Supporting Information

Cobalt (III) Catalysed Annulation of Indoles With Phenylethynyl ether For The Synthesis of ABC ring System of Ergot Alkaloids

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1. General Information:[1]

Reactions were performed using borosil Sealed tube under N_2 atmosphere. Column chromatography was done by using 100-200 & 230-400 mesh size silica gel of Finar Chemicals. Gradient elution was performed by using distilled petroleum ether and ethyl acetate. Merck TLC plates were detected under UV light at 254 nm. ^{1}H NMR and ^{13}C NMR were recorded on Bruker AV 400, 700 MHz spectrometer using $CDCl_3$ as NMR solvents. The residual $CHCl_3$ for ^{1}H NMR (δ = 7.26 ppm) and the deuterated solvent signal for ^{13}C NMR (δ = 77.00 ppm) is used as reference. Multiplicity (s = single, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet), integration, and coupling constants (*J*) in hertz (Hz). HRMS signal analysis was performed using a micro TOF Q-II mass spectrometer. X-ray analysis was conducted using Rigaku Smartlab X-ray diffractometer. Reagents and starting materials were purchased from Sigma Aldrich, Alfa Aesar, TCI, Avra, Spectrochem, Carbanio and other commercially available sources and used without further purification unless otherwise noted.

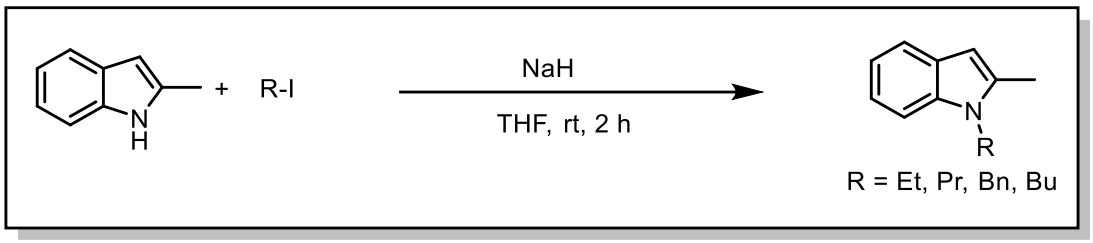
Abbreviation:

Cp*(1,2,3,4,5-Pentamethylcyclopentadiene), TFE (2,2,2-Trifluoroethanol), THF (Tetrahydrofuran), DMSO (Dimethylsulfoxide), HFIP (1,1,1,3,3,3-Hexafluoroisopropanol), DCE (1,2-Dichloroethane), DCM (Dichloromethane), PivOH (Pivalic acid), PivCl (Pivaloyl chloride), EtOAc (Ethylacetate), TLC (Thin Layer Chromatography), TBAF (Tetra Butyl Ammonium Fluoride), TFT (Triflurotoluene), DCM (Dichloromethane), DCE (Dichloroethane), DMF (Dimethylformamide).

2. Experimental procedure:

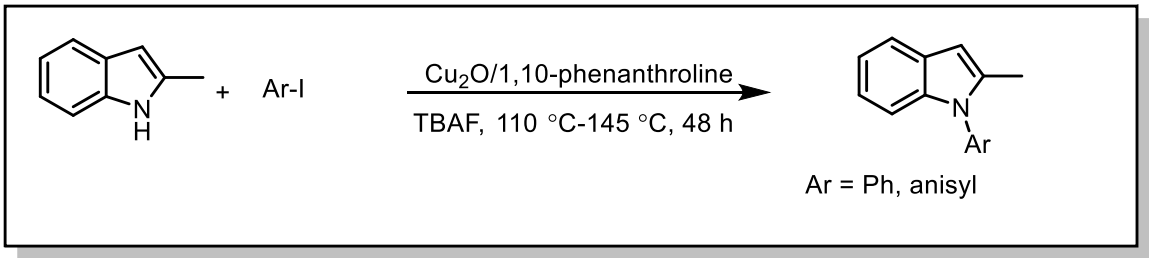
2.1 General procedure for preparation of *N*-protected indoles:

(a) *N*-alkyl indoles were prepared by following the reported procedure:[2]



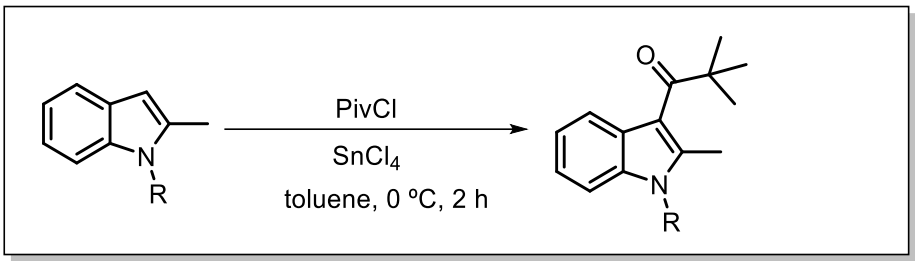
To a well-stirred solution of 2-methyl indole (10 mmol, 1 equiv) in THF (0.6 M, 16 mL w.r.t. indole) at 0 °C was added sodium hydride (60% in mineral oil, 15 mmol, 1.5 equiv) quickly. The reaction was warmed to room temperature and allowed to stir for 30 min. After 30 min, the reaction flask was cooled again to 0 °C, and alkyl halide (15 mmol, 1.5 equiv) was added dropwise. The reaction mixture was warmed to room temperature and allowed to stir until the reaction was completed (monitored by TLC) and then cooled to 0 °C and quenched with 20 ml of saturated aqueous NH_4Cl. The product was extracted with diethyl ether (3 x 20 mL) and dried over anhydrous Na_2SO_4. The organic phase was concentrated using rotary evaporator to obtain the crude mixture which was further purified by column chromatography (using 10% ethyl acetate/hexane) giving a white yellow oil up to 99% yield.

(b) *N*-aryl indoles were prepared by following the reported procedure:[3]



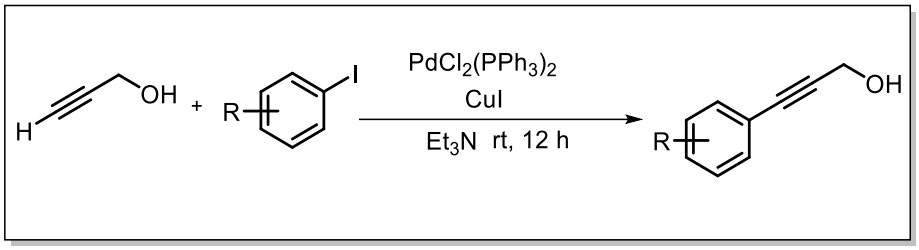
A mixture of 2-methyl indole (0.5 mmol, 1 equiv), aryl iodide (0.6 mmol, 1.2 equiv), Cu_2O (0.05 mmol, 0.1 equiv), 1,10-phenanthroline (0.1 mmol, 0.2 equiv), and TBAF (1.5 mmol, 3 equiv) was stirred at 110–145 °C for 24–48 h until complete consumption of the starting material was observed (monitored by TLC). After completion of the reaction, EtOAc (10 mL) was poured into the reaction mixture, which was then washed with saturated aqueous NaCl (3 × 5 mL) and extracted with Et_2O (2 × 10 mL). The organic layers were then dried over anhydrous Na_2SO_4 and evaporated using rotary evaporator. The crude residue was purified by flash column chromatography (hexane–EtOAc) to afford the desired product.

2.2 General procedure for the preparation of 3-pivaloyl indole:[4]



A two -neck round bottom flask containing a magnetic stir bar was charged with a solution of 2 methyl indole (5.13 mmol, 1 equiv) derivative and anhydrous toluene (50 mL w.r.t. methyl indole) The flask was cooled to 0 ℃ and pivaloyl chloride (7.69 mmol, 1.5 equiv) was added. After stirring for 15 min at 0 ℃, a solution of $SnCl_4$ (10.26 mmol, 2 equiv) in 24 mL of anhydrous toluene was added at 0 ℃ in a dropwise manner. The resultant solution was stirred for 2 h at 0 ℃ then 75 mL of 8% $NaHCO_3$ was added dropwise. The resultant slurry was diluted with 150 mL of EtOAc, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed using a rotary evaporator, and the crude residue was purified by column chromatography (using 10% ethyl acetate/hexane) to give the pure product.

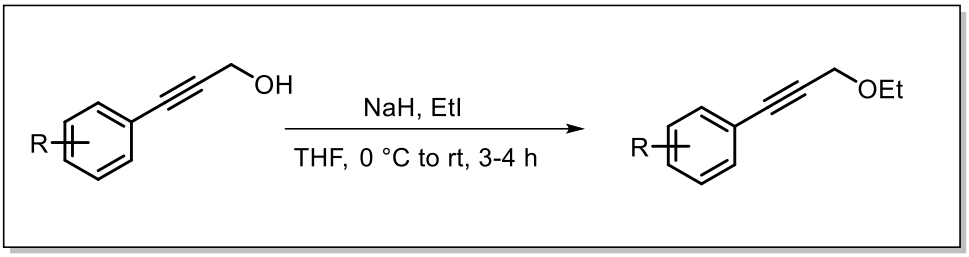
2.3 General preparation of propargyl alcohols: [5]



In an oven-dried 25 ml sealed tube with a magnetic stir bar, CuI (0.05 mmol, 5 mol %) was added, followed by the addition of Et_3N (5 mL, 0.2 M w.r.t. aryl iodide) and aryl iodide (1.0 mmol, 1 equiv). The sealed tube was flushed with N_2, taken inside glove box and $PdCl_2(PPh_3)_2$ (0.02 mmol, 2 mol %) was added and sealed, and then brought outside the glove box. The reaction was stirred at room temperature for 10 minutes and propargyl alcohol (1.5 mmol, 1.5 equiv) was added and flushed with N_2. The resulting mixture was stirred at room temperature overnight. After completion of reaction (monitored by TLC) the reaction was filtered through

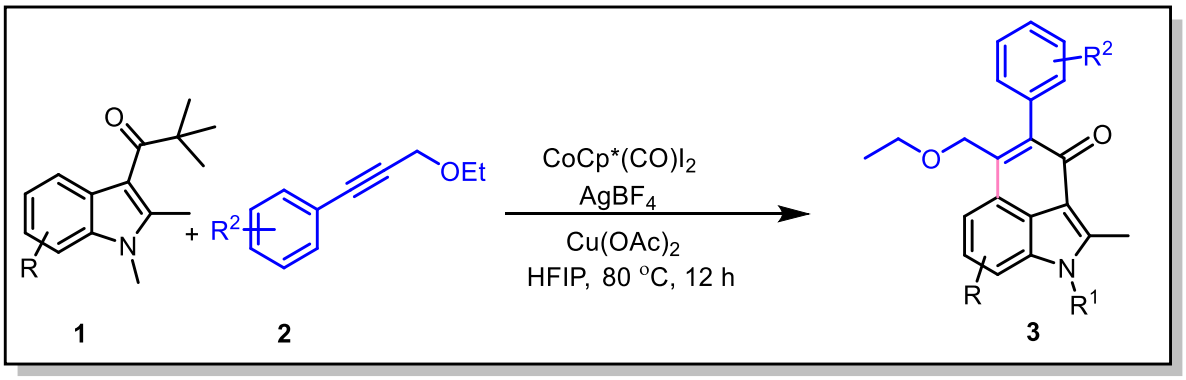
a pad of celite. The solvent was evaporated using rotary evaporator and purified using column chromatography, to get the desired product.

2.4 General preparation of propargyl ethers: [6]



In an oven-dried 25 mL 2-neck round-bottom flask containing a magnetic stir bar, the alcohol (2.0 mmol, 1 equiv) dissolved in THF (3.3 mL w.r.t. alcohol) was added. To this solution, NaH (60% in mineral oil, 3 mmol, 1.5 equiv) was added at 0 °C quickly. The reaction was stirred at room temperature for 30 minutes. After this, iodoethane (2.4 mmol, 1.2 equiv) was added to the solution at 0 °C. The final reaction mixture was stirred at room temperature for 3-4 h. After confirmation of product formation using TLC, the reaction was quenched, the organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated using rotary evaporator and purified using column chromatography, to get the desired product.
(Note: The column was first eluted with hexane to get rid of mineral oil)

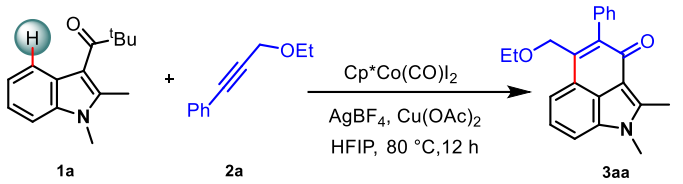
2.5 General procedure for C-4 annulation of *N*, 2 methyl 3-pivaloyl indole:



To a pre-dried 25ml sealed tube containing a magnetic stir bar under N_2, *N*-protected 2 methyl 3-pivaloyl indole **1** (0.1 mmol, 1 equiv), [CoCp*(CO)I_2] (0.02 mmol, 0.2 equiv), $Cu(OAc)_2$ (0.03 mmol, 0.3 equiv), dry HFIP (0.1 M w.r.t. **1**) and propargyl ether **2** (0.4 mmol, 4 equiv) were added sequentially. Then the sealed tube was taken inside the glove box and $AgBF_4$ (0.06 mmol, 0.6 equiv) was added. Then the sealed tube was brought outside the glove box and the reaction mixture was vigorously stirred at 80 °C on preheated aluminum block for 12 h. After 12 h (completion of reaction as monitored by TLC analysis), the reaction mixture was cooled

to room temperature and diluted with ethyl acetate and passed through a short celite pad, the solvent was evaporated using rotary evaporator and the residue was purified by column chromatography using EtOAc/hexane mixture on silica gel to give the pure product **3**.

2.6 Optimisation table:



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

entry	deviation from the standard condition	yield (%)
1[a]	**none**	**76**
2[b]	other solvents instead of HFIP	0
3	TFE as a solvent instead of HFIP	48
4	mixture of solvents TFE:HFIP (1:1)	50
5	10 mol % of $CoCp^*(CO)I_2$ instead of 20 mol %	57
6	$Cu(OAc)_2 \cdot H_2O$ instead of $Cu(OAc)_2$	24
7	Cu_2O instead of $Cu(OAc)_2$	16
8	LiOAc as an additive	15
9	$Zn(OAc)_2$ as an additive	50
10	AgOAc as an additive	38
11	CsOAc as an additive	54
12	Without $Cu(OAc)_2$	0
13	1.5 eq. of $Cu(OAc)_2$ instead of 30 mol %	51
14	without $CoCp^*(CO)I_2$	0

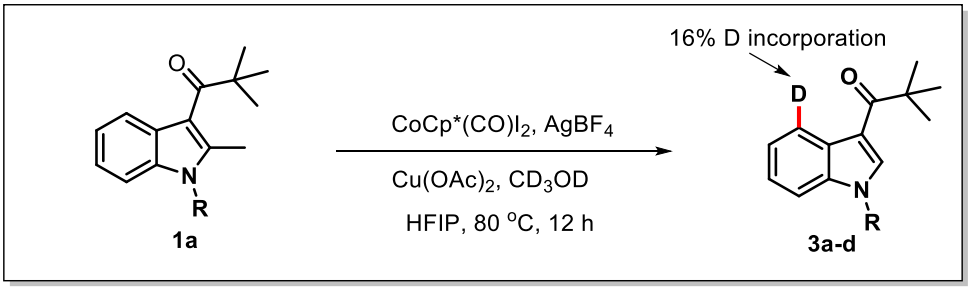
[a]Reaction Conditions: **1a** (0.1 mmol), **2a** (0.4 mmol), [Co $Cp^*(CO)I_2$] (20 mol %), $AgBF_4$ (60 mol %), $Cu(OAc)_2$ (30 mol %), HFIP (0.1 M w.r.t. **1a**), 80 °C, 12 h, N_2. [b]1,4-dioxane, DMF, chloroform, DCM, DCE, acetonitrile, toluene, methanol, and TFT.

Our investigation commenced with the reaction of N,2-di methyl-3-pivaloyl indole **1a** with the coupling partner (3-ethox yprop-1-yn-1-yl) benzene **2a**, under the catalytic influence of cobalt, silver salt, and an additive, this led to the synthesis of coveted phenyl benzoindole derivative **3aa**. After gaining in sights into the distinctive roles played by each component, We have begun optimizing the reaction conditions to develop a high-yielding process. We then carried out a systematic screen ing and found that the use of 20 mol % $Cp^*Co(CO)I_2$ catalyst, 60 mol % $AgBF_4$, and 30 mol % of $Cu(OAc)_2$ as the additive in a 0.1 M hexafluoroisopropanol (HFIP) yielded a striking 76% product yield (Table 1, entry 1). Scheme 1. Previous work vs our work Other solvents for e.g. 1.4 dioxane, DMF, DCE, Acetonitrile etc. failed to yield the desired product. (Table 1, entry 2). Although less efficient than HFIP, TFE and a 1:1 mixture of TFE:HFIP nevertheless yielded modest results of 48% and 50%, respectively (Table 1, entry 3, 4). When 10 mol % [$Cp^*Co(CO)I_2$] was used 57% of product was obtained. (Table 1, entry 5). Next, we screened the oxidant and found that using $Cu(OAc)_2 \cdot H_2O$ and Cu_2O instead of $Cu(OAc)_2$ yielded the product in 24% and 16% respectively (Table 1, entry 6,7), while other metal acetates such as LiOAc, $Zn(OAc)_2$, AgOAc, CsOAc yielded the results 15%, 50%, 38%,

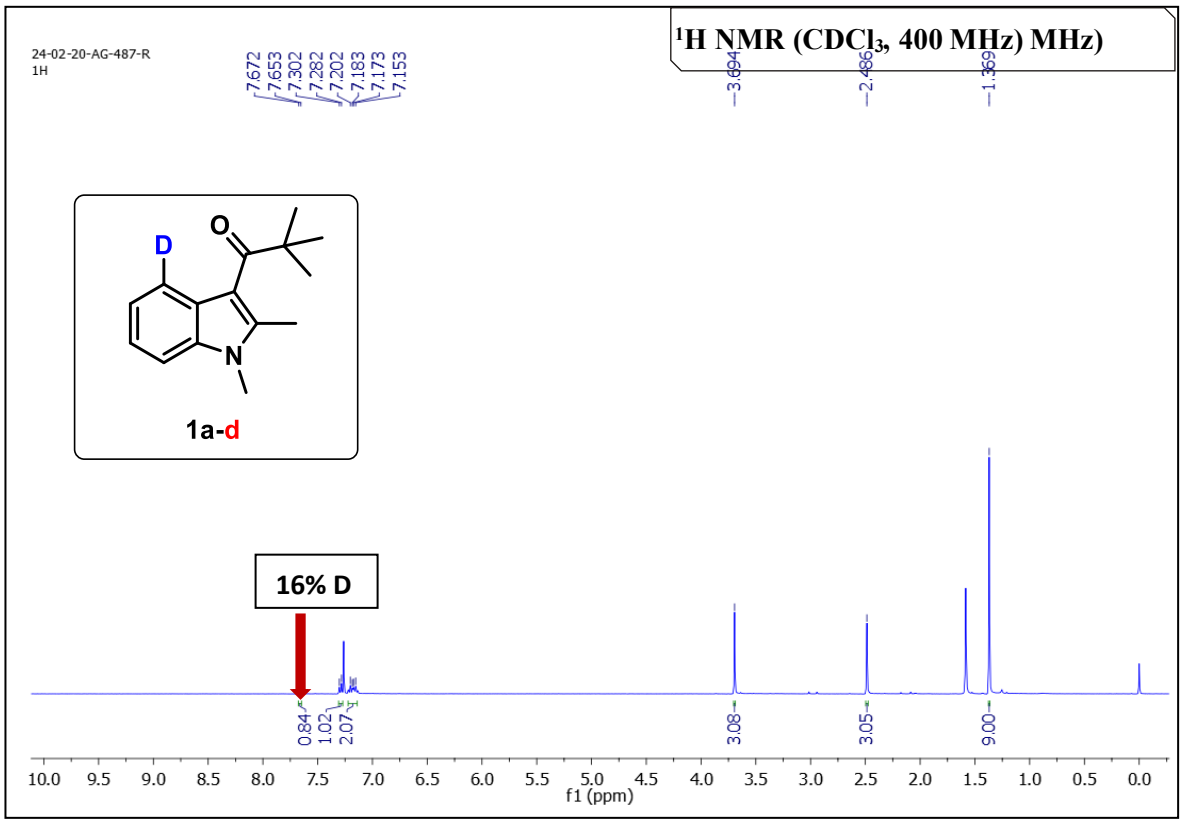
54% respectively (Table 1, entry 8-11), all of which failed to enhance the yield of the product. The absence of $Cu(OAc)_2$ in the reaction failed to furnish the expected product, highlighting sthe essential role of the copper catalyst in the success of the transformation (Table 1, entry 12). Then, 1.5 equiv. $Cu(OAc)_2$ was used which yielded 51% of the product (Table 1, entry 13). The absence of $[Cp^*Co(CO)I_2]$ failed to give the desired product (Table 1, entry 14).

3. Mechanistic Investigation:

3.1 H/D exchange experiment:

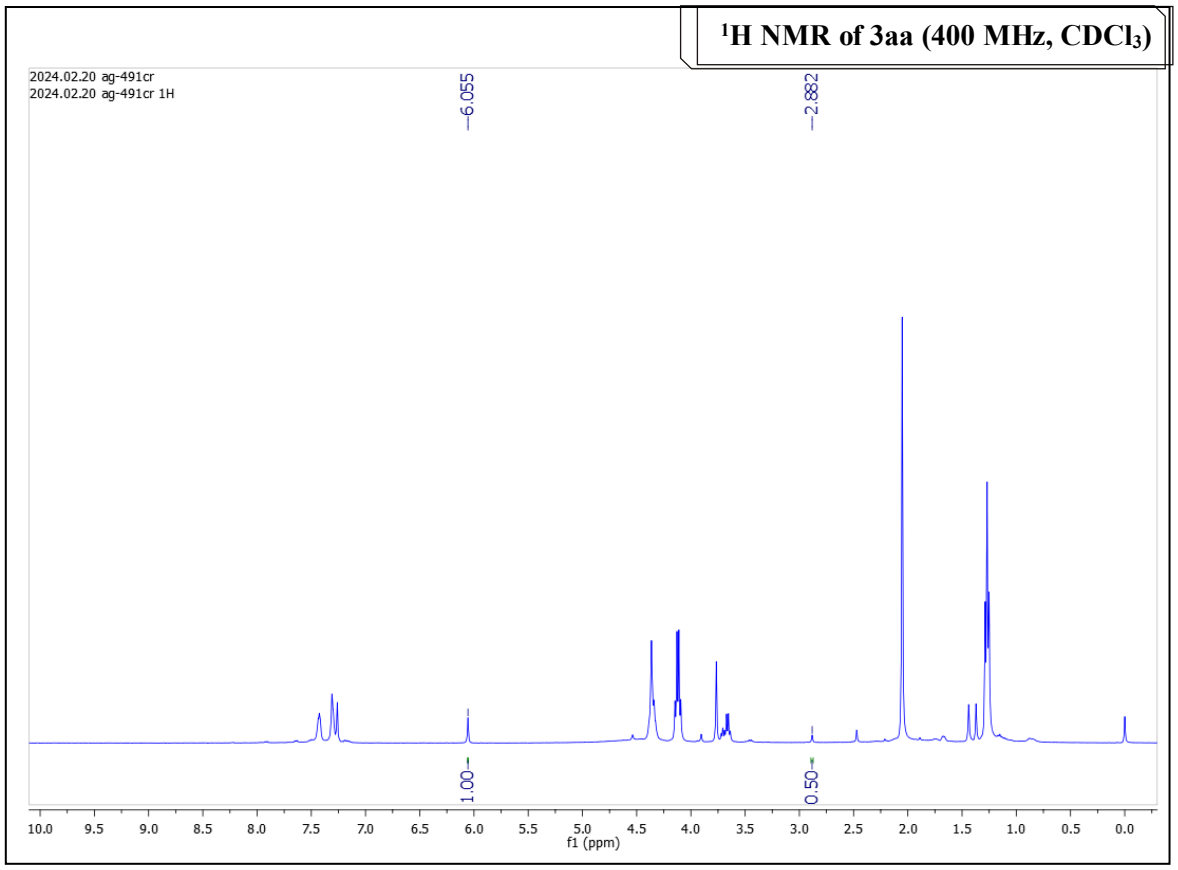


To a pre-dried 25 ml sealed tube under N_2, the mixture of *N*-substituted 3-pivaloyl indole **1a** (0.1 mmol, 1 equiv), CD_3OD (1 mmol, 10 equiv), $[Cp^*Co(CO)I_2]$ (0.02 mmol, 0.2 equiv), $Cu(OAc)_2$ (0.03 mmol, 0.3 equiv) and HFIP (0.1 M w.r.t **1a**) were added and sealed. Then the sealed tube was taken inside the glove box and $AgBF_4$ (0.06 mmol, 0.6 equiv) was added. The reaction mixture was vigorously stirred at 80 °C on the preheated aluminum block for 12 h. After 12 h (completion of the reaction as monitored by TLC analysis), the reaction mixture was cooled to room temperature and diluted with ethyl acetate and passed through a short celite pad, the solvent was evaporated using rotary evaporator and the residue was purified by column chromatography using EtOAc/hexane mixture on silica gel to give the pure product **3a-d**, where 16% deuterium incorporation has been observed in ^1H NMR.



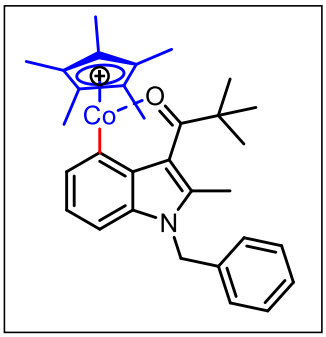
3.2 Reaction with radical scavenger (TEMPO)

To a pre-dried 25 ml sealed tube containing a magnetic stir bar under N_2, *N,2*-dimethyl 3-pivaloyl indole **1a** (21 mg, 0.1 mmol, 1 equiv), [CoCp*(CO)I_2] (10 mg, 0.02 mmol, 20 mol %), $Cu(OAc)_2$ (5.4 mg, 0.03 mmol, 0.3 equiv), TEMPO (16 mg, 0.1 mmol, 1 equiv), dry HFIP (1 mL, 0.1 M w.r.t. **1a**) and (3-ethoxyprop-1-yn-1-yl)benzene **2a** (64 mg, 0.4 mmol, 4 equiv) were added sequentially. Then the sealed tube was taken inside the glove box and $AgBF_4$ (12 mg, 0.06 mmol, 60 mol %) was added and sealed. Then the sealed tube was brought outside the glove box and the reaction mixture was vigorously stirred at 80 °C on preheated aluminum block for 12 h. After 12 h (completion of reaction as monitored by TLC analysis) the reaction mixture was cooled to room temperature and diluted with ethyl acetate and passed through a short celite pad, residue was submitted for NMR using internal standard trimethoxy benzene (1 mmol) to get to know the yield of the product **3aa** (50%).

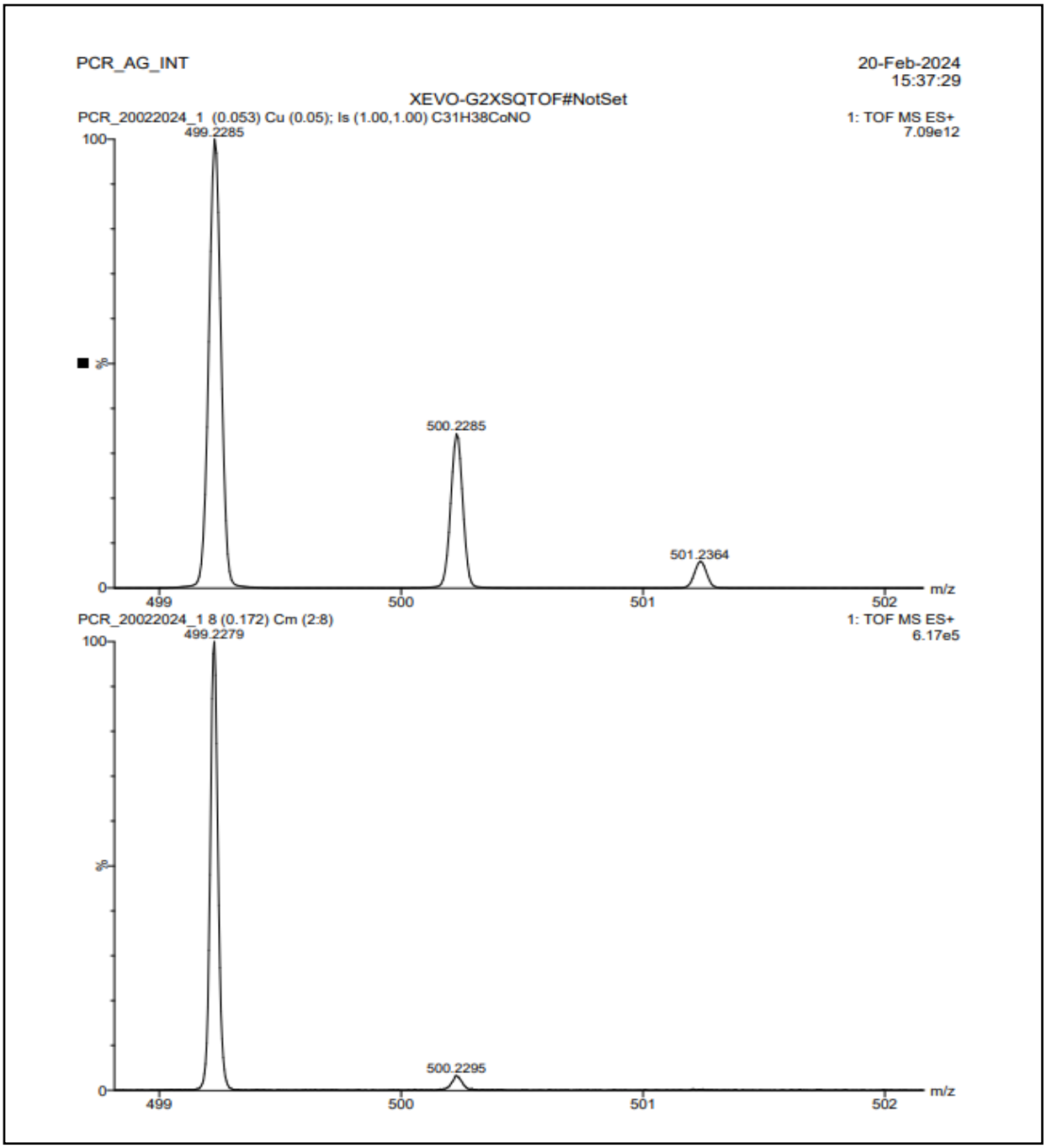


3.3 Detection of six-membered cobaltacycle intermediates:

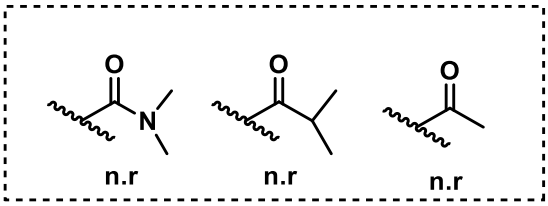
To a pre-dried 25ml sealed tube containing a magnetic stir bar under N_2, the mixture of *N*-protected 2 methyl 3-pivaloyl indole **1r** (30 mg, 0.1 mmol, 1 equiv), [CoCp*(CO)I_2] (48 mg, 0.1 mmol, 1 equiv), $Cu(OAc)_2$ (5 mg, 0.03 mmol, 0.3 equiv) and dry HFIP (1 mL, 0.1 M w.r.t. **1r**) were added sequentially. Then the sealed tube was taken inside the glove box and $AgBF_4$ (12 mg, 0.06 mmol, 0.6 equiv) was added and sealed. Then the sealed tube was brought outside the glove box and the reaction mixture was vigorously stirred at 80 °C on preheated aluminum block for the 12 h. After 12 h, the reaction mixture was cooled to room temperature and diluted with EtOAc/methanol (50:50) and passed through a short celite pad, the solvent was evaporated using rotary evaporator and the residue was submitted for HRMS.



