Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Rh(III)-Catalyzed [3+2]/[4+2] Annulation of Acetophenone Oxime Ethers with 3-Acetoxy-1,4-enynes involving C-H Activation

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(A)Typical Experimental Procedure

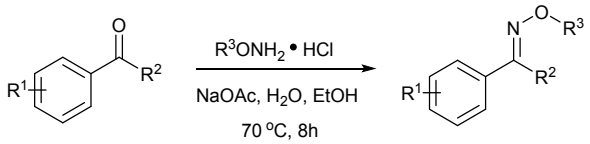
(a) General

The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ solvent on a NMR spectrometer using TMS as internal standard. Proton nuclear magnetic resonance (^{1}H NMR) spectra, carbon nuclear magnetic resonance (^{13}C NMR) spectra and fluorine nuclear magnetic resonance (^{19}F NMR) spectra were recorded at 500, 125 MHz and 471 MHz, respectively. LRMS was performed on a GC-MS instrument. HRMS was measured on an electrospray ionization (ESI) apparatus using time-of-flight (TOF) mass spectrometry. The X-ray crystal structure data were collected at room temperature on a Bruker APEX II area detector diffractometer equipped with a graphite-monochromator, using MoKα radiation (λ= 0.71073 Å) and ψ-ω scans. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.

Reagents and Materials. For thin layer chromatography (TLC), silica gel plates (XinNuo GF254) were used. Flash column chromatography was carried out using 300-400 mesh silica gel at increased pressure. All the solvents were commercial available without further purification. Bis[(pentamethylcyclopentadienyl) dichloro-rhodium] was purchased from Titan (Shanghai, China). Sliver bis(trifluoromethane sulfonimide), Methoxylamine hydrochloride and alkyne were purchased from Energy Chemical (Shanghai, China). Acetic anhydride was purchased from Xilong (Guangdong, China). Ketone and cinnamaldehyde was purchased from Innochem (Beijing China). *n*-Butyl lithium was purchased from Energy Chemical (Shanghai, China).

(b) Typical Experimental produce

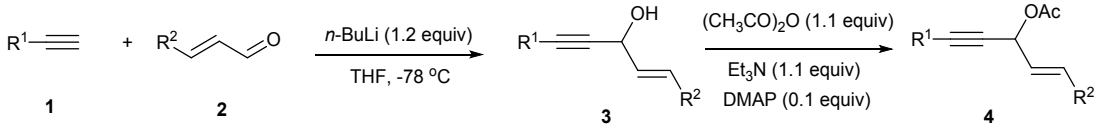
(1) Oximes were prepared following the published procedure [1].



To a 50mL round bottom flask equipped with a stir bar was added ketone (1.7 mmol, 1 equiv.), $MeONH_2$•HCl (380 mg, 4.6 mmol, 2.7 equiv.), NaOAc (610 mg, 7.5 mmol, 4.4 equiv.), H_2O (15 mL), and EtOH (5 mL). The flask was equipped with a reflux condenser and heated at 70 °C for 8 h. After cooling to room temperature, the mixture was extracted with EtOAc (3 x 15 mL). The organic layers were combined,

dried with Na_2SO_4, and concentrated. The purification was performed by flash column chromatography on silica gel to afford desired pure oximes.

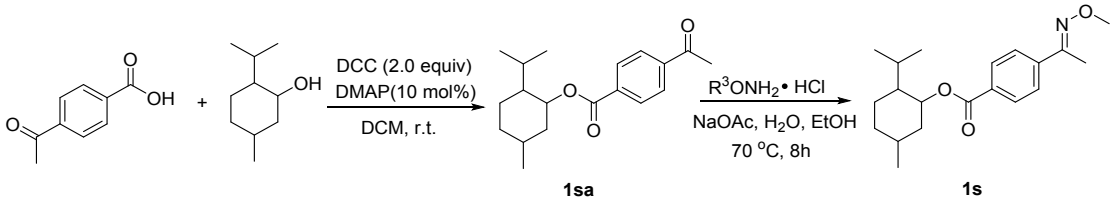
(2) All the 3-acetoxy-1,4-enynes were synthesized according to the known methods[2].



To a stirred solution of commercially available Alkyne **1** (5 mmol) in anhydrous THF (50 mL) was added *n*-BuLi (1.6 M in Hexane, 3.7 mL, 6 mmol) at -78 °C. The reaction mixture was stirred for 30 min at -78 °C and then commercially available Cinnamaldehyde **2** (5 mmol) in THF (5 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 40 min. Then the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl ether (2 x 40mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude materials were purified by flash column chromatography to obtain the products.

To a stirred solution of 1,4-enynes **3** in 20 mL DCM was slowly added Et_3N (1.1 equiv.), DMAP (0.1 equiv.) and acetic anhydride (1.1 equiv.) at room temperature, when the reaction was finished, 5 ml water was added. The organic layer was extracted with DCM (2 x 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel.

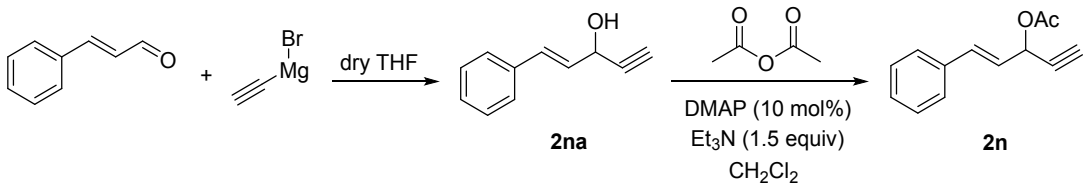
(3) General procedure for the synthesis of the starting compounds **1s**.[3]



A round-bottom flask was charged with 4-Acetylbenzoic acid (1.0 equiv.), N, N'-Dicyclohexylcarbodiimide (2.0 equiv.) and 4-dimethylaminopyridine (0.1 equiv.), Dichloromethane (20 mL) was added and the mixture was stirred vigorously in ice bath. Then DL-Menthol 1.7 g (1.1 equiv.) was slowly added and the mixture was allowed to stir until the acid was consumed (determined by TLC). The combined

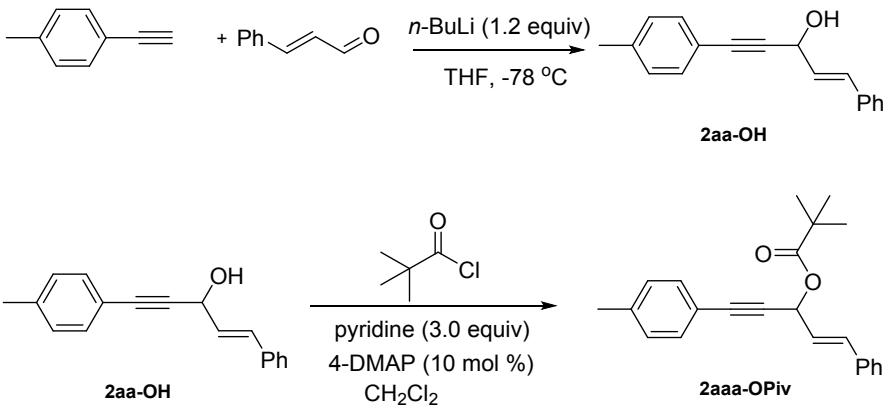
organic layers were washed with brine and ethyl acetate, the solvent was removed in vacuo and the crude product **1sa** purified by chromatography on silica gel. Then **1sa** was followed the previous procedure for the final product **1s.**

(4) General procedure for the synthesis of the starting compounds **2n**.[4]



Starting aldehyde was dissolved in tetrahydrofuran under argon to make a 2 M solution and cooled to 0 °C. Ethynylmagnesium bromide (0.5 M in tetrahydrofuran, 1.1 molar equivalents) was added, turning the solution orange from colourless. After completion of the addition the reaction mixture was warmed to room temperature. After 3 hours the reaction mixture was quenched with saturated ammonium chloride solution and extracted with ethyl acetate. The combined organic extracts were dried with magnesium sulfate, filtered and concentrated in vacuo to provide the crude product **2na**. Then add DMAP (10 mol %), triethylamine (1.5 equiv.), Ac_2O (1.5 equiv.) to a solution of **2na** (1.0 equiv.) in 15 mL CH_2Cl_2 at 0 °C. Stir the reaction mixture for 2 hours. After addition of an appropriate volume of aqueous water, extract the reaction with CH_2Cl_2 and wash the combined organic layer twice with saturated brine. Purify the crude product by flash chromatography on silica gel.

(5) General procedure for the synthesis of the starting compounds **2aaa**.

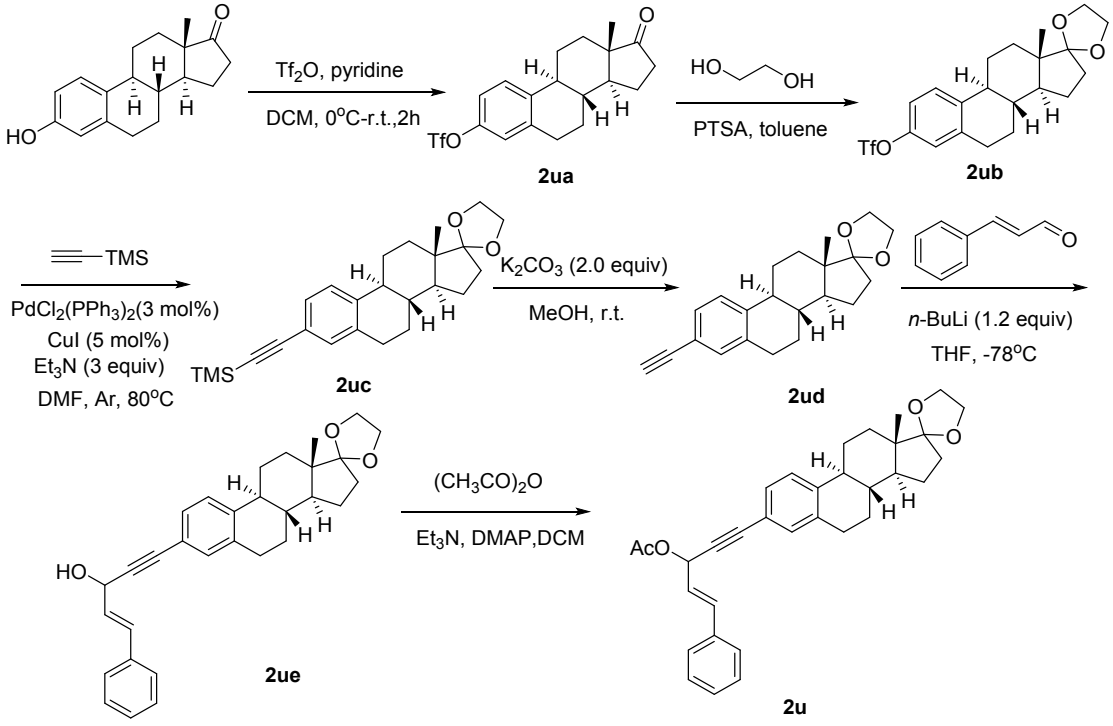


To a stirred solution of commercially available Alkyne (5 mmol) in anhydrous THF (30 mL) was added *n*-BuLi (1.6 M in Hexane, 3.7 mL, 6 mmol) at -78 °C. The

reaction mixture was stirred for 30 min at -78 °C and then commercially available Cinnamic aldehyde (5 mmol) in THF (5 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 40 min. Then the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl ether (2 x 40mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude materials were purified by flash column chromatography to obtain the products.

To a stirred solution of **2aa-OH** in 20 mL DCM was slowly added pyridine (3.0 equiv.) 4-DMAP (0.1 equiv.) and Pivaloyl chloride (1.1 equiv.) at 0 °C, when the reaction was finished, 5 ml water was added. The organic layer was extracted with DCM (2 x 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel.

(6) General procedure for the synthesis of the starting compounds **2u**.[2c][5]



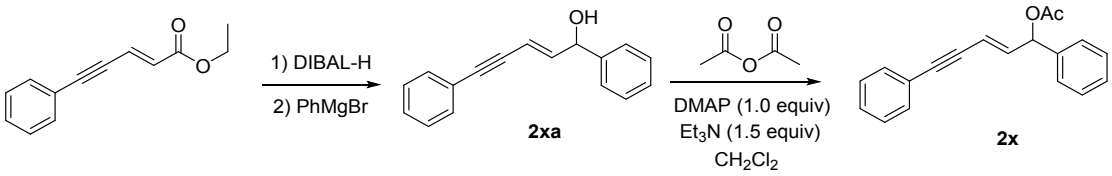
To a round bottom flask equipped with a magnetic stir bar was added estrone (2.7 g, 10 mmol), Et_3N (2.60 mL, 18.5 mmol) and CH_2Cl_2 (46 mL) at 0 °C.

Trifluoromethanesulfonic anhydride (1.71 mL, 10.2 mmol) was added dropwise. The reaction mixture was stirred at 0°C for 60 min, and quenched with saturated aqueous $NaHCO_3$ (50 mL). The organic layer was separated, and the aqueous phase was extracted with CH_2Cl_2. The combined organic layers were washed with brine (50 mL), dried over Na_2SO_4, and the volatiles were removed in vacuo. The residue was then purified by flash column chromatography on silica gel.

In 100 mL round bottom flask with Dean-Stark trap was added **2ua** (9 mmol), *p*-Toluenesulfonic Acid (0.01 equiv.), ethylene glycol (6.0 equiv.) and toluene solvent. The reaction took place at 150 °C for 12 hours, the crude product **2ub** was obtained by vacuum distillation of the filtrate after 3 times of extraction with saturated sodium chloride aqueous solution and ethyl acetate.

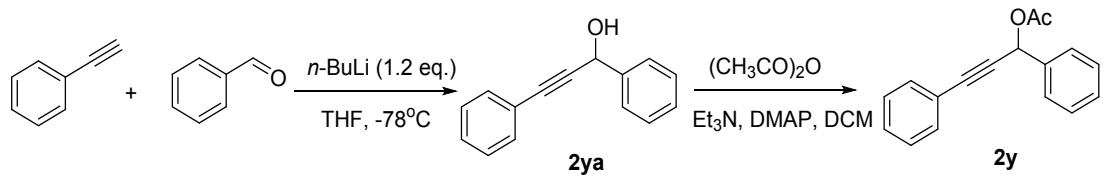
To a round bottom flask equipped with a magnetic stir bar was added the **2ub** (8 mmol), bis(triphenylphosphine) palladium(II) dichloride(10 mol%), and copper(I) iodide (10 mol%). The vessel was then sealed with a rubber septum, evacuated and backfilled with nitrogen. 40 mL DMF was added. After 5 min at room temperature, the ethynyltrimethylsilane (10 mmol) was added and the reaction mixture was stirred at 80 °C for 4 h under argon. Upon completion the mixture was concentrated, then diluted with CH_2Cl_2 and filtered through a plug of silica gel. The solvent was removed in vacuo and the residue dissolved in 40 mL MeOH and K_2CO_3 added (3 equivalents per silyl group). The reaction mixture was stirred at room temperature for 4 h. On completion the mixture was diluted with CH_2Cl_2, washed in turn with aqueous NaCl, and then dried over $MgSO_4$. The solvent was removed in vacuo and the crude product purified by chromatography on silica gel to give the estrone-containing alkyne **2ud**. Then the **2ud** followed the previous general procedure for the final product **2u.**

(7) General procedure for the synthesis of the starting compounds **2x**.[6]



To a solution of 5-phenyl-pent-2-en-4-ynoic acid ethyl ester (8.02 g, 40.0 mmol) in dry dichloromethane (200 mL) at -78 °C (internal temperature) was added dropwise of DIBAL-H (42 mL, 42 mmol, 1.0 M solution in toluene). The solution was stirred at -78 °C for 1.5 h, then quenched with 25 mL of 1 M HCl. The solution was diluted with 40 mL of ether and allowed to warm up to room temperature. The aqueous layer was extracted three times with ether. The combined organic layers were washed successively with 1M HCl, water, and saturated sodium chloride solution, and then dried over sodium sulfate. Purification by chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 10:1) afforded the crude aldehyde, which was used directly for the next step without further purification. To a solution containing above aldehyde in THF at 0 °C was added 2.0 equiv phenylmagnesium bromide (prepared from 2 equiv. of phenylbromide and magnesium turning). The mixture was stirred at room temperature until the reaction was complete as monitored by TLC. The reaction was quenched by saturated NH_4Cl solution and extracted with ether. The aqueous layer was extracted three times with ether. The combined organic layers were dried over Na2SO4. Purification by column chromatography on silica gel (eluent: petroleum ether : ethyl acetate = 7:1) afforded **2xa** as a yellow solid. Then the **2xa** followed the previous general procedure for the final product **2x**.

(8) General procedure for the synthesis of the starting compounds **2y**.[7]

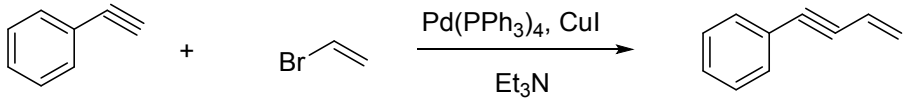


To a stirred solution of commercially available Alkyne (5 mmol) in anhydrous THF (30 mL) was added *n*-BuLi (1.6 M in Hexane, 3.7 mL, 6 mmol) at -78 °C. The reaction mixture was stirred for 30 min at -78 °C and then commercially available

Benzaldehyde (5 mmol) in THF (5 mL) was added dropwise. The reaction mixture was allowed to warm to room temperature and stirred for 40 min. Then the reaction was quenched with saturated NH_4Cl aqueous solution and extracted with ethyl ether (2 x 40mL). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The crude materials were purified by flash column chromatography to obtain the products **2ya**.

To a stirred solution of **2ya** in 20 mL DCM was slowly added Et_3N (1.1 equiv.) DMAP (0.1 equiv.) and acetic anhydride (1.1 equiv.) at 0 °C, when the reaction was finished, 5 ml water was added. The organic layer was extracted with DCM (2 x 20 mL). The combined organic phases were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation and purified by column chromatography on silica gel.

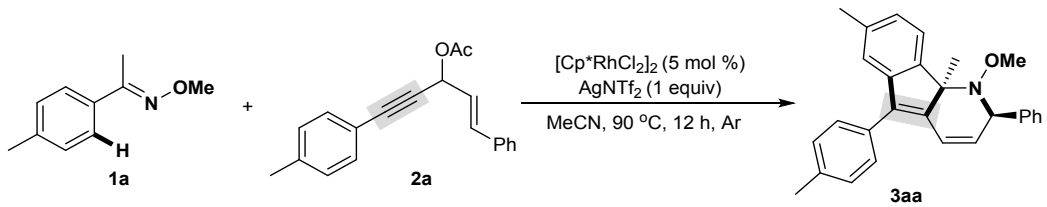
(9) General procedure for the synthesis of the starting compounds **2z**.[8]



2z

In an oven-dried flask, to a solution of ethynylbenzenes (10 mmol, 1 equiv.) in Et_3N (5 mL) were added CuI (0.5 mmol, 95.2 mg), $Pd(PPh_3)_4$ (0.3 mmol, 210 mg) and vinyl bromide (15 mmol, 1 M in THF, 15.0 mL) at 0 °C. After being stirred for 16 h at 25 °C, the mixture was then filtered through a pad of Celite with Et_2O (100 mL). The ether solution was washed with water (3×100 mL), dried over Na_2SO_4, concentrated in vacuo, and purified by column chromatography to give the product in almost quantitative yields.

(c) Typical Experimental Procedure for the Rh(III)-Catalyzed [3+2]/[2+4] Cycloaddition of Acetophenone Oxime Ethers (1) with 3-Acetoxy-1,4-enynes (2)



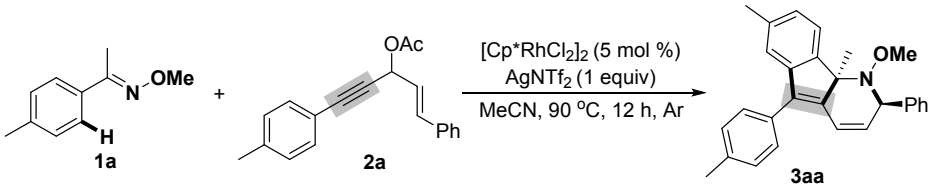
1a **2a** **3aa**

To a Schlenk tube was added (*E*)-1-(*p*-tolyl)ethan-1-one *O*-methyl oxime **1a** (0.1 mmol), *(E)*-1-phenyl-5-(*p*-tolyl)pent-1-en-4-yn-3-yl acetate **2a** (1.5 equiv.), $[Cp^*RhCl_2]_2$ (5 mol %), $AgNTf_2$ (1 equiv.) and MeCN (2 mL). Then the tube was charged with Argon, and was stirred at 90 ^oC (oil bath temperature) for the indicated time (about 12 h) until complete consumption of starting material as monitored by TLC. After the reaction was finished, the reaction mixture was cooled to room temperature, and the resulting residue was purified by silica gel column chromatography (petroleum ether/EtOAc = 100 : 1) to afford the desired product **3aa**.

(d) Table S1. Screening of Optimal Reaction Conditions

When oxime **1a** was treated with 1,4-enyne **2a**, 5 mol % $[Cp^*RhCl_2]_2$ and 1 equiv $AgNTf_2$ in MeCN at 90 ^oC for 12 h, the desired *trans*-2,9*b*-dihydro-1*H*-indeno [1,2-*b*]pyridine **3aa** was efficiently furnished in 70% yield with excellent selectivity (entry 1; Table S1). Both rhodium catalysts and silver salts were crucial for the reaction since negligence of each led to no reaction (entry 2). While a lower loading (2 mol%) of $[Cp^*RhCl_2]_2$ decreased the yield of **3aa** to 37% yield (entry 3), a higher loading (10 mol %) of $[Cp^*RhCl_2]_2$ delivered the same results to those at 5 mol % of $[Cp^*RhCl_2]_2$ (entry 4 versus entry 1). Using $[Cp^*Rh(MeCN)_3](SbF_6)_2$ afforded **3aa** in 50% yield (entry 5), but $RhCl_3$ was inert (entry 6). Testing both the loadings of $AgNTf_2$ and types of silver salts (e.g., $AgNTf_2$, AgOAc, $AgSbF_6$, AgO_2CCF_3) showed 1 equiv of $AgNTf_2$ as the best choice (entries 1 and 7-10). However, no reaction was observed when using $Cu(OAc)_2$ basic oxidant or other bases (e.g., K_2CO_3, NaOAc) to replace $AgNTf_2$ (entry 11). The reaction was sensitive to solvents: other solvents, including DMF, dioxane and $ClCH_2CH_2Cl$, exhibited lower reactivity (entry 12). Brief screening of temperatures indicated that the reaction at 90 ^oC gave the optimal results (entries 13-14). Notably, performing the reaction on 1 mmol scale of **1a** afforded **3aa** in good yield (entry 15).

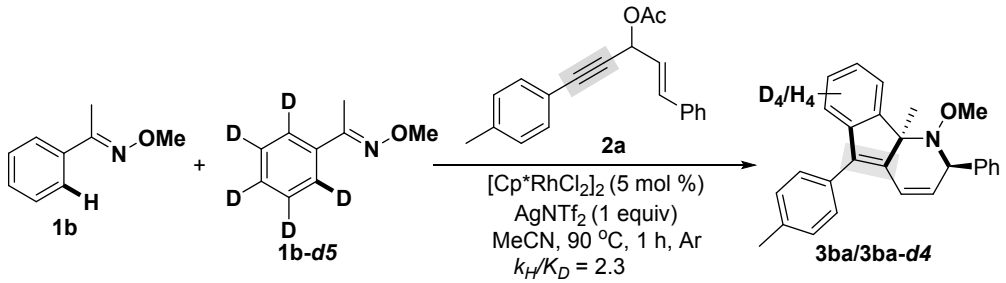
Table S1. Optimization of Reaction Conditions[a]



Entry	Variation from the standard conditions	Yield (%)
1	None	70
2	without $[Cp^*RhCl_2]_2$ or $AgNTf_2$	Trace
3	$[Cp^*RhCl_2]_2$ (2 mol%)	37
4	$[Cp^*RhCl_2]_2$ (10 mol%)	69
5	$[Cp^*Rh(MeCN)_3](SbF_6)_2$ instead of $[Cp^*RhCl_2]_2$	50
6	$RhCl_3$ instead of $[Cp^*RhCl_2]_2$	Trace
7	$AgNTf_2$ (0.5 equiv)	53
8	$AgNTf_2$ (1.5 equiv)	58
9	AgOAc instead of $AgNTf_2$	35
10	$AgSbF_6$ or AgO_2CCF_3 instead of $AgNTf_2$	49
11	$Cu(OAc)_2$, K_2CO_3 or NaOAc instead of $AgNTf_2$	0
12	DMF, dioxane or $ClCH_2CH_2Cl$ instead of MeCN	<5
13	at 80 °C	45
14	at 100 °C	62
15[b]	None	67

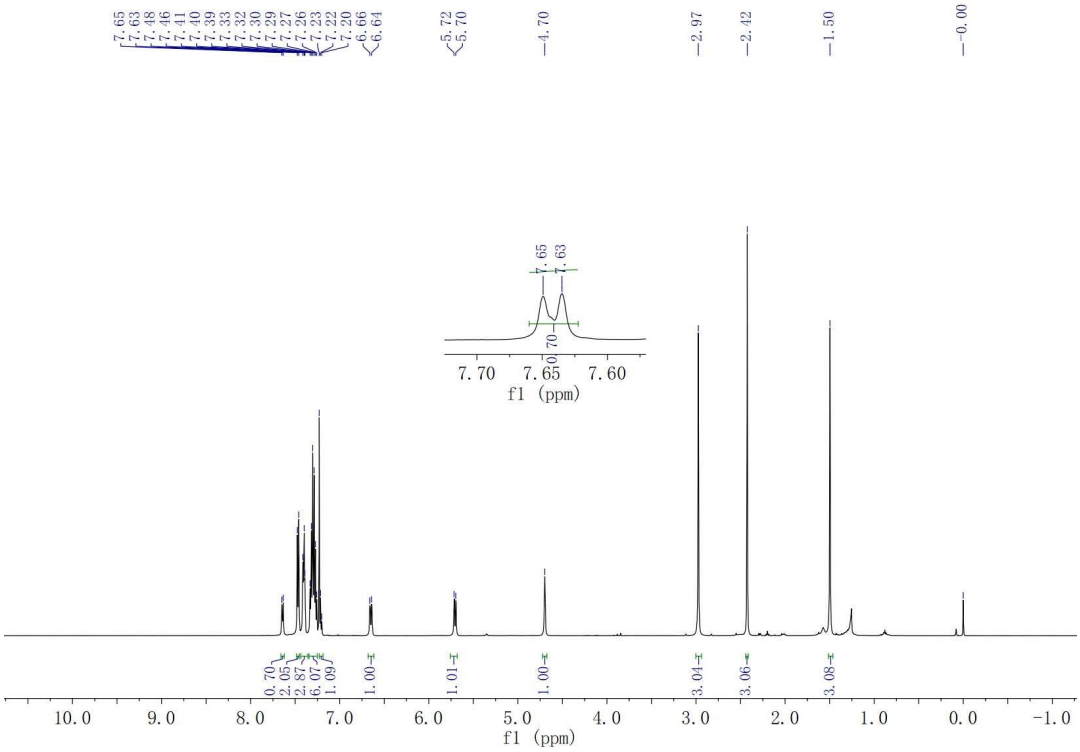
[a] Standard reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), $[Cp^*RhCl_2]_2$ (5 mol %), $AgNTf_2$ (1 equiv), MeCN (2 mL), argon, 90 °C and 12 h. Only *trans*-diastereoisomer (dr > 20:1) was obtained, which is determined by ^1H NMR or and GC-MS analysis of the crude product. [b] **1a** (1 mmol) for 20 h.

(e) Kinetic Isotopic Experiment

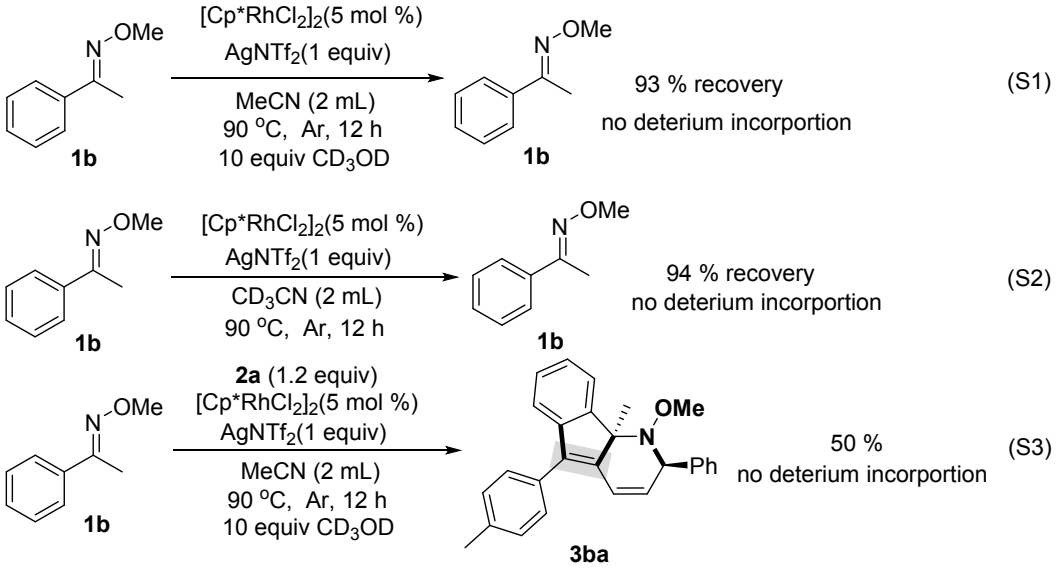


A sealed tube containing **1a** (30.1 mg, 0.2 mmol), **1a-*d5*** (29.9 mg, 0.2 mmol), **2a** (58.2 mg, 0.24 mmol), $[Cp^*RhCl_2]_2$ (5.3 mg, 5 mol %) and $AgNTF_2$ (76.3 mg, 1 equiv) was evacuated and purged with argon gas three times. Then MeCN (2 mL) was added via syringe under argon atmosphere and the reaction mixture was allowed to stir at 90 °C for 1 h. Then, the mixture was cooled, ethyl acetate (15 mL) was added,

and the solvents were removed in vacuo. Purification of the remaining residue by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired pure product. The ratio of **3aa** and **3aa-*d4*** was determined by ^{1}H NMR spectroscopy. The kinetic isotopic effect of this reaction was 2.3 (k_H/k_D).



(f) Deuterium Labelling Studies & Irreversibility of alkyne insertion



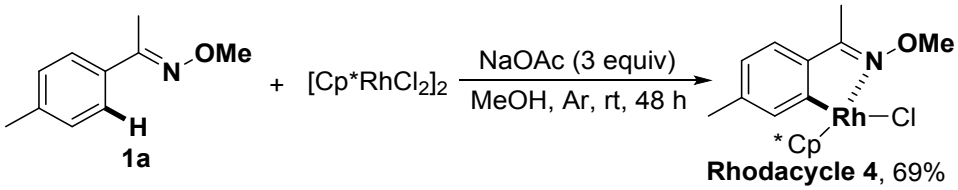
(Eq S1): A sealed tube containing **1b** (30.1 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (5.3 mg, 5 mol %), CD_3OD (10 equiv.) and $AgNTF_2$ (76.3 mg, 1 equiv.) was evacuated and purged with argon gas three times. Then MeCN (2 mL) was added via syringe under argon atmosphere and the reaction mixture was allowed to stir at 90 °C for 12 h. After the reaction was finished, the mixture was cooled, ethyl acetate (15 mL) was added, and the solvents were removed in vacuo. Purification of the remaining residue by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired pure product, no deuterium product was observed.

(Eq S2): A sealed tube containing **1b** (29.7 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (5.3 mg, 5 mol %) and $AgNTF_2$ (76.3 mg, 1 equiv.) was evacuated and purged with argon gas three times. Then CD_3CN (2 mL) was added via syringe under argon atmosphere and the reaction mixture was allowed to stir at 90 °C for 12 h. After the reaction was finished, the mixture was cooled, ethyl acetate (15 mL) was added, and the solvents were removed in vacuo. Purification of the remaining residue by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired pure product, no deuterium product was observed.

(Eq S3): A sealed tube containing **1b** (30.0 mg, 0.2 mmol), **2a** (72.7 mg, 0.3 mmol), $[Cp^*RhCl_2]_2$ (5.3 mg, 5 mol %), CD_3OD (34 mg, 10 equiv.) and $AgNTF_2$ (76.3 mg, 1 equiv.) was evacuated and purged with argon gas three times. Then MeCN (2 mL) was added via syringe under argon atmosphere and the reaction

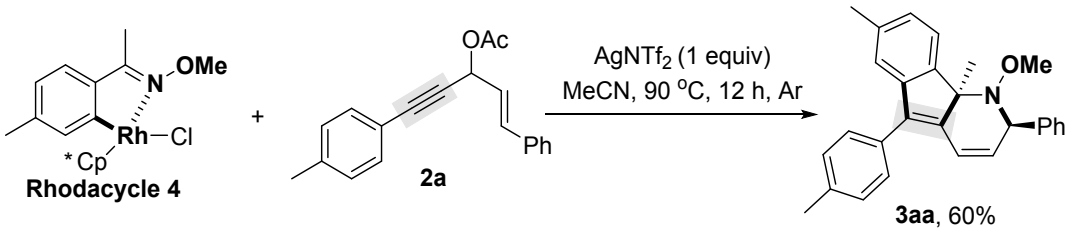
mixture was allowed to stir at 90 °C for 12 h. After the reaction was finished, the mixture was cooled, ethyl acetate (15 mL) was added, and the solvents were removed in vacuo. Purification of the remaining residue by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired pure product, no deuterium product was observed.

(g) Synthesis of Rhodacycle 4 and its Applications



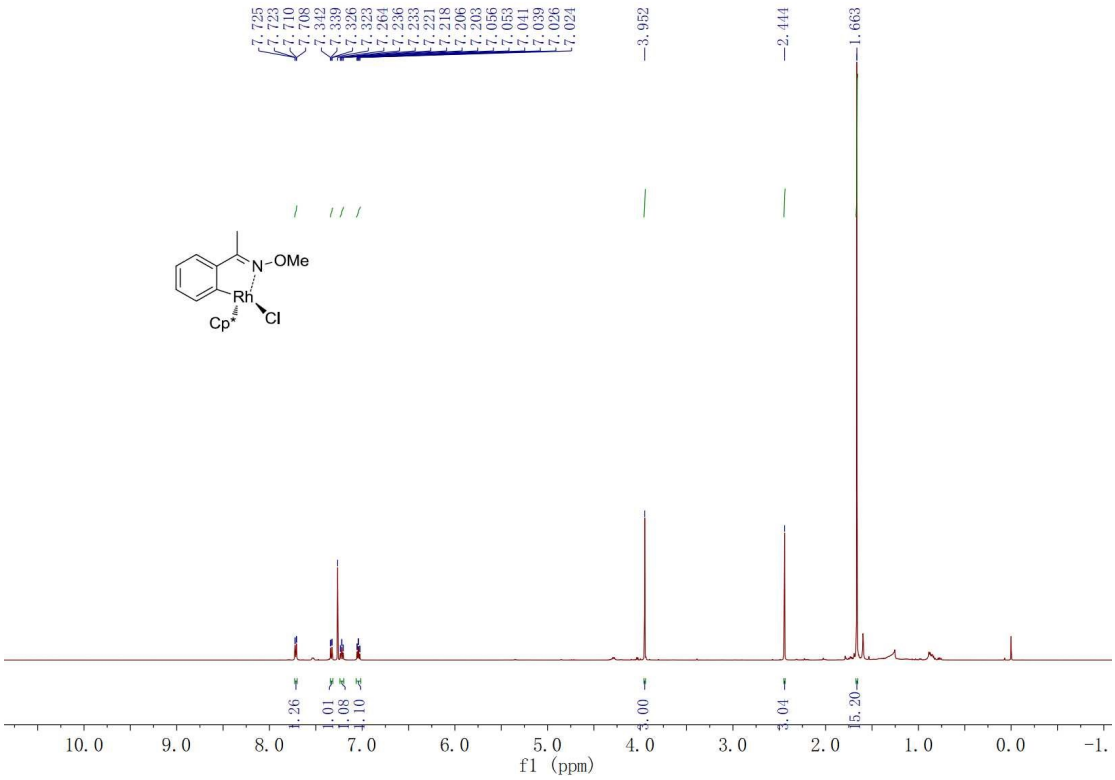
The Rhodium Complex was prepared according to the following literature procedures.[1a]

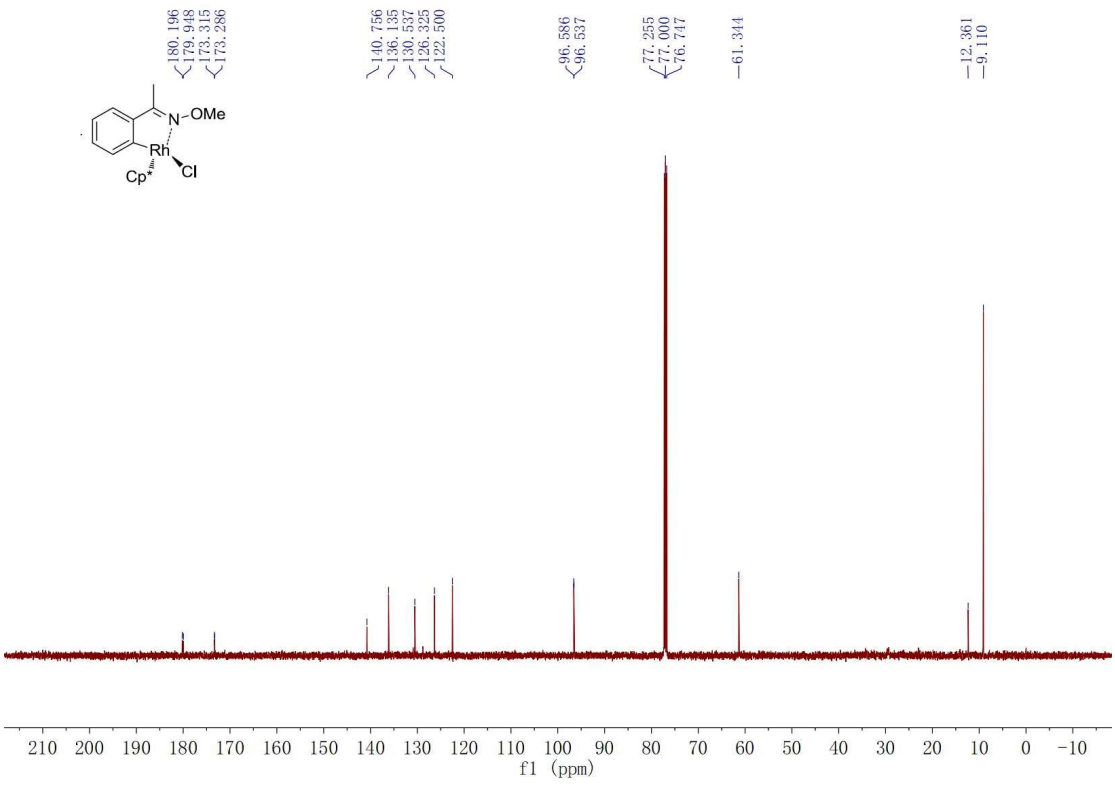
To a sealed tube equipped with a magnetic stir bar, the mixture of catalyst $[Cp^*RhCl_2]_2$ (91.3 mg, 0.15 mmol), NaOAc (36.9 mg, 3 equiv.) and MeOH (6.0 mL) was added under argon atmosphere. After stirred for 3 h at room temperature, compound **1b** (47.2 mg, 0.32 mmol) and NaOAc (36.9 mg, 3 equiv.) was added in one portion, then stirred for an additional 48 h at room temperature. After the reaction was finished, the solvent was removed under reduced pressure to afford the rhodacycle complex **4** by using column chromatography (eluent: CH_2Cl_2) in 69% yield (57.7 mg).



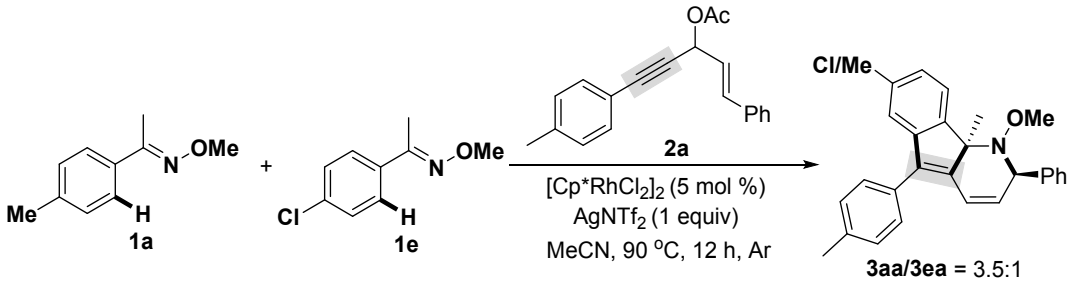
The mixture of rhodacycle complex **4** (0.1 mmol, 1 equiv.), 1-phenyl-5-(p-tolyl)pent-1-en-4-yn-3-yl acetate **2a** (0.12 mmol, 1.5 equiv.), $AgNTf_2$ (0.2 mmol, 1.0 equiv.) and MeCN (2.0 mL) was stirred at 90 °C for 12 h. The solvent was then removed under reduce pressure, and the residue was purified by silica gel column directly to give the corresponding product **3aa** (23.6 mg, 60%).

The spectra of the rhodacycle complex **4** are consistent with that reported in the literature.[1a]





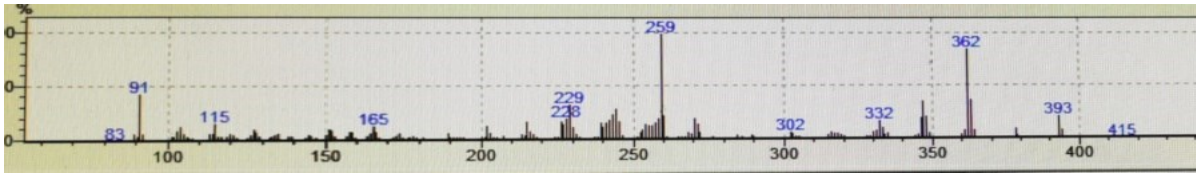
(h) Intermolecular Competition Experiments of *O*-Methyl Oximes.



A sealed tube containing **1a** (30.1 mg, 0.2 mmol), **1e** (29.9 mg, 0.20 mmol), **2a** (72.7 mg, 0.3 mmol), $[Cp^*RhCl_2]_2$ (5.3 mg, 5 mol %) and $AgNTF_2$ (76.3 mg, 1.0 eq) was evacuated and purged with argon gas three times. Then MeCN (2.0 mL) was added via syringe under argon atmosphere and the reaction mixture was allowed to stir at 90 °C for 12 h. After 12 hours, the mixture was cooled, ethyl acetate (15 mL) was added, and the solvents were removed in vacuo. Purification of the remaining residue by silica gel column chromatography using hexane/ethyl acetate as eluent to afford the desired pure products (**3aa** = 25.9 mg, **3ea** = 7.8 mg, **3aa/3ea** = 3.5:1).

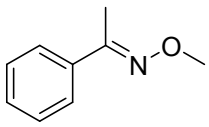
(g) The mass spectrum of 3ia.

3ia was determined by GC-MS:



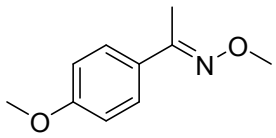
(B) Analytical data

(*E*)-1-phenylethan-1-one O-methyl oxime (1b)



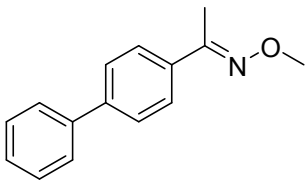
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62-7.60 (m, 2H), 7.29 (d, *J* = 5.5 Hz, 3H), 3.96 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 136.4, 128.8, 128.1, 125.8, 61.6, 12.2; LRMS (EI, 70 eV) *m/z* (%): 149 (M^+, 100), 121 (3), 104 (9).

(*E*)-1-(4-methoxyphenyl)ethan-1-one O-methyl oxime (**1c**)



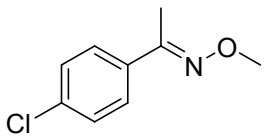
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74-7.49 (m, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.97 (d, *J* = 2.0 Hz, 3H), 3.80 (s, 3H), 2.19 (s, 3H);^{13}C NMR (125 MHz, $CDCl_3$) δ 160.3, 154.0, 129.1, 127.3, 113.7, 61.7, 55.2, 12.4; LRMS (EI, 70 eV) *m/z* (%): 179 (M^+, 100), 148 (94), 133 (18), 107 (27).

(*E*)-1-([1,1'-biphenyl]-4-yl) ethan-1-one O-methyl oxime (1d)



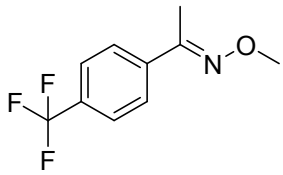
white solid; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.62 - 7.54 (m, 4H), 7.43 (t, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 1H), 4.01 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 141.7, 140.5, 135.5, 128.8, 127.5, 127.0, 127.0, 126.4, 61.9, 12.5; LRMS (EI, 70 eV) *m/z* (%): 225 (M^+, 100), 194 (63), 152 (58), 97 (12).

(*E*)-1-(4-chlorophenyl)ethan-1-one O-methyl oxime (1e)



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 3.95 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.8, 134.8, 134.7, 128.3, 127.0, 61.7, 11.9; LRMS (EI, 70 eV) *m/z* (%): 183 (M^+, 100), 152 (84), 137 (11), 111 (83).

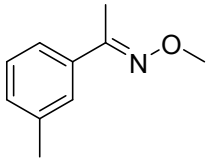
(*E*)-1-(4-(trifluoromethyl)phenyl)ethan-1-one O-methyl oxime (1f)



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 4.00 (s, 3H), 2.19 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.0, 140.0, 130.7(q, *J*=32.4), 126.2, 125.2, 125.2, 62.0, 12.0; ^{19}F NMR (471

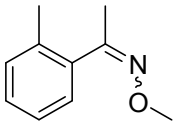
MHz, $CDCl_3$) δ -62.9; LRMS (EI, 70 eV) *m/z* (%): 217 (M^+, 94), 186 (75), 145 (100), 125 (11).

(*E*)-1-(m-tolyl)ethan-1-one O-methyl oxime (1g)



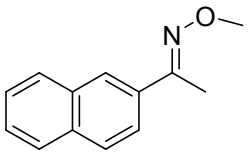
Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 7.5 Hz, 1H), 3.95 (s, 3H), 2.30 (s, 3H), 2.15 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.2, 137.6, 136.3, 129.5, 128.0, 126.3, 123.0, 61.5, 21.1, 12.2; LRMS (EI, 70 eV) *m/z* (%): 163 (M^+, 71), 132 (43), 107 (12), 91(100).

1-(O-tolyl)ethan-1-one O-methyl oxime (1i)



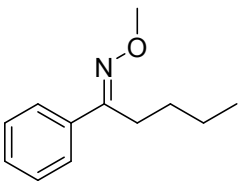
E/Z = 7.6, Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.17-7.12 (m, 4H), 3.92 (s, 2.65H), 3.75 (s, 0.35H), 2.31 (s, 2.65H), 2.19 (s, 0.35H), 2.11 (s, 2.65H), 2.07 (s, 0.35H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 137.1, 135.3, 134.0, 130.3, 129.5, 128.0, 127.9, 125.5,125.3, 61.2, 61.1, 21.5, 19.7, 19.0, 15.8; LRMS (EI, 70 eV) *m/z* (%): 163 (M^+, 79), 148 (38), 117 (100), 91(80).

(*E*)-1-(Naphthalen-2-yl)ethan-1-one *O*-methyl oxime (1j):



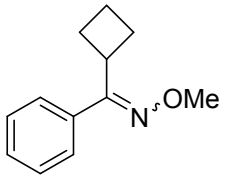
white solid; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.00 (s, 1H), 7.91 (d, *J* = 8.5 Hz, 1H), 7.84-7.86 (m, 1H), 7.79-7.82 (m, 2H), 7.46-7.48 (m, 2H), 4.04 (s, 3H), 2.33 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 154.4, 133.9, 133.6, 133.1, 128.4, 128.0, 127.6, 126.5, 126.2, 125.7, 123.4, 62.0, 12.4; LRMS (EI, 70 eV) m/z (%): 199 (M^+, 68), 168 (53), 158 (14), 153 (18), 127 (100).

(*E*)-1-Phenylpentan-1-one *O*-methyl oxime (1k):



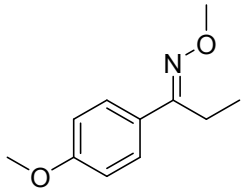
Colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.61-7.63 (m, 2H), 7.35-7.37 (m, 3H), 3.97 (s, 3H), 2.72-2.75 (m, 2H), 1.47-1.53 (m, 2H), 1.35-1.40 (m, 2H), 0.89-0.93 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 158.8, 135.9, 128.9, 128.4, 126.3, 61.8, 28.7, 26.4, 22.9, 13.8; LRMS (EI, 70 eV) m/z (%): 191 (M^+, 15), 149 (78), 119 (56), 104 (100), 91 (23).

Cyclobutyl(phenyl)methanone *O*-methyl oxime (1l):



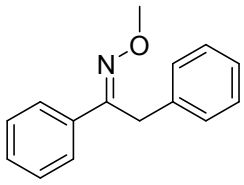
E/Z = 1.3, Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.28-7.38 (m, 5H), 3.91 (s, 1.3H), 3.83 (s, 1.7H), 3.78-3.79 (m, 0.5H), 3.66-3.42 (m, 0.5H), 2.18-2.32 (m, 2H), 2.03-2.13 (m, 2H), 1.88-1.98 (m, 1H), 1.67-1.80 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 162.6, 159.6, 135.5, 133.9, 128.4, 128.4, 128.2, 128.1, 127.7, 127.6, 61.9, 61.7, 39.9, 35.7, 28.4, 26.5, 19.6, 18.3; LRMS (EI, 70 eV) m/z (%): 189 (M^+, 38), 161 (20), 143 (37), 130 (100), 115 (15).

(*E*)-1-(4-methoxyphenyl)propan-1-one *O*-methyl oxime (1m):



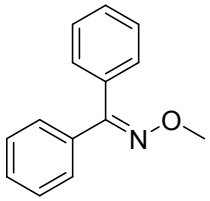
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.57 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.5 Hz, 2H), 3.95 (s, 3H), 3.76 (s, 3H), 2.68-2.73 (m, 2H), 1.09-1.13 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 160.4, 159.1, 128.1, 127.5, 113.8, 61.7, 55.2, 19.9, 11.3; LRMS (EI, 70 eV) m/z (%): 193 (M^+, 100), 163 (11), 162 (95), 147 (17), 134 (44).

(*E*)-1,2-diphenylethan-1-one *O*-methyl oxime (1n):



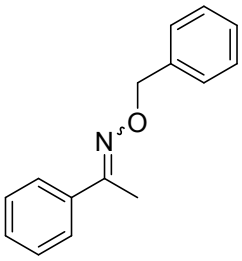
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.61-7.64 (m, 2H), 7.28-7.29 (m, 3H), 7.19-7.25 (m, 4H), 7.14-7.17 (m, 1H), 4.13 (m, 2H), 4.01 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 156.0, 136.6, 135.6, 129.0, 128.5, 128.4, 128.4, 126.4, 126.2, 62.0, 32.6; LRMS (EI, 70 eV) m/z (%): 225 (M^+, 11), 224 (16), 195 (8), 91 (100).

Diphenylmethanone O-methyl oxime (1o)



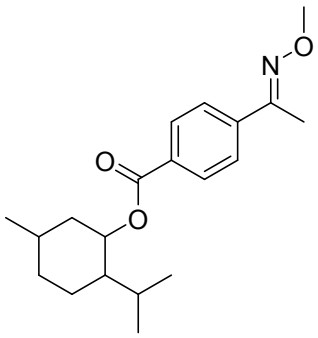
Colorless oil; ^{1}H NMR (500 MHz, CDCl3) δ 7.48 (d, J = 7.0 Hz, 2H), 7.45-7.37 (m, 3H), 7.37-7.23 (m, 5H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 136.4, 133.3, 129.2, 129.1, 128.8, 128.2, 128.1, 127.8, 62.4; LRMS (EI, 70 eV) *m/z* (%): 211 (M^+, 96), 180 (100), 165 (19), 108 (13).

1-Phenylethan-1-one *O*-benzyl oxime (1r):



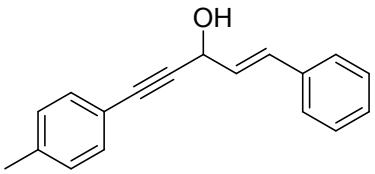
E/Z = 1.8; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.59-7.63 (m, 2H), 7.37-7.40 (m, 2H), 5.23 (s, 1.3H), 5.21 (s, 0.7H), 2.22 (s, 1.9H), 2.20 (s, 1.1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 154.8, 138.0, 138.0, 136.5, 136.5, 128.9, 128.9, 128.2, 128.2, 128.0, 128.0, 127.6, 127.6, 126.0, 125.9, 76.1, 12.7; LRMS (EI, 70 eV) m/z (%): 225 (M^+, 15), 193 (100), 165 (19), 119 (30).

2-Isopropyl-5-methylcyclohexyl (*E*)-4-(1-(methoxyimino)ethyl)benzoate (1s):



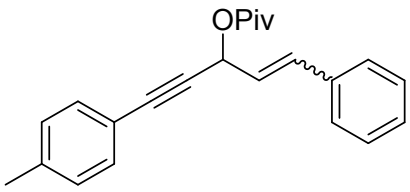
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.02 (d, *J* = 8.5 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 4.90-4.95 (m, 1H), 3.99 (s ,3H), 2.20 (s, 3H), 2.09-2.13 (m, 1H), 1.92-1.96 (m, H), 1.68-1.71 (m, 2H), 1.51-1.56 (m, 2H), 1.05-1.15 (m, 2H), 0.90 (t, *J* = 6.0 Hz, 6H), 0.78 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 165.5, 140.4, 130.9, 129.4, 125.7, 74.7, 61.9, 47.1, 40.8, 34.2, 31.3, 26.4, 23.6, 21.9, 20.6, 16.5, 12.2, 12.2; LRMS (EI, 70 eV) m/z (%): 331 (M^+, 6), 194 (49), 175 (78), 138(100), 117 (48).

(*E*)-1-Phenyl-5-(p-tolyl)pent-1-en-4-yn-3-ol (2aa-OH):



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.34-7.48 (m, 4H), 7.21-7.28 (m, 3H), 7.06 (d, *J* = 7.5Hz, 2H), 6.75-6.79 (m, 1H), 6.33-6.37 (m, 1H), 5.25 (d, *J* = 5.5Hz, 1H), 2.94 (s, 1H), 2.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 138.5, 136.0, 131.7, 131.5, 128.9, 128.4, 128.1, 127.9, 126.7, 119.2, 87.3, 86.4, 63.2, 21.3; LRMS (EI, 70 eV) m/z (%): 248 (M^+, 65), 232 (32), 215 (100), 202 (50), 189 (21).

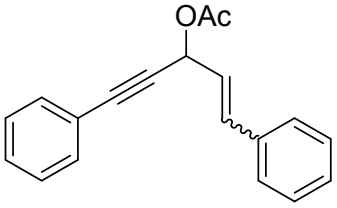
1-Phenyl-5-(p-tolyl)pent-1-en-4-yn-3-yl pivalate (2aaa-OPiv):



E/Z = 4.0; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.29-7.42 (m, 7H), 6.27-6.32(m, 2H), 5.92-5.95 (m, 1H), 2.34 (s, 0.6H), 2.33 (s, 2.4H), 1.25 (s, 1.8H), 1.23 (s, 7.2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 177.1, 140.2, 138.5, 138.5, 131.4, 129.1, 129.0, 128.6, 128.6,

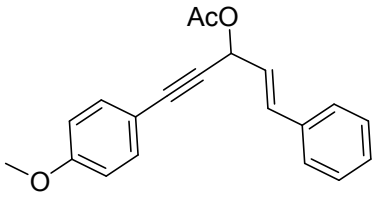
126.8, 124.3, 119.9, 112.0, 91.4, 86.3, 74.9, 38.9, 27.1, 21.4; LRMS (EI, 70 eV) m/z (%): 332 (M^+, 18), 275 (29), 248 (44), 215 (100).

1, 5-Diphenylpent-1-en-4-yn-3-yl acetate (2b):



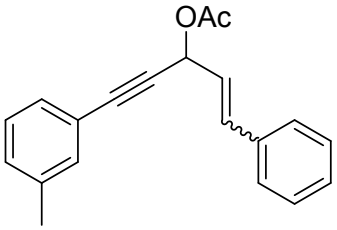
E/Z = 4.0; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.39-7.48 (m, 2H), 7.31-7.34 (m, 4H), 7.18-6.7.20 (m, 4H), 6.88-6.90 (m, 0.2H), 6.3-6.34 (m, 1.6H), 6.09-6.11 (m, 0.2H), 5.92-5.96 (m, 0.8H), 5.82-5.84 (m, 0.2H), 2.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.4, 140.1, 137.9, 131.4, 131.3, 128.5, 128.4, 128.2, 128.2, 128.2, 128.1, 127.9, 126.9, 126.3, 122.7, 112.1, 111.5, 96.0, 91.2, 86.7, 84.9, 75.0, 73.5, 20.8; LRMS (EI, 70 eV) m/z (%): 276 (M^+, 7), 233 (51), 215 (100), 201 (18), 115 (17).

(*E*)-5-(4-methoxyphenyl)-1-phenylpent-1-en-4-yn-3-yl acetate (2d):



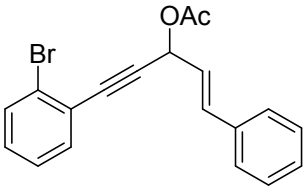
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.34-7.44 (m, 5H), 7.27-7.32 (m, 2H), 6.80-6.85 (m, 2H), 6.26-6.33 (m, 2H), 6.92-6.95 (m, 1H), 3.74 (m, 3H), 2.09 (s, 3H), 1.88-1.98 (m, 1H), 1.67-1.80 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.9, 159.8, 139.5, 138.3, 133.1, 128.7, 127.2, 126.6, 115.1, 114.1, 112.8, 91.6, 85.7, 75.5, 55.3, 21.2; LRMS (EI, 70 eV) m/z (%): 306 (M^+, 28), 263 (100), 245 (46), 215 (72).

1-phenyl-5-(m-tolyl)pent-1-en-4-yn-3-yl acetate (2h):



E/Z = 4.0; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.35-7.44 (m, 3H), 7.29-7.33 (m, 2H), 7.12-6.7.25 (m, 4H), 6.84-6.86 (m, 0.2H), 6.30-6.35 (m, 1.53H), 6.10-6.14 (m, 0.26H), 5.85-5.87 (m, 1H), 2.34 (s, 0.6H), 2.31 (s, 2.4H), 2.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.9, 140.1, 138.2, 138.0, 132.1, 129.5, 129.3, 128.7, 128.6, 128.5, 128.2, 128.1, 127.2, 126.6, 122.8, 112.5, 111.8, 91.6, 86.5, 75.4, 73.9, 21.3, 21.2; LRMS (EI, 70 eV) m/z (%): 290 (M^+, 9), 247 (70), 215 (100), 115 (28), 105 (33).

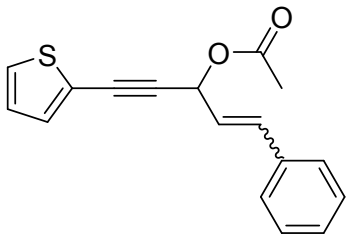
(*E*)-5-(2-bromophenyl)-1-phenylpent-1-en-4-yn-3-yl acetate (2i):



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.39-

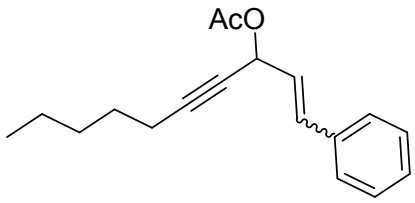
7.41 (m, 2H), 7.36-7.37 (m, 2H), 7.28-6.7.34 (m, 4H), 6.30-6.39 (m, 2H), 6.10-6.14 (m, 0.26H), 5.85-5.95 (m, 1H), 2.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.8, 140.2, 138.1, 131.5, 128.7, 128.4, 128.3, 128.3, 127.2, 122.9, 112.4, 91.3, 86.8, 75.3, 21.2; LRMS (EI, 70 eV) m/z (%): 354 (M^+, 4), 267 (6), 233 (51), 215 (100), 105 (33).

1-phenyl-5-(thiophen-2-yl)pent-1-en-4-yn-3-yl acetate (2j):



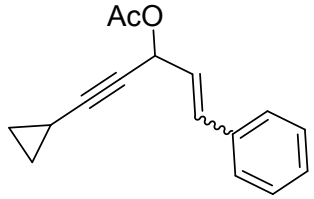
E/Z = 5.5; Red oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.29-7.37 (m, 5H), 7.24-7.28 (m, 2H), 7.17-7.20 (m, 1H), 6.95-7.00 (m, 1H), 6.30-6.35 (m, 1H), 5.92-5.97 (m, 0.85H), 5.85-5.89 (m, 0.15H), 2.23 (s, 0.46H), 2.18 (s, 2.56H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.8, 140.3, 138.1, 132.0, 128.7, 128.7, 128.7, 128.5, 127.5, 127.2, 127.1, 126.7, 123.0, 123.0, 112.0, 90.7, 84.6, 75.3, 21.2; LRMS (EI, 70 eV) m/z (%): 282 (M^+, 23), 240 (100), 221 (17), 211 (42), 178 (24).

