

Supporting Information

Electrochemically Driven Strain-Release Dearomative (3+2) Cyclization for the Synthesis of Bicyclo[2.1.1]hexane-Fused Polycyclic Spiroindolines

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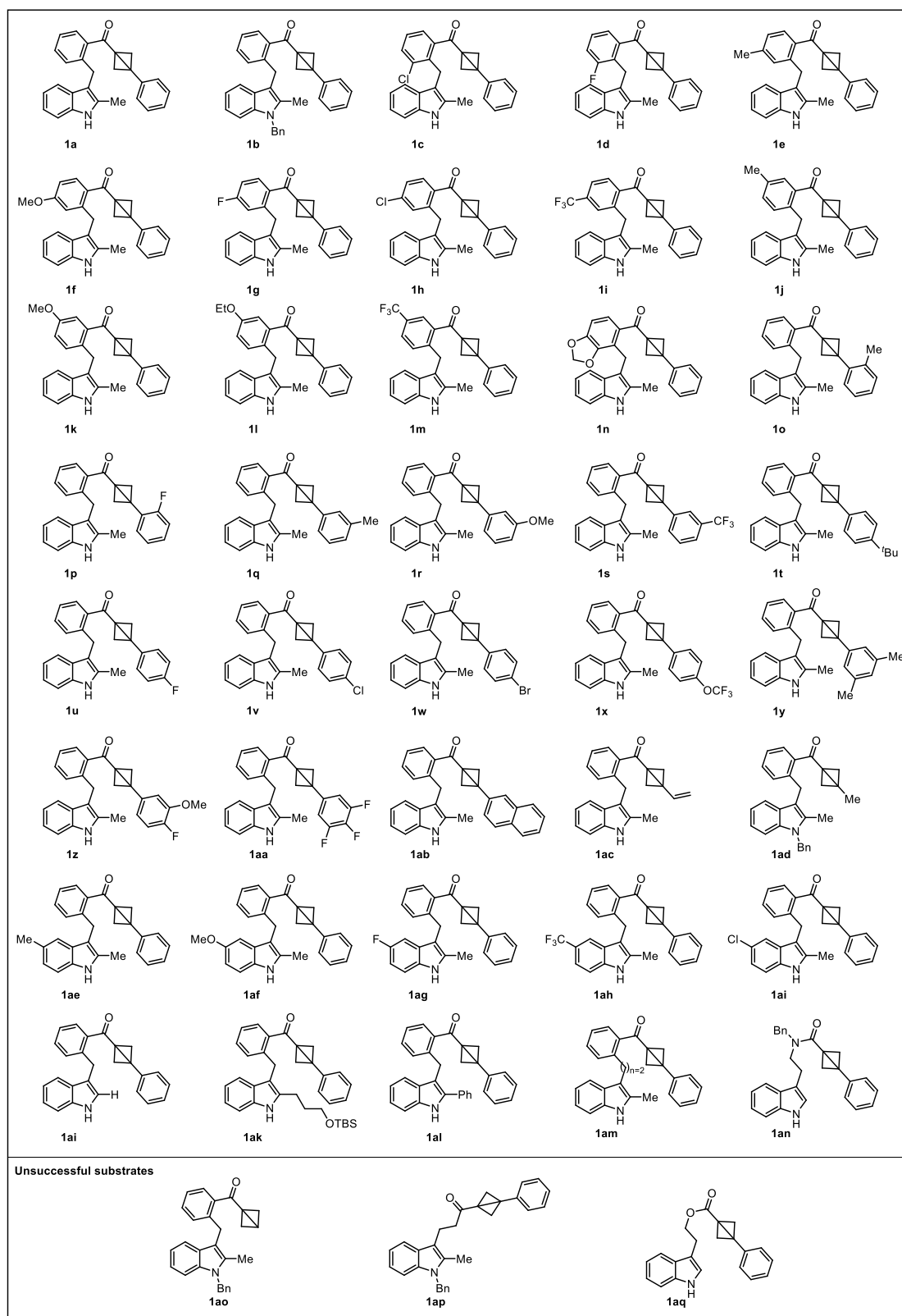
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1. General information

All compounds were characterized by ^1H NMR, ^{13}C NMR, ^{19}F NMR and HRMS. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 400 and 600 spectrometers. Chemical shifts are reported in parts per million (δ) referenced to tetramethylsilane (0.0 ppm), chloroform-*d* (7.26 ppm or 77.16 ppm). Data for ^1H NMR and ^{13}C NMR spectroscopy are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), and integration. X-Ray Single Crystal Diffraction Data were recorded on Bruker D8 QUEST and Bruker APEX DUO. High Resolution Mass spectra were taken on an AB QSTAR Pulsar mass spectrometer or Agilent LC/MSD TOF mass spectrometer. Melting points were measured on a Hanon MP 430 auto melting-point system and are uncorrected. Silica gel (200-300 mesh) for column chromatography and silica GF254 for TLC were obtained from Merck Chemicals Co. Ltd. (Shanghai). Electrolysis was performed using a SW-3211A dual display potentiostat (Guangzhou Swevy Instruments Co., China). All the electrochemical oxidations were performed in an oven-dried two-necked undivided cell equipped with a graphite felt anode (GF) (15 mm $\times$ 10 mm $\times$ 2 mm), Pt plate cathode (10 mm $\times$ 10 mm $\times$ 0.1 mm) unless otherwise noted. The boiling range of petroleum ether for column chromatography is 60–90 $^\circ\text{C}$. Anhydrous solvents were purchased from Adamas-beta[®] and used without further purification. Starting materials, solvents and reagents used in reactions were obtained commercially from Acros, Aldrich, Innochem and Adamas-beta[®], and were used without purification, unless otherwise indicated. All reactions were conducted in dried glassware. Reagents and starting materials were accordingly transferred via syringe or cannula. Reaction temperatures refer to the external oil bath temperature and are uncorrected.

2. Preparation of substrates

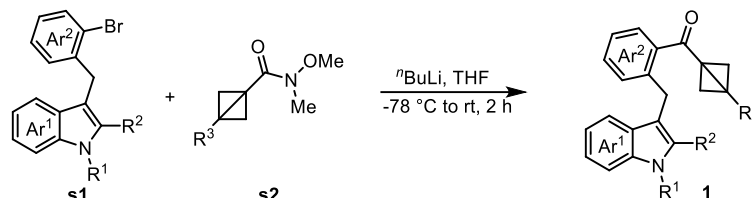
Procedures for the synthesis of C3-bicyclo[1.1.0]butane(BCB)-substituted indoles



s1 were synthesized according to the reported literature.^[1]

s2 were synthesized according to the reported literature.^[2]

General procedure A:



An oven-dried 100 mL round-bottom flask, equipped with a stir bar, was cooled under vacuum. After backfilling with N_2 ($\times 3$), the flask was capped with a septum. **S1** (1.1 equiv) and THF (20 mL) were added to the flask. The solution was then cooled to -78°C using a cooling bath, and $n\text{BuLi}$ (2.2 equiv) was added. The reaction mixture was stirred at -78°C for 40 min, after which a solution of amide **S2** (1.0 equiv) in THF (10 mL) was added. After stirring for 30 min, the cooling bath was removed, and the reaction mixture was stirred at room temperature for 1 h. The reaction was quenched with saturated NH_4Cl solution (20 mL). The aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with brine (25 mL), dried over anhydrous Na_2SO_4 , filtered, and concentrated by rotary evaporation. The residue was purified by column chromatography on silica gel to afford the BCBs **1**. (Note: When the benzyl-protected **S1** is used, the amount of $n\text{BuLi}$ is 1.1 equiv).

3. Detailed optimization of reaction conditions

Table S1. Optimization of solvent^a

0.75	Solvent	Yield% of 2a ^b
1	DCM	86
2	DCE	73
3	HFIP	0
4	TFE	0
5	MeOH	0
6	Acetone	35
7	EtOAc	46
8	THF	28
9	DMF	15
10	CH₃CN	93

^a Reaction conditions: graphite felt (GF) anode, platinum plate cathode, **1a** (0.20 mmol), ⁿBu₄NBF₄ (1.0 equiv), Solvent (4 mL), undivided cell, Ar, room temperature, constant current = 1 mA, 1 h. ^b Isolated yield.

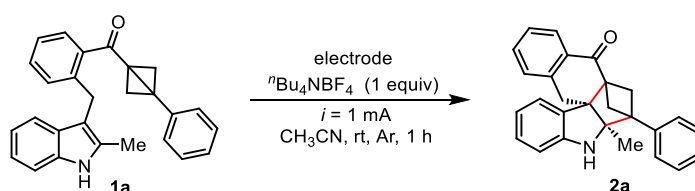
Table S2. Optimization of electrolyte^a

Entry	electrolyte	Yield% of 2a ^b
1	ⁿ Bu ₄ NPF ₆	88
2	ⁿBu₄NPF₄	93
3	ⁿ Bu ₄ NBr	62
4	ⁿ Bu ₄ NI	56

5	$n\text{Bu}_4\text{NClO}_4$	48
6	LiClO_4	35
7	NaClO_4	26

^a Reaction conditions: graphite felt (GF) anode, platinum plate cathode, **1a** (0.20 mmol), electrolyte (1.0 equiv), CH_3CN (4 mL), undivided cell, Ar, room temperature, constant current = 1 mA, 1 h. ^b Isolated yield.

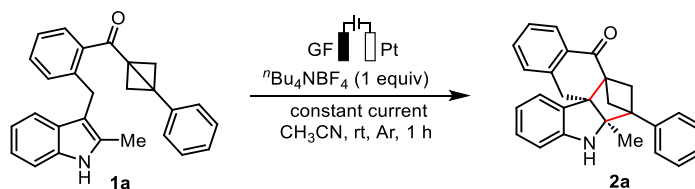
Table S3. Optimization of electrode^a



Entry	electrode	Yield% of 2a ^b
1	Carbon cloth(+)/(-)Pt	53
2	Carbon rod(+)/(-)Pt	Trace
3	Pt(+)/(-)Pt	Trace
4	graphite felt(+)/(-)Pt	93
5	graphite felt(+)/(-)graphite felt	78
6	graphite felt(+)/(-)Ni foam	37

^a Reaction conditions: electrode, **1a** (0.20 mmol), $n\text{Bu}_4\text{NBF}_4$ (1.0 equiv), CH_3CN (4 mL), undivided cell, Ar, room temperature, constant current = 1 mA, 1 h. ^b Isolated yield.

Table S4. Optimization of current^a

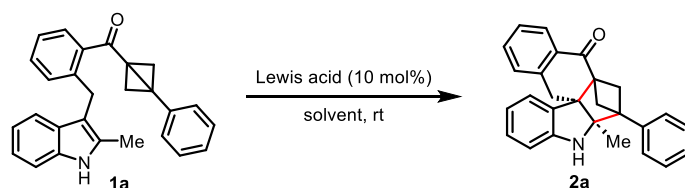


Entry	Constant current	Yield% of 2a ^b
1	No electricity	0
2	1 mA	93
3	2 mA	89

4	3 mA	92
5	4 mA	88
6	5 mA	90

^a Reaction conditions: graphite felt (GF) anode, platinum plate cathode, **1a** (0.20 mmol), ⁿBu₄NBF₄ (1.0 equiv), CH₃CN (4 mL), undivided cell, Ar, room temperature, constant current, 1 h. ^b Isolated yield.

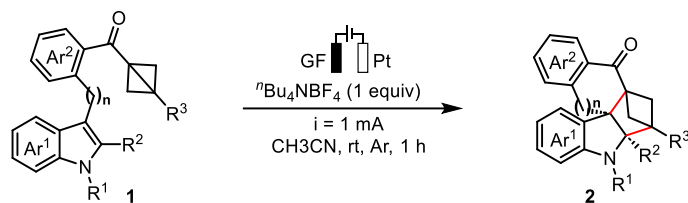
Table S5. Control experiments with different Lewis acids^a



Entry	Lewis acid	Solvent	Yield% ^b
1	AgOTf	CHCl ₃	68
2	Yb(OTf) ₃	CH ₂ Cl ₂	63
3	AgOTf	CH ₂ Cl ₂	65
4	Sc(OTf) ₃	CH ₂ Cl ₂	60
5	In(OTf)₃	CH₂Cl₂	71
6	Eu(OTf) ₃	CH ₂ Cl ₂	36
7	Bi(OTf) ₃	CH ₂ Cl ₂	47
8	Tb(OTf) ₃	CH ₂ Cl ₂	N.D.
9	La(OTf) ₃	CH ₂ Cl ₂	N.D.
10	TBSOTf	CH ₂ Cl ₂	59
11	BF ₃ ·Et ₂ O	CH ₂ Cl ₂	Trace
12	In(OTf) ₃	DCE	66
13	In(OTf) ₃	THF	49
14	In(OTf) ₃	EtOAc	56
15	In(OTf) ₃	CH ₃ CN	50
16	In(OTf) ₃	Toluene	42

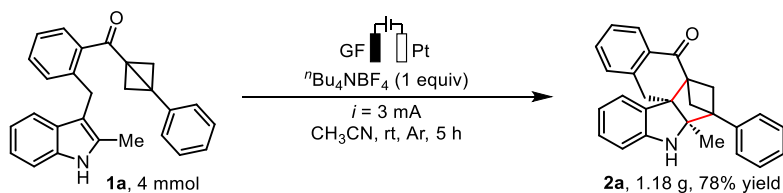
^a Reaction conditions: **1a** (0.20 mmol), Lewis acid (0.02 mmol, 10 mol %), solvent (4 mL), Ar, room temperature, 25 °C, 2 h. ^b Isolated yield.

4. General procedure electrochemical dearomative (3+2) cyclization



The electrocatalysis was carried out in an undivided cell with a graphite felt (GF) anode (15.0 mm $\times$ 10.0 mm $\times$ 2.0 mm) and a Pt plate cathode (10.0 mm $\times$ 10.0 mm $\times$ 0.1 mm). To a 10 mL oven-dried undivided electrochemical cell equipped with a magnetic bar were added C3-BCB-substituted indoles **1** (0.2 mmol, 1.0 equiv), $n\text{Bu}_4\text{NBF}_4$ (0.2 mmol, 1.0 equiv). Then CH_3CN (4.0 mL) was added under Ar. The electrocatalysis was performed at room temperature with a constant current of 1 mA maintained for 1 h. After completion of the reaction, the product was identified by TLC. The solvent was removed under reduced pressure by rotary evaporator, and then the crude product was purified by column chromatography to furnish the desired product **2**.

5. Scale up synthesis



The electrocatalysis was carried out in an undivided cell with a graphite felt (GF) anode (30 mm $\times$ 15 mm $\times$ 4 mm) and a Pt plate cathode (30 mm $\times$ 15 mm $\times$ 0.2 mm). To an oven-dried undivided two-necked bottle (50 mL) equipped with a magnetic bar were added C3-BCB-substituted indoles **1a** (4.0 mmol, 1.0 equiv), $n\text{Bu}_4\text{NBF}_4$ (1.32 g, 4.0 mmol, 1.0 equiv). Then CH_3CN (25 mL) was added under Ar. The electrocatalysis was performed at room temperature with a constant current of 3 mA maintained for 5 h. After completion of the reaction, the product was identified by TLC. The solvent was removed under reduced pressure by rotary evaporator, and then the crude product was

purified by column chromatography to furnish the desired product **2a** (1.18 g, 78% yield).

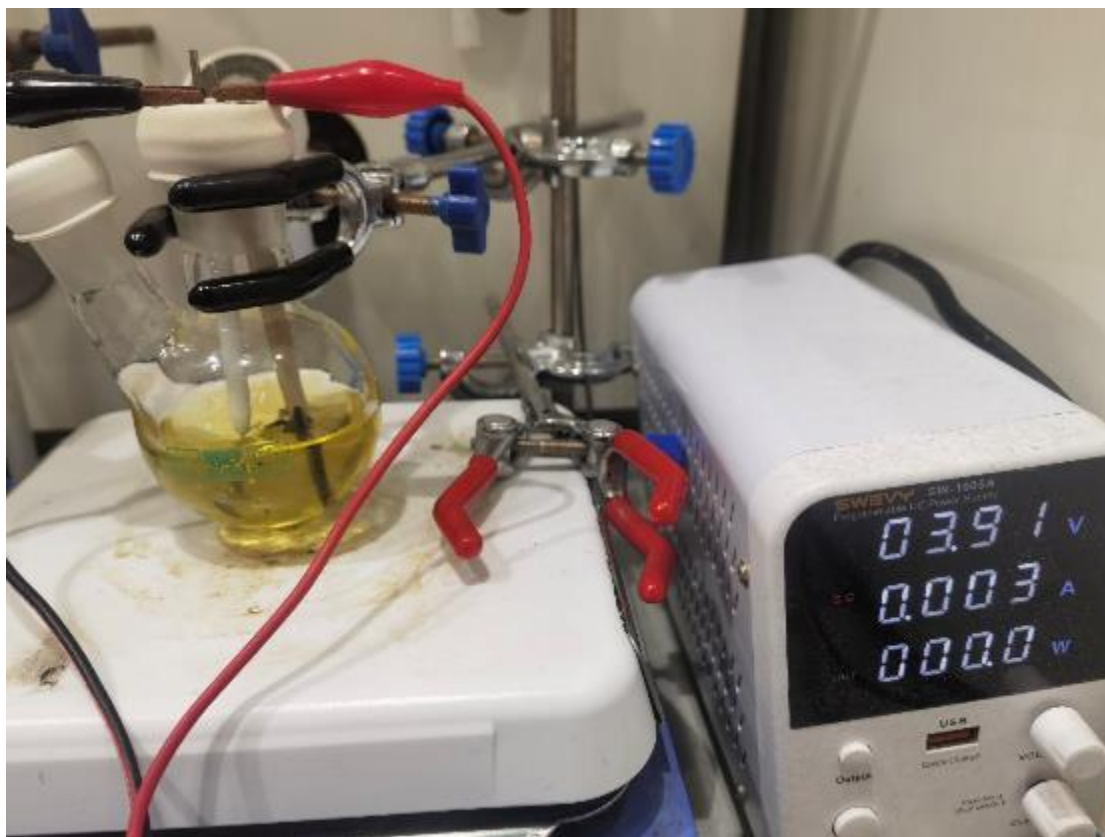
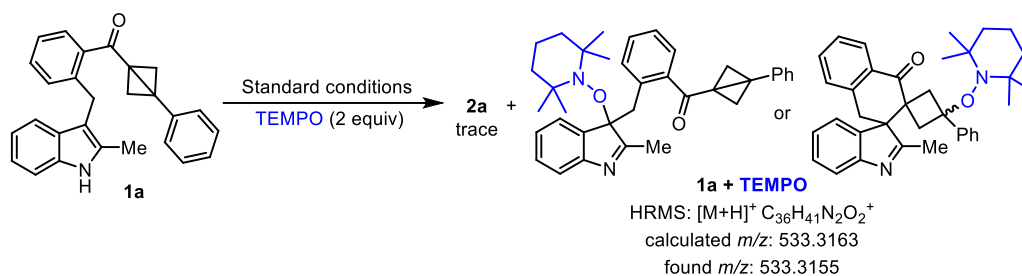


Figure S1. Electrolysis set-up for gram-scale experiments

6. Mechanistic investigation

6.1 Radical trapping experiment



The reaction was performed with the general procedure, and radical trap TEMPO (62.5 mg, 2.0 equiv) was added to the mixture, and the reaction mixture was stirred for 1 h. Then the reaction mixture was analyzed by HRMS.

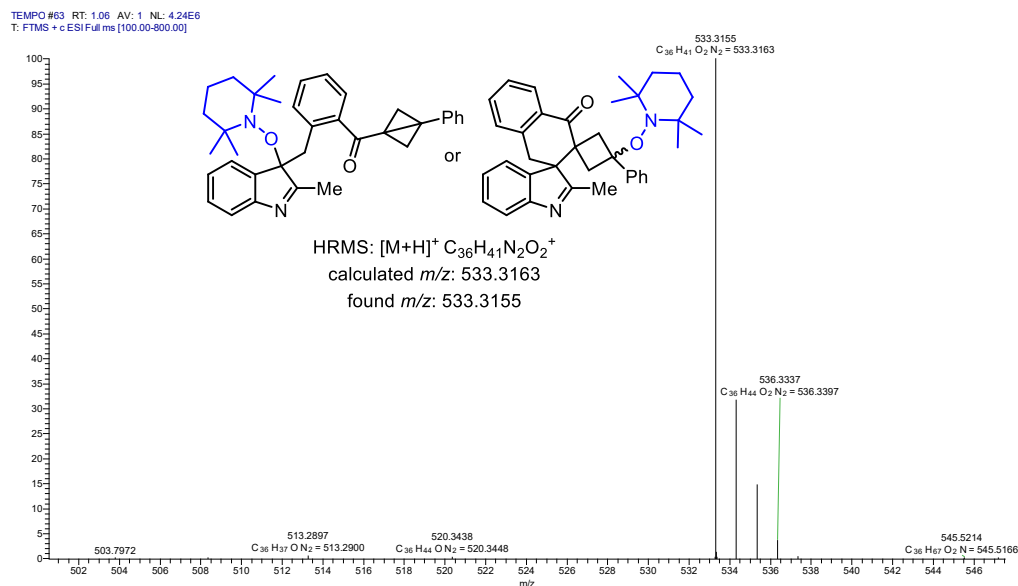
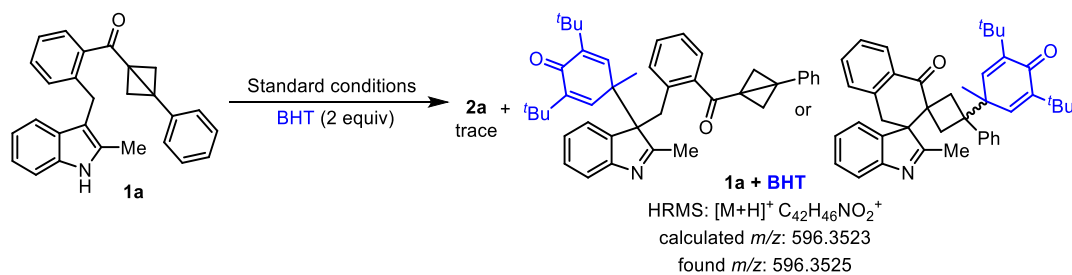


Figure S2. HRMS spectra of added TEMPO



The reaction was performed with the general procedure, and radical trap BHT (88.1 mg, 2.0 equiv) was added to the mixture, and the reaction mixture was stirred for 1 h. Then the reaction mixture was analyzed by HRMS.

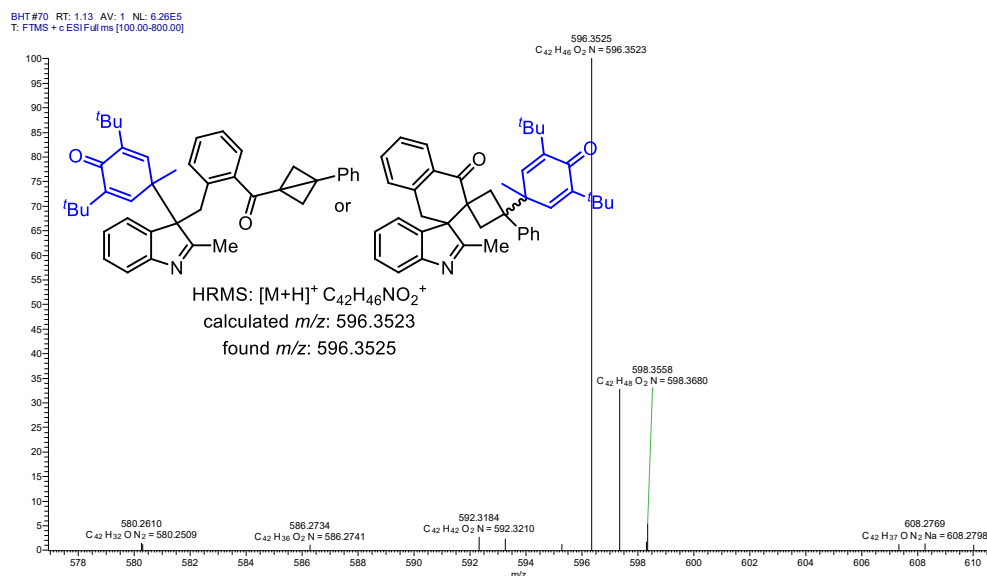
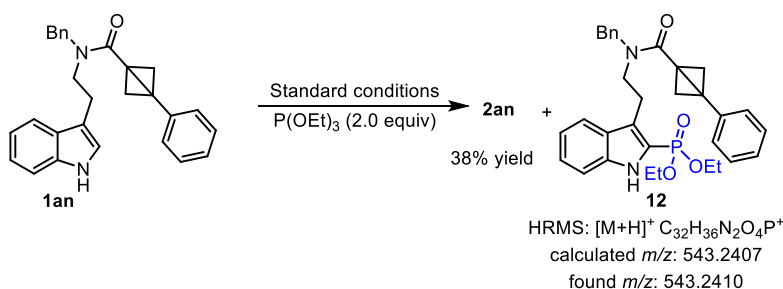


Figure S3. HRMS spectra of added BHT

6.2 Radical cation trapping experiment



The reaction was performed with the general procedure, and radical cation trap $\text{P}(\text{OEt})_3$ (68.5 μL , 2.0 equiv) was added to the mixture, and the reaction mixture was stirred for 5 h. After completion, the resulting mixture was filtered through a thin pad of silica gel, then the filtrate was concentrated in vacuo. The residue was analyzed by the HRMS and crude product was purified by prepared thin layer chromatography plate to give the product **2an** (30.6 mg, 38% yield) as a yellow oil.

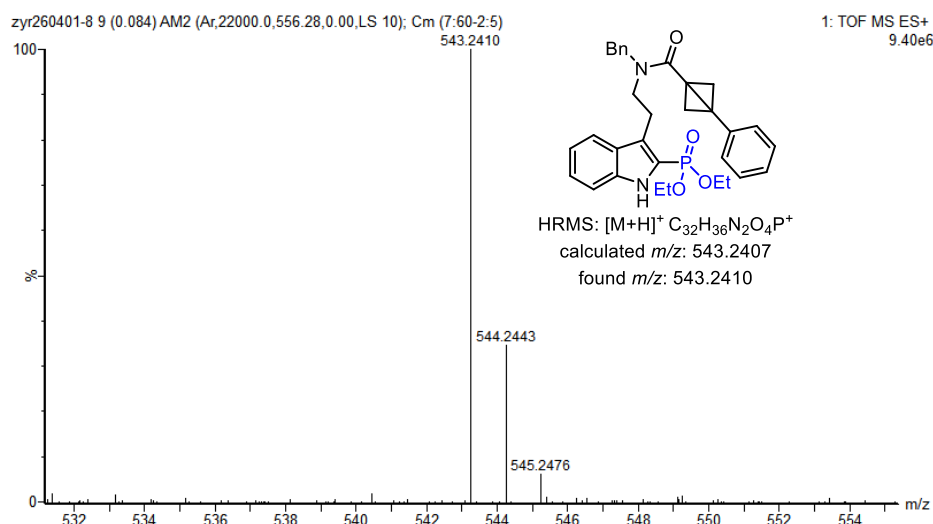


Figure S4. HRMS spectra of added $\text{P}(\text{OEt})_3$

6.3 Cyclic voltammetry (CV) experiments

Cyclic voltammetry experiments were performed in a three-electrode cell connected to three-necked bottles. The oxidation potential was measured at room temperature. Electrochemical Workstation model CHI710F used a glassy carbon working electrode, a platinum wire counter electrode, and a saturated calomel electrode (SCE) at 0.1 V/s scan rate. A solution of the corresponding substrates in MeCN (0.01 M) was tested with 0.1 M $n\text{Bu}_4\text{NPF}_6$ as the supporting electrolyte.

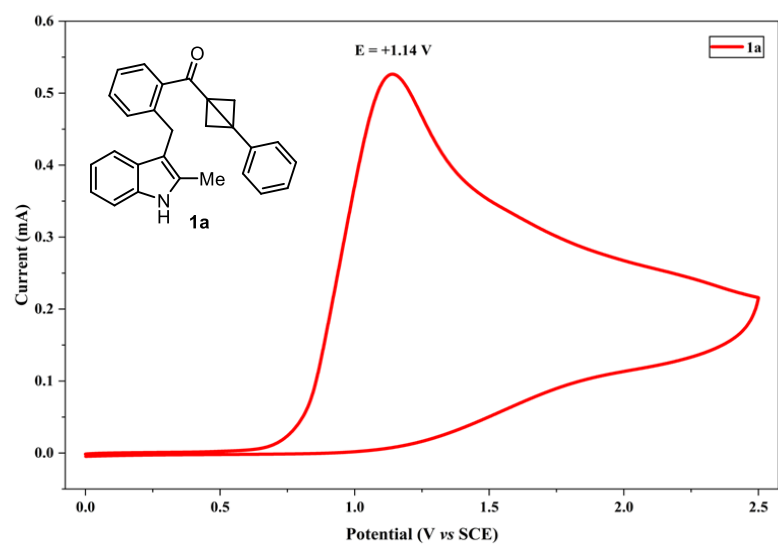


Figure S5. Cyclic voltammetry of **1a**

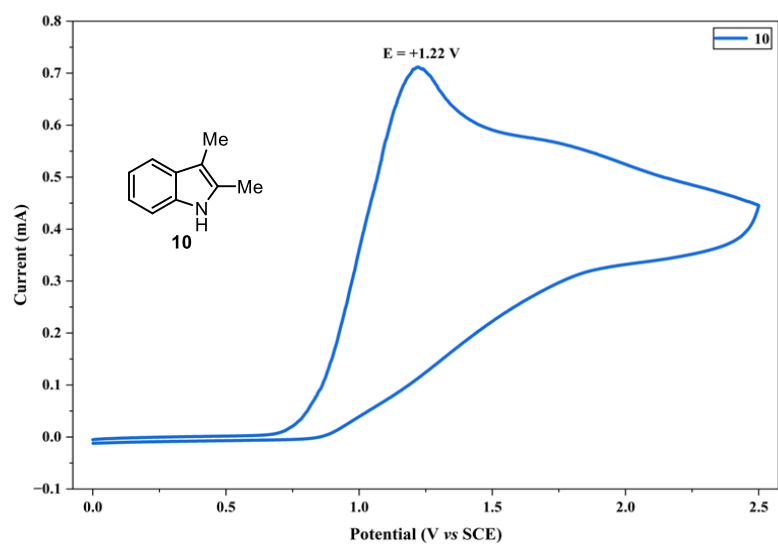


Figure S6. Cyclic voltammetry of **10**

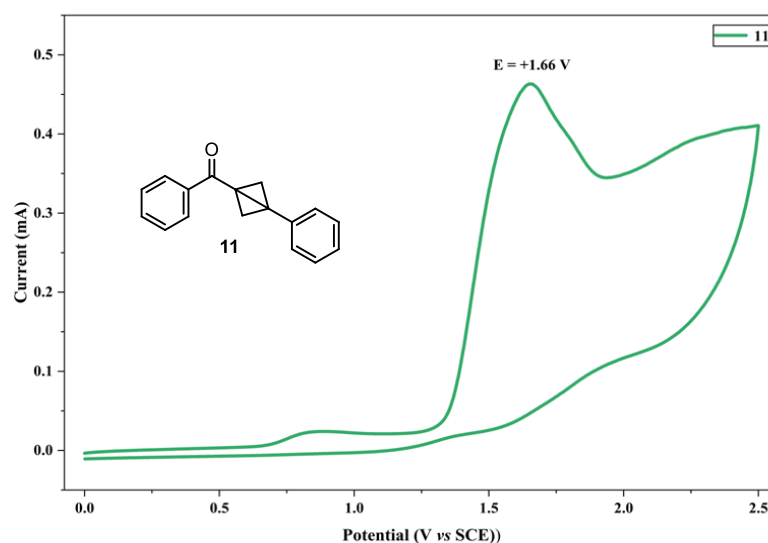
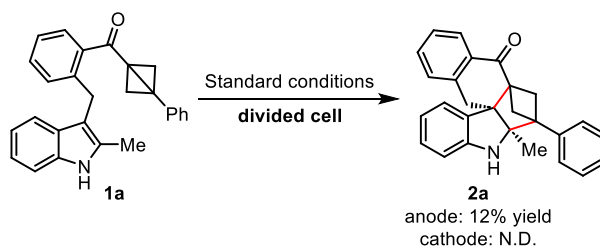


Figure S7. Cyclic voltammetry of **11**

6.4 Divided cell experiments



The experiment was conducted in divided cells separated by an anion-exchange membrane. A magnetic stir bar and a graphite felt (15 mm × 10 mm × 0.2 mm) electrode were placed in the anode cell; another magnetic stir bar and a Pt plate (10 mm × 10 mm × 0.1 mm) electrode were placed in the cathode cell, and then the same solvent containing 0.2 mmol **1a**, 0.2 mmol $n\text{-Bu}_4\text{NBF}_4$, and 10 mL CH_3CN was added into each cell. The reaction was stirred and electrolyzed at a constant current of 1 mA at room temperature for 1 h. After completion of the reaction, the starting material in the anode cell was completely consumed, and the target product **2a** (9.3 mg, 12% yield) was obtained. In contrast, no changes were observed in the starting material in the cathode cell, and no products were generated.

6.4 Faradaic efficiency calculation

The Faradaic efficiency (FE) was calculated according to the following equation:

$$FE = \frac{nZF}{It} \times 100\% = \frac{0.2 \times 93\% \times 10^{-3} \text{ mol} \times 1 \times 9.65 \times 10^4 \text{ C mol}^{-1}}{1 \times 10^{-3} \text{ A} \times 1 \times 3600 \text{ s}} \times 100\% \approx 500\%$$

Where n is the number of moles of the product, Z is the number of electrons transferred per molecule for the redox reaction ($Z = 1$ for oxidation of **1a**), and F is the Faraday constant ($9.65 \times 10^4 \text{ C mol}^{-1}$). According to $Q_1 = nFN$, the theoretical charge required for the formation of **2a** in 93% yield was calculated to be 17.95 C ($1 \times 9.65 \times 10^4 \text{ C mol}^{-1} \times 0.2 \times 10^{-3} \text{ mol} \times 93\%$). Based on the model reaction, complete conversion could be achieved by electrolysis in an undivided cell at a constant current of 1 mA for 1 h. According to $Q_2 = it$ (where i is the applied current and t is the reaction time), the total charge passed was calculated to be 3.6 C ($1 \times 10^{-3} \text{ A} \times 1 \times 3600 \text{ s}$). Therefore, the reaction was driven to completion with 0.2 equiv of the electric charge. The catalytic electric charge used for the reaction also supported the chain reaction mechanism.

6.5 Computational studies

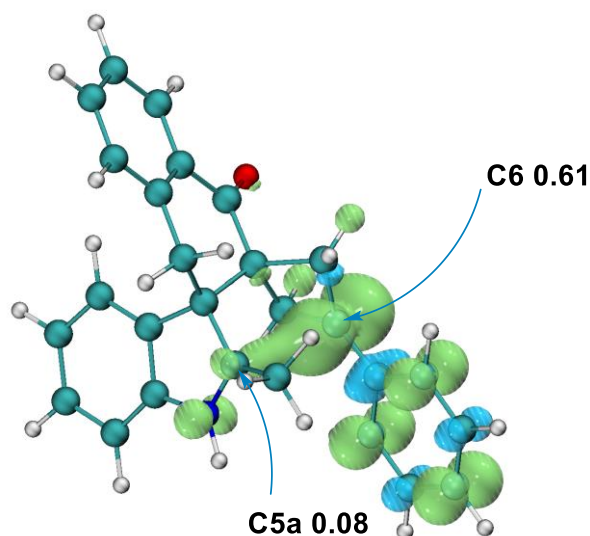
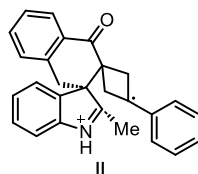


Fig S8. Spin density isovalue (0.004 a.u.) of intermediate II, calculated at the density functional theory (DFT) (U)M06-2X/6-31G(d) level, which is implemented in Gaussian 09.^[3] Mulliken spin population is 0.08 on C5a and 0.61 on C6, respectively.

Full Reference of Gaussian 09 Software

Gaussian 09, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

6.5.1 Cartesian Coordinates (Å) of Optimized Structures



Thermal correction to Gibbs free energy 0.380558 H

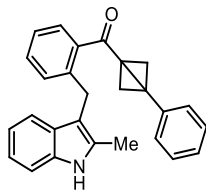
Sum of electronic and thermal free energies -1171.564204 H

C	0.021233	4.825458	-0.324159
C	0.928214	3.771630	-0.389675
C	2.253058	3.951081	0.004506
C	2.657743	5.215664	0.460081
C	1.745204	6.274910	0.516967
C	0.427445	6.080850	0.129914
H	-1.006332	4.667722	-0.635665
H	0.603532	2.800216	-0.752539
C	4.064880	5.478623	0.861440
H	2.097764	7.239119	0.869175
H	-0.281857	6.900050	0.176713
C	4.671692	3.245546	-0.232961
O	4.446347	6.563856	1.243038
C	5.037713	4.305968	0.855295
C	5.283360	3.673220	2.269522
C	6.552437	4.642070	0.829041
C	6.716386	3.544514	1.837145
H	4.706121	2.798478	2.582543
H	5.159673	4.458385	3.026990
H	7.085853	4.590490	-0.125246
H	6.698265	5.637587	1.267309
C	5.652696	2.084951	-0.147920
C	5.002426	3.819887	-1.604907
C	3.216363	2.785393	-0.043815
C	7.770788	2.668984	2.167030
C	7.625394	1.703974	3.195365
C	8.978829	2.690624	1.424297

C	8.642014	0.802597	3.460657
H	6.714621	1.692116	3.788965
C	9.986297	1.781429	1.698152
H	9.112940	3.441372	0.649917
C	9.823313	0.832470	2.712674
H	8.525080	0.076223	4.258261
H	10.911372	1.812825	1.131498
H	10.618832	0.127146	2.927915
H	3.146397	2.216353	0.893299
H	2.933615	2.103177	-0.852534
C	5.591555	0.864560	0.699004
H	4.908578	0.150820	0.218524
H	6.578375	0.400450	0.787511
H	5.213725	1.065192	1.699614
N	6.458589	2.129874	-1.185494
H	7.192223	1.445183	-1.348747
C	6.125692	3.159428	-2.103384
C	4.468203	4.868665	-2.341630
C	6.752395	3.472915	-3.296051
C	5.071004	5.201655	-3.559060
C	6.194294	4.520553	-4.028123
H	3.598552	5.417823	-1.998233
H	4.653957	6.009452	-4.150424
H	6.640901	4.805536	-4.974263
H	7.625507	2.933908	-3.648617

7. Analytical data of starting materials and products

(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1a)



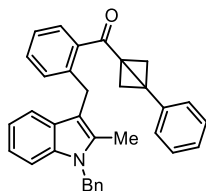
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1a** as a yellow oil (366 mg, 48% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.25 (d, *J* = 2.3 Hz, 3H), 7.17 (q, *J* = 7.9, 6.9 Hz, 3H), 7.11 – 7.02 (m, 4H), 7.00 – 6.93 (m, 2H), 6.85 (d, *J* = 7.5 Hz, 1H), 3.70 (s, 2H), 3.09 (s, 2H), 2.07 (s, 3H), 1.84 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.3, 139.9, 137.8, 135.3, 132.9, 132.5, 130.2, 128.9, 128.9, 128.6, 128.0, 127.5, 125.9, 124.9, 120.7, 118.9, 118.4, 110.2, 109.1, 40.2, 37.0, 34.4, 26.2, 11.5.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₄NO⁺ 378.1852, found 378.1858.

(2-((1-benzyl-2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1b)



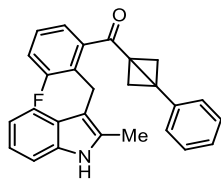
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) afforded **1b** as a yellow oil (455 mg, 60% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.32 (dd, *J* = 18.3, 8.4 Hz, 7H), 7.25 – 7.18 (m, 3H), 7.18 – 7.07 (m, 4H), 7.07 – 6.96 (m, 3H), 6.92 (d, *J* = 7.6 Hz, 1H), 5.32 (s, 2H), 3.81 (s, 2H), 3.17 (s, 2H), 2.15 (s, 3H), 1.91 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 199.9, 140.1, 138.1, 137.8, 136.6, 134.1, 133.1, 130.2, 128.9, 128.8, 128.7, 128.4, 128.2, 127.6, 127.3, 126.0, 125.0, 120.9, 119.1, 118.7, 109.5, 108.9, 46.6, 39.9, 37.1, 34.3, 26.5, 10.3.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₃₄H₃₀NO⁺ 468.2322, found 468.2324.

(3-fluoro-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1c)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1c** as a yellow oil (387 mg, 49% yield).

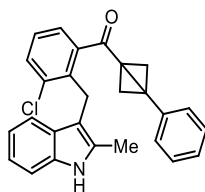
¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.17 (d, *J* = 5.5 Hz, 3H), 7.10 – 7.01 (m, 3H), 6.93 – 6.82 (m, 4H), 6.04 (d, *J* = 7.4 Hz, 1H), 3.89 (s, 2H), 2.72 (s, 2H), 2.00 (s, 3H), 1.42 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 199.0, 161.2 (d, *J* = 246.8 Hz), 141.7 (d, *J* = 3.4 Hz), 135.3, 132.9, 132.5, 128.8, 128.7, 127.7, 127.3 (d, *J* = 5.7 Hz), 127.2 (d, *J* = 12.1 Hz), 126.0, 121.7 (d, *J* = 3.5 Hz), 120.7, 119.0, 118.3, 116.8 (d, *J* = 23.1 Hz), 110.4, 108.9, 40.7, 36.6, 34.9, 21.1 (d, *J* = 4.3 Hz), 11.8.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -114.54.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₃FNO⁺ 396.1758, found 396.1751.

(3-chloro-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1d)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1d** as a yellow oil (369 mg, 45% yield).

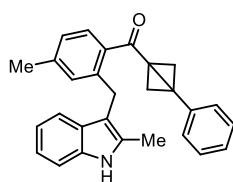
¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.27 (d, *J* = 8.0 Hz, 1H), 7.18 (d, *J* = 7.0 Hz, 3H), 7.10 (d, *J* = 3.5 Hz, 1H), 7.04 (d, *J* = 6.7 Hz, 2H), 6.95 (d, *J* = 4.0 Hz, 2H), 6.91 – 6.81 (m, 2H), 6.12 (d, *J* = 7.6 Hz, 1H), 3.99 (s, 2H), 2.65 (s, 2H), 1.93 (s,

3H), 1.34 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.7, 141.8, 137.0, 135.1, 135.1, 132.8, 132.4, 130.6, 128.6, 128.5, 127.4, 126.7, 125.8, 124.1, 120.4, 118.7, 118.0, 110.1, 108.4, 40.0, 36.1, 34.6, 25.8, 11.7.

HRMS (ESI⁺): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{23}^{35}\text{ClNO}^+$ 412.1463, found 412.1466; m/z : $[\text{M}+\text{H}]^+$ calcd $\text{C}_{27}\text{H}_{23}^{37}\text{ClNO}^+$, 414.1433, found 414.1432.

(4-methyl-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1e)



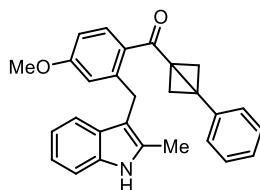
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1e** as a yellow oil (352 mg, 45% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.23 – 7.15 (m, 4H), 7.14 – 7.10 (m, 1H), 7.06 (dd, J = 7.8, 4.7 Hz, 2H), 7.03 – 6.95 (m, 2H), 6.92 (t, J = 7.3 Hz, 1H), 6.81 (d, J = 7.7 Hz, 1H), 6.64 (s, 1H), 3.64 (s, 2H), 3.07 (s, 2H), 1.99 (d, J = 3.2 Hz, 6H), 1.78 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.1, 140.4, 140.2, 135.3, 135.0, 132.9, 132.5, 129.6, 128.9, 128.6, 128.5, 127.4, 125.9, 125.6, 120.6, 118.8, 118.4, 110.2, 109.1, 39.7, 37.0, 34.2, 26.2, 21.4, 11.5.

HRMS (ESI⁺): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{NO}^+$ 392.2009, found 392.2013.

(4-methoxy-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1f)



This compound was prepared according to the **general procedure A**. Purification by

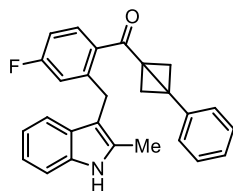
column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1f** as a yellow oil (371 mg, 46% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.82 (s, 1H), 7.32 – 7.27 (m, 5H), 7.23 – 7.17 (m, 2H), 7.09 – 6.99 (m, 2H), 6.99 – 6.93 (m, 1H), 6.61 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.38 (d, *J* = 2.6 Hz, 1H), 3.66 (s, 2H), 3.58 (s, 3H), 3.15 (s, 2H), 2.13 (s, 3H), 1.89 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 198.7, 161.3, 143.2, 135.4, 133.3, 132.4, 131.6, 130.4, 128.7, 127.5, 126.1, 120.9, 119.1, 118.6, 115.4, 110.1, 109.3, 109.3, 55.1, 39.0, 37.3, 33.9, 26.4, 11.7.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₆NO₂⁺ 408.1958, found 408.1952.

(4-fluoro-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1g)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1g** as a yellow oil (389 mg, 49% yield).

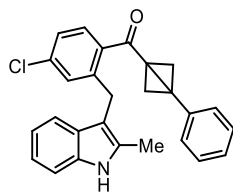
¹H NMR (400 MHz, CDCl₃) δ 8.02 (s, 1H), 7.30 – 7.22 (m, 4H), 7.20 – 7.15 (m, 2H), 7.12 – 6.95 (m, 4H), 6.71 (td, *J* = 8.2, 2.6 Hz, 1H), 6.50 (dd, *J* = 10.5, 2.6 Hz, 1H), 3.64 (s, 2H), 3.10 (s, 2H), 2.05 (s, 3H), 1.86 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 199.0, 163.9 (d, *J* = 250.1 Hz), 144.0 (d, *J* = 7.6 Hz), 135.3, 133.7 (d, *J* = 3.0 Hz), 132.6, 130.8 (d, *J* = 8.8 Hz), 128.7, 128.6, 127.7, 125.9, 120.9, 119.1, 118.3, 116.0 (d, *J* = 22.4 Hz), 111.9 (d, *J* = 21.9 Hz), 110.3, 108.3, 40.3, 37.2, 34.3, 26.2, 11.5.

¹⁹F NMR (376 MHz, CDCl₃) δ -109.04.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₃FNO⁺ 396.1758, found 396.1760.

(4-chloro-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1h)



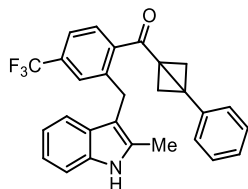
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1h** as a yellow oil (349 mg, 42% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.25 (d, *J* = 4.4 Hz, 4H), 7.19 (s, 1H), 7.15 (s, 1H), 7.08 – 7.00 (m, 3H), 6.98 – 6.90 (m, 2H), 6.81 (d, *J* = 2.1 Hz, 1H), 3.62 (s, 2H), 3.08 (s, 2H), 2.08 (s, 3H), 1.85 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 199.1, 142.5, 136.5, 136.1, 135.3, 132.7, 132.6, 129.6, 129.0, 128.7, 128.7, 127.7, 125.9, 125.3, 121.0, 119.2, 118.3, 110.3, 108.4, 40.6, 37.2, 34.4, 26.1, 11.6.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₃³⁵ClNO⁺ 412.1463, found 412.1466; *m/z*: [M+H]⁺ calcd C₂₇H₂₃³⁷ClNO⁺, 414.1433, found 414.1437.

(2-((2-methyl-1*H*-indol-3-yl)methyl)-4-(trifluoromethyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1i)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1i** as a yellow oil (297 mg, 33% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.39 – 7.33 (m, 5H), 7.28 (d, *J* = 2.3 Hz, 1H), 7.25 (dd, *J* = 5.4, 2.7 Hz, 2H), 7.18 – 7.10 (m, 2H), 7.08 – 7.01 (m, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 3.81 (s, 2H), 3.11 (s, 2H), 2.20 (s, 3H), 1.90 (s, 2H).

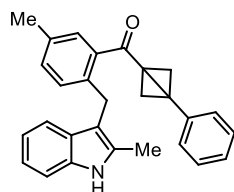
¹³C NMR (101 MHz, Chloroform-*d*) δ 199.2, 141.4, 141.0, 135.4, 132.7, 132.6, 131.7 (d, *J* = 32.3 Hz), 128.8, 128.7, 127.9, 127.7, 126.7 (d, *J* = 305.8 Hz), 126.0, 125.9 (dd, *J* = 7.0, 3.4 Hz), 122.2 (q, *J* = 3.3 Hz), 121.1, 119.3, 118.2, 110.3, 108.3, 41.3, 37.1,

34.7, 26.5, 11.7.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.71.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₃F₃NO⁺ 446.1726, found 446.1728.

(5-methyl-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1j)



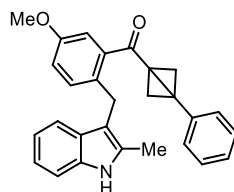
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1j** as a yellow oil (421 mg, 54% yield).

^1H NMR (400 MHz, CDCl₃) δ 8.04 (s, 1H), 7.20 – 7.12 (m, 4H), 7.09 – 7.04 (m, 2H), 7.03 – 6.97 (m, 1H), 6.96 – 6.90 (m, 1H), 6.82 (dd, *J* = 8.1, 2.0 Hz, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 6.54 (d, *J* = 2.0 Hz, 1H), 3.70 (s, 2H), 3.03 (s, 2H), 2.08 (s, 3H), 1.99 (s, 3H), 1.76 (s, 2H).

^{13}C NMR (101 MHz, CDCl₃) δ 200.6, 137.8, 136.7, 135.3, 134.4, 132.8, 132.4, 130.7, 128.8, 128.8, 128.4, 127.9, 127.4, 125.9, 120.5, 118.7, 118.3, 110.2, 109.0, 40.0, 36.9, 34.4, 26.0, 20.7, 11.4.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₆NO⁺ 392.2009, found 392.2011.

(5-methoxy-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1k)



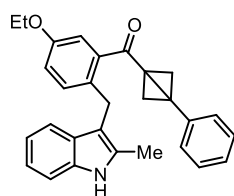
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1k** as a yellow oil (386 mg, 47% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (s, 1H), 7.26 (d, *J* = 3.9 Hz, 3H), 7.22 (s, 2H), 7.19 – 7.15 (m, 1H), 7.11 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.07 – 7.02 (m, 1H), 6.98 – 6.92 (m, 1H), 6.78 (d, *J* = 8.6 Hz, 1H), 6.62 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.25 (d, *J* = 2.8 Hz, 1H), 3.73 (s, 2H), 3.51 (s, 3H), 3.06 (s, 2H), 2.14 (s, 3H), 1.81 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.0, 156.9, 135.4, 133.1, 132.3, 131.7, 130.2, 129.0, 128.7, 127.6, 126.1, 120.9, 119.1, 118.5, 116.3, 111.8, 110.2, 55.2, 40.3, 37.1, 34.4, 25.8, 11.7.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₆NO₂⁺ 408.1958, found 408.1953.

(5-ethoxy-2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1l)



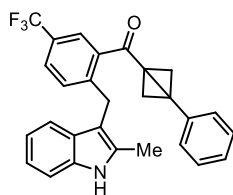
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1l** as a yellow oil (368 mg, 44% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (s, 1H), 7.31 (d, *J* = 4.3 Hz, 4H), 7.24 (d, *J* = 4.2 Hz, 1H), 7.18 (dd, *J* = 18.6, 7.9 Hz, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 8.6 Hz, 1H), 6.67 (dd, *J* = 8.6, 2.7 Hz, 1H), 6.39 (d, *J* = 2.7 Hz, 1H), 3.76 (d, *J* = 6.9 Hz, 4H), 3.12 (s, 2H), 2.16 (s, 3H), 1.86 (s, 2H), 1.34 (t, *J* = 7.0 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.1, 156.2, 138.8, 135.3, 133.1, 132.3, 131.6, 130.2, 128.9, 128.6, 127.5, 126.1, 120.8, 119.0, 118.5, 116.8, 112.7, 110.2, 109.6, 63.4, 40.3, 37.1, 34.4, 25.7, 14.8, 11.6.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₉H₂₈NO₂⁺ 422.2115, found 422.2110.

(2-((2-methyl-1*H*-indol-3-yl)methyl)-5-(trifluoromethyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1m)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1m** as a yellow oil (343 mg, 39% yield).

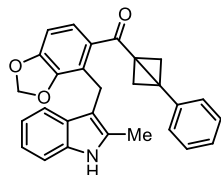
¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.39 – 7.30 (m, 6H), 7.28 (s, 1H), 7.16 – 7.10 (m, 2H), 7.09 – 7.02 (m, 3H), 3.83 (s, 2H), 3.13 (s, 2H), 2.21 (s, 3H), 1.94 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 198.9, 144.1, 138.5, 132.7, 132.5, 129.6, 128.9, 128.7, 128.0, 127.7 (d, J = 32.7 Hz), 126.6 (q, J = 3.3 Hz), 125.9, 124.3 (q), 123.9 (d, J = 272.1 Hz), 121.2, 119.4, 118.3, 110.3, 108.5, 41.3, 37.2, 34.6, 26.5, 11.7.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.43.

HRMS (ESI⁺): m/z : $[M+H]^+$ calcd for C₂₈H₂₃F₃NO⁺ 446.1726, found 446.1718.

(4-((2-methyl-1H-indol-3-yl)methyl)benzo[d][1,3]dioxol-5-yl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1n)



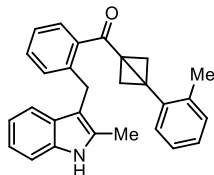
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1n** as a yellow oil (355 mg, 42% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 (s, 1H), 7.20 – 7.14 (m, 4H), 7.11 – 7.03 (m, 2H), 6.99 – 6.91 (m, 2H), 6.90 – 6.82 (m, 1H), 6.56 (s, 1H), 6.20 (s, 1H), 5.69 (s, 2H), 3.51 (s, 2H), 3.04 (s, 2H), 1.99 (s, 3H), 1.77 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 198.6, 149.3, 144.7, 136.3, 135.3, 132.4, 130.9, 128.8, 128.6, 127.6, 126.0, 120.9, 119.1, 118.5, 110.2, 109.5, 109.4, 108.9, 101.2, 40.0, 37.3, 34.0, 26.1, 11.6.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₈H₂₄NO₃⁺ 422.1751, found 422.1754.

(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-(*o*-tolyl)bicyclo[1.1.0]butan-1-yl)methanone (1o)



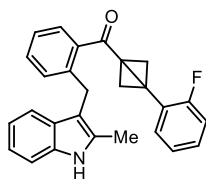
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1o** as a yellow oil (332 mg, 42% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 1H), 7.19 (dd, *J* = 7.1, 2.0 Hz, 1H), 7.13 (t, *J* = 2.0 Hz, 3H), 7.09 – 7.01 (m, 6H), 6.94 – 6.87 (m, 2H), 4.03 (s, 2H), 2.84 (s, 2H), 2.35 (s, 3H), 2.07 (s, 3H), 1.83 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 201.4, 140.1, 138.3, 138.2, 135.4, 132.6, 131.8, 131.0, 130.3, 129.2, 128.9, 127.9, 127.6, 126.0, 126.0, 125.1, 120.8, 119.0, 118.3, 110.2, 109.2, 40.5, 38.3, 32.3, 26.9, 20.6, 11.5.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₈H₂₆NO⁺ 392.2009, found 392.2011.

(3-(2-fluorophenyl)bicyclo[1.1.0]butan-1-yl)(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)methanone (1p)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1p** as a yellow oil (295 mg, 37% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.24 – 7.16 (m, 2H), 7.12 – 7.06 (m, 4H), 7.06 – 7.00 (m, 4H), 6.97 – 6.85 (m, 4H), 3.87 (s, 2H), 3.09 (s, 2H), 2.02 (s, 3H), 1.80 (s, 2H).

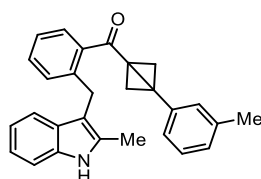
¹³C NMR (101 MHz, Chloroform-*d*) δ 200.3, 161.4 (d, *J* = 248.9 Hz), 140.2, 137.7,

135.3, 132.6, 130.4, 129.4 (d, $J = 3.0$ Hz), 129.1, 129.0 (d, $J = 8.1$ Hz), 128.8, 128.2, 125.0, 124.2 (d, $J = 3.6$ Hz), 120.8, 120.7, 118.9, 118.3, 115.9 (d, $J = 21.6$ Hz), 110.3, 108.9, 38.9 (d, $J = 4.0$ Hz), 34.9, 32.4, 26.6, 11.4.

^{19}F NMR (376 MHz, Chloroform- d) δ -114.41.

HRMS (ESI $^{+}$): m/z : $[\text{M}+\text{H}]^{+}$ calcd for $\text{C}_{27}\text{H}_{23}\text{FNO}^{+}$ 396.1758, found 396.1762.

(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-(*m*-tolyl)bicyclo[1.1.0]butan-1-yl)methanone (1q)



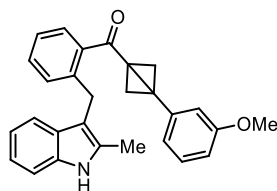
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1q** as a yellow oil (361 mg, 46% yield).

^1H NMR (400 MHz, Chloroform- d) δ 8.05 (s, 1H), 7.11 – 7.05 (m, 3H), 7.04 – 6.90 (m, 8H), 6.82 (d, $J = 7.5$ Hz, 1H), 3.72 (s, 2H), 3.04 (s, 2H), 2.21 (s, 3H), 2.00 (s, 3H), 1.77 (s, 2H).

^{13}C NMR (101 MHz, Chloroform- d) δ 139.9, 138.1, 137.9, 135.3, 132.6, 132.5, 130.1, 128.9, 128.8, 128.5, 128.4, 127.8, 126.7, 124.9, 123.0, 120.6, 118.8, 118.3, 110.2, 108.9, 37.0, 34.3, 26.2, 21.3, 11.4.

HRMS (ESI $^{+}$): m/z : $[\text{M}+\text{H}]^{+}$ calcd for $\text{C}_{28}\text{H}_{26}\text{NO}^{+}$ 392.2009, found 392.2006.

(3-(3-methoxyphenyl)bicyclo[1.1.0]butan-1-yl)(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)methanone (1r)



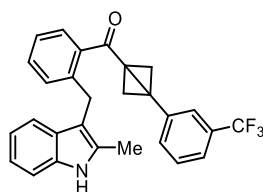
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1r** as a yellow oil (412 mg, 51% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.14 – 7.06 (m, 3H), 7.05 – 6.98 (m, 4H), 6.95 – 6.89 (m, 1H), 6.83 (dd, J = 7.7, 3.4 Hz, 2H), 6.75 (t, J = 2.1 Hz, 1H), 6.69 (dd, J = 8.2, 2.5 Hz, 1H), 3.72 (s, 2H), 3.61 (s, 3H), 3.04 (s, 2H), 2.01 (s, 3H), 1.78 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 159.6, 139.9, 135.3, 134.5, 132.5, 130.2, 129.6, 128.9, 128.8, 128.0, 124.9, 120.6, 118.9, 118.3, 118.3, 113.0, 111.7, 110.2, 108.9, 55.1, 40.0, 37.0, 34.4, 26.2, 11.4.

HRMS (ESI⁺): m/z : [M+H]⁺ calcd for C₂₈H₂₆NO₂⁺ 408.1958, found 408.1961.

(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-(3-(trifluoromethyl)phenyl)bicyclo[1.1.0]butan-1-yl)methanone (1s)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1s** as a yellow oil (382 mg, 43% yield).

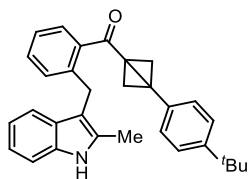
¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.53 – 7.47 (m, 3H), 7.41 – 7.36 (m, 1H), 7.20 – 7.06 (m, 5H), 7.04 – 6.91 (m, 3H), 3.83 (s, 2H), 3.13 (s, 2H), 2.13 (s, 3H), 1.91 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 199.8, 140.1, 137.7, 135.3, 134.6, 132.5, 130.9 (d, J = 32.3 Hz), 130.5, 129.3, 129.2, 129.0, 128.9, 127.7, 125.2, 124.0 (q, J = 3.5 Hz), 124.0 (d, J = 272.6 Hz), 122.9 (q, J = 3.8 Hz), 120.8, 119.1, 118.3, 110.2, 109.1, 38.4, 37.1, 34.6, 26.6, 11.4.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -62.49.

HRMS (ESI⁺): m/z : [M+H]⁺ calcd for C₂₈H₂₃F₃NO⁺ 446.1726, found 446.1728.

(3-(4-(tert-butyl)phenyl)bicyclo[1.1.0]butan-1-yl)(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)methanone (1t)



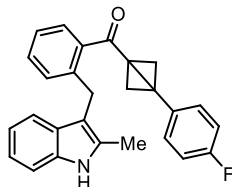
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1t** as a yellow oil (423 mg, 49% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.42 (q, *J* = 8.5 Hz, 4H), 7.33 – 7.29 (m, 2H), 7.25 – 7.12 (m, 5H), 7.11 – 7.04 (m, 1H), 3.87 (s, 2H), 3.32 (s, 2H), 2.24 (s, 3H), 2.02 (s, 2H), 1.32 (s, 9H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.6, 150.5, 139.8, 137.9, 135.3, 132.3, 130.0, 129.5, 129.0, 128.7, 128.0, 125.5, 124.8, 120.5, 118.6, 118.5, 110.2, 108.8, 40.7, 37.1, 34.3, 31.0, 26.2, 11.4.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₃₁H₃₂NO⁺ 434.2478, found 434.2475.

(3-(4-fluorophenyl)bicyclo[1.1.0]butan-1-yl)(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)methanone (1u)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1u** as a yellow oil (394 mg, 50% yield).

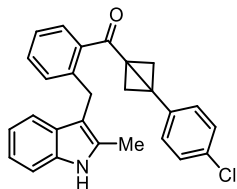
¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.18 – 7.14 (m, 3H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.07 – 6.98 (m, 4H), 6.96 – 6.84 (m, 5H), 3.75 (s, 2H), 3.00 (s, 2H), 2.03 (s, 3H), 1.79 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.2, 162.3 (d, *J* = 247.0 Hz), 140.0, 137.7, 135.3, 132.5, 130.3, 129.1, 128.8, 128.8, 127.9, 127.6 (d, *J* = 8.1 Hz), 125.1, 120.7, 118.9, 118.2, 115.6 (d, *J* = 21.8 Hz), 110.3, 108.9, 39.5, 37.1, 34.0, 26.5, 11.4.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -113.78.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₇H₂₃FNO⁺ 396.1758, found 396.1754.

(3-(4-chlorophenyl)bicyclo[1.1.0]butan-1-yl)(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)methanone (1v)



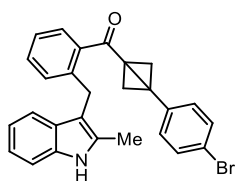
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1v** as a yellow oil (388 mg, 47% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (s, 1H), 7.29 (d, *J* = 8.6 Hz, 2H), 7.25 – 7.20 (m, 3H), 7.20 – 7.10 (m, 5H), 7.05 (t, *J* = 7.4 Hz, 1H), 7.01 – 6.95 (m, 1H), 3.84 (s, 2H), 3.11 (s, 2H), 2.14 (s, 3H), 1.90 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 199.9, 140.1, 137.5, 135.3, 133.3, 132.4, 131.7, 130.4, 129.2, 128.8, 128.7, 128.0, 127.3, 125.0, 120.7, 119.0, 118.2, 110.2, 108.9, 39.1, 37.1, 34.5, 26.4, 11.4.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₇H₂₃³⁵ClNO⁺ 412.1463, found 412.1467; [M+H]⁺ calcd for C₂₇H₂₃³⁷ClNO⁺ 414.1433, found 414.1435.

(3-(4-bromophenyl)bicyclo[1.1.0]butan-1-yl)(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)methanone (1w)



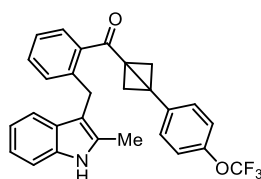
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1w** as a yellow oil (511 mg, 56% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 (s, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.06 (dd, *J* = 7.9, 4.5 Hz, 2H), 7.03 – 6.91 (m, 7H), 6.87 – 6.82 (m, 1H), 3.71 (s, 2H), 2.96 (s, 2H), 1.98 (s, 3H), 1.73 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 199.8, 140.0, 137.4, 135.2, 132.4, 132.1, 131.5, 130.3, 129.1, 128.7, 127.9, 127.5, 125.0, 121.3, 120.6, 118.9, 118.1, 110.2, 108.7, 39.1, 37.0, 34.5, 26.3, 11.3.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₃⁷⁹BrNO⁺ 456.0958, found 456.0956; [M+H]⁺ calcd for C₂₇H₂₃⁸¹BrNO⁺ 458.0937, found 458.0936.

(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-(4-(trifluoromethoxy)phenyl)bicyclo[1.1.0]butan-1-yl)methanone (1x)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1x** as a yellow oil (432 mg, 47% yield).

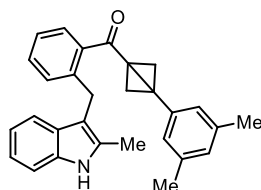
¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 (s, 1H), 7.18 (d, *J* = 8.7 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 7.08 – 6.99 (m, 5H), 6.95 – 6.84 (m, 3H), 3.78 (s, 2H), 2.99 (s, 2H), 2.02 (s, 3H), 1.79 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.0, 148.5 (d, *J* = 2.0 Hz), 140.1, 137.7, 135.3, 132.4, 132.0, 130.4, 129.2, 128.8, 127.7, 127.3, 125.2, 121.0, 120.8, 120.4 (q, *J* = 257.3 Hz), 119.0, 118.2, 110.3, 109.0, 38.8, 37.1, 34.3, 26.6, 11.3.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -57.66.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₃F₃NO₂⁺ 462.1675, found 462.1672.

(3-(3,5-dimethylphenyl)bicyclo[1.1.0]butan-1-yl)(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)methanone (1y)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1y**

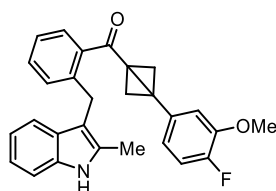
as a yellow oil (438 mg, 54% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.40 (s, 1H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.25 – 7.13 (m, 5H), 7.10 – 7.04 (m, 3H), 7.03 (s, 1H), 4.00 (s, 2H), 3.27 (s, 2H), 2.39 (s, 6H), 2.20 (s, 3H), 1.97 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.5, 139.8, 137.9, 137.8, 135.2, 132.4, 132.4, 130.0, 129.4, 128.8, 128.8, 127.6, 124.7, 123.8, 120.5, 118.7, 118.1, 110.2, 108.8, 36.9, 34.3, 26.2, 21.1, 11.1.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₉H₂₈NO⁺ 406.2165, found 406.2166.

(3-(4-fluoro-3-methoxyphenyl)bicyclo[1.1.0]butan-1-yl)(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)methanone (1z)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1z** as a yellow oil (375 mg, 44% yield).

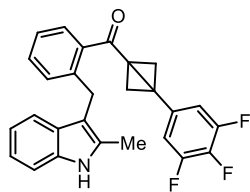
¹H NMR (400 MHz, Chloroform-*d*) δ 8.16 (s, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.19 – 7.13 (m, 2H), 7.13 – 7.07 (m, 2H), 7.05 – 6.96 (m, 4H), 6.88 – 6.80 (m, 2H), 3.90 (s, 2H), 3.80 (s, 3H), 3.08 (s, 2H), 2.14 (s, 3H), 1.88 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.0, 152.0 (d, *J* = 246.7 Hz), 147.5 (d, *J* = 11.0 Hz), 140.0, 137.8, 135.3, 132.4, 130.3, 129.4 (d, *J* = 3.6 Hz), 129.1, 128.8, 127.7, 125.0, 120.7, 119.0, 118.7 (d, *J* = 6.9 Hz), 118.1, 116.1 (d, *J* = 18.7 Hz), 110.8, 110.2, 108.9, 56.1, 39.7, 37.1, 34.1, 26.5, 11.3.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -135.67.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₅FNO₂⁺ 426.1864, found 426.1863.

(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-(3,4,5-trifluorophenyl)bicyclo[1.1.0]butan-1-yl)methanone (1aa)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1aa** as a yellow oil (364 mg, 42% yield).

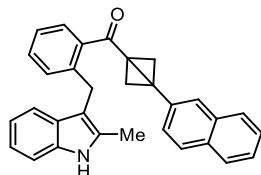
¹H NMR (400 MHz, CDCl₃) δ 8.13 (s, 1H), 7.25 – 7.12 (m, 6H), 7.11 – 7.01 (m, 2H), 6.94 (dd, *J* = 8.1, 6.2 Hz, 2H), 3.98 (s, 2H), 3.04 (s, 2H), 2.18 (s, 3H), 1.90 (s, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 199.3, 151.1 (ddd, *J* = 250.5, 10.2, 4.2 Hz), 140.2, 139.0 (dt, *J* = 253.1, 15.6 Hz), 137.2, 135.3, 132.5, 130.8, 130.3 (q, *J* = 12.6, 8.2 Hz), 129.4, 128.7, 128.0, 125.3, 120.8, 119.0, 118.0, 110.2 (d, *J* = 7.0 Hz), 110.1 (d, *J* = 5.9 Hz), 108.8, 37.5, 37.1, 34.5, 26.8, 11.2.

¹⁹F NMR (376 MHz, CDCl₃) δ -133.14 (d, *J* = 20.6 Hz), -160.95 (t, *J* = 20.6 Hz).

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₁F₃NO⁺ 432.1570, found 432.1568.

(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-(naphthalen-2-yl)bicyclo[1.1.0]butan-1-yl)methanone (1ab)



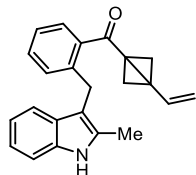
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1ab** as a yellow oil (418 mg, 49% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (s, 1H), 7.85 – 7.76 (m, 4H), 7.55 – 7.44 (m, 3H), 7.19 – 7.08 (m, 5H), 7.01 – 6.91 (m, 3H), 3.75 (s, 2H), 3.33 (s, 2H), 2.00 (s, 2H), 1.90 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.2, 140.0, 135.1, 133.2, 132.3, 130.5, 130.2, 129.0, 128.7, 128.3, 128.0, 127.7, 127.5, 126.5, 125.9, 125.6, 124.9, 123.2, 120.5, 118.8, 118.0, 110.1, 108.8, 40.6, 37.2, 34.7, 26.2, 11.0.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₃₁H₂₆NO⁺ 428.2009, found 428.2003.

(2-((2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-vinylbicyclo[1.1.0]butan-1-yl)methanone (1ac)



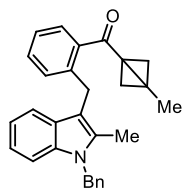
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1ac** as a yellow oil (236 mg, 36% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.22 (s, 1H), 7.38 – 7.31 (m, 1H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.12 – 7.07 (m, 3H), 7.05 – 6.99 (m, 1H), 6.98 – 6.89 (m, 2H), 5.90 (dd, *J* = 17.0, 10.3 Hz, 1H), 5.32 (dd, *J* = 17.0, 1.2 Hz, 1H), 5.16 (dd, *J* = 10.3, 1.2 Hz, 1H), 4.18 (s, 2H), 2.70 (s, 2H), 2.12 (s, 3H), 1.63 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.8, 140.0, 138.0, 135.3, 132.6, 130.5, 130.2, 129.2, 128.8, 127.8, 125.2, 120.6, 118.9, 118.9, 118.1, 110.3, 108.9, 41.0, 38.4, 31.3, 27.3, 11.5.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₃H₂₂NO⁺ 328.1696, found 328.1698.

(2-((1-benzyl-2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-methylbicyclo[1.1.0]butan-1-yl)methanone (1ad)



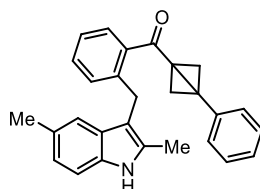
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) afforded **1ad** as a yellow oil (379 mg, 47% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.47 – 7.41 (m, 1H), 7.30 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.20 – 7.14 (m, 3H), 7.11 – 6.92 (m, 5H), 5.30 (s, 2H), 4.34 (s, 2H), 2.36 (s, 2H), 2.24 (s, 3H), 1.59 (s, 3H), 1.51 (d, *J* = 1.2 Hz, 2H).

^{13}C NMR (101 MHz, CDCl_3) δ 202.8, 140.1, 138.8, 138.1, 136.7, 134.2, 130.3, 129.3, 128.8, 128.4, 128.1, 127.3, 126.0, 125.4, 121.0, 119.2, 118.5, 109.7, 109.1, 46.6, 40.4, 36.0, 27.7, 24.5, 13.3, 10.4.

HRMS (ESI^+): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{29}\text{H}_{28}\text{NO}^+$ 406.2165, found 406.2166.

(2-((2,5-dimethyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1ae)



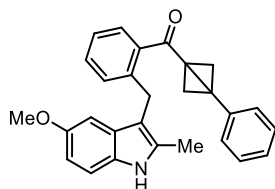
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1ae** as a yellow oil (397 mg, 51% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.04 (s, 1H), 7.42 – 7.34 (m, 4H), 7.34 – 7.28 (m, 1H), 7.20 – 7.11 (m, 4H), 7.07 (s, 1H), 7.02 (dd, J = 8.2, 1.6 Hz, 1H), 6.98 (d, J = 7.3 Hz, 1H), 3.83 (s, 2H), 3.24 (s, 2H), 2.51 (s, 3H), 2.13 (s, 3H), 1.98 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.0, 137.7, 133.6, 132.8, 132.6, 130.2, 129.1, 128.8, 128.6, 127.9, 127.8, 127.5, 125.9, 124.9, 122.2, 118.0, 109.9, 108.4, 40.1, 37.0, 34.4, 26.1, 21.5, 11.4.

HRMS (ESI^+): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{NO}^+$ 392.2009, found 392.2007.

(2-((5-methoxy-2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1af)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1af** as a yellow oil (366 mg, 45% yield).

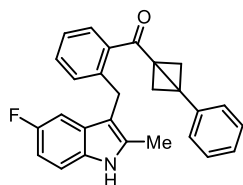
^1H NMR (400 MHz, Chloroform-*d*) δ 7.91 (s, 1H), 7.23 (d, J = 4.3 Hz, 4H), 7.18 (d, J

= 5.3 Hz, 1H), 7.11 – 7.04 (m, 1H), 7.00 (t, J = 7.3 Hz, 2H), 6.92 (dd, J = 7.6, 1.6 Hz, 1H), 6.86 (d, J = 7.7 Hz, 1H), 6.69 (dd, J = 8.6, 2.4 Hz, 1H), 6.64 (d, J = 2.4 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 2H), 3.06 (s, 2H), 2.03 (s, 3H), 1.82 (s, 2H).

^{13}C NMR (101 MHz, Chloroform- d) δ 153.6, 139.8, 138.0, 133.3, 132.9, 130.5, 130.2, 129.5, 129.0, 128.6, 127.8, 127.5, 125.9, 125.0, 110.8, 110.2, 109.1, 101.0, 55.9, 40.1, 37.0, 34.4, 26.2, 11.7.

HRMS (ESI $^{+}$): m/z : $[M+H]^{+}$ calcd for $\text{C}_{28}\text{H}_{26}\text{NO}_2^{+}$ 408.1958, found 408.1964.

(2-((5-fluoro-2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1ag)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1ag** as a yellow oil (325 mg, 41% yield).

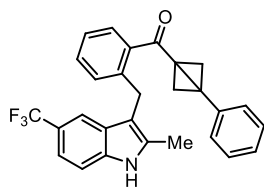
^1H NMR (400 MHz, Chloroform- d) δ 8.20 (s, 1H), 7.26 – 7.20 (m, 4H), 7.15 (d, J = 5.5 Hz, 1H), 7.08 – 7.00 (m, 3H), 6.96 (dd, J = 8.7, 4.4 Hz, 1H), 6.79 (d, J = 7.2 Hz, 1H), 6.72 (td, J = 9.1, 2.5 Hz, 1H), 6.64 (dd, J = 9.9, 2.5 Hz, 1H), 3.58 (s, 2H), 3.07 (s, 2H), 2.00 (s, 3H), 1.81 (s, 2H).

^{13}C NMR (101 MHz, Chloroform- d) δ 200.3, 157.5 (d, J = 232.7 Hz), 139.6, 137.7, 134.6, 132.8, 131.8, 130.3, 129.2 (d, J = 9.8 Hz), 128.9, 128.7, 128.3, 127.6, 125.9, 125.1, 110.7 (d, J = 9.7 Hz), 109.3 (d, J = 4.3 Hz), 108.6 (d, J = 26.0 Hz), 103.4 (d, J = 23.3 Hz), 40.3, 37.0, 34.5, 26.3, 11.5.

^{19}F NMR (376 MHz, Chloroform- d) δ -125.25.

HRMS (ESI $^{+}$): m/z : $[M+H]^{+}$ calcd for $\text{C}_{27}\text{H}_{23}\text{FNO}^{+}$ 396.1758, found 396.1755.

(2-((2-methyl-5-(trifluoromethyl)-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1ah)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1ah** as a yellow solid (428 mg, 48% yield), melting point: 205–207 °C.

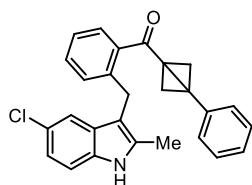
¹H NMR (400 MHz, DMSO) δ 11.31 (s, 1H), 7.46 – 7.35 (m, 2H), 7.35 – 7.02 (m, 9H), 6.77 (d, J = 7.6 Hz, 1H), 3.40 (s, 2H), 3.09 (s, 2H), 2.19 (s, 3H), 1.89 (s, 2H).

¹³C NMR (101 MHz, DMSO) δ 198.8, 139.1, 137.6, 136.9, 135.3, 132.9, 130.2, 128.7, 128.5, 128.2, 127.6, 127.3, 125.9, 125.8 (q, J = 271.1 Hz), 125.2, 119.0 (q, J = 30.6 Hz), 116.6, 115.0 (d, J = 4.6 Hz), 111.0, 109.2, 39.4, 36.7, 34.1, 25.1, 11.3.

¹⁹F NMR (376 MHz, DMSO) δ -58.20.

HRMS (ESI⁺): m/z : [M+H]⁺ calcd for C₂₈H₂₃F₃NO⁺ 446.1726, found 446.1725.

(2-((5-chloro-2-methyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1ai)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1ai** as a yellow oil (419 mg, 51% yield).

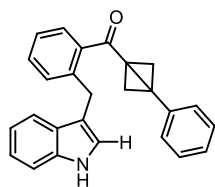
¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (s, 1H), 7.31 (d, J = 5.4 Hz, 3H), 7.23 (td, J = 5.7, 3.2 Hz, 1H), 7.18 – 7.12 (m, 2H), 7.11 (dd, J = 5.3, 2.4 Hz, 2H), 7.08 (s, 1H), 7.00 (dd, J = 8.5, 2.0 Hz, 1H), 6.97 (d, J = 2.0 Hz, 1H), 6.78 (dd, J = 7.3, 1.7 Hz, 1H), 3.56 (s, 2H), 3.13 (s, 2H), 2.12 (s, 3H), 1.89 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 139.5, 137.6, 134.2, 133.7, 133.0, 130.4, 130.1, 128.9, 128.8, 128.7, 127.7, 126.0, 125.2, 124.7, 121.1, 118.1, 111.1, 109.2, 40.1, 37.2,

34.4, 26.2, 11.7.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₇H₂₃³⁵ClNO⁺ 412.1463, found 412.1466;
[M+H]⁺ calcd for C₂₇H₂₃³⁷ClNO⁺ 414.1433, found 414.1428.

**(2-((1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone
(1aj)**



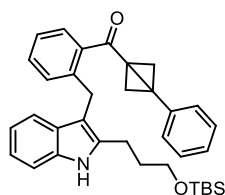
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1aj** as a yellow oil (216 mg, 30% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 8.09 (s, 1H), 7.31 (s, 2H), 7.21 (d, *J* = 1.9 Hz, 3H), 7.17 – 7.09 (m, 3H), 7.09 – 6.97 (m, 5H), 6.66 (d, *J* = 2.3 Hz, 1H), 3.67 (s, 2H), 3.07 (s, 2H), 1.83 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 200.2, 139.9, 138.1, 136.3, 132.9, 130.2, 129.9, 128.7, 128.2, 127.6, 126.0, 125.3, 123.2, 121.8, 119.2, 119.2, 114.7, 111.1, 40.2, 37.1, 34.4, 27.8.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₆H₂₂NO⁺ 364.1696, found 364.1697.

(2-((2-(3-((tert-butyldimethylsilyl)oxy)propyl)-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1ak)



This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1ak** as a yellow oil (548 mg, 51% yield).

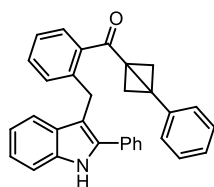
¹H NMR (400 MHz, CDCl₃) δ 8.57 (s, 1H), 7.26 – 7.24 (m, 2H), 7.21 – 7.16 (m, 3H),

7.08 – 6.97 (m, 5H), 6.96 – 6.90 (m, 1H), 6.85 – 6.78 (m, 1H), 3.69 (s, 2H), 3.59 (t, $J = 6.0$ Hz, 2H), 3.09 (d, $J = 1.3$ Hz, 2H), 2.64 (t, $J = 7.0$ Hz, 2H), 1.83 (s, 2H), 1.70 (p, $J = 6.6$ Hz, 2H), 0.92 (s, 9H), 0.07 (s, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 200.1, 140.2, 137.8, 136.6, 135.3, 133.0, 130.2, 129.0, 128.8, 128.6, 128.1, 127.5, 126.0, 124.9, 120.8, 118.8, 118.7, 110.2, 108.7, 62.8, 40.0, 37.1, 34.3, 31.8, 26.1, 26.1, 22.6, 18.4, -5.2.

HRMS (ESI⁺): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{35}\text{H}_{42}\text{NO}_2\text{Si}^+$ 536.2979, found 536.2975.

(2-((2-phenyl-1*H*-indol-3-yl)methyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1al)



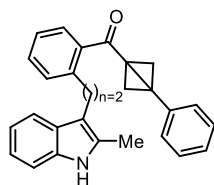
This compound was prepared according to the **general procedure A**. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1al** as a yellow oil (432 mg, 49% yield).

^1H NMR (400 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.32 (d, $J = 7.0$ Hz, 2H), 7.27 – 7.16 (m, 6H), 7.14 (d, $J = 7.3$ Hz, 2H), 7.11 – 6.98 (m, 5H), 6.98 – 6.87 (m, 3H), 3.91 (s, 2H), 3.04 (s, 2H), 1.76 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.3, 139.7, 138.1, 136.1, 135.8, 132.7, 132.7, 130.3, 129.2, 128.8, 128.7, 128.6, 128.0, 127.7, 127.6, 127.5, 125.8, 125.2, 122.2, 119.7, 119.4, 110.9, 109.9, 40.5, 37.1, 34.3, 27.0.

HRMS (ESI⁺): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{32}\text{H}_{26}\text{NO}^+$ 440.2009, found 440.2007.

(2-(2-(2-methyl-1*H*-indol-3-yl)ethyl)phenyl)(3-phenylbicyclo[1.1.0]butan-1-yl)methanone (1am)



This compound was prepared according to the **general procedure A**. Purification by

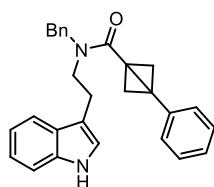
column chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) afforded **1am** as a yellow oil (369 mg, 47% yield).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.67 (s, 1H), 7.42 – 7.36 (m, 1H), 7.08 – 7.02 (m, 6H), 7.00 – 6.93 (m, 4H), 6.84 (d, *J* = 7.7 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 2.91 (s, 2H), 2.66 (t, 2H), 2.44 (t, 2H), 1.91 (s, 3H), 1.68 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 140.9, 138.5, 135.3, 132.7, 131.5, 130.5, 129.9, 128.6, 128.5, 127.9, 127.4, 125.9, 125.2, 120.6, 118.9, 118.1, 111.1, 110.2, 40.1, 37.0, 34.1, 34.0, 26.5, 11.3.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₆NO⁺ 392.2009, found 392.2013.

N-(2-(1*H*-indol-3-yl)ethyl)-N-benzyl-3-phenylbicyclo[1.1.0]butane-1-carboxamide (1an)



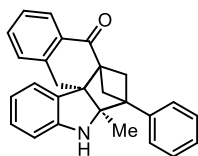
Compound **1an** was prepared following the literature.^[4] Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) as a white solid (438 mg, 59% yield), melting point: 99–101 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.93 (d, *J* = 132.4 Hz, 1H), 7.71 – 7.27 (m, 12H), 7.20 – 7.10 (m, 2H), 6.79 (d, *J* = 55.7 Hz, 1H), 4.81 (d, *J* = 75.8 Hz, 2H), 4.10 – 3.52 (m, 2H), 3.25 – 2.88 (m, 4H), 1.63 (d, *J* = 16.2 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 169.0, 137.6, 137.4, 136.4, 136.1, 134.0, 133.8, 128.7, 128.4, 128.3, 127.7, 127.4, 127.2, 127.0, 126.5, 126.4, 126.2, 122.4, 122.3, 121.7, 121.5, 119.0, 118.8, 118.4, 118.2, 112.2, 111.6, 111.4, 111.3, 52.1, 48.5, 47.0, 36.5, 36.3, 31.1, 30.9, 25.1, 23.0, 22.1.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₇N₂O⁺ 407.2118, found 407.2119.

(5a,13a)-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2a)



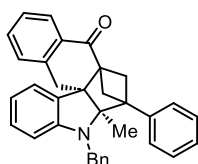
Compound **2a** (70.1 mg, 93% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.20 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.65 – 7.54 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.34 (m, 3H), 7.33 – 7.27 (m, 3H), 7.05 – 6.97 (m, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.43 – 6.31 (m, 2H), 3.76 (d, *J* = 17.4 Hz, 2H), 3.29 (d, *J* = 16.7 Hz, 1H), 2.73 – 2.63 (m, 1H), 2.23 (d, *J* = 7.5 Hz, 1H), 2.16 – 2.09 (m, 1H), 2.06 (d, *J* = 7.2 Hz, 1H), 1.31 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.9, 151.8, 142.2, 140.2, 134.1, 132.8, 132.0, 129.9, 128.6, 128.1, 127.5, 127.1, 126.8, 126.8, 123.3, 118.2, 108.6, 75.0, 60.5, 60.4, 58.0, 43.5, 37.3, 35.9, 19.3.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₄NO⁺ 378.1852, found 378.1856.