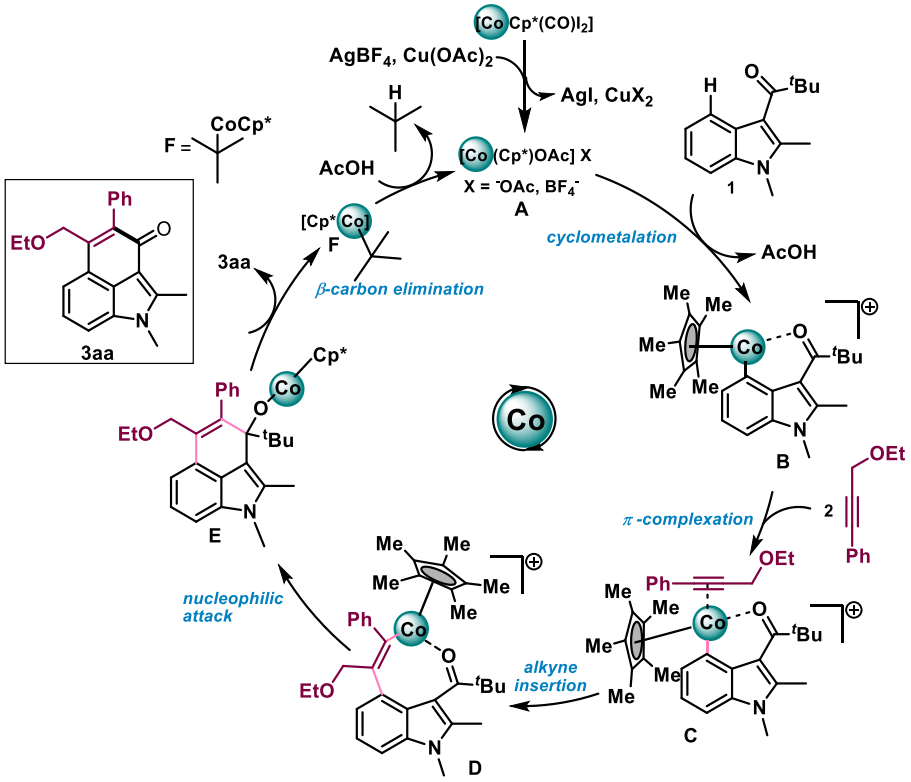
Intermediate HRMS: (ESI)*m/z* calcd for $C_{31}H_{38}CoNO$ $[M]^+$: 499.2285; found: 499.2279.



3.4 Variation in directing group:



3.5 Plausible mechanism of the reaction:

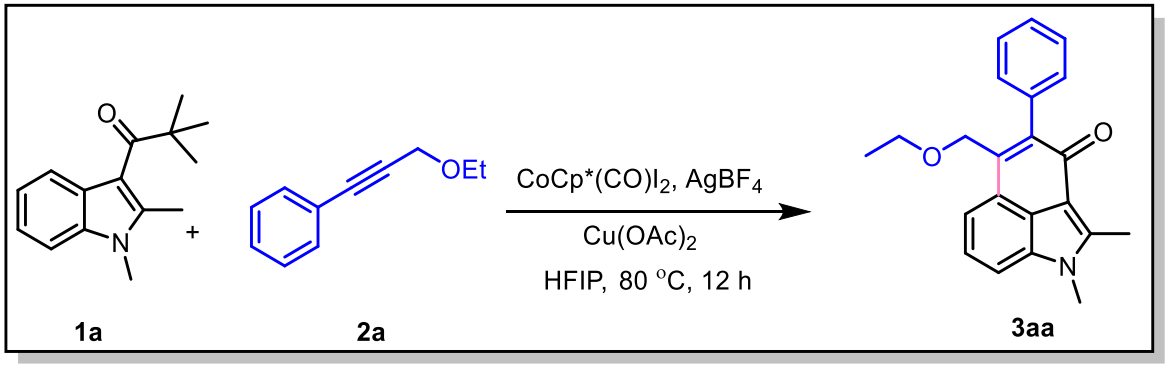


The proposed catalytic cycle described in **Scheme 3.5** highlights a series of key steps for the transformation, The initial step involves the reaction of the cobalt precursor, Cp*Co(CO)I_2, with a suitable silver or copper salt, such as $AgBF_4$ or $Cu(OAc)_2$. This reaction generates the active cationic cobalt (III) species **A**. The active catalyst **A** then triggers C–H activation at the C(4) position of the indole ring. This step is facilitated by the pivaloyl directing group at the indole and results in the formation of a six-membered cobaltacycle intermediate, identified as species **B**. The formation of this intermediate has been confirmed by High-Resolution Mass Spectrometry (HRMS) analysis. The next key step involves the coordination of the alkyne coupling partner, **2a**. The alkyne coordinates with the cobalt center of species **B** through a π-complexation mechanism. The newly formed alkene in species **D**, being bound to the cobalt center, acts as a nucleophile. After the migratory insertion of the alkyne into the Co–C bond of species **B**, the resulting intermediate **D** contains a newly formed alkene that is still coordinated to the cobalt center. Next, the cobalt-alkenyl species **D** attacks the electrophilic carbon of the pivaloyl group, leading to the formation of intermediate **E**. The feasibility of this

transformation is largely influenced by the spatial orientation of the pivaloyl group and the alkyl group at the C2 position of the pyrrole ring of the indole. The structural arrangement of these substituents can create an environment that promotes β-carbon elimination[9] and facilitates the generation of the desired product **3aa** alongside the alkyl metal intermediate **F** through a tertbutyl anion which undergoes protodemetallation to regenerate active catalyst Co (III) species **A**.

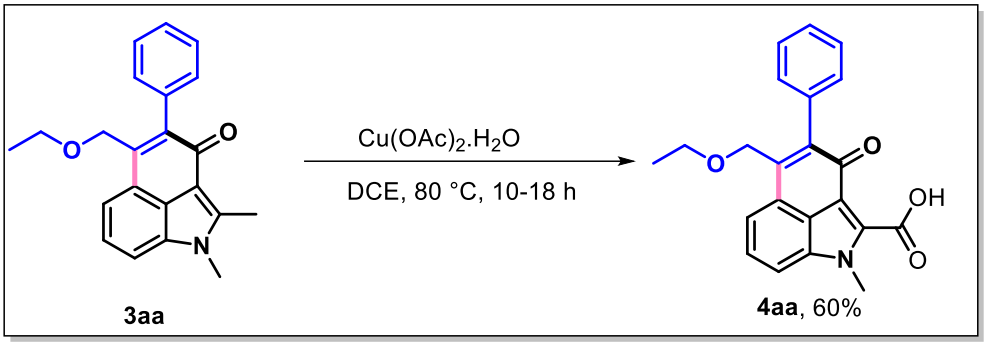
4. Synthetic utility

(a). Scale-up synthesis:



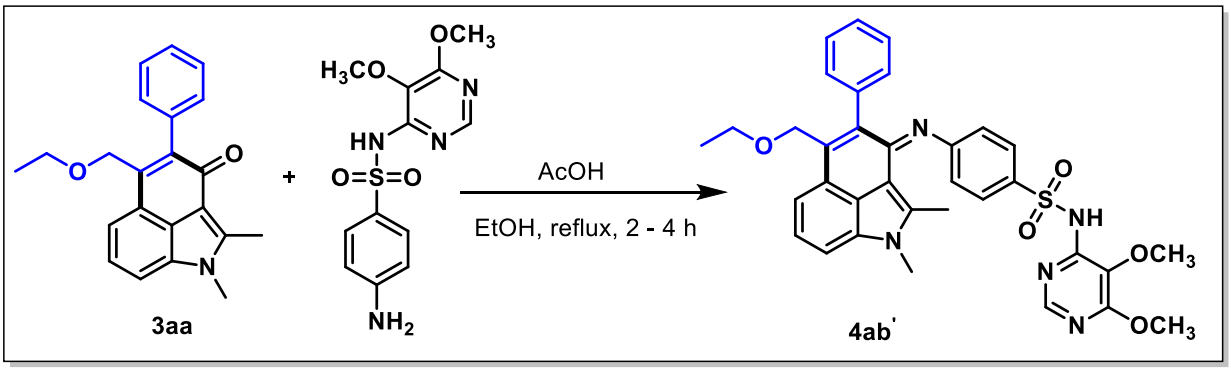
To a pre-dried sealed tube containing a magnetic stir bar under N_2, *N,2*-dimethyl 3-pivaloyl indole **1a** (229 mg, 1 mmol, 1 equiv), [CoCp*(CO)I_2] (96 mg, 0.2 mmol, 20 mol %), $Cu(OAc)_2$ (54 mg, 0.3 mmol, 0.3 equiv), dry HFIP (10 mL, 0.1 M w.r.t. **1a**) and (3-ethoxyprop-1-yn-1-yl)benzene **2a** (641 mg, 4 mmol, 4 equiv) were added sequentially. Then the sealed tube was taken inside the glove box and $AgBF_4$ (117 mg, 0.6 mmol, 60 mol %) was added and sealed. The reaction mixture was vigorously stirred at 80 °C on the preheated aluminum block for 20 h. After 20 h (completion of the reaction was monitored by TLC analysis), reaction mixture was diluted with ethyl acetate and passed through a short celite pad, the solvent was evaporated using rotary evaporator and the residue was purified by column chromatography using EtOAc/hexane mixture on silica gel to obtain 212 mg (64% yield) of the pure product **3aa**.

(b) Synthesis of Indole 5-(ethoxymethyl)-1-methyl-3-oxo-4-phenyl-1,3-dihydrobenzo[cd]indole-2-carboxylic acid:[7]



To an oven-dried seal 5(ethoxy methyl)1-methyl-2-methyl-4-phenyl benzo[cd] indol-3(1h)-sone (**3aa)** (1 mmol, 1 equiv, 331 mg), $Cu(OAc)_2.H_2O$ (1.2 mmol, 1.2 equiv, 240 mg), DCE (0.1 M w.r.t. **3aa**) were added under a N_2 atmosphere. The reaction mixture was vigorously stirred at 80°C on the preheated aluminum block for 18 h.The reaction mixture was cooled to room temperature and diluted with ethyl acetate and passed through a short celite pad, the solvent was evaporated using rotary evaporator and the residue was purified by column chromatography using EtOAc/hexane mixture on silica gel to give the pure product **4aa** in 60% yield.

(e) Synthesis of sulfadoxine derivative:[8]



To an oven-dried seal tube 5(ethoxy methyl)1-ethyl-2-methyl-4-phenyl benzo[cd] indol-3(1h)-one (**3aa**) (1 mmol, 1 equiv), Sulfadoxine (2 mmol, 1 equiv), AcOH (0.2 mmol, 0.2 equiv), EtOH (0.05 M w.r.t. **3aa**) were added under a N_2 atmosphere and refluxed for 2-4 hrs. The reaction mixture was worked up and diluted with ethyl acetate and the organic layer was washed with water and dried over anhydrous Na_2SO_4. The solvent was evaporated using rotary evaporator and purified using column chromatography using EtOAc/hexane mixture on silica gel to obtain the pure product **4ab'** in 56 % yield.

5. References:

[1] Banjare, S. K., Biswal, P., Ravikumar, P. C. *J. Org. Chem*. **2020**, *85*, 5330−5341.

[2] Kong, A., Han, X., Lu, X. *Org. Lett*. **2006**, *8*, 1339–1342.

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[4] MacKay, J. A., Bishop, R. L., Rawal, V. H. *Org. Lett*. **2005**, *7*, 3421−3424

[5] Lang, X.-D., You, F., He, X., Yu, Y.-C., He, L.-N. *Green Chem*.**2019**, *21*, 509-514.

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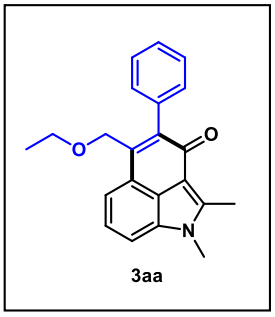
[8] Cordes E. H., Jencks, W. P. *J. Am. Chem. Soc.* **1962,** *84*, 832-837

[9] Souillart, L.; Cramer, N. *Chem. Sci*. **2014**, *5*, 837–840.

6. Experimental characterization data for products:



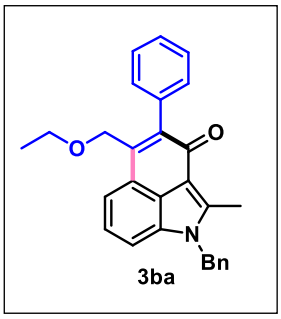
5-(ethoxymethyl)-1,2-dimethyl-4-phenylbenzo[*cd*]indol-3(1*H*)-one (3aa) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3aa** in 76% yield (25 mg).

Physical State: Yellow solid
m.p.: 130-132 °C
R_f-value: 0.4 (40% EtOAc/Hexane)

^{1}H NMR (CDCl$_3$,700 MHz): δ 7.86 (d, J = 7 Hz, 1H), 7.46 -7.40 (m, 4H), 7.39 -7.34 (m, 1H), 7.31-7.29 (m, 2H), 4.55 (s, 2H), 3.85 (s, 3H), 3.46 (q, J = 7 Hz, 2H), 2.88 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 180.2, 148.6, 143.9, 140.8, 136.7, 134.2, 130.3, 127.8,127.2, 125.4, 123.3, 123.0, 121.7, 112.6, 111.2, 68.0, 65.8, 30.2, 15.3, 12.2.

HRMS (ESI) m/z: [M+Na]$^+$Calcd for $C_{22}H_{21}NO_2Na$: 354.1469; Found 354.1473.



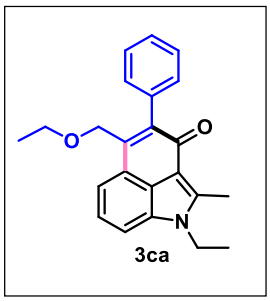
1-benzyl-5-(ethoxymethyl)-2-methyl-4- phenylbenzo[cd] indol-3(1H)-one (3ba) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ba** in 81% yield (33 mg).

Physical State: Yellow solid
m.p.: 190-193 °C
R_f-value: 0.6 (40% EtOAc/Hexane)

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.86 (d, J = 7.2 Hz, 1H), 7.43 (q, J = 7.2 Hz, 2H), 7.38-7.35 (m, 3H), 7.33-7.28 (m, 5H), 7.04 (d, J = 6 Hz, 2H), 5.47 (s, 2H), 4.56 (s, 2H), 3.48 (q, J = 7.2 Hz, 2H), 2.84 (s, 3H), 1.17 (t, J = 6.8 Hz, 3H).

^{13}C NMR (CDCl$_3$, 100 MHz): δ 180.6, 148.2, 144.0, 140.9, 136.7, 135.7, 134.0, 133.3, 129.1, 128.0, 127.8, 127.2, 126.1, 125.6, 123.5, 123.3, 121.7, 113.0, 111.7, 68.1, 65.9, 47.3, 15.3, 12.3.

HRMS (ESI) m/z: [M+H]$^+$ Calcd for $C_{28}H_{26}NO_2$: 408.1964; Found 408.1986.



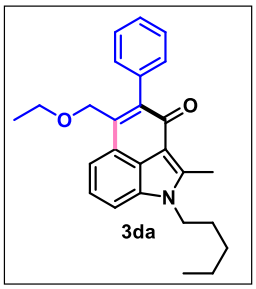
5-(ethoxymethyl)-1-ethyl-2-methyl-4- phenylbenzo [cd] indol-3(1H)-one (3ca) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ca** in 87% yield (30 mg).

Physical State: Yellow Liquid.
R_f-value: 0.3 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 7.6 Hz, 1H), 7.47-7.40 (m, 4H), 7.38-7.36 (m, 1H), 7.31-7.29 (m, 2H) , 4.55 (s, 2H), 4.35 (q, J = 7.6 Hz, 2H), 3.46 (q, J = 7.2 Hz, 2H), 2.88 (s, 3H), 1.46 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.2, 147.7, 144.0, 140.8, 136.8, 133.1, 130.3, 127.7, 127.2, 125.6, 123.4, 123.0, 121.6, 112.7, 111.3, 68.0, 65.8, 38.7, 15.5, 15.3, 12.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{24}NO_2$: 346.1807; Found 346.1785.



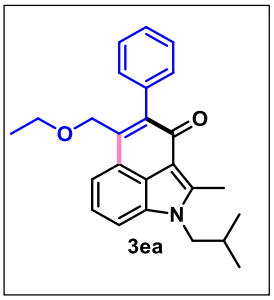
5-(ethoxymethyl)-2-methyl-1-pentyl-4-phenylbenzo [cd] indol-3(1H)-one (3da) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3da** in 49% yield (19 mg).

Physical State: Yellow liquid.
R_f-value: 0.3 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 7.6 Hz, 1H), 7.46-7.40 (m, 4H), 7.37 (d, J = 8 Hz, 1H), 7.30 (d, J = 7.2 Hz, 2H), 4.55 (s, 2H), 4.22 (t, J = 7.2 Hz, 2H), 3.46 (q, J = 6.8 Hz, 2H), 2.88 (s, 3H), 1.85 (m, J = 7.2 Hz, 2H), 1.37-1.33 (m, 4H), 1.16 (t, J = 6.8 Hz, 3H), 0.90 (t, J = 6.4 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.3, 148.0, 144.0, 140.7, 136.8, 133.6, 130.3, 127.7, 127.1, 125.6, 123.4, 122.9, 121.5, 112.6, 111.5, 68.0, 65.8, 44.0, 30.1, 29.0, 22.3, 15.3, 13.9, 12.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{30}NO_2$: 388.2198; Found 388.2215.



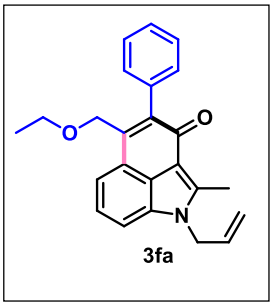
5-(ethoxymethyl)-1-isobutyl-2-methyl-4phenylbenzo[cd] indol-3(1H)-one (3ea) was prepared according to general procedure **(2.5)**. The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ea** in 48% yield (18 mg).

Physical State: Yellow solid
m.p.: 146-148 °C
R_f-value: 0.6 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (d, J = 7.6 Hz, 1H), 7.43 (t, J = 8 Hz, 3H), 7.39-7.35 (m, 2H), 7.32-7.29 (m, 2H), 4.55 (s, 2H), 4.03 (d, J = 8 Hz, 2H), 3.47 (q, J = 6.8 Hz, 2H), 2.88 (s, 3H), 2.31-2.23 (m, 1H), 1.16 (t, J = 7.6 Hz, 3H), 0.99 (d, J = 6.4 Hz, 6H).

^{13}C NMR ($CDCl_3$, 176 MHz): δ 180.3, 148.3, 144.0, 140.7, 139.1, 136.8, 134.0, 130.3, 127.7, 127.1, 122.9, 121.5, 112.7, 111.9, 68.0, 65.8, 51.4, 29.8, 20.2, 15.2, 12.6.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{28}NO_2$: 374.2120; Found 374.2105.



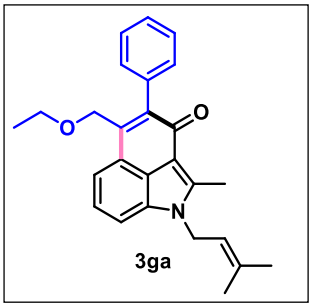
1-allyl-5-(ethoxymethyl)-2-methyl-4-phenylbenzo[cd]indol-3(1H)-one (3fa) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3fa** in 48% yield (17 mg).

Physical State: Yellow solid
m.p.: 120-124 °C
R_f-value: 0.5 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 7.6 Hz, 1H), 7.42 (t, J = 7.6 Hz, 3H), 7.38-7.34 (m, 2H), 7.32-7.30 (m, 2H), 6.05-5.95 (m, 1H), 5.23 (d, J = 10.4 Hz, 1H), 4.91 (d, J = 17.2 Hz, 1H), 4.85 (d, J = 4.4 Hz, 2H), 4.55 (s, 2H), 3.47 (q, J = 7.2 Hz, 2H), 2.85 (s, 3H), 1.16 (t, J = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 176 MHz): δ 180.5, 148.1, 143.9, 140.9, 136.7, 133.6, 131.6, 130.3, 127.7, 127.2, 125.6, 123.5, 123.1, 121.6, 117.4, 112.8, 111.5, 68.0, 65.8, 45.9, 15.3, 12.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{24}NO_2$: 358.1807; Found 358.1783.



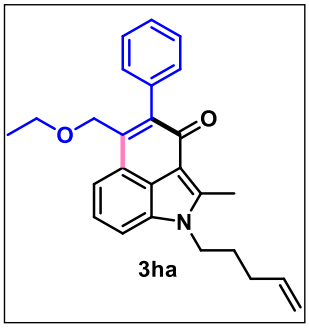
5-(ethoxymethyl)-2-methyl-1-(3-methylbut-2-en-1-yl)-4phenylbenzo[cd] indol 3(1H)-one (3ga) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ga** in 39% yield (15 mg).

Physical State: Yellow solid.
m.p.: 122-124 ℃
R_f-value: 0.6 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 7.2 Hz, 1H), 7.42 (t, J = 8.0 Hz, 3H), 7.39-7.35 (m, 2H), 7.31-7.29 (m, 2H), 5.22 (t, J = 6.8 Hz, 1H), 4.82 (d, J = 6.4 Hz, 2H), 4.55 (s, 2H), 3.45 (q, J = 7.2 Hz, 2H), 2.87 (s, 3H), 1.89 (s, 3H), 1.75 (s, 3H), 1.15 (t, J = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.3, 148.1, 144.0, 140.7, 136.8, 136.5, 133.5, 130.3, 127.7, 127.1, 125.6, 123.4, 122.9, 121.6, 118.9, 112.7, 111.6, 68.0, 65.7, 42.2, 25.6, 18.2, 15.3, 12.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{28}NO_2$: 386.2120; Found 386.2111.



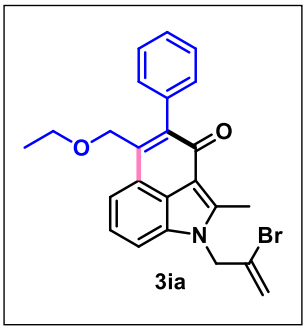
5-(ethoxymethyl)-2-methyl-1-(pent-4-en-1-yl)-4-phenylbenz [cd]indol-3(1H)-one (3ha) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ha** in 73% yield (28 mg).

Physical State: Yellow liquid.
R_f-value: 0.5 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 7.2 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.41-7.36 (m, 3H), 7.31-7.29 (m, 2H), 5.87-5.77 (m, 1H), 5.11-5.06 (m, 2H), 4.55 (s, 2H), 4.24 (t, J = 7.2 Hz, 2H), 3.46 (q, J = 7.2 Hz, 2H), 2.89 (s , 3H), 2.16 (q, J = 6 Hz, 2H), 1.97 (quintet, J = 7.6 Hz, 2H), 1.16 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.3, 148.0, 144.0, 140.8, 136.8, 136.6,133.6, 130.3, 127.8, 127.2, 125.6, 123.4, 123.0, 121.6, 116.2, 112.7, 111.5, 68.0, 65.8, 43.3, 30.7, 29.3, 15.3, 12.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{28}NO_2$: 386.2120; Found 386.2126.



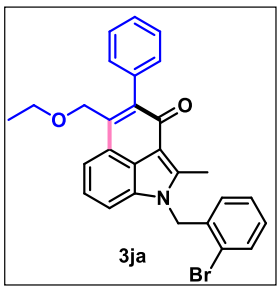
1-(2-bromoallyl)-5-(ethoxymethyl)-2-methyl-4-phenylbenzo [cd]indol-3(1H)-one (3ia) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ia** in 32% yield (14 mg).

Physical State: Yellow solid
m.p.: 115-117 °C
R_f-value: 0.5 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 7.2 Hz, 1H), 7.49-7.41 (m, 4H), 7.39-7.36 (m, 2H), 7.31-7.29 (m, 1H), 5.63 (d, J = 2.8 Hz, 1H), 5.36 (d, J = 2.4 Hz, 1H), 5.03 (s, 2H), 4.54 (s, 2H), 3.48 (q, J = 6.8 Hz, 2H), 2.87 (s, 3H) 1.17 (t, J = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.8, 147.5, 143.9, 141.1, 136.5, 133.4, 130.2, 127.8, 127.3, 127.2, 125.7, 125.5, 123.6 (2C), 121.9, 118.3, 111.5, 68.0, 66.0, 51.1, 15.3, 12.0.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{24}H_{23}BrNO_2$: 436.0912; Found 436.0903.



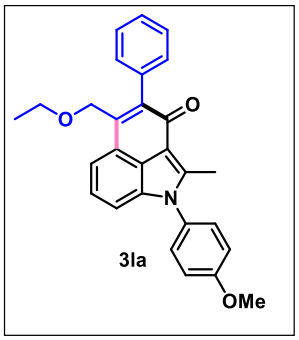
1-(2-bromobenzyl)-5-(ethoxymethyl)-2-methyl-4-phenylben zo[cd]indol-3(1H)-one (3ja) was prepared according to the general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ja** in 73% yield (35 mg).

Physical State: Brown solid.
m.p.: 138-140 °C
R_f-value: 0.8 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 (d, J = 6.4 Hz, 1H), 7.65 (d, J = 8 Hz, 1H), 7.45 (t, J = 7.2 Hz, 2H), 7.39-7.36 (m, 2H), 7.34-7.32 (m, 3H), 7.17-7.12 (m, 3H), 5.50 (s, 2H), 4.56 (s, 2H), 3.50 (q, J = 7.2 Hz, 2H), 2.81 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.7, 148.2, 144.0, 141.0, 136.6, 134.8, 133.8, 133.0, 130.2, 129.5, 128.1, 127.8, 127.3, 126.7, 125.6, 123.6, 123.5, 121.89, 121.81, 113.1, 111.6, 68.1, 66.0, 47.5, 15.3, 12.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{25}BrNO_2$: 486.1069; Found 488.1089.



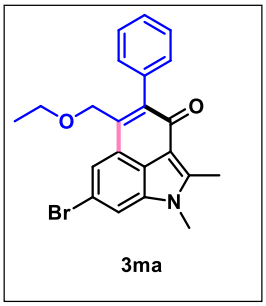
5-(ethoxymethyl)-1-(4-methoxyphenyl)-2-methyl-4-phenyl benzo [cd]indol-3(1H)-one (3la) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3la** in 59% yield (25 mg).

Physical State: Yellow solid
m.p.: 168-170 °C
R_f-value: 0.6 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.2 Hz, 2H), 7.39-7.32 (m, 7H), 7.22 (d, J = 8 Hz, 1H), 7.10 (d, J = 8.8 Hz, 1H), 4.59 (s, 2H), 3.92 (s, 3H), 3.47 (q, J = 7.2 Hz, 2H), 2.74 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.7, 160.0, 148.6, 144.0, 141.1, 136.7, 135.3, 130.3, 128.5, 128.4, 127.8, 127.2, 125.4, 123.44, 123.40, 121.8, 115.0, 113.9, 112.4, 68.1, 65.8, 55.6, 15.3, 13.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{28}H_{26}NO_3$: 424.1913; Found 424.1937.



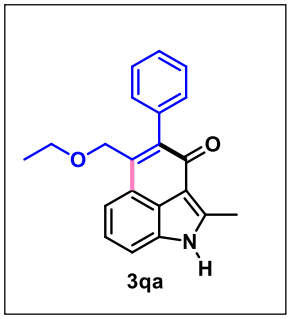
7-bromo-5-(ethoxymethyl)-1,2-dimethyl-4- phenylbenzo [cd]indol-3(1H)-one (3ma) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ma** in 73% yield (30 mg).

Physical State: Yellow solid
m.p.: 134-136 °C
R_f-value: 0.4 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.97 (s, 1H), 7.61 (s, 1H), 7.45-7.37 (m, 3H), 7.30-7.28 (m, 2H), 4.49 (s, 2H), 3.82 (s, 3H), 3.46 (q, J = 7.2 Hz, 2H), 2.86 (s, 3H), 1.18 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 176 MHz): δ 180.0, 149.0, 144.8, 140.0, 136.2, 134.7, 130.1, 127.8, 127.4, 124.5, 124.4 (2C), 124.3, 116.2, 114.1, 112.4, 67.9, 65.9, 30.3, 15.2, 12.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}BrNO_2$: 412.0756; Found 412.0766.



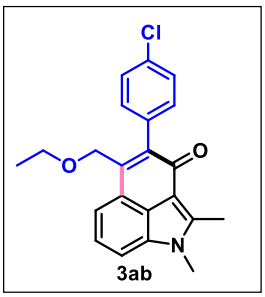
5-(ethoxymethyl)-2-methyl-4-phenylbenzo[cd]indol-3(1H)-one (3qa) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3qa** in 63% yield (20 mg).

Physical State: Yellow solid
m.p.: 240-242 °C
R_f-value: 0.4 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.24 (s, 1H), 7.85 (d, J = 7.2 Hz, 1H) , 7.43-7.39 (m, 3H), 7.37-7.33 (m, 2H), 7.32-7.29 (m, 2H), 4.55 (s, 2H), 3.47 (q, J = 6.8 Hz, 2H), 2.85 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 176 MHz): δ 180.9, 147.7, 143.7, 141.6, 136.7, 131.8, 131.4, 130.3, 127.8, 127.2, 126.3, 123.38, 123.31, 121.5, 112.9, 68.0, 65.9, 15.3, 14.1.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}NO_2$: 318.1494; Found 318.1517.



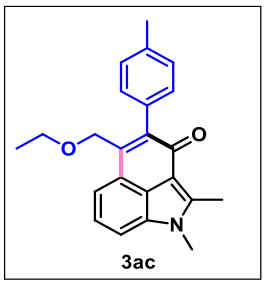
4-(4-chlorophenyl)-5-(ethoxymethyl)- 1,2dimethylbenzo [cd]indol-3(1H)-one (3ab) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ab** in 60% yield (22mg).

Physical State: Yellow solid
m.p.: 164-165 °C
R_f-value: 0.4 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 7.84 (d, J = 7.7 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.41-7.38 (m, 3H), 7.27-7.25 (m, 2H), 4.52 (s, 2H), 3.86 (s, 3H), 3.49 (q, J = 7 Hz, 2H), 2.88 (s, 3H), 1.18 (t, J = 7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 176 MHz): δ 179.9, 148.8, 142.7, 141.1, 135.2, 134.2, 133.2, 131.8, 128.0, 125.4, 123.19, 123.14, 121.8, 112.5, 111.5, 67.9, 66.1, 30.2, 15.3, 12.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}ClNO_2$: 366.1261; Found: 366.1252.



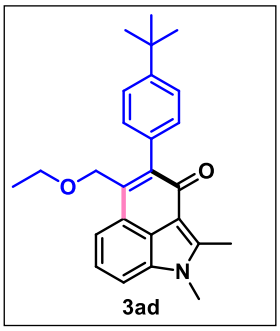
5-(ethoxymethyl)-1,2-dimethyl-4-(*p*-tolyl)benzo[cd]indol-3(1H)-one (3ac) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ac** in 52% yield (18 mg).

Physical State: Yellow solid
m.p.: 130-132 ℃
R$_f$-value: 0.4 (40% EtOAc/Hexane)

^{1}H NMR (CDCl$_3$, 400 MHz): δ 7.85 (d, J = 7.6 Hz, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.38 (t, J = 8 Hz, 1H), 7.25-7.17 (m, 4H), 4.56 (s, 2H), 3.84 (s, 3H), 3.47 (q, J = 6.8 Hz, 2H), 2.87 (s, 3H), 2.40 (s, 3H), 1.16 (t, J = 6.8 Hz, 3H).

^{13}C NMR (CDCl$_3$, 176 MHz): δ 180.4, 148.4, 143.9, 140.6, 136.8, 134.1, 133.6, 130.2, 128.5, 125.4, 123.4, 122.9, 121.6, 112.6, 111.0, 68.2, 65.8, 30.1, 21.3, 15.3, 12.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{24}NO_2$: 346.1807; Found 346.1805.



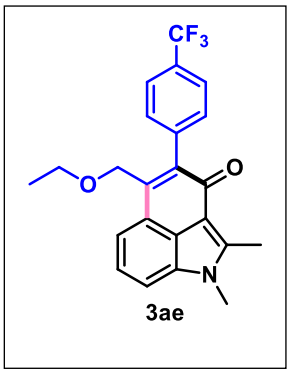
4-(4-(tert-butyl)phenyl)-5-(ethoxymethyl)-1,2-dimethylbenz o [cd]indol-3(1H)-one (3ad) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ad** in 44% yield (17 mg).

