Supporting Information

Electrochemical Nitrogen Atom Insertion Enabled by a Manganese Complex

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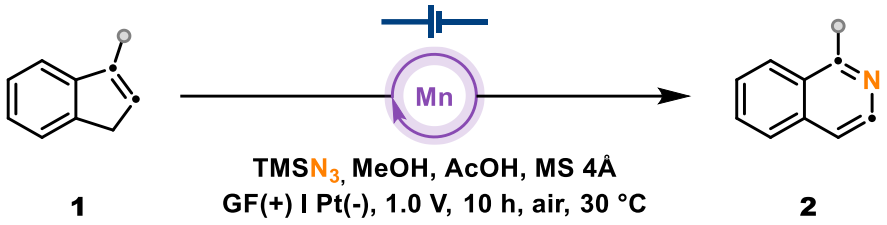
General Remarks

The electrochemical nitrogen insertion reaction using a manganese complex was performed in a Schlenk tube under an air atmosphere. Starting materials were synthesized according to previously described methods.[1] Other chemicals and solvents were obtained from commercial sources and were used without further purification. Platinum electrodes (10 mm × 20 mm × 0.2 mm, 99.99%; obtained from WizMAC, Daejeon, Republic of Korea) and graphite felt electrodes (10 mm × 25 mm × 4.2 mm, GF051BH, Areal Weight: 400 ± 50 (g/m²), Carbon Content: ≥ 99.0 wt.%, Electrical Resistance(TP): < 180 mΩ · cm^2, obtained from JNTG, Gyeonggi-do, Republic of Korea) were connected using house-made stainless steel adapters. During the reaction, the distance between the two electrodes was kept within 2.5 cm. After use, the platinum electrode was washed with ethyl acetate, soaked in 1 N HCl for 1 h, removed and neutralized with $NaHCO_3$, rinsed with distilled water, and finally washed with acetone and dried before the next use. Electrocatalysis was conducted using a power supply (HMP4040 ROHDE&SCHWARZ or MK-C3405 MKPOWER) in constant voltage mode. To minimize the influence of ambient temperature on the reaction, the temperature was maintained at 30 °C using an oil bath. Air: After evacuation under vacuum for 10 min, no N_2 purging was performed. Cyclic voltammetry studies were performed using a CH Instruments Electrochemical workstation and Origin Pro 2025 software. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^1H NMR. TLC: TLC Silica gel 60 F254, 25 Aluminium Sheets 20x20 cm detection under UV light at 254 nm. Chromatography: Separations were carried out on ZEOprep 60Å (40-63 micrometer, 230~400 mesh). NMR: ^1H, ^{13}C, and ^{19}F NMR spectra were recorded on Bruker 400 MHz spectrometers in $CDCl_3$ solutions, chemical shifts (δ) are given in ppm. GC–MS: GCMS-QP2020NX, column information is Rtx-5MS. IR: All spectra were recorded on a Bruker FT-IR Alpha device. (HRMS): Xevo G2-XS and Sciex (1290 infinity II / TripleTOF 5600 plus). M.p.: Barnstead Electrothermal: IA9100MK1 and AZ9003 MK4 melting point apparatus, all values are uncorrected. UV-Vis: All spectra were recorded on Agilent Technologies Cary 8454 UV-Vis. LCMS: Agilent G6135BA (NFEC-2024-11-300749)

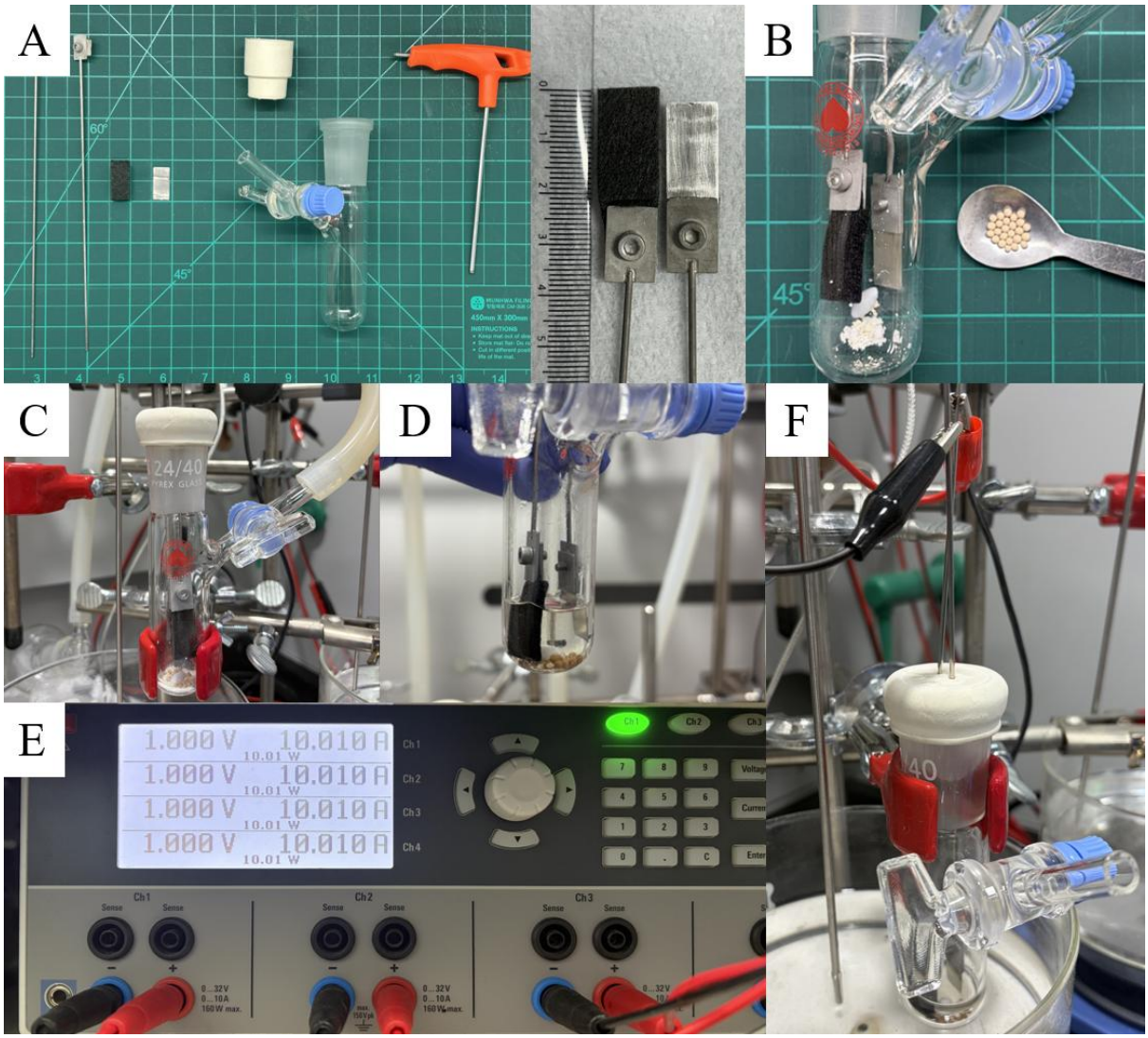
General Procedures

1) General procedure (**GP**) for electrochemical nitrogen atom insertion reactions:



In an oven-dried Schlenk tube, **1** (0.2 mmol), **[Mn]** (0.1 equiv, 10 mol%), Na_2CO_3 (1.0 equiv, 0.2 mmol), and activated 4Å molecular sieves (25 beads) were added, and the mixture was evacuated under vacuum for 10 min. The stopcock was then opened briefly to introduce air into the tube and subsequently closed. MeOH (4.0 mL) was added, followed by the addition of $TMSN_3$ (1.0 equiv, 0.2 mmol) to the reaction mixture. Additional MeOH (1.0 mL) and AcOH (1.0 mL) were then added sequentially. Electrolysis was carried out at 30 °C under constant voltage conditions (1.0 V) using a graphite felt anode and a platinum cathode in an undivided cell. After 10 h, the reaction was quenched and diluted with ethyl acetate (10.0 mL). The electrode was washed with ethyl acetate (10.0 mL). The resulting mixture was filtered through a pad composed of silica (2.0 cm), Celite (3.0 cm), and Na_2SO_4 (1.0 cm), layered sequentially. The filtrate was then concentrated under reduced pressure. Purification by column chromatography on silica gel using ethyl acetate and hexane as the mobile phase afforded the desired product.

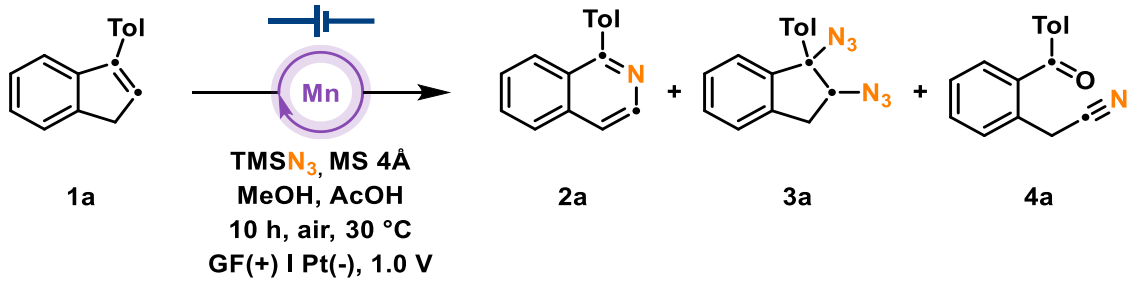
Electrochemical Setup



Scheme S1. Detailed electrochemical setup. A) Two stainless steel electrode holders, a graphite felt anode, a platinum plate cathode, septa, and a Schlenk tube were prepared. The anode was cut into a 1.0 cm × 2.5 cm piece so that a 1.0 cm × 2.0 cm portion was immersed in the reaction solution, while the cathode was a 1.0 cm × 2.0 cm platinum plate. B) After adding the solid reagents and 25 pellets of MS 4Å, the electrodes were installed. C) After evacuating under vacuum for 10 min, the tube was backfilled with ambient air, and the stopcock was immediately closed. D) After adding the liquid samples and solvent, the two electrodes were immersed in the solution, taking care to ensure that the electrode adapter was not submerged. E) The electrolysis was carried out using a four-channel power supply, with the desired constant voltage set on the power supply. F) The reaction was carried out in an oil bath maintained at 30 °C with stirring at 700 rpm; during the reaction, the two electrodes were kept from contacting each other and were immersed in the solution at the same height.

Optimization Studies

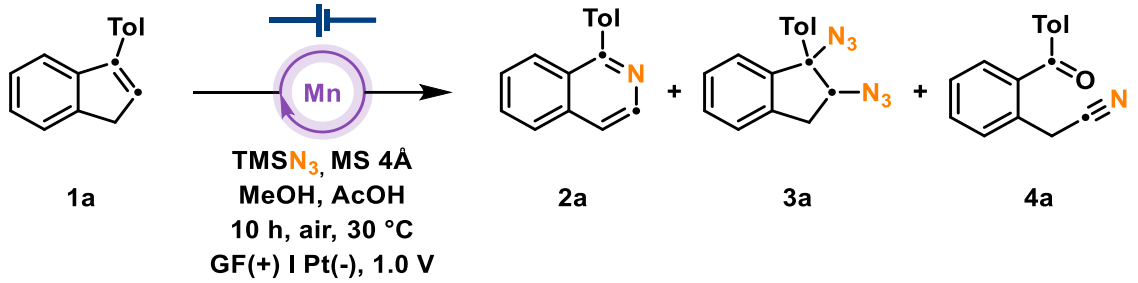
Table S1. Optimization studies for electrochemical nitrogen atom insertion reactions.



Entry[a]	Modified reaction conditions	**1a** (%)	**2a** (%)	**3a** (%)	**4a** (%)
1	None[b]	0	62	2	5
2	TFE, HFIP instead of AcOH	19-27	25	13-14	9-11
3	added $LiClO_4$	n.d.	n.d.	n.d.	n.d.
4	air instead of N_2	6	67	1	3
5	None[c]	0	59	5	4
6[d]	$MnCl_2·4H_2O$ instead of **[Mn-1]**	11	52	14	2
7	H_2O instead of AcOH	56	9	0	12
8	None[e]	0	70	4	2
9	$MnCl_2·4H_2O$ instead of **[Mn-1]**	0	58	5	3
10	60 °C instead of 30 °C	0	54	3	2
11	Without **[Mn-1]**	47	1	2	4
12	Without potential	90	n.d.	n.d.	n.d.

[a] Reaction conditions: **1a** (0.2 mmol), **[Mn-1]** (10 mol %), $TMSN_3$ (0.2 mmol), anode: GF, cathode: Pt, 30 °C, CPE: 1.0 V; [b] Reaction conditions: MeCN (5.0 mL), AcOH (1.0 mL), N_2, 16 h; [c] Reaction conditions: MeOH (5.0 mL), AcOH (1.0 mL), air, 10 h; [d] at 1.5 V. [e] Reaction conditions: MeOH (5.0 mL), AcOH (1.0 mL), Na_2CO_3 (0.2 mmol), MS 4Å, air, 10 h; Yield was determined by ^1H NMR with mesitylene as the internal standard. GF: Graphite Felt. **[Mn-1]**: bis(chloro)(Bathocuproine) manganese(II). HFIP: 1,1,1,3,3,3-Hexafluoropropan-2-ol. TFE: 2,2,2-Trifluoroethanol. AcOH: Acetic acid, glacial. $TMSN_3$: Trimethylsilyl azide. MS: molecular sieves. n.d.: not detected.

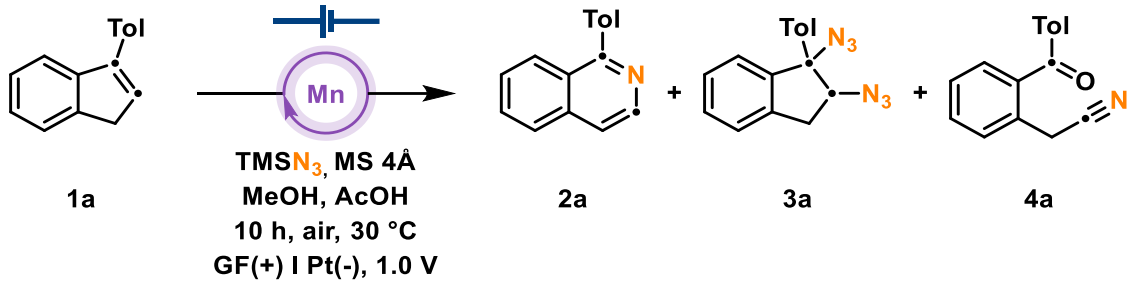
Table S2. Screening for solvents[a]



Entry	Modified reaction conditions	**1a** (%)	**2a** (%)	**3a** (%)	**4a** (%)
1	EtOH(5)/AcOH(1)	0	41	10	8
2	HFIP(5)/AcOH(1)	54	0	0	2
3	TFE(5)/AcOH(1)	0	16	2	10
4	*t*BuOH(5)/AcOH(1)	43	14	9	30
5	*i*PrOH(5)/AcOH(1)	20	11	0	3
6	DCM(5)/AcOH(1)	0	33	11	3
7	DCE(5)/AcOH(1)	75	13	2	1
8	DMA(5)/AcOH(1)	4	6	27	4

[a] Reaction conditions: **1a** (0.2 mmol), **[Mn-1]** (10 mol %), $TMSN_3$ (0.2 mmol), Na_2CO_3 (0.2 mmol), MS 4Å, anode: GF, cathode: Pt, 30 °C, air, 10h; Yield was determined by ^1H NMR with mesitylene as the internal standard. *t*BuOH: 2-Methyl-2-propanol. *i*PrOH: 2-Propanol. DCM: Dichloromethane. DCE: 1,2-Dichloroethane. DMA: *N,N*-dimethylacetamide.

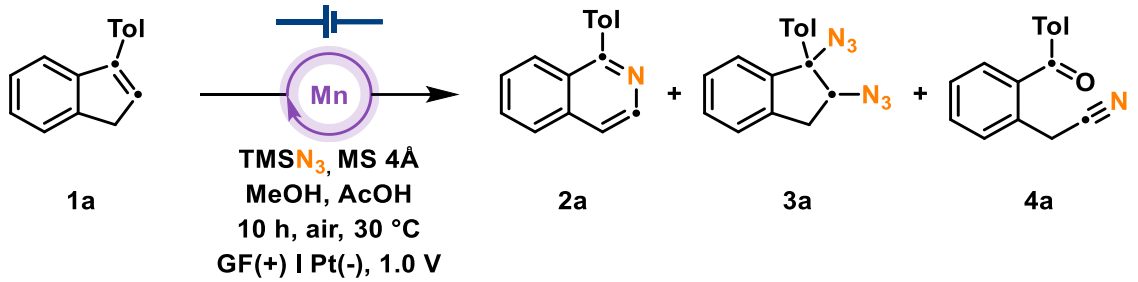
Table S3. Screening for electrodes[a]



Entry	Modified reaction conditions	**1a** (%)	**2a** (%)	**3a** (%)	**4a** (%)
1	Anode: GF / Cathode: GF	7	57	9	2
2	Anode: Pt / Cathode: GF	0	52	3	8
3	Anode: Pt / Cathode: Pt	0	31	6	15
4	Anode: Pt / Cathode: Zn	92	0	3	5
5	Anode: Fe / Cathode: Pt	54	9	0	6
6	Anode: Ni / Cathode: Pt	97	0	0	0
7	Anode: Pb / Cathode: Pt	92	6	0	0
8	Anode: Cu / Cathode: Pt	76	7	0	4

[a] Reaction conditions: **1a** (0.2 mmol), **[Mn-1]** (10 mol %), $TMSN_3$ (0.2 mmol), Na_2CO_3 (0.2 mmol), MS 4Å, MeOH (5.0 mL), AcOH (1.0 mL), 30 °C, air, 10h; Yield was determined by ^1H NMR with mesitylene as the internal standard.

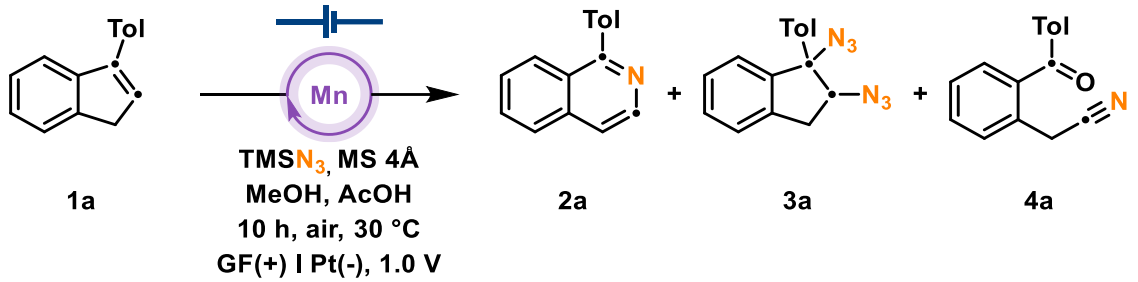
Table S4. Screening for bases[a]



Entry	Modified reaction conditions	**1a** (%)	**2a** (%)	**3a** (%)	**4a** (%)
1	Li_2CO_3 (0.2 mmol)	0	50	8	7
2	K_2CO_3 (0.2 mmol)	0	65	8	5
3	Cs_2CO_3 (0.2 mmol)	0	49	5	3
4	$NaHCO_3$ (0.2 mmol)	0	64	4	4
5	NaH_2PO_4 (0.2 mmol)	20	34	2	7
6	Na_2HPO_4 (0.2 mmol)	0	61	6	7
7	Na_3PO_4 (0.2 mmol)	75	3	3	3
8	TEA (0.2 mmol)	0	49	6	5
9	DBU (0.2 mmol)	7	50	9	1

[a] Reaction conditions: **1a** (0.2 mmol), **[Mn-1]** (10 mol %), $TMSN_3$ (0.2 mmol), MS 4Å, MeOH (5.0 mL), AcOH (1.0 mL), anode: GF, cathode: Pt, 30 °C, air, 10h; Yield was determined by ^1H NMR with mesitylene as the internal standard. TEA: Triethylamine. DBU: 1,8-Diazabicyclo[5.4.0]undec-7-ene.

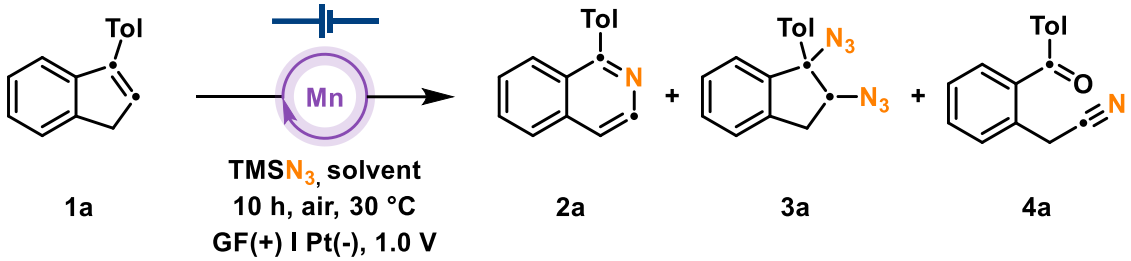
Table S5. Screening for azide sources and manganese complexes



Entry[a]	Modified reaction conditions	**1a** (%)	**2a** (%)	**3a** (%)	**4a** (%)
1[b]	$TBAN_3$ instead of $TMSN_3$	58	0	0	0
2[b]	NaN_3 instead of $TMSN_3$	57	0	0	0
3	**[Mn-2]** instead of **[Mn-1]**	0	62	6	2
4	**[Mn-3]** instead of **[Mn-1]**	21	40	20	11
5	**[Mn-4]** instead of **[Mn-1]**	18	42	18	6
6	**[Mn-5]** instead of **[Mn-1]**	18	37	19	8
7[c]	**[Mn-6]** instead of **[Mn-1]**	0	50	2	1
8	**[Mn-7]** instead of **[Mn-1]**	0	41	5	1
9	**[Ni]** instead of **[Mn-1]**	79	0	0	0

[a] Reaction conditions: **1a** (0.2 mmol), **[Mn-1]** (10 mol %), $TMSN_3$ (0.2 mmol), MS 4Å, MeOH (5.0 mL), AcOH (1.0 mL), anode: GF, cathode: Pt, 30 °C, air, 10h; [b] without **[Mn-1]**; [c] **1a** (0.1 mmol), **[Mn-6]** (50 mol %) without $TMSN_3$; Yield was determined by ^1H NMR with mesitylene as the internal standard. $TBAN_3$: Tetrabutylammonium azide. **[Mn-2]**: bis(chloro)(2,9-dimethyl-1,10-phenanthroline) manganese(II). **[Mn-3]**: bis(chloro)(4,7-diphenyl-1,10-phenanthroline) manganese(II). **[Mn-4]**: bis(chloro)(1,10-phenanthroline) manganese(II). **[Mn-5]**: bis(chloro)(2,2'-bipyridine) manganese(II). **[Mn-6]**: bis(azido)(bathocuproine) manganese(II). **[Mn-7]**: bis(chloro)(bathocuproine)$_2$ manganese(II). **[Ni]**: bis(chloro)(1,10-phenanthroline) nickel(II).

Examination of Byproducts



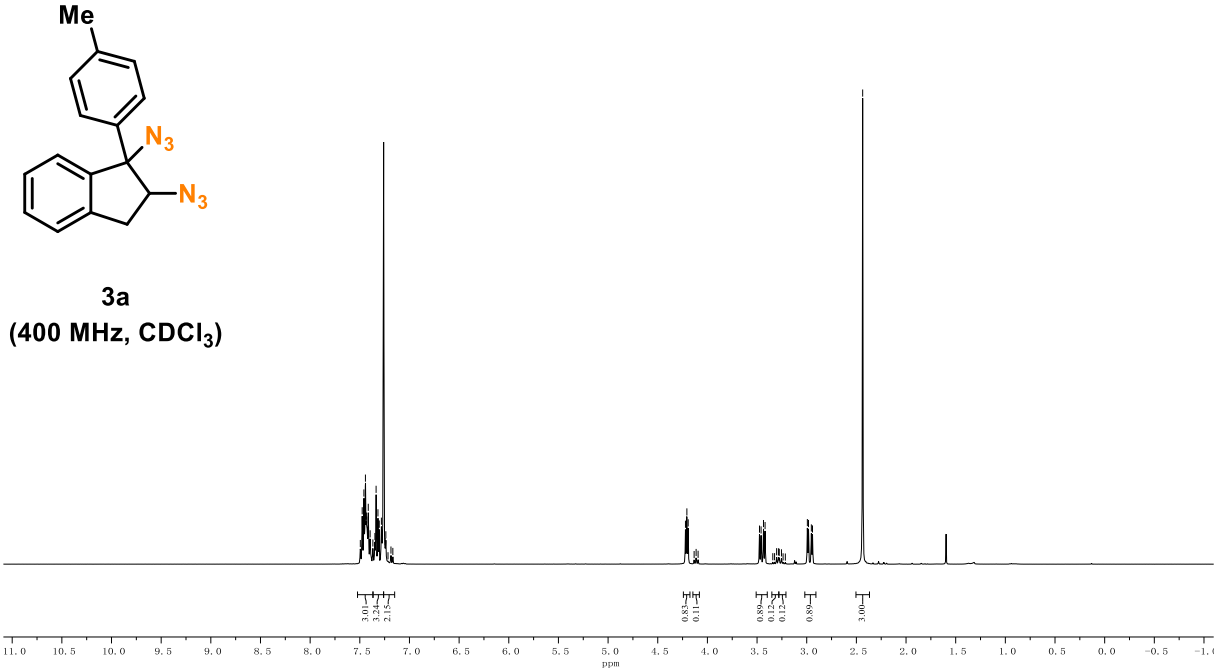
1) Analysis of diazidation byproduct **3a**

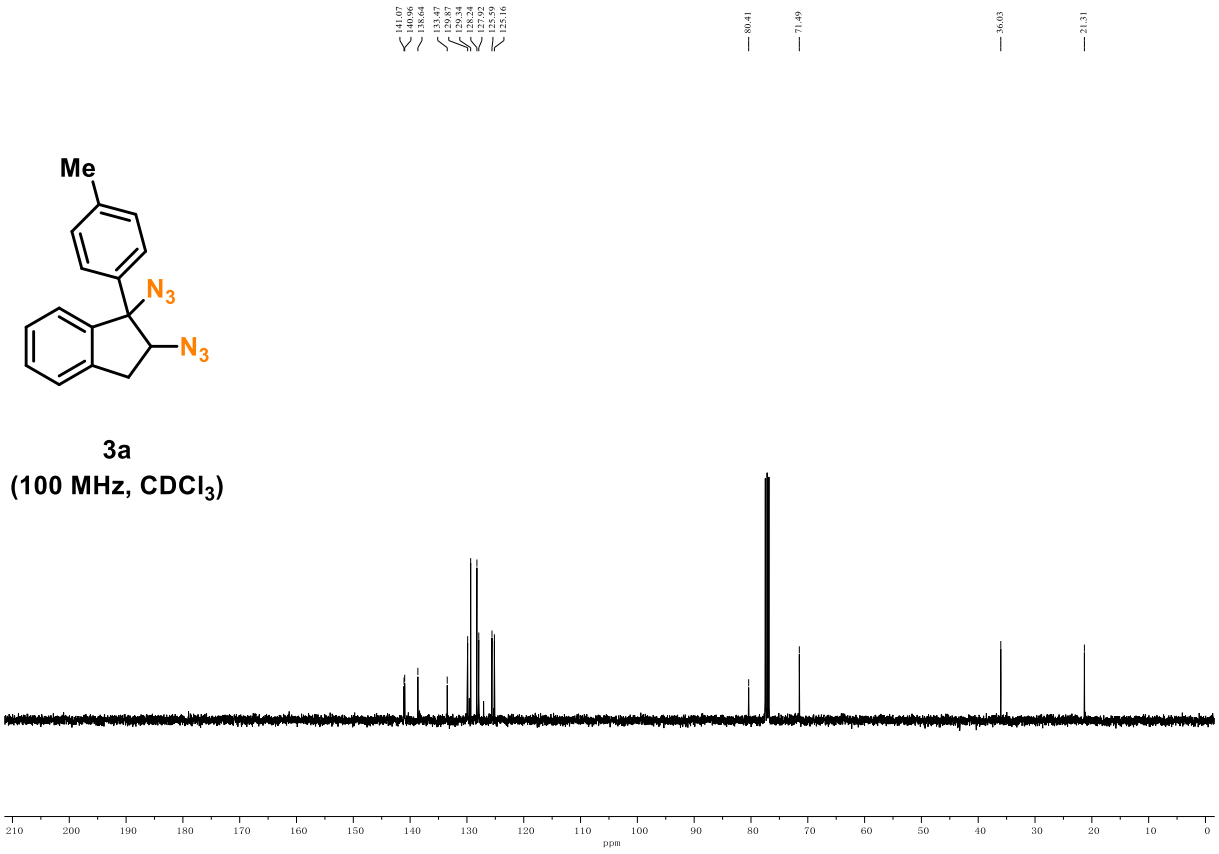
1,2-Diazido-1-(*p*-tolyl)-2,3-dihydro-1*H*-indene (3a)

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.40 (m, 3H), 7.37 – 7.28 (m, 3H), 7.24 – 7.17 (m, 2H), 4.21 (dd, J = 6.3, 4.8 Hz, 0.83H, major), 4.11 (dd, J = 9.0, 7.2 Hz, 0.11H, minor), 3.45 (dd, J = 16.1, 6.4 Hz, 0.89H), 3.31 (dd, J = 15.4, 7.2 Hz, 0.12H), 3.25 (dd, J = 15.4, 9.0 Hz, 0.12H), 2.97 (dd, J = 16.1, 4.7 Hz, 0.89H), 3.45 (dd, J = 16.1, 6.4 Hz, 0.89H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 141.1, 141.0, 138.6, 133.5, 130.0, 129.3, 128.2, 127.9, 125.6, 125.2, 80.4, 71.5, 36.0, 21.3.

HR-MS (APCI) $C_{16}H_{15}N$ $[M\text{-}N_4]^+$: 235.1230, found: 235.1249.




