.

Racemic **3aq**:

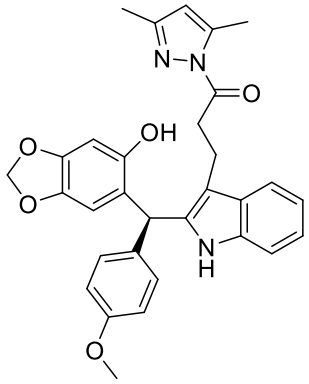


	Retention Time	Area	% Area
1	9.518	20194697	49.73
2	10.906	20415914	50.27

Chiral **3aq:**



	Retention Time	Area	% Area
1	9.730	767176	1.28
2	10.885	59011879	98.72



3ar

(*S*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-3-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propan-1-one (3ar)

0.1 mmol (**2r**) scale reaction:

Result: white solid, 51.8 mg, 99% yield, 95% ee, m.p. 71 – 73 ℃; $[\alpha]_D^{20}$ = –80.2 (*c* = 0.73 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 8.44 min, $t_r(_{major})$ = 12.21 min;

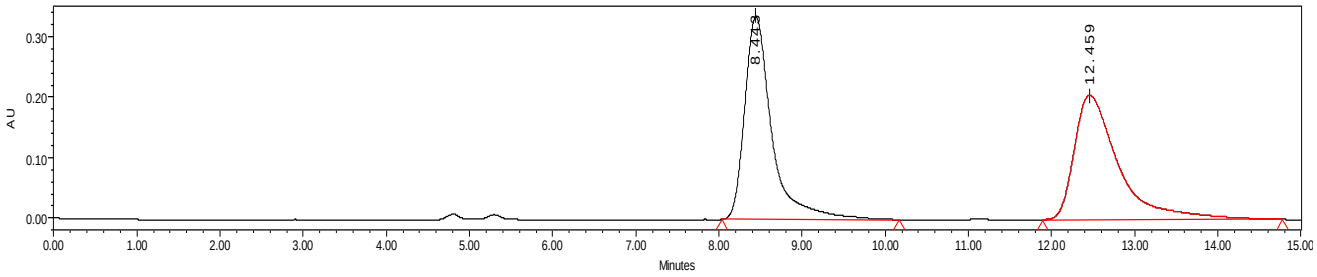
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.22 (m, 1H), 7.17 – 7.06 (m, 2H), 7.02 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.49 (s, 1H), 6.42 (s, 1H), 6.20 (s, 2H), 5.91 (s, 1H), 5.90 – 5.86 (m, 2H), 3.78 (s, 3H), 3.66 – 3.54 (m, 1H), 3.43 – 3.31 (m, 1H), 3.21 – 3.00 (m, 2H), 2.51 (s, 3H), 2.20 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 174.25, 158.41, 152.22, 148.86, 147.11, 144.30, 141.57, 135.36, 135.25, 133.57, 129.54, 128.28, 121.39, 120.57, 119.31, 118.43, 114.02, 111.28, 111.13, 110.86, 108.95, 101.10, 99.55, 55.22, 41.37, 35.66, 18.98, 14.57, 13.70;

ESI-HRMS calcd for $[C_{31}H_{29}N_3O_5+Na^+]$: 546.1999, found 546.2001;

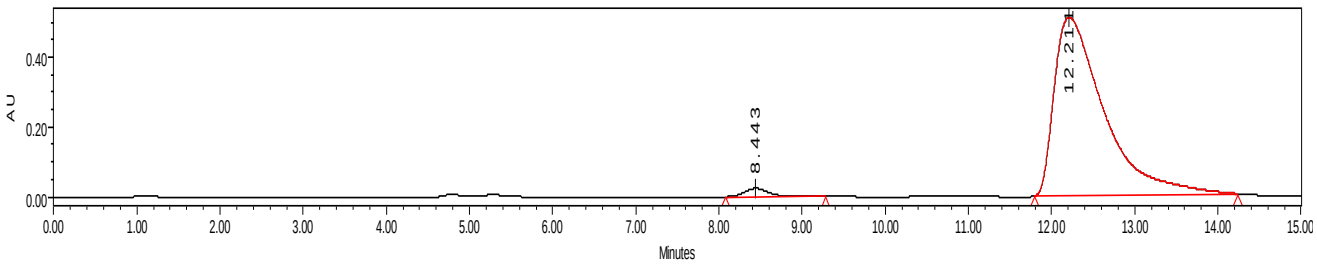
IR (film): $\tilde{\nu}$ (cm^{-1}) 3399, 3055, 2928, 2838, 1718, 1612, 1583, 1506, 1482, 1456, 1437, 1409, 1381, 1328, 1308, 1241, 1171, 1035, 964, 934, 910, 874, 828, 796, 735, 702, 617, 594, 518, 435.

Racemic **3ar**:

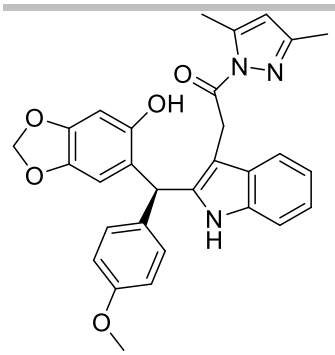


	Retention Time	Area	% Area
1	8.443	7642608	50.12
2	12.459	7605022	49.88

Chiral **3ar:**



	Retention Time	Area	% Area
1	8.443	511574	2.35
2	12.211	21296580	97.65



3as

(*S*)-1-(3,5-Dimethyl-1*H*-pyrazol-1-yl)-2-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}ethan-1-one (3as)

0.1 mmol (**2s**) scale reaction:

Result: white solid, 47.9 mg, 94% yield, 95% ee, m.p. 162 – 167 ℃; $[\alpha]_D^{21}$ = –39.9 (*c* = 0.81 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 7.89 min, $t_r(_{major})$ = 16.09 min;

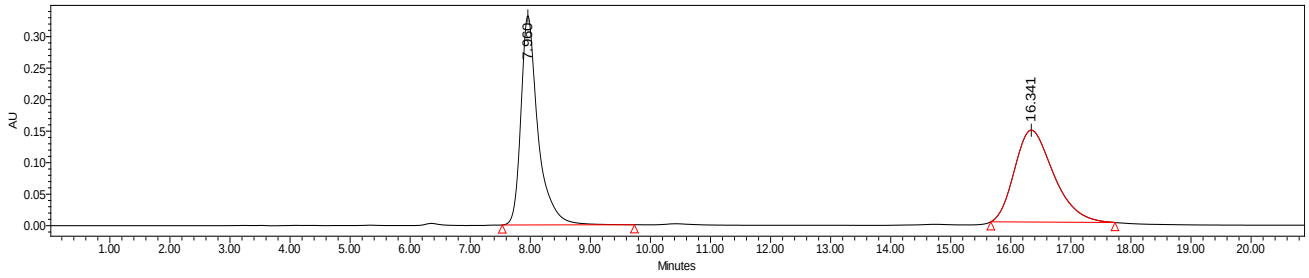
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.68 – 7.62 (m, 1H), 7.28 – 7.25 (m, 1H), 7.24 (s, 1H), 7.17 – 7.05 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.8 Hz, 2H), 6.48 (s, 1H), 6.32 (s, 1H), 5.99 (d, *J* = 9.2 Hz, 2H), 5.88 – 5.84 (m, 2H), 4.82 (d, *J* = 16.4 Hz, 1H), 4.13 (d, *J* = 16.8 Hz, 1H), 3.77 (s, 3H), 2.51 (s, 3H), 2.27 (s, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 172.79, 158.53, 152.83, 149.46, 147.28, 144.87, 141.31, 136.67, 135.18, 132.49, 129.65, 128.60, 121.82, 119.78, 119.70, 118.60, 114.04, 111.72, 110.93, 108.46, 105.42, 101.08, 99.44, 55.24, 41.65, 30.50, 14.67, 13.85;

ESI-HRMS calcd for [$C_{30}H_{27}N_3O_5$+Na^+]: 532.1843, found 532.1844;

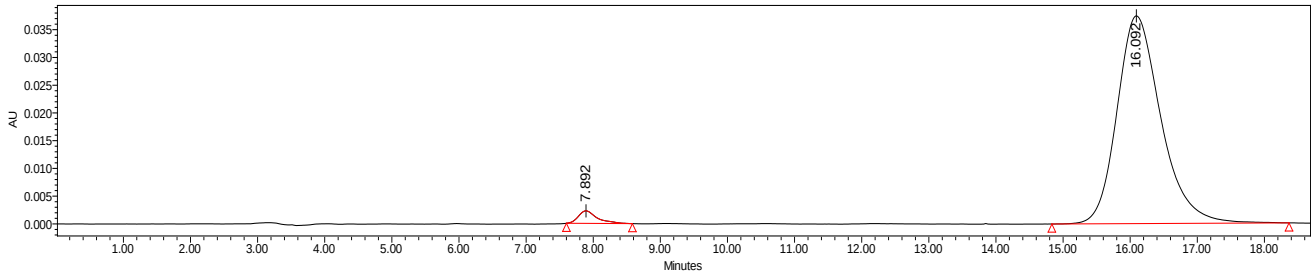
IR (film): $\tilde{\nu}$ (cm^{-1}) 3393, 3055, 2927, 2900, 2837, 1711, 1612, 1583, 1506, 1482, 1457, 1437, 1408, 1379, 1352, 1297, 1241, 1170, 1034, 964, 934, 874, 830, 797, 735, 632, 597, 534, 514, 485, 433.

Racemic **3as**:

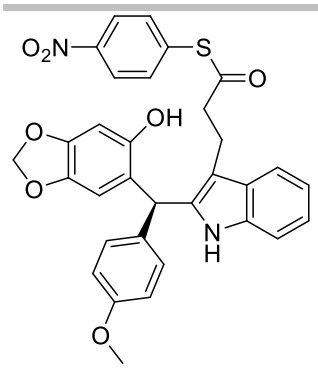


	Retention Time	Area	% Area
1	7.960	6546654	49.84
2	16.341	6589393	50.16

Chiral **3as**:



	Retention Time	Area	% Area
1	7.892	43849	2.52
2	16.092	1699463	97.48



3at

***S*-(4-Nitrophenyl) (*S*)-3-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3at)**

0.1 mmol (**2t**) scale reaction:

Result: yellow solid, 57.7 mg, 99% yield, 92% ee, m.p. 75 – 76 ℃; $[\alpha]_D^{20}$ = –41.5 (*c* = 0.76 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 21.65 min, $t_r(_{major})$ = 31.28 min;

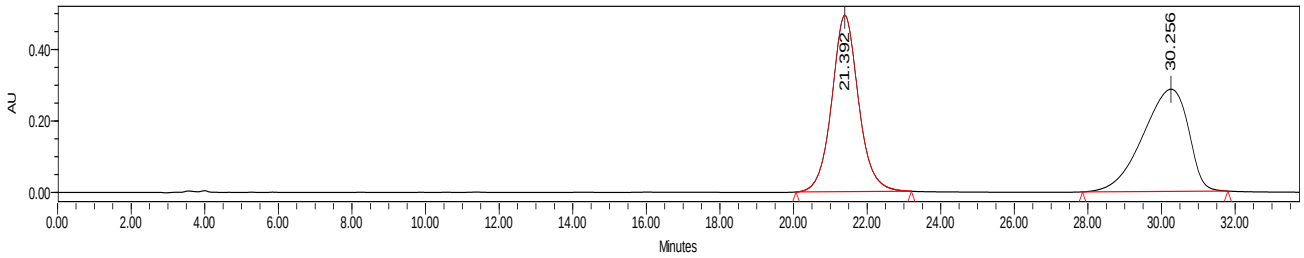
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.89 (s, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.30 – 7.25 (m, 1H), 7.20 – 7.10 (m, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 6.42 (s, 1H), 6.40 (s, 1H), 5.91 – 5.87 (m, 2H), 5.85 (s, 1H), 4.96 (s, 1H), 3.79 (s, 3H), 3.11 (t, *J* = 7.2 Hz, 2H), 3.00 – 2.85 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 195.89, 158.62, 148.00, 147.13, 141.81, 136.05, 135.67, 135.23, 134.64, 132.83, 129.44, 128.11, 123.82, 121.73, 120.62, 119.62, 118.17, 114.25, 111.05, 110.12, 109.19, 101.23, 99.29, 55.26, 44.17, 41.86, 20.10;

ESI-HRMS calcd for $[C_{32}H_{26}N_2O_7S+Na^+]$: 605.1353, found 605.1349;

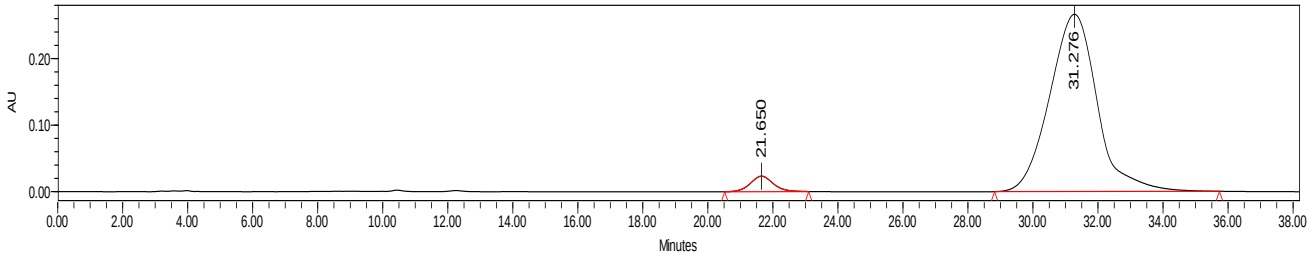
IR (film): $\tilde{\nu}$ (cm^{-1}) 3410, 3058, 2901, 2838, 2363, 2251, 1704, 1604, 1580, 1509, 1483, 1458, 1436, 1401, 1342, 1304, 1242, 1169, 1109, 1035, 934, 907, 877, 848, 793, 728, 648, 593, 549, 515, 455, 435.

Racemic **3at**:

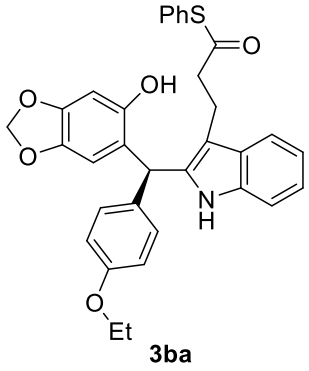


	Retention Time	Area	% Area
1	21.392	24899388	50.33
2	30.256	24569330	49.67

Chiral **3at:**



	Retention Time	Area	% Area
1	21.650	1133240	4.03
2	31.276	26991337	95.97



3ba

***S*-Phenyl (*S*)-3-{2-[(4-ethoxyphenyl)(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)methyl]-1*H*-indol-3-yl}propanethioate (3ba)**

0.1 mmol (**2a**) scale reaction:

Result: white solid, 54.6 mg, 99% yield, 93% ee, m.p. 65 – 68 ℃; $[\alpha]_D^{21}$ = –35.1 (*c* = 0.99 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IB, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 17.48 min, $t_r(_{major})$ = 19.40 min;

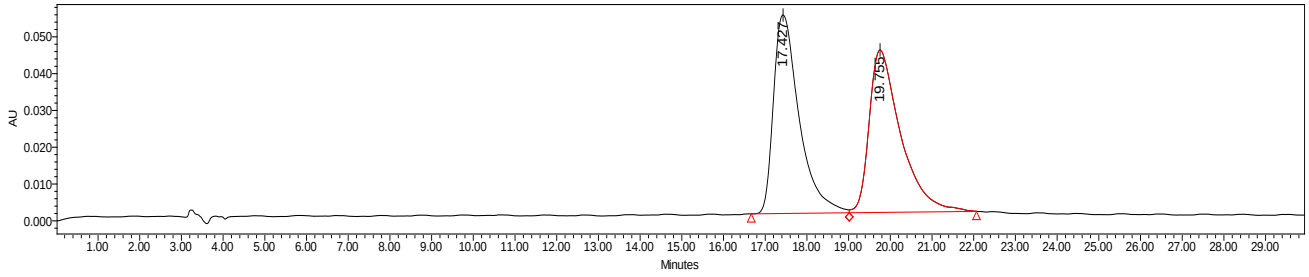
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 (s, 1H), 7.60 – 7.53 (m, 1H), 7.43 – 7.37 (m, 3H), 7.36 – 7.30 (m, 2H), 7.28 – 7.24 (m, 1H), 7.20 – 7.09 (m, 2H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.43 – 6.38 (m, 2H), 5.94 – 5.84 (m, 3H), 5.12 (s, 1H), 4.02 (q, *J* = 7.2 Hz, 2H), 3.14 – 3.02 (m, 2H), 2.97 – 2.82 (m, 2H), 1.42 (t, *J* = 6.8 Hz, 3H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.38, 157.94, 148.17, 147.04, 141.69, 135.60, 135.21, 134.43, 132.73, 129.49, 129.34, 129.11, 128.22, 127.57, 121.57, 120.65, 119.51, 118.26, 114.74, 110.96, 110.54, 109.14, 101.14, 99.31, 63.44, 43.72, 41.76, 20.07, 14.81;

ESI-HRMS calcd for [$C_{33}H_{29}NO_5S$+Na^+]: 574.1659, found 574.1656;

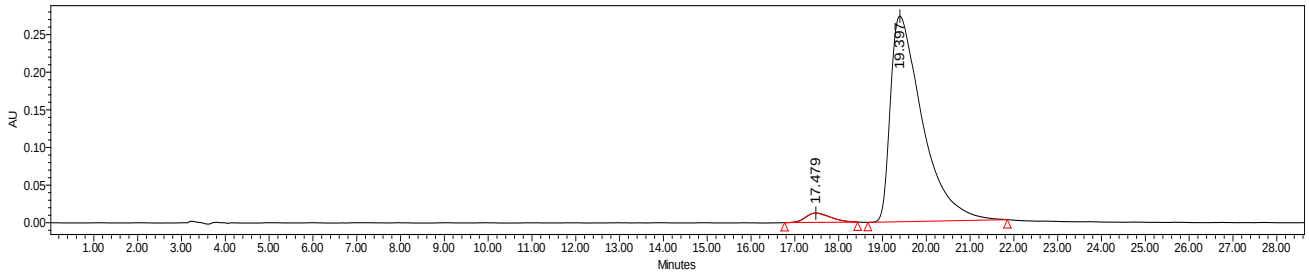
IR (film): $\tilde{\nu}$ (cm^{-1}) 3399, 3055, 2980, 2895, 2363, 2335, 1690, 1612, 1582, 1505, 1482, 1437, 1396, 1300, 1235, 1169, 1039, 931, 875, 846, 794, 739, 695, 597, 520, 458.

Racemic **3ba**:

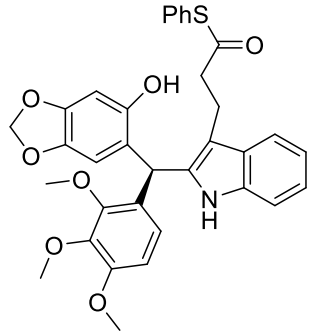


	Retention Time	Area	% Area
1	17.427	2310847	50.01
2	19.755	2309571	49.99

Chiral **3ba:**



	Retention Time	Area	% Area
1	17.479	486713	3.41
2	19.397	13801417	96.59



3ca

***S*-Phenyl (*R*)-3-{2-[(6-hydroxybenzo[*d*][1,3]dioxol-5-yl)(2,3,4-trimethoxyphenyl)methyl]-1*H*-indol-3-yl}propanethioate (3ca)**

0.1 mmol (**2a**) scale reaction:

Result: yellow solid, 53.2 mg, 89% yield, 90% ee, m.p. 76 – 80 ℃; $[\alpha]_D^{21} = -35.5$ (*c* = 0.70 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IA, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 15.06 min, $t_r(_{major})$ = 18.91 min;

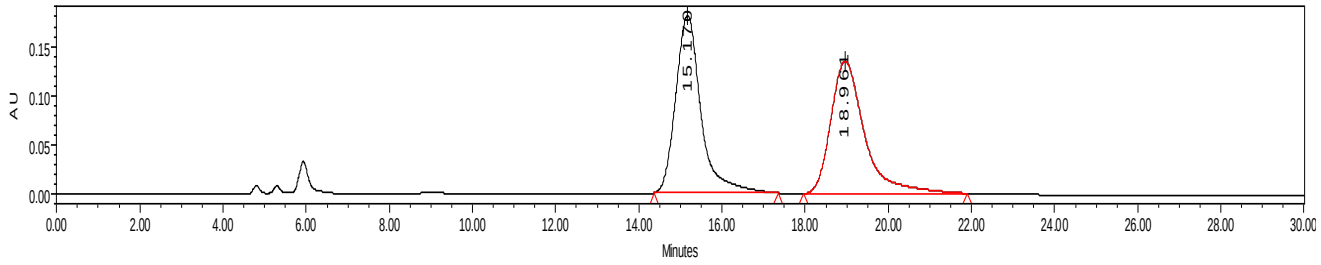
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.60 – 7.52 (m, 1H), 7.41 – 7.36 (m, 3H), 7.35 – 7.30 (m, 2H), 7.29 – 7.25 (m, 1H), 7.19 – 7.09 (m, 2H), 6.69 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.8 Hz, 1H), 6.43 (s, 1H), 6.39 (s, 1H), 6.08 (s, 1H), 5.90 – 5.85 (m, 2H), 5.23 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.59 (s, 3H), 3.13 – 3.00 (m, 2H), 2.93 – 2.80 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 197.95, 153.15, 151.37, 148.23, 146.93, 142.64, 141.50, 135.30, 135.05, 134.41, 129.28, 129.08, 128.37, 127.64, 127.41, 123.38, 121.45, 120.18, 119.47, 118.26, 110.88, 110.23, 108.61, 107.24, 101.08, 99.14, 60.72, 55.91, 43.70, 37.05, 20.11;

ESI-HRMS calcd for [$C_{34}H_{31}NO_7S$+Na^+]: 620.1713, found 620.1718;

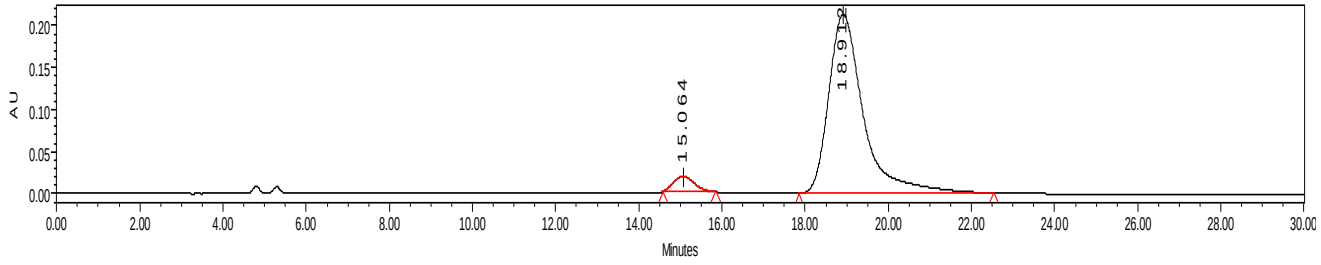
IR (film): $\tilde{\nu}$ (cm^{-1}) 3397, 3056, 2938, 2836, 2362, 2334, 1697, 1598, 1488, 1461, 1438, 1276, 1231, 1171, 1094, 1036, 934, 909, 871, 798, 742, 694, 597, 532, 489, 440.

Racemic **3ca**:

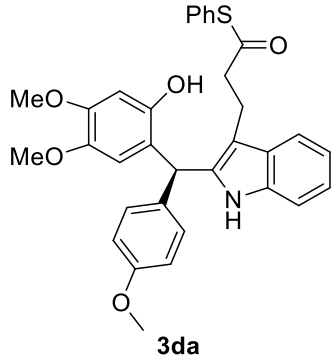


	Retention Time	Area	% Area
1	15.170	7629360	50.11
2	18.961	7595549	49.89

Chiral **3ca:**



	Retention Time	Area	% Area
1	15.064	643948	4.95
2	18.912	12377195	95.05



3da

_S_-Phenyl (_S_)-3-{2-[(2-hydroxy-4,5-dimethoxyphenyl)(4-methoxyphenyl)methyl]-1_H_-indol-3-yl}propanethioate (3da)

0.1 mmol (**2a**) scale reaction:

Result: white solid, 54.8 mg, 99% yield, 86% ee, m.p. 73 – 75 ℃; $[\alpha]_D^{21}$ = –54.8 (*c* = 1.74 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IB, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 10.18 min, $t_r(_{major})$ = 11.51 min;

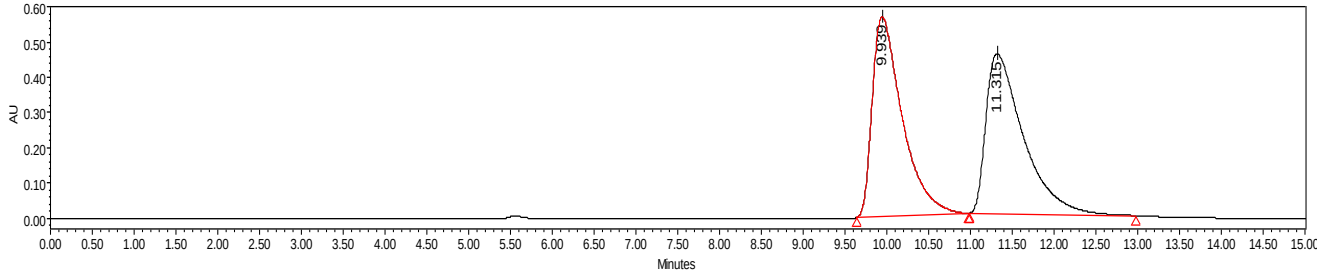
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.63 – 7.55 (m, 1H), 7.43 – 7.35 (m, 3H), 7.35 – 7.30 (m, 2H), 7.29 – 7.25 (m, 1H), 7.21 – 7.11 (m, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 6.55 (s, 1H), 6.46 (s, 1H), 5.89 (s, 1H), 5.33 (s, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.64 (s, 3H), 3.18 – 3.06 (m, 2H), 3.03 – 2.83 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.29, 158.39, 148.85, 147.58, 142.99, 135.67, 135.26, 134.35, 133.08, 129.35, 129.27, 129.04, 128.08, 127.49, 121.48, 119.40, 119.38, 118.16, 114.05, 113.82, 110.98, 110.46, 101.90, 56.49, 55.76, 55.17, 43.67, 42.19, 20.03;

ESI-HRMS calcd for [$C_{33}H_{31}NO_5S$+Na^+]: 576.1815, found 576.1825;

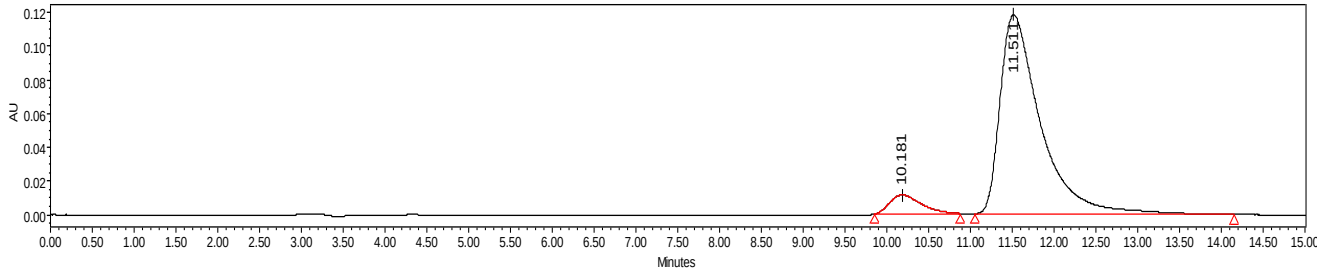
IR (film): $\tilde{\nu}$ (cm^{-1}) 3372, 3055, 3000, 2934, 2835, 1698, 1611, 1583, 1510, 1447, 1411, 1340, 1300, 1244, 1199, 1175, 1101, 1031, 997, 908, 849, 734, 695, 593, 518, 456.

Racemic **3da**:

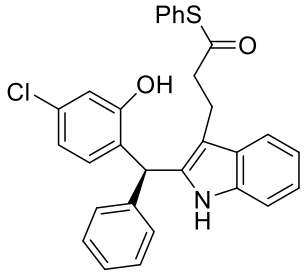


	Retention Time	Area	% Area
1	9.939	14120013	50.02
2	11.315	14107914	49.98

Chiral **3da:**



	Retention Time	Area	% Area
1	10.181	295769	6.93
2	11.511	3974629	93.07



3ea

***S*-Phenyl (*S*)-3-{2-[(4-chloro-2-hydroxyphenyl)(phenyl)methyl]-1*H*-indol-3-yl}propanethioate (3ea)**

0.1 mmol (**2a**) scale reaction:

Result: white solid, 43.3 mg, 87% yield, 91% ee, m.p. 64 – 66 ℃; $[\alpha]_D^{27}$ = –49.9 (*c* = 0.79 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH = 95/5, flow rate = 1.0 mL/min, λ = 230 nm, $t_r(_{major})$ = 41.91 min, $t_r(_{minor})$ = 47.90 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.31 – 7.25 (m, 5H), 7.24 – 7.18 (m, 2H), 7.17 – 7.09 (m, 2H), 7.09 – 7.04 (m, 3H), 6.90 – 6.86 (m, 1H), 6.65 (d, *J* = 8.8 Hz, 1H), 5.97 (s, 1H), 5.57 (s, 1H), 3.05 (t, *J* = 7.2 Hz, 2H), 2.86 (t, *J* = 7.2 Hz, 2H);

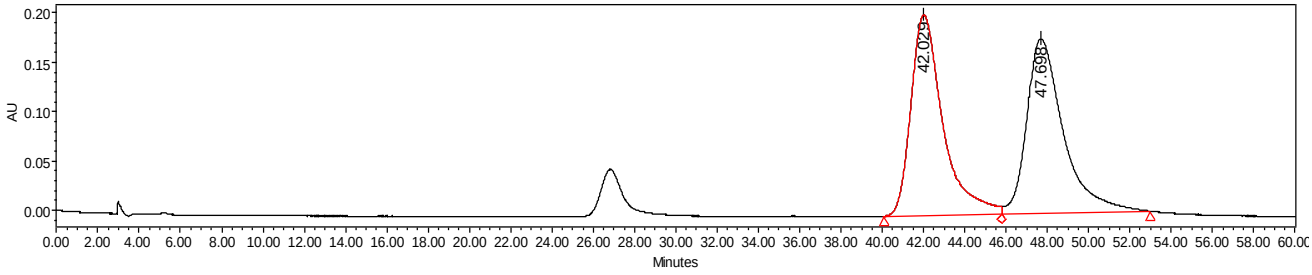
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.78, 152.22, 140.36, 135.36, 134.46, 134.43, 130.19, 129.70, 129.40, 129.14, 128.88, 128.49, 128.36, 128.11, 127.47, 127.23, 125.75, 121.80, 119.65, 118.36, 117.80, 111.06, 111.02, 43.66, 42.56, 20.08;

ESI-HRMS calcd for $[C_{30}H_{24}{}^{34.9689}ClNO_2S+Na^+]$: 520.1109, found 520.1099;

ESI-HRMS calcd for $[C_{30}H_{24}{}^{36.9659}ClNO_2S+Na^+]$: 522.1079, found 522.1072;

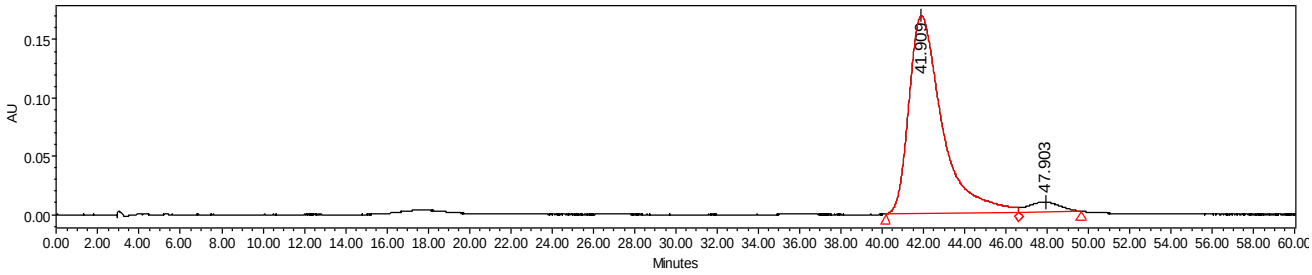
IR (film): $\tilde{\nu}$ (cm^{-1}) 3409, 3058, 3027, 2923, 2855, 1678, 1599, 1492, 1458, 1439, 1414, 1339, 1267, 1210, 1179, 1161, 1108, 1051, 1022, 997, 815, 740, 701, 646, 585, 499, 468.

Racemic **3ea**:

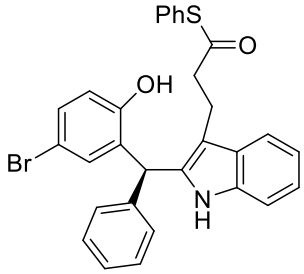


	Retention Time	Area	% Area
1	42.029	21790679	49.93
2	47.698	21851328	50.07

Chiral **3ea:**



	Retention Time	Area	% Area
1	41.909	18871381	95.38
2	47.903	913502	4.62



3fa

***S*-Phenyl (*S*)-3-{2-[(5-bromo-2-hydroxyphenyl)(phenyl)methyl]-1*H*-indol-3-yl}propanethioate (3fa)**

0.1 mmol (**2a**) scale reaction:

Result: white solid, 52.6 mg, 97% yield, 92% ee, m.p. 75 – 77 ℃; $[\alpha]_D^{28}$ = –52.0 (*c* = 0.76 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel ADH, *n*-hexane/*i*-PrOH = 90/10, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{major})$ = 15.54 min, $t_r(_{minor})$ = 18.84 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.73 (s, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.31 – 7.26 (m, 4H), 7.26 – 7.18 (m, 3H), 7.17 – 7.08 (m, 2H), 7.08 – 7.04 (m, 2H), 7.03 – 6.99 (m, 1H), 6.60 (d, *J* = 8.8 Hz, 1H), 5.97 (s, 1H), 5.51 (s, 1H), 3.10 – 2.99 (m, 2H), 2.92 – 2.80 (m, 2H);

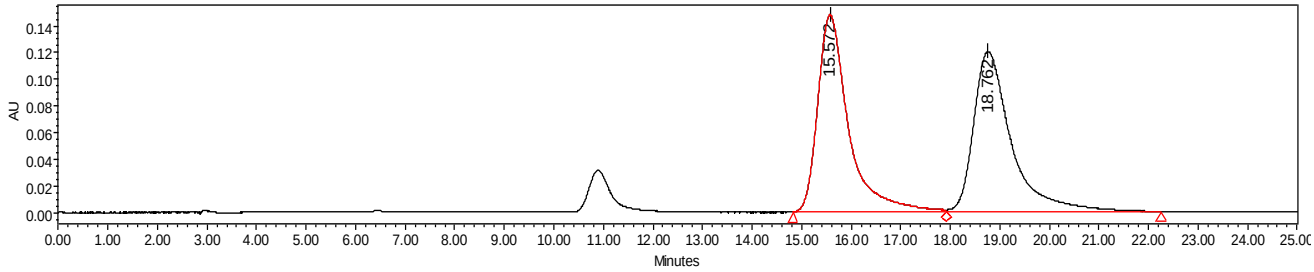
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 198.79, 152.74, 140.31, 135.37, 134.44, 134.39, 132.53, 131.36, 130.68, 129.40, 129.14, 128.90, 128.49, 128.11, 127.47, 127.26, 121.82, 119.66, 118.37, 118.32, 113.11, 111.07, 43.65, 42.55, 20.07;

ESI-HRMS calcd for $[C_{30}H_{24}{}^{78.9183}BrNO_2S+Na^+]$: 564.0603, found 564.0596;

ESI-HRMS calcd for $[C_{30}H_{24}{}^{80.9163}BrNO_2S+Na^+]$: 566.0583, found 566.0577;

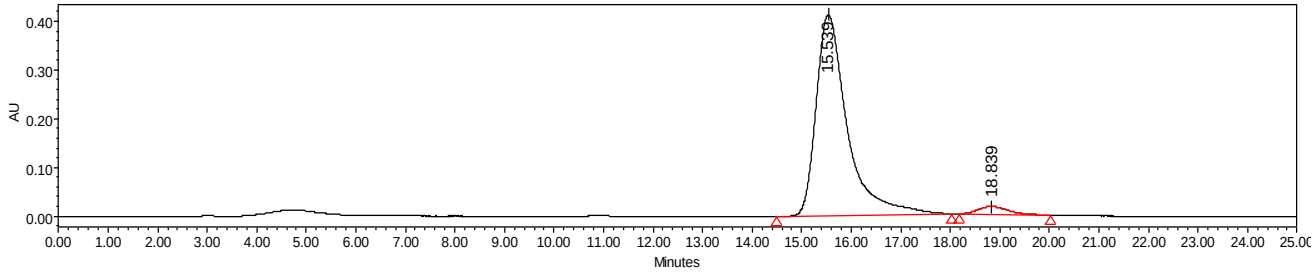
IR (film): $\tilde{\nu}$ (cm^{-1}) 3409, 3057, 2922, 2854, 1677, 1583, 1490, 1458, 1439, 1409, 1338, 1265, 1209, 1179, 1101, 1050, 995, 813, 736, 700, 622, 534, 498, 466, 435.

Racemic **3fa**:

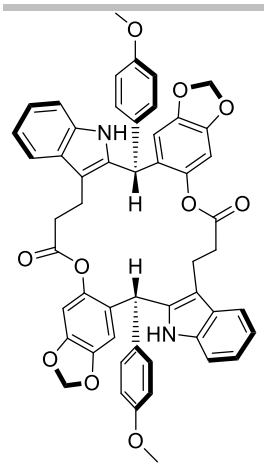


	Retention Time	Area	% Area
1	15.572	6416454	50.06
2	18.762	6399839	49.94

Chiral **3fa:**



	Retention Time	Area	% Area
1	15.539	17864380	96.20
2	18.839	704755	3.80



4aa

Compound 4aa

0.1 mmol (**2a**) scale reaction:

Result: yellow solid, 29.9 mg, 70% yield, 93:7 dr, 99% ee, m.p. 205 – 207 ℃; $[\alpha]_D^{21}$ = –68.0 (*c* = 1.26 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC[2] (Chiralcel IC-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 254 nm, $t_r(_{minor})$ = 5.43 min, $t_r(_{major})$ = 10.58 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 2H), 7.63 – 7.53 (m, 2H), 7.32 – 7.23 (m, 2H), 7.22 – 7.10 (m, 4H), 7.00 (d, *J* = 8.8 Hz, 4H), 6.82 (d, *J* = 8.8 Hz, 4H), 6.59 (s, 2H), 6.54 (s, 2H), 5.97 (s, 4H), 5.86 (s, 2H), 3.79 (s, 6H), 3.28 – 3.12 (m, 2H), 3.11 – 2.99 (m, 2H), 2.92 – 2.75 (m, 4H);

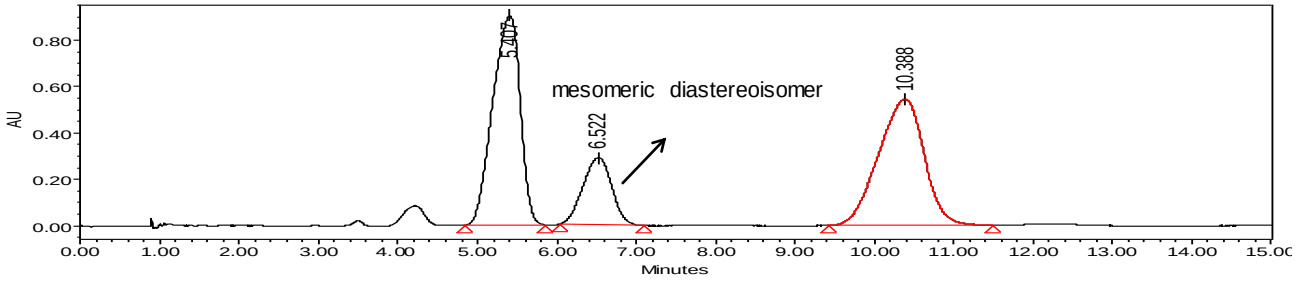
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.57, 158.45, 146.89, 145.82, 142.47, 135.19, 134.80, 133.11, 129.40, 128.09, 126.96, 121.61, 119.61, 118.19, 113.98, 110.96, 110.33, 108.55, 104.31, 101.84, 55.18, 40.77, 34.99, 19.46;

ESI-HRMS calcd for [$C_{52}H_{42}N_2O_{10}$+Na^+]: 877.2732, found 877.2717;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3785, 3411, 3053, 2903, 2837, 2393, 2285, 1751, 1609, 1584, 1506, 1479, 1457, 1367, 1344, 1298, 1243, 1178, 1123, 1032, 930, 871, 786, 736, 698, 592, 555, 515, 482, 433.

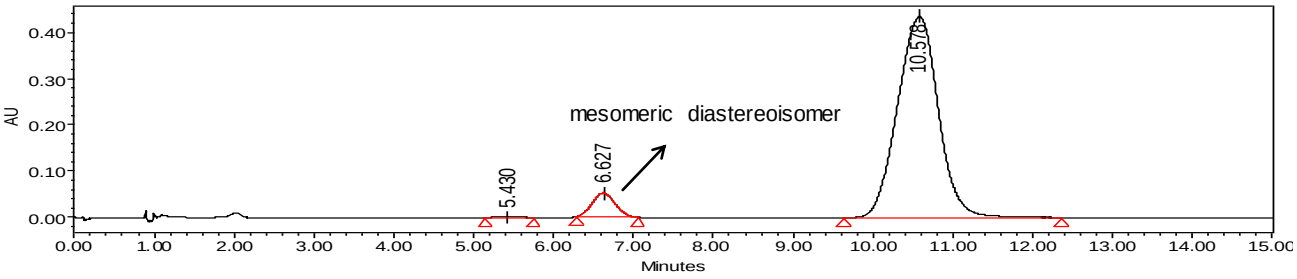
Reaction time: (**Step 1**) **1a** (0.1 mmol), **2a** (0.1 mmol), Sc(OTf)$_3$/**L$_3$-PiPr$_2$** (1:1, 5 mol%) in DCM (1.0 mL) at 35 °C for 4 h; (**Step 2**) Cs_2CO_3 (1.5 equiv) and ^{i}Pr$_2$NEt (0.5 equiv) were added, the resulting reaction mixture was stirred at 35 °C for 12 h.

Racemic **4aa**: (All racemic samples were filtered with nylon filter before injection)

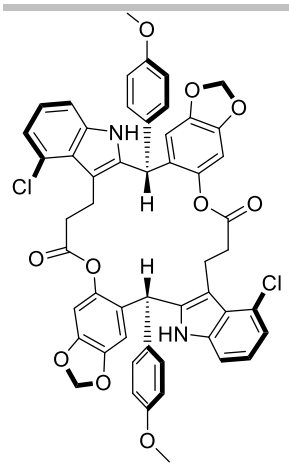


	Retention Time	Area	% Area
1	5.407	21702453	42.83
2	6.522	7274857	14.36
3	10.388	21688299	42.81

Chiral **4aa:**



	Retention Time	Area	% Area
1	5.430	33250	0.20
2	6.627	1041055	6.31
3	10.578	15414004	93.48



4ab

Compound 4ab

0.1 mmol (**2b**) scale reaction:

Result: white solid, 29.1 mg, 63% yield, 94:6 dr, 99% ee, m.p. 210 – 212 ℃; $[\alpha]_D^{20}$ = –29.9 (*c* = 0.32 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC[2] (Chiralcel OD-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 254 nm, $t_{r(minor)}$ =13.23 min, $t_{r(major)}$ = 18.40 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.72 (s, 2H), 7.18 – 7.11 (m, 2H), 7.09 – 7.00 (m, 4H), 6.97 (d, *J* = 8.8 Hz, 4H), 6.82 (d, *J* = 8.8 Hz, 4H), 6.64 (s, 2H), 6.47 (s, 2H), 6.00 – 5.93 (m, 4H), 5.82 (s, 2H), 3.78 (s, 6H), 3.45 – 3.33 (m, 2H), 3.16 – 3.02 (m, 2H), 2.96 – 2.77 (m, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.23, 158.69, 147.09, 145.86, 142.65, 136.52, 136.37, 132.76, 129.38, 126.56, 125.49, 125.10, 122.11, 120.78, 114.21, 110.91, 109.71, 108.44, 104.67, 101.92, 55.27, 40.86, 36.90, 19.79;

ESI-HRMS calcd for $[C_{52}H_{40}{}^{34.9689}Cl_2N_2O_{10}+Na^+]$: 945.1952, found 945.1929;

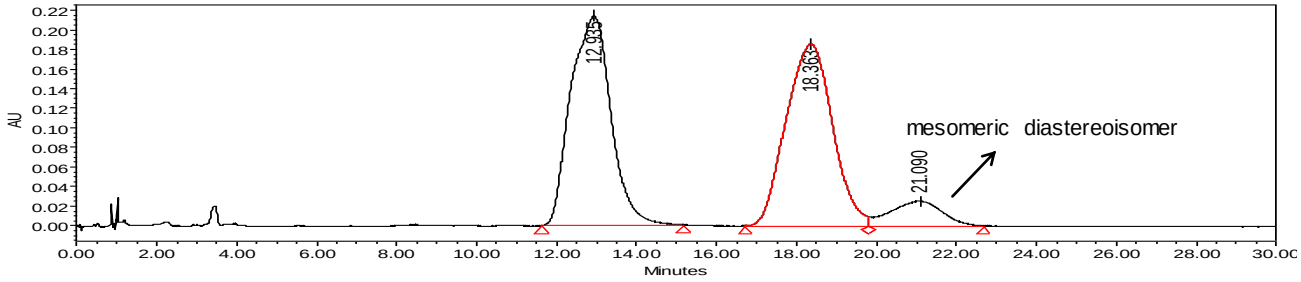
ESI-HRMS calcd for $[C_{52}H_{40}{}^{34.9689}Cl^{36.9659}Cl\ N_2O_{10}+Na^+]$: 947.1923, found 947.1918;

ESI-HRMS calcd for $[C_{52}H_{40}{}^{36.9659}Cl_2N_2O_{10}+Na^+]$: 949.1893, found 949.1899;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3402, 2957, 2923, 2853, 1751, 1610, 1506, 1479, 1450, 1426, 1371, 1324, 1254, 1179, 1121, 1031, 934, 869, 797, 735, 700, 566, 525.

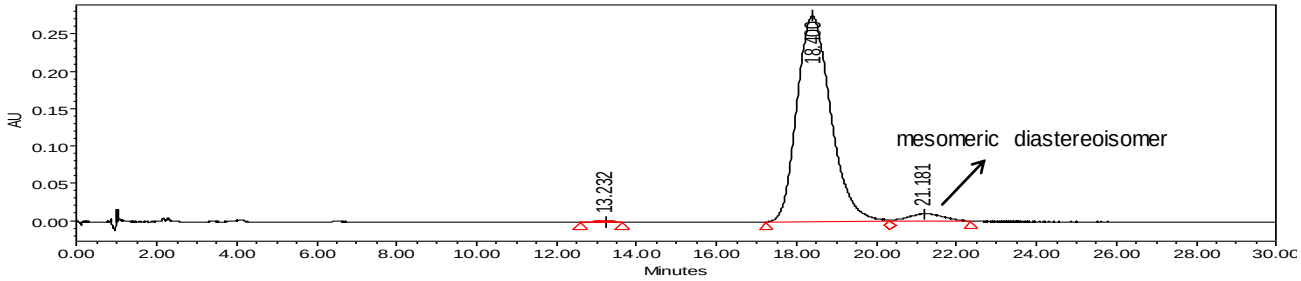
Reaction time: (**Step 1**) 47 h; (**Step 2**) 10 h.

Racemic **4ab**:

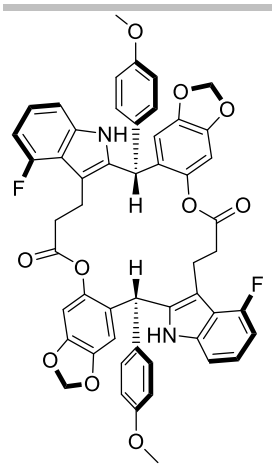


	Retention Time	Area	% Area
1	12.935	14966036	46.34
2	18.363	15029008	46.54
3	21.090	2299726	7.12

Chiral **4ab:**



	Retention Time	Area	% Area
1	13.232	13786	0.08
2	18.400	16287347	96.07
3	21.181	651726	3.84



4ac

Compound 4ac

0.1 mmol (**2c**) scale reaction:

Result: yellow solid, 25.8 mg, 58% yield, 93:7 dr, 99% ee, m.p. 241 – 242 ℃; $[\alpha]_D^{20}$ = –68.4 (*c* = 0.32 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel OD-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 254 nm, $t_r(_{minor})$ = 8.03 min, $t_r(_{major})$ = 10.05 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (s, 2H), 7.06 – 7.00 (m, 4H), 6.95 (d, *J* = 8.4 Hz, 4H), 6.81 (d, *J* = 8.4 Hz, 4H), 6.78 – 6.70 (m, 2H), 6.58 (s, 2H), 6.50 (s, 2H), 6.01 – 5.93 (m, 4H), 5.77 (s, 2H), 3.78 (s, 6H), 3.27 – 3.15 (m, 2H), 3.09 – 2.97 (m, 2H), 2.95 – 2.75 (m, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.37, 158.61, 156.62 (*J* = 243.8 Hz), 147.08, 145.88, 142.69, 137.86 (*J* = 11.7 Hz), 134.92, 133.09, 129.34, 126.82, 122.09 (*J* = 7.9 Hz), 116.95 (*J* = 19.7 Hz), 114.13, 109.07 (*J* = 2.7 Hz), 108.42, 107.08 (*J* = 3.0 Hz), 104.90 (*J* = 19.2 Hz), 104.58, 101.92, 55.26, 40.70, 35.78, 20.29;

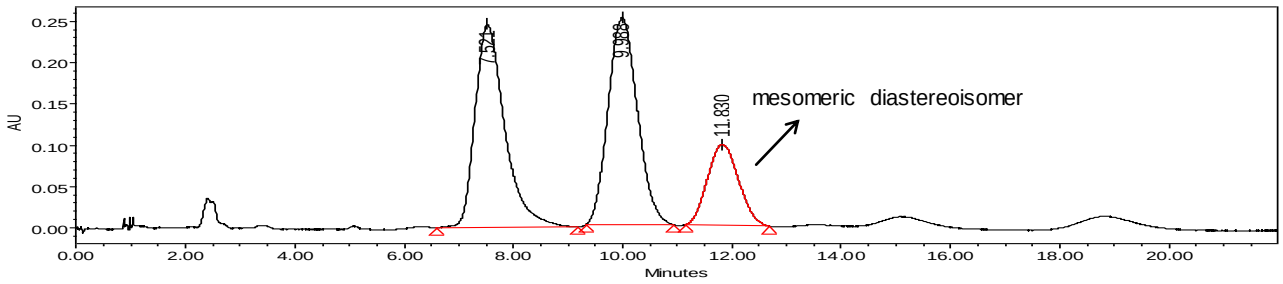
^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –124.43;

ESI-HRMS calcd for [$C_{52}H_{40}F_2N_2O_{10}$+Na$^+$]: 913.2543, found 913.2537;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3407, 2924, 2854, 1755, 1631, 1610, 1584, 1507, 1481, 1449, 1371, 1337, 1244, 1146, 1036, 934, 872, 777, 737, 700, 567, 478.

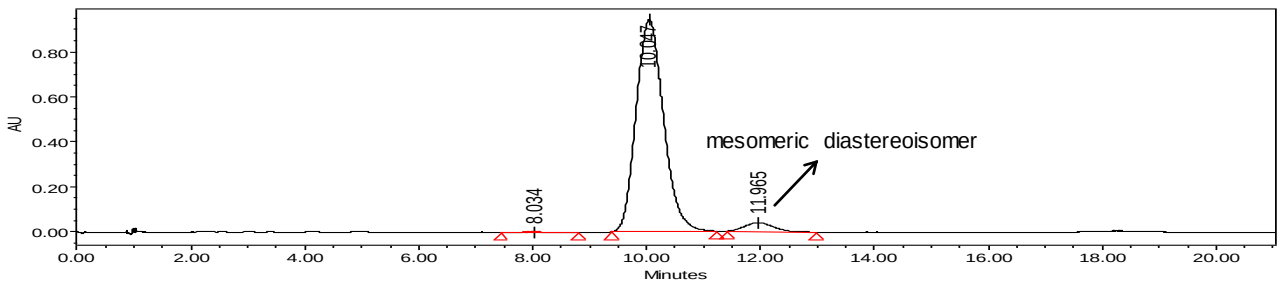
Reaction time: (**Step 1**) 47 h; (**Step 2**) 10 h.

Racemic **4ac**:

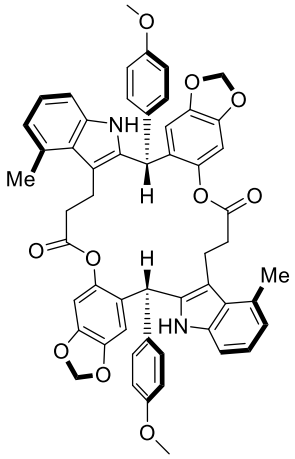


	Retention Time	Area	% Area
1	7.521	9335462	41.36
2	9.988	9363302	41.48
3	11.830	3874129	17.16

Chiral **4ac**:



	Retention Time	Area	% Area
1	8.034	37436	0.11
2	10.047	31516349	95.79
3	11.965	1346867	4.09



4ad

Compound 4ad

0.1 mmol (**2d**) scale reaction:

Result: yellow solid, 27.8 mg, 63% yield, 93:7 dr, 99% ee, m.p. 244 – 246 ℃; $[\alpha]_D^{20}$ = +19.1 (*c* = 0.32 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel IC-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 254 nm, $t_r(_{minor})$ = 5.46 min, $t_r(_{major})$ = 7.32 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (s, 2H), 7.13 – 7.08 (m, 2H), 7.06 – 6.98 (m, 6H), 6.88 – 6.80 (m, 6H), 6.63 (s, 2H), 6.51 (s, 2H), 5.99 – 5.95 (m, 4H), 5.88 (s, 2H), 3.78 (s, 6H), 3.29 – 3.16 (m, 2H), 3.15 – 3.04 (m, 2H), 2.82 – 2.68 (m, 4H), 2.67 (s, 6H);

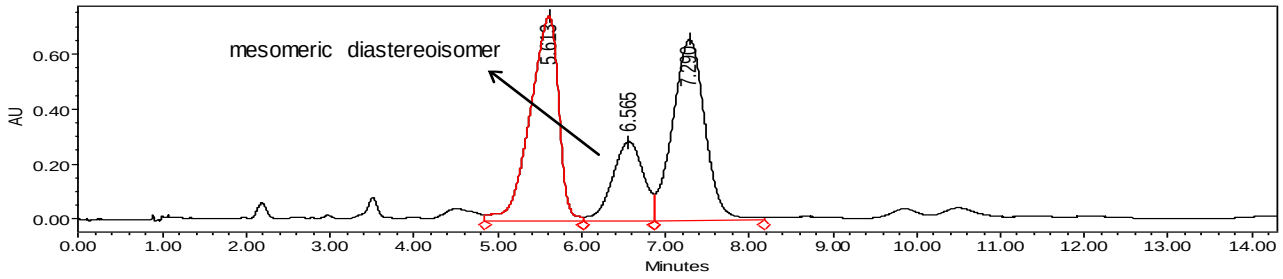
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.98, 158.64, 146.90, 145.77, 142.40, 135.41, 135.19, 132.82, 129.94, 129.41, 126.78, 126.59, 121.63, 121.57, 114.20, 111.48, 108.91, 108.61, 104.44, 101.85, 55.26, 40.96, 37.57, 20.72, 20.02;

ESI-HRMS calcd for [$C_{54}H_{46}N_2O_{10}$+Na$^+$]: 905.3045, found 905.3040;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3416, 2956, 2924, 2855, 1754, 1610, 1582, 1507, 1480, 1447, 1371, 1334, 1251, 1179, 1147, 1125, 1035, 932, 872, 801, 742, 702, 537, 480.

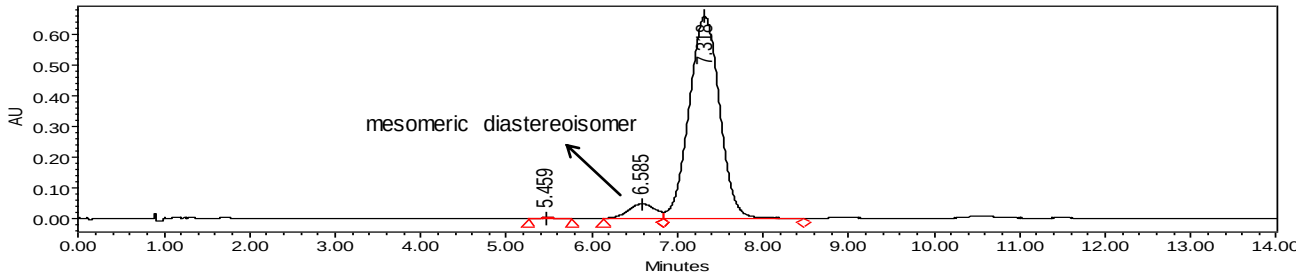
Reaction time: (**Step 1**) 14 h; (**Step 2**) 9 h.

Racemic **4ad**:

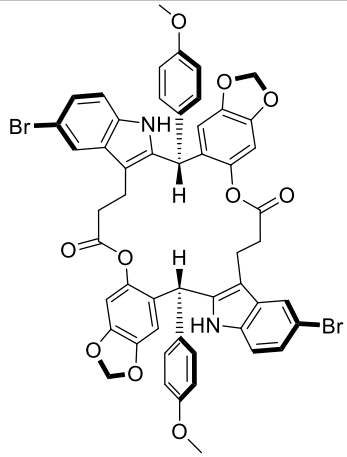


	Retention Time	Area	% Area
1	5.613	17685412	41.36
2	6.565	7390455	17.28
3	7.290	17686823	41.36

Chiral **4ad**:



	Retention Time	Area	% Area
1	5.459	26246	0.15
2	6.585	1024826	5.92
3	7.318	16256670	93.93



4ae

Compound 4ae

0.1 mmol (**2e**) scale reaction:

Result: white solid, 24.3 mg, 48% yield, 91:9 dr, 99% ee, m.p. 253 – 255 ℃; $[\alpha]_D^{18}$ = –96.5 (*c* = 0.28 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC[2] (Chiralcel OD-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 230 nm, $t_r(_{minor})$ = 17.54 min, $t_r(_{major})$ = 29.87 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 – 7.59 (m, 4H), 7.24 – 7.18 (m, 2H), 7.15 – 7.08 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 4H), 6.80 (d, *J* = 8.4 Hz, 4H), 6.55 (s, 2H), 6.49 (s, 2H), 6.02 – 5.94 (m, 4H), 5.77 (s, 2H), 3.78 (s, 6H), 3.10 – 2.99 (m, 2H), 2.97 – 2.85 (m, 2H), 2.84 – 2.64 (m, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.38, 158.65, 147.15, 146.01, 142.58, 136.34, 133.72, 132.77, 129.96, 129.40, 126.61, 124.48, 120.78, 114.15, 113.00, 112.44, 110.07, 108.47, 104.46, 101.97, 55.27, 40.89, 34.78, 19.22;

ESI-HRMS calcd for $[C_{52}H_{40}{}^{78.9183}Br\ {}_2N_2O_{10}+Na^+]$: 1033.0942, found 1033.0923;

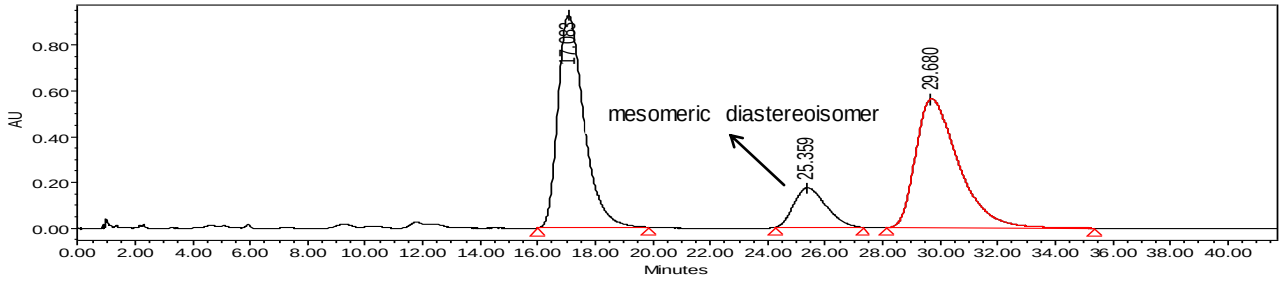
ESI-HRMS calcd for $[C_{52}H_{40}{}^{78.9183}Br\ {}^{80.9163}Br\ N_2O_{10}+Na^+]$: 1035.0921, found 1035.0916;

ESI-HRMS calcd for $[C_{52}H_{40}{}^{80.9163}Br\ {}_2N_2O_{10}+Na^+]$: 1037.0901, found 1037.0909;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3416, 2905, 2838, 1753, 1609, 1580, 1506, 1478, 1369, 1297, 1245, 1178, 1145, 1035, 932, 876, 795, 735, 703, 592, 528, 489, 430.

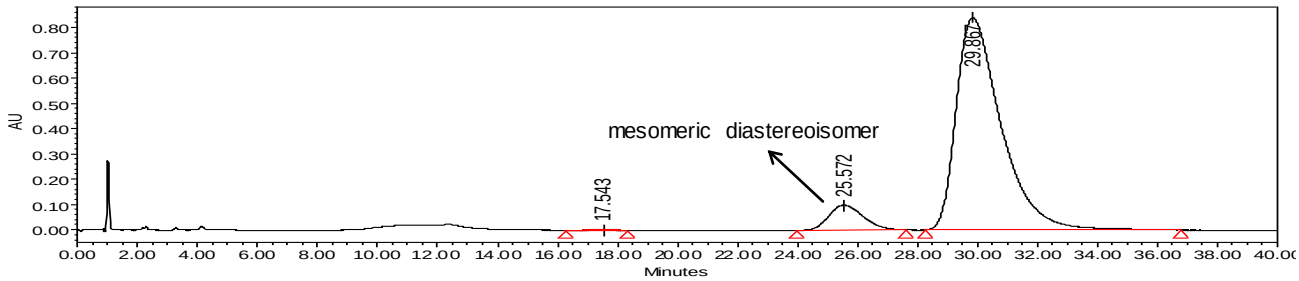
Reaction time: (**Step 1**) 30 h; (**Step 2**) 18 h.

Racemic **4ae**:

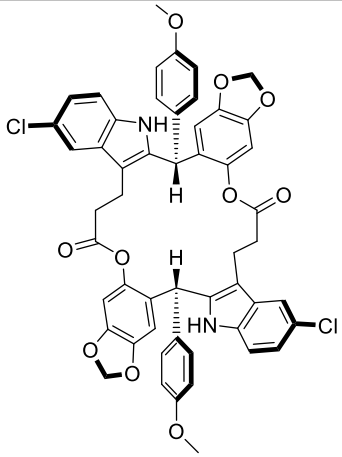


	Retention Time	Area	% Area
1	17.083	58578220	44.92
2	25.359	13346319	10.23
3	29.680	58490055	44.85

Chiral **4ae**:



	Retention Time	Area	% Area
1	17.543	86215	0.09
2	25.572	7833981	8.20
3	29.867	87657175	91.71



4af

Compound 4af

0.1 mmol (**2f**) scale reaction:

Result: yellow solid, 21.7 mg, 47% yield, 91:9 dr, 99% ee, m.p. 241 – 243 ℃; $[\alpha]_D^{20}$ = –100.4 (*c* = 0.24 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel OD-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 230 nm, $t_{r(minor)}$ = 13.34 min, $t_{r(major)}$ = 24.49 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (s, 2H), 7.53 – 7.45 (m, 2H), 7.20 – 7.13 (m, 2H), 7.12 – 7.05 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 4H), 6.80 (d, *J* = 8.8 Hz, 4H), 6.54 (s, 2H), 6.49 (s, 2H), 6.01 – 5.94 (m, 4H), 5.77 (s, 2H), 3.78 (s, 6H), 3.12 – 3.00 (m, 2H), 2.98 – 2.87 (m, 2H), 2.85 – 2.65 (m, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.39, 158.65, 147.14, 146.00, 142.58, 136.51, 133.45, 132.80, 129.40, 129.31, 126.64, 125.48, 121.92, 117.70, 114.15, 111.99, 110.16, 108.48, 104.46, 101.96, 55.27, 40.93, 34.77, 19.25;

ESI-HRMS calcd for $[C_{52}H_{40}{}^{34.9689}Cl_2N_2O_{10}+Na^+]$: 945.1952, found 945.1940;

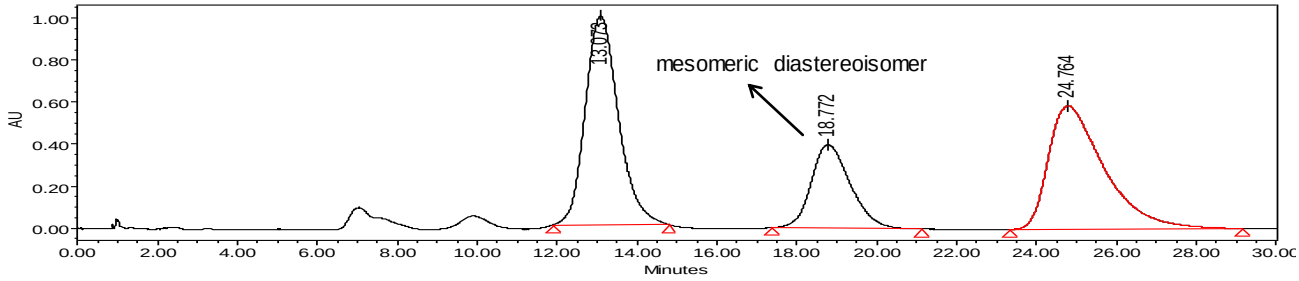
ESI-HRMS calcd for $[C_{52}H_{40}{}^{34.9689}Cl^{36.9659}Cl\ N_2O_{10}+Na^+]$: 947.1923, found 947.1930;

ESI-HRMS calcd for $[C_{52}H_{40}{}^{36.9659}Cl_2N_2O_{10}+Na^+]$: 949.1893, found 949.1899;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3412, 2919, 2854, 1751, 1608, 1579, 1506, 1477, 1368, 1294, 1243, 1178, 1143, 1122, 1032, 930, 874, 795, 733, 702, 595, 530, 489, 457, 430.

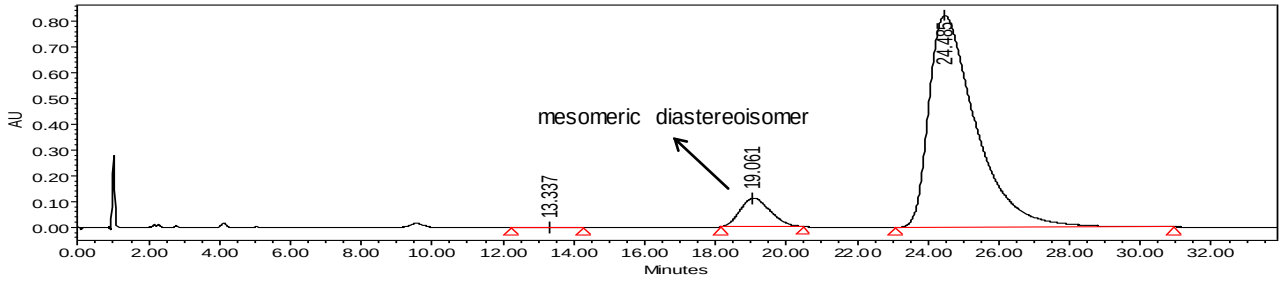
Reaction time: (**Step 1**) 30 h; (**Step 2**) 18 h.

Racemic **4af**:

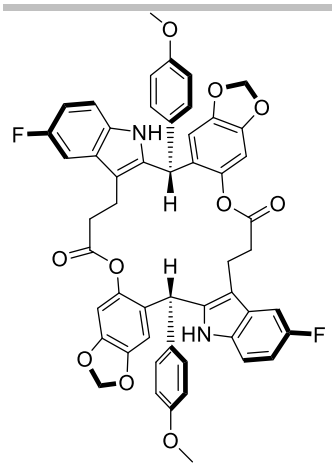


	Retention Time	Area	% Area
1	13.073	57467029	40.60
2	18.772	27058182	19.11
3	24.764	57033761	40.29

Chiral **4af**:



	Retention Time	Area	% Area
1	13.337	100877	0.12
2	19.061	6574654	7.97
3	24.485	75789063	91.90



4ag

Compound 4ag

0.1 mmol (**2g**) scale reaction:

Result: white solid, 25.4 mg, 57% yield, 93:7 dr, 99% ee, m.p. 234 – 235 ℃; $[\alpha]_D^{20}$ = –88.5 (*c* = 0.31 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC[2] (Chiralcel OD-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 254 nm, $t_r(_{minor})$ = 7.73 min, $t_r(_{major})$ = 12.23 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (s, 2H), 7.20 – 7.13 (m, 4H), 6.95 (d, *J* = 8.4 Hz, 4H), 6.92 – 6.84 (m, 2H), 6.81 (d, *J* = 8.4 Hz, 4H), 6.57 – 6.40 (m, 4H), 5.98 (d, *J* = 6.0 Hz, 4H), 5.78 (s, 2H), 3.78 (s, 6H), 3.09 – 2.99 (m, 2H), 2.98 – 2.88 (m, 2H), 2.82 – 2.67 (m, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.45, 157.90 (*J* = 233.5 Hz), 158.62, 147.07, 145.96, 142.55, 136.90, 132.87, 131.60, 129.42, 128.61 (*J* = 9.4 Hz), 126.71, 114.13, 111.61 (*J* = 9.5 Hz), 110.58 (*J* = 4.5 Hz), 109.87 (*J* = 26.0 Hz), 108.52, 104.42, 103.21 (*J* = 23.4 Hz), 101.93, 55.26, 41.00, 34.71, 19.37;

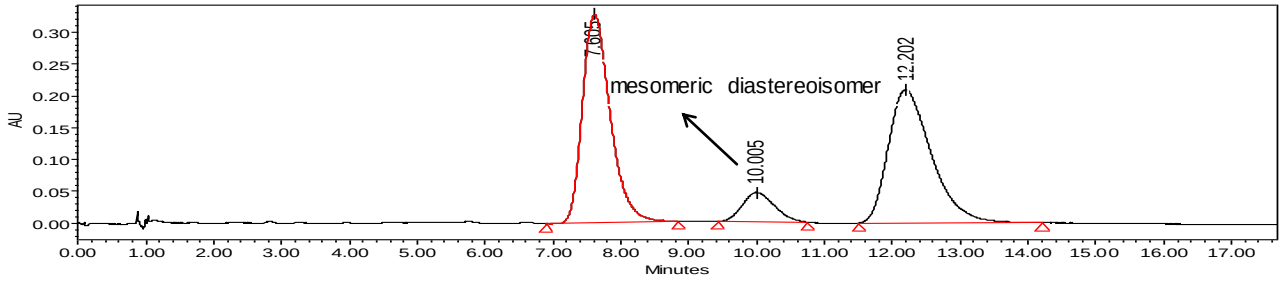
^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –124.06;

ESI-HRMS calcd for [$C_{52}H_{40}F_2N_2O_{10}$+Na^+]: 913.2543, found 913.2540;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3408, 2923, 2854, 2389, 2308, 2110, 1748, 1609, 1583, 1507, 1480, 1452, 1369, 1255, 1178, 1144, 1123, 1092, 1031, 931, 854, 797, 734, 701, 607, 538, 471, 434.

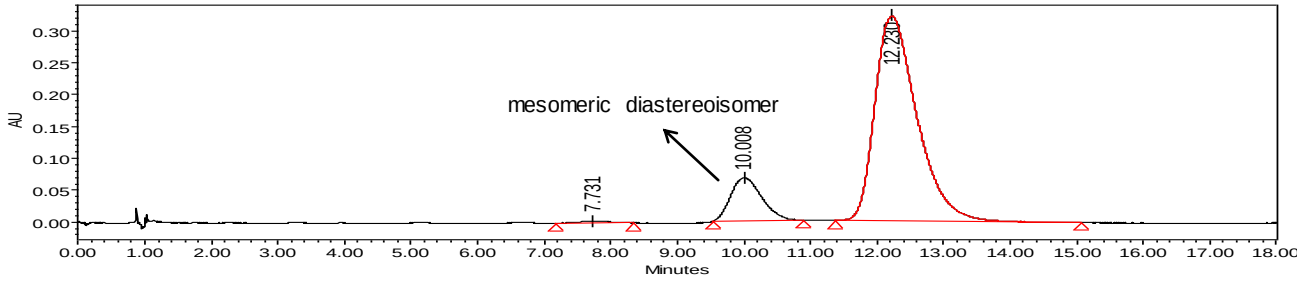
Reaction time: (**Step 1**) 14 h; (**Step 2**) 9 h.

Racemic **4ag**:

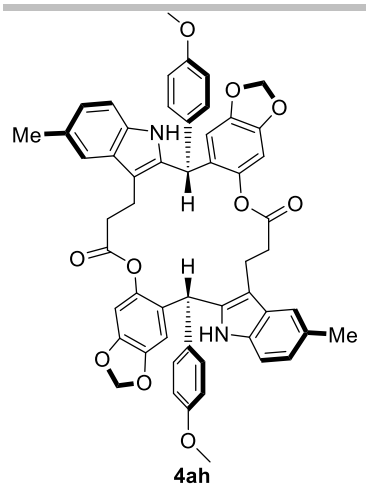


	Retention Time	Area	% Area
1	7.605	9328993	46.46
2	10.005	1493382	7.44
3	12.202	9256499	46.10

Chiral **4ag**:



	Retention Time	Area	% Area
1	7.731	93969	0.57
2	10.008	2194664	13.34
3	12.230	14162320	86.09



4ah

Compound 4ah

0.1 mmol (**2h**) scale reaction:

Result: yellow solid, 26.5 mg, 60% yield, 91:9 dr, 99% ee, m.p. 238 – 240 ℃; $[\alpha]_D^{17}$ = –47.4 (*c* = 0.34 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC[2] (Chiralcel IC-3, CO_2/MeOH = 70/30, flow rate = 1.5 mL/min, λ = 230 nm, t_r(minor) = 9.37 min, t_r(major) = 20.75 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (s, 2H), 7.34 (s, 2H), 7.20 – 7.12 (m, 2H), 7.03 – 6.91 (m, 6H), 6.84 – 6.75 (m, 4H), 6.54 (d, *J* = 3.2 Hz, 4H), 6.03 – 5.93 (m, 4H), 5.81 (s, 2H), 3.78 (s, 6H), 3.19 – 3.06 (m, 2H), 3.05 – 2.93 (m, 2H), 2.87 – 2.72 (m, 4H), 2.46 (s, 6H);

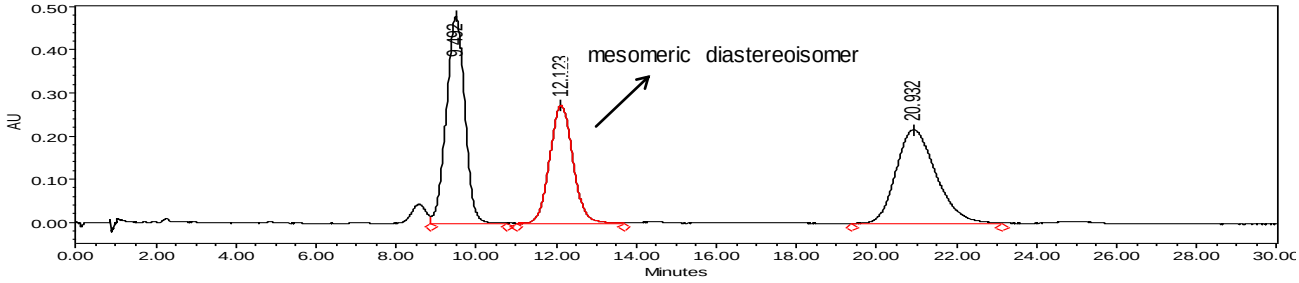
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.59, 158.52, 146.92, 145.85, 142.55, 134.97, 133.53, 133.24, 129.45, 128.98, 128.39, 127.05, 123.19, 117.95, 114.03, 110.68, 109.97, 108.59, 104.38, 101.86, 55.25, 40.85, 35.10, 21.48, 19.54;

ESI-HRMS calcd for [$C_{54}H_{46}N_2O_{10}$+Na^+]: 905.3045, found 905.3036;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3418, 2923, 2855, 2389, 2296, 1754, 1609, 1585, 1507, 1480, 1373, 1302, 1246, 1145, 1127, 1035, 932, 873, 796, 739, 698, 601, 539, 473, 435.

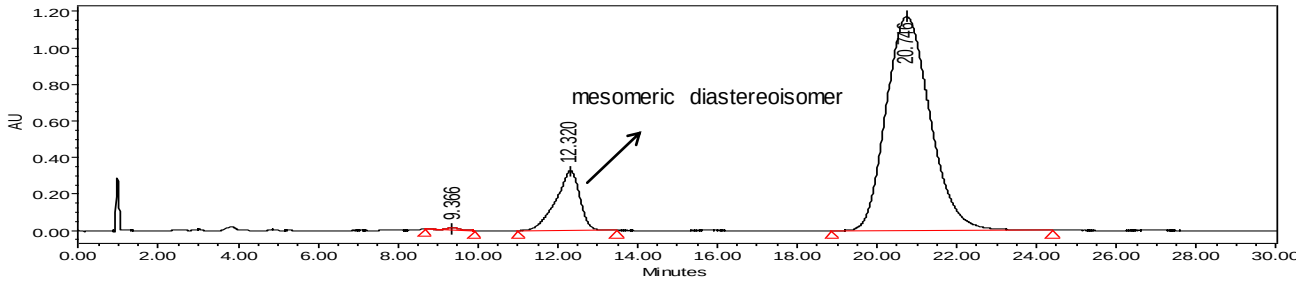
Reaction time: (**Step 1**) 11 h; (**Step 2**) 10 h.

Racemic **4ah**:

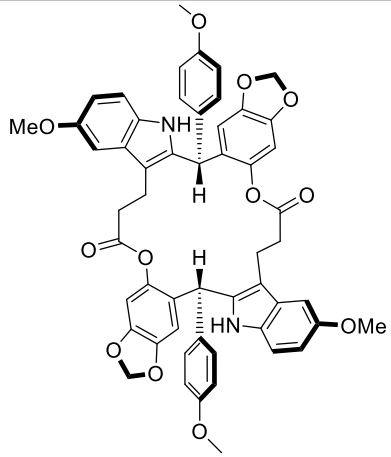


	Retention Time	Area	% Area
1	9.492	15397640	36.86
2	12.123	11067240	26.49
3	20.932	15310276	36.65

Chiral **4ah**:



	Retention Time	Area	% Area
1	9.366	239048	0.23
2	12.320	13696695	13.23
3	20.746	89573730	86.54



4ai

Compound 4ai

0.1 mmol (**2i**) scale reaction:

Result: yellow solid, 31.6 mg, 69% yield, 92:8 dr, 99% ee, m.p. 238 – 240 ℃; $[\alpha]_D^{19}$ = –80.5 (*c* = 0.31 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel OD-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 254 nm, $t_r(_{minor})$ = 11.45 min, $t_r(_{major})$ = 18.39 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (s, 2H), 7.19 – 7.12 (m, 2H), 7.00 – 6.93 (m, 6H), 6.84 – 6.78 (m, 6H), 6.54 (s, 4H), 6.00 – 5.94 (m, 4H), 5.81 (s, 2H), 3.86 (s, 6H), 3.78 (s, 6H), 3.15 – 3.04 (m, 2H), 3.03 – 2.92 (m, 2H), 2.84 – 2.70 (m, 4H);

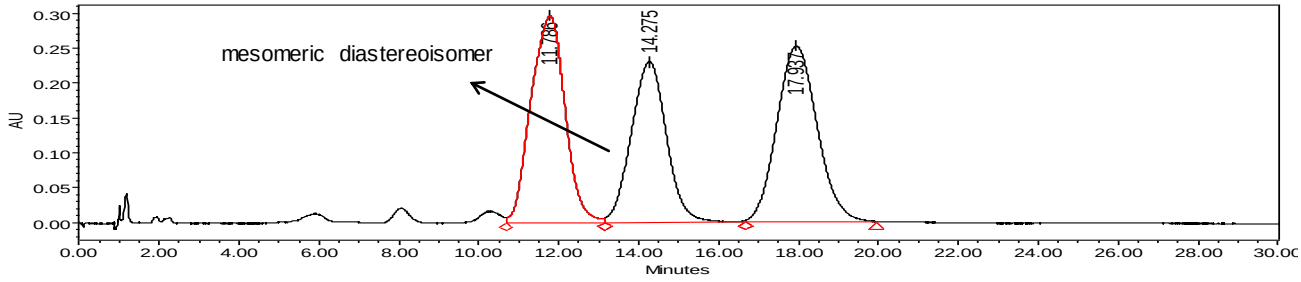
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.61, 158.55, 154.23, 146.94, 145.87, 142.49, 135.79, 133.13, 130.30, 129.44, 128.59, 126.95, 114.07, 111.72, 111.63, 110.24, 108.58, 104.35, 101.88, 100.28, 56.02, 55.25, 40.95, 34.94, 19.52;

ESI-HRMS calcd for [$C_{54}H_{46}N_2O_{12}$+Na^+]: 937.2943, found 937.2935;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3413, 2959, 2924, 2854, 2391, 2290, 1752, 1161, 1586, 1507, 1480, 1454, 1371, 1253, 1215, 1176, 1144, 1122, 1099, 1032, 931, 872, 798, 736, 699, 626, 531.

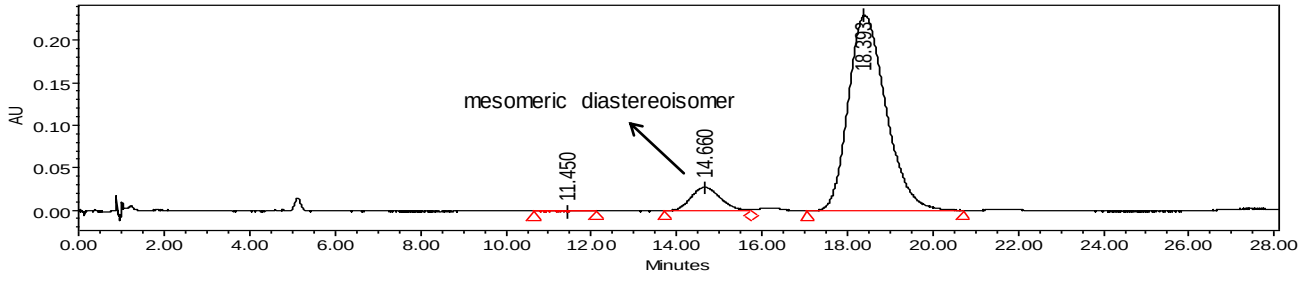
Reaction time: (**Step 1**) 5 h; (**Step 2**) 12 h.

Racemic **4ai**:

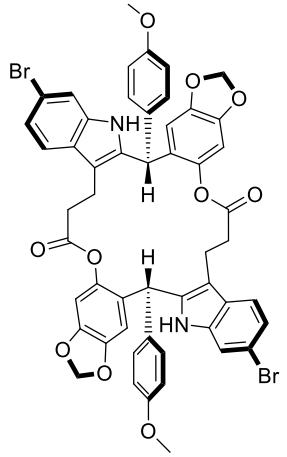


	Retention Time	Area	% Area
1	11.786	17527956	35.49
2	14.275	14128840	28.60
3	17.937	17737344	35.91

Chiral **4ai**:



	Retention Time	Area	% Area
1	11.450	18884	0.12
2	14.660	1371225	8.80
3	18.393	14196014	91.08



4aj

Compound 4aj

0.1 mmol (**2j**) scale reaction:

Result: white solid, 38.0 mg, 75% yield, 93:7 dr, 99% ee, m.p. 263 – 265 ℃; $[\alpha]_D^{20}$ = –68.2 (*c* = 0.33 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel IC-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 254 nm, $t_r(_{minor})$ = 6.47 min, $t_r(_{major})$ = 12.93 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (s, 2H), 7.43 – 7.40 (m, 2H), 7.39 – 7.35 (m, 2H), 7.22 – 7.14 (m, 2H), 6.93 (d, *J* = 8.8 Hz, 4H), 6.80 (d, *J* = 8.8 Hz, 4H), 6.55 – 6.43 (m, 4H), 6.00 – 5.98 (m, 4H), 5.76 (s, 2H), 3.77 (s, 6H), 3.12 – 3.00 (m, 2H), 2.99 – 2.87 (m, 2H), 2.84 – 2.67 (m, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.39, 158.64, 147.10, 145.99, 142.52, 135.88, 135.62, 132.71, 129.40, 127.06, 126.60, 122.96, 119.44, 115.12, 114.15, 113.95, 110.55, 108.47, 104.39, 101.96, 55.27, 40.91, 34.81, 19.29;

ESI-HRMS calcd for [$C_{52}H_{40}{}^{78.9183}Br_2N_2O_{10}$+Na$^+$]: 1033.0942, found 1033.0935;

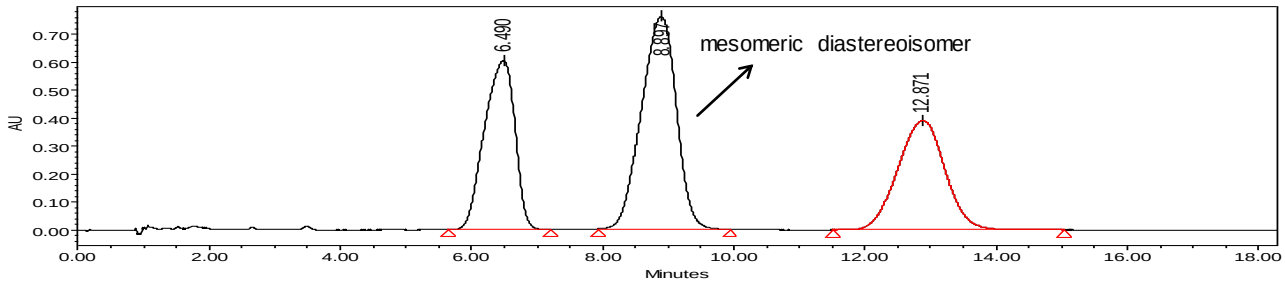
ESI-HRMS calcd for [$C_{52}H_{40}{}^{78.9183}Br\,{}^{80.9163}Br\,N_2O_{10}$+Na$^+$]: 1035.0921, found 1035.0925;

ESI-HRMS calcd for [$C_{52}H_{40}{}^{80.9163}Br_2N_2O_{10}$+Na$^+$]: 1037.0901, found 1037.0914;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3403, 2923, 2855, 2122, 1750, 1611, 1507, 1479, 1458, 1372, 1334, 1255, 1178, 1146, 1125, 1033, 932, 867, 799, 735, 703, 611, 568, 519, 487, 429.

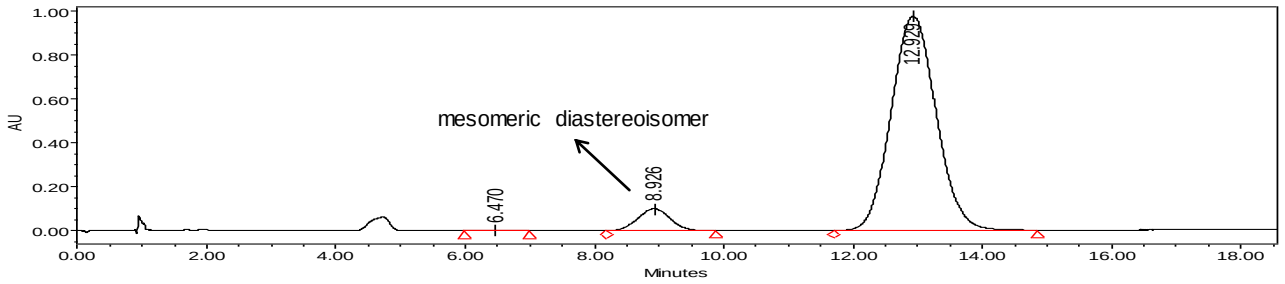
Reaction time: (**Step 1**) 29 h; (**Step 2**) 12 h.

Racemic **4aj**:

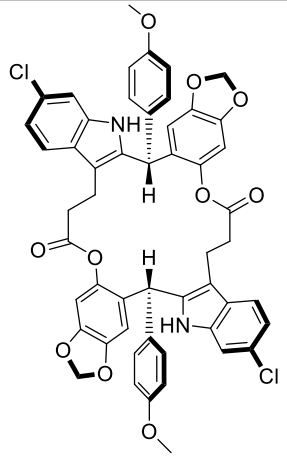


	Retention Time	Area	% Area
1	6.490	19554485	29.07
2	8.897	28194296	41.91
3	12.871	19528822	29.03

Chiral **4aj**:



	Retention Time	Area	% Area
1	6.470	87465	0.17
2	8.926	3517216	6.92
3	12.929	47231799	92.91



4ak

Compound 4ak

0.1 mmol (**2k**) scale reaction:

Result: white solid, 30.5 mg, 66% yield, 93:7 dr, 99% ee, m.p. 253 – 255 ℃; $[\alpha]_D^{28}$ = –66.3 (*c* = 0.46 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC[2] (Chiralcel IC-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 240 nm, $t_r(_{minor})$ = 5.06 min, $t_r(_{major})$ = 9.23 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (s, 2H), 7.45 – 7.38 (m, 2H), 7.25 – 7.22 (m, 2H), 7.10 – 7.03 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 4H), 6.80 (d, *J* = 8.8 Hz, 4H), 6.55 – 6.46 (m, 4H), 6.03 – 5.89 (m, 4H), 5.77 (s, 2H), 3.77 (s, 6H), 3.14 – 3.00 (m, 2H), 2.99 – 2.88 (m, 2H), 2.83 – 2.63 (m, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.43, 158.61, 147.07, 145.97, 142.50, 135.63, 135.45, 132.77, 129.40, 127.55, 126.73, 126.65, 120.36, 119.05, 114.12, 110.97, 110.48, 108.48, 104.37, 101.95, 55.27, 40.90, 34.82, 19.30;

ESI-HRMS calcd for $[C_{52}H_{40}{}^{34.9689}Cl_2N_2O_{10}+Na^+]$: 945.1952, found 945.1932;

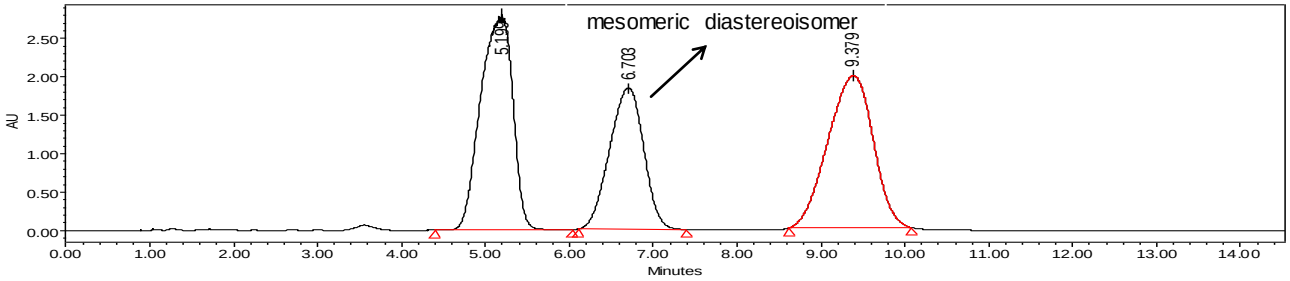
ESI-HRMS calcd for $[C_{52}H_{40}{}^{34.9689}Cl^{36.9659}Cl\ N_2O_{10}+Na^+]$: 947.1923, found 947.1922;

ESI-HRMS calcd for $[C_{52}H_{40}{}^{36.9659}Cl_2N_2O_{10}+Na^+]$: 949.1893, found 949.1903;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3415, 2908, 1754, 1610, 1583, 1507, 1480, 1460, 1424, 1367, 1336, 1245, 1179, 1146, 1126, 1064, 1035, 931, 875, 850, 799, 736, 702, 521.

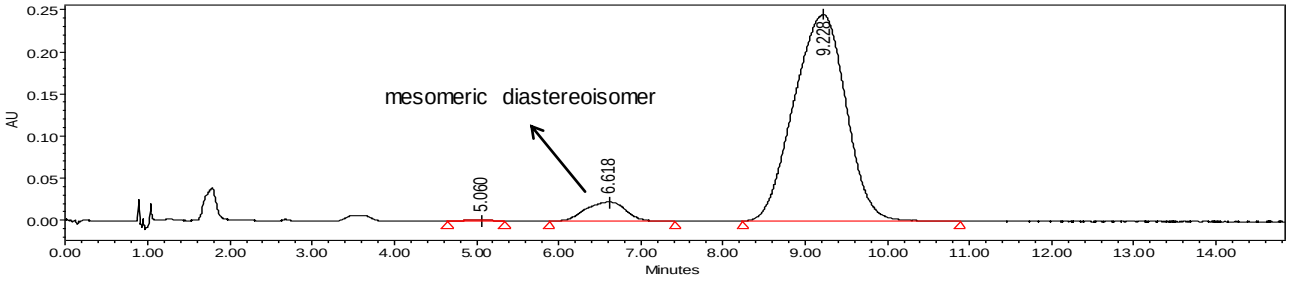
Reaction time: (**Step 1**) 12 h; (**Step 2**) 12 h.

Racemic **4ak**:

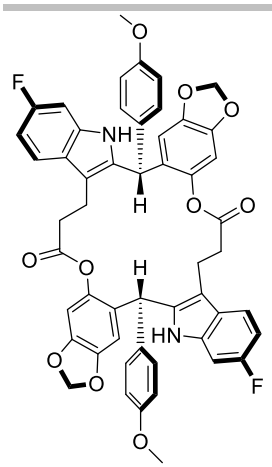


	Retention Time	Area	% Area
1	5.199	74200251	37.03
2	6.703	51934744	25.92
3	9.379	74218805	37.04

Racemic **4ak**:



	Retention Time	Area	% Area
1	5.060	25958	0.22
2	6.618	766390	6.59
3	9.228	10836040	93.19



4al

Compound 4al

0.1 mmol (**2l**) scale reaction:

Result: yellow solid, 26.7 mg, 60% yield, 93:7 dr, 99% ee, m.p. 239 – 241 ℃; $[\alpha]_D^{29}$ = –65.8 (*c* = 0.39 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel OD-3, CO_2/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 230 nm, t_r(minor) = 43.73 min, t_r(major) = 58.88 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (s, 2H), 7.46 – 7.38 (m, 2H), 6.99 – 6.91 (m, 6H), 6.90 – 6.84 (m, 2H), 6.80 (d, *J* = 8.8 Hz, 4H), 6.56 – 6.45 (m, 4H), 6.00 – 5.90 (m, 4H), 5.77 (s, 2H), 3.77 (s, 6H), 3.15 – 3.03 (m, 2H), 3.00 – 2.90 (m, 2H), 2.85 – 2.67 (m, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.48, 159.67 (*J* = 236.0 Hz), 158.55, 147.01, 145.94, 142.48, 135.09 (*J* = 5.5 Hz), 135.01 (*J* = 3.2 Hz), 132.97, 129.38, 126.82, 124.68, 118.86 (*J* = 10.2 Hz), 114.07, 110.35, 108.50, 108.26 (*J* = 24.1 Hz), 104.34, 101.93, 97.47 (*J* = 25.9 Hz), 55.25, 40.86, 34.91, 19.37;

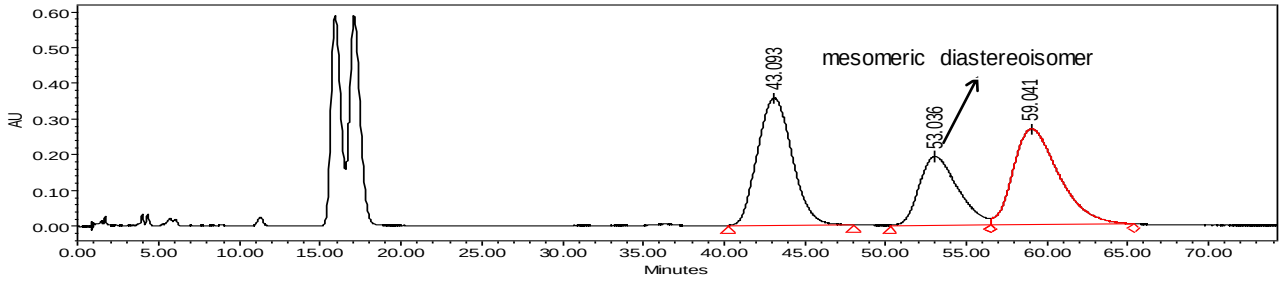
^{19}F{^{1}H} NMR (376 MHz, Chloroform-d) δ –121.29;

ESI-HRMS calcd for [$C_{52}H_{40}F_2N_2O_{10}$+Na^+]: 913.2543, found 913.2535;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3416, 2926, 1755, 1627, 1610, 1508, 1481, 1462, 1425, 1339, 1245, 1179, 1146, 1125, 1036, 960, 933, 875, 835, 797, 737, 524, 478.

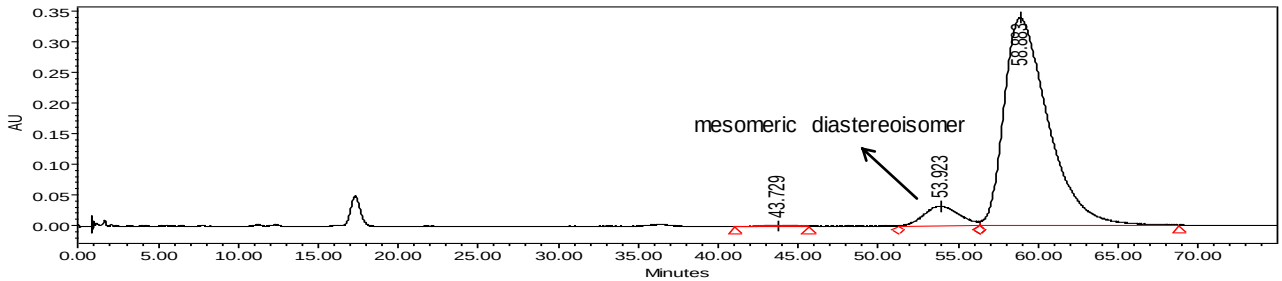
Reaction time: (**Step 1**) 12 h; (**Step 2**) 12 h.

Racemic **4al**:

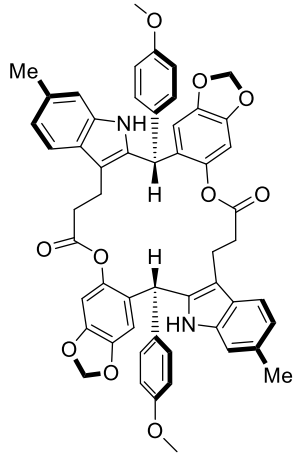


	Retention Time	Area	% Area
1	43.093	53122526	38.47
2	53.036	31876813	23.09
3	59.041	53071421	38.44

Chiral **4al**:



	Retention Time	Area	% Area
1	43.729	96398	0.14
2	53.923	5102438	7.25
3	58.883	65215842	92.62



4am

Compound 4am

0.1 mmol (**2m**) scale reaction:

Result: white solid, 26.0 mg, 59% yield, 92:8 dr, 99% ee, m.p. 242 – 245 ℃; $[\alpha]_D^{19}$ = –64.8 (*c* = 0.23 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel IC-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 254 nm, t_r(minor) = 5.37 min, t_r(major) = 11.70 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 (s, 2H), 7.45 – 7.40 (m, 2H), 7.07 (s, 2H), 6.99 – 6.90 (m, 6H), 6.79 (d, *J* = 8.4 Hz, 4H), 6.56 – 6.47 (m, 4H), 5.97 (d, *J* = 5.6 Hz, 4H), 5.80 (s, 2H), 3.77 (s, 6H), 3.17 – 3.06 (m, 2H), 3.05 – 2.93 (m, 2H), 2.84 – 2.70 (m, 4H), 2.44 (s, 6H);

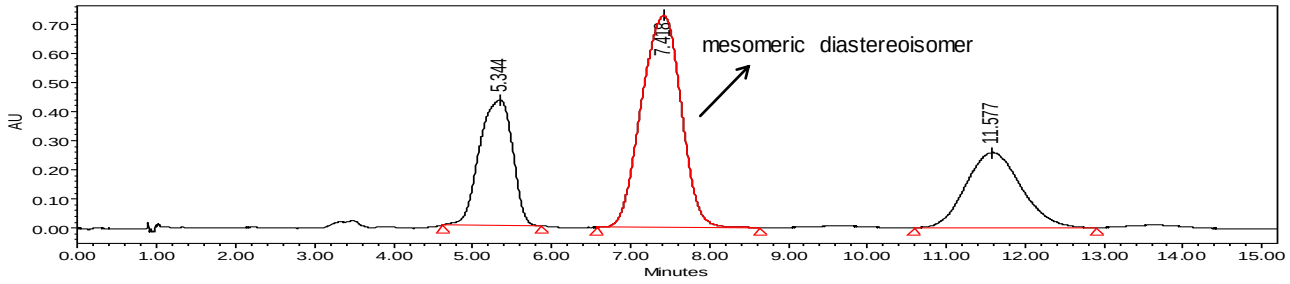
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.55, 158.52, 146.89, 145.82, 142.54, 135.69, 134.07, 133.29, 131.54, 129.44, 127.11, 125.98, 121.33, 117.96, 114.03, 111.00, 110.29, 108.56, 104.37, 101.85, 55.25, 40.83, 35.10, 21.64, 19.61;

ESI-HRMS calcd for [$C_{54}H_{46}N_2O_{10}$+Na^+]: 905.3045, found 905.3035;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3408, 2923, 2855, 2389, 2301, 1750, 1609, 1583, 1506, 1479, 1458, 1420, 1371, 1338, 1257, 1178, 1123, 1031, 932, 868, 799, 735, 701, 524, 475, 436.

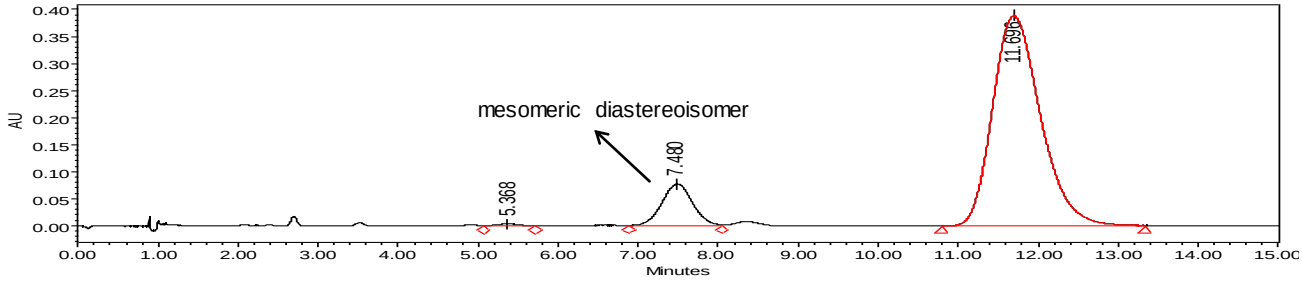
Reaction time: (**Step 1**) 11 h; (**Step 2**) 10 h.

Racemic **4am**:

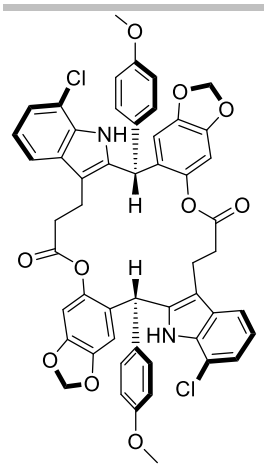


	Retention Time	Area	% Area
1	5.344	12526561	24.83
2	7.418	25425891	50.39
3	11.577	12501503	24.78

Chiral **4am**:



	Retention Time	Area	% Area
1	5.368	84933	0.46
2	7.480	2115092	11.53
3	11.696	16140257	88.00



4an

Compound 4an

0.1 mmol (**2n**) scale reaction:

Result: yellow solid, 32.3 mg, 70% yield, 94:6 dr, 99% ee, m.p. 229 – 230 ℃; $[\alpha]_D^{28}$ = –44.1 (*c* = 0.44 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel IE-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 230 nm, t_r(major) = 10.97 min, t_r(minor) = 13.91 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 (s, 2H), 7.47 – 7.40 (m, 2H), 7.17 – 7.10 (m, 2H), 7.08 – 7.01 (m, 2H), 6.97 (d, *J* = 8.8 Hz, 4H), 6.82 (d, *J* = 8.8 Hz, 4H), 6.58 – 6.54 (m, 4H), 6.04 – 5.94 (m, 4H), 5.82 (s, 2H), 3.79 (s, 6H), 3.15 – 3.05 (m, 2H), 3.04 – 2.92 (m, 2H), 2.78 (t, *J* = 8.4 Hz, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.40, 158.66, 147.14, 146.03, 142.51, 135.81, 132.70, 132.44, 129.58, 129.39, 126.51, 121.15, 120.54, 116.87, 116.48, 114.18, 111.64, 108.46, 104.38, 101.97, 55.26, 40.89, 34.85, 19.55;

ESI-HRMS calcd for [$C_{52}H_{40}{}^{34.9689}Cl_2N_2O_{10}$+$Na^+$]: 945.1952, found 945.1934;

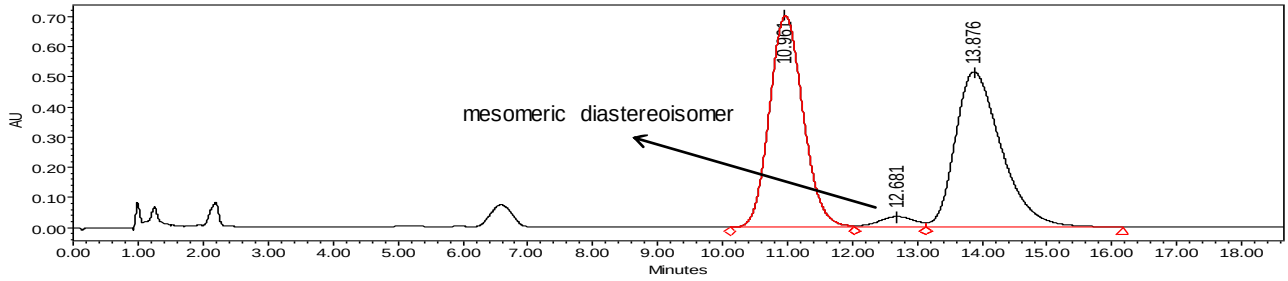
ESI-HRMS calcd for [$C_{52}H_{40}{}^{34.9689}Cl^{36.9659}ClN_2O_{10}$+$Na^+$]: 947.1923, found 947.1920;

ESI-HRMS calcd for [$C_{52}H_{40}{}^{36.9659}Cl_2N_2O_{10}$+$Na^+$]: 949.1893, found 949.1896;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3450, 2959, 2924, 2854, 1754, 1609, 1582, 1508, 1481, 1448, 1425, 1367, 1336, 1258, 1179, 1146, 1117, 1032, 931, 874, 797, 734, 702, 578, 535, 462.

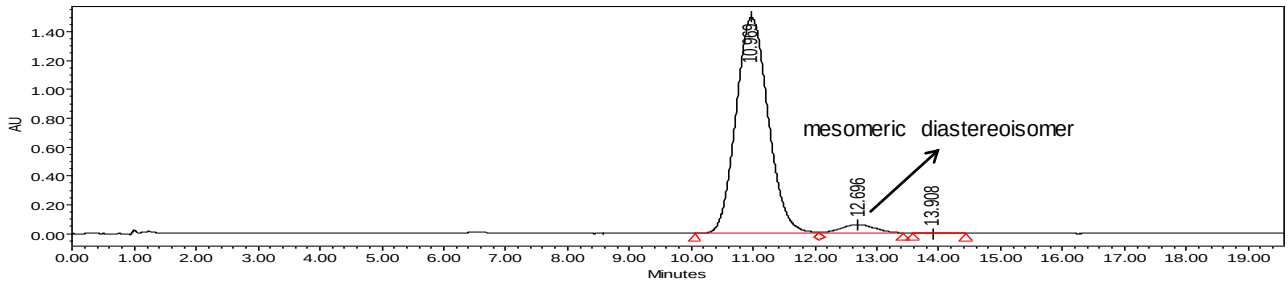
Reaction time: (**Step 1**) 59 h; (**Step 2**) 24 h.

Racemic **4an**:

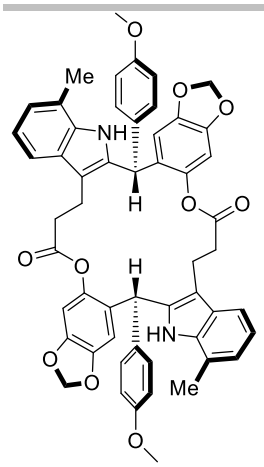


	Retention Time	Area	% Area
1	10.961	25327359	48.69
2	12.681	1370975	2.64
3	13.876	25320268	48.68

Chiral **4an**:



	Retention Time	Area	% Area
1	10.969	54064489	95.98
2	12.696	2252314	4.00
3	13.908	13443	0.02



4ao

Compound 4ao

0.1 mmol (**2o**) scale reaction:

Result: yellow solid, 22.1 mg, 50% yield, 93:7 dr, 99% ee, m.p. 232 – 235 ℃; $[\alpha]_D^{20}$ = –57.7 (*c* = 0.35 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel IC-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 230 nm, $t_{r(major)}$ = 14.63 min), $t_{r(minor)}$ = 17.26 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 (s, 2H), 7.42 – 7.38 (m, 2H), 7.08 – 7.03 (m, 2H), 7.02 – 6.94 (m, 6H), 6.81 (d, *J* = 8.8 Hz, 4H), 6.60 – 6.48 (m, 4H), 6.01 – 5.95 (m, 4H), 5.86 (s, 2H), 3.79 (s, 6H), 3.20 – 3.08 (m, 2H), 3.07 – 2.93 (m, 2H), 2.78 (t, *J* = 8.4 Hz, 4H), 2.39 (s, 6H);

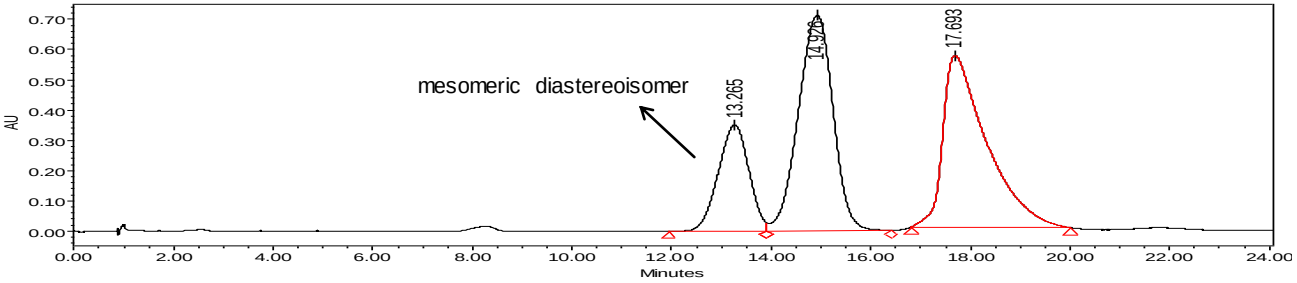
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.54, 158.54, 146.92, 145.83, 142.56, 134.82, 134.55, 133.17, 129.45, 127.72, 126.96, 122.38, 120.18, 119.95, 115.96, 114.06, 111.18, 108.50, 104.41, 101.87, 55.25, 40.91, 35.12, 19.64, 16.59;

ESI-HRMS calcd for [$C_{54}H_{46}N_2O_{10}$+Na$^+$]: 905.3045, found 905.3036;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3454, 3403, 2923, 2390, 2300, 1752, 1609, 1583, 1506, 1480, 1450, 1369, 1252, 1178, 1121, 1031, 931, 877, 798, 735, 701, 587, 536, 444.

