*Electronic Supplementary Information*

# Aryne and $CO_2$-based [2+2+2] annulation to access tetrahydroisoquinoline-fused benzoxazinones

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CONTENT

## 1. General information and starting materials

### 1.1 General information

Unless otherwise noted, all materials were purchased from commercial suppliers. Dichloromethane (DCM), acetonitrile and chlorobenzene were refluxed over $CaH_2$; tetrahydrofuran (THF) and toluene were refluxed over lithium aluminum hydride. The solvents were freshly distilled prior to use. Column chromatography was performed on silica gel (normal phase, 200-300 mesh) from Anhui Liangchen Silicon Material Co., Ltd, with petroleum ether (PE, bp. 60 – 90 °C) and ethyl acetate (EtOAc) as eluent. Reactions were monitored by thin-layer chromatography (TLC) on $GF_{254}$ silica gel plates (0.2 mm) from Anhui Liangchen Silicon Material Co., Ltd. The plates were visualized by UV light. $^{1}H$, $^{19}F$ and $^{13}C$ NMR spectra were recorded on a Bruker 400 MHz spectrometer, usually in $CDCl_3$ as an internal standard, and the chemical shifts ($\delta$) were reported in parts per million (ppm). Multiplicities are indicated as s (singlet), d (doublet), t (triplet), q (quartet), quint (quintet), dd (doublet of doublet), ddd (doublet of doublet of doublet), m (multiplet), and dq (doublet of quartet). Coupling constants ($J$) are reported in Hertz (Hz). HRMS measurements were carried out on an Agilent LC/MSD TOF mass spectrometer. GC-MS measurements were carried out on a Trace 1300 GC/ISQ QD mass spectrometer. Melting points were obtained on a Yanaco MP-500 melting point apparatus and are uncorrected. IR spectra (KBr pellets, $v$ ($cm^{-1}$)) were taken on a Bruker Tensor 27 spectrometer.

### 1.2 Preparation of aryne precursors

All aryne precursors in manuscript are listed below:

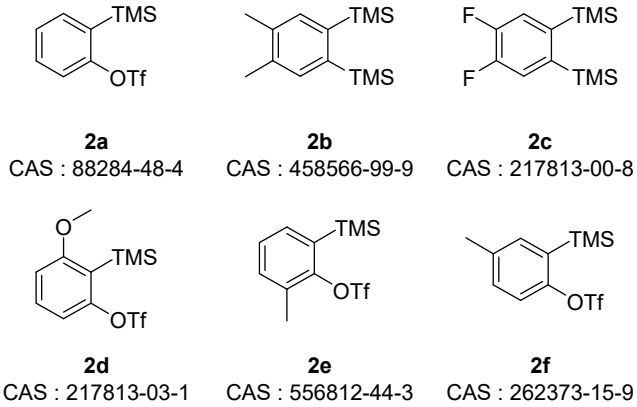


**Figure S1** The 2-(trimethylsilyl)phenyl trifluoromethanesulfonate substrates

The substrates **2a**, **2b, 2c**, **2e** and **2f** are purchased from commercial suppliers. **2d** was synthesized according to Peng's method.[1]

1.2.1 Synthesis of 3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2d):**

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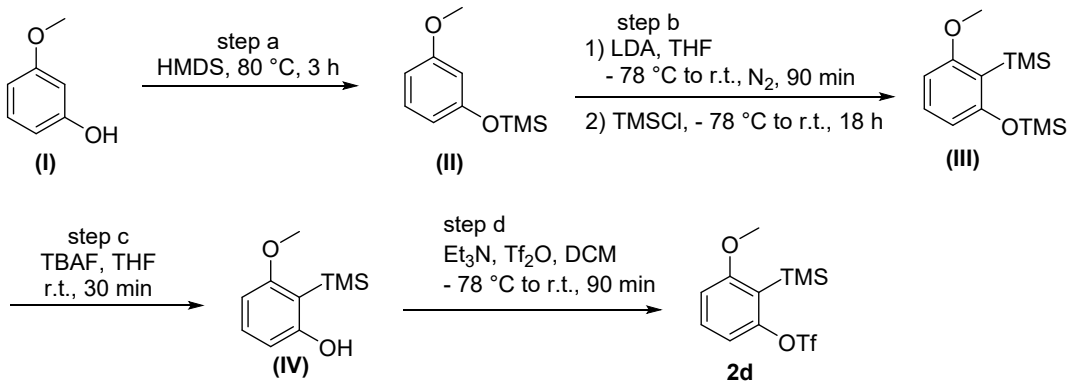
1 X. J. Li, Y. Sun, X. Huang, L. Zhang, L. Kong and B. Peng. Synthesis of *o*-Aryloxy Triarylsulfonium Salts via Aryne Insertion into Diaryl Sulfoxides. *Org. Lett.*, 2017, **19**, 838–841.




**Scheme S1** Four steps were needed to synthesize **2d.**[1]

(1)Step a: A mixture of 3-methoxyphenol (2.48 g, 20 mmol) and hexamethyl disilizane (HMDS; 4.84 g, 30 mmol) was stirred at 80 °C under nitrogen atmosphere for 3 h. Then, the volatile substances were removed under reduced pressure, affording the crude product **II** as a yellow oil which was used without further purification.
(2)Step b: To a solution of the obtained crude product in THF (40 mL) was added LDA (11 mL, 22 mmol, 2 M in THF) dropwise at -78 °C under nitrogen atmosphere. The mixture was warmed to room temperature and stirred for 90 min. After cooling to -78 °C again, TMSCl (6.1 mL, 48 mmol) was added to the mixture. The mixture was warmed to room temperature and stirred for 18 h. Afterwards, the mixture was quenched with saturated $NH_4Cl$ (5 mL; sat. aqueous solution). The aqueous layer was extracted with EtOAc (3 × 25 mL). The combined organic layers were dried over anhydrous $Na_2SO_4$. After filtration, the solvent was evaporated under reduced pressure. The obtained residue was purified by column chromatography on silica gel, affording desired product **III** as colorless oil, 3.716 g, 69% yield.
(3)Step c: To a solution of (3-methoxy-2-(trimethylsilyl)phenoxy) trimethylsilane (**II**; 2.51 g, 12.8 mmol) in THF (26 mL) was added TBAF (12.8 mL, 1 M solution in THF, 12.8 mmol) dropwise at room temperature. After stirring for 30 min, the mixture was filtered through a short plug of silica gel, and the residue was washed with PE/EtOAc (10:1). Concentration of the mixture *in vacuo* gave the phenol **IV** as a colorless oil, 1.759 g, 70% yield.
(4)Step d: To a solution of 3-methoxy-2-(trimethylsilyl)phenol (15 mmol) in $CH_2Cl_2$ (60 mL) was added $Et_3N$ (16.5 mmol) dropwise at -78 °C. After stirring for 30 min, $Tf_2O$ (16.5 mmol) was added dropwise and the whole system was then stirred for 30 min in -78 °C. The mixture was gradually warmed to room temperature and then was stirred for 1 h. Cold saturated $NaHCO_3$ (15 mL) and $H_2O$ (15 mL) were sequentially added to the mixture. The aqueous layer was extracted with $CH_2Cl_2$ (3 × 35 mL). The combined organic layers were dried over $Na_2SO_4$, filtered, and concentrated in vacuo. The obtained residue was purified by flash column chromatography on silica gel to afford the title compound **2d** as yellow oil, 1.936 g, 40% yield. **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.36 (t, $J$ = 8.4 Hz, 1H), 6.94 (d, $J$ = 8.0 Hz, 1H), 6.83 (d, $J$ = 8.0 Hz, 1H), 3.82 (s, 3H), 0.36 (s, 9H).

## 1.3 Synthesis of 3,4-dihydroisoquinoline 1

1.3.1 Structures of all prepared 3,4-dihydroisoquinolines **1**

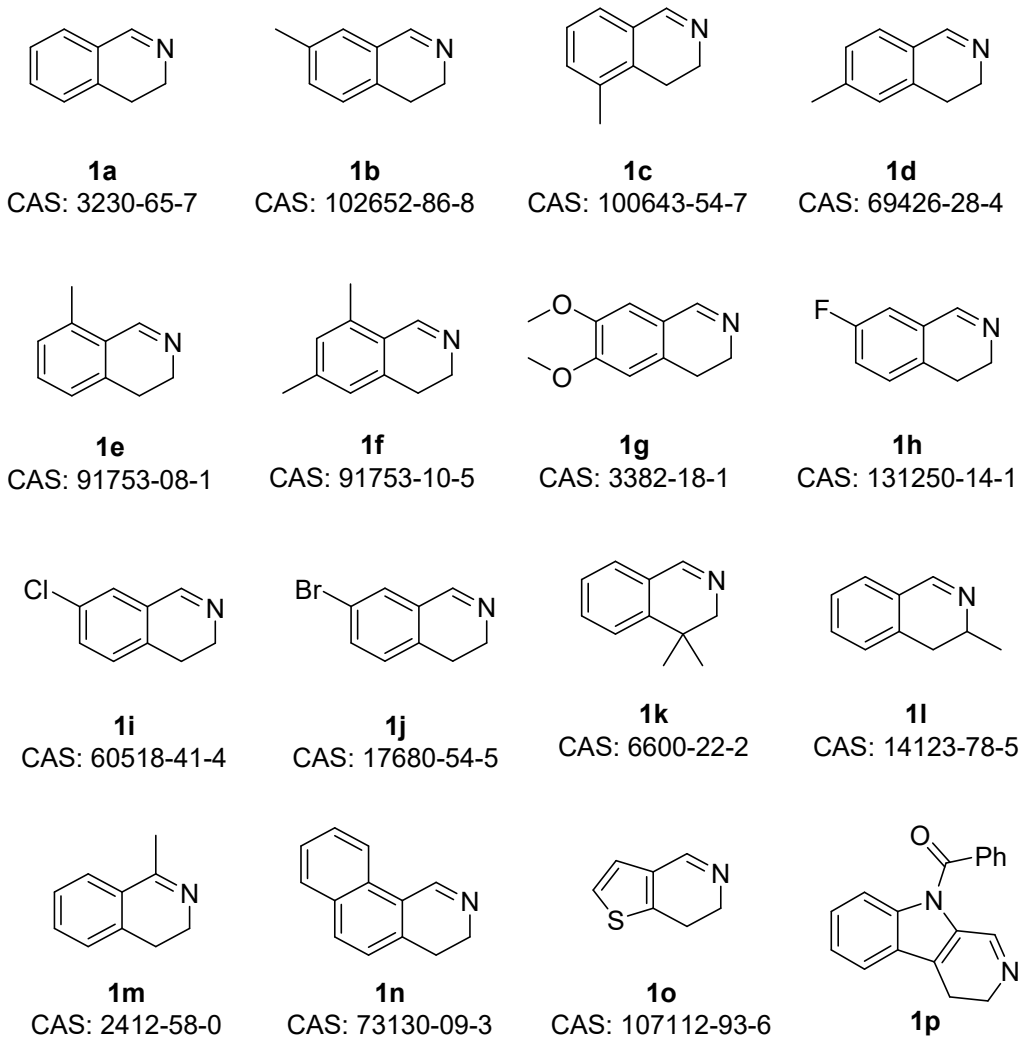
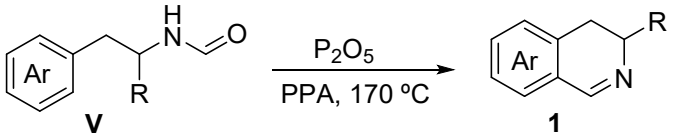



**Figure S2** The structure of 3,4-dihydroisoquinoline substrates **1**

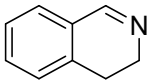
1.3.2 General Procedures for the preparation of dihydroisoquinoline **1**

*N*-phenylethyl formamides **V** were synthesized according the literatures.[2,3,4,5,6]




To a 25 mL flask was added 1 g sticky polyphosphoric acid (PPA), and heated to 90 °C. $P_2O_5$ (78 mg, 0.55 mmol) was added and the whole system was heated up to 170 °C for 1 h. Formamide **V** (1 mmol) was added and the reaction was stirred at 170 °C for 4 h. After cooling to 80 °C, 20% KOH solution was added to system until pH at 8 – 9. The aqueous solution was extracted with $CH_2Cl_2$ (5 mL × 5). The organic layers were collected, dried over $Na_2SO_4$. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel to obtain the dihydroisoquinoline **1**.[7]

3,4-dihydroisoquinoline **(1a).** [CAS: 3230-65-7][8]




Colorless oil, 2.10 g, 67%. $R_f$ = 0.08 (PE/EtOAc = 3:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.34 (s, 1H), 7.36 (dt, $J$ = 2.0, 7.2 Hz, 1H), 7.30 (t, $J$ = 7.2 Hz, 1H), 7.27 (dd, $J$ = 7.2, 2.4 Hz, 1H), 7.16 (d, $J$ = 7.6 Hz, 1H), 3.78 (dt, $J$ = 2.4, 7.6 Hz, 2H), 2.75 (t, $J$ = 7.6 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 160.4, 136.4, 131.1, 128.5, 127.4, 127.2, 127.1, 47.4, 25.0.

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2 R. N. Mitra, K. Show, D. Barman, S. Sarkar and D. K. Maiti. NHC-Catalyzed Dual Stetter Reaction: A Mild Cascade Annulation for the Syntheses of Naphthoquinones, Isoflavanones, and Sugar-Based Chiral Analogues. *J. Org. Chem.*, 2019, **84**, 42–52.

3 J. M. Rodríguez and M. Dolors Pujol, *Tetrahedron Lett*., 2011, **52**, 2629.

4 R. S. Varma and G. W. Kabalka. A Simple Route to Alkylamines Via the Reduction of Nitroalkenes. *Synth. Commun.*, 1985, **15**, 843–847.

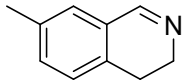
5 N. Esmati, A. R. Maddirala, N. Hussein, H. Amawi, A. K. Tiwari and P. R. Andreana. Efficient syntheses and anti-cancer activity of xenortides A–D including ent/epi-stereoisomers. *Org. Biomol. Chem*., 2018, **16**, 5332–5342.

6 D. Srinivas and G. Satyanarayana. Palladium-Catalyzed Distal *m*-C–H Functionalization of Arylacetic Acid Derivatives. *Org. Lett.*, 2021, **23**, 7353–7358.

7 S. Karin; K. Arno, V. Ludwig, B. Christian, M. Ingo, D. Frank, S. Wolfgang, E. Hansgeorg, B. Karl, M. Andrea, S. Martin. Process of producing bleach boosters containing isoquinolinium sulfuric acid innner salt. WO 2006134143. 2006. 12. 27

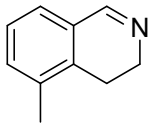
8 N. Sasamoto, C. Dubs, Y. Hamashima and M. Sodeoka. Pd(II)-Catalyzed Asymmetric Addition of Malonates to Dihydroisoquinolines. *J. Am. Chem. Soc.*, 2006, **128**, 14010–14011.

7-methyl-3,4-dihydroisoquinoline **(1b).** [CAS: 102652-86-8][8]



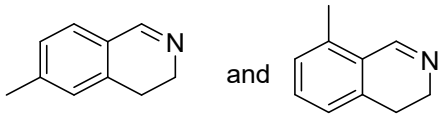
Yellow solid, 100 mg, 69%. $R_f$ = 0.14 (PE/EtOAc = 1:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.30 (t, *J* = 2.0 Hz, 1H), 7.17 (d, *J* =7.6 Hz, 1H), 7.0 9 (s, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 3.75 (ddd, *J* = 9.6, 6.0, 2.0 Hz, 2H), 2. 70 (t, *J* = 7.6 Hz, 2H), 2.36 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 160.6, 136.7, 133.3, 131.7, 128.4, 127.9, 127.3, 47.7, 24.7, 21.0.

5-methyl-3,4-dihydroisoquinoline **(1c).** [CAS: 100643-54-7][9]



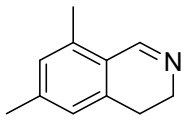
Yellow oil, 85 mg, 59%. $R_f$ = 0.15 (PE/EtOAc = 1:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.30 (t, *J* = 2.4 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.12 (dd, *J* = 7.2, 2.0 Hz, 1H), 3.78 (ddd, *J* = 9.6, 6.4, 2.0 Hz, 2H), 2.67 (t, *J* = 8.0 Hz, 2H), 2.27 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 160.8, 135.1, 134.7, 132.8, 128.3, 126.5, 125.3, 47.4, 21.7, 18.4.

6-methyl-3,4-dihydroisoquinoline **(1d)** [CAS: 69426-28-4][9] and 8-methyl-3,4-dihy droisoquinoline **(1e)** [CAS: 91753-08-1][9]**.** (This is the mixture).




Yellow oil, 103 mg, 71%. $R_f$ = 0.31 (PE/EtOAc = 1:2, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.63 (t, *J* = 2.4 Hz, 1H, **1e**), 8.28 (t, *J* = 2.4 Hz, 2.1 H, **1d**), 7.23 (t, *J* = 7.6 Hz, 1H, **1e**), 7.16 (d, *J* = 7.6 Hz, 2.2H, **1d**), 7.06 – 7.10 (m, 3.2H), 6.99 – 6.97 (m, 3.2H), 3.76 – 3.68 (m, 7.3H), 2.72 – 2.67 (m, 9.2H), 2.47 (s, 3H, **1e**), 2.36 (s, 7.1H, **1d**). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 1 60.2 (**1d**), 158.0 (**1e**), 141.4, 136.9 (**1e**), 136.4, 135.6 (**1e**), 130.8, 129.2, 128.2 (**1d**), 127.6 (**1d**), 127.2 (**1d**), 126.6 (**1e**), 126.3 (**1e**), 125.2, 47.4 (**1d**), 46.9 (**1e**), 25.7 (**1e**), 25.2 (**1d**), 21.7 (**1d**), 18.0 (**1e**).

6,8-dimethyl-3,4-dihydroisoquinoline **(1f).** [CAS: 91753-10-5][10]

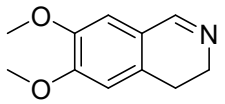


Yellow oil, 103 mg, 65%. $R_f$ = 0.17 (PE/EtOAc = 1:2, *v/v*). **$^1$H NMR** (400

9 B. Barna, D. T. Gáti, D. A. Kotschy and D. G. Tasnádi. Chemo-Enzymatic One-Pot Two-Step Functionalization of 1,2,3,4-Tetrahydroisoquinolines by Monoamine Oxidase-Ugi-Joullié Reaction Sequence. *Eur. J. Org.Chem.,* 2022, e20210154.
10 M. S. Gibson. The preparation of some isoquinoline derivatives. *J. Chem. Soc*., 1956, 808–812

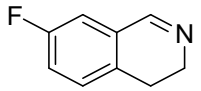
MHz, $CDCl_3$) $\delta$ (ppm) 8.59 (s, 1H), 6.89 (s, 1H), 6.80 (s, 1H), 3.68 (ddd, $J$ = 9.6, 6.0, 2.4 Hz, 2H), 2.65 (t, $J$ = 7.6 Hz, 2H), 2.43 (s, 3H), 2.30 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 158.0, 141.1, 137.0, 135.6, 129.8, 125.9, 124.3, 47.0 , 25.8, 21.5, 17.9.

6,7-dimethoxy-3,4-dihydroisoquinoline **(1g).** [CAS: 3382-18-1][8]



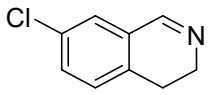
Yellow oil, 166 mg, 67%. $R_f$ = 0.05 (PE/EtOAc = 1:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.24 (t, $J$ = 2.4 Hz, 1H), 6.81 (s, 1H), 6.68 (s, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.74 (ddd, $J$ = 8.0, 5.6, 2.4 Hz, 2H), 2.68 (dd, $J$ = 7.6 , 6.4 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 159.6, 151.2, 147.8, 129.9, 121.5 , 110.4, 110.4, 56.1, 56.0, 47.4, 24.8.

7-fluoro-3,4-dihydroisoquinoline **(1h).** [CAS: 131250-14-1][11]



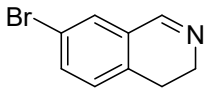
Yellow oil, 26 mg, 17%. $R_f$ = 0.14 (PE/EtOAc = 1:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.30 (s, 1H), 7.13 (dd, $J$ = 8.4, 5.6 Hz, 1H), 7.06 (dt, $J$ = 2.4, 8.4 Hz, 1H), 7.99 (dd, $J$ = 8.0, 2.4 Hz, 1H), 3.79 (dt, $J$ = 2.4, 8.4 Hz, 2H), 2.72 (t, $J$ = 7.6 Hz, 2H). **$^{19}$F NMR** (376 MHz, CDCl3) $\delta$ -115.0. **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 161.7 (d, $J$ = 246.6 Hz), 159.2 (d, $J$ = 2.0 Hz), 131.8 (d, $J$ = 3.3 Hz), 129.5 (d, $J$ = 7.2 Hz), 128.9 (d, $J$ = 7.3 Hz), 117.7 (d, $J$ = 21.5 Hz), 113.8 (d, $J$ = 21.9 Hz), 47.6, 24.3.

7-chloro-3,4-dihydroisoquinoline **(1i).** [CAS: 60518-41-4][11]



Yellow oil, 47 mg, 35%. $R_f$ = 0.28 (PE/EtOAc = 1:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.29 (t, $J$ = 2.4 Hz, 1H), 7.32 (dd, $J$ = 8.0, 2.0 Hz, 1H), 7.26 (d, $J$ = 2.4 Hz, 1H), 7.10 (d, $J$ = 8.0 Hz, 1H), 3.81 – 3.76 (m, 2H), 2.72 (t, $J$ = 8.4 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 159.0, 134.6, 132.7, 130.9, 129.6, 128.8, 127.1, 47.4, 24.4.

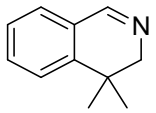
7-bromo-3,4-dihydroisoquinoline **(1j).** [CAS: 17680-54-5][8]



11 S. Huang, Y. Shih, W. Huang, D Lia and T. Yang. Tandem additions of 3,4-dihydroisoquinolines to γ-hydroxy-α,β-unsaturated ketones: a green and new access to oxazolo[2,3-*a*]tetrahydroisoquinolines. *RSC Adv*., 2016, **6**, 91870–91874.

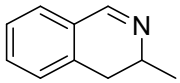
Yellow oil, 34 mg, 27%. $R_f$ = 0.15 (PE/EtOAc = 1:1, *v/v*). **$^1$H NMR** (400 M Hz, $CDCl_3$) $\delta$ (ppm) 8.28 (s, 1H), 7.48 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.41 (d, *J* = 2.0 Hz, 1H), 7.05 (d, *J* = 8.0 Hz, 1H), 3.78 (ddd, *J* = 8.0, 6.4, 2.4 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 158.9, 135.1, 133.8, 130.0, 129.9 129.1, 120.4, 47.3, 24.5.

4,4-dimethyl-3,4-dihydroisoquinoline **(1k).** [CAS: 6600-22-2][6]



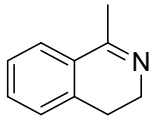

Yellow oil, 104 mg, 65%. $R_f$ = 0.30 (PE/EtOAc = 1:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.36 (t, *J* = 2.4 Hz, 1H), 7.43 (ddd, *J*= 7.6, 6.0, 2.4 Hz, 1H), 7.36 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.30 (dt, *J* = 1.2 , 7.2 Hz, 1H), 7.2 9 (d, *J* = 2.4 Hz, 1H), 3.61 (d, *J* = 2.0 Hz, 2H), 1.24 (s, 6H). **$^{13}$C NMR** (10 1 MHz, $CDCl_3$) $\delta$ 160.6, 145.4, 131.8, 127.6, 126.9, 126.7, 123.5, 61.0, 31.4, 26.4.

3-methyl-3,4-dihydroisoquinoline **(1l).** [CAS: 14123-78-5][12]




Brown oil, 89 mg, 61%. $R_f$ = 0.32 (PE/EtOAc = 1:1, *v/v*). **$^1$H NMR** (400 M Hz, $CDCl_3$) $\delta$ (ppm) 8.33 (s, 1H), 7.39 – 7.28 (m, 3H), 7.17 (d, *J* = 7.2 Hz, 1H), 3.79 – 3.68 (m, 1H), 2.83 (dd, *J* = 16.0, 5.6 Hz, 1H), 2.58 (dd, *J* = 16. 0, 12.0 Hz, 1H), 1.42 (d, *J* =6.8 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 15 9.3, 136.2, 131.1, 128.2, 127.6, 127.1, 127.1, 52.5, 32.5, 21.7.

1-methyl-3,4-dihydroisoquinoline **(1m).** [CAS: 2412-58-0][13]




Yellow oil, 102 mg, 70%. $R_f$ = 0.12 (PE/EtOAc = 1:2, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.48 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.35 (dt, *J* = 1.2, 7.2 Hz, 1H), 7.29 (dt, *J* = 1.6, 7.6 Hz, 1H), 7.18 (dd, *J* = 7.2, 1.6 Hz, 1H), 3.67 (tq, *J* = 7.6, 1.2 Hz, 2H), 2.71 (dd, *J* = 8.0, 5.6 Hz, 2H), 2.39 (t, *J* = 1.6 H z, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 164.3, 137.4, 130.6, 129.6, 127.4, 126.9 , 125.3, 46.9, 26.0, 23.3.

1,2-dihydrobenzo[*f*]isoquinoline **(1n).** [CAS: 73130-09-3][14]

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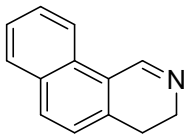
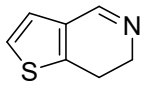
12 R. A. Fecik, P. Devasthale, S. Pillai. A. Keschavarz-Shokri, L. Shen and L. A. Mitscher, *J. Med. Chem*., 2005, **48**, 1229–1236.

13 J. Václavík, M. Kuzma, J. Přech and P. Kačer. Asymmetric Transfer Hydrogenation of Imines and Ketones Using Chiral $Ru^{II}Cl(\eta^6$-p-cymene)[(*S,S*)-*N*-TsDPEN] as a Catalyst: A Computational Study. *Organometallics*, 2011, **30**, 4822–4829.



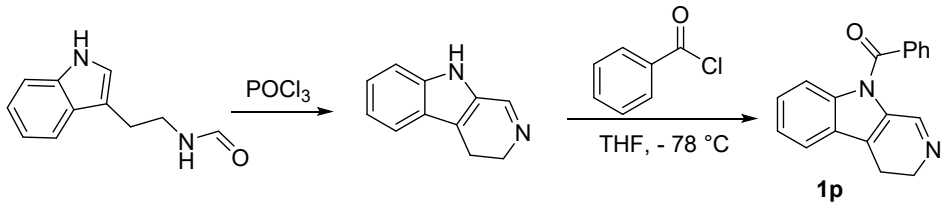
Yellow solid, 140 mg, 70%. $R_f$ = 0.12 (PE/EtOAc = 3:1, *v/v*). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ (ppm) 9.18 (s, 1H), 8.28 (d, $J$ = 8.4 Hz, 1H), 7.86 (d, $J$ = 6.0 Hz, 1H), 7.84 (d, $J$ = 6.0 Hz, 1H), 7.58 (ddd, $J$ = 8.4, 6.8, 1.2 Hz, 1H), 7.49 (ddd, $J$ = 8.0, 6.8, 1.2 Hz, 1H), 7.29 (d, $J$ = 8.4 Hz, 1H), 3.82 (dt, $J$ = 2.0, 8.0 Hz, 2H), 2.86 (t, $J$ = 8.0 Hz, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 156.8, 136.1, 132.9, 131.3, 129.8, 128.8, 127.4, 126.0, 125.6, 122.9, 121.4, 47.1, 26.0.

4,5-dihydrothieno[2,3-*c*]pyridine **(1o).** [CAS: 107112-93-6][15]



Yellow solid, 20 mg, 15%. $R_f$ = 0.35 (DCM/MeOH = 20:1, *v/v*). **$^1$H NMR** (4 00 MHz, $CDCl_3$) $\delta$ (ppm) 8.30 (s, 1H), 7.10 (d, $J$ = 5.2 Hz, 1H), 7.03 (d, $J$ = 5.2 Hz, 1H), 3.84 (dt, $J$ = 2.0, 8.4 Hz, 2H), 2.83 (t, $J$ = 8.4 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 154.9, 142.4, 131.1, 124.5, 122.8, 47.9, 22.0.

1.3.3 Synthesis of **1p**

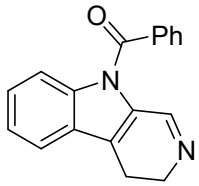



Formamide (376 mg, 2 mmol, 1 equiv) was dissolved in $CH_2Cl_2$ (3 mL), The whole system was stirred at 0 °C and then $POCl_3$ (838 mg, 5.5 mmol, 2.75 equiv) was added into the flask. Then the system was stirred for 2 h at room temperature. After removing the $CH_2Cl_2$ and $POCl_3$ in vacuo, the EtOAc (6 mL) was added into the system, and the organic phase was washed with 10% aqueous acetic acid solution (6 mL × 4). Before the system was extracted with $CH_2Cl_2$ (10 mL × 3), the ammonia was added to the aqueous acetic acid solution to PH = 9. The organic layers were collected, dried over $Na_2SO_4$. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel to obtain the imine.[16]

14 D. Beaumont, R. D. Waigh. Bischler-Napieralski cyclization of N-[2-(2-naphthyl)-ethyl] amides. *J. Chem. Res. Synop.*, 1979, **10**, 332.
15 I. Szatmári, P. Barta, A. Csámpai, F. Fülöp. Synthesis and detailed conformational analysis of new naphthoxazino[2,3-*a*]benz[*c*]azepine and naphthoxazino[2,3-a]thieno-[3,2-*c*]pyridine derivatives. *Tetrahedron*, 2017, **73**, 4790–4804.
16 G. Huang, B. Kling , F. H. Darras, J. Heilmann and M. Decker. Identification of a neuroprotective and selective butyrylcholinesterase inhibitor derived from the natural alkaloid evodiamine. *Eur. J. Med. Chem.*, 2014, **81**, 15–21.

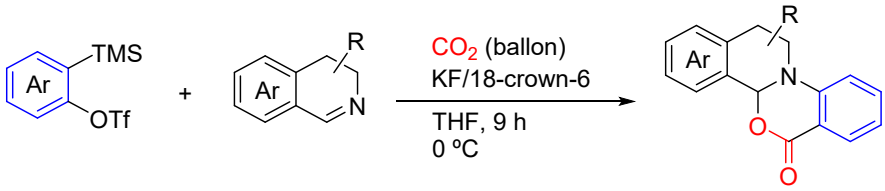
To a pre-dried 25 mL flask was added imide (474 mg, 2.79 mmol, 1 equiv), 60% NaH (134 mg, 3.35 mmol, 1.2 equiv) and charged with nitrogen balloon. In an ice-water bath, 10 mL of anhydrous THF was injected into the flask,and the whole system was stirred for 1 h. After then cooling the system to -78 °C, benzoyl chloride (391 mg, 2.79 mmol, 1 equiv) was added and the system was stirred at -78 °C for 50 min. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel to obtain the imine **1p**, with a yield of 14%.

(3,4-dihydro-9*H*-pyrido[3,4-*b*]indol-9-yl)(phenyl)methanone **(1p).**




Yellow solid, 30 mg, 7%. m.p. 107-108 °C. $R_f$ = 0.43 (DCM/MeOH = 20:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.89 (br, 1H), 7.73 – 7.70 (m, 3H), 7.64 (tt, *J* = 1.6, 6.8 Hz, 1H), 7.61 – 7.59 (m, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.32 (dquint, *J* = 1.6, 7.2 Hz, 2H), 3.89 (dt, *J* = 2.4, 8.8 Hz, 2H), 2.85 (t, *J* = 8.8 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 168.1, 151.3, 137.4, 135.2, 133.10, 129.6, 129.4, 129.0, 127.3, 127.1, 124.6, 123.9, 120.0, 116.1, 47.2, 19.0. **HRMS**-ESI (*m/z*): calcd for $C_{18}H_{15}N_2O^+$ $[M + H]^+$: 275.1179; found 275.1188.

## 2. General Procedures for the annulation of arynes, imines and $CO_2$

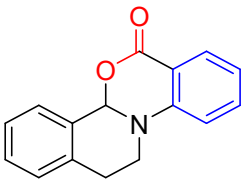



**2** **1** **3**

To a flame-dried Schlenk tube were added dihydroisoquinoline **1** (0.15 mmol), KF (35 mg, 0.60 mmol), and 18-crown-6 (158 mg, 0.60 mmol). The whole system was replaced with $CO_2$ three times and then charged with a $CO_2$ balloon. A solution of aryne precursor **2** (0.30 mmol) in 3 mL of THF was added dropwise into the tube and the resulting mixture was stirred at 0 °C for 9 h. The reaction mixture was quenched with water (5 mL), and then the system was extracted with $CH_2Cl_2$ (5 mL × 3). The organic layers were collected, dried over $Na_2SO_4$. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel to obtain the pure product **3**.

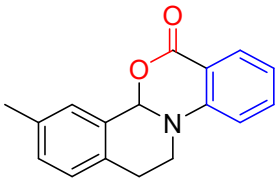
*4b*,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3aa).** [CAS:1435940-05-8][17]

17 X. Chen, C. Zhang, L. Yi, Z. Gao, Z. Wang and S. Ye. Intramolecular α-



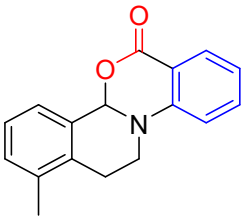
Colorless solid, 35 mg, 93%. m.p. 135-136 ℃. $R_f$ = 0.43 (PE/EtOAc = 3:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.10 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.58 – 7.54 (m, 2H), 7.36 (ddd, *J* = 10.8, 7.2, 2.0 Hz, 1H), 7.32 (ddd, *J* = 10.8, 7.2 , 2.0 Hz, 1H), 7.25 – 7.23 (m, 1H), 7.12 (d, *J* = 8.0, 1H), 7.10 (dt, *J* = 1.2, 7.6 Hz, 1H), 6.14 (s, 1H), 3.74 (quint, *J* = 6.0 Hz, 1H), 3.48 (quint, *J* = 5.6 Hz, 1H), 3.10 (t, *J* = 6.0 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 166.2, 15 3.9, 135.2, 134.7, 131.0, 130.0, 129.3, 128.6, 128.4, 126.6, 122.0, 117.2, 117.0, 85.2, 42.5, 26.4. **IR** (KBr) *v* ($cm^{-1}$) 1720. **HRMS**-ESI (*m/z*): calcd for $C_{16}H_{14}NO_2^+$ $[M + H]^+$: 252.1019; found 252.1024.

3-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ba).**



Colorless solid, 39 mg, 98%. m.p. 128-129 ℃. $R_f$ = 0.39 (PE/EtOAc = 5:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.11 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.56 (ddd, *J* =8.4, 7.2, 1.6 Hz, 1H), 7.39 (s, 1H), 7.15 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.12 (d, *J* = 4.4 Hz, 1H), 7.18 – 7.08 (m, 4H), 6.11 (s, 1H), 3.73 (quint, *J* = 6.0 Hz, 1H), 3.47 (quint, *J* = 6.0 Hz, 1H), 3.05 (t, *J* = 6.0 Hz, 2H), 2.37 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.1, 150.0, 136.7, 135.1, 131.6, 131.0, 130.2, 129.8, 128.9, 128.2, 121.9, 117.1, 116.9, 85.8, 43.7, 28.6, 21.0. **IR** (KB r) *v* ($cm^{-1}$) 1722. **HRMS**-ESI (*m/z*): calcd for $C_{17}H_{16}NO_2^+$ $[M + H]^+$: 266.1176; found 266.1173.

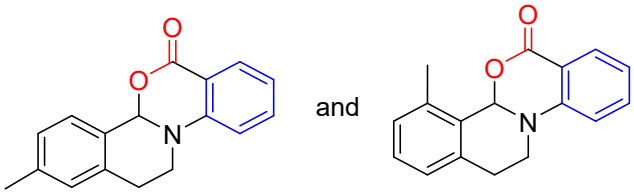
1-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ca).**



Colorless solid, 37 mg, 93%. m.p. 159-160 ℃. $R_f$ = 0.72 (PE/EtOAc = 2:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.57 (ddd, *J* = 8.4,

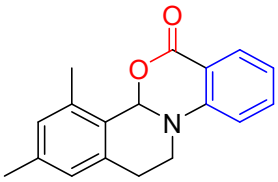
7.2, 1.6 Hz, 1H), 7.42 (dd, *J* = 7.6, 2.4 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.15 – 7.10 (m, 2H), 6.13 (s, 1H), 3.79 – 3.73 (m, 1H), 3.48 – 3.42 (m, 1H), 2.98 (dt, *J* =2.0, 5.6 Hz, 2H), 2.32 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) *δ* 165.1, 150.1, 135.9, 135.1, 133.2, 130.9, 130.6, 130.0, 126.6, 126.3, 122.2, 117.6, 117.2, 86.2, 43.4, 26.1, 19.3. **IR** (KBr) *v* ($cm^{-1}$) 1723. **HRMS**-ESI (*m/z*): calcd for $C_{17}H_{16}NO_2^+$ $[M + H]^+$: 266.1176; found 266.1180.

2-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3da)** and 4-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ea).** (**3da** and **3ea** were obtained as mixture from mixed **1d** and **1e**).



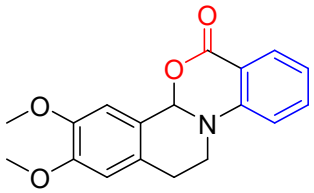

Yellow oil, 38 mg, 95%. $R_f$ = 0.20 (PE/EtOAc = 10:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) *δ* (ppm) 8.13 – 8.09 (m, 3.4H), 7.59 – 7.53 (m, 3.8H), 7.44 (d, *J* = 8.0 Hz, 2.6H, **3da**), 7.15 – 7.05 (m, 15.5H), 6.26 (s, 1H, 3**ea**), 6.11 (s, 2.4 H, **3da**), 3.75 – 3.68 (m, 4H), 3.49 – 3.42 (m, 4H), 3.10 (t, *J* = 6.0 Hz, 2H, **3ea**), 3.05 (t, *J* = 6.0 Hz, 5H, **3da**), 2.47 (s, 3H, 3**ea**), 2.36 (s, 7.7H, **3da**). **$^{13}$ C NMR** (101 MHz, $CDCl_3$) *δ* 165.2, 150.4 (**3ea**), 150.0 (**3da**), 139.3 (**3da**), 1 38.0 (**3ea**), 135.2 (**3ea**), 135.1 (**3da**), 135.0 (**3da**), 134.6 (**3ea**), 131.0 (**3da**), 13 0.8 (**3ea**), 129.4 (**3ea**), 129.2 (**3ea**), 128.9 (**3da**), 128.5 (**3da**), 128.0, 127.9 (**3d a**), 127.2, 126.3, 122.4, 121.9 (**3da**), 118.2, 117.6 (**3ea**), 117.1 (**3da**), 117.0, 8 5.8 (**3da**), 84.6 (**3ea**), 44.2 (**3ea**), 43.7 (**3da**), 29.6 (**3ea**), 28.9 (**3da**), 21.3 (**3d a**), 19.0 (**3ea**). **IR** (KBr) *v* ($cm^{-1}$) 1723. **HRMS**-ESI (*m/z*): calcd for $C_{17}H_{16}NO_2^+$ $[M + H]^+$: 266.1176; found 266.1171.

2,4-dimethyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3fa).**



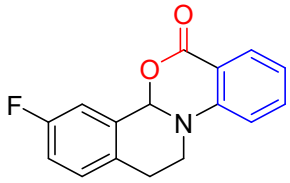

Yellow solid, 40 mg, 95%. m.p. 92-93 ℃. $R_f$ = 0.37 (PE/EtOAc = 10:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) *δ* (ppm) 8.12 – 8.10 (m, 1H), 7.58 – 7.54 (m, 1 H), 7.14 – 7.10 (m, 2H), 6.96 (s, 1H), 6.90 (s, 1H), 6.24 (s, 1H), 3.83 (quint, *J* = 6.0 Hz, 1H), 3.55 (quint, *J* = 6.0 Hz, 1H), 3.06 (t, *J* = 6.0 Hz, 2H), 2.43 (s, 3H), 2.32 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) *δ* 165.5, 150.5, 139.2, 13 7.8, 135.1, 134.9, 130.8, 130.1, 126.8, 125.2, 122.2, 118.1, 117.6, 84.7, 44.3, 2 9.5, 21.1, 18.8. **IR** (KBr) *v* ($cm^{-1}$) 1722. **HRMS**-ESI (*m/z*): calcd for $C_{18}H_{18}N O_2^+$ $[M + H]^+$: 280.1333; found 280.1330.

2,3-dimethoxy-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ga).**



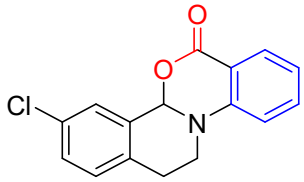
Yellow solid, 40 mg, 86%. m.p. 165-166 ℃. $R_f$ = 0.32 (PE/EtOAc = 1:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.09 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.55 (d dd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.11 – 7.07 (m, 2H), 7.00 (s, 1H), 6.68 (s, 1H), 6.08 (s, 1H), 3.90 (s, 3H), 3.89 (s, 3H), 3.71 (quint, *J* = 6.0 Hz, 1H), 3.45 (q uint, *J* = 6.0 Hz, 1H), 3.01 (t, *J* = 6.0 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.3, 150.0, 149.8, 148.2, 135.1, 130.9, 127.4, 122.0, 117.2, 116.9, 110.6, 1 10.6, 85.8, 56.1, 56.0, 43.7, 28.6. **IR** (KBr) *v* ($cm^{-1}$) 1721. **HRMS**-ESI (*m/z*): calcd for $C_{18}H_{18}NO_4^+$ [M + H]$^+$: 312.1231; found 312.1226.

3-fluoro-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ha).**



Colorless solid, 24 mg, 59%. m.p. 174-175 ℃. $R_f$ = 0.46 (PE/EtOAc = 3:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.12 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.59 (ddd, *J* = 8.8, 7.6, 2.0 Hz, 1H), 7.29 (dd, *J* = 9.2, 3.2 Hz, 1H), 7.22 (dd, *J* = 8.4, 5.2 Hz, 1H), 7.15 – 7.11 (m, 2H), 7.07 (dt, *J* = 2.8, 8.4 Hz, 1H), 6.11 ( s, 1H), 3.74 (quint, *J* = 5.6 Hz, 1H), 3.49 (quint, *J* = 5.6 Hz, 1H), 3.08 (t, *J* = 6.0 Hz, 2H). **$^{19}$F NMR** (376 MHz, CDCl3) $\delta$ -115.0. **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 164.6, 161.6 (d, *J* = 246.7 Hz), 149.7, 135.2, 131.8 (d, *J* = 7.9 Hz), 131.0, 130.3 (d, *J* = 2.8 H), 130.0 (d, *J* = 7.8 Hz), 122.3, 117.4, 117.0, 116.7 (d, *J* = 21.5 Hz), 115.1 (d, *J* = 22.7 Hz), 85.1, 43.7, 28.3. **IR** (KBr) *v* ($cm^{-1}$) 1726. **HRMS**-ESI (*m/z*): calcd for $C_{16}H_{13}FNO_2^+$ [M + H]$^+$: 270.0925; found 27 0.0921.

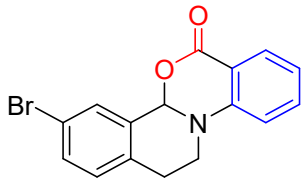
3-chloro-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one**(3ia).**



Colorless solid, 33 mg, 92%. m.p. 179-180 ℃. $R_f$ = 0.31 (PE/EtOAc = 3:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.60

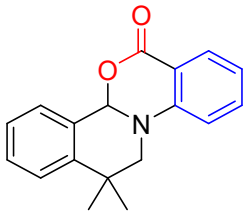
– 7.56 (m, 2H), 7.32 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 7.15 – 7.11 (m, 2H), 6.09 (s, 1H), 3.75 – 3.69 (m, 1H), 3.51 – 3.45 (m, 1H), 3.08 – 3.05 (m, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) *δ* 164.6, 149.7, 135.3, 133.1, 132.7, 131.7, 131.0, 129.8, 129.5, 128.5, 122.4, 117.5, 117.0, 85.0, 43.5, 28.5. HRMS-ESI (*m/z*): **IR** (KBr) *v* ($cm^{-1}$) 1724. **HRMS**-ESI (*m/z*): calcd for $C_{16}H_{13}ClNO_2^+$ $[M + H]^+$: 286.0630; found 286.0624.

3-bromo-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ja).** [17]



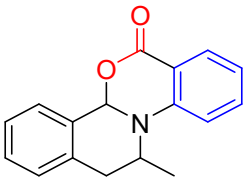

Colorless solid, 21 mg, 42%. m.p. 161-162 ℃. $R_f$ = 0.60 (PE/EtOAc = 3:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) *δ* (ppm) 8.11 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.73 (d, *J* = 2.4 Hz, 1H), 7.58 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.47 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.15 – 7.11 (m, 3H), 6.09 (s, 1H), 3.75 – 3.69 (m, 1H), 3.51 – 3.45 (m, 1H), 3.07 – 3.04 (m, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) *δ* 164.6, 149.7, 135.3, 133.6, 132.4, 132.0, 131.4, 131.0, 130.0, 122.4, 120.5, 117.5, 117.0, 84.9, 43.5, 28.5. **IR** (KBr) *v* ($cm^{-1}$) 1723. **HRMS**-ESI (*m/z*): calcd for $C_{16}H_{13}BrNO_2^+$ $[M + H]^+$: 330.0125; found 330.0122.

13,13-dimethyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ka).**



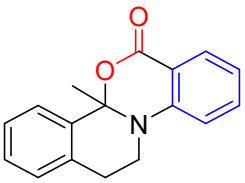

Yellow oil, 39 mg, 93%. $R_f$ = 0.30 (PE/EtOAc = 5:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) *δ* (ppm) 8.12 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.58 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.55 (dt, *J* = 1.6, 7.2 Hz, 1H), 7.43 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.40(dt, *J* = 1.6, 7.6 Hz, 1H), 7.32 (ddd, *J* = 8.0, 7.2, 2.0 Hz, 1H), 7.12 – 7.09 (m, 2H), 6.15 (s, 1H), 3.52 (d, *J* = 12.0 Hz, 1H), 3.20 (d, *J* = 12.0 Hz, 1H), 1.46 (s, 3H), 1.41 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) *δ* 165.1, 150.1, 143.8, 135.1, 131.0, 129.8, 128.8, 128.6, 126.7, 124.9, 122.0, 117.2, 117.1, 86.1, 56.2, 35.0, 28.0, 27.7. **IR** (KBr) *v* ($cm^{-1}$) 1727. **HRMS**-ESI (*m/z*): calcd for $C_{18}H_{18}NO_2^+$ $[M + H]^+$: 280.1259; found 280.1328.

12-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3la).**



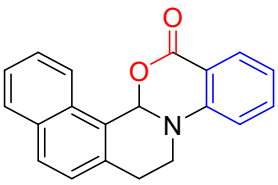
Yellow oil, 28 mg, 70%. $R_f$ = 0.48 (PE/EtOAc = 5:1, *v/v*). **$^1$H NMR** (400 M Hz, $CDCl_3$) $\delta$ (ppm) 8.15 (d, $J$ = 1.6 Hz, 1H), 8.10 (d, $J$ = 1.6 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.58 (ddd, $J$ = 1.6 Hz, 2H), 7.54 (dt, $J$ = 1.6, 7.6 Hz, 1H), 7.51 (dd, $J$ = 6.8, 1.6 Hz, 1H), 7.39 – 7.31 (m, 5H), 7.25 – 7.22 (m, 3H), 7. 14 (ddd, $J$ = 8.0, 7.2, 0.8 Hz, 1H), 7.03 – 7.00 (m, 2H), 6.20 (s, 1H), 6.10 ( s, 1H), 4.34 – 4.26 (m, 2H), 3.44 (t, $J$ = 4.8 Hz, 1H), 3.41 (t, $J$ = 4.4 Hz, 1 H), 2.85 (dd, $J$ = 16.0, 1.6 Hz, 1H), 2.77 (dd, $J$ = 15.6, 2.8 Hz, 1H), 1.19 (d, $J$ = 6.8 Hz, 3H), 1.08 (d, $J$ = 6.8 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.5, 165.2, 148.9, 148.5, 135.2, 134.9, 133.4, 132.4, 131.5, 130.8, 129.7, 129.5 , 129.4, 129.3, 129.1, 128.5, 128.2, 127.0, 126.9, 122.6, 120.2, 119.7, 119.2, 1 15.0, 113.9, 84.9, 84.0, 50.8, 48.8, 35.5, 35.3, 18.3, 16.9. **IR** (KBr) $v$ ($cm^{-1}$) 1 721. **HRMS**-ESI (*m/z*): calcd for $C_{17}H_{16}NO_2^+$ [M + H]$^+$: 266.1176; found 266. 1172.