141.07
140.96
138.64
133.47
129.87
129.34
126.34
127.92
125.59
125.16
80.41
71.49
36.03
21.31
Me
N3
N3
3a
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

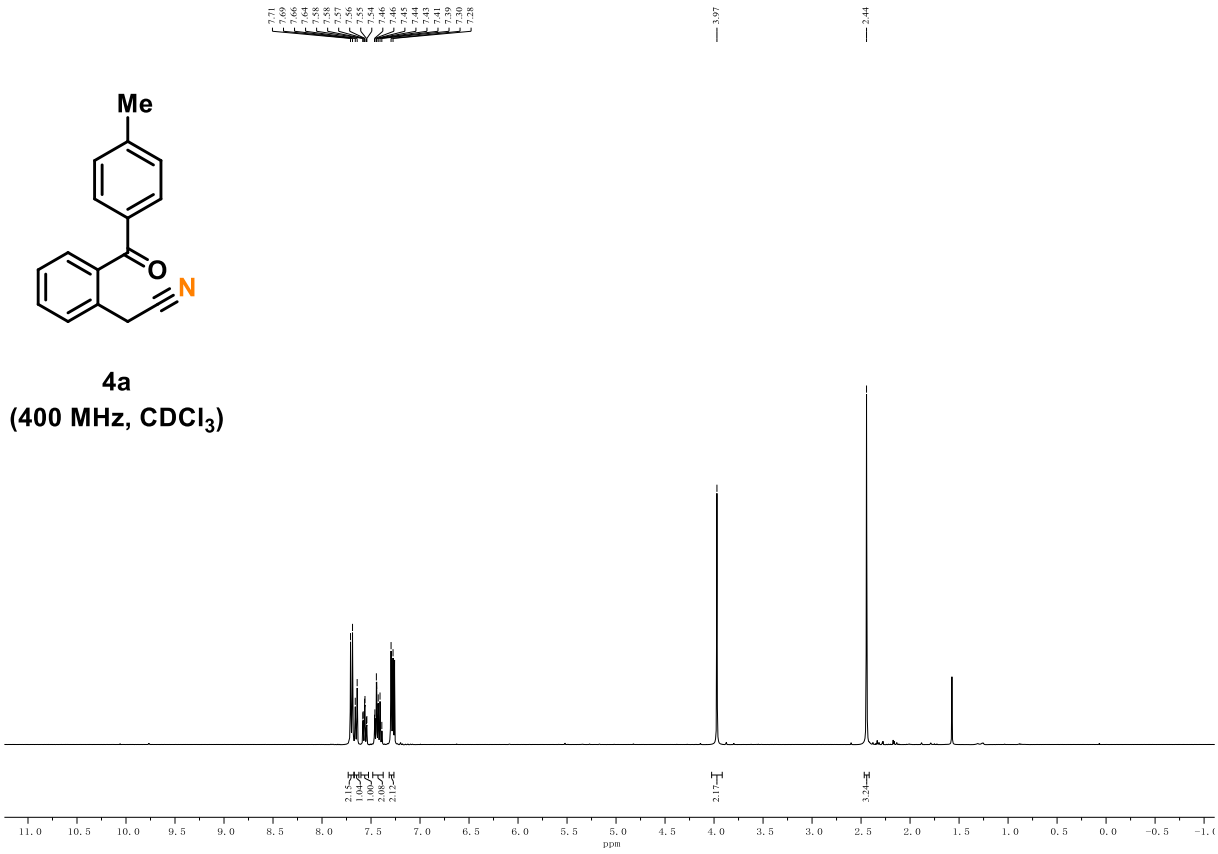
2) Analysis of nitrile byproduct **4a**

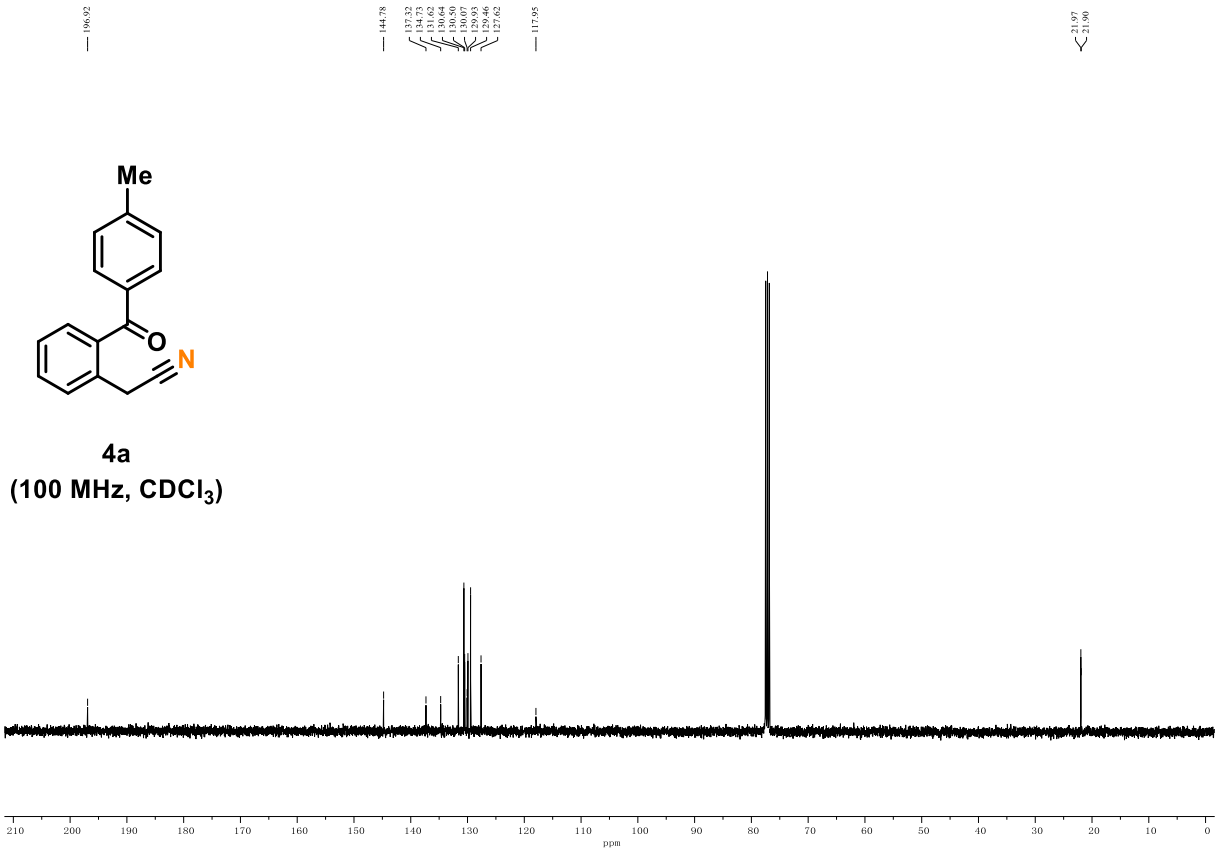
2-(2-(4-Methylbenzoyl) phenyl) acetonitrile (4a)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, J = 8.0, 2H), 7.65 (d, J = 7.5, 1H), 7.56 (td, J = 7.5, 1.6 Hz, 1H), 7.46 – 7.54 (m, 2H), 7.29 (d, J = 8.0, 2H), 3.97 (s, 2H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 144.8, 137.3, 134.7, 131.6, 130.6, 130.5, 130.1, 129.9, 129.5, 127.6, 118.0, 22.0, 21.9.

HR-MS (ESI) $C_{16}H_{14}NO$ $[M+H]^+$: 236.1070, found: 236.1068.

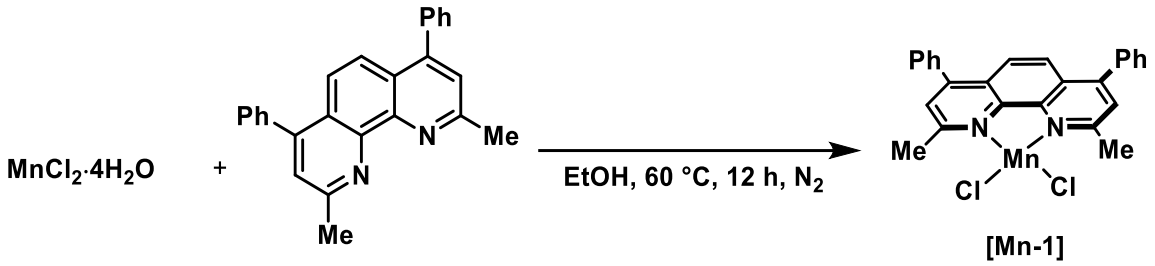



196.92
144.78
137.32
134.73
131.62
130.64
130.59
130.07
129.93
129.46
127.62
117.95
21.97
21.90
Me
O
N
4a
(100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

The Preparation of Transition Metal Complexes

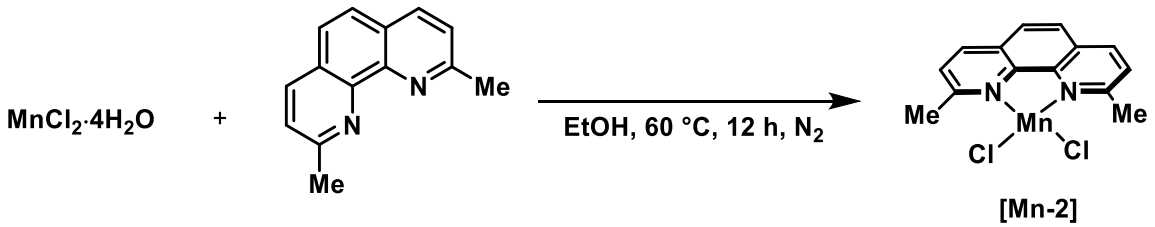
The polymeric versus monomeric nature of the manganese complex was not investigated. The complex is depicted as a monomeric species for clarity.[2]

1) Procedure for the synthesis of bis(chloro)(Bathocuproine) manganese(II) **[Mn-1]**
   The reaction was performed under the condition of the reported procedure.[3a] A suspension of $MnCl_2 \cdot 4H_2O$ (1.0 mmol) and bathocuproine (1.0 equiv) in ethanol (4.0 mL) was stirred at 60 °C for 12 h under N_2. After volatiles are evaporated under reduced pressure, residue dissolves in ethanol (3.0 mL). Diethyl ether slowly added into the solution until a solid is formed. Filtration with ethanol/diethyl ether (= 1:10 30 mL) gave pale yellow solid, which was dried *in vacuo* for 12 h.



[Mn-1]

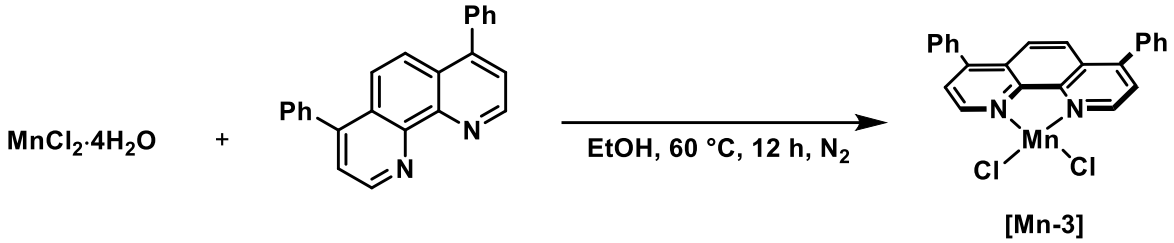
2) Procedure for the synthesis of bis(chloro)(2,9-dimethyl-1,10-phenanthroline) manganese(II) **[Mn-2]**
   The reaction was performed under the condition of the reported procedure.[3a] A suspension of $MnCl_2 \cdot 4H_2O$ (1.0 mmol) and 2,9-dimethyl-1,10-phenanthroline (1.0 equiv) in ethanol (4.0 mL) was stirred at 60 °C for 12 h under N_2. After volatiles are evaporated under reduced pressure, residue dissolves in ethanol (3.0 mL). Diethyl ether slowly added into the solution until a solid is formed. Filtration with ethanol/diethyl ether (= 1:10 30 mL) gave pale yellow solid, which was dried *in vacuo* for 12 h.



[Mn-2]

3) Procedure for the synthesis of bis(chloro)(4,7-diphenyl-1,10-phenanthroline) manganese(II) **[Mn-3]**

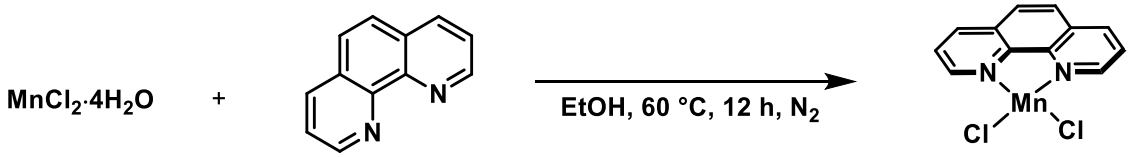
The reaction was performed under the condition of the reported procedure.[3a] A suspension of $MnCl_2 \cdot 4H_2O$ (1.0 mmol) and 4,7-diphenyl-1,10-phenanthroline (1.0 equiv) in ethanol (4.0 mL) was stirred at 60 °C for 12 h under N_2. After volatiles are evaporated under reduced pressure, residue dissolves in ethanol (3.0 mL). Diethyl ether slowly added into the solution until a solid is formed. Filtration with ethanol/diethyl ether (= 1:10 30 mL) gave pale yellow solid, which was dried *in vacuo* for 12 h.



[Mn-3]

4) Procedure for the synthesis of bis(chloro)(1,10-phenanthroline) manganese(II) **[Mn-4]**

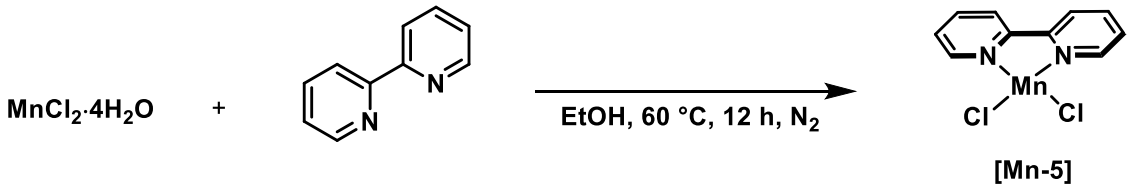
The reaction was performed under the condition of the reported procedure.[3a] A suspension of $MnCl_2 \cdot 4H_2O$ (1.0 mmol) and 1,10-phenanthroline (1.0 equiv) in ethanol (4.0 mL) was stirred at 60 °C for 12 h under N_2. After volatiles are evaporated under reduced pressure, residue dissolves in ethanol (3.0 mL). Diethyl ether slowly added into the solution until a solid is formed. Filtration with ethanol/diethyl ether (= 1:10 30 mL) gave pale yellow solid, which was dried *in vacuo* for 12 h.



[Mn-4]

5) Procedure for the synthesis of bis(chloro)(2,2'-bipyridine) manganese(II) **[Mn-5]**

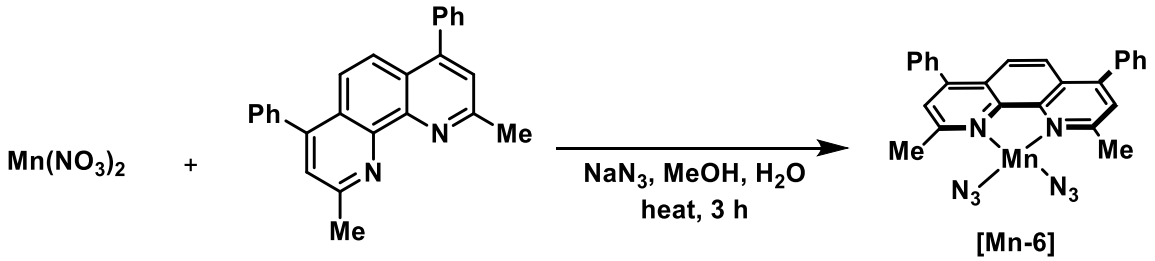
The reaction was performed under the condition of the reported procedure.[3a] A suspension of $MnCl_2 \cdot 4H_2O$ (1.0 mmol) and 2,2'-bipyridine (1.0 equiv) in ethanol (4.0 mL) was stirred at 60 °C for 12 h under N_2. After volatiles are evaporated under reduced pressure, residue dissolves in ethanol (3.0 mL). Diethyl ether slowly added into the solution until a solid is formed. Filtration with ethanol/diethyl ether (= 1:10 30 mL) gave pale yellow solid, which was dried *in vacuo* for 12 h.



[Mn-5]

6) Procedure for the synthesis of bis(azido)(Bathocuproine) manganese(II) **[Mn-6]**

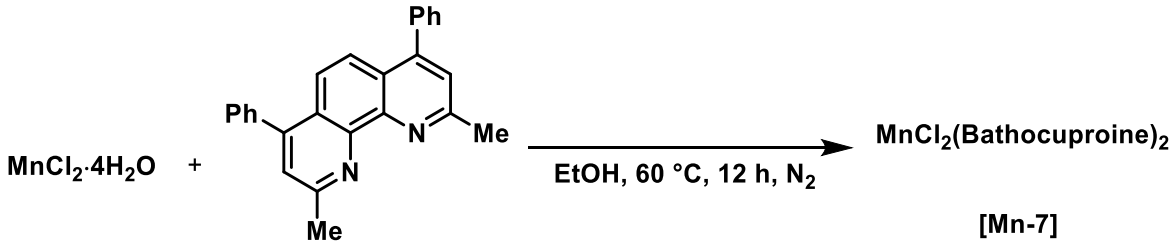
The reaction was performed according to the reported procedure.[3b] A suspension of $Mn(NO_3)_2$ (50 % aqueous solution, 1.0 mmol), bathocuproine (1.0 equiv), and sodium azide (1.0 equiv) in methanol/distilled water (1:1, 6 mL) was heated with stirring until a clear solution was obtained. After evaporation of the volatiles under reduced pressure, the residue was dissolved in methanol (3.0 mL). Diethyl ether was slowly added to the solution until a solid formed. Filtration with ethanol/diethyl ether (1:10, 30 mL) afforded a yellow solid, which was dried in vacuo for 12 h.



[Mn-6]

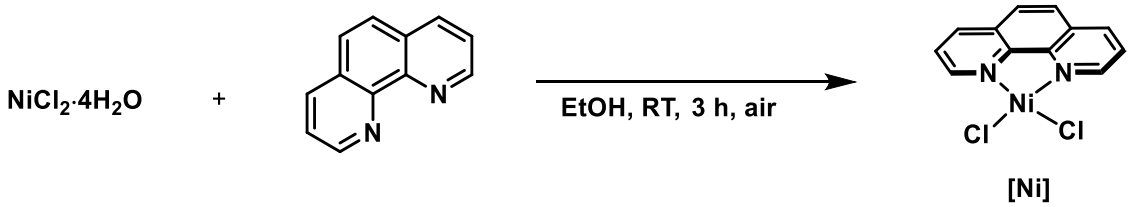
7) Procedure for the synthesis of bis(chloro)$_2$(Bathocuproine)$_2$ manganese(II) **[Mn-7]**

The reaction was performed under the condition of the reported procedure.[3c] A suspension of $MnCl_2 \cdot 4H_2O$ (1.0 mmol) and bathocuproine (2.0 equiv) in ethanol (4.0 mL) was stirred at 60 °C for 12 h under N_2. After volatiles are evaporated under reduced pressure, residue dissolves in ethanol (3.0 mL). Diethyl ether slowly added into the solution until a solid is formed. Filtration with ethanol/diethyl ether (= 1:10 30 mL) gave yellow solid, which was dried *in vacuo* for 12 h.



8) Procedure for the synthesis of bis(chloro)(1,10-phenanthroline) nickel(II) **[Ni]**

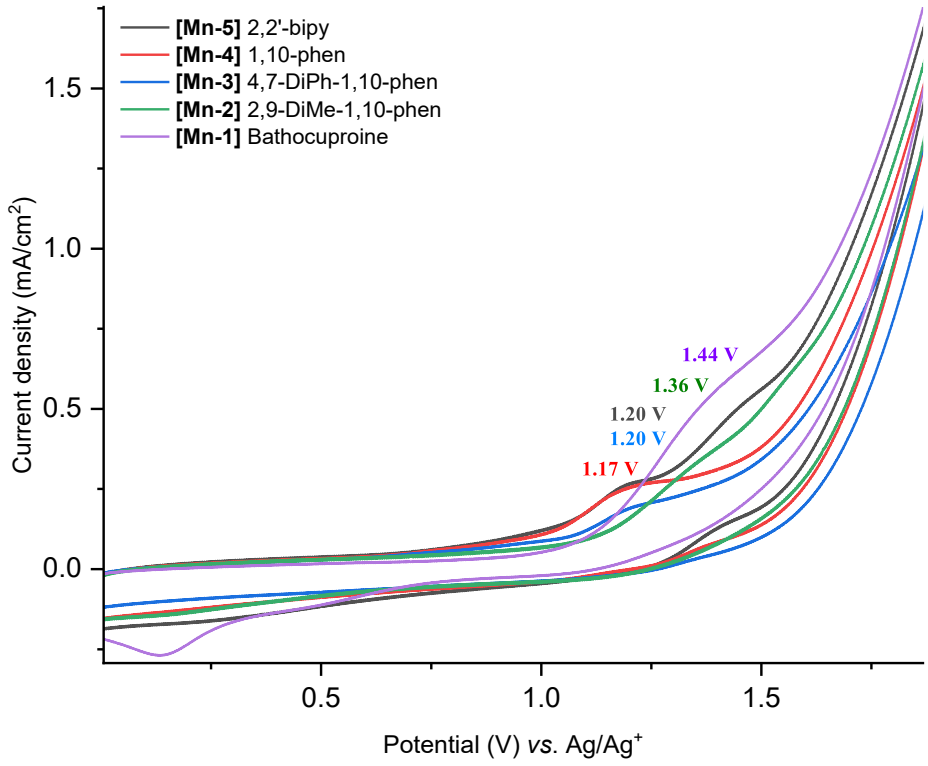
The reaction was performed under the condition of the reported procedure.[3d] A suspension of $NiCl_2 \cdot 6H_2O$ (1.0 mmol) and 1,10-phenanthroline (1.0 equiv) in methanol (4.0 mL) was stirred at RT for 3 h under air. After volatiles are evaporated under reduced pressure, residue dissolves in methanol (1.0 mL). Diethyl ether slowly added into the solution until a solid is formed. Filtration with methanol/diethyl ether (= 1:10 30 mL) gave pale blue green solid, which was dried *in vacuo* for 12 h.



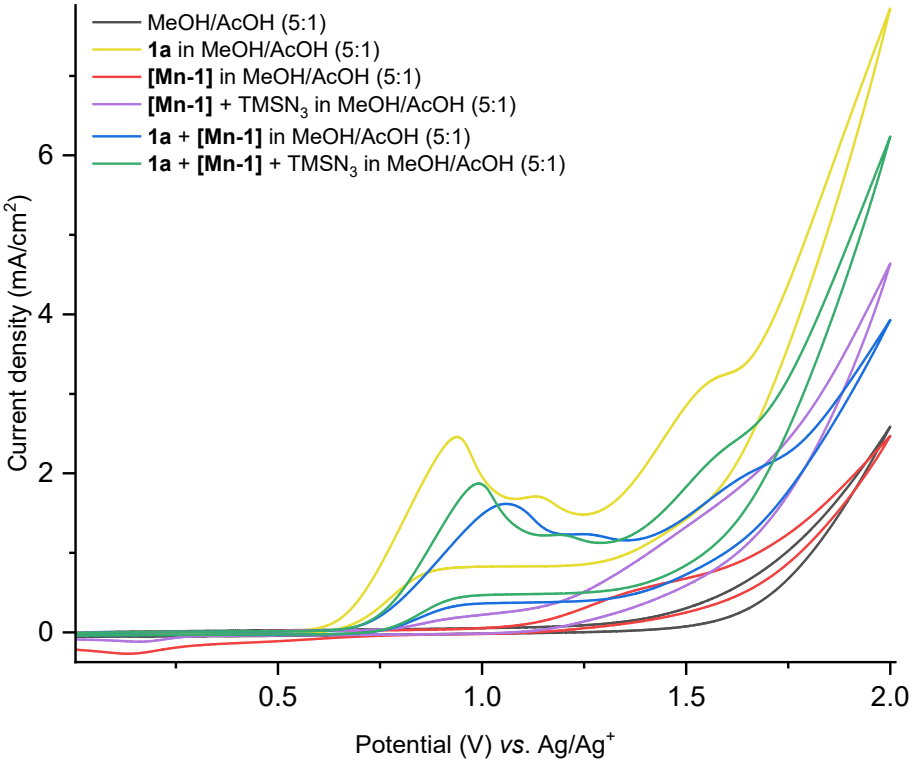
Cyclic Voltammetry Data

1) Procedure for cyclic voltametric study

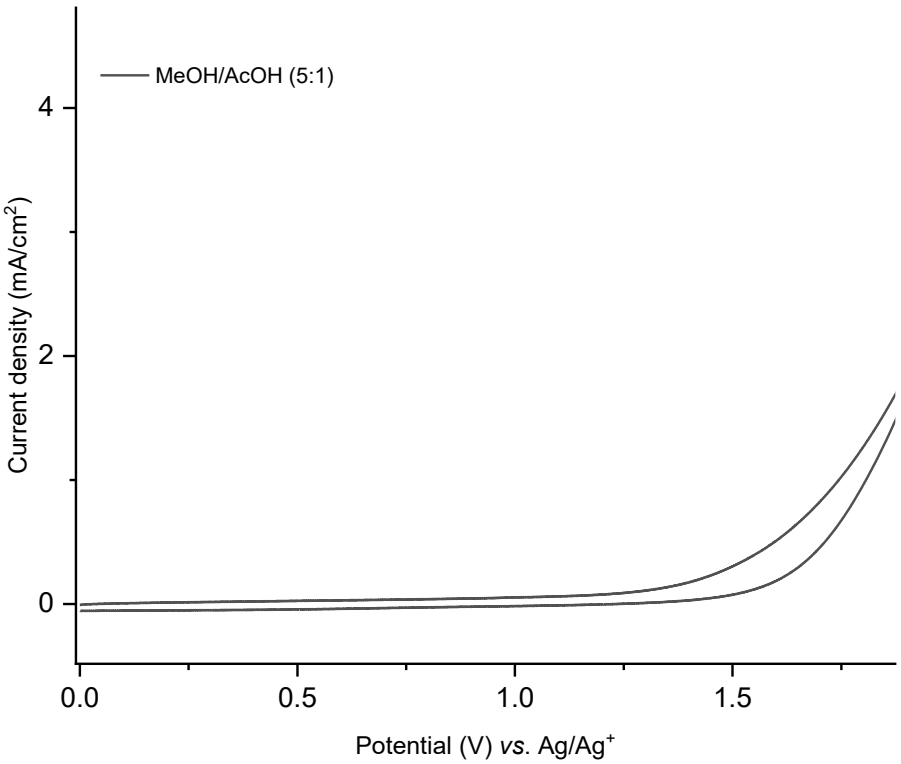
Cyclic voltammetry experiments were conducted using a glassy carbon disk working electrode (diameter: 3 mm), a coiled platinum wire counter electrode, and a Ag/Ag^+ reference electrode (Ag wire, 4 mm) immersed in 0.01 M $AgNO_3$ and 0.1 M $TBAPF_6$ in MeCN. The supporting electrolyte consisted of 0.1 M $TBAPF_6$ in MeOH/AcOH (5:1). The Mn complex (0.001 M) and the analyte (0.004 M) were prepared in the same supporting electrolyte. Cyclic voltammograms were recorded at a scan rate of 100 mV/s.



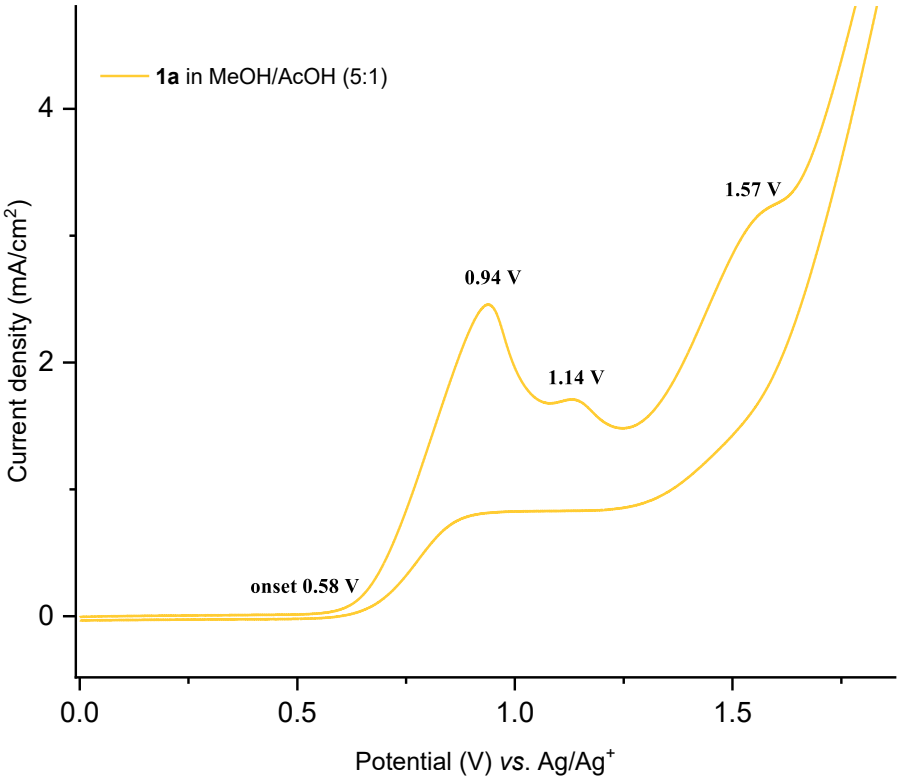
Scheme S2. CV comparison of oxidation potentials of manganese complexes



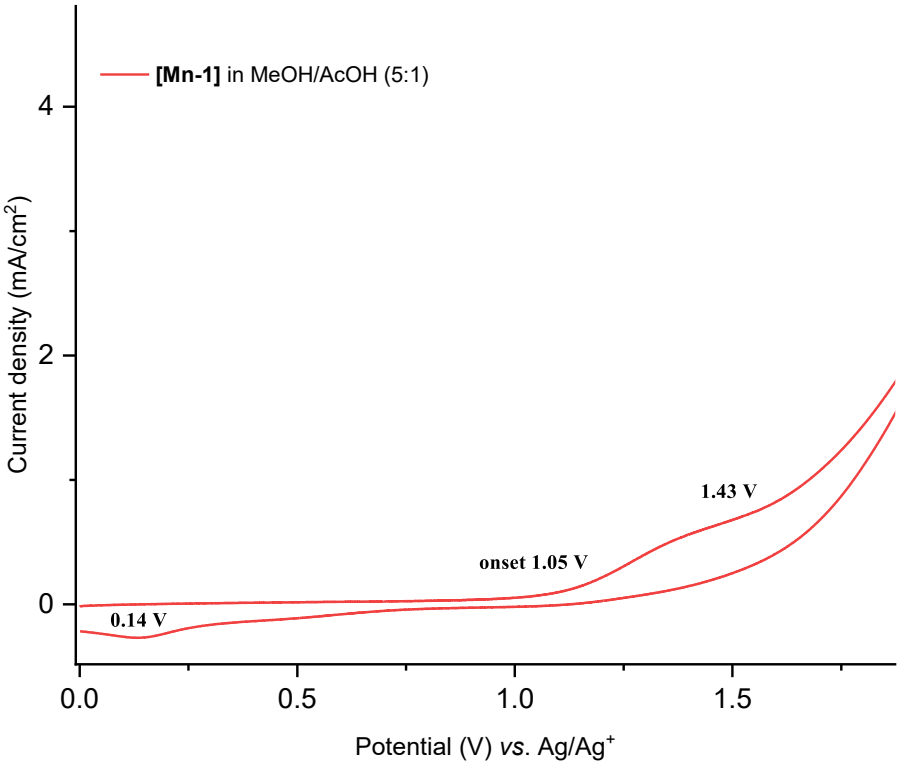
Scheme S3. CV analyses of **1a** and **[Mn-1]** in the presence of $TMSN_3$



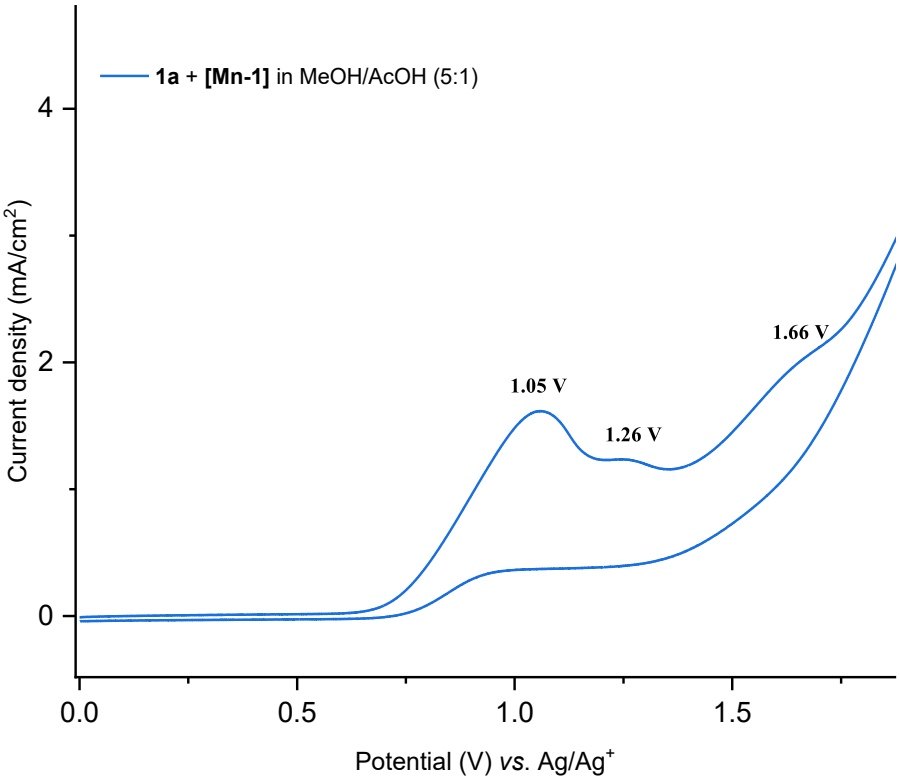
Scheme S4. CV analysis of the blank solution