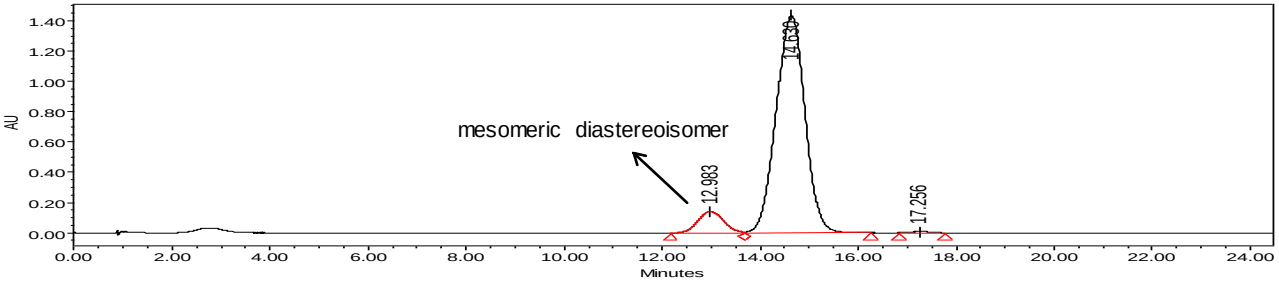
Reaction time: (**Step 1**) 24 h; (**Step 2**) 13 h.

Racemic **4ao**:

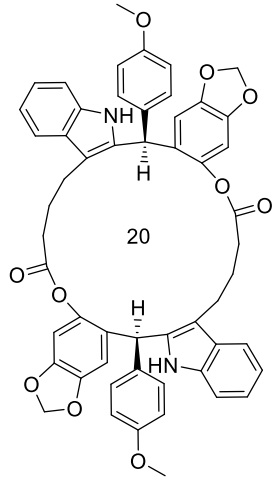


	Retention Time	Area	% Area
1	13.265	14949217	17.73
2	14.926	34645020	41.10
3	17.693	34698619	41.16

Chiral **4ao**:



	Retention Time	Area	% Area
1	12.983	5232539	8.12
2	14.630	58928369	91.49
3	17.256	251122	0.39



4ap

Compound 4ap

0.1 mmol (**2p**) scale reaction:

Result: yellow solid, 19.9 mg, 45% yield, 90:10 dr, 99% ee, m.p. 198 – 199 ℃; $[\alpha]_D^{20}$ = +34.3 (*c* = 0.23 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel IC-3, CO_2/MeOH = 70/30, flow rate = 1.5 mL/min, λ = 254 nm, t_r(minor) = 12.21 min, t_r(major) = 19.47 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 (s, 2H), 7.49 – 7.43 (m, 2H), 7.26 – 7.21 (m, 2H), 7.16 – 7.10 (m, 2H), 7.09 – 7.03 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 4H), 6.81 (d, *J* = 8.8 Hz, 4H), 6.57 (s, 2H), 6.45 (s, 2H), 5.96 (s, 4H), 5.77 (s, 2H), 3.77 (s, 6H), 2.73 – 2.57 (m, 4H), 2.56 – 2.48 (m, 2H), 2.48 – 2.32 (m, 2H), 1.98 – 1.78 (m, 4H);

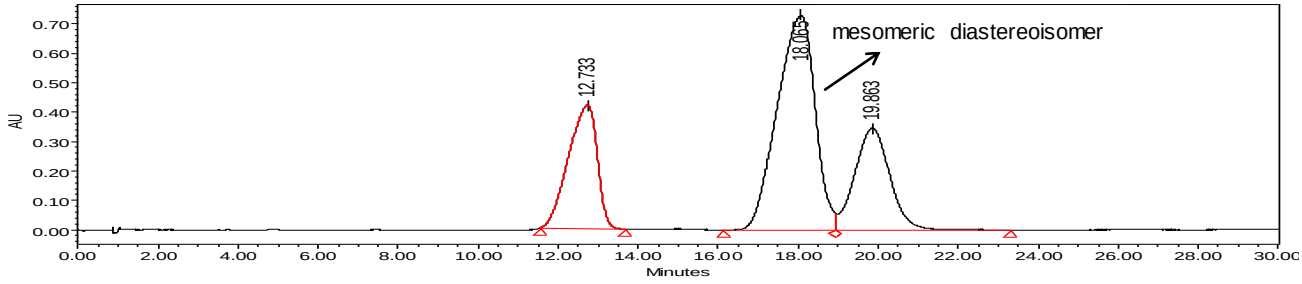
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 172.03, 158.56, 146.84, 145.70, 142.47, 135.22, 134.82, 132.99, 129.53, 128.61, 126.87, 121.49, 119.51, 118.49, 114.15, 111.51, 110.83, 108.79, 104.50, 101.81, 55.24, 41.51, 34.02, 25.45, 23.71;

ESI-HRMS calcd for [$C_{54}H_{46}N_2O_{10}$+Na$^+$]: 905.3045, found 905.3036;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3408, 2923, 2854, 2390, 2298, 1749, 1609, 1583, 1507, 1479, 1458, 1374, 1303, 1258, 1179, 1146, 1120, 1033, 931, 871, 797, 737, 704, 514, 488, 433.

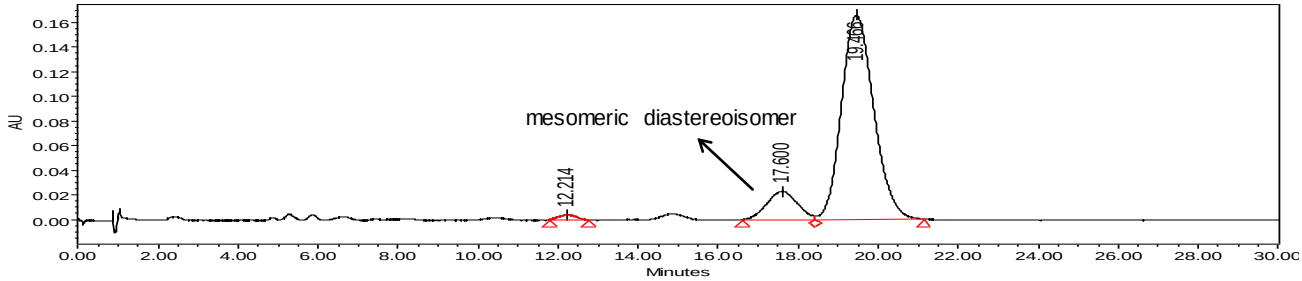
Reaction time: (**Step 1**) 18 h; (**Step 2**) 18 h.

Racemic **4ap**:

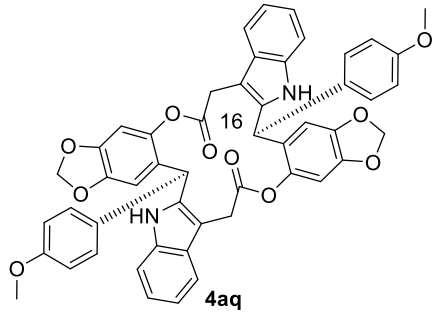


	Retention Time	Area	% Area
1	12.733	21173403	23.45
2	18.065	47974391	53.14
3	19.863	21125247	23.40

Chiral **4ap**:



	Retention Time	Area	% Area
1	12.214	127321	1.19
2	17.600	1233030	11.56
3	19.466	9304401	87.24



4aq

Compound 4aq

0.1 mmol (**2q**) scale reaction:

Result: yellow solid, 24.0 mg, 58% yield, >95:5 dr, 99% ee, m.p. 264 – 265 ℃; $[\alpha]_D^{28}$ = +39.9 (*c* = 0.72 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC[2] (Chiralcel ID-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 230 nm, $t_{r(major)}$ = 10.06 min, $t_{r(minor)}$ = 15.36 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 (s, 2H), 7.62 – 7.53 (m, 2H), 7.32 – 7.26 (m, 2H), 7.20 – 7.10 (m, 4H), 6.94 (d, *J* = 8.8 Hz, 4H), 6.77 (d, *J* = 8.8 Hz, 4H), 6.65 (s, 2H), 6.52 (s, 2H), 5.95 (s, 4H), 5.90 (s, 2H), 3.78 (s, 6H), 3.76 – 3.54 (m, 4H);

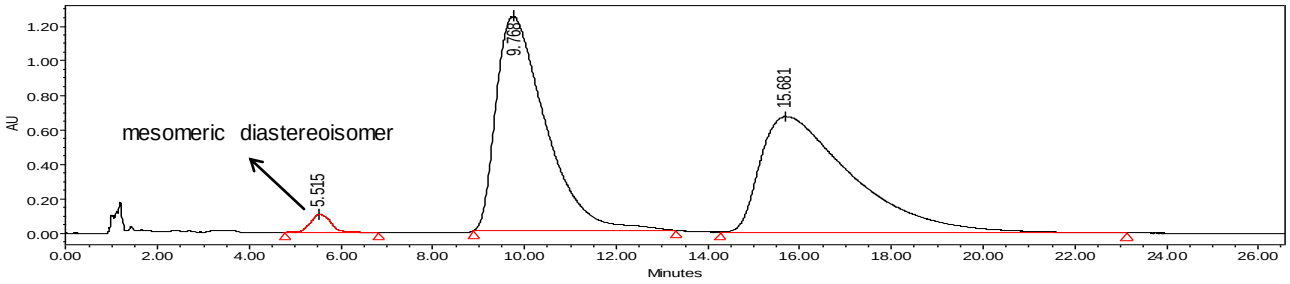
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.65, 158.66, 147.00, 145.80, 142.67, 136.77, 134.94, 132.47, 129.51, 128.79, 125.72, 121.85, 120.11, 118.10, 114.17, 111.05, 108.68, 104.66, 104.41, 101.86, 55.23, 41.34, 29.44;

ESI-HRMS calcd for [$C_{50}H_{38}N_2O_{10}$+Na^+]: 849.2419, found 849.2407;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3408, 2904, 2836, 1755, 1609, 1583, 1507, 1479, 1459, 1426, 1303, 1246, 1179, 1145, 1120, 1034, 932, 873, 851, 796, 741, 684, 516, 469.

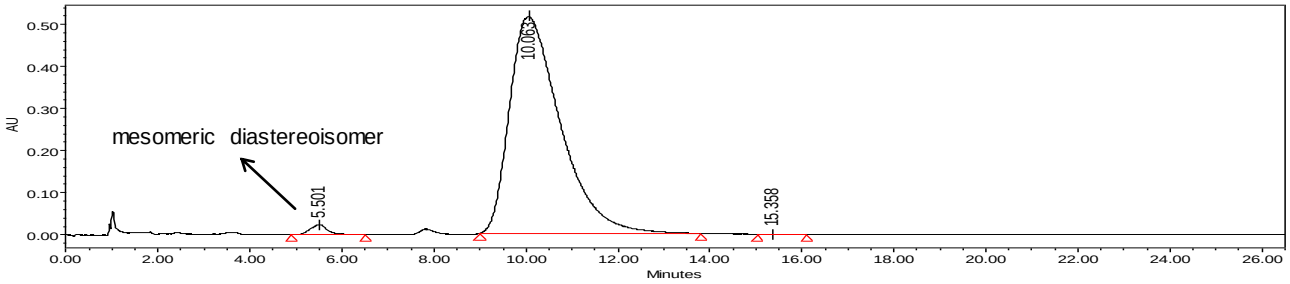
Reaction time: (**Step 1**) 12 h; (**Step 2**) 12 h.

Racemic **4aq**:

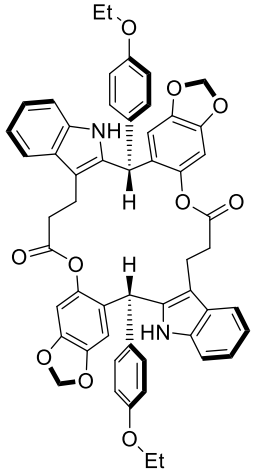


	Retention Time	Area	% Area
1	5.515	3298551	1.74
2	9.768	93201466	49.19
3	15.681	92990193	49.07

Chiral **4aq**:



	Retention Time	Area	% Area
1	5.501	580039	1.44
2	10.063	39651449	98.54
3	15.358	8284	0.02



4ba

Compound 4ba

0.1 mmol (**2a**) scale reaction:

Result: white solid, 30.0 mg, 68% yield, >95:5 dr, 99% ee, m.p. 184 – 187 ℃; $[\alpha]_D^{20}$ = −74.6 (*c* = 0.26 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel OD-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 254 nm, t_r(minor) = 11.40 min, t_r(major) = 21.31 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (s, 2H), 7.55 – 7.50 (m, 2H), 7.24 (s, 2H), 7.17 – 7.05 (m, 4H), 6.94 (d, *J* = 8.4 Hz, 4H), 6.77 (d, *J* = 8.4 Hz, 4H), 6.55 – 6.46 (m, 4H), 5.98 – 5.92 (m, 4H), 5.81 (s, 2H), 3.97 (q, *J* = 7.2 Hz, 4H), 3.18 – 3.06 (m, 2H), 3.06 – 2.92 (m, 2H), 2.85 – 2.69 (m, 4H), 1.37 (t, *J* = 6.8 Hz, 6H);

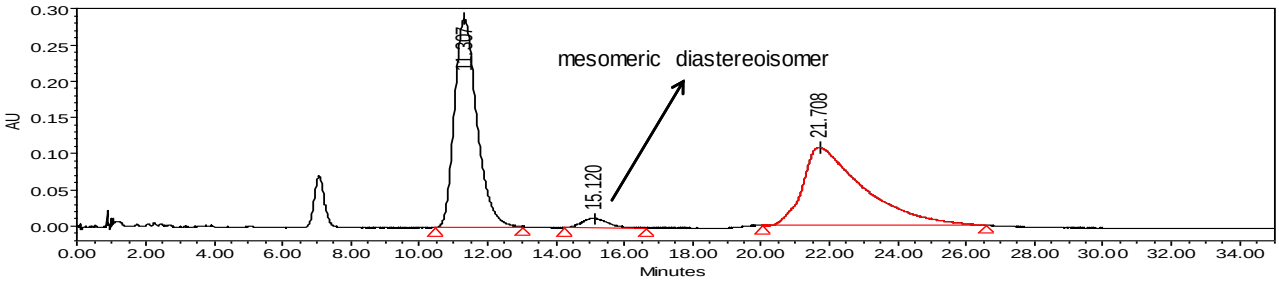
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.53, 157.94, 146.93, 145.86, 142.54, 135.23, 134.93, 132.96, 129.43, 128.19, 127.01, 121.66, 119.66, 118.25, 114.60, 110.98, 110.43, 108.59, 104.37, 101.87, 63.43, 40.88, 35.06, 19.52, 14.81;

ESI-HRMS calcd for [$C_{54}H_{46}N_2O_{10}$+Na$^+$]: 905.3045, found 905.3038;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3409, 2956, 2922, 2853, 2391, 2298, 2121, 1747, 1609, 1583, 1505, 1477, 1458, 1374, 1258, 1095, 1030, 928, 868, 798, 738, 700, 516, 486, 436.

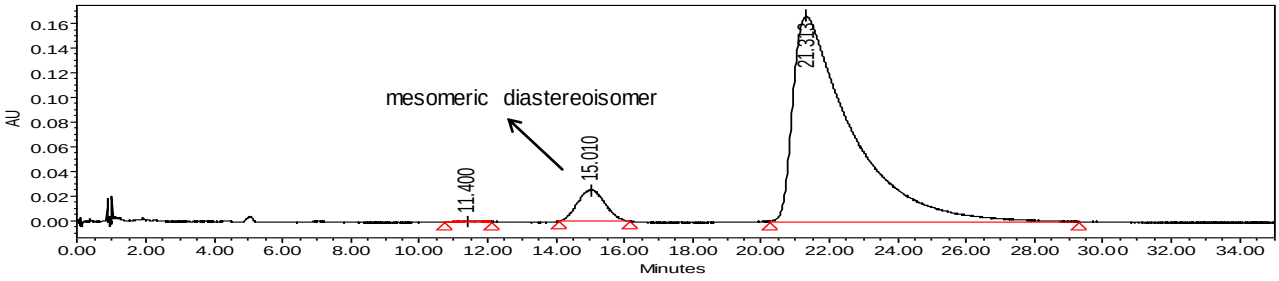
Reaction time: (**Step 1**) 4 h; (**Step 2**) 13 h.

Racemic **4ba**:

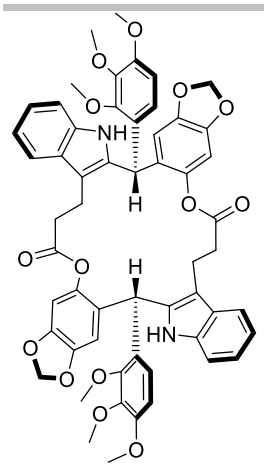


	Retention Time	Area	% Area
1	11.307	13240833	48.62
2	15.120	679061	2.49
3	21.708	13312251	48.88

Chiral **4ba**:



	Retention Time	Area	% Area
1	11.400	31980	0.15
2	15.010	1416866	6.73
3	21.313	19595989	93.12



4ca

Compound 4ca

0.1 mmol (**2a**) scale reaction:

Result: yellow solid, 27.8 mg, 57% yield, 92:8 dr, 99% ee, m.p. 230 – 233 ℃; $[\alpha]_D^{28}$ = +19.3 (*c* = 0.41 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel IE-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 230 nm, t_r(major) = 13.58 min, t_r(minor) = 24.09 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 (s, 2H), 7.58 – 7.48 (m, 2H), 7.32 – 7.27 (m, 2H), 7.17 – 7.08 (m, 4H), 6.69 – 6.55 (m, 6H), 6.47 (s, 2H), 6.22 (s, 2H), 5.98 – 5.92 (m, 4H), 3.87 – 3.80 (m, 12H), 3.52 (s, 6H), 3.27 – 3.16 (m, 2H), 3.15 – 3.03 (m, 2H), 2.88 – 2.75 (m, 4H);

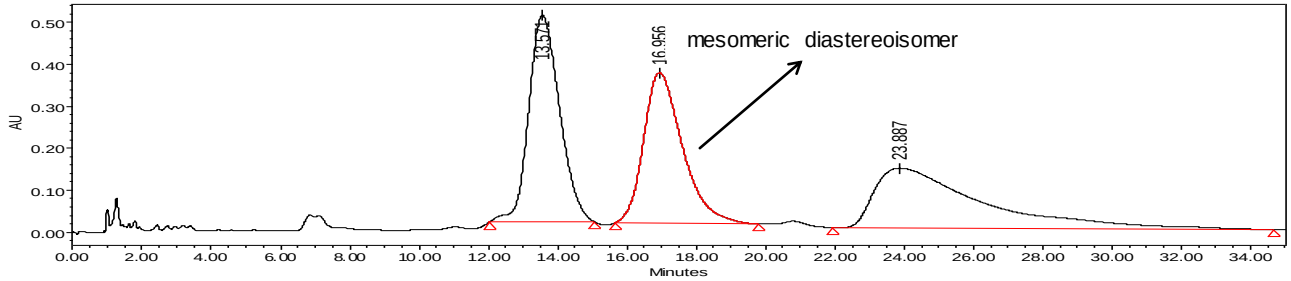
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.75, 153.12, 151.28, 146.44, 145.32, 142.53, 142.25, 135.38, 135.11, 128.35, 127.75, 126.47, 123.28, 121.44, 119.52, 118.13, 110.92, 109.98, 108.29, 106.97, 104.58, 101.75, 60.64, 60.53, 55.89, 36.73, 34.92, 19.48;

ESI-HRMS calcd for [$C_{56}H_{50}N_2O_{14}$+Na^+]: 997.3154, found 997.3141;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3374, 2924, 1753, 1598, 1481, 1460, 1415, 1373, 1259, 1148, 1121, 1093, 1034, 930, 870, 796, 735, 702, 591, 481, 436.

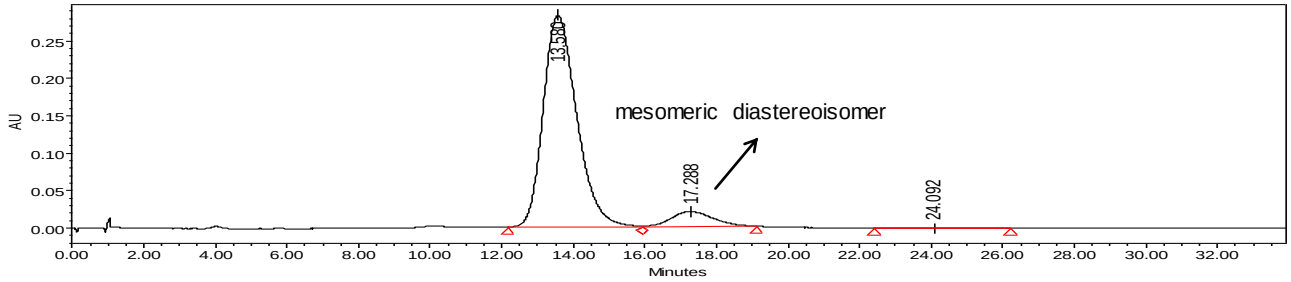
Reaction time: (**Step 1**) 42 h; (**Step 2**) 16 h.

Racemic **4ca**:

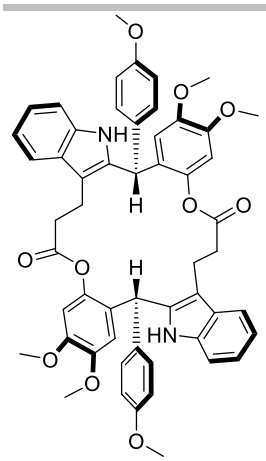


	Retention Time	Area	% Area
1	13.571	30577175	34.38
2	16.956	27969258	31.45
3	23.887	30385823	34.17

Chiral **4ca**:



	Retention Time	Area	% Area
1	13.580	18368481	91.85
2	17.288	1615507	8.08
3	24.092	14755	0.07



4da

Compound 4da

0.1 mmol (**2a**) scale reaction:

Result: white solid, 21.3 mg, 48% yield, 93:7 dr, 99% ee, m.p. 185 – 188 ℃; $[\alpha]_D^{29}$ = –77.7 (*c* = 0.29 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel OJ-3, CO_2/MeOH = 60/40, flow rate = 1.5 mL/min, λ = 230 nm, $t_{r(minor)}$ = 13.76 min, $t_{r(major)}$ = 25.15 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.54 (m, 4H), 7.29 – 7.23 (m, 2H), 7.18 – 7.08 (m, 4H), 7.00 (d, *J* = 8.0 Hz, 4H), 6.81 (d, *J* = 8.8 Hz, 4H), 6.55 (s, 2H), 6.44 (s, 2H), 5.84 (s, 2H), 3.79 (s, 6H), 3.77 (s, 6H), 3.69 (s, 6H), 3.24 – 3.10 (m, 2H), 3.05 – 2.94 (m, 2H), 2.92 – 2.82 (m, 2H), 2.79 – 2.66 (m, 2H);

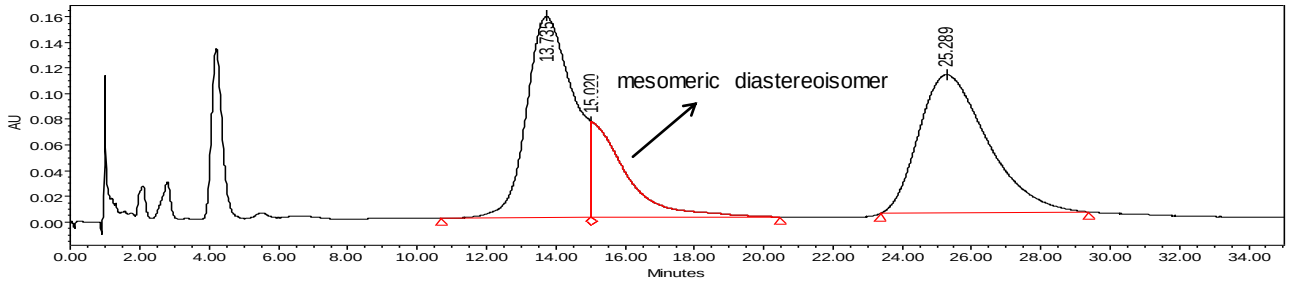
^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 171.91, 158.49, 148.61, 147.20, 142.09, 135.19, 135.11, 133.07, 129.61, 128.37, 125.52, 121.52, 119.61, 118.23, 113.97, 112.05, 110.97, 110.31, 106.51, 56.35, 56.03, 55.25, 40.72, 34.75, 19.57;

ESI-HRMS calcd for [$C_{54}H_{50}N_2O_{10}$+Na$^+$]: 909.3358, found 909.3356;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3376, 2930, 2834, 2362, 1752, 1610, 1582, 1508, 1458, 1441, 1398, 1342, 1302, 1246, 1206, 1175, 1123, 1090, 1031, 999, 912, 879, 863, 740, 700, 558, 518, 430.

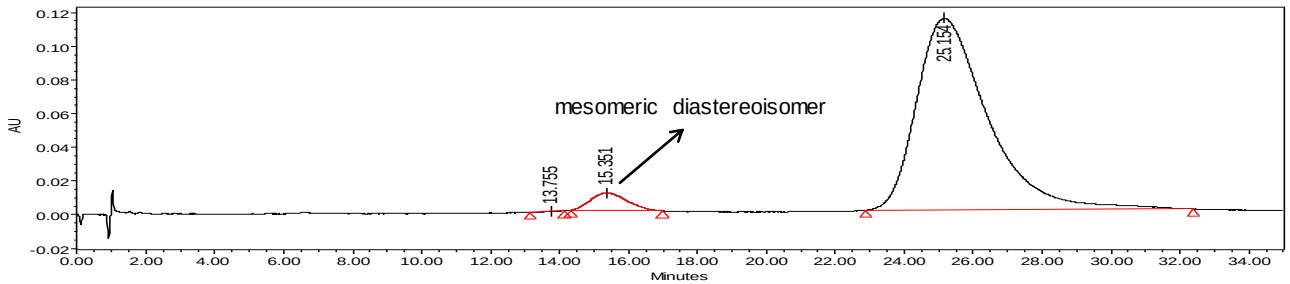
Reaction time: (**Step 1**) 12 h; (**Step 2**) 12 h.

Racemic **4da**:

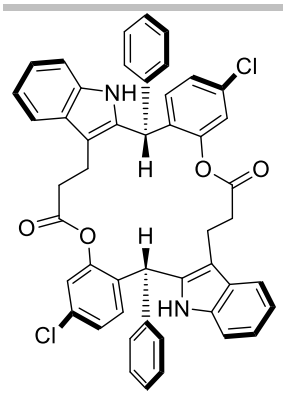


	Retention Time	Area	% Area
1	13.735	14835213	42.50
2	15.020	5222015	14.96
3	25.289	14848309	42.54

Chiral **4da**:



	Retention Time	Area	% Area
1	13.755	3028	0.02
2	15.351	761612	4.47
3	25.154	16291831	95.52



4ea

Compound 4ea

0.1 mmol (**2a**) scale reaction:

Result: white solid, 20.9 mg, 54% yield, 91:9 dr, 99% ee, m.p. 239 – 241 ℃; $[\alpha]_D^{28}$ = –41.2 (*c* = 0.31 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel OJ-3, CO_2/*i*-PrOH = 70/30, flow rate = 1.5 mL/min, λ = 270 nm, $t_{r(minor)}$ = 13.36 min, $t_{r(major)}$ = 23.16 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (s, 2H), 7.58 – 7.52 (m, 2H), 7.34 – 7.28 (m, 8H), 7.28 – 7.26 (m, 2H), 7.21 – 7.16 (m, 2H), 7.16 – 7.11 (m, 2H), 7.10 – 7.08 (m, 2H), 7.08 – 7.04 (m, 4H), 7.00 (d, *J* = 8.8 Hz, 2H), 6.00 (s, 2H), 3.22 – 3.08 (m, 2H), 3.08 – 2.98 (m, 2H), 2.85 – 2.75 (m, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.93, 147.21, 140.29, 136.01, 135.46, 133.66, 131.87, 129.71, 128.95, 128.57, 128.38, 128.01, 127.42, 124.38, 122.01, 119.87, 118.35, 111.15, 111.05, 41.96, 35.16, 19.45;

ESI-HRMS calcd for $[C_{48}H_{36}{}^{34.9689}Cl_2N_2O_4+Na^+]$: 797.1944, found 797.1932;

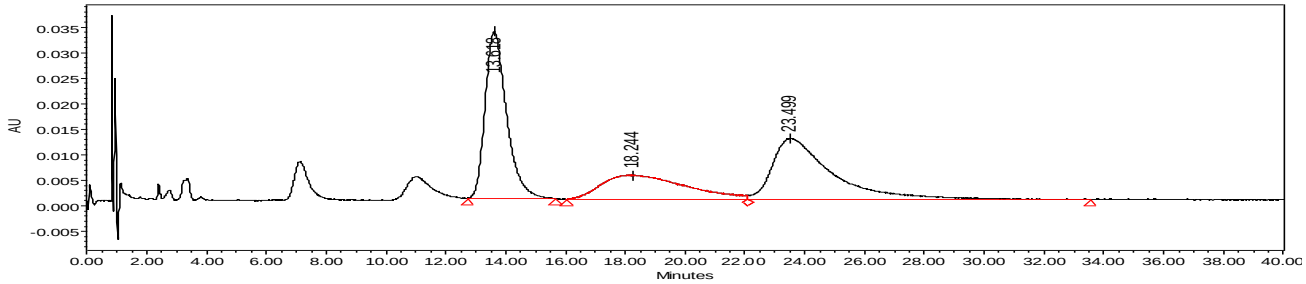
ESI-HRMS calcd for $[C_{48}H_{36}{}^{34.9689}Cl^{36.9659}Cl\ N_2O_4+Na^+]$: 799.1915, found 799.1920;

ESI-HRMS calcd for $[C_{48}H_{36}{}^{36.9659}Cl_{\ 2}N_2O_4+Na^+]$: 801.1885, found 801.1902;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3441, 3059, 2924, 2854, 2363, 1753, 1599, 1477, 1457, 1403, 1340, 1292, 1266, 1207, 1124, 1105, 1032, 900, 840, 740, 700, 582, 496, 472, 433.

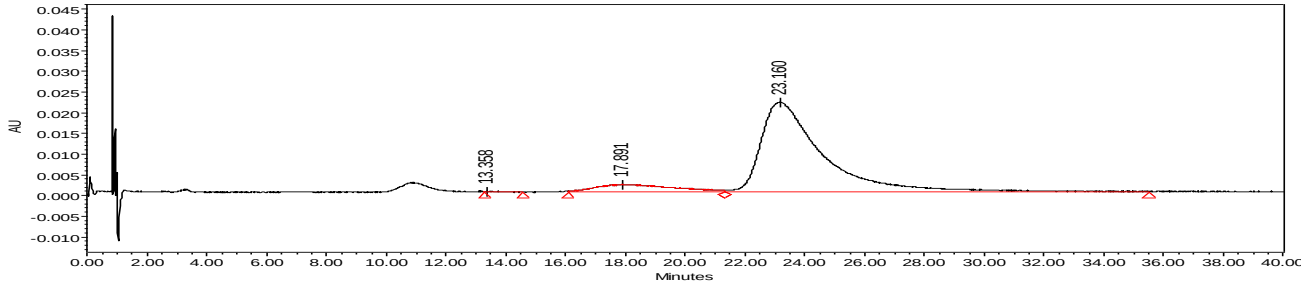
Reaction time: (**Step 1**) 12 h; (**Step 2**) 11 h.

Racemic **4ea**:

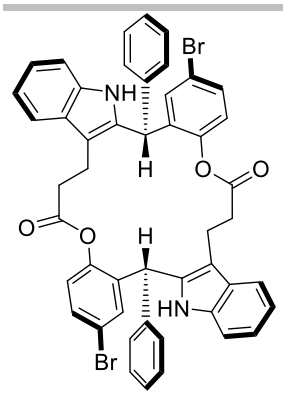


	Retention Time	Area	% Area
1	13.618	1630246	39.09
2	18.244	910739	21.84
3	23.499	1629548	39.07

Chiral **4ea**:



	Retention Time	Area	% Area
1	13.358	3933	0.12
2	17.891	300112	9.02
3	23.160	3023975	90.86



4fa

Compound 4fa

0.1 mmol (**2a**) scale reaction:

Result: white solid, 24.6 mg, 57% yield, 91:9 dr, 99% ee, m.p. 194 – 196 ℃; $[\alpha]_D^{29}$ = –52.9 (*c* = 0.38 g/100 mL, λ = 589 nm, in CH_2Cl_2); UPC^2 (Chiralcel AD-3, CO_2/MeOH = 80/20, flow rate = 1.5 mL/min, λ = 230 nm, $t_{r(major)}$ = 13.51 min, $t_{r(minor)}$ = 21.42 min;

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (s, 2H), 7.57 – 7.52 (m, 2H), 7.46 – 7.40 (m, 2H), 7.35 – 7.26 (m, 8H), 7.25 – 7.22 (m, 2H), 7.22 – 7.16 (m, 2H), 7.16 – 7.11 (m, 2H), 7.09 – 7.02 (m, 4H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.00 (m, 2H), 3.20 – 3.09 (m, 2H), 3.08 – 2.97 (m, 2H), 2.87 – 2.71 (m, 4H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 170.80, 147.76, 140.26, 136.37, 135.47, 133.65, 132.57, 131.57, 128.95, 128.37, 128.00, 127.43, 124.76, 122.01, 119.86, 119.63, 118.34, 111.16, 111.06, 41.92, 35.18, 19.46;

ESI-HRMS calcd for [$C_{48}H_{36}{}^{78.9183}Br_2N_2O_4$+$Na^+$]: 885.0934, found 885.0935;

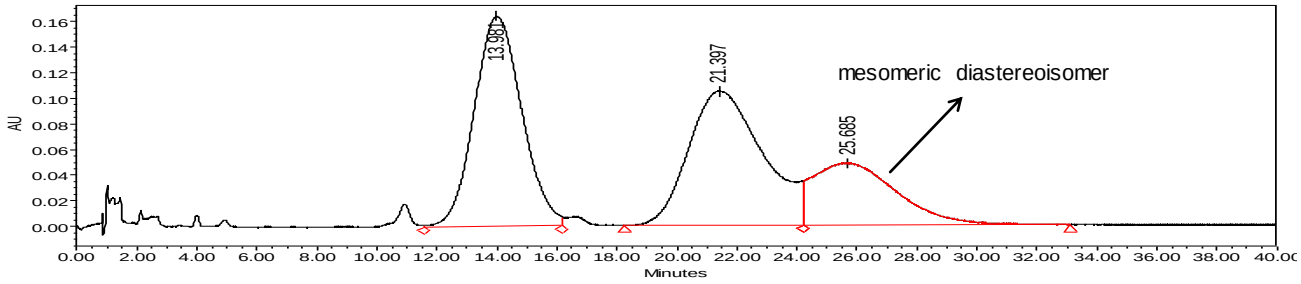
ESI-HRMS calcd for [$C_{48}H_{36}{}^{78.9183}Br\,{}^{80.9163}Br\,N_2O_4$+$Na^+$]: 887.0914, found 887.0930;

ESI-HRMS calcd for [$C_{48}H_{36}{}^{80.9163}Br_2N_2O_4$+$Na^+$]: 889.0893, found 889.0889;

IR (film): $\tilde{\nu}$ (cm^{-1}) 3423, 3058, 2924, 2854, 2362, 1753, 1598, 1476, 1457, 1340, 1291, 1266, 1206, 1124, 1100, 1032, 922, 894, 841, 740, 701, 495, 469, 434.

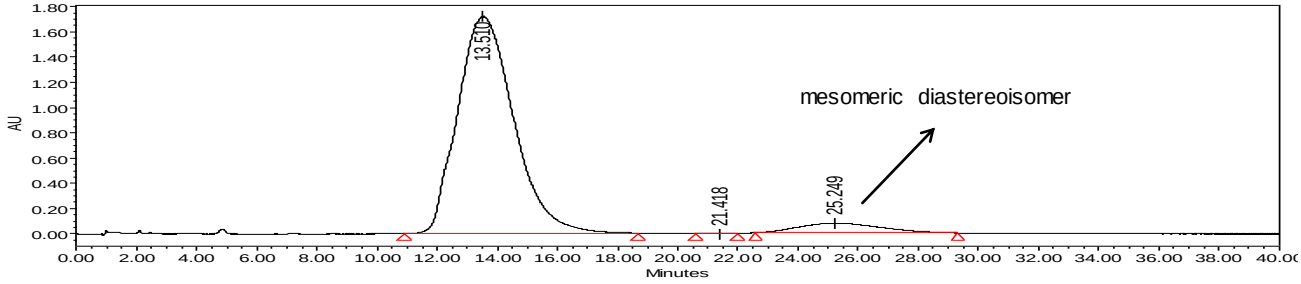
Reaction time: (**Step 1**) 12 h; (**Step 2**) 11 h.

Racemic **4fa**:

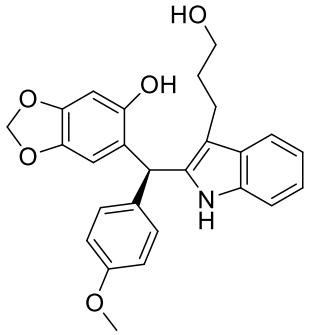


	Retention Time	Area	% Area
1	13.981	18057226	39.77
2	21.397	17952143	39.54
3	25.685	9395407	20.69

Chiral **4fa**:



	Retention Time	Area	% Area
1	13.510	222216264	93.90
2	21.418	42917	0.02
3	25.249	14397699	6.08



6aa

(*S*)-6-{[3-(3-Hydroxypropyl)-1*H*-indol-2-yl](4-methoxyphenyl)methyl}benzo[*d*][1,3]dioxol-5-ol (6aa)

0.05 mmol (**4aa**) scale reaction:

Result: colourless oil, 39.7 mg, 92% yield, 94% ee; $[\alpha]_D^{28} = -68.3$ (*c* = 0.58 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel IC, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, λ = 254 nm, $t_r(_{minor})$ = 5.40 min, $t_r(_{major})$ = 6.31 min;

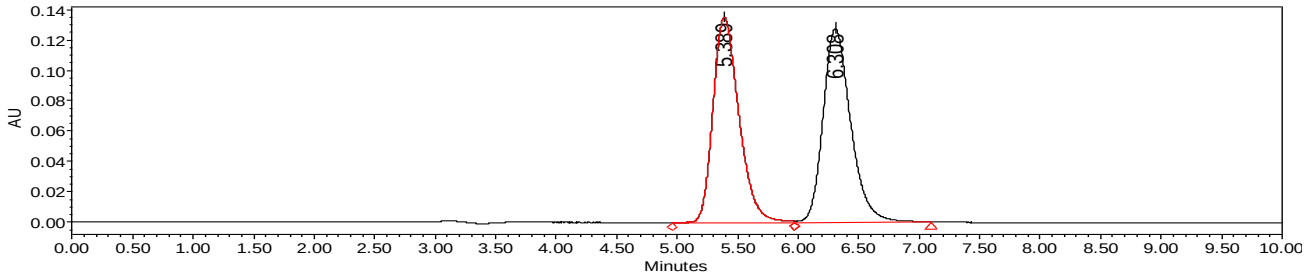
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.61 – 7.53 (m, 1H), 7.28 (s, 1H), 7.18 – 7.07 (m, 2H), 7.01 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 6.67 (s, 1H), 6.44 (s, 1H), 6.39 (s, 1H), 5.95 (s, 1H), 5.92 – 5.84 (m, 2H), 3.80 (s, 3H), 3.67 – 3.59 (m, 1H), 3.57 – 3.48 (m, 1H), 2.90 – 2.76 m, 2H), 2.12 (s, 1H), 1.98 – 1.83 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 158.38, 148.35, 146.90, 141.51, 135.49, 135.40, 133.66, 129.52, 128.57, 121.37, 120.93, 119.25, 118.60, 114.01, 111.46, 110.89, 109.04, 101.12, 99.09, 61.92, 55.23, 41.08, 31.74, 19.93;

ESI-HRMS calcd for $[C_{26}H_{25}NO_5+Na^+]$: 454.1625, found 454.1625;

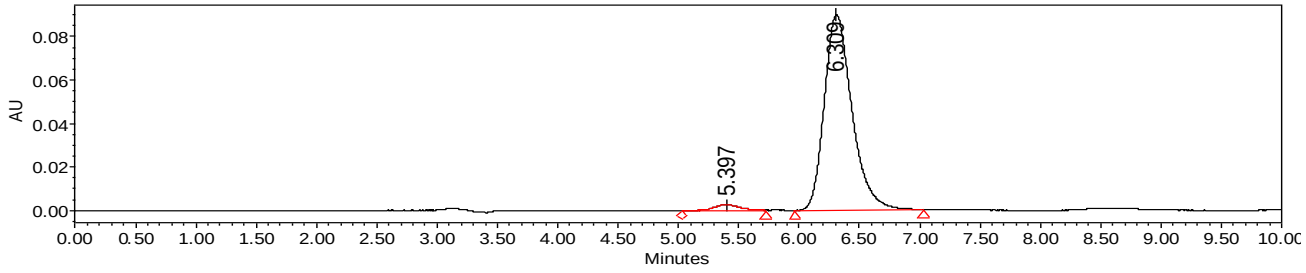
IR (film): $\tilde{\nu}$ (cm^{-1}) 3409, 3056, 2926, 1727, 1609, 1583, 1507, 1484, 1459, 1438, 1302, 1244, 1174, 1035, 934, 876, 849, 795, 738, 703, 608, 520, 478, 434.

Racemic **6aa**:

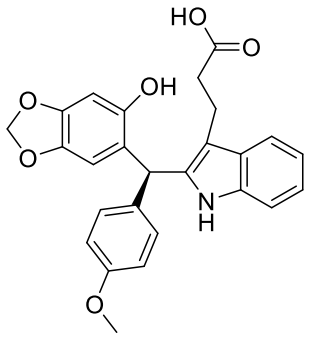


	Retention Time	Area	% Area
1	5.389	2027233	49.97
2	6.308	2029908	50.03

Chiral **6aa**:



	Retention Time	Area	% Area
1	5.397	41331	2.80
2	6.309	1436996	97.20



7aa

(*S*)-3-{2-[(6-Hydroxybenzo[*d*][1,3]dioxol-5-yl)(4-methoxyphenyl)methyl]-1*H*-indol-3-yl}propanoic acid (7aa)

0.05 mmol (**4aa**) scale reaction:

Result: yellow oil, 26.3 mg, 59% yield, 98% ee; $[\alpha]_D^{28} = -82.9$ (*c* = 0.42 g/100 mL, λ = 589 nm, in CH_2Cl_2); HPLC (Daicel chiralcel ID, *n*-hexane/*i*-PrOH = 70/30, flow rate = 1.0 mL/min, λ = 240 nm, $t_{r(major)}$ = 5.83 min, $t_{r(minor)}$ = 9.84 min);

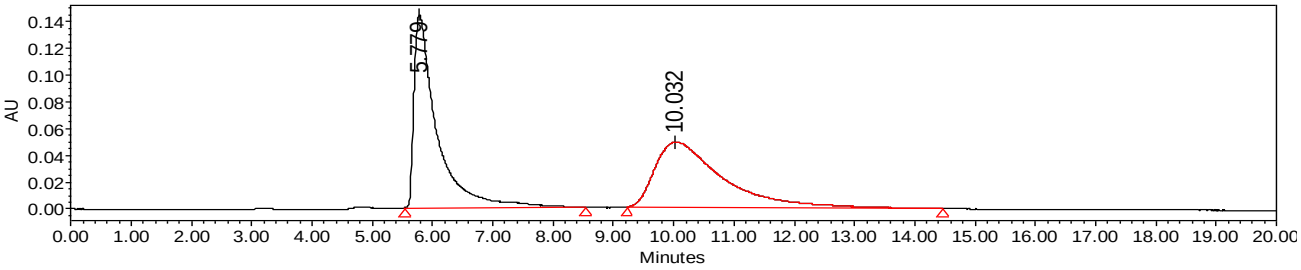
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.77 (s, 1H), 7.57 – 7.51 (m, 1H), 7.28 – 7.22 (m, 2H), 7.18 – 7.07 (m, 2H), 7.01 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.39 (s, 1H), 6.37 (s, 1H), 5.95 (s, 1H), 5.89 – 5.84 (m, 2H), 3.78 (s, 3H), 2.99 (m, 2H), 2.66 (m, 2H);

^{13}C{^{1}H} NMR (100 MHz, Chloroform-*d*) δ 178.60, 158.49, 148.15, 147.04, 141.68, 135.46, 135.27, 133.15, 129.51, 128.16, 121.57, 120.60, 119.49, 118.24, 114.16, 110.99, 110.81, 109.07, 101.16, 99.18, 55.26, 41.52, 33.93, 19.25;

ESI-HRMS calcd for $[C_{26}H_{23}NO_6+Na^+]$: 468.1418, found 468.1420;

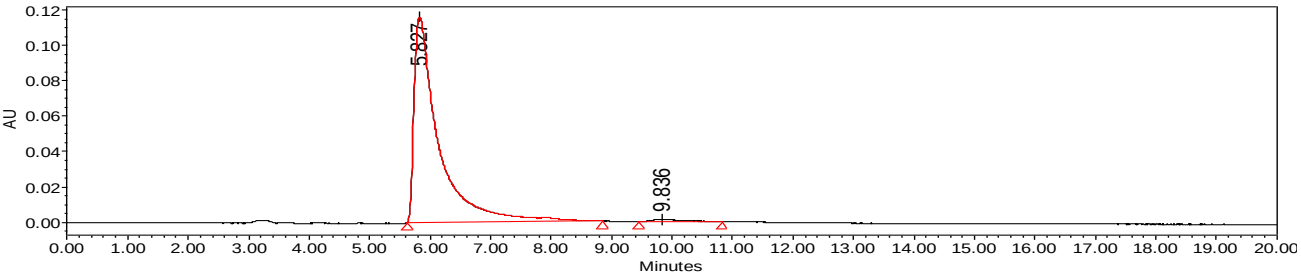
IR (film): $\tilde{\nu}$ (cm^{-1}) 3406, 3056, 2925, 1705, 1609, 1583, 1508, 1485, 1459, 1438, 1302, 1245, 1174, 1036, 934, 876, 849, 795, 741, 593, 518, 434.

Racemic **7aa**:



	Retention Time	Area	% Area
1	5.779	3816869	50.23
2	10.032	3782574	49.77

Chiral **7aa**:

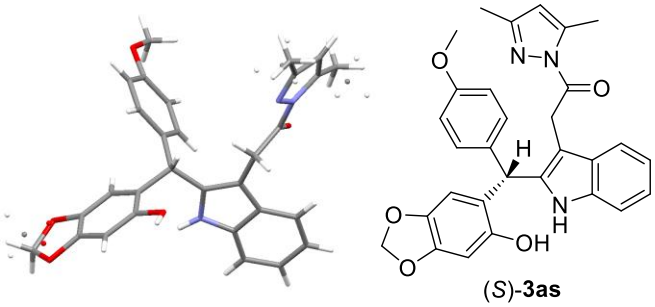


	Retention Time	Area	% Area
1	5.827	3291161	98.85
2	9.836	38427	1.15

12. Crystal Data of Product 3as, 4aa and 4ab

The absolute configuration of product **3as** was determined to be *S* by X-ray chromatography analysis. Single crystal of **3as** [$C_{30}H_{27}N_3O_5$] was obtained by recrystallization in CH_2Cl_2 at 25 °C. CCDC 2016694

The colourless crystal in block-shape, with approximate dimensions of 0.190 × 0.090 × 0.050 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 252(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package[5–7]. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested[8].



(*S*)-**3as**

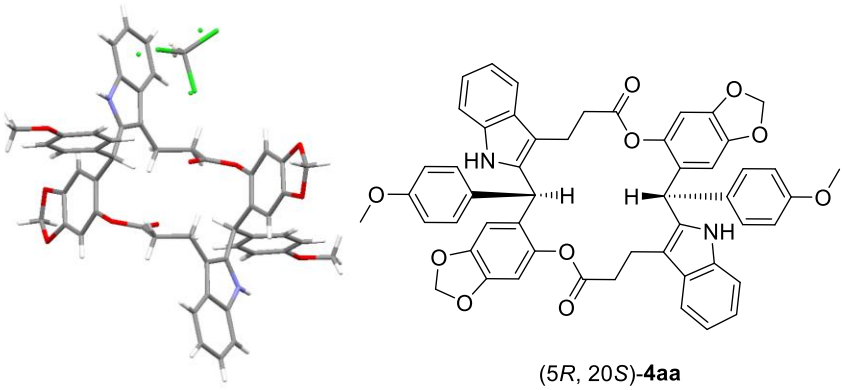
Crystal data and structure refinement for (*S*)-**3as**.

Empirical formula	$C_{30}H_{27}N_3O_5$
Formula weight	509.54
Temperature/K	252(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.8152(2)
b/Å	12.5754(2)
c/Å	20.1202(3)
α/°	90
β/°	90
γ/°	90
Volume/Å	2736.46(8)
Z	4
$\rho_{calc}g/cm^3$	1.237
μ/mm^{-1}	0.695
F(000)	1072.0
Crystal size/mm^3	0.190 × 0.090 × 0.050
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.292 to 130.184
Index ranges	-12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -22 ≤ l ≤ 23
Reflections collected	17740
Independent reflections	4659 [R_{int} = 0.0428, R_{sigma} = 0.0344]

Data/restraints/parameters	4659/48/367
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0363, wR_2 = 0.0857
Final R indexes [all data]	R_1 = 0.0430, wR_2 = 0.0925
Largest diff. peak/hole / e Å-3	0.22/-0.13
Flack parameter	-0.09(12)

The absolute configuration of product **4aa** was determined to be (5*R*,20*S*) by X-ray chromatography analysis. Single crystal of **4aa** [$C_{52}H_{42}N_2O_{10}$] was obtained by recrystallization in $CDCl_3$ at 25 °C. CCDC 2016020

The colourless crystal in block-shape, with approximate dimensions of 0.150 × 0.096 × 0.087 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 144(2)K equipped with micro-focus Cu radiation source (K_α = 1.54178Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.

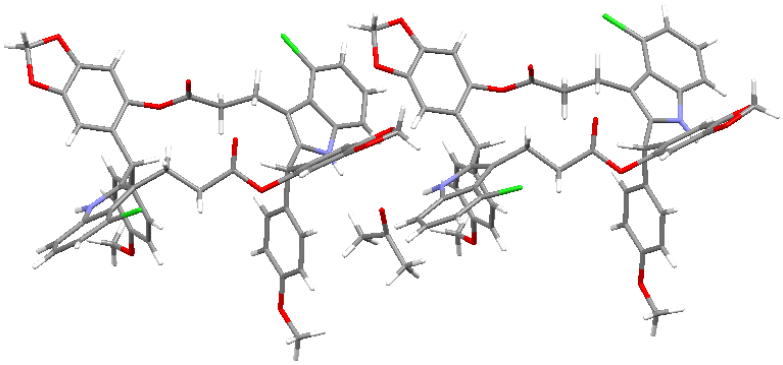


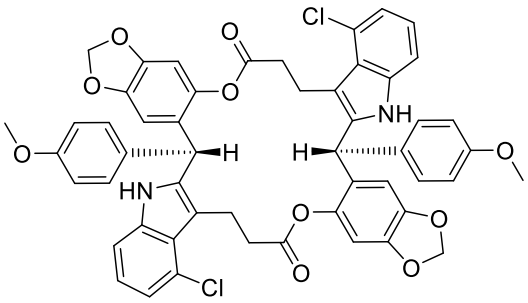
(5*R*, 20*S*)-**4aa**

Crystal data and structure refinement for (5*R*,20*S*)-**4aa**.

Empirical formula	$C_{54}H_{44}Cl_6N_2O_{10}$
Formula weight	1095.62
Temperature/K	144(2)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.8889(4)
b/Å	14.4911(5)
c/Å	14.9954(5)
α/°	90
β/°	104.794(2)
γ/°	90
Volume/Å	2497.81(15)
Z	2
ρ_{calc}g/cm^3	1.457
μ/mm^{-1}	3.660
F(000)	1128.0
Crystal size/mm^3	0.150 × 0.096 × 0.087

Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	8.51 to 161.416
Index ranges	-15 ≤ h ≤ 14, -18 ≤ k ≤ 16, -17 ≤ l ≤ 19
Reflections collected	35835
Independent reflections	5330 [R_{int} = 0.0632, R_{sigma} = 0.0380]
Data/restraints/parameters	5330/7/367
Goodness-of-fit on F^2	1.079
Final R indexes [I>=2σ (I)]	R_1 = 0.0869, wR_2 = 0.2166
Final R indexes [all data]	R_1 = 0.0968, wR_2 = 0.2220
Largest diff. peak/hole / e Å-3	1.17/-0.56





(5*S*, 20*S*)-**4ab**

The absolute configuration of product **4ab** was determined to be (5*S*, 20*S*) by X-ray chromatography analysis. Single crystal of **4ab** [$C_{52}H_{40}Cl_2N_2O_{10}$] was obtained by recrystallization in *i*-PrOH/CH_2Cl_2 at 25 °C. CCDC 2016695

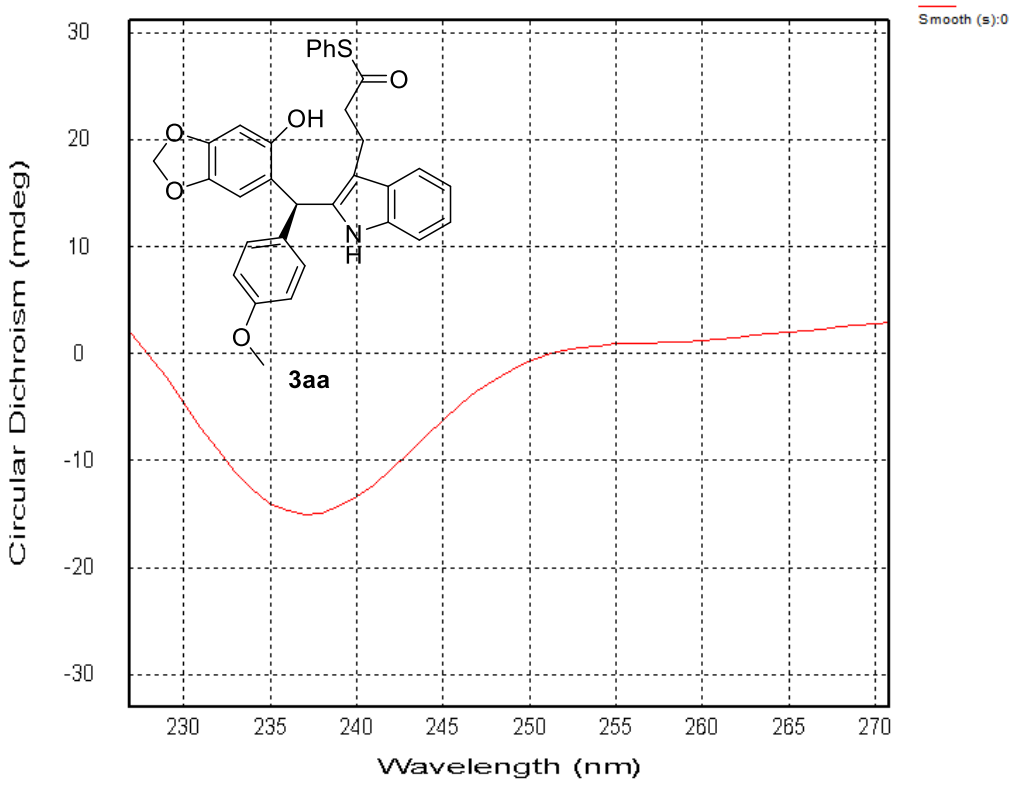
The colourless crystal in block-shape, with approximate dimensions of 0.24 × 0.09 × 0.08 mm^3, was selected and mounted for the single-crystal X-ray diffraction. The data set was collected by Bruker D8 Venture Photon II diffractometer at 193(2)K equipped with micro-focus Mo radiation source (K_α = 0.71073Å). Applied with face-indexed numerical absorption correction, the structure solution was solved and refinement was processed by SHELXTL (version 6.14) program package. The structure was analyzed by ADDSYM routine implemented in PLATON suite and no higher symmetry was suggested.

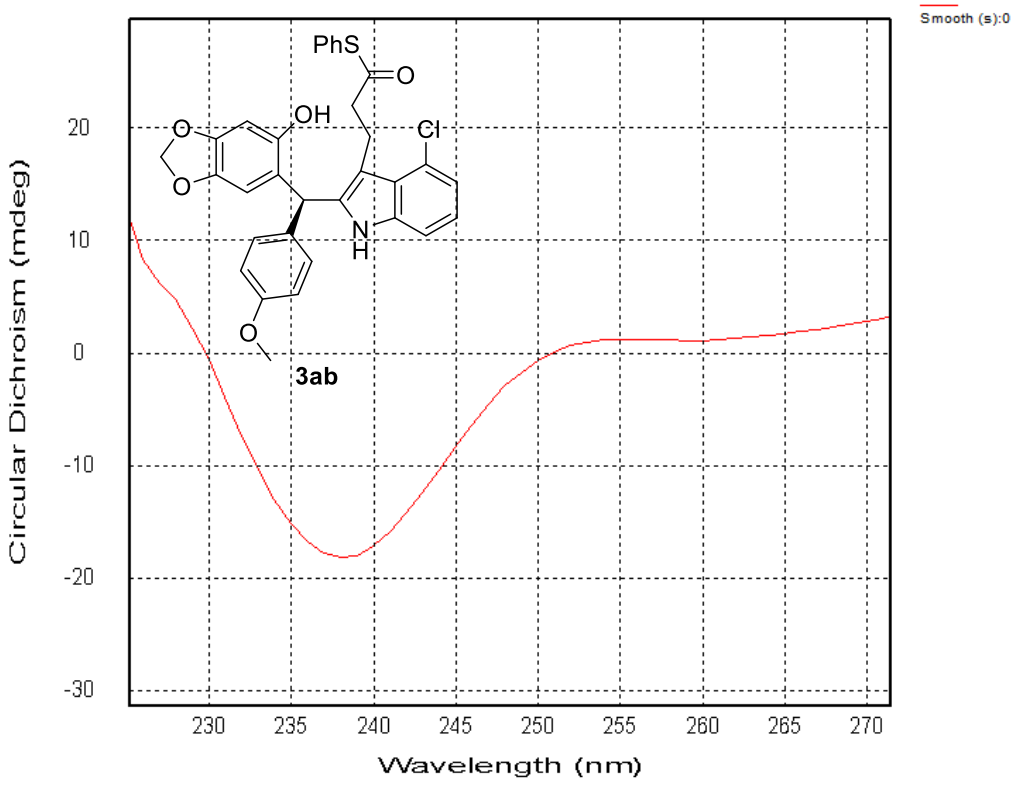
Crystal data and structure refinement for (5*S*, 20*S*)-**4ab**.

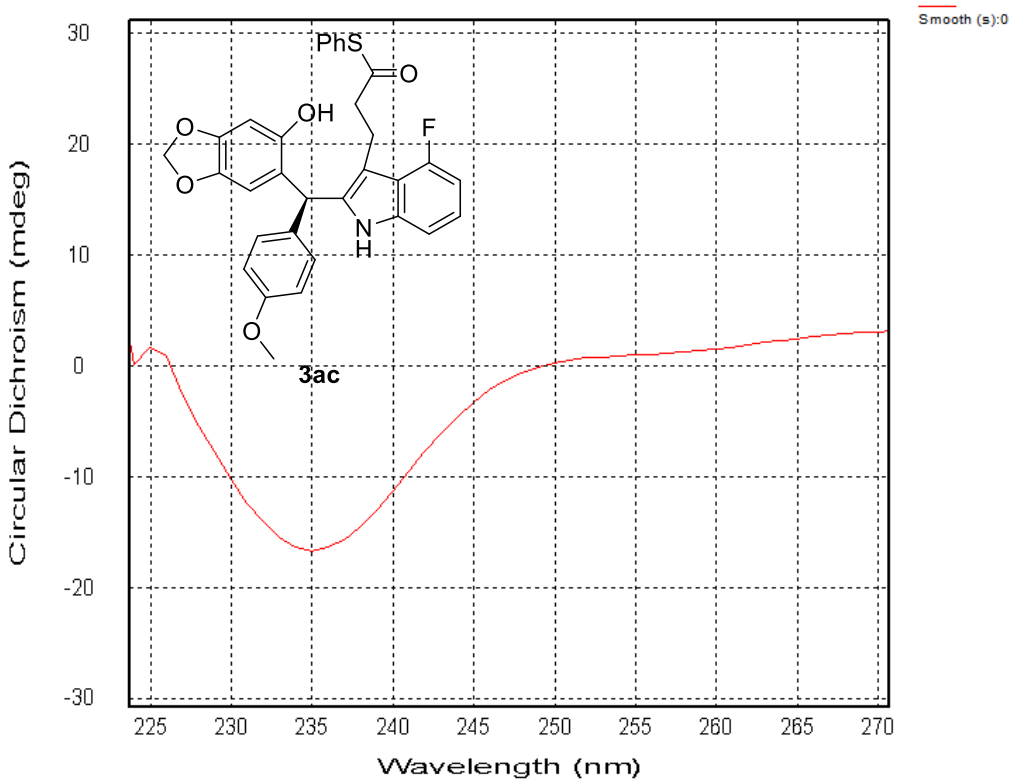
Empirical formula	$C_{55}H_{46}Cl_2N_2O_{11}$
Formula weight	981.84
Temperature/K	193(2)
Crystal system	tetragonal
Space group	$P4_12_12$
a/Å	19.2448(5)
b/Å	19.2448(5)
c/Å	26.8461(8)
α/°	90
β/°	90
γ/°	90
Volume/Å	9942.8(6)

Z	8
ρ_{calc}g/cm^3	1.312
μ/mm^{-1}	0.194
F(000)	4096.0
Crystal size/mm^3	0.24 × 0.09 × 0.08
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.732 to 56.984
Index ranges	-25 ≤ h ≤ 25, -25 ≤ k ≤ 25, -35 ≤ l ≤ 35
Reflections collected	445593
Independent reflections	12492 [R_{int} = 0.0913, R_{sigma} = 0.0234]
Data/restraints/parameters	12492/0/644
Goodness-of-fit on F^2	1.019
Final R indexes [I>=2σ (I)]	R_1 = 0.0477, wR_2 = 0.1107
Final R indexes [all data]	R_1 = 0.0791, wR_2 = 0.1330
Largest diff. peak/hole / e Å-3	0.45/-0.36
Flack parameter	-0.003(13)

13. Copies of CD Spectra for the Reaction Products in DCM






Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
225
230
235
240
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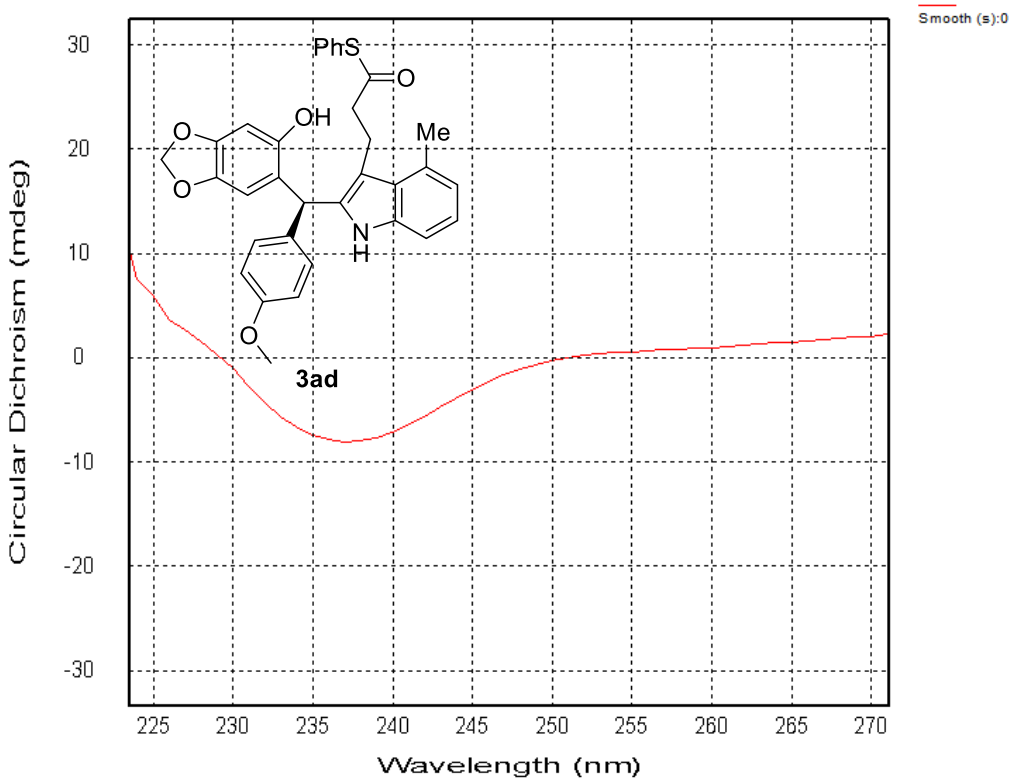
250
255
260
265
270
Wavelength (nm)
PhS
O
OH
F
O
O
N
H
O
3ac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Circular Dichroism (mdeg)
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20
10
0
-10
-20
-30
225
230
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240
245
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260
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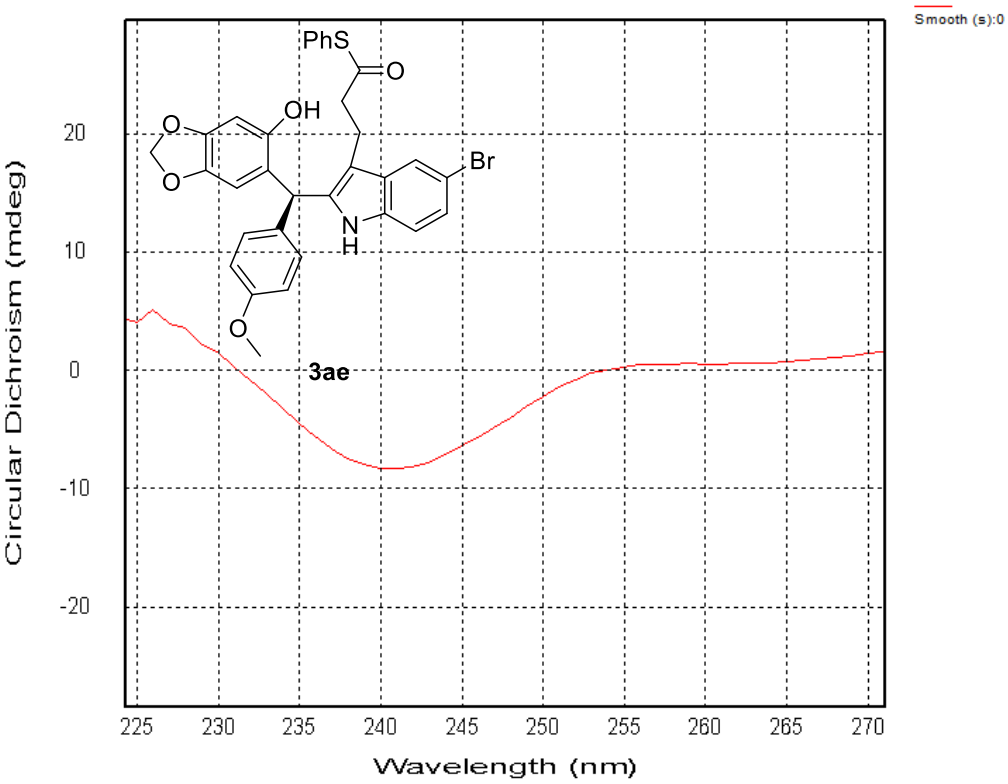
270
Wavelength (nm)
PhS
O
OH
Me
O
O
N
H
O
3ad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PhS
O
OH
O
O
Br
N
H
O
3ae
Circular Dichroism (mdeg)
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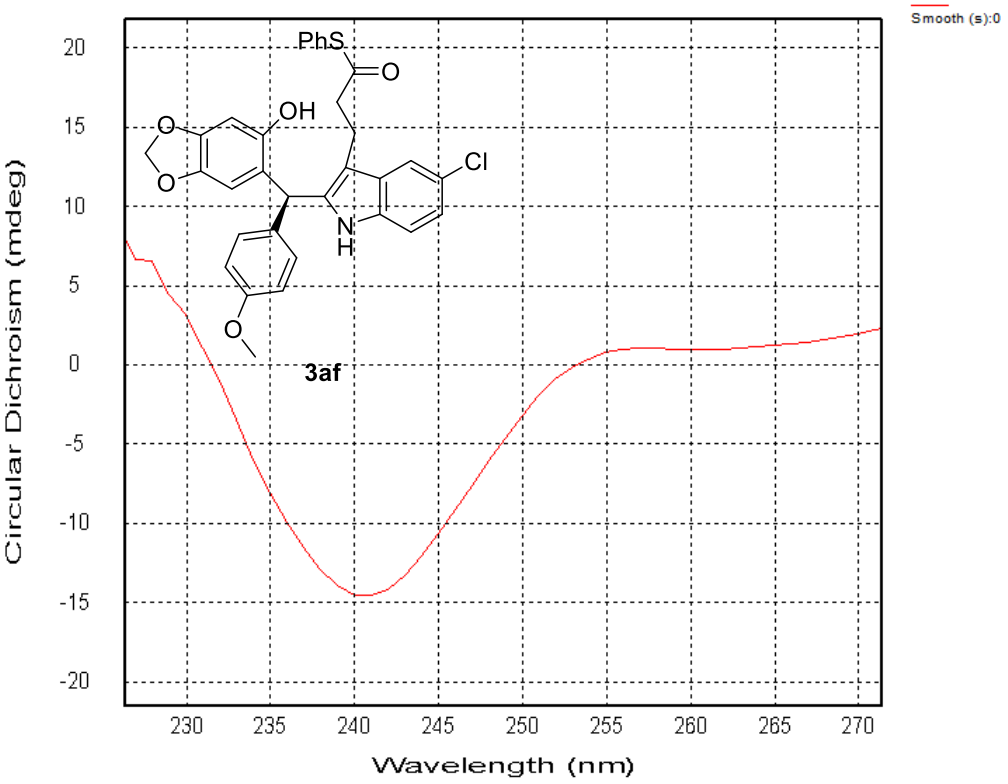
10
0
-10
-20
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)


Smooth (s):0
PhS
O
OH
O
O
Cl
N
H
O
3af
Circular Dichroism (mdeg)
20
15
10
5
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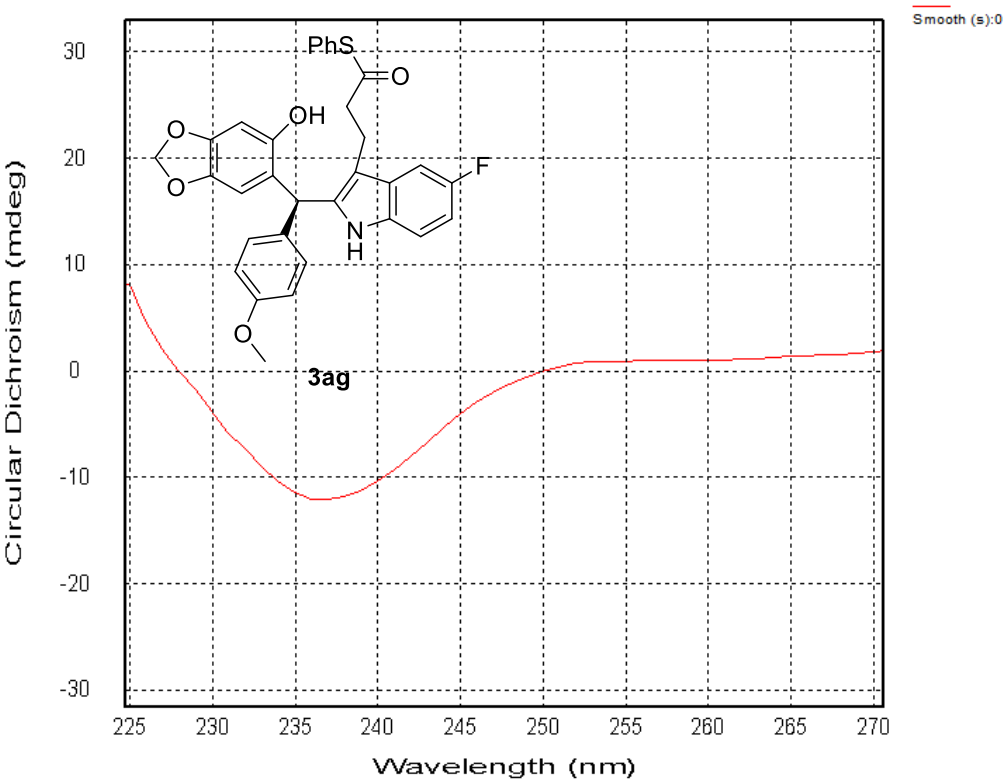
-10
-15
-20
230
235
240
245
250
255
260
265
270
Wavelength (nm)


Smooth (s):0
PhS
O
OH
O
O
F
N
H
O
3ag
Circular Dichroism (mdeg)
30
20
10
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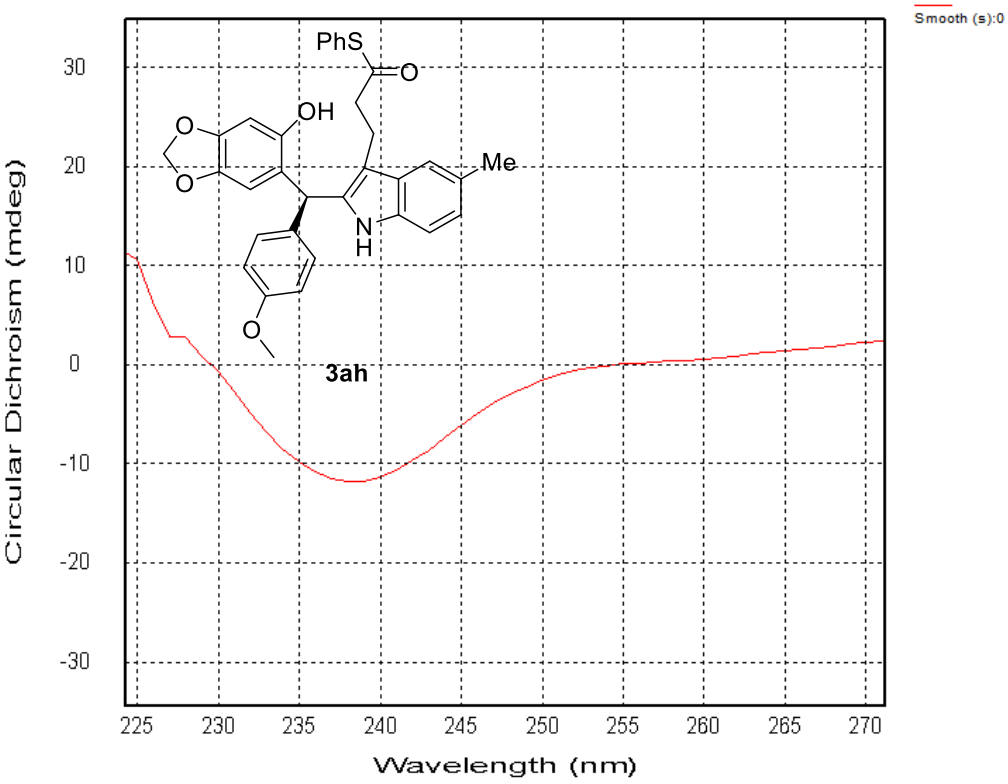
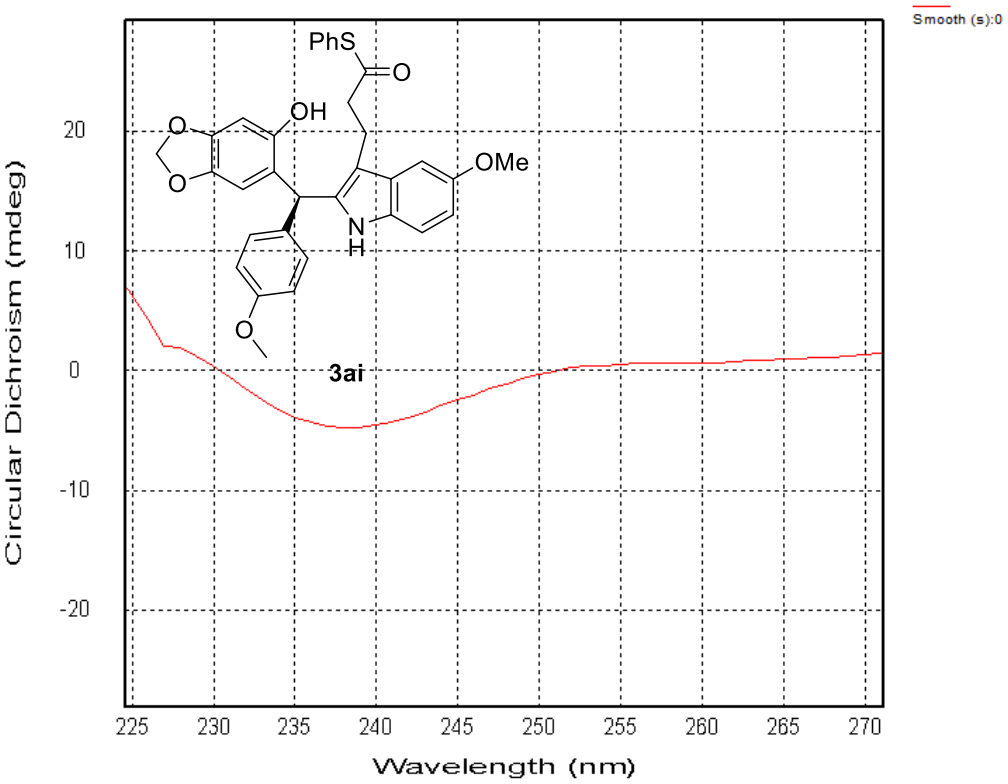
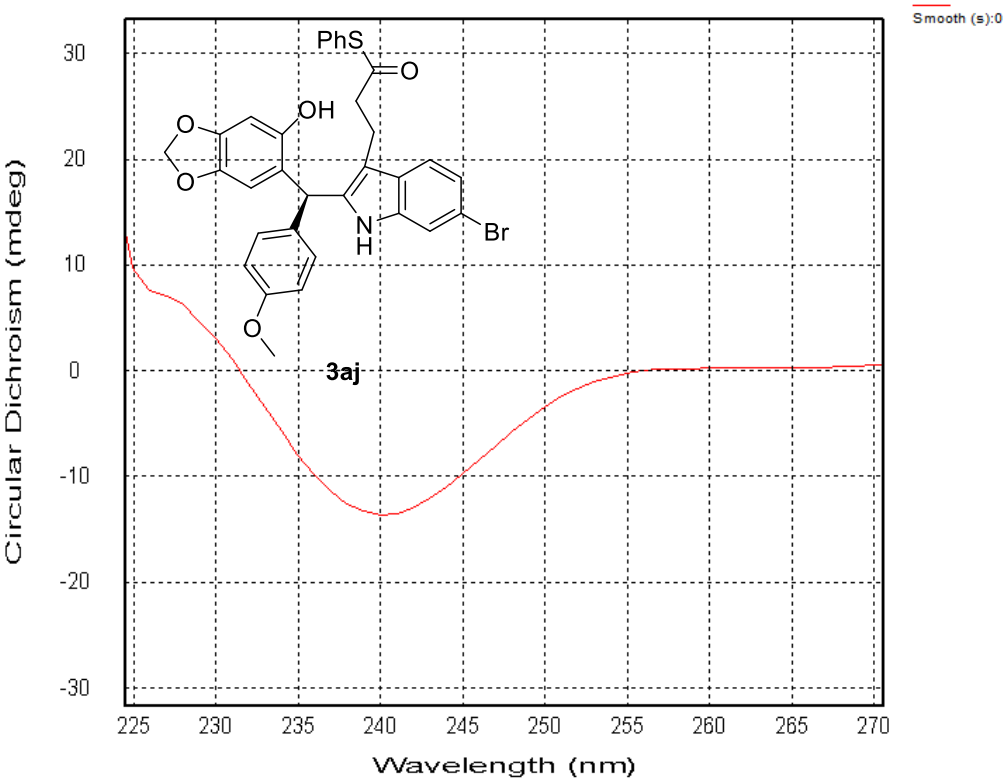
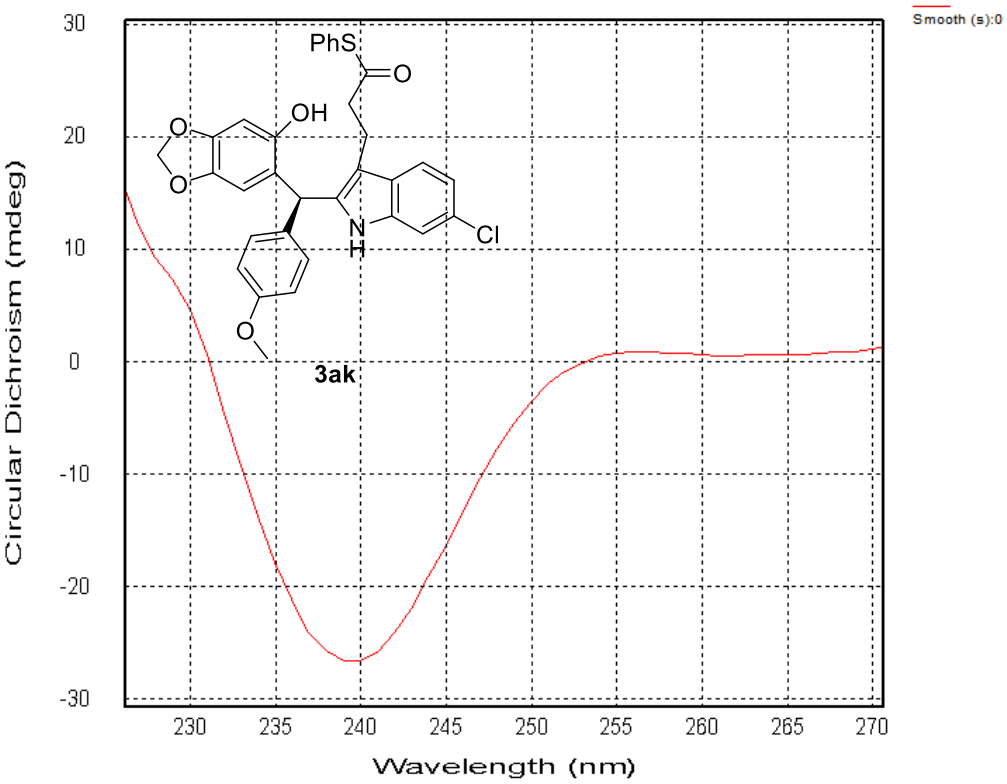
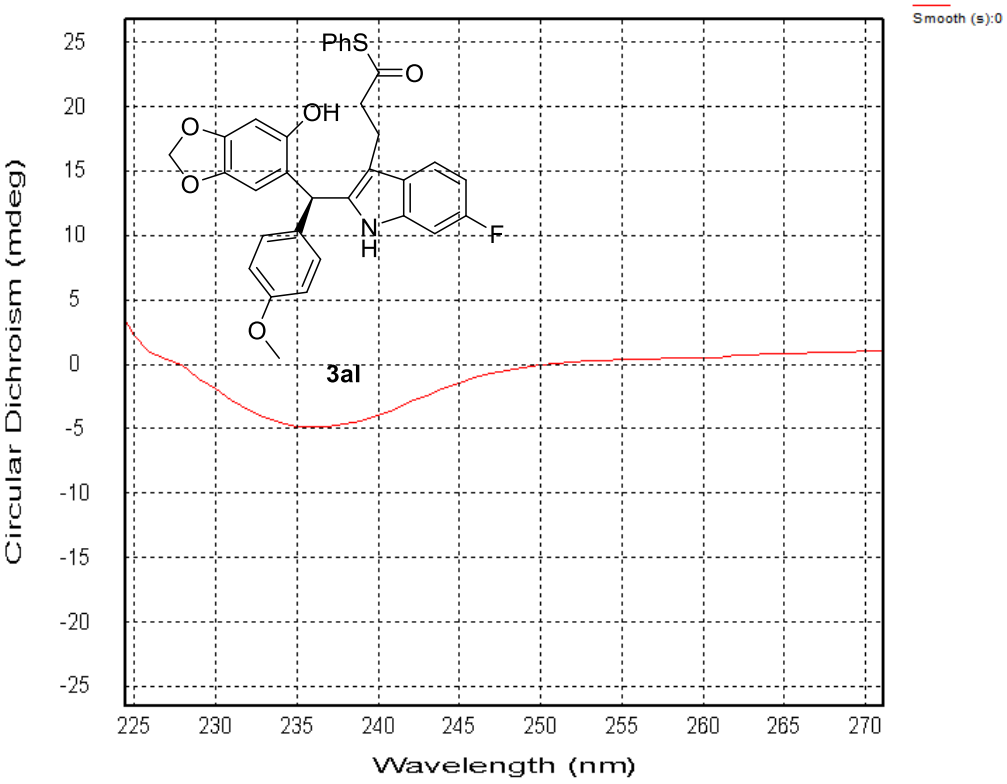
-10
-20
-30
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)

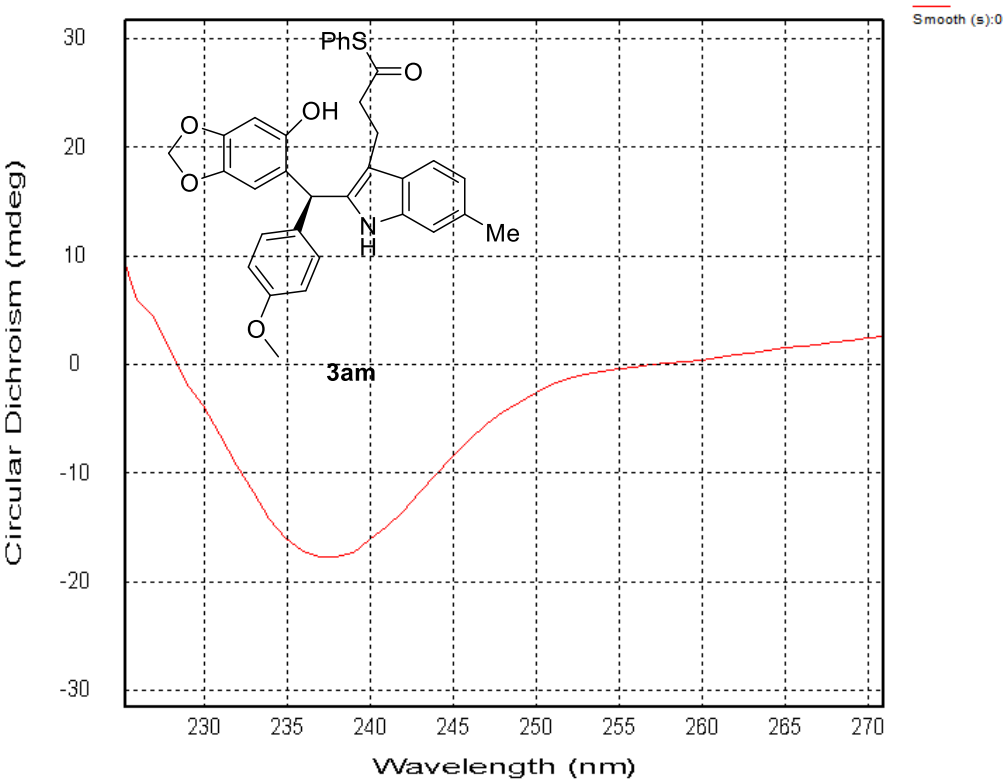

Smooth (s):0
PhS
O
OH
O
O
Me
N
H
O
3ah
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)

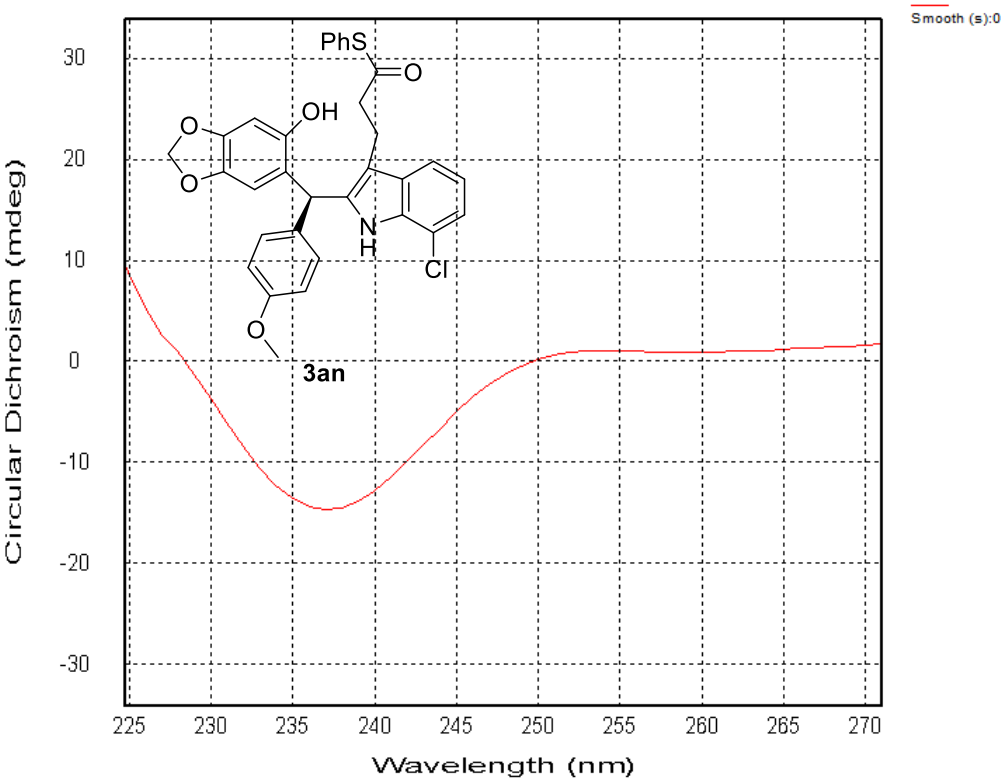

Smooth (s):0
PhS
O
OH
O
O
OMe
N
H
O
3ai
Circular Dichroism (mdeg)
20
10
0
-10
-20
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)

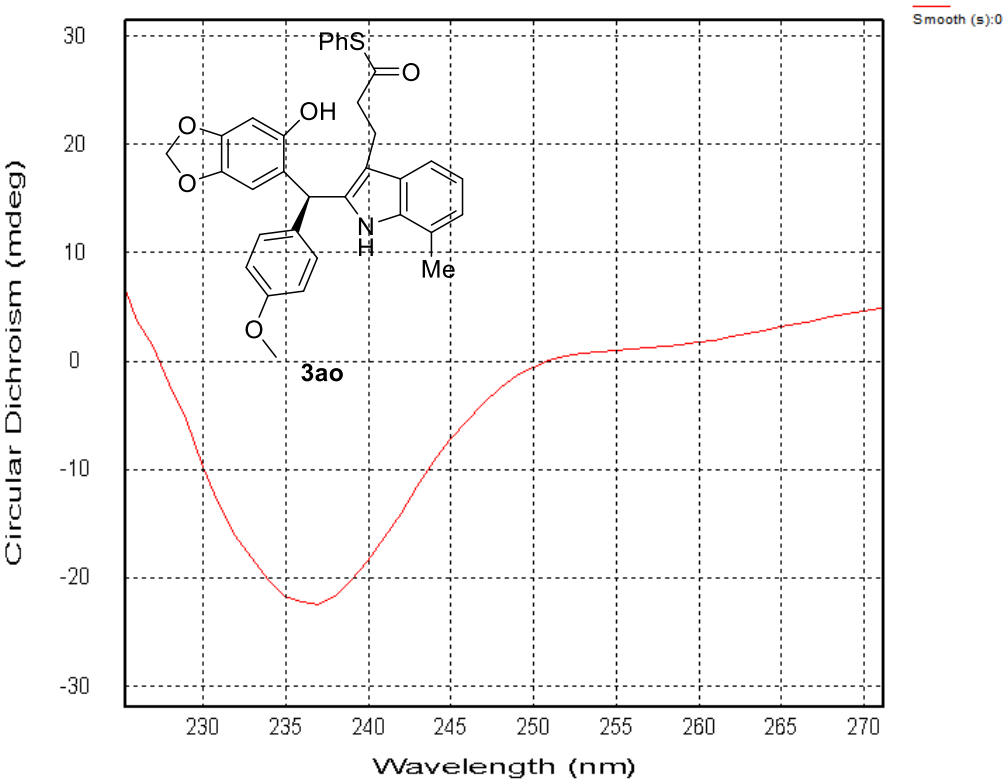

Smooth (s):0
PhS
O
OH
O
O
N
H
Br
O
3aj
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)

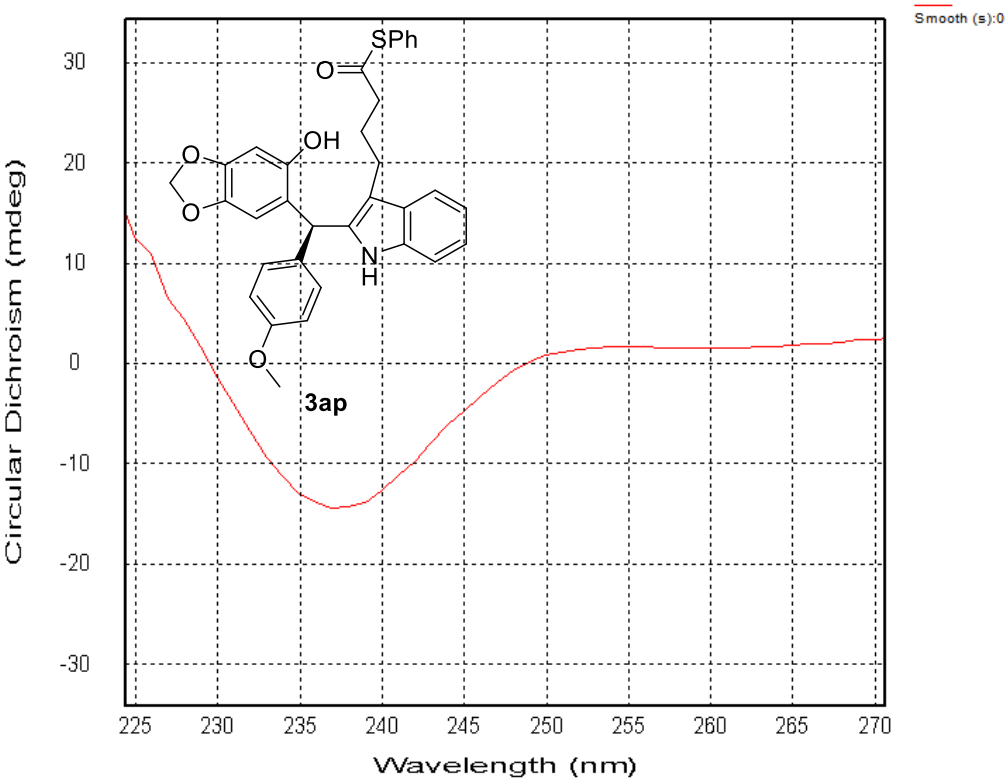

Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)
PhS
O
OH
O
O
N
H
Cl
O
3ak

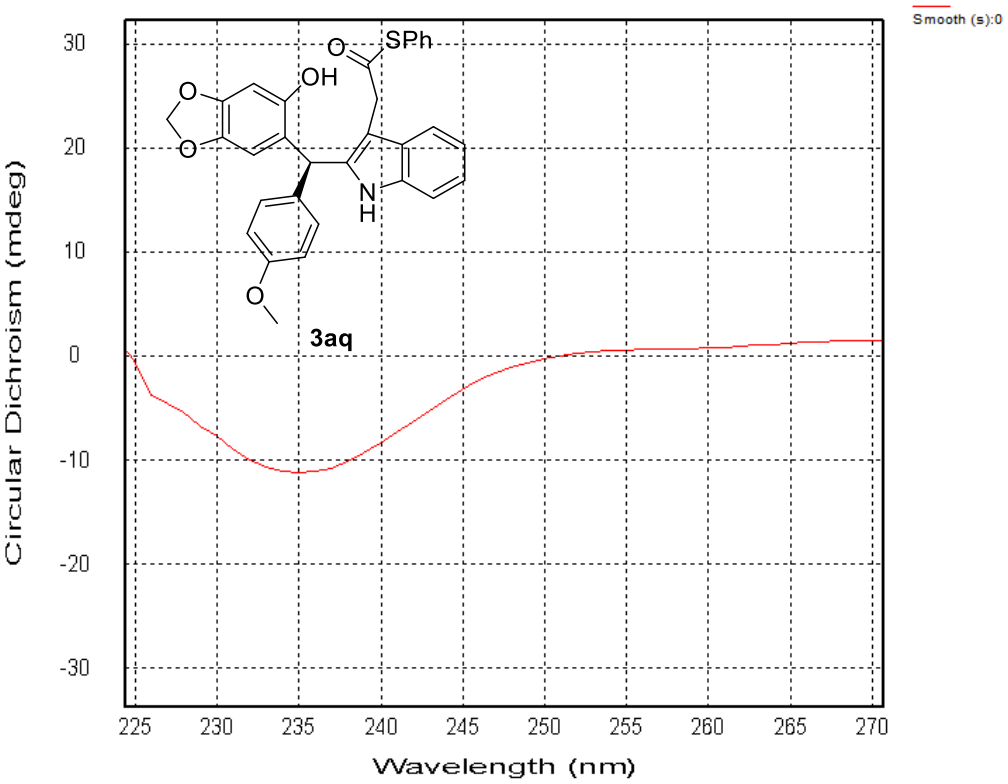

Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)
PhS
O
OH
O
O
N
H
F
O
3al

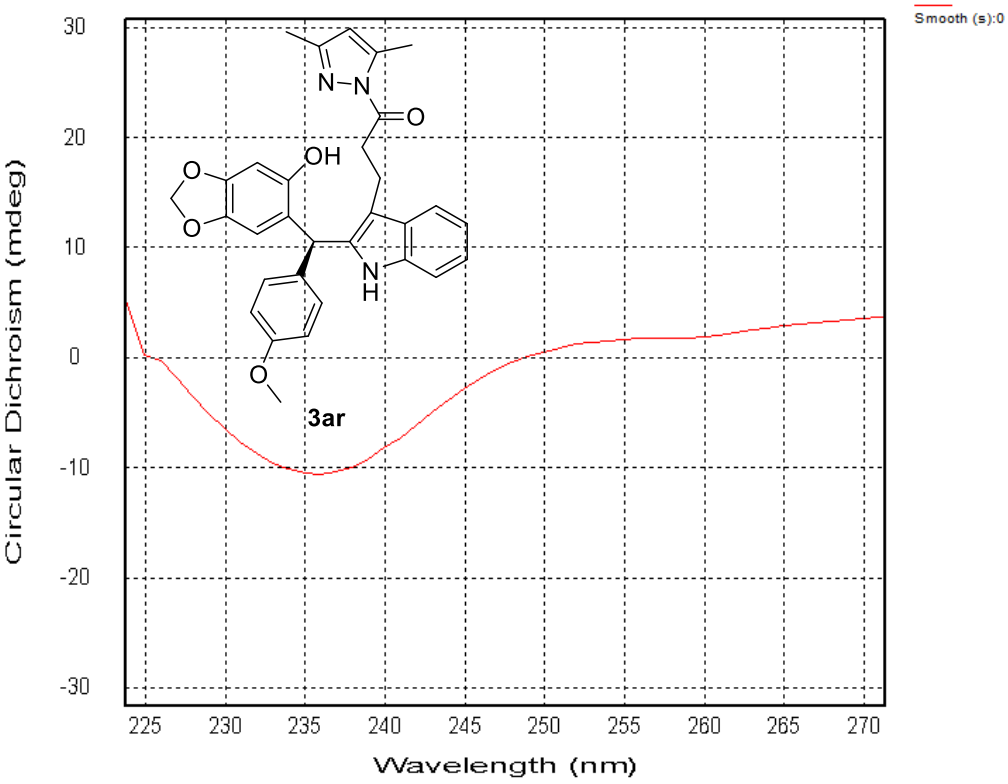

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
230
235
240
245
250
255
260
265
270
Wavelength (nm)
PhS
O
OH
O
O
N
H
Me
O
3am

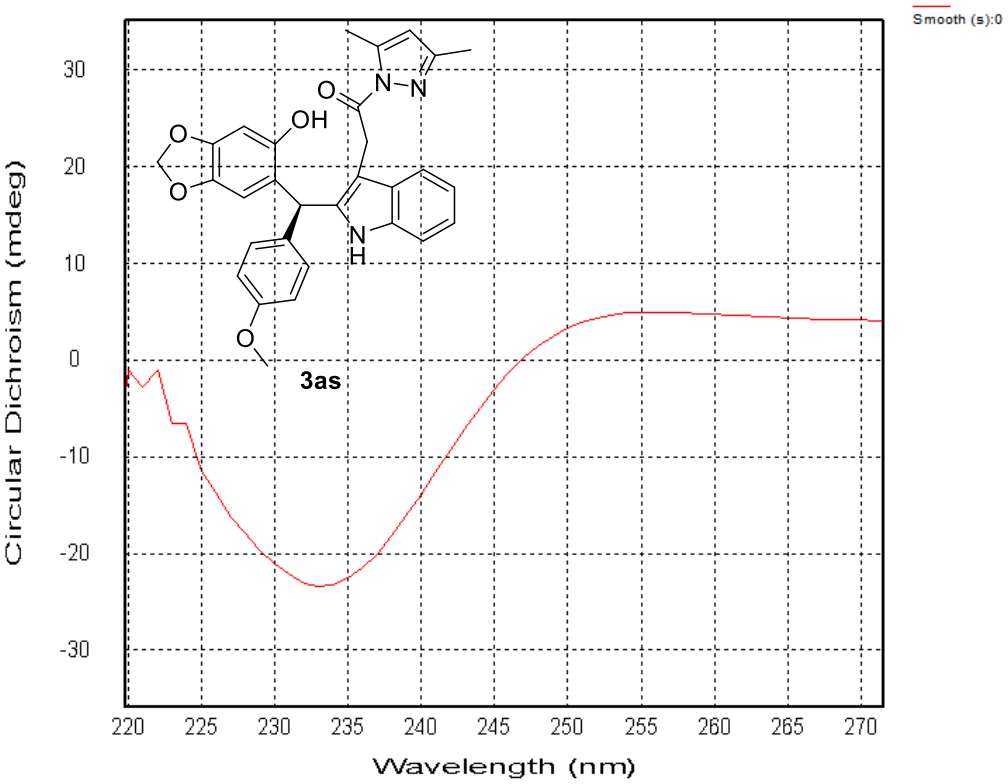

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)
PhS
O
OH
O
O
N
H
Cl
O
3an

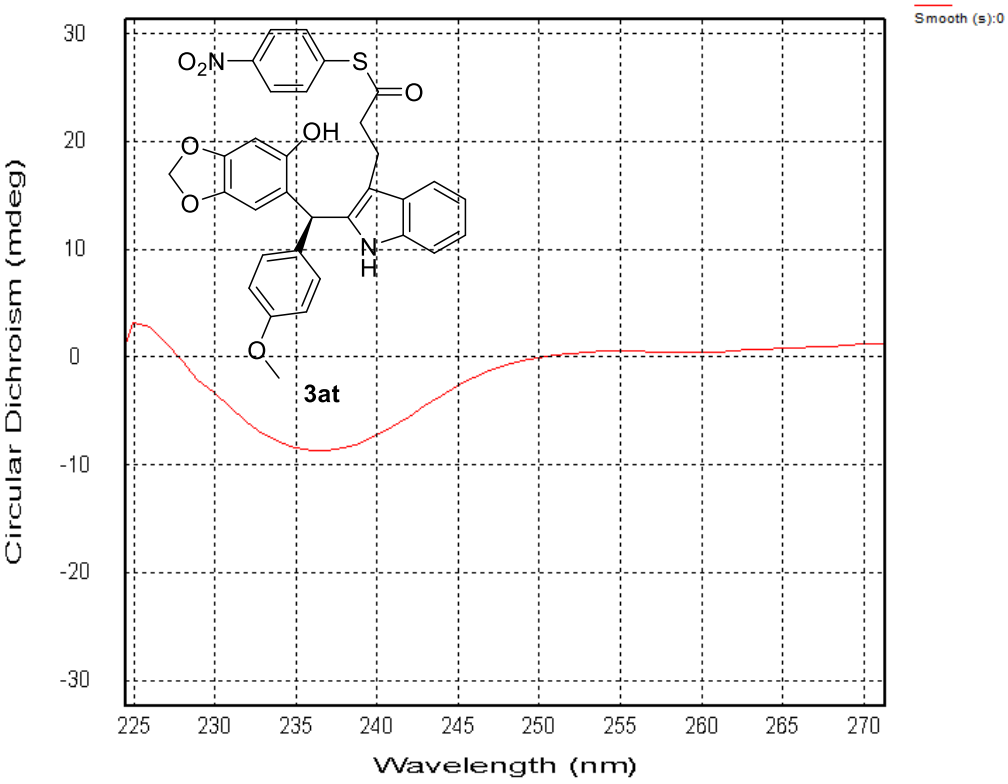

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
230
235
240
245
250
255
260
265
270
Wavelength (nm)
PhS
O
OH
O
O
N
H
Me
O
3ao

