Synthesis of 3,4-unsubstituted isoquinolone derivatives from benzimidates and vinylene carbonate *via* cobalt(III)-catalyzed C-H activation/cyclization

Weiyan Xu,[a] Haowen Dang,[a] Huiru Sheng,[b] Jiabin Shen,*[b] and Min Wang*[a]

[a] College of Material Chemistry and Chemical Engineering, Key Laboratory of Organosilicon Chemistry and Material Technology, Ministry of Education. Hangzhou Normal University, Hangzhou 310036, China.
[b] Key Laboratory of Pollution Exposure and Health Intervention of Zhejiang Province, College of Biology and Environmental Engineering, Zhejiang Shuren University Hangzhou 310015, P. R. China.

Email: shenjiabinhznu@163.com (Shen, J.);mwang@hznu.edu.cn (Wang, M.)

Supporting Information

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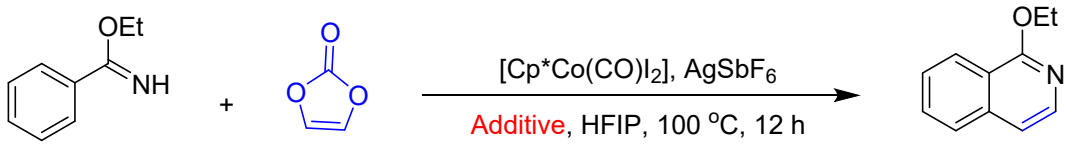
1. General Information

All the solvents involved in the reaction were dried by standard methods. The reagents were purchased from chemical reagent suppliers, such as Anergy, Bidet, etc, and were used without further purification. All products were separated by silica gel (200-300 mesh) column chromatography with petroleum ether (PE) (60-90°C) and ethyl acetate (EA). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Advance 500 spectrometer at ambient temperature with $CDCl_3$ as solvent and tetramethylsilane (TMS) as the internal standard. High resolution mass spectrometry (HRMS) data were recorded by Agilent LC 1200 / MS QTOF6520. Melting points were measured by WRS-1B type melting point apparatus and are uncorrected.

2. Experimental Section

2.1 **Screening of reaction conditions**

Table S1. Screening of reaction conditions for additive.

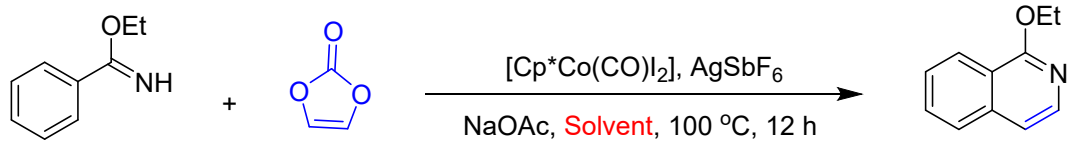


1a **2** **3a**

Entry	Additive	Yield (%)[b]
1	none	37
2	HOAc	31
3	**NaOAc**	**55**
4	$Zn(OAc)_2$	46
5	KOAc	45
6	AgOAc	39
7	CsOAc	trace
8	K_2CO_3	trace
9	Na_2CO_3	36
10	PhCOONa	43
11	1-AdCOOH	42
12	Ag_2O	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Cp*Co(CO)I_2 (10 mol%), $AgSbF_6$ (20 mol%), Additive (10 mol%), HFIP (2 mL) at 100 °C for 12 h under air atmosphere. [b] Yields were determined by ^{1}H NMR.

Table S2. Screening of reaction conditions for solvent.

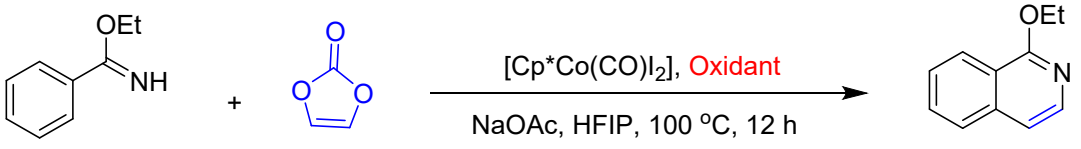


1a **2** **3a**

Entry	Solvent	Yield (%)[b]
1	DCE	16
2	THF	trace
3	DMSO	N.D.
4	EtOH	N.D.
5	TFE	23
6	Toluene	21
7	DMF	N.D.
8	1,4-dioxane	N.D.
9	PhCl	22
10	**HFIP**	**55**
11[c]	HFIP	33
12[d]	HFIP	45
13[e]	HFIP: EtOH	trace
14[f]	HFIP: TFE	31

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.4 mmol), Cp*Co(CO)I_2 (10 mol%), $AgSbF_6$ (20 mol%), NaOAc (10 mol%), Solvent (2 mL) at 100 °C for 12 h under air atmosphere. [b] Yields were determined by ^{1}H NMR. [c] 1 mL. [d] 3 mL. [e] HFIP: EtOH=1: 1. [f] HFIP: TFE=1: 1.

Table S3. Screening of reaction conditions for oxidants.



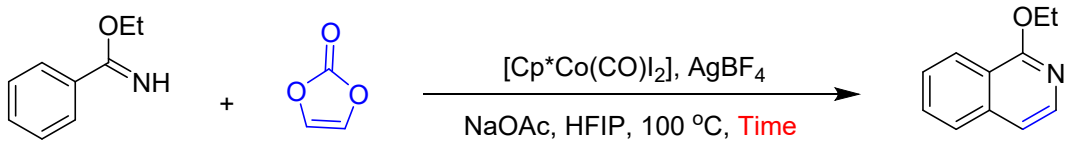
1a **2** **3a**

Entry	Oxidant	Yield (%)[b]
1	$AgSbF_6$	46
2	**$AgBF_4$**	**74**
3	$K_2S_2O_8$	19
4	$PhI(OAc)_2$	Trace

5	none	28

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), Cp*Co(CO)I_2 (10 mol%), Oxidant (20 mol%), NaOAc (10 mol%), HFIP (2 mL) at 100 °C for 12 h under air atmosphere. [b] Yields were determined by ^{1}H NMR.

Table S4. Screening of reaction conditions for time and atmosphere.

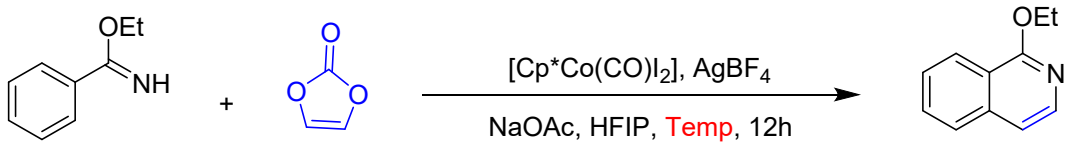


1a **2** **3a**

Entry	Time (h)	Yield (%)[b]
1	10	60
2	**12**	**74**
3[c]	12	15
4[d]	12	21
5	14	69

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), Cp*Co(CO)I_2 (10 mol%), $AgBF_4$ (20 mol%), NaOAc (10 mol%), HFIP (2 mL) at 100 °C for X h under air atmosphere. [b] Yields were determined by ^{1}H NMR. [c] under Ar atmosphere. [d] under N_2 atmosphere.

Table S5. Screening of reaction conditions for temperature.

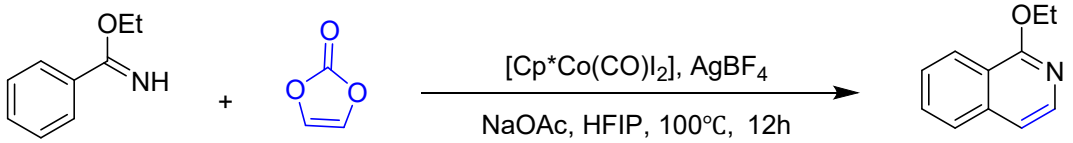


1a **2** **3a**

Entry	Temp (℃)	Yield (%)[b]
1	90	66
2	**100**	**74**
3	110	61

[a] Reaction conditions: **1a** (0.2 mmol), **2** (0.6 mmol), Cp*Co(CO)I_2 (10 mol%), $AgBF_4$ (20 mol%), NaOAc (10 mol%), HFIP(2 mL) at Y °C for 12 h under air atmosphere. [b] Yields were determined by ^{1}H NMR.

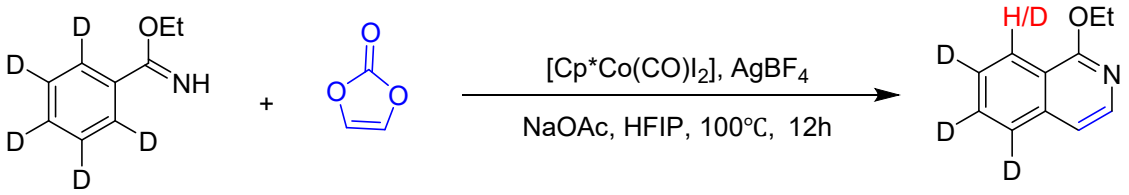
2.2 General procedure for synthesis of 3a.



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

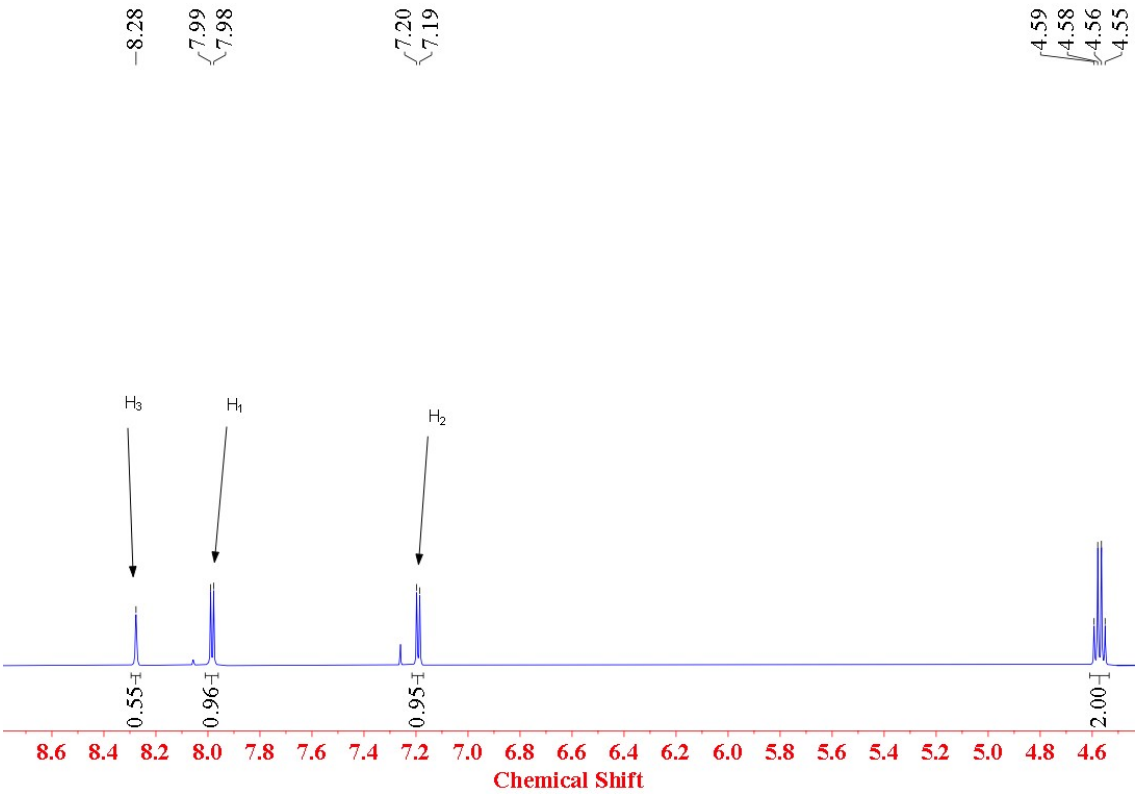
The synthesis of 1-ethoxyisoquinoline was taken as an example. Ethyl benzimidate **1a** (0.2 mmol), 1,3-dioxol-2-one **2a** (0.6 mmol), $Cp^*Co(CO)I_2$ (10 mol%), $AgBF_4$ (20 mol%), NaOAc (10 mol%) were dissolved in HFIP (2 mL). The reaction mixture was stirred at 100 °C for 12 h. The resulting mixture was cooled to room temperature. After concentrating on the solvent, the product was purified by flash chromatography with PE: EtOAc = 100: 1 to give the product **3a**.

2.3 General procedure for H / D exchange experiment.

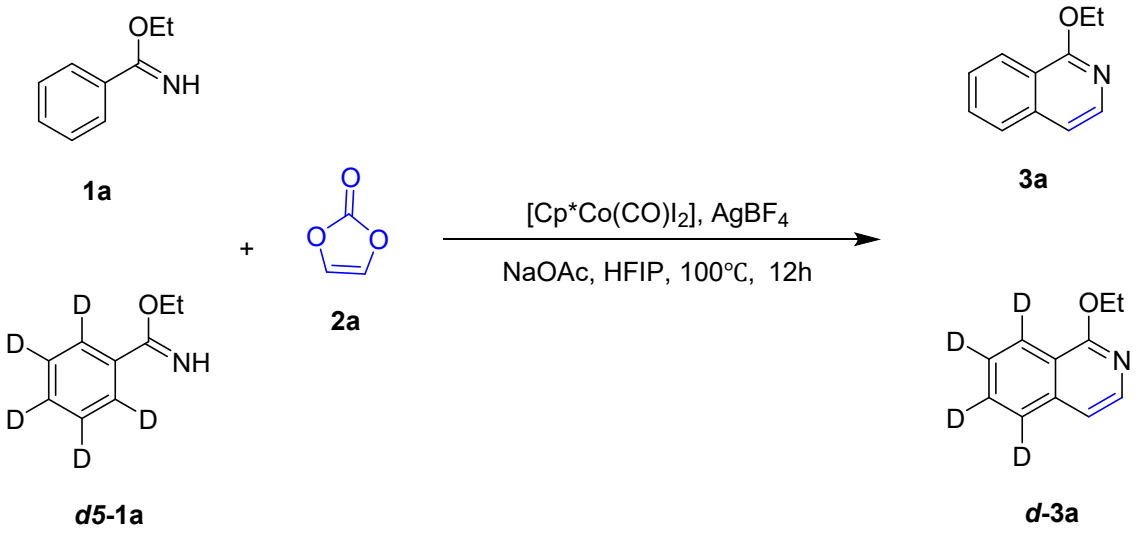


***d5*-1a** **2a** ***d*-3a**

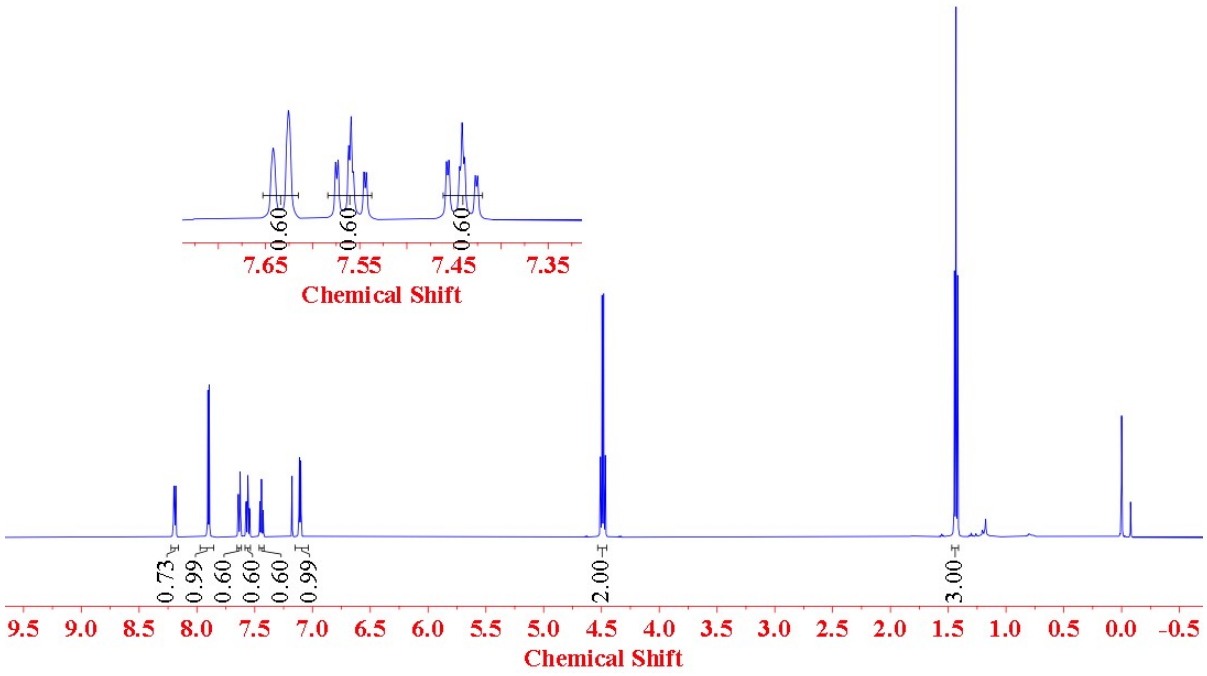
Ethyl benzimidate-2,3,4,5,6-d5 ***d*5-1a** (0.2 mmol), 1,3-dioxol-2-one **2a** (0.6 mmol), $Cp^*Co(CO)I_2$ (10 mol%), $AgBF_4$ (20 mol%), NaOAc (10 mol%) were dissolved in HFIP (2 mL). The reaction mixture was stirred at 100 °C for 12 h. The resulting mixture was cooled to room temperature. After concentrating on the solvent, the product was purified by flash chromatography with PE: EtOAc = 100: 1 to give the product ***d*-3a**. Through nuclear magnetic resonance hydrogen spectrum analysis, it was found that active hydrogen appeared in H_3, with an integral of 55%, and 45% was deuterated, indicating that the C-H activation process of this reaction is reversible.



2.4 General procedure for kinetic isotope experiments

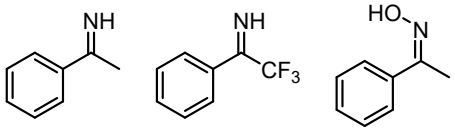


An equimolar mixture of ethyl benzoylimide **1a** (0.2 mmol) and ethyl deuterated benzoylimide ***d*5-1a** (0.2 mmol), 1,3-dioxol-2-one **2a** (0.6 mmol), Cp*Co(CO)I_2 (10 mol%), $AgBF_4$ (20 mol%), NaOAc (10 mol%) were dissolved in HFIP (2 mL). The reaction mixture was stirred at 100 °C for 12 h. The resulting mixture was cooled to room temperature. After concentrating on the solvent, the product was purified by flash chromatography with PE: EtOAc = 100: 1 to give the product. The KIE value (k_H / k_D = 1.5) was determined by ^{1}H NMR analysis, indicateing that the cleavage of the imine-directed ortho C-H bond may not be the rate-determining step of the reaction.

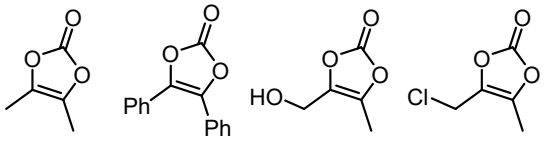


3. Unsuccessful substrate

imine/oxime:

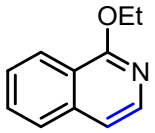


Substituted vinyl carbonate:



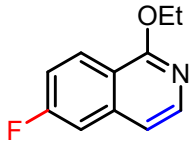
Characterization of Products

1-ethoxyisoquinoline (3a)



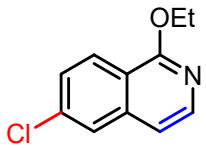
74% yield as a yellow oil.[1] R_f = 0.5 (PE: EA = 100: 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.5 Hz, 1H), 7.98 (d, *J* = 5.8 Hz, 1H), 7.72 (d, *J* = 8.1 Hz, 1H), 7.64 (tt, *J* = 8.0, 1.1 Hz, 1H), 7.53 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.19 (d, *J* = 5.9 Hz, 1H), 4.57 (q, *J* = 7.1 Hz, 2H), 1.52 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 139.6, 137.8, 130.3, 126.5, 126.0, 124.2, 119.8, 114.6, 62.0, 14.6. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{11}H_{12}NO$: 174.0913, found 174.0913.

1-ethoxy-6-fluoroisoquinoline (3b)



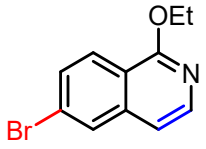
61% yield as a colorless oil. R_f = 0.5 (PE: EA = 100: 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.28 (dd, *J* = 9.1, 5.7 Hz, 1H), 8.00 – 7.95 (m, 1H), 7.32 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.25 (td, *J* = 8.8, 2.5 Hz, 1H), 7.13 (dd, *J* = 6.0, 0.9 Hz, 1H), 4.55 (q, *J* = 7.1 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 164.6, 162.6, 160.6, 141.0, 139.6 (d, *J* = 10 Hz), 127.4 (d, *J* = 8.75 Hz), 116.8, 116.2 (d, *J* = 25 Hz), 114.3 (d, *J* = 3.75 Hz), 109.8 (d, *J* = 20 Hz), 62.1, 14.6. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{11}H_{11}FNO$: 192.0819, found 192.0818.

6-chloro-1-ethoxyisoquinoline (3c)



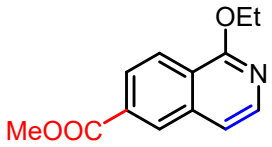
65% yield as a white solid.[2] M. p. = 43−45 °C. R_f = 0.6 (PE: EA = 80: 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 1H), 7.99 (d, *J* = 5.9 Hz, 1H), 7.70 (s, 1H), 7.45 (dt, *J* = 8.8, 1.6 Hz, 1H), 7.10 (dt, *J* = 6.0, 1.1 Hz, 1H), 4.56 (q, *J* = 7.0 Hz, 2H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 141.0, 138.8, 136.7, 127.3, 126.2, 125.0, 118.0, 113.8, 62.3, 14.6. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{11}H_{11}ClNO$: 208.0524, found 208.0525.

6-bromo-1-ethoxyisoquinoline (3d)



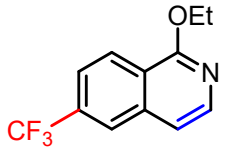
62% yield as a white solid. M. p. = 56−58 °C. R_f = 0.6 (PE: EA = 100: 1). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.9 Hz, 1H), 7.97 (d, *J* = 5.9 Hz, 1H), 7.84 (d, *J* = 1.9 Hz, 1H), 7.56 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.08 – 7.01 (m, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 1.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 141.0, 139.0, 129.8, 128.2, 126.1, 125.1, 118.2, 113.5, 62.2, 14.5. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{11}H_{11}BrNO$: 252.0019, found 252.0019.

Methyl 1-ethoxyisoquinoline-6-carboxylate (3e)



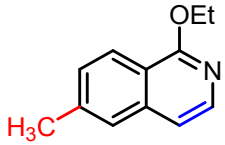
65% yield as a white solid. M. p. = 76−78 °C. R_f = 0.4 (PE: EA = 60: 1). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.51 (d, *J* = 1.6 Hz, 1H), 8.26 – 8.20 (m, 1H), 8.08 (d, *J* = 5.9 Hz, 1H), 8.05 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.54 (dd, *J* = 5.9, 0.9 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 3.95 (s, 3H), 1.45 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 165.7, 159.5, 140.6, 136.9, 131.1, 128.4, 125.9, 124.2, 120.6, 115.3, 61.9, 52.5, 14.3. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{13}H_{14}NO_3$: 232.0968, found 232.0966.

1-ethoxy-6-(trifluoromethyl)isoquinoline (3f)



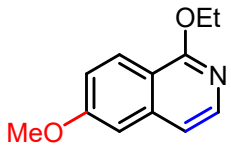
44% yield as a colorless oil. R_f = 0.7 (PE: EA = 100: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.30 (d, *J* = 8.5 Hz, 1H), 8.00 (dd, *J* = 5.8, 0.9 Hz, 1H), 7.94 (s, 1H), 7.62 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.18 (q, *J* = 2.1, 1.3 Hz, 1H), 4.51 (q, *J* = 7.0 Hz, 2H), 1.45 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 141.2 (q, *J* = 8.8 Hz), 137.1, 132.1 (q, *J* = 31.3 Hz), 125.6 (q, *J* = 2.5 Hz), 123.9 (q, *J* = 271.3 Hz), 123.7 (q, *J* = 3.8 Hz), 122.2, 121.1, 114.8 (q, *J* = 2.5 Hz), 62.5, 14.5. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{12}H_{11}F_3NO$: 242.0787, found 242.079.

1-ethoxy-6-methylisoquinoline (3g)



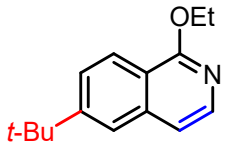
51% yield as a colorless oil. R_f = 0.6 (PE: EA = 100: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 5.9 Hz, 1H), 7.49 (s, 1H), 7.35 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.11 (d, *J* = 5.9 Hz, 1H), 4.55 (q, *J* = 7.0 Hz, 2H), 2.51 (s, 3H), 1.50 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 140.6, 139.7, 138.2, 128.5, 125.2, 124.1, 118.0, 114.3, 61.9, 21.9, 14.6. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{12}H_{14}NO$: 188.107, found 188.107.

1-ethoxy-6-methoxyisoquinoline (3h)



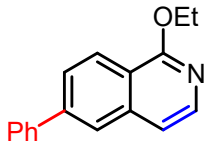
62% yield as a yellow oil. R_f = 0.6 (PE: EA = 100: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 9.1 Hz, 1H), 7.92 (d, *J* = 5.9 Hz, 1H), 7.12 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.11 – 7.07 (m, 1H), 6.99 (d, *J* = 2.4 Hz, 1H), 4.54 (q, *J* = 7.1 Hz, 2H), 3.91 (s, 3H), 1.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.0, 160.6, 140.4, 139.9, 126.1, 118.4, 114.7, 114.2, 104.6, 61.9, 55.3, 14.6. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{12}H_{14}NO_2$: 204.1019, found 204.1017.

6-(*tert*-butyl)-1-ethoxyisoquinoline (3i)



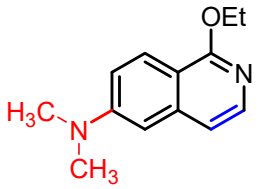
61% yield as a yellow oil.[2] R_f = 0.5 (PE: EA = 100: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 5.9 Hz, 1H), 7.65 (d, *J* = 1.9 Hz, 1H), 7.61 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.17 (d, *J* = 5.9 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.1 Hz, 3H), 1.41 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.5, 153.5, 139.6, 138.0, 125.2, 123.9, 121.3, 117.9, 114.9, 61.9, 35.1, 31.1, 14.7. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{15}H_{20}NO$: 230.1539, found 230.1545.

1-ethoxy-6-phenylisoquinoline (3j)



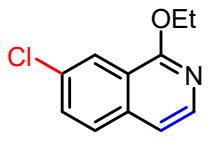
85% yield as a pale yellow oil.[1] R_f = 0.5 (PE: EA = 80: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 5.8 Hz, 1H), 7.78 (d, *J* = 2.0 Hz, 1H), 7.65 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.61 – 7.55 (m, 2H), 7.38 (dd, *J* = 8.4, 6.9 Hz, 2H), 7.33 – 7.27 (m, 1H), 7.12 (d, *J* = 6.0 Hz, 1H), 4.49 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 143.0, 140.4, 140.1, 138.2, 128.9, 127.9, 127.5, 126.0, 124.8, 123.9, 118.8, 114.8, 62.0, 14.6. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{17}H_{16}NO$: 250.1226, found 250.1225.

1-ethoxy-6-(dimethylamino)isoquinoline (3k)



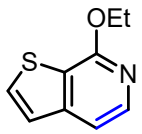
68% yield as a pale yellow solid, M. p. = 73−74 °C.[1] R_f = 0.3 (PE: EA = 60: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 9.2 Hz, 1H), 7.83 (d, *J* = 5.9 Hz, 1H), 7.04 (dt, *J* = 9.2, 2.5 Hz, 1H), 6.99 (d, *J* = 6.0 Hz, 1H), 6.69 (t, *J* = 2.2 Hz, 1H), 4.53 (q, *J* = 7.1 Hz, 2H), 3.05 (s, 6H), 1.49 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 151.3, 139.9, 139.8, 125.3, 114.8, 113.9, 111.7, 103.7, 61.5, 40.2, 14.7. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{13}H_{17}N_2O$: 217.1335, found 217.1346.

7-chloro-1-ethoxyisoquinoline (3m)



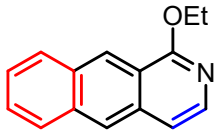
74% yield as a pale yellow solid. M. p. = 48−50 °C.[1] R_f = 0.5 (PE: EA = 80: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 – 8.22 (m, 1H), 7.98 (d, *J* = 5.8 Hz, 1H), 7.66 (dd, *J* = 8.8, 1.3 Hz, 1H), 7.61 – 7.56 (m, 1H), 7.16 (d, *J* = 5.9 Hz, 1H), 4.56 (q, *J* = 7.1 Hz, 2H), 1.51 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.8, 140.1, 136.1, 132.0, 131.2, 127.7, 123.5, 120.4, 114.2, 62.3, 14.6. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{11}H_{11}ClNO$: 208.0524, found 208.0524.

7-ethoxythieno[2,3-*c*]pyridine (3o)



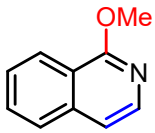
41% yield as a colorless oil.[1] R_f = 0.6 (PE: EA = 100: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 5.6 Hz, 1H), 7.65 – 7.60 (m, 1H), 7.32 (dd, *J* = 5.3, 1.4 Hz, 1H), 7.29 (dd, *J* = 5.6, 1.1 Hz, 1H), 4.58 (q, *J* = 7.0 Hz, 2H), 1.48 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 147.3, 140.5, 131.1, 123.4, 123.0, 112.0, 62.1, 14.7. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_9H_{10}NOS$: 180.0478, found 180.0478.

1-ethoxybenzo[*g*]isoquinoline (3p)



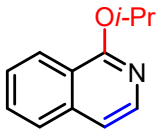
56% yield as a yellow solid. M. p. = 81−83 °C. R_f = 0.4 (PE: EA = 80: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (s, 1H), 8.23 (s, 1H), 8.07 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 6.2 Hz, 1H), 7.56 (ddd, *J* = 8.2, 6.5, 1.3 Hz, 1H), 7.50 (ddd, *J* = 7.9, 6.5, 1.3 Hz, 1H), 7.30 (d, *J* = 6.1 Hz, 1H), 4.65 (q, *J* = 7.1 Hz, 2H), 1.59 (t, J = 7.1 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.1, 137.8, 134.3, 134.1, 131.8, 129.2, 127.8, 127.3, 125.6, 124.4, 124.1, 119.2, 114.4, 62.2, 14.6. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{15}H_{14}NO$: 224.107, found 224.107.

1-methoxyisoquinoline (3q)



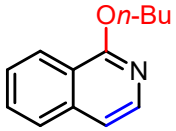
70% yield as a colorless oil.[1] R_f = 0.6 (PE: EA = 100: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.00 (d, *J* = 5.8 Hz, 1H), 7.76 – 7.70 (m, 1H), 7.66 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.54 (ddd, *J* = 8.3, 6.9, 1.3 Hz, 1H), 7.22 (dd, *J* = 5.8, 0.9 Hz, 1H), 4.15 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9, 139.4, 137.8, 130.5, 126.6, 126.1, 124.2, 119.8, 114.9, 53.8. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{10}H_{10}NO$: 160.0757, found 160.0757.

1-isopropoxyisoquinoline (3r)



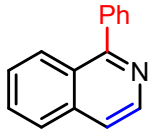
56% yield as a colorless oil. R_f = 0.7 (PE: EA = 100: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 8.4, 1.1 Hz, 1H), 7.98 (d, *J* = 5.9 Hz, 1H), 7.71 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.64 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.52 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.17 (dd, *J* = 5.9, 0.8 Hz, 1H), 5.57 (p, *J* = 6.2 Hz, 1H), 1.46 (d, *J* = 6.2 Hz, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.1, 139.6, 138.0, 130.3, 126.3, 126.0, 124.4, 120.2, 114.3, 68.5, 22.1. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{12}H_{14}NO$: 188.107, found 188.107.

1-butoxyisoquinoline (3s)



80% yield as a colorless oil.[3] R_f = 0.6 (PE: EA = 100: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.98 (d, *J* = 5.9 Hz, 1H), 7.72 (dt, *J* = 8.2, 0.9 Hz, 1H), 7.64 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 7.53 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.19 (dd, *J* = 5.9, 0.8 Hz, 1H), 4.51 (t, *J* = 6.6 Hz, 2H), 1.94 – 1.84 (m, 2H), 1.58 (m, *J* = 7.4 Hz, 2H), 1.03 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.8, 139.7, 137.8, 130.3, 126.5, 126.0, 124.2, 119.9, 114.6, 66.1, 31.1, 19.5, 13.9. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{13}H_{16}NO$: 202.1226, found 202.1226.

1-phenylisoquinoline (3t)



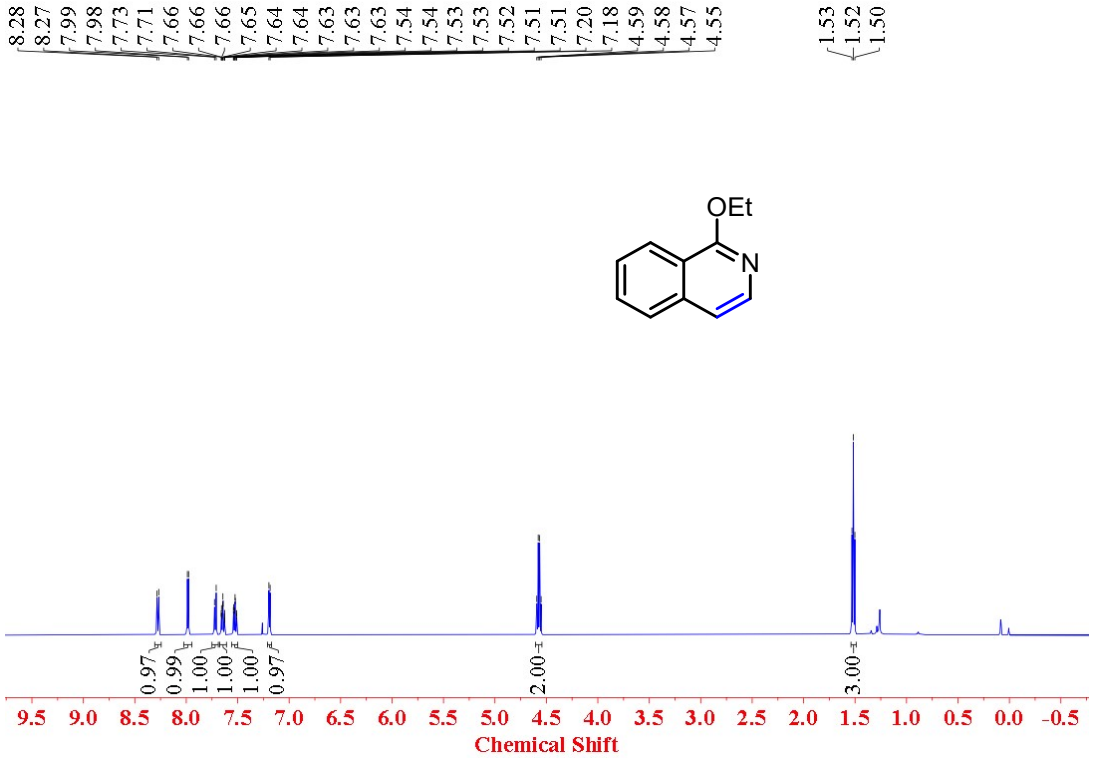
66% yield as a white solid foam.[1] R_f = 0.4 (PE: EA = 50: 1) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 5.7 Hz, 1H), 8.14 – 8.08 (m, 1H), 7.89 (d, *J* = 7.7 Hz, 1H), 7.75 – 7.62 (m, 4H), 7.58 – 7.47 (m, 4H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.7, 142.2, 139.5, 136.8, 130.0, 129.9, 128.5, 128.3, 127.6, 127.1, 126.9, 126.7, 119.9. HRMS (ESI-TOF) $[M+H]^+$ Calculated for $C_{15}H_{12}N$: 206.0964, found 206.097.

4. References

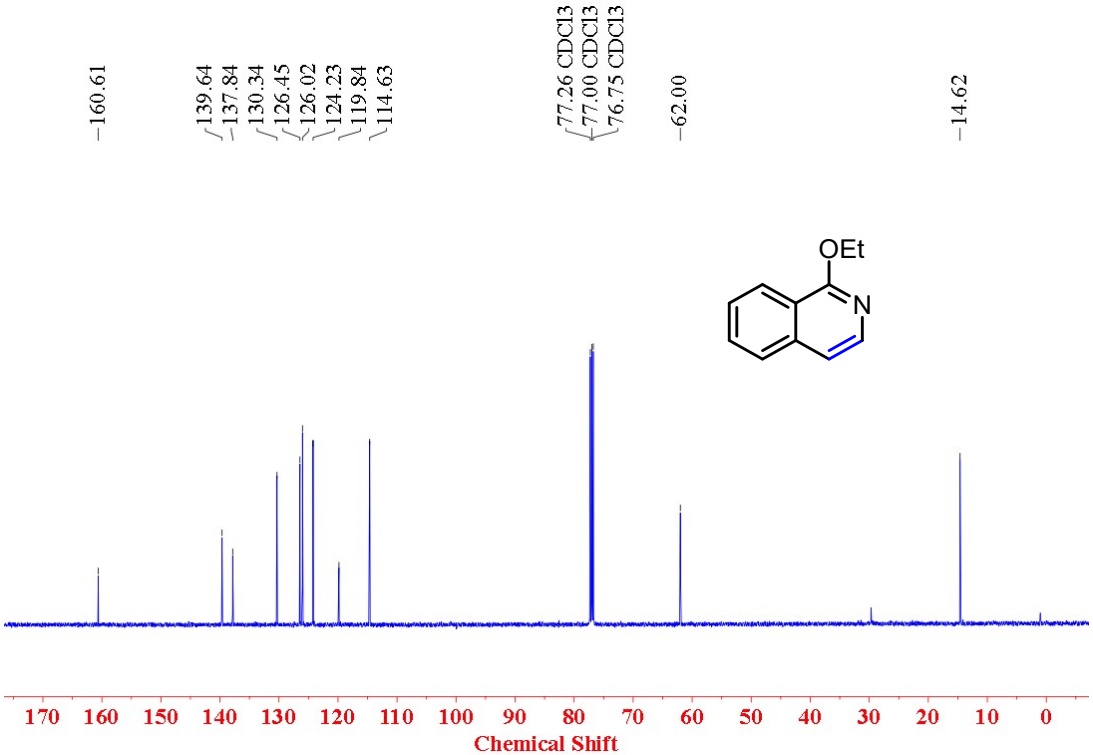
1. A. Inami, Y. Nishii, K. Hirano, M. Miura, *Org. Lett*., **2023**, *25*, 3206.
2. K. Ghosh, Y. Nishii, M. Miura, *ACS Catal*., **2019**, *9*, 11455.
3. T. Chen, P. Pedersen, N. Dow, R. Fayad, C. Hauke and D. MacMillan, *J. Am. Chem. Soc.*, **2022**, *144*, 8296.

5. Copies of ^{1}H and ^{13}C Spectra

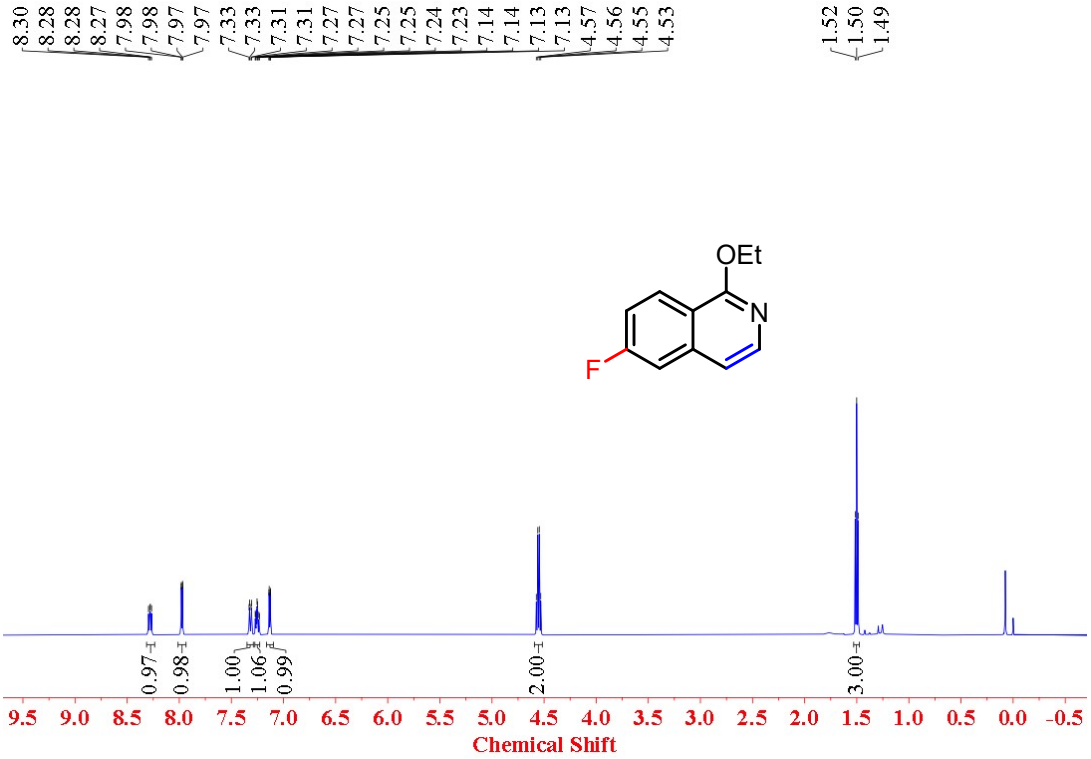
3a ^{1}H NMR



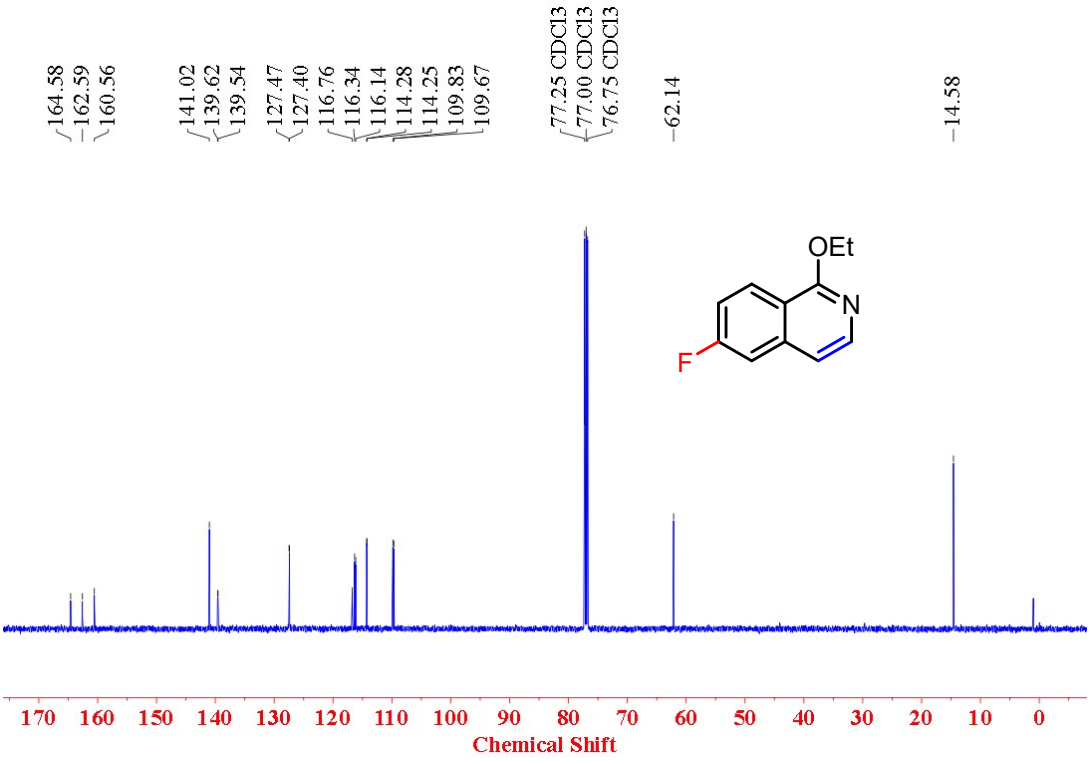
3a ^{13}C NMR



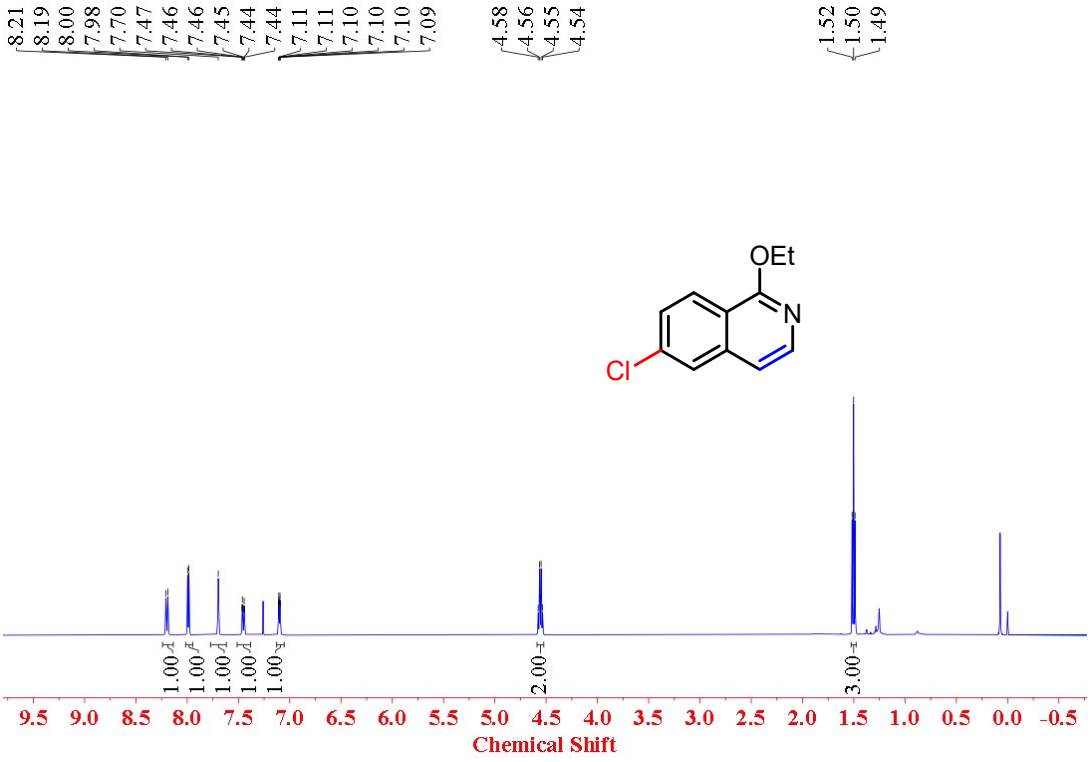
3b ^{1}H NMR



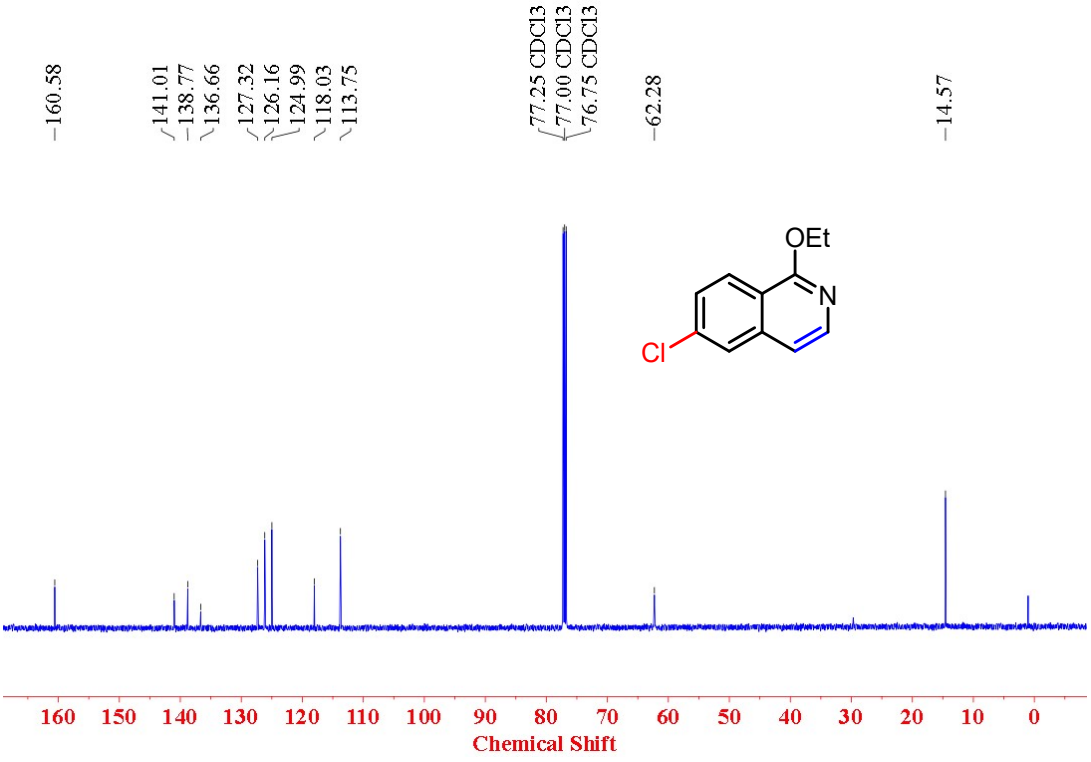
3b ^{13}C NMR



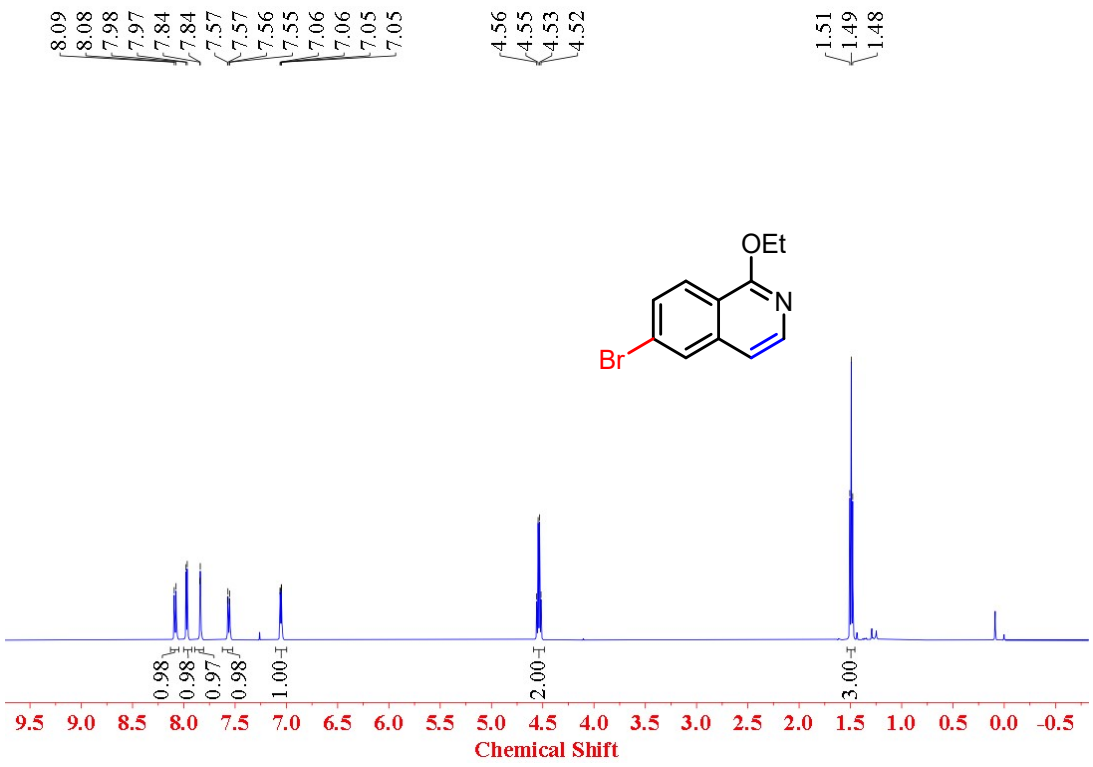
3c ^{1}H NMR



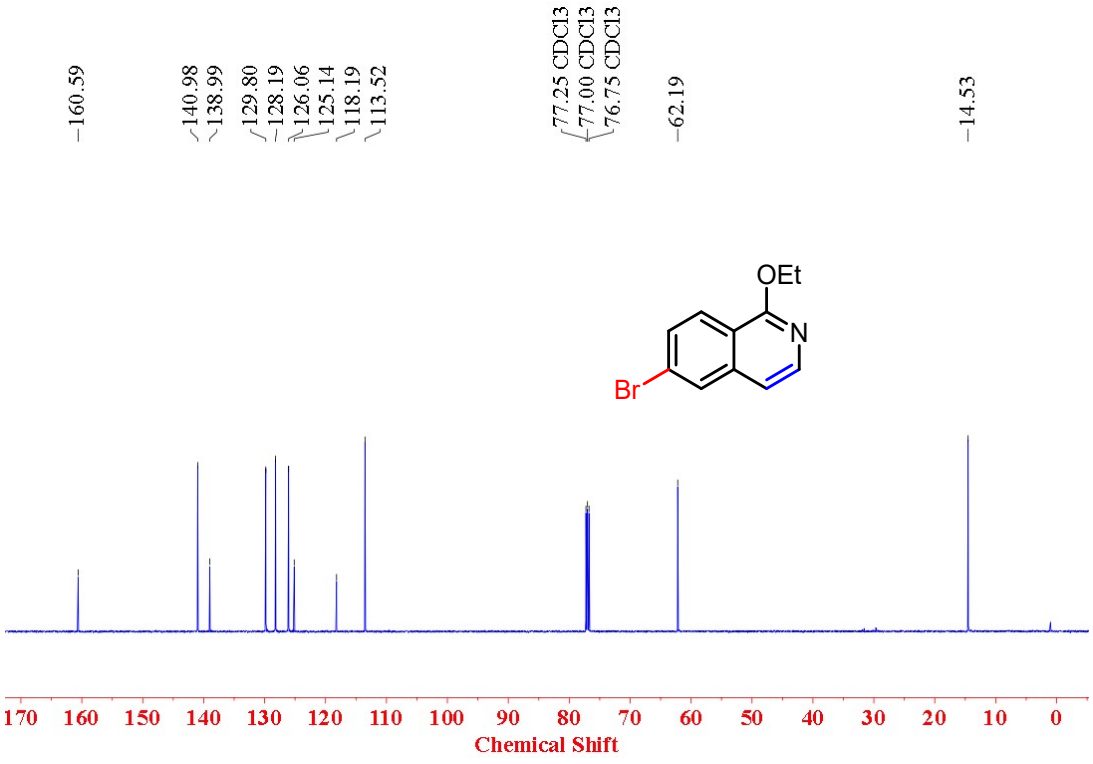
3c ^{13}C NMR



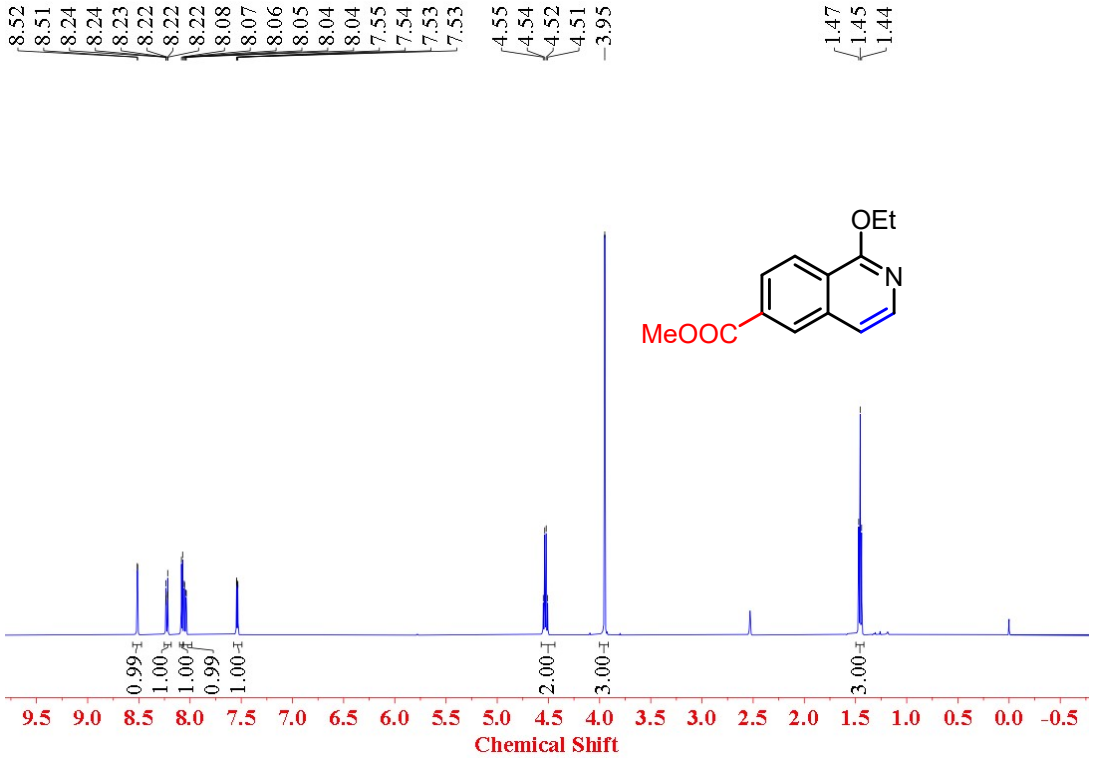
3d ^{1}H NMR



3d ^{13}C NMR



3e ^{1}H NMR



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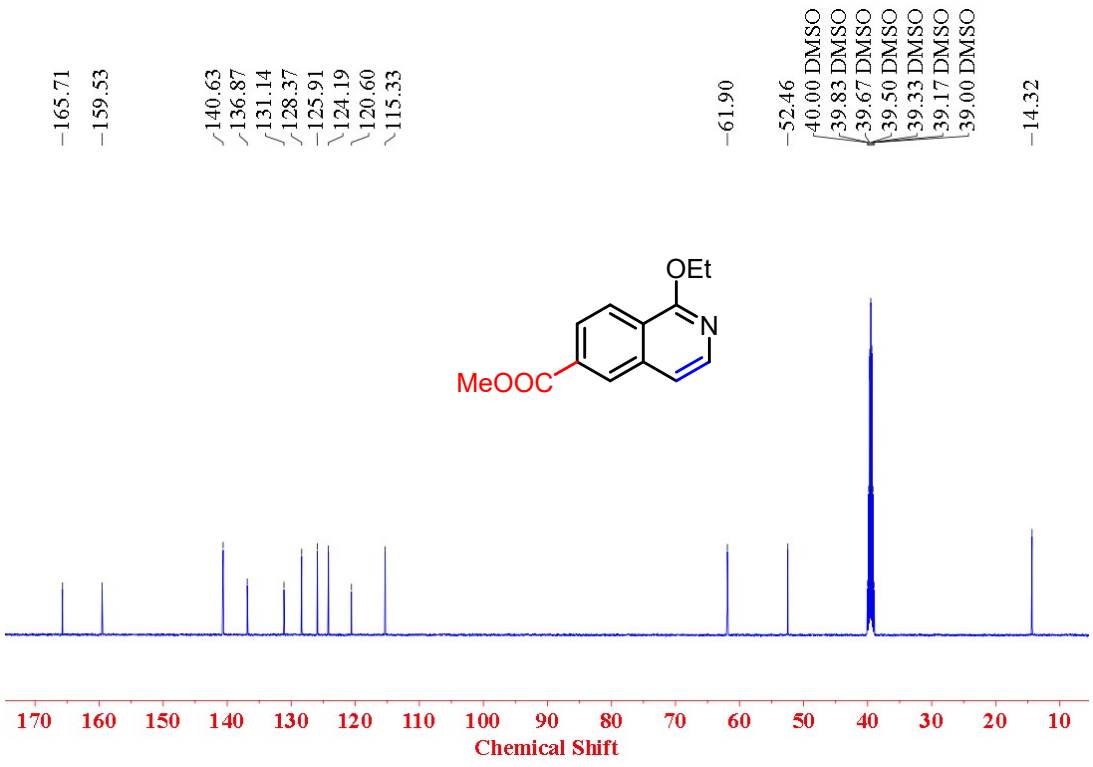
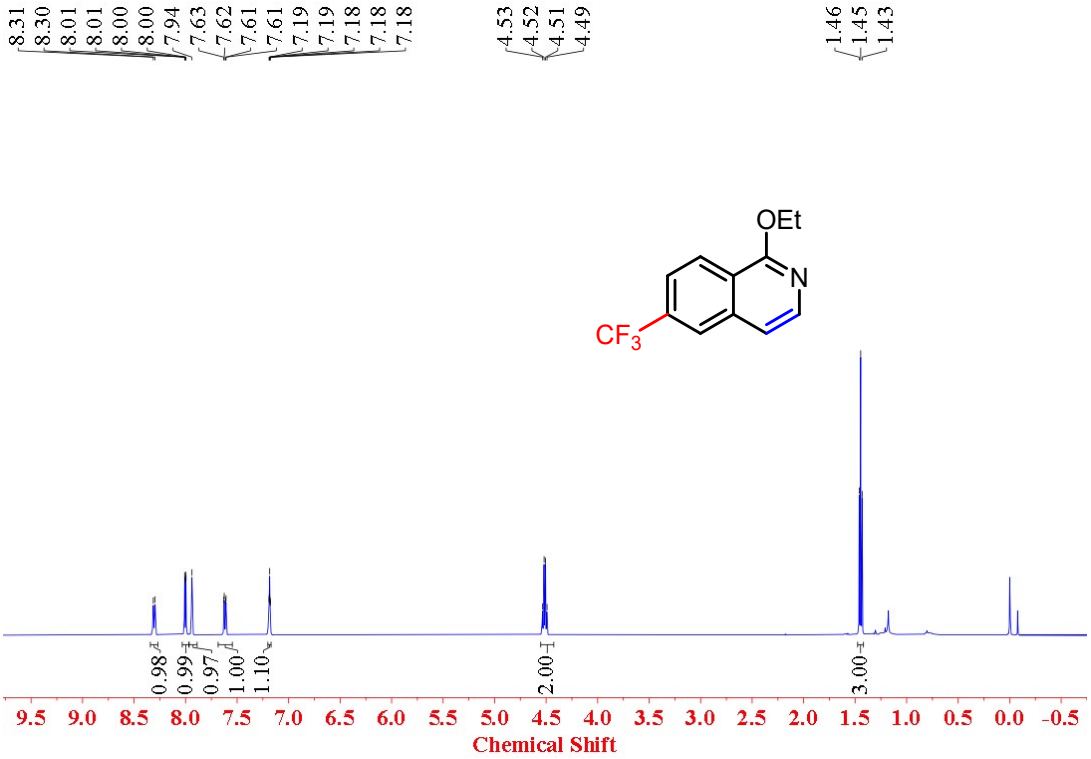
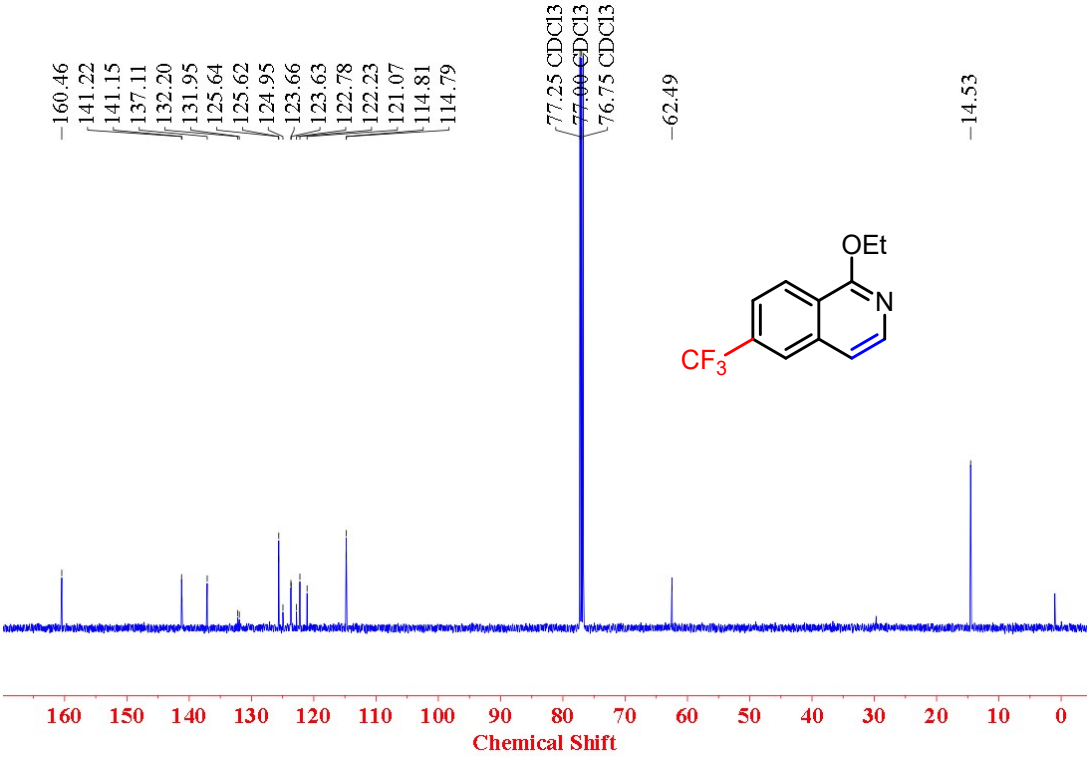


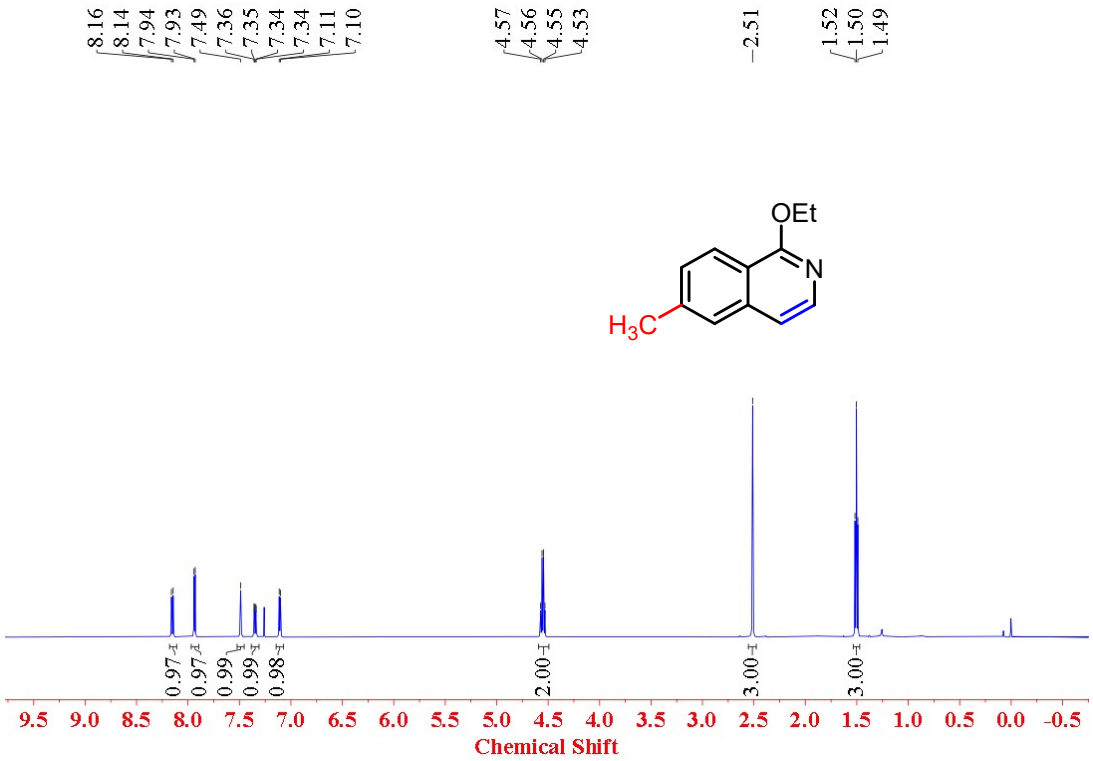
3f ^{1}H NMR



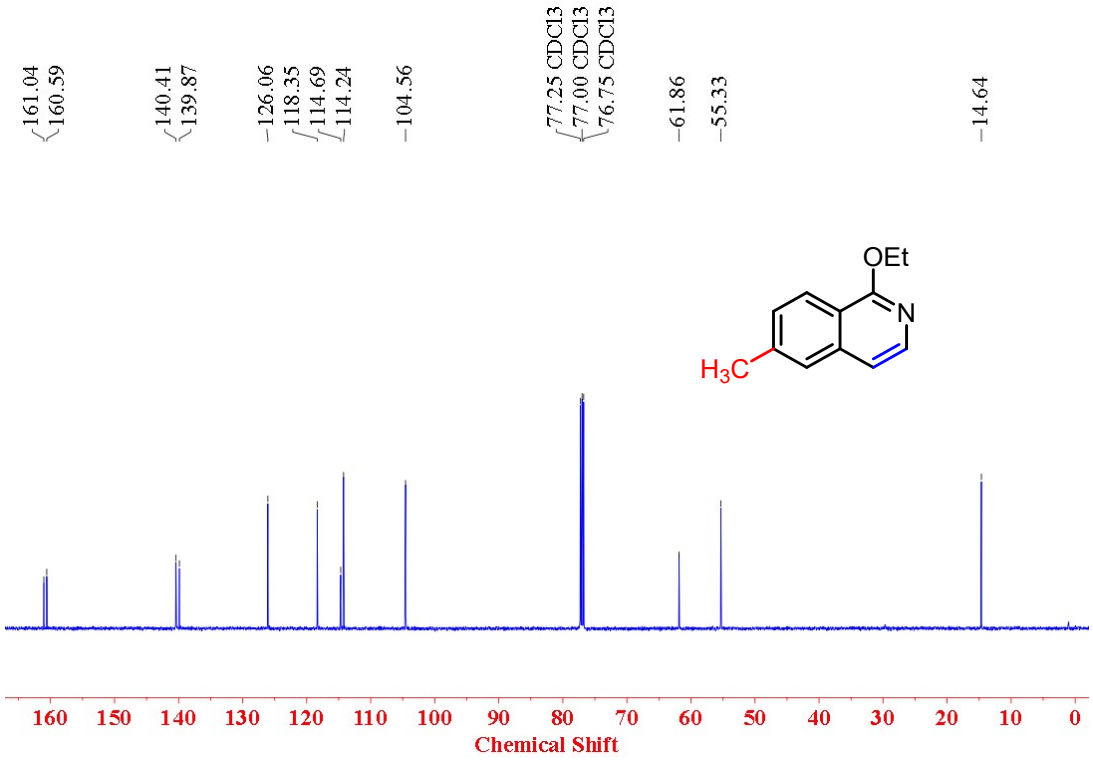
3f ^{13}C NMR



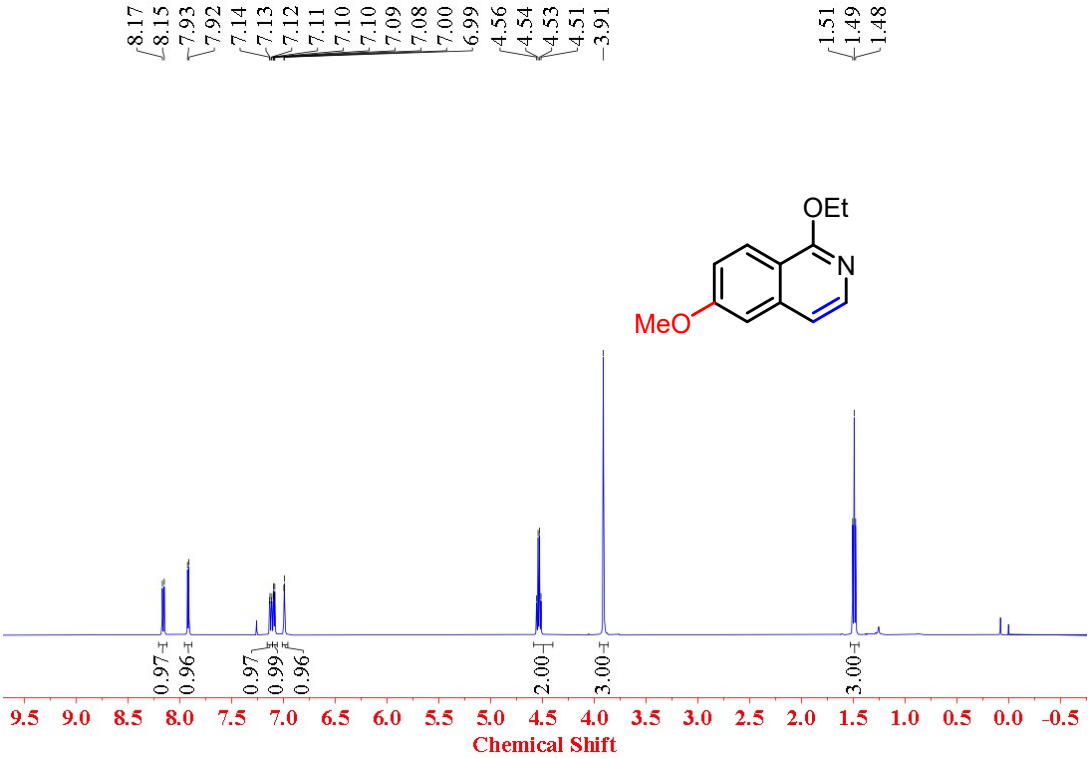
3g ^{1}H NMR



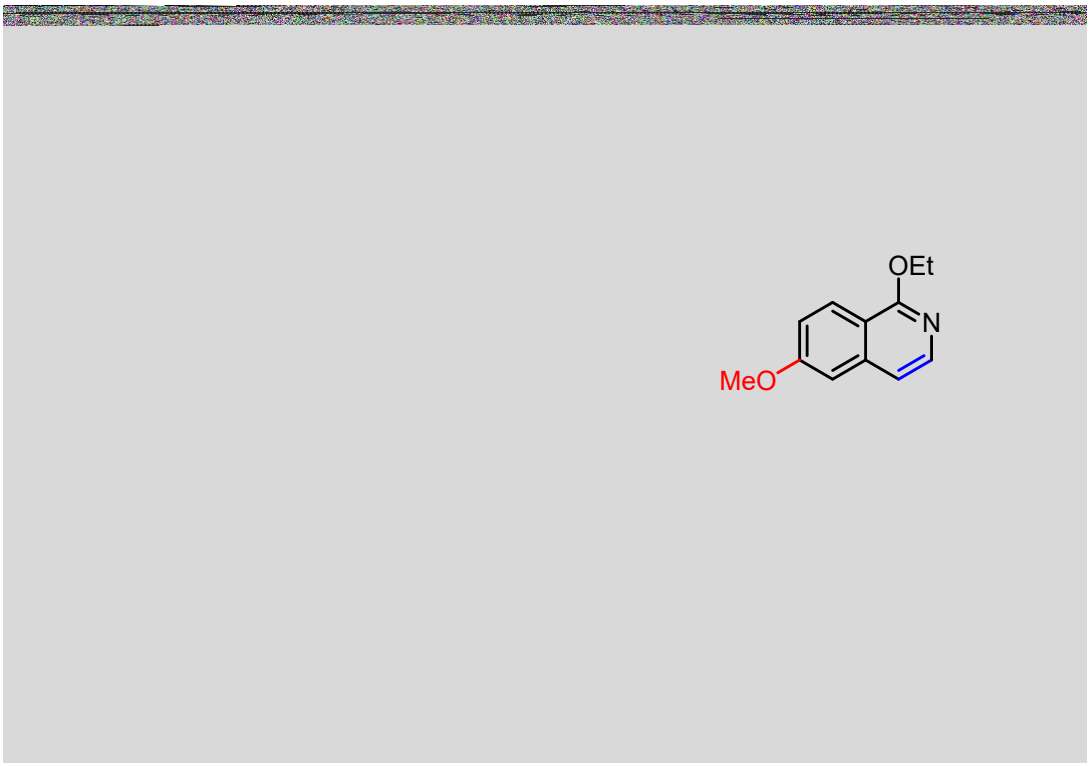
3g ^{13}C NMR



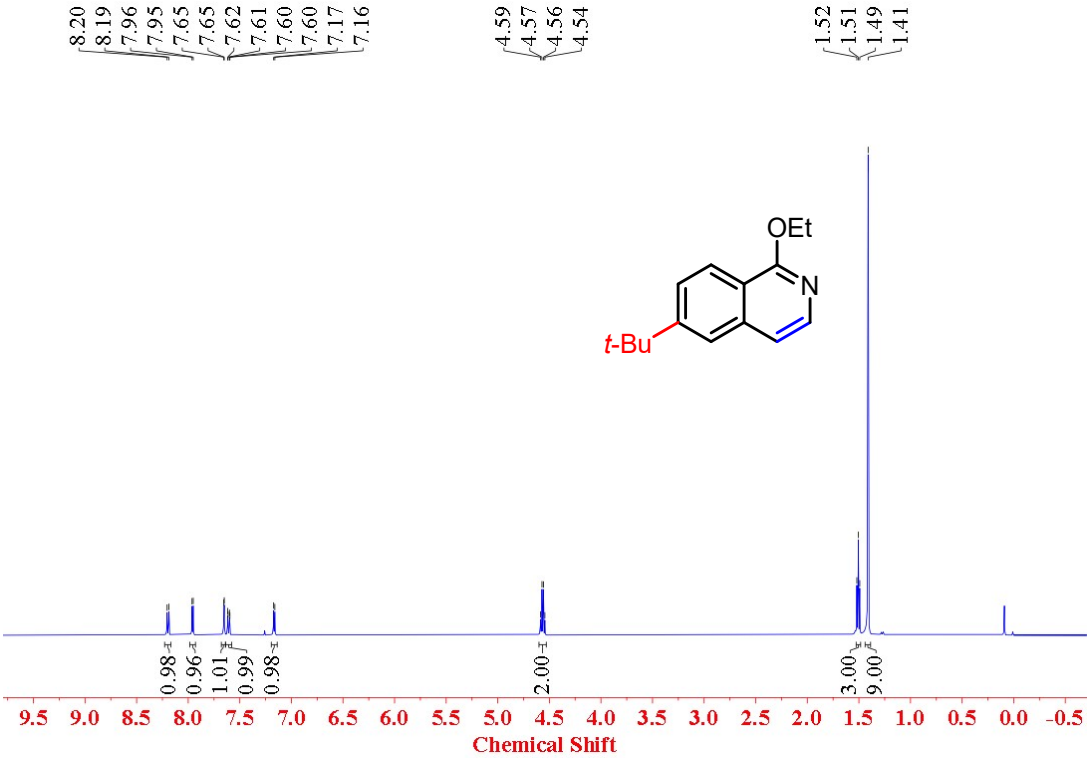
3h ^{1}H NMR



3h ^{13}C NMR



3i ^{1}H NMR



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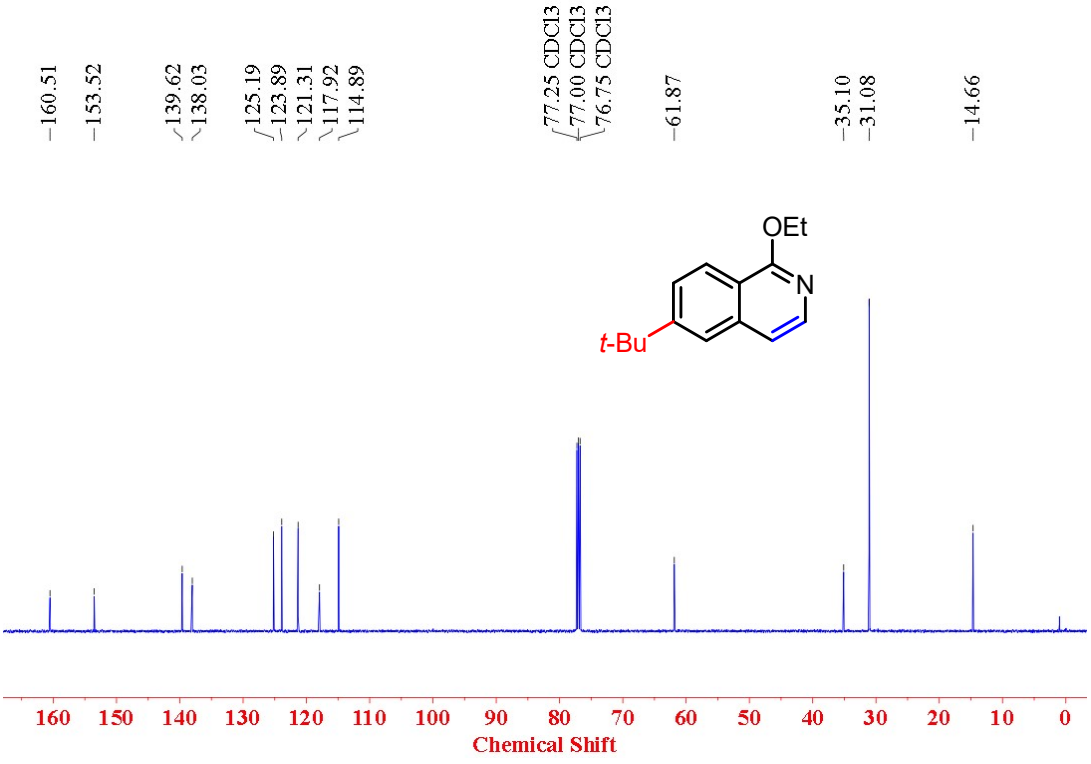

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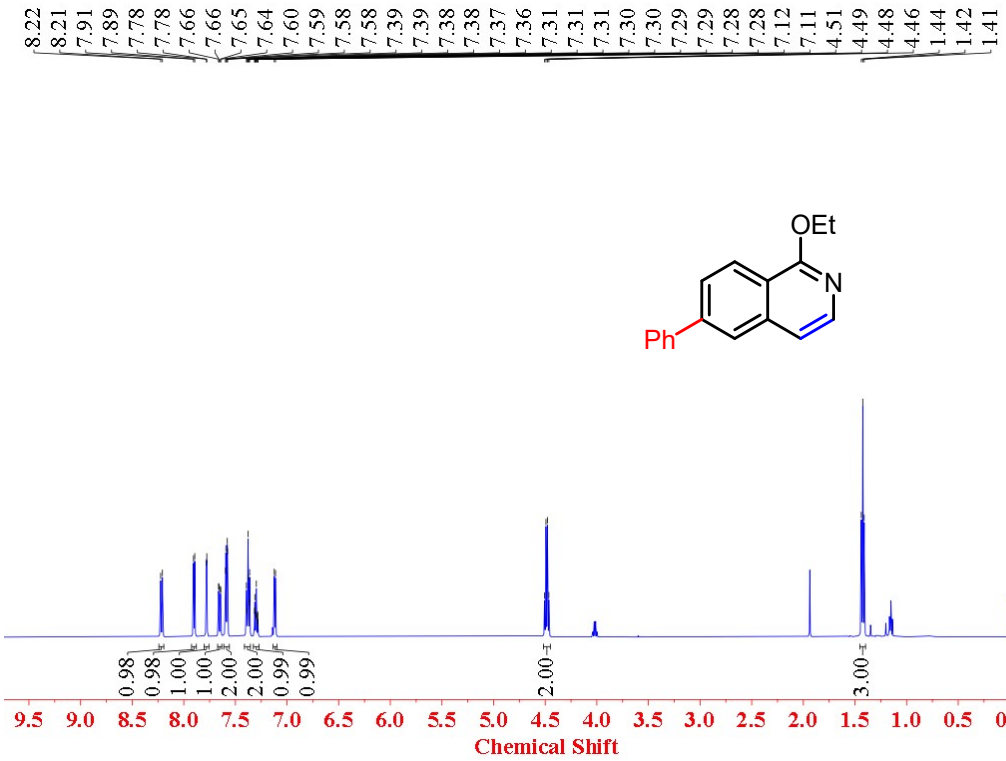
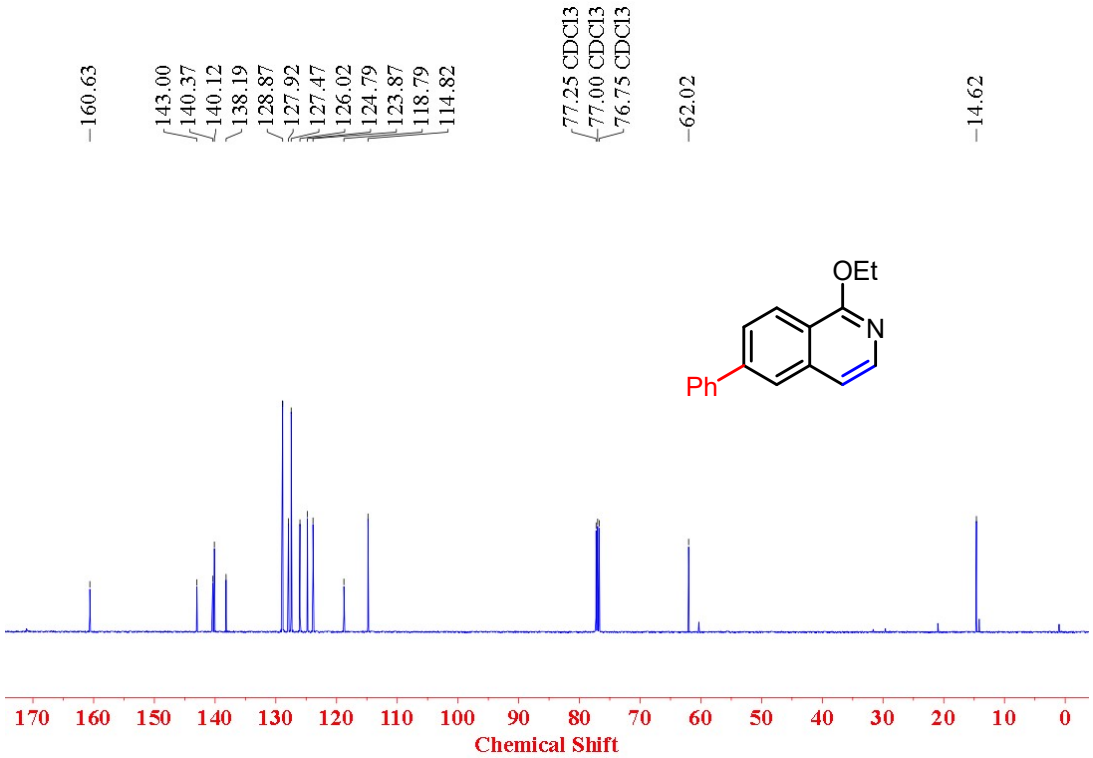
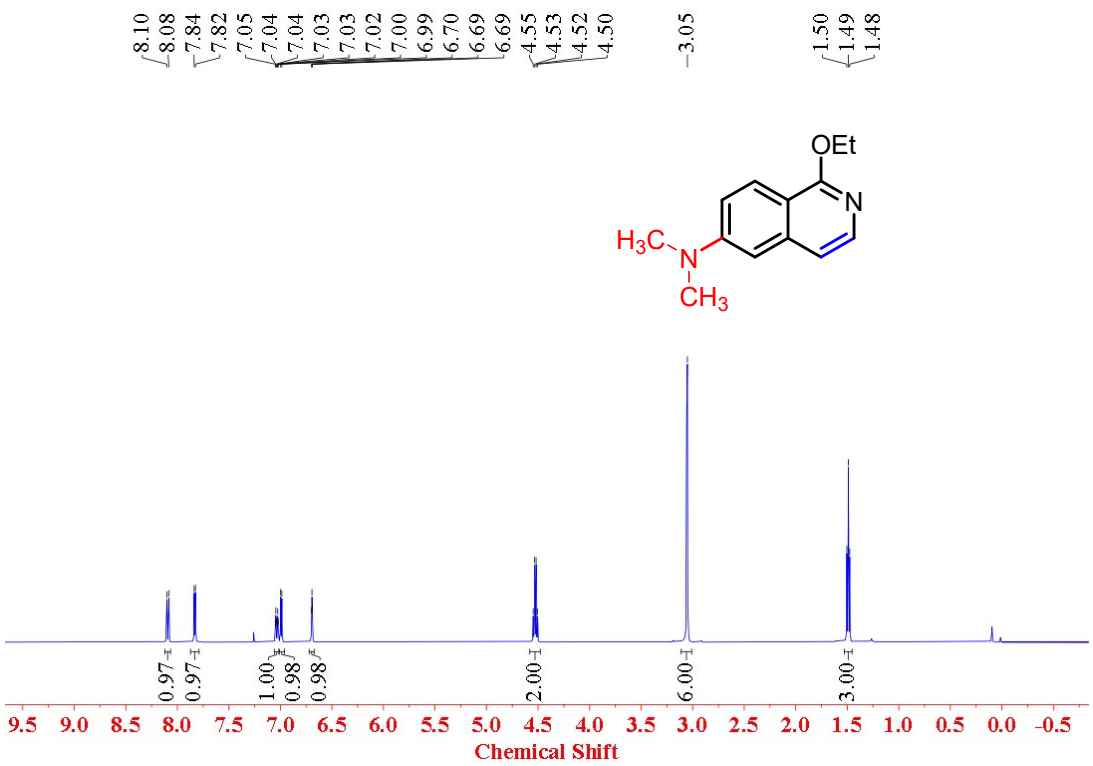


3j ^{13}C NMR



3k ^{1}H NMR



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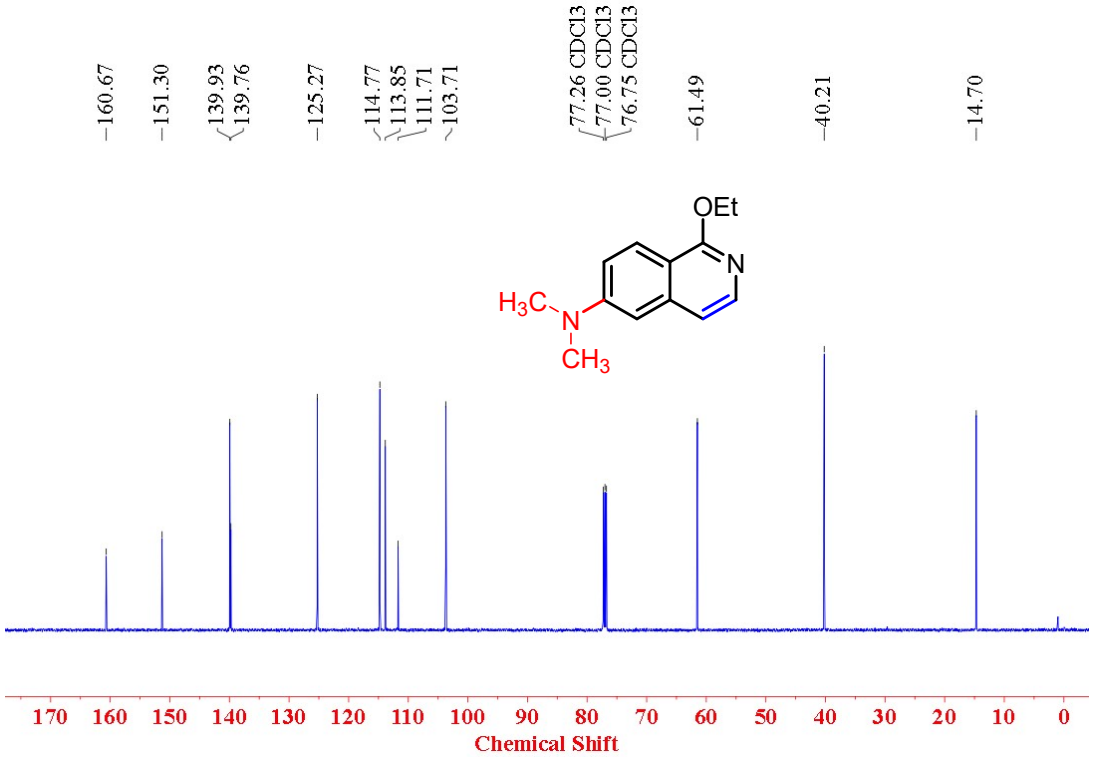
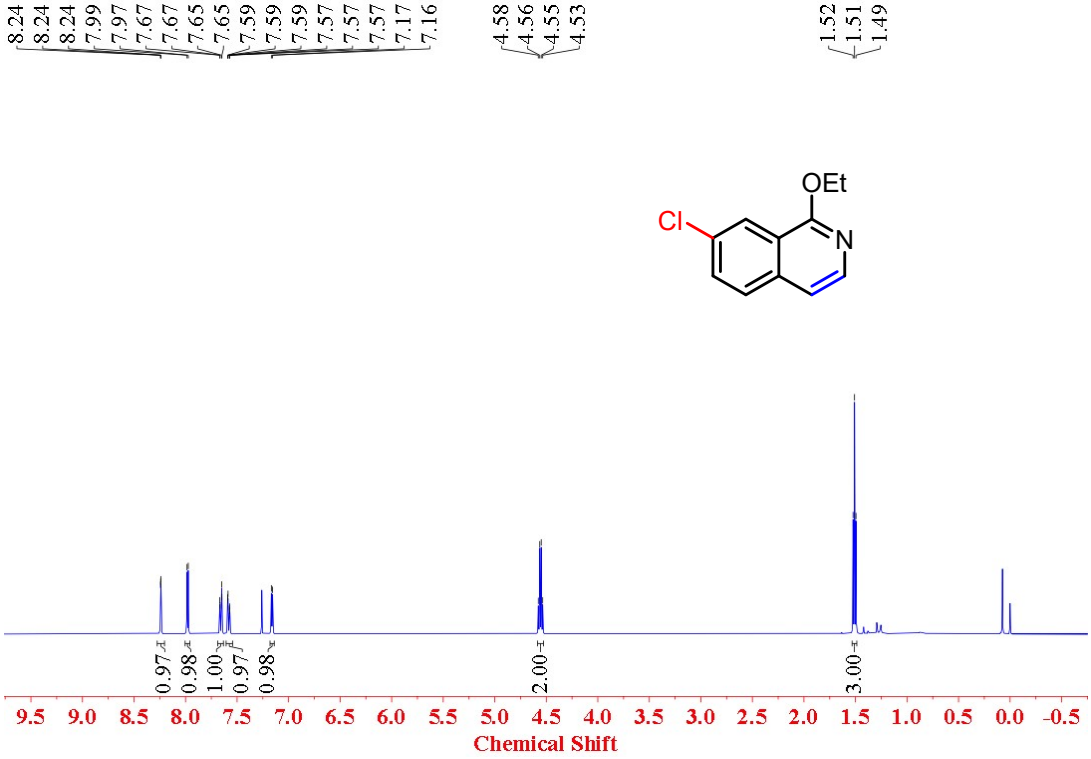


3m ^{1}H NMR



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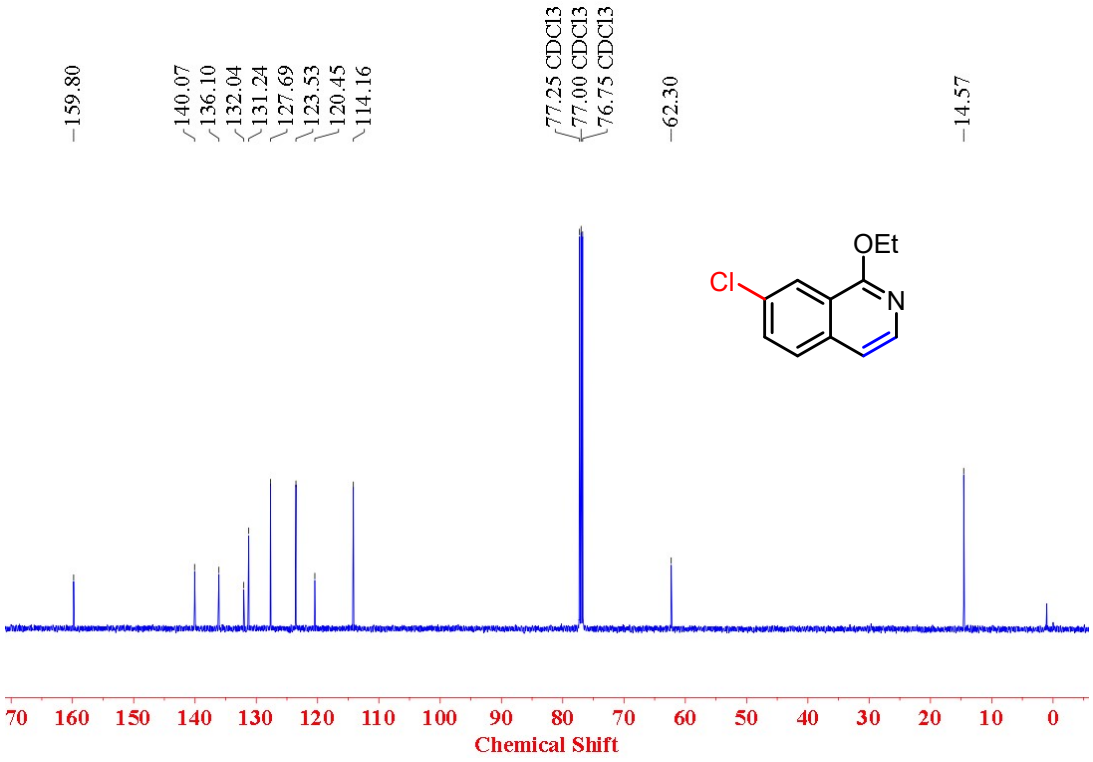
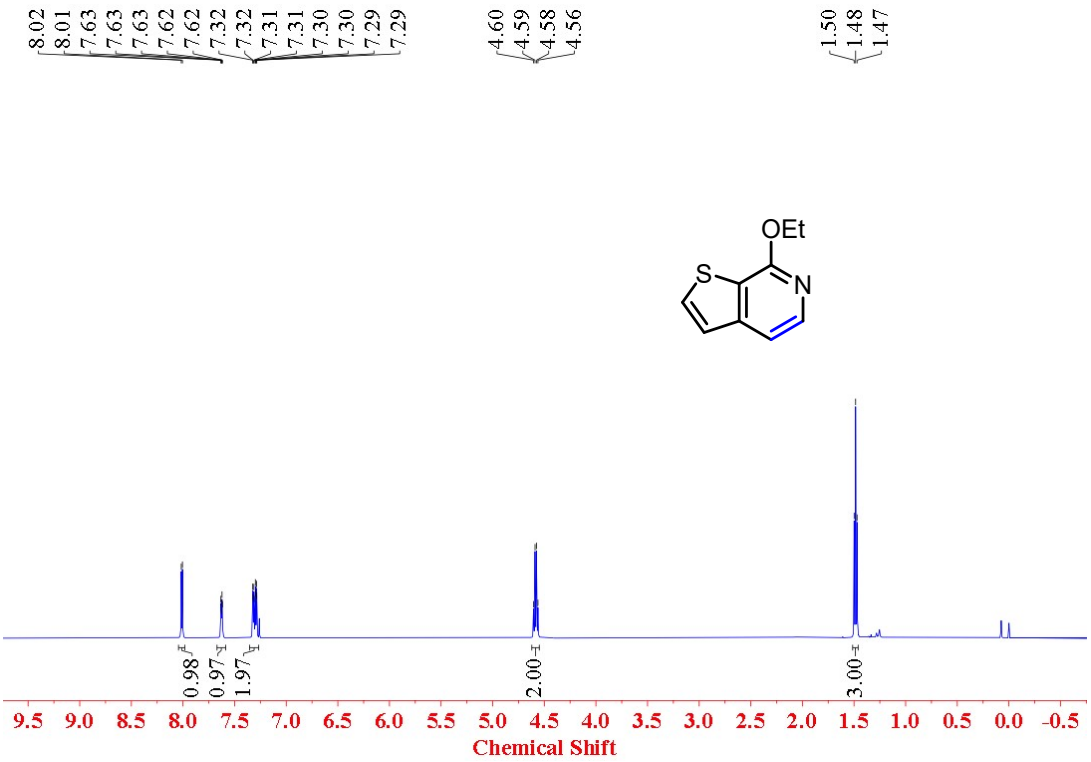
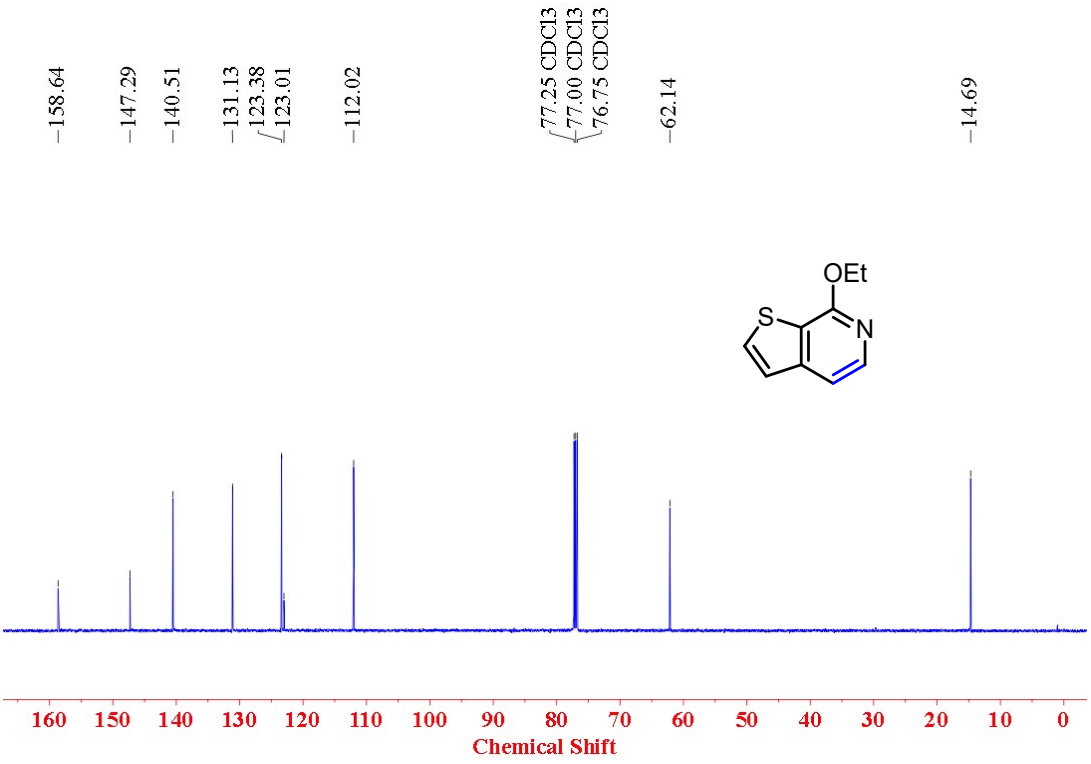


3o ^{1}H NMR



3o ^{13}C NMR



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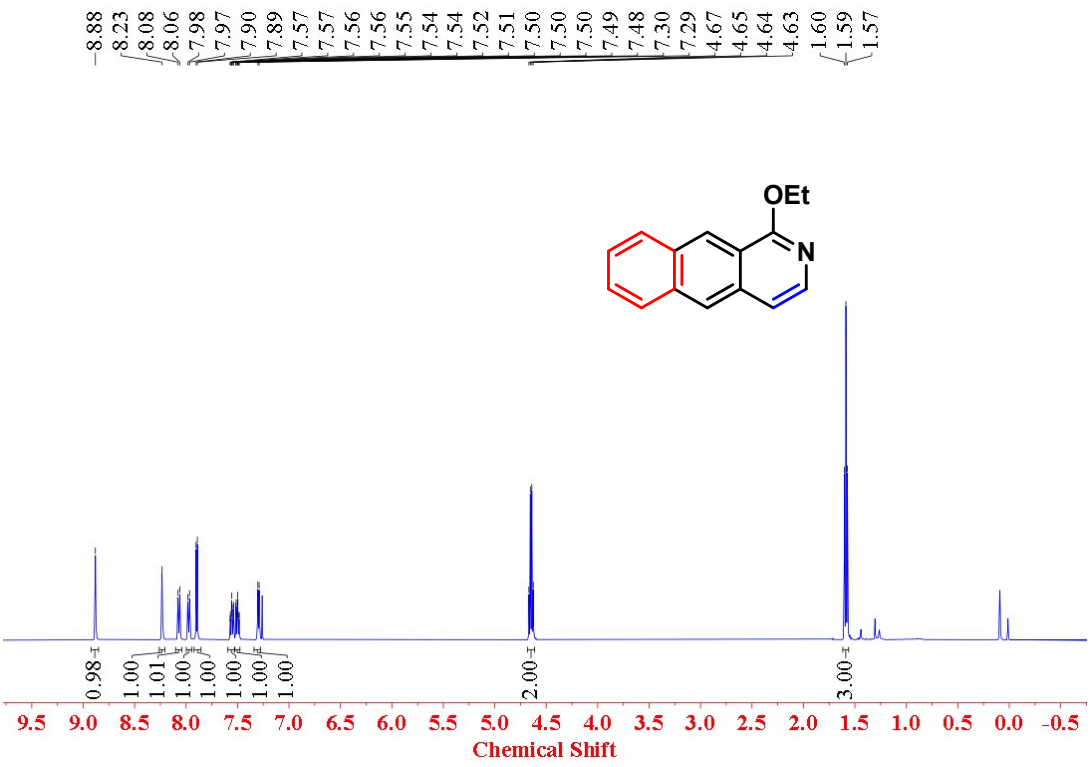
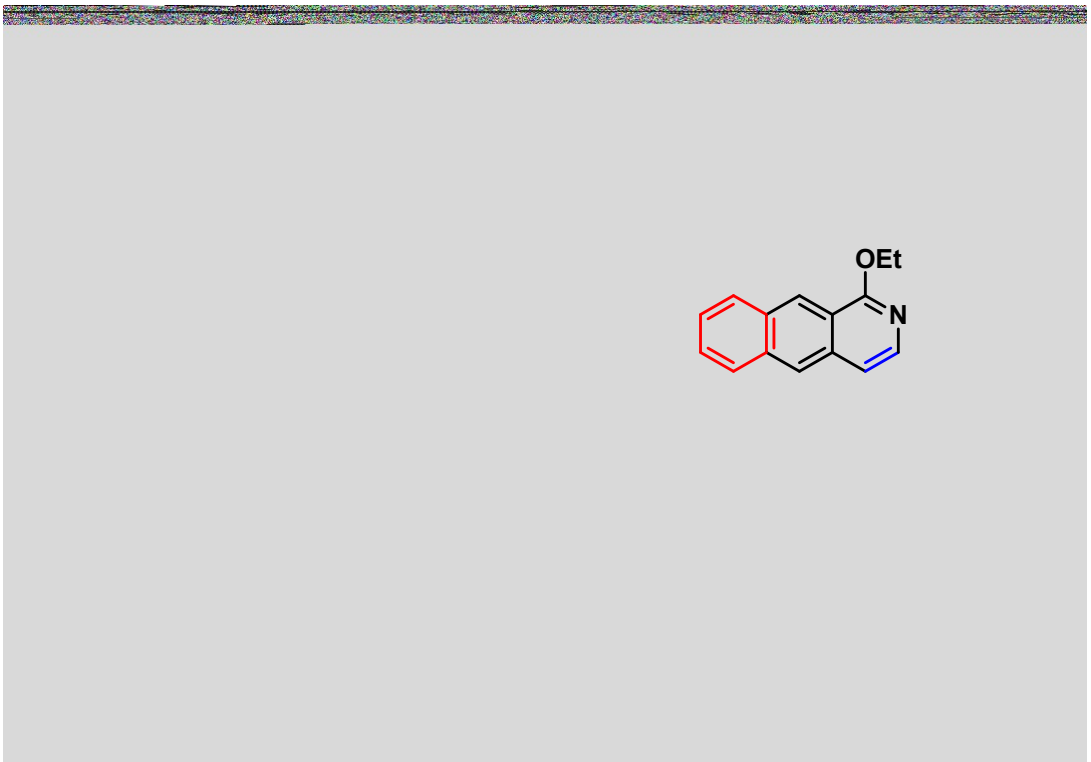
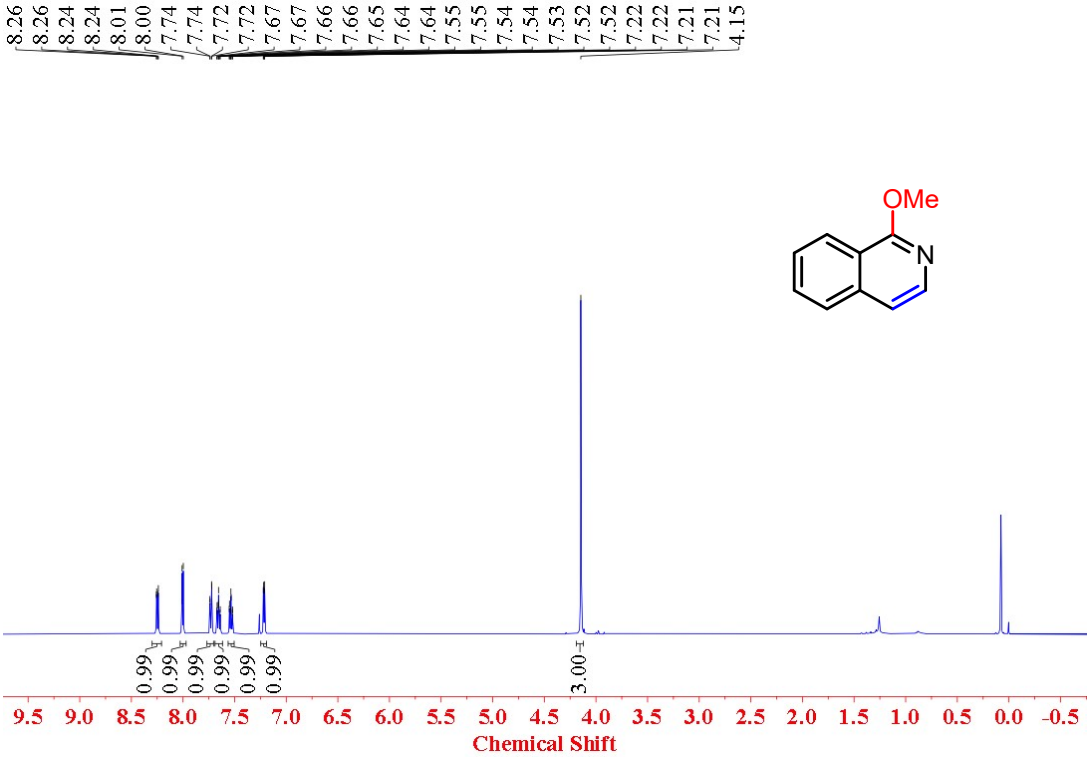


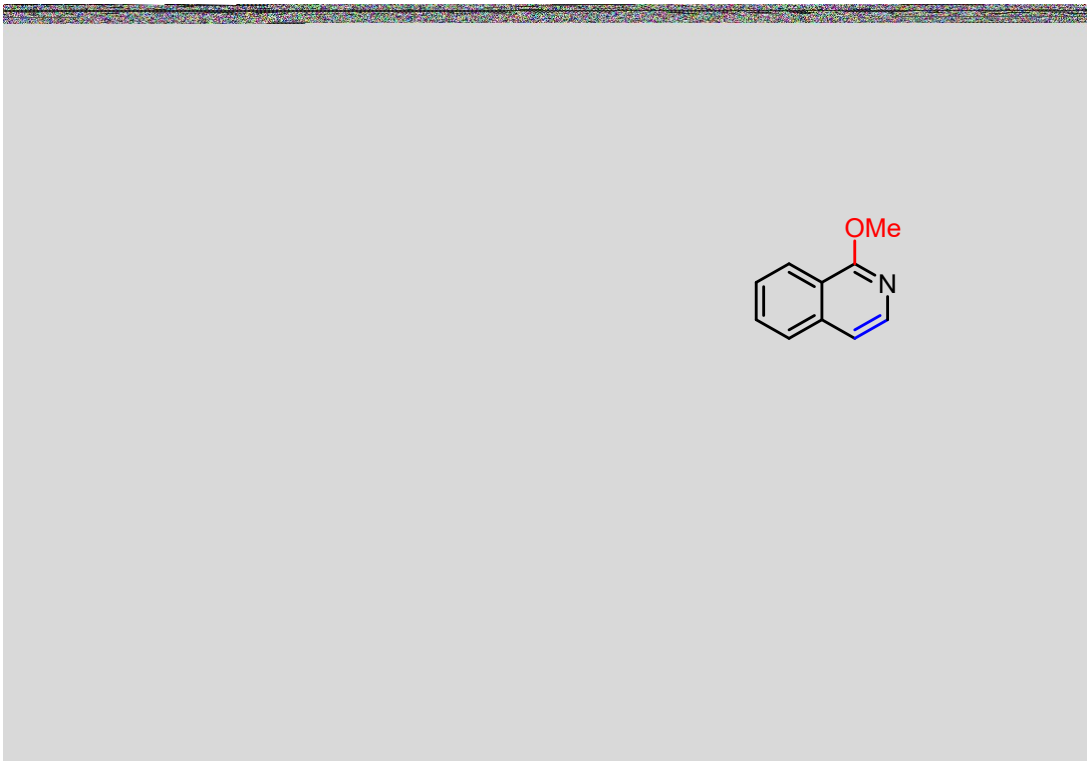
3p ^{13}C NMR



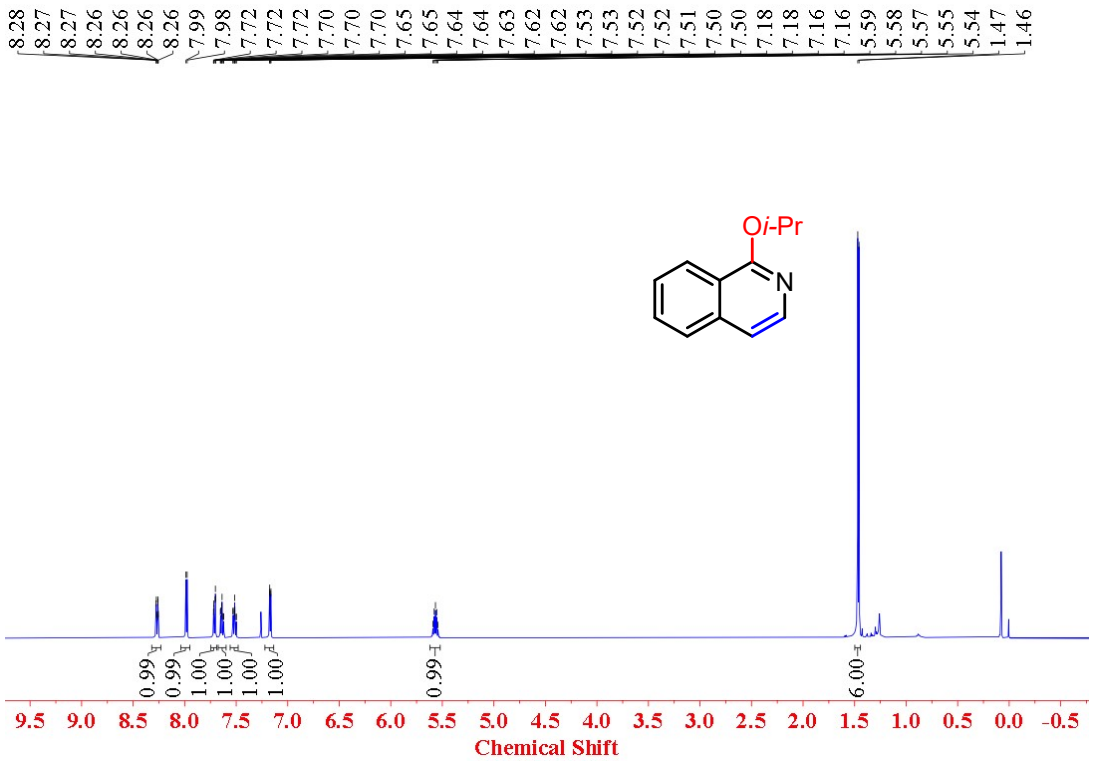
3q ^{1}H NMR



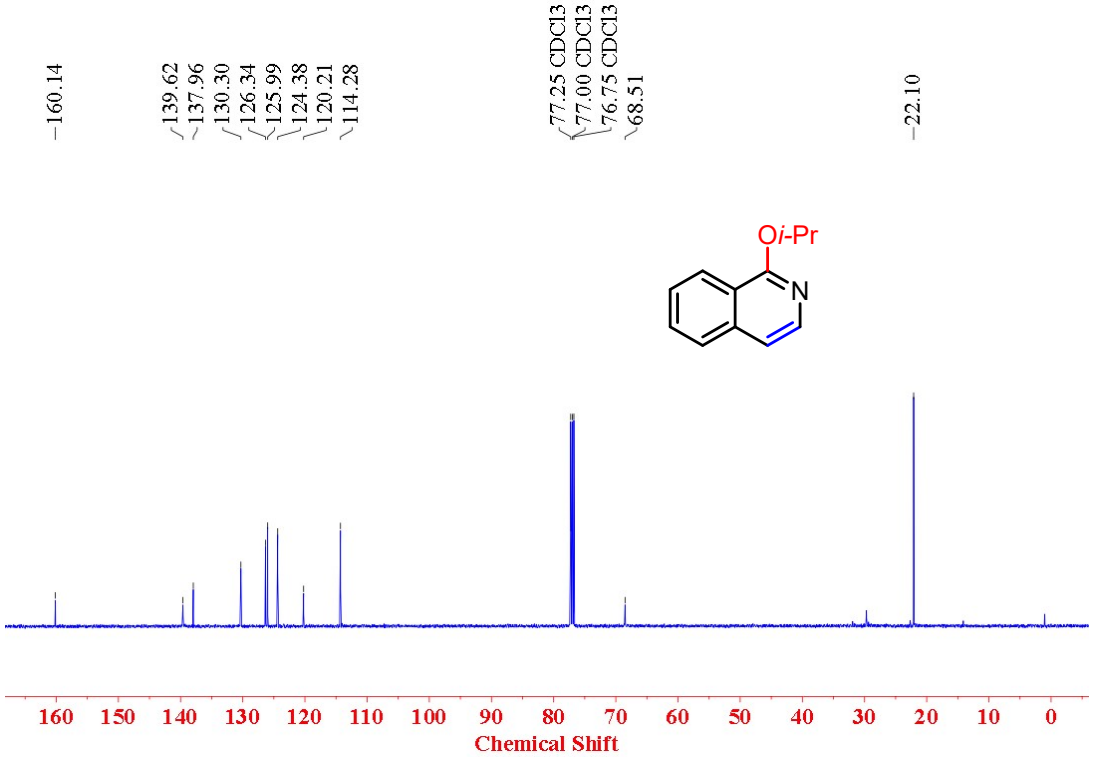
3q ^{13}C NMR



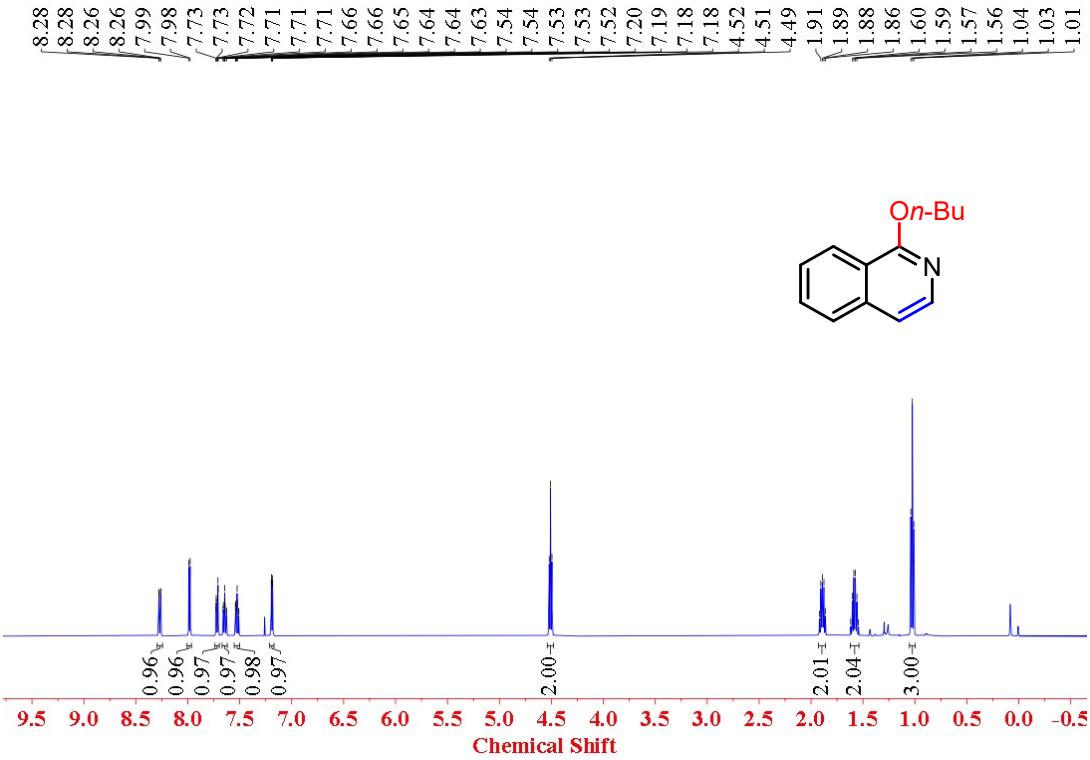
3r ^{1}H NMR



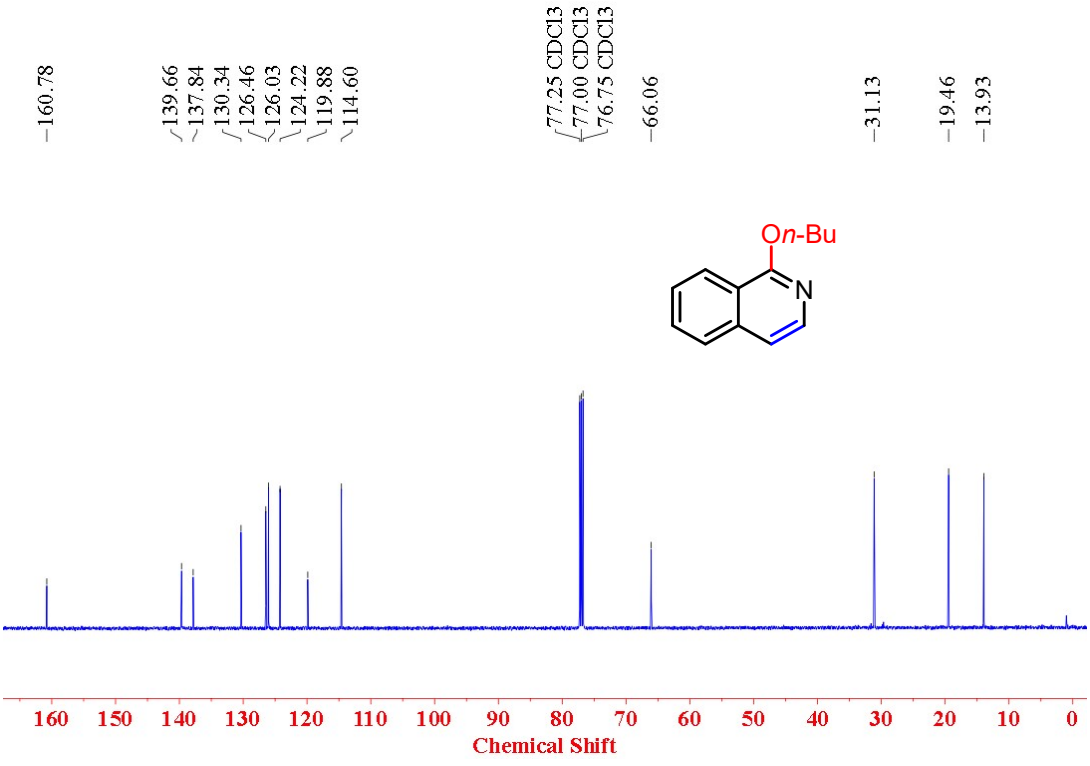
3r ^{13}C NMR



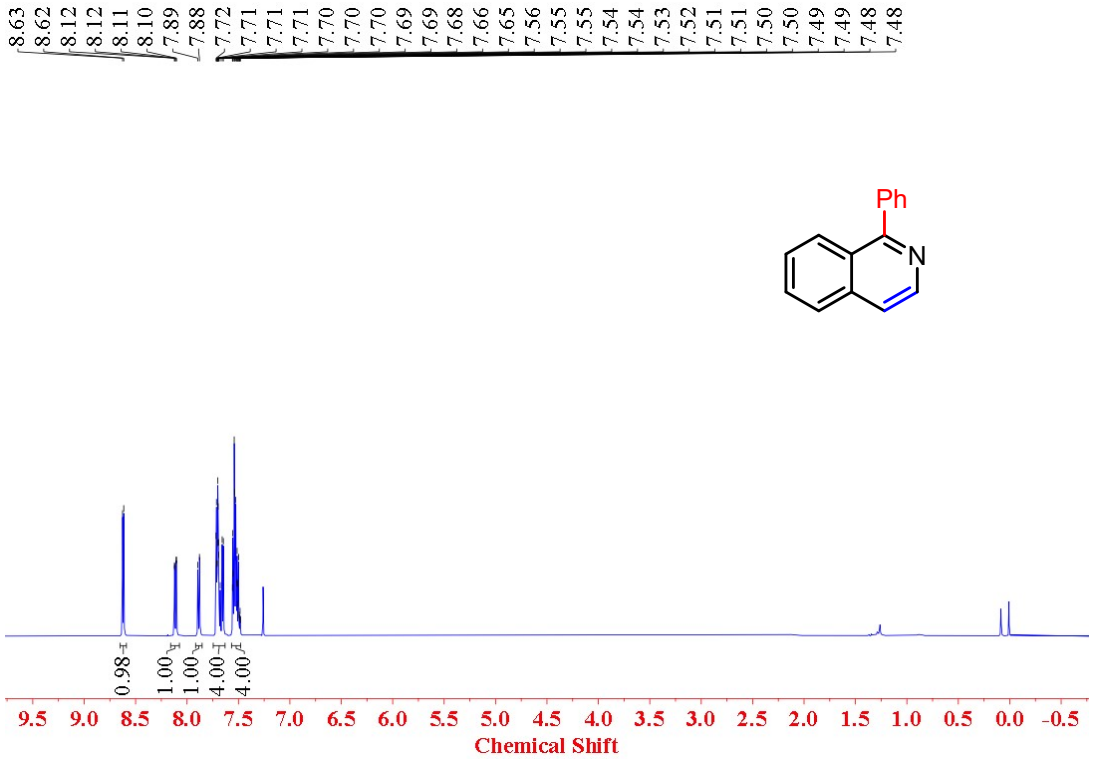
3s ^{1}H NMR



3s ^{13}C NMR



3t ^{1}H NMR



3t ^{13}C NMR