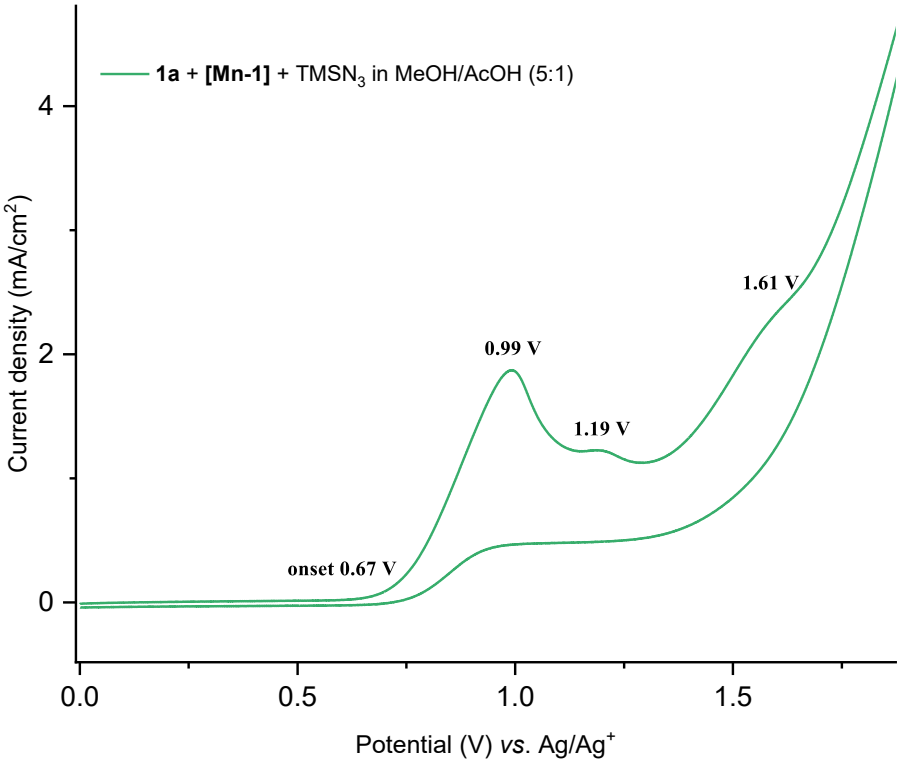
Scheme S5. CV analysis of **1a** in MeOH/AcOH



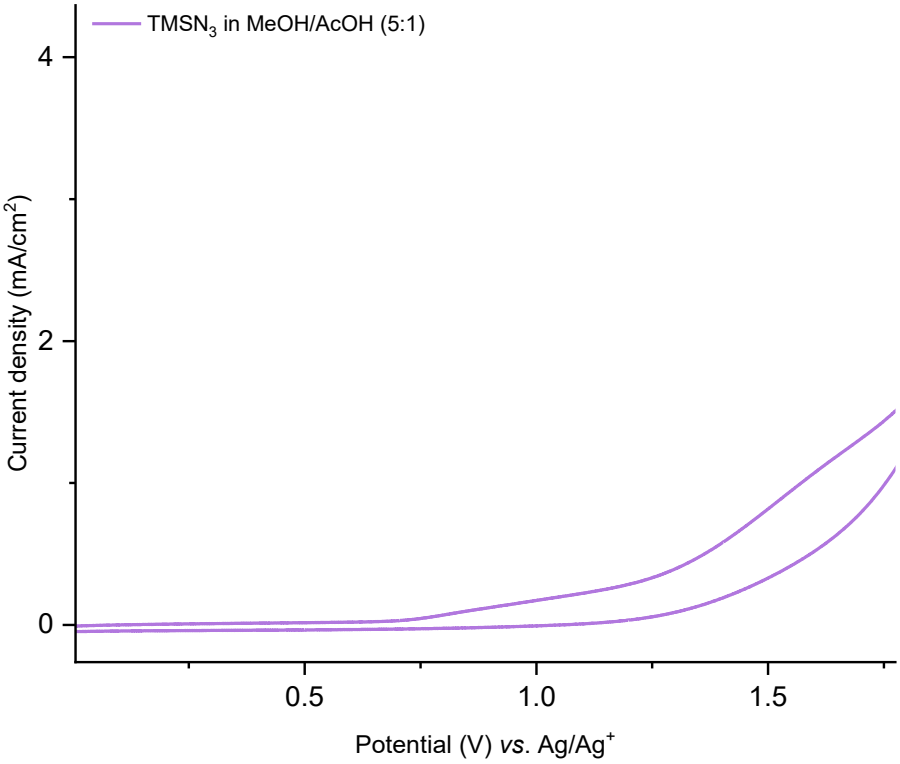
Scheme S6. CV analysis of **[Mn-1]** in MeOH/AcOH



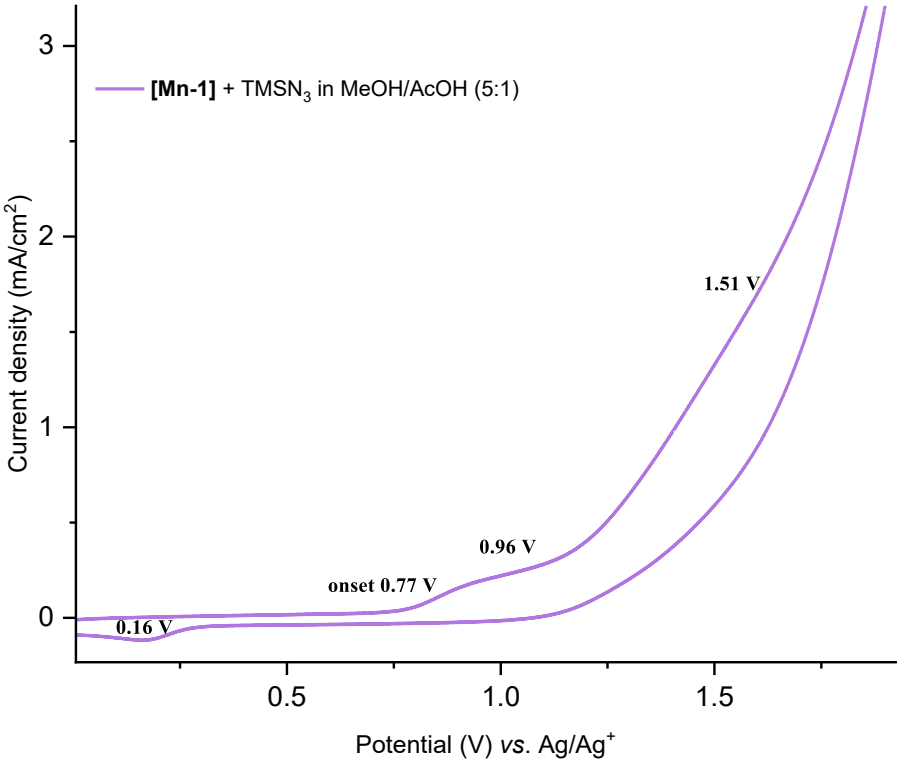
Scheme S7. CV analysis of **1a** + **[Mn-1]** in MeOH/AcOH



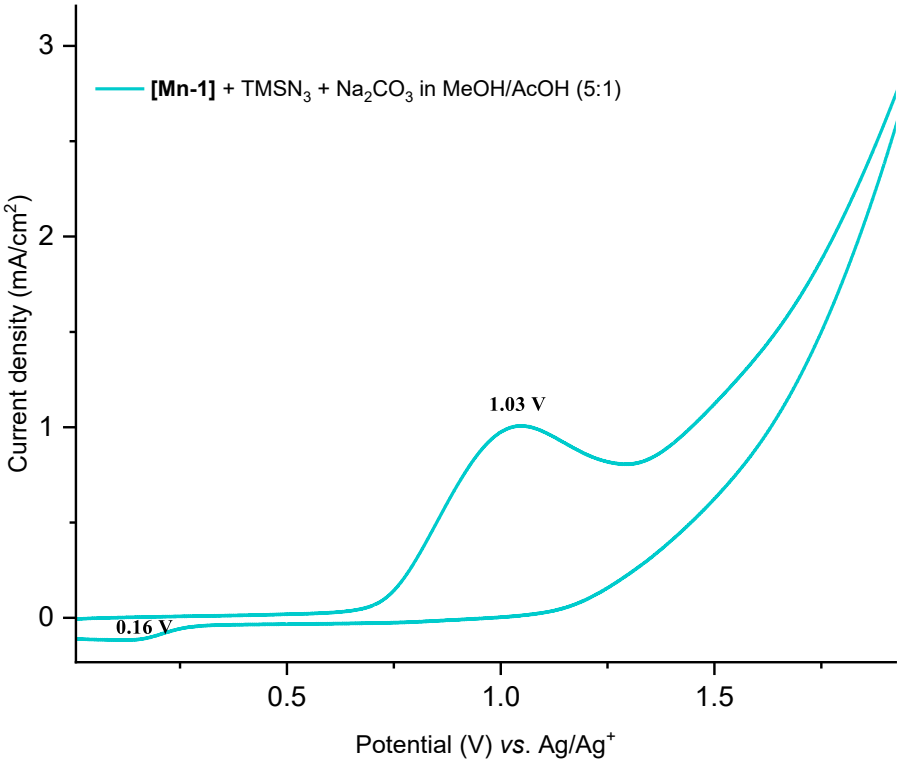
Scheme S8. CV analysis of **1a** + **[Mn-1]** + $TMSN_3$ in MeOH/AcOH



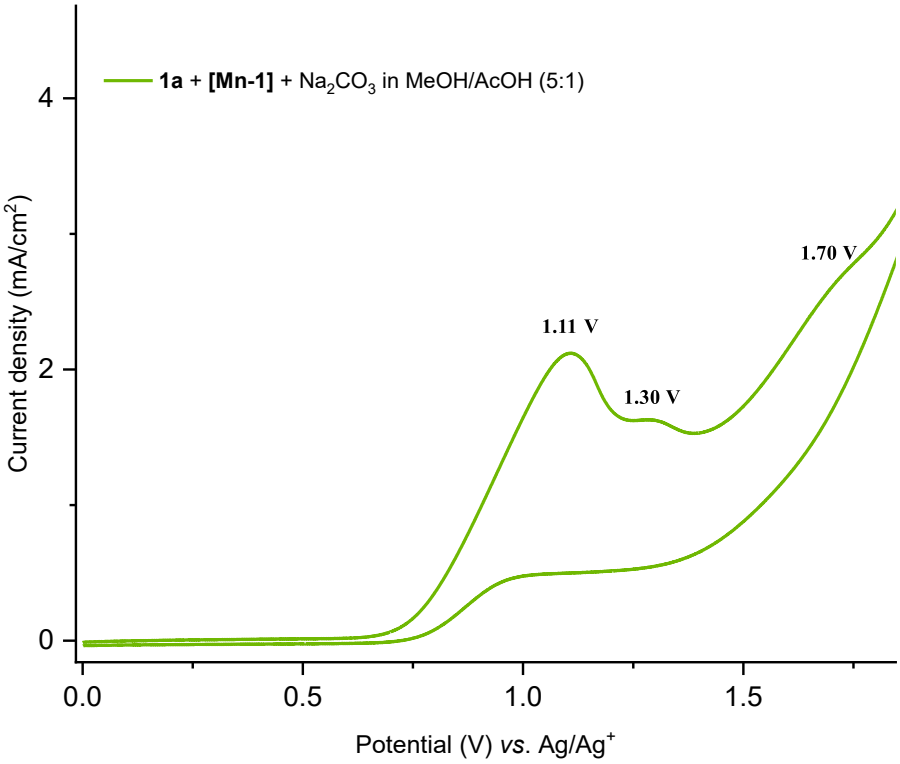
Scheme S9. CV analysis of $TMSN_3$ in MeOH/AcOH



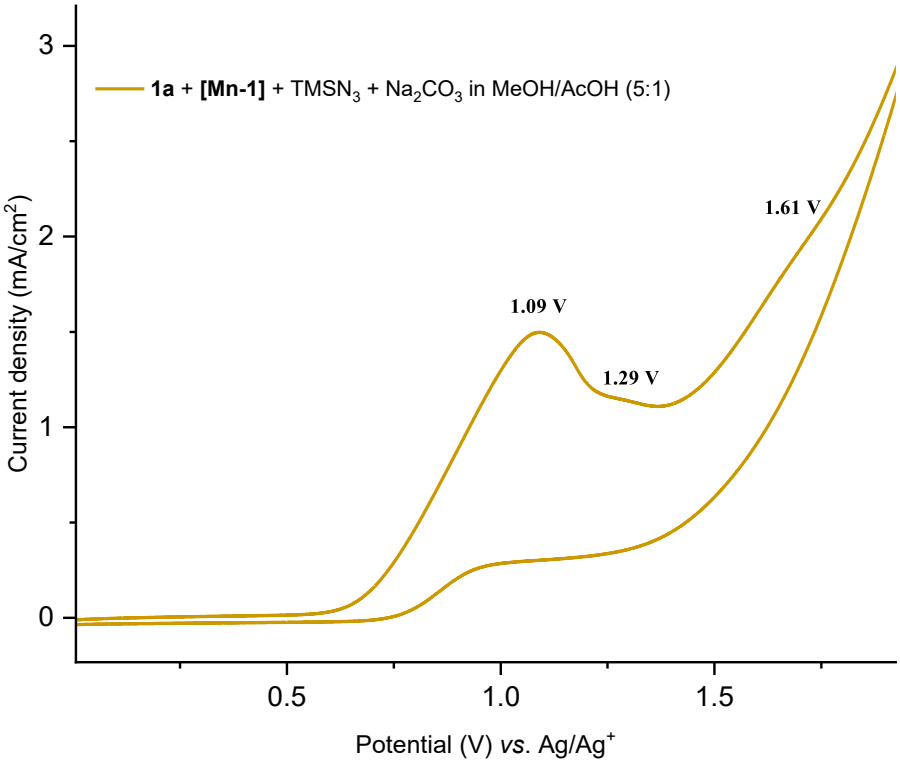
Scheme S10. CV analysis of **[Mn-1]** + $TMSN_3$ in MeOH/AcOH



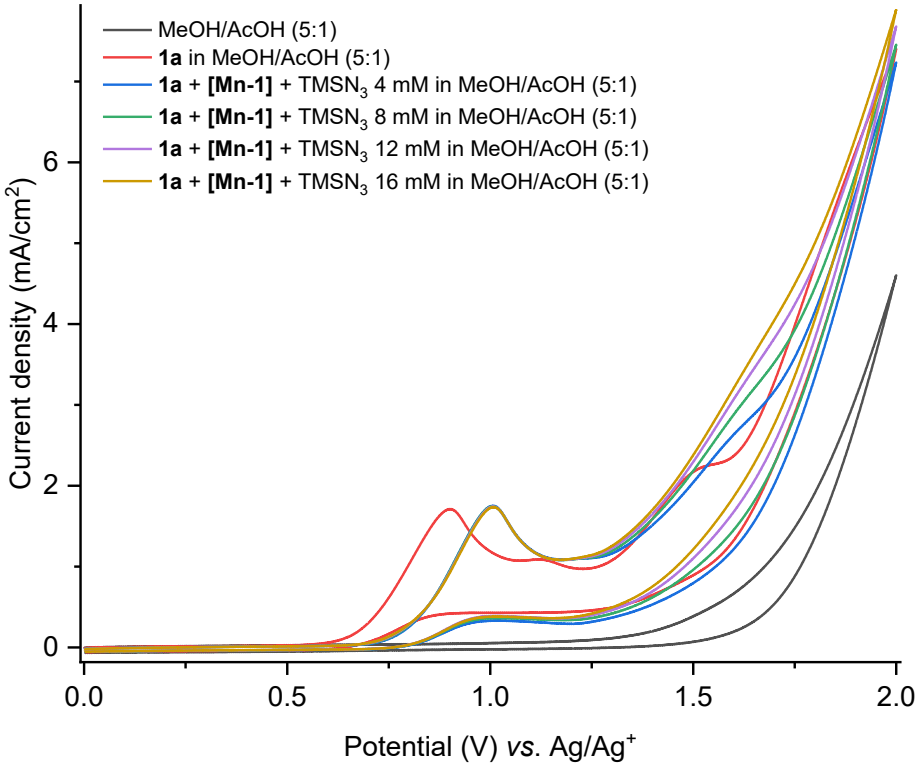
Scheme S11. CV analysis of **[Mn-1]** + $TMSN_3$ + Na_2CO_3 in MeOH/AcOH



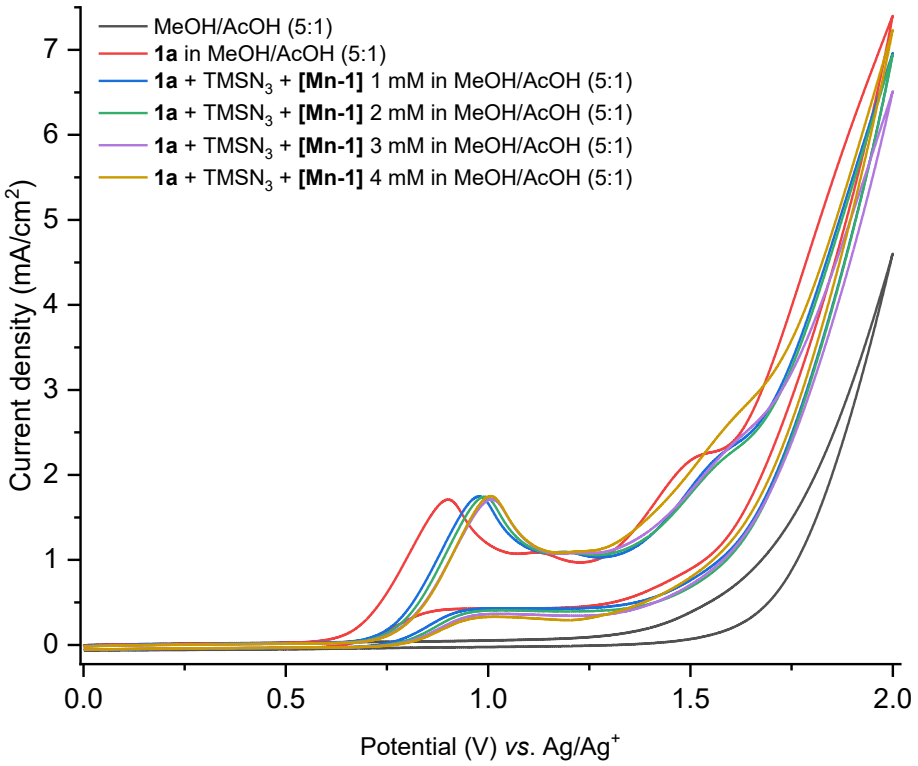
Scheme S12. CV analysis of **1a** + **[Mn-1]** + Na_2CO_3 in MeOH/AcOH



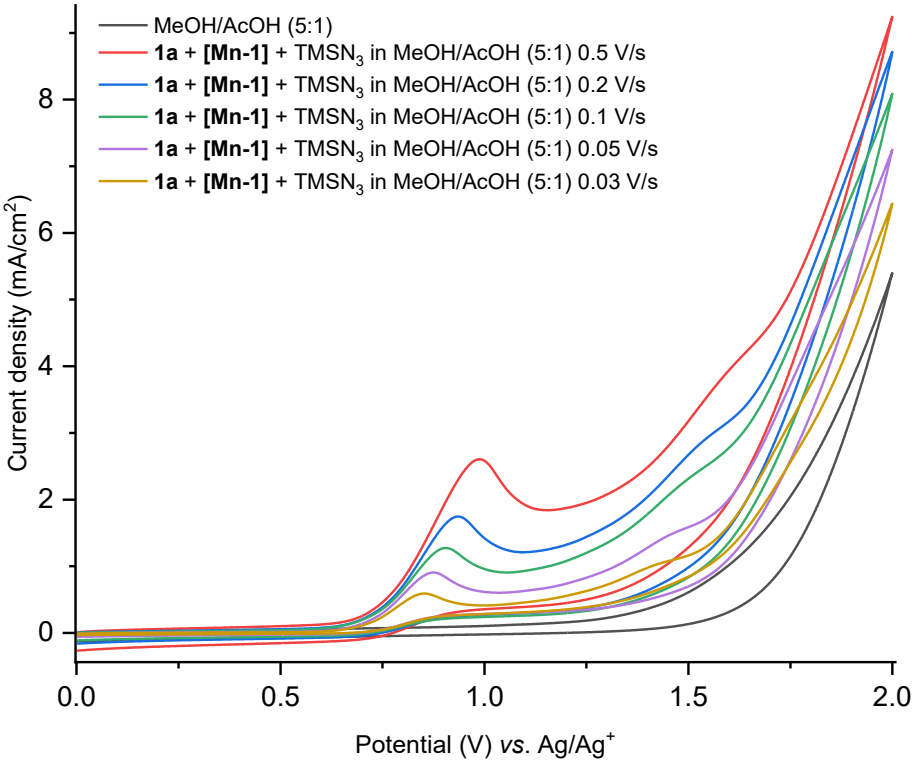
Scheme S13. CV analysis of **1a** + **[Mn-1]** + $TMSN_3$ + Na_2CO_3 in MeOH/AcOH



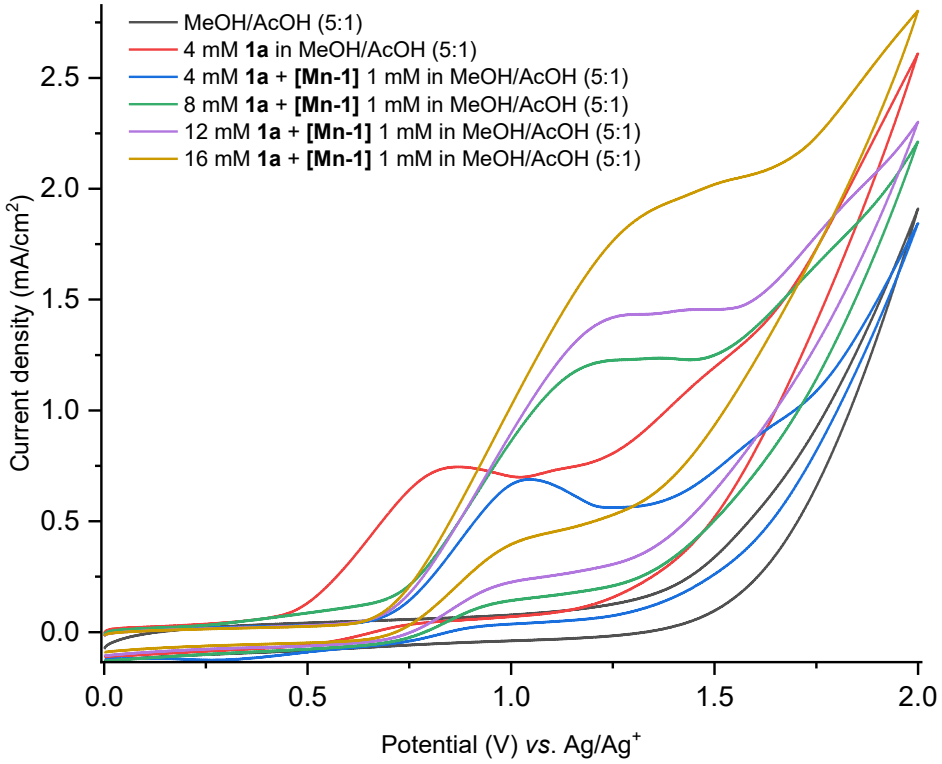
Scheme S14. CV analyses of $TMSN_3$ concentration dependence in the **1a** + **[Mn-1]** system



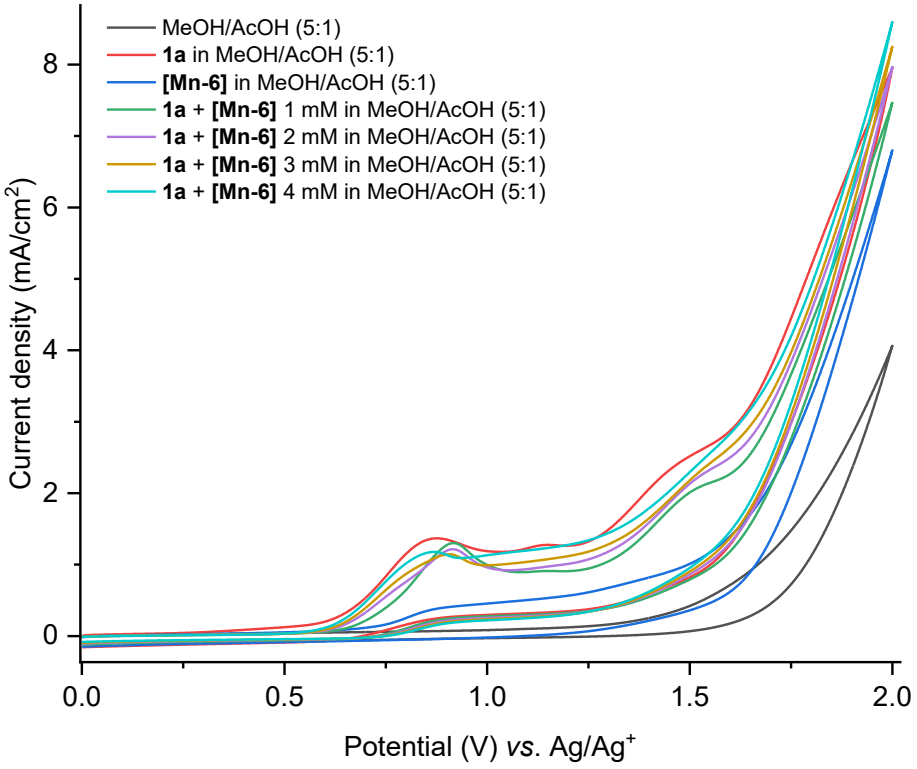
Scheme S15. CV analyses of **[Mn-1]** catalyst concentration dependence in the **1a** + $TMSN_3$ system



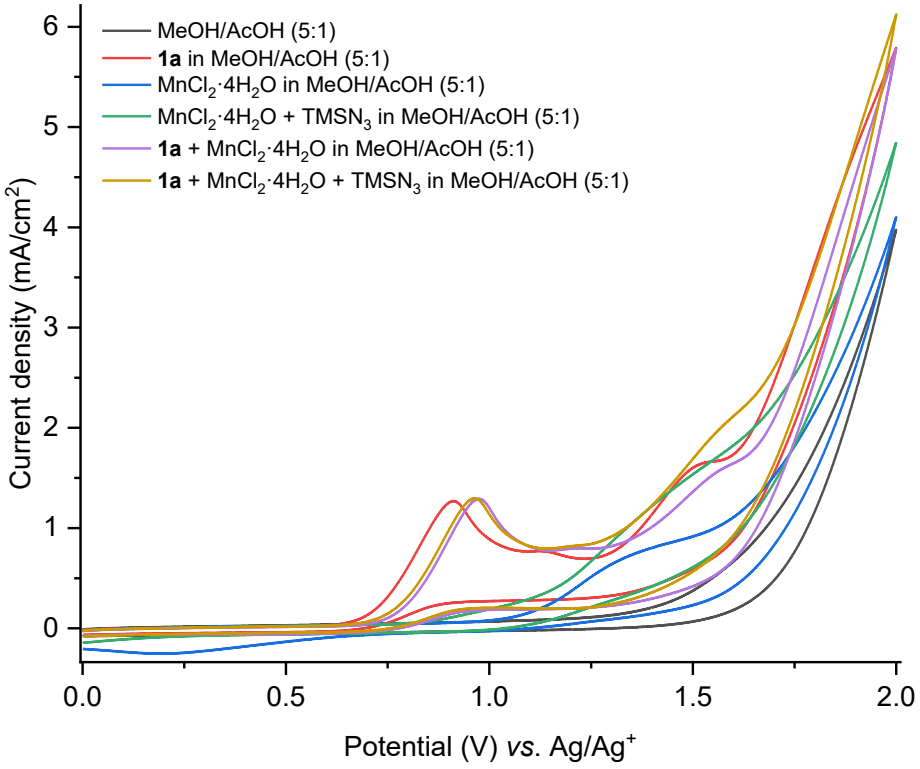
Scheme S16. CV analyses of **1a**, **[Mn-1]** and $TMSN_3$ at different scan rates



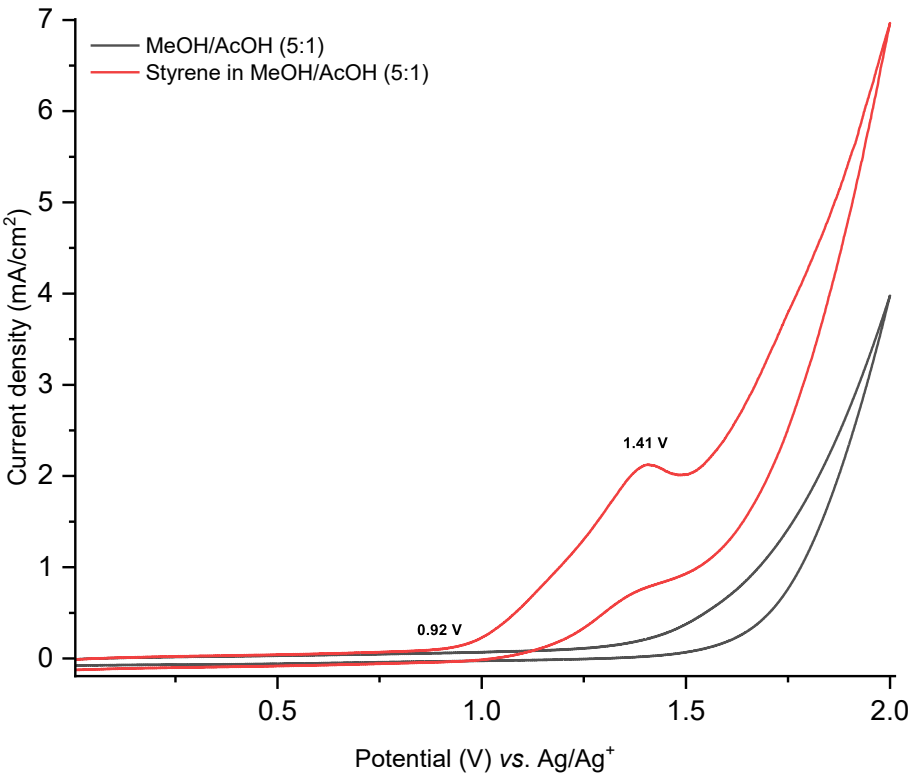
Scheme S17. CV analyses of **1a** concentration dependence in the **1a** + **[Mn-1]** system



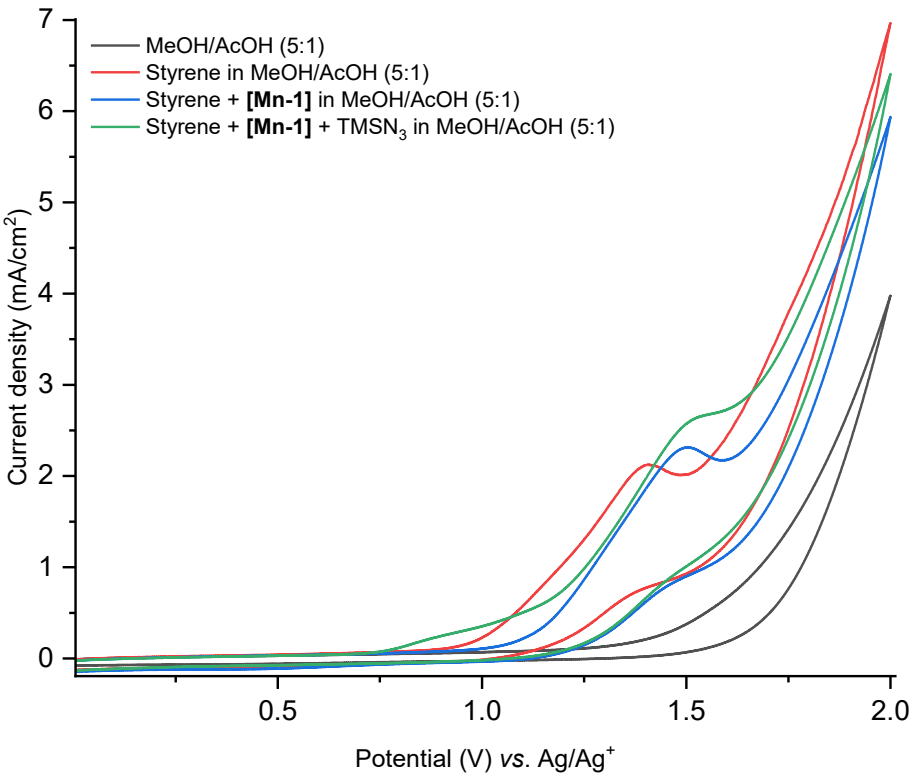
Scheme S18. CV analyses of **[Mn-6]** concentration dependence in the **1a** + **[Mn-6]** system