(5a,13a)-5-benzyl-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2b)



Compound **2b** (80.3 mg, 86% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) as a yellow solid, melting point: 207-209 °C.

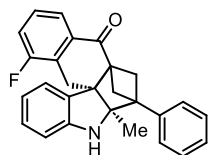
¹H NMR (400 MHz, CDCl₃) δ 8.17 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 – 7.51 (m, 1H), 7.43 – 7.36 (m, 2H), 7.29 (q, *J* = 5.6 Hz, 3H), 7.21 (dd, *J* = 7.9, 1.5 Hz, 4H), 7.17 – 7.10 (m, 1H), 7.06 – 7.00 (m, 2H), 6.85 (td, *J* = 7.6, 1.3 Hz, 1H), 6.33 (dd, *J* = 7.3, 1.3 Hz, 1H), 6.22 (td, *J* = 7.4, 1.0 Hz, 1H), 5.95 (d, *J* = 7.9 Hz, 1H), 4.22 (d, *J* = 17.6 Hz, 1H), 3.94 (d, *J* = 17.6 Hz, 1H), 3.80 (d, *J* = 16.6 Hz, 1H), 3.39 (d, *J* = 16.6 Hz, 1H), 2.68 (dd, *J* =

9.9, 7.3 Hz, 1H), 2.30 (d, $J = 7.5$ Hz, 1H), 2.19 (dd, $J = 9.9, 7.5$ Hz, 1H), 1.89 (d, $J = 7.3$ Hz, 1H), 1.52 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.7, 151.7, 142.2, 140.4, 139.0, 134.1, 132.7, 130.5, 130.0, 128.7, 128.3, 128.1, 127.5, 127.2, 127.1, 127.0, 126.5, 126.3, 122.5, 115.9, 105.1, 78.0, 61.4, 59.7, 57.8, 47.3, 44.5, 36.2, 35.8, 17.3.

HRMS (ESI^+): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{30}\text{NO}^+$ 468.2322, found 468.2325.

(5a,13a)-12-fluoro-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13*H*)-one (2c)



Compound **2c** (65.5 mg, 83% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

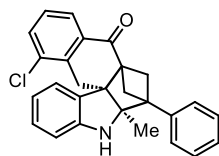
^1H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, $J = 7.7$ Hz, 1H), 7.46 – 7.32 (m, 5H), 7.32 – 7.27 (m, 3H), 7.05 – 6.99 (m, 1H), 6.58 (d, $J = 7.8$ Hz, 1H), 6.46 – 6.36 (m, 2H), 3.74 (s, 1H), 3.57 – 3.38 (m, 2H), 2.65 (dd, $J = 9.8, 7.1$ Hz, 1H), 2.20 (d, $J = 7.5$ Hz, 1H), 2.11 (dd, $J = 9.9, 7.6$ Hz, 1H), 2.06 (d, $J = 7.1$ Hz, 1H), 1.33 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 195.1, 160.9 (d, $J = 246.7$ Hz), 151.7, 140.0, 134.5 (d, $J = 3.0$ Hz), 131.8, 129.1 (d, $J = 16.9$ Hz), 128.8, 128.1, 127.9 (d, $J = 8.0$ Hz), 126.9, 126.7, 123.0 (d, $J = 3.4$ Hz), 122.9, 120.5 (d, $J = 22.1$ Hz), 118.3, 108.8, 75.2, 60.4, 59.8, 57.8, 43.7, 37.1, 28.3 (d, $J = 3.4$ Hz), 19.4.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -115.75.

HRMS (ESI^+): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{23}\text{FNO}^+$ 396.1758, found 396.1751.

(5a,13a)-12-chloro-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13*H*)-one (2d)



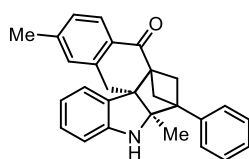
Compound **2d** (73.4 mg, 89% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.13 (dd, J = 7.8, 1.4 Hz, 1H), 7.69 (dd, J = 7.9, 1.4 Hz, 1H), 7.42 – 7.35 (m, 3H), 7.33 – 7.27 (m, 3H), 7.07 – 6.99 (m, 1H), 6.58 (d, J = 7.8 Hz, 1H), 6.47 – 6.37 (m, 2H), 3.75 (s, 1H), 3.68 – 3.45 (m, 2H), 2.64 (dd, J = 9.7, 7.1 Hz, 1H), 2.19 (d, J = 7.5 Hz, 1H), 2.12 (dd, J = 9.7, 7.6 Hz, 1H), 2.05 (d, J = 7.1 Hz, 1H), 1.35 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 151.6, 140.0, 139.5, 135.1, 134.7, 131.9, 128.8, 128.1, 127.7, 126.9, 126.7, 126.1, 122.9, 118.4, 108.8, 75.3, 60.4, 59.6, 57.3, 43.7, 37.1, 33.6, 19.5.

HRMS (ESI⁺): m/z : $[M+H]^+$ calcd for C₂₇H₂₃³⁵ClNO⁺ 412.1463, found 412.1467; $[M+H]^+$ calcd for C₂₇H₂₃³⁷ClNO⁺ 414.1433, found 414.1441.

(5a,13a)-5a,11-dimethyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2e)



Compound **2e** (71.5 mg, 91% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

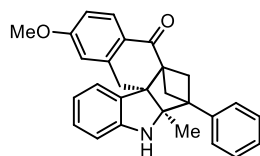
¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, J = 8.0 Hz, 1H), 7.36 (dd, J = 8.3, 6.3 Hz, 2H), 7.32 – 7.27 (m, 3H), 7.24 (d, J = 7.6 Hz, 1H), 7.17 (s, 1H), 7.03 – 6.97 (m, 1H), 6.56 (d, J = 7.8 Hz, 1H), 6.43 – 6.33 (m, 2H), 3.78 – 3.63 (m, 2H), 3.22 (d, J = 16.6 Hz, 1H), 2.65 (dd, J = 9.9, 7.1 Hz, 1H), 2.45 (s, 3H), 2.21 (d, J = 7.4 Hz, 1H), 2.14 – 2.06 (m,

1H), 2.04 (d, $J = 7.1$ Hz, 1H), 1.29 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.6, 151.7, 145.0, 142.2, 140.3, 132.1, 130.5, 130.4, 128.6, 128.1, 128.1, 127.6, 126.8, 126.8, 123.4, 118.1, 108.6, 74.9, 60.5, 60.4, 58.0, 43.5, 37.2, 35.8, 21.9, 19.3.

HRMS (ESI^+): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{NO}^+$ 392.2009, found 392.2015.

(5a,13a)-11-methoxy-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2f)



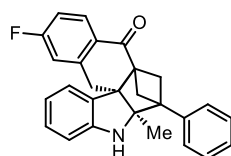
Compound **2f** (64.4 mg, 82% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a pale yellow solid, melting point: 212-214 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.18 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.62 – 7.54 (m, 1H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.39 – 7.33 (m, 3H), 7.30 (d, $J = 7.1$ Hz, 3H), 6.61 (dd, $J = 8.5, 2.6$ Hz, 1H), 6.52 (d, $J = 8.5$ Hz, 1H), 5.97 (d, $J = 2.6$ Hz, 1H), 3.74 (d, $J = 16.7$ Hz, 1H), 3.47 (s, 4H), 3.27 (d, $J = 16.7$ Hz, 1H), 2.66 (dd, $J = 9.9, 7.1$ Hz, 1H), 2.22 (d, $J = 7.4$ Hz, 1H), 2.16 – 2.07 (m, 1H), 2.05 (d, $J = 7.2$ Hz, 1H), 1.29 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.9, 152.8, 145.9, 141.9, 140.3, 134.1, 133.6, 132.7, 129.9, 128.0, 127.5, 127.1, 126.8, 126.8, 113.5, 110.2, 109.6, 75.6, 61.0, 60.3, 57.9, 55.7, 43.7, 37.3, 35.7, 19.4.

HRMS (ESI^+): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{NO}_2^+$ 408.1958, found 408.1960.

(5a,13a)-11-fluoro-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2g)



Compound **2g** (62.6 mg, 79% yield) was prepared following the general procedure.

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

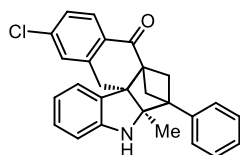
¹H NMR (400 MHz, Chloroform-*d*) δ 8.21 (dd, J = 8.7, 6.0 Hz, 1H), 7.36 (dd, J = 7.9, 6.3 Hz, 2H), 7.33 – 7.26 (m, 3H), 7.16 – 7.07 (m, 1H), 7.07 – 6.97 (m, 2H), 6.57 (d, J = 7.9 Hz, 1H), 6.41 (t, J = 7.4 Hz, 1H), 6.35 (dd, J = 7.6, 1.4 Hz, 1H), 3.78 – 3.66 (m, 2H), 3.26 (d, J = 16.8 Hz, 1H), 2.65 (dd, J = 9.9, 7.2 Hz, 1H), 2.21 (d, J = 7.5 Hz, 1H), 2.14 – 2.00 (m, 2H), 1.29 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 194.4, 166.2 (d, J = 256.1 Hz), 151.7, 145.4 (d, J = 8.8 Hz), 140.1, 131.7, 130.6 (d, J = 9.9 Hz), 129.5 (d, J = 2.7 Hz), 128.1, 126.9, 126.7, 123.2, 118.3, 116.2 (d, J = 21.4 Hz), 114.8 (d, J = 21.9 Hz), 108.7, 75.0, 60.5, 57.9, 43.5, 37.2, 36.1, 19.3.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -103.93.

HRMS (ESI⁺): m/z : [M+H]⁺ calcd for C₂₇H₂₃FNO⁺ 396.1758, found 396.1753.

(5a,13a)-11-chloro-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13*H*)-one (2h)



Compound **2h** (72.3 mg, 88% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

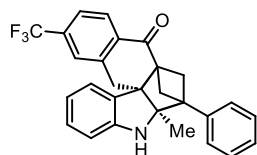
¹H NMR (400 MHz, CDCl₃) δ 8.12 (d, J = 8.4 Hz, 1H), 7.38 (dd, J = 17.7, 8.1 Hz, 4H), 7.33 – 7.26 (m, 3H), 7.02 (t, J = 7.6 Hz, 1H), 6.56 (d, J = 7.8 Hz, 1H), 6.42 (d, J = 7.4 Hz, 1H), 6.35 (d, J = 7.5 Hz, 1H), 3.79 – 3.62 (m, 2H), 3.24 (d, J = 16.8 Hz, 1H), 2.64 (dd, J = 9.9, 7.2 Hz, 1H), 2.20 (d, J = 7.5 Hz, 1H), 2.09 (dd, J = 9.8, 7.5 Hz, 1H), 2.05 (d, J = 7.1 Hz, 1H), 1.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 194.9, 151.7, 143.9, 140.3, 140.0, 131.6, 131.3, 129.7, 129.1, 128.8, 128.1, 127.6, 126.9, 126.7, 123.2, 118.3, 108.8, 75.0, 60.5, 60.5, 57.9,

43.6, 37.2, 35.7, 19.3.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₇H₂₃³⁵ClNO⁺ 412.1463, found 412.1465;
[M+H]⁺ calcd for C₂₇H₂₃³⁷ClNO⁺ 414.1433, found 414.1443.

(5a,13a)-5a-methyl-6-phenyl-11-(trifluoromethyl)-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2i)



Compound **2i** (67.8 mg, 76% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

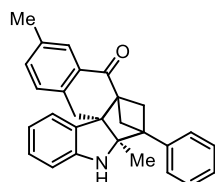
¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, *J* = 8.1 Hz, 1H), 7.74 – 7.63 (m, 2H), 7.37 (dd, *J* = 7.9, 6.4 Hz, 2H), 7.34 – 7.27 (m, 3H), 7.07 – 6.99 (m, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.45 – 6.36 (m, 1H), 6.31 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.87 – 3.68 (m, 2H), 3.37 (d, *J* = 17.0 Hz, 1H), 2.68 (dd, *J* = 9.9, 7.2 Hz, 1H), 2.22 (d, *J* = 7.6 Hz, 1H), 2.13 (dd, *J* = 9.9, 7.6 Hz, 1H), 2.07 (d, *J* = 7.1 Hz, 1H), 1.32 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.1, 151.7, 142.8, 139.9, 137.9 – 132.9 (m), 131.4, 128.9, 128.2, 128.2, 127.0, 126.9 (d, *J* = 3.8 Hz), 126.7, 123.9 (d, *J* = 3.7 Hz), 123.7 (d, *J* = 273.0 Hz), 123.0, 118.3, 108.9, 60.5, 60.4, 58.1, 43.6, 37.2, 35.9, 19.3.

¹⁹F NMR (376 MHz, CDCl₃) δ -63.07.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₈H₂₃F₃NO⁺ 446.1726, found 446.1728.

(5a,13a)-5a,10-dimethyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2j)



Compound **2j** (69.6 mg, 89% yield) was prepared following the general procedure.

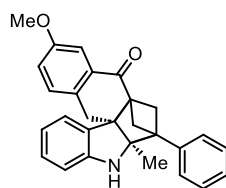
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a pale yellow solid, melting point: 224-226 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 2.0 Hz, 1H), 7.45 – 7.33 (m, 3H), 7.33 – 7.26 (m, 4H), 7.05 – 6.96 (m, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.42 – 6.33 (m, 2H), 3.77 – 3.62 (m, 2H), 3.24 (d, *J* = 16.6 Hz, 1H), 2.67 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.46 (s, 3H), 2.21 (d, *J* = 7.5 Hz, 1H), 2.10 (dd, *J* = 9.8, 7.5 Hz, 1H), 2.04 (d, *J* = 7.1 Hz, 1H), 1.29 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.2, 151.8, 140.3, 139.2, 136.8, 135.1, 132.6, 132.1, 129.8, 128.6, 128.1, 127.7, 126.8, 126.8, 123.4, 118.1, 108.6, 74.9, 60.6, 60.4, 58.1, 43.5, 37.3, 35.5, 21.1, 19.3.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₆NO⁺ 392.2009, found 392.2003.

(5a,13a)-10-methoxy-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2k)



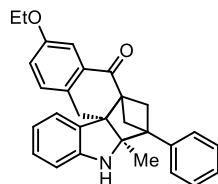
Compound **2k** (69.1 mg, 85% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow solid, melting point: 199-201 °C.

¹H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 2.9 Hz, 1H), 7.39 – 7.31 (m, 3H), 7.29 (dd, *J* = 7.6, 2.0 Hz, 3H), 7.16 (dd, *J* = 8.4, 2.9 Hz, 1H), 7.02 – 6.96 (m, 1H), 6.54 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.43 – 6.32 (m, 2H), 3.90 (s, 3H), 3.71 – 3.59 (m, 2H), 3.20 (d, *J* = 16.4 Hz, 1H), 2.66 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.20 (d, *J* = 7.5 Hz, 1H), 2.08 (dd, *J* = 9.8, 7.5 Hz, 1H), 2.02 (d, *J* = 7.1 Hz, 1H), 1.28 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.9, 158.8, 151.8, 140.3, 134.6, 133.7, 132.2, 131.1, 128.6, 128.1, 126.9, 126.8, 123.4, 122.3, 118.2, 109.6, 108.6, 74.9, 60.8, 60.5, 57.9, 55.7, 43.5, 37.4, 35.1, 29.8, 19.3.

HRMS (ESI⁺): m/z : $[M+H]^+$ calcd for $C_{28}H_{26}NO_2^+$ 408.1958, found 408.1961.

(5a,13a)-10-ethoxy-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13*H*)-one (2l)



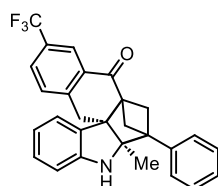
Compound **2l** (70.8 mg, 84% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, J = 2.8 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.34 – 7.27 (m, 4H), 7.22 – 7.16 (m, 1H), 7.06 – 6.98 (m, 1H), 6.57 (d, J = 7.8 Hz, 1H), 6.41 (d, J = 4.1 Hz, 2H), 4.21 – 4.10 (m, 2H), 3.75 (s, 1H), 3.69 (d, J = 16.4 Hz, 1H), 3.23 (d, J = 16.4 Hz, 1H), 2.76 – 2.64 (m, 1H), 2.23 (d, J = 7.4 Hz, 1H), 2.17 – 2.08 (m, 1H), 2.04 (d, J = 7.1 Hz, 1H), 1.49 (t, J = 6.9 Hz, 3H), 1.30 (s, 3H).

¹³C NMR (101 MHz, $CDCl_3$) δ 195.8, 158.0, 151.7, 140.2, 134.3, 133.5, 132.1, 131.0, 128.5, 128.1, 128.0, 126.7, 126.7, 123.3, 122.5, 118.0, 110.2, 108.5, 74.8, 63.8, 60.7, 60.4, 57.8, 43.3, 37.3, 35.0, 19.2, 14.9.

HRMS (ESI⁺): m/z : $[M+H]^+$ calcd for $C_{29}H_{28}NO_2^+$ 422.2115, found 422.2109.

(5a,13a)-5a-methyl-6-phenyl-10-(trifluoromethyl)-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13*H*)-one (2m)



Compound **2m** (71.3 mg, 80% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 7.82 (d, J = 8.1 Hz, 1H), 7.51 (d, J

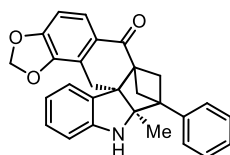
= 8.1 Hz, 1H), 7.37 (t, J = 7.3 Hz, 2H), 7.29 (dd, J = 8.5, 6.8 Hz, 3H), 7.03 (t, J = 7.6 Hz, 1H), 6.58 (d, J = 7.9 Hz, 1H), 6.41 (t, J = 7.5 Hz, 1H), 6.30 (d, J = 7.5 Hz, 1H), 3.77 (d, J = 18.6 Hz, 2H), 3.38 (d, J = 17.1 Hz, 1H), 2.73 – 2.60 (m, 1H), 2.23 (d, J = 7.6 Hz, 1H), 2.17 – 2.02 (m, 2H), 1.32 (s, 3H).

^{13}C NMR (101 MHz, Chloroform- d) δ 194.7, 151.7, 145.9, 139.9, 133.1, 131.4, 130.7, 130.2 (q, J = 3.2 Hz), 129.8 (d, J = 33.2 Hz), 128.9, 128.2, 127.0, 126.7, 124.7 (q, J = 3.6 Hz), 123.9 (d, J = 272.4 Hz), 123.0, 118.3, 108.9, 75.0, 60.6, 60.4, 58.0, 43.7, 37.2, 35.9, 19.3.

^{19}F NMR (376 MHz, Chloroform- d) δ -62.56.

HRMS (ESI $^{+}$): m/z : $[M+H]^{+}$ calcd for $\text{C}_{28}\text{H}_{23}\text{F}_3\text{NO}^{+}$ 446.1726, found 446.1728.

(8a,13b)-8a-methyl-8-phenyl-7,8,8a,9-tetrahydro-6a,8-methano[1,3]dioxolo[4'',5'':3',4']benzo[1',2':5,6]indeno[1,7a-*b*]indol-6(14*H*)-one (2n)



Compound **2n** (63.3 mg, 75% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow solid, melting point: 255-257 °C.

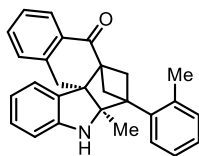
^1H NMR (400 MHz, CDCl_3) δ 7.60 (s, 1H), 7.35 (dd, J = 7.8, 6.4 Hz, 2H), 7.31 – 7.27 (m, 2H), 7.04 – 6.97 (m, 1H), 6.75 (s, 1H), 6.55 (d, J = 7.8 Hz, 1H), 6.50 – 6.38 (m, 2H), 6.08 (dd, J = 9.6, 1.3 Hz, 2H), 3.71 – 3.58 (m, 2H), 3.16 (d, J = 16.5 Hz, 1H), 2.63 (dd, J = 9.9, 7.1 Hz, 1H), 2.19 (d, J = 7.5 Hz, 1H), 2.10 – 2.00 (m, 2H), 1.27 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 194.1, 152.7, 151.8, 147.5, 140.3, 138.9, 132.0, 128.7, 128.1, 127.7, 126.8, 126.8, 123.4, 118.2, 109.0, 108.6, 106.6, 102.0, 74.9, 60.6, 60.5, 57.6, 43.3, 37.4, 36.2, 19.3.

HRMS (ESI $^{+}$): m/z : $[M+H]^{+}$ calcd for $\text{C}_{28}\text{H}_{24}\text{NO}_3^{+}$ 422.1751, found 422.1749.

(5a,13a)-5a-methyl-6-(*o*-tolyl)-5,5a,6,7-tetrahydro-6,7a-

methanobenzo[5,6]indeno[1,7a-b]indol-8(13*H*)-one (2o)



Compound **2o** (64.3 mg, 82% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

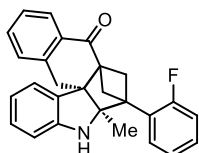
¹H NMR (400 MHz, CDCl₃) δ 8.20 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.60 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.26 (s, 2H), 7.19 (td, *J* = 6.7, 3.9 Hz, 4H), 7.02 (ddd, *J* = 8.2, 7.0, 1.8 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.44 – 6.31 (m, 2H), 3.83 – 3.68 (m, 2H), 3.29 (d, *J* = 16.7 Hz, 1H), 2.78 (dd, *J* = 10.0, 7.2 Hz, 1H), 2.46 (s, 3H), 2.35 (d, *J* = 7.6 Hz, 1H), 2.22 (dd, *J* = 9.9, 7.5 Hz, 1H), 2.12 (d, *J* = 7.2 Hz, 1H), 1.38 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.9, 151.5, 142.1, 138.1, 136.9, 134.1, 132.7, 131.9, 131.4, 129.9, 128.6, 128.5, 127.5, 127.1, 126.9, 125.4, 123.3, 118.1, 108.4, 76.4, 61.2, 60.2, 58.0, 45.2, 38.6, 35.8, 21.4, 19.3.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₆NO⁺ 392.2009, found 392.2007.

(5a,13a)-6-(2-fluorophenyl)-5a-methyl-5,5a,6,7-tetrahydro-6,7a-

methanobenzo[5,6]indeno[1,7a-b]indol-8(13*H*)-one (2p)



Compound **2p** (53.9 mg, 68% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.16 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.45 – 7.39 (m, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.29 (dd, *J* = 7.5, 1.8 Hz, 2H), 7.16 – 7.11 (m, 1H), 7.07 – 6.95 (m, 2H), 6.58 – 6.50 (m, 1H), 6.43 – 6.29 (m, 2H), 3.75 (t, *J* = 15.0 Hz, 2H), 3.27 (d, *J* = 16.7 Hz, 1H), 2.85 – 2.73 (m, 1H), 2.22 – 2.05 (m, 3H), 1.38 (d,

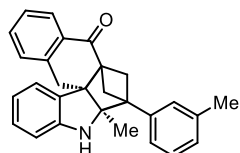
$J = 2.1$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 161.4 (d, $J = 245.7$ Hz), 151.7, 142.2, 134.1, 132.7, 131.9, 129.9 (d, $J = 4.7$ Hz), 129.8, 128.7, 128.6, 127.6, 127.1, 126.9 (d, $J = 15.3$ Hz), 123.9 (d, $J = 3.2$ Hz), 123.4, 118.3, 115.7 (d, $J = 22.4$ Hz), 108.7, 75.9, 60.2, 59.1, 57.5, 44.8 (d, $J = 3.9$ Hz), 37.6, 35.8, 19.0.

^{19}F NMR (376 MHz, CDCl_3) δ -114.96.

HRMS (ESI $^+$): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{23}\text{FNO}^+$ 396.1758, found 396.1753.

(5a,13a)-5a-methyl-6-(m-tolyl)-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2q)



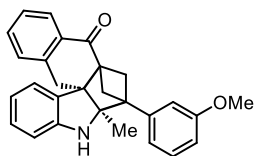
Compound **2q** (70.2 mg, 90% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 8.15 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.59 – 7.51 (m, 1H), 7.40 (t, $J = 7.6$ Hz, 1H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.22 (d, $J = 2.3$ Hz, 2H), 7.11 – 7.02 (m, 3H), 7.00 – 6.93 (m, 1H), 6.53 (d, $J = 7.8$ Hz, 1H), 6.39 – 6.27 (m, 2H), 3.76 – 3.66 (m, 2H), 3.25 (d, $J = 16.7$ Hz, 1H), 2.63 (dd, $J = 9.9, 7.1$ Hz, 1H), 2.36 (s, 3H), 2.17 (d, $J = 7.5$ Hz, 1H), 2.06 (dd, $J = 9.9, 7.5$ Hz, 1H), 2.00 (d, $J = 7.1$ Hz, 1H), 1.27 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 196.0, 151.8, 142.2, 140.2, 137.6, 134.0, 132.8, 132.0, 129.9, 128.6, 128.0, 127.6, 127.5, 127.4, 127.1, 123.8, 123.3, 118.1, 108.5, 74.9, 60.5, 60.4, 58.0, 43.5, 37.3, 35.8, 21.7, 19.3.

HRMS (ESI $^+$): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{26}\text{NO}^+$ 392.2009, found 392.2007.

(5a,13a)-6-(3-methoxyphenyl)-5a-methyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2r)



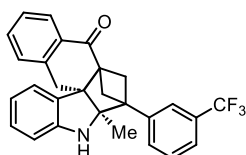
Compound **2r** (69.1 mg, 85% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.19 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.04 – 6.97 (m, 1H), 6.89 – 6.81 (m, 3H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.42 – 6.31 (m, 2H), 3.84 (s, 3H), 3.81 – 3.68 (m, 2H), 3.28 (d, *J* = 16.7 Hz, 1H), 2.66 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.21 (d, *J* = 7.5 Hz, 1H), 2.09 (dd, *J* = 9.9, 7.5 Hz, 1H), 2.04 (d, *J* = 7.1 Hz, 1H), 1.31 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.9, 159.4, 151.7, 142.1, 141.9, 134.1, 132.8, 131.9, 129.9, 129.1, 128.6, 127.5, 127.1, 123.3, 119.3, 118.1, 113.1, 111.5, 108.6, 75.0, 60.5, 60.4, 57.9, 55.3, 43.5, 37.3, 35.8, 19.3.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₆NO₂⁺ 408.1958, found 408.1961.

(5a,13a)-5a-methyl-6-(3-(trifluoromethyl)phenyl)-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2s)



Compound **2s** (73.2 mg, 82% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.19 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.62 – 7.42 (m, 6H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.06 – 6.99 (m, 1H), 6.61 (d, *J* = 7.8 Hz, 1H), 6.41 (d, *J* = 7.4 Hz, 1H), 6.35 (dd, *J* = 7.6, 1.4 Hz, 1H), 3.81 – 3.63 (m, 2H), 3.29 (d, *J* = 16.7 Hz, 1H), 2.70 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.23 (d, *J* = 7.4 Hz, 1H), 2.18 – 2.03 (m, 2H), 1.30 (s, 3H).

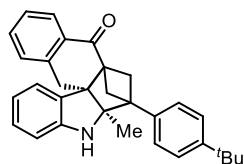
¹³C NMR (101 MHz, CDCl₃) δ 195.6, 151.7, 142.0, 141.4, 134.2, 132.7, 132.0, 130.5

(d, $J = 32.0$ Hz), 130.2, 129.9, 128.7, 128.6, 127.6, 127.2, 124.3 (d, $J = 272.3$ Hz), 123.7 (d, $J = 3.9$ Hz), 123.4 (d, $J = 3.9$ Hz), 123.3, 118.6, 109.2, 75.2, 60.7, 60.1, 58.0, 43.3, 37.5, 35.9, 19.1.

^{19}F NMR (376 MHz, CDCl_3) δ -62.32.

HRMS (ESI⁺): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{23}\text{F}_3\text{NO}^+$ 446.1726, found 446.1724.

(5a,13a)-6-(4-(tert-butyl)phenyl)-5a-methyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2t)



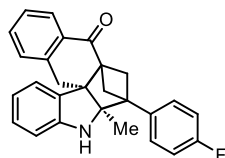
Compound **2t** (79.7 mg, 92% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

^1H NMR (400 MHz, CDCl_3) δ 8.22 (d, $J = 7.8$ Hz, 1H), 7.61 (t, $J = 7.3$ Hz, 1H), 7.51 – 7.37 (m, 4H), 7.30 – 7.26 (m, 2H), 7.09 – 6.98 (m, 1H), 6.63 – 6.53 (m, 1H), 6.40 (q, $J = 2.4$ Hz, 2H), 3.79 (d, $J = 15.6$ Hz, 2H), 3.32 (d, $J = 16.5$ Hz, 1H), 2.71 (t, $J = 8.5$ Hz, 1H), 2.24 (d, $J = 2.1$ Hz, 1H), 2.14 (t, $J = 8.5$ Hz, 1H), 2.11 – 2.03 (m, 1H), 1.40 (s, 9H), 1.36 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 196.0, 151.8, 149.5, 142.2, 137.1, 134.0, 132.7, 132.0, 129.9, 128.5, 127.4, 127.0, 126.4, 124.9, 123.2, 118.0, 108.5, 74.9, 60.4, 60.1, 58.0, 43.5, 37.1, 35.8, 34.5, 31.5, 19.3.

HRMS (ESI⁺): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{31}\text{H}_{32}\text{NO}^+$ 434.2478, found 434.2481.

(5a,13a)-6-(4-fluorophenyl)-5a-methyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2u)



Compound **2u** (66.5 mg, 84% yield) was prepared following the general procedure.

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

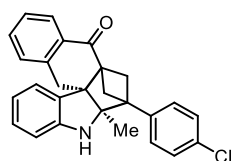
¹H NMR (400 MHz, CDCl₃) δ 8.15 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 – 7.52 (m, 1H), 7.40 (t, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 7.7 Hz, 1H), 7.22 (d, *J* = 3.2 Hz, 3H), 7.06 – 6.93 (m, 3H), 6.54 (d, *J* = 7.9 Hz, 1H), 6.41 – 6.26 (m, 2H), 3.70 (d, *J* = 16.7 Hz, 2H), 3.25 (d, *J* = 16.7 Hz, 1H), 2.62 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.15 (d, *J* = 7.5 Hz, 1H), 2.10 – 1.93 (m, 2H), 1.25 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.8, 162.0 (d, *J* = 244.7 Hz), 151.7, 142.1, 136.0 (d, *J* = 3.3 Hz), 134.1, 132.7, 132.0, 129.9, 128.6, 128.3 (d, *J* = 7.9 Hz), 127.5, 127.1, 123.3, 118.3, 114.9 (d, *J* = 21.0 Hz), 108.9, 74.9, 60.6, 59.8, 57.9, 43.4, 37.4, 35.8, 19.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -115.91.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₃FNO⁺ 396.1758, found 396.1757.

(5a,13a)-6-(4-chlorophenyl)-5a-methyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2v)



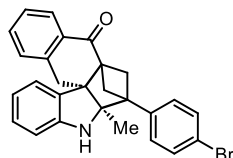
Compound **2v** (70.9 mg, 86% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.18 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.63 – 7.56 (m, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.29 (m, 3H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.05 – 6.97 (m, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.43 – 6.37 (m, 1H), 6.35 (d, *J* = 6.7 Hz, 1H), 3.78 – 3.62 (m, 2H), 3.28 (d, *J* = 16.6 Hz, 1H), 2.65 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.18 (d, *J* = 7.5 Hz, 1H), 2.12 – 2.05 (m, 1H), 2.02 (d, *J* = 7.1 Hz, 1H), 1.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.7, 151.7, 142.1, 138.8, 134.1, 132.7, 132.0, 129.9, 128.7, 128.2, 128.2, 127.5, 127.1, 123.3, 118.4, 108.9, 75.0, 60.6, 59.9, 57.9, 43.3, 37.4, 35.8, 19.1.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₇H₂₃³⁵ClNO⁺ 412.1463, found 412.1466;
[M+H]⁺ calcd for C₂₇H₂₃³⁷ClNO⁺ 414.1433, found 414.1446.

(5a,13a)-6-(4-bromophenyl)-5a-methyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2w)



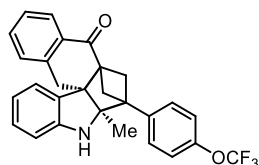
Compound **2w** (77.9 mg, 85% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.18 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.58 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.51 – 7.41 (m, 3H), 7.36 (d, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 8.4 Hz, 2H), 7.05 – 6.97 (m, 1H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.44 – 6.30 (m, 2H), 3.72 (d, *J* = 16.8 Hz, 2H), 3.28 (d, *J* = 16.7 Hz, 1H), 2.64 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.18 (d, *J* = 7.5 Hz, 1H), 2.07 (dd, *J* = 9.9, 7.4 Hz, 1H), 2.02 (d, *J* = 7.1 Hz, 1H), 1.28 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.7, 151.7, 142.0, 139.3, 134.2, 132.7, 131.9, 131.2, 129.9, 128.7, 128.5, 127.5, 127.1, 123.3, 120.8, 118.4, 108.9, 75.0, 60.6, 59.9, 57.9, 43.3, 37.4, 35.8, 19.1.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₇H₂₃⁷⁹BrNO⁺ 456.0958, found 456.0955;
[M+H]⁺ calcd for C₂₇H₂₃⁸¹BrNO⁺ 458.0937, found 458.0944.

(5a,13a)-5a-methyl-6-(4-(trifluoromethoxy)phenyl)-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2x)



Compound **2x** (73.8 mg, 80% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate =

10/1) as a yellow oil.

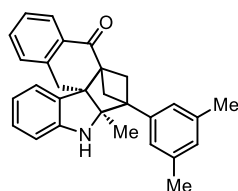
¹H NMR (400 MHz, CDCl₃) δ 8.23 – 8.16 (m, 1H), 7.64 – 7.56 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.39 (s, 1H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.06 – 6.97 (m, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.45 – 6.31 (m, 2H), 3.84 – 3.68 (m, 2H), 3.30 (d, *J* = 16.7 Hz, 1H), 2.68 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.21 (d, *J* = 7.5 Hz, 1H), 2.15 – 2.07 (m, 1H), 2.05 (d, *J* = 7.1 Hz, 1H), 1.31 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.7, 151.7, 148.2, 142.1, 139.1, 134.2, 132.7, 132.0, 129.9, 128.7, 128.1, 127.5, 127.1, 123.3, 120.6, 120.6 (q), 118.4, 109.0, 75.1, 60.6, 59.8, 57.9, 43.4, 37.4, 35.8, 19.1.

¹⁹F NMR (376 MHz, CDCl₃) δ -57.70.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₃F₃NO₂⁺ 462.1675, found 462.1676

(5a,13a)-6-(3,5-dimethylphenyl)-5a-methyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2y)



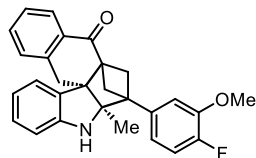
Compound **2y** (69.7 mg, 86% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 7.8 Hz, 1H), 7.64 – 7.55 (m, 1H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.01 (dd, *J* = 7.5, 1.6 Hz, 1H), 6.95 (s, 1H), 6.90 (s, 2H), 6.58 (d, *J* = 7.8 Hz, 1H), 6.43 – 6.29 (m, 2H), 3.83 – 3.68 (m, 2H), 3.29 (d, *J* = 16.6 Hz, 1H), 2.66 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.37 (s, 6H), 2.20 (d, *J* = 7.5 Hz, 1H), 2.09 (dd, *J* = 9.9, 7.5 Hz, 1H), 2.02 (d, *J* = 7.1 Hz, 1H), 1.33 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 196.0, 151.8, 142.2, 140.2, 137.5, 134.0, 132.8, 132.0, 129.9, 128.6, 128.5, 127.5, 127.1, 124.5, 123.3, 118.0, 108.5, 74.8, 60.5, 60.4, 58.0, 43.6, 37.3, 35.8, 21.5, 19.4.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₉H₂₈NO⁺ 406.2165, found 406.2168

(5a,13a)-6-(4-fluoro-3-methoxyphenyl)-5a-methyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2z)



Compound **2z** (67.4 mg, 79% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

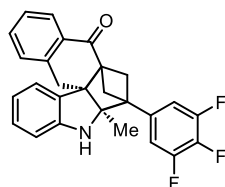
¹H NMR (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.09 – 6.96 (m, 2H), 6.88 (dd, *J* = 8.2, 2.0 Hz, 1H), 6.80 – 6.73 (m, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 6.43 – 6.35 (m, 1H), 6.32 (dd, *J* = 7.6, 1.3 Hz, 1H), 3.91 (s, 3H), 3.71 (d, *J* = 16.7 Hz, 2H), 3.26 (d, *J* = 16.7 Hz, 1H), 2.63 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.18 (d, *J* = 7.5 Hz, 1H), 2.10 – 1.98 (m, 2H), 1.29 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.8, 151.8, 142.1, 134.2, 132.8, 132.1, 129.9, 128.7, 127.6, 127.2, 123.4, 119.3, 119.2, 118.5, 115.7, 115.6, 112.3, 112.3, 109.0, 75.0, 60.7, 60.1, 57.8, 56.6, 43.5, 37.5, 35.9, 19.2.

¹⁹F NMR (376 MHz, Chloroform-*d*) δ -137.86.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₈H₂₅FNO₂⁺ 426.1864, found 426.1864.

(5a,13a)-5a-methyl-6-(3,4,5-trifluorophenyl)-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2aa)



Compound **2aa** (65.6 mg, 76% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate =

10/1) as a yellow oil.

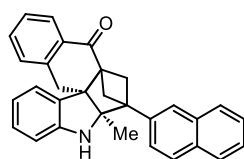
¹H NMR (600 MHz, CDCl₃) δ 8.17 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.60 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.02 (td, *J* = 7.6, 1.3 Hz, 1H), 6.93 (dd, *J* = 8.1, 6.4 Hz, 2H), 6.61 (d, *J* = 7.9 Hz, 1H), 6.42 (t, *J* = 7.4 Hz, 1H), 6.33 (d, *J* = 7.5 Hz, 1H), 3.69 (d, *J* = 16.5 Hz, 2H), 3.27 (d, *J* = 16.6 Hz, 1H), 2.59 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.16 (d, *J* = 7.4 Hz, 1H), 2.02 (dd, *J* = 10.0, 7.3 Hz, 2H), 1.28 (s, 3H).

¹³C NMR (151 MHz, CDCl₃) δ 195.4, 151.6, 151.0 (ddd, *J* = 249.8, 9.8, 4.0 Hz), 141.9, 138.8 (dt, *J* = 250.4, 15.4 Hz), 136.8 (q, *J* = 6.8 Hz), 134.3, 132.6, 131.9, 130.0, 128.8, 127.6, 127.3, 123.3, 118.9, 110.9 (dd, *J* = 16.4, 4.4 Hz), 109.5, 75.2, 60.7, 59.5, 57.6, 43.1, 37.7, 35.8, 19.0.

¹⁹F NMR (376 MHz, CDCl₃) δ -134.69 (d, *J* = 20.8 Hz), -163.02 (t, *J* = 20.5 Hz).

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₁F₃NO⁺ 432.1570, found 432.1566.

(5a,13a)-5a-methyl-6-(naphthalen-2-yl)-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2ab)



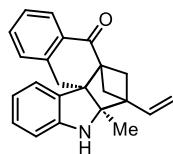
Compound **2ab** (69.9 mg, 82% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.21 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.90 – 7.81 (m, 3H), 7.69 (d, *J* = 1.7 Hz, 1H), 7.63 – 7.57 (m, 1H), 7.54 – 7.42 (m, 4H), 7.38 (d, *J* = 7.7 Hz, 1H), 7.07 – 6.99 (m, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 6.45 – 6.33 (m, 2H), 3.84 – 3.68 (m, 2H), 3.31 (d, *J* = 16.6 Hz, 1H), 2.77 (dd, *J* = 9.8, 7.1 Hz, 1H), 2.30 (d, *J* = 7.4 Hz, 1H), 2.21 (dd, *J* = 9.8, 7.5 Hz, 1H), 2.14 (d, *J* = 7.1 Hz, 1H), 1.32 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 196.0, 151.8, 142.2, 137.9, 134.1, 133.2, 132.8, 132.5, 132.0, 129.9, 128.7, 127.8, 127.8, 127.6, 127.6, 127.1, 126.2, 125.7, 125.3, 125.2, 123.4, 118.3, 108.7, 75.3, 60.7, 60.6, 58.1, 43.6, 37.5, 35.9, 19.4.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₃₁H₂₆NO⁺ 428.2009, found 428.2008.

(5a,13a)-5a-methyl-6-vinyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2ac)



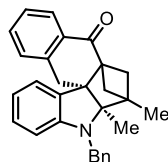
Compound **2ac** (21.8 mg, 33% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (600 MHz, Chloroform-*d*) δ 8.15 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.58 – 7.54 (m, 1H), 7.41 (q, *J* = 8.1, 7.5 Hz, 1H), 7.32 (d, *J* = 7.7 Hz, 1H), 6.99 – 6.94 (m, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 6.36 (dd, *J* = 8.0, 7.0 Hz, 1H), 6.28 (dd, *J* = 7.5, 1.3 Hz, 1H), 6.09 (dd, *J* = 17.3, 10.6 Hz, 1H), 5.25 (dd, *J* = 10.6, 1.8 Hz, 1H), 5.14 (dd, *J* = 17.3, 1.8 Hz, 1H), 3.79 (s, 1H), 3.62 (d, *J* = 16.6 Hz, 1H), 3.22 (d, *J* = 16.6 Hz, 1H), 2.31 (dd, *J* = 10.0, 7.1 Hz, 1H), 2.01 (d, *J* = 7.5 Hz, 1H), 1.81 (d, *J* = 7.2 Hz, 1H), 1.69 (dd, *J* = 10.0, 7.5 Hz, 1H), 1.40 (s, 3H).

¹³C NMR (151 MHz, Chloroform-*d*) δ 196.2, 151.7, 142.2, 135.5, 134.1, 132.1, 129.9, 128.6, 127.5, 127.1, 123.3, 118.4, 117.5, 108.9, 74.1, 60.5, 60.4, 57.9, 43.6, 36.7, 35.5, 19.3.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₃H₂₂NO⁺ 328.1696, found 328.1692.

(5a,13a)-5-benzyl-5a,6-dimethyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2ad)



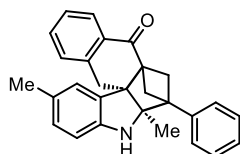
Compound **2ad** (61.8 mg, 76% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 15/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.15 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.55 (td, *J* = 7.5, 1.5 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.28 (m, 3H), 7.28 – 7.24 (m, 3H), 6.87 – 6.80 (m, 1H), 6.30 – 6.18 (m, 2H), 5.94 (d, *J* = 7.9 Hz, 1H), 4.65 – 4.48 (m, 2H), 3.66 (d, *J* = 16.5 Hz, 1H), 3.26 (d, *J* = 16.6 Hz, 1H), 2.23 (dd, *J* = 10.2, 7.3 Hz, 1H), 1.93 (d, *J* = 7.5 Hz, 1H), 1.75 (dd, *J* = 10.2, 7.5 Hz, 1H), 1.57 (d, *J* = 7.3 Hz, 1H), 1.50 (s, 3H), 1.21 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 196.1, 152.3, 142.3, 139.4, 134.0, 132.8, 130.8, 129.9, 128.7, 128.6, 127.5, 127.0, 126.8, 126.4, 122.6, 116.1, 105.5, 77.4, 60.1, 58.4, 55.1, 48.2, 45.7, 37.8, 36.0, 15.7, 15.1.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₉H₂₈NO⁺ 406.2165, found 406.2168.

(5a,13a)-2,5a-dimethyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2ae)



Compound **2ae** (72.3 mg, 92% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

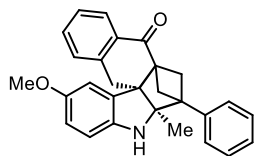
¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 3H), 7.30 (d, *J* = 7.7 Hz, 3H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 6.17 (s, 1H), 3.76 (d, *J* = 16.8 Hz, 1H), 3.60 (s, 1H), 3.29 (d, *J* = 16.9 Hz, 1H), 2.67 (t, *J* = 8.4 Hz, 1H), 2.22 (d, *J* = 7.4 Hz, 1H), 2.13 (d, *J* = 8.8 Hz, 1H), 2.05 (d, *J* = 7.0 Hz, 1H), 2.00 (s, 3H), 1.30 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 196.1, 149.5, 142.2, 140.3, 134.0, 132.7, 132.4, 129.9, 129.1, 128.0, 127.5, 127.0, 126.8, 123.8, 108.8, 75.2, 60.6, 60.3, 58.0, 43.7, 37.2, 35.8, 20.9, 19.3.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₆NO⁺ 392.2009, found 392.2005.

(5a,13a)-2-methoxy-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-

methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2af)



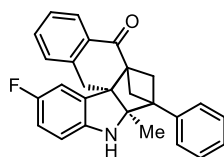
Compound **2af** (68.3 mg, 84% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow solid, melting point: 159-161 °C.

¹H NMR (400 MHz, CDCl₃) δ 8.18 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.58 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 – 7.33 (m, 4H), 7.30 (d, *J* = 7.1 Hz, 3H), 6.61 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.52 (d, *J* = 8.5 Hz, 1H), 5.97 (d, *J* = 2.6 Hz, 1H), 3.74 (d, *J* = 16.6 Hz, 1H), 3.47 (s, 4H), 3.27 (d, *J* = 16.7 Hz, 1H), 2.66 (dd, *J* = 9.9, 7.1 Hz, 1H), 2.22 (d, *J* = 7.4 Hz, 1H), 2.16 – 2.01 (m, 2H), 1.29 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.9, 152.8, 145.9, 141.9, 140.3, 134.1, 133.6, 132.7, 129.9, 128.0, 127.5, 127.1, 126.8, 126.8, 113.5, 110.2, 109.6, 75.6, 61.0, 60.3, 57.9, 55.7, 43.7, 37.3, 35.7, 19.4.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₈H₂₆NO₂⁺ 408.1958, found 408.1963.

(5a,13a)-2-fluoro-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (2ag)



Compound **2ag** (64.1 mg, 81% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.19 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.60 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.33 – 7.27 (m, 3H), 6.71 (td, *J* = 8.8, 2.7 Hz, 1H), 6.48 (dd, *J* = 8.6, 4.4 Hz, 1H), 6.07 (dd, *J* = 8.9, 2.7 Hz, 1H), 3.74 (d,

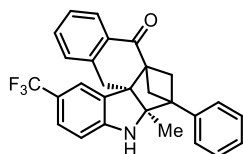
$J = 16.7$ Hz, 1H), 3.63 (s, 1H), 3.25 (d, $J = 16.8$ Hz, 1H), 2.66 (dd, $J = 9.9, 7.2$ Hz, 1H), 2.24 (d, $J = 7.5$ Hz, 1H), 2.14 – 2.00 (m, 2H), 1.30 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.6, 157.4, 155.0, 147.9, 141.6, 140.0, 134.3, 133.3, 133.2, 132.5, 129.9, 128.1, 127.6, 127.3, 126.9, 126.7, 114.9, 114.7, 110.6, 110.4, 109.1, 109.1, 75.8, 60.9, 60.8, 60.4, 57.9, 43.4, 37.2, 35.6, 19.2.

^{19}F NMR (376 MHz, CDCl_3) δ -125.99.

HRMS (ESI⁺): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{23}\text{FNO}^+$ 396.1758, found 396.1760.

(5a,13a)-5a-methyl-6-phenyl-2-(trifluoromethyl)-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2ah)



Compound **2ah** (58.6 mg, 66% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

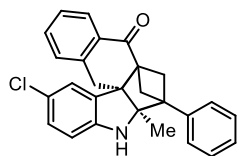
^1H NMR (400 MHz, CDCl_3) δ 8.15 (dd, $J = 7.8, 1.5$ Hz, 1H), 7.62 – 7.54 (m, 1H), 7.46 – 7.39 (m, 1H), 7.36 – 7.32 (m, 3H), 7.30 – 7.25 (m, 1H), 7.23 – 7.19 (m, 3H), 6.55 – 6.43 (m, 2H), 4.15 (s, 1H), 3.71 (d, $J = 16.6$ Hz, 1H), 3.23 (d, $J = 16.7$ Hz, 1H), 2.65 (dd, $J = 10.0, 7.3$ Hz, 1H), 2.22 (d, $J = 7.6$ Hz, 1H), 2.10 – 1.98 (m, 2H), 1.29 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.4, 154.3, 141.4, 139.6, 134.4, 132.5, 131.7, 129.9, 128.3, 127.7, 127.5, 127.1, 126.6, 124.7 (d, $J = 270.73$ Hz), 120.3 (d, $J = 3.88$ Hz), 119.3 (q, $J = 32.33$ Hz), 107.2, 75.6, 60.6, 60.0, 58.0, 43.2, 37.1, 35.6, 19.0.

^{19}F NMR (376 MHz, CDCl_3) δ -60.75.

HRMS (ESI⁺): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{28}\text{H}_{23}\text{F}_3\text{NO}^+$ 446.1726, found 446.1726.

(5a,13a)-2-chloro-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2ai)



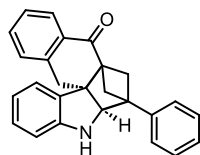
Compound **2ai** (70.2 mg, 85% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, CDCl₃) δ 8.14 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 – 7.53 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.32 (dd, *J* = 7.2, 5.4 Hz, 3H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.25 – 7.22 (m, 2H), 6.92 (dd, *J* = 8.4, 2.2 Hz, 1H), 6.43 (d, *J* = 8.4 Hz, 1H), 6.24 (d, *J* = 2.2 Hz, 1H), 3.80 – 3.64 (m, 2H), 3.21 (d, *J* = 16.8 Hz, 1H), 2.61 (dd, *J* = 9.9, 7.2 Hz, 1H), 2.19 (d, *J* = 7.6 Hz, 1H), 2.10 – 2.04 (m, 1H), 2.04 – 1.97 (m, 1H), 1.26 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.5, 150.3, 141.5, 139.8, 134.3, 133.7, 132.4, 129.9, 128.5, 128.1, 127.6, 127.3, 126.9, 126.7, 123.3, 122.2, 109.3, 75.7, 60.6, 60.5, 57.9, 43.4, 37.1, 35.6, 19.2.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₃³⁵ClNO⁺ 412.1463, found 412.1466; [M+H]⁺ calcd for C₂₇H₂₃³⁷ClNO⁺ 414.1433, found 414.1442.

(5a,13a)-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13*H*)-one (2aj)



Compound **2aj** (64.6 mg, 89% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

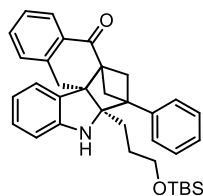
¹H NMR (400 MHz, Chloroform-*d*) δ 8.20 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.62 – 7.54 (m, 1H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.42 – 7.36 (m, 2H), 7.35 – 7.28 (m, 4H), 7.04 – 6.95 (m, 1H), 6.53 (d, *J* = 7.9 Hz, 1H), 6.44 – 6.32 (m, 2H), 4.32 (s, 1H), 4.07 (s, 1H), 3.78 (d, *J* = 16.8 Hz, 1H), 3.52 (d, *J* = 16.8 Hz, 1H), 2.68 (dd, *J* = 9.8, 6.9 Hz, 1H), 2.36 (d, *J* =

7.0 Hz, 1H), 2.01 (d, $J = 7.0$ Hz, 1H), 1.89 (dd, $J = 9.8, 7.6$ Hz, 1H).

^{13}C NMR (101 MHz, Chloroform- d) δ 153.0, 141.8, 140.5, 134.1, 132.9, 131.6, 129.8, 128.8, 128.6, 127.6, 127.2, 127.0, 126.4, 123.0, 118.4, 108.9, 74.4, 59.3, 58.7, 57.5, 45.8, 39.5, 35.3.

HRMS (ESI $^{+}$): m/z : $[M+H]^{+}$ calcd for $\text{C}_{26}\text{H}_{22}\text{NO}^{+}$ 364.1696, found 364.1693.

(5a,13a)-5a-(3-((tert-butyldimethylsilyl)oxy)propyl)-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2ak)



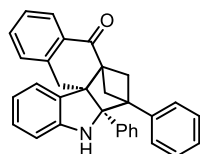
Compound **2ak** (91.2 mg, 85% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a white solid, melting point: 180 – 182 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.21 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.64 – 7.57 (m, 1H), 7.44 (t, $J = 7.3$ Hz, 1H), 7.41 – 7.27 (m, 6H), 7.07 – 7.00 (m, 1H), 6.63 (d, $J = 7.9$ Hz, 1H), 6.41 (dd, $J = 4.1, 1.2$ Hz, 2H), 4.40 (s, 1H), 3.87 (d, $J = 16.8$ Hz, 1H), 3.65 – 3.55 (m, 1H), 3.54 – 3.39 (m, 2H), 2.76 (t, $J = 8.1$ Hz, 1H), 2.26 – 2.16 (m, 2H), 2.16 – 2.03 (m, 2H), 1.78 – 1.64 (m, 1H), 1.60 – 1.40 (m, 2H), 0.91 (s, 9H), 0.02 (d, $J = 16.4$ Hz, 6H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.9, 152.7, 142.3, 140.8, 134.0, 132.7, 132.5, 129.9, 128.5, 128.0, 127.3, 127.0, 126.8, 126.7, 122.9, 117.8, 108.5, 78.4, 63.3, 60.7, 60.3, 58.2, 43.0, 37.6, 36.4, 28.4, 27.0, 26.0, 18.3, -5.4, -5.4.

HRMS (ESI $^{+}$): m/z : $[M+H]^{+}$ calcd for $\text{C}_{35}\text{H}_{42}\text{NO}_2\text{Si}^{+}$ 536.2979, found 536.2975.

(5a,13a)-5a,6-diphenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indol-8(13*H*)-one (2al)



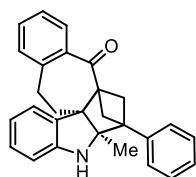
Compound **2al** (70.2 mg, 80% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

¹H NMR (400 MHz, Chloroform-*d*) δ 8.15 (dd, J = 7.9, 1.5 Hz, 1H), 7.65 – 7.58 (m, 2H), 7.53 – 7.47 (m, 1H), 7.42 – 7.31 (m, 6H), 7.26 – 7.20 (m, 3H), 7.18 – 7.06 (m, 2H), 6.74 (d, J = 7.9 Hz, 1H), 6.53 – 6.45 (m, 1H), 6.41 (dd, J = 7.5, 1.3 Hz, 1H), 4.63 (s, 1H), 2.93 (s, 3H), 2.53 (d, J = 7.2 Hz, 1H), 2.33 (d, J = 7.7 Hz, 1H), 2.26 (dd, J = 9.8, 7.8 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 153.1, 142.3, 141.4, 134.1, 131.3, 129.9, 128.9, 128.4, 128.1, 127.8, 127.4, 127.4, 127.0, 126.7, 123.6, 119.0, 108.6, 81.1, 64.6, 59.3, 57.9, 43.8, 42.2, 38.3.

HRMS (ESI⁺): m/z : [M+H]⁺ calcd for C₃₂H₂₆NO⁺ 440.2009, found 440.2003.

(5a,14a)-5a-methyl-6-phenyl-5,5a,6,7,13,14-hexahydro-8H-6,7a-methanobenzo[5,6]azuleno[1,8a-*b*]indol-8-one (2am)



Compound **2am** (60.8 mg, 78% yield) was prepared following the general procedure. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) as a yellow oil.

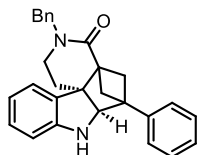
¹H NMR (400 MHz, Chloroform-*d*) δ 7.63 – 7.55 (m, 1H), 7.53 – 7.45 (m, 1H), 7.39 – 7.29 (m, 4H), 7.26 – 7.19 (m, 3H), 7.07 – 6.98 (m, 1H), 6.56 (d, J = 7.8 Hz, 1H), 6.51 (t, J = 7.4 Hz, 1H), 6.40 (d, J = 7.5 Hz, 1H), 3.77 – 3.62 (m, 1H), 3.46 – 3.33 (m, 1H), 3.14 – 2.98 (m, 1H), 2.74 – 2.60 (m, 1H), 2.45 (dd, J = 9.7, 7.2 Hz, 1H), 2.38 – 2.27 (m, 1H), 2.22 (dd, J = 9.7, 7.6 Hz, 1H), 2.03 (dd, J = 11.8, 7.4 Hz, 2H), 1.19 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 204.8, 152.0, 140.5, 140.1, 140.1, 133.1, 131.9, 129.9, 128.8, 128.2, 128.0, 127.1, 126.8, 126.7, 125.0, 118.2, 108.4, 76.2, 62.2, 59.9,

57.8, 43.1, 39.9, 34.0, 31.8, 20.1.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₈H₂₆NO⁺ 392.2009, found 392.2006.

(6a,11b)-3-benzyl-6-phenyl-2,3,5,6,6a,7-hexahydro-4a,6-methanopyrido[4',3':2,3]cyclopenta[1,2-*b*]indol-4(1*H*)-one (2an)



Compound **2an** (58.4 mg, 72% yield) was prepared based on the general procedure, with the reaction time extended to 5 h. Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 4/1) as a yellow oil.

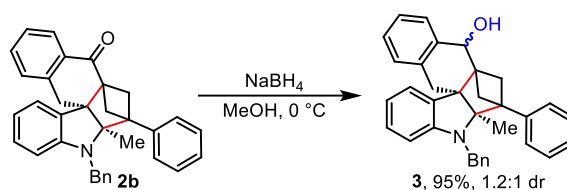
¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.34 (m, 7H), 7.31 – 7.27 (m, 1H), 7.26 – 7.21 (m, 2H), 7.01 (td, *J* = 7.6, 1.3 Hz, 1H), 6.61 (dd, *J* = 7.8, 1.4 Hz, 1H), 6.54 – 6.46 (m, 2H), 4.95 (d, *J* = 14.2 Hz, 1H), 4.56 (d, *J* = 14.2 Hz, 1H), 4.11 – 3.97 (m, 2H), 3.83 – 3.70 (m, 1H), 3.50 – 3.41 (m, 1H), 2.56 – 2.43 (m, 1H), 2.28 (dd, *J* = 9.8, 7.2 Hz, 3H), 2.17 (d, *J* = 6.9 Hz, 1H), 1.81 (dd, *J* = 9.8, 7.5 Hz, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 169.2, 153.0, 140.4, 137.2, 130.7, 128.9, 128.7, 128.6, 128.6, 127.8, 126.9, 126.3, 124.0, 118.4, 108.7, 73.8, 57.6, 55.9, 53.8, 50.1, 47.6, 45.1, 36.4, 30.3.

HRMS (ESI⁺): m/z: [M+H]⁺ calcd for C₂₈H₂₇N₂O⁺ 407.2118, found 407.2115.

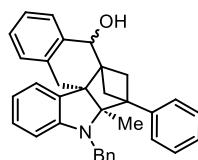
8. Synthetic transformations

Synthesis of 3



To a solution of **2b** (46.8, 0.1 mmol) in anhydrous MeOH (2.0 mL) at $0\text{ }^\circ\text{C}$, NaBH_4 (7.6 mg, 2.0 equiv) was added. After stirring for 2 h from $0\text{ }^\circ\text{C}$ to rt, the resulting mixture was added to H_2O (10 mL). The mixture was extracted with EA ($3 \times 15\text{ mL}$) and the combined organic layers were dried over Na_2SO_4 , filtered, and the solvent was removed under reduced pressure. The reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to afford the product **3** (44.5 mg, 95% yield) as a yellow oil with dr = 1.2:1.

(5a,13a)-5-benzyl-5a-methyl-6-phenyl-5,5a,6,7,8,13-hexahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8-ol (**3**)



More diastereomer: $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.52 (dd, $J = 7.2, 1.9\text{ Hz}$, 1H), 7.29 – 7.21 (m, 2H), 7.21 – 7.13 (m, 5H), 7.10 (s, 3H), 7.06 (t, $J = 7.2\text{ Hz}$, 1H), 6.95 (d, $J = 6.9\text{ Hz}$, 2H), 6.77 (td, $J = 7.7, 1.3\text{ Hz}$, 1H), 6.52 (dd, $J = 7.4, 1.3\text{ Hz}$, 1H), 6.25 – 6.18 (m, 1H), 5.87 (d, $J = 7.9\text{ Hz}$, 1H), 4.70 (s, 1H), 4.13 (d, $J = 17.5\text{ Hz}$, 1H), 3.91 (d, $J = 17.5\text{ Hz}$, 1H), 3.40 (d, $J = 16.5\text{ Hz}$, 1H), 3.12 (d, $J = 16.5\text{ Hz}$, 1H), 2.43 (dd, $J = 10.1, 7.3\text{ Hz}$, 1H), 2.24 – 2.12 (m, 1H), 1.94 (d, $J = 7.1\text{ Hz}$, 1H), 1.86 (d, $J = 7.3\text{ Hz}$, 1H), 1.56 (d, $J = 7.5\text{ Hz}$, 1H), 1.34 (s, 3H).

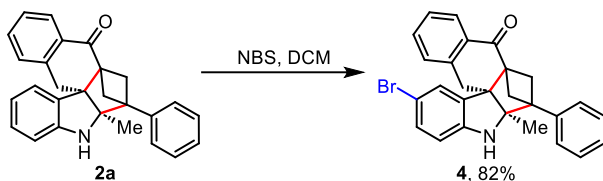
$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.3, 141.0, 139.0, 137.7, 135.0, 132.3, 131.3, 129.5, 128.4, 128.4, 128.3, 128.0, 127.2, 127.0, 126.7, 126.4, 126.4, 123.0, 116.0, 105.8, 78.1, 71.2, 60.2, 54.3, 53.2, 47.6, 43.9, 38.7, 35.9, 16.5.

Less diastereomer: ^1H NMR (600 MHz, CDCl_3) δ 7.75 (d, $J = 7.6$ Hz, 1H), 7.36 – 7.27 (m, 5H), 7.23 (dd, $J = 8.0, 3.0$ Hz, 5H), 7.18 (t, $J = 7.3$ Hz, 1H), 7.10 – 7.05 (m, 2H), 6.93 (td, $J = 7.6, 1.3$ Hz, 1H), 6.62 – 6.57 (m, 1H), 6.38 (td, $J = 7.4, 1.0$ Hz, 1H), 6.00 (d, $J = 7.9$ Hz, 1H), 5.00 (s, 1H), 4.28 (d, $J = 17.5$ Hz, 1H), 4.05 (d, $J = 17.4$ Hz, 1H), 3.58 (d, $J = 17.0$ Hz, 1H), 3.20 (d, $J = 17.0$ Hz, 1H), 2.16 (dd, $J = 10.0, 7.0$ Hz, 1H), 2.06 – 1.98 (m, 1H), 1.96 (d, $J = 6.9$ Hz, 1H), 1.84 (d, $J = 7.3$ Hz, 1H), 1.46 (s, 3H).

^{13}C NMR (151 MHz, CDCl_3) δ 151.9, 141.2, 139.2, 138.1, 135.1, 131.6, 129.4, 128.3, 128.3, 128.0, 127.8, 127.4, 127.4, 126.7, 126.7, 126.5, 126.4, 122.7, 115.7, 105.1, 78.4, 68.8, 60.7, 57.3, 54.2, 47.5, 39.4, 37.2, 35.2, 17.3.

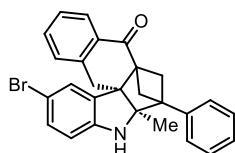
HRMS (ESI $^+$): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{34}\text{H}_{32}\text{NO}^+$ 470.2478, found 470.2475.

Synthesis of 4^[1b]



To a tube was added **2a** (27.5 mg, 0.1 mmol), NBS (17.8 mg, 1.0 equiv), and 4 mL DCM. The reaction mixture was allowed to stir at rt for 2 h. Then, the resulting mixture was added saturated aqueous NaHCO_3 (10 mL). The mixture was extracted with DCM (3×15 mL) and the combined organic layers were dried over Na_2SO_4 , filtered, and concentrated. The reaction mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1) to afford the product **4** (37.4 mg, 82% yield) as a brown solid, melting point: 156–158 °C.

(5a,13a)-2-bromo-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (4)

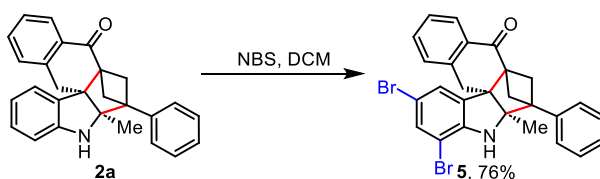


^1H NMR (400 MHz, CDCl_3) δ 8.07 (dd, $J = 7.9, 1.5$ Hz, 1H), 7.50 (td, $J = 7.5, 1.5$ Hz, 1H), 7.34 (t, $J = 7.5$ Hz, 1H), 7.29 – 7.22 (m, 3H), 7.22 – 7.17 (m, 1H), 7.14 (s, 1H), 6.98 (dd, $J = 8.4, 2.0$ Hz, 1H), 6.35 – 6.24 (m, 2H), 3.68 – 3.55 (m, 2H), 3.14 (d, $J = 16.8$ Hz, 1H), 2.53 (dd, $J = 10.0, 7.2$ Hz, 1H), 2.12 (d, $J = 7.6$ Hz, 1H), 2.01 – 1.89 (m, 2H), 1.18 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 195.5, 150.7, 141.4, 139.8, 134.4, 134.2, 132.4, 131.4, 130.0, 128.2, 127.7, 127.4, 127.0, 126.7, 126.2, 109.9, 109.3, 75.7, 60.5, 60.5, 57.9, 43.4, 37.1, 35.6, 19.3.

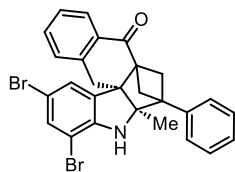
HRMS (ESI $^+$): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{23}^{79}\text{BrNO}^+$ 456.0958, found 456.0956; $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{27}\text{H}_{23}^{81}\text{BrNO}^+$ 458.0937, found 458.0930.

Synthesis of **5**



To a tube was added **2a** (37.8 mg, 0.1 mmol), NBS (35.6 mg, 2.0 equiv), and 4 mL DCM. The reaction mixture was allowed to stir at rt for 2 h. Then, the resulting mixture was added saturated aqueous NaHCO_3 (10 mL). The mixture was extracted with DCM (3 $\times$ 15 mL) and the combined organic layers were dried over Na_2SO_4 , filtered, and concentrated. The reaction mixture was purified by column chromatography (petroleum ether/ethyl acetate = 6/1) on silica gel to afford the product **5** (40.8 mg, 76% yield) as a brown solid, melting point: 254–256 $^\circ\text{C}$.

(5a,13a)-2,4-dibromo-5a-methyl-6-phenyl-5,5a,6,7-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-8(13H)-one (5**)**

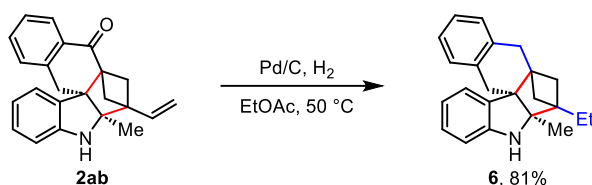


¹H NMR (400 MHz, CDCl₃) δ 8.17 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.61 (td, *J* = 7.5, 1.5 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.41 – 7.31 (m, 4H), 7.29 (d, *J* = 1.8 Hz, 2H), 7.24 (s, 1H), 6.30 (d, *J* = 1.8 Hz, 1H), 4.02 (s, 1H), 3.70 (d, *J* = 16.8 Hz, 1H), 3.24 (d, *J* = 16.8 Hz, 1H), 2.63 (dd, *J* = 10.0, 7.3 Hz, 1H), 2.25 (d, *J* = 7.8 Hz, 1H), 2.09 – 1.97 (m, 2H), 1.32 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 195.0, 149.0, 141.0, 139.4, 134.5, 134.5, 133.1, 132.4, 130.0, 128.4, 127.8, 127.6, 127.2, 126.6, 125.1, 108.8, 101.8, 75.2, 61.8, 60.6, 58.0, 43.2, 37.1, 35.5, 19.2.

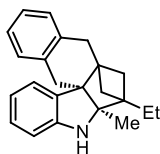
HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₇H₂₂⁷⁹Br₂NO⁺ 534.0063, found 534.0066; [M+H]⁺ calcd for C₂₇H₂₂⁷⁹Br⁸¹BrNO⁺ 536.0042, found 536.0042; [M+H]⁺ calcd for C₂₇H₂₂⁸¹Br₂NO⁺ 538.0022, found 538.0021.

Synthesis of 6



To an autoclave was added **2ab** (32.7 mg, 0.1 mmol), Pd/C (wetted with ca. 55% water) (10 mol%) and 4 mL ethyl acetate. The autoclave was then charged with H₂ (1 bar), and the reaction mixture was allowed to stir at 50 °C for 12 h. The Pd/C was filtered off and the filtrate was evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel to afford the desired product **6** (petroleum ether/ethyl acetate = 20/1) as a yellow oil (25.6 mg, 81% yield).

(5a,13a)-6-ethyl-5a-methyl-5,5a,6,7,8,13-hexahydro-6,7a-methanobenzo[5,6]indeno[1,7a-*b*]indole (6)

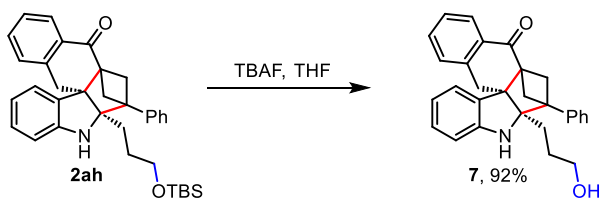


^1H NMR (400 MHz, CDCl_3) δ 7.21 – 7.12 (m, 4H), 6.99 (td, J = 7.5, 1.6 Hz, 1H), 6.58 – 6.43 (m, 3H), 3.72 (s, 1H), 3.30 (d, J = 16.9 Hz, 1H), 3.10 (d, J = 17.6 Hz, 1H), 2.94 (t, J = 16.6 Hz, 2H), 1.59 (dq, J = 15.5, 7.8 Hz, 1H), 1.53 – 1.45 (m, 2H), 1.38 (d, J = 7.4 Hz, 1H), 1.31 (d, J = 8.0 Hz, 5H), 0.97 (t, J = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 152.0, 135.8, 135.5, 134.2, 129.9, 129.5, 127.7, 126.0, 125.9, 123.7, 118.0, 108.4, 73.7, 58.6, 56.7, 48.5, 41.3, 38.1, 35.1, 32.6, 20.1, 18.5, 11.2.

HRMS (ESI $^+$): m/z : $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{23}\text{H}_{26}\text{N}^+$ 316.2060, found 316.2052.

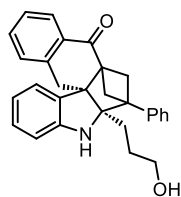
Synthesis of 7



Compound **2ah** (107.2 mg, 0.2 mmol) was dissolved in THF (4.0 mL). The solution of TBAF (0.4 mL, 1 M in THF, 2.0 equiv, 0.4 mmol) was added at 0 °C. The resultant mixture was stirred at 0 °C for 1 hour. The mixture was then stirred at room temperature until Compound **7** was complete (as monitored by TLC). The solvent was then removed under reduced pressure and the residue was diluted with water (4 mL). The aqueous layer was extracted with dichloromethane (3×10 mL). The combined organic phases were washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered, and concentrated under reduced pressure. The residue was purified by silica gel chromatography eluted with (petroleum ether/ethyl acetate = 5/1) to give compound **7** (77.2 mg, 92% yield) as a yellow solid, melting point: 242–244 °C.

(5a,13a)-5a-(3-hydroxypropyl)-6-phenyl-5,5a,6,7-tetrahydro-6,7a-

methanobenzo[5,6]indeno[1,7a-b]indol-8(13*H*)-one (7)

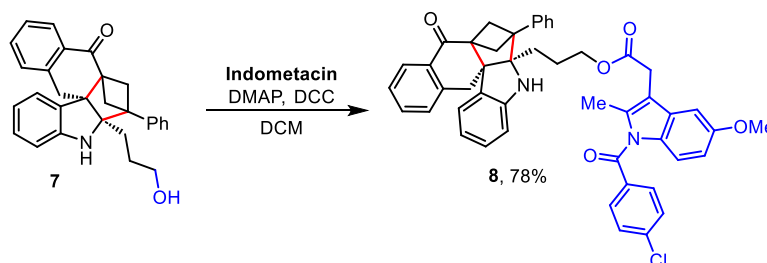


¹H NMR (400 MHz, CDCl₃) δ 8.14 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.31 (m, 3H), 7.30 – 7.26 (m, 3H), 7.01 – 6.95 (m, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 6.40 – 6.28 (m, 2H), 3.83 (d, *J* = 16.7 Hz, 1H), 3.58 – 3.50 (m, 2H), 3.43 (d, *J* = 16.7 Hz, 1H), 2.76 – 2.66 (m, 1H), 2.19 – 2.09 (m, 2H), 2.09 – 1.97 (m, 2H), 1.74 – 1.32 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 195.9, 152.1, 142.2, 140.8, 134.2, 132.5, 132.2, 130.0, 128.7, 128.2, 127.4, 127.1, 126.9, 126.7, 123.1, 118.0, 108.2, 77.8, 63.2, 60.9, 60.4, 58.3, 43.1, 37.4, 36.4, 29.0, 27.5.

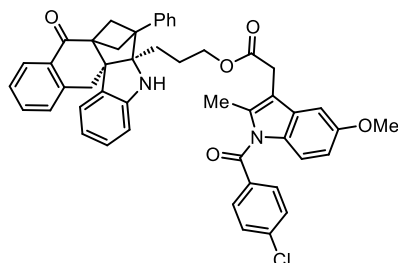
HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₉H₂₈NO₂⁺ 422.2115, found 422.2110.

Synthesis of 8



To a stirred solution of Indometacin (35.8 mg, 0.1 mmol) and DCC (dicyclohexylcarbodiimide) (29.1 mg, 0.15 mmol) in DCM (5 mL) were added DMAP (4-dimethylaminepyridine) (1.8 mg, 0.015 mmol) and **7** (42.2 mg, 0.1 mmol). The reaction mixture was stirred at rt for 24 h. After filtration, the filtrate was concentrated in vacuo and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 10/1) on silica gel to afford the product **8** (59.2 mg, 78% yield) as a white solid, melting point: 175-177 °C.

3-((5a,13a)-8-oxo-6-phenyl-6,7,8,13-tetrahydro-6,7a-methanobenzo[5,6]indeno[1,7a-b]indol-5a(5H)-yl)propyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)acetate (8)

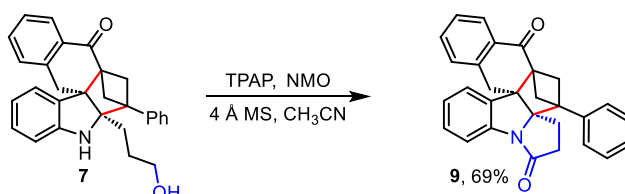


¹H NMR (400 MHz, CDCl₃) δ 8.15 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.61 – 7.52 (m, 3H), 7.48 – 7.38 (m, 3H), 7.33 – 7.26 (m, 4H), 7.07 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.01 – 6.92 (m, 2H), 6.77 (d, *J* = 9.1 Hz, 1H), 6.60 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.48 (d, *J* = 7.8 Hz, 1H), 6.36 – 6.24 (m, 2H), 4.12 – 4.02 (m, 1H), 4.02 – 3.92 (m, 1H), 3.86 (s, 1H), 3.72 (s, 3H), 3.64 (s, 2H), 3.53 (d, *J* = 16.2 Hz, 1H), 3.28 (d, *J* = 16.5 Hz, 1H), 2.38 (s, 4H), 2.15 – 2.02 (m, 2H), 1.87 (d, *J* = 7.2 Hz, 1H), 1.85 – 1.77 (m, 1H), 1.67 (t, *J* = 4.1 Hz, 1H), 1.50 – 1.40 (m, 1H), 1.36 – 1.32 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 195.6, 170.8, 168.2, 156.1, 151.7, 142.1, 140.5, 139.4, 136.1, 134.1, 133.8, 132.4, 131.7, 131.2, 130.8, 130.7, 130.0, 129.2, 128.7, 128.2, 127.4, 127.1, 127.0, 126.5, 123.0, 117.8, 115.1, 112.6, 111.2, 107.8, 101.8, 77.1, 65.4, 60.7, 60.3, 58.2, 55.6, 42.9, 37.1, 36.0, 30.6, 29.0, 23.8, 13.5.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₄₈H₄₂ClN₂O₅⁺ 761.2777, found 761.2781.

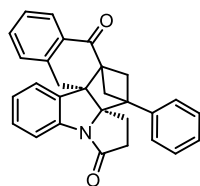
Synthesis of 9^[5]



In a dry Schlenk tube, 4Å molecular sieves (10 mg), NMO (N-methylmorpholine N-oxide) (35.1 mg, 0.3 mmol), and **7** (42.2 mg, 0.1 mmol) were stirred in 4 mL acetonitrile at room temperature. TPAP (Tetrapropylammonium perruthenate) (5.3 mg, 0.015 mmol)

was added and the mixture was stirred for 2 h until consumption of the alcohol was complete (as monitored by TLC). The reaction mixture was filtered through a plug of silica gel (washed with ethyl acetate) and purified by column chromatography (petroleum ether/ethyl acetate = 8/1) to afford product **9** (28.7 mg, 69% yield) as a white solid, melting point: 278–280 °C.

(7a,15b)-7-phenyl-6,7,8,9-tetrahydro-10H-5a,7-methanobenzo[5,6]indeno[1,7a-b]pyrrolo[1,2-a]indole-5,10(16H)-dione (9)



¹H NMR (400 MHz, CDCl₃) δ 8.19 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.76 (d, *J* = 7.9 Hz, 1H), 7.64 – 7.57 (m, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.41 – 7.32 (m, 4H), 7.26 (q, *J* = 2.7 Hz, 3H), 6.80 (td, *J* = 7.6, 1.1 Hz, 1H), 6.45 (dd, *J* = 7.7, 1.2 Hz, 1H), 3.68 (d, *J* = 16.4 Hz, 1H), 3.28 (d, *J* = 16.6 Hz, 1H), 2.69 (dd, *J* = 10.0, 7.3 Hz, 1H), 2.44 – 2.30 (m, 1H), 2.20 (dd, *J* = 16.3, 7.5 Hz, 3H), 2.02 (dd, *J* = 16.9, 8.9 Hz, 1H), 1.84 (dd, *J* = 10.0, 8.0 Hz, 1H), 1.51 – 1.37 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 194.9, 176.7, 142.5, 140.9, 138.8, 135.6, 134.5, 132.5, 130.0, 128.9, 128.7, 127.7, 127.6, 127.6, 126.0, 124.6, 123.0, 114.7, 82.2, 59.2, 58.9, 56.2, 43.5, 37.1, 34.5, 33.6, 27.8.

HRMS (ESI⁺): *m/z*: [M+H]⁺ calcd for C₂₉H₂₄NO₂⁺ 418.1802, found 418.1803.

9. X-ray characterization data.

The crystals of products **2k** were obtained by slow evaporation in n-hexane and acetone; the crystals of products **9** were obtained by slow evaporation in n-hexane and dichloromethane. The single crystal X-ray analysis determined the structure of products **2k** and **9** as expected.

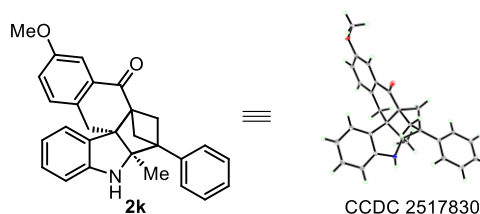


Figure S9. X-ray of **2k**. Displacement ellipsoids are drawn at the 50% probability level.

Table S5. Crystal data and structure refinement for **2k**.

Identification code	mo_250917A
Empirical formula	C ₂₈ H ₂₅ NO ₂
Formula weight	407.49 g/mol
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	$a = 9.6936(4) \text{ Å}$ $\alpha = 86.652(2)^\circ$. $b = 14.0626(5) \text{ Å}$ $\beta = 82.6790(10)$. $c = 16.2000(6) \text{ Å}$ $\gamma = 77.8870(10)$.
Volume	2140.43(14) Å ³
Z	4
Density (calculated)	1.265 g/cm ³
Absorption coefficient	0.079 mm ⁻¹
F(000)	864
Crystal size	0.130 x 0.180 x 0.220 mm

Theta range for data collection	1.98 to 27.56°
Index ranges	-12≤h≤12, -18≤k≤18, -20≤l≤21
Reflections collected	42828
Independent reflections	9870 [R(int) = 0.0810]
Completeness to theta = 25.242	99.8%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.6476
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	9870 / 0 / 563
Goodness-of-fit on F ²	1.059
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1229
R indices (all data)	R1 = 0.0839, wR2 = 0.1391
Extinction coefficient	n/a
Largest diff. peak and hole	0.285 and -0.331 eÅ ⁻³

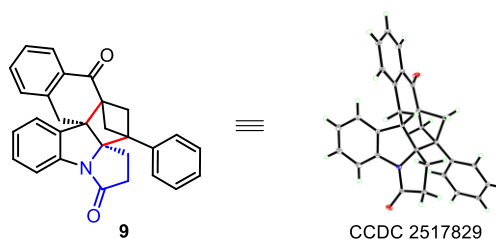


Figure S10. X-ray of **9**. Displacement ellipsoids are drawn at the 50% probability level.

Table S6. Crystal data and structure refinement for **9.**

Identification code	mo_251213A
Empirical formula	C ₂₉ H ₂₃ NO ₂
Formula weight	417.48 g/mol
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P 1 21/c 1
Unit cell dimensions	$a = 14.9928(5) \text{ Å}$ $\alpha = 90^\circ$. $b = 10.7897(4) \text{ Å}$ $\beta = 117.0260(10)^\circ$ $c = 14.3627(5) \text{ Å}$ $\gamma = 90^\circ$.
Volume	2069.71(13) Å ³
Z	4
Density (calculated)	1.340 g/cm ³
Absorption coefficient	0.084 mm ⁻¹
F(000)	880
Crystal size	0.180 x 0.200 x 0.240 mm
Theta range for data collection	2.43 to 28.32°
Index ranges	-20 ≤ h ≤ 19, -14 ≤ k ≤ 14, -19 ≤ l ≤ 19
Reflections collected	36335
Independent reflections	5153 [R(int) = 0.0774]
Completeness to theta = 25.242	99.9%

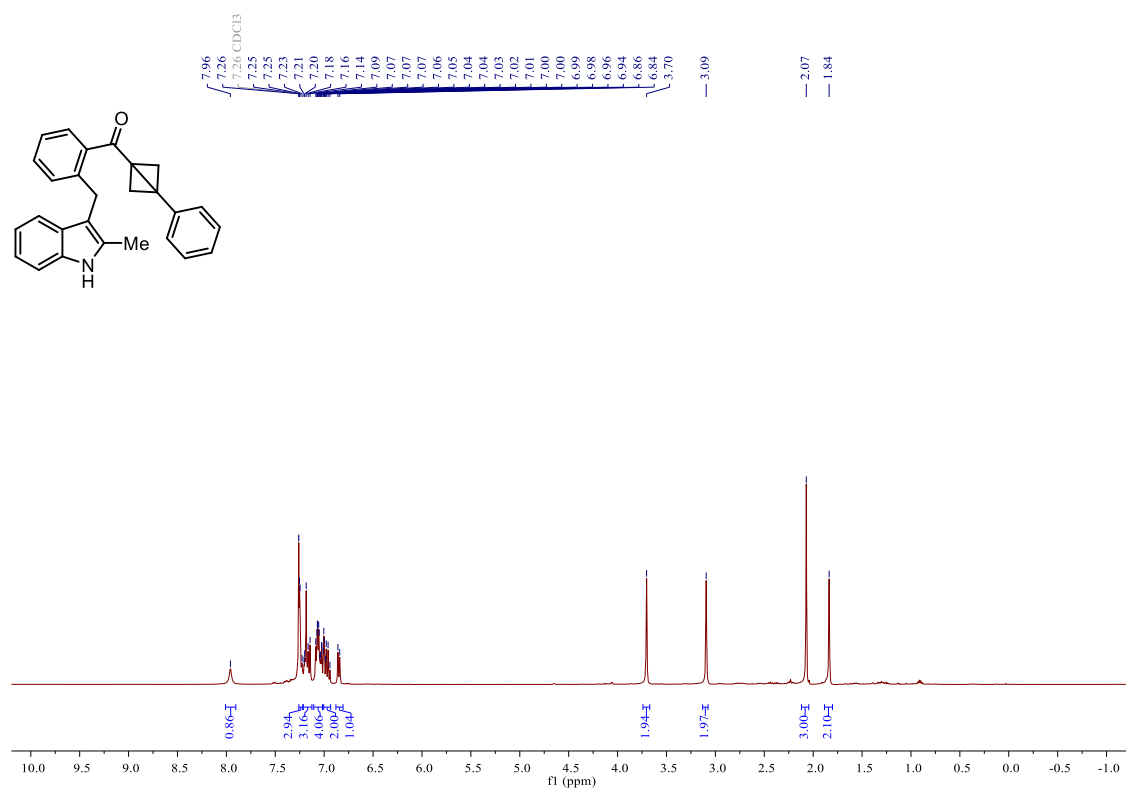
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7457 and 0.5204
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5153 / 0 / 289
Goodness-of-fit on F^2	1.063
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0528$, $wR_2 = 0.1167$
R indices (all data)	$R_1 = 0.0659$, $wR_2 = 0.1260$
Extinction coefficient	n/a
Largest diff. peak and hole	0.346 and -0.300 $e\text{\AA}^{-3}$

10. References

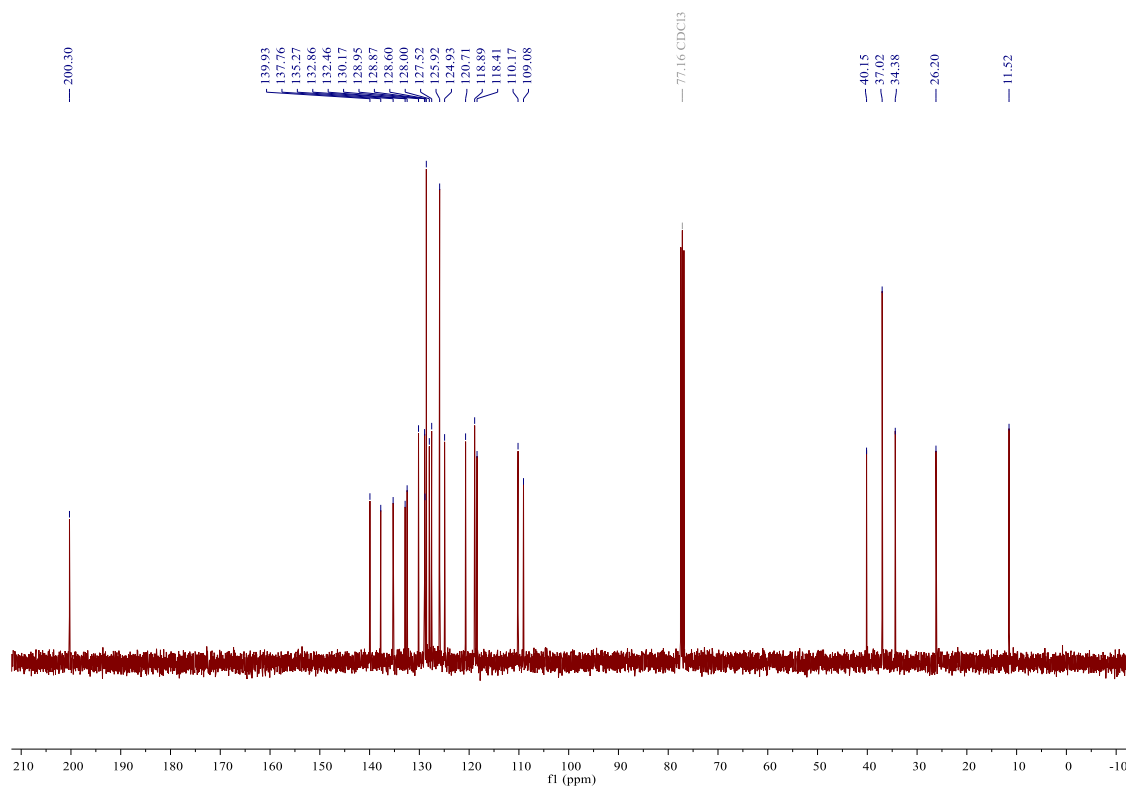
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- [5]a) Q. Yin, S.-L. You, *Chem. Sci.* **2011**, *2*, 1344-1348; b) L. Tang, Y. Xiao, F. Wu, J.-L. Zhou, T.-T. Xu, J.-J. Feng, *Angew. Chem., Int. Ed.* **2023**, *62*, e202310066.