4b-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3 ma).**



Yellow oil, 8 mg, 20%. $R_f$ = 0.44 (PE/EtOAc = :1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.05 (dd, $J$ = 8.0, 2.0 Hz, 1H), 7.69 (dd, $J$ = 7.2, 2.0 Hz, 1 H), 7.54 (ddd, $J$ = 8.8, 7.6, 1.6 Hz, 1H), 7.34 (dt, $J$ = 7.6, 1.6 Hz, 1H), 7.30 (dt, $J$ = 7.6, 1.6 Hz, 1H), 7.17 (d, $J$ = 6.8 Hz, 1H), 7.05 (d, $J$ = 8.4 Hz, 1H), 7.01 (t, $J$ = 7.6 Hz, 1H), 3.82 (dt, $J$ = 12.4, 5.6 Hz, 1H), 3.42 (ddd, $J$ = 12. 4, 8.0, 4.8 Hz, 1H), 3.16 – 2.98 (m, 2H), 1.81 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 163.4, 147.8, 136.4, 135.5, 133.0, 130.6, 128.5, 128.2, 127.1, 127.1, 120.5, 116.1, 115.5, 91.7, 42.9, 28.7, 25.4. **IR** (KBr) $v$ ($cm^{-1}$) 1720. **HRMS**-E SI (*m/z*): calcd for $C_{17}H_{16}NO_2^+$ [M + H]$^+$: 266.1176; found 266.1172.

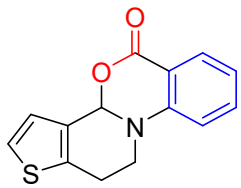
7,13c-dihydro-6*H*,15*H*-benzo[*h*]benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-15-one **(3n a).**



Yellow solid, 22 mg, 49%. m.p. 128-129 ℃. $R_f$ = 0.73 (PE/EtOAc = 1:1, *v/v*).

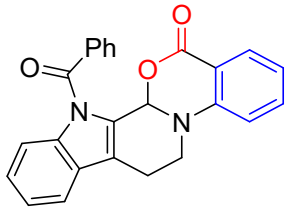
**$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.19 (dd, $J$ = 7.6, 1.2 Hz, 1H), 8.16 (d, $J$ = 8.4 Hz, 1H), 7.87 (d, $J$ = 8.4 Hz, 1H), 7.86 (d, $J$ = 7.6 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.51 (ddd, $J$ = 8.0, 6.8, 1.2 Hz, 1H), 7.34 (d, $J$ = 8.4 Hz,1H), 7.21 (d, $J$ = 8.4 Hz, 1H), 7.20 (t, $J$ = 8.0 Hz, 1H), 6.80 (s, 1H), 3.85 (ddd, $J$ = 13.2, 8.4, 4.8 Hz, 1H), 3.55 (quint, $J$ = 5.6 Hz, 1H), 3.36 – 3.20 (m, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.1, 150.5, 135.1, 133.6, 132.7, 131.0, 130.9, 130.3, 128.6, 127.4, 126.5, 125.7, 124.4, 123.3, 122.9, 118.9, 118.1, 84.2, 44.1, 29.8. **IR** (KBr) $\nu$ ($cm^{-1}$) 1722. **HRMS**-ESI (*m/z*): calcd for $C_{20}H_{16}NO_2^+$ [M + H]$^+$: 302.1176; found 302.1172.

3b,12-dihydro-5*H*,11*H*-benzo[d]thieno[3',2':3,4]pyrido[2,1-*b*][1,3]oxazin-5-one **(3oa).**



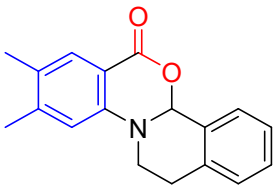

Colorless solid, 21 mg, 54%. m.p. 120-121 ℃. $R_f$ = 0.31 (PE/EtOAc = 5:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.14 – 8.12 (m, 1H), 7.60 (ddd, $J$ = 8.4, 7.2, 1.6 Hz, 1H), 7.25 (d, $J$ = 5.2 Hz, 1H), 7.18 (d, $J$ = 5.2 Hz, 2H), 7.16 (t, $J$ = 8.0 Hz, 1H), 6.16 (s, 1H), 3.83 (dt, $J$ = 12.0, 5.6 Hz, 1H), 3.58 (dt, $J$ = 12.0, 5.6 Hz, 1H), 3.23 – 3.11 (m, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 164.8, 149.9, 137.8, 135.1, 131.0, 130.4, 125.7, 124.3, 122.5, 118.2, 117.4, 83.8, 44.5, 25.2. **IR** (KBr) $\nu$ ($cm^{-1}$) 1722. **HRMS**-ESI (*m/z*): calcd for $C_{14}H_{12}NO_2S^+$ [M + H]$^+$: 258.0584; found 258.0580.

14-benzoyl-8,9,14,14b-tetrahydro-2*H*-benzo[4',5'][1,3]oxazino[3',2':1,2]pyrido[3,4-*b*]indol-2-one **(3pa).**



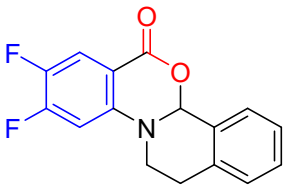

Yellow solid, 14 mg, 24%. m.p. 186-187 ℃. $R_f$ = 0.88 (DCM/MeOH = 50:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.05 (dd, $J$ = 8.0, 1.6 Hz, 1H), 7.81 (dd, $J$ = 8.0, 1.6 Hz, 2H), 7.64 (tt, $J$ = 1.6, 7.2 Hz, 1H), 7.60 – 7.56 (m, 2H), 7.51 (t, $J$ = 7.6 Hz, 2H), 7.22 (t, $J$ = 8.4 Hz, 2H), 7.18 – 7.12 (m, 2H), 6.86 (d, $J$ = 8.4 Hz, 1H), 6.73 (s, 1H), 3.76 (ddd, $J$ = 11.6, 8.8, 4.8 Hz, 1H), 3.60 (dt, $J$ = 12.0, 4.8 Hz, 1H), 3.20 – 3.13 (m, 1H), 3.07 (dt, $J$ = 16.4, 4.8 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 168.7, 164.0, 150.2, 137.4, 134.9, 134.7, 133.1, 130.9, 129.9, 129.4, 128.8, 127.6, 125.1, 123.2, 122.9, 119.7, 119.6, 119.4, 118.5, 114.9, 81.9, 44.6, 21.5. **IR** (KBr) $\nu$ ($cm^{-1}$) 1725, 1685. **LCMS**-ESI (*m/z*): calcd for $C_{25}H_{19}N_2O_3^+$ [M + H]$^+$: 395.1390; found 395.1383.

8,9-dimethyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ab).**



Colorless solid, 6 mg, 14%. m.p. 174-175 ℃. $R_f$ = 0.44 (PE/EtOAc = 3:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.86 (s, 1H), 7.57 – 7.55 (m, 1H), 7.37 – 7.30 (m, 2H), 7.24 – 7.22 (m, 1H), 6.94 (s, 1H), 6.11 (s, 1H), 3.67 (ddd, *J* = 12.0, 8.4, 4.8 Hz, 1H), 3.45 (quint, *J* = 5.6 Hz, 1H), 3.16 – 3.02 (m, 2H), 2.34 (s, 3H), 2.28 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.3, 148.2, 145.3, 134.7, 131.4, 131.0, 130.3, 129.2, 128.7, 128.3, 126.9, 119.1, 115.1, 85.9, 44.0, 29.1, 20.7, 19.0. **IR** (KBr) *v* ($cm^{-1}$) 1722. **HRMS**-ESI (*m/z*): calcd for $C_{18}H_{18}NO_2^+$ $[M + H]^+$: 280.1333; found 280.1327.

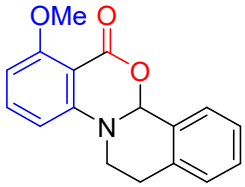
8,9-difluoro-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ac).**



Colorless solid, 42 mg, 97%. m.p. 149-150 ℃. $R_f$ = 0.44 (PE/EtOAc = 1:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.89 (dd, *J* = 9.6, 8.4 Hz, 1H), 7.54 (dd, *J* = 7.2, 2.0 Hz, 1H), 7.35 (dquint, *J* = 2.0, 7.2 Hz, 2H), 7.26 – 7.23 (m, 1H), 6.92 (dd, *J* = 11.2, 6.4 Hz, 1H), 6.15 (s, 1H), 3.67 (quint, *J* = 6.0 Hz, 1H), 3.47 (quint, *J* = 6.0 Hz, 1H), 3.10 (t, *J* = 5.6 Hz, 2H). **$^{19}$F NMR** (376 MHz, $CDCl_3$) $\delta$ -124.7 (d, *J* = 21.8 Hz) -143.8 (d, *J* = 21.8 Hz). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 163.4, 155.2 (dd, *J* = 259.1, 14.2 Hz), 147.4 (d, *J* = 2.0 Hz), 146.1 (dd, *J* = 247.5, 13.5 Hz), 134.4, 129.6, 129.4, 128.5, 128.4, 127.2, 118.9 (dd, *J* = 19.1, 2.2 Hz), 113.1, 106.4 (d, *J* = 20.6 Hz), 85.9, 44.1, 28.8. **IR** (KBr) *v* ($cm^{-1}$) 1726. **HRMS**-ESI (*m/z*): calcd for $C_{16}H_{12}F_2NO_2^+$ $[M + H]^+$: 288.0831; found 288.0827.

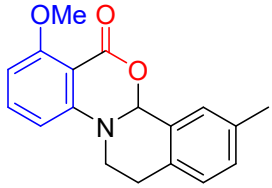
7-methoxy-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ad).** [CAS: 2414630-40-1][18]

18 Z. Gao, Z. Xia, L. Dai and S. Ye. N-Heterocyclic Carbene Catalyzed Photo-oxidation: Intramolecular Cross Dehydrogenative Coupling of Tetrahydroiso-Quinoline-Tethered Aldehydes. *Angew. Chem. Int. Ed.*, 2020, **362**, 1819–1824.



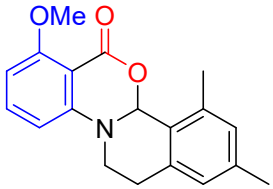

Colorless solid, 40 mg, 95%. m.p. 112-113 ℃. $R_f$ = 0.62 (PE/EtOAc = 1:2, *v*/*v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.52 – 7.49 (m, 1H), 7.45 (t, *J* = 8.4 Hz, 1H), 7.34 (ddd, *J* = 10.4, 7.2, 2.0 Hz, 1H), 7.30 (ddd, *J* = 10.4, 7.2, 2.0 Hz, 1H), 7.23 – 7.20 (m, 1H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 6.01 (s, 1H), 3.96 (s, 3H), 3.74 (ddd, *J* = 11.6, 6.8, 4.4 Hz, 1H), 3.47 (ddd, *J* = 12.0, 7.2, 4.8 Hz, 1H), 3.11 (ddd, *J* = 16.0, 7.2, 4.8 Hz, 1H), 3.04 (ddd, *J* = 16.0, 7.2, 4.8 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 162.4, 162.3, 152.3, 135.4, 134.7, 130.0, 129.2, 128.6, 128.3, 127.0, 108.7, 106.2, 104.5, 84.5, 56.3, 43.5, 28.9. **IR** (KBr) *v* ($cm^{-1}$) 1726. **HRMS**-ESI (*m/z*): calcd for $C_{17}H_{16}NO_3^+$ [M + H]$^+$: 282.1125; found 282.1122.

7-methoxy-3-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3bd).**




Colorless solid, 27 mg, 61%. m.p. 193-195 ℃. $R_f$ = 0.15 (PE/EtOAc = 4:1, *v*/*v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.45 (t, *J* = 8.4 Hz, 1H), 7.33 (s, 1H), 7.13 (dt, *J* = 1.6, 8.0 Hz, 1H), 7.11 (t, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 8.4 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 5.98 (s, 1H), 3.97 (s, 3H), 3.73 (ddd, *J* = 11.6, 6.8, 4.8 Hz, 1H), 3.46 (ddd, *J* = 12.0, 7.2, 4.8 Hz, 1H), 3.07 (ddd, *J* = 16.0, 7.2, 4.8 Hz, 1H), 2.99 (ddd, *J* = 16.0, 7.2, 4.8 Hz, 1H), 2.35 (s, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 162.4, 162.4, 152.4, 136.7, 135.3, 131.6, 130.1, 129.8, 128.9, 128.1, 108.6, 106.1, 104.4, 84.6, 56.3, 43.7, 28.5, 21.0. **IR** (KBr) *v* ($cm^{-1}$) 1724. **HRMS**-ESI (*m/z*): calcd for $C_{18}H_{18}NO_3^+$ [M + H]$^+$: 296.1282; found 296.1279.

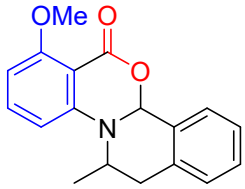
7-methoxy-2,4-dimethyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3fd).**




Colorless solid, 44 mg, 95%. m.p. 149-150 ℃. $R_f$ = 0.44 (PE/EtOAc = 1:1, *v*/*v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.44 (t, *J* = 8.4 Hz, 1H), 6.93 (s, 1H), 6.86 (s, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 6.59 (d, *J* = 8.4 Hz, 1H), 6.10 (s,

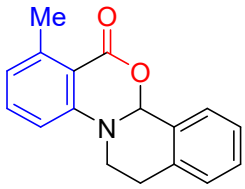
1H), 3.97 (s, 3H), 3.74 – 3.69 (m, 1H), 3.44 – 3.38 (m, 1H), 3.11 – 2.94 (m, 2H), 2.40 (s, 3H), 2.30 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 162.9, 162.3, 152.7, 139.1, 137.8, 135.2, 135.1, 130.1, 126.7, 125.1, 109.2, 106.6, 104.5, 83.4, 56.3, 44.0, 29.4, 21.1, 18.8. **IR** (KBr) $v$ ($cm^{-1}$) 1725. **HRMS**-ESI (*m/z*): calcd for $C_{19}H_{20}NO_3^+$ $[M + H]^+$: 310.1438; found 310.1433.

7-methoxy-12-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ld).**



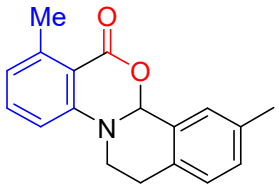

Yellow oil, 37 mg, 84%. $R_f$ = 0.10 (PE/EtOAc = 5:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 8.15 (dd, $J$ = 8.0, 1.6 Hz, 1H), 8.10 (dd, $J$ = 8.0, 1.6 Hz, 1H), 7.67 – 7.65 (m, 1H), 7.60 – 7.49 (m, 4H), 7.39 – 7.31 (m, 5H), 7.25 – 7.22 (m, 3H), 7.14 (ddd, $J$ = 8.0, 7.2, 0.8 Hz, 1H), 7.03 – 7.00 (m, 2H), 6.20 (s, 1H), 6.10 (s, 1H), 4.34 – 4.26 (m, 2H), 3.44 (t, $J$ = 4.8 Hz, 1H), 3.41 (t, $J$ = 4.4 Hz, 1H), 2.85 (dd, $J$ = 16.0, 1.6 Hz, 1H), 2.77 (dd, $J$ = 15.6, 2.8 Hz, 1H), 1.19 (d, $J$ = 6.8 Hz, 3H), 1.08 (d, $J$ = 6.8 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.5, 165.2, 148.9, 148.5, 135.2, 134.9, 133.4, 132.4, 131.5, 130.8, 129.7, 129.5, 129.4, 129.3, 129.1, 128.5, 128.2, 127.0, 126.9, 122.6, 120.2, 119.7, 119.2, 115.0, 113.9, 84.9, 84.0, 50.8, 48.8, 35.4, 35.3, 18.2, 16.9. **IR** (KBr) $v$ ($cm^{-1}$) 1722. **HRMS**-ESI (*m/z*): calcd for $C_{18}H_{18}NO_3^+$ $[M + H]^+$: 296.1282; found 296.1278.

7-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ae).**



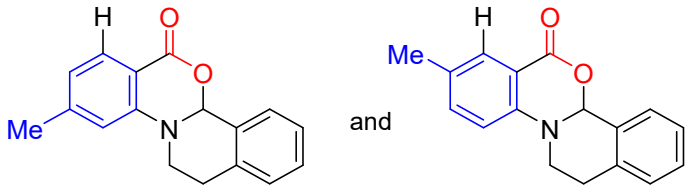

Yellow solid, 12 mg, 30%. m.p. 147-148 ℃. $R_f$ = 0.52 (PE/EtOAc = 3:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.56 – 7.51 (m, 1H), 7.40 (t, $J$ = 7.6 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.25 – 7.21 (m, 1H), 6.98 (d, $J$ = 8.4 Hz, 1H), 6.93 (d, $J$ = 7.6 Hz, 1H), 6.06 (s, 1H), 3.74 (dt, $J$ = 12.0, 5.6 Hz, 1H), 3.47 (dt, $J$ = 11.6, 5.6 Hz, 1H), 3.01 (t, $J$ = 5.4 Hz, 2H), 2.74 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 164.6, 151.4, 144.3, 134.9, 133.9, 130.3, 129.4, 128.7, 128.5, 127.1, 125.6, 116.4, 115.5, 85.1, 44.0, 29.2, 22.6. **IR** (KBr) $v$ ($cm^{-1}$) 1719. **HRMS**-ESI (*m/z*): calcd for $C_{17}H_{16}NO_2^+$ $[M + H]^+$: 266.1176; found 266.1173.

3,7-dimethyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3be).**



Colorless solid, 18 mg, 43%. m.p. 152-153 °C. $R_f$ = 0.47 (PE/EtOAc = 5:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.40 (t, *J* = 7.6 Hz, 1H), 7.36 (s, 1 H), 7.17 – 7.11 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.02 (s, 1H), 3.72 (quint, *J* = 6.0 Hz, 1H), 3.44 (quint, *J* = 5.6 Hz, 1H), 3.05 (t, *J* = 6.0 Hz, 2H), 2.74 (s, 3H), 2.36 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 164.5, 151.4, 144.1, 136.7, 133.8, 131.7, 130.1, 129.9, 128.9, 128.2, 125.3, 1 16.2, 115.3, 85.0, 43.9, 28.6, 22.5, 21.1. **IR** (KBr) *v* ($cm^{-1}$) 1709. **HRMS**-ESI (*m/z*): calcd for $C_{18}H_{18}NO_2^+$ [M + H]$^+$: 280.1332; found 280.1341.

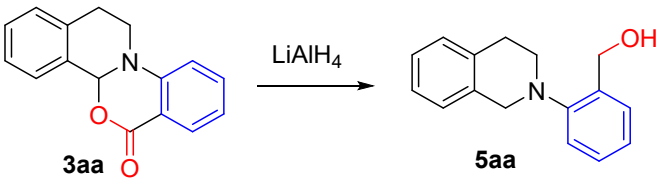
9-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3af)** [CAS: 2414630-31-0][17] and 8-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3af').** (**3af** and **3af'** were obtained as mixtures).



Yellow oil, 18 mg, 45%. $R_f$ = 0.49 (PE/EtOAc = 3:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.99 (d, *J* = 8.0 Hz, 1.3H, **3af**), 7.92 (d, *J* = 2.0 Hz, 1 H, **3af'**), 7.57 – 7.55 (m, 2.65H), 7.38 (dd, *J* = 8.4, 2.4 Hz, 1.3H, **3af**), 7.36 – 7.32 (m, 5H), 7.24 (d, *J* = 4.8 Hz, 1.4H, **3af**), 7.23 (d, *J* = 2.4 Hz, 1H, **3af'**), 7.06 (d, *J* = 8.0 Hz, 1.2H, **3af**), 6.93 – 6.91 (m, 2.9H), 6.13 (s, 1H, **3af'**), 6.12 (s, 1.3H, **3af**), 3.74 (quint, *J* = 6.0 Hz, 1.7H, **3af**), 3.67 (ddd, *J* = 12.4, 8.4, 4.8 Hz, 1H, **3af'**), 3.50 – 3.43 (m, 3H), 3.10 (t, *J* = 5.6 Hz, 4.4H), 2.42 (s, 4.4H, **3af**), 2.37 (s, 3H, **3af'**). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 165.3 (**3af'**), 165.1 (**3af**), 150.0, 147.8, 146.4, 136.2, 134.8 (**3af**), 134.7 (**3af'**), 132.2, 130.9, 130.6, 130.2, 130.2 (**3af'**), 129.3, 128.7 (**3af'**), 128.6 (**3af**), 128.4 (**3af'**), 128.4 (**3af**), 127.0 (**3af**), 126.9 (**3af'**), 123.4, 118.2 (**3af'**), 117.4 (**3s**), 117.3 (**3af'**), 1 14.4 (**3af**), 86.0 (**3af'**), 85.7 (**3af**), 44.1 (**3af'**), 43.6 (**3af**), 29.1 (**3af'**), 29.0 (**3af**), 22.2 (**3af**), 20.6 (**3af'**). **IR** (KBr) *v* ($cm^{-1}$) 1722. **HRMS**-ESI (*m/z*): calcd for $C_{17}H_{16}NO_2^+$ [M + H]$^+$: 266.1176; found 266.1172.

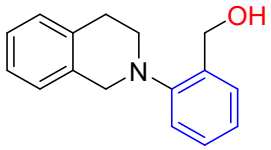
## 3. Procedures for the product derivatization

3.1 Synthesis of benzyl alcohol **5aa**



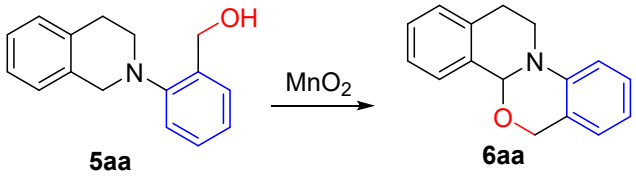
To a flame-dried Schlenk tube was added $LiAlH_4$ (30 mg, 0.8 mmol, 2 equiv), and charged with nitrogen balloon. **3aa** (100 mg, 0.4 mmol, 1 equiv) was dissolved into 3 mL of anhydrous THF, in an ice-water bath, THF solution was injected into the tube, and then the whole system was stirred at 70 °C for 1 h. $NH_4Cl$ solution (5 mL) was added to quench the system. The system was extracted with $CH_2Cl_2$ (5 mL × 3), The organic layers were collected, dried over $Na_2SO_4$. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel to obtain the pure product **5aa** with a yield of 98%.

(2-(3,4-dihydroisoquinolin-2(1*H*)-yl)phenyl)methanol **(5aa)**. [CAS: 1152514-66-3][19]




Colorless oil, 94 mg, 98%.$R_f$ = 0.49 (PE/EtOAc = 2:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.28 (dt, $J$ = 1.6, 6.8 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.18 – 7.10 (m, 4H), 7.05 – 7.03 (m, 1H), 4.98 (s, 1H), 4.80 (s, 2H), 4.13 (s, 2H), 3.26 (t, $J$ = 6.0, 2H), 3.01 (t, $J$ = 5.6 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 150.9, 136.0, 134.6, 133.9, 129.0, 128.8, 128.5, 126.6, 126.5, 126.0, 125.0, 121.0, 64.4, 55.0, 50.9, 29.7.

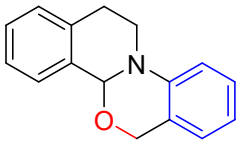
3.2 Synthesis of **6aa**




**5aa** **6aa**

To a Schlenk tube were added **5aa** (48 mg, 0.2 mmol, 1 equiv) and $CH_2Cl_2$ (2 mL). Then the $MnO_2$ (209 mg, 2.4 mmol, 12 equiv) was added into the tube, and the whole system was stirred for 3 h at room temperature. After the system was filtered, the residue was washed with $CH_2Cl_2$, The organic layers were collected, dried over $Na_2SO_4$. After removing the solvent in vacuo, the residue was purified by flash column chromatography on silica gel to obtain the pure product **6aa** with a yield of 59%.

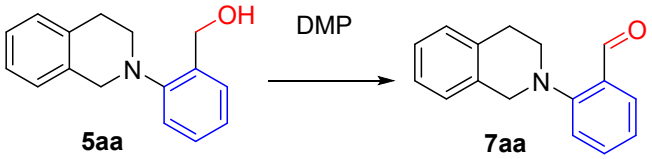
4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinoline **(6aa)**. [CAS: 1403831-53-7][19]




19 J. Xuan, Z. Feng, S. Duan and W. Xiao. Room temperature synthesis of isoquino[2,1-*a*][3,1]oxazine and isoquino[2,1-*a*]pyrimidine derivatives via visible light photoredox catalysis. *RSC Adv.*, 2012, **2**, 4065–4068.

Yellow oil, 28 mg, 59%. $R_f$ = 0.40 (PE/EtOAc = 20:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 7.48 – 7.43 (m, 1H), 7.30 – 7.25 (m, 2H), 7.23 – 7.18 (m, 2H), 7.11 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.01 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.97 (dt, *J* = 1.2, 6.4 Hz, 1H), 5.41 (s, 1H), 5.22 (d, *J* = 14.8 Hz, 1H), 4.97 (d, *J* = 14.8 Hz, 1H), 3.55 (ddd, *J* = 11.6, 10.4, 3.6 Hz, 1H), 3.46 (ddd, *J* = 11.6, 5.2, 3.6 Hz, 1H), 3.15 (ddd, *J* = 16.0, 10.8, 5.6 Hz, 1H), 2.91 (dt, *J* = 16.0, 3.6 Hz, 1H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 146.0, 135.3, 133.5, 128.7, 128.3, 128.3, 127.3, 126.4, 126.3, 125.0, 121.6, 121.2, 84.4, 68.3, 46.2, 29.8.

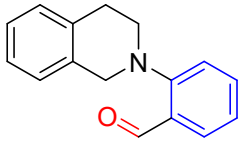
3.3 Synthesis of product derivatization **7aa**




**5aa** **7aa**

In an ice-water bath,to a Schlenk tube were added **5aa** (48 mg, 0.2 mmol, 1 equiv), $CH_2Cl_2$ (2.5 mL) and DMP (127 mg, 0.3 mmol, 1.5 equiv). The system was stirred for 2 h, and purified by flash column chromatography on silica gel to obtain the pure product **7aa** with a yield of 91%.

2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzaldehyde **(7aa).** [CAS: 124525-61-7][20]



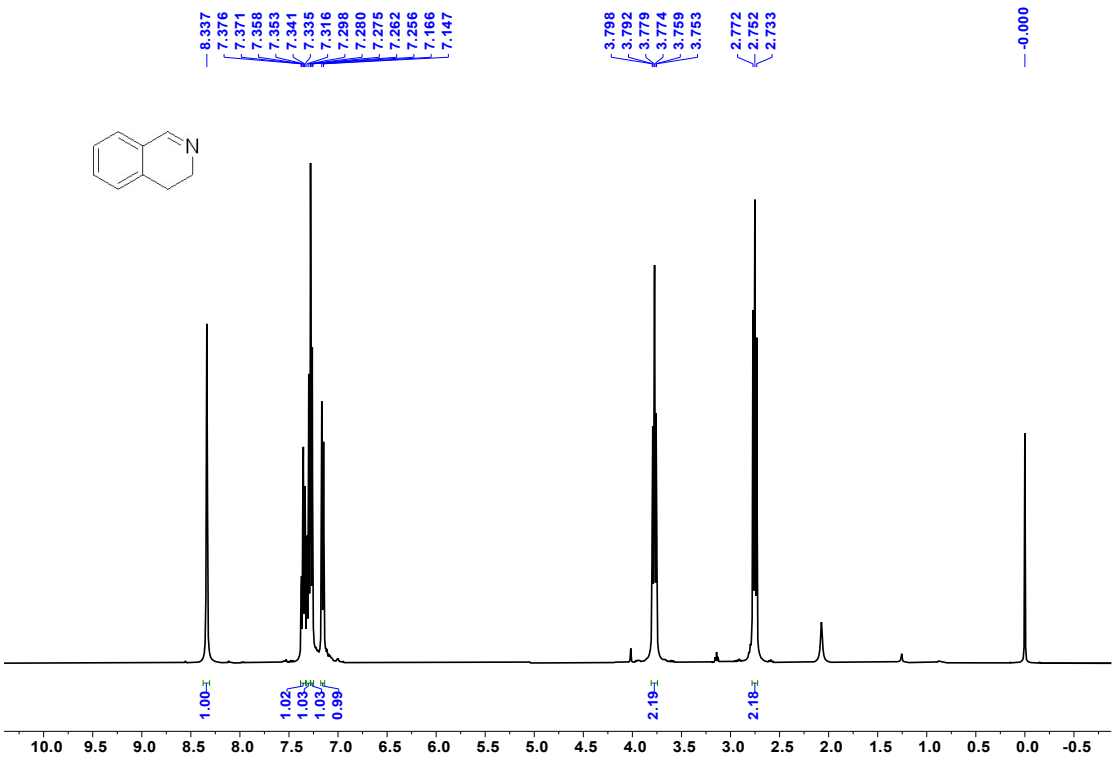

Green oil, 43 mg, 91%. $R_f$ = 0.45 (PE/EtOAc = 10:1, *v/v*). **$^1$H NMR** (400 MHz, $CDCl_3$) $\delta$ (ppm) 10.33 (s, 1H), 7.84 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.53 (ddd, *J* = 8.4, 7.2Hz, 2.0, 1H), 7.20 – 7.18 (m, 4H), 7.14 – 7.09 (m, 2H), 4.34 (s, 2H), 3.46 (t, *J* = 5.6 Hz, 2H), 3.06 (t, *J* = 6.0 Hz, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) $\delta$ 191.4, 155.2, 134.9, 134.2, 134.1, 130.0, 129.0, 128.6, 126.6, 126.4, 126.1, 122.3, 119.0, 54.8, 53.6, 29.1.

## 4. Copies of All NMR spectra of 1, 3, 5aa, 6aa, 7aa, and HRMS spectra of new compounds

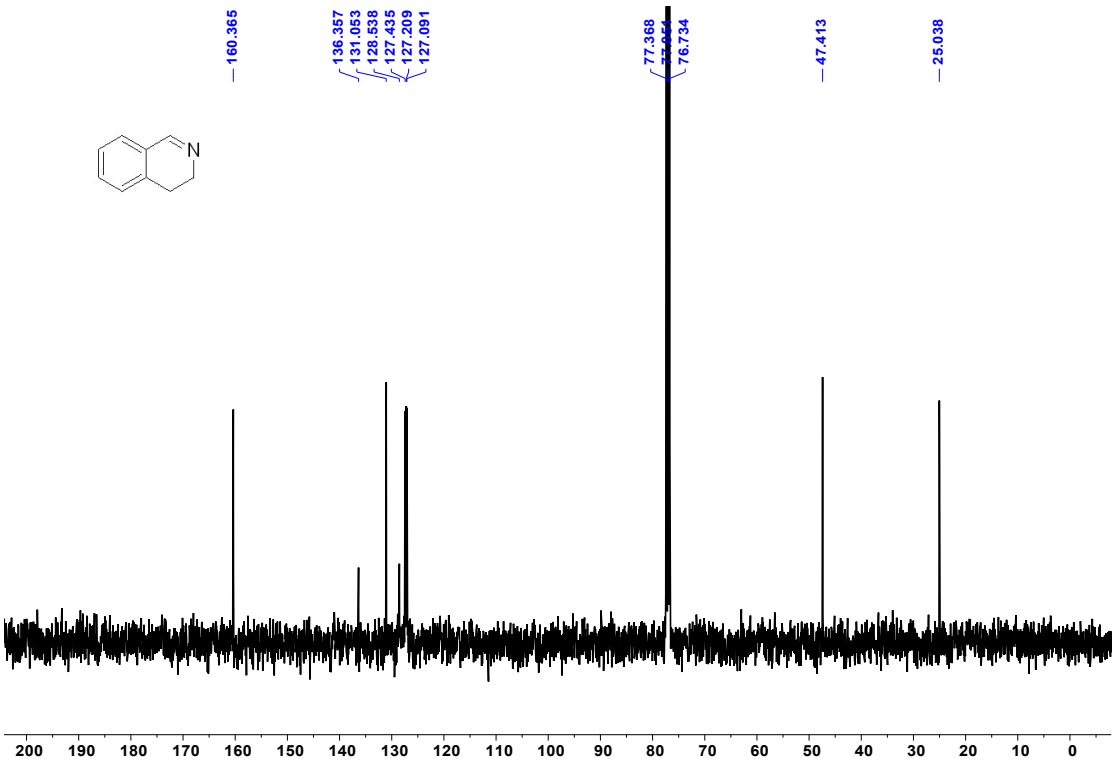
3,4-dihydroisoquinoline **(1a)**

**$^1$H NMR** (400 MHz, $CDCl_3$)

20 M. C. Haibach, I. Deb, C. K. De and D. Seidel. Redox-Neutral Indole Annulation Cascades. *J. Am. Chem. Soc.*, 2011, **133**, 2100–2103.

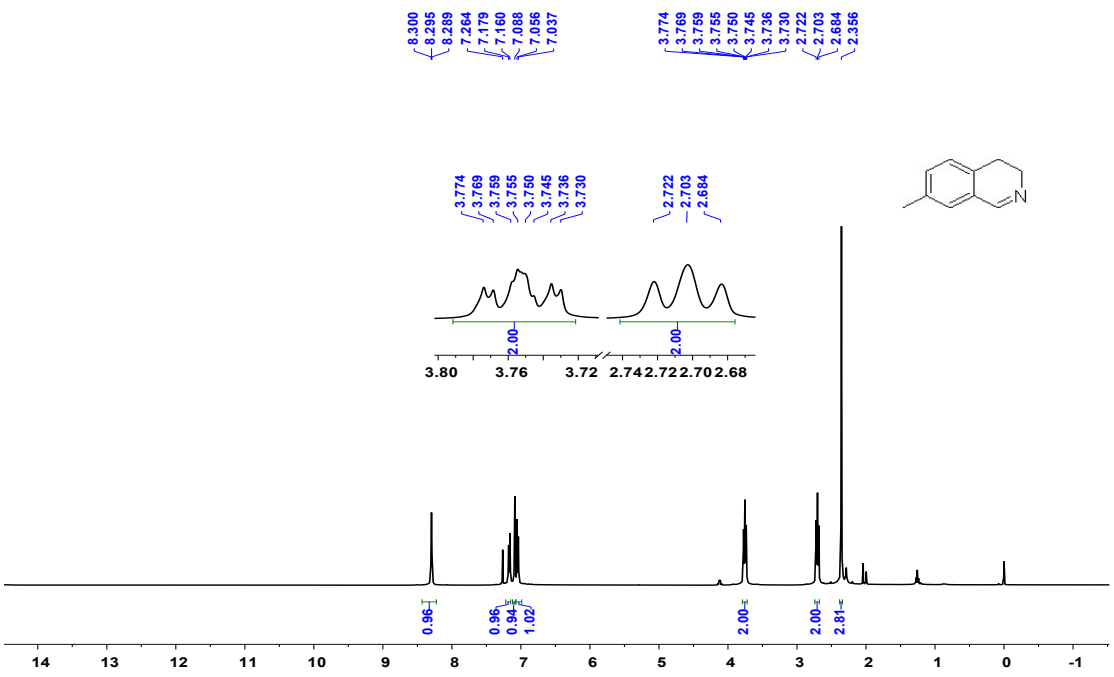



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

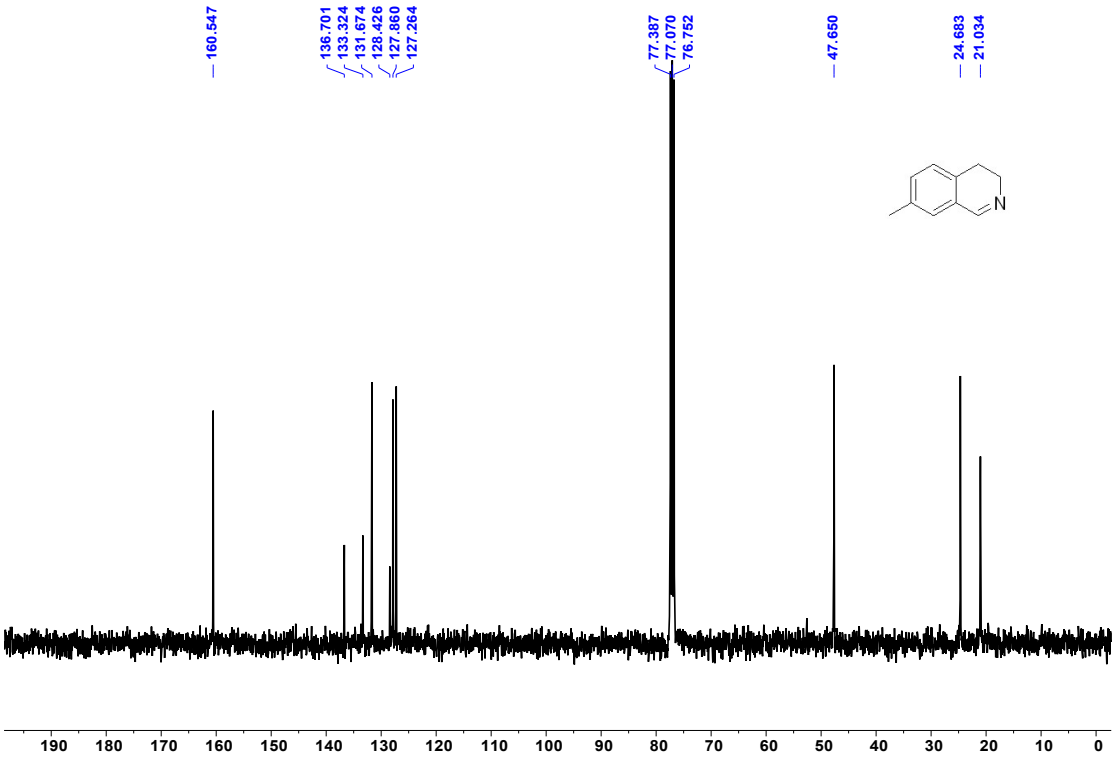



7-methyl-3,4-dihydroisoquinoline **(1b)**

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

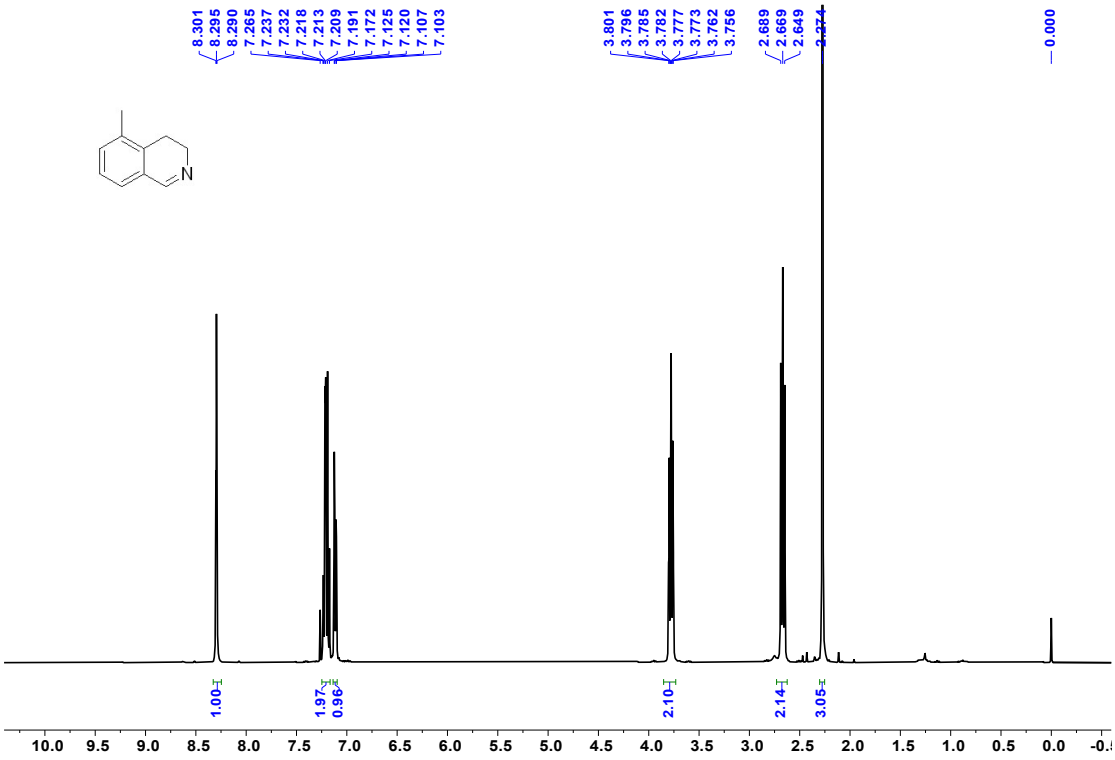



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

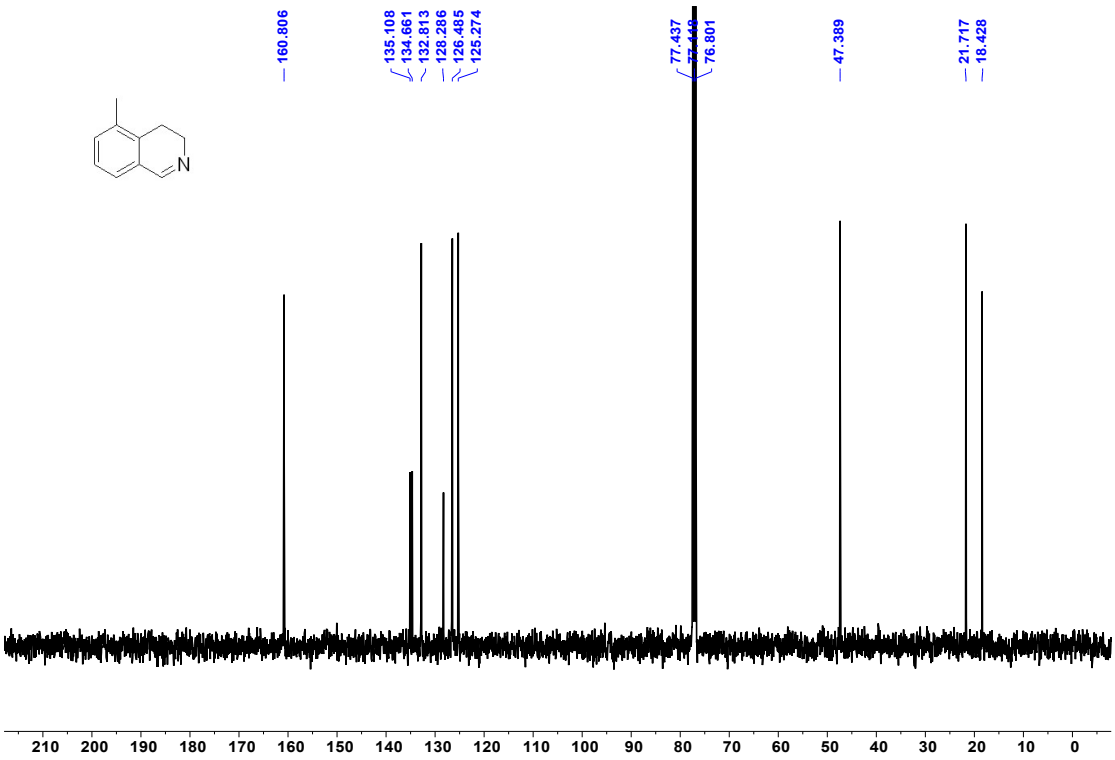


5-methyl-3,4-dihydroisoquinoline (**1c**)

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

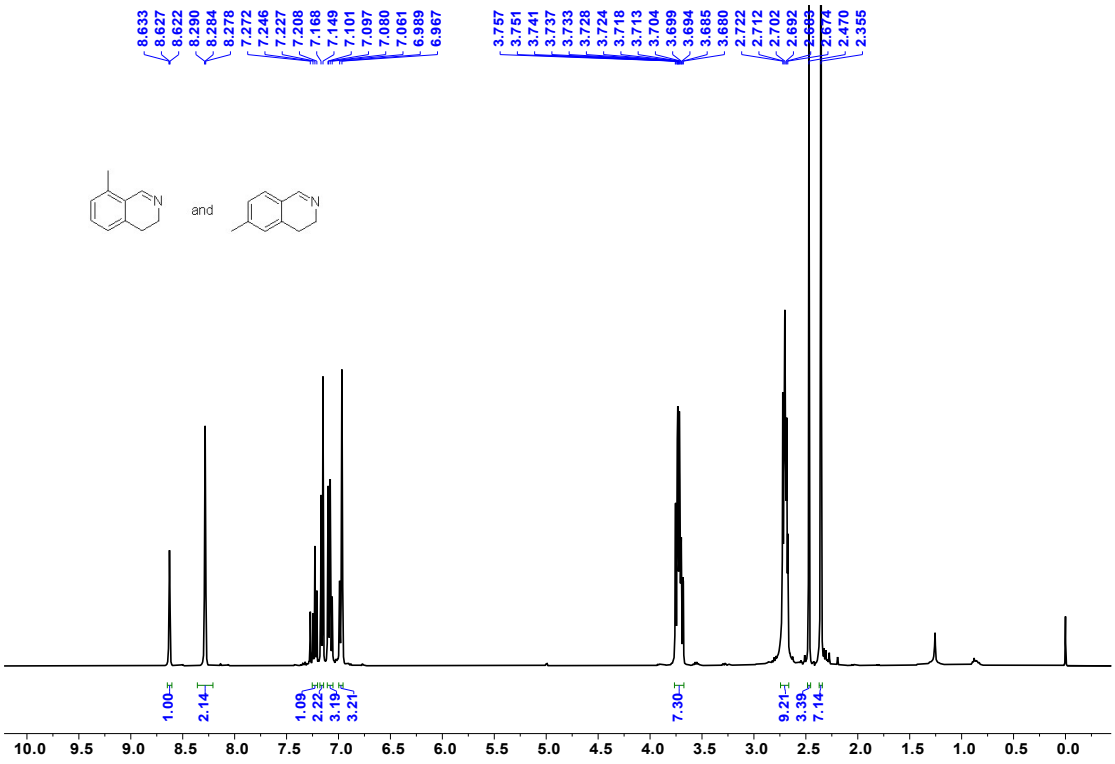



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

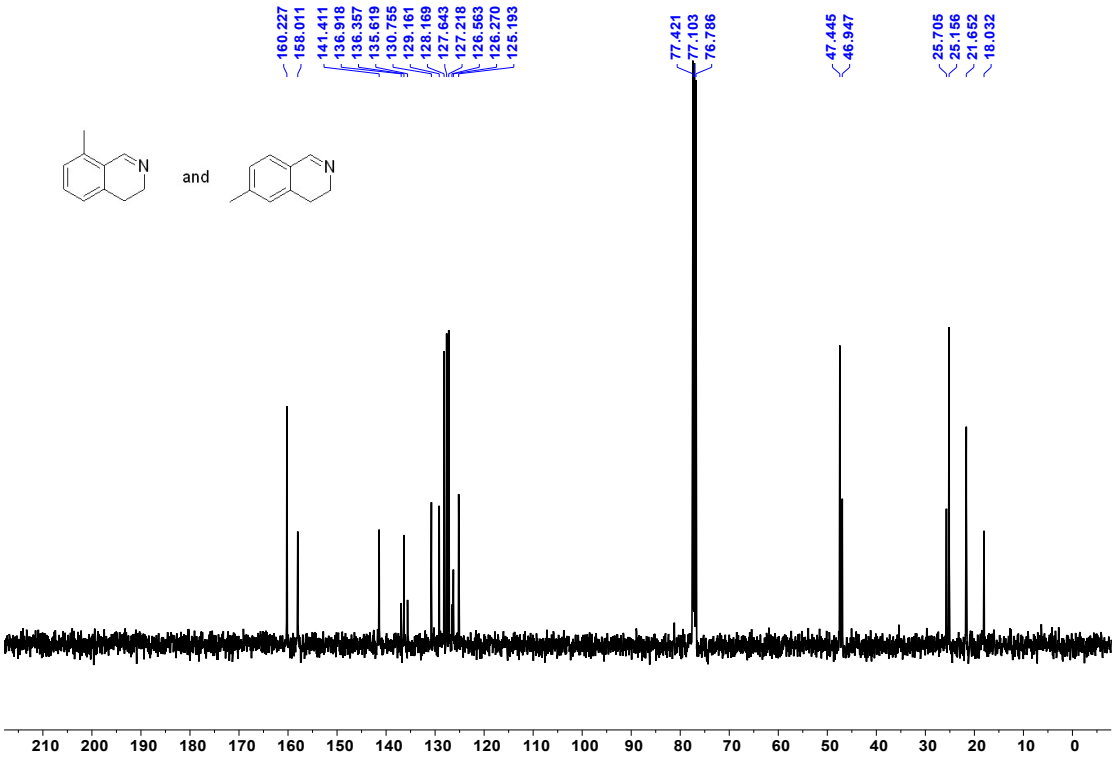


6-methyl-3,4-dihydroisoquinoline **(1d)** and 8-methyl-3,4-dihydroisoquinoline **(1e)**