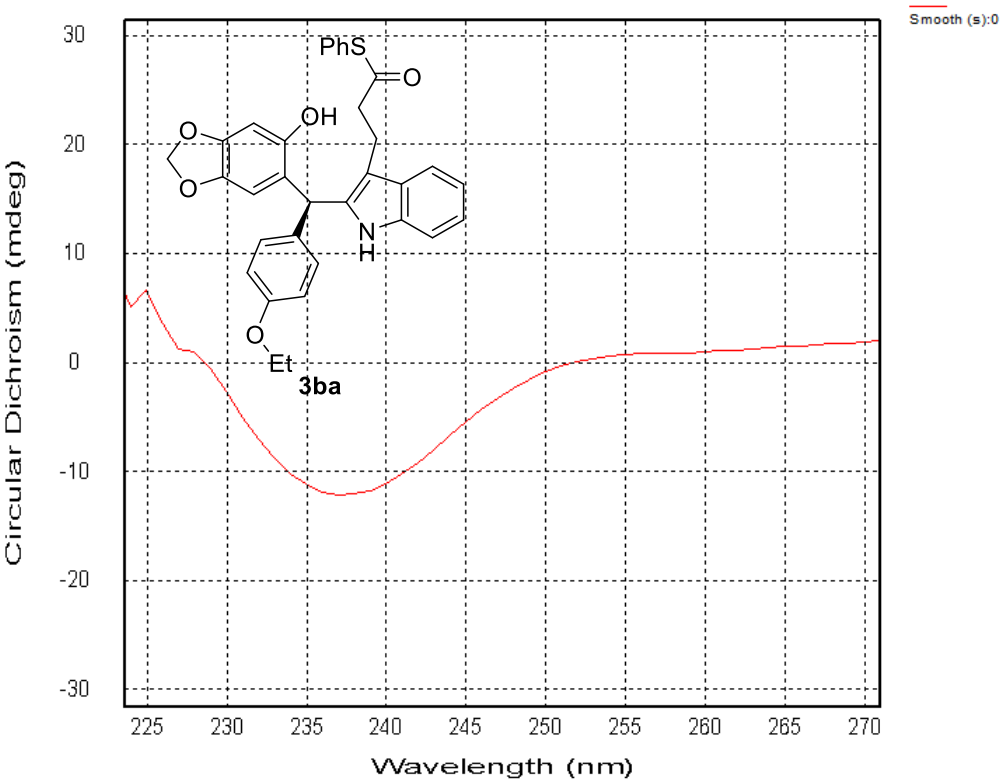

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)
SPh
O
OH
O
O
N
H
O
3ap

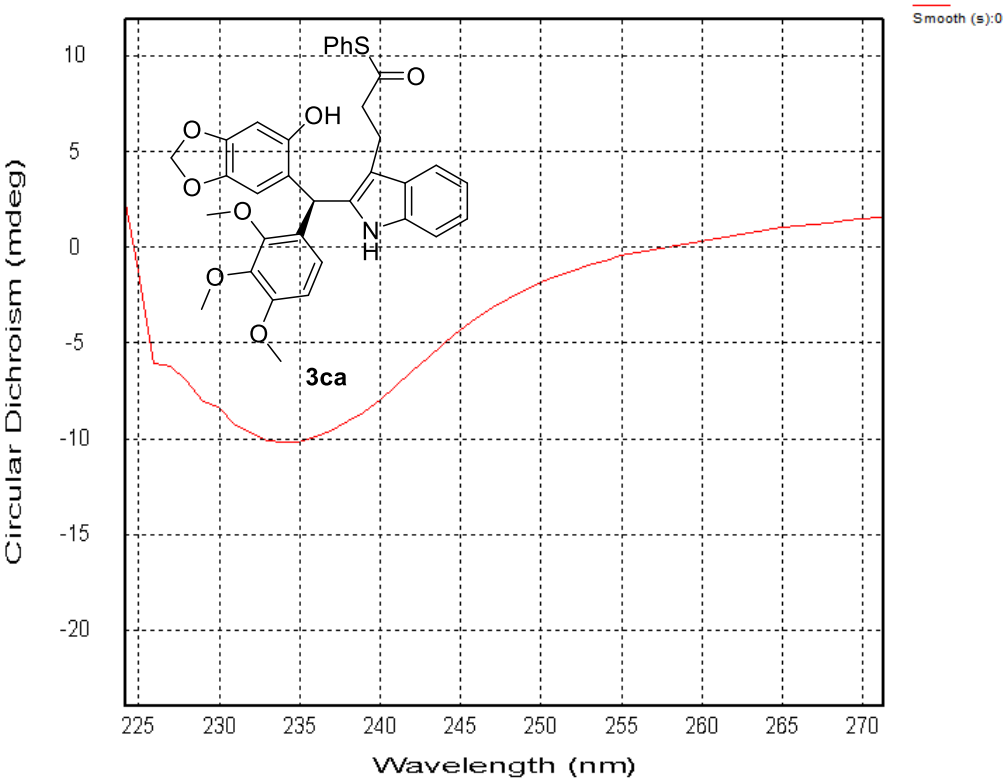

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)
O
SPh
OH
O
O
N
H
O
3aq

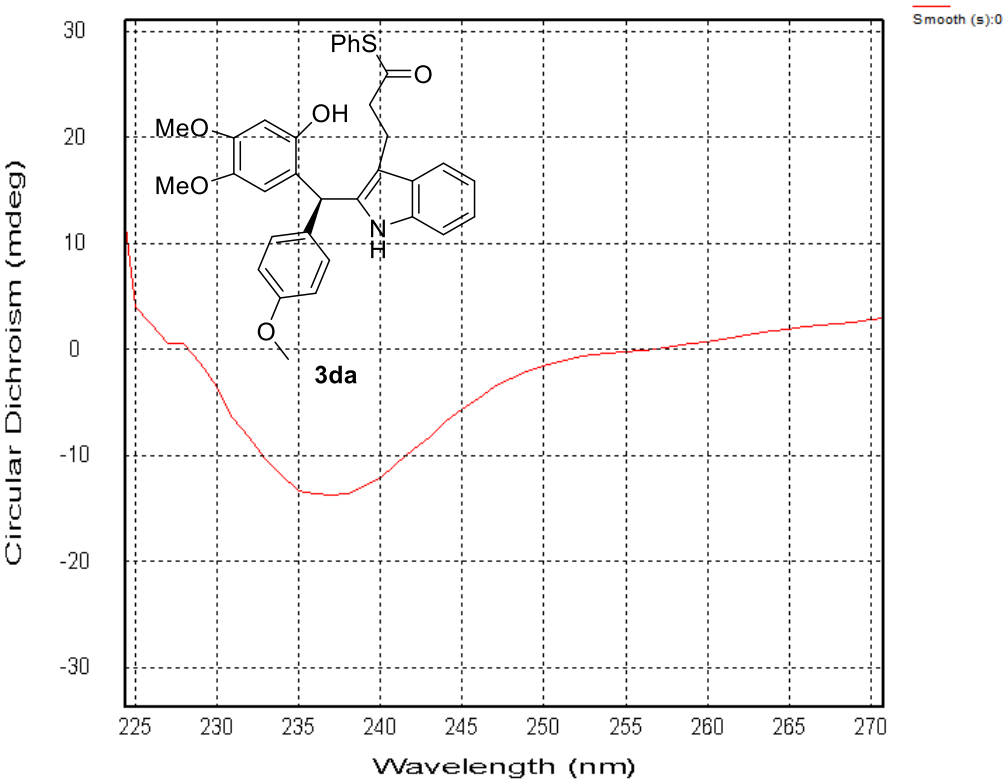

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)
N
N
O
OH
O
O
N
H
O
3ar

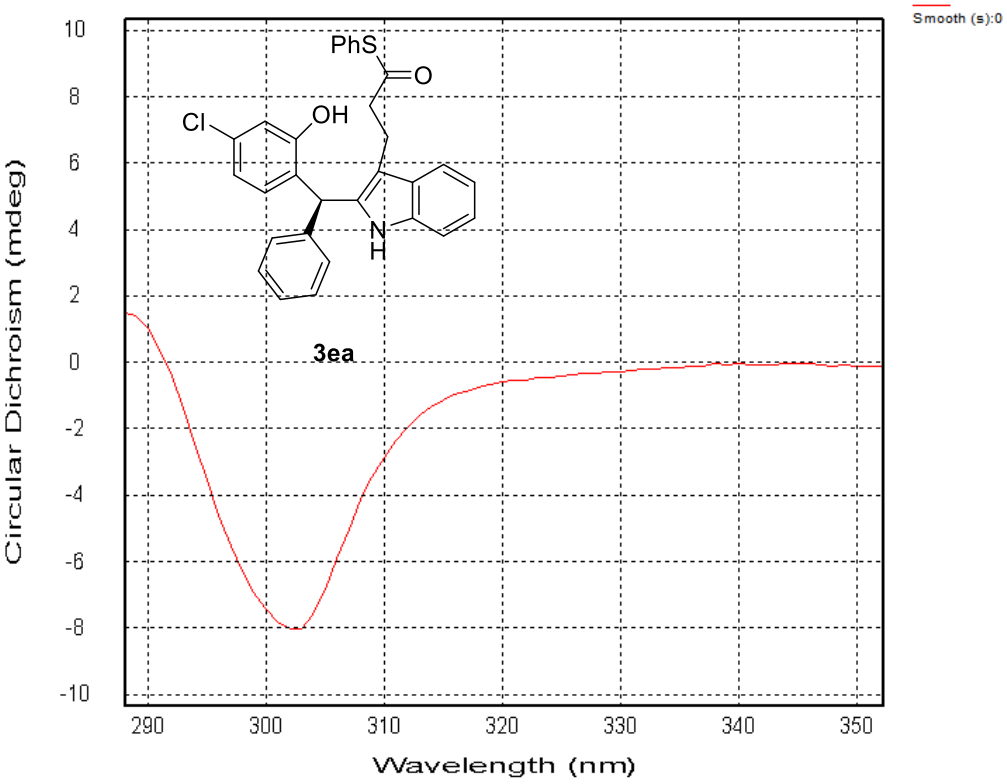

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
220
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)
OH
O
N
H
3as

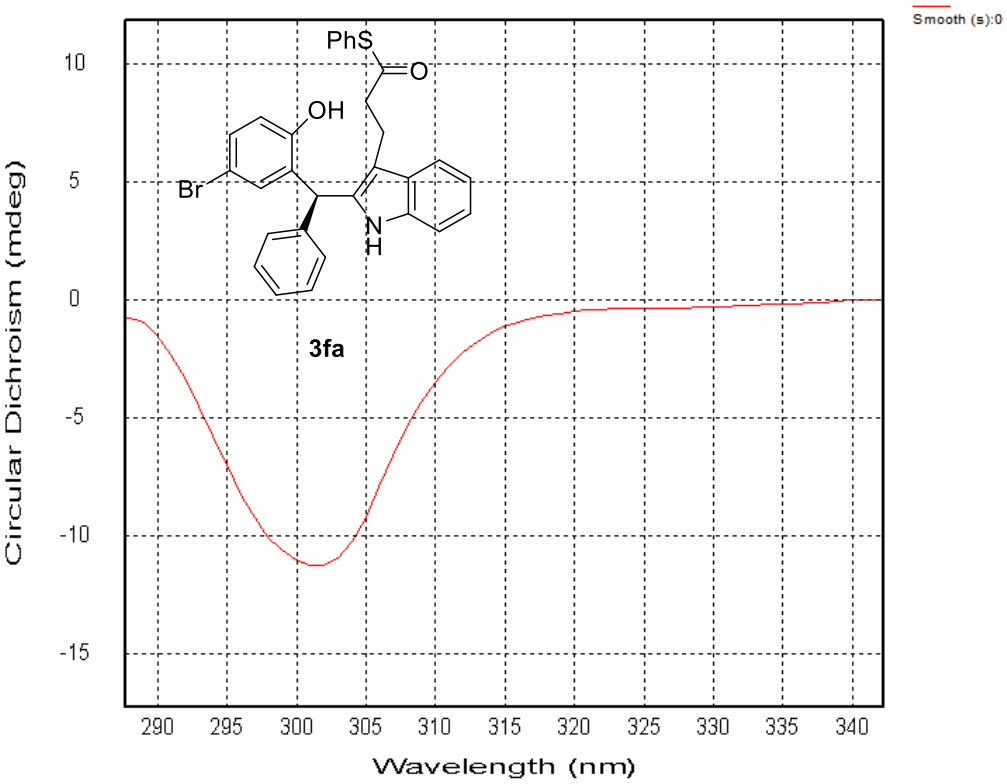

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)
O2N
S
O
OH
N
H
3at

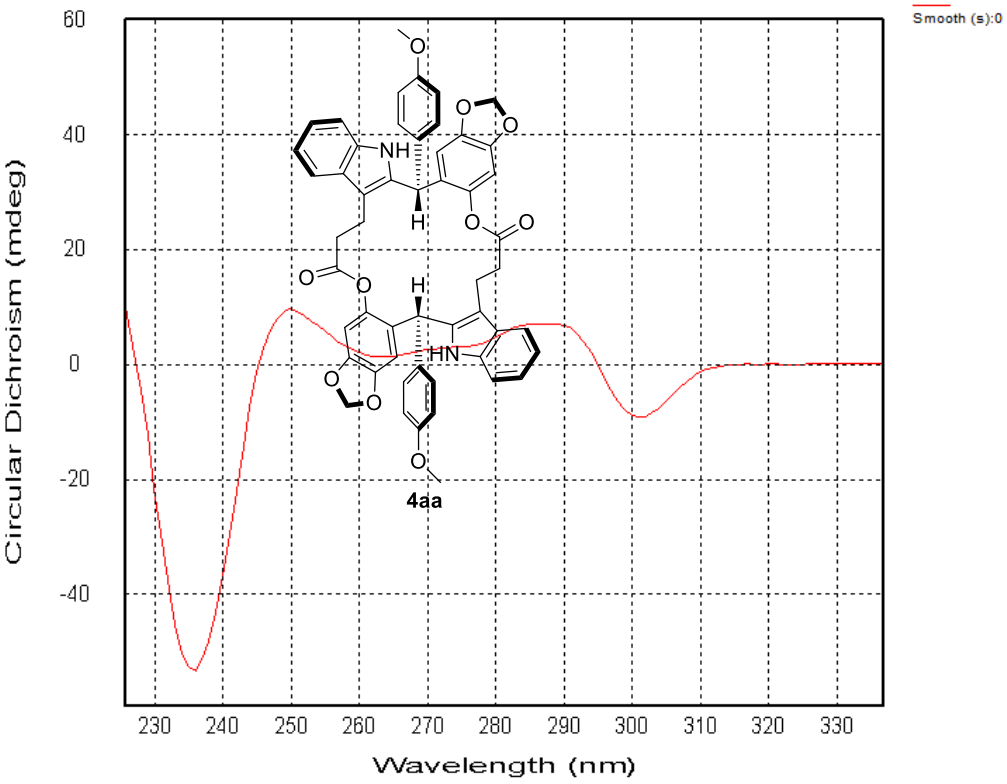

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)
PhS
O
OH
O
O
N
H
O
Et
3ba

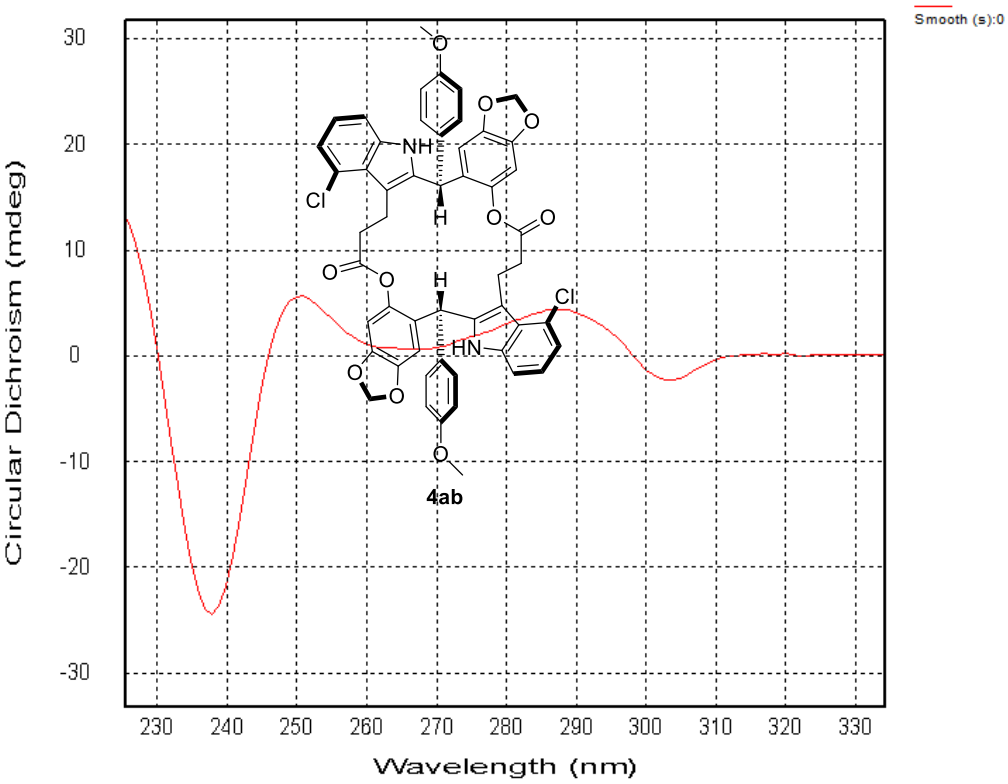

Smooth (s):0
Circular Dichroism (mdeg)
10
5
0
-5
-10
-15
-20
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)
PhS
O
OH
O
O
O
O
N
H
3ca

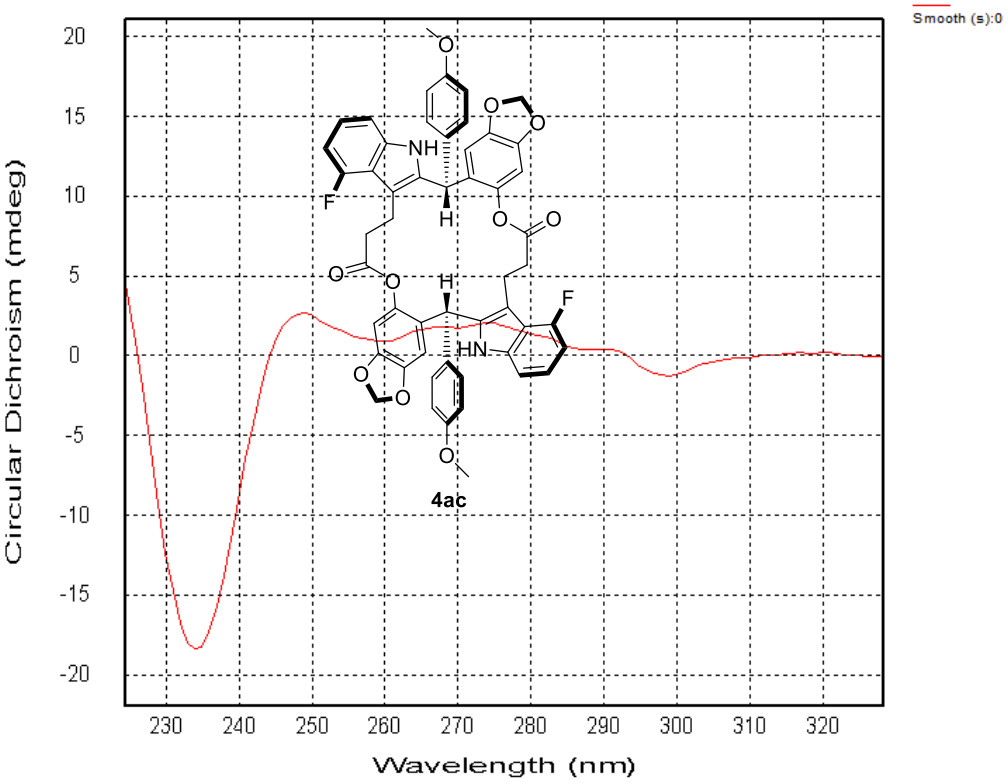

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
225
230
235
240
245
250
255
260
265
270
Wavelength (nm)
PhS
O
OH
MeO
MeO
N
H
O
3da

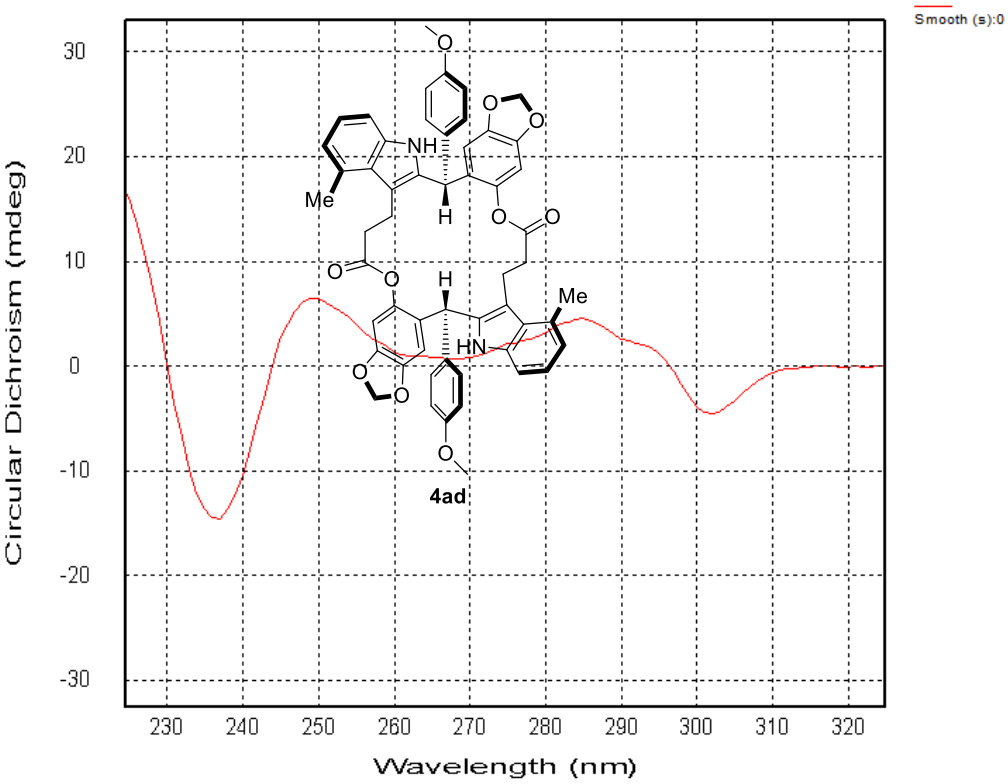

Smooth (s):0
Circular Dichroism (mdeg)
10
8
6
4
2
0
-2
-4
-6
-8
-10
290
300
310
320
330
340
350
Wavelength (nm)
PhS
O
Cl
OH
N
H
3ea

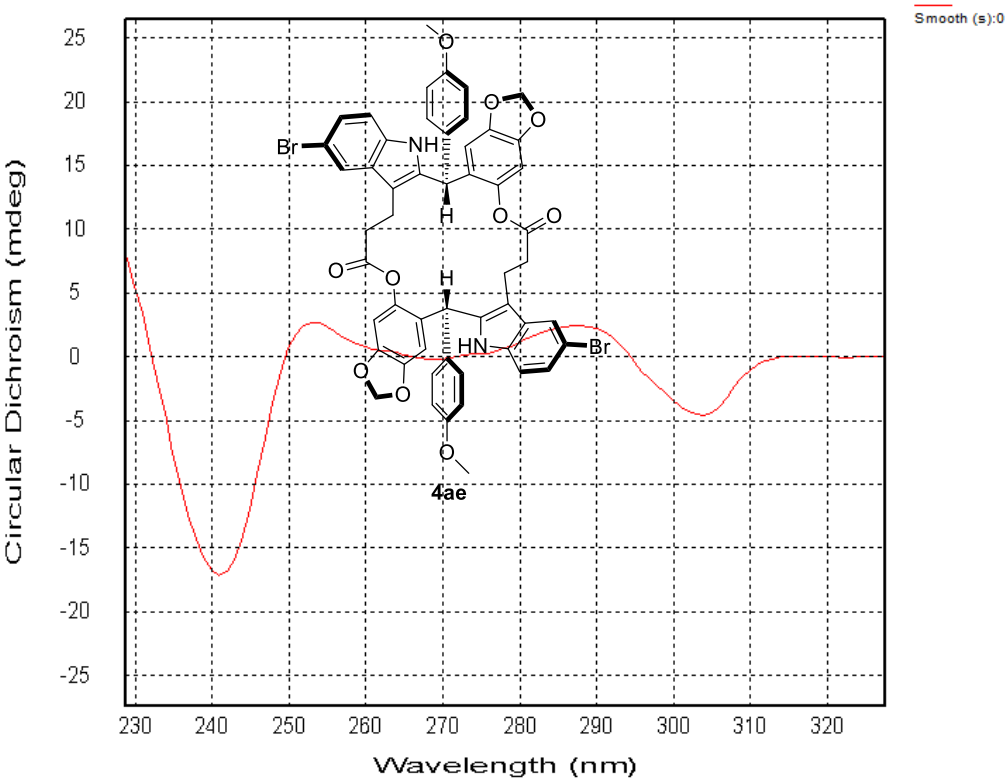

Smooth (s):0
Circular Dichroism (mdeg)
10
5
0
-5
-10
-15
290
295
300
305
310
315
320
325
330
335
340
Wavelength (nm)
PhS
O
OH
Br
N
H
3fa

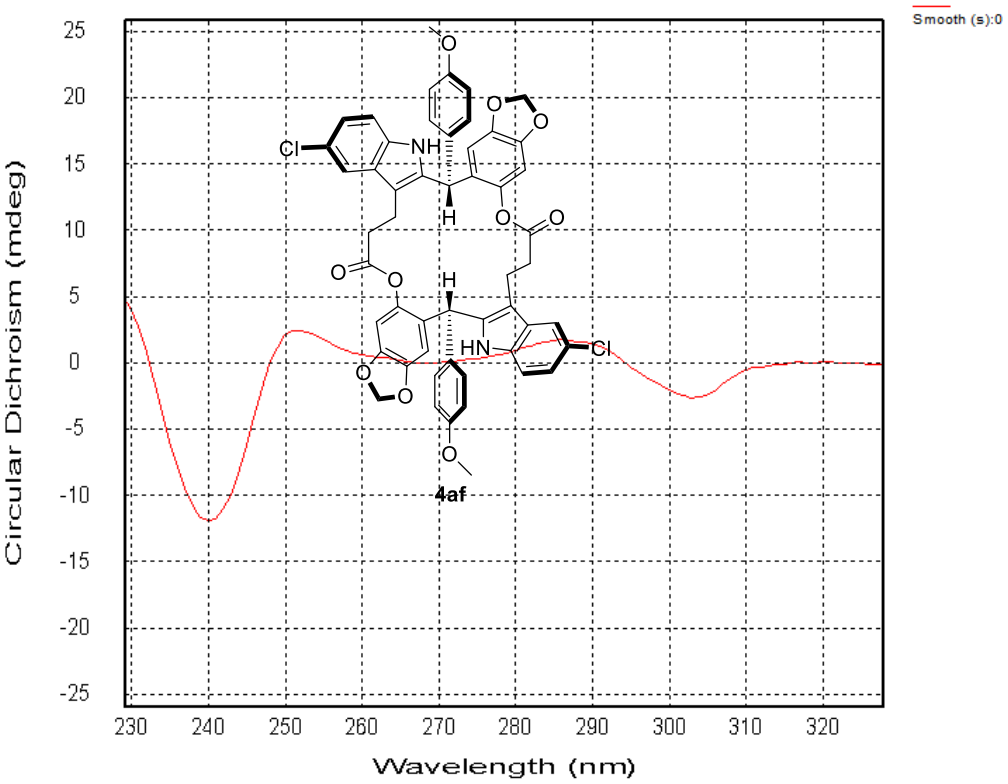

Smooth (s):0
Circular Dichroism (mdeg)
60
40
20
0
-20
-40
230
240
250
260
270
280
290
300
310
320
330
Wavelength (nm)
O
NH
H
O
O
O
O
O
O
H
HN
O
O
O
4aa

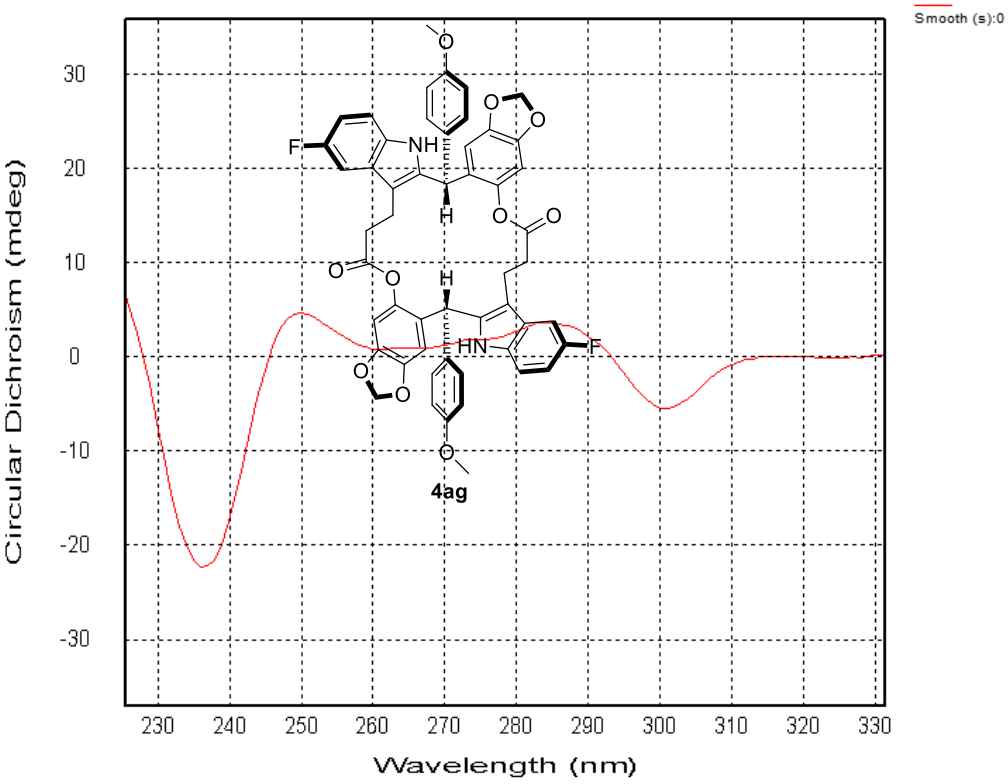

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
230
240
250
260
270
280
290
300
310
320
330
Wavelength (nm)
4ab

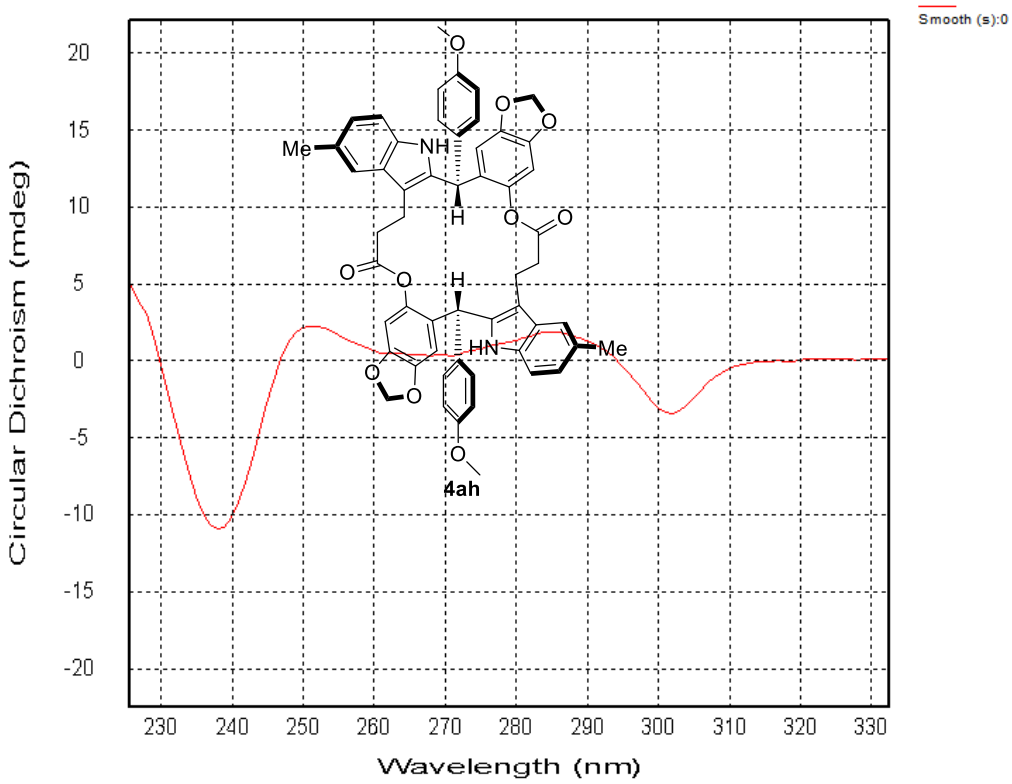

Smooth (s):0
Circular Dichroism (mdeg)
20
15
10
5
0
-5
-10
-15
-20
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
4ac

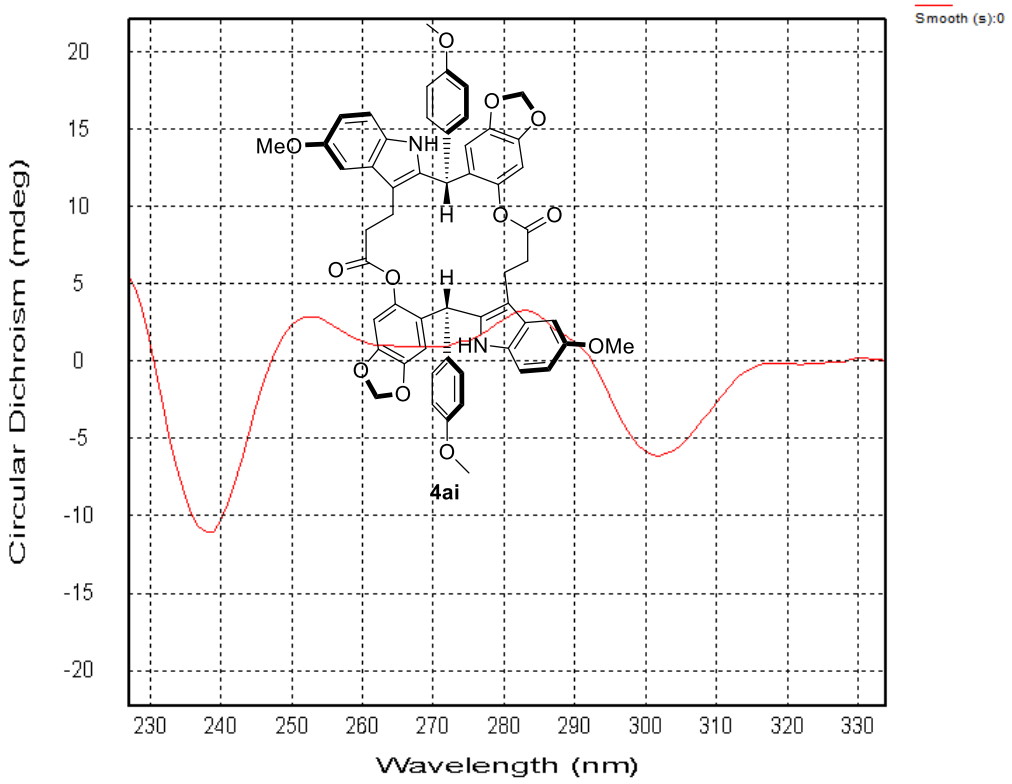

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
Me
NH
H
O
O
O
O
O
O
O
H
Me
HN
O
O
O
4ad

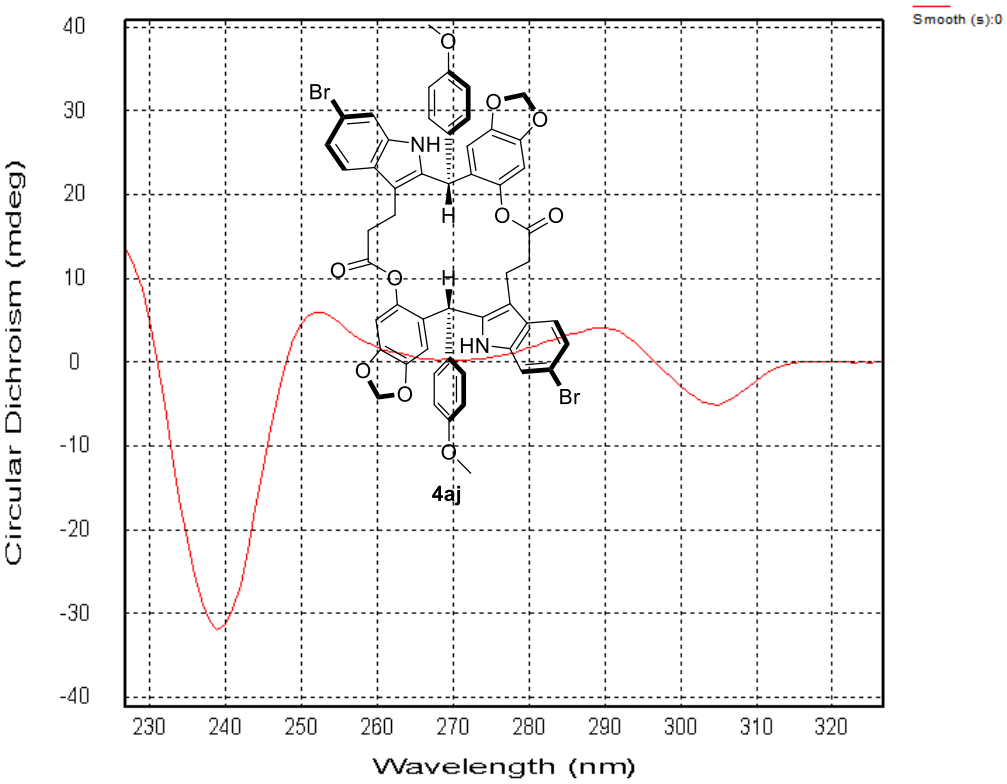

Smooth (s):0
Circular Dichroism (mdeg)
25
20
15
10
5
0
-5
-10
-15
-20
-25
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
Br
NH
H
O
O
O
O
O
O
O
H
HN
Br
O
O
O
4ae

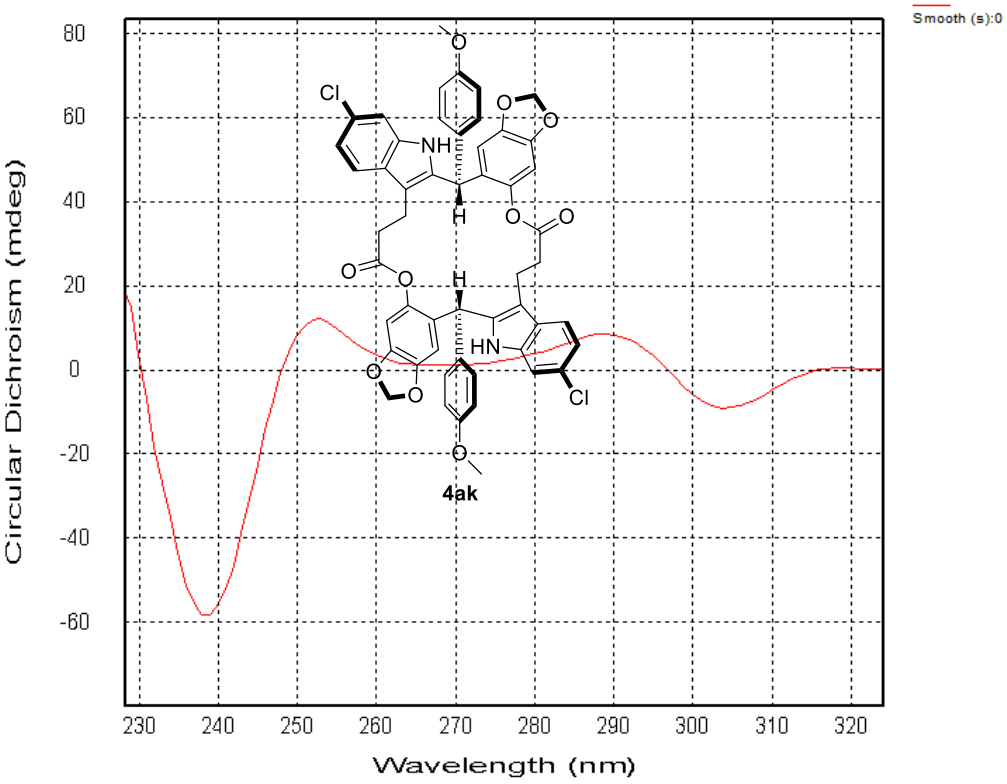

Smooth (s):0
Circular Dichroism (mdeg)
25
20
15
10
5
0
-5
-10
-15
-20
-25
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
Cl
NH
HN
Cl
4af

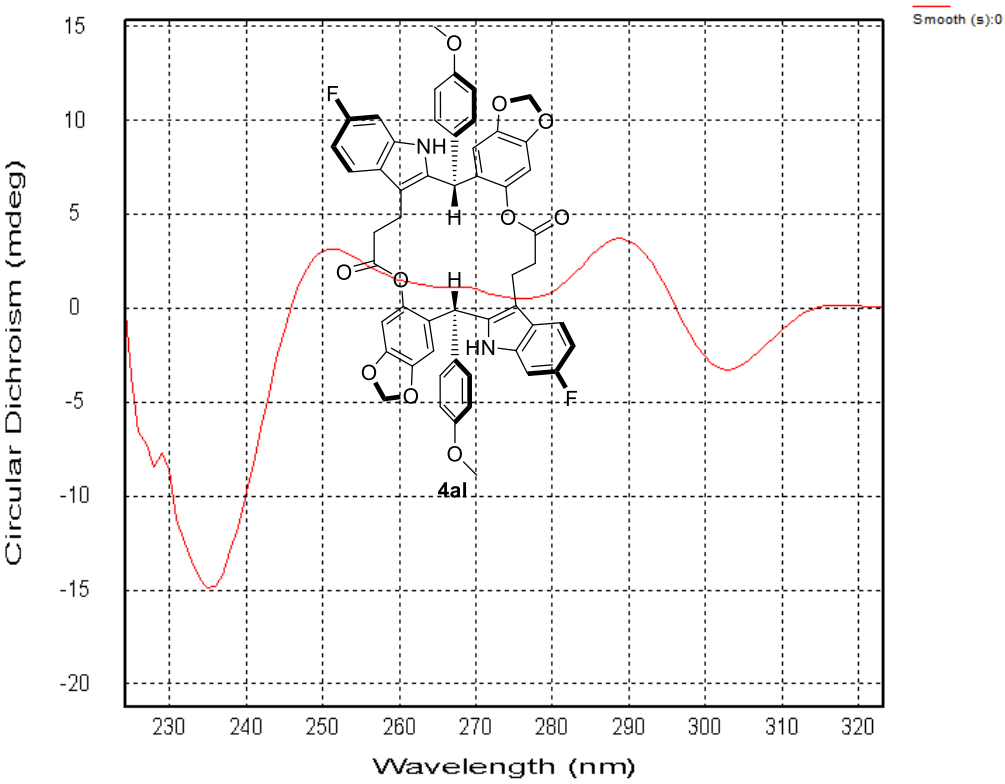

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
230
240
250
260
270
280
290
300
310
320
330
Wavelength (nm)
F
NH
HN
F
4ag

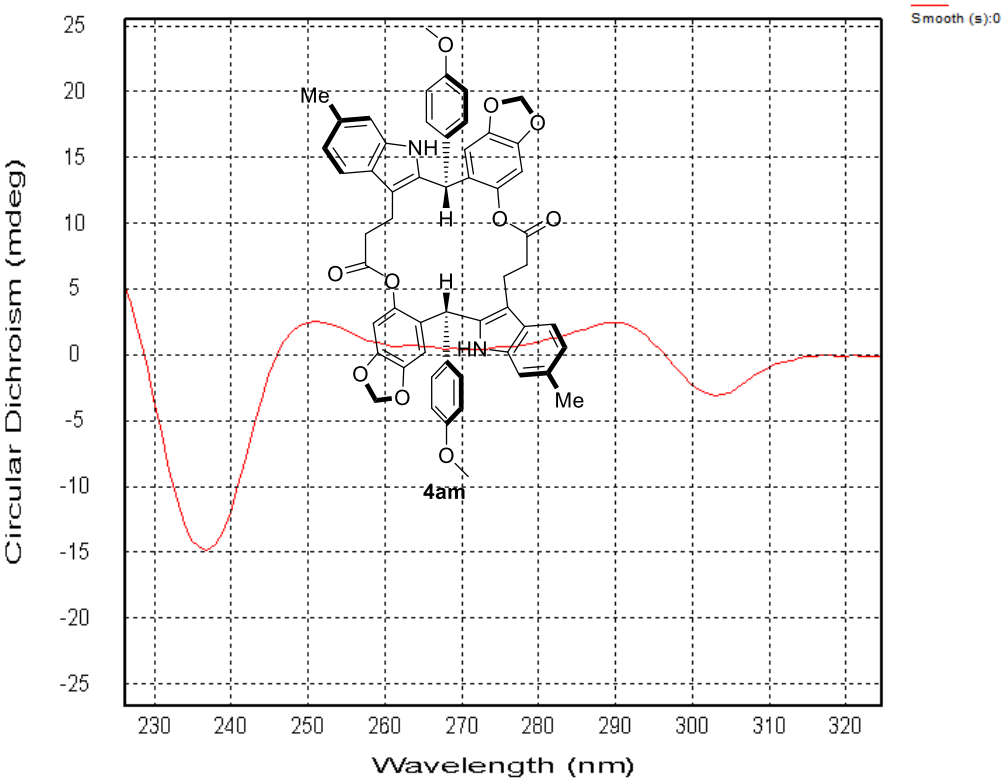

Smooth (s):0
Circular Dichroism (mdeg)
20
15
10
5
0
-5
-10
-15
-20
230
240
250
260
270
280
290
300
310
320
330
Wavelength (nm)
Me
NH
HN
Me
4ah

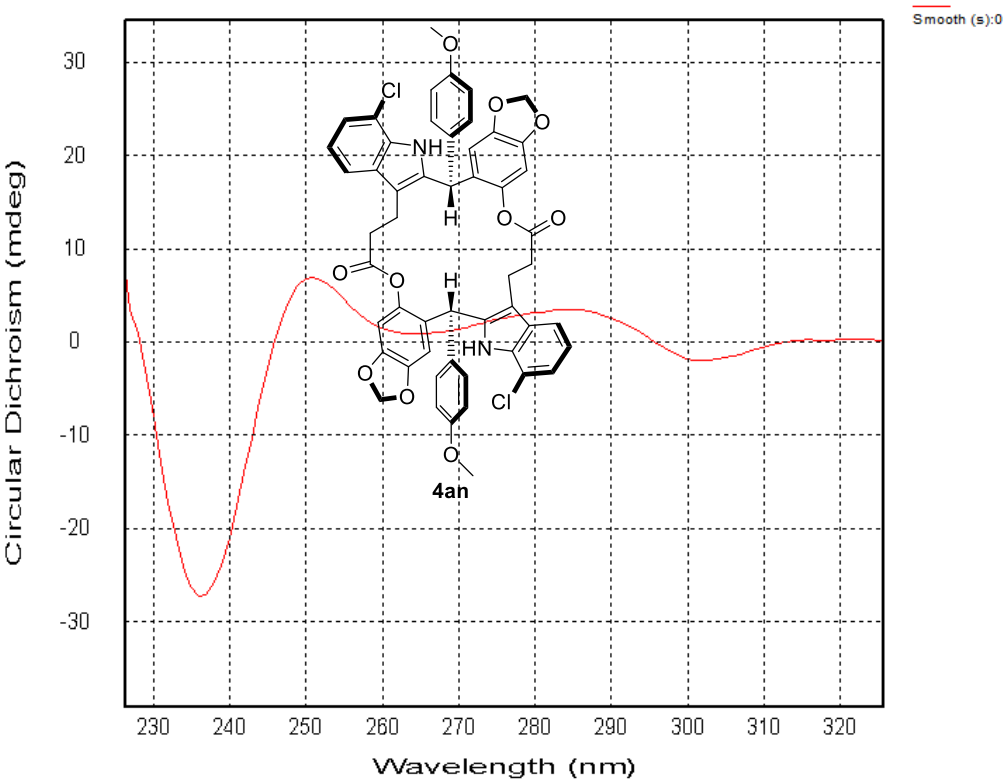

Smooth (s):0
Circular Dichroism (mdeg)
20
15
10
5
0
-5
-10
-15
-20
230
240
250
260
270
280
290
300
310
320
330
Wavelength (nm)
MeO
NH
HN
OMe
4ai

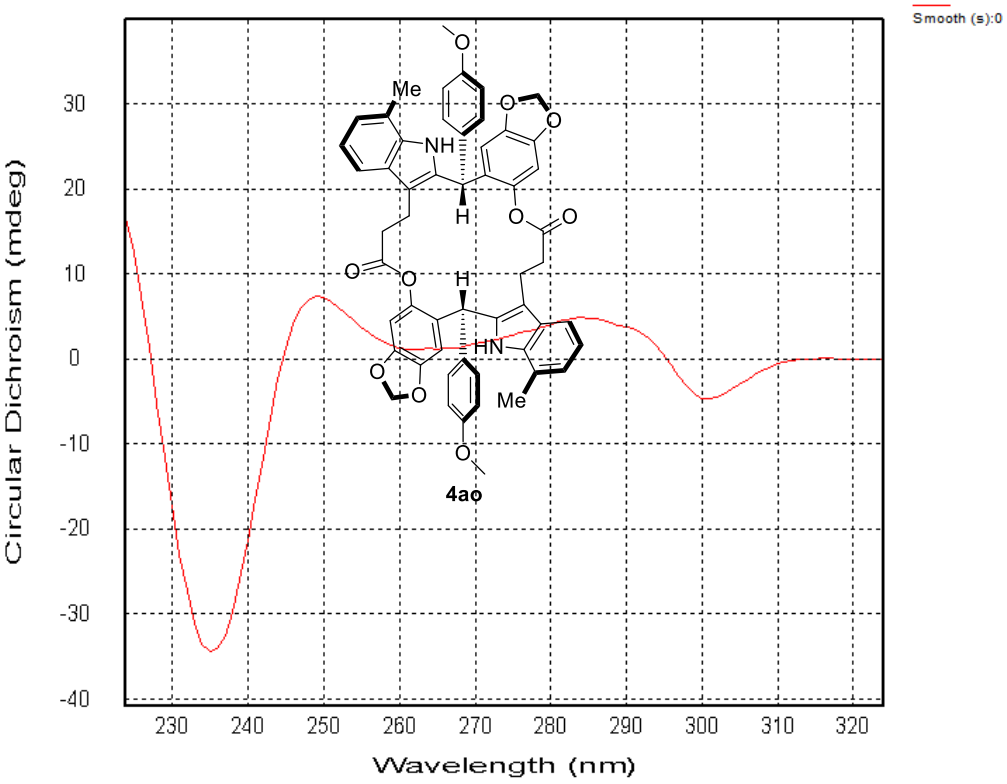

Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)
4aj

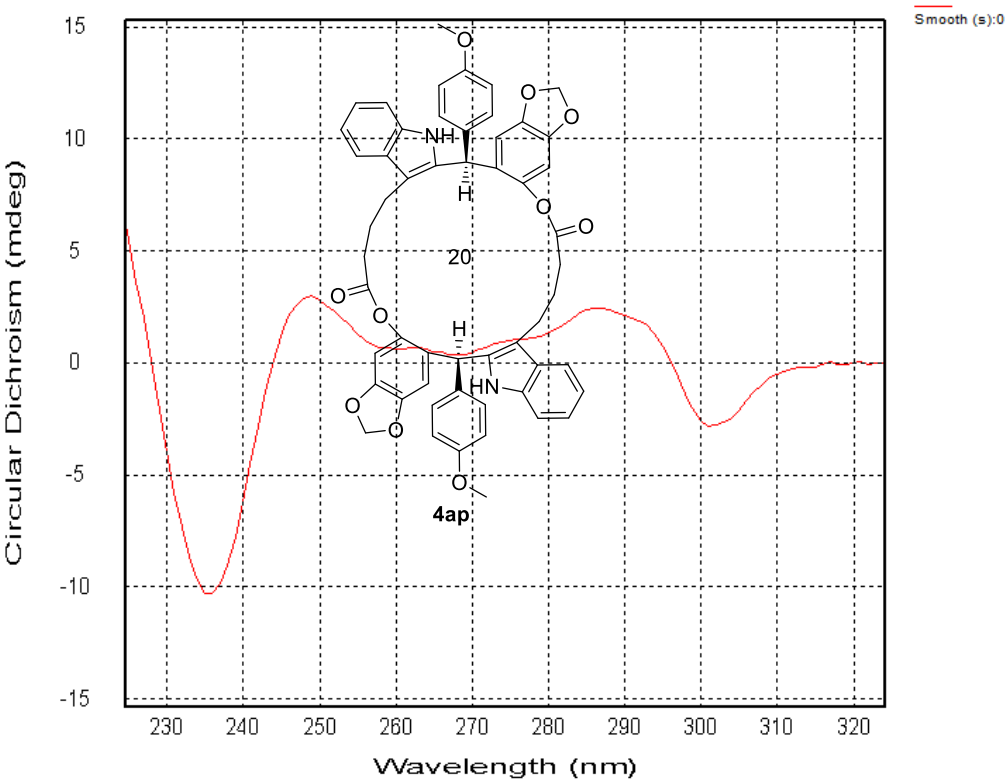

Smooth (s):0
Circular Dichroism (mdeg)
Wavelength (nm)
4ak

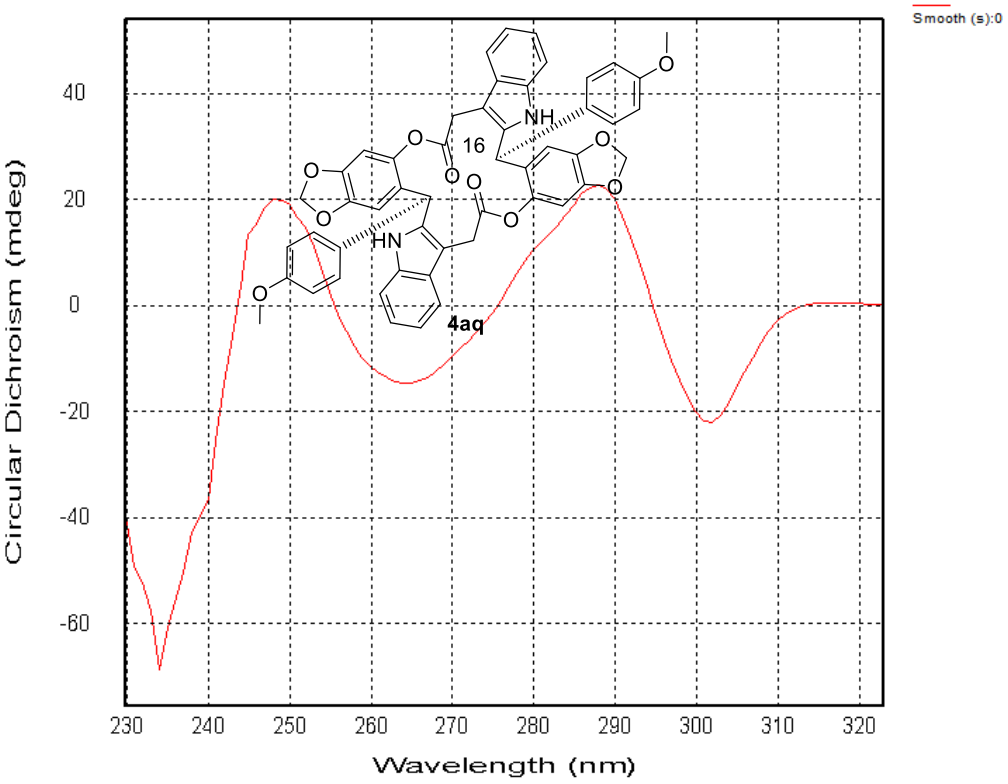

Smooth (s):0
Circular Dichroism (mdeg)
15
10
5
0
-5
-10
-15
-20
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
F
NH
H
HN
F
4al

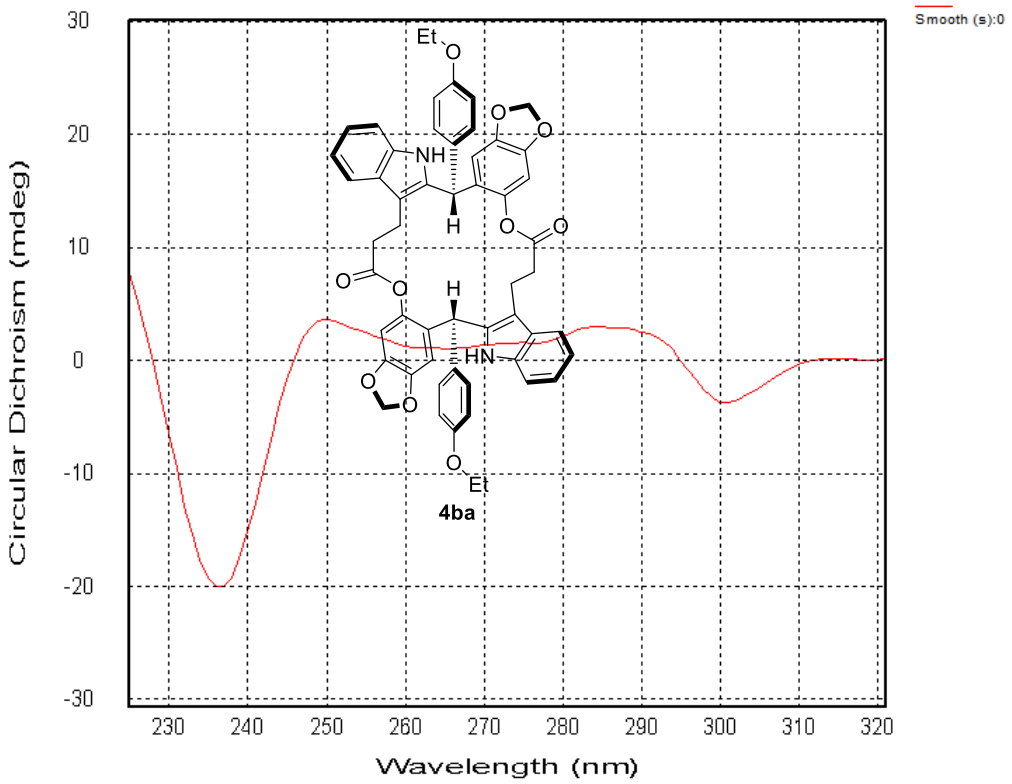

Smooth (s):0
Circular Dichroism (mdeg)
25
20
15
10
5
0
-5
-10
-15
-20
-25
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
Me
NH
H
HN
Me
4am

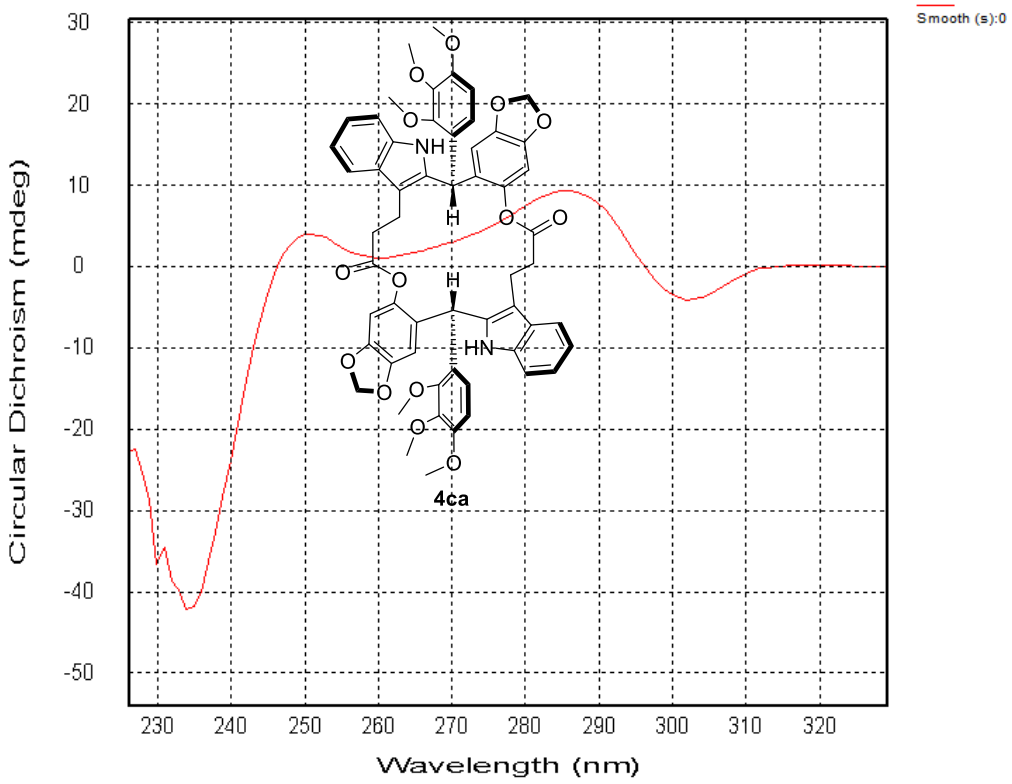

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
Cl
NH
H
O
HN
Cl
4an

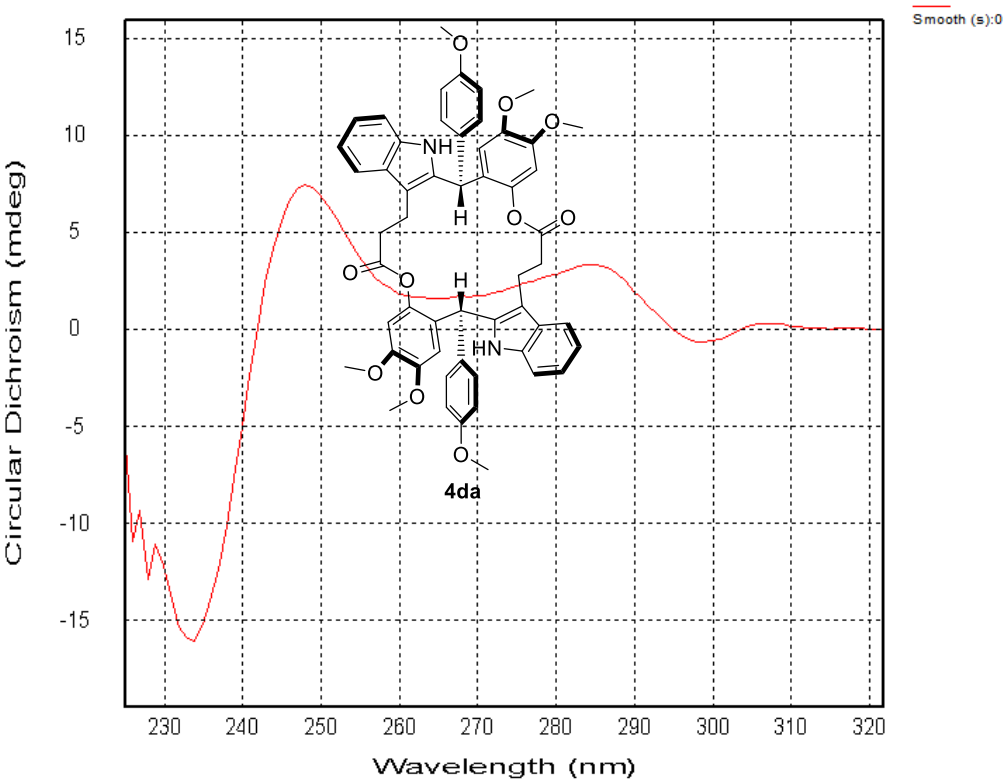

Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
-40
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
Me
NH
H
O
HN
Me
4ao


Smooth (s):0
Circular Dichroism (mdeg)
15
10
5
0
-5
-10
-15
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
NH
H
O
20
HN
4ap


Smooth (s):0
Circular Dichroism (mdeg)
40
20
0
-20
-40
-60
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
NH
HN
16
4aq


Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
Et
O
NH
H
HN
4ba


Smooth (s):0
Circular Dichroism (mdeg)
30
20
10
0
-10
-20
-30
-40
-50
230
240
250
260
270
280
290
300
310
320
Wavelength (nm)
O
NH
H
HN
4ca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Circular Dichroism (mdeg)
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10
5
0
-5
-10
-15
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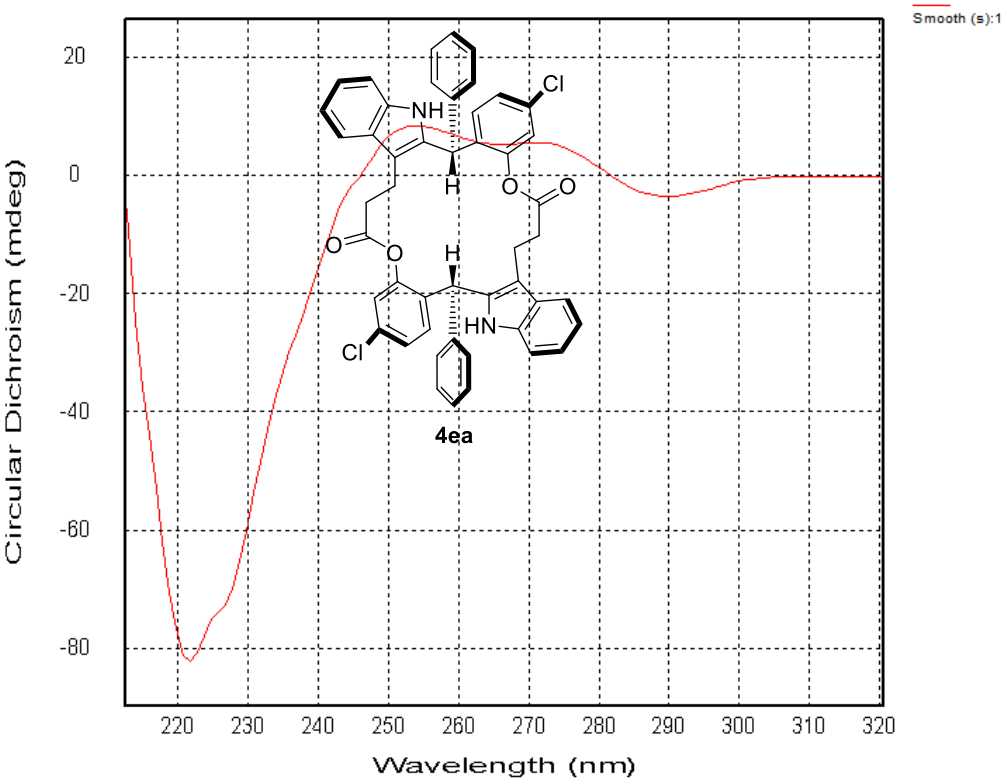
250
260
270
280
290
300
310
320
Wavelength (nm)
4da


Smooth (s):1
Circular Dichroism (mdeg)
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310
320
Wavelength (nm)
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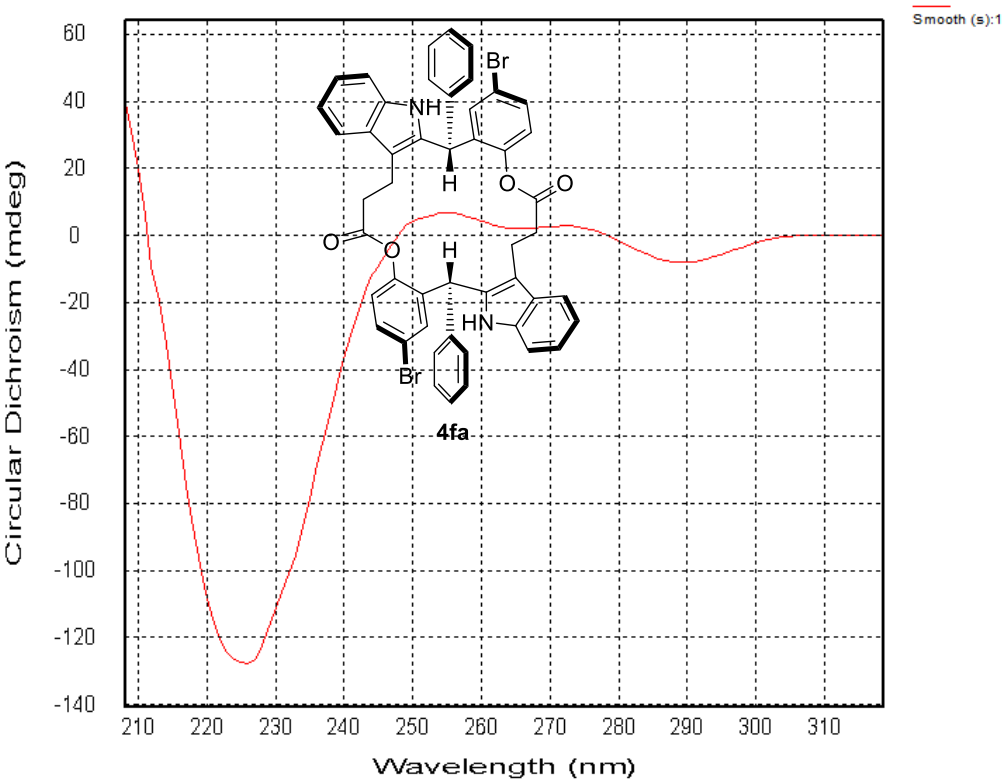
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Circular Dichroism (mdeg)
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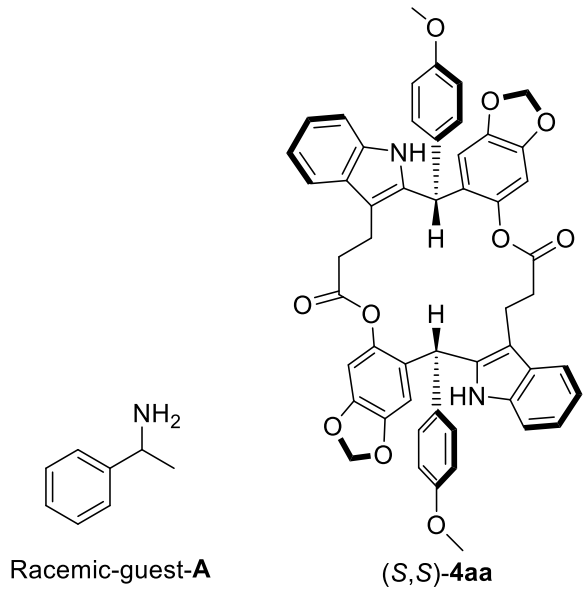
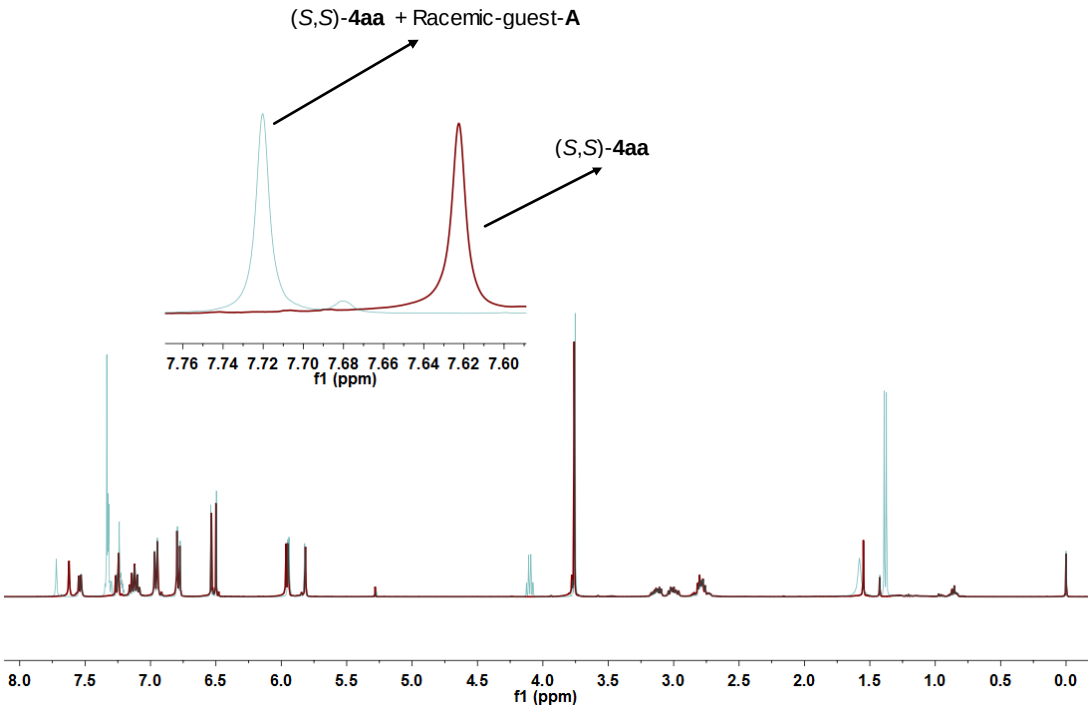
-20
-40
-60
-80
-100
-120
-140
210
220
230
240
250
260
270
280
290
300
310
Wavelength (nm)
Br
NH
H
O
O
O
O
H
HN
Br
4fa

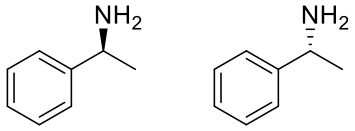
14. Chiral recognition of macrodiolide product (*S*,*S*)-4aa

14.1 Chiral recognition of (*S*,*S*)-4aa toward guests A—J by ^{1}H NMR analysis.

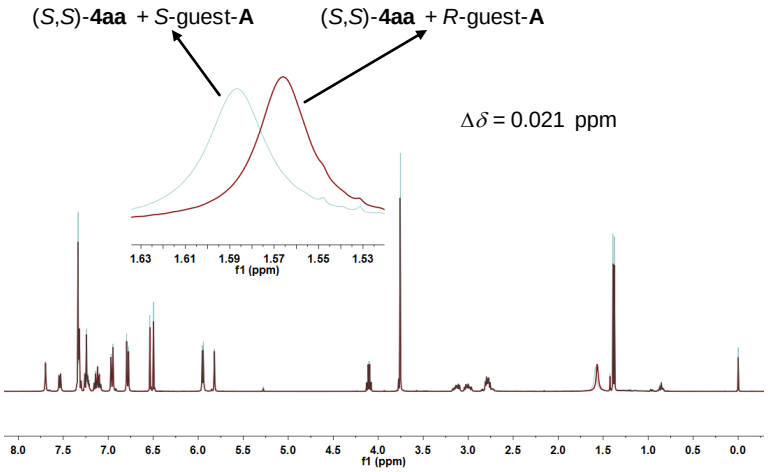




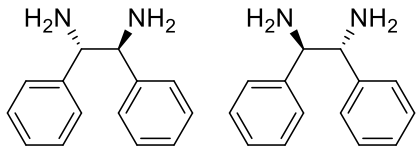
Procedure: The sample (red) was prepared by dissolving (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) in NMR tubes in $CDCl_3$ (0.7 mL) [36 mM of the (*S*,*S*)-**4aa**]. The sample (blue) was prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and racemic guest **A** (6.5 μL, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of racemic guest **A** in $CDCl_3$ (0.7 mL)]. ^{1}H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The N-H signals of (*S*,*S*)-**4aa** (red) compared with (*S*,*S*)-**4aa** with racemic guest **A** (blue) are shown in the figure. It is speculated that there exists hydrogen bond interactions between (*S*,*S*)-**4aa** and racemic guest **A**.



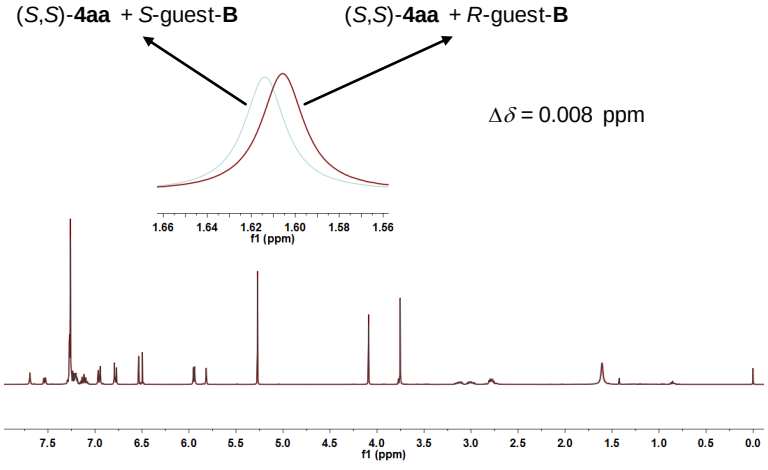
S-guest-**A** *R*-guest-**A**



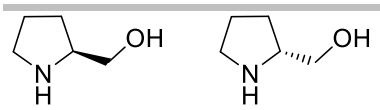
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *S*-guest-**A** (6.5 µL, 0.05 mmol) or *R*-guest-**A** (6.5 µL, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **A** in $CDCl_3$ (0.7 mL)]. ^1H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The N-H signals of *S*-guest-**A** with (*S*,*S*)-**4aa** (blue) compared with *R*-guest-**A** with (*S*,*S*)-**4aa** (red) are shown in the figure.



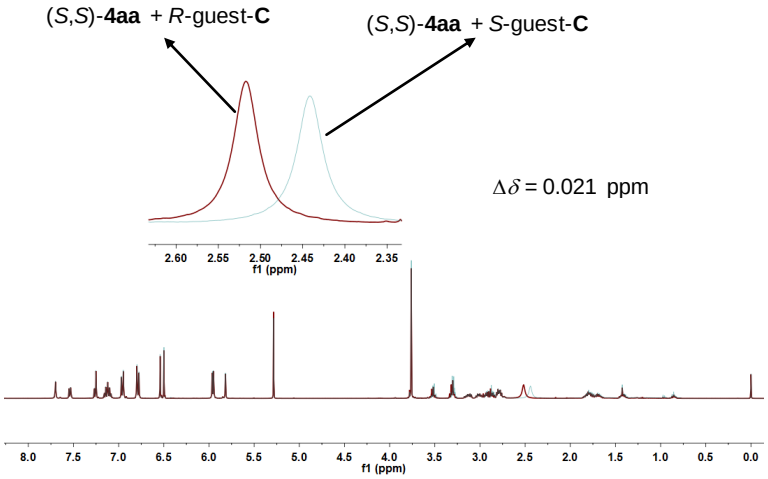
S-guest-**B** *R*-guest-**B**



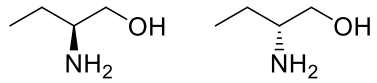
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *S*-guest-**B** (10.6 mg, 0.05 mmol) or *R*-guest-**B** (10.6 mg, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **B** in $CDCl_3$ (0.7 mL)]. ^1H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The N-H signals of *S*-guest-**B** with (*S*,*S*)-**4aa** (blue) compared with *R*-guest-**B** with (*S*,*S*)-**4aa** (red) are shown in the figure.



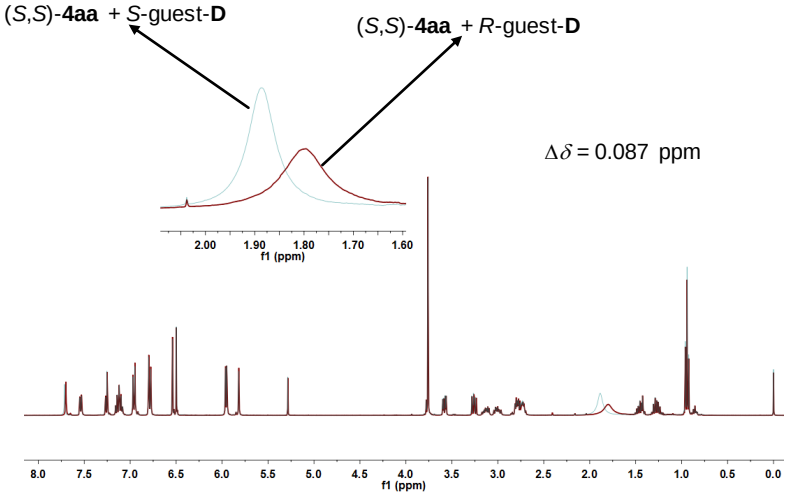
S-guest-**C** *R*-guest-**C**



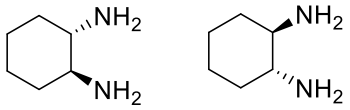
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *S*-guest-**C** (4.9 µL, 0.05 mmol) or *R*-guest-**C** (4.9 µL, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **C** in $CDCl_3$ (0.7 mL)]. ^{1}H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The N-H signals of *S*-guest-**C** with (*S*,*S*)-**4aa** (blue) compared with *R*-guest-**C** with (*S*,*S*)-**4aa** (red) are shown in the figure.



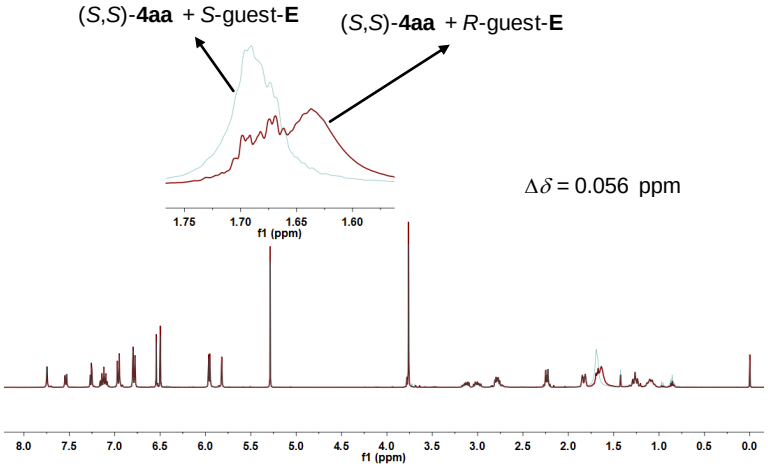
S-guest-**D** *R*-guest-**D**



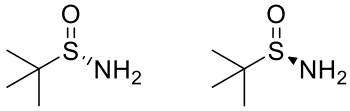
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *S*-guest-**D** (4.7 µL, 0.05 mmol) or *R*-guest-**D** (4.7 µL, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **D** in $CDCl_3$ (0.7 mL)]. ^{1}H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The N-H signals of *S*-guest-**D** with (*S*,*S*)-**4aa** (blue) compared with *R*-guest-**D** with (*S*,*S*)-**4aa** (red) are shown in the figure.



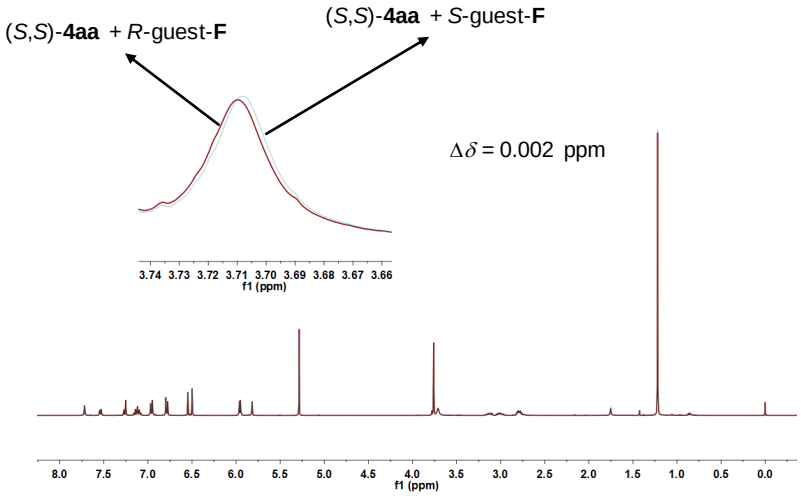
S-guest-**E** *R*-guest-**E**



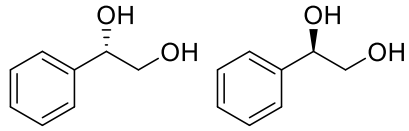
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *S*-guest-**E** (5.7 mg, 0.05 mmol) or *R*-guest-**E** (5.7 mg, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **E** in $CDCl_3$ (0.7 mL)]. ^{1}H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The N-H signals of *S*-guest-**E** with (*S*,*S*)-**4aa** (blue) compared with *R*-guest-**E** with (*S*,*S*)-**4aa** (red) are shown in the figure.



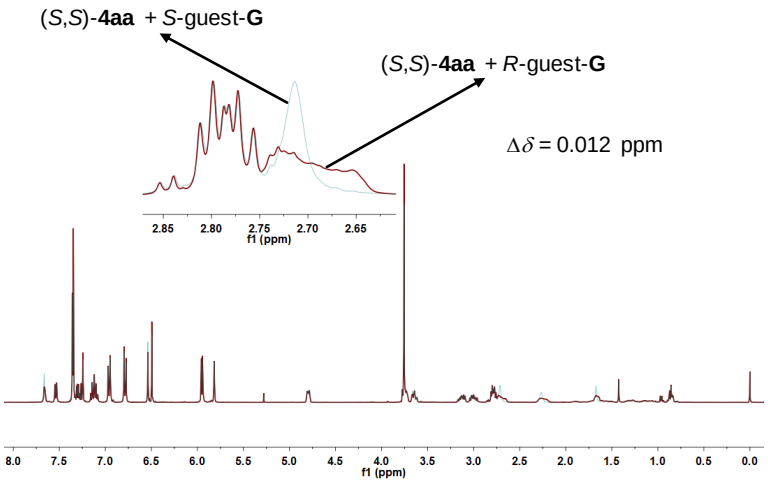
S-guest-**F** *R*-guest-**F**



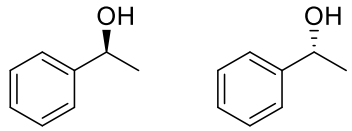
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *S*-guest-**F** (6.1 mg, 0.05 mmol) or *R*-guest-**F** (6.1 mg, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **F** in $CDCl_3$ (0.7 mL)]. ^{1}H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The N-H signals of *S*-guest-**F** with (*S*,*S*)-**4aa** (blue) compared with *R*-guest-**F** with (*S*,*S*)-**4aa** (red) are shown in the figure.



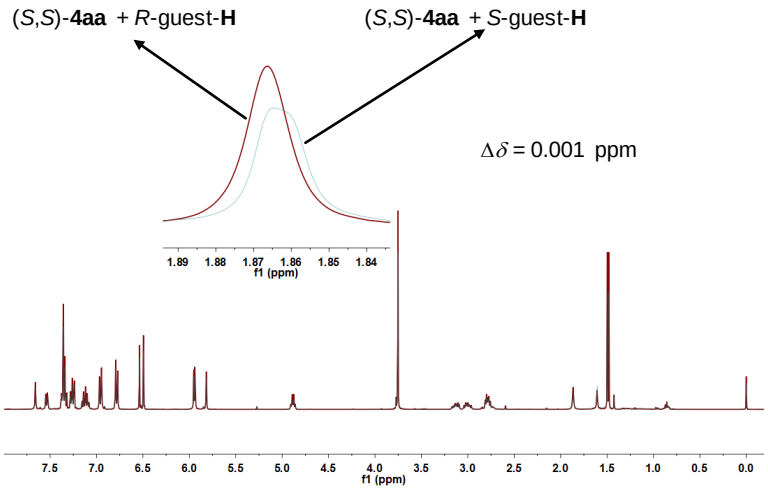
S-guest-**G** *R*-guest-**G**



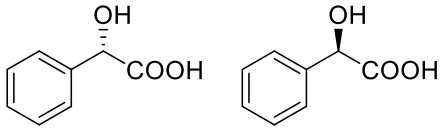
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *S*-guest-**G** (6.9 mg, 0.05 mmol) or *R*-guest-**G** (6.9 mg, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **G** in $CDCl_3$ (0.7 mL)]. ^{1}H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The O-H signals of *S*-guest-**G** with (*S*,*S*)-**4aa** (blue) compared with *R*-guest-**G** with (*S*,*S*)-**4aa** (red) are shown in the figure.



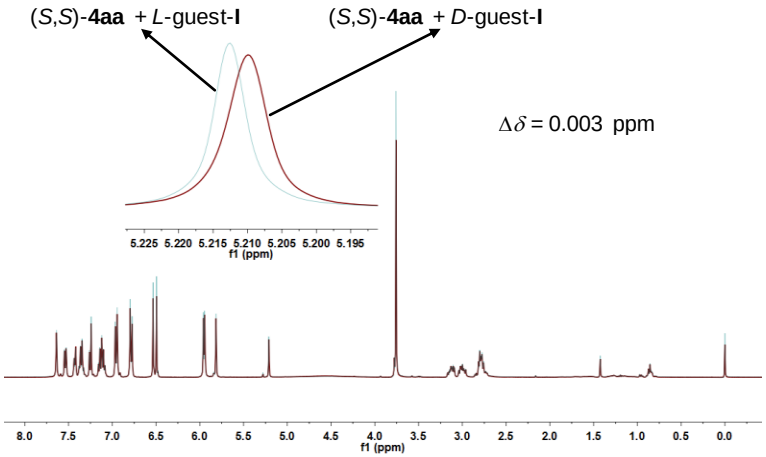
S-guest-**H** *R*-guest-**H**



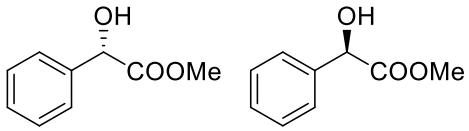
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *S*-guest-**H** (6.1 µL, 0.05 mmol) or *R*-guest-**H** (6.1 µL, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **A** in $CDCl_3$ (0.7 mL)]. ^{1}H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The O-H signals of *S*-guest-**H** with (*S*,*S*)-**4aa** (blue) compared with *R*-guest-**H** with (*S*,*S*)-**4aa** (red) are shown in the figure.



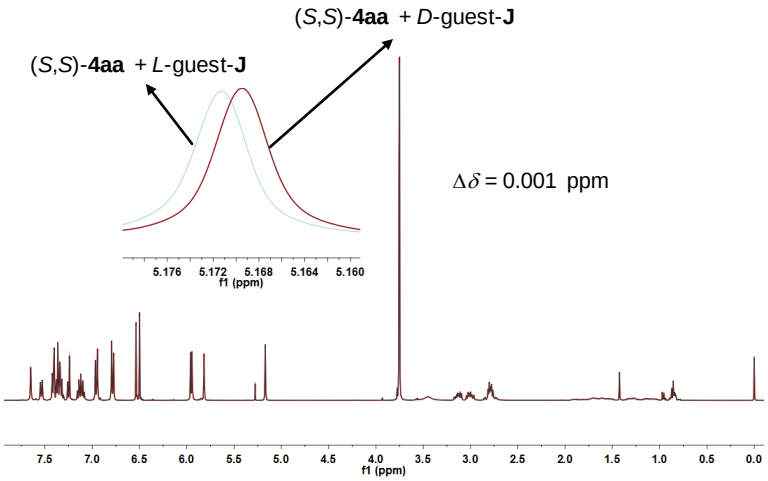
L-guest-**I** *D*-guest-**I**



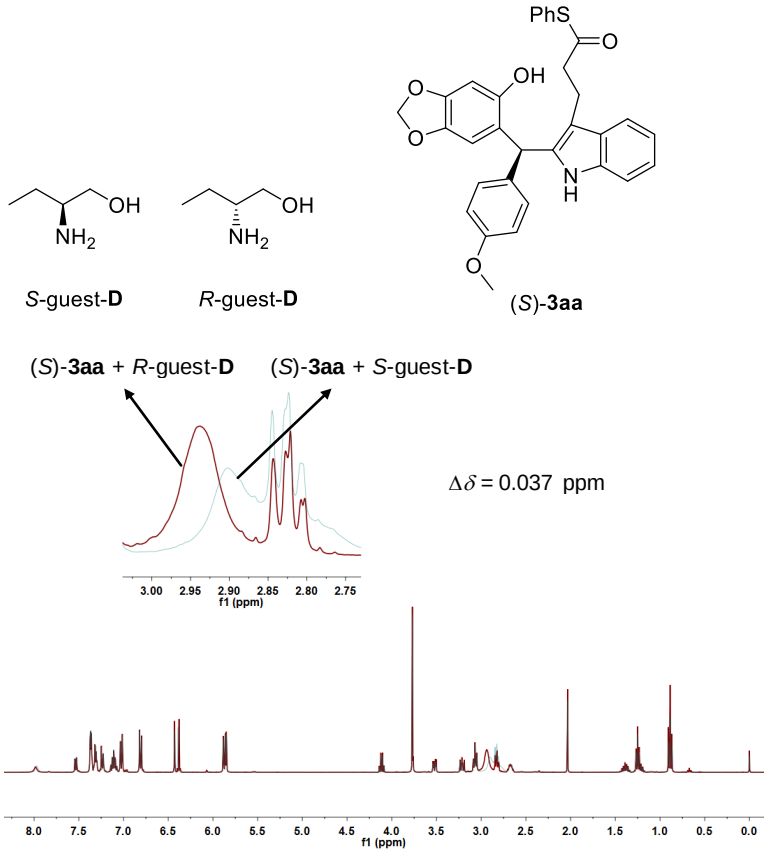
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *L*-guest-**I** (7.6 mg, 0.05 mmol) or *D*-guest-**I** (7.6 mg, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **I** in $CDCl_3$ (0.7 mL)]. ^{1}H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The O-H signals of *L*-guest-**I** with (*S*,*S*)-**4aa** (blue) compared with *D*-guest-**I** with (*S*,*S*)-**4aa** (red) are shown in the figure.



L-guest-**J** *D*-guest-**J**

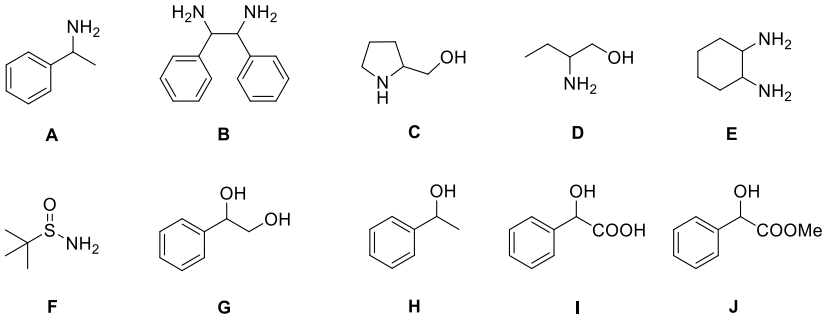


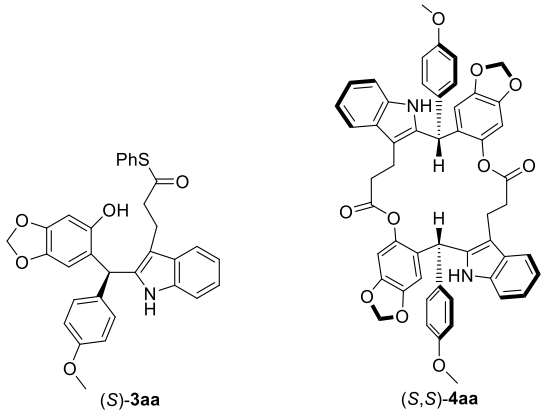
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *L*-guest-**J** (8.3 mg, 0.05 mmol) or *D*-guest-**J** (8.3 mg, 0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **J** in $CDCl_3$ (0.7 mL)]. ^{1}H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The O-H signals of *L*-guest-**J** with (*S*,*S*)-**4aa** (blue) compared with *D*-guest-**J** with (*S*,*S*)-**4aa** (red) are shown in the figure.



Procedure: The samples were prepared by mixing (*S*)-**3aa** (26.9 mg, 0.05 mmol) and *S*-guest-**D** (4.7 µL, 0.05 mmol) or *R*-guest-**D** (4.7 µL, 0.05 mmol) in NMR tubes [36 mM of (*S*)-**3aa** and 72 mM of guest **D** in $CDCl_3$ (0.7 mL)]. ^1H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. The N-H signals of *S*-guest-**D** with (*S*)-**3aa** (blue) compared with *R*-guest-**D** with (*S*)-**3aa** (red) are shown in the figure.

Table S13: Chiral recognition of (*S*,*S*)-**4aa** and (*S*)-**3aa** toward guests **A**–**J** by 1H NMR analysis.[a]

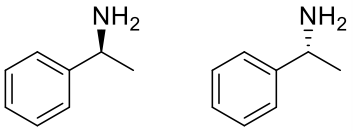




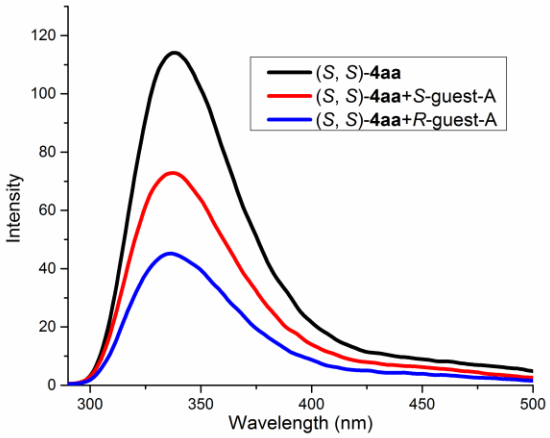
Entry	Guest	$\Delta\delta$ (ppm) [b]
1	**A**	0.021
2	**B**	0.008
3	**C**	0.076
4	**D**	0.087
5	**E**	0.056
6	**F**	0.002
7	**G**	0.012
8	**H**	0.001
9	**I**	0.003
10	**J**	0.001
11[c]	**D**	0.037

[a] The samples were prepared by mixing (*S*,*S*)-**4aa** (21.3 mg, 0.025 mmol) and *S*-guests-**A**–**J** (0.05 mmol) or *R*-guests-**A**–**J** (0.05 mmol) in NMR tubes [36 mM of (*S*,*S*)-**4aa** and 72 mM of guest **A**–**J** in $CDCl_3$ (0.7 mL)]. ^{1}H NMR data were collected on Bruker ASCEND (400 MHz) spectrometer at 25 °C. [b] $\Delta\delta$ of the N-H group or O-H group of guests **A**–**J**. [c] The sample was prepared by mixing (*S*)-**3aa** (26.9 mg, 0.05 mmol) and *S*-guest-**D** (4.7 μL, 0.05 mmol) or *R*-guest-**D** (4.7 μL, 0.05 mmol) in NMR tubes [36 mM of (*S*)-**3aa** and 72 mM of guest **D** in $CDCl_3$ (0.7 mL)].

14.2 Chiral recognition of (*S*,*S*)-4aa toward guests A—J by fluorescence spectra analysis.

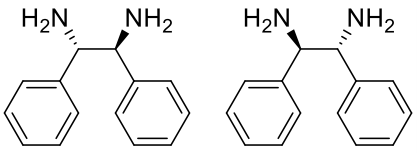


S-guest-**A** *R*-guest-**A**

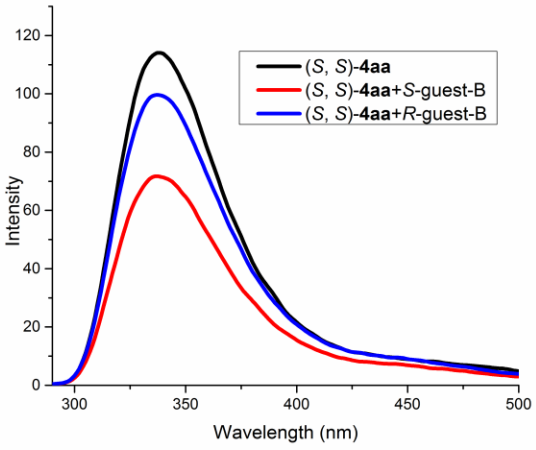


Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**A**	72.59 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**A**	45.13 (I_R)
ef		1.68 (0.60)

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**A** (500 μL, 10 mM in CH_3CN) or *R*-guest-**A** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guest **A** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**A** (red), (*S*,*S*)-**4aa** with *R*-guest-**A** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

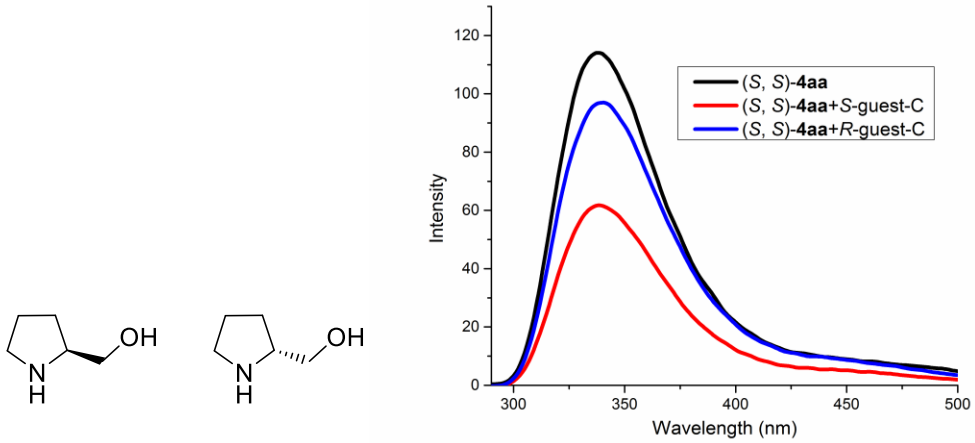


S-guest-**B** *R*-guest-**B**



Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**B**	71.48 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**B**	99.34 (I_R)
ef		3.02 (0.33)

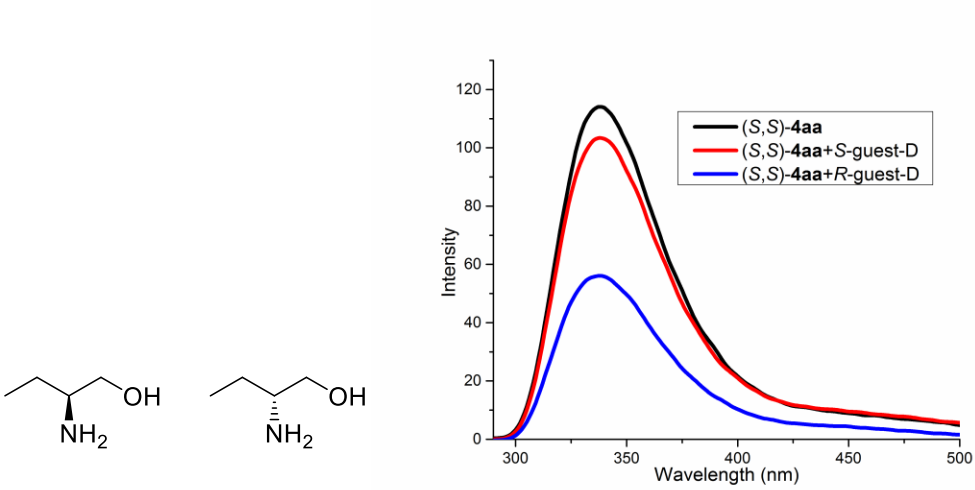
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**B** (500 μL, 10 mM in CH_3CN) or *R*-guest-**B** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guest **B** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**B** (red), (*S*,*S*)-**4aa** with *R*-guest-**B** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.



S-guest-**C** *R*-guest-**C**

Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**C**	60.91 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**C**	95.20 (I_R)
ef		2.92 (0.34)

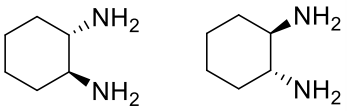
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**C** (500 μL, 10 mM in CH_3CN) or *R*-guest-**C** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guest **C** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**C** (red), (*S*,*S*)-**4aa** with *R*-guest-**C** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.



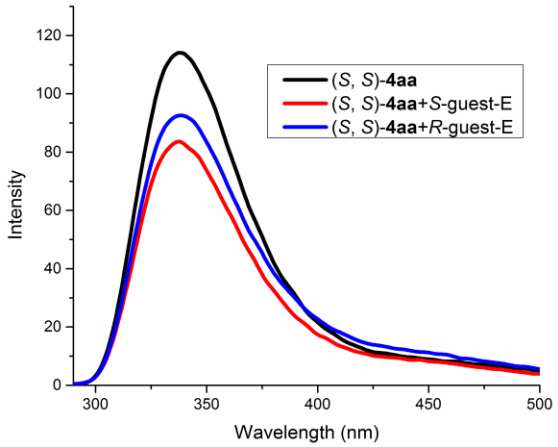
S-guest-**D** *R*-guest-**D**

Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**D**	102.60 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**D**	55.75 (I_R)
ef		5.46 (0.18)

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**D** (500 μL, 10 mM in CH_3CN) or *R*-guest-**D** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guest **D** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**D** (red), (*S*,*S*)-**4aa** with *R*-guest-**D** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

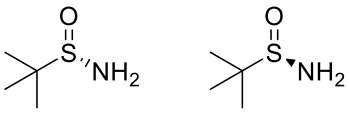


S-guest-**E** *R*-guest-**E**

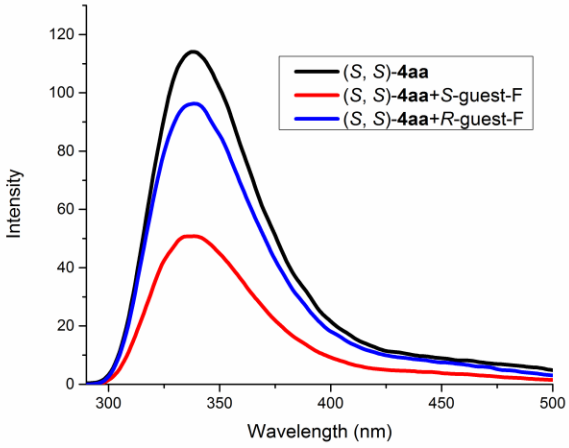


Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**E**	82.94 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**E**	91.83 (I_R)
ef		1.42 (0.70)

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**E** (500 μL, 10 mM in CH_3CN) or *R*-guest-**E** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guest **E** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**E** (red), (*S*,*S*)-**4aa** with *R*-guest-**E** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

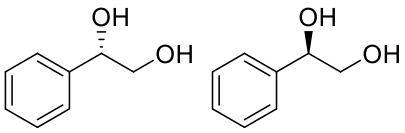


S-guest-**F** *R*-guest-**F**

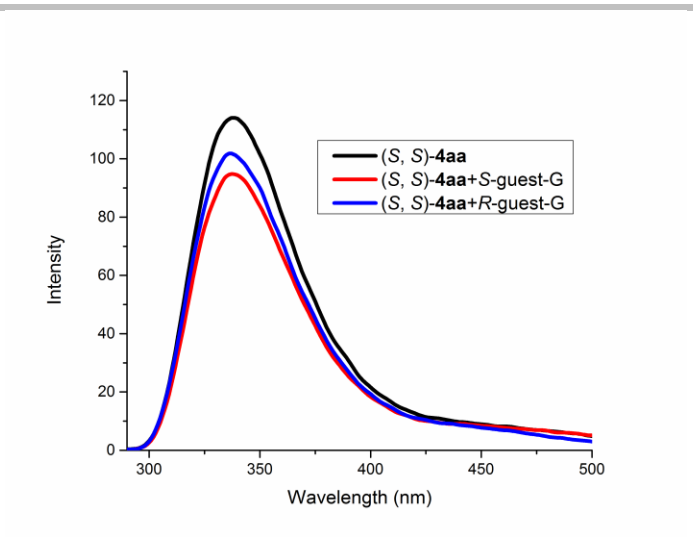


Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**F**	50.73 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**F**	95.71 (I_R)
ef		3.59 (0.28)

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**F** (500 μL, 10 mM in CH_3CN) or *R*-guest-**F** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guest **F** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**F** (red), (*S*,*S*)-**4aa** with *R*-guest-**F** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

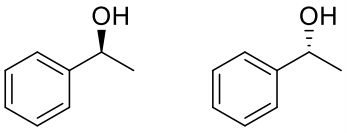


S-guest-**G** *R*-guest-**G**

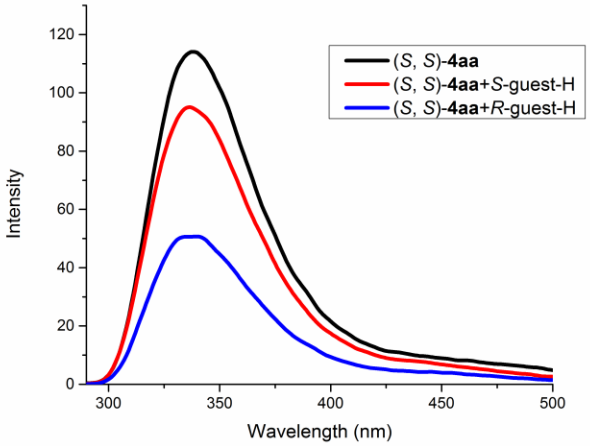


Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**G**	94.22 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**G**	101.50 (I_R)
ef		1.63 (0.61)

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**G** (500 μL, 10 mM in CH_3CN) or *R*-guest-**G** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guest **G** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**G** (red), (*S*,*S*)-**4aa** with *R*-guest-**G** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

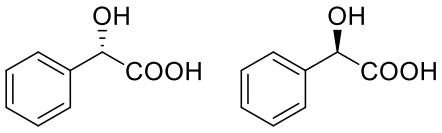


S-guest-**H** *R*-guest-**H**

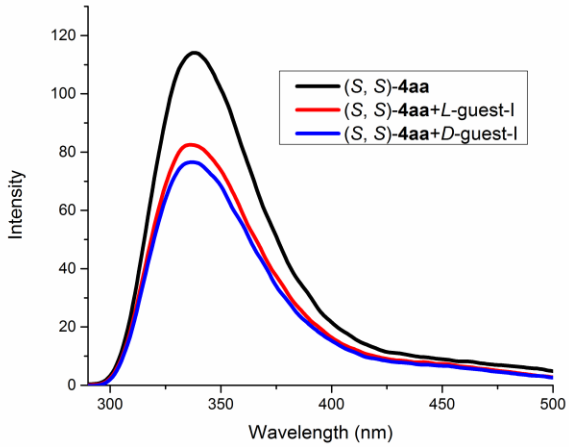


Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**H**	50.62 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**H**	94.92 (I_R)
ef		3.44 (0.29)

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**H** (500 μL, 10 mM in CH_3CN) or *R*-guest-**H** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guest **H** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**H** (red), (*S*,*S*)-**4aa** with *R*-guest-**H** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

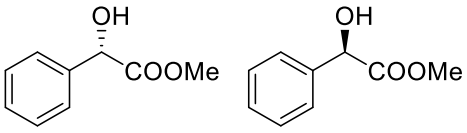


L-guest-**I** *D*-guest-**I**

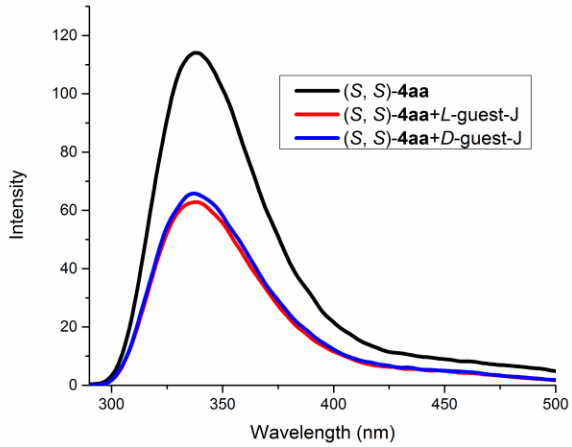


Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*L*-guest-**I**	82.46 (I_L)
3	(*S*,*S*)-**4aa**+*D*-guest-**I**	76.41 (I_D)
ef		1.20 (0.83)

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *L*-guest-**I** (500 μL, 10 mM in CH_3CN) or *D*-guest-**I** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guest **I** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *L*-guest-**I** (red), (*S*,*S*)-**4aa** with *D*-guest-**I** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

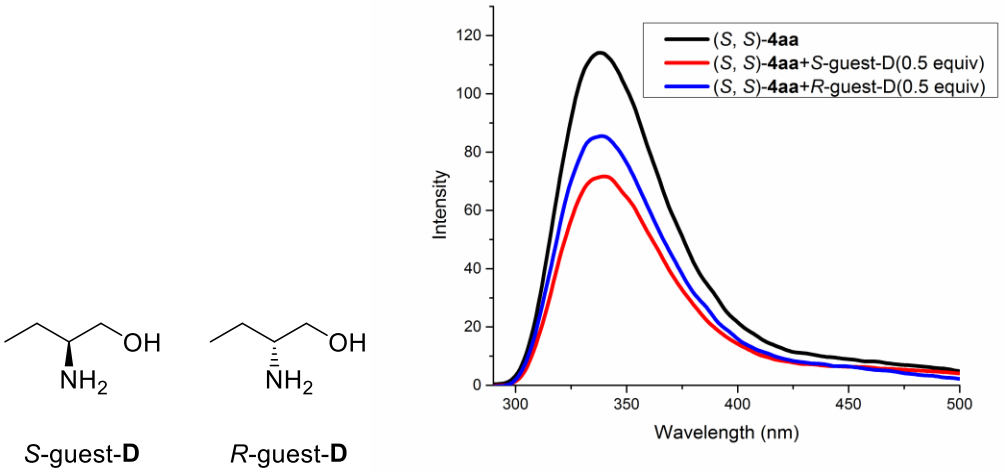


L-guest-**J** *D*-guest-**J**



Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*L*-guest-**J**	62.48 (I_L)
3	(*S*,*S*)-**4aa**+*D*-guest-**J**	65.53 (I_D)
ef		1.06 (0.94)

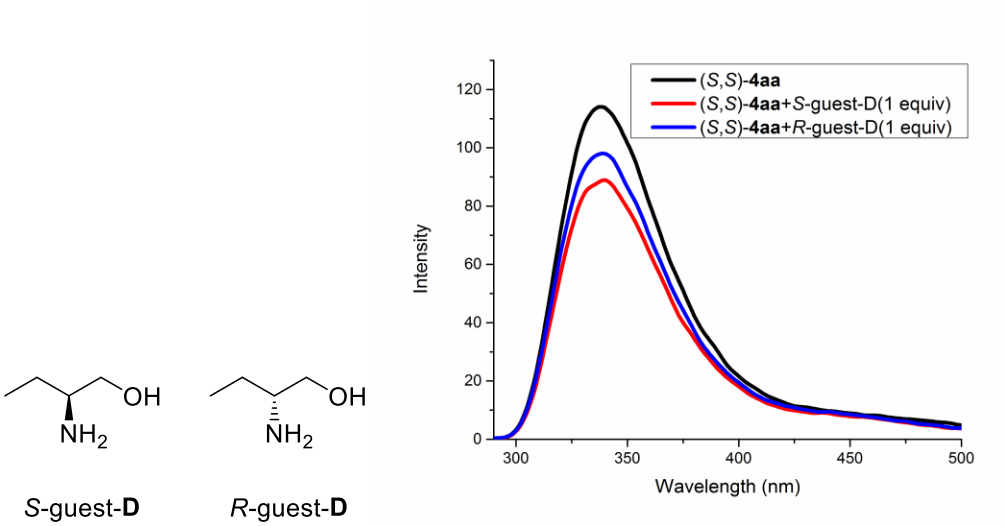
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *L*-guest-**J** (500 μL, 10 mM in CH_3CN) or *D*-guest-**J** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guest **J** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *L*-guest-**J** (red), (*S*,*S*)-**4aa** with *D*-guest-**J** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.