11. Copies of ^1H NMR, ^{13}C NMR and ^{19}F NMR spectra

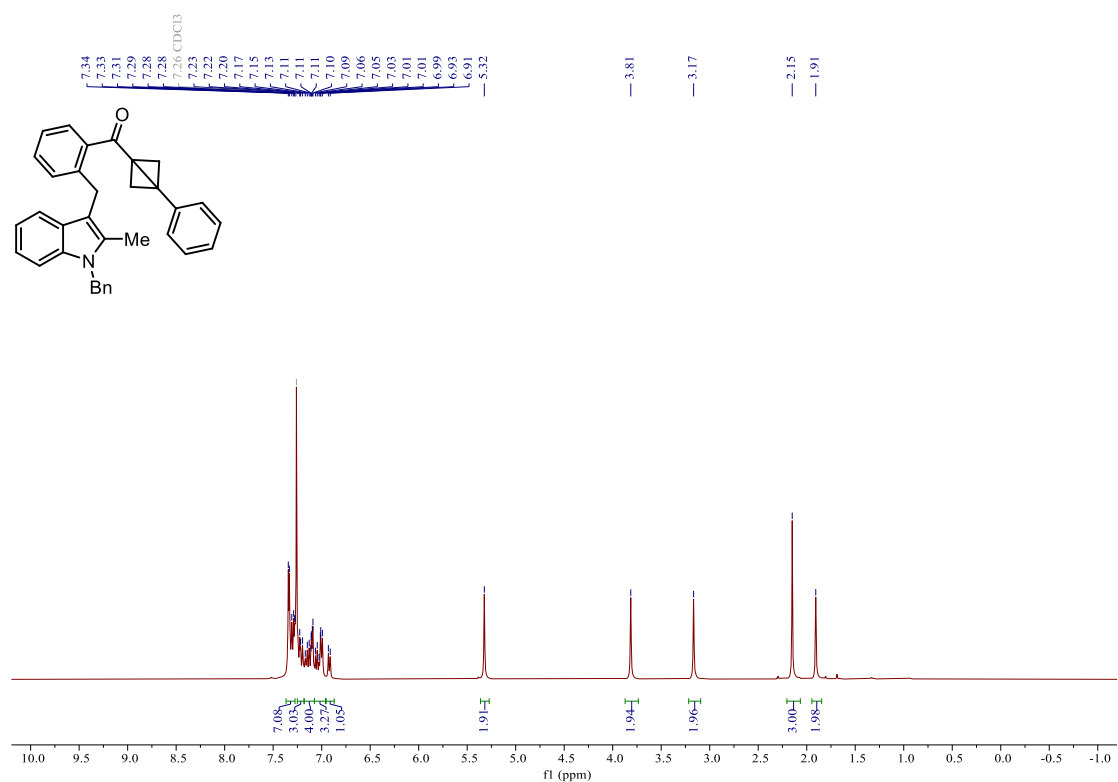
^1H NMR spectra of 1a (CDCl_3 , 400 MHz)



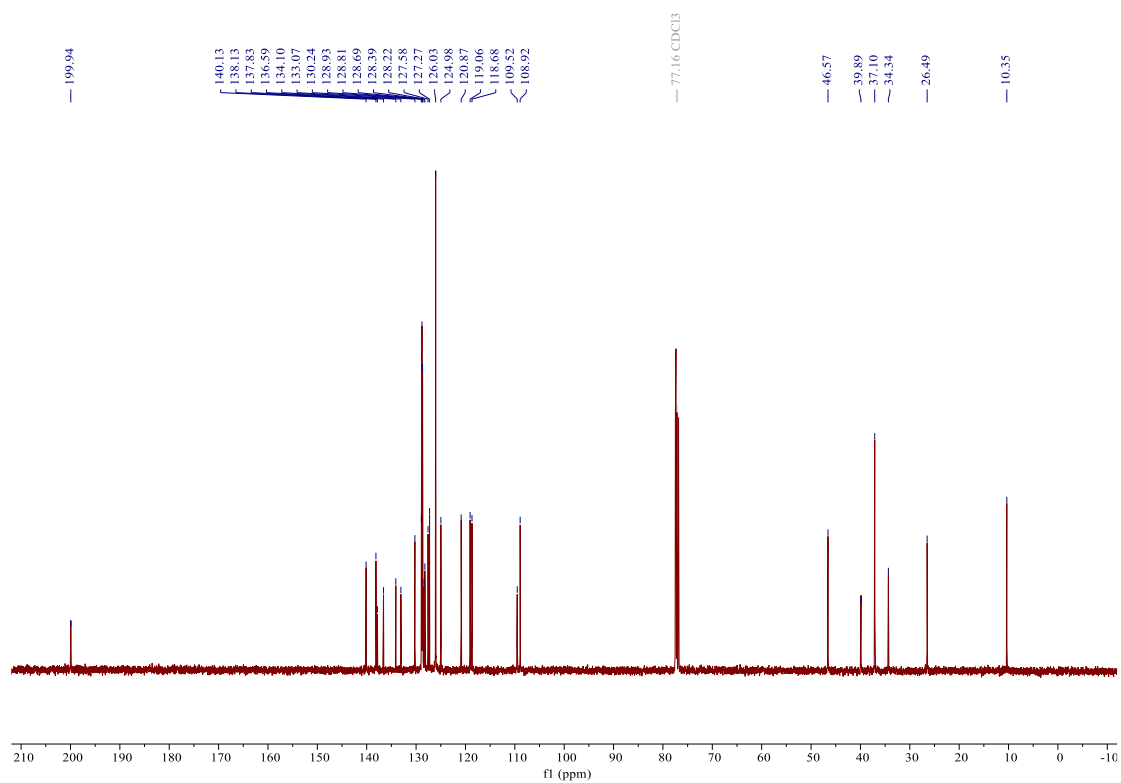
^{13}C NMR spectra of 1a (CDCl_3 , 101 MHz)



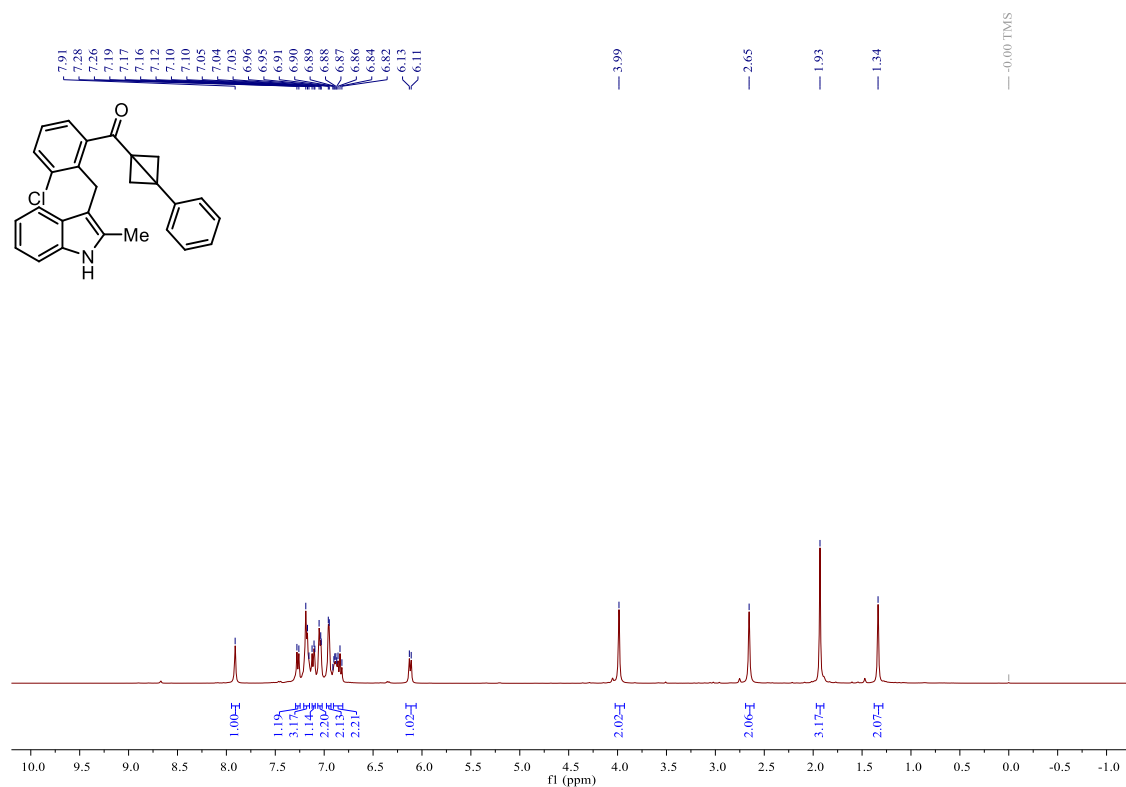
^1H NMR spectra of 1b (CDCl_3 , 400 MHz)



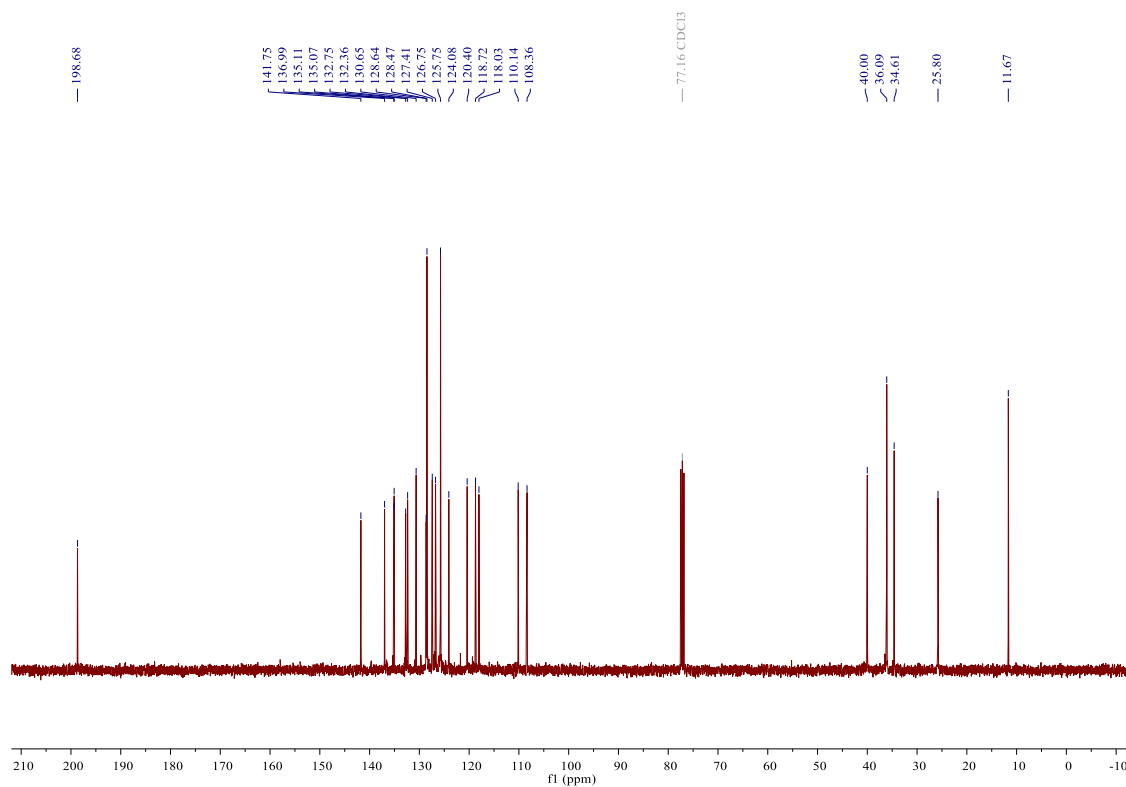
^{13}C NMR spectra of 1b (CDCl_3 , 101 MHz)



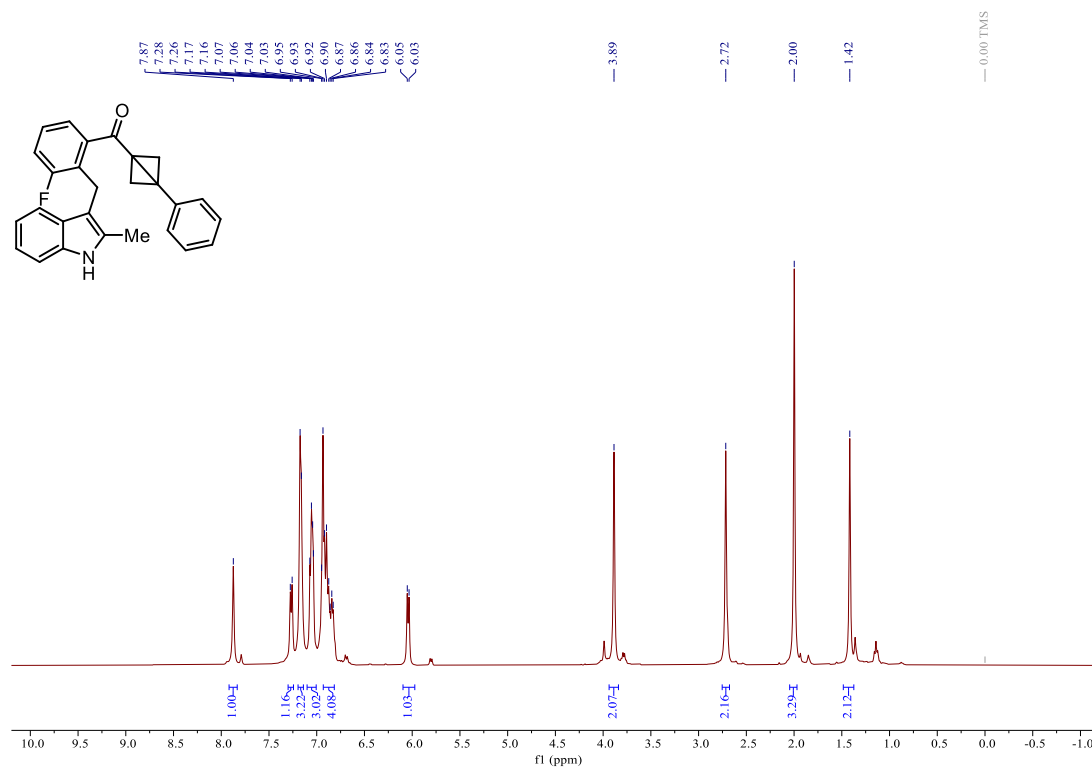
¹H NMR spectra of 1c (CDCl₃, 400 MHz)



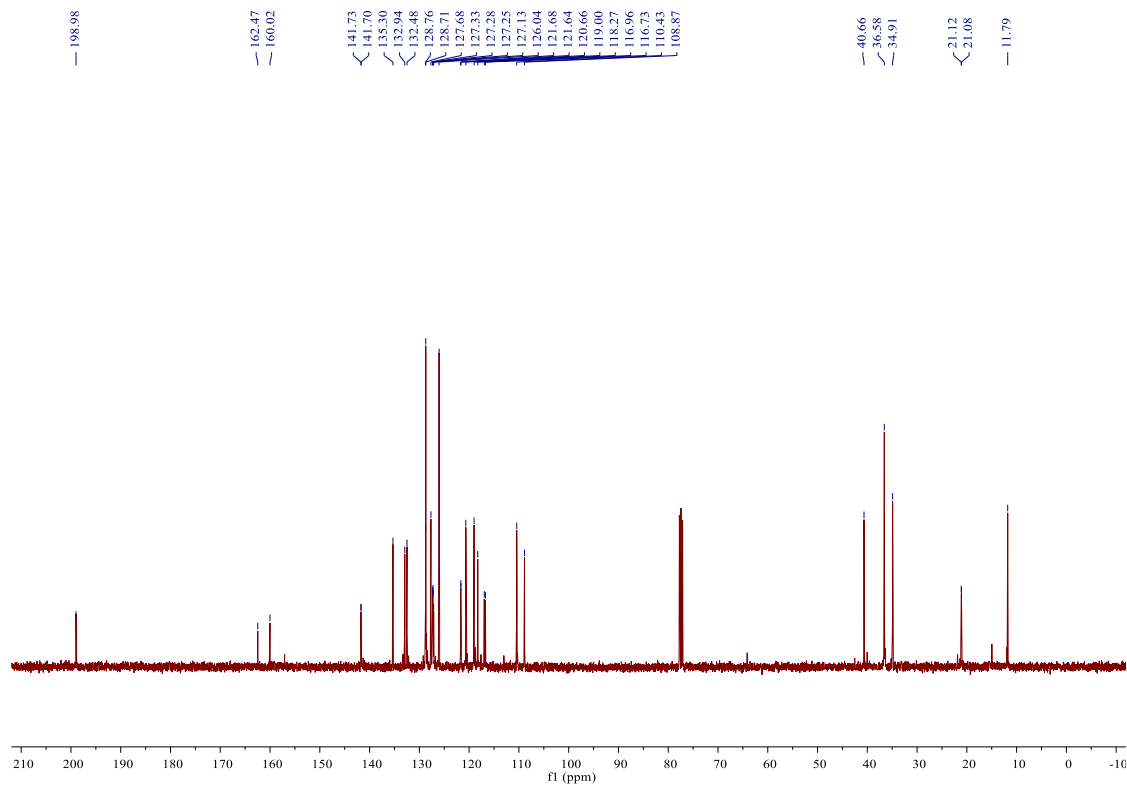
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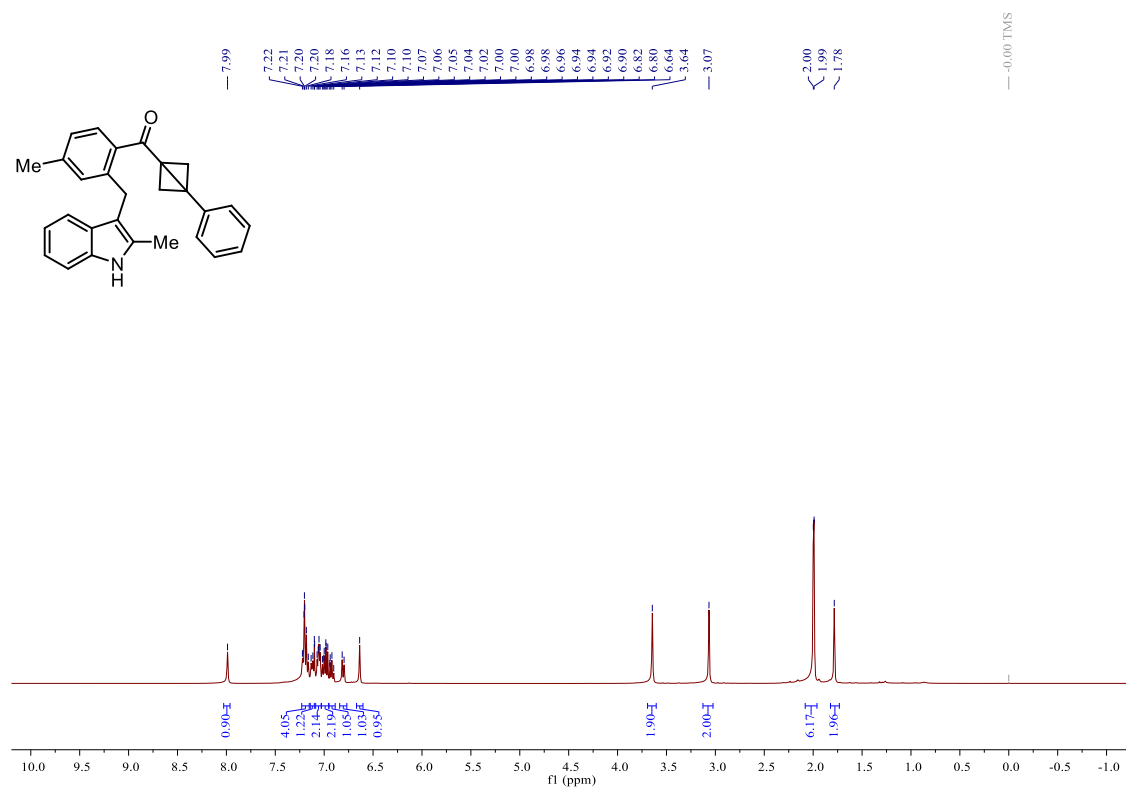
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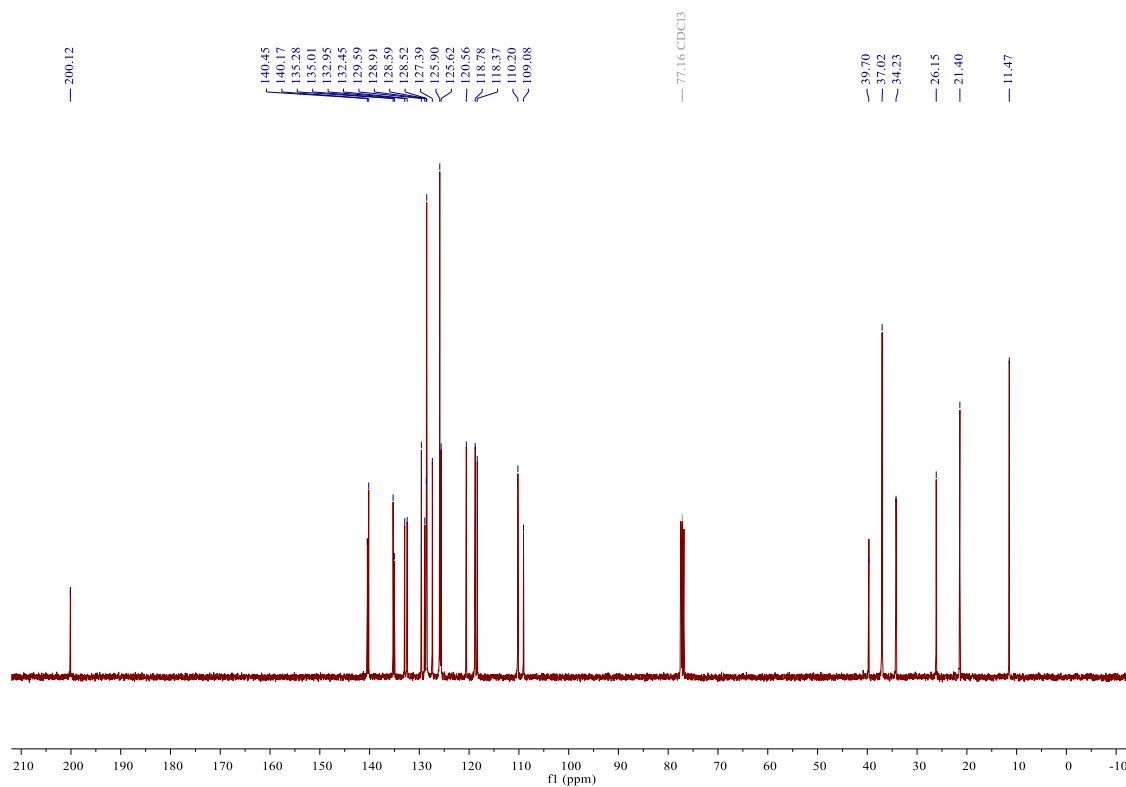
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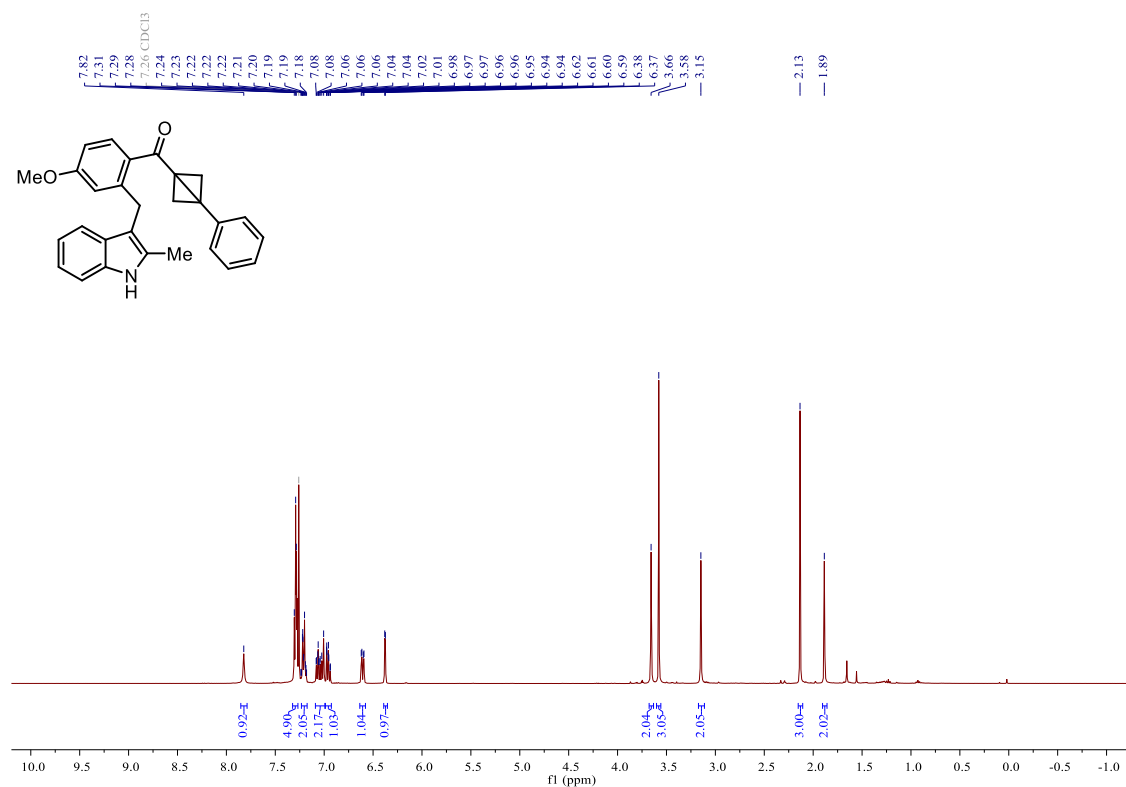
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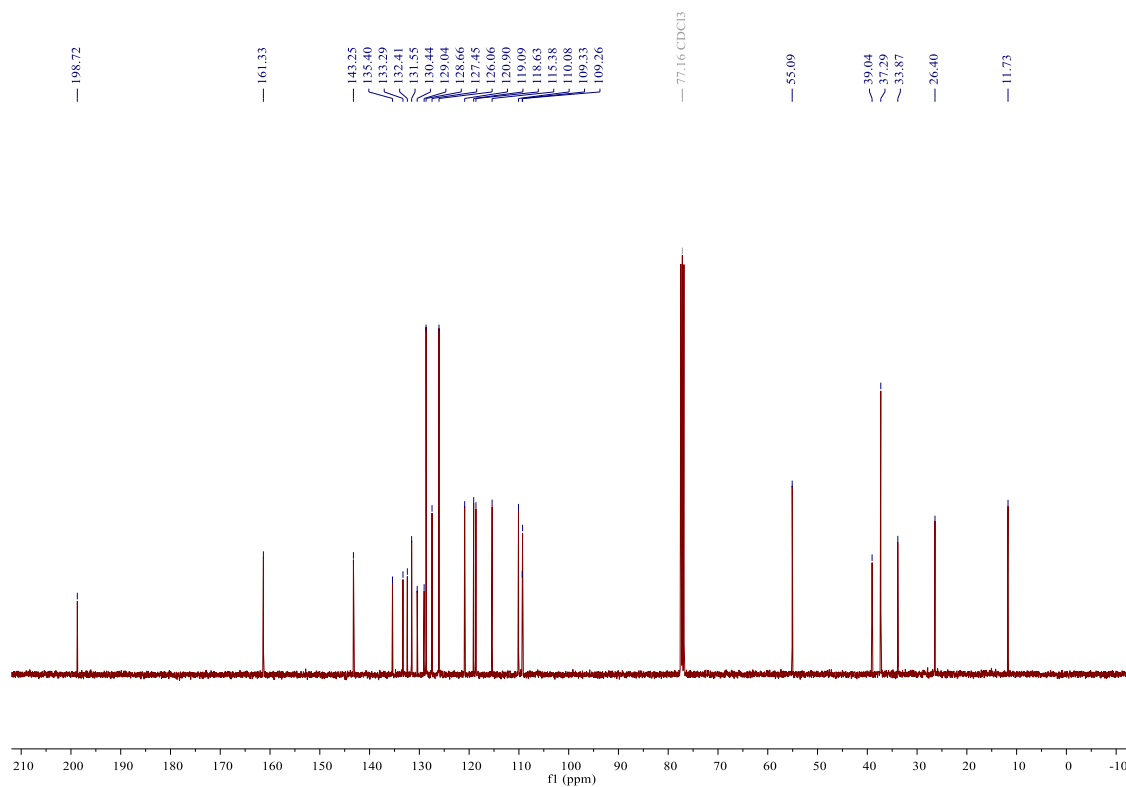
¹³C NMR spectra of 1e (CDCl₃, 101 MHz)



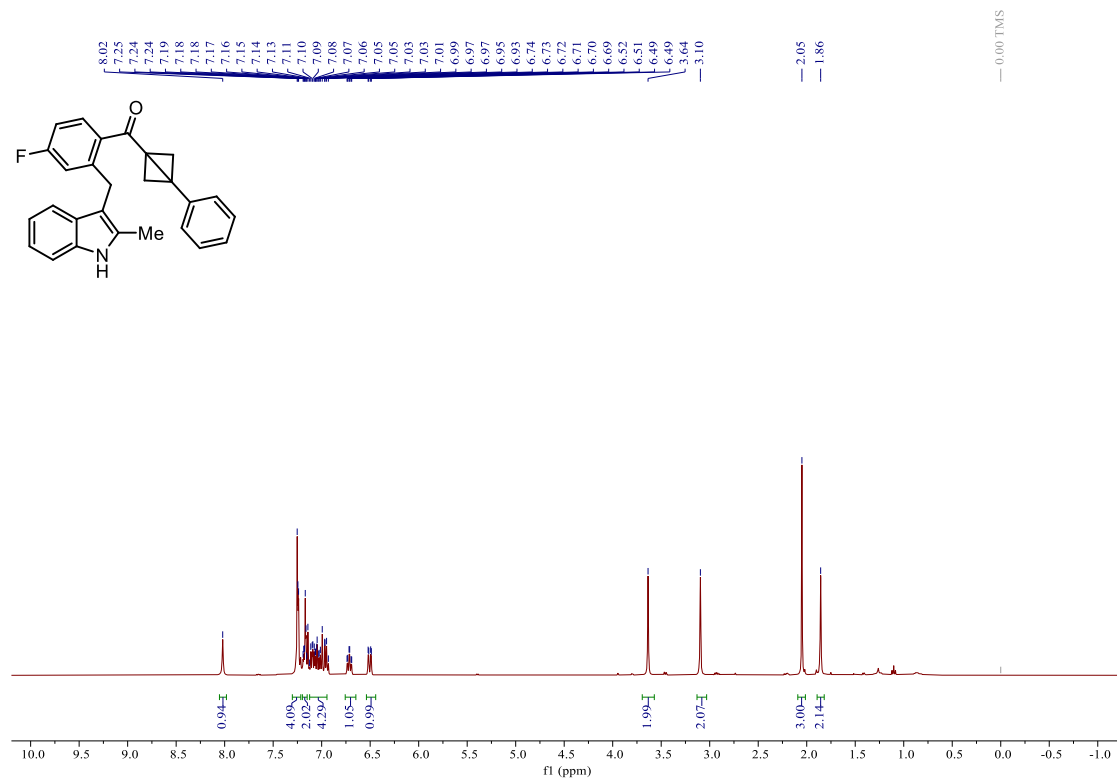
¹H NMR spectra of 1f (CDCl₃, 400 MHz)



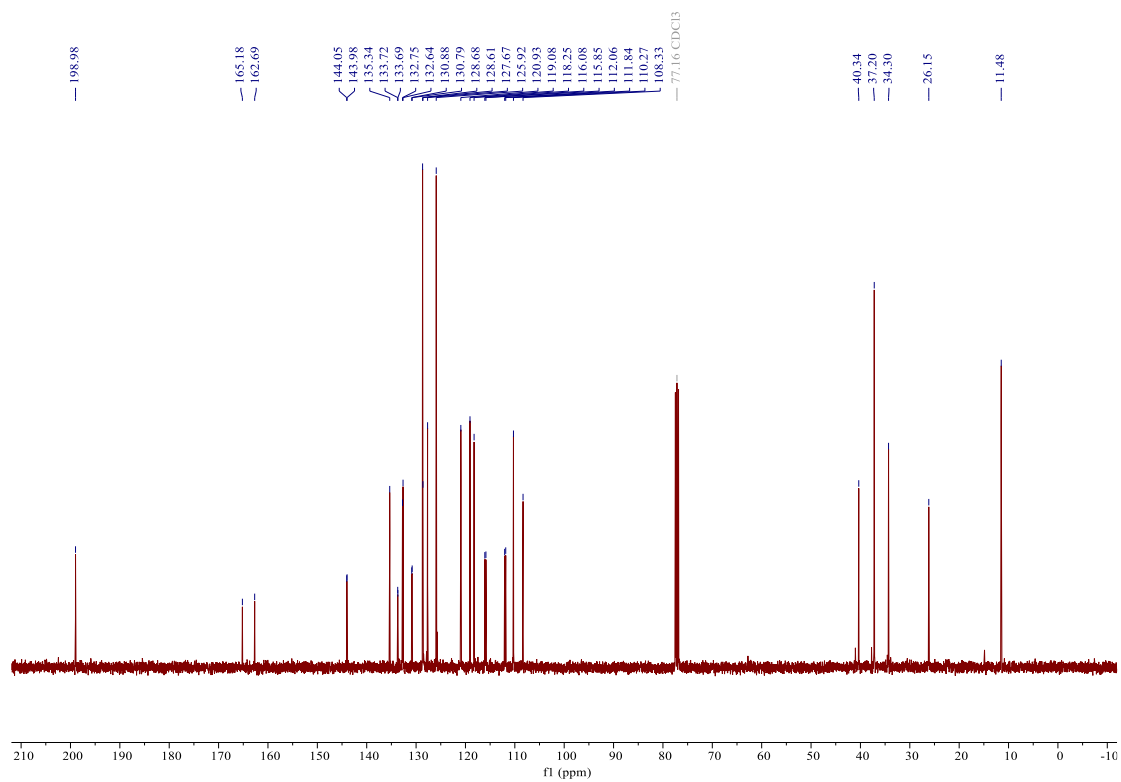
¹³C NMR spectra of 1f (CDCl₃, 101 MHz)



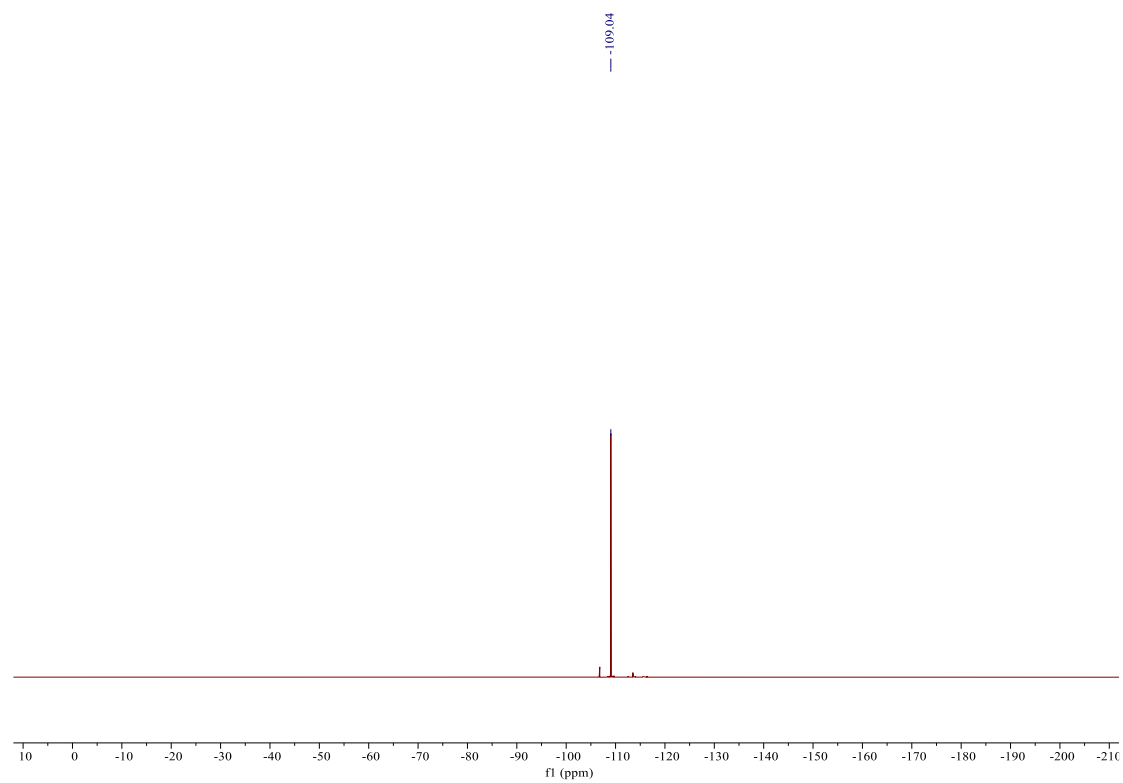
¹H NMR spectra of 1g (CDCl₃, 400 MHz)



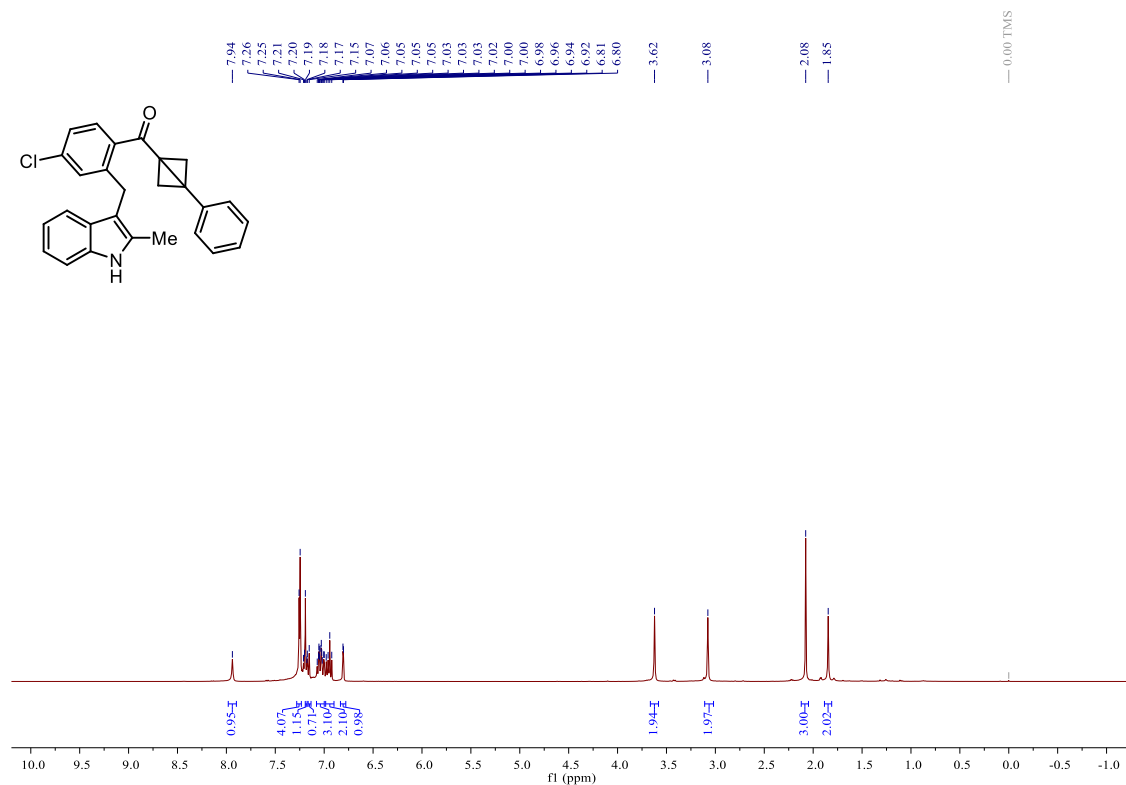
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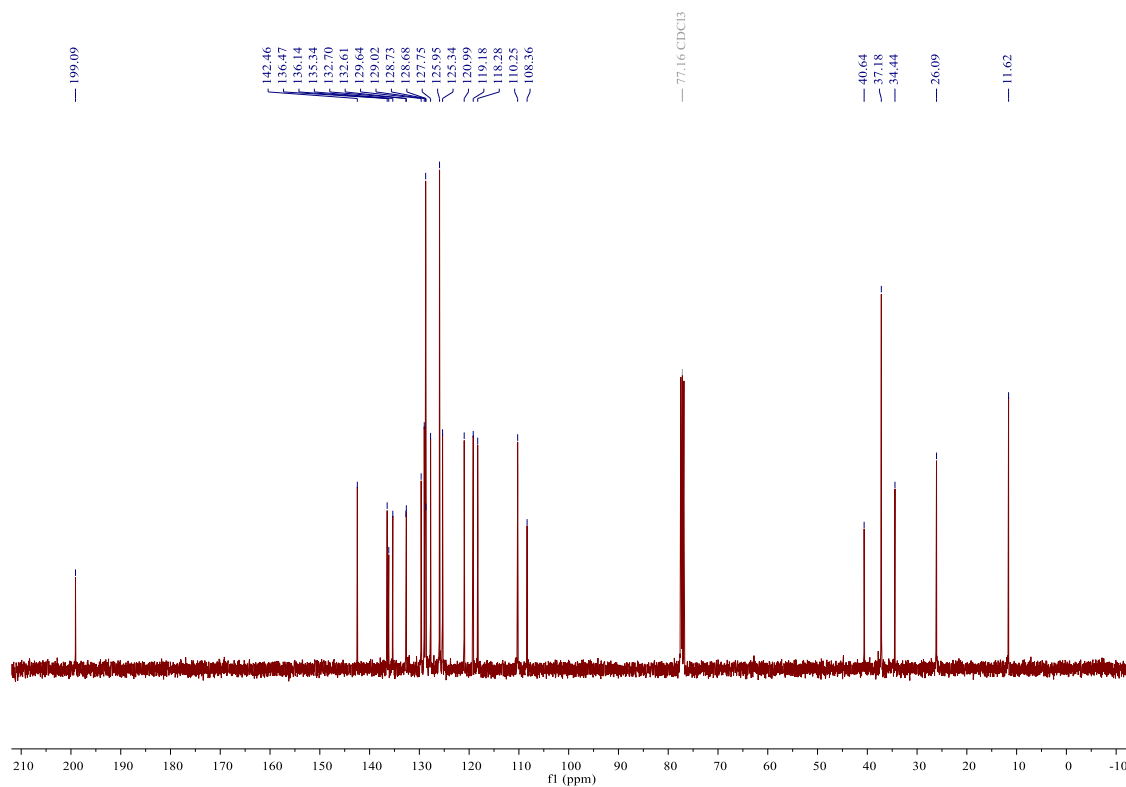
^{19}F NMR spectra of 1g (CDCl_3 , 376 MHz)



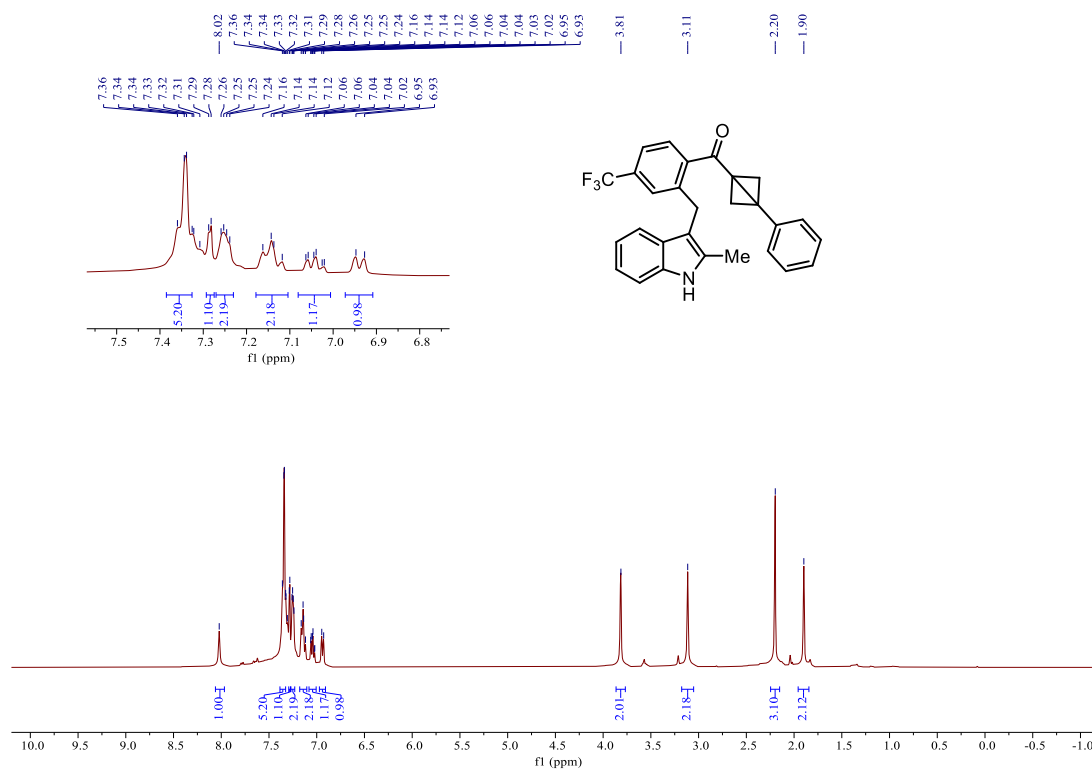
¹H NMR spectra of 1h (CDCl₃, 400 MHz)



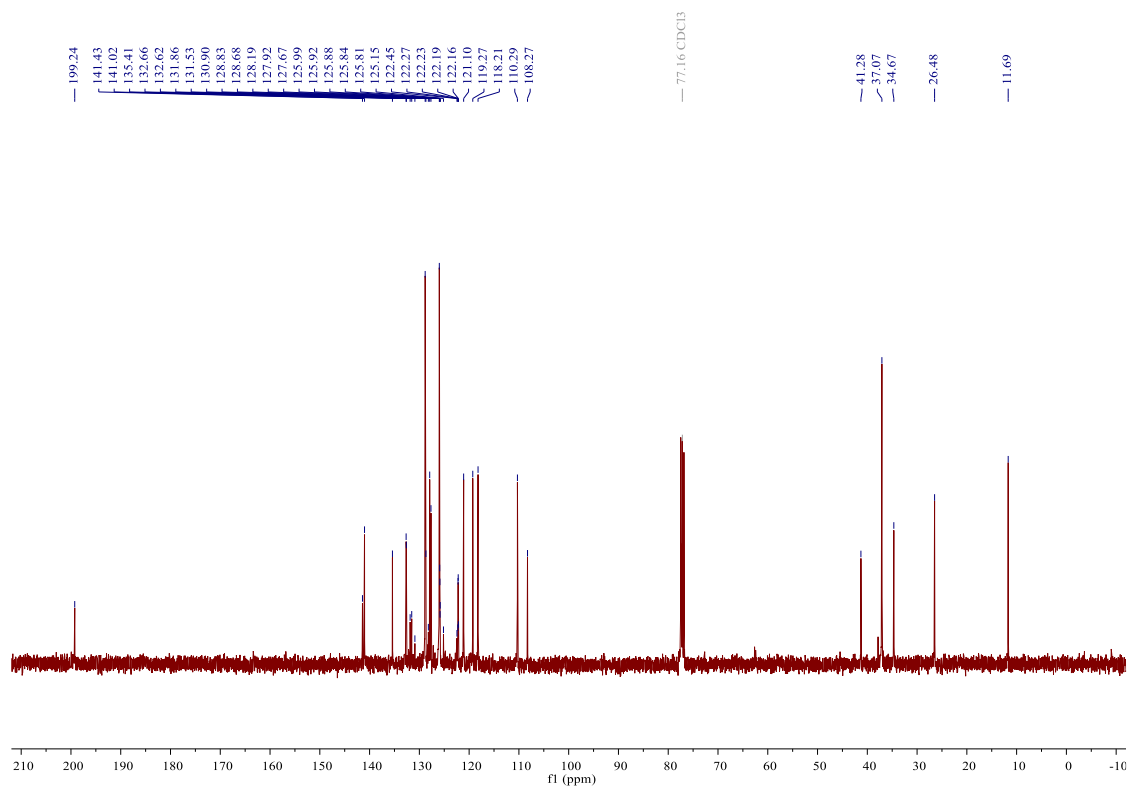
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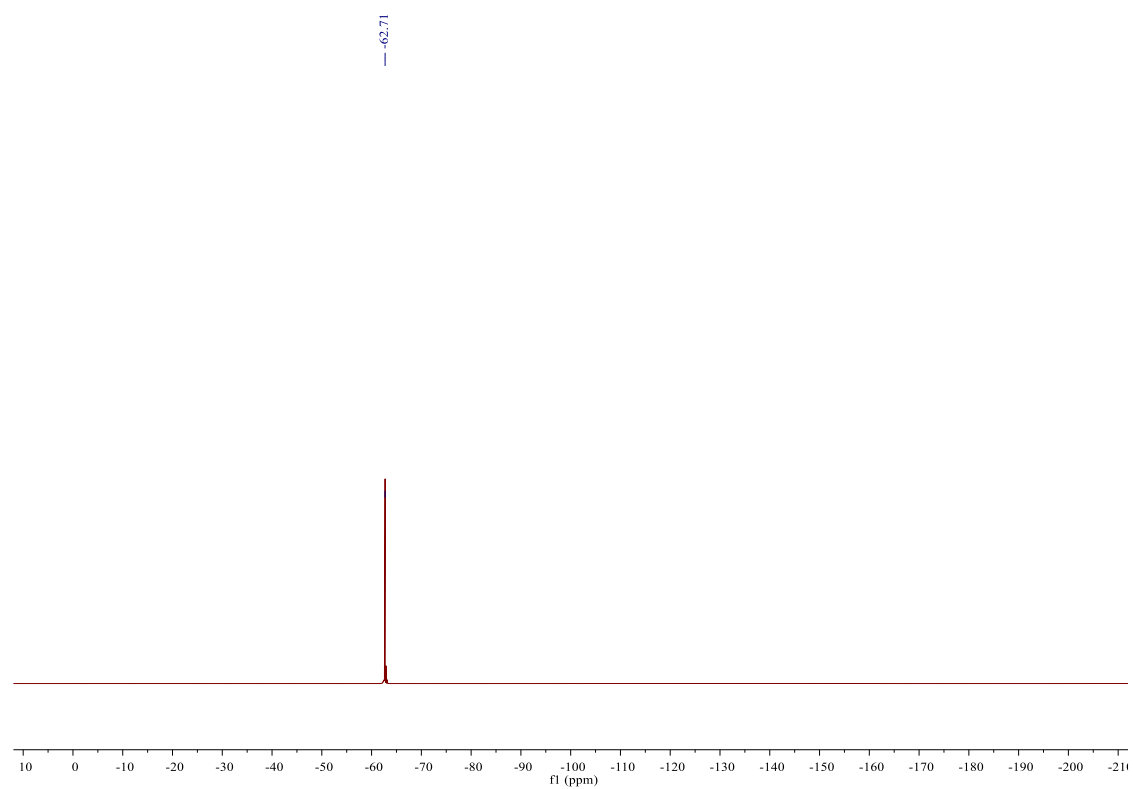
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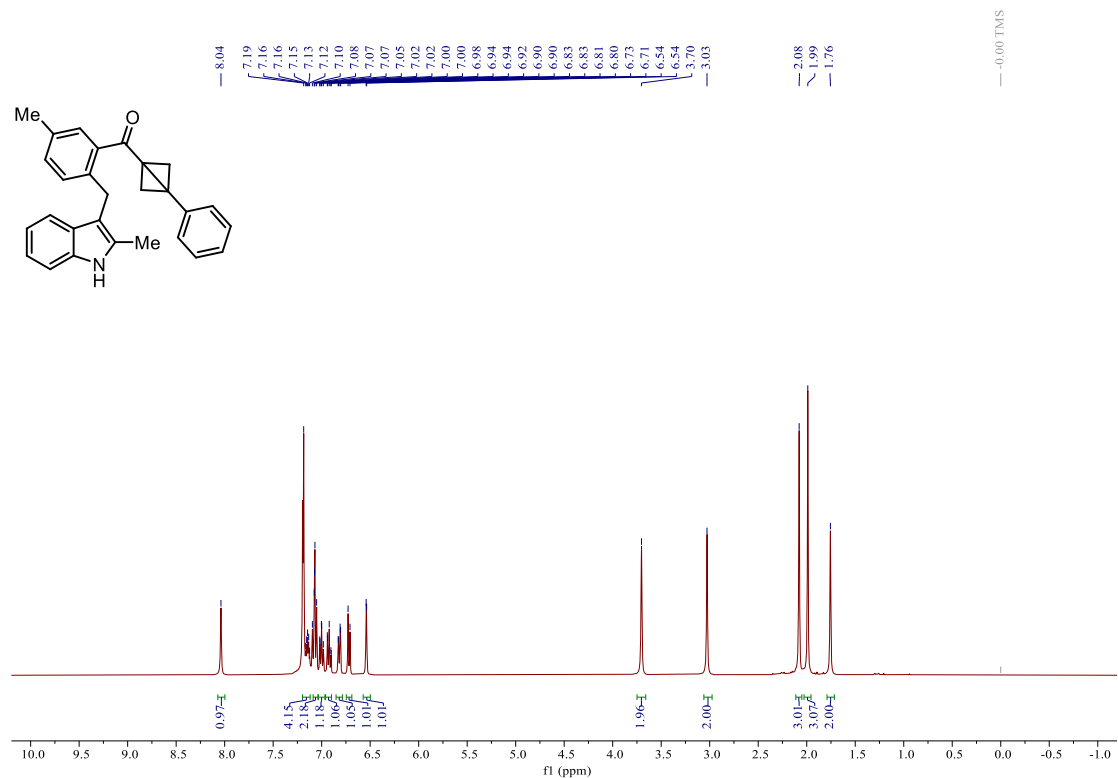
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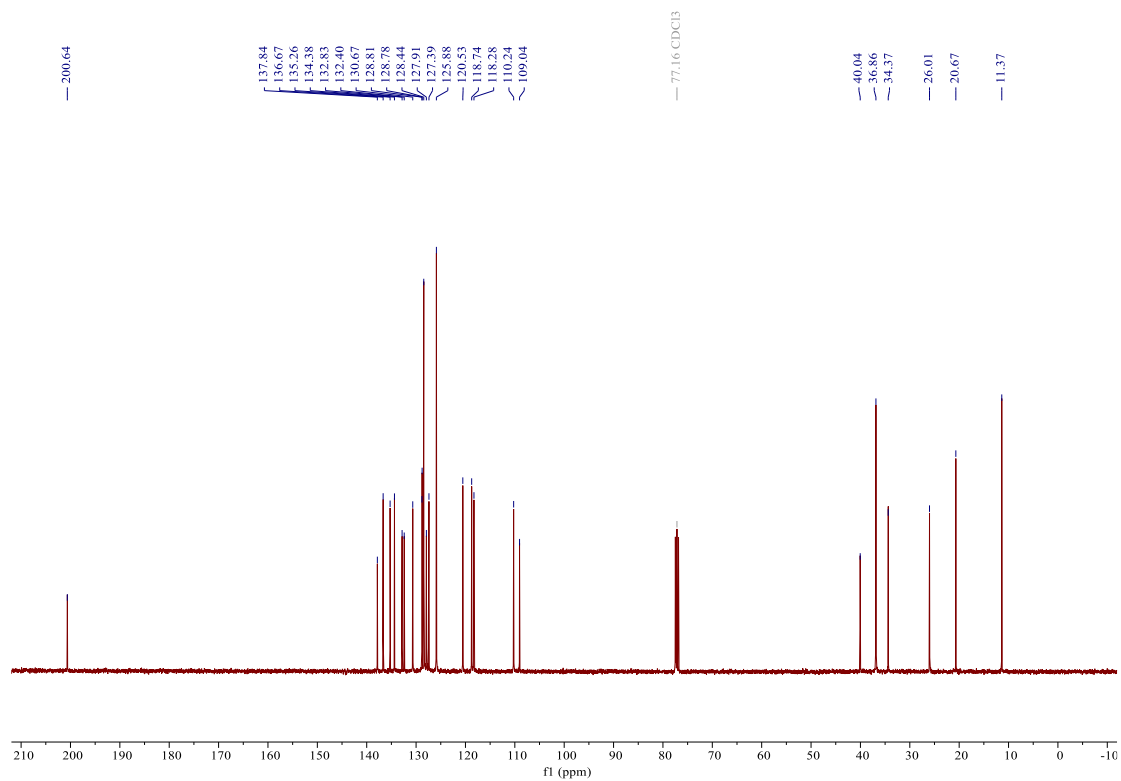
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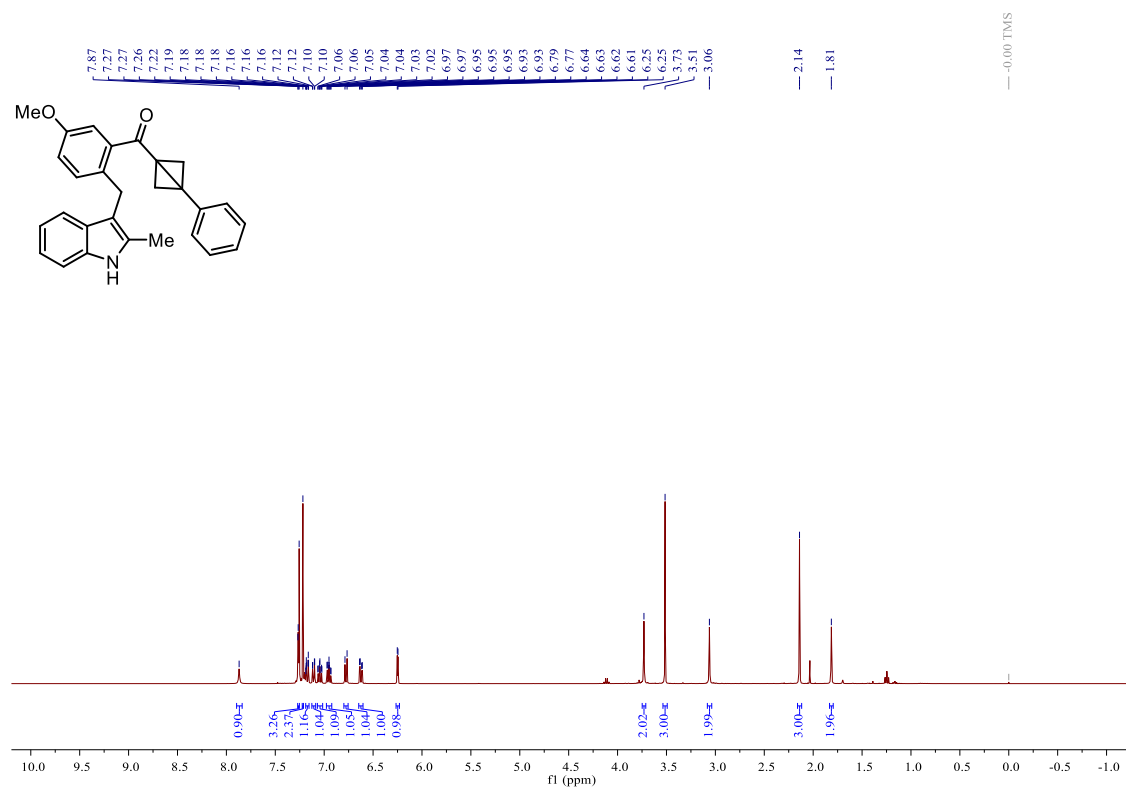
¹H NMR spectra of 1j (CDCl₃, 400 MHz)



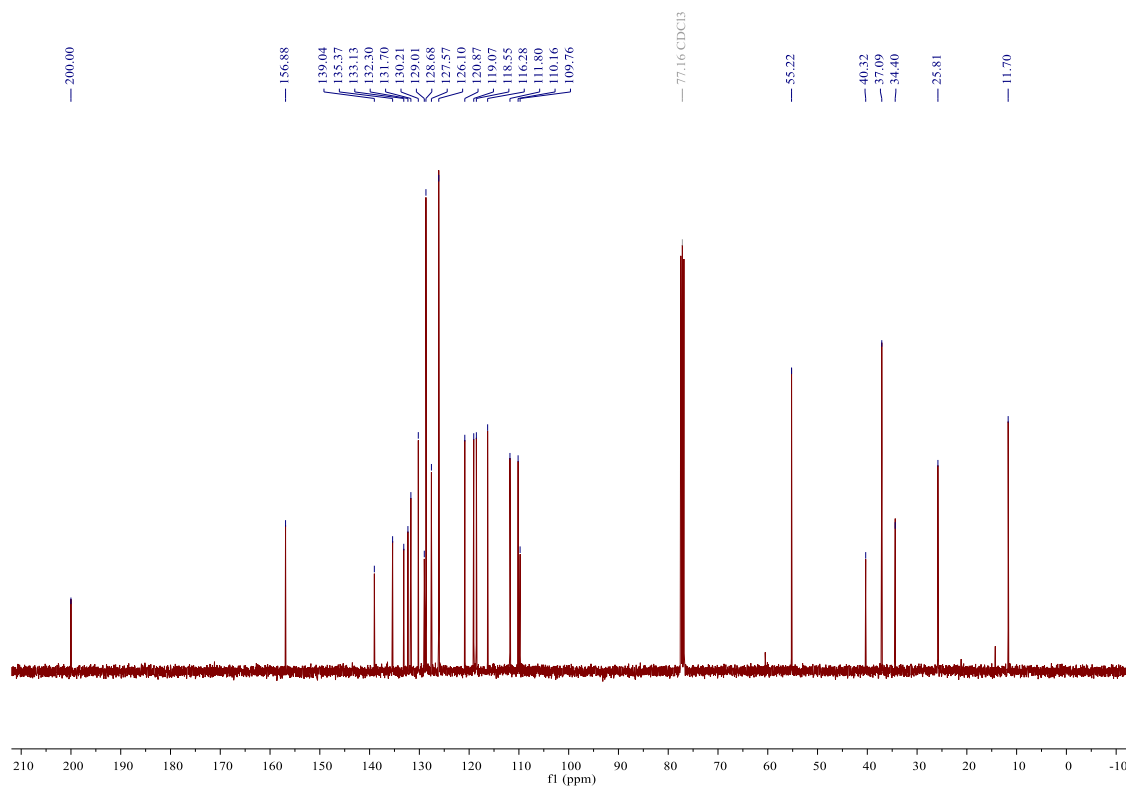
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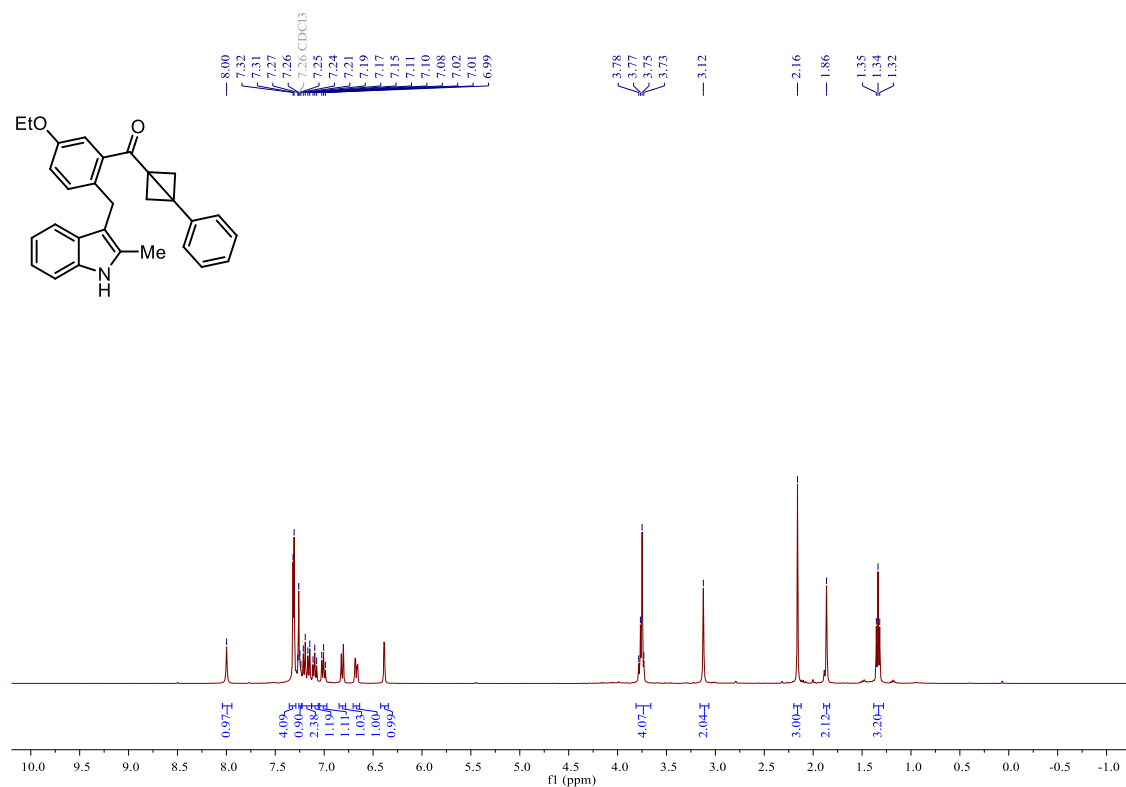
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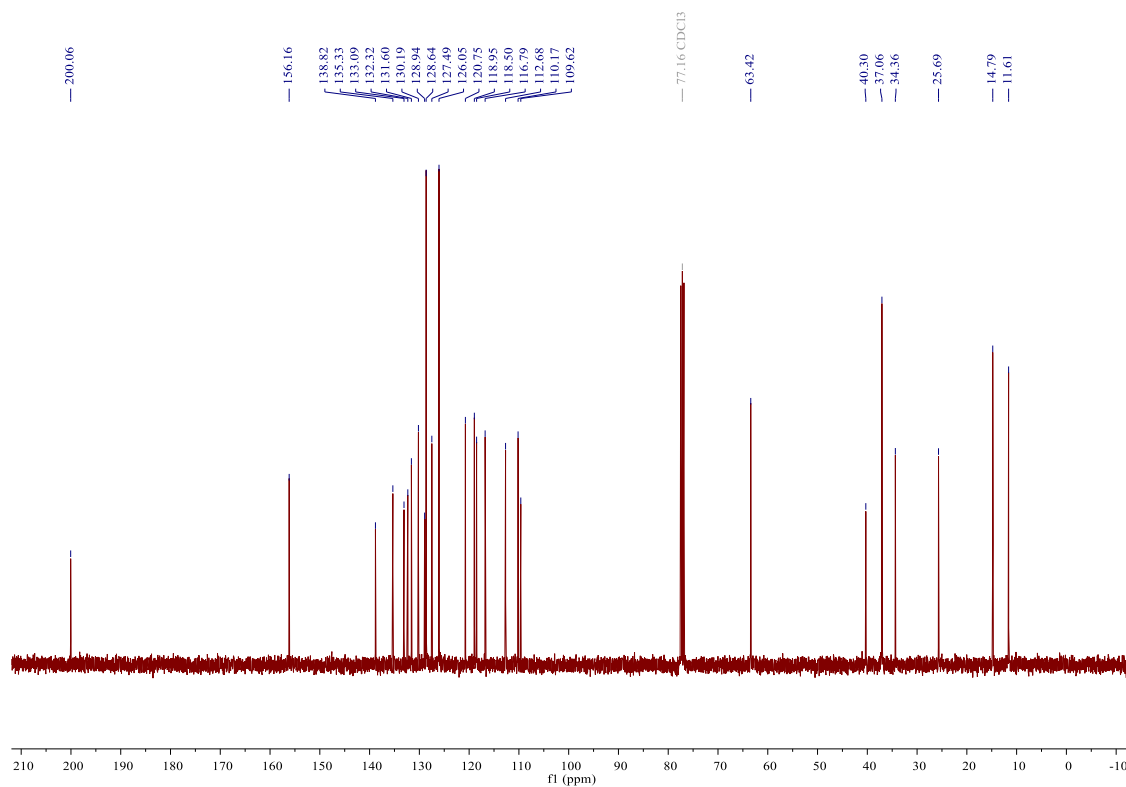
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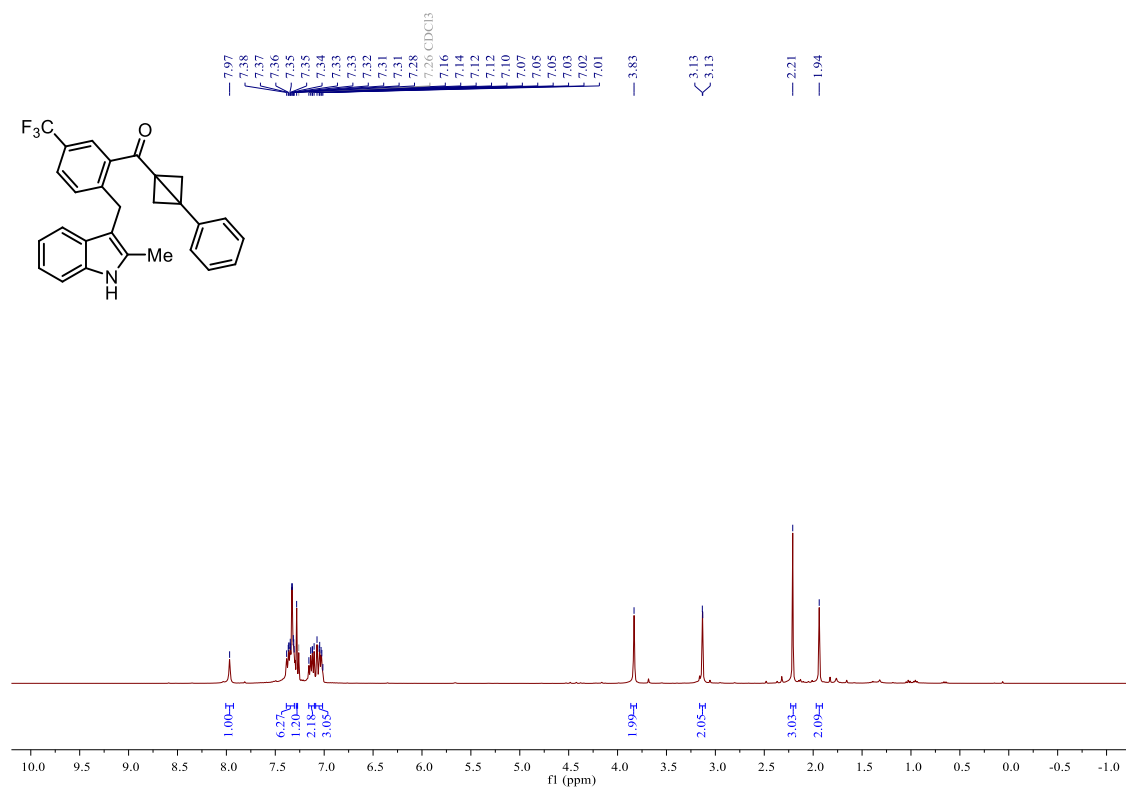
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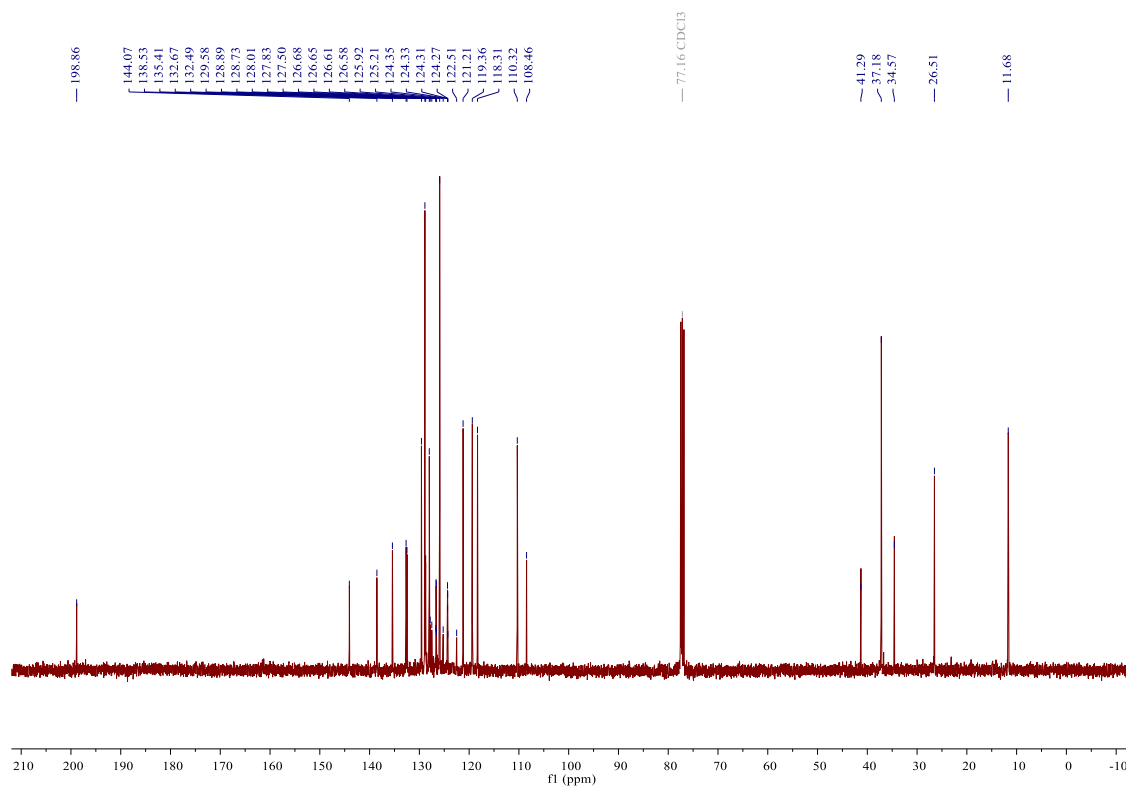
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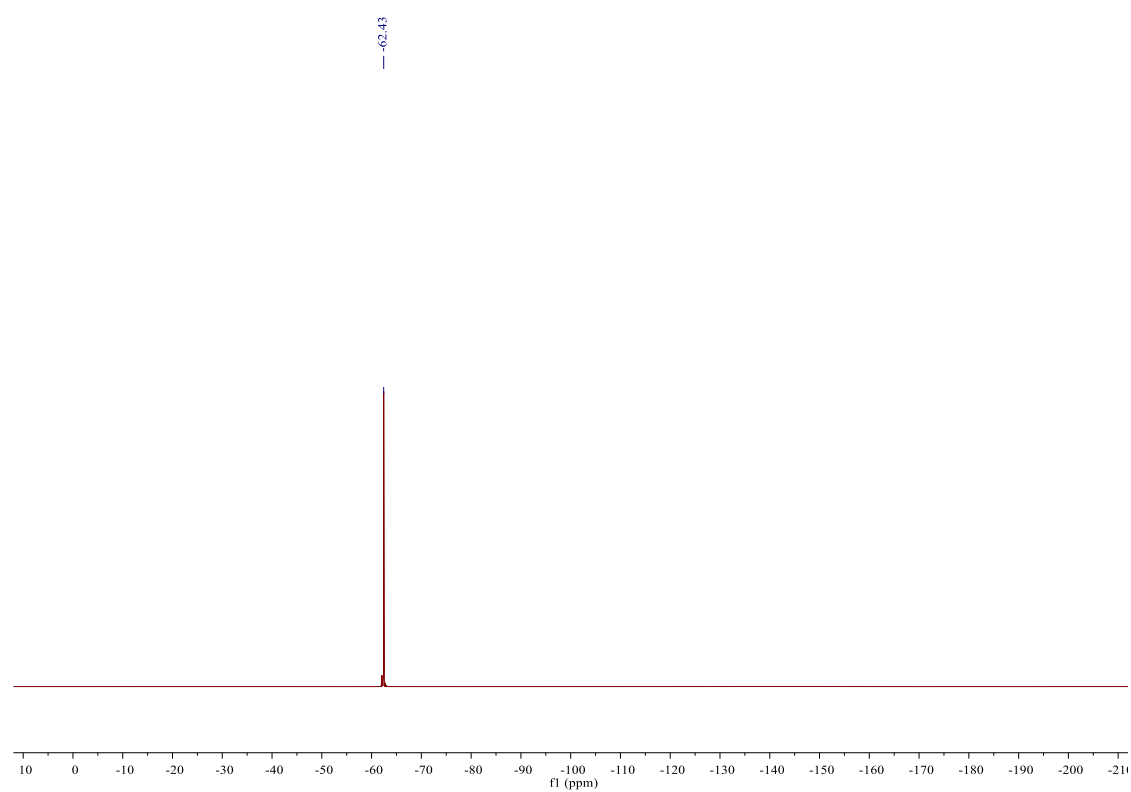
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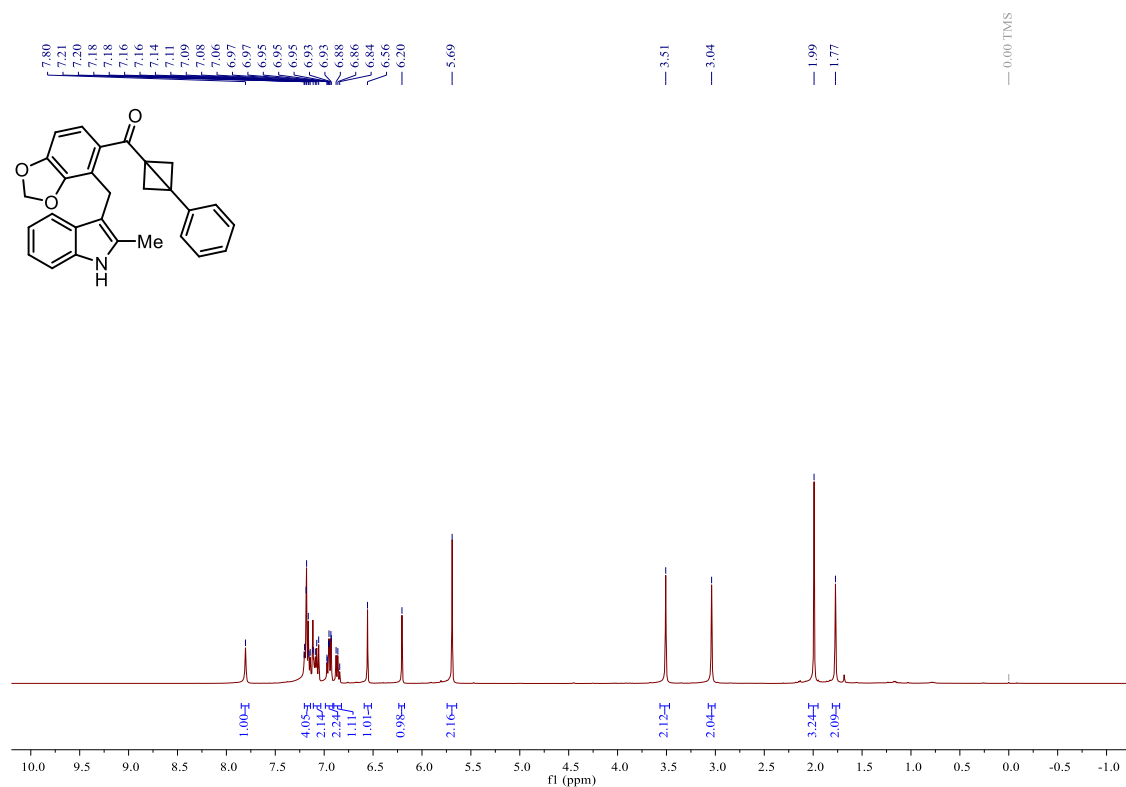
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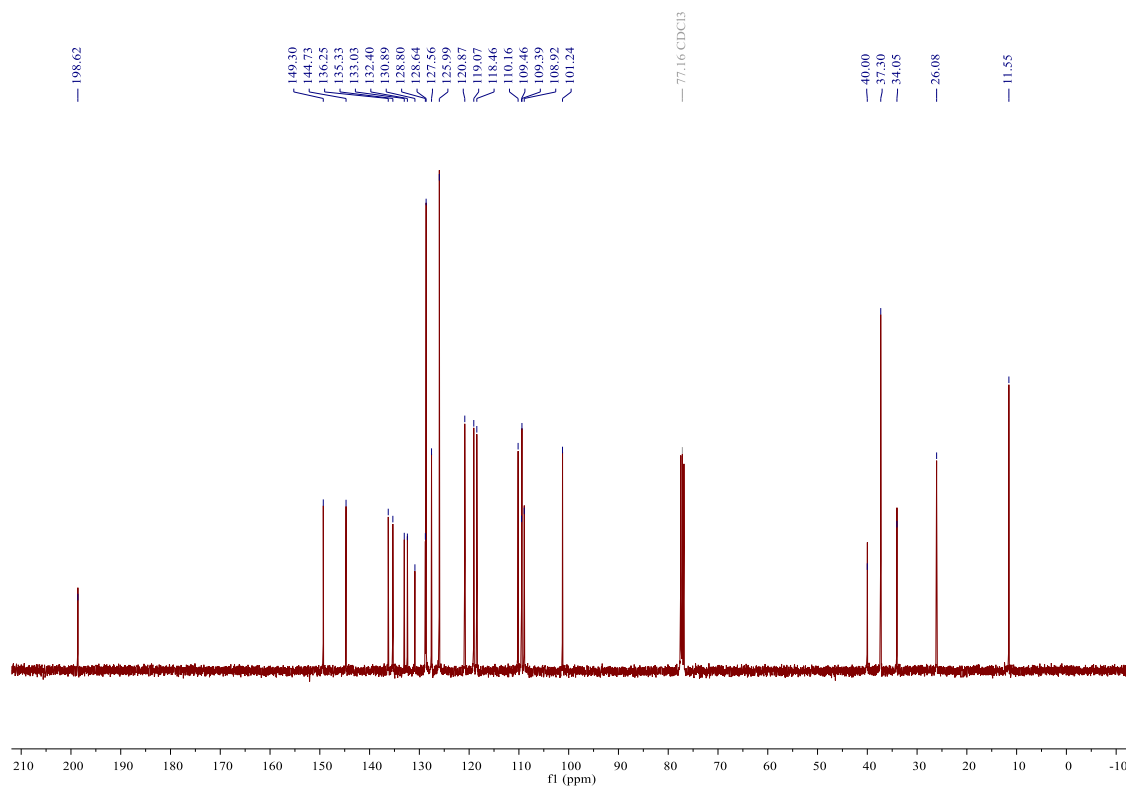
^{19}F NMR spectra of 1m (CDCl_3 , 376 MHz)