Physical State: Yellow solid
m.p.:173-175 ℃
R$_f$-value: 0.5 (40% EtOAc/Hexane)

^{1}H NMR (CDCl$_3$, 700 MHz): δ 7.85 (d, J = 7.7 Hz, 1H), 7.43 (d, J = 8.4 Hz, 3H), 7.37 (t, J = 7.7 Hz, 1H), 7.25-7.23 (m, 2H), 4.58 (s, 2H), 3.84 (s, 3H), 3.48 (q, J = 7 Hz, 2H), 2.87 (s, 3H), 1.36 (s, 9H), 1.17 (t, J = 7 Hz, 3H).

^{13}C NMR (CDCl$_3$, 176 MHz): δ 180.4, 149.8, 148.3, 143.9, 140.6, 134.1, 133.5, 129.9, 125.4, 124.6, 123.5, 122.9, 121.6, 112.6, 111.0, 68.2, 65.7, 34.5, 31.4, 30.1, 15.3, 12.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{30}NO_2$: 388.2277; Found 388.2263.



5-(ethoxymethyl)-1,2-dimethyl-4-(4--(trifluoromethyl)phenyl) benzo[cd]indol-3(1H)-one (3ae) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ae** in 48% yield (19 mg).

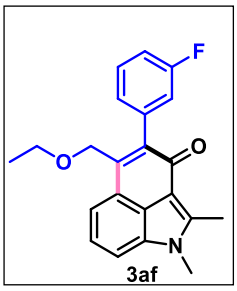
Physical State: Yellow solid
m.p.: 210-212 ℃
R_f-value: 0.3 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 700 MHz) δ 7.86 (d, J = 7.7 Hz, 1H), 7.69 (d, J = 7.7 Hz, 2H), 7.48 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 8.4 Hz, 2H), 7.41 (t, J = 7.7 Hz, 1H), 4.50 (s, 2H), 3.86 (s, 3H), 3.48 (q, J = 7 Hz, 2H), 2.88 (s, 3H), 1.18 (t, J = 7 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.6, 148.8, 142.6, 141.2, 140.7, 134.2, 130.8, 125.7, 124.7 (q, $J_{C\text{-}F}$ = 3.5 Hz), 124.3 (q, $J_{C\text{-}F}$ = 253.4 Hz), 123.1, 123.0, 122.9, 121.8, 112.5, 111.6, 67.9, 66.1, 30.3, 15.3, 12.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -62.4

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{21}F_3NO_2$: 400.1524; Found 400.1519.



5-(ethoxymethyl)-4-(3-fluorophenyl)- 1,2dimethylbenzo [cd] indol-3(1H)-one (3af) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3af** in 63% yield (22mg).

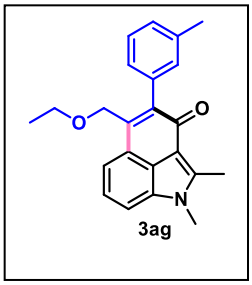
Physical State: Yellow solid
m.p.:169-171 ℃
R_f-value: 0.3 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8 Hz, 1H), 7.41-7.36 (m, 2H), 7.10-7.04 (m, 3H) , 4.53 (s, 2H), 3.85 (s, 3H), 3.48 (q, J = 7.2 Hz, 2H), 2.88 (s, 3H), 1.18 (t, J = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 179.8, 162.5 (d, $J_{C\text{-}F}$ = 243.7 Hz), 148.7, 142.7, 141.2, 139.0 (d, $J_{C\text{-}F}$ = 8 Hz), 134.2, 129.2 (d, $J_{C\text{-}F}$ = 8.5 Hz), 126.17, 127.14, 125.5, 123.1, 121.8, 117.4 (d, $J_{C\text{-}F}$ = 21.3 Hz), 114.1 (d, $J_{C\text{-}F}$ = 20.8 Hz), 112.5, 111.5, 67.9, 66.0, 30.2, 15.2, 12.3.

^{19}F NMR (376 MHz, $CDCl_3$): δ -114.3

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{21}FNO_2$: 350.1556; Found 350.1543.



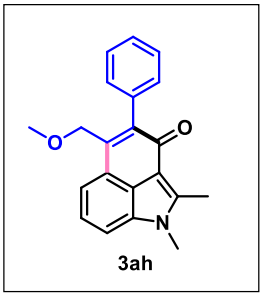
5-(ethoxymethyl)-1,2-dimethyl-4-(*m*-tolyl)benzo[cd]indol-3(1H)-one (3ag) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ag** in 60% yield (21 mg).

Physical State: Yellow solid
m.p.: 166-169 °C
R_f-value: 0.4 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.86 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 7.2 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.12 (s, 1H), 7.09 (d, J = 7.6 Hz, 1H), 4.54 (s, 2H), 3.85 (s, 3H), 3.47 (q, J = 6.8 Hz, 2H), 2.88 (s, 3H), 2.39 (s, 3H), 1.16 (t, J = 6.8 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.4, 148.3, 144.2, 140.6, 137.2, 136.6, 134.1, 130.9, 127.9, 127.7, 127.3, 125.4, 123.4, 122.9, 121.6, 112.6, 111.1, 68.1, 65.7, 30.2, 21.5, 15.3, 12.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{24}NO_2$: 346.1807; Found 346.1824



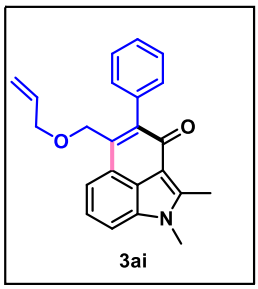
5-(methoxymethyl)-1,2-dimethyl-4-(*m*-tolyl)benzo[cd]indol-3(1H)-one (3ah) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ah** in 51% yield (16 mg).

Physical State: Yellow solid
m.p.: 207-209 °C
R_f-value: 0.2 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.83 (d, J = 7.2 Hz, 1H), 7.47-7.37 (m, 5H), 7.31-7.29 (m, 2H), 4.51 (s, 2H), 3.86 (s, 3H), 3.31 (s, 3H), 2.89 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.2, 148.5, 144.2, 140.4, 136.7, 134.2, 130.3, 127.8, 127.2, 125.4, 123.2, 123.0, 121.5, 112.6 , 111.2, 70.0, 58.2, 30.2, 12.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{21}H_{20}NO_2$: 318.1494; Found 318.1490



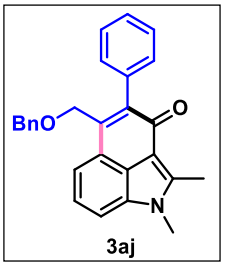
5-((allyloxy)methyl)-1,2-dimethyl-4-phenylbenzo[cd]indol-3(1H)-one (3ai) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3ai** in 32% yield (11 mg).

Physical State: Yellow solid
m.p.: 138-140 °C
R_f-value: 0.2 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 7.86 (d, J = 7 Hz, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.43 (t, J = 7 Hz, 2H), 7.40 (d, J = 7.7 Hz, 1H), 7.38-7.35 (m, 1H), 7.30-7.29 (m, 2H), 5.89-5.83 (m, 1H), 5.19 (dd, J = 16.8 Hz, 1H), 5.11(dd, J = 10.5 Hz, 1H), 4.56 (s, 2H), 3.95 (t, J = 1.4 Hz, 1H), 3.94 (t, J = 0.7 Hz, 1H) 3.85 (s, 3H), 2.88 (s, 3H).

^{13}C NMR ($CDCl_3$, 176 MHz): δ 180.2, 148.7, 144.1, 140.7, 136.7, 134.5, 134.2, 130.3, 127.8, 127.2, 125.4, 123.3, 123.0, 121.7, 112.6, 117.4, 111.3, 71.5, 67.6, 30.2, 12.3.

HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{23}H_{21}NO_2Na$: 366.1470; Found 366.1450.



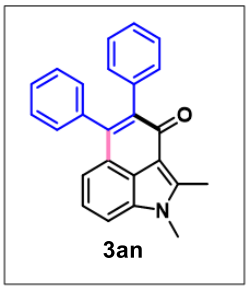
5-((benzyloxy)methyl)-1,2-dimethyl-4-phenylbenzo [cd]indole-3(1H)-one (3aj) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3aj** in 56% yield (22 mg).

Physical State: Yellow solid
m.p.: 172-174 °C
R_f-value: 0.4 (40% EtOAc/Hexane)

^{1}H NMR ($CDCl_3$, 700 MHz): δ 7.81 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 7.7 Hz, 1H), 7.41 (t, J = 7 Hz, 2H), 7.38-7.36 (m, 2H), 7.31-7.28 (m, 5H), 7.25 (m, 2H), 4.60 (s, 2H), 4.47 (s, 2H), 3.84 (s, 3H), 2.87 (s, 3H).

^{13}C NMR ($CDCl_3$, 176 MHz): δ 180.2, 148.6, 144.2, 140.5, 138.0, 136.6, 134.2, 130.3, 128.3, 128.0, 127.8, 127.6, 127.2, 125.4, 123.3, 123.0, 121.7, 112.6, 111.2, 72.6 , 67.8, 30.2, 12.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{27}H_{24}NO_2$: 394.1807; Found 394.1785.



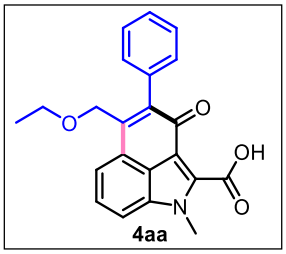
1,2-dimethyl-4,5-diphenylbenzo[cd]indol-3(1H)-one (3an) was prepared according to general procedure (**2.5**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **3an** in 33% yield (12 mg).

Physical State: Yellow solid.
R_f-value: 0.4 (40% EtOAc/Hexane)
m.p.: 146-148 °C

^{1}H NMR ($CDCl_3$, 700 MHz): δ 7.47 (d, J = 7.7 Hz, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.24-7.21 (m, 3H), 7.19-7.16 (m, 5H), 7.12-7.10 (m, 3H), 3.90 (s, 3H), 2.95 (s, 3H).

^{13}C NMR ($CDCl_3$, 176 MHz): δ 180.2, 160.5, 158.8, 148.6, 146.9, 137.3, 137.1, 131.1, 130.2, 127.5, 127.2, 127.0, 126.3, 125.2, 124.4, 123.0, 122.8, 118.1, 111.2, 30.3, 12.3.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{20}NO$: 350.1545; Found 350.1526.



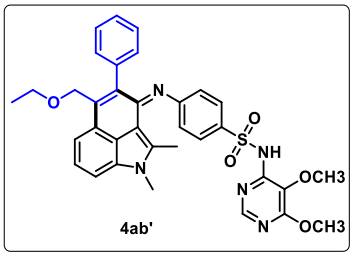
5-(ethoxymethyl)-1-methyl-3-oxo-4-phenyl-1,3- dihydrobenzo [cd]indole-2-carboxylic acid (4aa) was prepared according to general procedure (**5b**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **4aa** in 60 % yield (22 mg).

Physical State: Yellow solid
R_f-value: 0.5 (20 % EtOAc/Hexane)
m.p.: 136-138 °C

^{1}H NMR ($CDCl_3$, 400 MHz): δ 11.80 (brs, 1H), 8.06 (J =7.6 Hz, d, 1H), 7.70 (d, J = 8 Hz, 1H), 7.60 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 6.8 Hz, 2H), 7.43(d, J = 7.2 Hz, 1H), 7.30 (d, J = 7.2 Hz, 2H), 4.56 (s, 2H), 4.44 (s, 3H), 3.47 (q, J = 7.2 Hz, 2H), 1.17 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 180.6, 162.0, 143.0, 142.3, 136.4, 136.1, 135.5, 130.0, 128.1,127.8, 126.1, 124.9, 124.4, 124.1, 113.8, 113.3, 67.7, 66.1, 34.1, 15.2.

HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{20}NO_4$: 362.1392; Found 362.3304.



(R)-5-(ethoxymethyl)-1,2-dimethyl-4-phenyl-1,3-dihydrobenzo[cd]indol-3-ol (4ab) was prepared according to general procedure (**2.4**). The crude reaction mixture was purified by column chromatography using silica gel (100-200 mesh size) to obtain **4ab'** in 56% yield (35 mg).

Physical State: Brown liquid

R_f-value: 0.5 (5% EtOAc/Hexane)

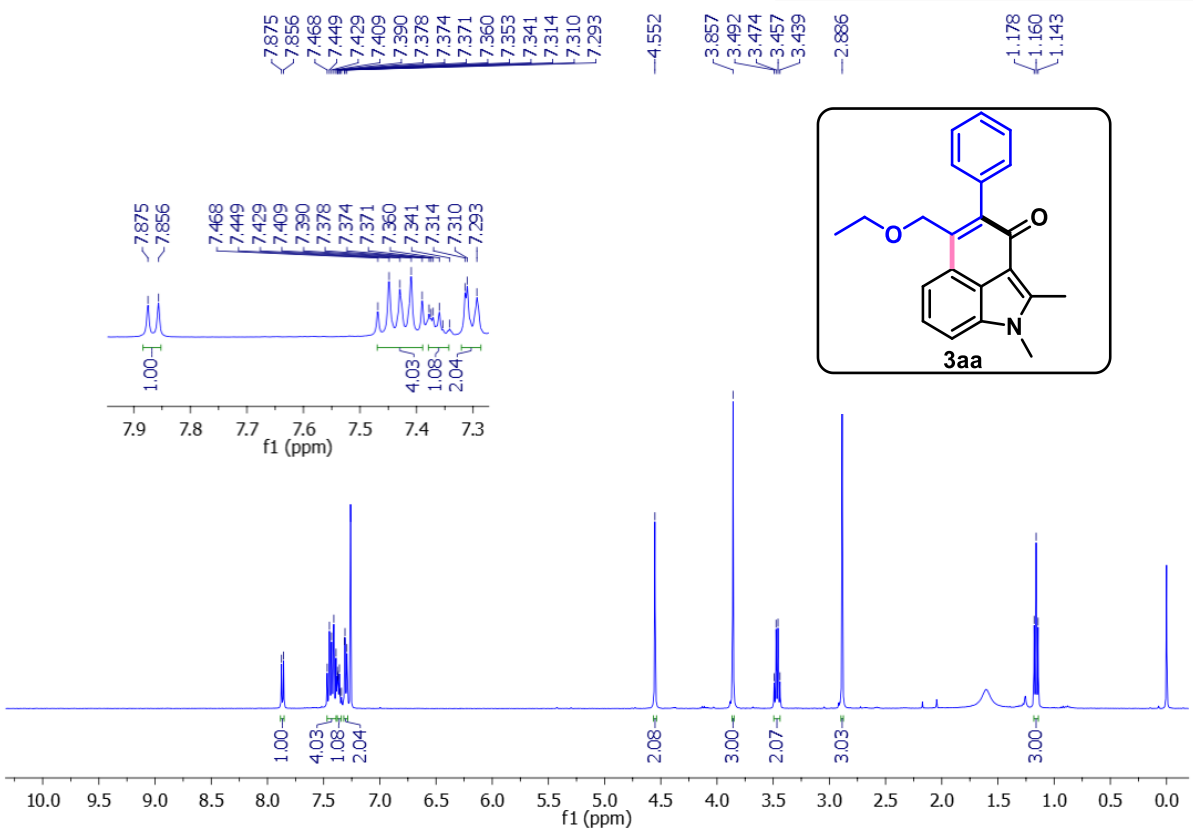
^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.17 (s, 1H), 7.91 (d, J = 8.8 Hz, 3H), 7.89 (d, J = 2 Hz, 1H), 7.88-7.85 (m, 1H) 7.76 (brs, 1H), 7.47-7.42 (m, 2H), 7.40 (d, J = 7.2 Hz, 1H), 7.38-7.34 (m, 1H), 7.31-7.29 (m, 2H), 6.65-6.63 (m, 3H), 4.55 (s, 2H), 3.97 (s, 3H), 3.86 (s, 3H), 3.83 (s, 3H), 3.46 (q, J = 6.8 Hz, 2H), 2,88 (s, 3H), 1.16 (t, J = 7.2 Hz, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ 160.7, 151.2, 151.1, 150.1, 148.5, 144.0, 140.8, 136.8, 134.2, 130.7, 130.3, 127.8, 127.2, 123.0, 121.7, 113.5, 111.2, 68.0, 65.8, 60.5, 54.1, 30.2, 15.3, 12.3.

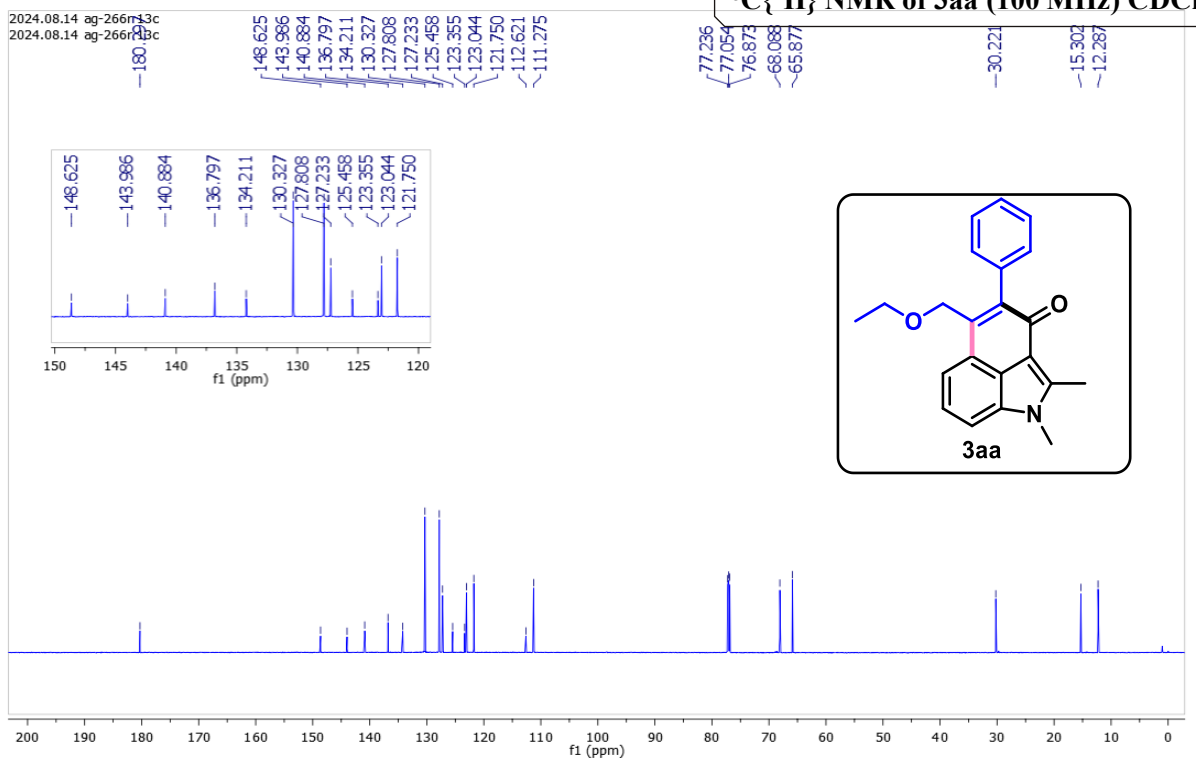
HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{34}H_{34}N_5O_5S$: 624.2280; Found 624.2332

7.Copies of ^{1}H NMR and ^{13}C NMR spectra of adducts:

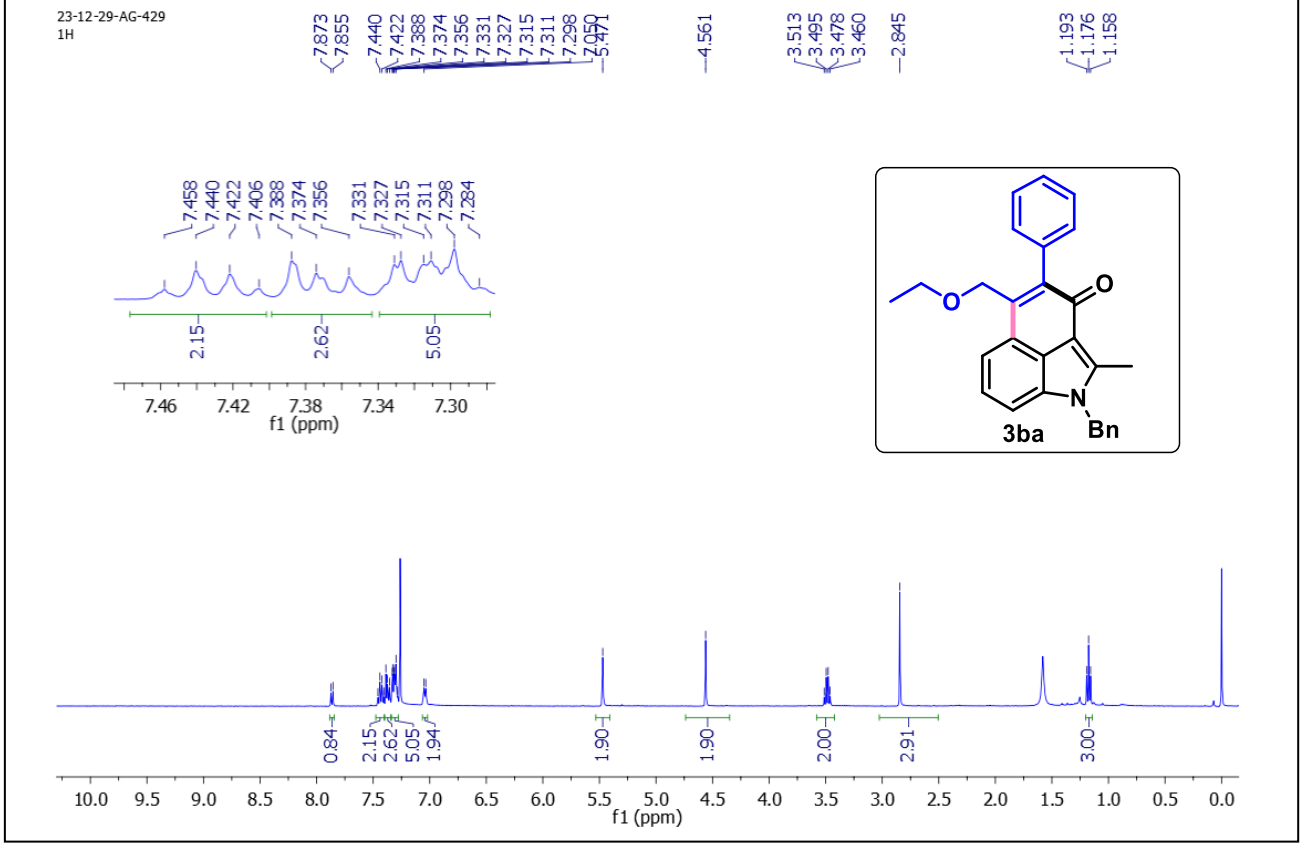
^{1}H NMR of 3aa (700 MHz, $CDCl_3$)



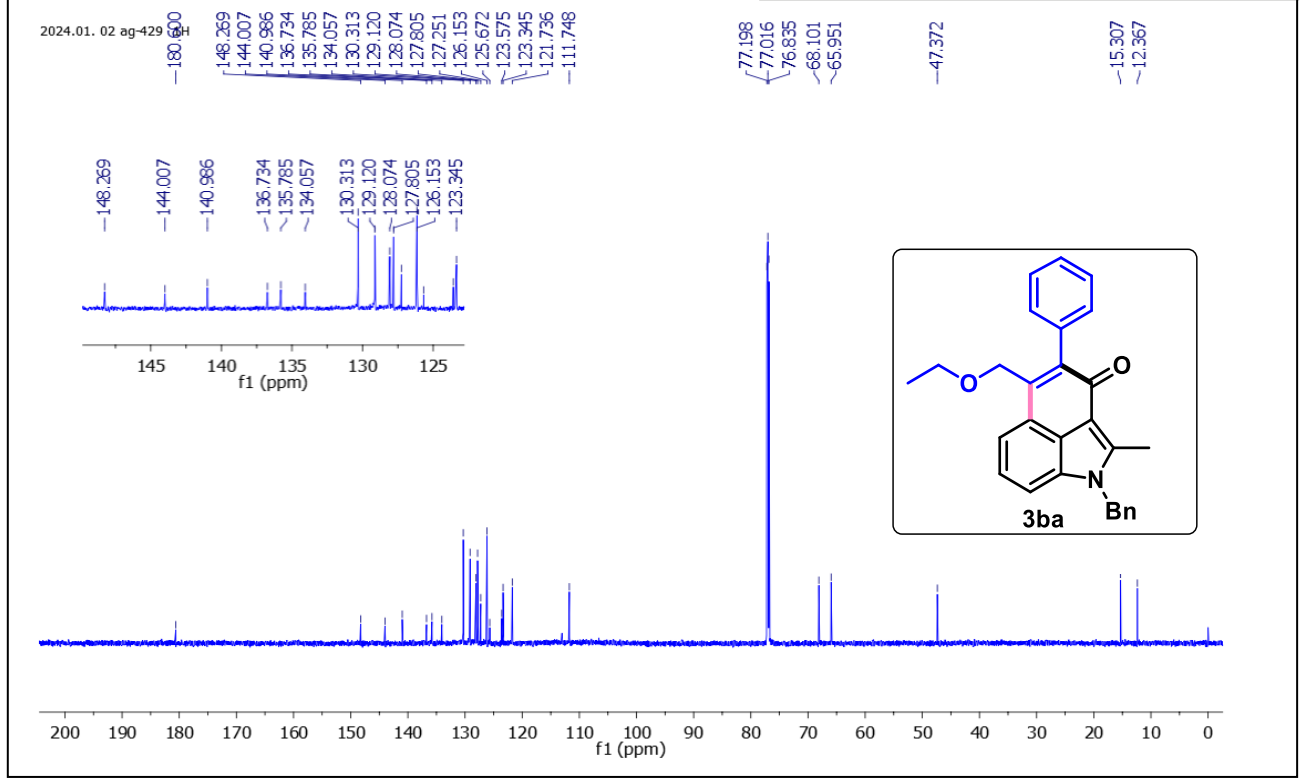
$^{13}C\{^{1}H\}$ NMR of 3aa (100 MHz) $CDCl_3$)



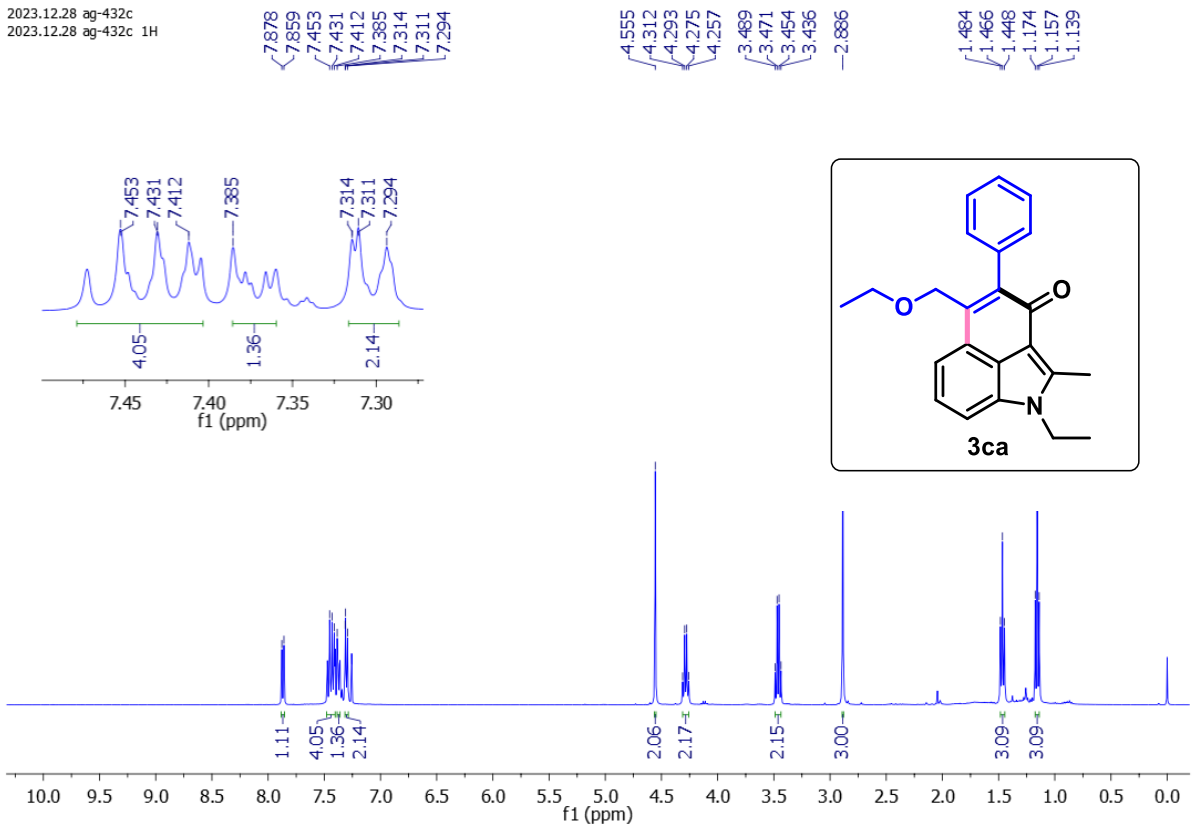
^{1}H NMR of 3ba (400 MHz, $CDCl_3$)



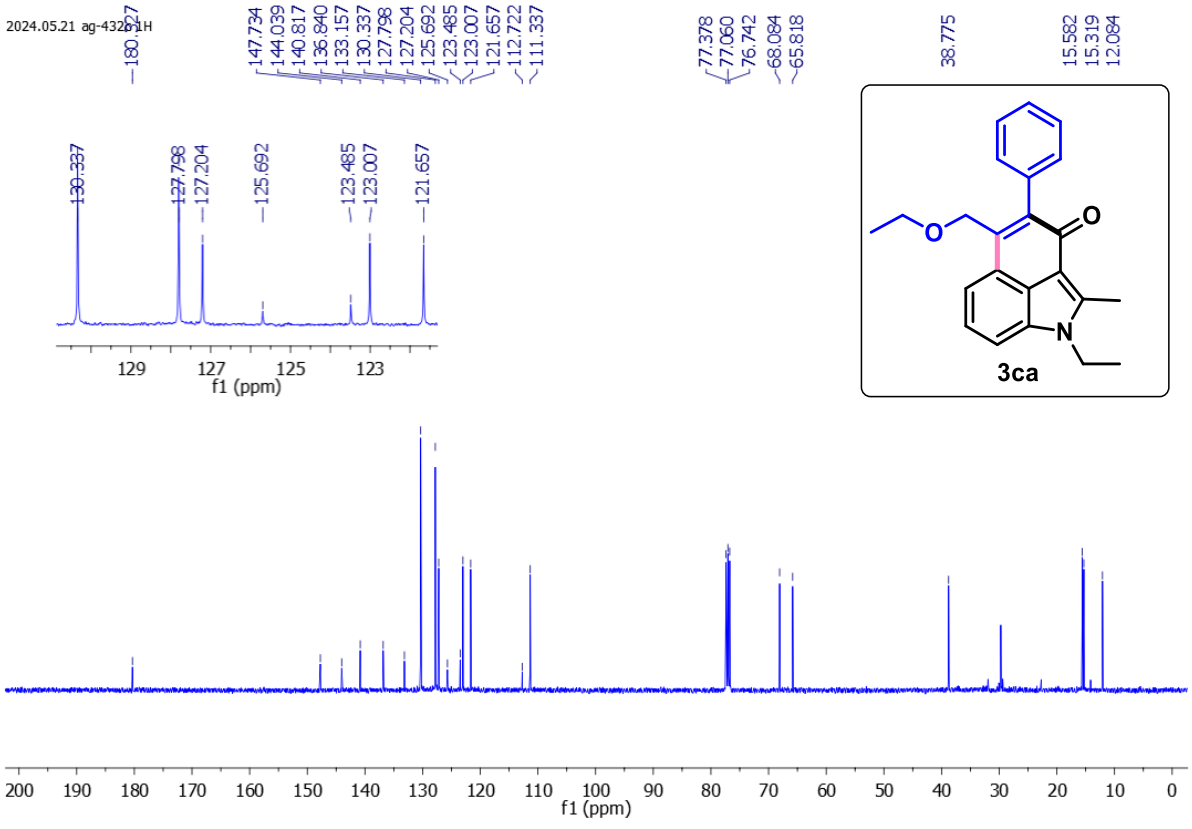
^{13}C{^{1}H} NMR of 3ba (100 MHz, $CDCl_3$)



