Supplementary Information

Enantioselective C–H Bond Oxidation using Bio-Inspired Chiral Fe-TAML Catalyst

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1. Materials and methods

Hydrogen peroxide (H_2O_2, 30%), aqueous sodium hypochlorite solution (4% Chlorine), Merck, was used directly without any purification. Meta-Chloroperoxybenzoic acid (mCPBA, Sigma Aldrich 77%) was purified following an established methodology[1]. Acetonitrile, n-hexane and iso propanol (LC-MS and HPLC grade, Sigma Aldrich) was passed through an activated neutral alumina column and distilled and used thereafter. All the other solvents required were purchased and used after distillation over drying agents. All the substrates required for desymmetrization and epoxidation were either bought from TCI, Sigma Aldrich, or Thermo-Fischer Scientific or synthesized following reported procedures.[2] Unless mentioned separately, the reactions were performed at room temperature under air. Analytical thin layer chromatography (TLC) was performed on TLC Silica gel 60 F254. Visualization was accomplished with short-wave UV light or with ninhydrin and PMA staining solutions followed by heating. Purification of desired products was performed by column chromatography using silica gel (230-400 mesh or 100-200 mesh) by standard techniques, eluting with solvents as indicated. All indicated solvents were purified before use as per standard literature protocols. All reagents were obtained commercially and used without further purification unless otherwise noted. Racemic $(Et4N)_2$[(Ph,Me-bTAML) FeIII-Cl] (1), (bTAML = biuret-modified tetraamidomacrocyclic ligands) was synthesized by our previously reported method[3].

2. General Instrumentation and techniques

NMR

^1H and ^{13}C NMR spectra were recorded on Bruker AV 500 or JEOL 400 instruments in solvents as indicated. Chemical shifts (δ) are given in ppm. The residual solvent signals ($CDCl_3$) were used as references, and the chemical shifts were converted to the TMS scale ($CDCl_3$: δH = 7.26 ppm, δC = 77.16 ppm).

Optical rotations

Measured on Perkin Elmer 241 MC polarimeter and $[\alpha]_D$ values quoted in 10^{-1} deg cm^2 g^{-1} with concentration (c) quoted in g (100 mL) $^{-1}$. The enantiomeric excess (ee) for the individual compound is given in brackets.

HPLC

Analytical HPLC (Dionex P580 pump, ASI-100 automated sample injector, UVD 340 U photodiode array detector) was performed using a chiral stationary phase (Daicel ChiralCell, Chemical Industries, flow rate: 1.0 mL/min, type and eluent is given for the corresponding compounds) and UV detection (λ = 210 or 254 nm) at 20 °C. The ***ent*-1** refers to the product mixture of the reaction of substrate with **(*S,S*)-1** catalyst and ***ent*-2** refers to the product mixture of the reaction of substrate with **(*R,R*)-1**

Gas Chromatography-Mass Spectrometry (GC-MS)

Gas Chromatography-Mass Spectrometry (GC-MS) was conducted on a Thermo Scientific ISQ QD Mass Spectrometer attached with Thermo Scientific TRACE 1300 gas chromatograph using an HP-5 ms capillary column (30 m × 0.25 mm × 0.25 μm, J&W Scientific) with helium as the carrier gas. The method was set as: oven temperature program, 31 min; initial

temperature, 60 °C, hold for 2.00 min; ramp-1, 15 °C min−1 to 250 °C, hold for 5 min; ramp-2, 20 °C to 280 °C, hold for 10 min; injector temperature, 230 °C; detector temperature, 280 °C.

Mass spectrometry

HRMS was performed in a WatersHAB213 spectrometer using an electrospray ionization source using methanol as an eluent.

Single Crystal X-ray Diffraction (SC-XRD) Measurements

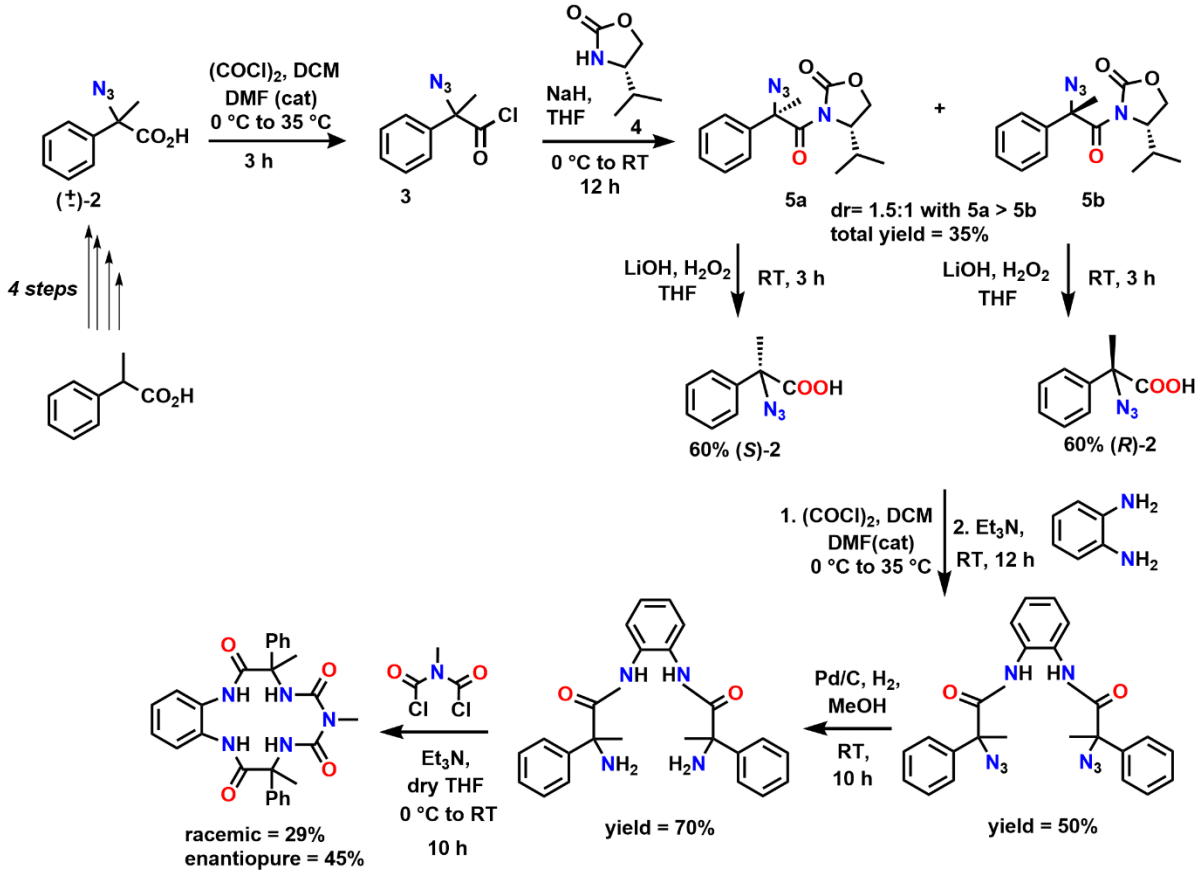
X-ray diffraction data for $(Et_4N)_2$[Fe-(Ph,Me-bTAML)]$^{2-}$ [(*R,R*)-1 and (*S,S*)-1] crystal was collected at 100 K on a SuperNova, Eos diffractometer using monochromatic Mo-Kα radiation (λ = 0.71073 Å) and Cu-Kα radiation (λ = 1.54178 Å) having a 300 μm beam size. Using Olex2 (1.2.9 version)[4] the structure was solved using the SHELXT[5] structure solution program following an intrinsic phasing solution method and refined with the ShelXL4[6] refinement package using Least Squares minimization. All the non-hydrogen atoms were refined anisotropically. All the crystal packing diagrams were prepared using Mercury (3.10.1 version) software

Quantum Chemistry Calculations:

The density functional theory (DFT) method was used for the geometry optimizations of the complexes under this study using the ORCA 6 program.[7] The geometry optimizations were carried out using the unrestricted B3LYP hybrid DFT model.[8] For all the calculations, the metal centre Fe has been described by the def2-SVP effective core potential basis set, while for the rest of the nonmetal atoms, an all-electron def2-TZVP basis set was used.[9] We have performed frequency calculations to make sure that all the positive frequencies were obtained, indicating a real minimum. All calculations were run with a solvent model (SMD) with a dielectric constant mimicking acetonitrile.

3. Experimental Results:

Scheme 1: Synthesis of enantiopure and racemic macrocycle:



Synthesis of 2-Azido-2-phenylpropanoyl chloride 3

In a 100 mL 2-neck RB, 2.54 g of 2 -Azido-2-phenylpropanoic acid **2** was taken and 30 mL dry DCM was added under inert atmosphere. At 0 °C, 2.3 mL oxalyl chloride (2 equiv.) was added slowly followed by addition of a catalytic amount (250 µL) of DMF (strong effervescence was observed after DMF addition). 0 °C was maintained for 15 mins. Then, the reaction was allowed to come to room temperature and slightly heated to 35 °C (with warm water). The reaction was continued for 4 h. The solvent was then evaporated by using a vacuum trap in liquid nitrogen. The RB content was washed with hexane twice, followed by drying under high vacuum. It was used as such for the next step (calculated 80% yield).

Synthesis of 3-(2-azido-2-phenylpropanoyl)-4-isopropyloxazolidin-2-one 5a and 5b:

All reactions were carried out under an argon atmosphere. Acid chloride **3** solution (1 equiv) was prepared by adding 35 mL dry toluene in that 2-neck RB used in the previous step. In another 250 mL 2-neck RB, 1.71 g of (4S)-4-Isopropyl-2-oxazolidinone (**4**) was taken and 30 mL dry THF was added. At 0 °C, 532 mg of NaH (1 equiv) was added to the oxazolidinone solution. The acid chloride solution was then added dropwise to the amine solution (for 20 mins). After addition, the temperature was maintained at 0 °C for 10 more mins, followed by stirring for 15 h at room temperature. After completion, the reaction mixture was filtered via frit funnel to remove insoluble salts. The filtrate was rota-evaporated to complete dryness.

Purification and separation by column chromatography (SiO_2, Hexane: EtOAc, 1:24 to 3:47) gave white solid as diastereomer **5a** (1.43 g, 35%) and pale yellow viscous liquid as diastereomer **5b** (1.02 g, 25%).

(*R*)-3-((*S*)-2-azido-2-phenylpropanoyl)-4-isopropyloxazolidin-2-one 5a:

R_f = 0.419 (1:4 ethyl acetate: hexane)

^{1}H NMR (500 MHz, $CDCl_3$) in ppm: δ 7.42 – 7.36 (m, 2H), 7.36 – 7.31 (m, 1H), 7.30 – 7.26 (m, 2H), 4.57 (ddd, *J* = 8.2, 4.0, 2.8 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.16 (dd, *J* = 9.2, 2.9 Hz, 1H), 2.46 – 2.39 (m, 1H), 2.04 (s, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H)

^{13}C NMR (126 MHz, $CDCl_3$) in ppm: δ 171.2, 151.3, 138.2, 129.0, 128.6, 125.3, 72.5, 63.8, 60.3, 28.9, 23.0, 18.3, 15.2.

Specific Rotation: $[\alpha]_D^{25.0}$ = 186 (c = 0.1, $CHCl_3$)

(*R*)-3-((*R*)-2-azido-2-phenylpropanoyl)-4-isopropyloxazolidin-2-one 5b:

R_f = 0.35 (1:4 ethyl acetate: hexane)

^{1}H NMR (500 MHz, $CDCl_3$) in ppm: δ 7.38 (dd, *J* = 8.0, 6.5 Hz, 2H), 7.34 – 7.31 (m, 1H), 7.31 – 7.27 (m, 2H), 4.60 – 4.51 (m, 1H), 4.28 – 4.22 (m, 1H), 4.17 (dd, *J* = 9.2, 2.9 Hz, 1H), 2.45 (m, 1H), 1.99 (s, 3H), 0.94 (d, *J* = 7.0 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 170.9, 151.0, 138.2, 128.6, 128.3, 125.3, 72.0, 63.2, 60.1, 28.2, 23.0, 18.2, 14.6.

Specific Rotation: $[\alpha]_D^{25.0}$ = 6 (c = 0.1, $CHCl_3$)

HRMS: Found $[M+Na]^+$ = 325.1265; $C_{15}H_{18}N_4O_3Na$ requires 325.1277

Synthesis of (*R*) and (*S*)-2-Azido-2-phenylpropanoic acid 2:

The removal of the chiral auxiliary was followed from the literature report with some modifications.[10] The diastereomers were taken separately in THF, and LiOH (1.5 equiv) was added along with H_2O_2 (4 equiv) at room temperature. The stirring was continued for 3 hours and the remaining H_2O_2 was quenched with Sodium hydrogen sulfite. The resulting mixture was extracted with ethyl acetate and Sodium bicarbonate. The organic part was discarded and the aqueous part was treated with 2 (N) HCl until pH reached 2. Then the aqueous part was treated with ethyl acetate and the compound was extracted in the organic part. The solution was passed through anhydrous sodium sulfate, followed by filtration and concentrated in rota vac to yield pale yellow oil (60%).

^{1}H NMR (500 MHz, $CDCl_3$**)** in ppm: δ 10.88 (s, 1H), 7.55 – 7.50 (m, 2H), 7.46 – 7.37 (m, 3H), 1.91 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) in ppm:δ 178.0, 138.3, 129.2, 129.2, 126.1, 69.2, 24.2.

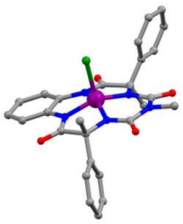
Specific Rotation: $[\alpha]_D^{25.0}$ of (*R*)-**2** = -26 and (*S*)-**2** = +24 (c = 0.1, $CHCl_3$)

****The macrocycles were synthesized following the exact literature method. The enantiomers and the racemic macrocycle will have the same NMR spectra.

^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.80 (s, 2H), 7.63 (dd, *J* = 6.0, 3.6 Hz, 2H), 7.55 (s, 2H), 7.49 – 7.46 (m, 4H), 7.45 – 7.41 (m, 4H), 7.40 – 7.34 (m, 2H), 7.11 – 7.05 (m, 2H), 3.15 (s, 3H), 1.95 (s, 6H).

Specific rotation: $[\alpha]_D^{25.0}$ of (*S,S*)-macrocycle = -101 and $[\alpha]_D^{25.0}$ of (*R,R*) macrocycle = +99 (c = 0.1, $CHCl_3$).

Chiral HPLC: Sample dissolved in i-PrOH. t_R [racemate] = 6.897 min and 10.295 min. t_R (*R,R*) = 6.7 min and t_R (*S,S*) = 10.347 min (IA, n-hexane/i-PrOH = 90:10, 1 mL/min, λ = 245 nm).



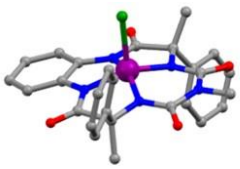
(***R,R***)-**1**

Figure S1: Crystal structure of (***R,R)*-1**

Table S1 Summary of X-ray crystallographic data of complex **(*R*,*R*)-1**

Identification code	DDB_CAT2_reduced
CCDC No	2491436
Empirical formula	$C_{43}H_{63}ClFeN_7O_4$
Formula weight	833.30
Temperature (K)	99.98(18)
Crystal system	Triclinic
Space group	P1
a (Å)	9.0356(2)
b (Å)	13.1688(2)
c (Å)	17.9549(3)
α (°)	88.500(2)
β (°)	81.057(2)
γ (°)	88.7800(10)
Volume (Å³)	2109.40(7)
Z	2
ρ_calc (g/cm³)	1.312
μ (mm⁻¹)	3.847
F(000)	890.0
Crystal size (mm³)	? × ? × ?
Radiation	Cu Kα (λ = 1.54184 Å)
2Θ range (°)	4.984 to 136.578
Index ranges	-10 ≤ h ≤ 10, -14 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	38828
Independent reflections	12102 [R_int = 0.0462, R_sigma = 0.0428]
Data/restraints/parameters	12102 / 3 / 1031
Goodness-of-fit on F²	1.061
Final R indexes [I ≥ 2σ(I)]	R_1 = 0.0622, wR_2 = 0.2049
Final R indexes [all data]	R_1 = 0.0641, wR_2 = 0.2062
Largest diff. peak/hole (e Å⁻³)	1.70 / -0.58
Flack parameter	0.004(4)

[a]$R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b]$wR_2 = \{\Sigma[w\,(|F_o|^2 - |F_c|^2)^2]/\Sigma[w\,(|F_o|^2)^2]\}^2$.



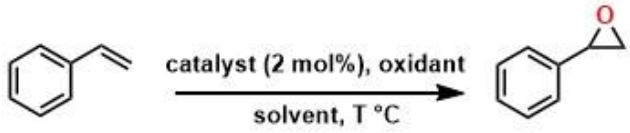
(*S*,*S*)-1

Figure S2: Crystal structure of (***S*,*S*)-1**

Table S2 Summary of X-ray crystallographic data of complex ***(S,S)*-1**

Identification code	ddb-cat1_reduced
CCDC No	2491428
Empirical formula	$C_{43}H_{63}ClFeN_7O_4$
Formula weight	833.30
Temperature (K)	100.15
Crystal system	Triclinic
Space group	P1
a (Å)	9.0318(2)
b (Å)	13.1643(4)
c (Å)	17.9475(3)
α (°)	88.547(2)
β (°)	81.094(2)
γ (°)	88.722(2)
Volume (Å³)	2107.14(9)
Z	2
ρ_calc (g/cm³)	1.313
μ (mm⁻¹)	3.851
F(000)	890.0
Crystal size (mm³)	0.6 × 0.4 × 0.2
Radiation	CuKα (λ = 1.54184 Å)
2Θ range (°)	4.986 to 133.194
Index ranges	-9 ≤ h ≤ 10, -15 ≤ k ≤ 15, -21 ≤ l ≤ 21
Reflections collected	11101
Independent reflections	11101 [R_int = ?, R_sigma = 0.0590]
Data/restraints/parameters	11101 / 3 / 1033
Goodness-of-fit on F²	1.057
Final R indexes [I ≥ 2σ(I)]	R_1 = 0.0589, wR_2 = 0.1866
Final R indexes [all data]	R_1 = 0.0619, wR_2 = 0.1884
Largest diff. peak/hole (e Å⁻³)	1.23 / -0.68
Flack parameter	0.013(4)

Table S3: Optimisation of AE of styrene in different solvents with different oxidants[a]



Entry	Oxidant	Temperature	Solvent	[c]ee%
1	**NaOCl**	**RT**	**MeCN: H_2O (9:1)**	**27**
2	NaOCl	0 °C	MeCN: H_2O (9:1)	27
3	NaOCl	RT	MeCN: H_2O (8:2)	18
4	NaOCl	RT	TFE: H_2O (9:1)	NR
5	PhI $(OAC)_2$	RT	MeCN: H_2O (9:1)	25
6	H_2O_2 (PBS, pH~ 8.5)	RT	MeCN: H_2O (1:1)	20
7	H_2O_2 (PBS, pH~ 8.5)	RT	100 % H_2O	5
8	H_2O_2 (PBS, pH~ 8.5)	RT	TFE: H_2O (1:1)	4

[a]Reaction conditions: 0.25 µmol (*R,R*) and (*S,S*)-**1**, styrene (12.5 µmol) dissolved in 1 mL solvent, H_2O= PBS (pH~ 8). Oxidant (13 µmol) added to it, and the reaction time was 30 mins. [c]ee values were determined by chiral HPLC, NR = no reaction.

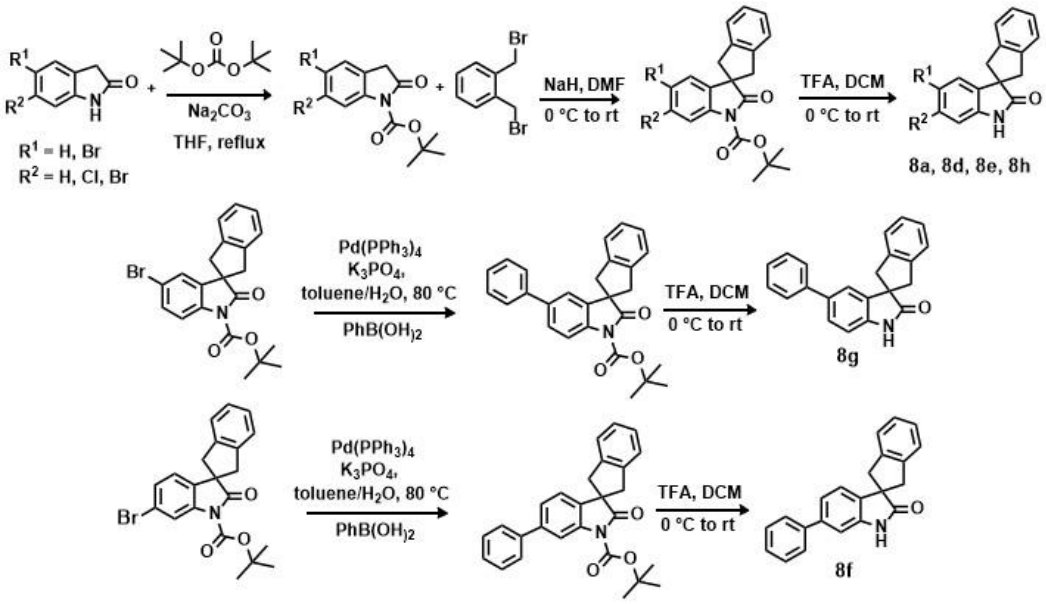
General procedure for asymmetric epoxidation of olefin.

For epoxidation, in a MeCN (0.9 mL) and water (0.1mL) solution of substrate **6a-d** (0.0125 mmol) and Fe catalyst (2 mol%), NaOCl (0.0131mmol) was added iteratively in a 2 mL vial at room temperature. The reaction was monitored by GC-MS. After completion of the reaction, the excess NaOCl was quenched by sodium thiosulfate. The product (**7a-d**) was extracted with hexane, passed through sodium sulfate followed by filtration. The enantiomeric excess was monitored by HPLC with chiral columns.

General procedure for synthesis of spirocyclic substrates (8a, 8d-h)

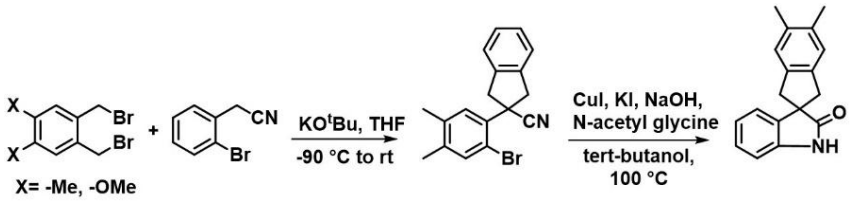
The spirocyclic oxindole and dihydroquinolinone substrates were synthesized according to the published strategies[2] (**Scheme 2**). To a solution of 2-oxindole (15.0 mmol) in THF (60 mL) at RT was added anhydrous Na_2CO_3 (14.3 g, 135.0 mmol) and Boc_2O (8.62 mL, 37.6 mmol) sequentially. The reaction mixture was heated to reflux and maintained at this temperature for 2 h after which it was cooled to RT. The resulting precipitated material was filtered off under suction using THF (3 × 10 mL) and concentrated in vacuo. Purification by column chromatography (SiO2, Petroleum ether/EtOAc, 50:1→20:1) gave the title compounds as a solid. Then, to a solution of above compounds (4.29 mmol) in DMF (68 mL) at 0 °C was added NaH (60% in mineral oil, 377 mg, 9.43 mmol) in one portion. The mixture was stirred for 1 h 30 min at 0 °C, after which a solution of o-xylylene dibromide (5.15 mmol) in DMF (6.3 mL) was added dropwise via syringe over 30 min. Following the addition, the mixture was allowed to warm to RT slowly over 16 h. The reaction was quenched with H_2O (40 mL) and diluted with EtOAc (40 mL). The layers were separated, and the aqueous layer was further extracted with EtOAc (40 mL). The combined organic layers were washed with brine (80 mL), dried ($MgSO_4$) and concentrated

Scheme 2: Synthesis of spirocyclic oxindoles **8a, 8d-h**



in vacuo. Purification by column chromatography (SiO_2, Petroleum ether/EtOAc, 20:1) gave the white compound which was further dissolved in DCM and trifluoroacetic acid (TFA) added at 0 °C. The reaction was warmed up at room temperature and was continued for 2 hours. Finally, the reaction mixture was concentrated in vacuo and purified by column chromatography (SiO_2, Hexane: EtOAc = 4:1 to 7:3) to get desired spirocyclic compounds **8a, 8d, 8e, 8h**. For **8f** and **8g** the phenyl group was incorporated to the Boc protected **8e** and **8h,** respectively by Suzuki cross coupling reaction. To a solution of Boc protected **8e** and **8h** (0.415g, 1.0 mmol) in Toluene/H_2O (10 mL/3 mL) separately at RT, $PhB(OH)_2$ (0.304 g, 1.5mmol), $Pd(PPh_3)_4$ (60 mg, 0.05 mmol) and K_3PO_4 (0.53g, 2.5 mmol) was added sequentially under argon atmosphere. The reaction mixture was heated to 80 °C and maintained at this temperature for 6 h after which it was cooled to RT. The reaction was extracted with toluene (10 mL) and the organic layer was washed with H_2O (3 × 5 mL), brine (10 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (SiO_2, dry load, Petroleum ether/EtOAc, 50:1) afforded a light yellow solid (353 mg, 86% isolated yield) which further dissolved in DCM and trifluoroacetic acid (TFA) added at 0 °C. The reaction was warmed up at room temperature and was continued for 2 hours. Finally, the reaction mixture was concentrated in vacuo and purified by column chromatography (SiO_2, Hexane: EtOAc = 4:1 to 7:3) to get desired spirocyclic compound **8g** and **8f** (212mg, 80% isolated yield).

Scheme 3: Synthesis of **8b** and **8c**:



To a solution of phenylene dibromide (5mmol) compound in 5mL dried THF, KO^{t}Bu (12.5 mmol) was added at -100 °C. After 30 mins rotation at the same temperature, a 2 mL THF

solution of 2-(2-bromophenyl) acetonitrile was added dropwise to it. Following the addition, the mixture was allowed to warm to RT slowly over 23 h. The reaction was quenched by the addition of sat. aq. $NaHCO_3$ (5 mL) and diluted with EtOAc (20 mL). The layers were separated and the aqueous layer further extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with H_2O (50 mL), brine (50 mL), dried (MgSO4) and concentrated in vacuo. Purification by column chromatography (SiO2, dry load, Hexane: EtOAc, 4:1→7:3) gave the title compound as a white solid (35%). To a suspension of the synthesised compound (0.13 mmol) in t-BuOH (3 mL) at RT was added CuI (3.9 µmol), KI (1.3 µmol), N-acetylglycine (7.8 µmol) and NaOH (0.39 mmol) sequentially. The reaction vessel was sealed and the mixture heated to 100 °C for 48 h. The reaction mixture was cooled to RT and concentrated in vacuo. Purification by column chromatography (SiO2, dry load, Hexane: EtOAc, 3:2→1:1→2:3) gave the title compound (31%) as an off-white solid.

Characterisations of substrates 8a-h:

1,3-dihydrospiro[indene-2,3'-indolin]-2'-one 8a:

^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 9.71 (s, 1H), 7.38 – 7.20 (m, 4H), 7.16 (td, *J* = 7.6, 1.5 Hz, 1H), 6.93 (dt, *J* = 7.9, 0.8 Hz, 1H), 6.86 (dtd, *J* = 15.0, 7.5, 1.2 Hz, 2H), 3.66 (d, *J* = 15.7 Hz, 2H), 3.13 (d, *J* = 15.7 Hz, 2H).

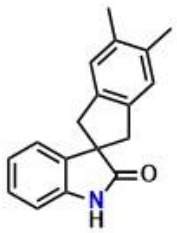
^{13}C NMR (126 MHz, $CDCl_3$) in ppm: δ 183.4, 141.3, 140.0, 136.8, 128.0, 127.1, 124.6, 122.7, 121.9, 110.2, 54.7, 44.0.

HRMS: Found $[M+H]^+$ = 236.1073; $C_{16}H_{14}O_1N_1$ requires 236.1075.

GC: tR = 16.024 min

IR (film)**:** ν_{max}/cm^{-1} 3138, 3073, 3024, 2895, 2838, 1701, 1613, 1466, 1436, 1341, 1306, 1262, 1252, 1226, 1140, 1101, 1007, 926, 889

5,6-dimethyl-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one 8b:



^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 9.03 (s, 1H), 7.17 (ddd, *J* = 7.8, 5.4, 3.5 Hz, 1H), 7.05 (s, 2H), 6.92 (d, *J* = 7.7 Hz, 1H), 6.90 – 6.84 (m, 2H), 3.58 (d, *J* = 15.5 Hz, 2H), 3.06 (d, *J* = 15.4 Hz, 2H), 2.28 (s, 6H).

^{13}C NMR (126 MHz, $CDCl_3$) in ppm: δ 183.2, 139.9, 138.7, 137.0, 135.3, 127.9, 125.7, 122.7, 122.0, 109.9, 54.8, 43.8, 19.9.

HRMS: Found $[M+H]^+$ = 264.1367; $C_{18}H_{18}O_1N_1$ requires 264.1388

GC: tR = 18.482 min

IR (film)**:** ν_{max}/cm^{-1} 3137, 3072, 3029, 2960, 2938, 2909, 2841, 1695, 1617, 1488, 1470, 1433, 1388, 1305, 1224, 875, 858, 797, 754

5,6-dimethoxy-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one 8c:

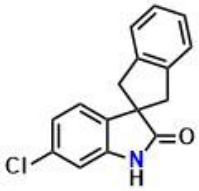
^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.58 (s, 1H), 7.21 – 7.16 (m, 1H), 6.95 – 6.88 (m, 3H), 6.79 (s, 2H), 3.88 (s, 6H), 3.57 (d, *J* = 15.3 Hz, 2H), 3.05 (d, *J* = 15.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) in ppm: δ 182.8, 148.7, 139.7, 137.0, 132.7, 128.1, 122.9, 122.1, 109.9, 107.8, 56.2, 54.9, 44.1.

HRMS: Found $[M+H]^+$ = 296.1298; $C_{18}H_{18}O_3N_1$ requires 296.1286

IR (film)**:** ν_{max}/cm^{-1} 3297, 2929, 2834, 1715, 1609, 1502, 1488, 1465, 1448, 1385, 1332, 1308, 1257, 1230, 1210, 1186, 1173, 1092, 1050, 1028, 1010, 988

6'-chloro-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one 8d:



^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 9.51 (s, 1H), 7.28 – 7.20 (m, 4H), 7.07 (d, *J* = 1.8 Hz, 1H), 6.97 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 3.60 (d, *J* = 15.6 Hz, 2H), 3.06 (d, *J* = 15.7 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) in ppm: δ 183.2, 141.1, 140.9, 135.1, 133.7, 127.3, 124.7, 122.9, 122.7, 110.7, 54.5, 44.0.

HRMS: Found $[M+H]^+$ = 270.0699; $C_{16}H_{13}O_1N_1Cl$ requires 270.0685

GC: tR = 18.388 min

IR (film)**:** ν_{max}/cm^{-1} 3184, 3168, 3121, 3064, 3022, 2958, 2918, 2853, 1708, 1610, 1480, 1452, 1335, 1298, 1262, 1225, 1105, 1068, 1016, 921

6'-bromo-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one 8e:

^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 9.53 (s, 1H), 7.31 – 7.20 (m, 4H), 7.09 (d, *J* = 1.8 Hz, 1H), 7.00 (dd, *J* = 7.9, 1.7 Hz, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 3.63 (d, *J* = 15.7 Hz, 2H), 3.09 (d, *J* = 15.7 Hz, 2H).

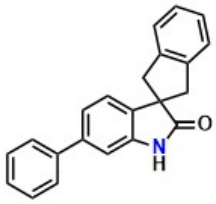
^{13}C NMR (126 MHz, $CDCl_3$) in ppm: δ 182.6, 141.0, 140.6, 135.4, 127.1, 125.4, 124.5, 123.0, 121.2, 113.2, 54.3, 43.8.

HRMS: Found $[M+H]^+$ = 314.018; $C_{16}H_{13}O_1N_1Br$ requires 314.0174

GC: tR =19.974 min

IR (film)**:** ν_{max}/cm^{-1} 3245, 3072, 3028, 2973, 2952, 2921, 2907, 2833, 1708, 1668, 1604, 1480, 1451, 1325, 1298, 1273, 1242, 1228, 1115, 1052, 1018

6'-phenyl-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one 8f:



^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.42 (s, 1H), 7.56 – 7.48 (m, 2H), 7.46 – 7.39 (m, 2H), 7.38 – 7.26 (m, 5H), 7.17 – 7.07 (m, 2H), 6.88 (d, *J* = 7.7 Hz, 1H), 3.68 (d, *J* = 15.7 Hz, 2H), 3.17 (d, *J* = 15.5 Hz, 2H).

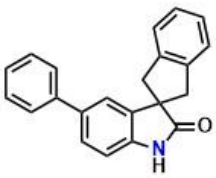
^{13}C NMR (101 MHz, $CDCl_3$) in ppm: δ 182.5, 141.7, 141.2, 141.0, 140.3, 135.8, 128.9, 127.6, 127.2, 127.2, 124.7, 122.3, 121.9, 108.7, 54.5, 44.2.

HRMS: Found $[M+H]^+$ = 312.1375; $C_{22}H_{18}NO$ requires 312.1388

GC: tR = 26.611 min

IR (film)**:** ν_{max}/cm^{-1} 3185, 3066, 3030, 2955, 2915, 2898, 2845, 1705, 1624, 1477, 1453, 1426, 1337, 1292, 1260, 1232, 1195, 1154, 1110, 1071, 1005, 915, 867

5'-phenyl-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one 8g:



^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 9.18 (s, 1H), 7.46 – 7.34 (m, 5H), 7.29 (dt, *J* = 8.8, 4.2 Hz, 5H), 7.09 (s, 1H), 7.02 (d, *J* = 8.0 Hz, 1H), 3.71 (d, *J* = 15.7 Hz, 2H), 3.23 (d, *J* = 15.8 Hz, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) in ppm: δ 182.9, 140.9, 140.8, 139.1, 137.2, 136.1, 128.6, 127.0, 126.8, 126.8, 126.7, 124.4, 120.6, 110.0, 54.4, 44.0.

HRMS: Found $[M+H]^+$ = 312.1373; $C_{22}H_{17}NO$ requires 312.1388

IR (film)**:** ν_{max}/cm^{-1} 3162, 3130, 3072, 3042, 3019, 2964, 2894, 2853, 2842, 1697, 1620, 1472, 1435, 1318, 1259, 1230, 1151, 1117, 1072, 1027, 931, 894

5'-bromo-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one 8h:

^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.68 (s, 1H), 7.31 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.27 (s, 4H), 6.92 (d, *J* = 2.0 Hz, 1H), 6.81 (d, *J* = 8.2 Hz, 1H), 3.64 (d, *J* = 15.7 Hz, 2H), 3.10 (s, 2H).

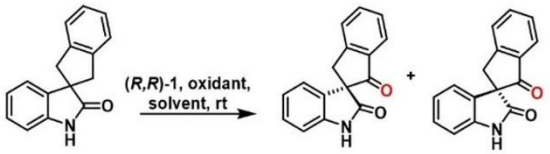
^{13}C NMR (101 MHz, $CDCl_3$) in ppm: δ 182.5, 141.0, 139.2, 131.3, 127.7, 125.6, 125.1, 115.8, 111.7, 55.1, 44.4.

HRMS: Found $[M+H]^+$ = 314.018; $C_{16}H_{12}O_1N_1Br$ requires 314.0174

GC: tR = 19.924 min

IR (film)**:** ν_{max}/cm^{-1} 3151, 3101, 3071, 3022, 2964, 2919, 2847, 1699, 1609, 1470, 1444, 1318, 1265, 1246, 1220, 1145, 1109, 1066, 1017, 884, 800

Table S4: Optimisation of desymmetrization of 8a[a]:

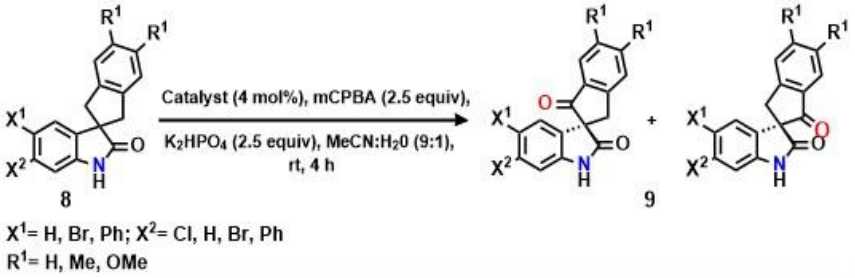


Entry	(*R,R*)- 1	oxidant	Solvent	Yield (%)[b]	ee (%)[c]
1	2 mol%	mCPBA (2.5 equiv)	MeCN: H_2O (9:1)	40	34
2	**4 mol%**	**mCPBA (2.5 equiv)**	**,,**	**86**	**34**
3	5 mol%	mCPBA (2.5 equiv)	,,	86	34
4	6 mol%	mCPBA (2.5 equiv)	,,	90	29
5	4 mol%	NaOCl (2.5 equiv)	,,	86	34
6	4 mol%	H_2O_2 (2.5 equiv)	100% H_2O	——	——
7		mCPBA	MeCN: H_2O (9:1)	——	——
8		NaOCl	MeCN: H_2O (9:1)	——	——
9	**(*S,S*)-1, 4 mol%**	**mCPBA (2.5 equiv)**	**,,**	**86**	**34**

[a]Reaction conditions: Reactions were performed at room temperature under stirring for 4 h. [b]isolated yield. [c]ee was checked by chiral HP LC.

General procedure for the asymmetric oxidation of spirocyclic substrate 8a-h by racemic, (*R*,*R*) and (*S*,*S*)-1

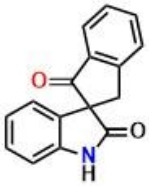
Scheme 4: Asymmetric C-H bond hydroxylation by **(*R*,*R*)** and **(*S*,*S*) -1**:



In 5mL vial equipped with magnetic stir bar, 3.6 mL MeCN, 0.4mL water, substrate **8a-h** (0.025 mmol), Fe catalyst (4 mol%) and K_2HPO_4 (0.07 mmol) was added and to this mCPBA (0.0625 mmol) was added portion wise at room temperature under stirring. The reaction was done at 4 different batches and monitored by TLC. After completion of the reaction, the reaction mixture was quenched by sodium bicarbonate (3 times). The product was extracted with chloroform, passed through sodium sulfate followed by filtration. The product was separated and isolated by silica gel column chromatography (hexane: ethyl acetate = 4:1 – 3:2). The products were analysed by NMR, GC, IR and HRMS. The enantiomeric excess was monitored by HPLC with chiral columns.

Characterisations of products 9a-h:

spiro[indene-2,3'-indoline]-1,2'(3H)-dione 9a:



^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.83 (s, 1H, N*H*), 7.71 (td, *J* = 7.5, 1.2 Hz, 2H), 7.62 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.02 – 6.93 (m, 2H), 6.90 (dt, *J* = 7.4, 0.8 Hz, 1H), 3.86 (d, *J* = 17.3 Hz, 1H), 3.47 (d, *J* = 17.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) in ppm: δ 200.3, 177.2, 154.2, 142.2, 136.2, 131.1, 129.4, 128.7, 127.0, 126.1, 123.5, 123.0, 110.7, 63.9, 37.9.

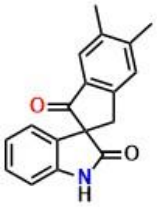
Chiral HPLC: Sample dissolved in 9:1 isopropanol: Methanol; tR [racemate] = 18.784 min, 25.617 min, tR for ***ent*-1** =18.672 min, 25.405 min and tR for ***ent*-2** = 18.721 min and 25.676 min; 34% ee (OD-H, n-hexane/i-PrOH = 93:7, 1 mL/min, λ = 214 nm)

HRMS (+ESI) Found $[M+H]^+$= 250.0864; $C_{16}H_{12}O_2N_1$ requires 250.0863.

GC: tR = 18.523 min

IR (film)**:** ν_{max}/cm^{-1} 2956, 2919, 2851, 1725, 1701, 1616, 1468, 1425, 1395, 1327, 1272, 1209, 1160, 1102, 1076, 1022, 1007, 969

5,6-dimethylspiro[indene-2,3'-indoline]-1,2'(3H)-dione 9b:



^{1}H NMR (500 MHz, $CDCl_3$) in ppm: δ 7.69 (s, 1H, N*H*), 7.58 (s, 1H), 7.38 (s, 1H), 7.23 (d, *J* = 6.6 Hz, 1H), 6.99 – 6.93 (m, 2H), 6.89 (d, *J* = 7.4 Hz, 1H), 3.75 (d, *J* = 17.1 Hz, 1H), 3.37 (d, *J* = 17.1 Hz, 1H), 2.40 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) in ppm: δ 199.2, 176.7, 152.1, 146.4, 141.8, 137.5, 133.2, 131.1, 128.9, 127.4, 125.9, 123.1, 122.7, 110.2, 63.8, 37.3, 21.0, 19.9.

Chiral HPLC: Sample dissolved in 9:1 isopropanol: Methanol; tR [racemate] = 12.165 min, 16.302 min, tR for ***ent*-1** =11.972 min, 15.799 min, tR for ***ent*-2** = 12.207 min and 16.673 min; 42% ee (OD-H, n-hexane/i-PrOH = 80:20, 1 mL/min, λ = 214 nm)

HRMS: Found $[M+H]^+$ = 278.1128; $C_{18}H_{16}O_2N$ requires 278.1181

GC: tR = 22.088 min

IR (film)**:** ν_{max}/cm^{-1} 3256, 2960, 2918, 2849, 1726, 1702, 1615, 1578, 1484, 1468, 1370, 1290, 1260, 1207, 1193, 1111, 1166, 1081, 1020

5,6-dimethoxyspiro[indene-2,3'-indoline]-1,2'(3H)-dione 9c:

^{1}H NMR (500 MHz, $CDCl_3$) in ppm: δ 7.65 (s, 1H, N*H*), 7.23 (d, *J* = 13.3 Hz, 2H), 7.03 – 6.91 (m, 4H), 4.02 (s, 3H), 3.92 (s, 3H), 3.74 (d, *J* = 17.0 Hz, 1H), 3.37 (d, *J* = 17.1 Hz, 1H).

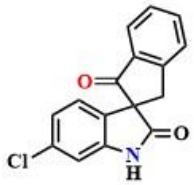
Chiral HPLC: Sample dissolved in ethanol; tR [racemate] = 19.803 min, 22.974 min, tR for ***ent*-1** =19.542 min, 22.996 min, tR for ***ent*-2** = 17.367 min, 20.429 min; 57% ee (IC, n-hexane/EtOH = 60:40, 1 mL/min, λ = 215 nm)

HRMS: Found $[M+H]^+$ = 310.1061; $C_{18}H_{16}O_4N$ requires 310.1079

GC: tR = 25.15 min

IR (film)**:** ν_{max}/cm^{-1} 3072, 2957, 2918, 2846, 1733, 1619, 1603, 1587, 1495, 1467, 1413, 1378, 1308, 1260, 1221, 1189, 1159, 1097, 1081, 1023

6'-chlorospiro[indene-2,3'-indoline]-1,2'(3H)-dione 9d:



^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 7.87 (s, 1H, N*H*), 7.82 (d, *J* = 7.7 Hz, 1H), 7.71 (t, *J* = 7.5 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 6.97 (dq, *J* = 3.8, 1.9 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 1H), 3.84 (d, *J* = 17.3 Hz, 1H), 3.44 (d, *J* = 17.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) in ppm: δ 199.1, 176.2, 153.7, 142.9, 136.1, 134.8, 129.1, 128.5, 126.7, 125.8, 123.7, 123.1, 111.0, 63.1, 37.5.

HRMS: Found $[M+H]^+$ = 284.0427; $C_{16}H_{11}ClO_2N$ requires 284.0478

GC: tR = 21.31 min

IR (film)**:** ν_{max}/cm^{-1} 3250, 2920, 1724, 1708, 1614, 1484, 1460, 1429, 1375, 1319, 1260, 1210, 1168, 1150, 1097, 1071, 1021, 923

Chiral HPLC: Sample dissolved in 9:1 isopropanol: Methanol; tR [racemate] = 9.718 min, 22.254 min, tR for ***ent*-1**= 10.589 min, 23.081 min and tR for ***ent*-2** = 10.035 min and 22.960 min; 50% ee (OJ-H, n-hexane/i-PrOH = 70:30, 1 mL/min, λ = 214 nm).

6'-bromospiro[indene-2,3'-indoline]-1,2'(3H)-dione 9e:

^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.16 (s, 1H, N*H*), 7.84 – 7.80 (m, 1H), 7.72 (td, *J* = 6.9, 6.1, 2.0 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.53 – 7.46 (m, 1H), 7.13 (dq, *J* = 3.8, 1.8 Hz, 1H), 7.00 – 6.90 (m, 1H), 6.84 – 6.74 (m, 1H), 3.84 (d, *J* = 17.3 Hz, 1H), 3.44 (d, *J* = 17.3 Hz, 1H).

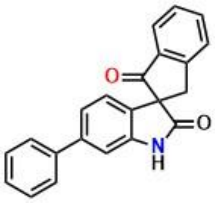
Chiral HPLC: Sample dissolved in 9:1 isopropanol: Methanol; tR [racemate] = 10.133 min, 36.885 min, tR for ***ent*-1**= 9.432 min, 31.391 min and tR for ***ent*-2**= 10.097 min and 37.081 min; 57% ee (AD-H, n-hexane/i-PrOH = 70:30, 1 mL/min, λ = 214 nm)

HRMS: Found $[M+H]^+$ = 327.9975; $C_{16}H_{11}O_2N_1Br$ requires 327.9973

GC: tR = 22.666 min

IR (film)**:** ν_{max}/cm^{-1} 3234, 1723, 1700, 1609, 1479, 1458, 1379, 1325, 1266, 1214, 1121, 1021, 916

6'-phenylspiro[indene-2,3'-indoline]-1,2'(3H)-dione 9f:



Chiral HPLC: Sample dissolved in 9:1 isopropanol: Methanol; tR [racemate] = 17.586 min, 22.405 min, tR for ***ent*-1** = 17.691 min, 22.895 min, tR for ***ent*-2** = 17.808 min and 22.283 min; 67% ee (OD-H, n-hexane/i-PrOH = 83:17, 1 mL/min, λ = 214 nm)

HRMS: Found $[M+H]^+$ = 326.1136; $C_{22}H_{16}O_2N$ requires 326.1181

5'-phenylspiro[indene-2,3'-indoline]-1,2'(3H)-dione 9g:

^{1}H NMR (500 MHz, $CDCl_3$) in ppm: δ 7.65 (s, 1H, N*H*), 7.57 – 7.29 (m, 4H), 7.26 (s, 7H), 7.15 – 6.95 (m, 1H), 3.67 (d, *J* = 15.8 Hz, 1H), 3.20 (d, *J* = 15.8 Hz, 1H)

Chiral HPLC: Sample dissolved in 9:1 isopropanol: Methanol; tR [racemate] = 12.7133 min, 15.056 min, tR for ***ent*-1** = 12.684 min, 15.181 min, tR for ***ent*-2** = 12.592 min and 14.978 min; 23% ee (OD-H, n-hexane/i-PrOH = 83:17, 1 mL/min, λ = 214 nm)

HRMS: Found $[M+H]^+$ = 326.1138; $C_{22}H_{16}O_2N$ requires 326.1181

GC: tR = 30.37 min

IR (film)**:** ν_{max}/cm^{-1} 3065, 3035, 2958, 2916, 2849, 1724, 1624, 1604, 1480, 1461, 1378, 1261, 1216, 1171, 1125, 1075, 1019, 823, 768

5'-bromo-5-methylspiro[indene-2,3'-indoline]-1,2'(3H)-dione 9h:

^{1}H NMR (400 MHz, $CDCl_3$) in ppm: δ 8.16 (s, 1H, N*H*), 7.84 – 7.80 (m, 1H), 7.72 (td, *J* = 6.9, 6.1, 2.0 Hz, 1H), 7.64 – 7.59 (m, 1H), 7.53 – 7.46 (m, 1H), 7.13 (dq, *J* = 3.8, 1.8 Hz, 1H), 7.00 – 6.90 (m, 1H), 6.84 – 6.74 (m, 1H), 3.84 (d, *J* = 17.3 Hz, 1H), 3.44 (d, *J* = 17.3 Hz, 1H).

Chiral HPLC: Sample dissolved in 9:1 isopropanol: Methanol; tR [racemate] = 8.688 min, 19.779 min, tR for ***ent*-1** = 8.549 min, 19.095 min, tR for ***ent*-1**= 8.728 min, 19.810 min; 9% ee (AD-H, n-hexane/i-PrOH = 70:30, 1 mL/min, λ = 214 nm)

HRMS: Found $[M+H]^+$ = 327.9962; $C_{16}H_{11}O_2N_1Br$ requires 327.9973

GC: tR = 22.547 min

IR (film)**:** ν_{max}/cm^{-1} 2922, 2854, 1729, 1706, 1611, 1590, 1471, 1430, 1294, 1265, 1211, 1167, 1122, 1099, 1019, 901, 811, 797

Quantum Chemistry Calculations:

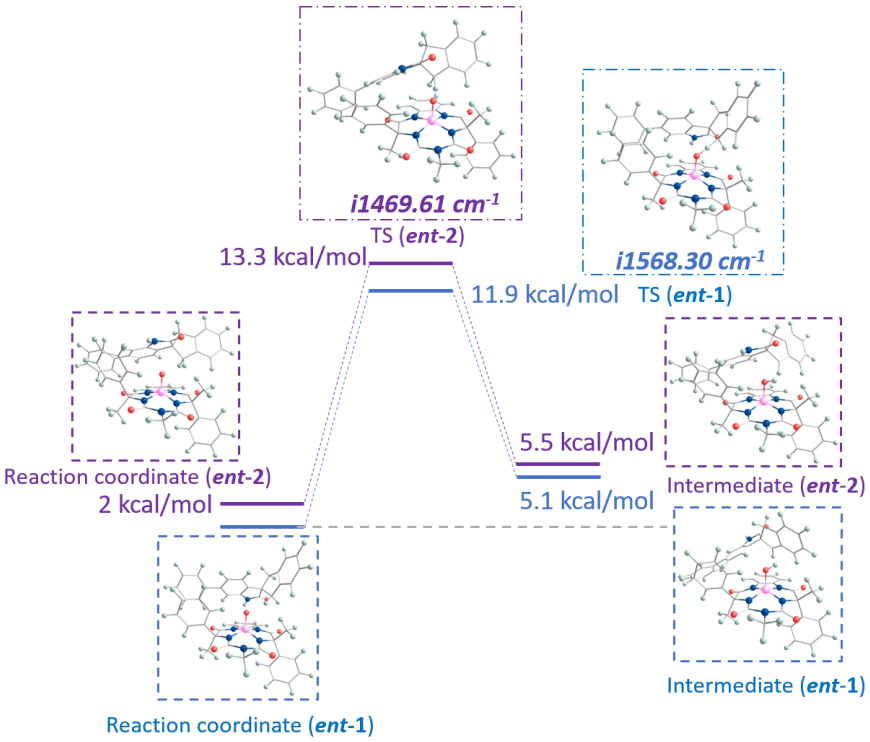
Coordinated:

(*S,S*)-(Ph,Me)bTAML-Fe(V)O

Charge: -1 and Multiplicity: 2

Intermendiate Lable	Energy	ZPE	Vibrational correction	Rotational Correction	Translational Correction	Enthalpy Correction	Entropy	Gibbs Free Energy
Reaction coordinate (*ent*-1)	-3931.86545320	0.79900093	0.04841156	0.00141627	0.00141627	0.00094421	-0.12715797	-3931.14142193
TS (*ent*-1)	-3931.83938221	0.78998601	0.04582966	0.00141627	0.00141627	0.00094421	-0.12131063	-3931.12110042
Intermediate (*ent*-1)	-3931.85228557	0.79551234	0.04950737	0.00141627	0.00141627	0.00094421	-0.12973503	-3931.13322414
Reaction coordinate (*ent*-2)	-3931.86140709	0.79895029	0.04856197	0.00141627	0.00141627	0.00094421	-0.12789342	-3931.13801150
TS (*ent*-2)	-3931.83733285	0.79216596	0.04811849	0.00141627	0.00141627	0.00094421	-0.12669203	-3931.11996368
Intermediate (*ent*-2)	-3931.85189050	0.79538047	0.04937061	0.00141627	0.00141627	0.00094421	-0.12925976	-3931.13262243

N.B.: (*ent*-1) refers to the more favourable enantiomer (major enantiomer of the product), and (*ent*-1) refers to the less favourable enantiomer (minor enantiomer of the product)



A reaction Coordinate has been optimized, followed by TS optimization. Here, the Energy of the reaction coordinate has been provided. The coordinates of this RC are given below:

Starting RC for the favourable enantiomer (Reaction coordinate (***ent*-1**))

Fe	-0.041853000000	1.289356000000	-0.487419000000
O	-3.332805000000	3.261005000000	-1.353803000000
O	1.226518000000	3.388376000000	-3.707176000000
O	0.885334000000	-0.026792000000	3.144057000000
O	3.936441000000	1.519700000000	-0.633159000000
N	0.128768000000	2.524171000000	-1.899832000000
N	2.448505000000	2.188771000000	-2.199396000000
N	-0.248505000000	0.899830000000	1.358056000000
N	-1.682992000000	2.116247000000	-0.230771000000
N	1.735566000000	1.383119000000	-0.059481000000
C	1.228753000000	2.743500000000	-2.662425000000
C	-1.405740000000	1.281374000000	-3.995616000000
H	-0.891622000000	0.632015000000	-3.286273000000
C	-2.547499000000	1.571371000000	-6.113710000000

H	-2.927274000000	1.155519000000	-7.050054000000
C	-1.603567000000	2.633765000000	-3.681703000000
C	-2.756615000000	2.915133000000	-5.802502000000
H	-3.296945000000	3.561058000000	-6.500035000000
C	3.607941000000	2.370037000000	-3.069633000000
H	3.240549000000	2.608123000000	-4.071855000000
H	4.210972000000	1.452701000000	-3.071809000000
H	4.250934000000	3.190647000000	-2.711453000000
C	-1.114297000000	3.174802000000	-2.333129000000
C	-1.516735000000	1.112599000000	1.876395000000
C	-1.871302000000	0.758772000000	-5.202152000000
H	-1.713269000000	-0.299648000000	-5.423213000000
C	2.758410000000	1.692035000000	-0.930154000000
C	-2.182813000000	2.853063000000	-1.270830000000
C	-3.654195000000	2.166014000000	1.325495000000
H	-4.274046000000	2.708970000000	0.616569000000
C	-3.296942000000	1.120519000000	3.498151000000
H	-3.680671000000	0.833244000000	4.479979000000
C	-2.346511000000	1.816153000000	0.962999000000
C	-1.990248000000	0.770714000000	3.149357000000
H	-1.341407000000	0.218670000000	3.824646000000
C	3.912671000000	1.269711000000	2.983778000000
H	4.130393000000	0.204780000000	3.059243000000
C	0.852286000000	0.480018000000	2.033955000000
C	-4.121339000000	1.806473000000	2.596294000000
H	-5.142693000000	2.071433000000	2.883205000000
C	2.139064000000	0.751708000000	1.214187000000
C	-2.290305000000	3.440685000000	-4.595503000000
H	-2.466654000000	4.492212000000	-4.371012000000
C	2.957732000000	1.723989000000	2.067731000000

C	4.593500000000	2.169167000000	3.807953000000
H	5.340362000000	1.794358000000	4.513554000000
C	4.324230000000	3.537571000000	3.734923000000
H	4.858821000000	4.241029000000	4.379285000000
C	2.683806000000	3.097411000000	2.009123000000
H	1.934138000000	3.458725000000	1.302918000000
C	3.362410000000	3.997661000000	2.830966000000
H	3.137727000000	5.065753000000	2.763976000000
C	2.818648000000	-0.608092000000	0.980958000000
H	3.838856000000	-0.472115000000	0.605952000000
H	2.822661000000	-1.184249000000	1.916510000000
H	2.234856000000	-1.167178000000	0.234977000000
C	-0.976283000000	4.712106000000	-2.305086000000
H	-0.324519000000	5.046910000000	-3.119545000000
H	-1.967281000000	5.178529000000	-2.385198000000
H	-0.533612000000	5.009267000000	-1.342176000000
O	-0.295535000000	-0.101537000000	-1.189960000000
C	-3.053704000000	-1.839595000000	-2.872984000000
C	-3.960429000000	-0.820184000000	-2.533233000000
C	-4.183108000000	-0.523819000000	-1.173342000000
C	-3.526942000000	-1.280994000000	-0.212028000000
C	-2.625775000000	-2.303425000000	-0.552090000000
C	-2.378977000000	-2.574644000000	-1.889612000000
N	-3.648757000000	-1.218280000000	1.177561000000
C	-2.865787000000	-2.155488000000	1.810930000000
C	-2.077104000000	-2.905301000000	0.720286000000
C	-0.541684000000	-2.666645000000	0.879473000000
C	0.059635000000	-3.951408000000	0.368136000000
C	-0.907132000000	-4.968833000000	0.328972000000
C	-2.232302000000	-4.445255000000	0.825782000000

C	1.369577000000	-4.211516000000	-0.033173000000
C	1.705820000000	-5.496750000000	-0.477868000000
C	0.741357000000	-6.509386000000	-0.517412000000
C	-0.573964000000	-6.248772000000	-0.110980000000
O	-2.805091000000	-2.351054000000	3.007182000000
H	-2.851225000000	-2.041405000000	-3.925990000000
H	-4.883090000000	0.260511000000	-0.884137000000
H	-1.659650000000	-3.346068000000	-2.174004000000
H	-4.147437000000	-0.494936000000	1.687429000000
H	-2.379360000000	-4.714981000000	1.887353000000
H	-3.098956000000	-4.816882000000	0.257560000000
H	2.121782000000	-3.420099000000	-0.011206000000
H	2.727897000000	-5.706476000000	-0.804905000000
H	1.013475000000	-7.506633000000	-0.874349000000
H	-1.330200000000	-7.038440000000	-0.146927000000
H	-0.295894000000	-2.512411000000	1.944939000000
H	-0.221158000000	-1.774813000000	0.325096000000
C	-4.702516000000	-0.080885000000	-3.584066000000
C	-4.977785000000	1.290904000000	-3.449260000000
C	-5.159036000000	-0.741736000000	-4.738477000000
C	-5.685025000000	1.973595000000	-4.438663000000
C	-5.868406000000	-0.057399000000	-5.726138000000
C	-6.137178000000	1.306036000000	-5.579475000000
H	-4.594546000000	1.846430000000	-2.592244000000
H	-4.971212000000	-1.811947000000	-4.851039000000
H	-5.860330000000	3.045906000000	-4.322482000000
H	-6.217860000000	-0.594170000000	-6.612828000000
H	-6.686525000000	1.846747000000	-6.355130000000

TS (***ent*-1**)

Fe	-0.000044000000	1.101955000000	-0.320859000000

O	-3.178061000000	3.261013000000	-1.367213000000
O	1.426739000000	2.887007000000	-3.617746000000
O	0.790435000000	0.075239000000	3.410415000000
O	4.036849000000	1.057402000000	-0.457146000000
N	0.250689000000	2.226427000000	-1.769403000000
N	2.543648000000	1.656285000000	-2.070522000000
N	-0.259107000000	0.873578000000	1.515653000000
N	-1.687894000000	1.943645000000	-0.198398000000
N	1.818732000000	1.019886000000	0.096429000000
C	1.381950000000	2.303089000000	-2.539292000000
C	-1.262856000000	0.953745000000	-3.860110000000
H	-0.740633000000	0.328066000000	-3.135294000000
C	-2.461113000000	1.161042000000	-5.957949000000
H	-2.865376000000	0.709186000000	-6.867205000000
C	-1.445048000000	2.319343000000	-3.597887000000
C	-2.659942000000	2.516597000000	-5.695518000000
H	-3.223812000000	3.133646000000	-6.399933000000
C	3.673436000000	1.703282000000	-2.995061000000
H	3.306160000000	1.531320000000	-4.013361000000
H	4.397813000000	0.940037000000	-2.693974000000
H	4.174166000000	2.686182000000	-2.975151000000
C	-0.949929000000	2.918840000000	-2.277455000000
C	-1.559458000000	1.100130000000	1.976242000000
C	-1.756581000000	0.385824000000	-5.034500000000
H	-1.596485000000	-0.678739000000	-5.221602000000
C	2.857136000000	1.227747000000	-0.757177000000
C	-2.084822000000	2.718300000000	-1.238184000000
C	-3.694745000000	2.084578000000	1.299674000000
H	-4.291402000000	2.592158000000	0.544982000000
C	-3.401970000000	1.146772000000	3.529155000000

H	-3.813853000000	0.905542000000	4.512244000000
C	-2.373957000000	1.731421000000	0.994688000000
C	-2.075306000000	0.805232000000	3.243066000000
H	-1.441273000000	0.303689000000	3.969704000000
C	3.799408000000	1.551091000000	3.221381000000
H	4.046262000000	0.528845000000	3.505920000000
C	0.817600000000	0.484314000000	2.260083000000
C	-4.201722000000	1.782502000000	2.570889000000
H	-5.232853000000	2.054008000000	2.814206000000
C	2.149600000000	0.640312000000	1.477481000000
C	-2.154237000000	3.089715000000	-4.526771000000
H	-2.325884000000	4.148637000000	-4.336866000000
C	2.885670000000	1.787693000000	2.187925000000
C	4.404982000000	2.613580000000	3.897315000000
H	5.121165000000	2.405134000000	4.697343000000
C	4.100559000000	3.933080000000	3.556603000000
H	4.575755000000	4.764384000000	4.084854000000
C	2.578694000000	3.116075000000	1.858926000000
H	1.865045000000	3.313396000000	1.057488000000
C	3.180764000000	4.178818000000	2.533310000000
H	2.929404000000	5.206064000000	2.255137000000
C	2.884959000000	-0.705000000000	1.571685000000
H	3.902169000000	-0.615570000000	1.175156000000
H	2.896799000000	-1.048631000000	2.614630000000
H	2.334172000000	-1.451211000000	0.984181000000
C	-0.714352000000	4.440625000000	-2.346892000000
H	-0.037689000000	4.682428000000	-3.174000000000
H	-1.674658000000	4.960077000000	-2.463211000000
H	-0.261030000000	4.770856000000	-1.399659000000
O	-0.322607000000	-0.434295000000	-0.961060000000

C	-3.383491000000	-1.781945000000	-2.916686000000
C	-4.224975000000	-0.737294000000	-2.498134000000
C	-4.366995000000	-0.471930000000	-1.120640000000
C	-3.661263000000	-1.256037000000	-0.217104000000
C	-2.787661000000	-2.267349000000	-0.644021000000
C	-2.649266000000	-2.537409000000	-1.995703000000
N	-3.676705000000	-1.222461000000	1.180995000000
C	-2.834108000000	-2.158179000000	1.734776000000
C	-2.083762000000	-2.831239000000	0.570077000000
C	-0.592176000000	-2.416262000000	0.572240000000
C	0.122631000000	-3.566592000000	-0.020381000000
C	-0.708837000000	-4.706052000000	-0.013184000000
C	-2.031541000000	-4.377842000000	0.634498000000
C	1.408271000000	-3.630760000000	-0.568662000000
C	1.859532000000	-4.844975000000	-1.093641000000
C	1.037982000000	-5.979640000000	-1.073590000000
C	-0.252746000000	-5.915231000000	-0.531315000000
O	-2.686301000000	-2.395154000000	2.914823000000
H	-3.260008000000	-1.967013000000	-3.983836000000
H	-5.024272000000	0.325831000000	-0.774878000000
H	-1.956278000000	-3.308473000000	-2.340214000000
H	-4.147125000000	-0.517550000000	1.742782000000
H	-2.029462000000	-4.682863000000	1.696373000000
H	-2.896283000000	-4.847710000000	0.141962000000
H	2.033589000000	-2.737769000000	-0.614307000000
H	2.857048000000	-4.904897000000	-1.536308000000
H	1.403269000000	-6.920588000000	-1.494028000000
H	-0.893693000000	-6.801361000000	-0.522039000000
H	-0.205749000000	-2.013523000000	1.519823000000
H	-0.439930000000	-1.384223000000	-0.206554000000

C	-4.945298000000	0.088227000000	-3.498330000000
C	-5.068231000000	1.477248000000	-3.326847000000
C	-5.503493000000	-0.496133000000	-4.649295000000
C	-5.732107000000	2.252502000000	-4.278267000000
C	-6.168291000000	0.280846000000	-5.598352000000
C	-6.287255000000	1.661747000000	-5.415572000000
H	-4.593424000000	1.970439000000	-2.477111000000
H	-5.427941000000	-1.576921000000	-4.790427000000
H	-5.788358000000	3.334534000000	-4.135172000000
H	-6.599151000000	-0.195381000000	-6.483779000000
H	-6.802035000000	2.273748000000	-6.161554000000

Reaction coordinates for Intermediate (***ent*-1**)

Fe	0.595595000000	0.807542000000	-0.574210000000
O	-2.794323000000	2.542076000000	-1.696968000000
O	1.817697000000	2.537690000000	-3.981366000000
O	1.443951000000	-0.067981000000	3.188457000000
O	4.573442000000	1.447240000000	-0.597303000000
N	0.711227000000	1.855719000000	-2.096663000000
N	3.073409000000	1.674887000000	-2.293297000000
N	0.329213000000	0.555418000000	1.262928000000
N	-1.190150000000	1.362478000000	-0.525965000000
N	2.380200000000	1.017629000000	-0.113955000000
C	1.834091000000	2.056707000000	-2.851625000000
C	-0.566313000000	0.246493000000	-4.072575000000
H	0.093434000000	-0.215781000000	-3.337967000000
C	-1.876946000000	0.070951000000	-6.105899000000
H	-2.224480000000	-0.512778000000	-6.962738000000
C	-0.981711000000	1.575689000000	-3.894965000000
C	-2.295031000000	1.392112000000	-5.934512000000
H	-2.975254000000	1.851149000000	-6.657526000000

C	4.223229000000	1.868003000000	-3.173527000000
H	3.923512000000	1.629127000000	-4.199590000000
H	5.038432000000	1.222400000000	-2.830840000000
H	4.579485000000	2.912285000000	-3.153581000000
C	-0.560910000000	2.354134000000	-2.643148000000
C	-1.004589000000	0.567720000000	1.669427000000
C	-1.011562000000	-0.497126000000	-5.166018000000
H	-0.680864000000	-1.532994000000	-5.280455000000
C	3.397619000000	1.382585000000	-0.947413000000
C	-1.663609000000	2.096779000000	-1.572963000000
C	-3.257834000000	1.083936000000	0.862828000000
H	-3.908762000000	1.422681000000	0.060296000000
C	-2.897491000000	0.307440000000	3.141965000000
H	-3.305377000000	0.033898000000	4.118836000000
C	-1.876996000000	1.018723000000	0.637171000000
C	-1.516738000000	0.234382000000	2.931104000000
H	-0.828400000000	-0.080902000000	3.712661000000
C	4.145802000000	1.849047000000	3.089485000000
H	4.518214000000	0.872626000000	3.398086000000
C	1.430822000000	0.341467000000	2.034644000000
C	-3.758308000000	0.713507000000	2.114278000000
H	-4.836947000000	0.749566000000	2.289460000000
C	2.739850000000	0.704235000000	1.277968000000
C	-1.857179000000	2.134908000000	-4.834474000000
H	-2.214497000000	3.155661000000	-4.705696000000
C	3.266034000000	1.950217000000	2.005298000000
C	4.553982000000	2.988760000000	3.787012000000
H	5.246320000000	2.887350000000	4.627718000000
C	4.082771000000	4.250193000000	3.416694000000
H	4.403394000000	5.142239000000	3.961976000000

C	2.789479000000	3.219352000000	1.647368000000
H	2.098230000000	3.309271000000	0.807865000000
C	3.195287000000	4.359090000000	2.342467000000
H	2.814944000000	5.339010000000	2.040981000000
C	3.685733000000	-0.504174000000	1.372594000000
H	4.699306000000	-0.221417000000	1.068834000000
H	3.680657000000	-0.899655000000	2.397923000000
H	3.319392000000	-1.290759000000	0.697679000000
C	-0.526043000000	3.877866000000	-2.864324000000
H	0.089208000000	4.124565000000	-3.736440000000
H	-1.549492000000	4.255530000000	-2.987463000000
H	-0.095054000000	4.355363000000	-1.970886000000
O	0.460098000000	-0.856443000000	-1.151652000000
C	-3.650838000000	-0.365184000000	-2.441271000000
C	-5.009849000000	-0.126861000000	-2.179627000000
C	-5.681878000000	-0.920117000000	-1.225832000000
C	-4.965454000000	-1.912338000000	-0.572668000000
C	-3.601185000000	-2.127365000000	-0.817891000000
C	-2.932699000000	-1.345597000000	-1.747803000000
N	-5.410377000000	-2.843357000000	0.377195000000
C	-4.419313000000	-3.725085000000	0.754759000000
C	-3.106147000000	-3.236180000000	0.089885000000
C	-2.152027000000	-2.682975000000	1.125554000000
C	-0.861619000000	-3.206739000000	0.933196000000
C	-0.881360000000	-4.177266000000	-0.114949000000
C	-2.298683000000	-4.377830000000	-0.592149000000
C	0.362016000000	-2.888590000000	1.576343000000
C	1.524985000000	-3.529898000000	1.154042000000
C	1.499658000000	-4.468118000000	0.107529000000
C	0.286893000000	-4.794144000000	-0.528718000000

O	-4.564132000000	-4.692139000000	1.470556000000
H	-3.131412000000	0.265527000000	-3.157427000000
H	-6.745072000000	-0.770750000000	-1.027287000000
H	-1.857995000000	-1.458255000000	-1.909577000000
H	-6.368874000000	-2.952708000000	0.684344000000
H	-2.683870000000	-5.350595000000	-0.240269000000
H	-2.396834000000	-4.349827000000	-1.687911000000
H	0.396186000000	-2.152595000000	2.380735000000
H	2.472684000000	-3.288793000000	1.639598000000
H	2.428702000000	-4.943551000000	-0.216281000000
H	0.272277000000	-5.526035000000	-1.341420000000
H	-2.432588000000	-1.898989000000	1.824750000000
H	0.638698000000	-1.487829000000	-0.434383000000
C	-5.717824000000	0.973989000000	-2.874726000000
C	-6.698768000000	1.736372000000	-2.216716000000
C	-5.411113000000	1.298584000000	-4.207568000000
C	-7.353117000000	2.783241000000	-2.867884000000
C	-6.062633000000	2.345344000000	-4.858779000000
C	-7.038971000000	3.093229000000	-4.193872000000
H	-6.925013000000	1.528242000000	-1.168541000000
H	-4.654460000000	0.721009000000	-4.738892000000
H	-8.101917000000	3.371183000000	-2.329861000000
H	-5.803164000000	2.578899000000	-5.895105000000
H	-7.545927000000	3.917160000000	-4.703294000000

Starting Reaction coordinate (***ent*-2**)

Fe	1.123647000000	-1.454424000000	-1.901877000000
O	0.048718000000	2.026526000000	-3.375857000000
O	2.825769000000	-1.722039000000	-5.560536000000
O	1.314227000000	-2.310629000000	1.957812000000

O	4.156144000000	-4.038727000000	-1.904293000000
N	1.828645000000	-1.059822000000	-3.611699000000
N	3.335135000000	-2.882896000000	-3.663906000000
N	0.985382000000	-1.181311000000	-0.029470000000
N	0.564262000000	0.308497000000	-1.938020000000
N	2.525131000000	-2.522906000000	-1.433665000000
C	2.646000000000	-1.849120000000	-4.351650000000
C	-0.311403000000	-1.766008000000	-5.338568000000
H	0.217313000000	-2.506899000000	-4.743827000000
C	-2.035155000000	-1.234156000000	-6.960670000000
H	-2.824557000000	-1.555802000000	-7.645627000000
C	0.016530000000	-0.409564000000	-5.207047000000
C	-1.732958000000	0.121687000000	-6.815398000000
H	-2.295783000000	0.875267000000	-7.370383000000
C	4.221362000000	-3.721042000000	-4.470568000000
H	4.059671000000	-3.458972000000	-5.519573000000
H	4.000596000000	-4.782587000000	-4.290309000000
H	5.273742000000	-3.551944000000	-4.194091000000
C	1.154860000000	0.058294000000	-4.279280000000
C	0.287671000000	-0.048079000000	0.357057000000
C	-1.322894000000	-2.174830000000	-6.210389000000
H	-1.548297000000	-3.240950000000	-6.310910000000
C	3.376012000000	-3.178034000000	-2.298088000000
C	0.521344000000	0.921330000000	-3.162224000000
C	-0.524660000000	2.078582000000	-0.525919000000
H	-0.648566000000	2.750418000000	-1.370095000000
C	-0.783445000000	1.528956000000	1.830228000000
H	-1.134166000000	1.804796000000	2.828528000000
C	0.081095000000	0.833653000000	-0.733953000000
C	-0.149429000000	0.297071000000	1.643131000000

H	0.023168000000	-0.399214000000	2.461789000000
C	4.344016000000	-3.696330000000	1.611495000000
H	3.775107000000	-4.589986000000	1.866534000000
C	1.524183000000	-2.136807000000	0.764825000000
C	-0.960917000000	2.412794000000	0.759301000000
H	-1.450202000000	3.376860000000	0.922647000000
C	2.506995000000	-3.024539000000	-0.039849000000
C	-0.720137000000	0.529269000000	-5.943897000000
H	-0.520739000000	1.592659000000	-5.813311000000
C	3.865609000000	-2.818948000000	0.633423000000
C	5.551619000000	-3.442010000000	2.266742000000
H	5.912339000000	-4.144120000000	3.023802000000
C	6.295722000000	-2.300991000000	1.959593000000
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Reaction coordinates for Intermediate (***ent*-2**)

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4. NMR Spectra

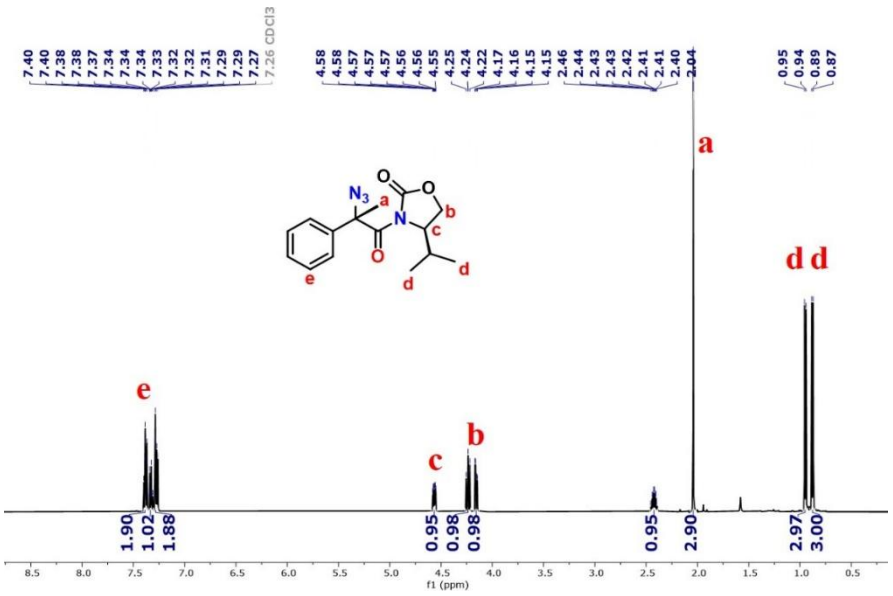


Figure 1A: ^{1}H NMR: (*R*)-3-((*S*)-2-azido-2-phenylpropanoyl)-4-isopropyloxazolidin-2-one **5a**

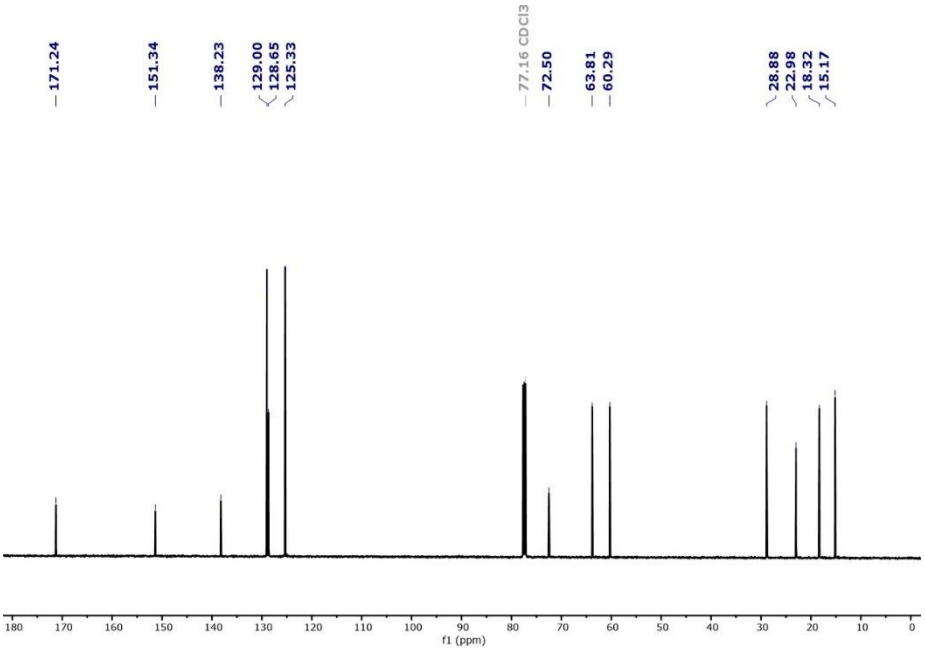


Figure 1B: ^{13}C NMR: (*R*)-3-((*S*)-2-azido-2-phenylpropanoyl)-4-isopropyloxazolidin-2-one **5a**

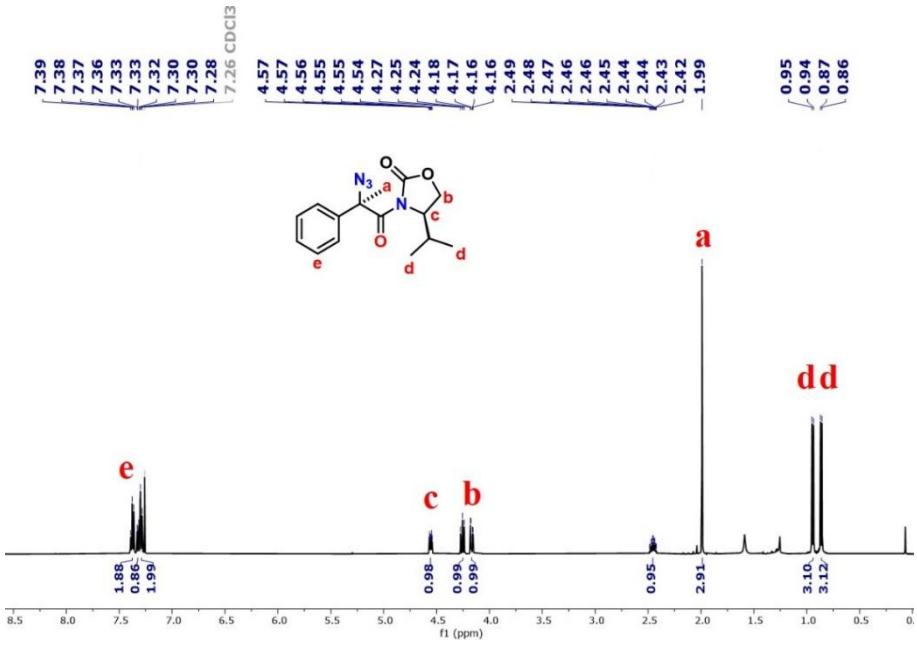


Figure 2A: ^{1}H NMR: (*R*)-3-((*R*)-2-azido-2-phenylpropanoyl)-4-isopropyloxazolidin-2-one **5b**

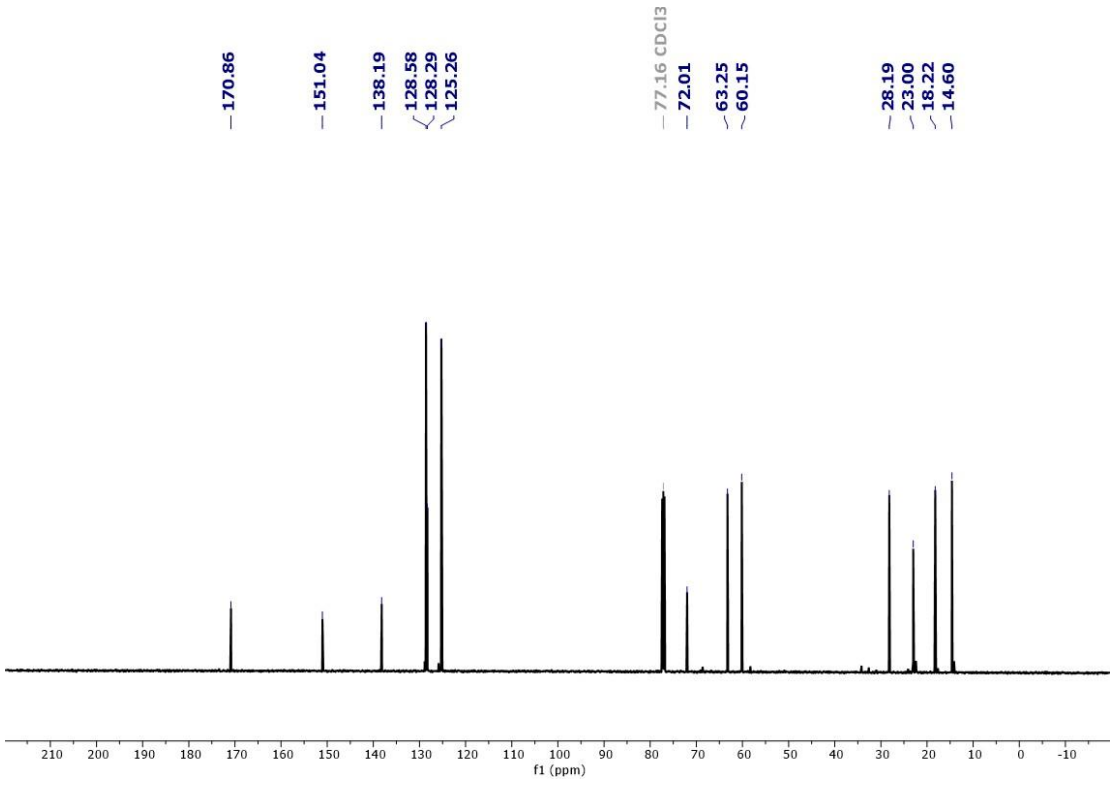


Figure 2B: ^{13}C NMR: (*R*)-3-((*R*)-2-azido-2-phenylpropanoyl)-4-isopropyloxazolidin-2-one **5b**

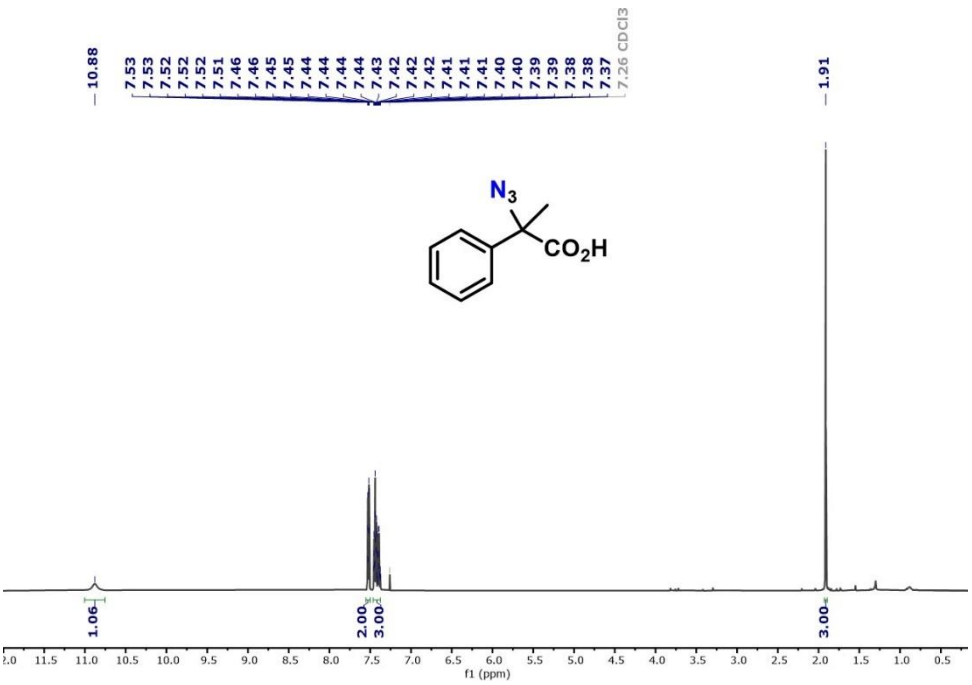


Figure 3A: ^{1}H NMR: 2-Azido-2-phenylpropanoic acid **2**

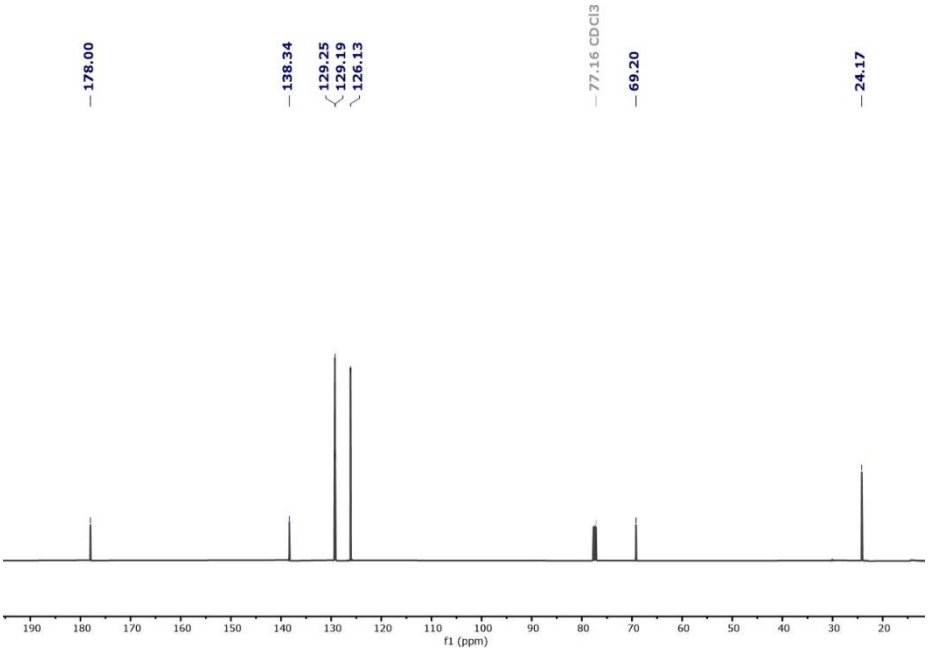


Figure 3B: ^{13}C NMR: 2-Azido-2-phenylpropanoic acid **2**

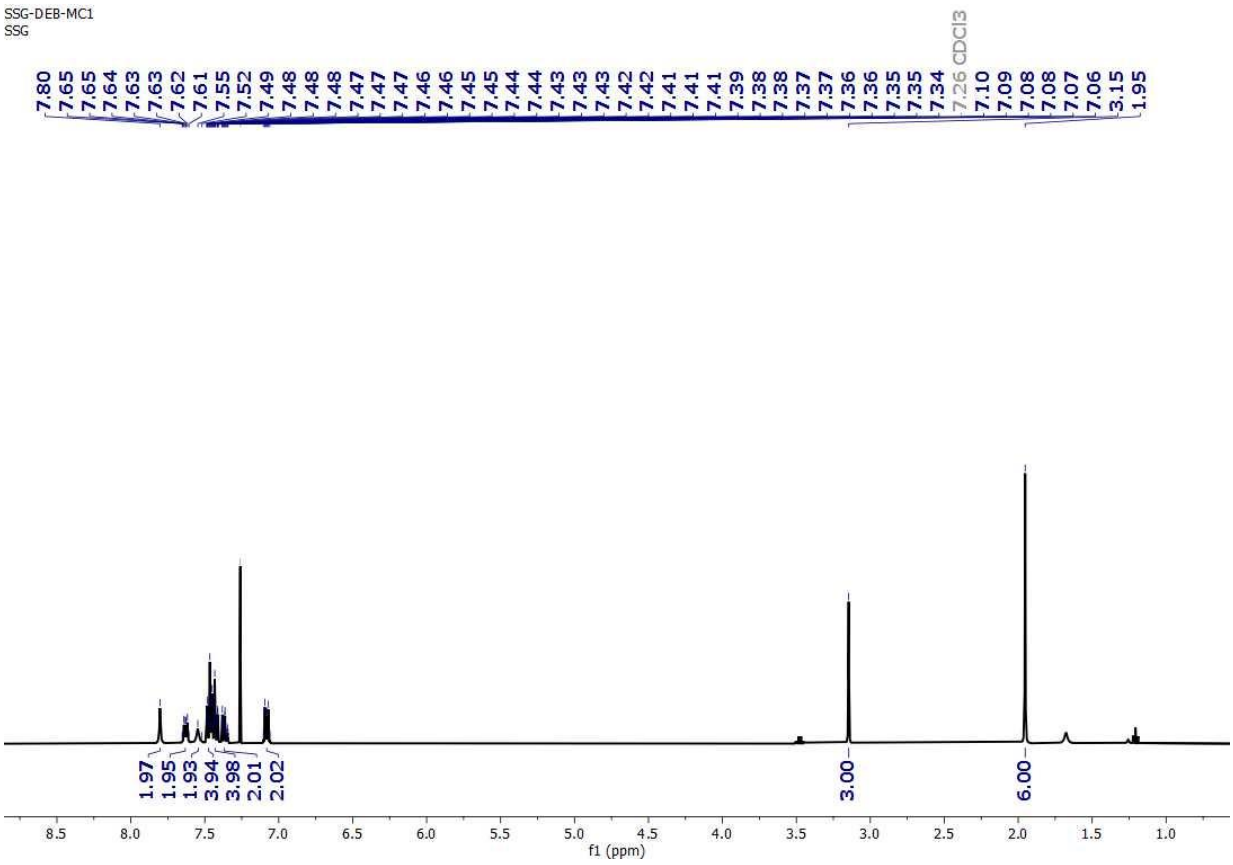


Figure 4: [1]H NMR of macrocycle

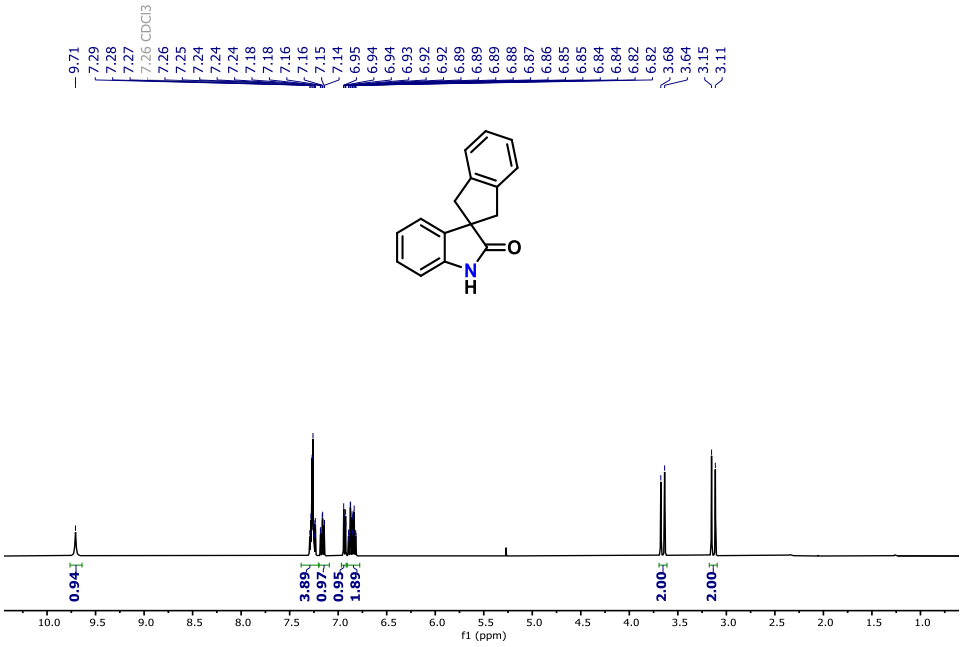


Figure 5A: [1]H NMR: 1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8a**

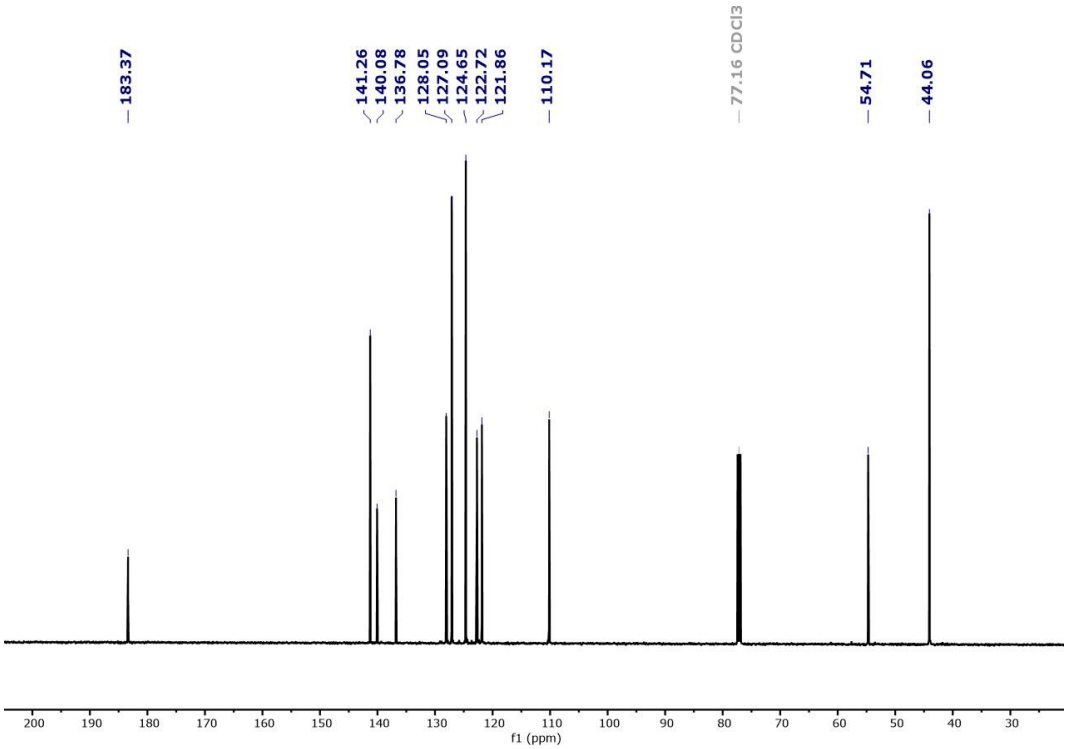


Figure 5B: ^{13}C NMR: 1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8a**

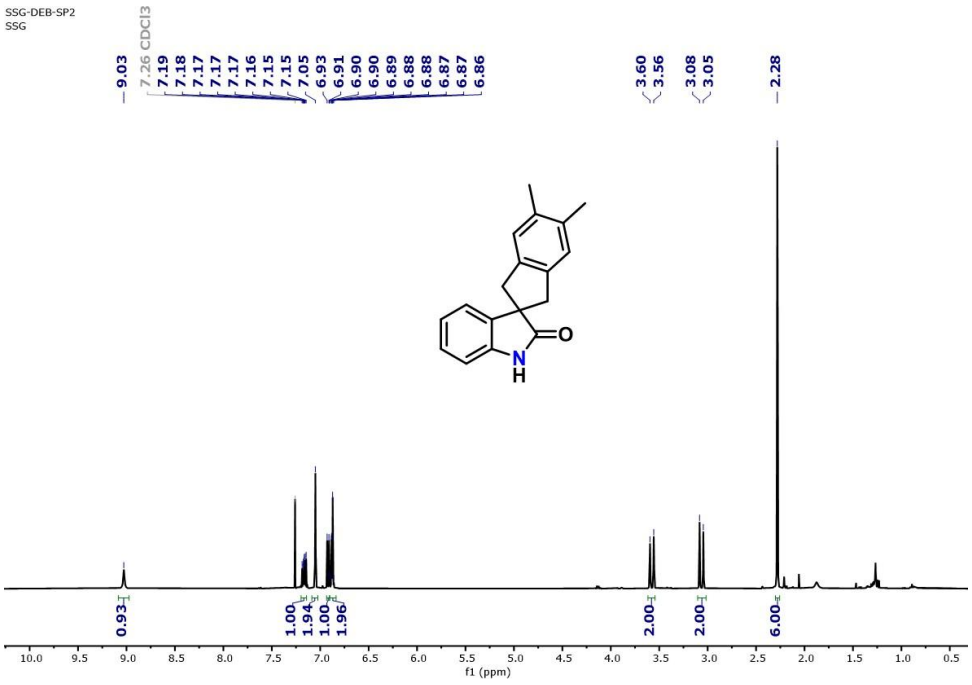


Figure 6A: ^{1}H NMR: 5,6-dimethyl-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8b**

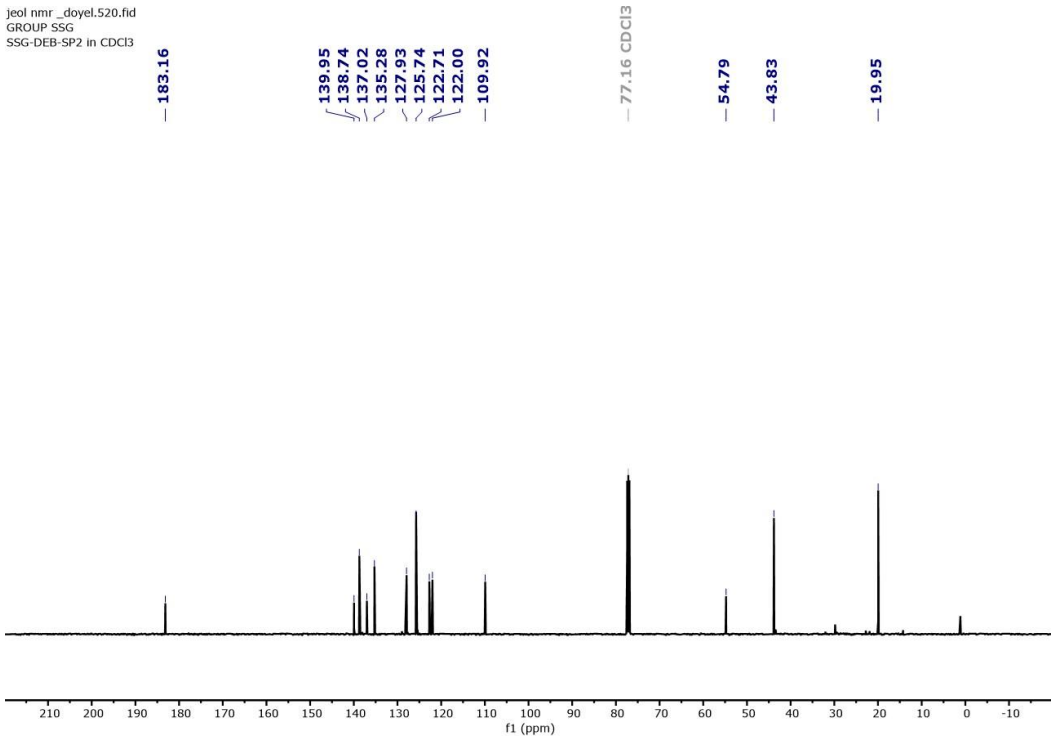


Figure 6B: ^{13}C NMR: 5,6-dimethyl-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8b**

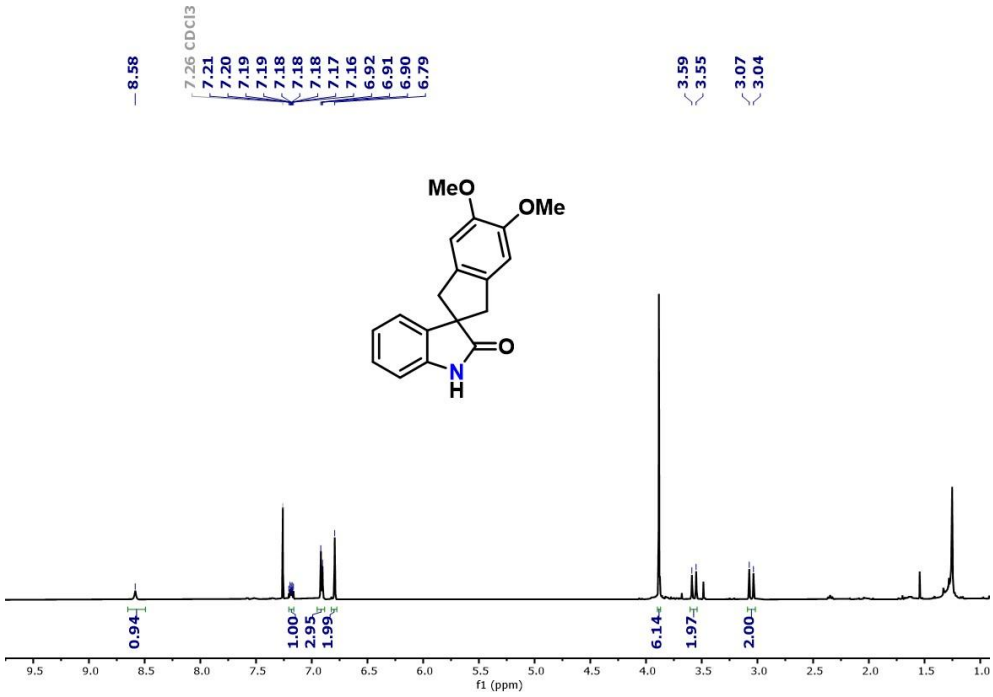


Figure 7A: ^{1}H-NMR: 5,6-dimethoxy-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8c**

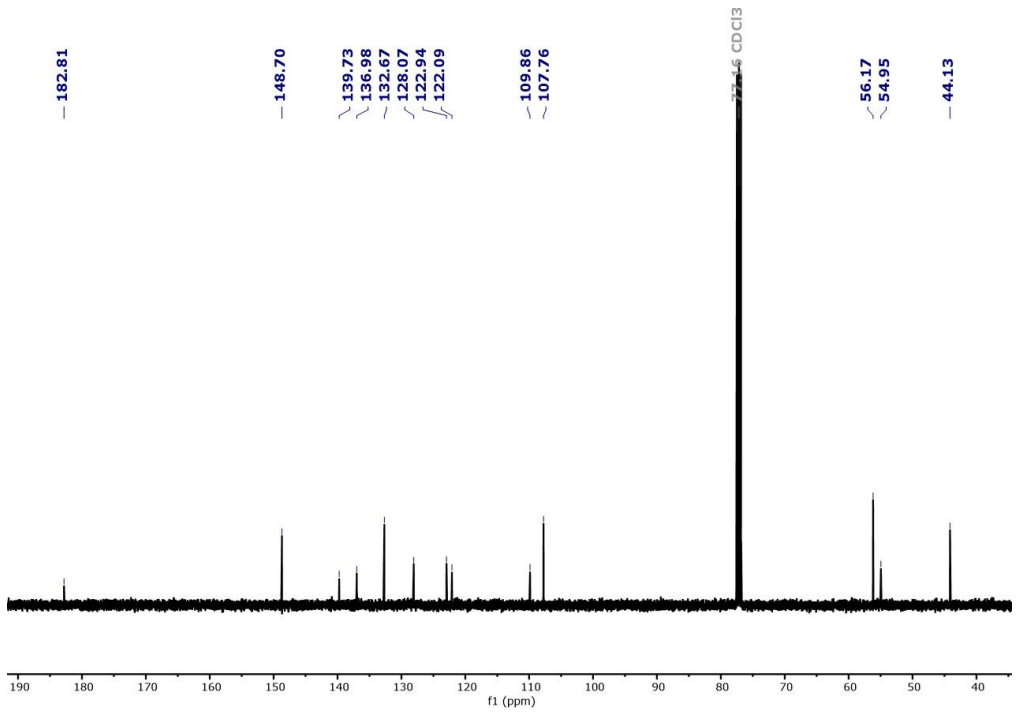


Figure 7B: ^{13}C-NMR: 5,6-dimethoxy-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8c**

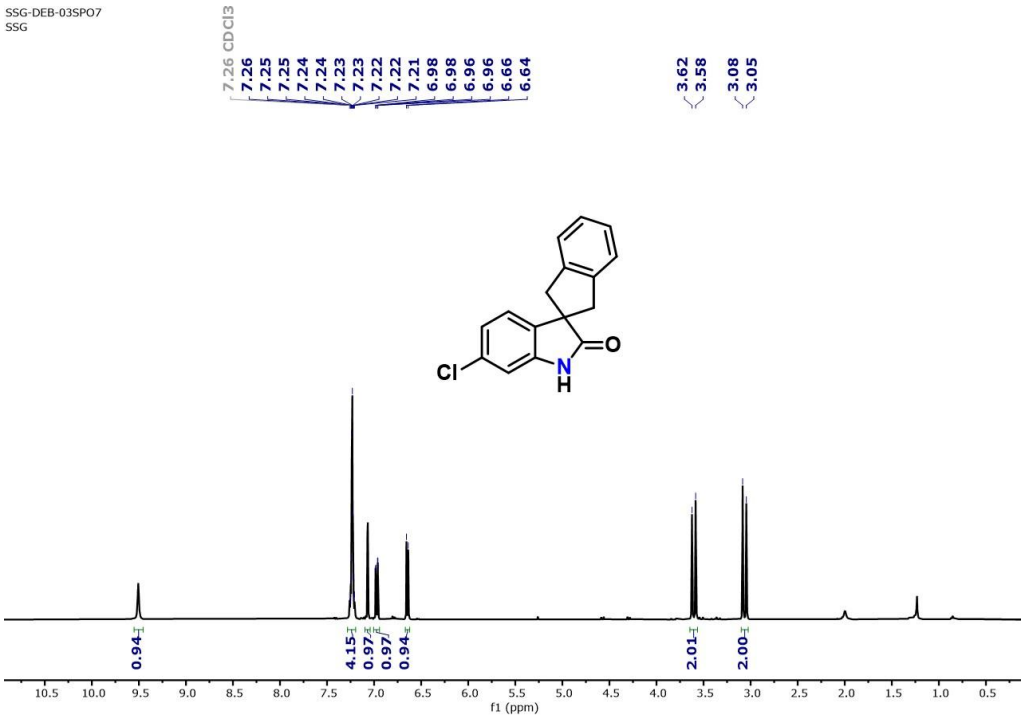


Figure 8A: ^{1}H NMR: 6'-chloro-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8d**

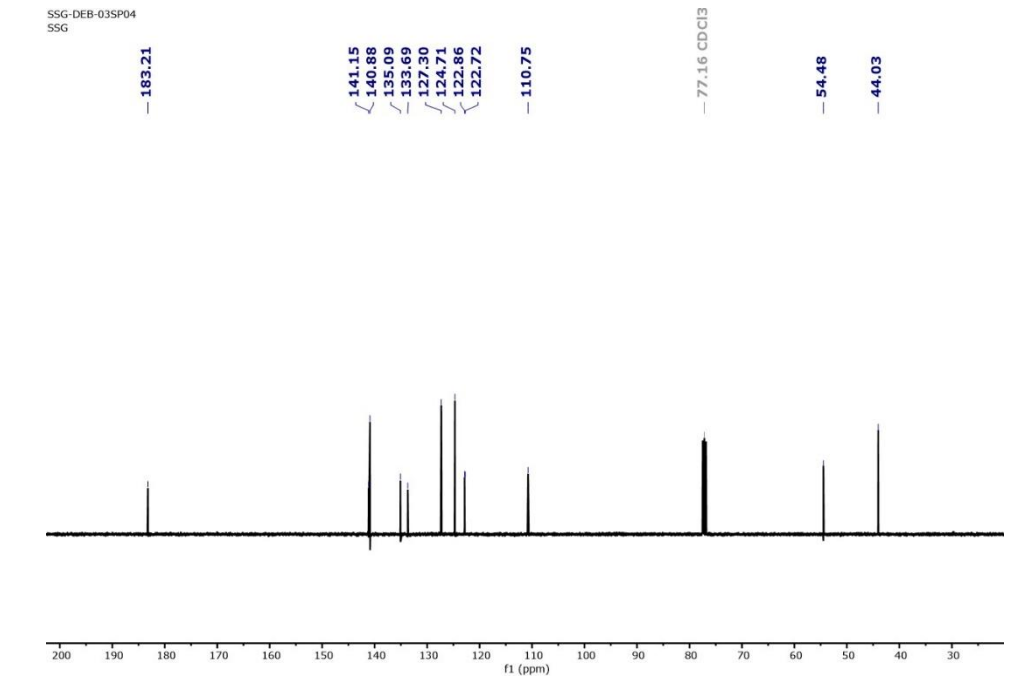


Figure 8B: ^{13}C NMR: 6'-chloro-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8d**

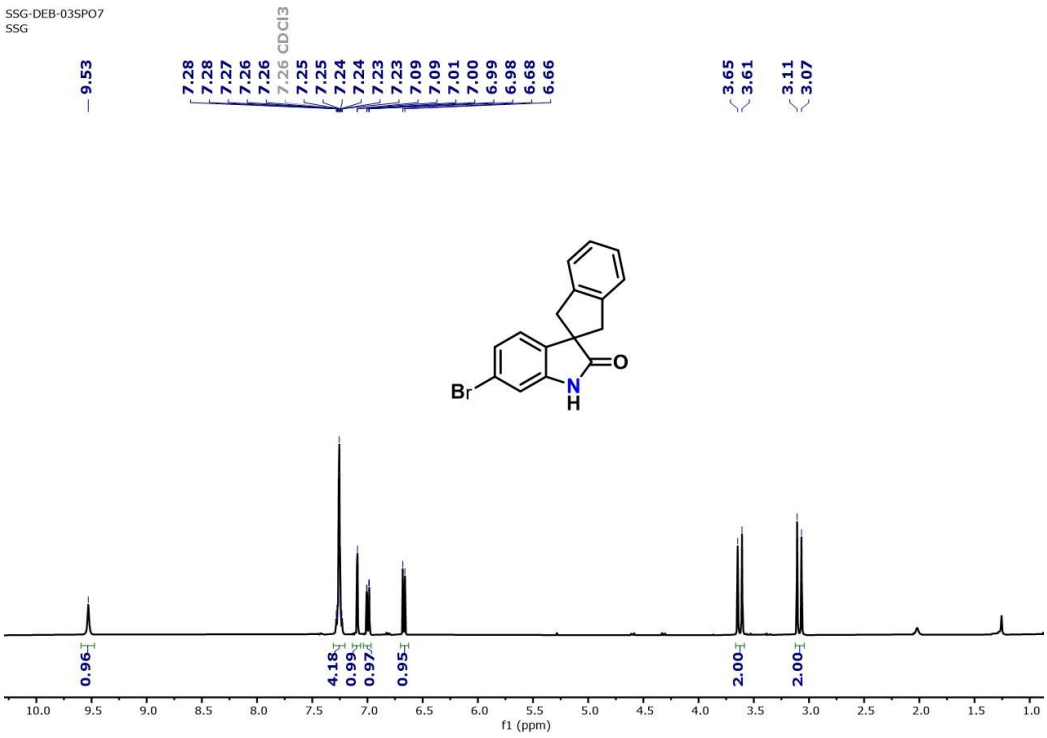


Figure 9A: ^{1}H NMR: 6'-bromo-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8e**

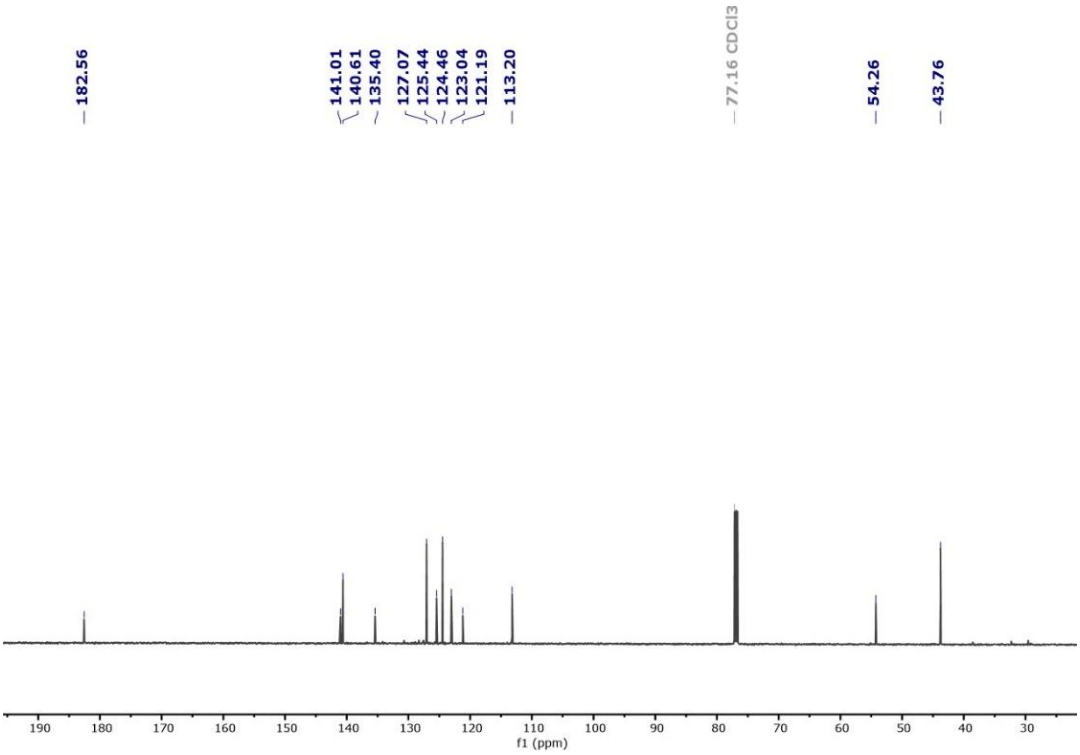


Figure 9B: ^{13}C NMR: 6'-bromo-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8e**

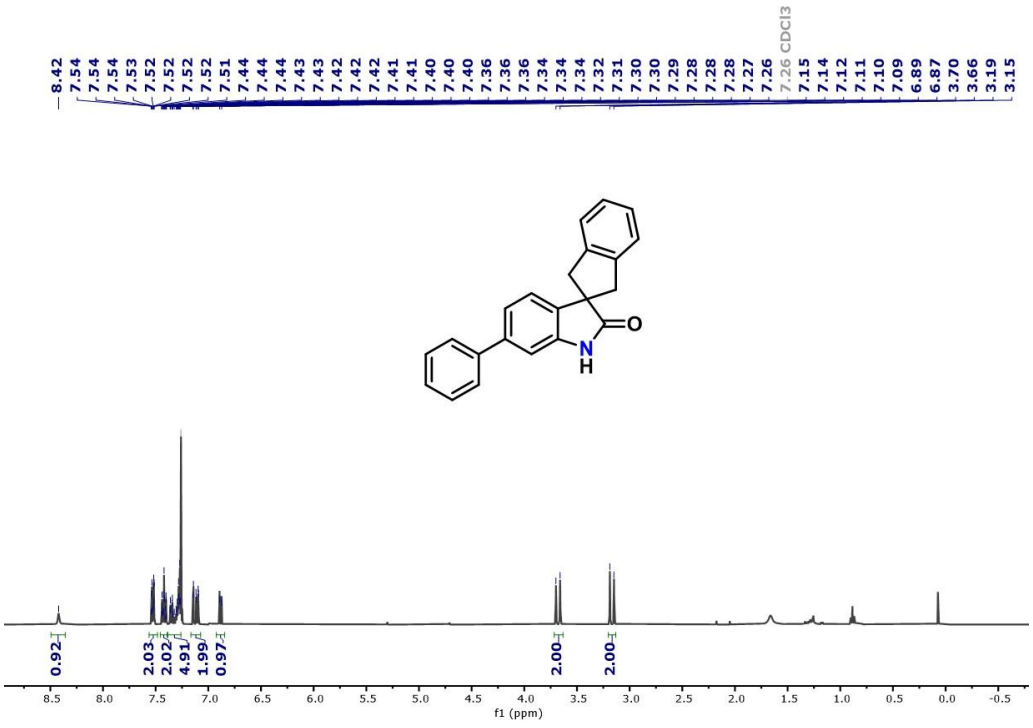


Figure 10A: ^{1}H NMR: 6'-phenyl-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8f**

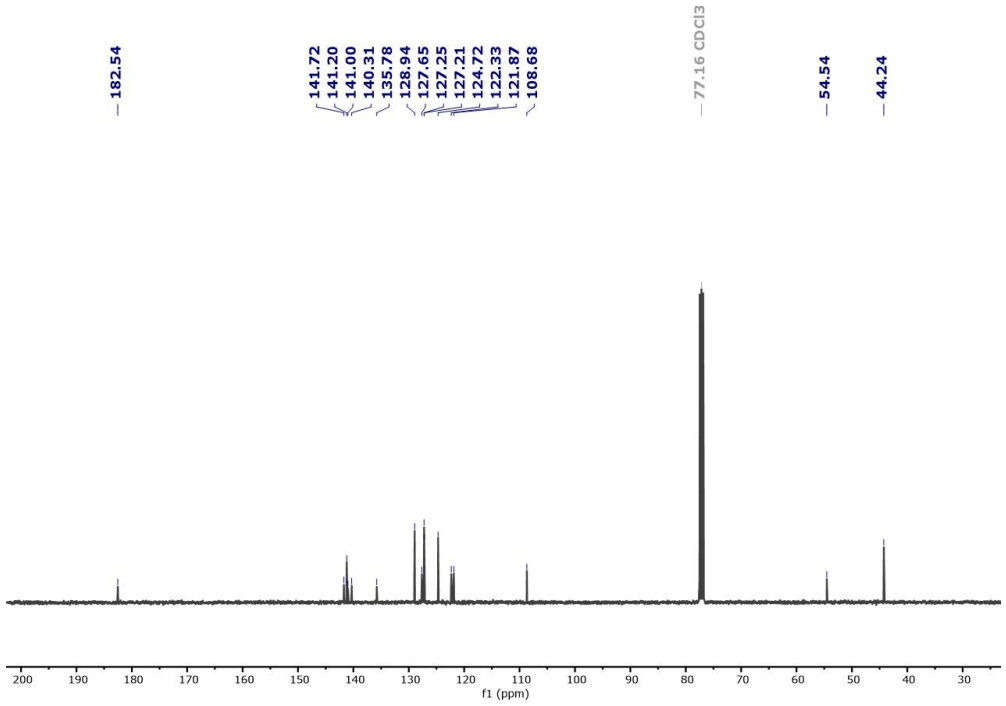


Figure 10B: ^{13}C NMR: 6'-phenyl-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8f**

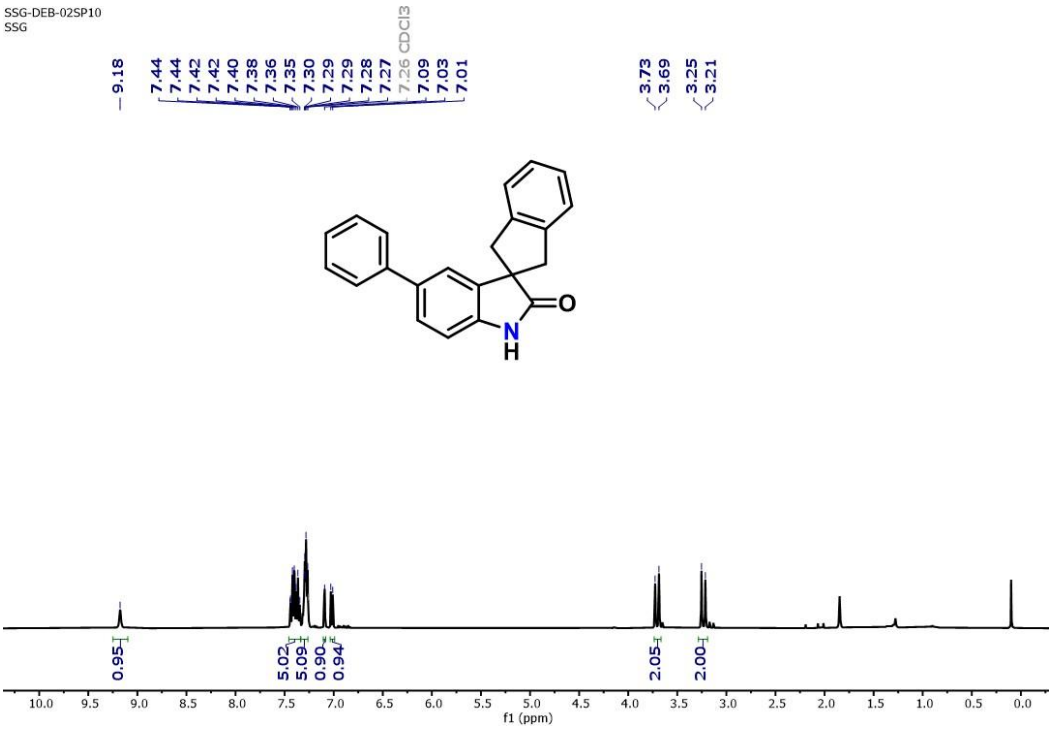


Figure 11A: ^{1}H NMR: 5'-phenyl-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8g**

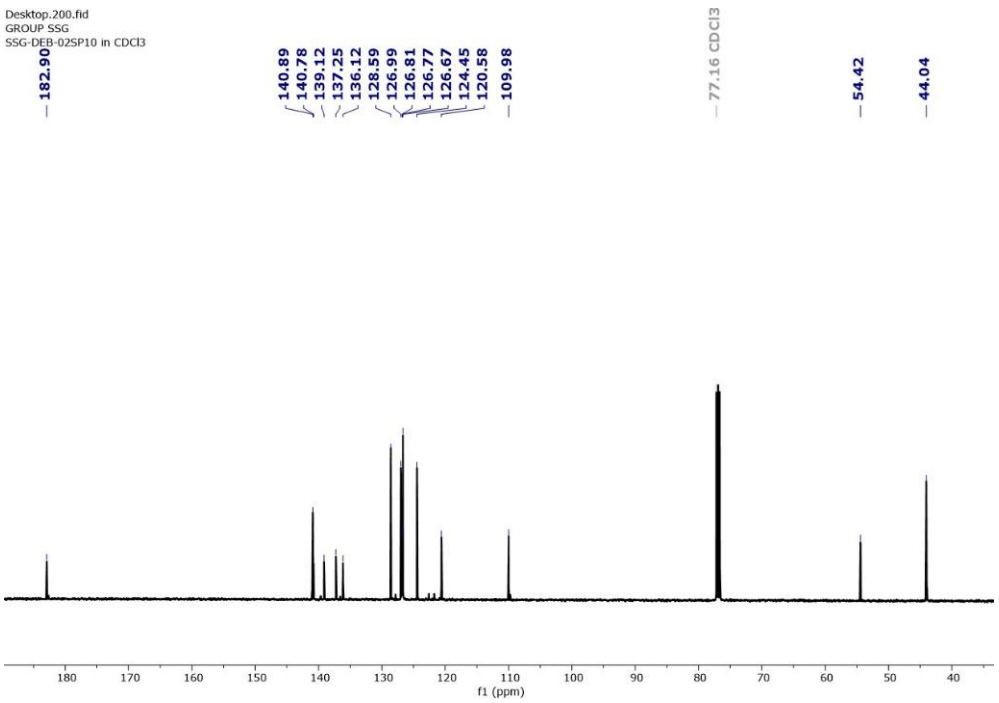


Figure 11B: ^{13}C NMR: 5'-phenyl-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8g**

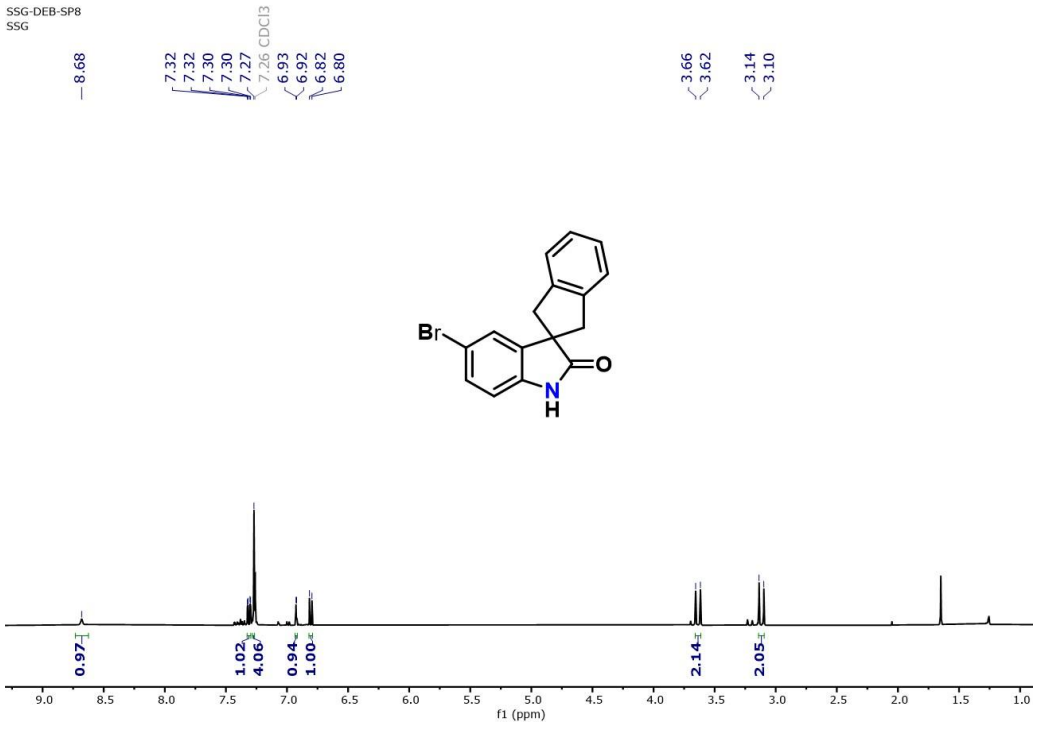


Figure 12A: ^{1}H NMR: 5'-bromo-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8h**

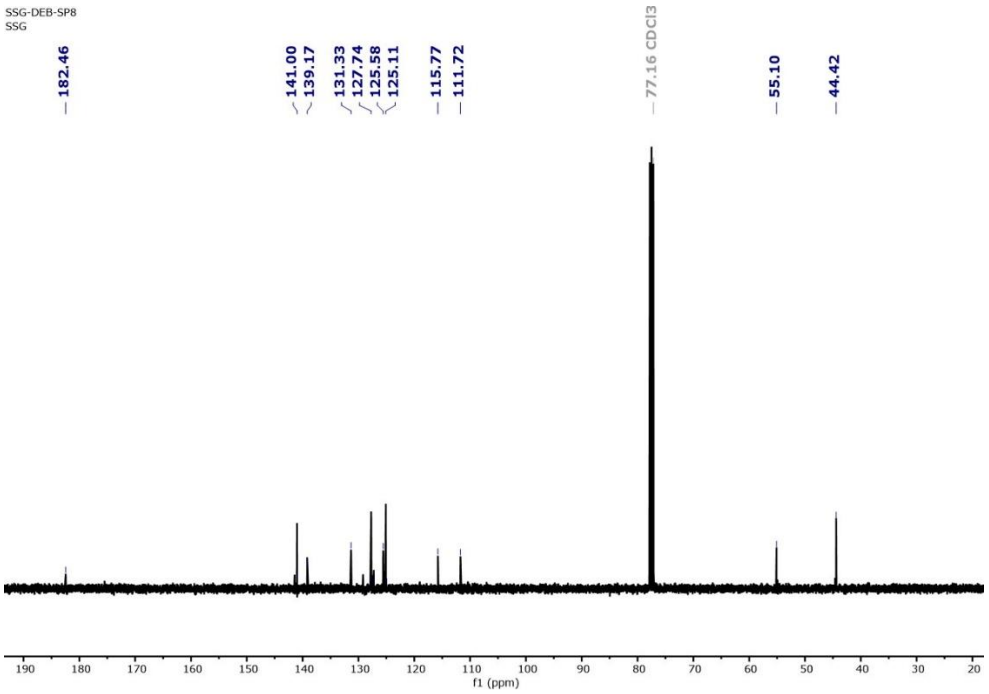


Figure 12B: ^{13}C NMR: 5'-bromo-1,3-dihydrospiro[indene-2,3'-indolin]-2'-one **8h**

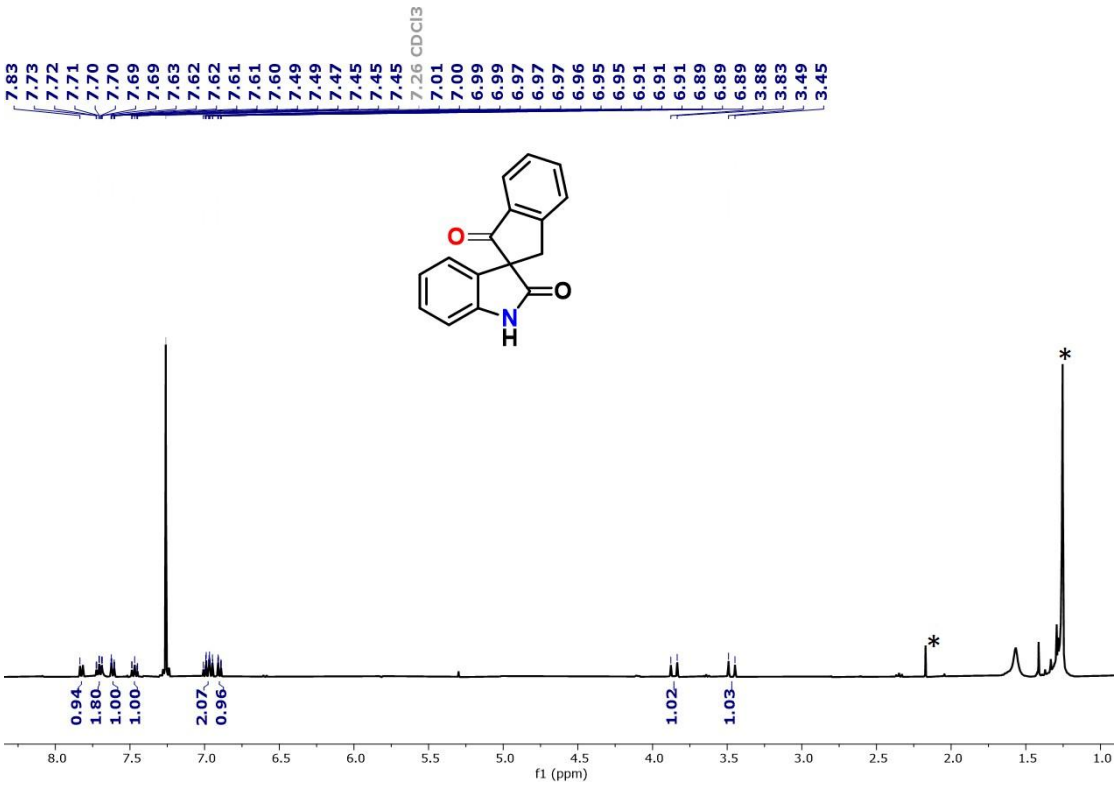


Figure 13A: ^{1}H NMR: spiro[indene-2,3'-indoline]-1,2'(3H)-dione **9a**

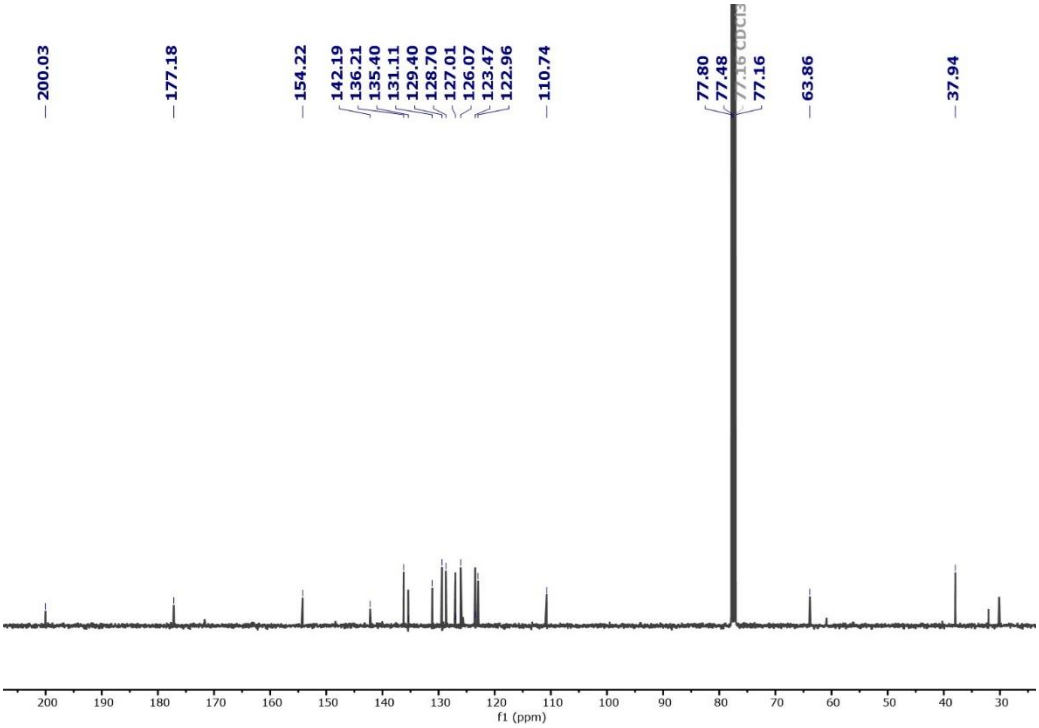


Figure 13B: ^{13}C NMR: spiro[indene-2,3'-indoline]-1,2'(3H)-dione **9a**

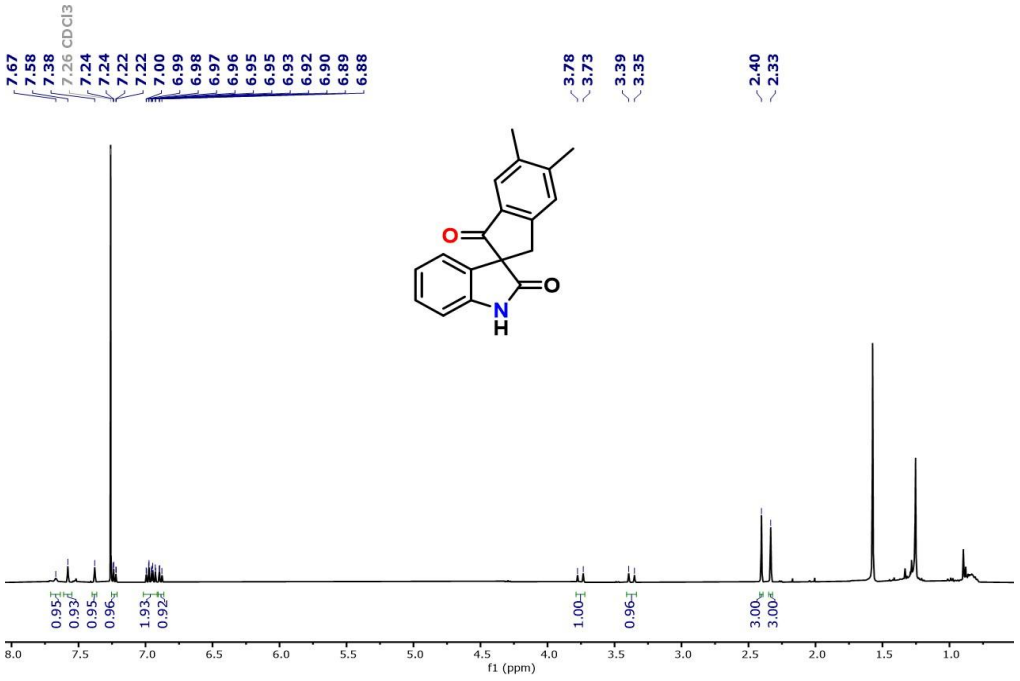


Figure 14A: ^{1}H NMR: 5,6-dimethylspiro[indene-2,3'-indoline]-1,2'(3H)-dione **9b**

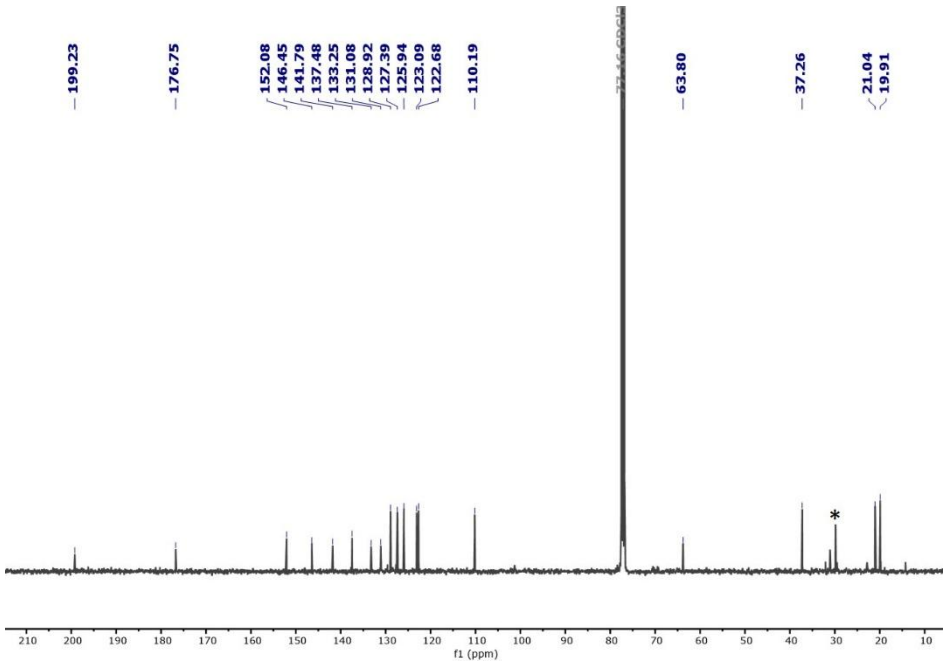


Figure 14B: ^{13}C NMR: 5,6-dimethylspiro[indene-2,3'-indoline]-1,2'(3H)-dione **9b**

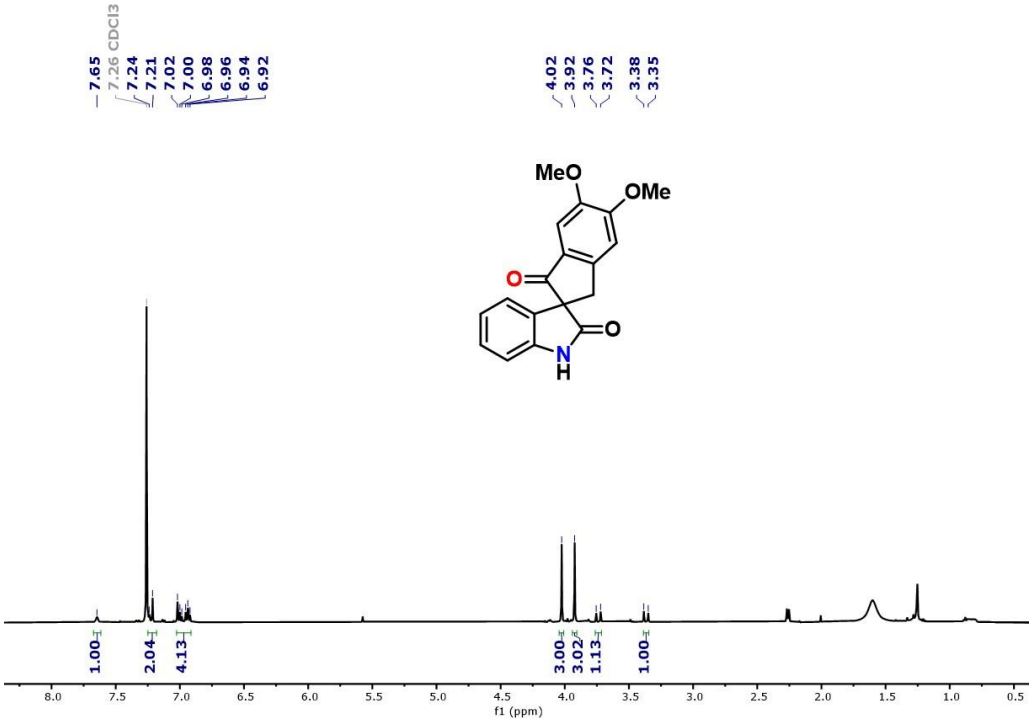


Figure 15A: ^{1}H NMR: 5,6-dimethoxyspiro[indene-2,3'-indoline]-1,2'(3H)-dione **9c**

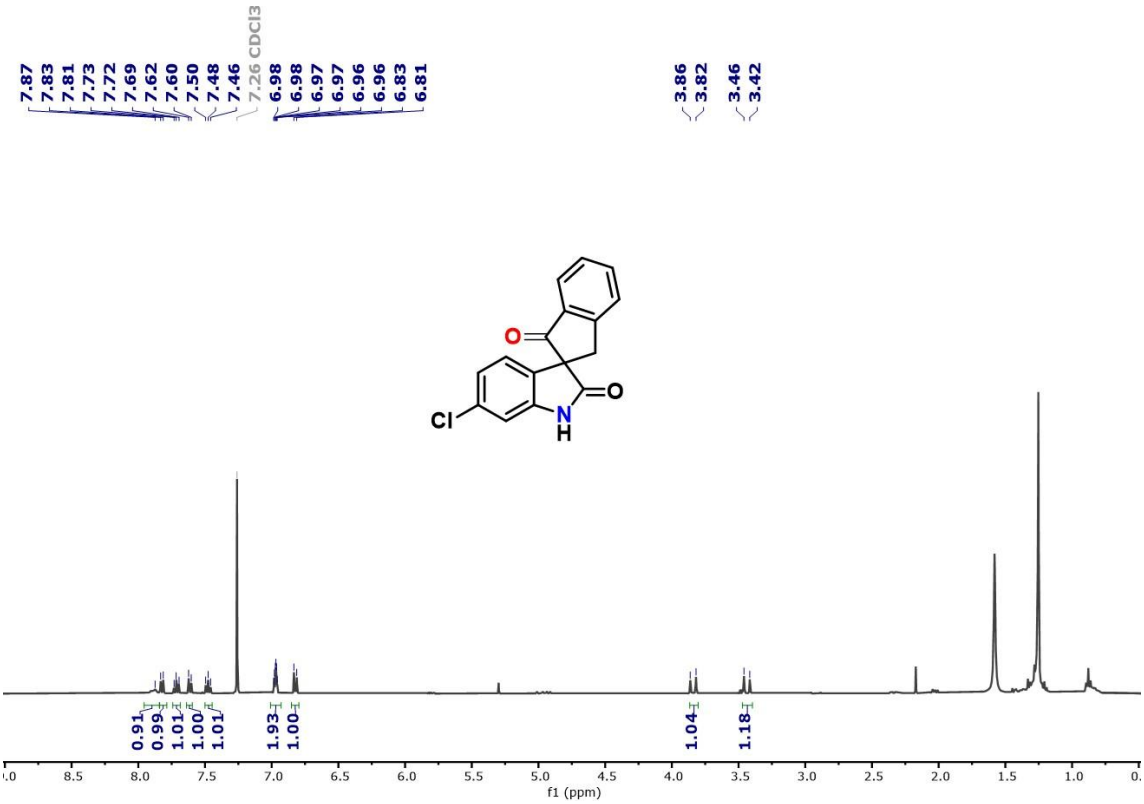


Figure 16A: ^{1}H NMR: 6'-chlorospiro[indene-2,3'-indoline]-1,2'(3H)-dione **9d**

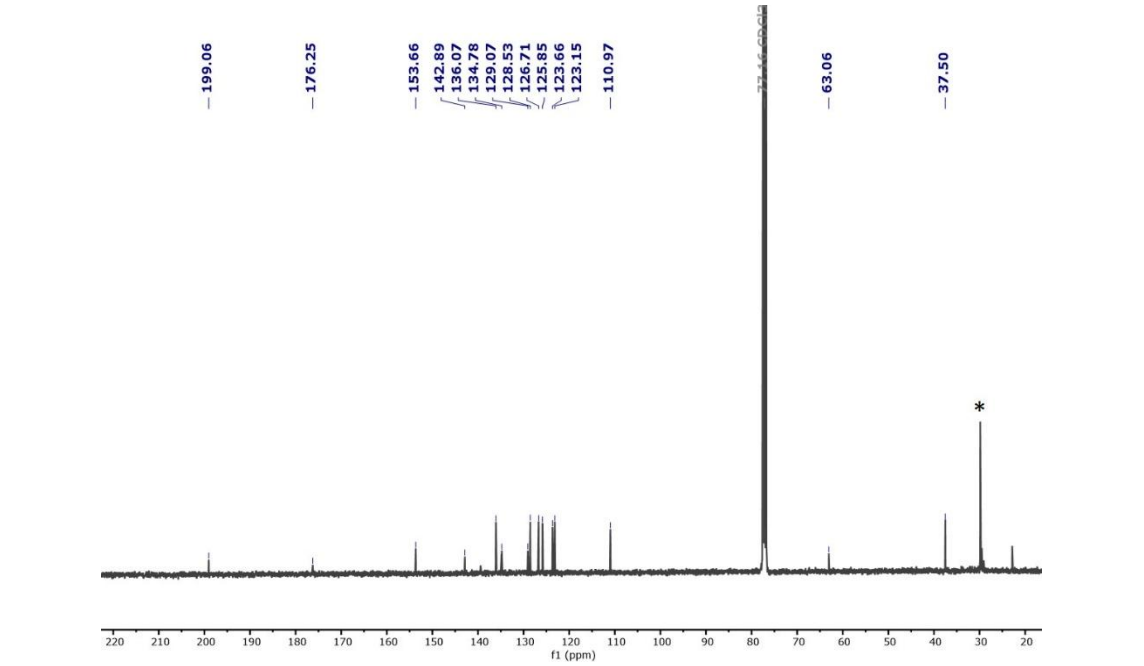


Figure 16B: ^{13}C NMR: 6'-chlorospiro[indene-2,3'-indoline]-1,2'(3H)-dione **9d**

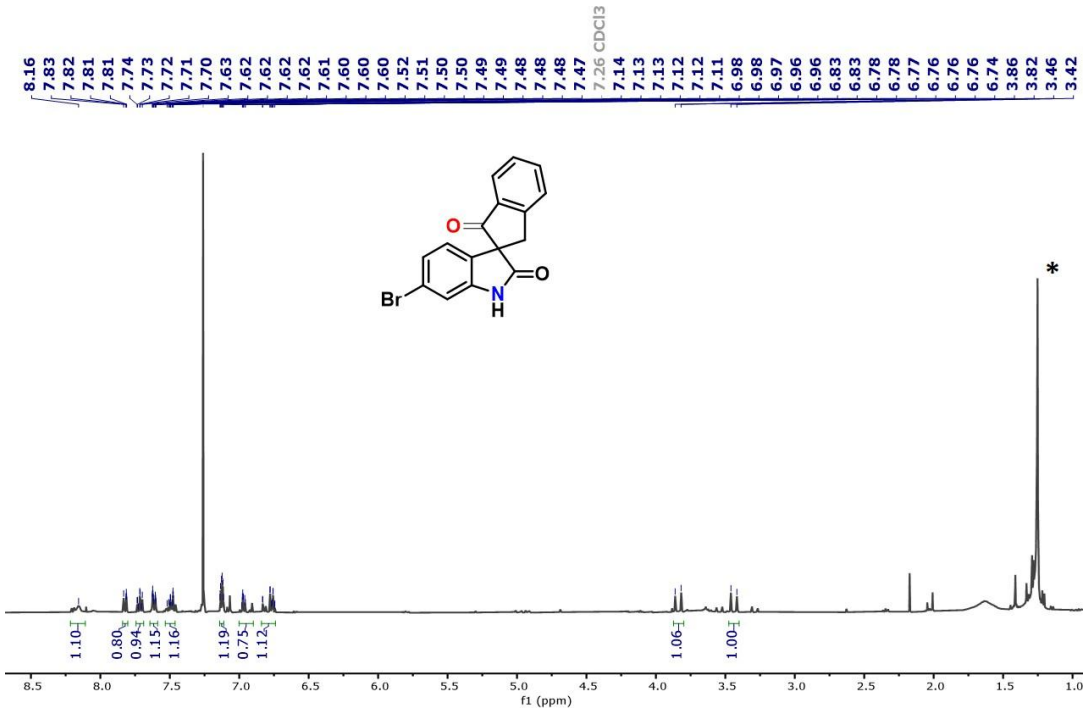


Figure 17: [1]H NMR: 6'-bromospiro[indene-2,3'-indoline]-1,2'(3H)-dione **9e**

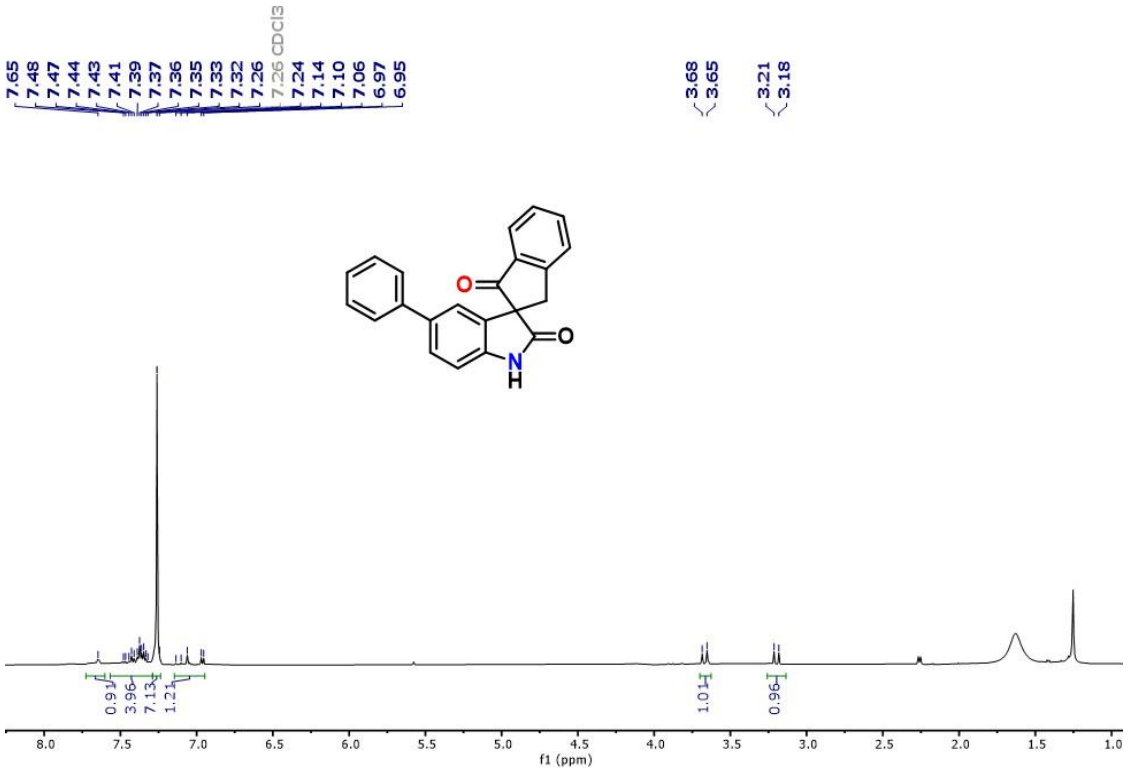


Figure 18: [1]H NMR of 5'-phenylspiro[indene-2,3'-indoline]-1,2'(3H)-dione **9g**

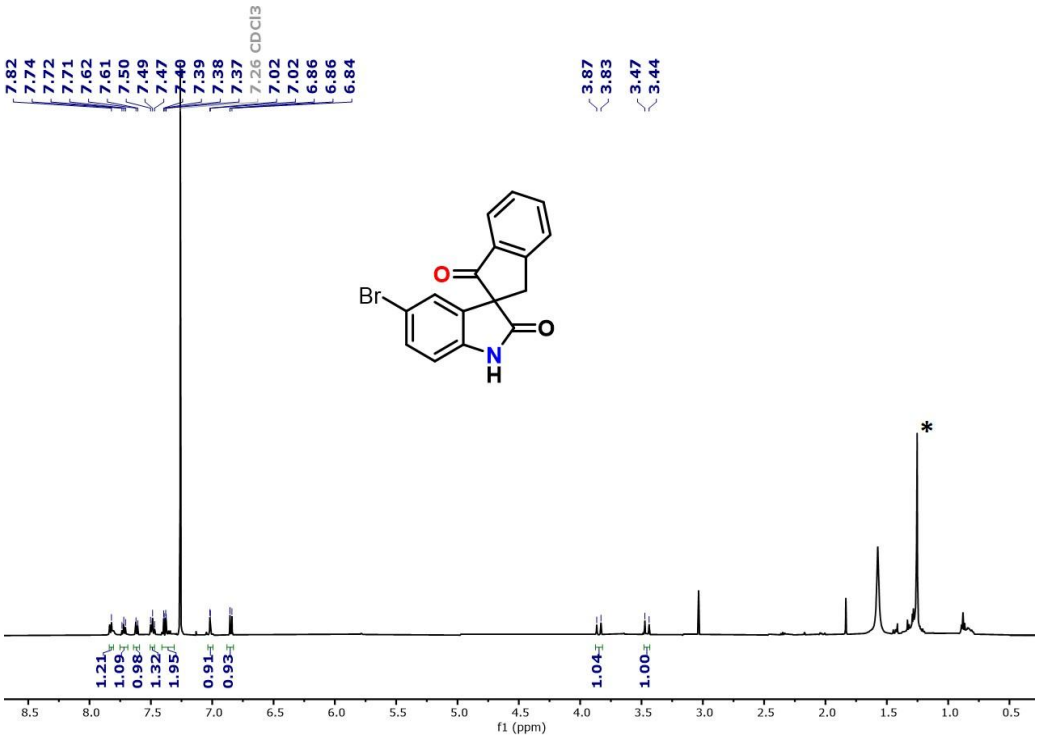
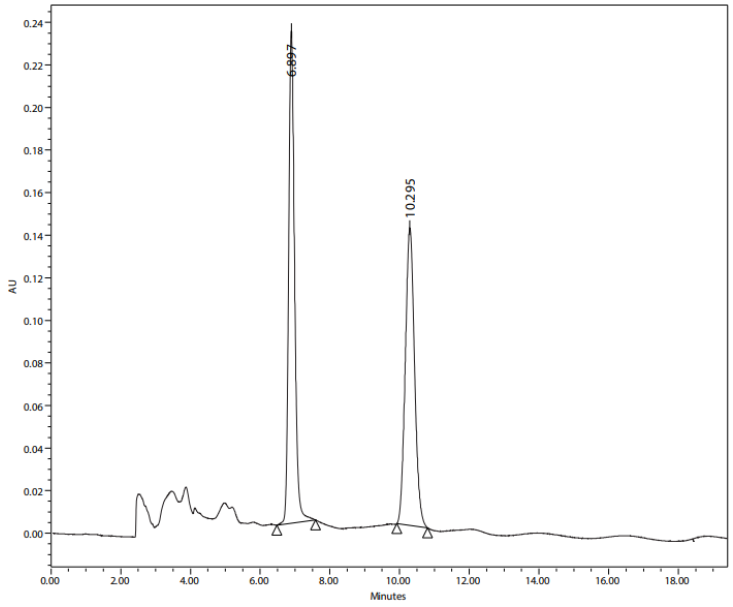


Figure 19: ^{1}H NMR: 5'-bromo-5-methylspiro[indene-2,3'-indoline]-1,2'(3H)-dione **9h**

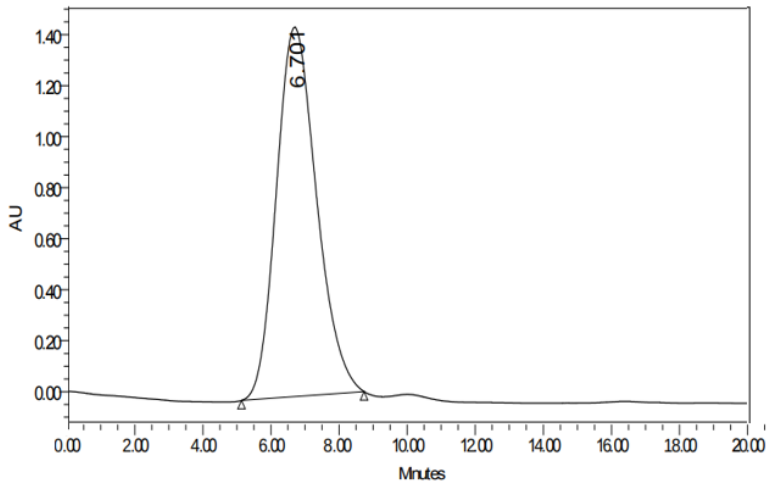
5. Copies of HPLC:

Racemic macrocycle:



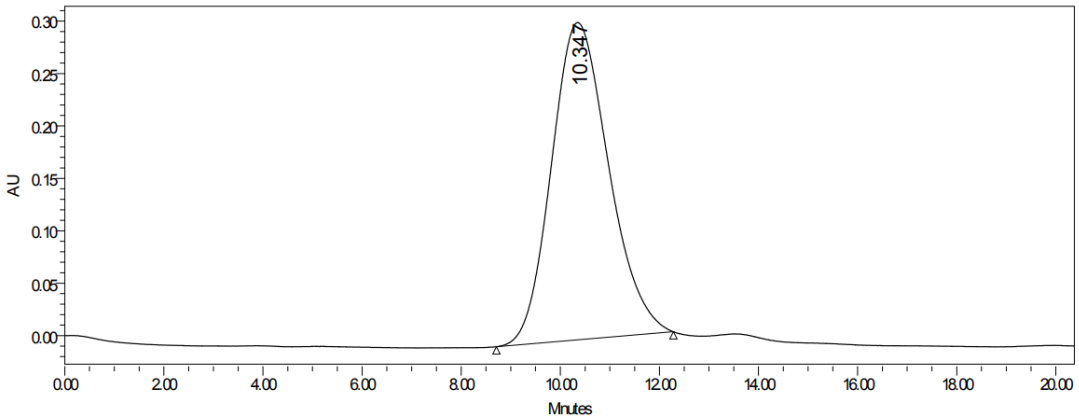
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	6.897	718185	51.27	231446
2	10.295	2583967	48.73	139738

(*R,R*)- macrocycle:



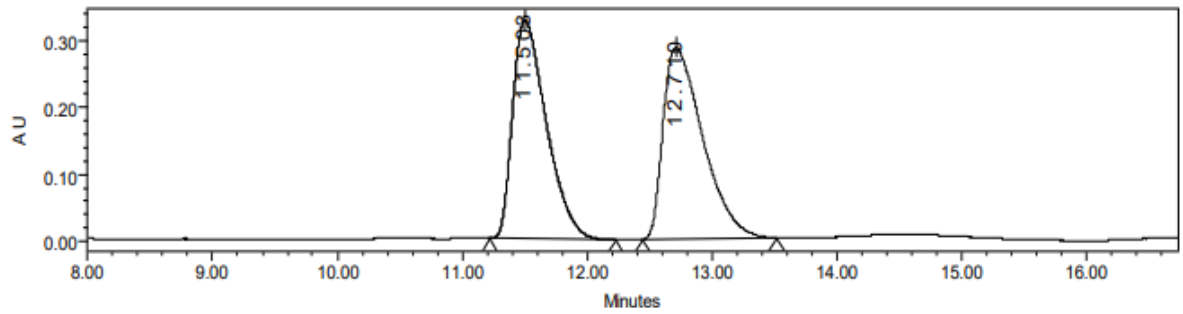
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	6.701	121109926	100.00	1477079

(*S,S*)- macrocycle:



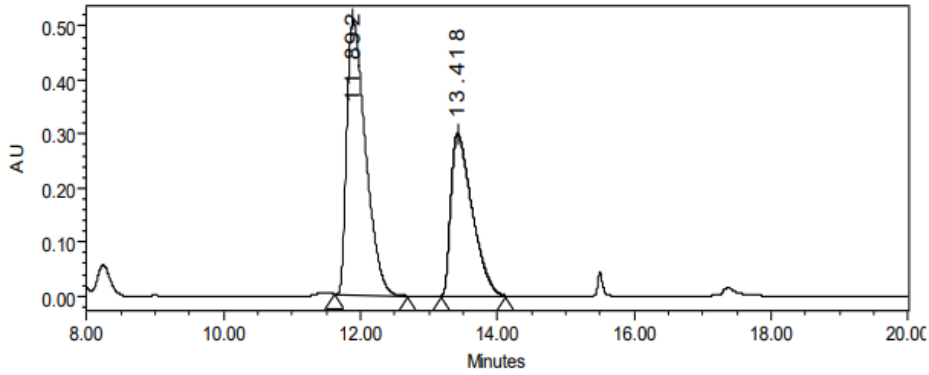
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	10.347	24250815	100.00	302589

Racemic 7a:



	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	11.503	6156236	49.31	327717
2	12.710	6327729	50.69	286350

***ent 1*-7a:**



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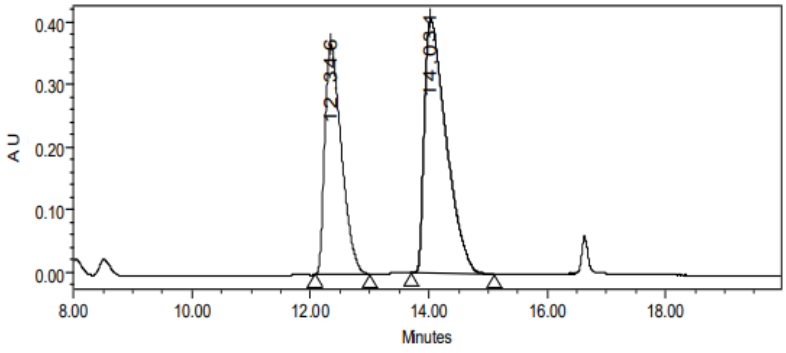
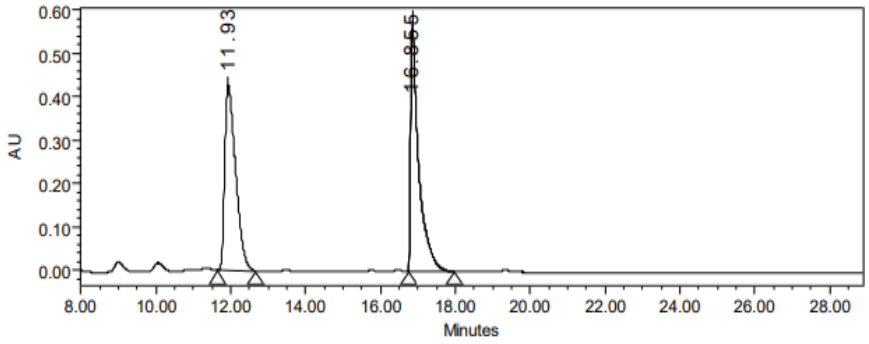
1	11.892	11048001	63.63	508884
2	13.418	6316078	36.37	299976

***ent 2*-7a**



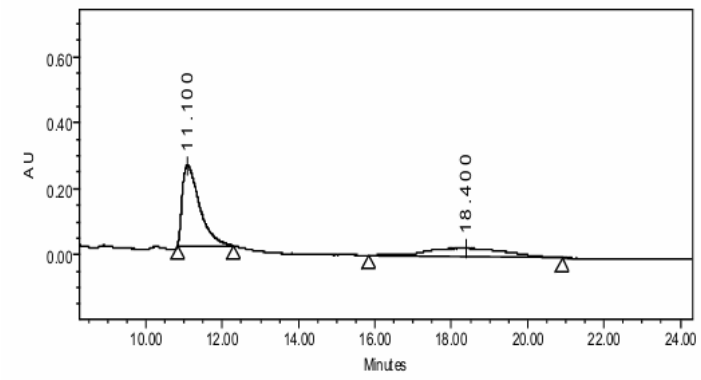
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	12.346	7387015	36.68	367953
2	14.031	12751401	63.32	40756

Racemic 7b:



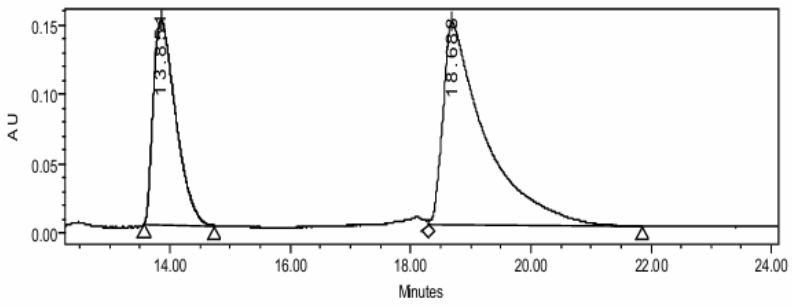
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	11.934	8703992	50.60	426370
2	16.855	8495930	49.40	579327

***ent 1*-7b:**



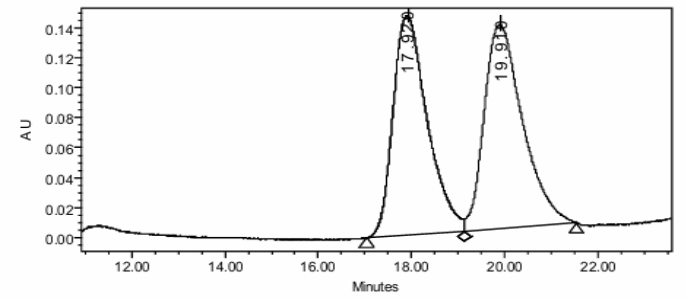
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	11.100	7692165	67.03	243724
2	18.400	3784335	32.97	25220

***ent 2*-7b:**



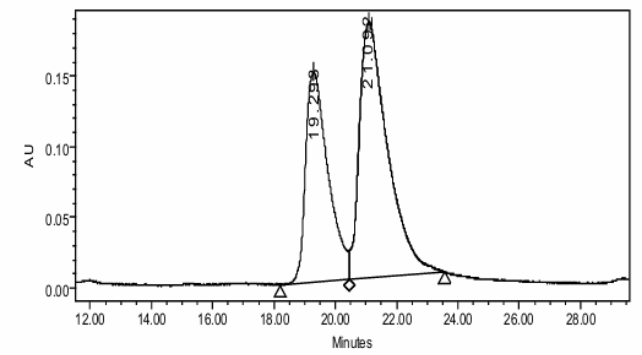
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	13.851	3795856	34.10	147449
2	18.688	7334593	65.90	146486

Racemic 7c:



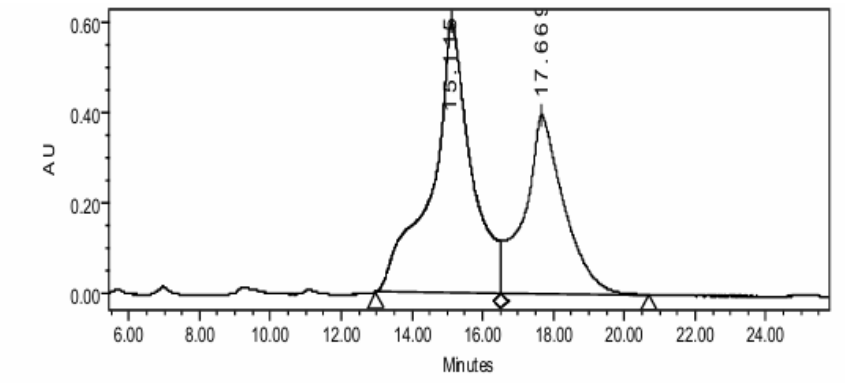
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	17.920	7474618	48.95	146364
2	19.910	7795219	51.05	136304

***ent 1*-7c:**



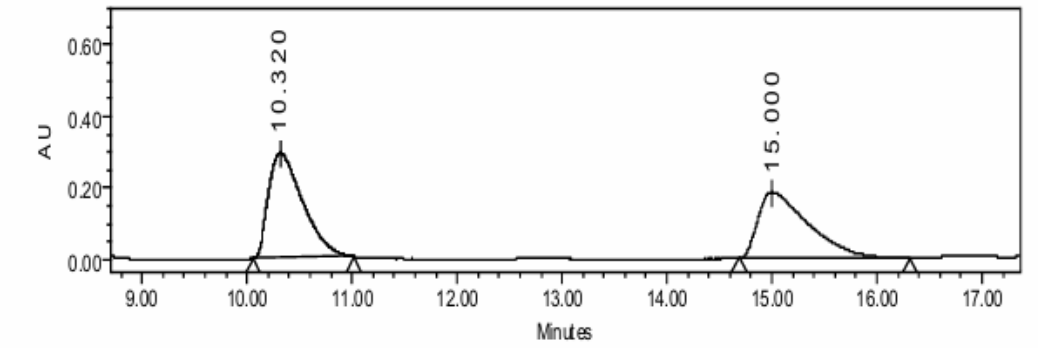
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	19.293	7610322	39.51	148783
2	21.092	11653276	60.49	181705

***ent 2*-7c**



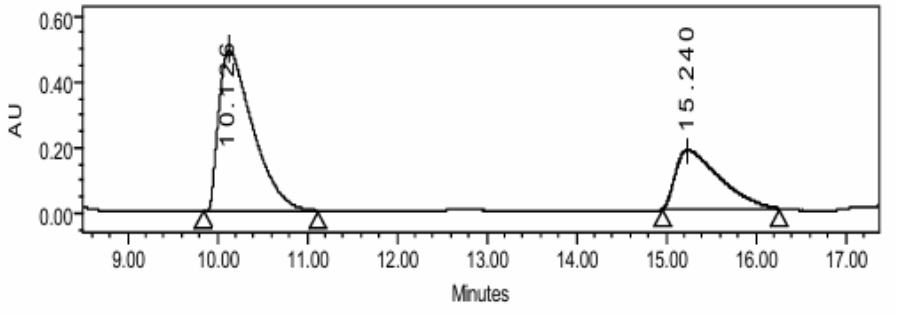
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	15.115	48084506	60.98	602112
2	17.669	30768831	39.02	397717

Racemic 7d:



	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	10.320	6351710	50.99	288681
2	15.000	6104302	49.01	184497

***ent 1*-7d:**



	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	10.126	12854881	67.62	490310
2	15.240	6154608	32.38	180717

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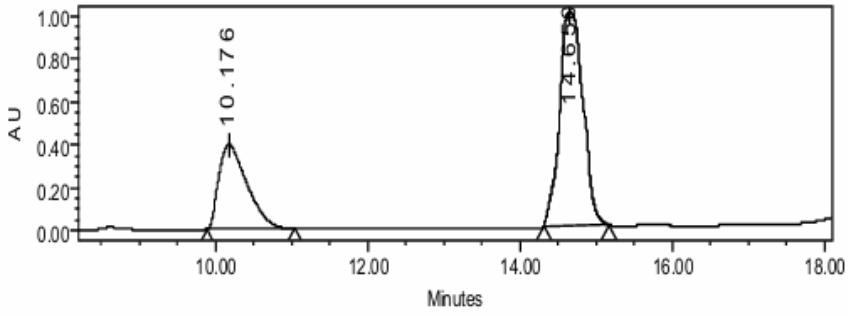
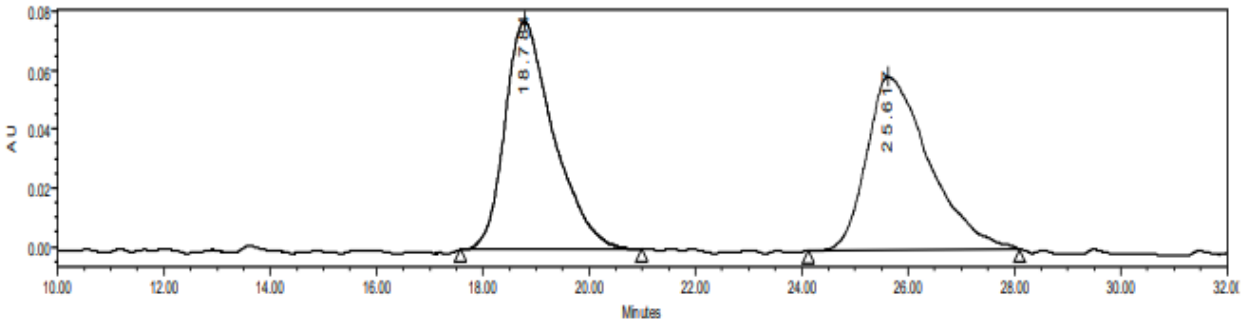


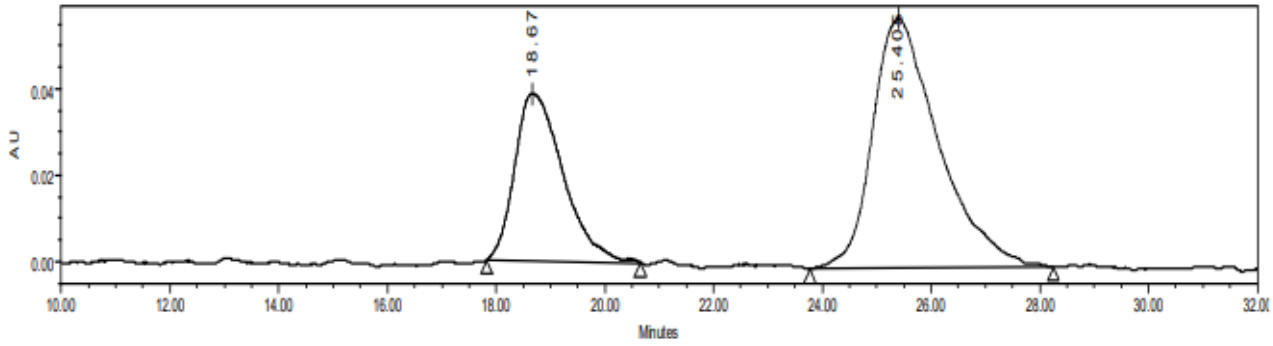
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	10.176	10222621	32.00	396826
2	14.650	21727749	68.00	1011167

Racemic 9a:



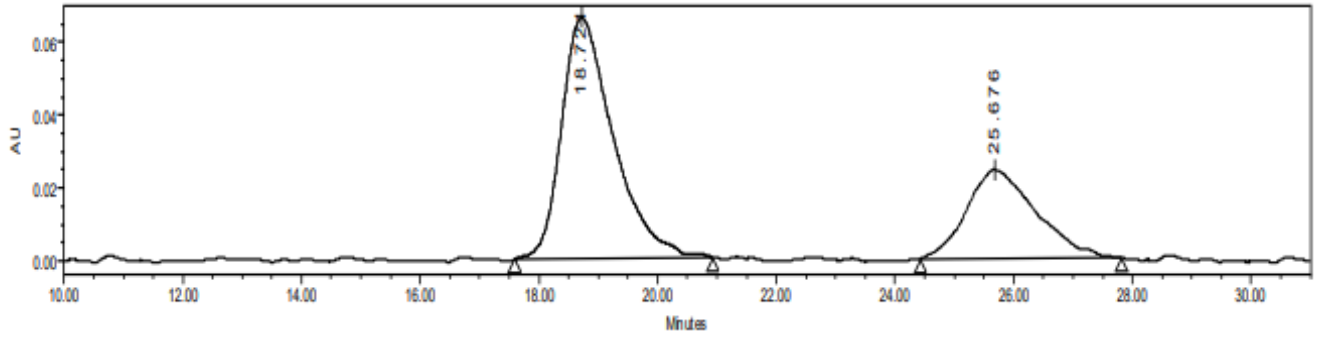
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	18.784	4921286	50.55	77529
2	25.617	4814122	49.45	58679

***ent 1*-9a:**



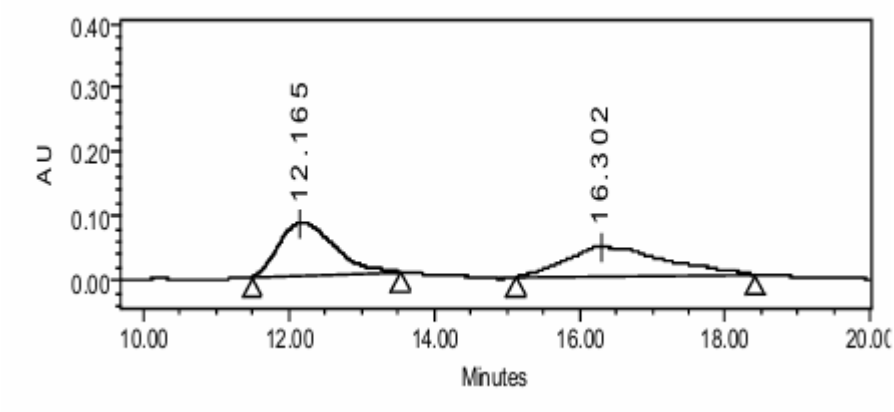
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	18.672	2401446	32.96	38860
2	25.405	4885158	67.04	57712

***ent 2*-9a:**



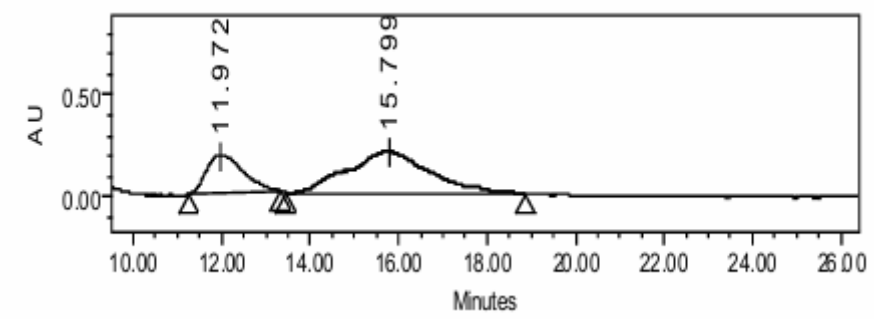
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	18.721	4012602	67.17	65956
2	25.676	1961561	32.83	24240

Racemic 9b:



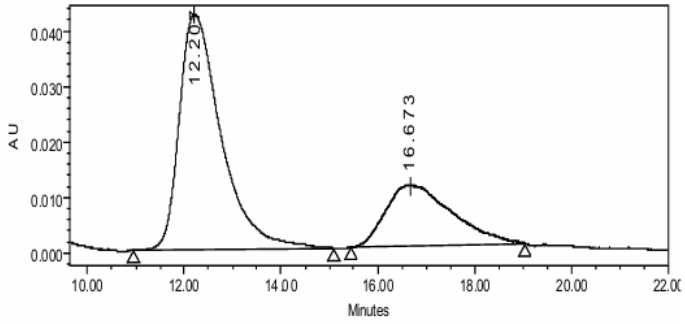
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	12.165	4299854	49.51	81988
2	16.302	4385589	50.49	46648

***ent 1*-9b:**



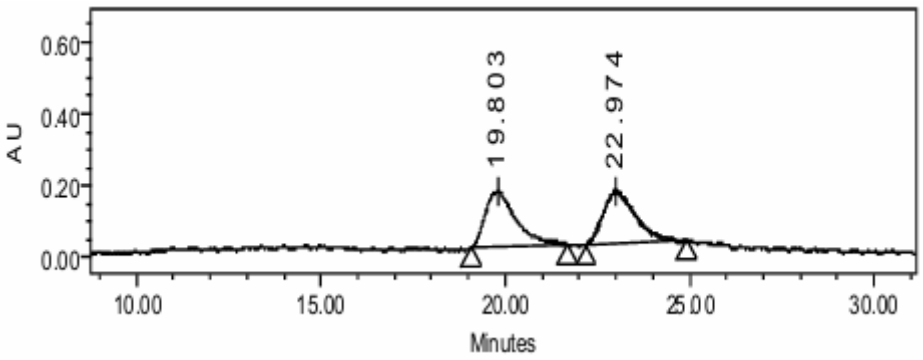
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	11.972	11005546	29.03	187208
2	15.799	26901711	70.97	210671

***ent 2*-9b:**



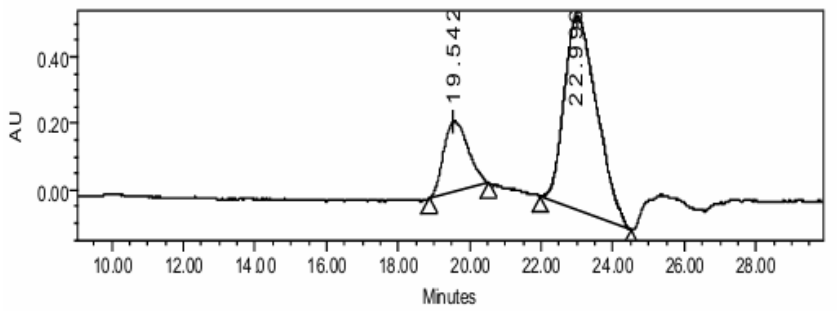
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	12.207	2545633	71.01	10896
2	16.673	1039255	28.99	42393

Racemic 9c:



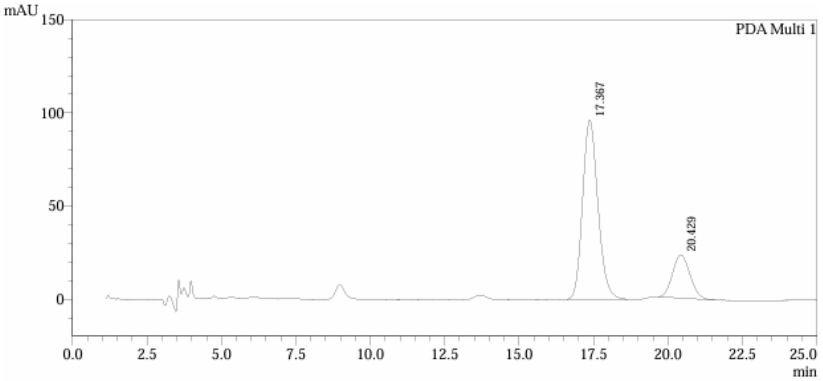
	RT (min)	Area (µV*sec)	% Area
1	19.803	8986580	50.21
2	22.974	8910638	49.79

***ent 1*-9c:**



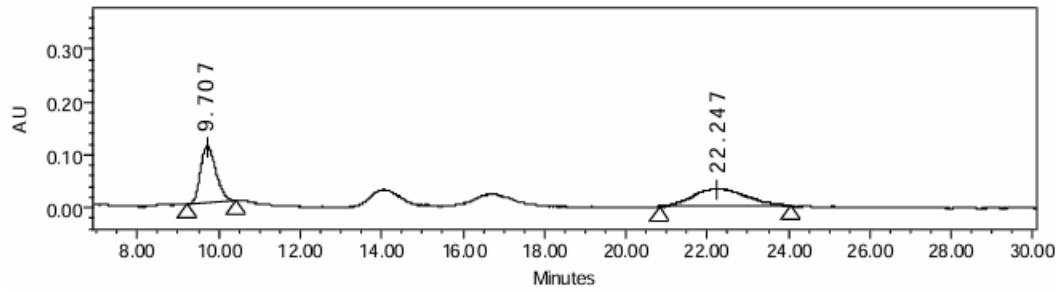
	RT (min)	Area (µV*sec)	% Area
1	19.542	10070123	21.41
2	22.996	36975425	78.59

***ent 2*-9c:**



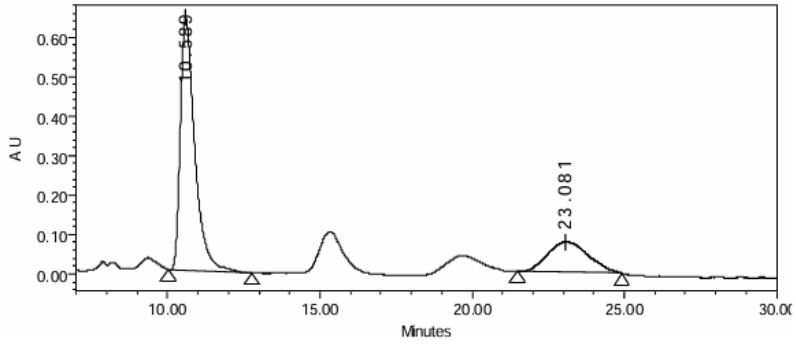
	RT (min)	Area (µV*sec)	% Area
1	17.367	3439619	78.665
2	20.429	932893	21.335

Racemic 9d:



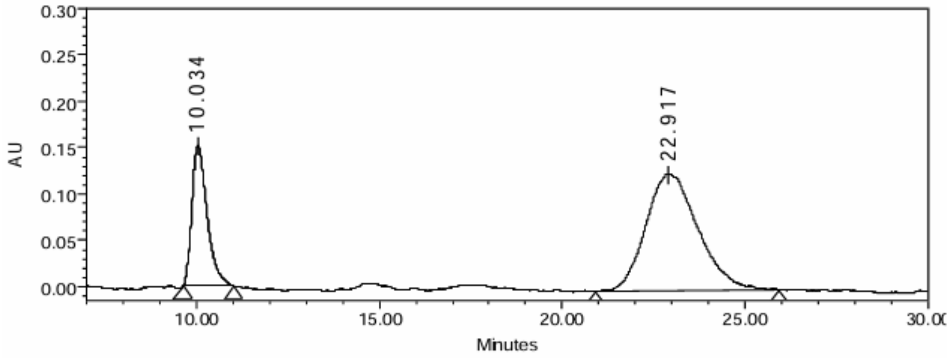
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	9.718	1388899	49.38	52088
2	22.254	1423655	50.62	15801

***ent 1*-9d:**



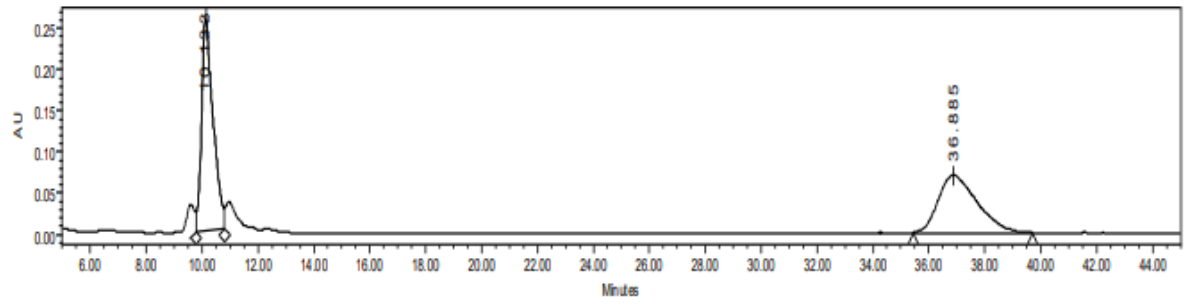
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	10.589	21106664	74.80	638310
2	23.081	7112135	25.20	76808

***ent 2*-9d:**



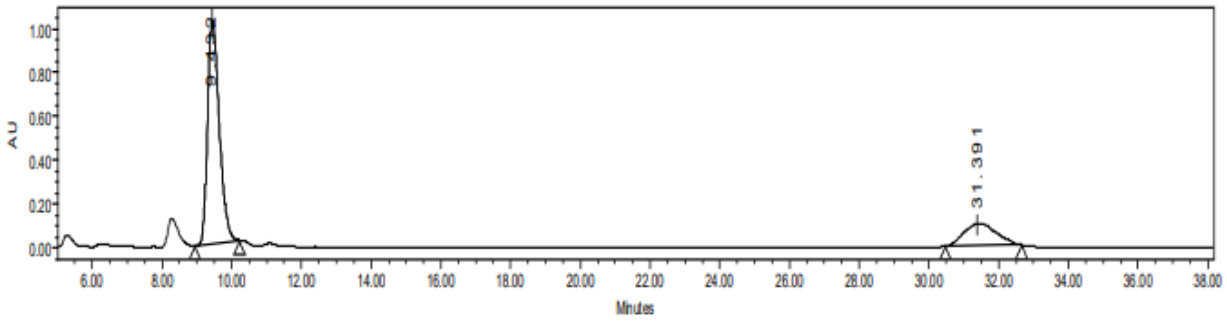
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	10.035	4209337	25.27	150958
2	22.960	12464769	74.73	124920

Racemic 9e:



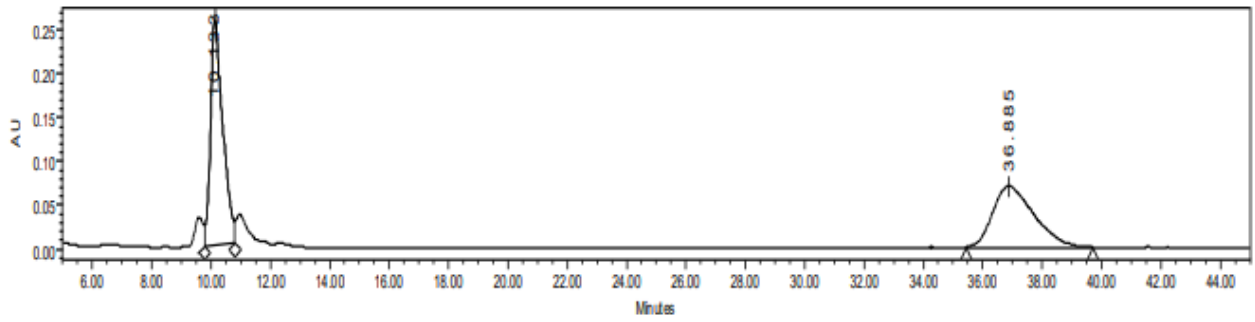
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	10.133	7050108	50.05	257241
2	36.885	7036022	49.95	70275

***ent 1*-9e:**



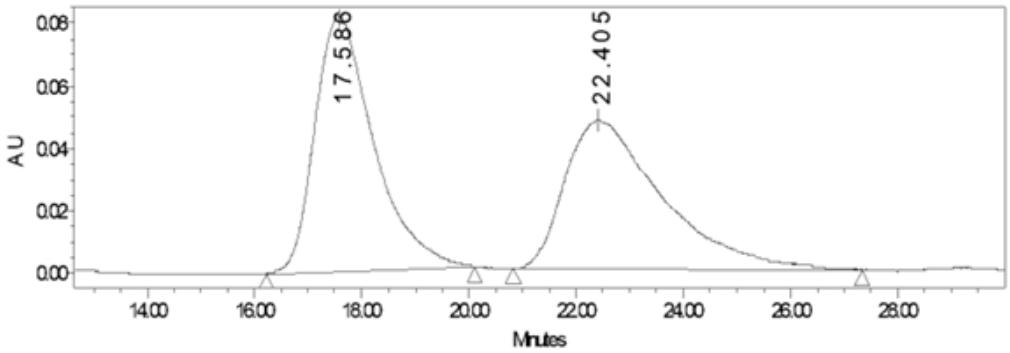
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	9.432	23858099	78.31	1025539
2	31.391	6608676	21.69	101422

***ent 2*-9e:**



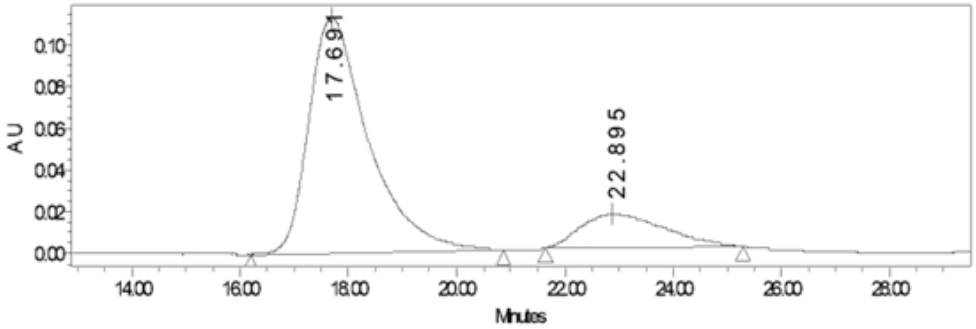
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	10.097	4094306	21.48	175888
2	37.081	14962290	78.52	149365

Racemic 9f:



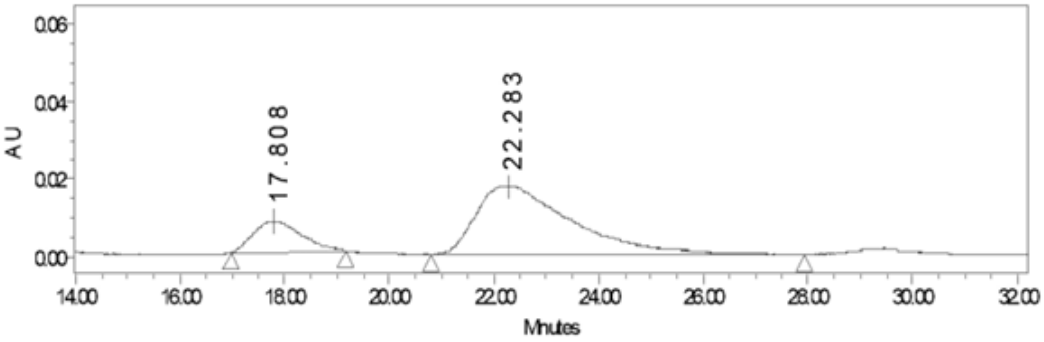
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	17.586	6232089	50.44	81469
2	22.405	6123807	49.56	47832

***ent 1*-9f:**



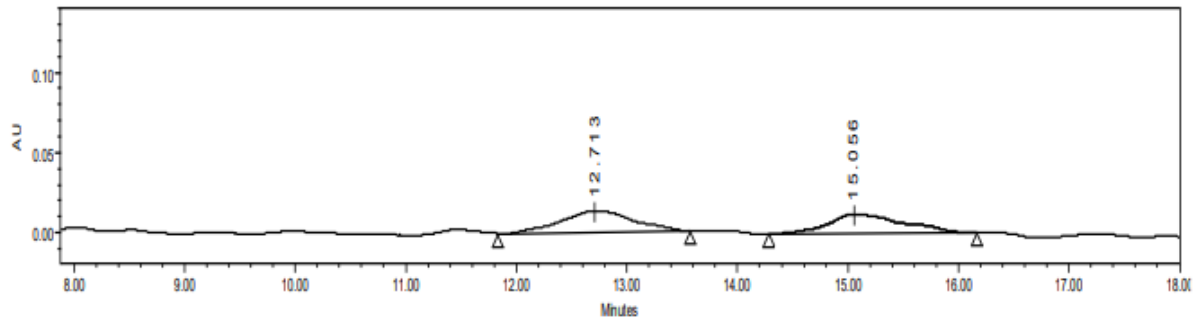
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	17.691	8725810	83.47	113211
2	22.895	1728483	16.53	16133

***ent 2*- 9f:**



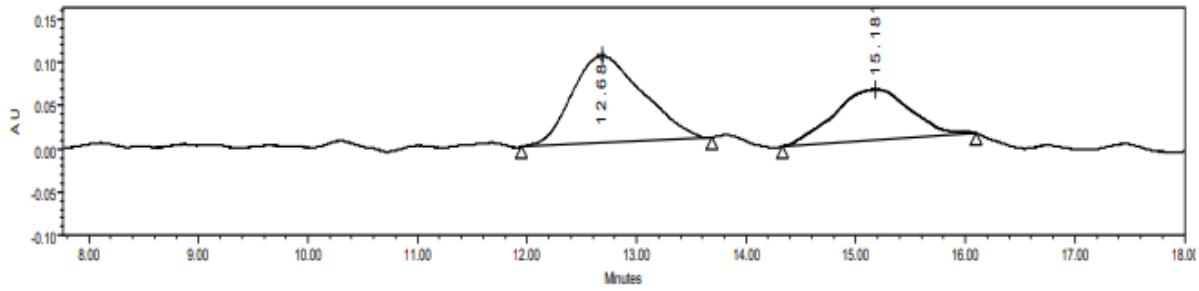
	RT (min)	Area (µV*sec)	% Area	Height (µV)
1	17.808	463997	17.19	7703
2	22.283	2234938	82.81	17583

Racemic 9g:



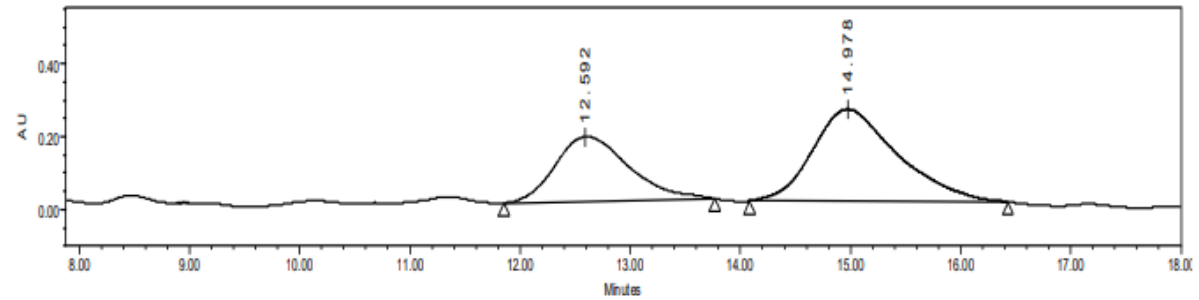
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	12.713	531595	49.35	12502
2	15.056	545503	50.65	11807

***ent 1*-9g:**



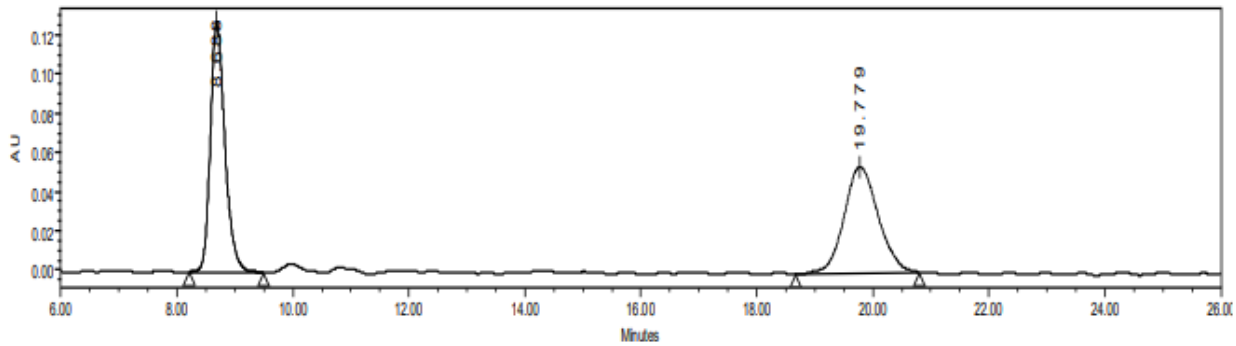
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	12.684	4519452	61.36	100224
2	15.181	2845633	38.64	59004

***ent 2*-9g:**



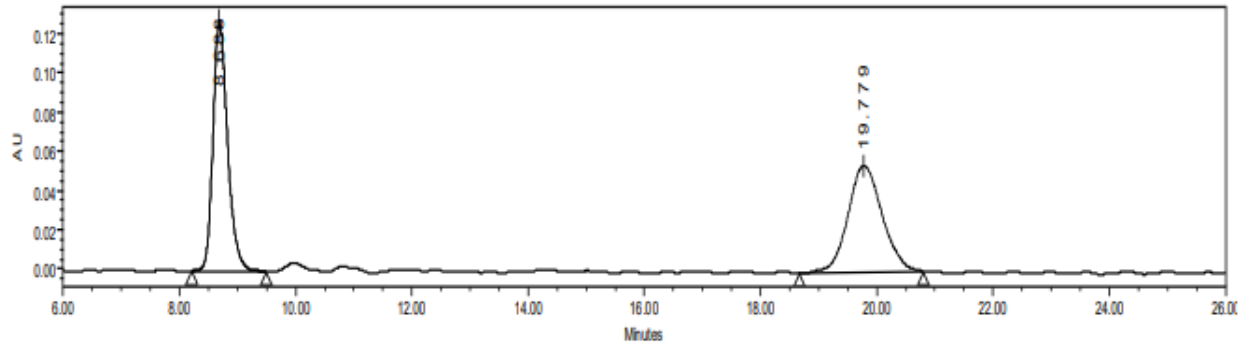
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	12.592	8790591	38.13	180238
2	14.978	14263210	61.87	256685

Racemic 9h:



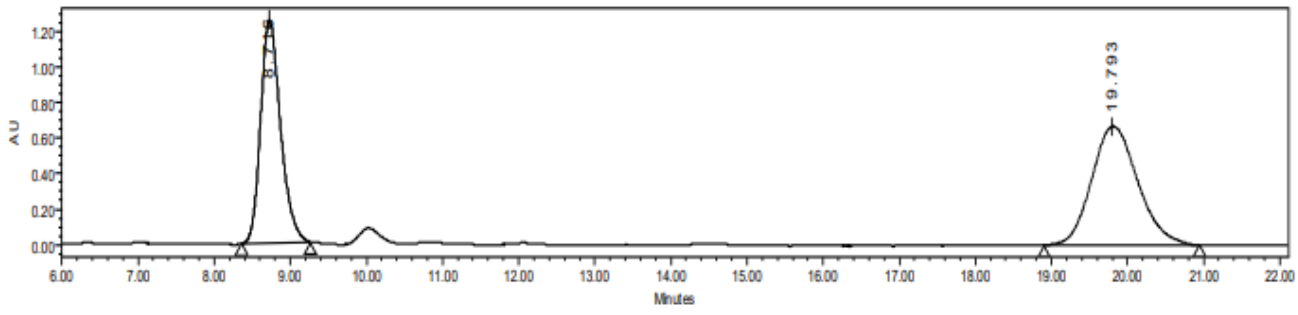
	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	8.688	2236378	50.07	128269
2	19.779	2230539	49.93	54564

***ent 1*-9h :**



	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	8.549	7825651	54.50	481791
2	19.095	6533249	45.50	196561

***ent 2*-9h:**



	RT (min)	Area (μV*sec)	% Area	Height (μV)
1	8.728	16513172	45.28	909812
2	19.810	19952056	54.72	476184

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