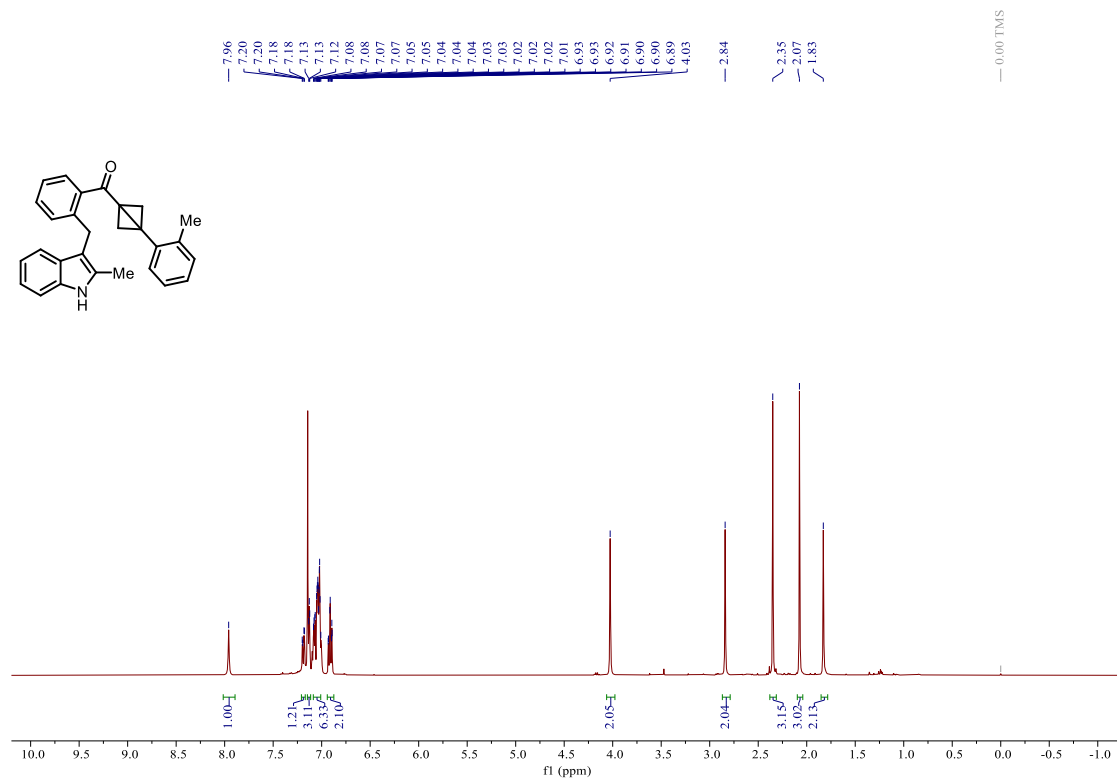
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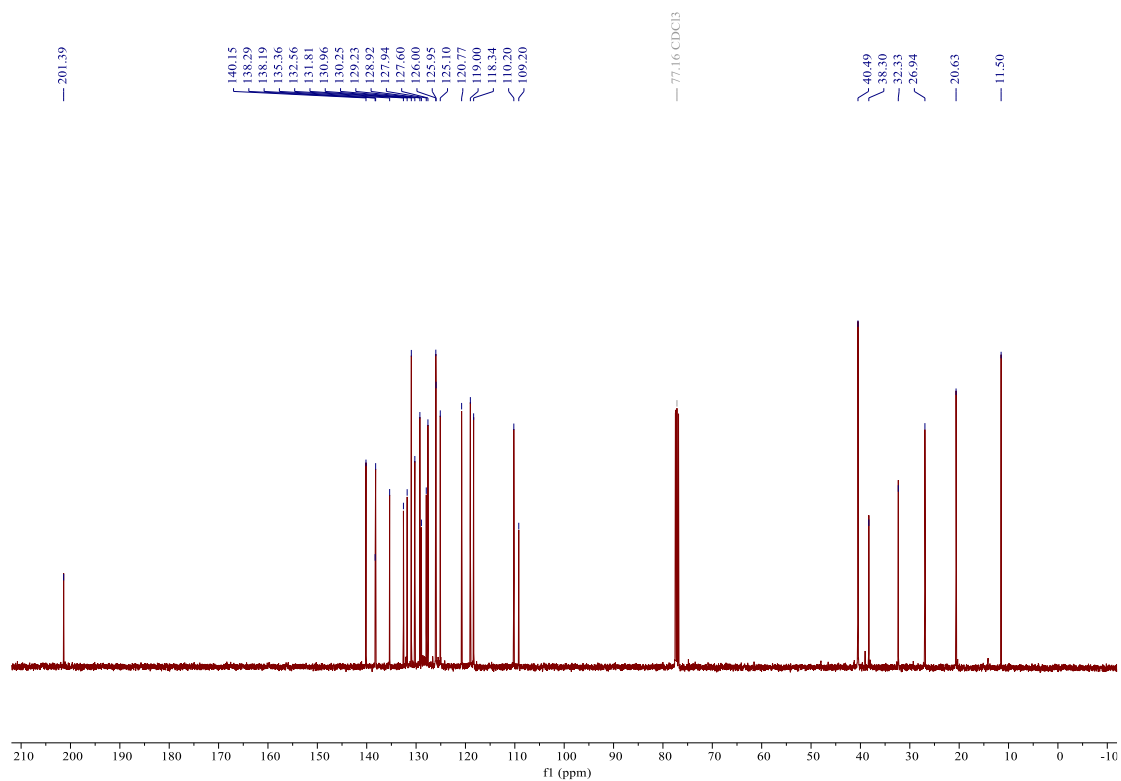
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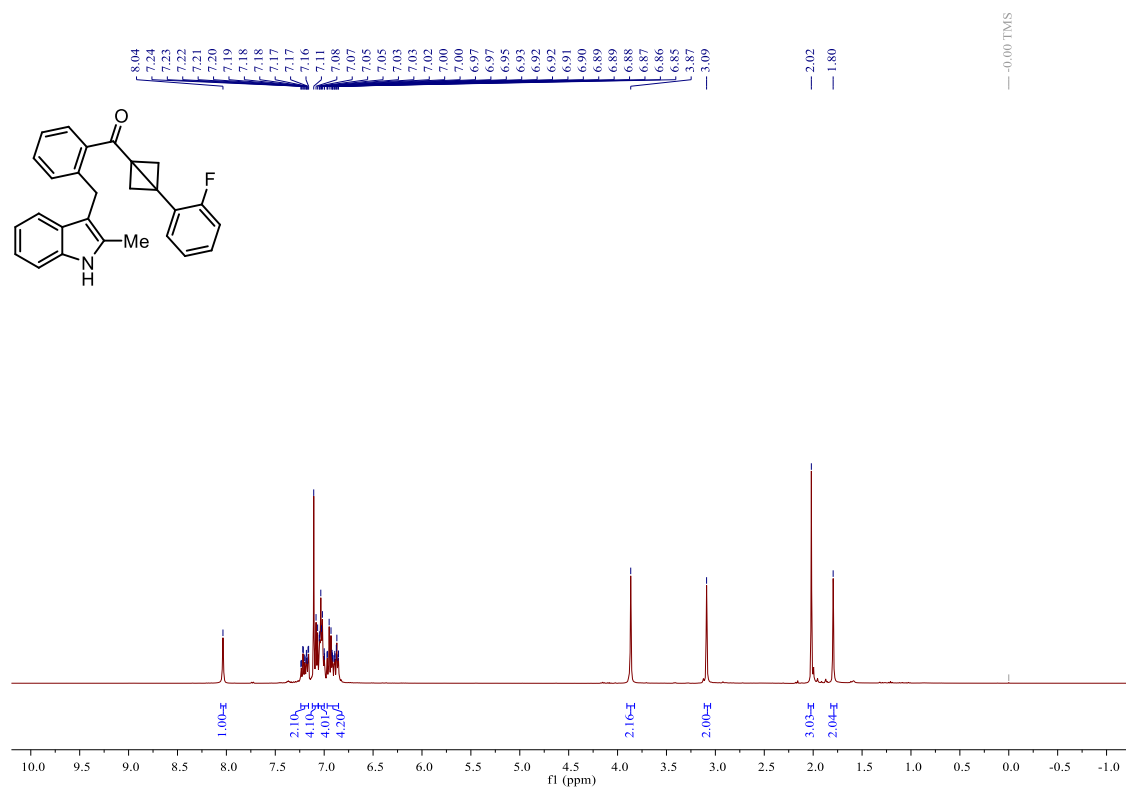
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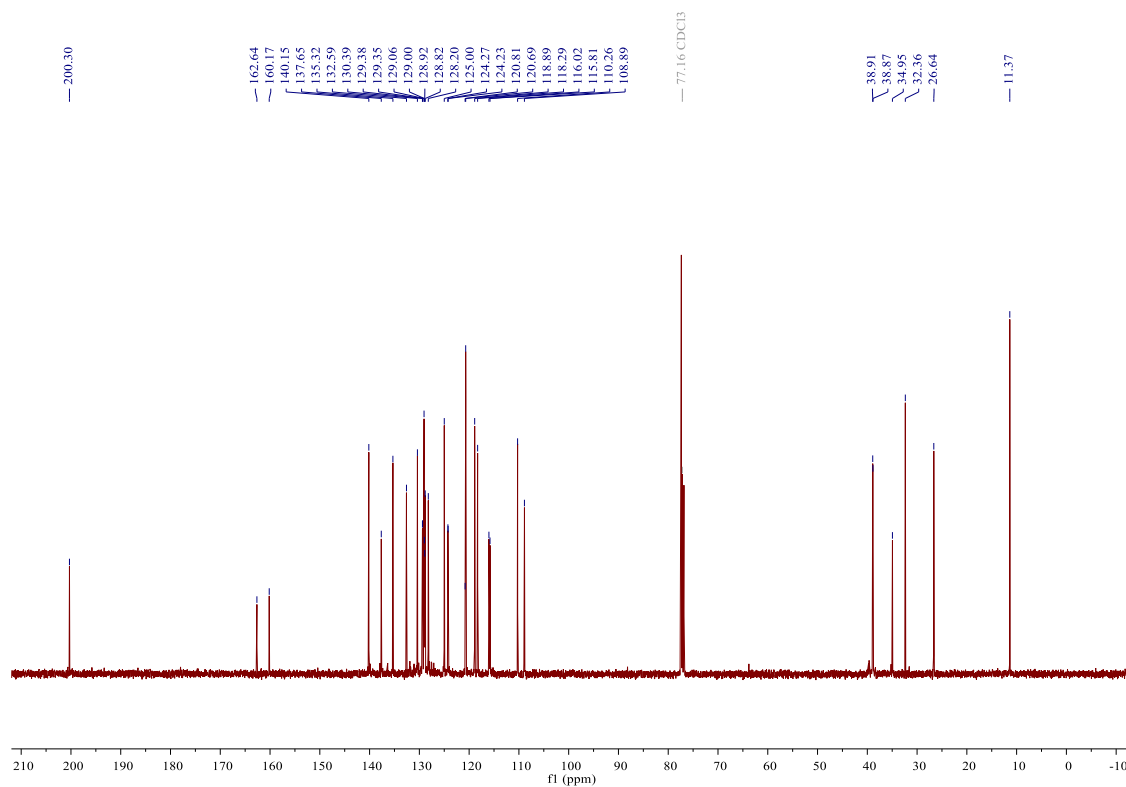
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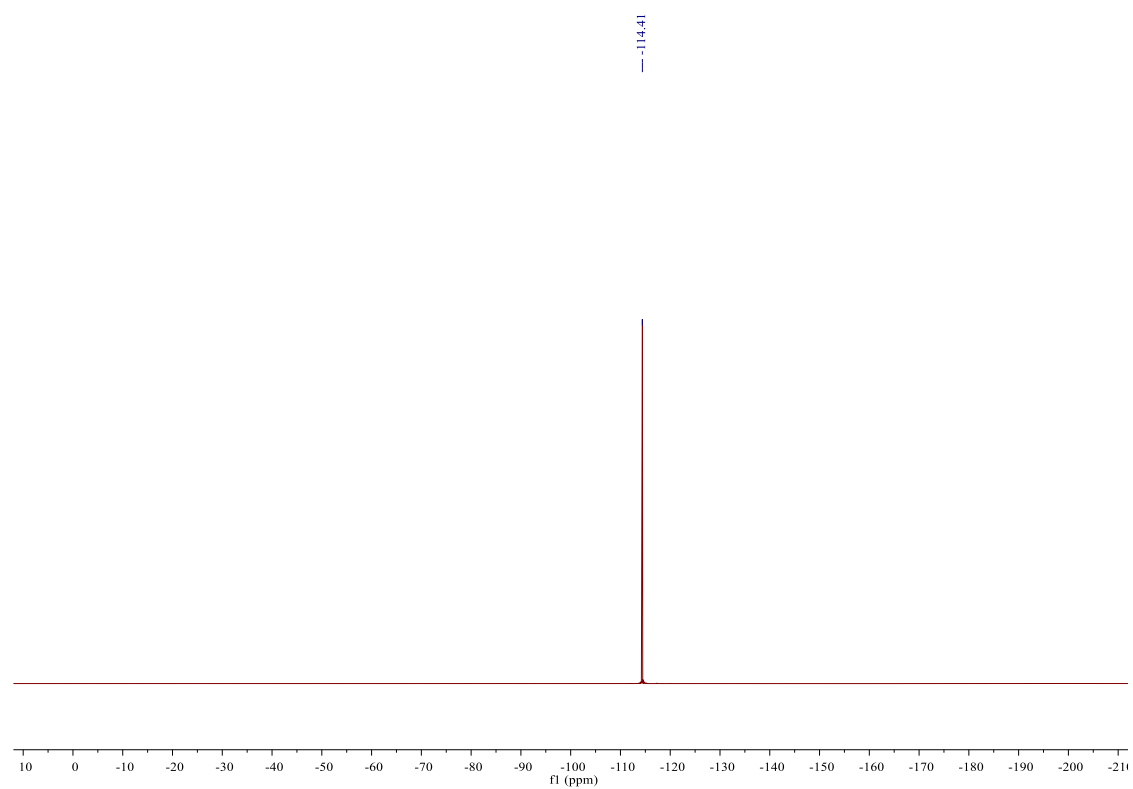
¹H NMR spectra of 1p (CDCl₃, 400 MHz)



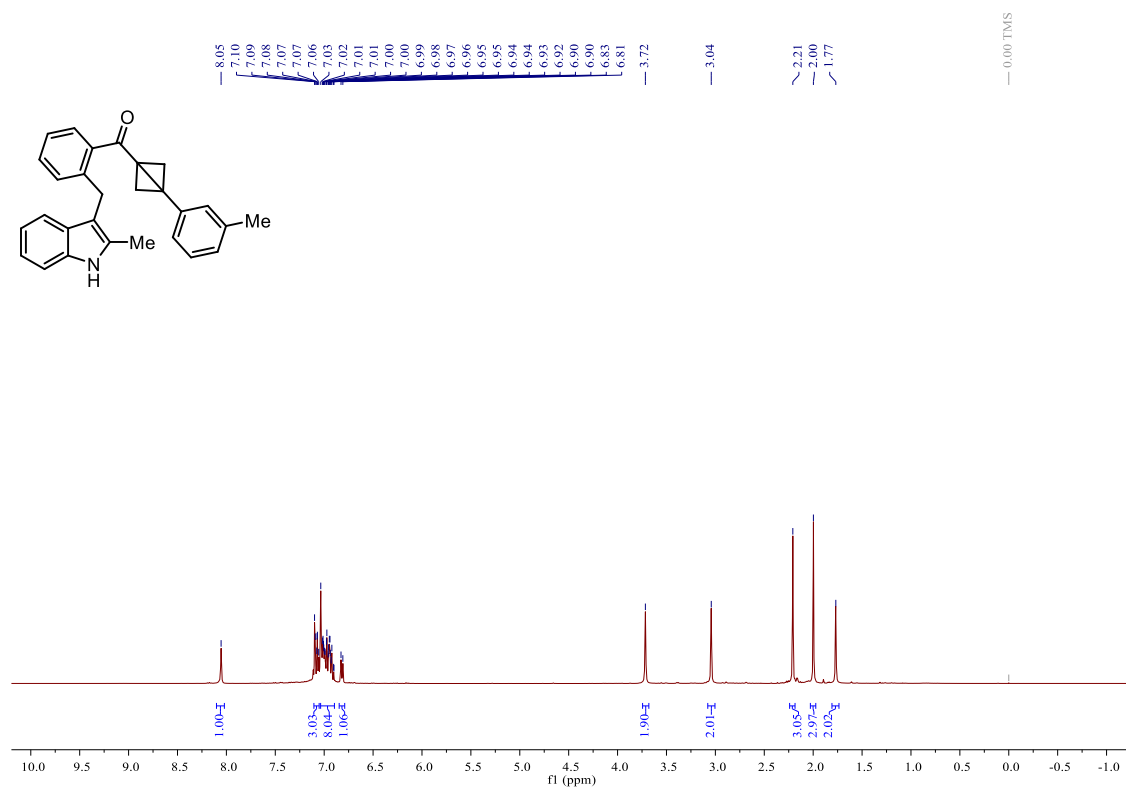
¹³C NMR spectra of 1p (CDCl₃, 101 MHz)



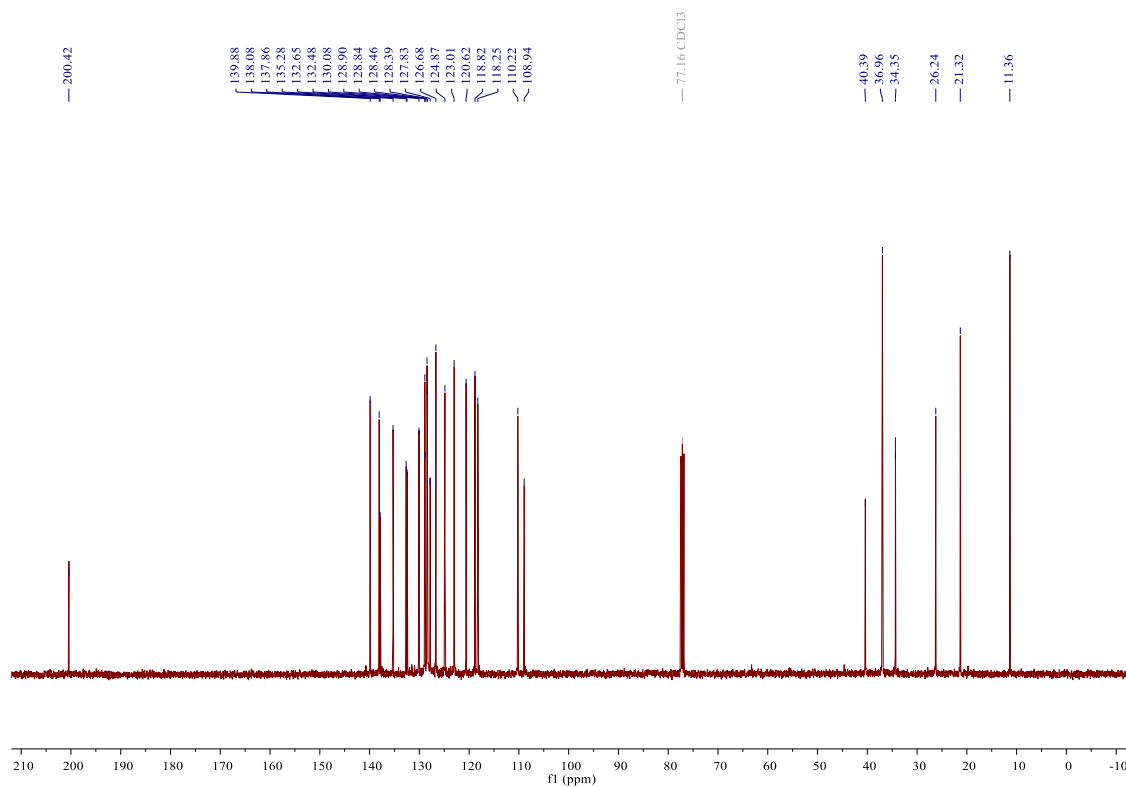
^{19}F NMR spectra of 1p (CDCl_3 , 376 MHz)



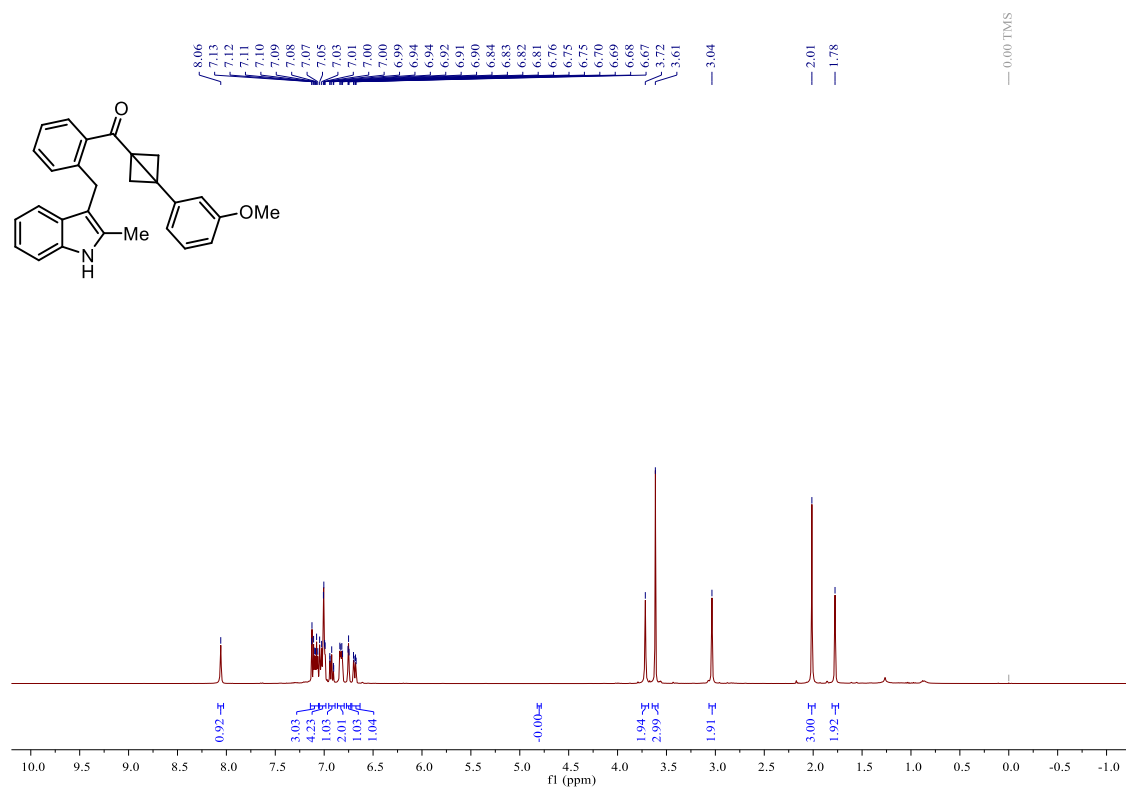
^1H NMR spectra of 1q (CDCl₃, 400 MHz)



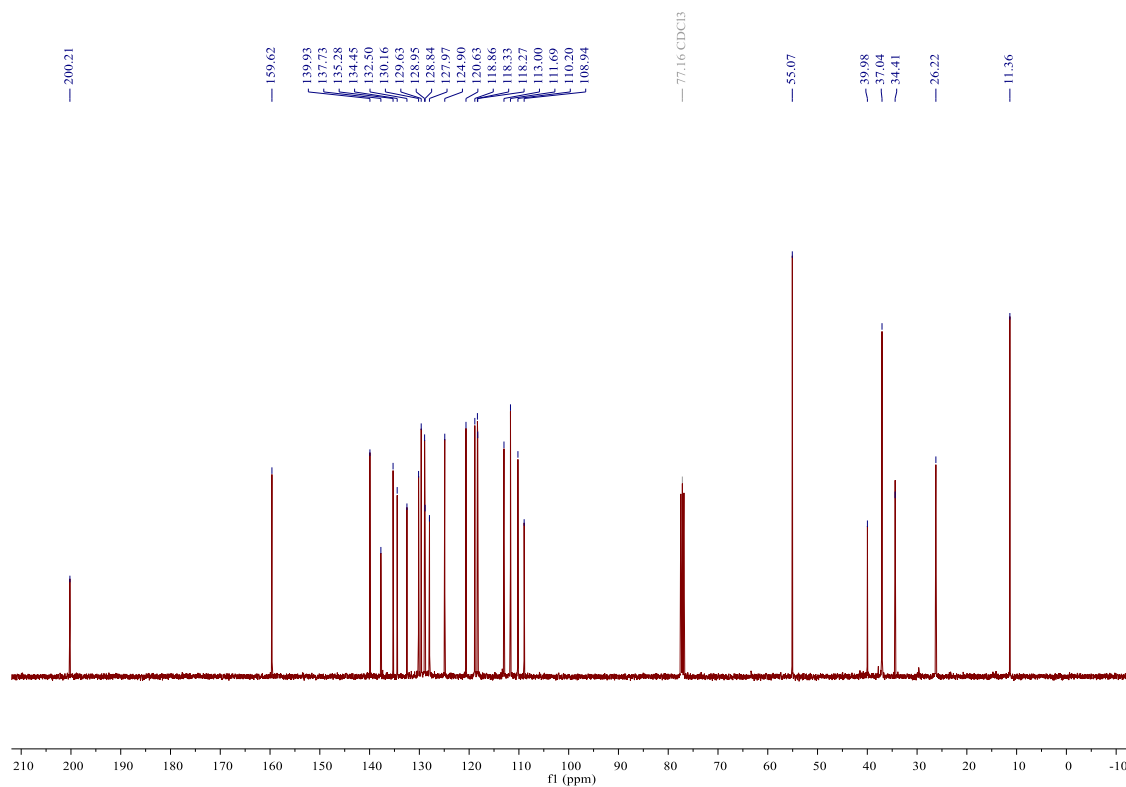
^{13}C NMR spectra of 1q (CDCl₃, 101 MHz)



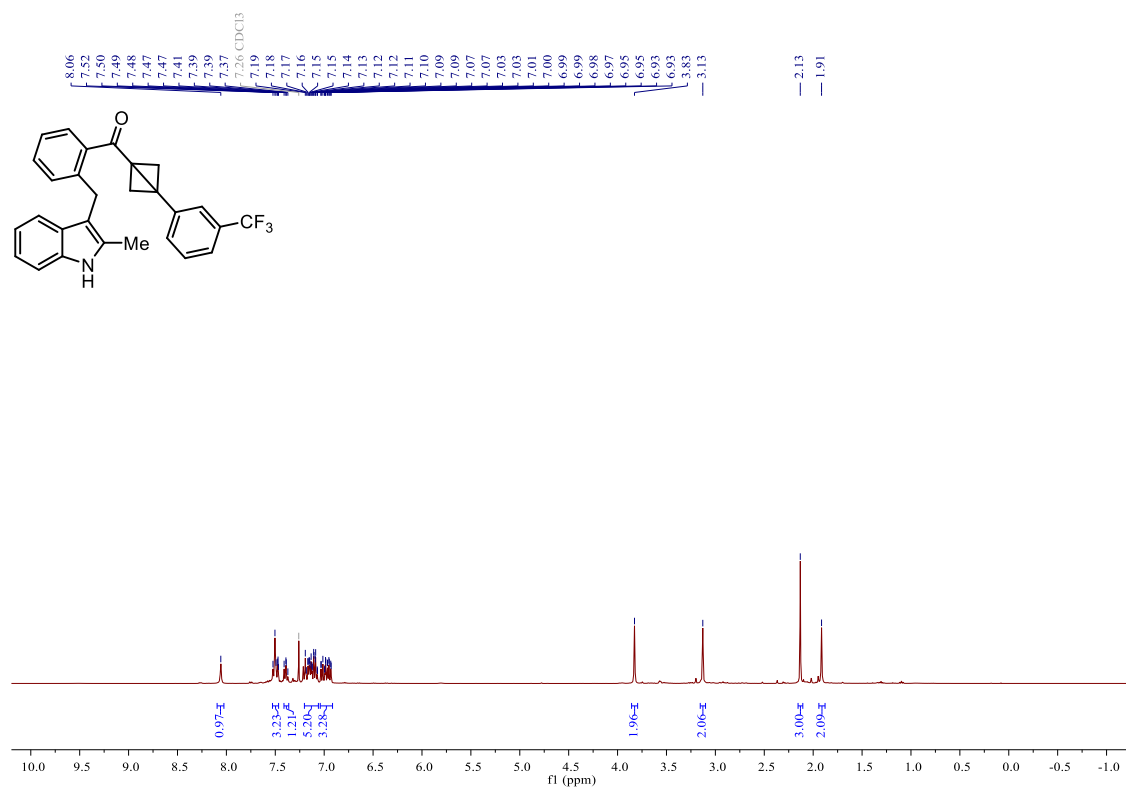
¹H NMR spectra of 1r (CDCl₃, 400 MHz)



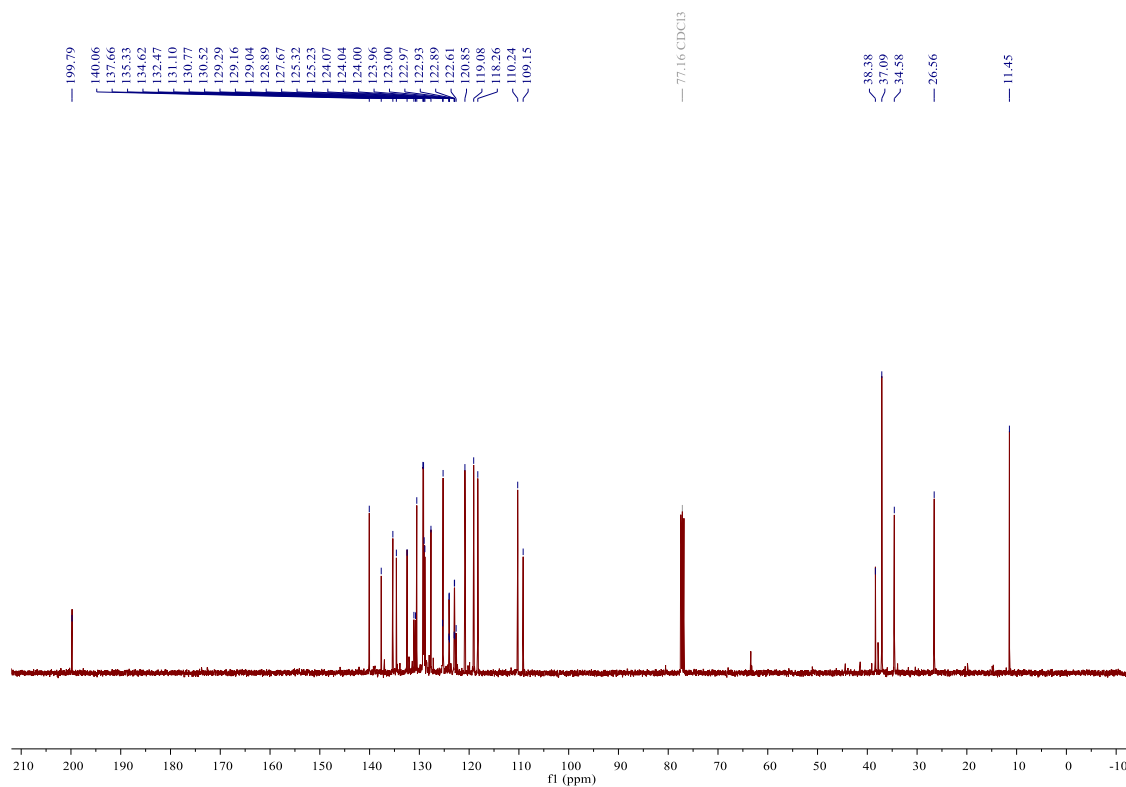
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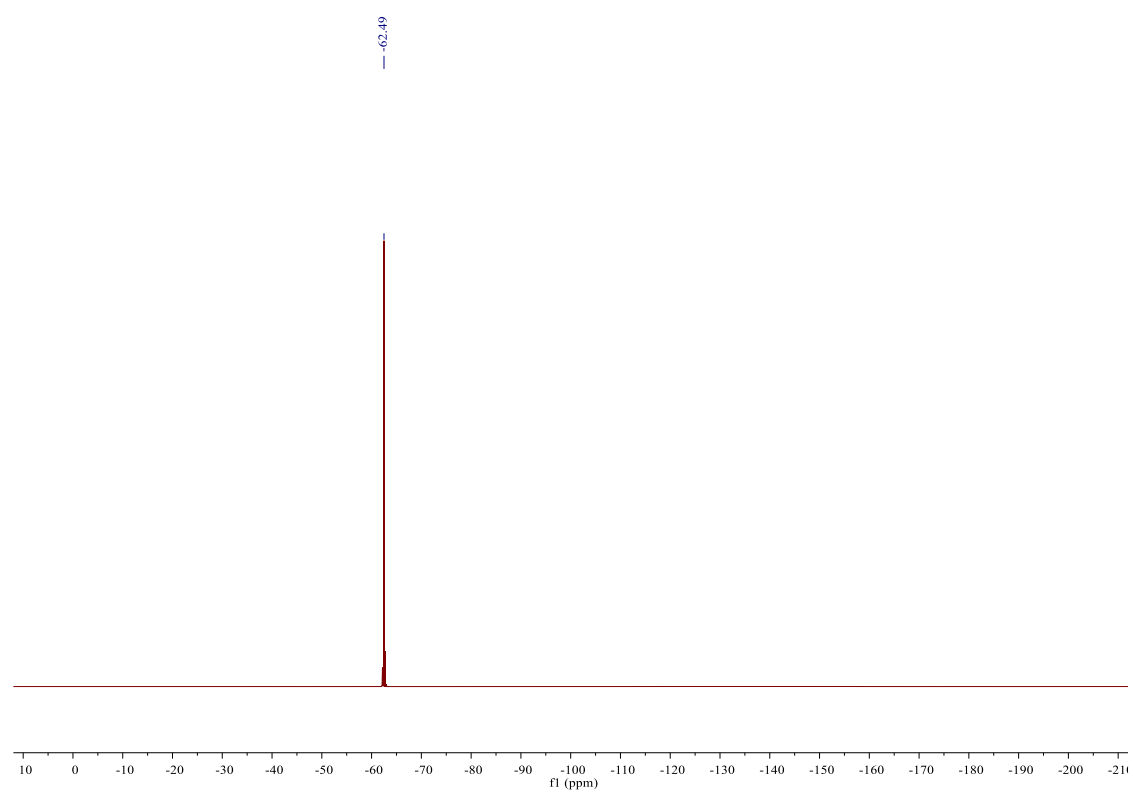
^1H NMR spectra of 1s (CDCl_3 , 400 MHz)



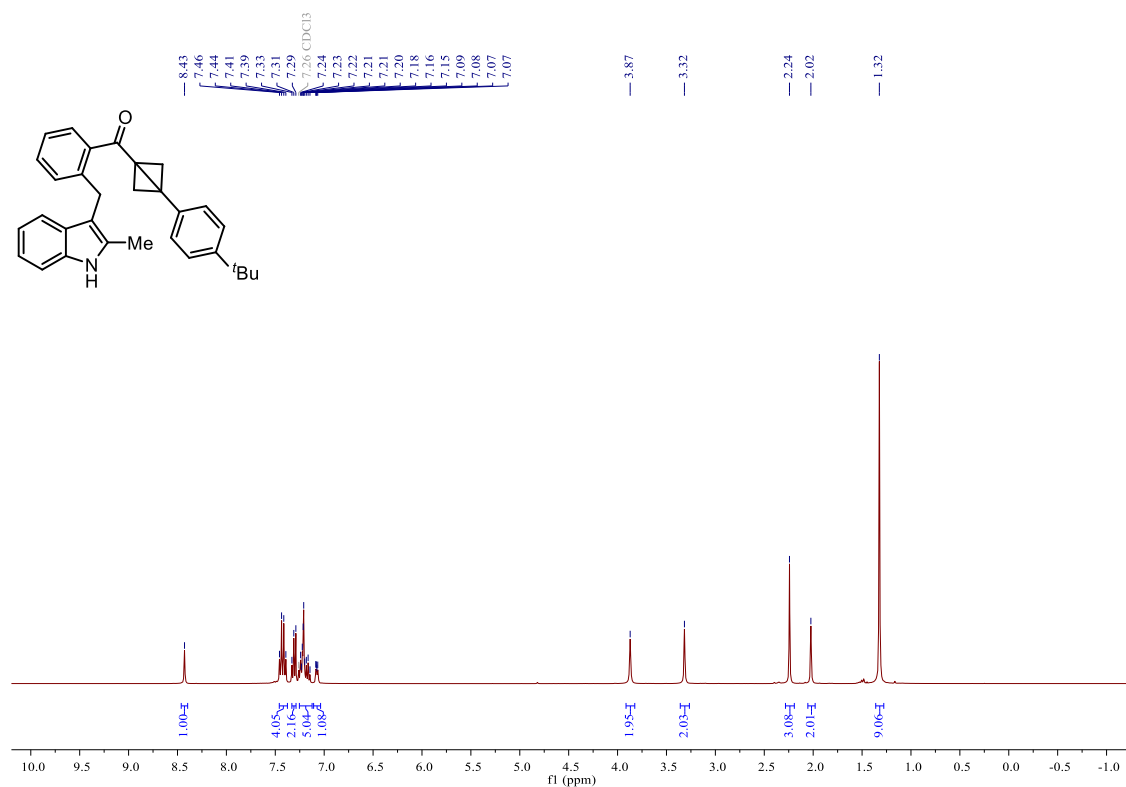
^{13}C NMR spectra of 1s (CDCl_3 , 101 MHz)



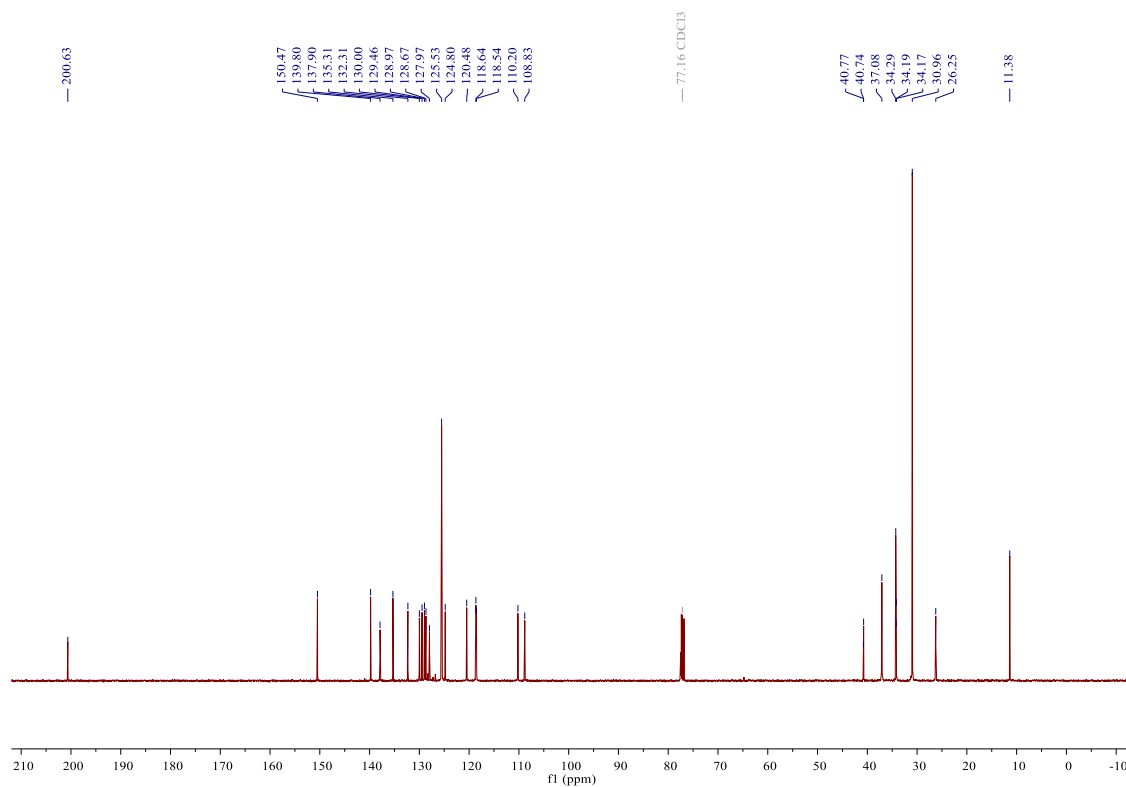
^{19}F NMR spectra of 1s (CDCl₃, 376 MHz)



¹H NMR spectra of 1t (CDCl₃, 400 MHz)



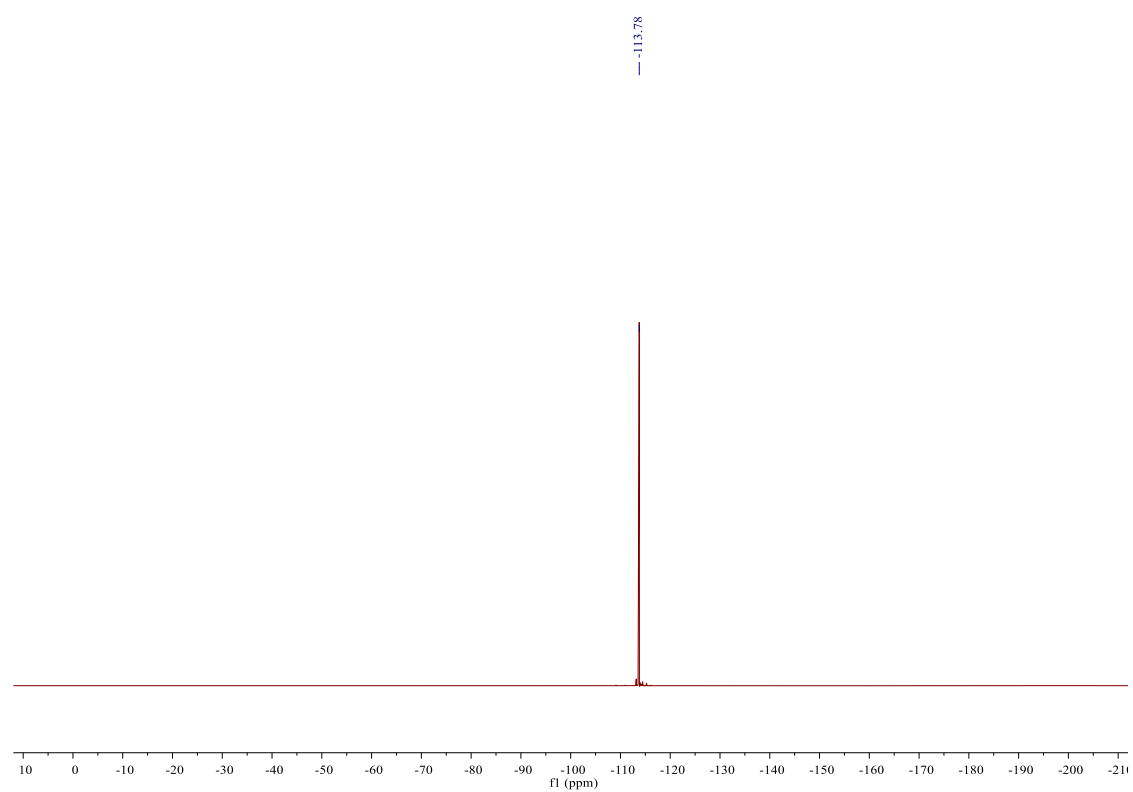
¹³C NMR spectra of 1t (CDCl₃, 101 MHz)



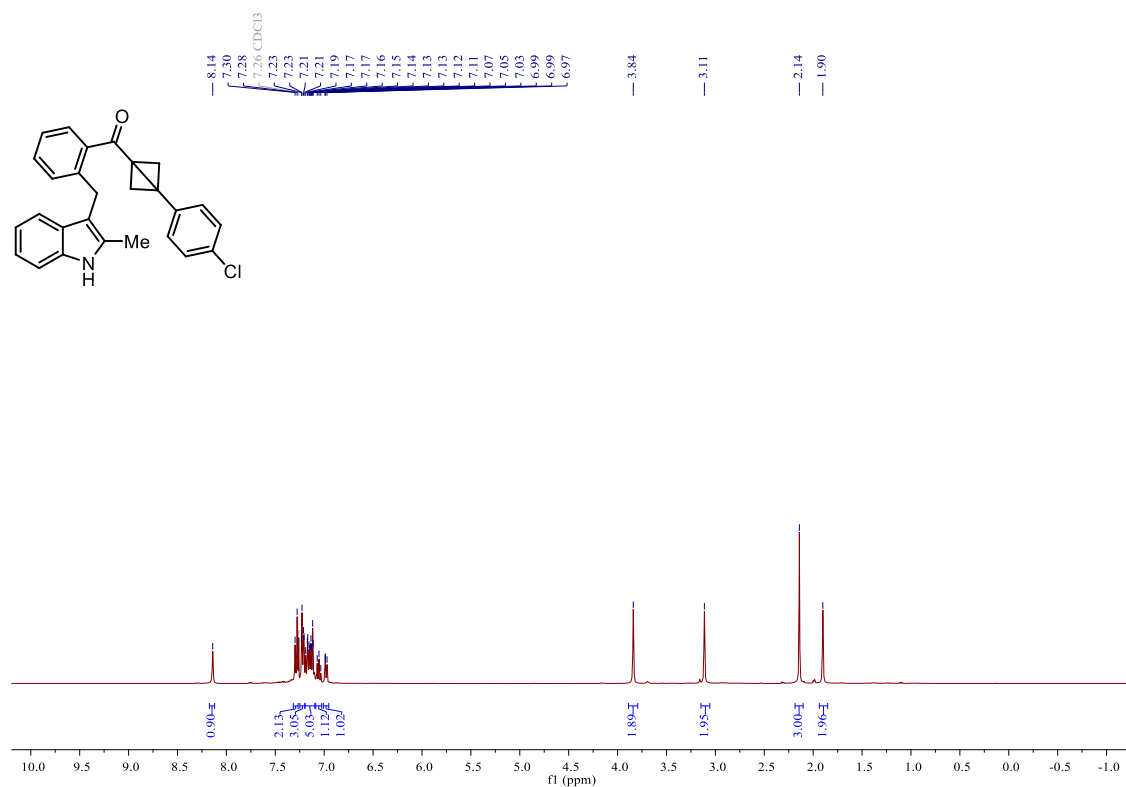
Chemical structure of compound 10 is shown. The ^1H NMR spectrum (CDCl₃) displays peaks corresponding to the structure. The x-axis represents the chemical shift in ppm, ranging from 10.0 to -1.0. The y-axis represents the intensity. The spectrum shows a complex multiplet between 6.8 and 8.0 ppm, a singlet at approximately 3.75 ppm, and a doublet at approximately 2.0 ppm. Integration values are provided below the baseline: 0.94, 2.98, 1.00, 4.23, 5.18, 1.98, 1.98, 3.00, and 2.06. A list of chemical shifts (delta) in ppm is shown at the top: 8.02, 7.17, 7.16, 7.15, 7.14, 7.11, 7.09, 7.06, 7.05, 7.04, 7.03, 7.02, 7.00, 6.99, 6.98, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 3.75, 3.00, 2.03, 1.79, and 0.00 TMS.

13C NMR spectrum of compound 10 in CDCl₃. The x-axis represents chemical shift in ppm, ranging from 210 to -10. The spectrum shows several sharp peaks. A peak at 200.15 ppm is labeled. A cluster of peaks between 100 and 160 ppm is labeled with values: 163.52, 161.07, 139.97, 137.70, 135.30, 135.30, 132.47, 130.31, 129.07, 128.81, 128.78, 127.88, 127.66, 127.58, 125.06, 120.74, 118.94, 118.19, 115.73, 115.52, 110.26, and 108.90. A triplet for the solvent CDCl₃ is centered at 77.16 ppm. Peaks at 39.52, 37.13, 34.01, and 26.45 ppm are labeled. A peak at 11.37 ppm is labeled.

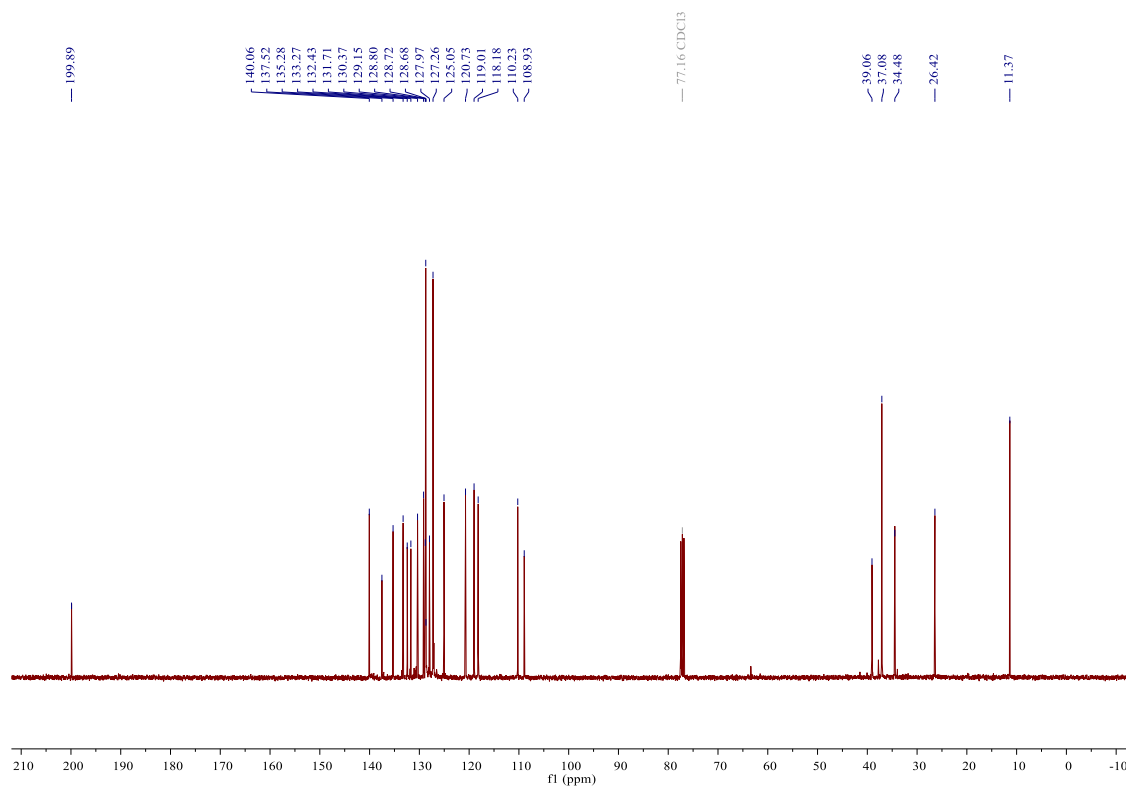
^{19}F NMR spectra of 1u (CDCl_3 , 376 MHz)



^1H NMR spectra of 1v (CDCl_3 , 400 MHz)



^{13}C NMR spectra of 1v (CDCl_3 , 101 MHz)



Chemical structure of compound 10: Cc1c(C(=O)c2ccccc2)c3ccccc3n1C4(CCC4Cc5ccc(Br)cc5)C6=CC=CC=C6

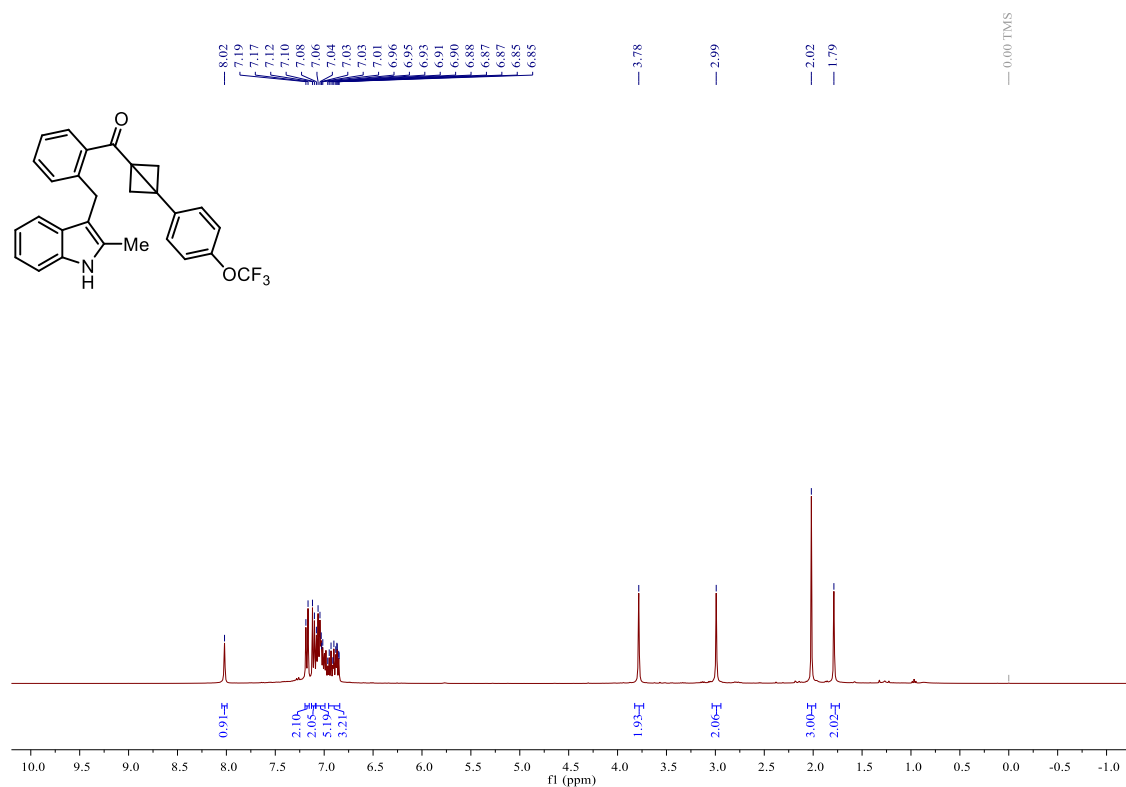
¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from 10.0 to -1.0. The spectrum shows several peaks, with integration values provided below the baseline.

Integration values (from left to right): 1.00, 2.13, 2.18, 7.02, 1.07, 1.98, 1.94, 2.98, 1.95.

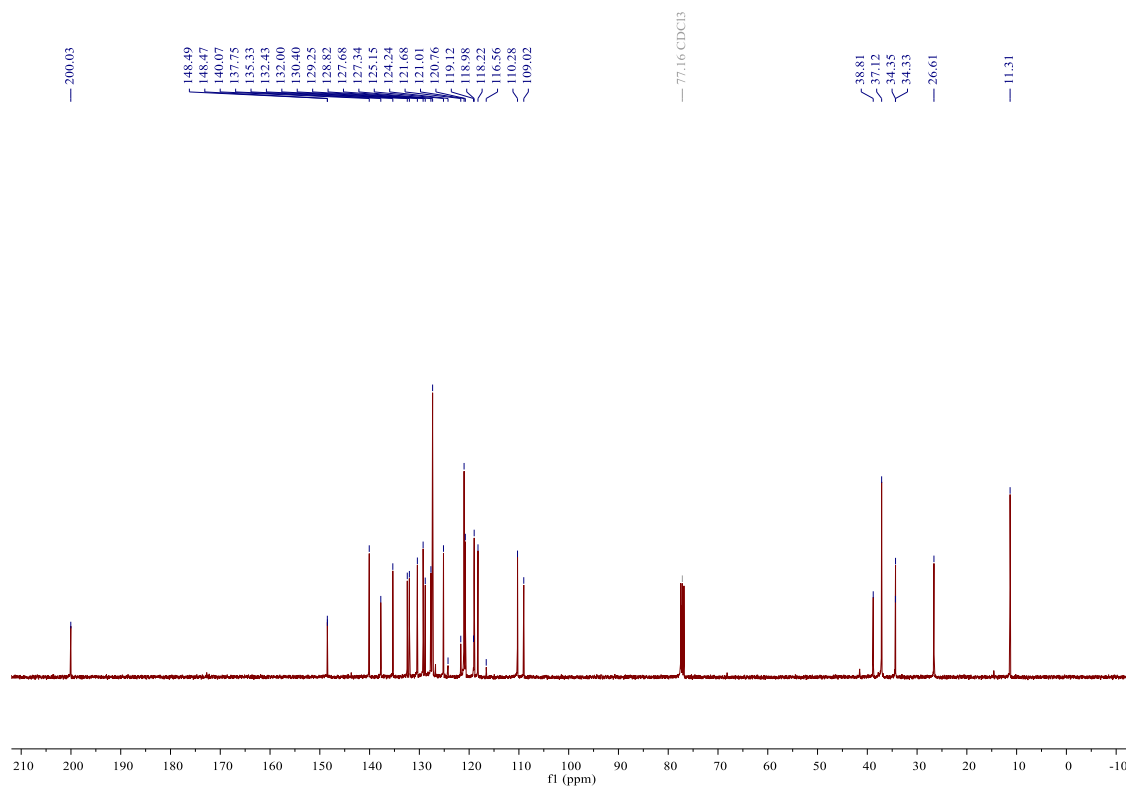
Chemical shift values (ppm) labeled above the peaks: 8.06, 7.28, 7.26, 7.08, 7.07, 7.06, 7.05, 7.02, 7.02, 7.01, 6.99, 6.97, 6.95, 6.93, 6.91, 6.86, 6.85, 6.84, 3.71, 2.96, 1.98, 1.73, 0.00 TMS.

Chemical shifts (ppm): 199.84, 139.99, 137.36, 135.19, 132.39, 132.09, 131.52, 130.30, 129.09, 128.69, 127.90, 127.46, 124.97, 123.77, 120.60, 118.92, 118.07, 110.23, 108.73, 77.16 (CDCl₃), 39.06, 36.95, 34.51, 26.32, 11.28.

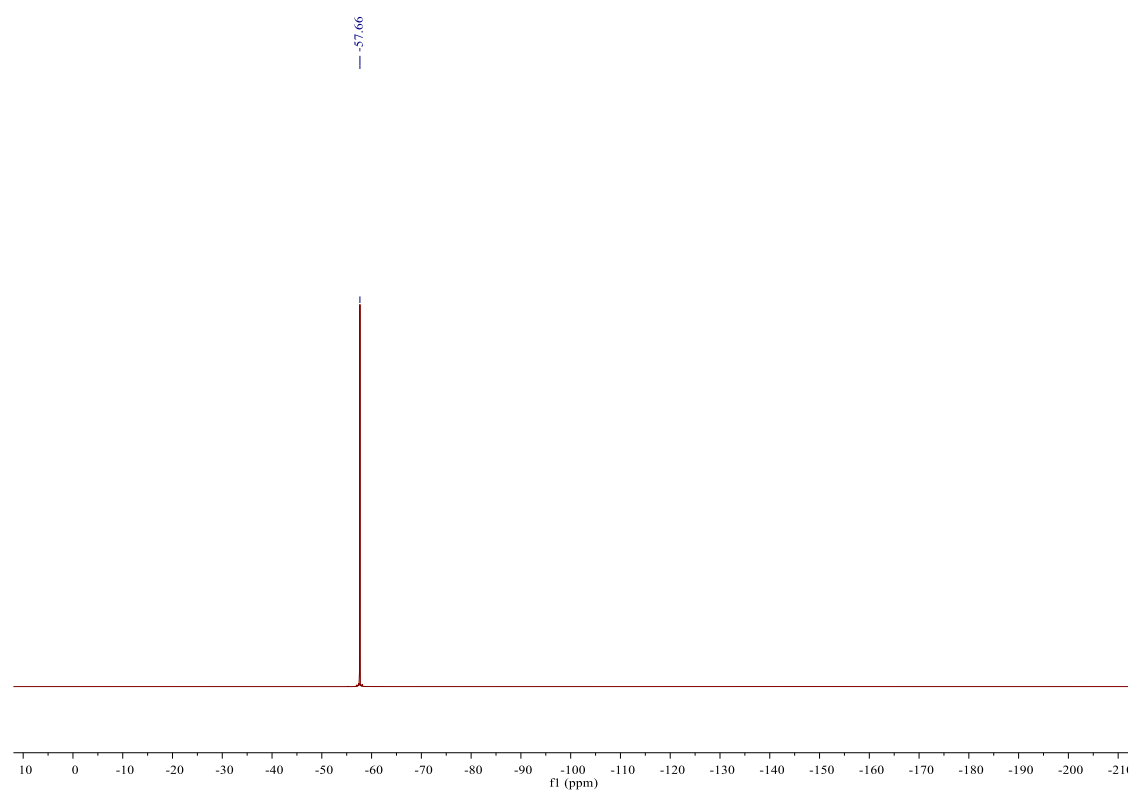
¹H NMR spectra of 1x (CDCl₃, 400 MHz)



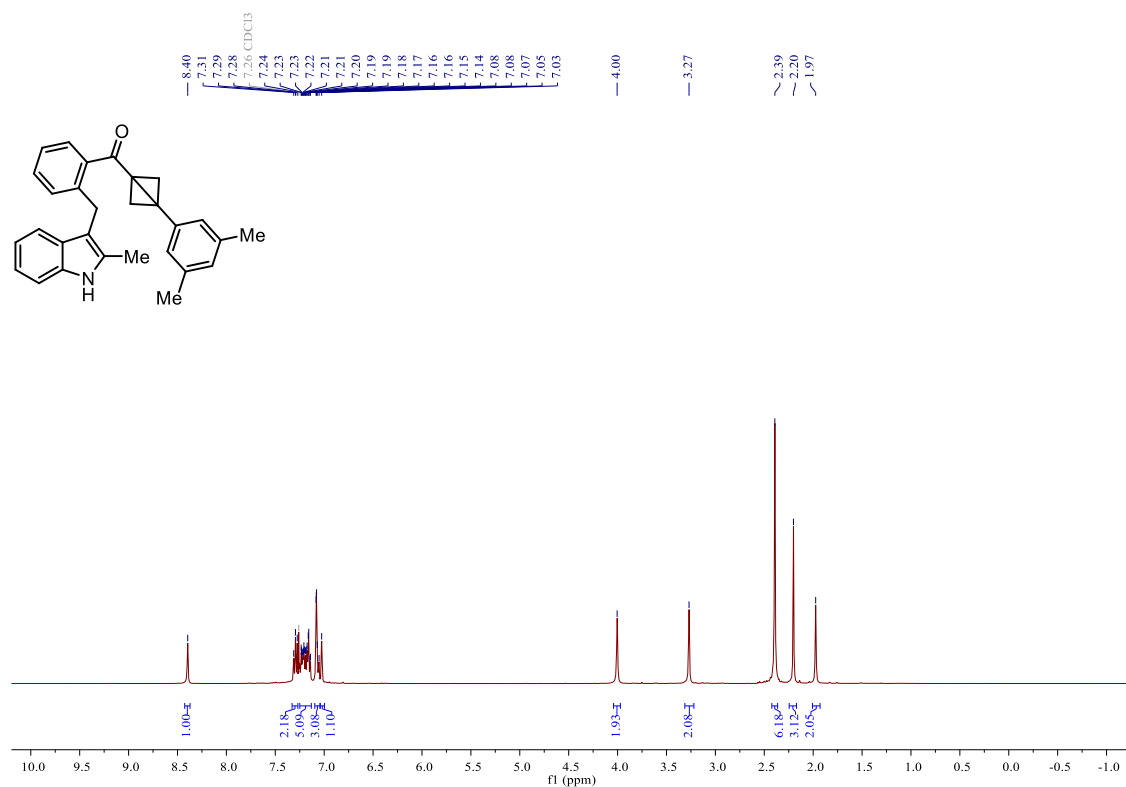
¹³C NMR spectra of 1x (CDCl₃, 101 MHz)



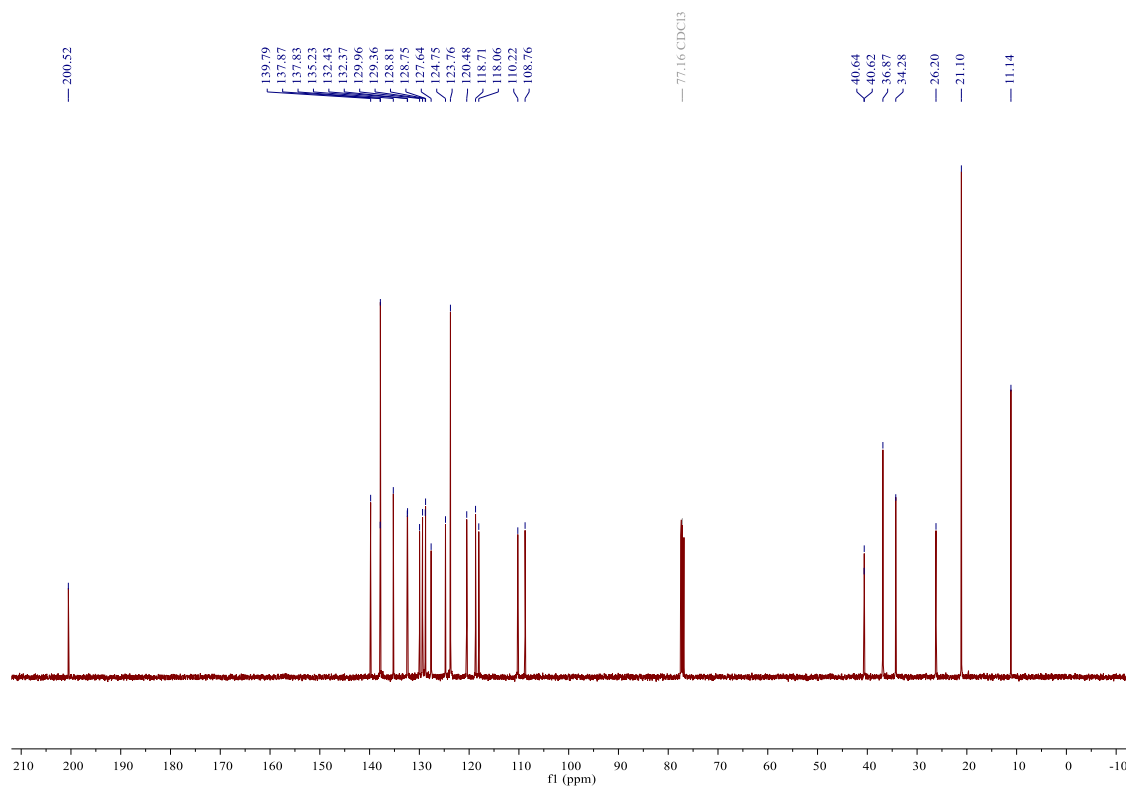
^{19}F NMR spectra of 1x (CDCl_3 , 376 MHz)



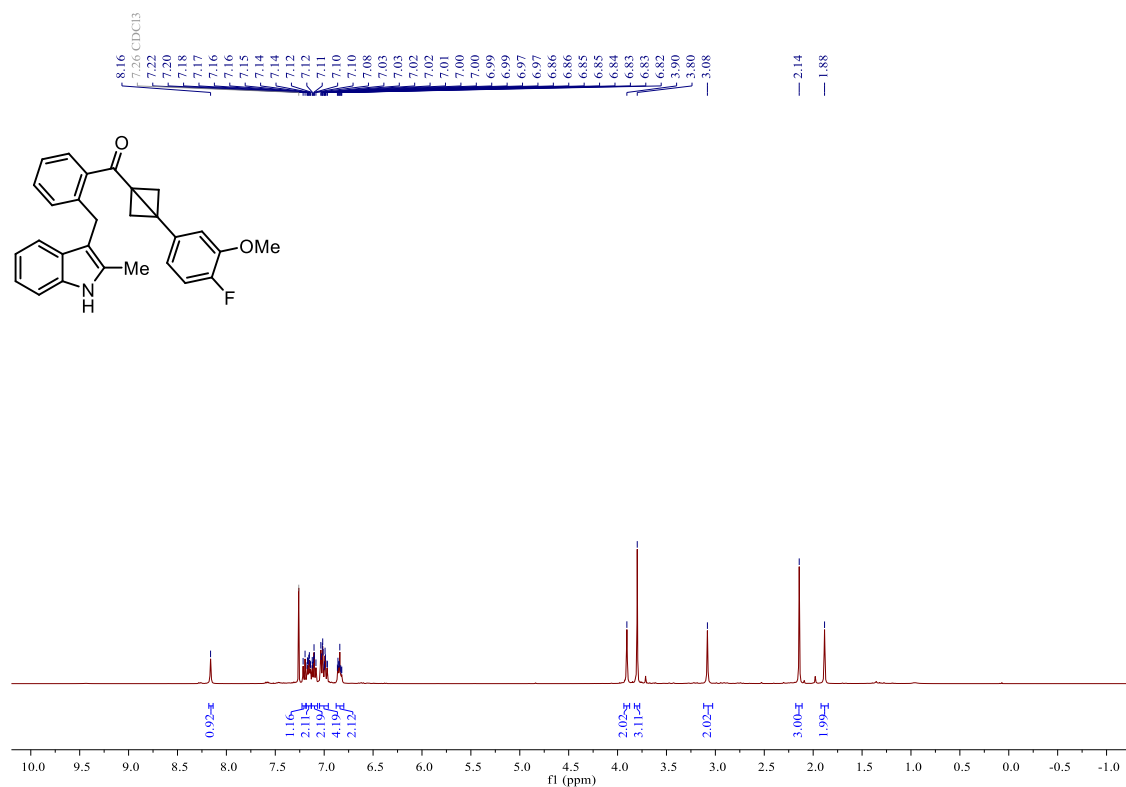
^1H NMR spectra of 1y (CDCl_3 , 400 MHz)



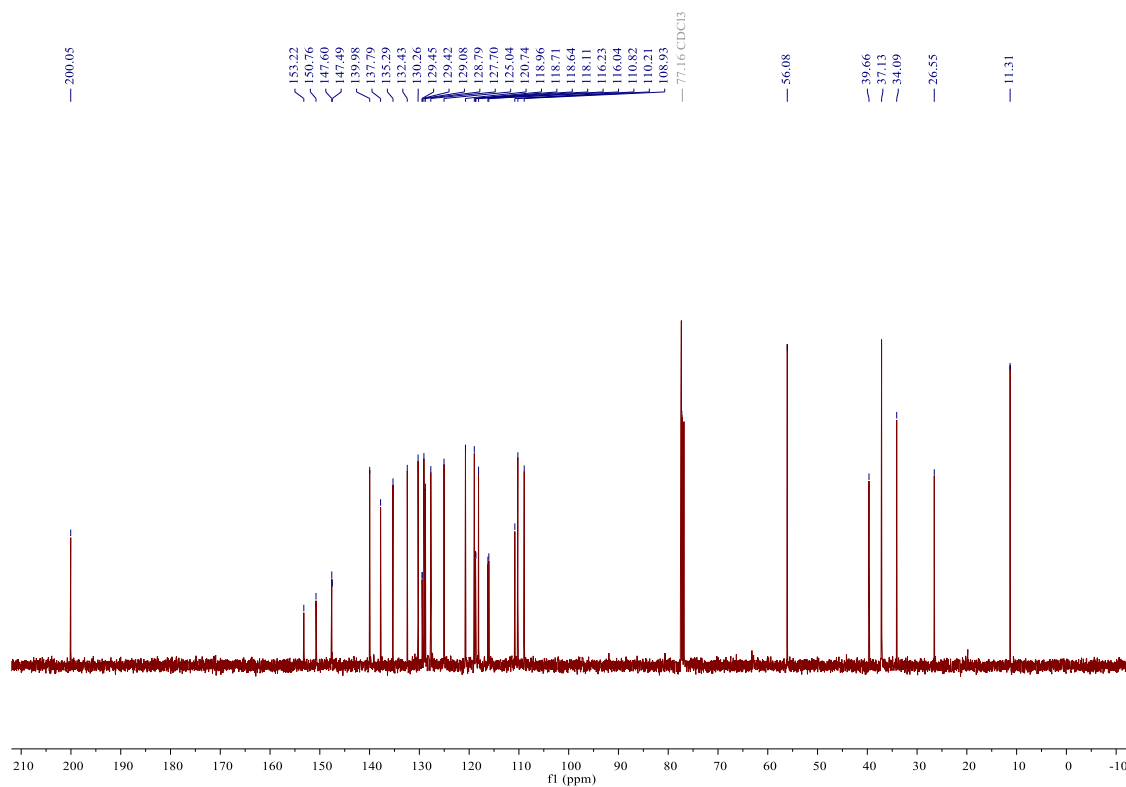
^{13}C NMR spectra of 1y (CDCl_3 , 101 MHz)



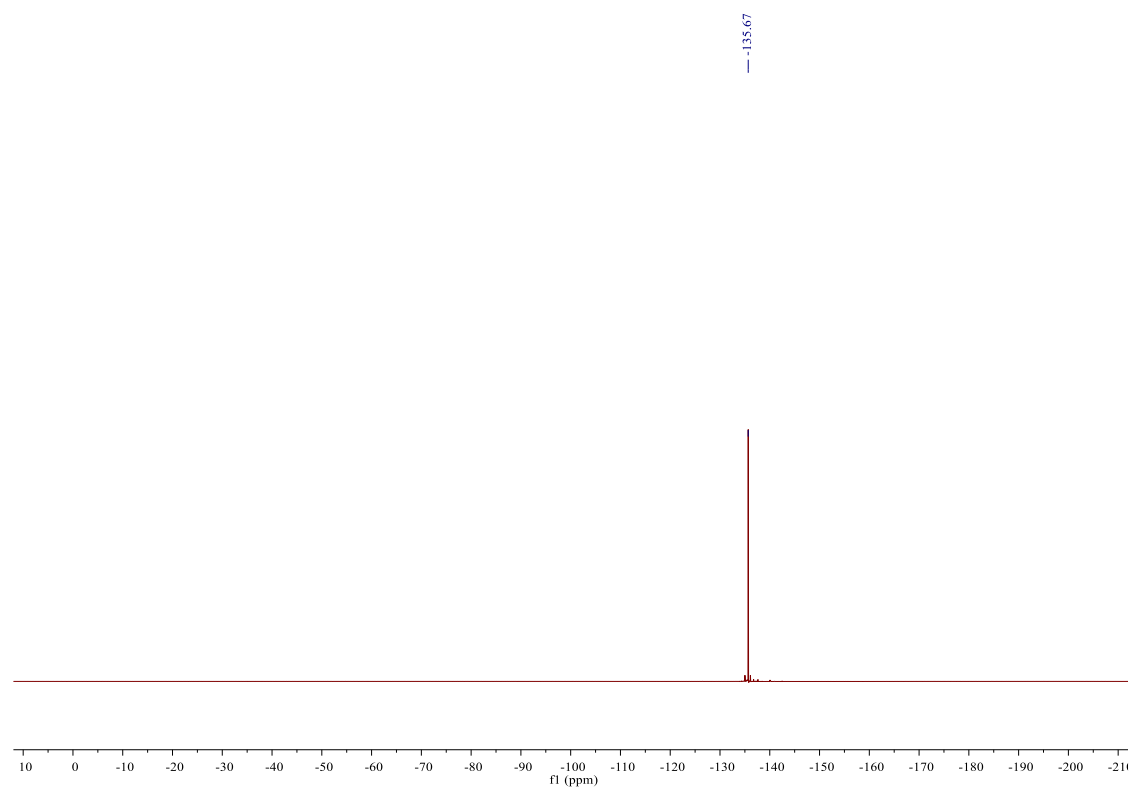
¹H NMR spectra of 1z (CDCl₃, 400 MHz)



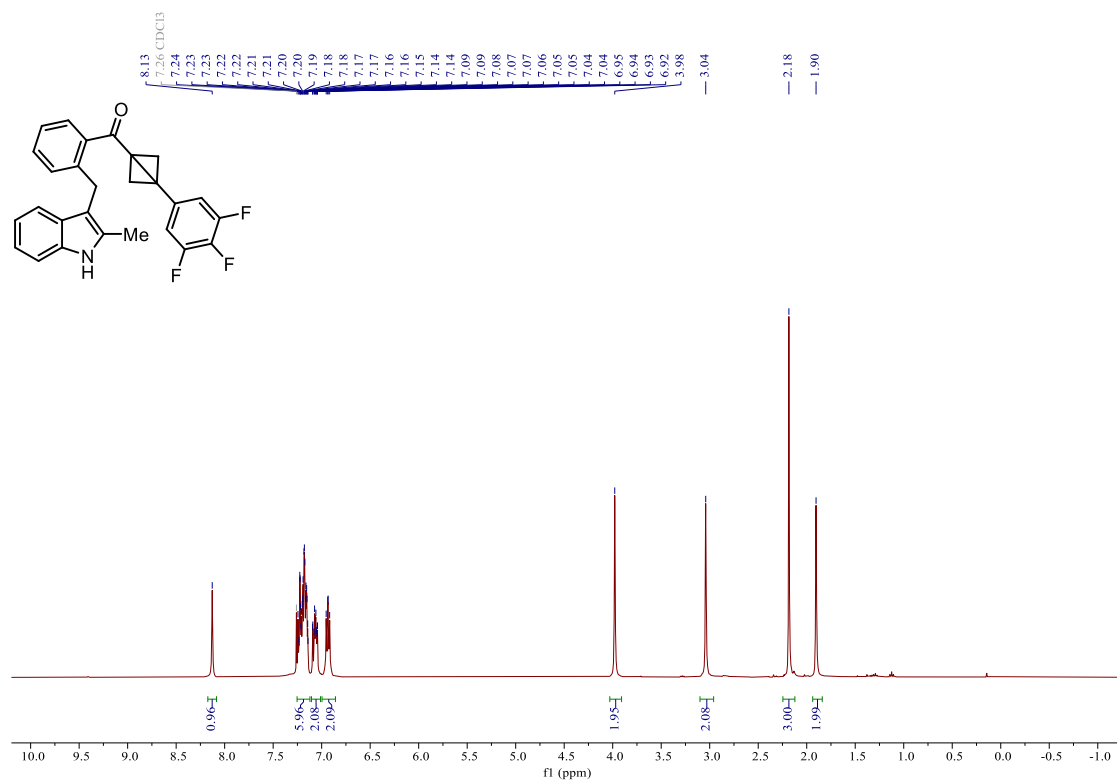
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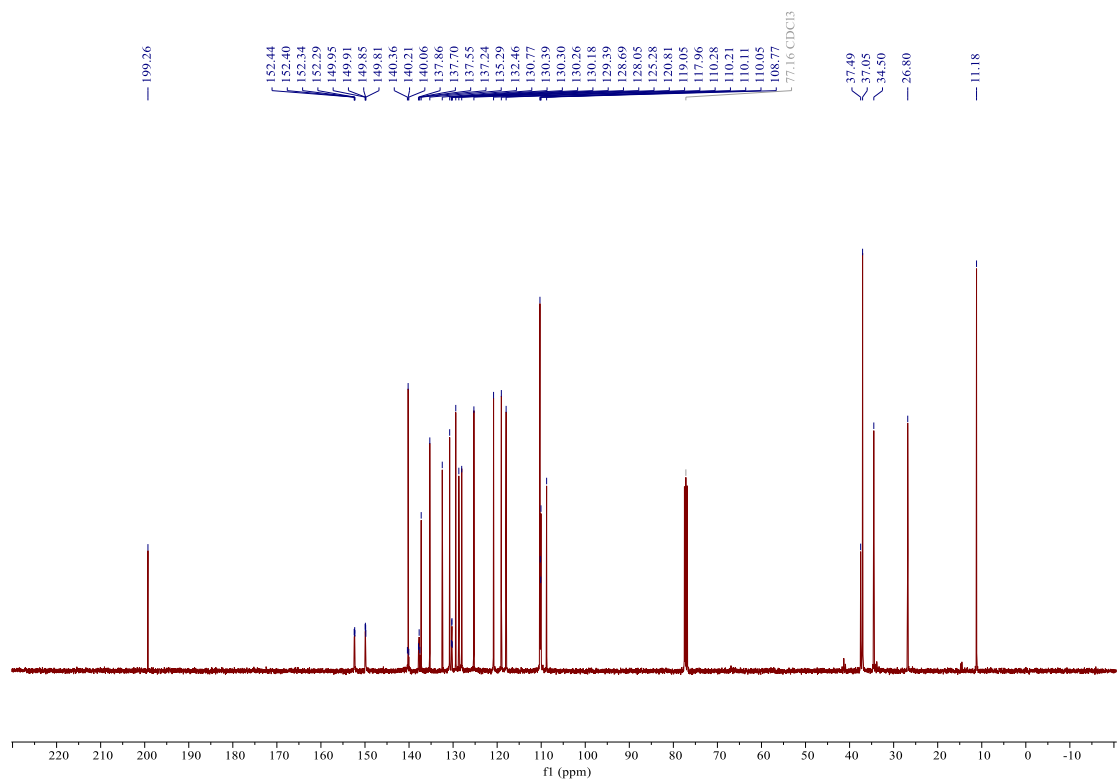
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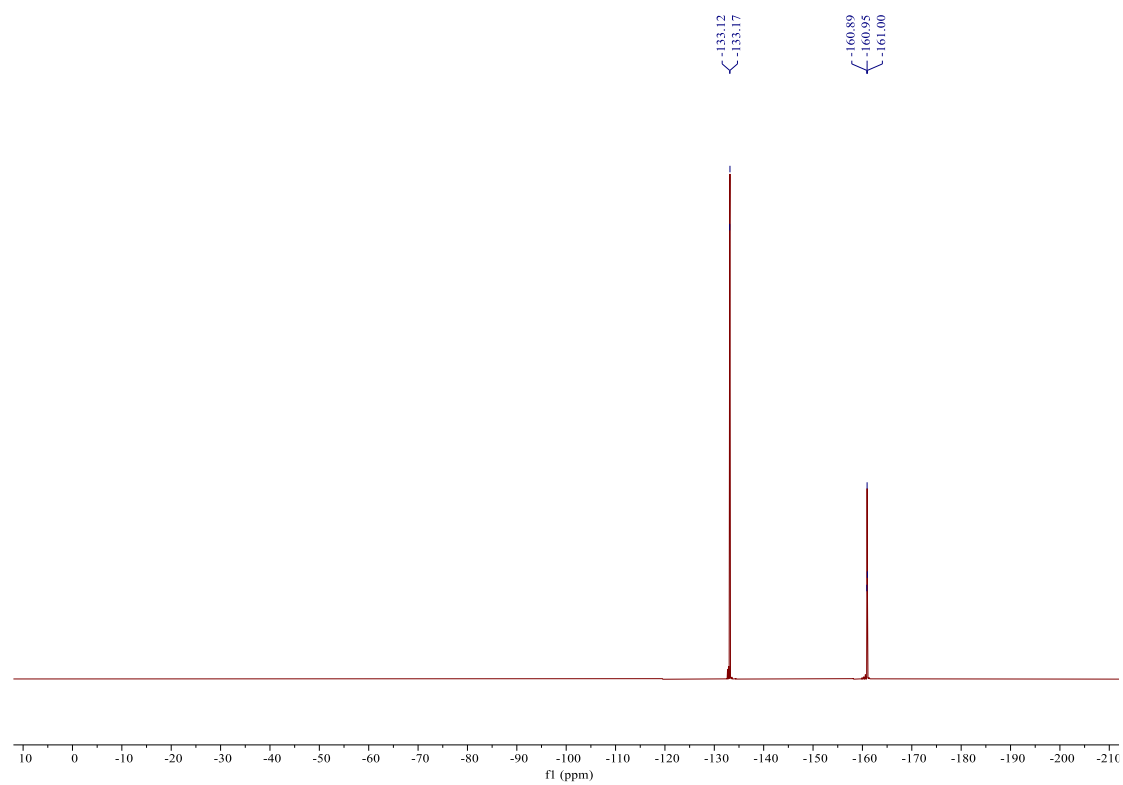
¹H NMR spectra of 1aa (CDCl₃, 400 MHz)



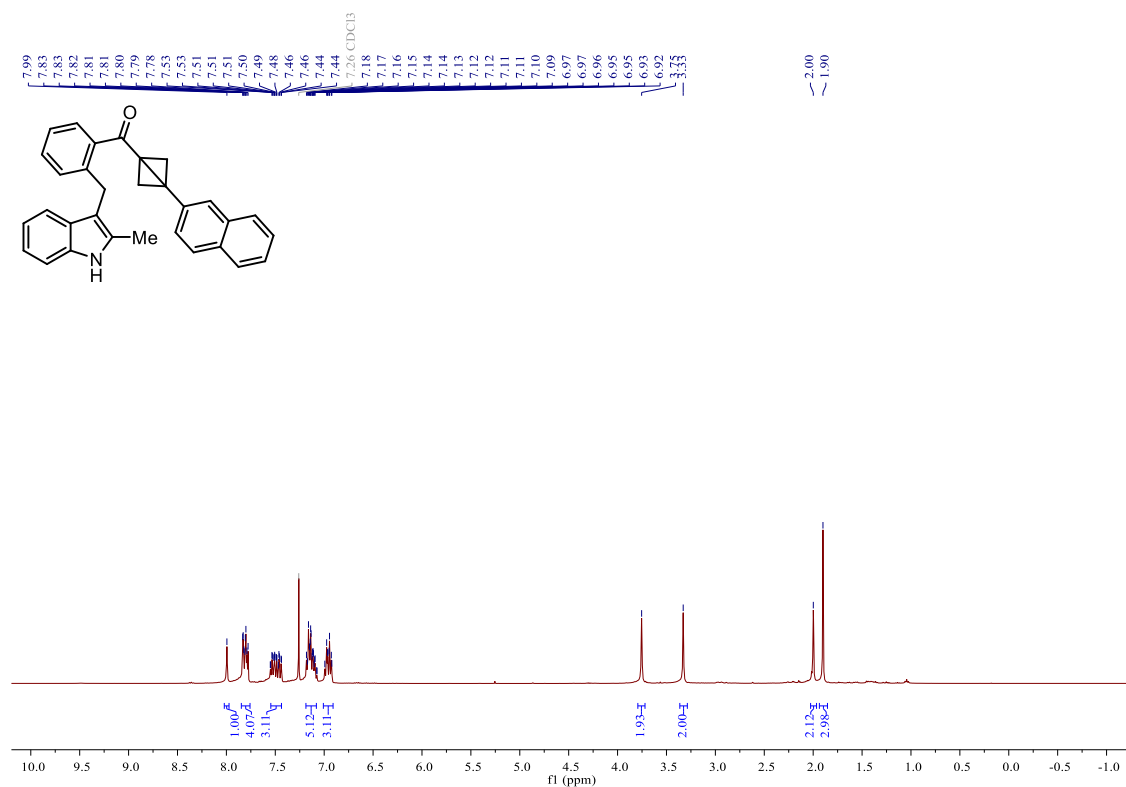
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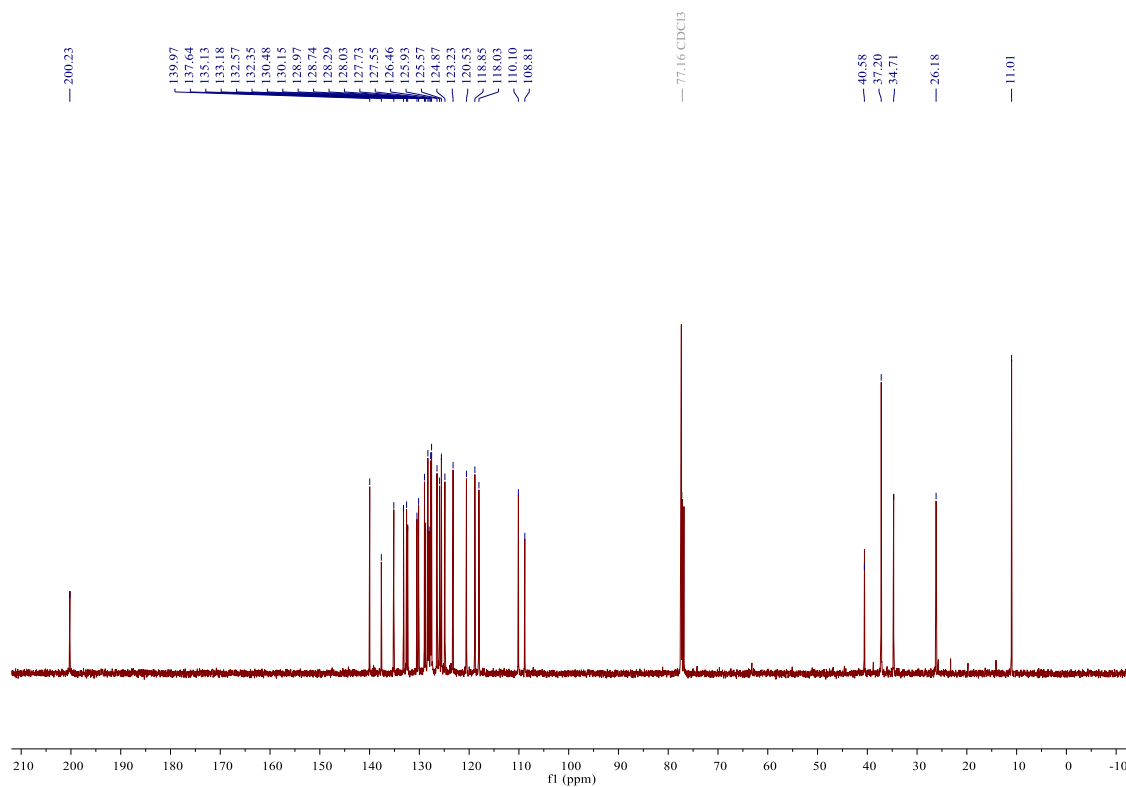
^{19}F NMR spectra of 1aa (CDCl_3 , 376 MHz)