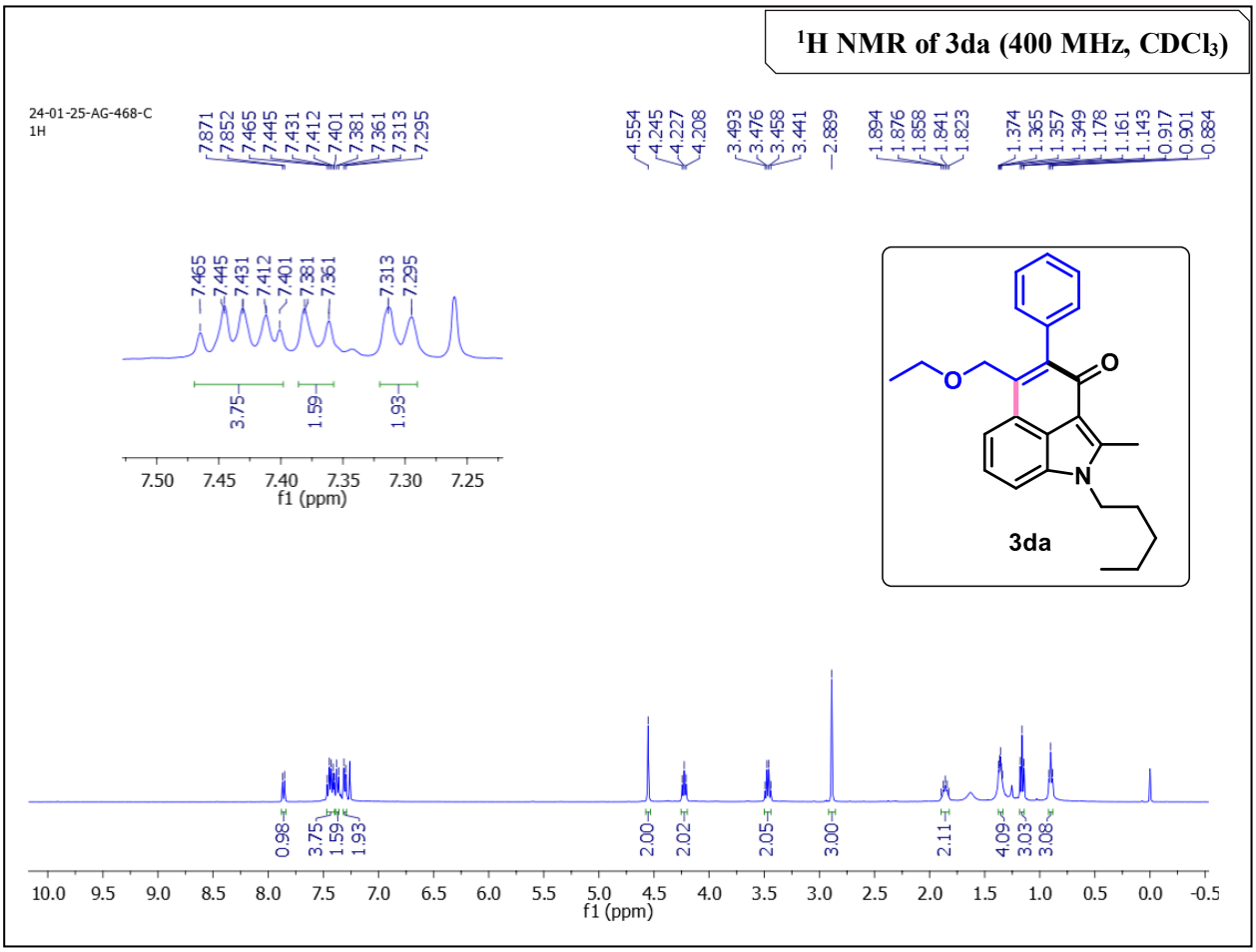
^{1}H NMR of 3ca (400 MHz, $CDCl_3$)



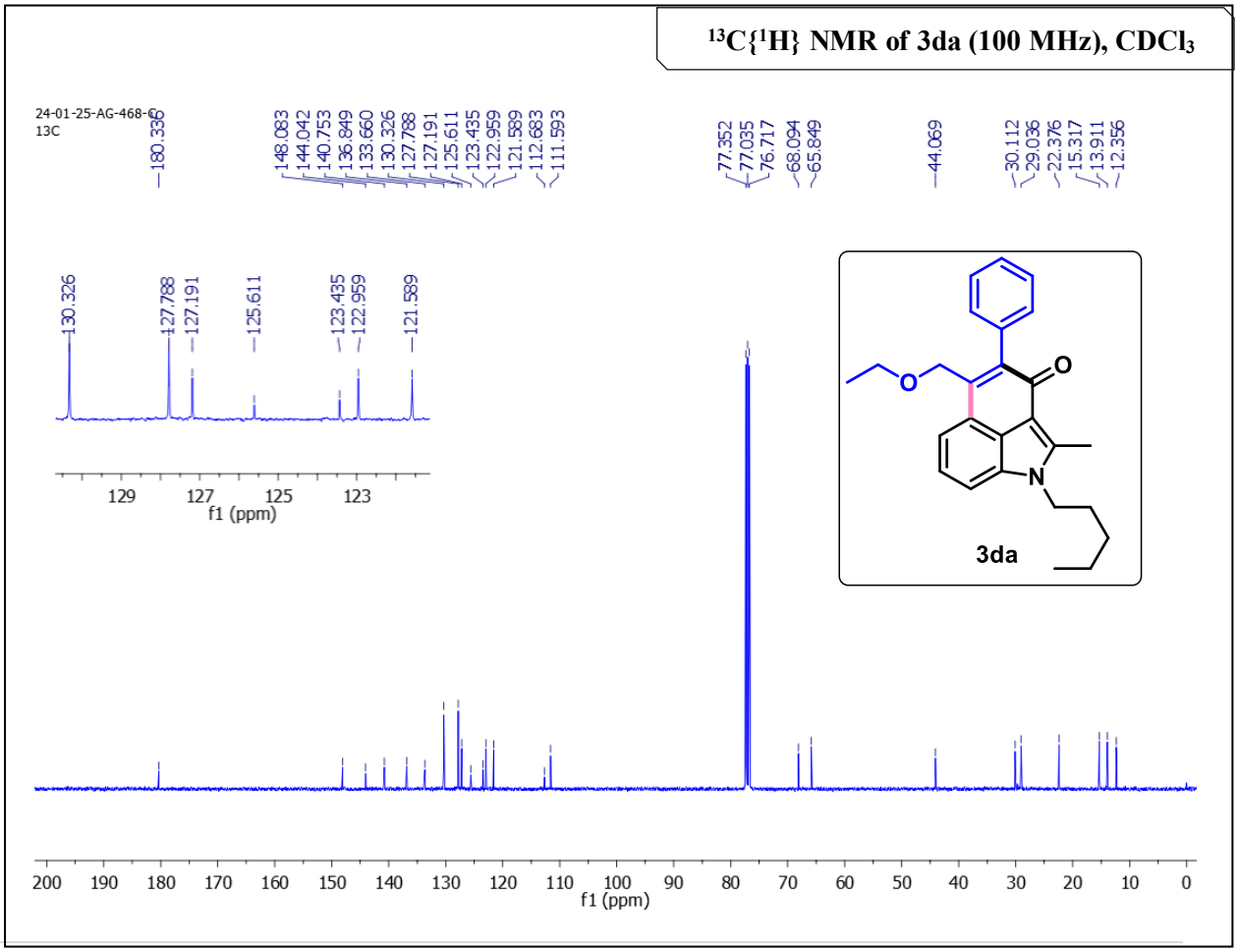
^{13}C{^{1}H} NMR of 3ca (100 MHz, $CDCl_3$)



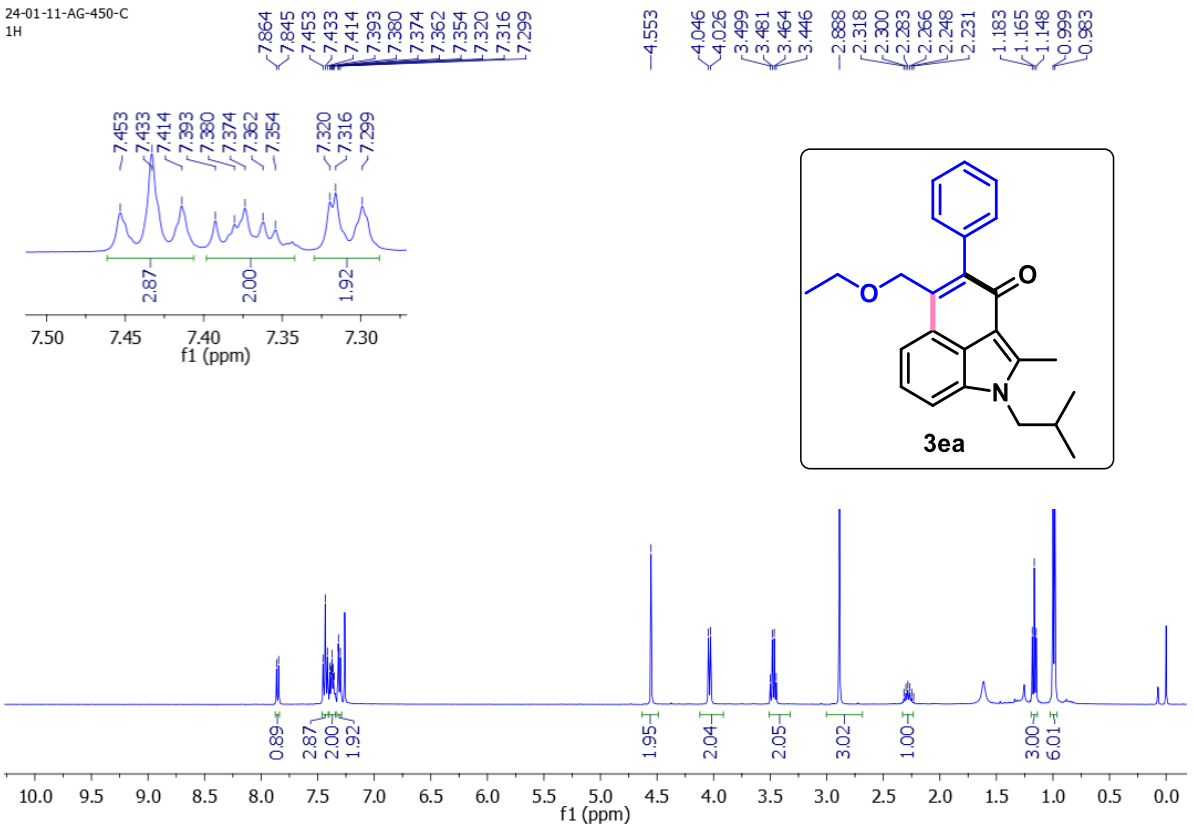
^{1}H NMR of 3da (400 MHz, $CDCl_3$)



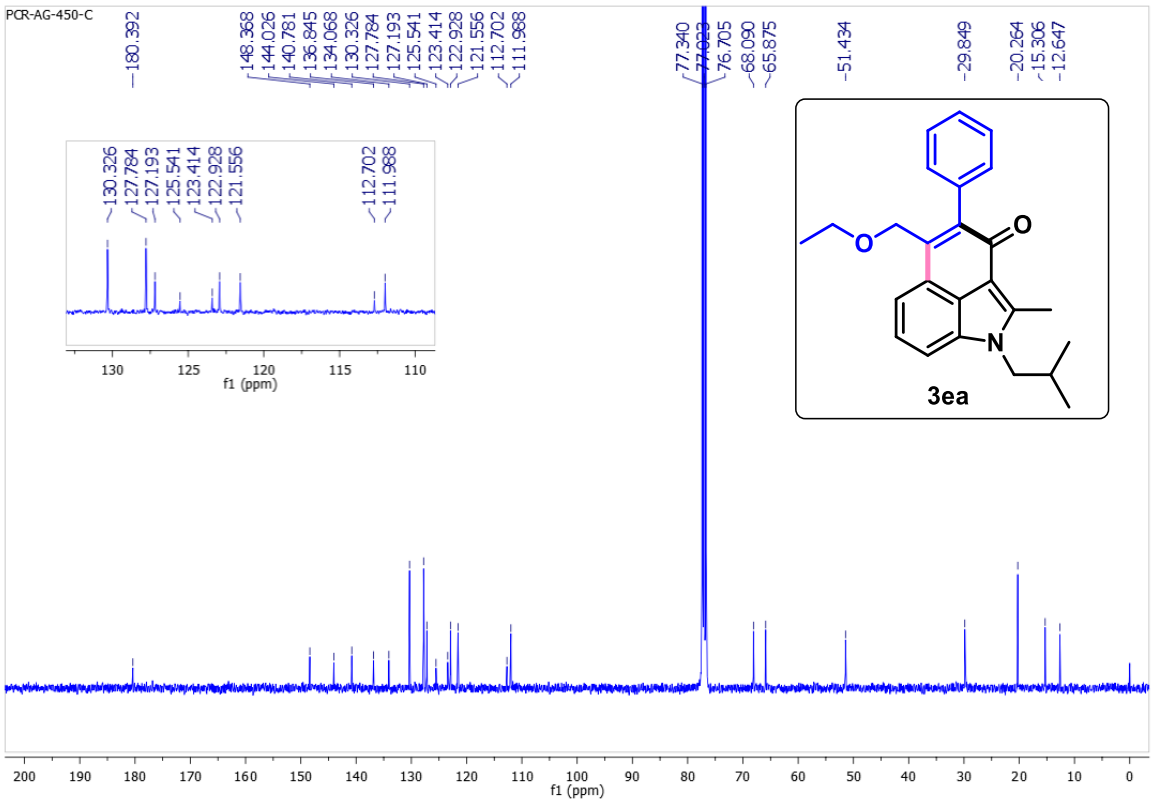
$^{13}C\{^{1}H\}$ NMR of 3da (100 MHz), $CDCl_3$



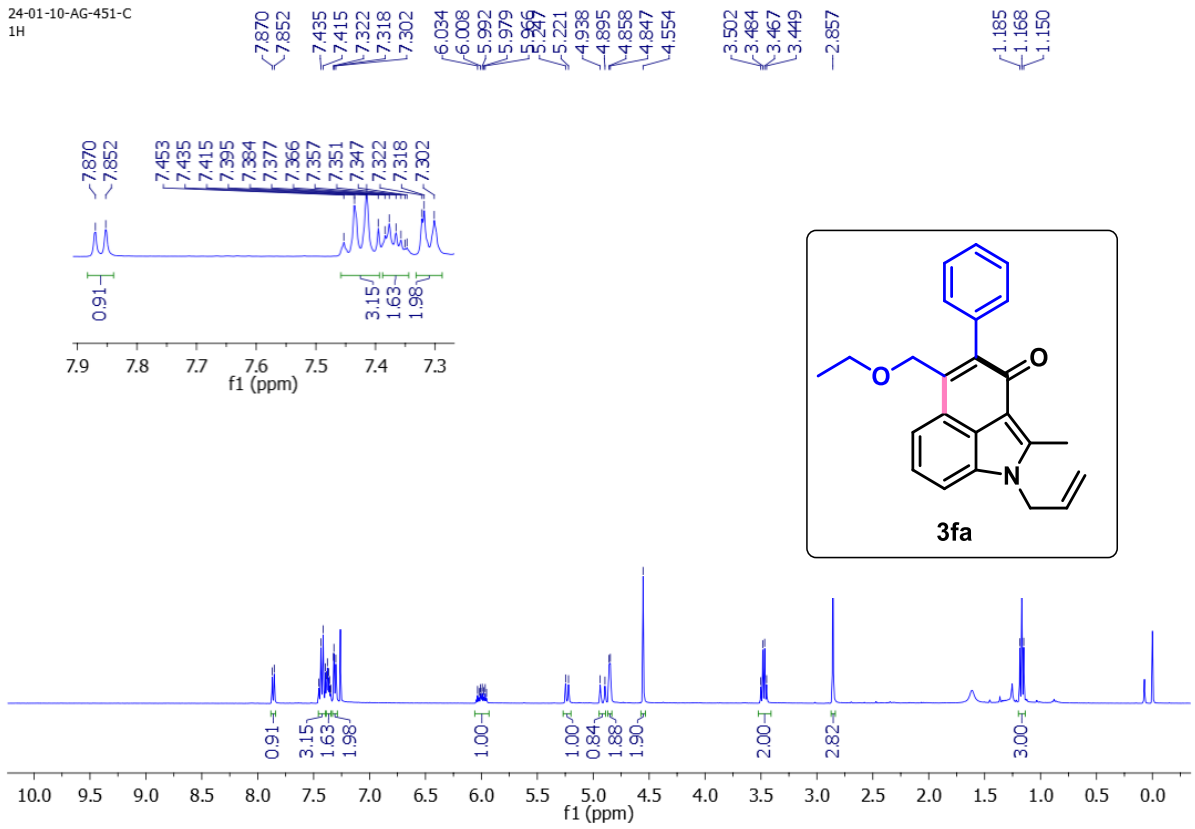
^{1}H NMR of 3ea (400 MHz, $CDCl_3$)



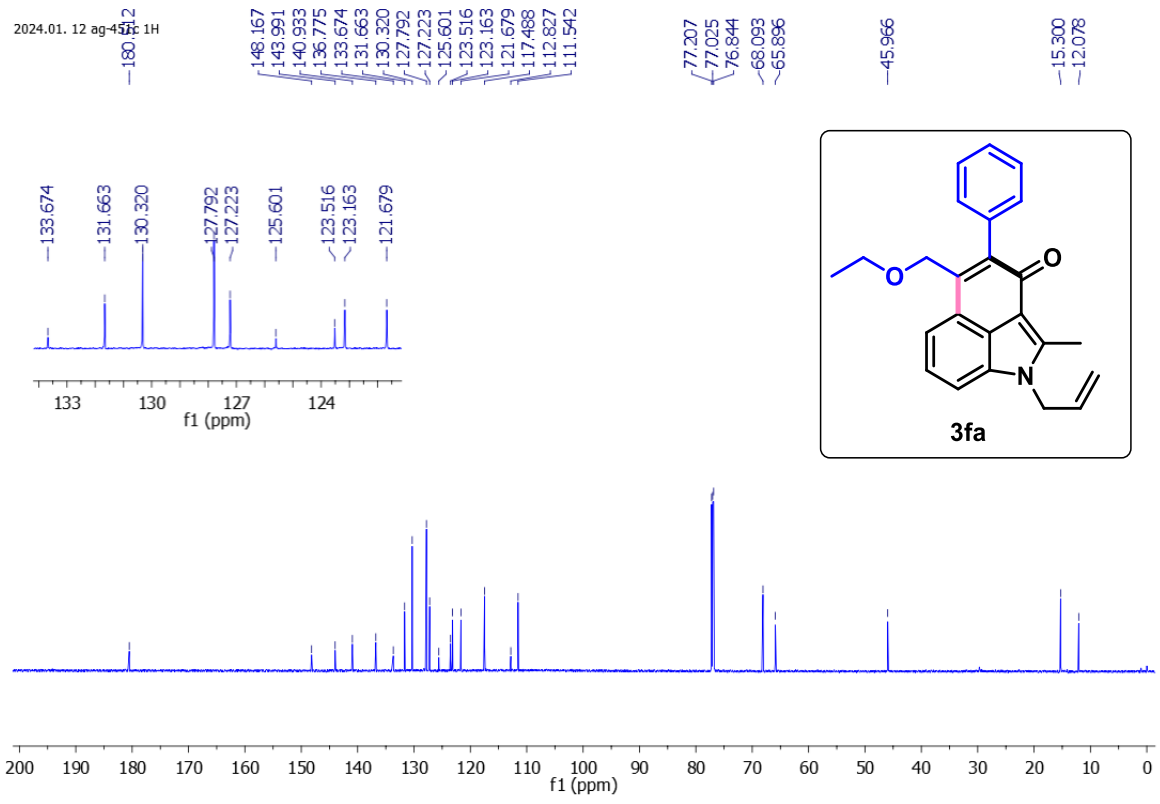
^{13}C{^{1}H} NMR of 3ea (176 MHz), $CDCl_3$



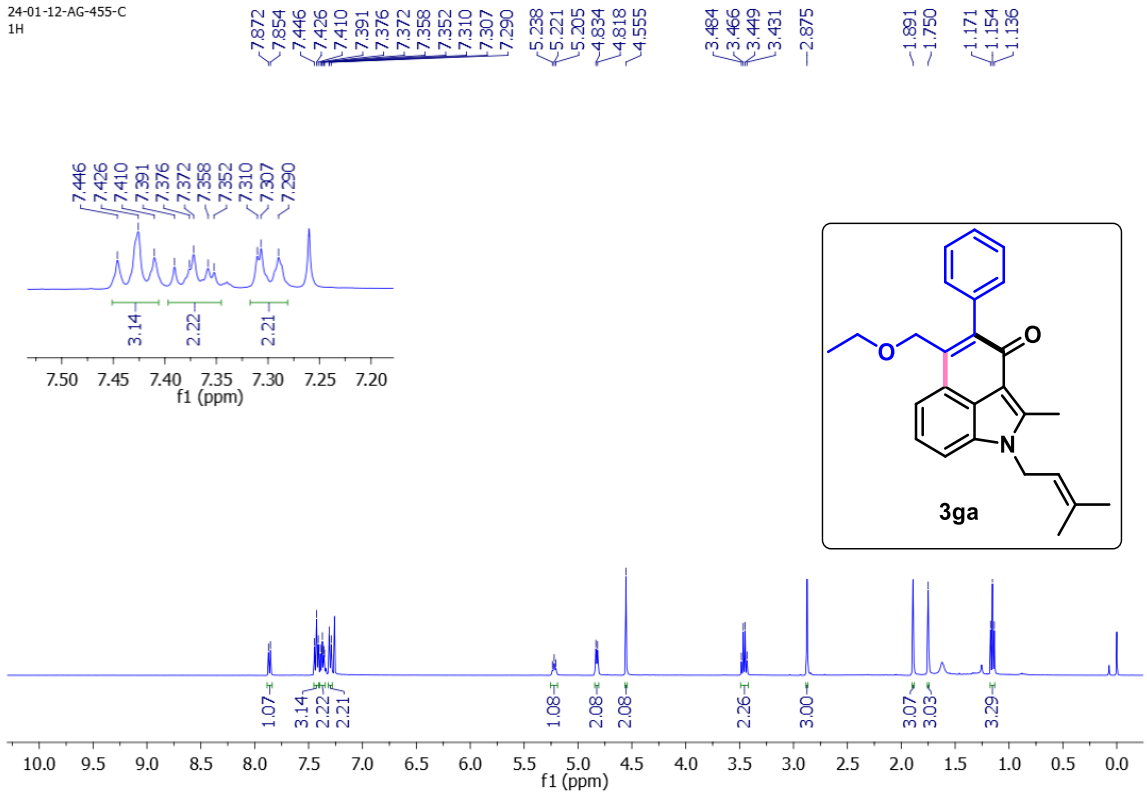
^{1}H NMR of 3fa (400 MHz, $CDCl_3$)



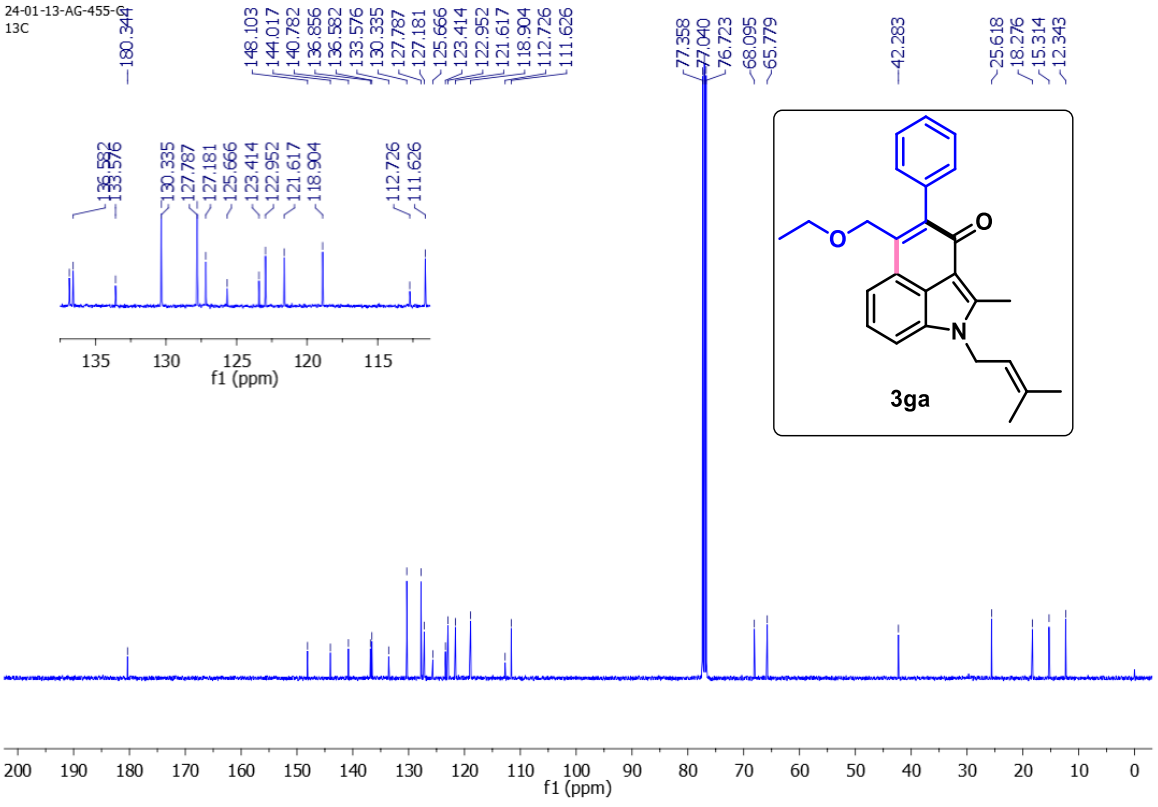
^{13}C{^{1}H} NMR of 3fa (176 MHz), $CDCl_3$



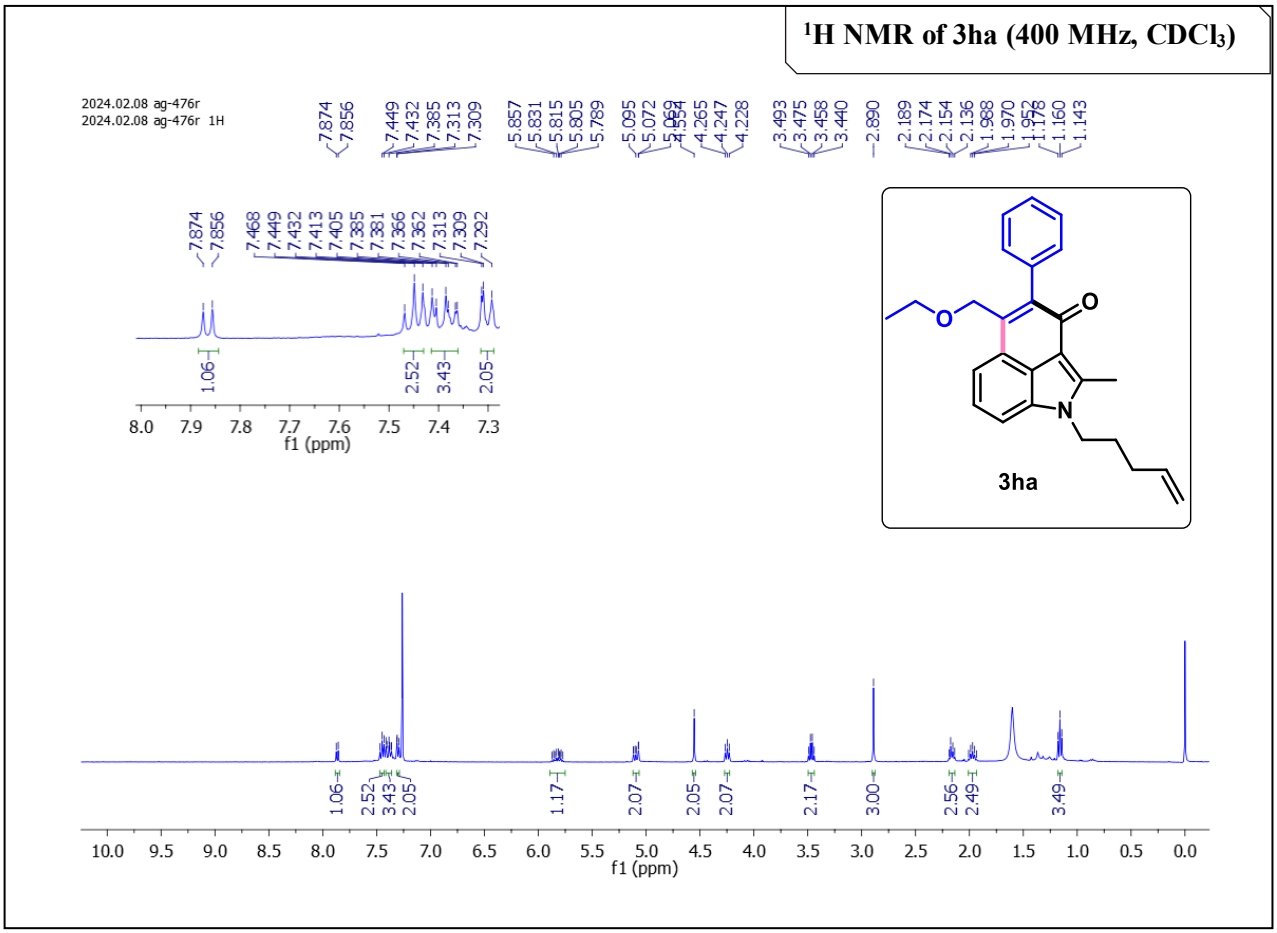
^{1}H NMR of 3ga (400 MHz, $CDCl_3$)



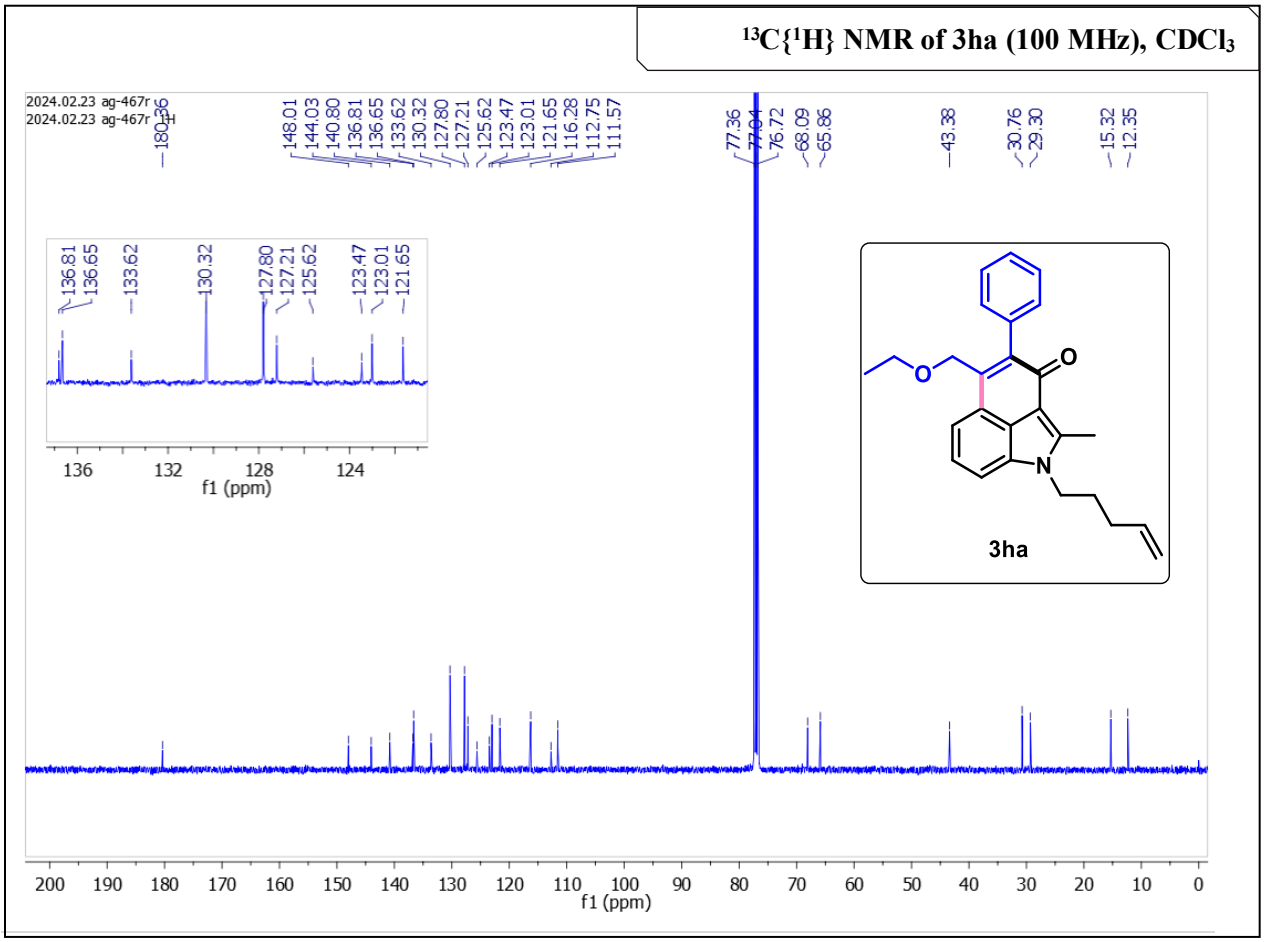
^{13}C{^{1}H} NMR of 3ga (100 MHz), $CDCl_3$

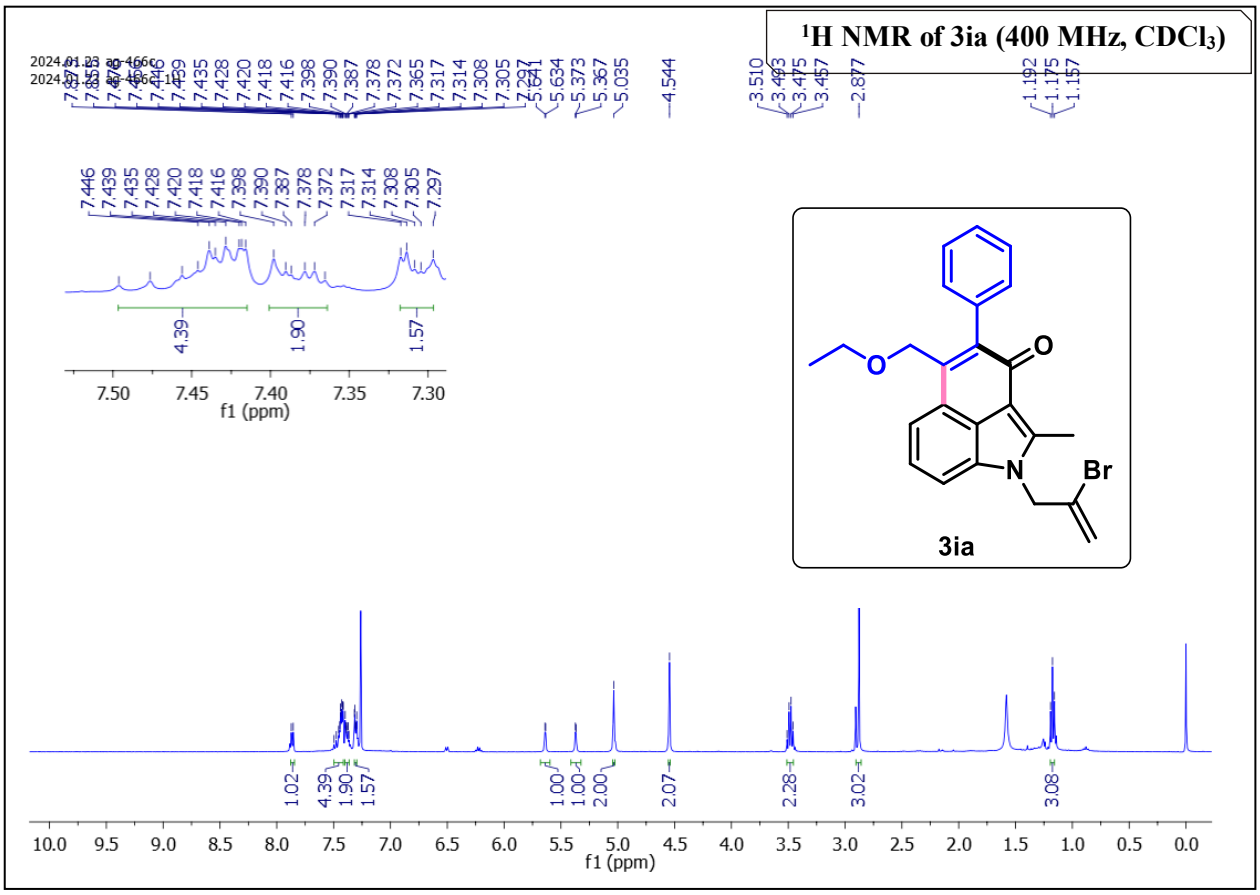


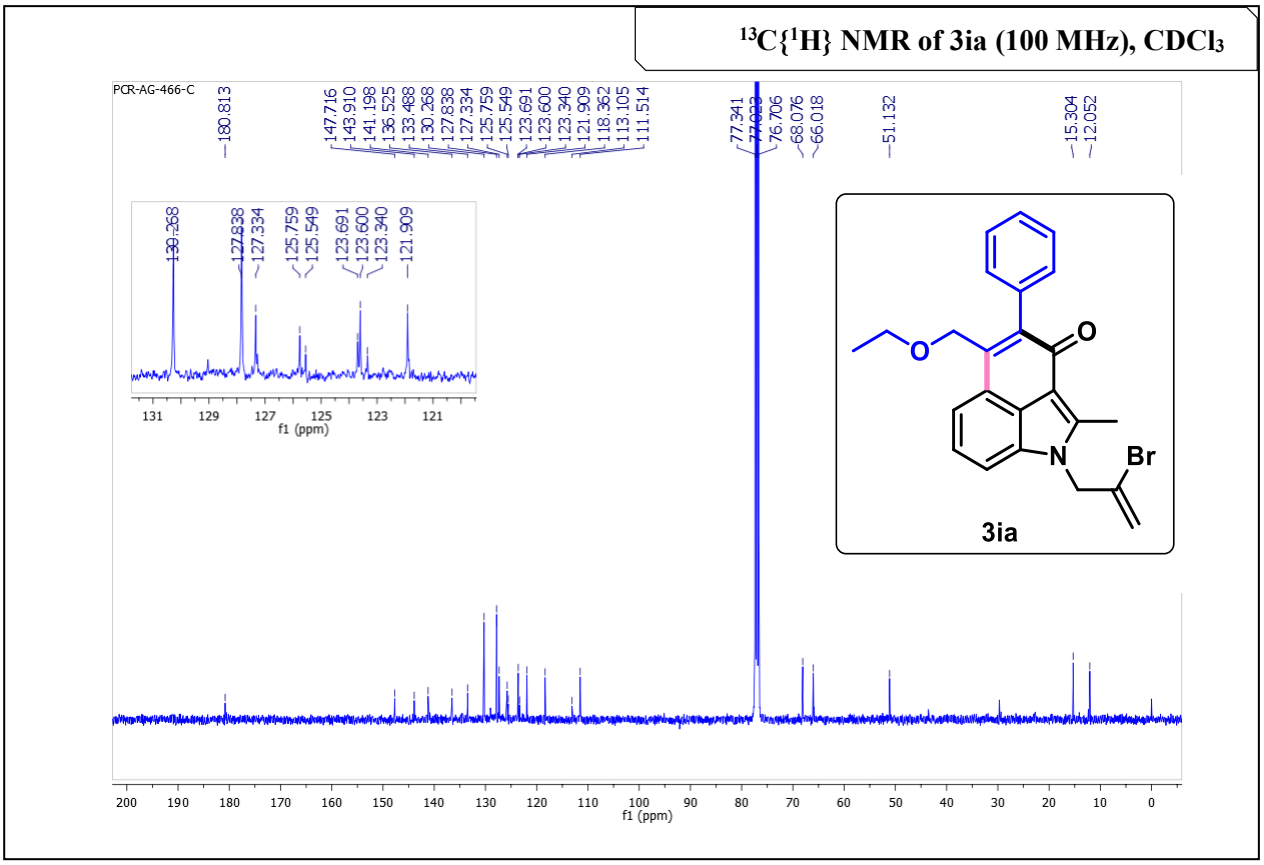
^{1}H NMR of 3ha (400 MHz, $CDCl_3$)



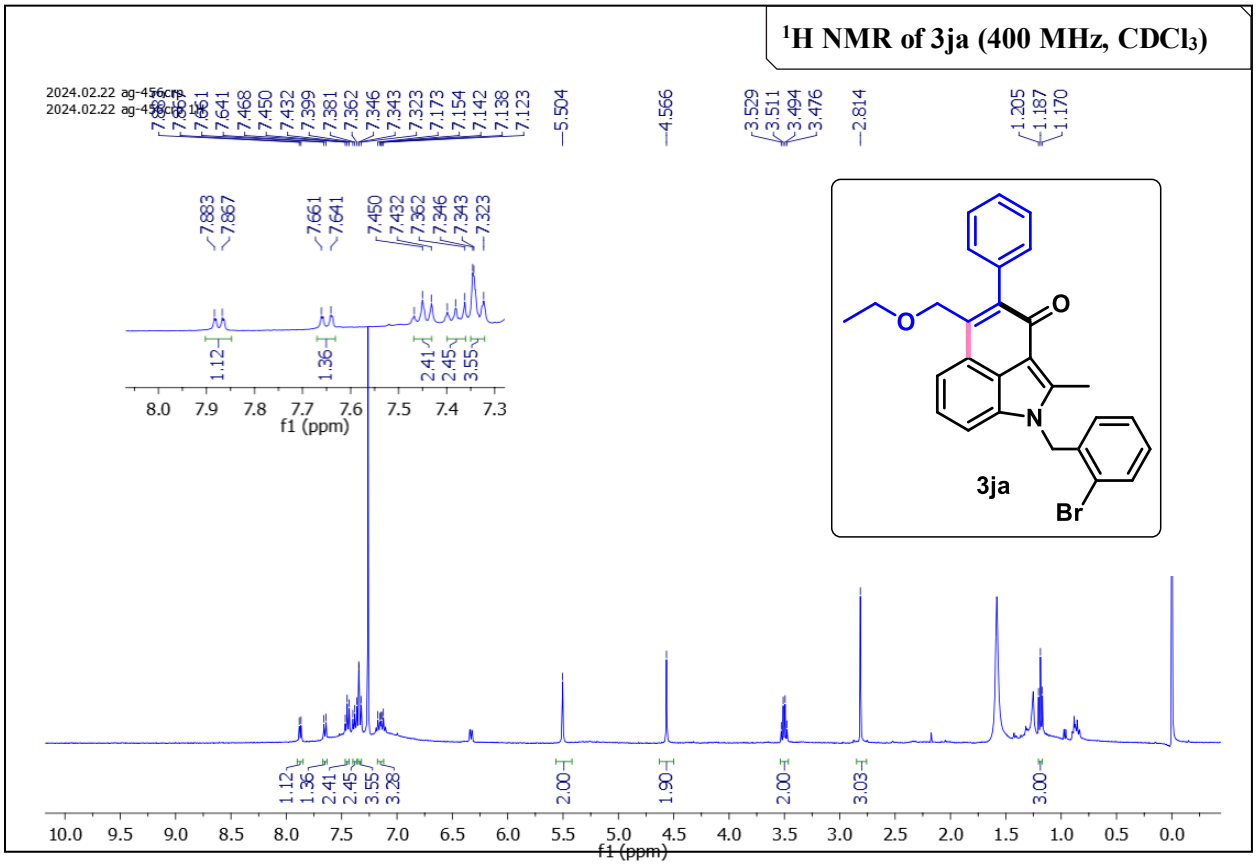
$^{13}C\{^{1}H\}$ NMR of 3ha (100 MHz), $CDCl_3$



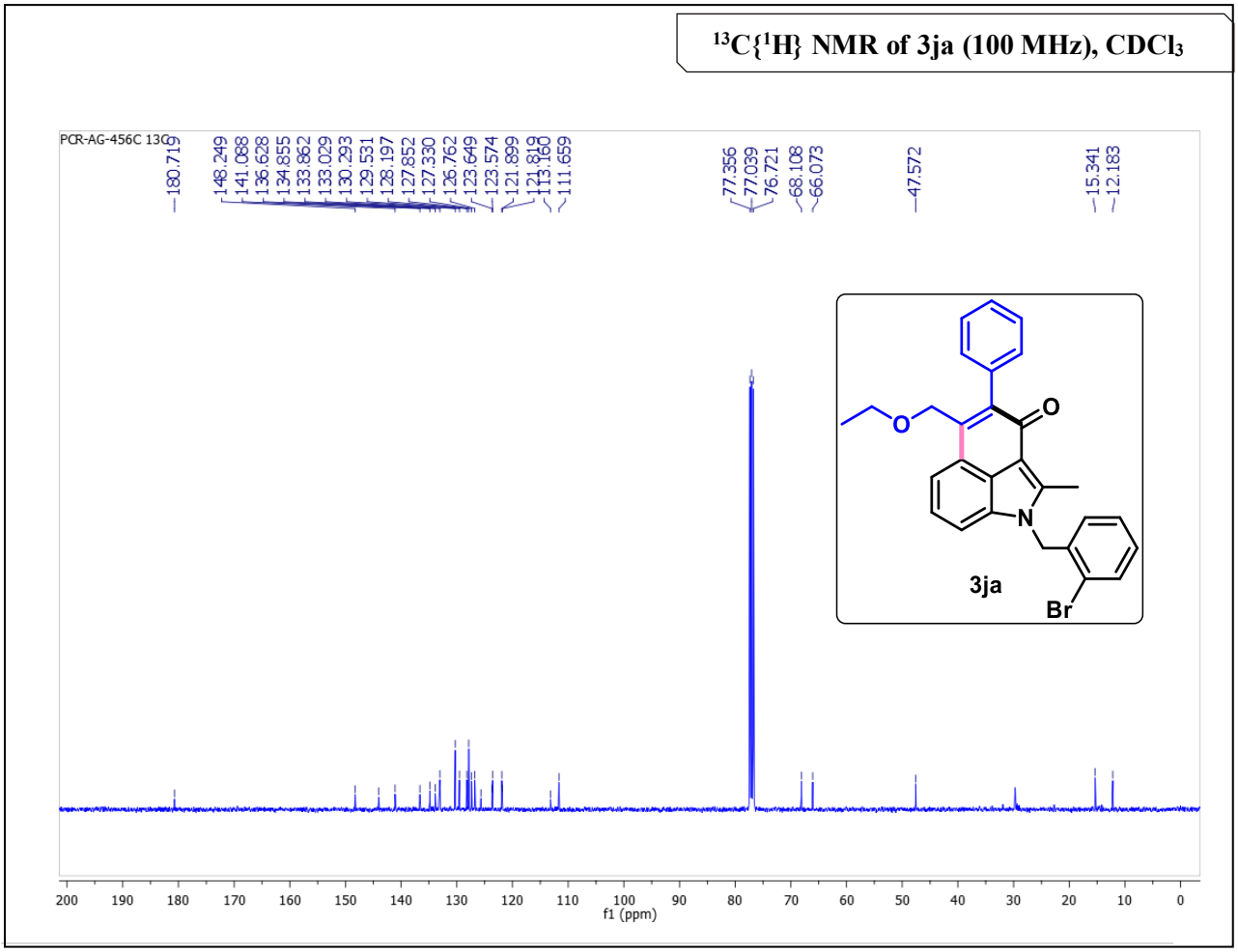

^{1}H NMR of 3ia (400 MHz, CDCl$_3$)
3ia
f1 (ppm)


^{13}C{^{1}H} NMR of 3ia (100 MHz), CDCl$_3$
PCR-AG-466-C
3ia
f1 (ppm)

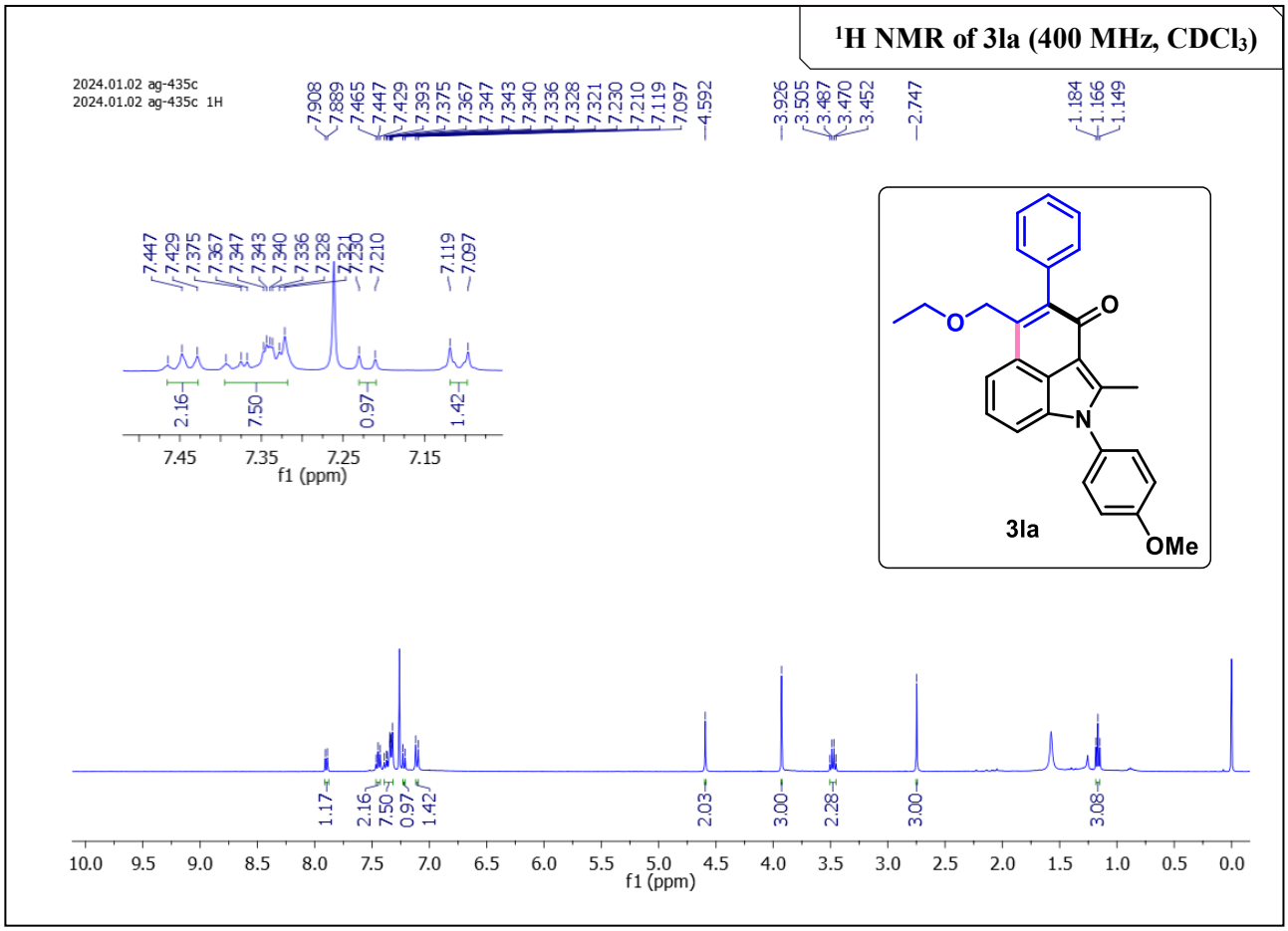
^{1}H NMR of 3ja (400 MHz, $CDCl_3$)



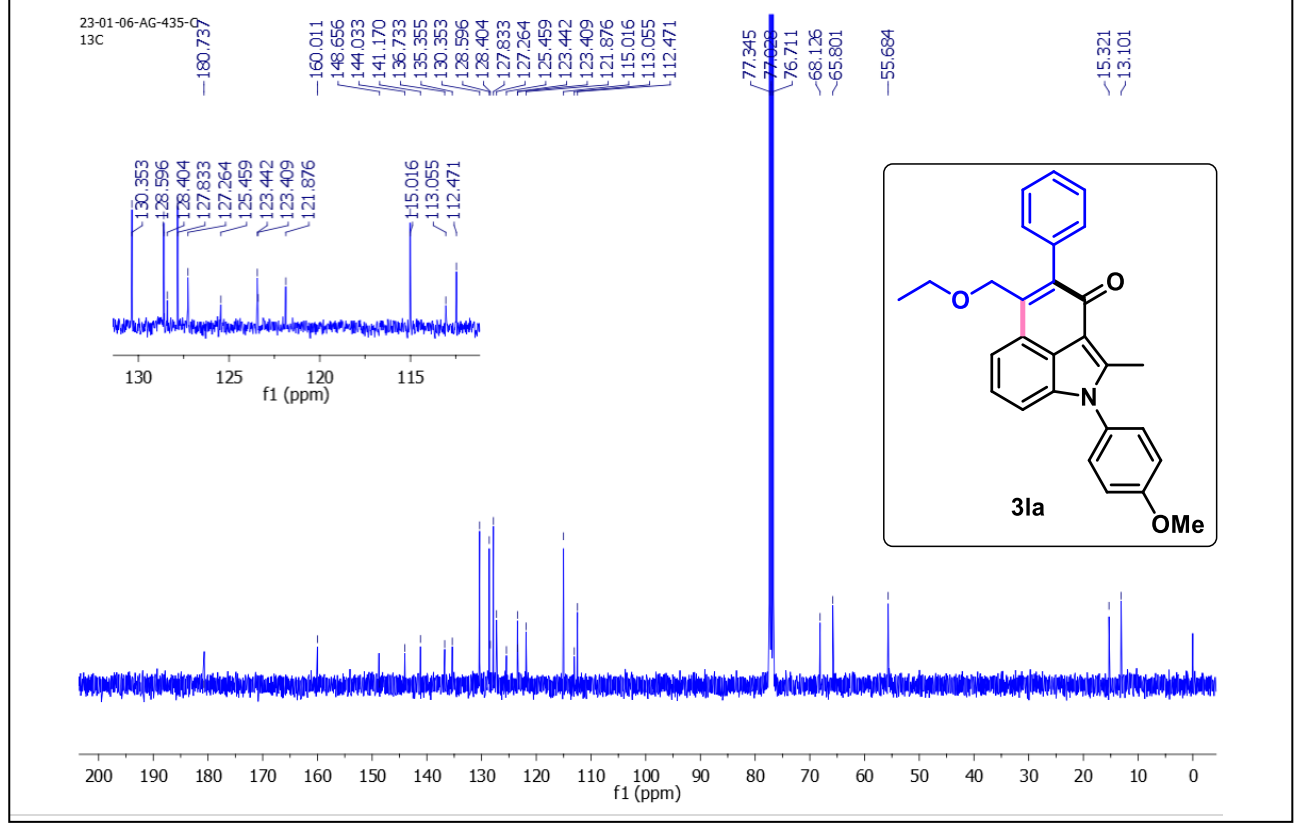
^{13}C{^{1}H} NMR of 3ja (100 MHz), $CDCl_3$



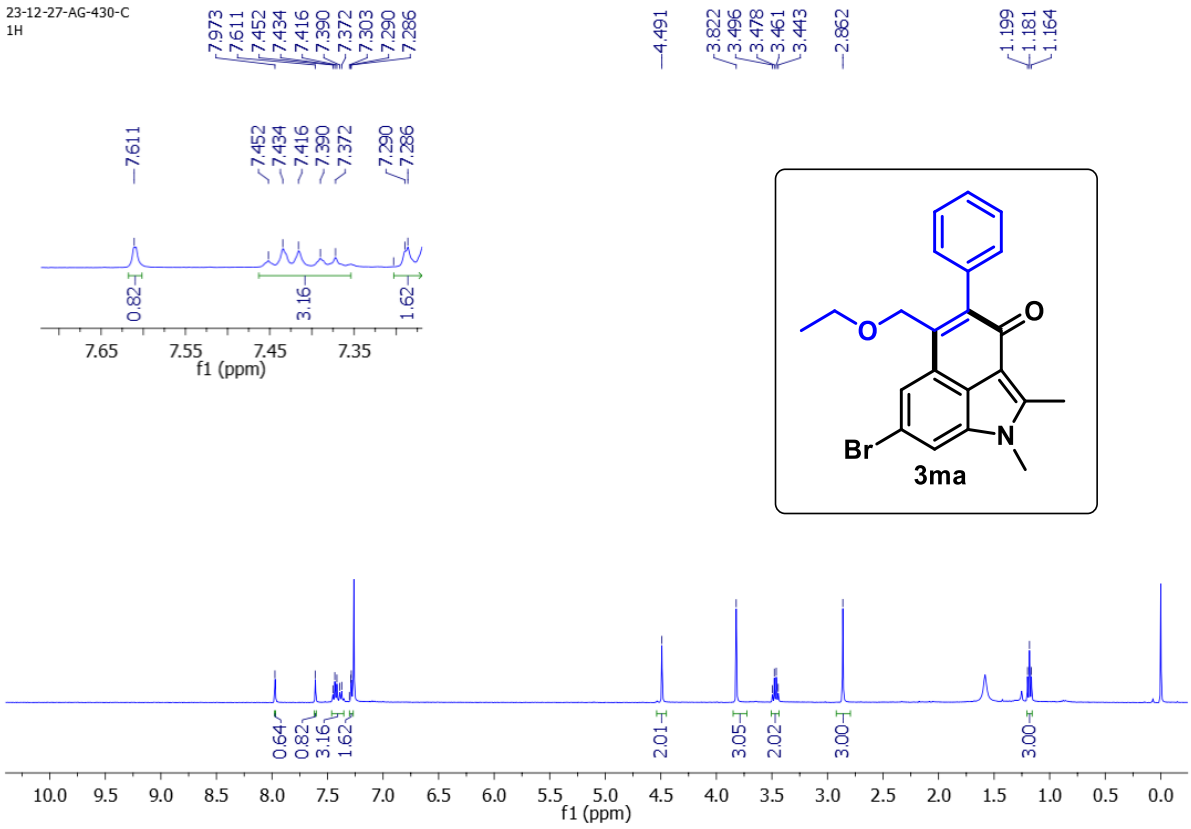
^{1}H NMR of 3la (400 MHz, $CDCl_3$)



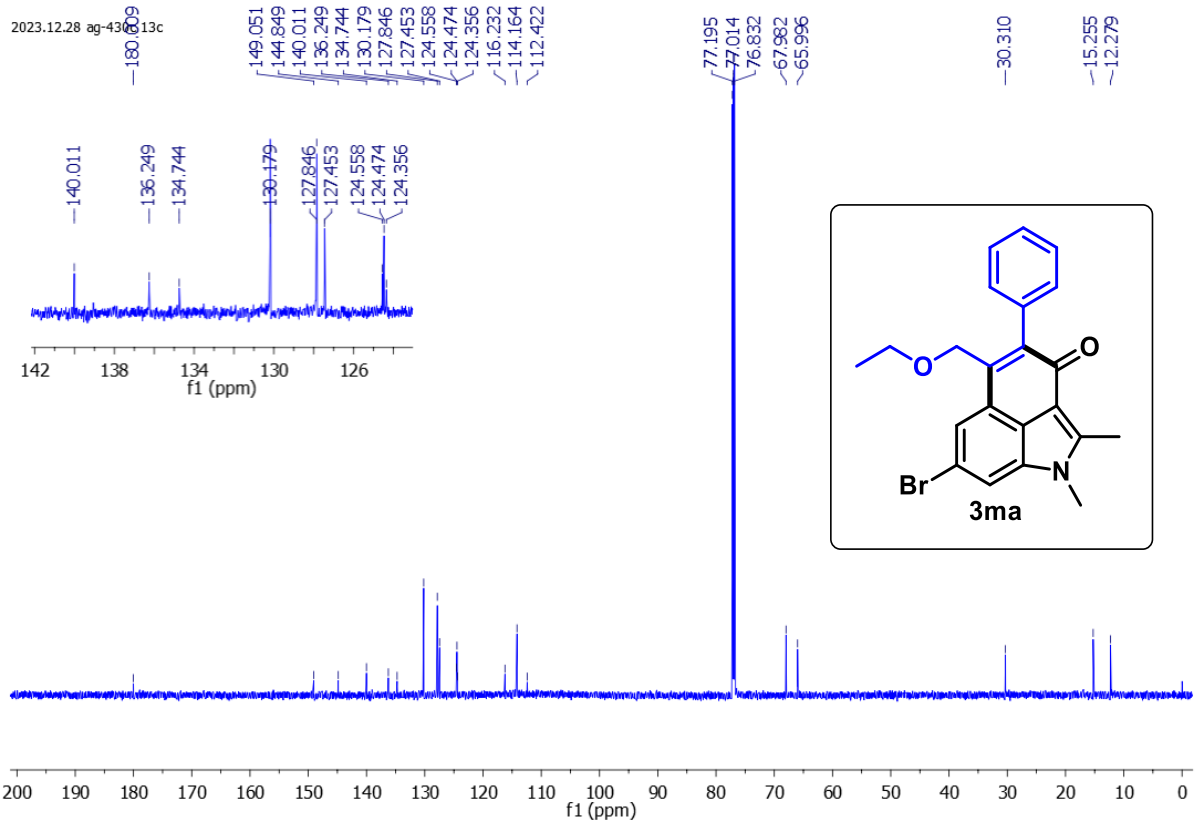
^{13}C{^{1}H} NMR of 3la (100 MHz), $CDCl_3$



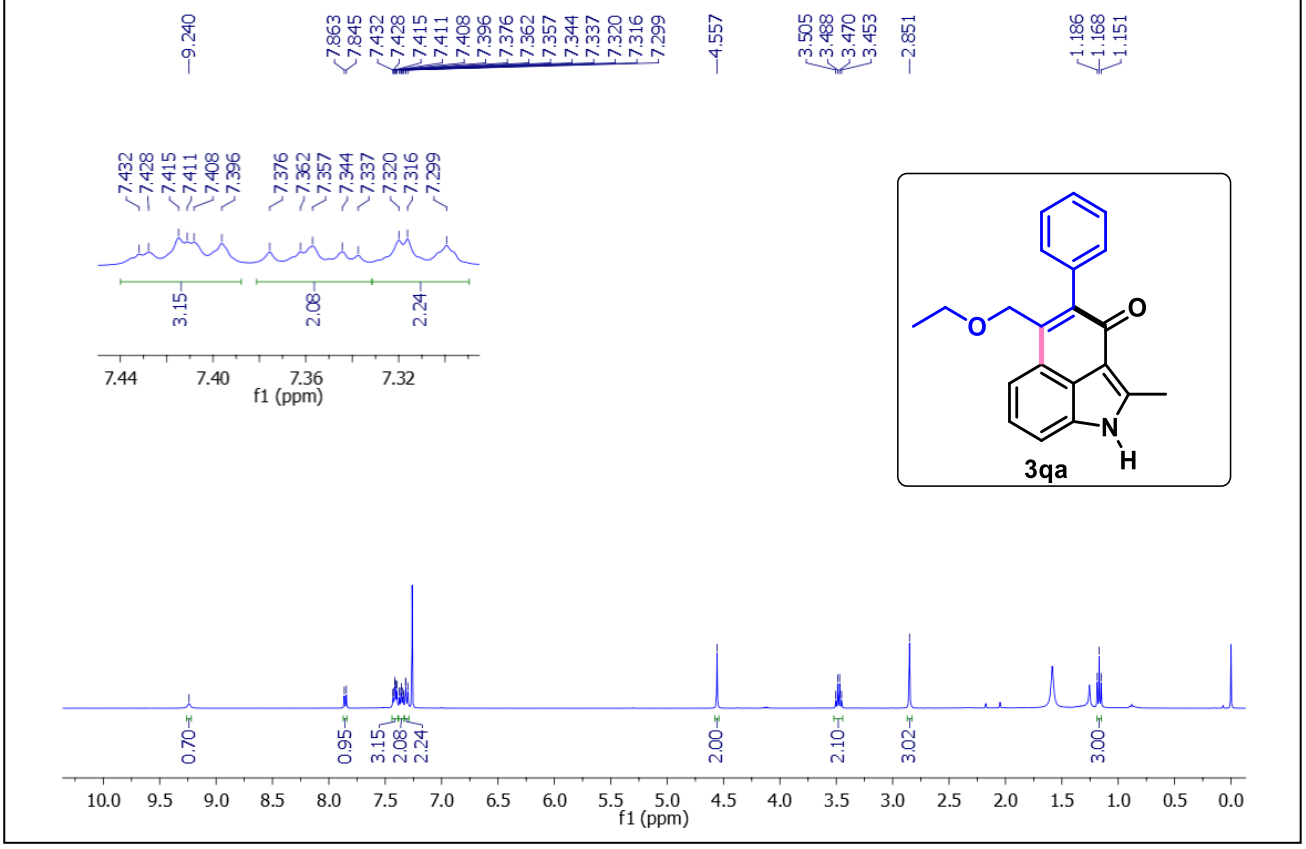
^{1}H NMR of 3ma (400 MHz, $CDCl_3$)