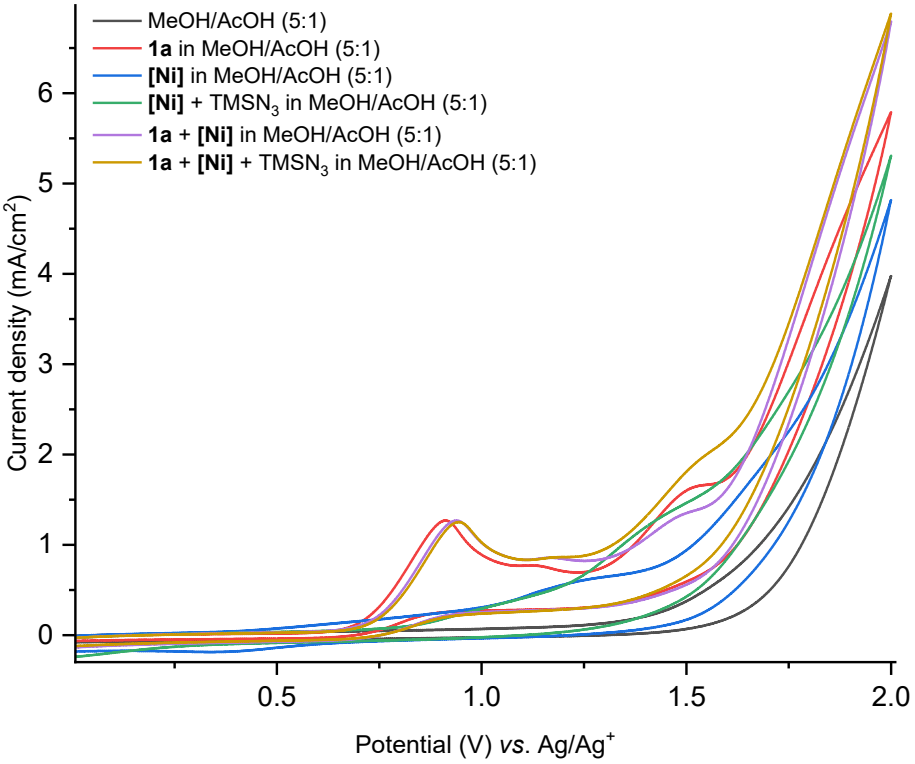
Scheme S19. Correlated CV analyses of **1a**, $MnCl_2 \cdot 4H_2O$, and $TMSN_3$



Scheme S20. CV analysis of styrene in MeOH/AcOH



Scheme S21. CV analyses of styrene in the presence of **[Mn-1]** and $TMSN_3$



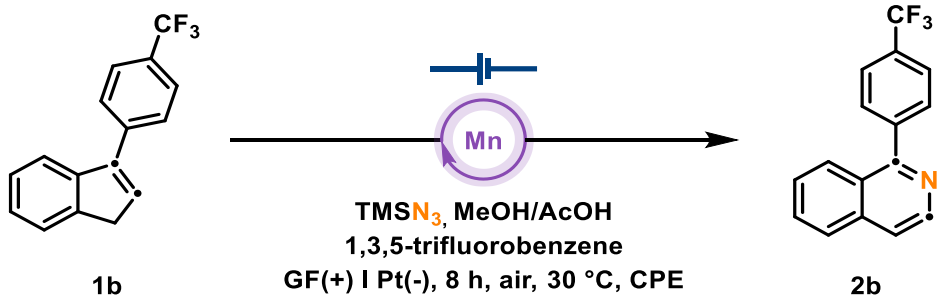
Scheme S22. CV analyses of **1a** and nickel complexes in the presence of $TMSN_3$

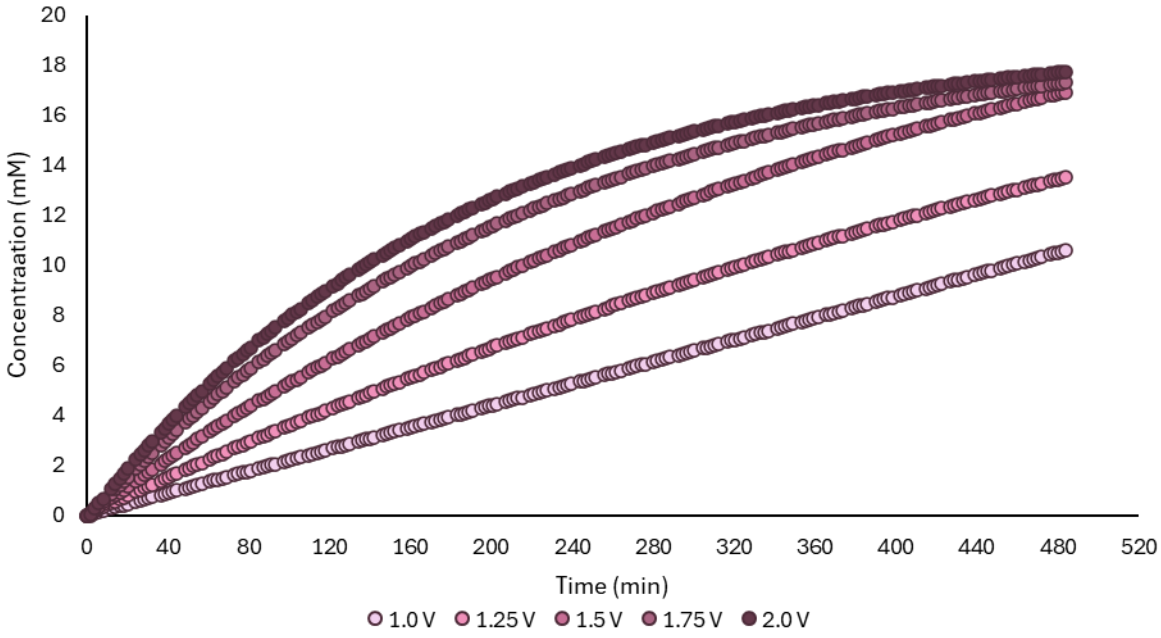
Potential-Dependence Analysis

The detailed reaction setup for in-operando NMR studies has been described in our group's previous work.[4]

1) Analysis of potential dependence

GP was followed using 3-(4-(trifluoromethyl)phenyl)-1*H*-indene **1b** (0.2 mmol, 52.1 mg), **[Mn-1]** (0.02 mmol, 9.7 mg), $TMSN_3$ (0.2 mmol, 25.8 μL), Na_2CO_3 (0.2 mmol, 21.2 mg) and 1,3,5-trifluorobenzene (0.2 mmol, 21.2 μL) in a mixture of MeOH (6.67 mL) and AcOH (1.33 mL) at 30 °C under open conditions. The reaction was conducted at constant voltages of 1.0, 1.25, 1.5, 1.75, and 2.0 V. Reaction progress under each condition was monitored using an *in-operando* NMR setup.



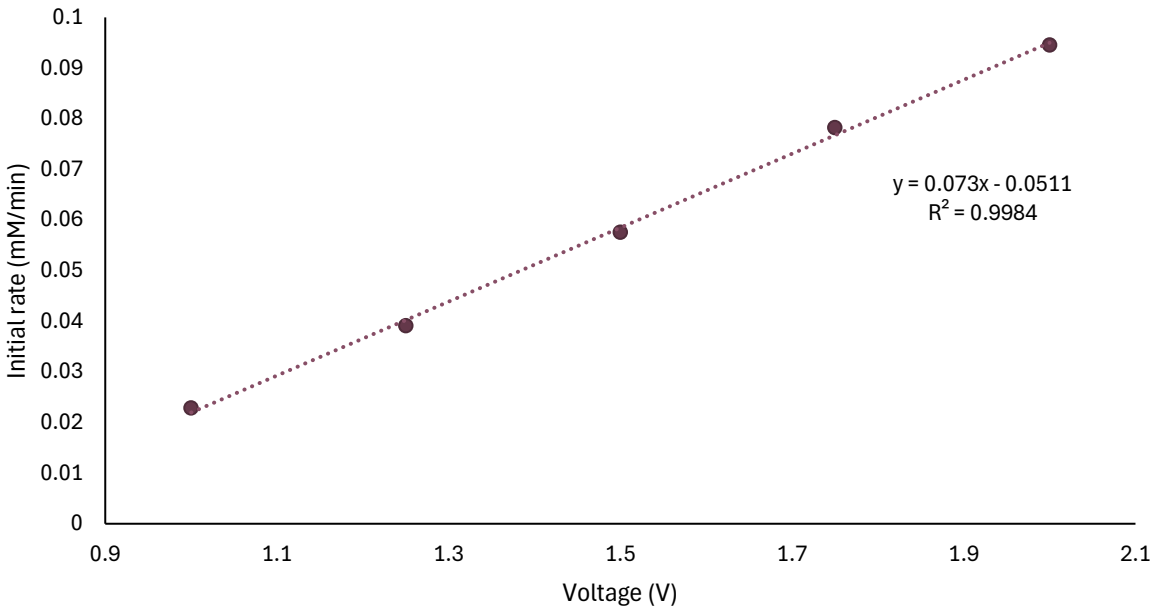


Scheme S23. Time–concentration profiles under different applied voltage

Table S6. In1itial reaction rates at different applied voltages

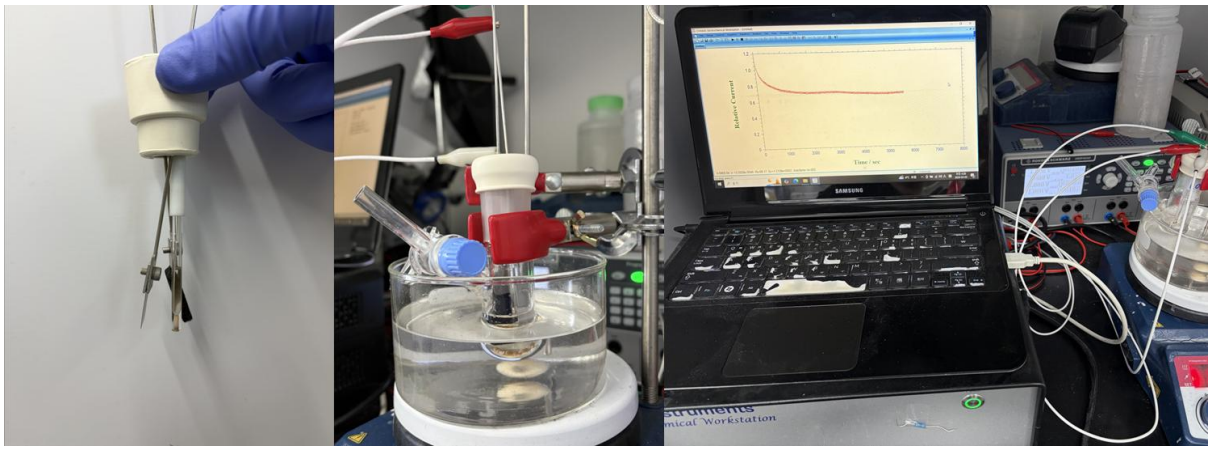
Voltage (V)	Initial rate (mM/min)
1.0	0.0229
1.25	0.0391
1.5	0.0576
1.75	0.0783
2.0	0.0946

To determine initial reaction rates, time–concentration profiles were analyzed by focusing on the early reaction stage (0–14 min), where the concentration change exhibited an approximately linear behavior.



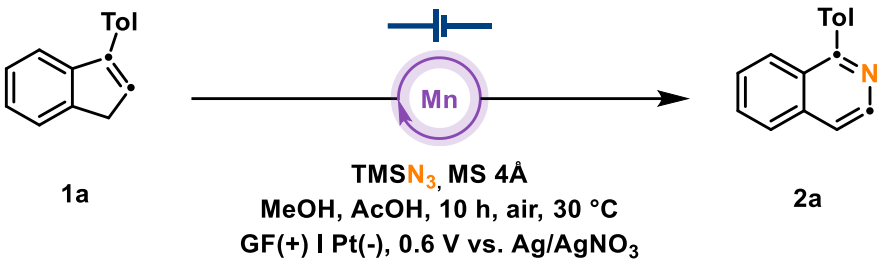
Scheme S24. Slope of the initial rate as a function of the applied voltage

Controlled Potential Electrolysis Experiments



Scheme S25. Controlled potential electrolysis (CPE) experiments were performed in a 10 mL divided cell equipped with a three-electrode setup, consisting of a graphite felt (1 cm × 2 cm) working electrode, a Pt plate (1 cm × 2 cm) counter electrode, and an $Ag/AgNO_3$ reference electrode. **1a** (0.2 mmol), **[Mn-1]** (0.1 equiv, 10 mol%), Na_2CO_3 (1.0 equiv, 0.2 mmol), and activated 4Å molecular sieves (25 beads) were added, and the mixture was evacuated under vacuum for 10 min. The stopcock was then opened briefly to introduce air into the tube and subsequently closed. MeOH (4.0 mL) was added, followed by the addition of $TMSN_3$ (1.0 equiv, 0.2 mmol) to the reaction mixture. Additional MeOH (1.0 mL) and AcOH (1.0 mL) were then added sequentially. Electrolysis was carried out at applied potentials of 0.6 V and 1.0 V vs $Ag/AgNO_3$ and continued for 10 h. The reaction work-up was performed according to the general procedure (GP). The crude yield was determined by ^1H NMR analysis using mesitylene as an internal standard.

1) Electrolysis was carried out at applied potentials of 0.6 V vs $Ag/AgNO_3$

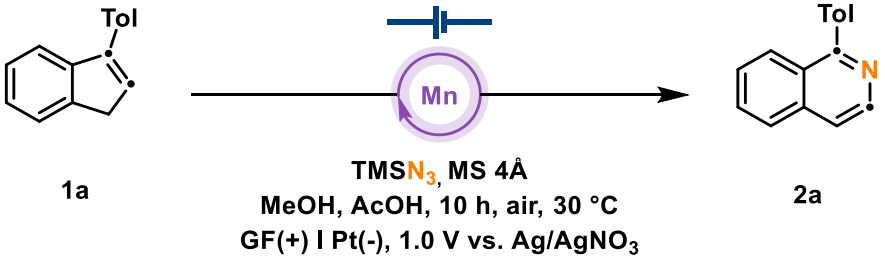


Potential	1a	2a	3a	4a
0.6 V	0%	0%	0%	0%

Yield was determined by ^1H NMR with mesitylene as internal standard.

The starting material **1a** was fully decomposed, and no formation of the desired product **2a** was detected. A black passivation layer was formed on the Pt plate counter electrode.

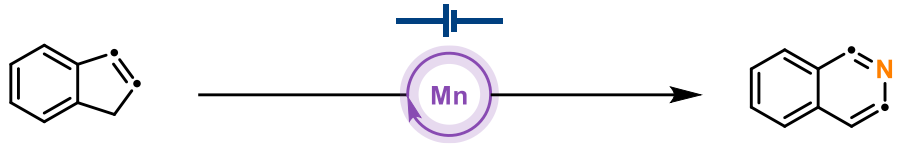
2) Electrolysis was carried out at applied potentials of 1.0 V vs $Ag/AgNO_3$



Potential	1a	2a	3a	4a
1.0 V	0%	55%	3%	2%

Yield was determined by ^1H NMR with mesitylene as internal standard.

Additional Substrate Scope

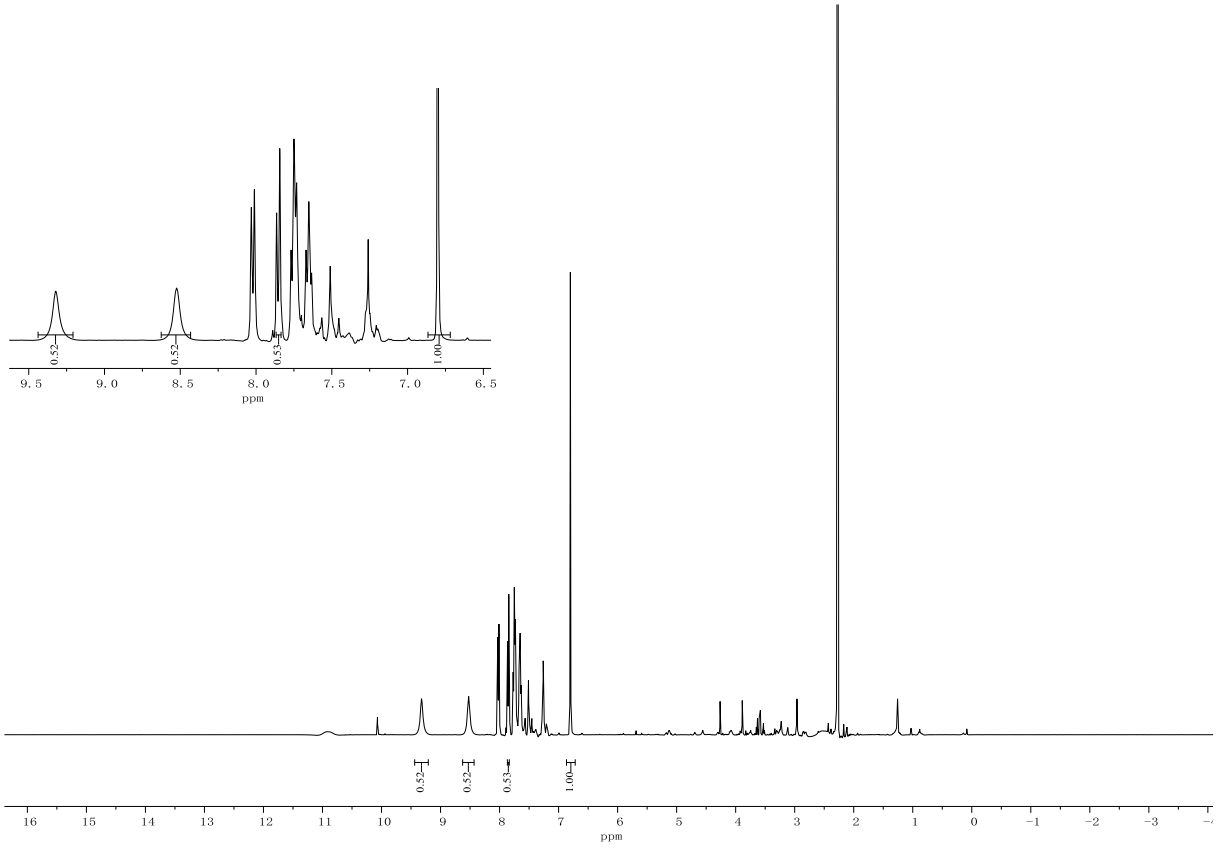


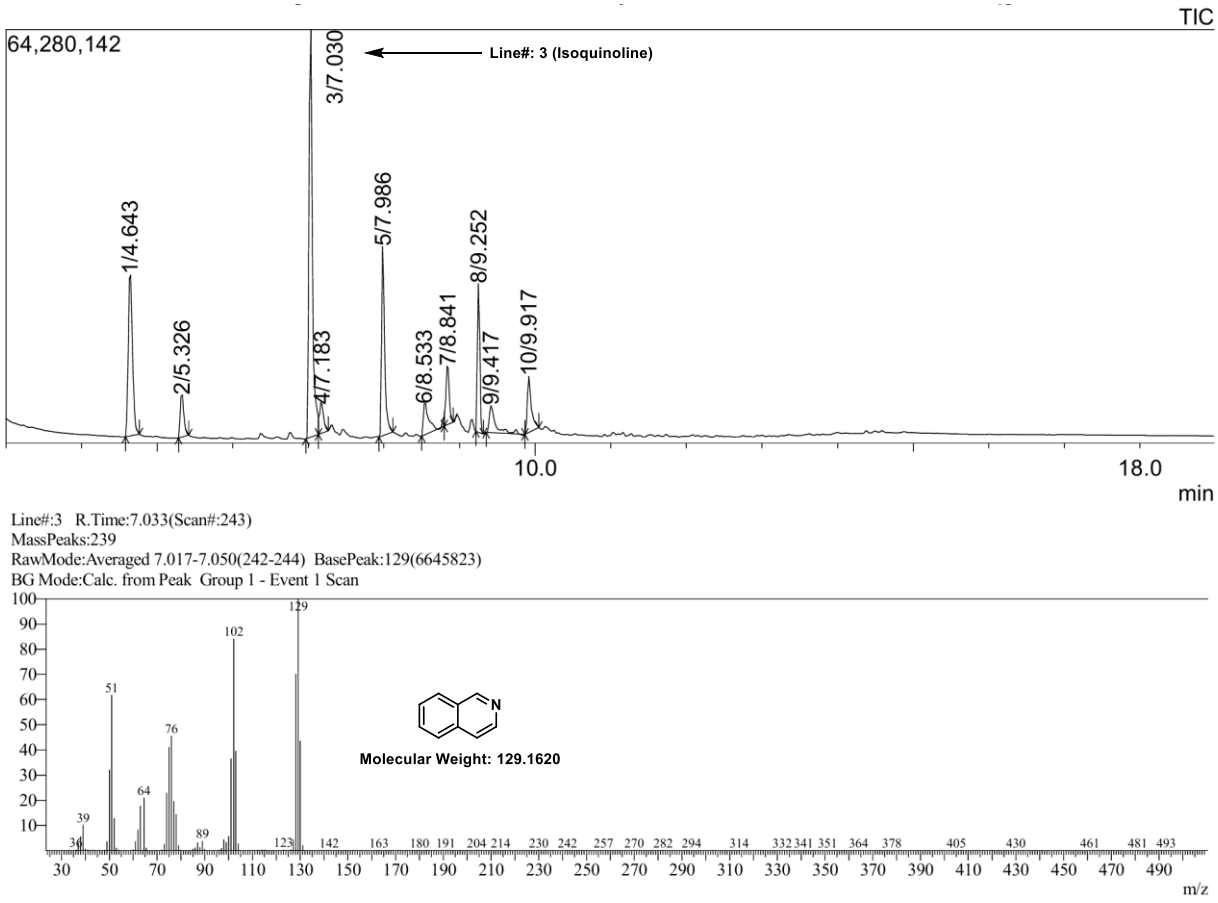
1*H*-indene

TMSN_3, MS 4Å
MeOH, AcOH, 10 h, air, 30 °C
GF(+) I Pt(-), 1.0 V

Isoquinoline

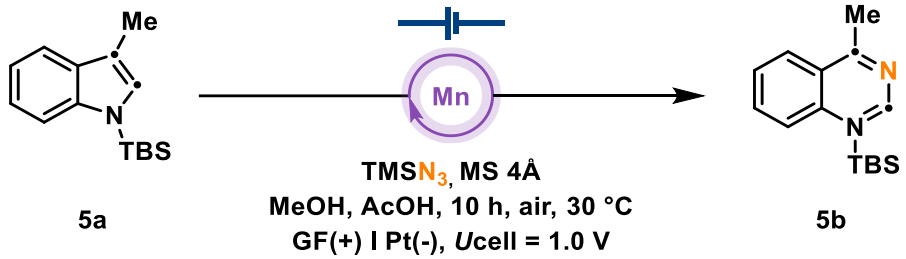
GP was followed using 1*H*-indene (0.2 mmol, 23.3 μL), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Due to the volatility of isoquinoline under high-vacuum conditions, the isolated yield could not be accurately determined. Therefore, the crude yield was quantified by ^{1}H NMR analysis using mesitylene (0.66 mmol, 9.2 μL) as an internal standard. (52 %)[5]



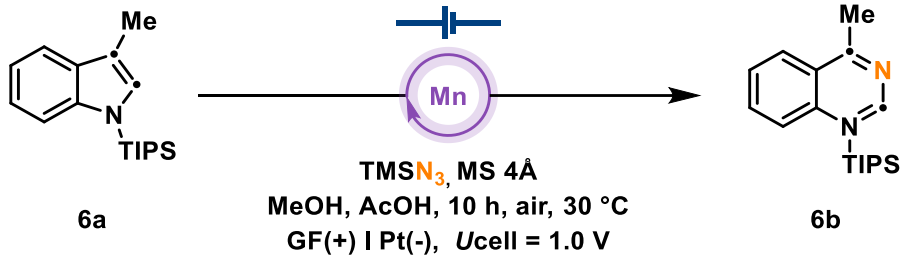


Scheme S26. Crude GC–MS analysis of the reaction using simple indene

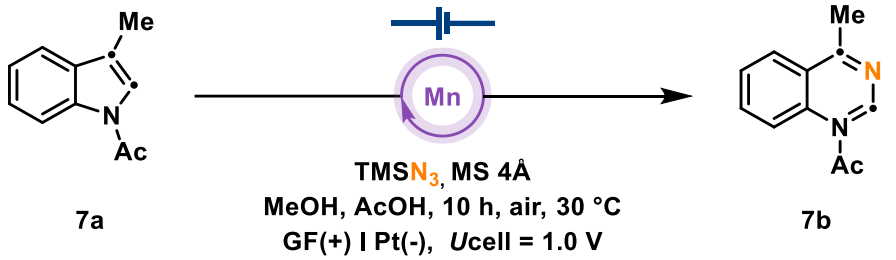
Unsuccessful Reactions



GP was followed using **5a** (0.2 mmol, 49.0 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). After quenching, based on TLC and crude NMR analysis, the starting material remained unchanged and no formation of **5b** was observed.



GP was followed using **6a** (0.2 mmol, 57.5 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). After quenching, based on TLC and crude NMR analysis, the starting material remained unchanged and no formation of **6b** was observed.

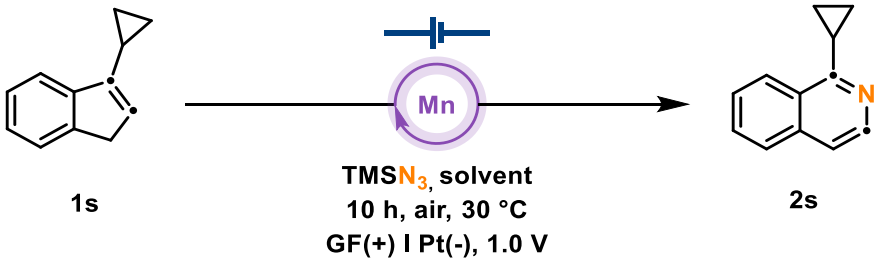


GP was followed using **7a** (0.2 mmol, 34.6 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). After quenching, based on TLC and crude NMR analysis, the starting material remained unchanged and no formation of **7b** was observed.

Radical Clock Experiment

1) Under the optimized conditions

GP was followed using **1s** (0.2 mmol, 31.2 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2s** (17.6 mg, 52 %) as a colorless oil.



1-Cyclopropylisoquinoline (2s)

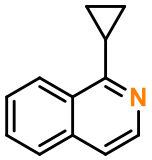
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J =8.4 Hz, 1H), 8.36 (d, J = 5.7 Hz, 1H), 7.79 (d, J = 7.8 Hz, 1H), 7.69-7.60 (m, 2H), 7.44 (d, J = 5.7 Hz, 1H), 2.78-2.71 (m, 1H), 1.30-1.25 (m, 2H), 1.17-1.12 (m, 2H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 162.0, 141.8, 136.1, 130.0, 127.8, 127.4, 127.1, 125.3, 118.6, 13.6, 9.6.

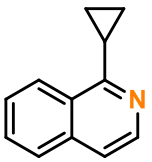
IR (ATR): 3051, 3006, 2925, 2853, 2103, 1622, 1410, 1014, 902, 865 cm^{-1}.

HR-MS (ESI) $C_{12}H_{12}N$ $[M+H]^+$: 170.0964, found: 170.0970.

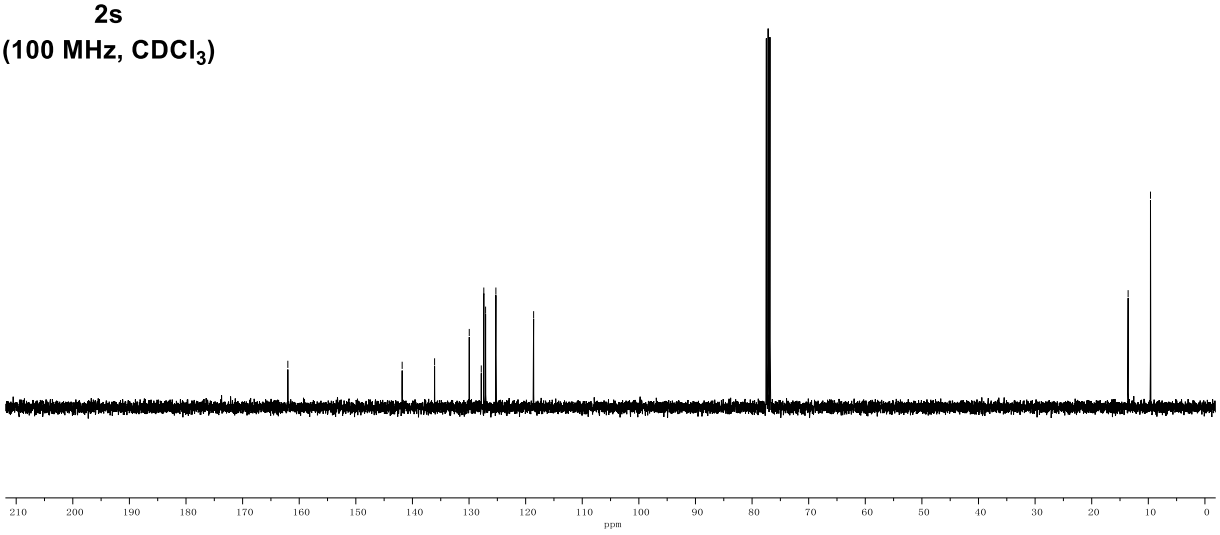
The spectral data were in accordance with those reported in the literature.[11]



2s
(400 MHz, $CDCl_3$)

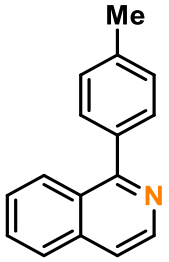


2s
(100 MHz, $CDCl_3$)



Characterization Data of Products

1-(*p*-Tolyl)isoquinoline (2a)



GP was followed using **1a** (0.2 mmol, 41.2 mg), $TMSN_3$ (0.2 mmol, 26.3 μL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2a** (29.3 mg, 67%) as a colorless oil.

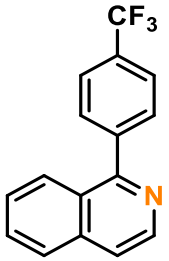
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J =5.7 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.73-7.67 (m, 1H), 7.64 (d, J = 5.7 Hz, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.58-7.50 (m, 1H), 7.35 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 141.7, 138.7, 137.0, 136.2, 130.2, 129.9, 129.1, 127.8, 127.2, 127.0, 126.7, 119.8, 21.4

IR (ATR): 2980, 2971, 1733, 1557, 1384, 1208, 1166, 1127, 955, 823 cm^{-1}.

HR-MS (ESI) $C_{16}H_{14}N$ $[M+H]^+$: 220.1121, found: 220.1120.

1-(4-(Trifluoromethyl)phenyl)isoquinoline (2b)



GP was followed using **1b** (0.2 mmol, 52.0 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2b** (32.6 mg, 65%) as a white solid.

M. p. 112-114 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, J =5.7 Hz, 1H), 8.03 (d, J = 8.5 Hz, 1H), 7.92 (d, J = 8.2 Hz, 1H), 7.84-7.79 (m, 4H), 7.75-7.68 (m, 2H), 7.60-7.54 (m, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 143.2, 142.4, 137.0, 130.8 (q, J = 32.5 Hz), 130.4, 130.3, 127.8, 127.3, 127.1, 126.7, 125.5 (q, J = 3.8 Hz), 124.2 (q, J = 273.6 Hz), 120.7

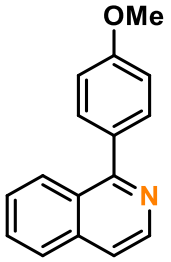
^{19}F NMR (471 MHz, $CDCl_3$) δ -105.5.

IR (ATR): 2980, 2889, 1616, 1518, 1105, 1016, 967, 800, 680, 497 cm^{-1}.

HR-MS (ESI) $C_{16}H_{11}{}^{19}F_3N$ $[M+H]^+$: 274.0838, found: 274.0837.