S-guest-**D** *R*-guest-**D**

Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**D**	70.74 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**D**	84.82 (I_R)
ef		1.50 (0.67)

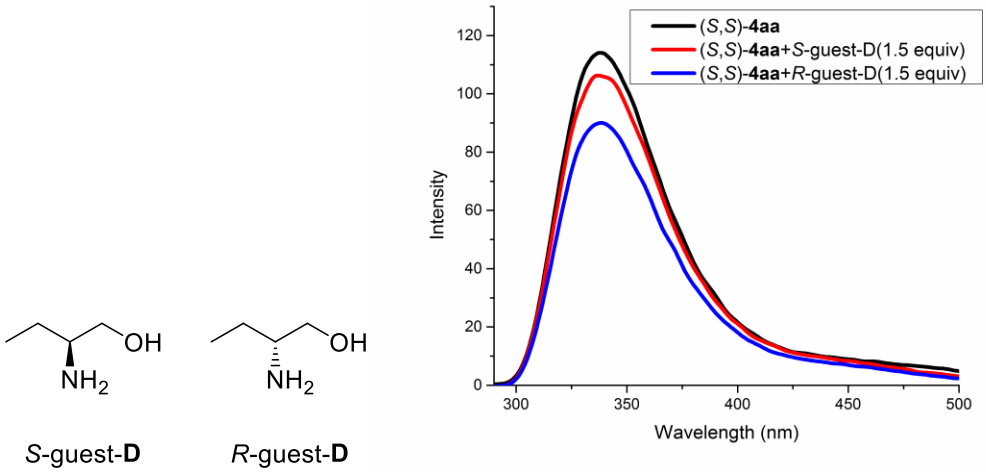
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**D** (125 μL, 10 mM in CH_3CN) or *R*-guest-**D** (125 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 0.25 mM of guest **D** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**D** (red), (*S*,*S*)-**4aa** with *R*-guest-**D** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.



S-guest-**D** *R*-guest-**D**

Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**D**	87.24 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**D**	96.89 (I_R)
ef		1.60 (0.63)

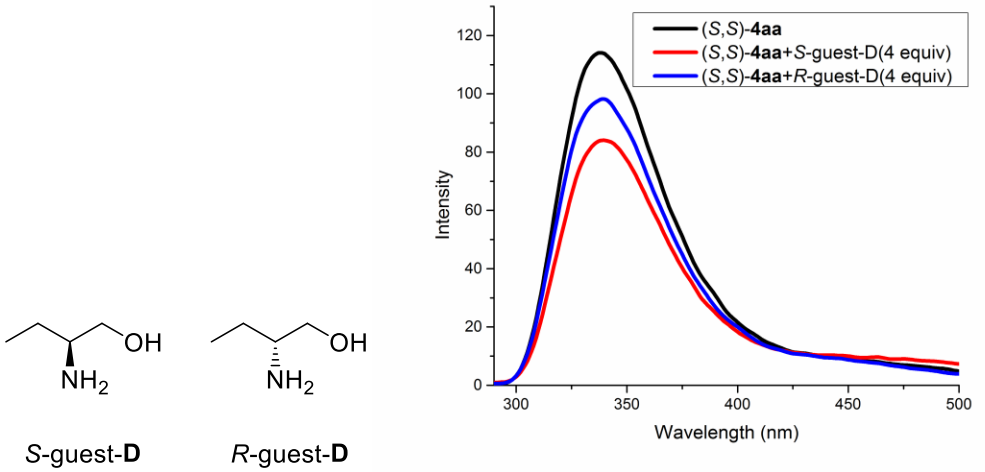
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**D** (250 μL, 10 mM in CH_3CN) or *R*-guest-**D** (250 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 0.5 mM of guest **D** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**D** (red), (*S*,*S*)-**4aa** with *R*-guest-**D** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.



S-guest-**D** *R*-guest-**D**

Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**D**	105.70 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**D**	89.13 (I_R)
ef		3.24 (0.31)

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**D** (375 μL, 10 mM in CH_3CN) or *R*-guest-**D** (375 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 0.75 mM of guest **D** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**D** (red), (*S*,*S*)-**4aa** with *R*-guest-**D** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

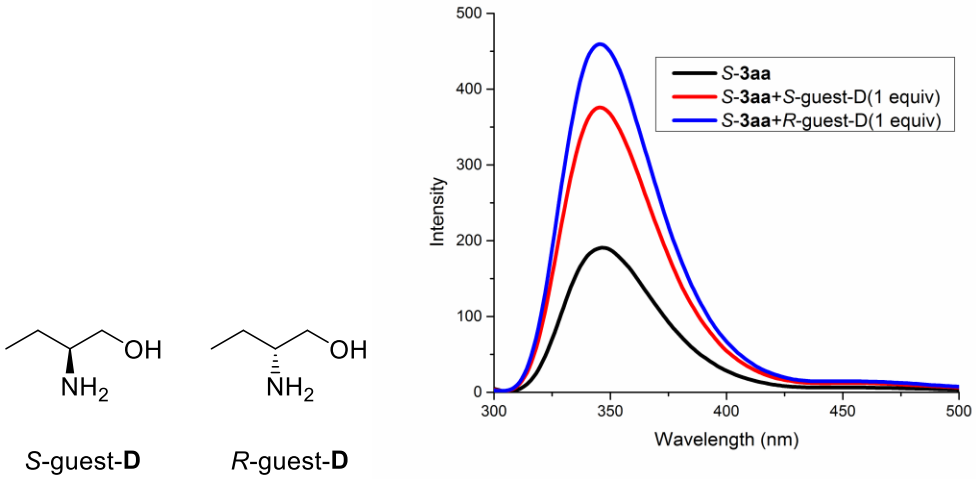


S-guest-**D** *R*-guest-**D**

Entry	Sample	Fluorescence Intensity (λ_{em} = 335.2 nm)
1	(*S*,*S*)-**4aa**	113.10 (I_0)
2	(*S*,*S*)-**4aa**+*S*-guest-**D**	82.55 (I_S)
3	(*S*,*S*)-**4aa**+*R*-guest-**D**	96.61 (I_R)
ef		1.85 (0.54)

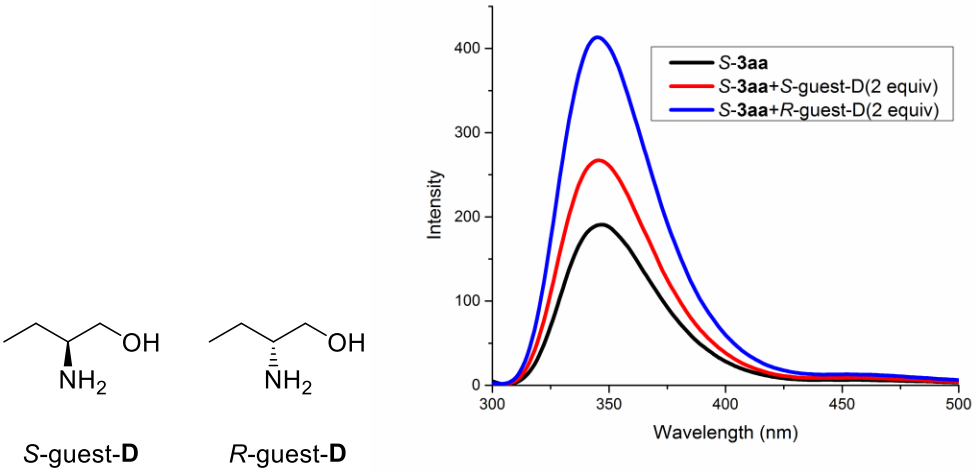
Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**D** (1000 μL, 10 mM in CH_3CN) or *R*-guest-**D** (1000 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 2 mM of guest **D** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** (black), (*S*,*S*)-**4aa** with *S*-guest-**D** (red), (*S*,*S*)-**4aa** with *R*-guest-**D** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

14.3 Chiral recognition of (*S*)-3aa toward guest D by fluorescence spectra analysis.



Entry	Sample	Fluorescence Intensity (λ_{em} = 345 nm)
1	(*S*)-**3aa**	190.00 (I_0)
2	(*S*)-**3aa**+*S*-guest-**D**	375.60 (I_S)
3	(*S*)-**3aa**+*R*-guest-**D**	459.30 (I_R)
ef		1.45 (0.69)

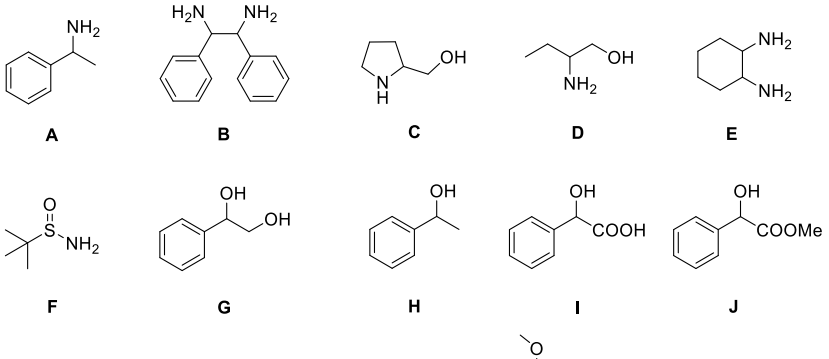
Procedure: The samples were prepared by mixing (*S*)-**3aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**D** (250 μL, 10 mM in CH_3CN) or *R*-guest-**D** (250 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*)-**3aa** and 0.5 mM of guest **D** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*)-**3aa** (black), (*S*)-**3aa** with *S*-guest-**D** (red), (*S*)-**3aa** with *R*-guest-**D** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 285 nm, slits: 2.5/20 nm, λ_{em} = 345 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

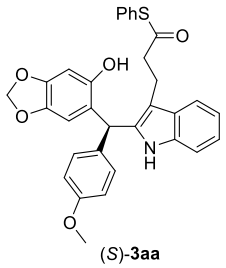


Entry	Sample	Fluorescence Intensity (λ_{em} = 345 nm)
1	(*S*)-**3aa**	190.00 (I_0)
2	(*S*)-**3aa**+*S*-guest-**D**	267.00 (I_S)
3	(*S*)-**3aa**+*R*-guest-**D**	413.30 (I_R)
ef		2.90 (0.34)

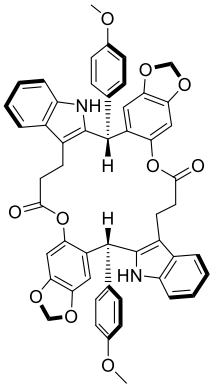
Procedure: The samples were prepared by mixing (*S*)-**3aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**D** (500 μL, 10 mM in CH_3CN) or *R*-guest-**D** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*)-**3aa** and 1 mM of guest **D** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*)-**3aa** (black), (*S*)-**3aa** with *S*-guest-**D** (red), (*S*)-**3aa** with *R*-guest-**D** (blue) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 285 nm, slits: 2.5/20 nm, λ_{em} = 345 nm). The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$.

Table S14: Chiral recognition of (*S*,*S*)-**4aa** and (*S*)-**3aa** toward guests **A**–**J** by fluorescence analysis.[a]





(*S*)-**3aa**



(*S*,*S*)-**4aa**

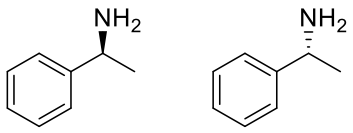
Entry	Guest	ef[b]
1	**A**	1.68 (0.60)
2	**B**	3.02 (0.33)
3	**C**	2.92 (0.34)
4	**D**	5.46 (0.18)
5	**E**	1.42 (0.70)
6	**F**	3.59 (0.28)
7	**G**	1.63 (0.61)
8	**H**	3.44 (0.29)
9	**I**	1.20 (0.83)
10	**J**	1.06 (0.94)
11[c]	**D** (0.5 equiv)	1.50 (0.67)
12[d]	**D** (1.0 equiv)	1.60 (0.63)
13[e]	**D** (1.5 equiv)	3.24 (0.31)
14[f]	**D** (4.0 equiv)	1.85 (0.54)
15[g]	**D**	1.45 (0.69)

[a] The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guests-**A**–**J** (500 μL, 10 mM in CH_3CN) or *R*-guests-**A**–**J** (500 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks at 25 °C for 12 hours [0.5 mM of (*S*,*S*)-**4aa** and 1 mM of guests **A**–**J** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa**, (*S*,*S*)-**4aa** with *S*-guests-**A**–**J**, (*S*,*S*)-**4aa** with *R*-guests-**A**–**J** were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 335.2 nm). [b] The enantiomeric fluorescence difference ratio, ef = $(I_0–I_R)/(I_0–I_S)$ or $(I_0–I_S)/(I_0–I_R)$. [c] (*S*,*S*)-**4aa**:guest **D** = 1:0.5. [d] (*S*,*S*)-**4aa**:guest **D** = 1:1. [e] (*S*,*S*)-**4aa**:guest **D** = 1:1.5. [f] (*S*,*S*)-**4aa**:guest **D** = 1:4. [g] The sample were prepared by mixing (*S*)-**3aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**D** (250 μL, 10 mM in CH_3CN) or *R*-guest-**D** (250 μL, 10 mM in CH_3CN) in 5 mL volumetric flasks [0.5 mM of (*S*)-**3aa** and 0.5 mM of guest **D** in CH_3CN (5 mL). Fluorescence spectra of (*S*)-**3aa**, (*S*)-**3aa** with *S*-guest-**D**, (*S*)-**3aa** with *R*-guest-**D** were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 285 nm, slits: 2.5/20 nm, λ_{em} = 345 nm).

14.4 Stern-Volmer plots of (*S*,*S*)-4aa toward guests A–J by fluorescence spectra analysis.

Generally, the fluorescence quenching followed the Stern-Volmer equation: $I_0/I = 1 + K_{SV}$ [Q].

Here I and I_0 are the fluorescent intensity of the fluorophore with and without the quencher, [Q] is the concentration of the quencher, and K_{SV} is the Stern-Volmer constant. For static quenching, K_{SV} represents the association constant of the fluorophore with the quencher.

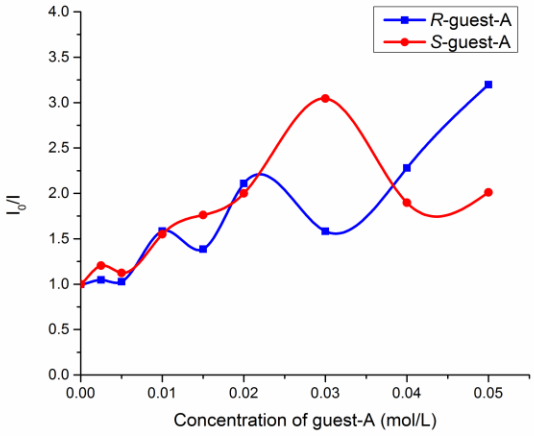


S-guest-**A** *R*-guest-**A**

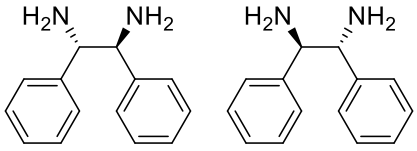
Entry	$C_{S\text{-guest-A}}$ (mol/L)	I	I_0/I
1	0	135.50 (I_0)	1
2	0.0025	112.50	1.20444
3	0.005	120.70	1.12262
4	0.01	87.45	1.54946
5	0.015	76.88	1.76249
6	0.02	67.76	1.99970
7	0.03	44.51	3.04426
8	0.04	71.44	1.89670
9	0.05	67.35	2.01188

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**A** (from 0 μL to 2000 μL, 125 mM in CH_3CN) or *R*-guest-**A** (from 0 μL to 2000 μL, 125 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.5 mM of (*S*,*S*)-**4aa** and 0 to 50 mM of guest **A** in CH_3CN(5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa**, (*S*,*S*)-**4aa** with *S*-guest-**A**, (*S*,*S*)-**4aa** with *R*-guest-**A** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

Entry	$C_{R\text{-guest-A}}$ (mol/L)	I	I_0/I
1	0	133.50 (I_0)	1
2	0.0025	127.50	1.04706
3	0.005	130.00	1.02692
4	0.01	84.26	1.58438
5	0.015	96.31	1.38615
6	0.02	63.31	2.10867
7	0.03	84.41	1.58157
8	0.04	58.55	2.28010
9	0.05	41.76	3.19684



Conclusion: The Stern-Volmer plot shows that (*S*,*S*)-**4aa** fluorescence quenching by guests **A** in CH_3CN is non-linear.

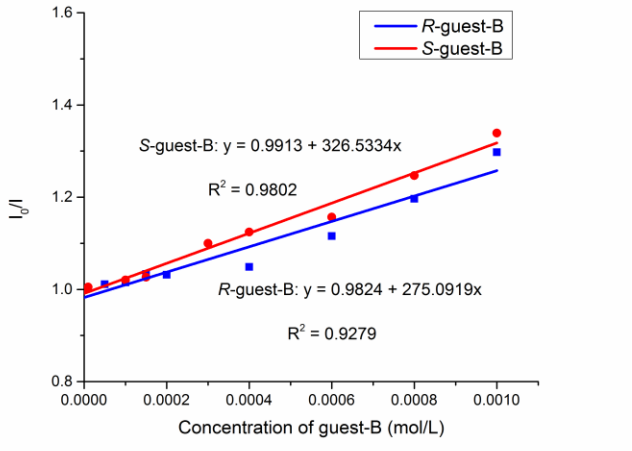


S-guest-**B** *R*-guest-**B**

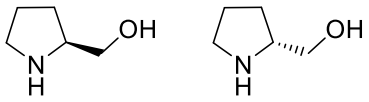
Entry	$C_{S\text{-guest-B}}$ (mol/L)	I	I_0/I
1	0	587.40 (I_0)	1
2	0.00001	584.40	1.00513
3	0.0001	575.70	1.02032
4	0.00015	572.20	1.02656
5	0.0003	534.00	1.10000
6	0.0004	522.40	1.12443
7	0.0006	507.90	1.15653
8	0.0008	471.20	1.24660
9	0.001	438.70	1.33896

Procedure: The samples were prepared by mixing (*S,S*)-**4aa** (100 μL, 0.5 mM in CH_3CN) and *S*-guest-**B** (from 0 μL to 1000 μL, 5 mM in CH_3CN) or *R*-guest-**B** (from 0 μL to 1000 μL, 5 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.01 mM of (*S,S*)-**4aa** and 0 to 1 mM of guest **B** in CH_3CN(5 mL)]. Fluorescence spectra of (*S,S*)-**4aa**, (*S,S*)-**4aa** with *S*-guest-**B**, (*S,S*)-**4aa** with *R*-guest-**B** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

Entry	$C_{R\text{-guest-B}}$ (mol/L)	I	I_0/I
1	0	565.90 (I_0)	1
2	0.00005	559.70	1.01108
3	0.0001	557.50	1.01507
4	0.00015	547.60	1.03342
5	0.0002	548.40	1.03191
6	0.0004	539.60	1.04874
7	0.0006	507.20	1.11573
8	0.0008	473.00	1.19641
9	0.001	436.20	1.29734



Conclusion: The Stern-Volmer plot shows that (*S,S*)-**4aa** fluorescence quenching by guests **B** in CH_3CN is linear in a certain concentration range. The Stern-Volmer constant of (*S,S*)-**4aa** is 326.53 M^{-1} [K_{SV}(S-S)] in the presence of *S*-guest-**B** and 275.09 M^{-1} [K_{SV}(S-R)] in the presence of *R*-guest-**B**. The ratio of Stern-Volmer constant [K_{SV}(S-S)]/[K_{SV}(S-R)] = 1.19.

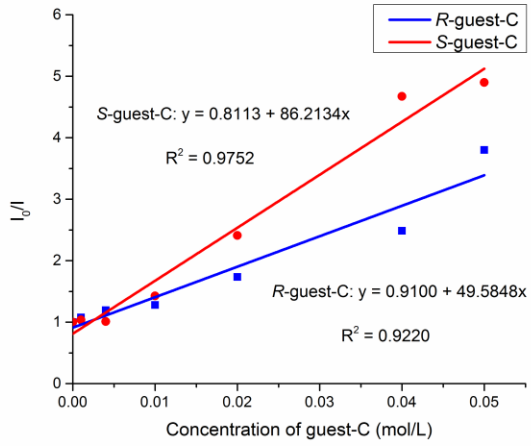


S-guest-**C** *R*-guest-**C**

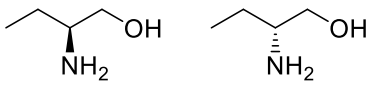
Entry	$C_{S\text{-guest-C}}$ (mol/L)	I	I_0/I
1	0	150.40 (I_0)	1
2	0.001	145.20	1.03581
3	0.004	149.00	1.00940
4	0.01	105.40	1.42694
5	0.02	62.39	2.41064
6	0.04	32.18	4.67371
7	0.05	30.70	4.89902

Procedure: The samples were prepared by mixing (*S,S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**C** (from 0 μL to 2000 μL, 125 mM in CH_3CN) or *R*-guest-**C** (from 0 μL to 2000 μL, 125 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.5 mM of (*S,S*)-**4aa** and 0 to 50 mM of guest **C** in CH_3CN(5 mL)]. Fluorescence spectra of (*S,S*)-**4aa**, (*S,S*)-**4aa** with *S*-guest-**C**, (*S,S*)-**4aa** with *R*-guest-**C** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

Entry	$C_{R\text{-guest-C}}$ (mol/L)	I	I_0/I
1	0	150.40 (I_0)	1
2	0.001	139.70	1.07659
3	0.004	125.90	1.19460
4	0.01	117.60	1.27891
5	0.02	86.76	1.73352
6	0.04	60.51	2.48554
7	0.05	39.59	3.79894



Conclusion: The Stern-Volmer plot shows that (*S,S*)-**4aa** fluorescence quenching by guests **C** in CH_3CN is linear in a certain concentration range. The Stern-Volmer constant of (*S,S*)-**4aa** is 86.21 M^{-1} [K_{SV}(S-S)] in the presence of *S*-guest-**C** and 49.58 M^{-1} [K_{SV}(S-R)] in the presence of *R*-guest-**C**. The ratio of Stern-Volmer constant [K_{SV}(S-S)]/[K_{SV}(S-R)] = 1.74.

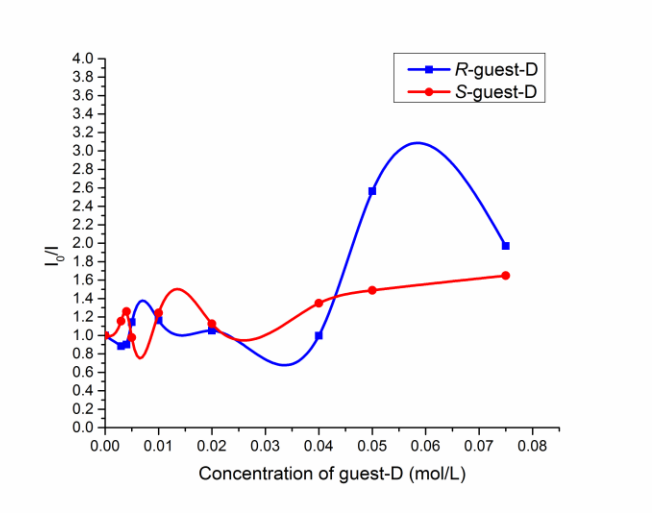


S-guest-**D** *R*-guest-**D**

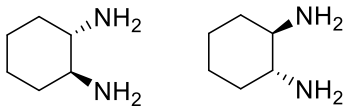
Entry	$C_{S\text{-guest-D}}$ (mol/L)	I	I_0/I
1	0	150.40 (I_0)	1
2	0.003	130.20	1.15515
3	0.004	119.40	1.25963
4	0.005	154.00	0.97662
5	0.01	120.90	1.24400
6	0.02	133.70	1.12491
7	0.04	111.50	1.34888
8	0.05	101.00	1.48911
9	0.075	91.20	1.64912

Procedure: The samples were prepared by mixing (*S,S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**D** (from 0 μL to 3000 μL, 125 mM in CH_3CN) or *R*-guest-**D** (from 0 μL to 3000 μL, 125 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.5 mM of (*S,S*)-**4aa** and 0 to 75 mM of guest **D** in CH_3CN(5 mL)]. Fluorescence spectra of (*S,S*)-**4aa**, (*S,S*)-**4aa** with *S*-guest-**D**, (*S,S*)-**4aa** with *R*-guest-**D** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

Entry	$C_{R\text{-guest-D}}$ (mol/L)	I	I_0/I
1	0	150.40 (I_0)	1
2	0.003	170.30	0.88315
3	0.004	166.90	0.90114
4	0.005	131.60	1.14286
5	0.01	129.30	1.16319
6	0.02	143.20	1.05028
7	0.04	151.00	0.99603
8	0.05	58.68	2.56305
9	0.075	76.33	1.97039



Conclusion: The Stern-Volmer plot shows that (*S,S*)-**4aa** fluorescence quenching by guests **D** in CH_3CN is non-linear.

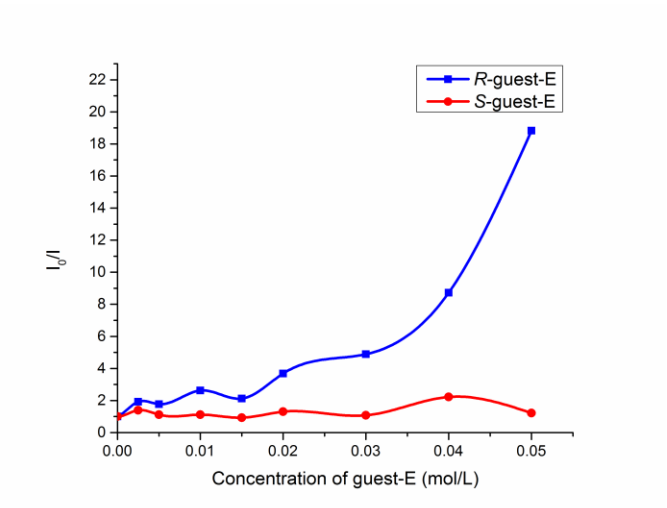


S-guest-**E** *R*-guest-**E**

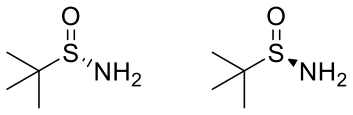
Entry	$C_{S\text{-guest-E}}$ (mol/L)	I	I_0/I
1	0	145.80 (I_0)	1
2	0.0025	104.10	1.40058
3	0.005	130.80	1.11468
4	0.01	130.30	1.11896
5	0.015	156.30	0.93282
6	0.02	111.40	1.30880
7	0.03	134.90	1.08080
8	0.04	65.42	2.22868
9	0.05	119.70	1.21805

Procedure: The samples were prepared by mixing (*S,S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**E** (from 0 μL to 2000 μL, 125 mM in CH_3CN) or *R*-guest-**E** (from 0 μL to 2000 μL, 125 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.5 mM of (*S,S*)-**4aa** and 0 to 50 mM of guest **E** in CH_3CN(5 mL)]. Fluorescence spectra of (*S,S*)-**4aa**, (*S,S*)-**4aa** with *S*-guest-**E**, (*S,S*)-**4aa** with *R*-guest-**E** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

Entry	$C_{R\text{-guest-E}}$ (mol/L)	I	I_0/I
1	0	132.70 (I_0)	1
2	0.0025	68.98	1.92375
3	0.005	74.71	1.77620
4	0.01	50.50	2.62772
5	0.015	62.46	2.12456
6	0.02	36.05	3.68100
7	0.03	27.15	4.88766
8	0.04	15.22	8.71879
9	0.05	7.05	18.82270



Conclusion: The Stern-Volmer plot shows that (*S,S*)-**4aa** fluorescence quenching by guests **E** in CH_3CN is non-linear.

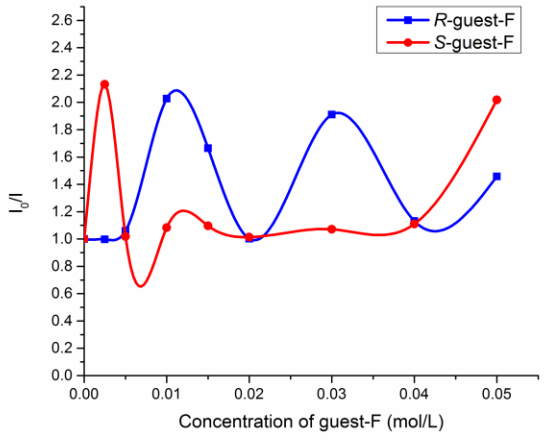


S-guest-**F** *R*-guest-**F**

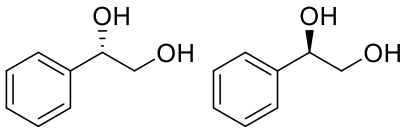
Entry	$C_{S\text{-guest-F}}$ (mol/L)	I	I_0/I
1	0	145.80 (I_0)	1
2	0.0025	68.39	2.13189
3	0.005	143.30	1.01745
4	0.01	134.60	1.08321
5	0.015	133.00	1.09624
6	0.02	143.90	1.01320
7	0.03	136.10	1.07127
8	0.04	131.40	1.10959
9	0.05	72.24	2.01827

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**F** (from 0 μL to 2000 μL, 125 mM in CH_3CN) or *R*-guest-**F** (from 0 μL to 2000 μL, 125 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.5 mM of (*S*,*S*)-**4aa** and 0 to 50 mM of guest **F** in CH_3CN(5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa**, (*S*,*S*)-**4aa** with *S*-guest-**F**, (*S*,*S*)-**4aa** with *R*-guest-**F** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

Entry	$C_{R\text{-guest-F}}$ (mol/L)	I	I_0/I
1	0	145.80 (I_0)	1
2	0.0025	146.20	0.99726
3	0.005	137.70	1.05882
4	0.01	71.91	2.02753
5	0.015	87.62	1.66400
6	0.02	145.60	1.00137
7	0.03	76.28	1.91138
8	0.04	128.80	1.13199
9	0.05	99.97	1.45844



Conclusion: The Stern-Volmer plot shows that (*S*,*S*)-**4aa** fluorescence quenching by guests **F** in CH_3CN is non-linear.

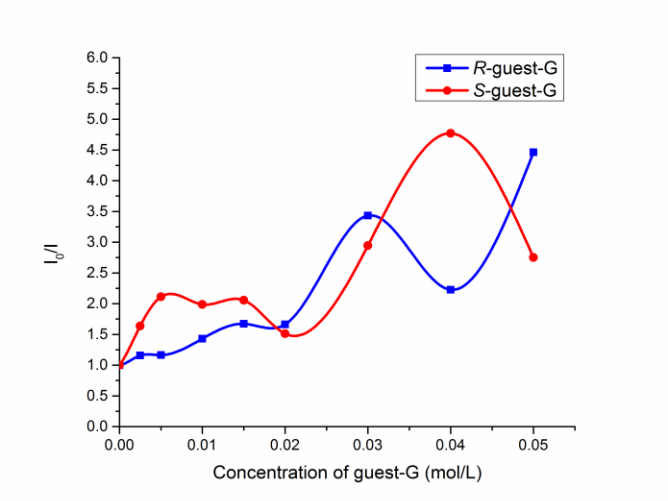


S-guest-**G** *R*-guest-**G**

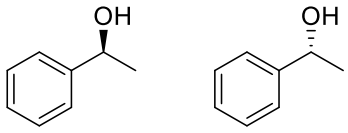
Entry	$C_{S\text{-guest-G}}$ (mol/L)	I	I_0/I
1	0	129.00 (I_0)	1
2	0.0025	78.79	1.63726
3	0.005	61.10	2.11129
4	0.01	64.88	1.98829
5	0.015	62.71	2.05709
6	0.02	85.27	1.51284
7	0.03	43.83	2.94319
8	0.04	27.04	4.77071
9	0.05	46.88	2.75171

Procedure: The samples were prepared by mixing (*S,S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**G** (from 0 μL to 2000 μL, 125 mM in CH_3CN) or *R*-guest-**G** (from 0 μL to 2000 μL, 125 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.5 mM of (*S,S*)-**4aa** and 0 to 50 mM of guest **G** in CH_3CN (5 mL)]. Fluorescence spectra of (*S,S*)-**4aa**, (*S,S*)-**4aa** with *S*-guest-**G**, (*S,S*)-**4aa** with *R*-guest-**G** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

Entry	$C_{R\text{-guest-G}}$ (mol/L)	I	I_0/I
1	0	145.80 (I_0)	1
2	0.0025	125.90	1.15806
3	0.005	125.10	1.16547
4	0.01	102.10	1.42801
5	0.015	87.21	1.67183
6	0.02	87.66	1.66324
7	0.03	42.47	3.43301
8	0.04	65.51	2.22561
9	0.05	32.68	4.46144



Conclusion: The Stern-Volmer plot shows that (*S,S*)-**4aa** fluorescence quenching by guests **G** in CH_3CN is non-linear.

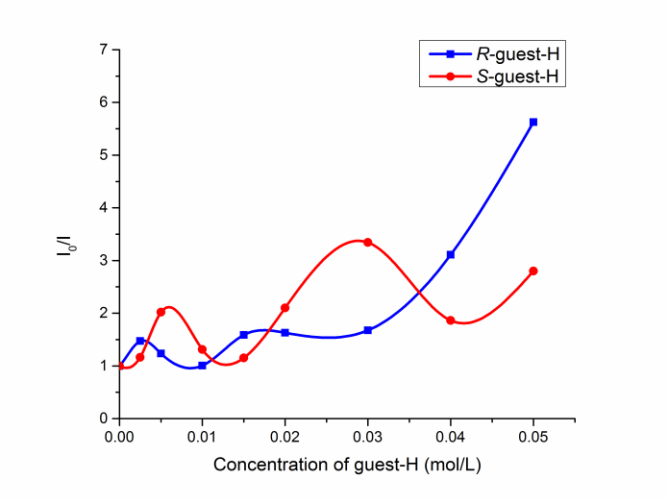


S-guest-**H** *R*-guest-**H**

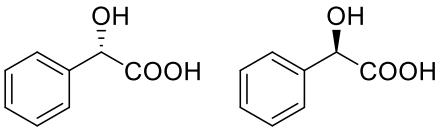
Entry	$C_{S\text{-guest-H}}$ (mol/L)	I	I_0/I
1	0	113.90 (I_0)	1
2	0.0025	97.80	1.16462
3	0.005	56.43	2.01843
4	0.01	86.76	1.31282
5	0.015	98.94	1.15120
6	0.02	54.21	2.10109
7	0.03	34.08	3.34214
8	0.04	61.17	1.86202
9	0.05	40.68	2.79990

Procedure: The samples were prepared by mixing (*S,S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guest-**H** (from 0 μL to 2000 μL, 125 mM in CH_3CN) or *R*-guest-**H** (from 0 μL to 2000 μL, 125 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.5 mM of (*S,S*)-**4aa** and 0 to 50 mM of guest **H** in CH_3CN (5 mL)]. Fluorescence spectra of (*S,S*)-**4aa**, (*S,S*)-**4aa** with *S*-guest-**H**, (*S,S*)-**4aa** with *R*-guest-**H** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

Entry	$C_{R\text{-guest-H}}$ (mol/L)	I	I_0/I
1	0	113.90 (I_0)	1
2	0.0025	77.40	1.47158
3	0.005	92.12	1.23643
4	0.01	113.20	1.00618
5	0.015	71.70	1.58856
6	0.02	69.96	1.62807
7	0.03	67.91	1.67722
8	0.04	36.64	3.10862
9	0.05	20.24	5.62747



Conclusion: The Stern-Volmer plot shows that (*S,S*)-**4aa** fluorescence quenching by guests **H** in CH_3CN is non-linear.

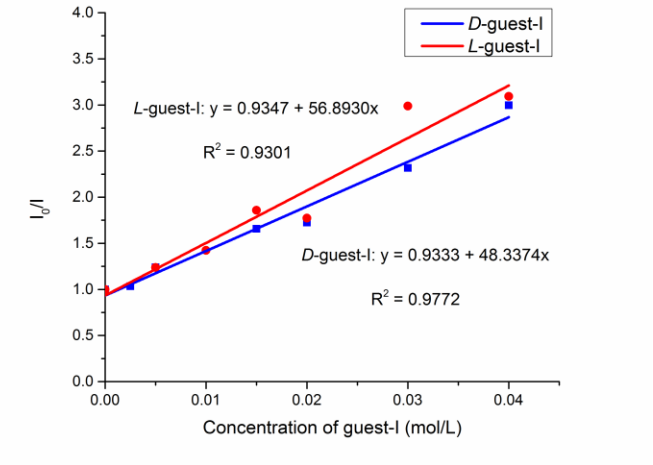


L-guest-**I** *D*-guest-**I**

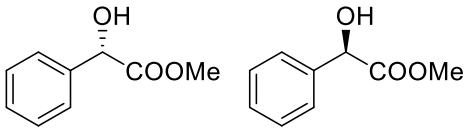
Entry	$C_{L\text{-guest-I}}$ (mol/L)	I	I_0/I
1	0	139.40 (I_0)	1
2	0.005	112.70	1.23691
3	0.01	98.04	1.42187
4	0.015	75.02	1.85817
5	0.02	78.62	1.77309
6	0.03	46.67	2.98693
7	0.04	45.07	3.09297

Procedure: The samples were prepared by mixing (*S,S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *L*-guest-**I** (from 0 μL to 1600 μL, 125 mM in CH_3CN) or *D*-guest-**I** (from 0 μL to 1600 μL, 125 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.5 mM of (*S,S*)-**4aa** and 0 to 40 mM of guest **I** in CH_3CN (5 mL)]. Fluorescence spectra of (*S,S*)-**4aa**, (*S,S*)-**4aa** with *L*-guest-**I**, (*S,S*)-**4aa** with *D*-guest-**I** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

Entry	$C_{D\text{-guest-I}}$ (mol/L)	I	I_0/I
1	0	139.40 (I_0)	1
2	0.0025	134.80	1.03412
3	0.005	112.40	1.24021
4	0.015	84.14	1.65676
5	0.02	80.81	1.72503
6	0.03	60.14	2.31792
7	0.04	46.51	2.99720



Conclusion: The Stern-Volmer plot shows that (*S,S*)-**4aa** fluorescence quenching by guests **I** in CH_3CN is linear in a certain concentration range. The Stern-Volmer constant of (*S,S*)-**4aa** is 56.89 M^{-1} [K_{SV}(S-L)] in the presence of *L*-guest-**I** and 48.34 M^{-1} [K_{SV}(S-D)] in the presence of *D*-guest-**I**. The ratio of Stern-Volmer constant [K_{SV}(S-L)]/[K_{SV}(S-D)] = 1.18.

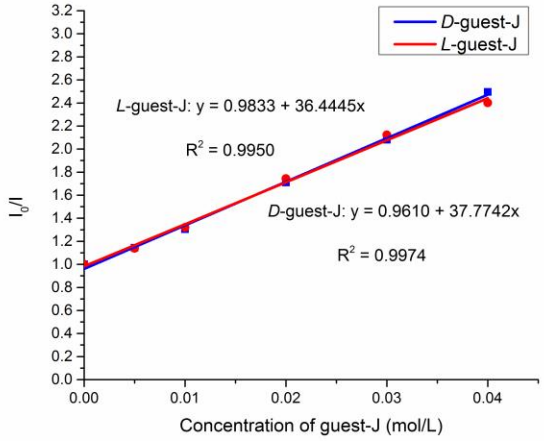


L-guest-**J** *D*-guest-**J**

Entry	$C_{L\text{-guest-J}}$ (mol/L)	I	I_0/I
1	0	130.20 (I_0)	1
2	0.005	114.30	1.13911
3	0.01	98.60	1.32049
4	0.02	74.69	1.74321
5	0.03	61.34	2.12260
6	0.04	54.22	2.40133

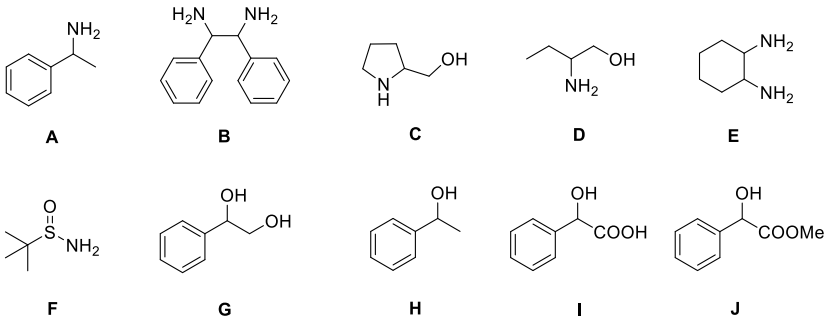
Procedure: The samples were prepared by mixing (*S,S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *L*-guest-**J** (from 0 μL to 1600 μL, 125 mM in CH_3CN) or *D*-guest-**J** (from 0 μL to 1600 μL, 125 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.5 mM of (*S,S*)-**4aa** and 0 to 40 mM of guest **J** in CH_3CN (5 mL)]. Fluorescence spectra of (*S,S*)-**4aa**, (*S,S*)-**4aa** with *L*-guest-**J**, (*S,S*)-**4aa** with *D*-guest-**J** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

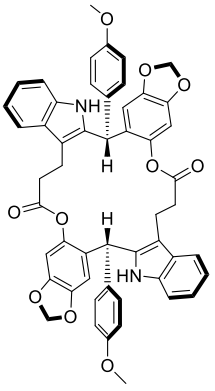
Entry	$C_{D\text{-guest-J}}$ (mol/L)	I	I_0/I
1	0	130.20 (I_0)	1
2	0.005	113.90	1.14311
3	0.01	99.87	1.30369
4	0.02	76.15	1.70978
5	0.03	62.58	2.08054
6	0.04	52.18	2.49521



Conclusion: The Stern-Volmer plot shows that (*S,S*)-**4aa** fluorescence quenching by guests **J** in CH_3CN is linear in a certain concentration range. The Stern-Volmer constant of (*S,S*)-**4aa** is 36.44 M^{-1} [K_{SV}(S-L)] in the presence of *L*-guest-**J** and 37.77 M^{-1} [K_{SV}(S-D)] in the presence of *D*-guest-**J**. The ratio of Stern-Volmer constant [K_{SV}(S-L)]/[K_{SV}(S-D)] = 0.96.

Table S15: Stern-Volmer quenching constants of (*S*,*S*)-**4aa** toward guests **A**–**J** by fluorescence analysis.[a]





(*S*,*S*)-**4aa**

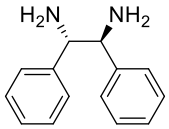
Entry	Guest	K_{SV} (M^{-1})	K_{SV}(S-S)/K_{SV}(S-R)
1	*S*-guest-**A** *R*-guest-**A**	non-linear	--
2[b]	*S*-guest-**B** *R*-guest-**B**	326.53 275.09	1.19
3	*S*-guest-**C** *R*-guest-**C**	86.21 49.58	1.74
4	*S*-guest-**D** *R*-guest-**D**	non-linear	--
5	*S*-guest-**E** *R*-guest-**E**	non-linear	--
6	*S*-guest-**F** *R*-guest-**F**	non-linear	--
7	*S*-guest-**G** *R*-guest-**G**	non-linear	--
8	*S*-guest-**H** *R*-guest-**H**	non-linear	--
9	*L*-guest-**I** *D*-guest-**I**	56.89 48.34	1.18
10	*L*-guest-**J** *D*-guest-**J**	36.44 37.77	0.96

[a] The samples were prepared by mixing (*S*,*S*)-**4aa** (500 μL, 5 mM in CH_3CN) and *S*-guests-**A**–**J** (from 0 to 3000 μL, 125 mM in CH_3CN) or *R*-guests-**A**–**J** (from 0 μL to 3000 μL, 125 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.5 mM of (*S*,*S*)-**4aa** and 0 to 75 mM of guests **A**–**J** in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa** with *S*-guests-**A**–**J**, (*S*,*S*)-**4aa** with *R*-guests-**A**–**J** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). [b] The samples were prepared by mixing (*S*,*S*)-**4aa** (100 μL, 0.5 mM in CH_3CN) and *S*-guest-**B** (from 0 μL to 1000 μL, 5 mM in CH_3CN) or *R*-guest-**B** (from 0 μL to 1000 μL, 5 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.01 mM of (*S*,*S*)-**4aa** and 0 to 1 mM of guest **B** in CH_3CN (5 mL)].

Conclusion: The table shows that (*S*,*S*)-**4aa** fluorescence quenching by guests **B**, **C**, **I**, **J** in CH_3CN is linear in a certain concentration range. However the (*S*,*S*)-**4aa** fluorescence quenching by other guests is non-linear.

14.5 Stern-Volmer plots of (*S,S*)-4aa toward guest B with the temperature change.

The method to make a distinction between dynamic quenching and static quenching is to inspect their relationship with the temperature change. For dynamic quenching, since it heavily depends on the collision, rising of the temperature will be advantageous, thus enlarge its *Ksv* value. While for static quenching, rising of the temperature will be unfavorable to the stability of the complex, thus reduce the value of the formation constant (*Ksv*) of the complex.



S-guest-**B**

Fluorescence quenching experiments at 20 °C

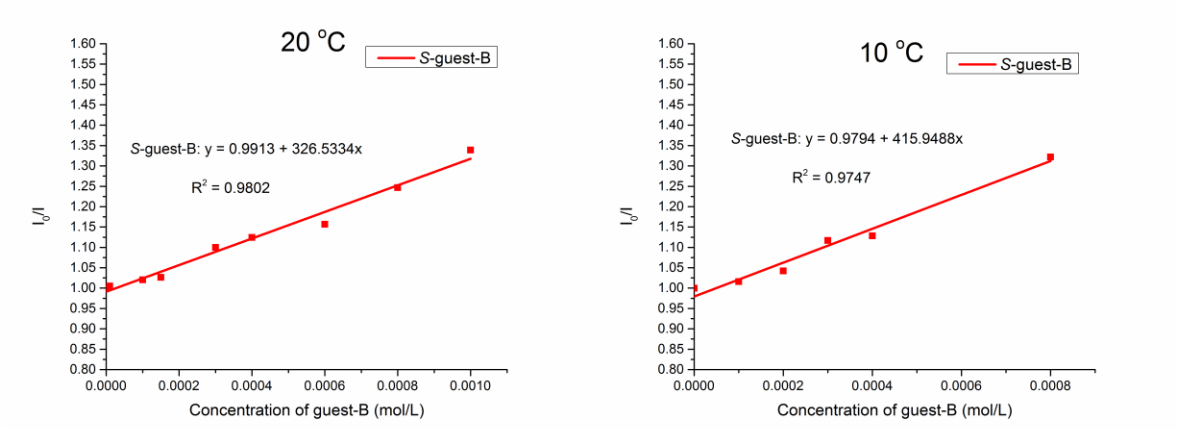
Entry	$C_{S\text{-guest-B}}$ (mol/L)	I	I_0/I
1	0	587.40 (I_0)	1
2	0.00001	584.40	1.00513
3	0.0001	575.70	1.02032
4	0.00015	572.20	1.02656
5	0.0003	534.00	1.10000
6	0.0004	522.40	1.12443
7	0.0006	507.90	1.15653
8	0.0008	471.20	1.24660
9	0.001	438.70	1.33896

Procedure 1 : The samples were prepared by mixing (*S,S*)-**4aa** (100 μL, 0.5 mM in CH_3CN) and *S*-guest-**B** (from 0 μL to 1000 μL, 5 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.01 mM of (*S,S*)-**4aa** and 0 to 1 mM of *S*-guest **B** in CH_3CN(5 mL)]. Fluorescence spectra of (*S,S*)-**4aa**, (*S,S*)-**4aa** with *S*-guest-**B** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm).

Fluorescence quenching experiments at 10 °C

Entry	$C_{S\text{-guest-B}}$ (mol/L)	I	I_0/I
1	0	570.10 (I_0)	1
2	0.0001	561.20	1.01586
3	0.0002	547.10	1.04204
4	0.0003	510.40	1.11697
5	0.0004	505.20	1.12846
6	0.0008	431.30	1.32182

Procedure 2 : The samples were measured according to **Procedure 1** at 10 °C.

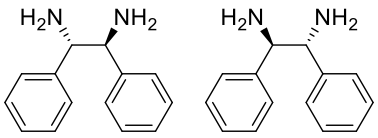


Conclusion: The Stern-Volmer constant of (*S,S*)-**4aa** is 326.53 M^{-1} [K_{SV}(20 °C)] in the presence of *S*-guest-**B** at 20 °C and 415.95 M^{-1} [K_{SV}(10 °C)] at 10 °C. Due to K_{SV}(10 °C) > K_{SV}(20 °C), the process of quenching is not the dynamic quenching induced by the collision of molecules, but the static quenching by forming a complex.

14.6 Calculation for association constant (K_A) and binding sites (n) of (*S*,*S*)-4aa toward guest B.

Correlative static quenching equation: $\lg [(I_0 - I)/I] = \lg K_A + n \lg [Q]$.

Here I and I_0 are the fluorescent intensity of the fluorophore with and without the quencher, [Q] is the concentration of the quencher, and K_A is the association constant of (*S*,*S*)-**4aa** with guest **B** and n is binding sites of (*S*,*S*)-**4aa**.

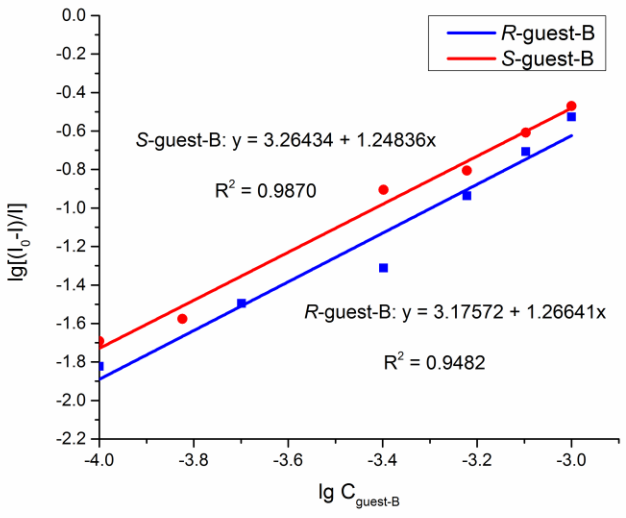


S-guest-**B** *R*-guest-**B**

Entry	$C_{S\text{-guest-B}}$ (mol/L)	I	lg $C_{S\text{-guest-B}}$	$(I_0 - I)/I$	lg $[(I_0 - I)/I]$
1	0	587.40 (I_0)	--	0	--
2	0.0001	575.70	-4	0.02032	-1.69201
3	0.00015	572.20	-3.82391	0.02656	-1.5757
4	0.0004	522.40	-3.39794	0.12443	-0.90509
5	0.0006	507.90	-3.22185	0.15653	-0.80541
6	0.0008	471.20	-3.09691	0.2466	-0.608
7	0.001	438.70	-3	0.33896	-0.46986

Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (100 μL, 0.5 mM in CH_3CN) and *S*-guest-**B** (from 0 μL to 1000 μL, 5 mM in CH_3CN) or *R*-guest-**B** (from 0 μL to 1000 μL, 5 mM in CH_3CN) in 5 mL volumetric flasks at 20 °C for 24 hours [0.01 mM of (*S*,*S*)-**4aa** and 0 to 1 mM of guest **B** in CH_3CN(5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa**, (*S*,*S*)-**4aa** with *S*-guest-**B**, (*S*,*S*)-**4aa** with *R*-guest-**B** were collected on fluorescence spectrometer at 20 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm, λ_{em} = 338 nm). I_0 was measured again before measuring another set of samples.

Entry	$C_{R\text{-guest-B}}$ (mol/L)	I	lg $C_{R\text{-guest-B}}$	$(I_0 - I)/I$	lg $[(I_0 - I)/I]$
1	0	565.90 (I_0)	--	0	--
2	0.0001	557.50	-4	0.01507	-1.82197
3	0.0002	548.40	-3.69897	0.03191	-1.49606
4	0.0004	539.60	-3.39794	0.04874	-1.31212
5	0.0006	507.20	-3.22185	0.11573	-0.93654
6	0.0008	473.00	-3.09691	0.19641	-0.70685
7	0.001	436.20	-3	0.29734	-0.52675



Conclusion: By applying correlative static quenching equation: lg $[(I_0 - I)/I]$ = lg K_A + n lg [Q], through the plots of linear equations calculated by lg $[(I_0 - I)/I]$ compared with lg $C_{guest\text{-}B}$, we calculated the values of association constant K_A and binding sites n.

Guest	n	lg K_A	K_A (M^{-1})	K_A(S)/K_A(R)
S-guest-**B**	1.24836	3.26434	1837.98	1.23
R-guest-**B**	1.26641	3.17572	1498.71	

The equation of Gibbs free energy: $\Delta G = -RT \ln K_A$.

Here R is 8.314 J • K^{-1} • mol^{-1}, T is 293 K, and K_A is the association constant of (*S*,*S*)-**4aa** with guest **B**.

Guest	K_A (M^{-1})	ΔG (kJ • mol^{-1})	$\Delta\Delta G$ (kJ • mol^{-1})
S-guest-**B**	1837.98	− 18.310	0.497
R-guest-**B**	1498.71	− 17.813	

15. Metal ion recognition of macrodiolide product (*S*,*S*)-4aa

15.1 Metal ion recognition of (*S*,*S*)-4aa by UV-vis absorption spectra analysis.

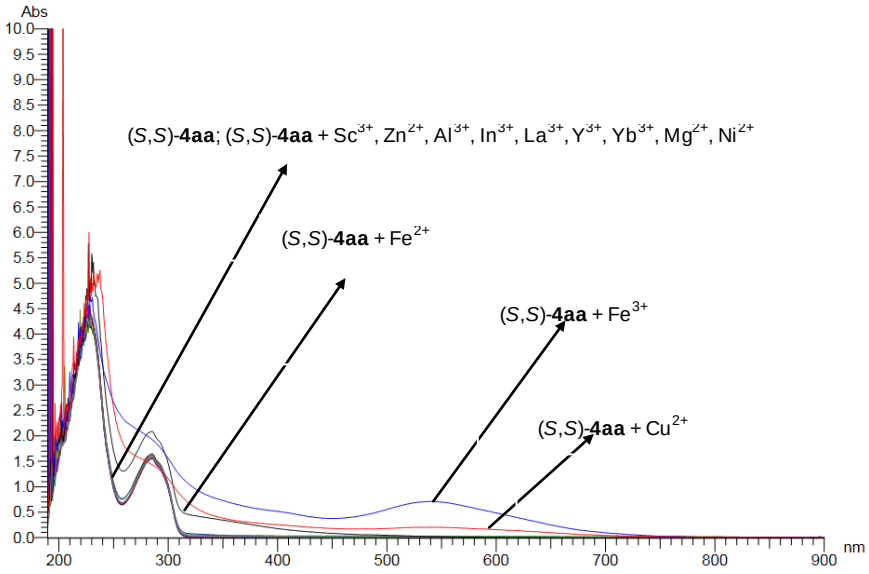


Fig. S1 Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (50 μL, 5 mM in CH_3CN) and metal salts (5 μmol) in 5 mL volumetric flasks [0.05 mM of (*S*,*S*)-**4aa** and 1 mM of metal salts in CH_3CN (5 mL)]. UV-Vis absorption spectra of (*S*,*S*)-**4aa**, (*S*,*S*)-**4aa** with metal salts [$Sc(OTf)_3$, $Zn(OTf)_2$, $Al(OTf)_3$, $In(OTf)_3$, $La(OTf)_3$, $Y(OTf)_3$, $Yb(OTf)_3$, $Mg(OTf)_2$, $Ni(OTf)_2$, $Fe(OTf)_2$, $Fe(OTf)_3$, $Cu(OTf)_2$] were collected on UV-Vis absorption spectrometer at 25 °C.

15.2 Metal ion recognition of (*S*,*S*)-4aa by fluorscence spectra analysis.

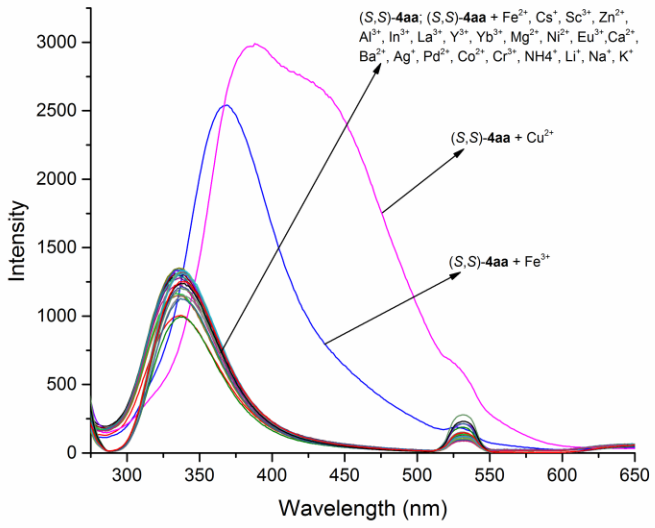


Fig. S2 Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (50 μL, 5 mM in CH_3CN) and metal salts (50 μL, 5 mM in CH_3CN or CH_3CN : H_2O = 1:1) in 5 mL volumetric flasks [0.05 mM of (*S*,*S*)-**4aa** and 0.05 mM of metal salts in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa**, (*S*,*S*)-**4aa** with metal salts [$Sc(OTf)_3$, $Zn(OTf)_2$, $Al(OTf)_3$, $In(OTf)_3$, $La(OTf)_3$, $Y(OTf)_3$, $Yb(OTf)_3$, $Mg(OTf)_2$, $Ni(OTf)_2$, $Fe(OTf)_2$, $Fe(OTf)_3$, $Cu(OTf)_2$, $Eu(OTf)_3$, $Ca(OTf)_2$, $Ba(OTf)_2$, AgOTf, $Pd(CH_3CN)_4(OTf)_2$, $Co(OTf)_2$, $CrCl_3 \cdot 6H_20$, NH_4Cl, Li_2CO_3, Na_2CO_3, K_2CO_3, Cs_2CO_3] were collected on fluorescence spectrometer at 25 °C [(*S*,*S*)-**4aa**:metal ions = 1:1, λ_{ex} = 265 nm, slits: 2.5/20 nm].

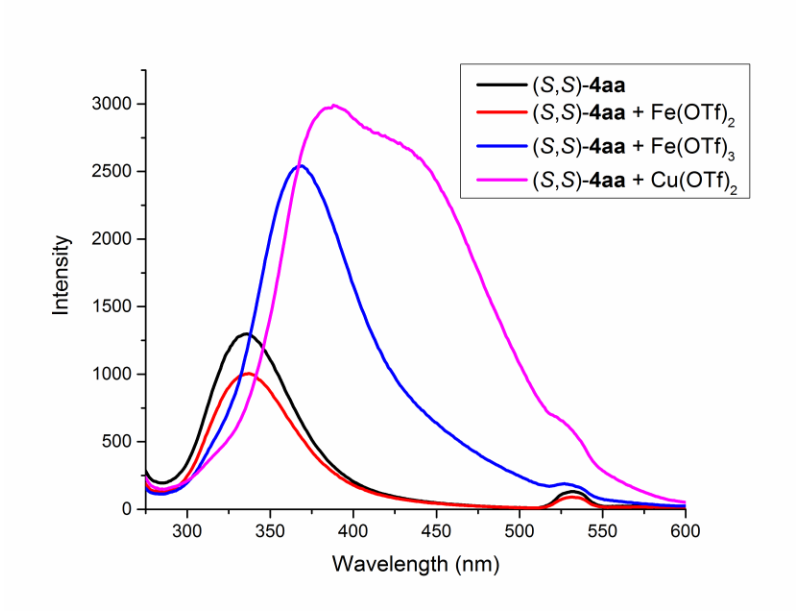


Fig. S3 Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (50 μL, 5 mM in CH_3CN) and metal salts (50 μL, 5 mM in CH_3CN) in 5 mL volumetric flasks [0.05 mM of (*S*,*S*)-**4aa** and 0.05 mM of metal salts in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa**, (*S*,*S*)-**4aa** with metal salts [$Fe(OTf)_3$, $Fe(OTf)_2$, $Cu(OTf)_2$] were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm).

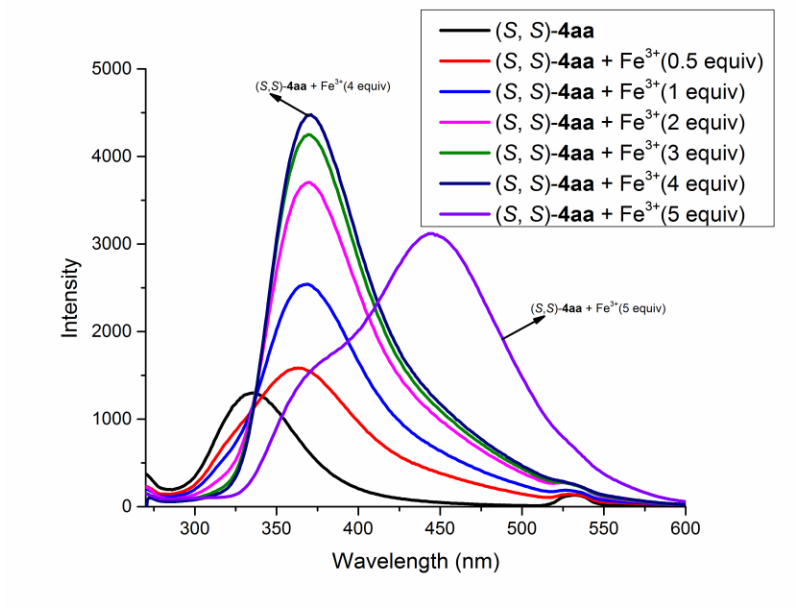


Fig. S4 Procedure: The samples were prepared by mixing (*S*,*S*)-**4aa** (50 μL, 5 mM in CH_3CN) and $Fe(OTf)_3$ (25 μL, 50 μL, 100 μL, 150 μL, 200 μL, 250 μL, 5 mM in CH_3CN) in 5 mL volumetric flasks [0.05 mM of (*S*,*S*)-**4aa** and 0.025–0.25 mM of $Fe(OTf)_3$ in CH_3CN (5 mL)]. Fluorescence spectra of (*S*,*S*)-**4aa**, (*S*,*S*)-**4aa** with $Fe(OTf)_3$ (0.5 equiv, 1 equiv, 2 equiv, 3 equiv, 4 equiv, 5 equiv) were collected on fluorescence spectrometer at 25 °C (λ_{ex} = 265 nm, slits: 2.5/20 nm).

15.3 Metal ion recognition of (*S*,*S*)-4aa by visualization.

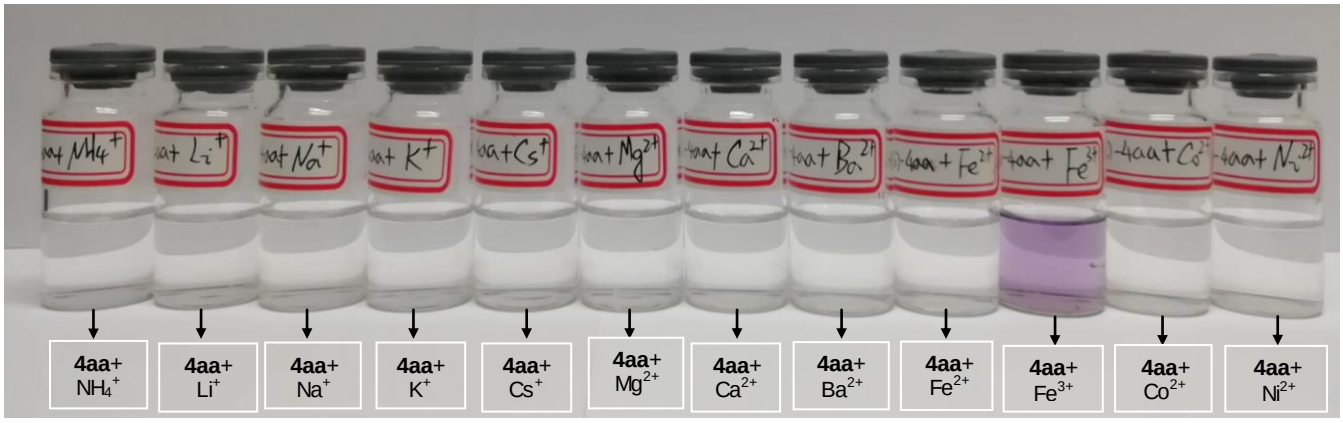


Fig. S5 From left to right : (*S*,*S*)-**4aa** (0.05 mM in 5 mL CH_3CN) with metal ions (NH_4^+, Li^+, Na^+, K^+, Cs^+, Mg^{2+}, Ca^{2+}, Ba^{2+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, 0.25mM in CH_3CN).

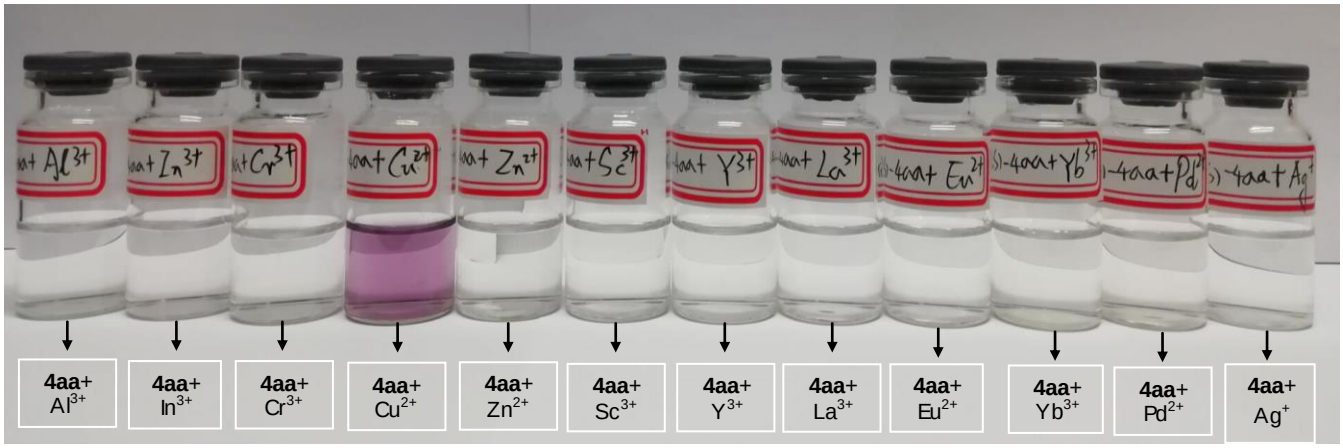


Fig. S6 From left to right : (*S*,*S*)-**4aa** (0.05 mM in 5 mL CH_3CN) with metal ions (Al^{3+}, In^{3+}, Cr^{3+}, Cu^{2+}, Zn^{2+}, Sc^{3+}, Y^{3+}, La^{3+}, Eu^{2+}, Yb^{3+}, Pd^{2+}, Ag^+, 0.25mM in CH_3CN).

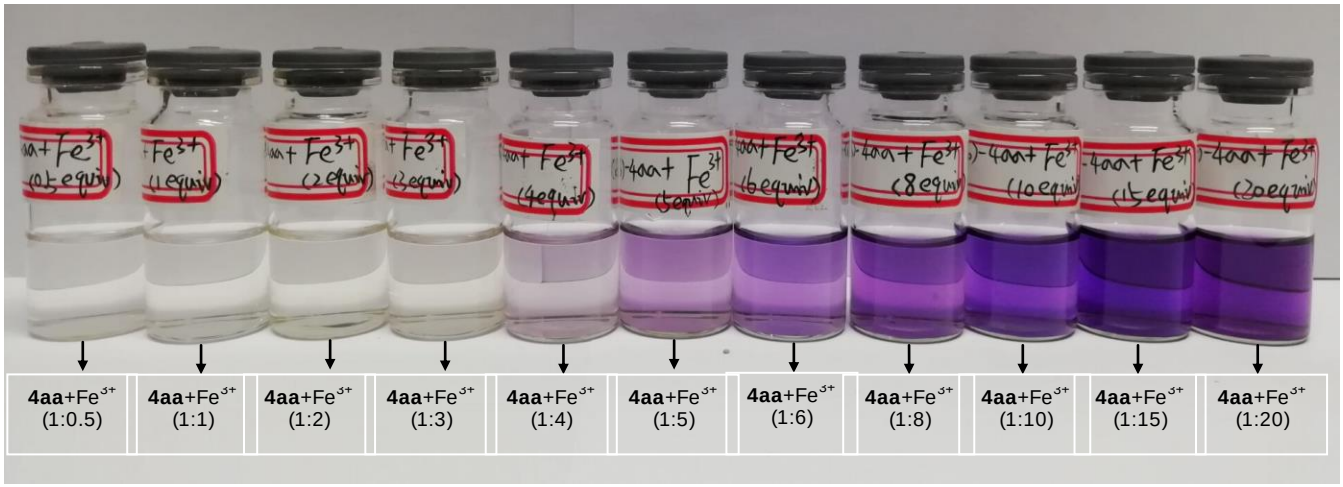


Fig. S7 From left to right : (*S*,*S*)-**4aa** (0.05 mM in 5 mL CH_3CN) with Fe^{3+} (0.025 mM, 0.05 mM, 0.1 mM, 0.15 mM, 0.2 mM, 0.25 mM, 0.3 mM, 0.4 mM, 0.5 mM, 0.75 mM, 1mM in CH_3CN).

16. DFT Calculation of Reaction Mechanism

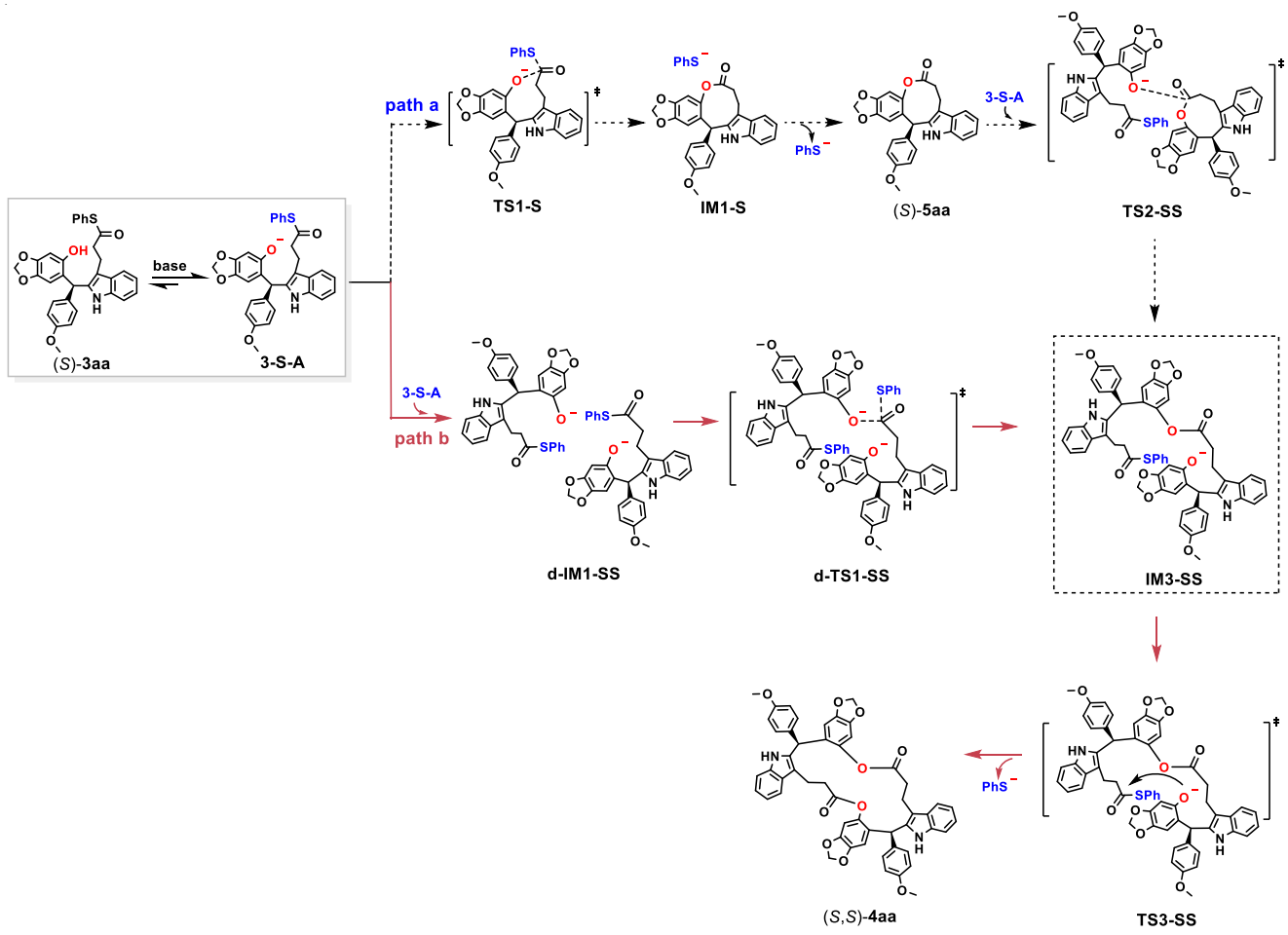


Fig. S8 Schematic reaction mechanism for the transformation from **3aa** to **4aa** along path a and b.

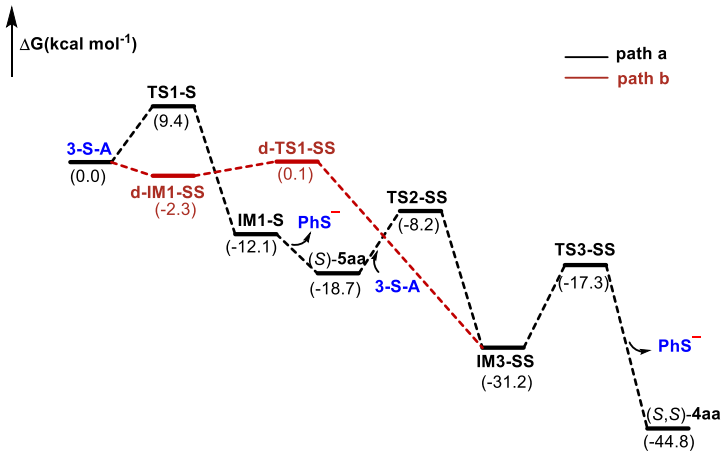


Fig. S9 Energy profiles for the transformation from **3-S-A** to **4aa** along path a and b.

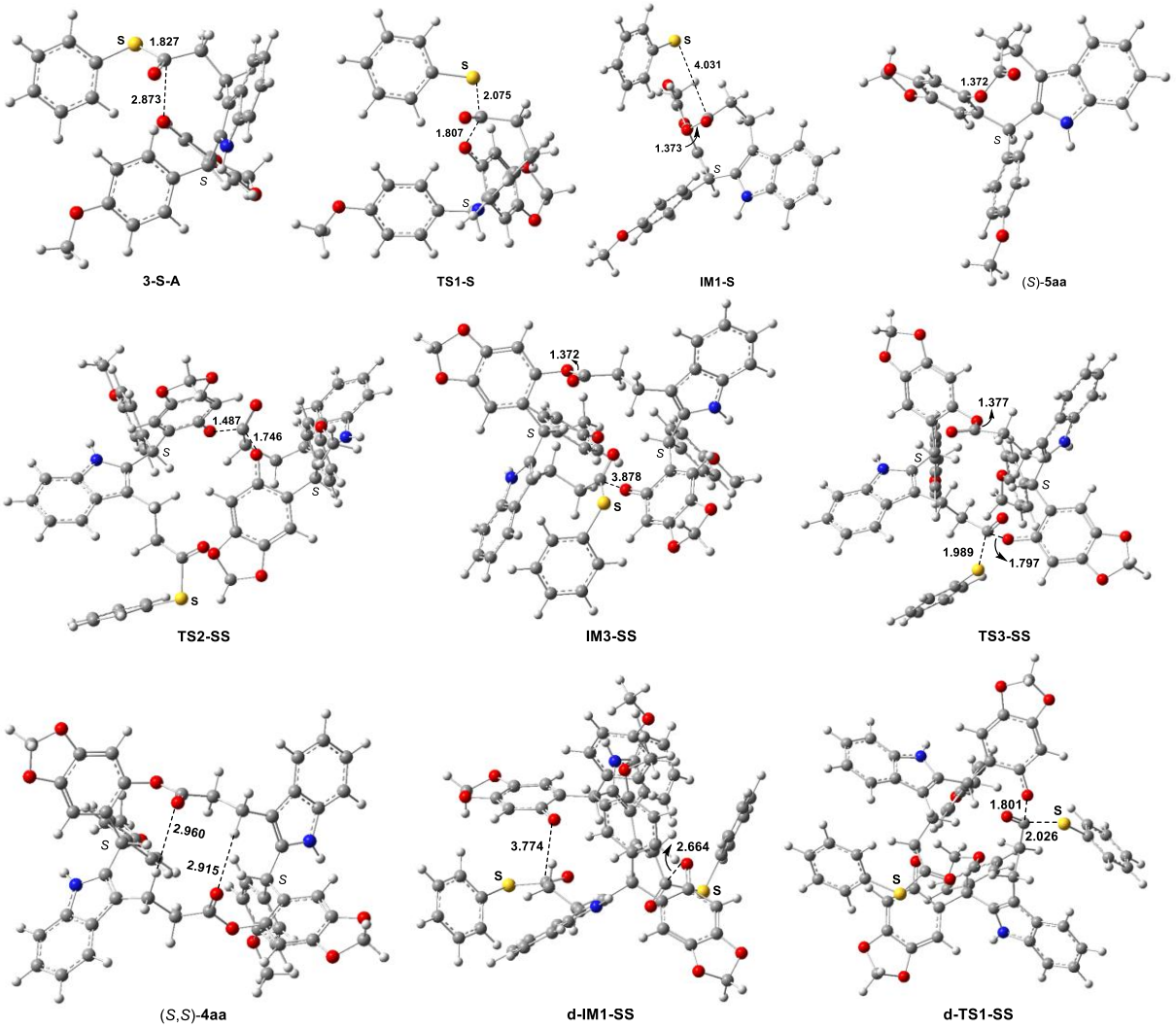


Fig. S10 Optimized geometry of transition states and intermediates for the formation of **4aa**.

To understand the formation of the eighteen-membered-ring product **4aa**, DFT calculation was performed at the B3LYP-D3(BJ)/6-31G(d,p) (SMD, CH_2Cl_2) theoretical level. Two pathways (path a and b) were studied, in which the intramolecular or intermolecular cyclization reactions were involved.

As shown in Fig. S8, **3aa** underwent a deportation process by base reagent (e.g. Cs_2CO_3), producing the corresponding anion **3-S-A**. Then, an intramolecular cyclization reaction occurred *via* transition state **TS1-S**, accompanying with the releasing of a SPh anion (path a). The process was exothermic by 12.1 kcal/mol, with the energy barrier of 9.4 kcal/mol (Fig. S9). The nine-membered ring intermediate **5aa** exhibited a boat-like conformation (Fig. S10), in which two aromatic rings was connected by the planar ester group as well as -$(CH_2)_2$ chain. This less stable rigid structure could occur ring-open reaction when another **3-S-A** attacked the C atom of carbonyl group of **5aa**. Consequently, the intermediate **IM3-SS** was formed, with the ΔG of –31.2 kcal/mol. In the final step, **4aa** with eighteen-membered ring was generated *via* transition state **TS3-SS**, with the activation barrier ($\Delta G^{\neq}$) of 13.9 kcal/mol. This step was exothermic by 13.6 kcal/mol. Compared to **5aa** with nine-membered ring, **4aa** had the lower the relative Gibbs free energy of formation (ΔG=–44.8 kcal/mol), suggesting eighteen-membered-ring product **4aa** was more stable thermodynamically.

The eighteen-membered ring in **4aa** could also be constructed by coupling of **3aa** with its anion **3-S-A** *via* intermolecular cyclization along path b. Starting from molecular complex **d-IM1-SS**, two C-O bonds were formed sequentially *via* transition states **TS1-SS-1** and **TS3-SS**, with the activation barriers of 2.4 and 13.9 kcal/mol, respectively (Fig. S11). The activation barrier in the first C-O bond formation step *via* **TS1-SS-1** was 7.0 kcal/mol lower than *via* **TS1-S** in ring-closure reaction for nine-membered ring intermediate **IM1-S** (2.4 vs 9.4 kcal/mol). These results indicated that **3-S-A** was more possible to occur the intermolecular nucleophilic reaction, producing the eighteen-membered-ring product **4aa**.

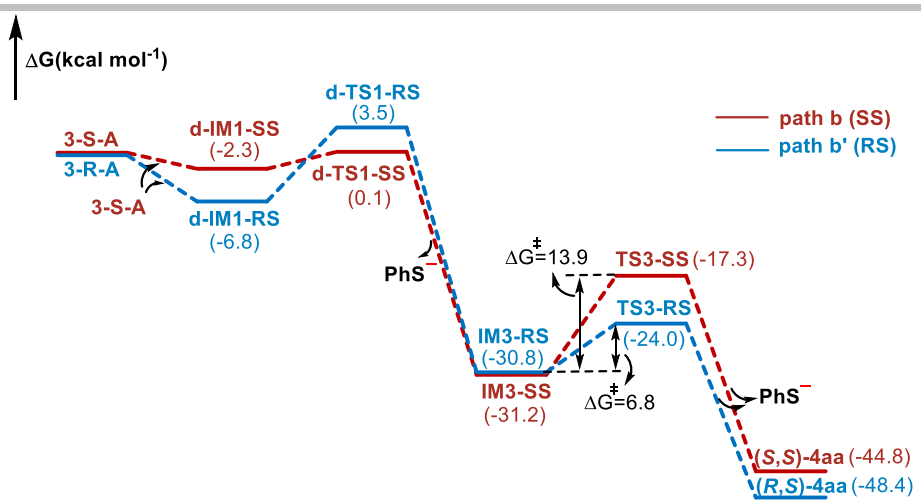


Fig. S11 Gibbs free energy (ΔG, kcal/mol) of transition states and intermediates for the formation of (*S*,*S*)-**4aa** **vs** (*R*,*S*)-**4aa**.

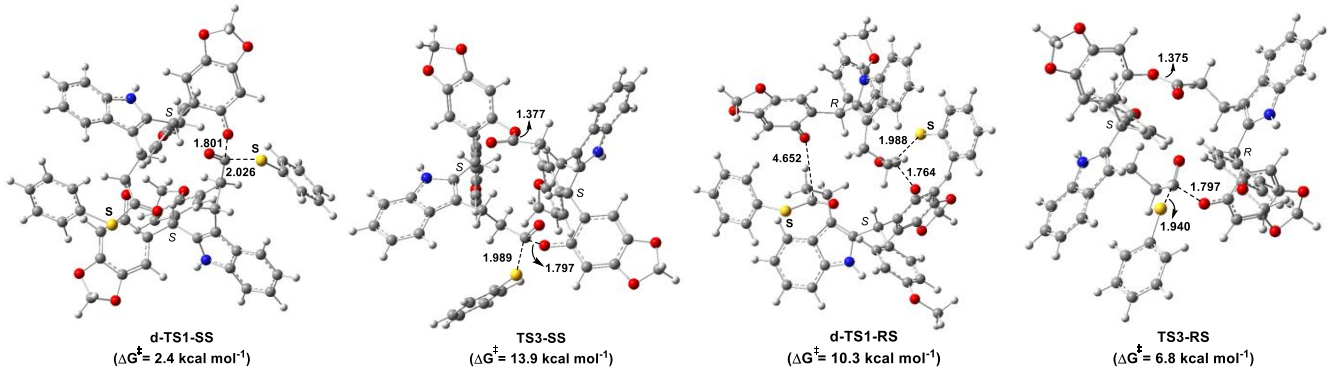


Fig. S12 Optimized geometry of transition states in two C-O bond formation steps. Activation energy barriers were in the parentheses.

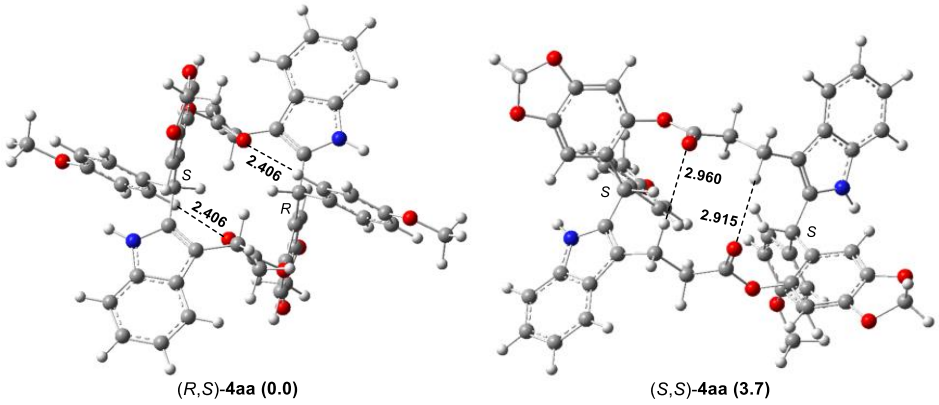


Fig. S13 Optimized geometry of intermediates (*R*,*S*)-**4aa** and (*S*,*S*)-**4aa**. Relative Gibbs free energy (ΔG, kcal/mol) of (*R*,*S*)-**4aa** was set to zero.

For comparison, we studied the formation of mesoisomer (*R*,*S*)-**4aa** by interacting between **3-S-A** and its enantiomer **3-R-A** along path b at the same theoretical level. The optimized geometries of the two C-O bond formation transition states (**d-TS1-RS** and **TS3-RS**) were shown in Fig. S12. The relative Gibbs free energy of **d-TS1-RS** was 3.4 kcal/mol higher than that of d-TS1-SS in the first C-O bond formation (3.5 vs 0.1 kcal/mol). Different from **TS3-SS**, the PhOMe groups in **TS3-RS** in the second C-O bond formation step was placed to be trans-position. This favorable spatial arrangement minimized the steric repulsion of two interplaying partners.

As a result, the activation barrier associated with the second C-O bond formation *via* **TS3-RS** was lower than *via* **TS3-SS-1** by 7.1 kcal/mol (6.8 vs 13.9 kcal/mol, Figs. S11–S12). In addition, the (*R*,*S*)-**4aa** was more stable thermodynamically than (*S*,*S*)-**4aa** by 3.7 kcal/mol (Fig. S13). These results indicated that **3-R-A** was facile to interact with **3-S-A**, contributing to high ee values observed in the experiment.

Computational details

All calculations were performed using Gaussian 09 program package,[9] employing the B3LYP density functional with the 6-31G(d,p) basis set. Geometries were optimized in CH_2Cl_2 solvent and characterized by frequency analysis at 298 K. The self-consistent reaction field (SCRF) method based on the universal solvation model SMD[10] was adopted to evaluate the effect of solvent. Dispersion corrections were computed with Grimme's D3(BJ) method in optimization.[11–12] The intrinsic reaction coordinate (IRC) path was traced to check the energy profiles connecting each transition state to two associated minima of the proposed mechanism.[13]

Cartesian coordinates and the corresponding energies of all stationary points in this work.

3-S-A

Zero-point correction = 0.50891 a.u.

Thermal correction to Gibbs Free Energy = 0.44065 a.u.

Sum of electronic and zero-point Energies = -2063.93252 a.u.

Sum of electronic and thermal Free Energies = -2064.00077 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-3.068780	-2.575544	3.550488
2	7	0	0.851655	2.403021	2.124368
3	1	0	0.763179	2.069908	3.072848
4	8	0	-1.735741	1.532753	-1.090699
5	8	0	0.250071	-0.919832	-0.978625
6	6	0	-1.090615	1.361505	-2.097551
7	6	0	0.145612	2.148904	-2.473063
8	1	0	-0.159704	3.200710	-2.458733
9	1	0	0.446358	1.905562	-3.496722
10	6	0	1.362079	1.942507	-1.533929
11	1	0	2.173267	2.548499	-1.960263
12	1	0	1.669138	0.902955	-1.586118
13	6	0	1.159074	1.582339	1.039864
14	6	0	1.132609	2.350003	-0.110238
15	6	0	0.808959	3.700819	0.295619

16	6	0	0.626433	3.690958	1.708318
17	6	0	0.300362	4.841500	2.431503
18	6	0	0.672455	4.920484	-0.389689
19	6	0	1.477682	0.145367	1.401458
20	1	0	2.188392	0.241454	2.234614
21	6	0	0.255455	-0.562897	1.999014
22	6	0	-1.052408	-0.279397	1.580743
23	1	0	-1.213901	0.464660	0.811726
24	6	0	0.437709	-1.545450	2.971839
25	1	0	1.445316	-1.786088	3.303130
26	6	0	-2.136014	-0.956262	2.126475
27	1	0	-3.147727	-0.742315	1.796982
28	6	0	-0.640482	-2.246654	3.524736
29	1	0	-0.457148	-3.005876	4.275408
30	6	0	-1.937888	-1.952625	3.093563
31	6	0	2.193440	-0.724514	0.379610
32	6	0	3.538550	-1.064965	0.613916
33	1	0	4.069766	-0.655214	1.469455
34	6	0	4.166533	-1.935692	-0.255783
35	6	0	3.476755	-2.490845	-1.328794
36	6	0	2.158988	-2.196811	-1.597982
37	1	0	1.633324	-2.627034	-2.444492
38	6	0	1.456919	-1.269540	-0.738093
39	8	0	5.457440	-2.478796	-0.200237
40	8	0	4.314351	-3.370852	-2.000619
41	16	0	-1.621290	0.217610	-3.419835
42	6	0	-2.967976	-0.637884	-2.609457
43	6	0	-2.701795	-1.454631	-1.501896
44	6	0	-4.271145	-0.505848	-3.100985
45	6	0	-3.757293	-2.130263	-0.888040

46	6	0	-5.315936	-1.199160	-2.486506
47	6	0	-5.060902	-2.007734	-1.377216
48	1	0	-4.466875	0.136440	-3.954004
49	1	0	-1.676913	-1.534777	-1.144397
50	1	0	-3.558422	-2.754675	-0.021946
51	1	0	-5.875707	-2.540295	-0.895153
52	1	0	-6.327534	-1.098565	-2.869020
53	6	0	0.161205	6.031865	1.721193
54	6	0	0.349833	6.071345	0.325363
55	1	0	0.242543	7.016535	-0.199349
56	1	0	-0.091246	6.944386	2.253606
57	1	0	0.164254	4.806768	3.508577
58	1	0	0.825051	4.971933	-1.463693
59	6	0	-2.910014	-3.599131	4.524305
60	1	0	-2.296445	-4.426443	4.146869
61	1	0	-3.913642	-3.969237	4.741948
62	1	0	-2.462495	-3.213830	5.449083
63	6	0	5.620562	-3.075522	-1.483617
64	1	0	6.192008	-4.001848	-1.388974
65	1	0	6.123015	-2.368990	-2.165149

TS1-S

Zero-point correction = 0.50862 a.u.

Thermal correction to Gibbs Free Energy = 0.44464 a.u.

Sum of electronic and zero-point Energies = -2063.92174 a.u.

Sum of electronic and thermal Free Energies = -2063.98571 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-4.085040	-0.647073	3.692233
2	7	0	0.881787	2.755046	1.654445

3	1	0	0.409006	2.751208	2.546041
4	8	0	-0.798487	1.220957	-1.738628
5	8	0	0.038674	-0.742851	-0.575230
6	6	0	-0.009832	0.340898	-2.020405
7	6	0	1.444010	0.578967	-2.414979
8	1	0	1.379550	1.318553	-3.220733
9	1	0	1.865861	-0.332776	-2.845896
10	6	0	2.403427	1.088312	-1.306112
11	1	0	3.198988	1.650519	-1.810692
12	1	0	2.887140	0.229344	-0.844773
13	6	0	1.325193	1.605737	1.003710
14	6	0	1.807613	1.960050	-0.240995
15	6	0	1.629272	3.386100	-0.366717
16	6	0	1.038809	3.852804	0.842545
17	6	0	0.728802	5.199636	1.051004
18	6	0	1.910471	4.312073	-1.384611
19	6	0	1.212237	0.304274	1.766850
20	1	0	1.843733	0.425242	2.657967
21	6	0	-0.209091	0.079016	2.297491
22	6	0	-1.349053	0.509670	1.598932
23	1	0	-1.229412	1.017191	0.649931
24	6	0	-0.392742	-0.603817	3.499867
25	1	0	0.476696	-0.945665	4.056515
26	6	0	-2.622313	0.255444	2.092601
27	1	0	-3.503922	0.583183	1.550581
28	6	0	-1.667973	-0.873194	4.009258
29	1	0	-1.768555	-1.408091	4.945833
30	6	0	-2.792269	-0.443173	3.297505
31	6	0	1.752356	-0.920851	1.041778
32	6	0	2.890654	-1.576288	1.545631
33	1	0	3.375993	-1.230793	2.453337

34	6	0	3.382837	-2.659166	0.842653
35	6	0	2.769552	-3.105609	-0.323171
36	6	0	1.636555	-2.507688	-0.835972
37	1	0	1.147380	-2.853526	-1.738737
38	6	0	1.114327	-1.380656	-0.143444
39	8	0	4.452572	-3.489547	1.151641
40	8	0	3.440653	-4.216914	-0.796975
41	16	0	-0.694887	-1.016702	-3.432241
42	6	0	-2.419143	-1.032277	-3.004885
43	6	0	-2.834277	-1.079753	-1.661702
44	6	0	-3.395396	-1.017451	-4.014574
45	6	0	-4.192239	-1.107206	-1.347142
46	6	0	-4.752835	-1.064688	-3.691860
47	6	0	-5.159633	-1.104012	-2.356364
48	1	0	-3.087500	-0.966823	-5.055210
49	1	0	-2.079485	-1.094770	-0.884891
50	1	0	-4.493885	-1.142326	-0.303264
51	1	0	-6.216228	-1.131461	-2.105427
52	1	0	-5.493388	-1.058238	-4.487525
53	6	0	1.018197	6.093824	0.022377
54	6	0	1.604095	5.655009	-1.182680
55	1	0	1.814463	6.378238	-1.965457
56	1	0	0.786025	7.147084	0.151254
57	1	0	0.276672	5.534531	1.980081
58	1	0	2.355711	3.982802	-2.319585
59	6	0	-4.303644	-1.362849	4.902164
60	1	0	-3.897347	-2.380334	4.849477
61	1	0	-5.386184	-1.415689	5.030884
62	1	0	-3.865454	-0.844532	5.764056
63	6	0	4.663453	-4.244855	-0.044569
64	1	0	4.909855	-5.277368	0.211260

65	1	0	5.464484	-3.779854	-0.639713

IM1-S

Zero-point correction = 0.51068 a.u.

Thermal correction to Gibbs Free Energy = 0.44228 a.u.

Sum of electronic and zero-point Energies = -2063.95161 a.u.

Sum of electronic and thermal Free Energies = -2064.0200 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	2.160478	5.405740	-1.178939
2	7	0	3.604780	-0.733285	-0.381821
3	1	0	4.147289	0.117921	-0.384108
4	8	0	-0.447652	-0.704911	-2.186527
5	8	0	-0.552347	0.089809	-0.135546
6	6	0	-0.533963	-0.968862	-1.009690
7	6	0	-0.610418	-2.371792	-0.452880
8	1	0	-0.632591	-3.020511	-1.329726
9	1	0	-1.563384	-2.487046	0.072905
10	6	0	0.586956	-2.749634	0.461984
11	1	0	0.679977	-3.840076	0.440258
12	1	0	0.366436	-2.481416	1.494334
13	6	0	2.408032	-0.890839	0.306386
14	6	0	1.884700	-2.137905	0.012521
15	6	0	2.791331	-2.756103	-0.926851
16	6	0	3.859626	-1.843114	-1.152183
17	6	0	4.918555	-2.130982	-2.018432
18	6	0	2.799843	-3.990896	-1.596921
19	6	0	1.987291	0.229258	1.229768
20	1	0	2.736967	0.251289	2.030845
21	6	0	2.056006	1.609371	0.566202

22	6	0	1.780519	1.816004	-0.794008
23	1	0	1.519791	0.977628	-1.428492
24	6	0	2.378871	2.720428	1.347923
25	1	0	2.598268	2.583185	2.403772
26	6	0	1.823433	3.090691	-1.344233
27	1	0	1.606308	3.250398	-2.395448
28	6	0	2.423518	4.009798	0.812634
29	1	0	2.678939	4.845322	1.452596
30	6	0	2.142970	4.198267	-0.545501
31	6	0	0.655566	0.004390	1.935074
32	6	0	0.646850	-0.129616	3.339570
33	1	0	1.568793	-0.067423	3.906795
34	6	0	-0.562432	-0.351397	3.965273
35	6	0	-1.754192	-0.441170	3.249630
36	6	0	-1.793449	-0.306547	1.877090
37	1	0	-2.705668	-0.417748	1.291744
38	6	0	-0.559161	-0.087597	1.247355
39	8	0	-0.816344	-0.486135	5.308476
40	8	0	-2.799907	-0.637663	4.116536
41	16	0	-4.471428	-1.552078	-0.371098
42	6	0	-4.651599	-0.313420	-1.616244
43	6	0	-3.721736	0.744202	-1.766790
44	6	0	-5.740000	-0.322790	-2.521978
45	6	0	-3.871568	1.719283	-2.751422
46	6	0	-5.889529	0.654343	-3.505112
47	6	0	-4.956811	1.688546	-3.633341
48	1	0	-6.475782	-1.118454	-2.439368
49	1	0	-2.868718	0.789710	-1.097696
50	1	0	-3.129330	2.510784	-2.830939
51	1	0	-5.071607	2.448997	-4.400446
52	1	0	-6.742591	0.606267	-4.178871

53	6	0	4.899202	-3.361862	-2.668235
54	6	0	3.851542	-4.282859	-2.459351
55	1	0	3.867656	-5.233299	-2.984575
56	1	0	5.705870	-3.616775	-3.349229
57	1	0	5.722447	-1.418721	-2.178239
58	1	0	1.995071	-4.705021	-1.447070
59	6	0	2.480499	6.558667	-0.406380
60	1	0	1.759173	6.714944	0.404521
61	1	0	2.434407	7.403899	-1.094932
62	1	0	3.490627	6.492981	0.015679
63	6	0	-2.194746	-0.888741	5.395219
64	1	0	-2.699721	-0.295800	6.160699
65	1	0	-2.247302	-1.962226	5.620825

(*S*)-**5aa**

Zero-point correction = 0.41982 a.u.

Thermal correction to Gibbs Free Energy = 0.36367 a.u.

Sum of electronic and zero-point Energies = -1434.03958 a.u.

Sum of electronic and thermal Free Energies = -1434.09573 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	0.177612	5.714941	0.769641
2	7	0	-2.370112	0.252604	-1.189269
3	1	0	-2.399038	1.208336	-1.512838
4	8	0	-1.147201	-0.620361	3.017315
5	8	0	0.625330	-0.290114	1.753312
6	6	0	-0.364520	-1.108541	2.235793
7	6	0	-0.413630	-2.549738	1.774210
8	1	0	-1.238716	-2.994088	2.332533
9	1	0	0.509205	-3.059684	2.069332

10	6	0	-0.650481	-2.720189	0.247231
11	1	0	-1.115132	-3.700341	0.101281
12	1	0	0.304449	-2.751711	-0.275821
13	6	0	-1.209719	-0.406379	-0.805424
14	6	0	-1.546124	-1.661215	-0.329505
15	6	0	-2.984633	-1.760929	-0.401261
16	6	0	-3.468445	-0.538570	-0.945277
17	6	0	-4.830991	-0.298539	-1.147695
18	6	0	-3.905078	-2.765657	-0.059299
19	6	0	0.106351	0.298023	-1.037597
20	1	0	0.229745	0.353628	-2.126320
21	6	0	0.102570	1.751952	-0.551877
22	6	0	-0.620101	2.179819	0.572157
23	1	0	-1.220757	1.473347	1.132717
24	6	0	0.866044	2.695860	-1.242046
25	1	0	1.431656	2.385978	-2.117081
26	6	0	-0.574004	3.504867	0.986416
27	1	0	-1.134140	3.836317	1.854853
28	6	0	0.927207	4.031229	-0.837937
29	1	0	1.529456	4.733045	-1.401408
30	6	0	0.200638	4.441115	0.286067
31	6	0	1.333070	-0.456323	-0.538069
32	6	0	2.293224	-0.885699	-1.478614
33	1	0	2.153517	-0.691712	-2.535957
34	6	0	3.403296	-1.563148	-1.018494
35	6	0	3.602075	-1.814874	0.337724
36	6	0	2.692389	-1.402628	1.289116
37	1	0	2.831406	-1.581437	2.348451
38	6	0	1.553524	-0.733489	0.814470
39	8	0	4.469310	-2.044597	-1.736408
40	8	0	4.796524	-2.459771	0.520862

41	6	0	-5.719040	-1.311486	-0.797435
42	6	0	-5.261458	-2.533210	-0.261006
43	1	0	-5.983087	-3.301540	0.000374
44	1	0	-6.784467	-1.157966	-0.940911
45	1	0	-5.180275	0.643068	-1.560403
46	1	0	-3.561756	-3.708480	0.357452
47	6	0	0.924530	6.706679	0.070554
48	1	0	1.996191	6.474615	0.063320
49	1	0	0.764691	7.640558	0.611699
50	1	0	0.572193	6.822721	-0.961307
51	6	0	5.237998	-2.819964	-0.801102
52	1	0	6.297030	-2.579443	-0.910229
53	1	0	5.047865	-3.888014	-0.969238

TS2-SS

Zero-point correction = 0.92869 a.u.

Thermal correction to Gibbs Free Energy = 0.82776 a.u.

Sum of electronic and zero-point Energies = -3497.97874 a.u.

Sum of electronic and thermal Free Energies = -3498.07967 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	5.062713	-2.624473	4.701567
2	7	0	6.171363	-0.791129	-1.261493
3	1	0	6.681192	-1.386820	-0.626376
4	8	0	3.257726	1.968964	-0.017708
5	8	0	2.241970	-0.214460	-0.032861
6	6	0	2.275079	1.450416	-0.558485
7	6	0	2.141072	1.429002	-2.087181
8	1	0	2.362090	2.460090	-2.384818
9	1	0	1.103497	1.234048	-2.367679

10	6	0	3.049666	0.450790	-2.875395
11	1	0	3.188552	0.879618	-3.875775
12	1	0	2.507643	-0.482076	-3.026205
13	6	0	4.804155	-0.906588	-1.507613
14	6	0	4.406747	0.147860	-2.307341
15	6	0	5.578949	0.955577	-2.541480
16	6	0	6.669273	0.339311	-1.862508
17	6	0	7.959080	0.876962	-1.877981
18	6	0	5.812013	2.140329	-3.258761
19	6	0	4.106910	-2.110512	-0.910635
20	1	0	4.571827	-2.989239	-1.379037
21	6	0	4.391440	-2.245809	0.590422
22	6	0	4.535470	-1.129668	1.431373
23	1	0	4.440297	-0.137298	1.008336
24	6	0	4.486191	-3.515636	1.159911
25	1	0	4.376691	-4.393605	0.527745
26	6	0	4.758044	-1.289701	2.792889
27	1	0	4.858176	-0.428222	3.446199
28	6	0	4.708091	-3.695379	2.529424
29	1	0	4.773817	-4.698174	2.933765
30	6	0	4.842471	-2.573317	3.353085
31	6	0	2.621388	-2.212411	-1.222624
32	6	0	2.145440	-3.286242	-1.995570
33	1	0	2.819235	-4.062488	-2.345080
34	6	0	0.801665	-3.309207	-2.318188
35	6	0	-0.060676	-2.308557	-1.888000
36	6	0	0.360411	-1.256904	-1.100881
37	1	0	-0.311448	-0.481106	-0.761048
38	6	0	1.738203	-1.200509	-0.758205
39	8	0	0.090947	-4.262786	-3.035044
40	8	0	-1.339385	-2.580869	-2.341533

41	6	0	8.157902	2.055225	-2.594786
42	6	0	7.095405	2.679918	-3.279602
43	1	0	7.283721	3.598467	-3.828368
44	1	0	9.148278	2.500569	-2.623895
45	1	0	8.775078	0.393731	-1.348286
46	1	0	4.998074	2.633242	-3.783472
47	6	0	5.151968	-3.908146	5.308210
48	1	0	4.224038	-4.479487	5.183742
49	1	0	5.322986	-3.729306	6.371264
50	1	0	5.989520	-4.489033	4.902502
51	6	0	-1.170786	-3.644419	-3.294000
52	1	0	-1.969266	-4.376129	-3.163484
53	1	0	-1.175850	-3.218316	-4.308763
54	6	0	-7.304932	0.230085	2.221451
55	1	0	-8.101825	-0.423355	2.564810
56	7	0	-4.150533	2.548683	0.925816
57	1	0	-4.046410	3.522391	0.680118
58	8	0	-1.857891	6.755570	-2.765096
59	8	0	0.920091	1.846159	-0.090196
60	8	0	-0.423759	2.097838	5.230031
61	8	0	1.827185	1.879453	4.729854
62	8	0	-1.799311	-3.548397	0.788596
63	6	0	0.611860	1.889062	1.230689
64	6	0	-6.574777	2.480069	1.615883
65	1	0	-6.772567	3.539960	1.485423
66	6	0	-7.567413	1.605375	2.050017
67	6	0	-6.046046	-0.300431	1.959262
68	1	0	-5.856063	-1.361036	2.097122
69	6	0	-5.310270	1.944200	1.355671
70	6	0	-0.766877	1.990343	1.524732
71	6	0	-3.640651	0.363913	1.149172

72	6	0	-0.255230	2.009203	3.857616
73	6	0	-5.022649	0.555956	1.514656
74	6	0	-1.205821	2.066470	2.860676
75	1	0	-2.260866	2.144802	3.093995
76	6	0	-2.808600	-3.272999	0.182772
77	6	0	-1.752571	1.985084	0.360318
78	1	0	-1.411850	1.205638	-0.326698
79	6	0	-2.894174	-0.936676	1.168185
80	1	0	-2.985830	-1.407578	2.154583
81	1	0	-1.826607	-0.772548	1.008764
82	6	0	1.095649	1.883401	3.558913
83	6	0	-1.744692	3.283888	-0.438818
84	6	0	1.572044	1.824810	2.266515
85	1	0	2.619637	1.741128	2.022767
86	6	0	-3.437484	-1.905222	0.107507
87	1	0	-4.521532	-2.002872	0.193401
88	1	0	-3.249999	-1.521002	-0.901245
89	6	0	-3.148663	1.601614	0.785767
90	6	0	-1.877884	3.249851	-1.834319
91	1	0	-1.950011	2.289566	-2.338183
92	6	0	0.850029	1.722375	5.769366
93	1	0	0.821084	0.668738	6.084300
94	1	0	1.099644	2.378403	6.606320
95	6	0	-1.909988	4.418234	-2.583660
96	1	0	-2.001411	4.390161	-3.664833
97	6	0	-1.815780	5.664872	-1.946476
98	6	0	-1.649397	4.530423	0.181674
99	1	0	-1.528620	4.582465	1.259451
100	6	0	-1.685080	5.719310	-0.554763
101	1	0	-1.600818	6.667521	-0.038001
102	6	0	-1.741932	8.041863	-2.164834

103	1	0	-2.565570	8.237355	-1.467436
104	1	0	-1.787147	8.762070	-2.983393
105	1	0	-0.787325	8.155649	-1.637575
106	1	0	-8.560893	1.989587	2.261959
107	16	0	-3.643800	-4.650282	-0.694799
108	6	0	-5.107294	-3.901392	-1.411028
109	6	0	-6.336917	-4.016106	-0.750256
110	6	0	-5.027333	-3.210129	-2.626290
111	6	0	-7.477911	-3.430726	-1.299711
112	6	0	-6.171182	-2.624449	-3.167741
113	6	0	-7.396277	-2.732929	-2.506184
114	1	0	-4.073539	-3.115430	-3.132706
115	1	0	-6.394294	-4.551663	0.191684
116	1	0	-8.428249	-3.516832	-0.781920
117	1	0	-8.284537	-2.274480	-2.929737
118	1	0	-6.103795	-2.081802	-4.105644

IM3-SS

Zero-point correction = 0.93000 a.u.

Thermal correction to Gibbs Free Energy = 0.82746 a.u.

Sum of electronic and zero-point Energies = -3498.01385 a.u.

Sum of electronic and thermal Free Energies = -3498.11639 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.562641	2.844425	2.496872
2	1	0	-5.964831	3.844174	2.634072
3	7	0	-3.900360	-0.871377	1.819527
4	1	0	-3.854113	-1.725022	2.356935
5	8	0	0.628243	-4.445211	4.131404
6	8	0	-0.970195	-3.189275	-1.924546

7	8	0	-6.409076	-3.853939	-1.861402
8	8	0	-5.213661	-4.975905	-3.499268
9	8	0	0.018524	2.196491	-2.214319
10	6	0	-2.365531	-3.274593	-1.899344
11	6	0	-5.398491	0.537670	3.283371
12	1	0	-5.652911	-0.243765	3.993264
13	6	0	-5.899656	1.830241	3.417471
14	6	0	-4.717895	2.586983	1.422553
15	1	0	-4.456121	3.375680	0.725287
16	6	0	-4.547727	0.283482	2.203718
17	6	0	-3.058405	-2.573729	-0.908157
18	6	0	-3.300207	0.691279	0.304216
19	6	0	-5.074378	-3.538187	-1.757516
20	6	0	-4.195021	1.293368	1.261556
21	6	0	-4.459330	-2.716998	-0.835176
22	1	0	-5.033304	-2.194629	-0.080098
23	6	0	-0.686767	2.851537	-1.477207
24	6	0	-2.282198	-1.695138	0.068421
25	1	0	-1.524421	-1.159152	-0.507904
26	6	0	-2.619612	1.388485	-0.834033
27	1	0	-3.339788	2.003407	-1.387708
28	1	0	-2.216364	0.660824	-1.543594
29	6	0	-4.358500	-4.217365	-2.740566
30	6	0	-1.530212	-2.492565	1.136051
31	6	0	-2.986552	-4.107491	-2.840238
32	1	0	-2.407999	-4.626873	-3.594481
33	6	0	-1.464139	2.284512	-0.321405
34	1	0	-1.859508	3.070028	0.320984
35	1	0	-0.770106	1.677167	0.273064
36	6	0	-3.129377	-0.620172	0.692975
37	6	0	-0.445060	-1.885241	1.790960

38	1	0	-0.124731	-0.877340	1.528837
39	6	0	-6.533699	-4.555842	-3.108160
40	1	0	-6.941223	-3.879376	-3.871440
41	1	0	-7.168476	-5.433331	-2.971622
42	6	0	0.245024	-2.559915	2.788195
43	1	0	1.089373	-2.094782	3.284496
44	6	0	-0.126183	-3.863298	3.153029
45	6	0	-1.900987	-3.782080	1.513594
46	1	0	-2.733194	-4.272703	1.018631
47	6	0	-1.208342	-4.475887	2.514296
48	1	0	-1.517009	-5.480940	2.775214
49	6	0	0.286637	-5.765865	4.536204
50	1	0	-0.729554	-5.813001	4.946625
51	1	0	1.000697	-6.036477	5.315797
52	1	0	0.372460	-6.478270	3.706550
53	1	0	-6.559047	2.061045	4.249051
54	16	0	-0.863299	4.615973	-1.933936
55	6	0	-1.935269	5.342678	-0.697108
56	6	0	-3.318483	5.391994	-0.912182
57	6	0	-1.383214	5.895151	0.466258
58	6	0	-4.149335	5.975126	0.045754
59	6	0	-2.222887	6.466617	1.423019
60	6	0	-3.603778	6.504768	1.217173
61	1	0	-0.308465	5.874816	0.613122
62	1	0	-3.738560	4.971270	-1.819802
63	1	0	-5.221667	6.008683	-0.121331
64	1	0	-4.252738	6.950653	1.964713
65	1	0	-1.795677	6.884628	2.329537
66	8	0	5.408594	-2.607864	4.523554
67	8	0	3.829556	4.896173	-0.824125
68	8	0	0.808761	0.986600	1.576354

69	8	0	2.046955	5.549518	0.489638
70	8	0	-1.062358	-1.369325	-3.277514
71	7	0	5.053582	-0.488160	-1.210306
72	1	0	5.646179	-0.358846	-0.403219
73	6	0	-0.410400	-2.145009	-2.616478
74	6	0	3.170008	-0.722697	-2.426587
75	6	0	4.300973	-1.025291	-3.266186
76	6	0	5.472976	-0.869334	-2.465109
77	6	0	1.574062	1.858545	1.024530
78	6	0	3.493590	2.422578	-0.466555
79	1	0	4.324118	2.113193	-1.093279
80	6	0	4.851362	-1.910366	3.488987
81	6	0	3.669454	-0.412490	-1.177362
82	6	0	1.716824	-0.779868	-2.796638
83	1	0	1.595601	-0.622208	-3.872995
84	1	0	1.167234	0.030533	-2.309338
85	6	0	1.078898	-2.122215	-2.406974
86	1	0	1.515232	-2.948162	-2.983125
87	1	0	1.269191	-2.353488	-1.354692
88	6	0	5.726010	-1.633483	-5.115002
89	1	0	5.848639	-1.931994	-6.152339
90	6	0	6.757019	-1.091924	-2.969191
91	1	0	7.634666	-0.967227	-2.341541
92	6	0	2.701325	1.475727	0.201791
93	6	0	3.593229	-0.655928	1.296747
94	6	0	4.448467	-1.412707	-4.609513
95	1	0	3.575025	-1.536478	-5.244089
96	6	0	2.116146	4.160730	0.483336
97	6	0	3.174979	3.761719	-0.321596
98	6	0	1.313708	3.270258	1.161578
99	1	0	0.476977	3.596690	1.768895

100	6	0	6.868794	-1.476590	-4.303366
101	6	0	5.061632	-0.550555	3.242319
102	1	0	5.698895	0.041789	3.887748
103	6	0	4.430560	0.059599	2.151354
104	1	0	4.582081	1.120019	1.976923
105	6	0	4.013177	-2.645474	2.636266
106	1	0	3.842243	-3.696251	2.848216
107	6	0	2.932215	-0.019206	0.072698
108	1	0	1.933011	-0.462210	0.006936
109	6	0	2.883113	5.938749	-0.614027
110	1	0	2.254072	6.063950	-1.509276
111	1	0	3.404364	6.864888	-0.362264
112	6	0	3.403461	-2.022258	1.555858
113	1	0	2.754236	-2.601118	0.905281
114	6	0	6.251651	-1.897343	5.423250
115	1	0	5.711758	-1.088926	5.931031
116	1	0	7.127695	-1.479652	4.912092
117	1	0	6.584230	-2.626420	6.164268
118	1	0	7.853191	-1.656421	-4.725557

TS3-SS

Zero-point correction = 0.93045 a.u.