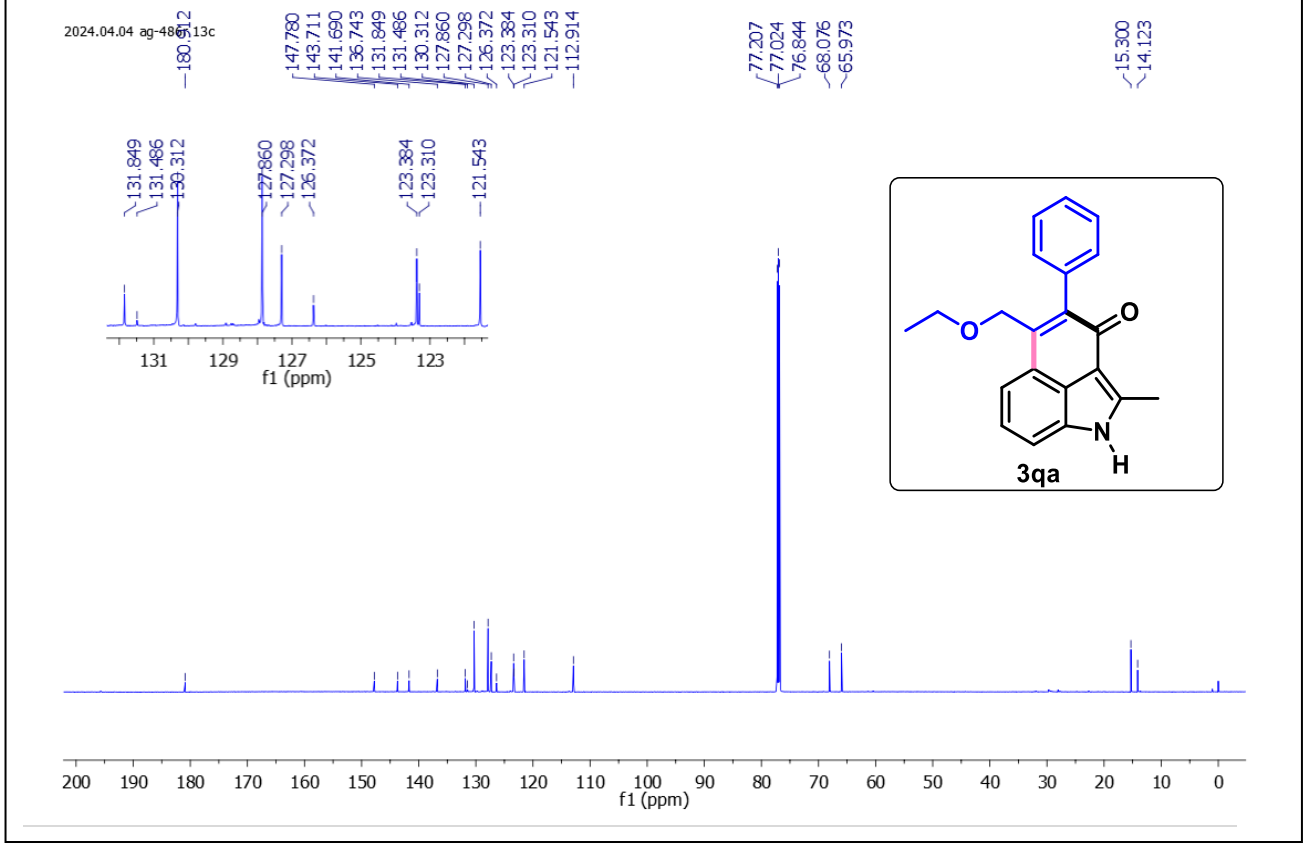
^{13}C{^{1}H} NMR of 3ma (176 MHz, $CDCl_3$)



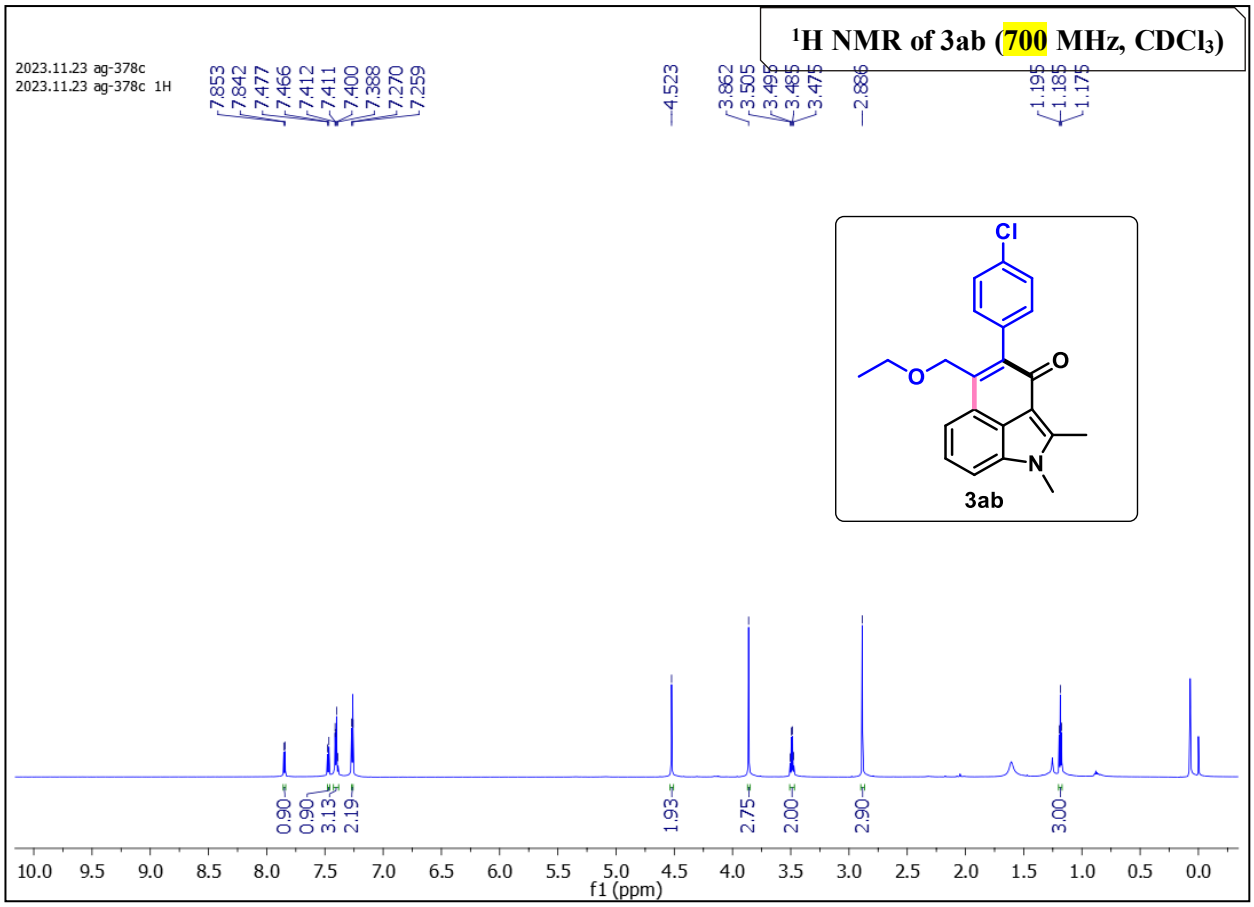
^{1}H NMR of 3qa (400 MHz, $CDCl_3$)



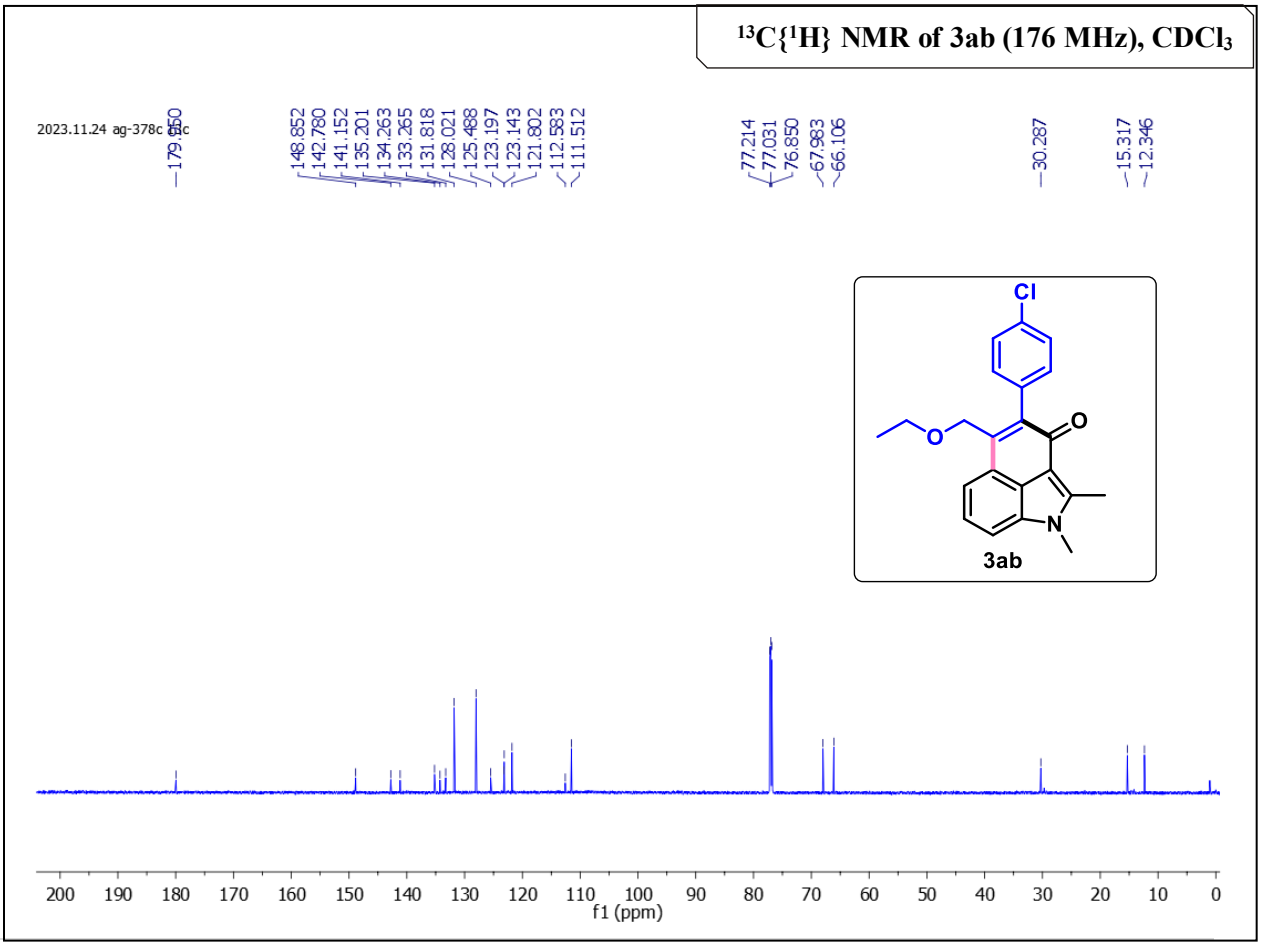
^{13}C{^{1}H} NMR of 3qa (400 MHz, $CDCl_3$)



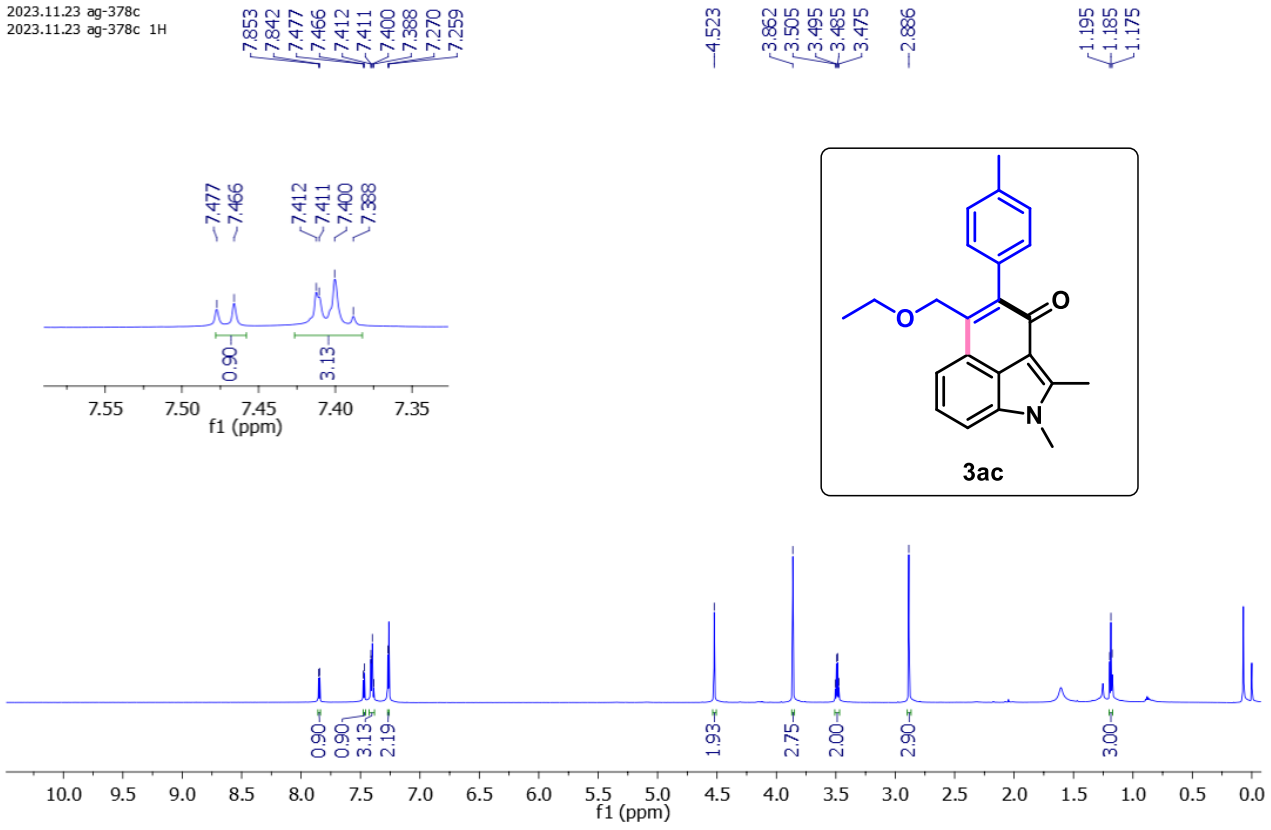
^{1}H NMR of 3ab (700 MHz, $CDCl_3$)



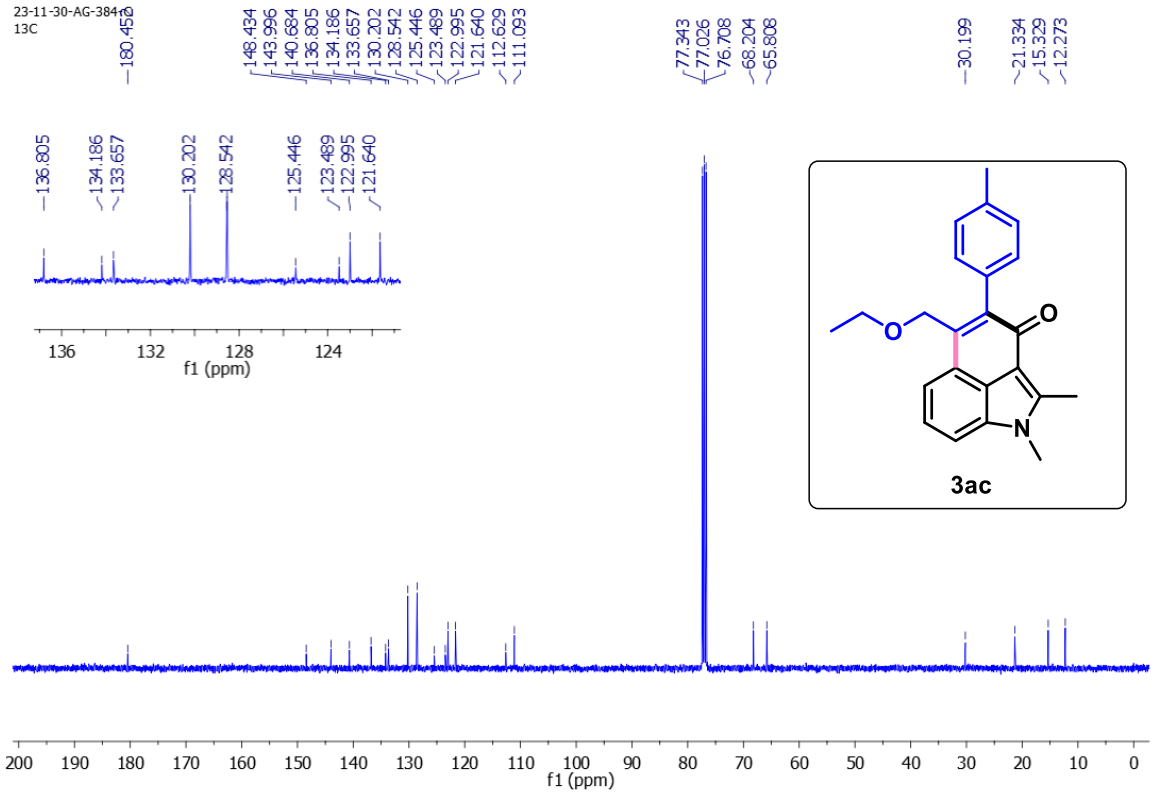
^{13}C{^{1}H} NMR of 3ab (176 MHz), $CDCl_3$



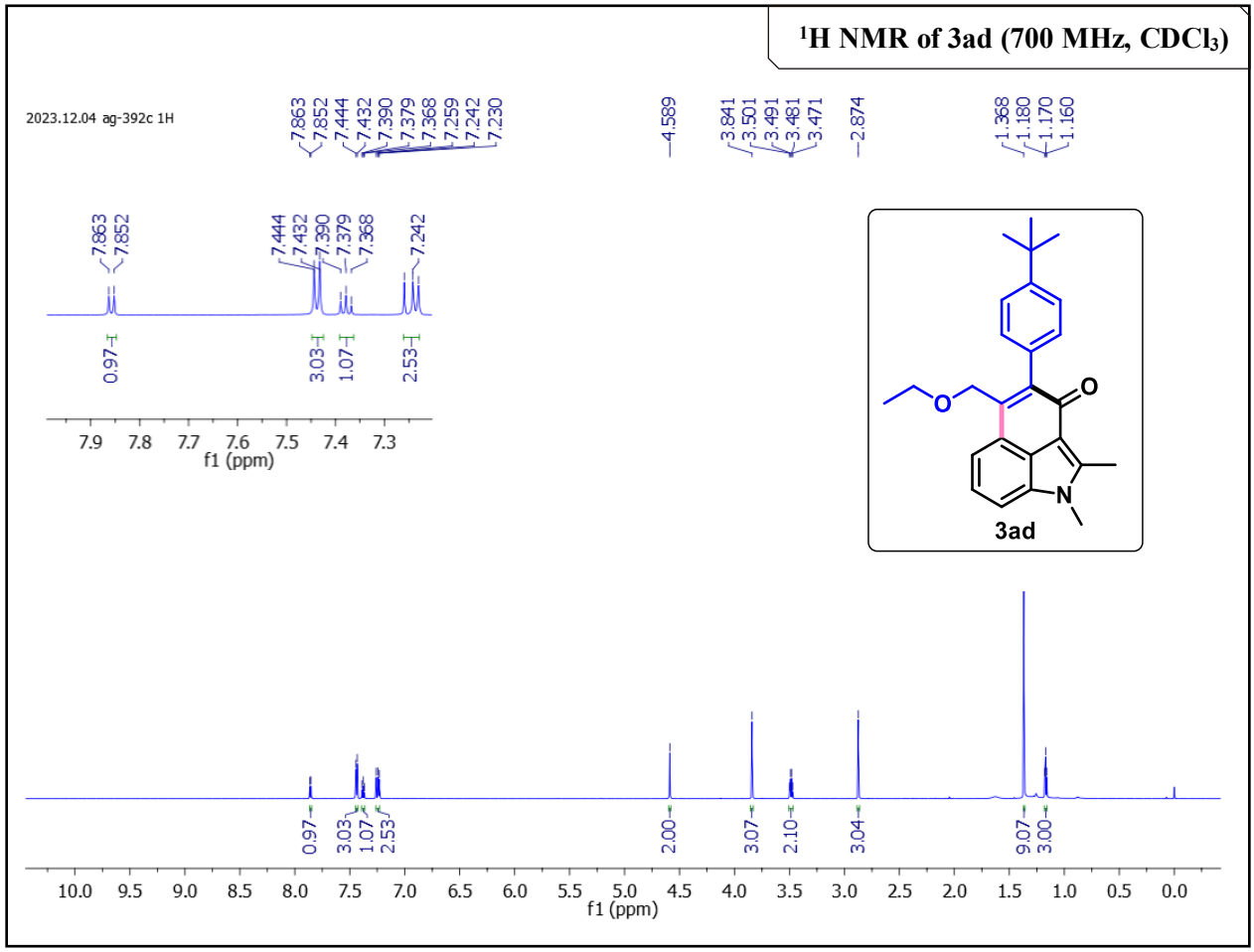
^{1}H NMR of 3ac (400 MHz, $CDCl_3$)



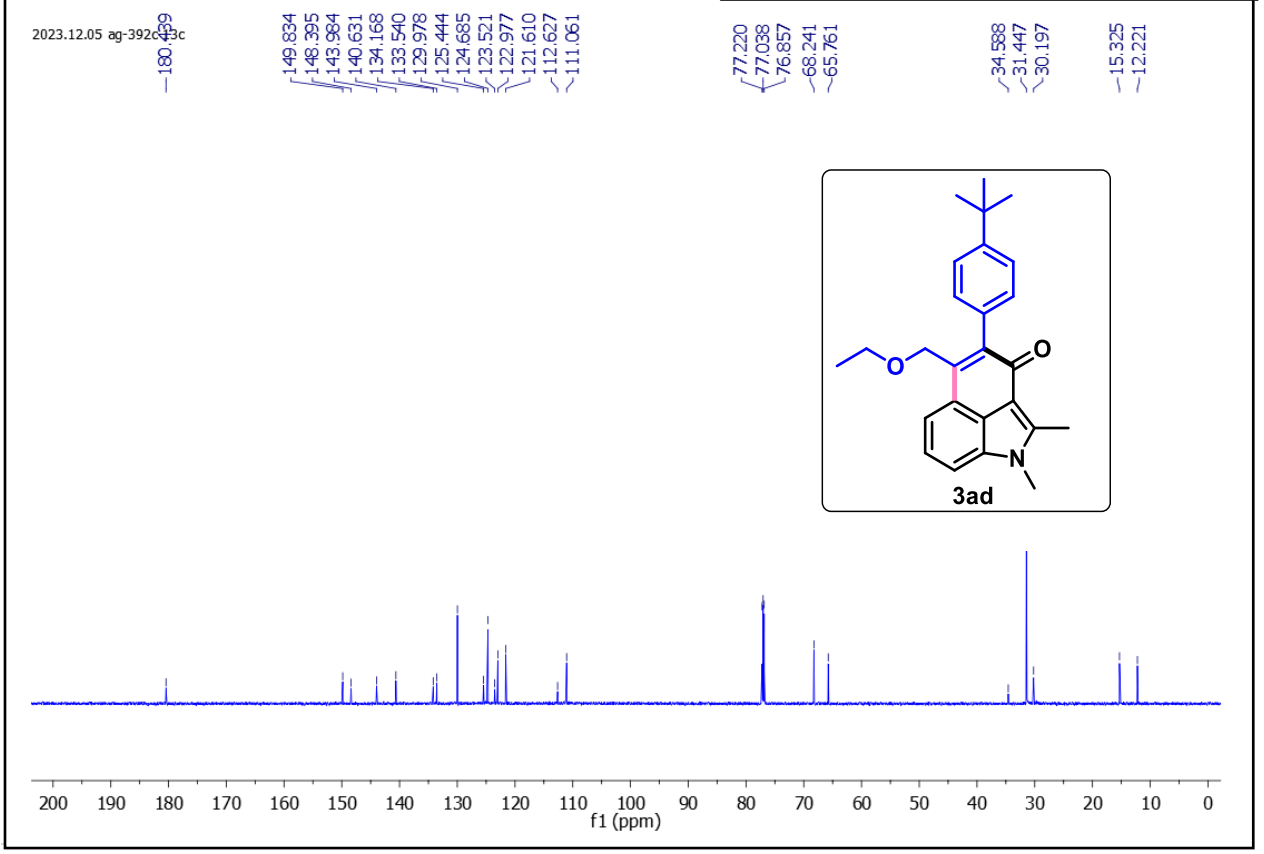
^{13}C{^{1}H} NMR of 3ac (100 MHz), $CDCl_3$



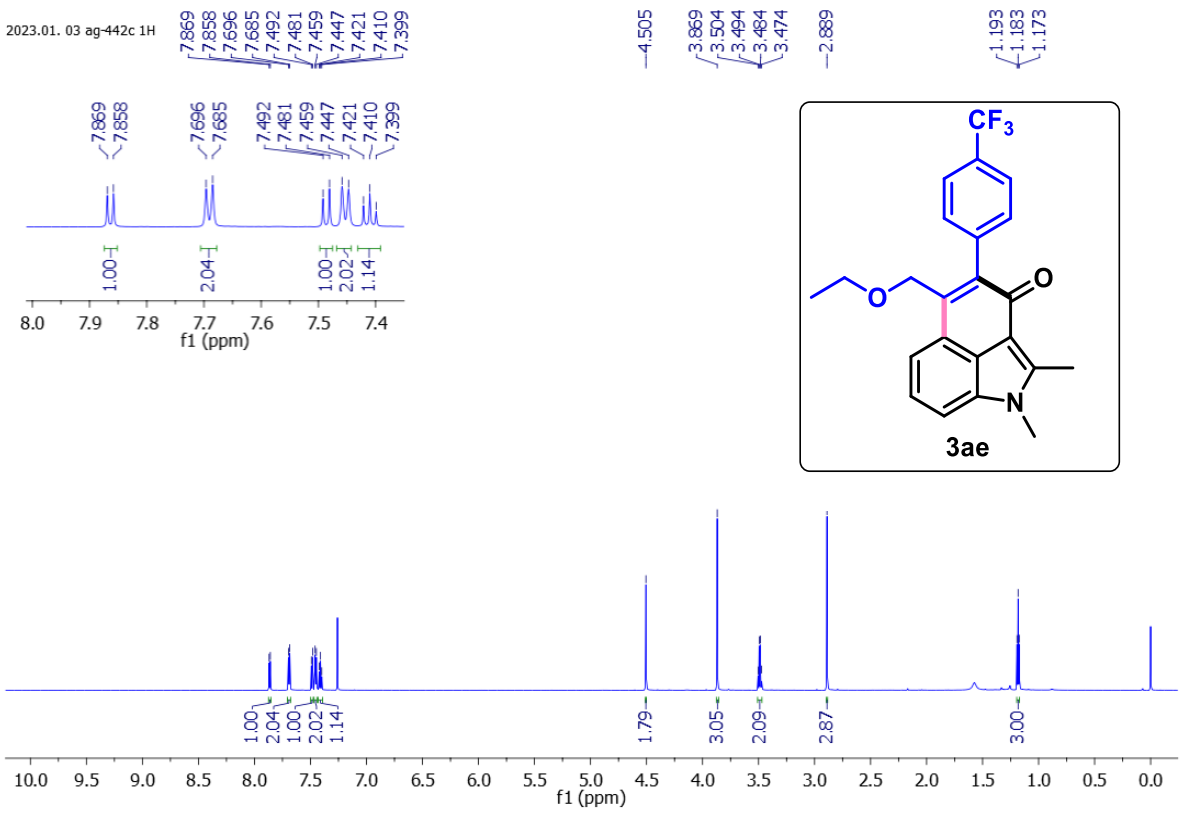
^{1}H NMR of 3ad (700 MHz, $CDCl_3$)



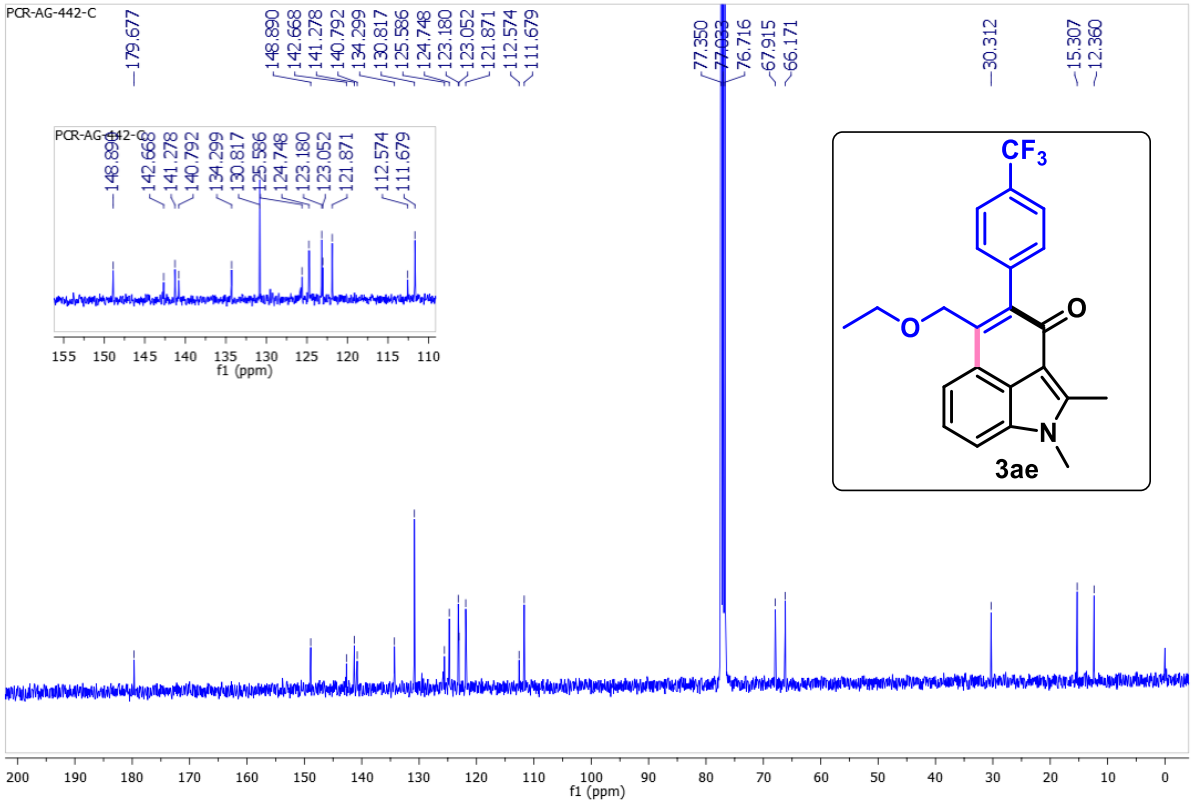
^{13}C{^{1}H} NMR of 3ad (176 MHz), $CDCl_3$



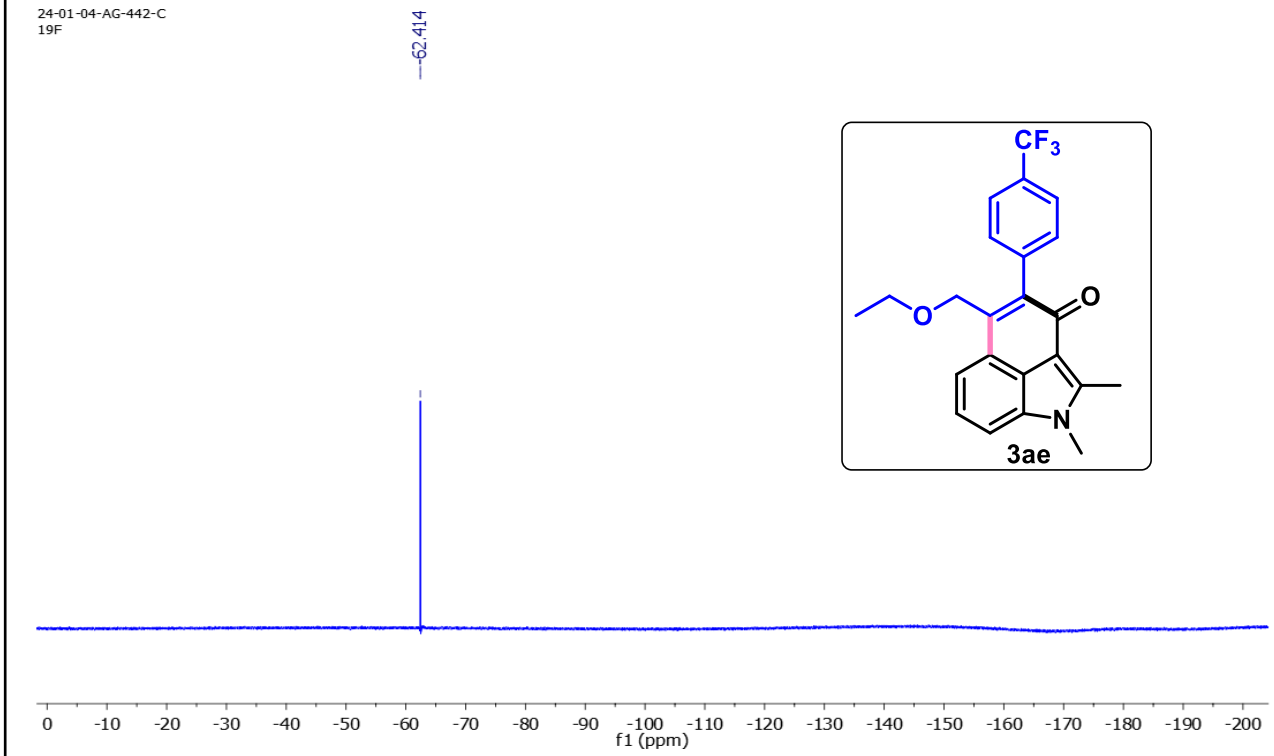
^{1}H NMR of 3ae (700 MHz, $CDCl_3$)

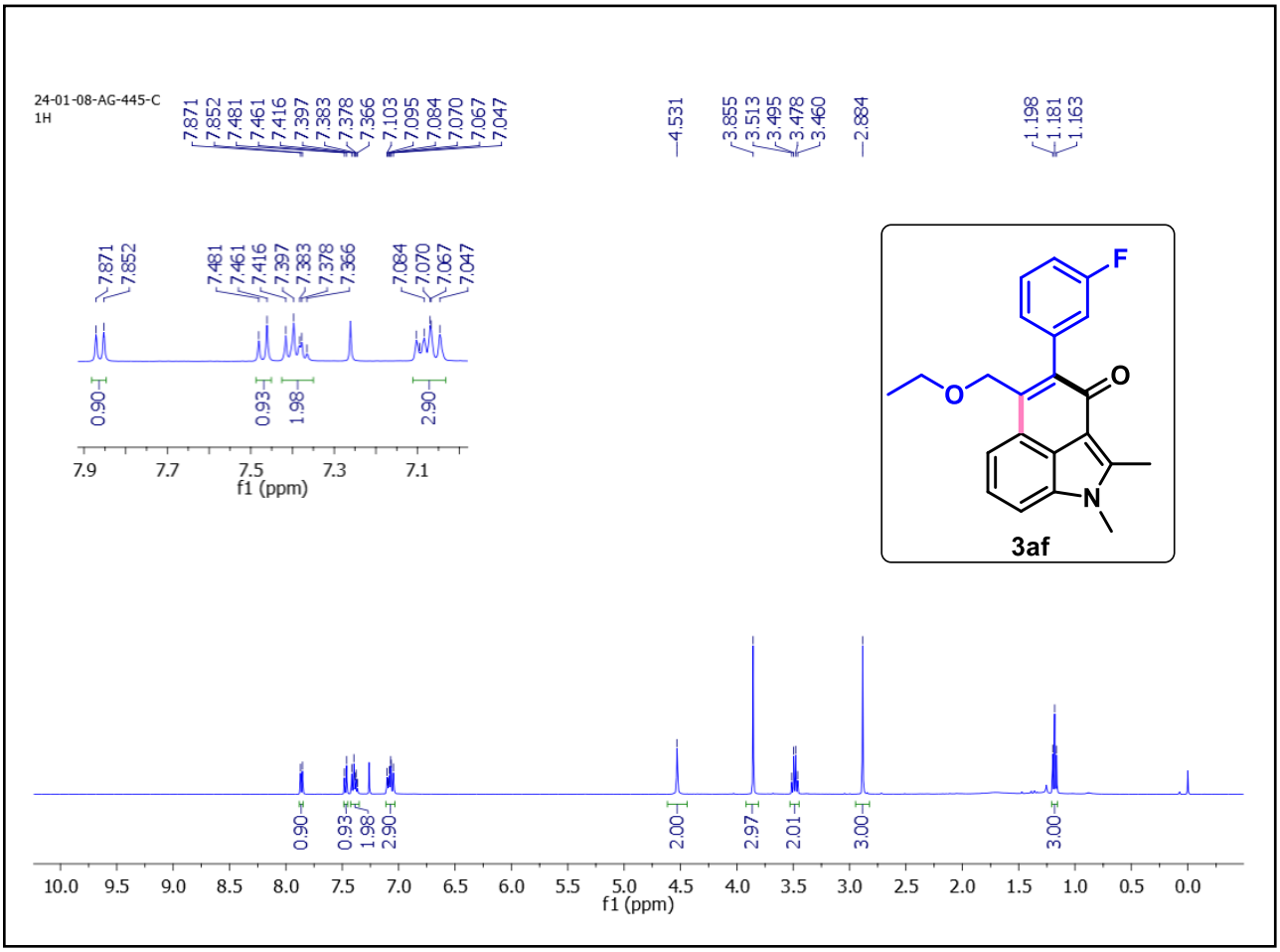


^{13}C{^{1}H} NMR of 3ae (100 MHz, $CDCl_3$)

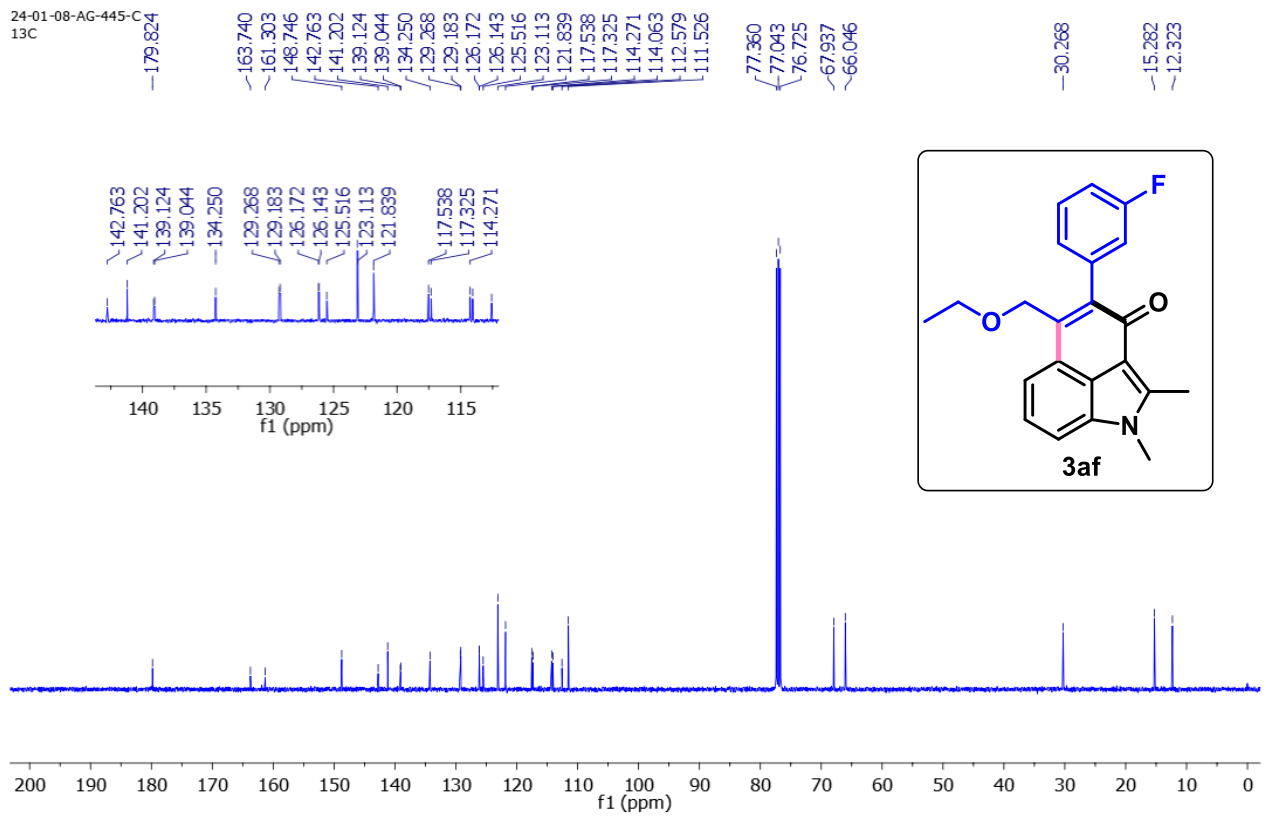


$^{19}F\{^{1}H\}$ NMR of 3ae (376 MHz, $CDCl_3$)

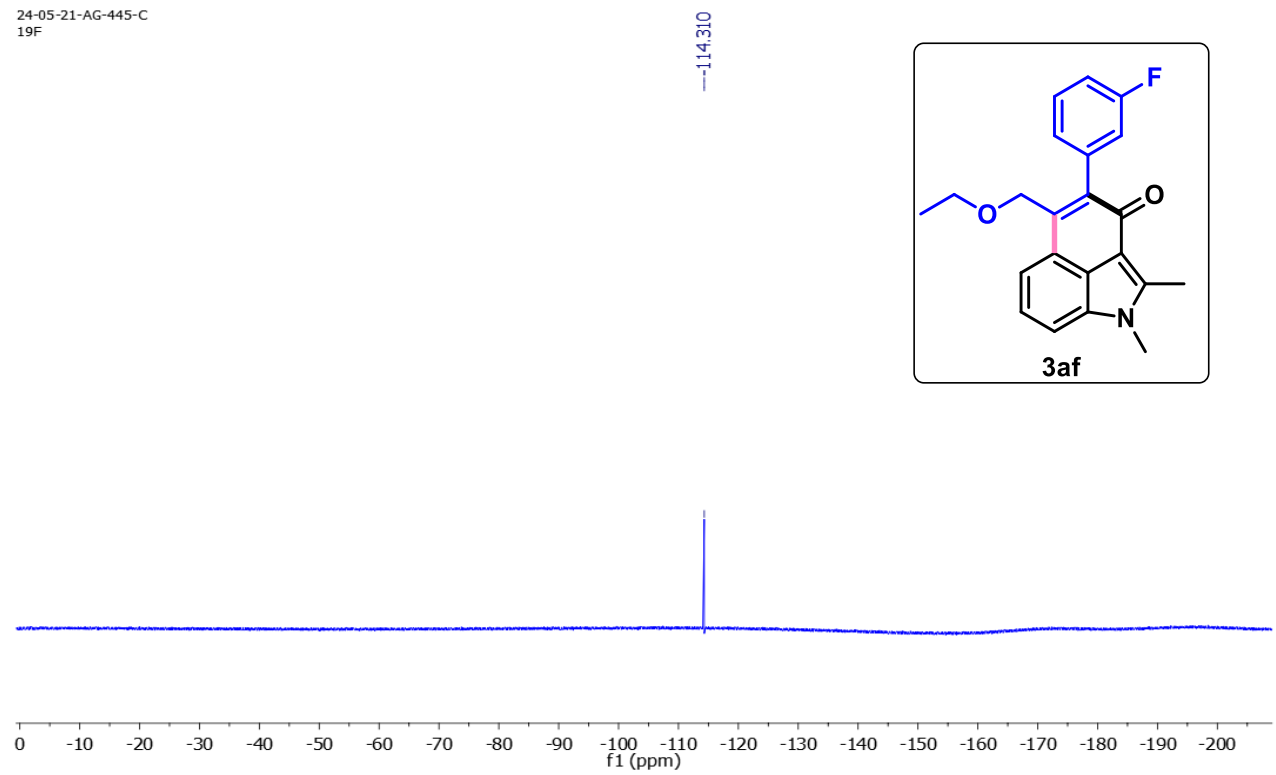




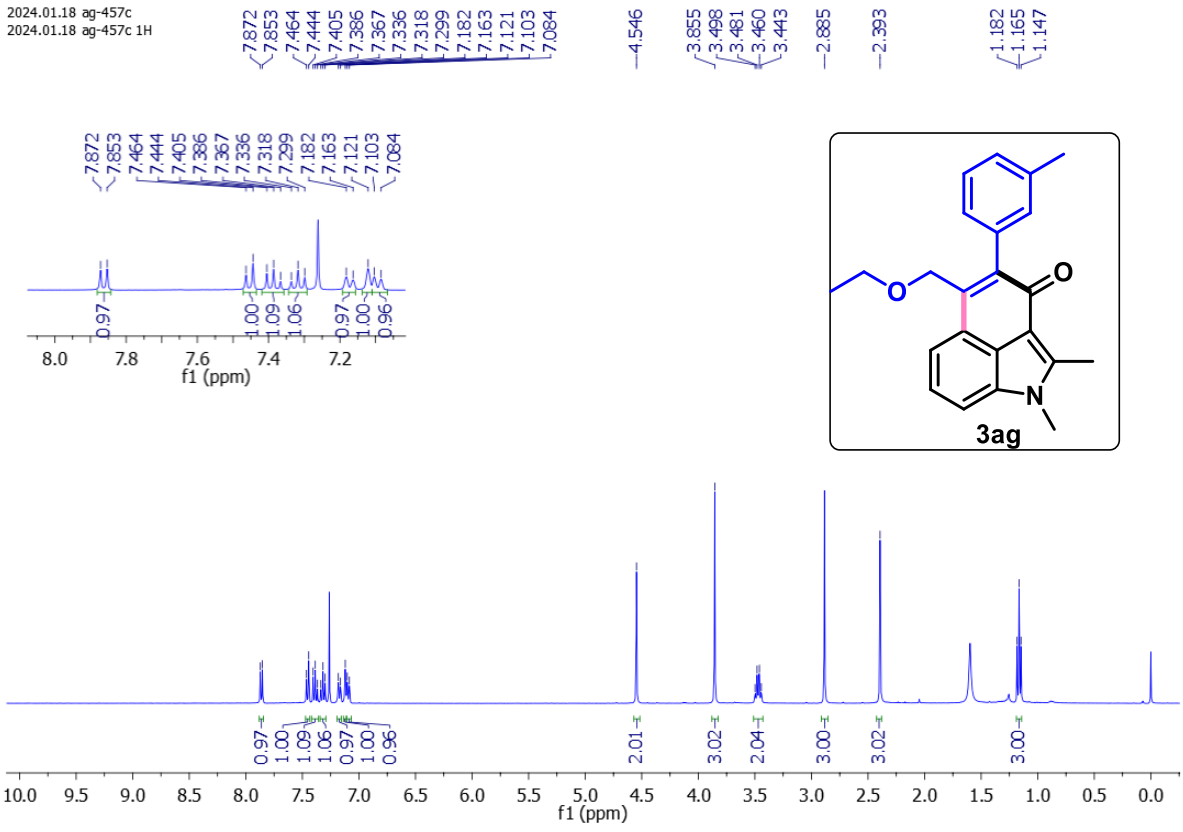
$^{13}C\{^{1}H\}$ NMR of 3af (100 MHz)



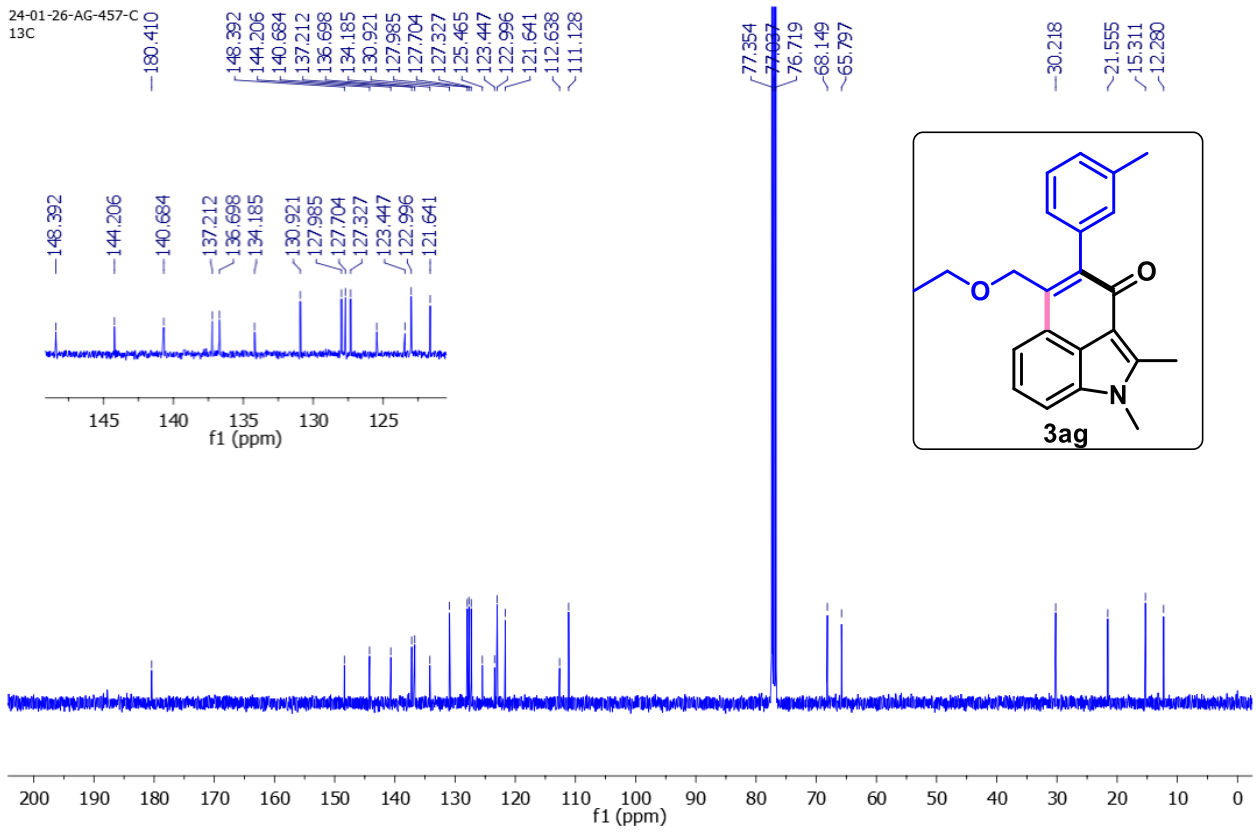
$^{19}F\{^{1}H\}$ NMR of 3af (376 MHz, $CDCl_3$)



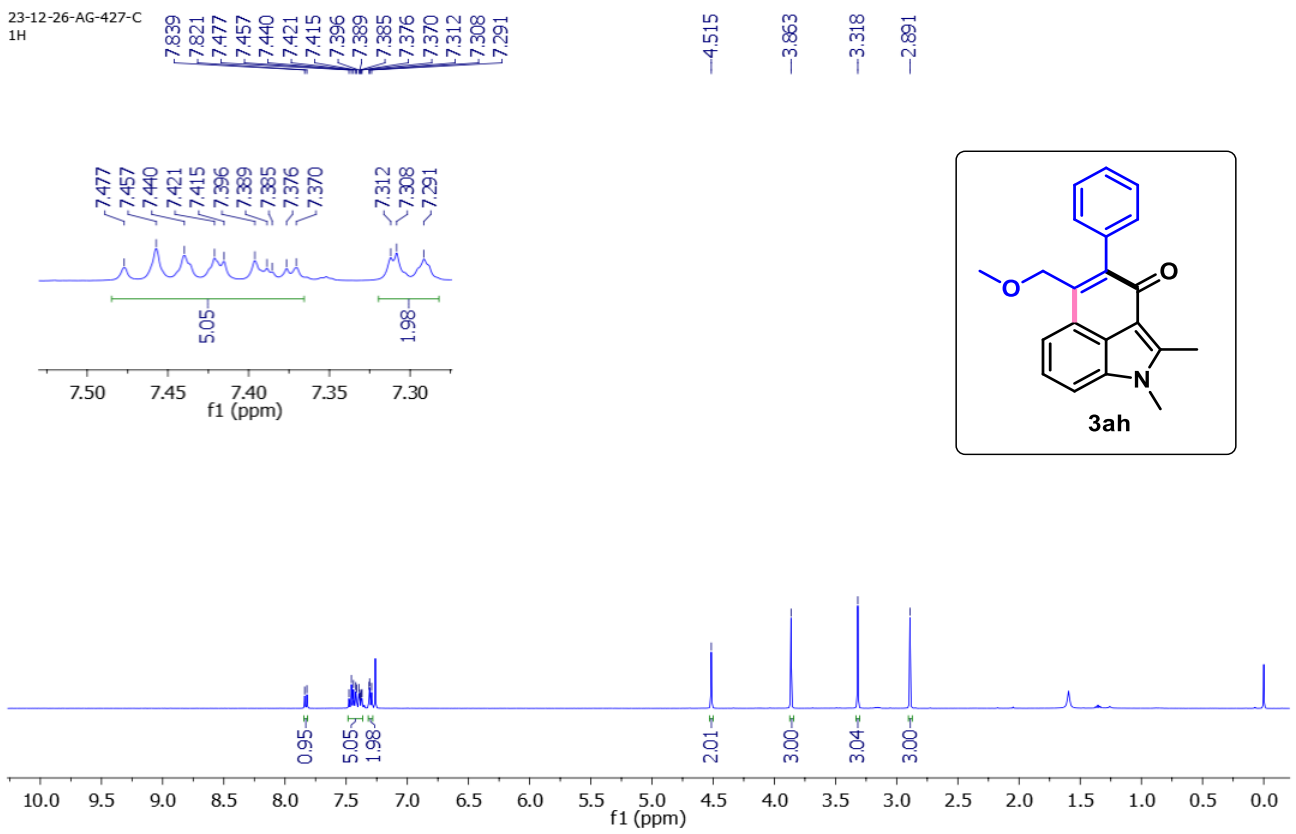
^{1}H NMR of 3ag (400 MHz, $CDCl_3$)



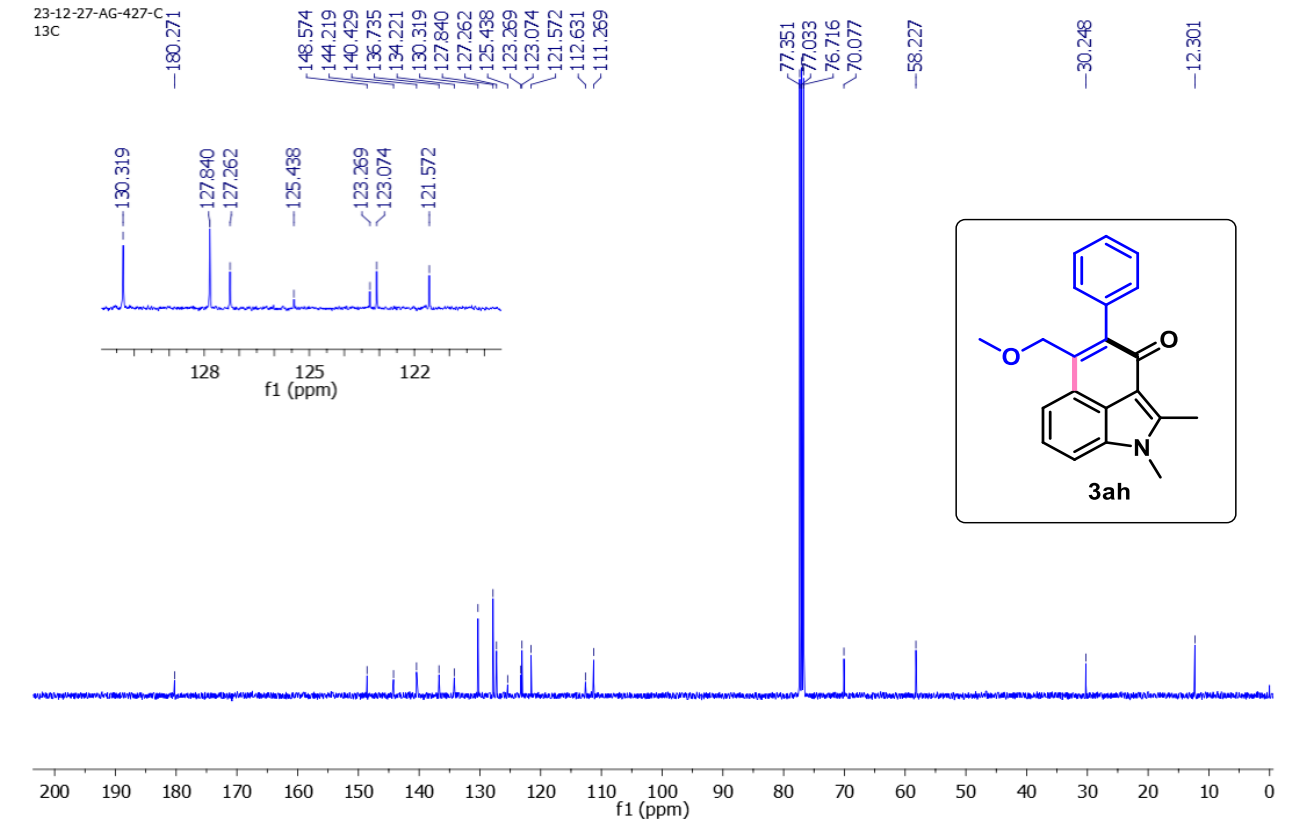
^{13}C{^{1}H} NMR of 3ag (100 MHz, $CDCl_3$)



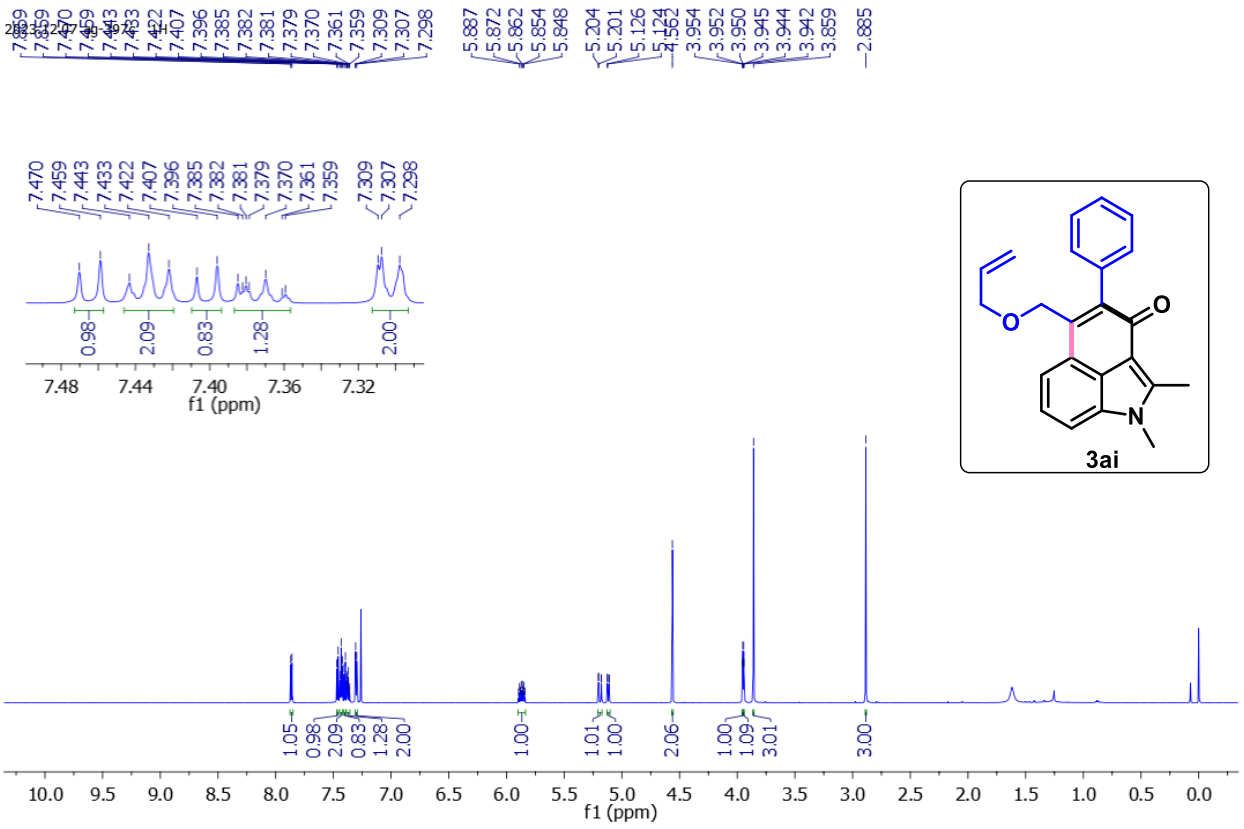
^{1}H NMR of 3ah (400 MHz, $CDCl_3$)



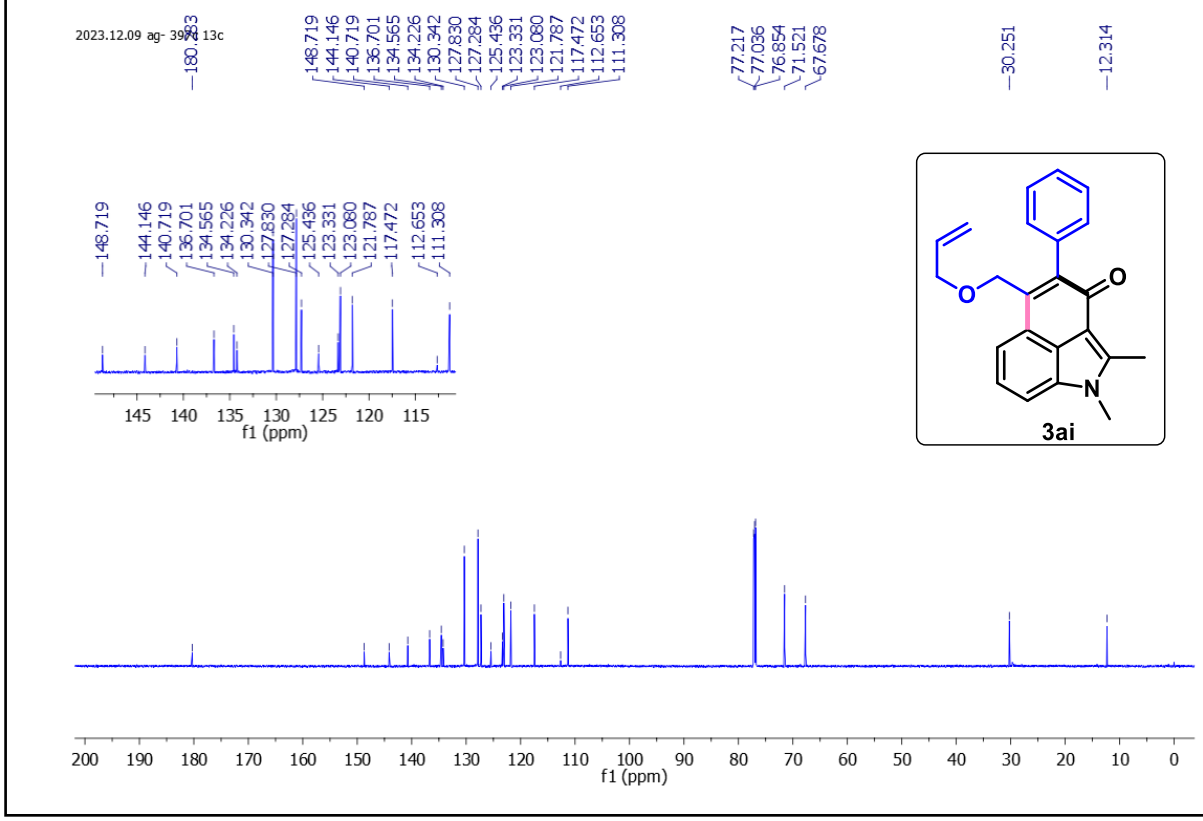
^{13}C{^{1}H} NMR of 3ah (100 MHz, $CDCl_3$)

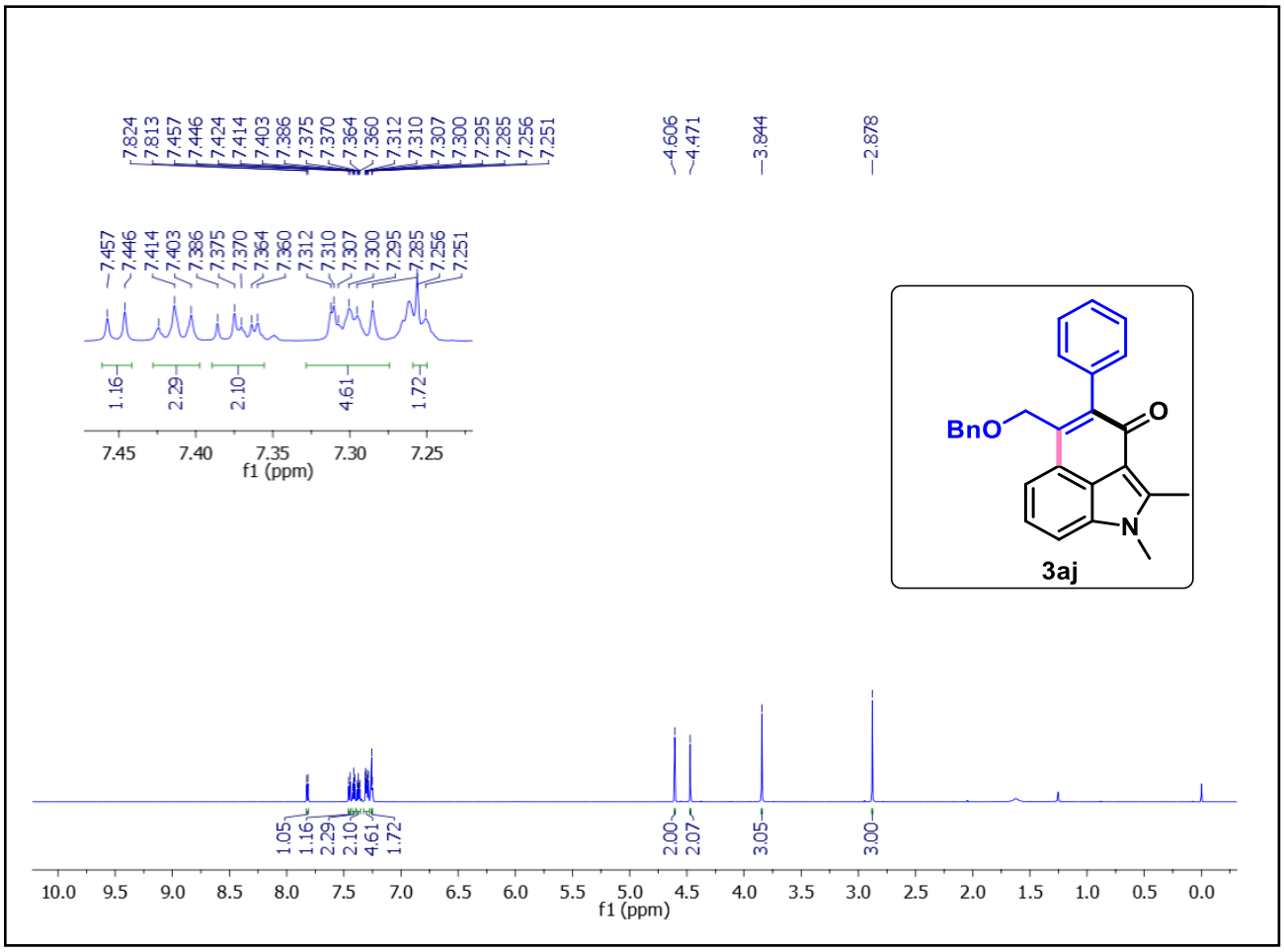


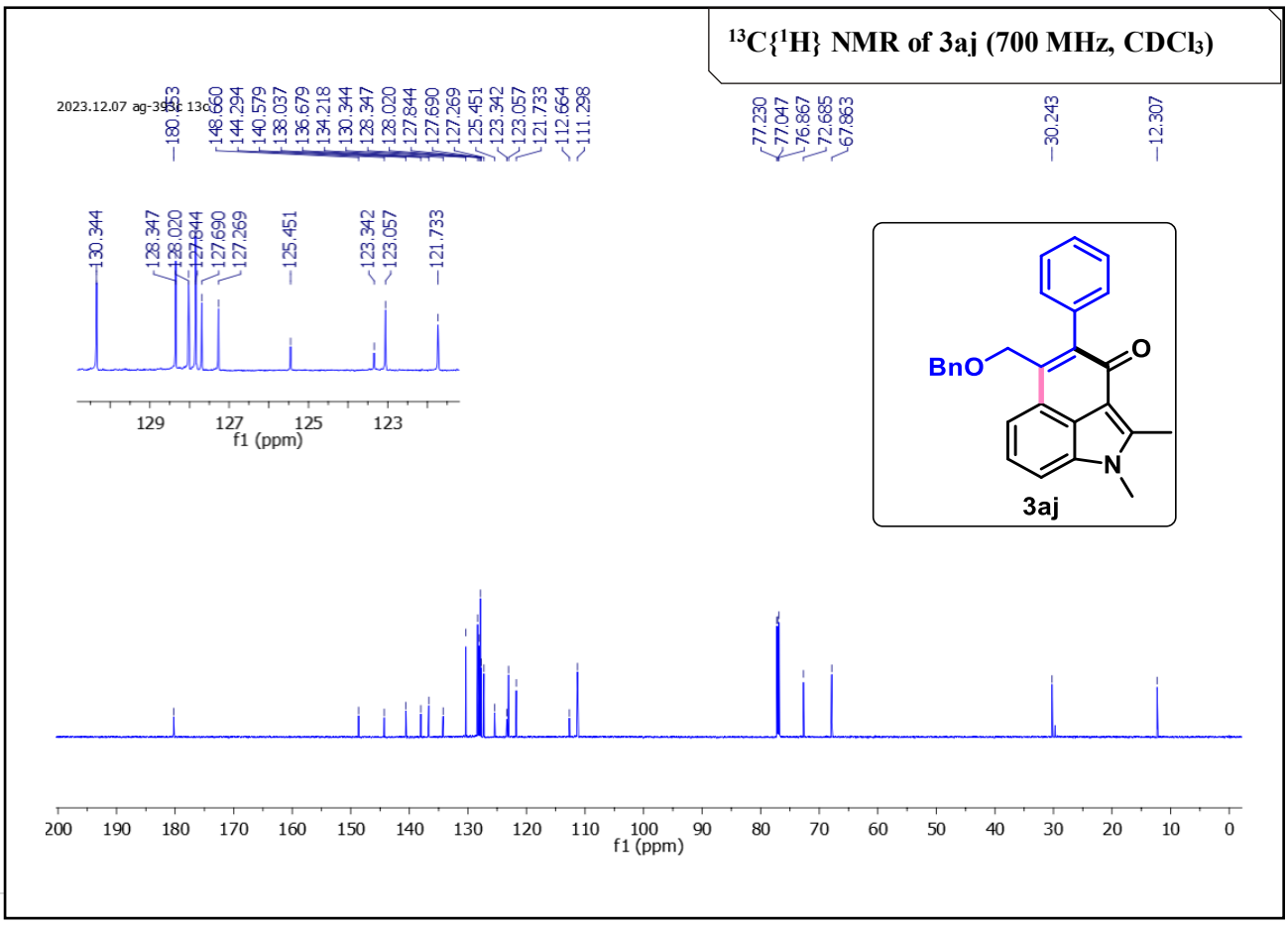
^{1}H NMR of 3ai (700 MHz, $CDCl_3$)



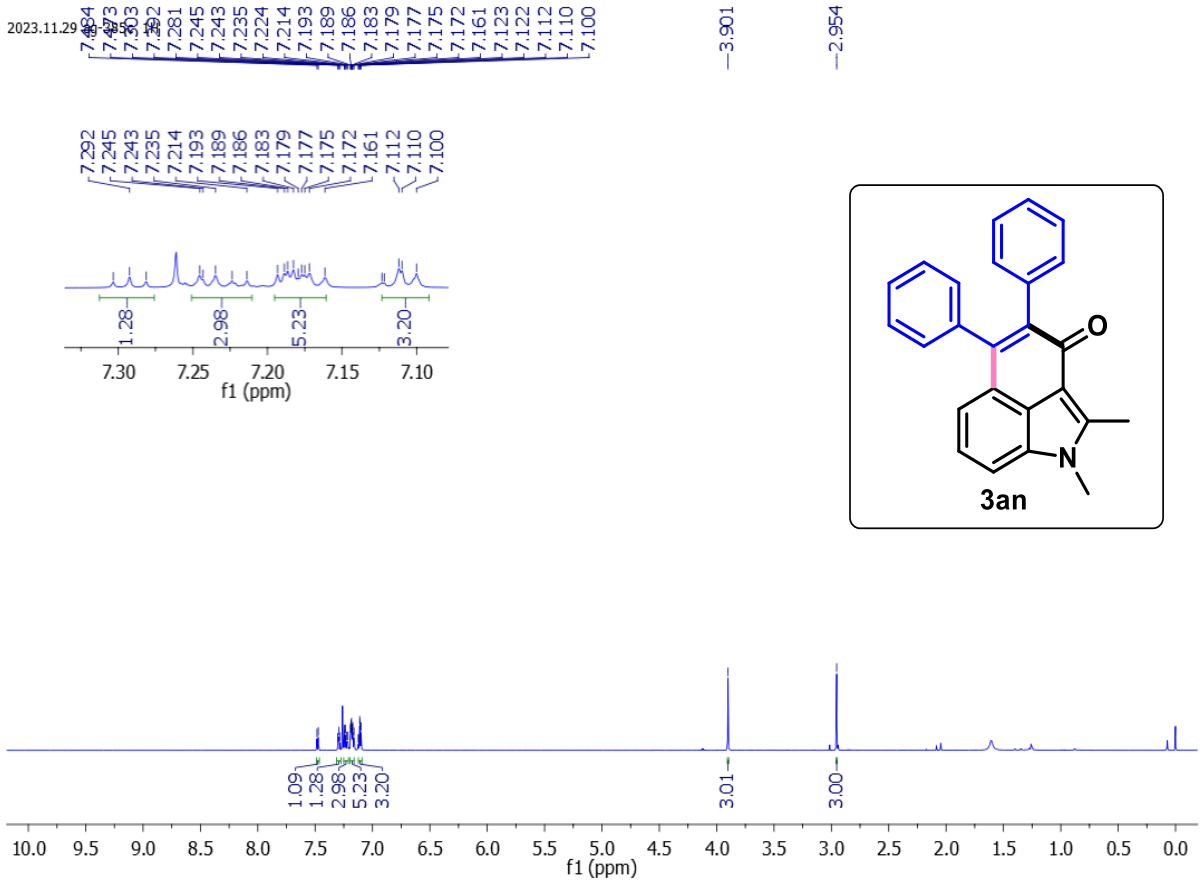
^{13}C{^{1}H} NMR of 3ai (176 MHz, $CDCl_3$)



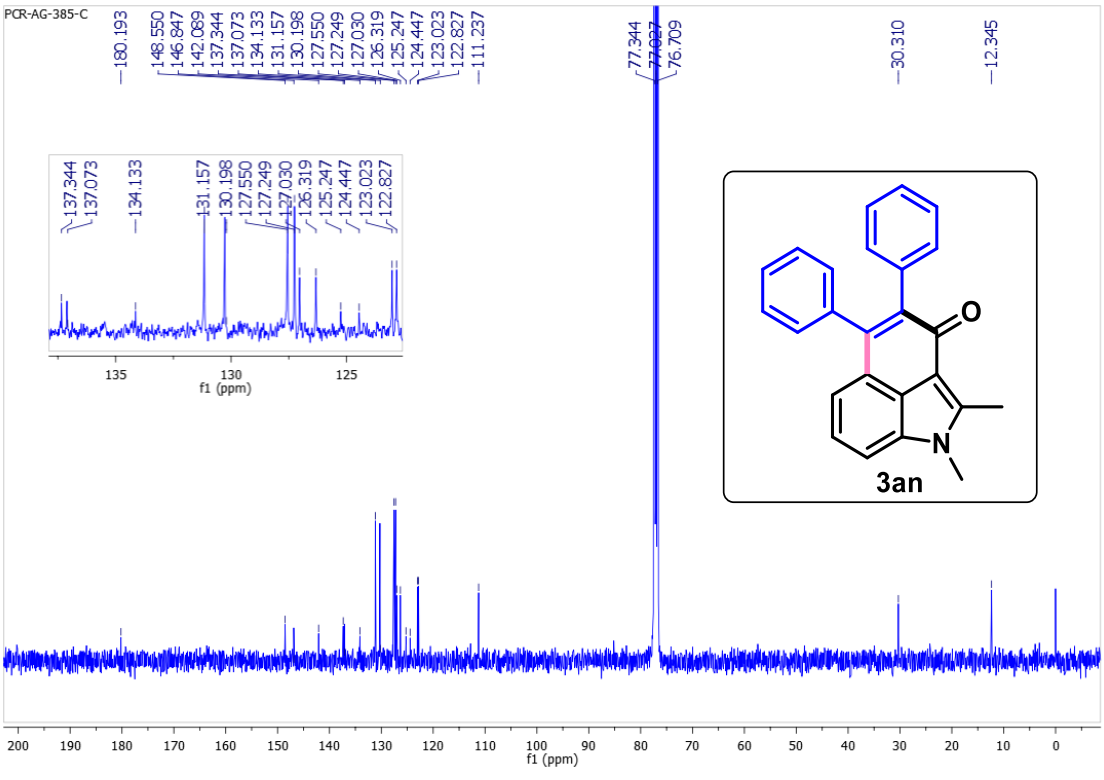

7.824
7.813
7.457
7.446
7.424
7.414
7.403
7.386
7.375
7.370
7.364
7.360
7.312
7.310
7.307
7.300
7.295
7.285
7.256
7.251
4.606
4.471
3.844
2.878
1.16
2.29
2.10
4.61
1.72
7.45
7.40
7.35
7.30
7.25
f1 (ppm)
BnO
O
N
3aj
1.05
1.16
2.29
2.10
4.61
1.72
2.00
2.07
3.05
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


$^{13}C\{^{1}H\}$ NMR of 3aj (700 MHz, $CDCl_3$)
2023.12.07 ag-3931 13C
180.453
148.660
144.294
140.579
138.037
136.679
134.218
130.344
128.347
128.020
127.844
127.690
127.269
125.451
123.342
123.057
121.733
112.664
111.298
77.230
77.047
76.867
72.685
67.863
30.243
12.307
130.344
128.347
128.020
127.844
127.690
127.269
125.451
123.342
123.057
121.733
129
127
125
123
f1 (ppm)
BnO
O
N
3aj
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

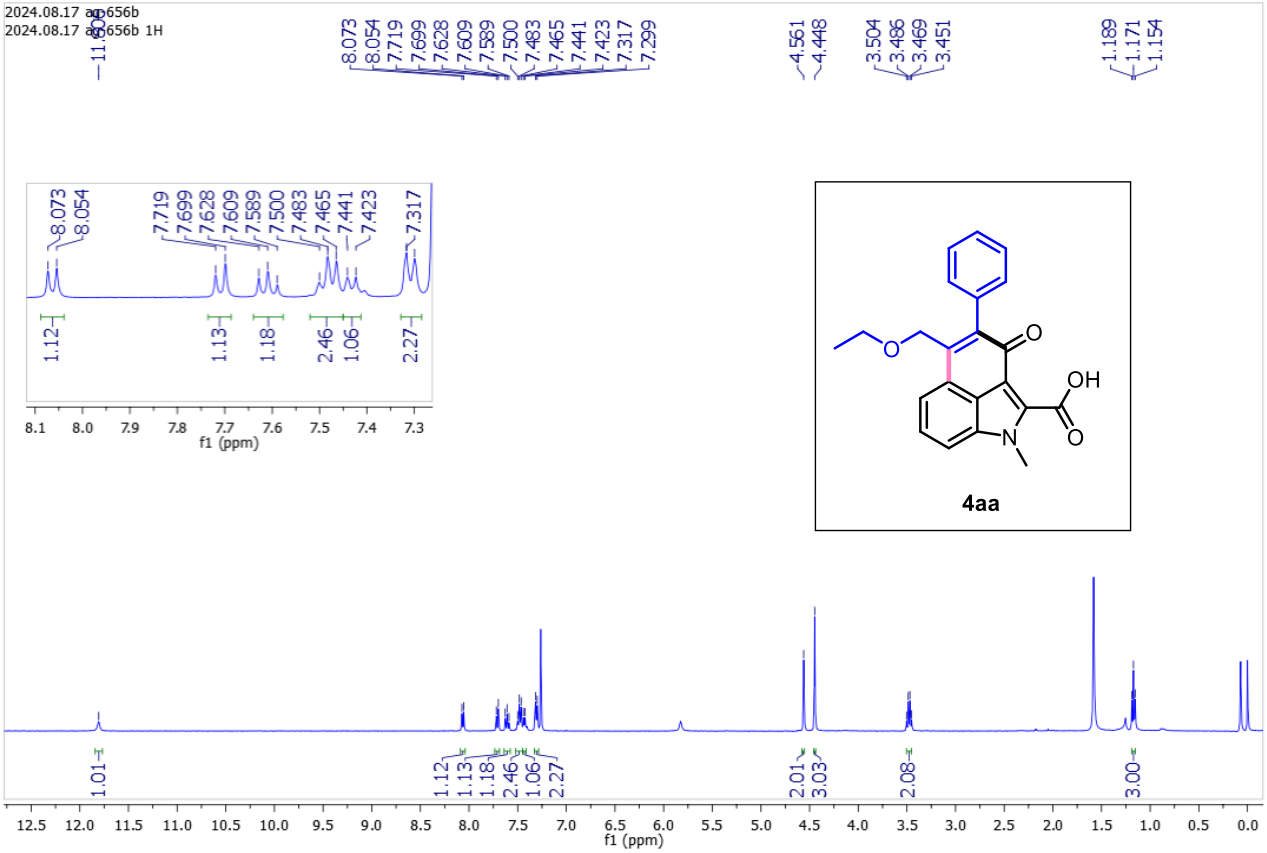
^{1}H NMR of 3an (700 MHz, $CDCl_3$)



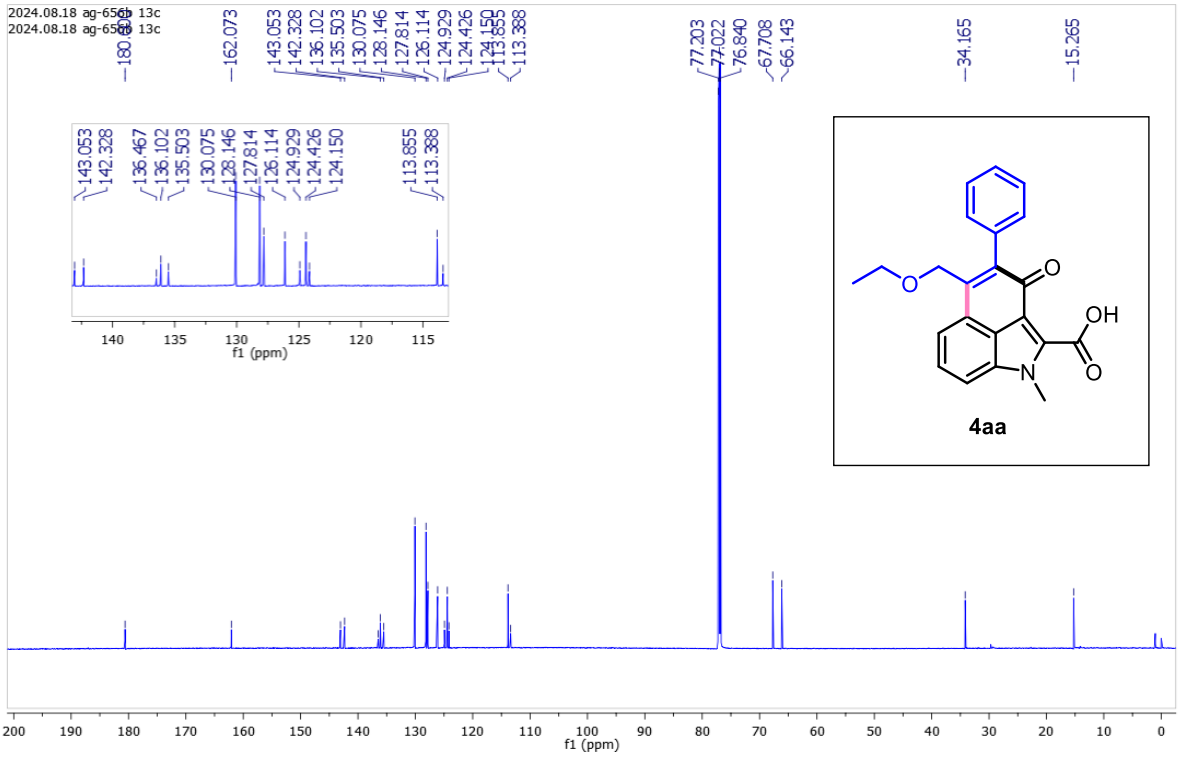
^{13}C{^{1}H} NMR of 3an (176 MHz), CDCl3



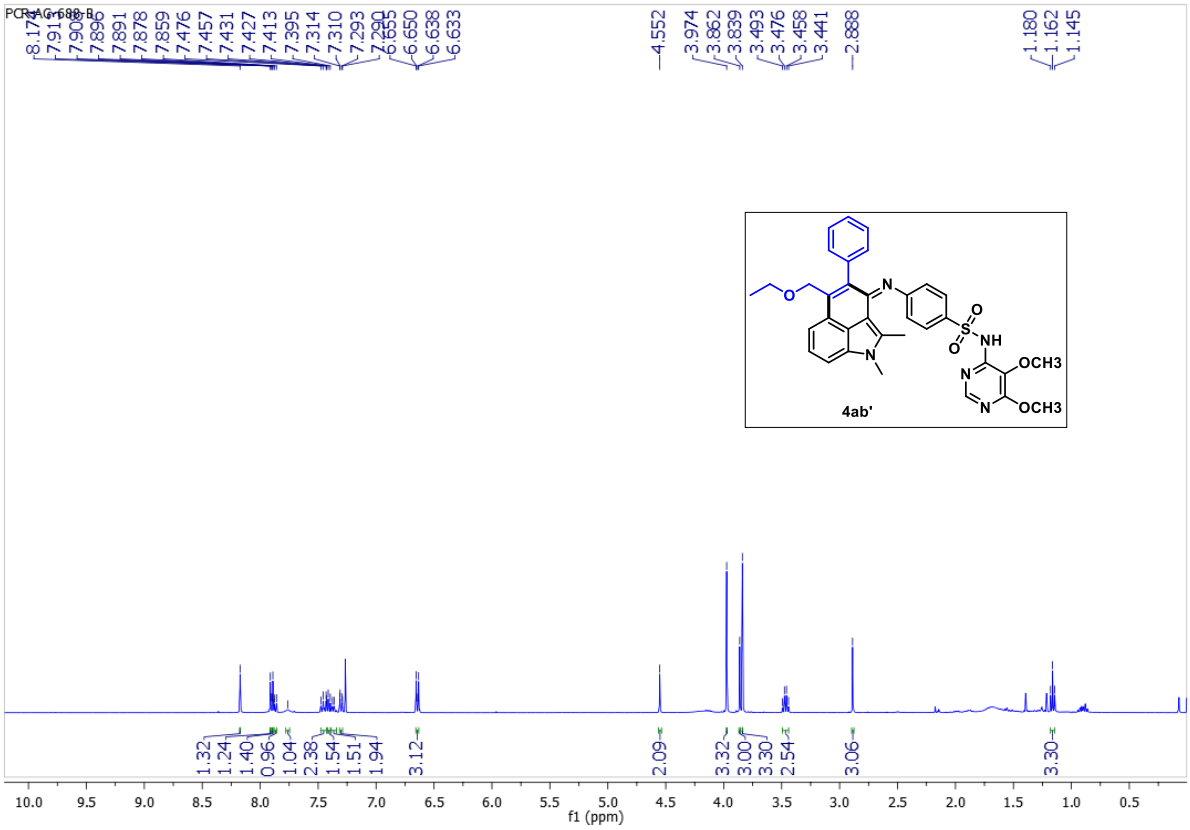
^{1}H NMR of 4aa (400 MHz, $CDCl_3$)



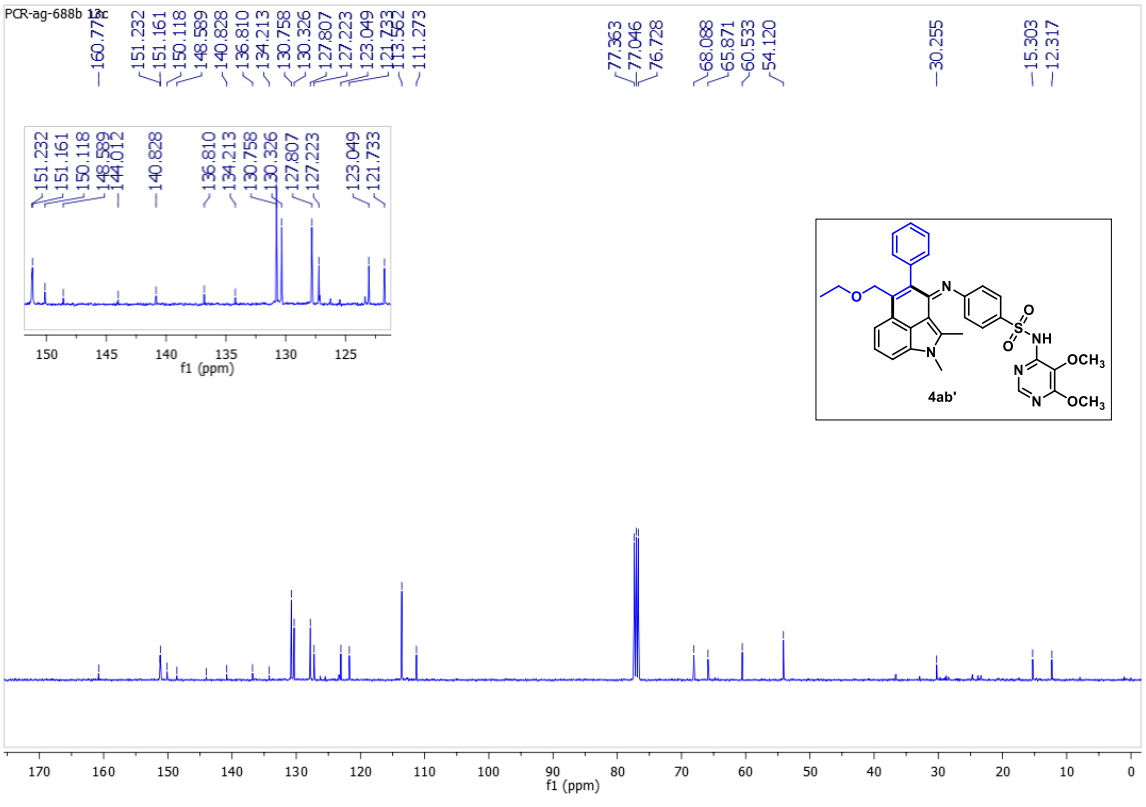
^{13}C{^{1}H} NMR of 4aa (100 MHz), $CDCl_3$



^{1}H NMR of 4ab' (100 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR of 4ab' (100 MHz, $CDCl_3$)



8.Crystallographic data

Crystals of the compounds **3aa** 5-(ethoxymethyl)-1,2-dimethyl-4-phenylbenzo[cd]indol-3(1H)-one were obtained after slow evaporation of methanol. Crystals suited for single crystal X-Ray diffraction measurements were mounted on a glass fiber. Geometry and intensity data were collected with a Rigaku Smartlab X-ray diffractometer equipped with graphite-monochromated (Mo-Kα radiation, λ = 0.71073, multilayer optics). Temperature was controlled using an Oxford Cryostream 700 instrument. Intensities were integrated with SAINT and SMART software packages and corrected for absorption with SADABS. The structure was solved by direct methods and refined on F2 with SHELXL-97 using Olex-2 software.

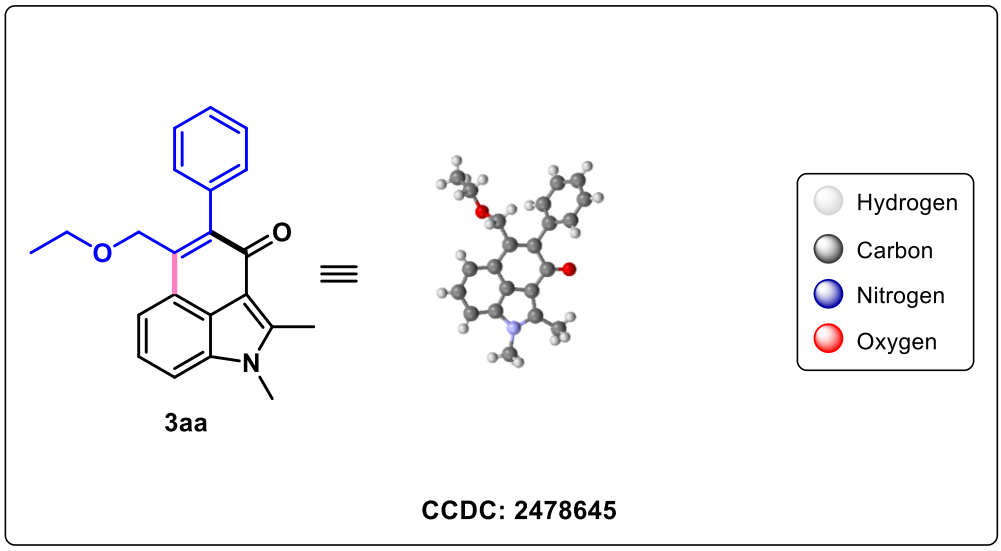
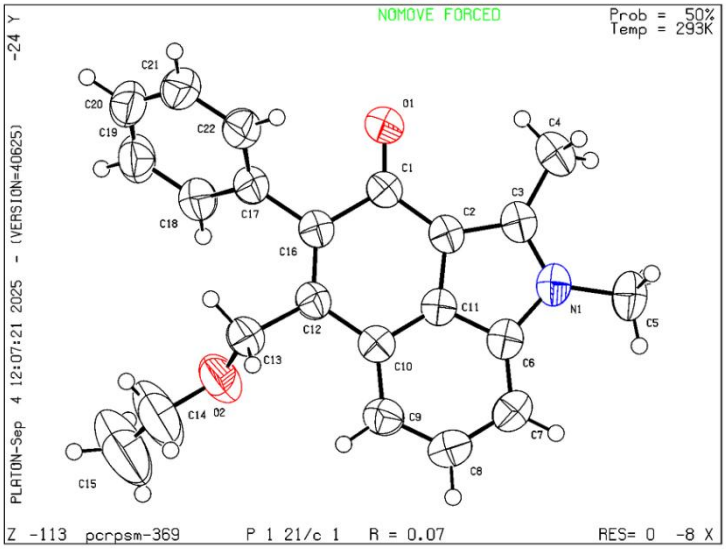


Figure S1. Crystal structure of **3aa** (50% ellipsoid probability).



Bond precision: C-C = 0.0035 A Wavelength=1.54184

Cell: a=8.7902(2) b=31.2988(5) c=7.0352(1)
alpha=90 beta=110.298(2) gamma=90
Temperature: 293 K

	Calculated	Reported
Volume	1815.35(6)	1815.35(6)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C22 H21 N O2	C22 H21 N O2
Sum formula	C22 H21 N O2	C22 H21 N O2
Mr	331.40	331.40
Dx,g cm-3	1.213	1.213
Z	4	4
Mu (mm-1)	0.611	0.611
F000	704.0	704.0
F000'	706.01	
h,k,lmax	11,39,8	11,39,8
Nref	3890	3795
Tmin,Tmax		0.766,1.000
Tmin'		

Correction method= # Reported T Limits: Tmin=0.766 Tmax=1.000
AbsCorr = MULTI-SCAN