The spectral data were in accordance with those reported in the literature.[6]

1-(4-Methoxyphenyl)isoquinoline (2c)



GP was followed using **1c** (0.2 mmol, 44.4 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2c** (33.4 mg, 71%) as a orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J =5.7 Hz, 1H), 8.15 (d, J = 8.2 Hz, 1H), 7.87 (d, J = 8.2 Hz, 1H), 7.71-7.64 (m, 3H), 7.61 (d, J = 5.7 Hz, 1H), 7.57-7.50 (m, 1H), 7.07 (d, J = 8.6 Hz, 2H), 3.90 (s, 3H)

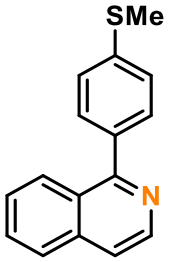
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.3, 160.0, 142.1, 136.9, 132.0, 131.3, 129.9, 127.6, 127.1, 127.0, 126.7, 119.5, 113.8, 55.4

IR (ATR): 3047, 2980, 1607, 1582, 1454, 1109, 1029, 973, 873, 822 cm^{-1}

HR-MS (ESI) $C_{16}H_{14}NO$ $[M+H]^+$: 236.1070, found: 236.1069.

The spectral data were in accordance with those reported in the literature.[6]

1-(4-(Methylthio)phenyl)isoquinoline (2d)



GP was followed using **1d** (0.2 mmol, 47.6 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2d** (36.6 mg, 67%) as a colorless oil.

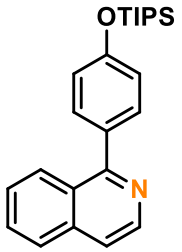
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J =5.7 Hz, 1H), 8.10 (d, J = 8.5 Hz, 1H), 7.85 (d, J = 8.5 Hz, 1H), 7.69-7.62 (m, 3H), 7.60 (d, J = 5.7 Hz, 1H), 7.55-7.47 (m, 1H), 7.40 (d, J = 8.3 Hz, 2H), 2.54 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.0, 142.2, 139.4, 132.9, 136.2, 130.4, 130.0, 127.4, 127.2, 127.0, 126.6, 126.1, 119.8, 15.6

IR (ATR): 3046, 2980, 2917, 1617, 1544, 1382, 1243, 1124, 873, 674 cm^{-1}

HR-MS (ESI) $C_{16}H_{14}NS$ $[M+H]^+$: 252.0841, found: 252.0855.

1-(4-((Triisopropylsilyl)oxy)phenyl)isoquinoline (2e)



GP was followed using **1i** (0.2 mmol, 72.9 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2i** (52.1 mg, 69%) as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J =5.7 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.70-7.63 (m, 1H), 7.63-7.57 (m, 3H), 7.53 (ddd, J = 8.2, 6.9, 1.1 Hz, 1H), 7.08-7.00 (m, 2H), 1.38-1.26 (m, 3H), 1.15 (d, J = 7.4, 18H)

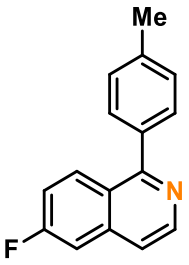
^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 156.7, 142.1, 136.9, 132.2, 131.2, 129.9, 127.7, 127.0, 126.9, 126.7, 119.8, 119.5, 18.0, 12.7

IR (ATR): 3048, 2943, 2865, 1604, 1583, 1261, 1138, 1014, 996, 799 cm^{-1}.

HR-MS (TOF) $C_{24}H_{32}NOSi$ $[M+H]^+$: 378.2248, found: 378.2240.

The spectral data were in accordance with those reported in the literature.[6]

6-Fluoro-1-(*p*-tolyl)isoquinoline (2f)



GP was followed using **1f** (0.2 mmol, 44.8 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2f** (34.6 mg, 73%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (d, J =5.7 Hz, 1H), 8.15 (dd, J = 9.3, 5.6 Hz, 1H), 7.61-7.53 (m, 3H), 7.47 (dd, J = 9.3, 2.5 Hz, 1H), 7.34 (d, J = 7.8 Hz, 2H), 7.31-7.22 (m, 1H), 2.46 (s, 3H).

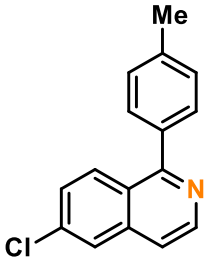
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1 (d, J =252.8 Hz), 160.9 (d, J =1.1 Hz), 143.2, 138.9, 138.7 (d, J =9.5 Hz), 131.2 (d, J =9.5 Hz), 136.5, 129.9, 129.3, 124.1, 119.5 (d, J =5.1 Hz), 117.5 (d, J =25.0 Hz), 110.3 (d, J =20.6 Hz), 21.5

^{19}F NMR (376 MHz, $CDCl_3$) δ -108.12.

IR (ATR): 3047, 2958, 1732, 1515, 1353, 1247, 1205, 1136, 1019, 947 cm^{-1}.

HR-MS (ESI) $C_{16}H_{13}{}^{19}FN$ $[M+H]^+$: 238.1027, found: 238.1026.

6-Chloro-1-(*p*-tolyl)isoquinoline (2g)



GP was followed using **1g** (0.2 mmol, 48.1 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 10/1) yielded **2g** (38.5 mg, 76%) as a pale yellow oil.

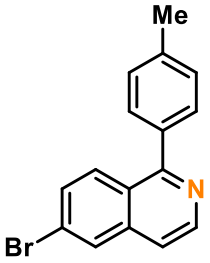
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J =5.7 Hz, 1H), 8.06 (d, J = 9.0 Hz, 1H), 7.84 (d, J = 2.0 Hz, 1H), 7.57 (d, J = 8.0 Hz, 2H), 7.52 (d, J = 5.7 Hz, 1H), 7.45 (dd, J = 9.0, 2.0 Hz, 1H), 7.34 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 143.40, 143.39, 138.9, 137.8, 136.3, 129.9, 129.7, 129.3, 128.1, 125.8, 125.0, 118.9, 21.5

IR (ATR): 3052, 2969, 1610, 1449, 1243, 1080, 1020, 935, 809, 770 cm^{-1}.

HR-MS (ESI) $C_{16}H_{13}{}^{35}ClN$ $[M+H]^+$: 254.0737, found: 254.0747.

6-Bromo-1-(*p*-tolyl)isoquinoline (2h)



GP was followed using **1h** (0.2 mmol, 57.0 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2h** (44.7 mg, 75%) as yellow oil.

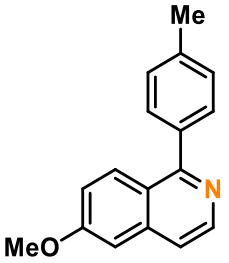
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, J = 5.7 Hz, 1H), 8.01 (d, J = 1.9 Hz, 1H), 7.98 (d, J = 9.0 Hz, 1H), 7.59-7.53 (m, 3H), 7.50 (d, J = 5.7 Hz, 1H), 7.34 (d, J = 7.8 Hz, 2H), 2.47 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.9, 143.2, 143.2, 138.9, 138.0, 136.1, 130.5, 129.5, 129.2, 129.0, 125.1, 124.8, 118.6, 21.4

IR (ATR): 3042, 2919, 2850, 1604, 1443, 1299, 909, 836, 722, 686 cm^{-1}.

HR-MS (TOF) $C_{16}H_{13}{}^{79}BrN$ $[M+H]^+$: 298.0226, found: 298.0233.

6-Methoxy-1-(*p*-tolyl)isoquinoline (2i)



GP was followed using **1i** (0.2 mmol, 47.2 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2i** (27.4 mg, 55%) as a brown oil.

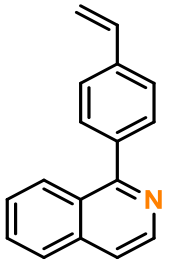
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J =5.7 Hz, 1H), 8.02 (d, J = 9.2 Hz, 1H), 7.58 (d, J = 8.1 Hz, 2H), 7.52 (d, J =5.7 Hz, 1H), 7.33 (d, J = 8.1 Hz, 2H), 7.14 (dd, J = 9.2, 2.5 Hz, 1H), 7.11 (d, J = 2.5 Hz, 1H), 3.95 (s, 3H), 2.45 (s, 3H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.5, 160.1, 142.7, 139.0, 138.4, 136.6, 129.8, 129.6, 129.0, 122.4, 119.9, 119.1, 104.4, 55.5, 21.3

IR (ATR): 2948, 2938, 1623, 1315, 1217, 1153, 1085, 1019, 807, 734 cm^{-1}.

HR-MS (TOF) $C_{17}H_{16}NO$ $[M+H]^+$: 250.1226, found: 250.1225.

1-(4-Vinylphenyl)isoquinoline (2j)



GP was followed using **1j** (0.2 mmol, 43.6 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2j** (26.8 mg, 58%) as a colorless oil.

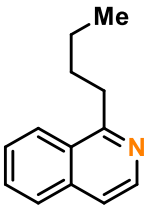
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J =5.7 Hz, 1H), 8.13 (d, J = 8.2 Hz, 1H), 7.89 (d, J = 8.2 Hz, 1H), 7.72-7.67 (m, 3H), 7.65 (d, J = 5.7 Hz, 1H), 7.59 (d, J = 8.1 Hz, 2H), 7.57-7.52 (m, 1H), 6.83 (dd, J = 16.9, 10.9 Hz, 1H), 5.87 (d, J = 16.9 Hz, 1H), 5.34 (d, J = 10.9 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 142.1, 138.8, 137.9, 136.9, 136.4, 130.2, 130.1, 127.5, 127.2, 127.0, 126.6, 126.2, 120.0, 114.7

IR (ATR): 2980, 2887, 1558, 1541, 1382, 1248, 1072, 754, 843, 571 cm^{-1}.

HR-MS (ESI) $C_{17}H_{14}N$ $[M+H]^+$: 232.1121, found: 232.1134.

1-Butylisoquinoline (2k)



GP was followed using **1k** (0.2 mmol, 34.4 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2k** (24.8 mg, 67%) as a orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J =5.7 Hz, 1H), 8.16 (dd, J = 8.2, 1.2 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.67 (ddd, J = 8.2, 6.6, 1.3 Hz, 1H), 7.59 (ddd, J = 8.2, 6.6, 1.3 Hz, 1H), 7.50 (d, J = 5.7 Hz, 1H), 3.46-3.19 (m, 2H), 1.91-1.79 (m, 2H), 1.57-1.44 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H)

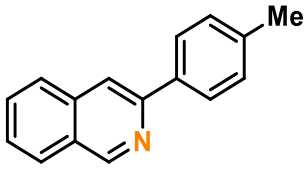
^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4, 141.6, 136.3, 129.8, 127.4, 127.0, 126.9, 125.4, 119.2, 35.2, 31.9, 23.0, 14.0

IR (ATR): 2956, 2925, 2855, 1732, 1683, 1624, 1125, 1070, 1020, 974 cm^{-1}.

HR-MS (ESI) $C_{13}H_{16}N$ $[M+H]^+$: 186.1277, found: 186.1282.

The spectral data were in accordance with those reported in the literature.[6]

3-(*p*-Tolyl)isoquinoline (2l)



GP was followed using **1l** (0.2 mmol, 41.2 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 9/1) yielded **2l** (29.8 mg, 68%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.33. (s, 1H), 8.07-8.01 (m, 3H), 7.97 (d, J = 8.2 Hz, 1H), 7.85 (d, J = 8.2 Hz, 1H), 7.73-7.62 (m, 1H), 7.60-7.52 (m, 1H), 7.33 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H)

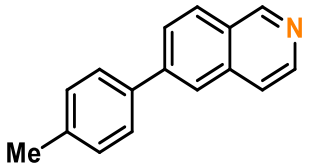
^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 151.3, 138.4, 136.7, 136.7, 130.5, 129.5, 129.5, 127.6, 127.5, 126.8, 126.8, 116.0, 21.3

IR (ATR): 3053, 2969, 2099, 1547, 1514, 1367, 1160, 1033, 972, 742 cm^{-1}.

HR-MS (ESI) $C_{16}H_{14}N$ $[M+H]^+$: 220.1121, found: 220.1135.

The spectral data were in accordance with those reported in the literature.[7]

6-(p-Tolyl)isoquinoline (2m)



GP was followed using **1m** (0.2 mmol, 41.2 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 5/1) yielded **2m** (20.6 mg, 47%) as a colorless oil.

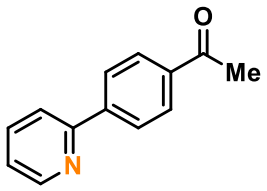
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.33. (s, 1H), 8.52 (d, J = 5.7 Hz, 1H), 8.24 (d, J = 1.8 Hz, 1H), 8.20-8.18 (m, 1H), 8.01 (dd, J = 8.6 Hz, J = 1.8 Hz, 1H), 7.87 (d, J = 5.7 Hz, 1H), 7.76 (d, J = 7.8 Hz, 2H), 7.36 (d, J = 7.8 Hz, 2H), 2.38 (s, 3H)

^{13}C NMR (100 MHz, DMSO-d_6) δ 152.1, 143.3, 141.79, 141.78, 137.9, 136.3, 135.7, 129.8, 128.3, 127.2, 126.6, 123.3, 120.6, 20.8

IR (ATR): 3023, 2921, 2853, 1732, 1625, 1488, 1382, 947, 856, 803 cm^{-1}.

HR-MS (ESI) $C_{16}H_{14}N$ $[M+H]^+$: 220.1121, found: 220.1118.

1-(4-(Pyridin-2-yl)phenyl)ethan-1-one (2n)



GP was followed using **1n** (0.2 mmol, 37.2 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2n** (28.4 mg, 72%) as a white solid.

M. p. 103-105 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J =4.8 Hz, 1H), 8.12-8.03 (m, 4H), 7.82-7.76 (m, 2H), 7.33-7.26 (m, 1H), 2.64 (s, 3H)

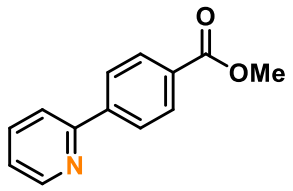
^{13}C NMR (100 MHz, $CDCl_3$) δ 197.8, 156.0, 149.9, 143.5, 137.3, 137.0, 128.8, 127.0, 122.9, 121.0, 26.8

IR (ATR): 3048, 2920, 2011, 1675, 1583, 1399, 1263, 1112, 987, 957 cm^{-1}.

HR-MS (ESI) $C_{13}H_{12}NO$ $[M+H]^+$: 198.0913, found: 198.0917.

The spectral data were in accordance with those reported in the literature.[8]

Methyl 4-(pyridin-2-yl)benzoate (2o)



GP was followed using **1o** (0.2 mmol, 40.4 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2o** (33.2 mg, 78%) as an off-white solid.

M. p. 60-62 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 4.8 Hz, 1H), 8.18-8.03 (m, 4H), 7.82-7.70 (m, 2H), 7.31-7.27 (m, 1H), 3.94 (s, 3H)

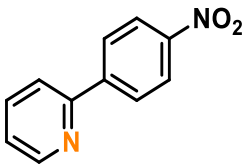
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.9, 156.2, 149.8, 143.4, 136.9, 130.3, 130.0, 126.8, 122.9, 121.0, 52.2

IR (ATR): 2942, 2845, 2102, 1705, 1604, 1434, 1317, 1182, 1012, 868 cm^{-1}.

HR-MS (ESI) $C_{13}H_{12}NO_2$ $[M+H]^+$: 214.0863, found: 214.0867.

The spectral data were in accordance with those reported in the literature.[9]

2-(4-Nitrophenyl)pyridine (2p)



GP was followed using **1p** (0.2 mmol, 37.8 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 20/1 to 15/1) yielded **2p** (13.4 mg, 34%) as a white solid.

M. p. 121-123 °C

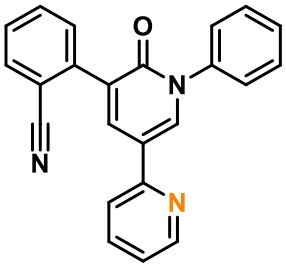
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, J =4.8 Hz, 1H), 8.37-8.31 (m, 2H), 8.23-8.13 (m, 2H), 7.87-7.79 (m, 2H), 7.64 (ddd, J = 6.8, 4.8, 2.2 Hz, 1H)

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 150.1, 148.1, 145.2, 137.1, 127.7, 124.0, 123.5, 121.2

IR (ATR): 2920, 2851, 1597, 1597, 1567, 1465, 1404, 1343, 989, 855 cm^{-1}.

HR-MS (ESI) $C_{11}H_9N_2O_2$ $[M+H]^+$: 201.0659, found: 201.0663.

2-(6'-Oxo-1'-phenyl-1',6'-dihydro-[2,3'-bipyridin]-5'-yl)benzonitrile (2q)



GP was followed using **1q** (0.2 mmol, 41.2 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 2/1) yielded **2q** (21.0 mg, 30%) as a yellow solid.

M. p. 176-178 °C

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.59 (d, J = 4.7 Hz, 1H), 8.53 (d, J = 2.5 Hz, 1H), 8.48 (d, J = 2.5 Hz, 1H), 8.01 (d, J = 7.6 Hz, 1H), 7.93 (d, J = 7.6 Hz, 1H), 7.84 (td, J = 7.6, 1.8 Hz, 1H), 7.81-7.75 (m, 1H), 7.74-7.70 (m, 1H), 7.63-7.55 (m, 5H), 7.53-7.46 (m, 1H), 7.30 (td, J = 7.6, 1.8 Hz, 1H)

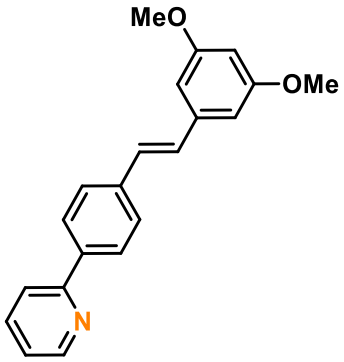
^{13}C NMR (100 MHz, DMSO-d_6) δ 159.4, 152.2, 149.2, 140.8, 140.4, 138.6, 138.3, 137.3, 133.0, 132.9, 130.9, 129.16 (2C), 128.6, 128.5, 126.82 (2C), 122.14, 122.13, 119.1, 118.2, 117.1, 112.0

IR (ATR): 3065, 2217, 1979, 1621, 1585, 1547, 1474, 1316, 1274, 875, 784 cm^{-1}.

HR-MS (ESI) $C_{23}H_{16}N_3O$ $[M+H]^+$: 350.1293, found: 350.1295.

The spectral data were in accordance with those reported in the literature.[10]

(*E*)-2-(4-(3,5-Dimethoxystyryl)phenyl)pyridine (2r)



GP was followed using **1r** (0.2 mmol, 61.3 mg), $TMSN_3$ (0.2 mmol, 26.3 µL) **[Mn-1]** (10 mol%, 9.7 mg), Na_2CO_3 (0.2 mmol, 21.2 mg), activated 4Å molecular sieves (25 beads), AcOH (1.0 mL) and MeOH (5.0 mL). Purification by column chromatography on silica gel (*n*-hexane/EtOAc: 2/1) yielded **2r** (37.0 mg, 58%) as a yellow oil.

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.69 (d, J = 4.2 Hz, 1H), 8.12 (d, J = 8.1 Hz, 2H), 8.04 (d, J = 7.9 Hz, 1H), 7.99–7.91 (m, 1H), 7.73 (d, J = 8.1 Hz, 2H), 7.42-7.39 (m, 1H), 7.38-7.27 (m, 2H), 6.82 (d, J = 1.8 Hz, 2H), 6.45-6.43 (m, 1H), 3.79 (s, 6H)

^{13}C NMR (100 MHz, DMSO-d_6) δ 160.7, 155.0, 148.8, 138.9, 138.1, 138.0, 136.9, 129.4, 128.3, 127.0, 126.9, 122.8, 120.6, 104.6, 100.1, 55.2

IR (ATR): 3001, 2931, 2835, 1584, 1464, 1297, 1202, 1148, 1057, 961, 776 cm^{-1}.

HR-MS (ESI) $C_{21}H_{20}NO_2$ $[M+H]^+$: 318.1494, found: 318.1490.

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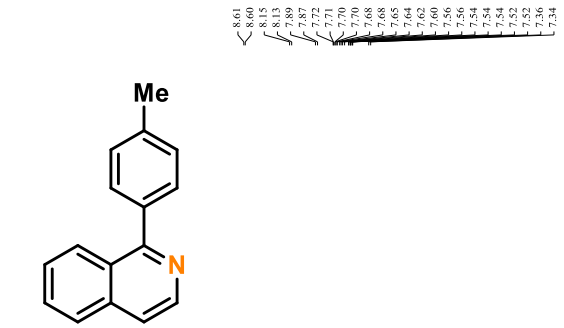
^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra



2a
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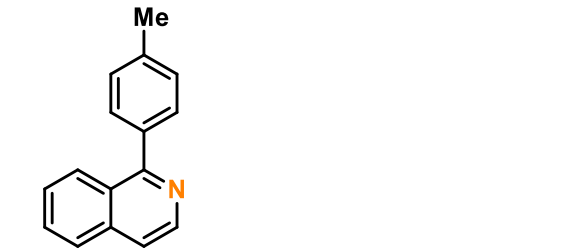
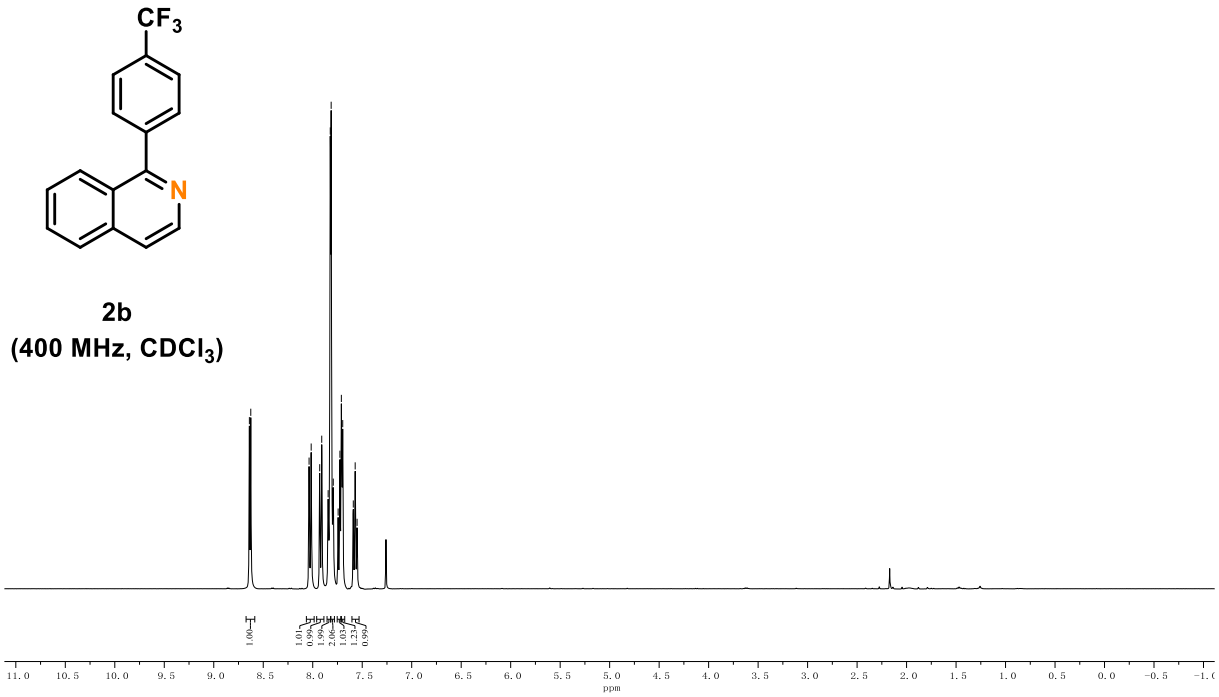


2a
(100 MHz, $CDCl_3$)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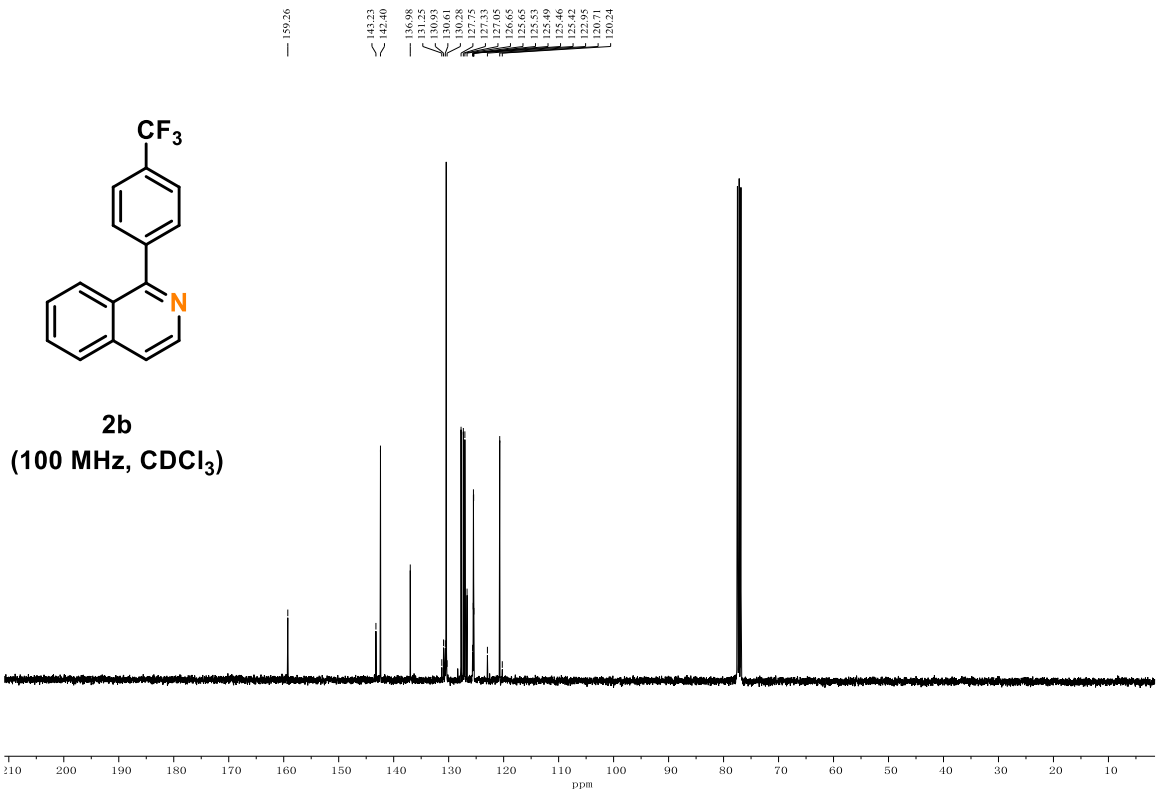
8.04
8.02
7.93
7.91
7.84
7.82
7.81
7.79
7.74
7.73
7.71
7.70
7.59
7.57
7.55
CF3
N
2b
(400 MHz, CDCl3)
1.00
1.01
0.99
1.99
2.08
1.04
1.23
0.99
ppm


159.26
143.23
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131.25
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130.28
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127.33
127.05
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125.65
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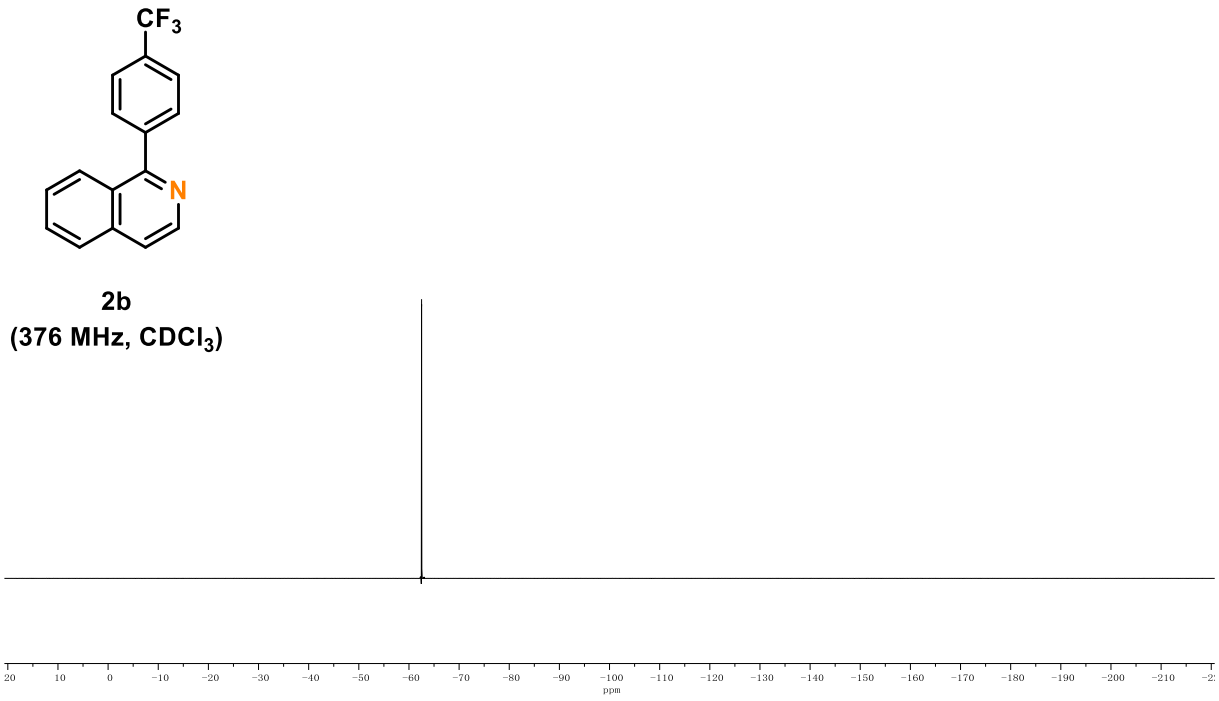
125.46
125.42
122.95
120.71
120.24
CF3
N
2b
(100 MHz, CDCl3)
ppm