Thermal correction to Gibbs Free Energy = 0.83400 a.u.

Sum of electronic and zero-point Energies = -3497.99782 a.u.

Sum of electronic and thermal Free Energies = -3498.09428 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.365989	-6.632737	-1.912951
2	1	0	2.283619	-7.451459	-2.622150
3	7	0	2.686889	-3.385756	0.605202

4	1	0	2.860724	-3.285048	1.594083
5	8	0	0.307595	-0.698446	5.620590
6	8	0	2.486474	1.876402	-0.110392
7	8	0	7.317324	-0.707711	-0.225058
8	8	0	7.307111	1.575297	-0.615063
9	8	0	-1.786385	-1.404872	-3.574540
10	6	0	3.626529	1.189961	-0.179408
11	6	0	2.883370	-5.883205	0.350199
12	1	0	3.189931	-6.087183	1.372029
13	6	0	2.750450	-6.906731	-0.584785
14	6	0	2.095520	-5.332866	-2.330737
15	1	0	1.814095	-5.140301	-3.361519
16	6	0	2.615838	-4.579434	-0.075197
17	6	0	3.633402	-0.215789	0.019648
18	6	0	1.999902	-2.848243	-1.475661
19	6	0	6.011972	-0.238640	-0.217724
20	6	0	2.202533	-4.277237	-1.407060
21	6	0	4.844592	-0.935258	0.017833
22	1	0	4.859653	-2.006206	0.185939
23	6	0	-0.943305	-1.989408	-2.931820
24	6	0	2.298524	-0.917024	0.260403
25	1	0	1.575507	-0.385913	-0.361884
26	6	0	1.671469	-2.047131	-2.698963
27	1	0	2.490336	-2.171856	-3.420590
28	1	0	1.651945	-0.978848	-2.469594
29	6	0	6.009462	1.133849	-0.442276
30	6	0	1.797926	-0.818656	1.707032
31	6	0	4.846157	1.873206	-0.432578
32	1	0	4.833208	2.942055	-0.606944
33	6	0	0.390285	-2.433842	-3.471700
34	1	0	0.445050	-2.019366	-4.480375

35	1	0	0.322907	-3.523790	-3.567446
36	6	0	2.297942	-2.342951	-0.226119
37	6	0	0.741392	-1.637834	2.142807
38	1	0	0.278369	-2.331878	1.448267
39	6	0	8.085596	0.377167	-0.756853
40	1	0	8.286703	0.199347	-1.824052
41	1	0	9.015300	0.478525	-0.192193
42	6	0	0.276427	-1.587176	3.448793
43	1	0	-0.532572	-2.228469	3.777323
44	6	0	0.827760	-0.674629	4.357082
45	6	0	2.330888	0.087837	2.623534
46	1	0	3.136899	0.743511	2.317358
47	6	0	1.853034	0.175733	3.935167
48	1	0	2.291431	0.900238	4.610708
49	6	0	0.717277	0.323187	6.522483
50	1	0	1.788399	0.255362	6.748707
51	1	0	0.150725	0.162482	7.440635
52	1	0	0.490755	1.319411	6.128111
53	1	0	2.952281	-7.931410	-0.286569
54	16	0	2.121246	3.790217	-2.304824
55	6	0	1.396849	4.943650	-1.153510
56	6	0	1.574107	4.813469	0.235092
57	6	0	0.627943	6.012632	-1.642158
58	6	0	0.982318	5.727555	1.106590
59	6	0	0.056892	6.935361	-0.764965
60	6	0	0.226886	6.795160	0.614055
61	1	0	0.473377	6.111837	-2.712410
62	1	0	2.144890	3.969429	0.606944
63	1	0	1.116225	5.606608	2.178394
64	1	0	-0.229147	7.505887	1.297029
65	1	0	-0.535966	7.755407	-1.160901

66	8	0	-2.349305	0.922666	5.503778
67	8	0	-6.470097	-3.160548	-0.426630
68	8	0	-1.169657	-2.396300	-1.636190
69	8	0	-5.366966	-4.813369	-1.622134
70	8	0	2.041286	1.123970	-2.481606
71	7	0	-4.145501	1.556323	-0.526269
72	1	0	-4.745882	1.230703	0.215663
73	6	0	1.625533	1.966611	-1.685212
74	6	0	-2.235772	1.865054	-1.692810
75	6	0	-3.123360	2.975413	-1.944583
76	6	0	-4.310871	2.749965	-1.190892
77	6	0	-2.524858	-2.481135	-1.273829
78	6	0	-4.528590	-1.636464	-0.234909
79	1	0	-5.064287	-0.895594	0.343340
80	6	0	-2.394016	0.556870	4.190923
81	6	0	-2.888645	1.029437	-0.808584
82	6	0	-0.836409	1.741752	-2.222238
83	1	0	-0.685985	2.491063	-3.006201
84	1	0	-0.673780	0.769670	-2.694912
85	6	0	0.213027	1.948075	-1.120721
86	1	0	0.006228	2.862043	-0.563509
87	1	0	0.168605	1.127952	-0.401383
88	6	0	-4.081951	5.044941	-2.721811
89	1	0	-4.011247	5.954949	-3.310709
90	6	0	-5.382916	3.647419	-1.199161
91	1	0	-6.280133	3.456301	-0.617657
92	6	0	-3.156731	-1.469931	-0.549780
93	6	0	-2.417242	0.008336	1.417621
94	6	0	-3.021274	4.145195	-2.716559
95	1	0	-2.123506	4.345845	-3.293994
96	6	0	-4.508392	-3.775832	-1.368066

97	6	0	-5.170009	-2.778047	-0.653796
98	6	0	-3.177191	-3.656878	-1.692499
99	1	0	-2.640125	-4.416889	-2.246937
100	6	0	-5.251094	4.797985	-1.971979
101	6	0	-2.953287	-0.629364	3.712235
102	1	0	-3.379239	-1.359227	4.389417
103	6	0	-2.948830	-0.895056	2.337397
104	1	0	-3.370709	-1.832774	1.996581
105	6	0	-1.833970	1.465638	3.281046
106	1	0	-1.389966	2.380561	3.659670
107	6	0	-2.406798	-0.219817	-0.105854
108	1	0	-1.365962	-0.354563	-0.407910
109	6	0	-6.667316	-4.335476	-1.229676
110	1	0	-7.244224	-4.074617	-2.126573
111	1	0	-7.172464	-5.101712	-0.638299
112	6	0	-1.854803	1.194909	1.922113
113	1	0	-1.429318	1.918371	1.235533
114	6	0	-2.798422	-0.024022	6.467342
115	1	0	-2.217853	-0.950569	6.409943
116	1	0	-3.864907	-0.248856	6.343381
117	1	0	-2.646418	0.441908	7.442305
118	1	0	-6.062613	5.519585	-1.995861

(*S*,*S*)-4aa

Zero-point correction = 0.84011 a.u.

Thermal correction to Gibbs Free Energy = 0.74936 a.u.

Sum of electronic and zero-point Energies = -2868.11241 a.u.

Sum of electronic and thermal Free Energies = -2868.20316 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.183066	-5.960145	-0.738397
2	1	0	4.080470	-6.976830	-1.106239
3	7	0	4.421600	-2.042718	0.534838
4	1	0	4.951951	-1.572327	1.254053
5	8	0	2.014074	1.136834	5.442699
6	8	0	-3.368343	-1.768428	5.363277
7	8	0	-7.018562	-1.006435	-2.921135
8	8	0	-2.054023	-2.458874	-1.111048
9	8	0	-6.115999	-2.980125	-3.740393
10	8	0	2.308428	2.645423	-0.660646
11	8	0	7.426117	1.363423	-2.139717
12	8	0	6.669230	3.500045	-2.631974
13	8	0	1.377745	1.762199	-2.533140
14	8	0	-1.002239	-1.530731	-2.895533
15	6	0	3.585810	2.239664	-1.065721
16	7	0	-4.338193	2.039747	0.511009
17	1	0	-4.959602	1.548070	1.136871
18	6	0	5.345779	-4.383417	0.720341
19	1	0	6.109693	-4.159055	1.458687
20	6	0	1.249336	2.297614	-1.455468
21	6	0	5.175287	-5.671904	0.221998
22	6	0	-2.549297	2.436955	-0.807177
23	6	0	-3.220924	3.687213	-0.548281
24	6	0	3.337296	-4.965866	-1.218177
25	1	0	2.576301	-5.196740	-1.958358
26	6	0	4.493465	-3.386460	0.236448
27	6	0	4.008716	0.942401	-0.760224
28	6	0	2.800681	-2.411592	-0.992669

29	6	0	6.118177	1.495201	-1.740770
30	6	0	-4.339567	3.399348	0.287081
31	6	0	-3.294401	-2.012415	-1.583072
32	6	0	3.482542	-3.655142	-0.732705
33	6	0	-5.086481	-0.398294	-1.497717
34	1	0	-5.522493	0.522016	-1.130158
35	6	0	-3.350215	-1.413180	4.048629
36	6	0	5.320327	0.561793	-1.111364
37	1	0	5.690845	-0.433120	-0.899491
38	6	0	-0.944382	-2.118938	-1.840311
39	6	0	3.045111	-0.003740	-0.049700
40	1	0	2.077468	0.094620	-0.546176
41	6	0	1.597064	-2.210358	-1.865818
42	1	0	1.667445	-2.833335	-2.763641
43	1	0	1.545934	-1.176174	-2.217499
44	6	0	5.668215	2.779927	-2.034618
45	6	0	2.817501	0.355914	1.419015
46	6	0	4.391200	3.189220	-1.707908
47	1	0	4.018501	4.182532	-1.926303
48	6	0	-3.255742	1.461143	-0.135878
49	6	0	-1.283869	2.247700	-1.589571
50	1	0	-1.310754	2.845454	-2.507181
51	1	0	-1.185934	1.207398	-1.911661
52	6	0	-0.046001	2.639717	-0.770616
53	1	0	-0.043710	3.709110	-0.532665
54	1	0	-0.041209	2.124078	0.197221
55	6	0	0.301240	-2.547211	-1.113257
56	1	0	0.229452	-3.618372	-0.895457
57	1	0	0.286753	-2.049212	-0.136436
58	6	0	3.397055	-1.457891	-0.194923
59	6	0	-3.853211	6.011410	-0.493972

60	1	0	-3.683434	7.042806	-0.788685
61	6	0	-5.210691	4.396143	0.736519
62	1	0	-6.056844	4.156402	1.373383
63	6	0	-3.806262	-0.816336	-1.076089
64	6	0	-3.147903	-0.533872	1.376410
65	6	0	1.611552	-0.018391	2.031523
66	1	0	0.852363	-0.533657	1.449139
67	6	0	7.714290	2.546574	-2.902137
68	1	0	7.715072	2.302874	-3.972457
69	1	0	8.673995	2.960337	-2.585760
70	6	0	-2.988248	5.017181	-0.938609
71	1	0	-2.145400	5.263301	-1.578346
72	6	0	-5.223603	-2.380429	-2.891488
73	6	0	-5.762401	-1.193020	-2.398674
74	6	0	-3.977855	-2.824177	-2.500195
75	1	0	-3.538977	-3.743197	-2.868931
76	6	0	-4.951987	5.703681	0.335441
77	6	0	1.371088	0.251444	3.370740
78	1	0	0.438116	-0.039282	3.840552
79	6	0	-4.158168	-1.979186	3.059105
80	1	0	-4.868512	-2.761142	3.297755
81	6	0	-4.050333	-1.532509	1.736598
82	1	0	-4.683841	-1.985743	0.982034
83	6	0	-2.442314	-0.398925	3.701201
84	1	0	-1.826076	0.039617	4.479315
85	6	0	-2.996641	-0.018883	-0.059071
86	1	0	-1.942733	-0.141848	-0.322629
87	6	0	-7.165852	-2.014101	-3.935033
88	1	0	-7.058618	-1.556062	-4.926721
89	1	0	-8.135115	-2.504724	-3.824527
90	6	0	2.343613	0.909569	4.140365

91	6	0	-2.346273	0.027740	2.385269
92	1	0	-1.642065	0.815959	2.134318
93	6	0	3.777070	1.004625	2.194590
94	1	0	4.714774	1.313490	1.743568
95	6	0	3.553197	1.285037	3.547191
96	1	0	4.319428	1.795542	4.117471
97	6	0	-4.236700	-2.828961	5.754190
98	1	0	-3.989707	-3.761042	5.232294
99	1	0	-5.288152	-2.578719	5.569740
100	1	0	-4.082156	-2.964888	6.825593
101	6	0	2.964403	1.812575	6.261917
102	1	0	3.898021	1.243697	6.346028
103	1	0	2.505385	1.897843	7.247980
104	1	0	3.184770	2.815701	5.878133
105	1	0	5.820212	-6.469689	0.578162
106	1	0	-5.609443	6.501771	0.667206

(*R*,*S*)-**4aa**

Zero-point correction = 0.84044 a.u.

Thermal correction to Gibbs Free Energy = 0.74812 a.u.

Sum of electronic and zero-point Energies = -2868.11666 a.u.

Sum of electronic and thermal Free Energies = -2868.20898 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	3.115445	-5.050402	3.258210
2	7	0	-4.322646	-0.772047	-1.619388
3	1	0	-4.791425	0.094270	-1.841220
4	6	0	-5.693362	-3.752313	-3.372431
5	1	0	-6.478613	-4.096436	-4.038973
6	8	0	5.525133	0.942981	-3.824903

7	7	0	4.323032	0.772049	1.619097
8	1	0	4.791941	-0.094280	1.840610
9	6	0	-4.746014	-4.675907	-2.883208
10	1	0	-4.819084	-5.718210	-3.179867
11	8	0	4.579670	-0.650005	-5.220612
12	6	0	-3.724266	-4.273558	-2.029382
13	1	0	-3.002213	-4.994110	-1.655709
14	8	0	-4.580604	0.649885	5.220405
15	6	0	-3.642031	-2.921333	-1.653140
16	6	0	-4.617011	-2.007234	-2.153010
17	8	0	-5.526094	-0.942757	3.824354
18	8	0	-3.114518	5.050405	-3.258523
19	6	0	-5.642950	-2.408006	-3.013746
20	1	0	-6.373815	-1.695902	-3.385332
21	6	0	-2.746860	-2.168661	-0.809826
22	8	0	-1.685717	2.360150	1.733653
23	8	0	-0.017229	0.836420	1.607865
24	6	0	-3.192403	-0.863734	-0.823772
25	6	0	-2.634177	0.330618	-0.098539
26	1	0	-1.562478	0.139116	-0.031448
27	8	0	0.016743	-0.836598	-1.607606
28	6	0	-3.930609	2.421649	-0.791455
29	1	0	-4.702465	2.163456	-0.072403
30	6	0	-5.390936	-0.540275	5.197076
31	1	0	-6.376066	-0.317336	5.611567
32	1	0	-4.886637	-1.333784	5.763966
33	8	0	1.685450	-2.360116	-1.733246
34	6	0	-4.080571	3.580757	-1.559232
35	1	0	-4.966125	4.191877	-1.434888
36	6	0	-1.942031	3.128190	-2.601843
37	1	0	-1.173431	3.418306	-3.311286

38	6	0	-3.078840	3.940462	-2.467773
39	6	0	-2.803486	1.608641	-0.913717
40	6	0	-1.813305	1.975638	-1.837500
41	1	0	-0.939754	1.342793	-1.956585
42	6	0	-3.150715	0.458341	1.335298
43	6	0	-4.551407	-0.251080	3.145424
44	6	0	-4.157577	-0.395877	1.831452
45	1	0	-4.602900	-1.150762	1.195843
46	6	0	-3.988961	0.705977	3.984945
47	6	0	-3.007939	1.566625	3.537582
48	1	0	-2.560654	2.326044	4.167188
49	6	0	-2.607878	1.415404	2.202282
50	6	0	-0.413465	1.968945	1.439324
51	6	0	0.370912	3.132635	0.890783
52	1	0	0.689386	3.740586	1.746715
53	1	0	-0.316322	3.750392	0.306873
54	6	0	1.583292	2.717705	0.039254
55	1	0	1.906145	3.609561	-0.511001
56	1	0	1.257337	1.996937	-0.716021
57	6	0	3.192503	0.863806	0.823877
58	6	0	2.746922	2.168719	0.810271
59	6	0	3.642293	2.921278	1.653475
60	6	0	4.617478	2.007140	2.152870
61	6	0	5.643657	2.407812	3.013371
62	1	0	6.374675	1.695683	3.384607
63	6	0	5.694082	3.752051	3.372316
64	1	0	6.479514	4.096085	4.038690
65	6	0	4.746521	4.675677	2.883571
66	1	0	4.819605	5.717923	3.180426
67	6	0	3.724536	4.273431	2.029978
68	1	0	3.002311	4.994006	1.656683

69	6	0	2.634097	-0.330447	0.098630
70	1	0	1.562407	-0.138886	0.031817
71	6	0	2.803563	-1.608580	0.913606
72	6	0	3.930882	-2.421316	0.791280
73	1	0	4.702646	-2.162950	0.072185
74	6	0	1.813418	-1.975936	1.837298
75	1	0	0.939713	-1.343306	1.956371
76	6	0	4.081126	-3.580463	1.558959
77	1	0	4.966818	-4.191370	1.434553
78	6	0	1.942414	-3.128538	2.601494
79	1	0	1.173836	-3.418986	3.310828
80	6	0	3.079472	-3.940469	2.467449
81	6	0	4.269459	-5.882412	3.183225
82	1	0	4.397924	-6.303710	2.178927
83	1	0	4.102904	-6.694471	3.892594
84	1	0	5.177740	-5.336740	3.465866
85	6	0	3.150322	-0.458119	-1.335315
86	6	0	4.156989	0.396167	-1.831736
87	1	0	4.602302	1.151198	-1.196295
88	6	0	4.550650	0.251241	-3.145746
89	6	0	3.988229	-0.706016	-3.985051
90	6	0	5.389968	0.540188	-5.197537
91	1	0	6.375107	0.317181	-5.611977
92	1	0	4.885652	1.333564	-5.764588
93	6	0	3.007391	-1.566736	-3.537417
94	1	0	2.560087	-2.326274	-4.166868
95	6	0	2.607462	-1.415364	-2.202091
96	6	0	0.413225	-1.968968	-1.438669
97	6	0	-0.370861	-3.132601	-0.889600
98	1	0	-0.689045	-3.741126	-1.745229
99	1	0	0.316509	-3.749814	-0.305267

100	6	0	-1.583421	-2.717508	-0.038416
101	1	0	-1.906378	-3.609230	0.511994
102	1	0	-1.257625	-1.996541	0.716736
103	6	0	-4.268555	5.882443	-3.184035
104	1	0	-4.101900	6.694190	-3.893735
105	1	0	-4.397162	6.304131	-2.179921
106	1	0	-5.176790	5.336659	-3.466598

d-TS1-SS

Zero-point correction = 1.02059 a.u.

Thermal correction to Gibbs Free Energy = 0.91366 a.u.

Sum of electronic and zero-point Energies = -4127.89441 a.u.

Sum of electronic and thermal Free Energies = -4128.00134 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	5.188665	4.747926	0.319588
2	1	0	6.222649	4.876703	0.012106
3	7	0	1.242130	4.112413	1.328788
4	1	0	0.665748	4.387940	2.110234
5	8	0	-1.566433	0.637306	5.634740
6	8	0	-3.015876	1.721123	-0.662695
7	8	0	-2.400909	7.161992	-0.869586
8	8	0	-4.366642	6.267289	-1.702507
9	8	0	1.957359	-0.807440	-2.788799
10	6	0	-2.792827	3.031331	-0.711204
11	6	0	3.386885	5.327057	1.861289
12	1	0	3.009880	5.878911	2.717512
13	6	0	4.705257	5.465779	1.432461
14	6	0	4.365349	3.874771	-0.385341
15	1	0	4.751464	3.324129	-1.236927

16	6	0	2.564145	4.448868	1.150654
17	6	0	-1.576743	3.582924	-0.220229
18	6	0	1.931933	2.898813	-0.444682
19	6	0	-2.357881	5.776448	-0.780761
20	6	0	3.032377	3.707604	0.026090
21	6	0	-1.367152	4.975696	-0.248822
22	1	0	-0.451135	5.412374	0.130030
23	6	0	2.948004	-0.314409	-2.293413
24	6	0	-0.546403	2.627373	0.376044
25	1	0	-0.526582	1.754503	-0.276222
26	6	0	1.999755	1.905706	-1.567409
27	1	0	2.370933	2.394114	-2.478813
28	1	0	1.003747	1.522829	-1.801763
29	6	0	-3.541679	5.242480	-1.272935
30	6	0	-0.900405	2.127386	1.782010
31	6	0	-3.787902	3.885948	-1.258861
32	1	0	-4.702206	3.455346	-1.648353
33	6	0	2.941139	0.727247	-1.213681
34	1	0	3.948429	1.085462	-1.006764
35	1	0	2.577315	0.234813	-0.294923
36	6	0	0.857107	3.172634	0.378063
37	6	0	-0.119525	1.098107	2.336871
38	1	0	0.675950	0.629324	1.763320
39	6	0	-3.518148	7.425043	-1.723902
40	1	0	-3.165014	7.596451	-2.752428
41	1	0	-4.070332	8.289457	-1.348239
42	6	0	-0.358288	0.636455	3.621441
43	1	0	0.234576	-0.170260	4.036092
44	6	0	-1.406855	1.170044	4.382508
45	6	0	-1.936866	2.655238	2.549287
46	1	0	-2.563132	3.439582	2.136712

47	6	0	-2.206181	2.179470	3.841009
48	1	0	-3.032228	2.599821	4.402862
49	6	0	-2.776740	0.920393	6.321408
50	1	0	-2.860247	1.983130	6.582339
51	1	0	-2.751390	0.333833	7.241109
52	1	0	-3.651677	0.625541	5.729852
53	1	0	5.371139	6.138149	1.965923
54	16	0	4.529537	-0.921665	-3.005927
55	6	0	5.851076	-0.067586	-2.152496
56	6	0	6.209064	1.235568	-2.523709
57	6	0	6.557586	-0.726046	-1.138137
58	6	0	7.250445	1.885857	-1.861538
59	6	0	7.600736	-0.069686	-0.483449
60	6	0	7.943522	1.236498	-0.837382
61	1	0	6.291914	-1.740713	-0.864010
62	1	0	5.667821	1.736513	-3.319723
63	1	0	7.519690	2.898315	-2.146936
64	1	0	8.751342	1.745792	-0.320729
65	1	0	8.140948	-0.580402	0.308084
66	16	0	-3.747879	0.746640	-3.358535
67	6	0	-5.035382	-0.267291	-2.661174
68	6	0	-5.489821	-0.090334	-1.341799
69	6	0	-5.620922	-1.275410	-3.446467
70	6	0	-6.491572	-0.913112	-0.827020
71	6	0	-6.636981	-2.080624	-2.931344
72	6	0	-7.074978	-1.907723	-1.616619
73	1	0	-5.268515	-1.430905	-4.461766
74	1	0	-5.019824	0.673258	-0.730799
75	1	0	-6.820398	-0.772885	0.199493
76	1	0	-7.855749	-2.544209	-1.210577
77	1	0	-7.073252	-2.856623	-3.554607

78	8	0	-2.305733	-2.471136	5.750850
79	8	0	4.122998	-5.525489	-0.554141
80	8	0	2.156575	-0.785257	1.389208
81	8	0	5.635249	-3.914820	0.120877
82	8	0	-1.295764	1.455107	-2.502366
83	7	0	-1.133893	-4.623824	-0.062296
84	1	0	-0.875669	-5.114264	0.780853
85	6	0	-2.231984	0.828820	-2.016751
86	6	0	-1.387818	-2.902080	-1.499543
87	6	0	-2.234830	-3.990416	-1.921170
88	6	0	-2.054395	-5.056410	-0.989264
89	6	0	2.555662	-1.924098	0.949201
90	6	0	2.068458	-4.165045	-0.021409
91	1	0	1.363583	-4.913309	-0.368360
92	6	0	-1.642554	-2.532532	4.555819
93	6	0	-0.744958	-3.318699	-0.352296
94	6	0	-1.329002	-1.540099	-2.128924
95	1	0	-1.773126	-1.588184	-3.128869
96	1	0	-0.295600	-1.209069	-2.260295
97	6	0	-2.089647	-0.497107	-1.293559
98	1	0	-3.068815	-0.880271	-1.006962
99	1	0	-1.546697	-0.289051	-0.368210
100	6	0	-3.847542	-5.357714	-3.080040
101	1	0	-4.562307	-5.493245	-3.886939
102	6	0	-2.746879	-6.265735	-1.097842
103	1	0	-2.594798	-7.065853	-0.378940
104	6	0	1.625346	-2.941603	0.506321
105	6	0	-0.451140	-2.582881	1.994746
106	6	0	-3.150380	-4.158102	-2.973429
107	1	0	-3.320082	-3.354871	-3.684141
108	6	0	4.344325	-3.430815	0.310154

109	6	0	3.431204	-4.386104	-0.114935
110	6	0	3.962155	-2.218202	0.838735
111	1	0	4.681394	-1.466877	1.145805
112	6	0	-3.647081	-6.401458	-2.152743
113	6	0	-0.297192	-2.882978	4.410607
114	1	0	0.311391	-3.125811	5.273667
115	6	0	0.281443	-2.904941	3.134632
116	1	0	1.328625	-3.168924	3.032594
117	6	0	-2.398580	-2.224057	3.416665
118	1	0	-3.440445	-1.944972	3.538831
119	6	0	0.155917	-2.560506	0.581602
120	1	0	0.123514	-1.510427	0.269591
121	6	0	5.449851	-5.048369	-0.745164
122	1	0	5.587502	-4.722659	-1.789084
123	1	0	6.165157	-5.828956	-0.477088
124	6	0	-1.805351	-2.245855	2.162537
125	1	0	-2.401912	-1.989277	1.292611
126	6	0	-1.520482	-2.524420	6.934655
127	1	0	-0.755542	-1.740234	6.937275
128	1	0	-1.039270	-3.502516	7.061944
129	1	0	-2.209967	-2.363874	7.765753
130	1	0	-4.205615	-7.326999	-2.260541

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Zero-point correction = 1.01985 a.u.

Thermal correction to Gibbs Free Energy = 0.91439 a.u.

Sum of electronic and zero-point Energies = -4127.89047 a.u.

Sum of electronic and thermal Free Energies = -4127.99593 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	8	0	-5.227008	-2.053165	5.190638
2	8	0	-5.366625	3.796746	-2.294543
3	7	0	-4.481438	-1.526335	-0.840408
4	1	0	-5.215137	-1.502429	-0.147806
5	8	0	-4.498914	5.462743	-0.953745
6	8	0	-0.072957	-1.239812	0.736143
7	8	0	-2.164435	2.309294	1.921802
8	6	0	0.092231	-2.090706	-0.147162
9	6	0	0.056007	-1.737265	-1.636248
10	1	0	-0.038963	-2.638177	-2.244885
11	1	0	1.023939	-1.288454	-1.872651
12	6	0	-1.045990	-0.718252	-1.976675
13	1	0	-0.913710	-0.430687	-3.028301
14	1	0	-0.868307	0.184255	-1.389657
15	6	0	-3.282807	-0.831417	-0.721015
16	6	0	-2.445758	-1.200011	-1.753023
17	6	0	-3.149071	-2.183919	-2.534935
18	6	0	-4.424213	-2.377811	-1.920450
19	6	0	-5.356220	-3.295346	-2.412252
20	1	0	-6.316408	-3.434732	-1.923427
21	6	0	-5.009451	-4.023815	-3.549520
22	1	0	-5.712229	-4.746391	-3.954740
23	6	0	-3.763184	-3.836872	-4.181668
24	1	0	-3.521668	-4.422836	-5.064048
25	6	0	-2.833789	-2.927438	-3.684564
26	1	0	-1.869739	-2.805509	-4.170085
27	6	0	-3.048395	0.153341	0.394008
28	1	0	-1.968479	0.162604	0.562398
29	6	0	-3.658349	-0.370302	1.693304
30	6	0	-4.976196	-0.096088	2.057319
31	1	0	-5.569716	0.569713	1.437116

32	6	0	-2.902127	-1.210392	2.526892
33	1	0	-1.872898	-1.424875	2.252440
34	6	0	-5.546551	-0.637461	3.216916
35	1	0	-6.572247	-0.396397	3.469921
36	6	0	-3.449648	-1.752539	3.682264
37	1	0	-2.863905	-2.396462	4.331617
38	6	0	-4.778845	-1.471765	4.034063
39	6	0	-6.568686	-1.795514	5.581597
40	1	0	-6.742668	-0.726799	5.758569
41	1	0	-6.722508	-2.341644	6.514366
42	1	0	-7.286081	-2.155505	4.833316
43	6	0	-3.462814	1.578356	0.057576
44	6	0	-4.268711	1.891570	-1.045933
45	1	0	-4.655135	1.108916	-1.691829
46	6	0	-4.545048	3.224862	-1.304926
47	6	0	-4.045860	4.228861	-0.485619
48	6	0	-4.985081	5.164943	-2.272671
49	1	0	-5.850208	5.795754	-2.489493
50	1	0	-4.173497	5.343301	-2.998824
51	6	0	-3.253756	3.976381	0.613377
52	1	0	-2.847990	4.775249	1.225493
53	6	0	-2.918514	2.604235	0.937371
54	16	0	-0.997406	-3.696797	0.281348
55	6	0	-0.801790	-4.876096	-1.033787
56	6	0	-1.938222	-5.552972	-1.509415
57	6	0	0.448349	-5.165214	-1.610050
58	6	0	-1.827512	-6.498898	-2.527686
59	6	0	0.546952	-6.096129	-2.644409
60	6	0	-0.585582	-6.772831	-3.105823
61	1	0	1.321130	-4.634347	-1.245093
62	1	0	-2.912346	-5.316200	-1.093781

63	1	0	-2.720450	-7.003576	-2.886323
64	1	0	-0.502564	-7.499357	-3.909040
65	1	0	1.518445	-6.299738	-3.087758
66	7	0	4.660318	1.517858	1.052162
67	1	0	5.519474	1.035972	0.832579
68	6	0	5.126843	5.022121	2.212156
69	1	0	5.869915	5.768542	2.478160
70	6	0	3.757262	5.352542	2.276181
71	1	0	3.464727	6.349805	2.592707
72	6	0	2.776393	4.422778	1.942660
73	1	0	1.725129	4.688341	1.998886
74	8	0	2.825231	-4.277503	4.392445
75	6	0	3.164736	3.135497	1.530275
76	6	0	4.557111	2.823302	1.478048
77	8	0	4.093064	-2.394960	4.838453
78	8	0	7.166586	-1.534862	-3.670083
79	6	0	5.544152	3.753602	1.814690
80	1	0	6.598127	3.495140	1.766037
81	6	0	2.445504	1.959239	1.104702
82	8	0	1.723106	-2.760072	-0.094903
83	6	0	3.393481	1.001637	0.805815
84	6	0	3.204637	-0.400636	0.290395
85	1	0	2.260199	-0.390055	-0.252359
86	8	0	1.404717	1.507282	-1.913728
87	6	0	5.305337	-1.672461	-0.473533
88	1	0	5.328571	-2.188753	0.480264
89	6	0	3.378394	-3.476147	5.446427
90	1	0	4.065739	-4.081207	6.041549
91	1	0	2.561233	-3.075781	6.065469
92	6	0	6.291096	-1.964630	-1.424894
93	1	0	7.058005	-2.692834	-1.189506

94	6	0	5.253129	-0.387459	-2.936748
95	1	0	5.240440	0.101038	-3.906284
96	6	0	6.264530	-1.322221	-2.665272
97	6	0	4.289967	-0.752244	-0.731285
98	6	0	4.284561	-0.110361	-1.982401
99	1	0	3.500622	0.607309	-2.204268
100	6	0	3.055579	-1.442496	1.389588
101	6	0	3.537182	-2.291651	3.570969
102	6	0	3.693489	-1.288423	2.635575
103	1	0	4.281485	-0.404667	2.857384
104	6	0	2.782411	-3.427660	3.301156
105	6	0	2.151467	-3.616030	2.089581
106	1	0	1.551433	-4.490987	1.873772
107	6	0	2.299320	-2.608281	1.101208
108	6	0	1.005885	2.564523	-1.472412
109	6	0	0.382726	2.764054	-0.119855
110	1	0	0.477380	3.804972	0.185641
111	1	0	-0.691656	2.579054	-0.234778
112	6	0	0.960726	1.819642	0.947887
113	1	0	0.429868	2.059504	1.874833
114	1	0	0.700955	0.786816	0.712092
115	6	0	8.166180	-2.525341	-3.460292
116	1	0	8.753966	-2.562202	-4.379234
117	1	0	7.723517	-3.511970	-3.276861
118	1	0	8.825737	-2.266184	-2.622935
119	16	0	1.166616	3.999378	-2.595314
120	6	0	0.514497	5.387300	-1.668848
121	6	0	-0.862959	5.635703	-1.651866
122	6	0	1.389205	6.217056	-0.955437
123	6	0	-1.365057	6.707812	-0.913917
124	6	0	0.880863	7.289747	-0.223175

125	6	0	-0.494279	7.534786	-0.200974
126	1	0	2.453427	6.008547	-0.957769
127	1	0	-1.536219	4.977848	-2.190444
128	1	0	-2.436668	6.874962	-0.885767
129	1	0	-0.887592	8.365329	0.377596
130	1	0	1.559452	7.925527	0.337539

TS3-RS

Zero-point correction = 0.9304 a.u.

Thermal correction to Gibbs Free Energy = 0.83188 a.u.

Sum of electronic and zero-point Energies = -3498.00639 a.u.

Sum of electronic and thermal Free Energies = -3498.10494 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	5.357567	1.587691	-5.146510
2	7	0	-4.466846	0.992081	-0.093147
3	1	0	-5.036538	0.603520	0.643979
4	6	0	-5.503929	4.395262	-1.187087
5	1	0	-6.264353	5.162143	-1.070983
6	8	0	5.070906	1.077140	4.165133
7	7	0	4.597681	-2.192966	-0.502553
8	1	0	5.202543	-1.716248	-1.155152
9	6	0	-4.414489	4.624621	-2.052950
10	1	0	-4.349186	5.568512	-2.586137
11	8	0	3.883863	3.060502	4.269049
12	6	0	-3.417041	3.669614	-2.219625
13	1	0	-2.571545	3.863199	-2.873142
14	8	0	-4.195136	-5.111643	-3.592470
15	6	0	-3.504614	2.459020	-1.512405
16	6	0	-4.622146	2.242461	-0.651045

17	8	0	-5.295347	-3.087379	-3.857275
18	8	0	-4.130906	-1.706746	5.418714
19	6	0	-5.623511	3.202509	-0.476942
20	1	0	-6.462049	3.024021	0.190023
21	6	0	-2.665759	1.291794	-1.421081
22	8	0	-1.638431	-3.475557	0.204482
23	8	0	0.124133	-2.667308	-0.977056
24	6	0	-3.276045	0.431351	-0.536762
25	6	0	-2.787827	-0.910422	-0.062273
26	1	0	-1.698274	-0.819600	-0.071031
27	8	0	0.097304	0.410448	0.391609
28	6	0	-4.387484	-1.790060	1.730298
29	1	0	-5.055310	-2.140144	0.948217
30	6	0	-5.021371	-4.347436	-4.489344
31	1	0	-5.958718	-4.880735	-4.662283
32	1	0	-4.477746	-4.177842	-5.428459
33	8	0	1.747991	2.286686	-0.022456
34	6	0	-4.748212	-1.987649	3.068048
35	1	0	-5.687487	-2.474606	3.300501
36	6	0	-2.671181	-0.942990	3.747753
37	1	0	-2.010321	-0.621577	4.546772
38	6	0	-3.885328	-1.562223	4.083552
39	6	0	-3.185103	-1.172785	1.385686
40	6	0	-2.330274	-0.749796	2.415594
41	1	0	-1.393028	-0.267795	2.151928
42	6	0	-3.161362	-2.053598	-1.000668
43	6	0	-4.383015	-2.988187	-2.832097
44	6	0	-4.124657	-1.903501	-2.018747
45	1	0	-4.638282	-0.960422	-2.160033
46	6	0	-3.725468	-4.205015	-2.674909
47	6	0	-2.779066	-4.392278	-1.687762

48	1	0	-2.259163	-5.331492	-1.542795
49	6	0	-2.519540	-3.289001	-0.862728
50	6	0	-0.324873	-3.096088	0.058829
51	6	0	0.402520	-3.335689	1.357143
52	1	0	0.753428	-4.374785	1.332892
53	1	0	-0.331671	-3.273037	2.164267
54	6	0	1.568079	-2.366716	1.625446
55	1	0	1.815474	-2.466606	2.690817
56	1	0	1.213460	-1.343345	1.482279
57	6	0	3.426455	-1.654388	0.006897
58	6	0	2.807839	-2.590855	0.811197
59	6	0	3.640699	-3.768034	0.796037
60	6	0	4.753574	-3.484660	-0.053767
61	6	0	5.764221	-4.417831	-0.299448
62	1	0	6.599003	-4.179911	-0.952426
63	6	0	5.667099	-5.656546	0.330188
64	1	0	6.438327	-6.402526	0.162056
65	6	0	4.587314	-5.954916	1.186504
66	1	0	4.545643	-6.926942	1.669811
67	6	0	3.579167	-5.025436	1.424433
68	1	0	2.759076	-5.267177	2.094324
69	6	0	3.022867	-0.227907	-0.266359
70	1	0	1.945404	-0.244173	-0.442264
71	6	0	3.674705	0.303475	-1.536636
72	6	0	4.874915	1.014756	-1.523069
73	1	0	5.349383	1.239724	-0.572885
74	6	0	3.080944	0.039137	-2.781151
75	1	0	2.148336	-0.517591	-2.814833
76	6	0	5.474629	1.464958	-2.704680
77	1	0	6.402248	2.021908	-2.651775
78	6	0	3.658647	0.479676	-3.964866

79	1	0	3.191408	0.283073	-4.924818
80	6	0	4.864212	1.197105	-3.933990
81	6	0	6.545658	2.371655	-5.156744
82	1	0	6.411702	3.313402	-4.611071
83	1	0	6.754007	2.590991	-6.205341
84	1	0	7.395308	1.825430	-4.729054
85	6	0	3.233095	0.678432	0.945834
86	6	0	4.113574	0.320916	1.985174
87	1	0	4.661824	-0.613612	1.954244
88	6	0	4.245219	1.184946	3.054134
89	6	0	3.540831	2.381319	3.113947
90	6	0	4.593356	2.091473	5.054926
91	1	0	5.438806	2.573033	5.550777
92	1	0	3.904645	1.644210	5.788228
93	6	0	2.681588	2.773380	2.109207
94	1	0	2.133660	3.706725	2.145578
95	6	0	2.529408	1.912314	0.988973
96	6	0	0.094505	1.581783	-0.025262
97	6	0	-0.192143	1.914914	-1.491804
98	1	0	-0.386939	2.981958	-1.610498
99	1	0	0.726885	1.691260	-2.039768
100	6	0	-1.339212	1.078685	-2.083432
101	1	0	-1.412101	1.321917	-3.151554
102	1	0	-1.064521	0.021924	-2.024402
103	6	0	-5.353279	-2.324269	5.806716
104	1	0	-5.351377	-2.337195	6.898004
105	1	0	-5.421642	-3.353692	5.434274
106	1	0	-6.222717	-1.755558	5.454974
107	16	0	-0.827533	2.707428	1.257356
108	6	0	-0.916073	4.365809	0.617463
109	6	0	0.166280	4.989094	-0.027202

110	6	0	-2.110544	5.084680	0.791789
111	6	0	0.042109	6.298016	-0.494823
112	6	0	-2.217704	6.399679	0.341633
113	6	0	-1.143759	7.012900	-0.308184
114	1	0	-2.961536	4.601228	1.260889
115	1	0	1.082600	4.424907	-0.165072
116	1	0	0.883136	6.764703	-1.001052
117	1	0	-1.232197	8.033354	-0.669477
118	1	0	-3.151499	6.937383	0.480556

SPh

Zero-point correction = 0.09009 a.u.

Thermal correction to Gibbs Free Energy = 0.06029 a.u.

Sum of electronic and zero-point Energies = -629.90506 a.u.

Sum of electronic and thermal Free Energies = -629.93486 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	16	0	-3.173525	2.379050	-3.049742
2	6	0	-4.755950	1.786863	-2.545855
3	6	0	-5.210844	1.900822	-1.207830
4	6	0	-5.652304	1.168960	-3.454138
5	6	0	-6.461920	1.432837	-0.809967
6	6	0	-6.903289	0.701480	-3.055537
7	6	0	-7.326064	0.826499	-1.727901
8	1	0	-5.345291	1.060612	-4.491118
9	1	0	-4.556487	2.368485	-0.476806
10	1	0	-6.765414	1.543194	0.229202
11	1	0	-8.301122	0.462006	-1.417613
12	1	0	-7.555489	0.233890	-3.790495

d-IM1-SS

Zero-point correction = 1.02114 a.u.

Thermal correction to Gibbs Free Energy = 0.91559 a.u.

Sum of electronic and zero-point Energies = -4127.89964 a.u.

Sum of electronic and thermal Free Energies = -4128.00519 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.927570	4.970360	-0.254583
2	1	0	5.947987	5.097326	-0.605166
3	7	0	1.035935	4.318533	0.935735
4	1	0	0.460675	4.682405	1.680821
5	8	0	-1.163427	1.180051	5.782820
6	8	0	-3.208765	1.549884	-0.356557
7	8	0	-2.874918	6.931009	-1.405153
8	8	0	-4.862438	5.854380	-1.886743
9	8	0	1.939175	-1.006490	-2.611130
10	6	0	-3.074283	2.804511	-0.595275
11	6	0	3.136747	5.677283	1.245258
12	1	0	2.754557	6.322737	2.030874
13	6	0	4.438618	5.810223	0.766500
14	6	0	4.126642	3.979603	-0.815321
15	1	0	4.517962	3.339064	-1.598798
16	6	0	2.337436	4.679816	0.680273
17	6	0	-1.829195	3.496242	-0.324542
18	6	0	1.734192	2.910325	-0.681354
19	6	0	-2.749918	5.560972	-1.125412
20	6	0	2.811209	3.814756	-0.349592
21	6	0	-1.681217	4.868714	-0.584730
22	1	0	-0.748460	5.380347	-0.374221

23	6	0	2.910212	-0.452122	-2.140446
24	6	0	-0.710511	2.651480	0.271332
25	1	0	-0.707595	1.712675	-0.288193
26	6	0	1.827499	1.777249	-1.661674
27	1	0	2.126931	2.156472	-2.648372
28	1	0	0.851971	1.307149	-1.798730
29	6	0	-3.952340	4.923885	-1.398112
30	6	0	-0.920734	2.275142	1.747120
31	6	0	-4.151490	3.581793	-1.157874
32	1	0	-5.094393	3.094828	-1.382819
33	6	0	2.857166	0.717051	-1.201740
34	1	0	3.842479	1.161158	-1.072611
35	1	0	2.554194	0.317718	-0.217455
36	6	0	0.665077	3.248936	0.127287
37	6	0	-0.003186	1.396498	2.346657
38	1	0	0.787738	0.934991	1.764531
39	6	0	-4.050292	6.993703	-2.206251
40	1	0	-3.779609	6.952225	-3.274842
41	1	0	-4.603209	7.908347	-1.979110
42	6	0	-0.098841	1.062030	3.688348
43	1	0	0.607049	0.369535	4.133022
44	6	0	-1.140715	1.578557	4.470554
45	6	0	-1.950432	2.783756	2.534083
46	1	0	-2.679177	3.454319	2.090032
47	6	0	-2.076251	2.436978	3.887122
48	1	0	-2.900772	2.839622	4.463793
49	6	0	-2.307345	1.523519	6.551532
50	1	0	-2.410199	2.610115	6.665965
51	1	0	-2.156751	1.080023	7.537263
52	1	0	-3.223865	1.117355	6.108478
53	1	0	5.086253	6.573801	1.187934

54	16	0	4.514816	-1.163136	-2.674023
55	6	0	5.798917	-0.111020	-2.006705
56	6	0	6.073583	1.128988	-2.599554
57	6	0	6.563065	-0.553373	-0.919744
58	6	0	7.088443	1.935621	-2.086044
59	6	0	7.583298	0.256523	-0.417951
60	6	0	7.842346	1.502122	-0.992847
61	1	0	6.360527	-1.520766	-0.473479
62	1	0	5.487202	1.459696	-3.450531
63	1	0	7.291382	2.899654	-2.542627
64	1	0	8.631524	2.132105	-0.593876
65	1	0	8.171178	-0.085713	0.428411
66	16	0	-3.752467	0.385465	-3.508170
67	6	0	-4.800756	-0.811904	-2.683769
68	6	0	-5.223742	-0.595755	-1.363710
69	6	0	-5.215181	-1.953044	-3.379741
70	6	0	-6.043881	-1.540064	-0.746685
71	6	0	-6.050203	-2.882597	-2.756673
72	6	0	-6.461685	-2.680574	-1.438821
73	1	0	-4.878215	-2.117114	-4.398326
74	1	0	-4.849998	0.279649	-0.833251
75	1	0	-6.355998	-1.385208	0.282391
76	1	0	-7.098662	-3.412020	-0.950281
77	1	0	-6.361334	-3.771920	-3.296551
78	8	0	-2.581013	-1.741975	5.582204
79	8	0	4.302888	-5.323463	-0.159030
80	8	0	2.150040	-0.579927	1.554342
81	8	0	5.744295	-3.689387	0.608619
82	8	0	-1.384103	1.270269	-2.903177
83	7	0	-0.938567	-4.574717	0.260285
84	1	0	-0.668495	-4.922020	1.168617

85	6	0	-2.185224	0.432126	-2.547072
86	6	0	-1.230965	-3.113227	-1.432219
87	6	0	-1.981496	-4.312869	-1.715025
88	6	0	-1.775678	-5.210753	-0.625408
89	6	0	2.589368	-1.727886	1.186247
90	6	0	2.200176	-3.984599	0.211111
91	1	0	1.534789	-4.746935	-0.179213
92	6	0	-1.839401	-1.933725	4.448000
93	6	0	-0.613363	-3.307656	-0.211851
94	6	0	-1.226236	-1.876645	-2.285948
95	1	0	-1.764793	-2.096289	-3.213898
96	1	0	-0.212129	-1.585493	-2.566609
97	6	0	-1.905060	-0.680860	-1.576240
98	1	0	-2.820115	-1.011220	-1.094705
99	1	0	-1.255574	-0.269845	-0.805164
100	6	0	-3.411814	-5.970934	-2.726318
101	1	0	-4.059052	-6.287810	-3.539392
102	6	0	-2.372468	-6.473945	-0.575331
103	1	0	-2.202875	-7.140496	0.265252
104	6	0	1.702835	-2.763449	0.696061
105	6	0	-0.465077	-2.228229	1.999043
106	6	0	-2.813242	-4.715415	-2.773405
107	1	0	-2.992646	-4.051116	-3.613062
108	6	0	4.437308	-3.222043	0.706556
109	6	0	3.568084	-4.189624	0.220975
110	6	0	4.002437	-2.011568	1.195839
111	1	0	4.687004	-1.244580	1.541045
112	6	0	-3.193912	-6.841737	-1.638508
113	6	0	-0.545099	-2.459916	4.425366
114	1	0	-0.044170	-2.748181	5.341684
115	6	0	0.124653	-2.602769	3.202932

116	1	0	1.134242	-2.999984	3.195874
117	6	0	-2.452684	-1.563729	3.242720
118	1	0	-3.450209	-1.137043	3.269344
119	6	0	0.227826	-2.390123	0.634516
120	1	0	0.197093	-1.399770	0.169929
121	6	0	5.633471	-4.830150	-0.261370
122	1	0	5.839185	-4.509098	-1.295498
123	1	0	6.338734	-5.599720	0.060024
124	6	0	-1.769699	-1.706928	2.043820
125	1	0	-2.252691	-1.391355	1.125621
126	6	0	-1.932546	-1.953591	6.829653
127	1	0	-1.047405	-1.315922	6.929024
128	1	0	-1.642041	-3.003433	6.963337
129	1	0	-2.660248	-1.689106	7.598958
130	1	0	-3.675104	-7.815570	-1.628428

d-IM1-RS

Zero-point correction = 1.02105 a.u.

Thermal correction to Gibbs Free Energy = 0.90889 a.u.

Sum of electronic and zero-point Energies = -4127.90028 a.u.

Sum of electronic and thermal Free Energies = -4128.01244 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	-6.178648	0.042832	5.106865
2	8	0	-3.982481	4.263044	-3.240498
3	7	0	-4.991098	-0.755614	-0.706901
4	1	0	-5.691686	-0.422448	-0.060942
5	8	0	-2.826944	5.854289	-2.029484
6	8	0	-0.886088	-1.849114	0.864154
7	8	0	-1.895590	2.794956	1.629567

8	6	0	-0.916715	-2.635271	-0.060219
9	6	0	-0.688672	-2.255395	-1.503374
10	1	0	-0.958757	-3.076046	-2.164499
11	1	0	0.391055	-2.096313	-1.599162
12	6	0	-1.480082	-0.986244	-1.868929
13	1	0	-1.292200	-0.776541	-2.928854
14	1	0	-1.076719	-0.143557	-1.314954
15	6	0	-3.660697	-0.361248	-0.670334
16	6	0	-2.949607	-1.097977	-1.597437
17	6	0	-3.878032	-2.017504	-2.207010
18	6	0	-5.154503	-1.778128	-1.613687
19	6	0	-6.288533	-2.518392	-1.958795
20	1	0	-7.249040	-2.322207	-1.491057
21	6	0	-6.139375	-3.519063	-2.916846
22	1	0	-7.000855	-4.115634	-3.202941
23	6	0	-4.889562	-3.771533	-3.518821
24	1	0	-4.805409	-4.561349	-4.259949
25	6	0	-3.762308	-3.030669	-3.175001
26	1	0	-2.805443	-3.239115	-3.643730
27	6	0	-3.184517	0.699912	0.291618
28	1	0	-2.159215	0.425962	0.555467
29	6	0	-3.981945	0.603729	1.590421
30	6	0	-5.096529	1.402777	1.837775
31	1	0	-5.363672	2.172306	1.119661
32	6	0	-3.643208	-0.373624	2.539492
33	1	0	-2.781619	-1.010236	2.357365
34	6	0	-5.862945	1.252459	3.000327
35	1	0	-6.718053	1.897654	3.162817
36	6	0	-4.389254	-0.535736	3.699193
37	1	0	-4.122447	-1.285398	4.437872
38	6	0	-5.507676	0.277924	3.937273

39	6	0	-7.325202	0.837367	5.381345
40	1	0	-7.075354	1.903488	5.445976
41	1	0	-7.703524	0.500819	6.348470
42	1	0	-8.105882	0.697666	4.622878
43	6	0	-3.129598	2.103365	-0.295325
44	6	0	-3.665785	2.408865	-1.556010
45	1	0	-4.182014	1.651969	-2.138555
46	6	0	-3.498228	3.690775	-2.051552
47	6	0	-2.825417	4.658384	-1.315755
48	6	0	-3.228310	5.463098	-3.352549
49	1	0	-3.847134	6.249537	-3.790741
50	1	0	-2.325649	5.286185	-3.961590
51	6	0	-2.290473	4.414300	-0.070340
52	1	0	-1.739641	5.173248	0.474568
53	6	0	-2.415532	3.091003	0.499063
54	16	0	-1.349067	-4.347949	0.368500
55	6	0	-1.073289	-5.298485	-1.123956
56	6	0	-2.152352	-5.961549	-1.719750
57	6	0	0.214347	-5.394847	-1.671829
58	6	0	-1.943517	-6.732835	-2.864439
59	6	0	0.404617	-6.156086	-2.825514
60	6	0	-0.666373	-6.829528	-3.419939
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62	1	0	-3.147830	-5.862745	-1.300101
63	1	0	-2.782568	-7.243734	-3.327555
64	1	0	-0.507088	-7.422118	-4.316181
65	1	0	1.396620	-6.220239	-3.263802
66	7	0	4.098193	1.300678	1.605994
67	1	0	5.055655	0.982258	1.621482
68	6	0	3.513468	4.572752	3.289198
69	1	0	3.987271	5.366235	3.860642

70	6	0	2.133091	4.651446	3.006546
71	1	0	1.566775	5.505277	3.368249
72	6	0	1.488618	3.660046	2.271803
73	1	0	0.419841	3.704369	2.069633
74	8	0	2.366129	-4.955685	3.960917
75	6	0	2.244234	2.565181	1.818327
76	6	0	3.632324	2.485013	2.138181
77	8	0	3.194642	-2.992720	4.851281
78	8	0	8.267678	-0.847193	-2.429766
79	6	0	4.280959	3.488553	2.863746
80	1	0	5.340266	3.421813	3.095467
81	6	0	1.916030	1.391739	1.052745
82	8	0	2.223098	-3.175543	-0.560243
83	6	0	3.066656	0.640130	0.944517
84	6	0	3.257101	-0.716009	0.317638
85	1	0	2.501416	-0.812633	-0.465100
86	8	0	1.491431	0.541009	-2.361023
87	6	0	5.746173	-1.317329	0.238437
88	1	0	5.657966	-1.722387	1.241655
89	6	0	2.450718	-4.167454	5.157006
90	1	0	2.965693	-4.739034	5.932827
91	1	0	1.431422	-3.893980	5.477589
92	6	0	6.990930	-1.348923	-0.401358
93	1	0	7.846726	-1.762080	0.118841
94	6	0	5.973878	-0.344976	-2.353321
95	1	0	6.075683	0.019511	-3.371081
96	6	0	7.106990	-0.860450	-1.705903
97	6	0	4.611026	-0.803514	-0.389414
98	6	0	4.748219	-0.318725	-1.700195
99	1	0	3.873359	0.070521	-2.213014
100	6	0	2.993632	-1.861917	1.282548

101	6	0	2.978734	-2.830835	3.473322
102	6	0	3.235857	-1.741971	2.661071
103	1	0	3.609404	-0.813210	3.081017
104	6	0	2.494698	-4.019224	2.940525
105	6	0	2.237589	-4.185025	1.597492
106	1	0	1.836468	-5.112704	1.204639
107	6	0	2.472528	-3.081222	0.697175
108	6	0	1.338276	1.662154	-1.917104
109	6	0	0.374854	2.013680	-0.817074
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111	1	0	-0.632108	1.875306	-1.225913
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121	6	0	0.780718	5.175933	-2.129013
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123	6	0	0.483450	6.357023	-1.450274
124	6	0	2.547975	6.165535	-0.202134
125	6	0	1.368142	6.854185	-0.490240
126	1	0	3.744389	4.421287	-0.623863
127	1	0	0.090080	4.779785	-2.865717
128	1	0	-0.449777	6.868254	-1.661665
129	1	0	1.133178	7.772086	0.040196
130	1	0	3.228068	6.537766	0.556925

IM3-RS

Zero-point correction = 0.93072 a.u.

Thermal correction to Gibbs Free Energy = 0.82890 a.u.

Sum of electronic and zero-point Energies = -3498.01403 a.u.

Sum of electronic and thermal Free Energies = -3498.11585 a.u.

Standard orientation

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	8	0	2.850138	0.684044	-5.655850
2	7	0	-4.439984	1.402844	-0.252820
3	1	0	-5.189006	1.138585	0.370459
4	6	0	-4.882145	4.745839	-1.823962
5	1	0	-5.568315	5.579990	-1.936957
6	8	0	7.467954	0.404191	2.463657
7	7	0	4.208264	-2.600185	-0.541821
8	1	0	4.776950	-2.217838	-1.282764
9	6	0	-3.618561	4.798113	-2.448722
10	1	0	-3.350112	5.674655	-3.030922
11	8	0	6.925199	2.606896	2.908465
12	6	0	-2.710944	3.751731	-2.323228
13	1	0	-1.736063	3.806720	-2.798608
14	8	0	-4.290625	-4.993734	-3.073528
15	6	0	-3.067277	2.627807	-1.558494
16	6	0	-4.352218	2.594214	-0.939511
17	8	0	-5.374202	-2.985914	-3.484611
18	8	0	-5.491558	-0.721872	5.429543
19	6	0	-5.266675	3.644263	-1.063480
20	1	0	-6.237839	3.602704	-0.579200
21	6	0	-2.387783	1.408720	-1.194972
22	8	0	-1.862945	-3.166052	0.722338

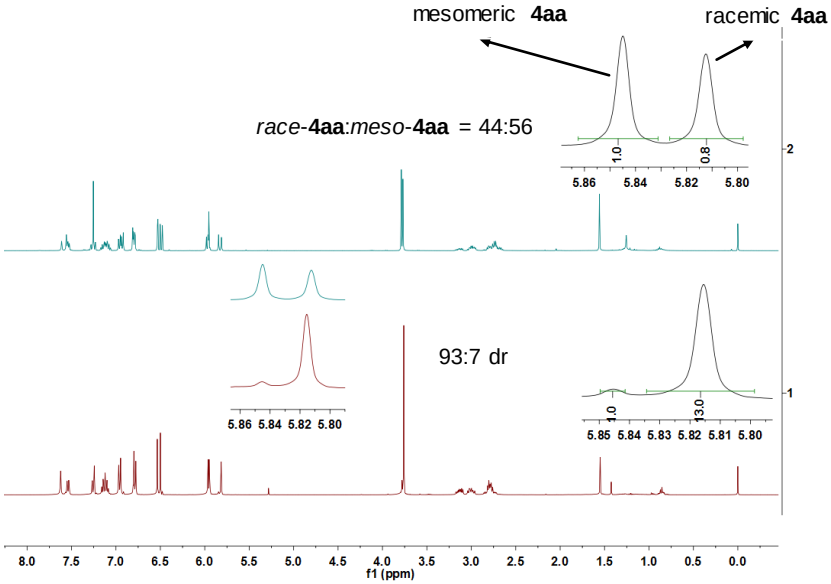
23	8	0	-0.104594	-2.402206	-0.486072
24	6	0	-3.249018	0.702459	-0.382204
25	6	0	-3.022230	-0.624168	0.292530
26	1	0	-1.951340	-0.655886	0.492023
27	8	0	-0.126010	0.498192	1.244073
28	6	0	-5.047367	-1.102212	1.779417
29	1	0	-5.602954	-1.419891	0.901806
30	6	0	-5.071491	-4.273531	-4.044426
31	1	0	-5.999831	-4.815086	-4.237651
32	1	0	-4.482605	-4.145589	-4.962339
33	8	0	2.689490	2.322060	0.546031
34	6	0	-5.684579	-1.120143	3.024408
35	1	0	-6.717755	-1.438626	3.089776
36	6	0	-3.633708	-0.340285	4.049323
37	1	0	-3.092906	-0.052665	4.945379
38	6	0	-4.974440	-0.737516	4.167581
39	6	0	-3.716833	-0.701071	1.648220
40	6	0	-3.018294	-0.321384	2.804803
41	1	0	-1.981070	-0.010296	2.719169
42	6	0	-3.347920	-1.809975	-0.607253
43	6	0	-4.503352	-2.834346	-2.431483
44	6	0	-4.270158	-1.708765	-1.669008
45	1	0	-4.773420	-0.772973	-1.879840
46	6	0	-3.855528	-4.042813	-2.185151
47	6	0	-2.948469	-4.180094	-1.154458
48	1	0	-2.434865	-5.110341	-0.944126
49	6	0	-2.718521	-3.035866	-0.376674
50	6	0	-0.541921	-2.818783	0.560129
51	6	0	0.199061	-3.078149	1.845854
52	1	0	0.352571	-4.163315	1.892818
53	1	0	-0.477450	-2.833817	2.670064

54	6	0	1.530486	-2.326258	2.010778
55	1	0	1.864803	-2.515767	3.039290
56	1	0	1.335113	-1.254447	1.942518
57	6	0	3.267006	-1.869455	0.170319
58	6	0	2.614504	-2.711022	1.048469
59	6	0	3.188617	-4.024114	0.875153
60	6	0	4.183576	-3.916630	-0.143877
61	6	0	4.942353	-5.010606	-0.567554
62	1	0	5.692630	-4.903749	-1.345612
63	6	0	4.706330	-6.237925	0.047791
64	1	0	5.281509	-7.107041	-0.257987
65	6	0	3.739142	-6.367941	1.065005
66	1	0	3.585642	-7.336633	1.532194
67	6	0	2.982786	-5.276171	1.482151
68	1	0	2.250810	-5.390424	2.276346
69	6	0	3.129987	-0.387048	-0.045903
70	1	0	2.140013	-0.103008	0.322555
71	6	0	3.116551	-0.072337	-1.547180
72	6	0	4.060950	0.748989	-2.157820
73	1	0	4.844750	1.192800	-1.553211
74	6	0	2.106097	-0.627087	-2.351797
75	1	0	1.364872	-1.274372	-1.893343
76	6	0	4.013383	1.029129	-3.529059
77	1	0	4.762740	1.678620	-3.965327
78	6	0	2.040587	-0.358858	-3.712561
79	1	0	1.255770	-0.784330	-4.330725
80	6	0	2.996790	0.476047	-4.312192
81	6	0	3.787672	1.539731	-6.298473
82	1	0	3.760892	2.554572	-5.883115
83	1	0	3.493959	1.574803	-7.349120
84	1	0	4.809905	1.148396	-6.224958

85	6	0	4.133315	0.432730	0.754500
86	6	0	5.336448	-0.117512	1.226766
87	1	0	5.590659	-1.153981	1.030574
88	6	0	6.193663	0.689768	1.951453
89	6	0	5.882334	2.019630	2.203806
90	6	0	7.719508	1.493121	3.345972
91	1	0	8.777440	1.763247	3.306382
92	1	0	7.420030	1.222898	4.372551
93	6	0	4.718768	2.608401	1.757822
94	1	0	4.486037	3.647429	1.968441
95	6	0	3.781816	1.818590	0.994186
96	6	0	-0.143295	1.617928	0.760898
97	6	0	0.032230	1.885879	-0.713451
98	1	0	-0.099941	2.942452	-0.937114
99	1	0	1.069751	1.629378	-0.938882
100	6	0	-0.970288	1.043235	-1.526330
101	1	0	-0.766080	1.212184	-2.589502
102	1	0	-0.792914	-0.017726	-1.336844
103	6	0	-6.853717	-1.103418	5.594306
104	1	0	-7.064779	-1.013528	6.661117
105	1	0	-7.023398	-2.140249	5.280004
106	1	0	-7.527298	-0.442108	5.036030
107	16	0	-0.537593	2.953321	1.912779
108	6	0	-0.376019	4.474260	0.981991
109	6	0	0.881738	4.888287	0.521226
110	6	0	-1.514606	5.252908	0.749078
111	6	0	0.982752	6.087694	-0.183711
112	6	0	-1.396781	6.456445	0.051968
113	6	0	-0.149668	6.874308	-0.415328
114	1	0	-2.485182	4.911987	1.093098
115	1	0	1.742612	4.237139	0.673572

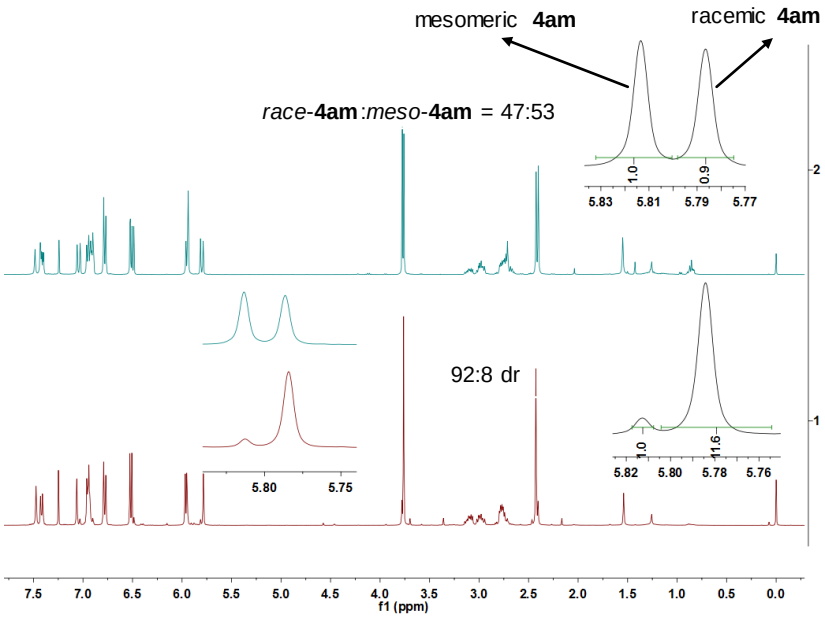
116	1	0	1.951597	6.408819	-0.555605
117	1	0	-0.060152	7.807293	-0.964078
118	1	0	-2.282878	7.053953	-0.138563

The ratio of mesomeric 4aa and racemic 4aa determined by ^{1}H NMR analysis



Determined by ^{1}H NMR analysis , the ratio of racemic **4aa** [(*R*,*R*)-**4aa** and (*S*,*S*)-**4aa**] and mesomeric **4aa** [(*R*,*S*)-**4aa**] was 44:56 (blue, up) under the racemic conditions: **1a** (0.1 mmol), **2a** (0.1 mmol), Sc(OTf)$_3$/ *rac*-**L$_3$-PiPr$_2$** (1:1, 5 mol%) in DCM (1.0 mL) at 35 °C, then Cs_2CO_3 (1.5 equiv) and ^{i}Pr$_2$NEt (0.5 equiv) were added, the resulting reaction mixture was stirred at 35 °C. And the ratio of (*S*,*S*)-**4aa** and (*R*,*S*)-**4aa** was 93:7 (red, down) under the optimized asymmetric catalytic condition as a control.

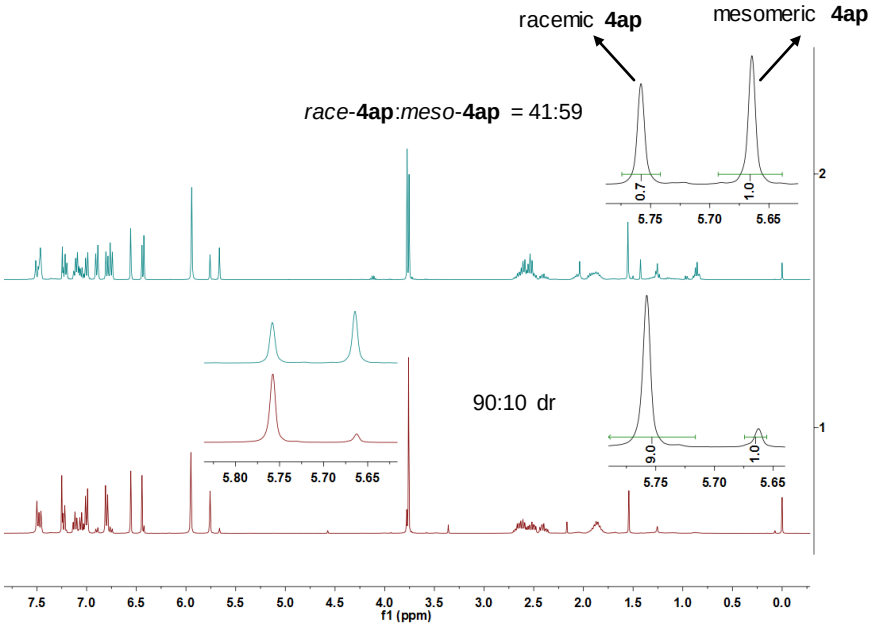
The ratio of mesomeric 4am and racemic 4am determined by ^{1}H NMR analysis



Determined by ^{1}H NMR analysis , the ratio of racemic **4am** [(*R*,*R*)-**4am** and (*S*,*S*)-**4am**] and mesomeric **4am** [(*R*,*S*)-**4am**] was 41:59 (blue, up) under the racemic conditions: **1a** (0.1 mmol), **2m** (0.1 mmol), Sc(OTf)$_3$/ *rac*-**L$_3$-PiPr$_2$** (1:1, 5 mol%) in DCM (1.0 mL) at 35

°C, then Cs_2CO_3 (1.5 equiv) and $^iPr_2NEt$ (0.5 equiv) were added, the resulting reaction mixture was stirred at 35 °C. And the ratio of (*S*,*S*)-**4am** and (*R*,*S*)-**4am** was 92:8 (red, down) under the optimized asymmetric catalytic condition as a control.

The ratio of mesomeric 4ap and racemic 4ap determined by ^{1}H NMR analysis



Determined by ^{1}H NMR analysis , the ratio of racemic **4ap** [(*R*,*R*)-**4ap** and (*S*,*S*)-**4ap**] and mesomeric **4ap** [(*R*,*S*)-**4ap**] was 41:59 (blue, up) under the racemic conditions: **1a** (0.1 mmol), **2p** (0.1 mmol), $Sc(OTf)_3$/ *rac*-**L_3-$PiPr_2$** (1:1, 5 mol%) in DCM (1.0 mL) at 35 °C, then Cs_2CO_3 (1.5 equiv) and $^iPr_2NEt$ (0.5 equiv) were added, the resulting reaction mixture was stirred at 35 °C. And the ratio of (*S*,*S*)-**4ap** and (*R*,*S*)-**4ap** was 90:10 (red, down) under the optimized asymmetric catalytic condition as a control.

The experimental results showed that the formation of mesomeric products (*R*,*S*)-**4** were easier than their enantiomers.

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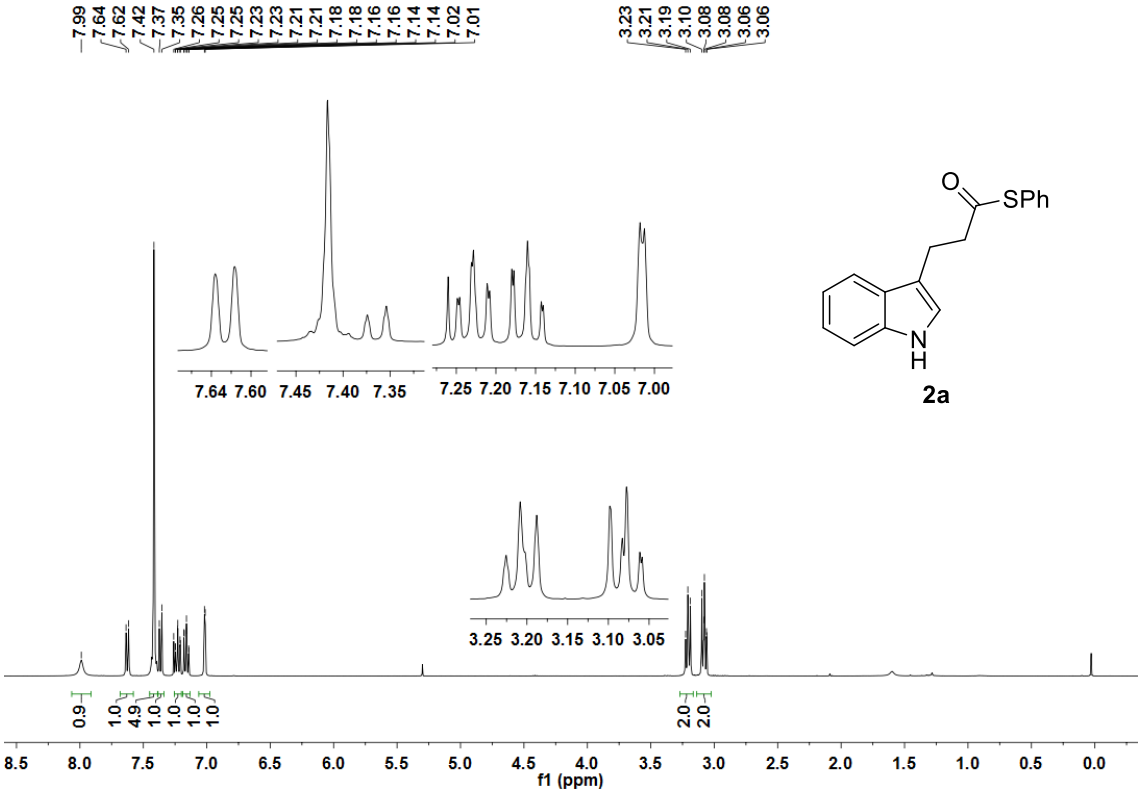
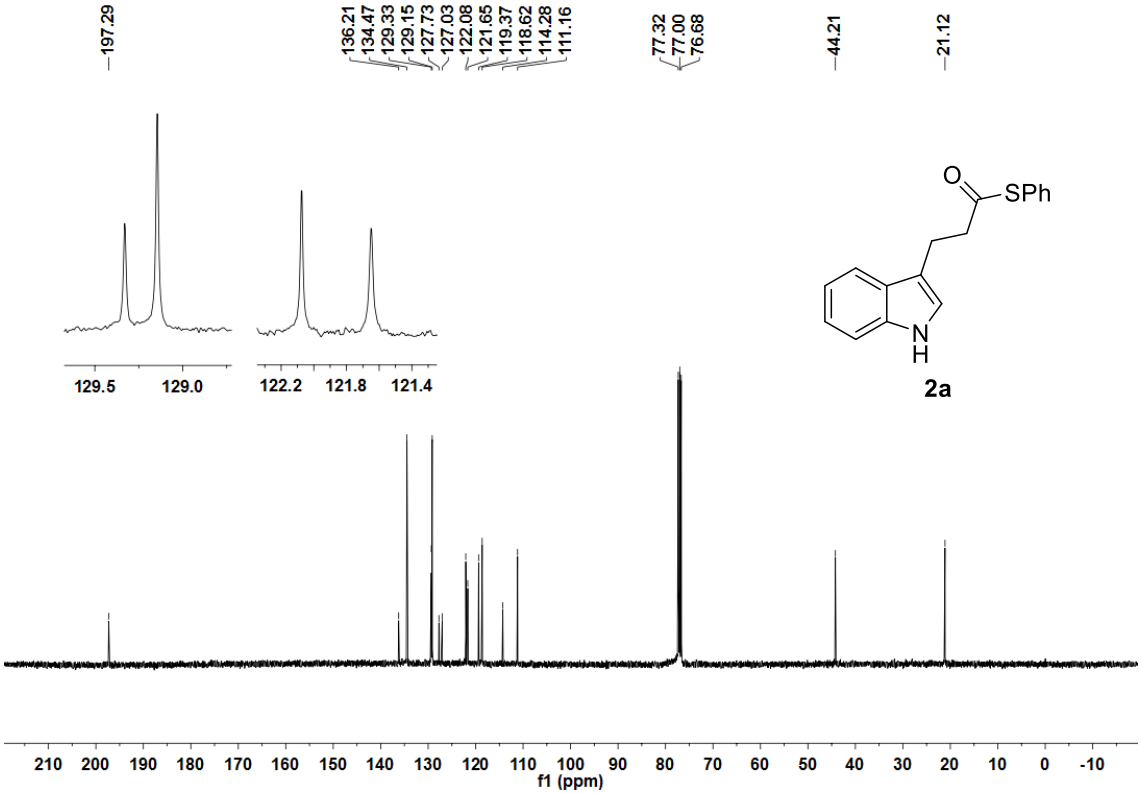
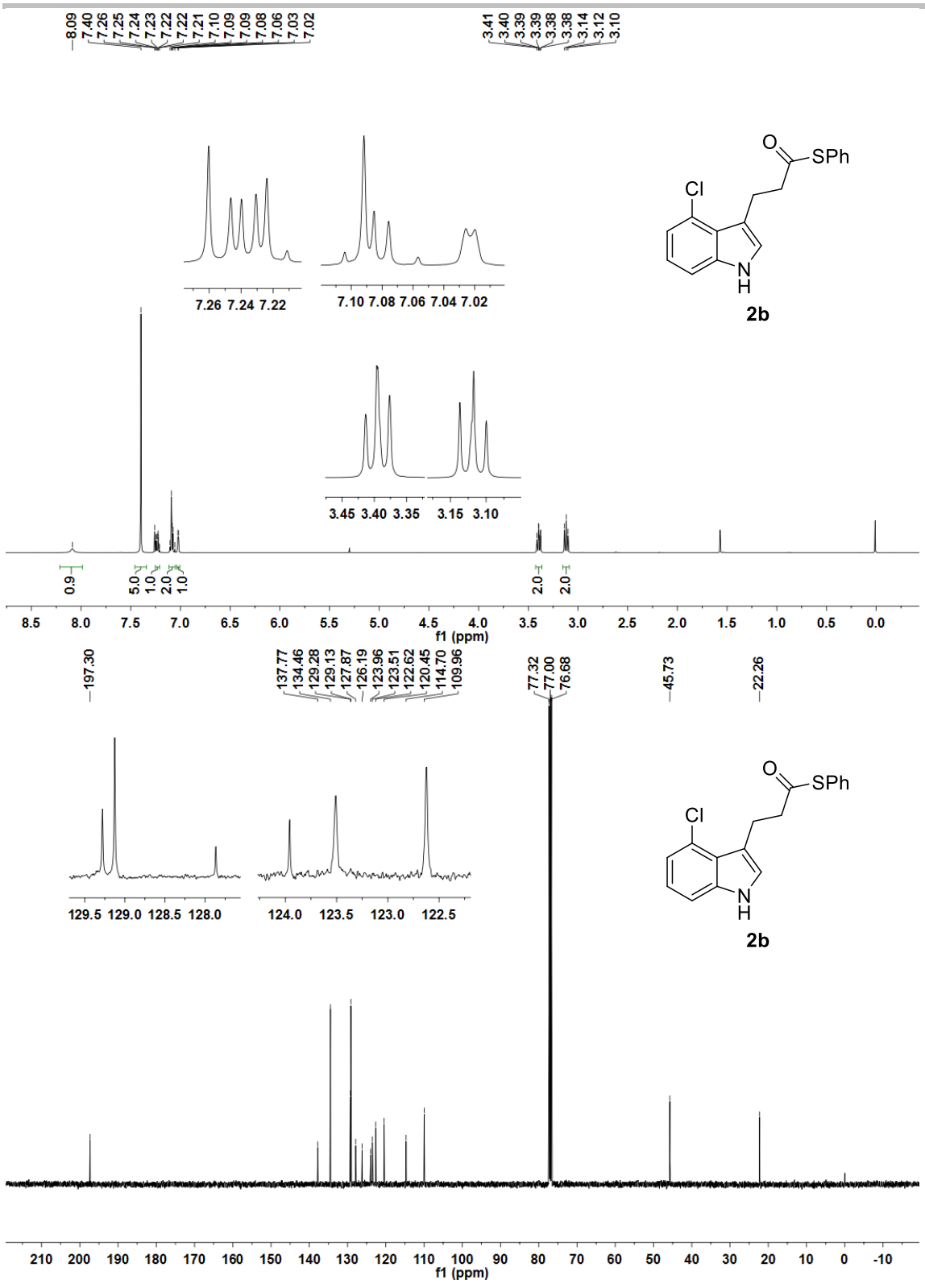
18. Copies of NMR Spectra for the Reaction Substrates and Products



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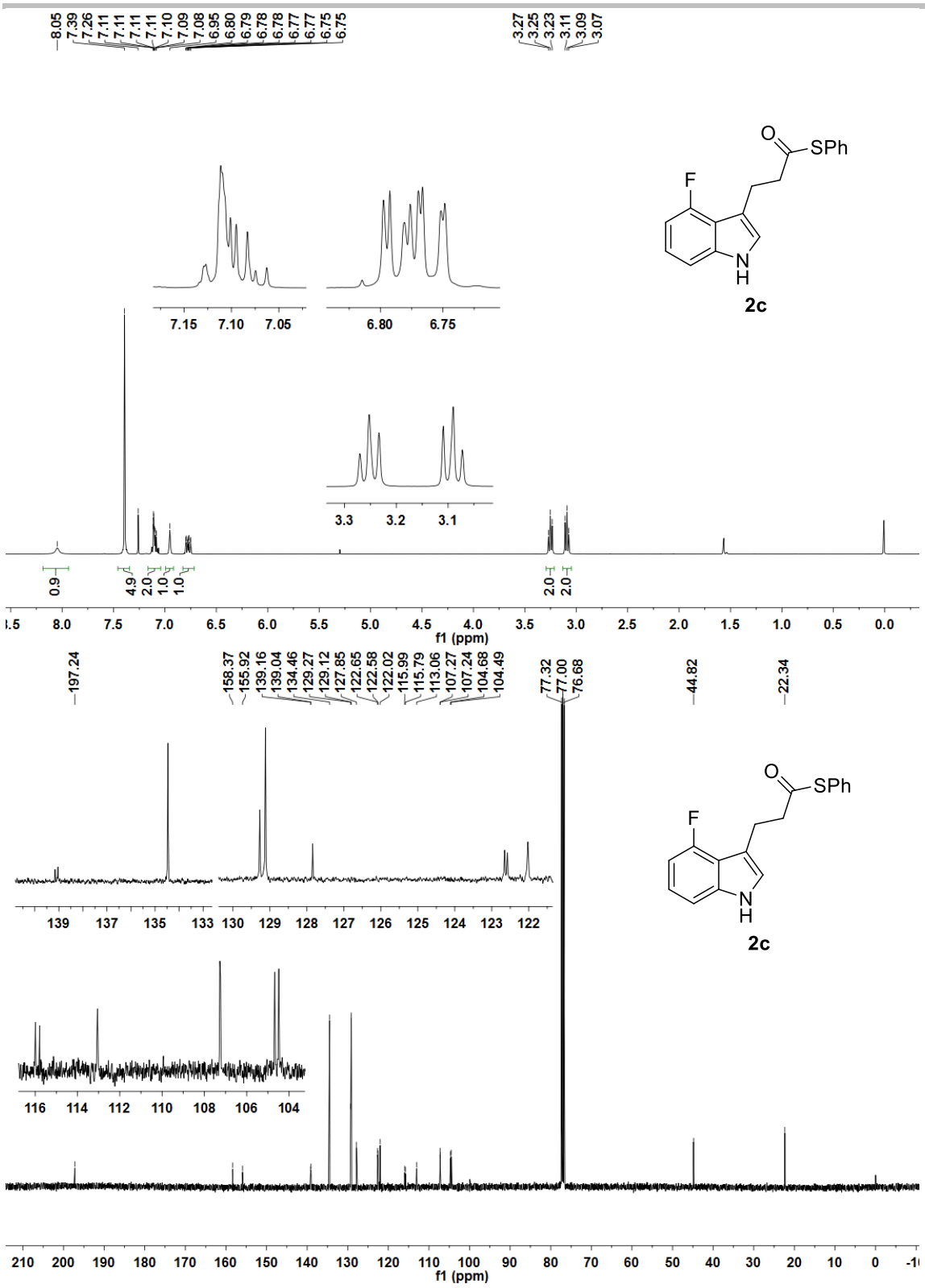
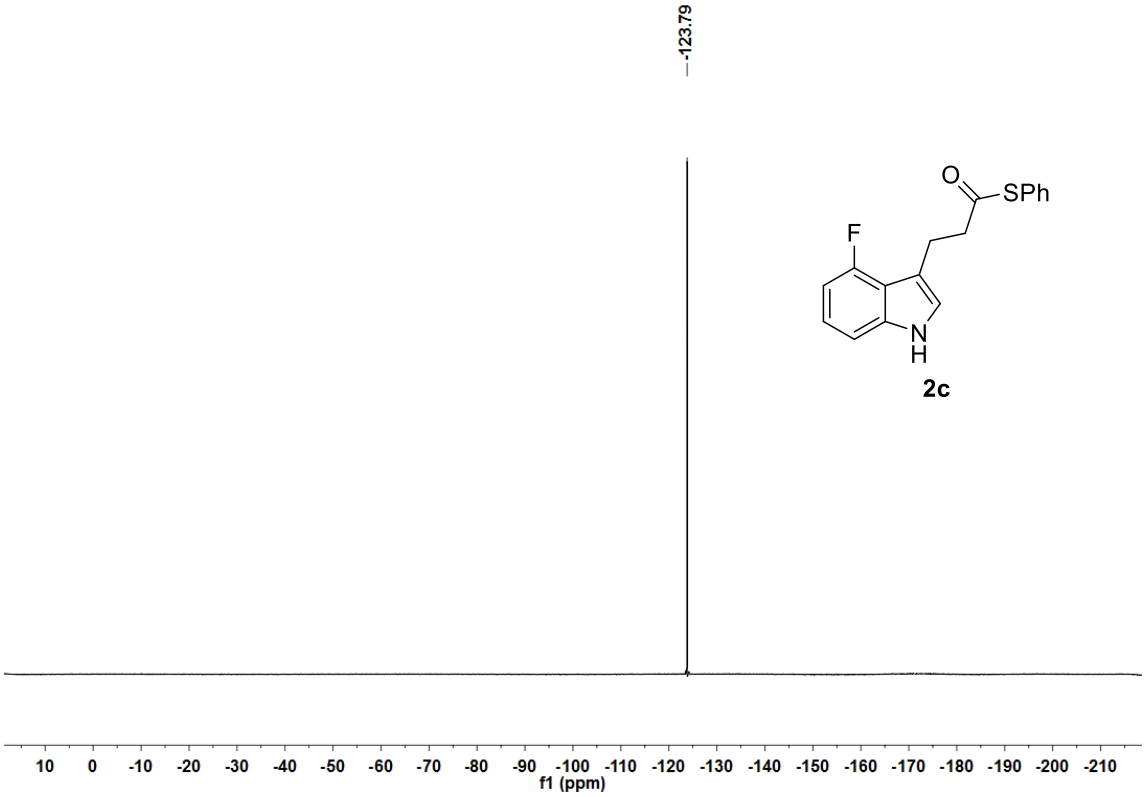
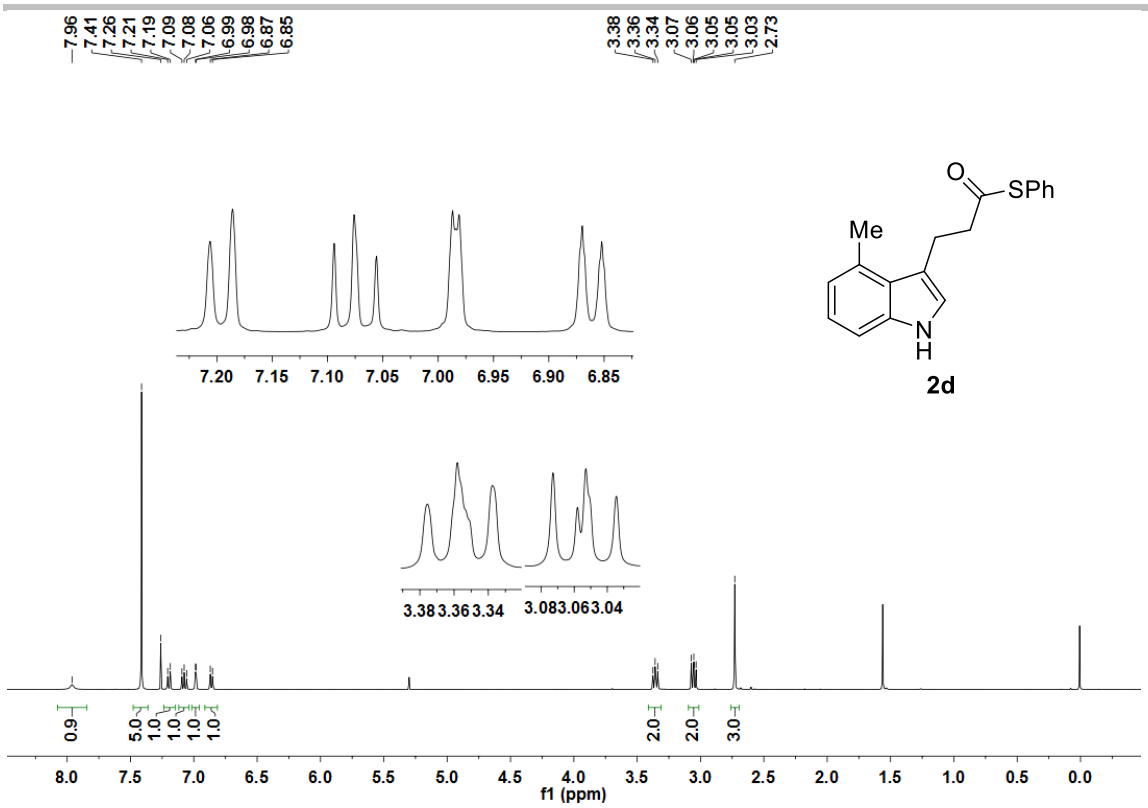
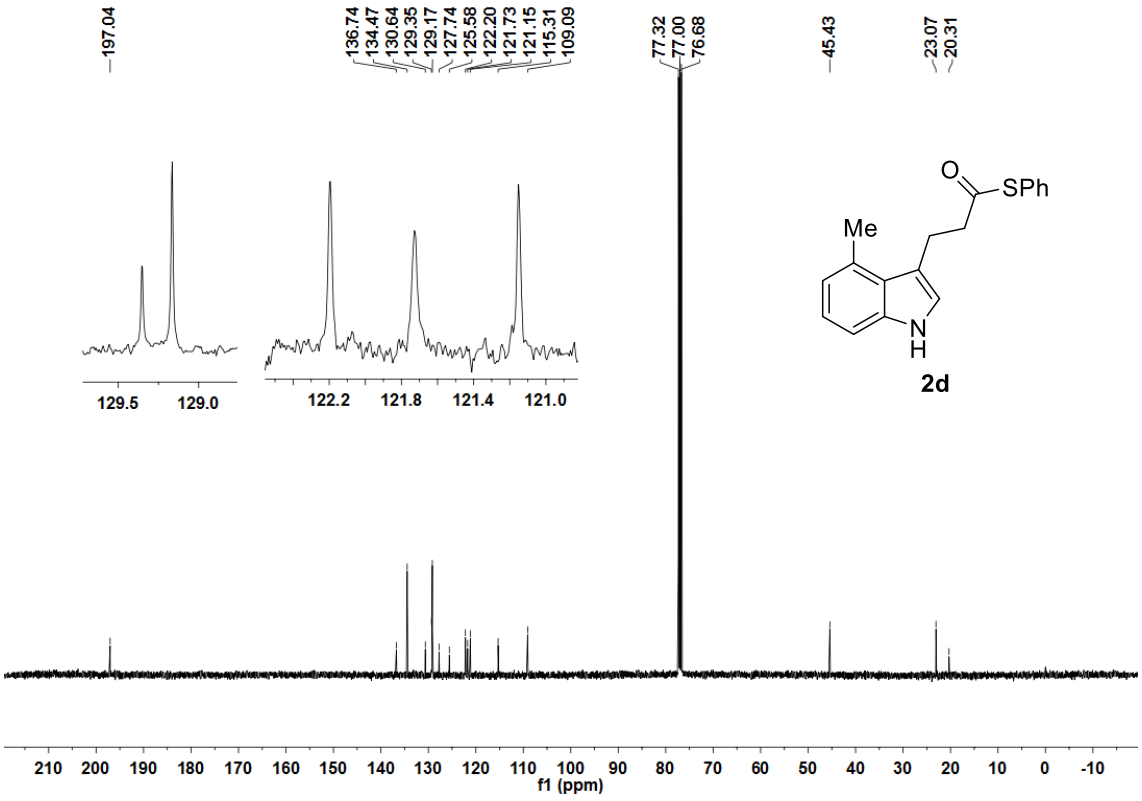
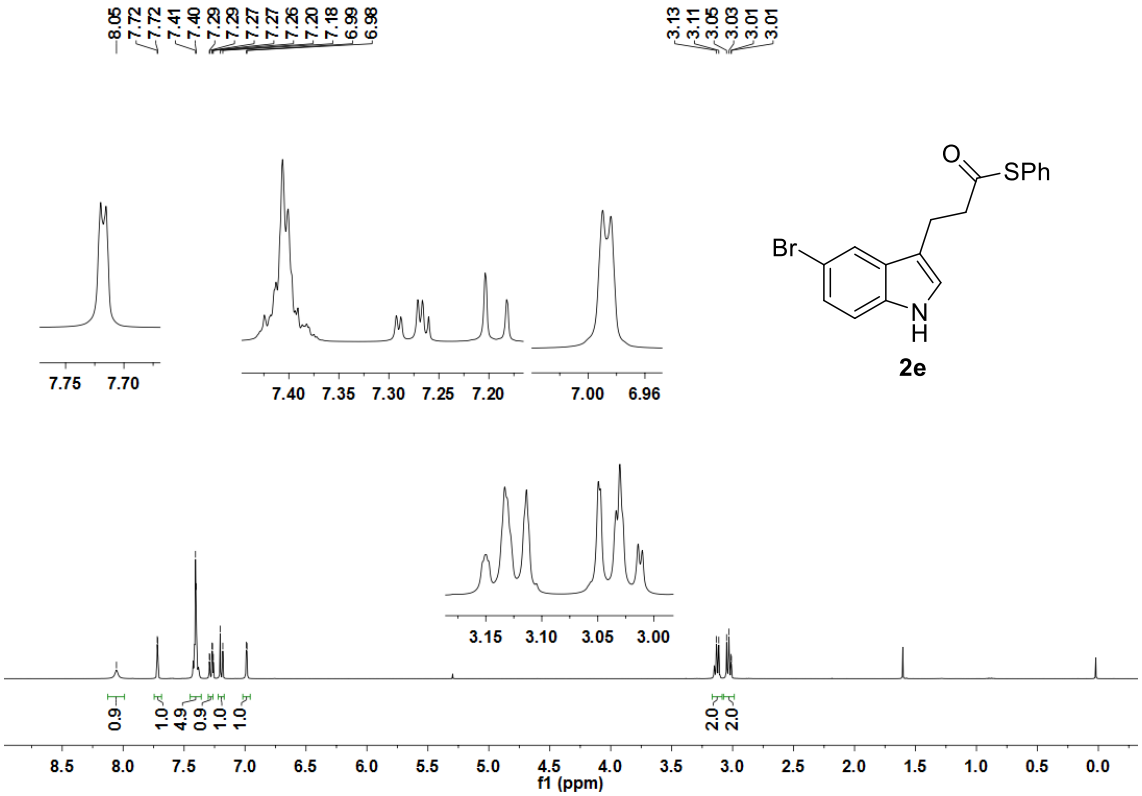
7.40
7.26
7.25
7.24
7.23
7.22
7.22
7.21
7.10
7.09
7.09
7.08
7.06
7.03
7.02
3.41
3.40
3.39
3.39
3.38
3.14
3.12
3.10
7.26 7.24 7.22
7.10 7.08 7.06 7.04 7.02
3.45 3.40 3.35
3.15 3.10
O
SPh
Cl
N
H
2b
0.9
5.0
1.0
2.0
1.0
2.0
2.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
197.30
137.77
134.46
129.28
129.13
127.87
126.19
123.96
123.51
122.62
120.45
114.70
109.96
77.32
77.00
76.68
45.73
22.26
129.5 129.0 128.5 128.0
124.0 123.5 123.0 122.5
O
SPh
Cl
N
H
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

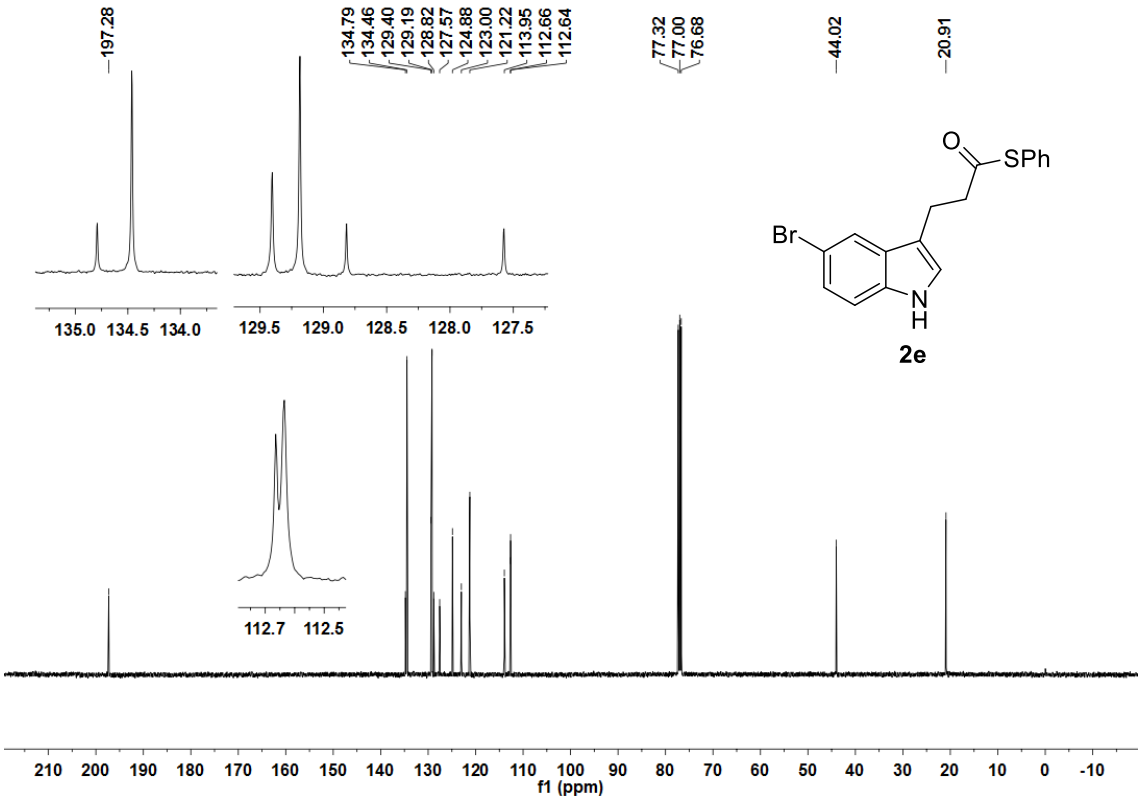

8.05
7.39
7.26
7.11
7.11
7.11
7.11
7.10
7.09
7.08
6.95
6.80
6.79
6.78
6.78
6.77
6.77
6.75
6.75
3.27
3.25
3.23
3.11
3.09
3.07
O
SPh
F
N
H
2c
7.15
7.10
7.05
6.80
6.75
3.3
3.2
3.1
0.9
4.9
2.0
1.0
1.0
2.0
2.0
f1 (ppm)
197.24
158.37
155.92
139.16
139.04
134.46
129.27
129.12
127.85
122.65
122.58
122.02
115.99
115.79
113.06
107.27
107.24
104.68
104.49
77.32
77.00
76.68
44.82
22.34
O
SPh
F
N
H
2c
139
137
135
133
130
129
128
127
126
125
124
123
122
116
114
112
110
108
106
104
f1 (ppm)

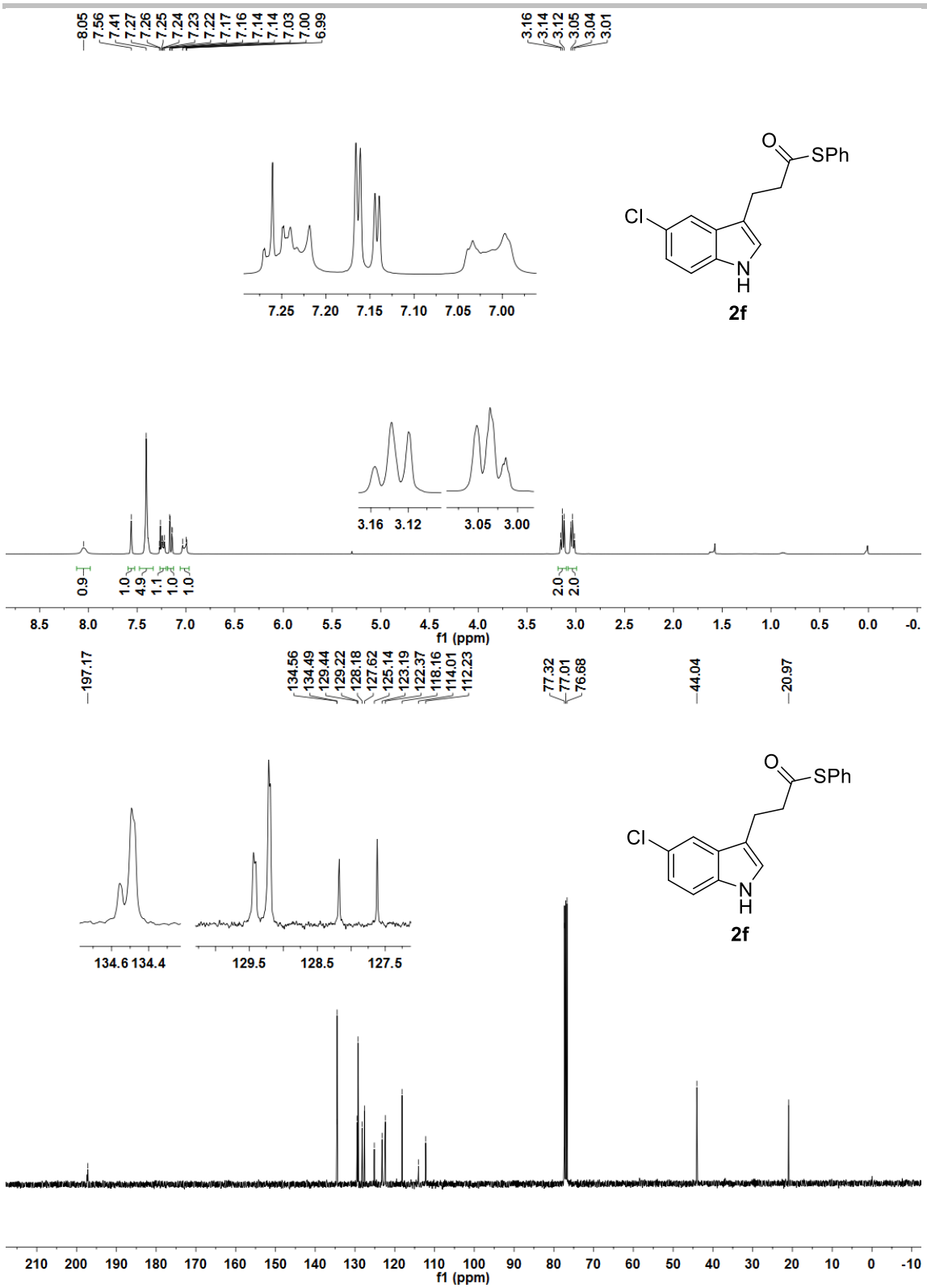

-123.79
O
SPh
F
N
H
2c
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

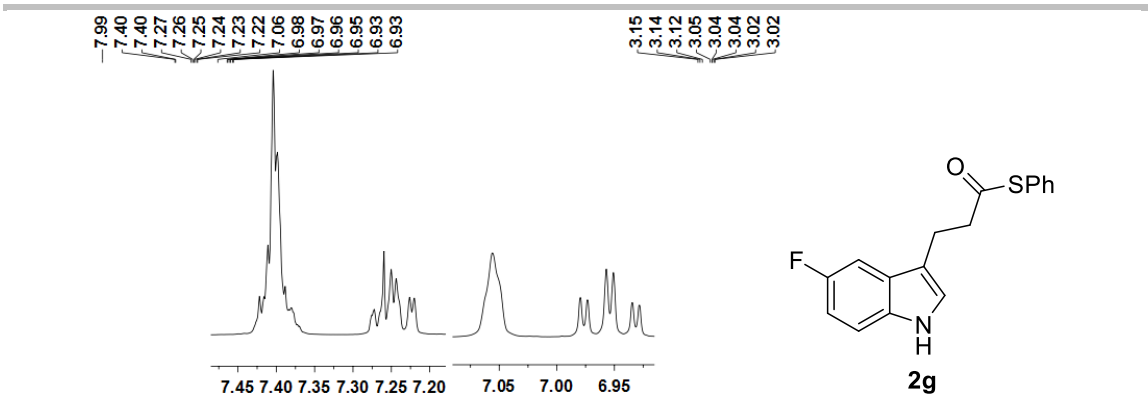

7.96
7.41
7.26
7.21
7.19
7.09
7.08
7.06
6.99
6.98
6.87
6.85
3.38
3.36
3.34
3.07
3.06
3.05
3.05
3.03
2.73
O
SPh
Me
N
H
2d
7.20 7.15 7.10 7.05 7.00 6.95 6.90 6.85
3.38 3.36 3.34
3.08 3.06 3.04
0.9
5.0
1.0
1.0
1.0
1.0
2.0
2.0
3.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


197.04
136.74
134.47
130.64
129.35
129.17
127.74
125.58
122.20
121.73
121.15
115.31
109.09
77.32
77.00
76.68
45.43
23.07
20.31
O
SPh
Me
N
H
2d
129.5 129.0
122.2 121.8 121.4 121.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

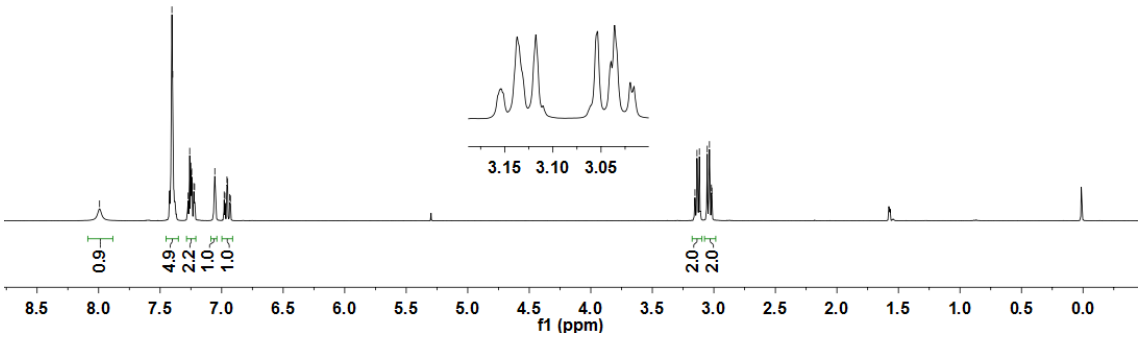

8.05
7.72
7.72
7.41
7.40
7.29
7.29
7.27
7.27
7.26
7.20
7.18
6.99
6.98
3.13
3.11
3.05
3.03
3.01
3.01
7.75 7.70
7.40 7.35 7.30 7.25 7.20
7.00 6.96
3.15 3.10 3.05 3.00
0.9
1.0
4.9
0.9
1.0
1.0
2.0
2.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
SPh
Br
N
H
2e

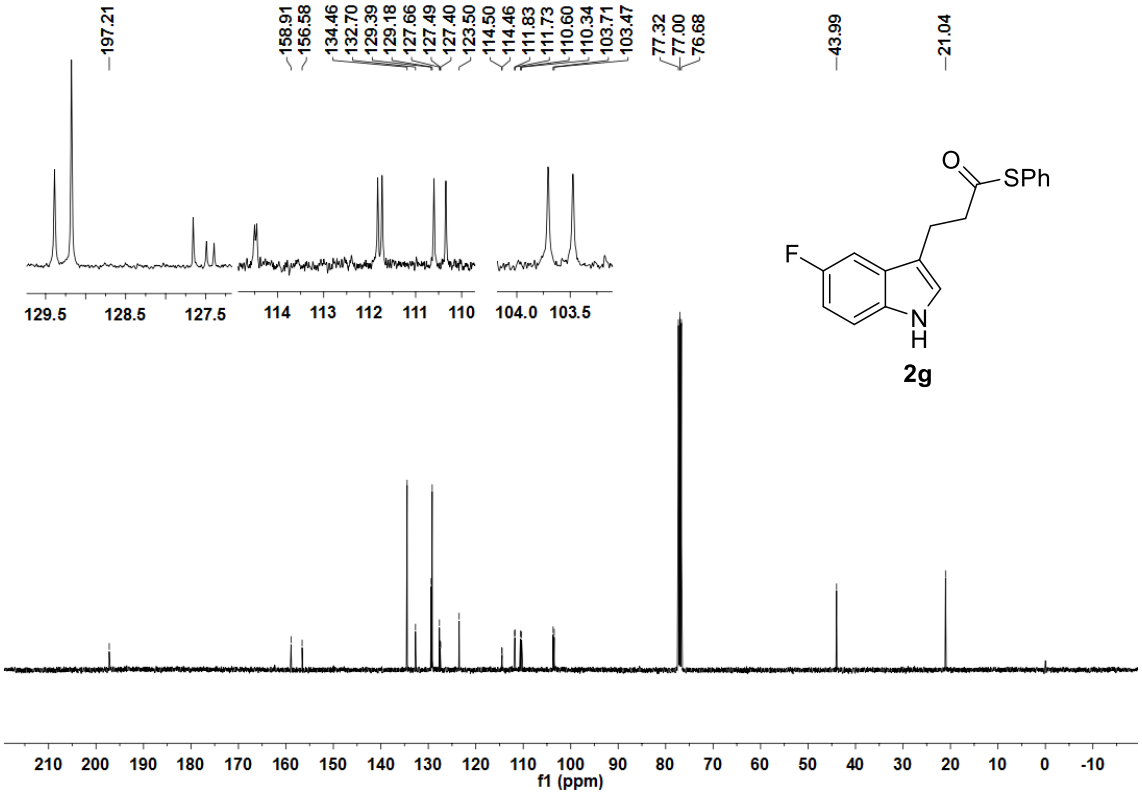

197.28
134.79
134.46
129.40
129.19
128.82
127.57
124.88
123.00
121.22
113.95
112.66
112.64
77.32
77.00
76.68
44.02
20.91
135.0 134.5 134.0
129.5 129.0 128.5 128.0 127.5
112.7 112.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
O
SPh
Br
N
H
2e