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

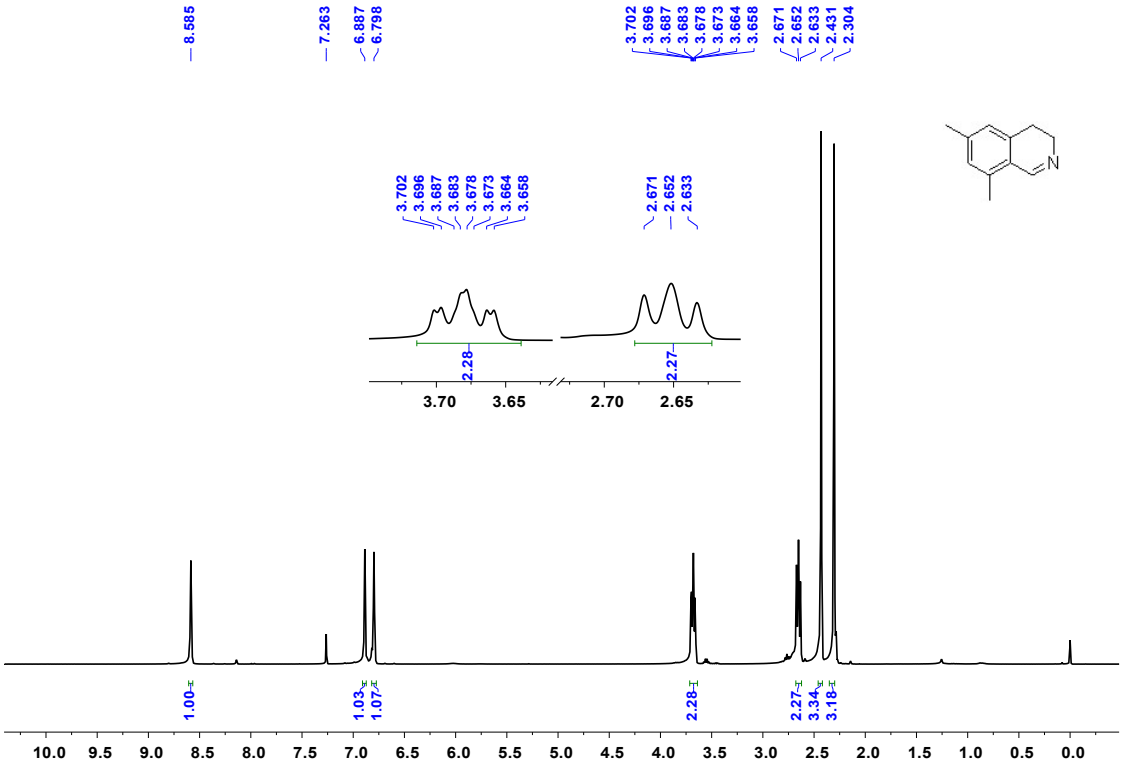



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

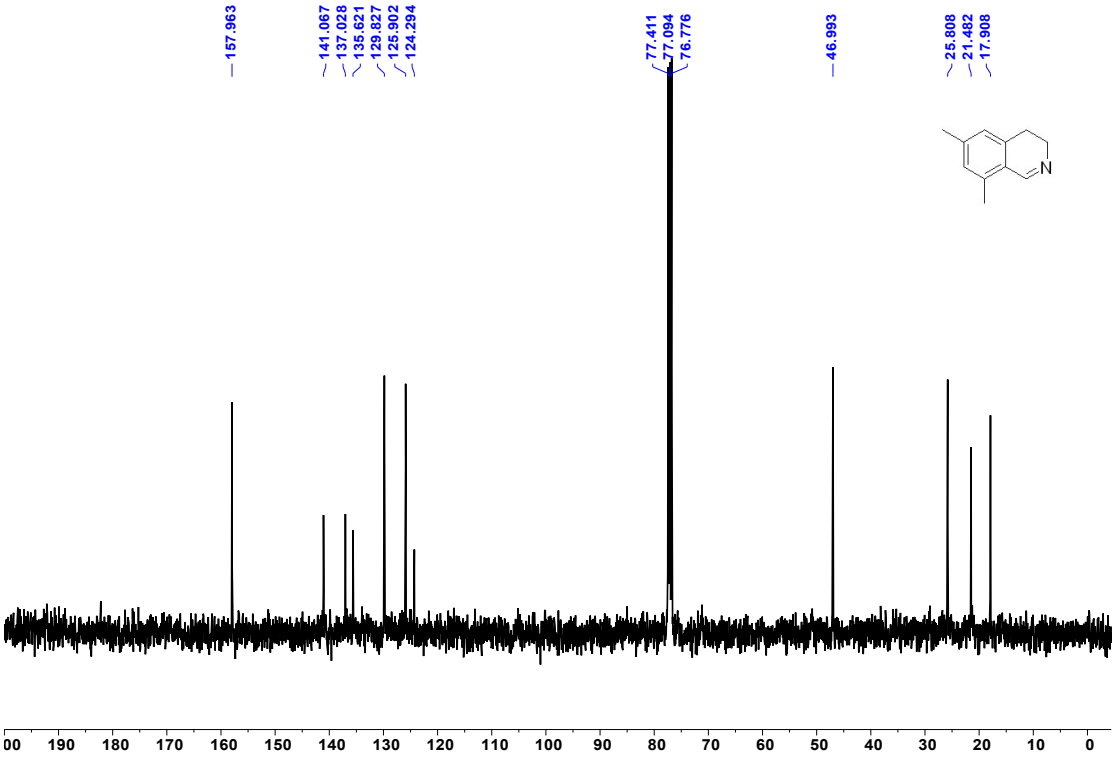


6,8-dimethyl-3,4-dihydroisoquinoline **(1f)**

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

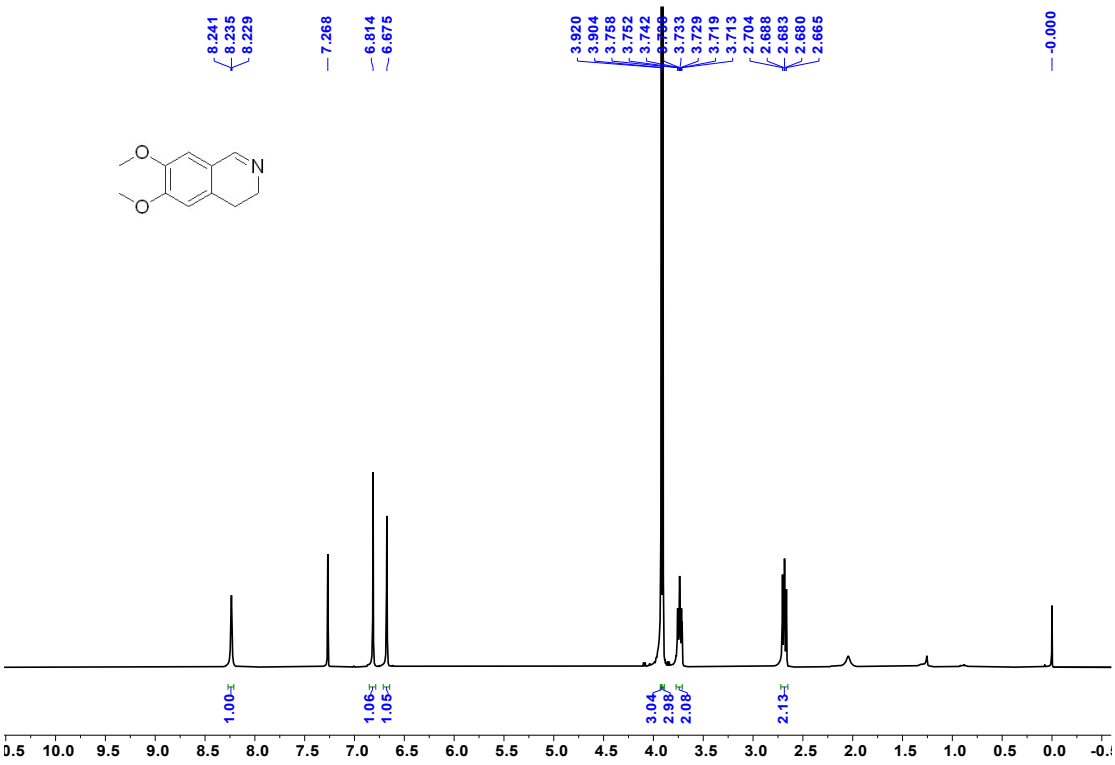



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

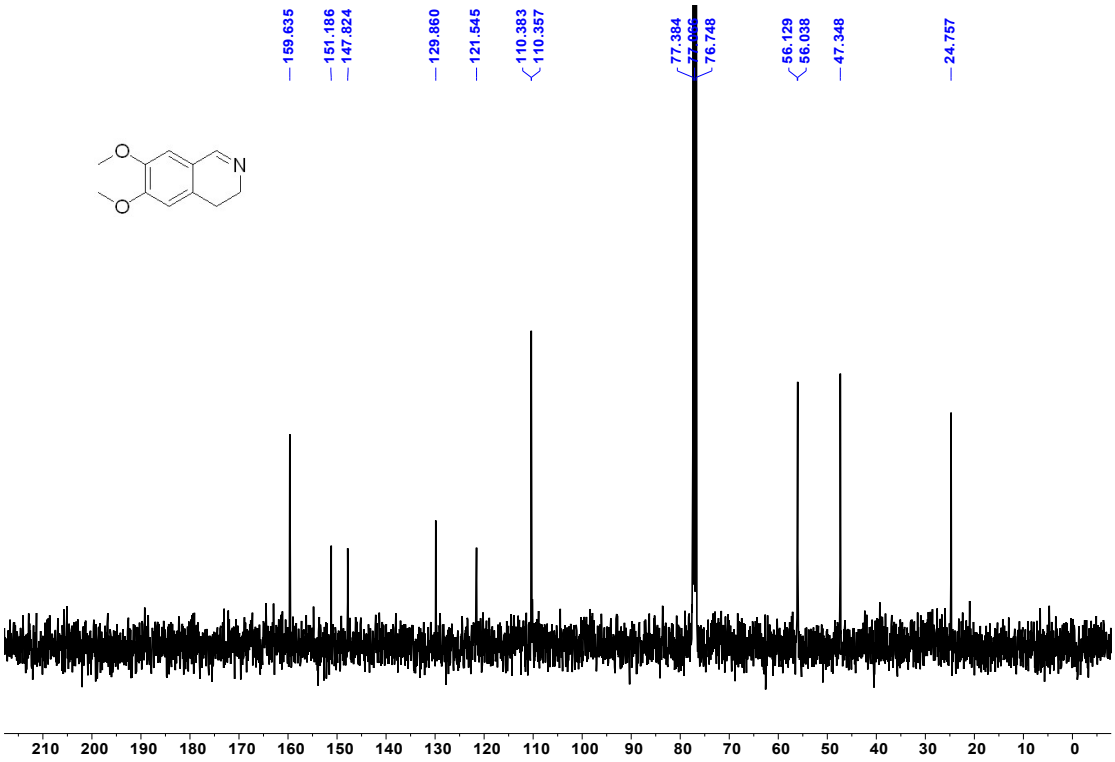


6,7-dimethoxy-3,4-dihydroisoquinoline **(1g)**

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

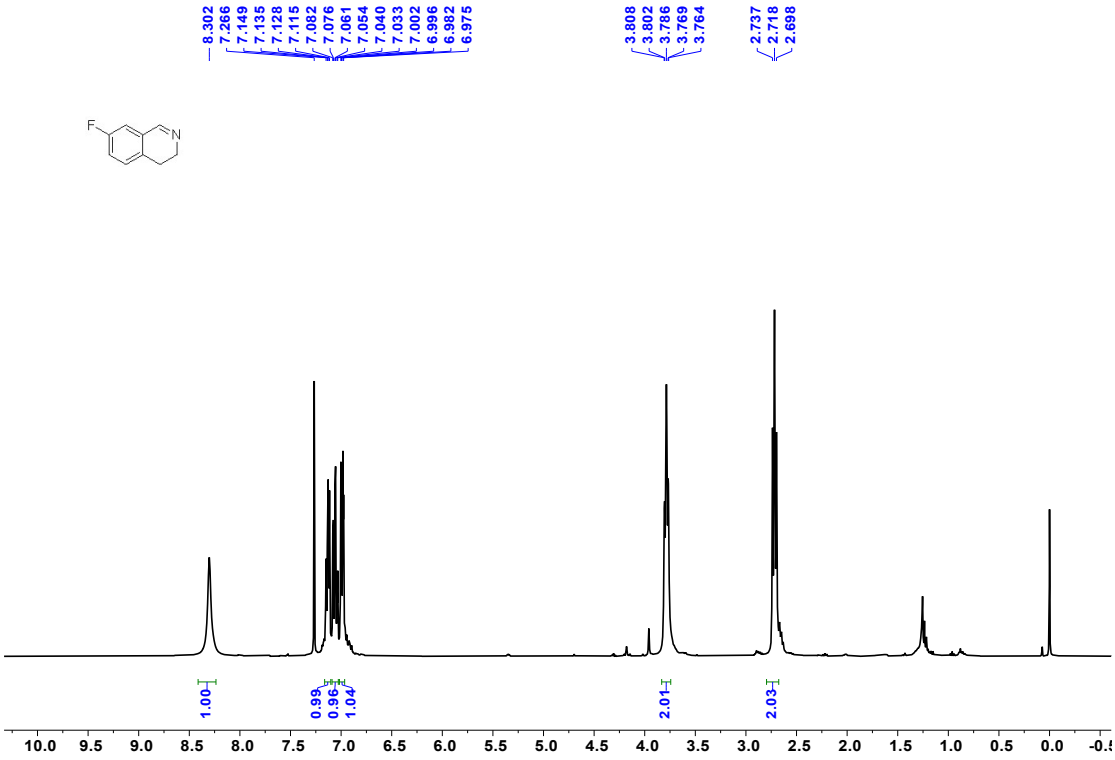



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

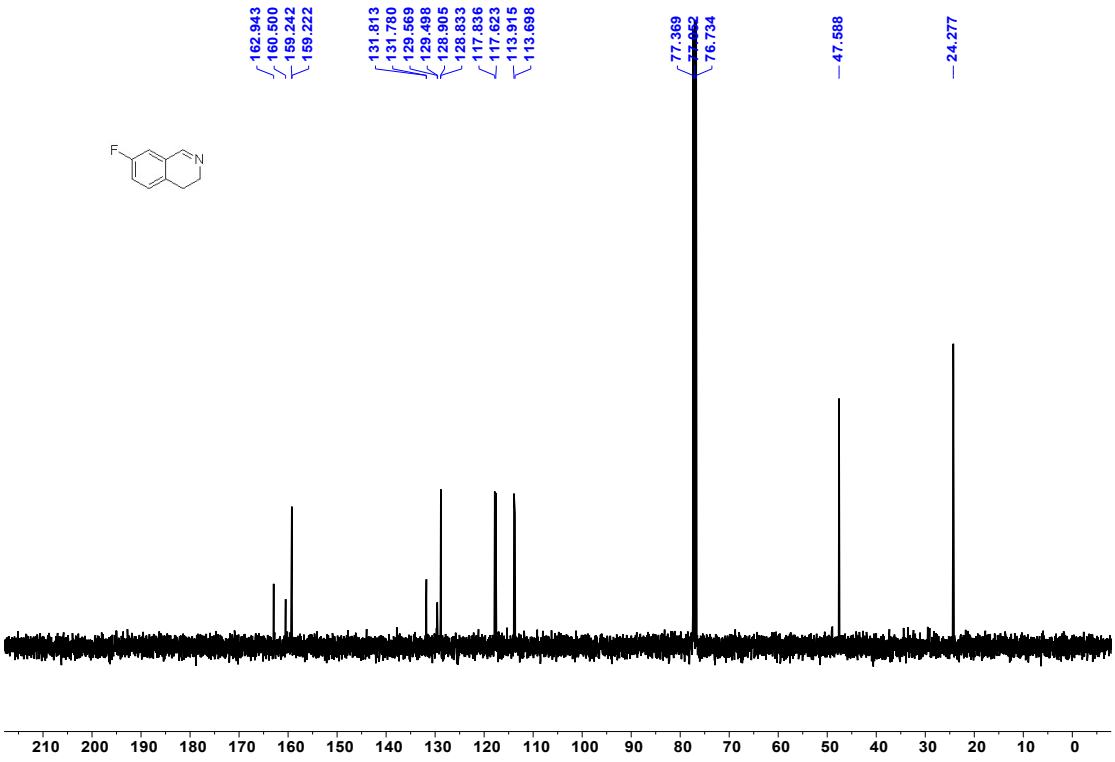


7-fluoro-3,4-dihydroisoquinoline **(1h)**

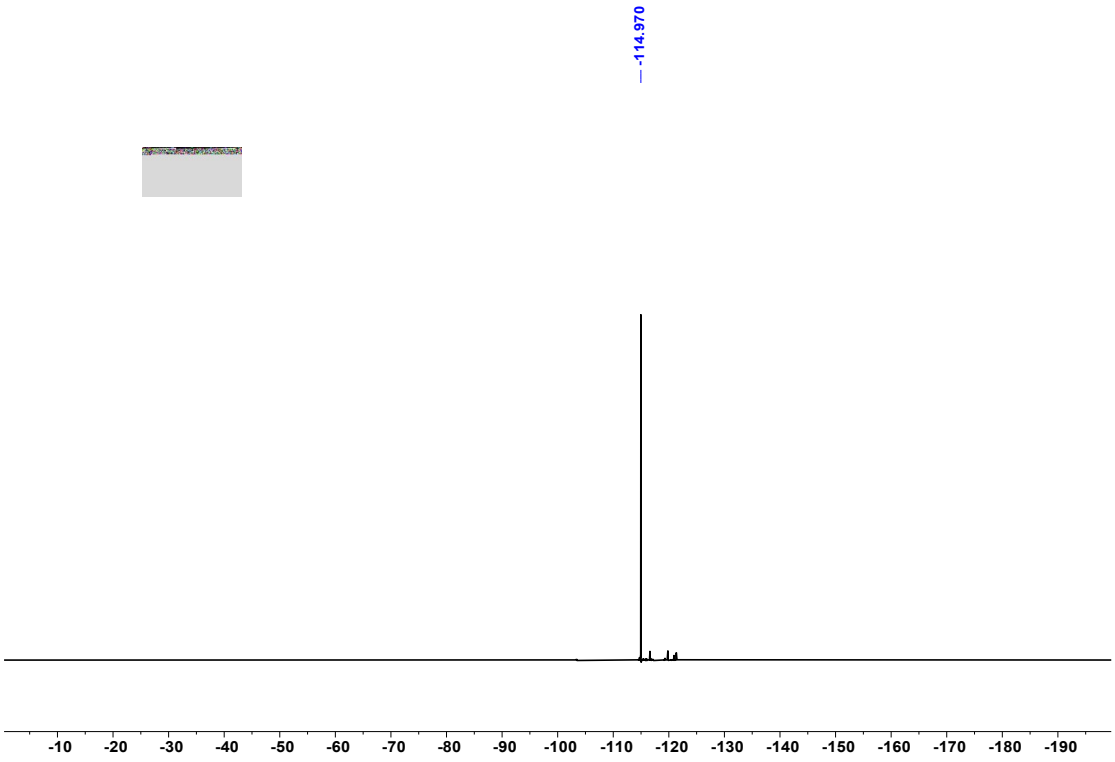
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