-62.52
CF3
N
2b
(376 MHz, CDCl3)
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
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−100
−110
−120
−130
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−150
−160
−170
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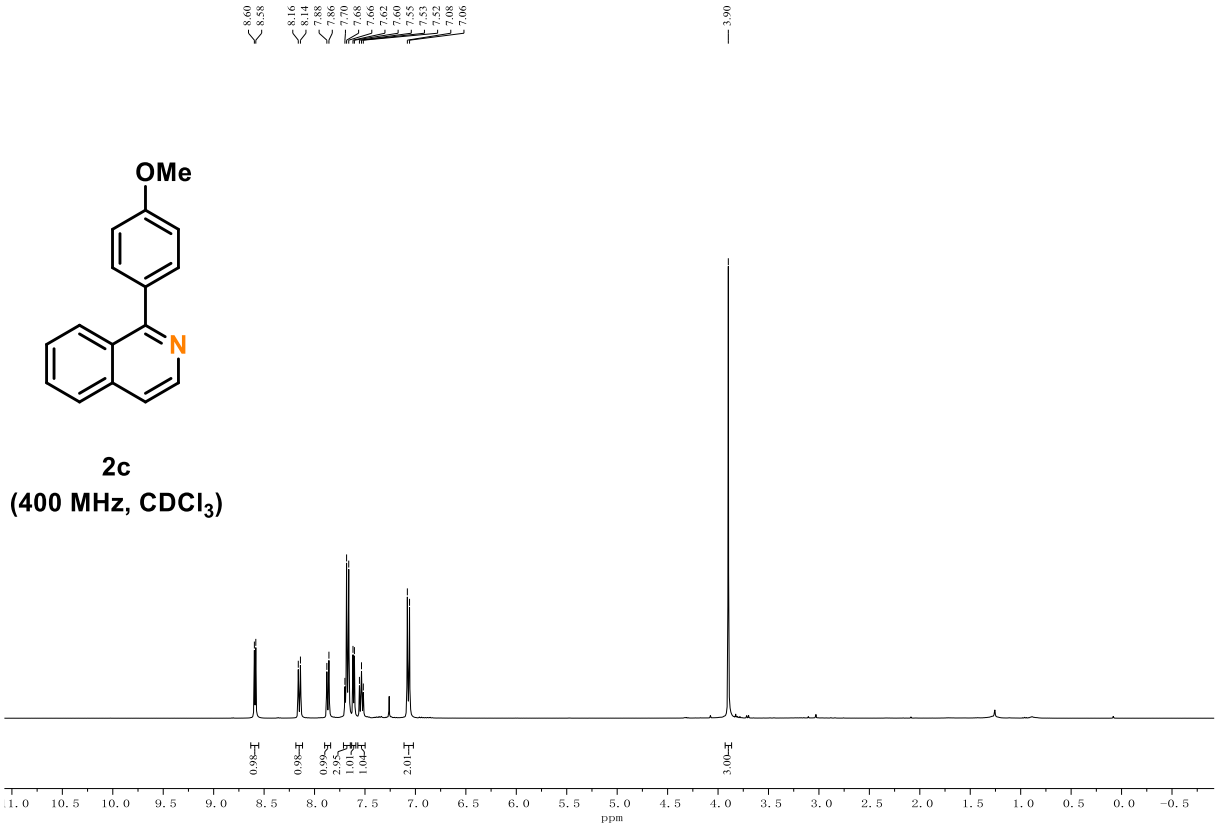
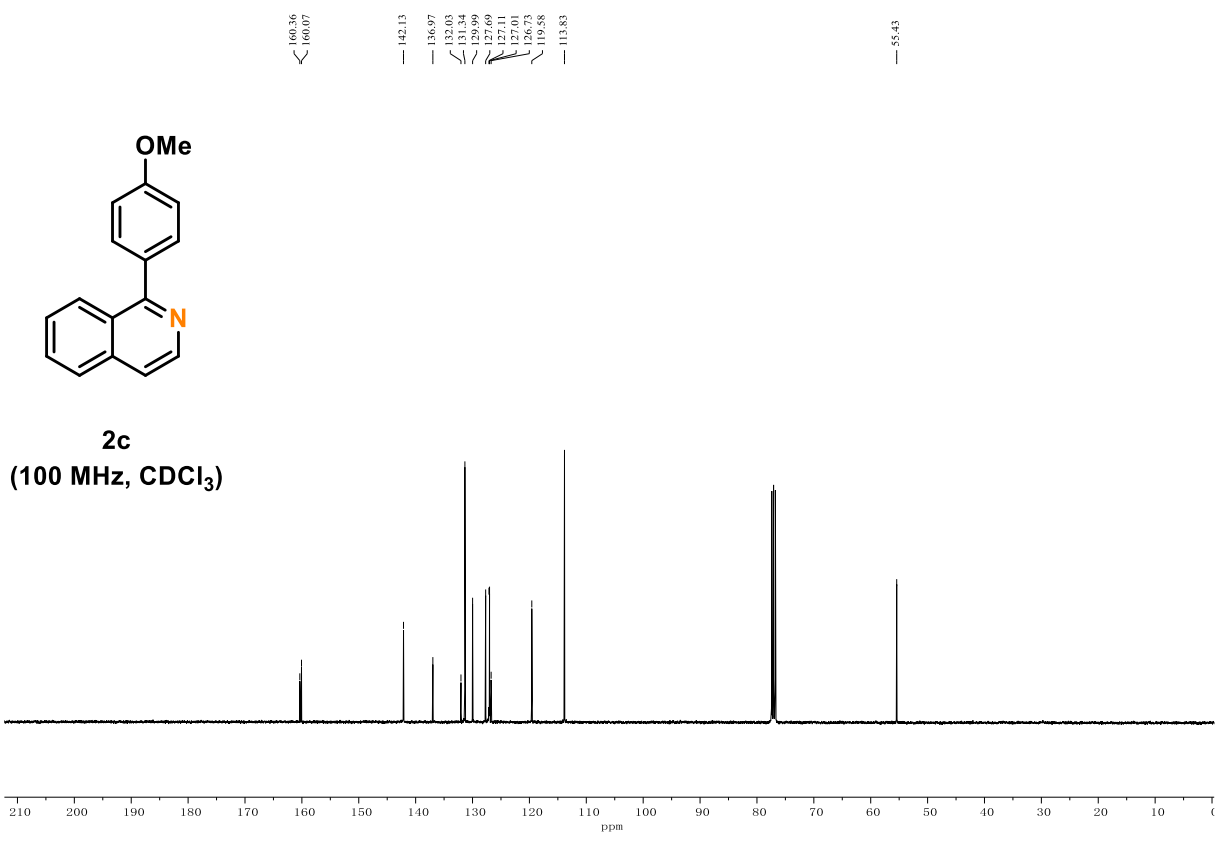
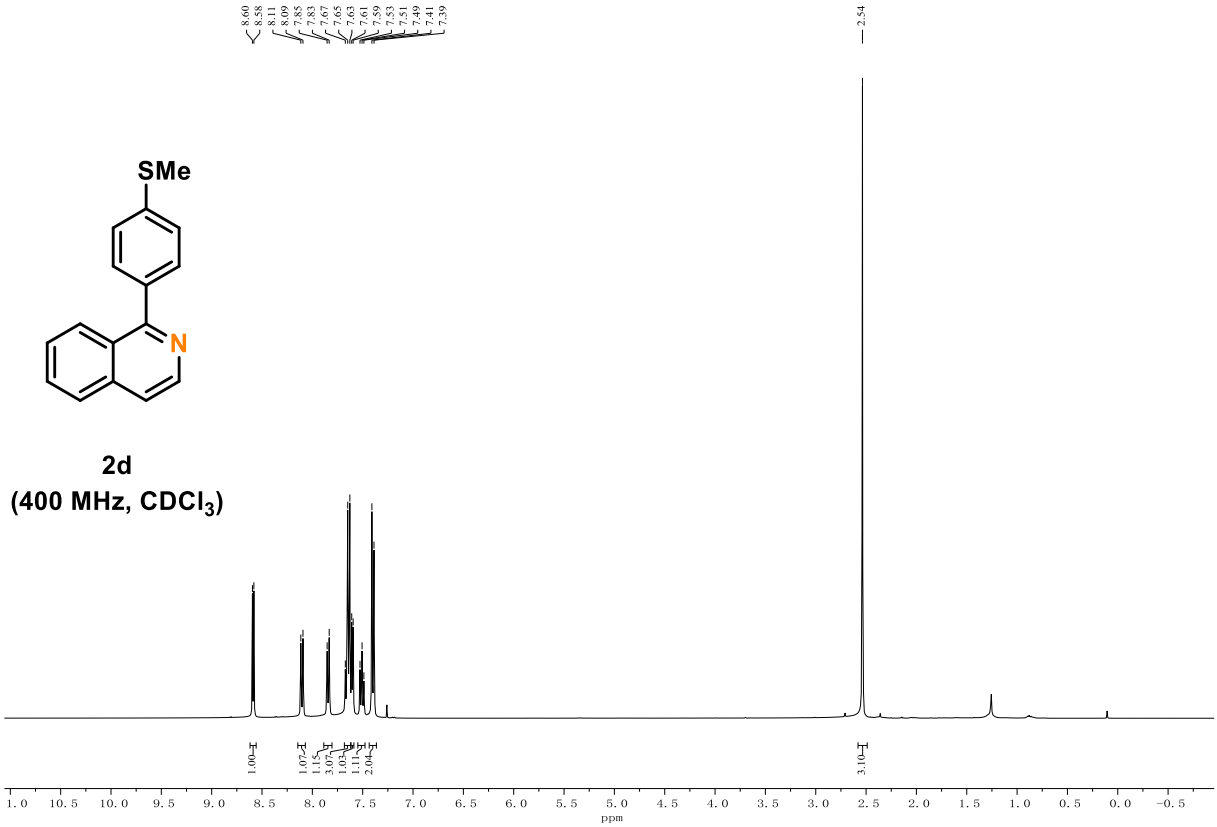
−200
−210
ppm



2c
(400 MHz, $CDCl_3$)



2c
(100 MHz, $CDCl_3$)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N
2d
(400 MHz, CDCl3)
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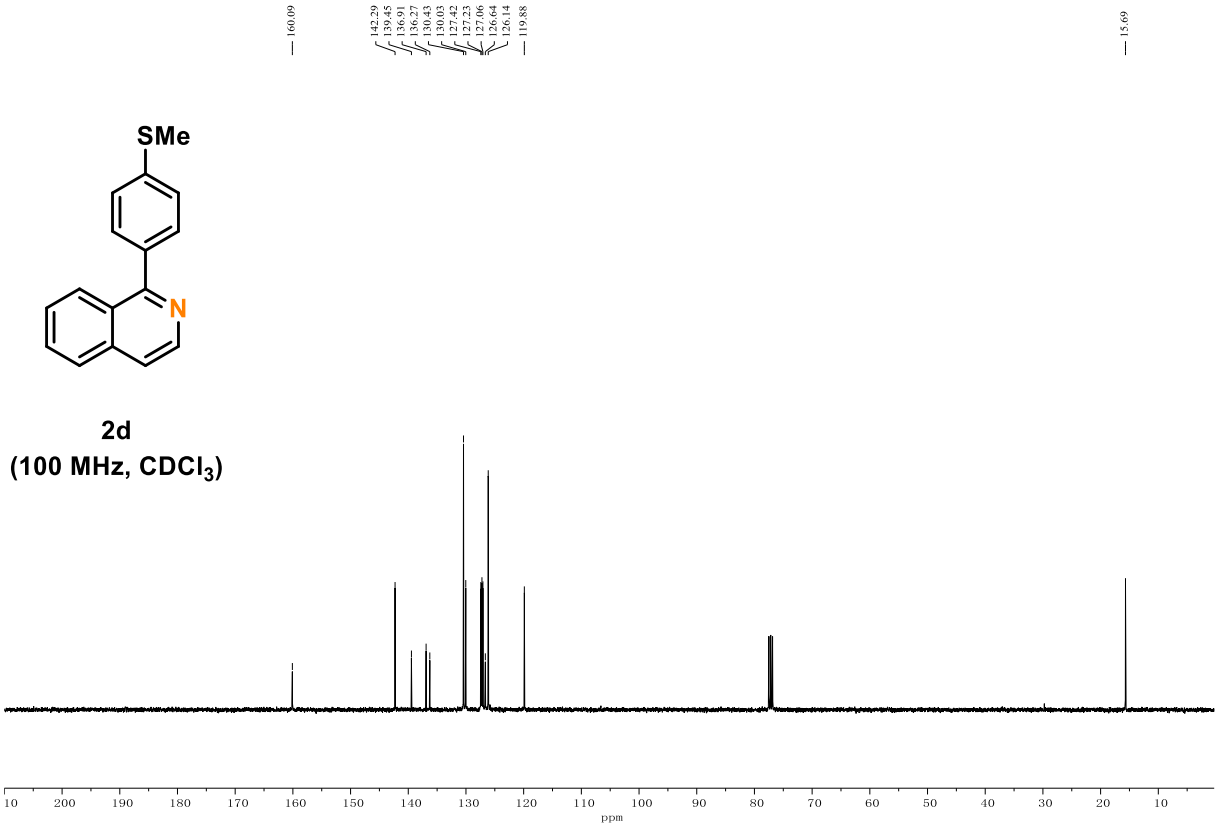
8.11
8.09
7.85
7.83
7.67
7.65
7.63
7.61
7.59
7.53
7.51
7.49
7.41
7.39
2.54
1.00
1.07
1.15
1.07
1.03
1.11
2.04
3.10
ppm


SMe
N
2d
(100 MHz, CDCl3)
160.09
142.29
139.45
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130.03
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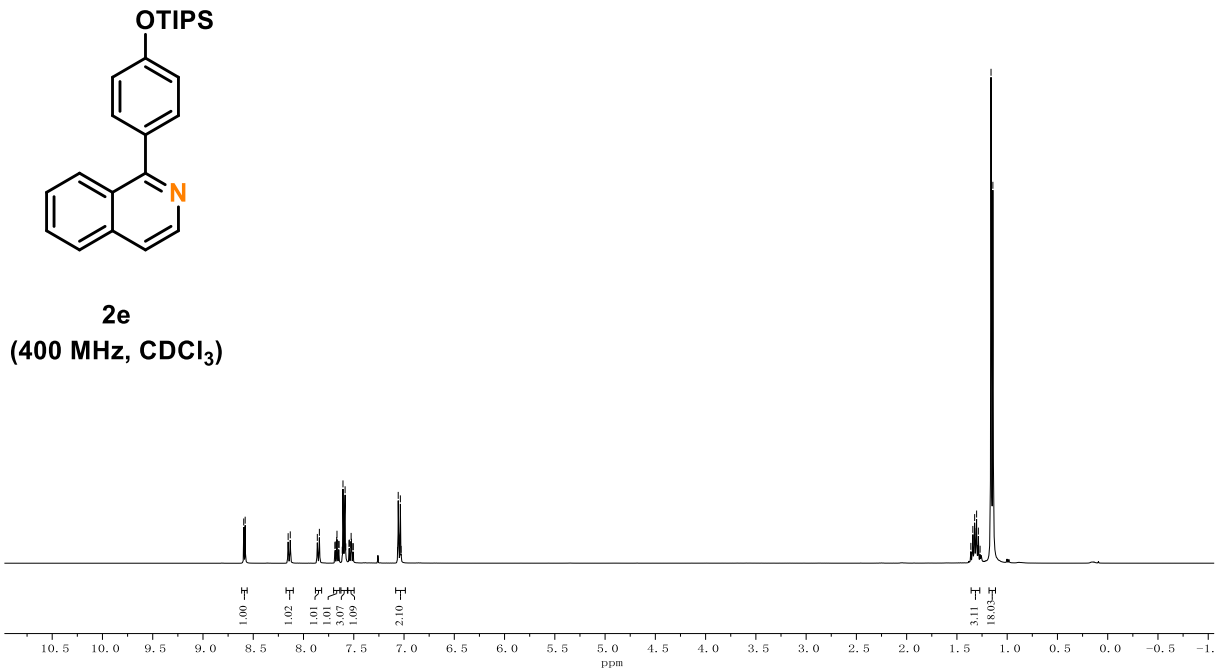
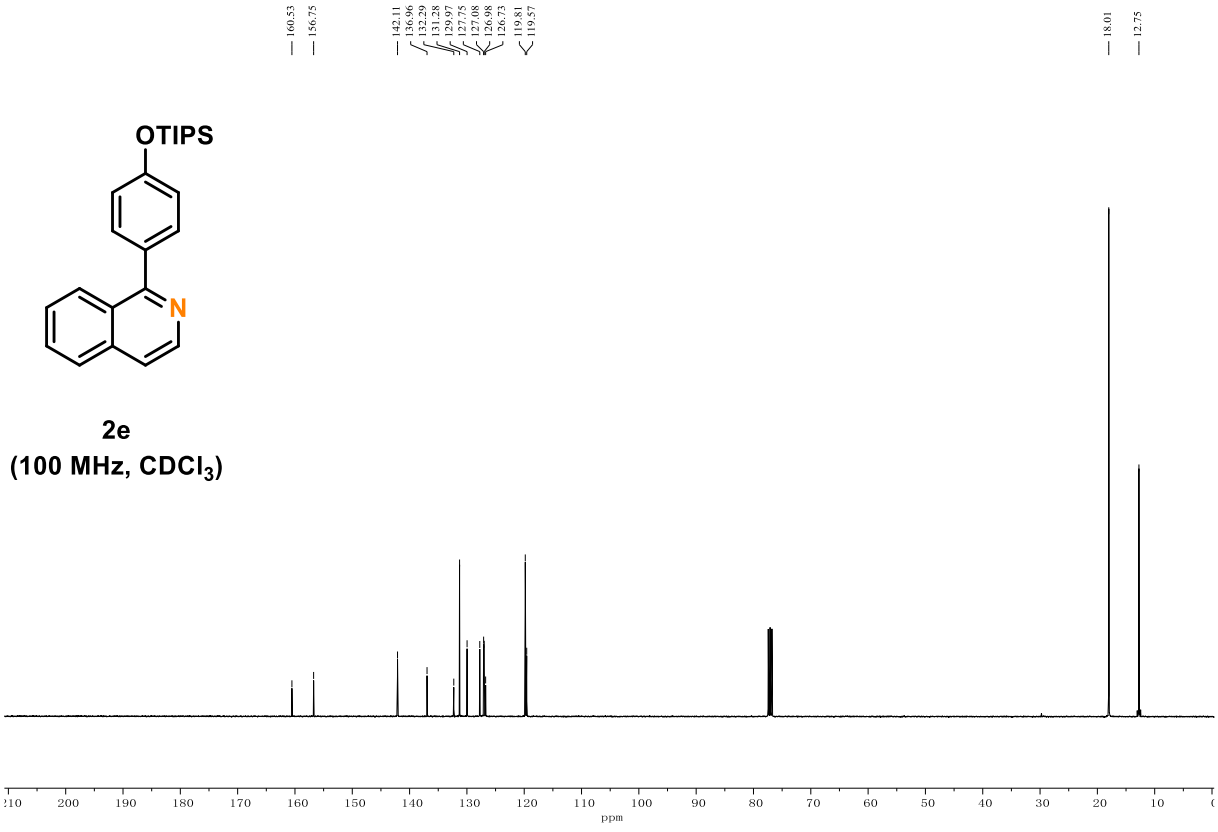
127.23
127.06
126.64
126.14
119.88
15.69
ppm


OTIPS
N
2e
(400 MHz, CDCl3)
ppm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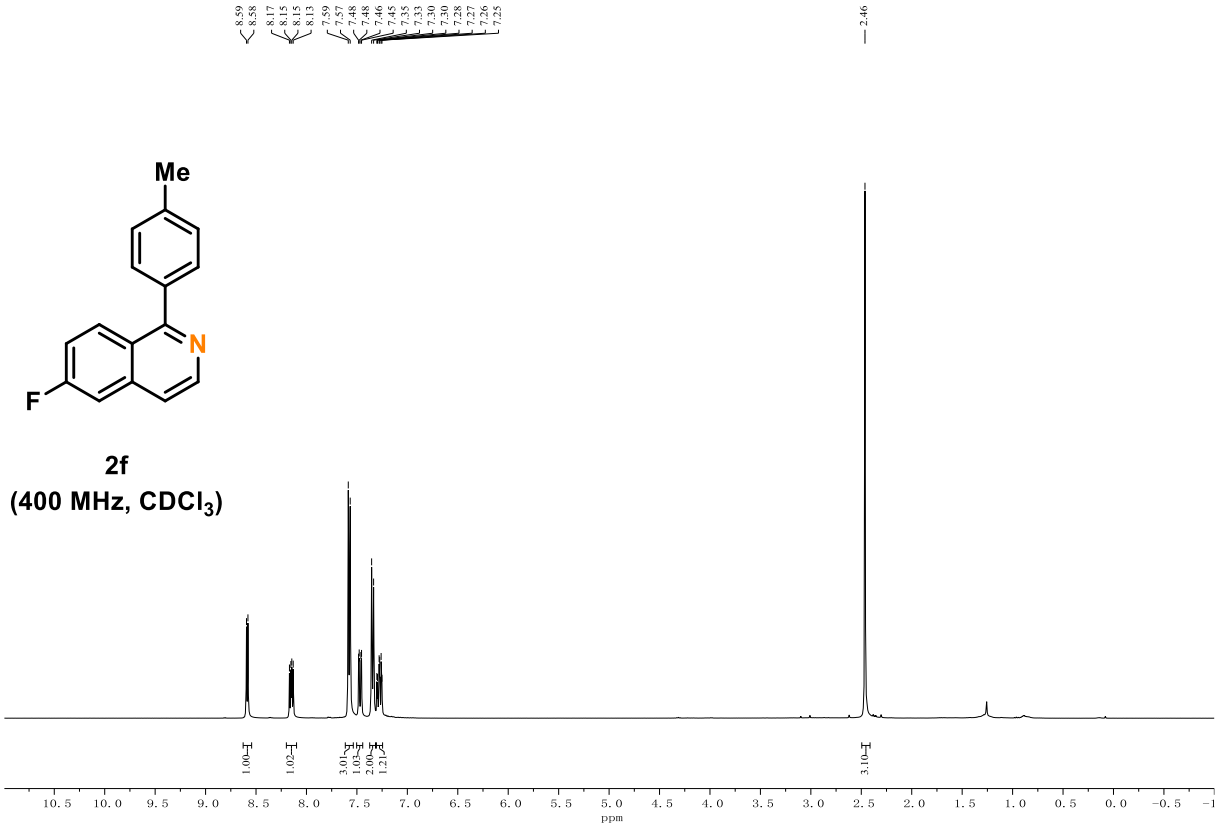
N
2e
(100 MHz, CDCl3)
ppm


Me
N
F
2f
(400 MHz, CDCl3)
8.59
8.58
8.17
8.15
8.15
8.13
7.59
7.57
7.48
7.48
7.46
7.45
7.35
7.33
7.30
7.30
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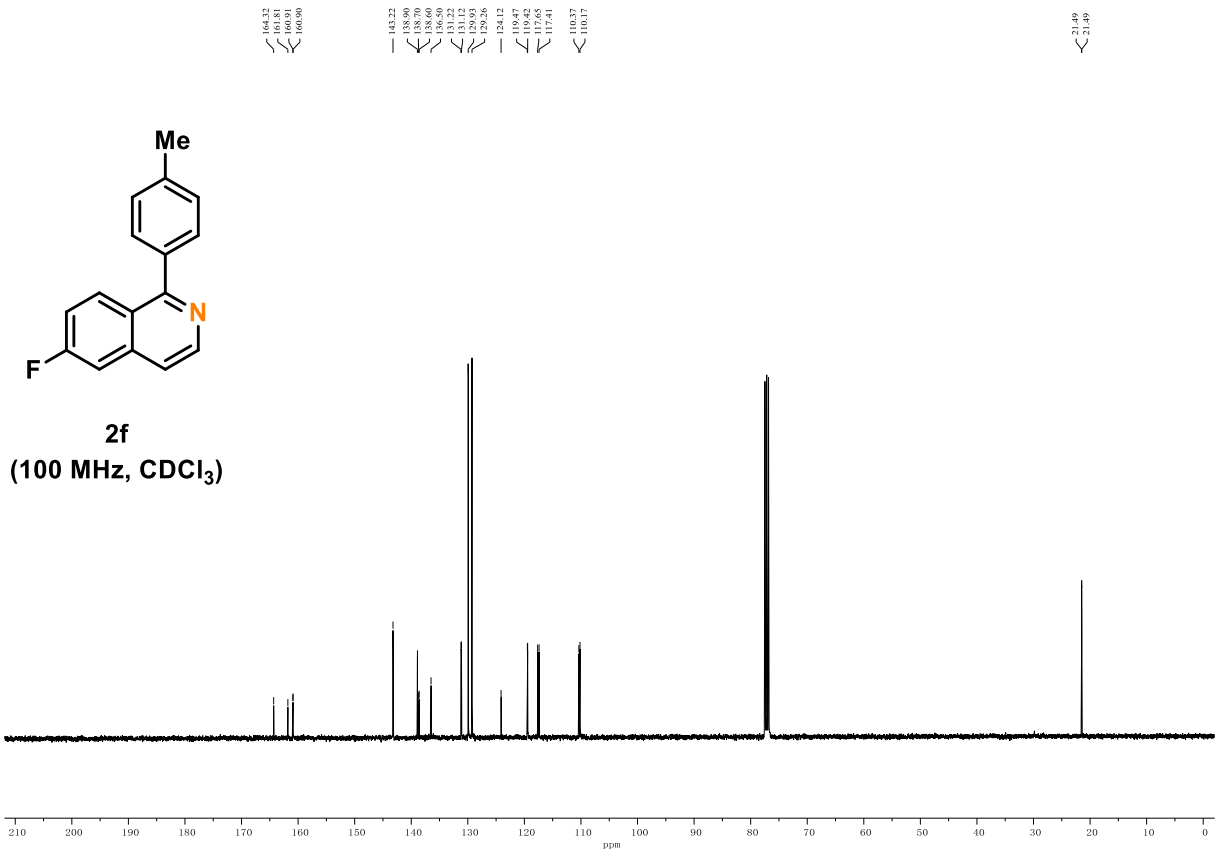
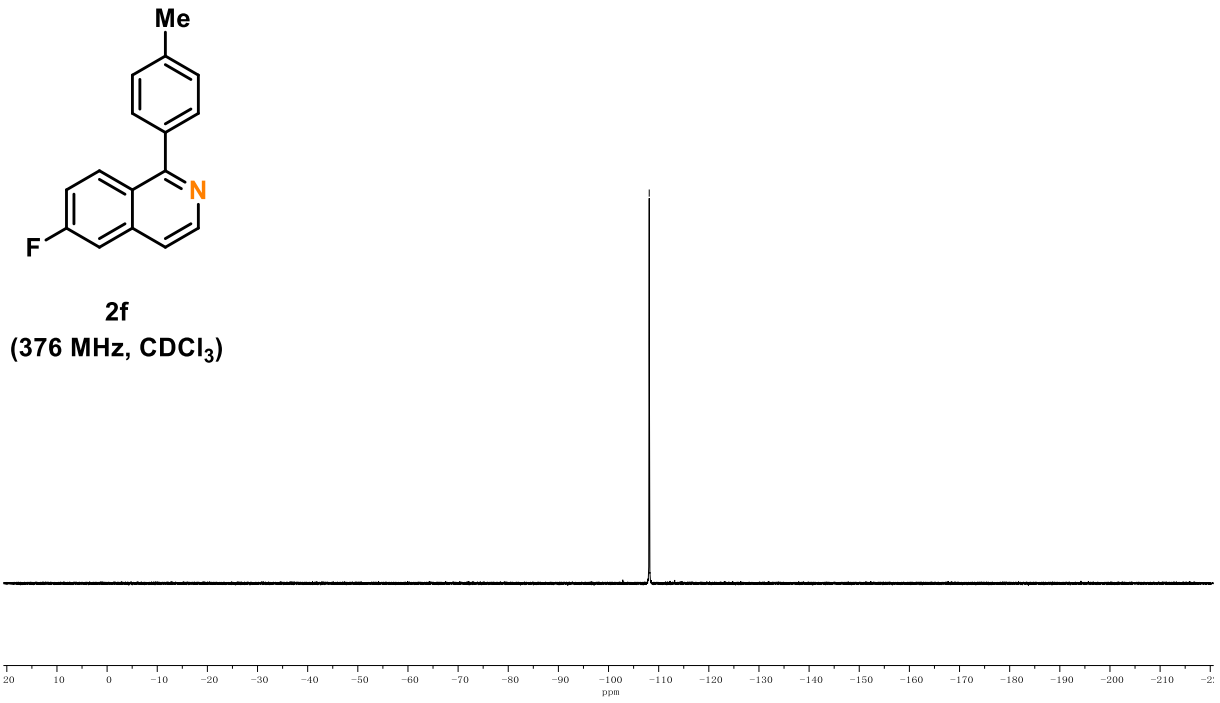
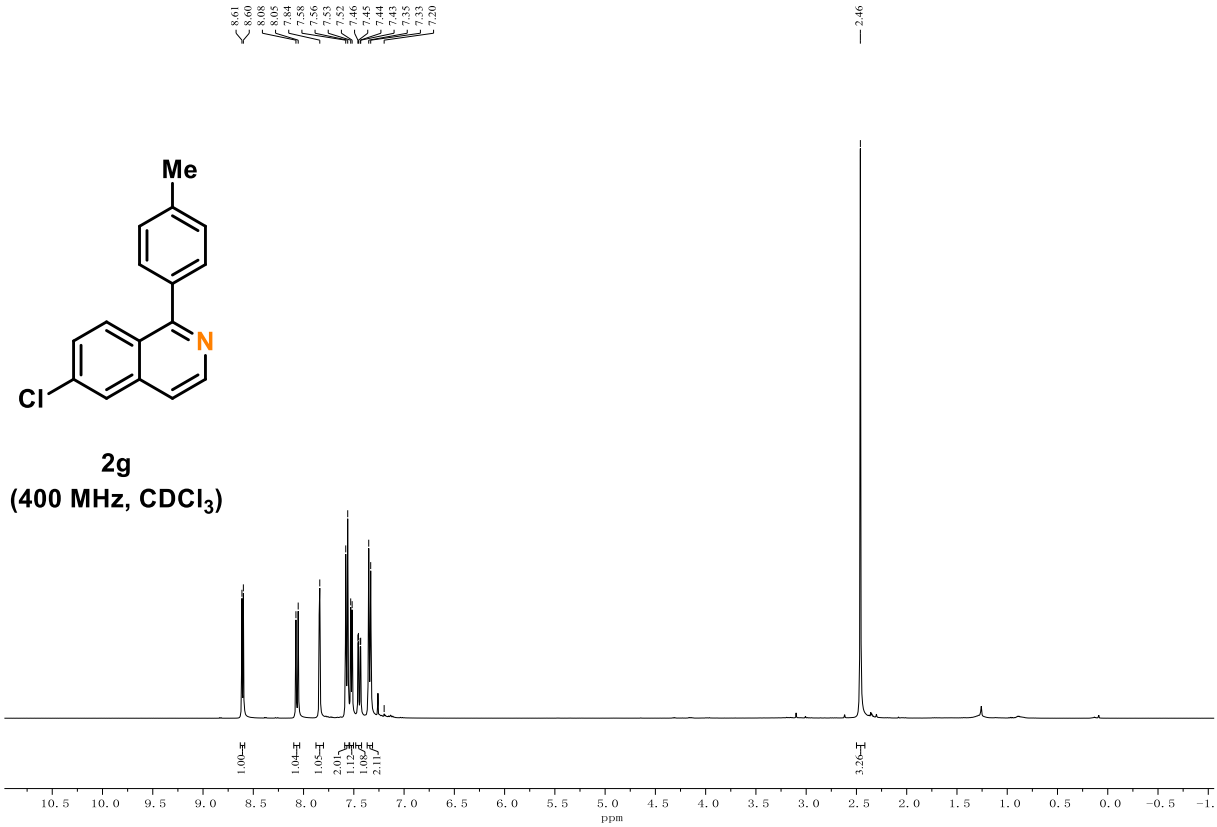
1.03
2.00
1.21
3.10
ppm


Me
N
F
2f
(100 MHz, CDCl3)
164.32
161.81
160.93
160.90
143.22
138.90
138.70
138.60
138.50
131.22
131.12
129.93
129.26
124.12
119.47
119.42
117.56
117.41
110.37
110.17
21.49
21.49
ppm