8.05
7.56
7.41
7.27
7.26
7.25
7.24
7.23
7.22
7.17
7.16
7.14
7.14
7.03
7.00
6.99
3.16
3.14
3.12
3.05
3.04
3.01
7.25 7.20 7.15 7.10 7.05 7.00
O
SPh
Cl
N
H
2f
3.16 3.12
3.05 3.00
0.9
1.0
4.9
1.1
1.0
1.0
2.0
2.0
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.
f1 (ppm)
197.17
134.56
134.49
129.44
129.22
128.18
127.62
125.14
123.19
122.37
118.16
114.01
112.23
77.32
77.01
76.68
44.04
20.97
134.6 134.4
129.5 128.5 127.5
O
SPh
Cl
N
H
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

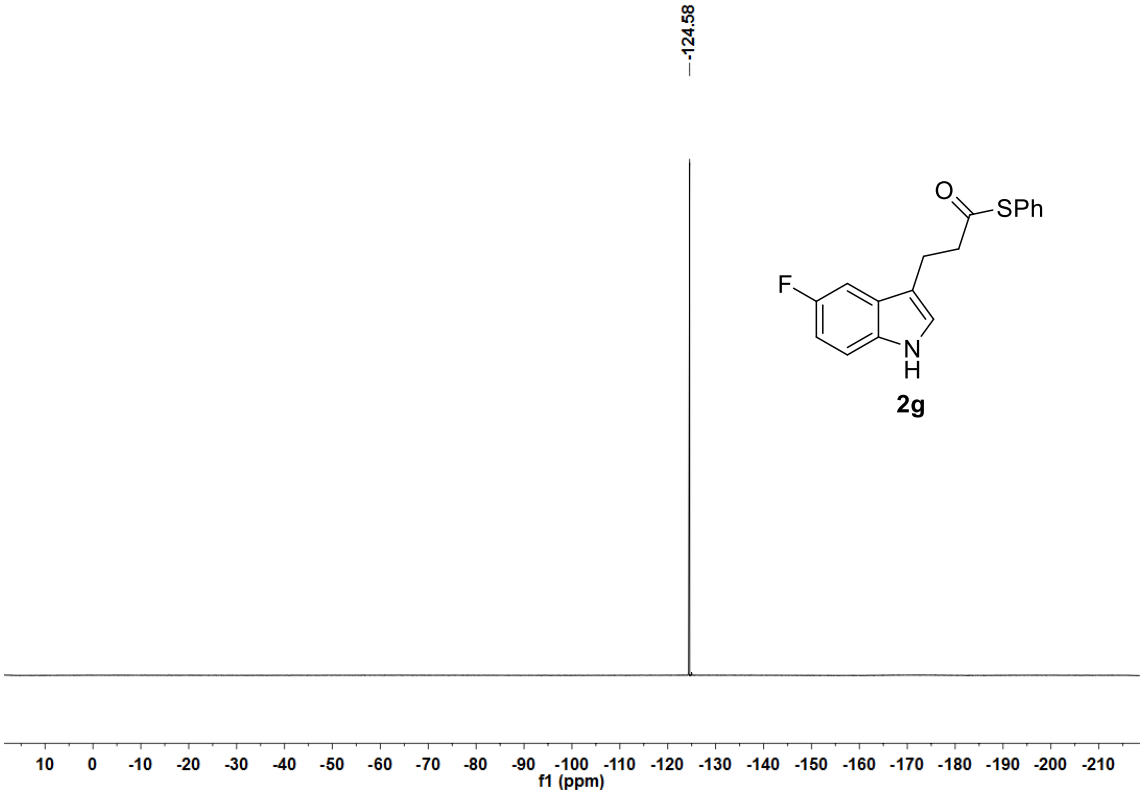

7.99
7.40
7.40
7.27
7.26
7.25
7.24
7.23
7.22
7.06
6.98
6.97
6.96
6.95
6.93
6.93
3.15
3.14
3.12
3.05
3.04
3.04
3.02
3.02
7.45 7.40 7.35 7.30 7.25 7.20
7.05
7.00
6.95
O
SPh
F
N
H

2g

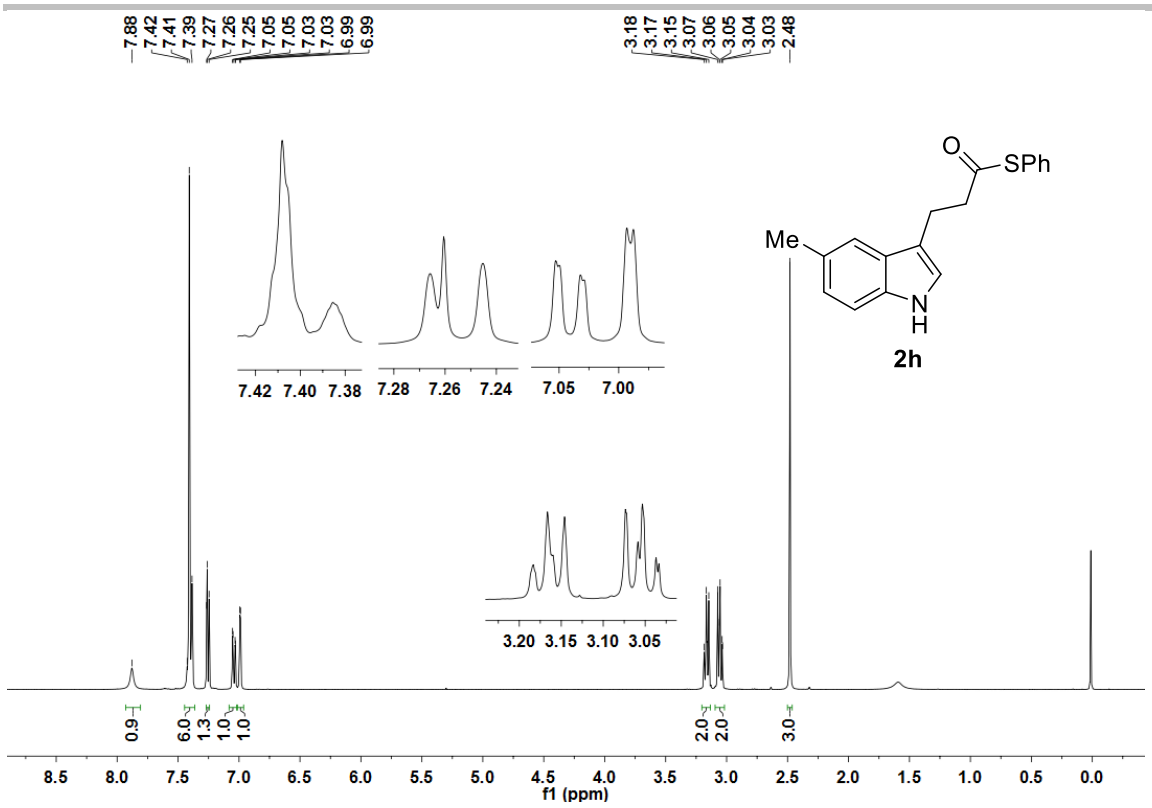

3.15 3.10 3.05
0.9
4.9
2.2
1.0
1.0
2.0
2.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

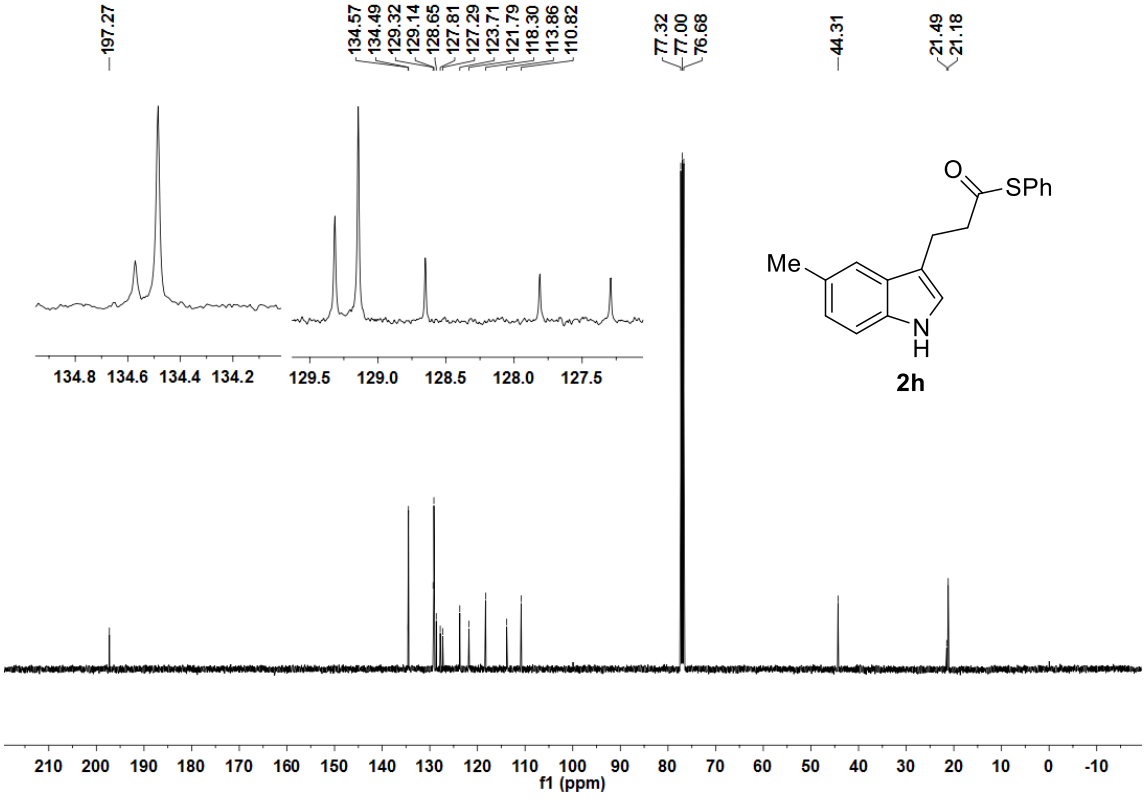

197.21
158.91
156.58
134.46
132.70
129.39
129.18
127.66
127.49
127.40
123.50
114.50
114.46
111.83
111.73
110.60
110.34
103.71
103.47
77.32
77.00
76.68
43.99
21.04
129.5 128.5 127.5
114 113 112 111 110
104.0 103.5
O
SPh
F
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

2g


-124.58
O
SPh
F
N
H
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

2g


7.88
7.42
7.41
7.39
7.27
7.26
7.25
7.05
7.05
7.03
7.03
6.99
6.99
3.18
3.17
3.15
3.07
3.06
3.05
3.04
3.03
2.48
7.42 7.40 7.38
7.28 7.26 7.24
7.05 7.00
3.20 3.15 3.10 3.05
0.9
6.0
1.3
1.0
1.0
2.0
2.0
3.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
SPh
Me
N
H
2h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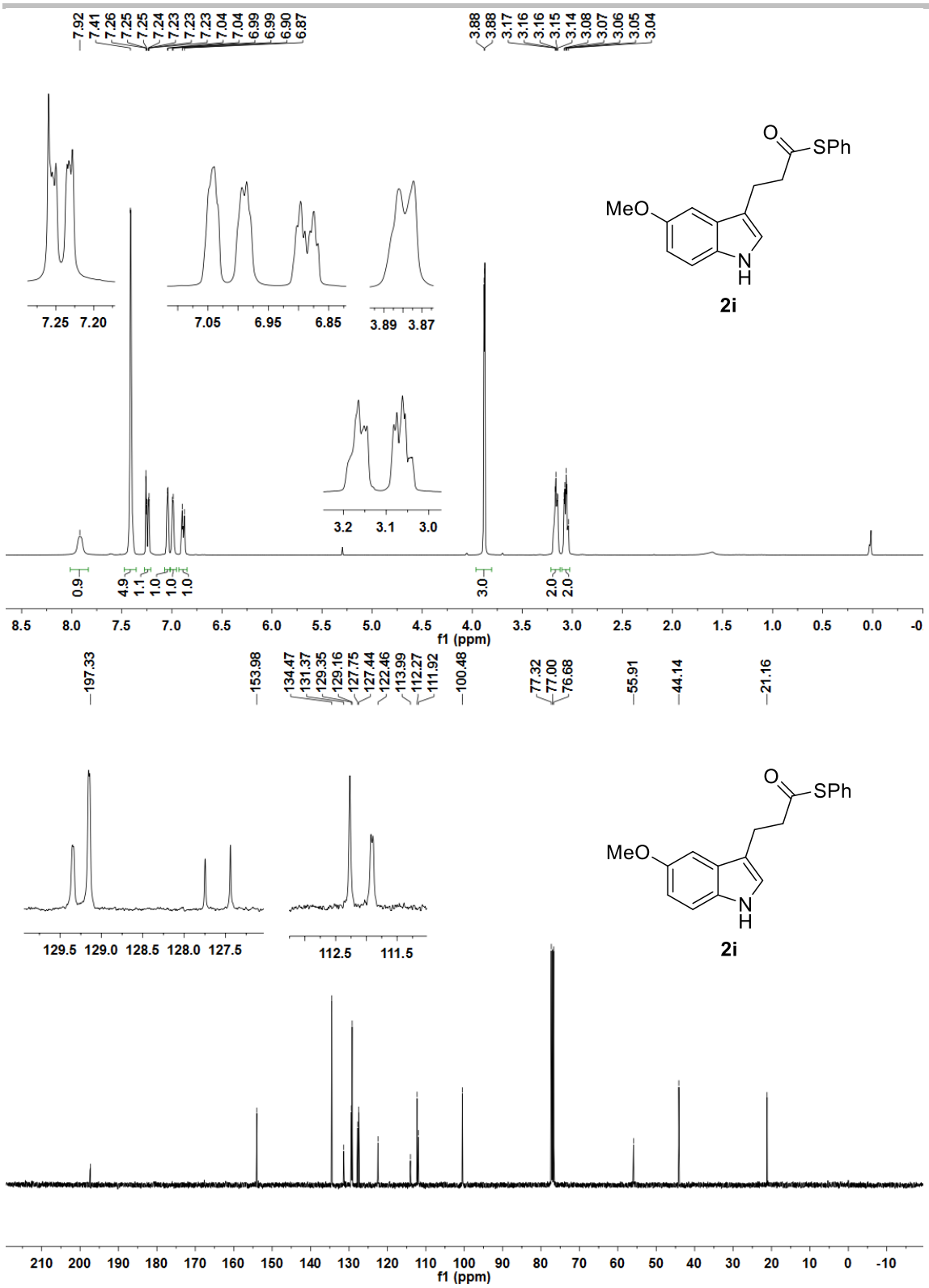
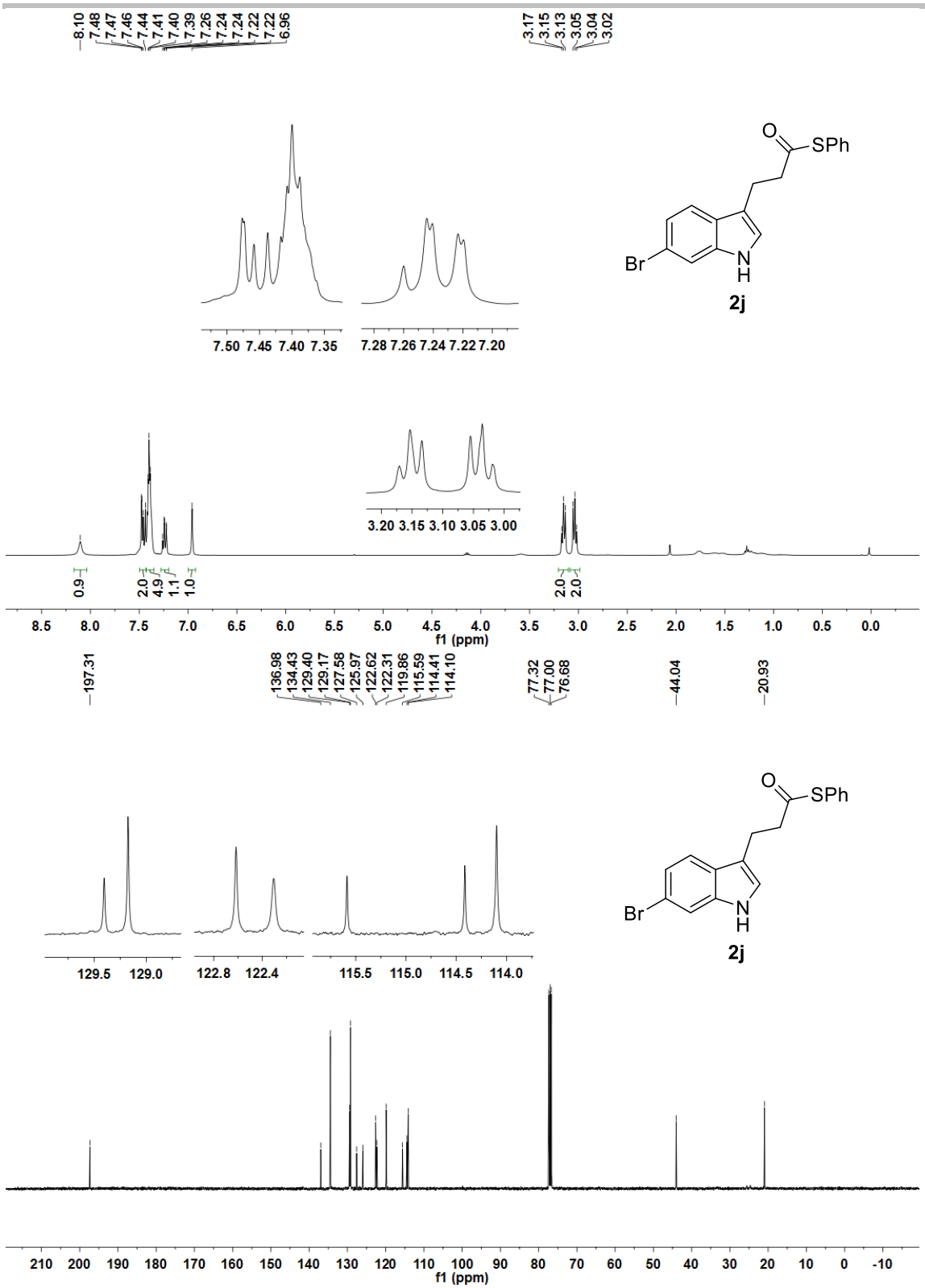
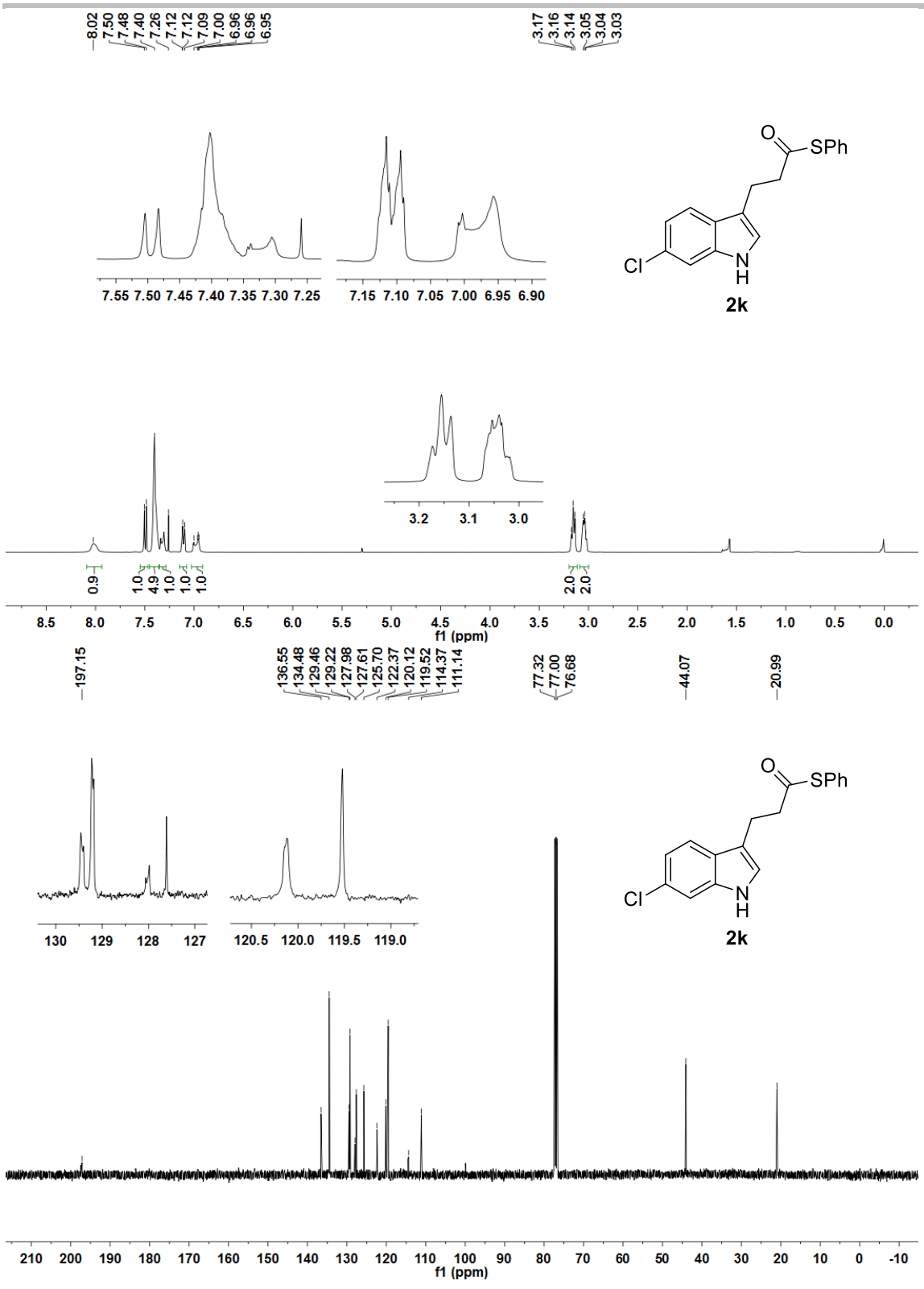
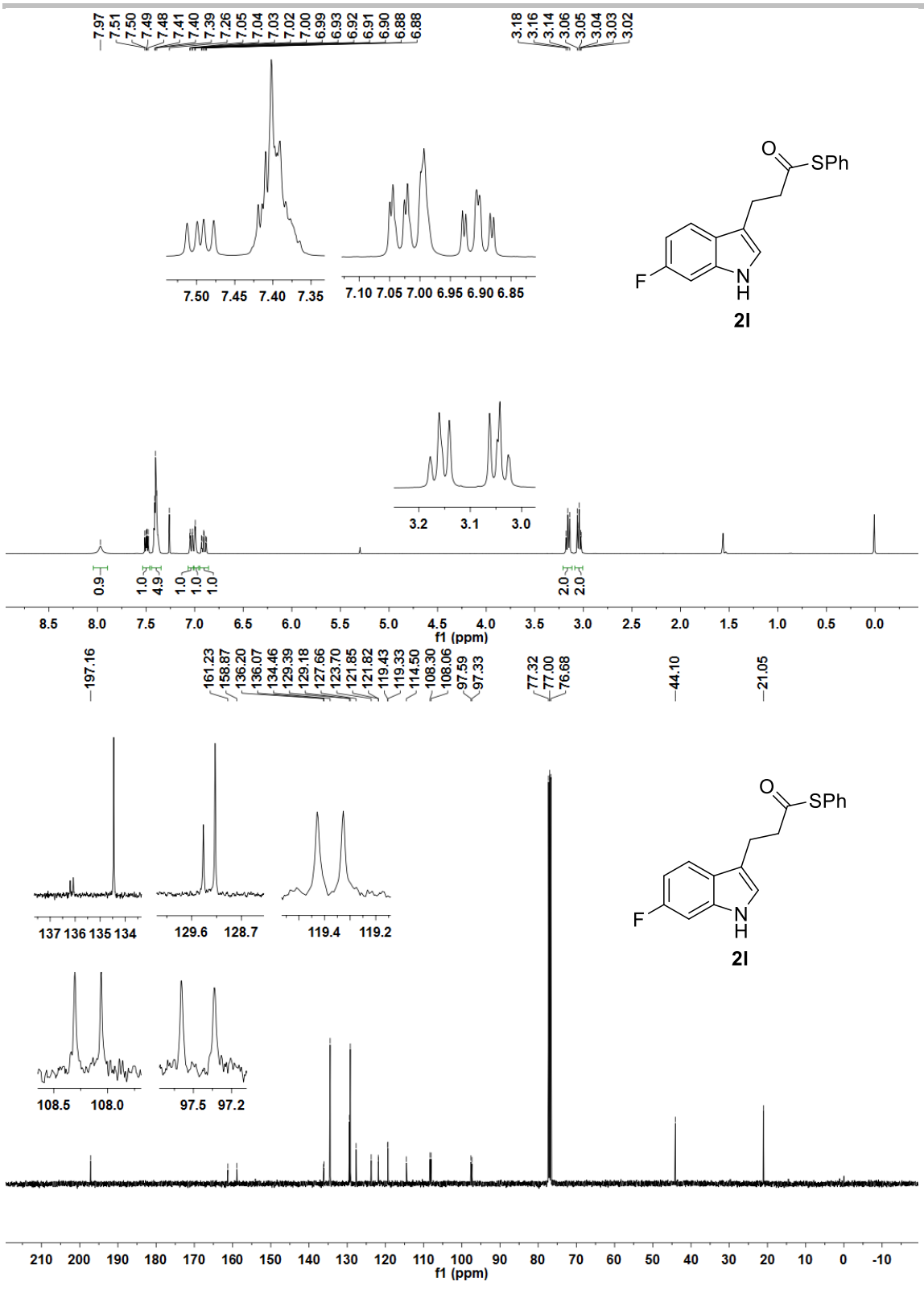
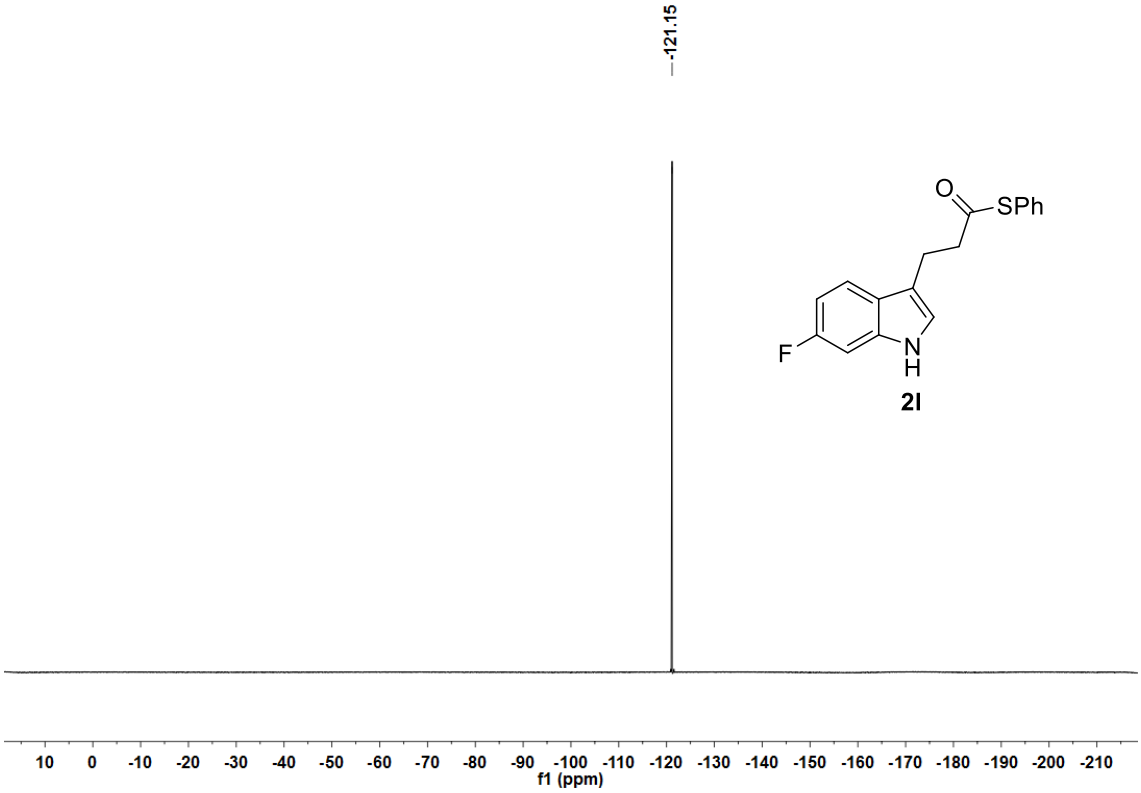
134.57
134.49
129.32
129.14
128.65
127.81
127.29
123.71
121.79
118.30
113.86
110.82
77.32
77.00
76.68
44.31
21.49
21.18
134.8 134.6 134.4 134.2
129.5 129.0 128.5 128.0 127.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
O
SPh
Me
N
H
2h


7.92
7.41
7.26
7.25
7.25
7.24
7.23
7.23
7.04
7.04
6.99
6.90
6.87
3.88
3.88
3.17
3.16
3.16
3.15
3.14
3.08
3.07
3.06
3.05
3.04
O
SPh
MeO
N
H
2i
7.25 7.20
7.05 6.95 6.85
3.89 3.87
3.2 3.1 3.0
0.9
4.9
1.1
1.0
1.0
1.0
3.0
2.0
2.0
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
f1 (ppm)
197.33
153.98
134.47
131.37
129.35
129.16
127.75
127.44
122.46
113.99
112.27
111.92
100.48
77.32
77.00
76.68
55.91
44.14
21.16
O
SPh
MeO
N
H
2i
129.5 129.0 128.5 128.0 127.5
112.5 111.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

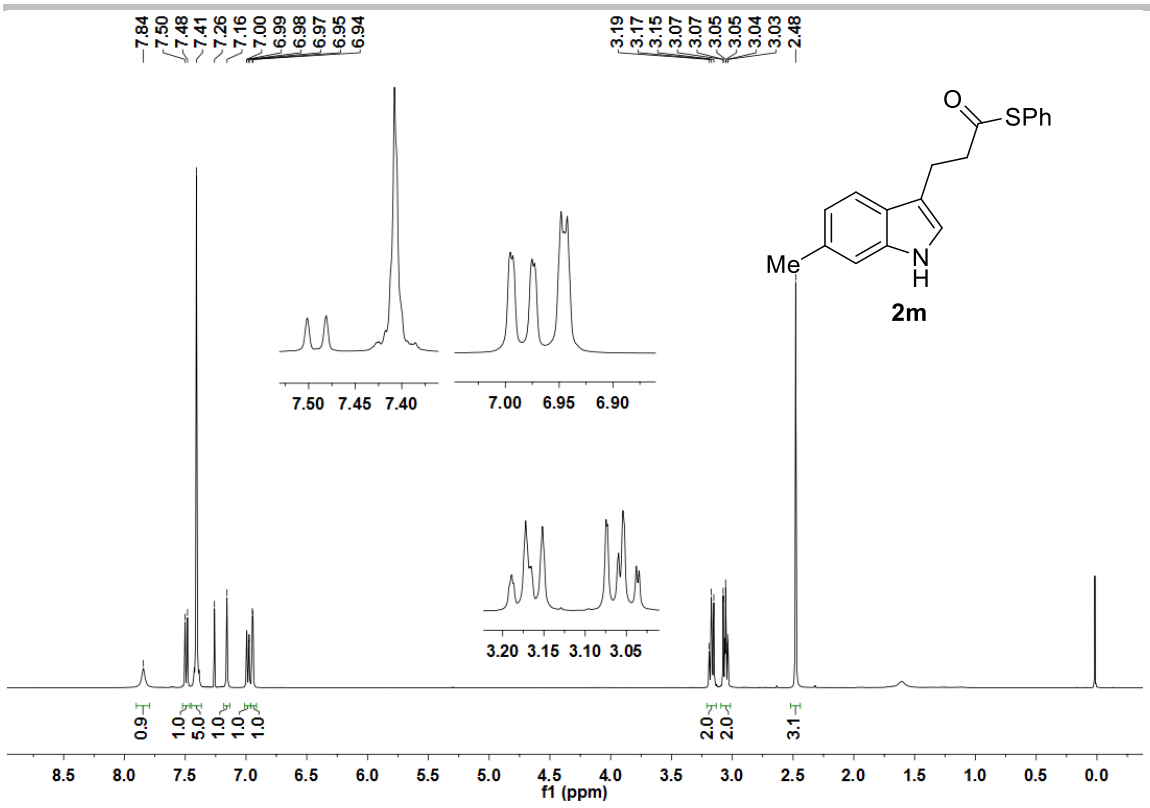

8.10
7.48
7.47
7.46
7.44
7.41
7.40
7.39
7.26
7.24
7.24
7.22
7.22
6.96
3.17
3.15
3.13
3.05
3.04
3.02
O
SPh
Br
N
H
2j
7.50 7.45 7.40 7.35
7.28 7.26 7.24 7.22 7.20
3.20 3.15 3.10 3.05 3.00
0.9
2.0
4.9
1.1
1.0
2.0
2.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
197.31
136.98
134.43
129.40
129.17
127.58
125.97
122.62
122.31
119.86
115.59
114.41
114.10
77.32
77.00
76.68
44.04
20.93
O
SPh
Br
N
H
2j
129.5 129.0
122.8 122.4
115.5 115.0 114.5 114.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

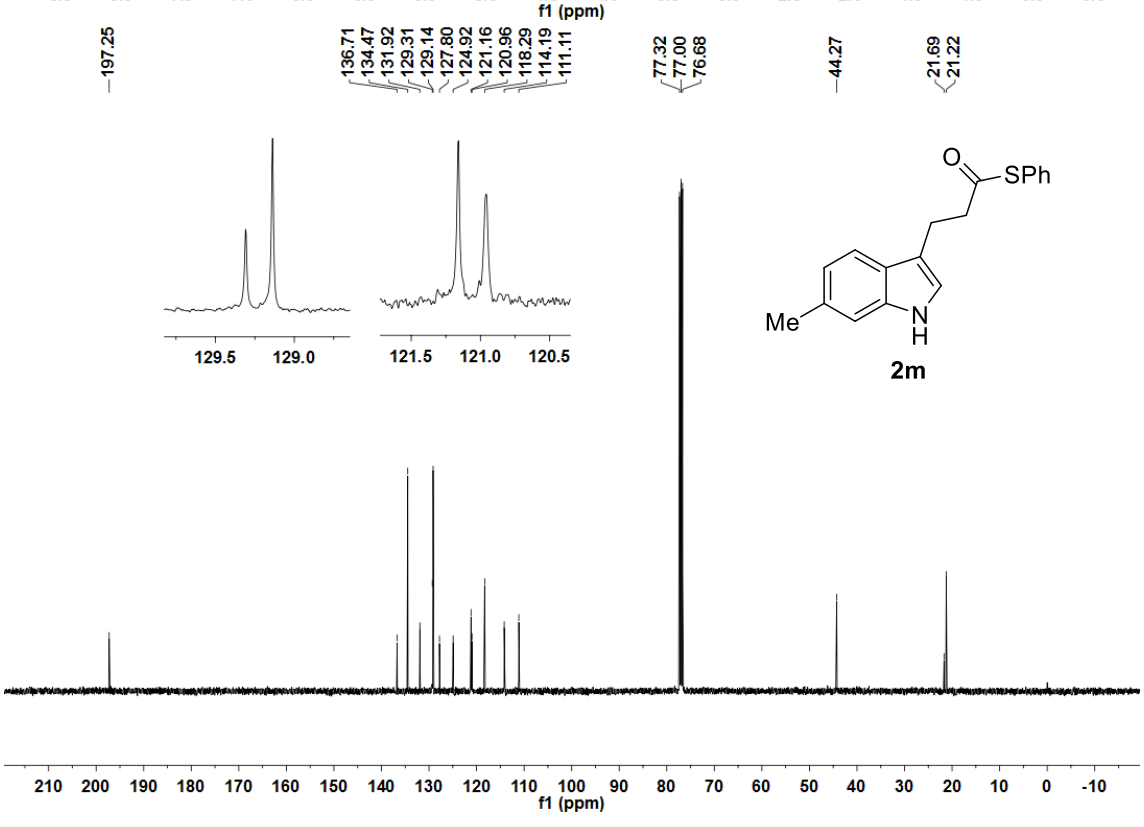

8.02
7.50
7.48
7.40
7.26
7.12
7.12
7.09
7.00
6.96
6.96
6.95
3.17
3.16
3.14
3.05
3.04
3.03
7.55 7.50 7.45 7.40 7.35 7.30 7.25
7.15 7.10 7.05 7.00 6.95 6.90
O
SPh
Cl
N
H
2k
3.2 3.1 3.0
0.9
1.0
4.9
1.0
1.0
1.0
2.0
2.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
197.15
136.55
134.48
129.46
129.22
127.98
127.61
125.70
122.37
120.12
119.52
114.37
111.14
77.32
77.00
76.68
44.07
20.99
130 129 128 127
120.5 120.0 119.5 119.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

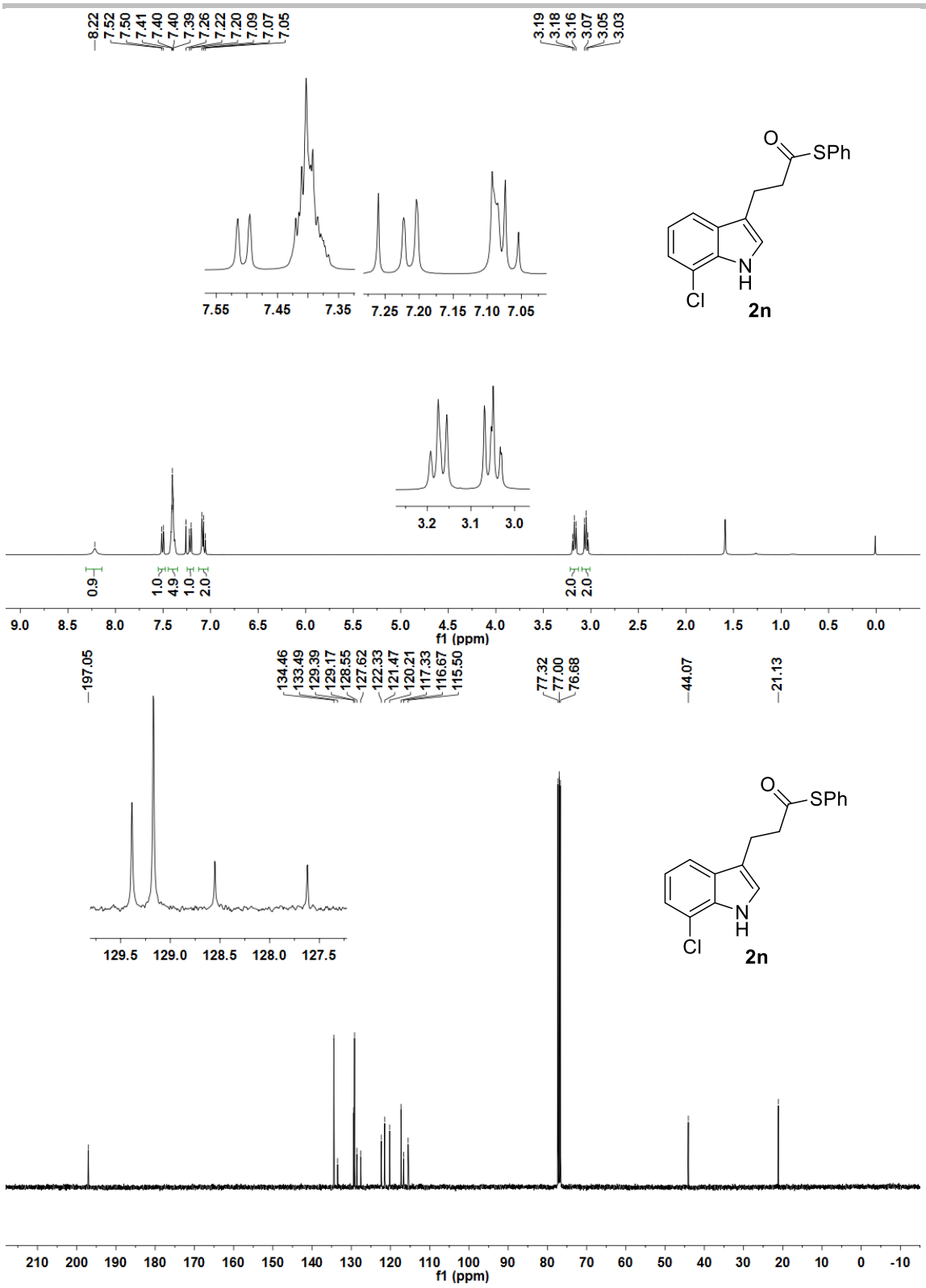

7.97 7.51 7.50 7.49 7.48 7.41 7.40 7.39 7.26 7.05 7.04 7.03 7.02 7.00 6.99 6.93 6.92 6.91 6.90 6.88 6.88
3.18 3.16 3.14 3.06 3.05 3.04 3.03 3.02
7.50 7.45 7.40 7.35
7.10 7.05 7.00 6.95 6.90 6.85
O
SPh
F
N
H
2l
3.2 3.1 3.0
0.9 1.0 4.9 1.0 1.0 1.0 2.0 2.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
197.16 161.23 158.87 136.20 136.07 134.46 129.39 129.18 127.66 123.70 121.85 121.82 119.43 119.33 114.50 108.30 108.06 97.59 97.33 77.32 77.00 76.68 44.10 21.05
137 136 135 134
129.6 128.7
119.4 119.2
108.5 108.0
97.5 97.2
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

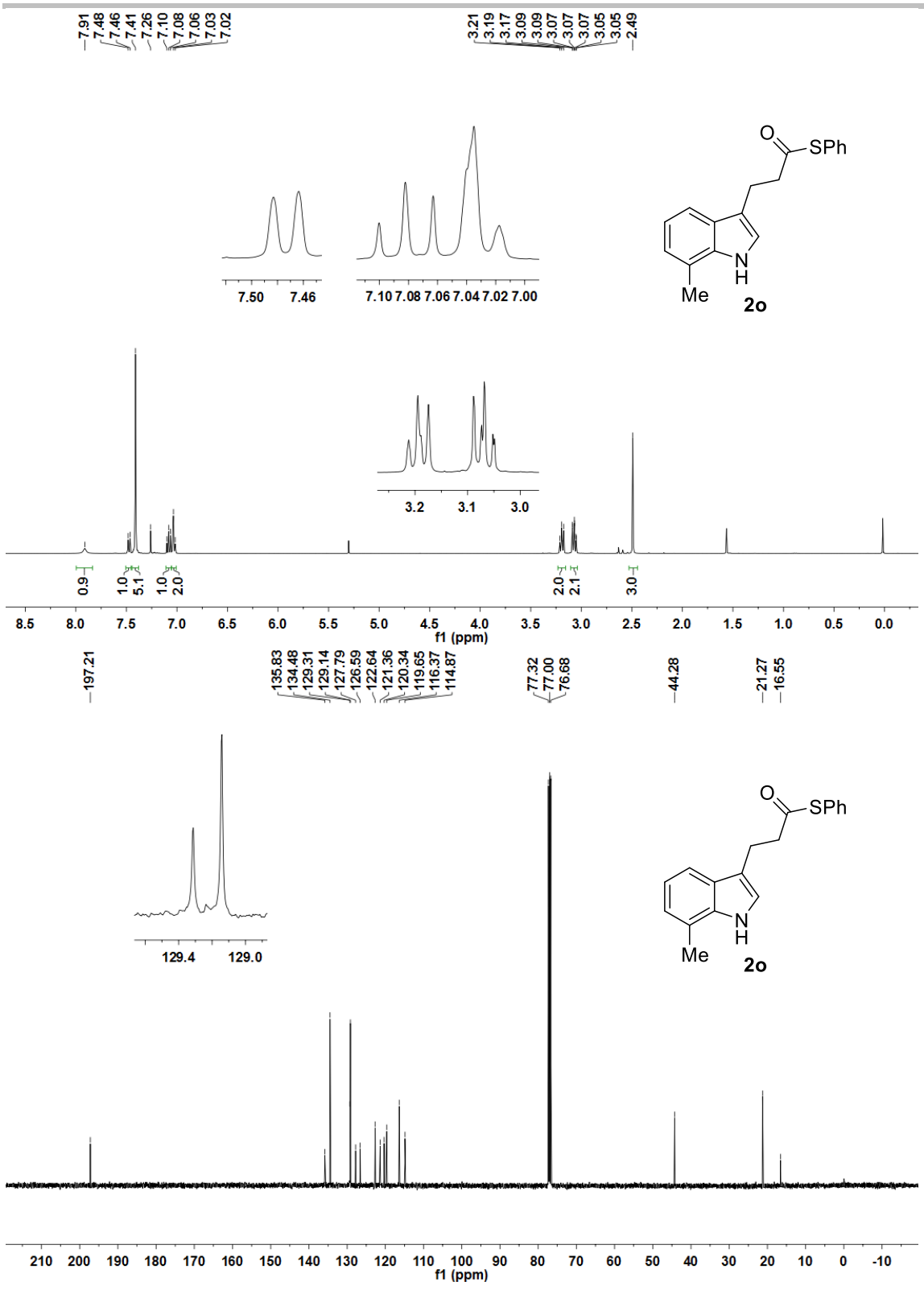

-121.15
O
SPh
F
N
H
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

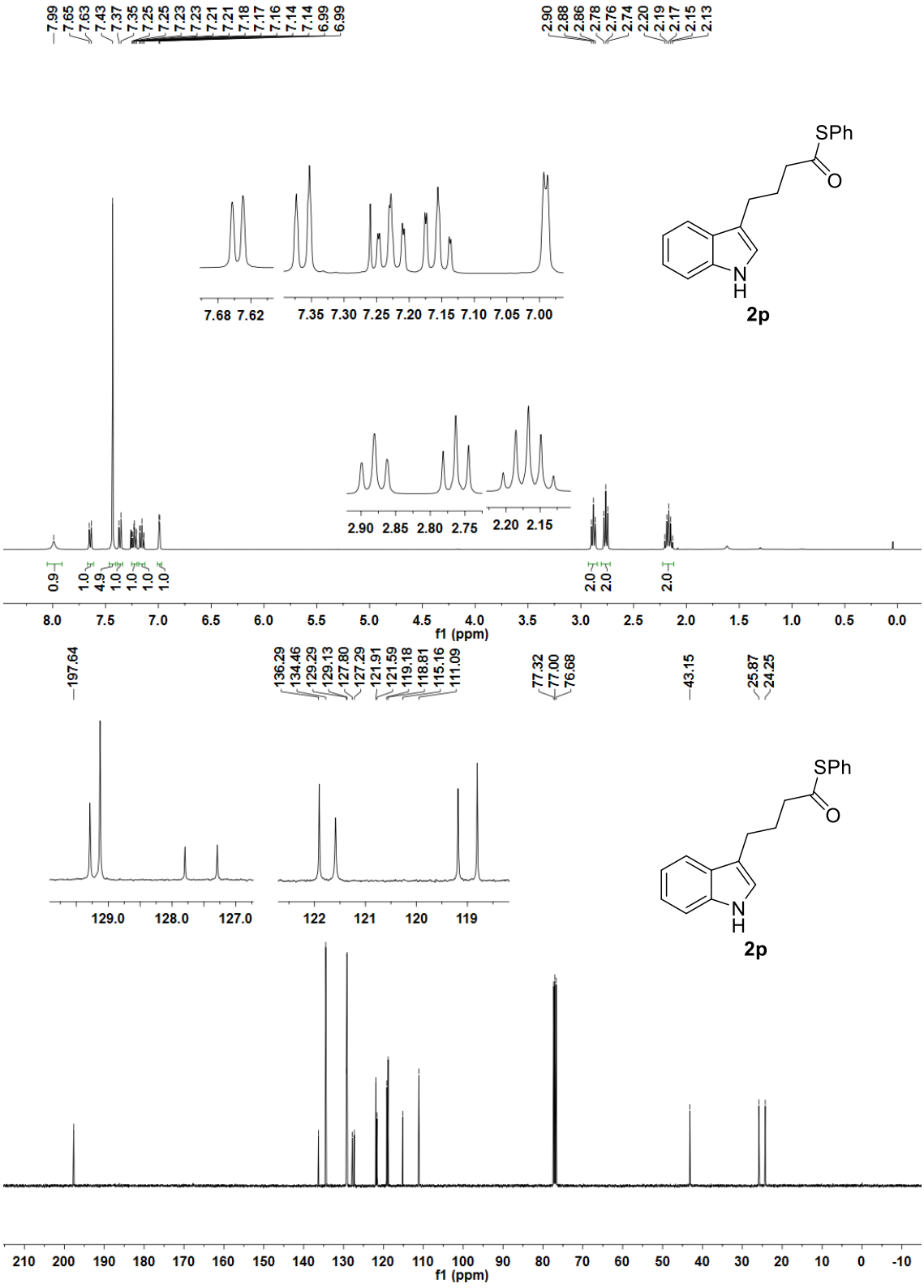
2l

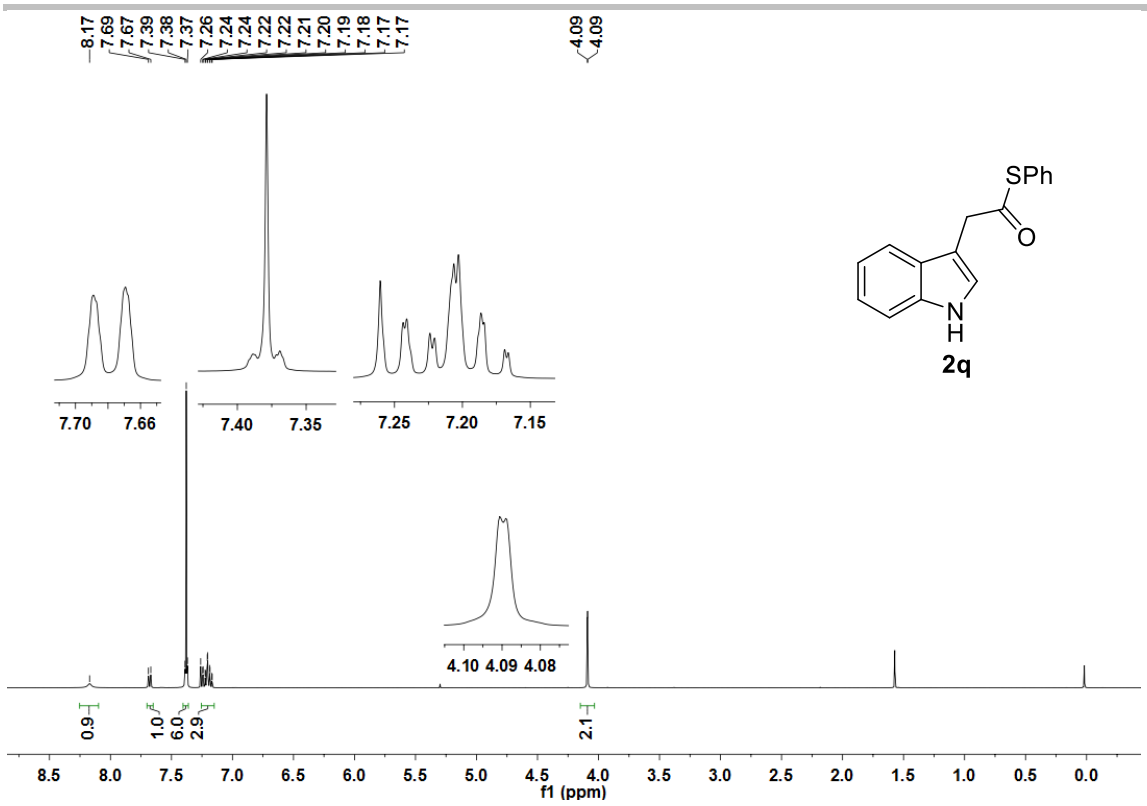

7.84
7.50
7.48
7.41
7.26
7.16
7.00
6.99
6.98
6.97
6.95
6.94
3.19
3.17
3.15
3.07
3.07
3.05
3.05
3.04
3.03
2.48
O
SPh
Me
N
H
2m
7.50 7.45 7.40
7.00 6.95 6.90
3.20 3.15 3.10 3.05
0.9
1.0
5.0
1.0
1.0
1.0
2.0
2.0
3.1
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

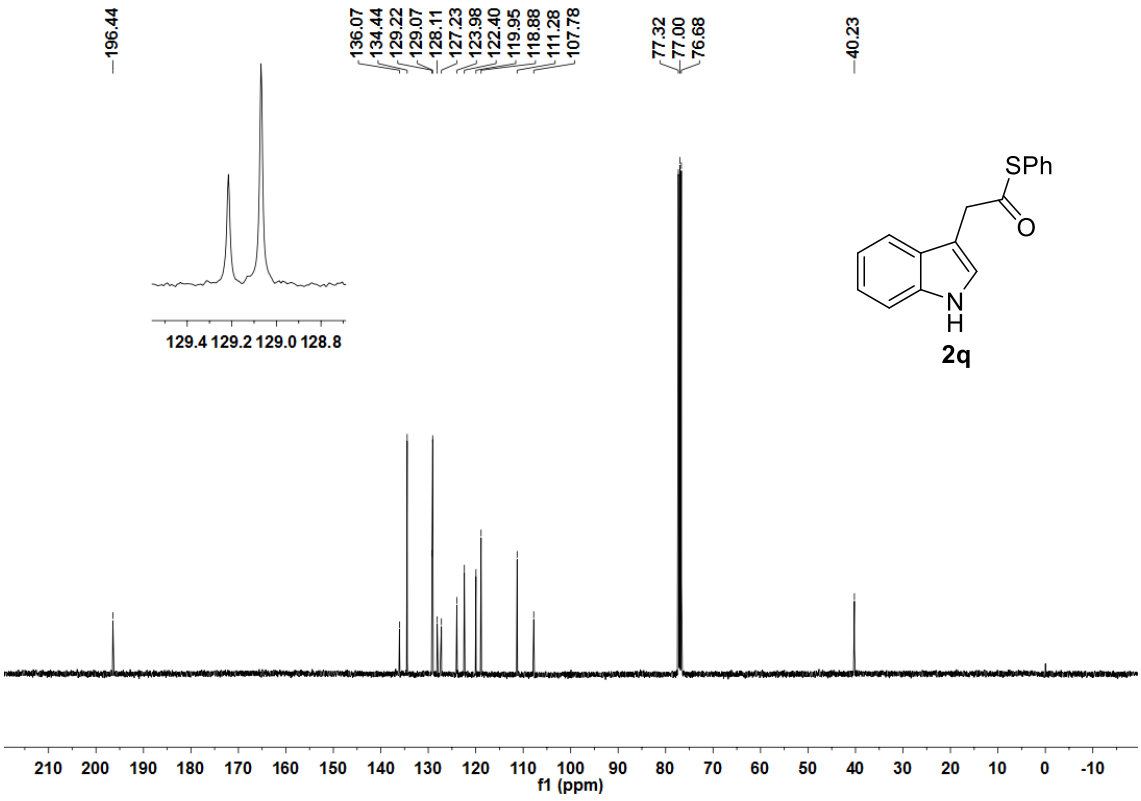

197.25
136.71
134.47
131.92
129.31
129.14
127.80
124.92
121.16
120.96
118.29
114.19
111.11
77.32
77.00
76.68
44.27
21.69
21.22
O
SPh
Me
N
H
2m
129.5 129.0
121.5 121.0 120.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

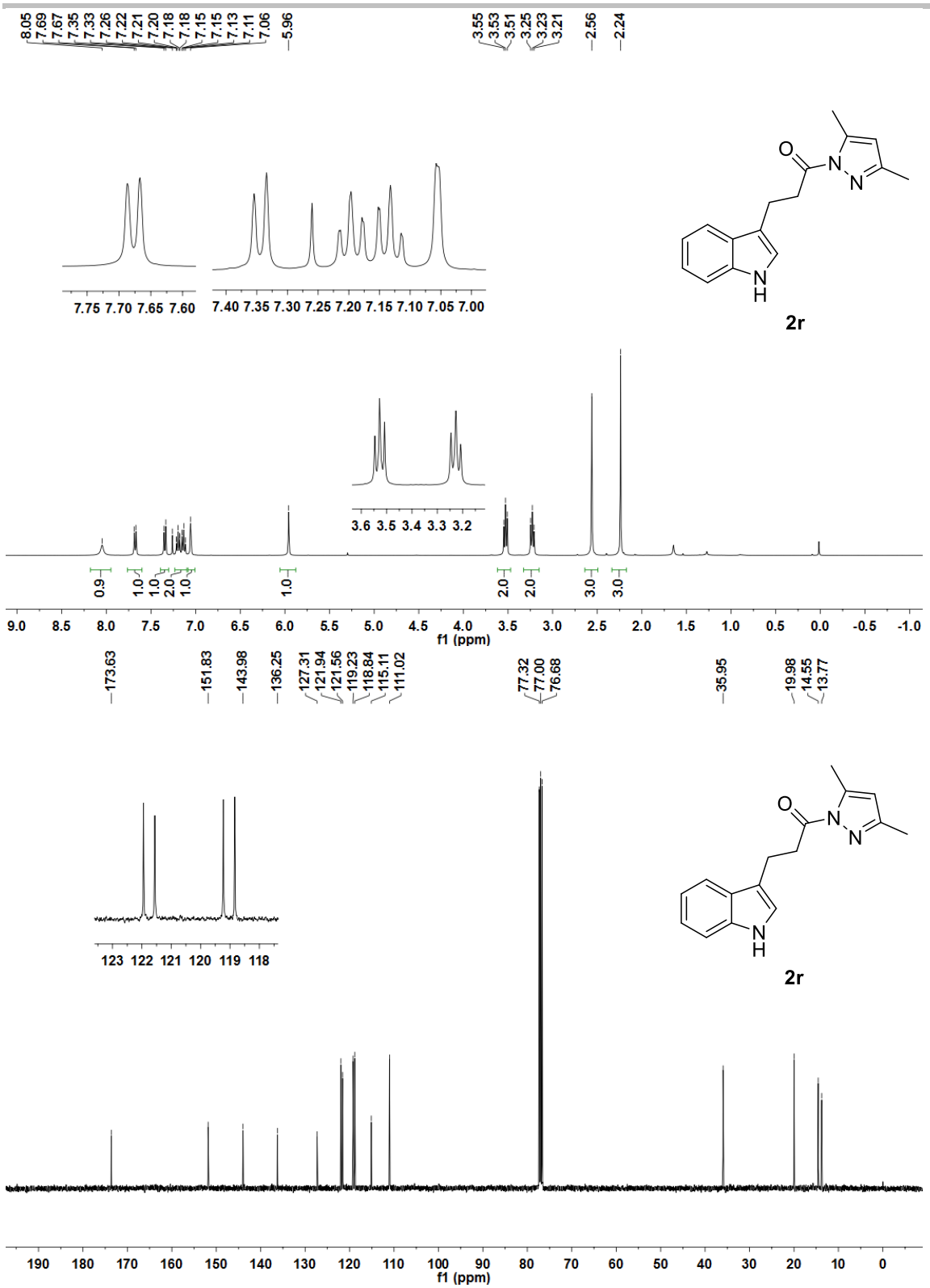

8.22
7.52
7.50
7.41
7.40
7.40
7.39
7.26
7.22
7.20
7.09
7.07
7.05
3.19
3.18
3.16
3.07
3.05
3.03
O
SPh
N
H
Cl
2n
0.9
1.0
4.9
1.0
2.0
2.0
2.0
f1 (ppm)
197.05
134.46
133.49
129.39
129.17
128.55
127.62
122.33
121.47
120.21
117.33
116.67
115.50
77.32
77.00
76.68
44.07
21.13
f1 (ppm)

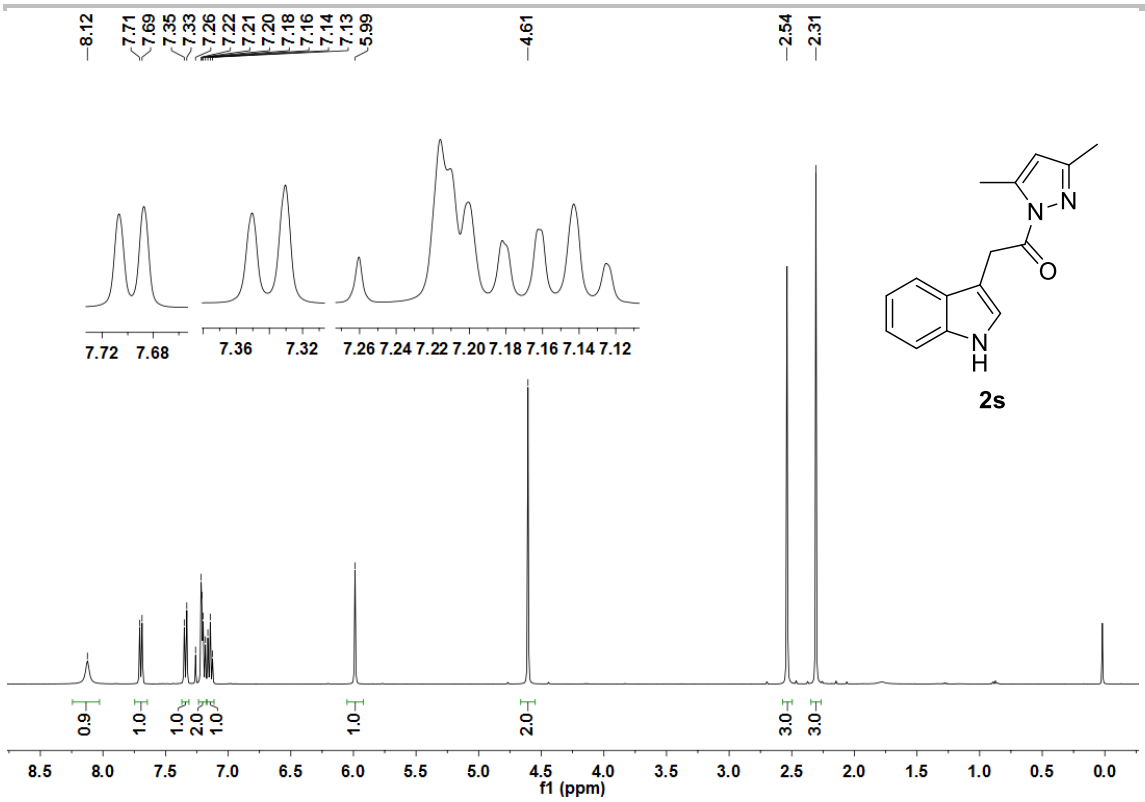

7.91
7.48
7.46
7.41
7.26
7.10
7.08
7.06
7.03
7.02
3.21
3.19
3.17
3.09
3.09
3.07
3.07
3.07
3.05
3.05
2.49
7.50
7.46
7.10 7.08 7.06 7.04 7.02 7.00
O
SPh
N
H
Me
2o
3.2
3.1
3.0
0.9
1.0
5.1
1.0
2.0
2.0
2.1
3.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
197.21
135.83
134.48
129.31
129.14
127.79
126.59
122.64
121.36
120.34
119.65
116.37
114.87
77.32
77.00
76.68
44.28
21.27
16.55
129.4
129.0
O
SPh
N
H
Me
2o
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

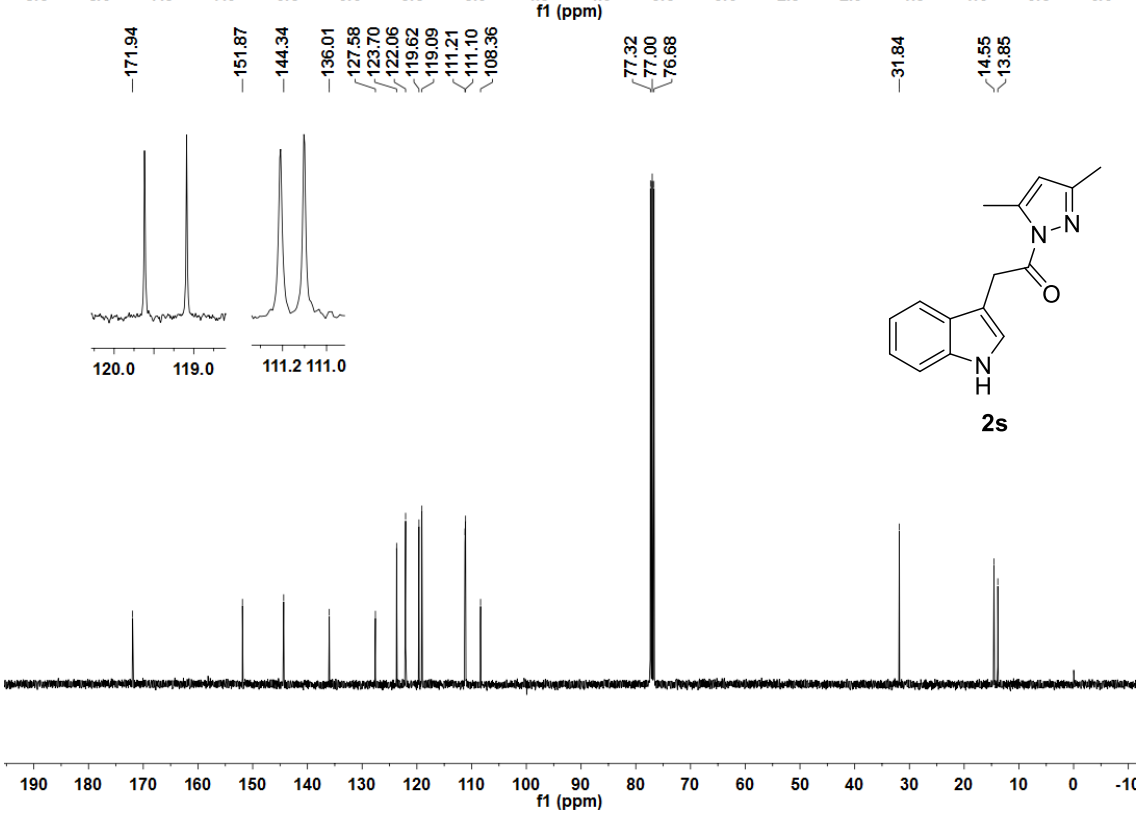

7.99 7.65 7.63 7.43 7.37 7.35 7.25 7.25 7.23 7.23 7.21 7.21 7.18 7.17 7.16 7.14 7.14 6.99 6.99
2.90 2.88 2.86 2.78 2.76 2.74 2.20 2.19 2.17 2.15 2.13
SPh
O
N
H
2p
7.68 7.62
7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
2.90 2.85 2.80 2.75
2.20 2.15
0.9 1.0 4.9 1.0 1.0 1.0 2.0 2.0 2.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
197.64
136.29 134.46 129.29 129.13 127.80 127.29 121.91 121.59 119.18 118.81 115.16 111.09
77.32 77.00 76.68
43.15
25.87 24.25
SPh
O
N
H
2p
129.0 128.0 127.0
122 121 120 119
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

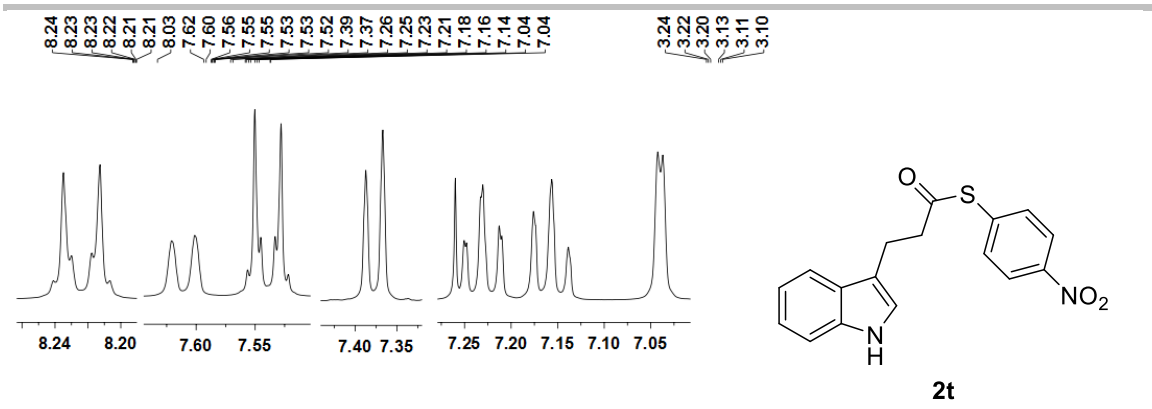

8.17
7.69
7.67
7.39
7.38
7.37
7.26
7.24
7.24
7.22
7.22
7.21
7.20
7.19
7.18
7.17
7.17
4.09
4.09
SPh
O
N
H
2q
7.70 7.66
7.40 7.35
7.25 7.20 7.15
4.10 4.09 4.08
0.9
1.0
6.0
2.9
2.1
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


196.44
136.07
134.44
129.22
129.07
128.11
127.23
123.98
122.40
119.95
118.88
111.28
107.78
77.32
77.00
76.68
40.23
SPh
O
N
H
2q
129.4 129.2 129.0 128.8
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

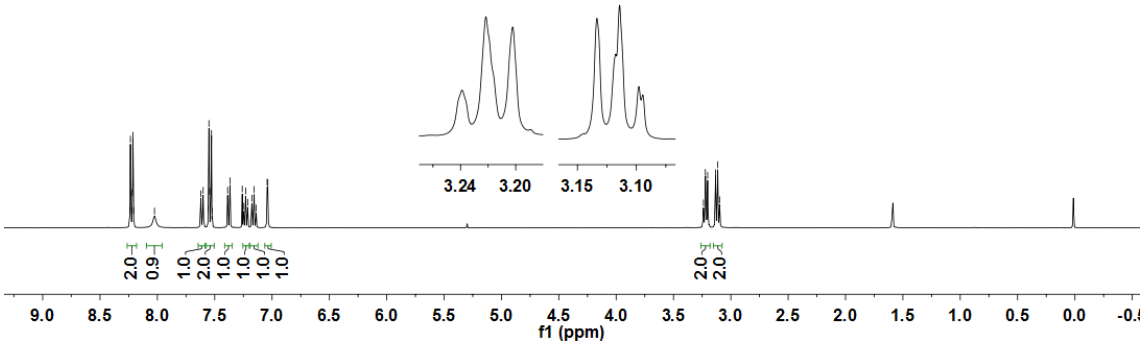

8.05
7.69
7.67
7.35
7.33
7.26
7.22
7.21
7.20
7.18
7.18
7.15
7.15
7.13
7.11
7.06
5.96
3.55
3.53
3.51
3.25
3.23
3.21
2.56
2.24
7.75 7.70 7.65 7.60
7.40 7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
O
N
N
N
H
2r
3.6 3.5 3.4 3.3 3.2
0.9
1.0
1.0
2.0
1.0
1.0
2.0
2.0
3.0
3.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)
173.63
151.83
143.98
136.25
127.31
121.94
121.56
119.23
118.84
115.11
111.02
77.32
77.00
76.68
35.95
19.98
14.55
13.77
123 122 121 120 119 118
O
N
N
N
H
2r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

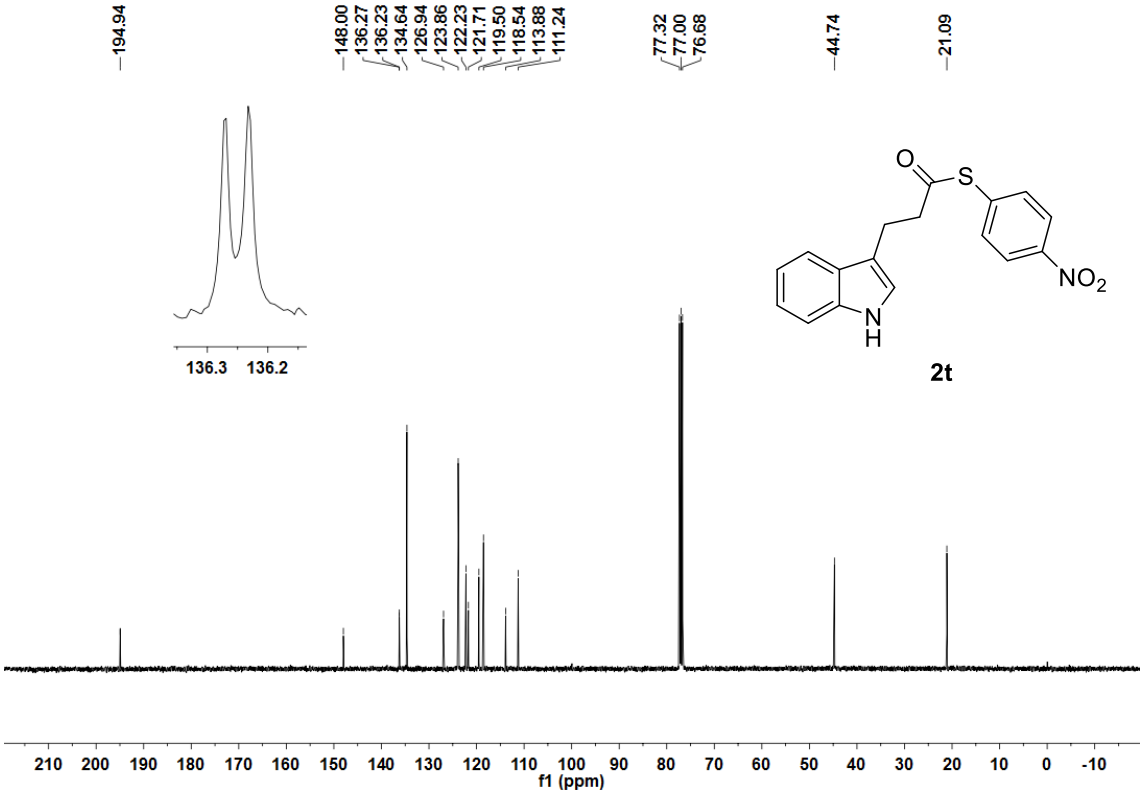

8.12
7.71
7.69
7.35
7.33
7.26
7.22
7.21
7.20
7.18
7.16
7.14
7.13
5.99
4.61
2.54
2.31
7.72 7.68
7.36 7.32
7.26 7.24 7.22 7.20 7.18 7.16 7.14 7.12
0.9
1.0
1.0
2.0
1.0
1.0
2.0
3.0
3.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
N
N
O
N
H
2s


171.94
151.87
144.34
136.01
127.58
123.70
122.06
119.62
119.09
111.21
111.10
108.36
77.32
77.00
76.68
31.84
14.55
13.85
120.0 119.0
111.2 111.0
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)
N
N
O
N
H
2s

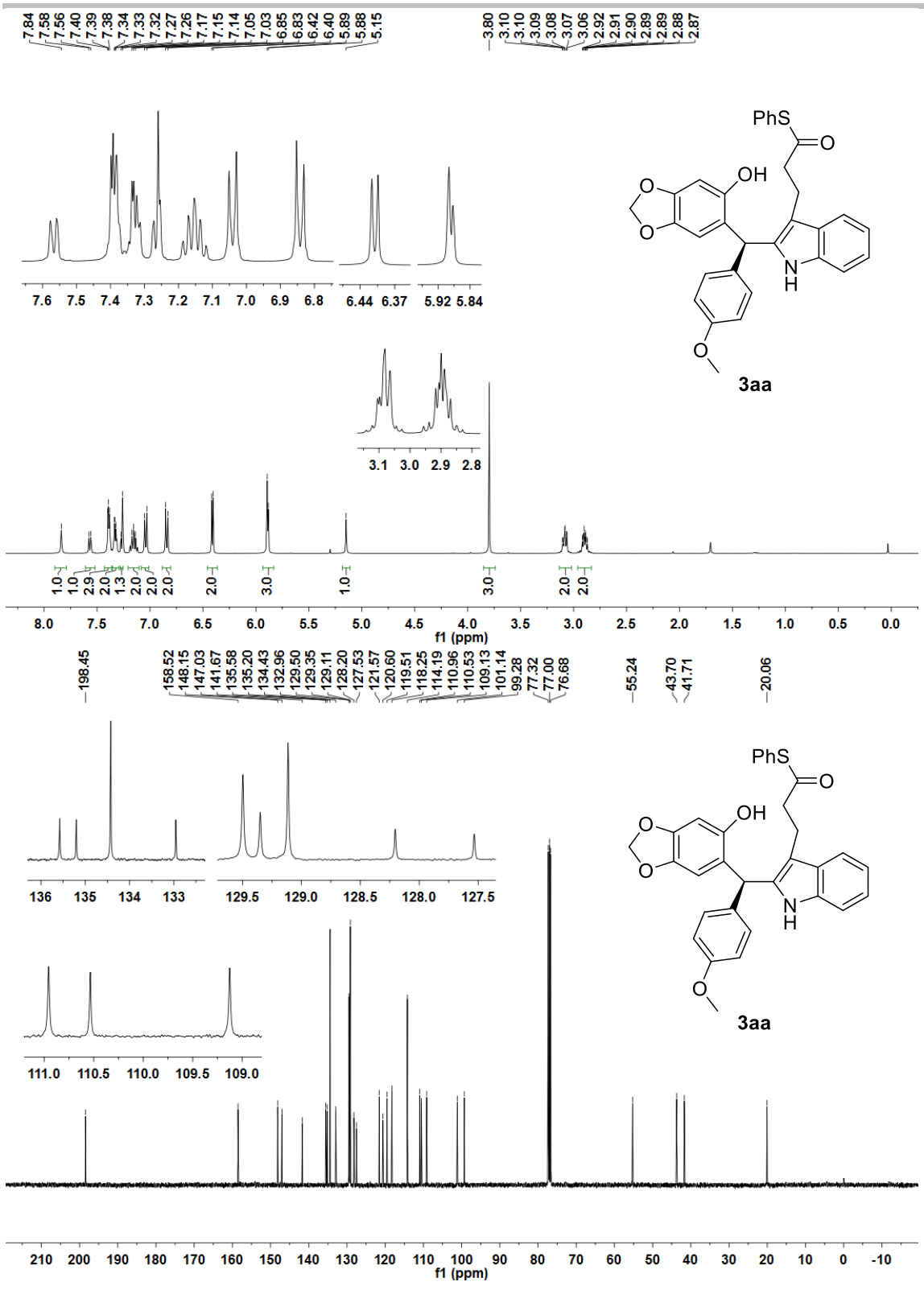

8.24 8.23 8.23 8.22 8.21 8.21 8.03 7.62 7.60 7.56 7.55 7.55 7.53 7.53 7.52 7.39 7.37 7.26 7.25 7.23 7.21 7.18 7.16 7.14 7.04 7.04
3.24 3.22 3.20 3.13 3.11 3.10
8.24 8.20
7.60 7.55
7.40 7.35
7.25 7.20 7.15 7.10 7.05
O
S
NO2
N
H

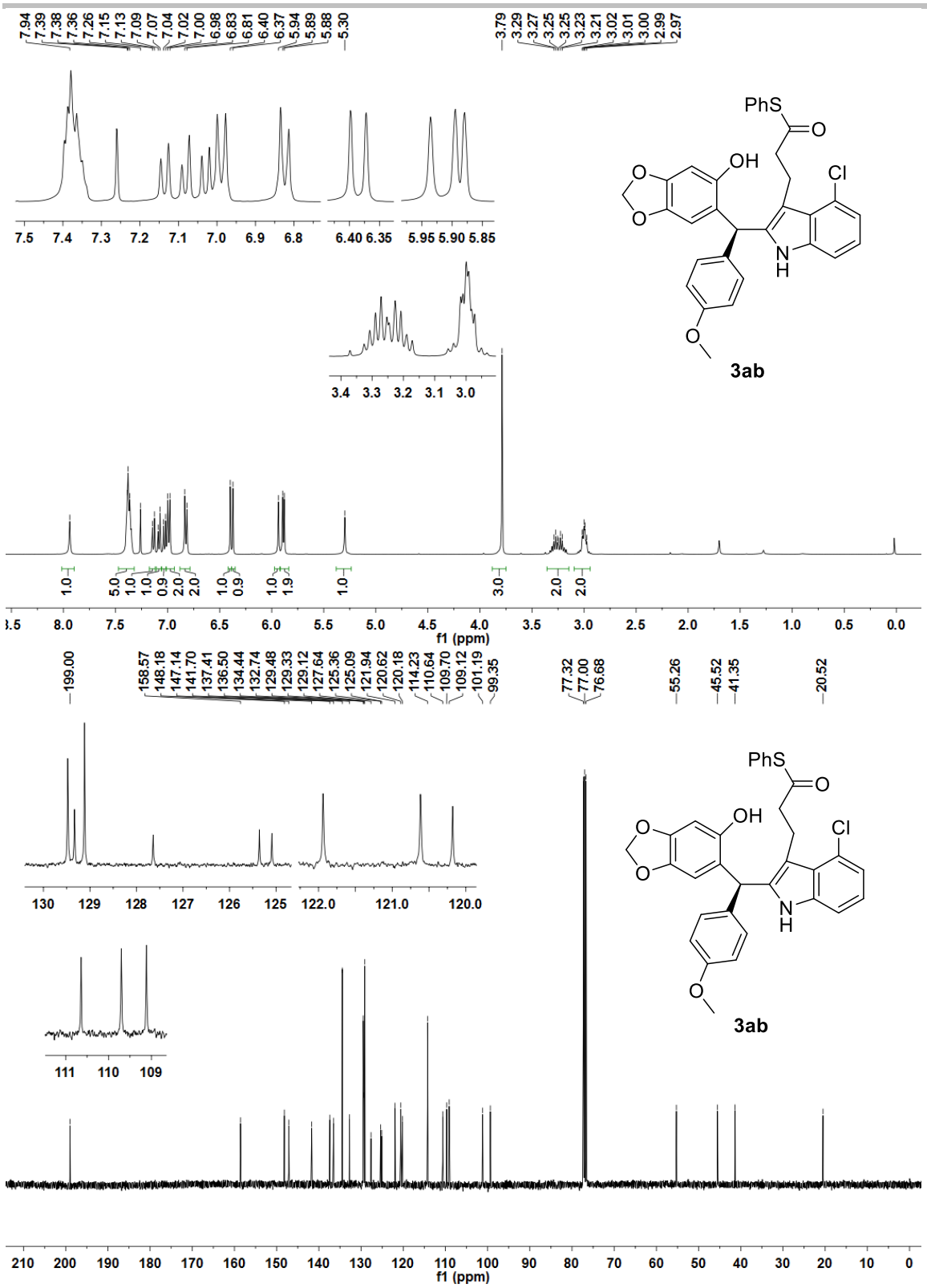
2t

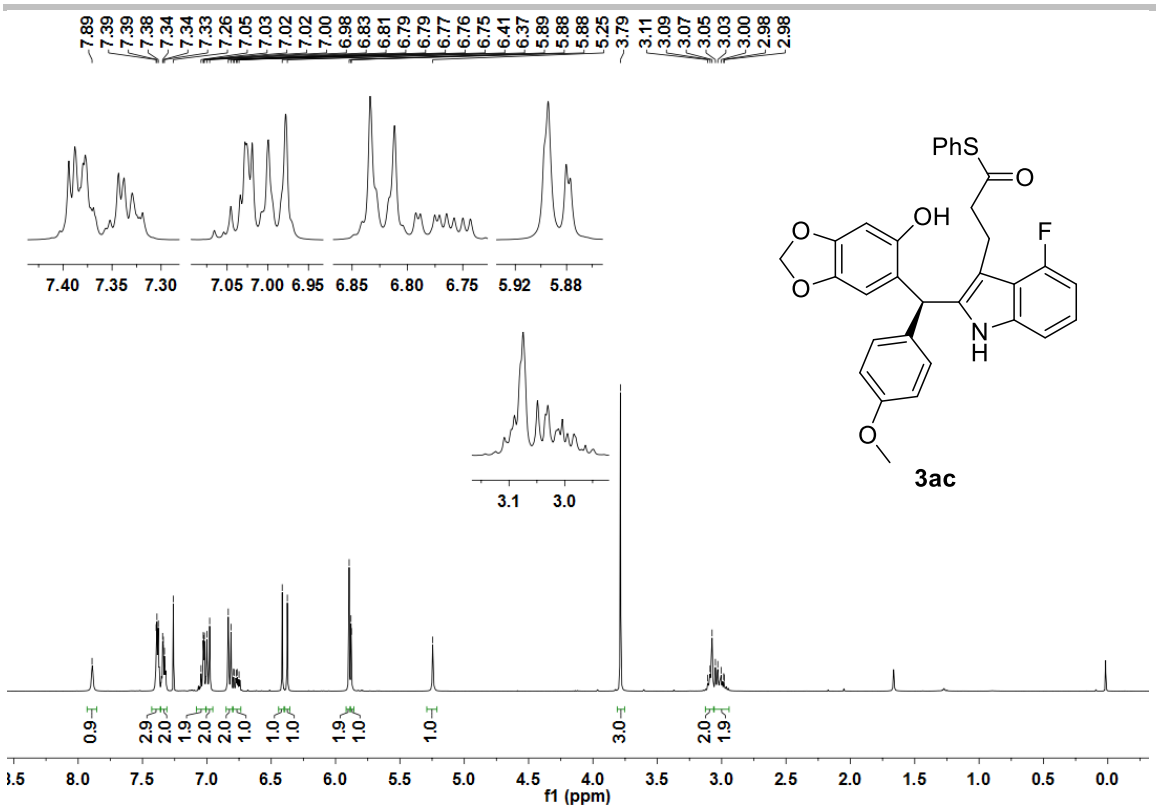

3.24 3.20
3.15 3.10
2.0 0.9 1.0 2.0 1.0 1.0 1.0 1.0 2.0 2.0
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

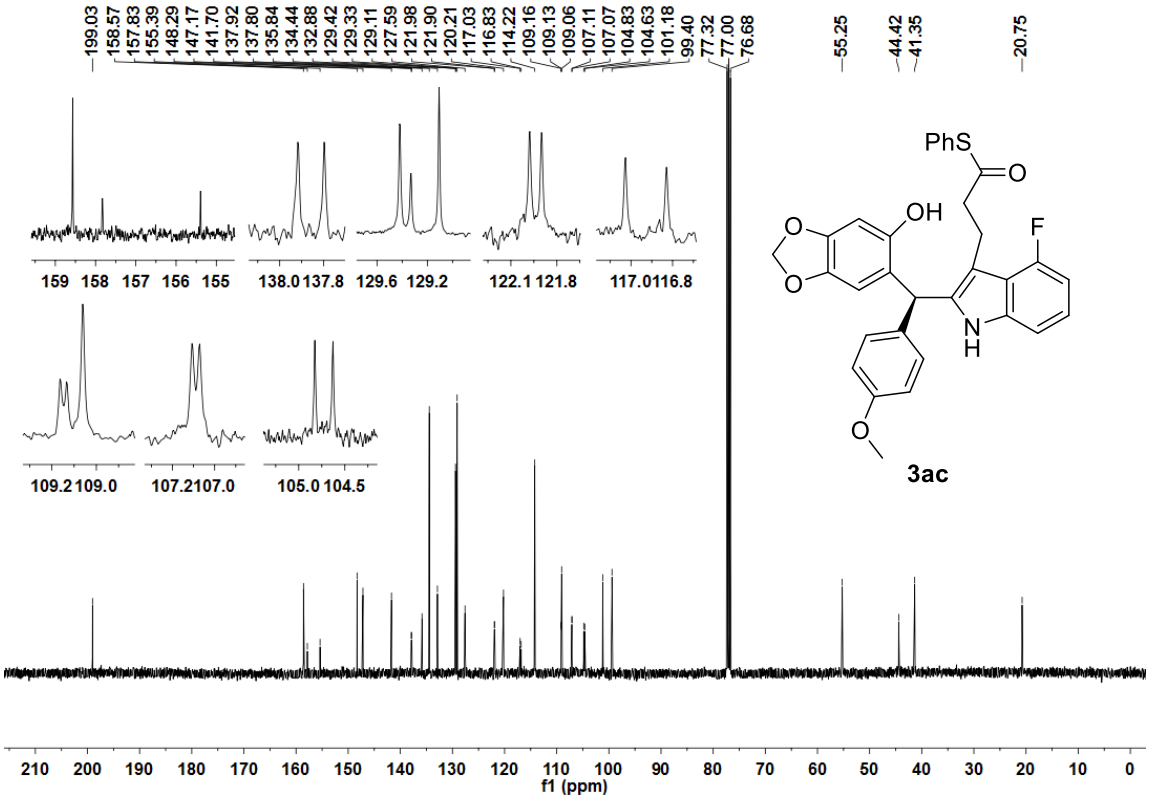

194.94
148.00 136.27 136.23 134.64 126.94 123.86 122.23 121.71 119.50 118.54 113.88 111.24
77.32 77.00 76.68
44.74
21.09
136.3 136.2
O
S
NO2
N
H
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

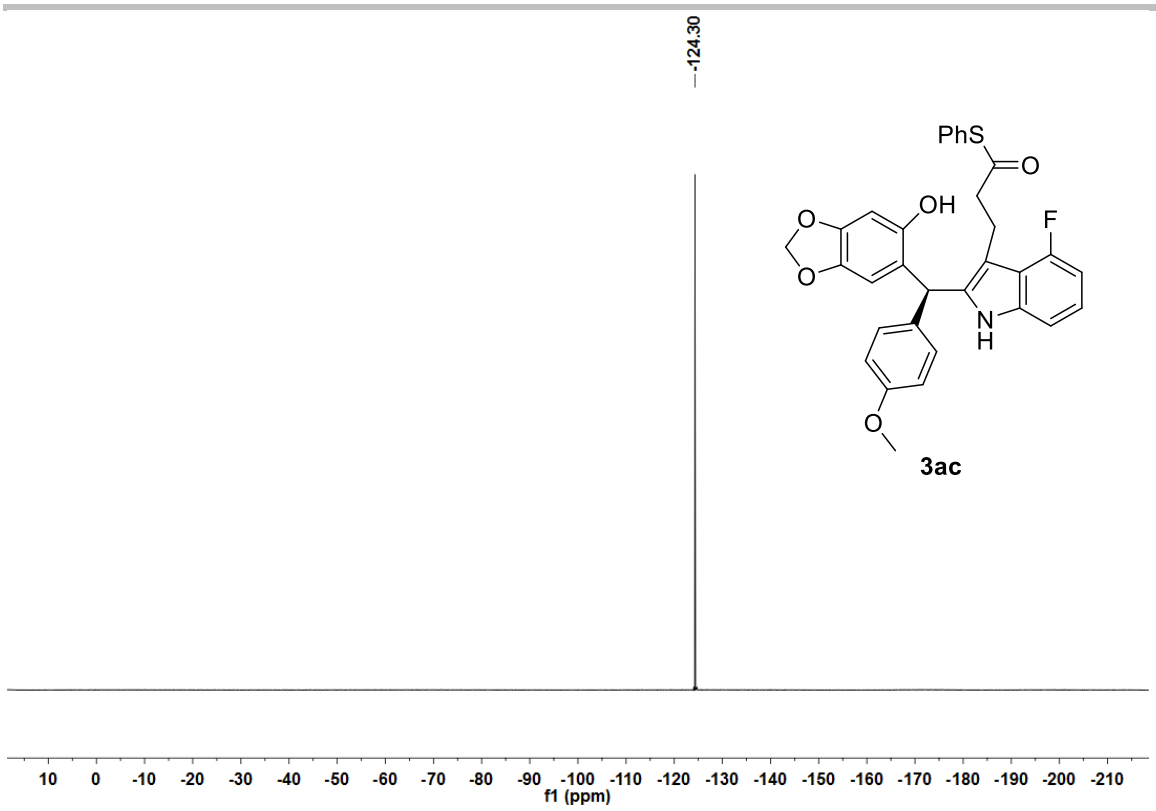
2t

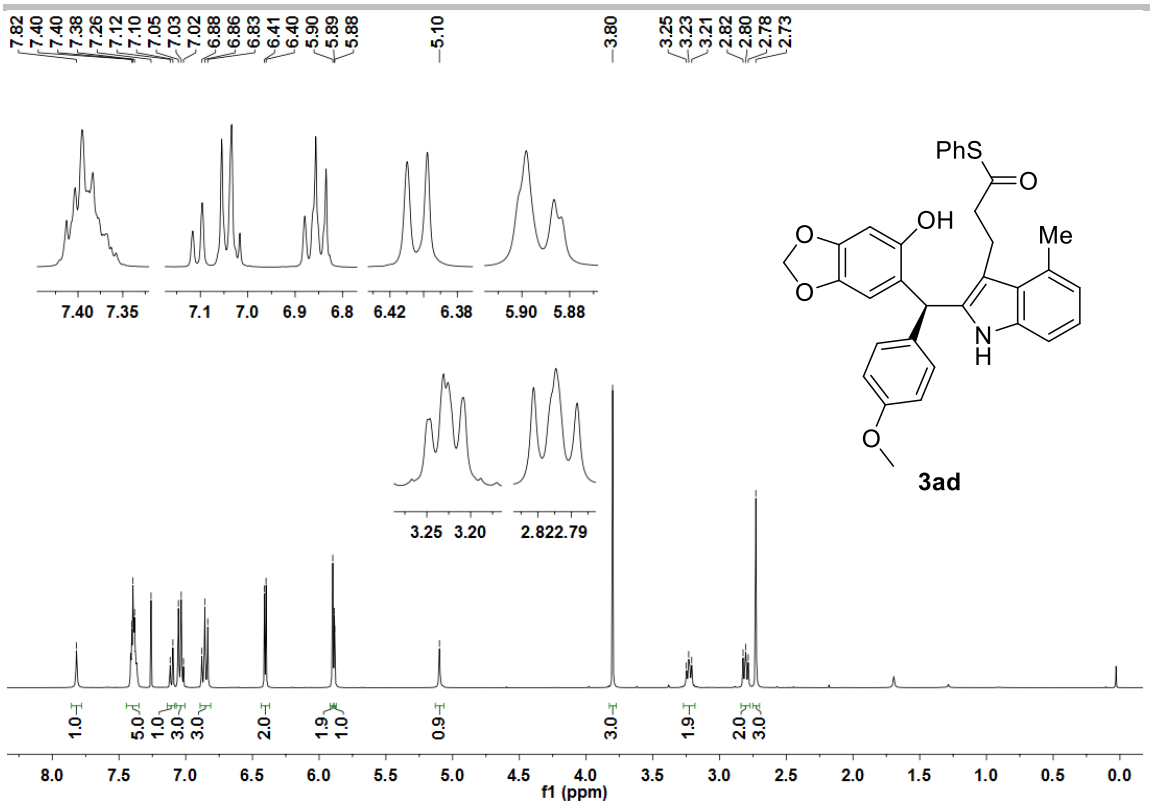

7.84 7.58 7.56 7.40 7.39 7.38 7.34 7.33 7.32 7.27 7.26 7.17 7.15 7.14 7.05 7.03 6.85 6.83 6.42 6.40 5.89 5.88 5.15
3.80 3.10 3.10 3.09 3.08 3.07 3.06 2.92 2.91 2.90 2.89 2.89 2.88 2.87
PhS
O
OH
O
O
N
H
O
3aa
f1 (ppm)
198.45 158.52 148.15 147.03 141.67 135.58 135.20 134.43 132.96 129.50 129.35 129.11 128.20 127.53 121.57 120.60 119.51 118.25 114.19 110.96 110.53 109.13 101.14 99.28 77.32 77.00 76.68 55.24 43.70 41.71 20.06
f1 (ppm)

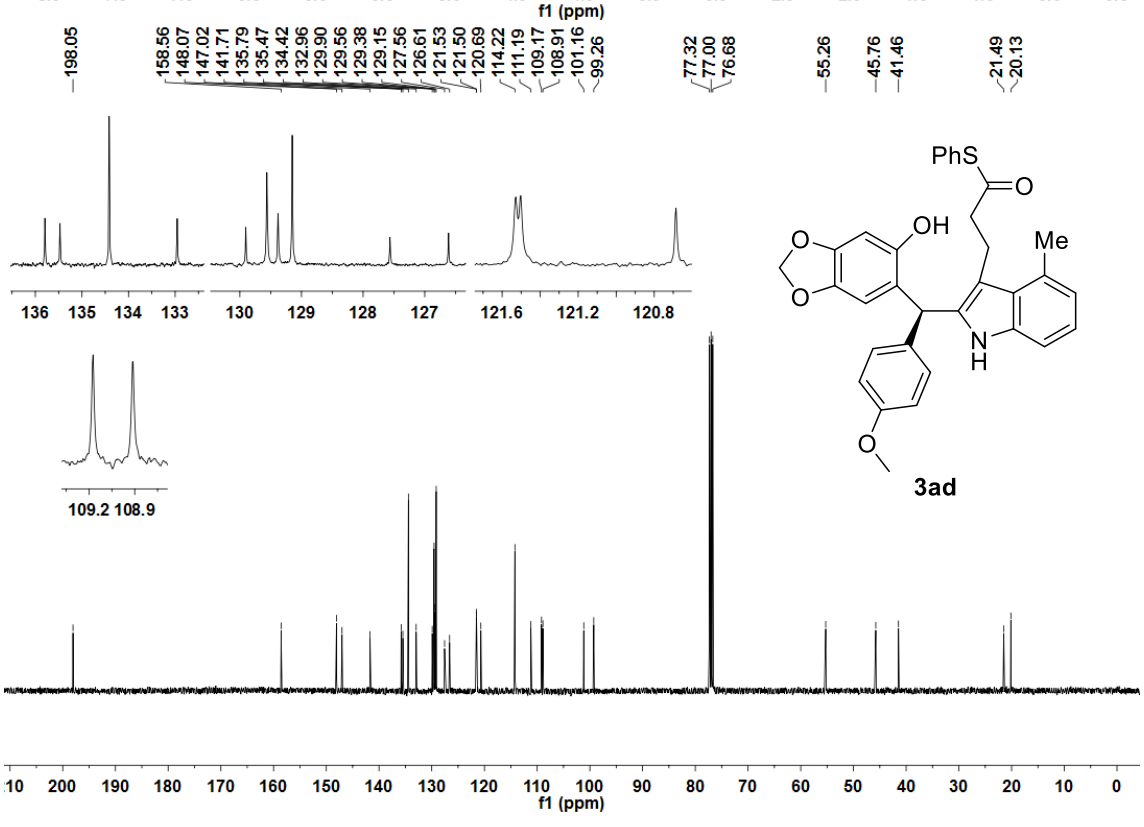

PhS
O
OH
Cl
O
O
N
H
O
3ab
f1 (ppm)
PhS
O
OH
Cl
O
O
N
H
O
3ab
f1 (ppm)

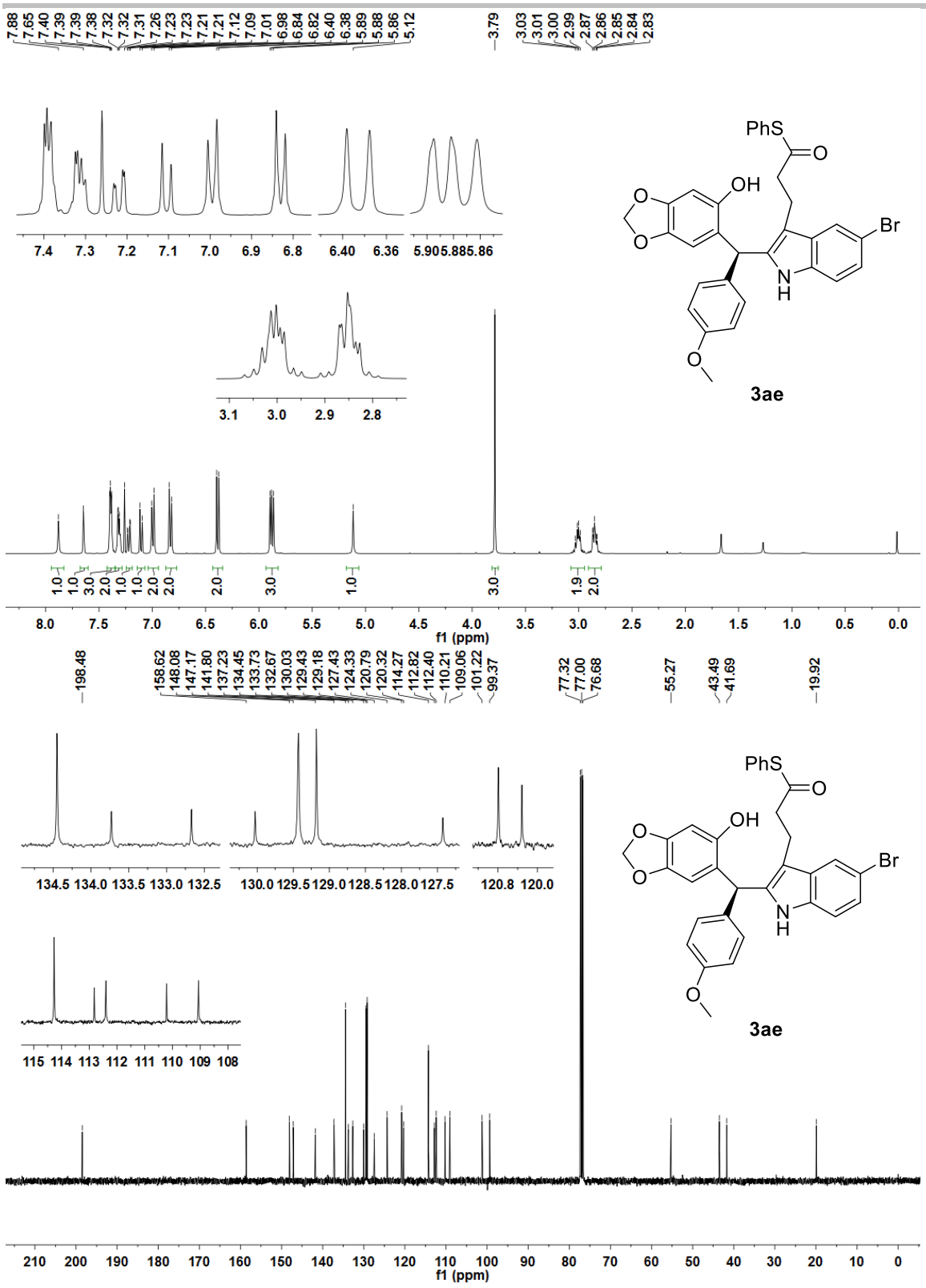

PhS
O
OH
F
O
O
N
H
O
3ac

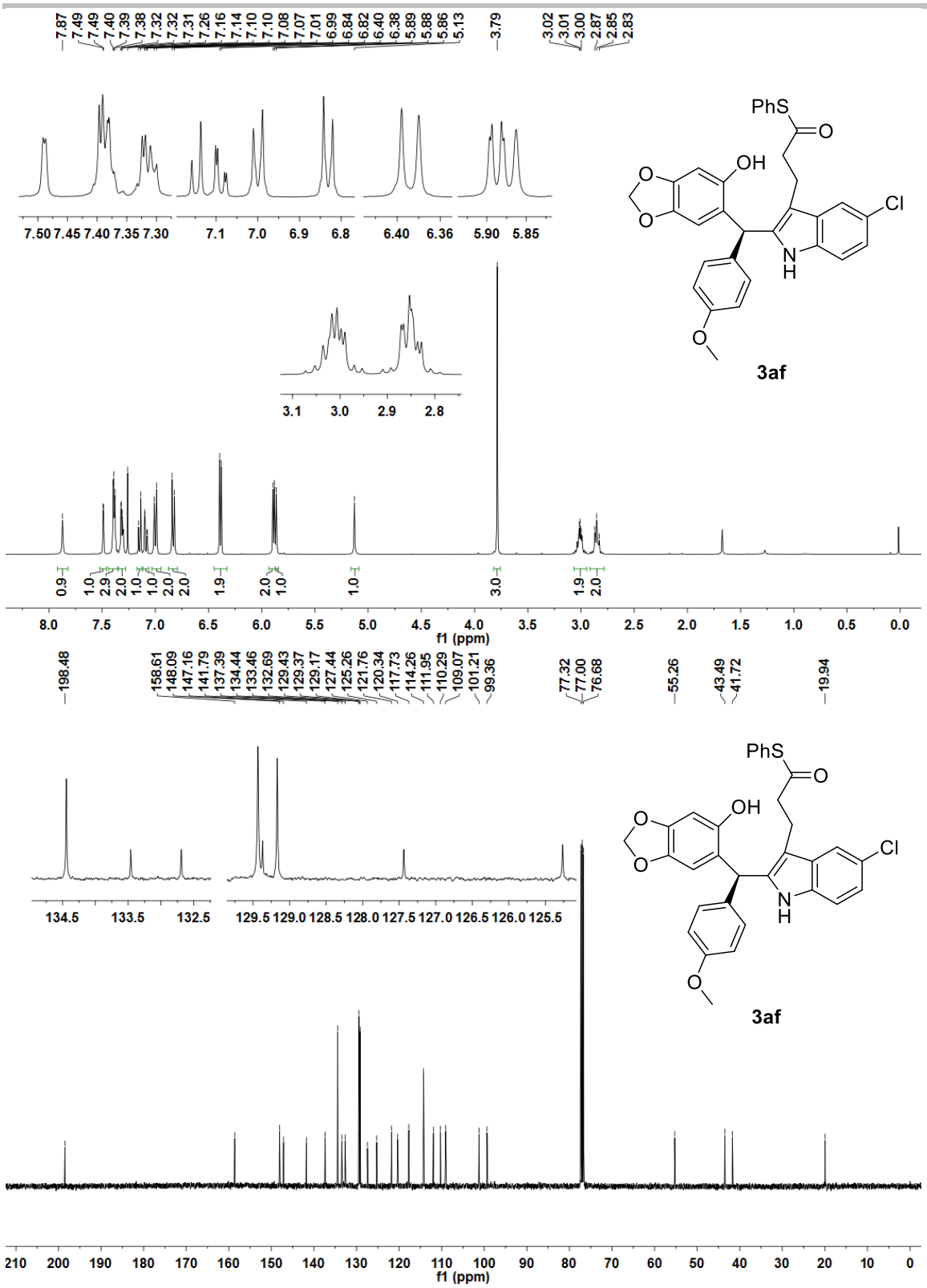

PhS
O
OH
F
O
O
N
H
O
3ac

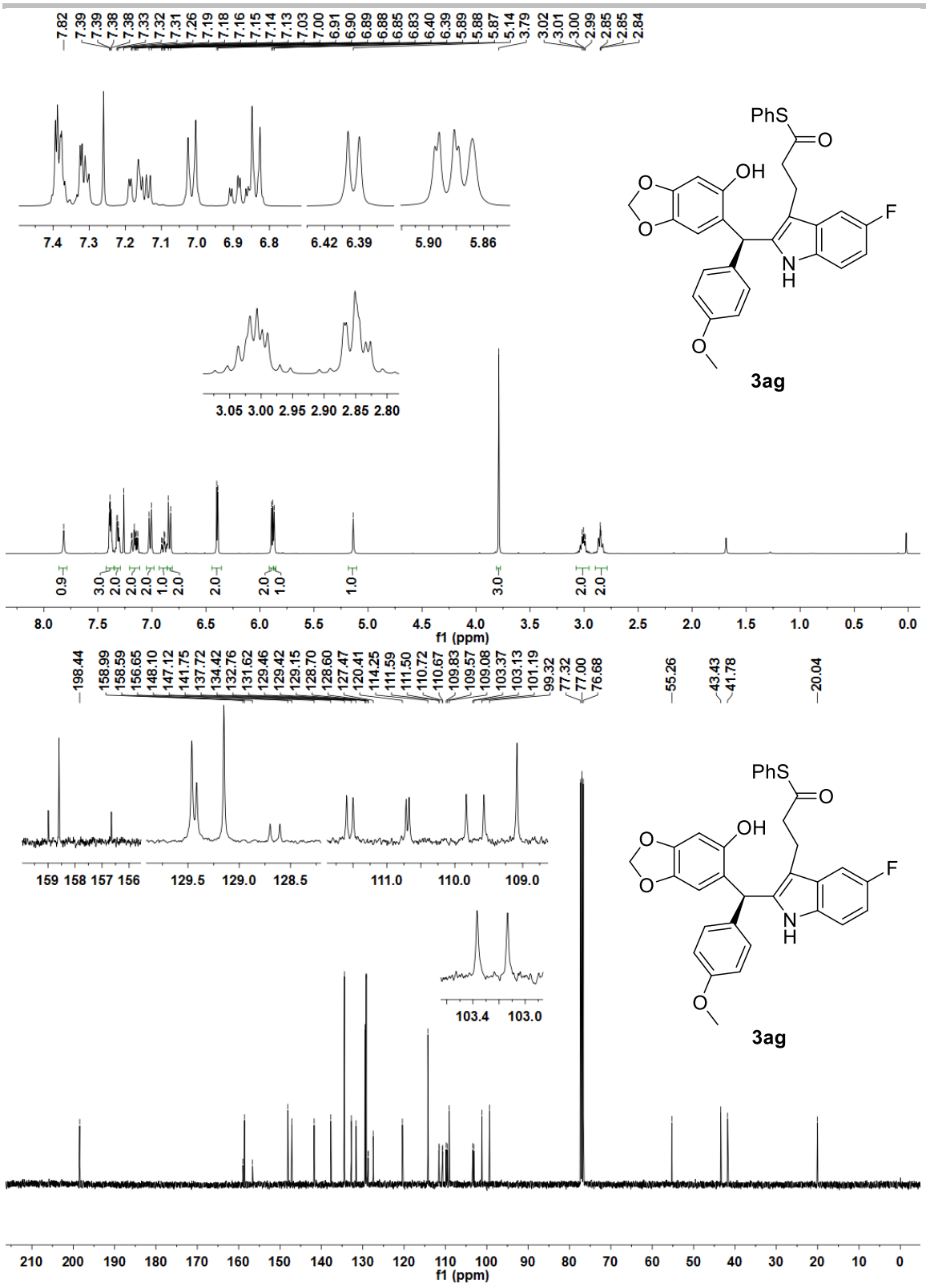

-124.30
PhS
O
OH
F
O
O
N
H
O
3ac
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

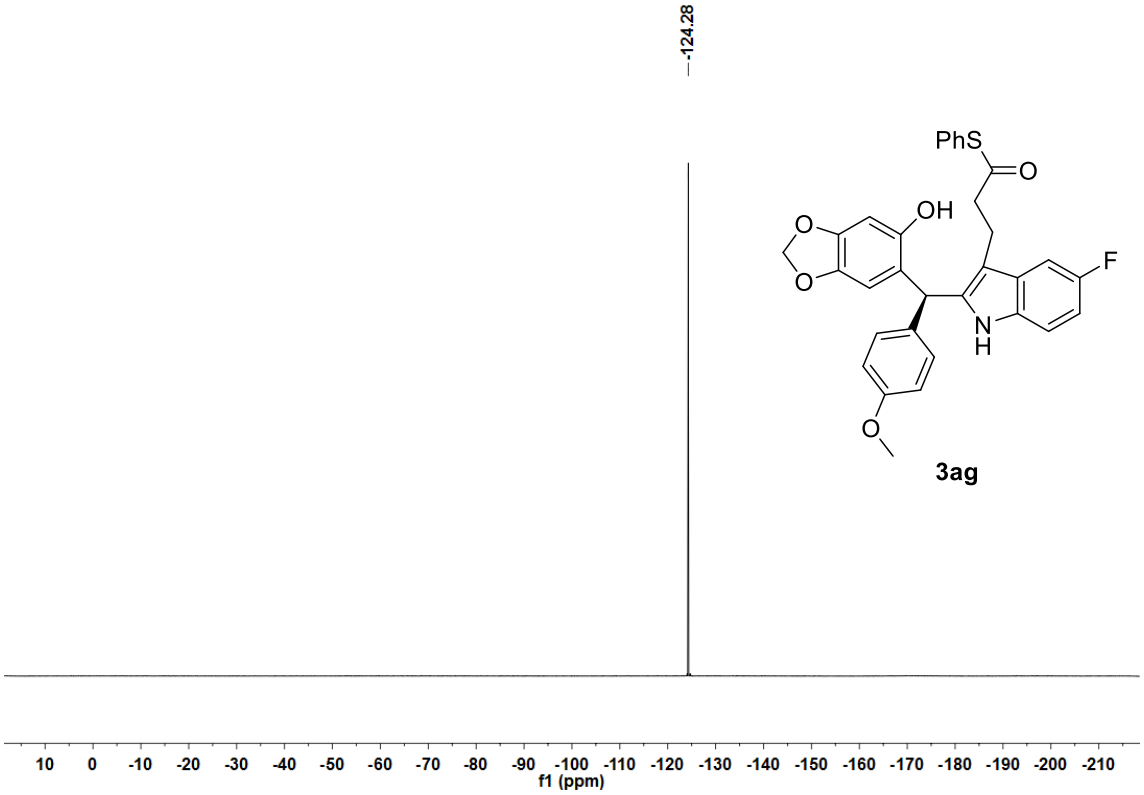

7.82 7.40 7.40 7.38 7.26 7.12 7.10 7.05 7.03 7.02 6.88 6.86 6.83 6.41 6.40 5.90 5.89 5.88
5.10
3.80
3.25 3.23 3.21 2.82 2.80 2.78 2.73
7.40 7.35
7.1 7.0 6.9 6.8
6.42 6.38
5.90 5.88
3.25 3.20
2.822.79
PhS
O
OH
Me
O
O
N
H
O
3ad
1.0 5.0 1.0 3.0 3.0 2.0 1.9 1.0 0.9 3.0 1.9 2.0 3.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

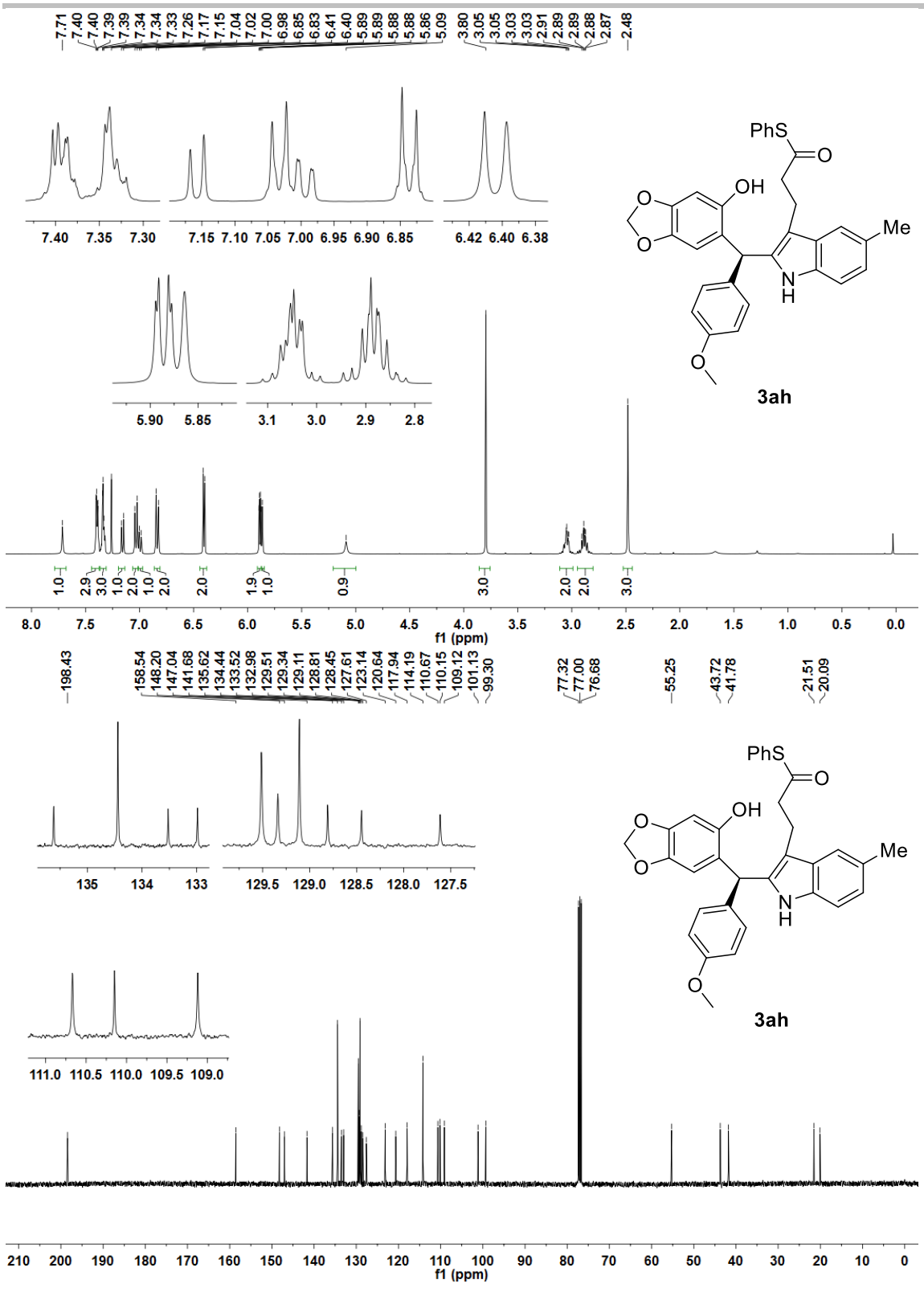

198.05
158.56 148.07 147.02 141.71 135.79 135.47 134.42 132.96 129.90 129.56 129.38 129.15 127.56 126.61 121.53 121.50 120.69 114.22 111.19 109.17 108.91 101.16 99.26
77.32 77.00 76.68
55.26
45.76 41.46
21.49 20.13
136 135 134 133
130 129 128 127
121.6 121.2 120.8
109.2 108.9
PhS
O
OH
Me
O
O
N
H
O
3ad
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

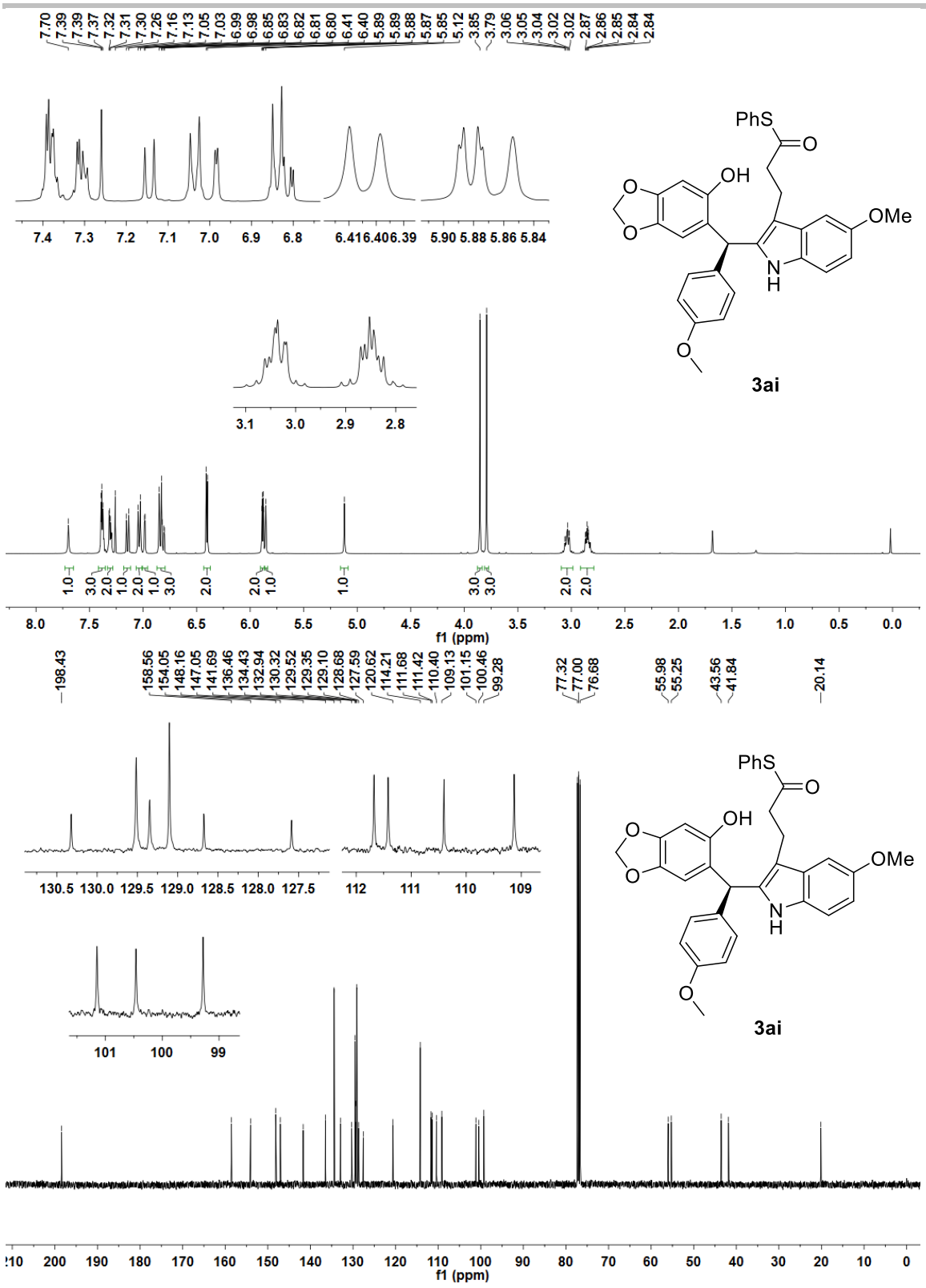

7.88 7.65 7.40 7.39 7.39 7.38 7.32 7.32 7.31 7.26 7.23 7.23 7.21 7.21 7.12 7.09 7.01 6.98 6.84 6.82 6.40 6.38 5.89 5.88 5.86 5.12
3.79
3.03 3.01 3.00 2.99 2.87 2.86 2.85 2.84 2.83
PhS
O
OH
O
O
Br
N
H
O
3ae
1.0 1.0 3.0 2.0 1.0 2.0 2.0 2.0 3.0 1.0 3.0 1.9 2.0
f1 (ppm)
198.48
158.62 148.08 147.17 141.80 137.23 134.45 133.73 132.67 130.03 129.43 129.18 127.43 124.33 120.79 120.32 114.27 112.82 112.40 110.21 109.06 101.22 99.37
77.32 77.00 76.68
55.27
43.49 41.69
19.92
134.5 134.0 133.5 133.0 132.5
130.0 129.5 129.0 128.5 128.0 127.5
120.8 120.0
115 114 113 112 111 110 109 108
f1 (ppm)

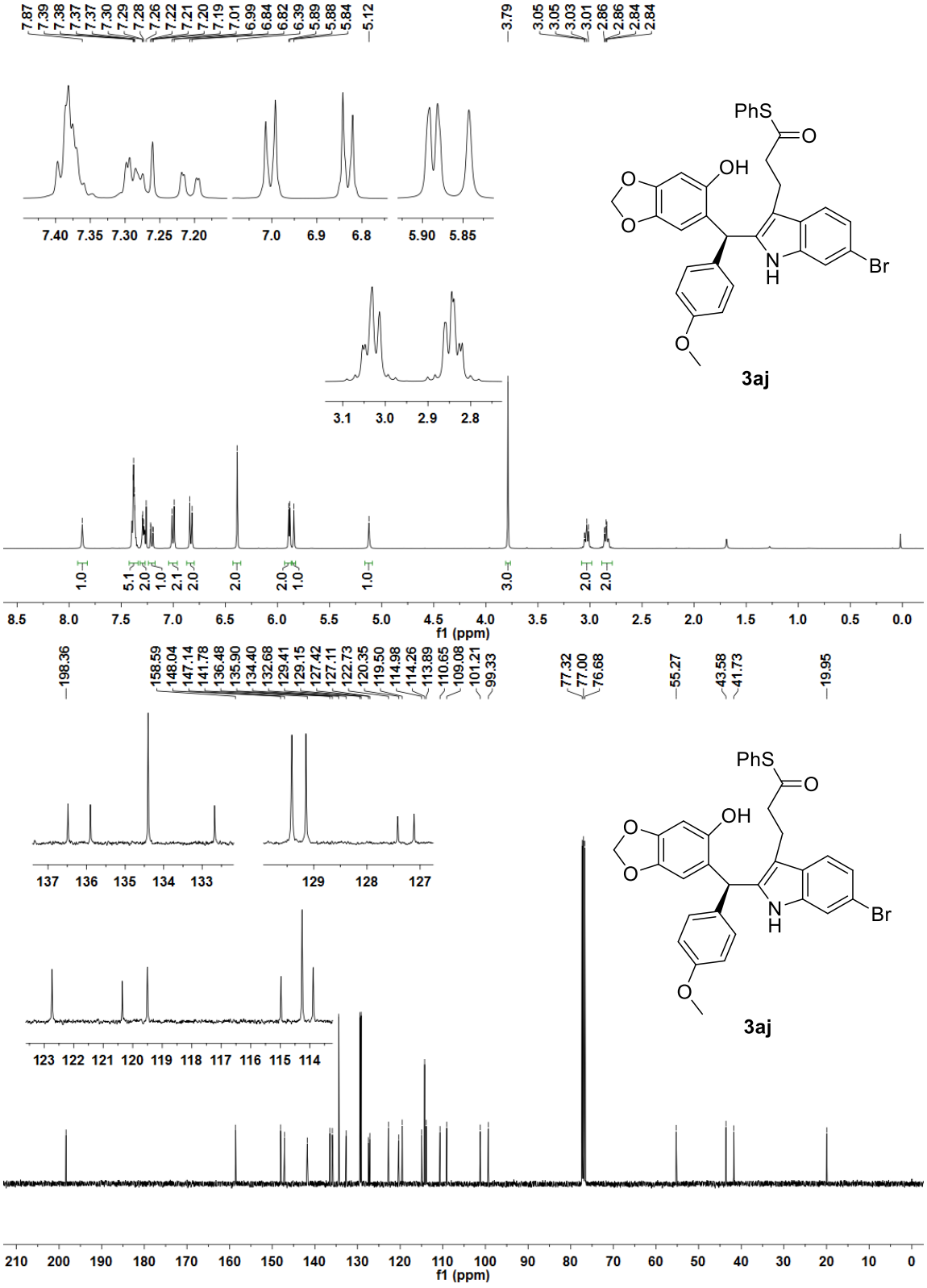

7.87 7.49 7.49 7.40 7.39 7.38 7.32 7.32 7.31 7.26 7.16 7.14 7.10 7.10 7.08 7.07 7.01 6.99 6.84 6.82 6.40 6.38 5.89 5.88 5.86 5.13 3.79 3.02 3.01 3.00 2.87 2.85 2.83
7.50 7.45 7.40 7.35 7.30 7.1 7.0 6.9 6.8 6.40 6.36 5.90 5.85
3.1 3.0 2.9 2.8
PhS O OH O O Cl N H O
3af
0.9 1.0 2.9 2.0 1.0 1.0 2.0 2.0 1.9 2.0 1.0 1.0 3.0 1.9 2.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
198.48 158.61 148.09 147.16 141.79 137.39 134.44 133.46 132.69 129.43 129.37 129.17 127.44 125.26 121.76 120.34 117.73 114.26 111.95 110.29 109.07 101.21 99.36 77.32 77.00 76.68 55.26 43.49 41.72 19.94
134.5 133.5 132.5 129.5 129.0 128.5 128.0 127.5 127.0 126.5 126.0 125.5
PhS O OH O O Cl N H O
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

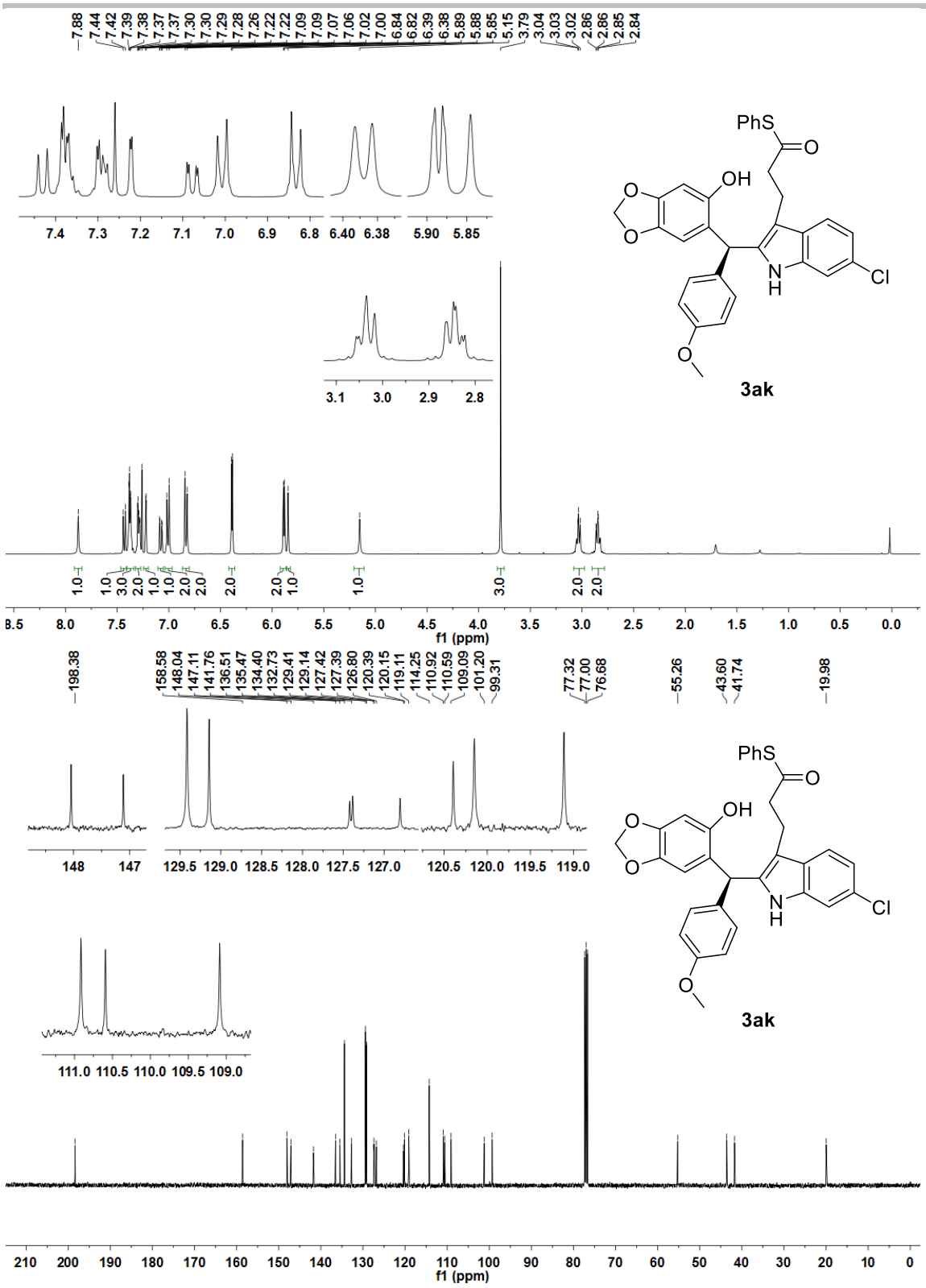

7.82 7.39 7.39 7.38 7.38 7.33 7.32 7.31 7.26 7.19 7.18 7.16 7.15 7.14 7.13 7.03 7.00 6.91 6.90 6.89 6.88 6.85 6.83 6.40 6.39 5.89 5.88 5.87 5.14 3.79 3.02 3.01 3.00 2.99 2.85 2.85 2.84
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.42 6.39 5.90 5.86
3.05 3.00 2.95 2.90 2.85 2.80
PhS
O
OH
O
O
F
N
H
O
3ag
0.9 3.0 2.0 2.0 2.0 1.0 2.0 2.0 1.0 1.0 3.0 2.0 2.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
198.44 158.99 158.59 156.65 148.10 147.12 141.75 137.72 134.42 132.76 131.62 129.46 129.42 129.15 128.70 128.60 127.47 120.41 114.25 111.59 111.50 110.72 110.67 109.83 109.57 109.08 103.37 103.13 101.19 99.32 77.32 77.00 76.68 55.26 43.43 41.78 20.04
159 158 157 156 129.5 129.0 128.5 111.0 110.0 109.0
103.4 103.0
PhS
O
OH
O
O
F
N
H
O
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


-124.28
PhS
O
OH
O
O
F
N
H
O
3ag
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


PhS
O
OH
O
O
Me
N
H
O
3ah
f1 (ppm)
PhS
O
OH
O
O
Me
N
H
O
3ah
f1 (ppm)


7.70 7.39 7.39 7.37 7.32 7.31 7.30 7.26 7.16 7.13 7.05 7.03 6.99 6.98 6.85 6.83 6.82 6.81 6.80 6.41 6.40 5.89 5.89 5.88 5.87 5.85 5.12 3.85 3.79 3.06 3.05 3.04 3.02 3.02 2.87 2.86 2.85 2.84 2.84
7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.41 6.40 6.39 5.90 5.88 5.86 5.84
3.1 3.0 2.9 2.8
1.0 3.0 2.0 1.0 2.0 1.0 3.0 2.0 2.0 1.0 1.0 3.0 3.0 2.0 2.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
PhS
O
OH
O
O
OMe
N
H
O
3ai
198.43 158.56 154.05 148.16 147.05 141.69 136.46 134.43 132.94 130.32 129.52 129.35 129.10 128.68 127.59 120.62 114.21 111.68 111.42 110.40 109.13 101.15 100.46 99.28 77.32 77.00 76.68 55.98 55.25 43.56 41.84 20.14
130.5 130.0 129.5 129.0 128.5 128.0 127.5
112 111 110 109
101 100 99
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.87 7.39 7.38 7.37 7.37 7.30 7.29 7.28 7.26 7.22 7.21 7.20 7.19 7.01 6.99 6.84 6.82 6.39 5.89 5.88 5.84 5.12
3.79 3.05 3.05 3.03 3.01 2.86 2.86 2.84 2.84
PhS
O
OH
O
O
N
H
Br
O
3aj
f1 (ppm)
198.36 158.59 148.04 147.14 141.78 136.48 135.90 134.40 132.68 129.41 129.15 127.42 127.11 122.73 120.35 119.50 114.98 114.26 113.89 110.65 109.08 101.21 99.33 77.32 77.00 76.68 55.27 43.58 41.73 19.95
f1 (ppm)


PhS
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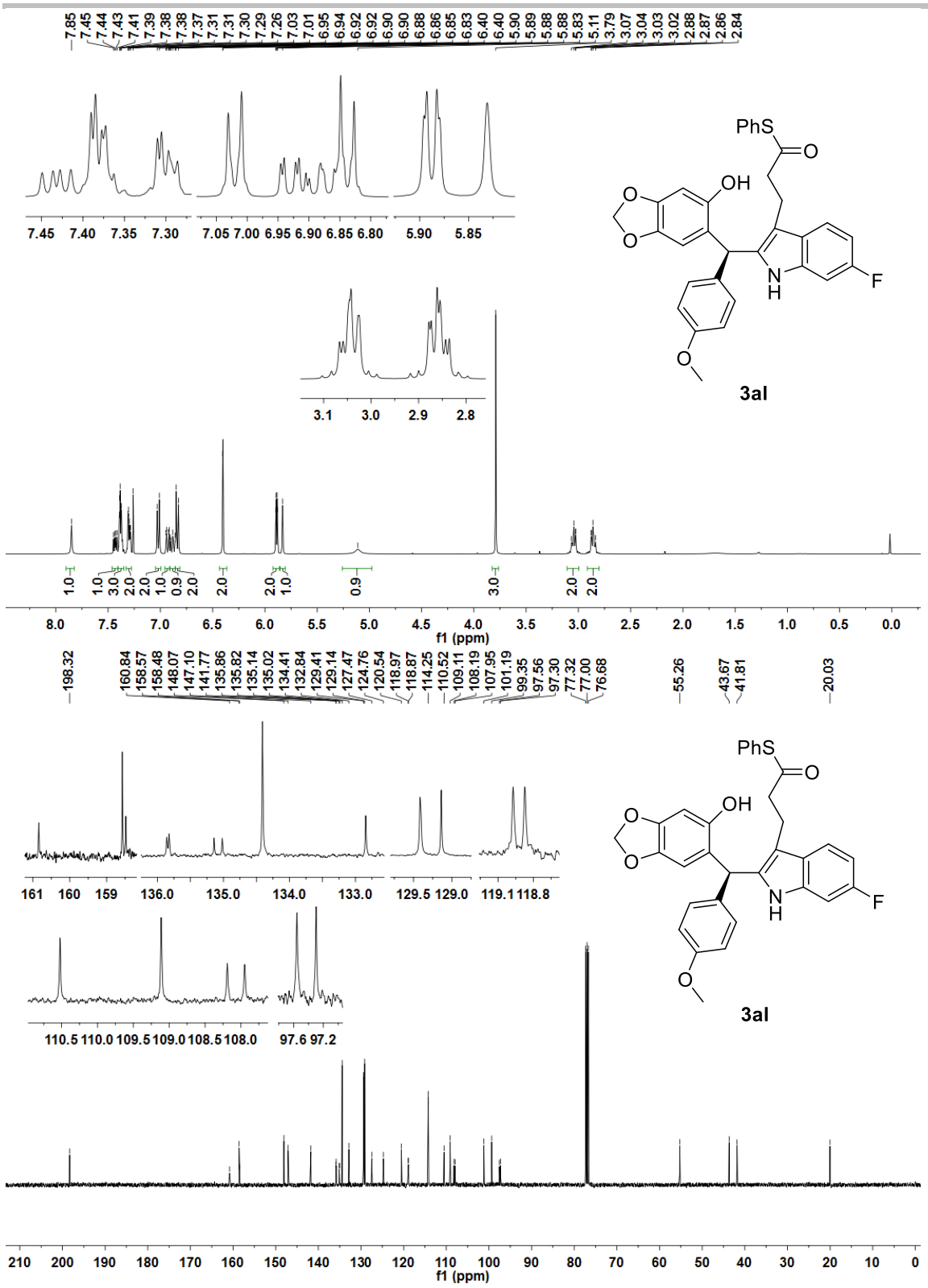
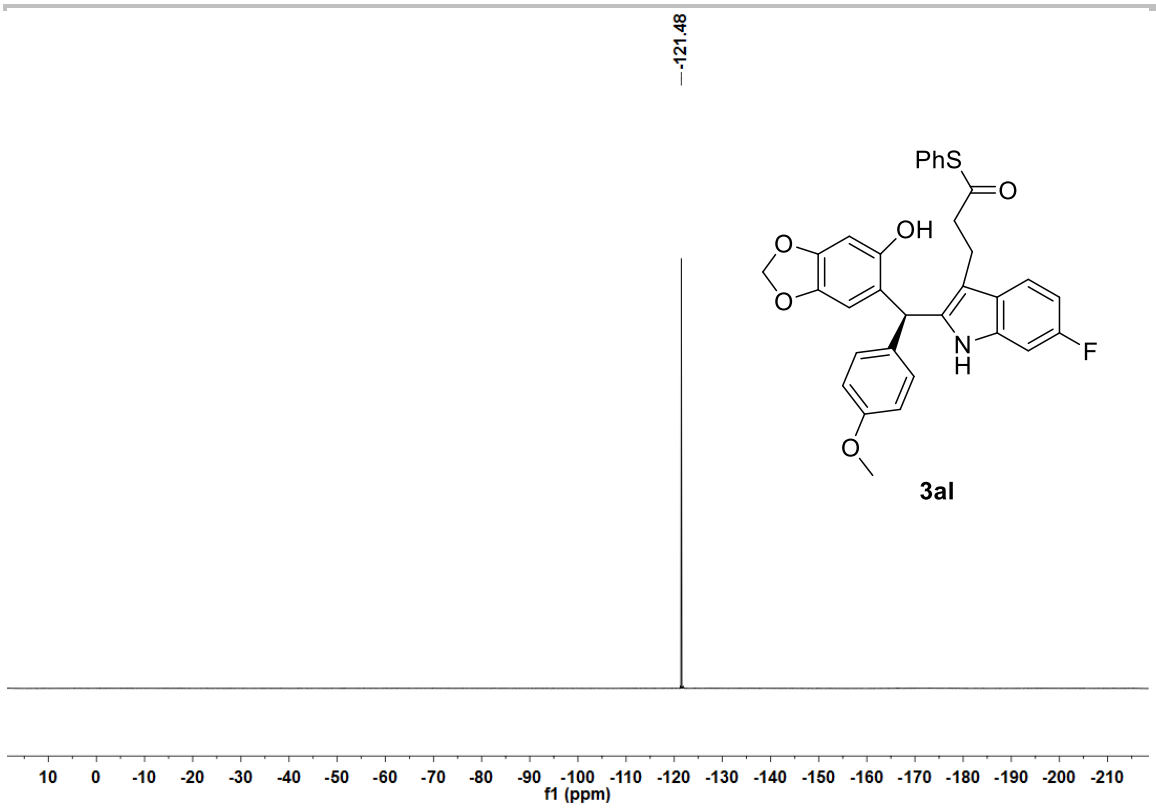
OH
O
O
N
H
Cl
O
3ak
f1 (ppm)
PhS
O
OH
O
O
N
H
Cl
O
3ak
f1 (ppm)


PhS
O
OH
O
O
N
H
F
O
3al
f1 (ppm)
PhS
O
OH
O
O
N
H
F
O
3al
f1 (ppm)


-121.48
PhS
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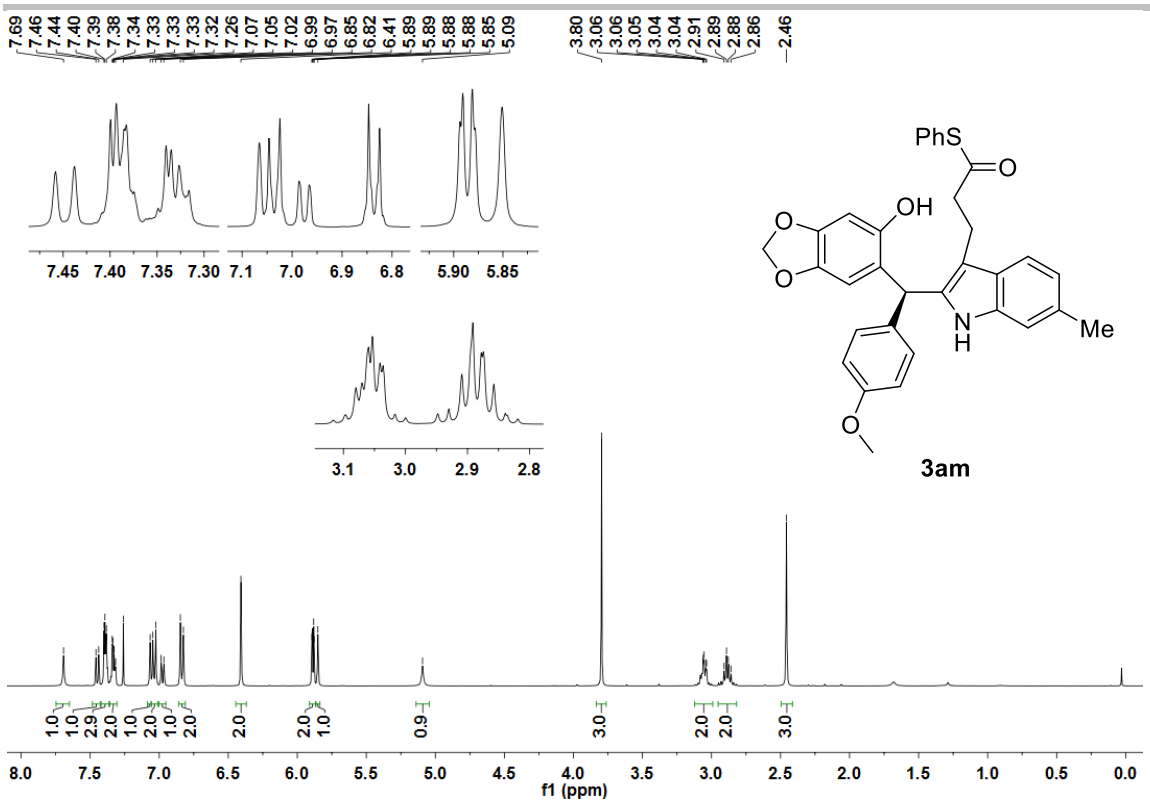
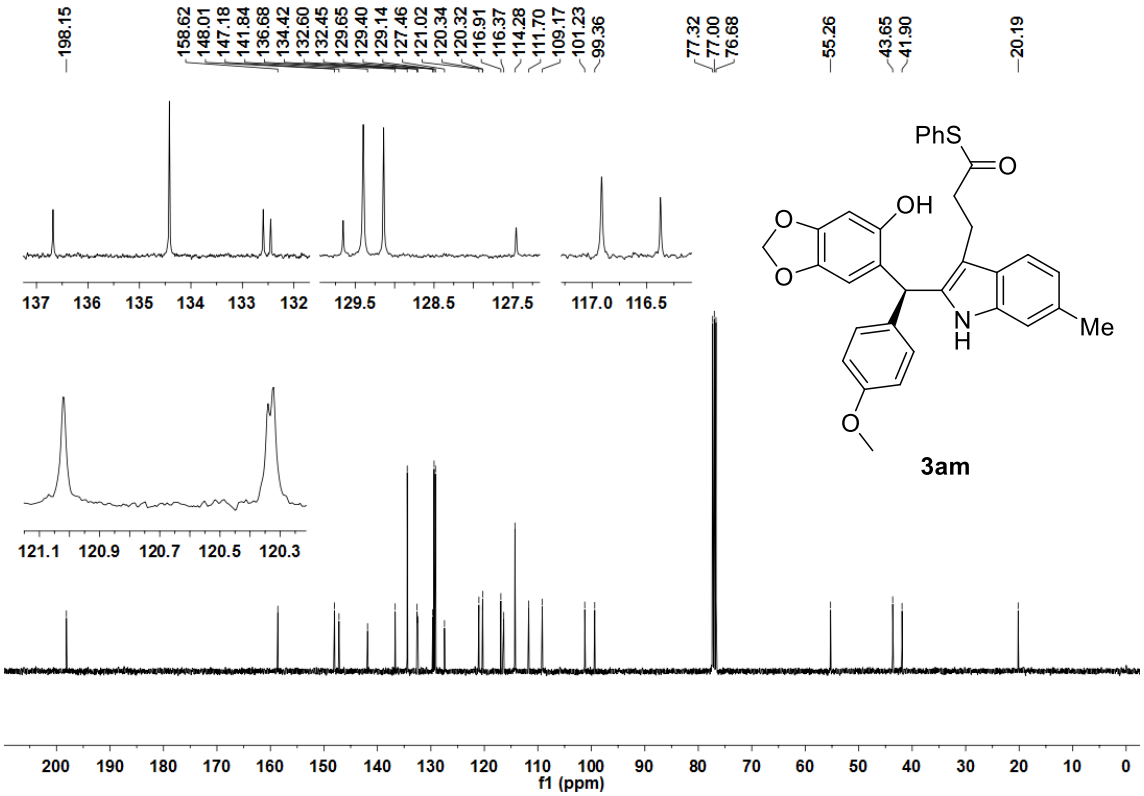
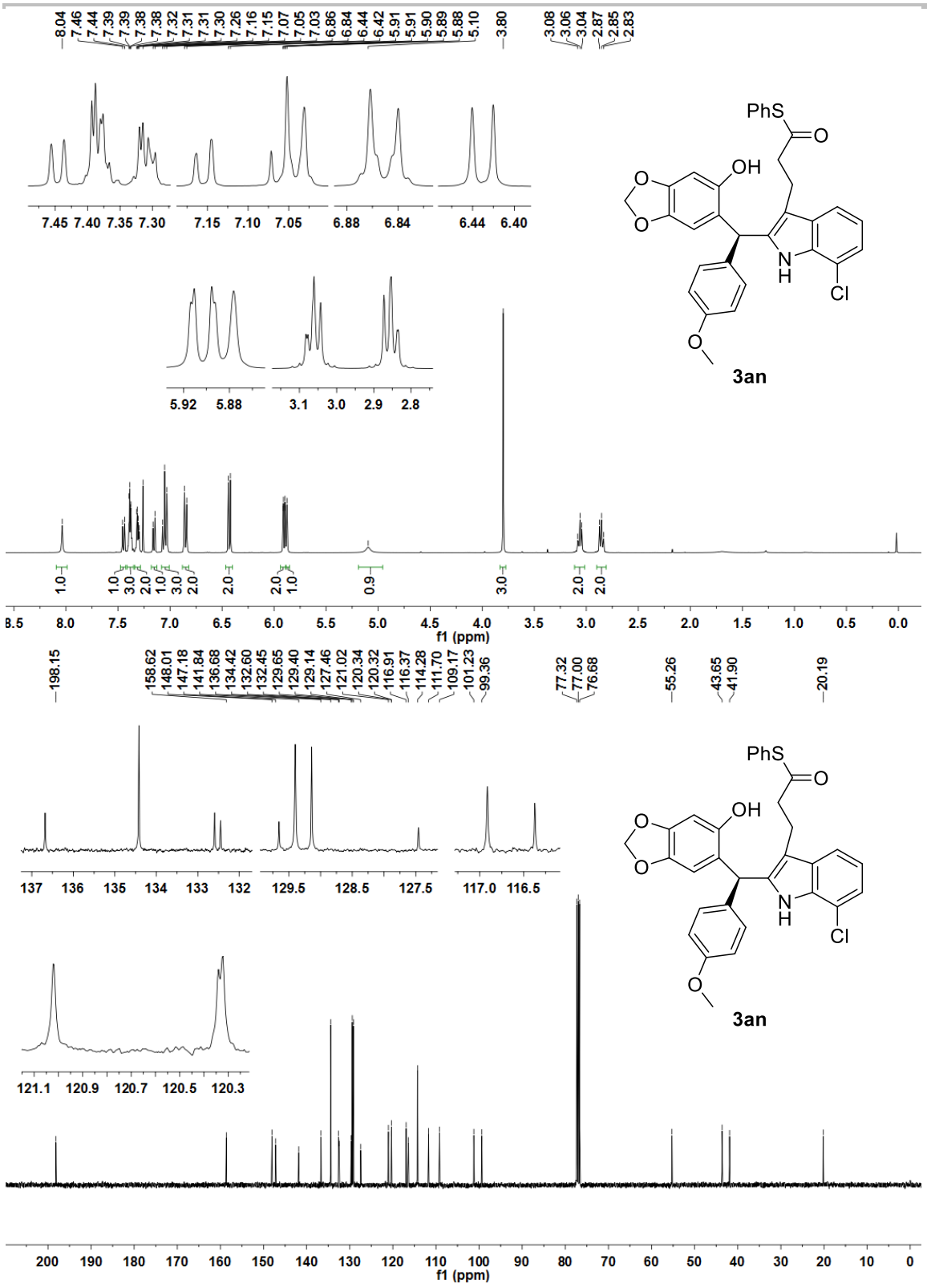
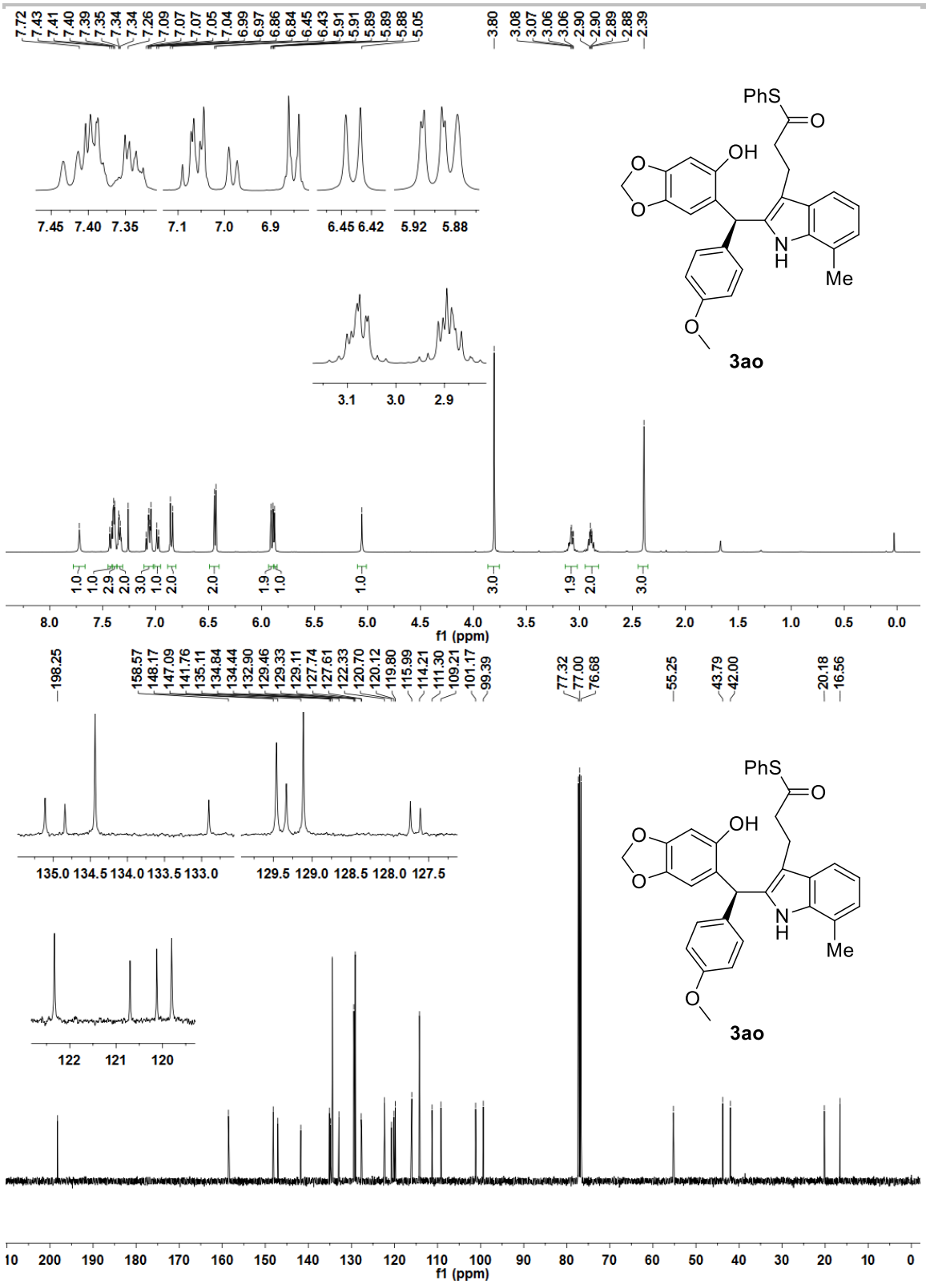
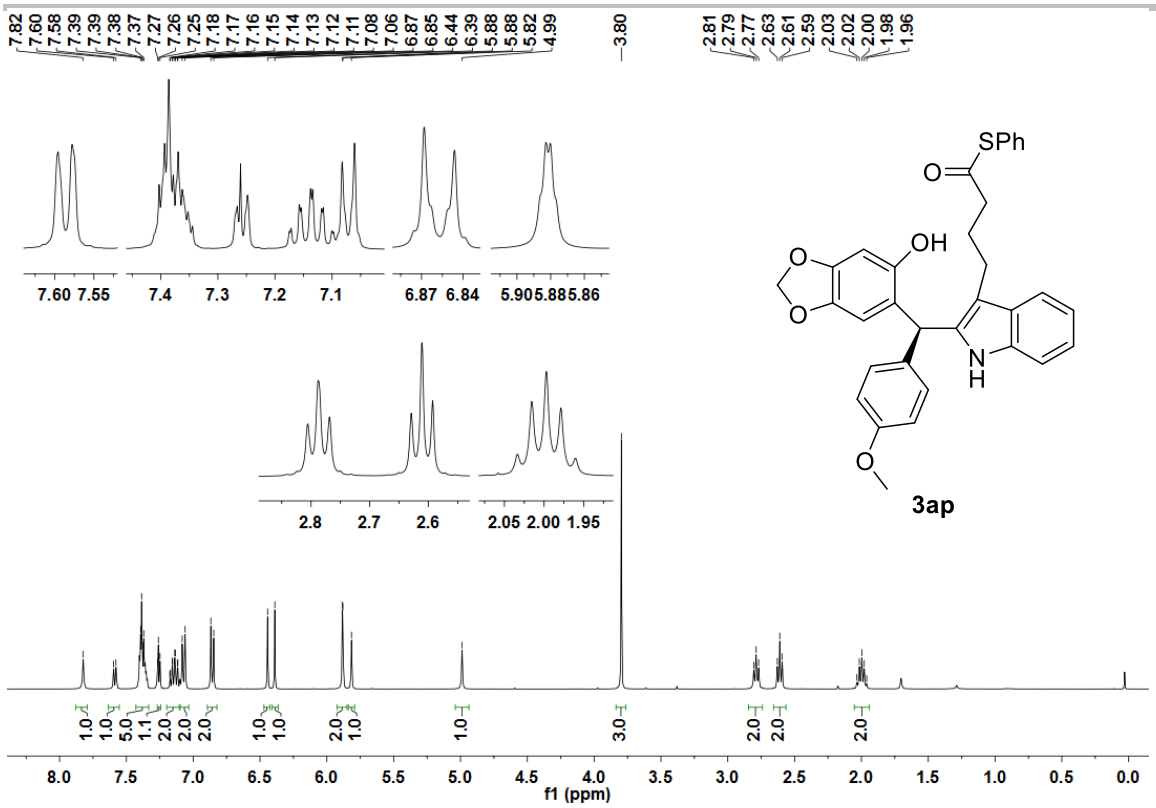
OH
O
O
N
H
F
O
3al
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

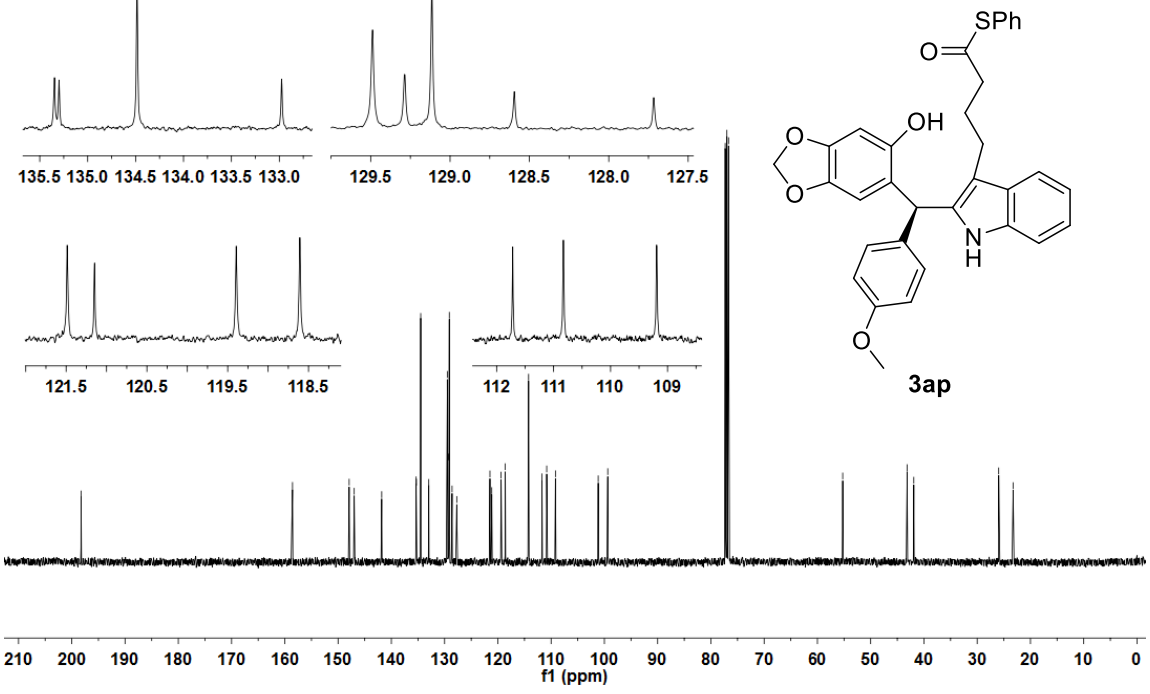

PhS
O
OH
O
O
N
H
Me
O
3am

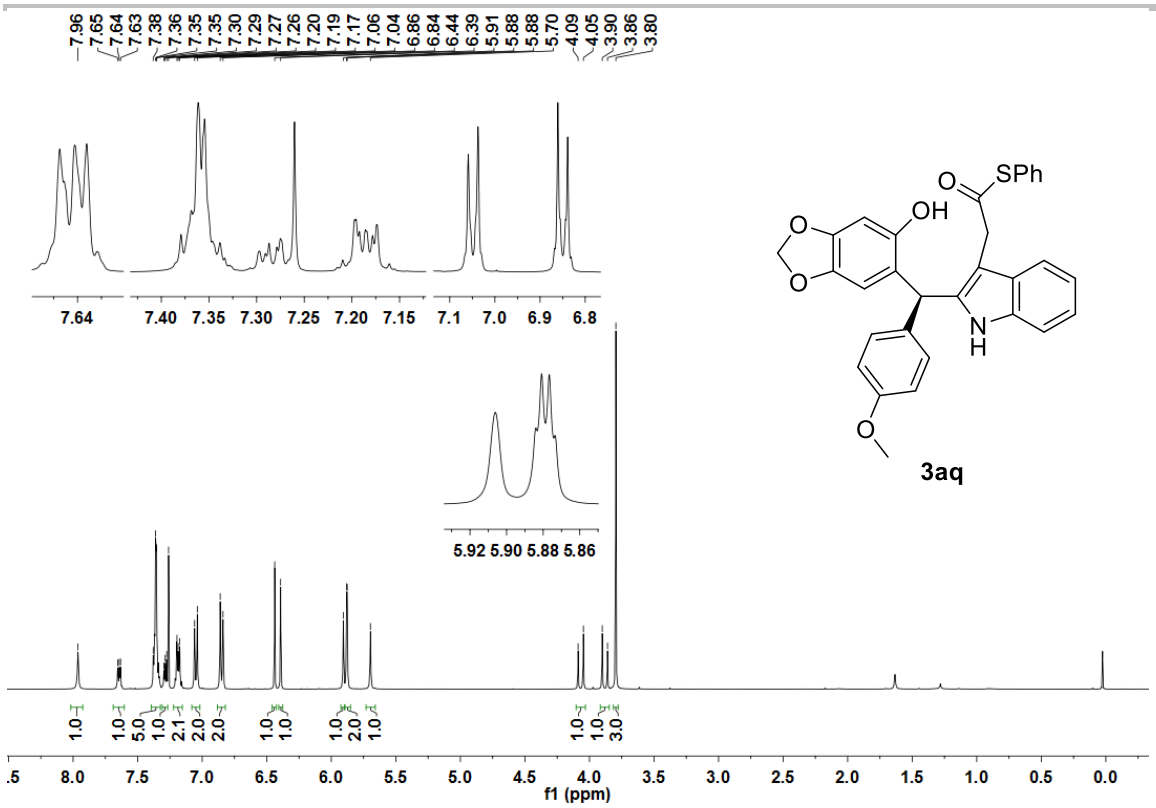

PhS
O
OH
O
O
N
H
Me
O
3am

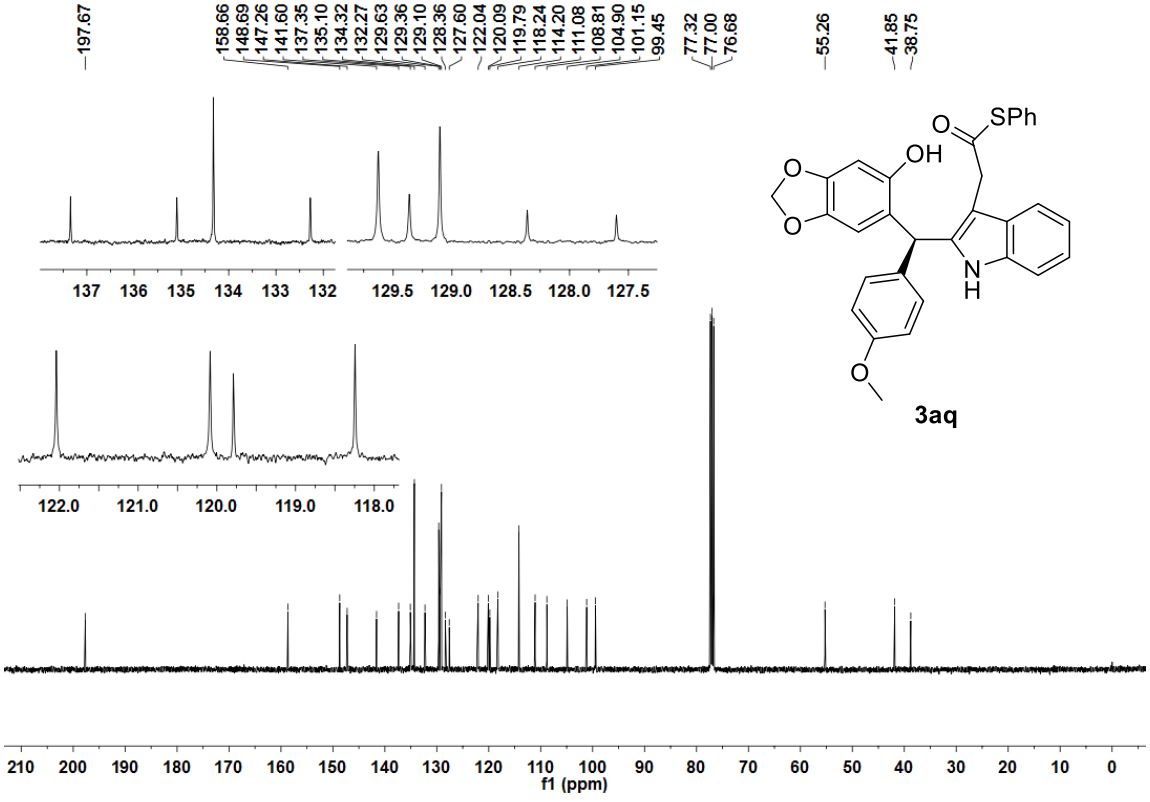

PhS
O
OH
O
O
N
H
Cl
O
3an
f1 (ppm)
PhS
O
OH
O
O
N
H
Cl
O
3an
f1 (ppm)

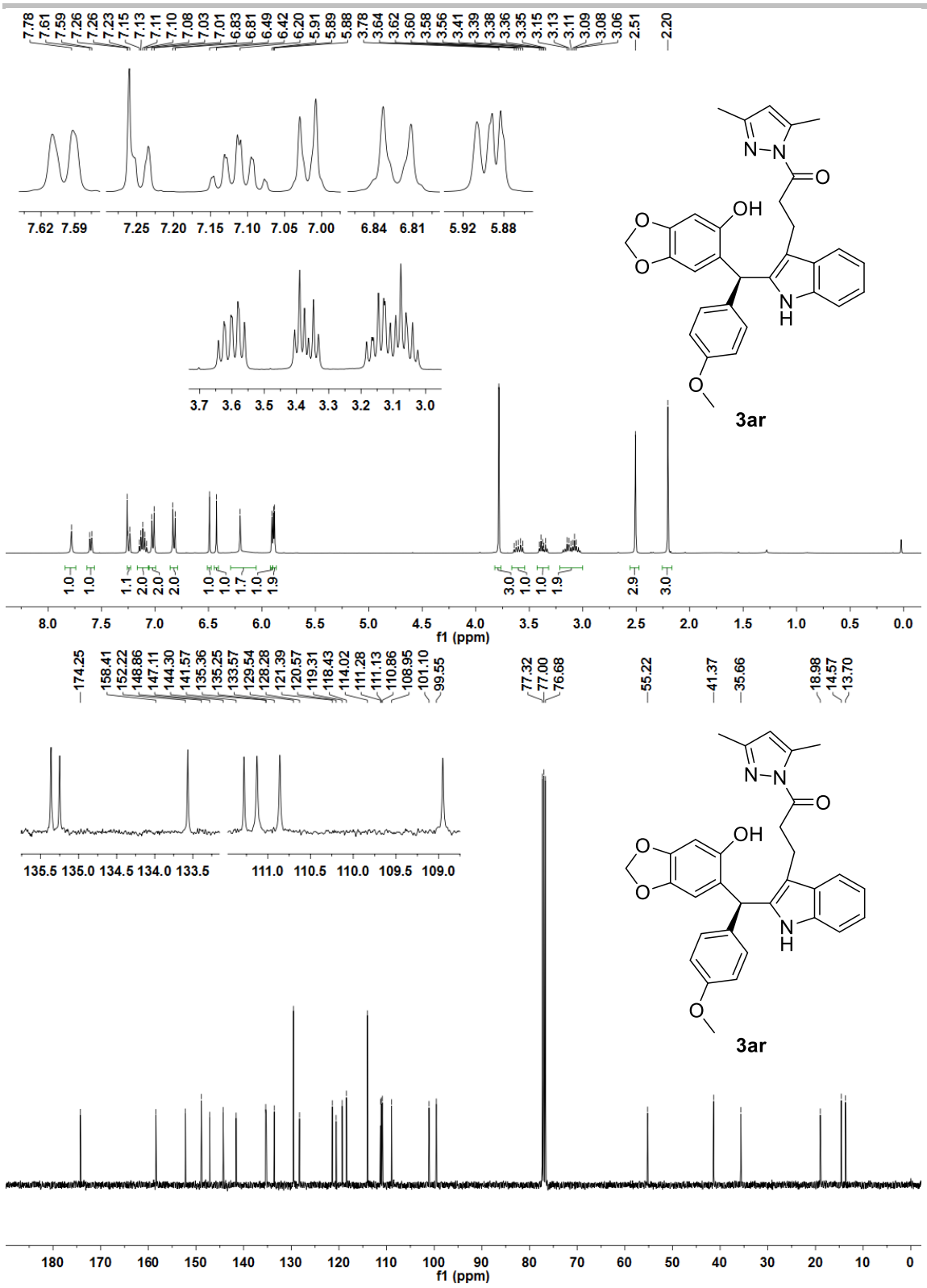

7.72 7.43 7.41 7.40 7.39 7.35 7.34 7.34 7.26 7.09 7.07 7.07 7.05 7.04 6.99 6.97 6.86 6.84 6.45 6.43 5.91 5.91 5.89 5.89 5.88 5.05
3.80 3.08 3.07 3.06 3.06 2.90 2.90 2.89 2.88 2.39
7.45 7.40 7.35 7.1 7.0 6.9 6.45 6.42 5.92 5.88
3.1 3.0 2.9
PhS O OH O O N H Me O
3ao
1.0 1.0 2.9 2.0 3.0 1.0 2.0 2.0 1.9 1.0 1.0 3.0 1.9 2.0 3.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
198.25 158.57 148.17 147.09 141.76 135.11 134.84 134.44 132.90 129.46 129.33 129.11 127.74 127.61 122.33 120.70 120.12 119.80 115.99 114.21 111.30 109.21 101.17 99.39 77.32 77.00 76.68 55.25 43.79 42.00 20.18 16.56
135.0 134.5 134.0 133.5 133.0 129.5 129.0 128.5 128.0 127.5
122 121 120
PhS O OH O O N H Me O
3ao
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

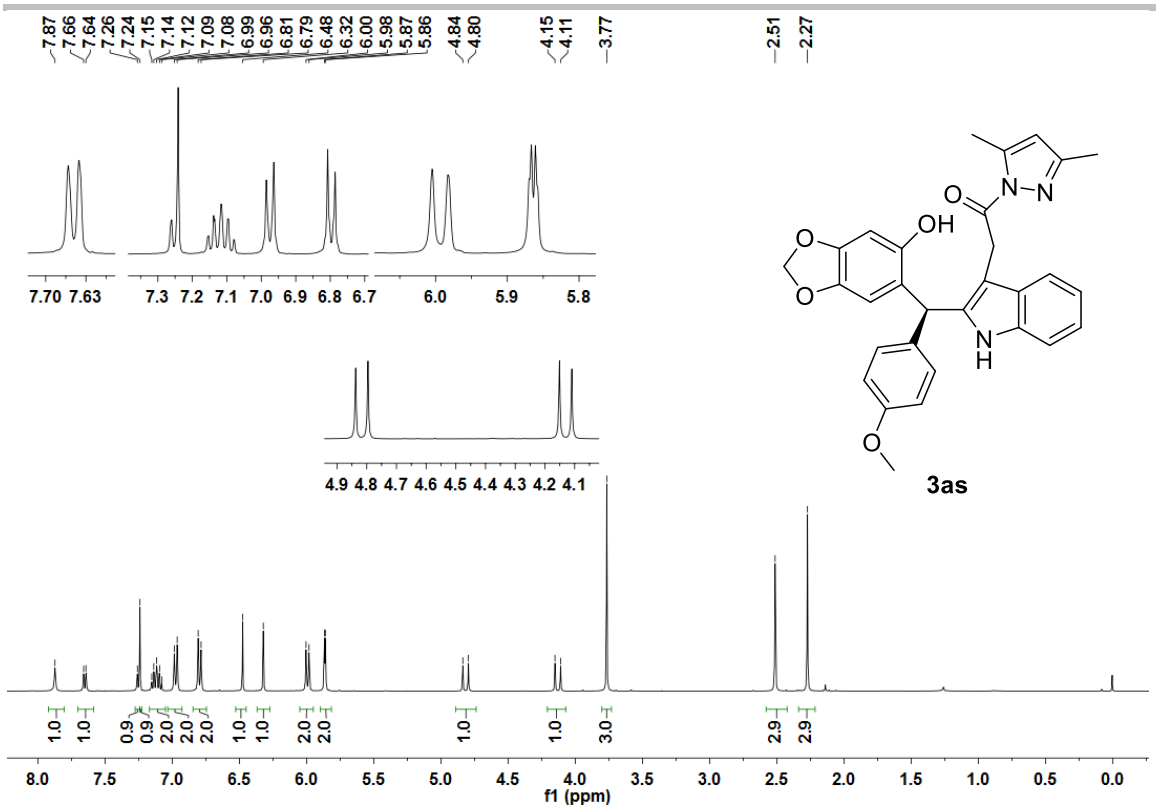

SPh
O
OH
O
O
N
H
O
3ap

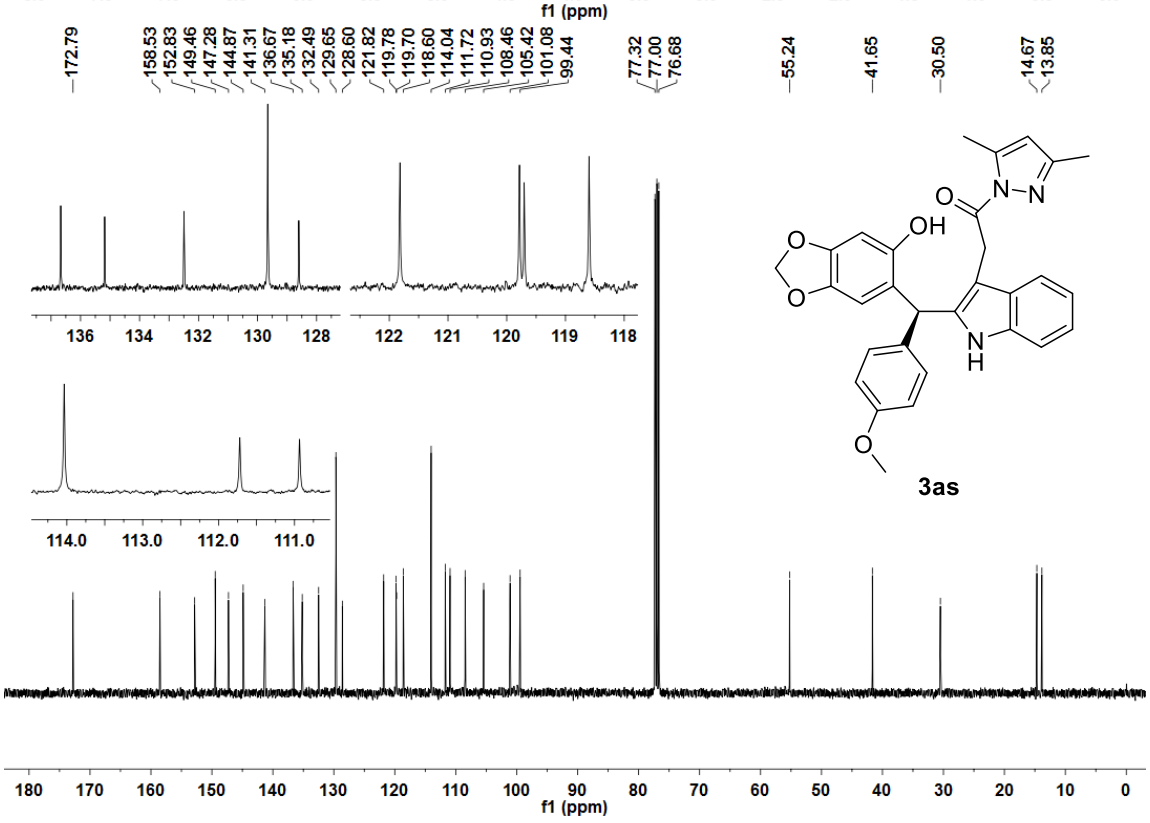

SPh
O
OH
O
O
N
H
O
3ap

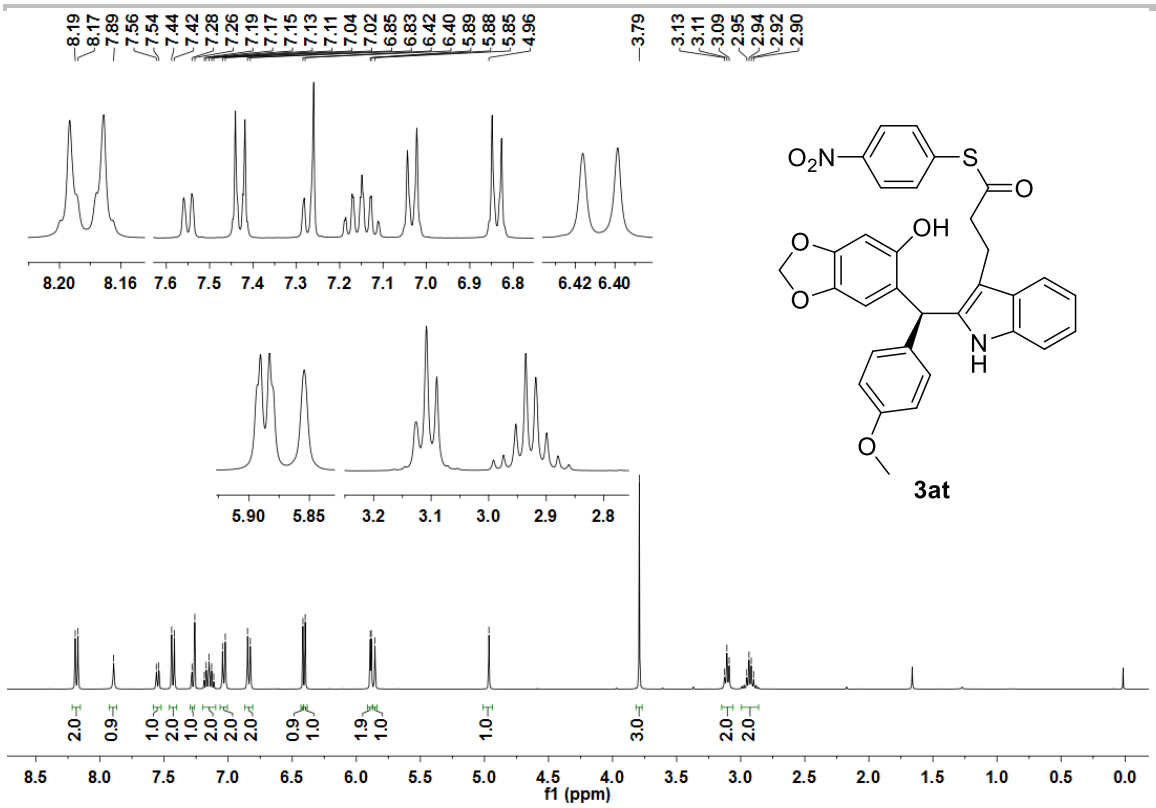

7.96 7.65 7.64 7.63 7.38 7.36 7.35 7.35 7.30 7.29 7.27 7.26 7.20 7.19 7.17 7.06 7.04 6.86 6.84 6.44 6.39 5.91 5.88 5.88 5.70 4.09 4.05 3.90 3.86 3.80
7.64 7.40 7.35 7.30 7.25 7.20 7.15 7.1 7.0 6.9 6.8
5.92 5.90 5.88 5.86
1.0 1.0 5.0 1.0 2.1 2.0 2.0 1.0 1.0 1.0 2.0 1.0 1.0 1.0 3.0
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
SPh
OH
O
O
N
H
O
3aq

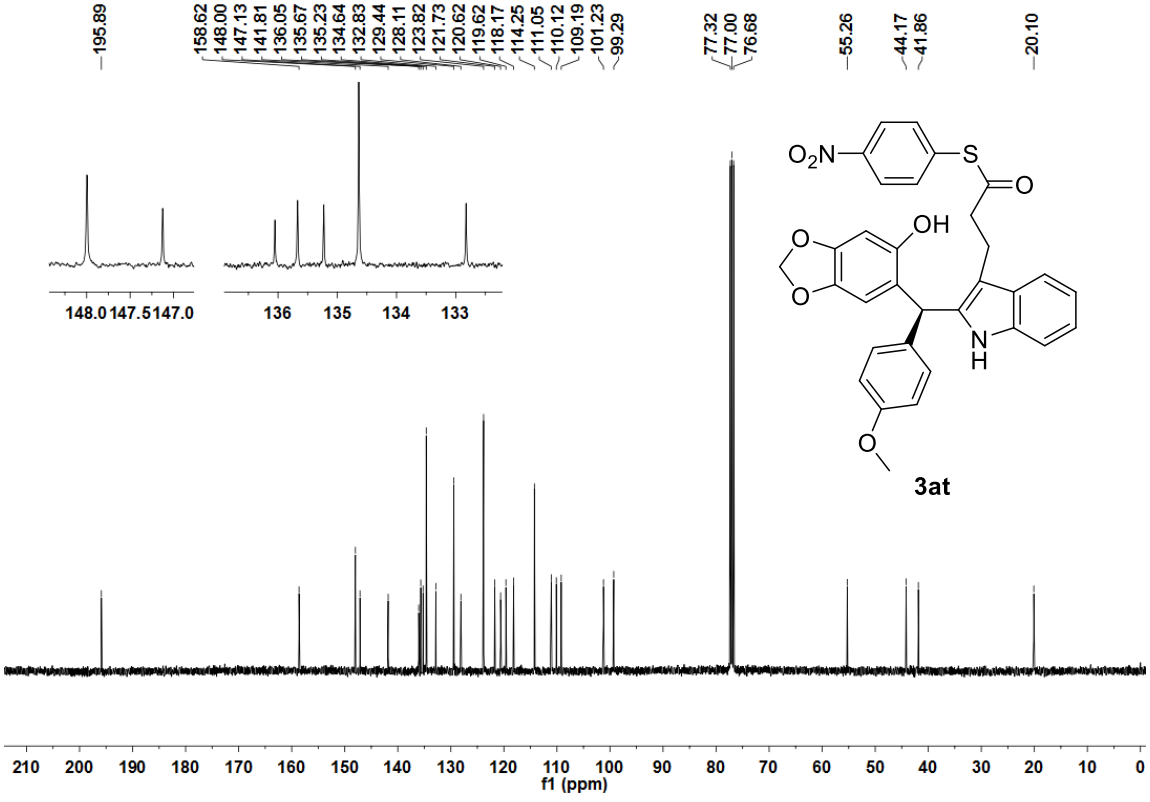

197.67
158.66 148.69 147.26 141.60 137.35 135.10 134.32 132.27 129.63 129.36 129.10 128.36 127.60 122.04 120.09 119.79 118.24 114.20 111.08 108.81 104.90 101.15 99.45
77.32 77.00 76.68
55.26
41.85 38.75
137 136 135 134 133 132
129.5 129.0 128.5 128.0 127.5
122.0 121.0 120.0 119.0 118.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
SPh
OH
O
O
N
H
O
3aq

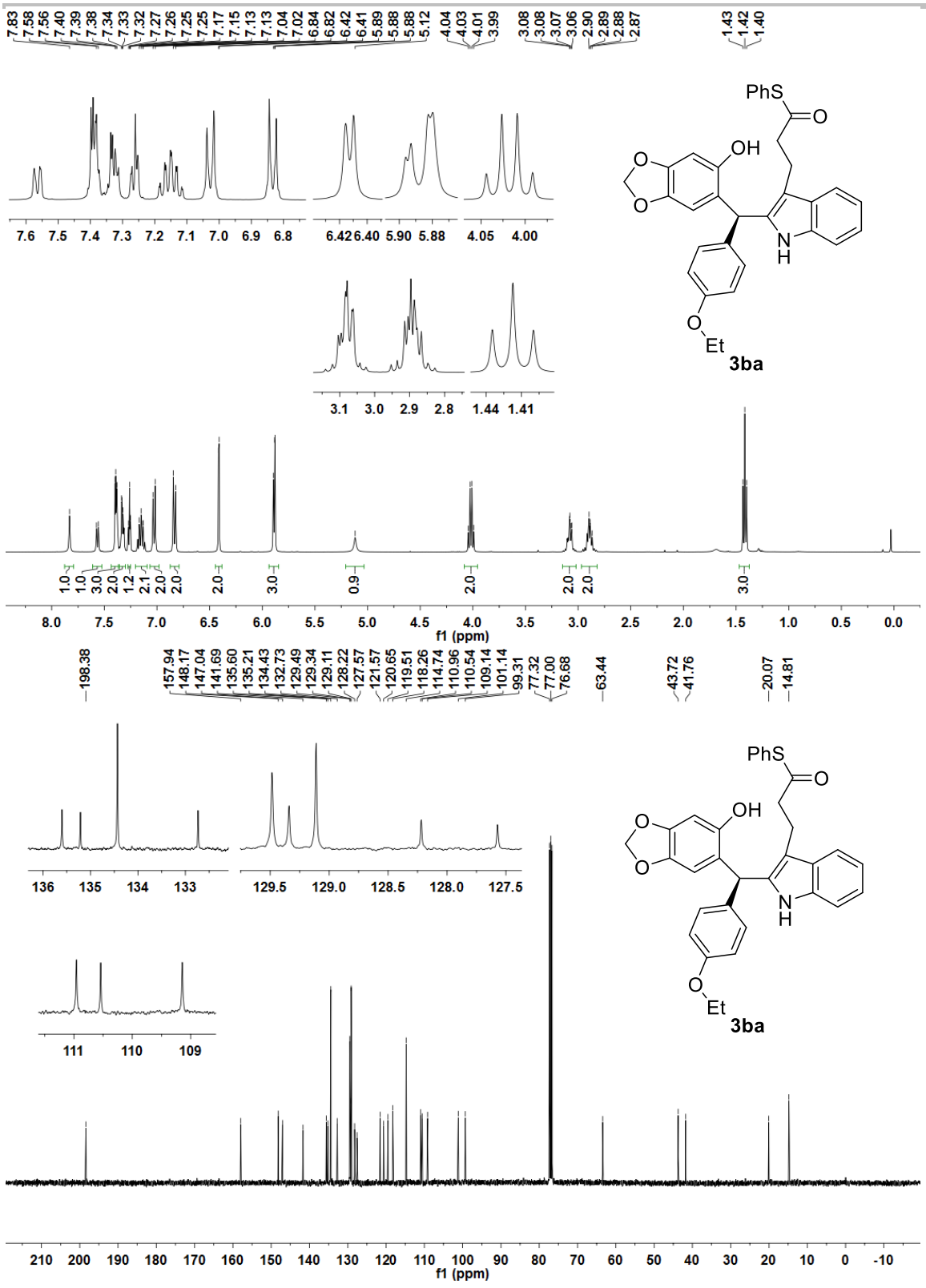

7.78 7.61 7.59 7.26 7.26 7.23 7.15 7.13 7.11 7.10 7.08 7.03 7.01 6.83 6.81 6.49 6.42 6.20 5.91 5.89 5.88 3.78 3.64 3.62 3.60 3.58 3.56 3.41 3.39 3.38 3.36 3.35 3.15 3.13 3.11 3.09 3.08 3.06 2.51 2.20
7.62 7.59
7.25 7.20 7.15 7.10 7.05 7.00
6.84 6.81
5.92 5.88
3.7 3.6 3.5 3.4 3.3 3.2 3.1 3.0
1.0 1.0 1.1 2.0 2.0 2.0 1.0 1.0 1.7 1.0 1.9 3.0 1.0 1.0 1.9 2.9 3.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
3ar
174.25 158.41 152.22 148.86 147.11 144.30 141.57 135.36 135.25 133.57 129.54 128.28 121.39 120.57 119.31 118.43 114.02 111.28 111.13 110.86 108.95 101.10 99.55 77.32 77.00 76.68 55.22 41.37 35.66 18.98 14.57 13.70
135.5 135.0 134.5 134.0 133.5
111.0 110.5 110.0 109.5 109.0
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
3ar

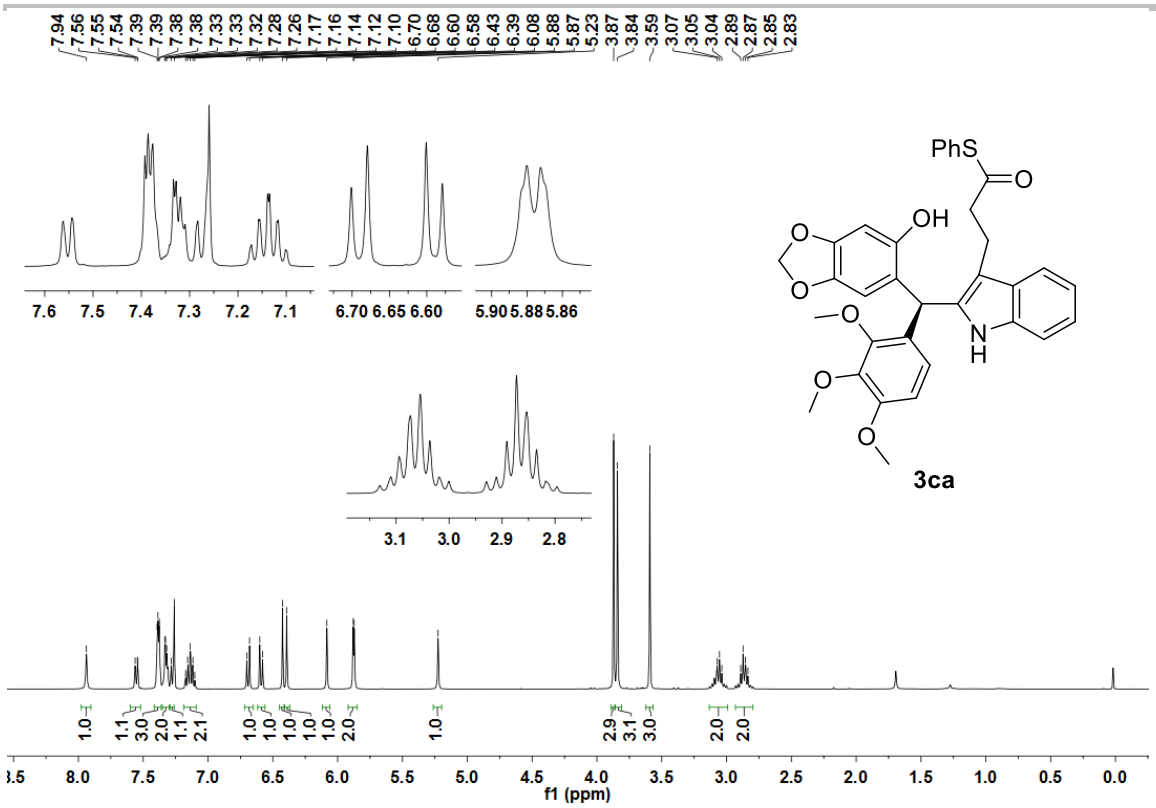

7.87
7.66
7.64
7.26
7.24
7.15
7.14
7.12
7.09
7.08
6.99
6.96
6.81
6.79
6.48
6.32
6.00
5.98
5.87
5.86
4.84
4.80
4.15
4.11
3.77
2.51
2.27
7.70 7.63
7.3 7.2 7.1 7.0 6.9 6.8 6.7
6.0
5.9
5.8
4.9 4.8 4.7 4.6 4.5 4.4 4.3 4.2 4.1
1.0 1.0 0.9 0.9 2.0 2.0 1.0 1.0 2.0 2.0 1.0 1.0 3.0 2.9 2.9
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O
N
N
OH
O
O
N
H
O
3as

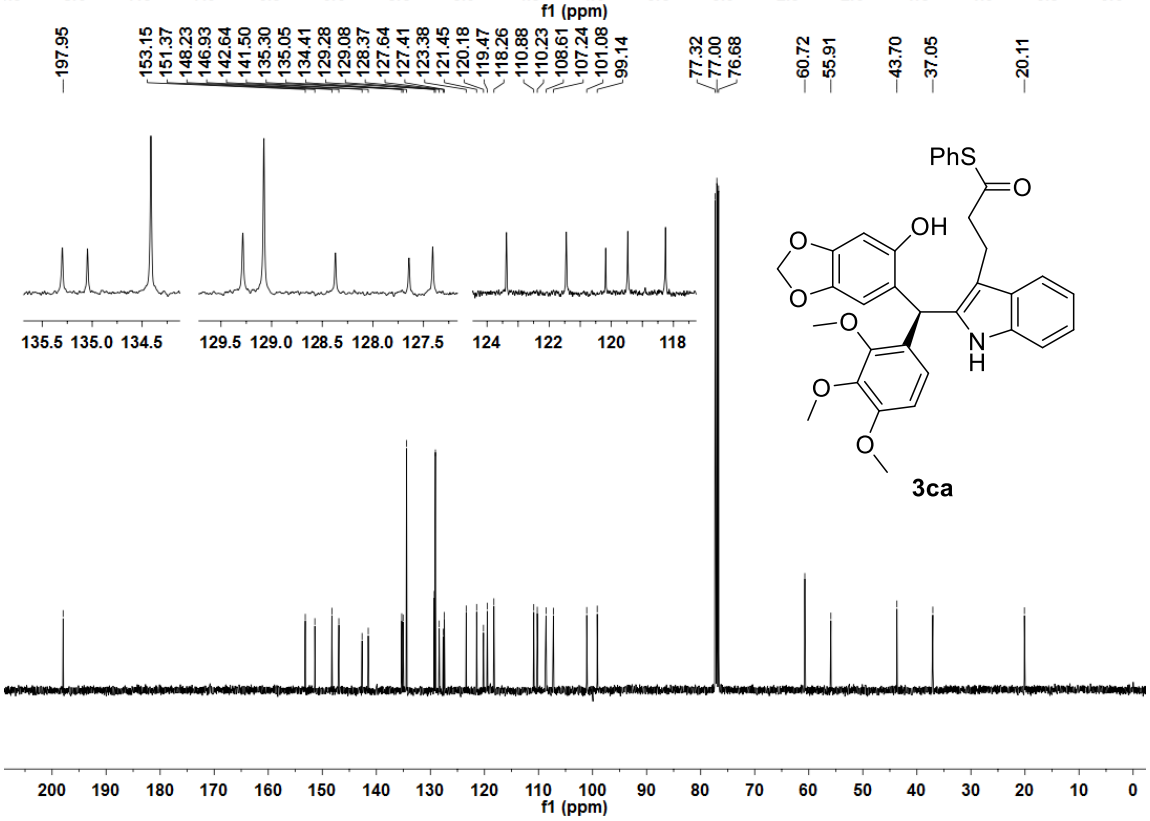

172.79
158.53
152.83
149.46
147.28
144.87
141.31
136.67
135.18
132.49
129.65
128.60
121.82
119.78
119.70
118.60
114.04
111.72
110.93
108.46
105.42
101.08
99.44
77.32
77.00
76.68
55.24
41.65
30.50
14.67
13.85
136 134 132 130 128
122 121 120 119 118
114.0 113.0 112.0 111.0
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O
N
N
OH
O
O
N
H
O
3as

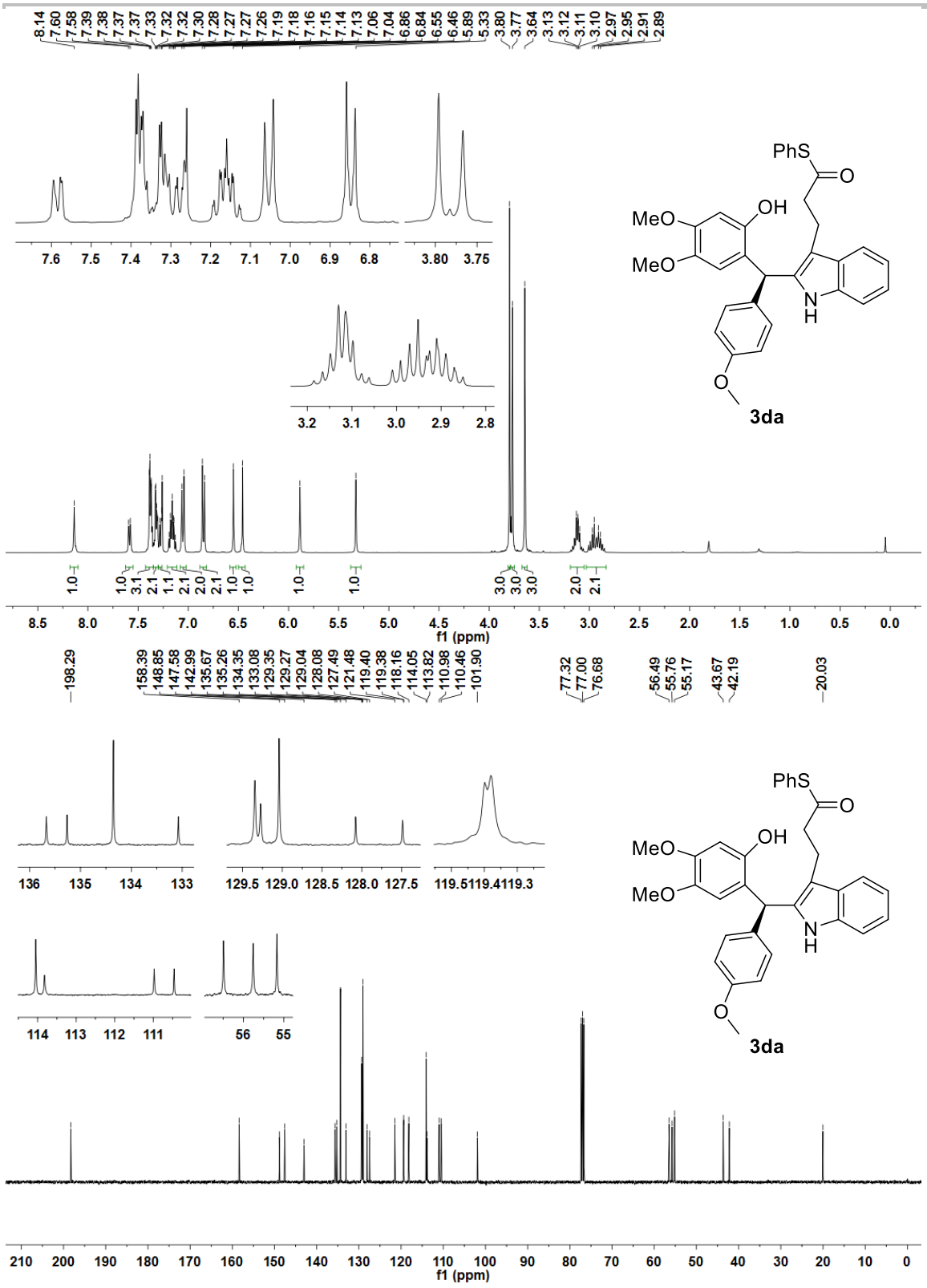

8.19
8.17
7.89
7.56
7.54
7.44
7.42
7.28
7.26
7.19
7.17
7.15
7.13
7.11
7.04
7.02
6.85
6.83
6.42
6.40
5.89
5.88
5.85
4.96
3.79
3.13
3.11
3.09
2.95
2.94
2.92
2.90
8.20 8.16 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.42 6.40
5.90 5.85 3.2 3.1 3.0 2.9 2.8
2.0 0.9 1.0 2.0 1.0 2.0 2.0 2.0 0.9 1.0 1.9 1.0 1.0 3.0 2.0 2.0
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
O2N
S
O
OH
O
O
N
H
O
3at

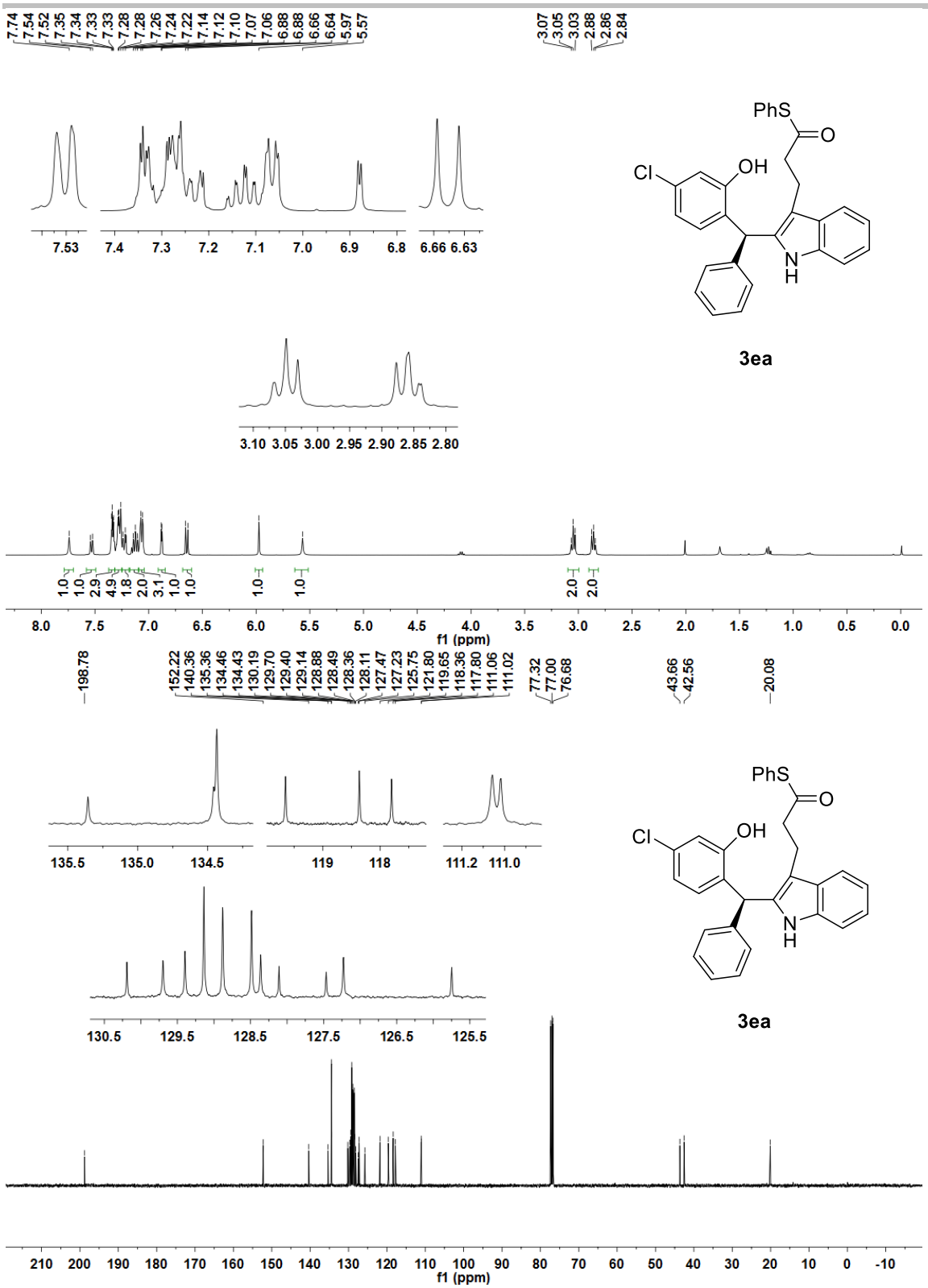

195.89
158.62
148.00
147.13
141.81
136.05
135.67
135.23
134.64
132.83
129.44
128.11
123.82
121.73
120.62
119.62
118.17
114.25
111.05
110.12
109.19
101.23
99.29
77.32
77.00
76.68
55.26
44.17
41.86
20.10
148.0 147.5 147.0 136 135 134 133
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
O2N
S
O
OH
O
O
N
H
O
3at

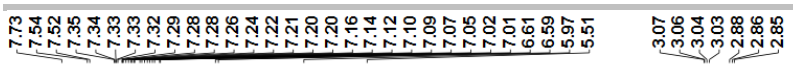

PhS
O
OH
O
O
N
H
O
Et
3ba

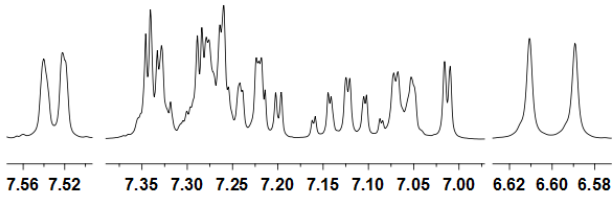

7.94 7.56 7.55 7.54 7.39 7.39 7.38 7.38 7.33 7.33 7.32 7.28 7.26 7.17 7.16 7.14 7.12 7.10 6.70 6.68 6.60 6.58 6.43 6.39 6.08 5.88 5.87 5.23 3.87 3.84 3.59 3.07 3.05 3.04 2.89 2.87 2.85 2.83
7.6 7.5 7.4 7.3 7.2 7.1
6.70 6.65 6.60
5.90 5.88 5.86
3.1 3.0 2.9 2.8
PhS
O
OH
O
O
O
O
O
N
H
3ca
1.0 1.1 3.0 2.0 1.1 2.1 1.0 1.0 1.0 1.0 2.0 1.0 2.9 3.1 3.0 2.0 2.0
f1 (ppm)

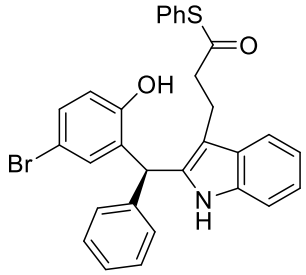

197.95
153.15 151.37 148.23 146.93 142.64 141.50 135.30 135.05 134.41 129.28 129.08 128.37 127.64 127.41 123.38 121.45 120.18 119.47 118.26 110.88 110.23 108.61 107.24 101.08 99.14
77.32 77.00 76.68
60.72 55.91 43.70 37.05 20.11
135.5 135.0 134.5
129.5 129.0 128.5 128.0 127.5
124 122 120 118
PhS
O
OH
O
O
O
O
O
N
H
3ca
f1 (ppm)


PhS
O
OH
MeO
MeO
N
H
O
3da
f1 (ppm)

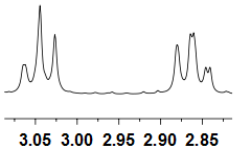

7.74 7.54 7.52 7.35 7.34 7.33 7.33 7.28 7.28 7.26 7.24 7.22 7.14 7.12 7.10 7.07 7.06 6.88 6.88 6.66 6.64 5.97 5.57
3.07 3.05 3.03 2.88 2.86 2.84
7.53 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.66 6.63
3.10 3.05 3.00 2.95 2.90 2.85 2.80
PhS O Cl OH N H
3ea
1.0 1.0 2.9 4.9 1.8 2.0 3.1 1.0 1.0 1.0 1.0 2.0 2.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
198.78 152.22 140.36 135.36 134.46 134.43 130.19 129.70 129.40 129.14 128.88 128.49 128.36 128.11 127.47 127.23 125.75 121.80 119.65 118.36 117.80 111.06 111.02 77.32 77.00 76.68 43.66 42.56 20.08
135.5 135.0 134.5 119 118 111.2 111.0
130.5 129.5 128.5 127.5 126.5 125.5
PhS O Cl OH N H
3ea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

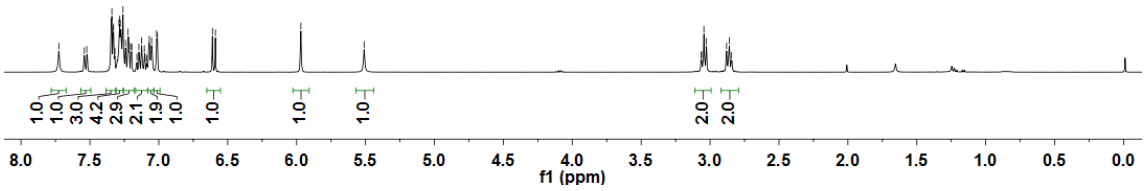

7.73
7.54
7.52
7.35
7.34
7.33
7.33
7.32
7.29
7.28
7.28
7.26
7.24
7.22
7.21
7.20
7.20
7.16
7.14
7.12
7.10
7.09
7.07
7.05
7.02
7.01
6.61
6.59
5.97
5.51
3.07
3.06
3.04
3.03
2.88
2.86
2.85

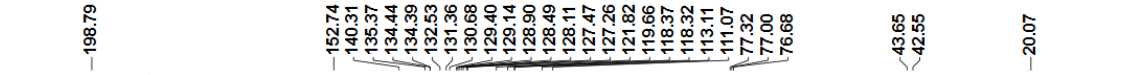

7.56 7.52
7.35 7.30 7.25 7.20 7.15 7.10 7.05 7.00
6.62 6.60 6.58

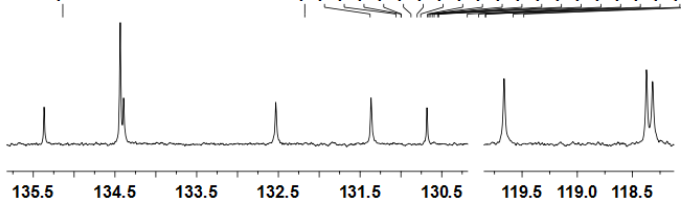

PhS
O
OH
Br
N
H

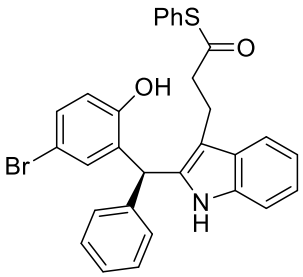
3fa


3.05 3.00 2.95 2.90 2.85

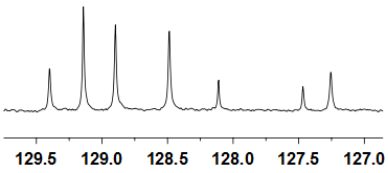

1.0
1.0
3.0
4.2
2.9
2.1
1.9
1.0
1.0
1.0
1.0
2.0
2.0
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

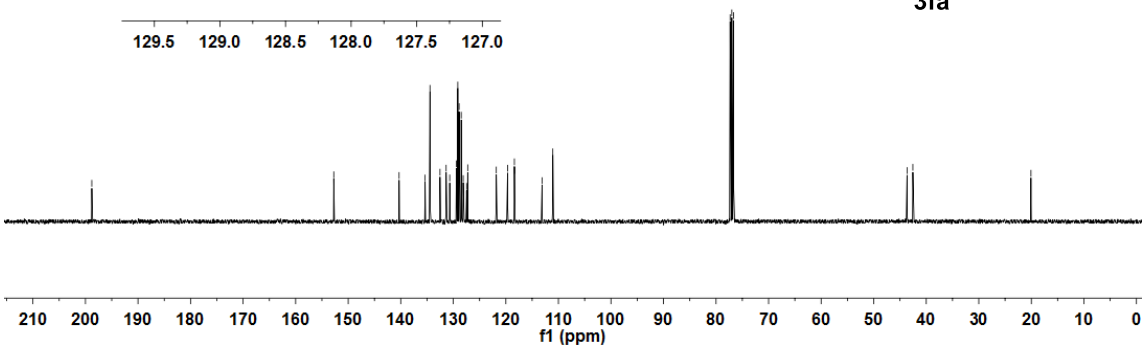

198.79
152.74
140.31
135.37
134.44
134.39
132.53
131.36
130.68
129.40
129.14
128.90
128.49
128.11
127.47
127.26
121.82
119.66
118.37
118.32
113.11
111.07
77.32
77.00
76.68
43.65
42.55
20.07

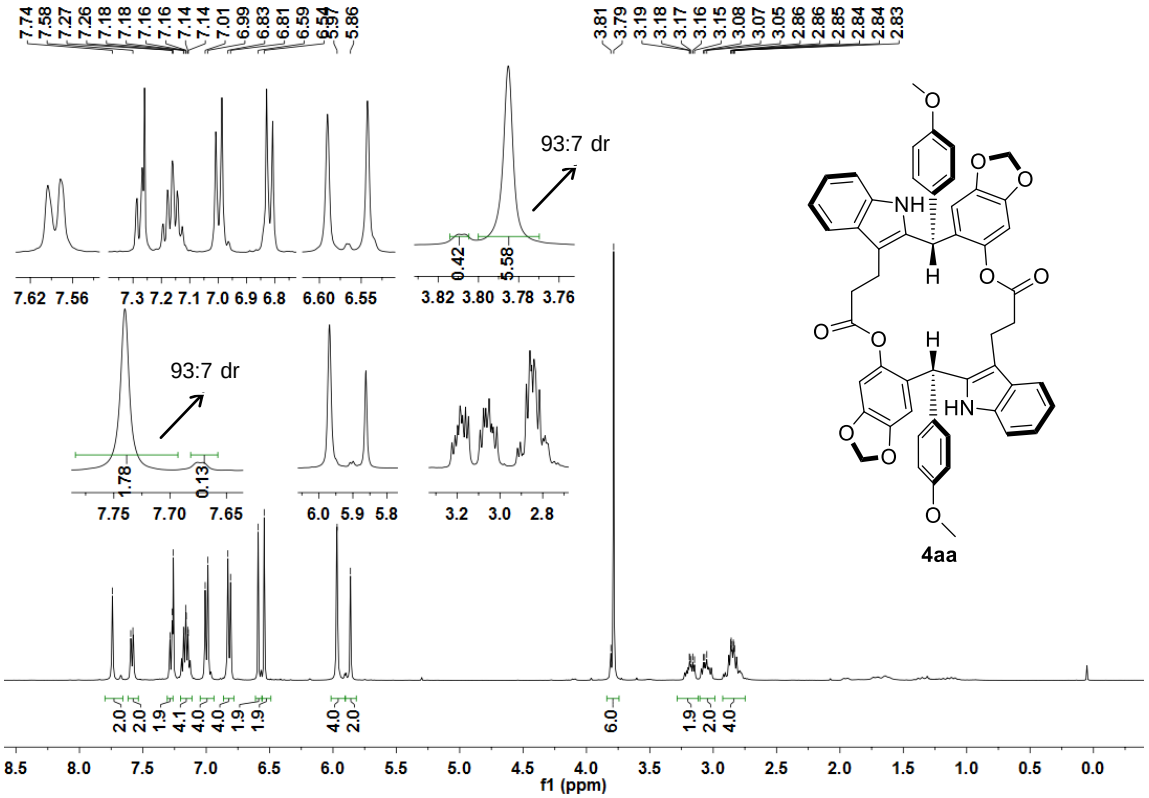

135.5
134.5
133.5
132.5
131.5
130.5
119.5
119.0
118.5

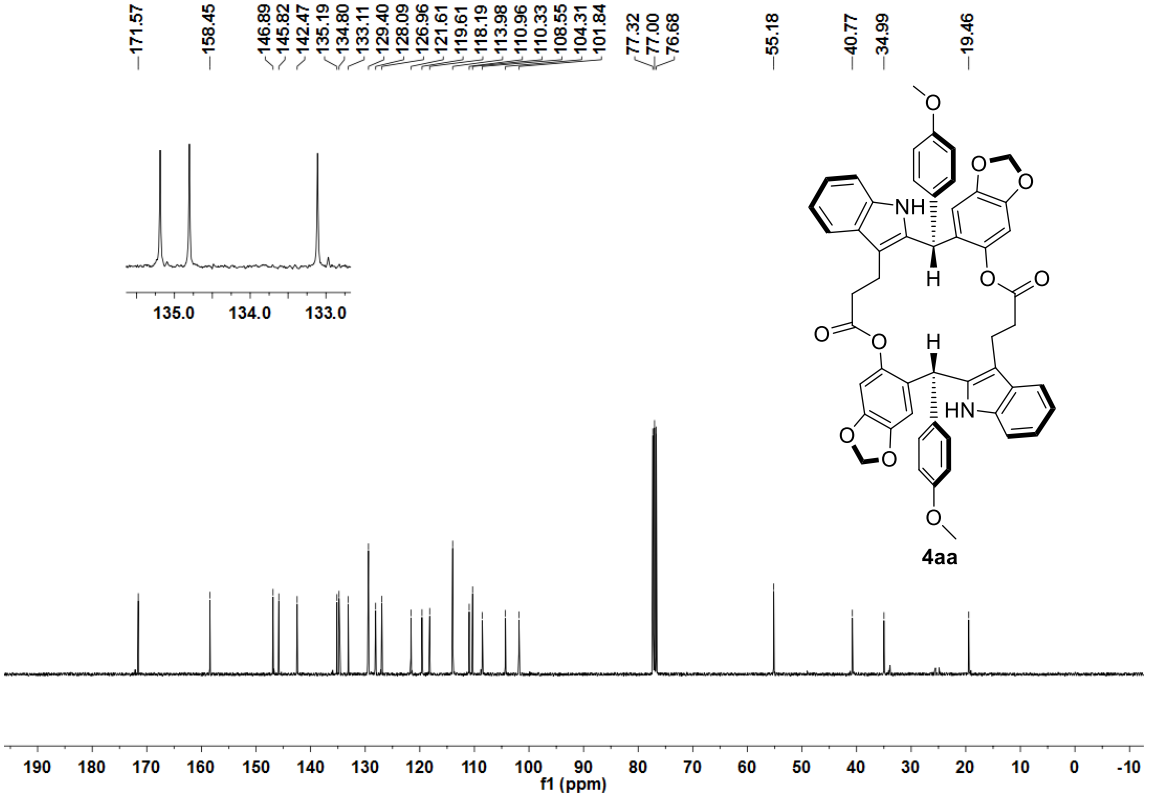

PhS
O
OH
Br
N
H

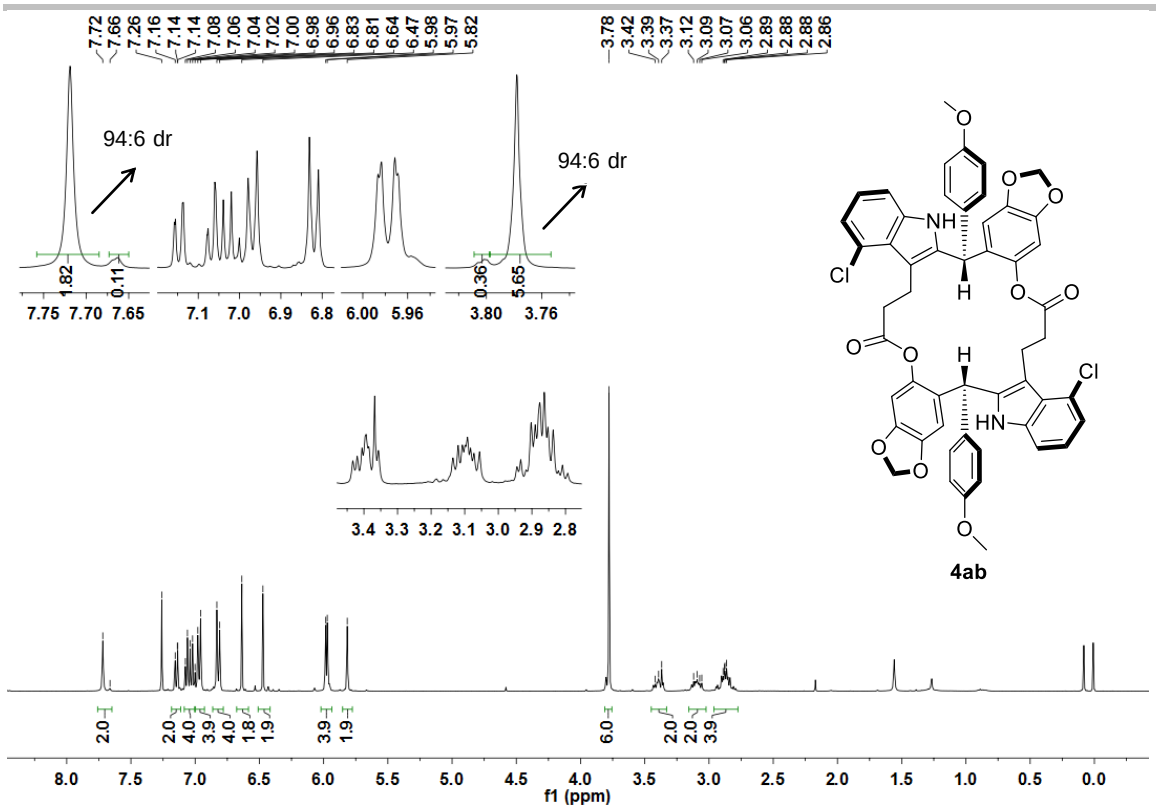
3fa

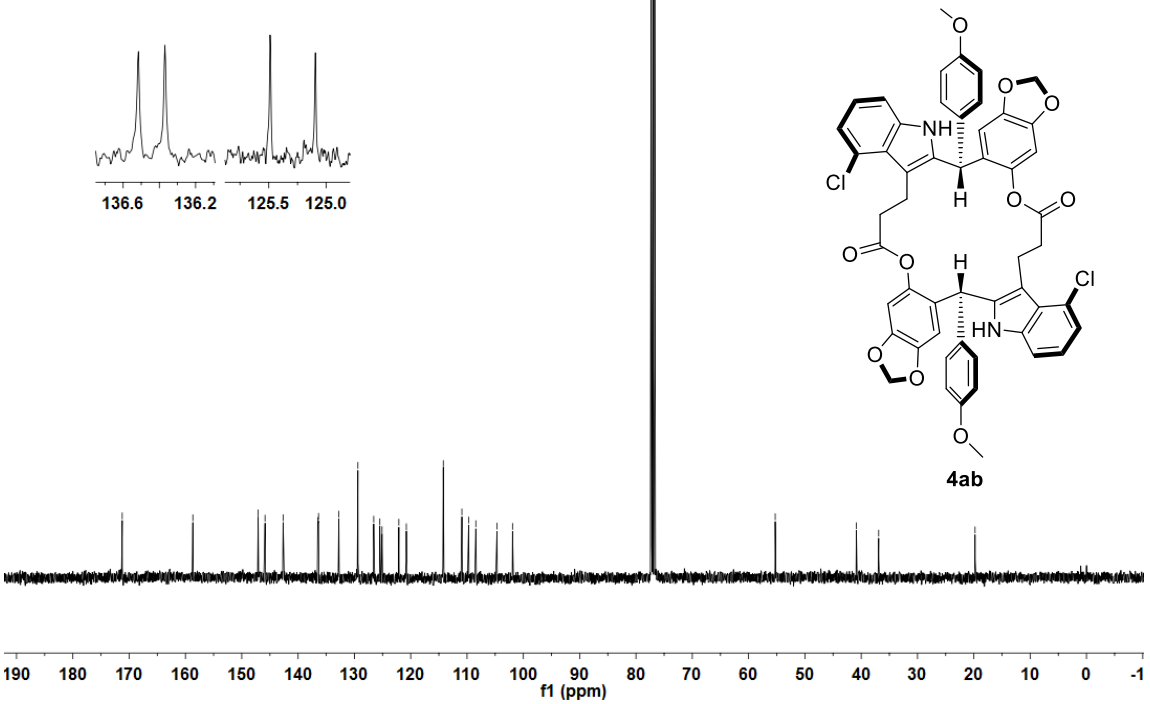

129.5
129.0
128.5
128.0
127.5
127.0

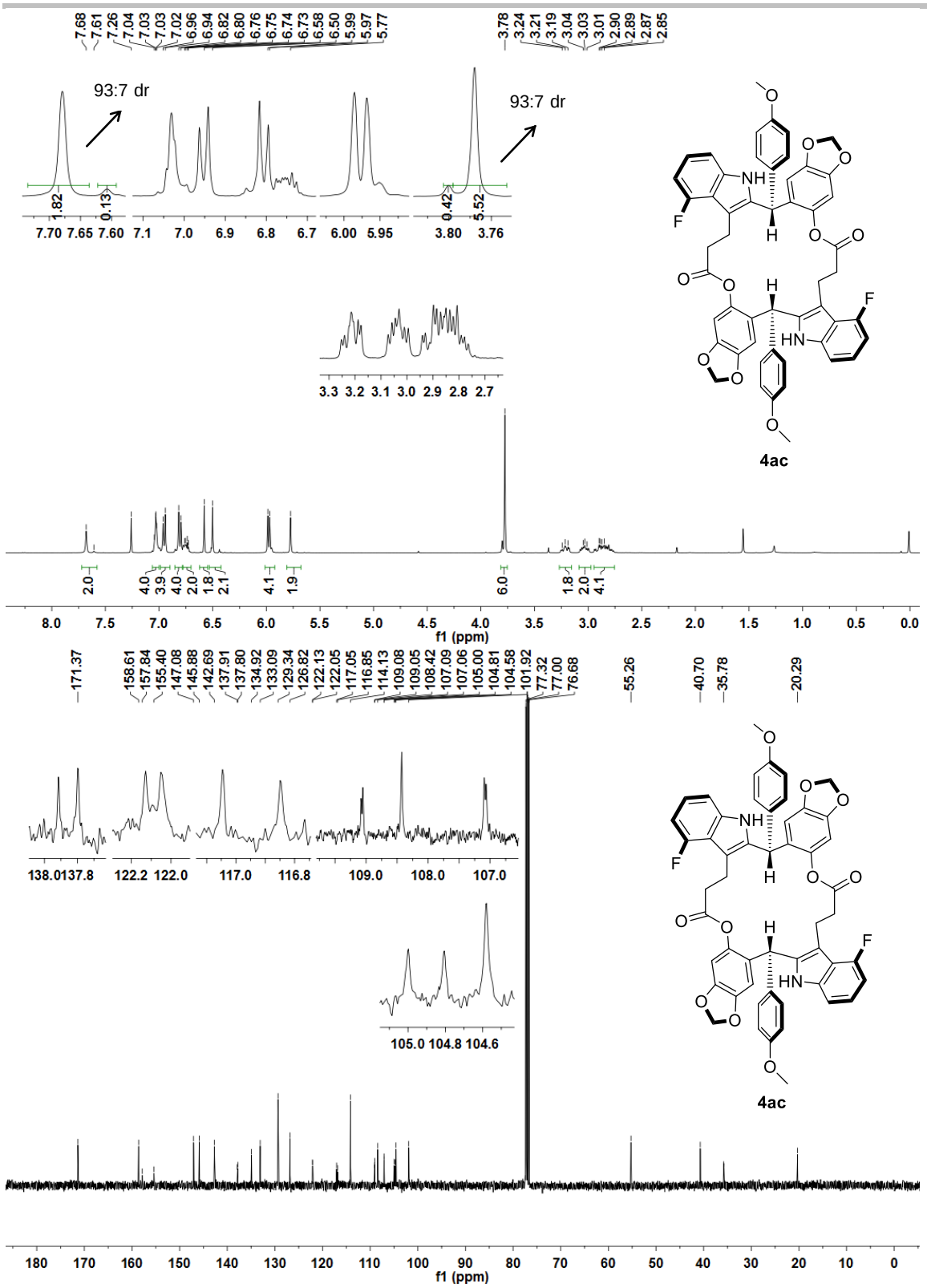

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

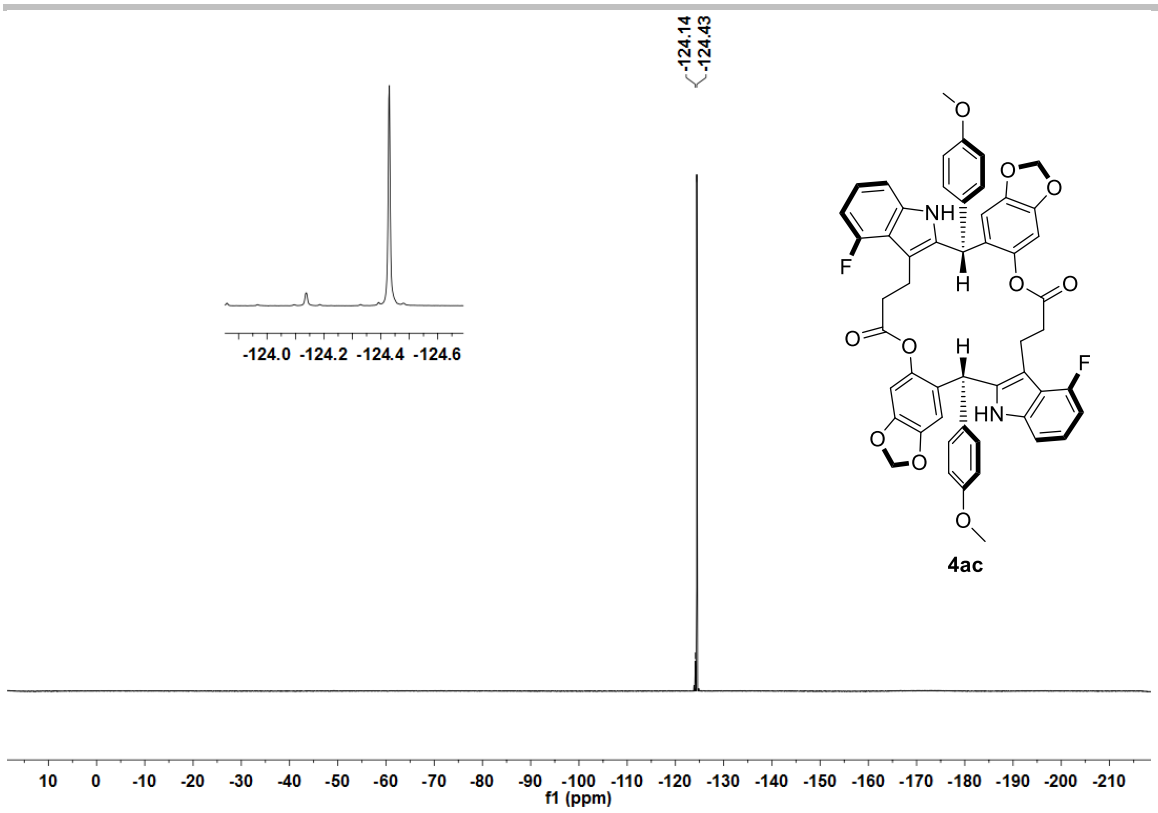

93:7 dr
93:7 dr
4aa
f1 (ppm)

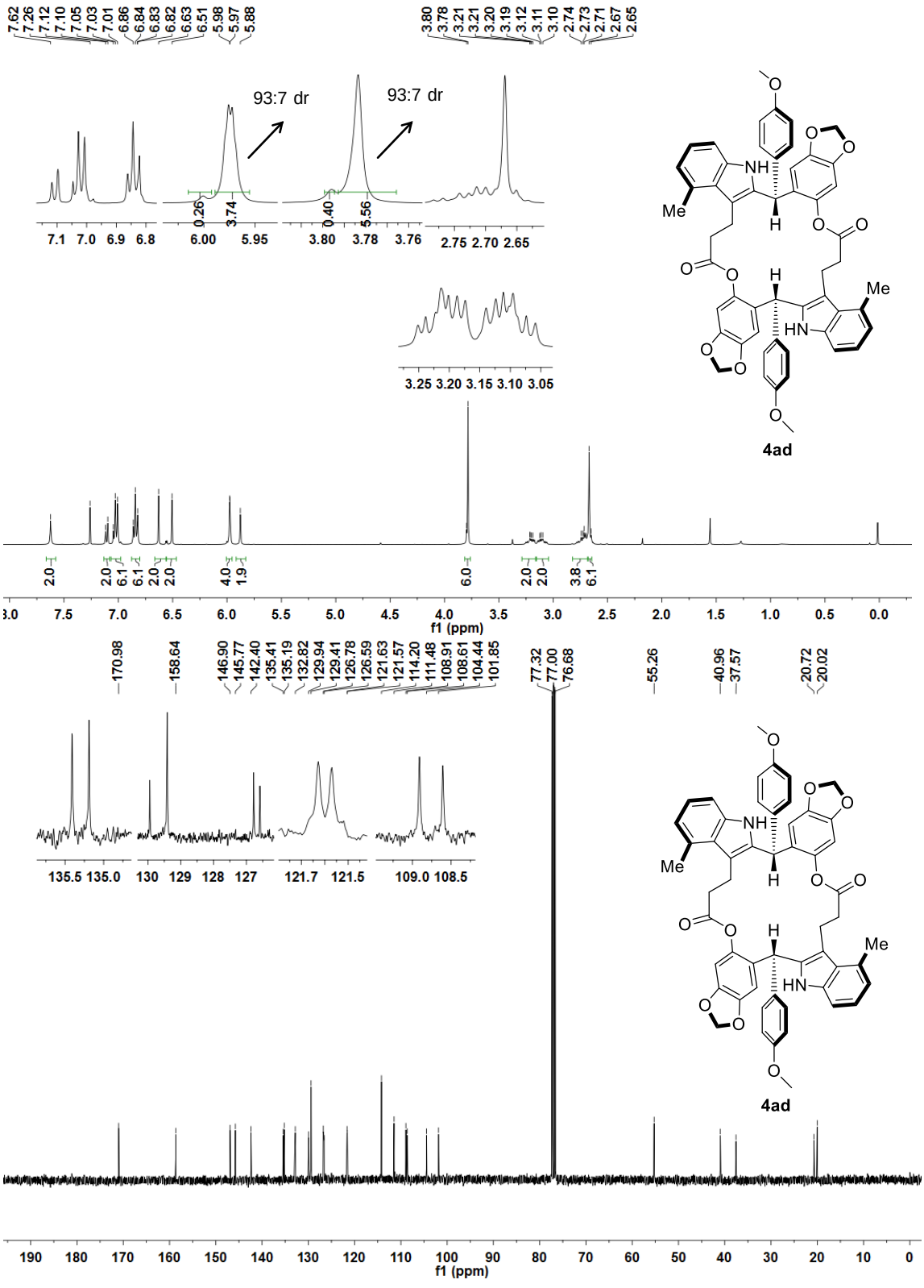

4aa
f1 (ppm)

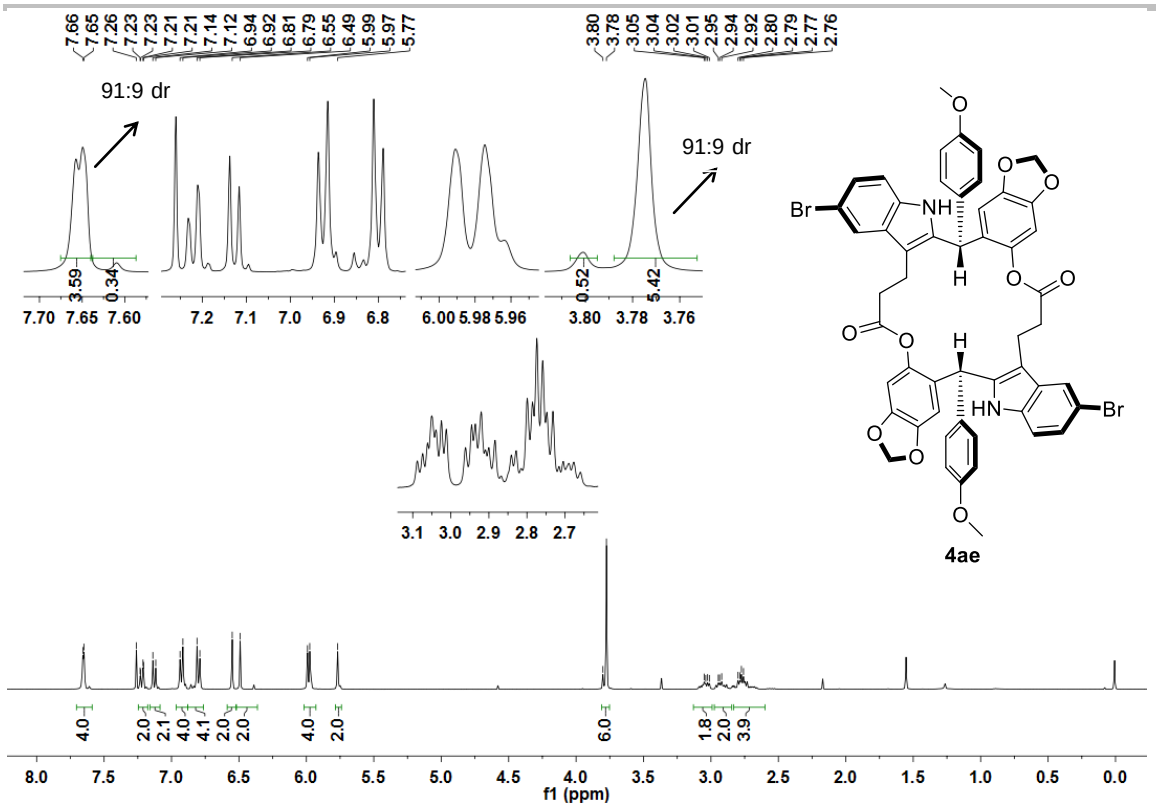

94:6 dr
94:6 dr
4ab

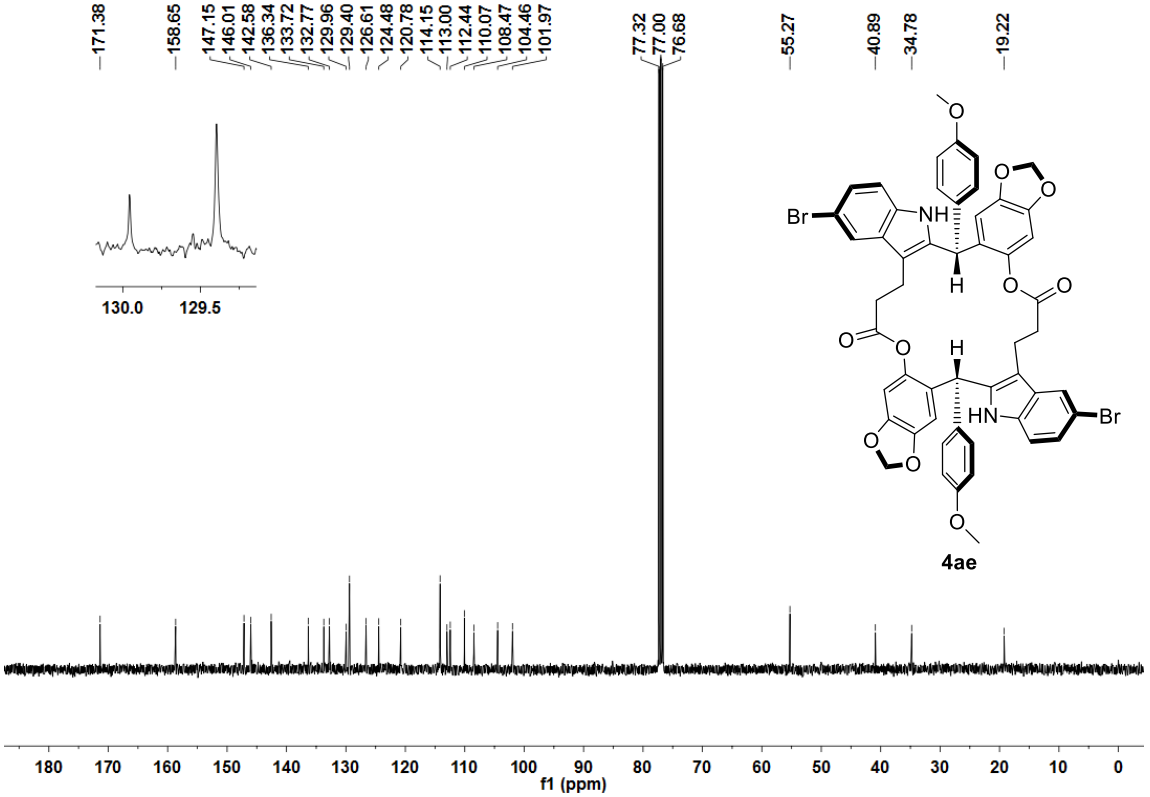

4ab

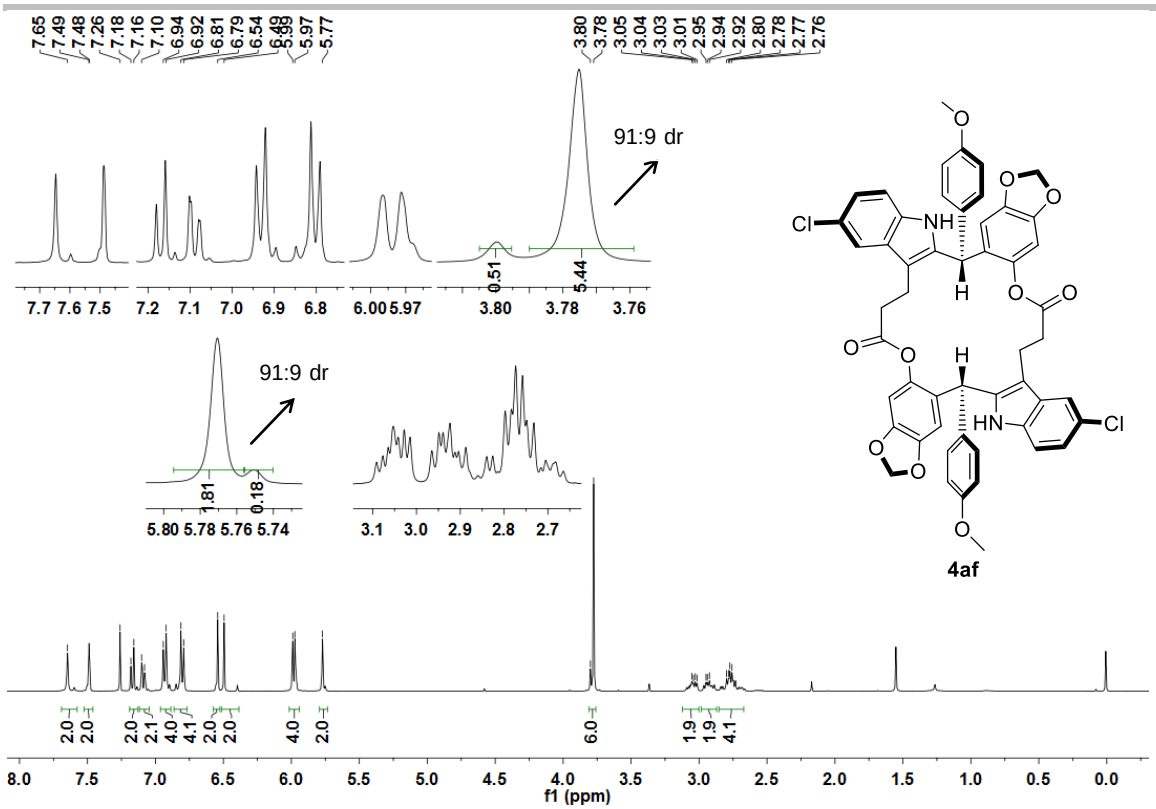

93:7 dr
93:7 dr
4ac
4ac
f1 (ppm)
f1 (ppm)

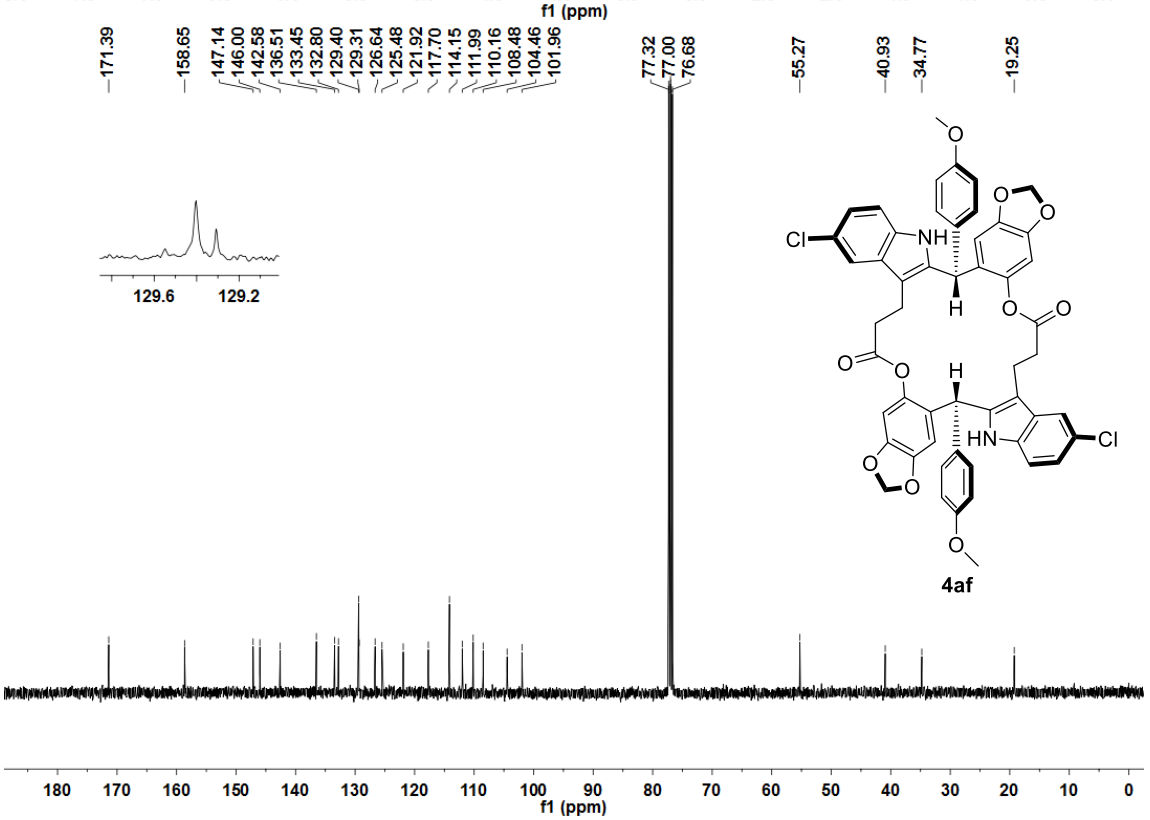

-124.14
-124.43
-124.0 -124.2 -124.4 -124.6
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
NH
HN
F
F
O
H
4ac

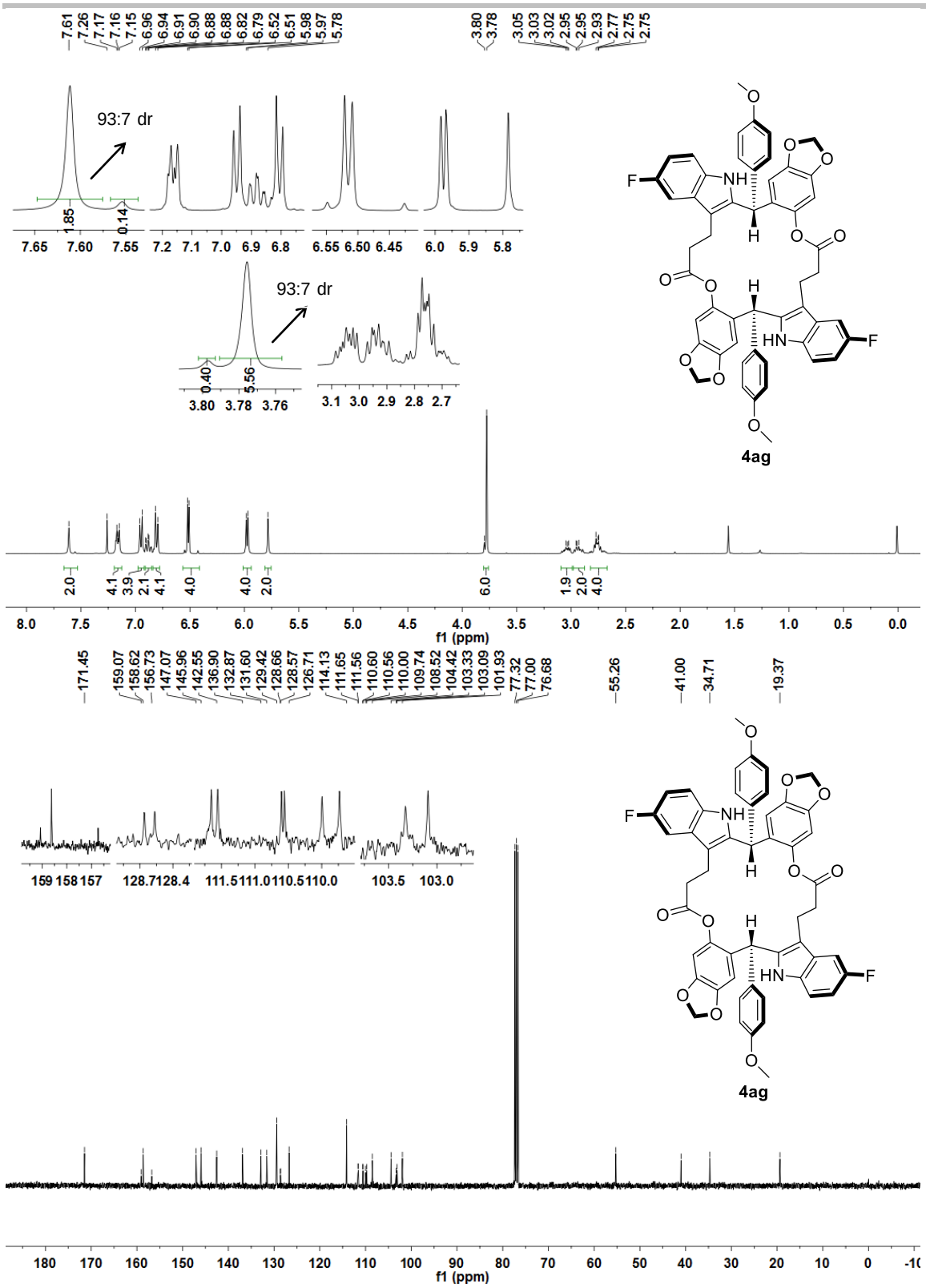

93:7 dr
93:7 dr
4ad
4ad
f1 (ppm)
f1 (ppm)

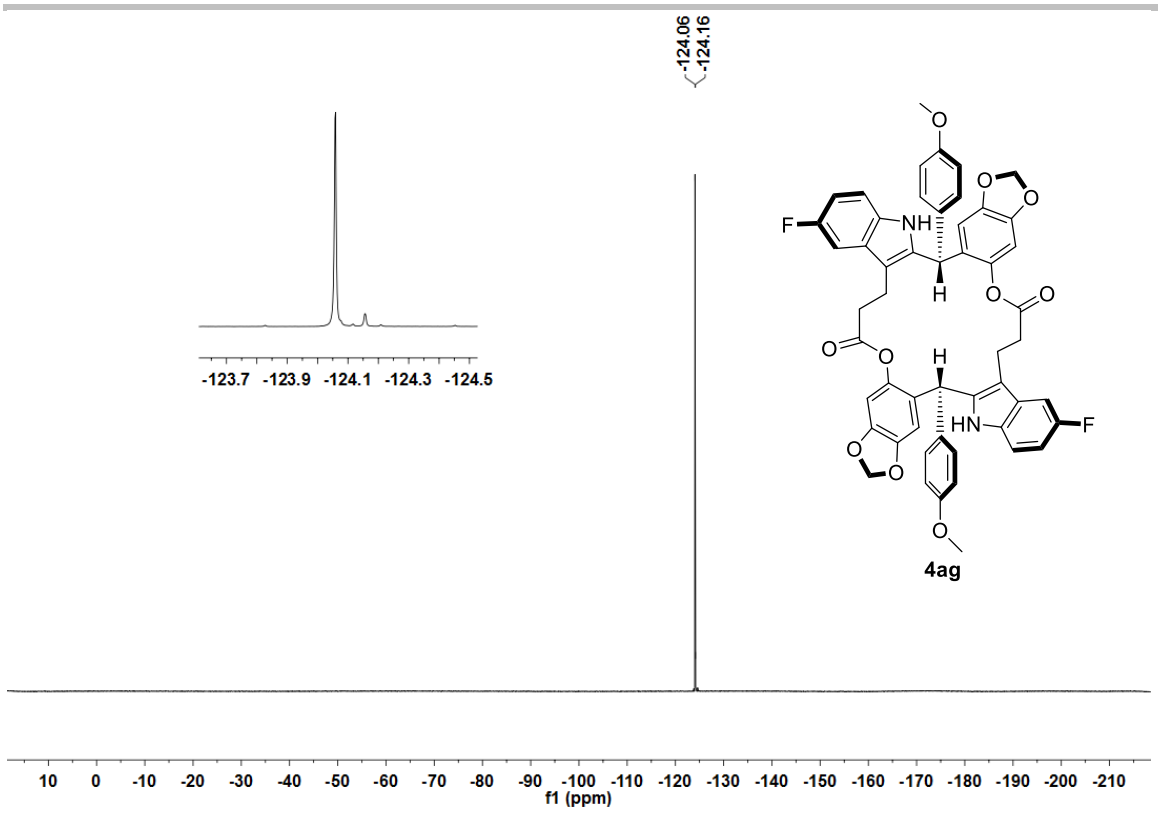

91:9 dr
91:9 dr
4ae

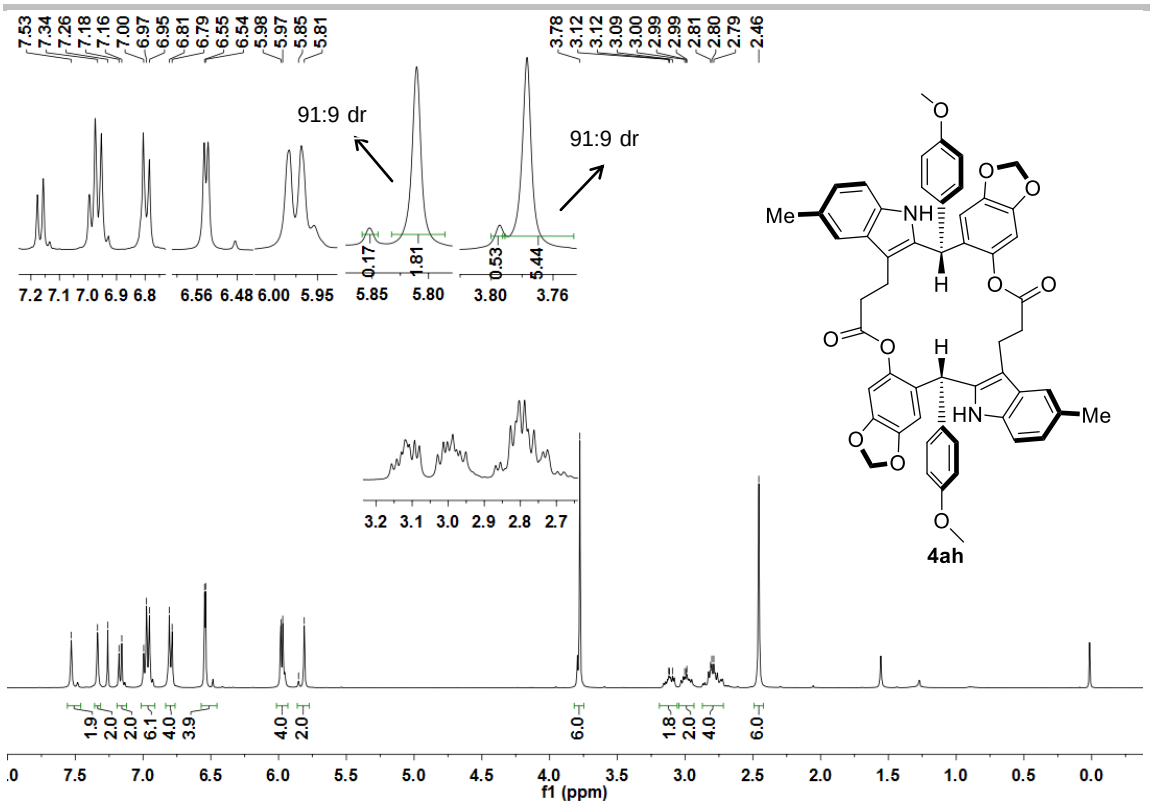

4ae

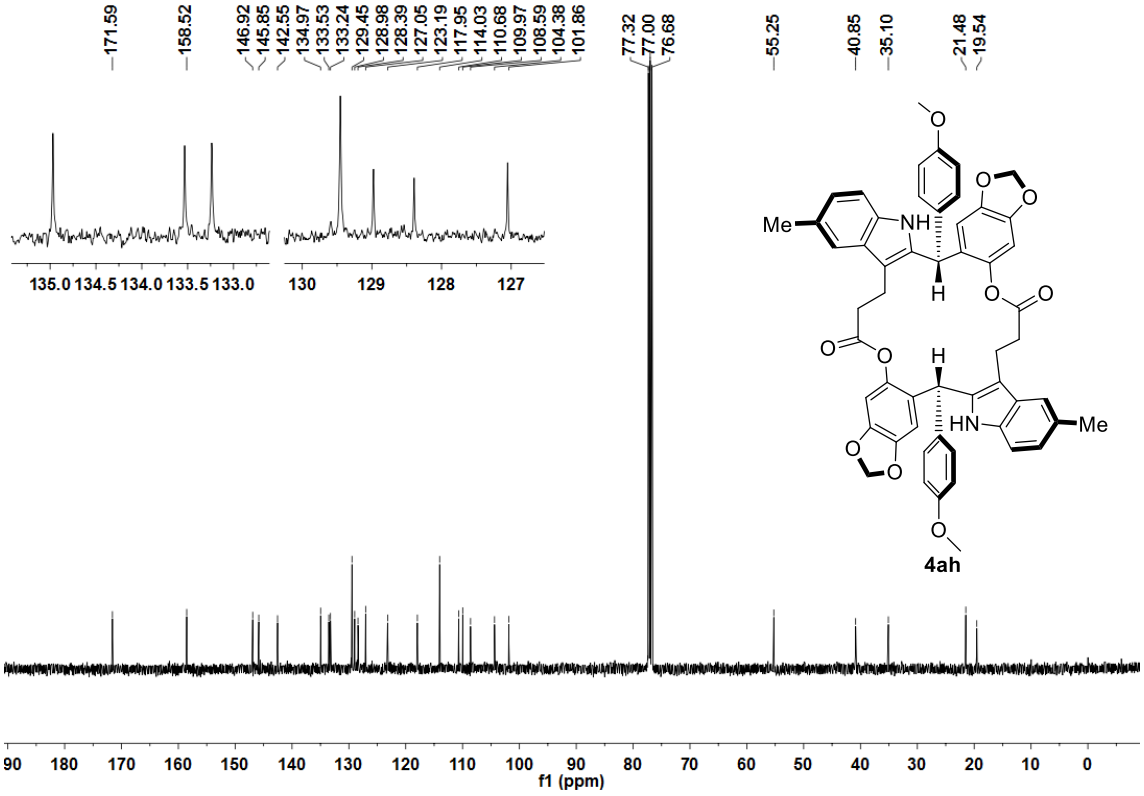

91:9 dr
91:9 dr
4af

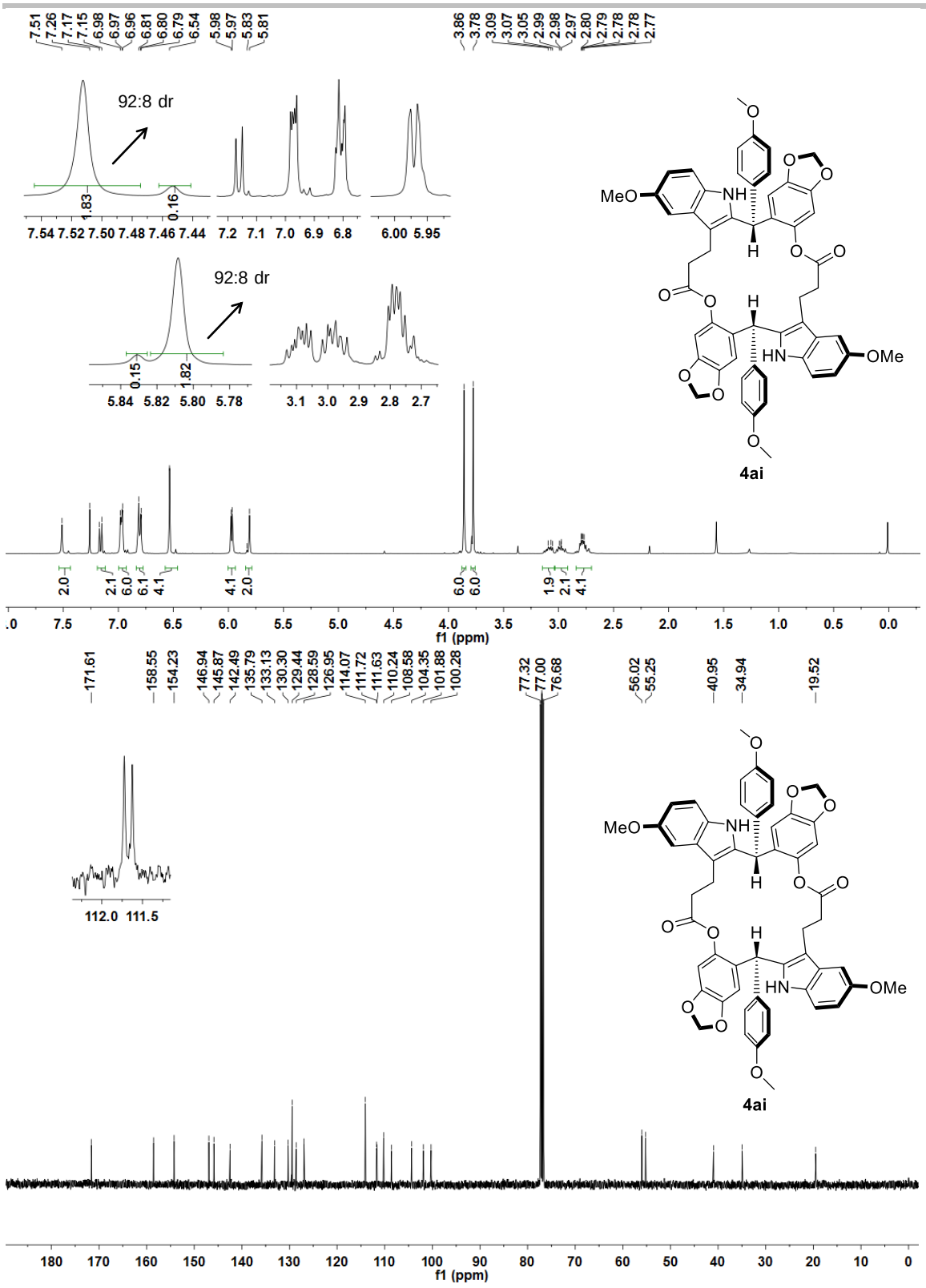

4af

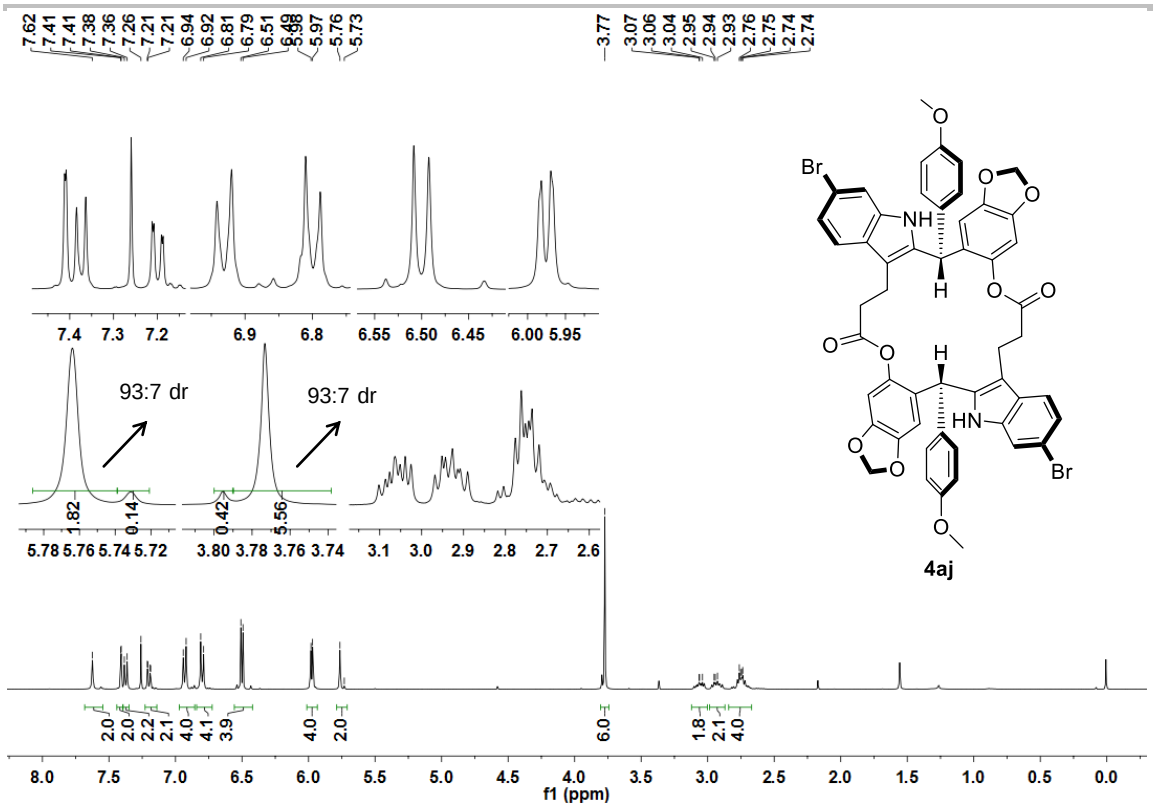

93:7 dr
93:7 dr
4ag
4ag
f1 (ppm)
f1 (ppm)

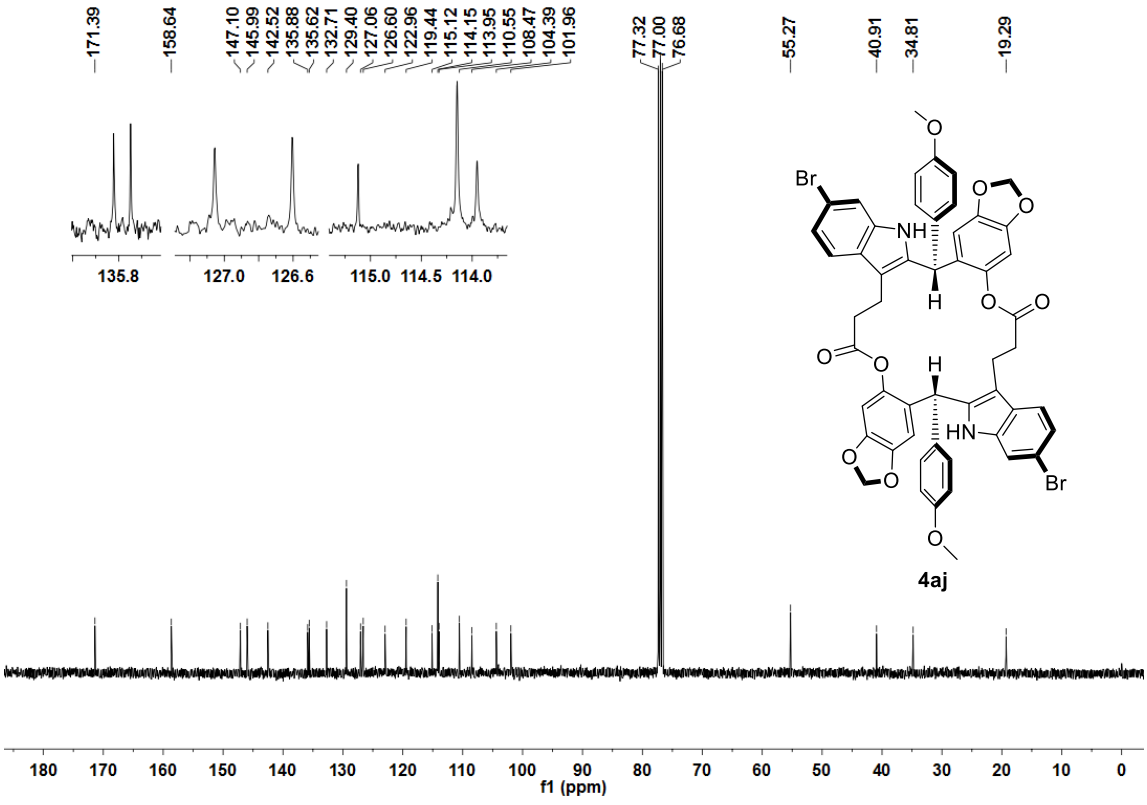

-124.06
-124.16
-123.7
-123.9
-124.1
-124.3
-124.5
F
NH
H
O
HN
4ag
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

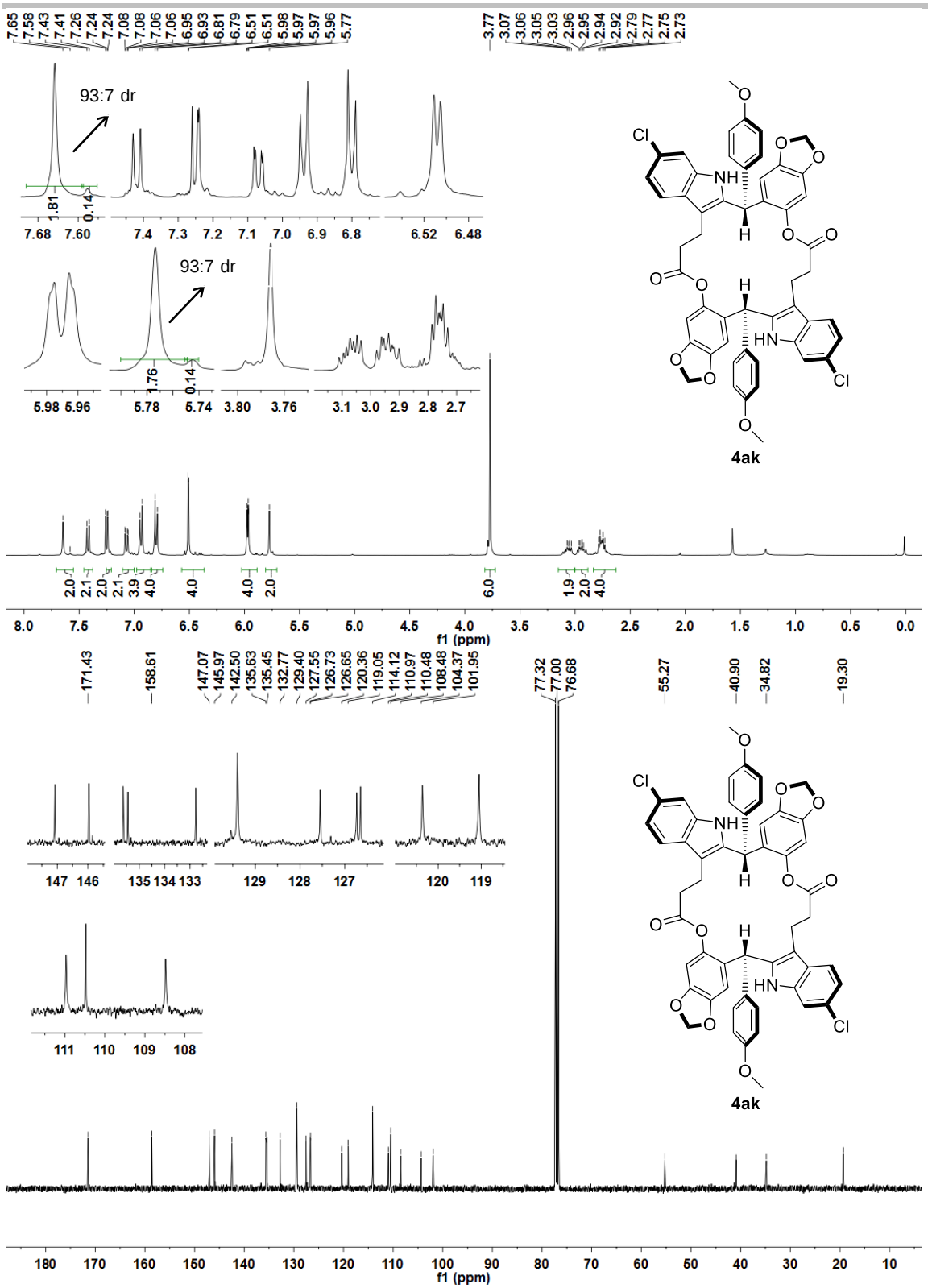

91:9 dr
91:9 dr
4ah

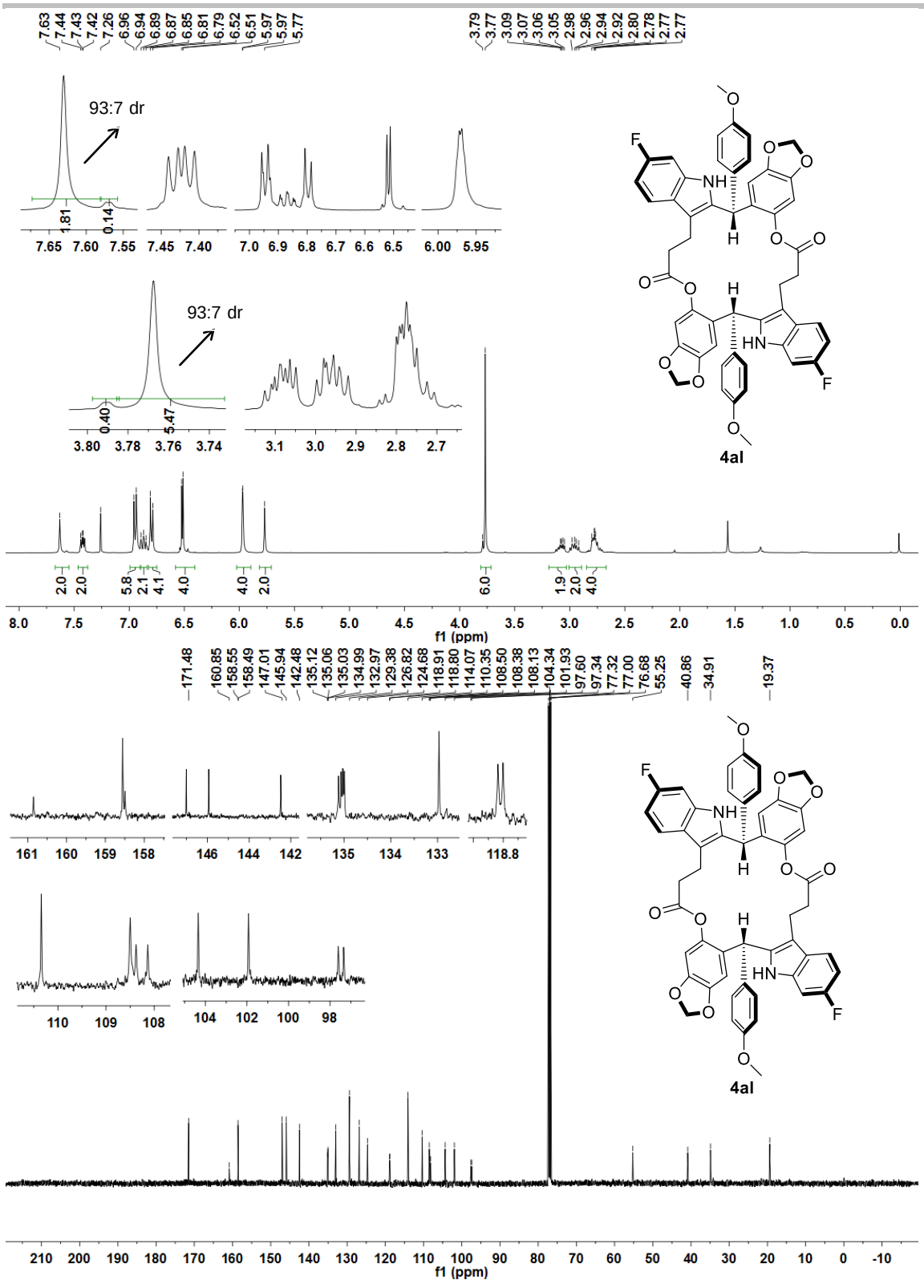

4ah

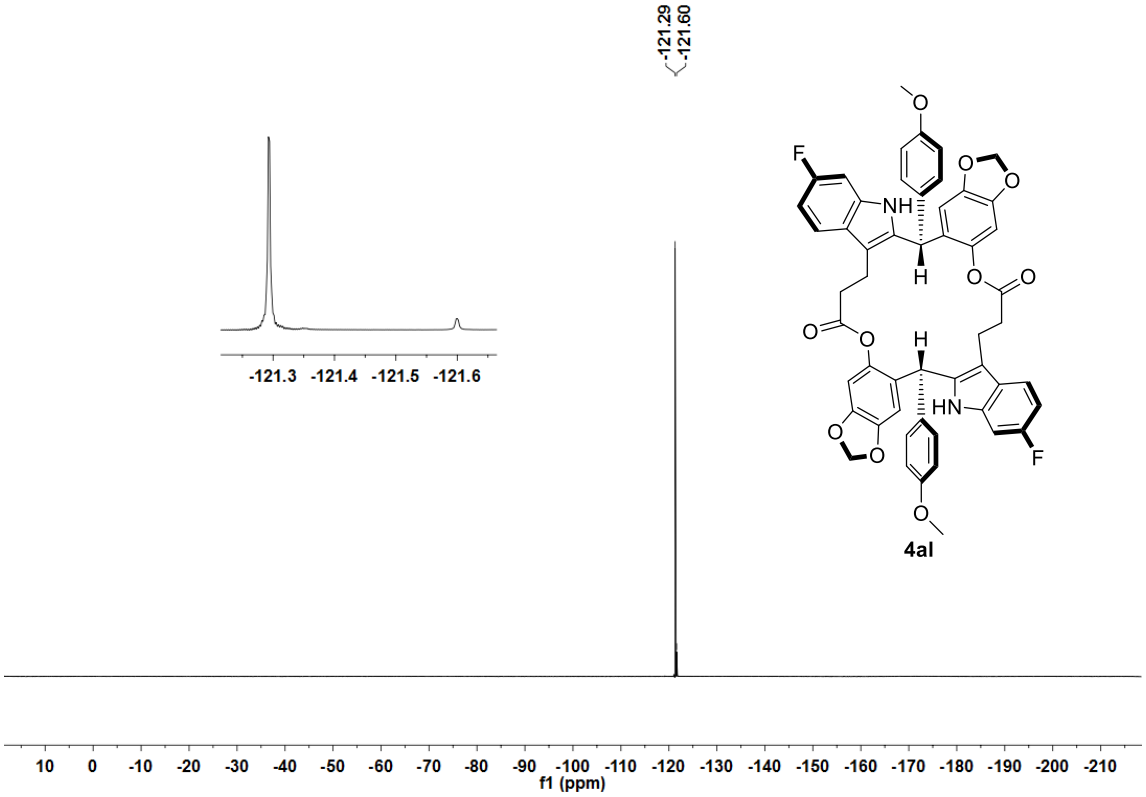

92:8 dr
92:8 dr
4ai
4ai
f1 (ppm)
f1 (ppm)

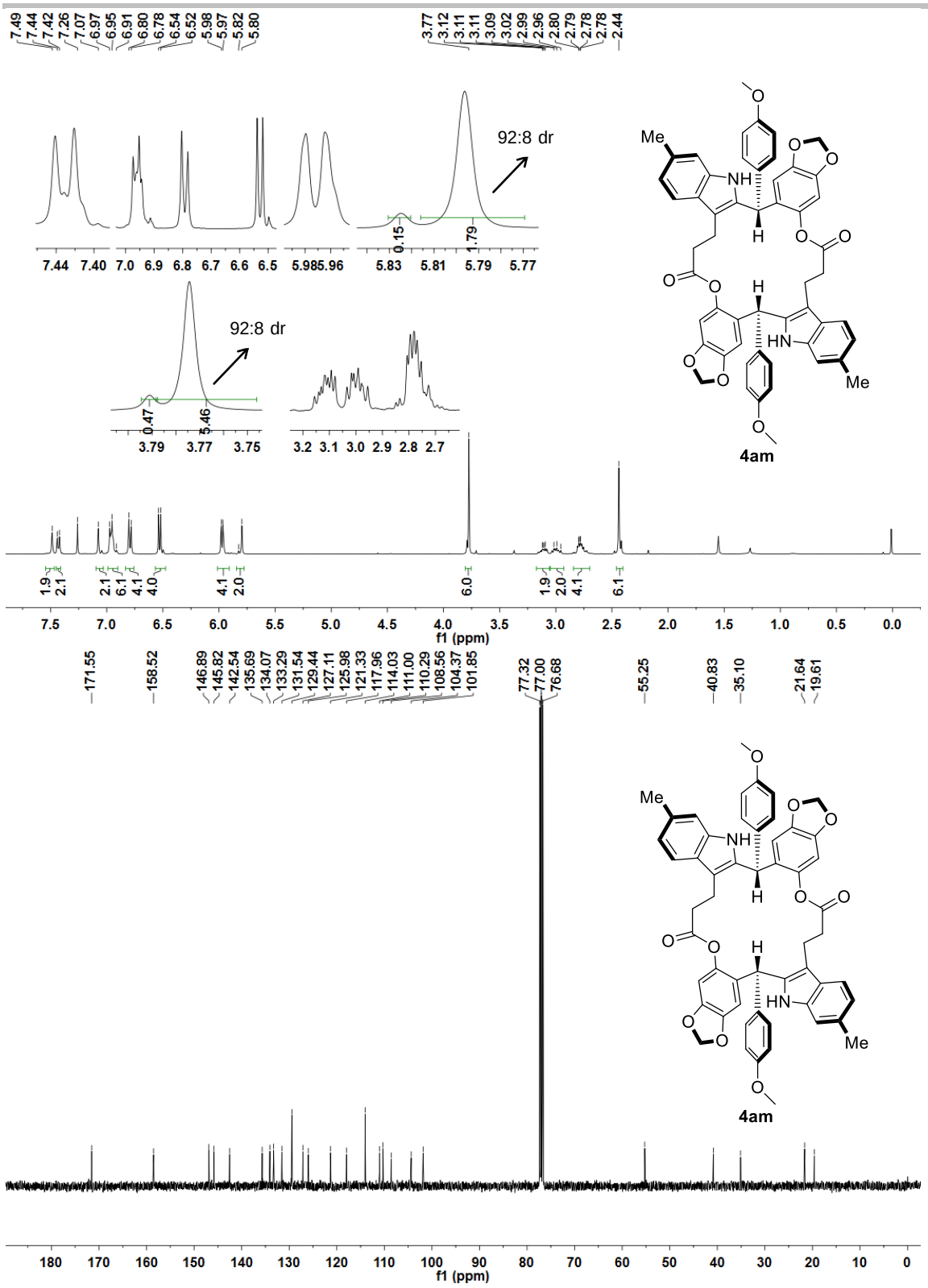

7.62 7.41 7.41 7.38 7.36 7.26 7.21 7.21 6.94 6.92 6.81 6.79 6.51 6.49 5.98 5.97 5.76 5.73
3.77 3.07 3.06 3.04 2.95 2.94 2.93 2.76 2.75 2.74 2.74
93:7 dr
93:7 dr
1.82
0.14
0.42
5.56
2.0 2.0 2.2 2.1 4.0 4.1 3.9 4.0 2.0 6.0 1.8 2.1 4.0
f1 (ppm)
Br
NH
HN
Br
4aj

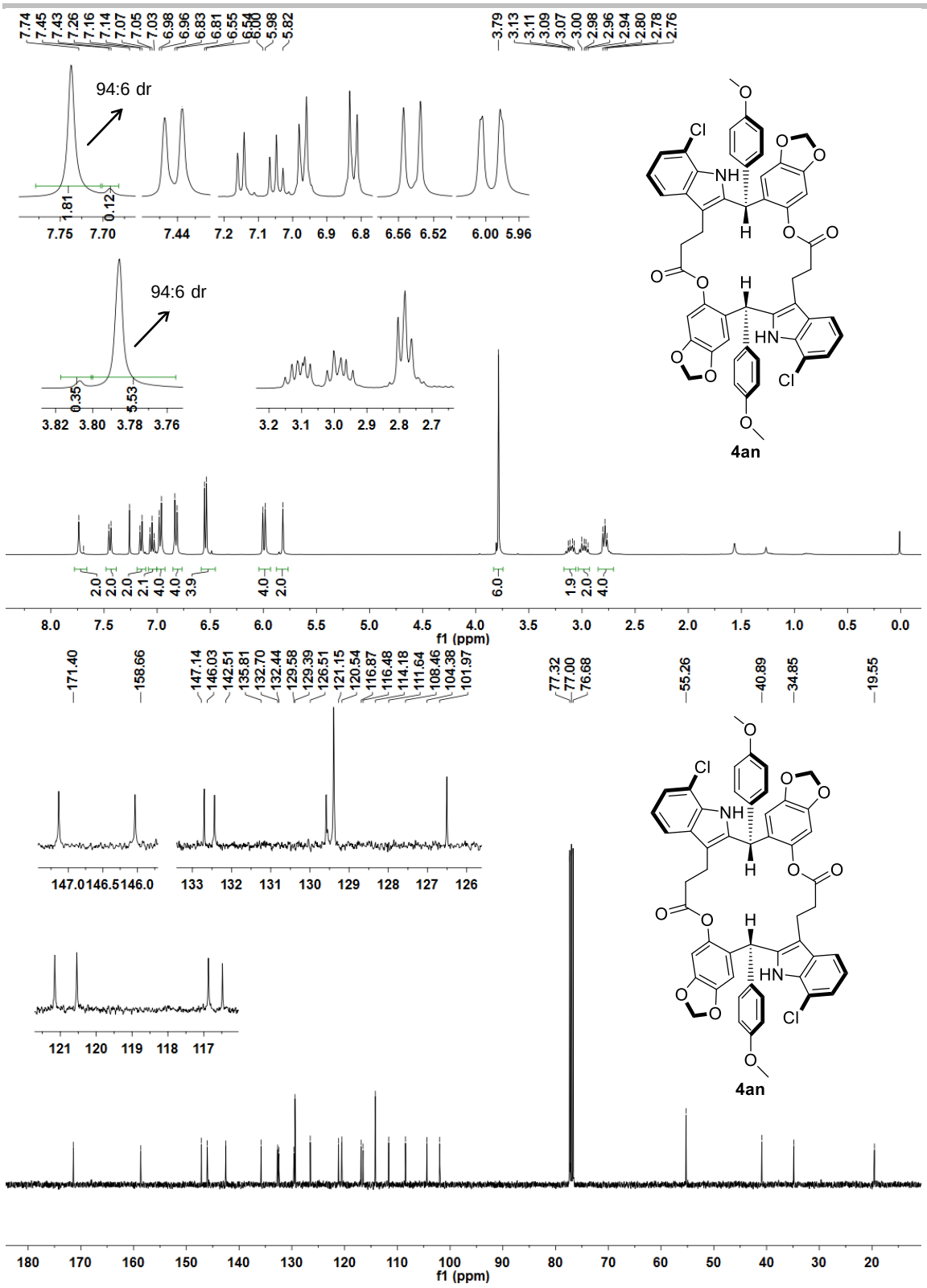

171.39 158.64 147.10 145.99 142.52 135.88 135.62 132.71 129.40 127.06 126.60 122.96 119.44 115.12 114.15 113.95 110.55 108.47 104.39 101.96
77.32 77.00 76.68
55.27 40.91 34.81 19.29
135.8 127.0 126.6 115.0 114.5 114.0
f1 (ppm)
Br
NH
HN
Br
4aj

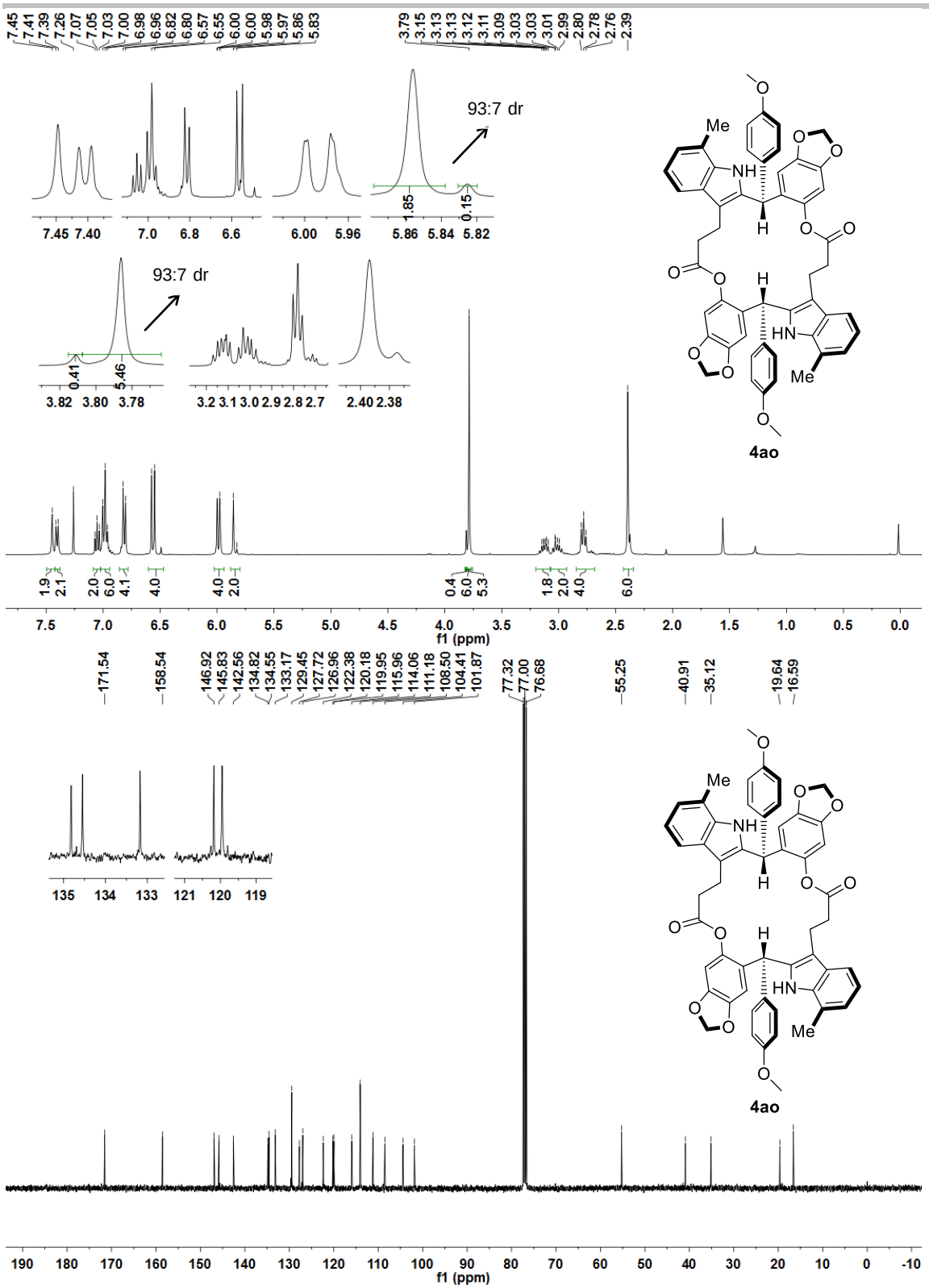

93:7 dr
93:7 dr
4ak
4ak
f1 (ppm)
f1 (ppm)

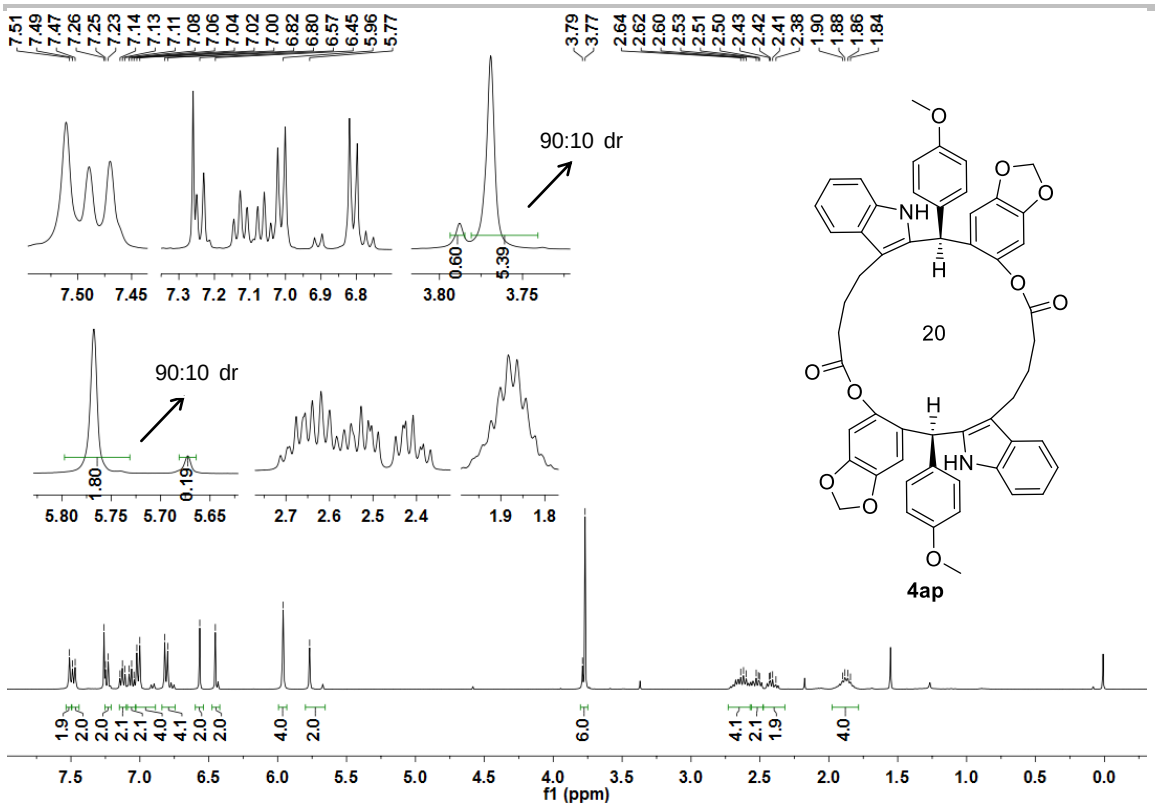

93:7 dr
93:7 dr
4al
4al
f1 (ppm)
f1 (ppm)

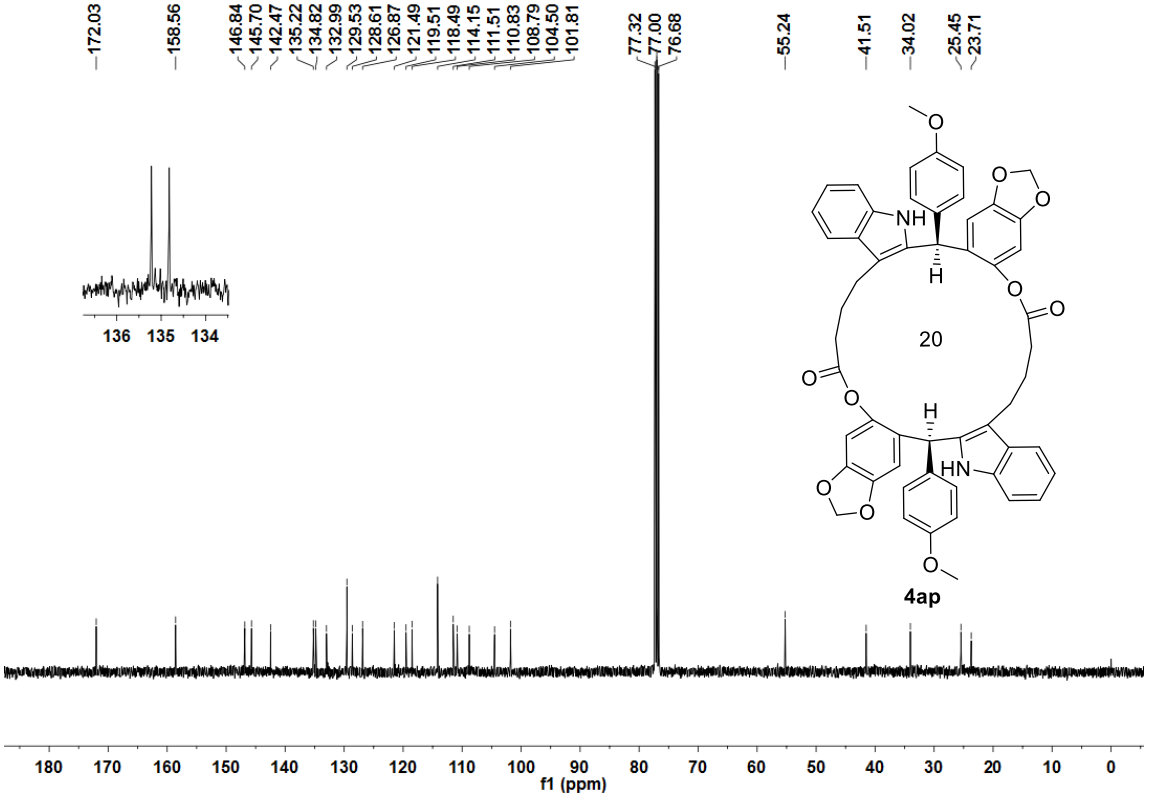

-121.29
-121.60
-121.3
-121.4
-121.5
-121.6
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)
F
NH
O
O
O
O
H
O
O
O
H
HN
O
O
F
O
4al

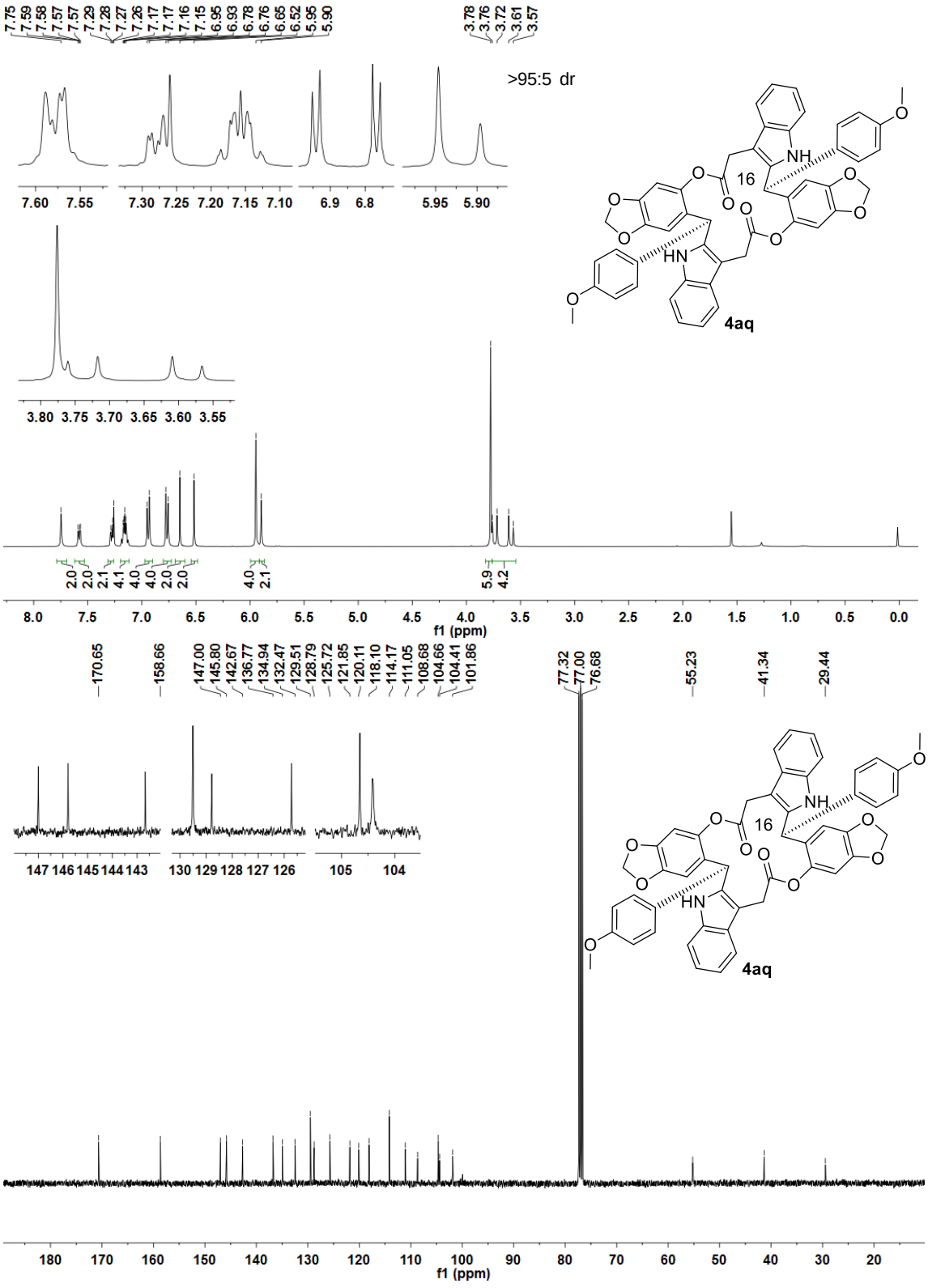

92:8 dr
92:8 dr
4am
4am
f1 (ppm)
f1 (ppm)

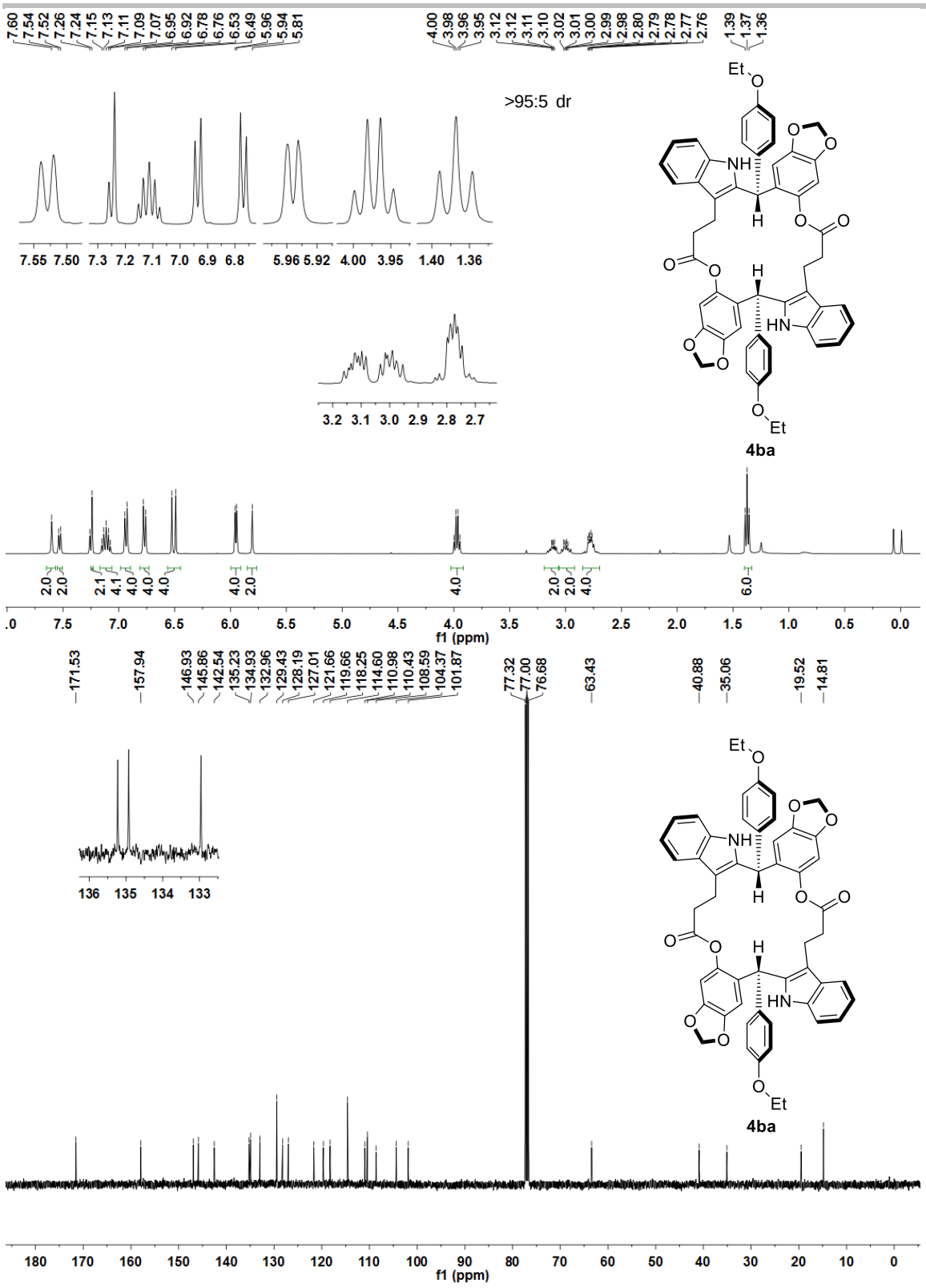

94:6 dr
94:6 dr
4an
4an
f1 (ppm)
f1 (ppm)

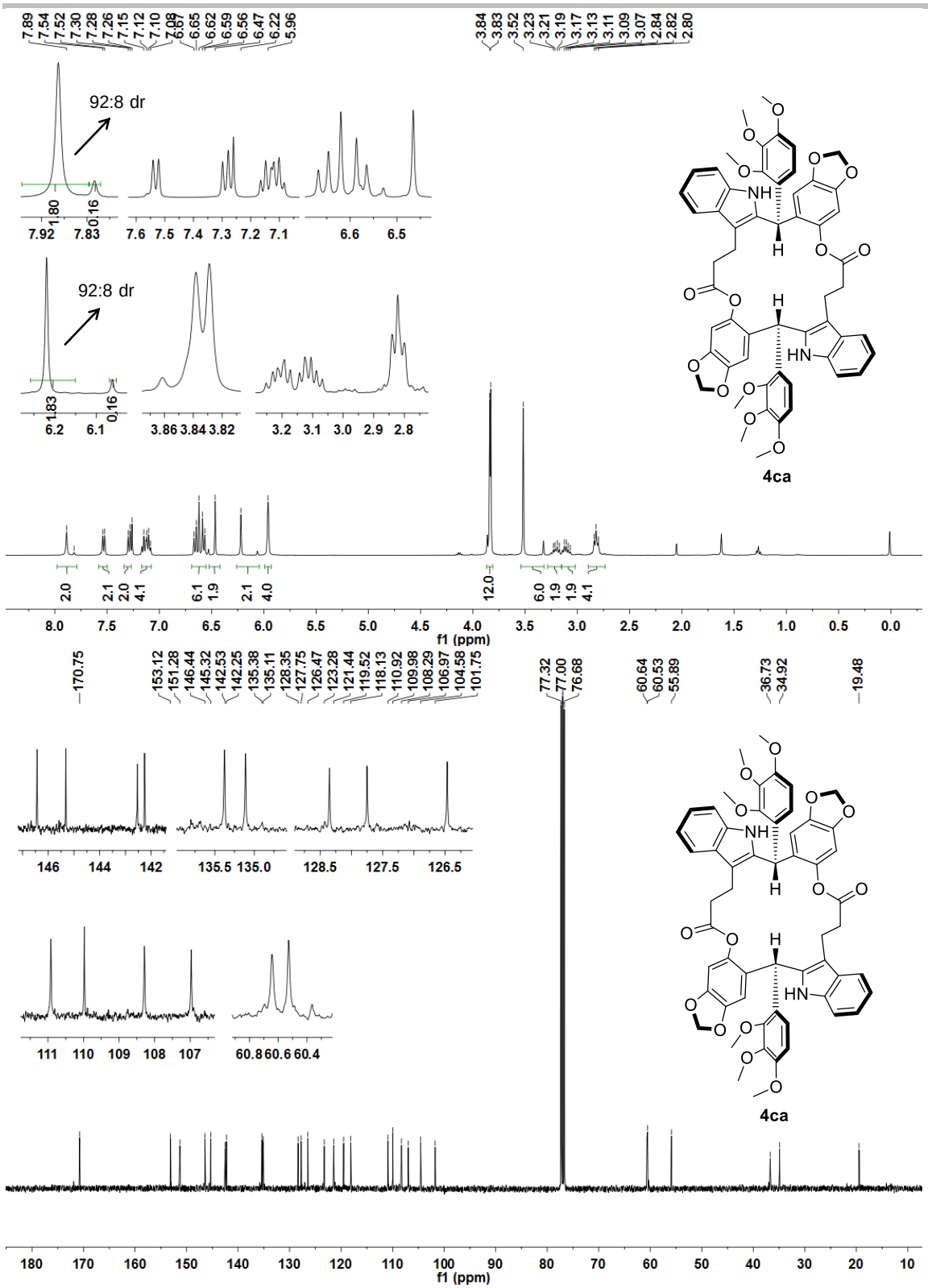

93:7 dr
93:7 dr
4ao
4ao
f1 (ppm)
f1 (ppm)

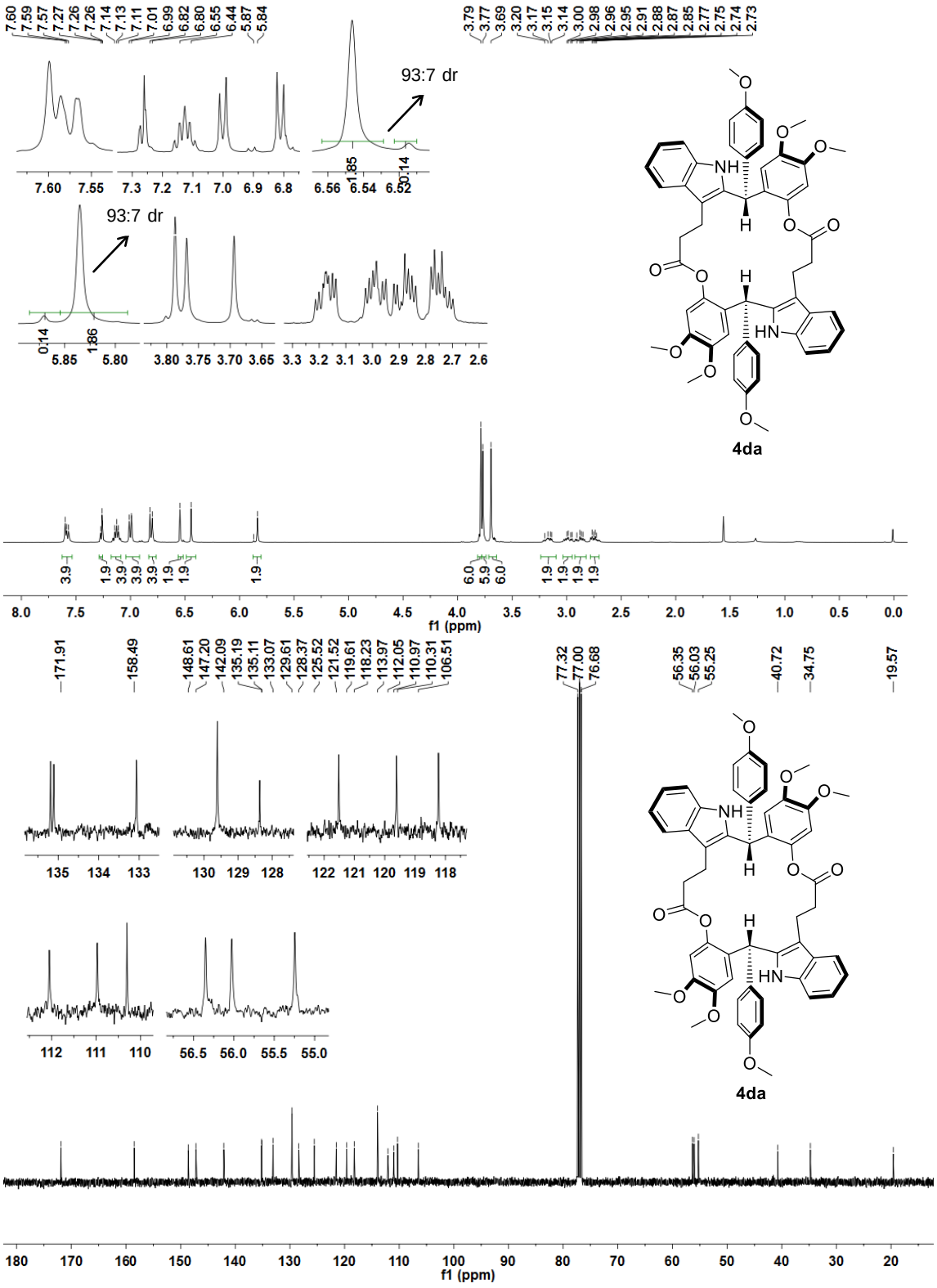

90:10 dr
90:10 dr
4ap

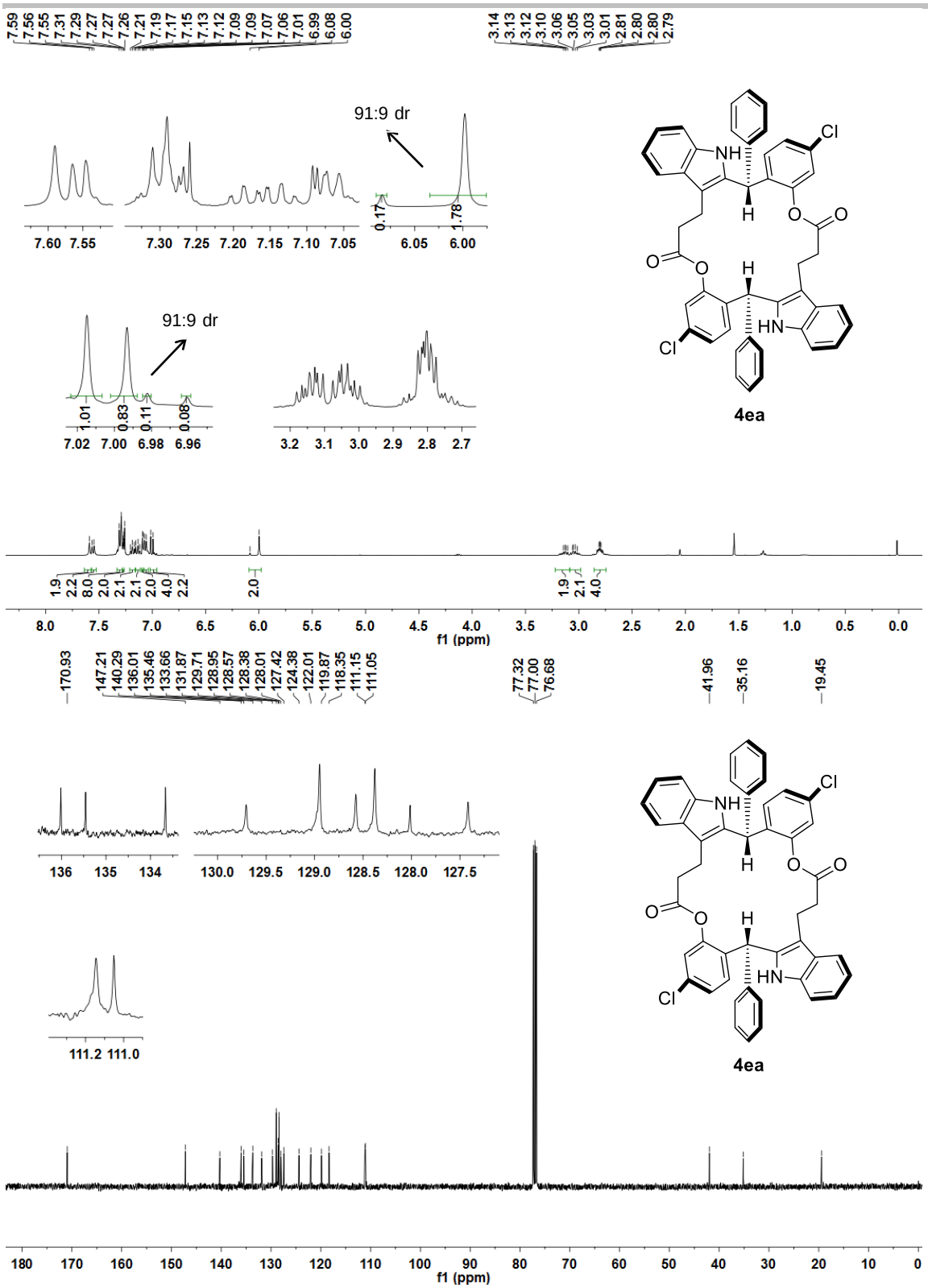

4ap

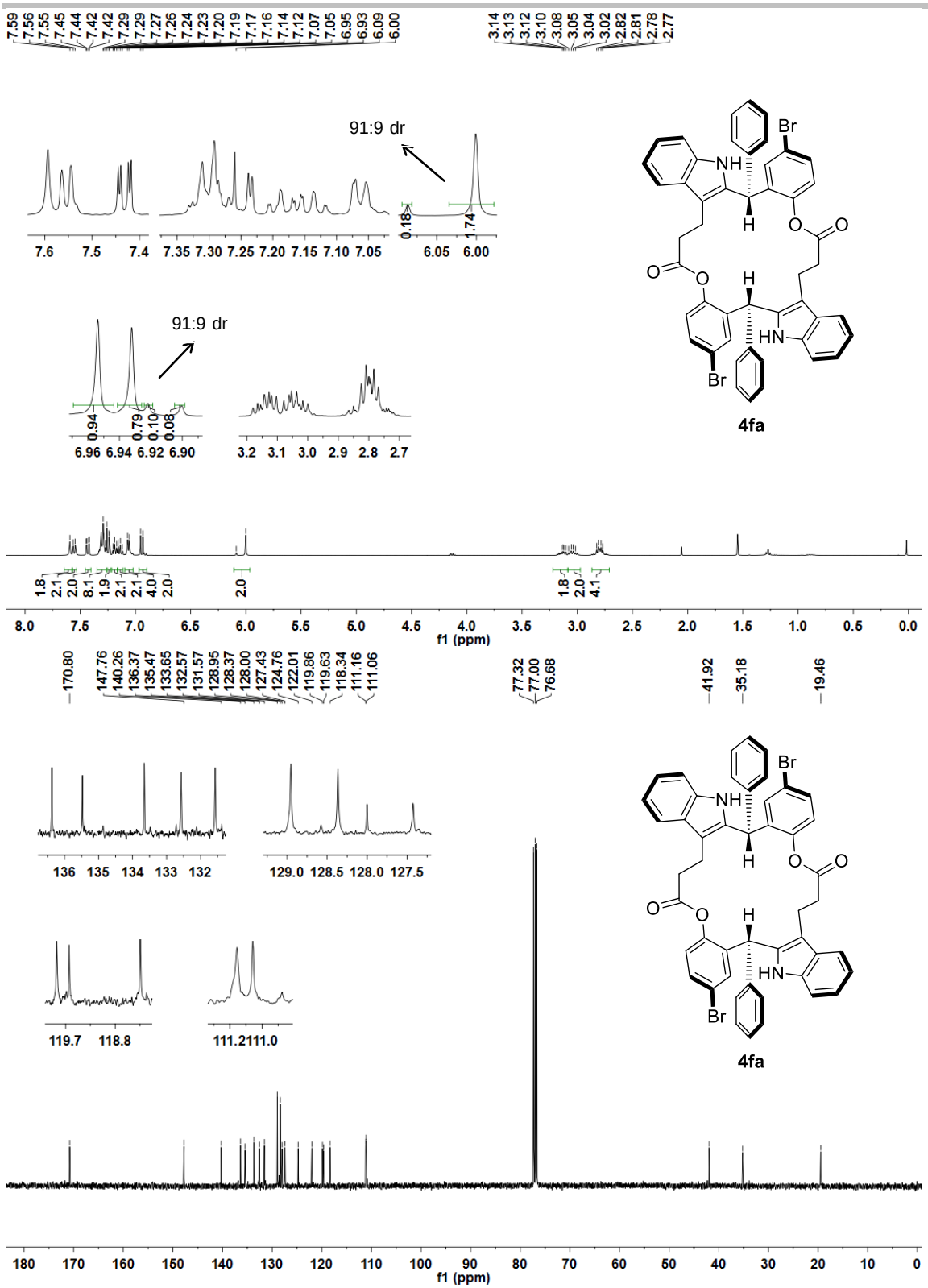

>95:5 dr
4aq
f1 (ppm)
4aq
f1 (ppm)

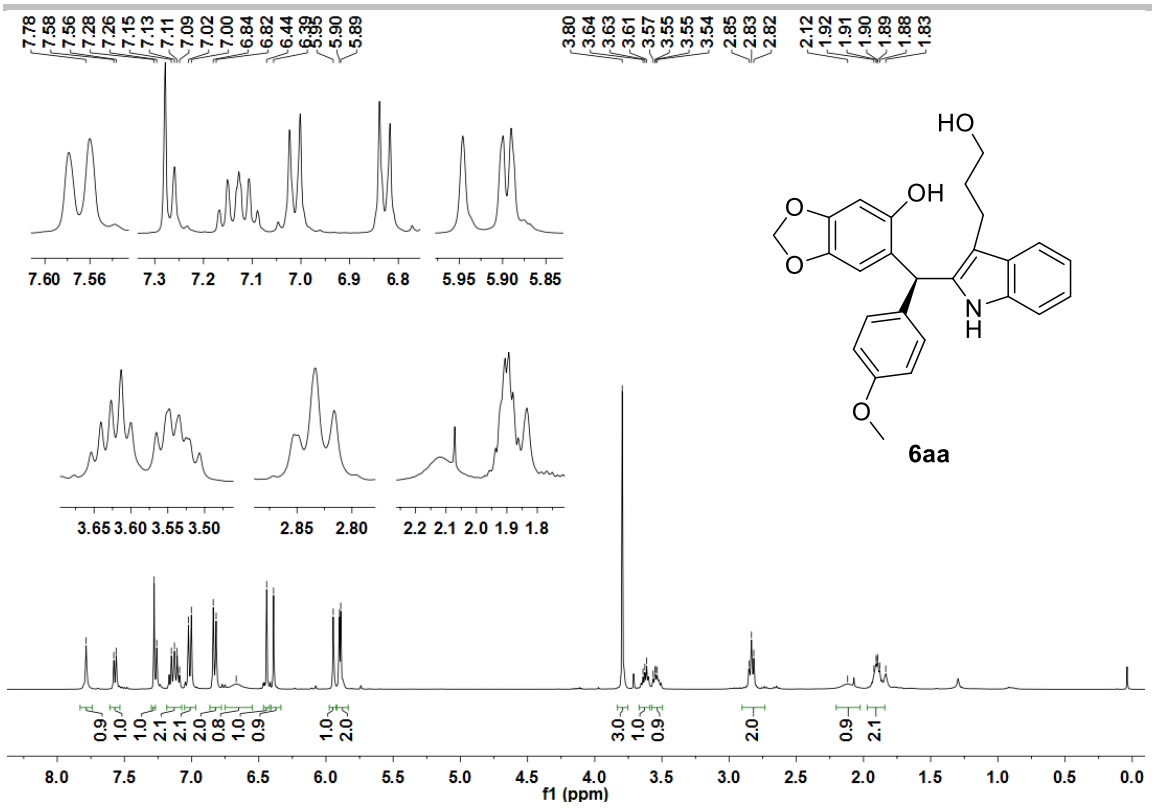

>95:5 dr
4ba
4ba
f1 (ppm)
f1 (ppm)

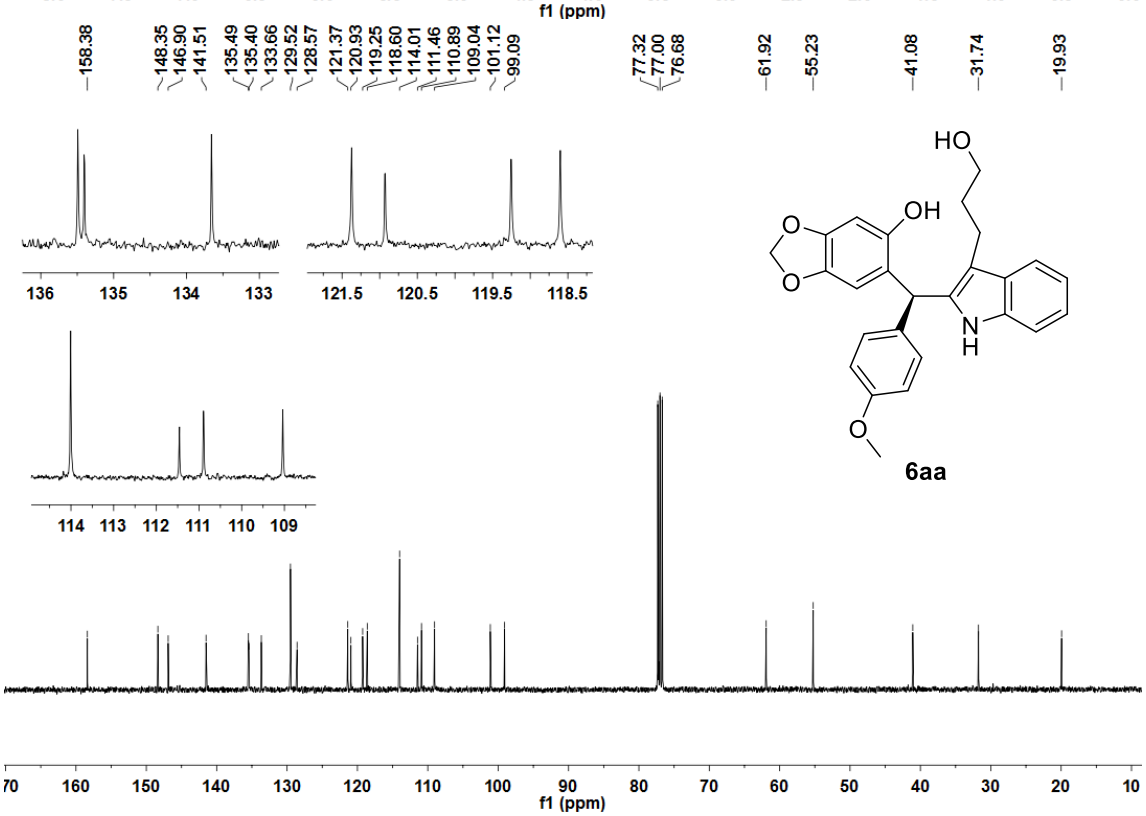

92:8 dr
92:8 dr
4ca
4ca
f1 (ppm)
f1 (ppm)

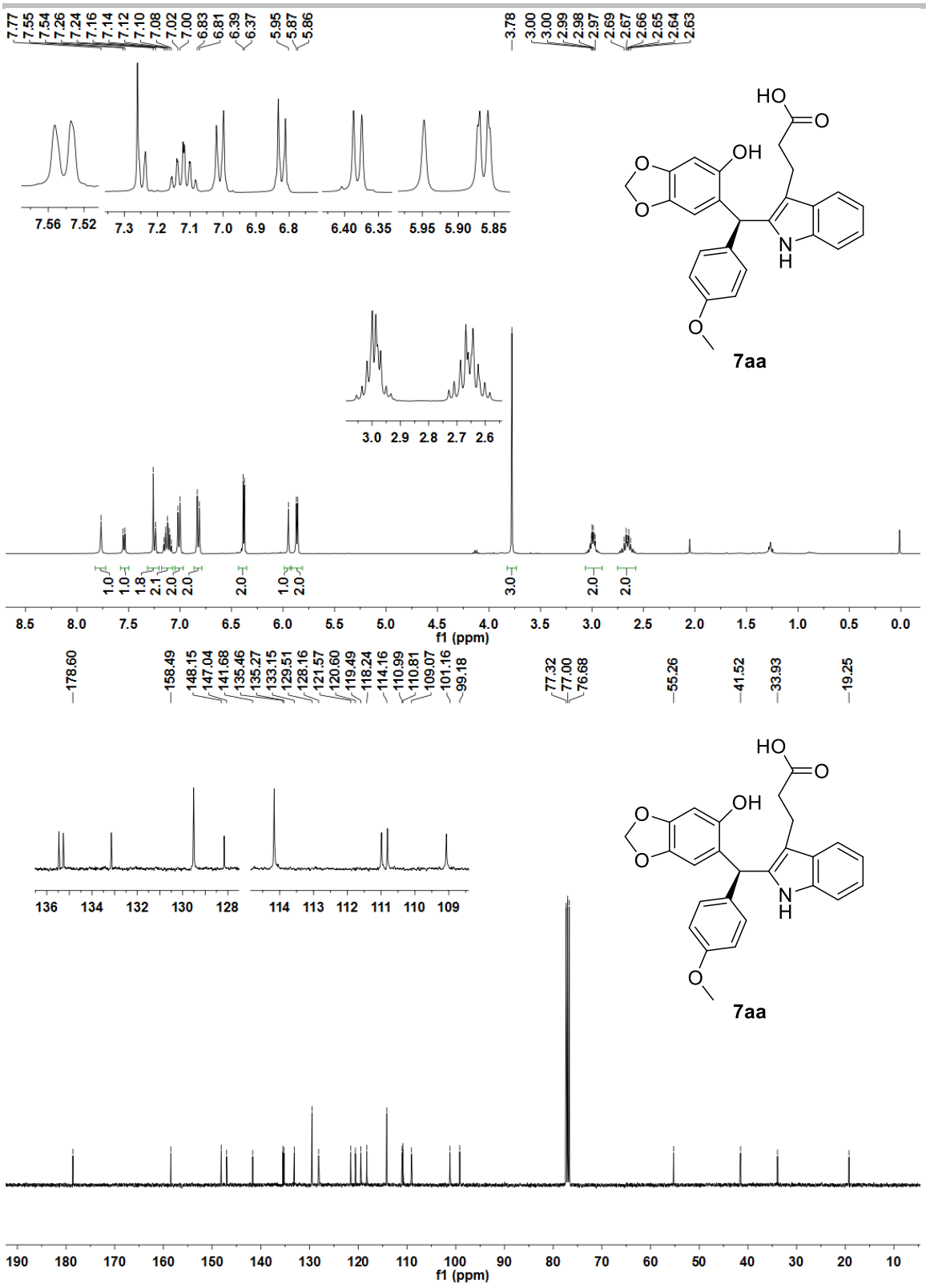

93:7 dr
93:7 dr
4da
4da
f1 (ppm)
f1 (ppm)


91:9 dr
91:9 dr
4ea
4ea
f1 (ppm)
f1 (ppm)


91:9 dr
91:9 dr
4fa
4fa
f1 (ppm)
f1 (ppm)


7.78 7.58 7.56 7.28 7.26 7.15 7.13 7.11 7.09 7.02 7.00 6.84 6.82 6.44 6.39 5.95 5.90 5.89
3.80 3.64 3.63 3.61 3.57 3.55 3.55 3.54 2.85 2.83 2.82
2.12 1.92 1.91 1.90 1.89 1.88 1.83
HO
OH
O
O
N
H
O
6aa
7.60 7.56 7.3 7.2 7.1 7.0 6.9 6.8 5.95 5.90 5.85
3.65 3.60 3.55 3.50 2.85 2.80 2.2 2.1 2.0 1.9 1.8
0.9 1.0 1.0 2.1 2.1 2.0 0.8 1.0 0.9 1.0 2.0 3.0 1.0 0.9 2.0 0.9 2.1
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


158.38 148.35 146.90 141.51 135.49 135.40 133.66 129.52 128.57 121.37 120.93 119.25 118.60 114.01 111.46 110.89 109.04 101.12 99.09
77.32 77.00 76.68 61.92 55.23 41.08 31.74 19.93
HO
OH
O
O
N
H
O
6aa
136 135 134 133 121.5 120.5 119.5 118.5
114 113 112 111 110 109
70 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


7.77 7.55 7.54 7.26 7.24 7.16 7.14 7.12 7.10 7.08 7.02 7.00 6.83 6.81 6.39 6.37 5.95 5.87 5.86
3.78 3.00 3.00 2.99 2.98 2.97 2.69 2.67 2.66 2.65 2.64 2.63
HO
O
OH
O
O
N
H
O
7aa
f1 (ppm)
178.60 158.49 148.15 147.04 141.68 135.46 135.27 133.15 129.51 128.16 121.57 120.60 119.49 118.24 114.16 110.99 110.81 109.07 101.16 99.18 77.32 77.00 76.68 55.26 41.52 33.93 19.25
f1 (ppm)