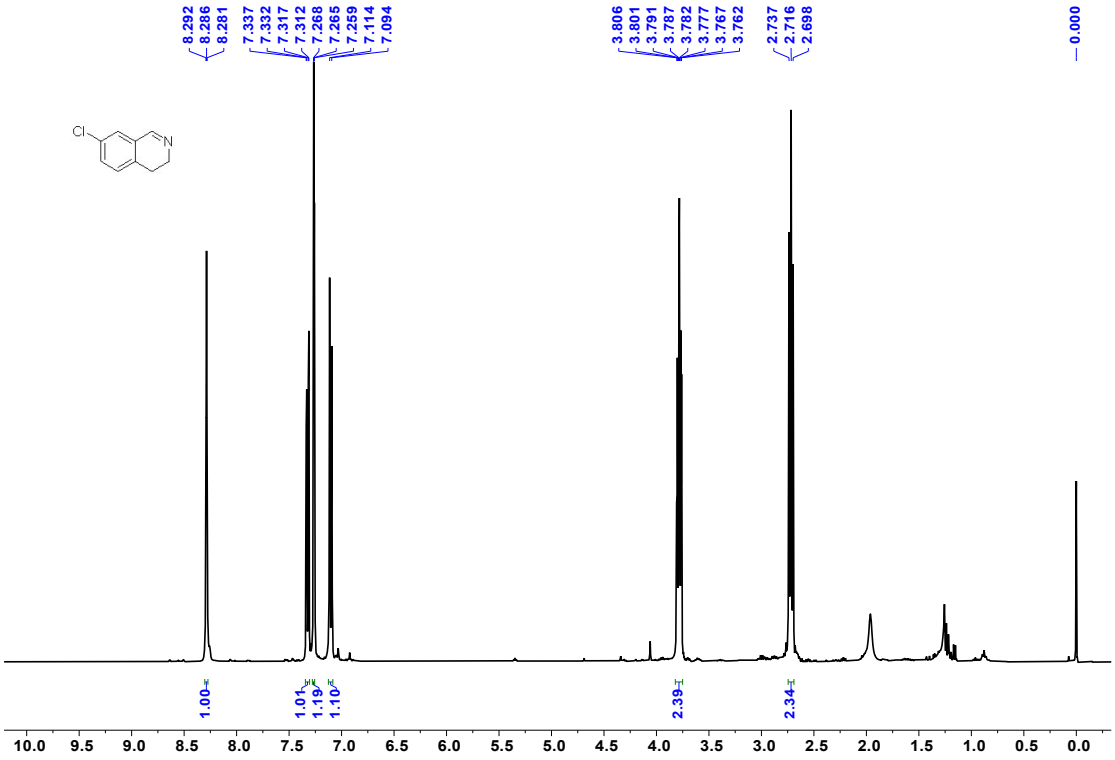


**$^{19}$F NMR** (376 MHz, $CDCl_3$)

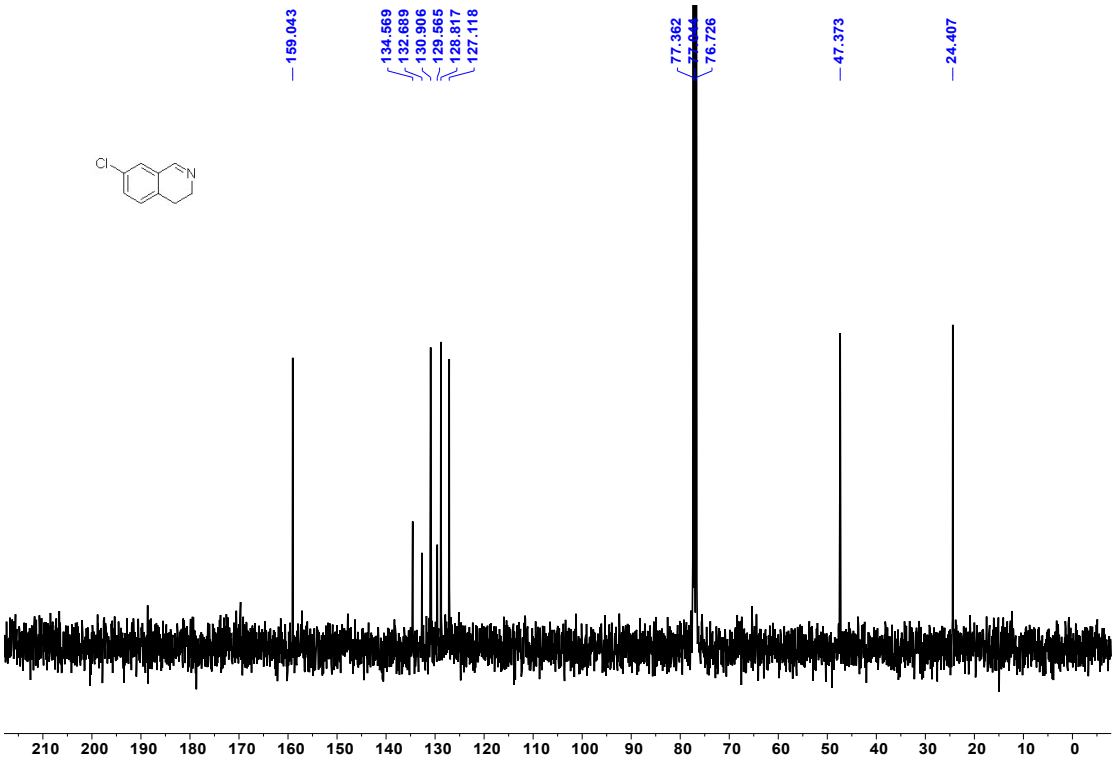


7-chloro-3,4-dihydroisoquinoline **(1i)**

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

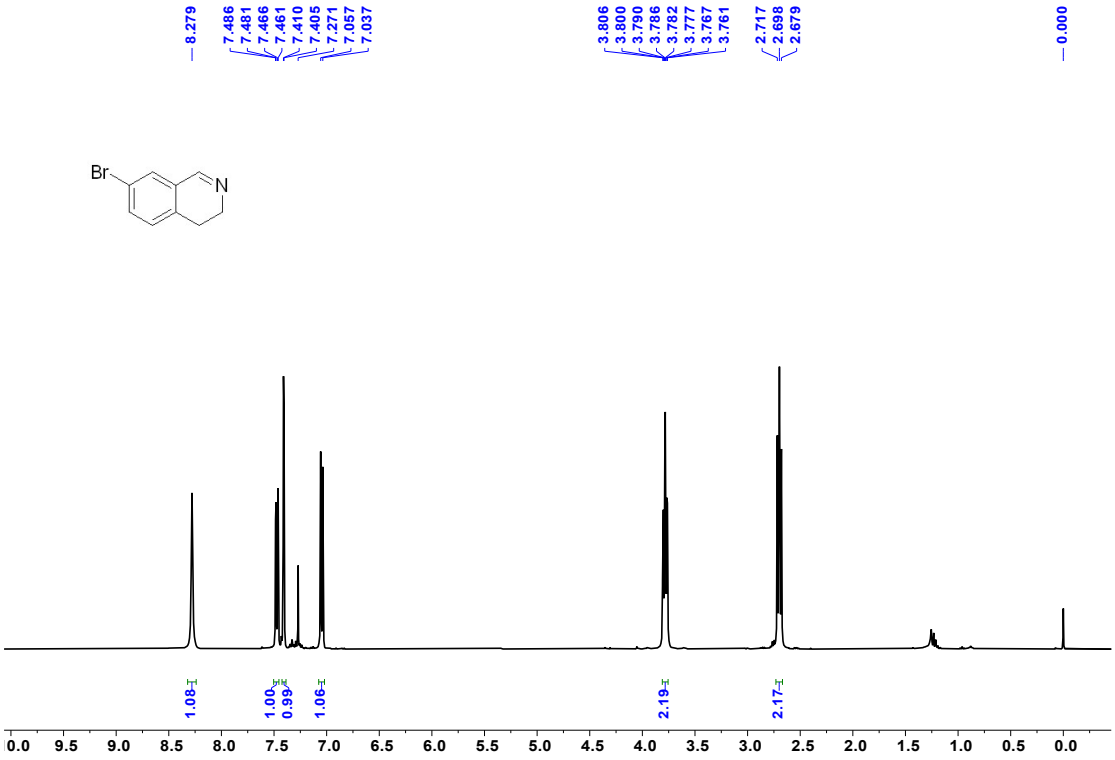



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

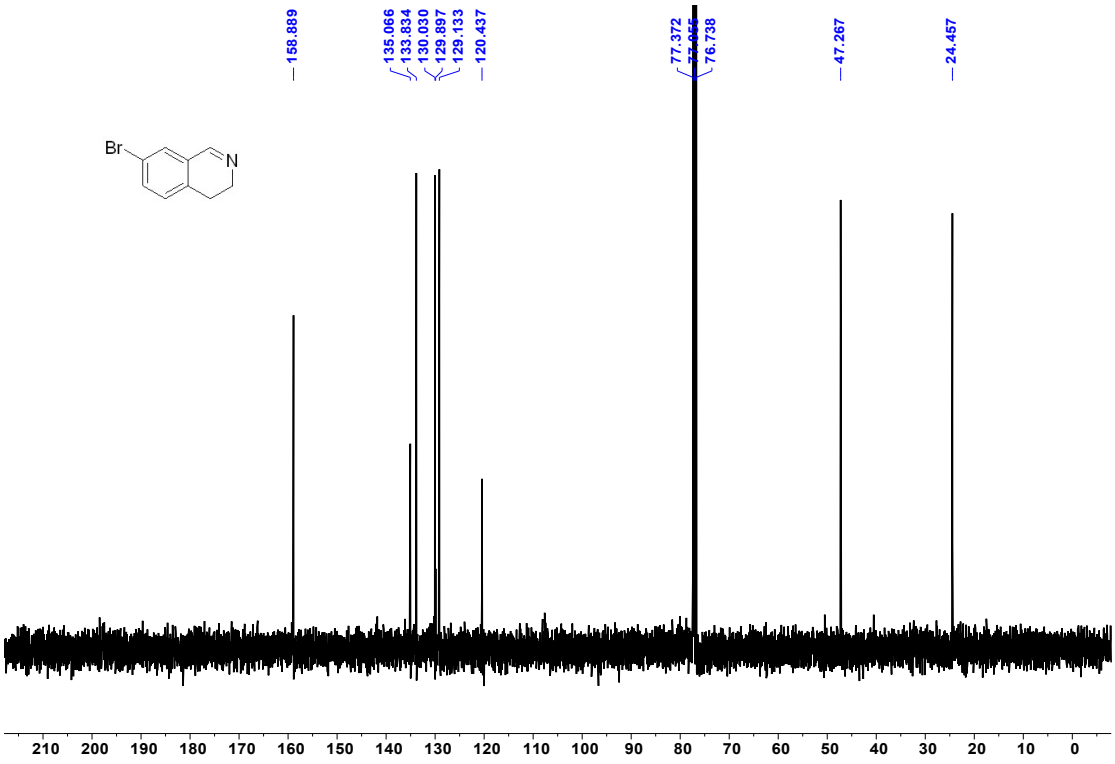


7-bromo-3,4-dihydroisoquinoline **(1j)**

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

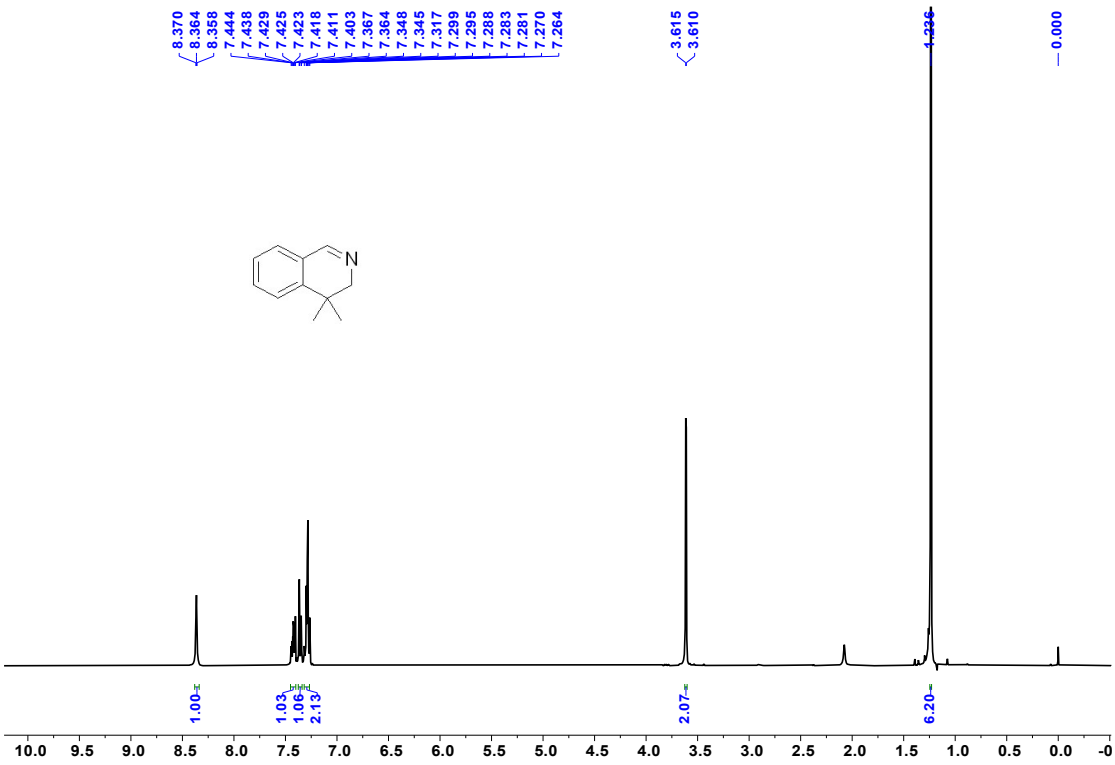



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

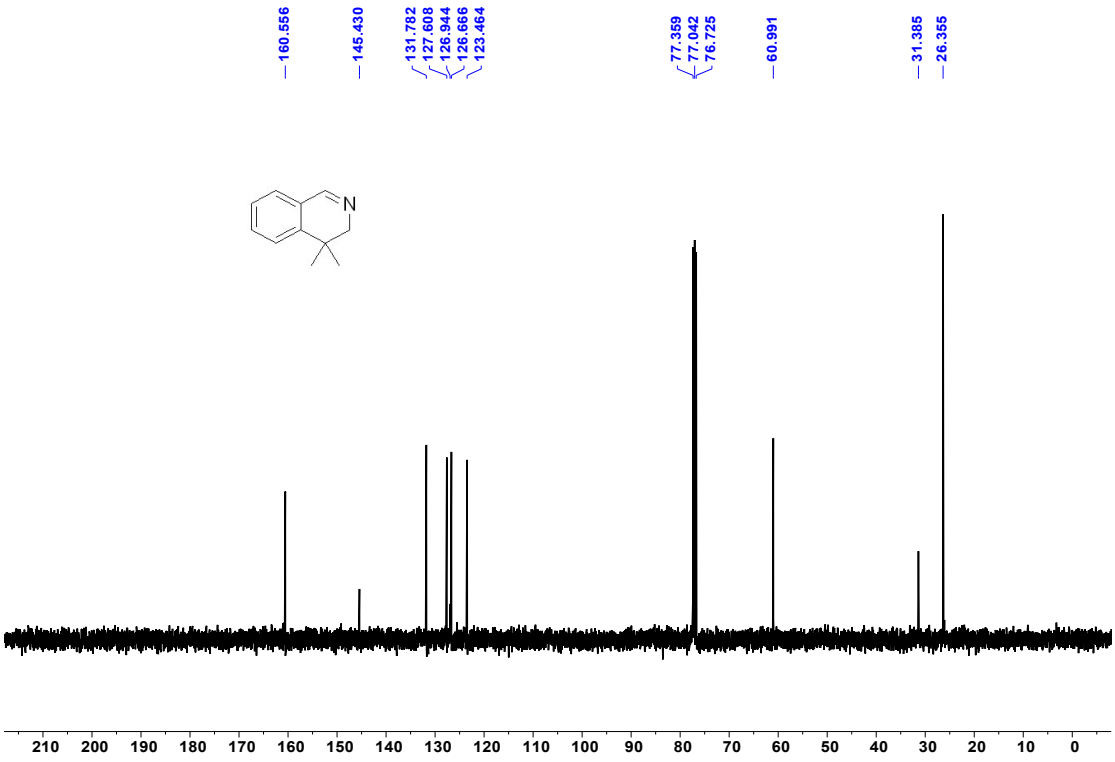


4,4-dimethyl-3,4-dihydroisoquinoline **(1k)**

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

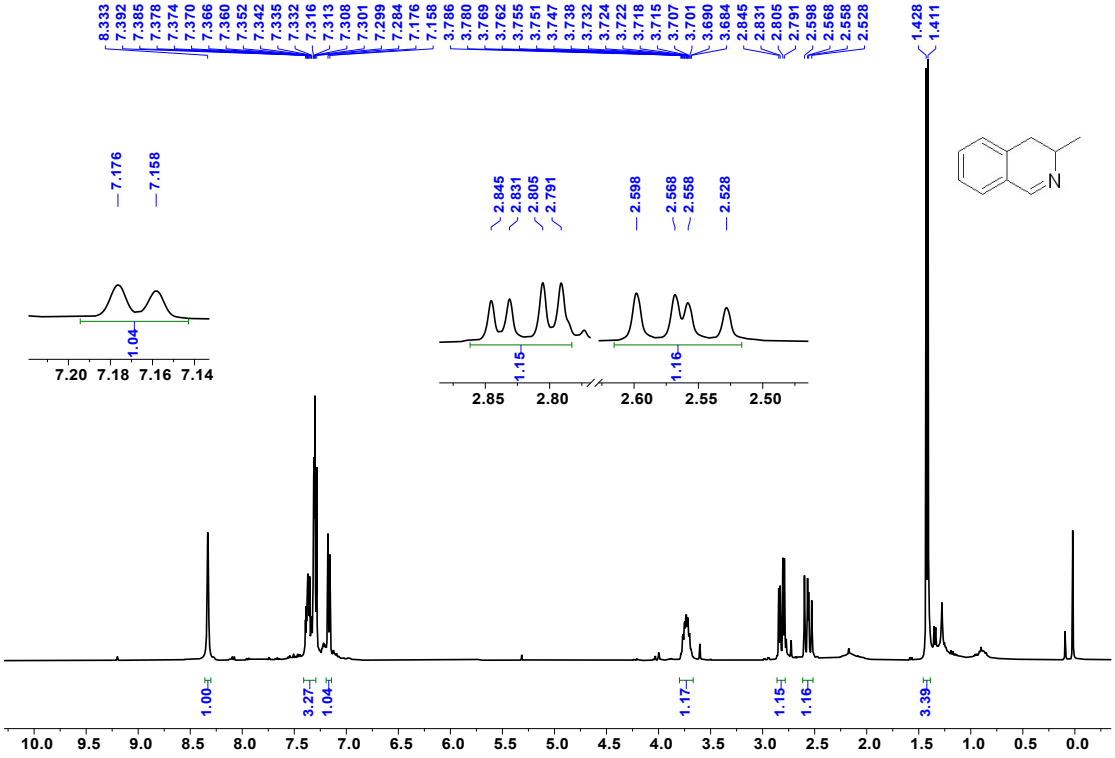



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

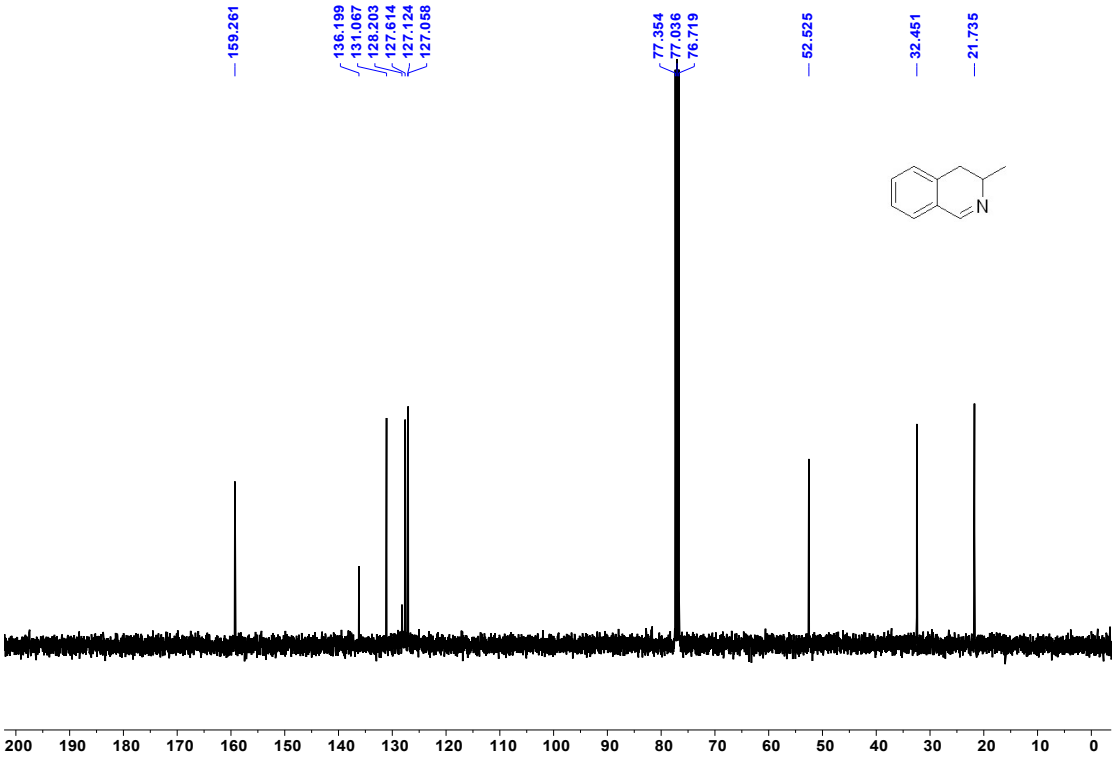


3-methyl-3,4-dihydroisoquinoline **(1l)**

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

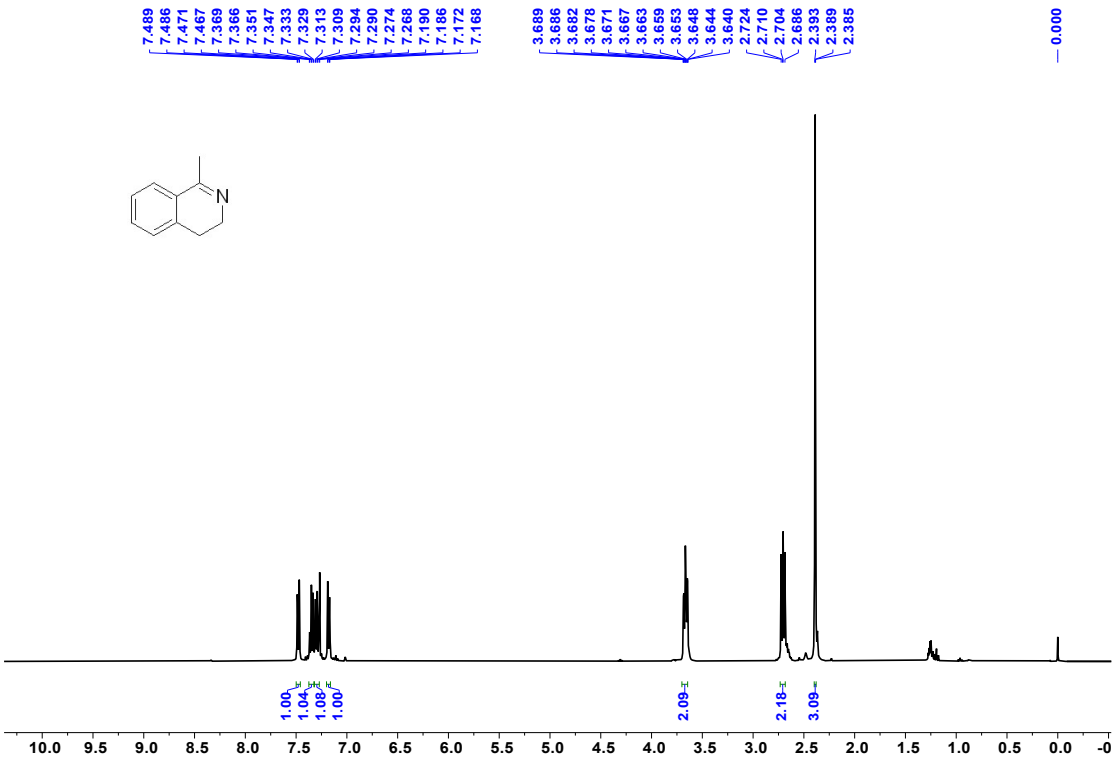


**$^{13}$C NMR** (101 MHz, $CDCl_3$)

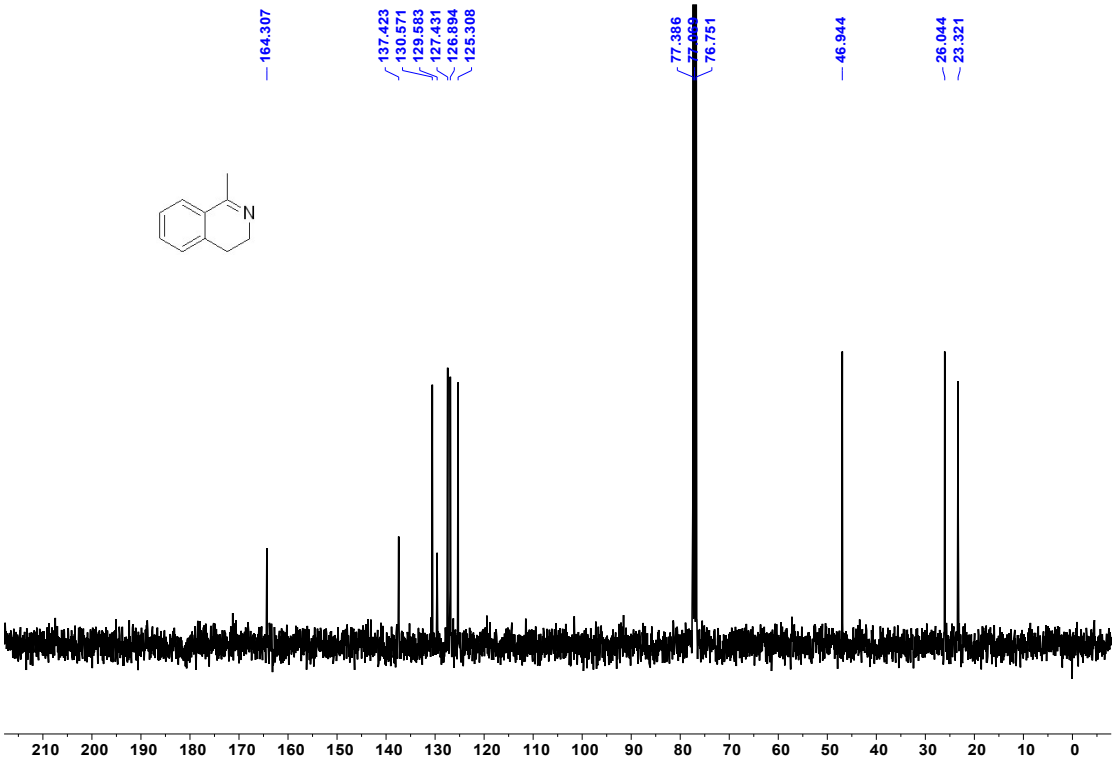


1-methyl-3,4-dihydroisoquinoline **(1m)**

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

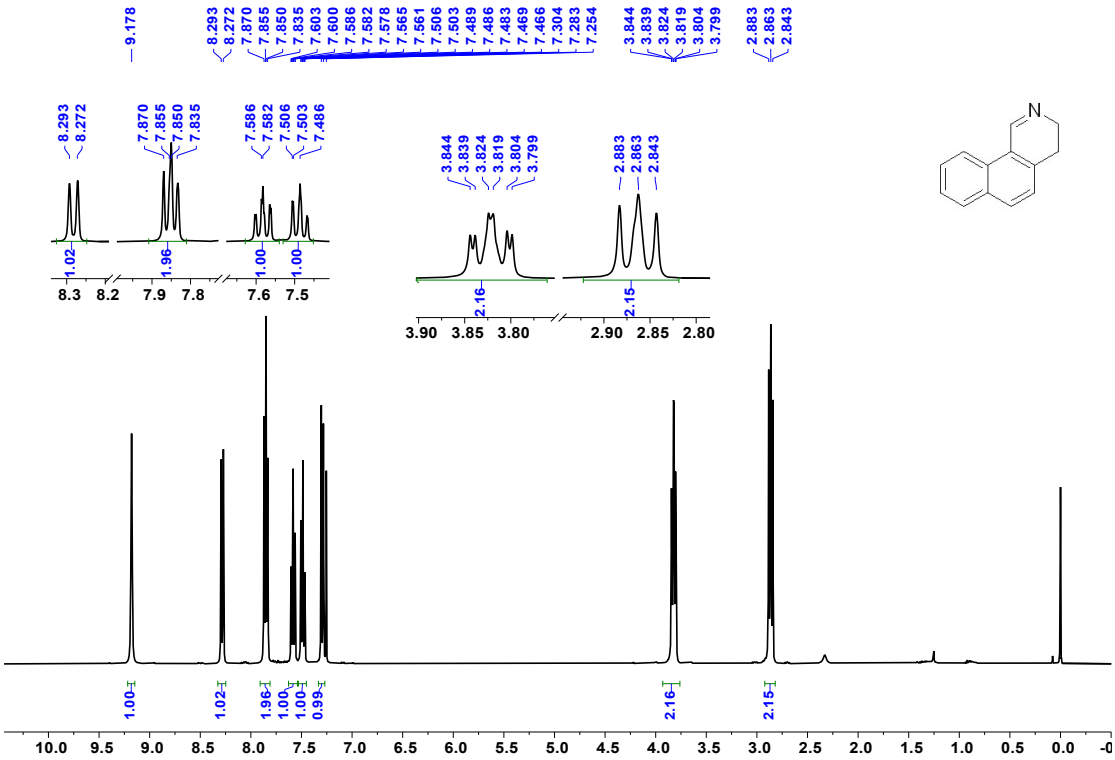



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

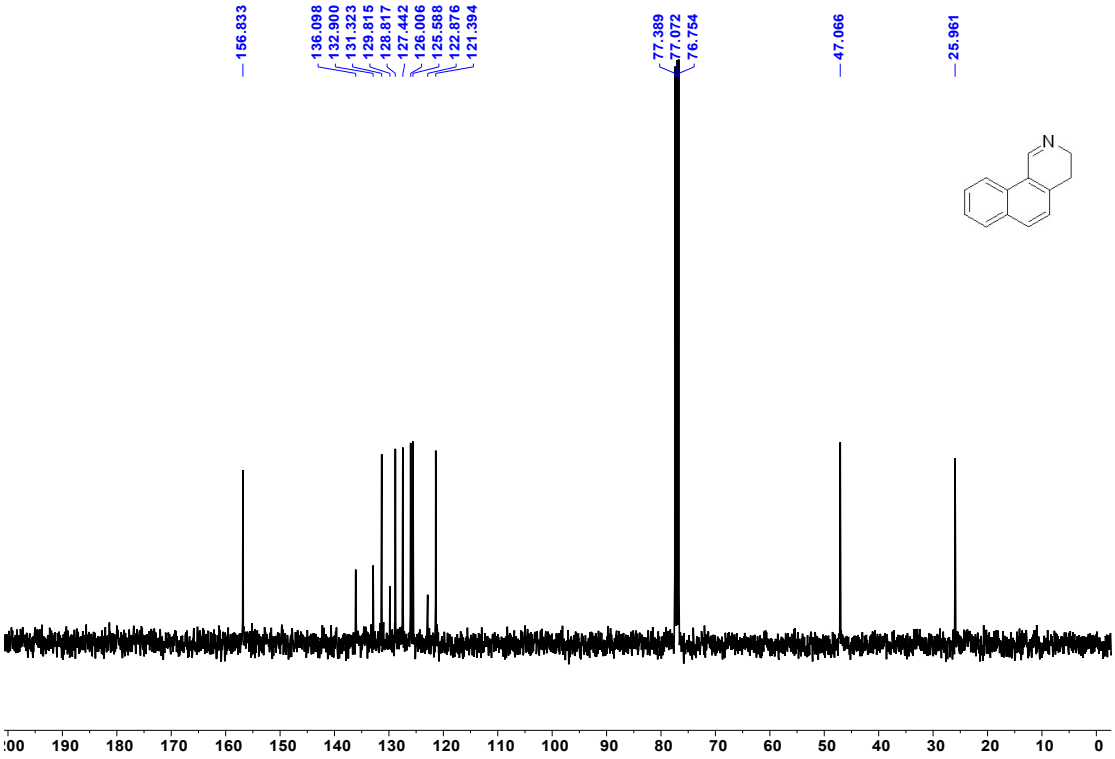


1,2-dihydrobenzo[*f*]isoquinoline **(1n)**

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

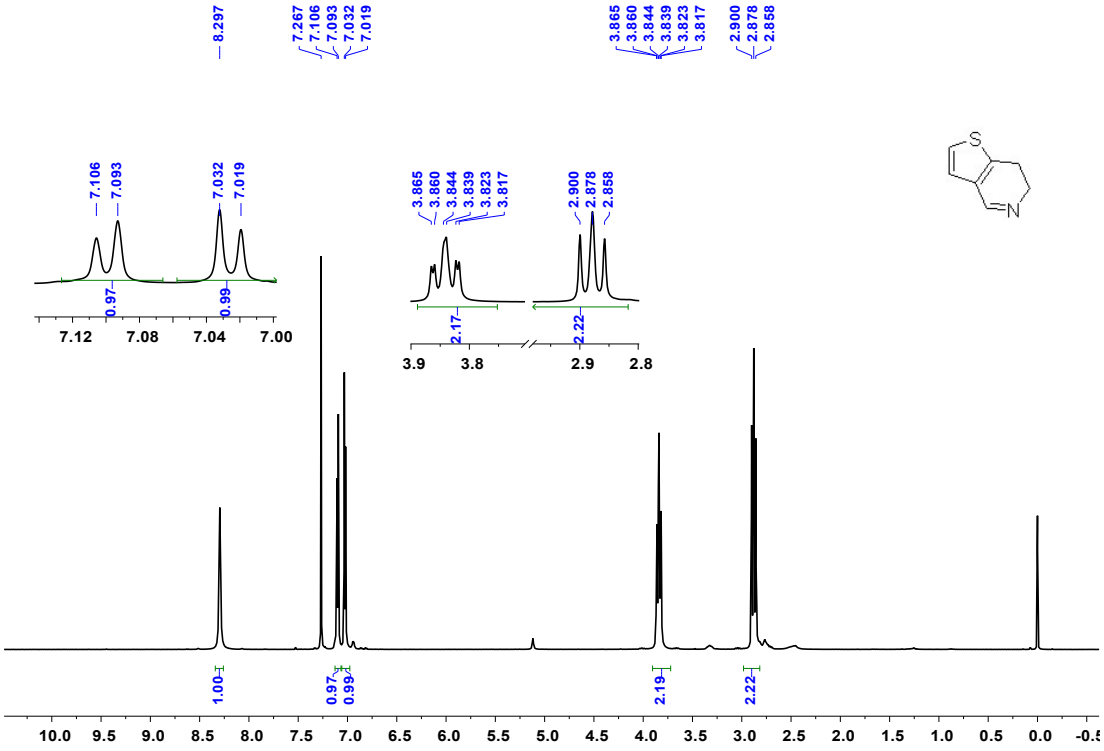


**$^{13}$C NMR** (101 MHz, $CDCl_3$)

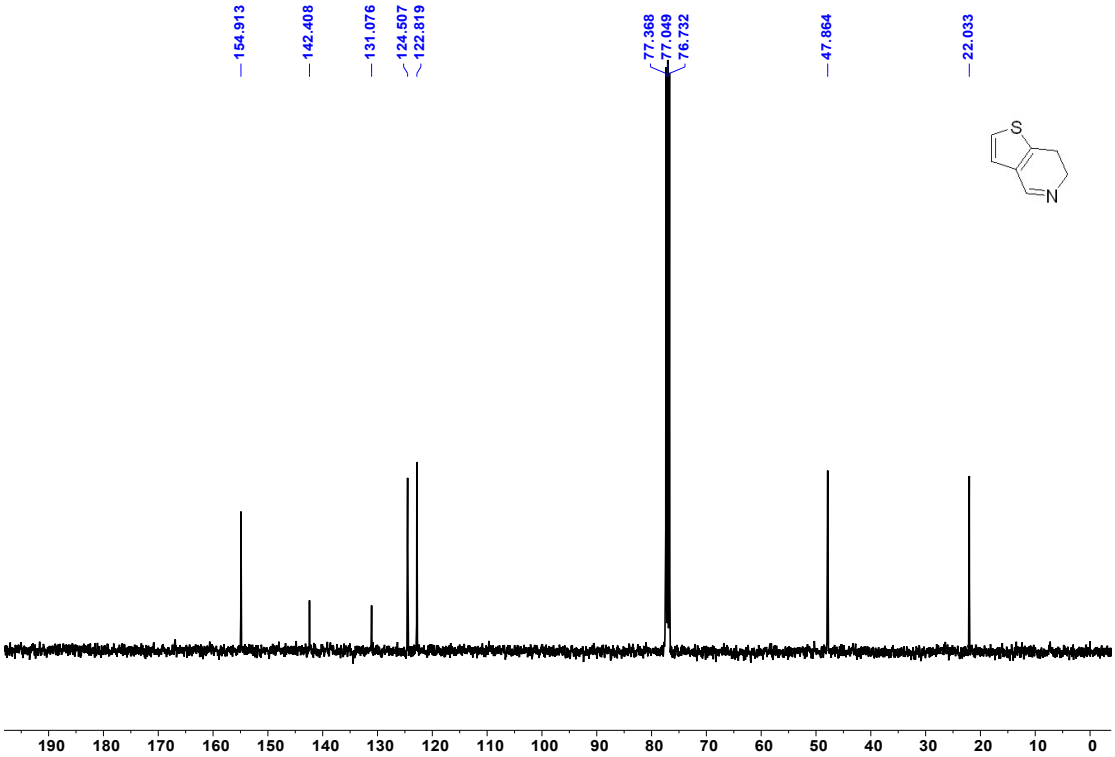


4,5-dihydrothieno[2,3-*c*]pyridine **(1o)**

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

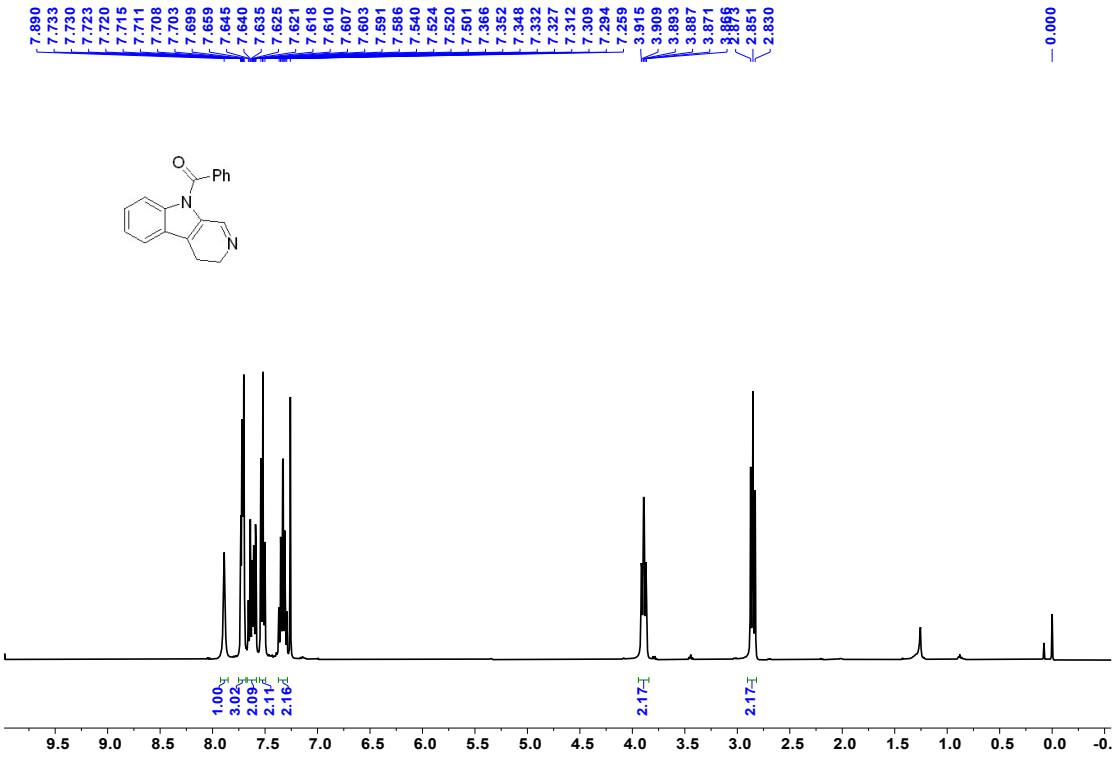



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

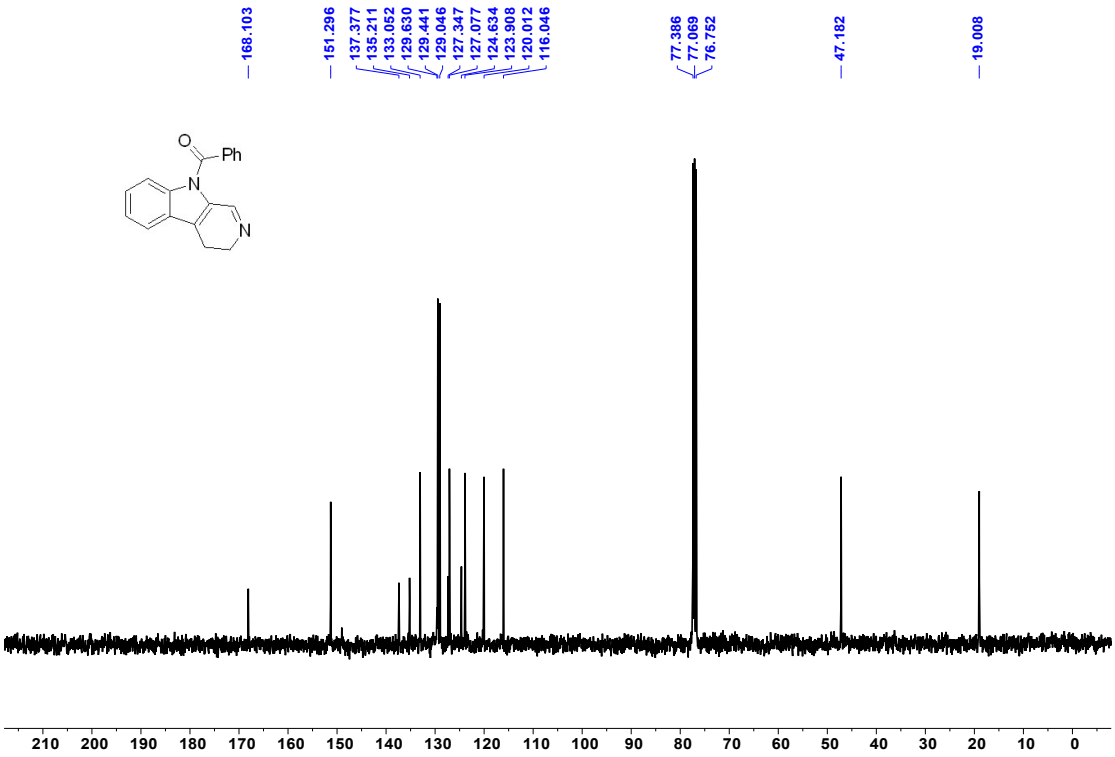


(3,4-dihydro-9*H*-pyrido[3,4-*b*]indol-9-yl)(phenyl)methanone **(1p)**

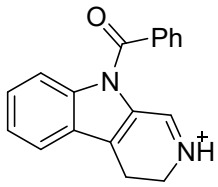
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



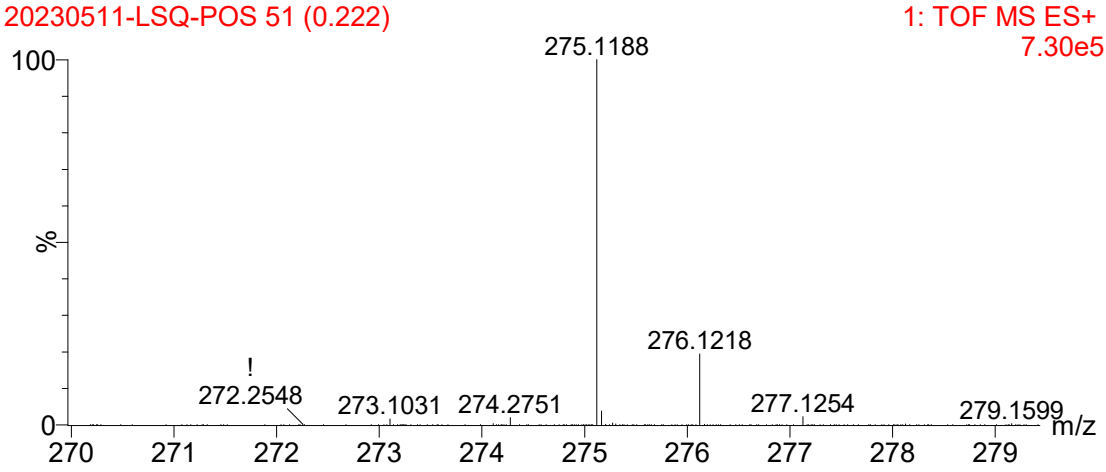

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



**HRMS** (ESI)

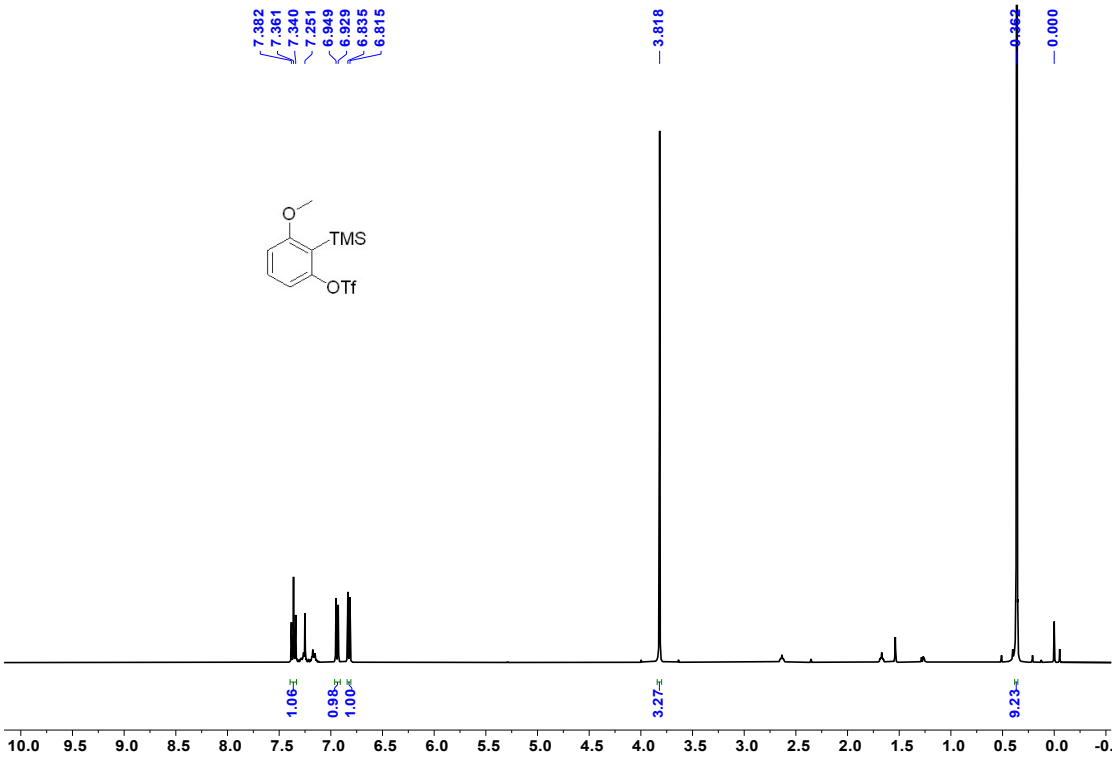



Chemical Formula: $C_{18}H_{15}N_2O^+$
m/z: 275.1179 (100.0%), 276.1212 (19.5%), 277.1246 (1.8%)



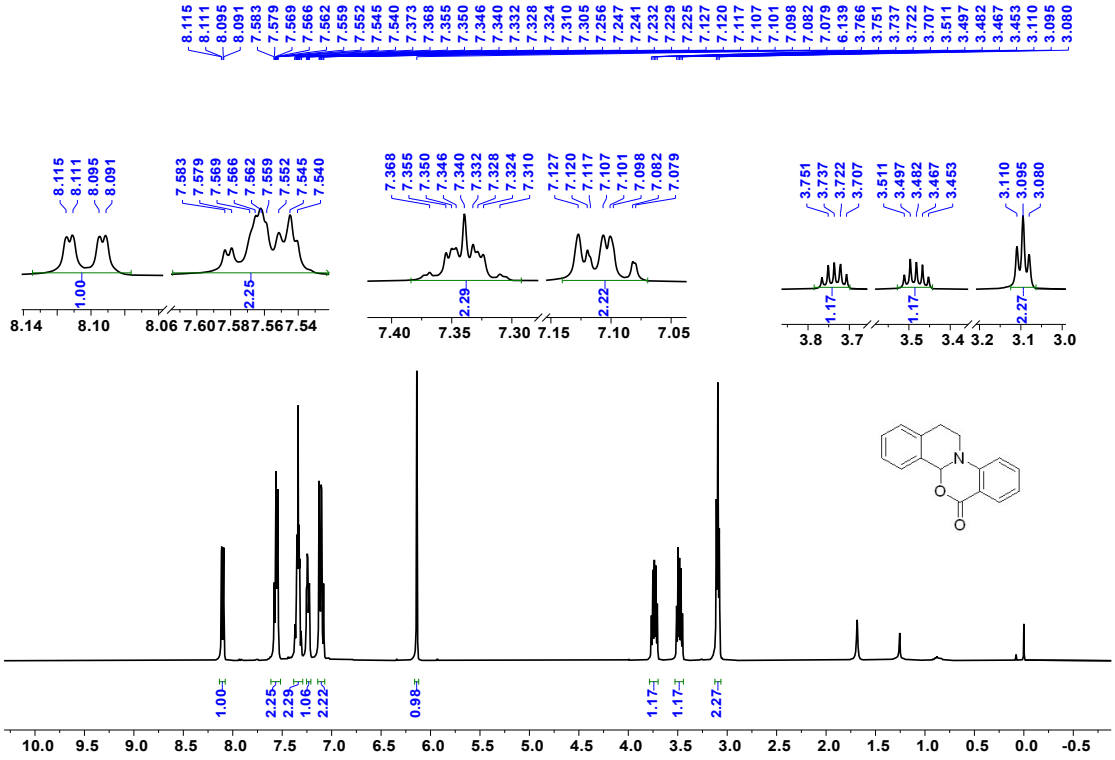
3-methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate **(2d)**

**$^1$H NMR** (400 MHz, $CDCl_3$)

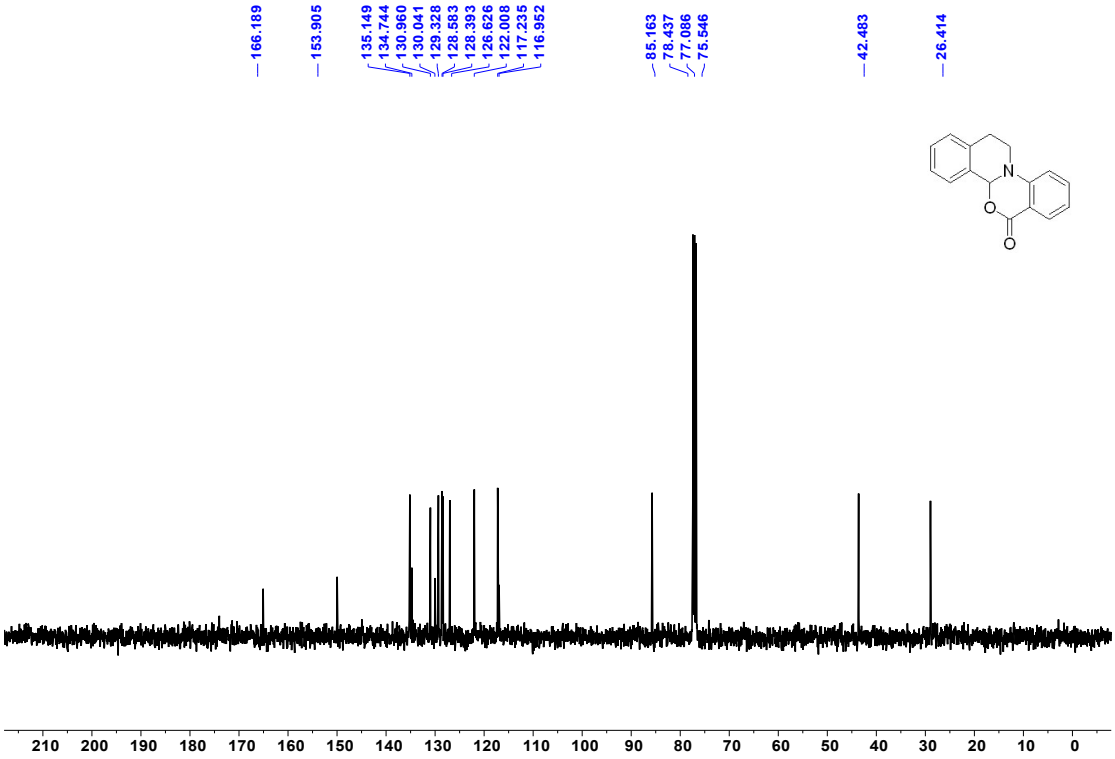


4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3aa)**

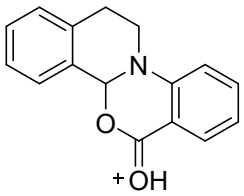
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



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

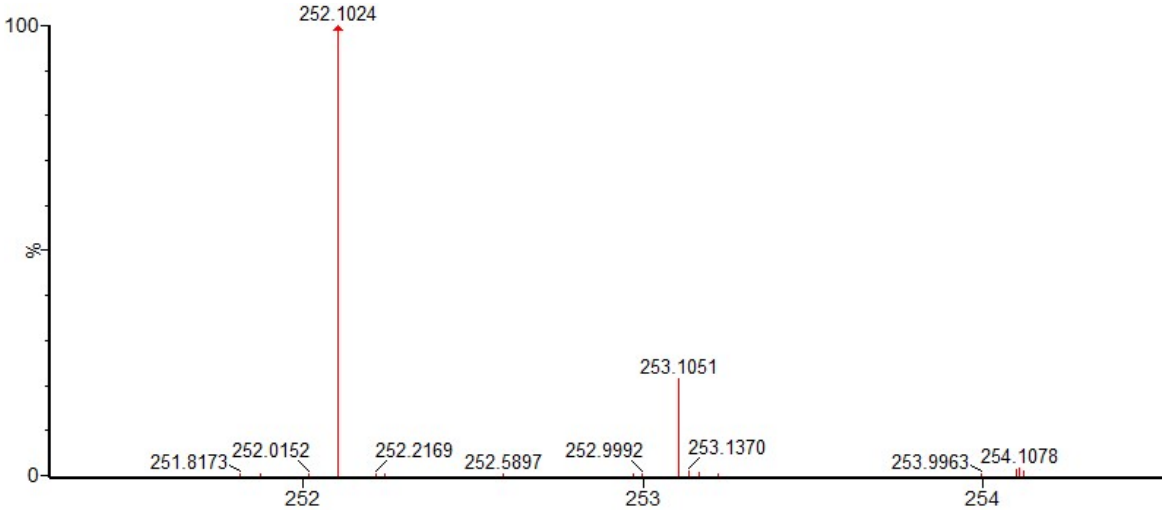


**HRMS** (ESI)

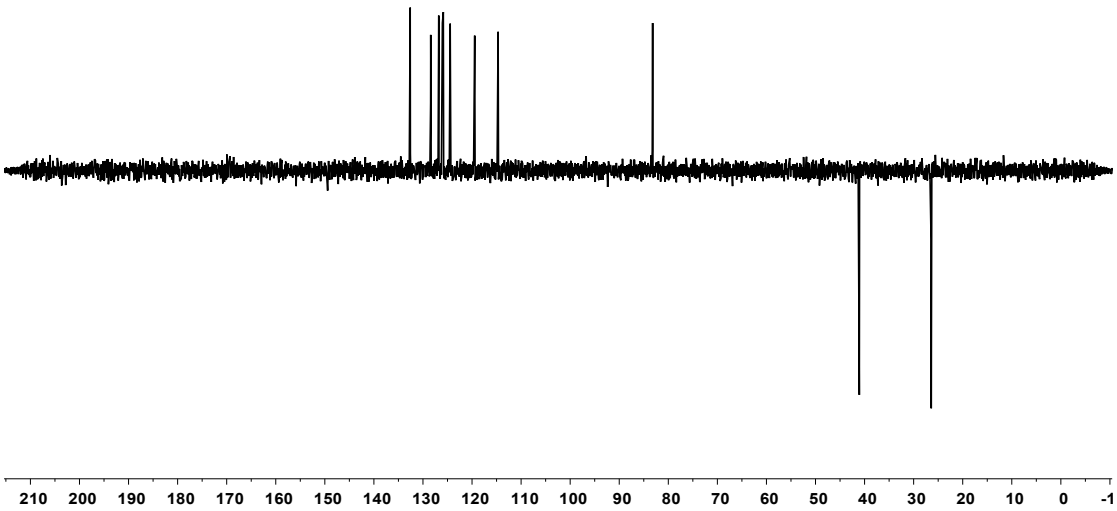



Chemical Formula: $C_{16}H_{14}NO_2^+$

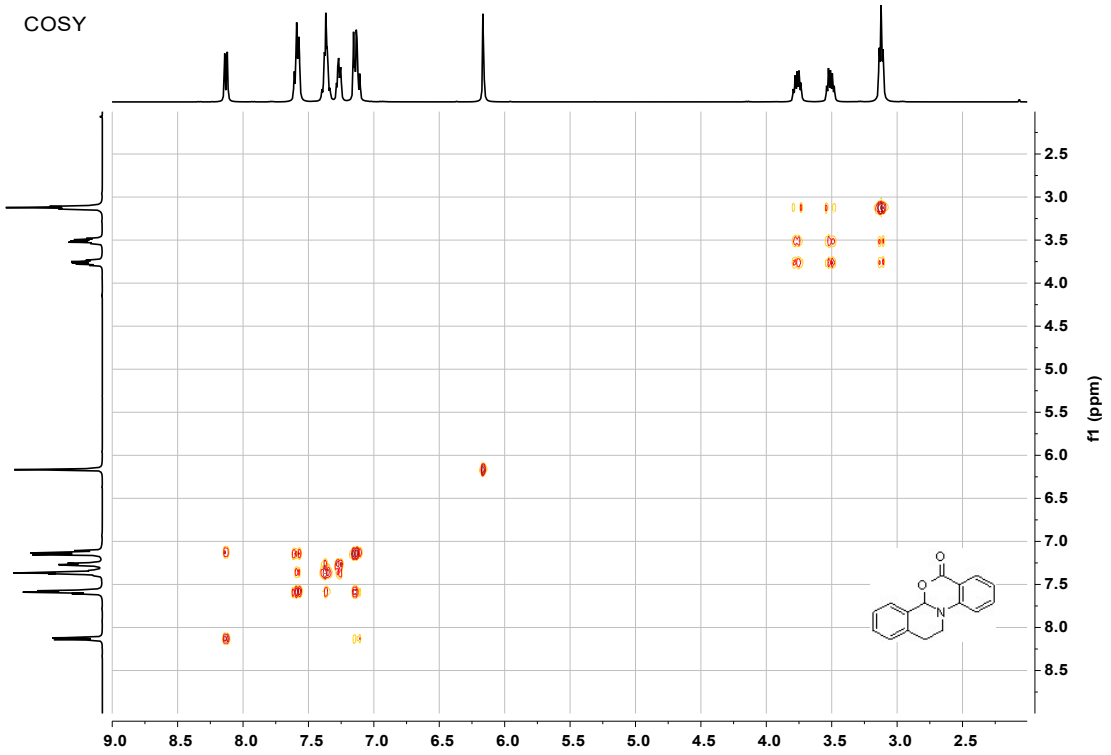
m/z: 252.1019 (100.0%), 253.1053 (17.3%), 254.1086 (1.4%)



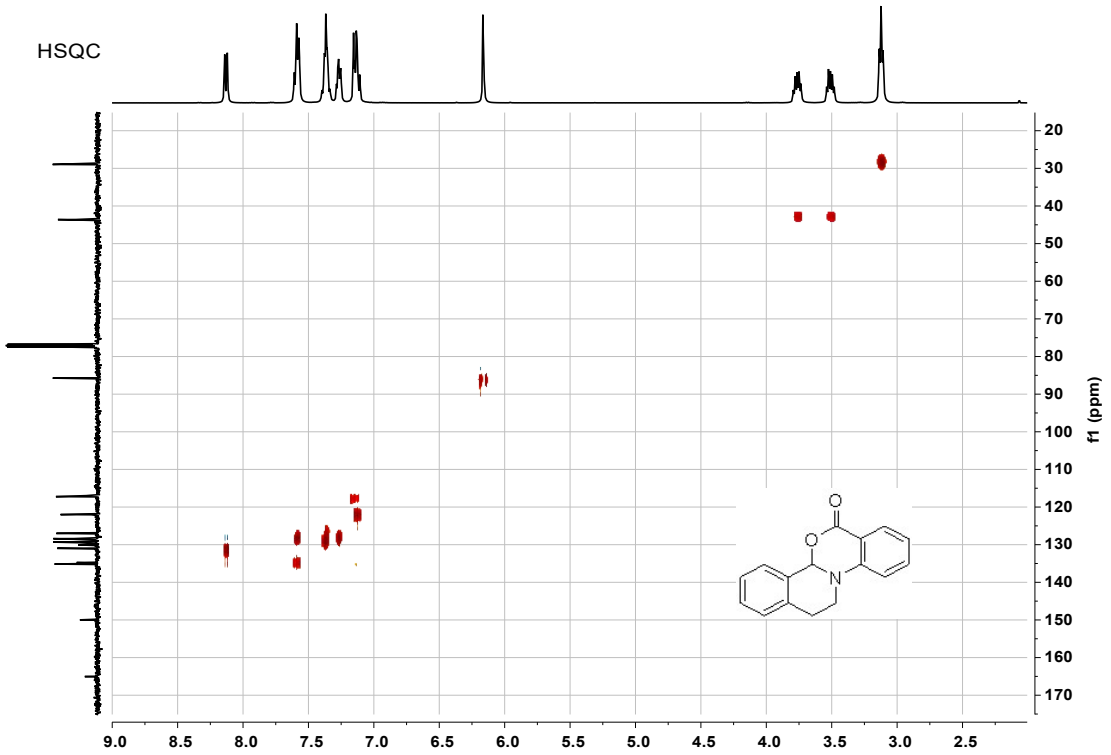

**DEPT-135**



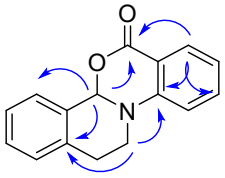
H-H COSY of **3aa**




HSQC of **3aa**

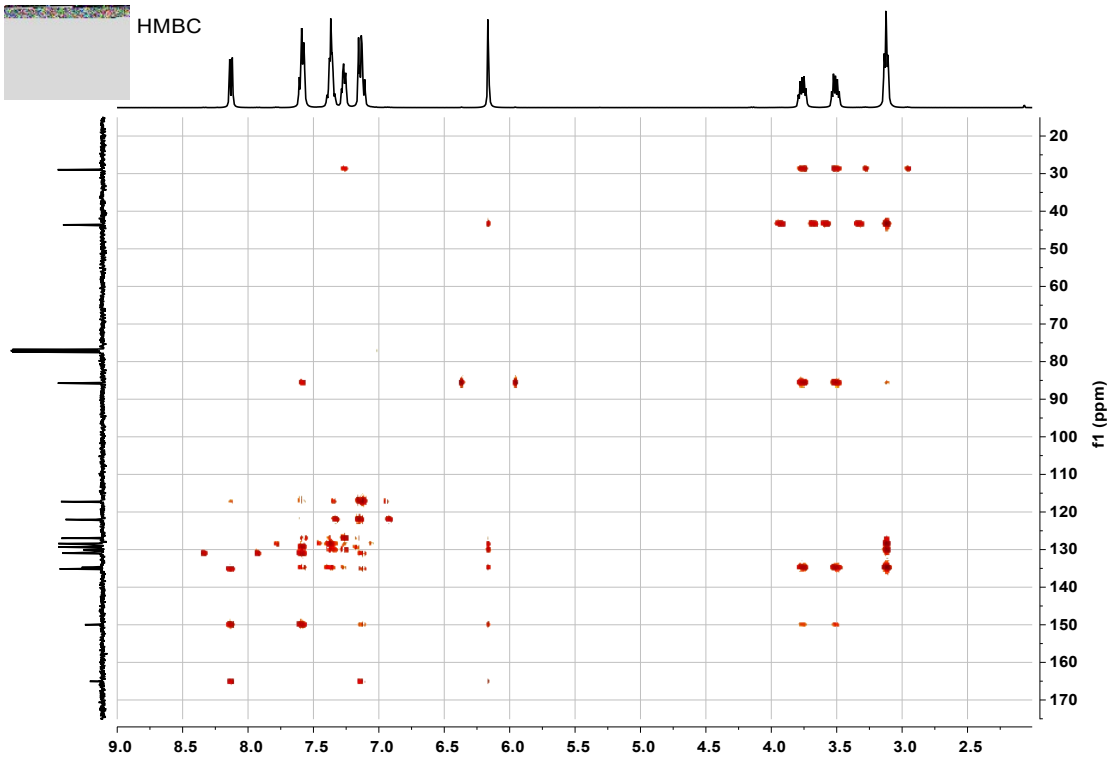


HMBC of **3aa**



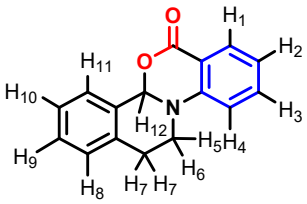
**3aa**

Key correlation in HMBC:



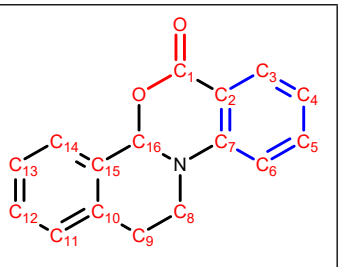

Assignment of protons

| | ppm | | ppm | | ppm |
|---|---|---|---|---|---|
| H1 | 8.10 | H5 | 3.74 | H9 | 7.32 |
| H2 | 7.10 | H6 | 3.48 | H10 | 7.36 |
| H3 | 7.56 | H7 | 3.10 | H11 | 7.54 |
| H4 | 7.12 | H8 | 7.24 | H12 | 6.14 |




Assignment of carbons

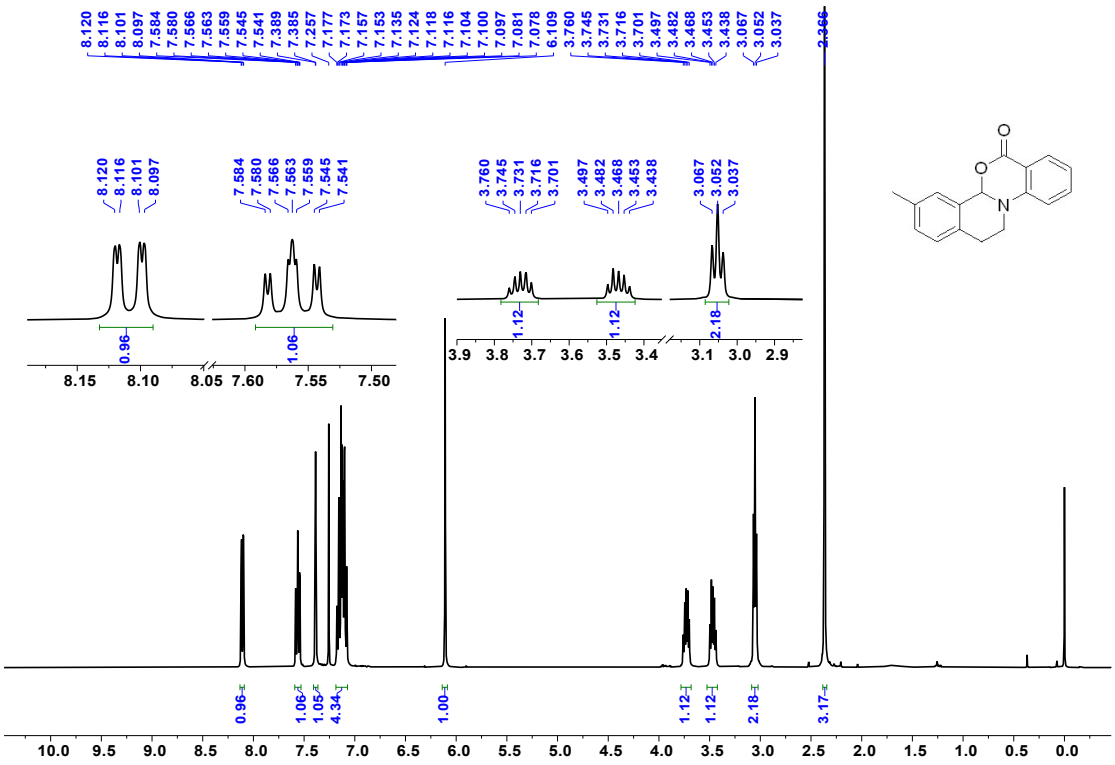
| | ppm | | ppm | | ppm |
|---|---|---|---|---|---|
| C1 | 166.2 | C7 | 153.9 | C13 | 126.6 |
| C2 | 117.0 | C8 | 42.5 | C14 | 128.6 |
| C3 | 131.0 | C9 | 26.4 | C15 | 130.0 |
| C4 | 122.0 | C10 | 134.7 | C16 | 85.2 |
| C5 | 135.2 | C11 | 128.4 | | |
| C6 | 117.2 | C12 | 129.3 | | |



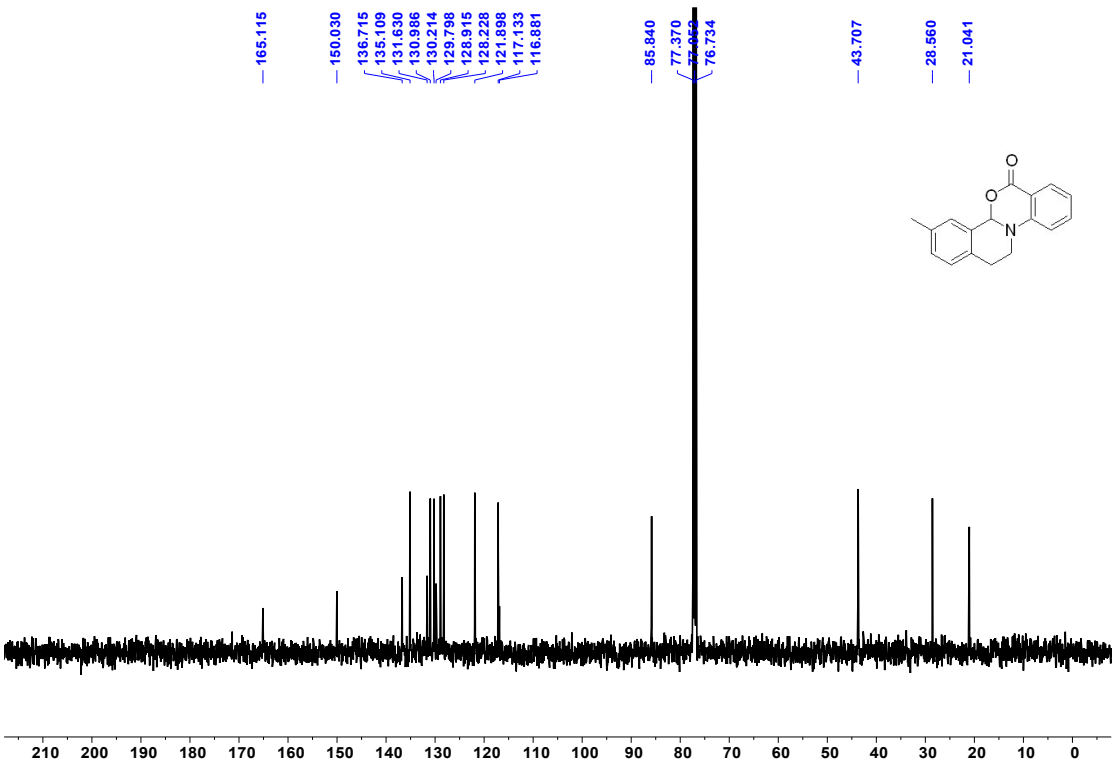
3-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one

**(3ba)**

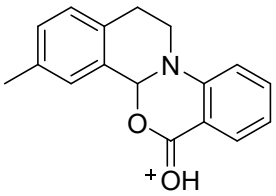
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



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

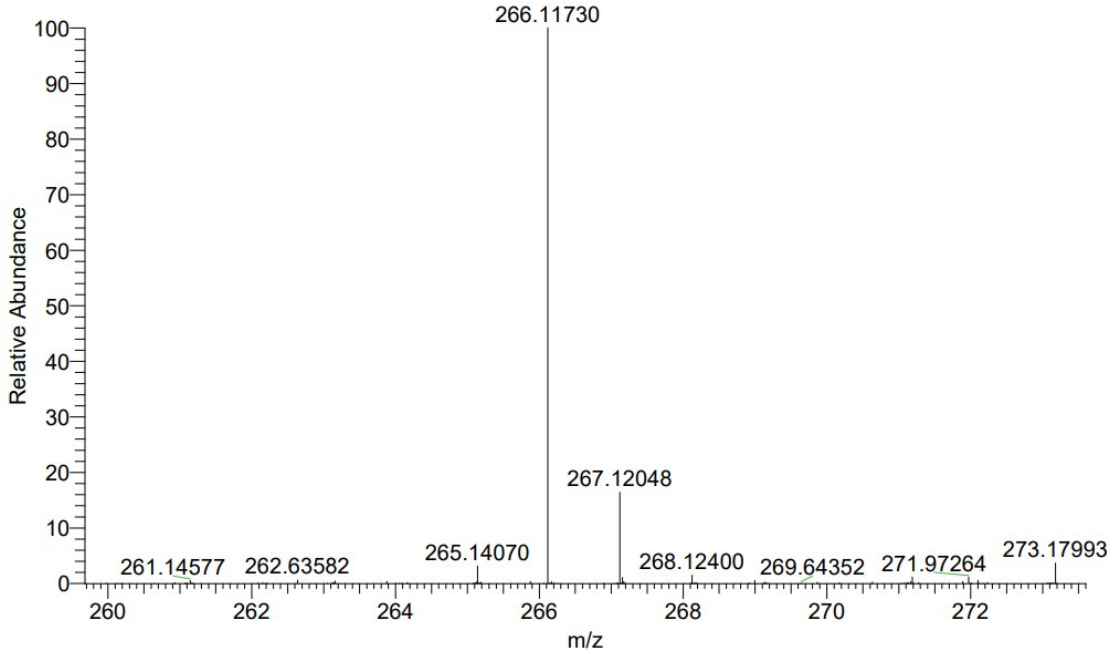


**HRMS** (ESI)



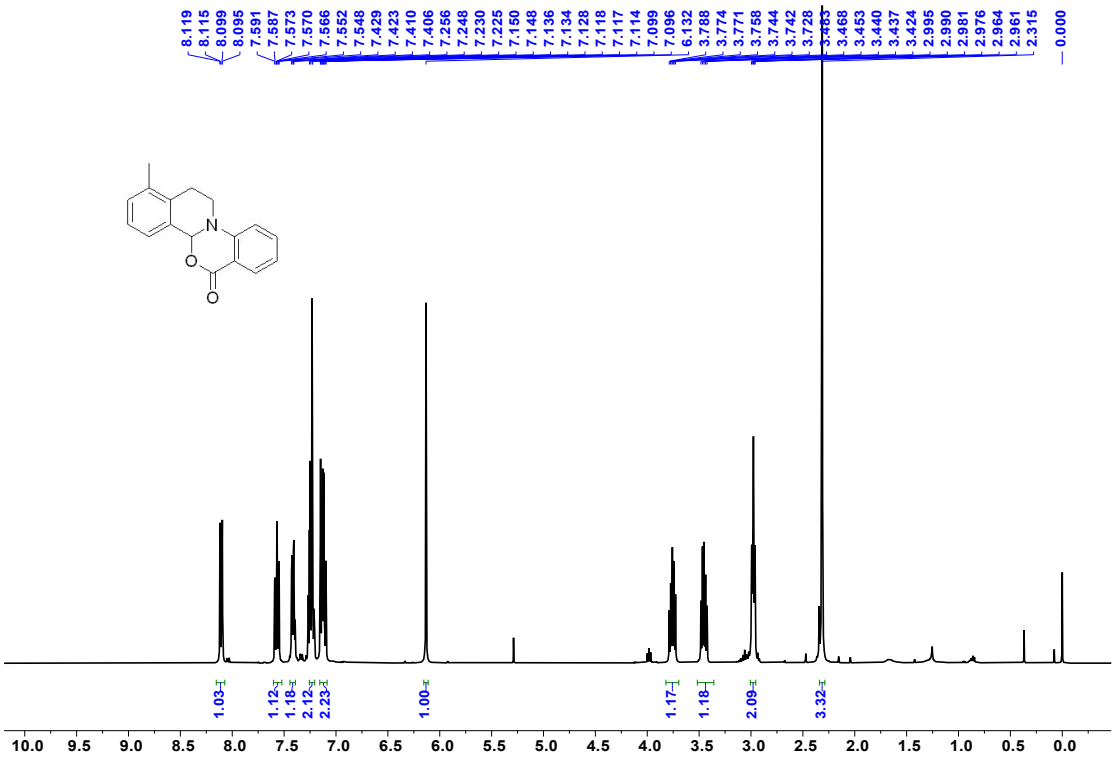

Chemical Formula: $C_{17}H_{16}NO_2^+$

m/z: 266.1176 (100.0%), 267.1209 (18.4%), 268.1243 (1.6%)

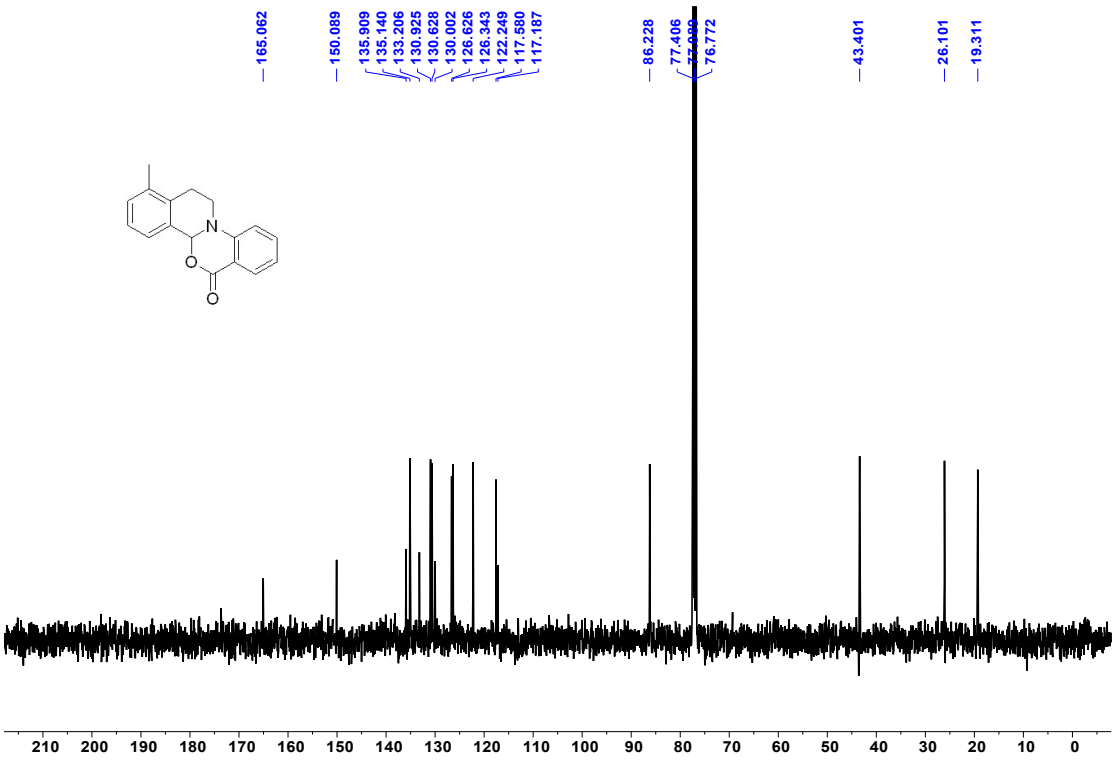


1-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one (**3ca**).

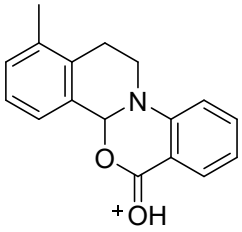
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



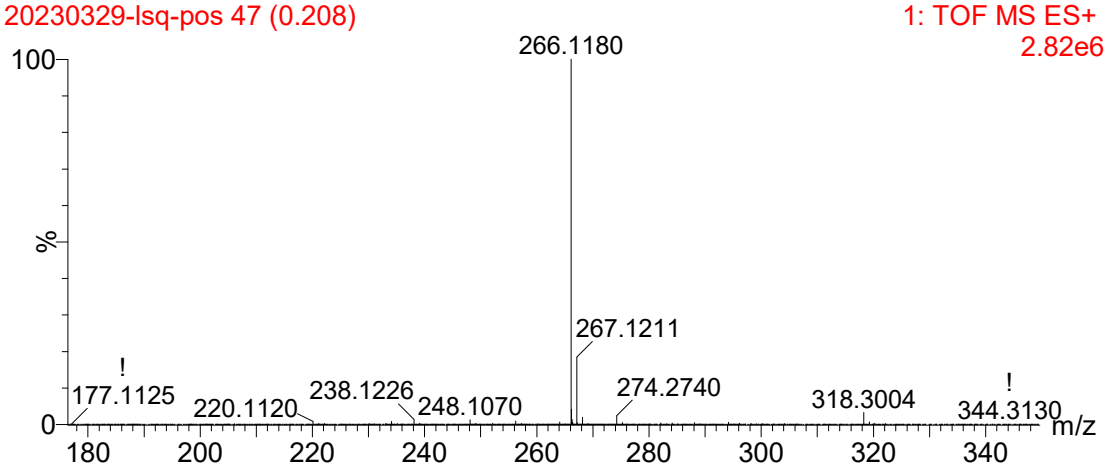

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



**HRMS** (ESI)

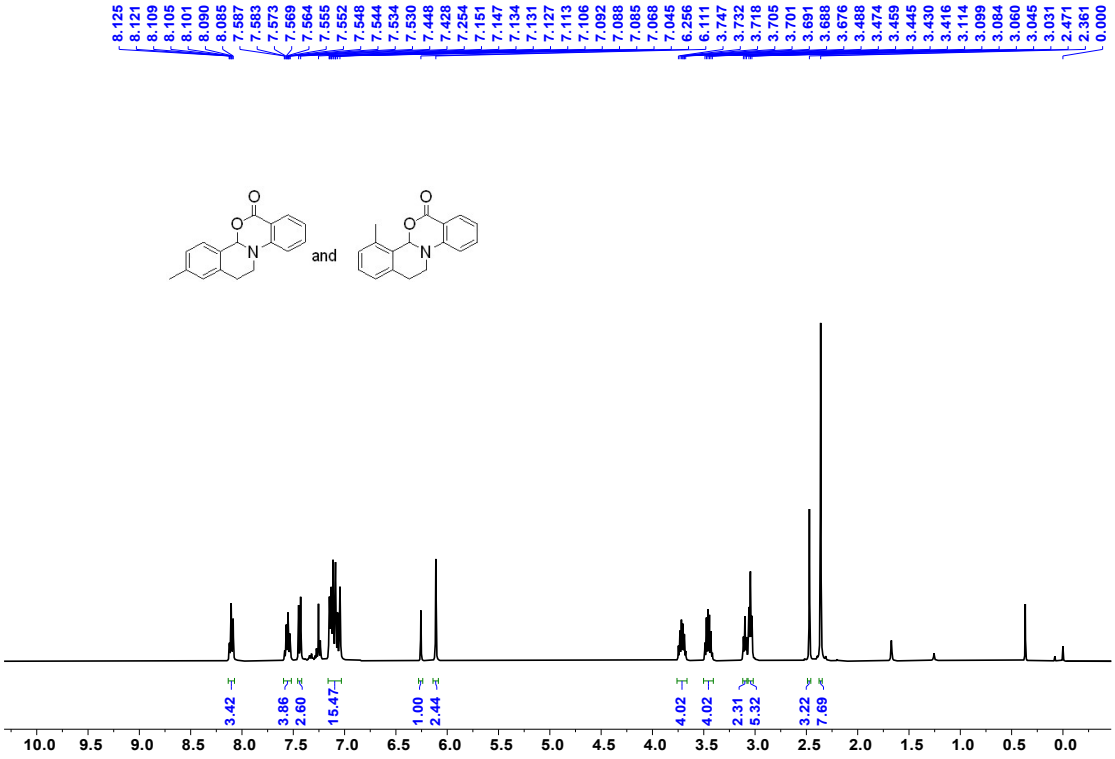



Chemical Formula: $C_{17}H_{16}NO_2^+$
m/z: 266.1176 (100.0%), 267.1209 (18.4%), 268.1243 (1.6%)

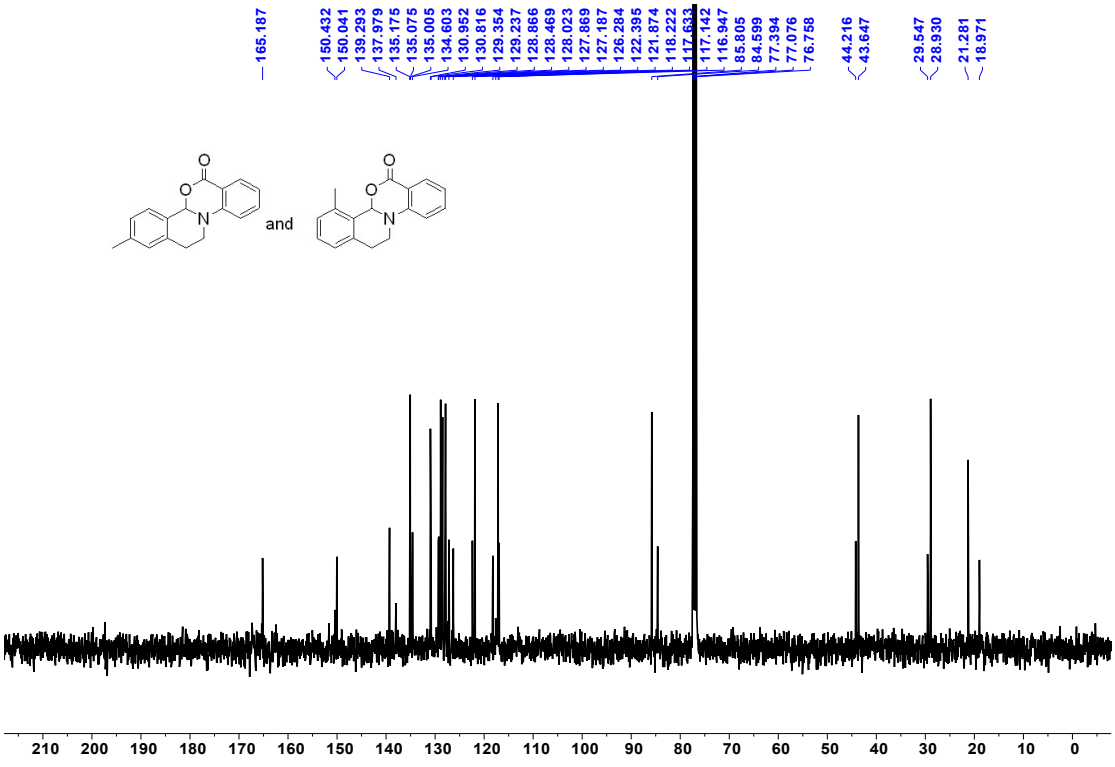


2-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3da)** and 4-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ea)**

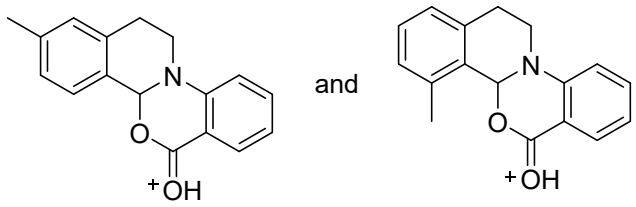
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

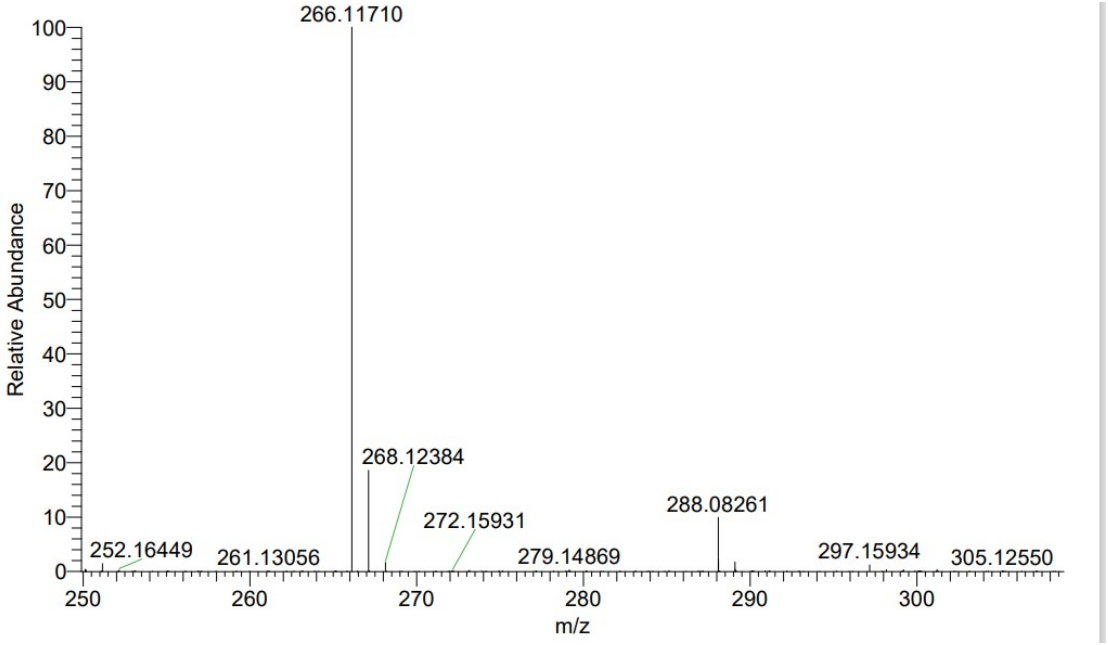


**HRMS** (ESI)



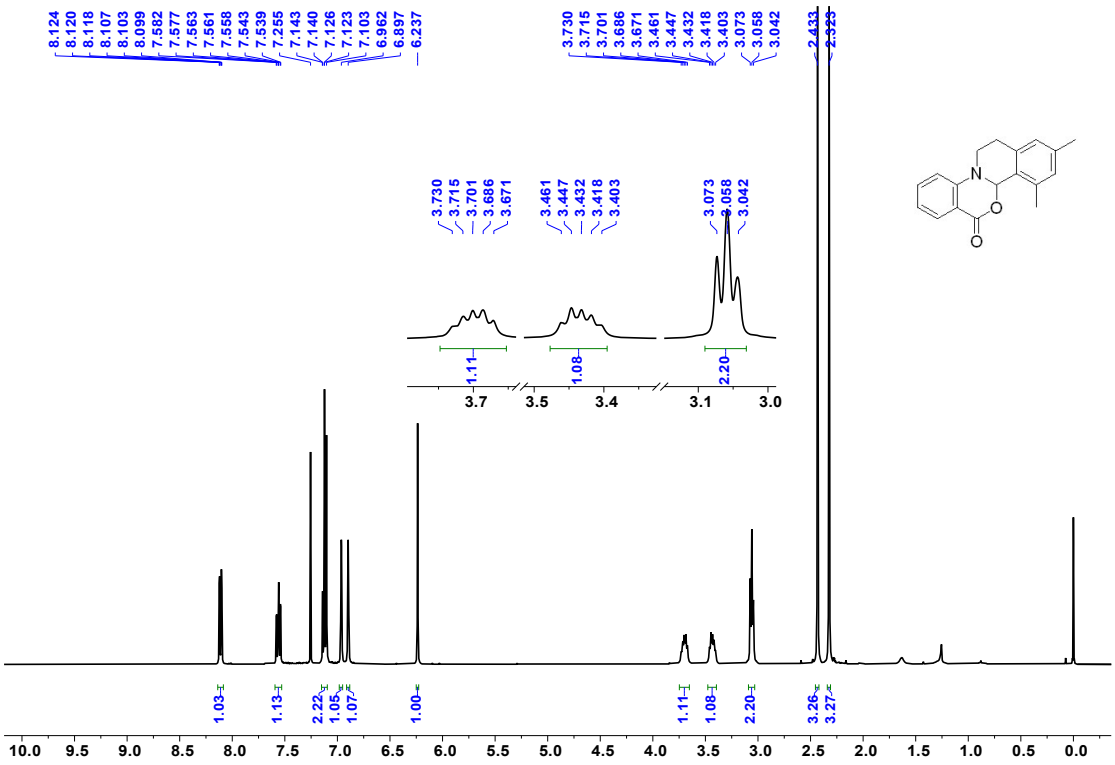
Chemical Formula: $C_{17}H_{16}NO_2^+$

m/z: 266.1176 (100.0%), 267.1209 (18.4%), 268.1243 (1.6%)

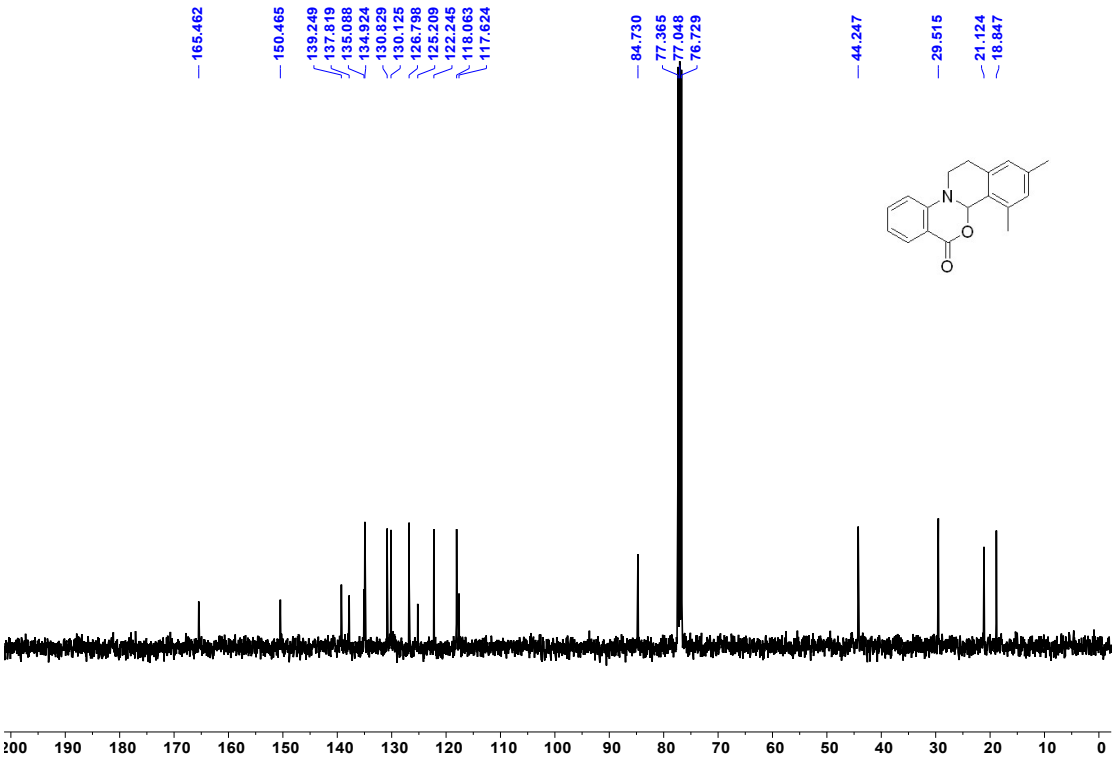


2,4-dimethyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3fa)**

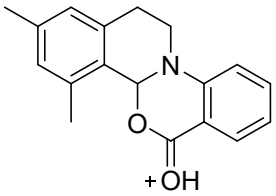
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

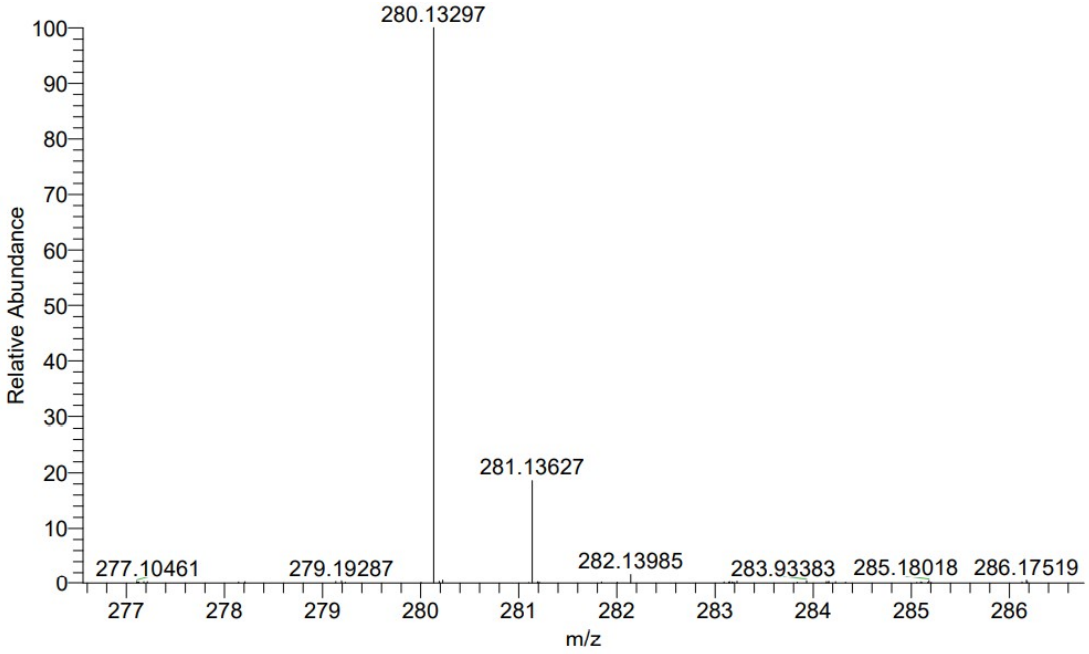


**HRMS** (ESI)



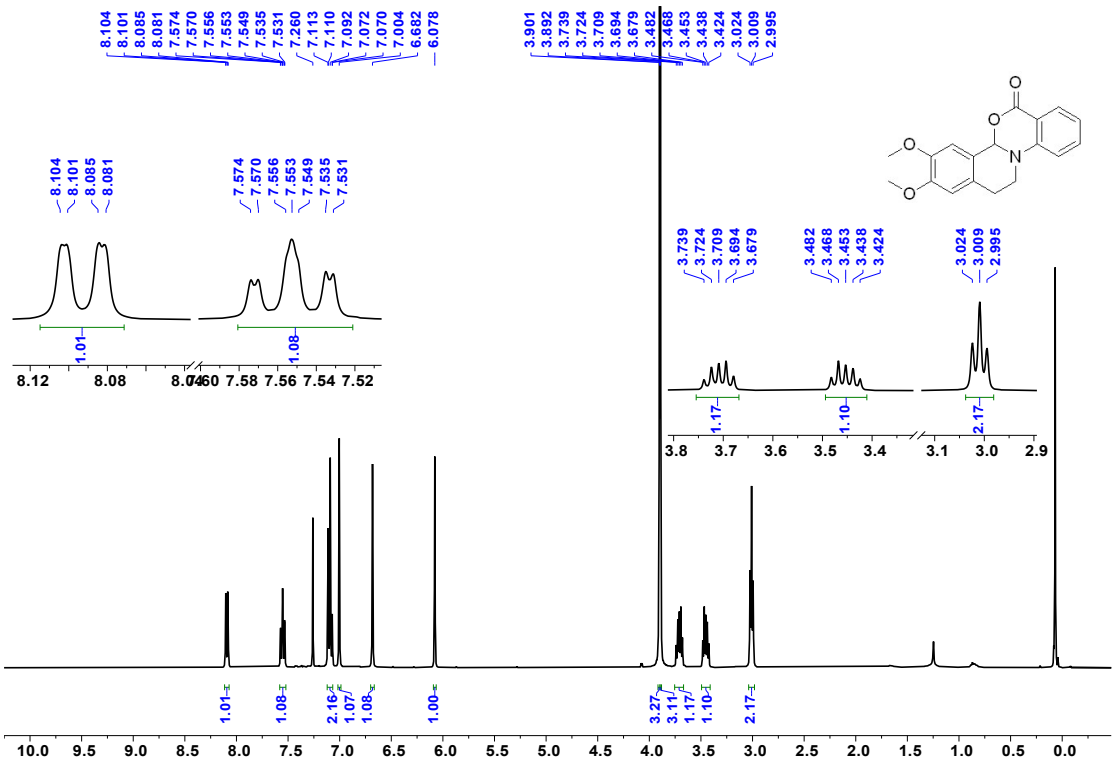

Chemical Formula: $C_{18}H_{18}NO_2^+$

m/z: 280.1332 (100.0%), 281.1366 (19.5%), 282.1399 (1.8%)

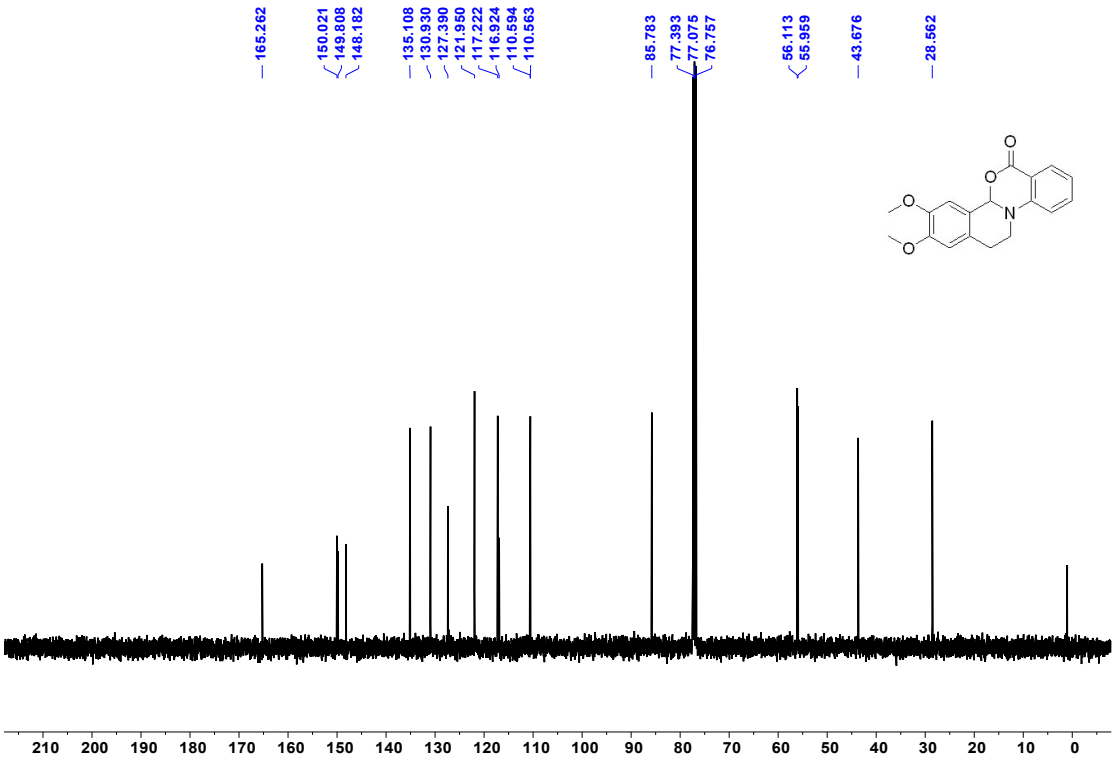


2,3-dimethoxy-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ga)**

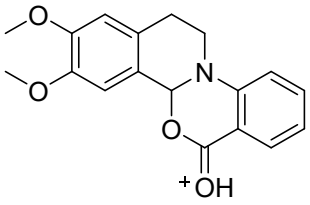
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

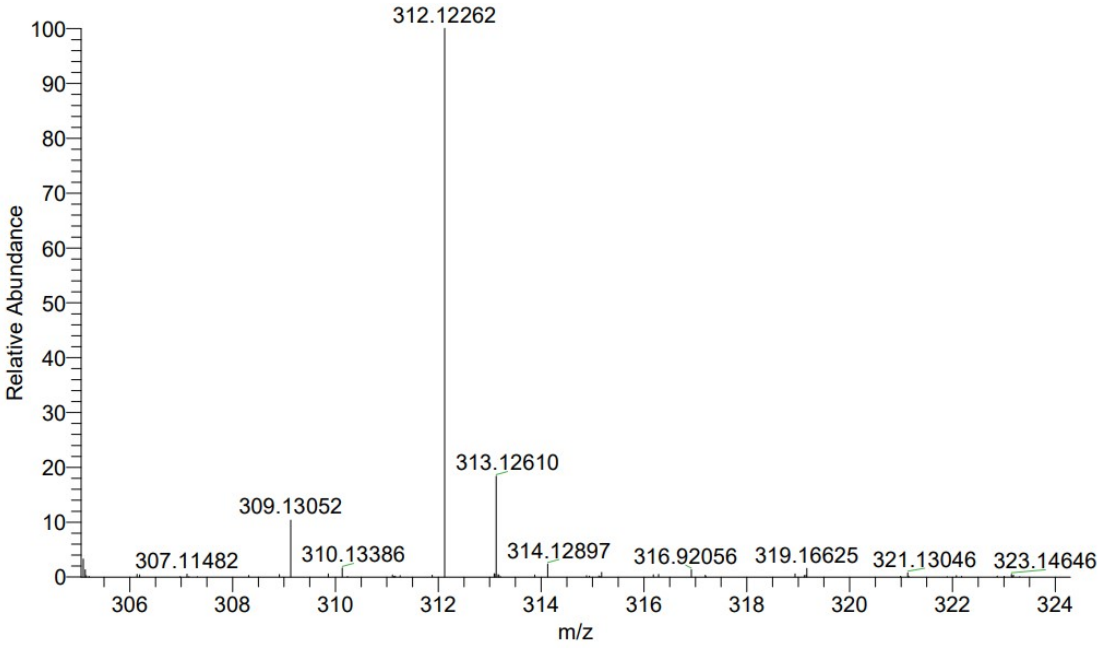


**HRMS** (ESI)



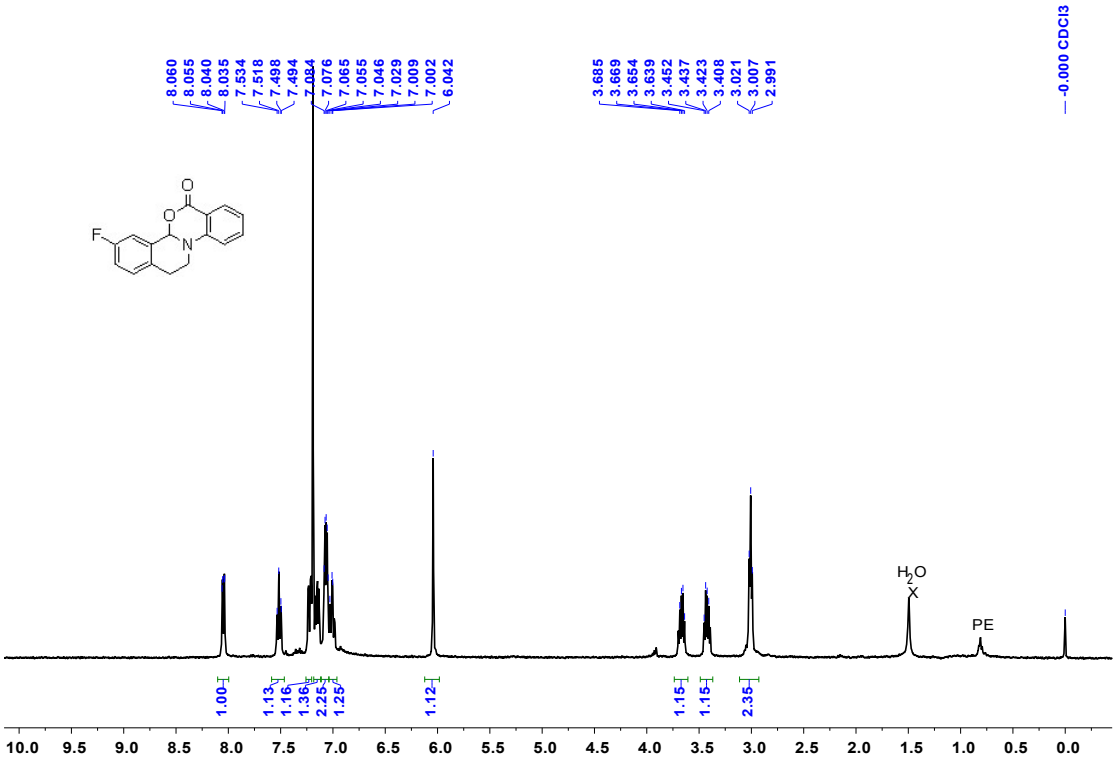

Chemical Formula: $C_{18}H_{18}NO_4^+$

m/z: 312.1230 (100.0%), 313.1264 (19.5%), 314.1297 (1.8%)

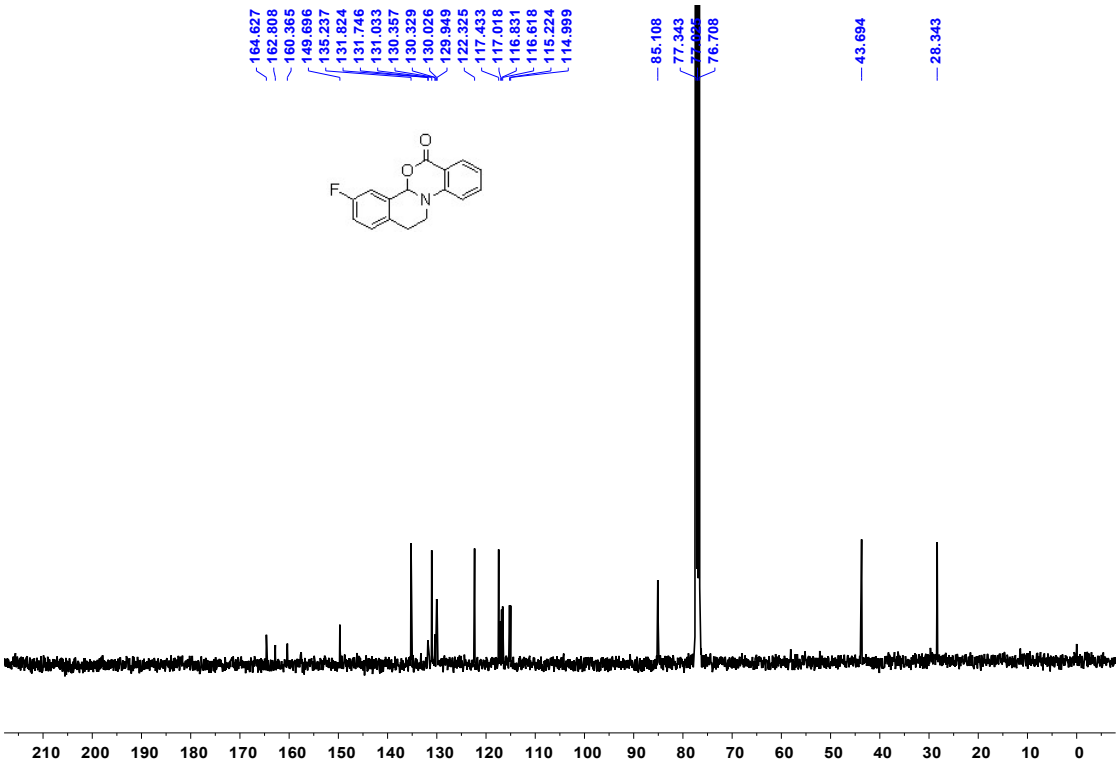


3-fluoro-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ha)**

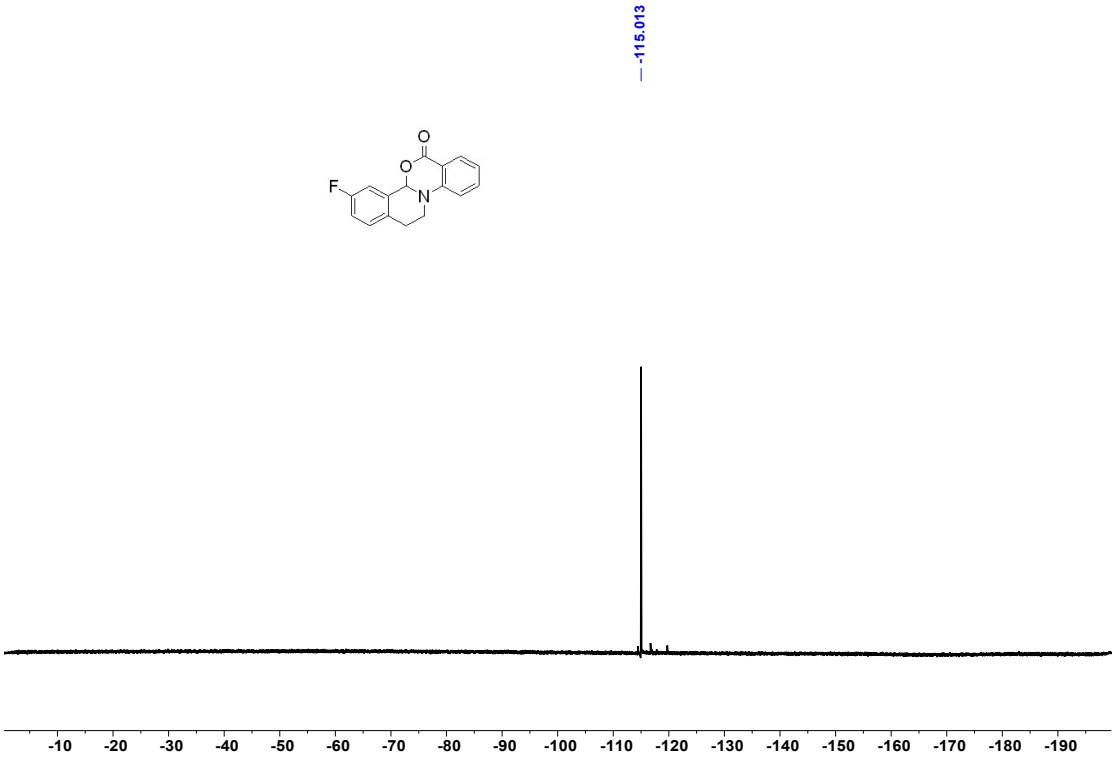
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



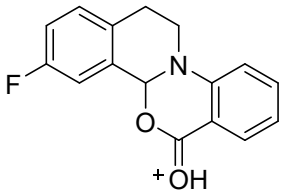

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



**$^{19}$F NMR** (376 MHz, CDCl3)

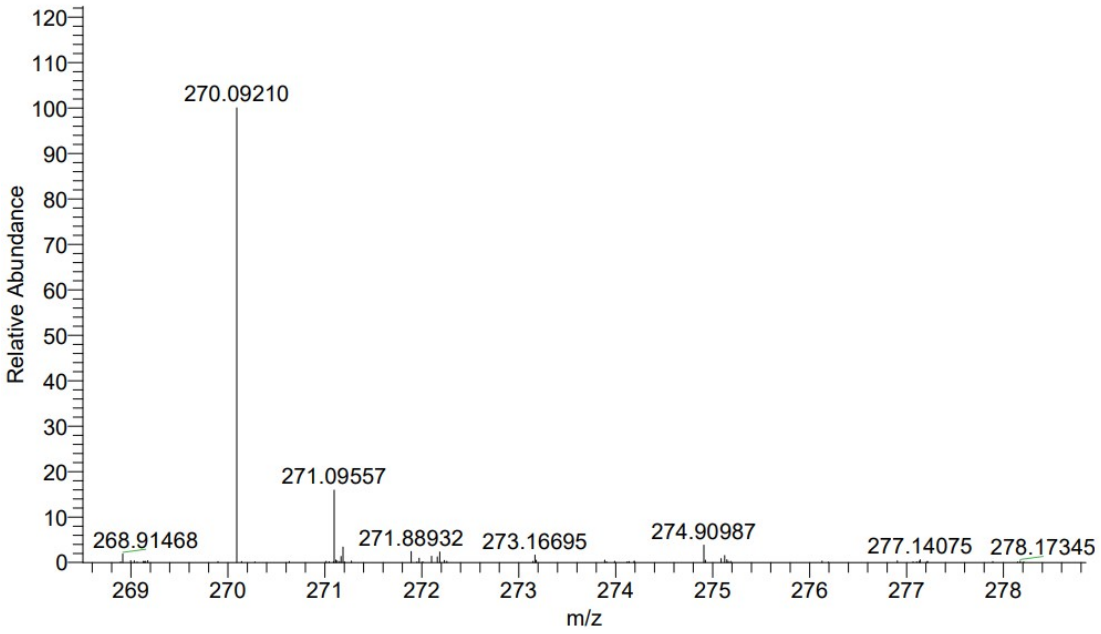



**HRMS** (ESI)



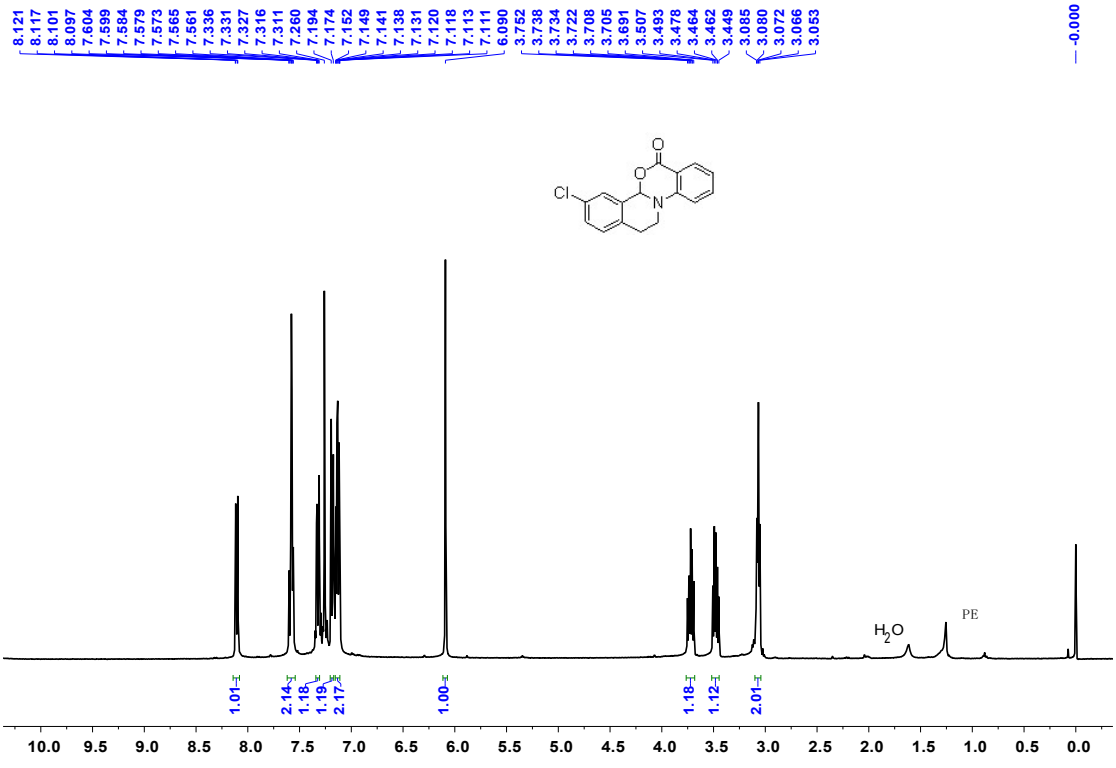

Chemical Formula: $C_{16}H_{13}FNO_2^+$

m/z: 270.0925 (100.0%), 271.0958 (17.3%), 272.0992 (1.4%)

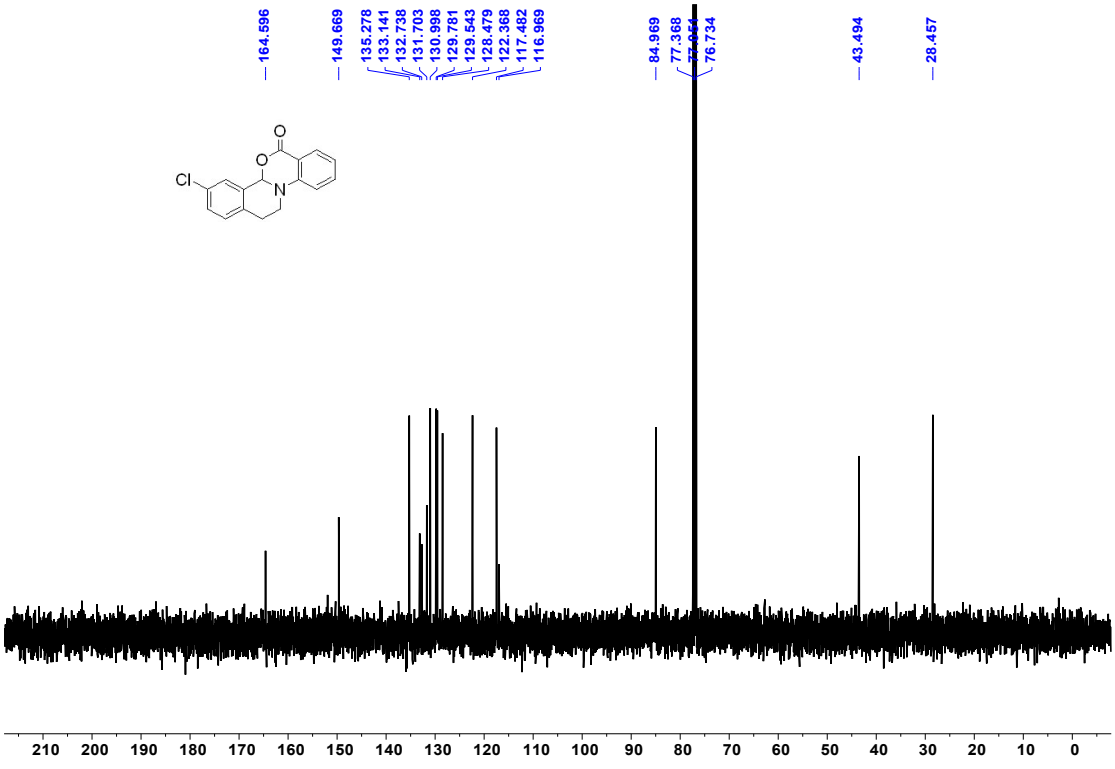



3-chloro-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ia)**

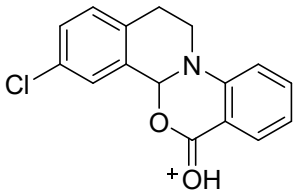
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

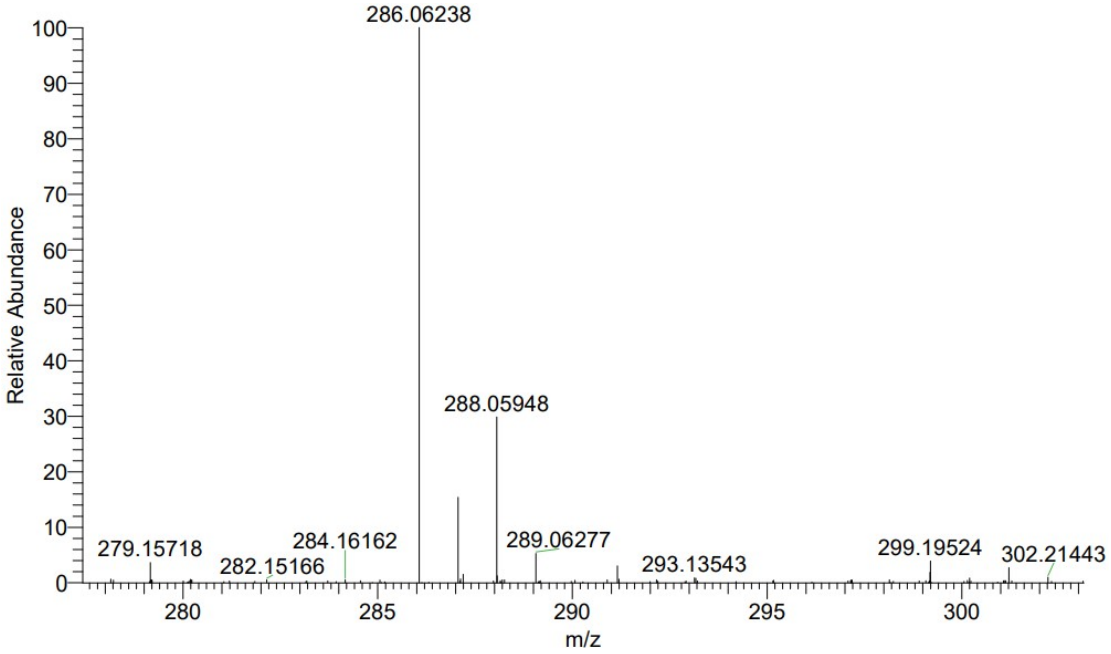



**HRMS** (ESI)



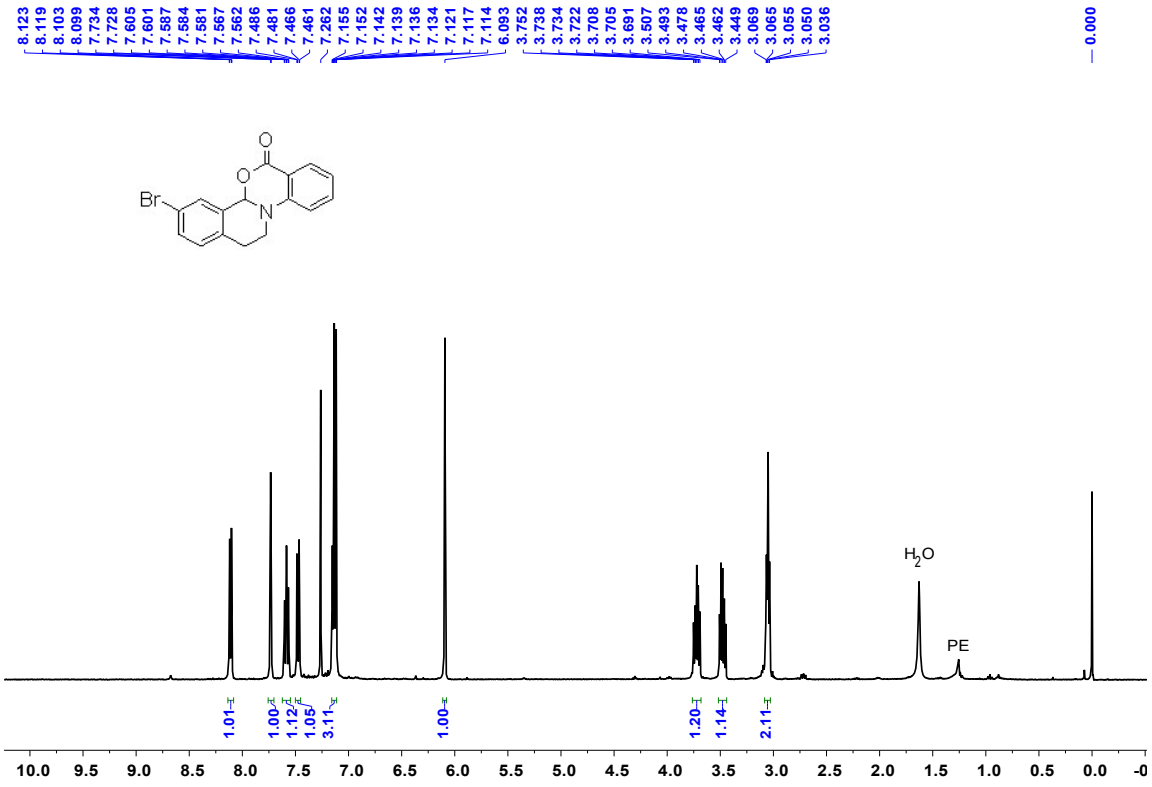

Chemical Formula: $C_{16}H_{13}ClNO_2^+$

m/z: 286.0629 (100.0%), 288.0600 (32.0%), 287.0663 (17.3%)