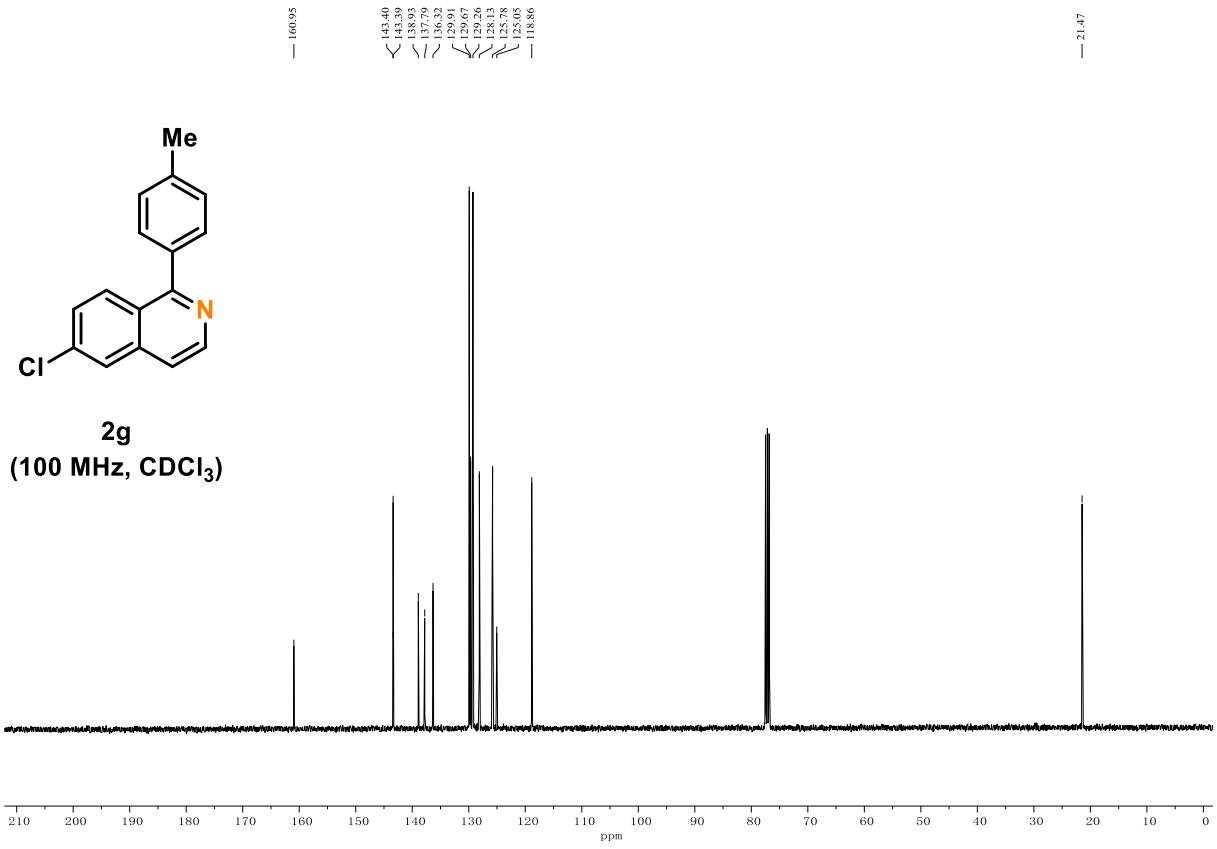


2f

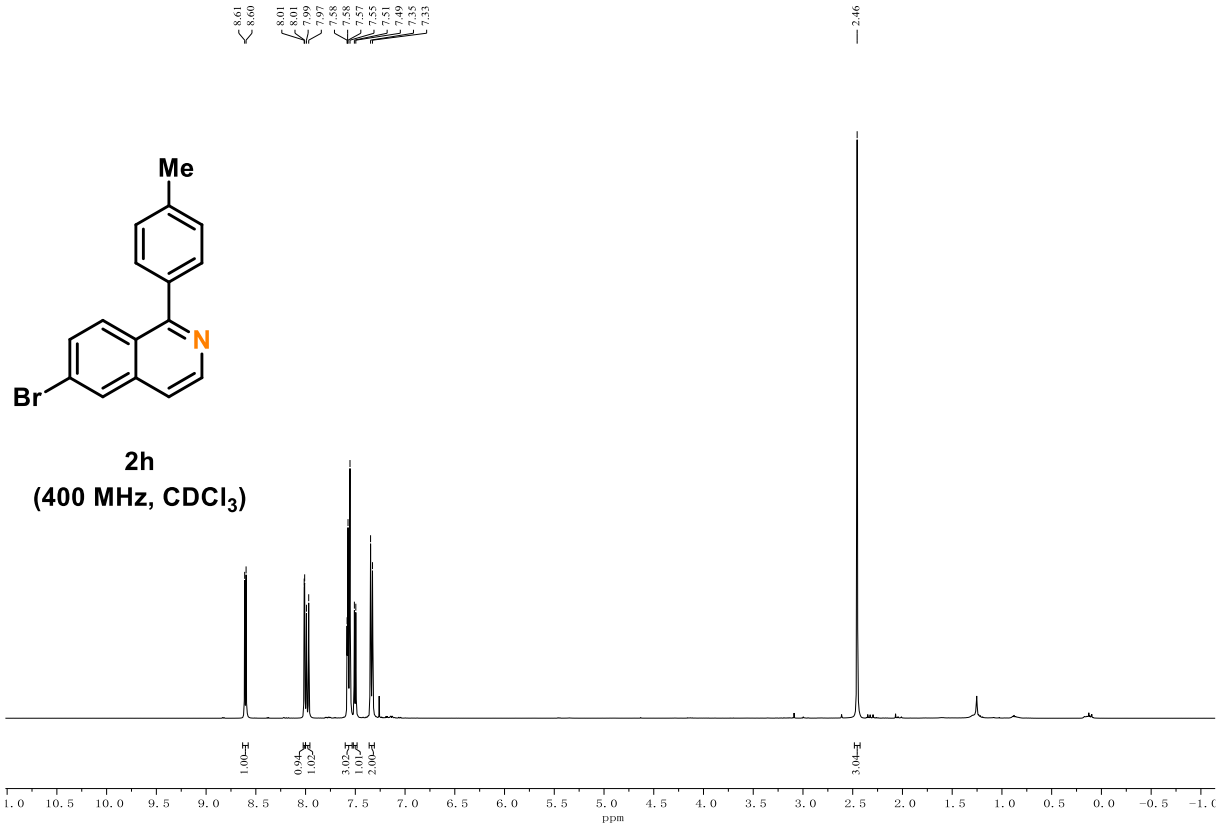
(376 MHz, $CDCl_3$)



2g
(400 MHz, $CDCl_3$)



2g
(100 MHz, $CDCl_3$)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7.97
7.58
7.58
7.57
7.55
7.51
7.49
7.35
7.33
2.46
Me
N
Br
2h
(400 MHz, CDCl3)
1.00
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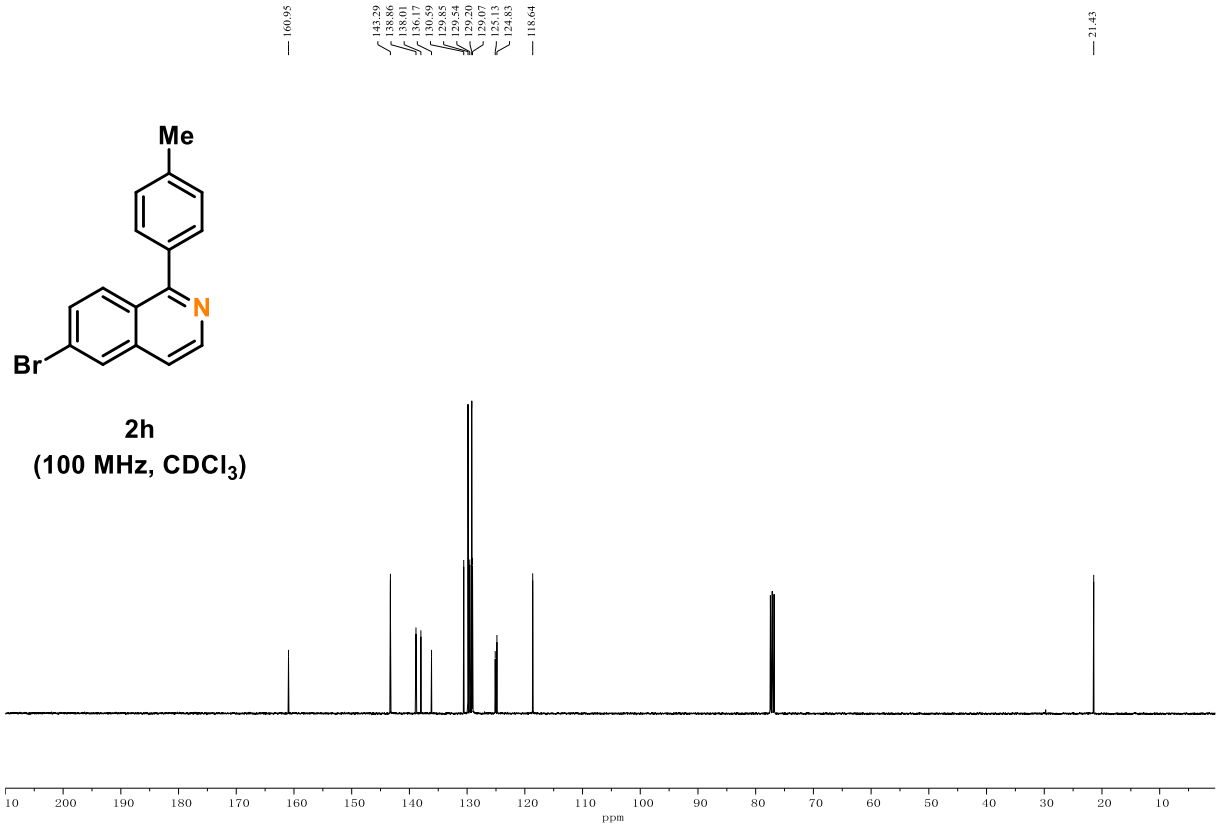
1.02
3.02
1.07
2.00
3.04
ppm


160.95
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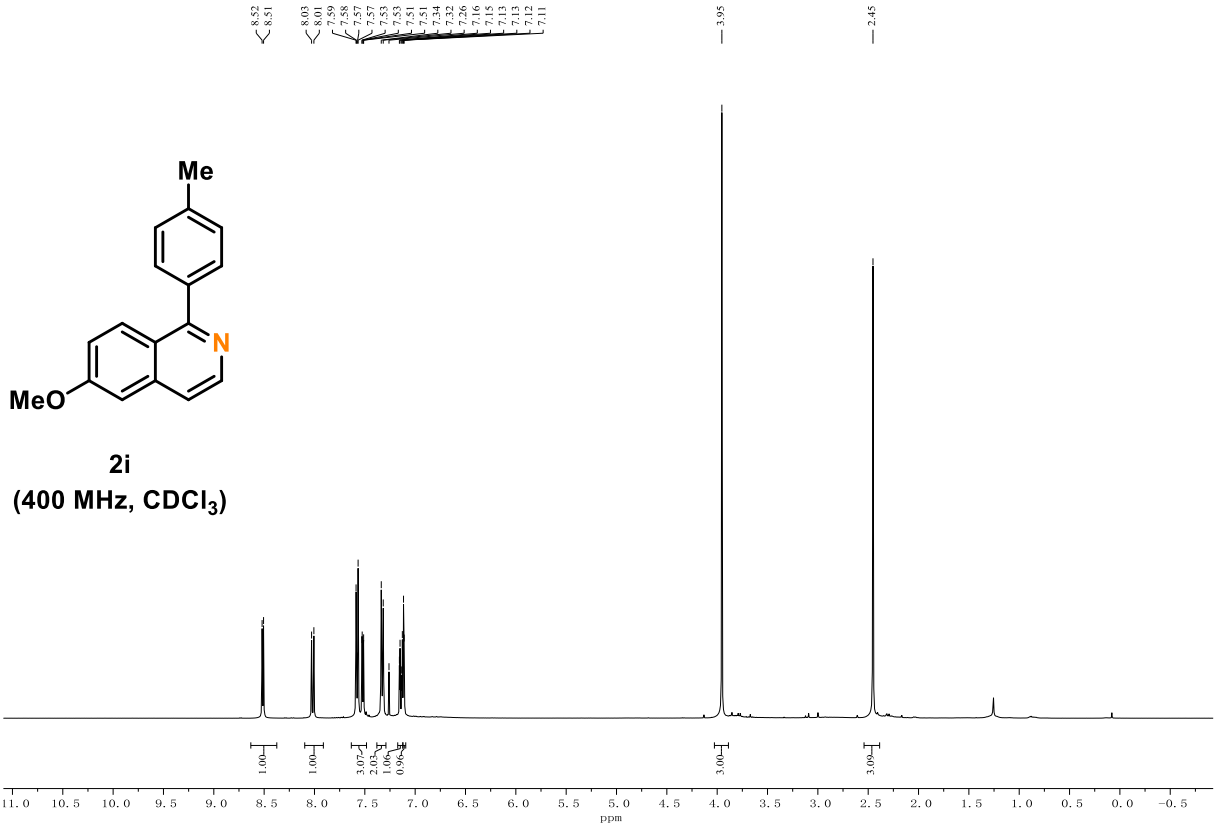
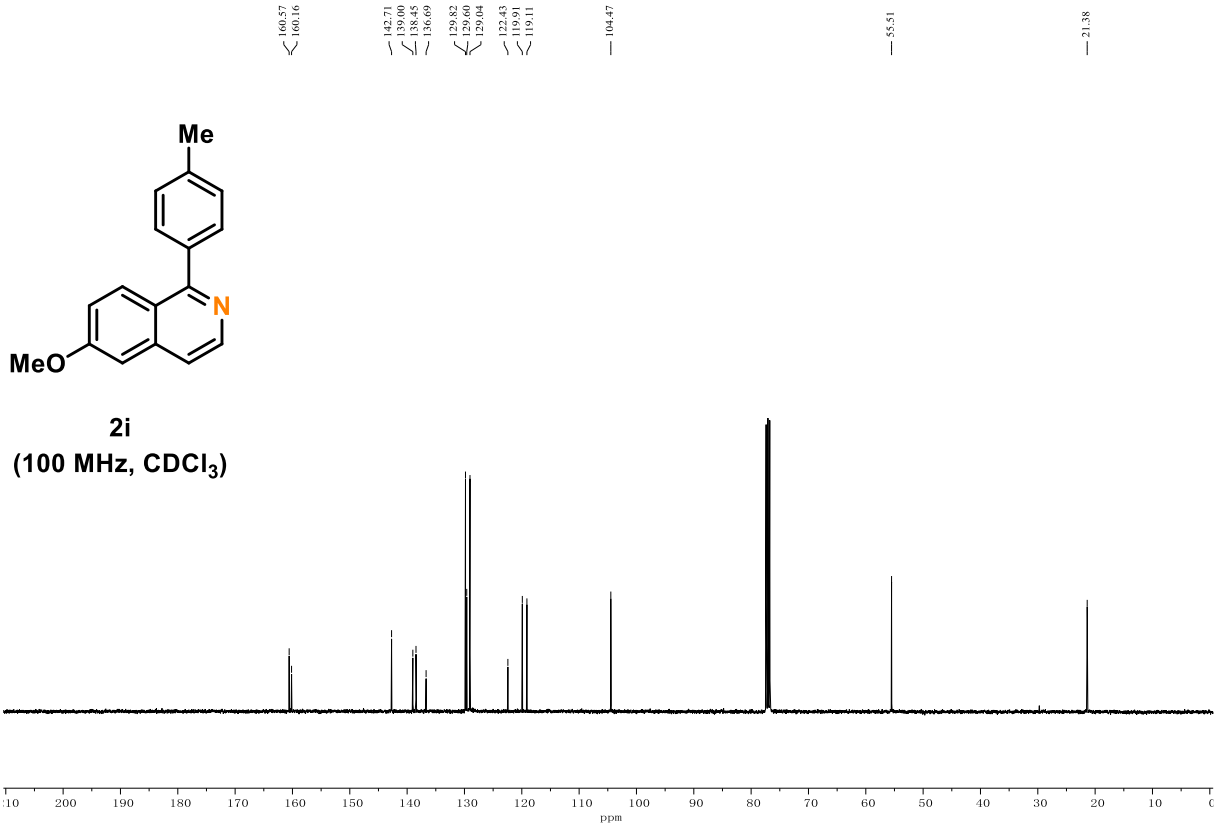
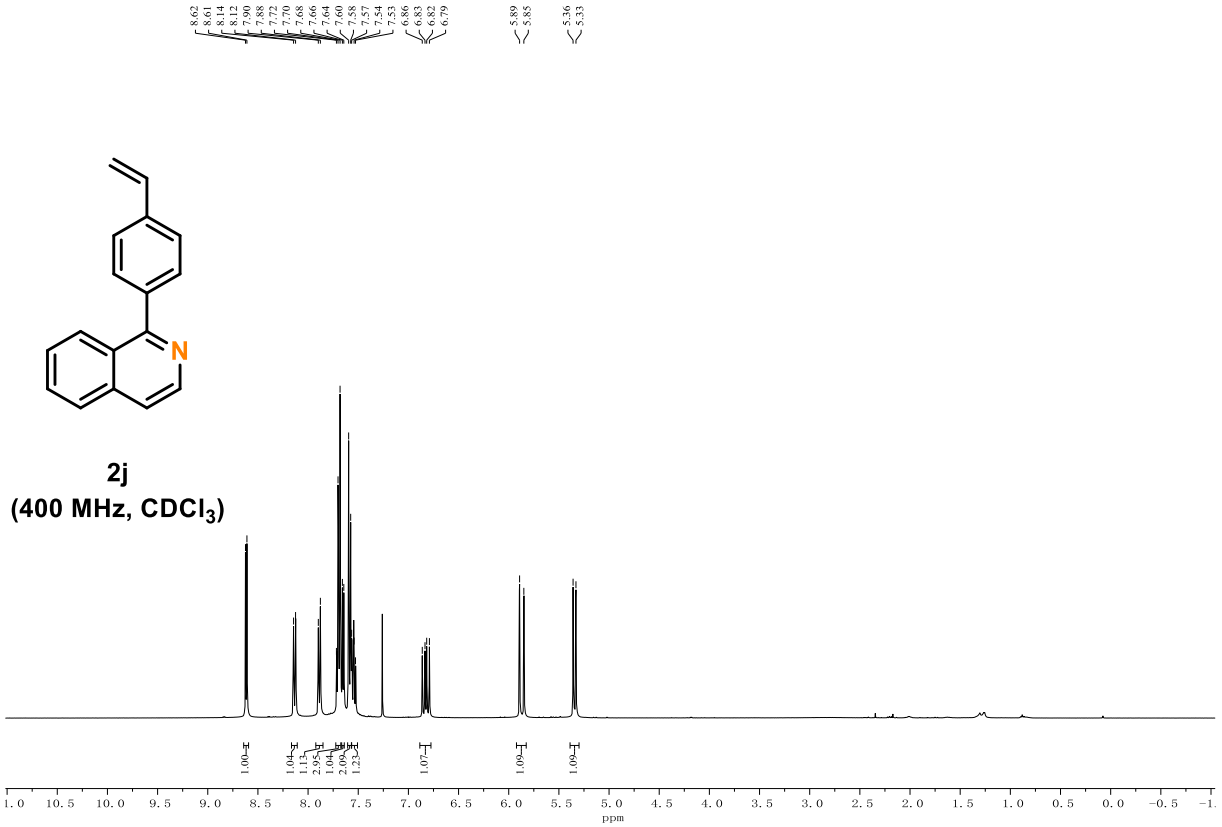
Me
N
Br
2h
(100 MHz, CDCl3)
ppm



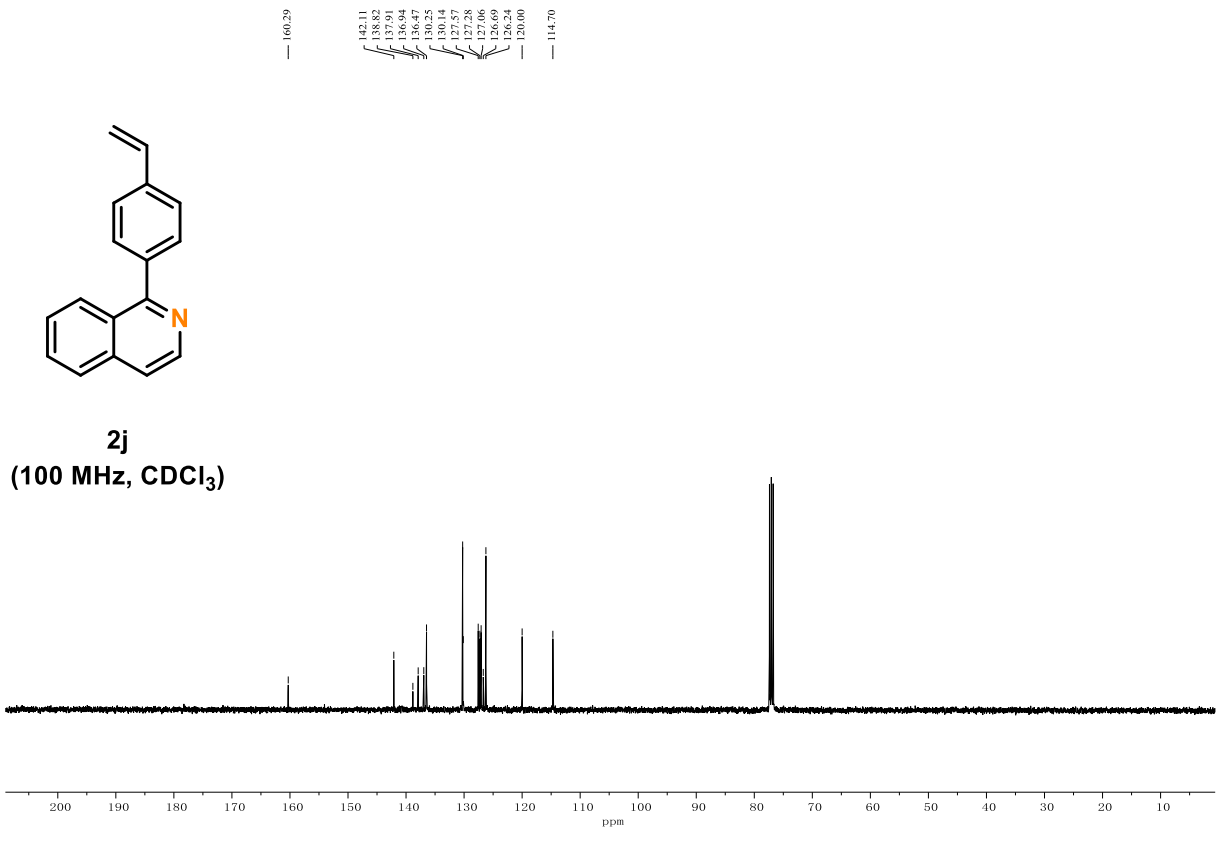
2i
(400 MHz, $CDCl_3$)



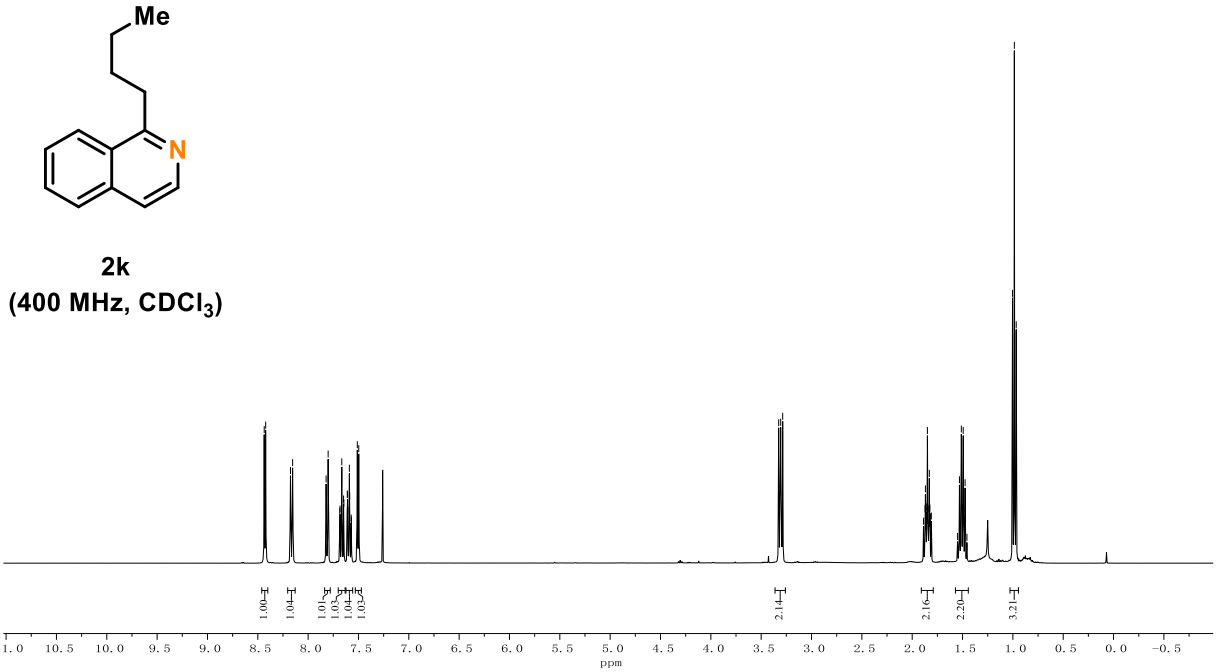
2i
(100 MHz, $CDCl_3$)

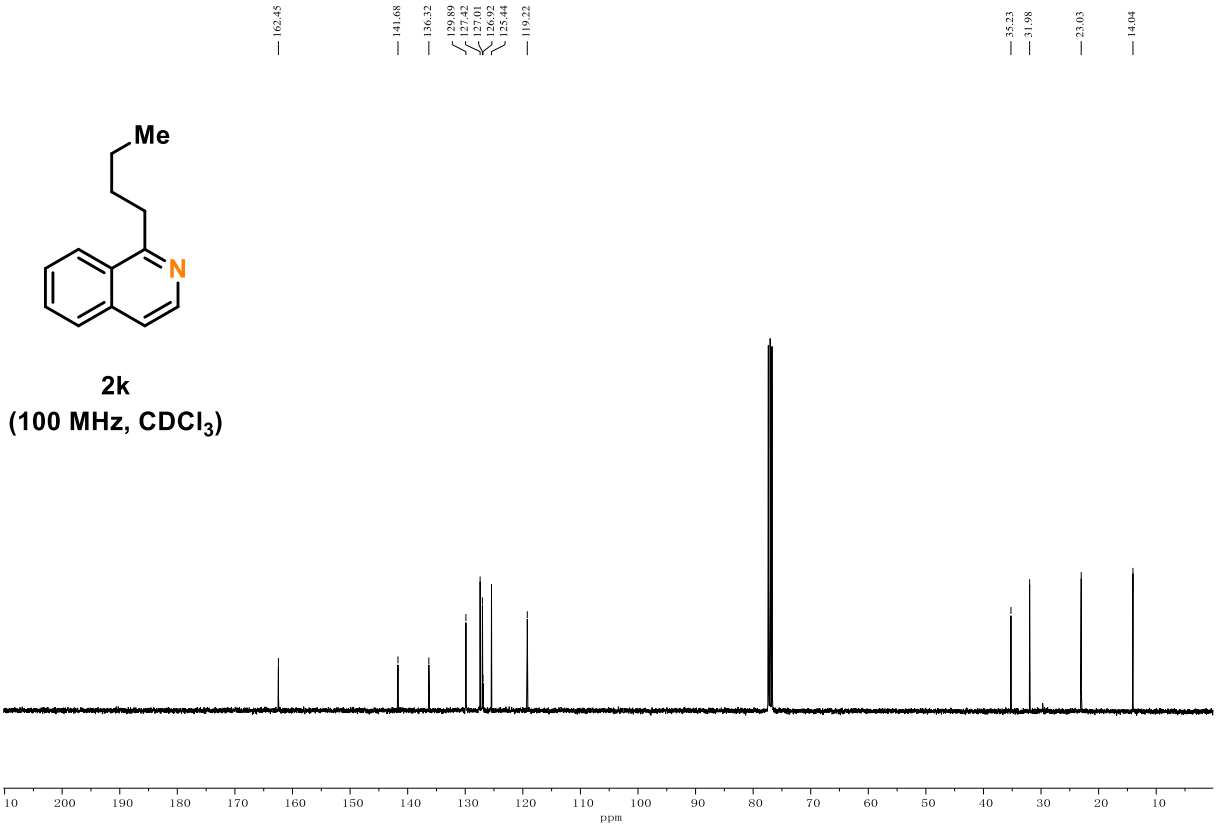


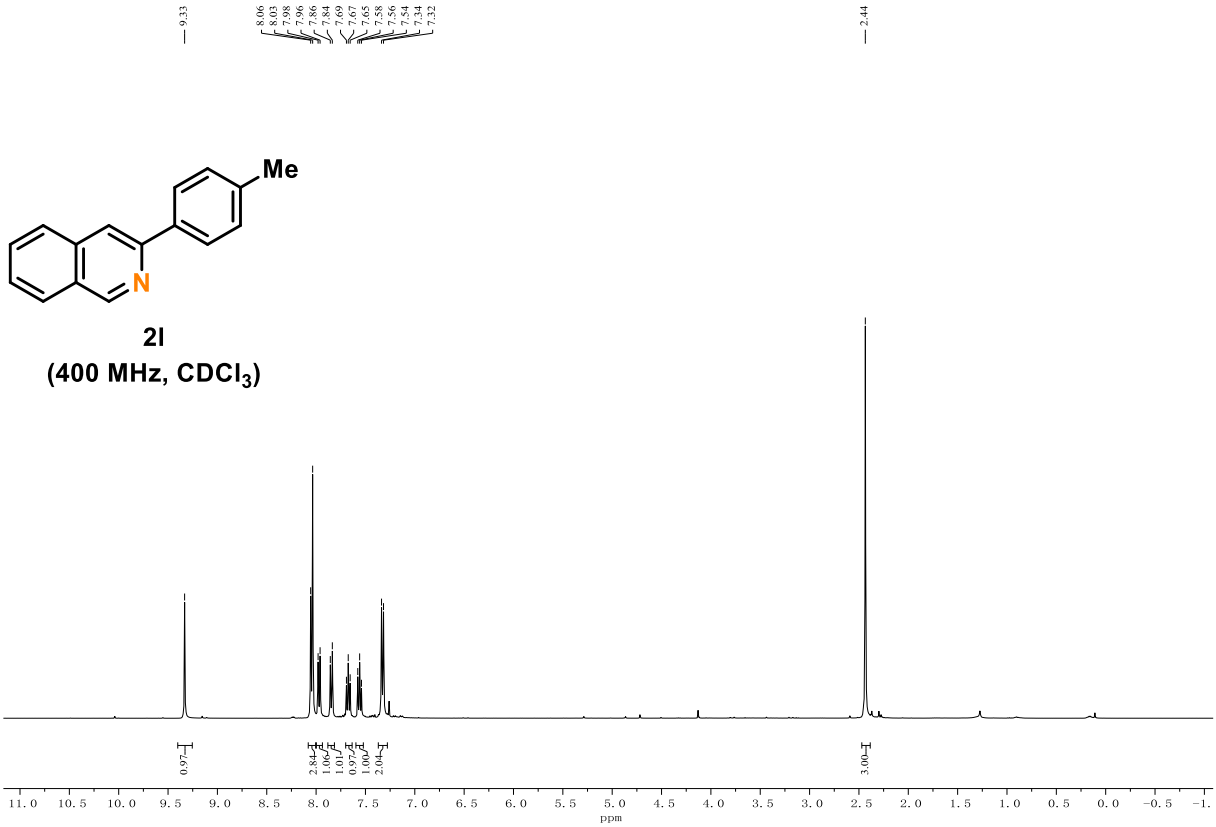
2j
(400 MHz, $CDCl_3$)



2j
(100 MHz, $CDCl_3$)

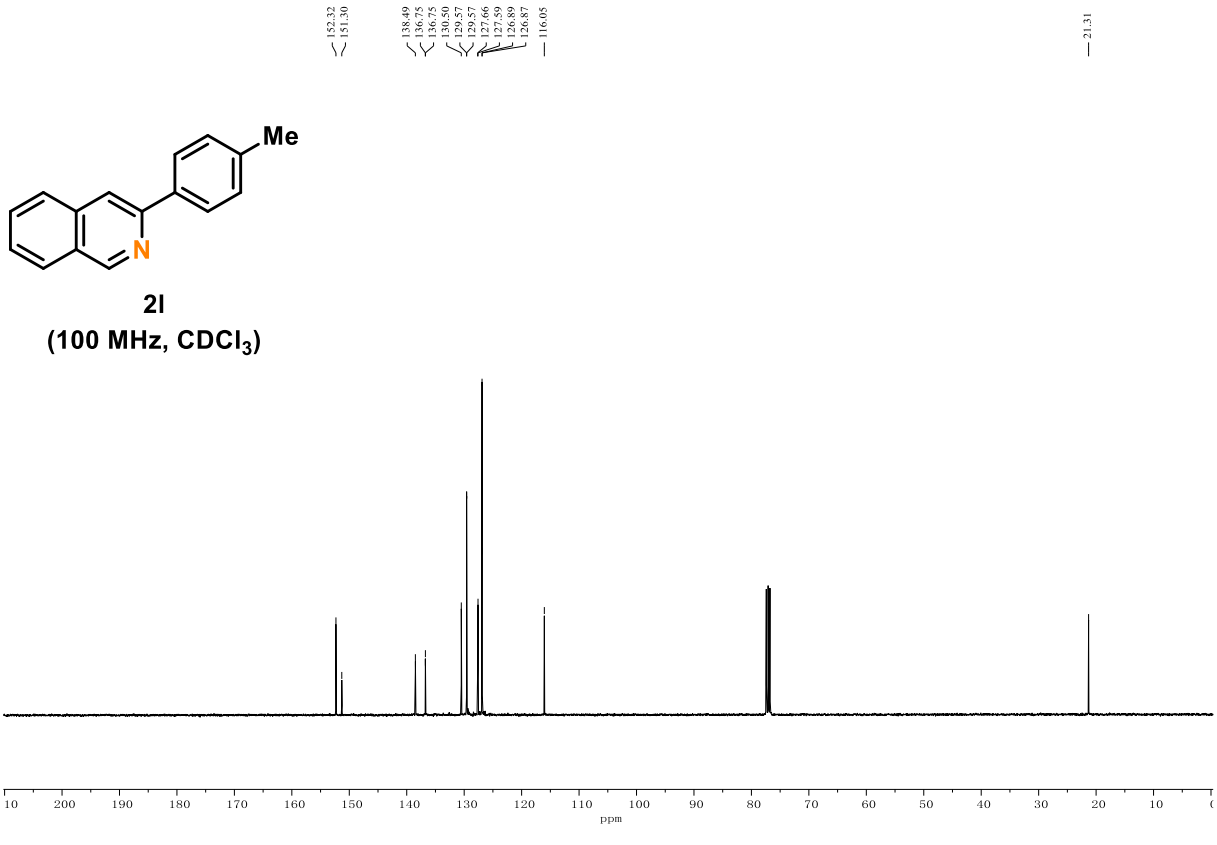

8.44
8.42
8.18
8.15
7.82
7.80
7.69
7.68
7.67
7.67
7.65
7.65
7.61
7.61
7.59
7.59
7.59
7.57
7.57
7.51
7.50
3.33
3.31
3.29
1.89
1.87
1.87
1.86
1.86
1.85
1.84
1.83
1.82
1.81
1.55
1.53
1.51
1.49
1.47
1.46
1.00
0.99
0.97
Me
N
2k
(400 MHz, CDCl3)
1.00
1.04
1.01
1.03
1.04
1.03
2.14
2.16
2.20
3.21
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
ppm