1-Phenyldec-1-en-4-yn-3-yl acetate (2l):



E/Z = 5.6; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.3-7.4 (m, 5H), 6.56-6.75 (m, 0.15H), 5.96-6.28 (m, 1.85H), 5.62-5.8 (m, 1H), 2.36-2.39 (m, 0.3H), 2.26-2.29 (m, 1.7H), 2.09 (s, 3H), 1.47-1.56 (m, 2H), 1.28-1.39 (m, 4H), 0.89 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.8, 138.7, 138.4, 128.6, 128.3, 127.1, 113.2, 92.8, 77.9, 75.4, 31.0, 28.3, 22.2, 21.2, 19.3, 13.9; LRMS (EI, 70 eV) m/z (%): 270 (M^+, 6), 228 (49), 213 (23), 195 (15), 105 (100).

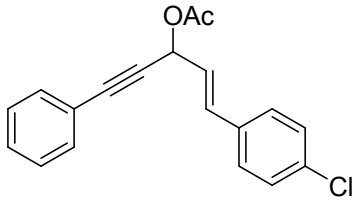
5-Cyclopropyl-1-phenylpent-1-en-4-yn-3-yl acetate (2m):



E/Z = 2.8; Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.28-7.39 (m, 5H), 7.28-7.29 (m, 3H), 6.63-6.70 (m, 0.26H), 5.97-6.25 (m, 1.74H), 5.60-5.69 (m, 1H), 2.09 (s, 0.8H), 2.08 (s, 2.2H), 1.29-1.36 (m, 1H), 0.76-0.96 (m, 2.5H); 0.67-0.70 (m, 1.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.7, 138.7, 138.3, 128.5, 128.4, 128.2, 126.9, 126.3, 112.9, 95.7, 75.3, 73.2, 21.0, 8.7, 8.4, 0.0;

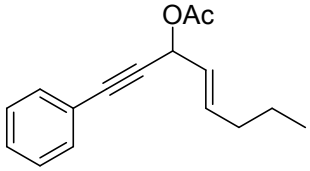
LRMS (EI, 70 eV) m/z (%): 240 (M^+, 5), 198 (48), 179 (68), 165 (91), 105 (100).

(*E*)-1-(4-Chlorophenyl)-5-phenylpent-1-en-4-yn-3-yl acetate (2q):



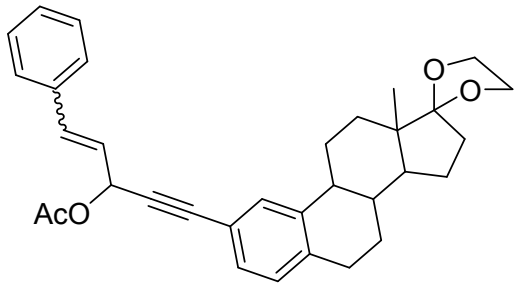
Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.48-7.50 (m, 2H), 7.32-7.34 (m, 4H), 7.27-7.30 (m, 3H), 6.83-6.88 (m, 1H), 6.25-6.30 (m, 2H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.6, 134.1, 133.1, 131.8, 131.4, 128.8, 128.7, 128.2, 128.0, 124.5, 121.8, 87.1, 84.3, 64.5, 21.0; LRMS (EI, 70 eV) m/z (%): 310 (M^+, 6), 267 (29), 215 (100), 139 (12), 105 (18).

(*E*)-1-Phenyloct-4-en-1-yn-3-yl acetate (2r):



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.45-7.48 (m, 2H), 7.28-7.34 (m, 3H), 6.03-6.13 (m, 2H), 5.60-5.64 (m, 1H), 2.06-2.11(m, 5H), 1.42-1.47 (m, 2H), 0.92 (t, *J* = 7.0Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.8, 136.6, 131.9, 128.7, 128.3, 125.1, 122.2, 86.4, 85.2, 64.9, 34.1, 21.9, 21.2, 13.7; LRMS (EI, 70 eV) m/z (%): 242 (M^+, 14), 227 (14), 199 (100), 171 (24), 157 (53).

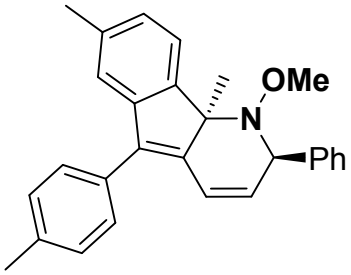
5-(13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-2-yl)-1-phenylpent-1-en-4-yn-3-yl acetate (2u):



E/Z = 5.2; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.42-7.44 (m, 0.4H), 7.36-7.37 (m, 3.5H), 7.28-6.7.33 (m, 1.2H), 7.25-7.26 (m, 0.4H), 7.21-7.23 (m, 0.8H), 7.16-7.18 (m, 0.7H), 7.13-7.16 (m, 1H), 6.83-6.85 (m, 0.2H), 6.28-6.34 (m, 1.6H), 6.08-6.12 (m, 0.2), 5.84-5.94 (m, 1H), 3.87-3.97 (m, 4H), 2.80-2.87 (m, 2H), 2.23-2.33 (m, 2H), 2.12 (s, 3H), 1.99-2.20 (m, 1H), 1.82-1.91 (m, 4H), 1.61-1.67 (m, 2H), 1.45-1.55 (m, 2H), 1.30-1.37 (m, 3H), 0.89 (s, 0.5H), 0.87 (s, 2.5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 169.8, 141.2, 139.7, 139.7, 139.2, 138.2, 136.9, 136.8, 132.0, 131.9, 128.8, 128.6, 128.6, 128.6, 128.4, 128.0, 127.1, 126.5, 125.4, 125.4, 119.9, 119.3, 119.3, 112.7, 91.7, 86.0, 75.3, 73.9, 65.2, 64.5, 49.4, 49.4, 46.0, 44.1, 38.6, 38.6, 34.2, 30.6, 30.6, 29.2, 29.2, 26.7, 26.7,

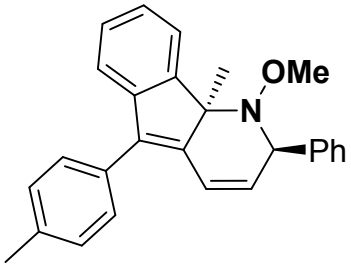
25.7, 22.3, 21.2, 14.3.

1-Methoxy-7,9*b*-dimethyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3aa):



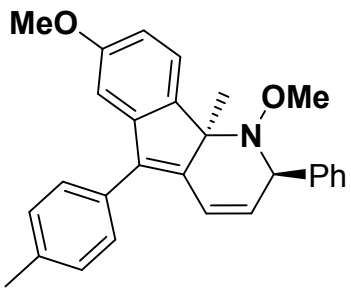
70%, 27.5 mg; Yellow solid; mp 120.7-121.5 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.52 (d, *J* = 7.5 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.34-7.26 (m, 5H), 7.20 (s, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.63-6.61 (d, *J* = 9.5 Hz, 1H), 5.69 (d, *J* = 9.0 Hz, 1H), 4.68 (s, 1H), 2.97 (s, 3H), 2.43 (s, 3H), 2.34 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 145.6, 144.4, 143.5, 142.0, 137.4, 137.4, 135.5, 132.2, 131.1, 129.5, 129.2, 129.0, 128.1, 127.5, 126.6, 124.3, 121.4, 120.1, 71.0, 67.9, 62.7, 21.6, 21.4, 15.4; LRMS (EI, 70 eV) *m/z* (%): 393 (M^+, 22), 378 (37), 362 (69), 347 (34), 259 (100); HRMS *m/z* (ESI) calcd for $C_{28}H_{27}NO$ ($[M+H]^+$) 394.2165, found 394.2169.

1-Methoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ba):



65%, 24.6 mg; Yellow solid; mp 113.3-113.8 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 7.5 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.31 (t, *J* = 6.5 Hz ,3H), 7.24-7.16 (m, 6H), 7.14-7.11 (m, 1H), 6.55 (d, *J* = 9.5 Hz, 1H), 5.61 (d, *J* = 9.5 Hz, 1H), 4.61 (s, 1H), 2.88 (s, 3H), 2.33 (s, 3H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.3, 144.1, 143.3, 141.9, 137.5, 135.5, 132.3, 131.0, 129.5, 129.2, 128.9, 128.1, 127.6, 127.6, 125.9, 124.6, 120.8, 120.1, 71.4, 67.9, 62.7, 21.3, 15.3; LRMS (EI, 70 eV) *m/z* (%): 379 (M^+, 22), 348 (62), 333 (33), 245 (100), 215 (39); HRMS *m/z* (ESI) calcd for $C_{27}H_{25}NO$ ($[M+H]^+$) 380.2009, found 380.2009.

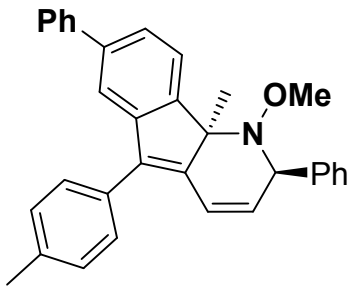
1,7-Dimethoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ca):



75%, 30.6 mg; Yellow solid; mp 117.4-118.3 °C

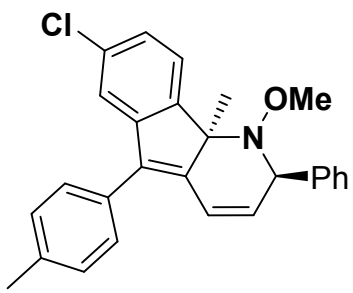
(uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.52 (d, *J* = 8.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.24-7.33 (m, 5H), 6.94-6.95 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.63 (d, *J* = 9.5 Hz, 1H), 5.70 (d, *J* = 9.5 Hz, 1H), 4.67 (s, 1H), 3.78 (s, 3H), 2.97 (s, 3H), 2.47 (s, 3H), 1.47 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 159.7, 145.3, 144.9, 141.9, 140.9, 137.5, 135.3, 132.5, 130.9, 129.6, 129.3, 128.9, 128.1, 127.6, 125.1, 120.1, 111.3, 106.6, 70.7, 67.9, 62.7, 55.4, 21.3, 15.4; LRMS (EI, 70 eV) m/z (%): 409 (M^+, 29), 394 (66), 378 (96), 275 (100), 91 (44); HRMS m/z (ESI) calcd for $C_{28}H_{27}NO_2$ ($[M+H]^+$) 410.2115, found 410.2112.

1-Methoxy-9*b*-methyl-2,7-diphenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3da):



82%, 37.3 mg; White solid; mp 140.8-141.4 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.70 (d, *J* = 7.5 Hz, 1H), 7.60 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.45-7.38 (m, 5H), 7.34-7.28 (m, 6H), 6.67-6.65 (m, 1H), 5.73-5.71 (m, 1H), 4.71 (s, 1H), 3.01 (s, 3H), 2.43 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 147.4, 144.7, 144.0, 141.9, 141.7, 141.1, 137.6, 135.4, 132.5, 131.0, 129.6, 129.3, 129.0, 128.6, 128.2, 127.6, 127.3, 127.1, 125.1, 124.8, 120.0, 119.6, 71.2, 67.9, 62.8, 21.4, 15.3; HRMS *m/z* (ESI) calcd for $C_{33}H_{29}NO$ ($[M+H]^+$) 456.2322, found 456.2327.

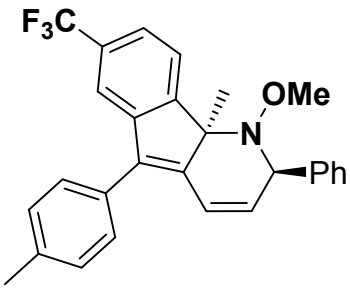
7-Chloro-1-methoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ea):



56%, 23.1 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.46 (d, *J* = 8.0 Hz, 1H), 7.36-7.34 (m, 2H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 2.0 Hz, 1H), 7.24-7.20 (m, 4H), 7.15 (s, 1H), 7.11-7.10 (m, 1H), 6.54 (d, *J*

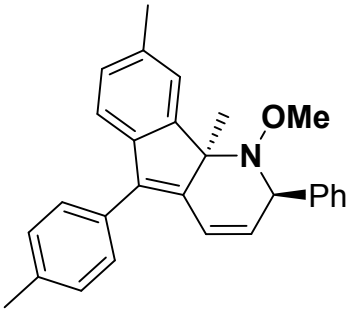
= 9.5 Hz, 1H), 5.66 (d, *J* = 10.0 Hz, 1H), 4.60 (s, 1H), 2.87 (s, 3H), 2.35 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 146.6, 145.5, 145.2, 141.6, 137.83, 134.6, 133.7, 133.2, 130.4, 129.5, 129.4, 128.8, 128.2, 127.7, 125.7, 125.5, 120.9, 119.9, 71.0, 67.8, 62.7, 21.3, 15.2; LRMS (EI, 70 eV) *m/z* (%): 415 (M^++2, 10), 413 (M^+, 29), 382 (68), 332 (36), 279 (100), 229 (47); HRMS *m/z* (ESI) calcd for $C_{27}H_{24}{}^{25}ClNO$ ($[M+H]^+$) 414.1619, found 414.1624.

1-Methoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-7-(trifluoromethyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3fa):



45%, 20.1 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.73 (d, *J* = 7.5 Hz, 1H), 7.61 (s, 1H), 7.49 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 7.0 Hz, 2H), 7.35- 7.28 (m, 5H), 6.67-6.64 (m, 1H), 5.78-5.76 (m, 1H), 4.71 (s, 1H), 2.95 (s, 3H), 2.45 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 151.6, 145.6 144.1, 143.4, 141.5, 138.0, 134.6, 133.4, 130.2 (q, *J* = 6.4 z, 1C), 130.0, 129.5, 128.8, 128.3, 127.8, 124.7, 123.4, 123.2 (q, *J* = 5.0 Hz, 1C), 122.8 (q, *J* = 3.2 Hz, 1C), 118.6 (q, *J* = 294.2, 1C), 71.3, 67.8, 62.7, 21.4, 15.1; ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm) -62.0; LRMS (EI, 70 eV) *m/z* (%): 447 (M^+, 28), 416 (53), 401 (27), 313 (100), 91(61); HRMS *m/z* (ESI) calcd for $C_{28}H_{24}F_3NO$ ($[M+H]^+$) 448.1883, found 448.1888.

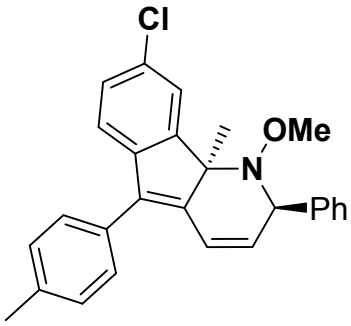
1-Methoxy-8,9*b*-dimethyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ga):



55%, 21.6 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.37 (m, 3H), 7.32 (d, *J* = 7.0 Hz, 2H), 7.25-7.19 (m, 6H), 7.00 (d, *J* = 7.5 Hz, 1H), 6.55 (d, *J* = 9.5 Hz, 1H), 5.58 (d, *J* = 9.5 Hz, 1H), 4.60 (s, 1H), 2.90 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H), 1.40 (s, 3H); ^{13}C NMR

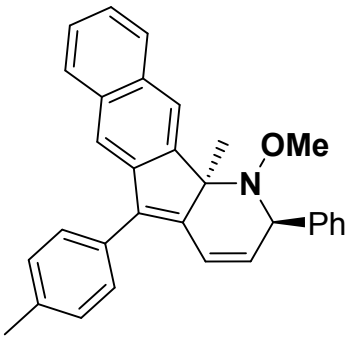
(125 MHz, $CDCl_3$) δ (ppm): 148.6, 143.2, 142.0, 140.7, 137.4, 135.7, 135.4, 131.8, 131.28, 129.6, 129.2, 128.9, 128.2 ,128.1, 127.5, 125.5, 120.5, 120.1, 71.2, 67.9, 62.6, 21.6, 21.3, 15.4; LRMS (EI, 70 eV) *m/z* (%): 393 (M^+, 19), 378 (22), 362 (71), 259 (100), 244 (31); HRMS *m/z* (ESI) calcd for $C_{28}H_{27}NO$ ($[M+H]^+$) 394.2165, found 394.2163.

8-Chloro-1-methoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ha):



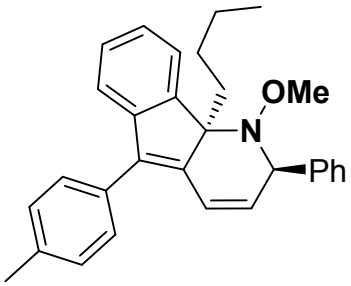
45%, 18.5 mg; Yellow oil; ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.59 (d, *J* = 1.0 Hz, 1H), 7.44-7.39 (m, 4H), 7.34-7.29 (m, 6H), 7.25-7.24 (m, 1H), 6.63 (d, *J* = 9.5 Hz, 1H), 5.72 (d, *J* = 9.5 Hz, 1H), 4.68 (s, 1H), 2.98 (s, 3H), 2.43 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 149.9, 144.4, 141.9, 141.6, 137.8, 134.7, 132.8, 131.8, 130.6, 129.5, 129.3, 128.8, 128.2, 127.7, 125.1, 121.6, 119.9, 71.4, 67.9, 62.7, 21.3, 15.2; LRMS (EI, 70 eV) *m/z* (%): 415 (M^++2, 7), 413 (M^+, 20), 382 (60), 379 (100), 229 (50), 91 (61); HRMS *m/z* (ESI) calcd for $C_{27}H_{24}{}^{35}ClNO$ ($[M+H]^+$) 414.1619, found 414.1617.

1-Methoxy-11*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,11*b*-dihydro-1*H*-benzo[5,6]indeno[1,2-*b*]pyridine (3ja):



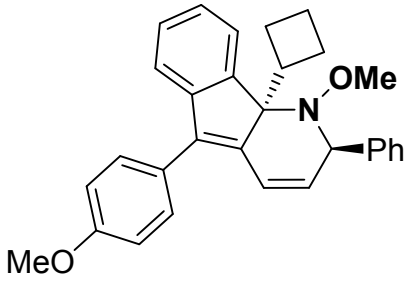
70%, 30.0 mg; Yellow solid; mp 142.9-143.8 °C (uncorrected); ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.02 (s, 1H), 7.83 (s, 1H), 7.77-7.74 (m, 2H), 7.54 (d, *J* = 6.5 Hz, 2H), 7.44-7.38 (m, 4H), 7.36-7.28 (m, 5H), 6.66 (d, *J* = 9.5 Hz, 1H), 5.75 (d, *J* = 9.5 Hz, 1H), 4.77 (s, 1H), 3.03 (s, 3H), 2.45 (d, *J* = 1.0 Hz, 3H), 1.59 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 146.1, 145.2, 142.2, 141.8, 137.7, 135.6, 133.7, 133.1, 132.6, 131.0, 129.6, 129.3, 129.1, 128.2, 128.0, 127.6, 125.7, 125.2, 123.5, 120.1, 118.8, 71.0, 68.0, 62.9, 21.4, 16.0; LRMS (EI, 70 eV) *m/z* (%): 429 (M^+, 31), 414 (50), 398 (65), 295 (78), 207 (100); HRMS *m/z* (ESI) calcd for $C_{31}H_{27}NO$ ($[M+H]^+$) 430.2165, found 430.2166.

9*b*-Butyl-1-methoxy-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ka):



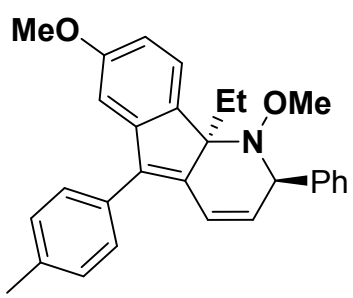
46%, 19.4 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.61 (d, *J* = 7.0 Hz, 1H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.41-7.37 (m, 3H), 7.34 -7.25 (m, 6H), 7.21 (t, *J* = 7.0 Hz, 1H), 6.63 (d, *J* = 8.5 Hz, 1H), 5.69 (d, *J* = 9.5 Hz, 1H), 4.86 (s, 1H), 2.96 (s, 3H), 2.43 (s, 3H), 2.00-2.06 (m, 1H), 1.27-1.29 (m, 1H), 1.19-1.15 (m, 2H), 0.81-0.67 (m, 4H), 0.50-0.46 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 146.3, 144.8, 142.1, 142.0, 137.5, 136.6, 132.5, 131.1, 129.5, 129.2, 128.9, 128.1, 127.6, 127.5, 125.8, 124.8, 120.3, 120.1, 74.8, 67.6, 62.9, 27.3, 25.2, 23.1, 21.3, 13.9; LRMS (EI, 70 eV) *m/z* (%): 421 (M^+, 1), 365 (30), 364 (100), 333 (41), 215 (10); HRMS *m/z* (ESI) calcd for $C_{30}H_{31}NO$ ($[M+H]^+$) 422.2478, found 422.2477.

9*b*-Cyclobutyl-1-methoxy-5-(4-methoxyphenyl)-2-phenyl-2,9*b*-dihydro-1H-indeno[1,2-*b*]pyridine (3la):



50%, 21.7 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.63 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.26-7.28 (m, 2H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.03 (d, *J* = 8.5 Hz, 2H), 6.69 (d, *J* = 9.5 Hz, 1H), 5.68 (d, *J* = 9.5 Hz, 1H), 4.84 (s, 1H), 3.88 (s, 3H), 3.55 (s, 1H), 2.95 (s, 3H), 1.83-1.85 (m, 1H), 1.70-1.76 (m, 2H), 1.62-1.64 (m, 2H), 1.44-1.49 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 159.2, 144.7, 142.2, 141.0, 137.3, 132.4, 130.3, 130.3, 129.7, 129.6, 128.1, 127.5, 127.5, 126.5, 125.5, 121.1, 120.3, 114.0, 68.4, 62.8, 55.3, 36.3, 26.9, 26.2, 18.9; HRMS *m/z* (ESI) calcd for $C_{30}H_{29}NO_2$ ($[M+H]^+$) 436.2271, found 436.2276.

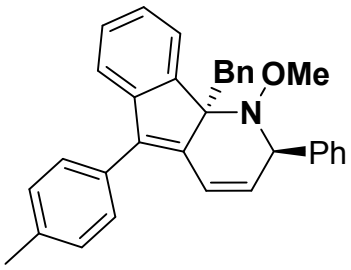
9*b*-Ethyl-1,7-dimethoxy-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ma):



62%, 26.2 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.48 (d, *J* = 8.5 Hz, 1H), 7.45 (d, *J* = 8.0 Hz,

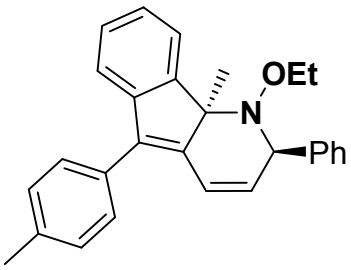
2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.28-7.32 (m, 5H), 6.92 (d, *J* = 2.5 Hz, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 5.69 (d, *J* = 9.5 Hz, 1H), 4.81 (s, 1H), 3.83 (s, 3H), 2.97 (s, 3H), 2.38-2.42 (m, 4H), 2.04-2.10 (m, 1H), 0.37-0.39 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 159.7, 146.5, 142.8, 142.1, 138.2, 137.5, 136.7, 132.8, 131.0, 129.5, 129.3, 128.9, 128.1, 127.5, 125.3, 120.0, 111.2, 106.2, 74.7, 67.6, 62.8, 55.4, 21.3, 20.5, 7.7; LRMS (EI, 70 eV) *m/z* (%): 423 (M^+, 3), 393 (100), 363 (21), 348 (12), 181 (9); HRMS *m/z* (ESI) calcd for $C_{29}H_{29}NO_2$ ($[M+H]^+$) 424.2271, found 424.2274.

9*b*-Benzyl-1-methoxy-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3na):



60%, 27.3 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.80 (d, *J* = 7.5 Hz, 1 H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28-7.31 (m, 1H), 7.18-7.23 (m, 3H), 7.14 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.91-6.96 (m, 2H), 6.87 (t, *J* = 7.5 Hz, 2H), 6.69 (d, *J* = 9.0 Hz, 1H), 6.60 (d, *J* = 7.0 Hz, 2H), 5.80 (d, *J* = 9.5 Hz, 1H), 4.99 (s, 1H), 3.63 (d, *J* = 13.5 Hz, 1H), 3.37 (d, *J* = 12.0 Hz, 1H), 3.07 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 145.1, 144.9, 142.0, 140.6, 137.6, 137.4, 136.3, 132.3, 130.9, 130.1, 129.7, 129.1, 128.7, 128.3, 127.8, 127.8, 126.6, 125.6, 125.5, 125.4, 120.4, 120.1, 75.6, 68.1, 63.0, 34.6, 21.4; HRMS *m/z* (ESI) calcd for $C_{33}H_{29}NO$ ($[M+H]^+$) 456.2322, found 456.2325.

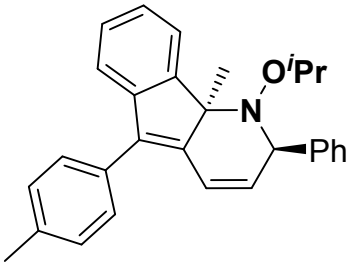
1-Ethoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3pa):



64%, 25.1 mg; Yellow solid; mp 128.0-128.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.61 (d, *J* = 7.0 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.38-7.40 (m, 3H), 7.26-7.32 (m, 6H), 7.20 (t, *J* = 7.5 Hz, 1H), 6.66 (d, *J* = 9.5 Hz, 1H), 5.72 (d, *J* = 9.5 Hz, 1H), 4.71 (s, 1H), 3.40-3.43 (m, 1H), 2.63-2.66 (m, 1H), 2.43 (s, 3H), 1.51 (s, 3H), 0.88 (t, *J* = 3.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.5, 144.2, 143.4, 141.9, 137.4,

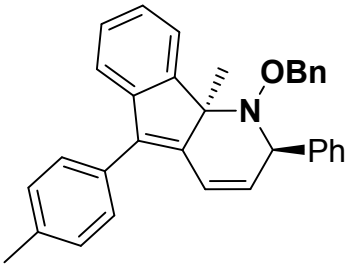
135.4, 132.3, 131.1, 129.6, 129.2, 129.0, 128.0, 127.6, 127.6, 125.8, 124.3, 120.8, 120.2, 71.4, 69.6, 67.8, 21.3, 15.4, 13.1; LRMS (EI, 70 eV) *m/z* (%): 393 (M^+, 19), 348 (98), 331 (27), 245 (100); HRMS *m/z* (ESI) calcd for $C_{28}H_{27}NO$ ($[M+H]^+$) 394.2165, found 394.2169.

1-Isopropoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3qa):



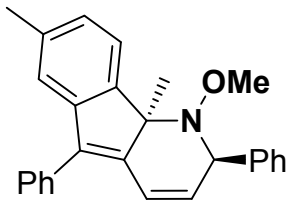
66%, 26.8 mg; Yellow solid; 130.1-130.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.66 (d, *J* = 6.5 Hz, 1H), 7.47 (d, *J* = 7.5 Hz, 2H), 7.37-7.38 (m, 3H), 7.26-7.30 (m, 6H), 7.18 (t, *J* = 7.5 Hz, 1H), 6.61 (d, *J* = 8.5 Hz, 1H), 5.70 (d, *J* = 8.5 Hz, 1H), 4.70 (s, 1H), 3.09-3.14 (m, 1H), 2.43 (s, 3H), 1.51 (s, 3H), 0.76 (s, 3H), 0.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.4, 144.6, 143.5, 142.5, 137.3, 134.9, 133.3, 131.2, 129.9, 129.2, 129.0, 129.0, 127.9, 127.5, 125.9, 124.9, 120.4, 119.6, 73.5, 71.8, 68.9, 21.3, 20.7, 15.6; LRMS (EI, 70 eV) *m/z* (%): 407 (M^+, 3), 393 (46), 318 (20), 256 (17); HRMS *m/z* (ESI) calcd for $C_{29}H_{29}NO$ ($[M+H]^+$) 408.2322, found 408.2318.

1-(Benzyloxy)-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ra) :



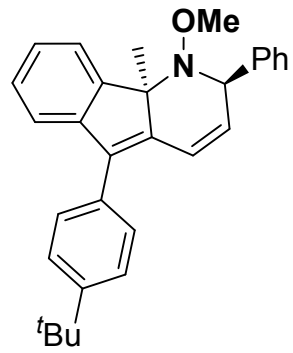
71%, 32.3 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.73 (d, *J* = 7.0 Hz, 1H), 7.51-7.42 (m, 5H), 7.36-7.24 (m, 10H), 7.07 (d, *J* = 6.0 Hz, 2H), 6.68 (d, *J* = 9.5 Hz, 1H), 5.74 (d, *J* = 9.5 Hz, 1H), 4.82 (s, 1H), 4.38 (d, *J* = 9.5 Hz, 1H), 3.67 (d, *J* = 9.0 Hz, 1H), 2.42 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.3, 144.2, 143.5, 141.8, 137.5, 136.6, 135.5, 132.4, 131.0, 129.8, 129.2, 129.0, 128.9, 128.21, 127.8, 125.8, 124.9, 120.8, 120.1, 76.5, 71.6, 68.0, 21.3, 15.4; LRMS (EI, 70 eV) *m/z* (%): 455 (M^+, 1), 349 (91), 334 (100), 257 (47), 104 (47); HRMS *m/z* (ESI) calcd for $C_{33}H_{29}NO$ ($[M+H]^+$) 456.2322, found 456.2325.

1-Methoxy-7,9*b*-dimethyl-2,5-diphenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3gb):



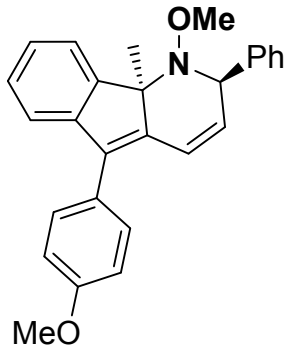
60%, 22.7mg; Yellow solid; mp 165.6-166.7 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.56 (d, *J* = 7.5 Hz, 2H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.37-7.41 (m, 3H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.25-7.28 (m, 1H), 7.20 (s, 1H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 9.5 Hz, 1H), 5.70 (d, *J* = 9.5 Hz, 1H), 4.68 (s, 1H), 2.98 (s, 3H), 2.35 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 145.7, 144.8, 143.5, 142.0, 137.5, 135.6, 134.2, 132.6, 129.6, 129.2, 128.6, 128.2, 127.7, 127.6, 126.8, 124.4, 121.5, 120.0, 77.3, 77.1, 76.8, 71.2, 68.0, 62.8, 21.6, 15.4; LRMS (EI, 70 eV) *m/z* (%): 379 (M^+, 12), 348 (69), 332 (39), 319 (10), 245 (100); HRMS *m/z* (ESI) calcd for $C_{27}H_{25}NO$ ($[M+H]^+$) 380.2009, found 380.2013.

5-(4-(*tert*-Butyl)phenyl)-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ac):



61%, 25.6 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.66 (d, *J* = 7.0 Hz, 1H), 7.49-7.52 (m, 4H), 7.40-7.44 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 7.5, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 6.68 (d, *J* = 9.5 Hz, 1H), 5.70 (d, *J* = 9.5 Hz, 1H), 4.70 (s, 1H), 2.98 (s, 3H), 1.50 (s, 3H), 1.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 150.6, 148.4, 144.1, 143.4, 142.0, 135.5, 132.3, 131.0, 129.6, 128.7, 128.1, 127.6, 127.6, 125.9, 125.4, 124.6, 120.9, 120.2, 71.4, 67.9, 62.7, 34.7, 31.4, 15.4; LRMS (EI, 70 eV) *m/z* (%): 421 (M^+, 21), 390 (100), 334 (57), 287 (99), 231 (15); HRMS *m/z* (ESI) calcd for $C_{30}H_{31}NO$ ($[M+H]^+$) 422.2478, found 422.2475.

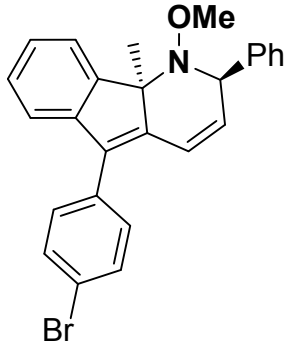
1-Methoxy-5-(4-methoxyphenyl)-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ad) :



72%, 28.4 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.64 (d, *J* = 7.5 Hz, 1H), 7.51 (d, *J* = 9.0 Hz, 2H), 7.40 (t, *J* = 7.0 Hz, 3H), 7.33-7.26 (m, 4H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.65 (d, *J* = 10.0 Hz,1H), 5.70 (d, *J* = 10.0 Hz, 1H), 4.70 (s, 1H), 3.87 (s, 3H), 2.97 (s,

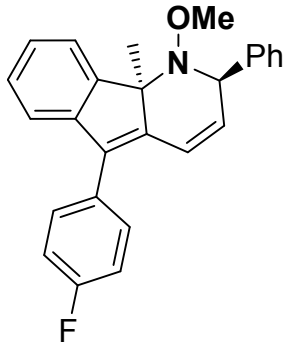
3H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 159.1, 148.3, 143.7, 143.4, 141.9, 135.1, 132.2, 130.2, 129.6, 128.2, 127.6,127.6, 126.3, 125.9, 124.6, 120.7, 120.1, 113.9, 71.3, 67.9, 62.7, 55.3, 15.3; LRMS (EI, 70 eV) *m/z* (%): 395 (M^+, 23), 364 (86), 349 (31), 261 (100), 334 (30); HRMS *m/z* (ESI) calcd for $C_{27}H_{25}NO_2$ ($[M+H]^+$) 396.1958, found 396.1956.

5-(4-Bromophenyl)-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine(3ae)：



dr = 3.3:1; 58%, 25.6 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.65 (d, *J* = 7.5 Hz, 1H), 7.56-7.62 (m, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.39-7.45 (m, 4H), 7.30-7.34 (m, 2H), 7.27-7.29 (m, 2H), 7.21-7.23 (m, 1H), 6.65 (d, *J* = 10.0 Hz, 1H), 5.72 (d, *J* = 10.0 Hz, 1H), 4.70 (s, 1H), 2.98 (s, 2.3H), 2.91 (s, 0.7H), 1.50 (s, 2.3H), 1.49 (s, 0.7H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.3, 144.4, 143.2, 141.8, 135.5, 134.0, 133.2, 132.6, 131.8, 130.7, 129.6, 129.1, 128.5, 128.2, 127.7,127.6, 126.0, 124.6, 120.7, 120.5, 120.0, 71.4, 67.9, 62.7, 15.3; LRMS (EI, 70 eV) *m/z* (%): 445 (M^++2, 19), 443 (M^+, 19), 318 (69), 230 (83), 215 (100), 91 (86); HRMS *m/z* (ESI) calcd for $C_{26}H_{22}{}^{79}BrNO$ ($[M+H]^+$) 444.0958, found 444.0960.

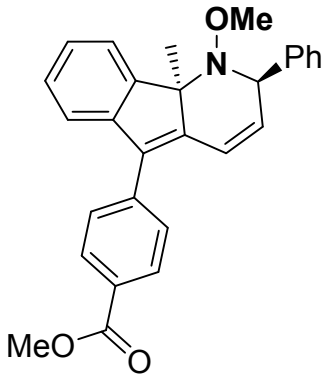
5-(4-Fluorophenyl)-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3af):



63%, 24.0 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.65 (d, *J* = 7.5 Hz, 1H), 7.52-7.55 (m, 2H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.27-7.35 (m, 5H), 7.16-7.24 (m, 3H), 6.60 (d, *J* = 10.0 Hz, 1H), 5.75 (d, *J* = 10.0 Hz, 1H), 4.70 (s, 1H), 2.97 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 162.3 (d, *J* = 245.5 Hz), 148.3, 144.6, 143.1, 141.7, 134.5, 132.9, 130.7 (d, *J* = 7.9 Hz, 1C), 129.9 (d, *J* = 3.2 Hz, 1C), 129.5, 128.2, 127.7 (d, *J* = 9.6 Hz, 1C), 126.1, 124.7, 120.5, 119.7, 115.5 (d, *J* = 21.2 Hz, 1C), 71.4, 67.9, 62.7, 15.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ (ppm): -113.8; LRMS (EI, 70 eV) *m/z* (%): 383 (M^+, 0), 381 (30), 380 (100), 349 (29), 334 (19); HRMS *m/z* (ESI) calcd for

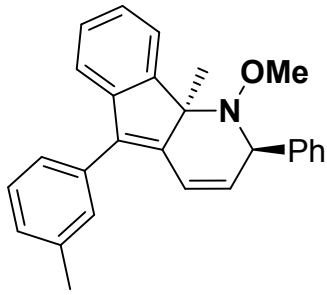
$C_{26}H_{22}FNO$ ([M+H]$^+$) 384.1758, found 384.1759.

Methyl 4-(1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]-pyridin-5-yl)benzoate (3ag):



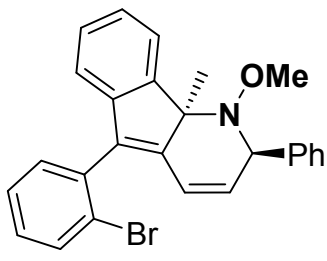
40 %, 16.9 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.16 (d, *J* = 8.0 Hz, 2H), 7.64-7.66 (m, 3H), 7.40 (d, *J* = 7.0 Hz, 2H), 7.28-7.36 (m, 5H), 7.23-7.25 (m, 1H), 6.62 (d, *J* = 8.0 Hz, 1H), 5.78 (d, *J* = 9.5 Hz, 1H), 4.72 (s, 1H), 3.96 (s, 3H), 2.98 (s, 3H), 1.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 166.9, 148.2, 145.6, 142.6, 141.6, 138.9, 134.6, 133.7, 129.8, 129.5, 129.3, 129.1, 128.2, 127.8, 127.7, 126.3, 124.8, 120.6, 119.6, 71.6, 67.9, 62.8, 52.2, 15.3; HRMS *m/z* (ESI) calcd for $C_{28}H_{25}NO_3$ ([M+H]$^+$) 424.1907, found 424.1906.

1-Methoxy-9*b*-methyl-2-phenyl-5-(*m*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ah):



70%, 26.5 mg; White solid; mp 147.5-148.3 ^{o}C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.64 (d, *J* = 7.5 Hz, 1H), 7.42-7.36 (m, 6H), 7.33-7.26 (m, 4H), 7.23-7.20 (m, 2H), 6.64 (d, *J* = 10.0 Hz, 1H), 5.71 (d, *J* = 9.5 Hz, 1H), 4.70 (s, 1H), 2.97 (s, 3H), 2.43 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.3, 144.3, 143.3, 141.9, 138.1, 135.7, 133.9, 132.5, 129.6, 129.6, 128.5, 128.4, 128.2, 127.6,127.6, 126.2, 126.0, 124.6, 120.8, 120.0, 71.4, 67.9, 62.7, 21.5, 15.3; LRMS (EI, 70 eV) *m/z* (%): 379 (M$^+$, 27), 348 (65), 333 (36), 245 (100), 215 (44); HRMS *m/z* (ESI) calcd for $C_{27}H_{25}NO$ ([M+H]$^+$) 380.2009, found 380.2012.

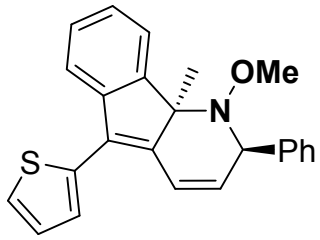
5-(2-Bromophenyl)-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ai):



45%, 19.9 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.65 (d, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41-7.37 (m, 4H), 7.33-7.26 (m, 4H), 6.64 (d, *J* = 9.5 Hz, 1H), 5.72 (d, *J* = 9.5 Hz, 1H),

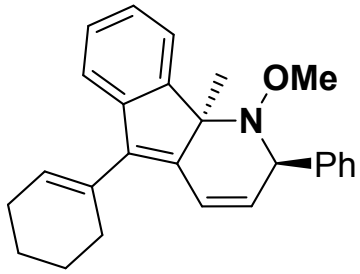
4.70 (s, 1H), 2.98 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.3, 143.2, 141.9, 135.6, 134.0, 132.7, 129.6, 129.1, 128.5, 128.2, 127.7, 127.7, 126.0, 124.6, 120.7, 120.0, 71.4, 67.9, 62.7, 15.3; LRMS (EI, 70 eV) *m/z* (%): 445 (M^++2, 1), 443 (M^+, 1), 365 (28), 350 (35), 334 (50), 231 (100); HRMS *m/z* (ESI) calcd for $C_{26}H_{22}{}^{79}BrNO$ ($[M+H]^+$) 444.0958, found 444.0960.

1-Methoxy-9*b*-methyl-2-phenyl-5-(thiophen-2-yl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3aj):



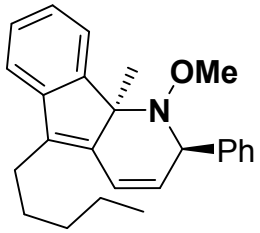
40%, 14.8 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.71-7.59 (m, 2H), 7.47-7.36 (m, 4H), 7.36-7.27 (m, 4H), 7.25 (s, 1H), 7.20-7.18 (m, 1H), 6.90 (d, *J* = 10.0 Hz, 1H), 5.79 (d, *J* = 10.0 Hz, 1H), 4.71 (s, 1H), 2.96 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.0, 144.9, 142.6, 141.7, 135.3, 133.3, 129.6, 128.4, 128.2, 127.8, 127.7, 127.4, 127.1, 126.2, 125.6, 124.7, 121.0, 120.1, 71.4, 67.9, 62.8, 15.4; LRMS (EI, 70 eV) *m/z* (%): 371 (M^+, 24), 340 (80), 325 (46), 237 (100), 91 (26); HRMS *m/z* (ESI) calcd for $C_{24}H_{21}NOS$ ($[M+H]^+$) 372.1417, found 372.1415.

(2R,9bR)-5-(cyclohex-1-en-1-yl)-1-methoxy-9b-methyl-2-phenyl-2,9b-dihydro-1H-indeno[1,2-b]pyridine (3ak):



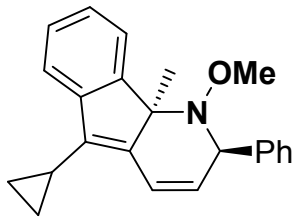
46%, 16.9 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.57 (d, *J* = 7.5 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 2H), 7.29-7.34 (m, 3H), 7.24-7.28 (m, 3H), 7.16 (t, *J* = 7.5 Hz, 1H), 6.60 (d, *J* = 9.5 Hz, 1H), 5.91 (s, 1H), 5.62 (d, *J* = 9.5 Hz, 1H), 4.64 (s, 1H), 2.94 (s, 3H), 2.37 (s, 1H), 2.23-2.56 (m, 2H), 1.78-1.81 (m, 2H), 1.71-1.77 (m, 2H), 1.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.4, 143.6, 142.8, 142.1, 138.4, 131.6, 130.9, 129.5, 128.2, 128.1, 127.5, 127.5, 125.5, 124.4, 120.9, 120.3, 71.0, 67.8, 62.7, 28.8, 25.4, 22.9, 22.3, 15.3; LRMS (EI, 70 eV) *m/z* (%): 369 (M^+, 17), 354 (19), 338 (100), 220 (69); HRMS *m/z* (ESI) calcd for $C_{26}H_{27}NO$ ($[M+H]^+$) 370.2165, found 370.2163.

1-Methoxy-9*b*-methyl-5-pentyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3al):



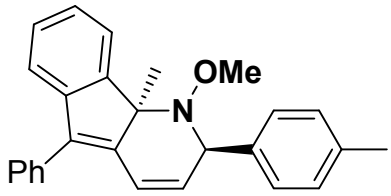
68%, 24.4 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.57 (d, *J* = 7.5 Hz, 1H), 7.38 (d, *J* = 7.0 Hz, 2H), 7.32-7.25(m, 5H), 7.17 (t, *J* = 6.5 Hz, 1H), 6.60-6.57 (m, 1H), 5.65-5.63 (m, 1H), 4.64 (s, 1H), 2.92 (s, 3H), 2.62-2.58 (m, 2H), 1.70-1.64 (m, 2H), 1.39-1.36 (m, 7H), 0.91 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.5, 144.0, 143.4, 142.1, 136.0, 130.7, 129.5, 128.1, 127.5, 125.5, 124.3, 119.7, 119.3, 71.1, 67.8, 62.6, 31.9, 28.4, 25.3, 22.5, 15.1, 14.1; LRMS (EI, 70 eV) *m/z* (%): 359 (M^+, 35), 344 (67), 288 (61), 256 (71), 225 (100); HRMS *m/z* (ESI) calcd for $C_{25}H_{29}NO$ ($[M+H]^+$) 360.2322, found 360.2318.

5-Cyclopropyl-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3am):



55%, 18.0 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.55 (d, *J* = 7.0 Hz, 1H), 7.42-7.38 (m, 3H), 7.33-7.26 (m, 4H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.74 (d, *J* = 9.5 Hz, 1H), 5.65 (d, *J* = 10.0 Hz, 1H), 4.62 (s, 1H), 2.91 (s, 3H), 1.77 (s, 1H), 1.36 (s, 3H), 0.97-0.81 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.1, 144.2, 143.9, 141.9, 136.1, 130.6, 129.6, 128.1, 127.6, 127.5, 125.6, 124.2, 120.3, 119.7, 71.1, 67.7, 62.6, 15.0, 7.7, 5.2, 5.0; LRMS (EI, 70 eV) *m/z* (%): 329 (M^+, 31), 298 (67), 282 (44), 181 (100), 165 (79); HRMS *m/z* (ESI) calcd for $C_{23}H_{23}NO$ ($[M+H]^+$) 330.1852, found 330.1848.

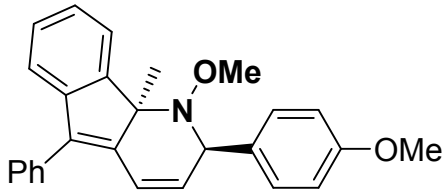
1-Methoxy-9*b*-methyl-5-phenyl-2-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ao):



54%, 20.4 mg; Yellow solid; mp 133.4-135.1 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.65 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.40 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 8.5 Hz, 3H), 7.22 (t, *J* = 7.0 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 2H), 6.65-6.62 (m, 1H), 5.72-5.70 (m, 1H), 4.67 (s, 1H), 3.00 (s, 3H), 2.34 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.4, 144.6, 143.2, 138.9, 137.2, 135.4, 134.0, 132.9, 129.4, 129.1, 128.9, 128.5, 127.7, 127.6, 126.0, 124.6, 120.7, 119.8, 71.4, 67.6,

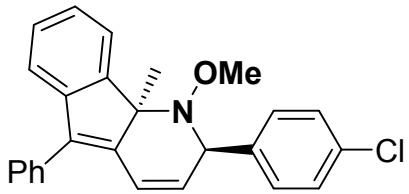
62.8, 21.2, 15.3; LRMS (EI, 70 eV) *m/z* (%): 379 (M^+, 33), 348 (61), 333 (33), 231 (100), 215 (44); HRMS *m/z* (ESI) calcd for $C_{27}H_{25}NO$ ($[M+H]^+$) 380.2009, found 380.2014.

1-Methoxy-2-(4-methoxyphenyl)-9*b*-methyl-5-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ap):



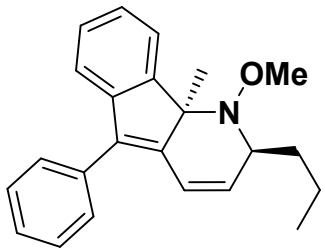
50%, 19.7 mg; Yellow solid; mp 143.70-143.9 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.65 (d, *J* = 7.0 Hz, 1H), 7.57 (d, *J* = 7.0 Hz, 2H), 7.49 (t, *J* = 7.5Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.33-7.26 (m, 3H), 7.23 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 2H), 6.65-6.63 (m, 1H), 5.73-5.70 (m, 1H), 4.66 (s, 1H), 3.80 (s, 3H), 3.00 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 159.1, 148.4, 144.6, 143.2, 135.4 (s), 134.0, 132.9, 130.6, 129.1 (2C), 128.5, 127.7, 127.6, 126.0, 124.6, 120.7, 119.9, 113.5, 71.4, 67.2, 62.7, 55.2, 15.3; LRMS (EI, 70 eV) *m/z* (%): 395 (M^+, 65), 364 (100), 349 (43), 216 (50), 121 (45); HRMS *m/z* (ESI) calcd for $C_{27}H_{25}NO_2$ ($[M+H]^+$) 396.1958, found 396.1955.

2-(4-Chlorophenyl)-1-methoxy-9*b*-methyl-5-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3aq):



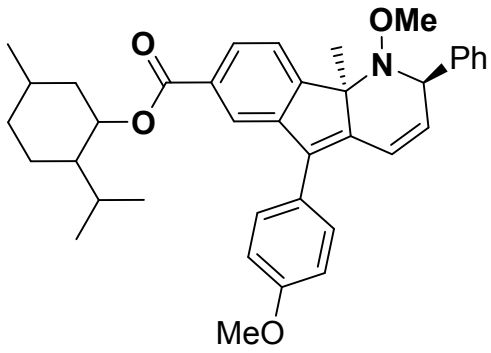
43%, 17.1 mg; White solid; mp 130.7-131.5 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.64 (d, *J* = 7.5 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 8.0 Hz, 3H), 7.24 (d, *J* = 7.5 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 5.65 (d, *J* = 9.5 Hz, 1H), 4.68 (s, 1H), 3.00 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.2, 144.2, 143.2, 140.5, 135.9, 133.9, 133.4, 132.0, 130.9, 129.1, 128.6, 128.3, 127.8, 127.8, 126.1, 124.6, 120.8, 120.3, 71.4, 67.2, 62.9, 29.7, 15.3; LRMS (EI, 70 eV) *m/z* (%): 401 (M^++2, 6), 399 (M^+, 18), 384 (28), 368 (45), 231 (100), 216 (43); HRMS *m/z* (ESI) calcd for $C_{26}H_{22}{}^{35}ClNO$ ($[M+H]^+$) 400.1463, found 400.1462.

1-Methoxy-9*b*-methyl-5-phenyl-2-propyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ar):



51 %, 16.8 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.66 (d, *J* = 7.0 Hz, 1H), 7.51 (d, *J* = 7.0 Hz, 2H), 7.43-7.46 (m, 2H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.22-7.28 (m, 2H), 6.53 (d, *J* = 10.0 Hz, 1H), 5.78 (d, *J* = 10.0 Hz, 1H), 3.74 (s, 1H), 3.62 (s, 3H), 1.56-1.65 (m, 3H), 1.33-1.43 (m, 4H), 0.96 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.3, 144.7, 143.4, 134.9, 134.1, 132.4, 129.1, 128.5, 127.6, 125.8, 124.8, 120.6, 120.1, 71.0, 63.9, 63.3, 35.1, 18.4, 15.1, 14.5; LRMS (EI, 70 eV) *m/z* (%): 331 (M^+, 46), 288 (64), 242 (100), 216 (39), 231 (19); HRMS *m/z* (ESI) calcd for $C_{23}H_{25}NO$ ($[M+H]^+$) 332.2009, found 332.2008.

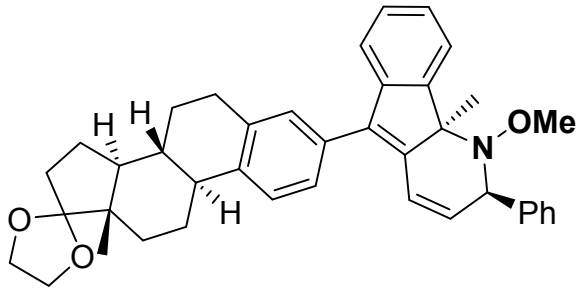
2-Isopropyl-5-methylcyclohexyl 1-methoxy-5-(4-methoxyphenyl)-9*b*-methyl- 2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine-7-carboxylate (3sd):



52%, 30.0 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 8.06 (d, *J* = 3.5 Hz, 1H), 7.94 (t, *J* = 7.0 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.51-7.53 (m, 2H), 7.39-7.41 (m, 2H), 7.28-7.33 (m, 3H), 7.05 (d, *J* = 8.0, 2H), 6.65 (t, *J* = 8.0 Hz, 1H), 5.73 (d, *J* = 9.5 Hz, 1H), 4.88-4.93 (m, 1H), 4.71 (s, 1H), 3.89 (s, 3H), 2.96 (d, *J* = 6.5 Hz, 3H), 2.10-2.13 (m, 1H), 1.91-1.96 (m, 1H), 1.71 (d, *J* = 11.0 Hz, 2H), 1.49-1.56 (m, 5H), 1.04-1.66 (m, 2H), 0.89-0.93 (m, 7H), 0,79-0.81 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 166.3 (d, *J* = 3.1 Hz, 1C), 159.3, 152.8, 144.5, 143.8, 141.7, 134.6 (d, *J* = 21.2 Hz, 1C), 132.8, 130.5 (d, *J* = 4.4 Hz, 1C), 130.2 (d, *J* = 3.6 Hz, 1C), 129.5, 128.2, 127.7, 127.5, 125.9 (d, *J* = 1.6 Hz, 1C), 124.3 (d, *J* = 2.7 Hz, 1C), 121.7 (d, *J* = 6.0 Hz, 1C),

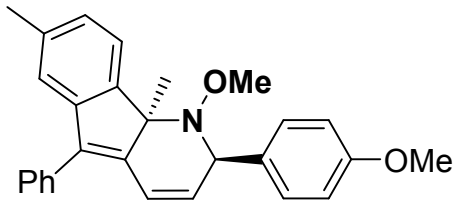
119.9 (d, *J* = 9.0 Hz, 1C), 114.1, 74.8 (d, *J* = 4.0 Hz, 1C), 71.3, 67.9, 62.7 (d, *J* = 4.4 Hz, 1C), 55.3, 47.2 (d, *J* = 7.4 Hz, 1C), 40.9 (d, *J* = 3.4 Hz, 1C), 34.3, 31.4, 26.7 (d, *J* = 15.9 Hz, 1C), 23.8 (d, *J* = 12.5 Hz, 1C), 22.0, 20.7 (d, *J* = 5.2 Hz, 1C), 16.7 (d, *J* = 14.0 Hz, 1C), 15.1; HRMS *m/z* (ESI) calcd for $C_{38}H_{43}NO_4$ ([M+H]$^+$) 578.3265, found 578.3264.

1-Methoxy-9*b*-methyl-5-((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3bu):



57%, 33.3 mg; Yellow solid; mp 152.4-153.3 °C (uncorrected); ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.64 (d, *J* = 7.0 Hz, 1H), 7.40-7.43 (m, 4H), 7.30-7.36 (m, 4H), 7.26-7.28 (m, 2H), 7.21 (t, *J* = 7.5Hz, 1H), 6.67 (d, *J* = 9.5 Hz, 1H), 5.69 (d, *J* = 9.5 Hz, 1H), 4.69 (s, 1H), 3.99-3.90 (m, 4H), 2.97 (s, 3H), 2.44-2.33 (m, 2H), 2.03-2.08 (m, 1H), 1.95-1.98 (m, 1H), 1.79-1.90 (m, 3H), 1.36-1.71(m, 11H), 0.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 148.34 (s), 144.0, 143.3, 141.9, 140.0, 136.9, 135.5, 132.2, 131.2, 129.5, 129.4, 128.1, 127.6, 126.3, 125.9, 125.5, 124.5, 120.9, 120.2, 119.4, 71.3, 67.9, 65.2, 64.6, 62.7, 49.5, 46.1, 44.1, 38.8, 34.2, 30.7, 29.6, 26.9, 25.9, 22.3, 15.3, 14.3; HRMS *m/z* (ESI) calcd for $C_{40}H_{43}NO_3$ ([M+H]$^+$) 586.3316, found 586.3314.

1-Methoxy-2-(4-methoxyphenyl)-7,9*b*-dimethyl-5-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3av):



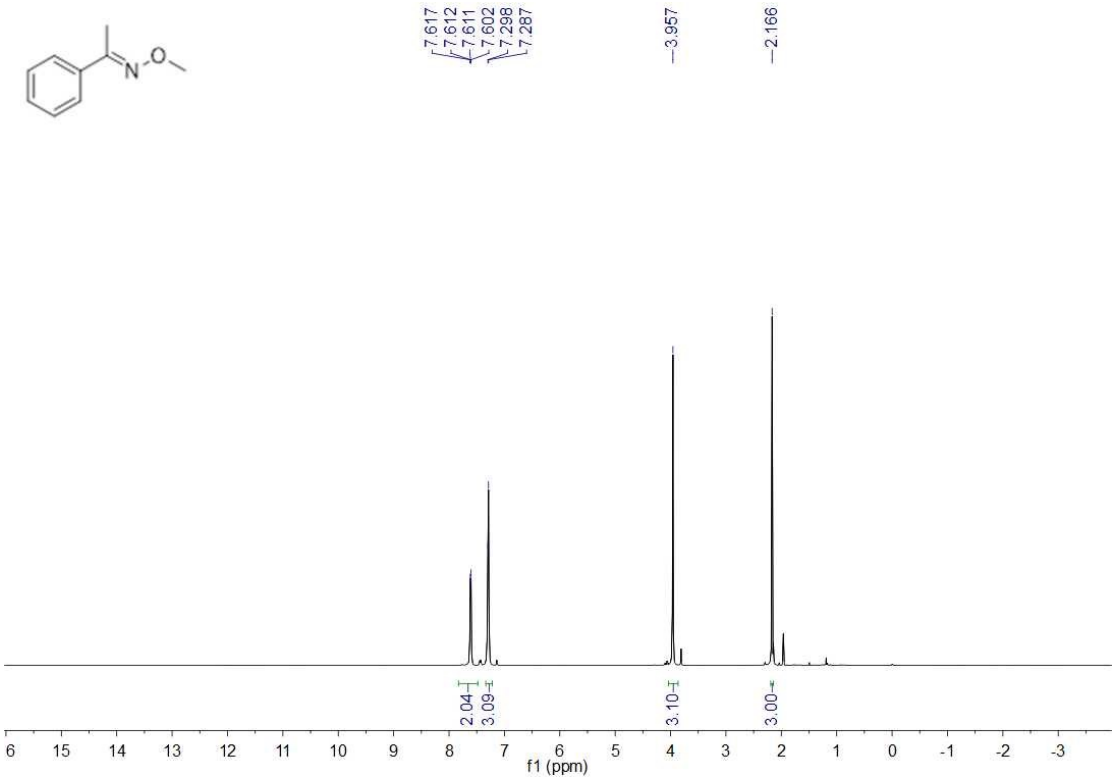
46%, 18.8 mg; Yellow oil; ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.58 (d, *J* = 7.0 Hz, 2H), 7.55 (d, *J* = 8.0 Hz, 1H), 7.49-7.52 (m, 2H), 7.40-7.43 (m, 2Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 8.0 Hz, 1H), 5.71 (d, *J* = 9.5Hz, 1H), 4.67 (s, 1H), 3.81 (s, 3H), 3.17 (s, 3H), 2.37 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 159.0, 145.7, 144.9, 143.4, 137.3, 135.4, 134.1, 132.8, 130.6, 129.1, 128.5, 127.6, 126.7, 124.3, 121.4, 119.9, 113.5, 71.1, 67.2, 62.7, 55.2, 21.6,

15.4; HRMS *m/z* (ESI) calcd for $C_{28}H_{27}NO_2$ ($[M+H]^+$) 410.2115, found 410.2114.