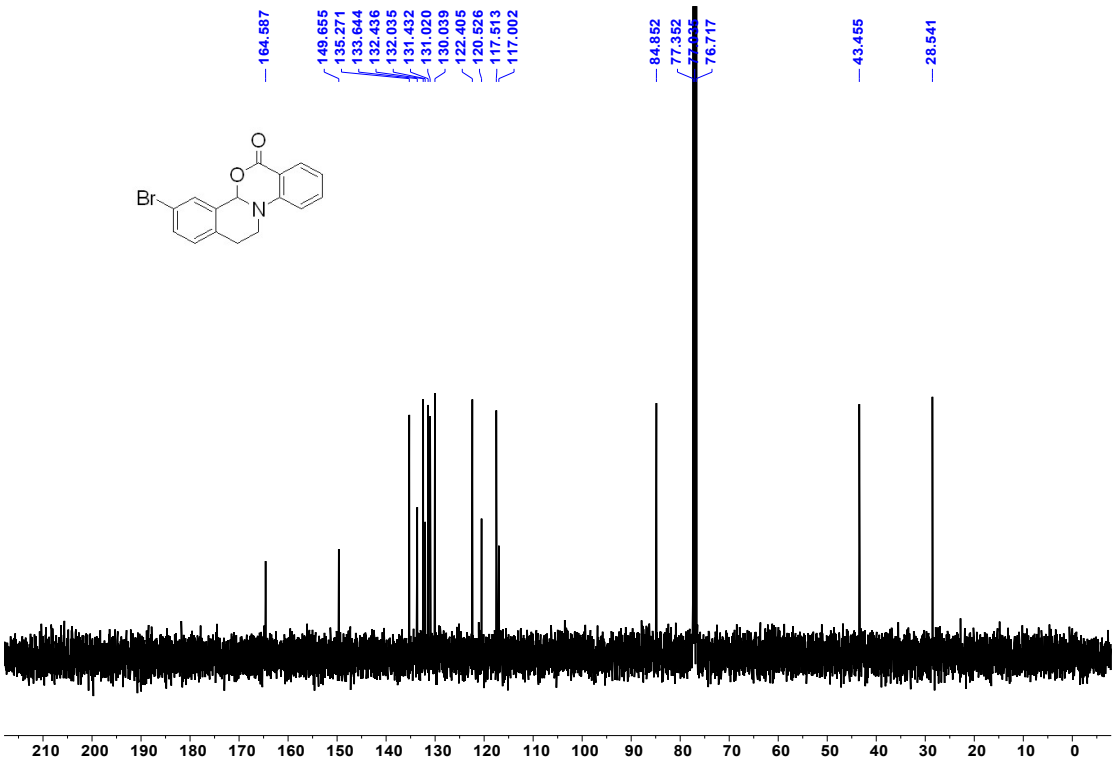

286.06238
288.05948
279.15718
282.15166
284.16162
289.06277
293.13543
299.19524
302.21443
Relative Abundance
m/z
100
90
80
70
60
50
40
30
20
10
0
280
285
290
295
300

3-bromo-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ja)**

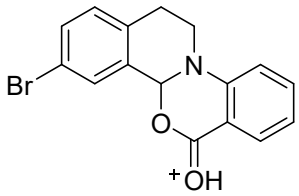
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

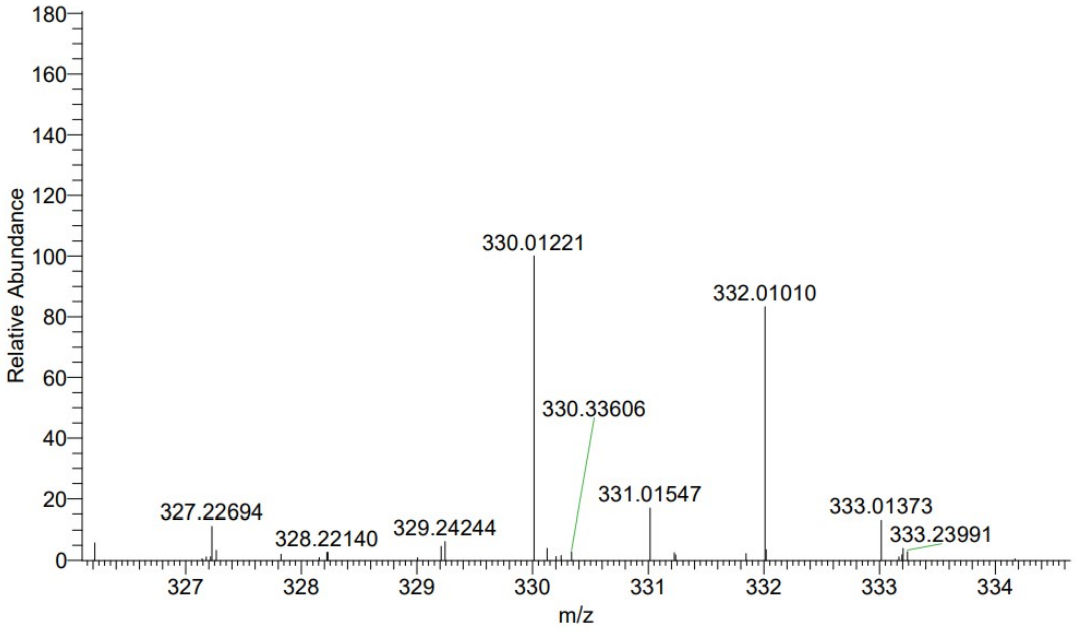


**HRMS** (ESI)



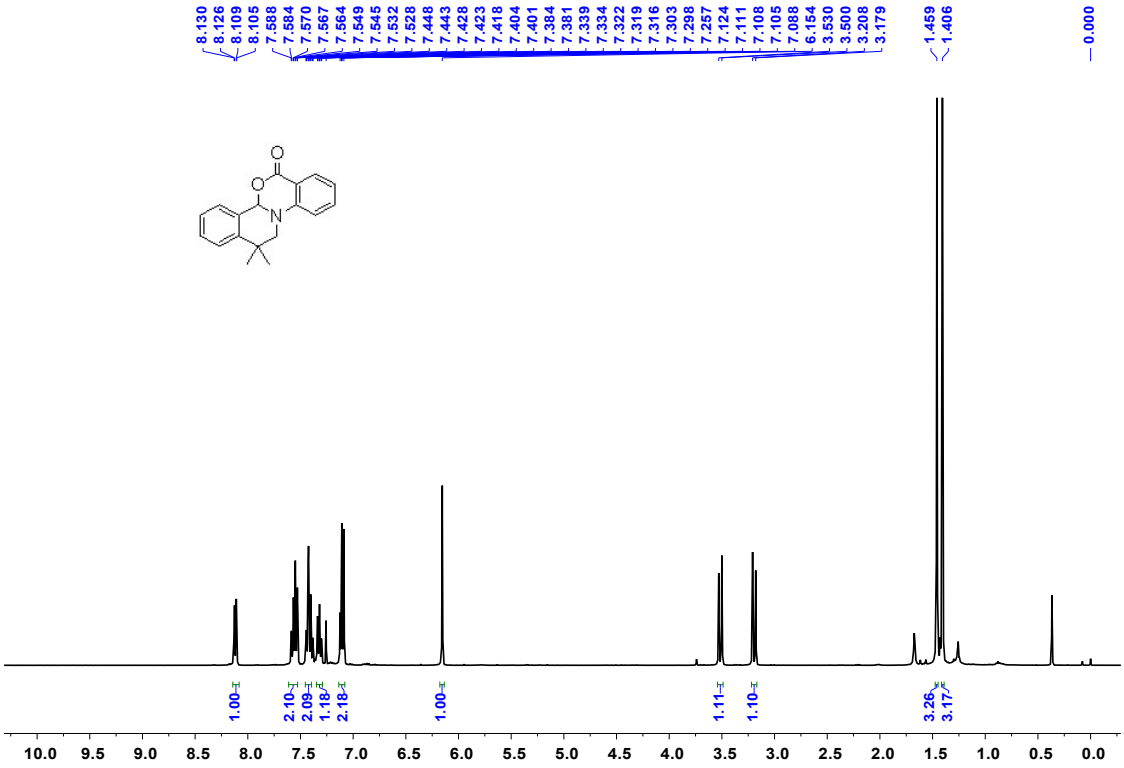

Chemical Formula: $C_{16}H_{13}BrNO_2^+$

m/z: 330.0124 (100.0%), 332.0104 (97.3%)

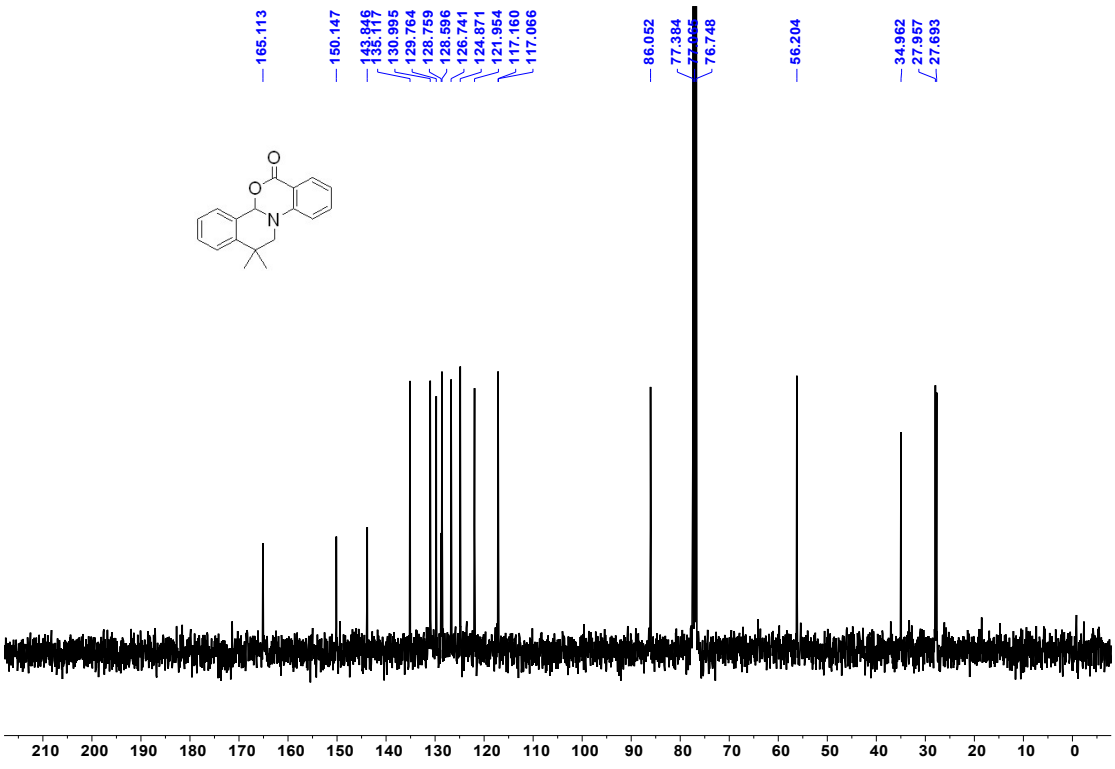


13,13-dimethyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ka)**

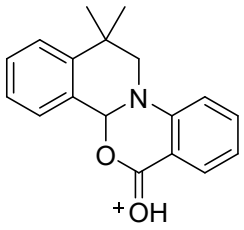
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

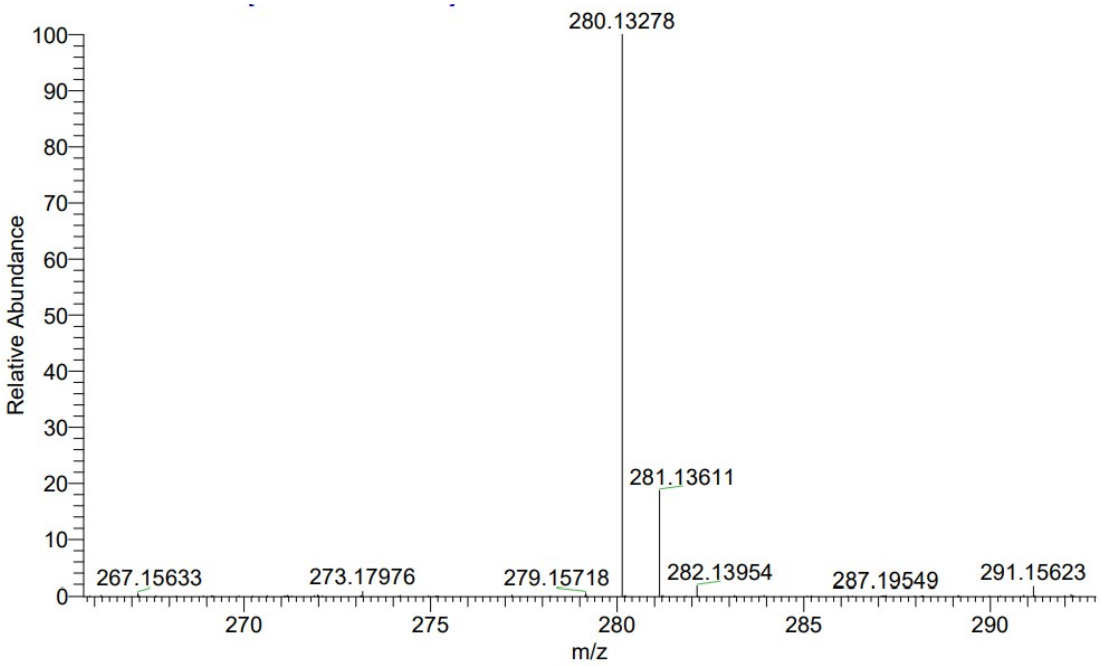


**HRMS** (ESI)



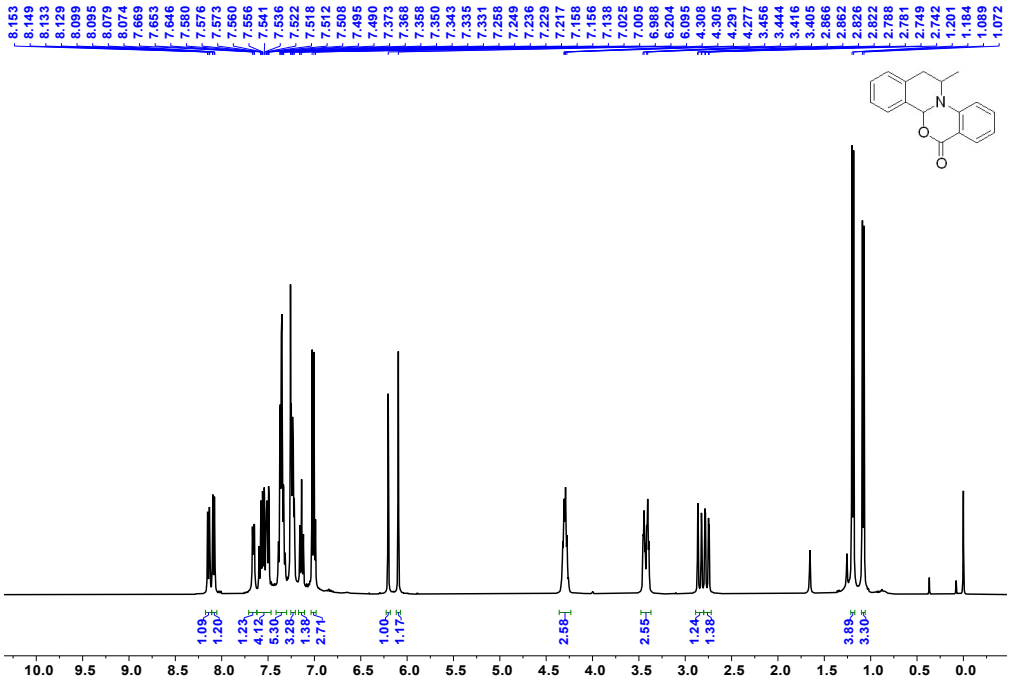

Chemical Formula: $C_{18}H_{18}NO_2^+$

m/z: 280.1332 (100.0%), 281.1366 (19.5%), 282.1399 (1.8%)

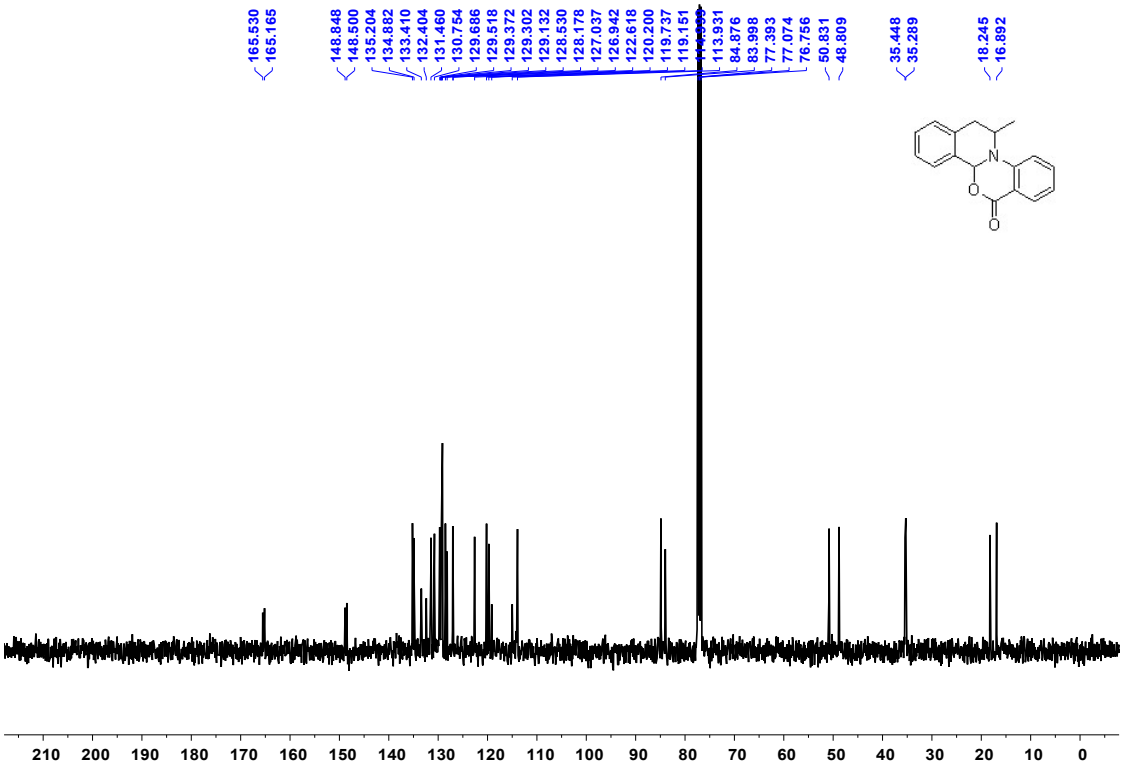


12-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3la)**

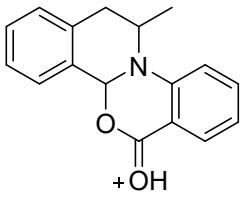
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



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

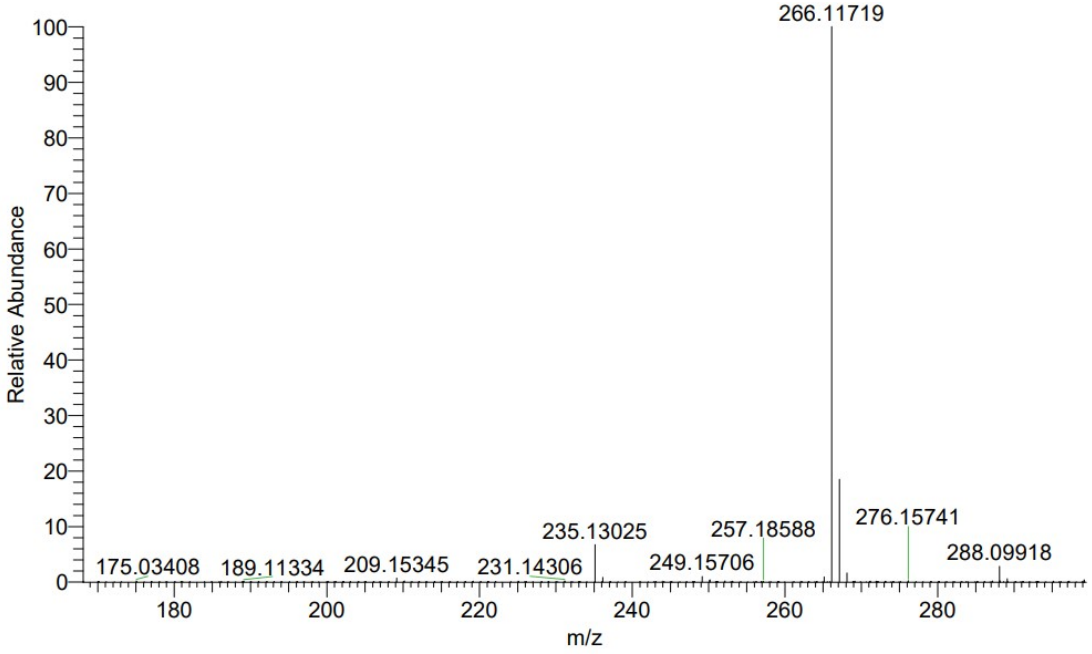


**HRMS** (ESI)



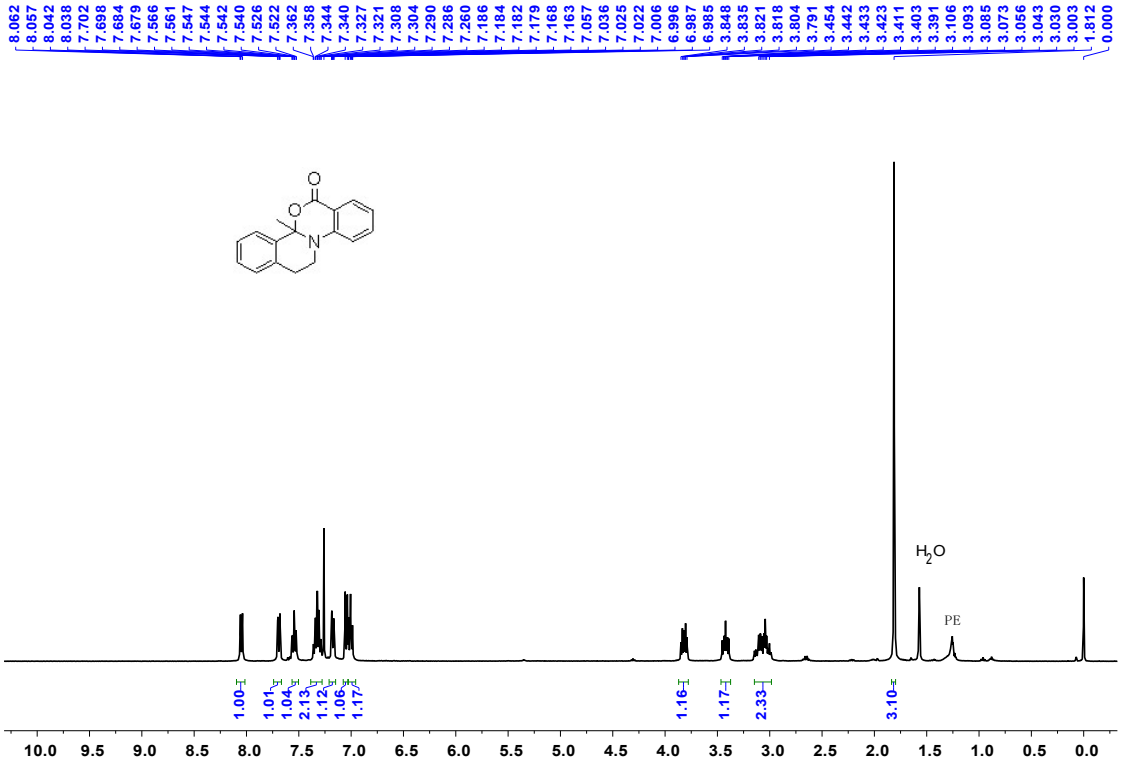

Chemical Formula: $C_{17}H_{16}NO_2^+$

m/z: 266.1176 (100.0%), 267.1209 (18.4%), 268.1243 (1.6%)

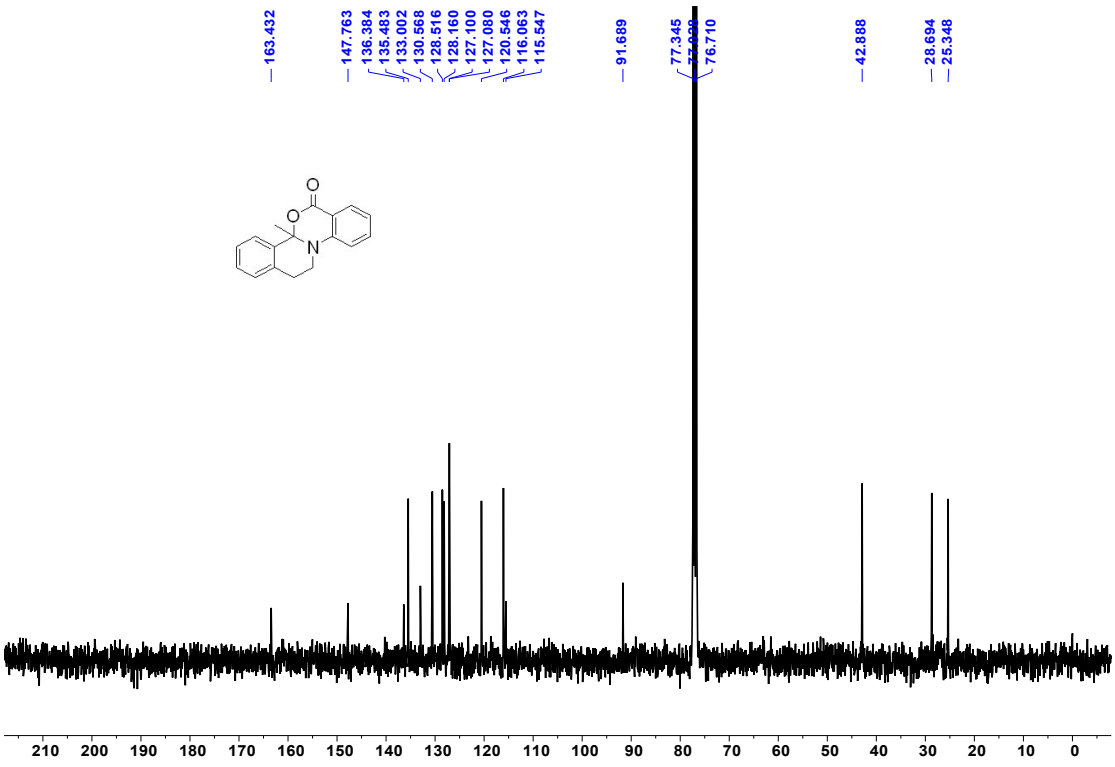


4b-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ma)**

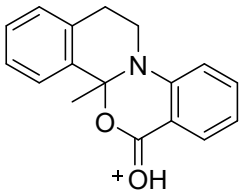
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

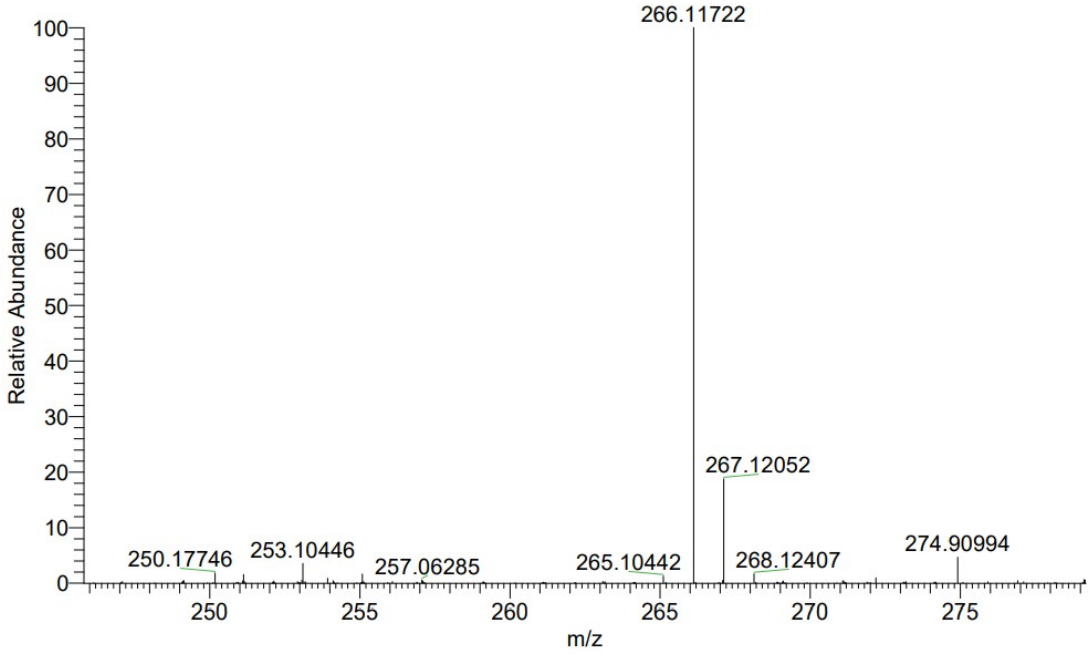


**HRMS** (ESI)




Chemical Formula: $C_{17}H_{16}NO_2^+$

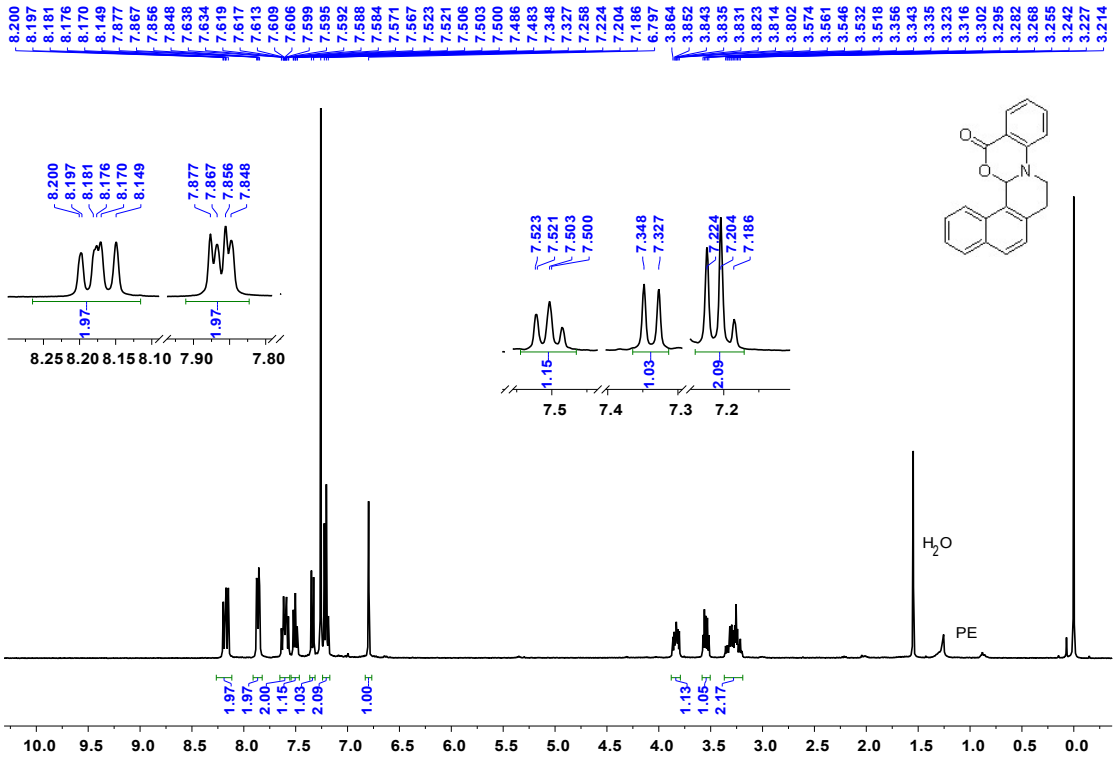
m/z: 266.1176 (100.0%), 267.1209 (18.4%), 268.1243 (1.6%)



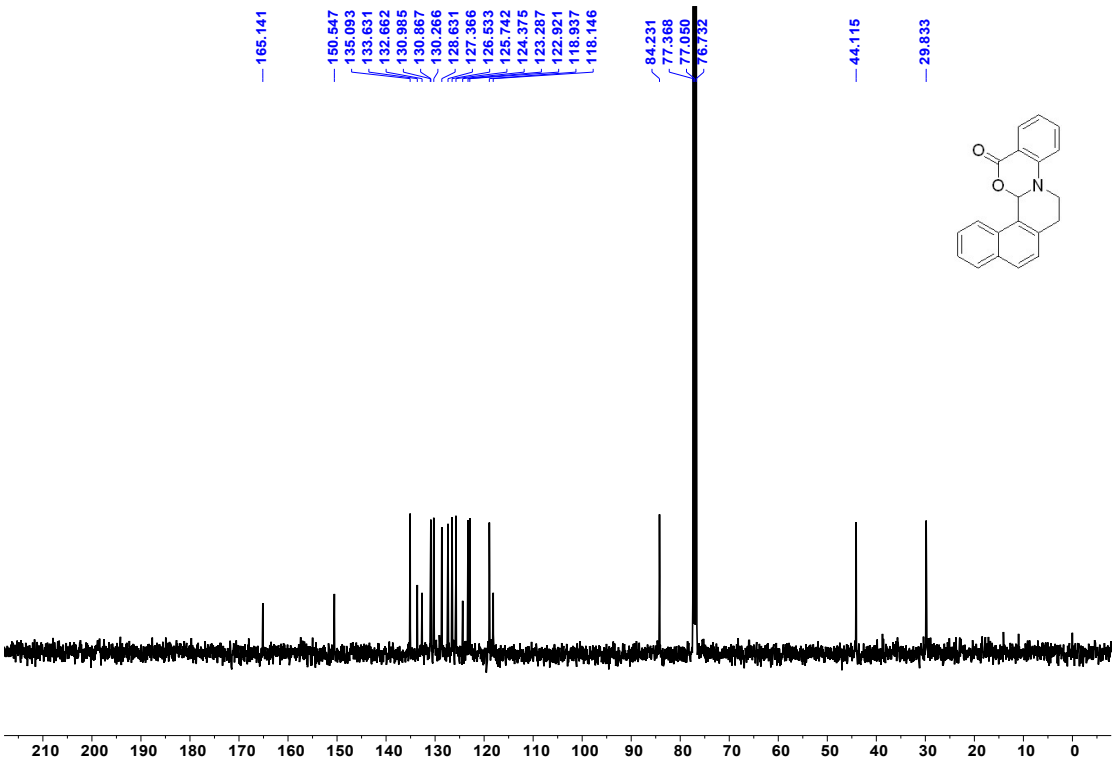
7,13c-dihydro-6*H*,15*H*-benzo[h]benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-15-one

**(3na)**

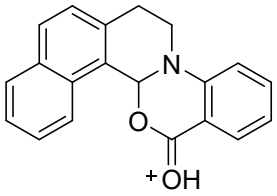
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

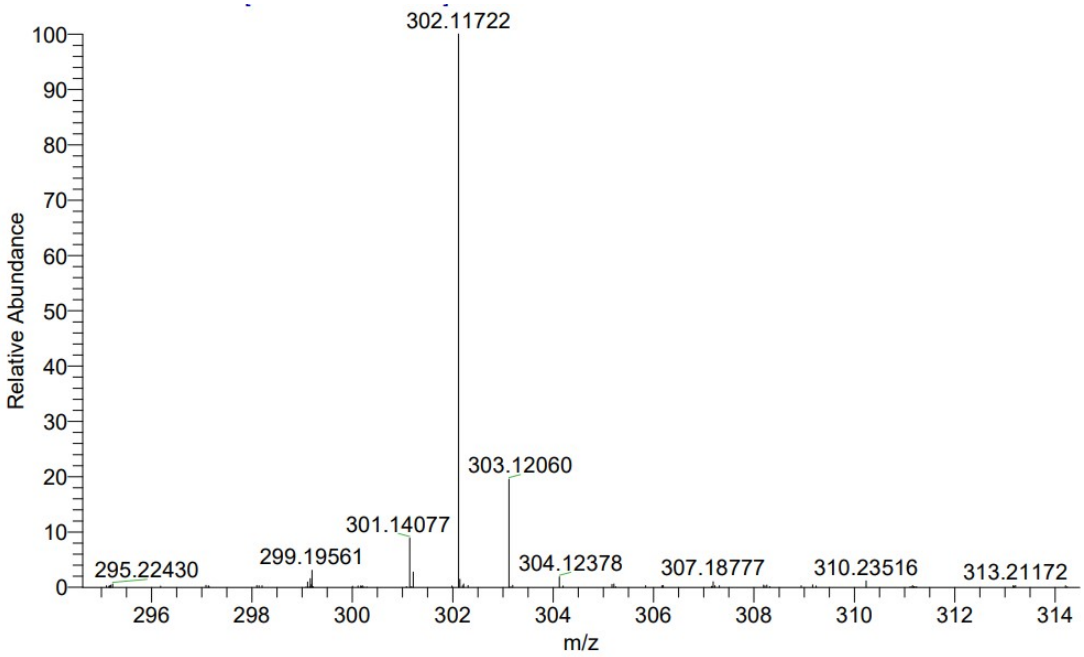


**HRMS** (ESI)



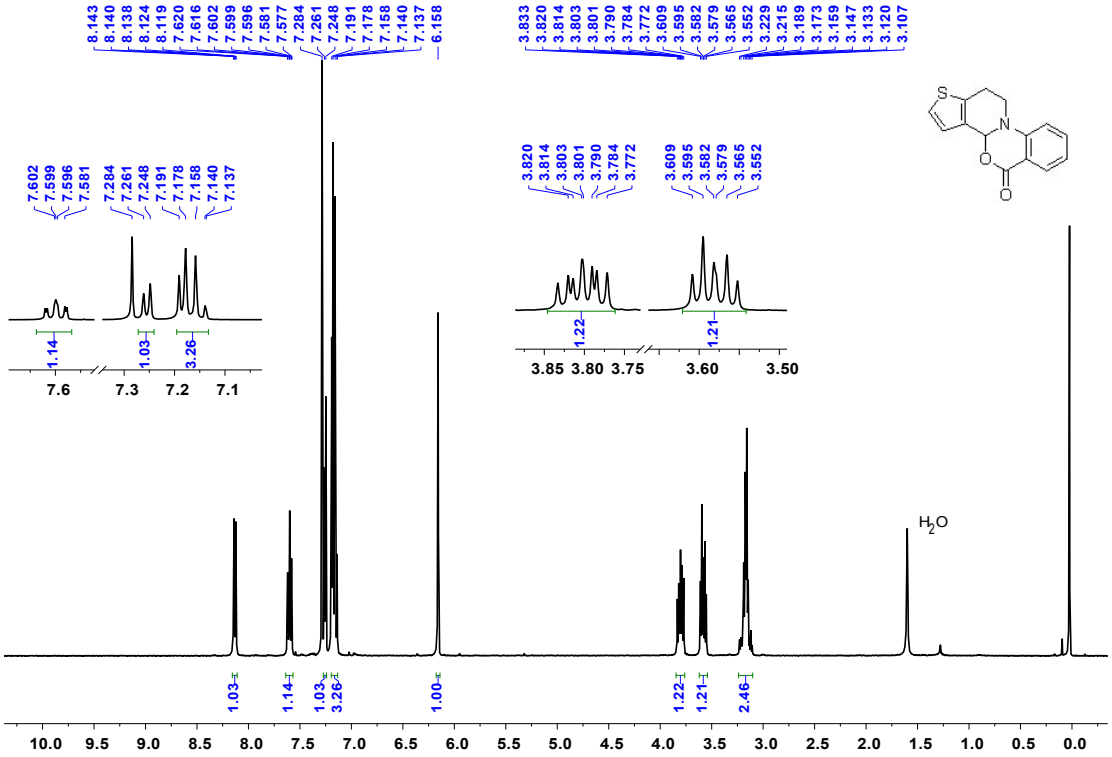

Chemical Formula: $C_{20}H_{16}NO_2^+$

m/z: 302.1176 (100.0%), 303.1209 (21.6%), 304.1243 (2.2%)

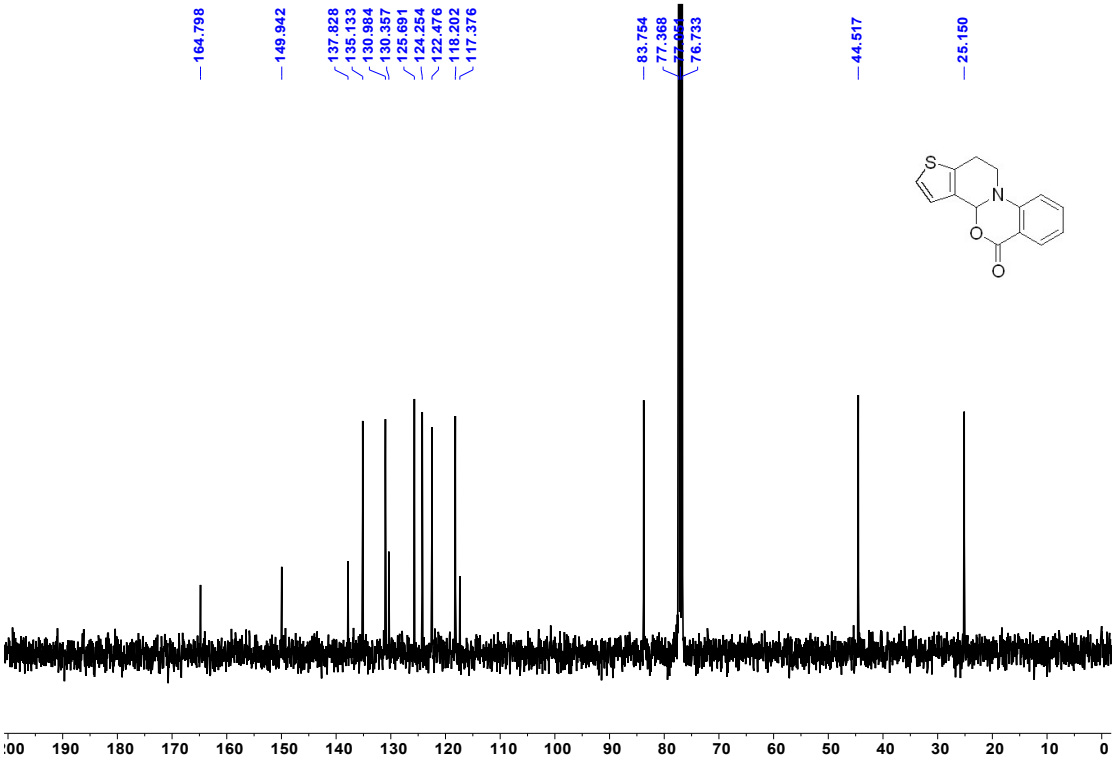


3b,12-dihydro-5*H*,11*H*-benzo[d]thieno[3',2':3,4]pyrido[2,1-*b*][1,3]oxazin-5-one **(3oa)**

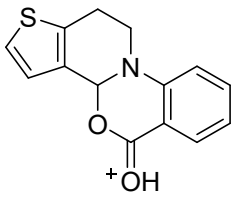
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

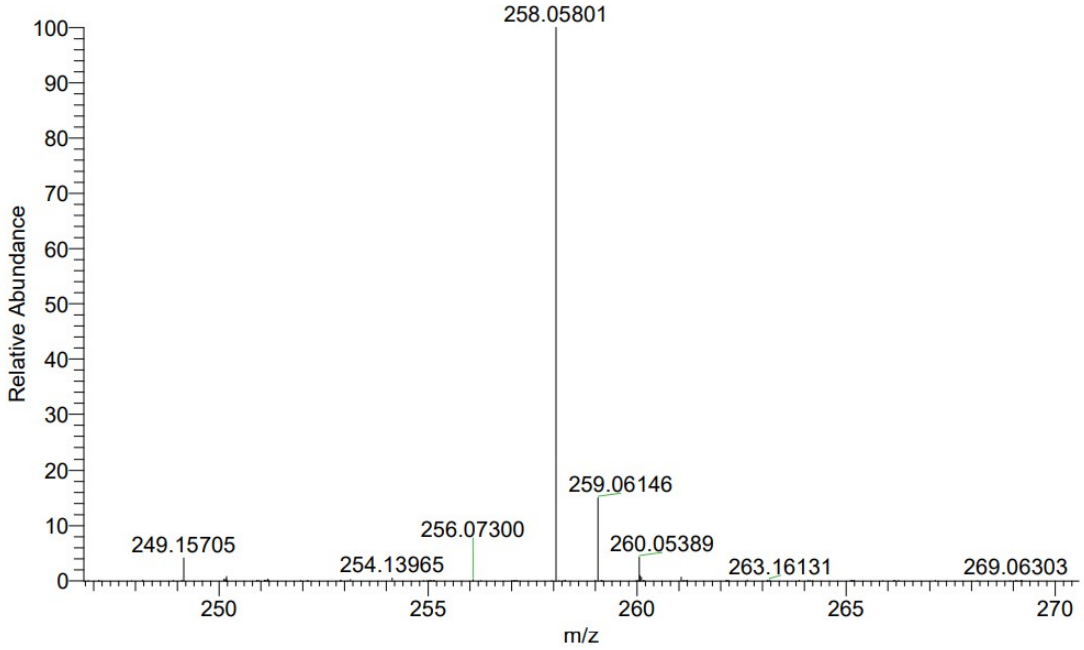


**HRMS** (ESI)



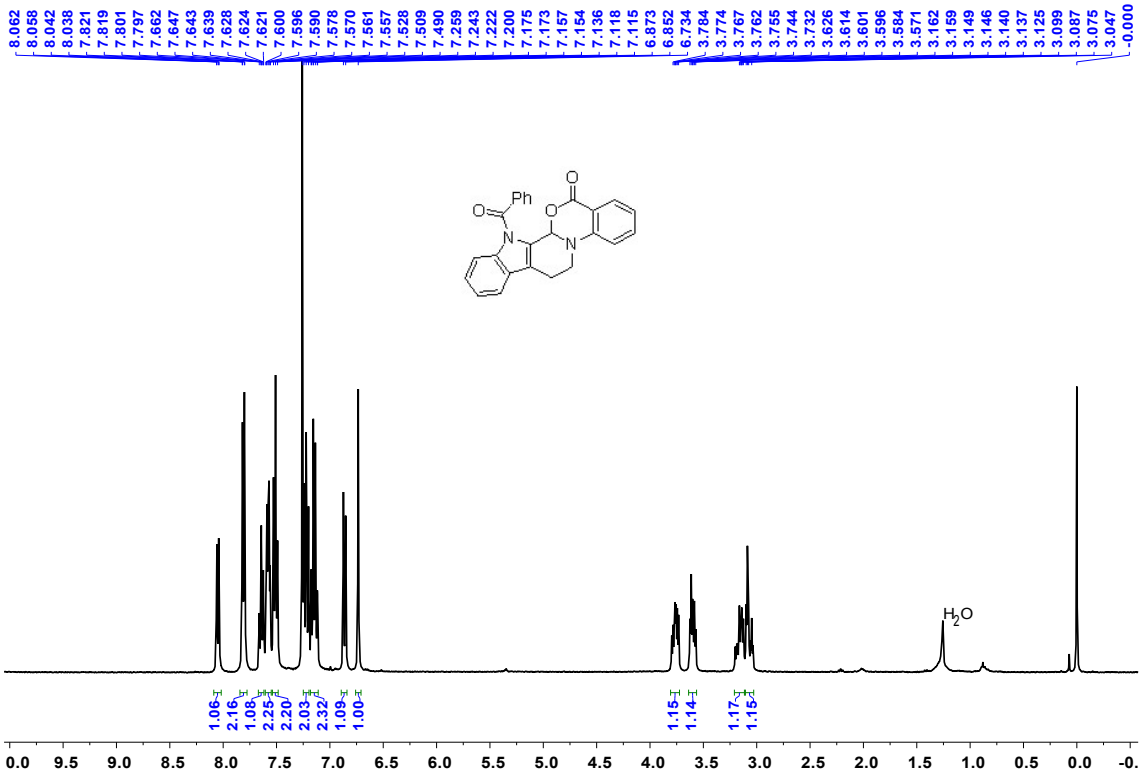

Chemical Formula: $C_{14}H_{12}NO_2S^+$

m/z: 258.0583 (100.0%), 259.0617 (15.1%), 260.0541 (4.5%), 260.0650 (1.1%)

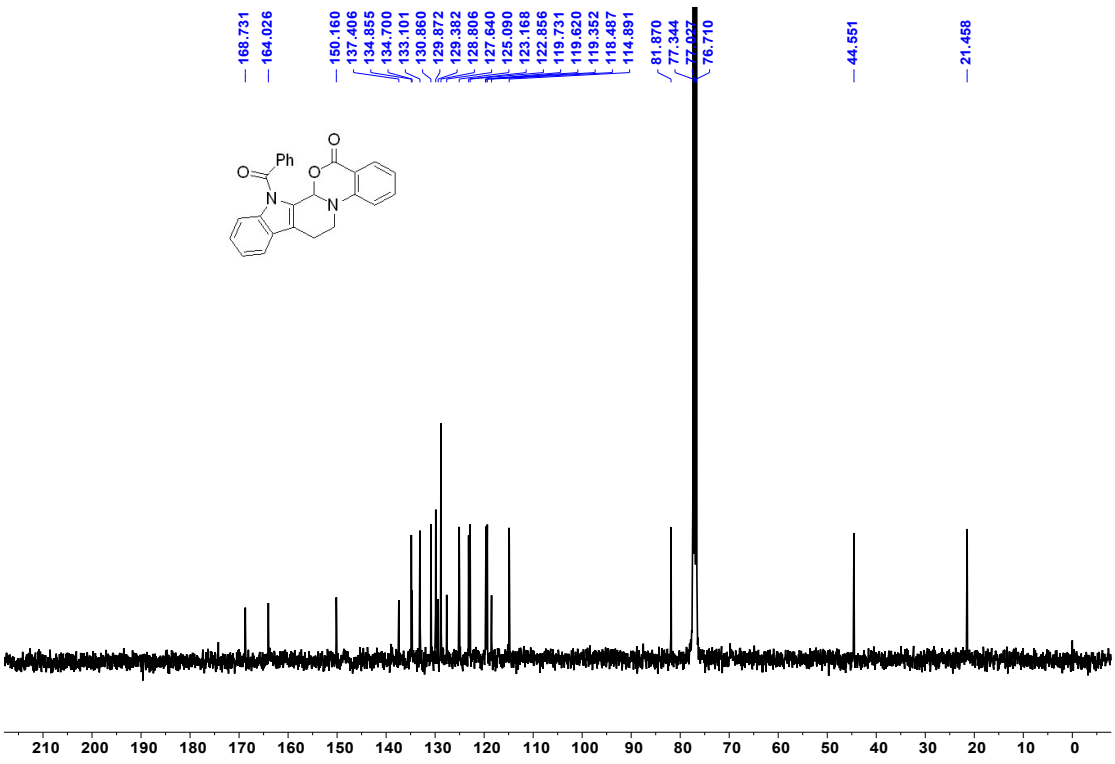


14-benzoyl-8,9,14,14b-tetrahydro-2*H*-benzo[4',5'][1,3]oxazino[3',2':1,2]pyrido[3,4-*b*]indol-2-one **(3pa)**

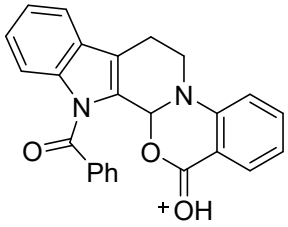
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



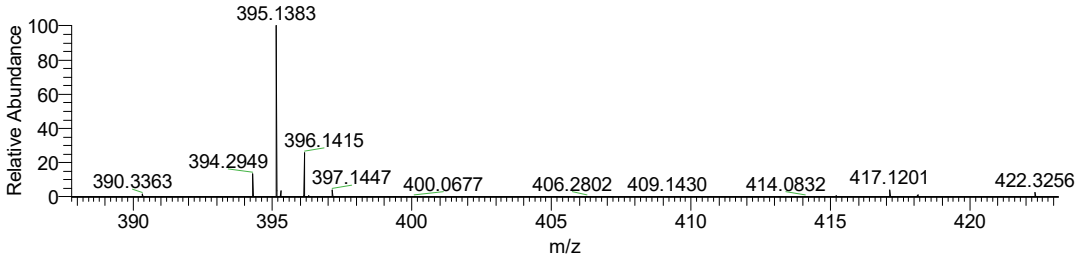

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



**LC-MS (**ESI**)**

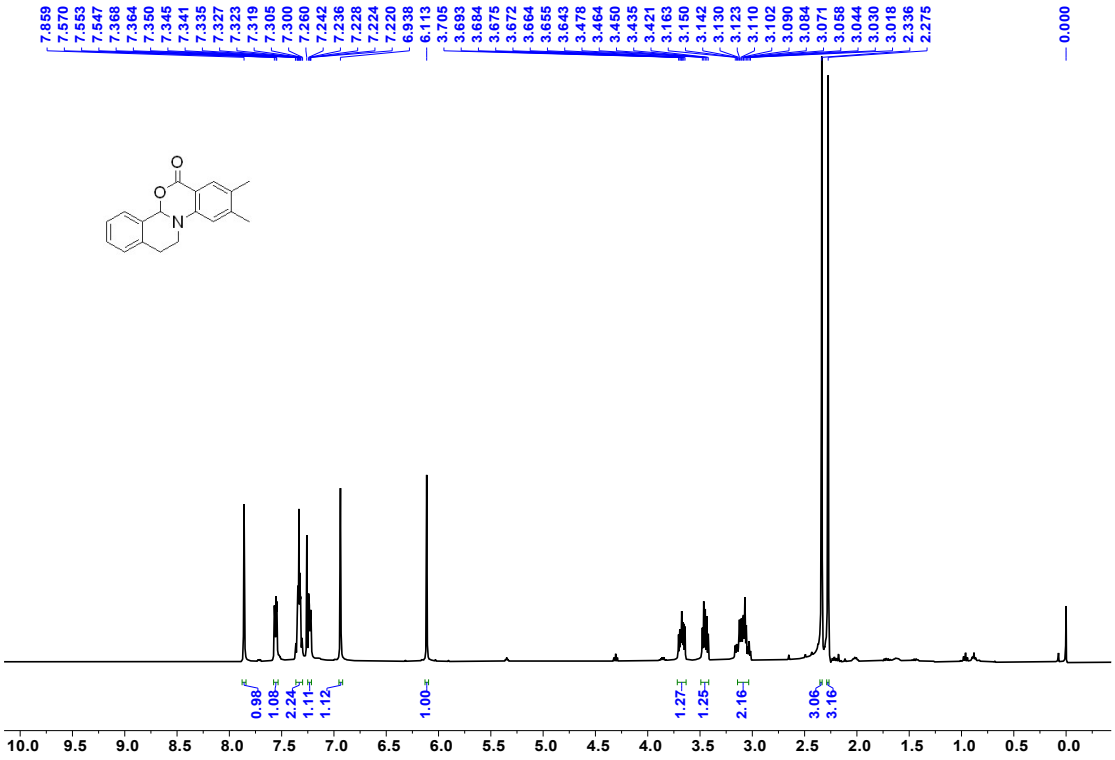



Chemical Formula: $C_{25}H_{19}N_2O_3^+$
m/z: 395.1390 (100.0%), 396.1424 (27.0%), 397.1457 (2.7%)

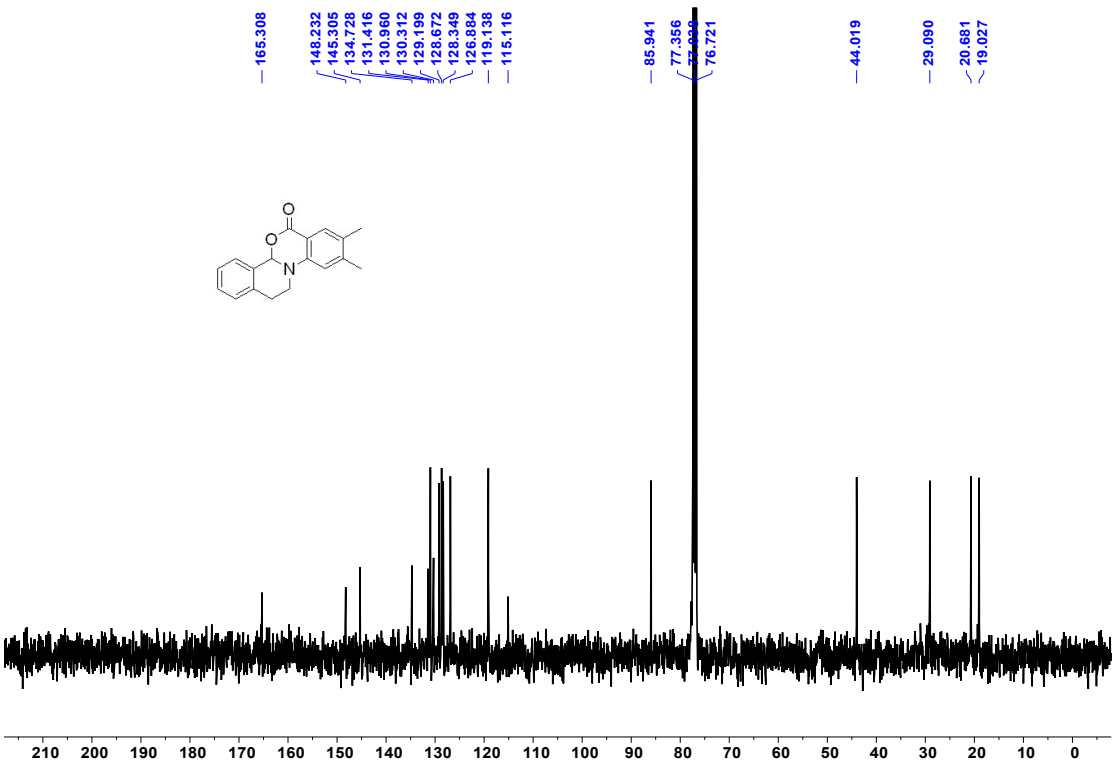


8,9-dimethyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ab)**

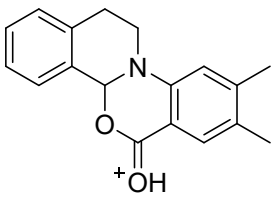
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

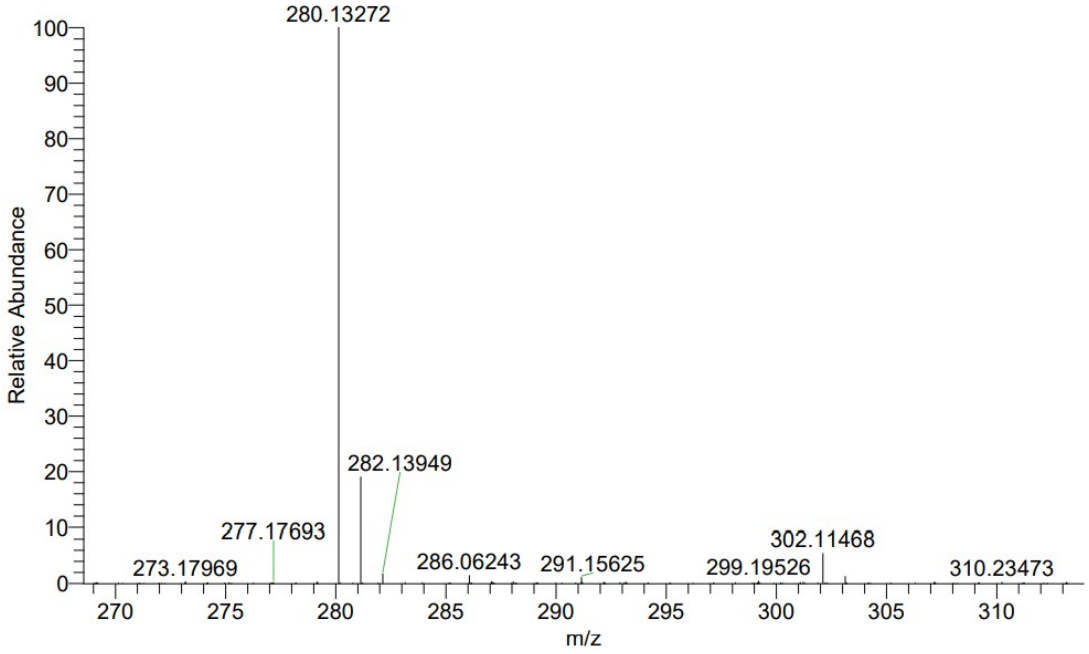


**HRMS** (ESI)



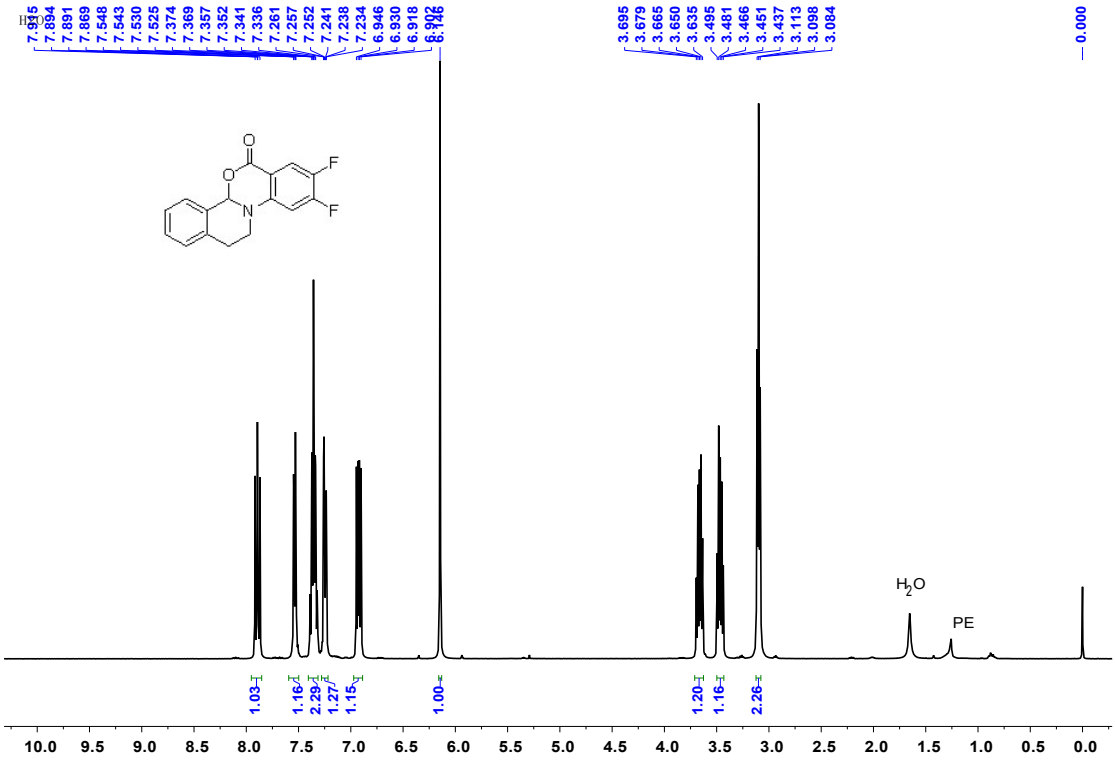

Chemical Formula: $C_{18}H_{18}NO_2^+$

m/z: 280.1332 (100.0%), 281.1366 (19.5%), 282.1399 (1.8%)

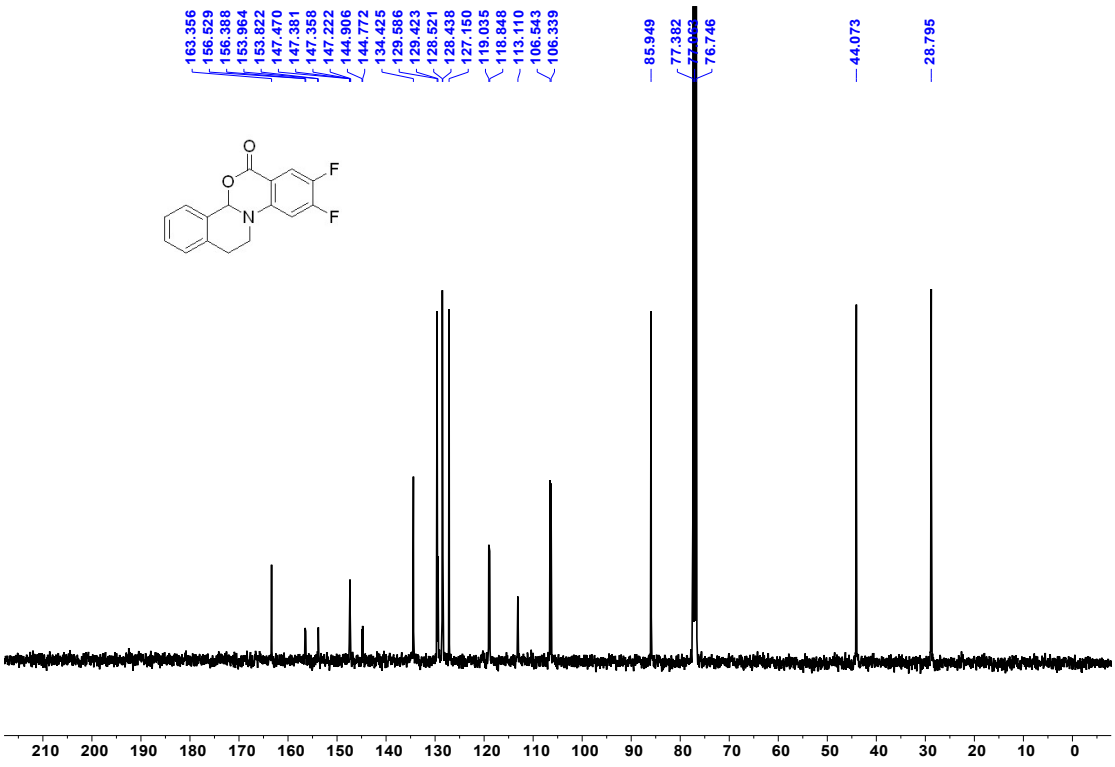


8,9-difluoro-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ac)**

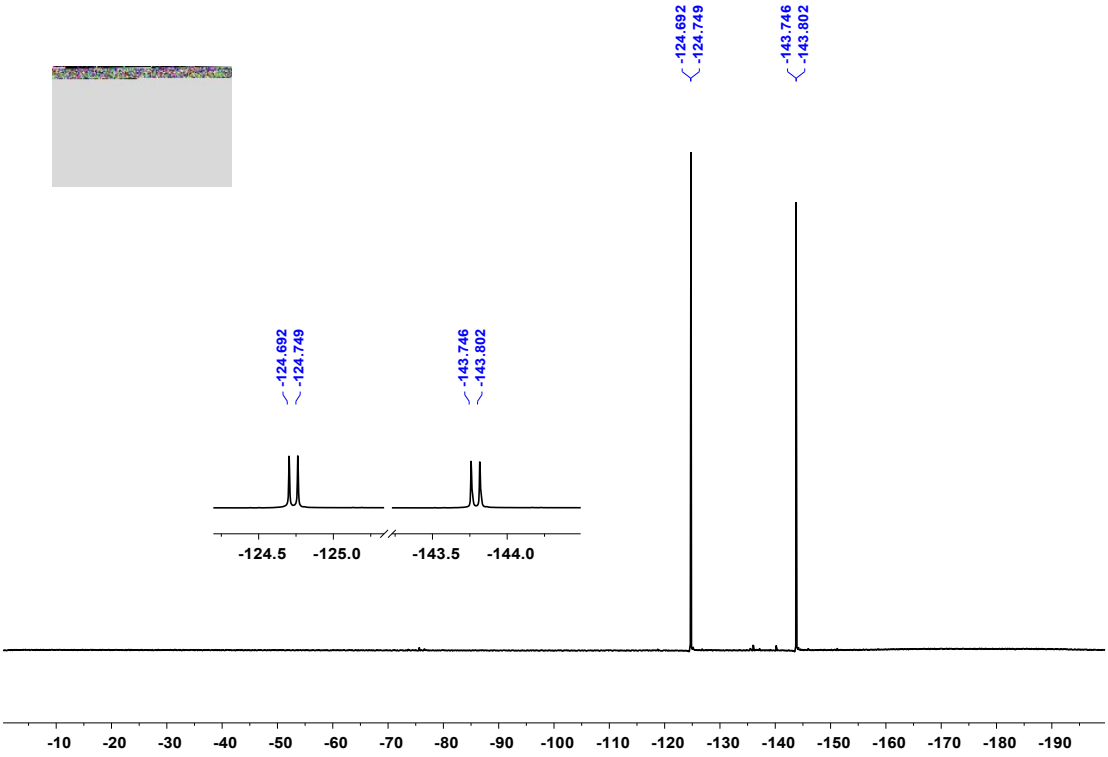
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



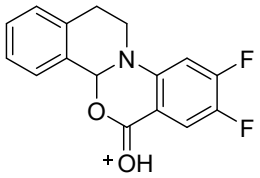

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



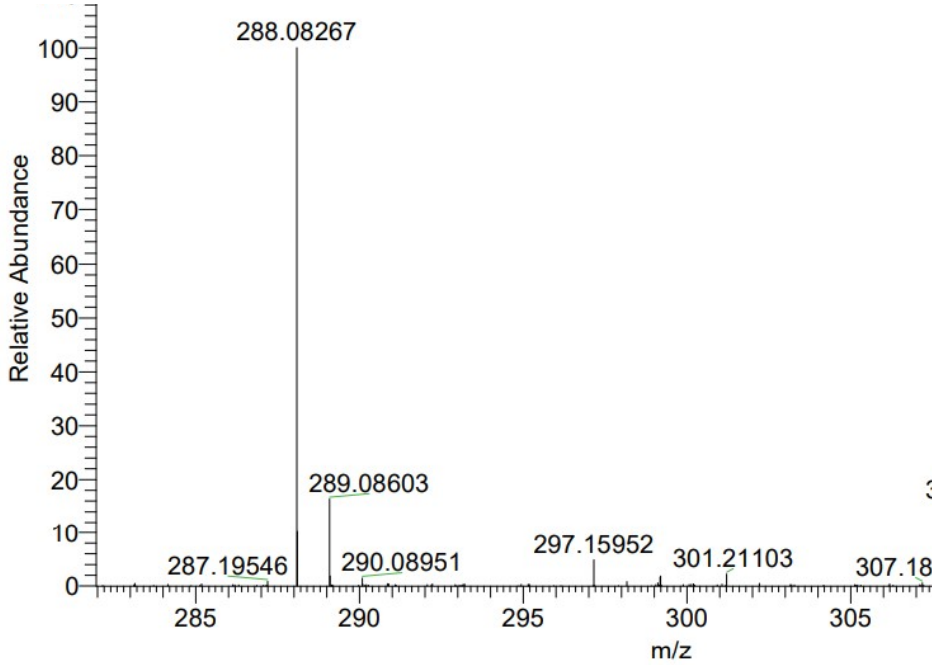
**$^{19}$F NMR** (376 MHz, $CDCl_3$)




**HRMS** (ESI)

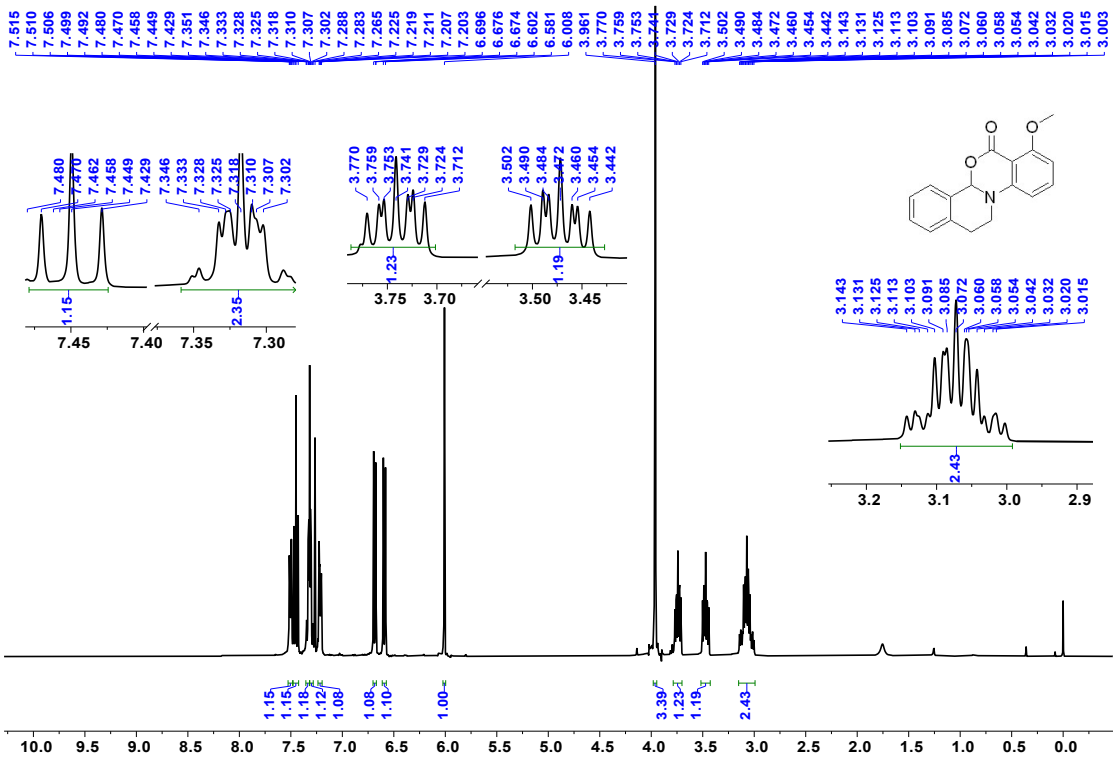



Chemical Formula: $C_{16}H_{12}F_2NO_2^+$
m/z: 288.0831 (100.0%), 289.0864 (17.3%), 290.0898 (1.4%)

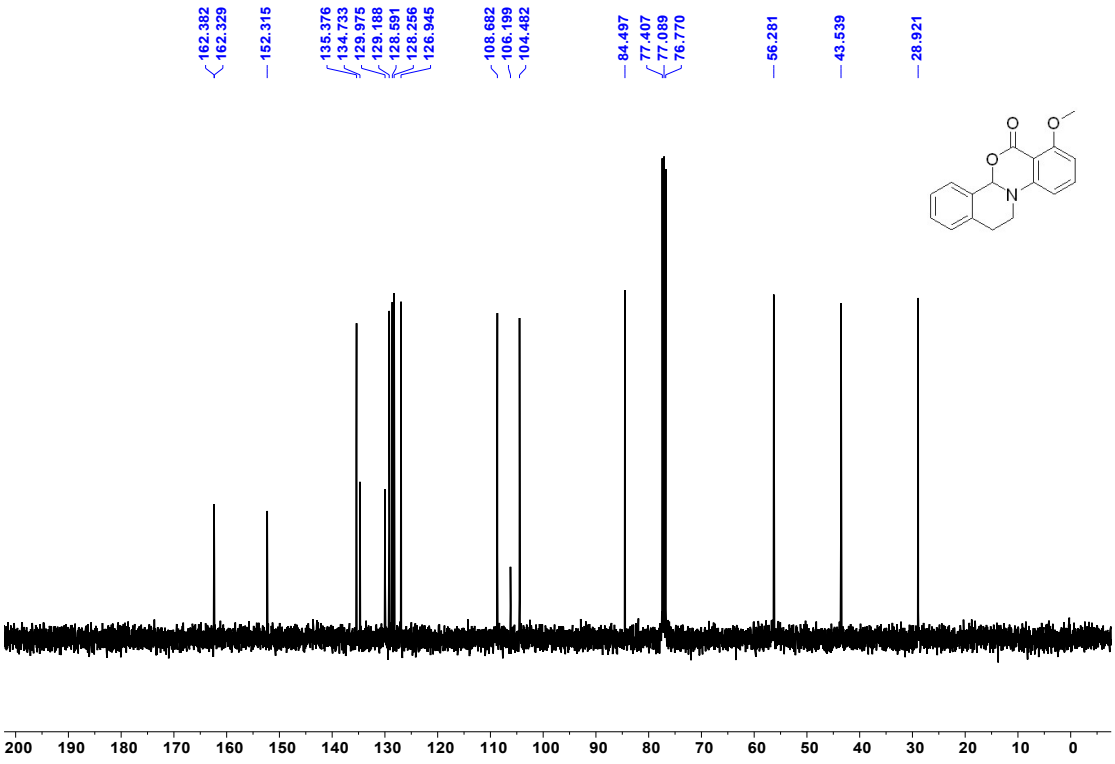



7-methoxy-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ad)**

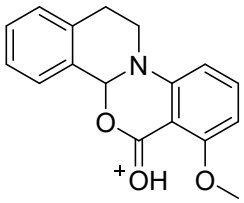
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



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

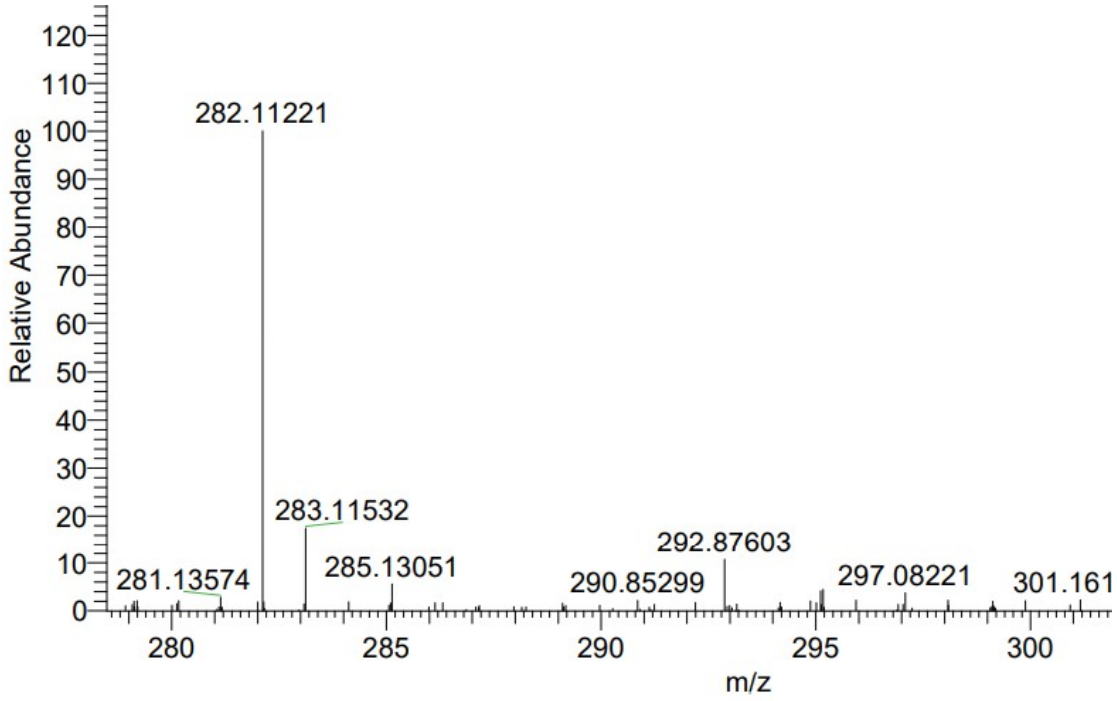



**HRMS** (ESI)



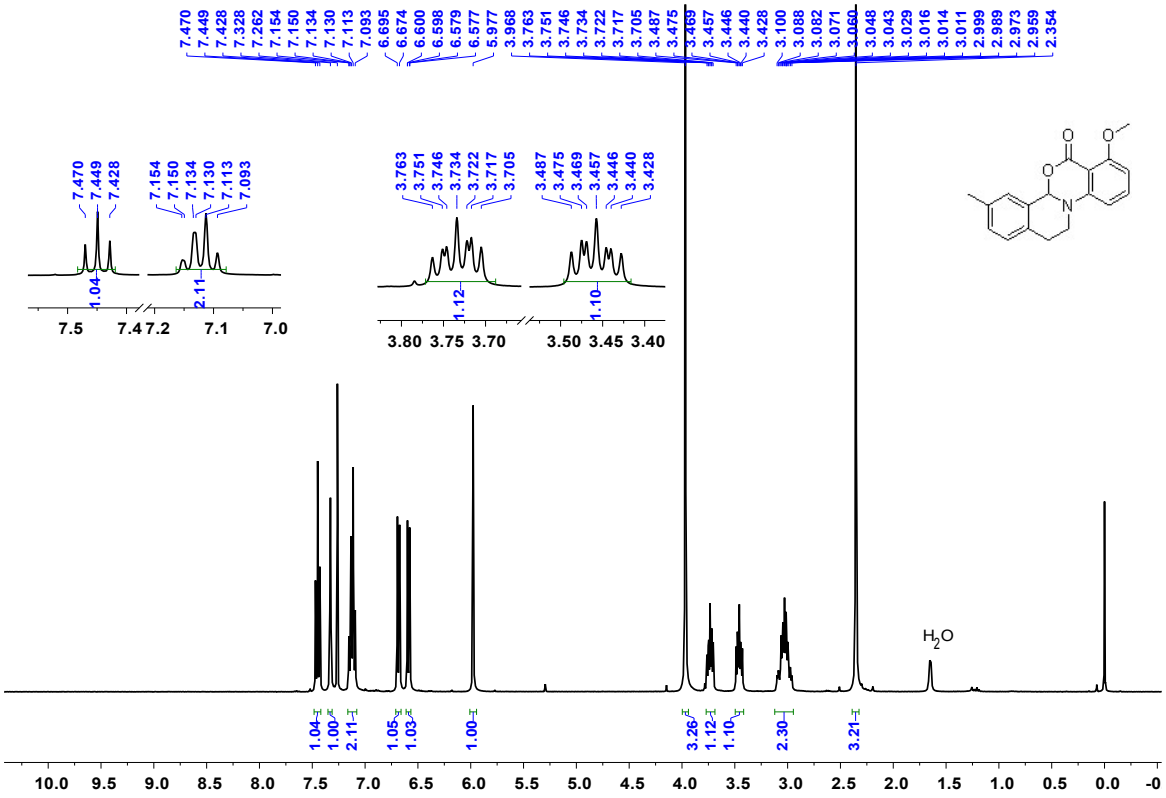
Chemical Formula: $C_{17}H_{16}NO_3^+$

m/z: 282.1125 (100.0%), 283.1158 (18.4%), 284.1192 (1.6%)

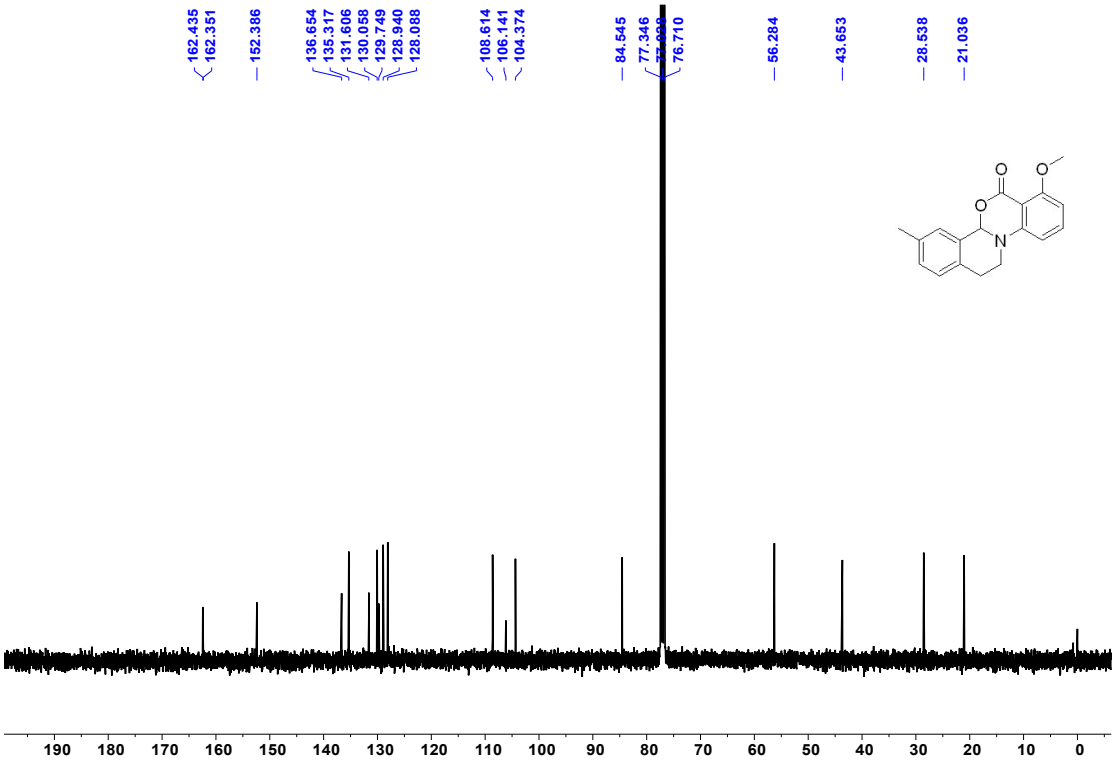

Relative Abundance
120
110
100
90
80
70
60
50
40
30
20
10
0
282.11221
283.11532
285.13051
281.13574
290.85299
292.87603
297.08221
301.161
280
285
290
295
300
m/z

7-methoxy-3-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3bd)**

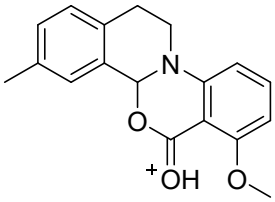
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



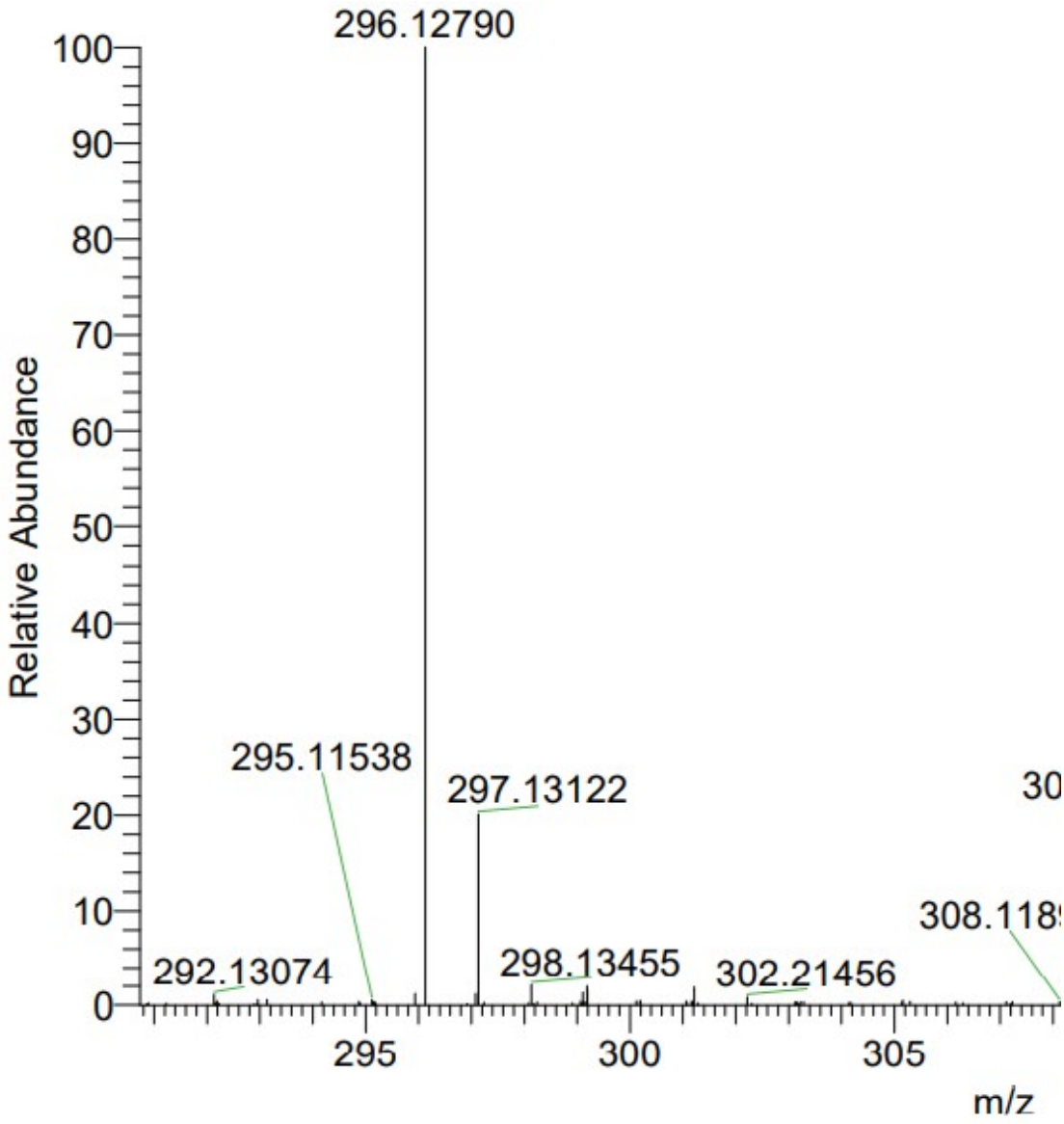

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



**HRMS** (ESI)

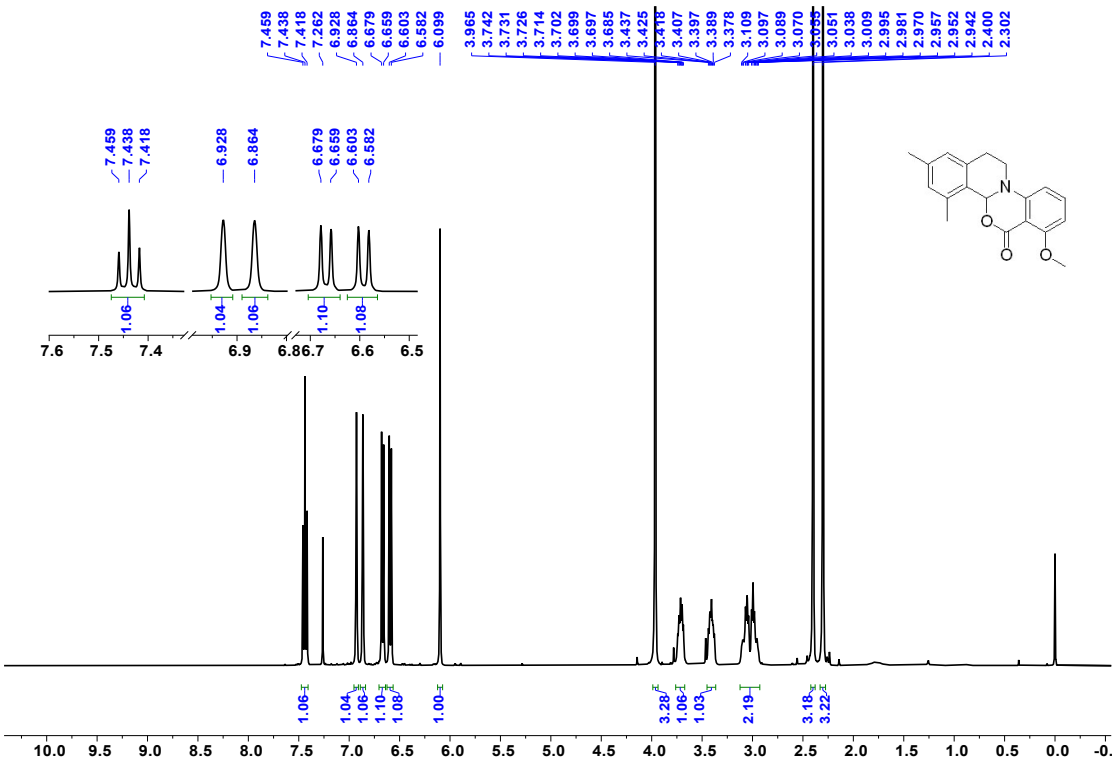



Chemical Formula: $C_{18}H_{18}NO_3^+$
m/z: 296.1281 (100.0%), 297.1315 (19.5%), 298.1348 (1.8%)

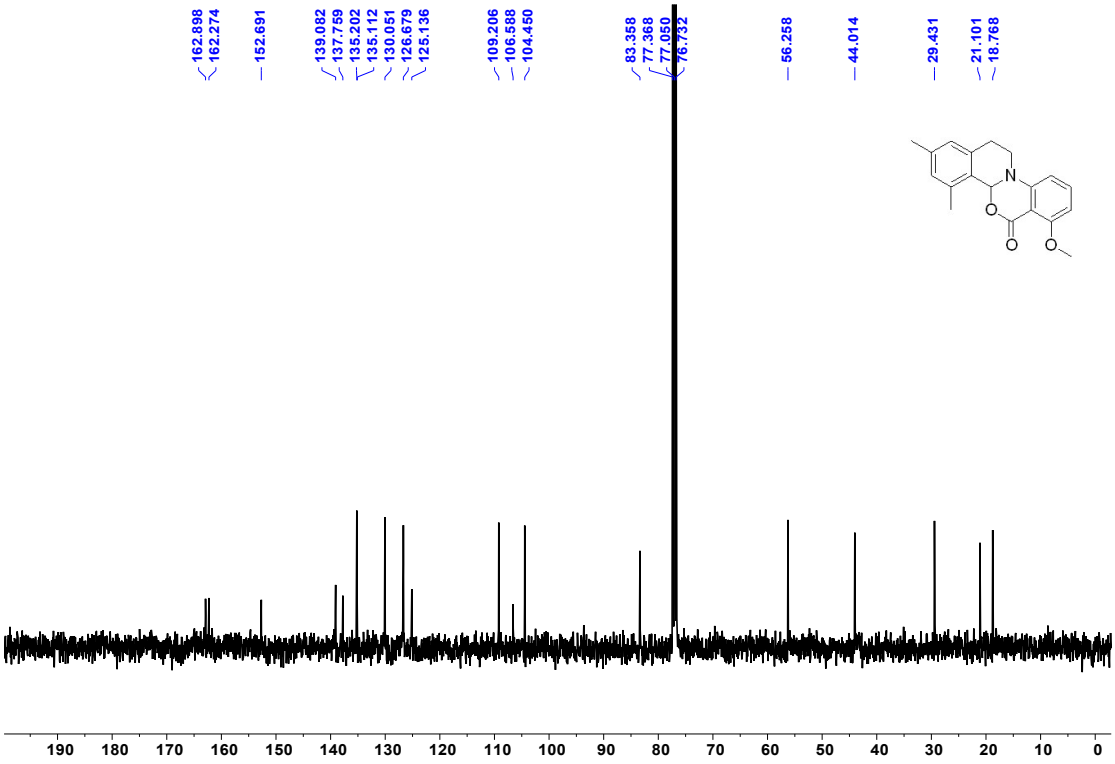


7-methoxy-2,4-dimethyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3fd)**

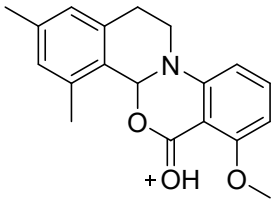
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



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

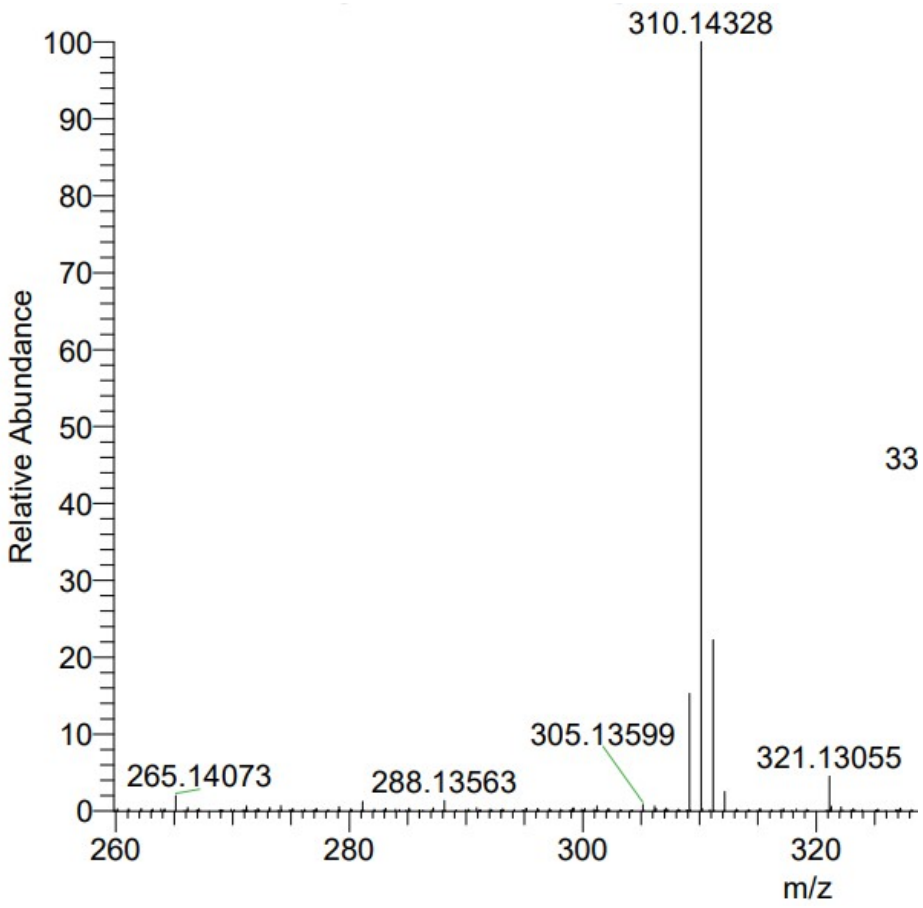


**HRMS** (ESI)



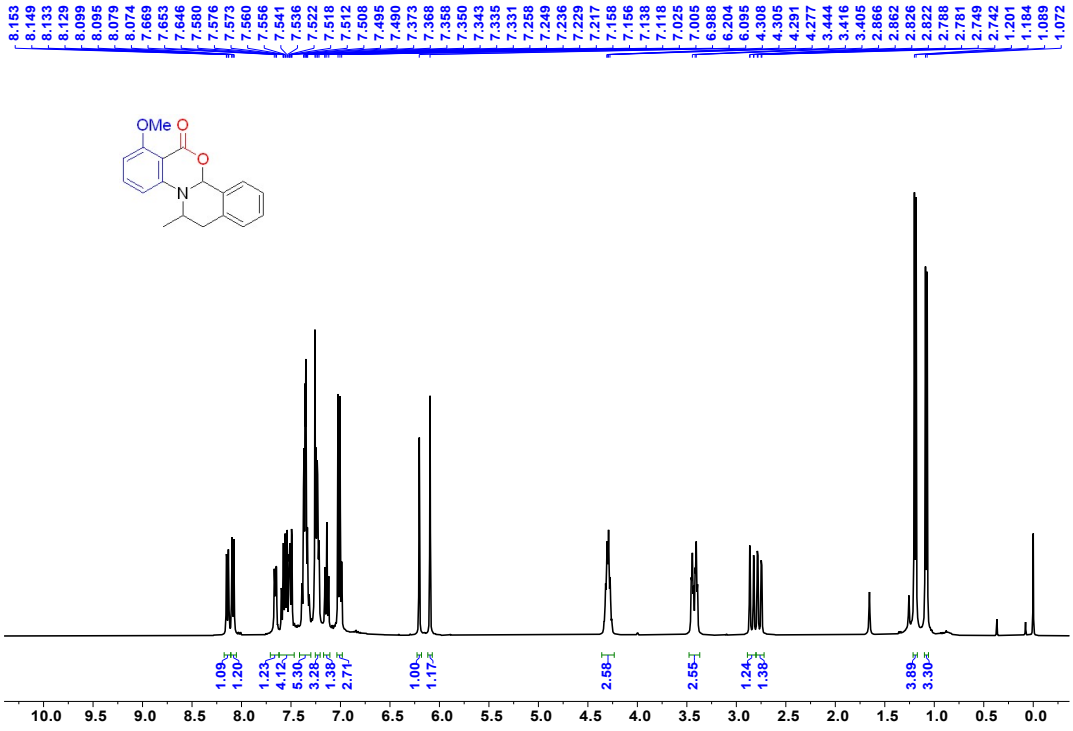

Chemical Formula: $C_{19}H_{20}NO_3^+$

m/z: 310.1438 (100.0%), 311.1471 (20.5%), 312.1505 (2.0%)

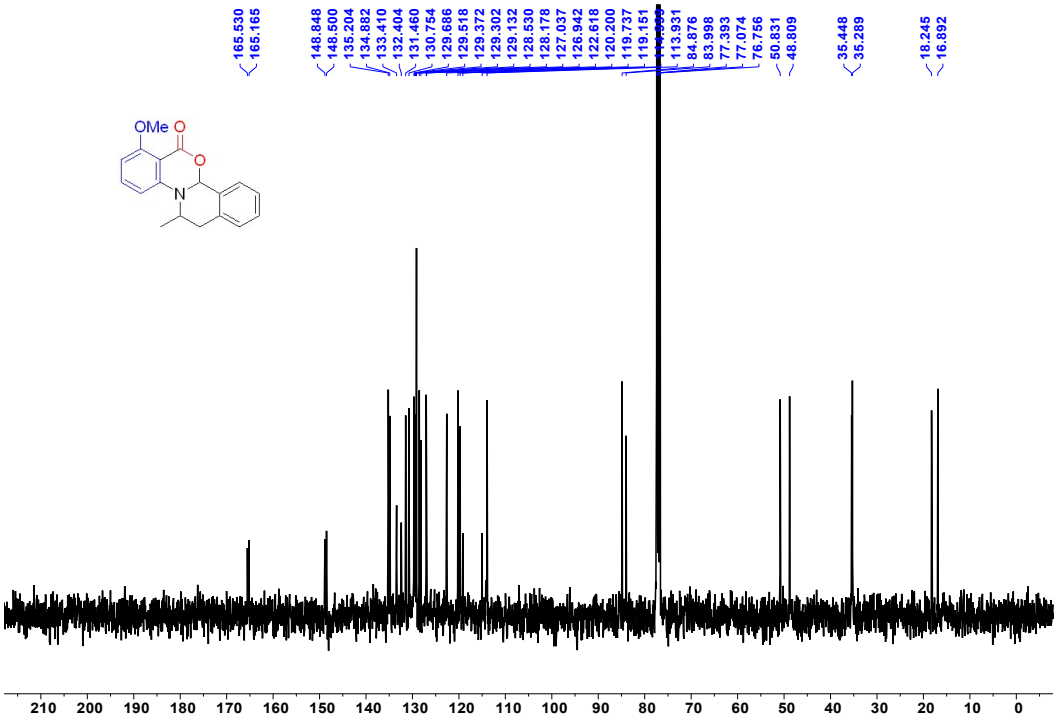


7-methoxy-12-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3ld)**

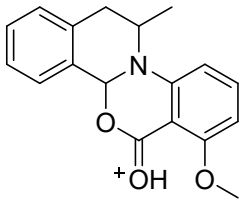
**$^{1}$H NMR** (400 MHz, $CDCl_3$)



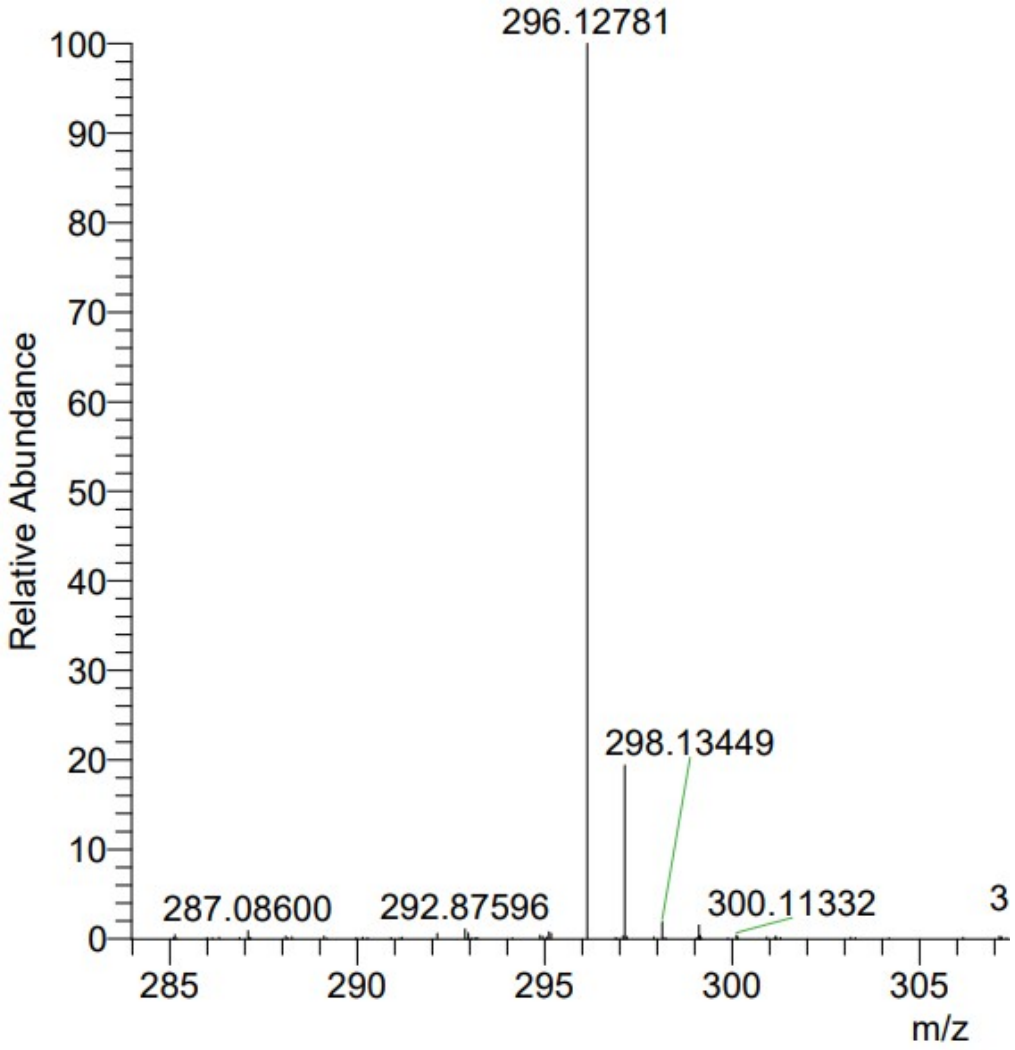

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



**HRMS** (ESI)



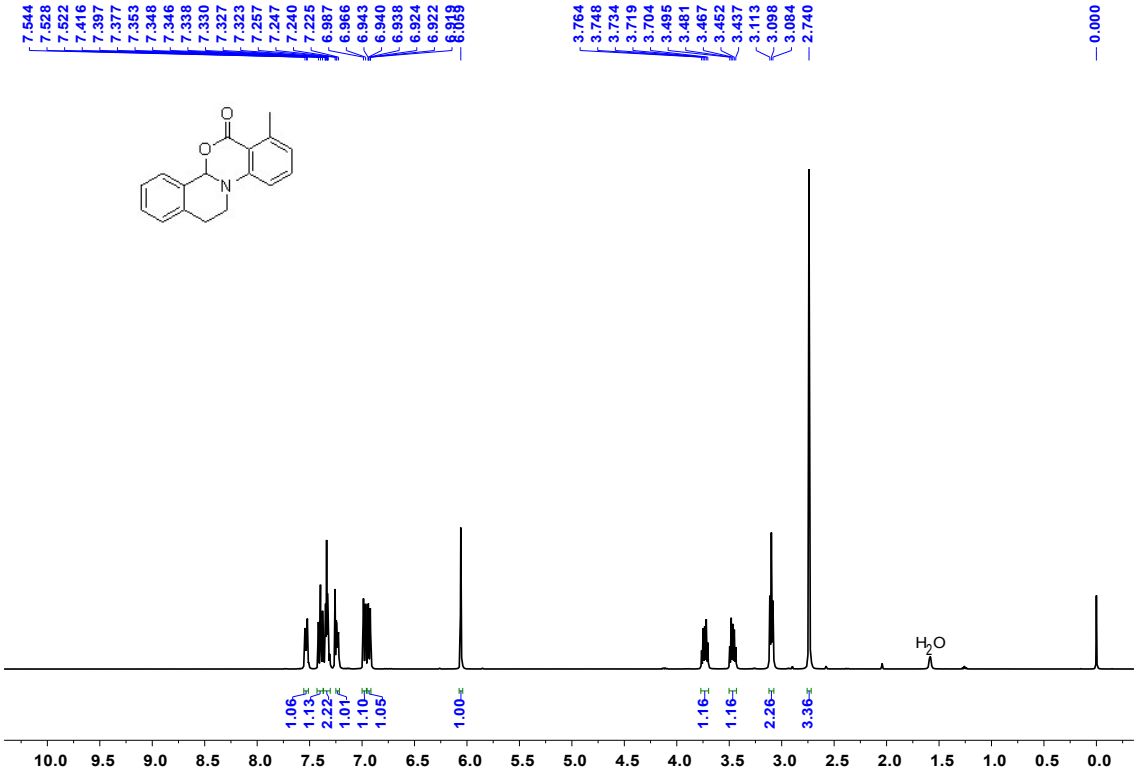

Chemical Formula: $C_{18}H_{18}NO_3^+$
m/z: 296.1281 (100.0%), 297.1315 (19.5%), 298.1348 (1.8%)



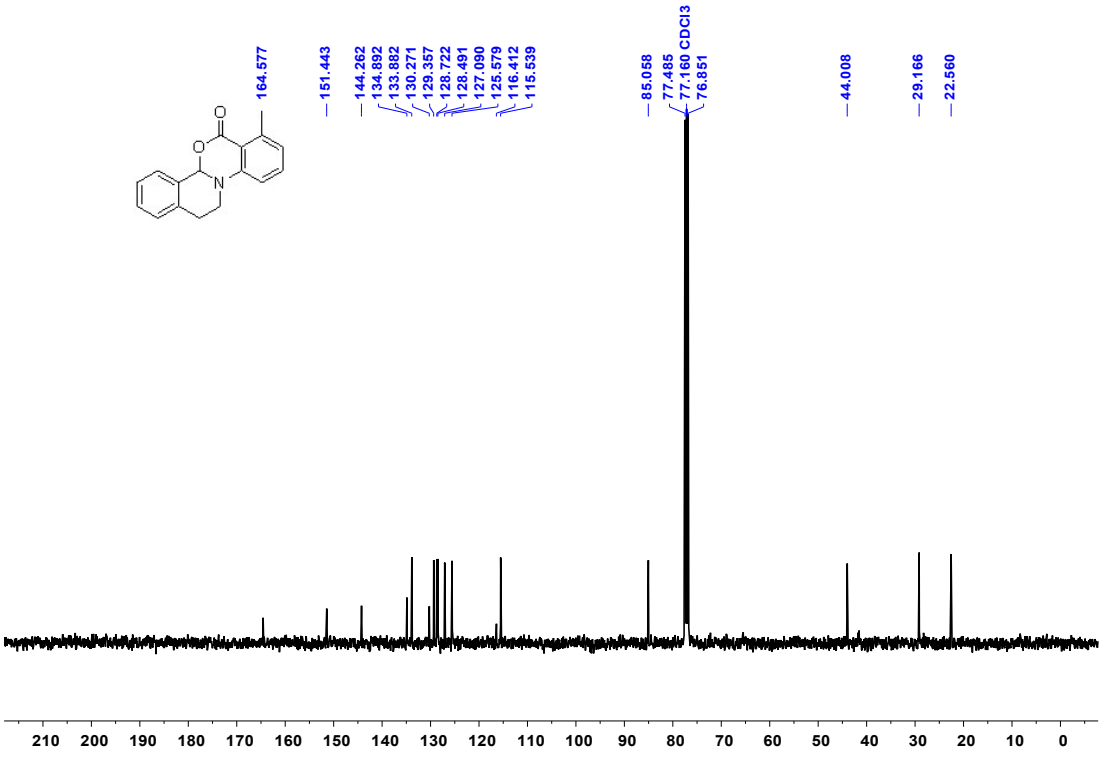
7-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one

**(3ae)**

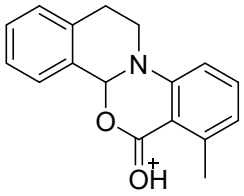
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

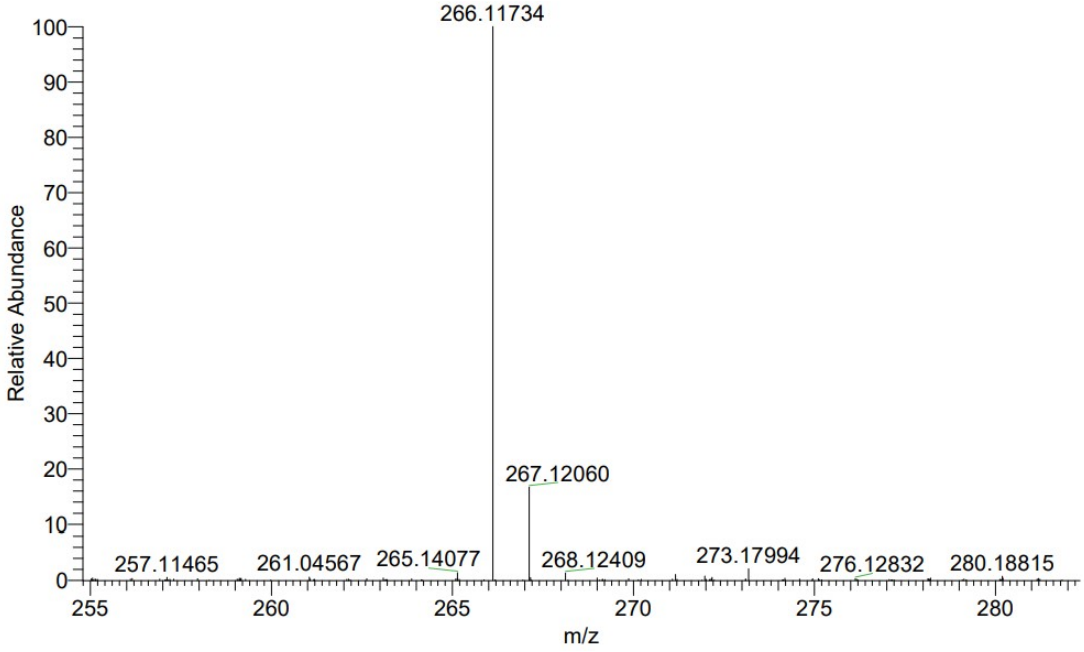


**HRMS** (ESI)



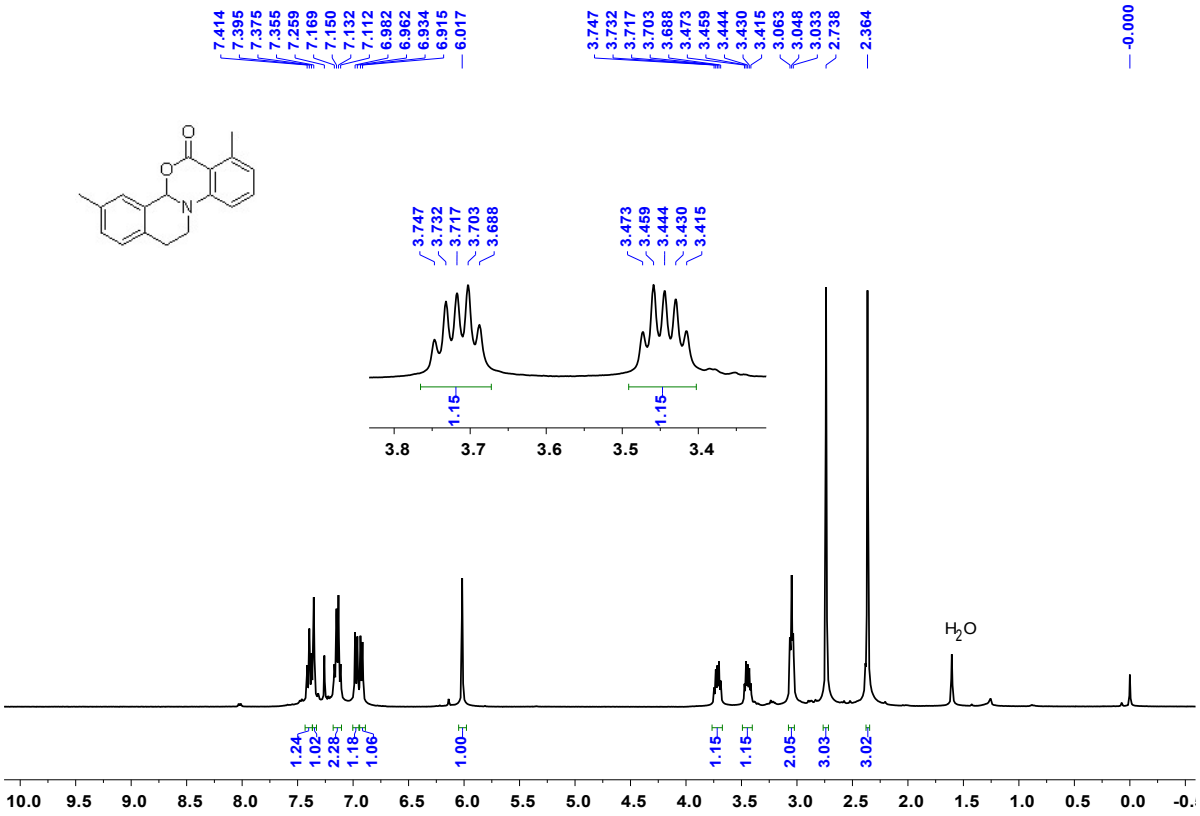

Chemical Formula: $C_{17}H_{16}NO_2^+$

m/z: 266.1176 (100.0%), 267.1209 (18.4%), 268.1243 (1.6%)

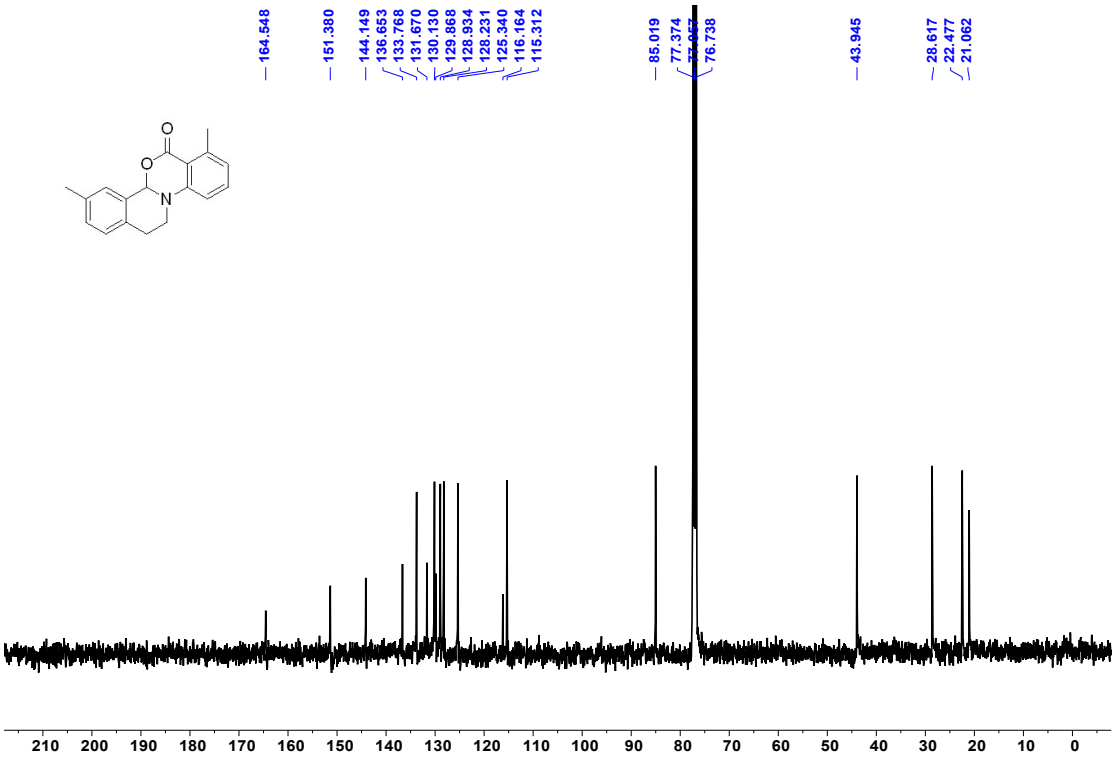


3,7-dimethyl-4b,13-dihydro-6H,12H-benzo[4,5][1,3]oxazino[2,3-a]isoquinolin-6-one **(3be)**

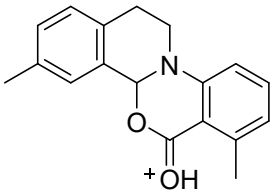
**$^{1}$H NMR** (400 MHz, $CDCl_3$)




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

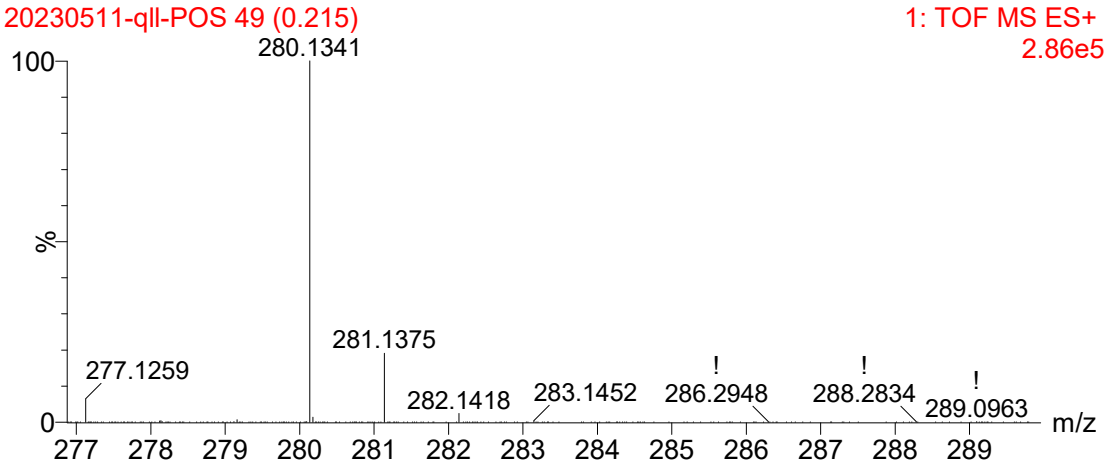


**HRMS** (ESI)



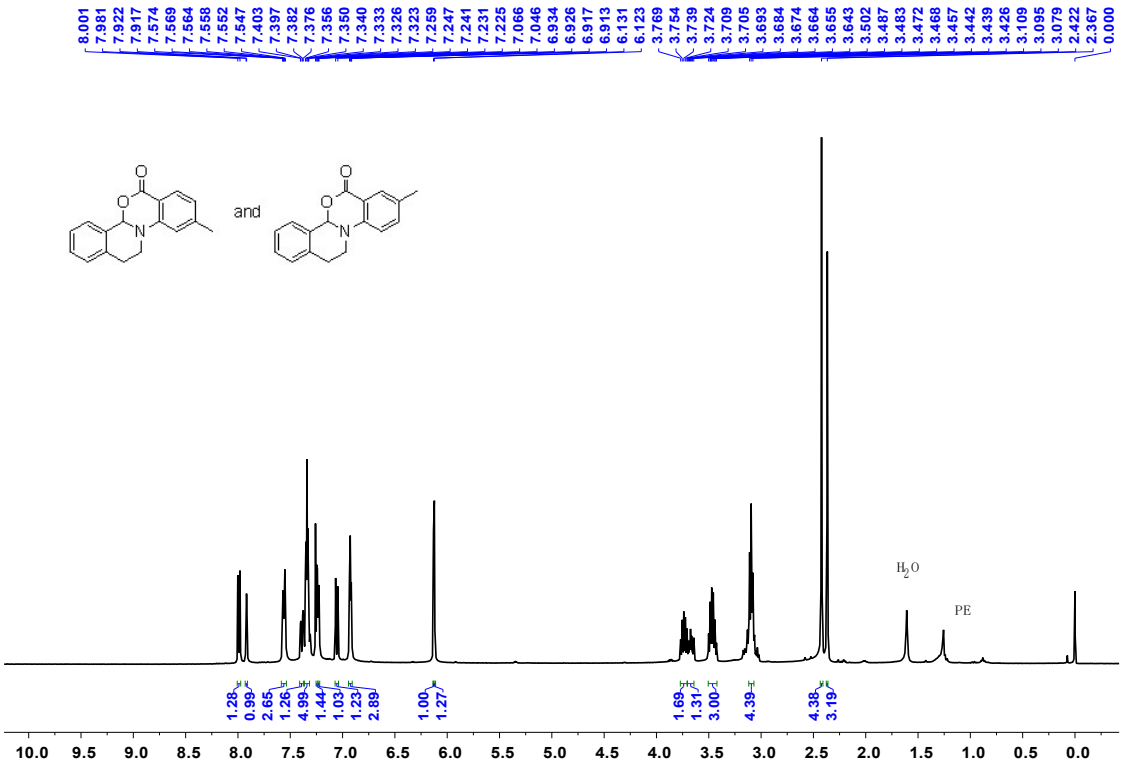

Chemical Formula: $C_{18}H_{18}NO_2^+$

m/z: 280.1332 (100.0%), 281.1366 (19.5%), 282.1399 (1.8%)

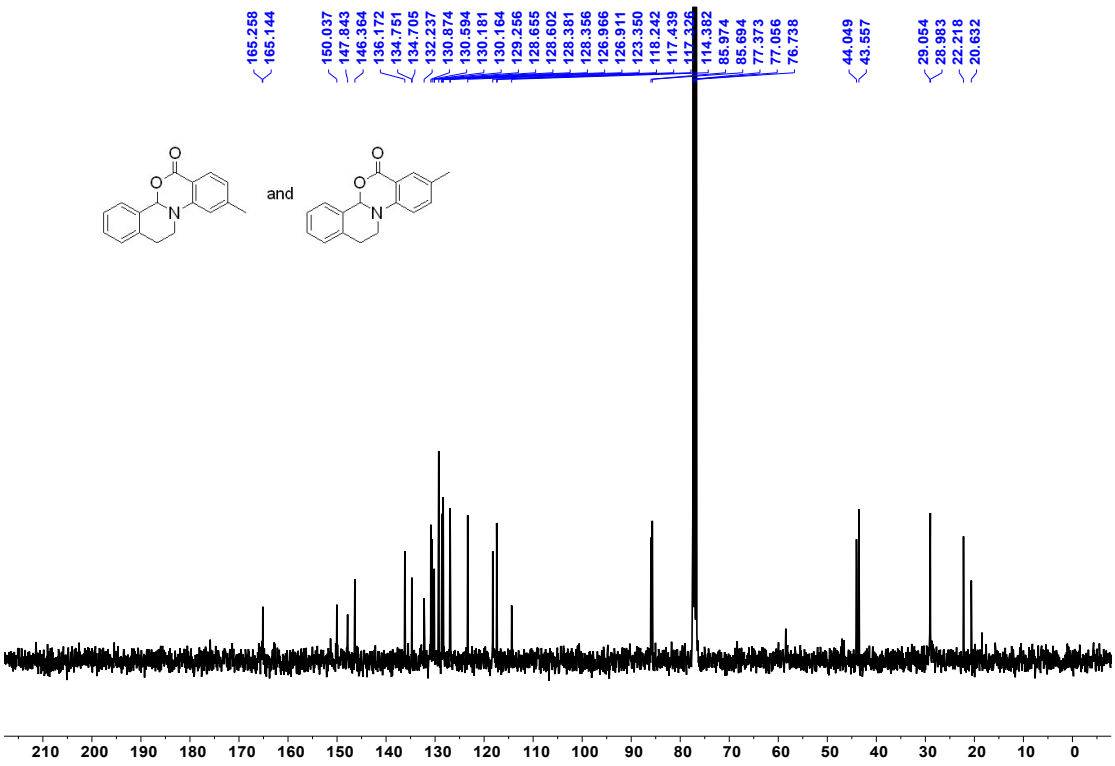


9-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3af)** and 8-methyl-4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinolin-6-one **(3af')**

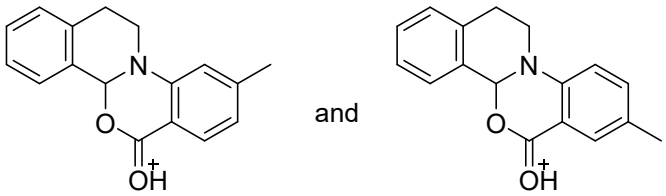
**$^1$H NMR** (400 MHz, $CDCl_3$)




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

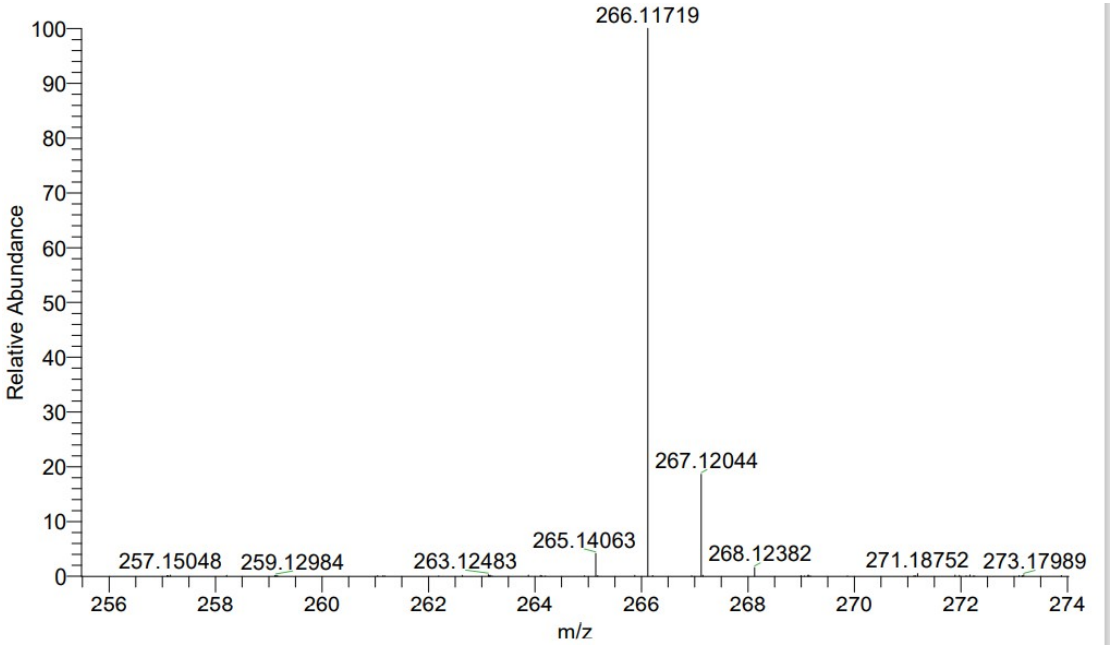


**HRMS** (ESI)



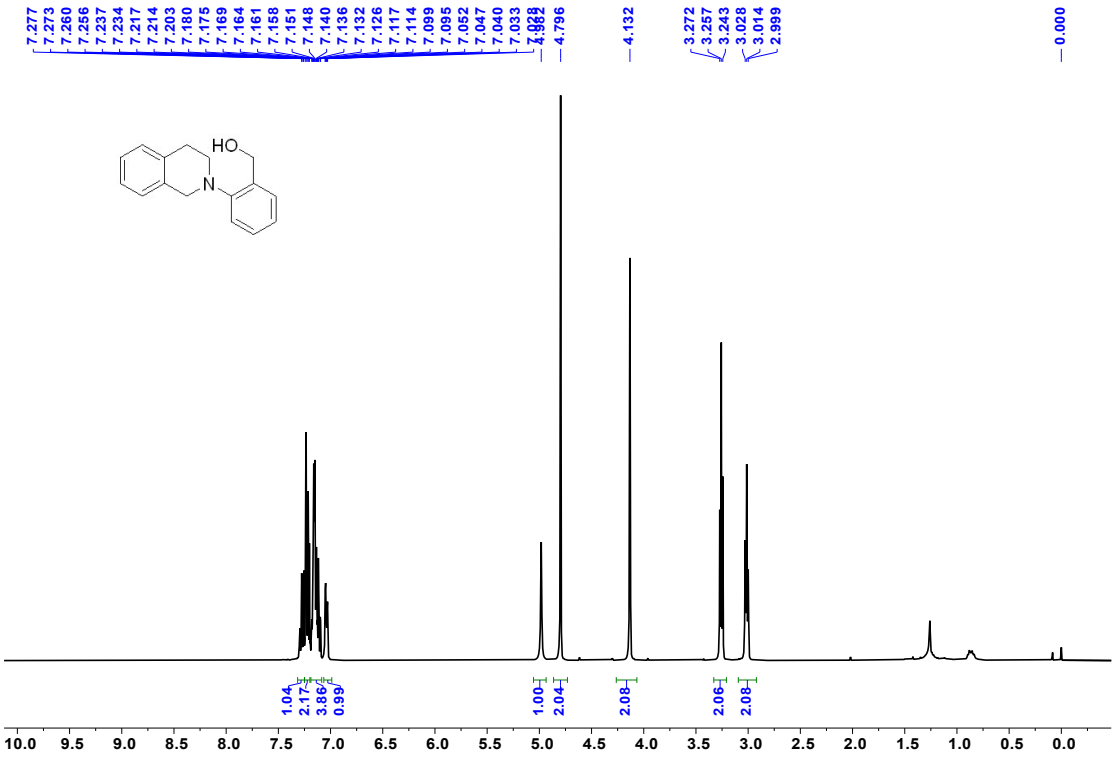
Chemical Formula: $C_{17}H_{16}NO_2^+$

m/z: 266.1176 (100.0%), 267.1209 (18.4%), 268.1243 (1.6%)

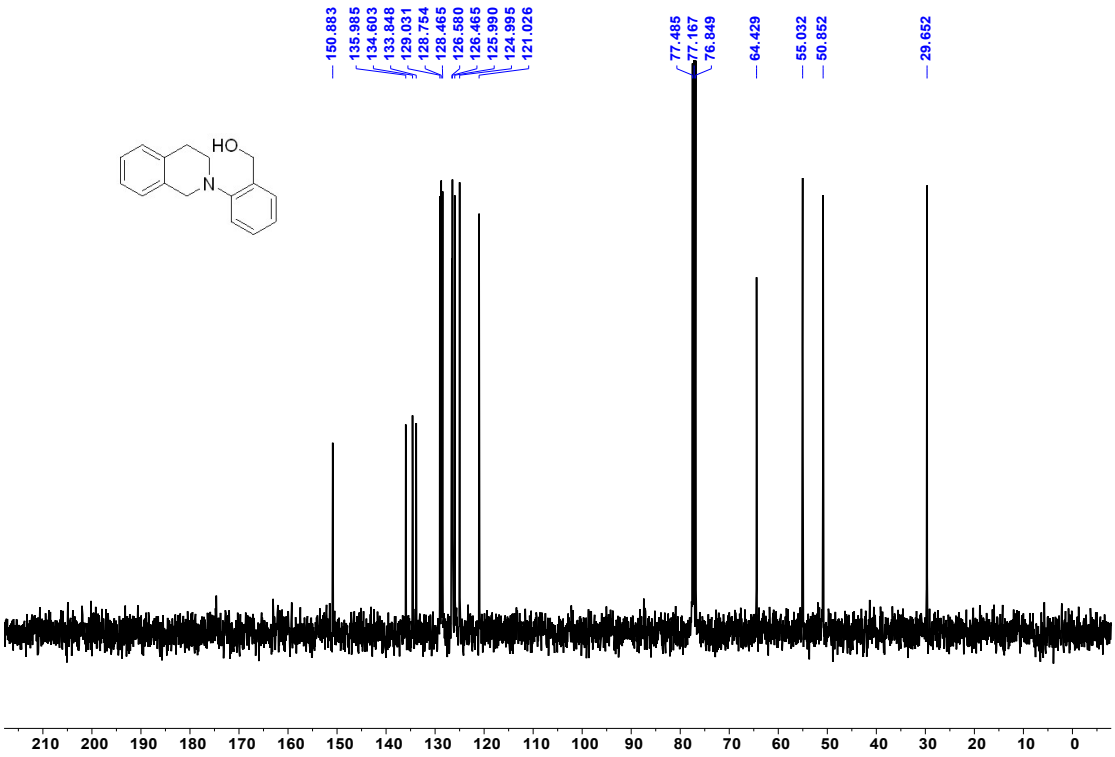


(2-(3,4-dihydroisoquinolin-2(1*H*)-yl)phenyl)methanol (**5aa**).

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

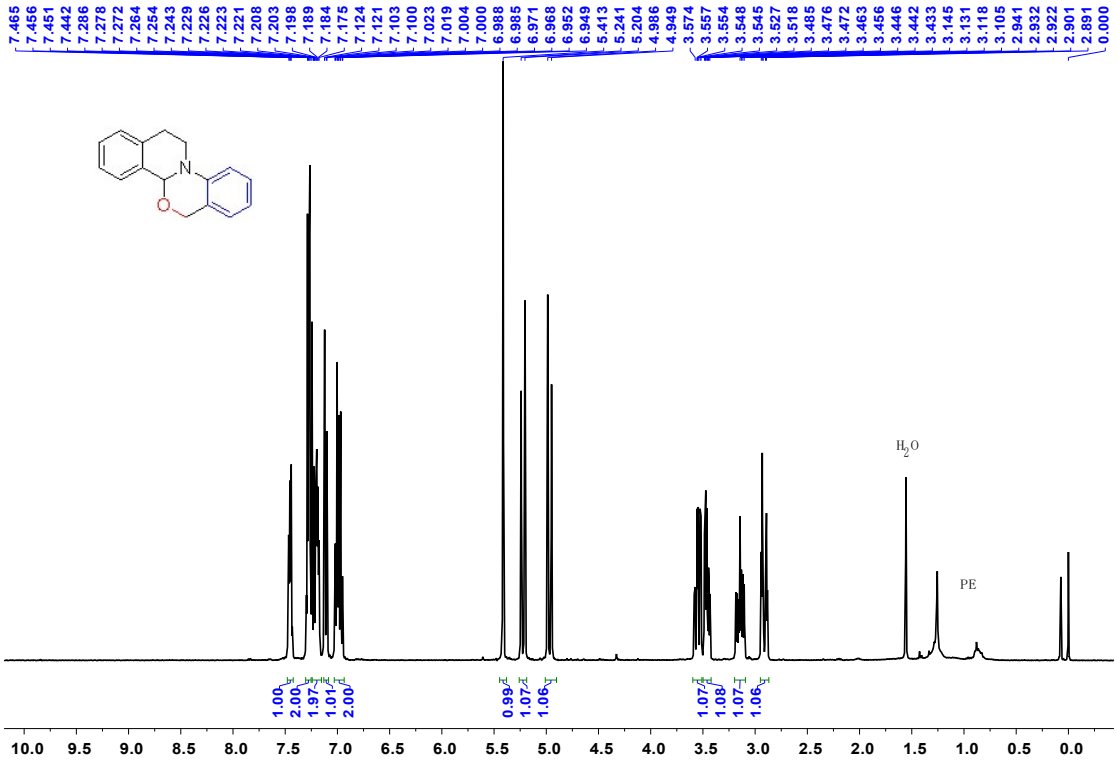



**$^{13}$C NMR** (101 MHz, $CDCl_3$)

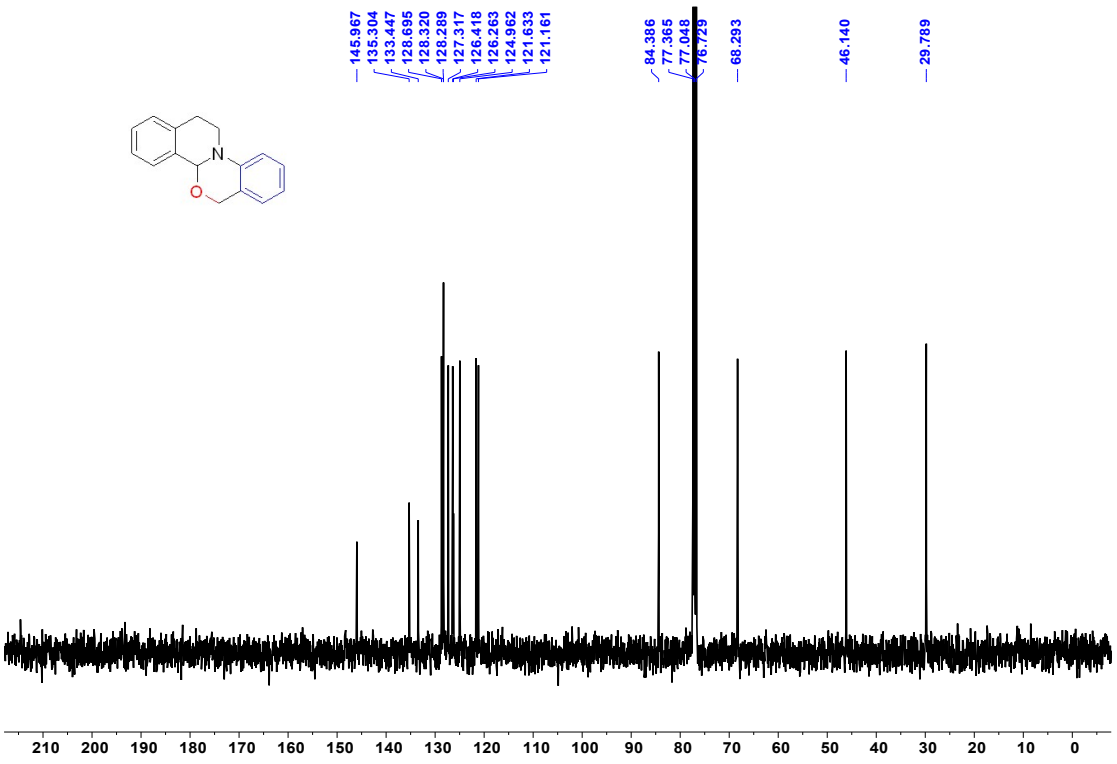


4b,13-dihydro-6*H*,12*H*-benzo[4,5][1,3]oxazino[2,3-*a*]isoquinoline (**6aa**)

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

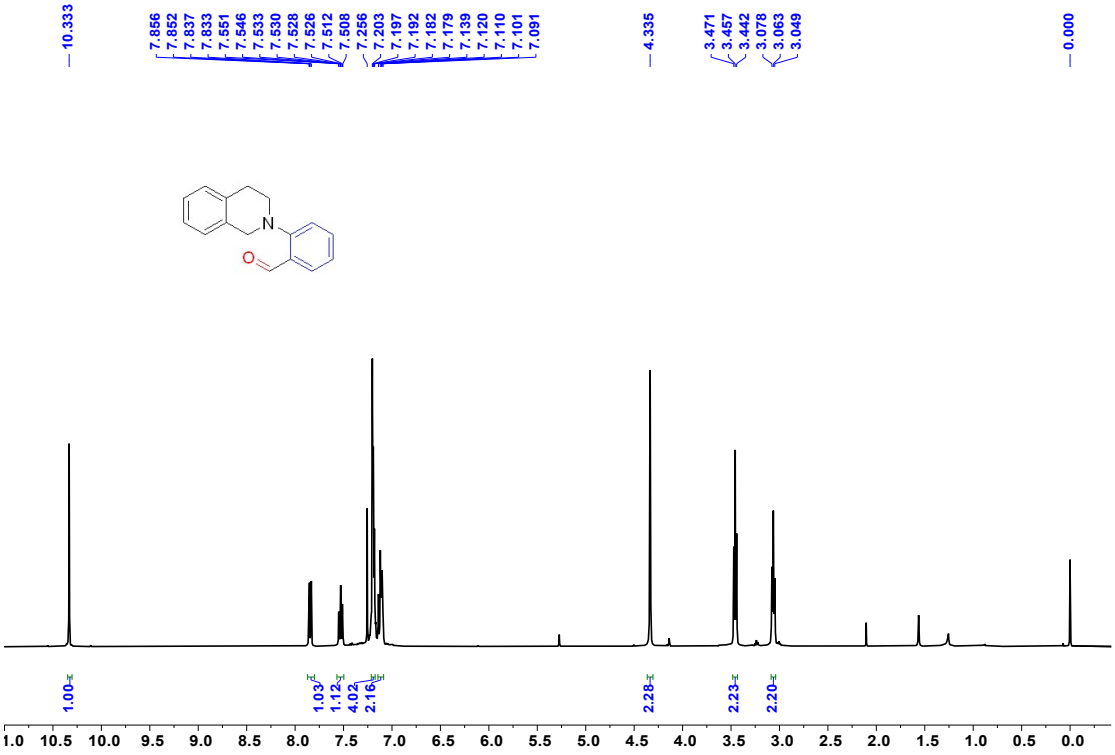



**$^{13}$C NMR** (101 MHz, $CDCl_3$)



2-(3,4-dihydroisoquinolin-2(1*H*)-yl)benzaldehyde **(7aa)**

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




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