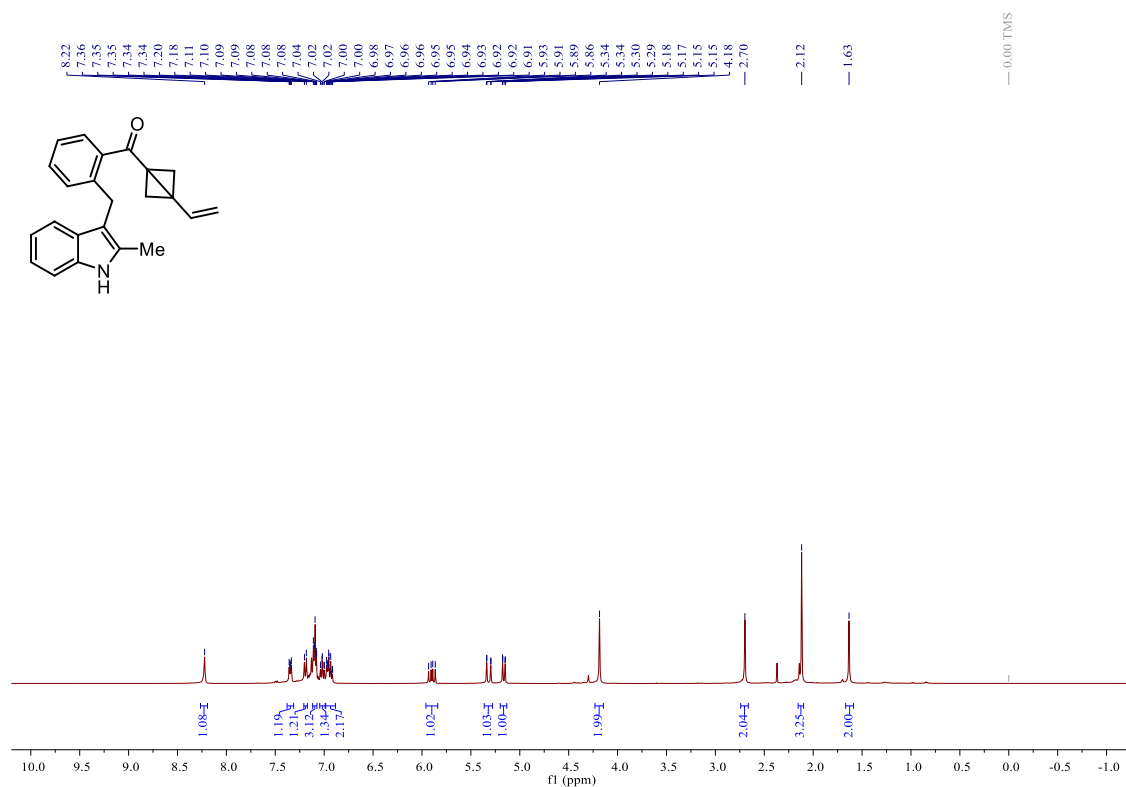
¹H NMR spectra of 1ab (CDCl₃, 400 MHz)



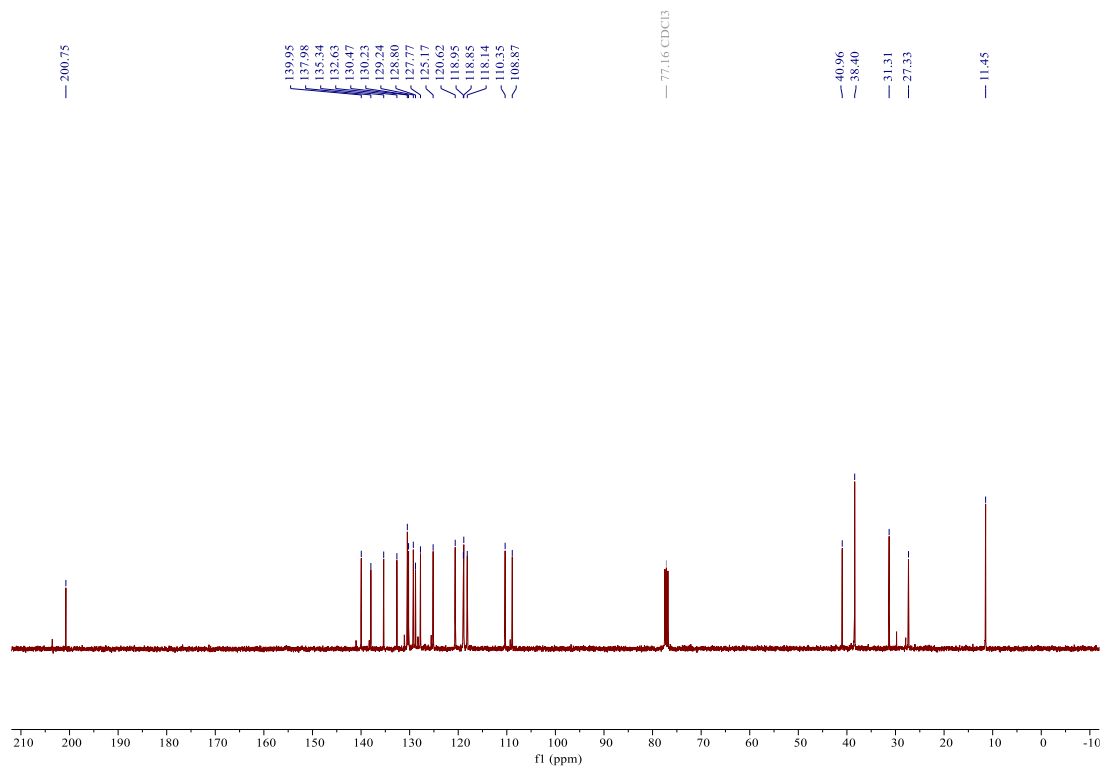
¹³C NMR spectra of 1ab (CDCl₃, 101 MHz)



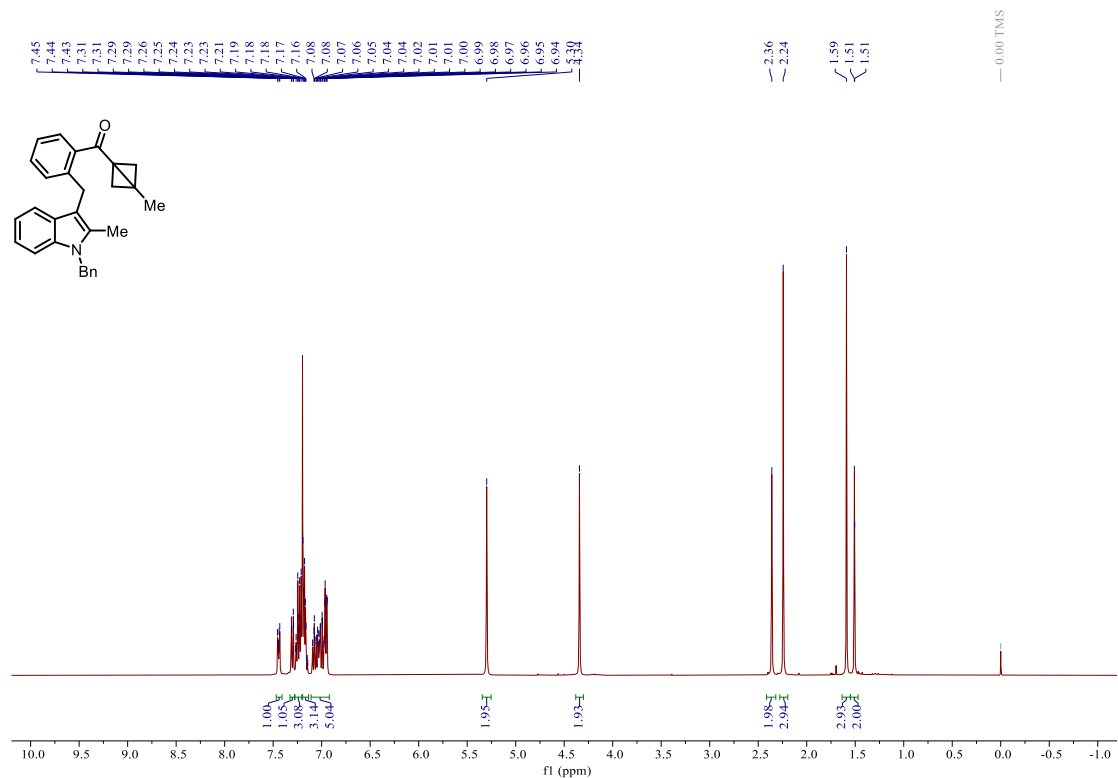
¹H NMR spectra of 1ac (CDCl₃, 400 MHz)



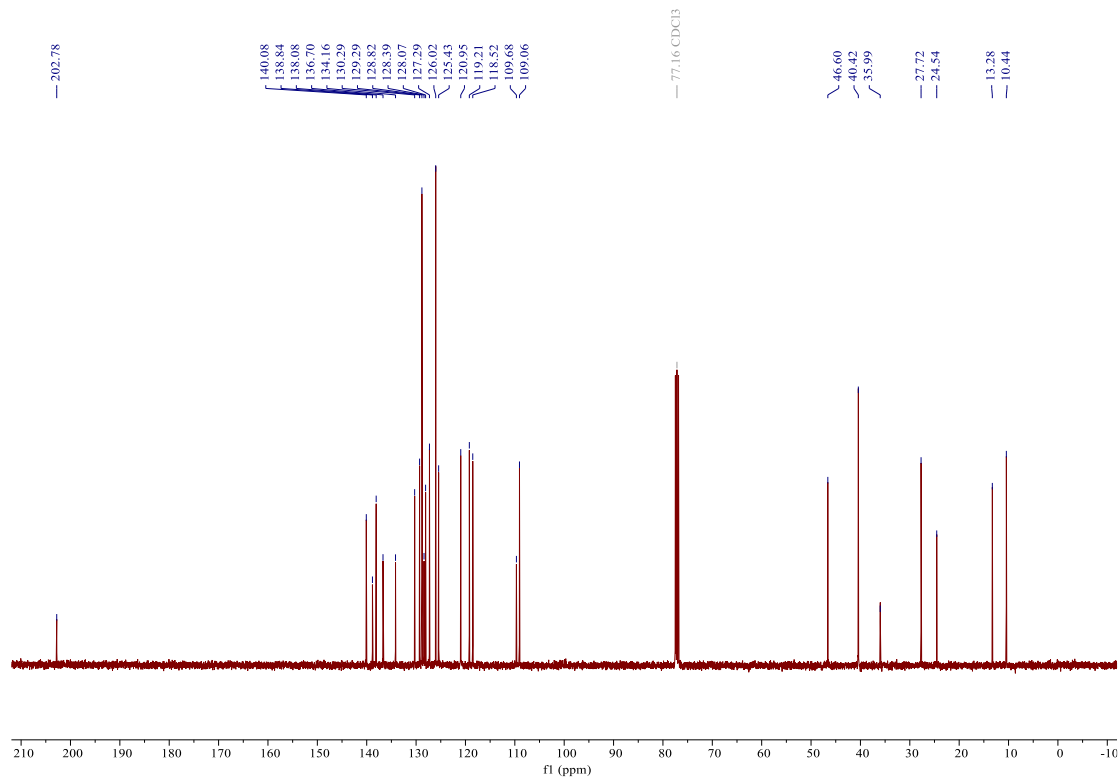
¹³C NMR spectra of 1ac (CDCl₃, 101 MHz)



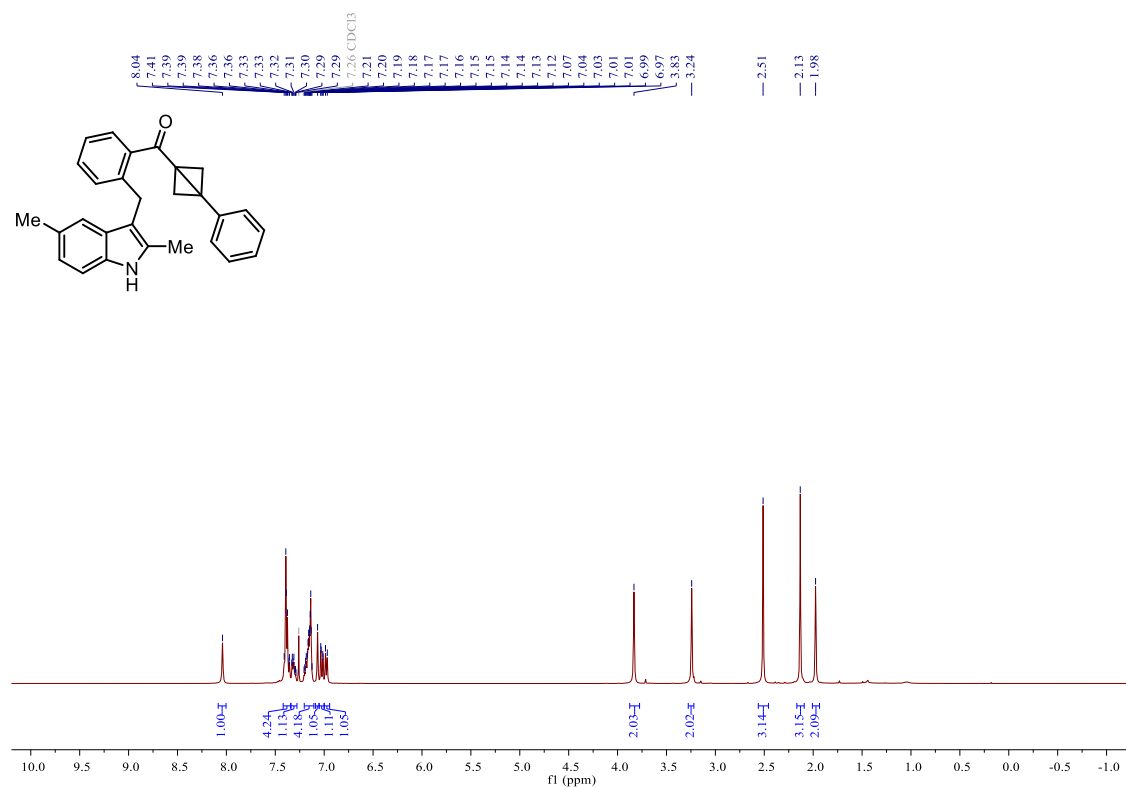
¹H NMR spectra of 1ad (CDCl₃, 400 MHz)



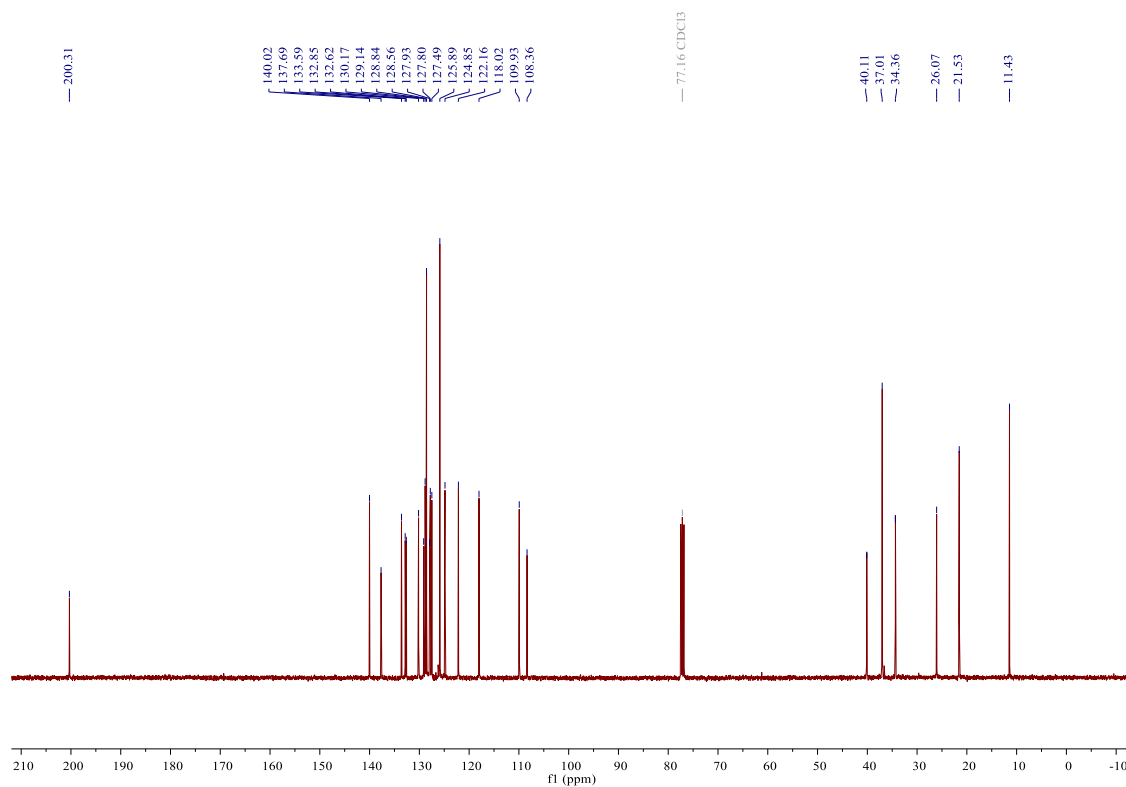
¹³C NMR spectra of 1ad (CDCl₃, 101 MHz)



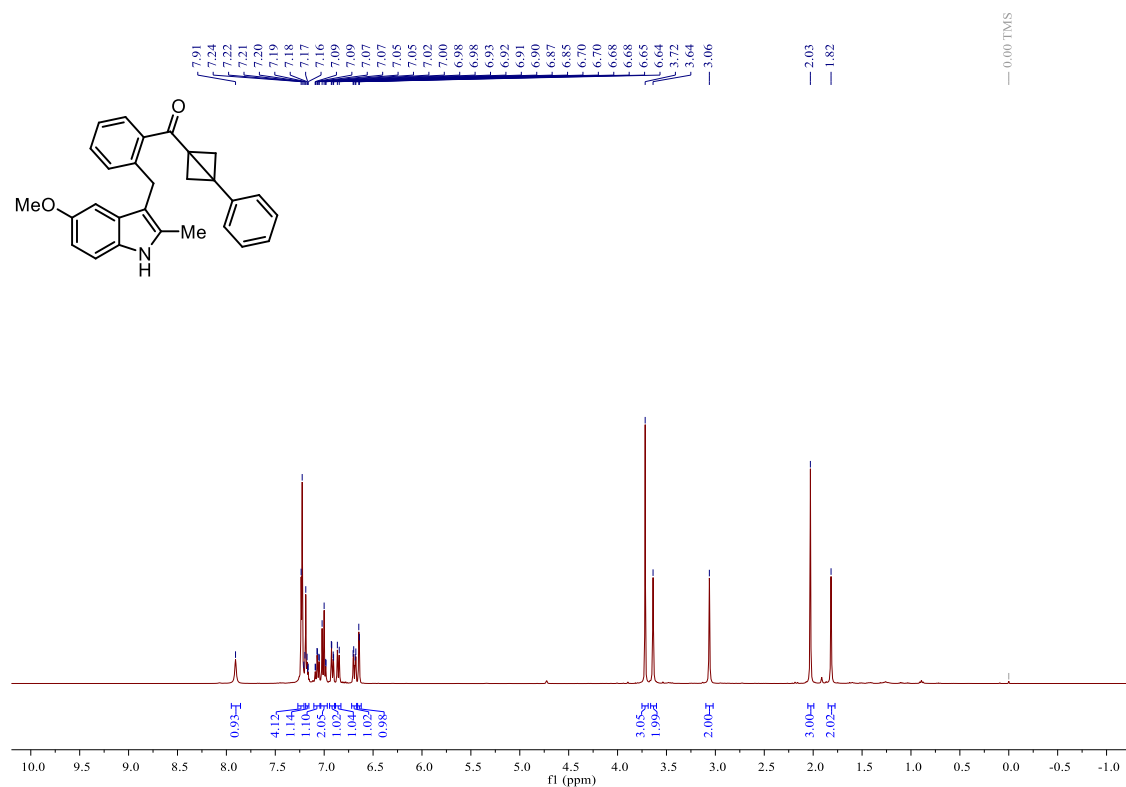
¹H NMR spectra of 1ae (CDCl₃, 400 MHz)



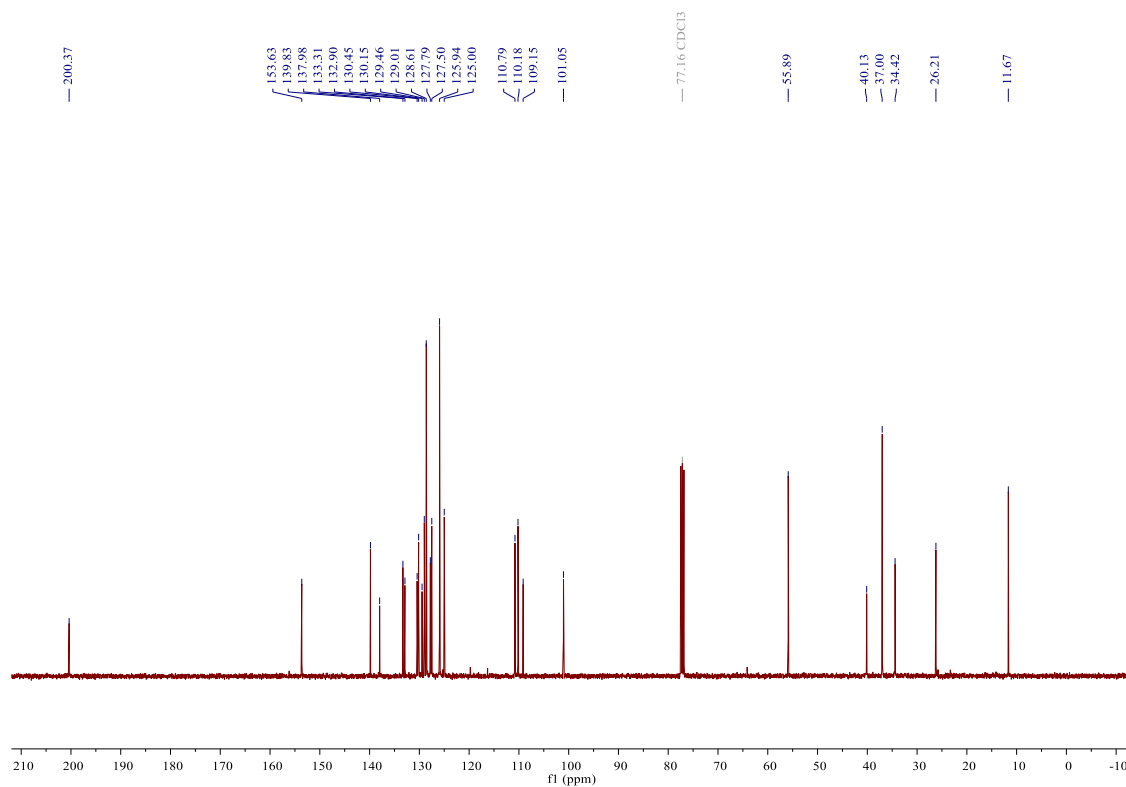
¹³C NMR spectra of 1ae (CDCl₃, 101 MHz)



¹H NMR spectra of 1af (CDCl₃, 400 MHz)



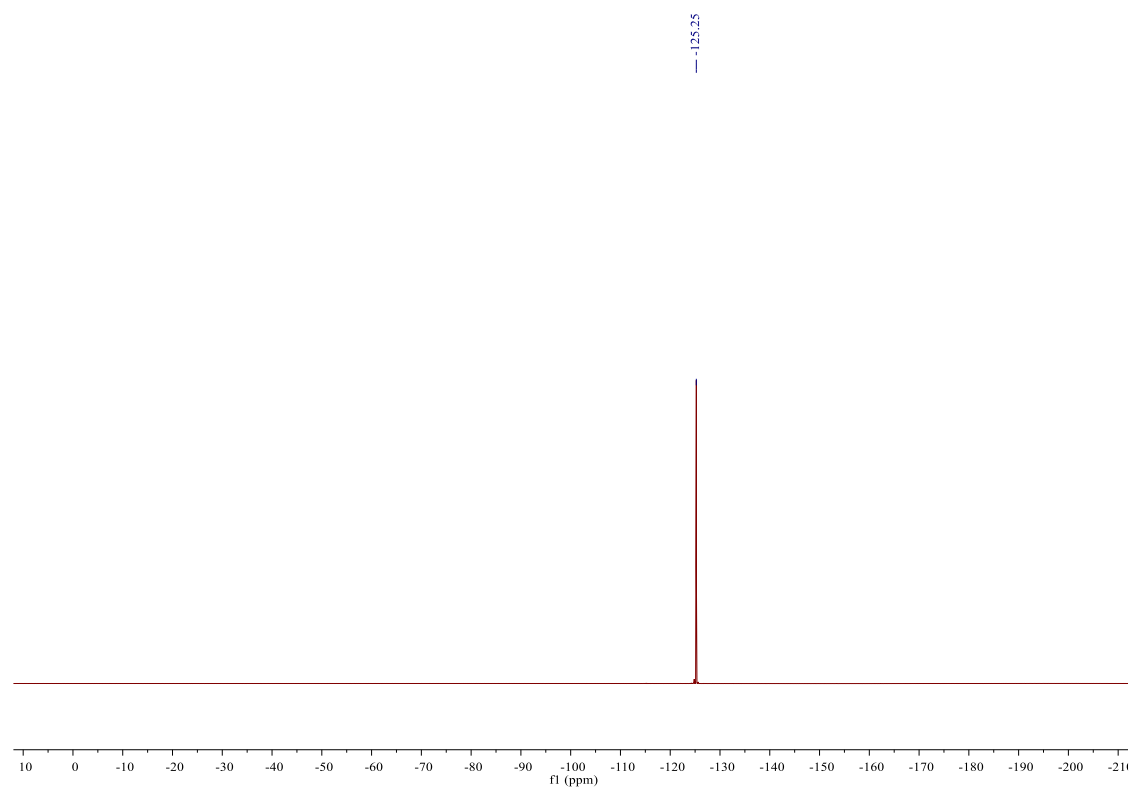
¹³C NMR spectra of 1af (CDCl₃, 101 MHz)



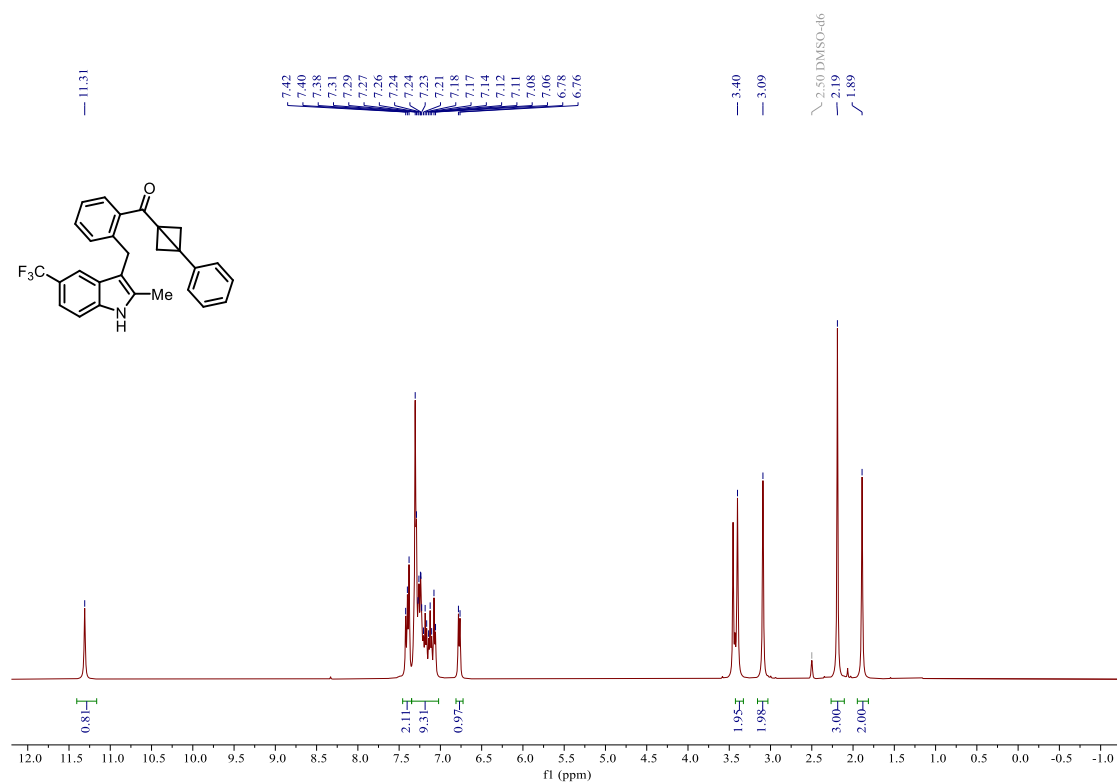
[illegible]

Chemical shifts (ppm): 200.34, 158.65, 156.34, 139.57, 137.66, 134.63, 132.80, 131.79, 130.29, 129.24, 129.14, 128.90, 128.67, 128.34, 127.62, 125.90, 125.09, 110.73, 110.63, 109.50, 109.26, 108.80, 108.44, 103.50, 103.27, 77.16 (CDCl₃), 40.33, 37.03, 34.46, 26.31, 11.54.

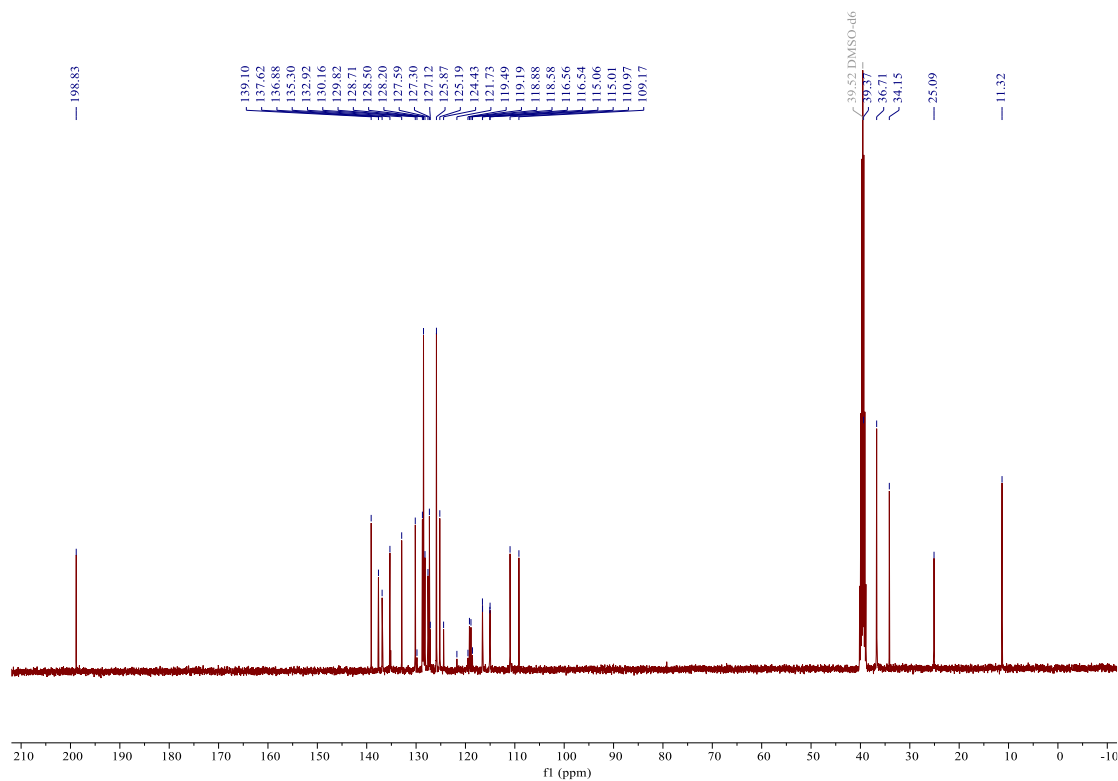
^{19}F NMR spectra of 1ag (CDCl_3 , 376 MHz)



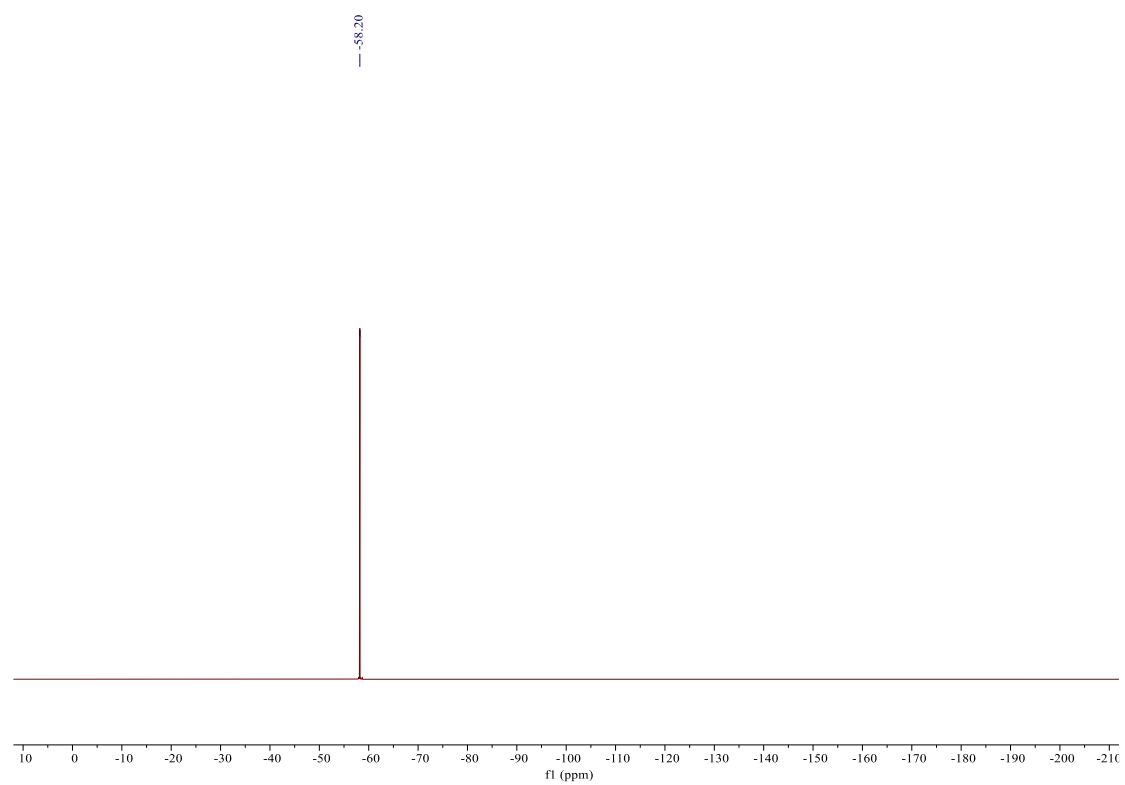
¹H NMR spectra of 1ah (DMSO, 400 MHz)



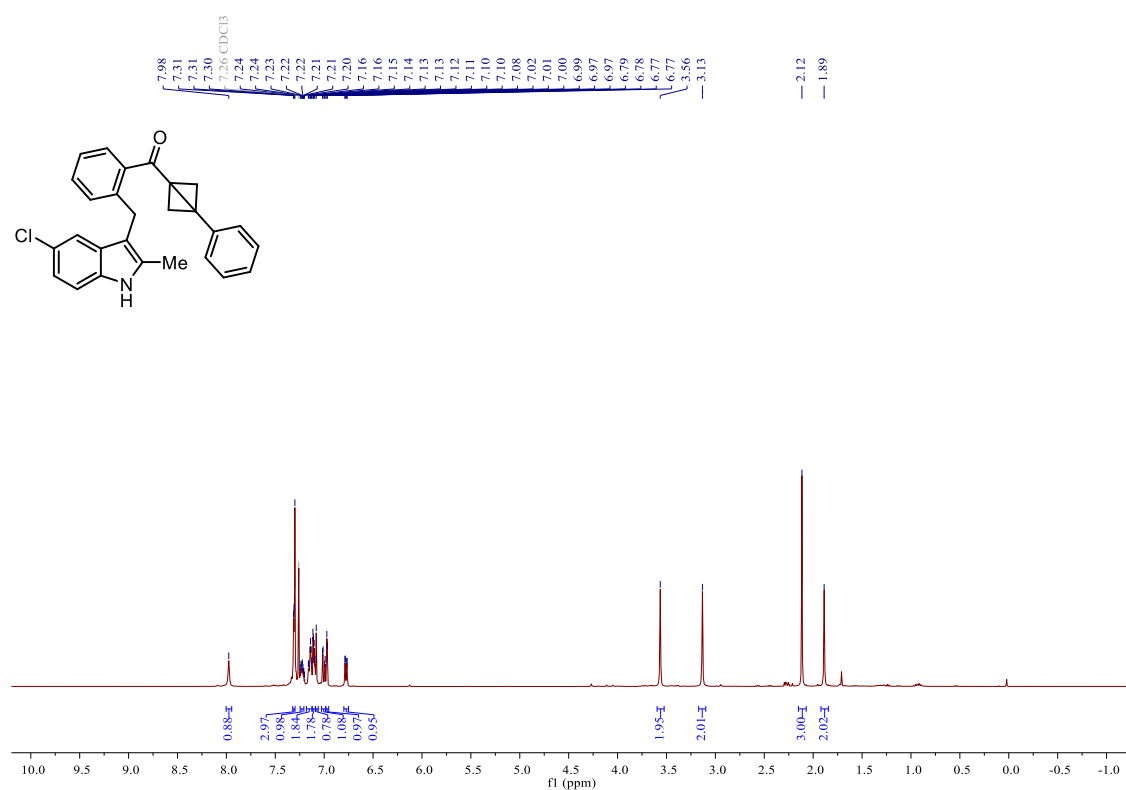
¹³C NMR spectra of 1ah (DMSO, 101 MHz)



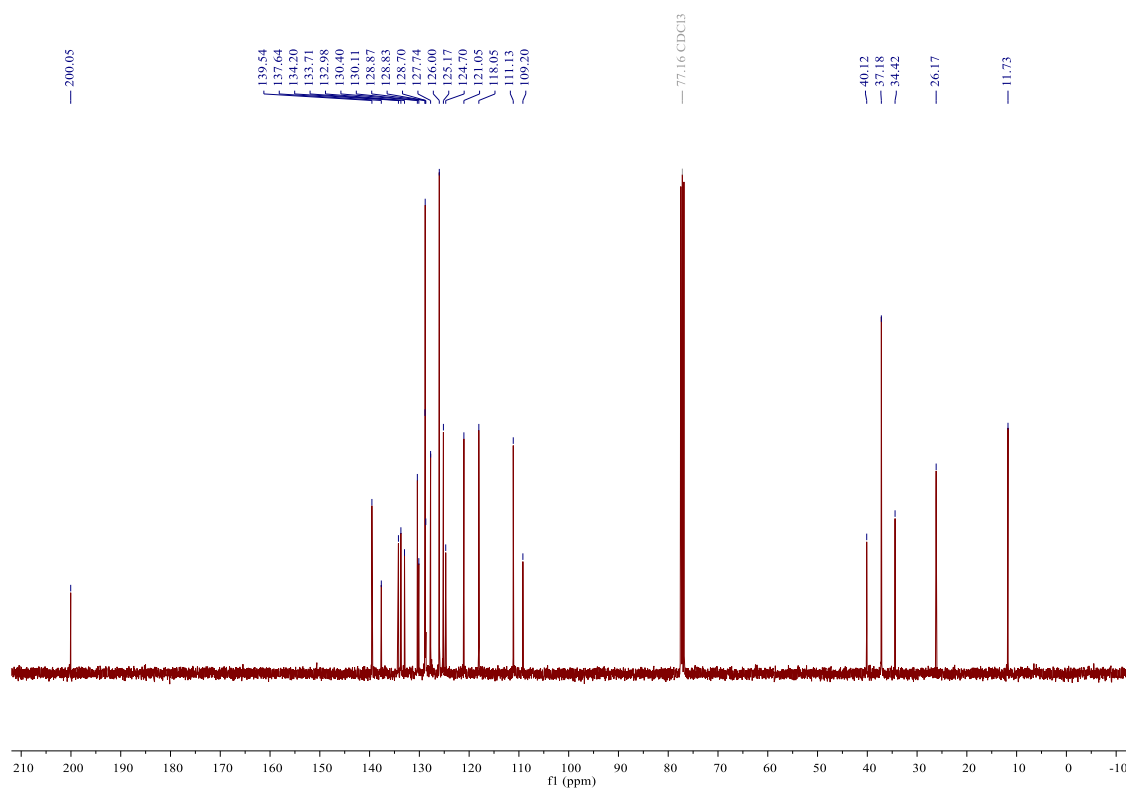
^{19}F NMR spectra of 1ah (DMSO, 376 MHz)



^1H NMR spectra of 1ai (CDCl₃, 400 MHz)



^{13}C NMR spectra of 1ai (CDCl₃, 101 MHz)



Chemical structure of compound 10 is shown above the spectrum. The structure is a benzimidazole derivative with a cyclopropane ring and a phenyl group.

Integration values are provided below the peaks: 1.00, 2.03, 2.00, 3.00, 5.14, 1.11, 2.07, 2.11, and 2.34.

200.18

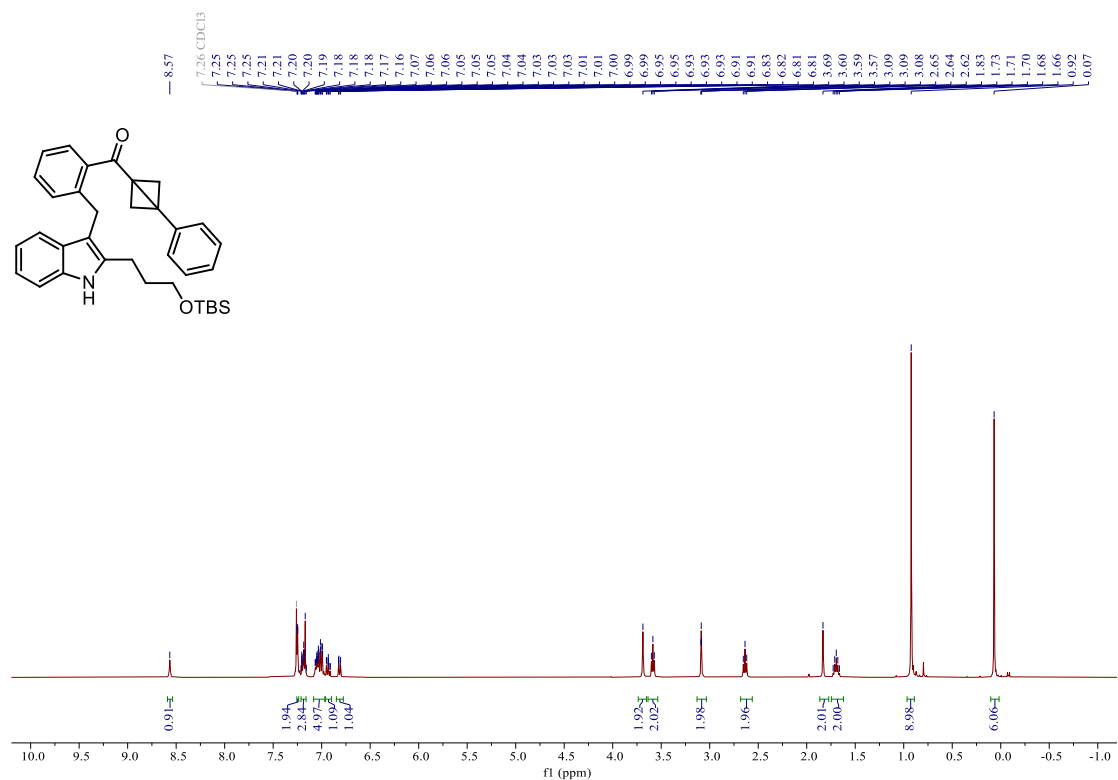
139.86
138.13
136.35
132.94
130.23
129.89
128.65
128.17
127.55
126.01
125.27
123.16
121.83
119.21
119.16
114.72
111.14

77.16 CDCl₃

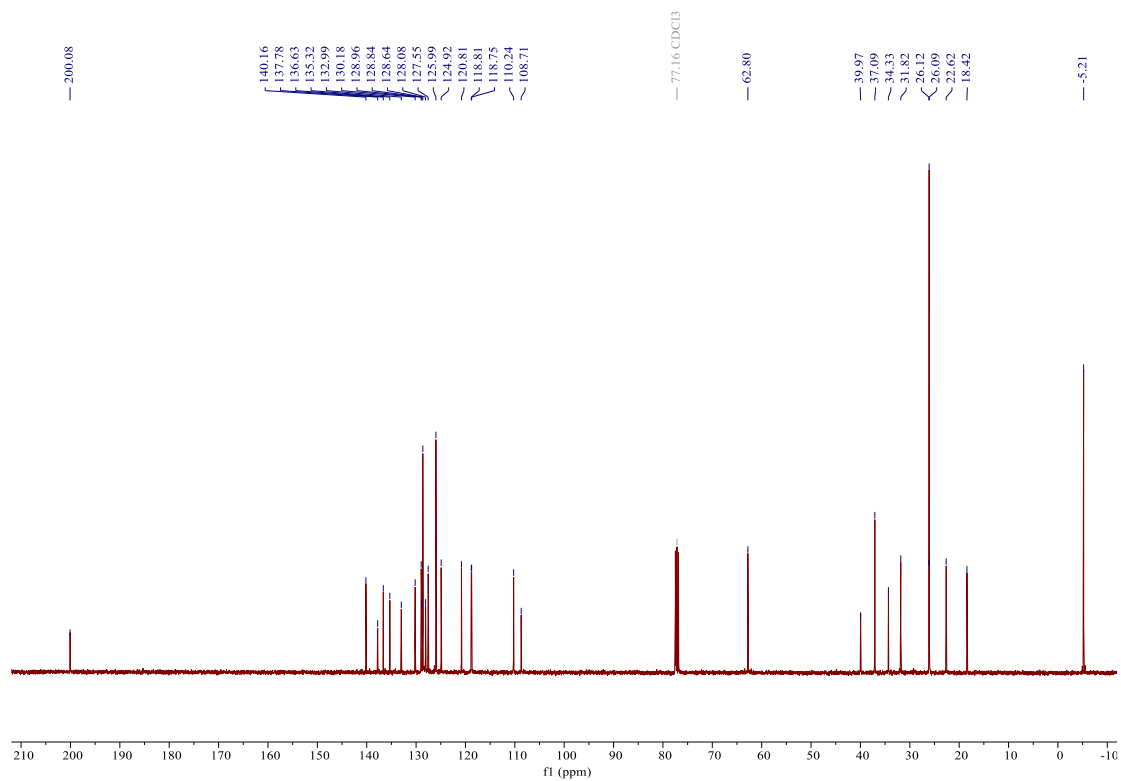
40.19
37.15
34.36
27.80

ppm

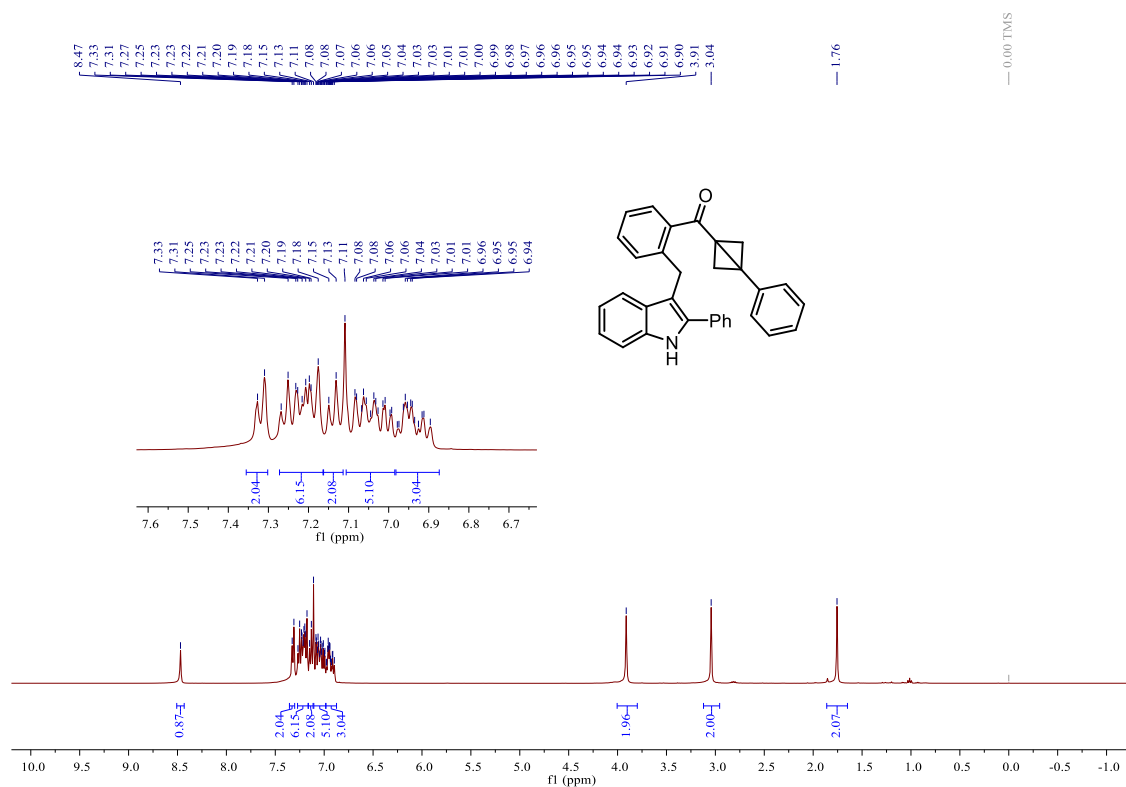
¹H NMR spectra of 1ak (CDCl₃, 400 MHz)



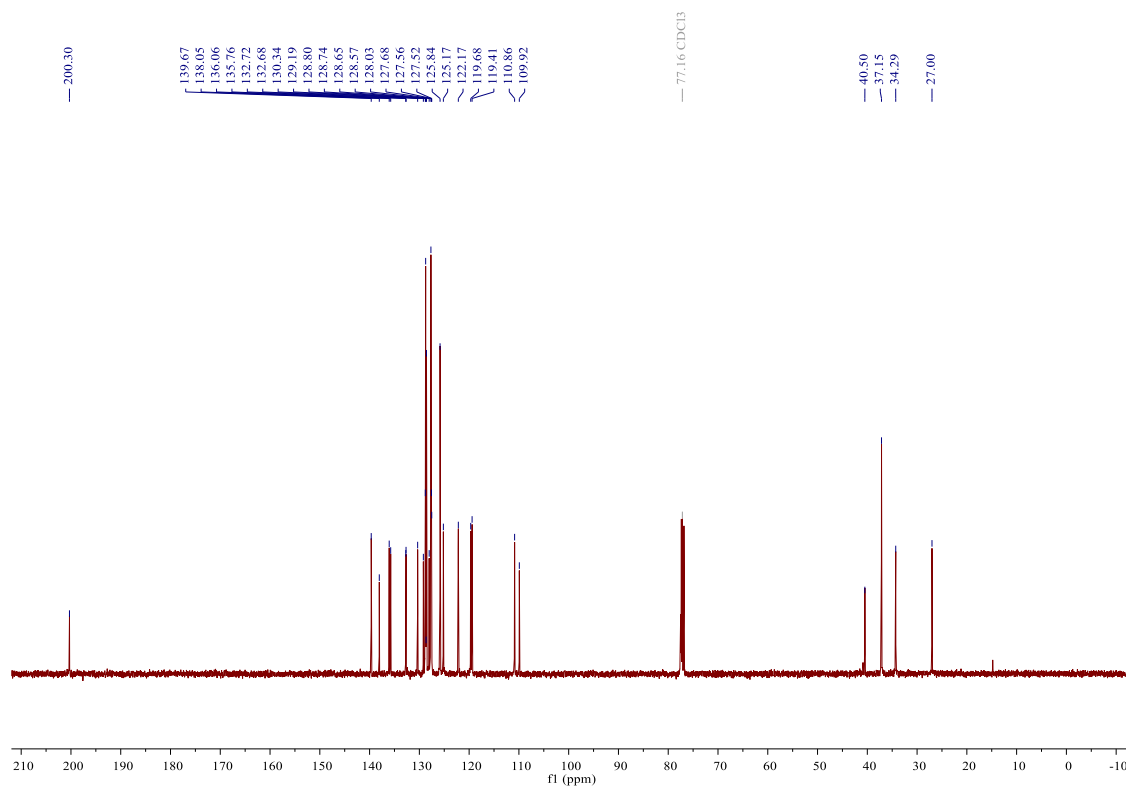
¹³C NMR spectra of 1ak (CDCl₃, 101 MHz)



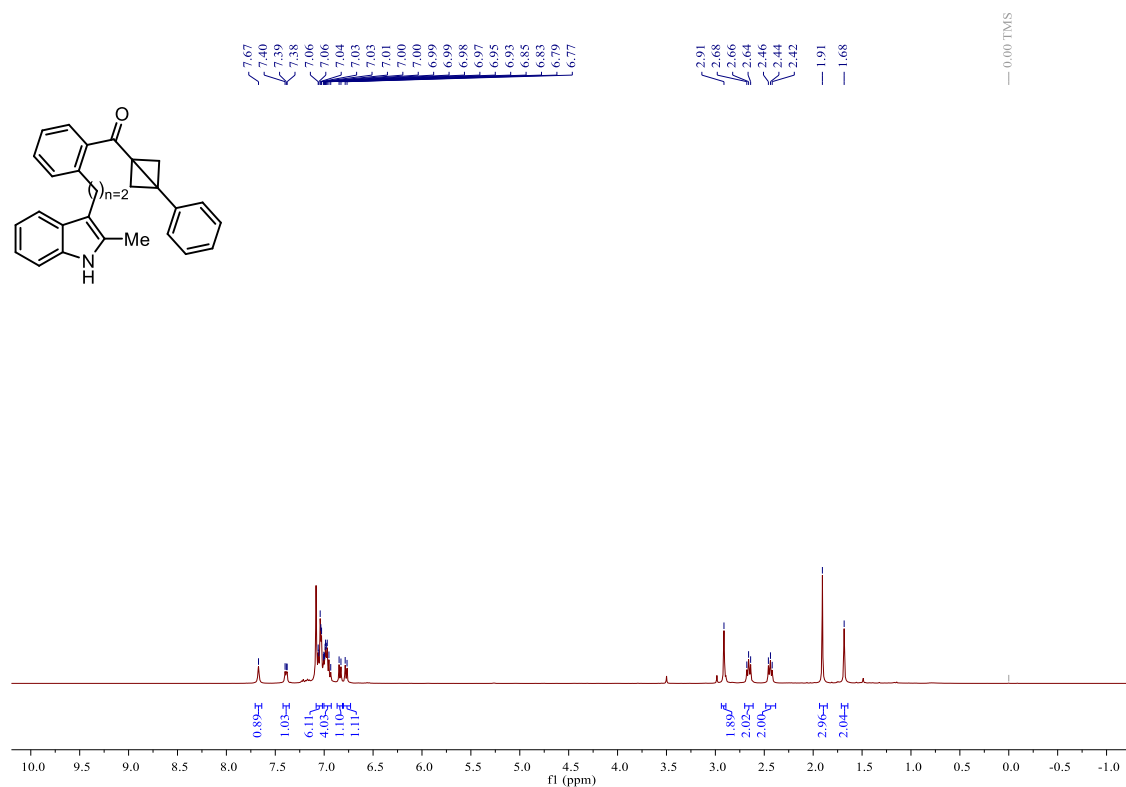
¹H NMR spectra of 1a (CDCl₃, 400 MHz)



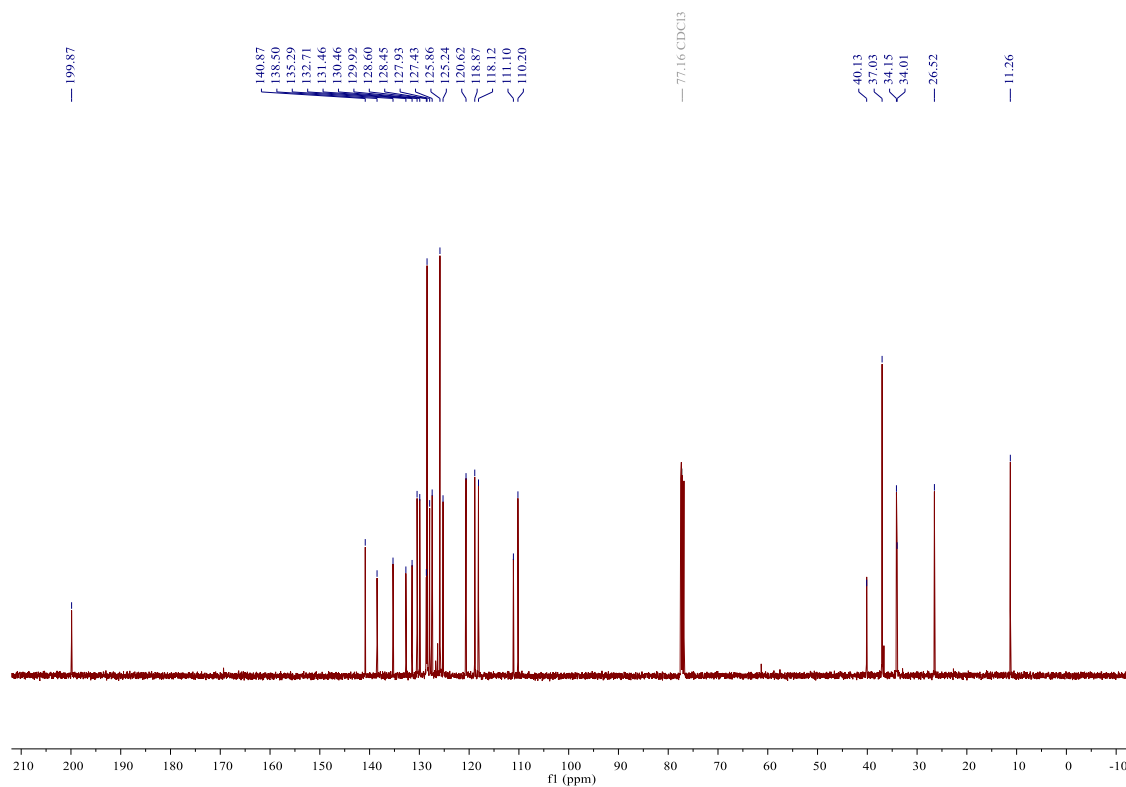
¹³C NMR spectra of 1a (CDCl₃, 101 MHz)



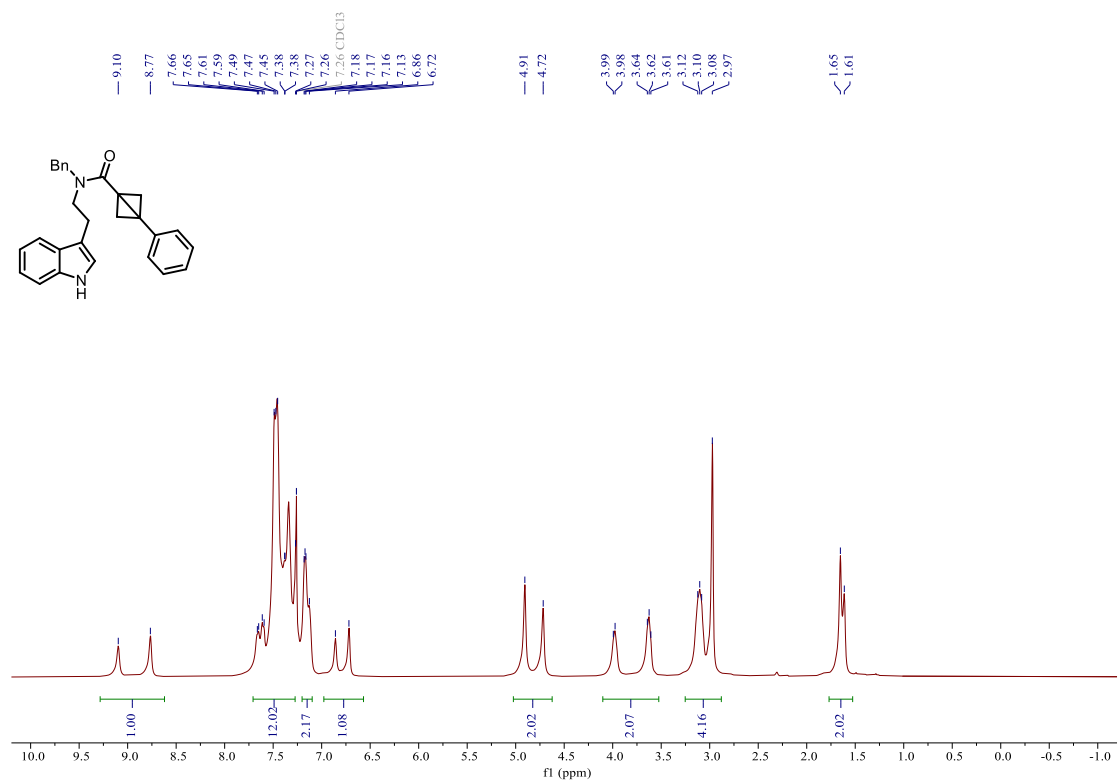
¹H NMR spectra of 1am (CDCl₃, 400 MHz)



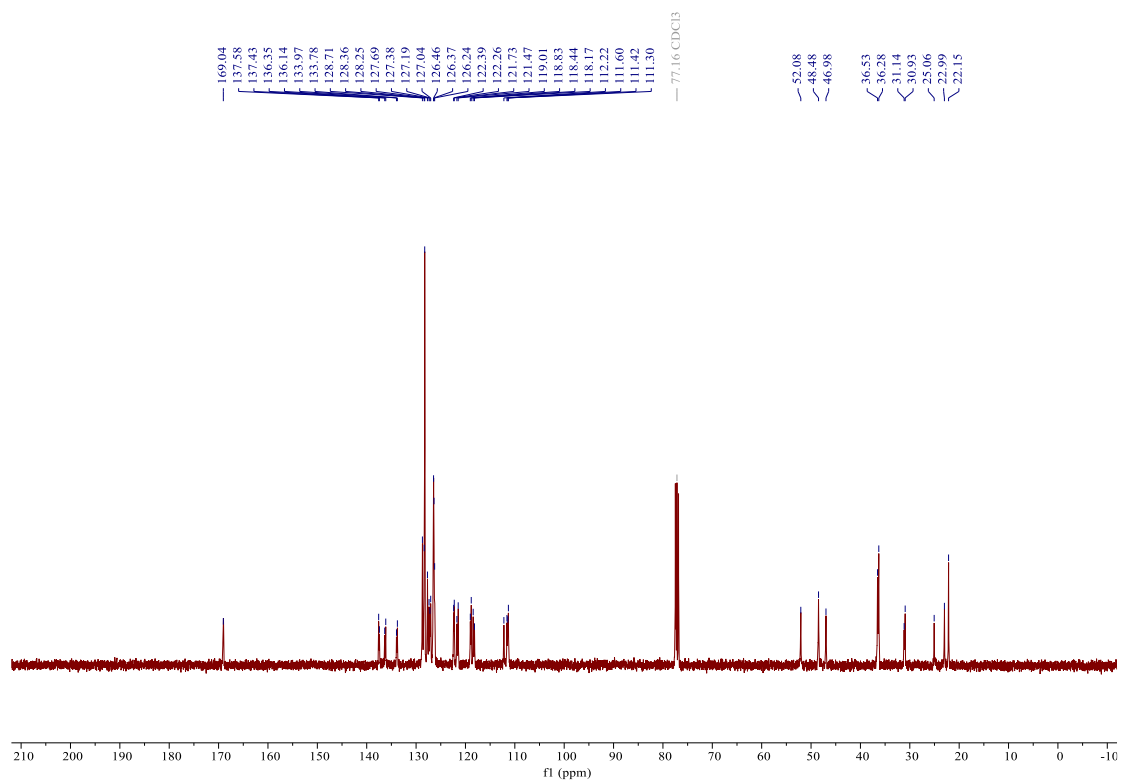
¹³C NMR spectra of 1am (CDCl₃, 101 MHz)



¹H NMR spectra of 1an (CDCl₃, 400 MHz)



¹³C NMR spectra of 1an (CDCl₃, 101 MHz)



Chemical structure of 1-methyl-1-phenyl-2,3,4,5-tetrahydro-1H-indeno[1,2-b]pyridine-3-carbonyl compound:

C[C@H]1Cc2ccccc2[C@@H]3C(=O)c4ccccc4N3

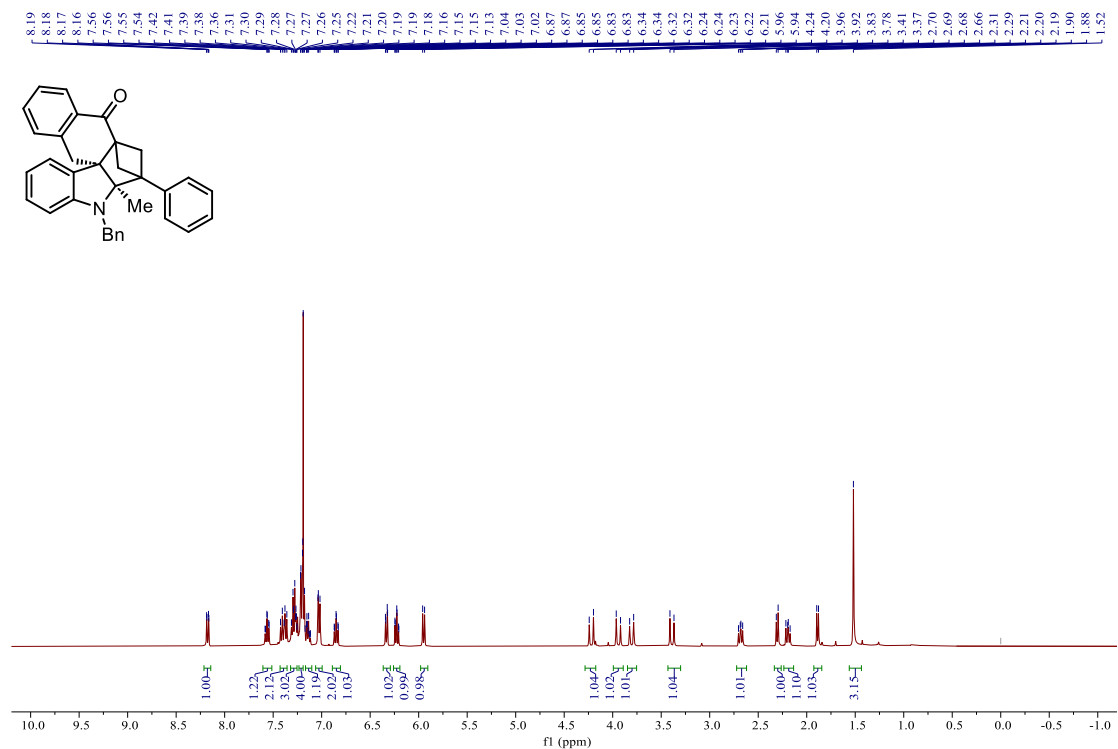
¹H NMR spectrum (CDCl₃) showing peaks from 1.31 to 8.21 ppm. Integration values are provided below the peaks:

Chemical Shift (ppm)	Integration
8.21	1.00
7.26	1.06
7.03	1.07
6.99	3.04
6.95	1.02
6.41	1.01
6.37	2.02
6.36	1.99
6.35	1.01
6.34	1.01
6.33	1.02
6.32	1.06
1.31	3.14

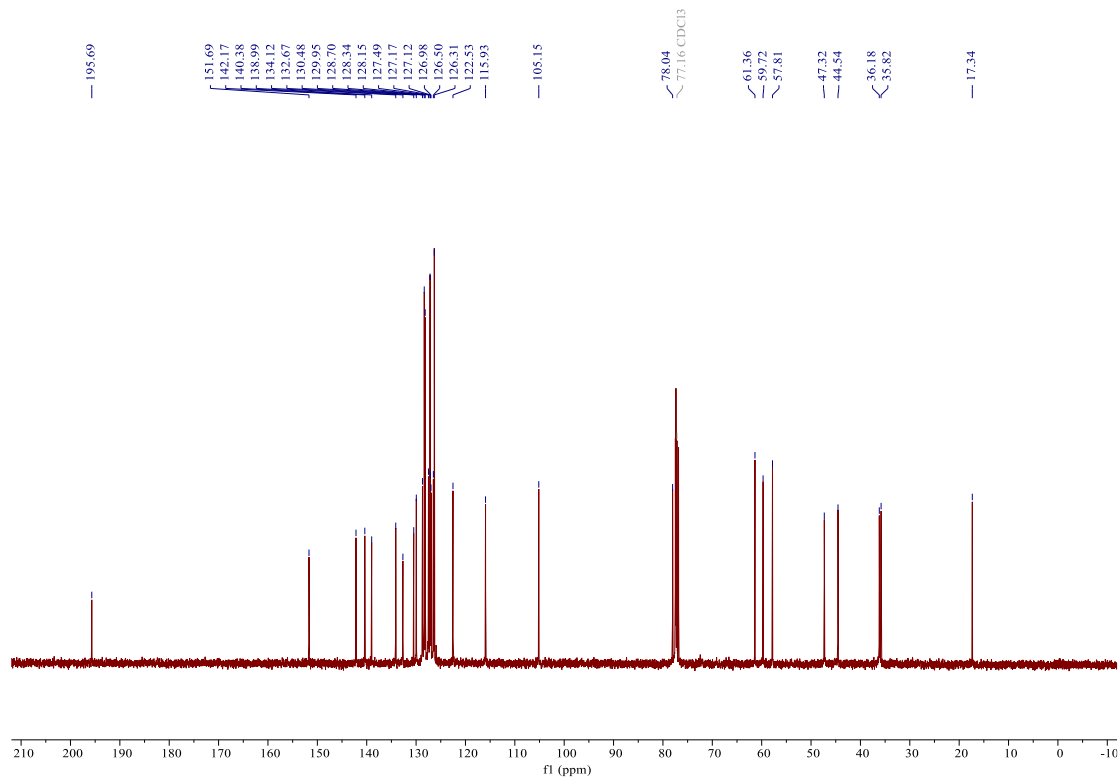
¹³C NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from 210 to -10. The spectrum shows several peaks, with the following chemical shifts (ppm) labeled above the corresponding peaks:

- 195.93
- 151.76
- 142.17
- 140.23
- 134.07
- 132.79
- 131.99
- 129.91
- 128.62
- 128.09
- 127.53
- 127.08
- 126.83
- 126.75
- 123.30
- 118.15
- 108.61
- 77.16 (CDCl₃)
- 74.96
- 60.55
- 60.45
- 58.03
- 43.49
- 37.27
- 35.86
- 19.28

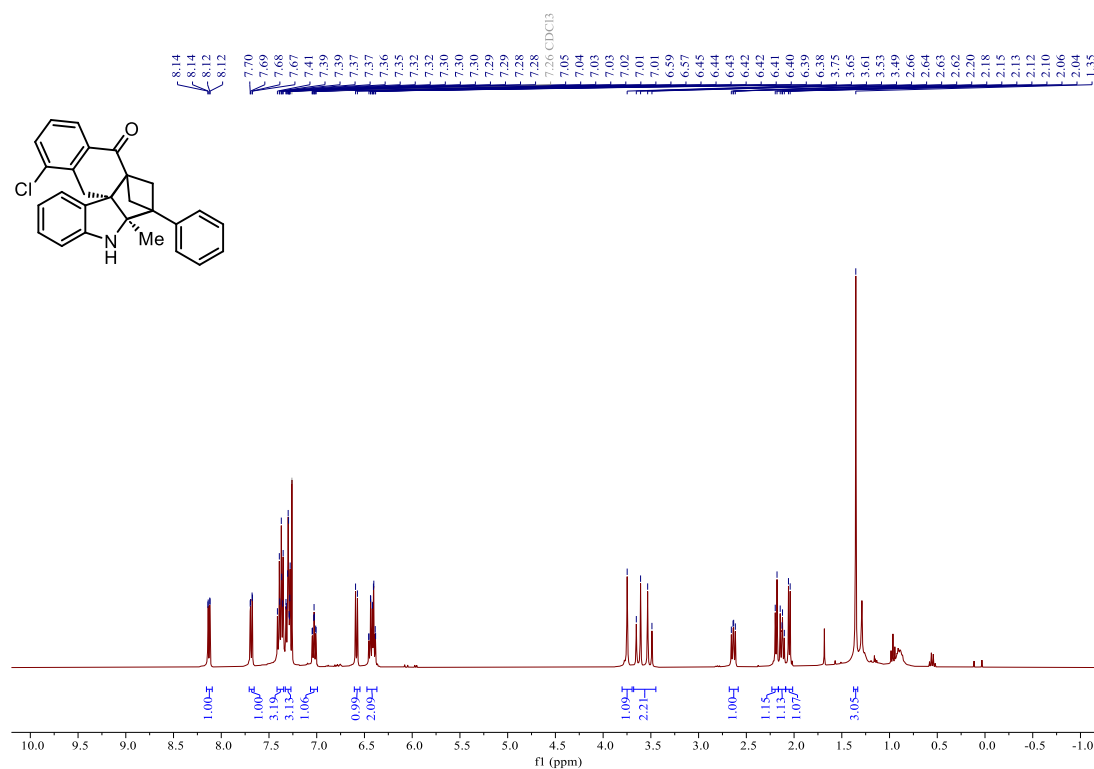
¹H NMR spectra of 2b (CDCl₃, 400 MHz)



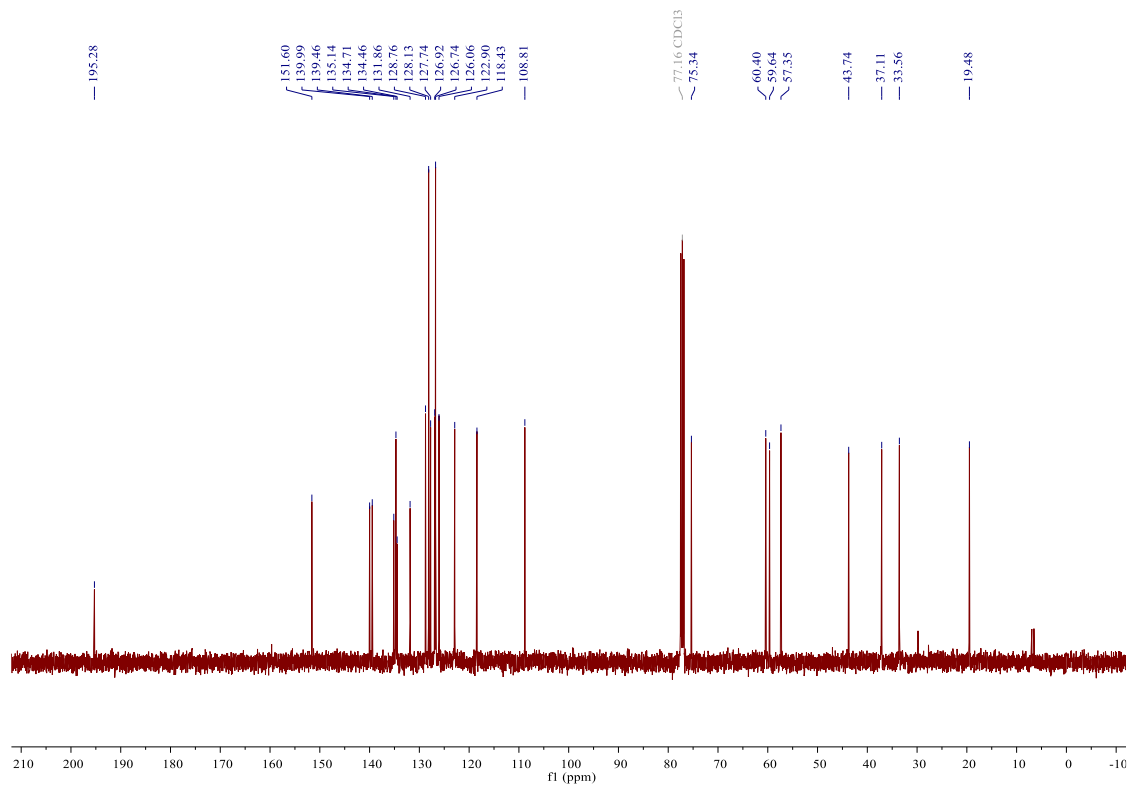
¹³C NMR spectra of 2b (CDCl₃, 101 MHz)



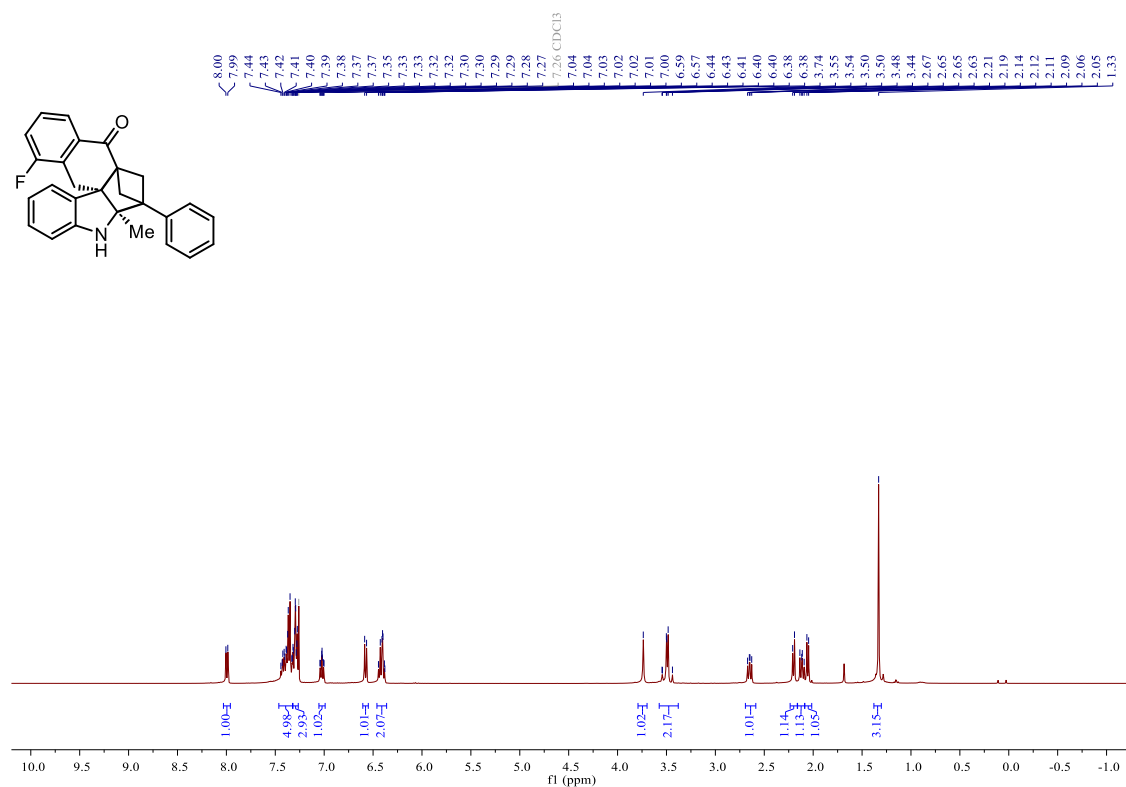
¹H NMR spectra of 2c (CDCl₃, 400 MHz)



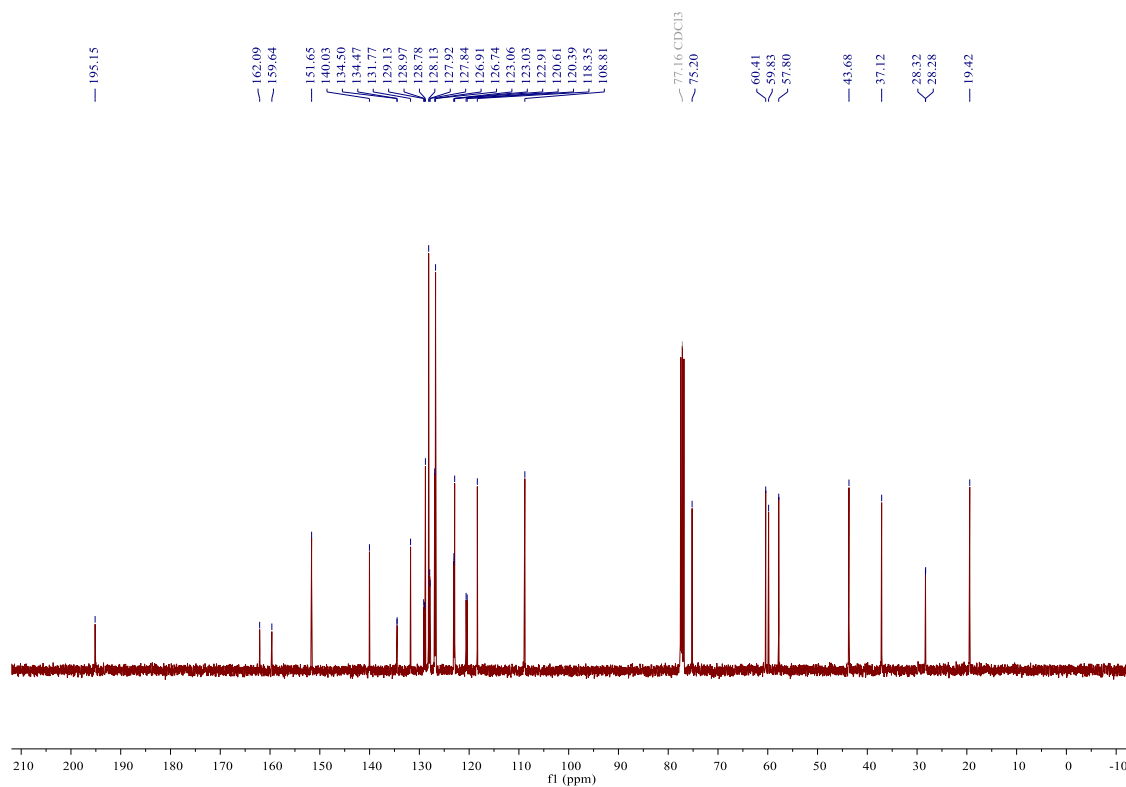
¹³C NMR spectra of 2c (CDCl₃, 101 MHz)



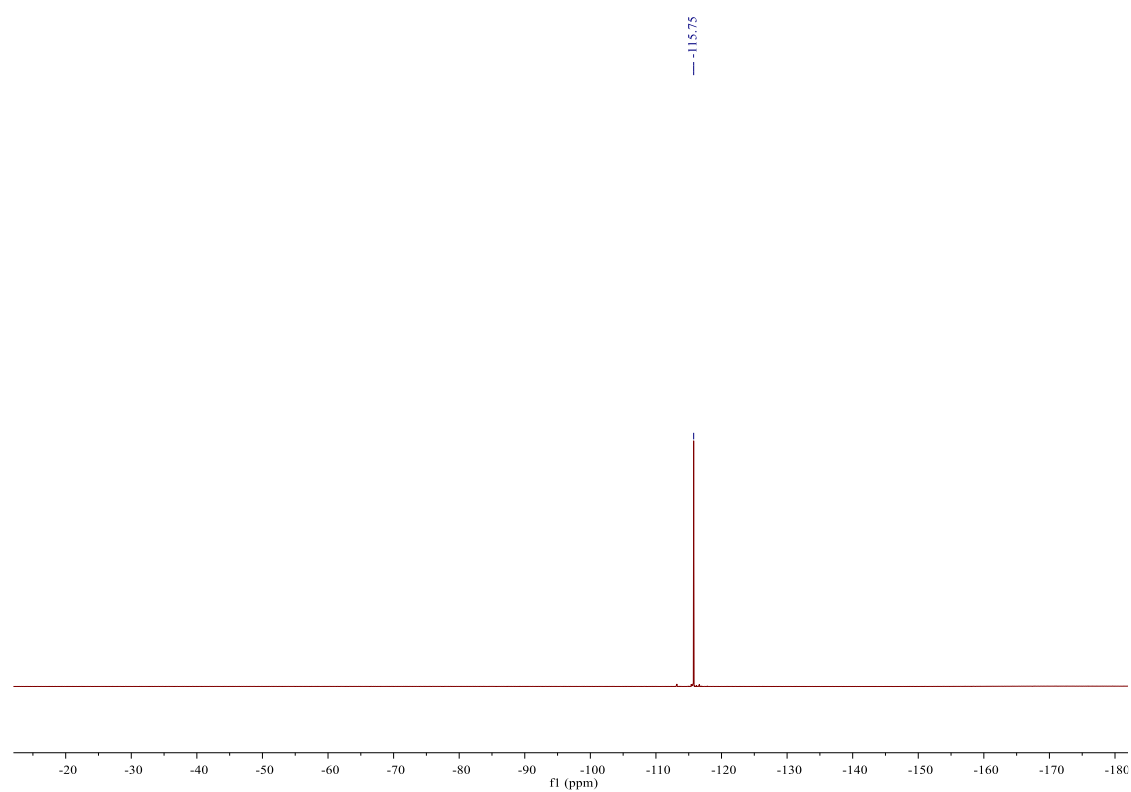
^1H NMR spectra of 2d (CDCl_3 , 400 MHz)



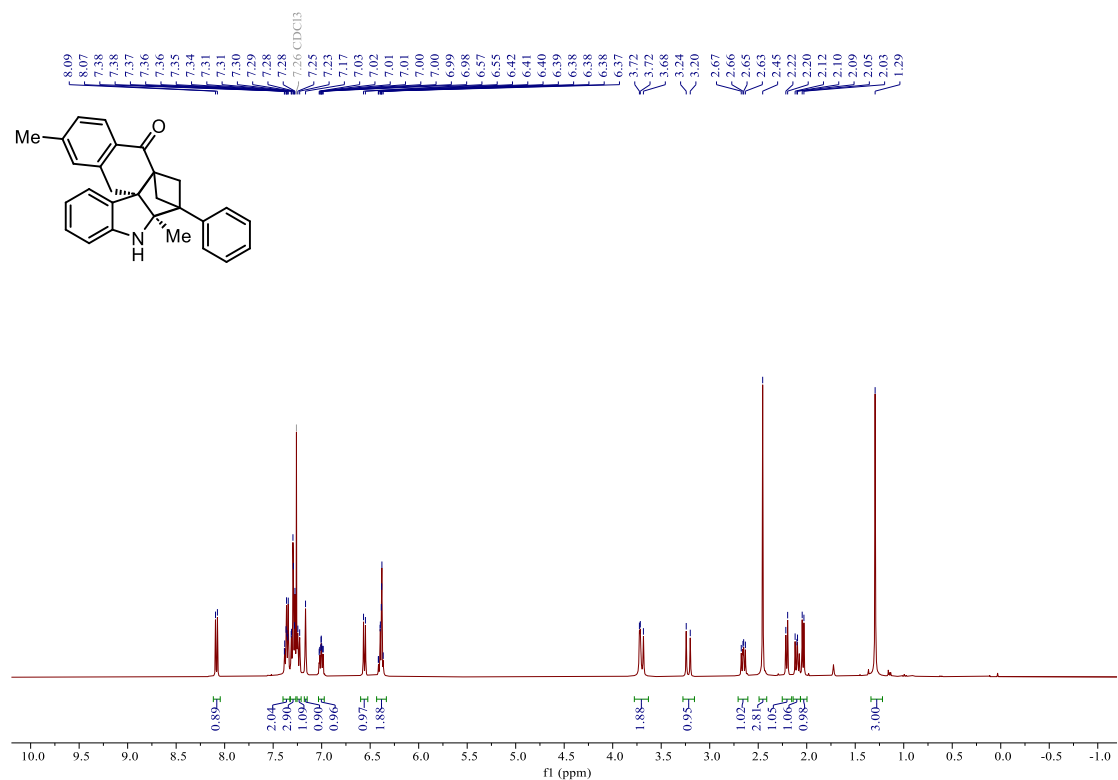
^{13}C NMR spectra of 2d (CDCl_3 , 101 MHz)



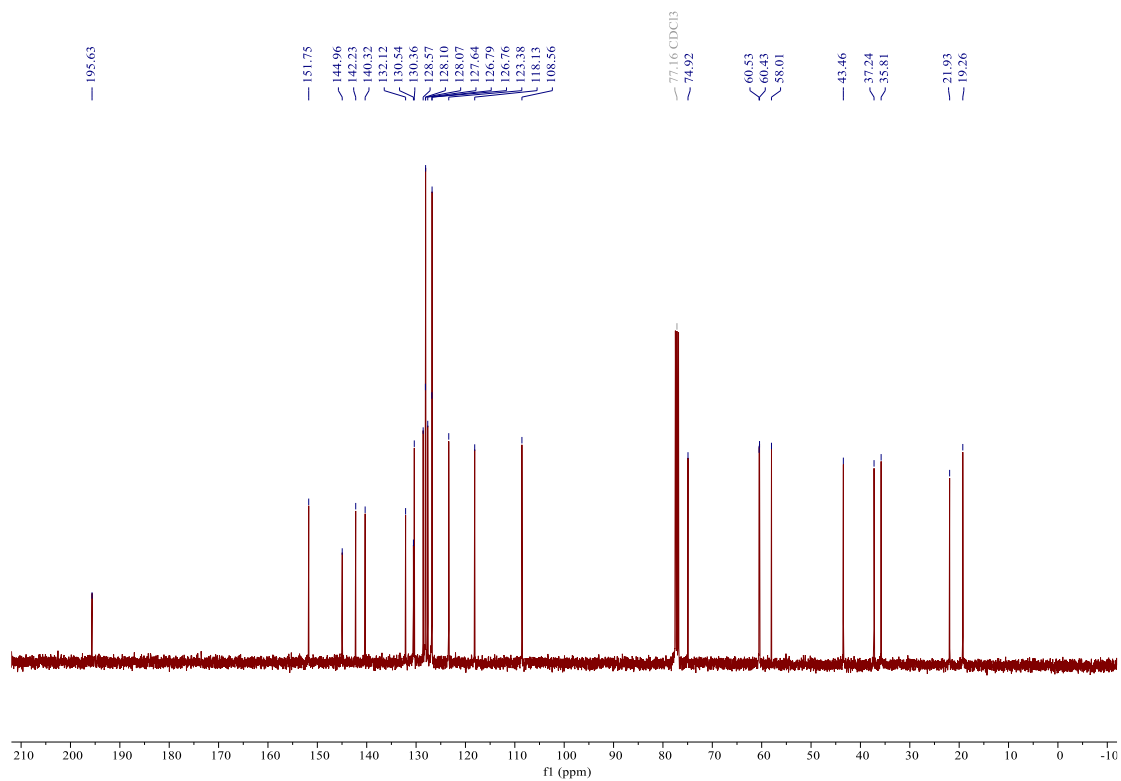
^{19}F NMR spectra of 2d (CDCl_3 , 376 MHz)



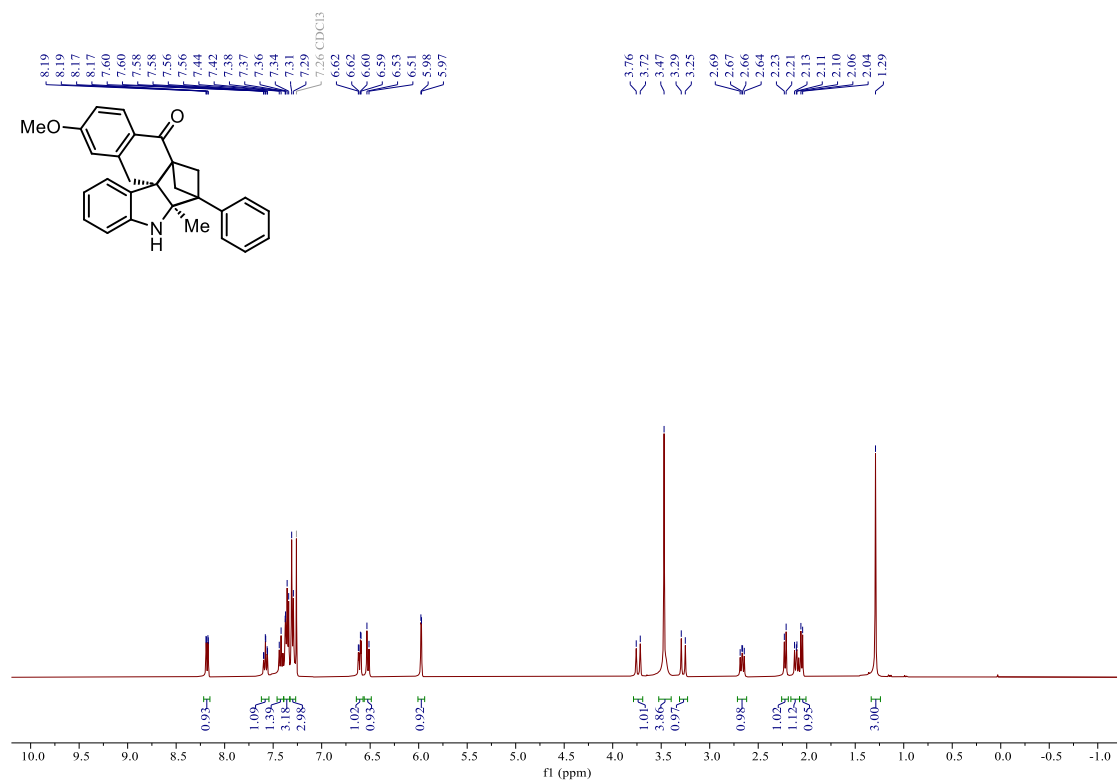
¹H NMR spectra of 2e (CDCl₃, 400 MHz)



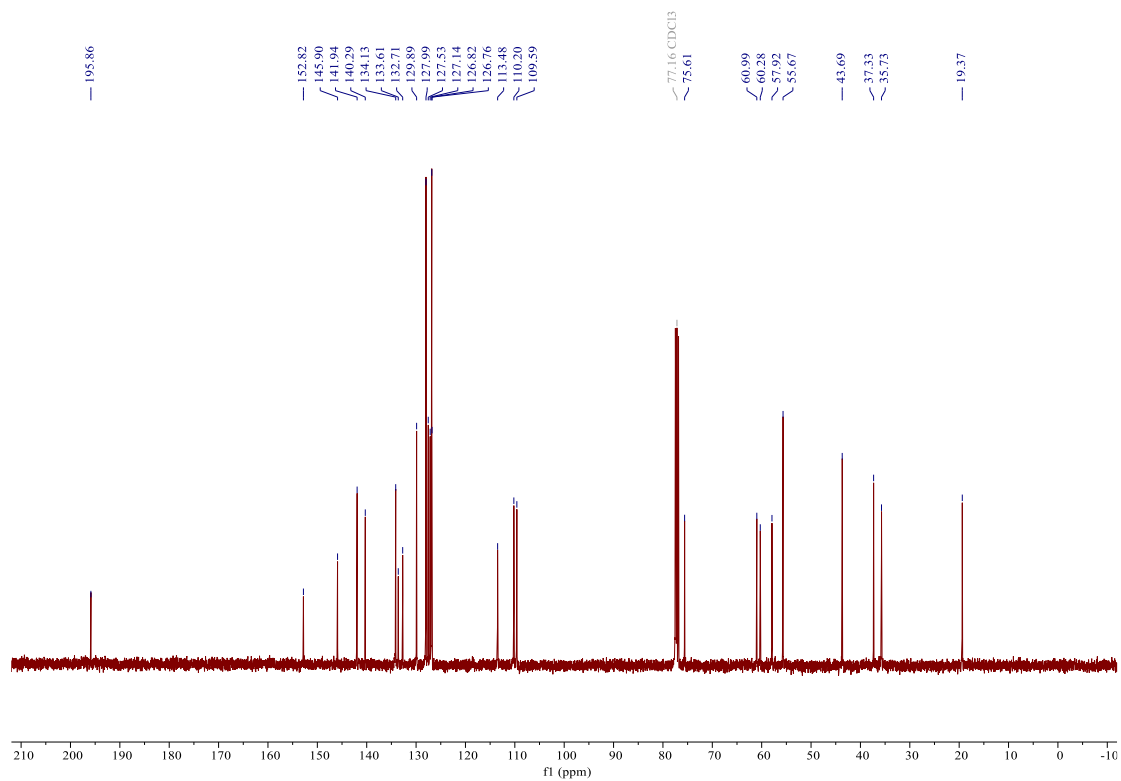
¹³C NMR spectra of 2e (CDCl₃, 101 MHz)



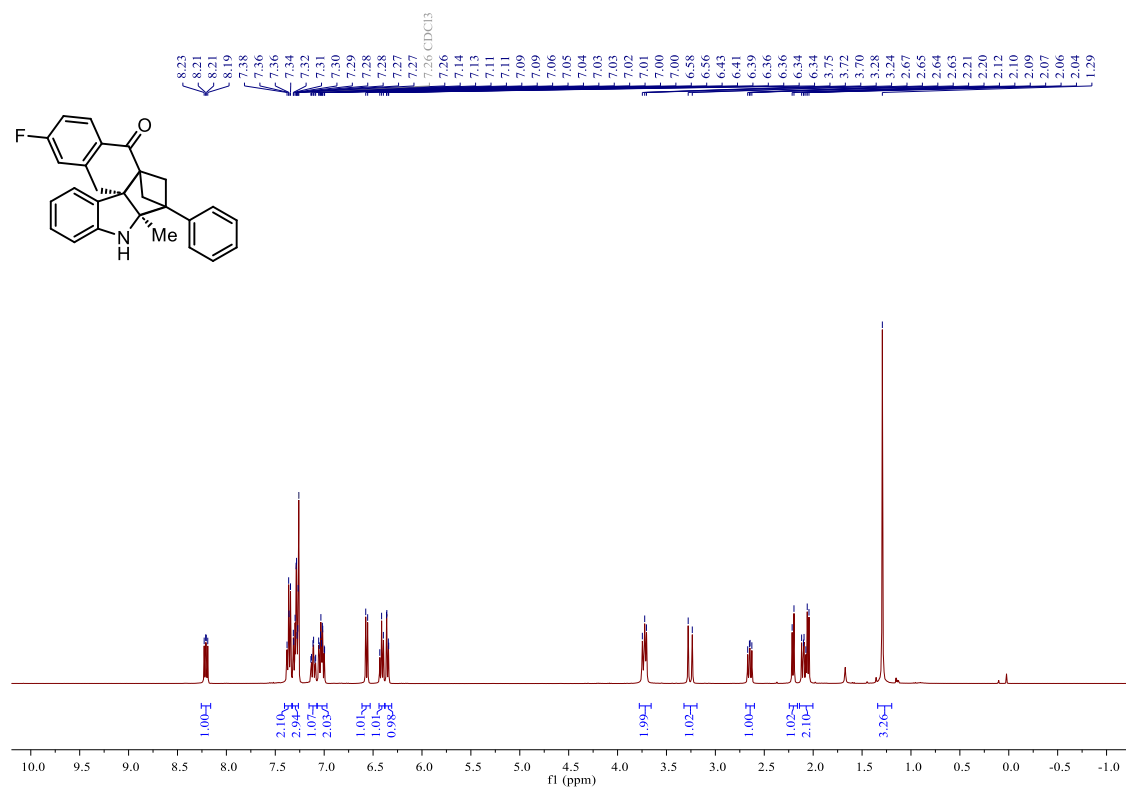
¹H NMR spectra of 2f (CDCl₃, 400 MHz)



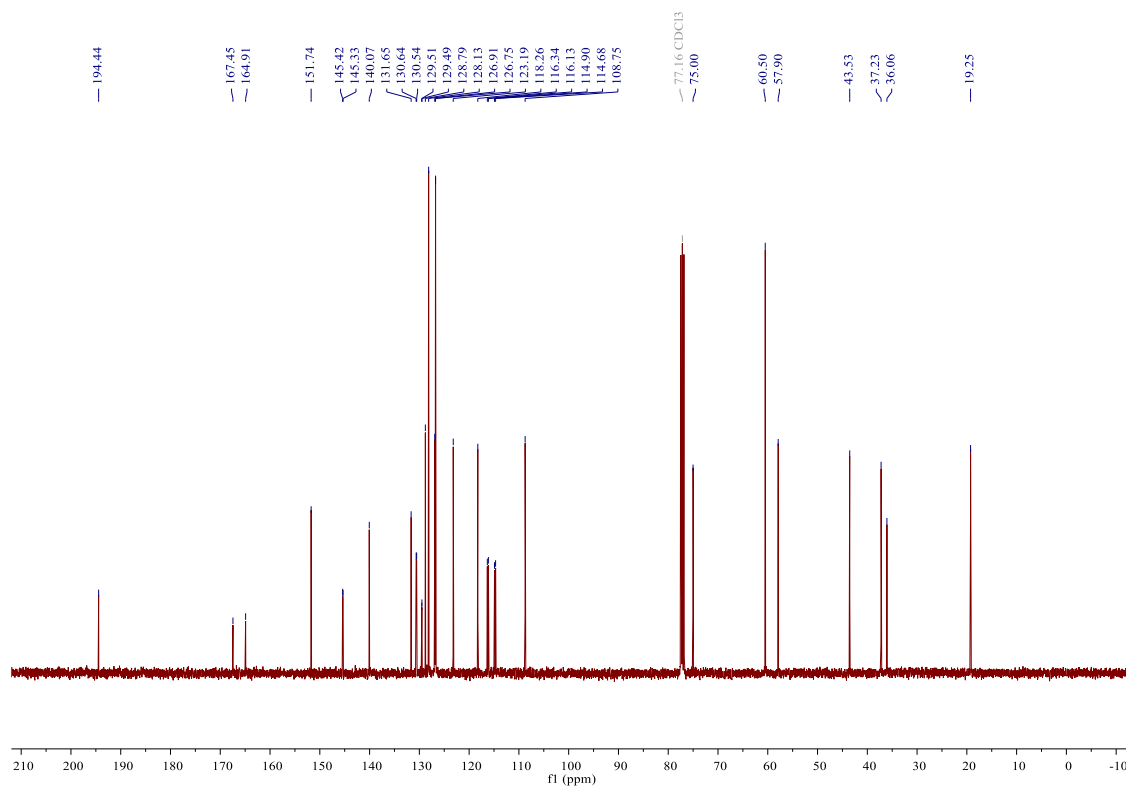
¹³C NMR spectra of 2f (CDCl₃, 101 MHz)



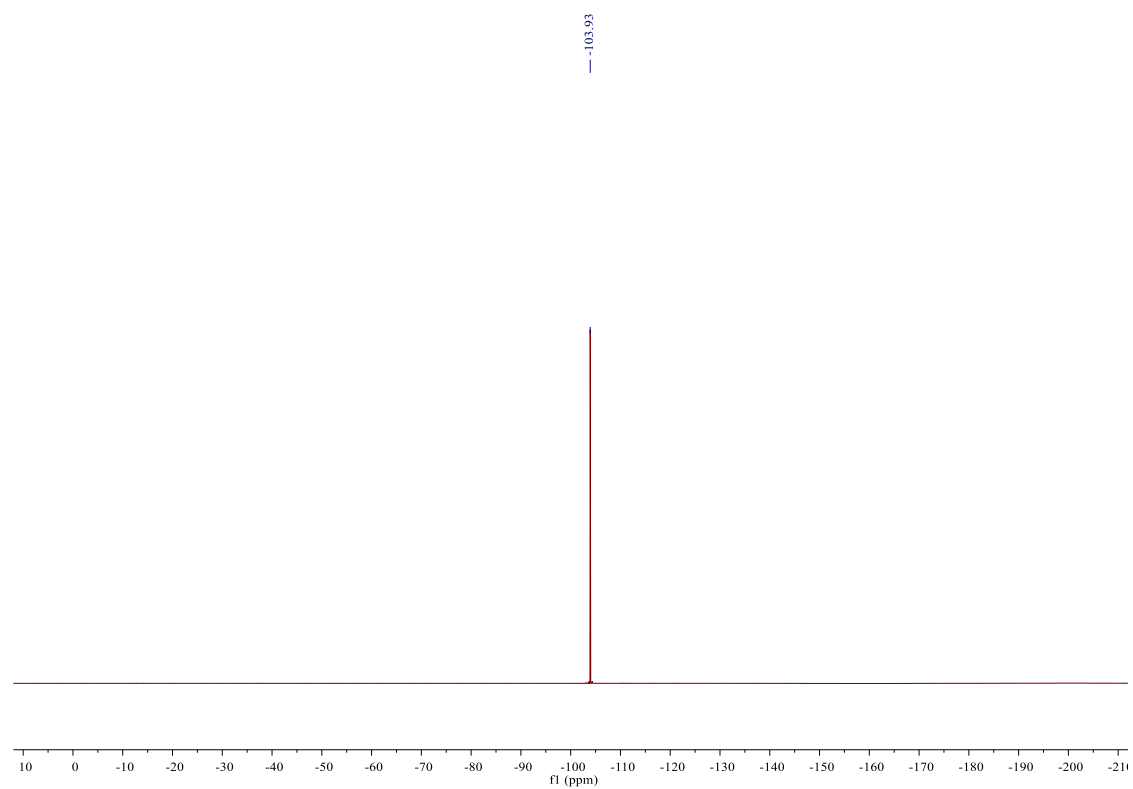
^1H NMR spectra of 2g (CDCl_3 , 400 MHz)



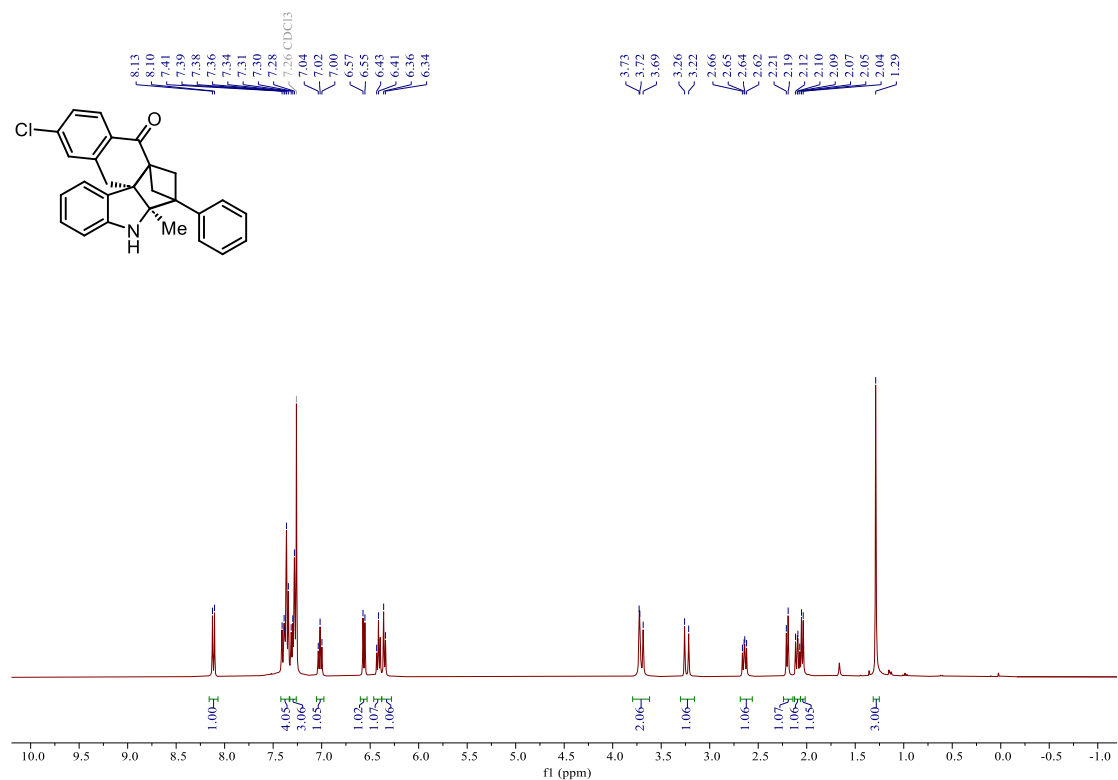
^{13}C NMR spectra of 2g (CDCl_3 , 101 MHz)



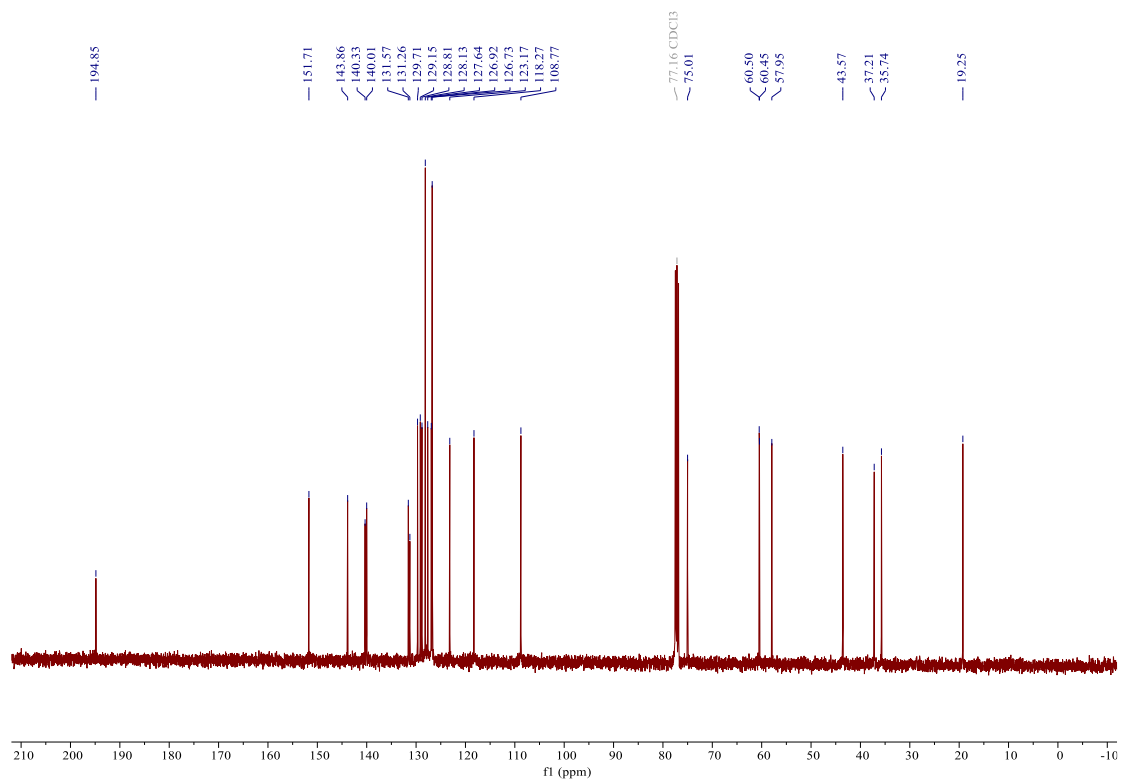
^{19}F NMR spectra of 2g (CDCl_3 , 376 MHz)



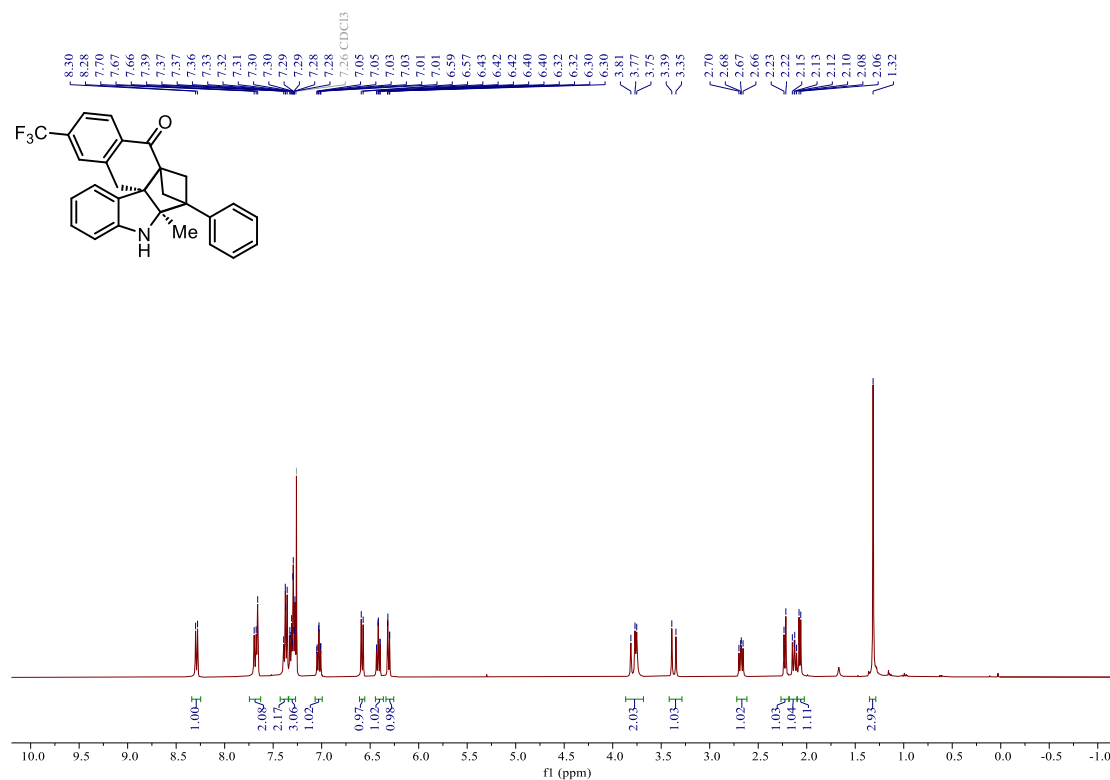
¹H NMR spectra of 2h (CDCl₃, 400 MHz)



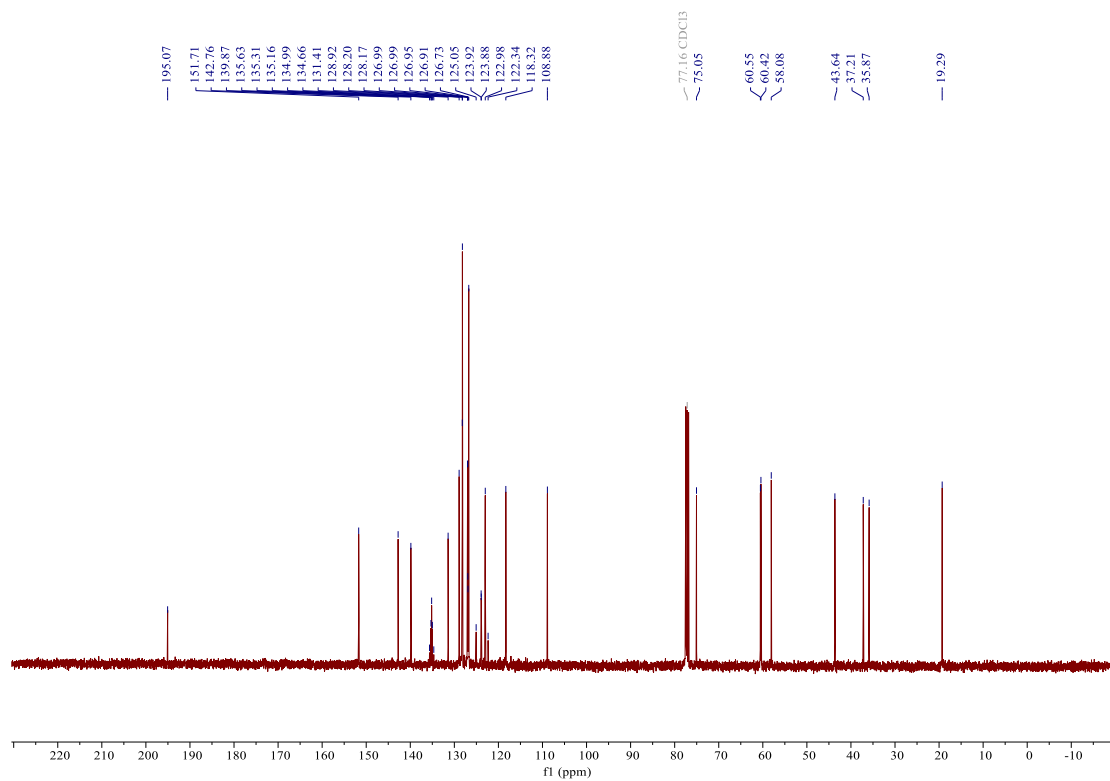
¹³C NMR spectra of 2h (CDCl₃, 101 MHz)



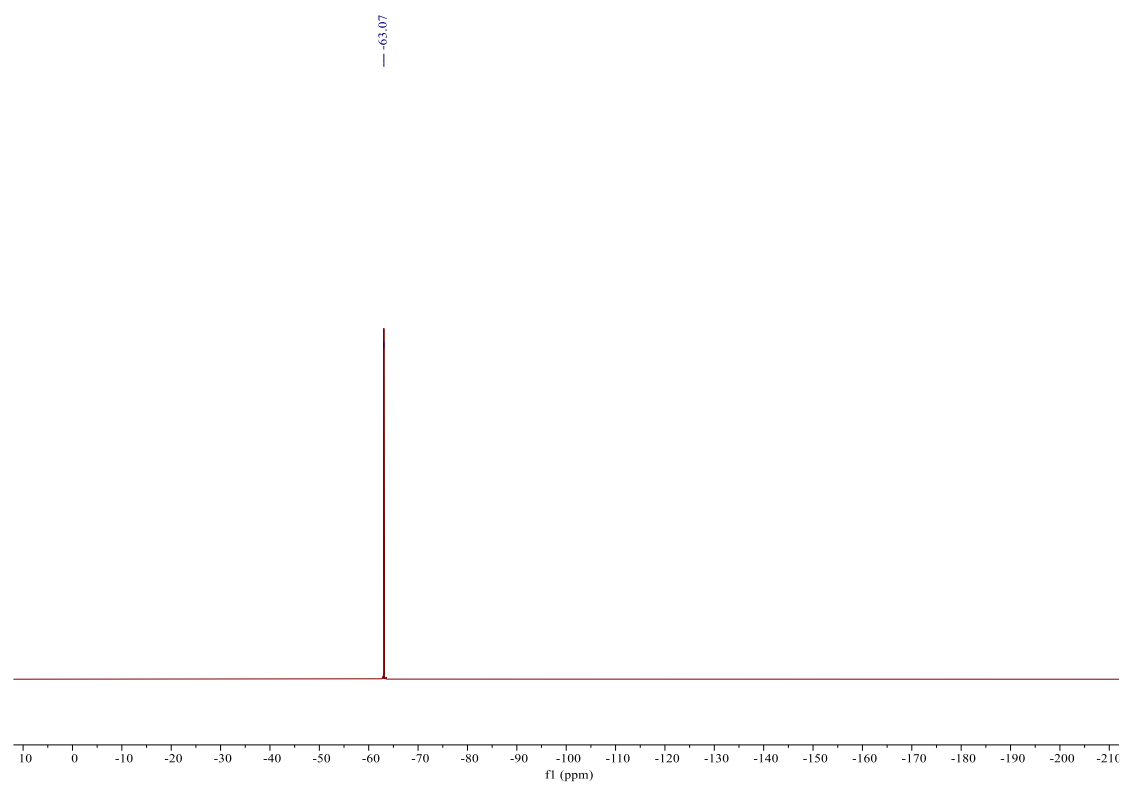
¹H NMR spectra of 2i (CDCl₃, 400 MHz)



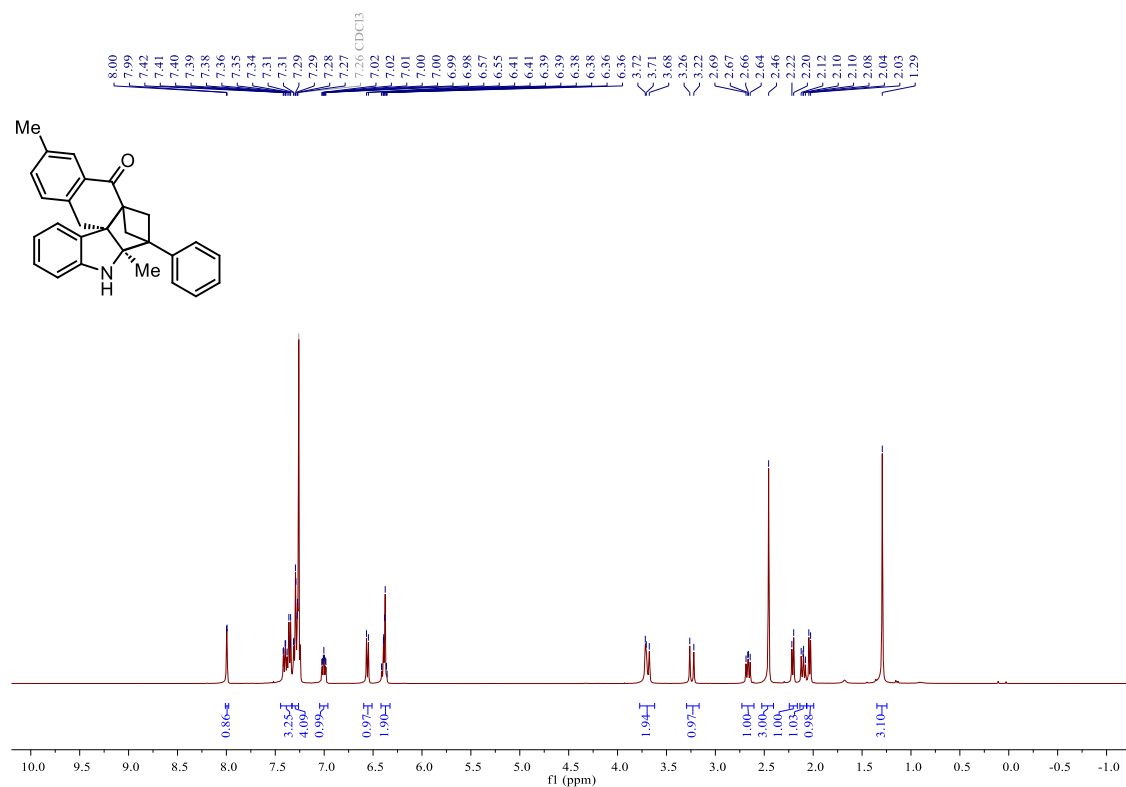
¹³C NMR spectra of 2i (CDCl₃, 101 MHz)



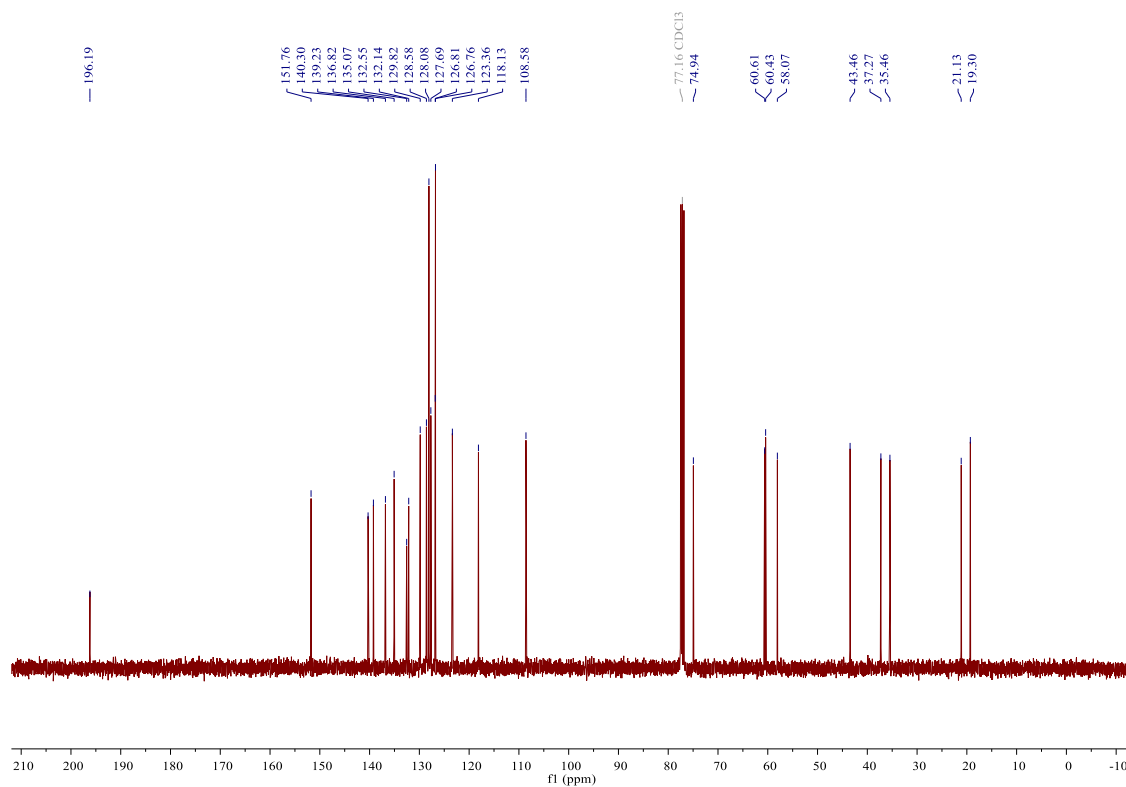
^{19}F NMR spectra of 2i (CDCl₃, 376 MHz)



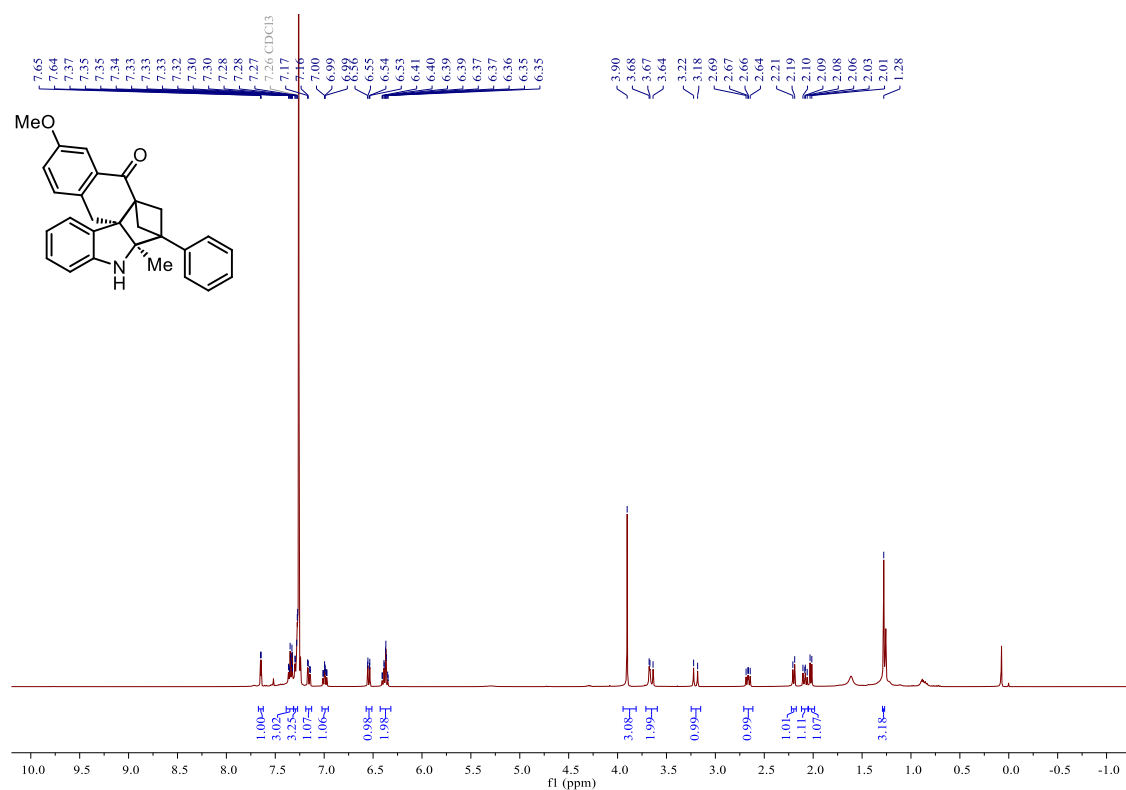
¹H NMR spectra of 2j (CDCl₃, 400 MHz)



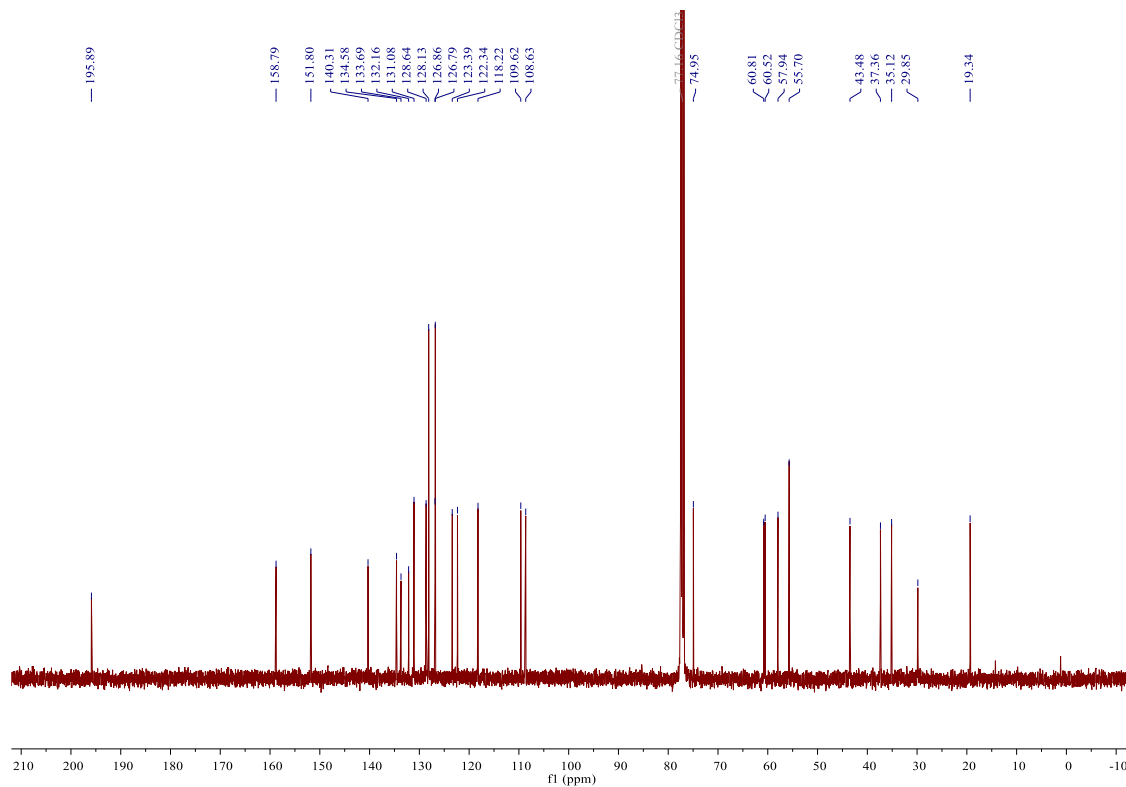
¹³C NMR spectra of 2j (CDCl₃, 101 MHz)



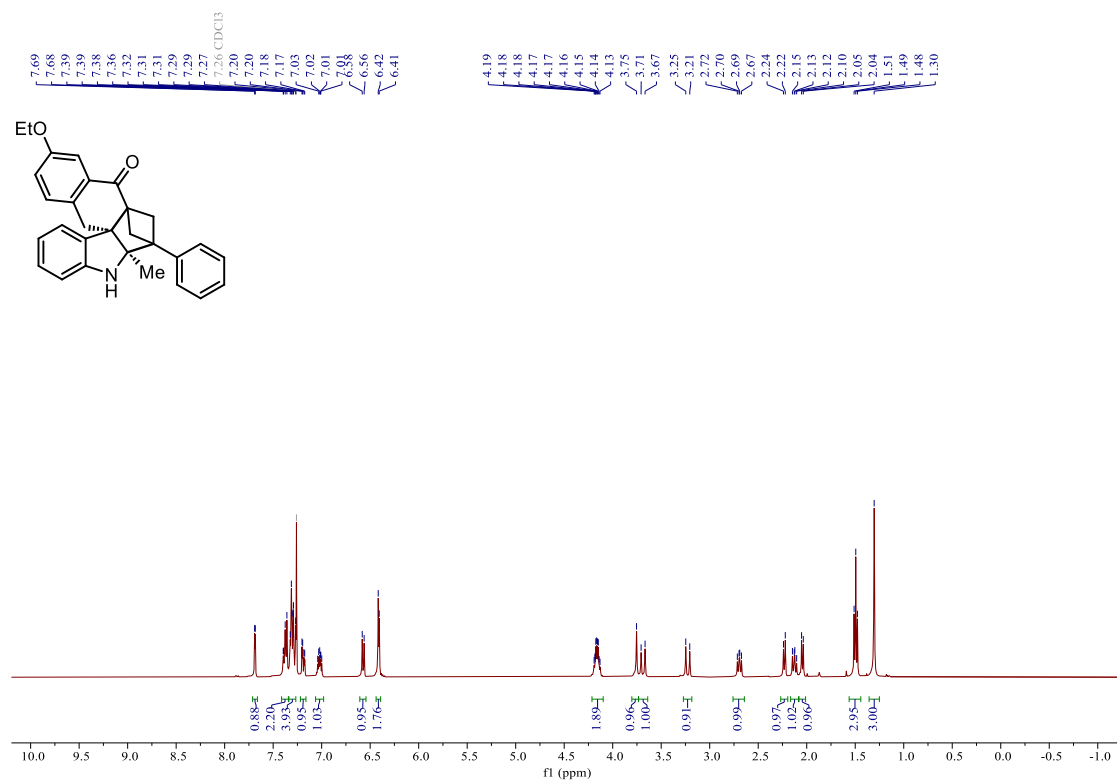
^1H NMR spectra of 2k (CDCl_3 , 400 MHz)



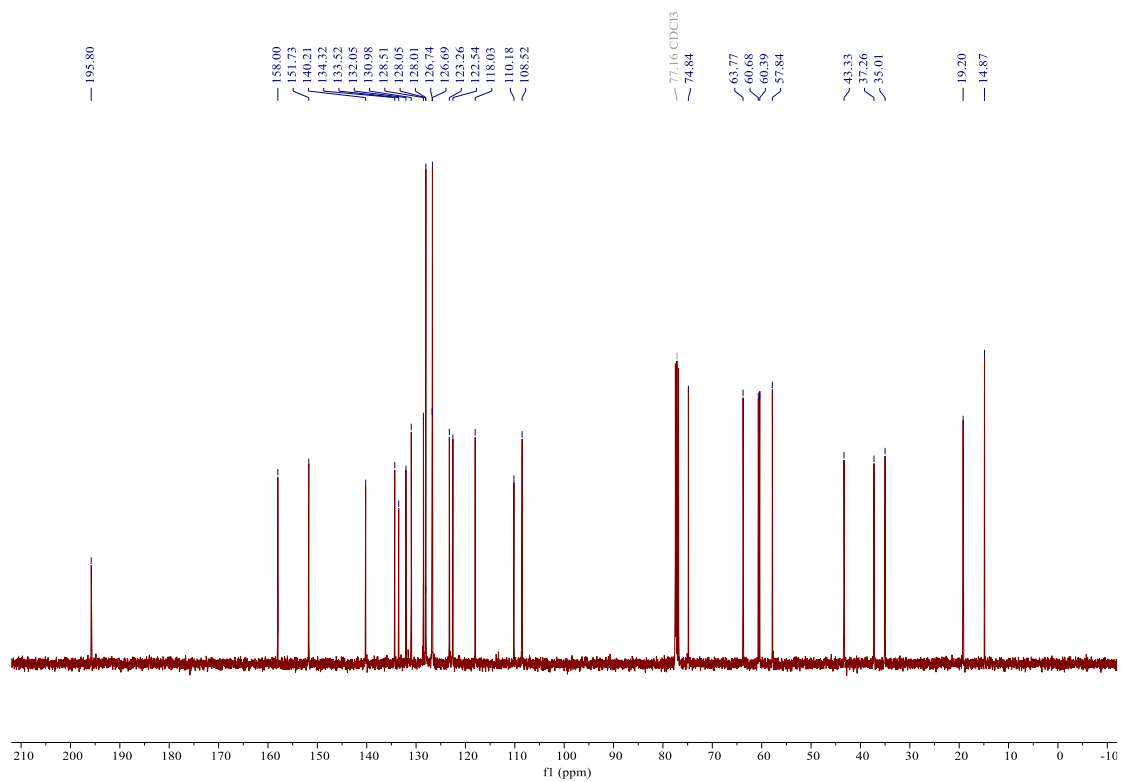
^{13}C NMR spectra of 2k (CDCl_3 , 101 MHz)



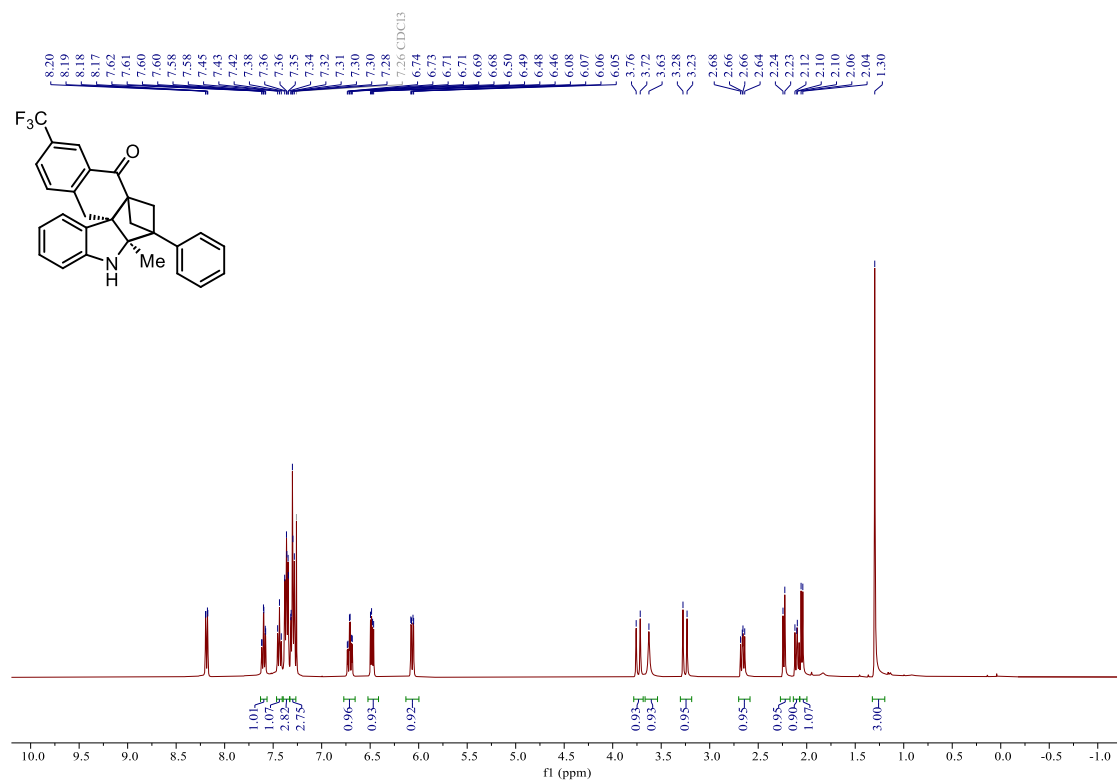
¹H NMR spectra of 2l (CDCl₃, 400 MHz)



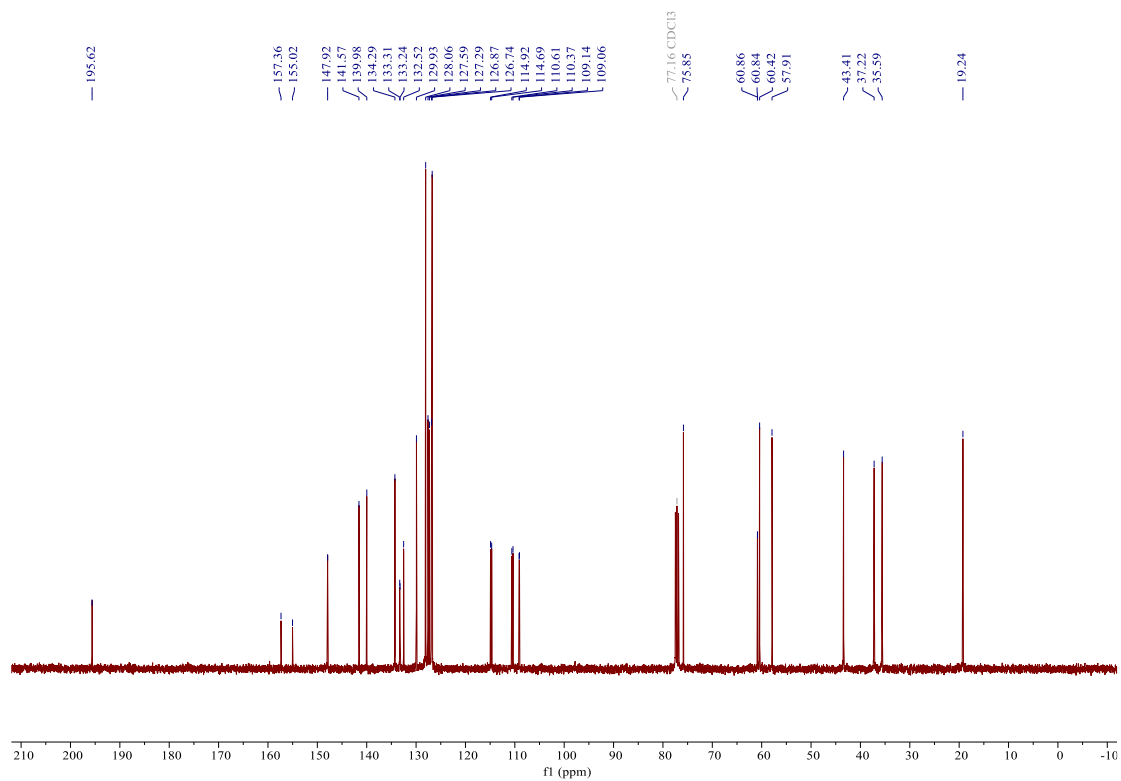
¹³C NMR spectra of 2l (CDCl₃, 101 MHz)



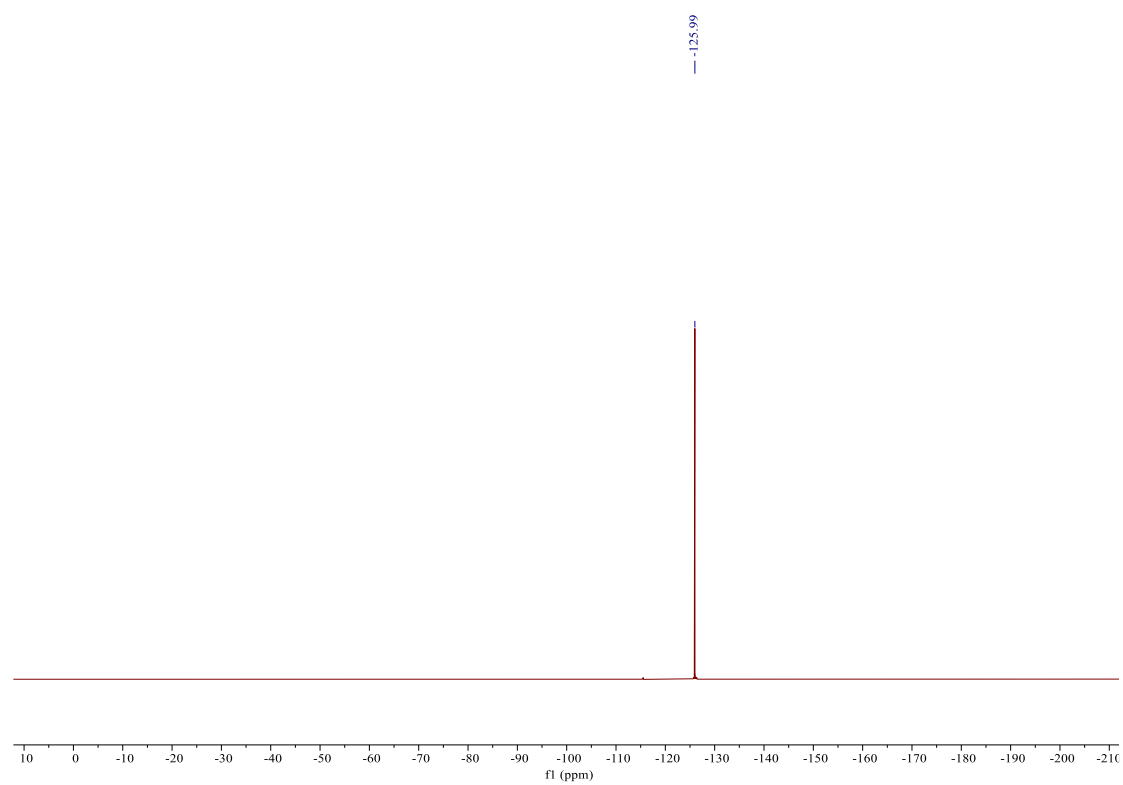
¹H NMR spectra of 2m (CDCl₃, 400 MHz)



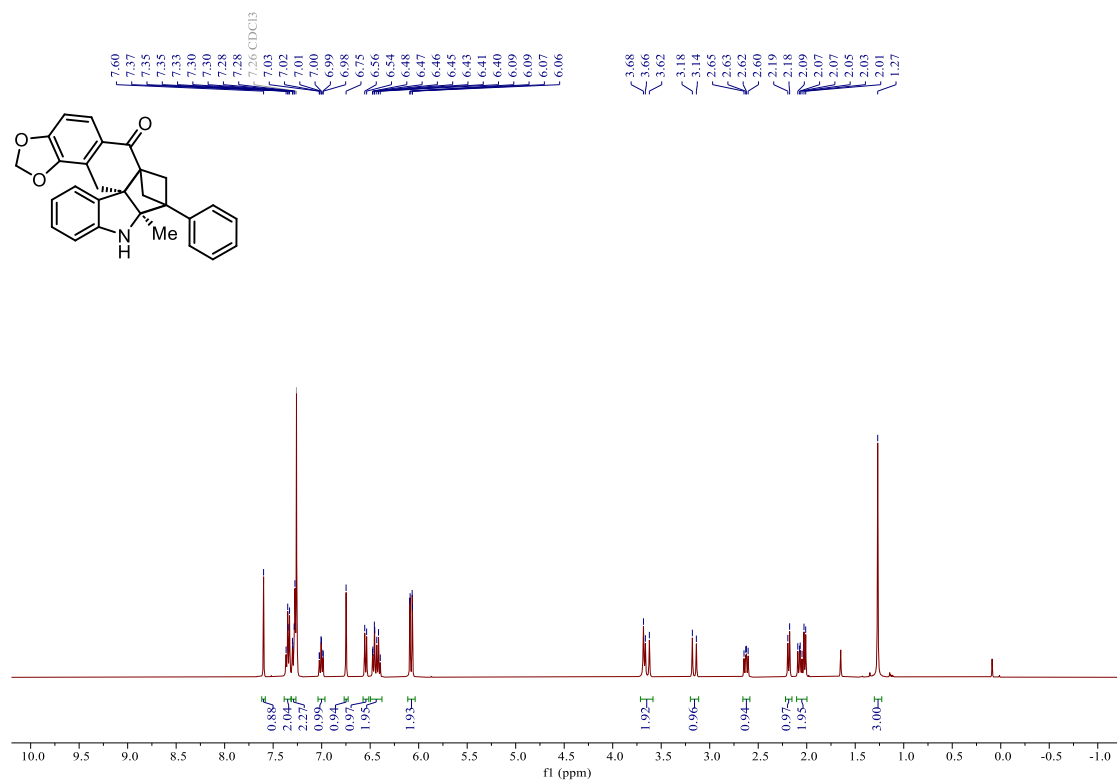
¹³C NMR spectra of 2m (CDCl₃, 101 MHz)



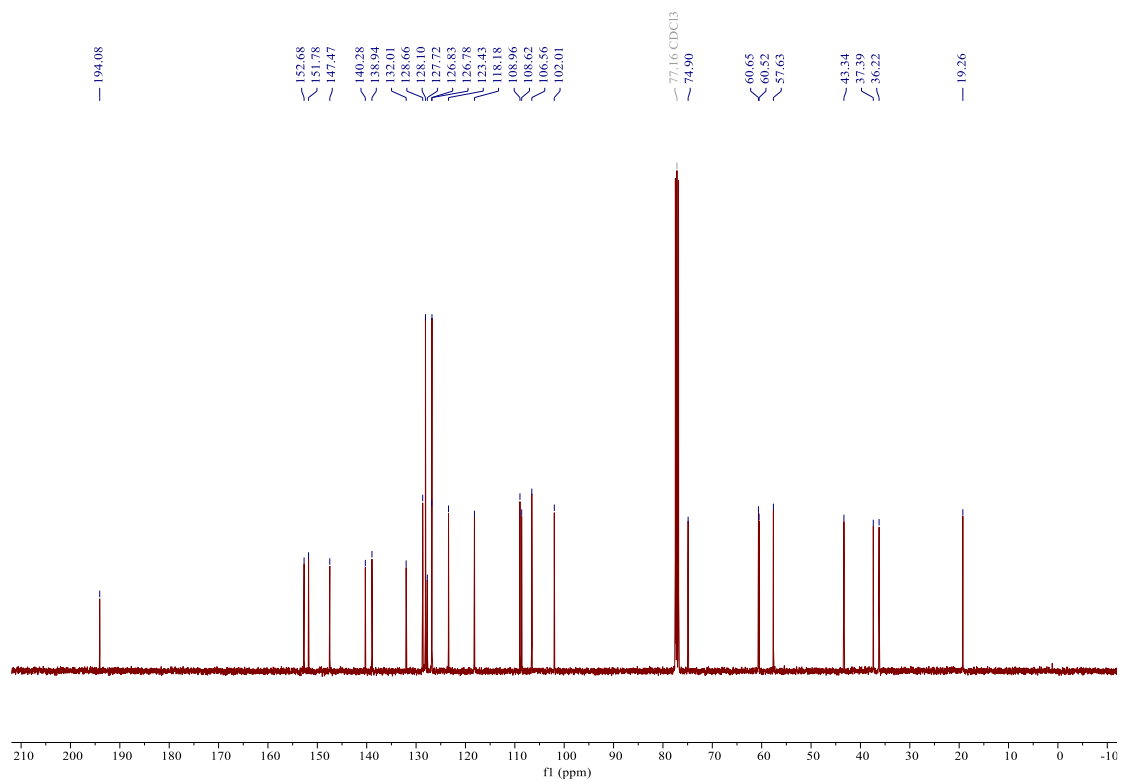
^{19}F NMR spectra of 2m (CDCl_3 , 376 MHz)



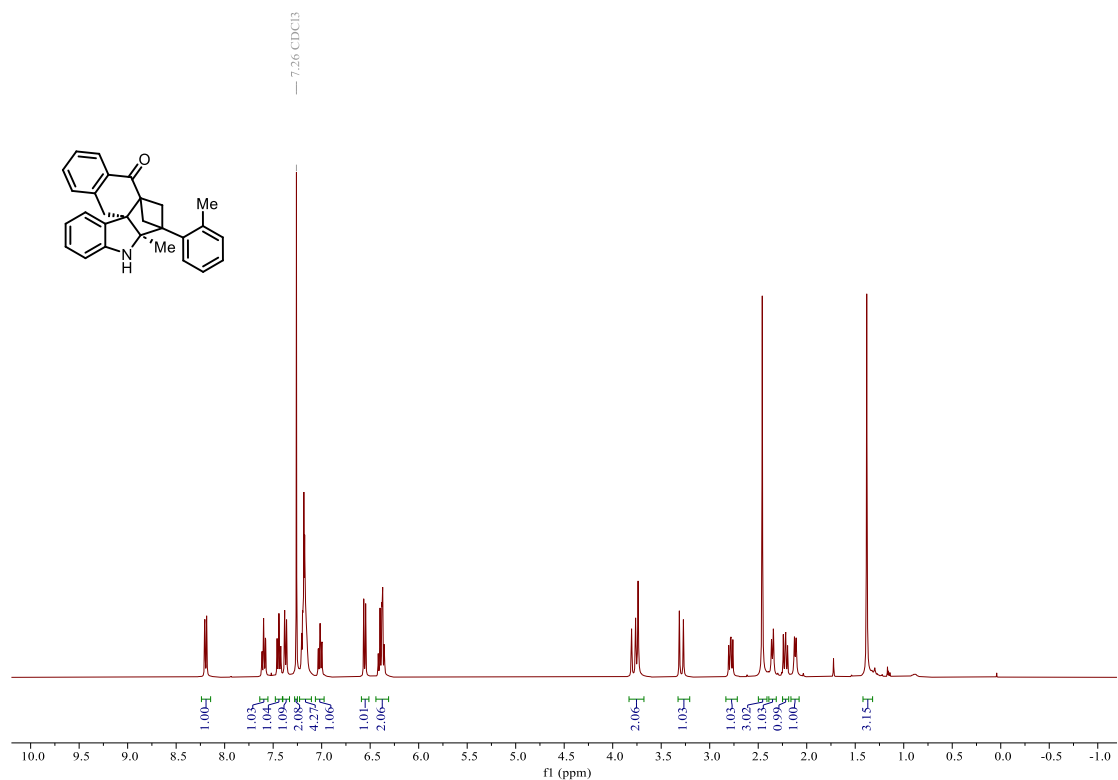
¹H NMR spectra of 2n (CDCl₃, 400 MHz)



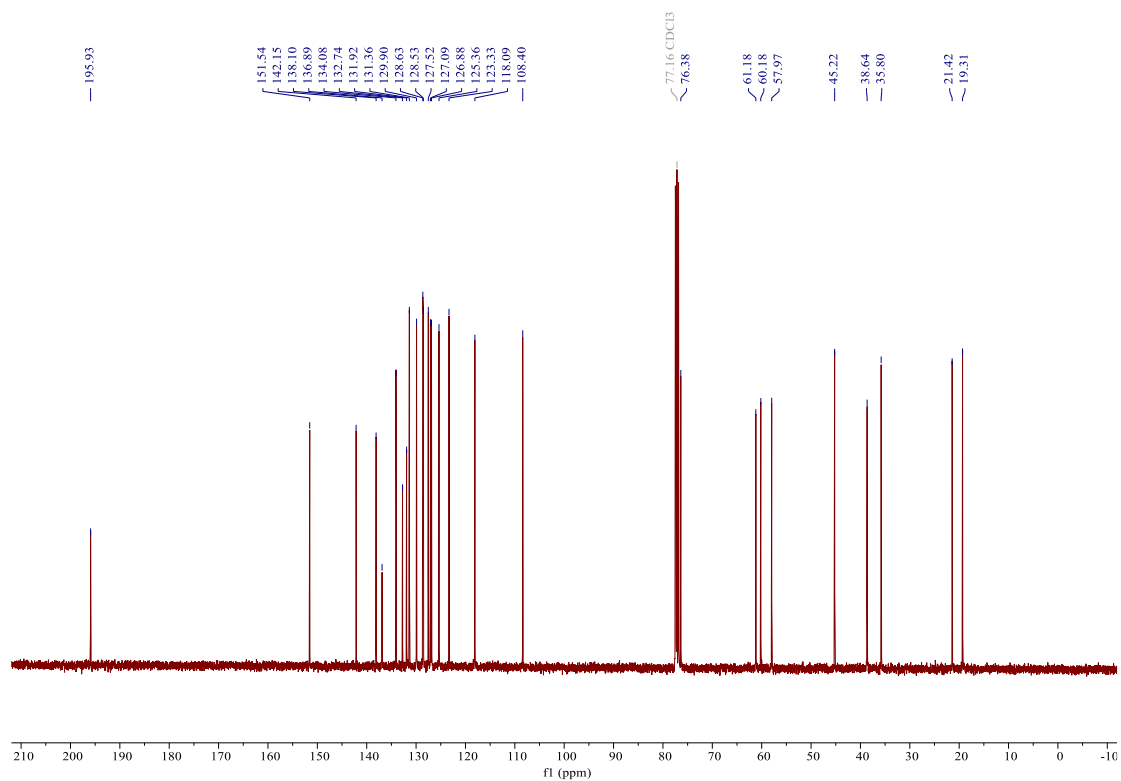
¹³C NMR spectra of 2n (CDCl₃, 101 MHz)



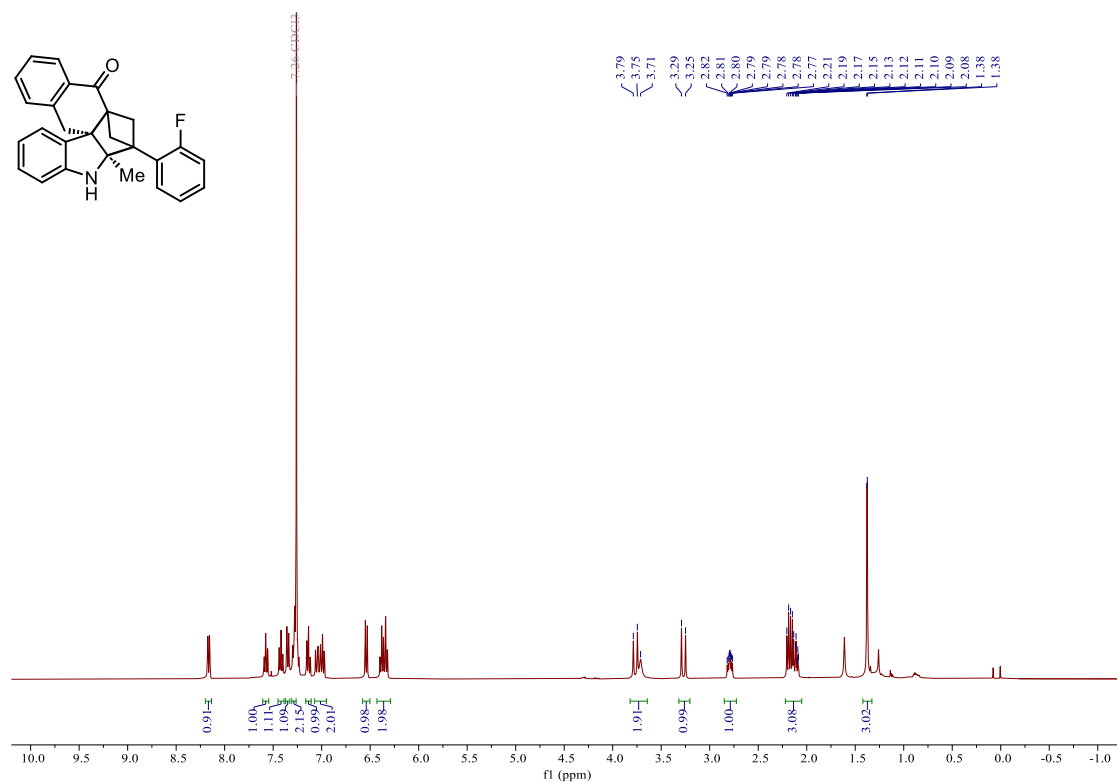
^1H NMR spectra of 2o (CDCl₃, 400 MHz)



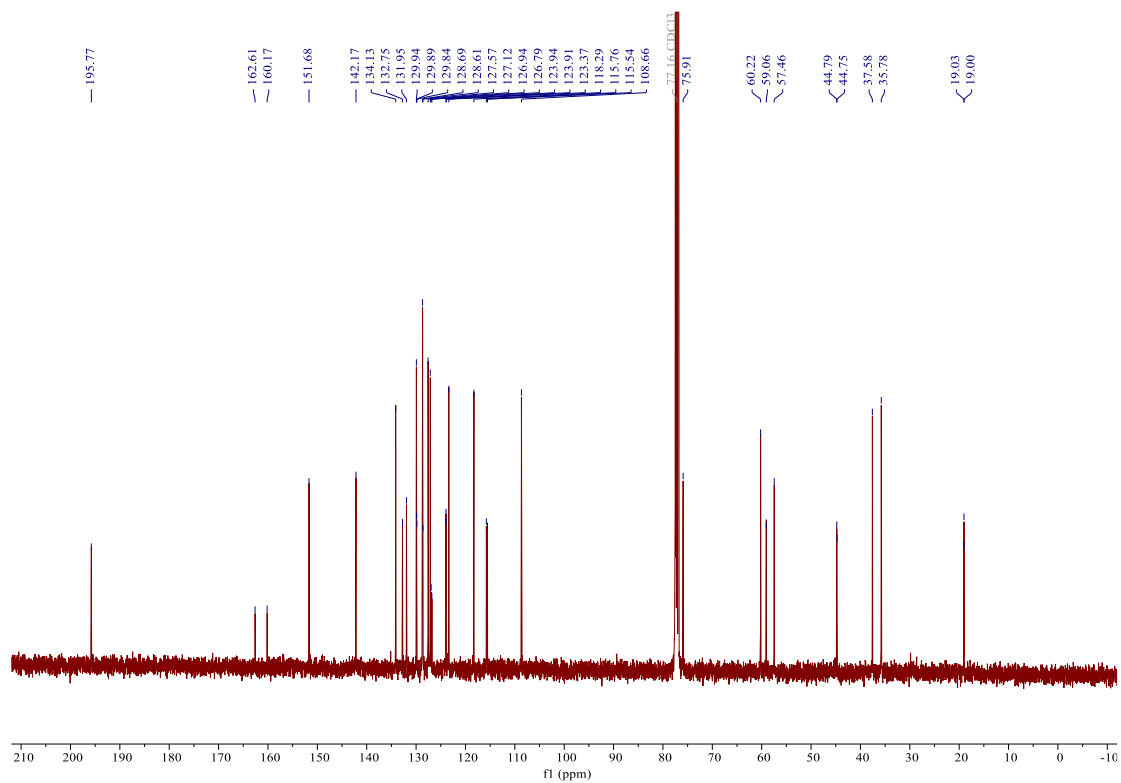
^{13}C NMR spectra of 2o (CDCl₃, 101 MHz)



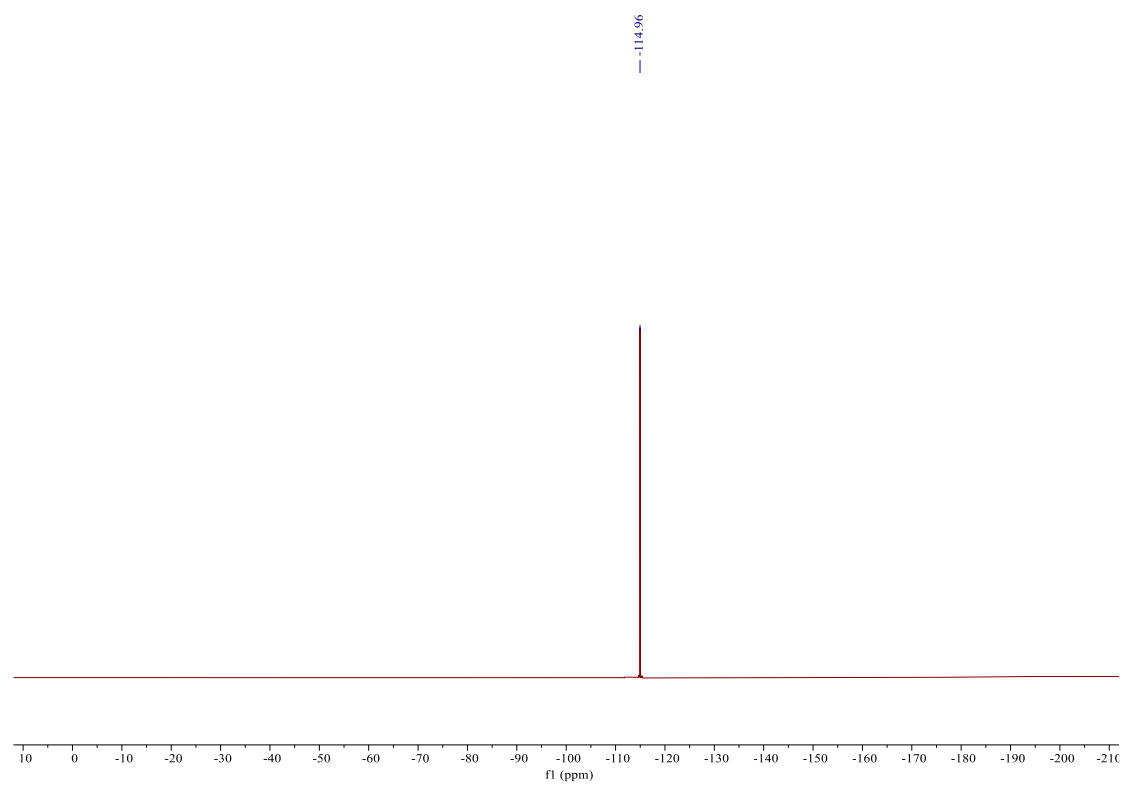
^1H NMR spectra of 2p (CDCl₃, 400 MHz)



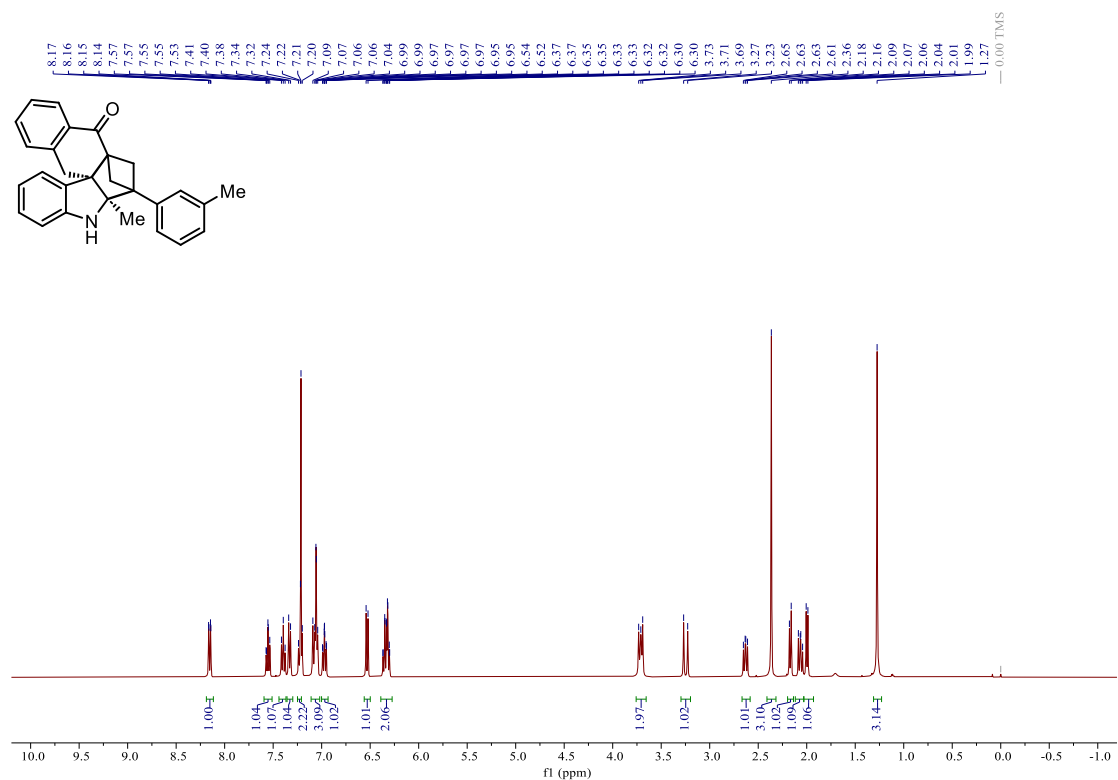
^{13}C NMR spectra of 2p (CDCl₃, 101 MHz)



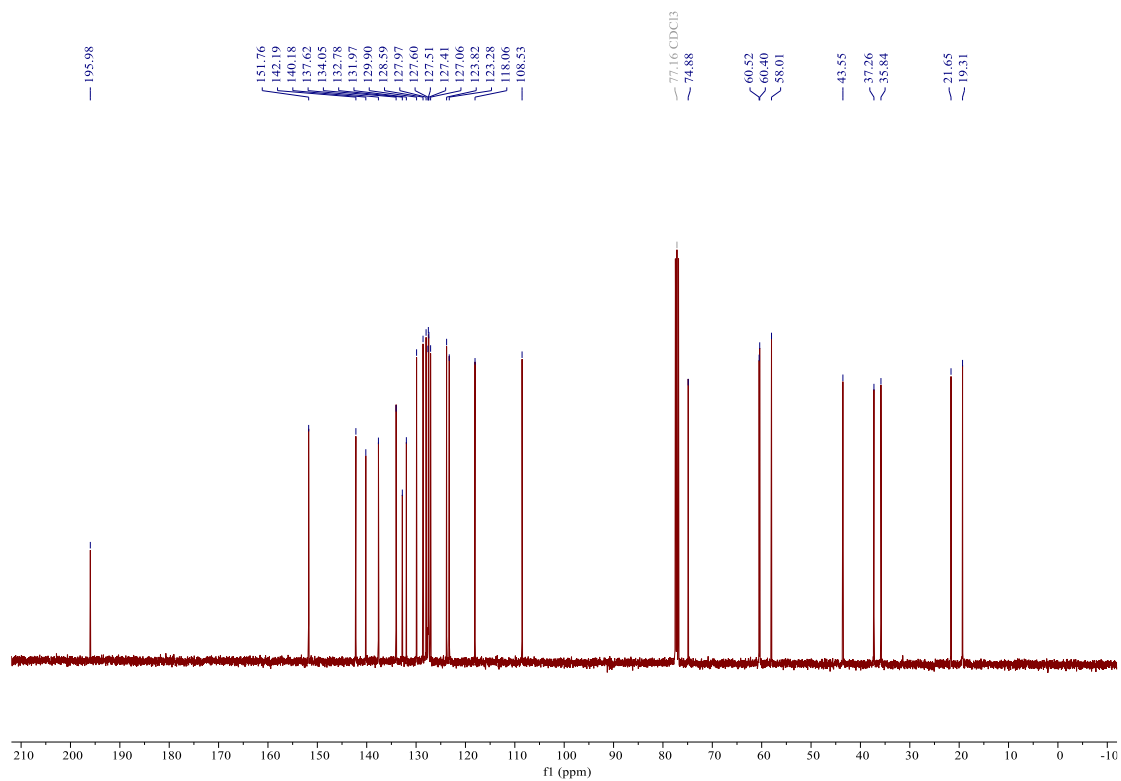
^{19}F NMR spectra of 2p (CDCl_3 , 376 MHz)



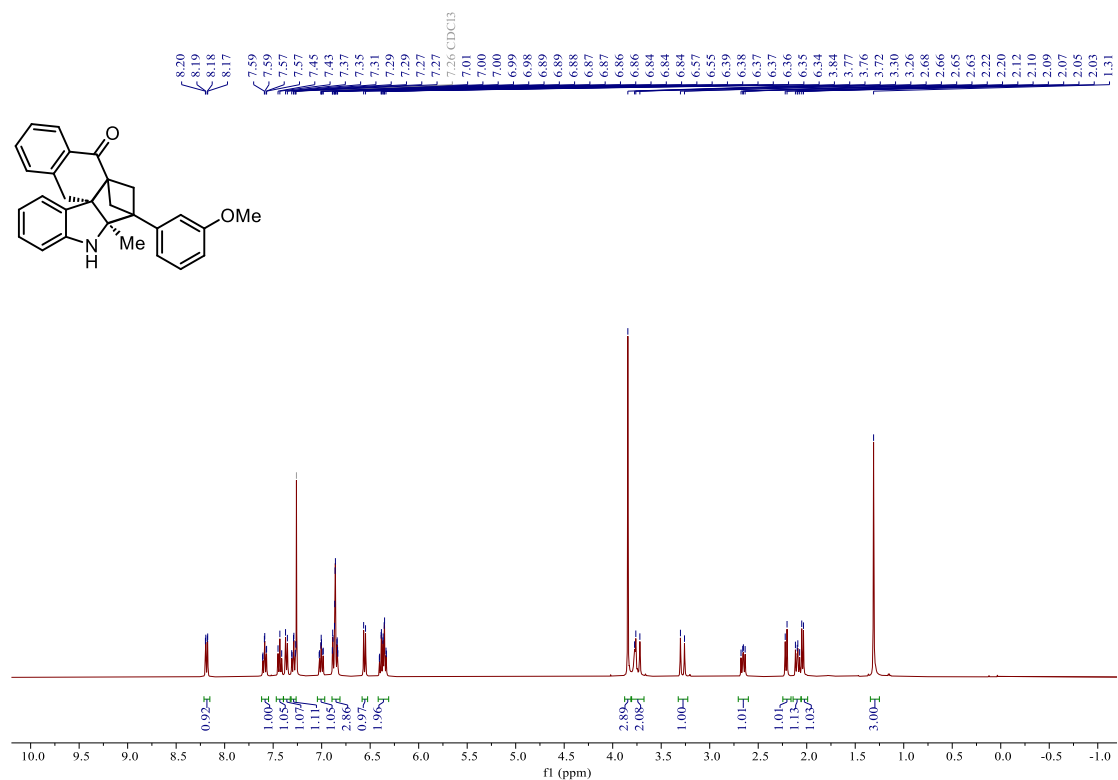
¹H NMR spectra of 2q (CDCl₃, 400 MHz)



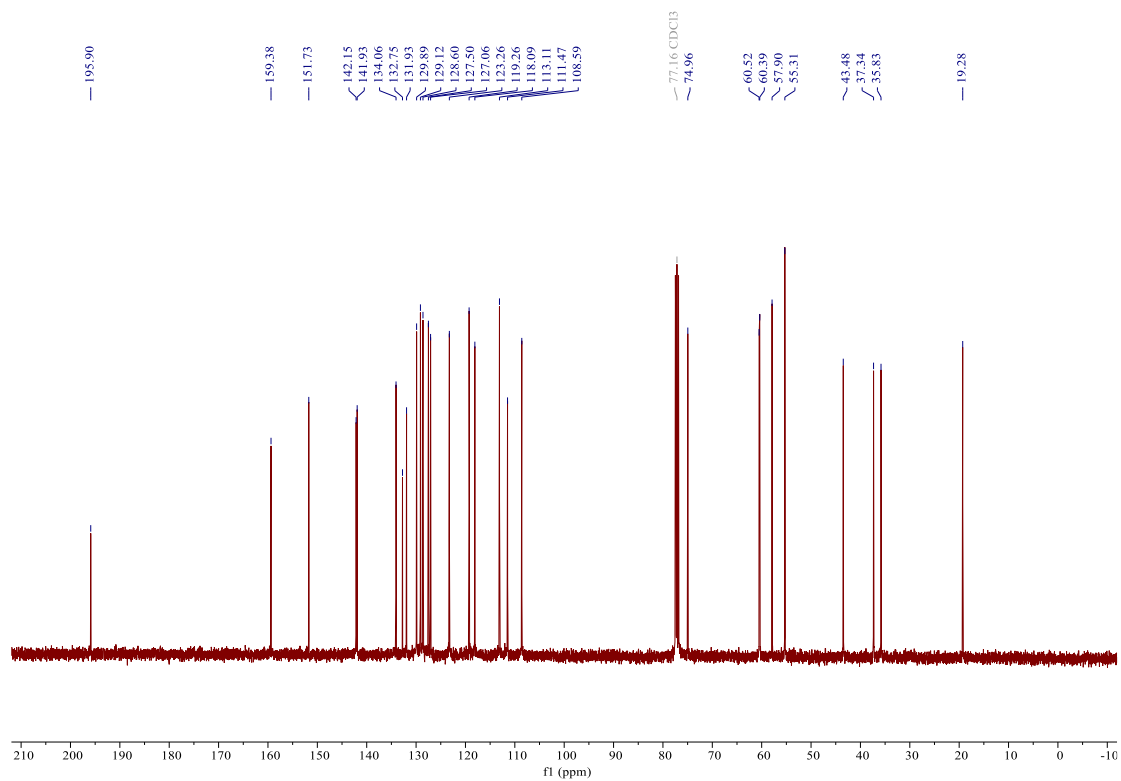
¹³C NMR spectra of 2q (CDCl₃, 101 MHz)



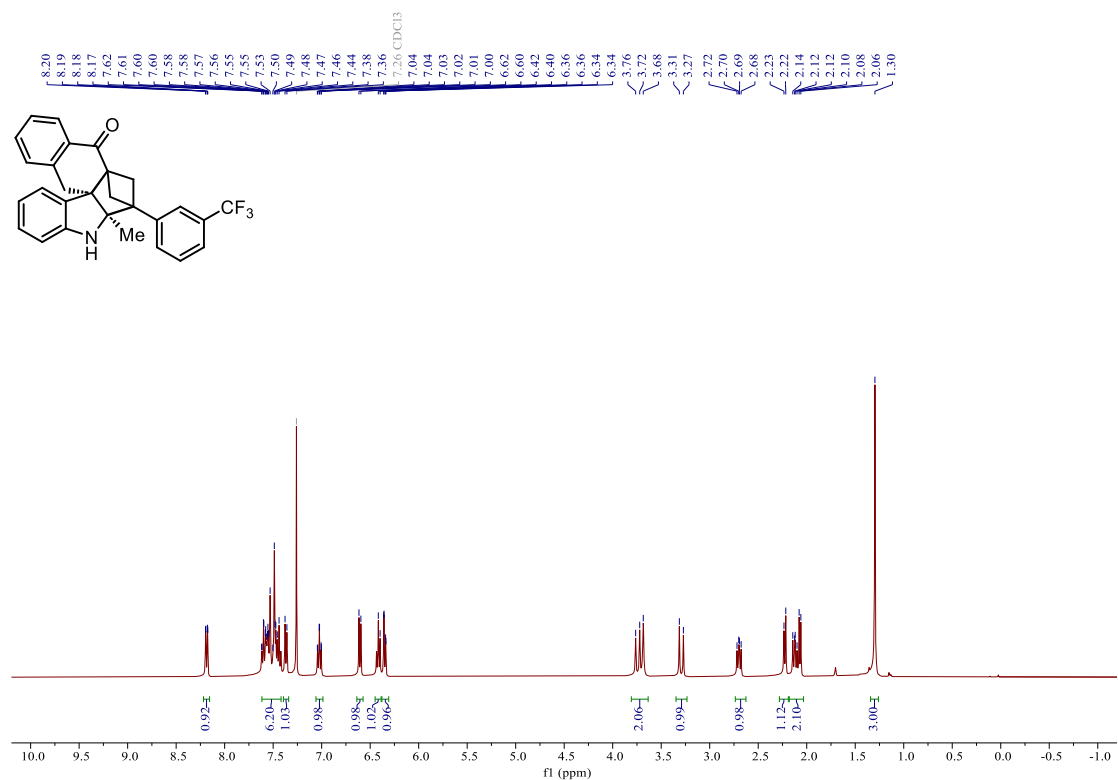
^1H NMR spectra of 2r (CDCl_3 , 400 MHz)



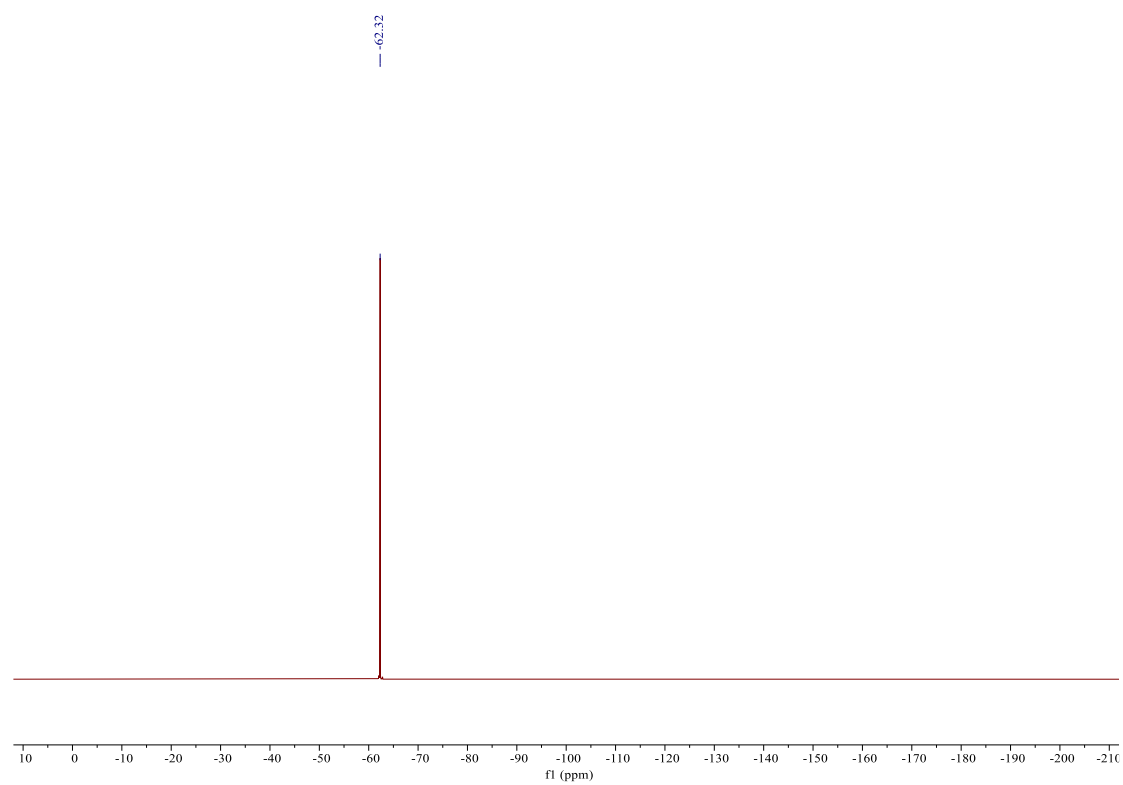
^{13}C NMR spectra of 2r (CDCl_3 , 101 MHz)



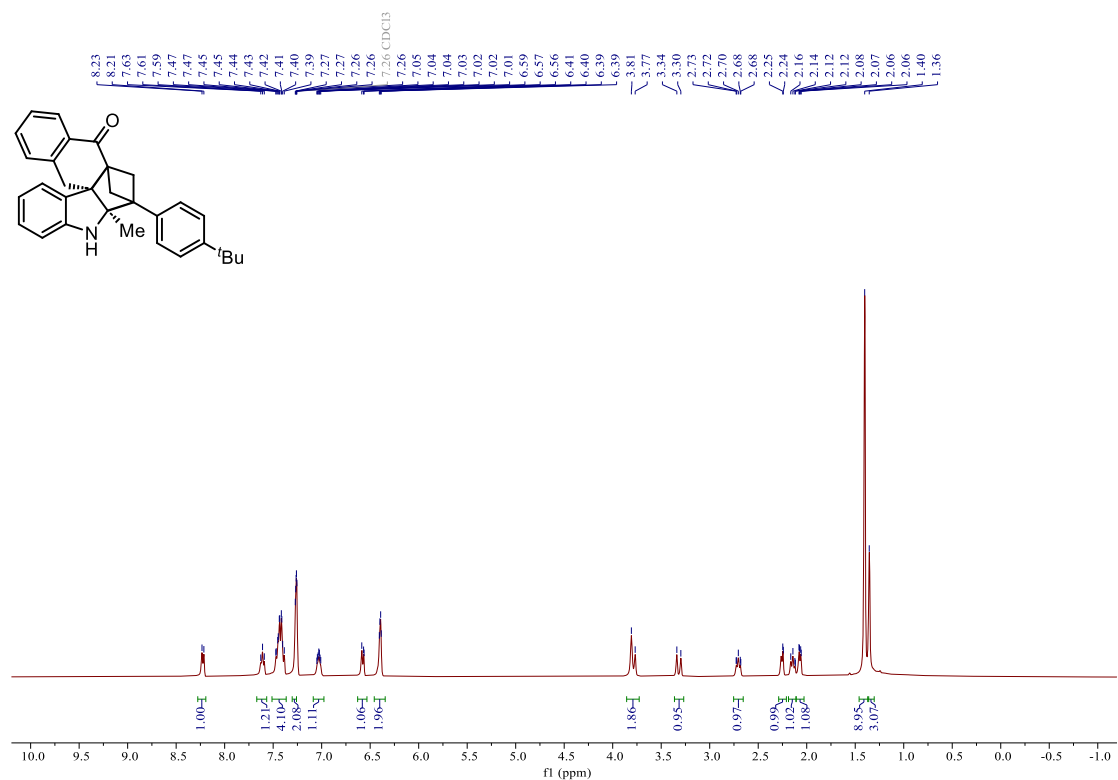
¹H NMR spectra of 2s (CDCl₃, 400 MHz)



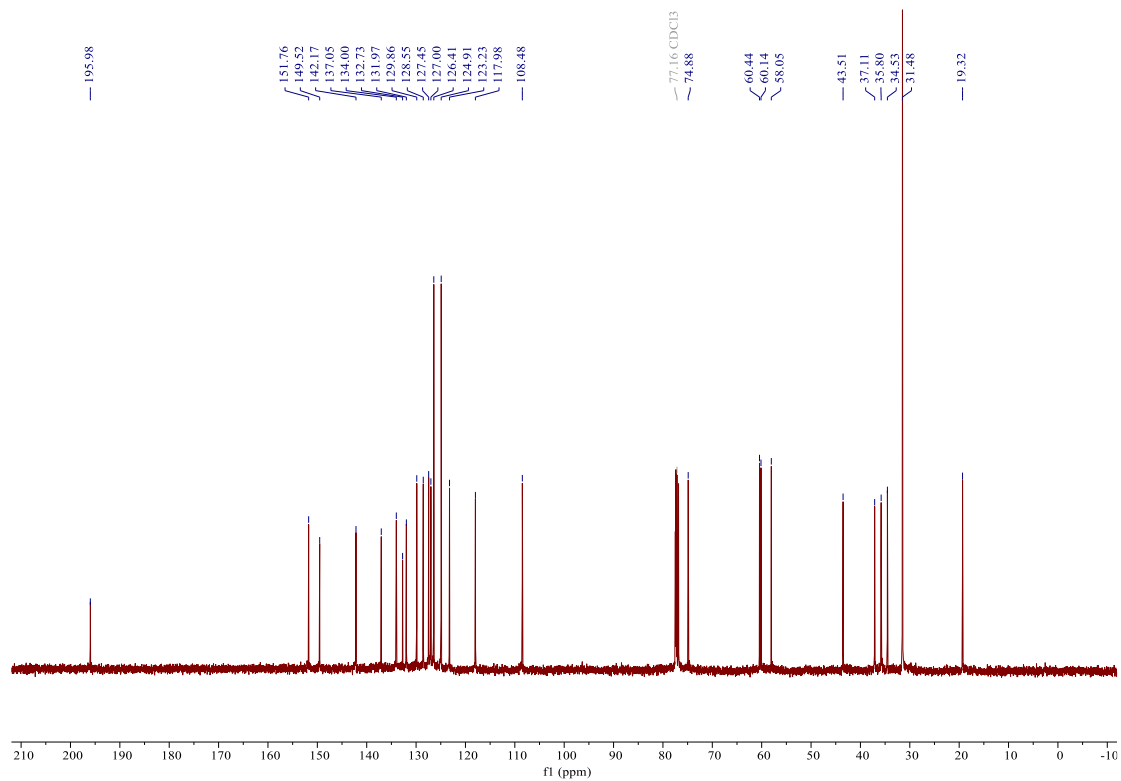
^{19}F NMR spectra of 2s (CDCl_3 , 376 MHz)



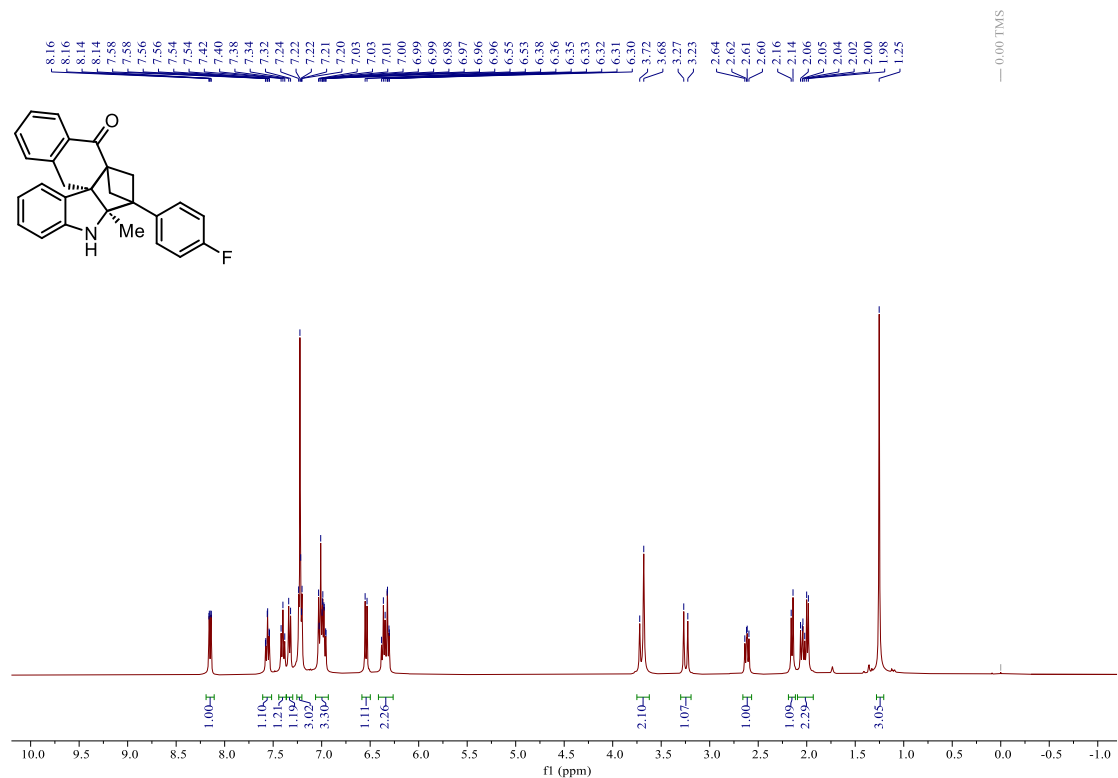
¹H NMR spectra of 2t (CDCl₃, 400 MHz)



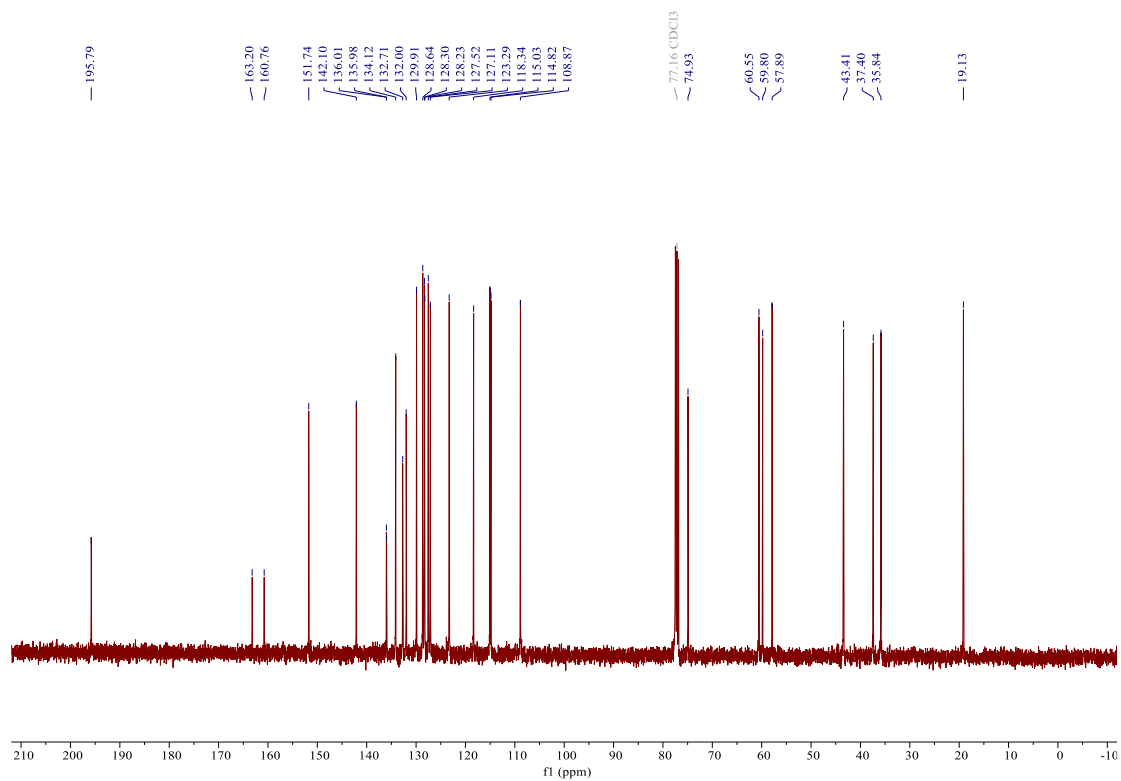
¹³C NMR spectra of 2t (CDCl₃, 101 MHz)



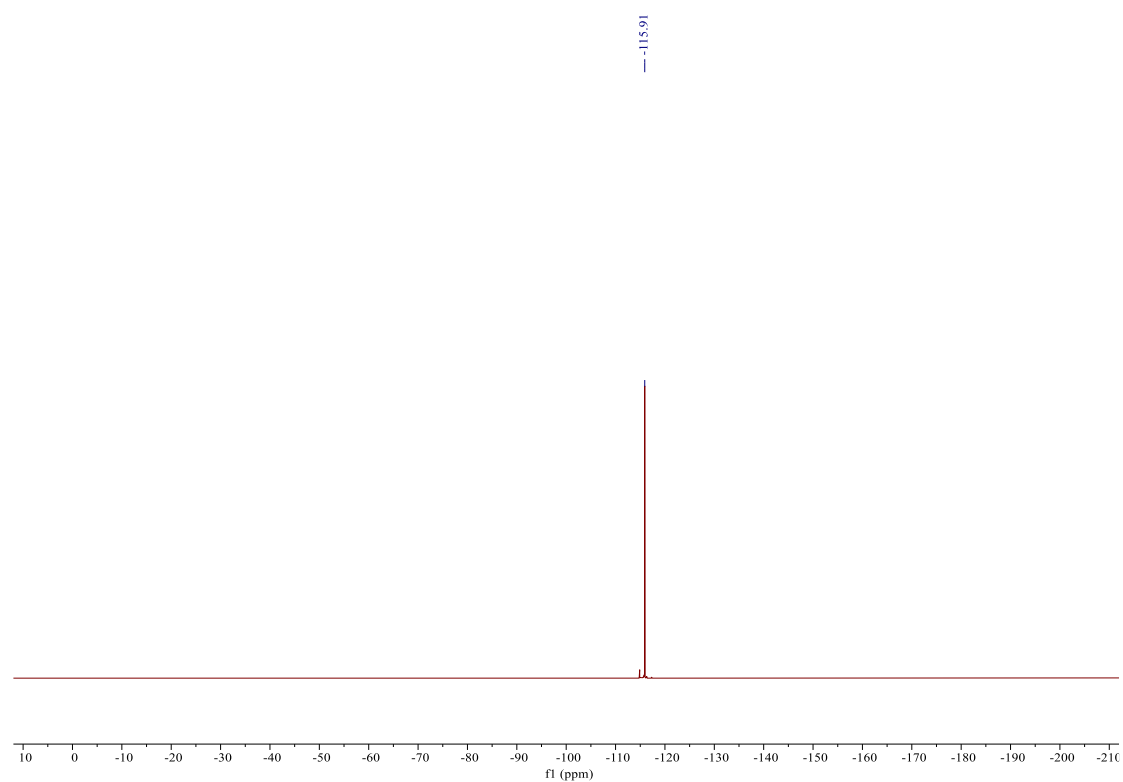
¹H NMR spectra of 2u (CDCl₃, 400 MHz)



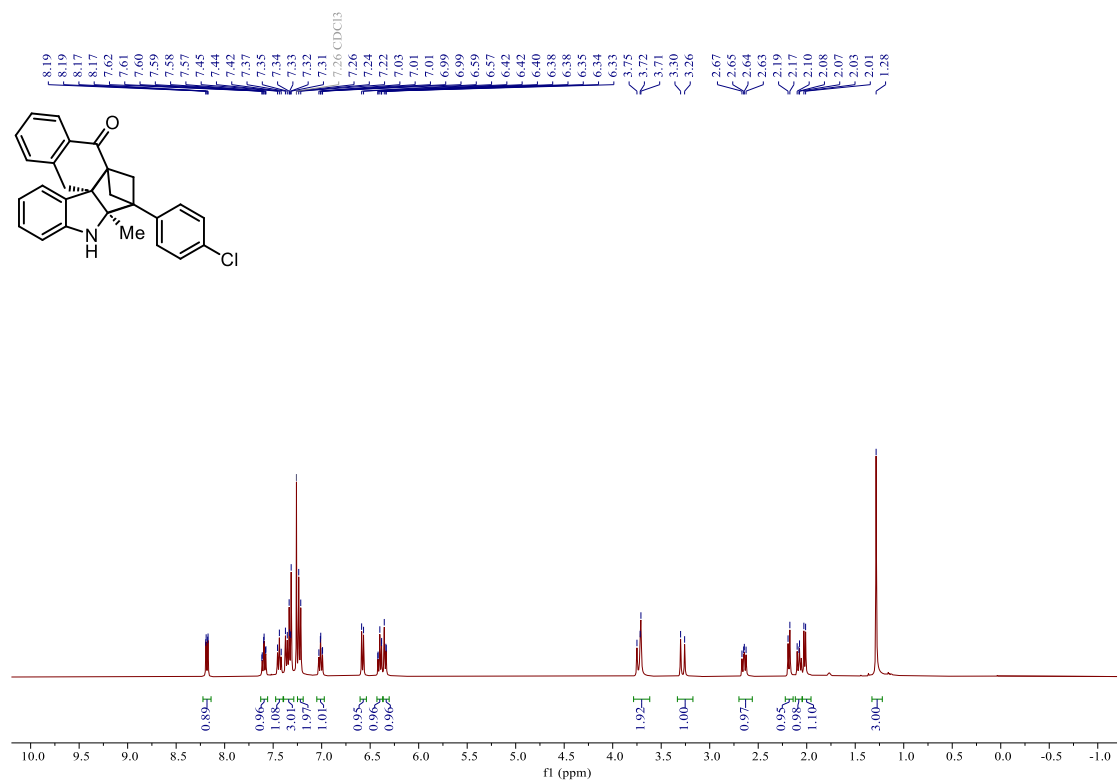
¹³C NMR spectra of 2u (CDCl₃, 101 MHz)



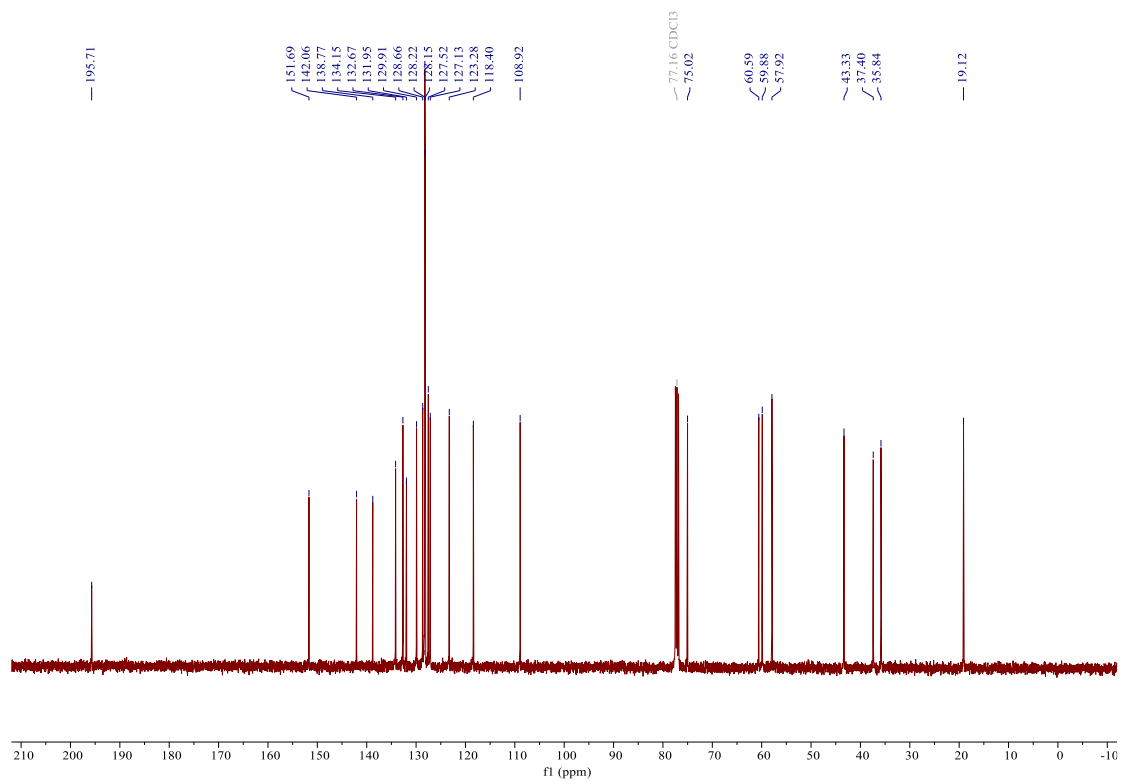
^{13}C NMR spectra of 2u (CDCl_3 , 101 MHz)



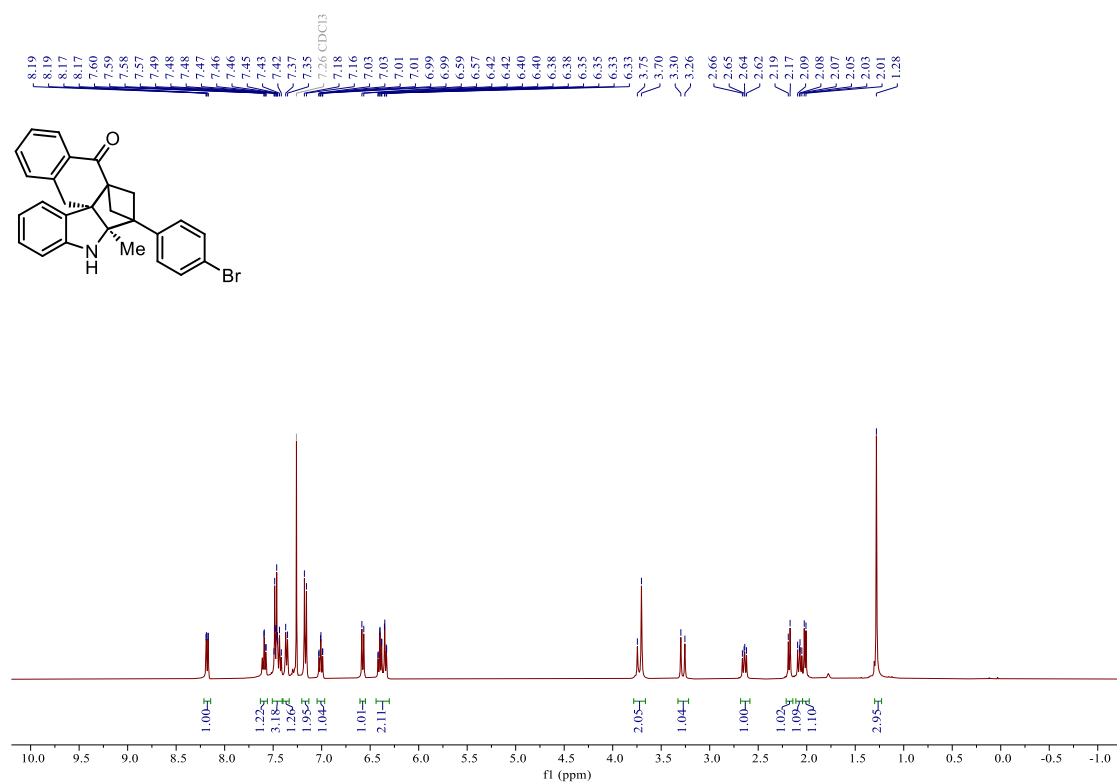
¹H NMR spectra of 2v (CDCl₃, 400 MHz)



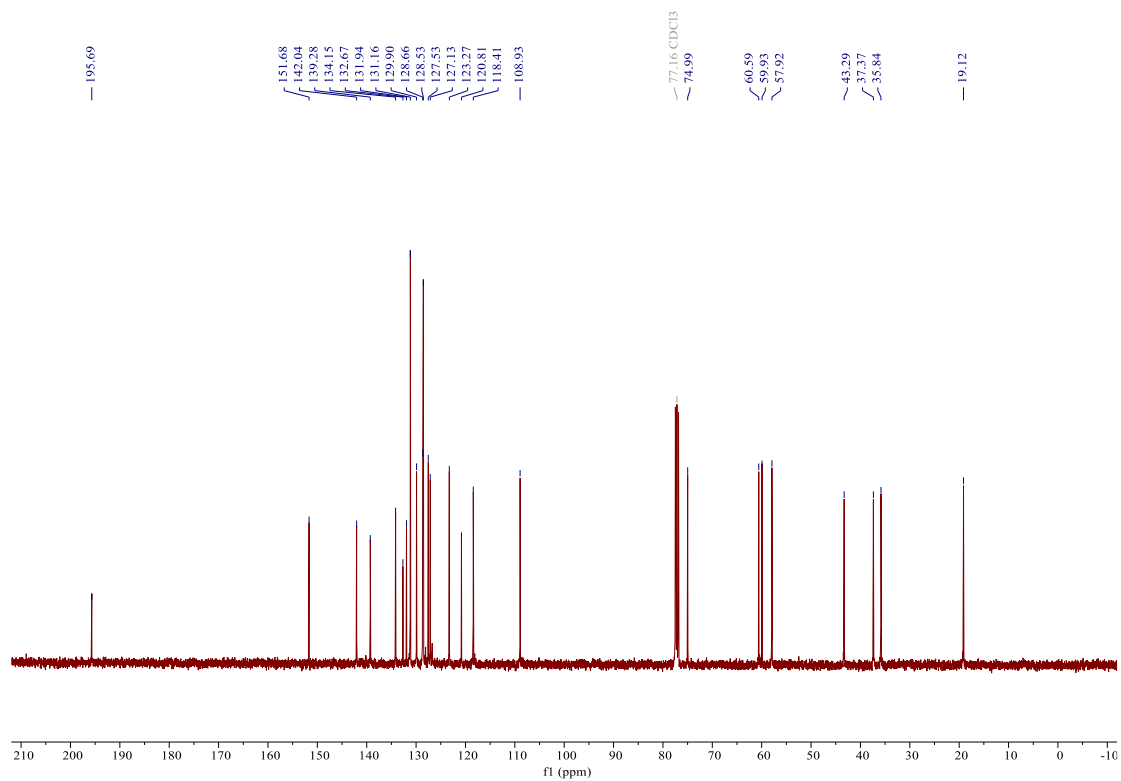
¹³C NMR spectra of 2v (CDCl₃, 101 MHz)



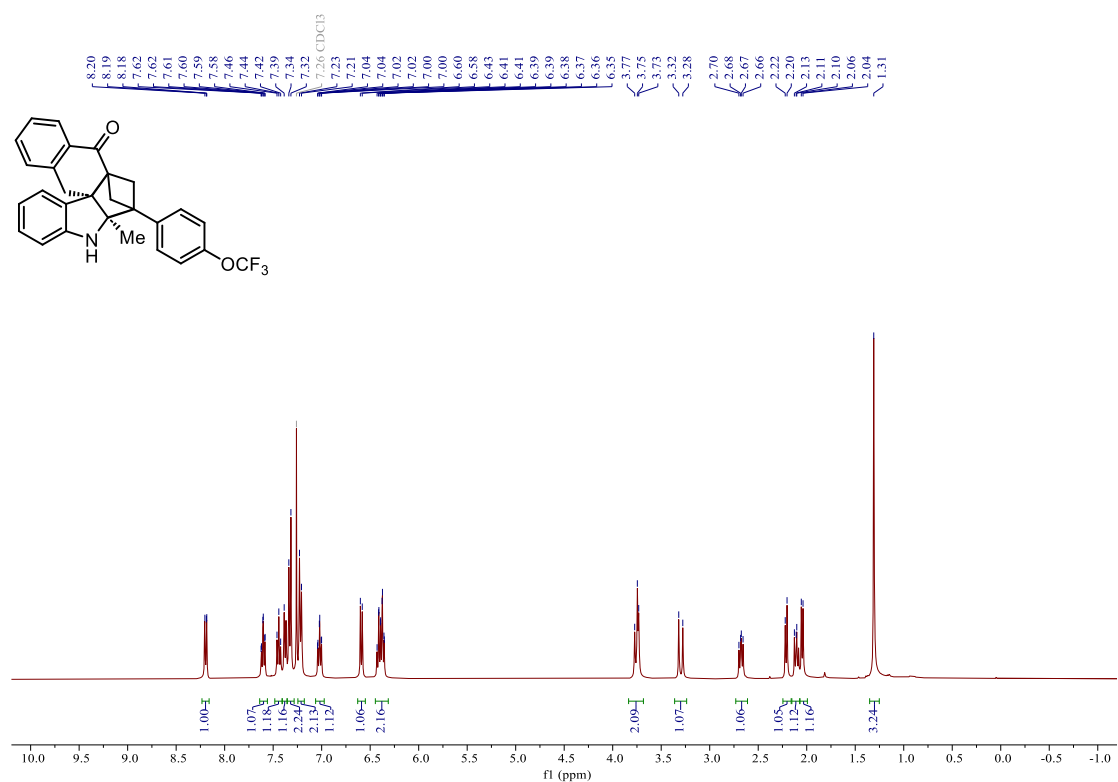
¹H NMR spectra of 2w (CDCl₃, 400 MHz)



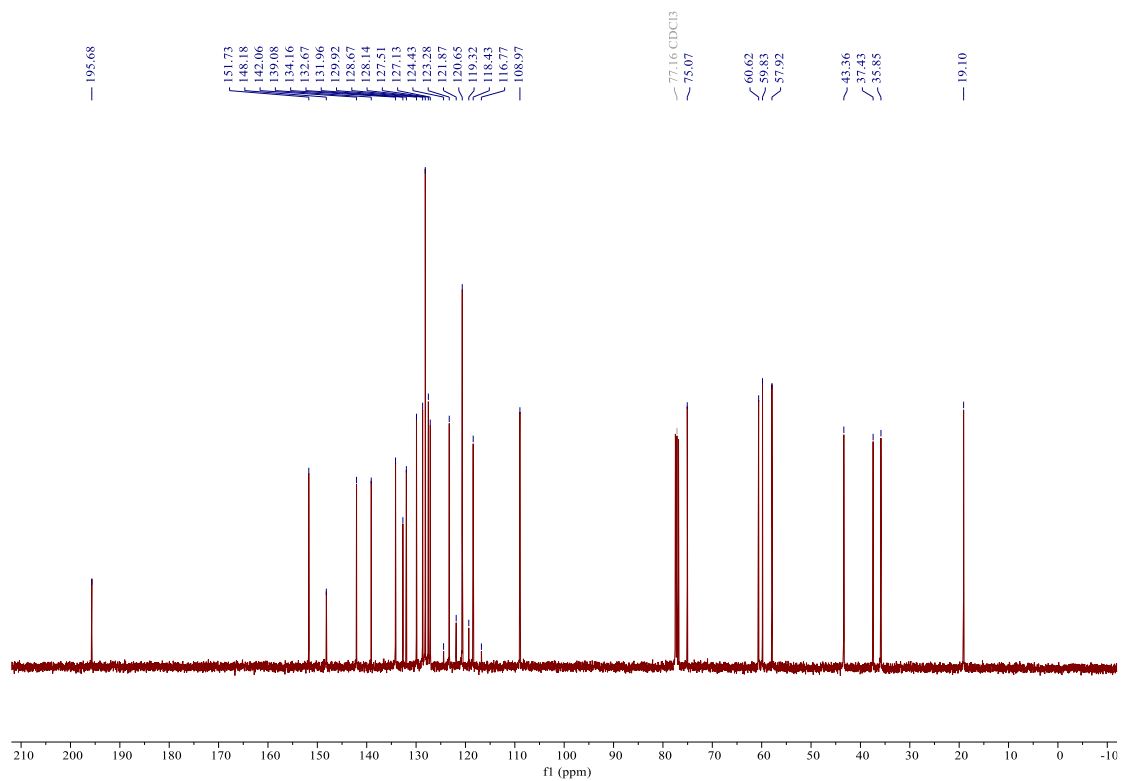
¹³C NMR spectra of 2w (CDCl₃, 101 MHz)



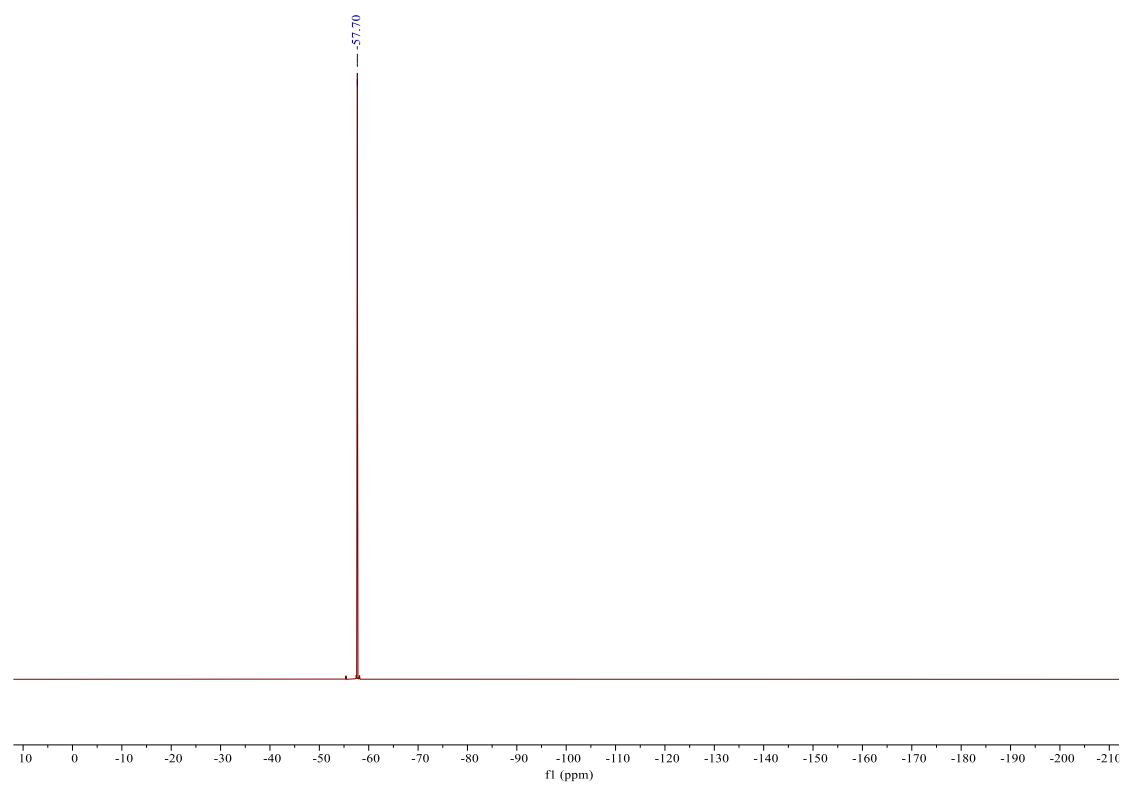
¹H NMR spectra of 2x (CDCl₃, 400 MHz)



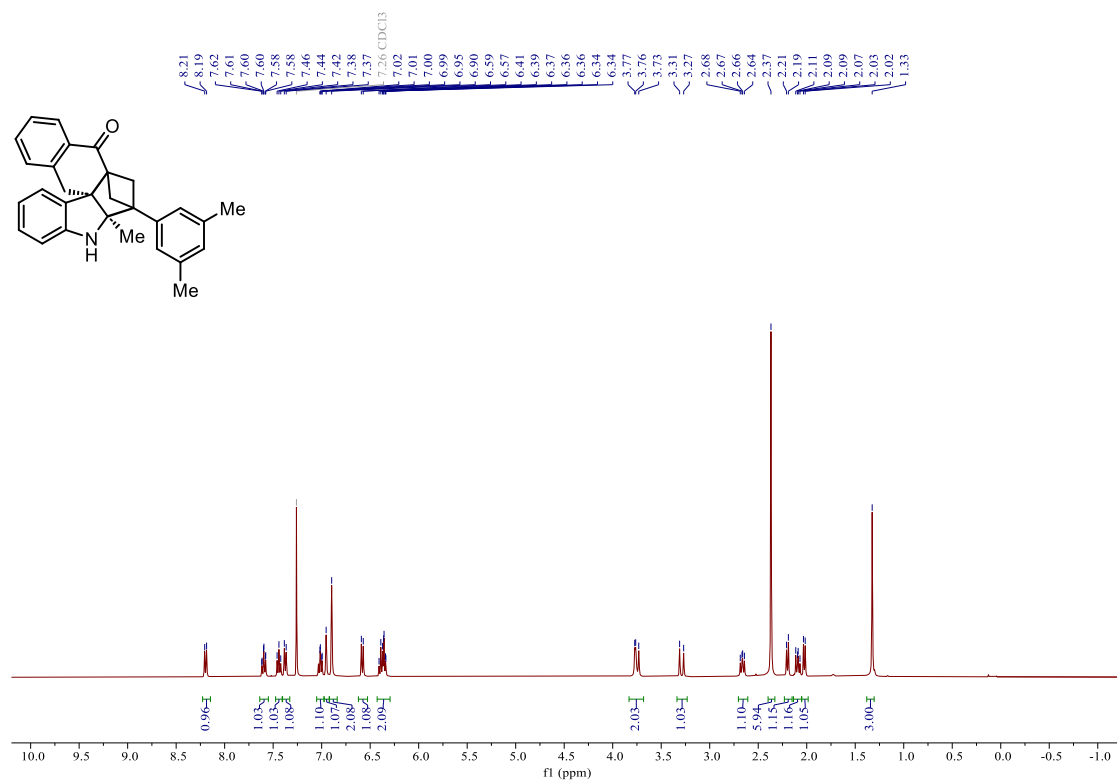
¹³C NMR spectra of 2x (CDCl₃, 101 MHz)



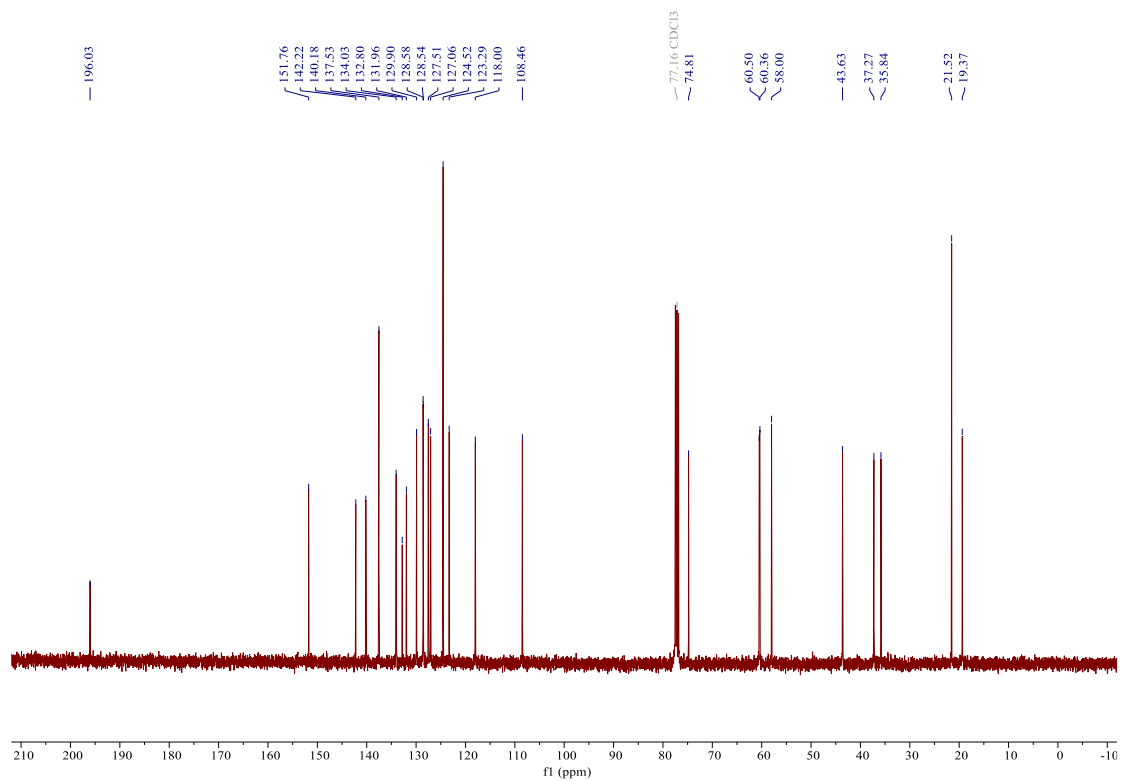
^{19}F NMR spectra of 2x (CDCl₃, 376 MHz)



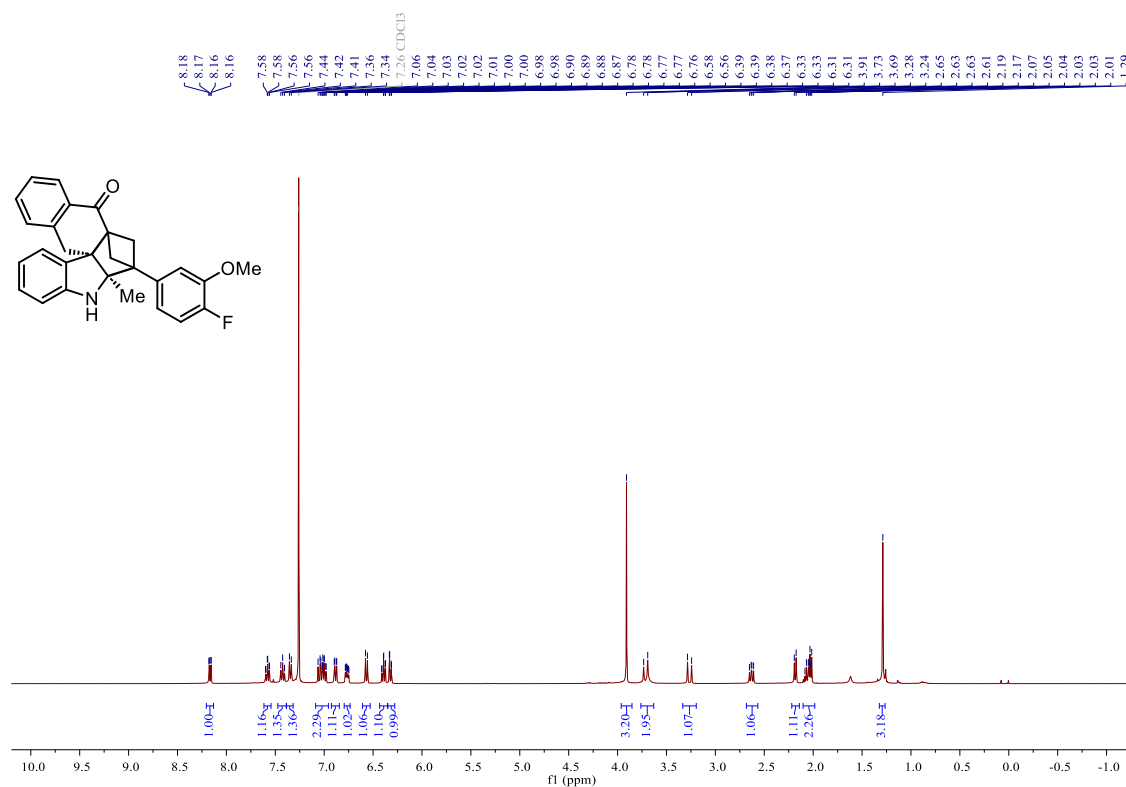
^1H NMR spectra of 2y (CDCl_3 , 400 MHz)



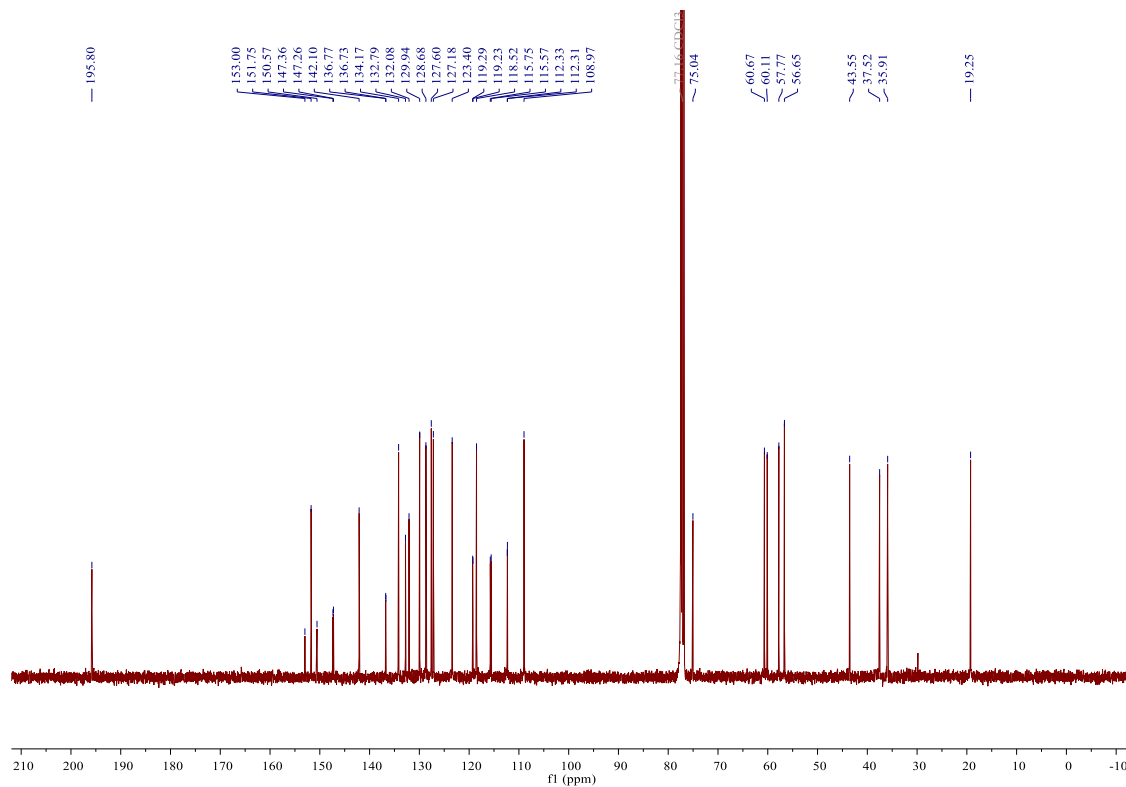
^{13}C NMR spectra of 2y (CDCl_3 , 101 MHz)



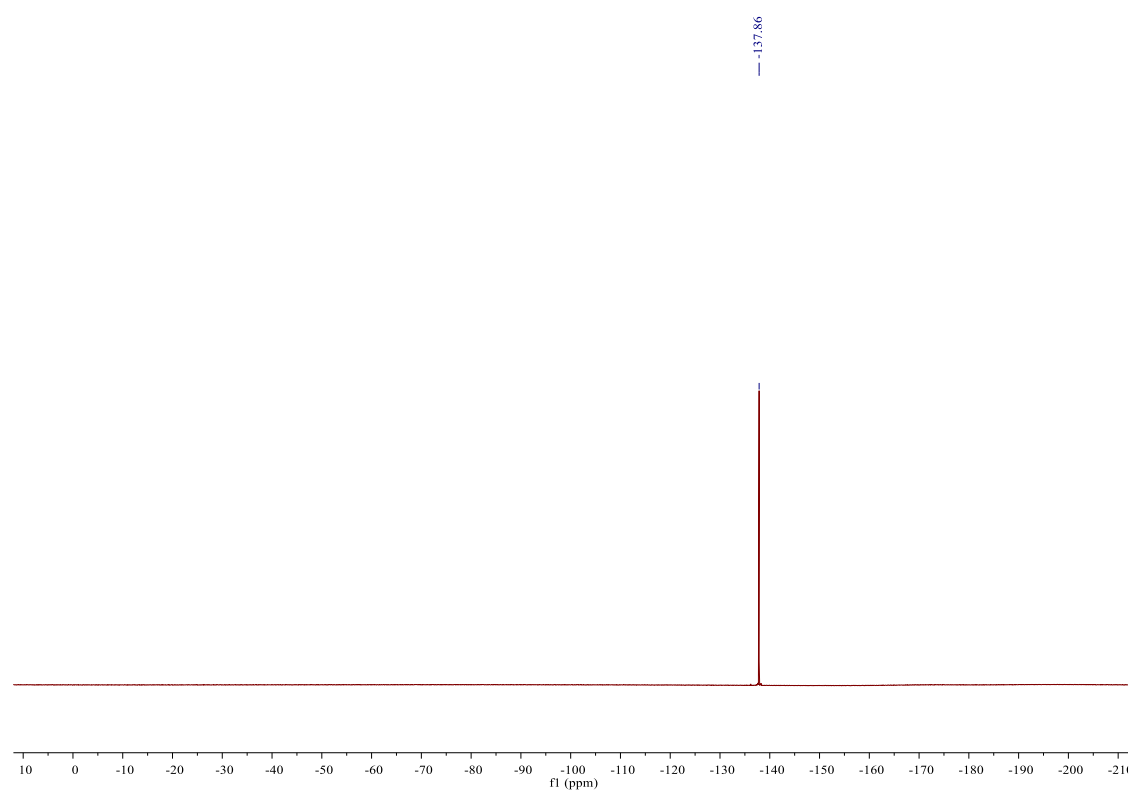
^1H NMR spectra of 2z (CDCl₃, 400 MHz)



^{13}C NMR spectra of 2z (CDCl₃, 101 MHz)



^{19}F NMR spectra of 2z (CDCl₃, 376 MHz)



Chemical structure of compound 10 is shown in the top left. The ^1H NMR spectrum (CDCl₃) is displayed below, showing peaks from 0 to 10 ppm. The chemical shifts (δ) are listed on the right, and the integrations are shown below the peaks.

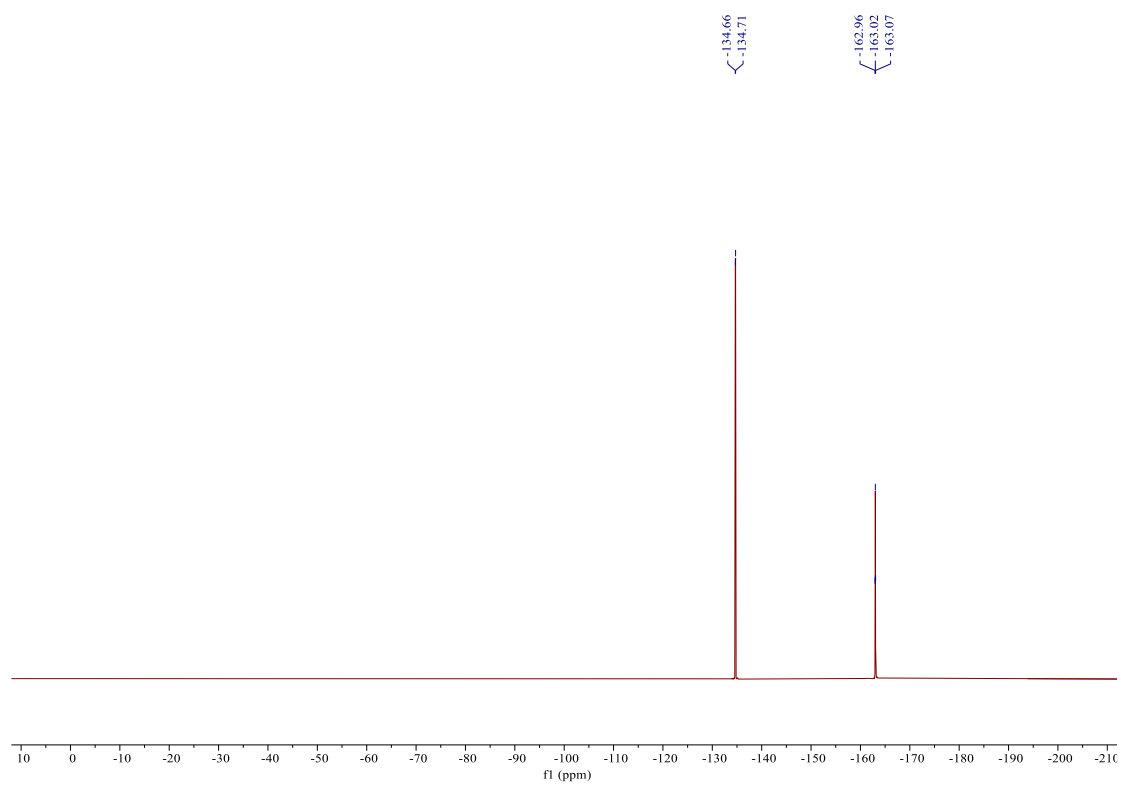
Chemical shifts (δ): 8.17, 8.16, 8.16, 7.61, 7.60, 7.59, 7.58, 7.58, 7.45, 7.44, 7.42, 7.36, 7.35, 7.26, 7.25, 7.03, 7.02, 7.02, 7.01, 7.01, 6.94, 6.93, 6.92, 6.91, 6.62, 6.60, 6.43, 6.42, 6.41, 6.33, 6.32, 3.71, 3.68, 3.28, 3.26, 2.61, 2.60, 2.59, 2.58, 2.17, 2.15, 2.03, 2.02, 2.01, 2.00, 1.28.

Integrations: 0.97, 1.00, 1.00, 1.00, 1.98, 0.98, 0.98, 1.86, 1.03, 1.04, 1.03, 2.04, 3.17.

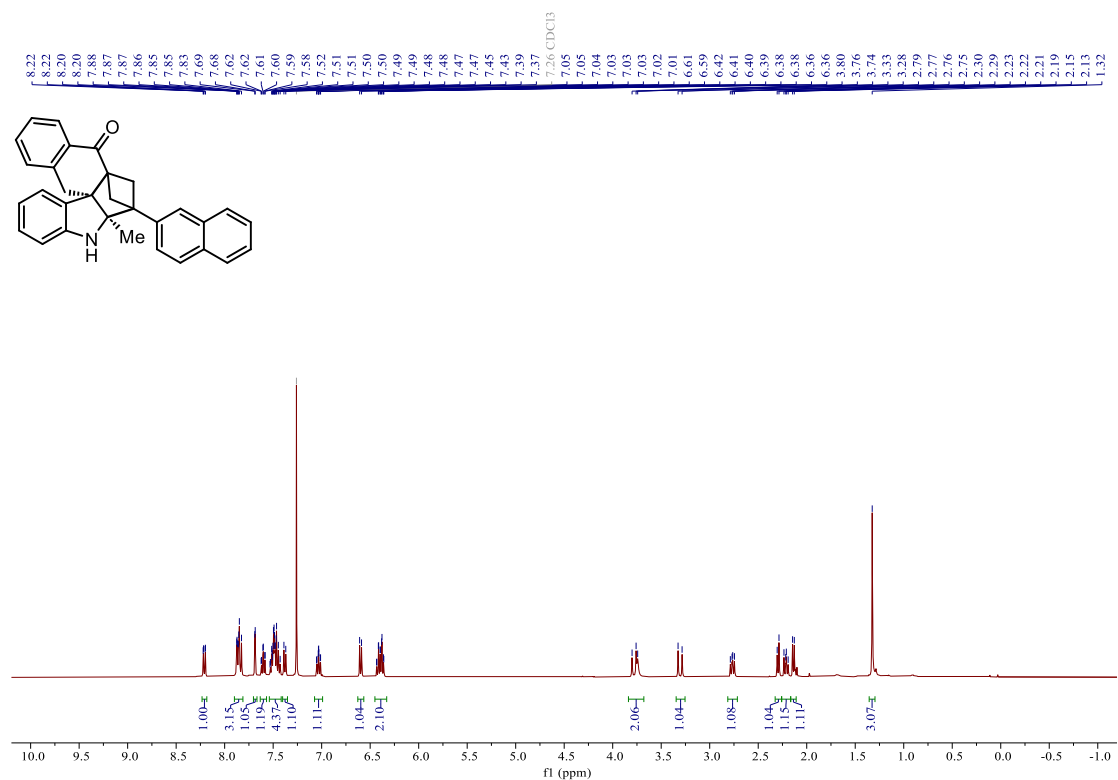
13C NMR spectrum of compound 10 in CDCl₃. The x-axis represents the chemical shift in ppm, ranging from 210 to -10. The spectrum shows several sharp peaks. A list of peak chemical shifts is provided on the right side of the plot.

Chemical Shift (ppm)
195.38
151.89
151.87
151.83
151.80
151.60
150.24
150.21
150.17
150.15
141.90
139.77
139.67
139.57
138.11
138.01
137.91
136.84
136.80
136.77
136.72
134.31
132.59
131.94
129.95
128.80
127.59
127.25
123.33
118.91
110.97
110.94
110.86
110.84
109.48
77.16 (CDCl ₃)
75.22
60.75
59.52
57.57
43.07
37.72
35.84
19.03

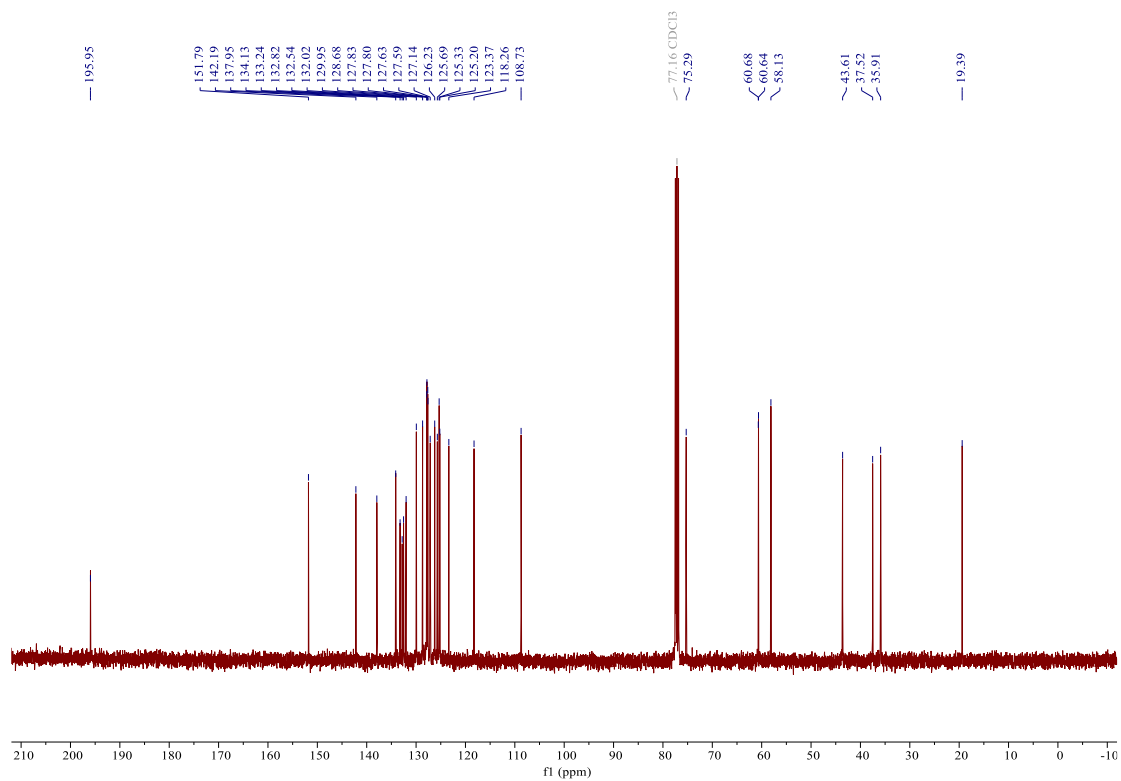
^{19}F NMR spectra of 2aa (CDCl_3 , 376 MHz)



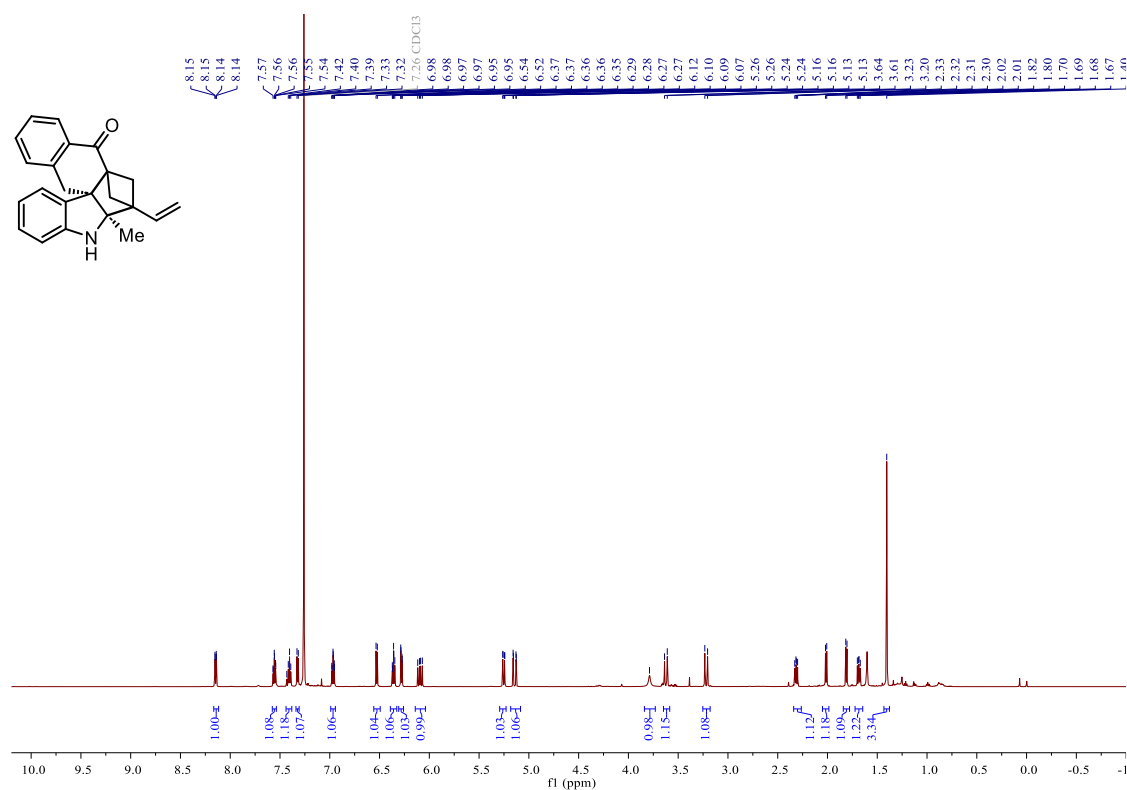
¹H NMR spectra of 2ab (CDCl₃, 400 MHz)



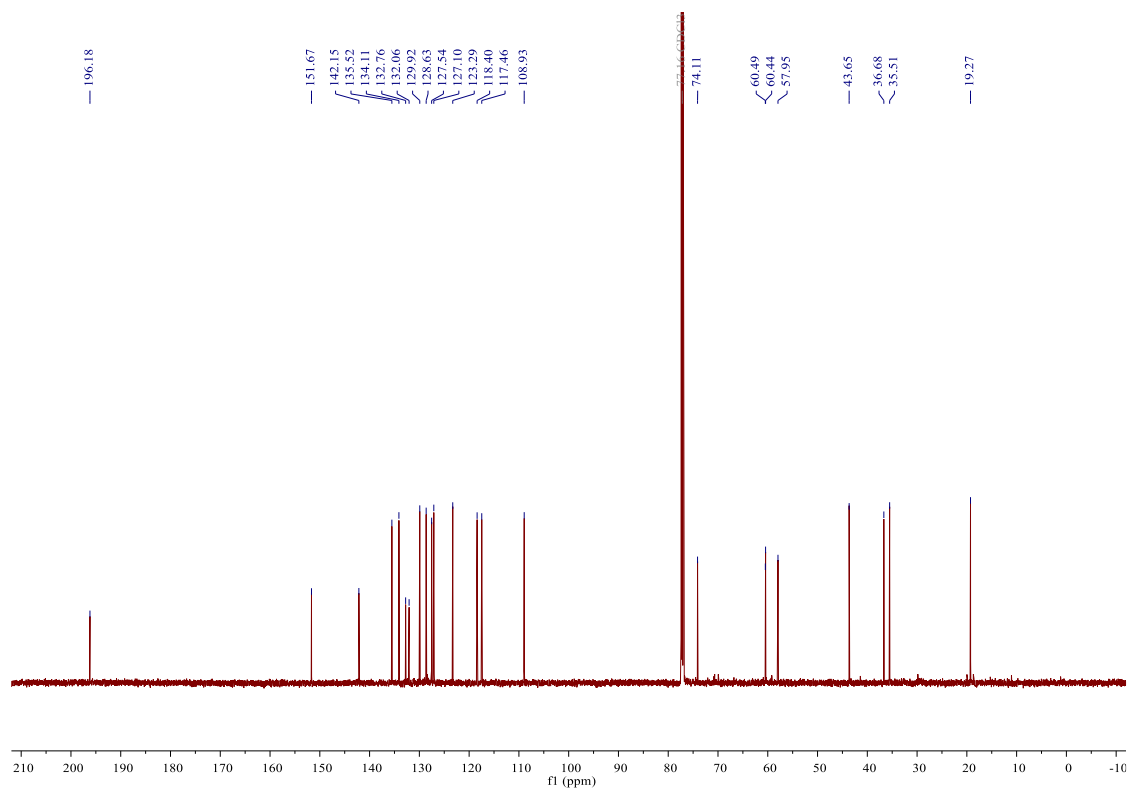
¹³C NMR spectra of 2ab (CDCl₃, 101 MHz)



^1H NMR spectra of 2ac (CDCl_3 , 400 MHz)



^{13}C NMR spectra of 2ac (CDCl_3 , 101 MHz)



Chemical structure of compound 10: C[C@H]1[C@@H](C(=O)c2ccccc2)[C@H](c3ccccc3)N(Cc4ccccc4)[C@H]1c5ccccc5

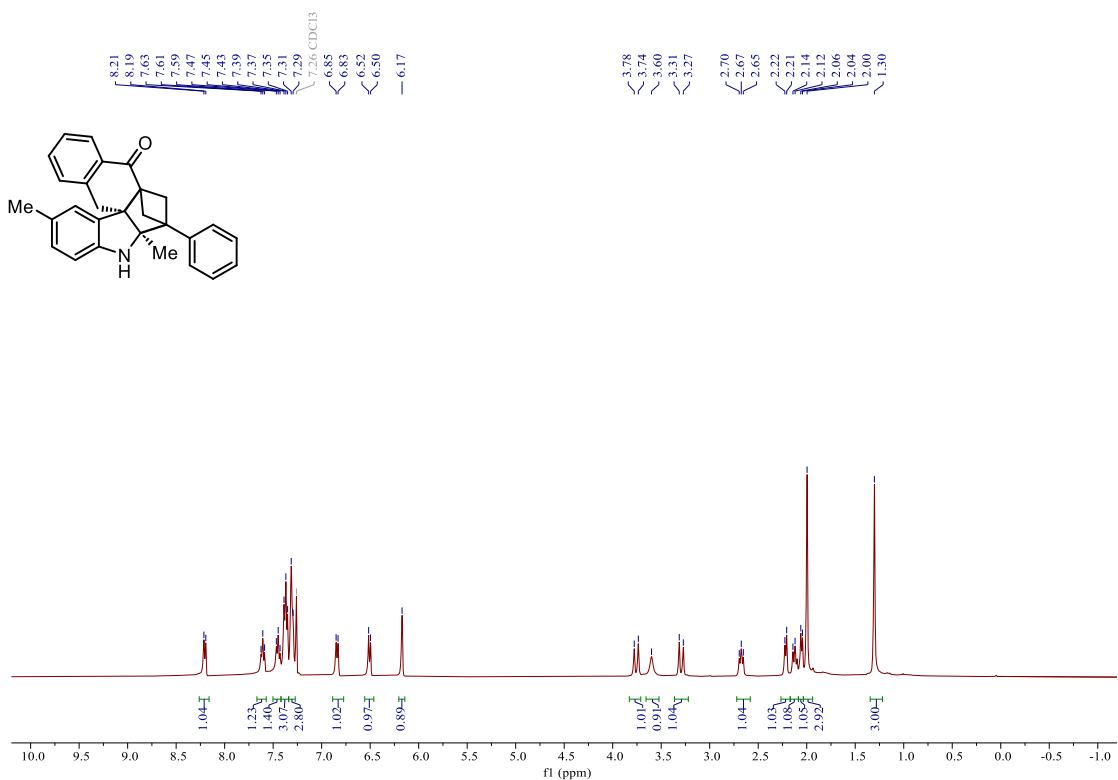
¹H NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from 10.0 to -1.0. The spectrum shows several multiplets and singlets, with integration values indicated below the baseline.

Integration values (from left to right): 1.00, 1.12, 1.13, 3.18, 1.01, 2.06, 1.01, 2.11, 1.03, 1.02, 1.04, 1.01, 1.08, 1.08, 3.03, 3.23.

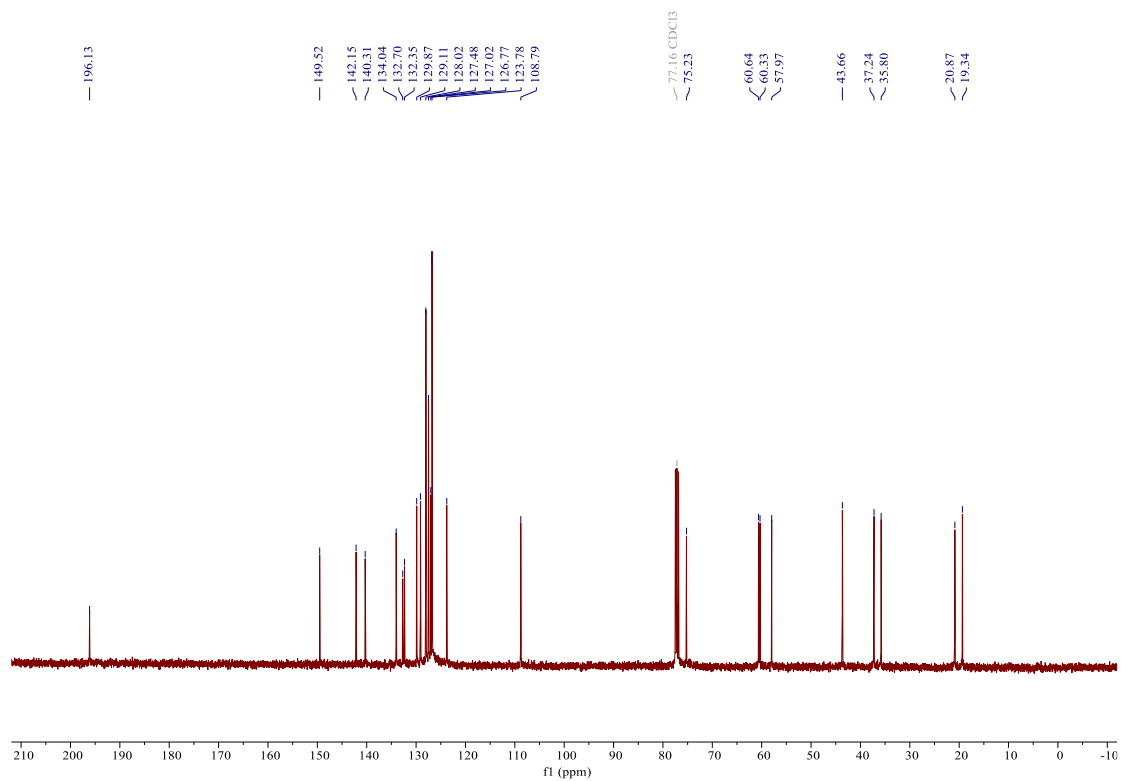
Chemical shift values (ppm) labeled above the spectrum: 8.16, 8.16, 8.14, 7.55, 7.55, 7.53, 7.41, 7.40, 7.38, 7.33, 7.33, 7.32, 7.31, 7.29, 7.27, 7.27, 7.25, 7.24, 6.86, 6.85, 6.84, 6.83, 6.83, 6.82, 6.81, 6.28, 6.28, 6.26, 6.26, 6.23, 6.23, 6.22, 6.21, 5.95, 5.95, 5.93, 4.64, 4.60, 4.54, 4.50, 3.68, 3.64, 3.58, 3.58, 2.26, 2.24, 2.23, 2.21, 1.94, 1.92, 1.77, 1.75, 1.74, 1.72, 1.58, 1.56, 1.50, 1.21.

¹³C NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from 210 to -10. The spectrum shows several peaks, with the most intense at 77.16 ppm (CDCl₃ solvent). Other labeled peaks include 196.08, 152.32, 142.28, 139.40, 134.03, 132.78, 130.80, 129.90, 128.69, 128.59, 127.50, 127.04, 126.79, 126.39, 122.56, 116.14, 105.54, 77.36, 77.16 (CDCl₃), 60.07, 58.42, 55.14, 48.20, 45.70, 37.81, 35.99, 15.69, and 15.12.

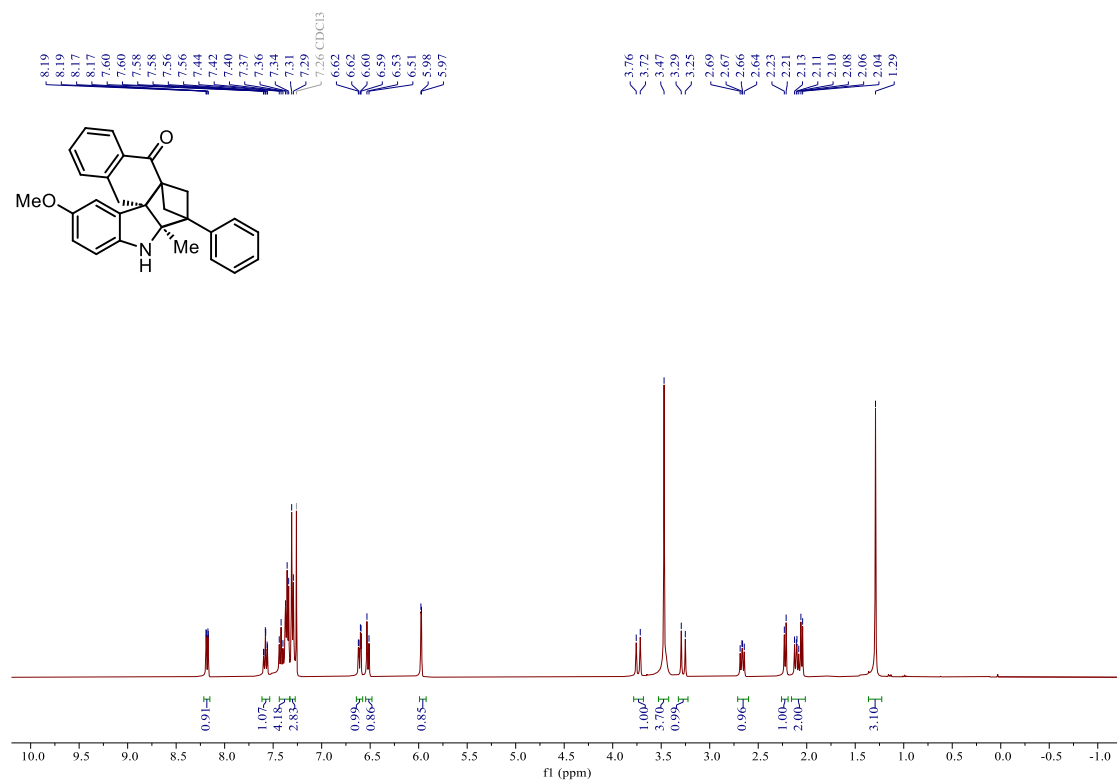
^1H NMR spectra of 2ae (CDCl_3 , 400 MHz)



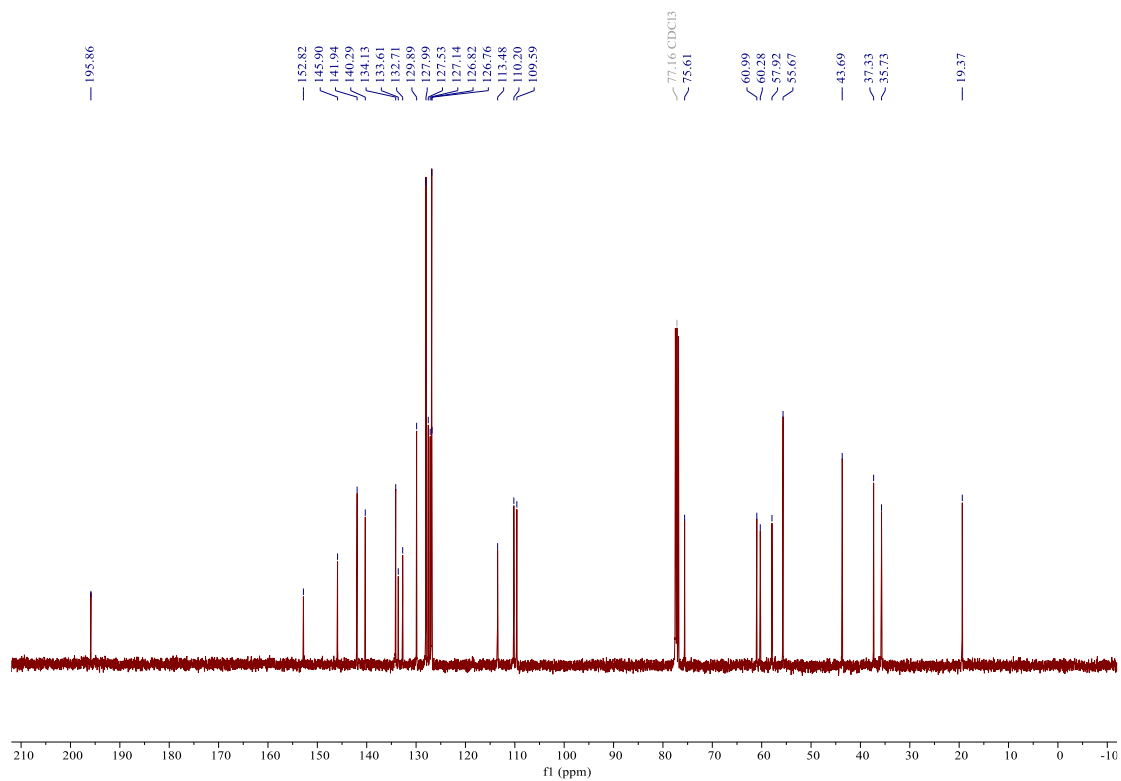
^{13}C NMR spectra of 2ae (CDCl_3 , 101 MHz)



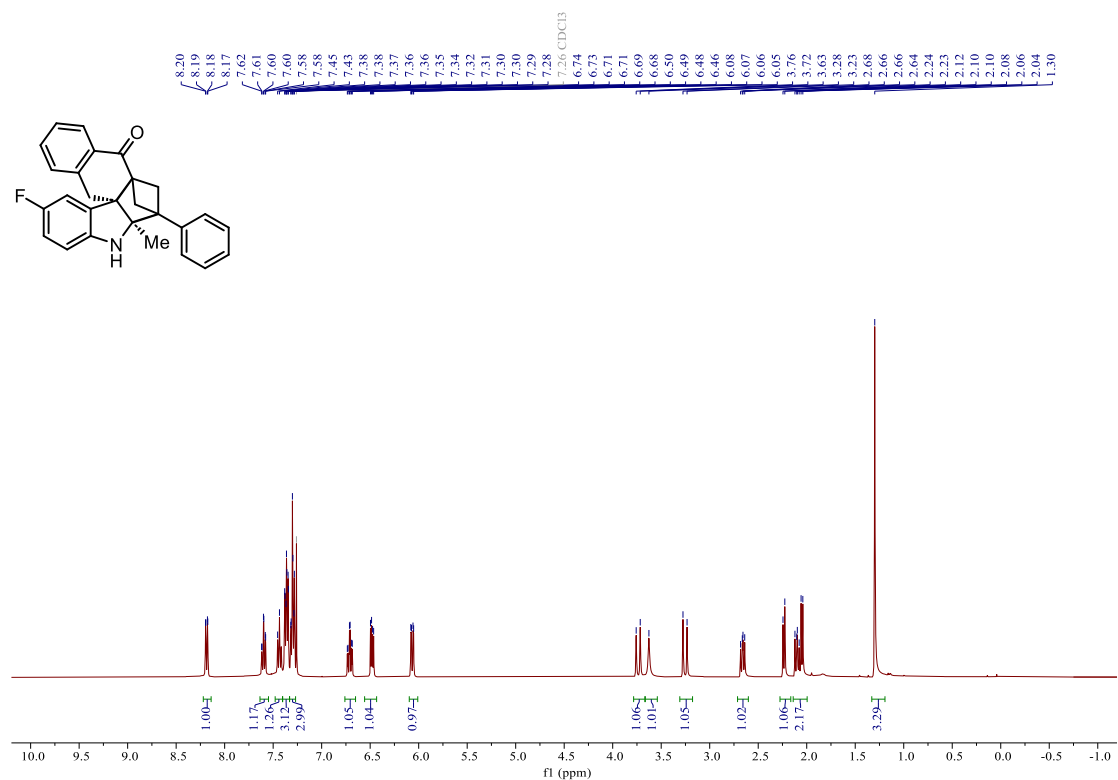
¹H NMR spectra of 2af (CDCl₃, 400 MHz)



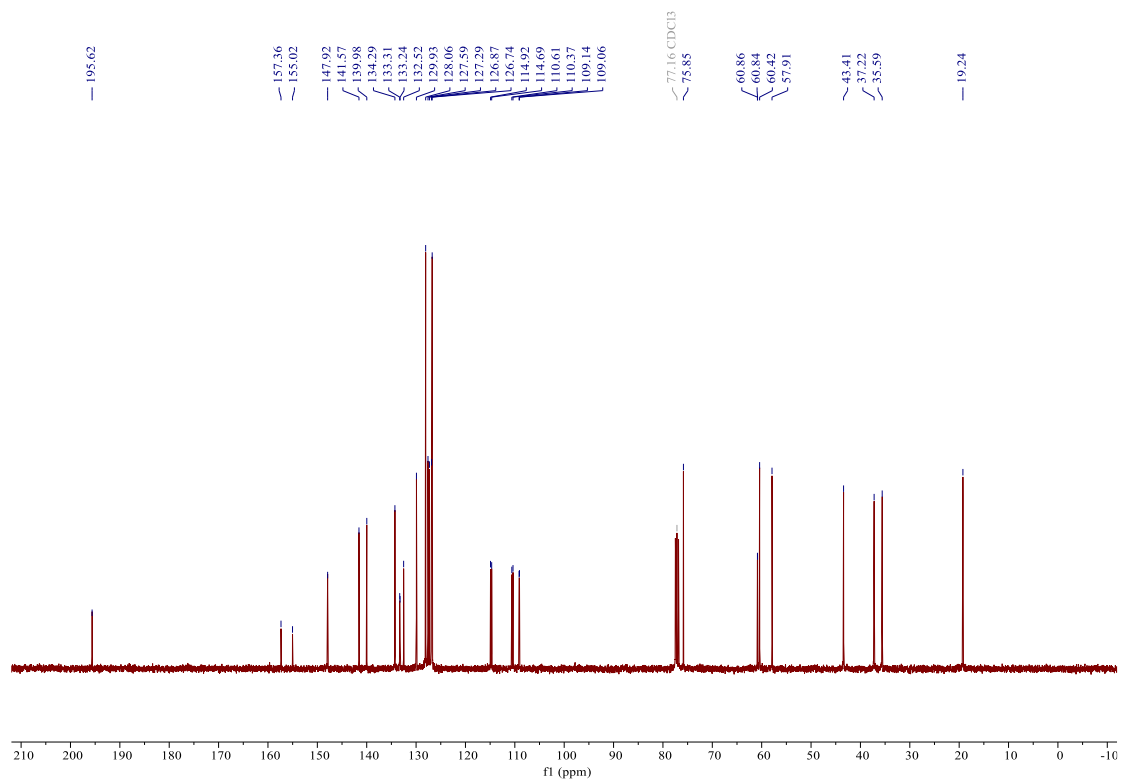
¹³C NMR spectra of 2af (CDCl₃, 101 MHz)



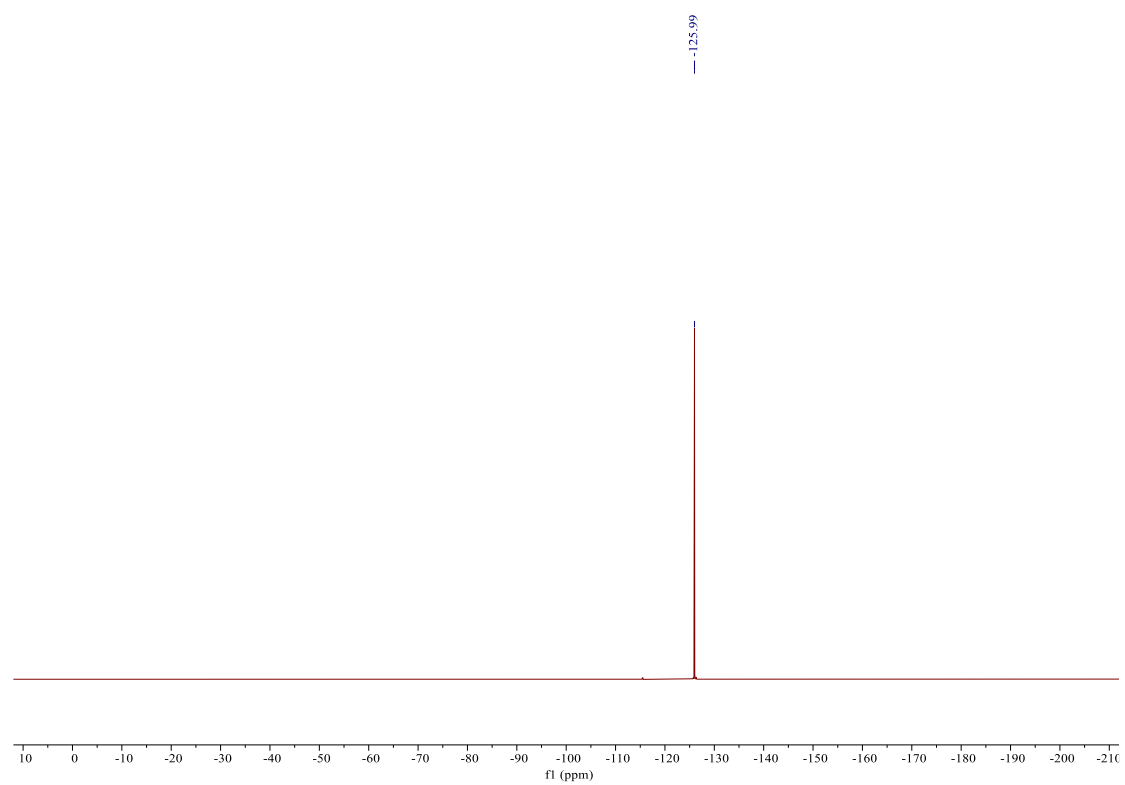
¹H NMR spectra of 2ag (CDCl₃, 400 MHz)



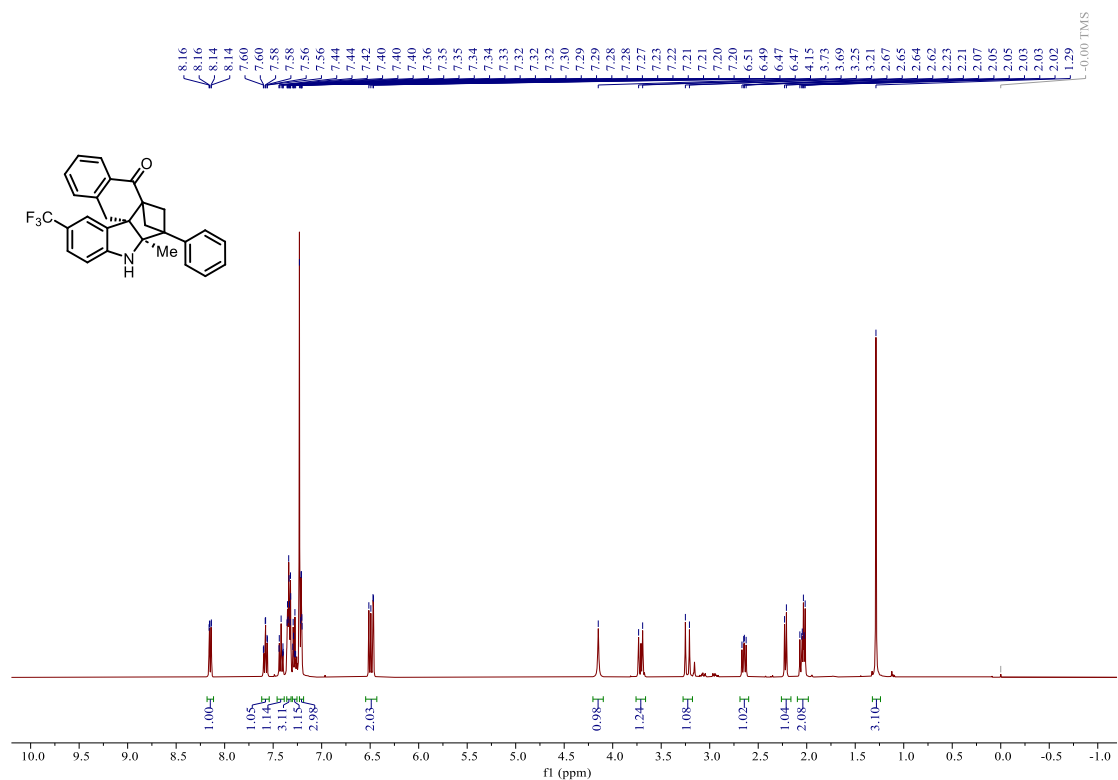
¹³C NMR spectra of 2ag (CDCl₃, 101 MHz)



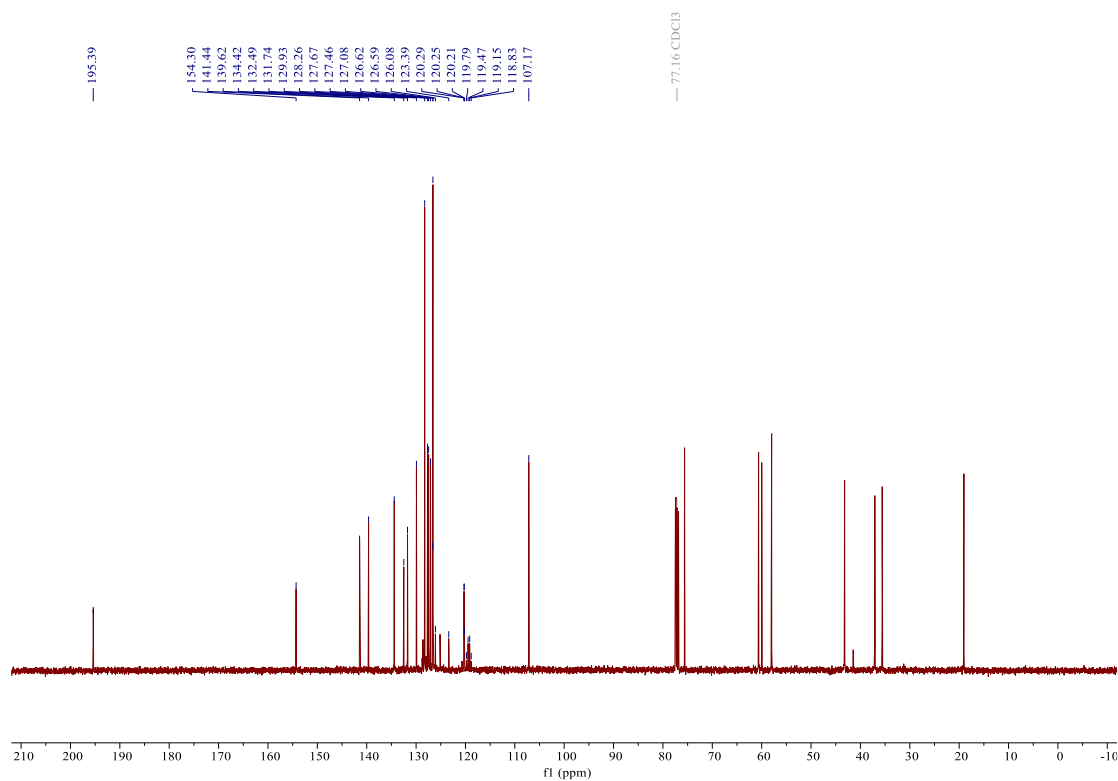
^{19}F NMR spectra of 2ag (CDCl_3 , 376 MHz)



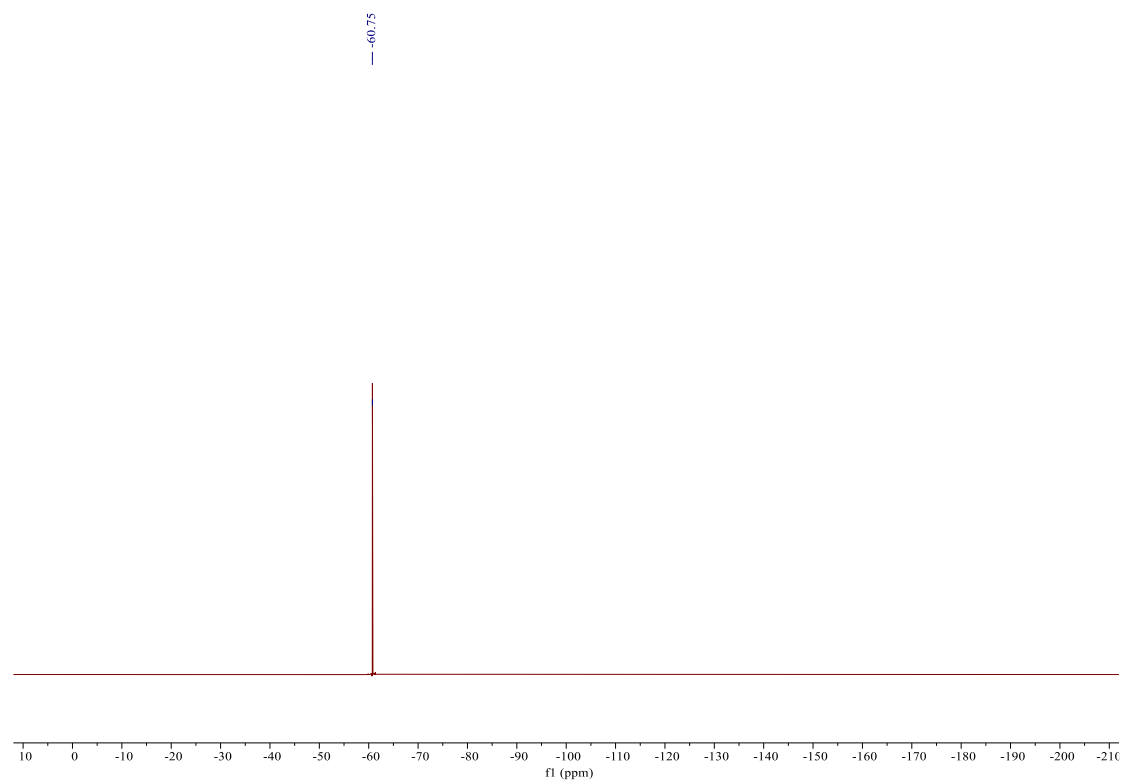
¹H NMR spectra of 2ah (CDCl₃, 400 MHz)



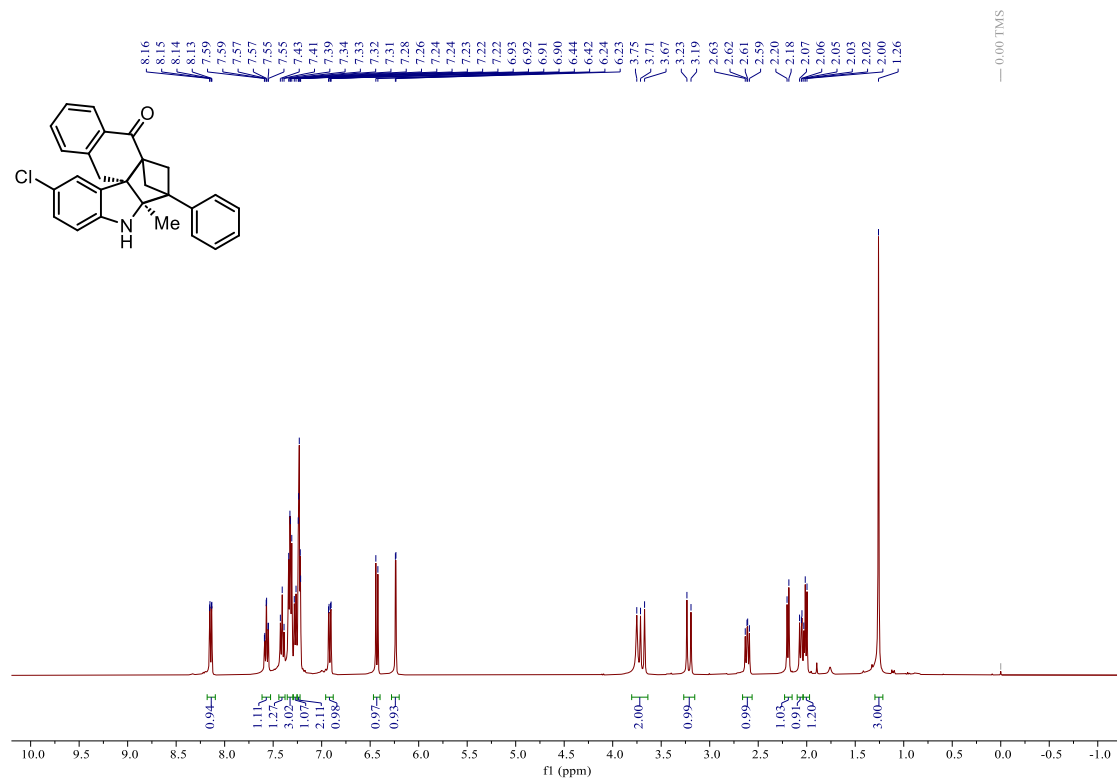
¹³C NMR spectra of 2ah (CDCl₃, 101 MHz)



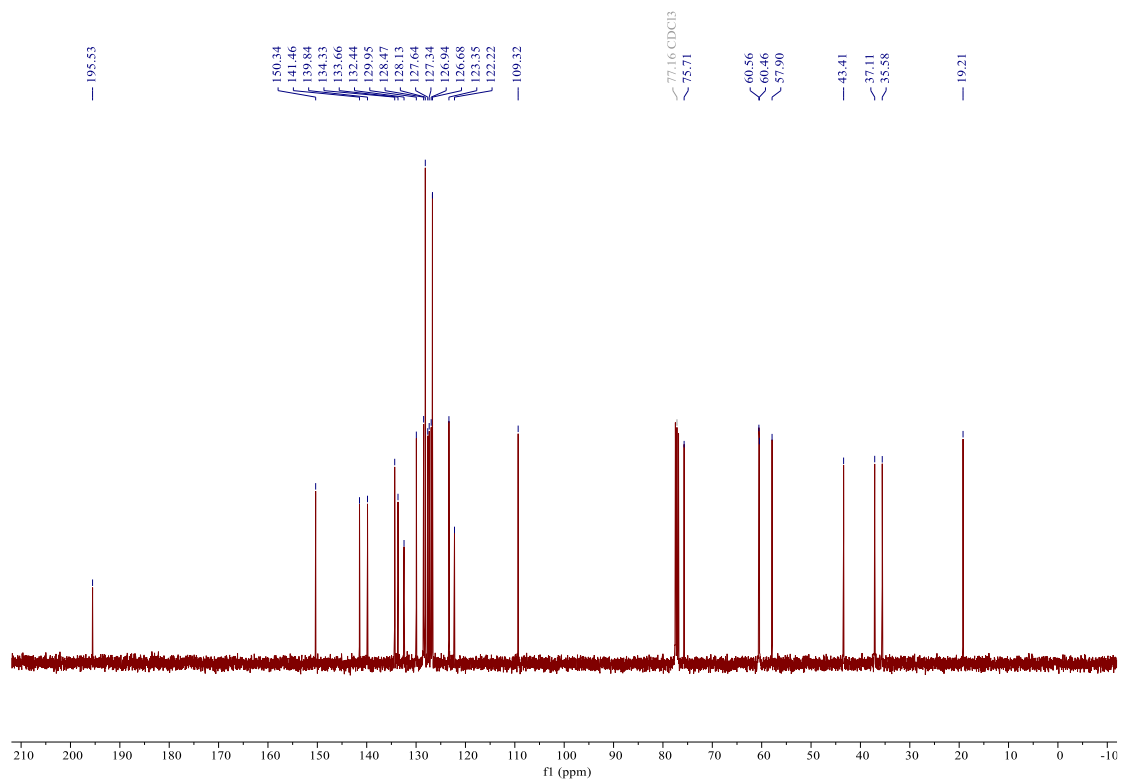
^{19}F NMR spectra of 2ah (CDCl_3 , 376 MHz)



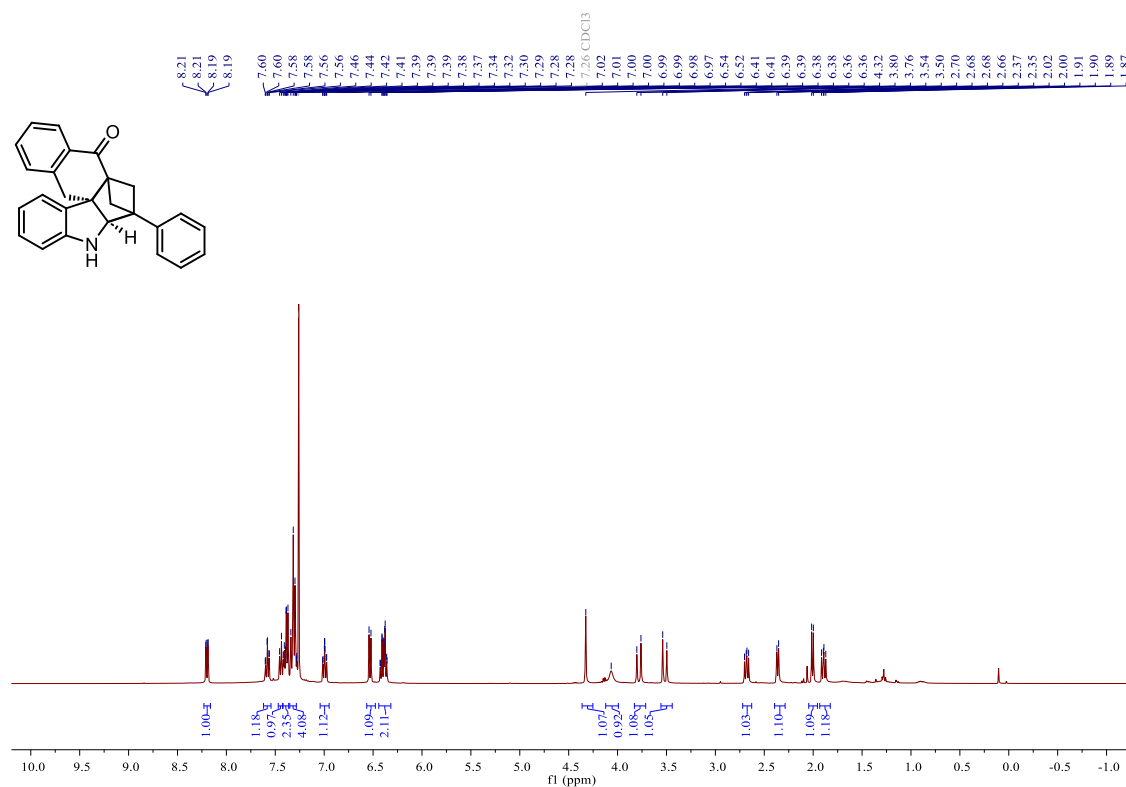
¹H NMR spectra of 2ai (CDCl₃, 400 MHz)



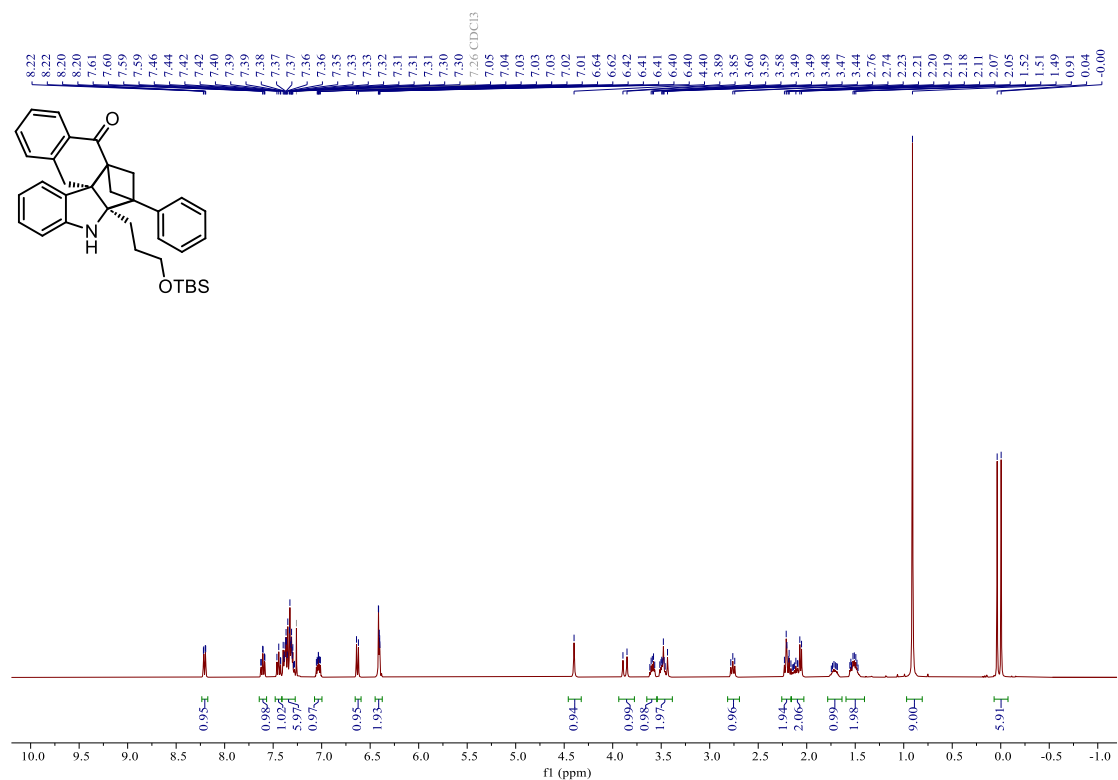
¹³C NMR spectra of 2ai (CDCl₃, 101 MHz)



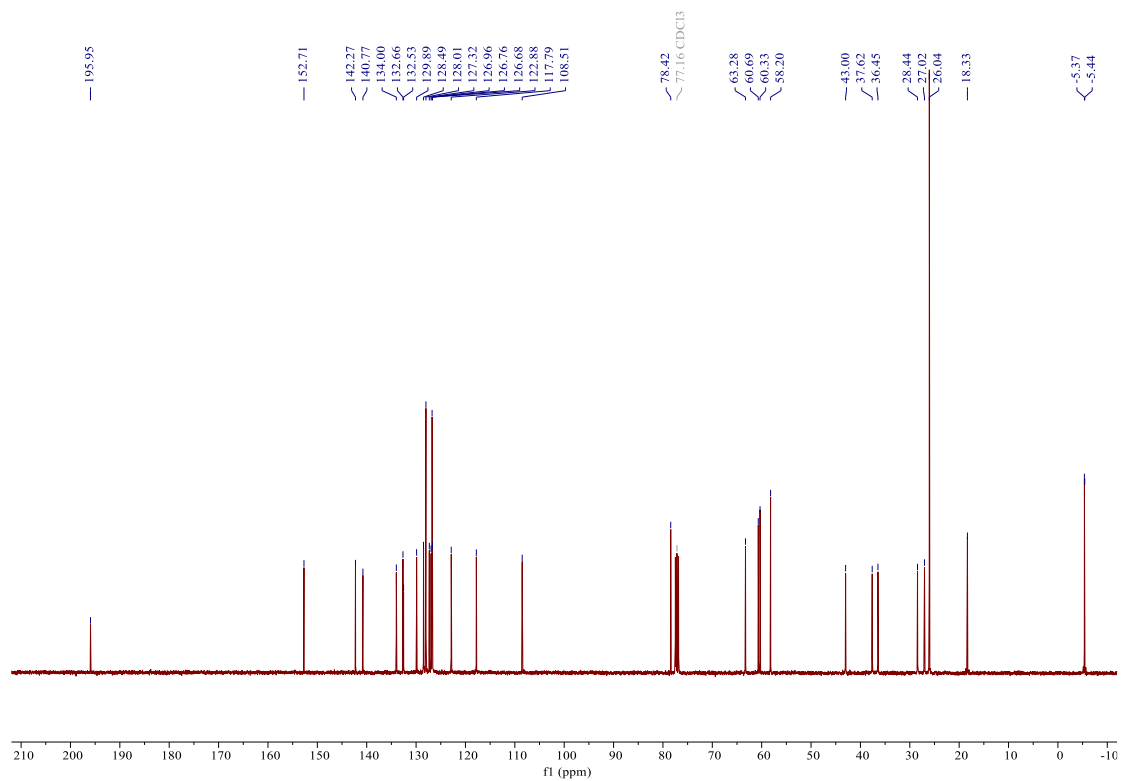
^1H NMR spectra of 2aj (CDCl₃, 400 MHz)



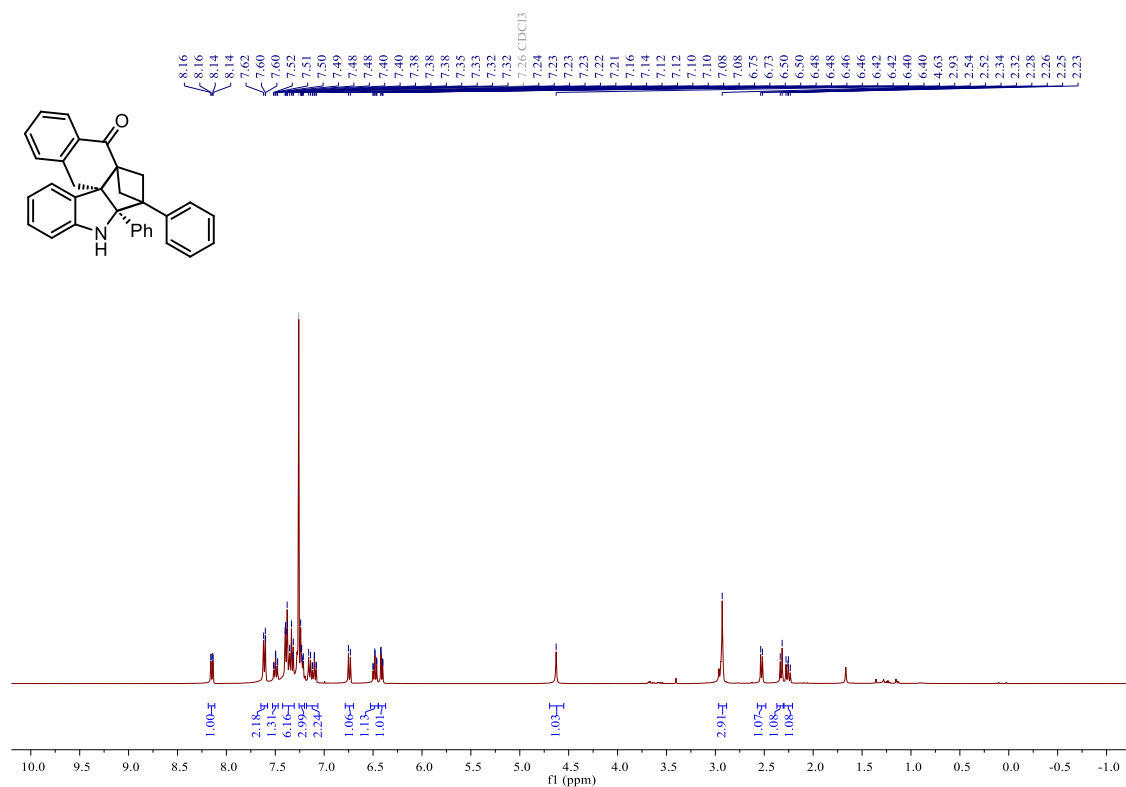
¹H NMR spectra of 2ak (CDCl₃, 400 MHz)



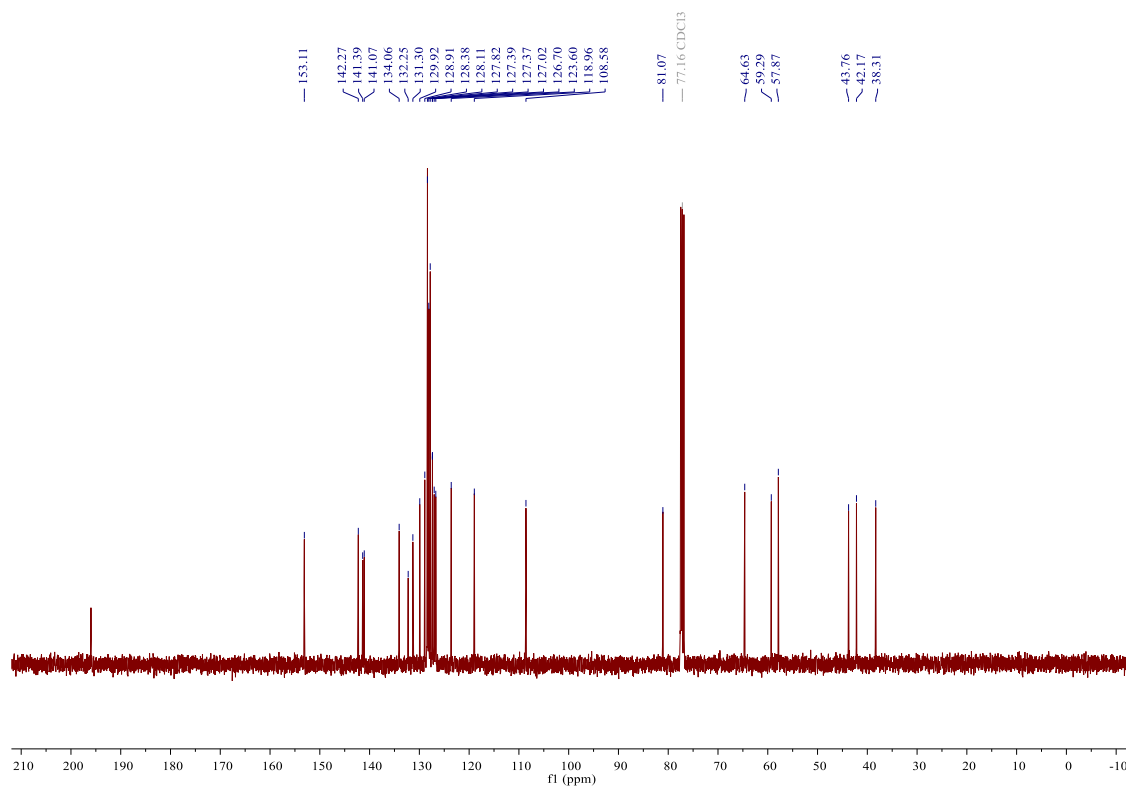
¹³C NMR spectra of 2ak (CDCl₃, 101 MHz)



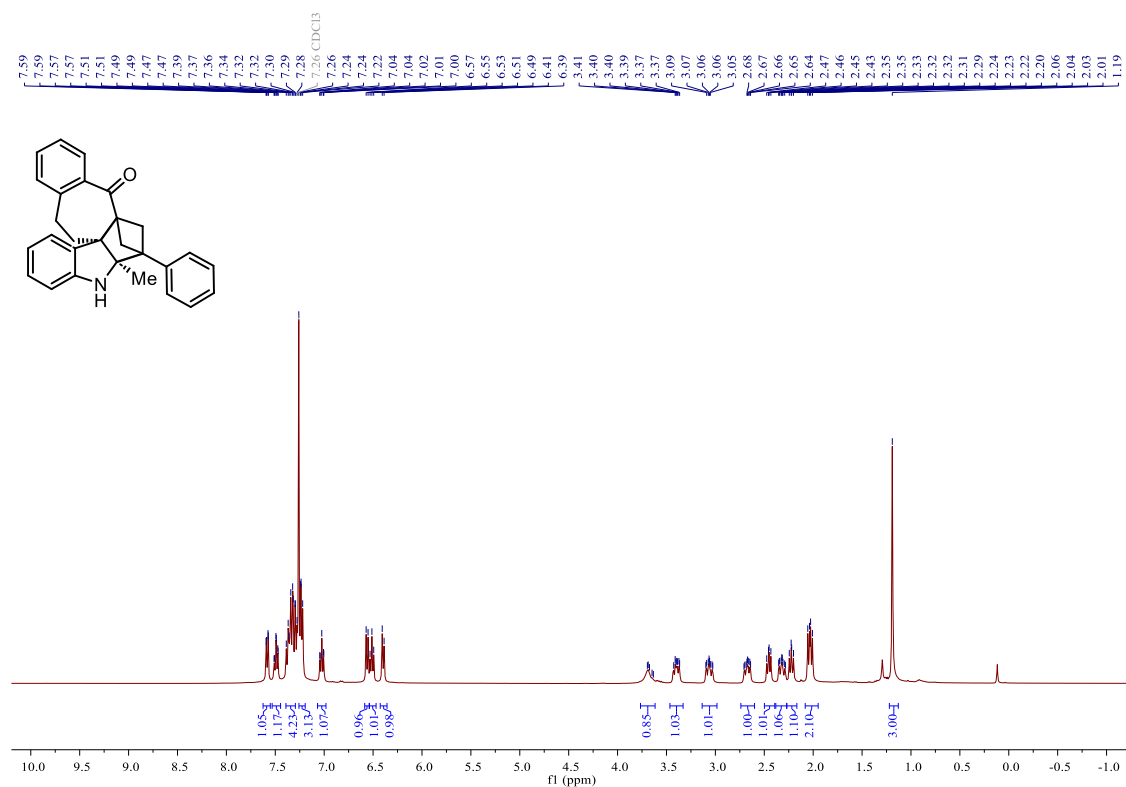
^1H NMR spectra of 2aI (CDCl_3 , 400 MHz)



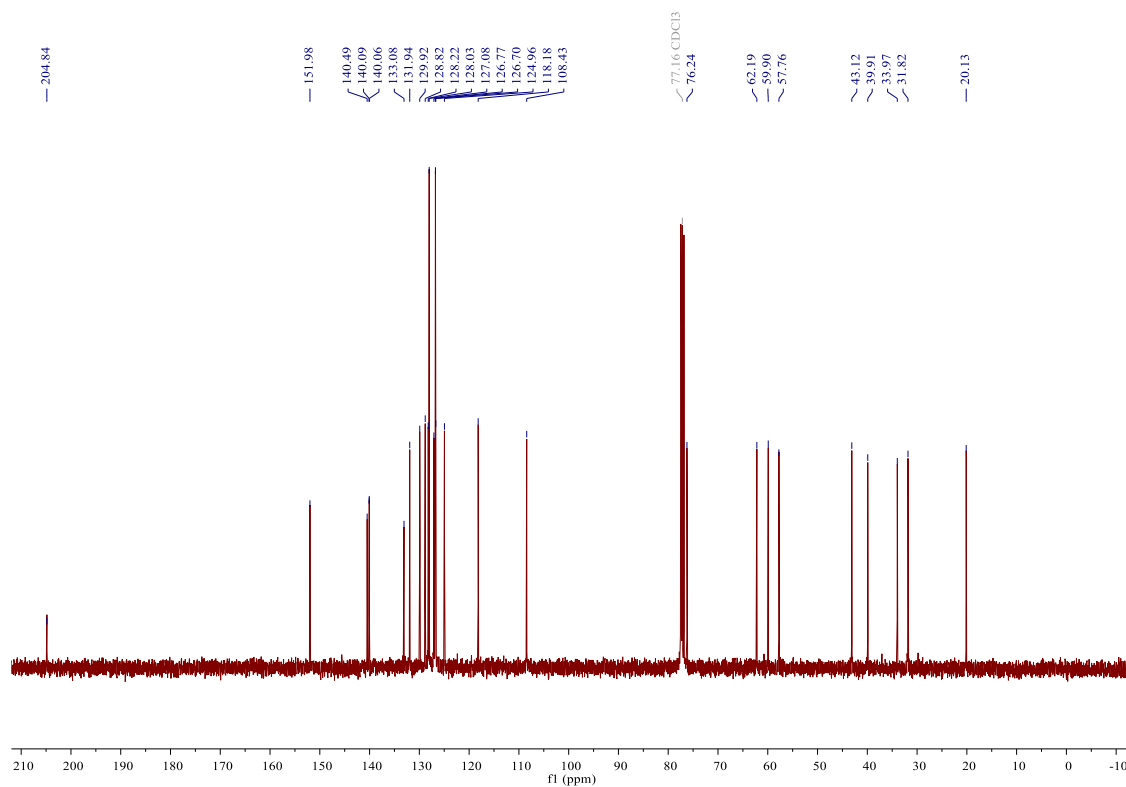
^{13}C NMR spectra of 2aI (CDCl_3 , 101 MHz)



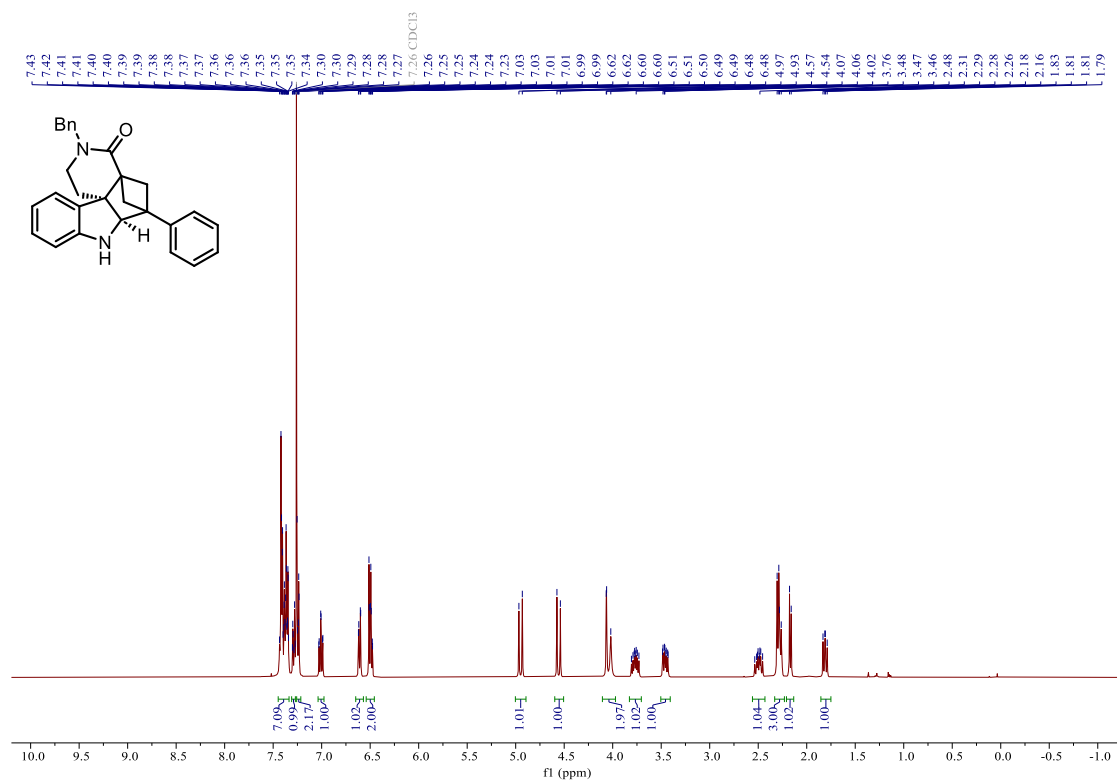
¹H NMR spectra of 2am (CDCl₃, 400 MHz)



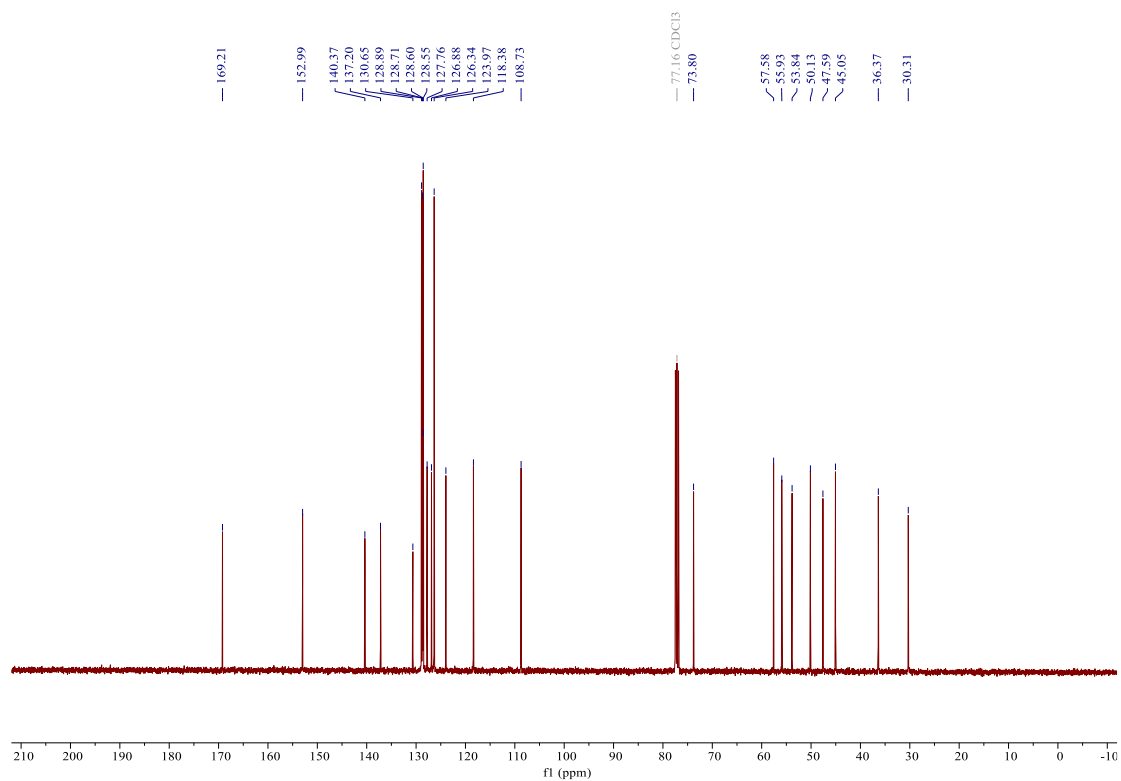
¹³C NMR spectra of 2am (CDCl₃, 101 MHz)



¹H NMR spectra of 2an (CDCl₃, 400 MHz)



¹³C NMR spectra of 2an (CDCl₃, 101 MHz)



Chemical structure of compound 10 is shown in the top left. The ¹H NMR spectrum (CDCl₃) is displayed below, with chemical shifts (ppm) listed along the top axis and integration values provided below the baseline.

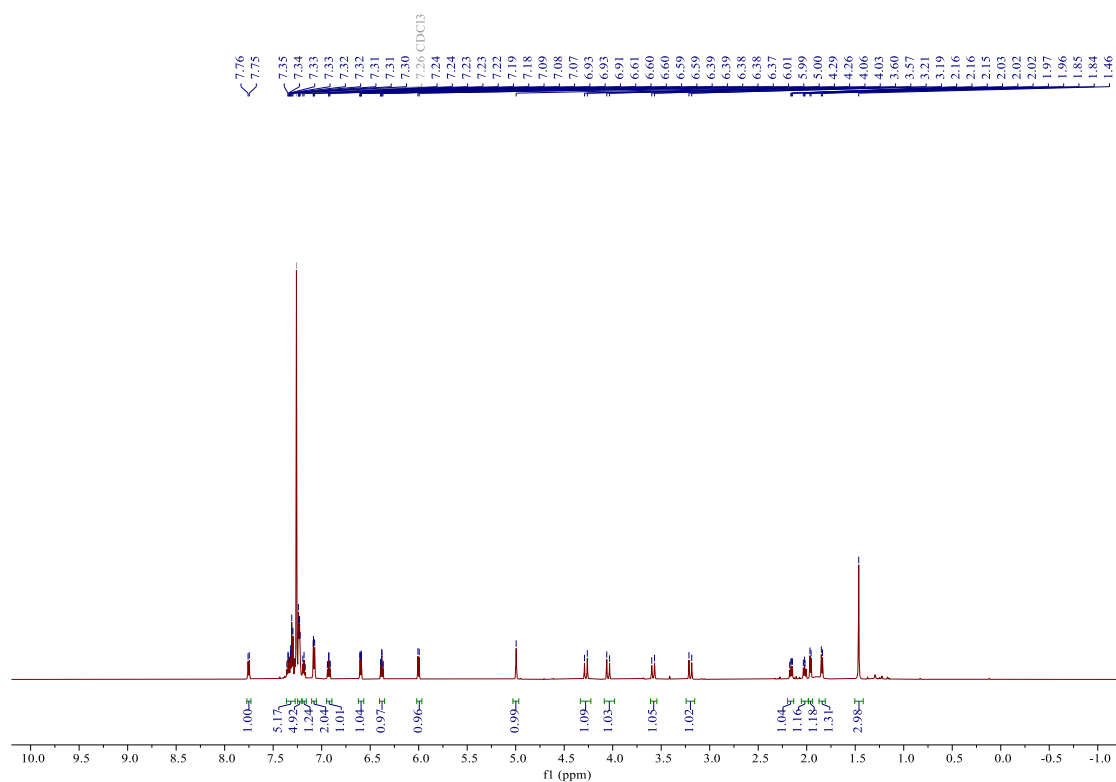
Chemical Shift (ppm)	Integration
7.54	1.00
7.53	2.14
7.52	5.07
7.51	2.90
7.29	1.15
7.27	2.06
7.26	0.96
7.25	0.96
7.24	0.94
7.23	0.94
7.22	0.94
7.20	0.94
7.19	0.94
7.18	0.94
7.17	0.94
7.16	0.94
7.15	0.94
7.14	0.94
7.12	0.94
7.10	0.94
7.08	0.94
7.07	0.94
7.06	0.94
6.96	0.94
6.94	0.94
6.79	0.94
6.78	0.94
6.77	0.94
6.75	0.94
6.75	0.94
6.53	0.94
6.53	0.94
6.51	0.94
6.51	0.94
6.23	0.94
6.23	0.94
6.22	0.94
6.21	0.94
6.21	0.94
5.88	0.94
5.86	0.94
4.70	0.94
4.15	0.94
4.11	0.94
3.93	0.94
3.88	0.94
3.42	0.94
3.38	0.94
3.14	0.94
3.10	0.94
2.45	0.94
2.43	0.94
2.41	0.94
2.21	0.94
2.19	0.94
2.19	0.94
2.17	0.94
1.93	0.94
1.87	0.94
1.85	0.94
1.83	0.94
1.82	0.94
1.57	0.94
1.55	0.94
1.34	0.94

¹³C NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from -10 to 210. The spectrum shows a complex pattern of peaks, with a large cluster between 110-140 ppm and a smaller cluster between 30-70 ppm. Solvent peaks for CDCl₃ are visible at 77.16 ppm.

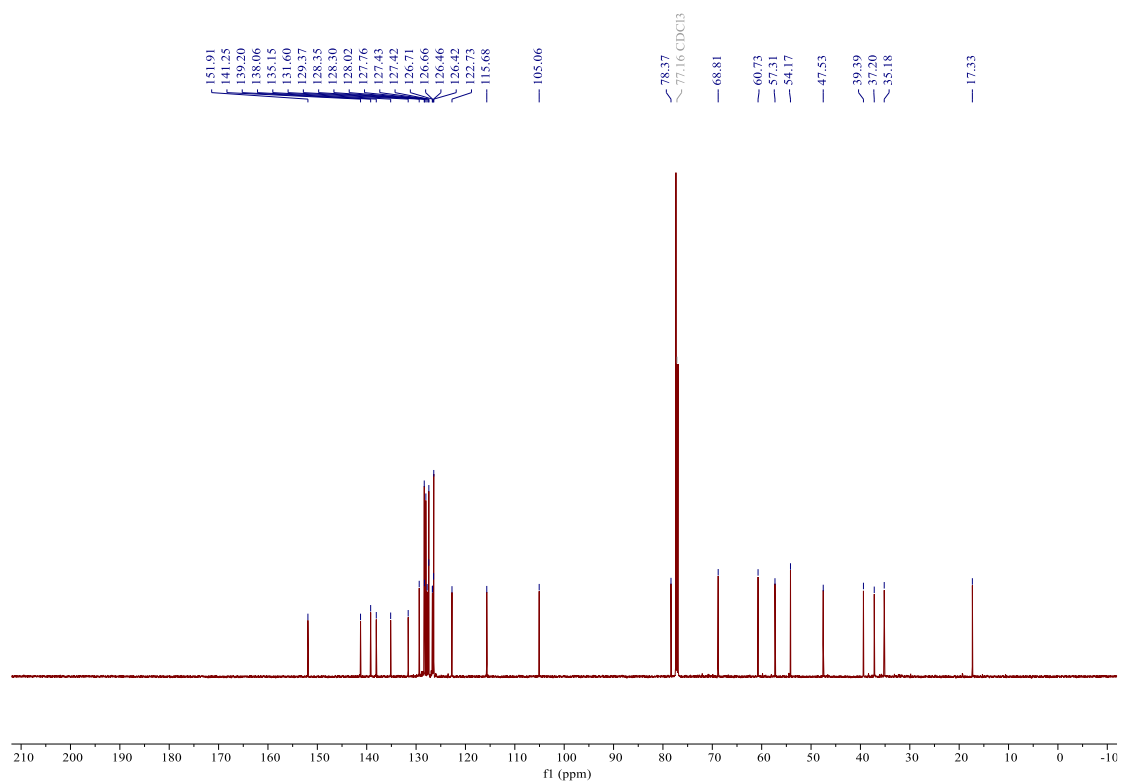
Chemical shift values (ppm) labeled on the spectrum:

- 152.26
- 140.97
- 139.00
- 137.70
- 135.01
- 132.31
- 131.33
- 129.54
- 128.41
- 128.39
- 128.32
- 128.02
- 127.24
- 127.01
- 126.70
- 126.44
- 126.40
- 122.96
- 115.96
- 105.78
- 78.12
- 77.16 (CDCl₃)
- 71.16
- 60.20
- 54.34
- 53.16
- 47.64
- 43.87
- 38.66
- 35.93
- 16.54

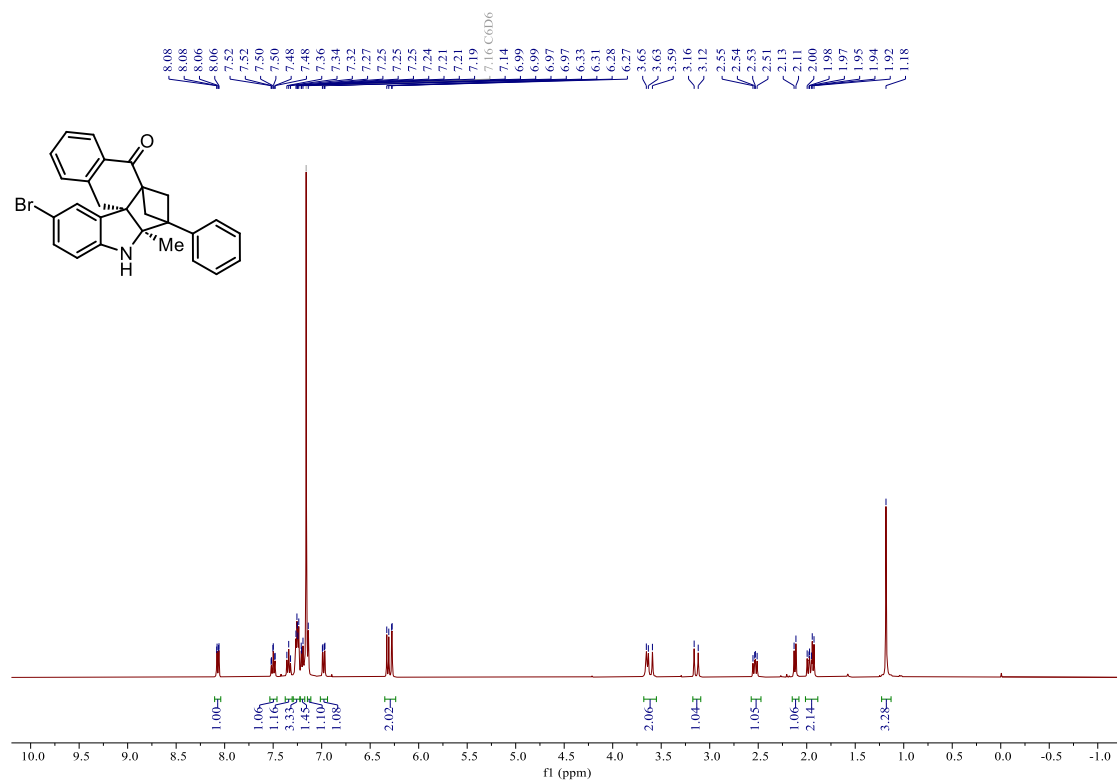
^1H NMR spectra of 3 (CDCl_3 , 600 MHz)



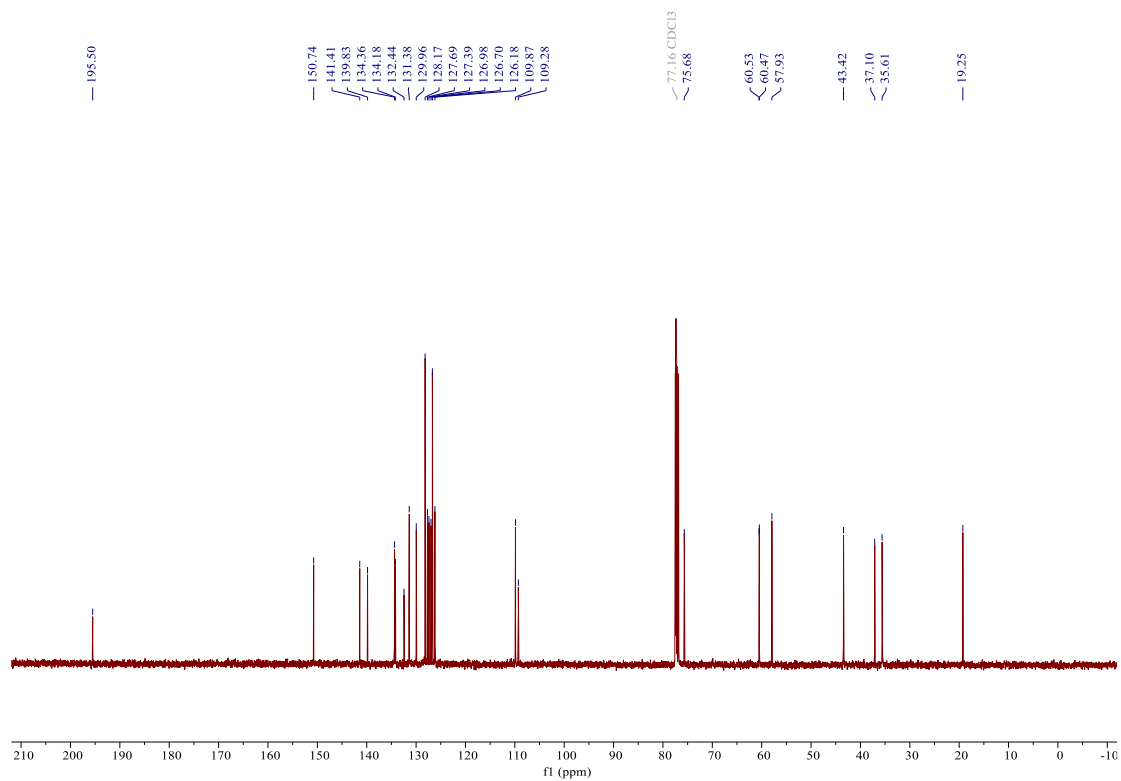
^{13}C NMR spectra of 3 (CDCl_3 , 151 MHz)



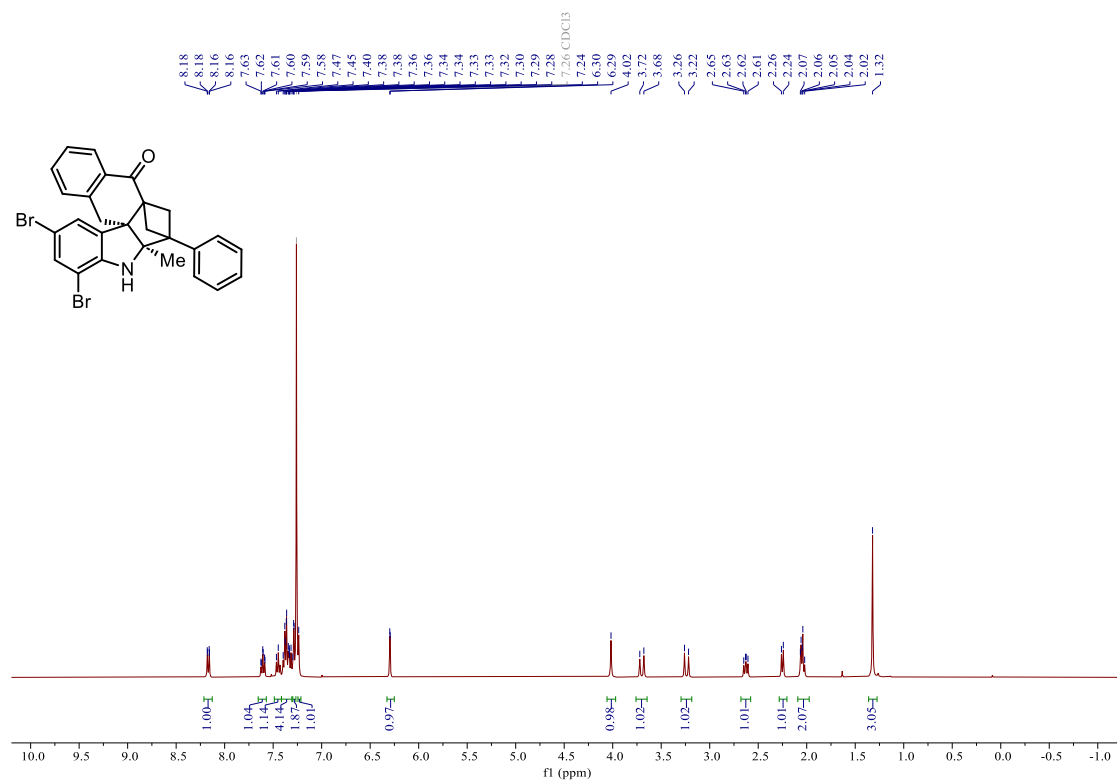
¹H NMR spectra of 4 (CDCl₃, 400 MHz)



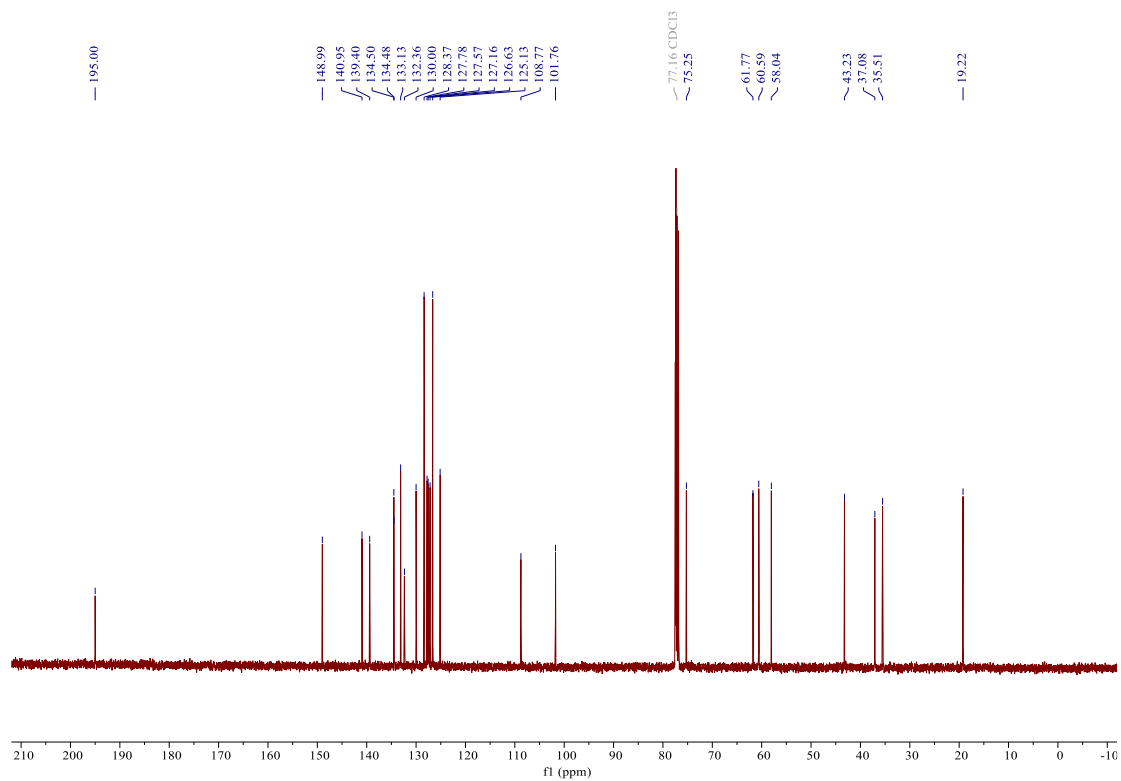
¹³C NMR spectra of 4 (CDCl₃, 101 MHz)



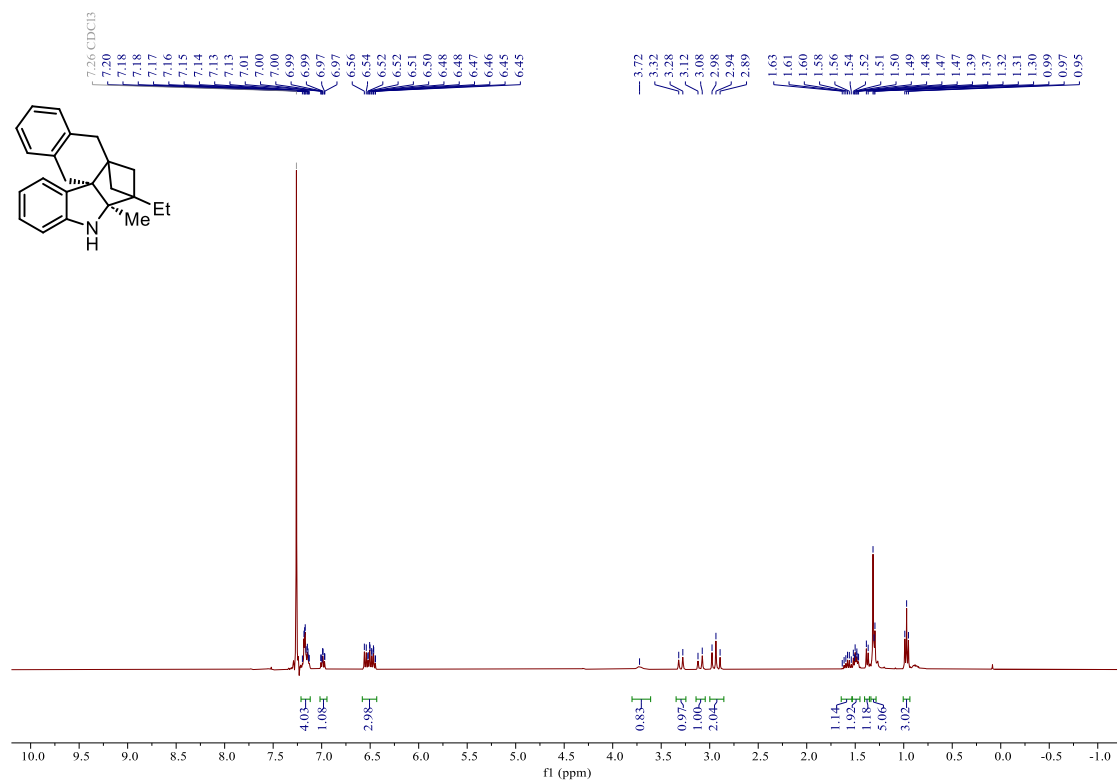
¹H NMR spectra of 5 (CDCl₃, 400 MHz)



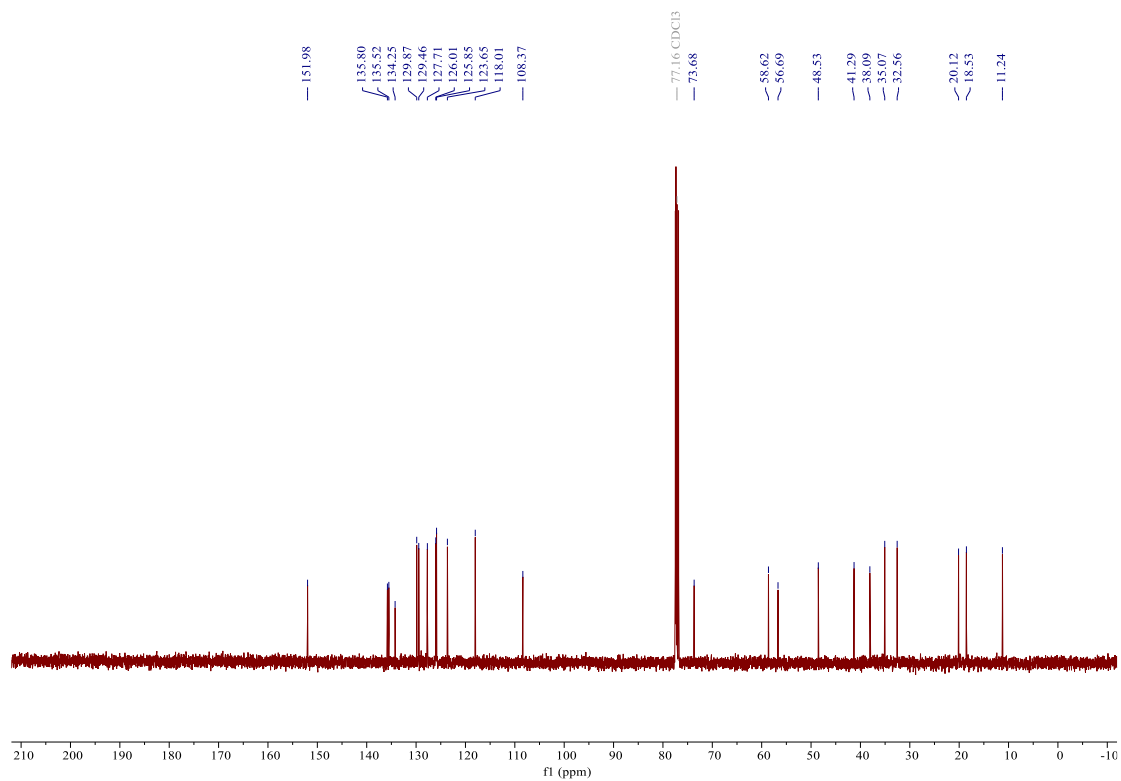
¹³C NMR spectra of 5 (CDCl₃, 101 MHz)



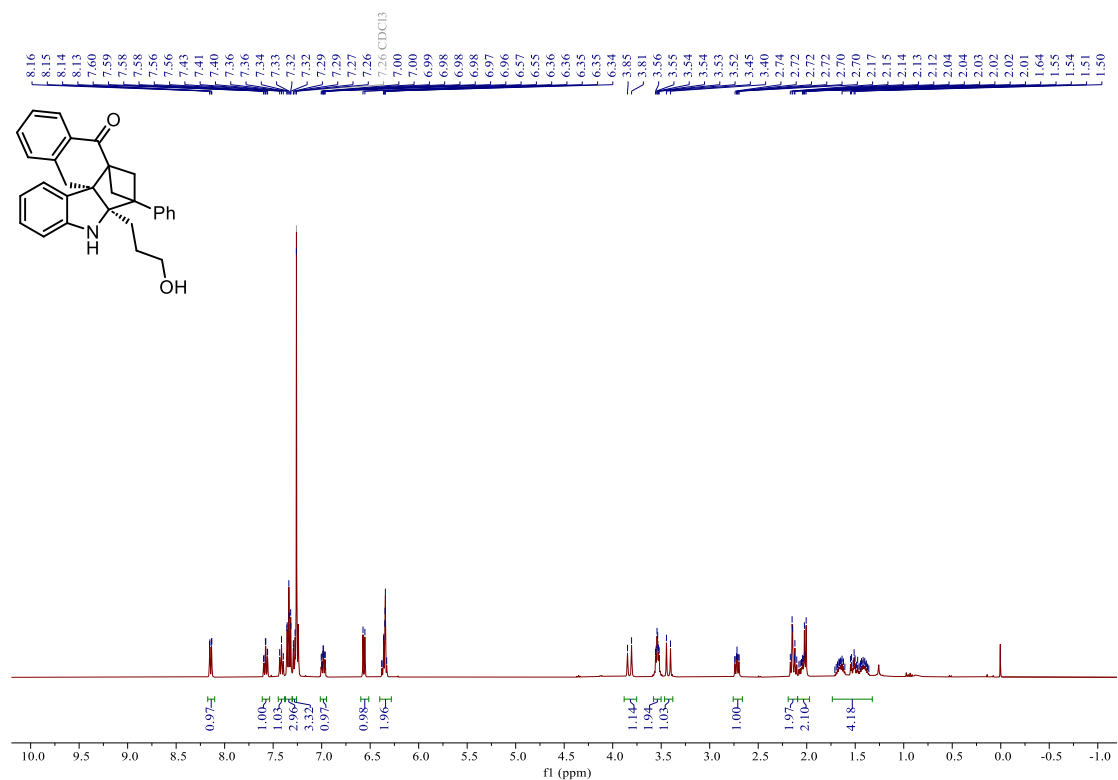
¹H NMR spectra of 6 (CDCl₃, 400 MHz)



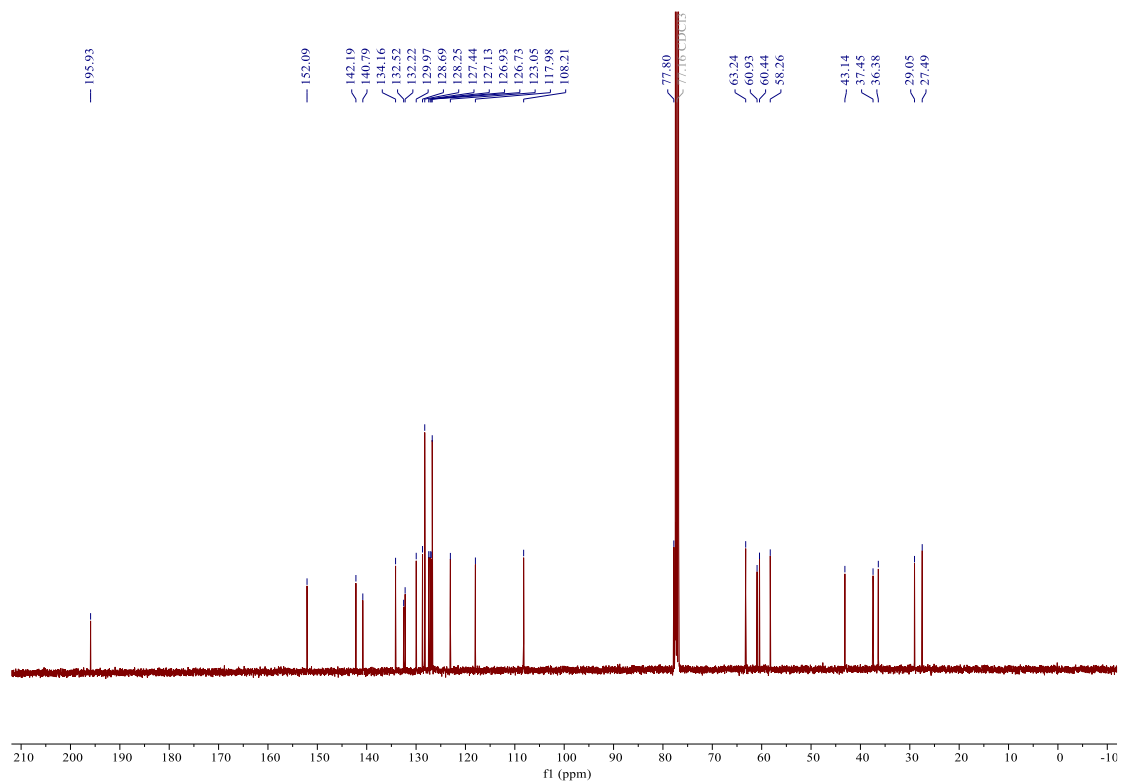
¹³C NMR spectra of 6 (CDCl₃, 101 MHz)



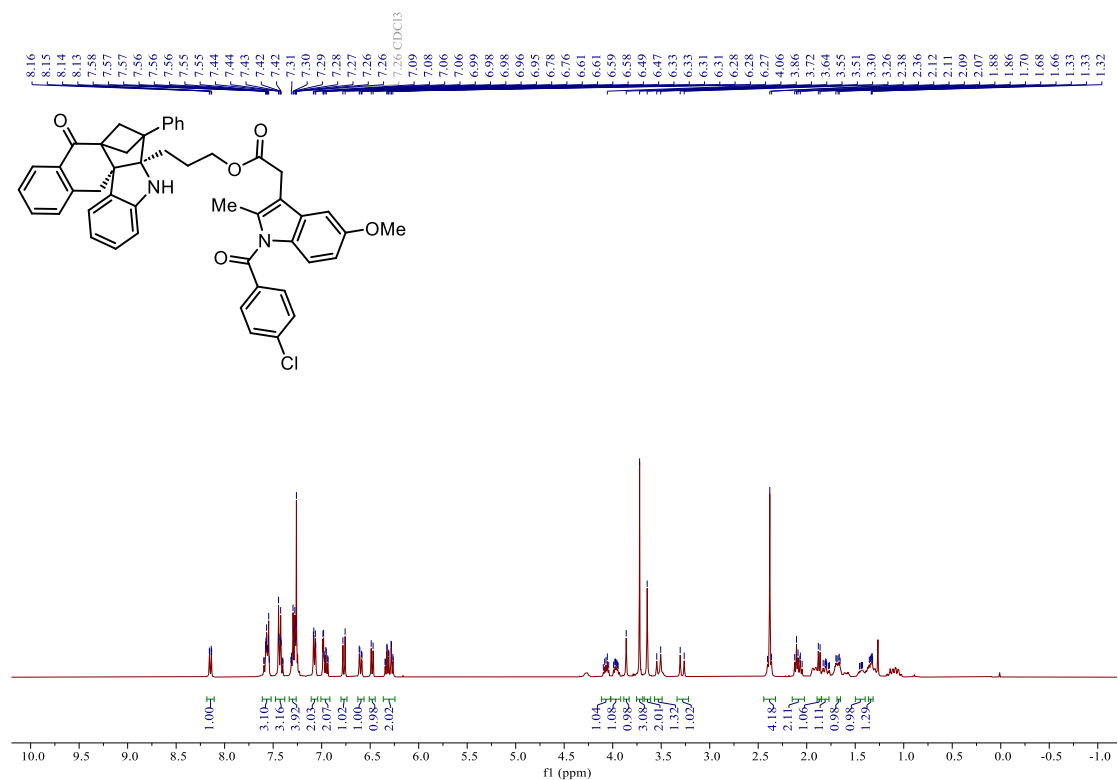
¹H NMR spectra of 7 (CDCl₃, 400 MHz)



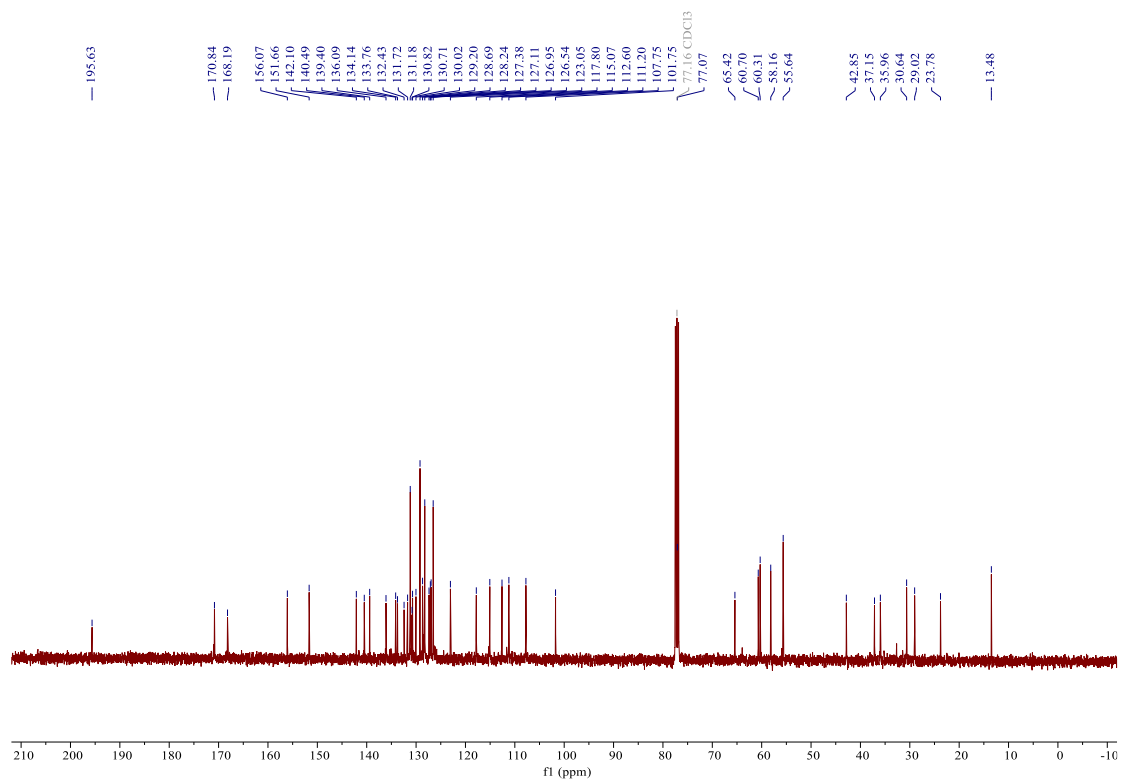
¹³C NMR spectra of 7 (CDCl₃, 101 MHz)



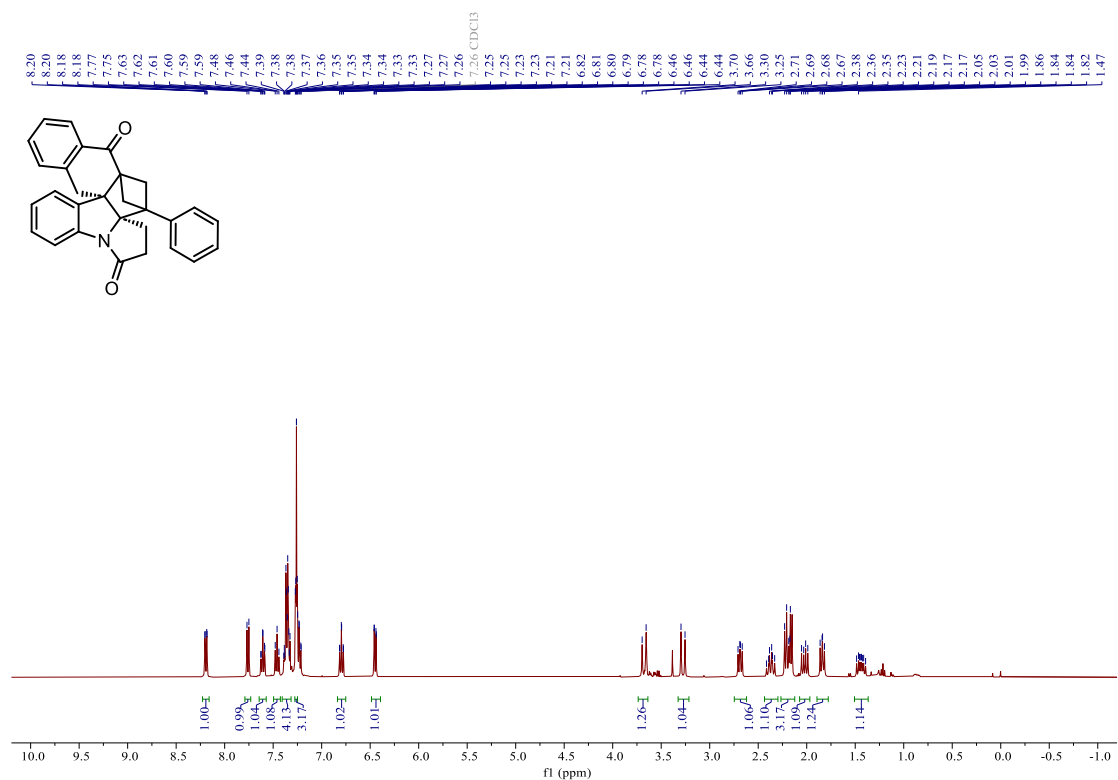
¹H NMR spectra of 8 (CDCl₃, 400 MHz)



¹³C NMR spectra of 8 (CDCl₃, 101 MHz)



¹H NMR spectra of 9 (CDCl₃, 400 MHz)



¹³C NMR spectra of 9 (CDCl₃, 101 MHz)