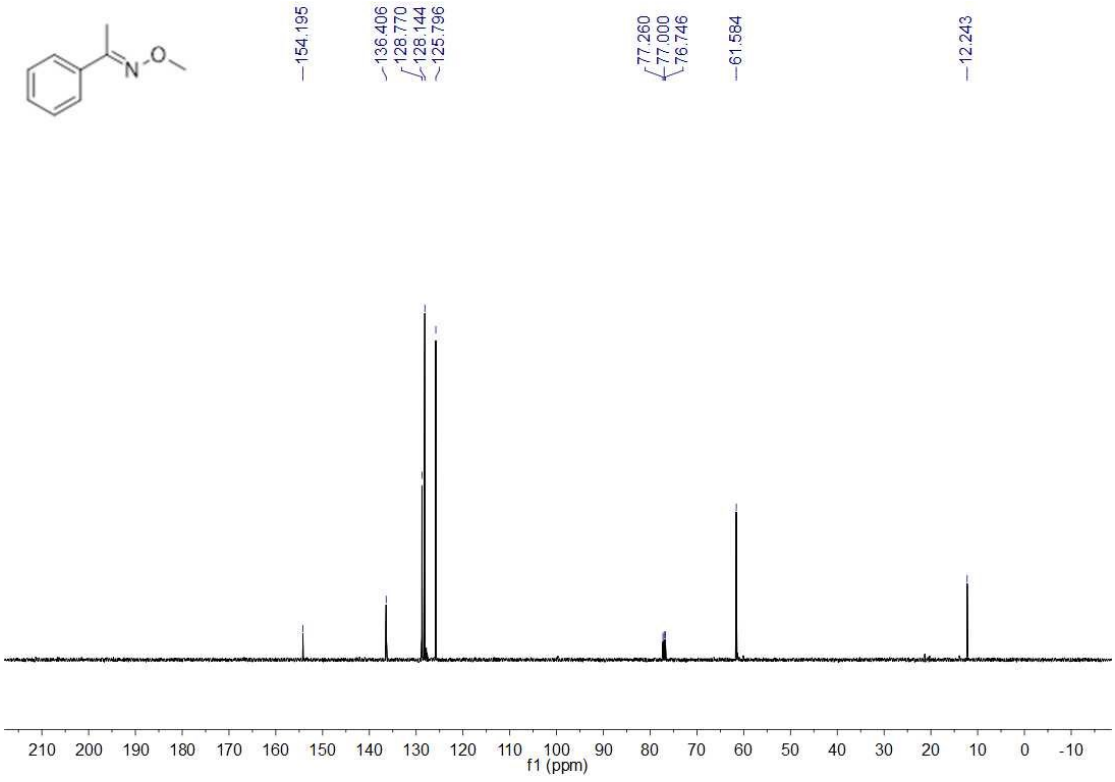
(C) Spectra

(*E*)-1-phenylethan-1-one O-methyl oxime (1b)

^{1}H NMR (125MHz, $CDCl_3$)

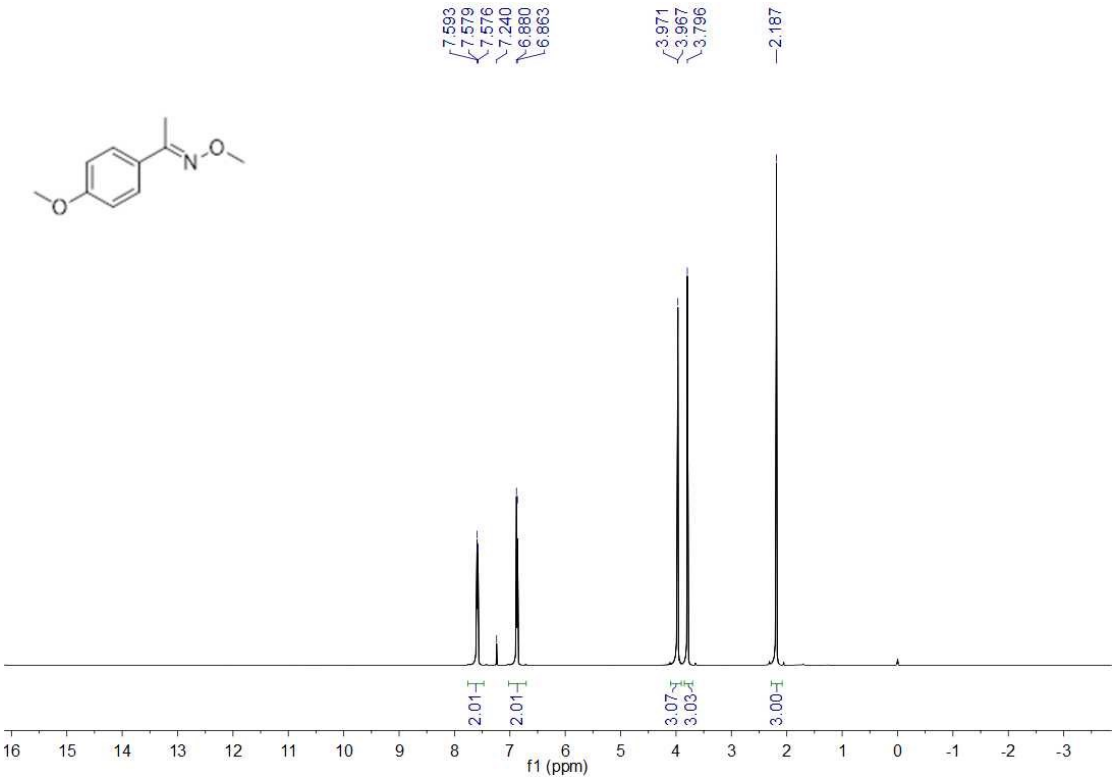


^{13}C NMR (125MHz, $CDCl_3$)

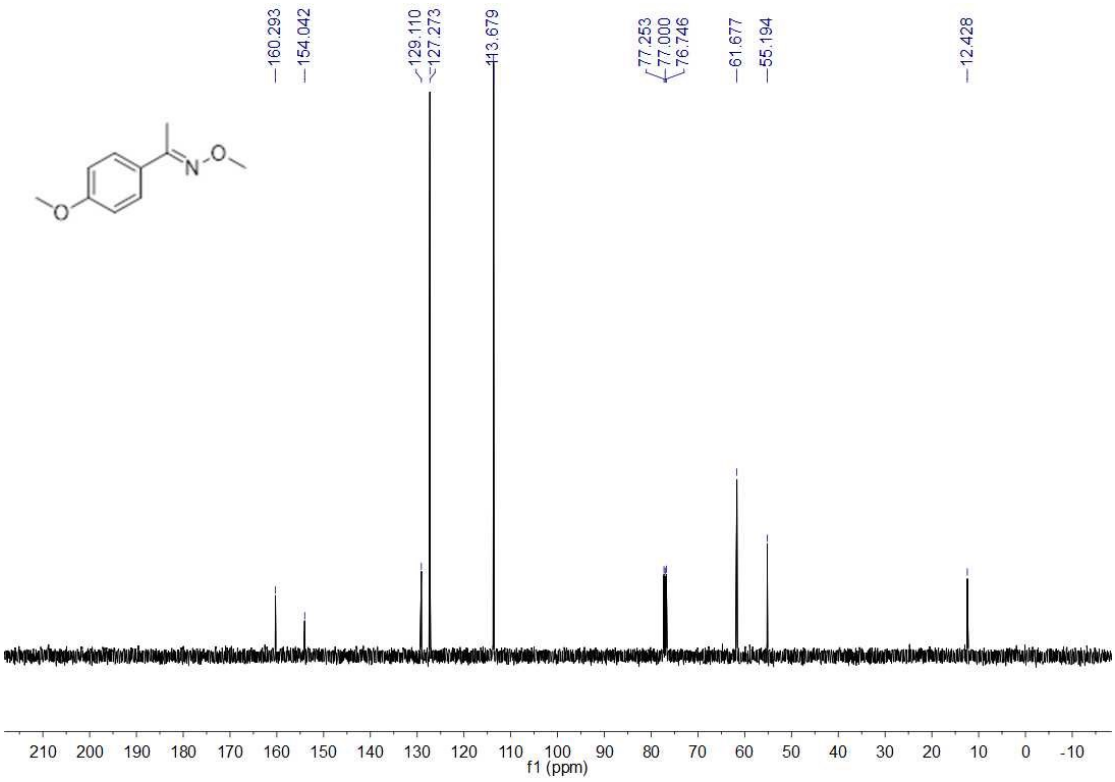


(*E*)-1-(4-methoxyphenyl)ethan-1-one O-methyl oxime(1c)

^{1}H NMR (125MHz, $CDCl_3$)

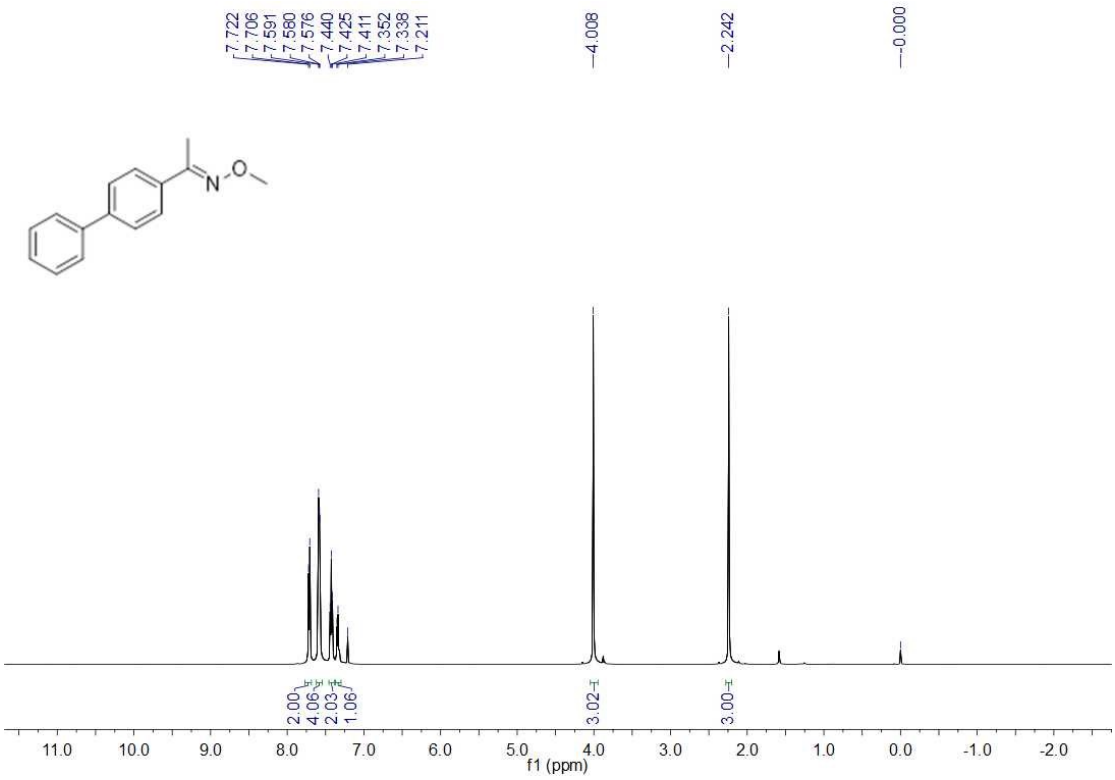


^{13}C NMR (125MHz, $CDCl_3$)

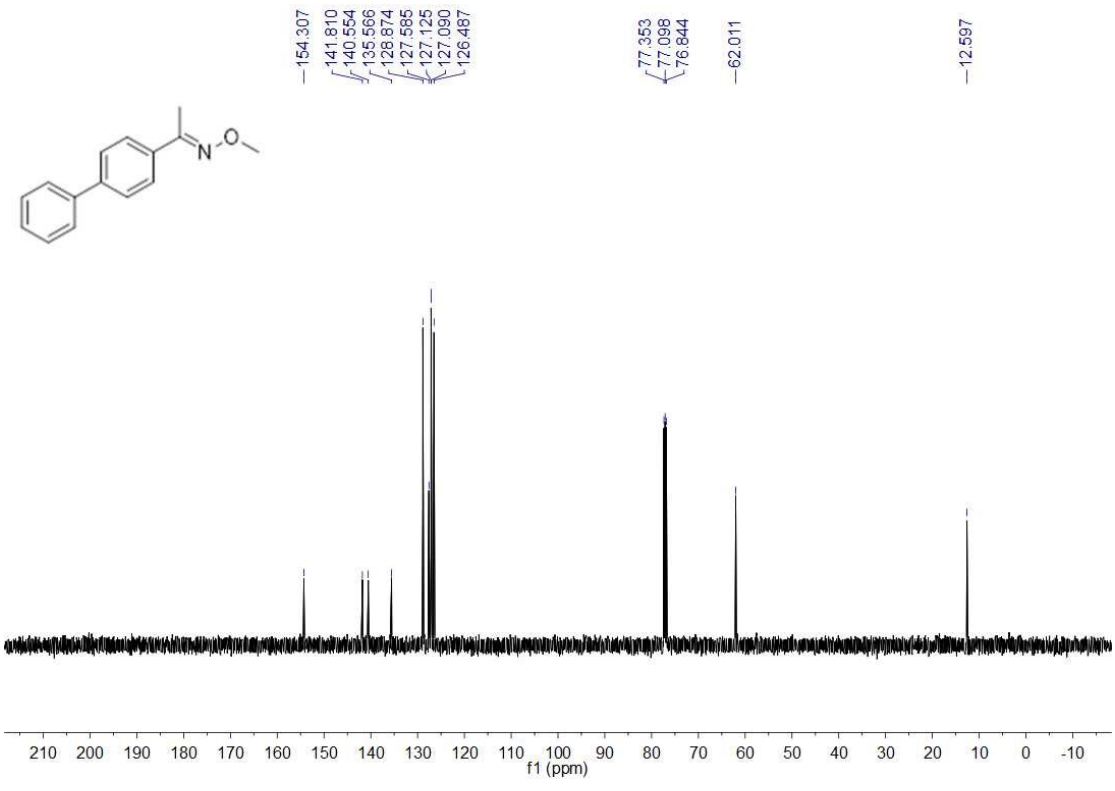


(*E*)-1-([1,1'-biphenyl]-4-yl) ethan-1-one O-methyl oxime (1d)

^{1}H NMR (125MHz, $CDCl_3$)

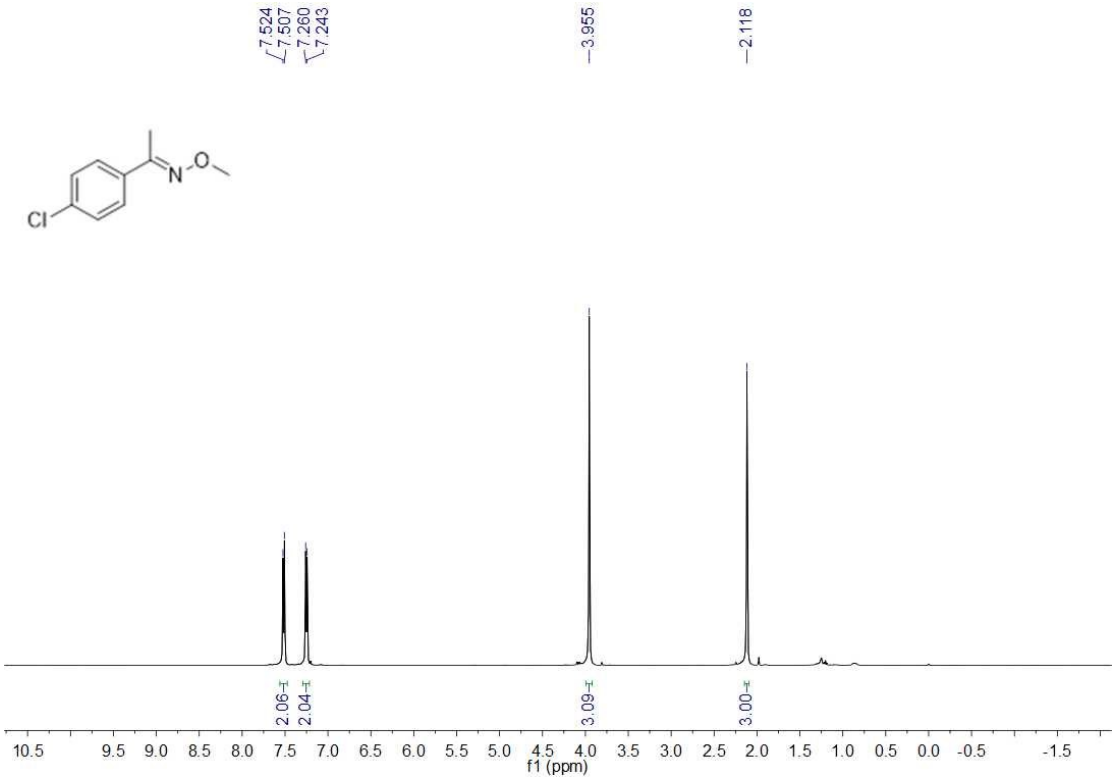


^{13}C NMR (125MHz, $CDCl_3$)

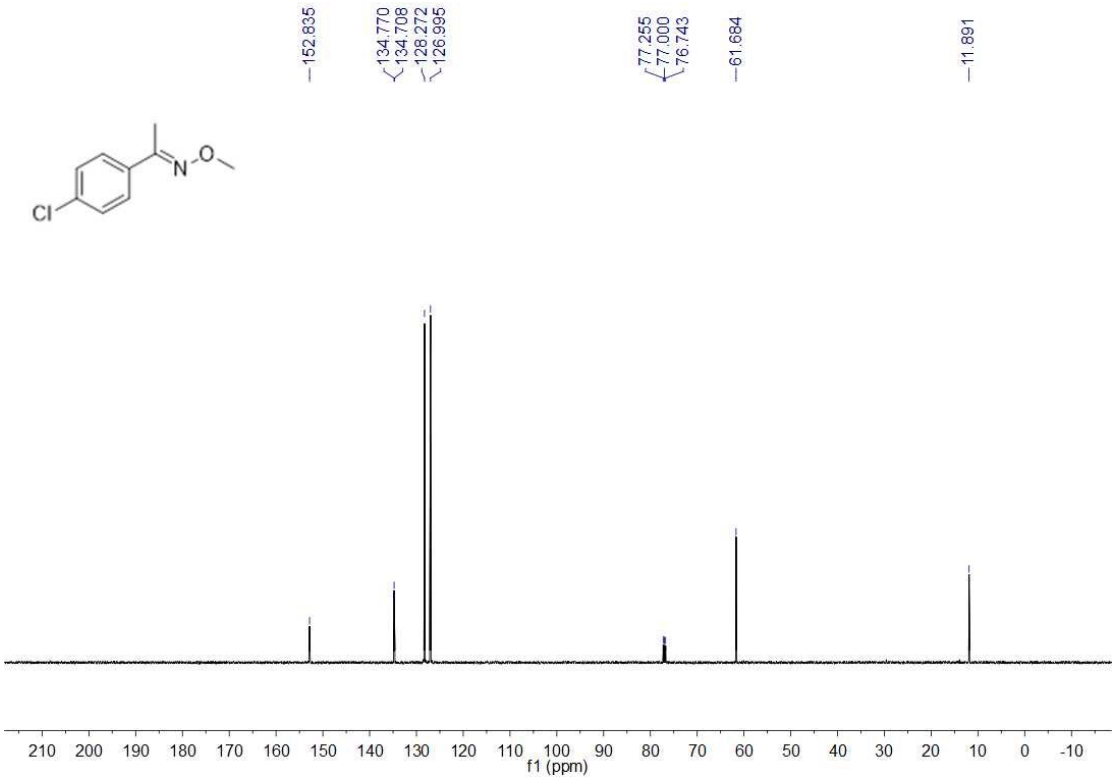


(*E*)-1-(4-chlorophenyl)ethan-1-one O-methyl oxime (1e)

^{1}H NMR (125MHz, $CDCl_3$)

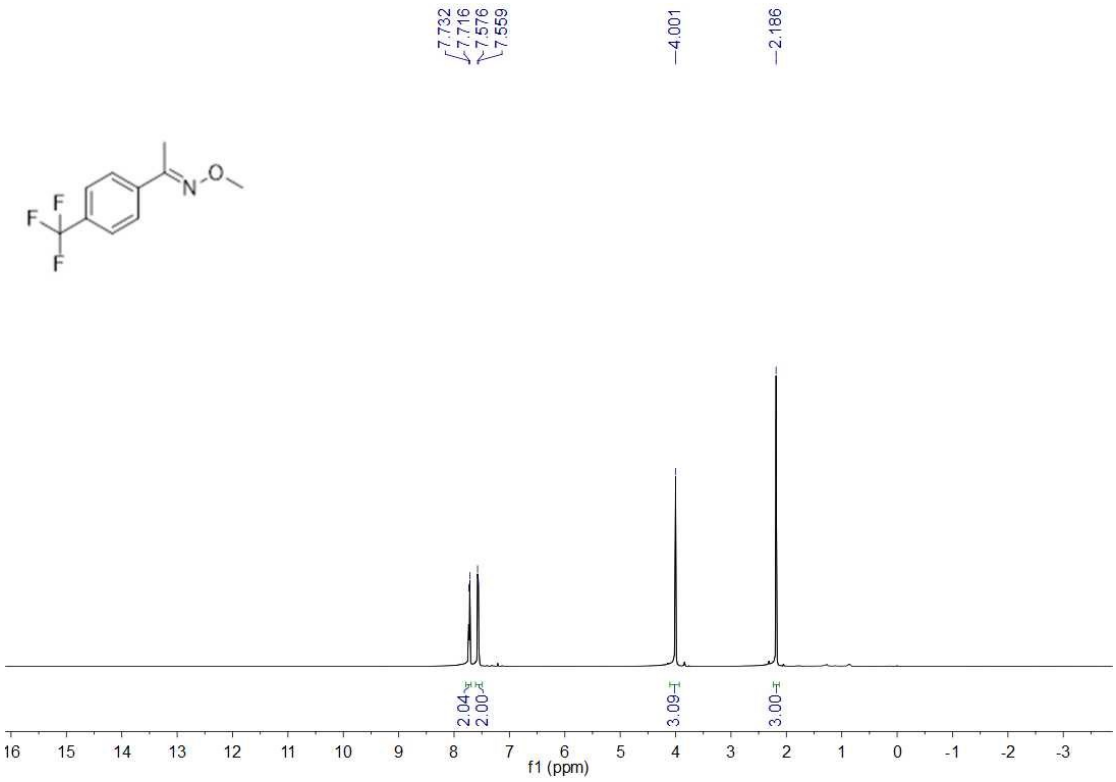


^{13}C NMR (125MHz, $CDCl_3$)

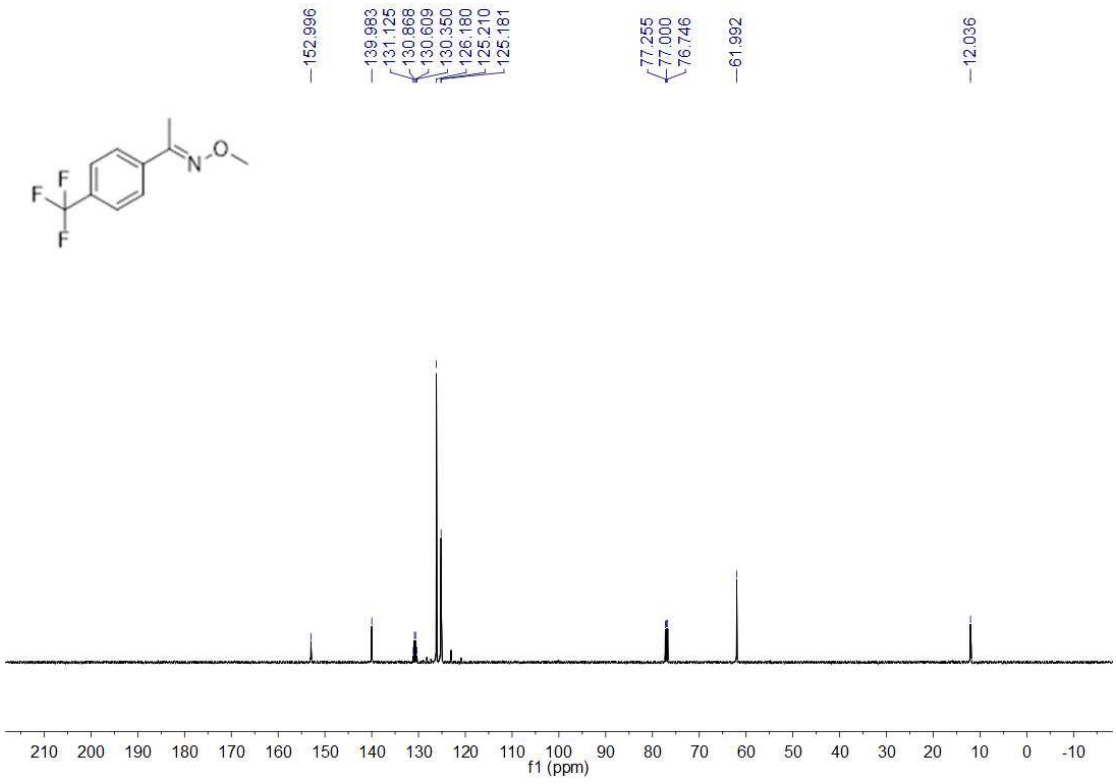


(*E*)-1-(4-(trifluoromethyl)phenyl)ethan-1-one O-methyl oxime (1f)

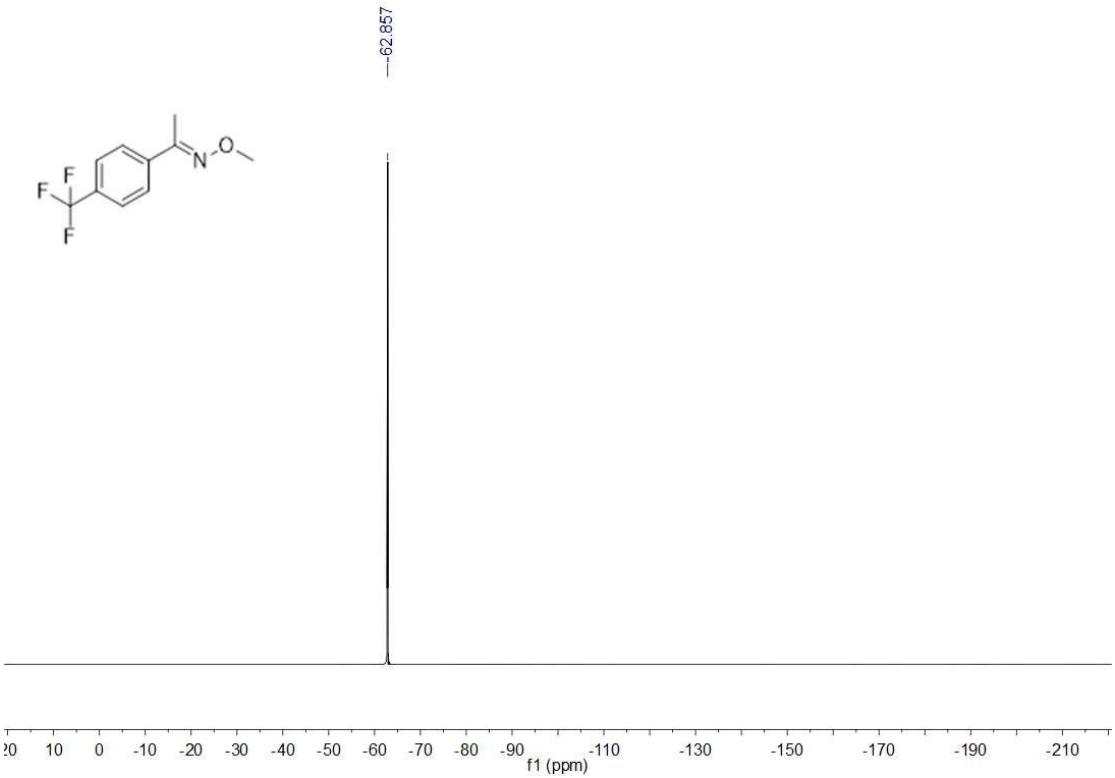
^{1}H NMR (125MHz, $CDCl_3$)



^{13}C NMR (125MHz, $CDCl_3$)

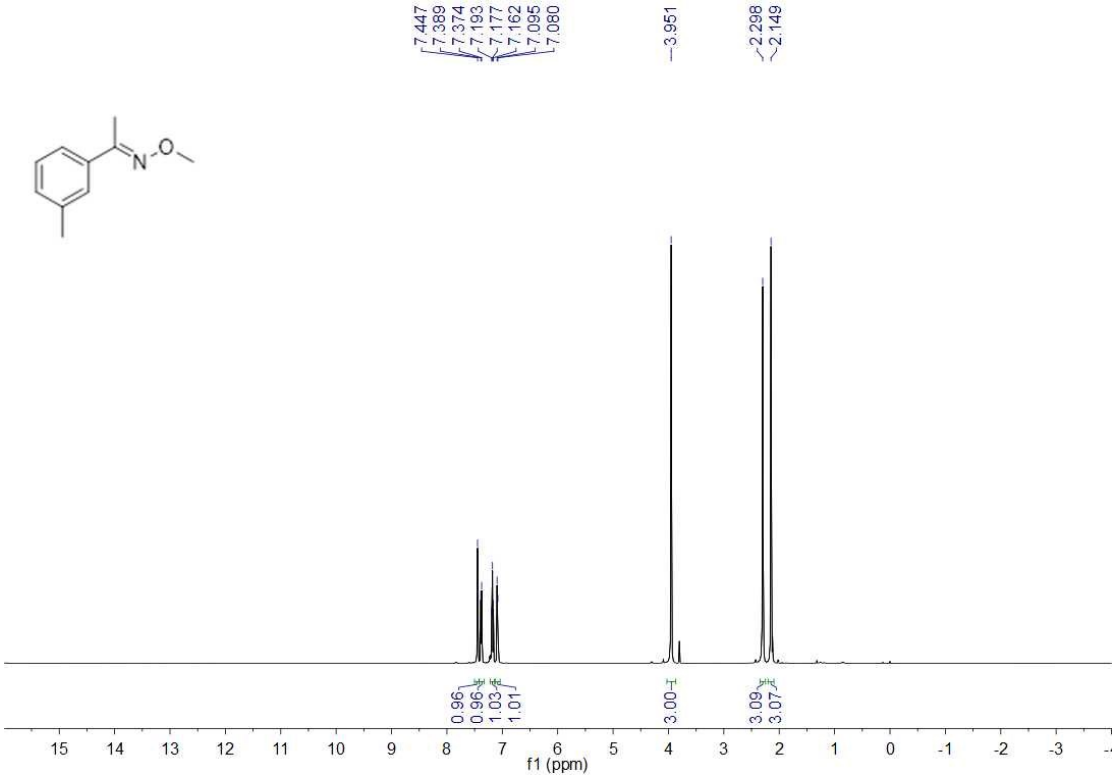


^{19}F NMR (471MHz, $CDCl_3$)

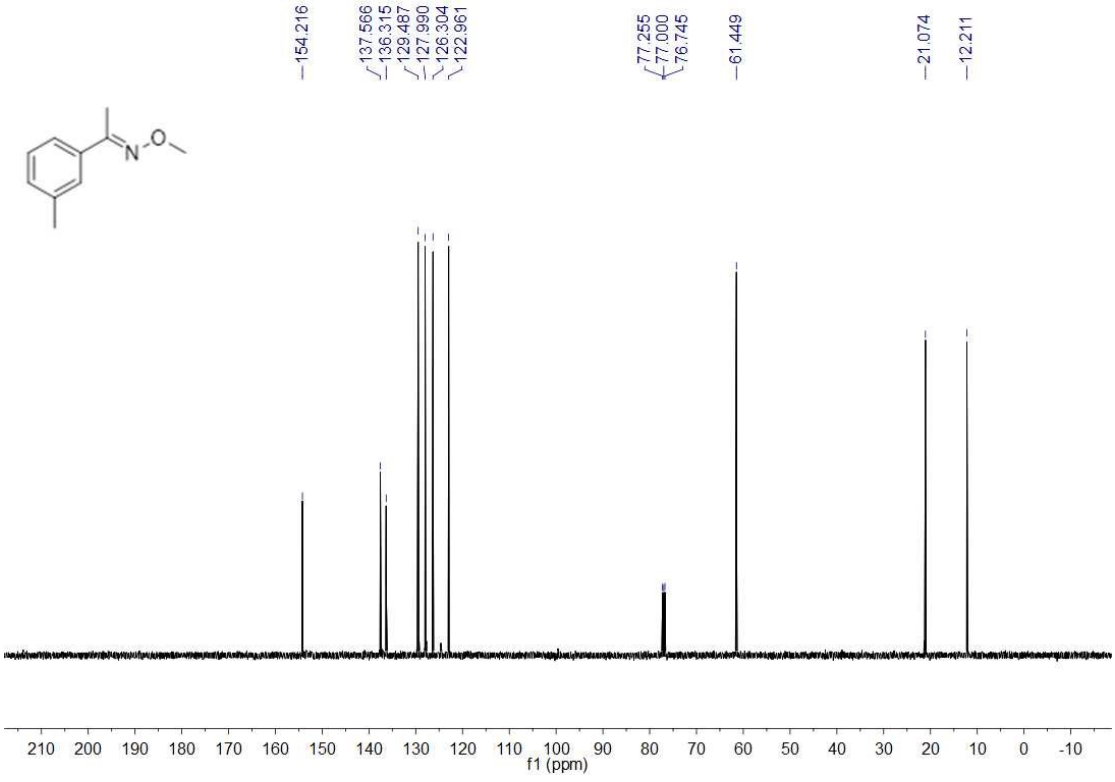

-62.857
F
F
F
N
O
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-110
-130
-150
-170
-190
-210
f1 (ppm)

(*E*)-1-(m-tolyl)ethan-1-one O-methyl oxime (1g)

^{1}H NMR (125MHz, $CDCl_3$)

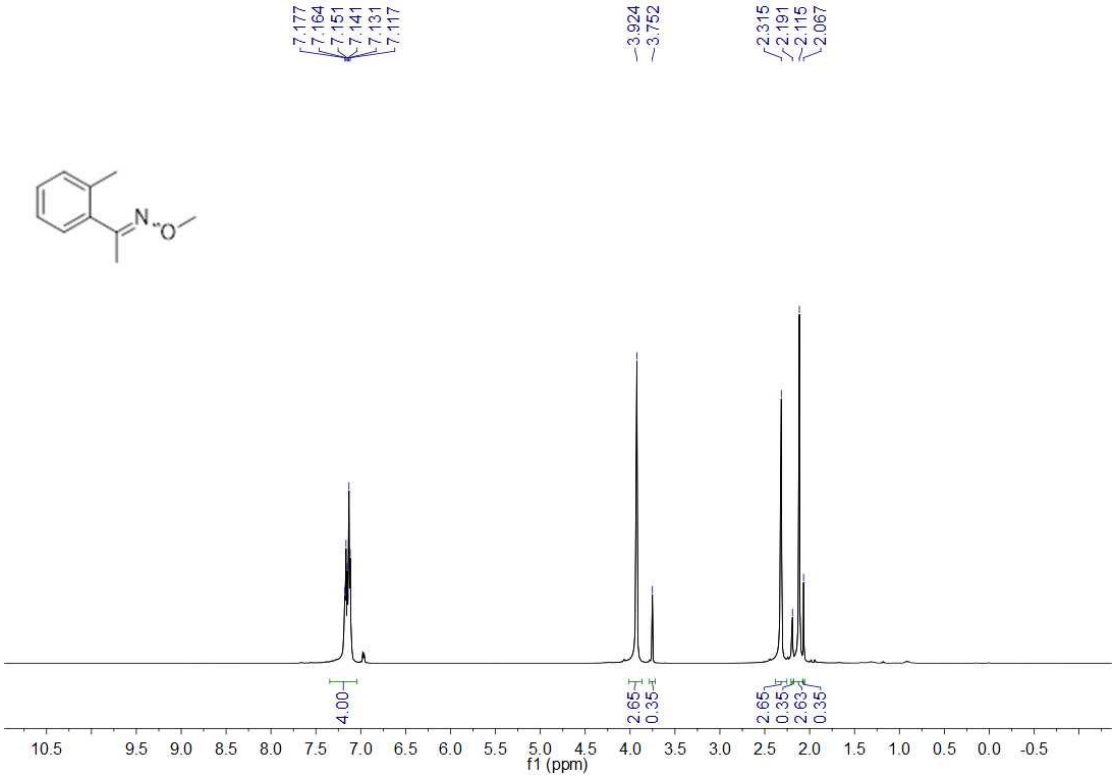


^{13}C NMR (125MHz, $CDCl_3$)

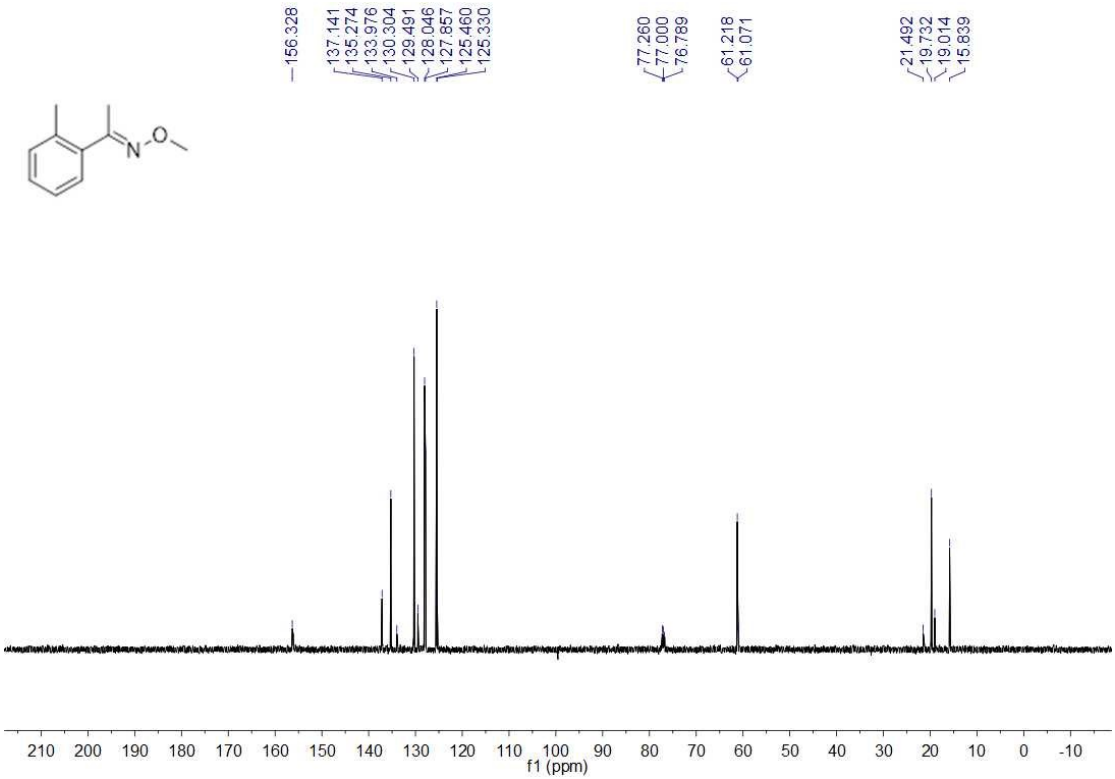


1-(o-tolyl)ethan-1-one O-methyl oxime (1i)

^{1}H NMR (125MHz, $CDCl_3$)

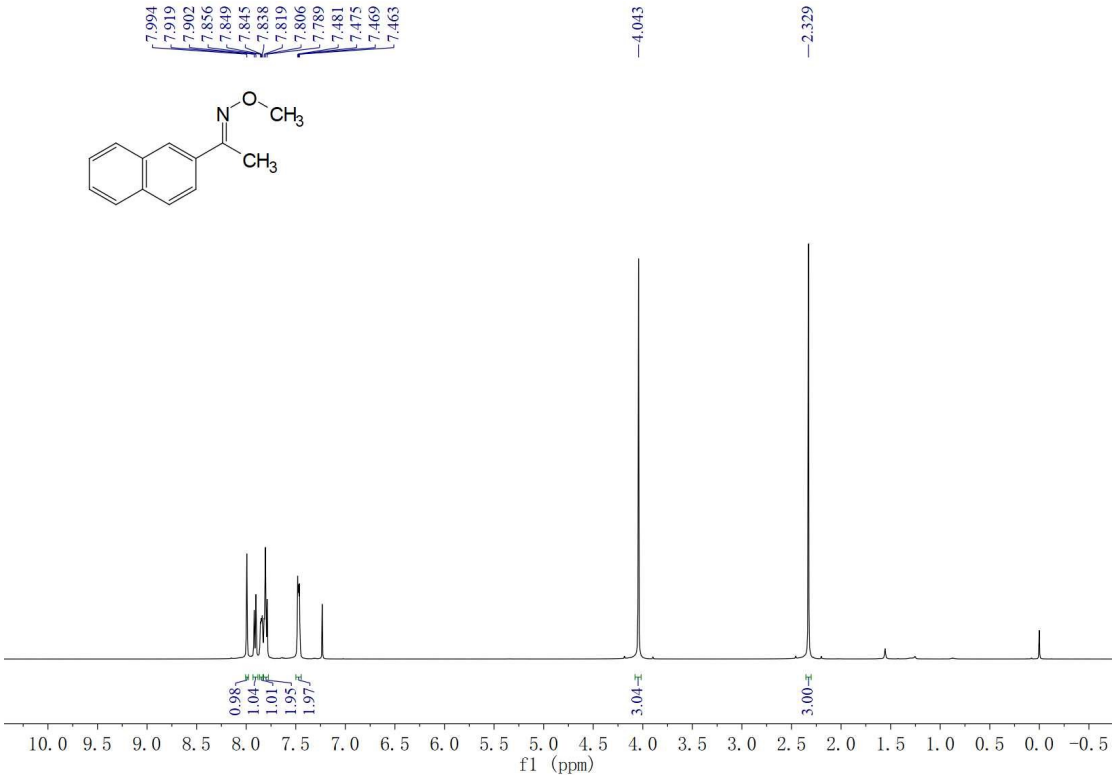


^{13}C NMR (125MHz, $CDCl_3$)

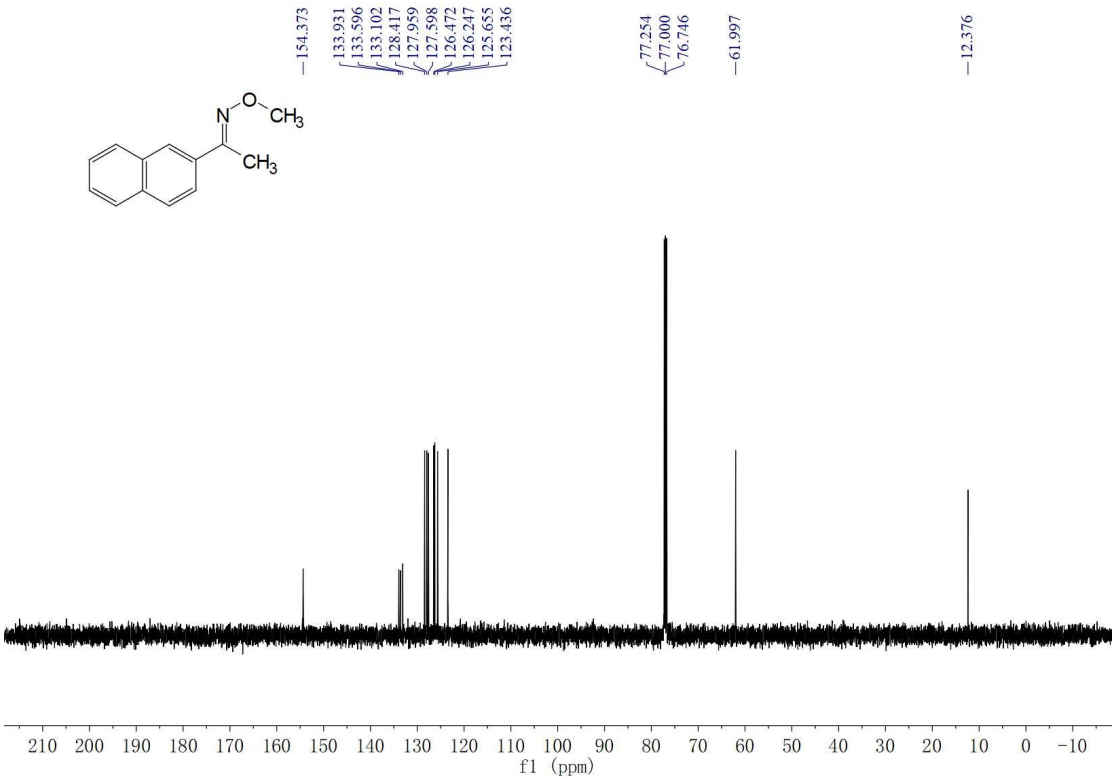


(*E*)-1-(Naphthalen-2-yl)ethan-1-one *O*-methyl oxime (1j):

^{1}H NMR (500 MHz, $CDCl_3$)

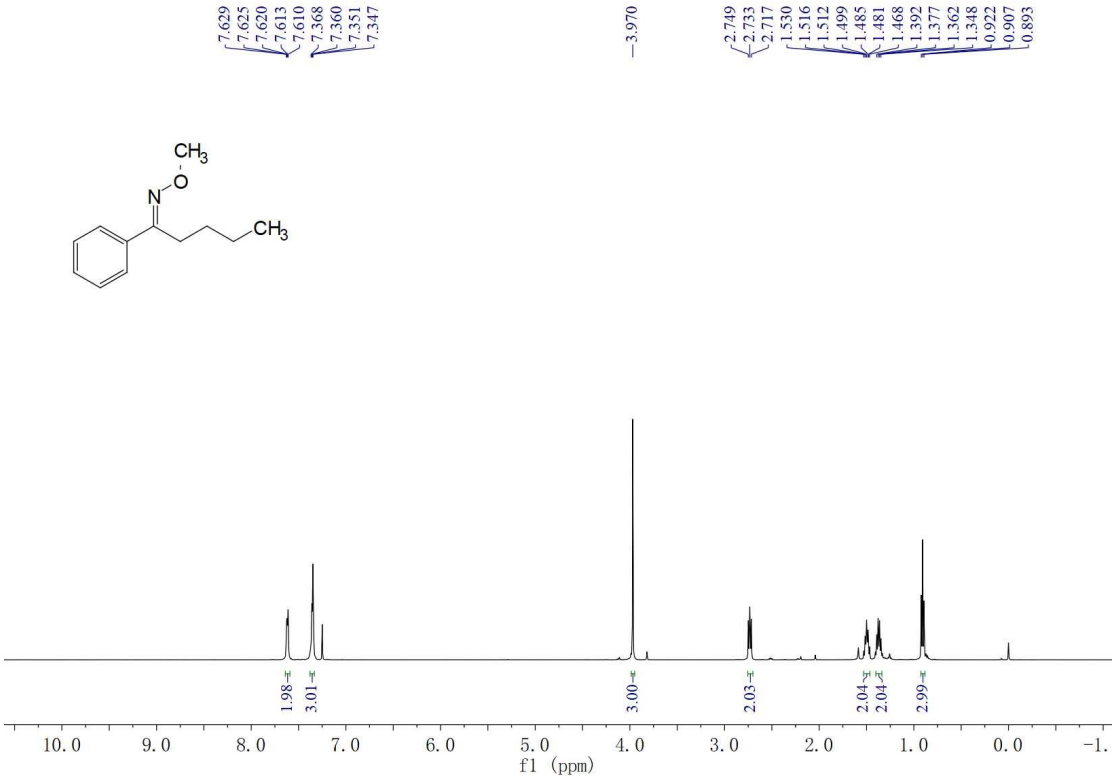


^{13}C NMR (125 MHz, $CDCl_3$)

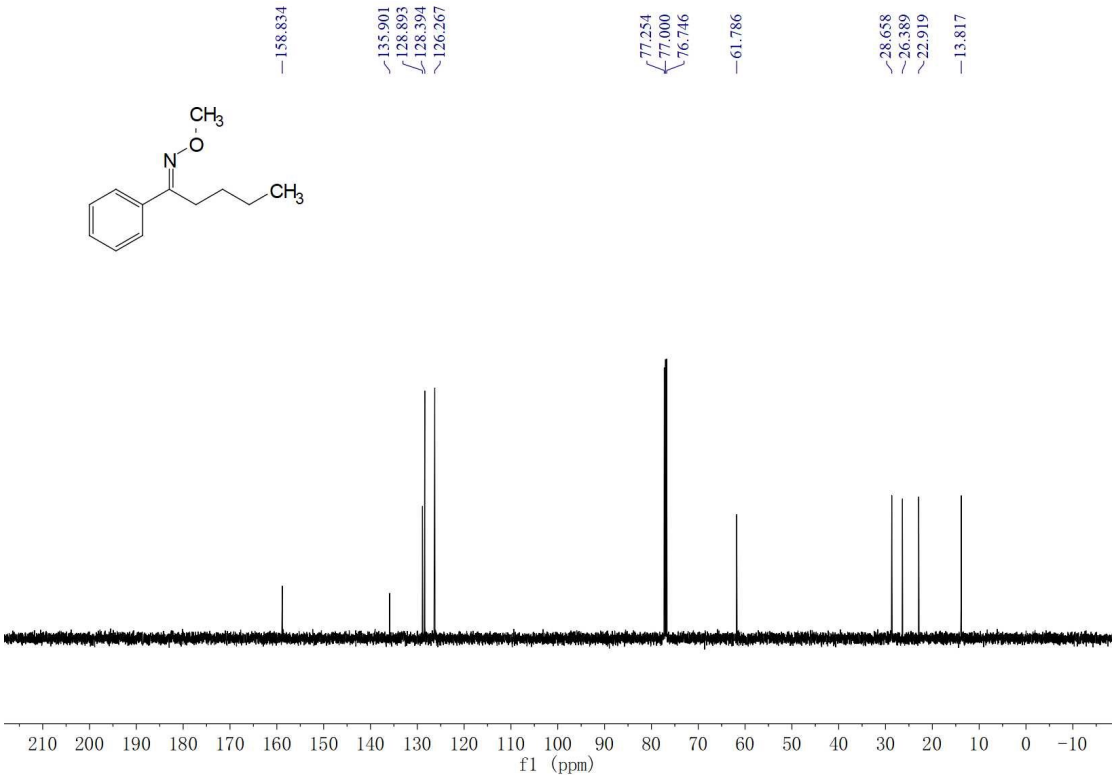


(*E*)-1-Phenylpentan-1-one *O*-methyl oxime (1k):

^{1}H NMR (500 MHz, $CDCl_3$)

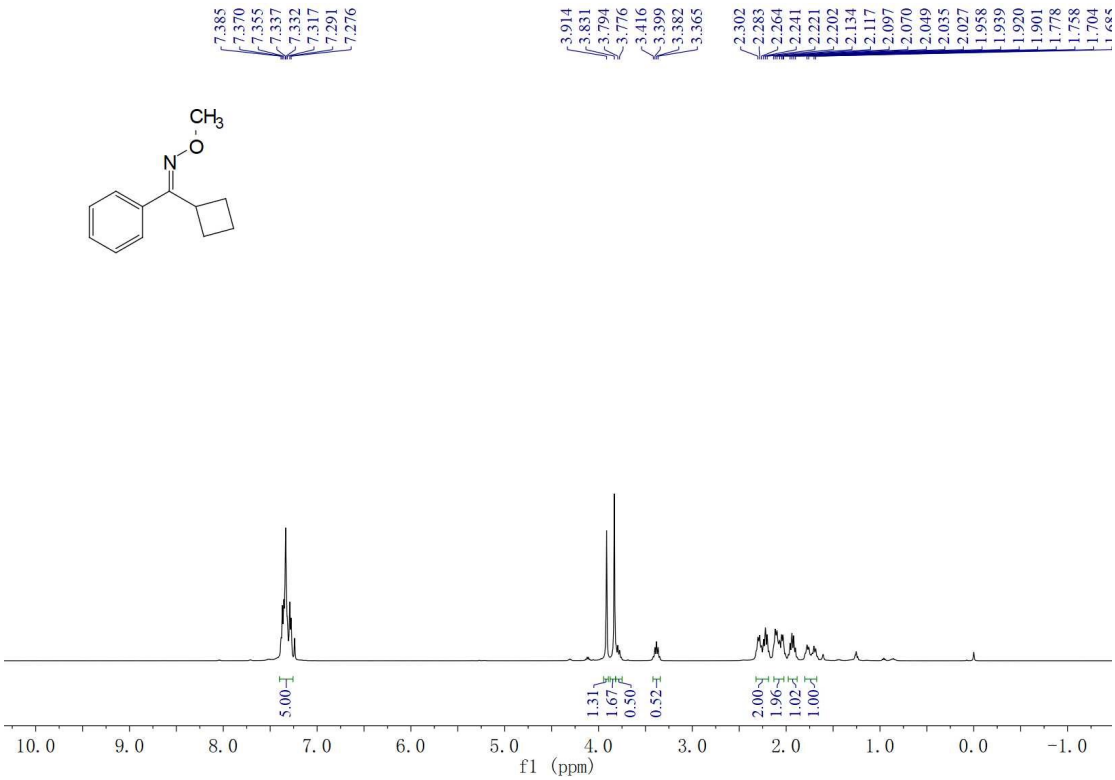


^{13}C NMR (125 MHz, $CDCl_3$)

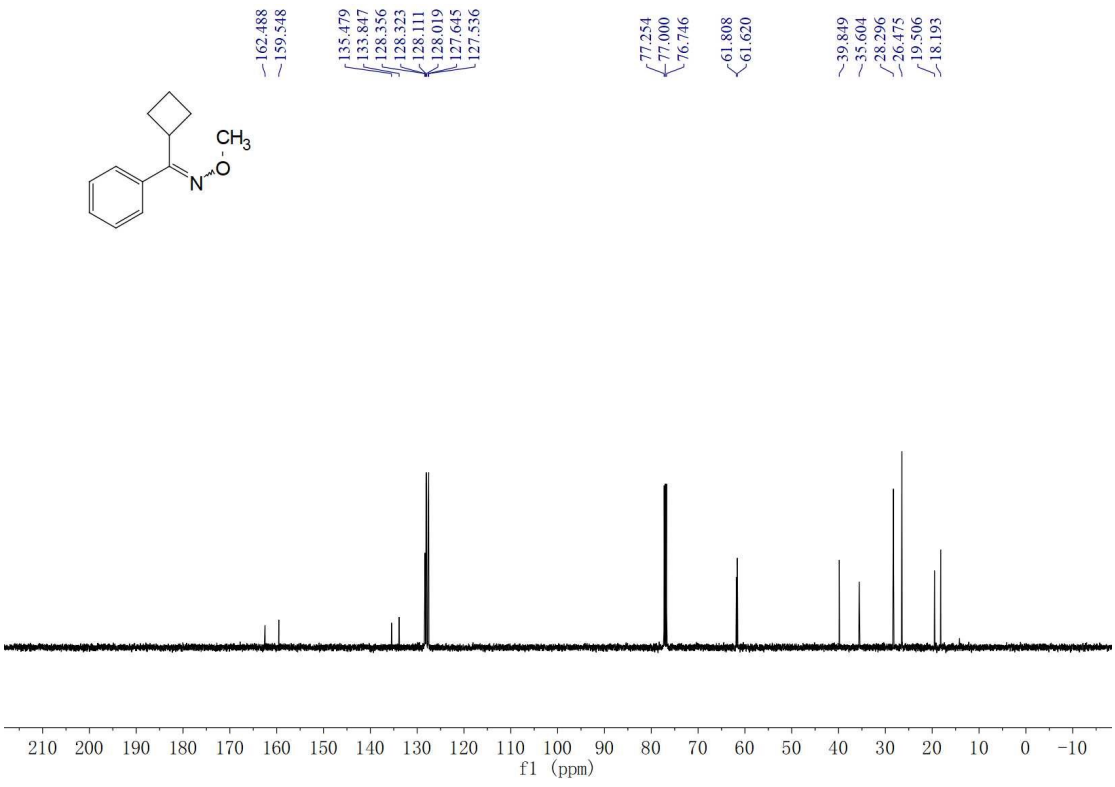


Cyclobutyl(phenyl)methanone *O*-methyl oxime (1l):

^{1}H NMR (500 MHz, $CDCl_3$)

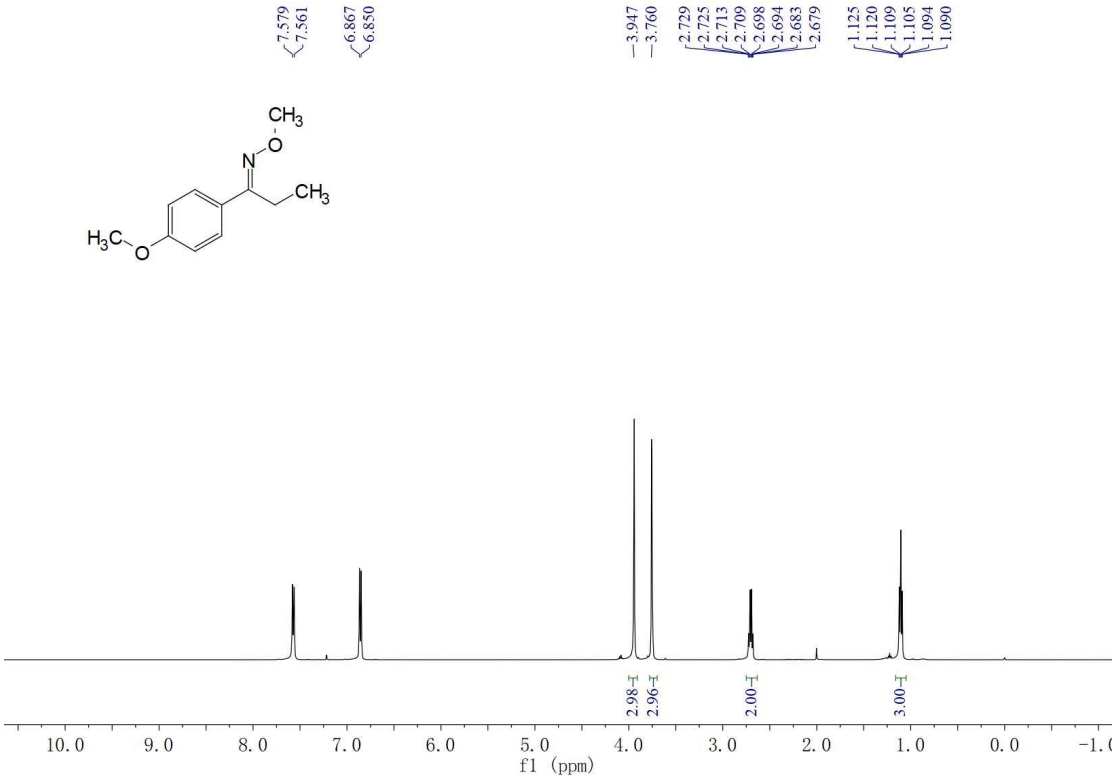


^{13}C NMR (125 MHz, $CDCl_3$)

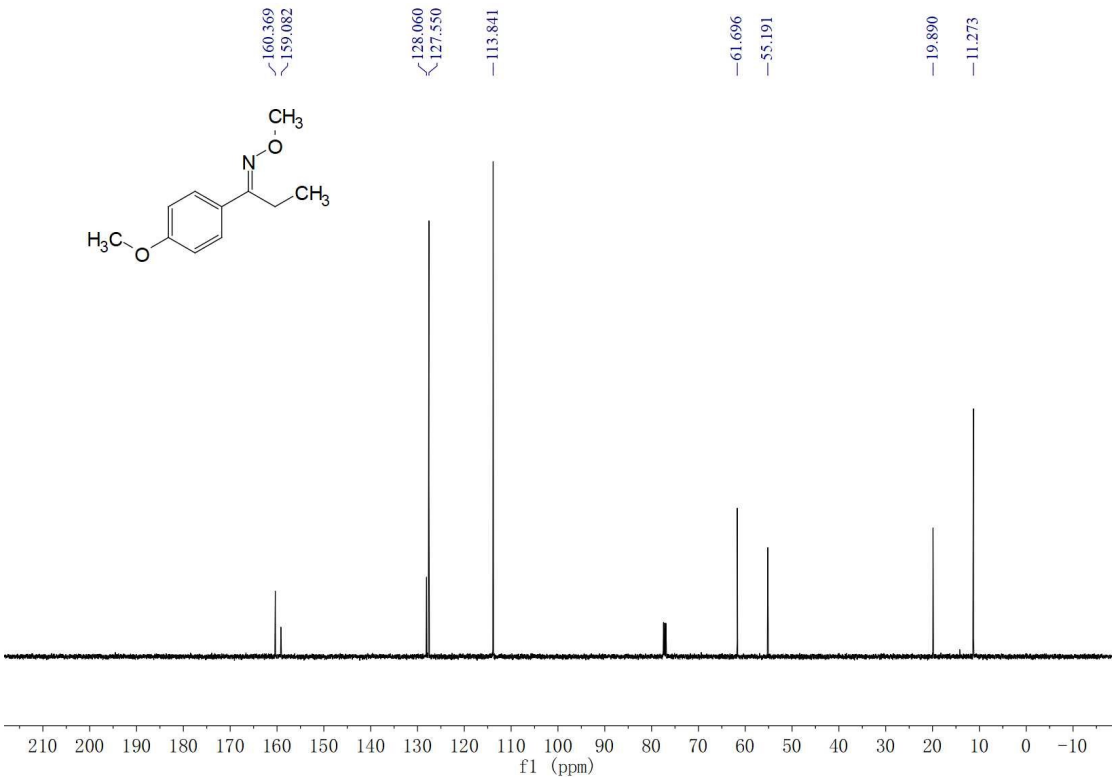


(*E*)-1-(4-methoxyphenyl)propan-1-one *O*-methyl oxime (1m):

^{1}H NMR (500 MHz, $CDCl_3$)

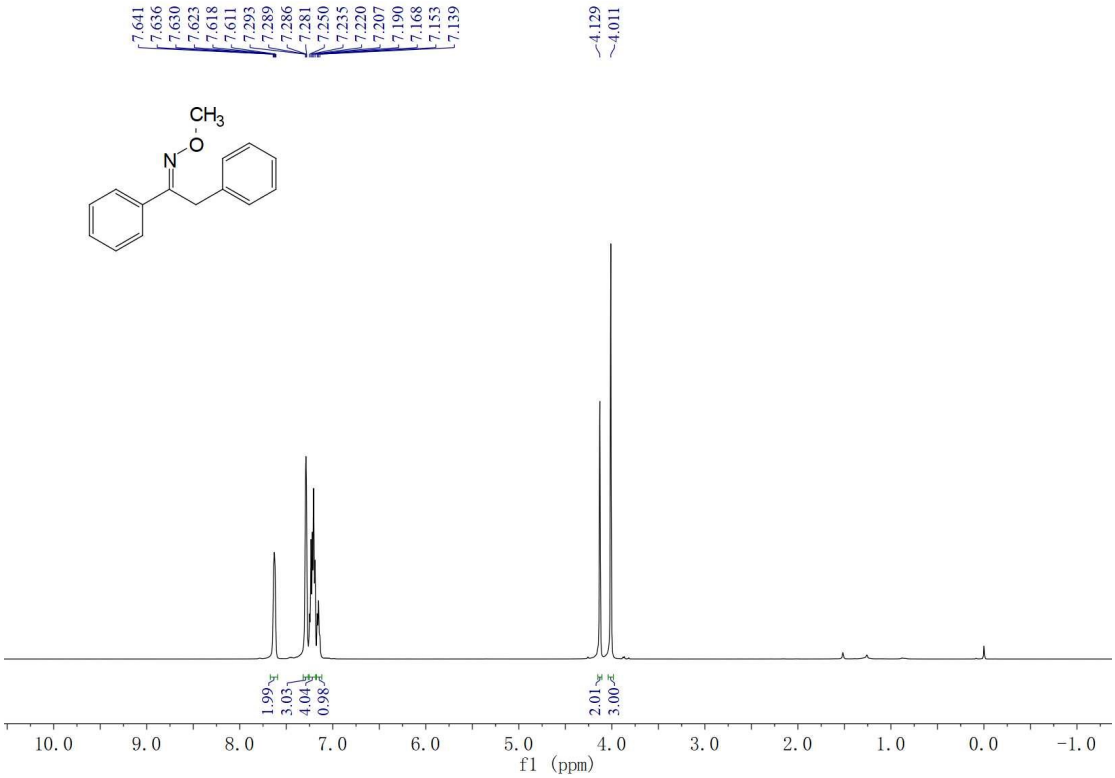


^{13}C NMR (125 MHz, $CDCl_3$)

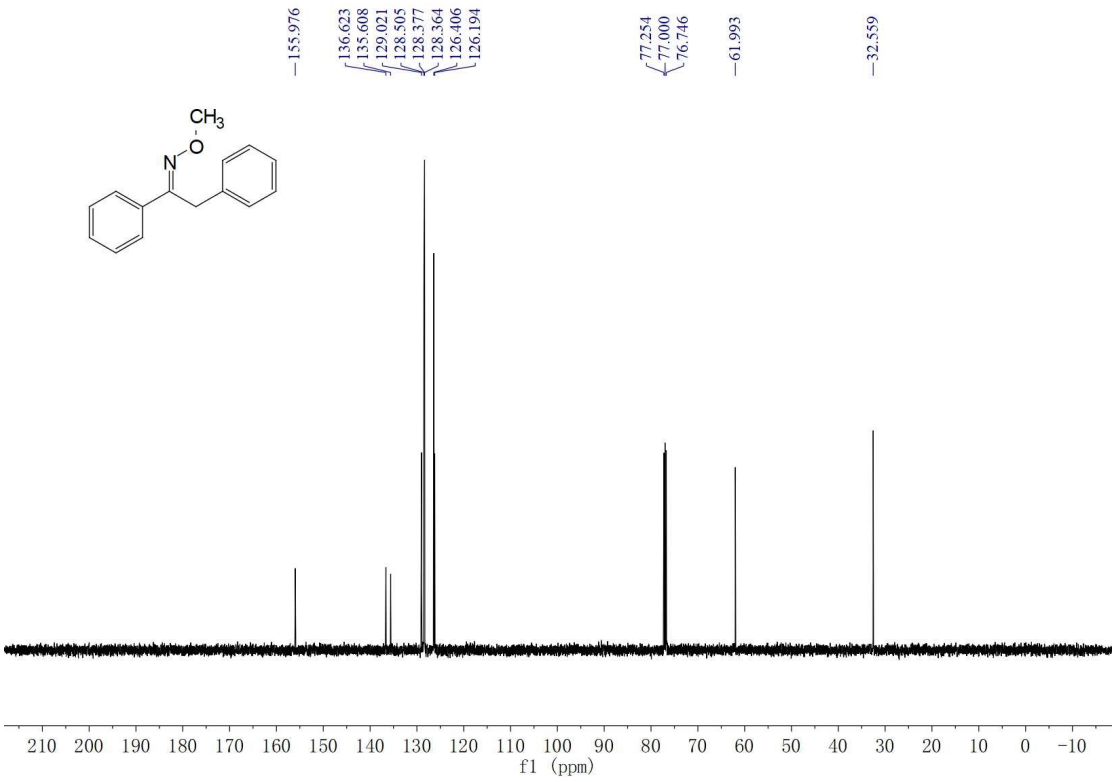


(*E*)-1,2-diphenylethan-1-one *O*-methyl oxime (1n):

^{1}H NMR (500 MHz, $CDCl_3$)

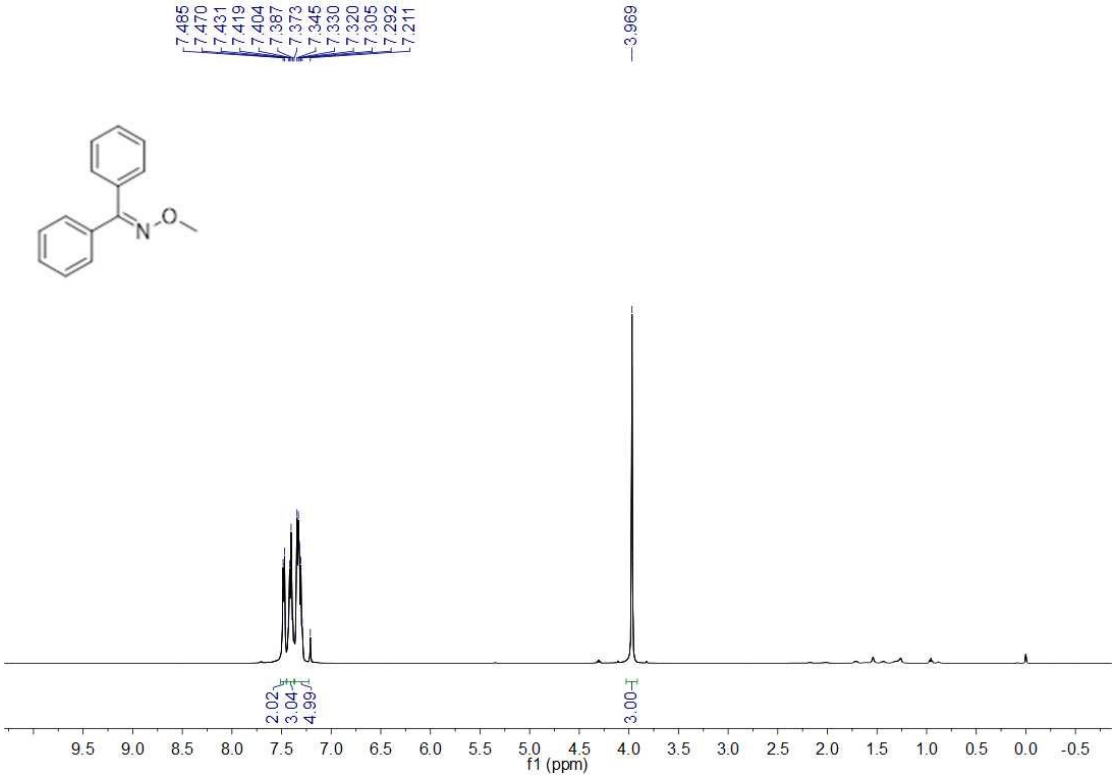


^{13}C NMR (125 MHz, $CDCl_3$)

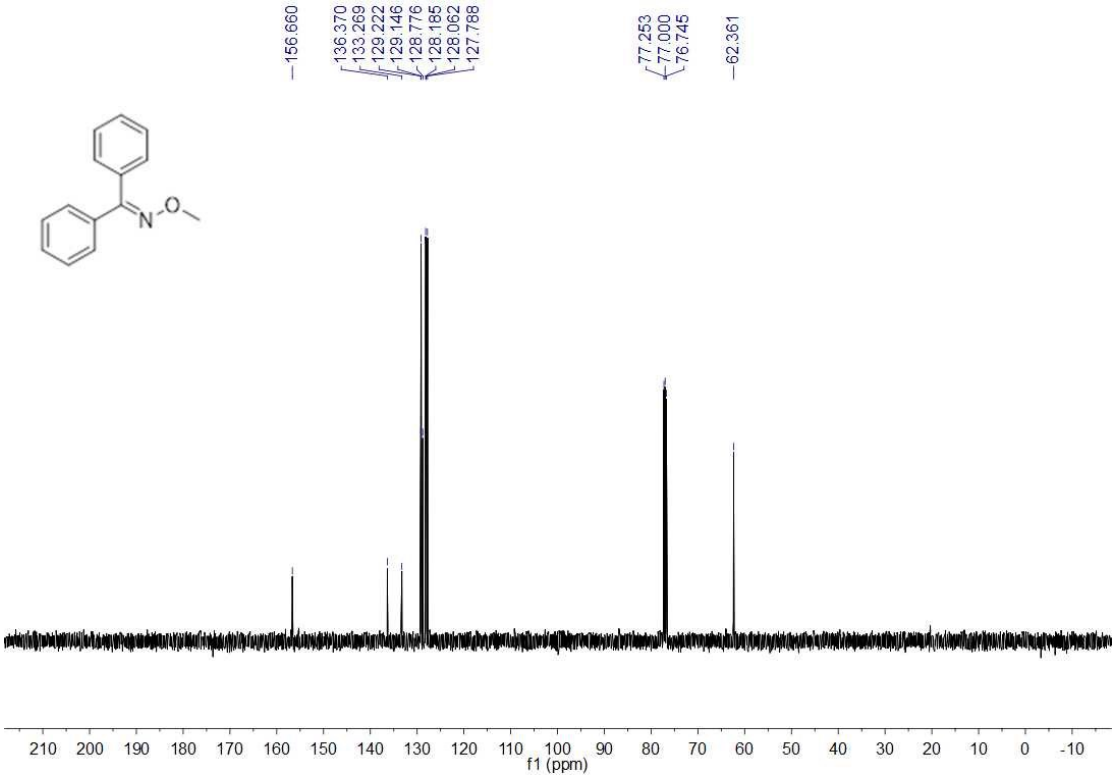


*D*iphenylmethanone O-methyl oxime(1o)

^{1}H NMR (125MHz, $CDCl_3$)

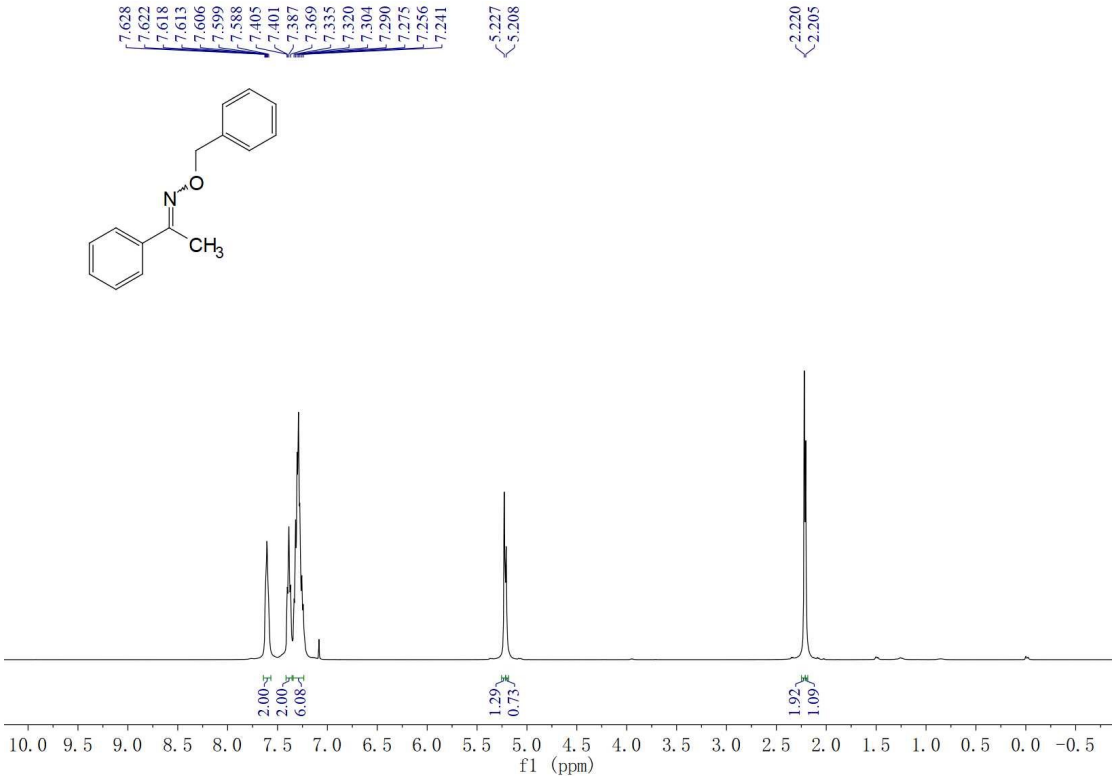


^{13}C NMR (125MHz, $CDCl_3$)

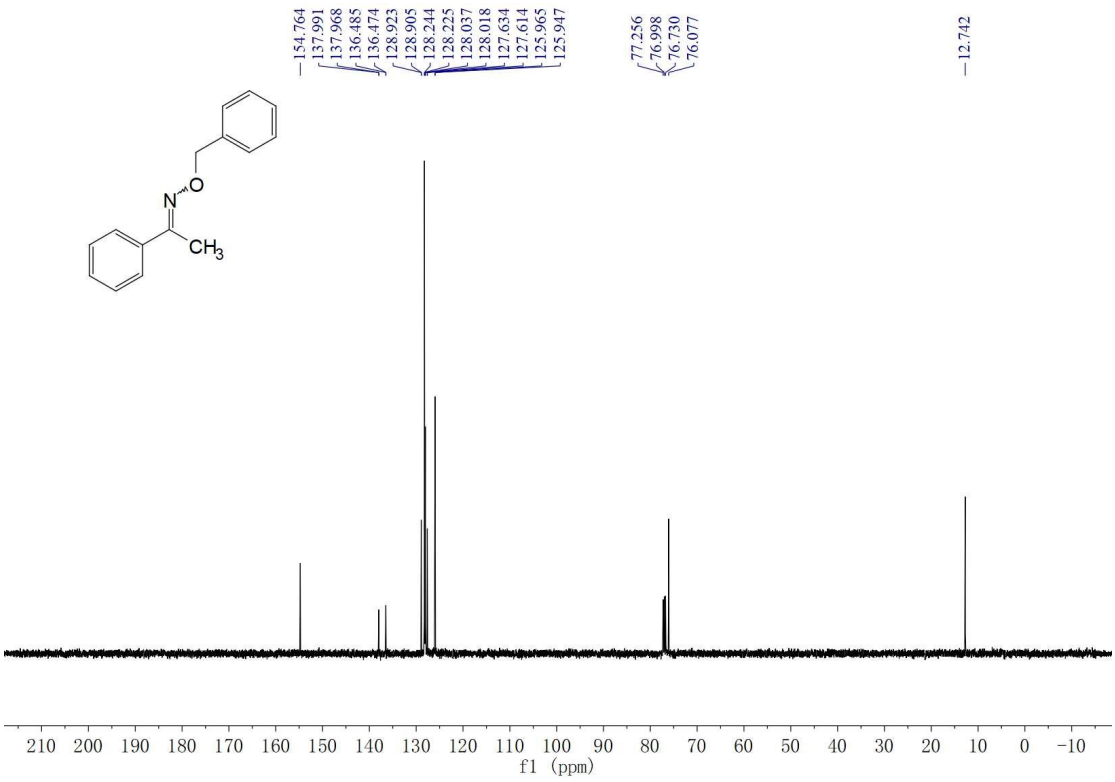


1-Phenylethan-1-one *O*-benzyl oxime (1r):

^{1}H NMR (500 MHz, $CDCl_3$)

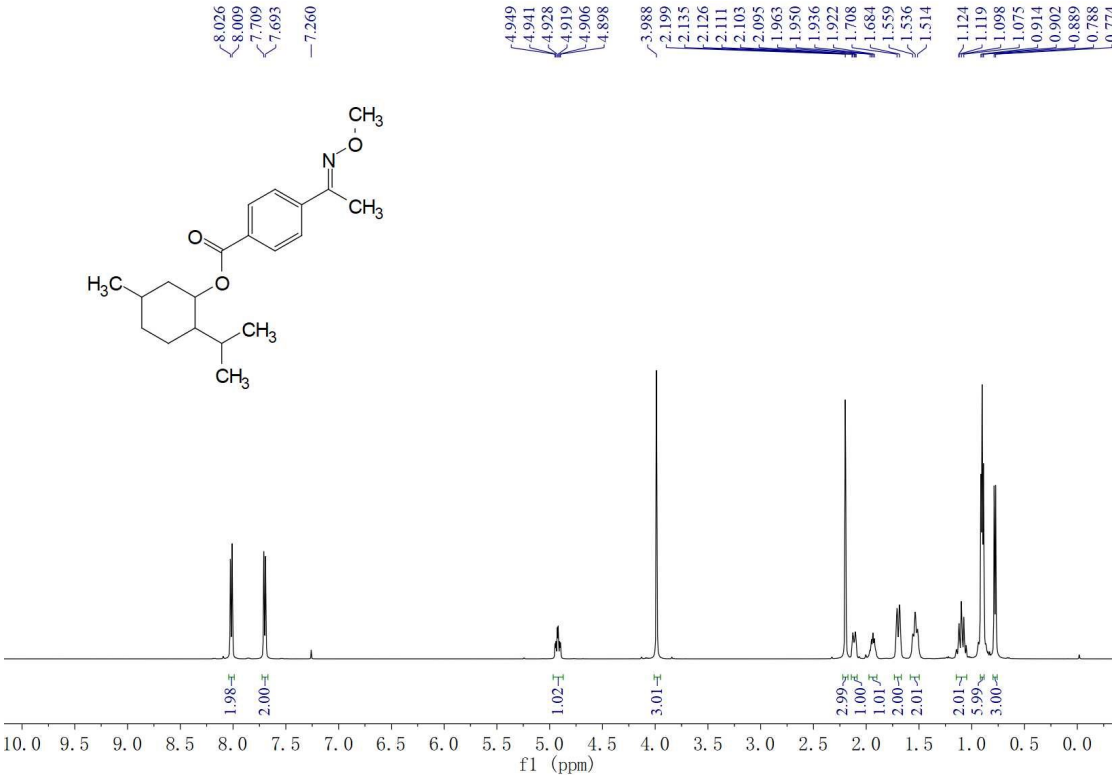


^{13}C NMR (125 MHz, $CDCl_3$)

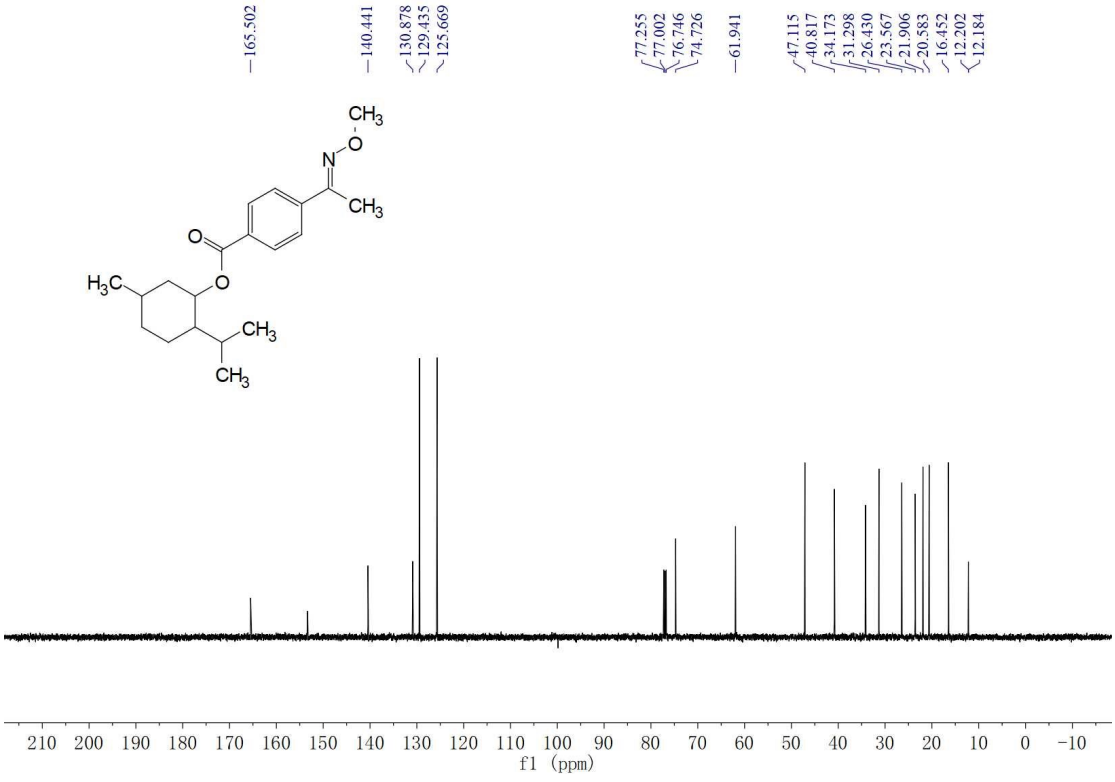


2-Isopropyl-5-methylcyclohexyl (*E*)-4-(1-(methoxyimino)ethyl)benzoate (1s):

^{1}H NMR (500 MHz, $CDCl_3$)

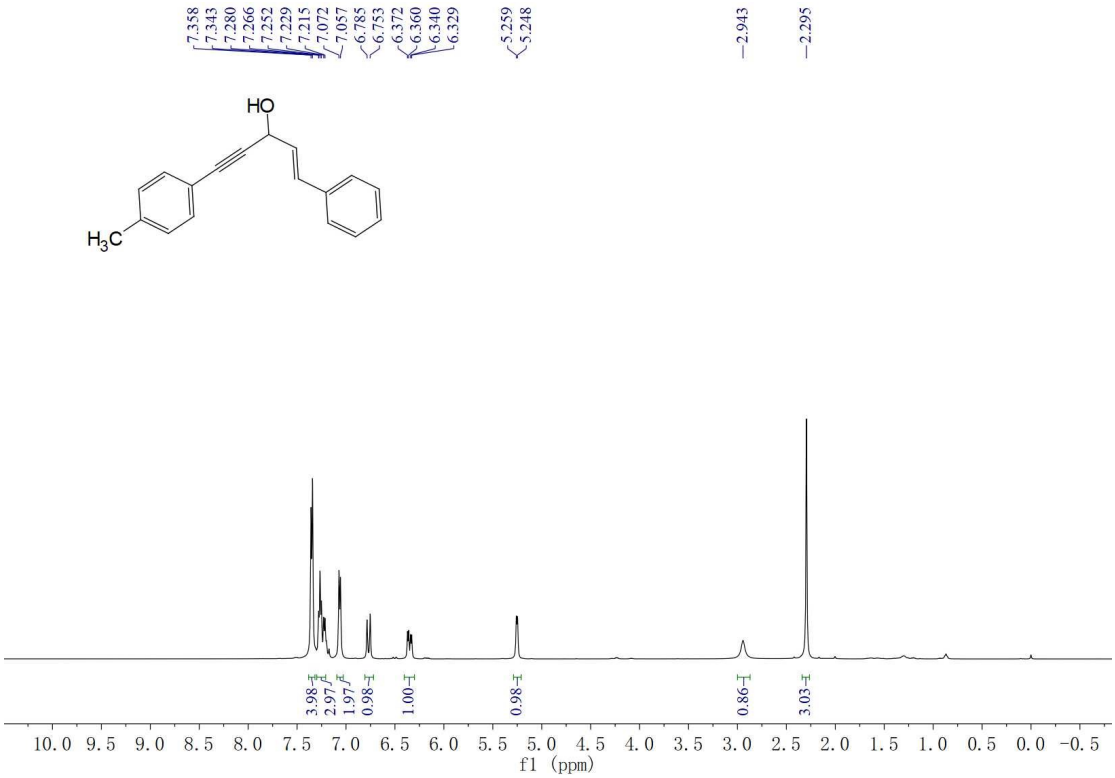


^{13}C NMR (125 MHz, $CDCl_3$)

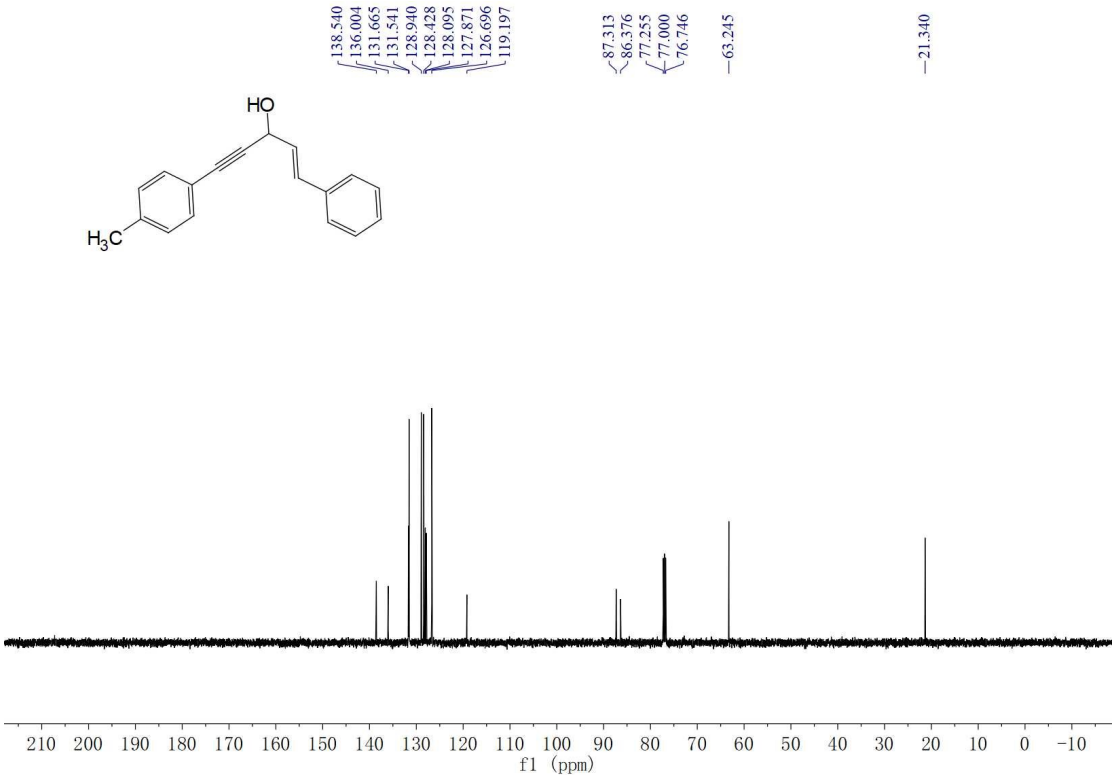


(*E*)-1-Phenyl-5-(p-tolyl)pent-1-en-4-yn-3-ol (2aa-OH):

^{1}H NMR (500 MHz, $CDCl_3$)

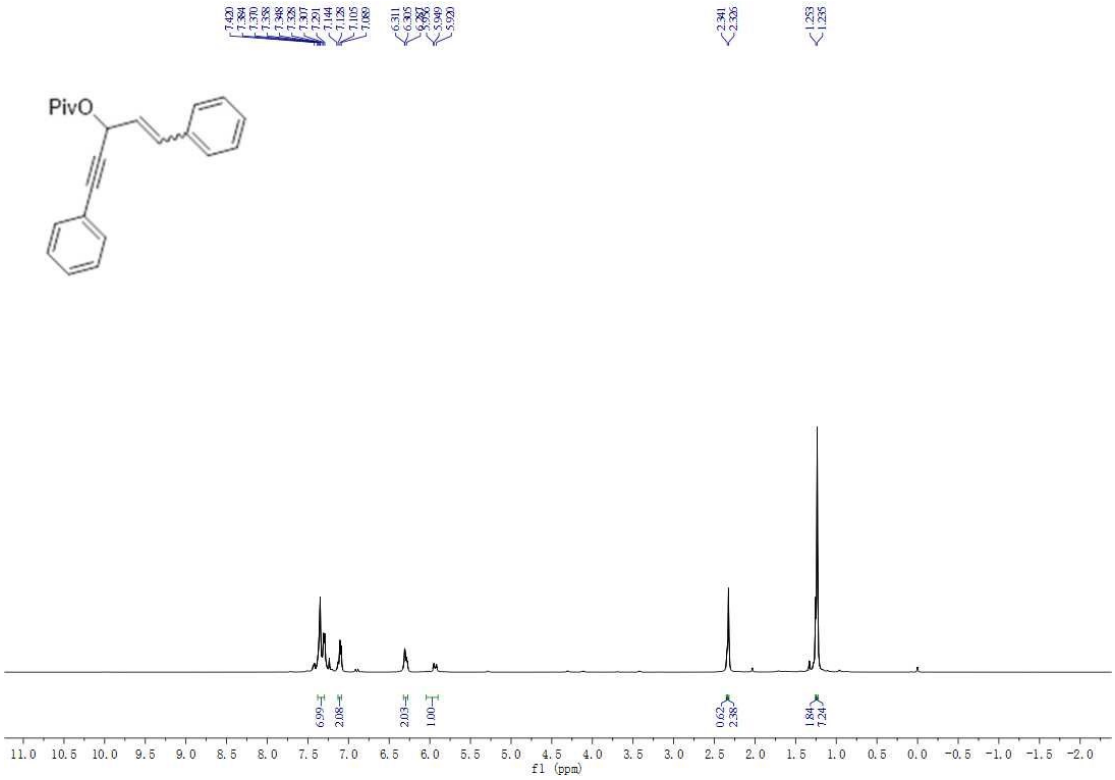


^{13}C NMR (125 MHz, $CDCl_3$)

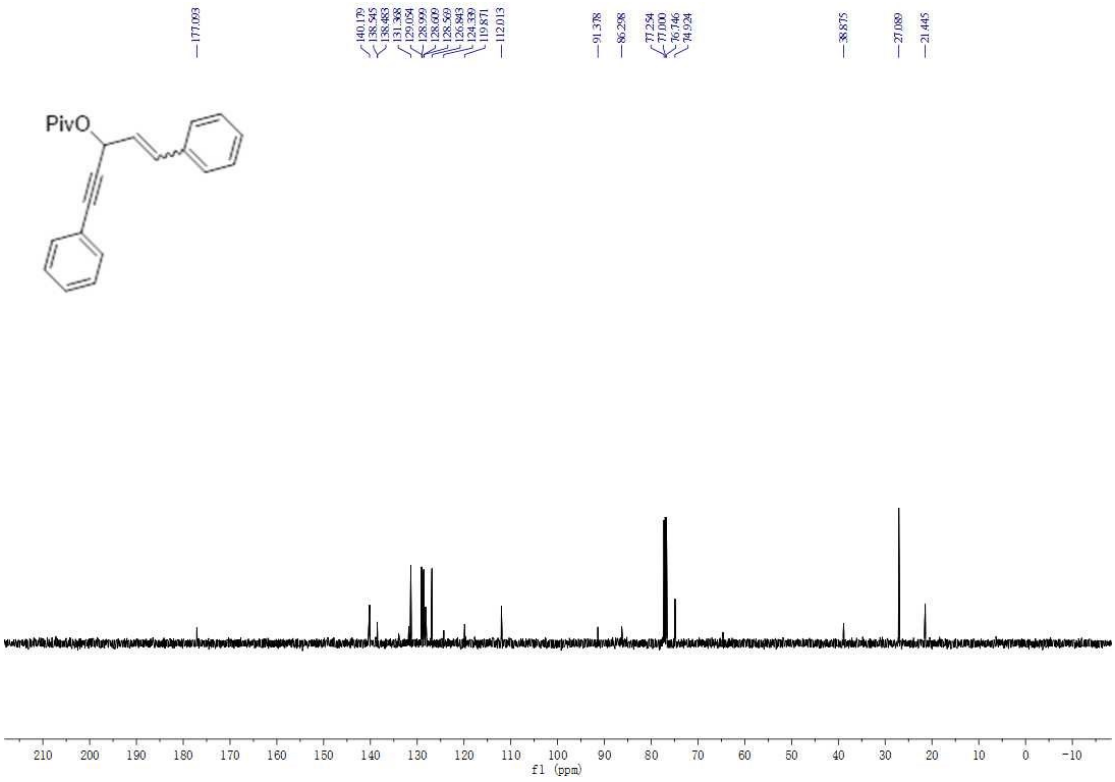


1-Phenyl-5-(p-tolyl)pent-1-en-4-yn-3-yl pivalate (2aaa-OPiv):

^{1}H NMR (500 MHz, $CDCl_3$)

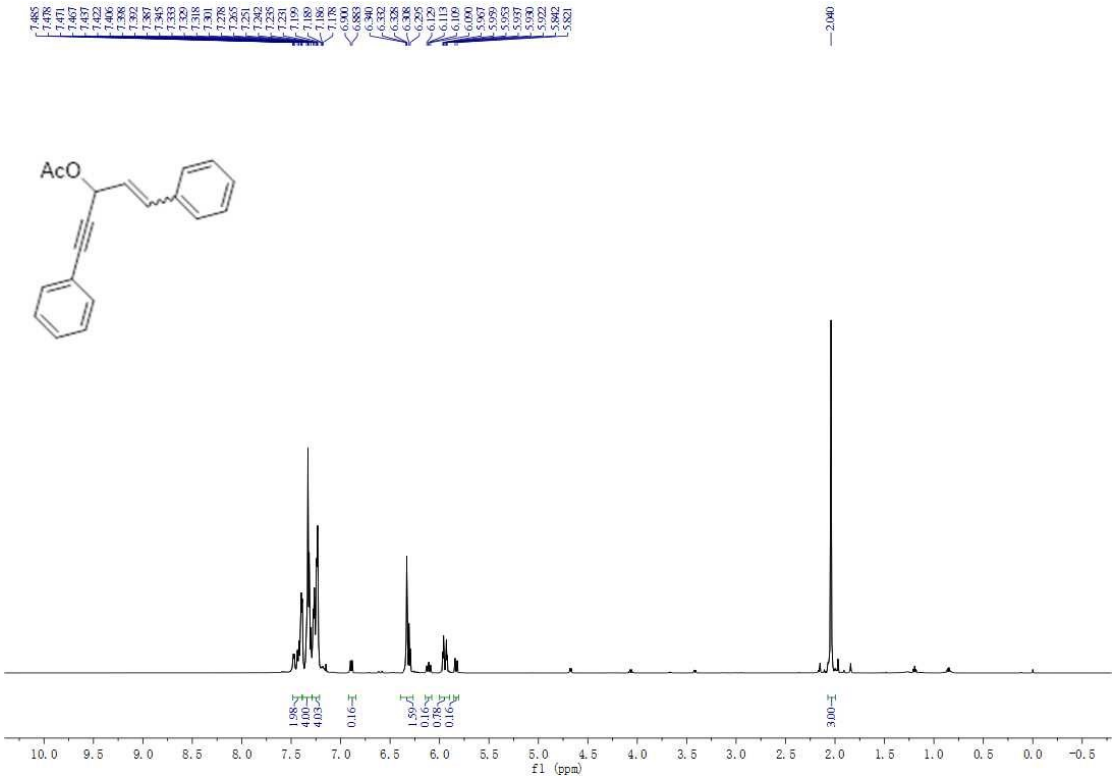


^{13}C NMR (125 MHz, $CDCl_3$)

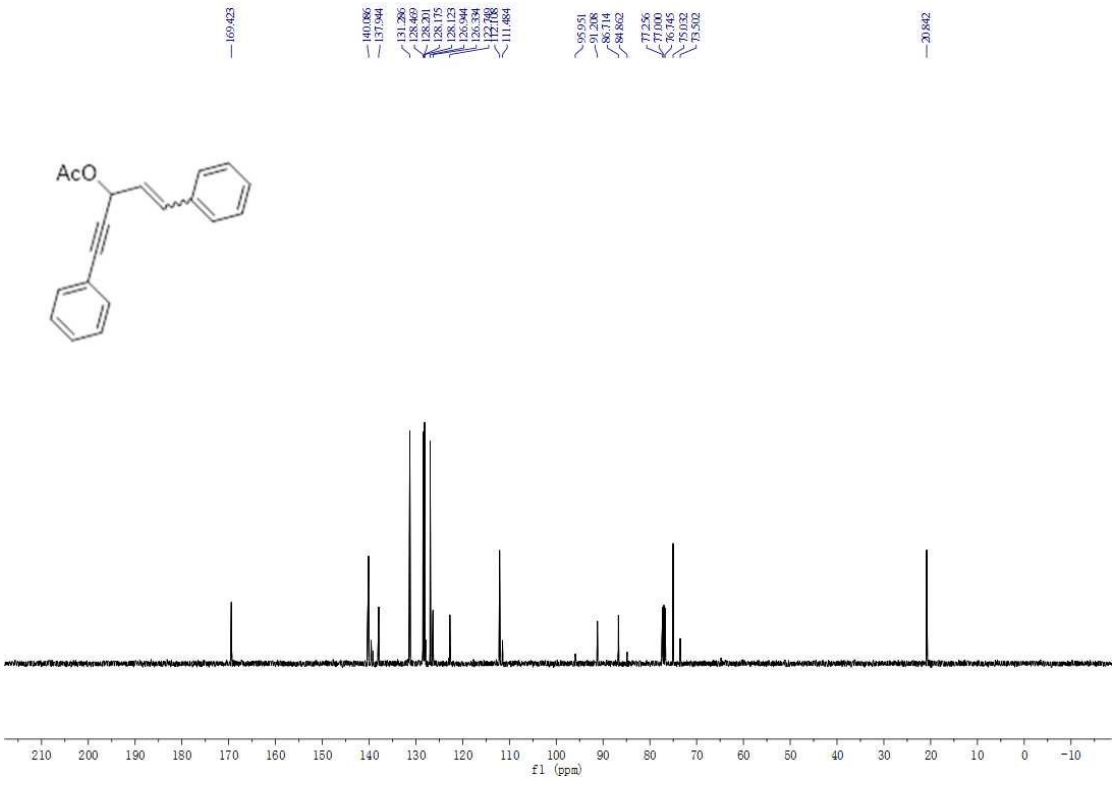


1,5-Diphenylpent-1-en-4-yn-3-yl acetate (2b):

^{1}H NMR (500 MHz, $CDCl_3$)

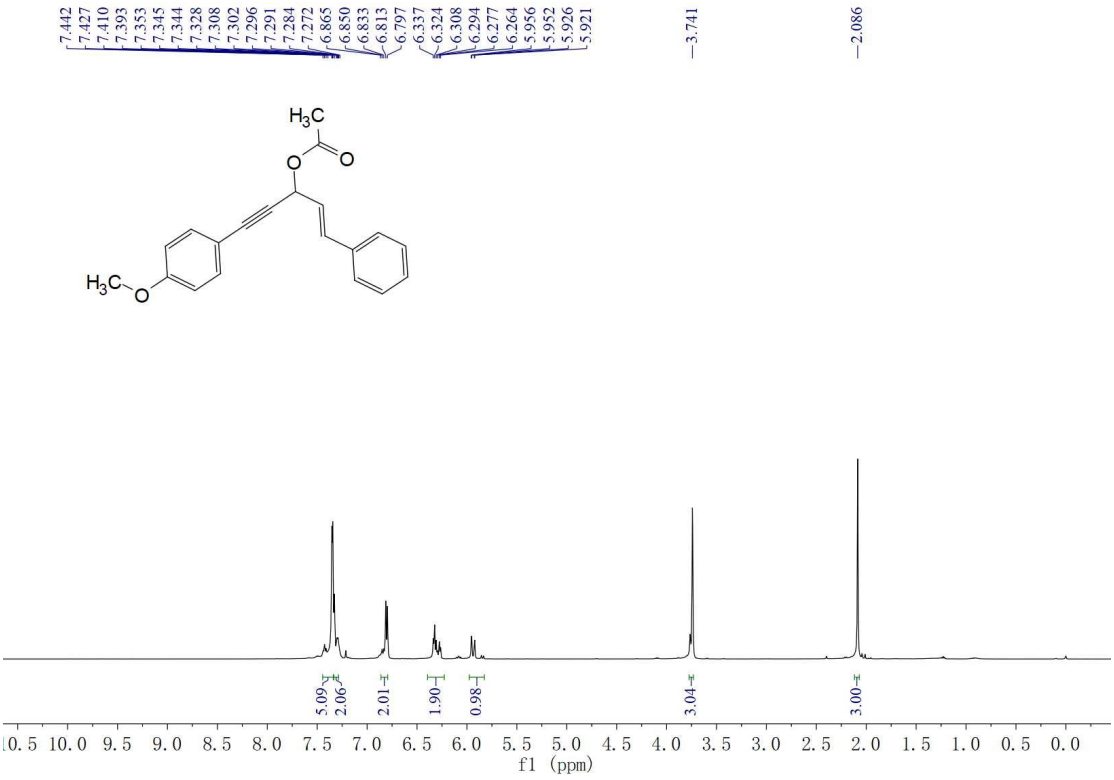


^{13}C NMR (125 MHz, $CDCl_3$)

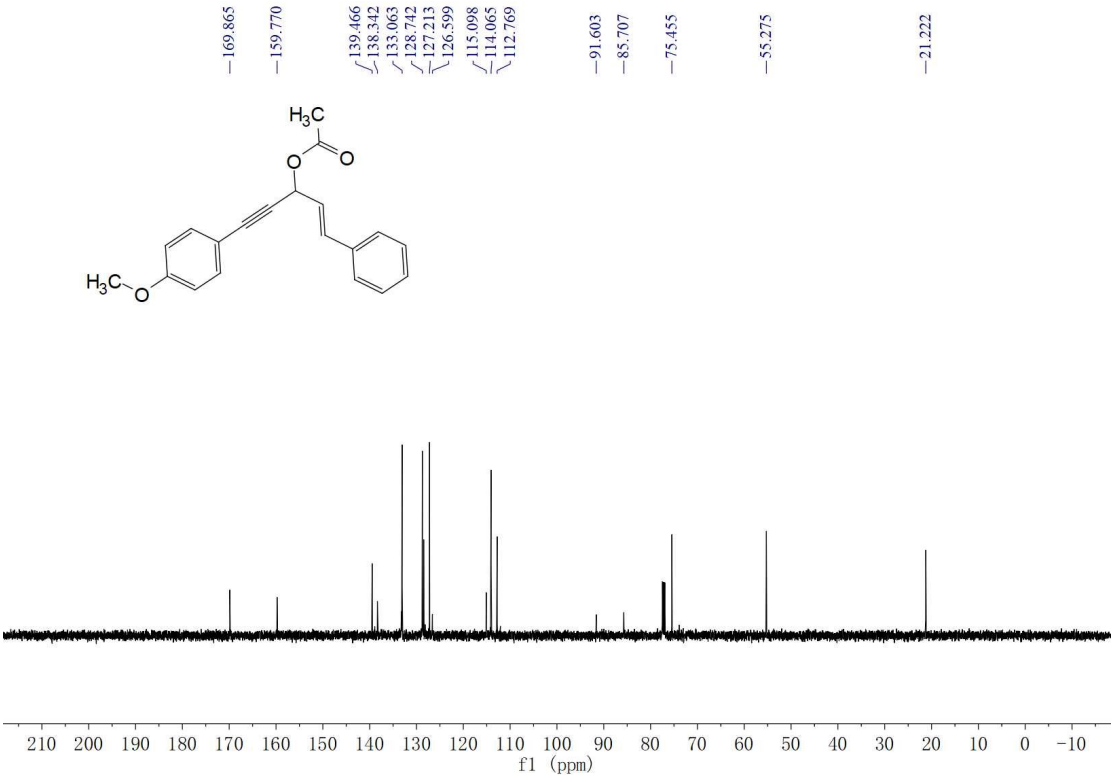


(*E*)-5-(4-methoxyphenyl)-1-phenylpent-1-en-4-yn-3-yl acetate (2d):

^{1}H NMR (500 MHz, $CDCl_3$)

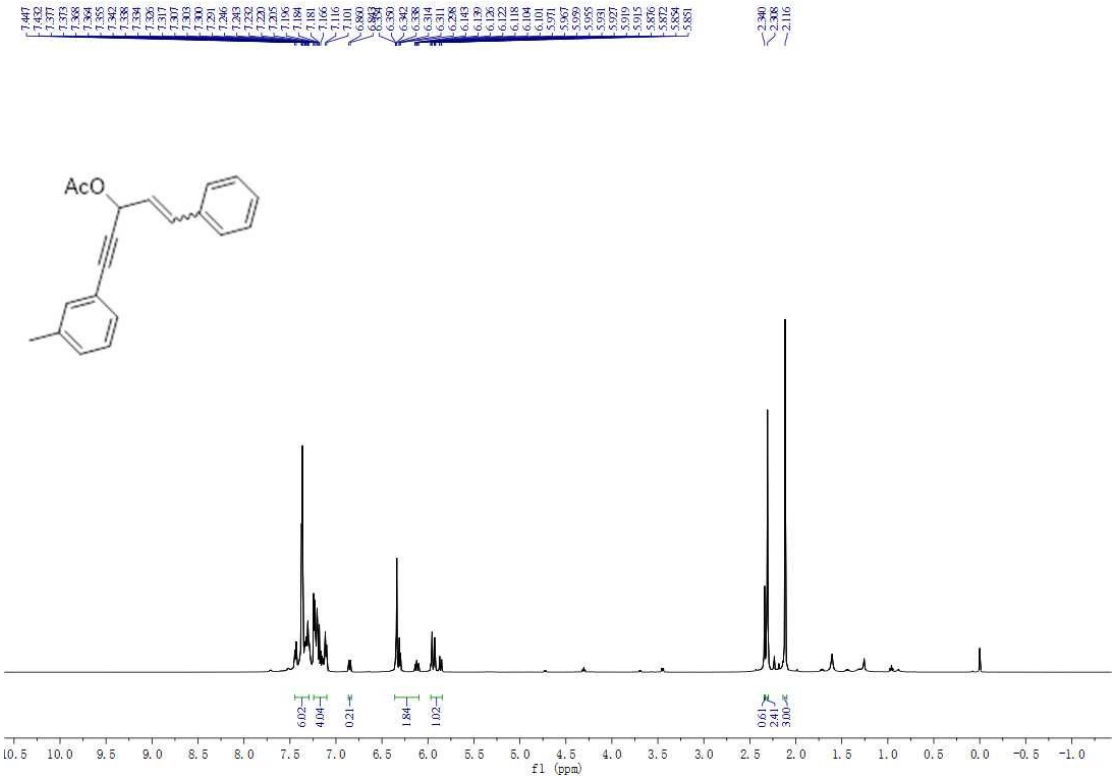


^{13}C NMR (125 MHz, $CDCl_3$)

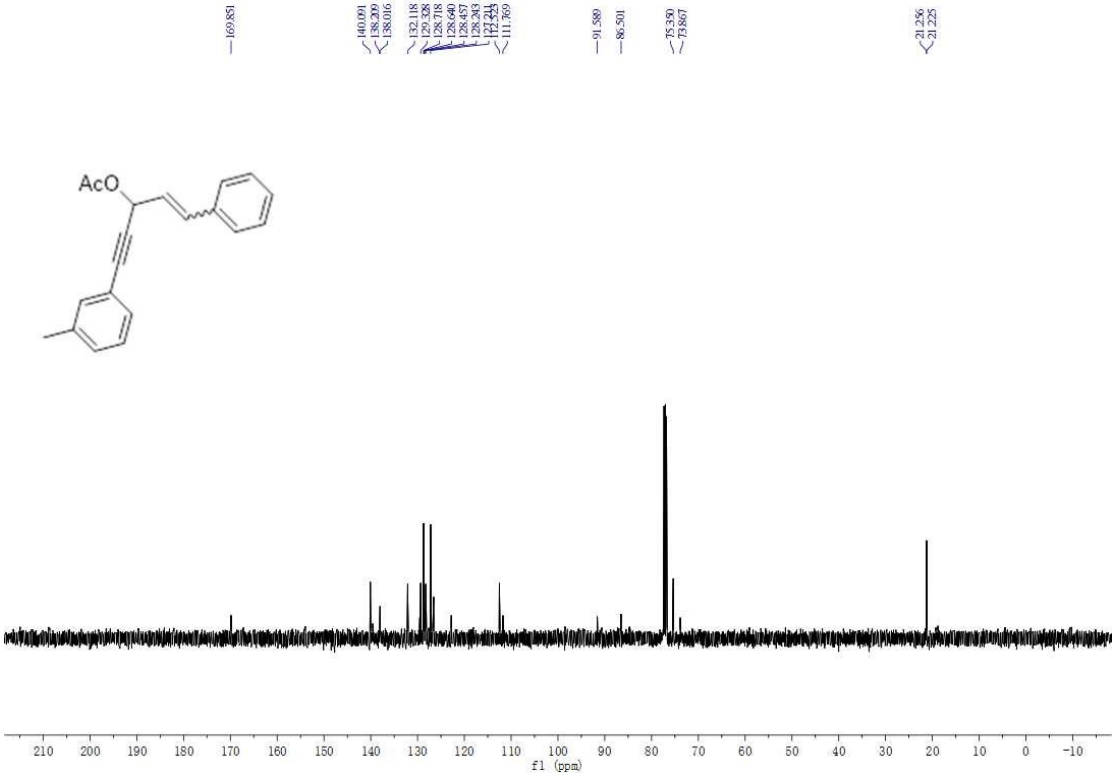


1-phenyl-5-(m-tolyl)pent-1-en-4-yn-3-yl acetate (2h):

^{1}H NMR (500 MHz, $CDCl_3$)

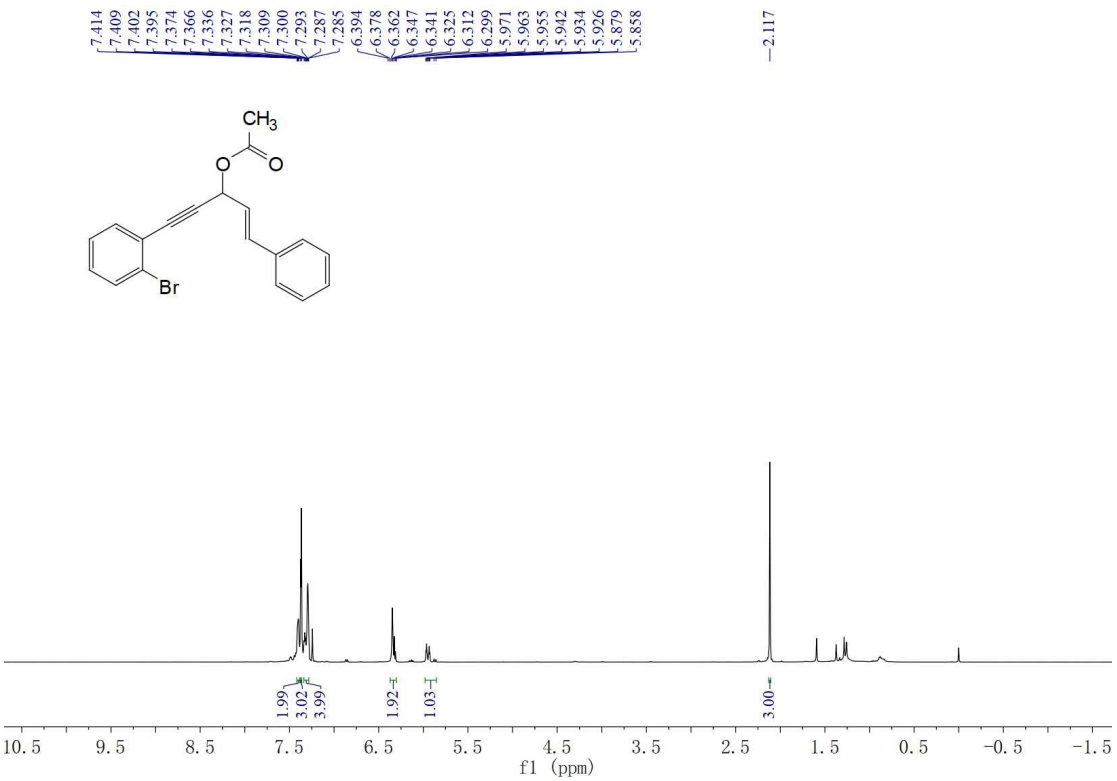


^{13}C NMR (125 MHz, $CDCl_3$)

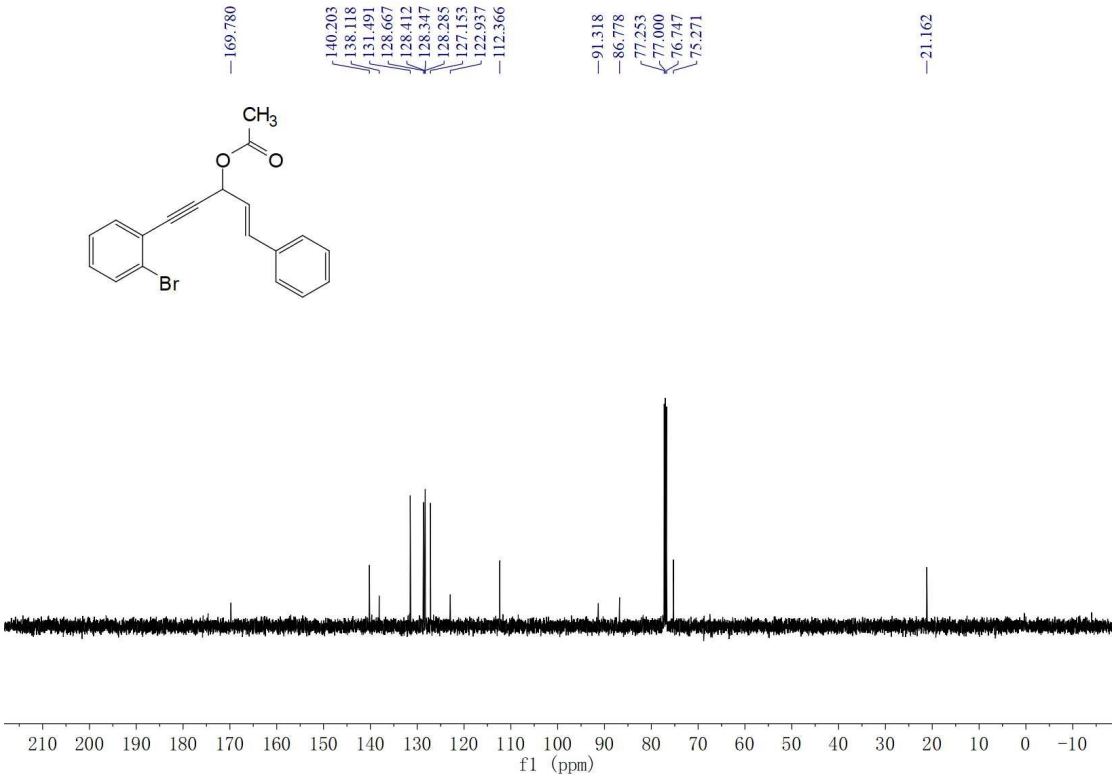


(*E*)-5-(2-bromophenyl)-1-phenylpent-1-en-4-yn-3-yl acetate (2i):

^{1}H NMR (500 MHz, $CDCl_3$)

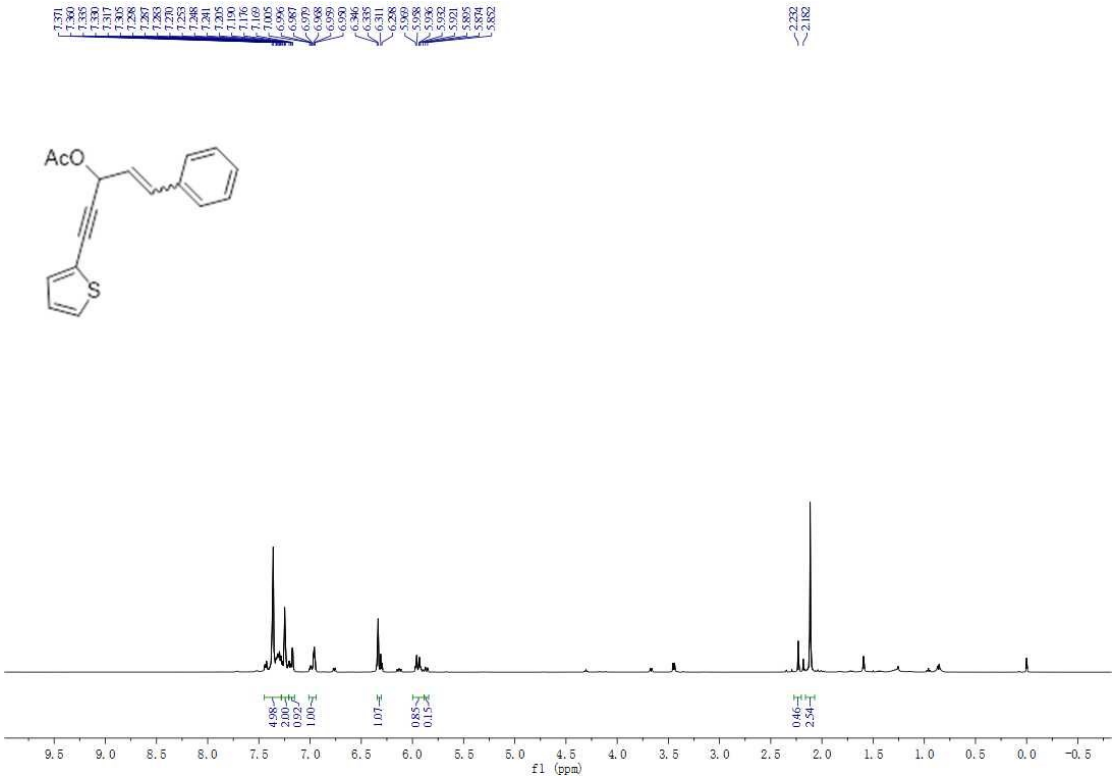


^{13}C NMR (125 MHz, $CDCl_3$)

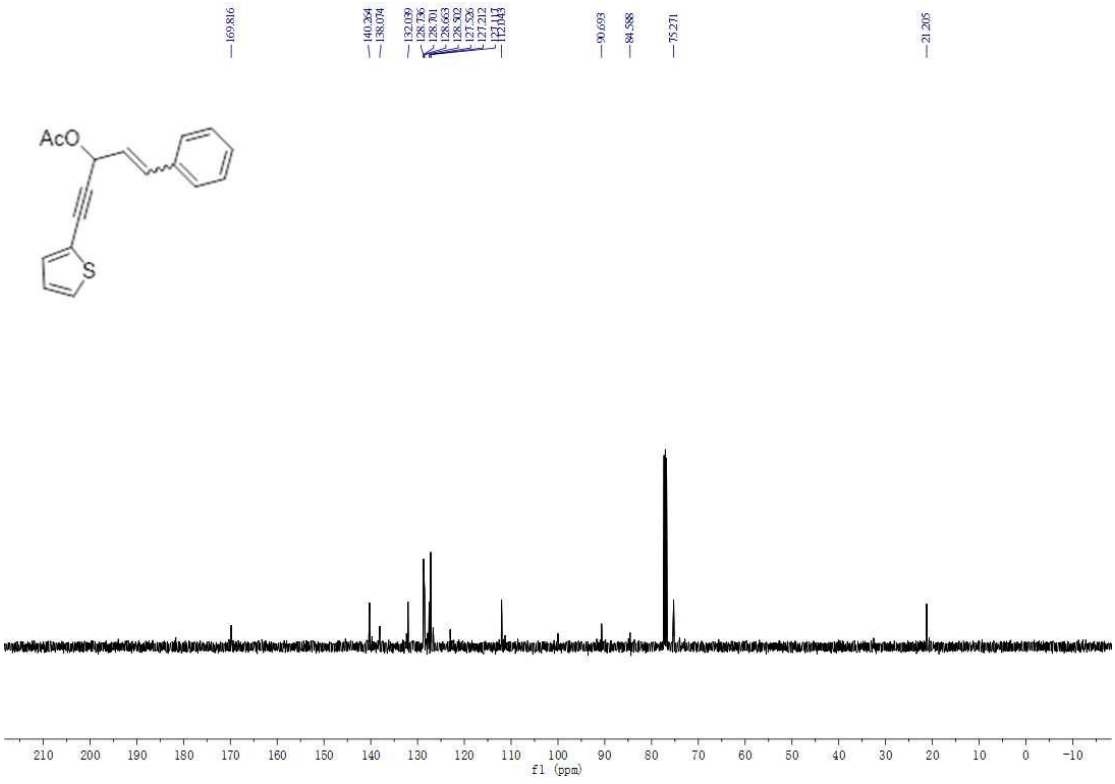


1-phenyl-5-(thiophen-2-yl)pent-1-en-4-yn-3-yl acetate (2j):

^{1}H NMR (500 MHz, $CDCl_3$)

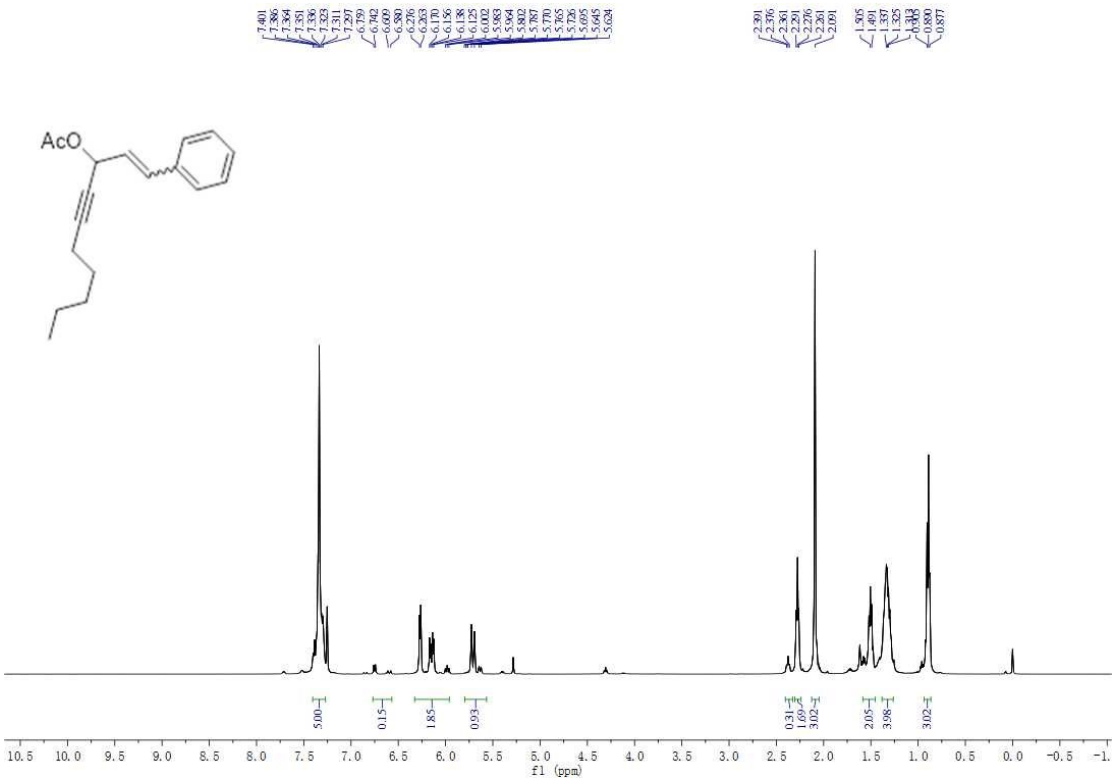


^{13}C NMR (125 MHz, $CDCl_3$)

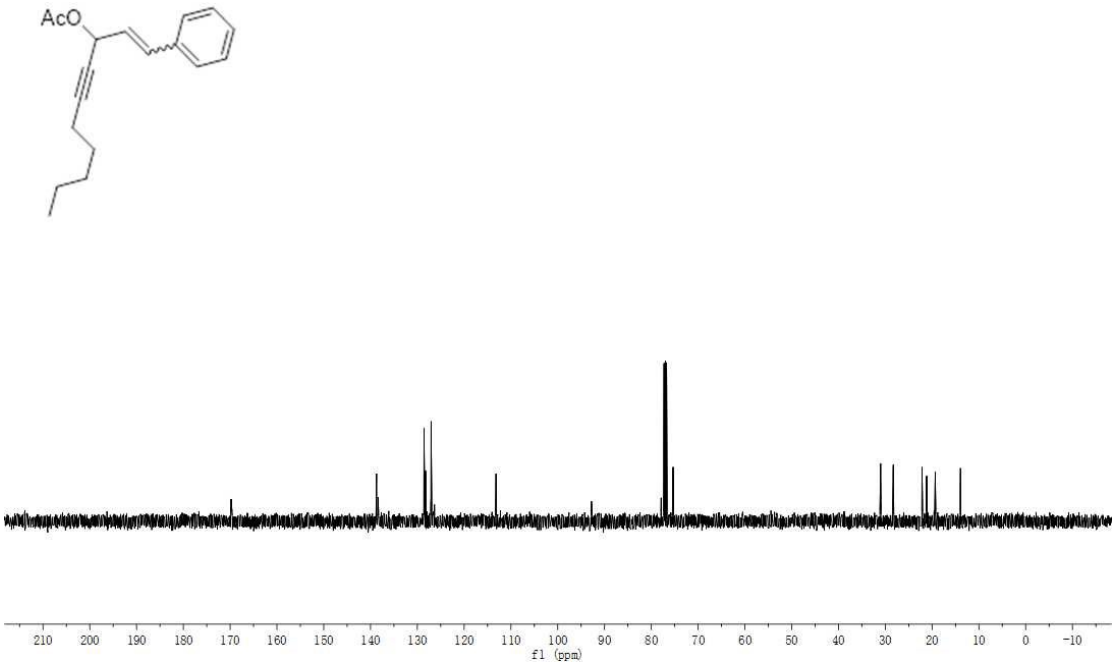


1-Phenyldec-1-en-4-yn-3-yl acetate (2l):

^{1}H NMR (500 MHz, $CDCl_3$)

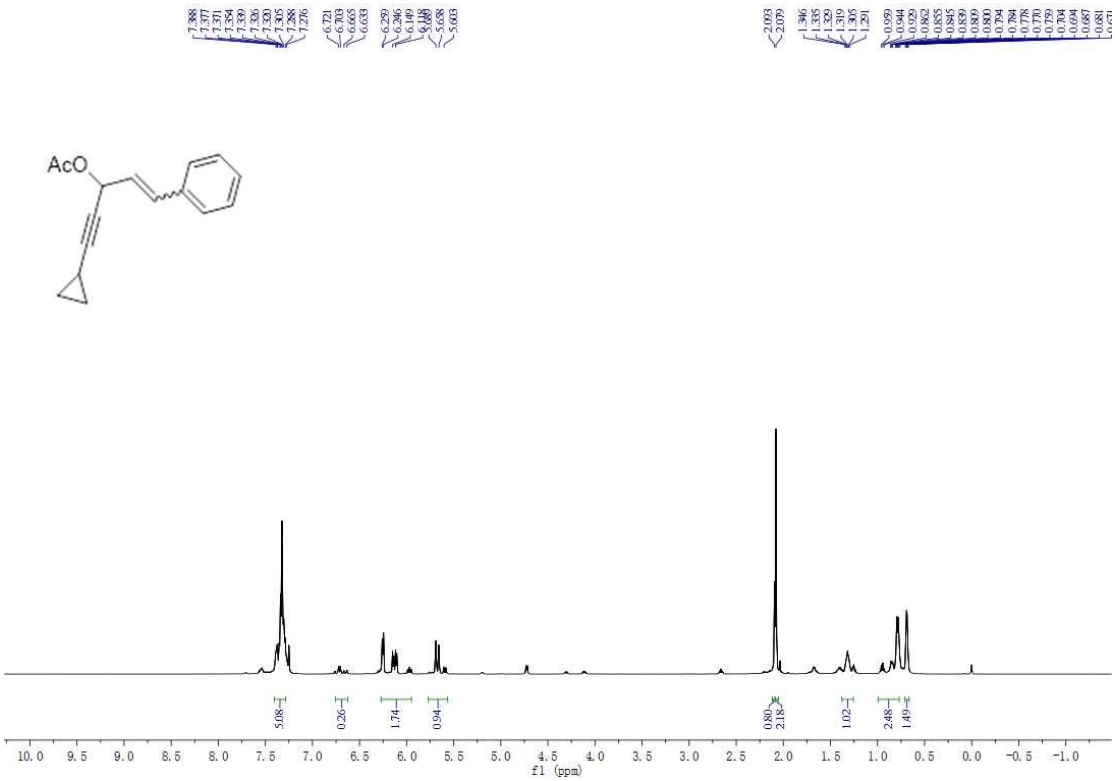


^{13}C NMR (125 MHz, $CDCl_3$)

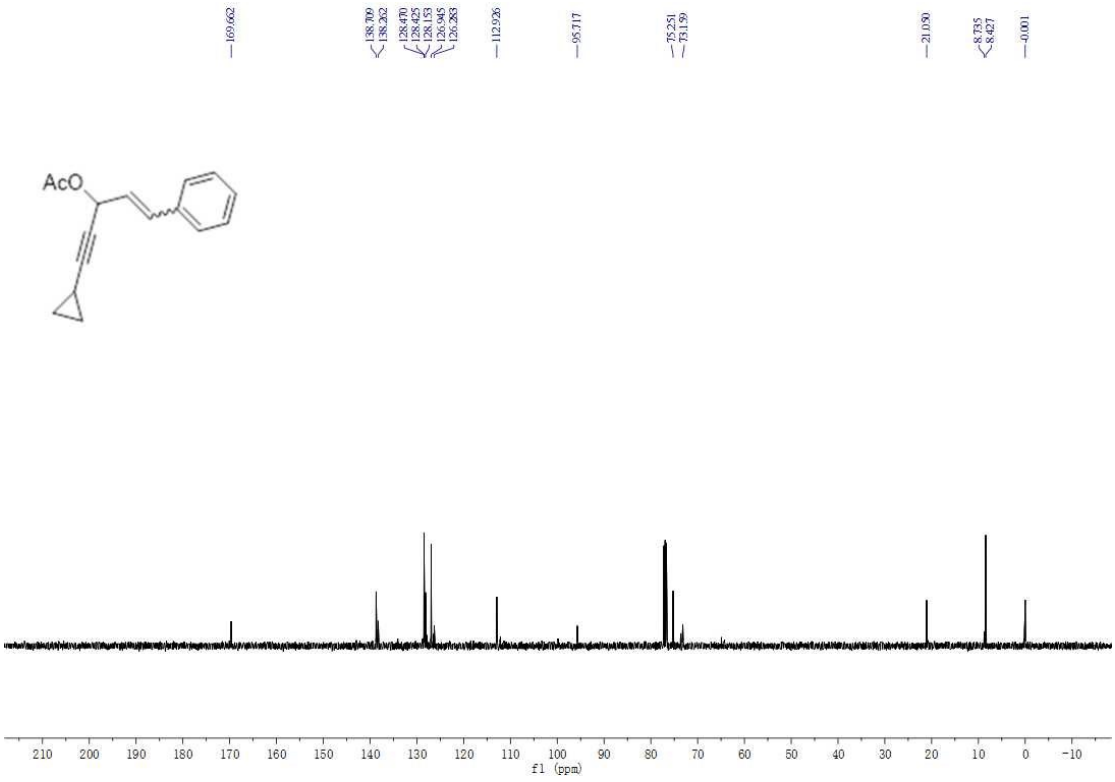


5-Cyclopropyl-1-phenylpent-1-en-4-yn-3-yl acetate (2m):

^{1}H NMR (500 MHz, $CDCl_3$)

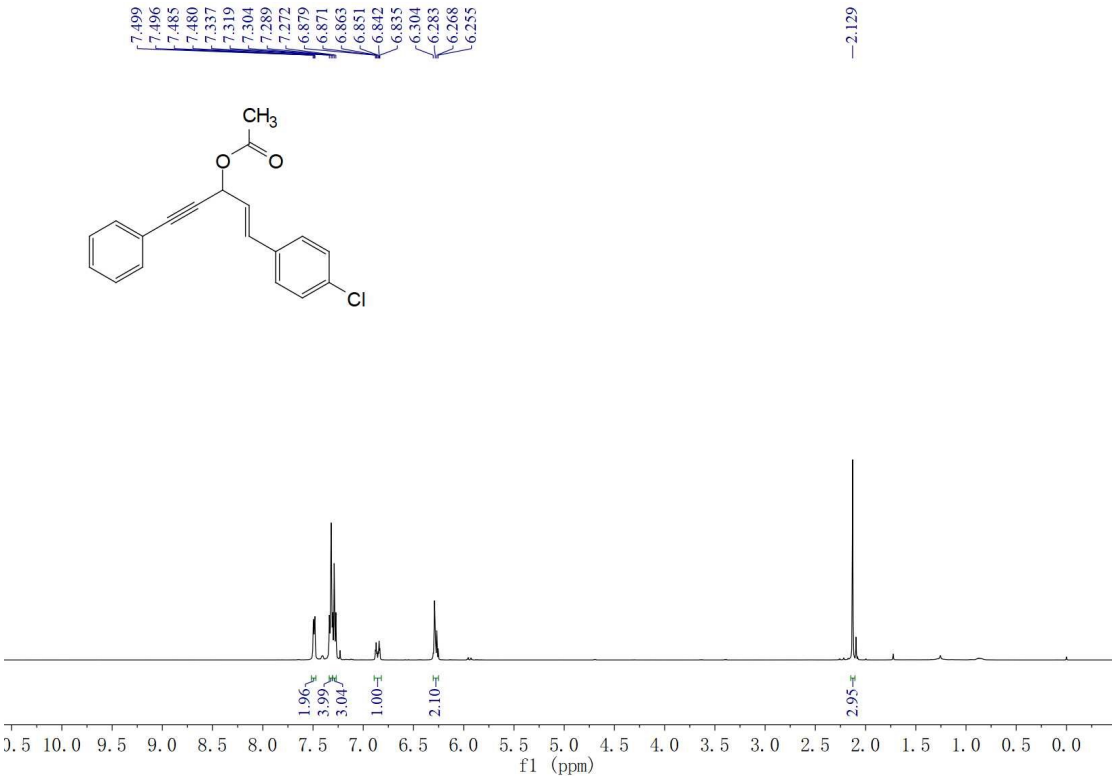


^{13}C NMR (125 MHz, $CDCl_3$)

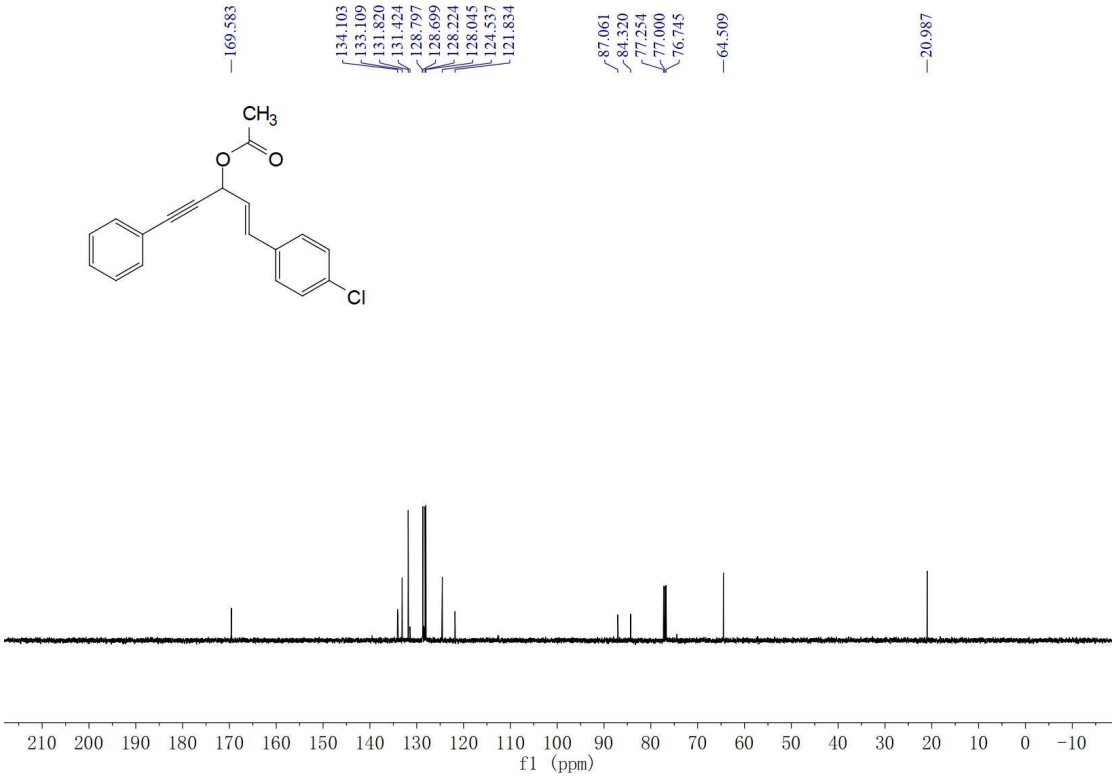


(*E*)-1-(4-Chlorophenyl)-5-phenylpent-1-en-4-yn-3-yl acetate (2q):

^{1}H NMR (500 MHz, $CDCl_3$)

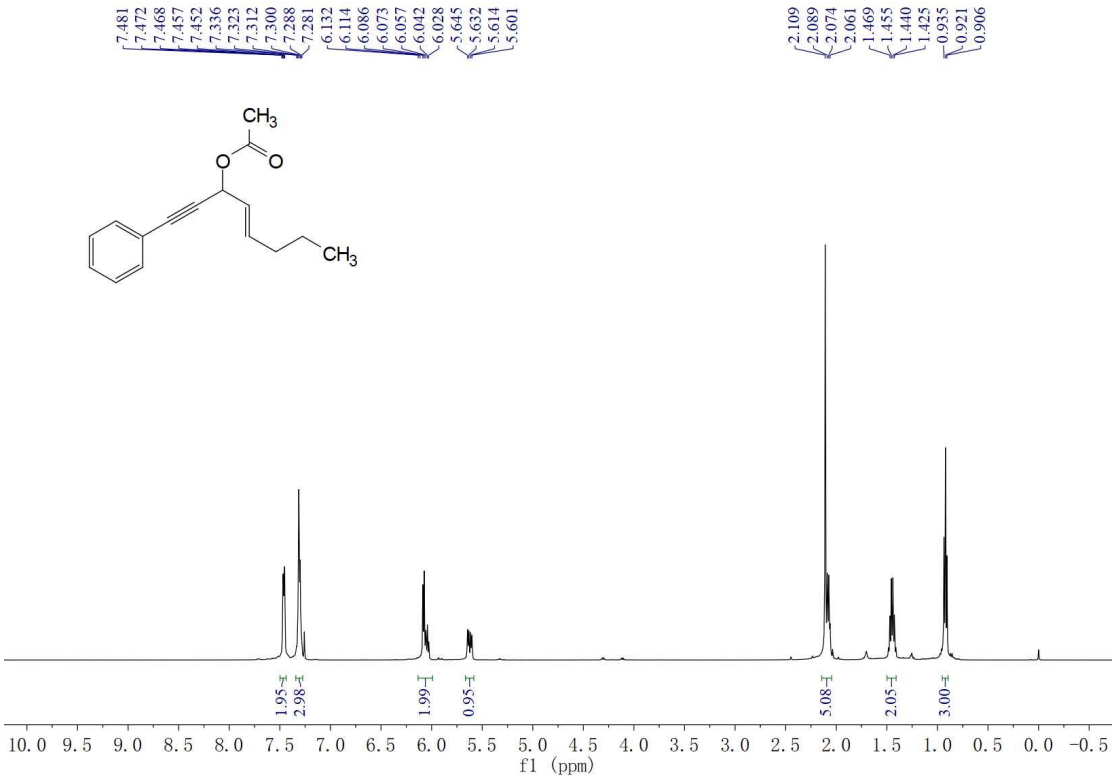


^{13}C NMR (125 MHz, $CDCl_3$)

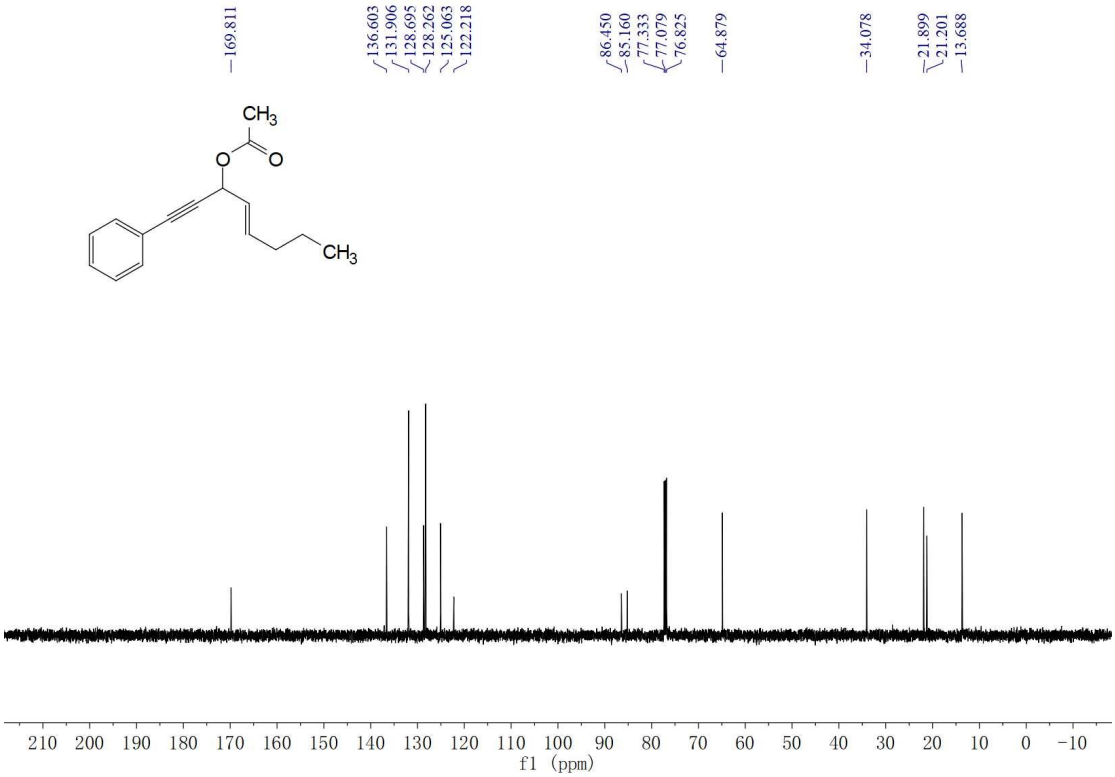


(*E*)-1-Phenyloct-4-en-1-yn-3-yl acetate (2r):

^{1}H NMR (500 MHz, $CDCl_3$)

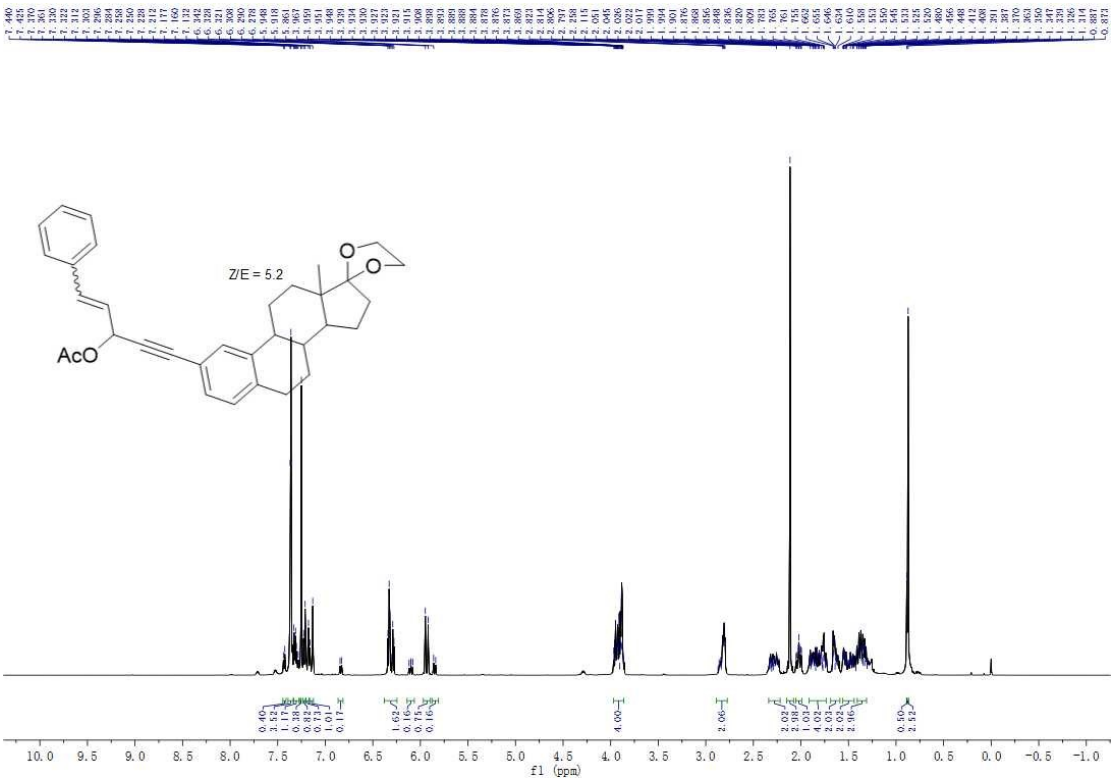


^{13}C NMR (125 MHz, $CDCl_3$)

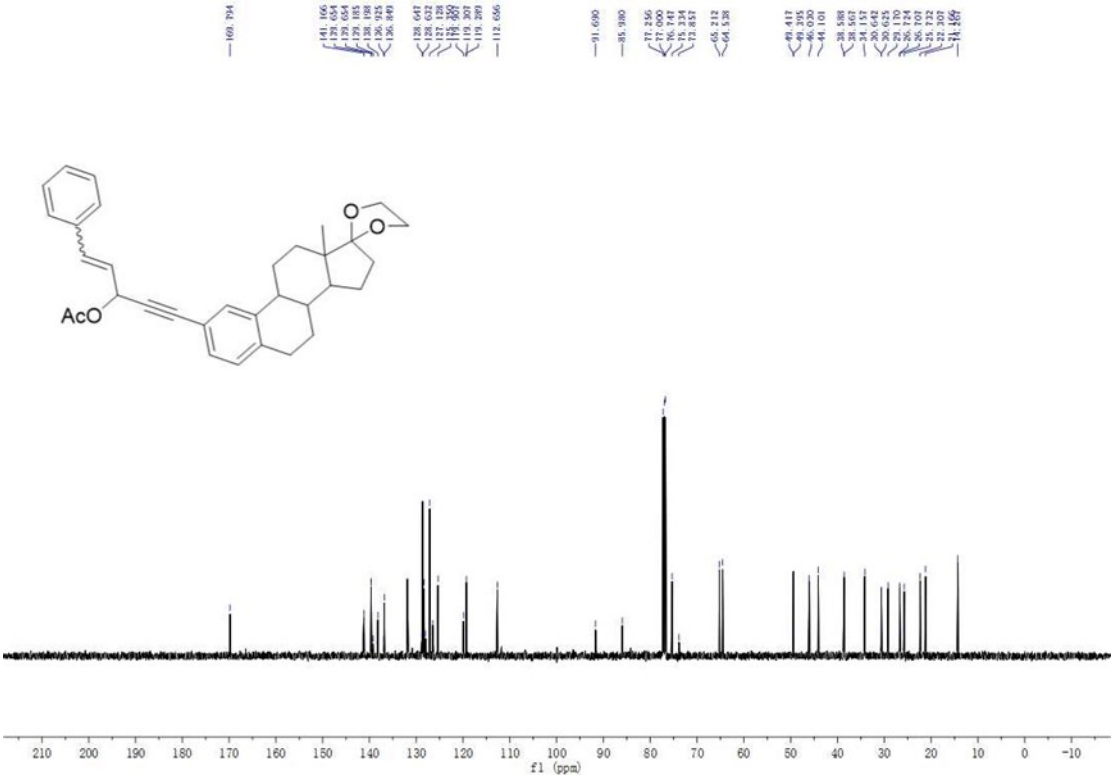


5-(13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[a]phenanthrene-17,2'-[1,3]dioxolan]-2-yl)-1-phenylpent-1-en-4-yn-3-yl acetate (2u):

^{1}H NMR (500 MHz, $CDCl_3$)

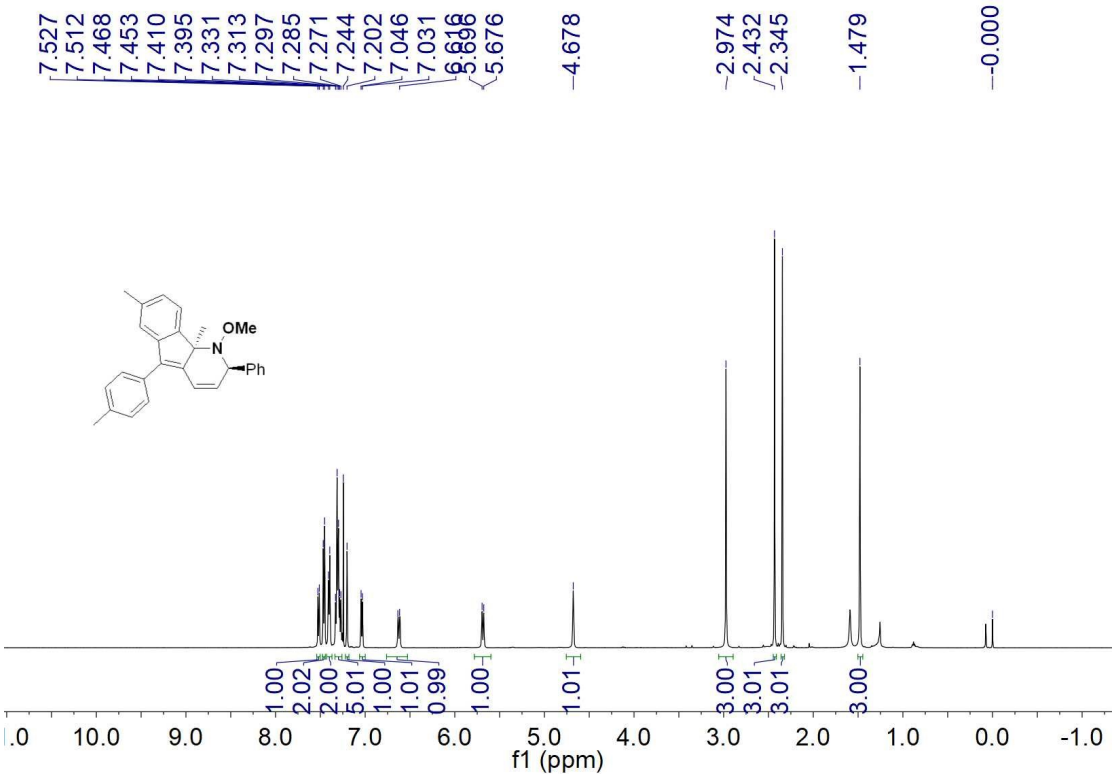


^{13}C NMR (125 MHz, $CDCl_3$)

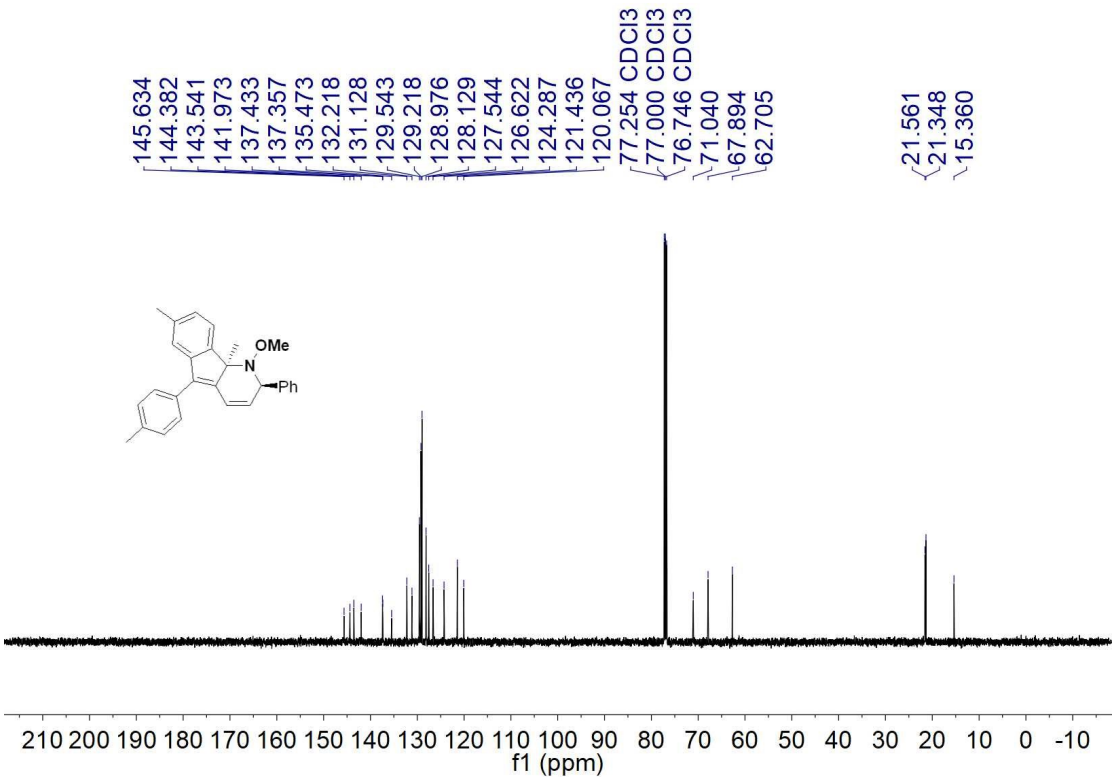


1-Methoxy-7,9*b*-dimethyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3aa):

^{1}H NMR (500 MHz, $CDCl_3$)

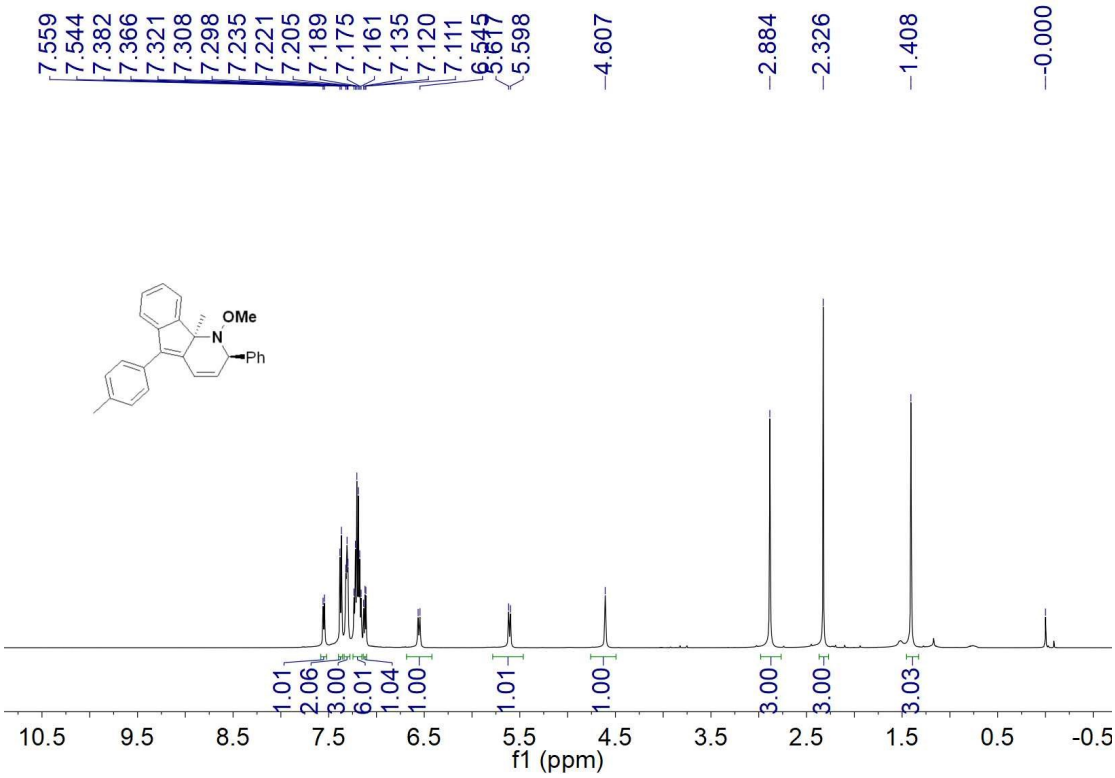


^{13}C NMR (125 MHz, $CDCl_3$)

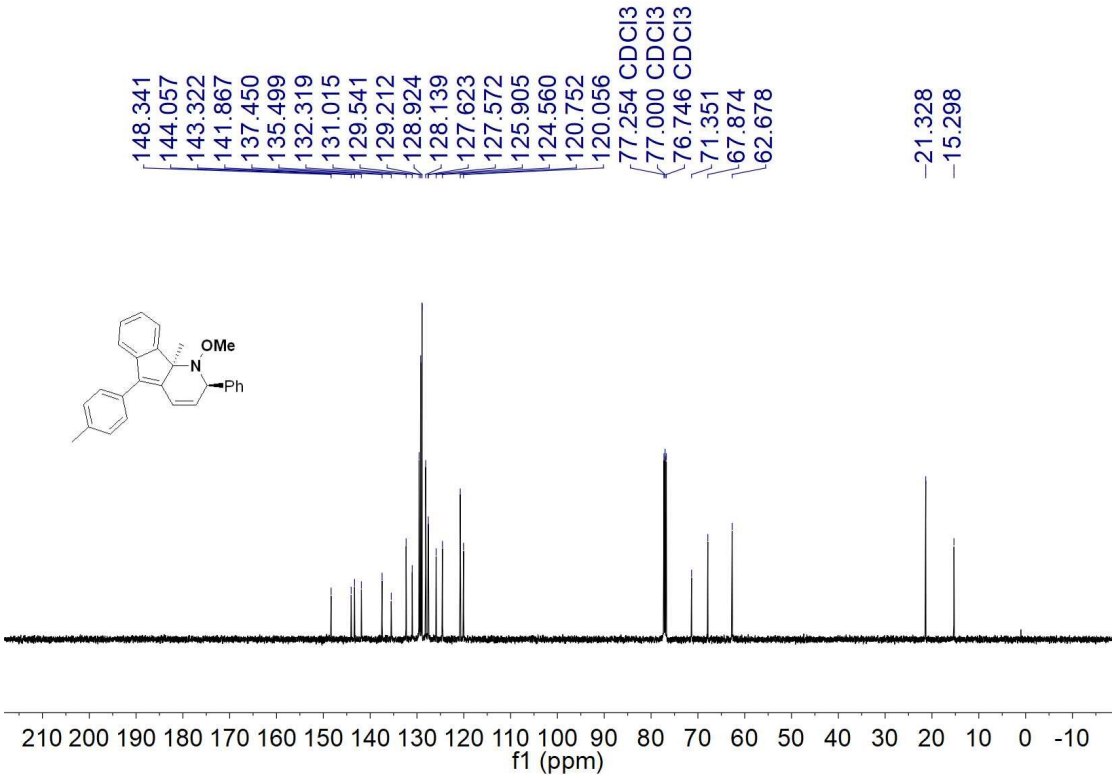


1-Methoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ba):

^{1}H NMR (500 MHz, $CDCl_3$)

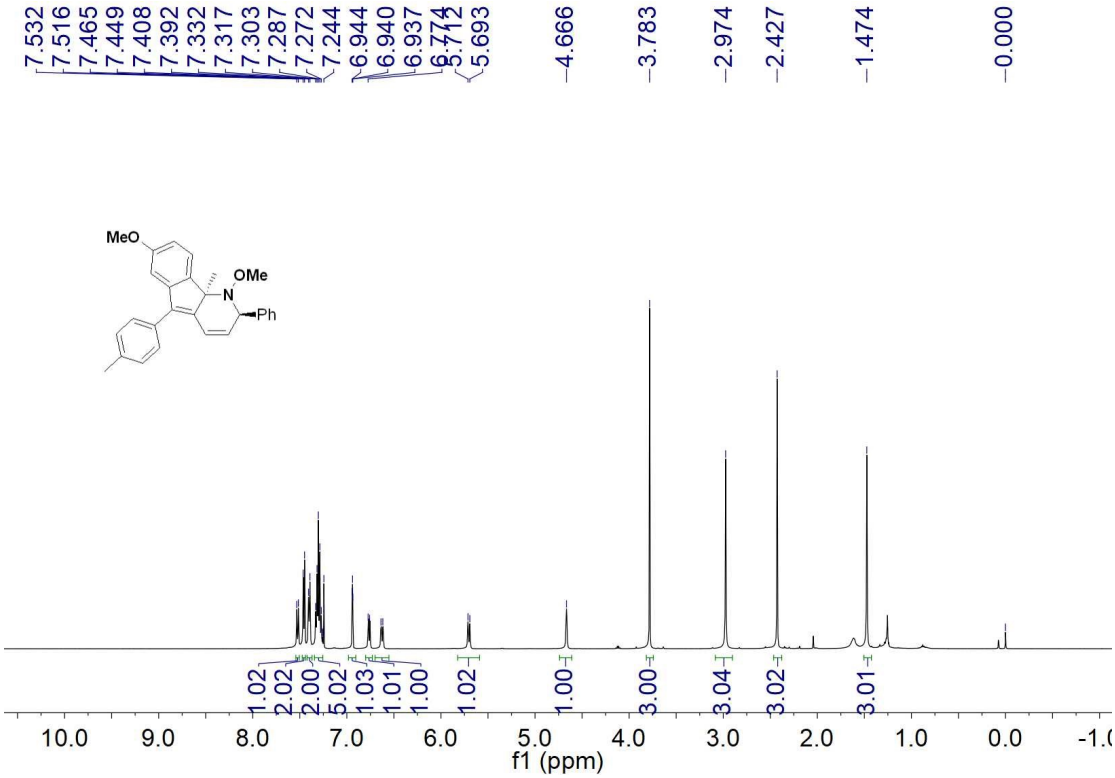


^{13}C NMR (125 MHz, $CDCl_3$)

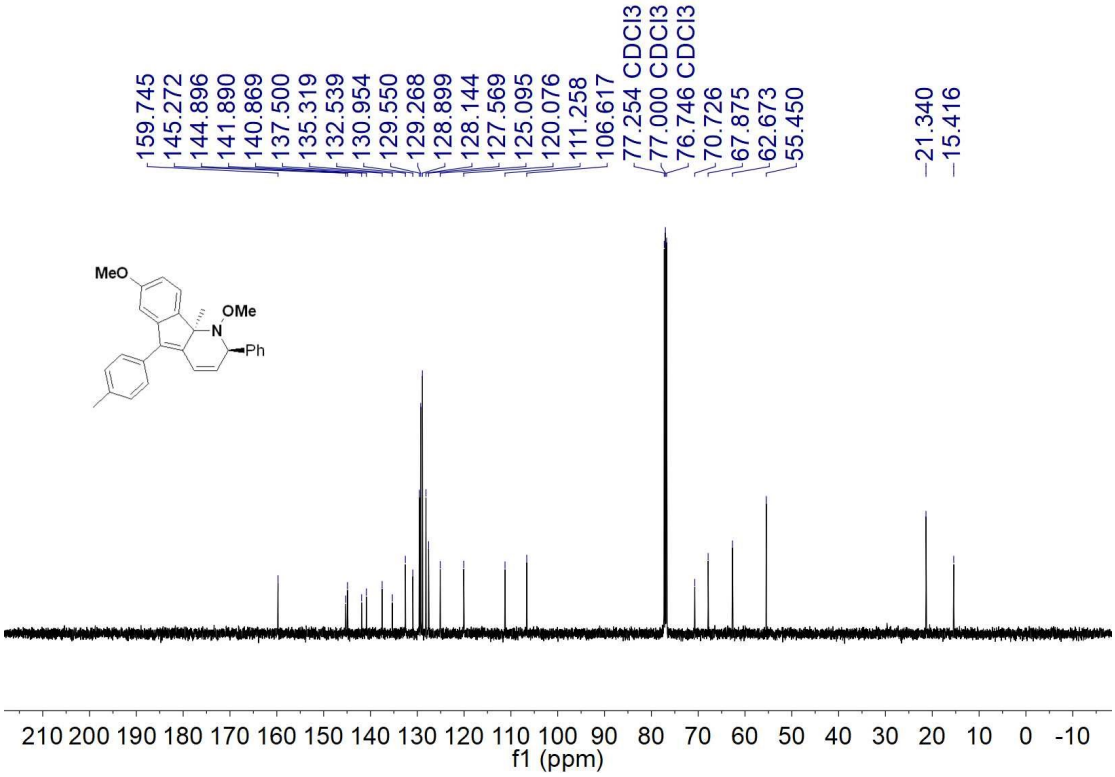


1,7-Dimethoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ca):

^{1}H NMR (500 MHz, $CDCl_3$)

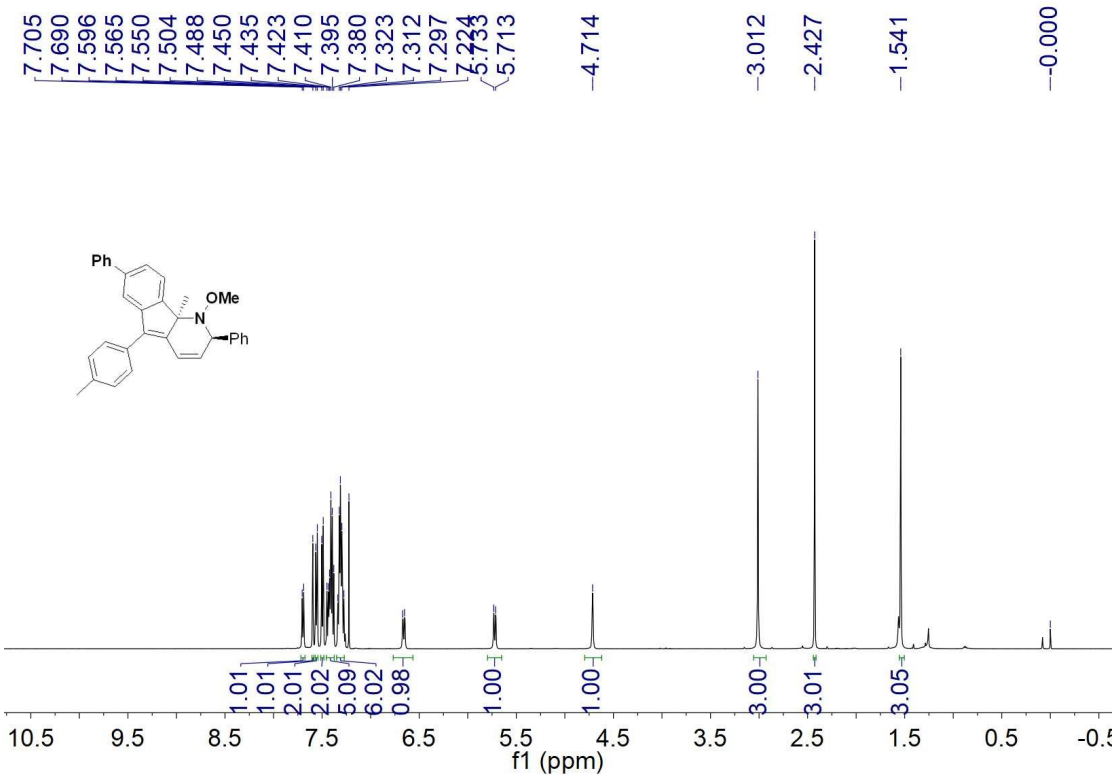


^{13}C NMR (125 MHz, $CDCl_3$)

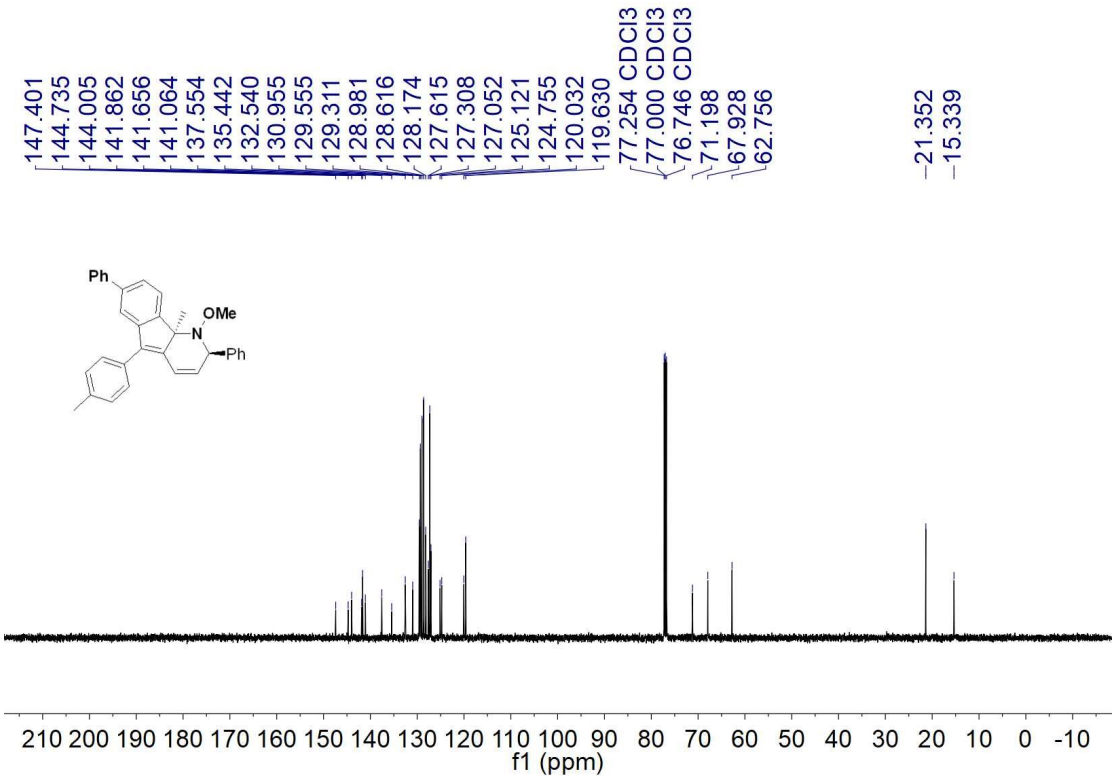


1-Methoxy-9*b*-methyl-2,7-diphenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3da):

^{1}H NMR (500 MHz, $CDCl_3$)

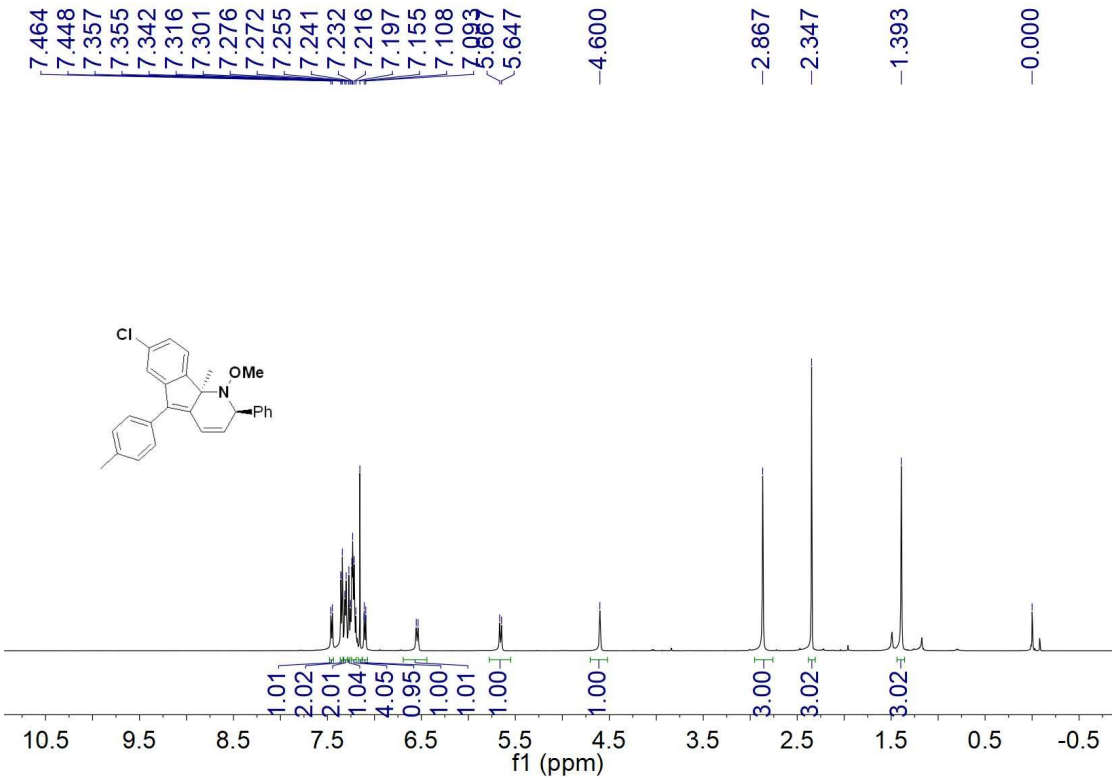


^{13}C NMR (125 MHz, $CDCl_3$)

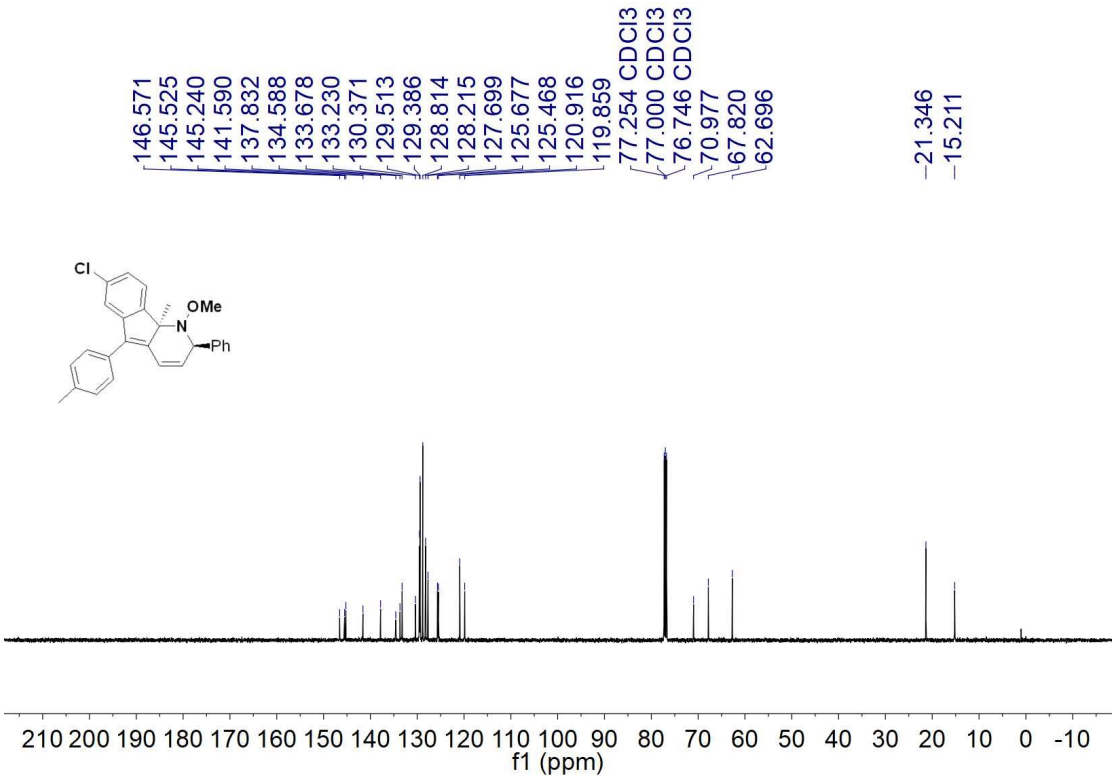


7-Chloro-1-methoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ea):

^{1}H NMR (500 MHz, $CDCl_3$)

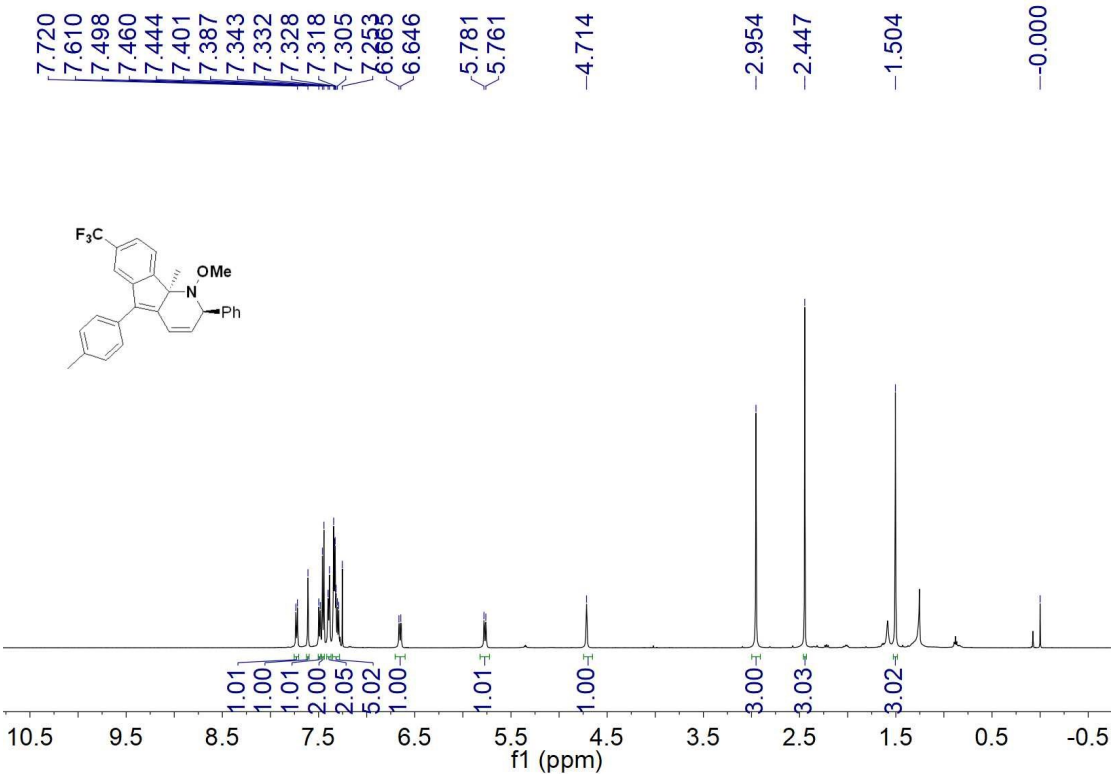


^{13}C NMR (125 MHz, $CDCl_3$)

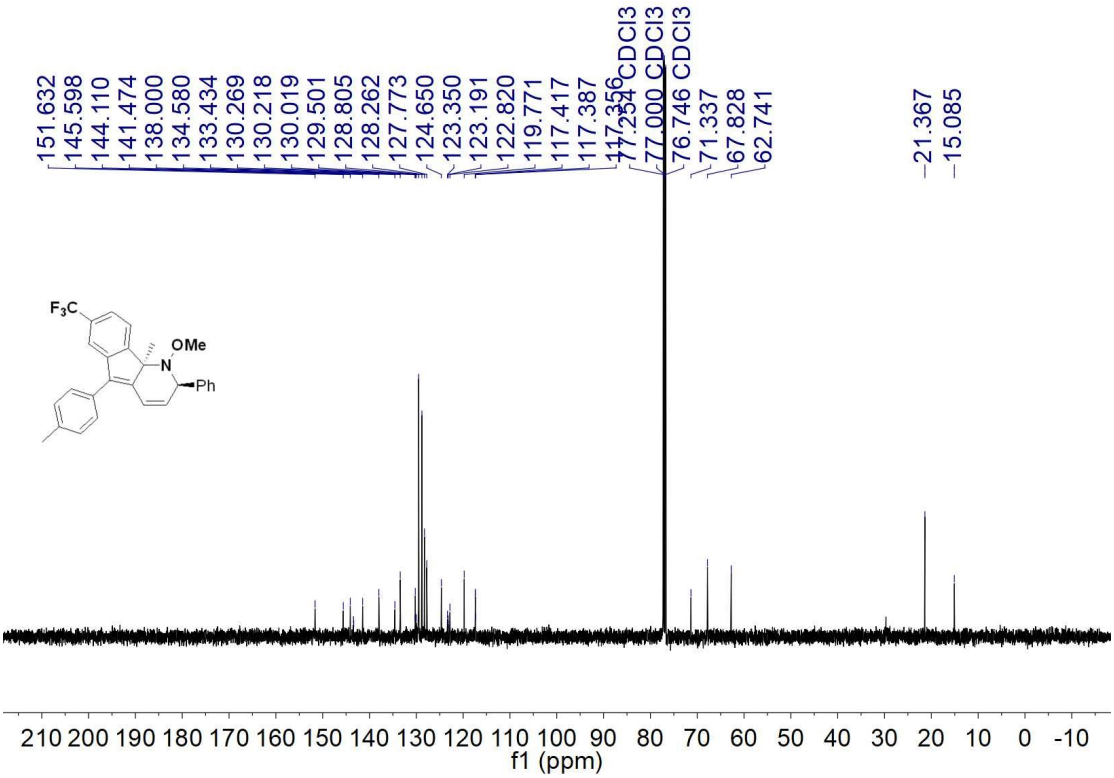


1-Methoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-7-(trifluoromethyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3fa):

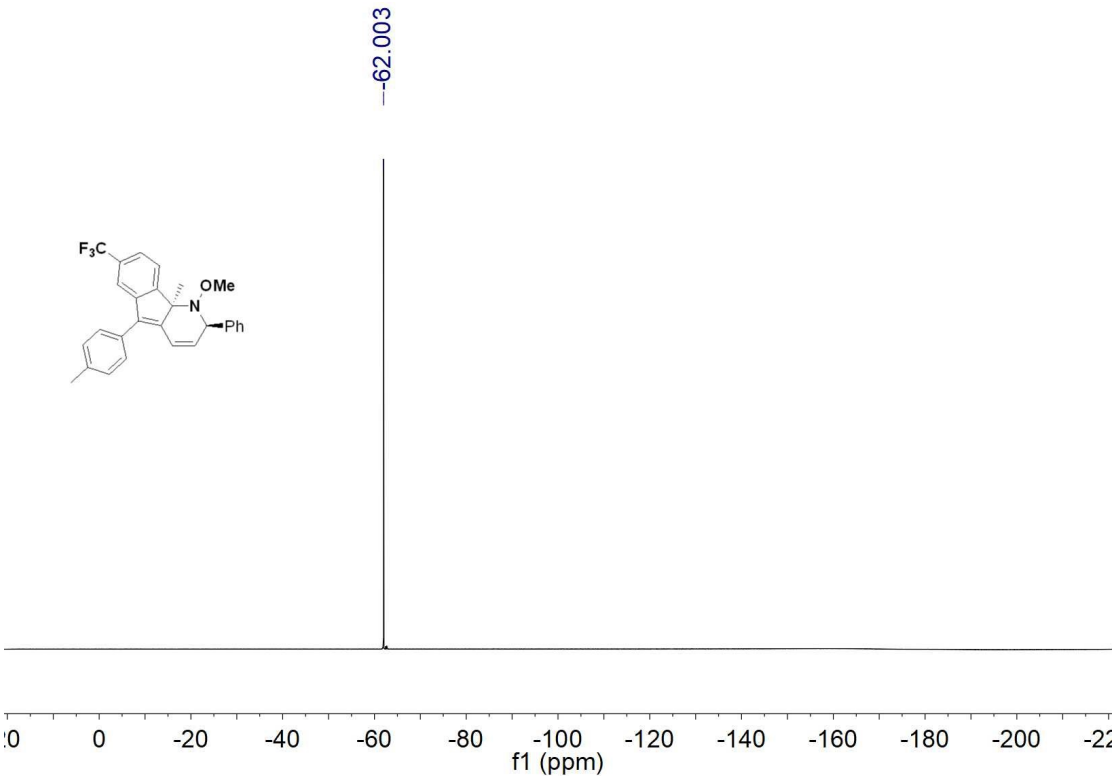
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

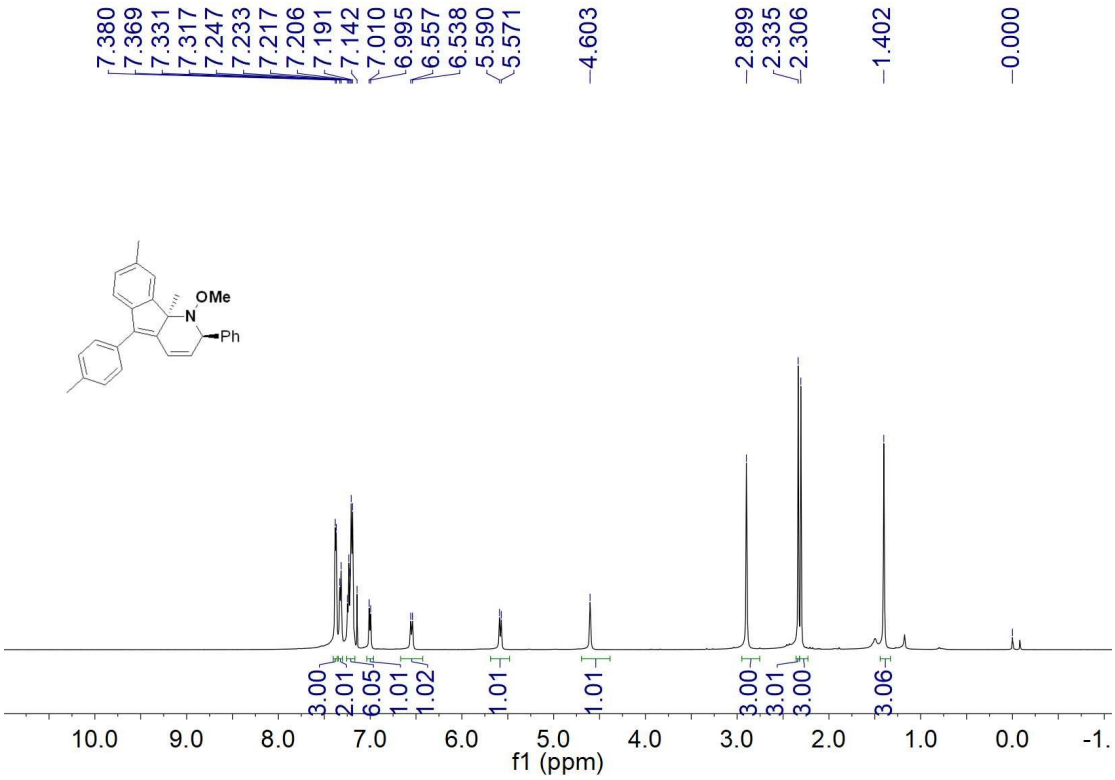


^{19}F NMR (471 MHz, $CDCl_3$)

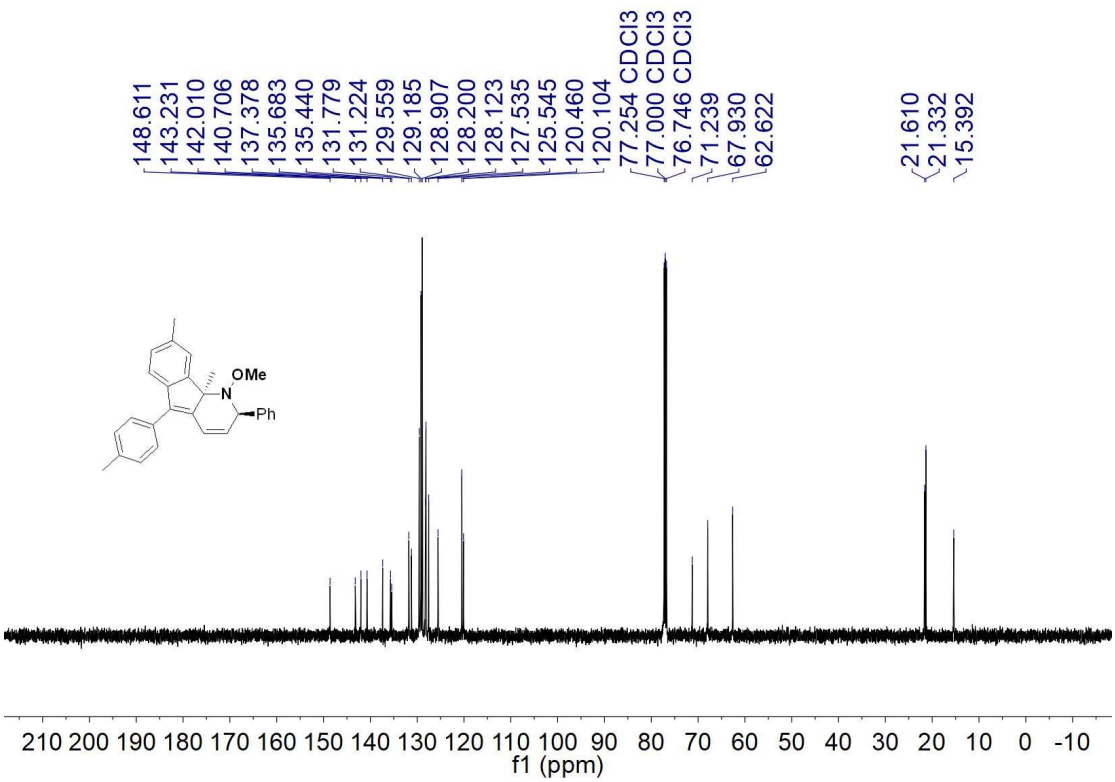


1-Methoxy-8,9*b*-dimethyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ga):

^{1}H NMR (500 MHz, $CDCl_3$)



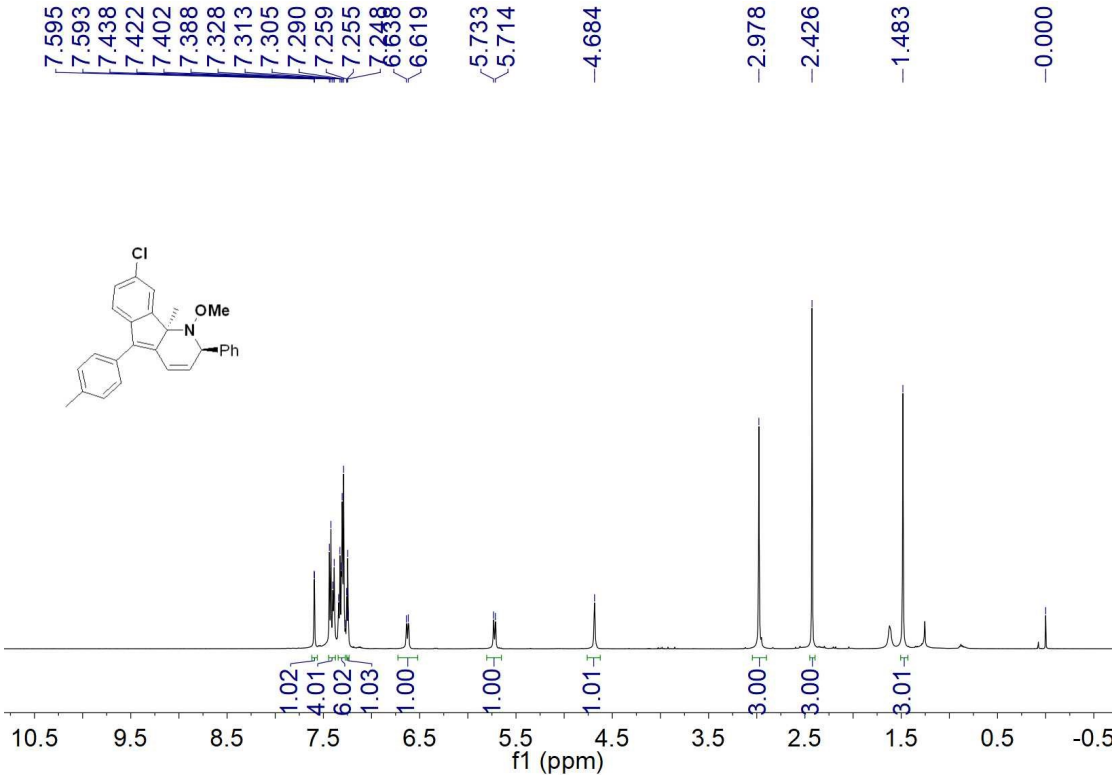
^{13}C NMR (125 MHz, $CDCl_3$)



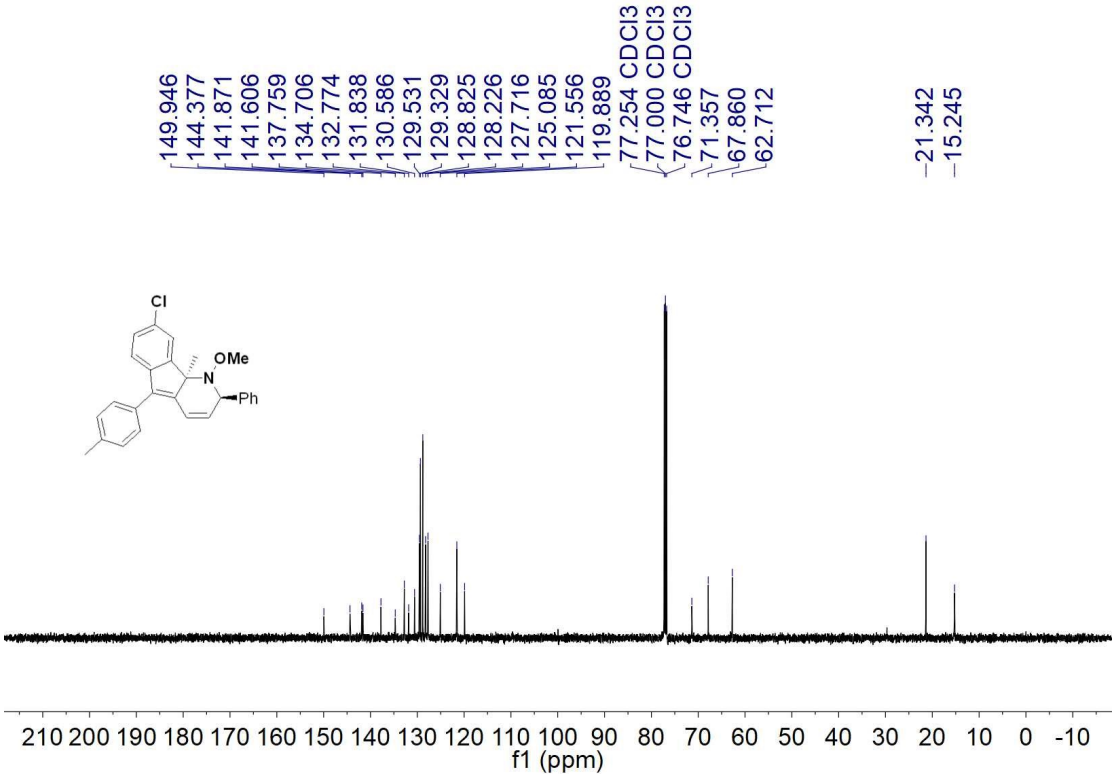
8-Chloro-1-methoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-

***b*]pyridine (3ha):**

^{1}H NMR (500 MHz, $CDCl_3$)



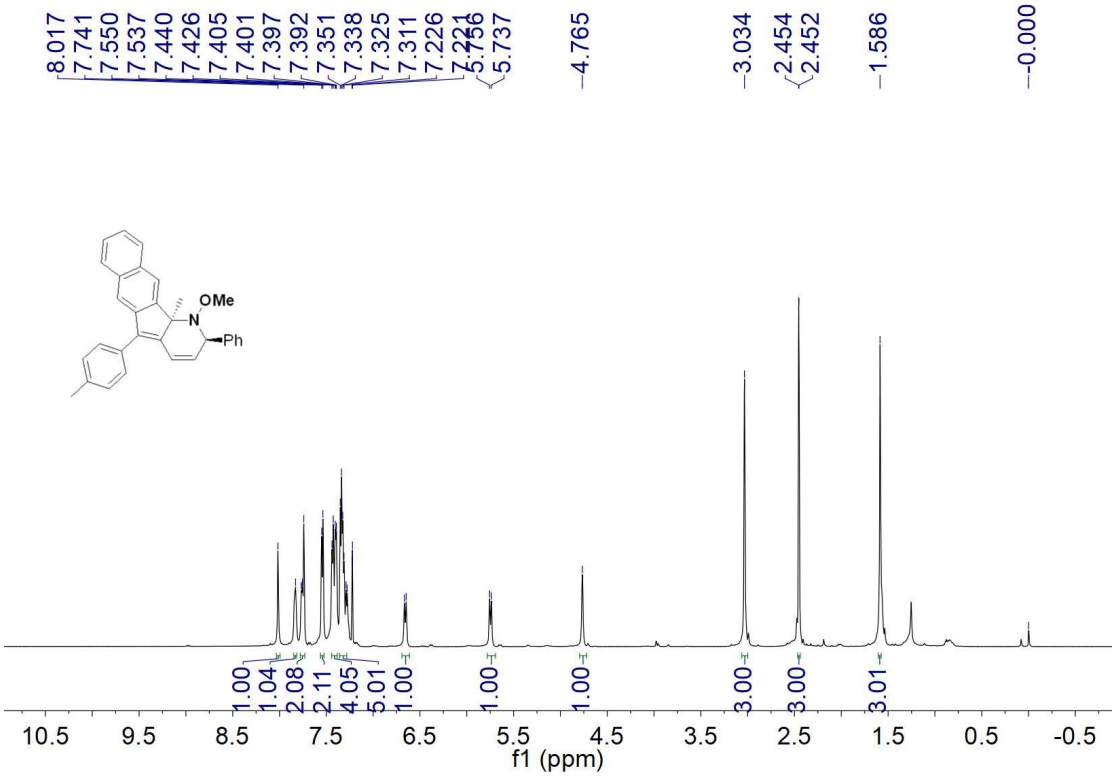
^{13}C NMR (125 MHz, $CDCl_3$)



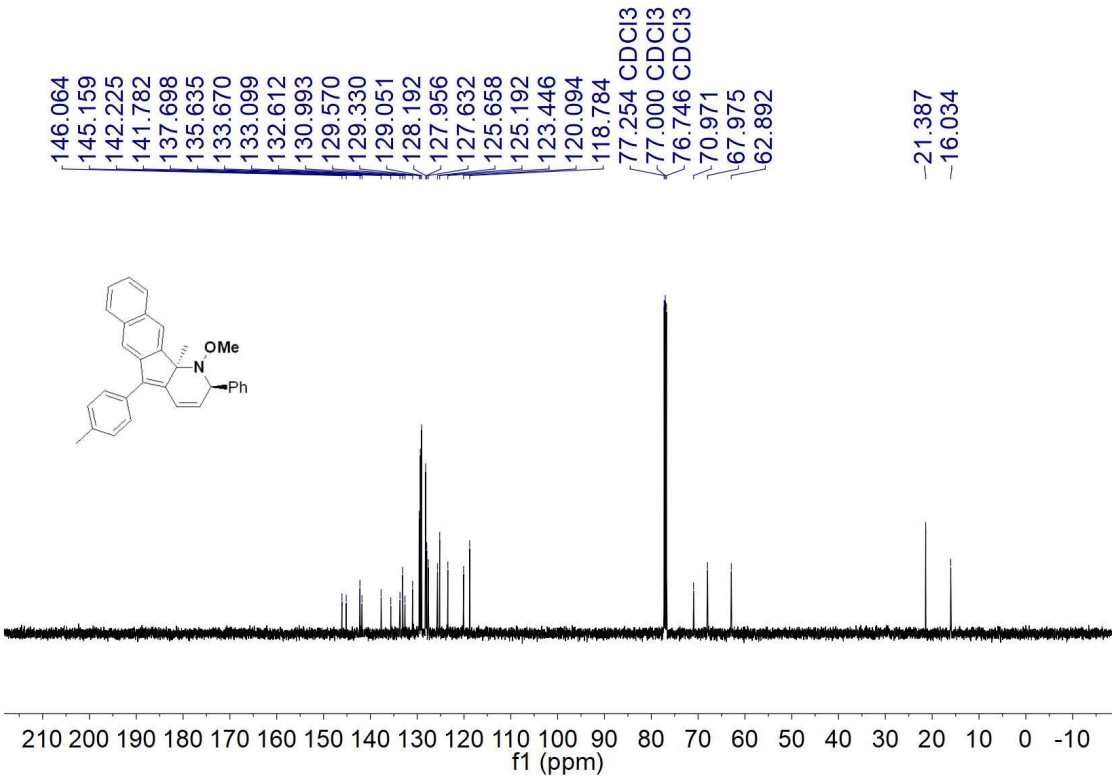
1-Methoxy-11*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,11*b*-dihydro-1*H*-

benzo[5,6]indeno[1,2-*b*]pyridine (3ja):

^{1}H NMR (500 MHz, $CDCl_3$)

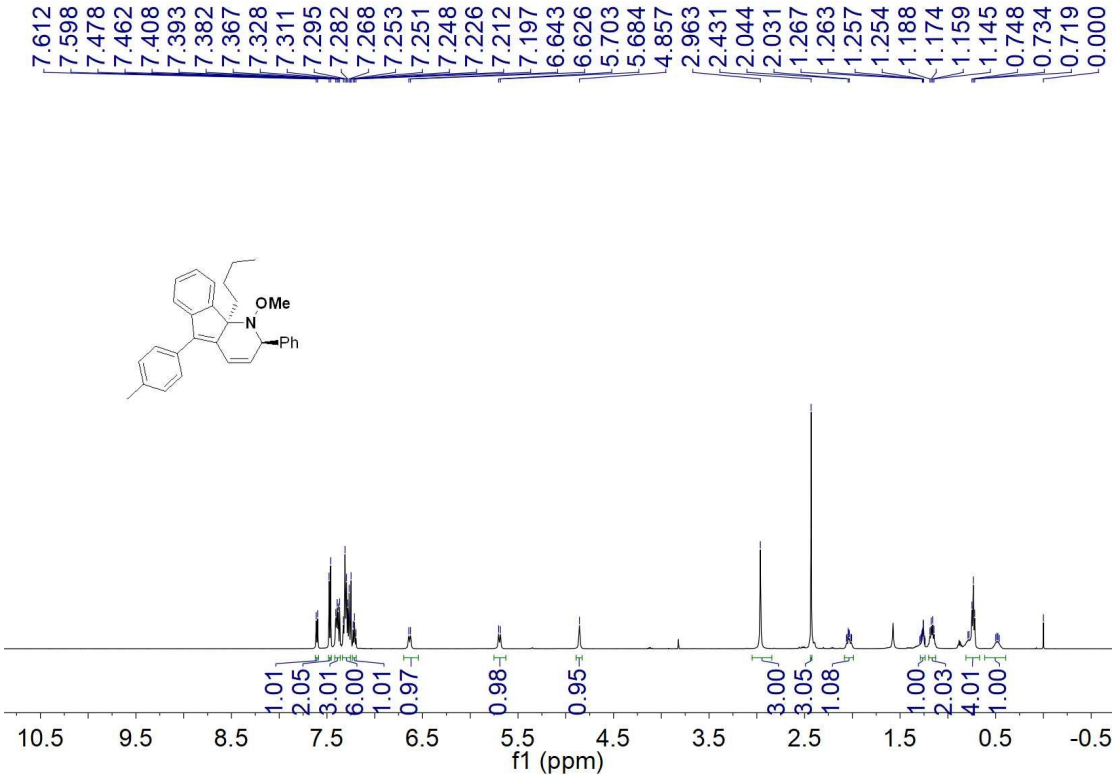


^{13}C NMR (125 MHz, $CDCl_3$)

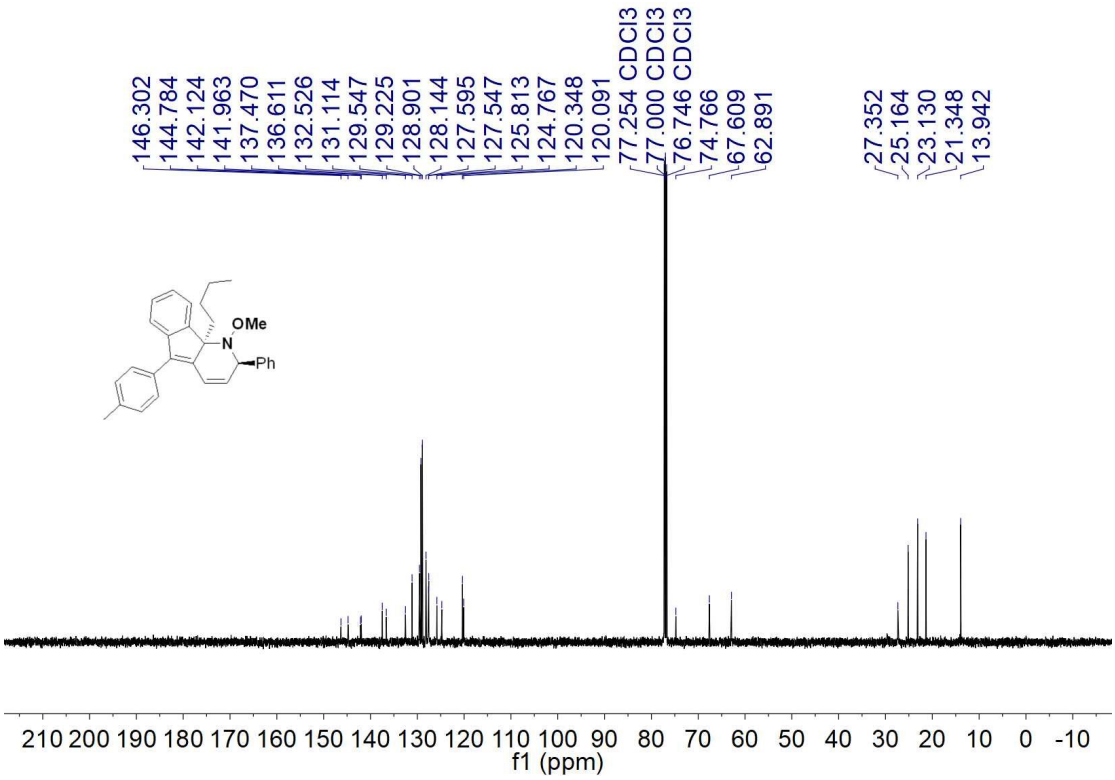


9*b*-Butyl-1-methoxy-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ka):

^{1}H NMR (500 MHz, $CDCl_3$)

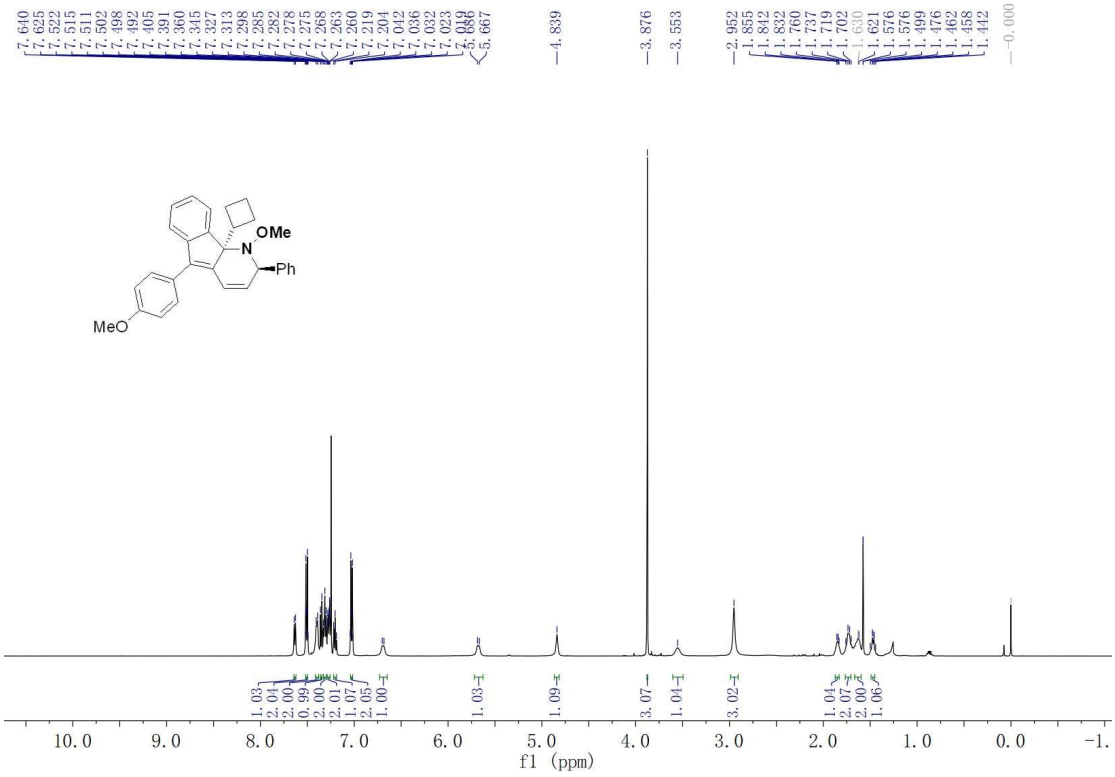


^{13}C NMR (125 MHz, $CDCl_3$)

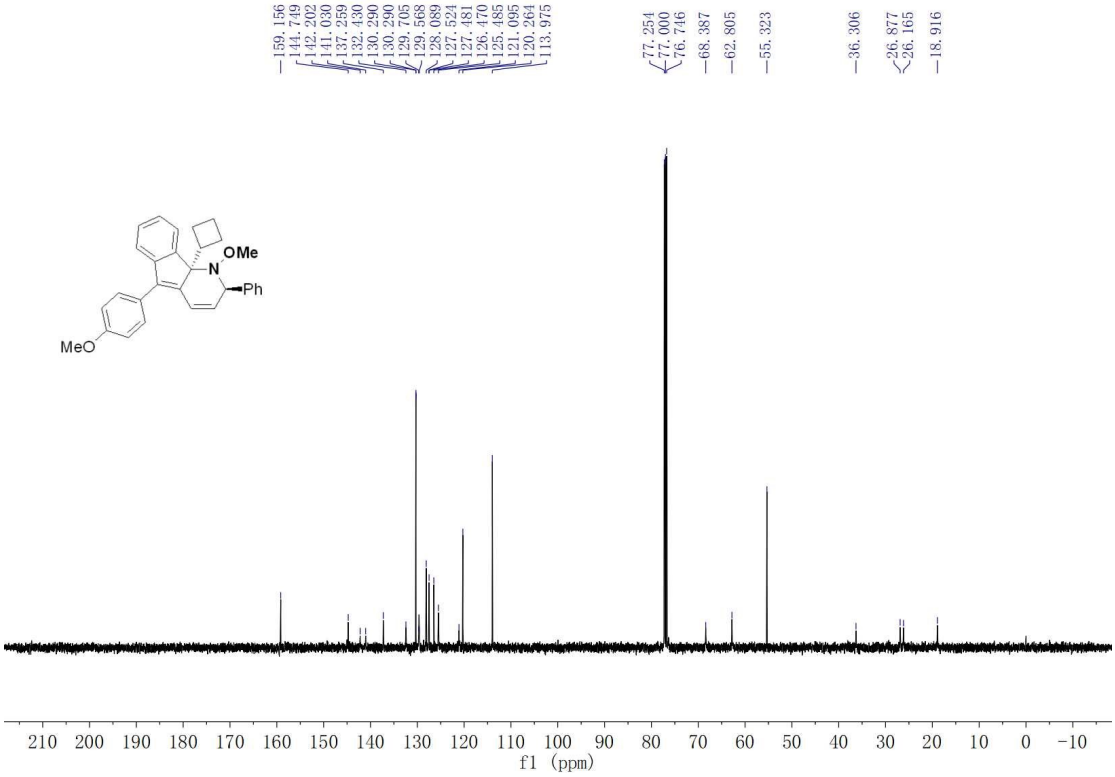


9*b*-Cyclobutyl-1-methoxy-5-(4-methoxyphenyl)-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3la):

^{1}H NMR (500 MHz, $CDCl_3$)

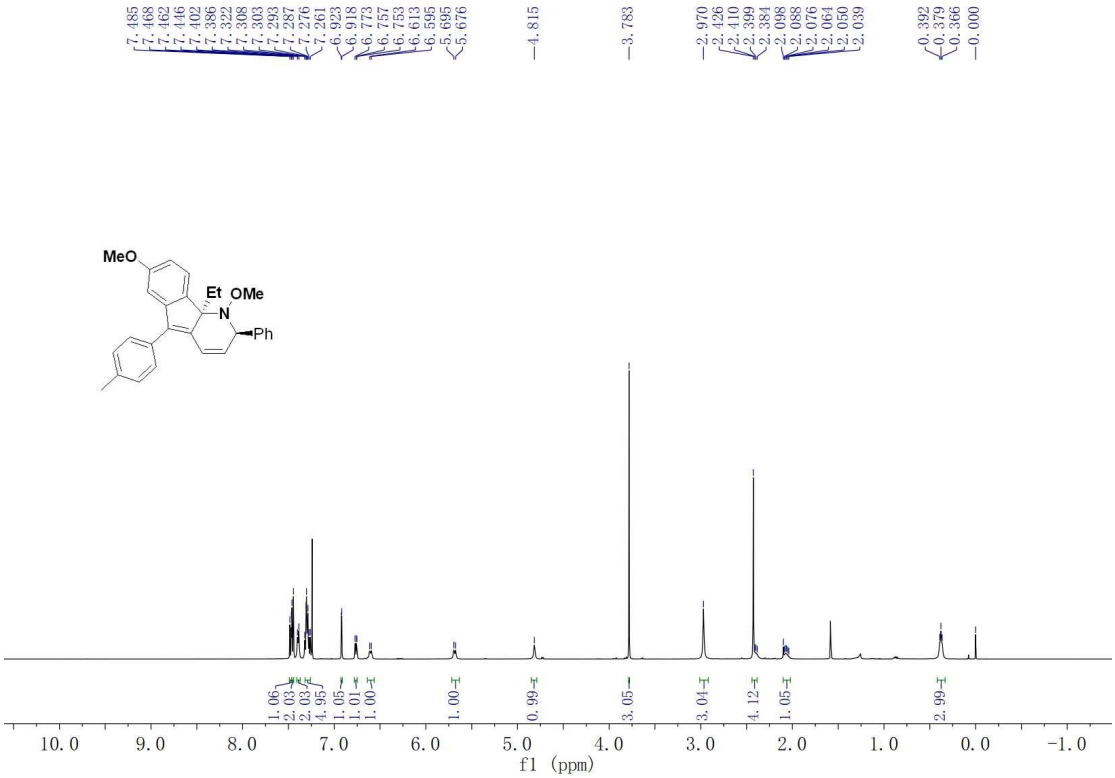


^{13}C NMR (125 MHz, $CDCl_3$)

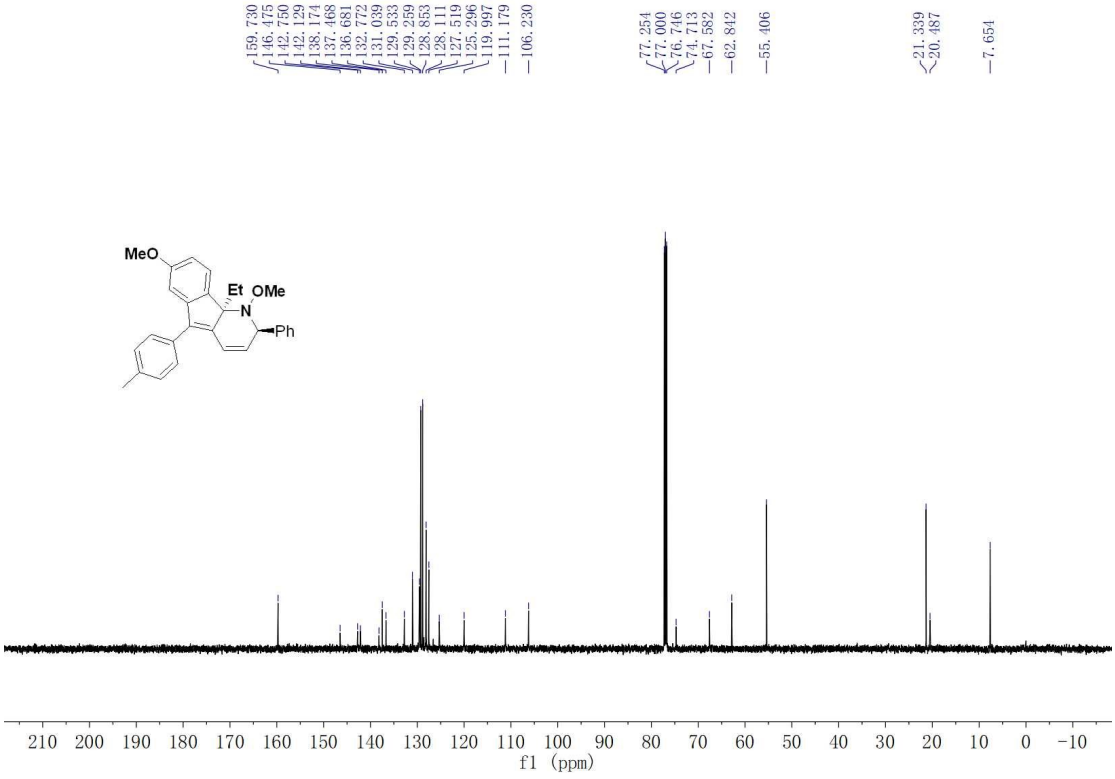


9*b*-Ethyl-1,7-dimethoxy-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ma):

^{1}H NMR (500 MHz, $CDCl_3$)

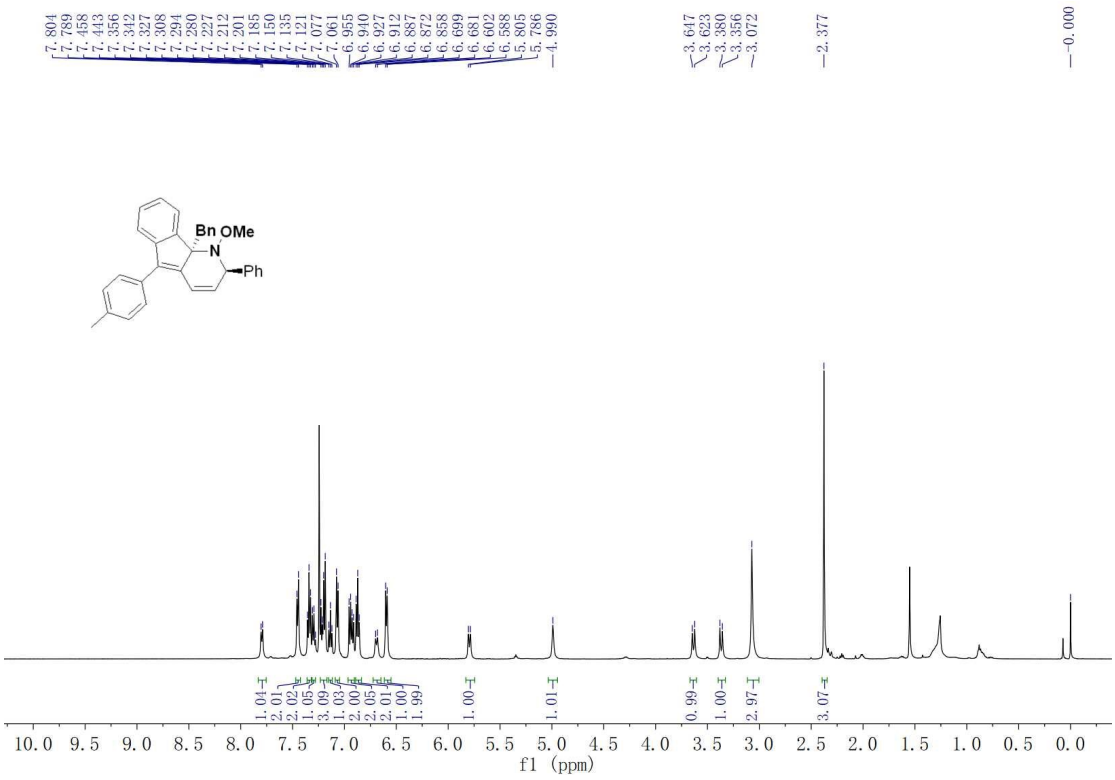


^{13}C NMR (125 MHz, $CDCl_3$)

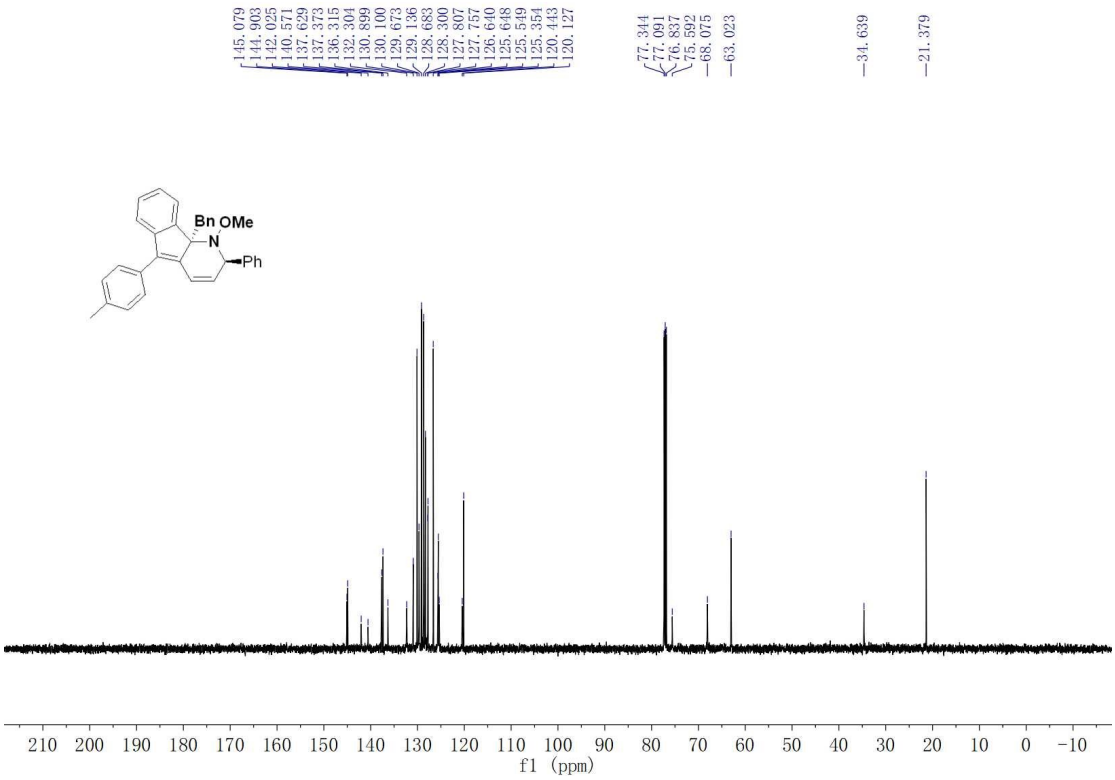


9*b*-Benzyl-1-methoxy-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3na):

^{1}H NMR (500 MHz, $CDCl_3$)

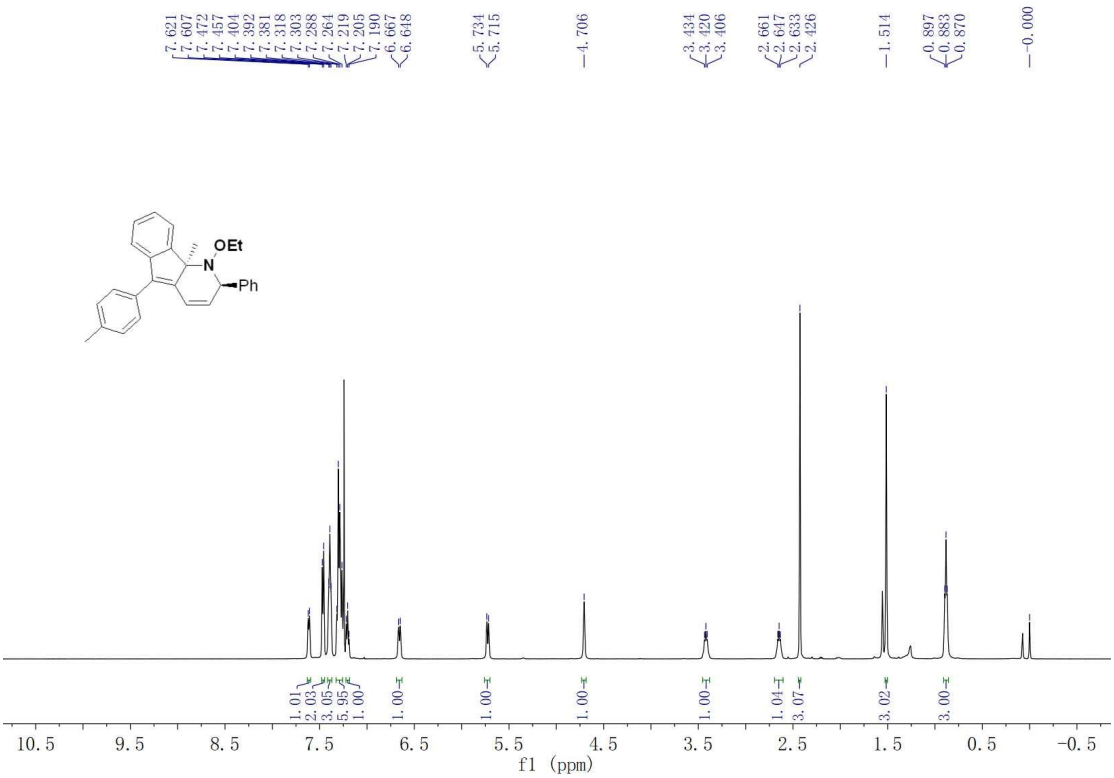


^{13}C NMR (125 MHz, $CDCl_3$)

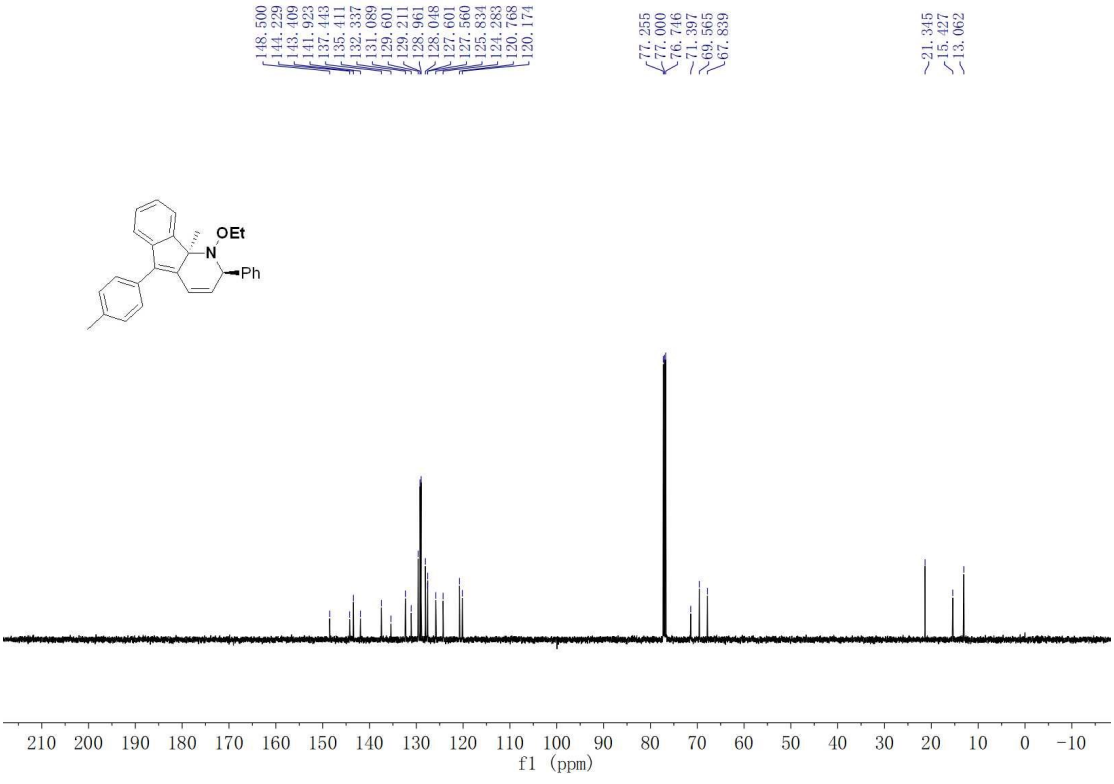


1-Ethoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3pa):

^{1}H NMR (500 MHz, $CDCl_3$)

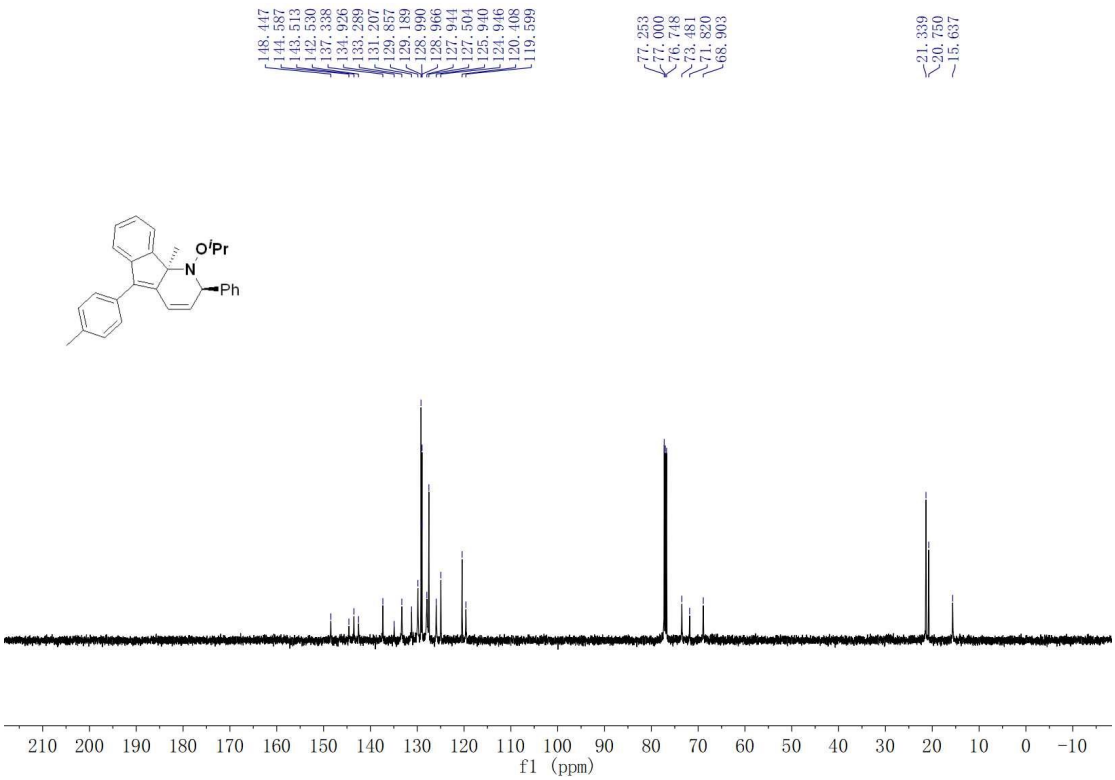


^{13}C NMR (125 MHz, $CDCl_3$)

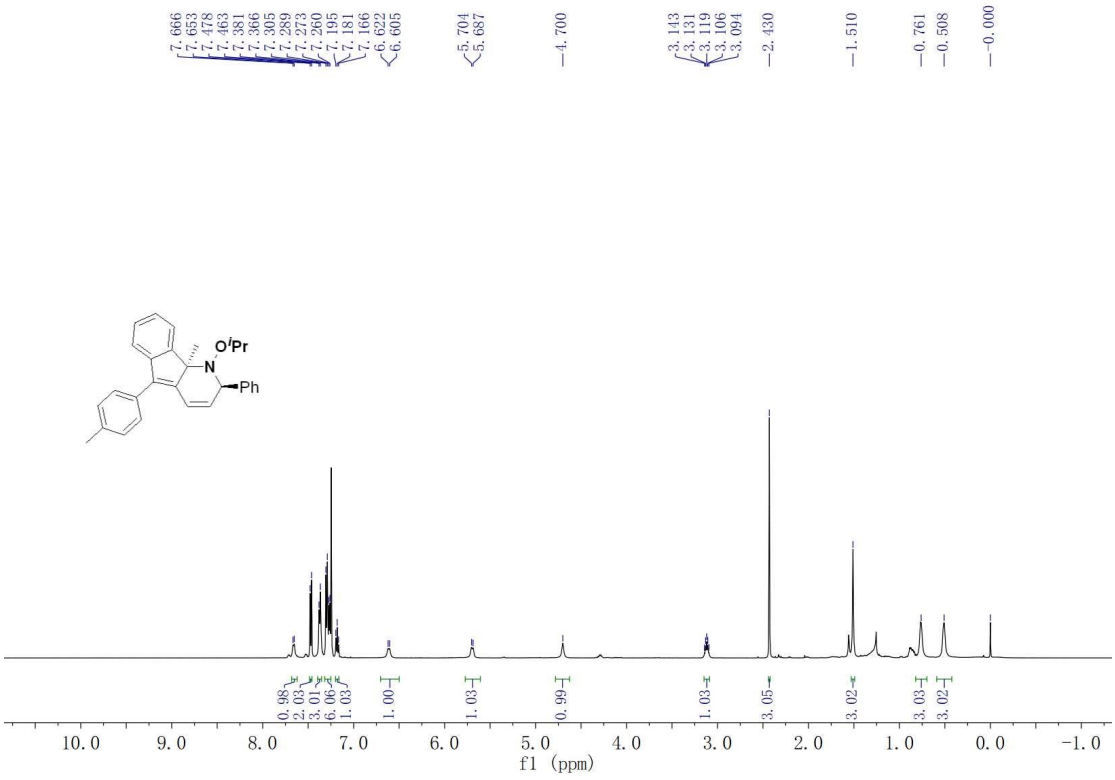


1-Isopropoxy-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3qa):

^{1}H NMR (500 MHz, $CDCl_3$)

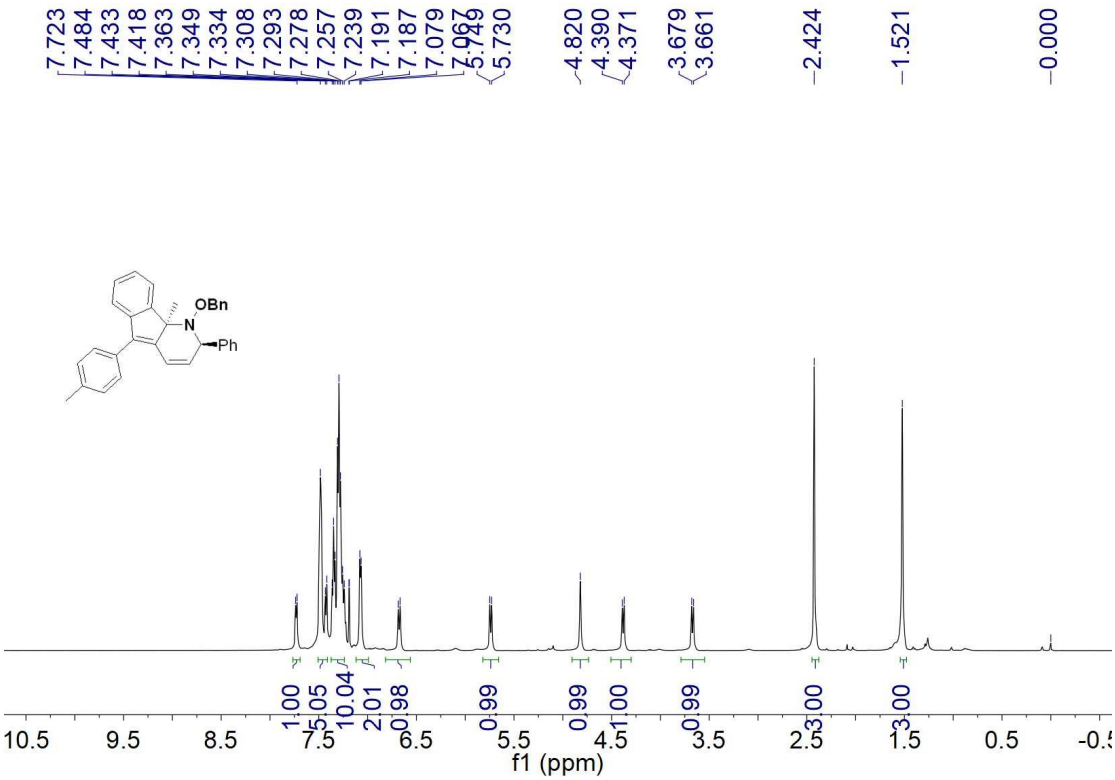


^{13}C NMR (125 MHz, $CDCl_3$)

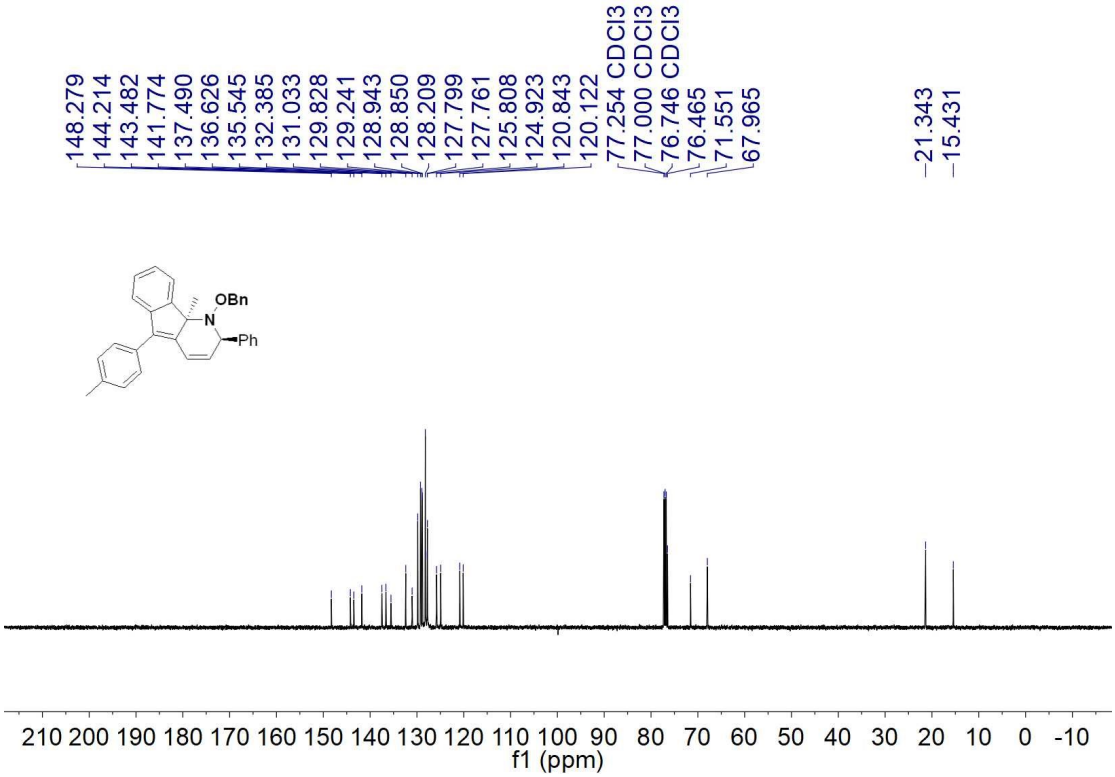


1-(Benzyloxy)-9*b*-methyl-2-phenyl-5-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ra) :

^{1}H NMR (500 MHz, $CDCl_3$)

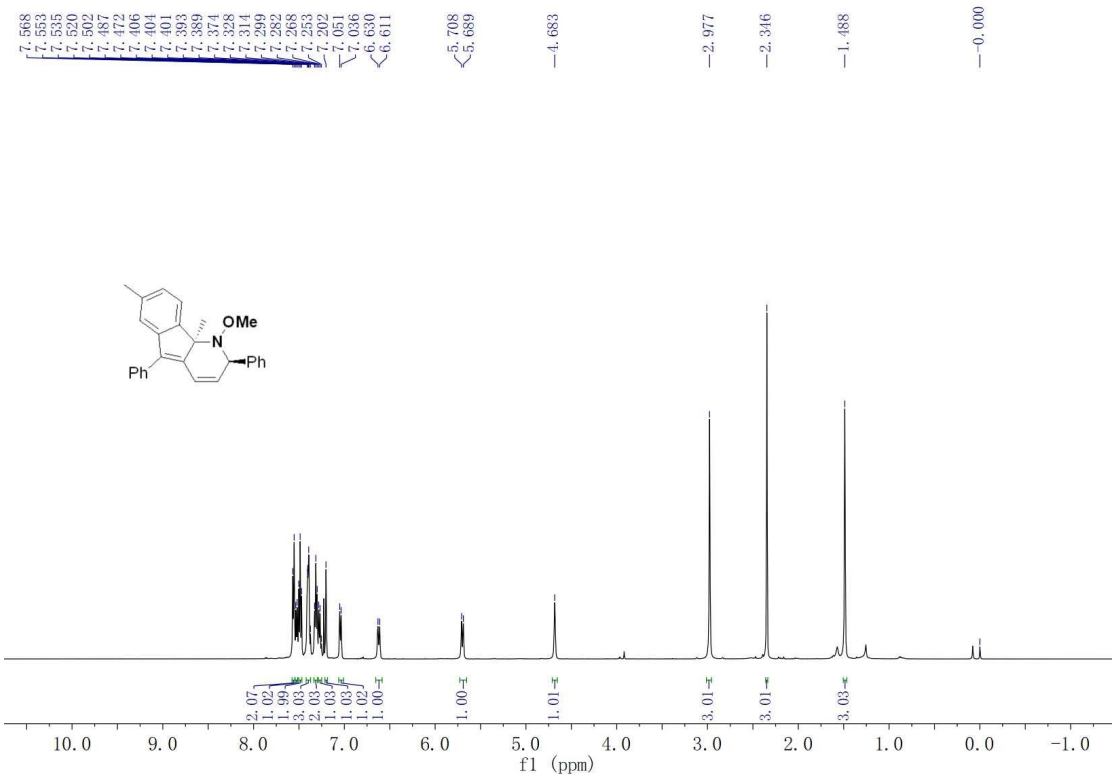


^{13}C NMR (125 MHz, $CDCl_3$)

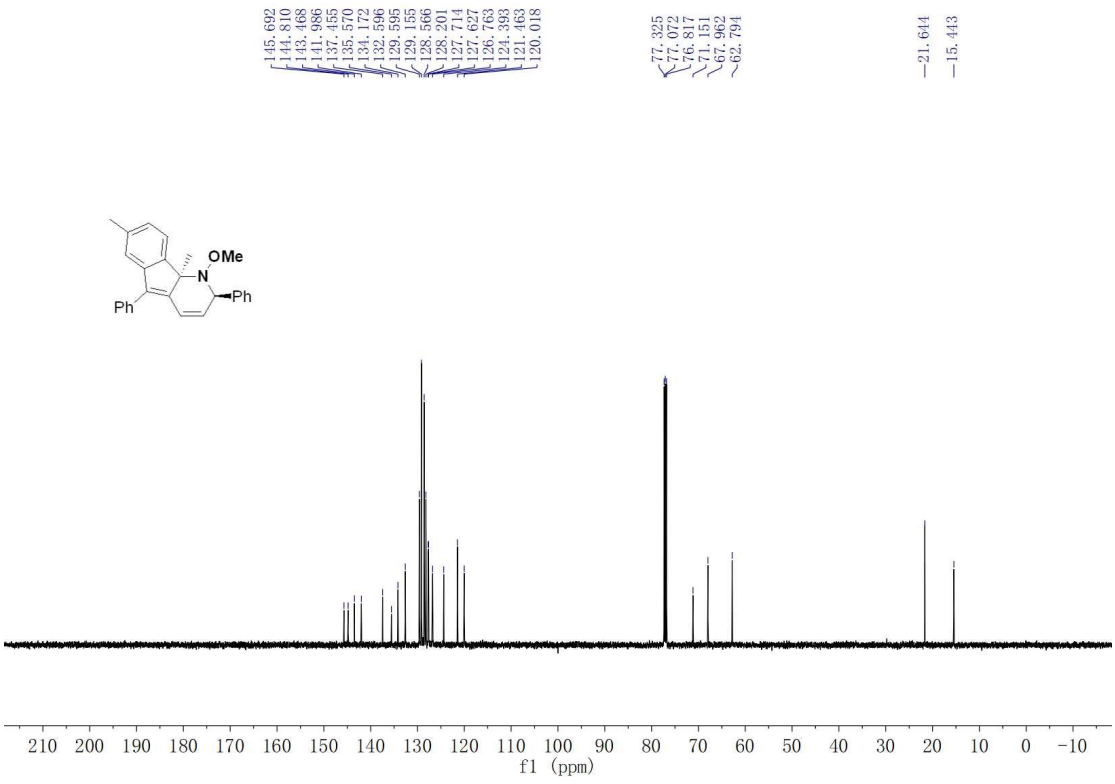


1-Methoxy-7,9*b*-dimethyl-2,5-diphenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3gb):

^{1}H NMR (500 MHz, $CDCl_3$)

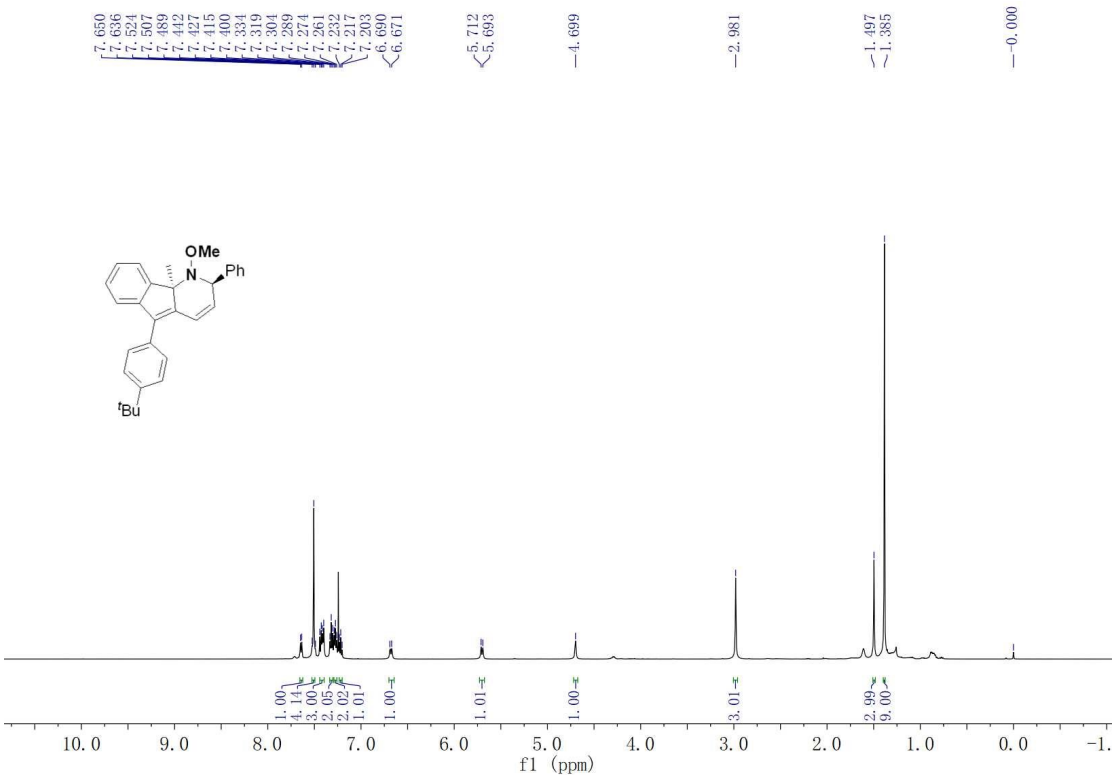


^{13}C NMR (125 MHz, $CDCl_3$)

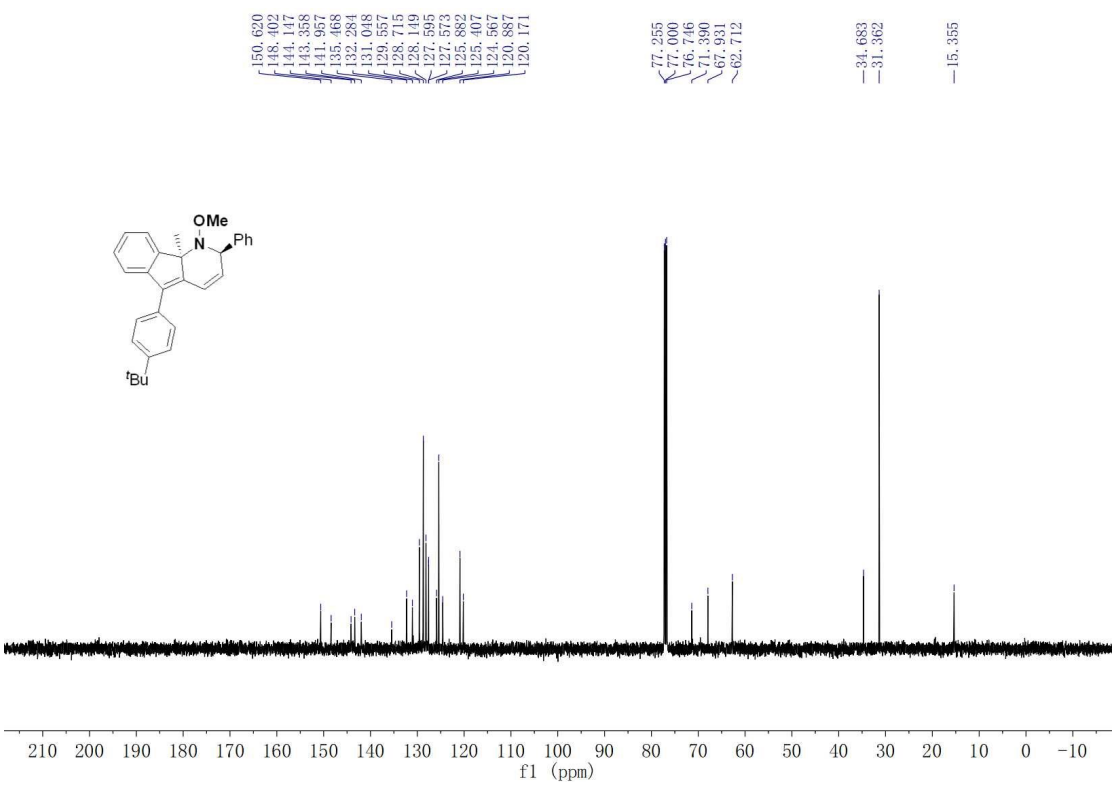


5-(4-(*tert*-Butyl)phenyl)-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ac):

^{1}H NMR (500 MHz, $CDCl_3$)

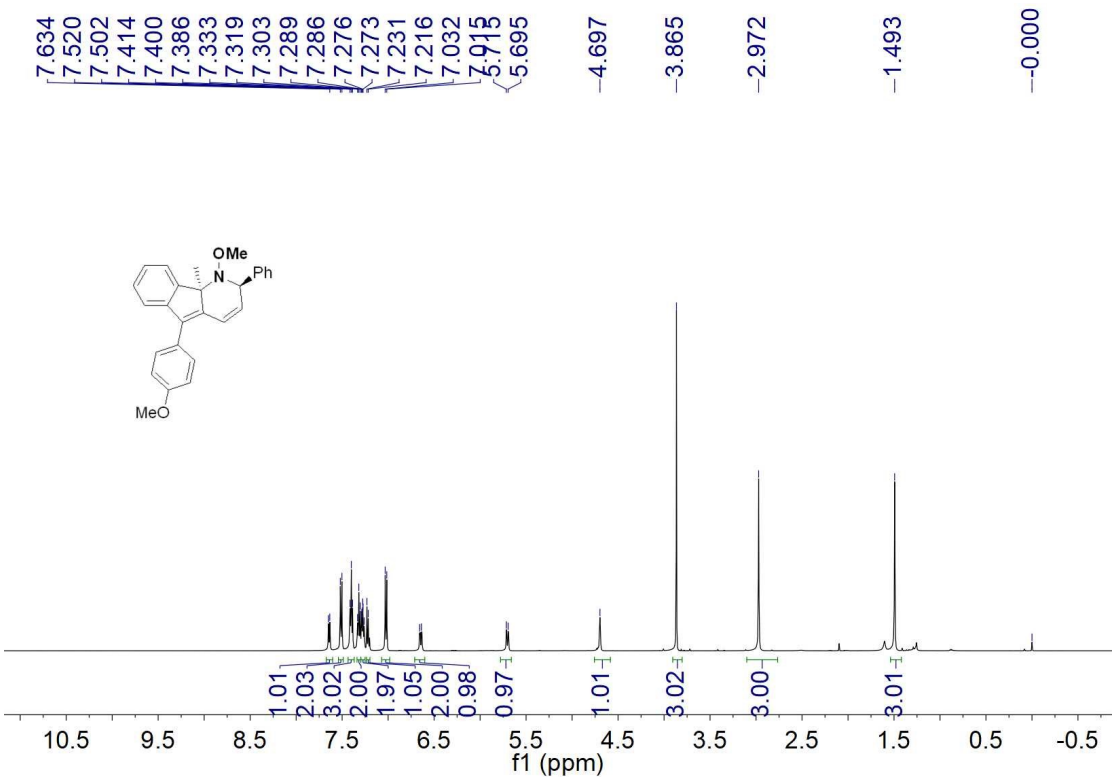


^{13}C NMR (125 MHz, $CDCl_3$)

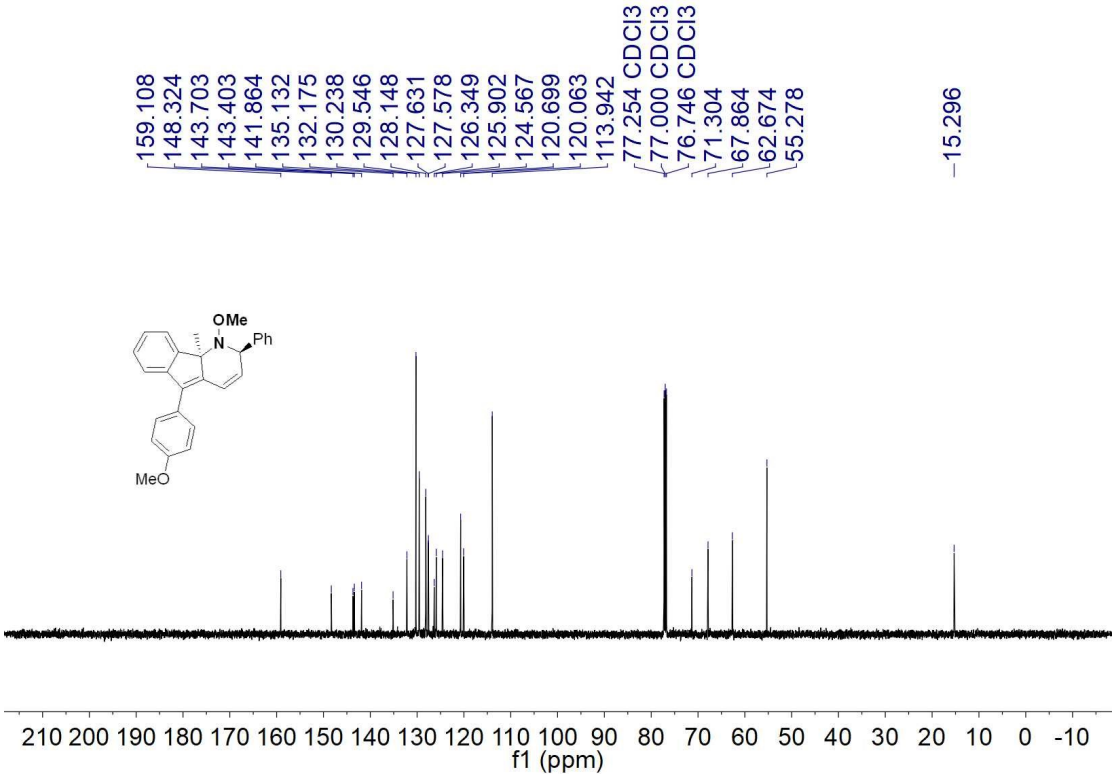


1-Methoxy-5-(4-methoxyphenyl)-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ad) :

^{1}H NMR (500 MHz, $CDCl_3$)

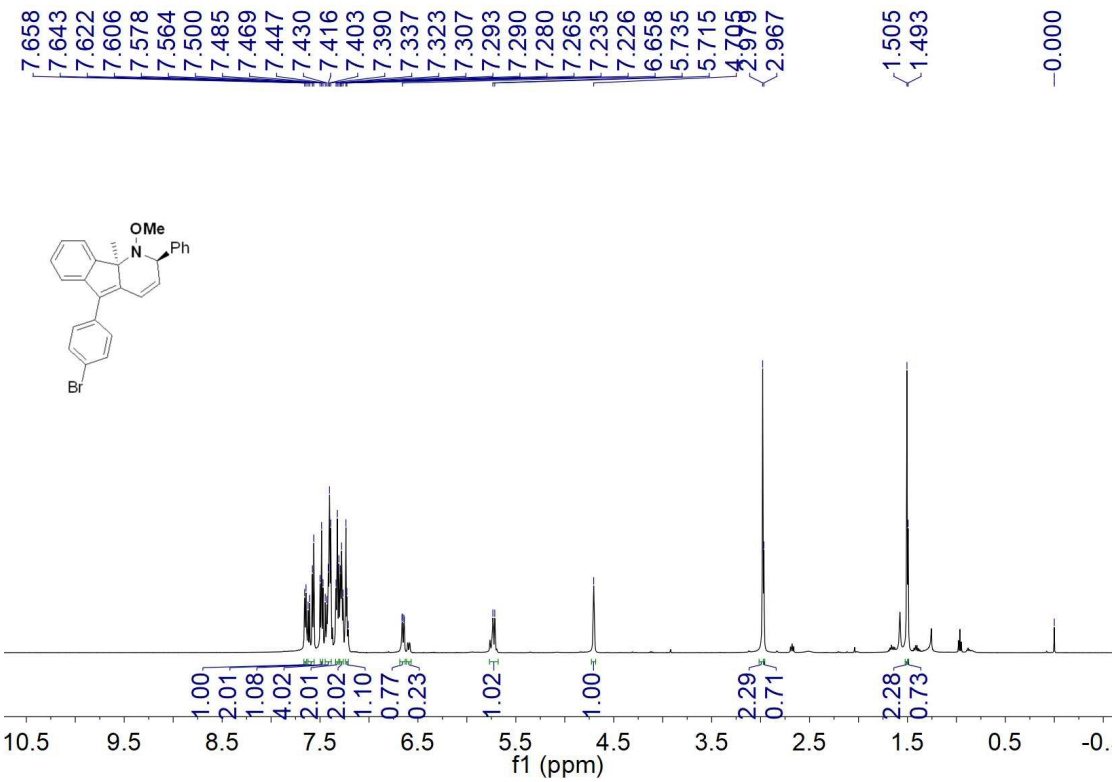


^{13}C NMR (125 MHz, $CDCl_3$)

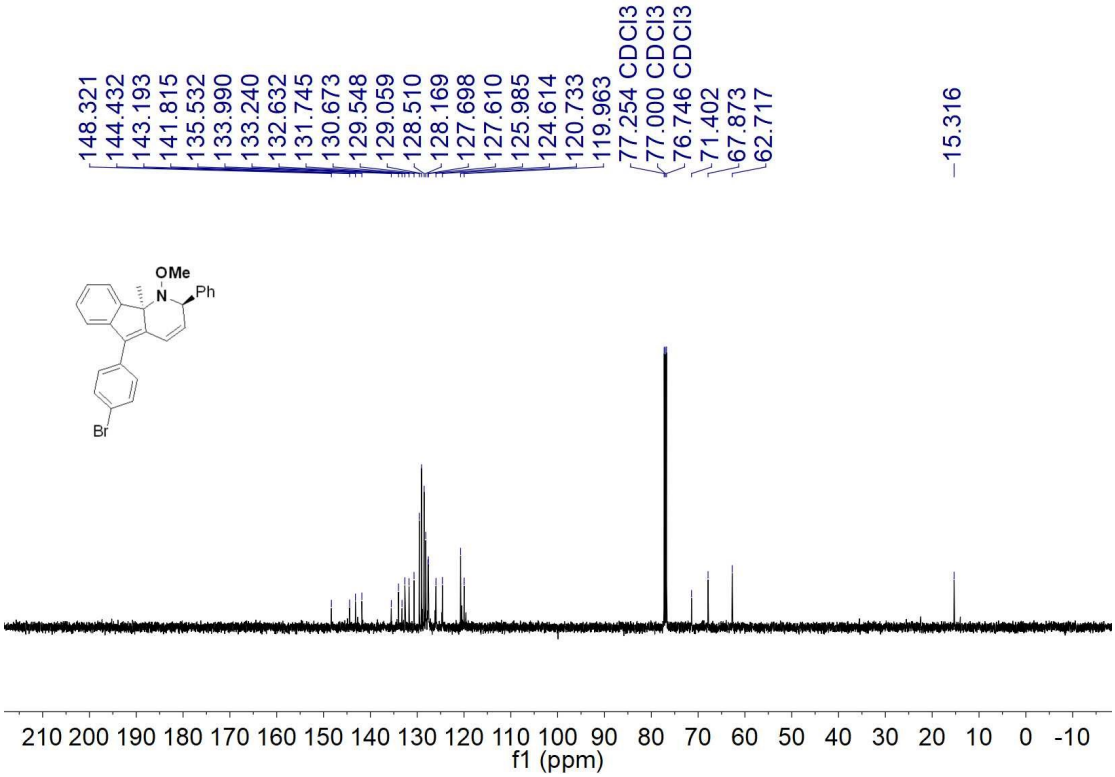


5-(4-Bromophenyl)-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ae):

^{1}H NMR (500 MHz, $CDCl_3$)

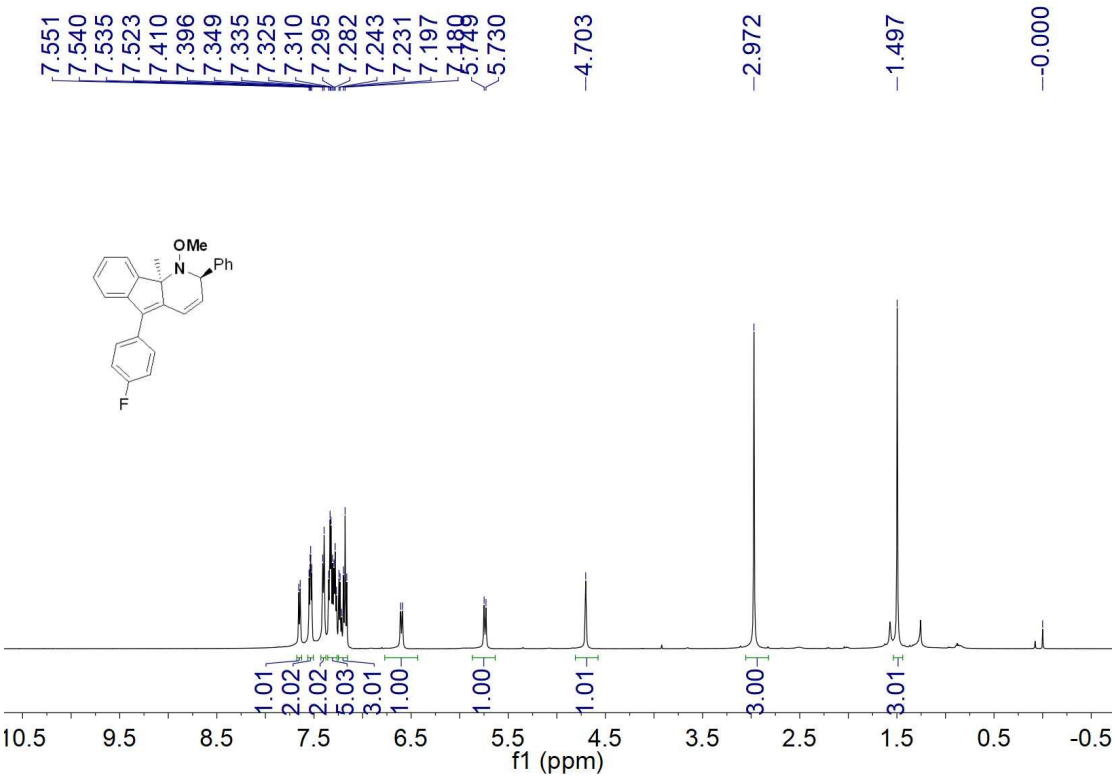


^{13}C NMR (125 MHz, $CDCl_3$)

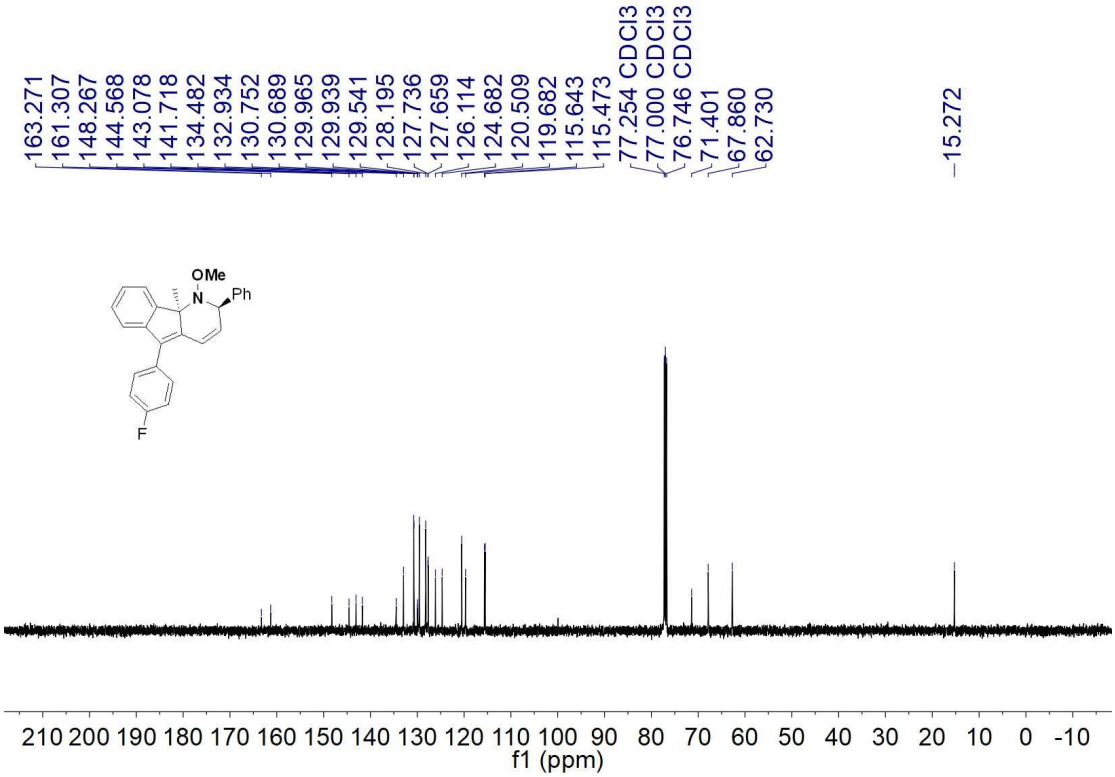


5-(4-Fluorophenyl)-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3af):

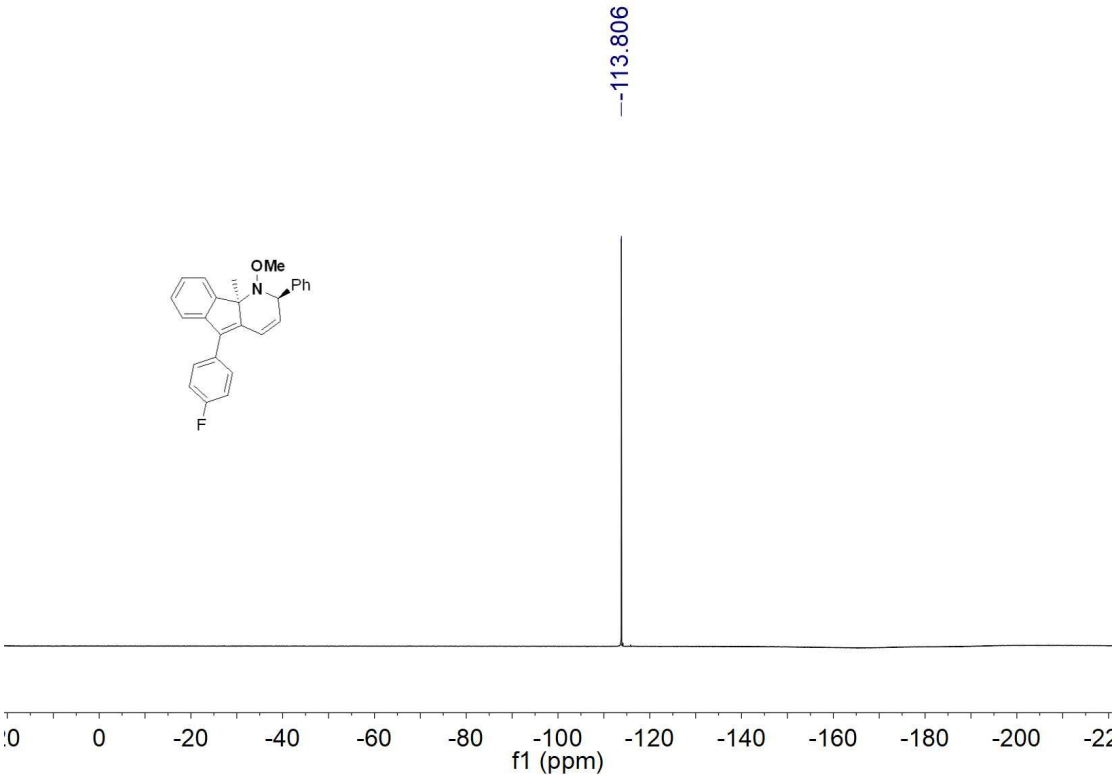
^{1}H NMR (500 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)

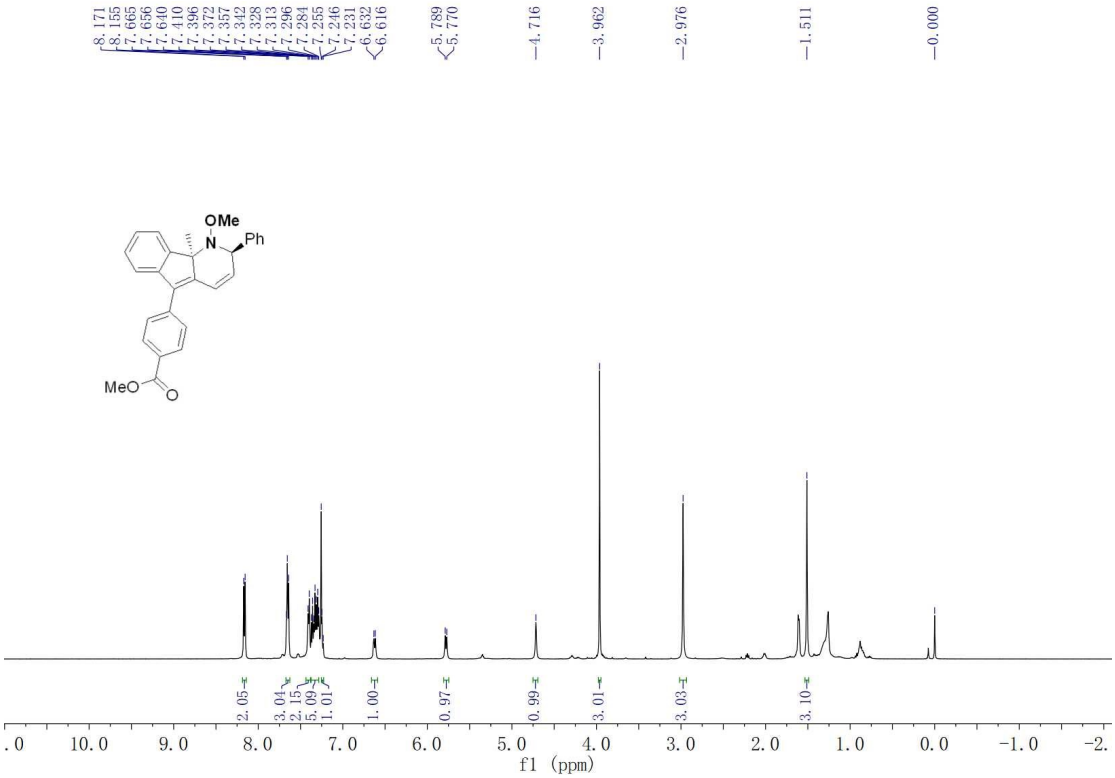


^{19}F NMR (471 MHz, $CDCl_3$)

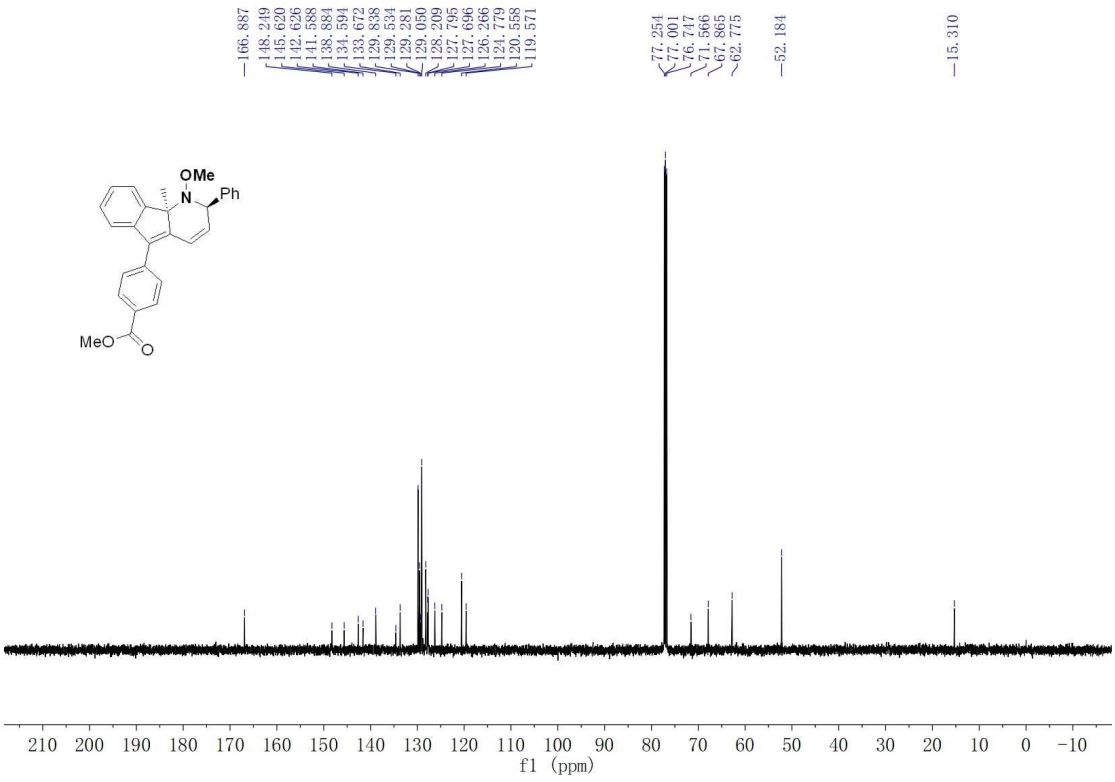


Methyl 4-(1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]-pyridin-5-yl)benzoate (3ag):

^{1}H NMR (500 MHz, $CDCl_3$)

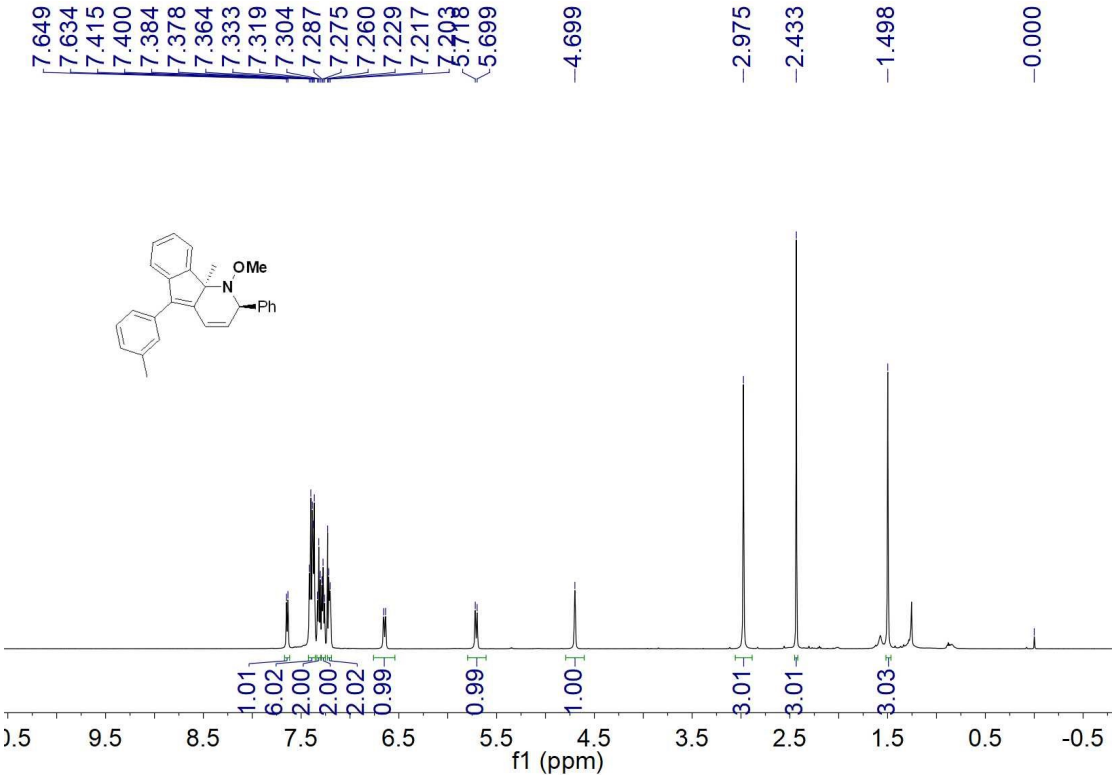


^{13}C NMR (125 MHz, $CDCl_3$)

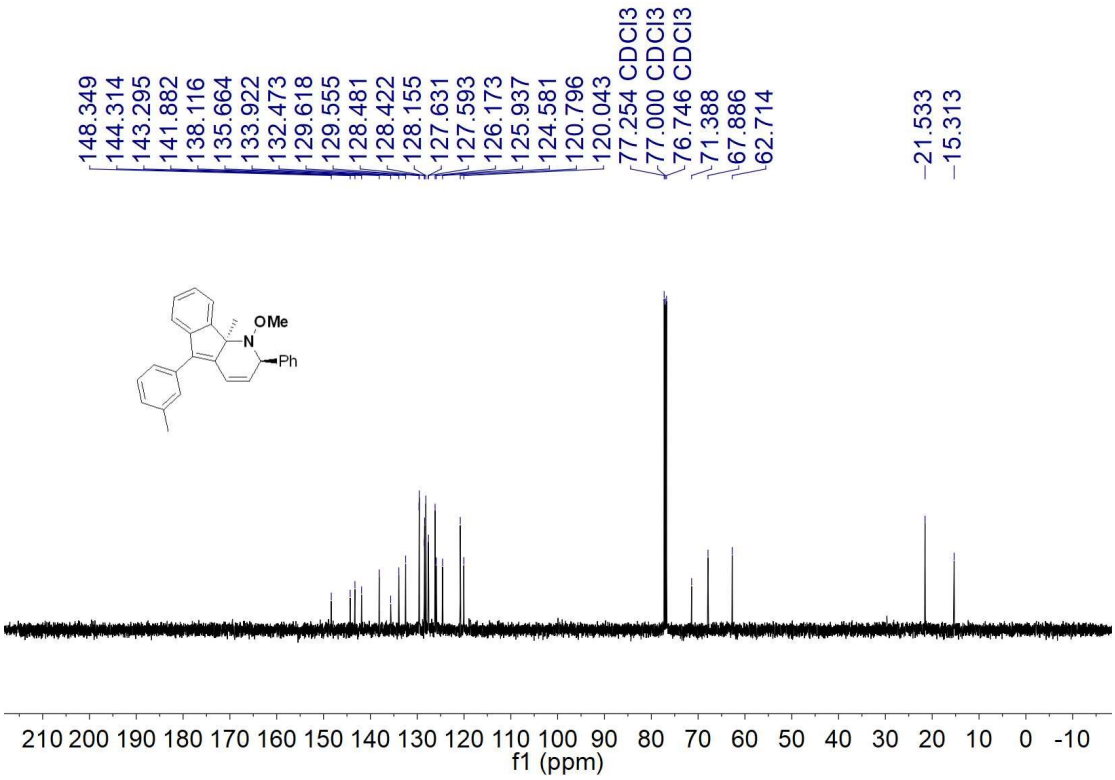


1-Methoxy-9*b*-methyl-2-phenyl-5-(m-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ah):

^{1}H NMR (500 MHz, $CDCl_3$)

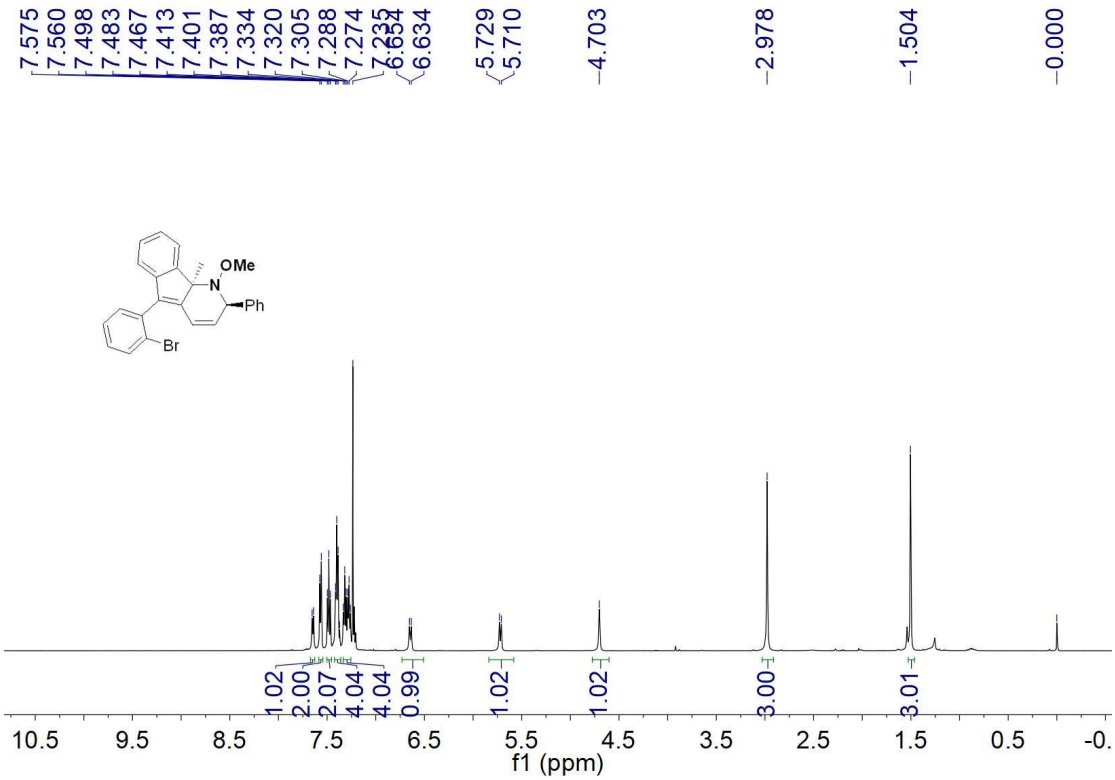


^{13}C NMR (125 MHz, $CDCl_3$)

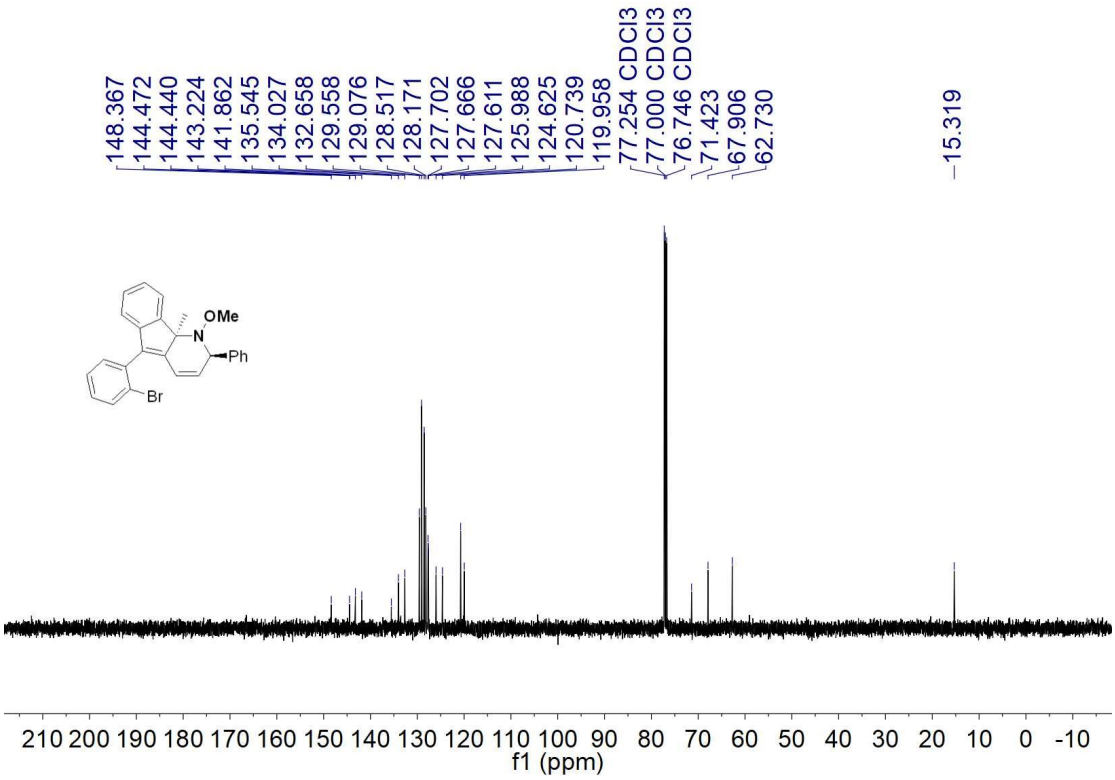


5-(2-Bromophenyl)-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ai):

^{1}H NMR (500 MHz, $CDCl_3$)

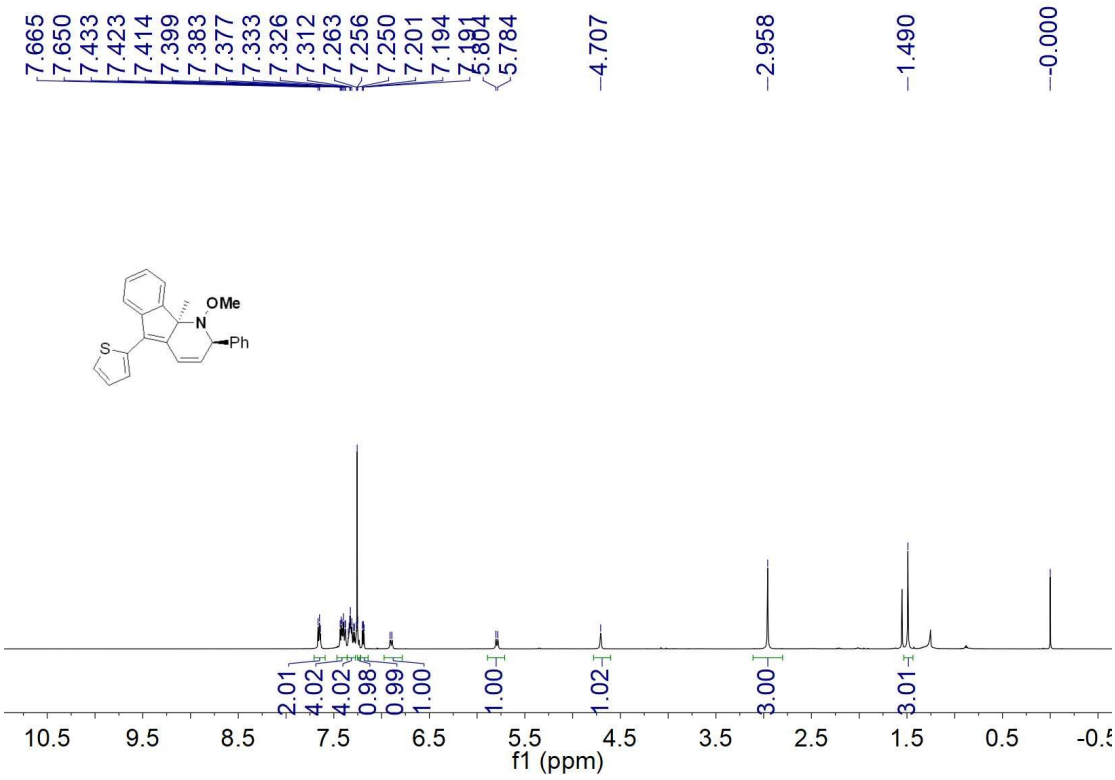


^{13}C NMR (125 MHz, $CDCl_3$)

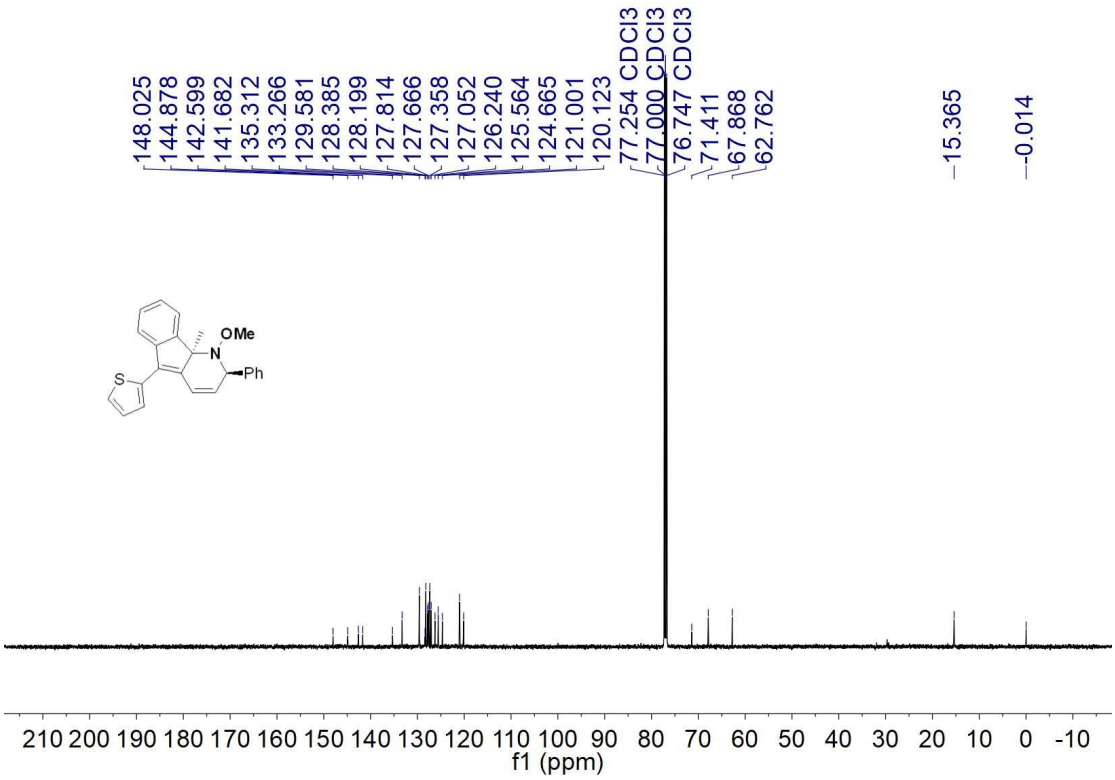


1-Methoxy-9*b*-methyl-2-phenyl-5-(thiophen-2-yl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3aj):

^{1}H NMR (500 MHz, $CDCl_3$)

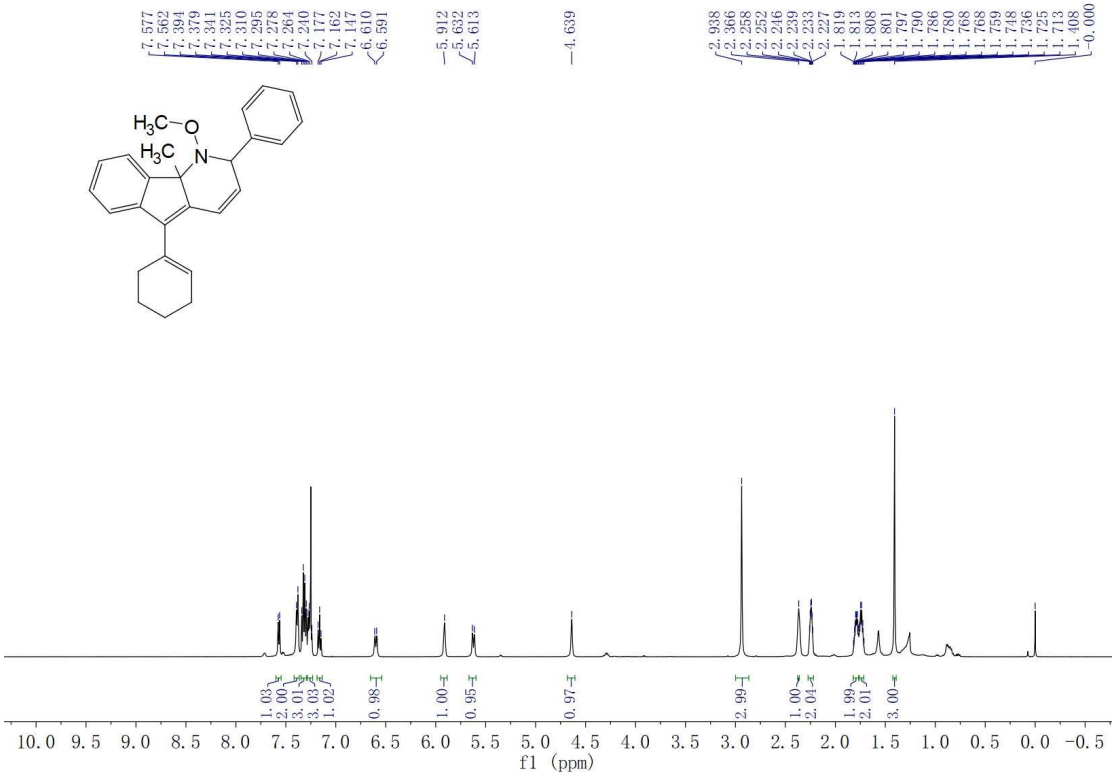


^{13}C NMR (125 MHz, $CDCl_3$)

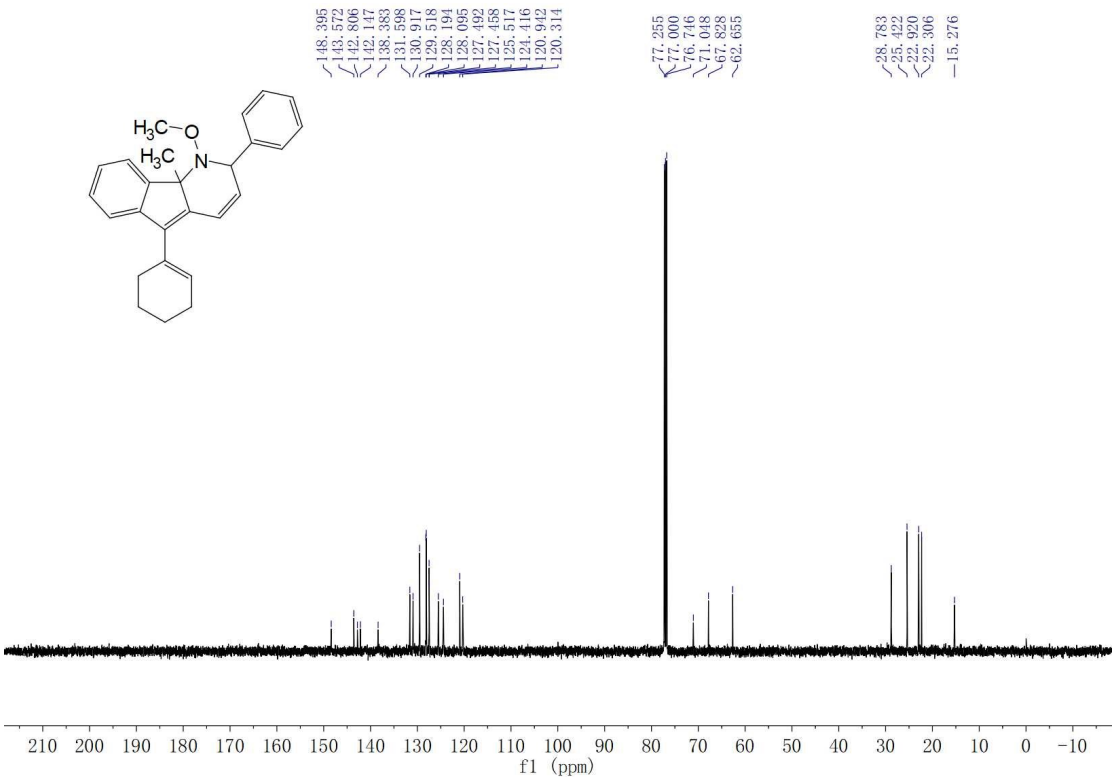


5-(Cyclohex-2-en-1-yl)-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ak):

^{1}H NMR (500 MHz, $CDCl_3$)

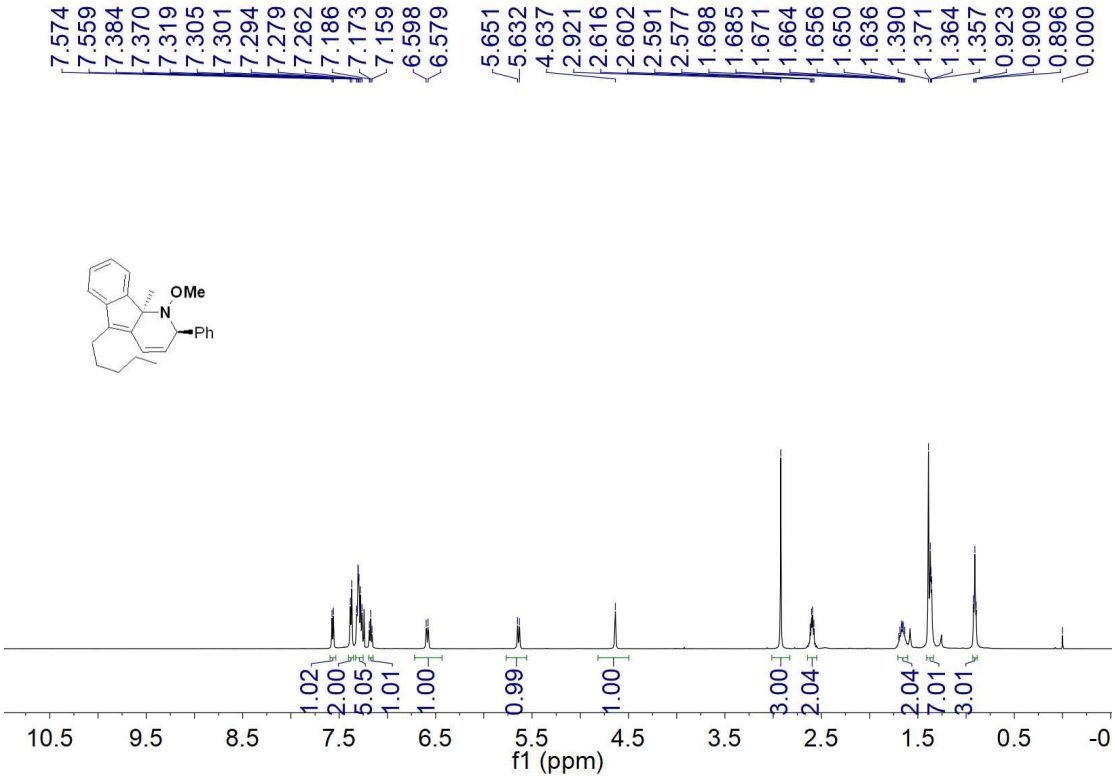


^{13}C NMR (125 MHz, $CDCl_3$)

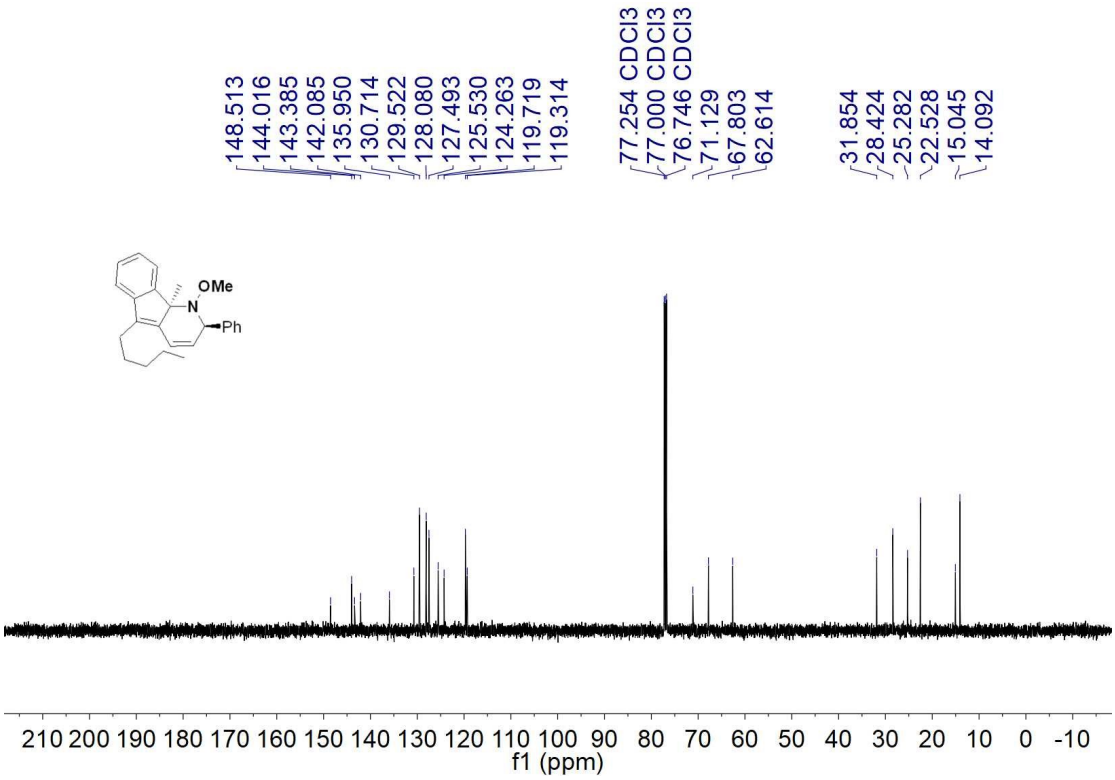


1-Methoxy-9*b*-methyl-5-pentyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3al):

^{1}H NMR (500 MHz, $CDCl_3$)

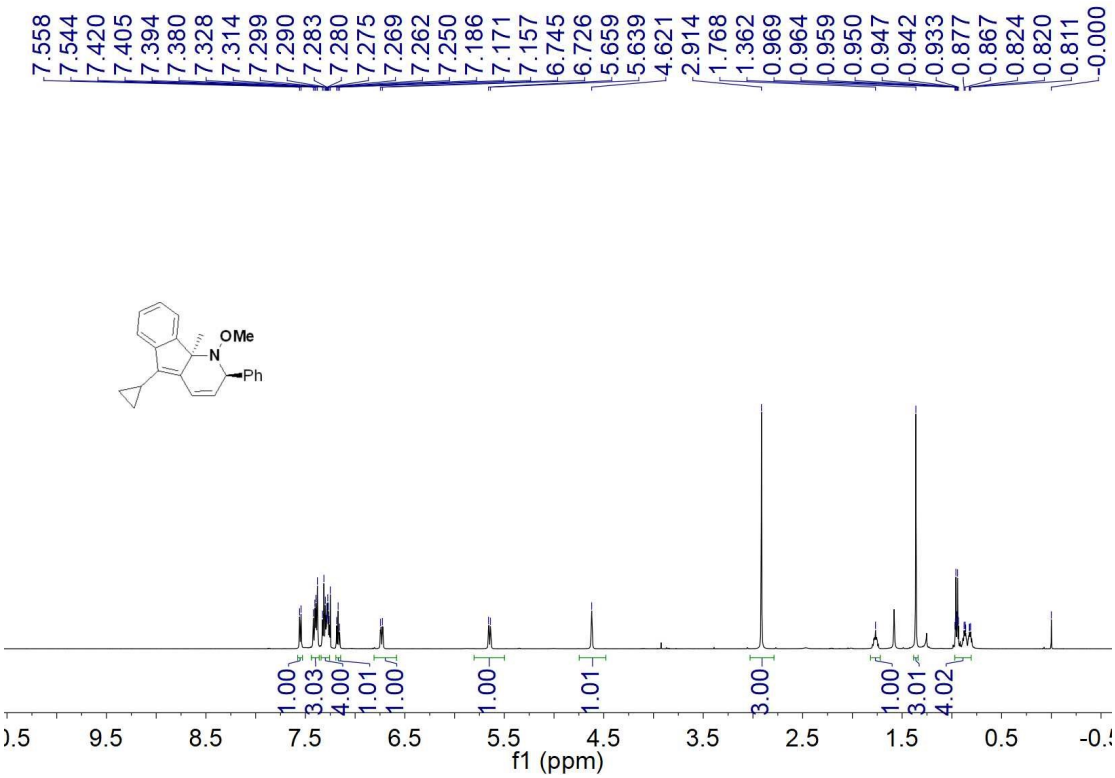


^{13}C NMR (125 MHz, $CDCl_3$)

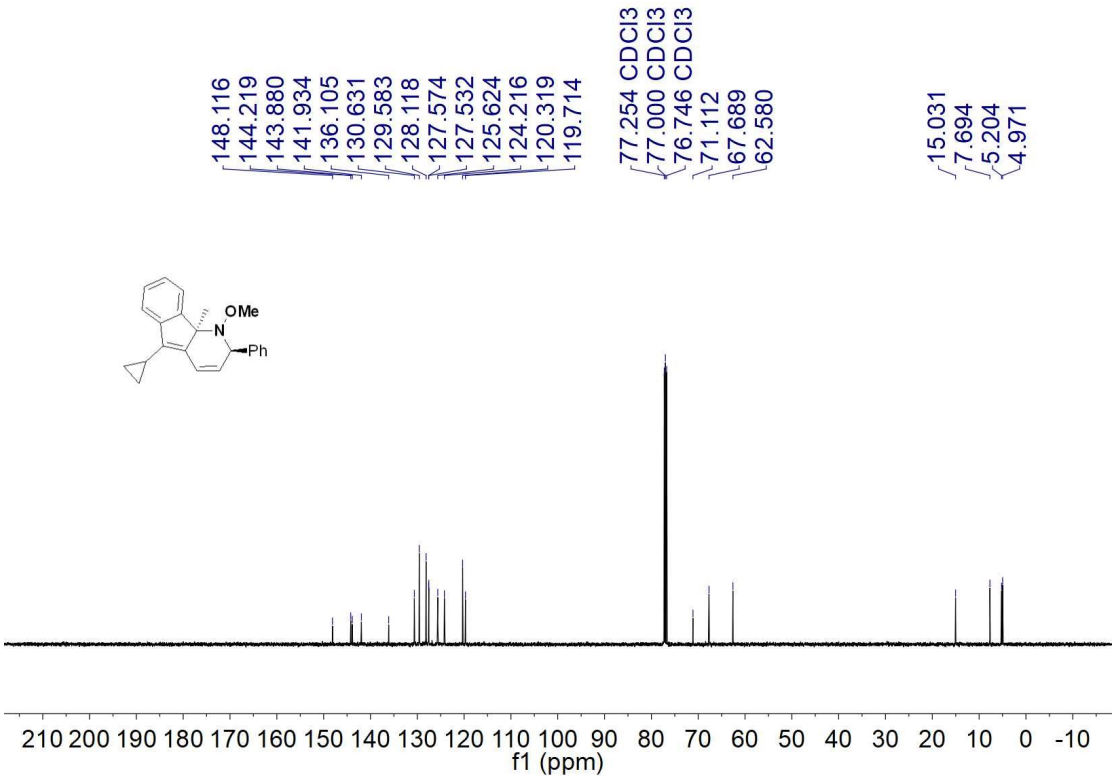


5-Cyclopropyl-1-methoxy-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3am) :

^{1}H NMR (500 MHz, $CDCl_3$)

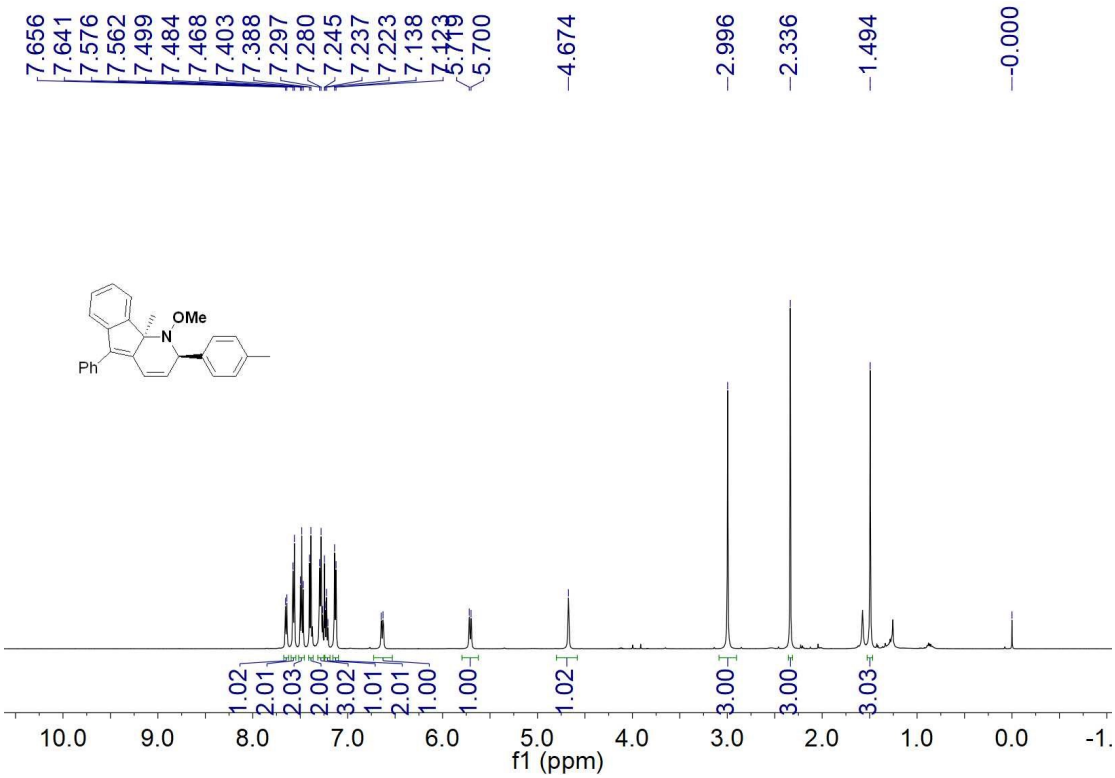


^{13}C NMR (125 MHz, $CDCl_3$)

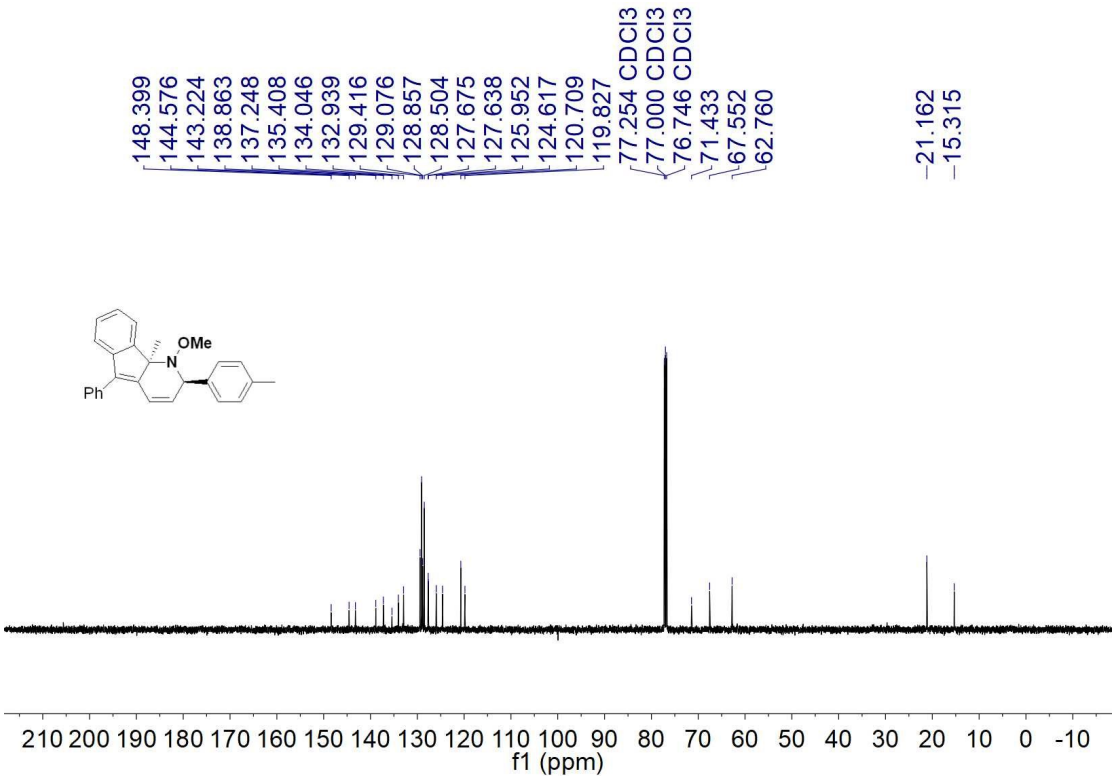


1-Methoxy-9*b*-methyl-5-phenyl-2-(*p*-tolyl)-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ao):

^{1}H NMR (500 MHz, $CDCl_3$)

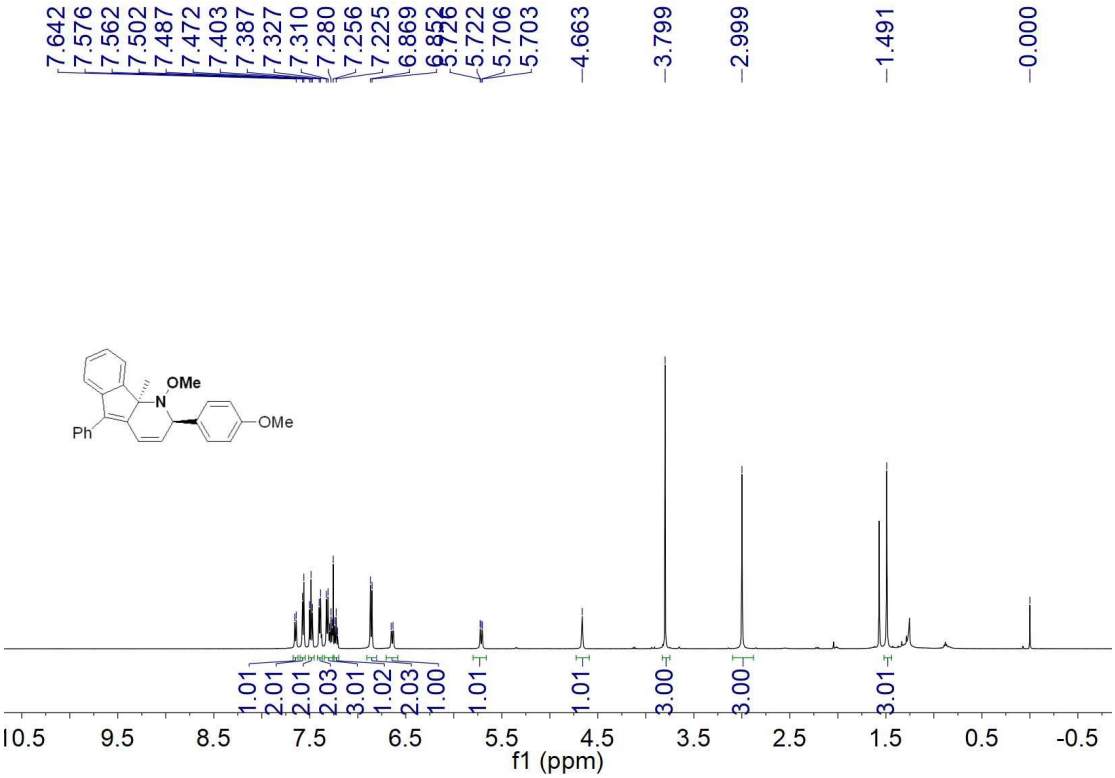


^{13}C NMR (125 MHz, $CDCl_3$)

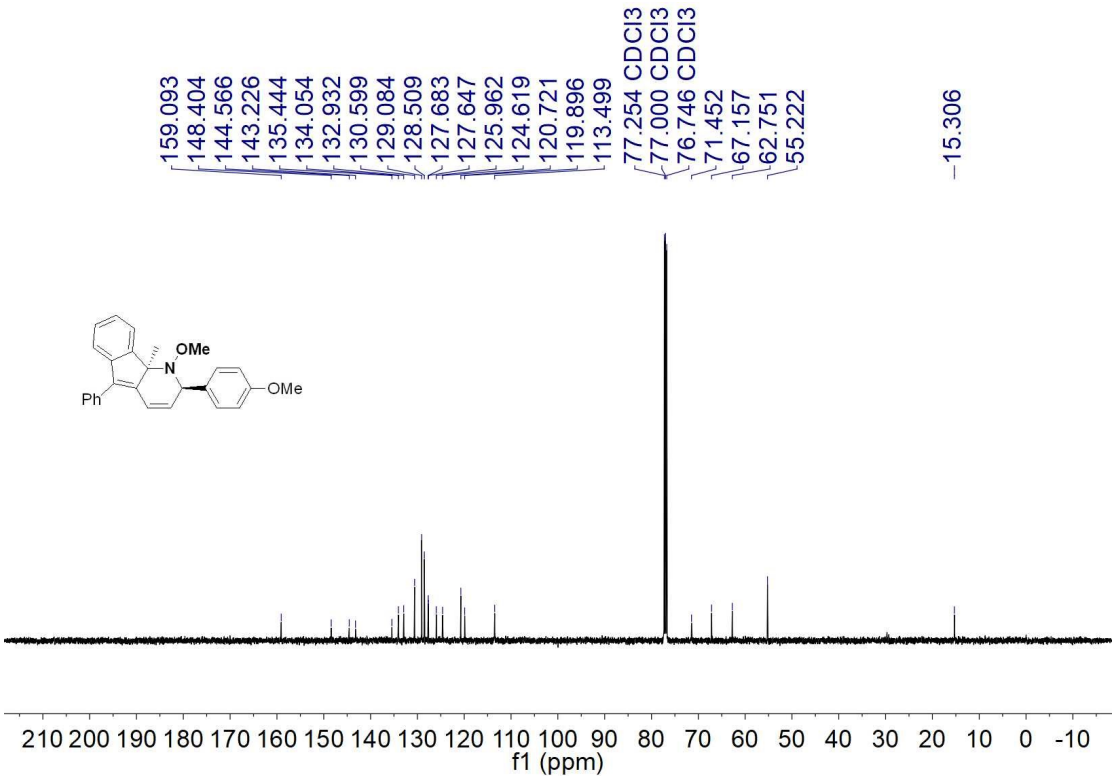


1-Methoxy-2-(4-methoxyphenyl)-9*b*-methyl-5-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ap):

^{1}H NMR (500 MHz, $CDCl_3$)

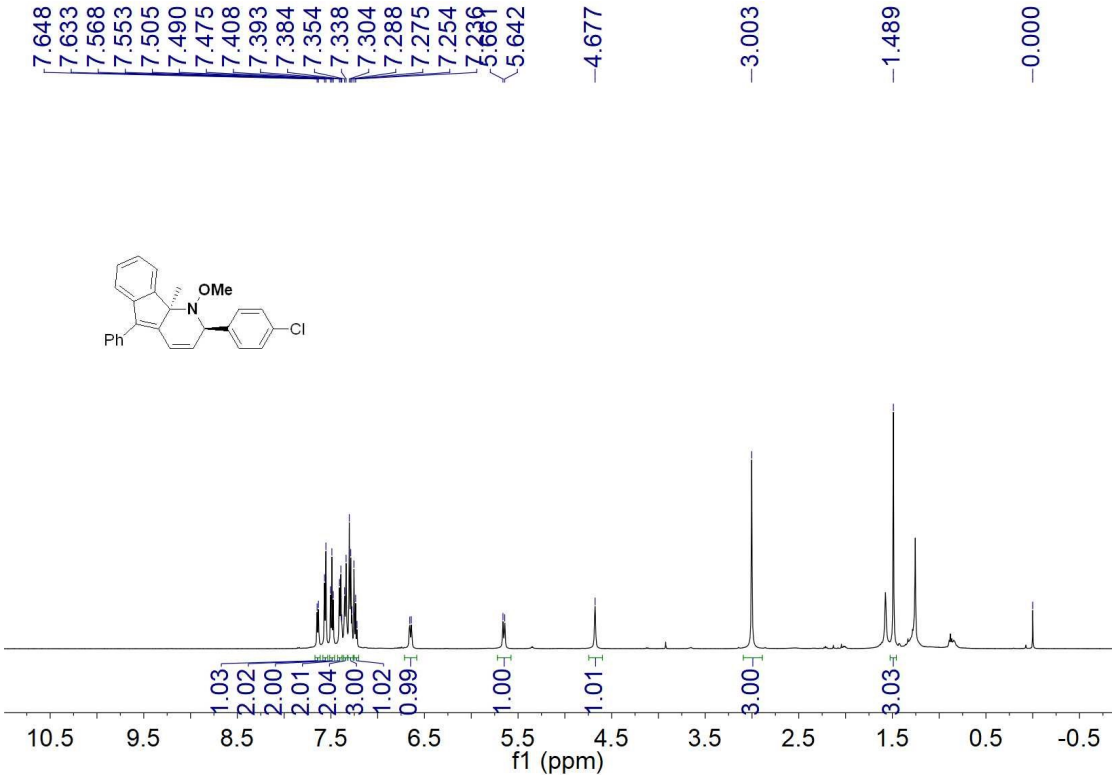


^{13}C NMR (125 MHz, $CDCl_3$)

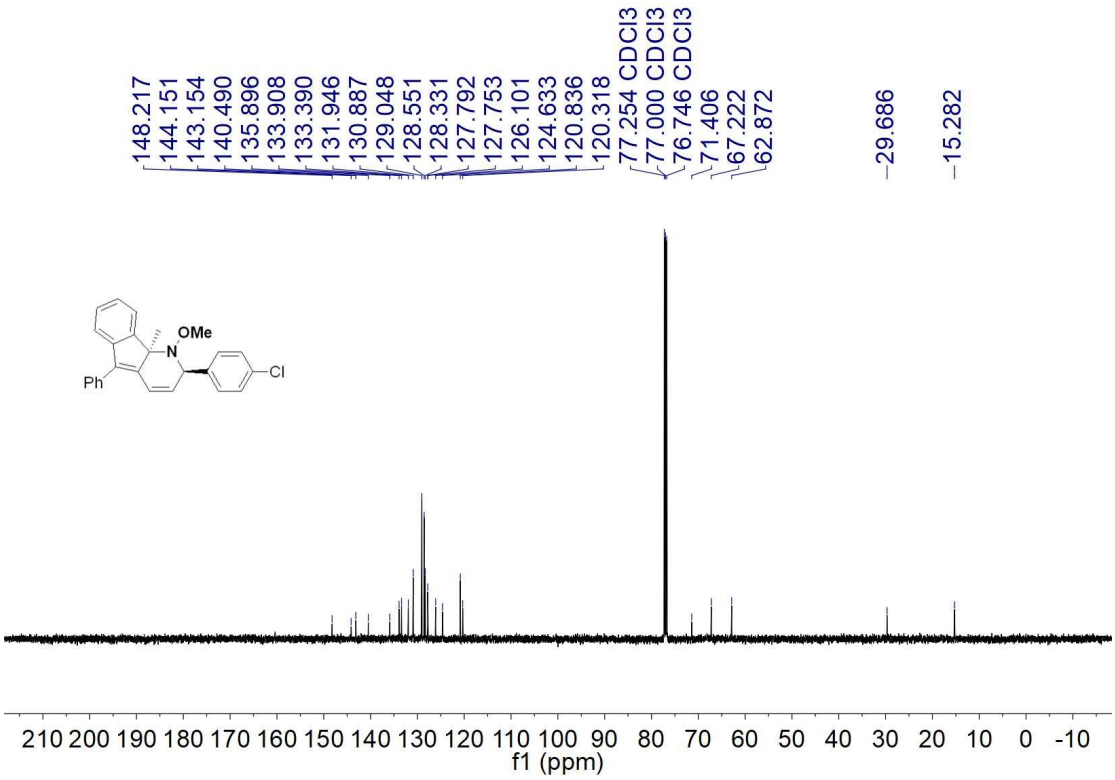


2-(4-Chlorophenyl)-1-methoxy-9*b*-methyl-5-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3aq):

^{1}H NMR (500 MHz, $CDCl_3$)

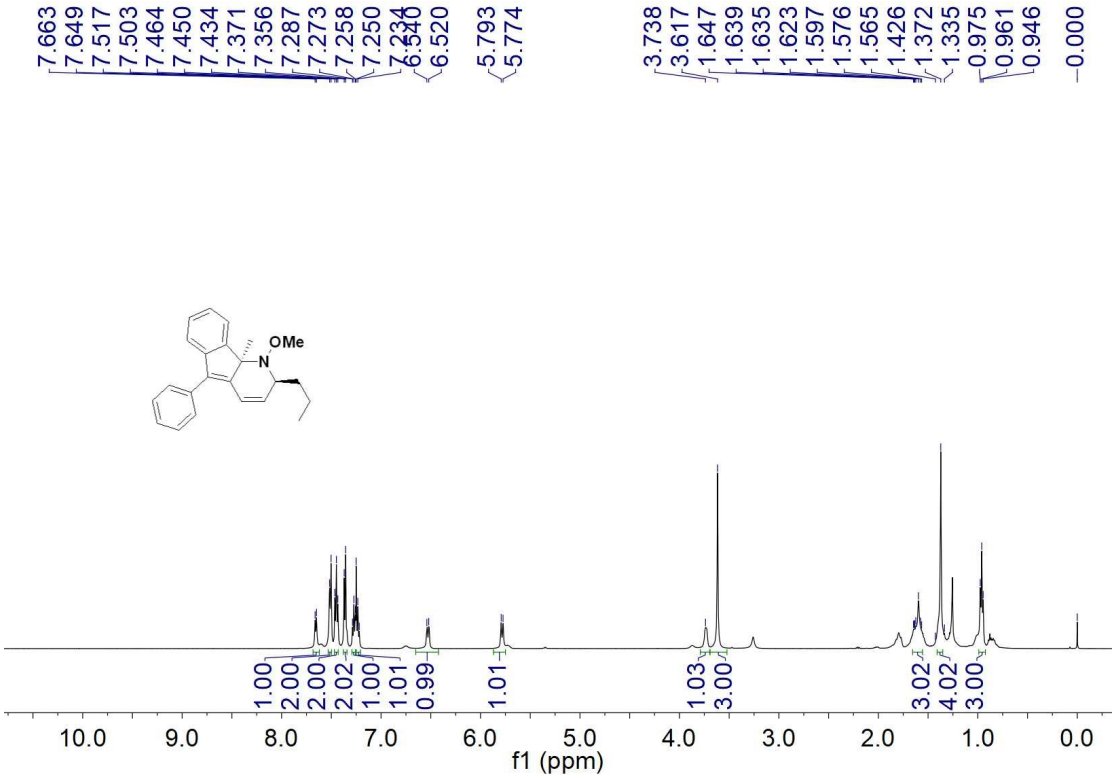


^{13}C NMR (125 MHz, $CDCl_3$)

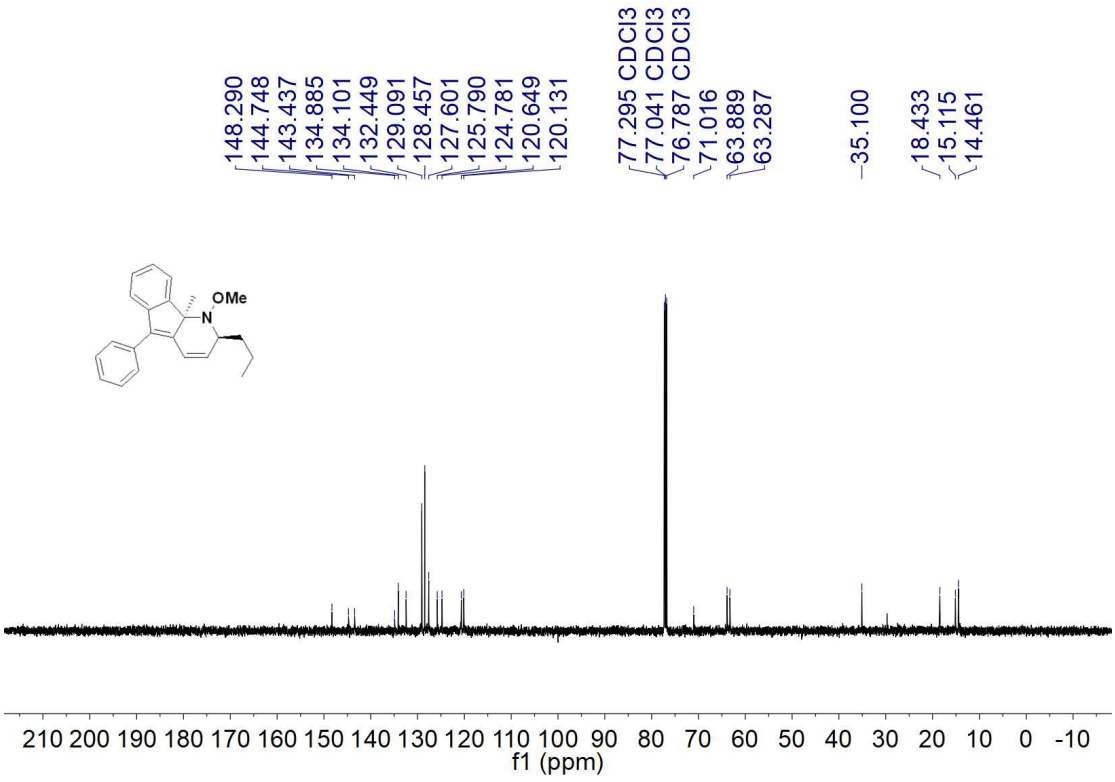


1-Methoxy-9*b*-methyl-5-phenyl-2-propyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3ar) :

^{1}H NMR (500 MHz, $CDCl_3$)

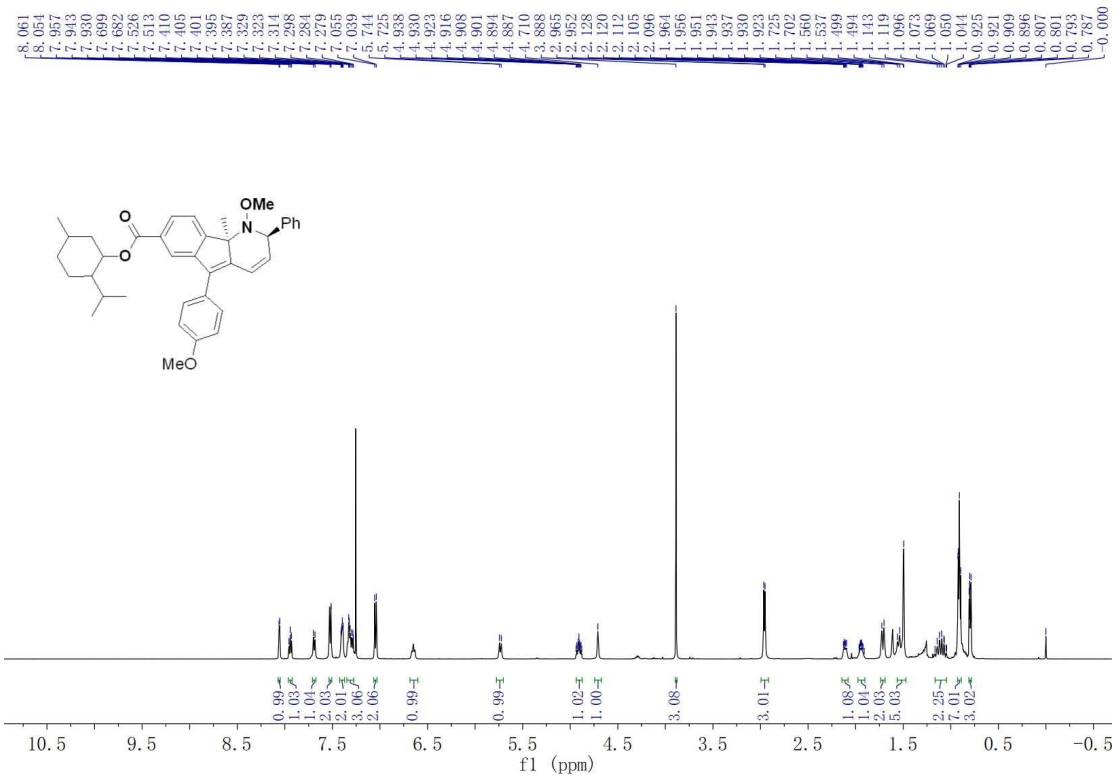


^{13}C NMR (125 MHz, $CDCl_3$)

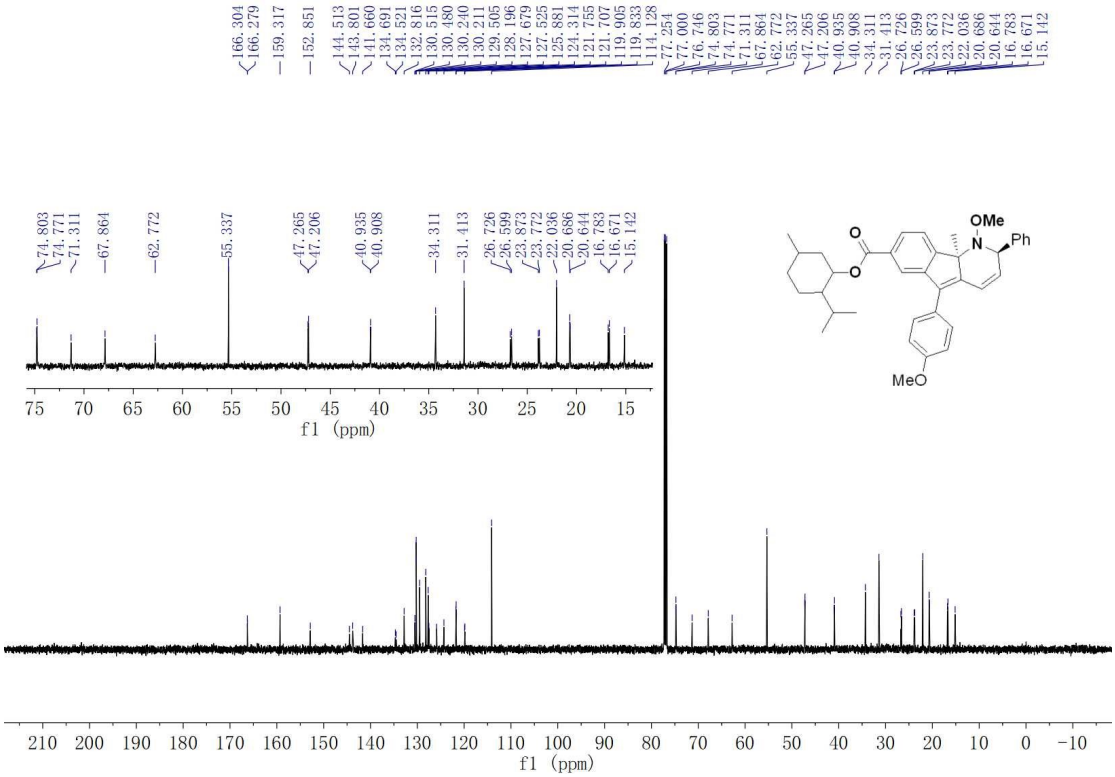


2-Isopropyl-5-methylcyclohexyl 1-methoxy-5-(4-methoxyphenyl)-9*b*-methyl-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine-7-carboxylate (3sd):

^{1}H NMR (500 MHz, $CDCl_3$)

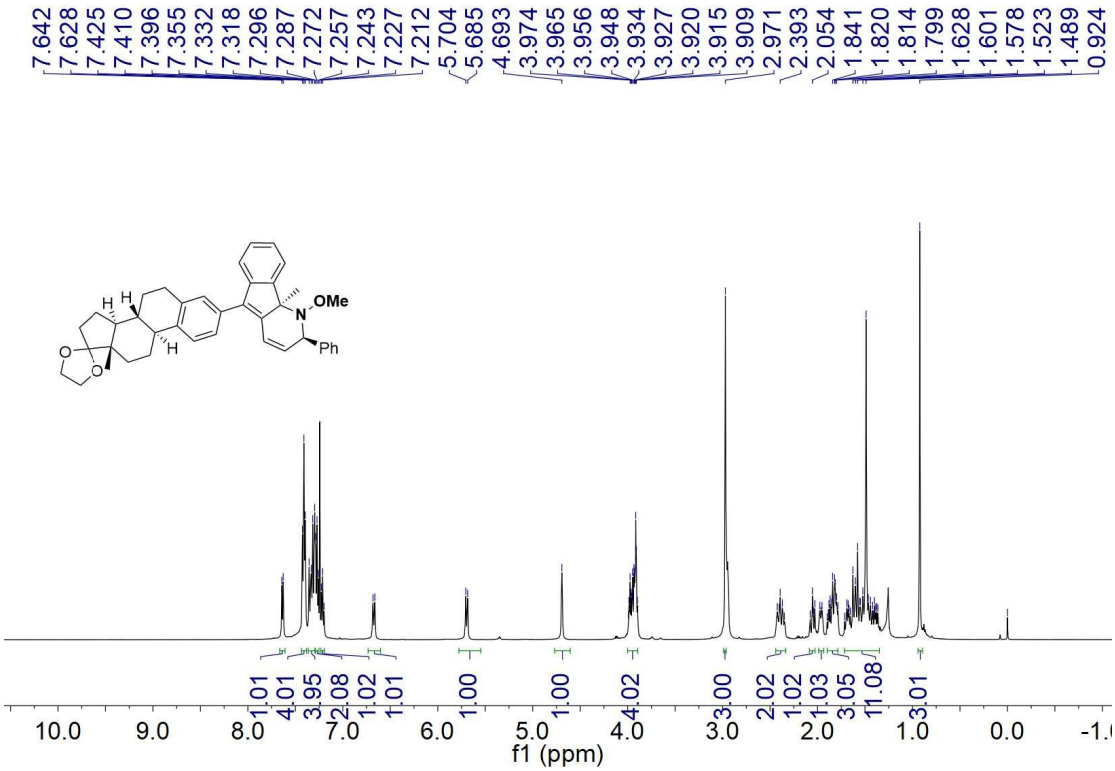


^{13}C NMR (125 MHz, $CDCl_3$)

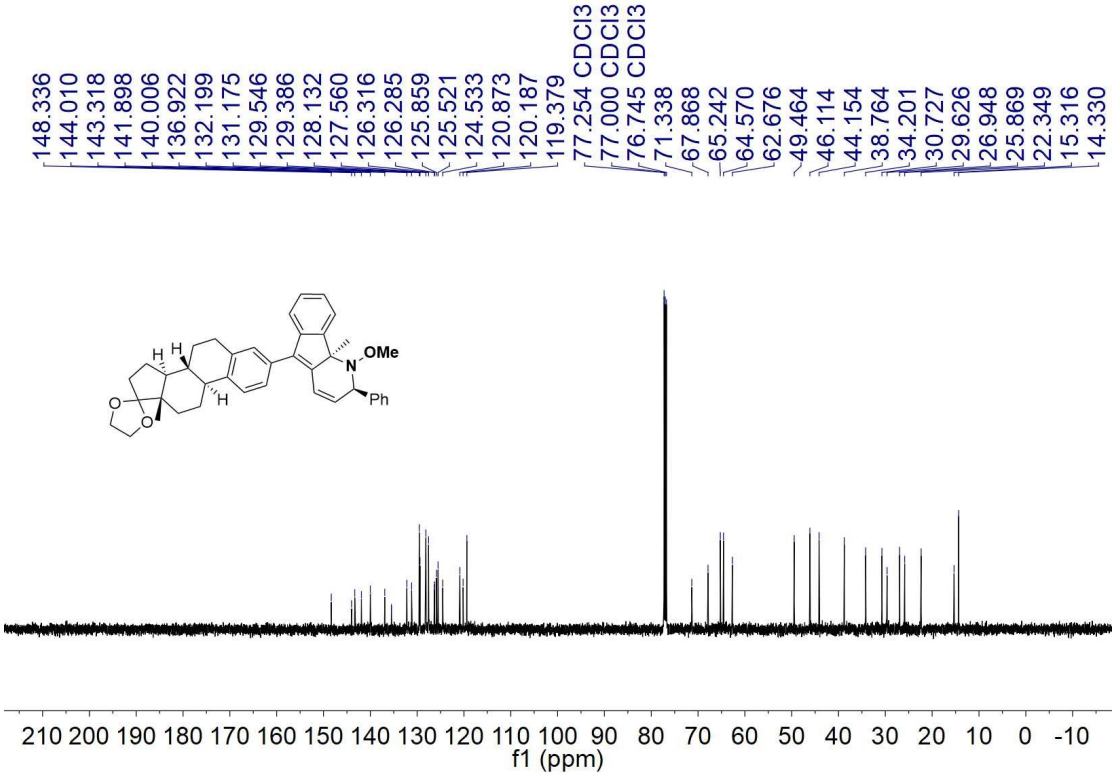


1-Methoxy-9*b*-methyl-5-((8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-yl)-2-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3bu):

^{1}H NMR (500 MHz, $CDCl_3$)

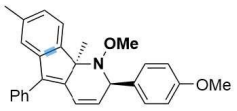


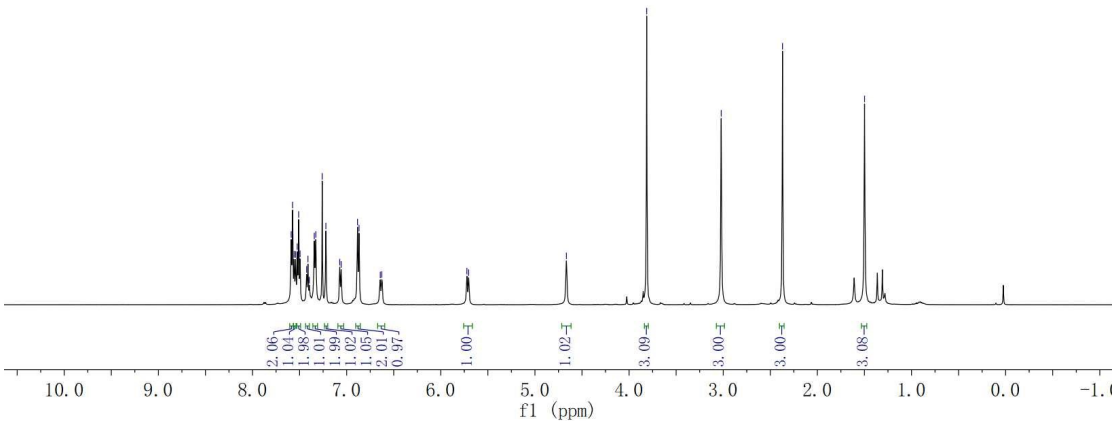
^{13}C NMR (125 MHz, $CDCl_3$)



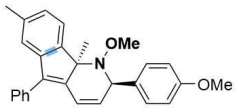
1-Methoxy-2-(4-methoxyphenyl)-7,9*b*-dimethyl-5-phenyl-2,9*b*-dihydro-1*H*-indeno[1,2-*b*]pyridine (3av):

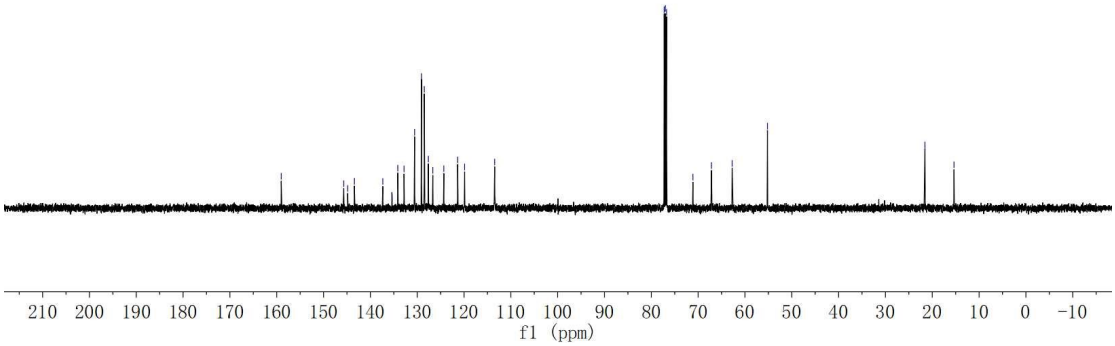
^{1}H NMR (500 MHz, $CDCl_3$)





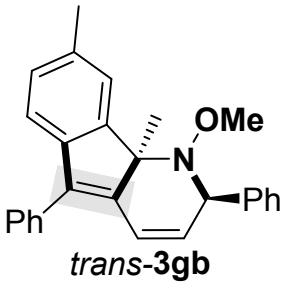
^{13}C NMR (125 MHz, $CDCl_3$)



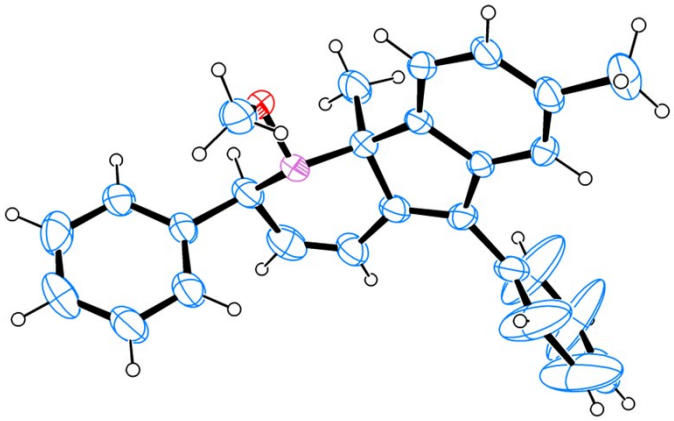


(D) The X-ray structure of 3gb.

CCDC 2013160 contains the supplementary crystallographic data which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



trans-**3gb**



The thermal ellipsoid plot of 4aba with 30 % displacement ellipsoids

Table S2. Crystal data and structure refinement for A.

Identification code	A	
Empirical formula	C27 H25 N O	
Formula weight	379.48	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/c$	
Unit cell dimensions	a = 14.865(5) Å	α= 90°.
	b = 14.925(5) Å	β= 109.544(5)°.
	c = 10.074(4) Å	γ = 90°.
Volume	2106.2(13) $Å^3$	
Z	4	
Density (calculated)	1.197 Mg/m^3	
Absorption coefficient	0.072 mm^{-1}	
F(000)	808	
Crystal size	? x ? x ? mm^3	
Theta range for data collection	2.543 to 25.496°.	

Index ranges	-18<=h<=17, -18<=k<=17, -12<=l<=12
Reflections collected	15966
Independent reflections	3915 [R(int) = 0.1148]
Completeness to theta = 25.242°	99.9 %
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3915 / 0 / 253
Goodness-of-fit on F^2	3.295
Final R indices [I>2sigma(I)]	R1 = 0.1412, wR2 = 0.2530
R indices (all data)	R1 = 0.2083, wR2 = 0.2679
Extinction coefficient	n/a
Largest diff. peak and hole	1.069 and -0.599 e.$Å^{-3}$

Table S3. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for A. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(22)	985(4)	7351(4)	6021(5)	82(2)
C(23)	1322(5)	8115(5)	5555(10)	274(10)
C(24)	724(7)	8849(5)	5084(11)	540(30)
C(25)	-212(6)	8818(4)	5079(8)	248(9)
C(26)	-549(4)	8053(5)	5545(11)	253(10)
C(27)	49(5)	7319(4)	6016(10)	249(9)
C(1)	2782(6)	4732(5)	2670(7)	91(2)
C(2)	3161(6)	4561(6)	1654(7)	101(3)
C(3)	3392(6)	3702(7)	1418(8)	102(3)
C(4)	3216(6)	3019(5)	2189(9)	95(2)
C(5)	2808(5)	3197(4)	3230(7)	83(2)
C(6)	2614(5)	4064(4)	3454(6)	71(2)
C(7)	2162(6)	4262(4)	4577(6)	78(2)
C(8)	1220(6)	4752(6)	3939(7)	96(3)
C(9)	951(5)	5436(5)	4505(7)	77(2)
C(10)	1561(4)	5770(4)	5818(6)	62(2)
C(11)	2367(4)	5174(4)	6701(6)	58(2)
C(12)	1983(5)	4418(4)	7422(7)	84(2)
C(13)	4457(5)	4504(5)	6301(7)	89(2)
C(14)	2979(4)	5801(4)	7780(6)	52(2)
C(15)	2490(4)	6627(4)	7670(6)	50(1)
C(16)	1631(4)	6586(4)	6465(6)	58(2)
C(17)	3841(4)	5708(4)	8825(6)	59(2)
C(18)	4211(4)	6395(5)	9726(6)	66(2)
C(19)	3748(5)	7191(4)	9655(6)	66(2)
C(20)	2876(4)	7303(4)	8622(6)	59(2)
C(21)	4152(5)	7916(4)	10721(7)	91(2)
N(1)	2817(4)	4825(3)	5684(5)	60(1)
O(1)	3570(3)	4230(2)	6472(4)	70(1)

Table S4. Bond lengths [Å] and angles [°] for A.

C(22)-C(23)	1.3900
C(22)-C(27)	1.3900
C(22)-C(16)	1.462(7)
C(23)-C(24)	1.3900
C(23)-H(23)	0.9300
C(24)-C(25)	1.3900
C(24)-H(24)	0.9300
C(25)-C(26)	1.3900
C(25)-H(25)	0.9300
C(26)-C(27)	1.3900
C(26)-H(26)	0.9300
C(27)-H(27)	0.9300
C(1)-C(2)	1.347(10)
C(1)-C(6)	1.346(9)
C(1)-H(1)	0.9300
C(2)-C(3)	1.368(10)
C(2)-H(2)	0.9300
C(3)-C(4)	1.358(10)
C(3)-H(3)	0.9300
C(4)-C(5)	1.401(10)
C(4)-H(4)	0.9300
C(5)-C(6)	1.360(8)
C(5)-H(5)	0.9300
C(6)-C(7)	1.526(9)
C(7)-N(1)	1.473(7)
C(7)-C(8)	1.519(10)
C(7)-H(7)	0.9800
C(8)-C(9)	1.296(9)
C(8)-H(8)	0.9300
C(9)-C(10)	1.420(8)
C(9)-H(9)	0.9300
C(10)-C(16)	1.369(8)
C(10)-C(11)	1.518(8)
C(11)-N(1)	1.493(7)
C(11)-C(14)	1.491(8)
C(11)-C(12)	1.550(8)

C(12)-H(12A)	0.9600
C(12)-H(12B)	0.9600
C(12)-H(12C)	0.9600
C(13)-O(1)	1.444(8)
C(13)-H(13A)	0.9600
C(13)-H(13B)	0.9600
C(13)-H(13C)	0.9600
C(14)-C(17)	1.366(7)
C(14)-C(15)	1.416(7)
C(15)-C(20)	1.378(7)
C(15)-C(16)	1.439(8)
C(17)-C(18)	1.358(8)
C(17)-H(17)	0.9300
C(18)-C(19)	1.363(8)
C(18)-H(18)	0.9300
C(19)-C(20)	1.374(7)
C(19)-C(21)	1.501(8)
C(20)-H(20)	0.9300
C(21)-H(21A)	0.9600
C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600
N(1)-O(1)	1.442(5)

C(23)-C(22)-C(27)	120.0
C(23)-C(22)-C(16)	118.0(5)
C(27)-C(22)-C(16)	122.0(5)
C(24)-C(23)-C(22)	120.0
C(24)-C(23)-H(23)	120.0
C(22)-C(23)-H(23)	120.0
C(23)-C(24)-C(25)	120.0
C(23)-C(24)-H(24)	120.0
C(25)-C(24)-H(24)	120.0
C(26)-C(25)-C(24)	120.0
C(26)-C(25)-H(25)	120.0
C(24)-C(25)-H(25)	120.0
C(25)-C(26)-C(27)	120.0
C(25)-C(26)-H(26)	120.0
C(27)-C(26)-H(26)	120.0

C(26)-C(27)-C(22)	120.0
C(26)-C(27)-H(27)	120.0
C(22)-C(27)-H(27)	120.0
C(2)-C(1)-C(6)	120.8(7)
C(2)-C(1)-H(1)	119.6
C(6)-C(1)-H(1)	119.6
C(3)-C(2)-C(1)	120.1(8)
C(3)-C(2)-H(2)	119.9
C(1)-C(2)-H(2)	119.9
C(4)-C(3)-C(2)	119.8(8)
C(4)-C(3)-H(3)	120.1
C(2)-C(3)-H(3)	120.1
C(3)-C(4)-C(5)	120.0(7)
C(3)-C(4)-H(4)	120.0
C(5)-C(4)-H(4)	120.0
C(6)-C(5)-C(4)	118.2(7)
C(6)-C(5)-H(5)	120.9
C(4)-C(5)-H(5)	120.9
C(5)-C(6)-C(1)	121.0(7)
C(5)-C(6)-C(7)	118.5(6)
C(1)-C(6)-C(7)	120.4(6)
N(1)-C(7)-C(6)	109.2(6)
N(1)-C(7)-C(8)	109.1(5)
C(6)-C(7)-C(8)	110.6(6)
N(1)-C(7)-H(7)	109.3
C(6)-C(7)-H(7)	109.3
C(8)-C(7)-H(7)	109.3
C(9)-C(8)-C(7)	124.7(6)
C(9)-C(8)-H(8)	117.6
C(7)-C(8)-H(8)	117.6
C(8)-C(9)-C(10)	119.4(6)
C(8)-C(9)-H(9)	120.3
C(10)-C(9)-H(9)	120.3
C(16)-C(10)-C(9)	132.8(6)
C(16)-C(10)-C(11)	108.8(5)
C(9)-C(10)-C(11)	118.2(6)
N(1)-C(11)-C(10)	104.4(4)
N(1)-C(11)-C(14)	114.6(5)

C(10)-C(11)-C(14)	103.2(4)
N(1)-C(11)-C(12)	112.8(4)
C(10)-C(11)-C(12)	111.1(5)
C(14)-C(11)-C(12)	110.2(5)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
O(1)-C(13)-H(13A)	109.5
O(1)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
O(1)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(17)-C(14)-C(15)	118.2(5)
C(17)-C(14)-C(11)	133.2(5)
C(15)-C(14)-C(11)	108.5(5)
C(20)-C(15)-C(14)	120.0(5)
C(20)-C(15)-C(16)	131.5(5)
C(14)-C(15)-C(16)	108.5(5)
C(10)-C(16)-C(15)	110.1(5)
C(10)-C(16)-C(22)	127.6(6)
C(15)-C(16)-C(22)	122.2(6)
C(14)-C(17)-C(18)	120.3(6)
C(14)-C(17)-H(17)	119.9
C(18)-C(17)-H(17)	119.9
C(17)-C(18)-C(19)	122.6(6)
C(17)-C(18)-H(18)	118.7
C(19)-C(18)-H(18)	118.7
C(18)-C(19)-C(20)	118.5(6)
C(18)-C(19)-C(21)	121.1(6)
C(20)-C(19)-C(21)	120.3(6)
C(19)-C(20)-C(15)	120.4(5)
C(19)-C(20)-H(20)	119.8
C(15)-C(20)-H(20)	119.8
C(19)-C(21)-H(21A)	109.5

C(19)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(19)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
O(1)-N(1)-C(7)	105.1(4)
O(1)-N(1)-C(11)	106.3(4)
C(7)-N(1)-C(11)	112.6(5)
C(13)-O(1)-N(1)	109.4(4)

Symmetry transformations used to generate equivalent atoms:

Table S5. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for A. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(22)	100(5)	100(5)	51(4)	26(4)	33(4)	46(5)
C(23)	326(18)	288(16)	312(18)	217(15)	246(16)	241(15)
C(24)	890(60)	570(40)	370(30)	370(30)	480(30)	670(40)
C(25)	370(20)	271(15)	93(7)	23(8)	69(10)	276(15)
C(26)	64(6)	65(5)	630(30)	-11(11)	114(11)	13(5)
C(27)	163(10)	104(7)	560(30)	98(11)	228(14)	62(8)
C(1)	151(7)	67(5)	63(4)	-9(4)	46(5)	-6(5)
C(2)	154(8)	99(7)	60(5)	-6(4)	49(5)	-8(6)
C(3)	111(6)	136(8)	63(5)	-39(5)	36(5)	-22(6)
C(4)	108(6)	77(5)	92(6)	-36(5)	24(5)	-2(5)
C(5)	128(7)	59(5)	55(4)	-8(3)	22(4)	2(4)
C(6)	113(5)	55(4)	48(4)	-8(3)	31(4)	1(4)
C(7)	124(6)	63(4)	48(4)	-4(3)	29(4)	-5(4)
C(8)	98(6)	121(7)	55(4)	-10(5)	6(4)	-13(5)
C(9)	71(5)	102(5)	53(4)	-6(4)	13(4)	17(4)
C(10)	61(4)	76(4)	44(4)	5(3)	13(3)	11(4)
C(11)	75(4)	53(4)	45(3)	-1(3)	17(3)	6(3)
C(12)	128(6)	74(4)	63(4)	1(3)	50(4)	-9(4)
C(13)	100(6)	104(5)	72(5)	16(4)	43(4)	33(5)
C(14)	61(4)	59(4)	37(3)	6(3)	20(3)	13(3)
C(15)	56(4)	60(4)	39(3)	5(3)	24(3)	16(3)
C(16)	60(4)	67(4)	55(4)	15(3)	28(3)	25(3)
C(17)	70(4)	65(4)	45(4)	6(3)	22(3)	25(3)
C(18)	64(4)	92(5)	39(3)	-6(3)	14(3)	27(4)
C(19)	85(5)	68(4)	54(4)	-10(3)	37(4)	-4(4)
C(20)	64(4)	59(4)	58(4)	5(3)	25(3)	26(3)
C(21)	110(6)	90(5)	79(5)	-31(4)	40(4)	-15(5)
N(1)	82(3)	58(3)	39(3)	1(2)	17(3)	10(3)
O(1)	105(3)	54(2)	57(3)	11(2)	34(2)	29(3)

Table S6. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for A.

	x	y	z	U(eq)
H(23)	1948	8136	5559	328
H(24)	950	9361	4773	652
H(25)	-612	9308	4764	298
H(26)	-1175	8032	5541	303
H(27)	-177	6807	6327	299
H(1)	2635	5318	2831	109
H(2)	3266	5028	1112	121
H(3)	3668	3585	733	122
H(4)	3366	2434	2026	114
H(5)	2673	2735	3754	99
H(7)	2050	3697	4994	94
H(8)	807	4546	3080	116
H(9)	364	5706	4056	93
H(12A)	2506	4056	7982	126
H(12B)	1542	4053	6716	126
H(12C)	1664	4678	8015	126
H(13A)	4566	5127	6530	133
H(13B)	4422	4409	5342	133
H(13C)	4972	4157	6916	133
H(17)	4176	5172	8920	71
H(18)	4804	6320	10419	79
H(20)	2545	7838	8564	71
H(21A)	4756	8107	10668	136
H(21B)	4240	7690	11648	136
H(21C)	3720	8415	10528	136

Table S7. Torsion angles [°] for A.

C(27)-C(22)-C(23)-C(24)	0.0
C(16)-C(22)-C(23)-C(24)	178.1(5)
C(22)-C(23)-C(24)-C(25)	0.0
C(23)-C(24)-C(25)-C(26)	0.0
C(24)-C(25)-C(26)-C(27)	0.0
C(25)-C(26)-C(27)-C(22)	0.0
C(23)-C(22)-C(27)-C(26)	0.0
C(16)-C(22)-C(27)-C(26)	-178.1(5)
C(6)-C(1)-C(2)-C(3)	-0.8(12)
C(1)-C(2)-C(3)-C(4)	1.6(12)
C(2)-C(3)-C(4)-C(5)	-0.6(12)
C(3)-C(4)-C(5)-C(6)	-1.2(11)
C(4)-C(5)-C(6)-C(1)	2.0(11)
C(4)-C(5)-C(6)-C(7)	179.5(6)
C(2)-C(1)-C(6)-C(5)	-1.0(11)
C(2)-C(1)-C(6)-C(7)	-178.5(7)
C(5)-C(6)-C(7)-N(1)	117.9(6)
C(1)-C(6)-C(7)-N(1)	-64.6(8)
C(5)-C(6)-C(7)-C(8)	-122.0(7)
C(1)-C(6)-C(7)-C(8)	55.5(9)
N(1)-C(7)-C(8)-C(9)	-16.2(10)
C(6)-C(7)-C(8)-C(9)	-136.2(7)
C(7)-C(8)-C(9)-C(10)	-0.1(11)
C(8)-C(9)-C(10)-C(16)	157.6(7)
C(8)-C(9)-C(10)-C(11)	-16.7(10)
C(16)-C(10)-C(11)-N(1)	-129.0(5)
C(9)-C(10)-C(11)-N(1)	46.6(7)
C(16)-C(10)-C(11)-C(14)	-8.9(6)
C(9)-C(10)-C(11)-C(14)	166.7(6)
C(16)-C(10)-C(11)-C(12)	109.2(6)
C(9)-C(10)-C(11)-C(12)	-75.3(7)
N(1)-C(11)-C(14)-C(17)	-62.0(8)
C(10)-C(11)-C(14)-C(17)	-174.9(6)
C(12)-C(11)-C(14)-C(17)	66.4(8)
N(1)-C(11)-C(14)-C(15)	121.8(5)
C(10)-C(11)-C(14)-C(15)	8.9(6)
C(12)-C(11)-C(14)-C(15)	-109.8(5)
C(17)-C(14)-C(15)-C(20)	-1.4(8)
C(11)-C(14)-C(15)-C(20)	175.4(5)

C(17)-C(14)-C(15)-C(16)	177.2(5)
C(11)-C(14)-C(15)-C(16)	-6.0(6)
C(9)-C(10)-C(16)-C(15)	-169.0(7)
C(11)-C(10)-C(16)-C(15)	5.7(7)
C(9)-C(10)-C(16)-C(22)	8.2(11)
C(11)-C(10)-C(16)-C(22)	-177.1(6)
C(20)-C(15)-C(16)-C(10)	178.5(6)
C(14)-C(15)-C(16)-C(10)	0.1(6)
C(20)-C(15)-C(16)-C(22)	1.1(9)
C(14)-C(15)-C(16)-C(22)	-177.2(5)
C(23)-C(22)-C(16)-C(10)	-112.0(7)
C(27)-C(22)-C(16)-C(10)	66.1(8)
C(23)-C(22)-C(16)-C(15)	64.8(7)
C(27)-C(22)-C(16)-C(15)	-117.1(7)
C(15)-C(14)-C(17)-C(18)	0.0(8)
C(11)-C(14)-C(17)-C(18)	-175.9(6)
C(14)-C(17)-C(18)-C(19)	1.1(9)
C(17)-C(18)-C(19)-C(20)	-0.6(9)
C(17)-C(18)-C(19)-C(21)	176.4(6)
C(18)-C(19)-C(20)-C(15)	-0.9(8)
C(21)-C(19)-C(20)-C(15)	-177.9(6)
C(14)-C(15)-C(20)-C(19)	1.9(8)
C(16)-C(15)-C(20)-C(19)	-176.3(6)
C(6)-C(7)-N(1)-O(1)	-74.1(6)
C(8)-C(7)-N(1)-O(1)	164.9(5)
C(6)-C(7)-N(1)-C(11)	170.6(5)
C(8)-C(7)-N(1)-C(11)	49.7(6)
C(10)-C(11)-N(1)-O(1)	-178.2(4)
C(14)-C(11)-N(1)-O(1)	69.6(5)
C(12)-C(11)-N(1)-O(1)	-57.5(6)
C(10)-C(11)-N(1)-C(7)	-63.7(6)
C(14)-C(11)-N(1)-C(7)	-175.8(5)
C(12)-C(11)-N(1)-C(7)	57.0(6)
C(7)-N(1)-O(1)-C(13)	114.9(5)
C(11)-N(1)-O(1)-C(13)	-125.6(5)

Symmetry transformations used to generate equivalent atoms:

(E) Reference

1.(a) W. Gong, Z. Zhou, J. Shi, B. Wu, B. Huang and W. Yi,Catalyst-Controlled [3 + 2] and [4 + 2] Annulations of Oximes with Propargyl Alcohols: Divergent Access to Indenamines and Isoquinolines, *Org. Lett.,* 2018, **20**, 182-185; (b) E. Tan, M. Zanini and A. M, Iridium-Catalyzed β-Alkynylation of Aliphatic Oximes as Masked Carbonyl Compounds and Alcohols, *Angew. Chem. Int. Ed.*, 2020, **59**, 10470-10473.

2. (a) X. Li, S. Huang, C. M. Schienebeck, D. Shu and W. Tang, Rhodium-Catalyzed Carbonylation of 3-Acyloxy-1,4-enynes for the Synthesis of Cyclopentenones, *Org. Lett.*, 2012, **14**, 1584-1587; (b) M. Skaria, P. Sharma and R.-S. Liu，Gold(I)-Catalyzed 1,3-Carbofunctionalizations of Anthranils with Vinyl Propargyl Esters To Yield 1,3-Dihydrobenzo[c]-isoxazoles, *Org. Lett.*, 2019, **21**, 2876-2879; (c)L-J Wu, R-J Song, S-L Luo, J-H Li, Palladium-Catalyzed Reductive [5+1] Cycloaddition of 3-Acetoxy-1,4-enynes with CO: Access to Phenols Enabled by Hydrosilanes, *Angew. Chem. Int. Ed.*, 2018, **57**, 13308-13312.

3. H-Y Liu, Y Lu, Y Li, J-H Li, Photocatalytic Decarboxylative [2 + 2 + m] Cyclization of 1,7-Enynes Mediated by Tricyclohexylphosphine and Potassium Iodide, *Org. Lett.*, 2020**, 22**, 8819-8823.

4. J Zhao, S Yang, X Xie, X Li, and Y Liu, Ligand-Effect in Gold(I)-Catalyzed Rautenstrauch Rearrangement: Regio- and Stereoselective Synthesis of Bicyclo[3.2.1]octa-3,6-dienes through Cyclodimerization of 1-Ethynyl-2-propenyl Esters, *J. Org. Chem.,* **2018,** 83, 1287-1297.

5. C Song, X Dong, Z Wang, K Liu, C.-W. Chiang, A Lei, Visible-Light-Induced [4+2] Annulation of Thiophenes and Alkynes to Construct Benzene Rings, *Angew. Chem. Int. Ed.*, 2019, **58**, 12206-12210.

6. X Du, H Chen, Y Liu, New Synthetic Approach for the Construction of Multisubstituted 2-Acyl Furans by the IBX-Mediated Cascade Oxidation/Cyclization of *cis*-2-En-4-yn-1-ols (IBX=2-Iodoxybenzoic Acid), *Chem. Eur. J.*, 2008, 14, 9495-9498.

7. N Sakai, K Enomoto, M Takayanagi, T Konakahara, Y Ogiwara, Copper-catalyzed [3+2] annulation of propargylic acetates with anilines in the presence of trimethylsilyl chloride leading to 2,3-disubstituted indoles via an aza-Claisen rearrangement, *Tetrahedron Letters*, 2016, **57**, 2175-2178.

8. Y Li, D Shi, X He, Y Wang, Y Tang, J Zhang, and S Xu, Redox-Neutral Annulation of Alkynylcyclopropanes with N-Aryloxyamides via Rhodium(III)-Catalyzed Sequential C-H/C-C Activation, *J. Org. Chem.*, 2019**, 84**, 1588-1595.