162.45
141.68
136.32
129.89
127.42
127.01
126.92
125.44
119.22
35.23
31.98
23.03
14.04
Me
N
2k
(100 MHz, CDCl3)
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



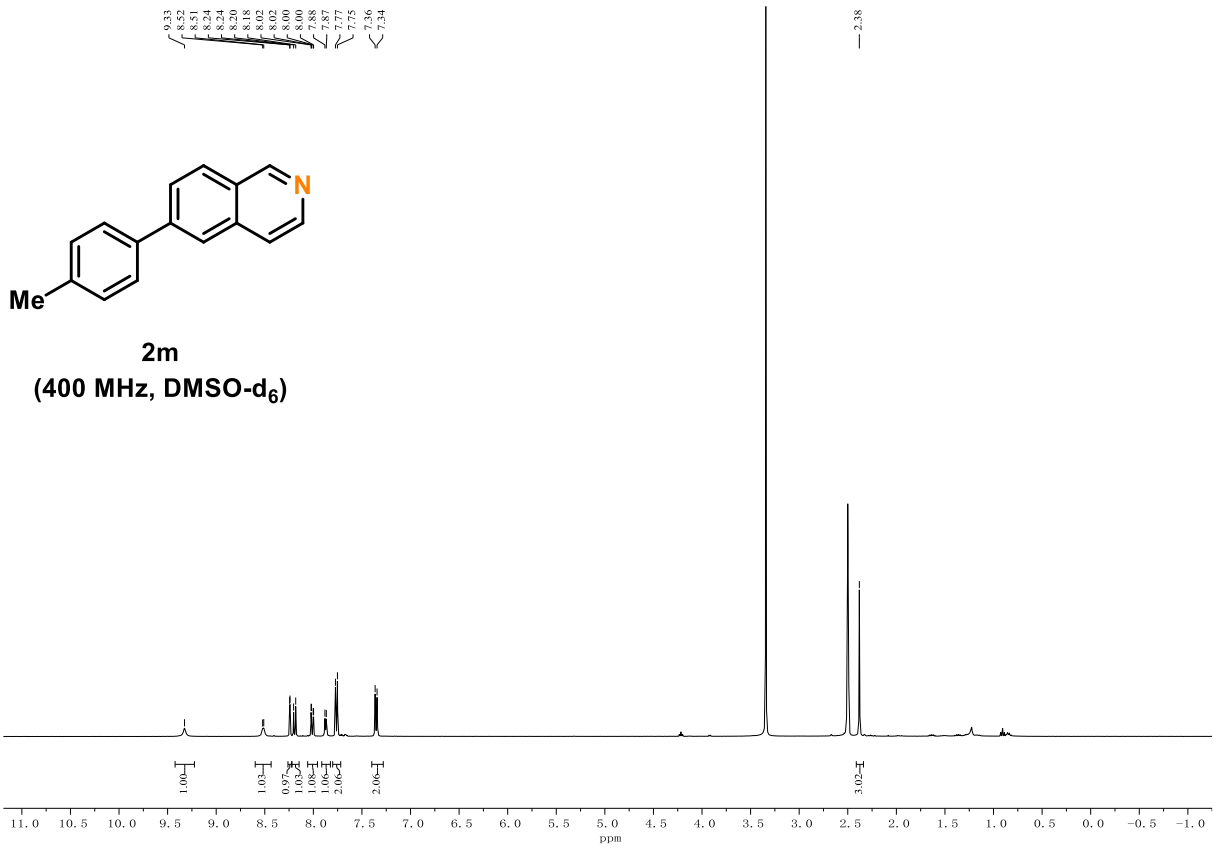
2l

(400 MHz, $CDCl_3$)

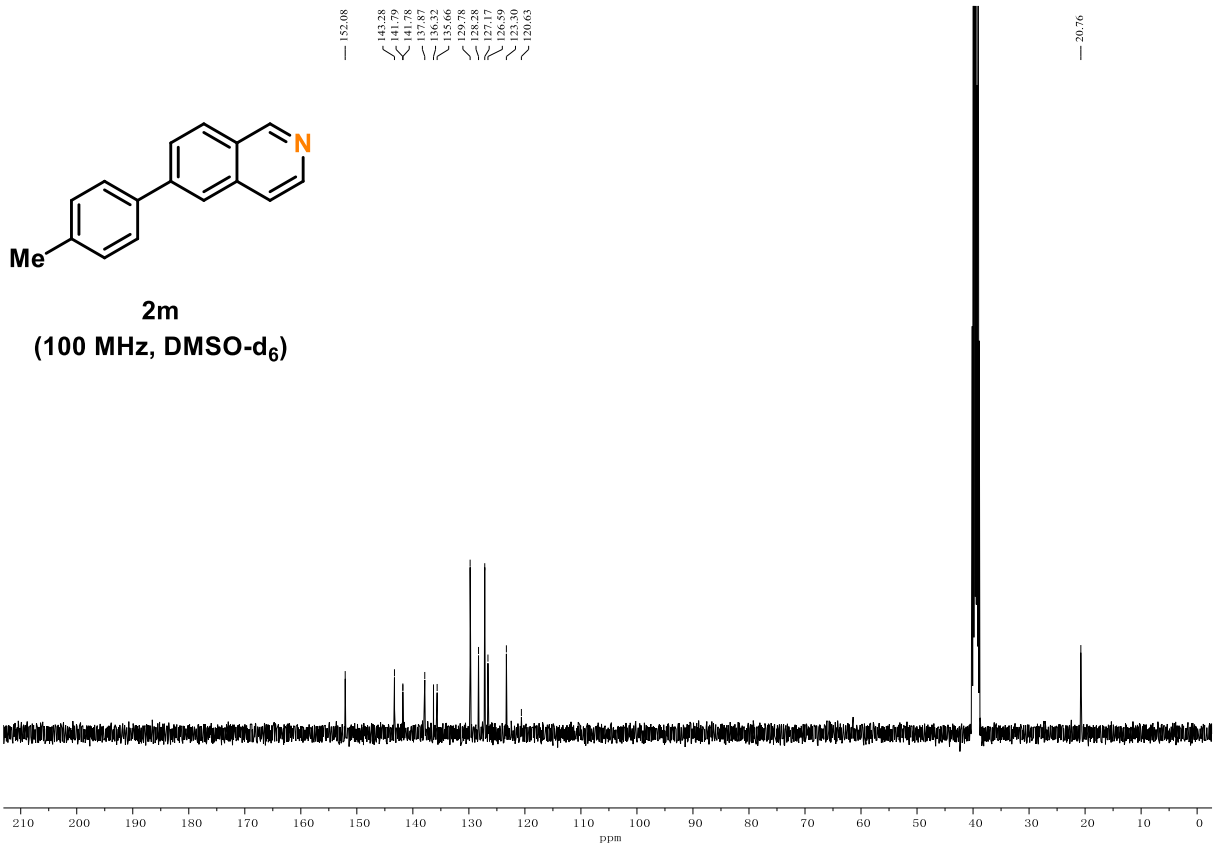


2l

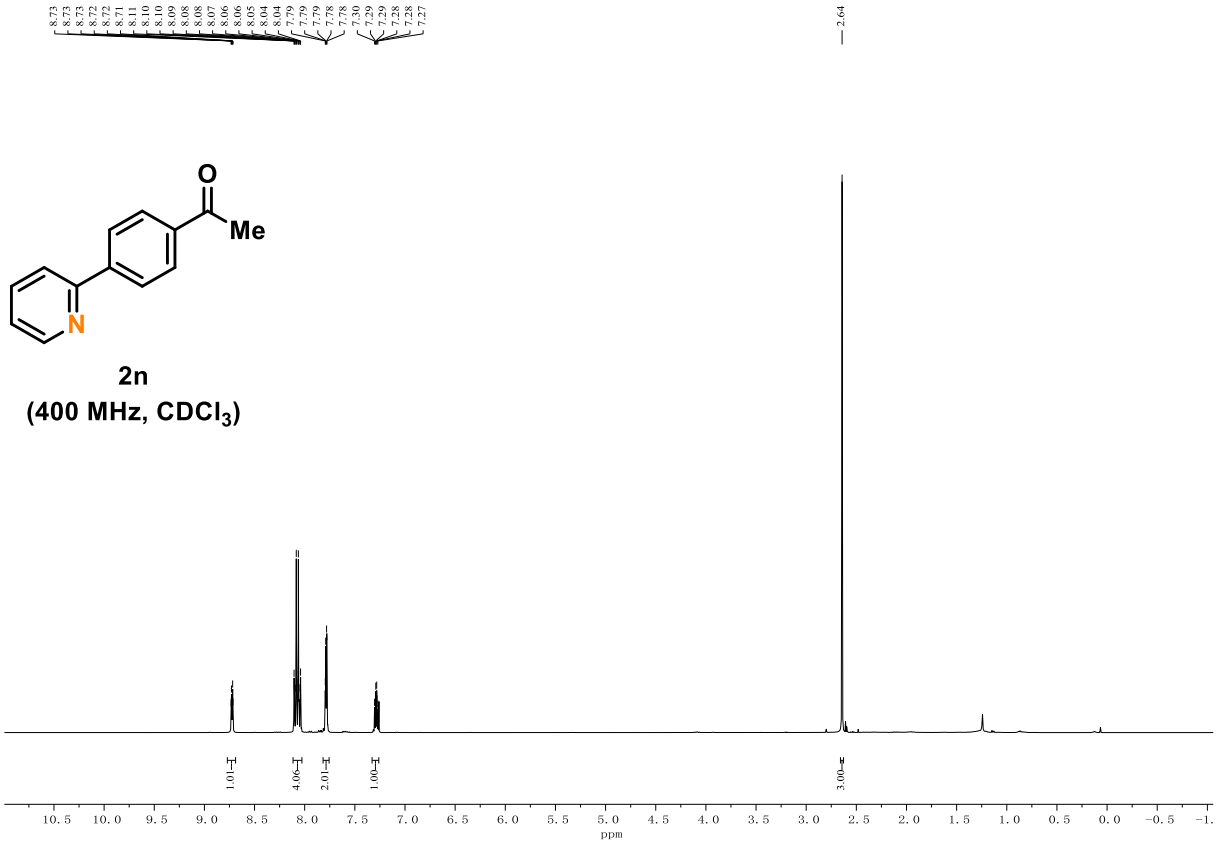
(100 MHz, $CDCl_3$)



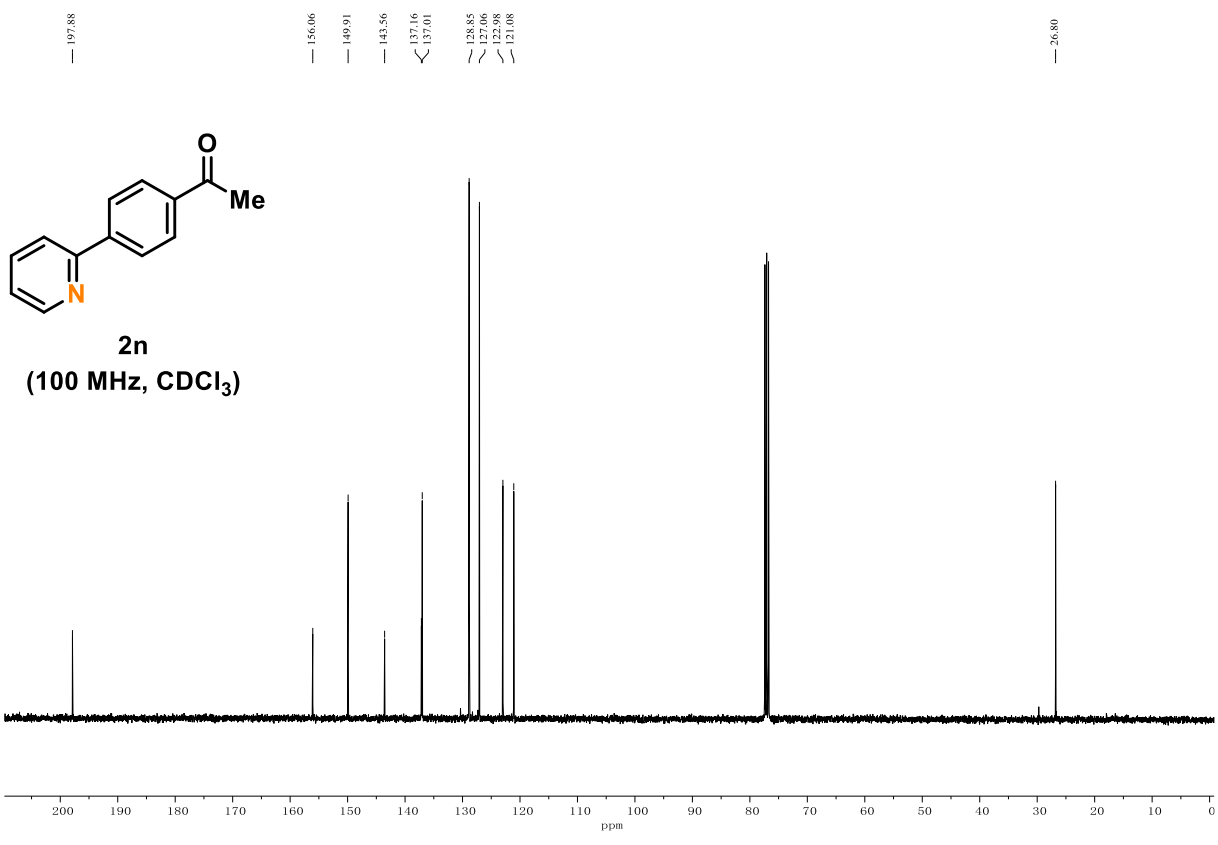
2m
(400 MHz, DMSO-d_6)



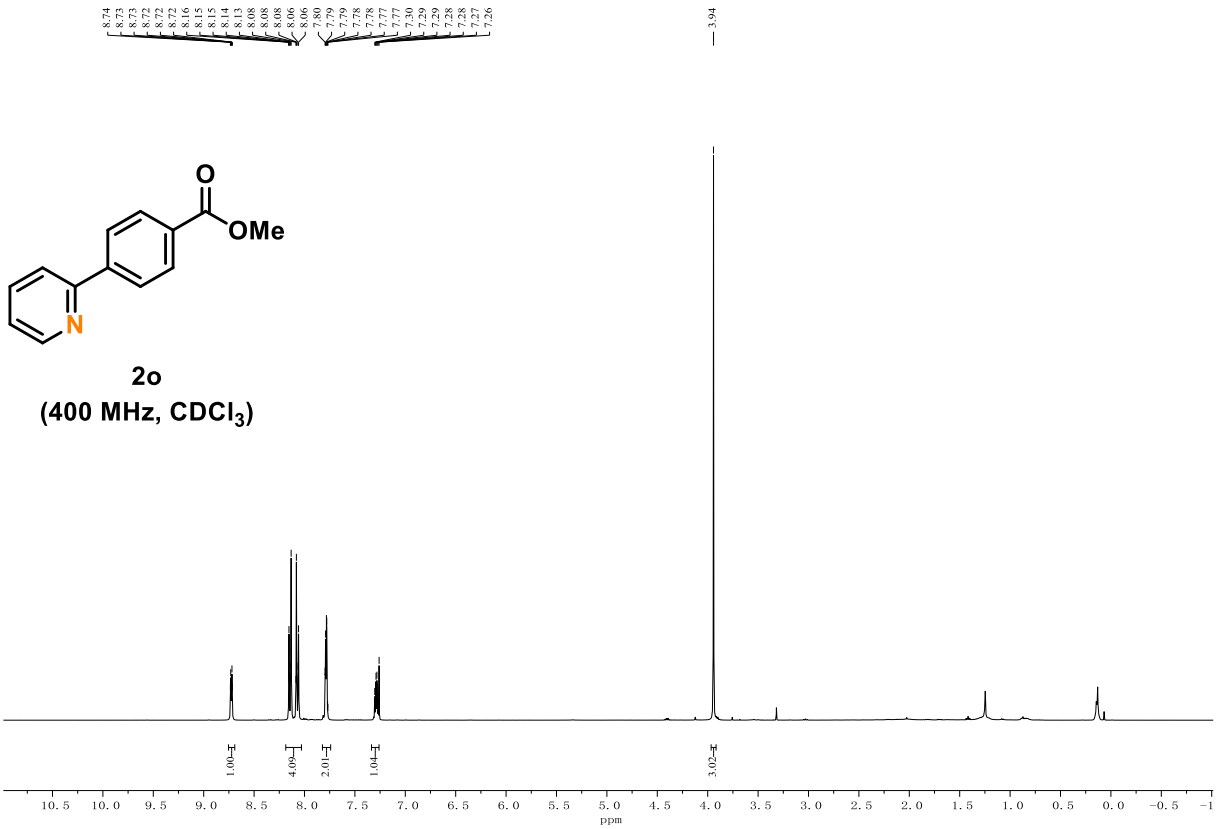
2m
(100 MHz, DMSO-d_6)



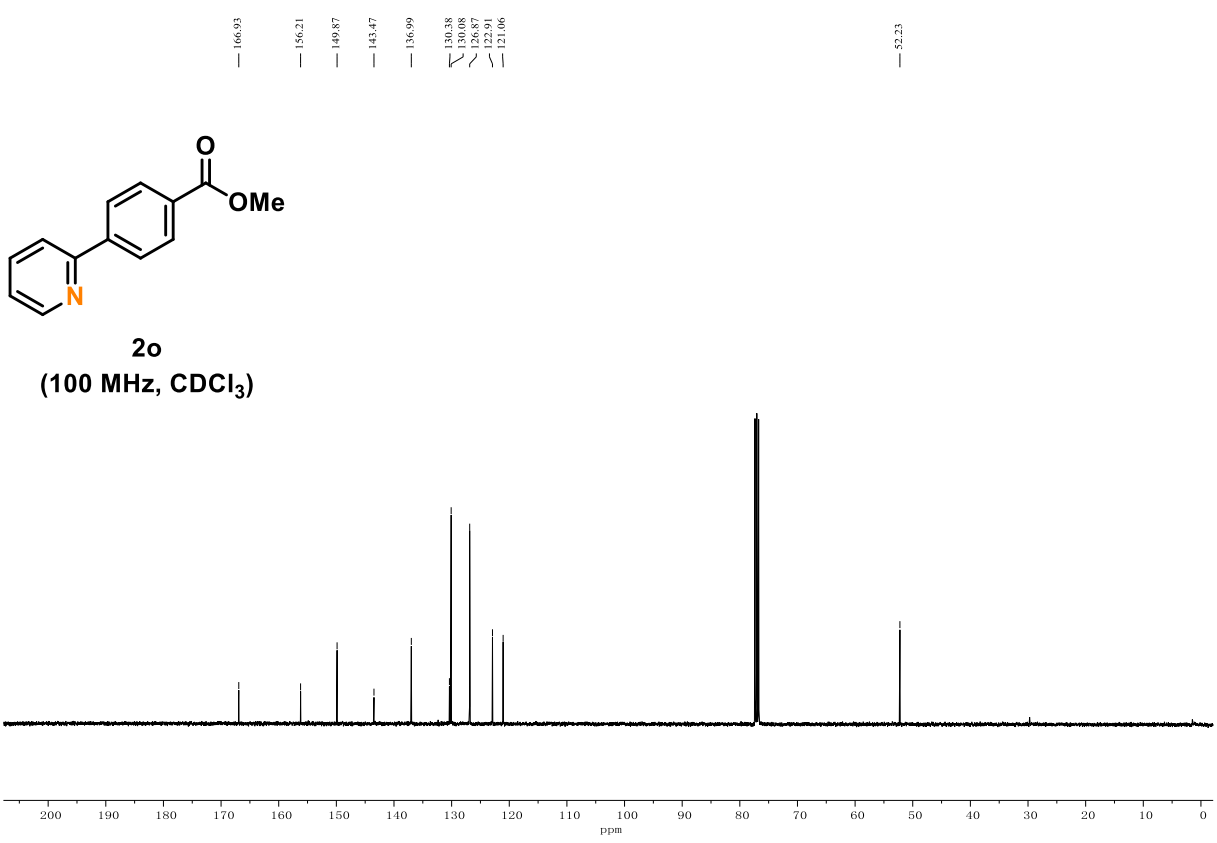
2n
(400 MHz, $CDCl_3$)



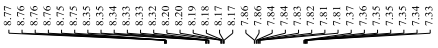
2n
(100 MHz, $CDCl_3$)

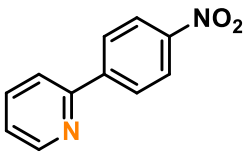


2o
(400 MHz, $CDCl_3$)

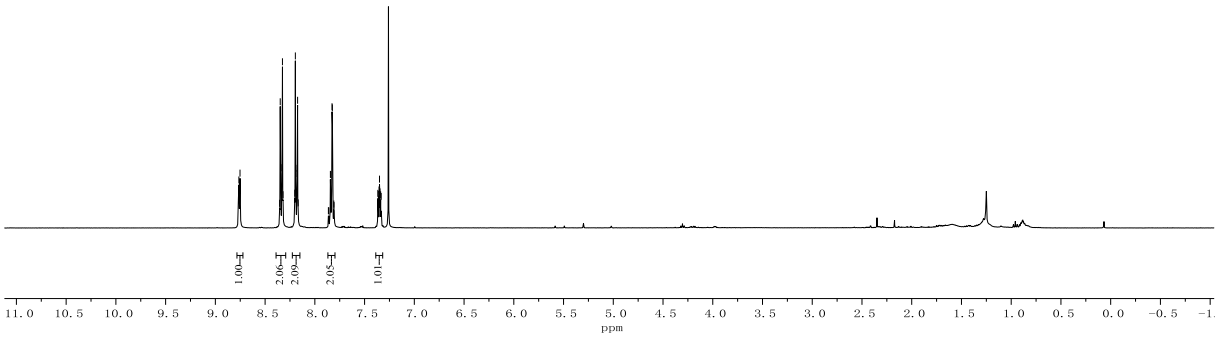


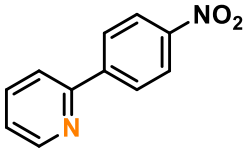
2o
(100 MHz, $CDCl_3$)



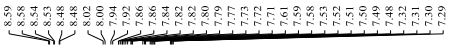


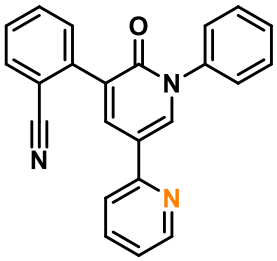
2p
(400 MHz, $CDCl_3$)



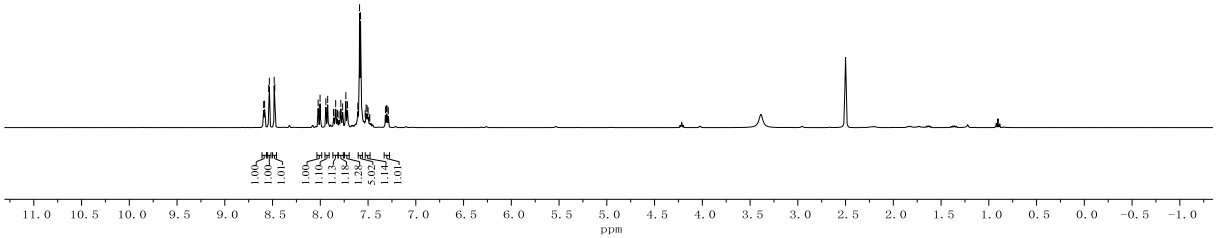


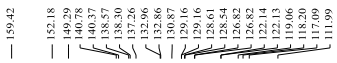
2p
(100 MHz, $CDCl_3$)

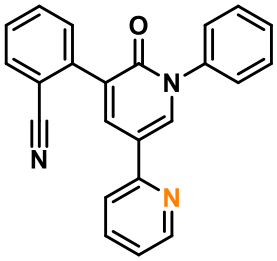




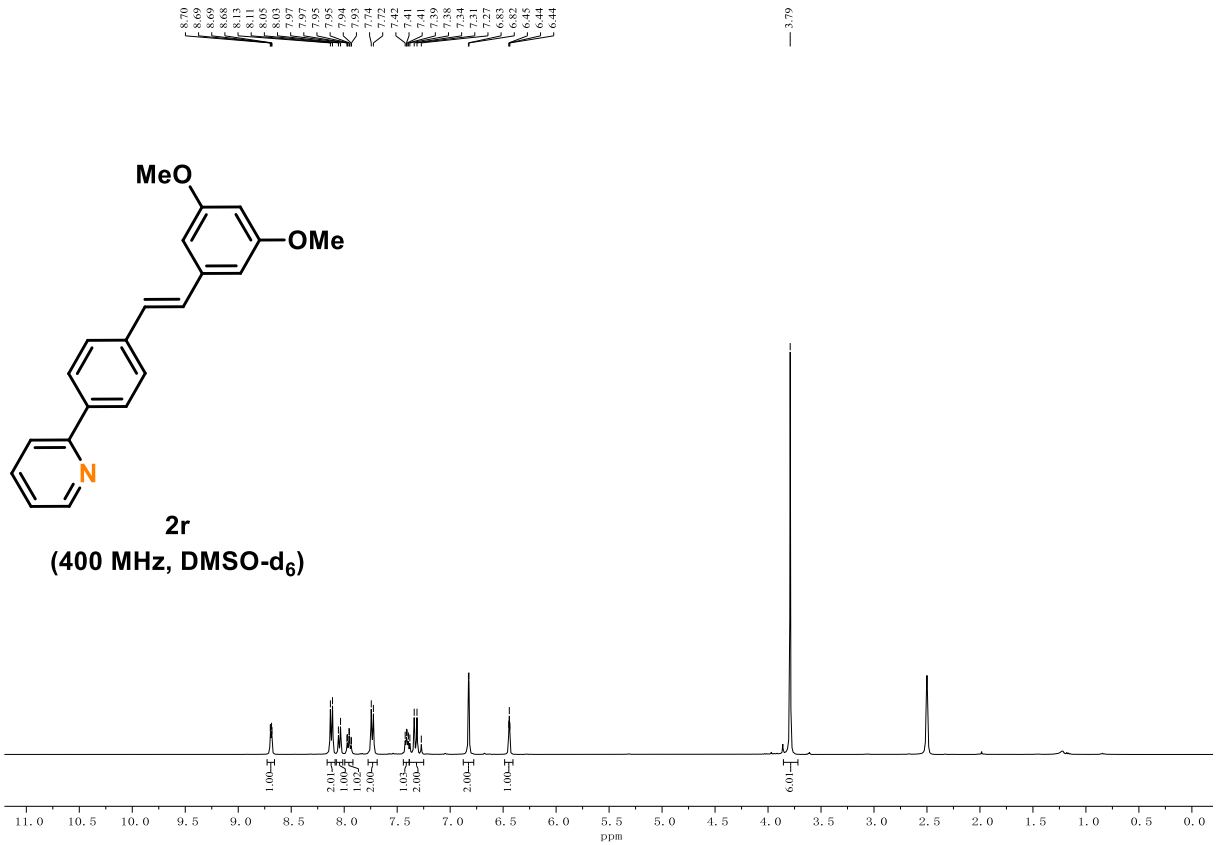
2q
(400 MHz, DMSO-d_6)

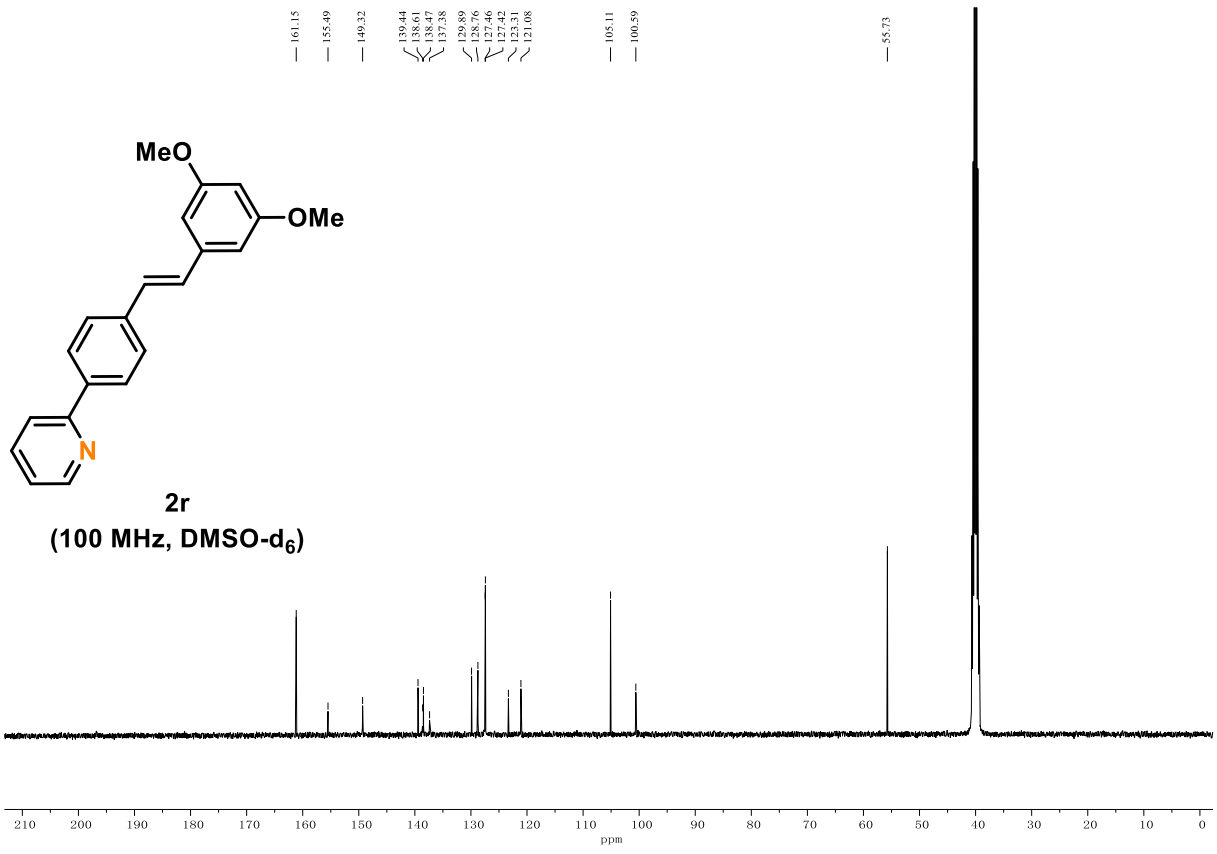






2q
(100 MHz, DMSO-d_6)


8.70
8.69
8.69
8.68
8.13
8.11
8.05
8.03
7.97
7.97
7.95
7.95
7.94
7.93
7.74
7.72
7.42
7.41
7.41
7.39
7.38
7.34
7.31
7.27
6.83
6.82
6.45
6.44
6.44
3.79
MeO
OMe
N
2r
(400 MHz, DMSO-d6)
1.00
2.01
1.02
1.00
2.00
1.03
2.00
2.00
1.00
6.01
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
ppm


161.15
155.49
149.32
139.44
138.61
138.47
137.38
129.89
128.76
127.46
127.42
123.31
121.08
105.11
100.59
55.73
MeO
OMe
N
2r
(100 MHz, DMSO-d6)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm