Supporting Information

Redox-Neutral Functionalization of α-Csp^3-H Bond of Secondary Cyclic Amines: Highly Atom-Economic Strategy for N-Arylative/Formal Cross-Dehydrogenative Couplings

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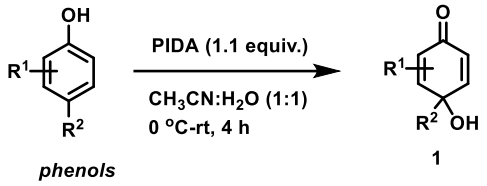
[1] General

^{1}H and ^{13}C nuclear magnetic resonance spectra were recorded on Bruker Avance III 400 spectrometer at 25 °C. The chemical shifts in ^{1}H NMR and ^{13}C{^{1}H} NMR spectra are reported in parts per million (ppm) and are referenced to the residual solvent signal as the internal standard; ^{1}H NMR spectra ($CDCl_3$ δ 7.26 ppm), ^{13}C ($CDCl_3$ δ 77.16). Coupling constants (*J*) are quoted in Hz. Splitting patterns are denoted as "s" for singlet; "d" for doublet; "t" for triplet; "q" for quartet; "sext" for sextet; "sept" for septet; "m"for multiplet, "br" for broad; "dt" for doublet of triplets; "td" for triplet of doublets, and "app" for apparent. Assignment of proton signals was assisted by ^{1}H, ^{1}H COSY, HSQC and HMBC experiments. ^{13}C NMR spectra were recorded at 100 MHz using a Bruker AVANCE 400. High Resolution Mass Spectra (HRMS) were recorded on Q-TOF mass spectrometer at SAIF department in CSIR-CDRI, Lucknow, India. Reactions were performed using borosil sealed tube vial or Schlenk tube. Temperature mentioned for any reaction is corresponding to the oil bath temperature. Column chromatography was done in 60-120 Å or 100-200 Å mesh silica gel of Merck Company. All solvents were distilled for purification in column chromatography. Reagents and starting materials were used as received from company. THF and toluene were distilled from sodium benzophenone ketyl and other solvents were distilled under standard procedures. Starting materials, *p*-quinols were synthesized with the procedures that reported in literature.[1]

[2] Preparation of starting materials

Oxidative dearomatization of phenol to p-quinol was reported with many oxidizing agents; such as Oxone, Hypervalent iodine (III) reagents (most common are PIDA and PIFA), dimethyldioxirane (DMDO), H_2O_2, *m*-CPBA, $O_2/P(OEt)_3$, and molecular oxygen in the presence of photosensitizer. Considering all these methods, photo catalyzed oxidation with singlet oxygen seems to be attractive. However, it requires reductive work up with dimethylsulphide or PPh_3, generate eventual DMSO or triphenylphosphineoxide as by-products. Among all, PIDA has been commonly employed for this particular transformation due to the quick reaction time and user friendly. PIFA is relatively more reactive, however costlier. We used PIDA for the synthesis of *p*-quinols.



phenols **1**

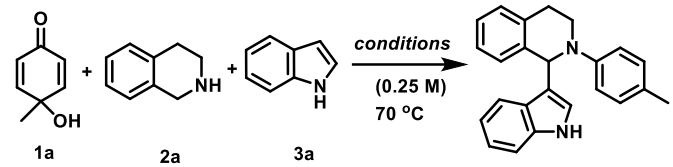
The general experimental procedures for the preparation of *p*-quinol were followed as reported previously. (Diacetoxyiodo)benzene (PIDA; 1.1 equiv.) was added portion wise to a stirred solution of 4-substituted phenol (1-10 mmol; 1.0 equiv.) in acetonitrile and water (2:1; 10 mL/mmol) at 0 °C. The solution was allowed to warm to room temperature for 2-4 h. After the completion of reaction (monitored by TLC), reaction mixture was quenched with saturated aqueous $NaHCO_3$ solution to neutralize the acidic reaction mixture and extracted with EtOAc for three times. The combined organic phases were washed with brine, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (20-30% EtOAc in hexane) to give pure *p*-quinol **1**. Spectral data for *p*-quinols matched that provided in the literature.[1]

[3] Evaluation of redox-neutral conditions for CDC reactions with Indole (Table 1)

General Procedure for optimization (Table 1): To the reaction vial/Schlenk tube, a mixture of *p*-quinol (**1a**, 0.5 mmol), THIQ (0.6 mmol), and indole (0.5-0.6 mmol) was taken in different solvents (0.4 M). It was degassed and refilled with nitrogen and then heated at 70 °C with/without an additive (RCO_2H; 10-20 mol%) in the presence of an internal standard, 4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dien-1-one (0.25 mmol). After the completion of reaction as monitored by TLC with reference to *p*-quinol, solvent was evaporated and yields were calculated on the basis of ^1H NMR. The product **4a** was purified by silica gel column chromatography and isolated yield was mentioned in parentheses (entries 12 and 13).
R_f 0.5; 20% EtOAc in hexane; eluted with 10% EtOAc in hexane.

Entry 14; Reaction mixture was heated at 70 °C in toluene in open air.

Table 1.



1a (0.5 mmol) 2a (1.2 equiv) 3a (1.2 equiv) 4a

run	solvent	additive (mol%)	time (h)	yield (4a, %)[a]
1	Neat	-	24	39
2	CH_3CN	-	36	62
3	THF	-	48	36
4	HFIP	-	36	nd
5	DCE	-	36	nd
6	MeOH	-	18	49
7	Dioxane	-	48	nd
8	Toluene	-	12	60
9[b]	Toluene	-	12	59
10	Toluene	$PhCO_2H$ (20)	6	77
11	Toluene	AcOH (20)	6	98
12[b]	Toluene	AcOH (20)	6	98 (81)[c]
13[b]	Toluene	AcOH (10)	9	94 (78)[c]
14[b,d]	Toluene	AcOH (20)	10	83 (72)[c]

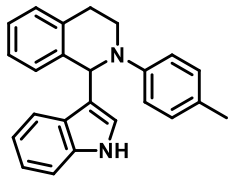
[a]NMR yield was calculated using 4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dien-1-one as an internal standard. [b]1.0eqiv indol was used. [c]Isolated yields are mentioned in parentheses. [d]Open air reaction. nd = not determined due to complex reaction mixture.

[4] Synthesis and spectral data for indole addition products (4)

General Procedure (run 12, Table 1):

To the Schlenk tube, a mixture of *p*-quinol (**1a**, 0.8 mmol), THIQ/amine (0.96 mmol), indole (0.8 mmol) and acetic acid (0.16 mmol) was taken in toluene (2.0 mL). Reaction tube was degassed and refilled with nitrogen and then heated at 70 °C for specified reaction time as mentioned for different entities. After the completion of reaction with reference to *p*-quinol, (monitored by TLC under UV or I_2), toluene was evaporated under reduced pressure and loaded to the pad of silica gel for purification. Yields are calculated with respect to corresponding *p*-quinols (**1**).

1-(1H-Indol-3-yl)-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (4a): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), indole (95.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) at 70 °C for 6 h to furnish **4a** as a white solid (222.0 mg, 0.66 mmol, 81% yield).



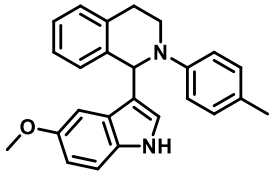
4a

Purification: Silica gel Flash chromatography, eluted with 4% EtOAc in hexane
R_f 0.5 (10% EtOAc in hexane)

The spectral data was completely in match with previously reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (bs, 1H), 7.50 (d, *J* = 7.9 Hz, 1H), 7.23–7.18 (m, 1H), 7.17 (s, 1H), 7.16–7.07 (m, 4H), 7.05–6.94 (m, 3H), 6.90 (d, *J* = 7.2 Hz, 2H), 6.45 (d, *J* = 2.3 Hz, 1H), 6.07 (s, 1H), 3.57–3.49 (m, 2H), 3.07–2.95 (m, 1H), 2.72 (dd, *J* = 16.2, 3.7 Hz, 1H), 2.23 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 147.8, 137.4, 136.6, 135.6, 129.7, 128.9, 128.1, 127.7, 126.7, 126.6, 125.6,

124.2, 122.1, 120.2, 119.6, 119.5, 116.6, 111.0, 56.9, 42.7, 26.5, 20.4.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{24}H_{23}N_2$: 339.1861, found 339.1848

1-(5-Methoxy-1H-indol-3-yl)-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (4b): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), 5-methoxy-1H-indole (119.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4b** as a white solid (232.0 mg, 0.63 mmol, 78% yield).

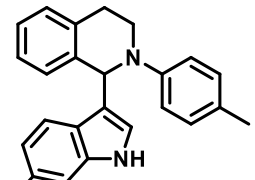


4b

Purification: Silica gel Flash chromatography, eluted with 70% $CHCl_3$ in hexane R_f 0.50 (80% $CHCl_3$ in hexane).

The spectral data was completely in match with previously reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (bs, 1H), 7.26–7.14 (m, 5H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.95 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 2.2 Hz, 1H), 6.80 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.56 (d, *J* = 2.1 Hz, 1H), 6.08 (s, 1H), 3.67 (s, 3H), 3.60–3.53 (m, 2H), 3.14–3.02 (m, 1H), 2.80 (dt, *J* = 16.3, 4.0 Hz, 1H), 2.27 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 153.9, 148.2, 137.7, 135.5, 131.6, 129.7, 128.9,128.1, 128.1, 127.1, 126.6, 125.7, 125.2, 118.7, 117.3, 112.3, 111.6, 102.0, 57.4, 55.7, 42.5, 27.0, 20.5.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{25}H_{25}N_2O$: 369.1967, found 369.1955

1-(6-Fluoro-1H-indol-3-yl)-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (4c): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), 6-fluoro-1H-indole (109.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4c** as a white solid (201.0 mg, 0.57 mmol, 70% yield).

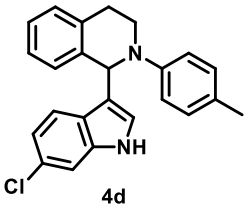


4c

Purification: Silica gel Flash chromatography, eluted with 45% $CHCl_3$ in hexane R_f 0.50 (70% $CHCl_3$ in hexane).

Melting Point: 183-185 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (s, 1H), 7.45–7.39 (m, 1H), 7.24 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.23–7.14 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.98 (dd, *J* = 9.6, 2.3 Hz, 1H), 6.94 (d, *J* = 8.6 Hz, 2H), 6.83–6.74 (m, 1H), 6.56 (d, *J* = 1.5 Hz, 1H), 6.07 (s, 1H), 3.62–3.51 (m, 2H), 3.12–3.01 (m, 1H), 2.76 (dt, *J* = 16.4, 4.1 Hz, 1H), 2.27 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 159.9 (d, $^1J_{C\text{-}F}$ = 237.2 Hz), 147.8, 137.2, 136.5 (d, $^3J_{C\text{-}F}$ = 12.4 Hz), 135.5, 129.7, 129.0, 128.1, 126.7, 125.7, 124.5 (d, $^4J_{C\text{-}F}$ = 3.4 Hz), 123.3, 121.0 (d, $^3J_{C\text{-}F}$ = 10.7 Hz), 119.6, 116.9, 108.3 (d, $^2J_{C\text{-}F}$ = 24.3 Hz), 97.2 (d, $^2J_{C\text{-}F}$ = 25.8 Hz), 56.9, 42.7, 26.4, 20.4.
^{19}F NMR (376 MHz, $CDCl_3$): δ -121.11
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{24}H_{22}N_2F$: 357.1767, found 357.1763.

1-(6-Chloro-1H-indol-3-yl)-2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinoline (4d): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), 6-chloro-1H-indole (123.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4d** as a white solid (229.0 mg, 0.61 mmol, 76% yield).

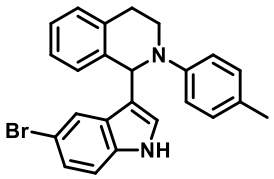


4d

Purification: Silica gel Flash chromatography, eluted with 50% $CHCl_3$ in hexane R_f 0.50 (70% $CHCl_3$ in hexane).

The spectral data was completely in match with previously reported data.[2]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (bs, 1H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.24 (d, *J* = 7.4 Hz , 1H), 7.22–7.14 (m, 3H), 7.06 (d, *J* = 8.3 Hz, 2H), 6.98 (dd, *J* = 8.5, 1.8 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.57 (d, *J* = 1.6 Hz, 1H), 6.06 (s, 1H), 3.60–3.52 (m, 2H), 3.12–3.01 (m, 1H), 2.78 (dt, *J* =16.3, 4.0 Hz, 1H), 2.28 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 147.8, 137.1, 136.9, 135.5, 129.7, 129.0, 128.2, 128.1, 128.0, 126.7, 125.7, 125.3, 124.8, 121.2, 120.3, 119.6, 117.0, 110.9, 56.9, 42.8, 26.6, 20.4.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{24}H_{22}N_2Cl$: 373.1472 , found 373.1468.

1-(5-Bromo-1H-indol-3-yl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (4e): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), 5-bromo-1H-indole (159.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) at 120 °C for 12 h to furnish **4e** as a white solid (252.7 mg, 0.61 mmol, 75% yield).

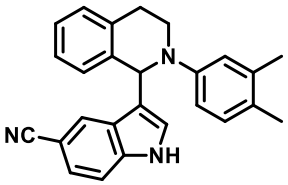


4e

Purification: Silica gel Flash chromatography, eluted with 70% $CHCl_3$ in hexane R_f 0.50 (80% $CHCl_3$ in hexane).

The spectral data was completely in match with previously reported data.[3]
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (bs, 1H), 7.54 (d, *J* =1.8 Hz, 1H), 7.26–7.13 (m, 6H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.60–6.54 (m, 1H), 6.01 (s, 1H), 3.58–3.51 (m, 2H), 3.11–3.06 (m, 1H), 2.78 (dt, *J* = 16.3, 4.0 Hz, 1H), 2.28 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 148.0, 137.1, 135.4, 135.1, 129.7, 129.0, 128.7, 128.4, 128.0, 126.7, 125.7, 125.5, 125.0, 122.9, 119.2, 117.6, 113.0, 112.3, 57.2, 42.9, 26.6, 20.4.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{24}H_{22}N_2Br$: 417.0966, found 417.0967, 419.0942

3-(2-(3,4-Dimethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1H-indole-5-carbonitrile (4f): General procedure was followed with 4-hydroxy-3,4-dimethylcyclohexa-2,5-dien-1-one (112.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), 1H-indole-5-carbonitrile (115.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4f** as a white solid (198.5 mg, 0.53 mmol, 65% yield).



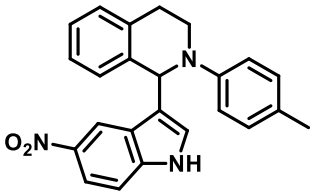
4f

Purification: Silica gel Flash chromatography, eluted with 1% in EtOAc in CH_2Cl_2
R_f 0.40 (5% EtOAc in CH_2Cl_2).

Melting Point: 195-197 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (s, 1H), 7.73 (s, 1H), 7.37–7.33 (m, 2H), 7.23–7.15 (m, 4H), 7.00 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 2.5 Hz, 1H), 6.73 (dd, *J* = 8.1 Hz, 2.5, 1H), 6.70 (d, *J* = 2.3 Hz, 1H), 6.05 (s, 1H), 3.60–3.52 (m, 1H), 3.50–3.41 (m, 1H), 3.13–3.02 (m, 1H), 2.77 (d, *J* = 16.5, 4.1 Hz, 1H), 2.23 (s, 3H),

2.20 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 148.2, 138.2, 137.3, 136.7, 135.4, 130.3, 129.1, 128.0, 126.9, 126.5, 126.4, 126.3, 125.8, 125.0, 120.8, 120.3, 119.4, 115.1, 111.8, 102.6, 57.1, 42.9, 26.7, 20.3, 18.8.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{24}N_3$: 378.1970, found 378.1955.

1-(5-Nitro-1H-indol-3-yl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (4g): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), 5-nitro-1H-indole (162.0 mg, 0.97 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4g** as a white solid (222.0 mg, 0.58 mmol, 72% yield).

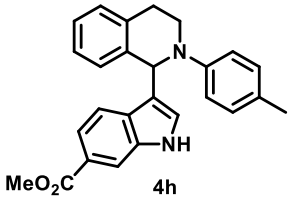


4g

Purification: Silica gel Flash chromatography, eluted with 100% in $CHCl_3$
R_f 0.40 (100% in $CHCl_3$).

Melting Point: 205-207 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (bs, 1H), 8.33 (d, *J* = 1.8 Hz, 1H), 8.04 (dd, *J* = 8.7, 2.4 Hz, 1H), 7.31 (d, *J* = 9.0 Hz, 1H), 7.24–7.18 (m, 4H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.77 (d, *J* = 1.8 Hz, 1H), 6.07 (s, 1H), 3.54–3.48 (m, 2H), 3.13–3.04 (m, 1H), 2.86 (dt, *J* = 16.4, 4.2 Hz, 1H), 2.27 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 141.8, 139.4, 136.7, 135.4, 129.8, 129.4, 129.0, 127.9, 127.1, 127.0, 126.0, 125.9, 121.7, 118.1, 117.8, 110.9, 57.4, 43.4, 27.1, 20.4.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{24}H_{22}N_3O_2$: 384.1712, found 384.1705.

Methyl 3-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1H-indole-6-carboxylate (4h): General procedure was followed **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), methyl 1H-indole-6-carboxylate (175.0 mg, 0.97mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4h** as a white solid (198.0 mg, 0.50 mmol, 62% yield).

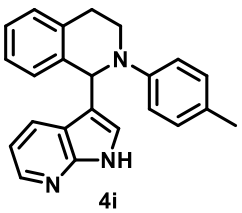


4h

Purification: Silica gel Flash chromatography, eluted with 1% in EtOAc in CH_2Cl_2
R_f 0.50 (5% EtOAc in CH_2Cl_2).

Melting Point: 203-205 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (bs, 1H), 8.07 (d, *J* = 0.8 Hz, 1H), 7.69 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.50 (d, *J* = 8.6 Hz, 1H), 7.26–7.22 (m, 1H), 7.22–7.14 (m, 3H), 7.05 (d, *J* = 8.2 Hz, 2H), 6.93 (d, *J* = 8.6 Hz, 2H), 6.76 (d, *J* = 1.8 Hz, 1H), 6.09 (s, 1H), 3.92 (s, 3H), 3.60–3.50 (m, 2H), 3.14–3.00 (m, 1H), 2.89 (dt, *J* = 16.5, 4.0 Hz, 1H), 2.27 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 168.2, 147.8, 137.1, 135.9, 135.5, 130.2, 129.7, 129.0, 128.3, 128.0, 127.5, 126.7, 125.8, 123.7, 120.6, 119.8, 117.1, 113.4, 56.9, 51.9, 42.9, 26.7, 20.4.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{25}N_2O_2$: 397.1916, found 397.1901.

1-(1H-Pyrrolo[2,3-b]pyridin-3-yl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (4i): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), 1H-pyrrolo[2,3-b]pyridine (118.0 mg, 0.97 mmol), and acetic acid (9 µL, 0.16 mmol) at 100 °C for 13 h to furnish **4i** as a white solid (170.0 mg, 0.50 mol, 62% yield).

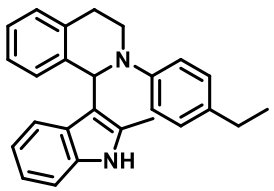


4i

Purification: Silica gel Flash chromatography, eluted with 25% EtOAc in $CHCl_3$
R_f 0.50 (50% EtOAc in $CHCl_3$).

Melting Point: 218-220 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.16 (bs, 1H), 8.31–8.21 (m, 1H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.26–7.22 (m, 1H), 7.21–7.16 (m, 3H), 7.06 (d, *J* = 8.2 Hz, 2H), 6.96–6.88 (m, 3H), 6.75 (s, 1H), 6.08 (s, 1H), 3.58–3.51 (m, 2H), 3.16–2.92 (m, 1H), 2.80 (dt, *J* = 16.3, 3.6 Hz, 1H), 2.28 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 149.0, 147.9, 142.6, 136.9, 135.5, 129.7, 129.0, 128.8, 128.3, 128.0, 126.8, 125.7, 124.7, 119.5, 117.5, 117.1, 115.6, 57.4, 42.7, 26.8, 20.4.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{23}H_{22}N_3$: 340.1814, found 340.1804.

2-(4-Ethylphenyl)-1-(2-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (4j): General procedure was followed with 4-ethyl-4-hydroxycyclohexa-2,5-dien-1-one (112.0 mg, 0.81 mmol), THIQ (123 µL, 0.97 mmol), 2-methyl-1H-indole (106.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4j** as a white solid (187.0 mg, 0.51 mmol, 63% yield).

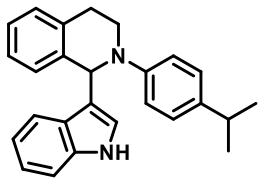


4j

Purification: Silica gel Flash chromatography, eluted with 50% $CHCl_3$ in hexane R_f 0.20 (50% $CHCl_3$ in hexane).

Melting Point: 128-130 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (bs, 1H), 7.20 (s, 2H), 7.17 (s, 1H), 7.12–7.04 (m, 4H), 7.02 (d, *J* = 7.9 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 7.6 Hz, 1H), 5.90 (s, 1H), 3.73–3.63 (m, 1H), 3.62–3.53 (m, 1H), 3.13–3.03 (m, 2H), 2.57 (q, *J* = 7.6 Hz, 2H), 2.00 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 138.3, 136.4, 135.3, 134.9, 133.4, 128.7, 128.6, 128.2, 128.1, 126.2, 126.0, 120.7, 120.1, 119.4, 119.3, 113.5, 110.0, 57.6, 46.6, 28.2, 28.0, 15.7, 12.2.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{27}N_2$: 367.2174, found 367.2159.

1-(1H-Indol-3-yl)-2-(4-isopropylphenyl)-1,2,3,4-tetrahydroisoquinoline (4k): General procedure was followed with 4-hydroxy-4-isopropylcyclohexa-2,5-dien-1-one (123.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), indole (95.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4k** as a white solid (160.0 mg, 0.44 mmol 54% yield).

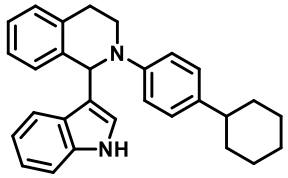


4k

Purification: Silica gel Flash chromatography, eluted with 70% $CHCl_3$ in hexane R_f 0.20 (80% $CHCl_3$ in hexane).

Melting Point: 137-139 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (bs, 1H), 7.52 (d, *J* = 7.5 Hz, 1H), 7.31–7.21 (m, 2H), 7.20–7.05 (m, 6H), 7.04–6.91 (m, 3H), 6.56 (s, 1H), 6.11(s, 1H), 3.65–3.50 (m, 2H), 3.14–2.96 (m, 1H), 2.89–2.69 (m, 2H), 1.21 (s, 6H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 138.8, 137.6, 136.6, 135.6, 128.9, 128.1, 127.1, 126.6, 125.6, 124.3, 122.1, 120.2, 119.6, 119.5, 116.3, 111.0, 57.0, 42.5, 33.1, 26.6, 24.2.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{27}N_2$: 367.2174, found 367.2170.

2-(4-Cyclohexylphenyl)-1-(1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (4l): General procedure was followed with 1-hydroxy-[1,1'-bi(cyclohexane)]-2,5-dien-4-one (155.5 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), indole (95.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4l** as a white solid (187 mg, 0.46 mmol, 57% yield).



4l

Purification: Silica gel Flash chromatography, eluted with 6% EtOAc in hexane R_f 0.40 (5% EtOAc in hexane).

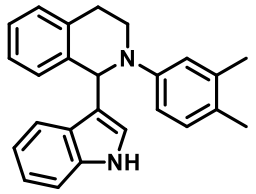
Melting Point: 170-172 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (bs, 1H), 7.51 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.25–7.23 (m, 1H), 7.18–7.14 (m, 2H), 7.14–7.11 (m, 2H), 7.06 (d, *J* = 8.6 Hz, 2H), 7.02–6.98 (m, 1H), 6.94 (d, *J* = 8.7 Hz, 2H), 6.55 (d, *J* = 1.7 Hz, 1H), 6.10 (s, 1H), 3.60–3.54 (m, 2H), 3.15–2.97 (m, 1H), 2.76 (dt, *J* = 16.3, 4.3 Hz, 1H), 2.48–2.31 (m, 1H), 1.89–1.66 (m, 6H), 1.36 (t, *J* = 9.6 Hz, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 138.2, 137.6, 136.6, 135.6, 128.9, 128.1, 127.4, 126.6, 125.6, 124.3, 122.0, 120.2, 119.6, 119.5, 116.2, 111.0, 57.1, 43.6, 42.4, 34.7, 27.0, 26.6, 26.3.

HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{29}H_{31}N_2$: 407.2487, found 407.2468.

2-(3,4-dimethylphenyl)-1-(1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline (4m): General procedure was followed with 4-hydroxy-3,4-dimethylcyclohexa-2,5-dien-1-one (112.0 mg, 0.81 mmol), THIQ (123.0 µL, 0.97 mmol), indole (95.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4m** as a white solid (162 mg, 0.46, 57% yield).



4m

Purification: Silica gel Flash chromatography, eluted with 5% EtOAc in hexane R_f 0.30 (5% EtOAc in hexane).

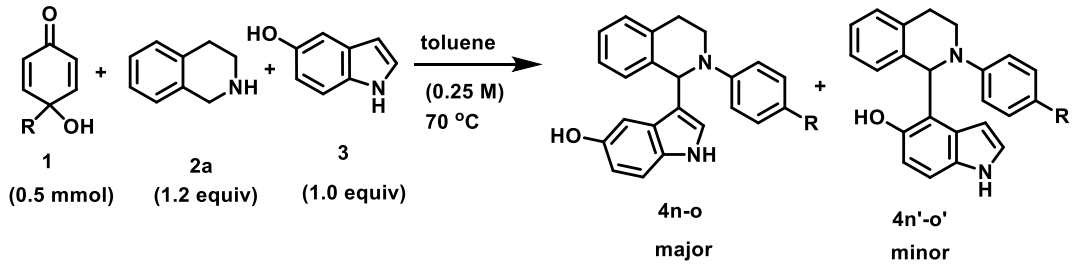
Melting Point: 108-110 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (bs, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.25–7.18 (m, 2H), 7.18–7.08 (m, 4H), 7.0 (d, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.85 (s, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 6.48 (s, 1H), 6.10 (s, 1H), 3.62–3.49 (m, 2H), 3.11–2.95 (m, 1H), 2.71 (dt, *J* = 16.3, 3.7 Hz, 1H), 2.19 (s, 3H), 2.15 (s, 3H).

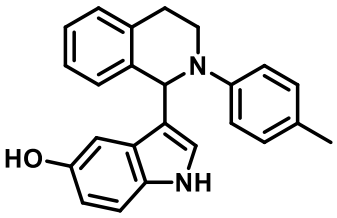
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 137.6, 137.2, 136.6, 135.7, 130.3, 129.0, 128.2, 126.7, 126.6, 126.5, 125.7, 124.4, 122.1, 120.3, 119.6, 119.5, 118.1, 113.9, 111.1, 56.8, 42.6, 26.5, 20.4, 18.8.

HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{25}H_{25}N_2$: 353.2018, found 353.2002.

Reaction with 5-hydroxyindole: Under the optimized conditions, a mixture of CDC products was obtained at C3 (**4n** and **4o**) and C4 positions (**4n'** and **4o'**).



3-(2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1H-indol-5-ol (4n): General procedure was followed with **1a** (112.0 mg, 0.81 mmol), THIQ (123 µL, 0.97 mmol), 1H-indol-5-ol (108.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4n** as a white solid (173.0 mg, 0.49 mmol, 60% yield).
The minor regio-isomer **4n'** was isolated as a white solid (19.0 mg, 0.053 mmol, *ca* 6% yield).



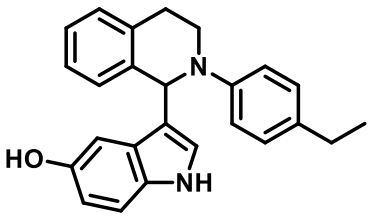
4n

Purification: Silica gel Flash chromatography, both the regioisomers were eluted with 12% EtOAc in hexane

Major isomer (4n): R_f 0.30 (30% EtOAc in hexane).
Melting Point: 136-138 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (bs, 1H), 7.25 (like d, *J* = 7.8 Hz, 1H), 7.20–7.17 (m, 2H), 7.16–7.12 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = Hz 1.6, 1H), 6.74 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.54 (d, *J* = 1.6 Hz, 1H), 6.03 (s, 1H), 4.61 (bs,1H), 3.63–3.56 (m, 2H), 3.12–2.99 (m, 1H), 2.74 (dt, *J* = 16.4, 3.9 Hz, 1H), 2.27(s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ149.4, 147.8, 137.3, 135.5, 131.8, 129.8, 129.0, 128.2, 127.9, 127.3, 126.6, 125.6, 125.4, 118.8, 116.8, 111.9, 111.7, 104.6, 56.8, 42.6, 26.3, 20.4.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{24}H_{23}N_2O$: 355.1810, found 355.1805.

Minor isomer (4n'): R_f 0.40 (30% EtOAc in hexane).
Melting Point: 198-200 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.72 (bs, 1H), 8.0 (bs, 1H), 7.21 (d, *J* = 8.3 Hz, 3H), 7.18–7.09 (m, 2H), 7.06 (d, *J* = 8.6 Hz, 1H), 6.98–6.91 (m, 4H), 6.65 (dd, *J* = 2.5, 2.4 Hz, 1H), 6.61 (d, *J* = 8.6 Hz, 1H), 6.00 (s, 1H), 3.70–3.63 (m, 1H), 3.59–3.48 (m, 1H), 3.32 (td, *J* = 11.8, 3.1 Hz, 1H), 2.96 (dt, *J* = 15.9, 3.0 Hz, 1H), 2.17 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 147.9, 137.0, 134.3, 133.4, 130.1, 129.6, 128.3, 127.7, 126.4, 125.0, 122.7, 117.0, 113.4 110.8, 99.8, 61.5, 54.9, 30.6, 20.7.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{24}H_{23}N_2O$: 355.1810, found 355.1805.

3-(2-(4-Ethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1H-indol-5-ol (4o): General procedure was followed with 4-ethyl-4-hydroxycyclohexa-2,5-dien-1-one (112.0 mg, 0.81 mmol), THIQ (123 µL, 0.97 mmol), 1H-indol-5-ol (108.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4o** as a white solid (188 mg, 0.51 mmol, 63% yield).
The minor regio-isomer **4o'** was isolated as (18 mg, 0.050 mmol, 6% yield).



4o

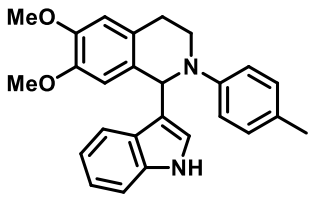
Purification: Silica gel Flash chromatography, both the regioisomers were eluted with 12% EtOAc in hexane

Major isomer (4o): R_f 0.30 (30% EtOAc in hexane).
Melting Point: 143-145 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (bs, 1H), 7.25 (like d, *J* = 7.6 Hz, 1H), 7.21–7.13 (m, 4H), 7.09 (d, *J* = 8.3 Hz, 2H), 6.98 (d, *J* = 8.4 Hz, 2H), 6.90 (d, *J* = 1.9 Hz, 1H), 6.74 (dd, *J* = 8.6 Hz, 2.1, 1H), 6.54 (bs, 1H), 6.05 (s, 1H), 3.64–3.57 (m, 2H), 3.12–3.01 (m, 1H), 2.74 (dt, *J* = 16.3, 4.0 Hz, 1H), 2.58 (q, *J* = 7.5, Hz 2H), 1.22(t, *J* = 7.5 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 148.0, 131.8, 129.0, 128.6, 128.2, 127.2, 126.6, 125.7, 125.5, 118.8, 116.7, 111.9, 111.7, 104.6, 56.8, 42.5, 27.9, 26.3, 15.8.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{25}H_{25}N_2O$: 369.1967, found 369.1967.

Minor isomer (4o'): R_f 0.40 (30% EtOAc in hexane).
Melting Point: 201-203 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.73 (bs, 1H), 8.02 (bs, 1H), 7.23 (d, *J* = 7.8 Hz, 3H), 7.18–7.06 (m, 3H), 6.98 (d, *J* = 8.3 Hz, 2H), 6.95 (d, *J* = 5.9 Hz, 2H), 6.66 (s, 1H), 6.60 (d, *J* = 8.5 Hz, 1H), 6.00 (s, 1H), 3.67 (dd, *J* = 11.8, 3.8 Hz, 1H), 3.53 (td, *J* = 16.7, 4.5 Hz, 1H), 3.32 (td, *J* = 11.4, 2.1 Hz, 1H), 2.96 (d, *J* = 16.2 Hz, 1H), 2.48 (q, *J* = 7.7 Hz, 2H), 1.12 (t, *J* = 7.7 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 148.0, 140.4, 137.0, 133.5, 130.1, 128.9, 128.3, 128.3, 127.7, 126.4, 126.4, 125.0, 122.6, 117.0, 113.4, 110.7, 99.9, 61.4, 54.9, 30.6, 28.1, 15.1.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{25}H_{25}N_2O$: 369.1967, found 369.1962.

1-(1H-Indol-3-yl)-6,7-dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (4p): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (187.6 mg, 0.97 mmol), indole (95.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4p** as a white solid (257.8 mg, 0.65 mmol, 80% yield).

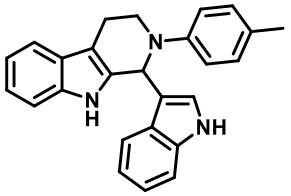


4p

Purification: Silica gel Flash chromatography, eluted with 20% EtOAc in hexane R_f 0.60 (30% EtOAc in hexane).

Melting Point: 186-188 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (bs, 1H), 7.55 (d, *J* = 7.9 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.18 (dd, *J* = 8.0 7.1 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 7.3 Hz, 1H), 7.00 (dd, *J* = 8.1, 8.0 Hz, 2H), 6.76 (s, 1H), 6.65 (s, 1H), 6.60 (d, *J* = 2.0 Hz, 1H), 6.06 (s, 1H), 3.88 (s, 3H), 3.81 (s, 3H), 3.62–3.51 (m, 2H), 3.05–2.94 (m, 1H), 2.61 (dt, *J* = 16.1, 3.8 Hz, 1H), 2.29 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 147.9, 147.7, 147.0, 136.6, 129.7, 129.1, 128.0, 127.5, 126.8, 124.4, 122.1, 120.2, 119.6, 117.2, 111.6, 111.1, 111.0, 56.4, 56.0, 55.9, 42.4, 25.6, 20.4.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{27}N_2O_2$: 399.2073, found 399.2064.

1-(1H-Indol-3-yl)-2-(p-tolyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (4q): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), Triptoline (172.2 mg, 0.97 mmol), indole (95.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4q** as a white solid (155 mg, 0.41 mmol, 51% yield).

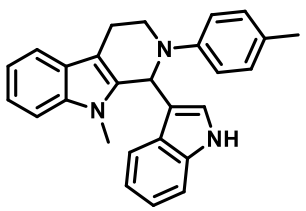


4q

Purification: Silica gel Flash chromatography, eluted with 4% EtOAc in hexane R_f 0.50 (10% EtOAc in hexane).

Melting Point: 213-215 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (bs, 1H), 7.70 (bs, 1H), 7.52 (d, *J* = 8.2, 7.6 Hz, 2H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 7.6 Hz 1H), 7.19 – 7.09 (m, 3H), 7.06 – 6.96 (m, 5H), 6.78 (s, 1H), 6.05 (s, 1H), 3.75 – 3.55 (m, 2H), 3.03 – 2.92 (m, 1H), 2.79 (dt, *J* = 15.1, 5.0 Hz, 1H), 2.24 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 148.1, 136.5, 136.0, 134.6, 129.4, 128.2, 126.9, 126.6, 124.8, 121.3, 120.8, 119.3, 119.0, 118.4, 118.0, 117.7, 115.7, 111.3, 111.1, 108.3, 52.9, 43.4, 20.3, 19.6.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{24}N_3$: 378.1970, found 378.1956.

1-(1H-indol-3-yl)-9-methyl-2-(p-tolyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indole (4r): General procedure was followed with **1a** (100 mg, 0.81 mmol), N-methyl Triptoline (223.0 mg, 1.2 mmol), indole (95.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **4r** as a white solid (155.2 mg, 0.40 mmol, 49% yield).



4r

Purification: Silica gel Flash chromatography, eluted with 10% EtOAc in hexane R_f 0.50 (20% EtOAc in hexane).

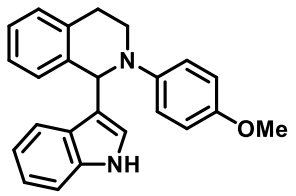
Melting Point: 218-220 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (bs, 1H), 7.54 (d, J = 7.8 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 7.25 (s, 1H), 7.22 (dd, J = 7.8, 7.7 Hz, 1H), 7.18 – 7.10 (m, 2H), 7.08 (m, 5H), 6.44 (s, 1H), 6.15 (s, 1H), 3.67 (dd, *J* = 13.7, 5.0 Hz, 1H), 3.55 – 3.49 (m, 1H), 3.47 (s, 3H), 3.05 – 2.91 (m, 1H), 2.64 (dd, *J* = 15.2, 3.6 Hz, 1H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 137.1, 136.5, 135.3, 129.8, 129.1, 127.1, 126.6, 124.6, 122.3, 121.2, 119.9, 119.7, 118.9, 118.4, 118.4, 116.2, 111.2, 109.0, 108.9, 52.0, 42.4, 29.6, 20.5, 19.2.

HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{27}H_{26}N_3$: 392.2127, found 392.2114.

1-(1H-Indol-3-yl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline (4s): General procedure was followed with *p*-quinone dimethyl monoketal (100.0 mg, 0.65 mmol), **2a** (99 µL, 0.78 mmol), indole (76 mg, 0.65 mmol), and acetic acid (7 µL, 0.13 mmol) at 70 °C to furnish **4s** as a white solid (182.0 mg, 0.51 mmol, 79% yield).



4s

Purification: Silica gel Flash chromatography, eluted with 10% EtOAc in hexane
R_f 0.5 (20% EtOAc in hexane)

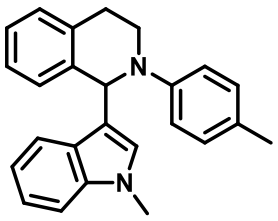
Melting Point: 173-175 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (s, 1H), 7.44 (d, *J*=8.0 Hz, 1H), 7.30 (d, *J*=8.1 Hz, 1H), 7.24–7.13 (m, 5H), 7.01 (dd, *J*=7.8, 7.3 Hz, 1H), 6.97 (d, *J*=8.8 Hz, 2H), 6.81 (d, *J*=8.9 Hz, 2H), 6.56 (s,1H), 5.98 (s, 1H), 3.77 (s, 3H), 3.62–3.53 (m, 1H), 3.53–3.45 (m, 1H), 3.14–2.99 (m, 1H), 2.82 (dt, *J*=16.5, 4.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 153.4, 144.8, 137.6, 136.5, 135.4, 128.9, 128.2, 126.9, 126.5, 125.7, 124.3, 122.0, 120.3, 119.7, 119.6, 119.2, 114.5, 111.0, 58.0, 55.6, 43.8, 26.9.

HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{24}H_{23}N_2O$: 355.1810, found 339.1802

1-(1-methyl-1H-indol-3-yl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline: General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), 1-methyl-1H-indole (101.2 µL, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) at 70 °C for 14 h to furnish **4t** as a white solid (133.9 mg, 0.38 mmol, 47% yield).



Purification Silica gel Flash chromatography, eluted with 4 % EtOAc in hexane
R_f 0.5 (10% EtOAc in hexane)

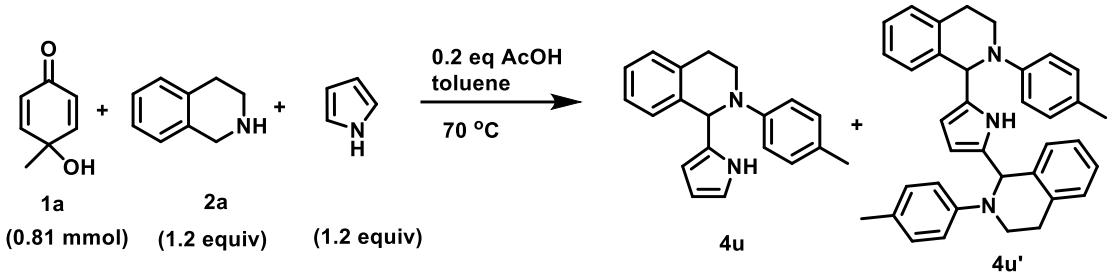
Melting Point: 86-88 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J*=8.1 Hz, 1H), 7.30–7.25 (m, 2H), 7.23–7.14 (m, 4H), 7.06(d, *J*=8.0 Hz, 2H), 7.02 (d, *J*=7.4Hz, 1H), 6.96 (d, *J*=8.2 Hz, 2H), 6.49 (s, 1H), 6.13 (s, 1H), 3.67 (s, 3H), 3.65–3.53 (m, 2H), 3.14–2.98 (m, 1H), 2.78 (td, *J*=16.4, 4.2 Hz, 1H), 2.28 (s, 3H).

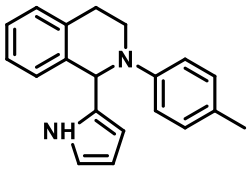
^{13}C NMR (101 MHz, $CDCl_3$): δ147.9, 137.8, 137.5, 135.7, 129.8, 129.0, 129.0, 128.3, 127.6, 127.2, 126.6,

125.7, 121.7, 120.4, 119.2, 118.0, 116.5, 109.2, 56.9, 42.6, 32.8, 26.5, 20.5.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{25}H_{25}N_2$: 353.2018, found 353.2002.

Reaction with pyrrol

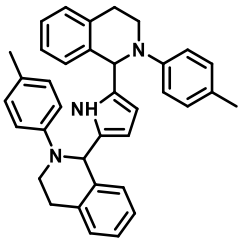


1-(1H-pyrrol-2-yl)-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinoline (4u): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), 1H-pyrrole (67 µL, 0.97 mmol), and acetic acid (9 µL, 0.16 mmol) at 70 °C for 12 h to furnish mono addition product at C2 (**4u**; 25 mg, 0.0.087 mmol, 11 % yield) along with C2 and C5 bis addition product (**4u'**; 12 mg, 0.023 mmol, 3 % yield) as a thick oil.



Purification: Both the compounds were isolated with silica gel Flash chromatography, eluted at 4-5 % EtOAc in hexane
4u: R_f 0.5 (10% EtOAc in hexane)
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (bs, 1H), 7.31–7.27 (m, 1H), 7.25–7.20 (m, 2H), 7.19–7.14 (m, 1H), 7.09 (d, *J*=8.3 Hz, 2H), 6.92(d, *J* = 8.5 Hz, 2H), 6.69–6.64 (m, 1H), 6.11–6.05 (m, 1H), 5.85 (s, 1H), 5.73–5.66 (m,1H), 3.63–3.51 (m, 1H), 3.50–3.37 (m, 1H), 3.07–2.93 (m, 1H), 2.75 (td, *J*=16.3, 4.5 Hz,1H), 2.30 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 147.5, 135.6, 135.0, 133.3, 129.6, 128.6, 128.3, 127.7, 126.8, 125.6, 116.8, 116.2, 107.9, 107.5, 57.7, 42.9, 26.8, 20.2.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{20}H_{21}N_2$: 289.1705, found 289.1691.

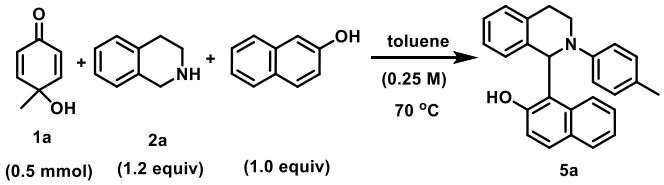
2,5-bis(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-1H-pyrrole (4u'):



R_f 0.6 (10% EtOAc in hexane)
^{1}H NMR (400 MHz, $CDCl_3$): δ7.83 (d, J=13.3Hz, 1H), 7.22–7.13 (m, 6H), 7.12–7.06 (m, 2H), 7.06–6.99 (m, 4H), 6.85–6.18 (m, 4H), 5.72 (s, 1H), 5.69 (s, 1H), 5.47 (d, *J* = 2.6 Hz, 1H), 5.39 (d, *J* = 2.7 Hz, 1H), 3.50–3.36 (m, 2H), 3.35–3.25 (m, 1H), 3.25–3.14 (m,1H), 3.01–2.87 (m, 2H), 2.73–2.59 (m, 2H), 2.29 (s, 3H), 2.27 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 147.9, 147.8, 139.2, 135.6, 134.9, 132.7, 132.5, 129.7,129.6, 128.6, 128.6, 127.9, 127.9, 126.7, 126.7,125.6, 125.5, 123.4, 117.0, 116.9, 114.0, 107.6, 107.5, 58.1, 58.1 42.9, 42.5, 27.0, 27.0, 20.4, 20.4.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{36}H_{36}N_3$: 510.2909, found 510.2902.

[5] Synthesis and spectral data for phenol addition products (5)

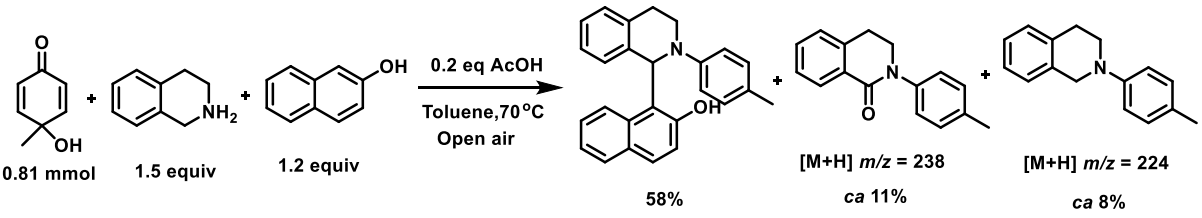
Table S1: Optimization of reaction parameters for phenols (Table S1)



run	veriation from standard conditions	time (h)	yield (4a, %)[a]
1	-	30	48
2	1.2 equiv of 2-naphthol was used	24	55
3	1.2 equiv of 2-naphthol & 20 mol%AcOH	20	69
4	1.5 equiv of 2-naphthol was used	18	58
5	1.5 equiv of 2-naphthol & 20 mol%AcOH	11	60
6	1.5 equiv of THIQ, 1.2 equiv of 2-naphthol & 20 mol% AcOH	20	72 (65)[b]
7[c]	1.5 equiv of THIQ, 1.2 equiv of 2-naphthol & 20 mol% AcOH	25	58 (51)[b]

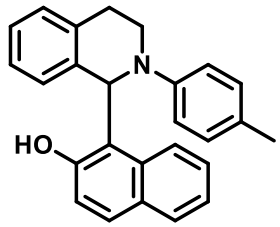
[a]NMR yield was calculated using 4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dien-1-one as an internal standard. [b]Isolated yields are mentioned in parenthesis. [c]Open air reaction

Entry 7: Reaction was conducted at 70 °C in toluene in open air flask. Some minor by-products were also detected as below. Yields were calculated based on ^{1}H NMR.



General Procedure: To the reaction vial/Schlenk tube, a mixture of *p*-quinol (**1a**, 0.5 mmol), THIQ/amine (0.6 mmol), and 2-naphthol (0.5 mmol) was dissolved in toluene (1.2 mL), degassed and refilled with nitrogen. The flask was heated in an oil bath at 70 °C with/without an additive (CH_3CO_2H; 20 mol%) in the presence of an internal standard, 4-hydroxy-2,4,6-trimethylcyclohexa-2,5-dien-1-one (0.25 mmol). The progress of reaction was monitored by TLC with reference to *p*-quinol (monitored by TLC) and NMR yields was primarily checked by ^{1}H NMR and isolated yields were calculated after column chromatography. Yields are calculated with respect to corresponding *p*-quinols. (R_f 0.5; 20% EtOAc in hexane, eluted at 10%). The best result (**Table S1, entry 6**) was employed for substrate scope (**5**).

1-(2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-2-ol (5a): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), β-naphthol (117.0 mg, 0.81 mmol) , and acetic acid (9 µL, 0.16 mmol) to furnish **5a** as a white solid (193.0 mg, 0.53 mmol, 65% yield).



5a

Purification: Silica gel Flash chromatography, eluted with 2% EtOAc in hexane R_f 0.40 (5% EtOAc in hexane).

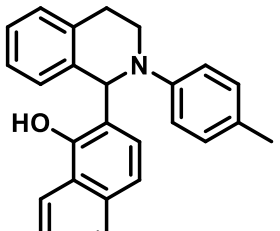
Melting Point: 148-150 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 11.19 (bs, 1H), 8.16 (d, *J* = 8.6 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.6 Hz, 1H), 7.51 (dd, *J* = 8.3, 7.2 Hz, 1H), 7.28 (dd, *J* = 7.7, 7.2 Hz, 1H), 7.18 (s, 1H), 7.16 d, *J* = 1.2 Hz, 1H), 7.13 (s, 1H), 7.09 (dd, *J* = 7.4, 7.1 Hz, 1H), 6.91 (dd, *J* = 8.6, 1.5 Hz, 1H), 6.89–6.83 (m, 3H), 6.67 (d, *J* = 7.2 Hz, 1H), 6.36 (s, 1H), 3.69–3.42 (m, 2H), 3.42–3.26 (m, 1H), 2.95 (pseudo d, *J* = 15.8 Hz, 1H), 2.09 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 154.8, 147.5, 136.5, 135.2, 133.7, 133.4, 129.7, 129.5, 129.0, 128.4, 128.3, 127.5, 127.1, 126.6, 126.5, 123.0, 122.4, 121.1, 119.7, 118.5, 59.7, 55.4, 30.6, 20.7.

HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{24}NO$ 366.1858, found 366.1852

2-(2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl) naphthalen-1-ol (5b): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), **α**-naphthol (117.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **5b** as a white solid (201.0 mg, 0.55 mmol, 68% yield).



5b

Purification: Silica gel Flash chromatography, eluted with 2% EtOAc in hexane R_f 0.50 (5% EtOAc in hexane).

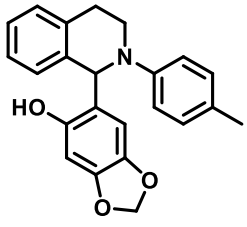
Melting Point: 128-130 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.76 (bs, 1H), 8.21–8.13 (m, 1H), 7.71–7.65 (m, 1H), 7.40–7.34 (m, 2H), 7.25 (d, *J* = 8.3 Hz, 1H), 7.18–7.12 (m, 4H), 7.11–7.06 (m, 2H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 5.71 (s, 1H), 3.58 (dt, *J* = 12.8, 5.5 Hz, 1H), 3.46–3.37 (m, 1H), 3.22–3.11 (m, 1H), 2.90 (dt, *J* = 16.8, 5.5 Hz, 1H), 2.19 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 146.9, 135.5, 134.0, 133.9, 129.8, 128.9, 128.5, 127.6, 127.2, 126.9, 126.2, 126.1, 125.4, 124.8, 122.4, 122.2, 120.0, 118.3, 115.9, 64.7, 51.1, 28.2, 20.7.

HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{24}NO$: 366.1858, found 366.1848.

6-(2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)benzo[d][1,3]dioxol-5-ol (5c): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol),), benzo[d][1,3]dioxol-5-ol (112.0 mg, 0.81 mmol) , and acetic acid (9 µL, 0.16 mmol) to furnish **5c** as a white solid (180 mg, 0.50 mmol, 62% yield).



5c

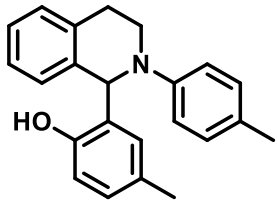
Purification: Silica gel Flash chromatography, eluted with 2% EtOAc in hexane R_f 0.40 (5% EtOAc in hexane).

Melting Point: 198-200 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.69 (bs, 1H), 7.21–7.15 (m, 2H), 7.14–7.10 (m, 1H), 7.09–7.02 (m, 5H), 6.36 (s, 1H), 6.32 (s, 1H), 5.81 (ABq, *J* = 4.1, 1.2 Hz, 2H), 5.48 (s, 1H), 3.56–3.48 (m, 1H), 3.46–3.38 (m, 1H), 2.98 (dt, J = 17.2, 6.1 Hz, 1H), 2.85 (dt, *J* = 17.4, 5.5 Hz, 1H), 2.25 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$ and 3 drops DMSO-d_6): δ 151.1, 147.3, 146.6, 140.1, 135.2, 134.1, 132.9, 129.7, 128.8, 128.3, 126.8, 126.1, 121.2, 119.2, 109.2, 100.7, 99.0, 63.0, 49.1, 27.4, 20.6.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{23}H_{22}NO_3$: 360.1600, found 360.1593.

4-Methyl-2-(2-(*p*-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phenol (5d): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), p-Cresol (87.5 mg, 0.81 mmol) , and acetic acid (9 µL, 0.16 mmol) to furnish **5d** as a white solid (148.0 mg, 0.45 mmol, 55% yield).

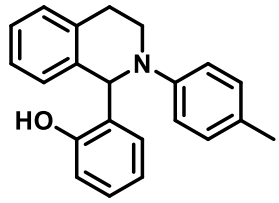


5d

Purification: Silica gel Flash chromatography, eluted with 1% EtOAc in hexane R_f 0.50 (5% EtOAc in hexane).

Melting Point: 132-134 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.66 (bs, 1H), 7.15 (dd, *J* = 8.0,7.6 Hz, 2H), 7.12 (s, 1H), 7.09 (s, 1H), 7.07 (s, 1H) 7.03 (dd, *J* = 9.0, 8.5 Hz, 3H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.64 (s, 1H), 5.55 (s, 1H), 3.57–3.47 (m, 1H), 3.46–3.36 (m, 1H), 3.0 (dt, *J* = 16.8, 6.4 Hz, 1H), 2.85 (dt, *J* = 17.2, 5.8 Hz, 1H), 2.22 (s, 3H), 2.17 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 154.0, 146.8, 134.8, 134.2, 133.5, 130.4, 129.8, 129.4, 129.1, 128.6, 128.2, 126.9, 126.9, 126.2, 121.9, 116.7, 64.1, 49.7, 27.5, 20.7, 20.7.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{23}H_{24}NO$: 330.1858, found 330.1848.

2-(2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phenol (5e): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), phenol (76.0 mg, 1.2 mmol) , and acetic acid (9 µL, 0.16 mmol) to furnish **5e** as a white solid (123.0 mg, 0.39 mmol, 48% yield).

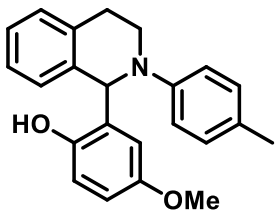


5e

Purification: Silica gel Flash chromatography, eluted with 1% EtOAc in hexane R_f 0.50 (5% EtOAc in hexane).

Melting Point: 138-140 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.96 (bs, 1H), 7.26–7.13 (m, 6H), 7.11–7.06 (m, 3H), 6.90 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.84 (dd, *J* = 8.1, 1.1 Hz, 1H), 6.79 (ddd, *J* = 7.6, 7.4, 1.2 Hz, 1H), 5.65 (s, 1H), 3.62–3.54 (m, 1H), 3.53–3.46 (m, 1H), 3.06 (dt, *J* = 16.9, 6.2 Hz, 1H), 2.92 (dt, *J* = 17.0, 5.5 Hz, 1H), 2.29 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 156.4, 146.6, 134.7, 134.2, 133.7, 129.9, 129.8, 129.1, 128.9, 128.6, 127.2, 127.0, 126.2, 122.0, 119.2, 117.0, 64.1, 49.7, 27.4, 20.7.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{22}H_{22}NO$: 316.1701, found 316.1690.

4-Methoxy-2-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phenol (5f): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), 4-methoxyphenol (100.5 mg, 0.81 mmol) , and acetic acid (9 µL, 0.16 mmol) to furnish **5f** as a white solid (159 mg, 0.46 mmol, 57% yield).



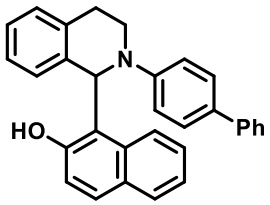
5f

Purification: Silica gel Flash chromatography, eluted with 10% $CHCl_3$ in hexane R_f 0.50 (20% $CHCl_3$ in hexane).

Melting Point: 120-122 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.37 (bs, 1H), 7.23–7.12 (m, 3H), 7.11 (d, *J* = 1.8 Hz, 1H), 7.09 (s, 2H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.74 (d, *J* = 8.7 Hz, 1H), 6.69 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.44 (d, *J* = 2.7 Hz, 1H), 5.58 (s, 1H), 3.69 (s, 3H), 3.58–3.43 (m, 2H), 3.11–2.74 (m, 2H), 2.26 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.5, 150.2, 146.6, 134.4, 134.2, 133.5, 129.8, 129.1, 128.5, 128.2, 127.1, 126.2, 121.7, 117.1, 116.5, 113.0, 63.8, 55.6, 49.4, 27.1, 20.7.
HRMS (ESI^+): *m/z*: $[M+H]^+$ Calculated for $C_{23}H_{24}NO_2$: 346.1807, found 346.1814.

1-(2-([1,1'-Biphenyl]-4-yl)-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-2-ol (5g): General procedure was followed with 1-hydroxy-[1,1'-biphenyl]-4(1H)-one (150.6 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), β naphthol (117.0 mg, 0.81 mmol) , and acetic acid (9 µL, 0.16 mmol) to furnish **5g** as a white solid (209 mg, 0.49 mmol, 60% yield).

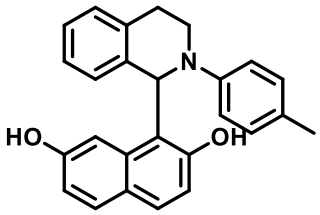


5g

Purification: Silica gel Flash chromatography, eluted with 50% $CHCl_3$ in hexane
R_f 0.30 (70% $CHCl_3$ in hexane).

Melting Point: 193-195 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.98 (bs, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.57 (dd, *J* = 8.5, 7.7 Hz, 2H), 7.37 (d, J = 7.5 Hz, 2H), 7.35–7.28 (m, 7H), 7.25–7.22 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.15–7.09 (m, 1H), 6.93 (d, *J* = 8.8 Hz, 1H), 6.89 (d, *J* = 7.4 Hz, 1H), 6.70 (d, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 3.75 (dd, *J* = 11.7, 4.6 Hz, 1H), 3.67–3.55 (m, 1H), 3.40 (td, *J* = 12.3, 3.1 Hz, 1H), 3.02 (d, *J* = 16.4 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 154.7, 149.3, 140.2, 138.1, 136.3, 133.7, 133.4, 129.6, 129.1, 128.6, 128.5, 128.4, 127.7, 127.6, 127.3, 127.1, 126.8, 126.7, 126.6, 123.3, 122.6, 121.1, 119.7, 118.4, 59.3, 55.5, 30.7.
HRMS (ESI^+): *m/z*: $[M+H]^+$ Calculated for $C_{31}H_{26}NO$: 428.2014, found 428.2011.

1-(2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalene-2,7-diol (5h): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), naphthalene-2,7-diol (129.7 mg, 0.81 mmol) , and acetic acid (9 µL, 0.16 mmol) to furnish **5h** as a white solid (179 mg, 0.47 mmol, 58% yield).

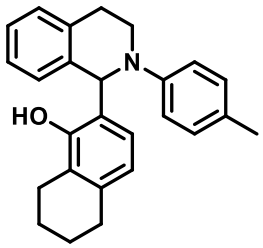


5h

Purification: Silica gel Flash chromatography, eluted with 10% EtOAc in hexane
R_f 0.50 (30% EtOAc in hexane).

Melting Point: 150-152 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.9 Hz, 1H), 7.53 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 8.9 Hz, 1H), 7.21–7.17 (m, 3H), 7.14 (dd, *J* = 7.5, 7.2 Hz, 1H), 6.95–6.87 (m, 4H), 6.78 (d, *J* = 8.8 Hz, 1H), 6.76 (d, *J* = 8.0 Hz, 1H), 6.21 (s, 1H), 3.69–3.53 (m, 2H), 3.35 (td, *J* = 10.7, 4.3 Hz, 1H), 3.00 (like d, *J* = 16.5 Hz, 1H), 2.14 (s, 3H). [2 H missing]
^{13}C NMR (100 MHz, $CDCl_3$): δ 155.4, 155.0, 147.4, 136.4, 135.1, 135.1, 133.4, 130.8, 129.7, 129.3, 128.3, 127.5, 126.7, 126.5, 123.8, 122.8, 117.5, 117.1, 114.2, 103.9, 59.8, 55.5, 30.6, 20.7.
HRMS (ESI^+): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{24}NO_2$: 382.1807, found 382.1793.

2-(2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-5,6,7,8-tetrahydronaphthalen-1-ol (5i): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), 5,6,7,8-tetrahydronaphthalen-1-ol (120.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **5i** as a white solid (182.3 mg, 0.49 mmol, 61% yield).



5i

Purification: Silica gel Flash chromatography, eluted with 2% EtOAc in hexane R_f 0.40 (5% EtOAc in hexane).

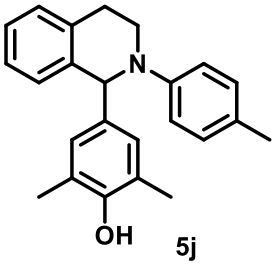
Melting Point: 154-156 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.02 (bs, 1H), 7.24–7.16 (m, 2H), 7.15–7.10 (m, 4H), 7.06 (d, *J* = 8.5, Hz, 2H), 6.58 (d, *J* = 7.9 Hz, 1H), 6.51 (d, *J* = 7.7 Hz, 1H), 5.64 (s, 1H), 3.63–3.55 (m, 1H), 3.54–3.45 (m, 1H), 3.02–2.86 (m, 2H), 2.71 (dd, J = 6.0, 5.3 Hz, 2H), 2.65 (dd, J = 6.2, 5.5 Hz, 2H), 2.28 (s, 3H), 1.82 –1.74 (m, 4H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 154.1, 146.6, 138.0, 134.9, 134.3, 133.1, 129.8, 129.1 128.8, 126.9, 126.4, 126.0, 125.2, 123.2, 121.6, 119.4, 63.4, 48.9, 29.6, 26.8, 22.9, 22.9, 20.7.

HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{28}NO$: 370.2171, found 370.2164.

2,6-Dimethyl-4-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)phenol (5j): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), 2,6-dimethylphenol (99.0 mg, 0.81 mmol) , and acetic acid (9 µL, 0.16 mmol) to furnish **5j** as a white solid (127 mg, 0.37 mmol, 46% yield).



5j

Purification: Silica gel Flash chromatography, eluted with 70% $CHCl_3$ in hexane R_f 0.50 (70% $CHCl_3$ in hexane).

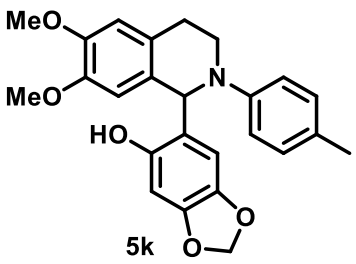
Melting Point: 138-140 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25–7.13 (m, 4H), 7.04 (d, *J* = 8.2 Hz, 2H), 6.85 (m, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 5.68 (s, 1H), 4.51 (s, 1H), 3.75–3.61 (m, 1H), 3.55–3.44 (m, 1H), 3.03–2.87 (m, 2H), 2.27 (s, 3H), 2.17 (s, 6H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.0, 147.7, 138.1, 135.6, 135.2, 129.6, 128.2, 127.9, 127.8, 126.9, 126.7, 126.0, 122.6, 114.7, 62.8, 43.7, 27.8, 20.3, 16.1.

HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{24}H_{26}NO$: 344.2014, found 344.1998 .

6-(6,7-Dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)benzo[d][1,3]dioxol-5-ol (5k): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (234 mg, 1.21 mmol), benzo[d][1,3]dioxol-5-ol (112.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **5k** as a white solid (230.8 mg, 0.55 mmol, 68% yield).



5k

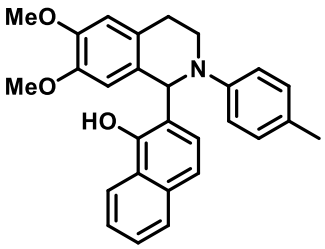
Purification: Silica gel Flash chromatography, eluted with 10% EtOAc in hexane R_f 0.50 (20% EtOAc in hexane).

Melting Point: 140-142 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.62 (bs, 1H), 7.06 (s, 4H), 6.60 (s, 1H), 6.56 (s, 1H), 6.41 (s, 1H), 6.32 (s, 1H), 5.84 (AB q, *J* = 3.9, 1.3 Hz, 2H), 5.45 (s, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.54–3.40 (m, 2H), 2.85–2.73 (m, 2H), 2.27 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 151.7, 148.4, 147.7, 146.6, 140.5, 133.5, 130.0, 126.7, 126.5, 121.9, 119.2, 111.8, 111.3, 109.3, 101.0, 99.5, 63.0, 56.2, 56.0, 48.8, 26.4, 20.9.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{25}H_{26}NO_5$: 420.1811, found 420.1798.

2-(6,7-Dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-1-ol (5l): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (234 mg, 1.21 mmol), α-naphthol (117.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **5l** as a white solid (244.4 mg, 0.58 mmol, 71% yield).

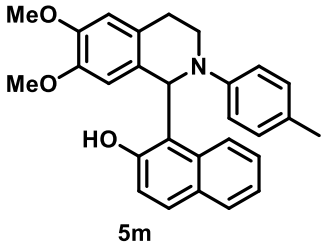


5l

Purification: Silica gel Flash chromatography, eluted with 6% EtOAc in hexane R_f 0.40 (10% EtOAc in hexane).

Melting Point: 168-170 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.69 (bs, 1H), 8.18 (like d, *J* = 7.8 Hz, 1H), 7.80–7.61 (m, 1H), 7.43–7.36 (m, 2H), 7.25 (s, 1H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.07 (d, *J* = 8.2 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.61 (s, 1H), 6.54 (s, 1H), 5.67 (s, 1H), 3.84 (s, 3H), 3.69 (s, 3H), 3.61–3.52 (m, 1H), 3.48–3.38 (m, 1H), 3.01 (dt, *J* = 16.7, 6.2 Hz, 1H), 2.82 (dt, *J* = 16.7, 5.6 Hz, 1H), 2.22 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.2, 148.1, 147.5, 146.7, 133.9, 133.7, 129.8, 127.2, 127.0, 126.3, 126.1, 125.4, 124.8, 122.4, 122.0, 120.1, 118.4, 111.4, 111.2, 63.9, 55.9, 55.8, 50.4, 27.2, 20.7
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{28}H_{28}NO_3$: 426.2069, found 426.2084.

1-(6,7-Dimethoxy-2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-2-ol: (5m): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (234.0 mg, 1.21 mmol), β-naphthol (117.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **5m** as a white solid (234.1 mg, 0.55 mol, 68% yield).

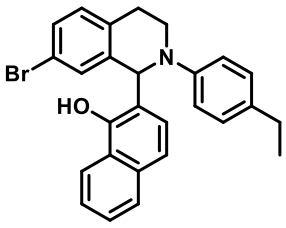


5m

Purification: Silica gel Flash chromatography, eluted with 6% EtOAc in hexane R_f 0.40 (10% EtOAc in hexane).

Melting Point: 183-185 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.32 (bs, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 7.9 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.55 (like d, *J* = 7.9 Hz, 1H), 7.31 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.22 (d, *J* = 8.3 Hz, 2H), 6.98–6.89 (m, 3H), 6.65 (s, 1H), 6.35 (s, 1H), 6.21 (s, 1H), 3.84 (s, 3H), 3.69–3.62 (m, 1H), 3.58–3.48 (m, 1H), 3.35 (td, *J* = 12.0, 3.4 Hz, 1H), 3.25 (s, 3H), 2.90 (d, *J* = 15.8 Hz, 1H), 2.15 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 154.8, 147.9, 147.6, 147.5, 135.1, 133.5, 129.7, 129.4, 129.0, 128.4, 128.3, 127.0, 125.7, 122.9, 122.4, 120.9, 119.7, 118.4, 110.7, 110.5, 59.3, 55.8, 55.5, 30.2, 20.7.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{28}H_{28}NO_3$: 426.2069, found 426.2057.

2-(7-Bromo-2-(4-ethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-1-ol (5n): General procedure was followed with 4-ethyl-4-hydroxycyclohexa-2,5-dien-1-one (100.0 mg, 0.81 mmol), 6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline (256 mg, 1.21 mmol), α-naphthol (117.0 mg, 0.81 mmol) , and acetic acid (9 µL, 0.16 mmol) to furnish **5n** as a white solid (224.6 mg, 0.49 mmol, 60% yield).

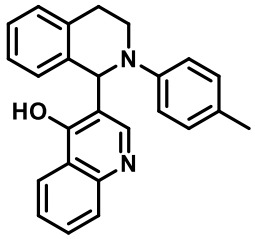


5n

Purification: Silica gel Flash chromatography, eluted with 6% EtOAc in hexane R_f 0.40 (10% EtOAc in hexane).

Melting Point: 200-202 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.60 (bs, 1H), 8.19 (like d, *J* = 8.0 Hz, 1H), 7.74 (like d, *J* = 7.7, 1H), 7.47–7.39 (m, 2H), 7.36–7.28 (m, 2H), 7.21 (s, 1H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.06 (dd, *J* = 8.0, 7.6 Hz, 4H), 5.71 (s, 1H), 3.66–3.56 (m, 1H), 3.49–3.39 (m, 1H), 3.18–3.07 (m, 1H), 2.89 (dt, *J* = 16.9, 5.2 Hz, 1H), 2.55 (q, *J* = 7.4 Hz, 2H), 1.17 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 152.1, 146.6, 140.4, 137.7, 134.0, 133.0, 131.2, 130.6, 130.1, 128.6, 127.3, 126.2, 125.4, 124.9, 122.4, 122.1, 119.9, 119.3, 118.7, 64.1, 50.6, 28.1, 27.6, 15.3.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ calculated for $C_{27}H_{25}BrNO$: 458.1120 found 458.1112, 460.1088

3-(2-(*p*-Tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)quinolin-4-ol (5o): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), quinolin-4-ol (117.6 mg, 0.81 mmol) , and acetic acid (9 µL, 0.16 mmol) to furnish **5o** as a white solid (130.0 mg, 0.36 mmol, 44% yield).

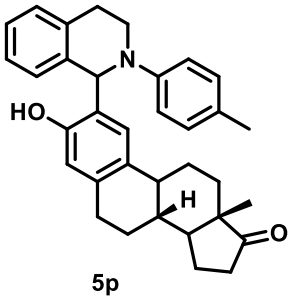


5o

Purification: Silica gel Flash chromatography, eluted with 4% CH_2Cl_2 in EtOAc R_f 0.50 (10% CH_2Cl_2 in EtOAc).

Melting Point: 233-235 °C
^{1}H NMR (400 MHz, $CDCl_3$ and 3 Drops DMSO-d_6): δ 11.00 (d, *J* = 3.0 Hz, 1H), 8.18 (dd, *J* = 8.3, 1.3 Hz, 1H), 7.44–7.38 (m, 1H), 7.37–7.34 (m, 1H), 7.31 (dd, J = 8.3, 1.3 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 1H), 7.09 (ddd, *J* = 8.3, 8.1, 1.0 Hz, 1H), 6.93–6.89 (m, 3H), 6.77 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 6.06 (s, 1H), 3.71–3.60 (m, 1H), 3.32–3.26 (m, 1H), 2.92– 2.81 (m, 2H), 1.99 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$ and 3 Drops DMSO-d_6): δ 176.7, 147.1, 139.4, 137.9, 136.8, 134.7, 131.2, 129.4, 128.2, 127.7, 126.7, 126.2, 126.0, 125.8, 124.4, 123.1, 117.8, 114.8, 55.7, 44.9, 28.4, 20.1.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{25}H_{23}N_2O$: 367.1810, found 367.1797 .

(8R,13S)-3-Hydroxy-13-methyl-2-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (5p): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), estrone (219.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **5p** (dr 1:1) as a white solid (159.0 mg, 0.32 mmol, 40% yield).



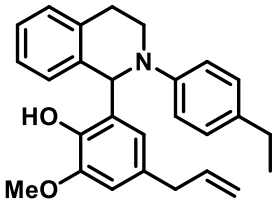
5p

Purification: Silica gel Flash chromatography, both diastereomers was eluted together with 50% $CHCl_3$ in hexane
R_f 0.60 (80% $CHCl_3$ in hexane).

Melting Point: 196-198 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26−7.02 (m, 18H), 6.80 (s, 1H), 6.73 (s, 1H), 6.56 (s, 1H), 6.51 (s, 1H),

5.65 (s, 1H), 5.55 (s, 1H), 3.62−3.44 (m, 4H), 2 .98−2.79 (m, 8H), 2.55−2.48 (m, 2H), 2.28 (s, 6H), 2.24−1.87 (m, 14H), 1.69−1.36 (m, 14H), 0.93 (s, 3H), 0.92 (s, 3H). (mixture of two diastereomers; dr 1:1).
^{13}C NMR (100 MHz, $CDCl_3$): δ 221.1, 154.2, 154.0, 146.4, 137.1, 137.0, 135.0, 134.4, 134.2, 134.0, 133.6, 133.0, 130.3, 129.8, 129.2, 129.0, 128.7, 128.4, 127.0, 126.8, 126.7, 126.1, 126.0, 124.5, 122.1, 121.5, 116.7, 64.4, 63.1, 50.4, 50.3, 48.8, 48.0, 44.1, 43.9, 38.4, 35.9, 31.6, 29.2, 27.8, 26.5, 26.0. (some carbon peaks overlap)
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{34}H_{38}NO_2$: 492.2903 found 492.2898.

4-Allyl-2-(2-(4-ethylphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)-6-methoxyphenol (5q): General procedure was followed with 4-ethyl-4-hydroxycyclohexa-2,5-dien-1-one (112.0 mg, 0.81 mmol), **2a** (154 µL, 1.21 mmol), 4-allyl-2-methoxyphenol (126.0 µL, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **5q** as a yellow liquid (184.0 mg, 0.46 mmol, 57% yield).

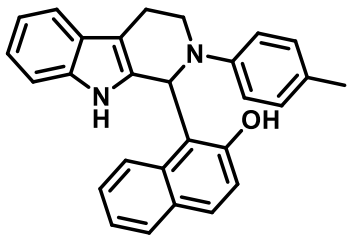


5q

Purification: Silica gel Flash chromatography, eluted with 6% EtOAc in hexane R_f 0.40 (10% EtOAc in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ8.99 (bs, 1H), 7.20−7.13 (m, 4H), 7.09−7.05 (m, 4H), 6.58 (d, *J* = 1.8 Hz, 1H), 6.41 (d, *J* = 1.6 Hz, 1H), 5.96−5.83 (m, 1H), 5.74 (s, 1H), 5.04−4.94 (m, 2H), 3.82 (s, 3H), 3.69−3.60 (m, 1H), 3.51−3.41 (m, 1H), 3.23 (d, *J* = 6.6 Hz, 2H), 3.13−3.02 (m, 1H), 2.98−2.86 (m, 1H), 2.56 (q, *J* = 7.6 Hz, 2H), 1.87 (t, *J* = 7.6 Hz, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 147.0, 143.2, 138.2, 137.9, 135.6, 134.4, 130.3, 128.7, 128.5, 128.0, 126.7, 126.1, 121.5, 120.1, 115.4, 111.1, 62.4, 55.9, 48.6, 39.9, 28.0, 27.7, 15.5.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ calculated for $C_{27}H_{30}NO_2$: 400.2277 found 400.2267

1-(2-(*p*-Tolyl)-2,3,4,9-tetrahydro-1H-pyrido[3,4-b]indol-1-yl)naphthalen-2-ol (5r): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), triptoline (208 mg, 1.21 mmol), β-naphthol (117.0 mg, 0.81 mmol), and acetic acid (9 µL, 0.16 mmol) to furnish **5r** as a white solid (167.0 mg, 0.41 mmol, 51% yield).



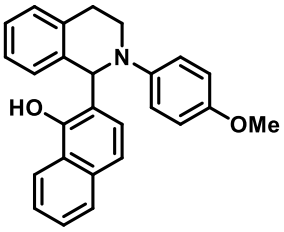
5r

Purification: Silica gel Flash chromatography, eluted with 2% EtOAc in hexane
R_f 0.40 (5% EtOAc in hexane).

Melting Point: 188-190 °C
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.45 (bs, 1H), 8.21 (d, *J* = 8.9 Hz, 1H), 7.78 (d, *J* = 8.3 Hz, 1H), 7.65–7.56 (m, 2H), 7.51 (like d, *J* = 7.7 Hz, 1H), 7.36 (dd, *J* = 7.2, 7.1 Hz, 1H), 7.21 (d, *J* = 8.3 Hz, 3H), 7.10–7.01 (m, 3H), 6.95 (d, *J* = 7.7 Hz, 2H), 6.90 (d, *J* = 8.3 Hz, 1H), 6.49 (s, 1H), 3.85–3.75 (m, 1H), 3.49–3.27 (m, 2H), 3.00 (d, *J* = 14.2 Hz, 1H), 2.16 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 155.9, 146.9, 136.4, 135.1, 132.6, 132.4, 130.0, 129.9 129.5, 128.7, 127.6, 126.8, 122.8, 122.0, 119.9, 119.6, 118.3, 113.8, 111.0, 108.6, 56.6, 56.5, 22.7, 20.8.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{28}H_{25}N_2O$: 405.1967, found 405.1954.

2-(2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)naphthalen-1-ol (5s): General procedure was followed with *p*-quinone dimethyl monoketal (100.0 mg, 0.65 mmol), **2a** (99 µL, 0.78 mmol), α-naphthol (93.6 mg, 0.65 mmol) , and acetic acid (7 µL, 0.13 mmol) to furnish **5s** as a white solid (165.4 mg, 0.43 mmol, 67% yield).



5s

Purification: Silica gel Flash chromatography, eluted with 5% EtOAc in hexane R_f 0.50 (10% EtOAc in hexane).

Melting Point: 168-170 °C

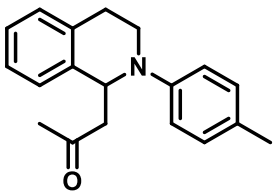
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.89 (s, 1H), 8.15 (d, *J*=7.27 Hz, 1H), 7.69 (d, *J*=7.27 Hz, 1H), 7.44–7.33 (m, 2H), 7.25 (d, *J*=8.6 Hz, 1H), 7.20 (d, *J*=8.5 Hz, 2H), 7.17–7.03 (m, 4H), 6.98 (d, *J*=7.7 Hz, 1H), 6.72 (d, *J*=8.6 Hz, 2H), 5.60 (s, 1H), 3.67 (s, 3H), 3.59–3.50 (m, 1H), 3.46–3.34 (m, 1H), 3.33–3.19 (m, 1H), 2.92 (d, *J*=16.5 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$): δ 156.8, 152.1, 142.8, 135.8, 133.9, 133.7, 128.8, 128.3, 127.7, 127.2, 126.8, 126.3, 126.1, 125.4, 124.7, 124.0, 122.4, 120.1, 118.3, 114.4, 65.9, 55.3, 52.1, 28.8.

HRMS (ESI$^+$): *m/z*: $[M+H]^+$ Calculated for $C_{26}H_{24}NO_2$: 382.1807, found 339.1784

[6] Synthesis and spectral data for ketone addition products (6)

1-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6a): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), acetone (600 µL, 8.1 mmol) , and acetic acid (9 µL, 0.16 mmol) in toluene at 70 °C for 12 h to furnish **6a** as a yellowish liquid (128 mg, 0.46 mmol, 57% yield).



6a

Purification: Silica gel Flash chromatography, eluted with 2% EtOAc in hexane R_f 0.5 (5% EtOAc in hexane).

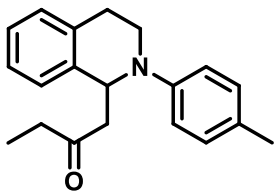
The spectral data was completely in match with previously reported data.[3]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22–7.14 (m, 4H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 5.35 (t, *J* = 6. Hz, 1H), 3.67 (dt, *J* = 12.8, 5.0 Hz, 1H), 3.58–3.49 (m, 1H), 3.13–3.03 (m, 2H), 2.87–2.78 (m, 2H), 2.30 (s, 3H), 2.10 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 147.0, 138.4, 134.5, 129.9, 128.9, 128.0, 126.9, 126.8, 126.2, 115.7, 55.2, 50.1, 42.2, 31.0, 27.1, 20.4.

HRMS (ESI$^+$): *m/z*: $[M+H]^+$ calculated for $C_{19}H_{22}NO$: 280.1701 found 280.1687.

1-(2-(p-tolyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)butan-2-one (6b): General procedure was followed with **1a** (100.0 mg, 0.81 mmol), **2a** (123 µL, 0.97 mmol), butanone (724 µL, 8.1 mmol) , and acetic acid (9 µL, 0.16 mmol) in toluene at 70 °C for 12 h to furnish **6b** as a yellowish liquid (141 mg, 0.48 mmol, 60% yield).



6b

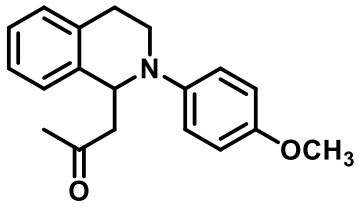
Purification: Silica gel Flash chromatography, eluted with 3% acetone in hexane R_f 0.30 (5% acetone in hexane).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.12 (m, 4H), 7.06 (d, *J* = 8.1 Hz, 2H), 6.87 (d, *J* = 8.6 Hz, 2H), 5.37 (t, *J* = 6.5 Hz, 1H), 3.67–3.60 (m, 1H), 3.55–3.46 (m, 1H), 3.11–2.99 (m, 2H), 2.83–2.73 (m, 2H), 2.40–2.28 (m, 2H), 2.26 (s, 3H), 0.99 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.0, 146.9, 138.4, 134.4, 129.8, 128.8, 127.8, 126.9, 126.7, 126.2, 115.5,

55.5, 48.8, 42.1, 37.2, 27.1, 20.3, 7.5.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ calculated for $C_{20}H_{24}NO$: 294.1858 found 294.1849.

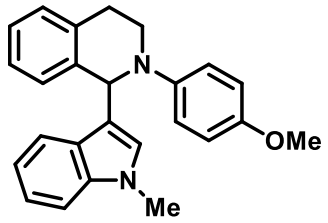
1-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)propan-2-one (6c): General procedure was followed with *p*-quinonedimethyl monoketal (100.0 mg, 0.65 mmol), **2a** (99 µL, 0.78 mmol), acetone (390 µL, 8.1 mmol), and acetic acid (7 µL, 0.13 mmol) to furnish **6c** as a yellowish liquid (140.0 mg, 0.47 mmol, 73% yield).



6c

Purification: Silica gel Flash chromatography, eluted with 6% EtOAc in hexane R_f 0.50 (10% EtOAc in hexane).
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.13 (m, 3H), 7.12–7.08 (m, 1H), 6.91 (d, *J*= 9.0 Hz, 2H), 6.81 (d, *J* = 9.0 Hz, 2H), 5.24 (t, *J* = 6.5 Hz, 1H), 3.74 (s, 3H), 3.57–3.52 (m, 1H), 3.50–3.41 (m, 1H), 3.04–2.94 (m, 2H), 2.80–2.68 (m, 2H), 2.05 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 153.3, 143.7, 138.3, 134.3, 129.0, 126.8, 126.6, 126.2, 118.4, 114.7, 56.0, 55.6, 50.0, 42.9, 30.9, 26.8.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ calculated for $C_{19}H_{22}NO_2$: 296.1651 found 296.1637.

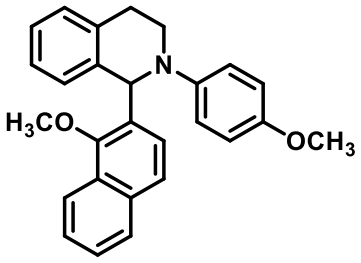
2-(4-methoxyphenyl)-1-(1-methyl-1H-indol-3-yl)-1,2,3,4-tetrahydroisoquinoline: Compound **4s** (100 mg, 0.28 mmol) was dissolved in 1 mL DMF and NaH (13.5 mg, 0.56 mmol, 60% suspension in mineral oil) was added slowly at 0 °C. The reaction mixture was then warmed to room temperature and stirred for 30 min. After cooling again to 0 °C, iodomethane (52 µL, 0.84 mmol) was added dropwise. The reaction mixture was warmed to room temperature and stirred overnight to afford methylated product as a white solid (85 mg, 0.23 mmol 82 % yield).



Purification: Silica gel Flash chromatography, eluted with 8% EtOAc in hexane
R_f 0.5 (20% EtOAc in hexane)
Melting Point: 123-125 °C

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48(d, *J* =7.9 Hz, 1H), 7.30–7.23 (m, 3H), 7.22–7.18 (m, 3H), 7.05 (d, *J* =7.9 Hz, 1H), 7.03–6.98 (m, 2H), 6.87–6.81 (m, 2H), 6.47 (s, 1H), 6.03 (s, 1H), 3.79 (s, 3H), 3.67 (s, 3H), 3.63–3.57 (m, 1H), 3.55–3.48 (m, 1H), 3.14–3.02 (m, 1H), 2.83 (d, *J* =16.4 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ153.2, 144.7, 137.8, 137.3, 135.4, 129.0, 128.9, 128.3, 127.3, 126.5, 125.7, 121.6, 120.3, 119.4, 119.1, 117.1, 114.5, 109.1, 57.8, 55.7, 43.6, 32.7, 26.8.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ calculated for $C_{25}H_{25}N_2O$: 369.1967 observed 369.1961

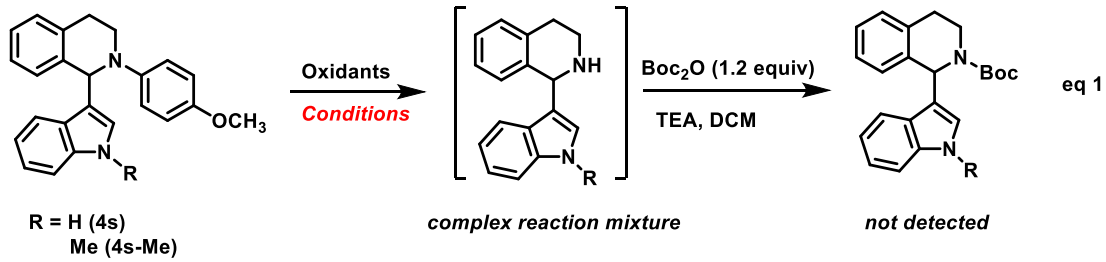
1-(1-methoxynaphthalen-2-yl)-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinoline: A mixture of compound **5s** (100 mg, 0.26 mmol), K_2CO_3 (72 mg, 0.52 mmol), and iodomethane (32.83 µL, 0.52 mmol) in 1 mL DMF was stirred at room temperature for overnight to furnish the corresponding O-methylated product as a yellow solid (83 mg, 0.21 mmol, 81 %).

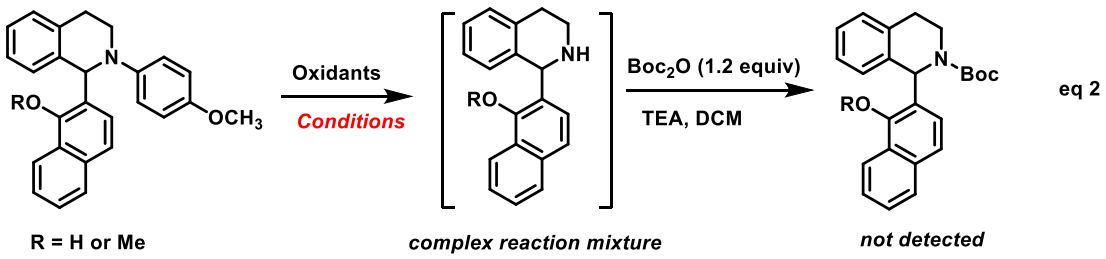


Purification: Silica gel Flash chromatography, eluted with 4% EtOAc in hexane R_f 0.50 (10% EtOAc in hexane).
Melting Point: 98-100°C

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 (d, *J* = 8.4 Hz, 1H), 7.82 (d, *J* = 8.1 Hz, 1H), 7.57–7.51 (m, 2H), 7.51–7.46 (m, 1H), 7.31 (d, *J* = 8.7 Hz, 1H), 7.25–7.16 (m, 2H), 7.10 (d, *J* = 8.2 Hz, 1H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.78 (d, *J* = 9.0 Hz, 2H), 6.19 (s, 1H), 3.86 (s, 3H), 3.74(s, 3H), 3.70–3.59 (m, 2H), 3.16 (dt, *J* = 16.3, 5.8 Hz, 1H), 3.04 (dt, *J* = 16.5, 5.0 Hz, 1H).
^{13}C NMR (100 MHz, $CDCl_3$): δ154.5, 153.9, 145.2, 138.0, 135.4, 135.4, 133.1, 128.7, 128.7, 128.1, 127.9, 127.9, 126.3, 126.1, 126.0, 125.8, 123.8, 122.6, 121.9, 114.2, 62.3, 59.8, 55.5, 47.4, 28.2.
HRMS (ESI^+): *m/z*: $[M+H]^+$ calculated for $C_{27}H_{26}NO_2$: 396.1964 observed 396.1953

Attempts for the Oxidative cleavage of PMP group from 4s and 5s: Various oxidative conditions were examined to deprotect PMP group from **4s** and **5s** (eq 1 and 2). A complex reaction mixture was obtained in all of our attempts (See Table below).

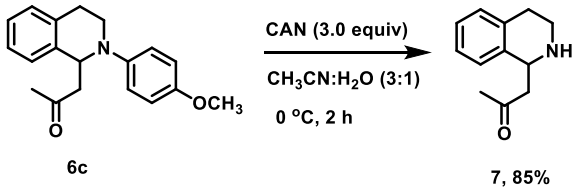




entry	R	oxidation conditions (for eq. 1 and 2)	inference
1	Indol (N*H*)	CAN (3 eq), CH_3CN:H_2O (3:1), 0 °C- rt	complex
2	Indol (NH)	CAN (1.5 eq), CH_3CN:H_2O (3:1), 0 °C	complex
3	Indol (N*H*)	CAN (3 eq), CH_3CN:H_2O (3:1), 0 °C	complex
4	Indol (N*H*)	CAN (3 eq), CH_3CN:H_2O (3:1), -20 °C	complex
5[a]	Indol (N*H*)	H_5IO_6 & H_2SO_4 (1 eq, each), CH_3CN:H_2O (1:1), rt	complex
6	Indol (NH)	NIS & H_2SO_4 (1 eq, each), CH_3CN:H_2O (1:1), rt	complex
7	Indol (NH)	TCCA (0.5 eq), H_2SO_4 (1 eq, each), CH_3CN:H_2O (1:1), rt	complex
8	Indol (NCH_3)	CAN (1.5 eq), CH_3CN:H_2O (3:1), 0 °C	complex
9	Indol (NCH_3)	CAN (1 eq), CH_3CN:H_2O (3:1), 0 °C	complex
10	Indol (NCH_3)	TCCA (0.5 eq), H_2SO_4 (1 eq, each), CH_3CN:H_2O (1:1), rt	complex
11	1-Naphthol (O*H*)	CAN (1.5 eq), CH_3CN:H_2O (3:1), 0 °C	complex
12	1-Naphthol (O*H*)	CAN (3 eq), CH_3CN:H_2O (3:1), -20 °C	complex
13	1-Naphthol (O*H*)	CAN (3 eq), CH_3CN:H_2O (3:1) , 0 °C	complex
14	1-Naphthol (O*H*)	CAN (3 eq), CH_3CN:H_2O (3:1), 0 °C- rt	complex
15	1-Naphthol (O*H*)	TCCA (0.5 eq) & H_2SO_4 (1 eq), CH_3CN:H_2O (3:1), rt	complex
16[a]	1-Naphthol (O*H*)	H_5IO_6 & H_2SO_4 (1 eq, each), CH_3CN:H_2O (1:1), rt	complex
17	1-Naphthol (O*H*)	NIS & H_2SO_4 (1 eq, each), CH_3CN:H_2O (1:1), rt	complex
18	1-Naphthol (O*Me*)	CAN (3 eq), CH_3CN:H_2O (3:1), 0 °C	complex
19	1-Naphthol (O*Me*)	CAN (1.5 eq), CH_3CN:H_2O (3:1), 0 °C	complex
20[a]	1-Naphthol (O*Me*)	TCCA (0.5 eq), H_2SO_4 (1 eq, each), CH_3CN:H_2O (1:1), rt	complex

[a]Treament of complex reaction mixture with Boc anhydride didn't give any isolable product

Deprotection of *p*-methoxyphenyl (PMP) group from 6c:



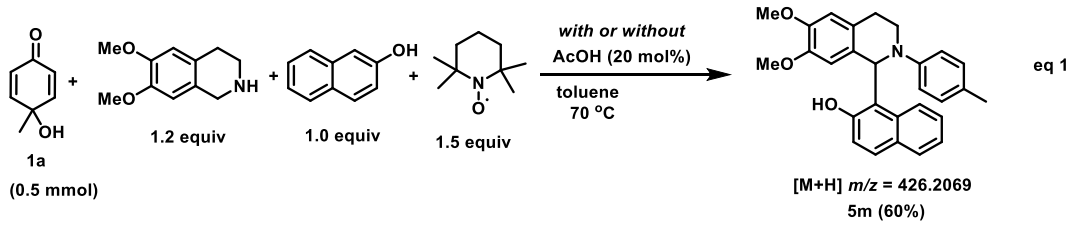
1-(1,2,3,4-Tetrahydroisoquinolin-1-yl)propan-2-one (7): Compound **6c** (59 mg, 0.2 mmol) was dissolved in acetonitrile (2 mL) and was added dropwise a solution of CAN (328 mg, 0.6 mmol) in water (0.6 mL) at 0 °C and stirred at the same temperature for 2 h. After the completion of reaction, 50 ml water added and reaction mixture was washed with diethylether (2×20 mL). The pH of the aqueous layer was adjusted to 9 with 1M NaOH and extracted with diethyl ether (3×30 mL). The combined organic phases were washed once with saturated aq NaCl (40 mL) and dried over anhydrous Na_2SO_4. Evaporation of the solvent gave the residue in pure form of free amine (**7**; 32 mg, 0.17 mmol, 85.0% yield) as yellow oil.

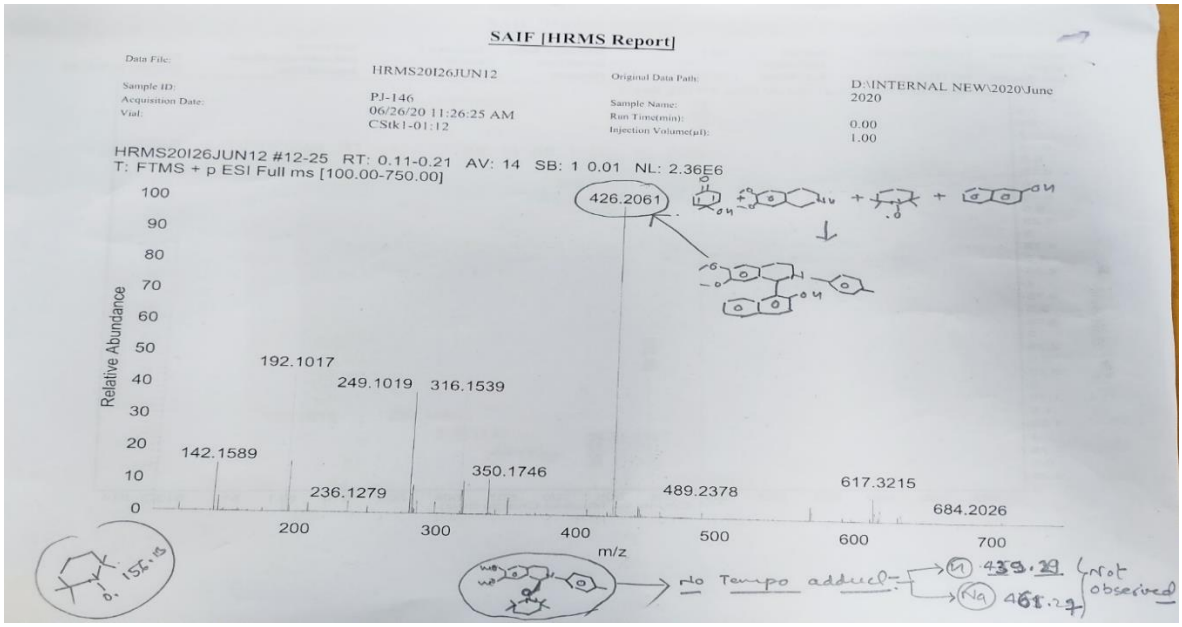
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16-7.12 (m, 2H), 7.11 – 7.07 (m, 1H), 7.06 – 7.03 (m, 1H), 4.49 (dd, *J* = 9.3 Hz, 1H), 3.17 (dt, *J* = 12.3, 5.3 Hz, 1H), 3.04–2.97 (m, 1H), 2.96–2.83 (m, 3H), 2.73 (dt, *J* = 16.3, 4.8 Hz, 1H), 2.21 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ 208.3, 137.9, 135.5, 129.5, 126.2, 125.9, 125.6, 51.9, 50.5, 41.1, 30.7, 29.8.
HRMS (ESI$^+$): *m/z*: $[M+H]^+$ calculated for $C_{12}H_{16}NO$: 190.1232, found: 190.1226.

[7] Mechanistic studies

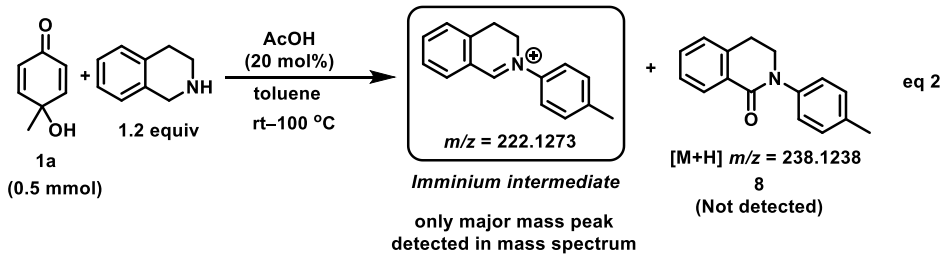
Some controlled experiments were conducted to rule out the any possibility of radical pathway under the standard (degassed) reaction conditions**.**

Eq 1: A control experiment was conducted with **1a** (0.5 mmol), 6,7-dimethoxy-THIQ (1.2 equiv), 2-naphthol (1.0 equiv) and a stable free radical TEMPO (1.5 equiv) in toluene in the absence or presence of AcOH (20 mol%). The reaction mixture was degassed and refilled with the stream of nitrogen and heated the tube at 70-100 °C. The aliquot was subjected for mass spectrometry at different intervals for analysis. There was no peak corresponding to TEMPO adduct (**6**). The desired CDC product **5m** was isolated in 60% yield after column chromatography.

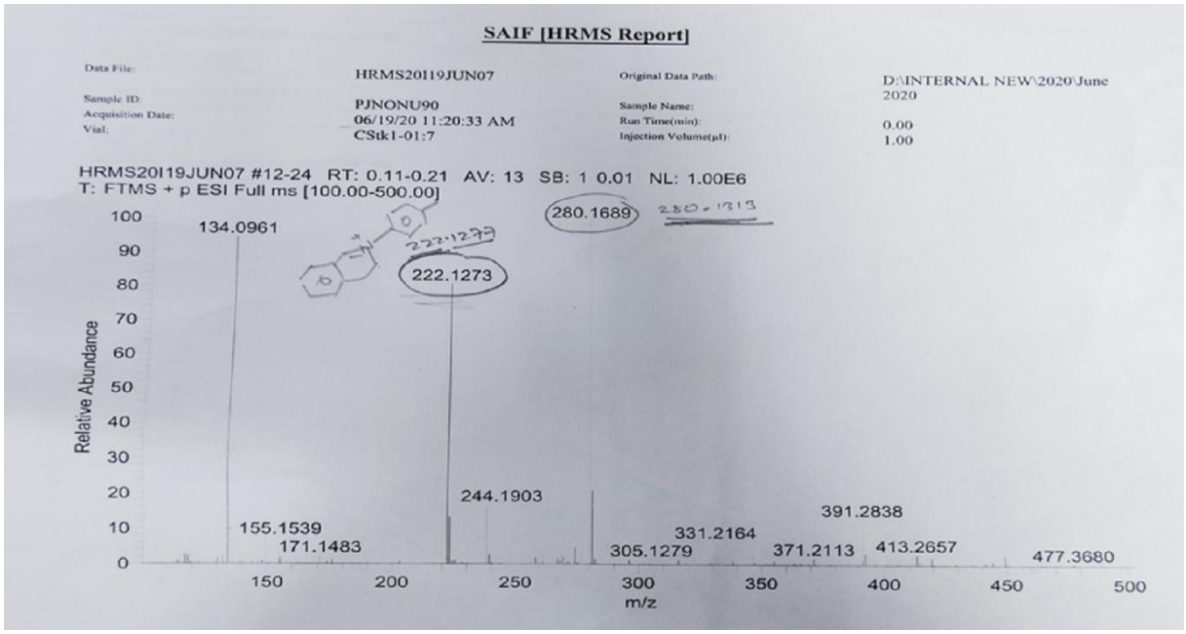




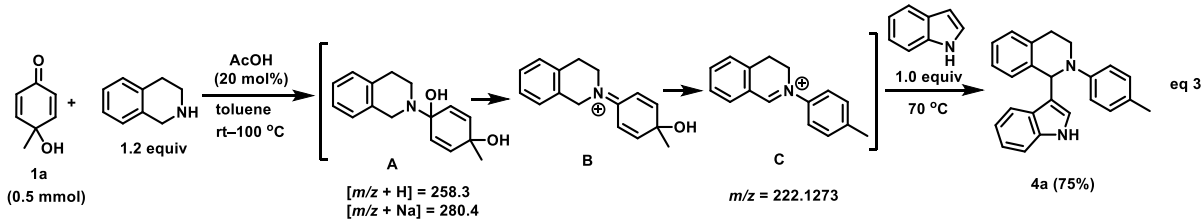
Eq 2: Another control experiment was performed in the absence of any nucleophile. A mixture of **1a** (0.5 mmol), THIQ (1.2 equiv) and AcOH (20 mol%) in toluene was degassed and refilled with the stream of nitrogen and heated the tube at 70-100 °C. The aliquot was subjected for mass spectrometry at different intervals for analysis. A mass peak corresponding peak for *N*-aryliminium was observed in HRMS (*m/z* 222.1273; calculated 222.1277).

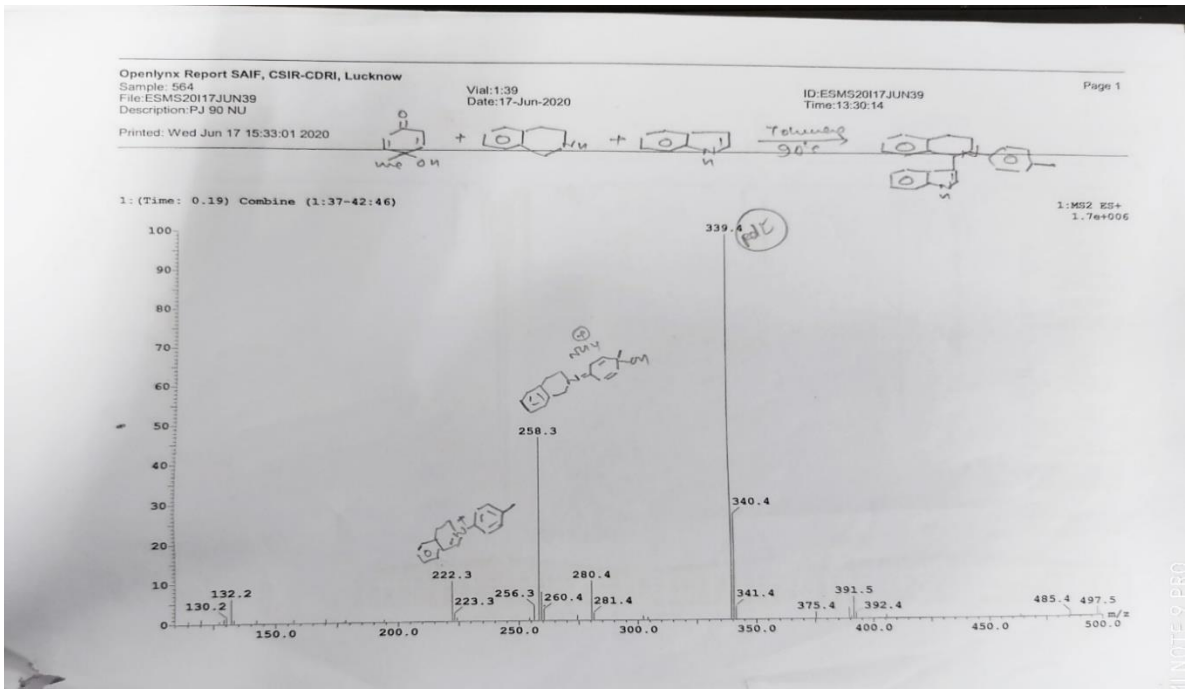


There is no detection of cyclic amide product (**6**) in mass spectra, it rules out the possibility of any radical pathway**.**



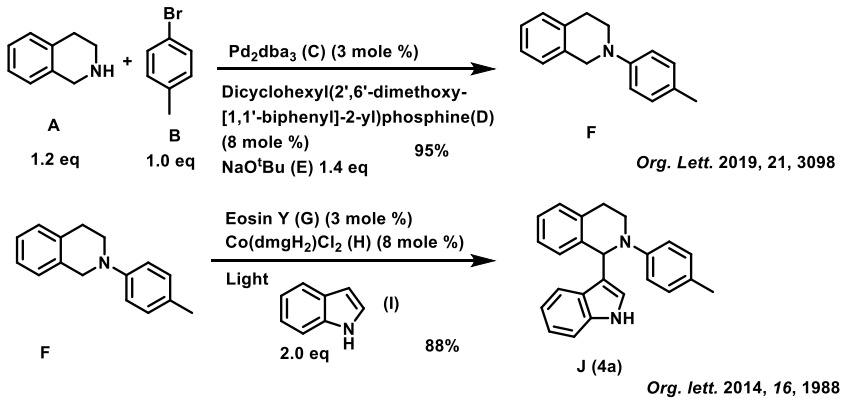
Eq 3: A mixture of **1a** (0.5 mmol), THIQ (1.2 equiv), indole (0.5 mmol) and AcOH (20 mol%) in toluene was degassed and refilled with the stream of nitrogen. The aliquot was subjected for mass spectrometry at different intervals for analysis. The spectrum showed the mass peaks corresponding to hemiaminal (**A**) and *N*-aryliminium (**C**) intermediates along with an indole addition product **4a** (*ca* 20%) at room temperature. Reaction was completed in 6 h when heated to 70 °C. The desired product **4a** was isolated in 75% yield (eq. 3, see chart below).





[8] Calculations of Green Chemistry Metrics

Previous report [Selected from the literature reports[5] of maximum yield for each steps; based on Scifinder search]



Steps involved in this process are:

The reactants and reagents efficiently participate in product formation excluding intermediates. The Green Chemistry Metrics[4] were calculated based on general formula as below:

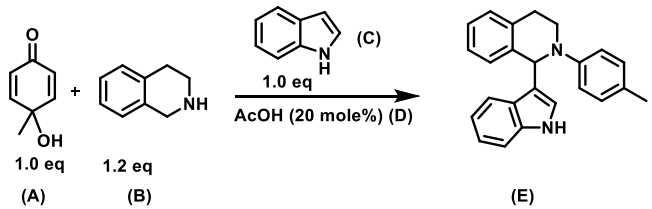
1. No. of steps = No. of steps involved in the process
2. Atom Economy = [(M.W. of product **J**)/(M.W. of **A** + M.W. of **B** + M.W. of **E** + M.W. of **I**)] x 100
3. % yield = (Observed yield/ Calculated yield) x100
4. Atom Efficiency = % yield (over two steps) x Atom economy
5. Process Mass Intensity (PMI) = (Total mass used in the process / Mass of the product)
6. Mass Productivity = (1/ Mass intensity) x100
7. E-factor = (Mass intensity – 1)

Green Metrics Calculation for J (4a), starting from 1-bromo-4-methylbenzene (B):

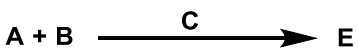
1. No. of steps = 2
2. Atom Economy = [(338.45)/ (133.19 + 171.04 + 117.15 + 96)] x 100 = 65.42%
[Contribution from catalysts was excluded]
3. % yield = (95 x 88)/100 = 83.60%
4. Atom efficiency = (83.6/100) x 65.42 = 54.69
5. Process Mass Intensity = {(15.98 + 17.1 + 2.74 + 3.28 + 13.44 + 2.07 + 2.31 + 23.43)/29.78} = (80.35/29.78) = 2.70 kg/kg
[Contribution of catalysts was included]
6. Mass Productivity = (1/2.70) x 100 = 37.03%
7. E- factor = (2.70 – 1) = 1.70 kg/kg

Basic Green Chemistry metrics were calculated for some representative examples of synthesized compounds (**4a** and **5m**).

Our methodology:



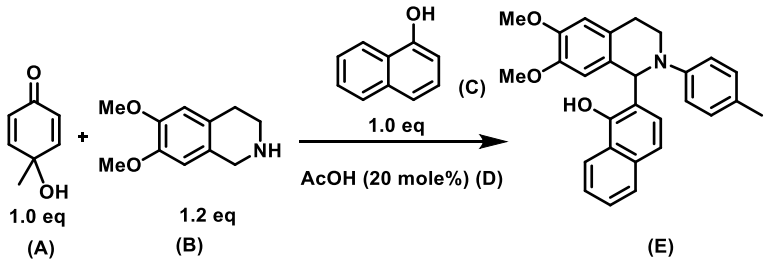
Steps involved in this process are:



Green Metrics Calculation for E (4a), starting from *p*-quinol (1a)

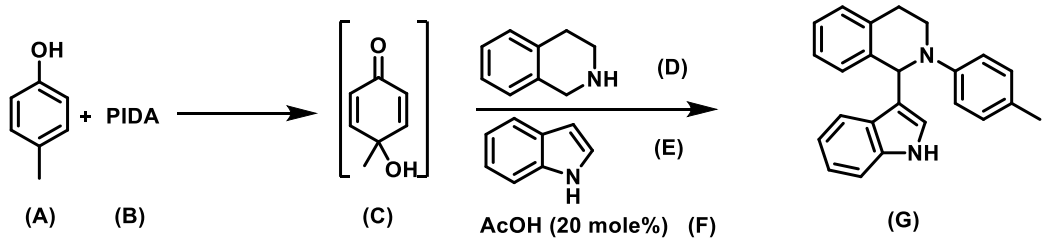
1. No. of steps = 1
2. Atom Economy = [(338.45)/ (124.0 + 133.19 + 117.15)] x 100 = 90.41%
3. % yield = (0.66/ 0.81) x100 = 81%
4. Atom Efficiency = (81/100) x 90.41 = 73.23
5. Process Mass Intensity = (100.0 + 129.46 + 94.89 + 9.6/222) = 1.50 kg/kg
6. Mass Productivity = (1/1.50) x 100 = 66.66%
7. E-factor = (1.50 – 1) = 0.50 kg/kg

Green Metrics Calculation for E (5l), starting from *p*-quinol (1a)

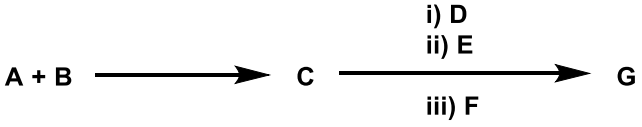


1. No. of steps = 1
2. Atom Economy = [(425.52)/ (124 + 193 + 144)] x 100 = [(425.52/461)] x 100 = 92.30%
3. % yield = (0.58/ 0.81) x 100 = 71%
4. Atom Efficiency = (71/100) x 92.30 = 65.53.
5. Process Mass Intensity (PMI) = [(100 + 234 + 117 + 9.6)/244] = (460.6/244) = 1.89 kg/kg
6. Mass Productivity = (1/1.89) x100 = 52.91%
7. E-factor = (1.89 – 1) = 0.89 kg/kg

Green Metrics Calculation for E (4a), starting from *p*-cresol

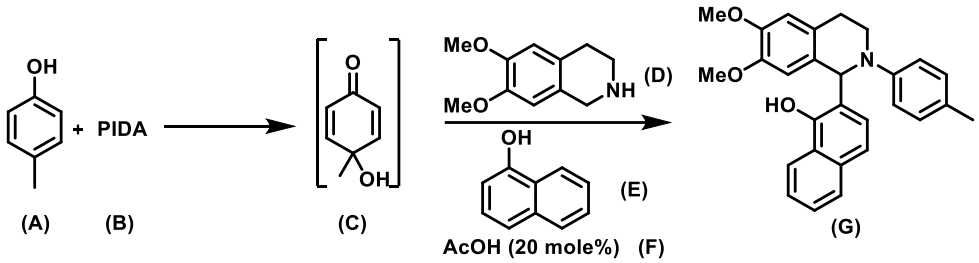


Steps involved in this process are:



Green Metrics Calculation for E (4a), starting from *p*-quinol (1a)

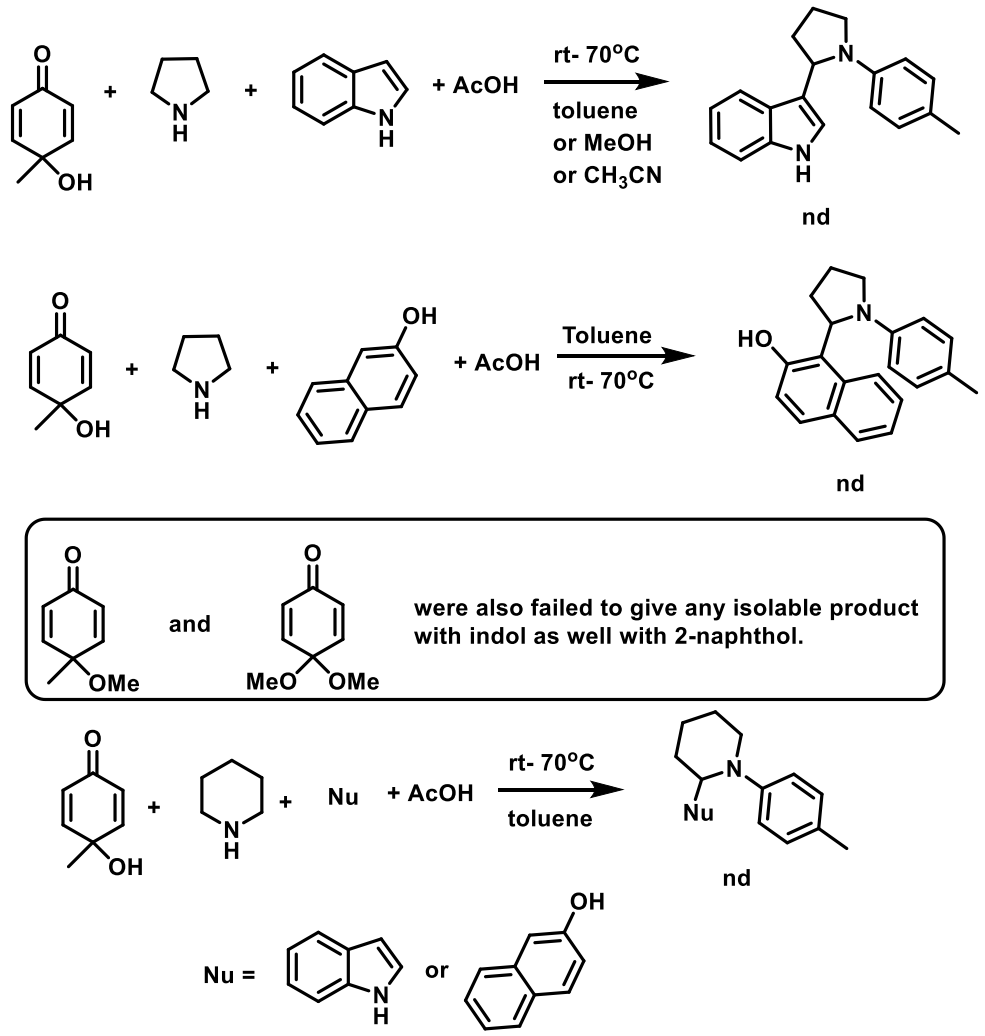
1. No. of steps = 2
2. Atom Economy = [(338.45)/ (108.0 + 322 + 133.19 + 117.15)] x 100 = 49.75%
3. % yield = (75 x 81)/100 = 60%
4. Atom Efficiency = (60/100) x 49.75 = 29.85
5. Process Mass Intensity = (116.60 + 382.40 + 129.46 + 94.89 + 9.6/222) = 3.30 kg/kg
6. Mass Productivity = (1/3.30) x 100 = 30.3%
7. E-factor = (3.30 - 1) = 2.30 kg/kg



Green Metrics Calculation for E (5a), starting from *p*-quinol (1a)

1. No. of steps = 2
2. Atom Economy = [(425.52)/ (108 + 322 + 193 + 144)] x 100 = [(425.52/767)]x100 = 55.48%
3. % yield = (75 x 71)/100 = 53.25%
4. Atom Efficiency = (53.25/100) x 55.48 = 29.54
5. Process Mass Intensity (PMI) = [(116.6 + 382.4 + 234 + 117 + 9.6)/244] = (859.6/244) = 3.52 kg/kg
6. Mass Productivity = (1/3.52) x100 = 28.41%
7. E-factor = (3.52 - 1) = 2.52 kg/kg

Attempts for sp^3 functionalization with pyrrolidine and piperdines: We investigated three types of dienones with pyrrolidine and indole (NH) as well as 2-naphthol in the presence of AcOH (20-40%). Indole and 2-naphthol were majorly recovered and there was decomposition of p-quinol in all of our attempts.

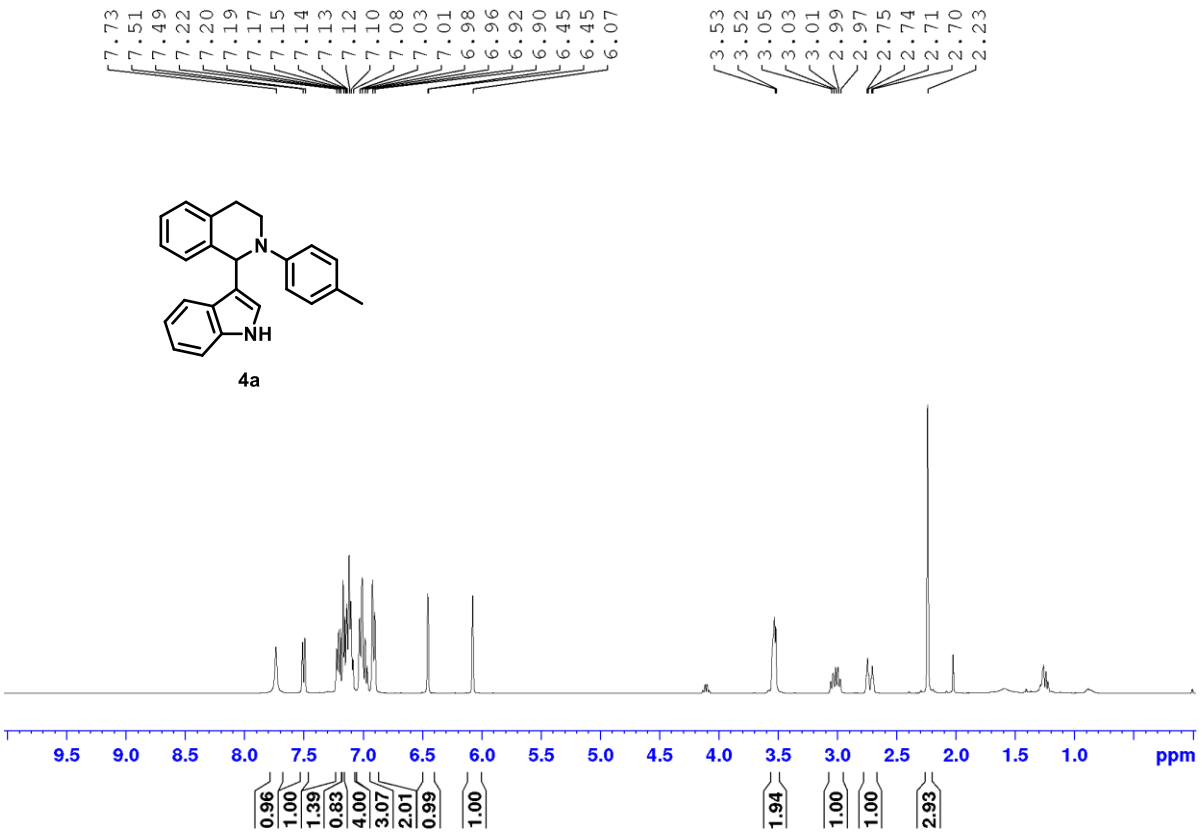


[9] References:

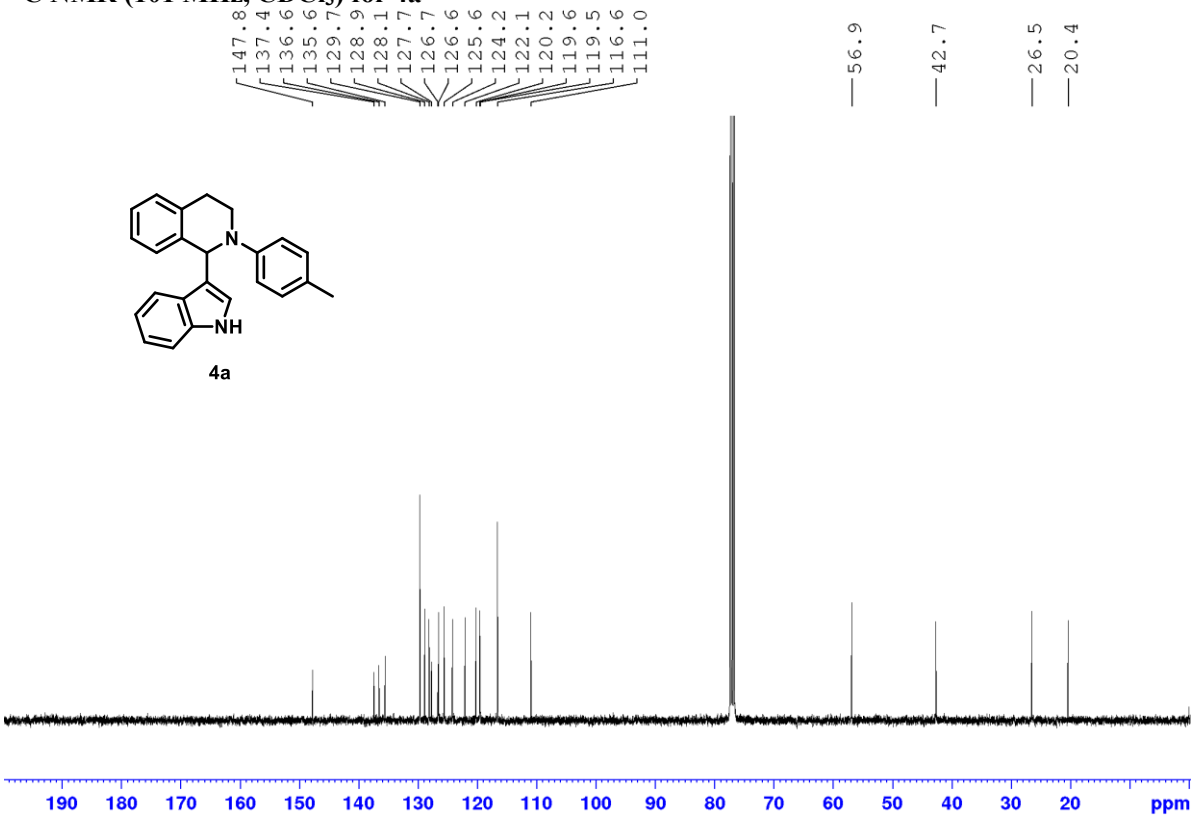
1. a) Novak, M.; Glover, S. A. *J. Am. Chem. Soc.* **2004**, *126*, 7748–7749; b) Green, N. J.; Connolly, C. A.; Rietdijk, K. P. W.; Nichol, G. S.; Duarte, F.; Lawrence, A. L. .
2. Dutta, B.; Sharma, V.; Sassu, N.; Dang, Y.; Weerakkody, C.; Macharia, J.; Miao, R.; Howell, A. R.; Suib, S. L. *Green Chem.,* **2017***, 19***,** 5350–5355.
3. Patil, M. R.; Dedhia, N. P.; Kapdi, A. R.; Kumar, A.V. *J. Org. Chem.* **2018**, *83*, 4477–4490.
4. a) David J. C. Constable, Alan D. Curzons and Virginia L. Cunningham, *Green Chem.*, **2002**, *4*, 521–527; b) Alan D. Curzons, David J. C. Constable, David N. Mortimer and Virginia L. Cunningham, *Green Chem.*, **2001**, *3*, 1–6.
5. a) for *N*-arylation step; C. Mudithanapelli, L. P. Dhorma and M. Kim, *Org. Lett.* 2019, **21**, 3098-3102; b) for Cross Dehydrogenative Coupling step; J.-J. Zhong, Q.-Y. Meng, B. Liu, X.-B. Li, X.-W. Gao, T. Lei, C.-J. Wu, Z.-J. Li, C.-H. Tung and L.-Z. Wu, *Org. lett.* 2014, **16**, 1988-1991.

[10] ^{1}H and ^{13}C NMR spectra

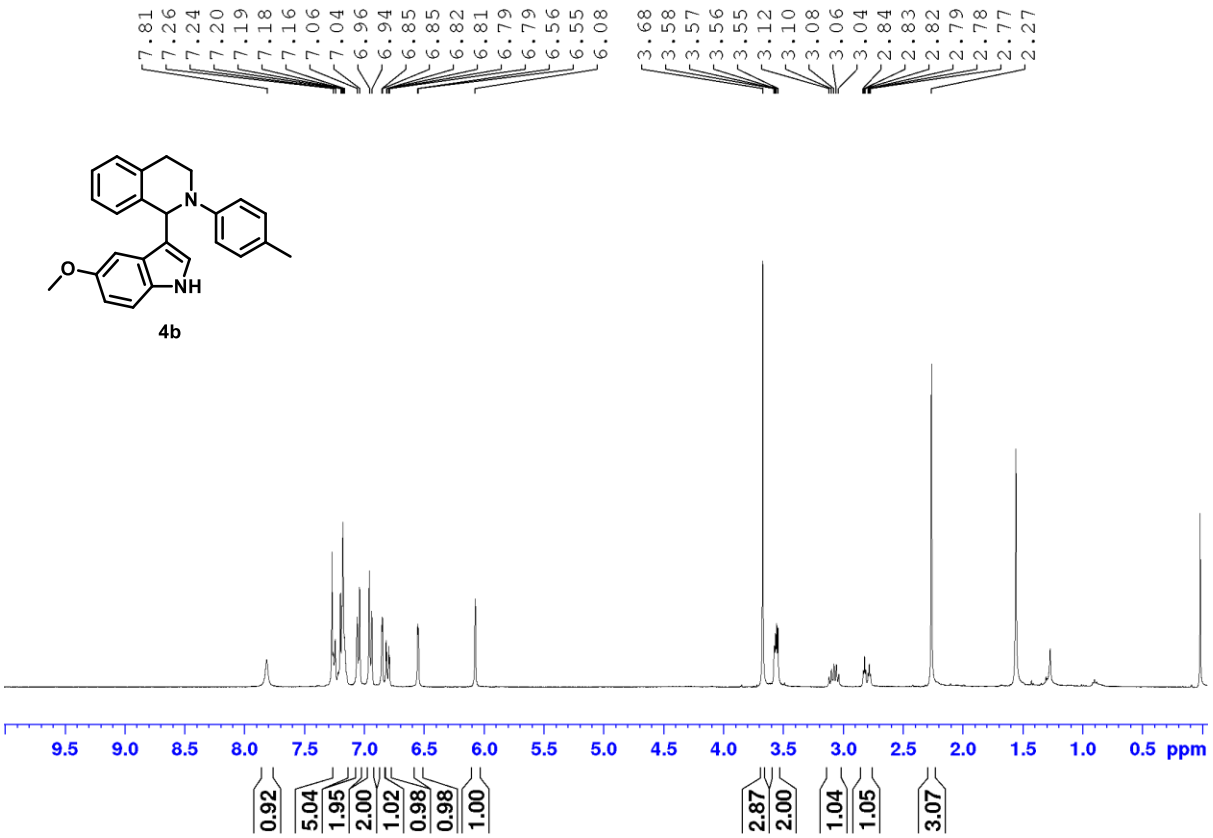
^{1}H NMR (400 MHz, $CDCl_3$) for 4a



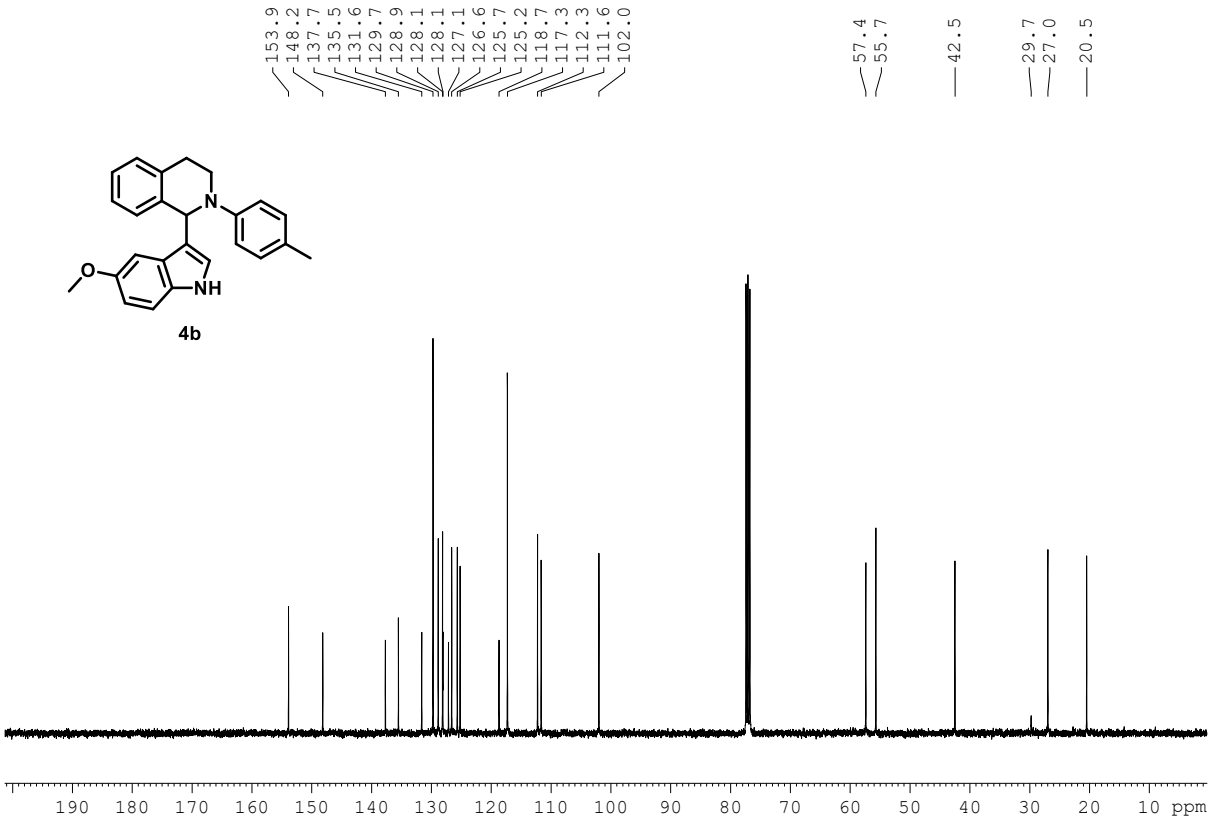
^{13}C NMR (101 MHz, $CDCl_3$) for 4a



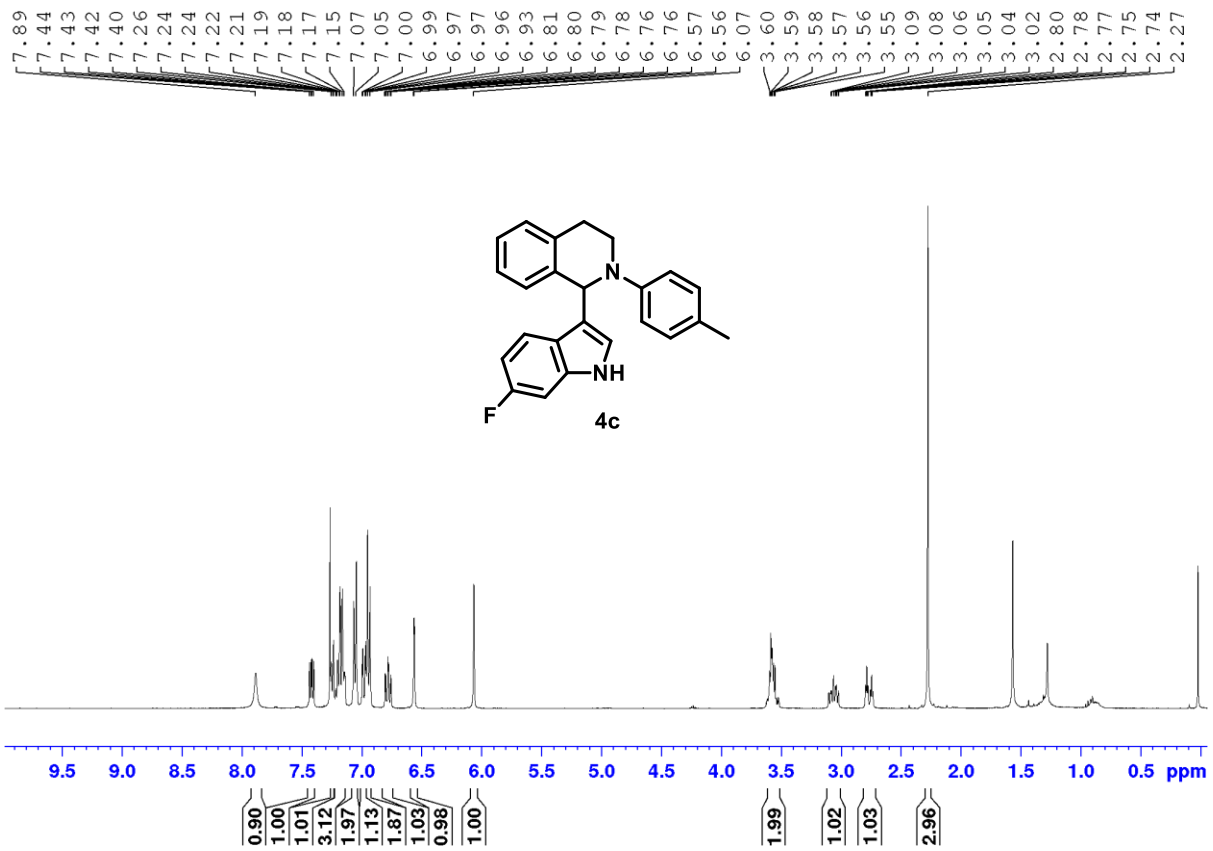
^{1}H NMR (400 MHz, $CDCl_3$) for 4b



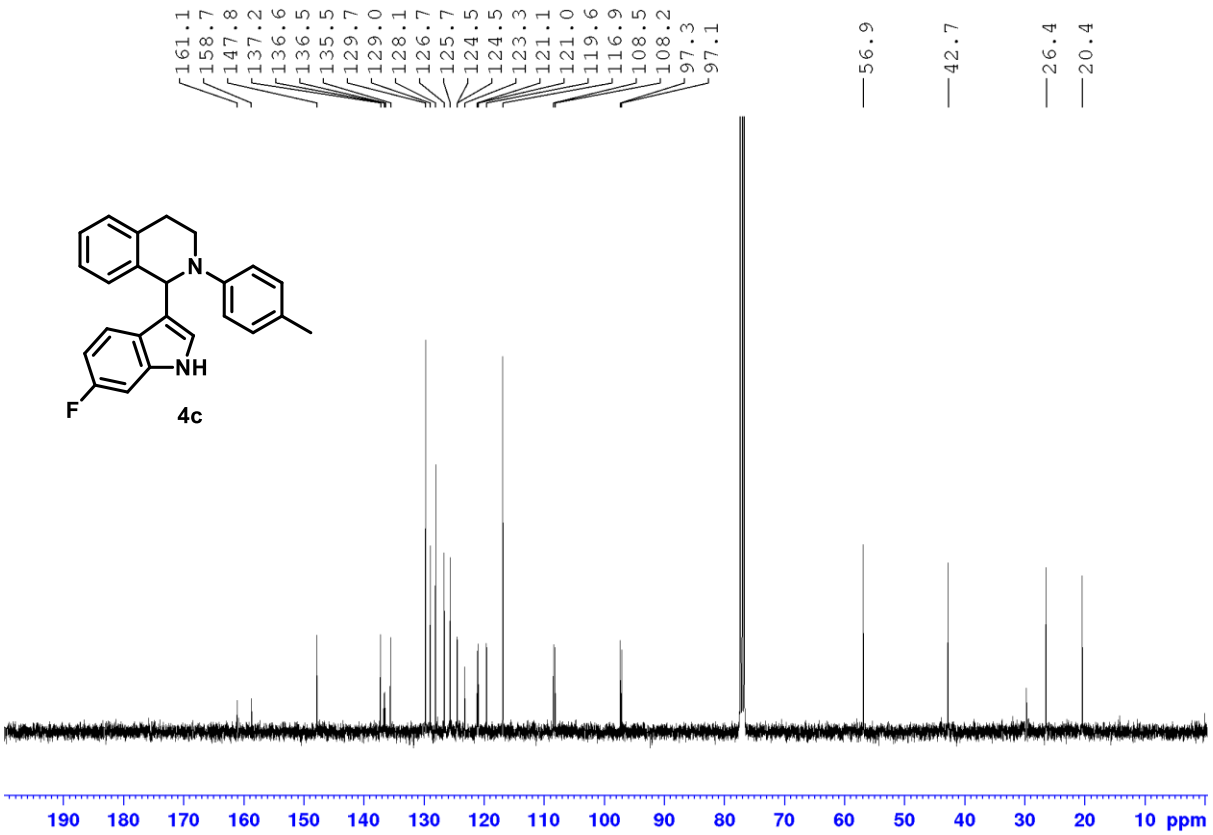
^{13}C NMR (101 MHz, $CDCl_3$) for 4b



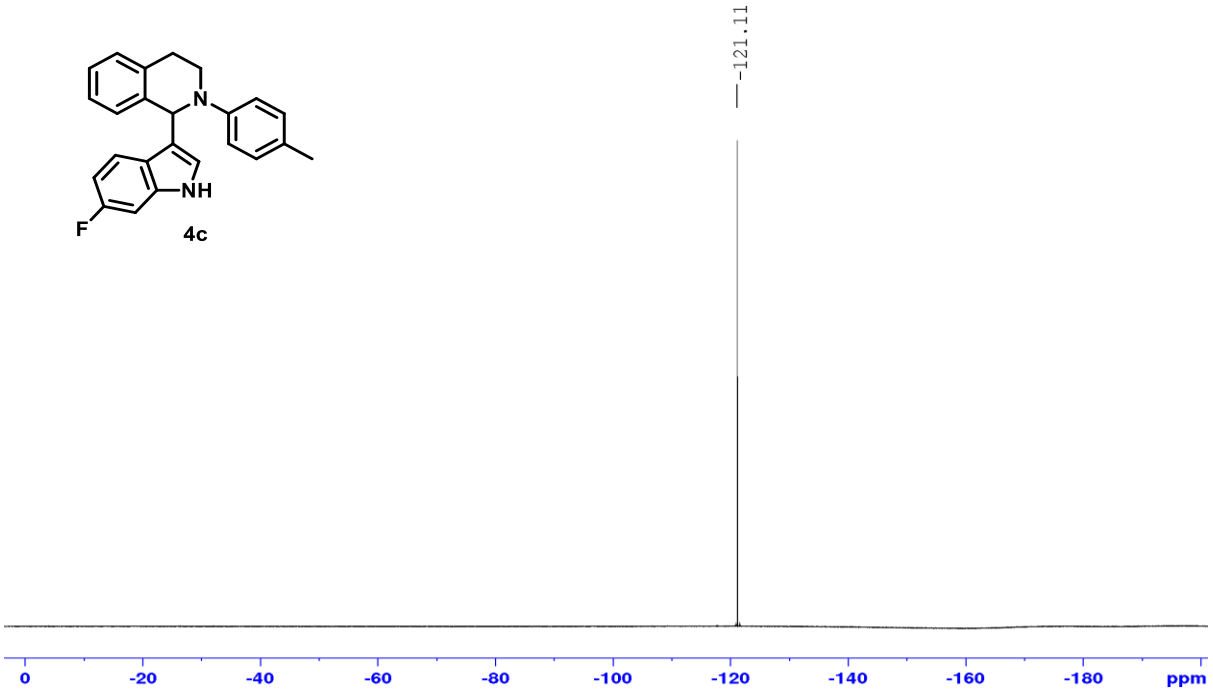
^{1}H NMR (400 MHz, $CDCl_3$) for 4c



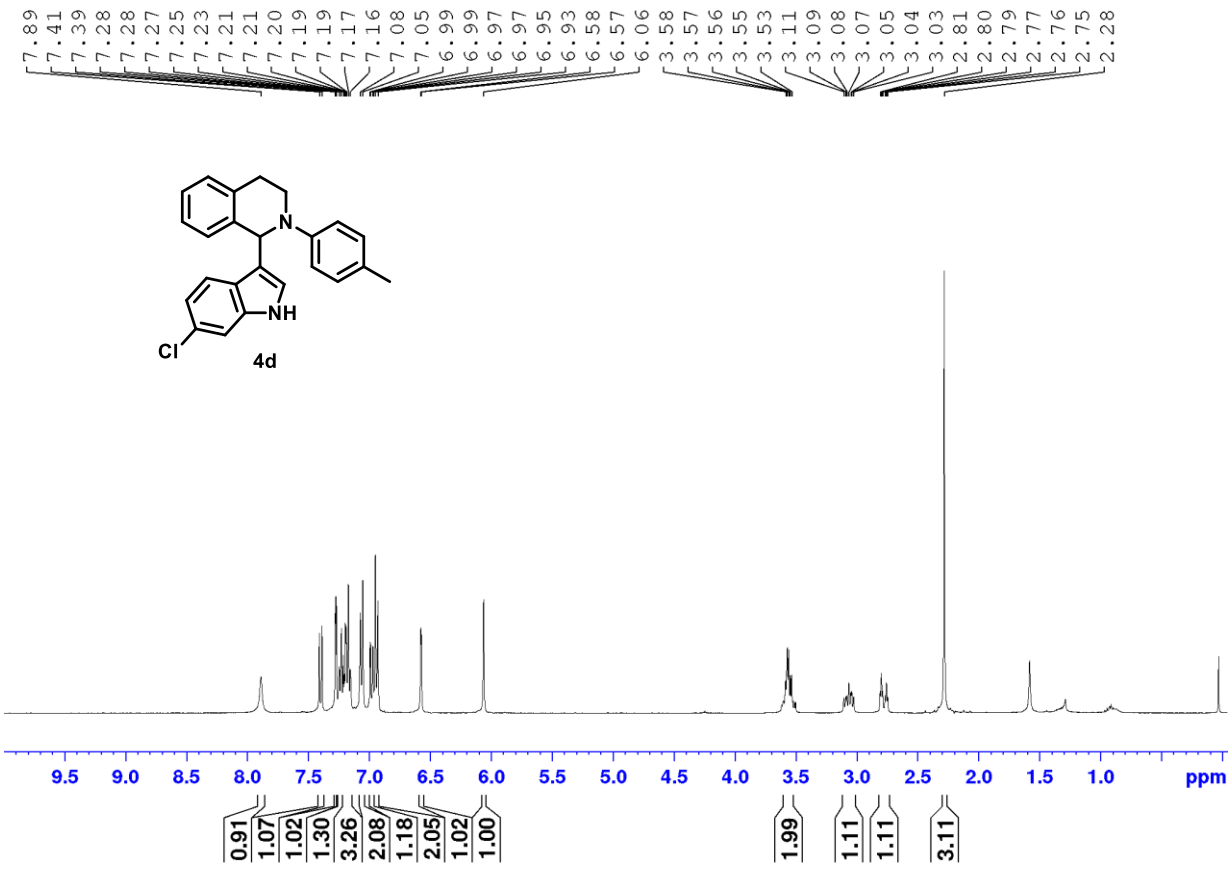
^{13}C NMR (101 MHz, $CDCl_3$) for 4c



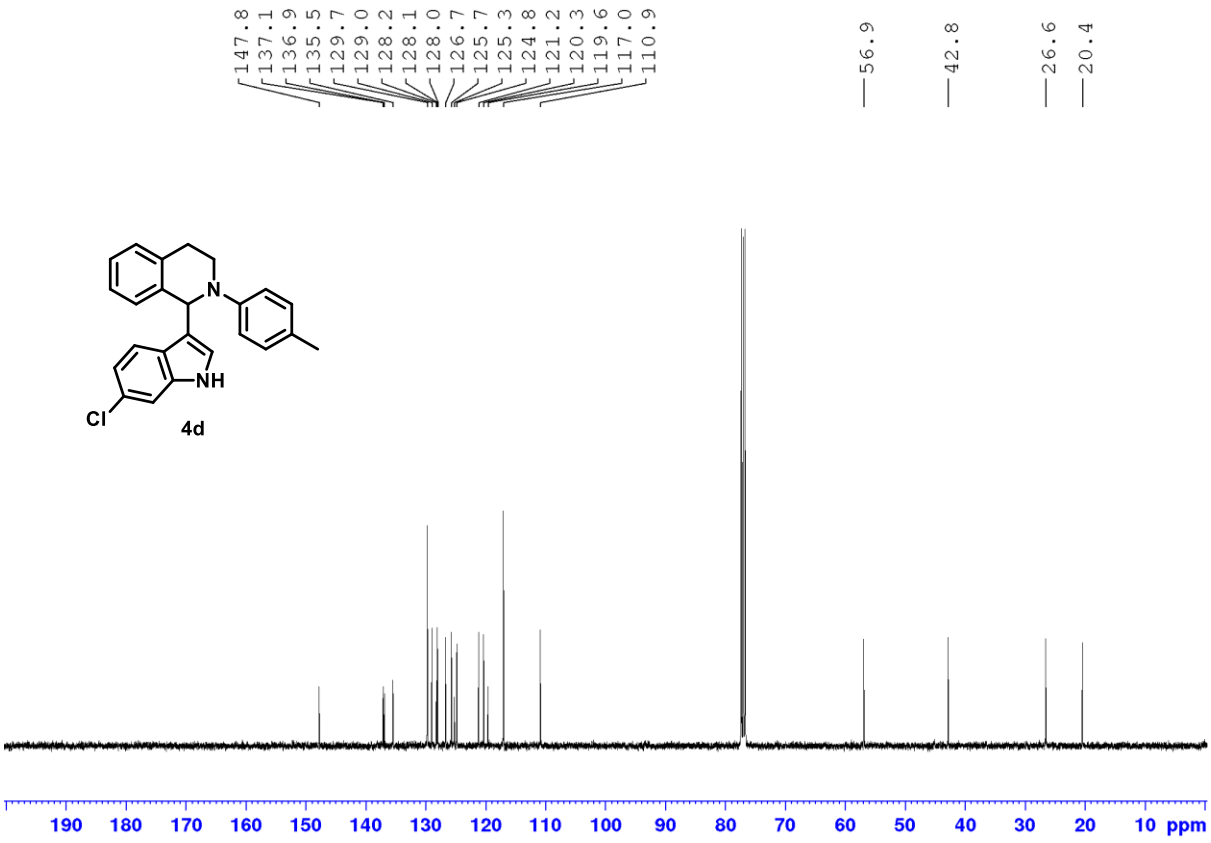
^{19}F NMR (376 MHz, $CDCl_3$) for 4c



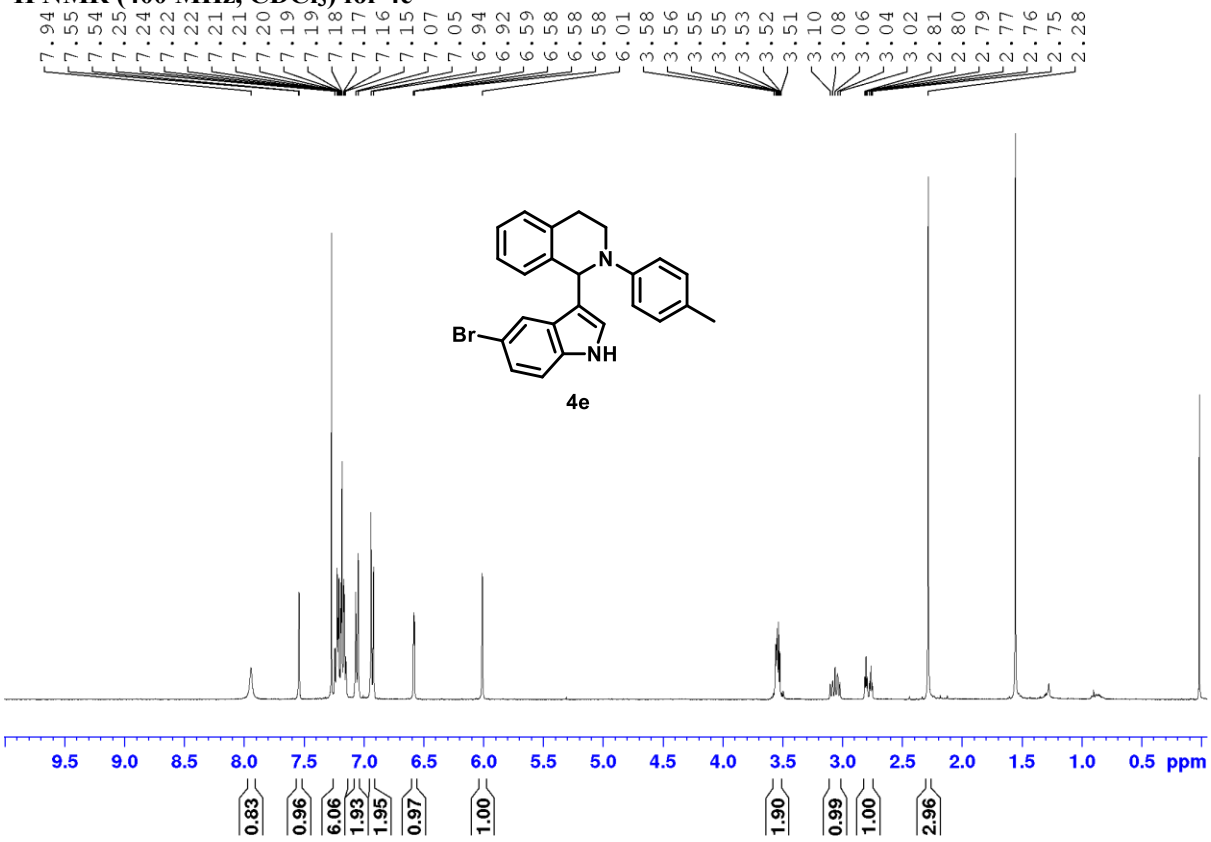
^{1}H NMR (400 MHz, $CDCl_3$) for 4d



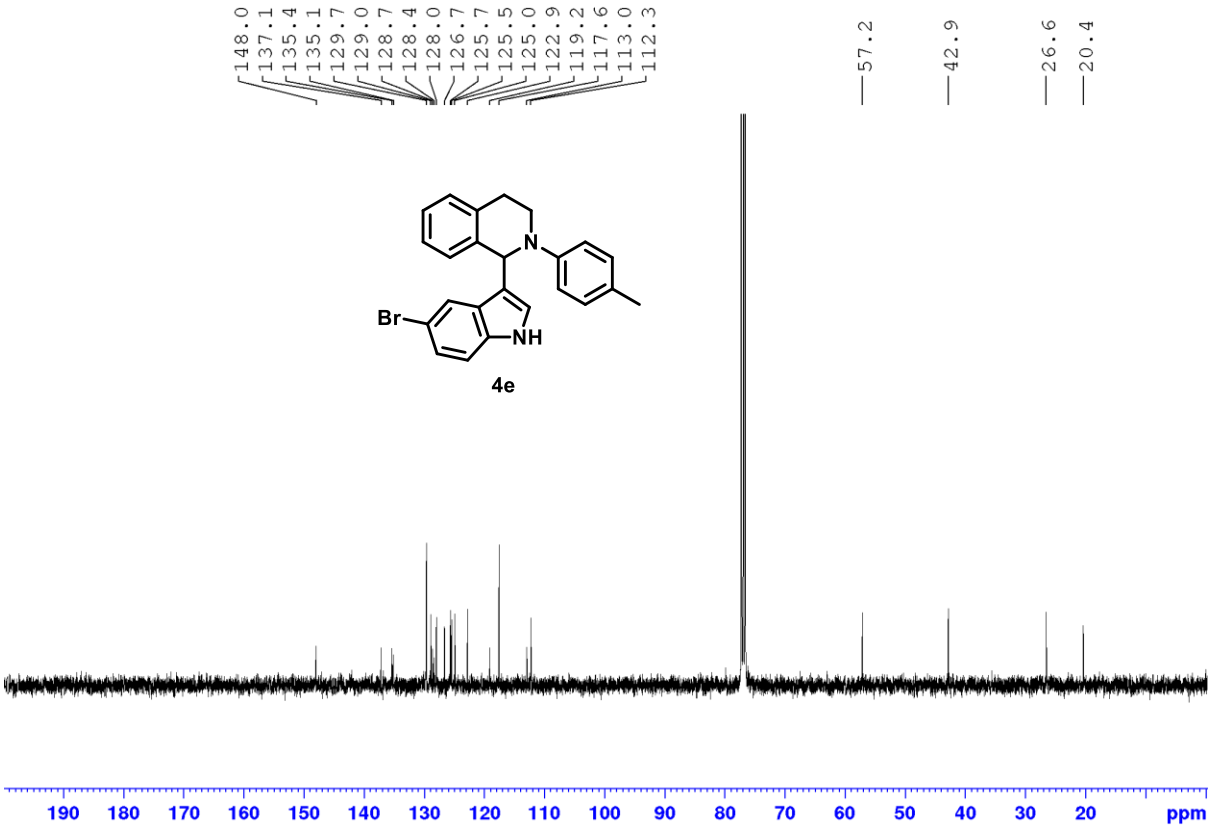
^{13}C NMR (101 MHz, $CDCl_3$) for 4d



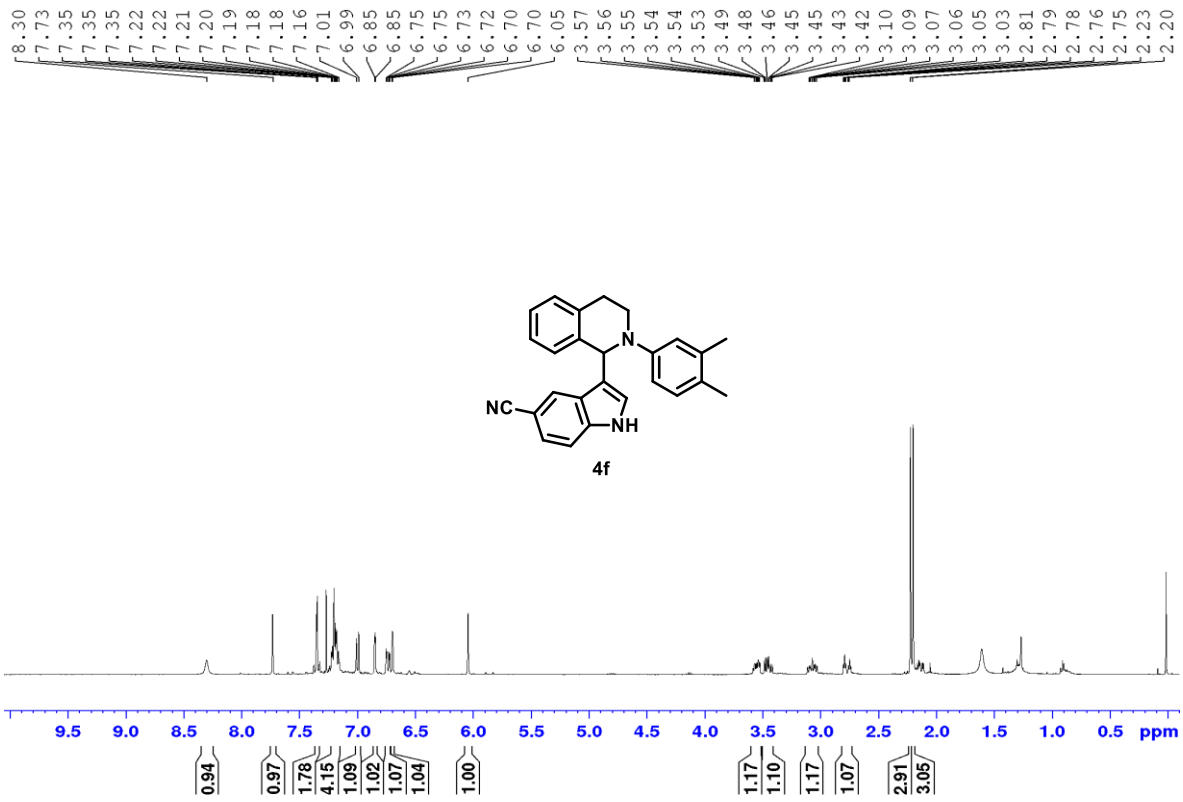
^{1}H NMR (400 MHz, $CDCl_3$) for 4e



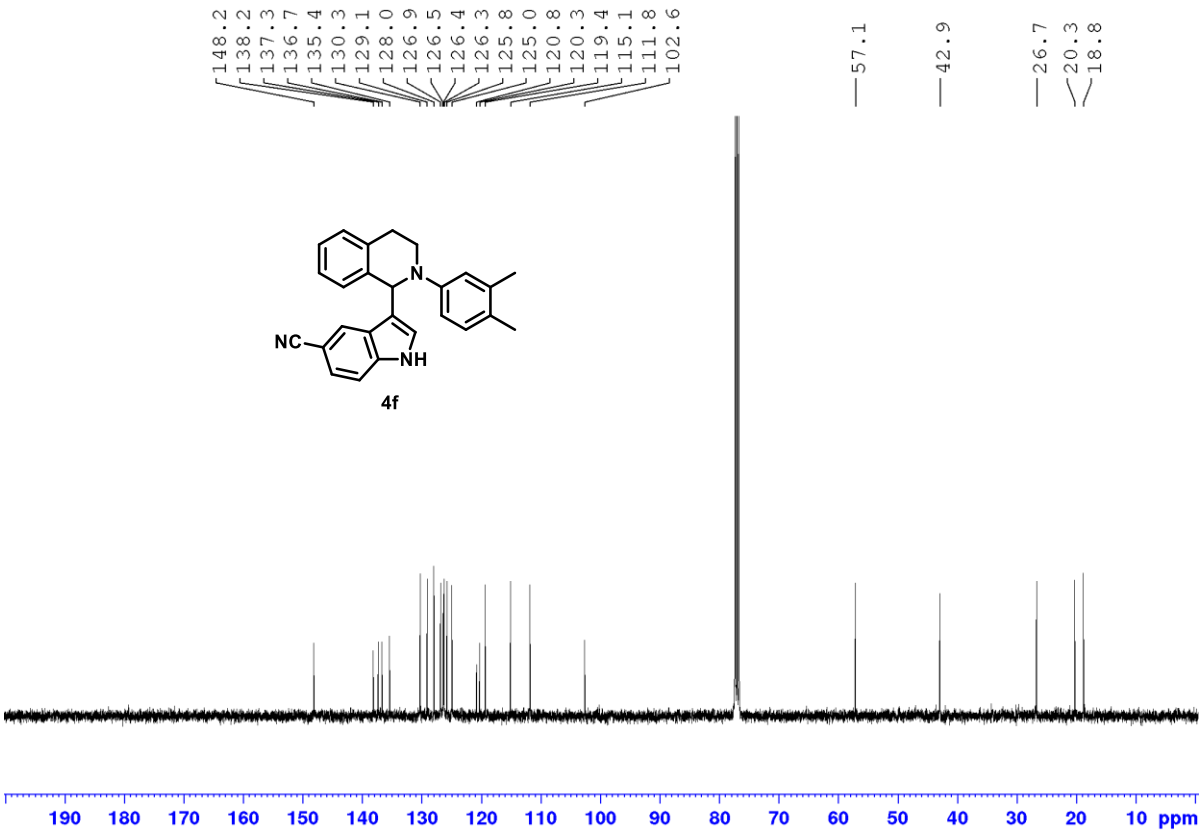
^{13}C NMR (101 MHz, $CDCl_3$) for 4e



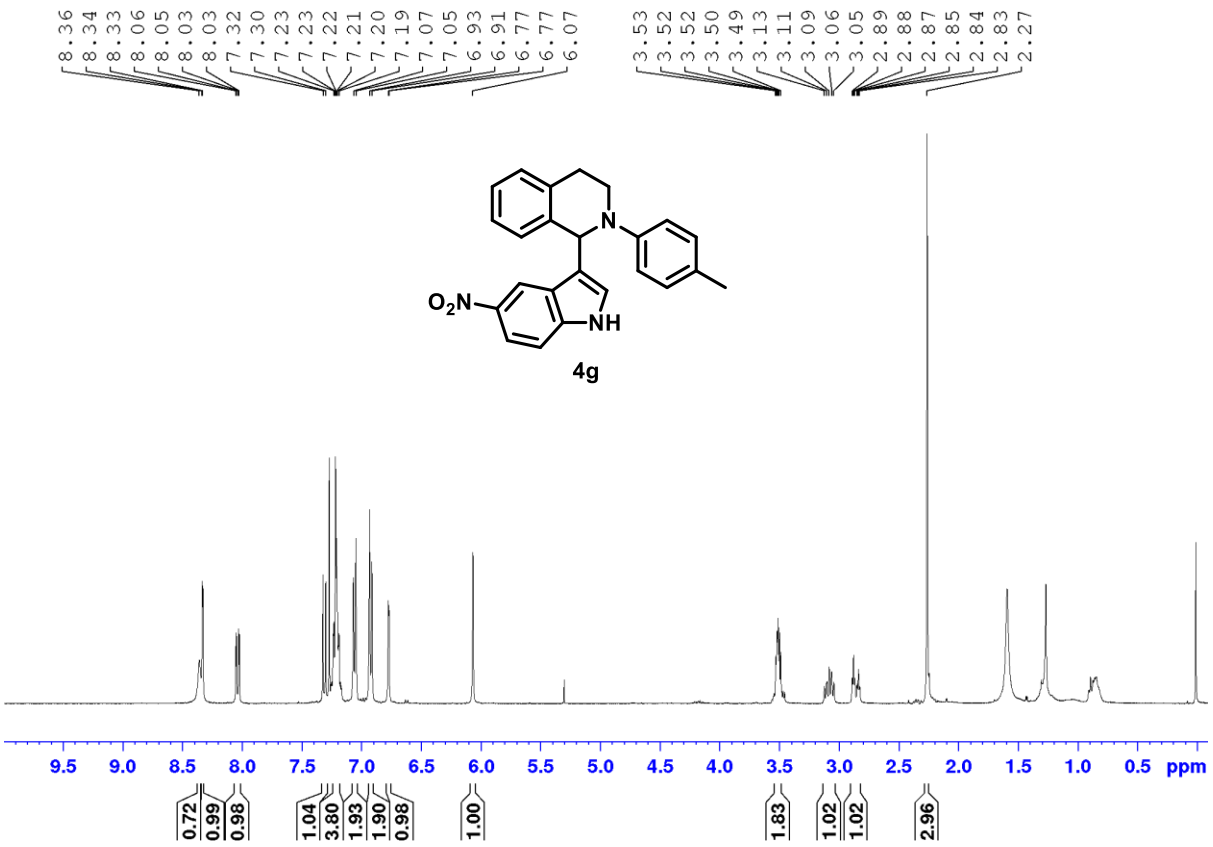
^{1}H NMR (400 MHz, $CDCl_3$) for 4f



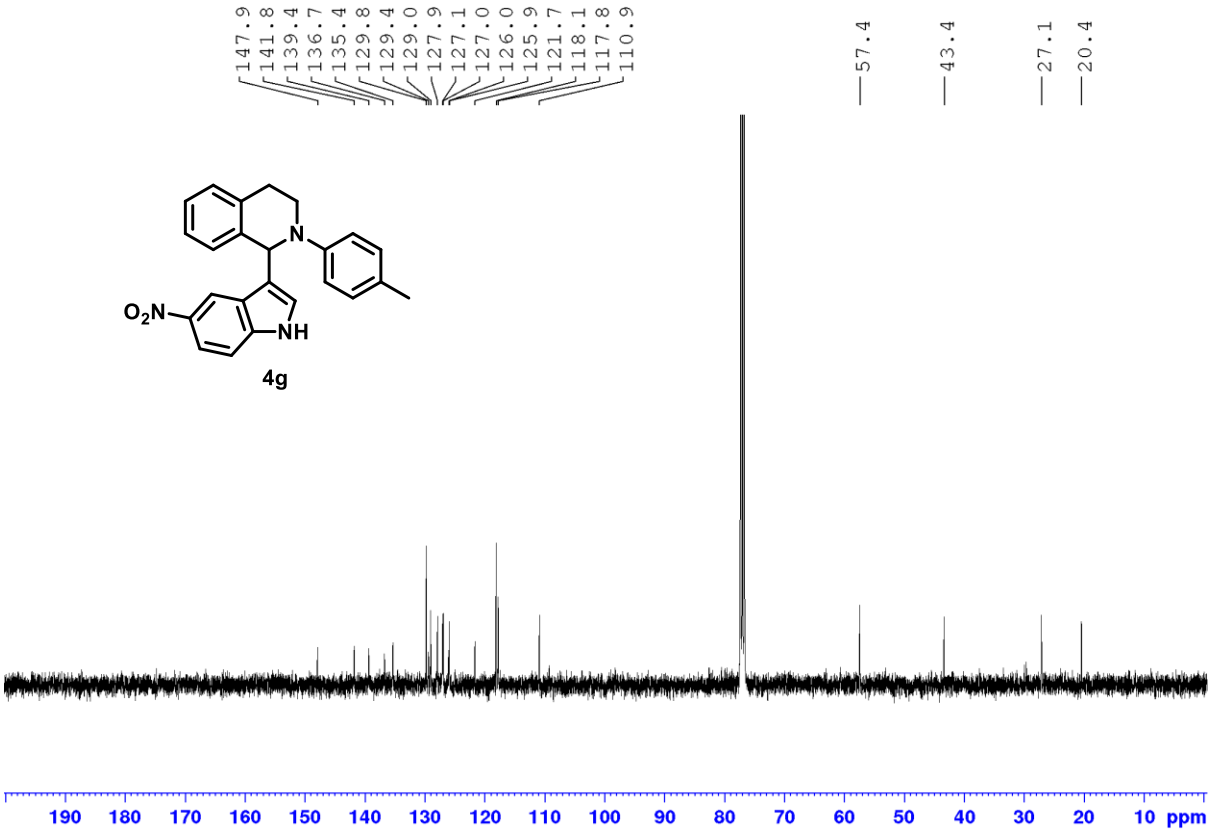
^{13}C NMR (100 MHz, $CDCl_3$) for 4f



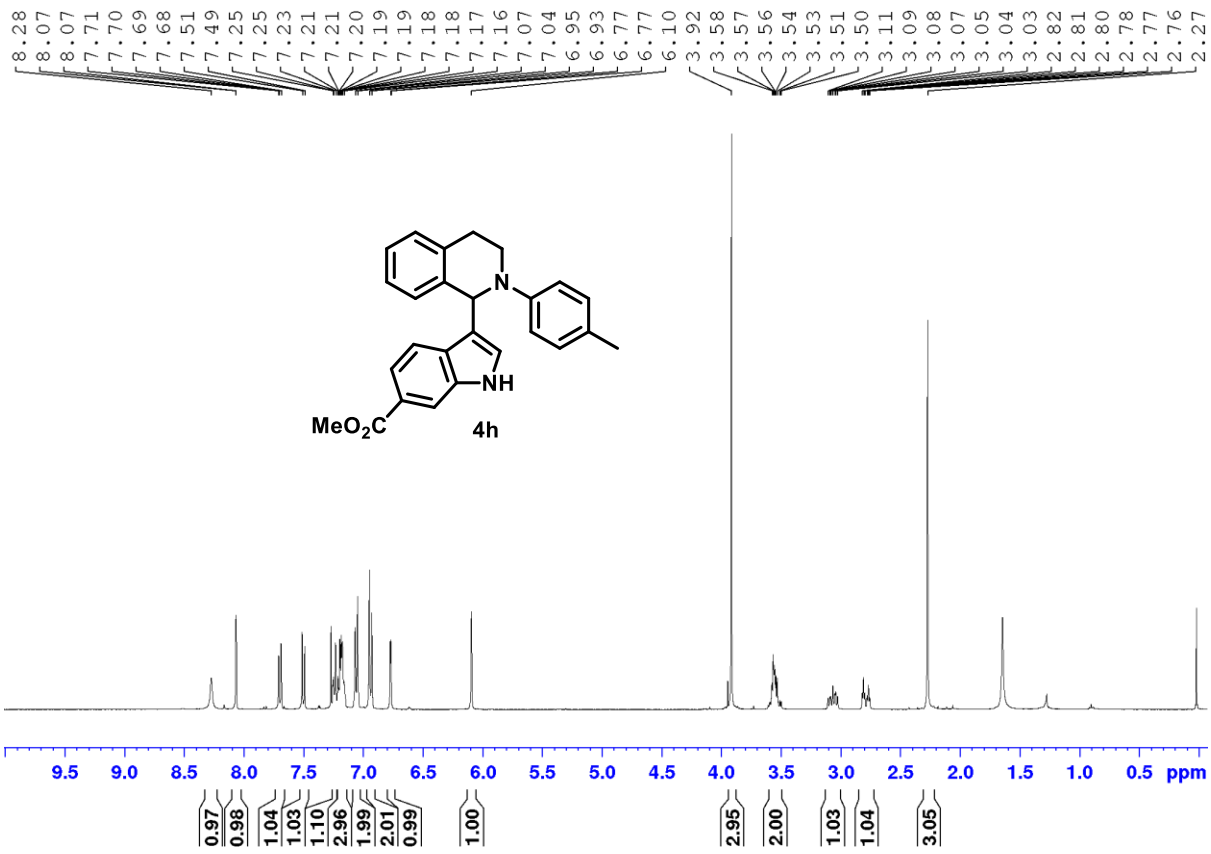
^{1}H NMR (400 MHz, $CDCl_3$) for 4g



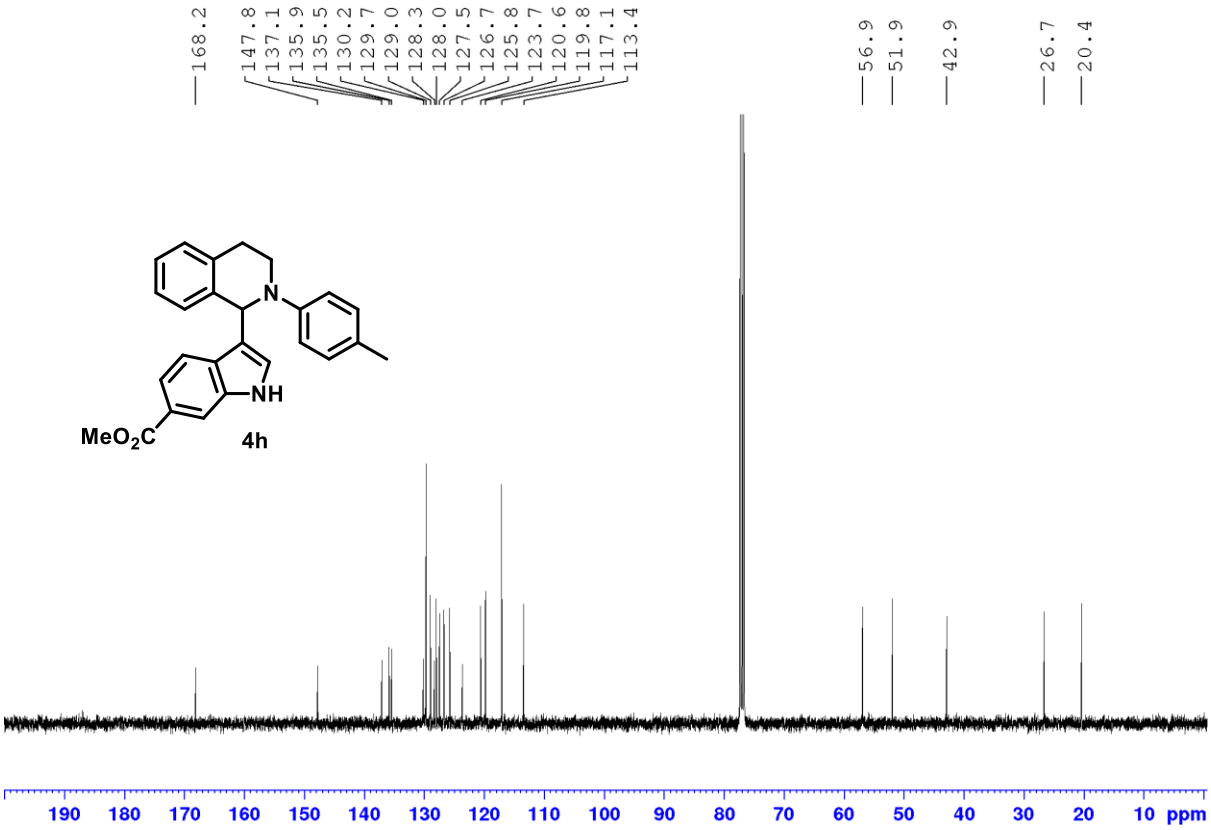
^{13}C NMR (101 MHz, $CDCl_3$) for 4g



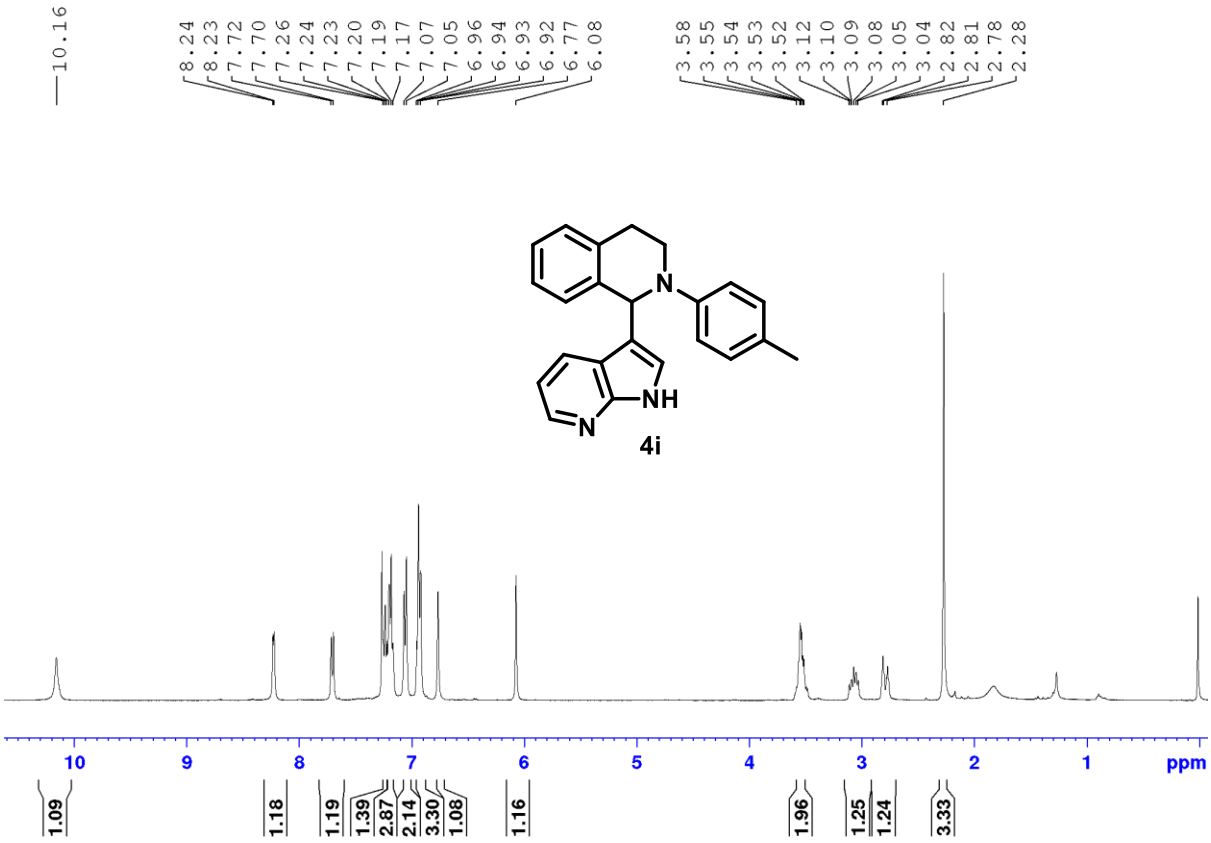
^{1}H NMR (400 MHz, $CDCl_3$) for 4h



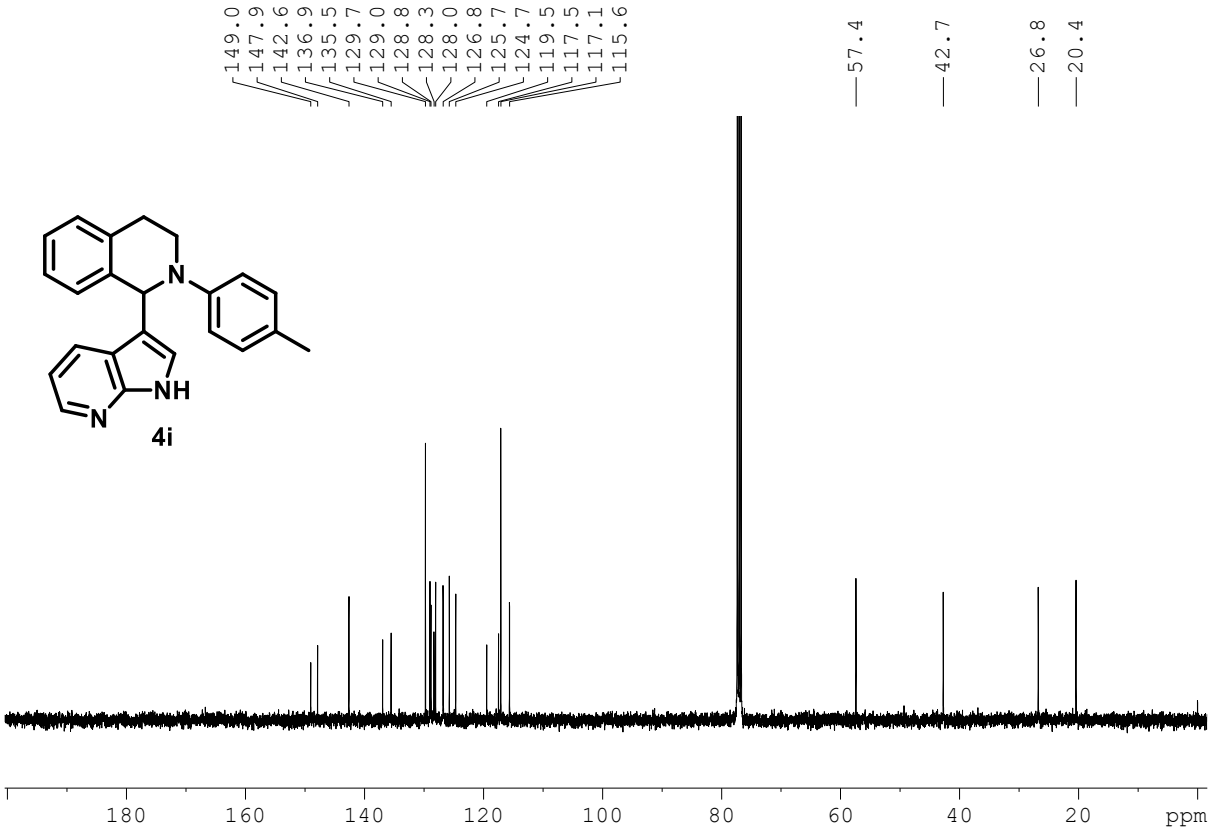
^{13}C NMR (101 MHz, $CDCl_3$) for 4h



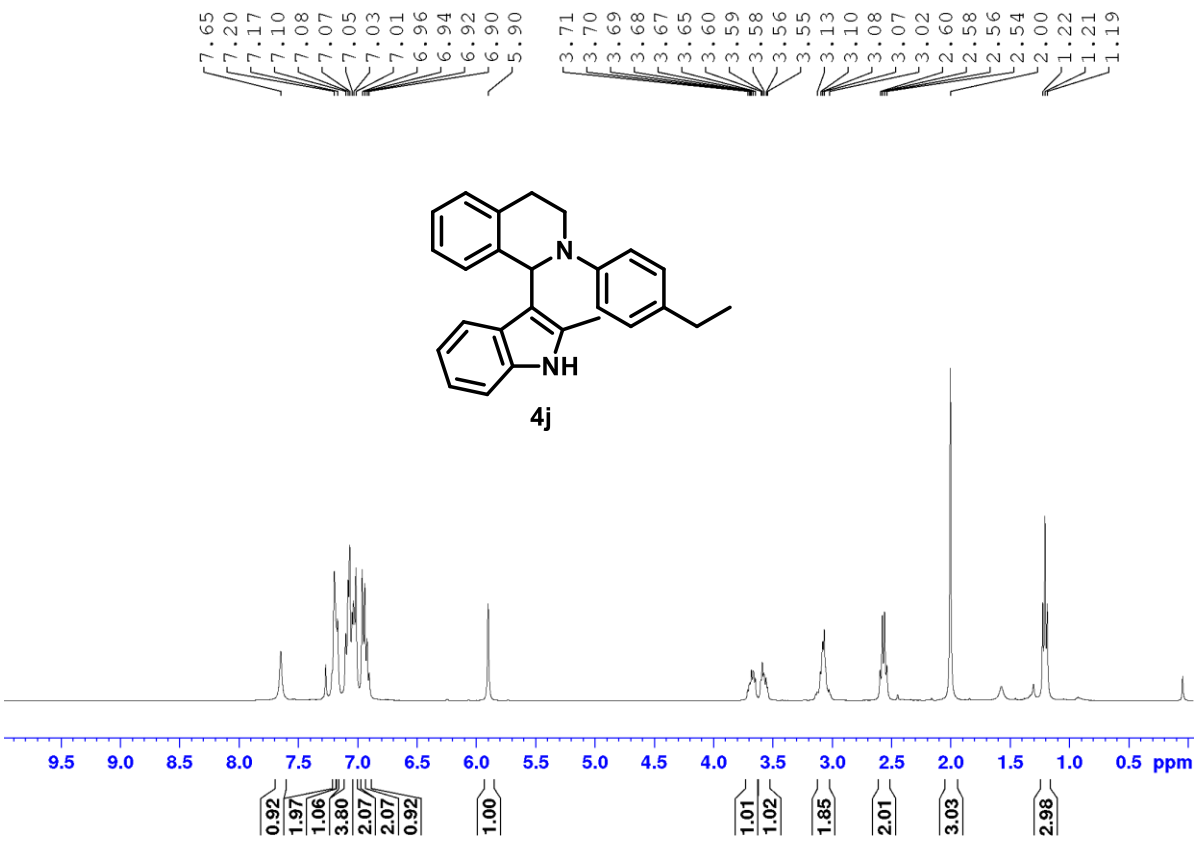
^{1}H NMR (400 MHz, $CDCl_3$) for 4i



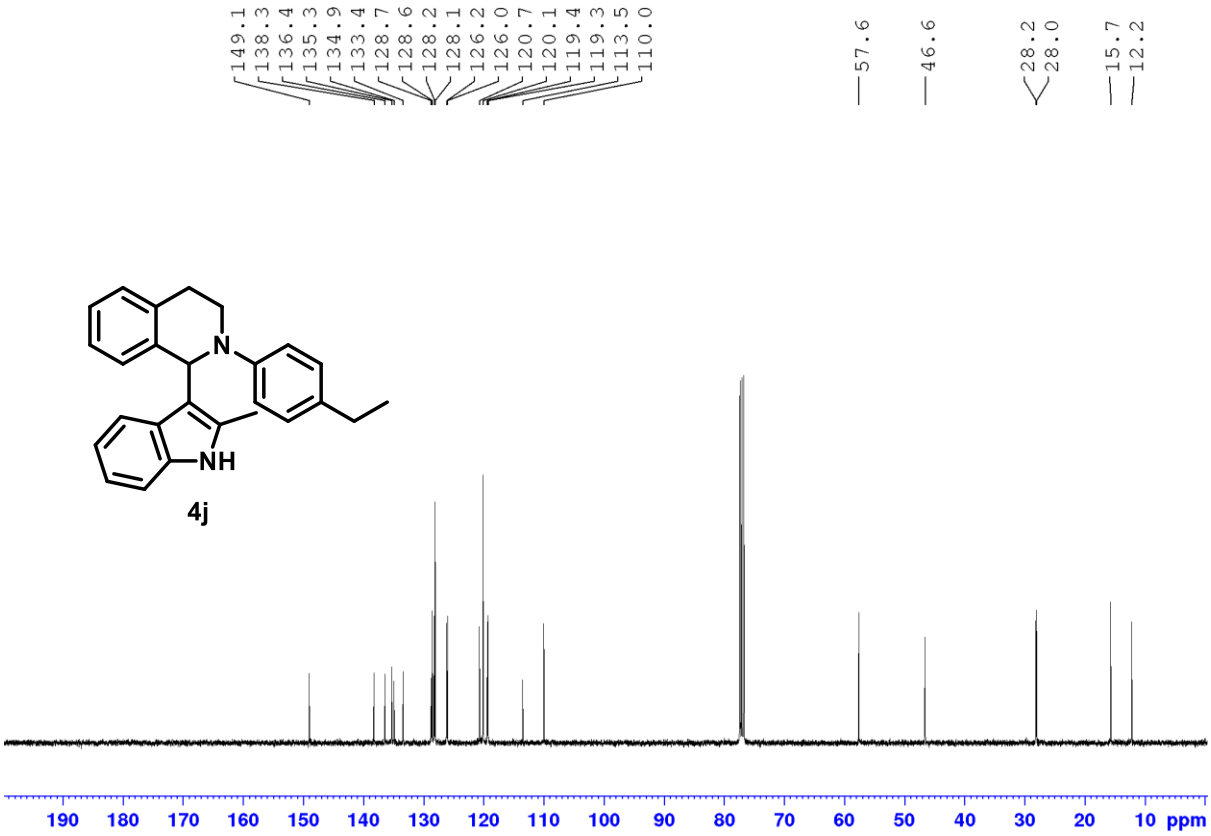
^{13}C NMR (101 MHz, $CDCl_3$) for 4i



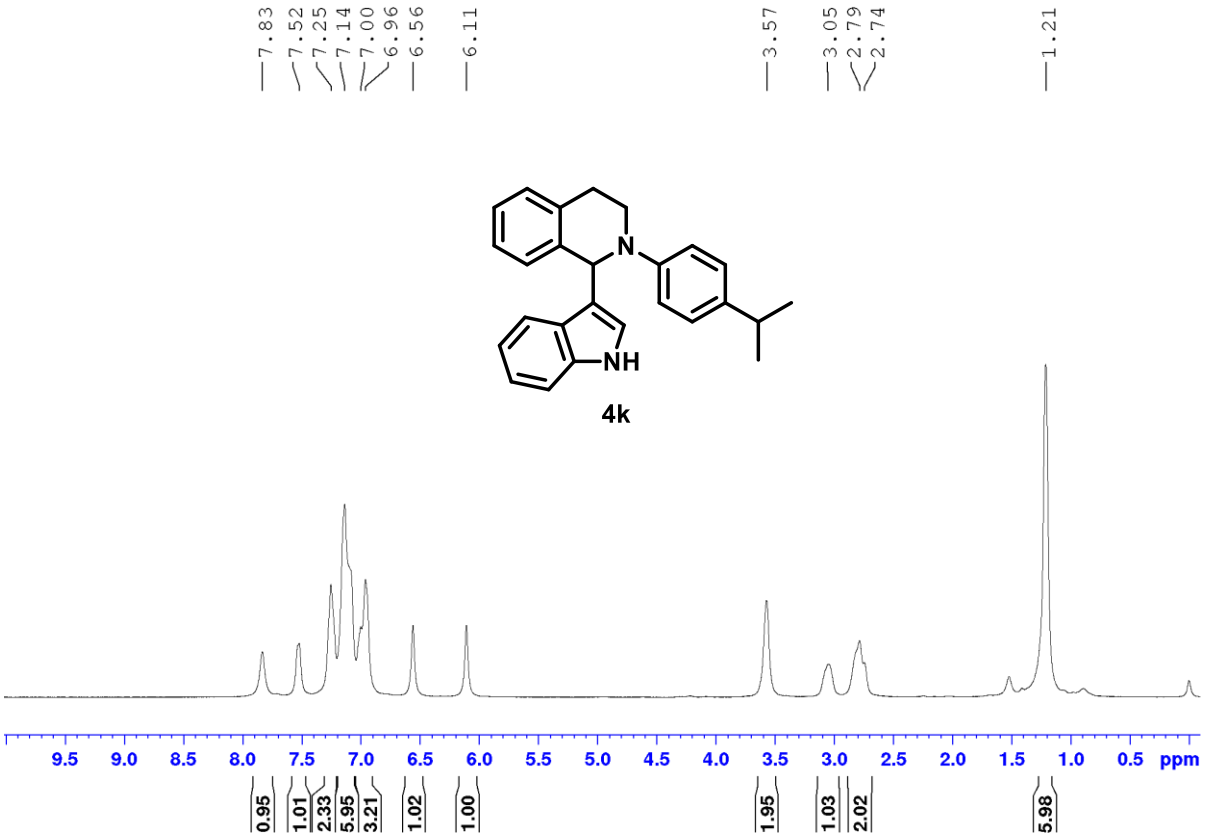
^{1}H NMR (400 MHz, $CDCl_3$) for 4j



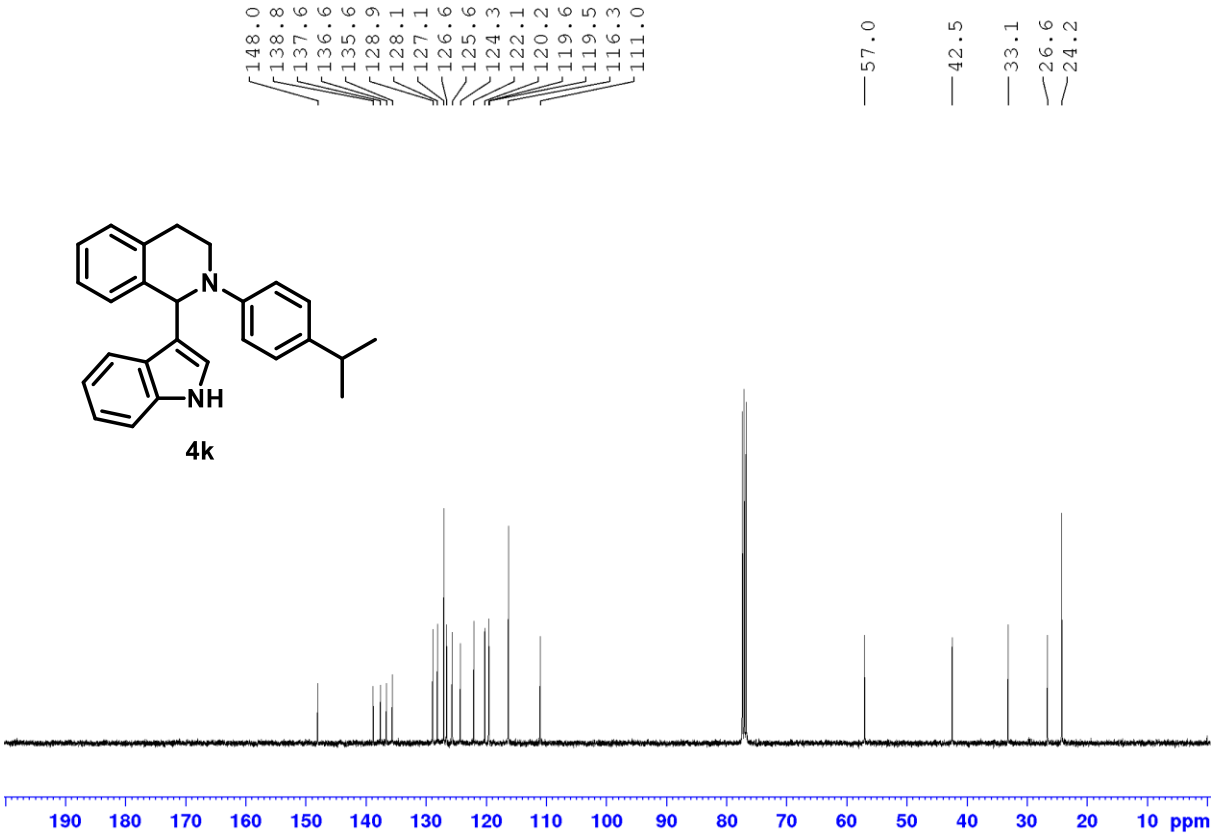
^{13}C NMR (101 MHz, $CDCl_3$) for 4j



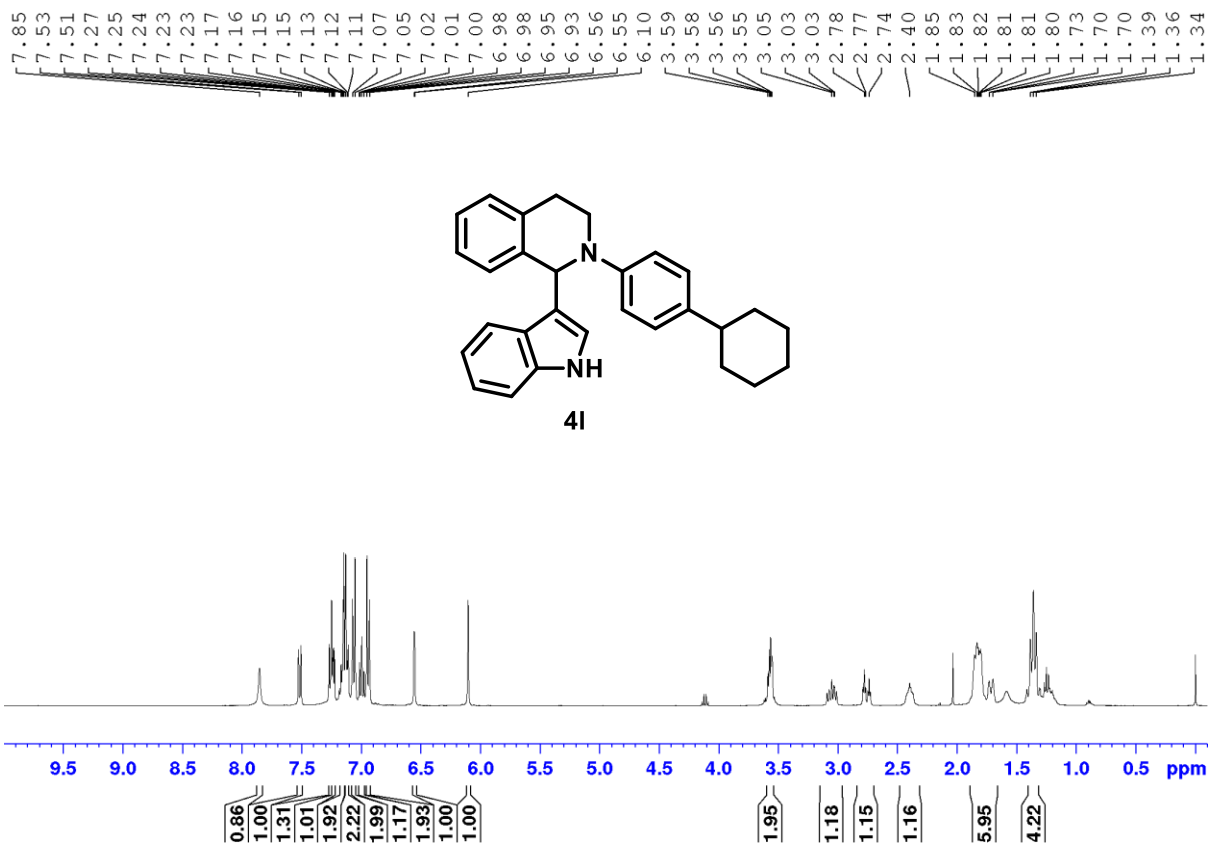
^{1}H NMR (400 MHz, $CDCl_3$) for 4k



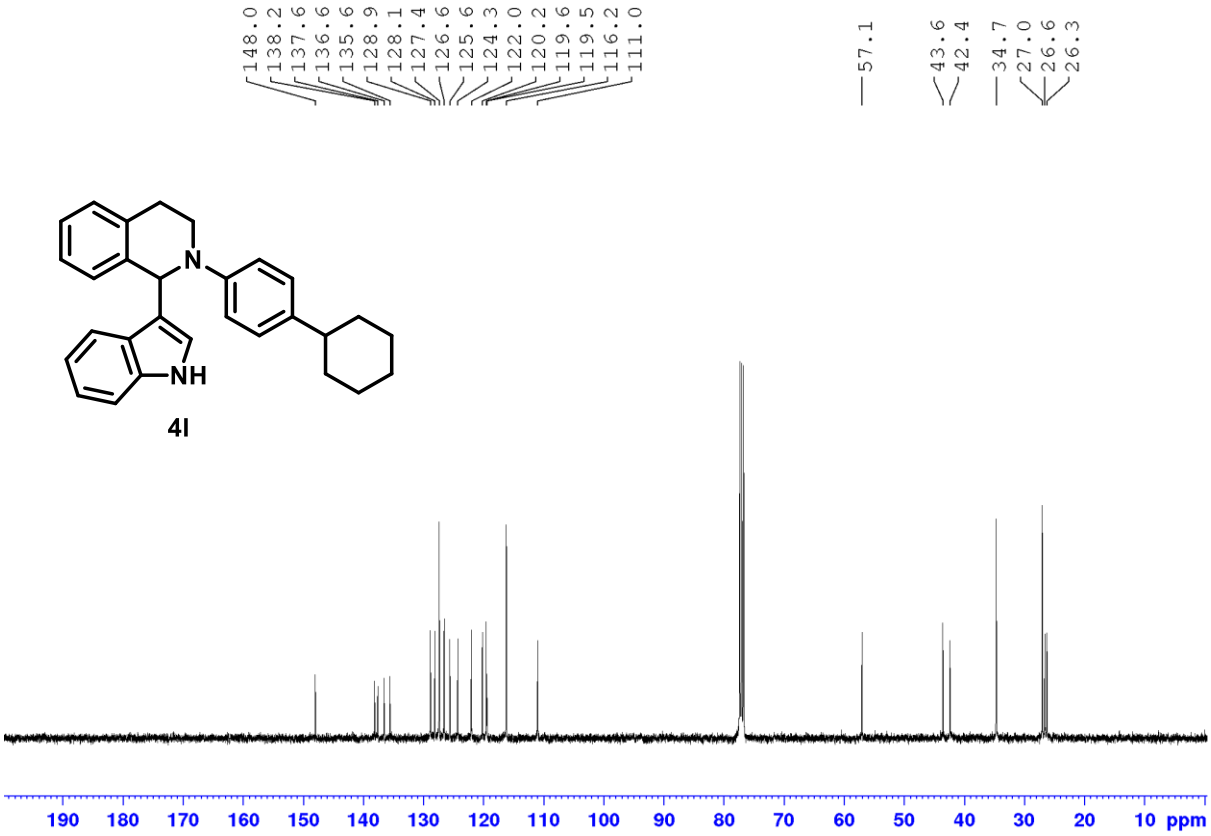
^{13}C NMR (101 MHz, $CDCl_3$) for 4k



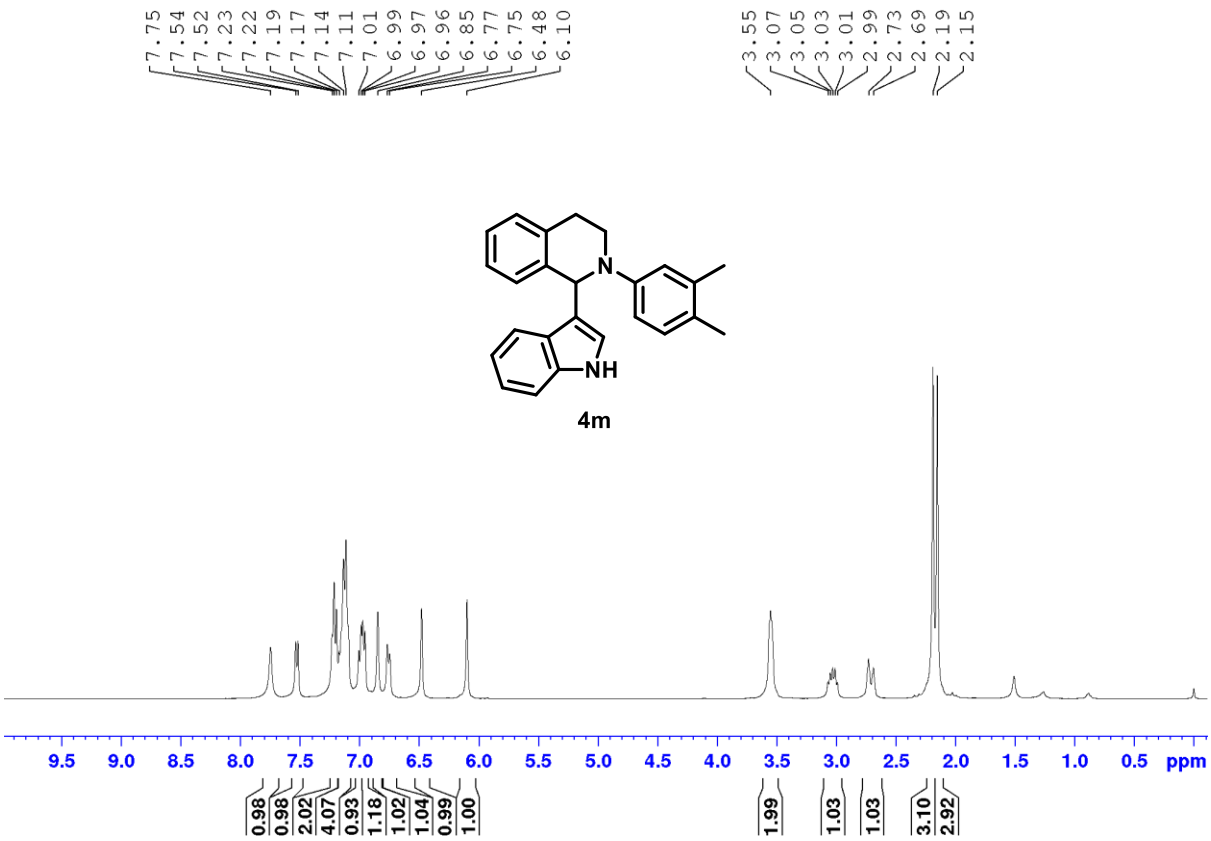
^{1}H NMR (400 MHz, $CDCl_3$) for 4l



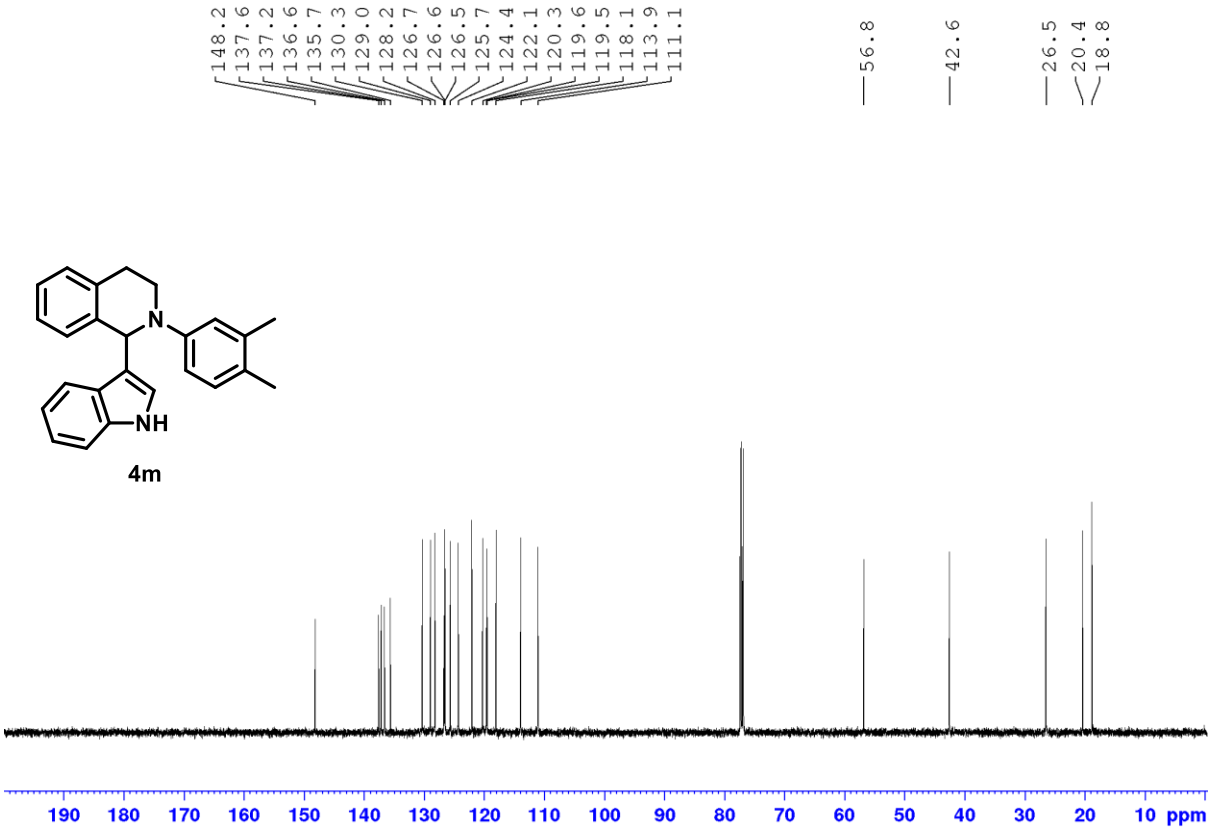
^{13}C NMR (101 MHz, $CDCl_3$) for 4l



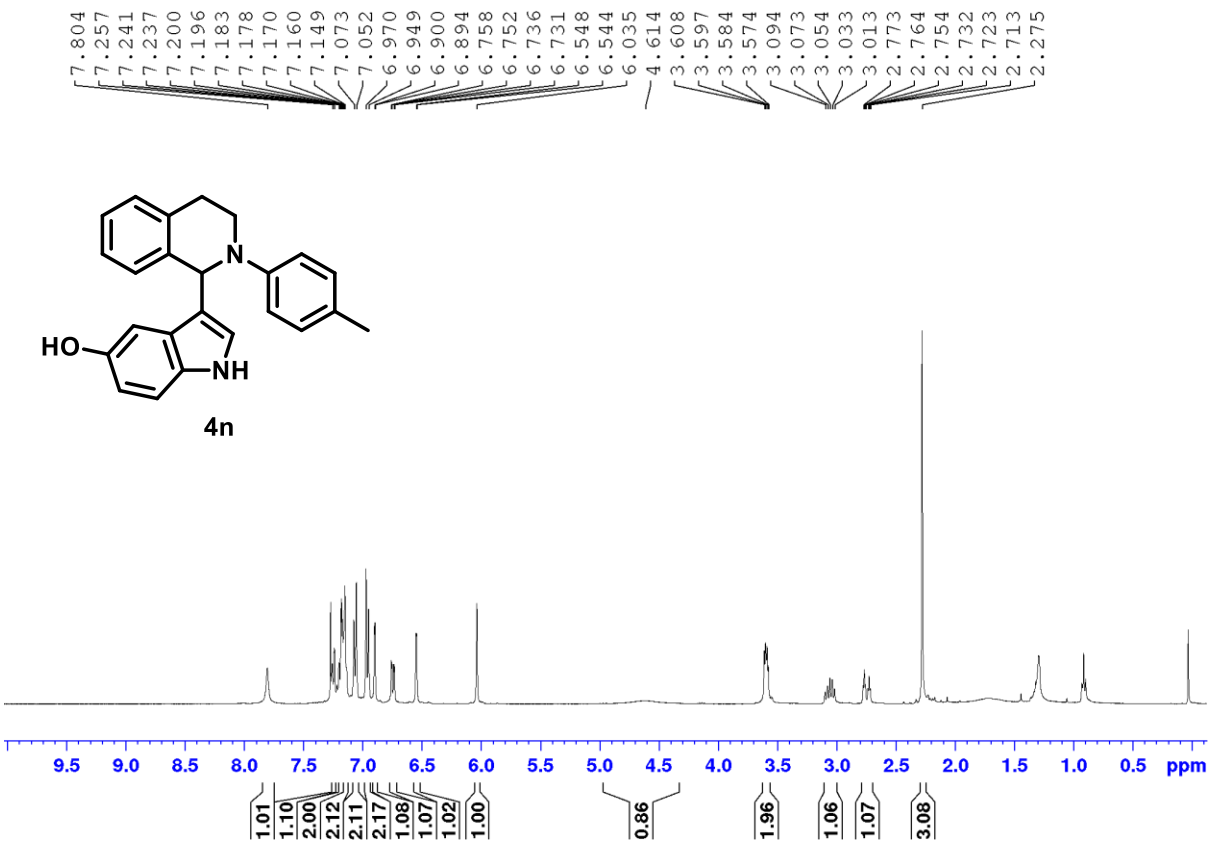
^{1}H NMR (400 MHz, $CDCl_3$) for 4m



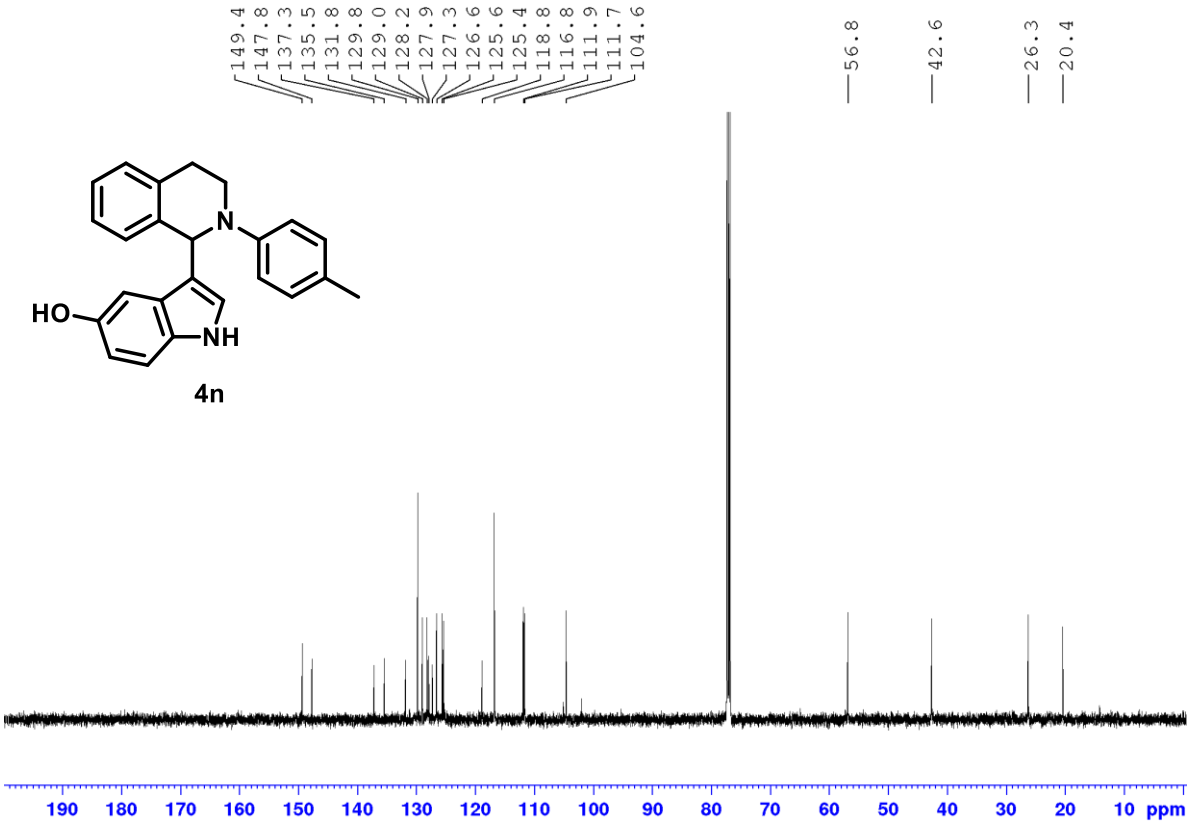
^{13}C NMR (101 MHz, $CDCl_3$) for 4m



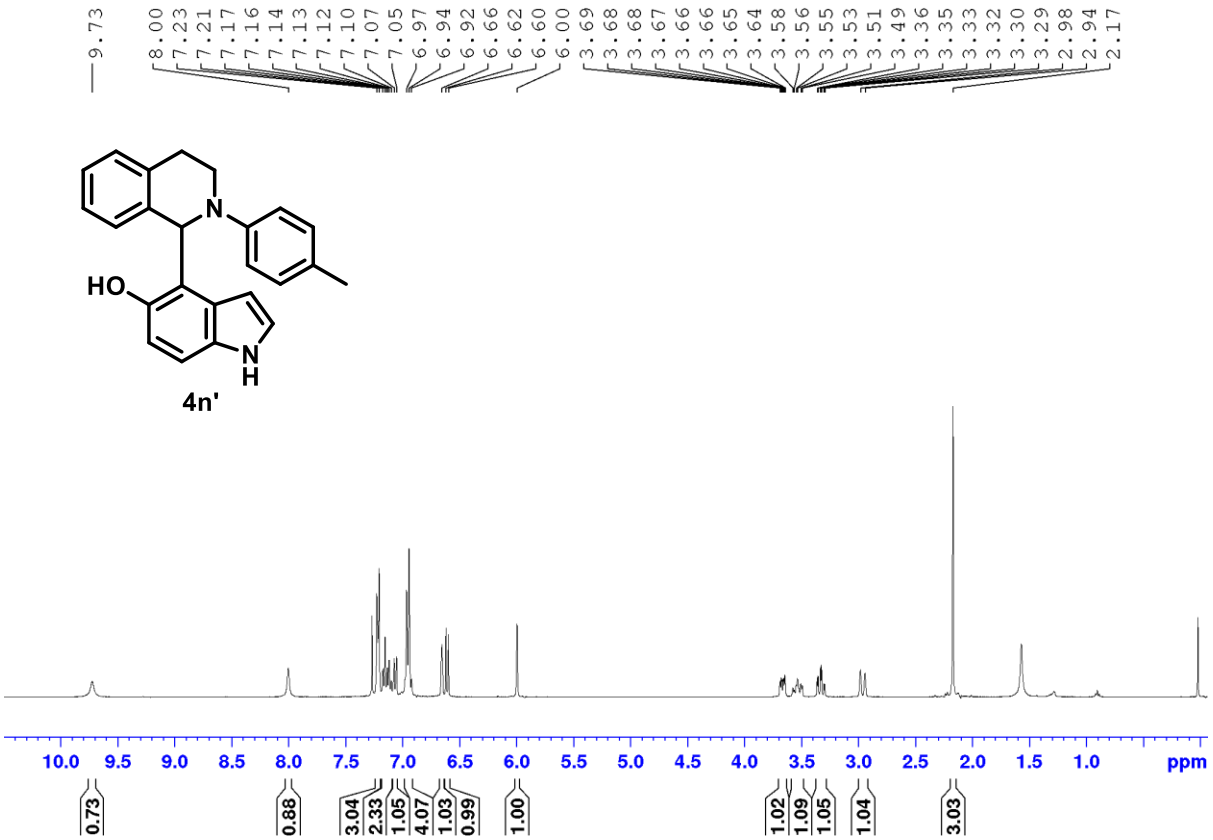
^{1}H NMR (400 MHz, $CDCl_3$) for 4n



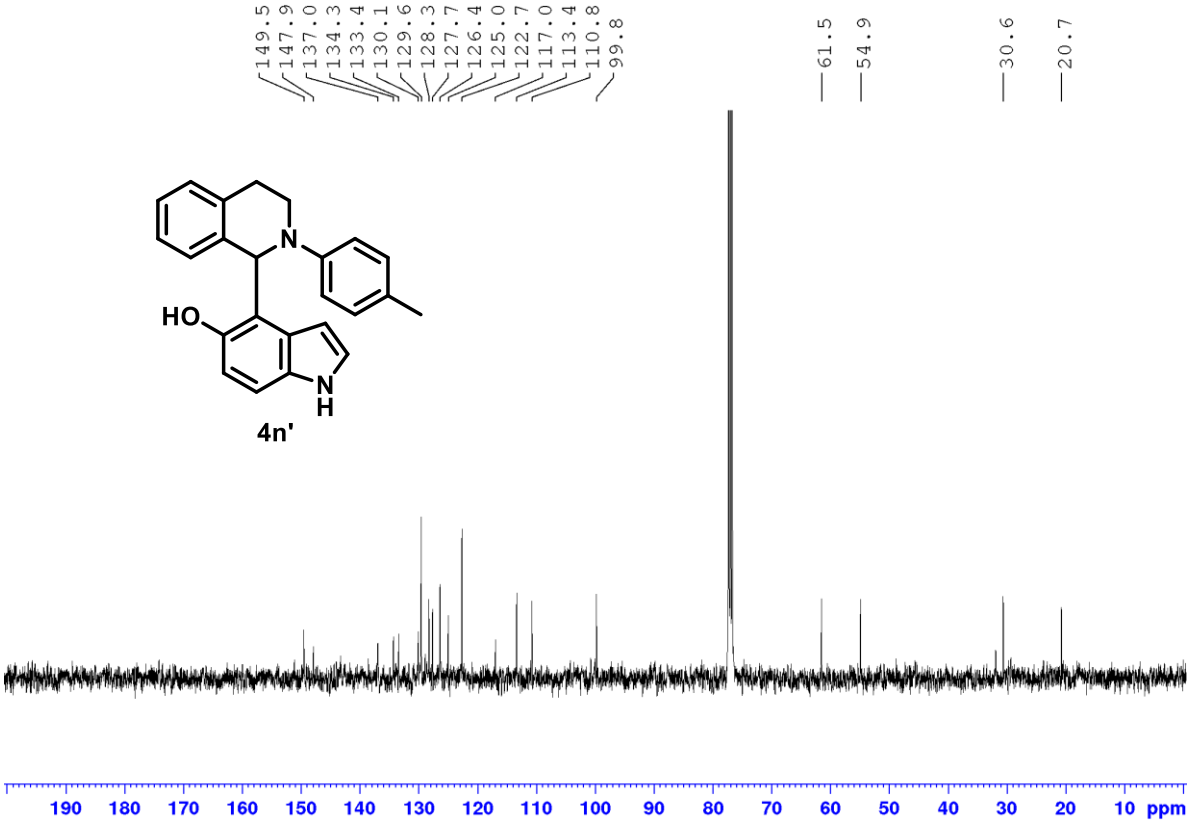
^{13}C NMR (101 MHz, $CDCl_3$) for 4n



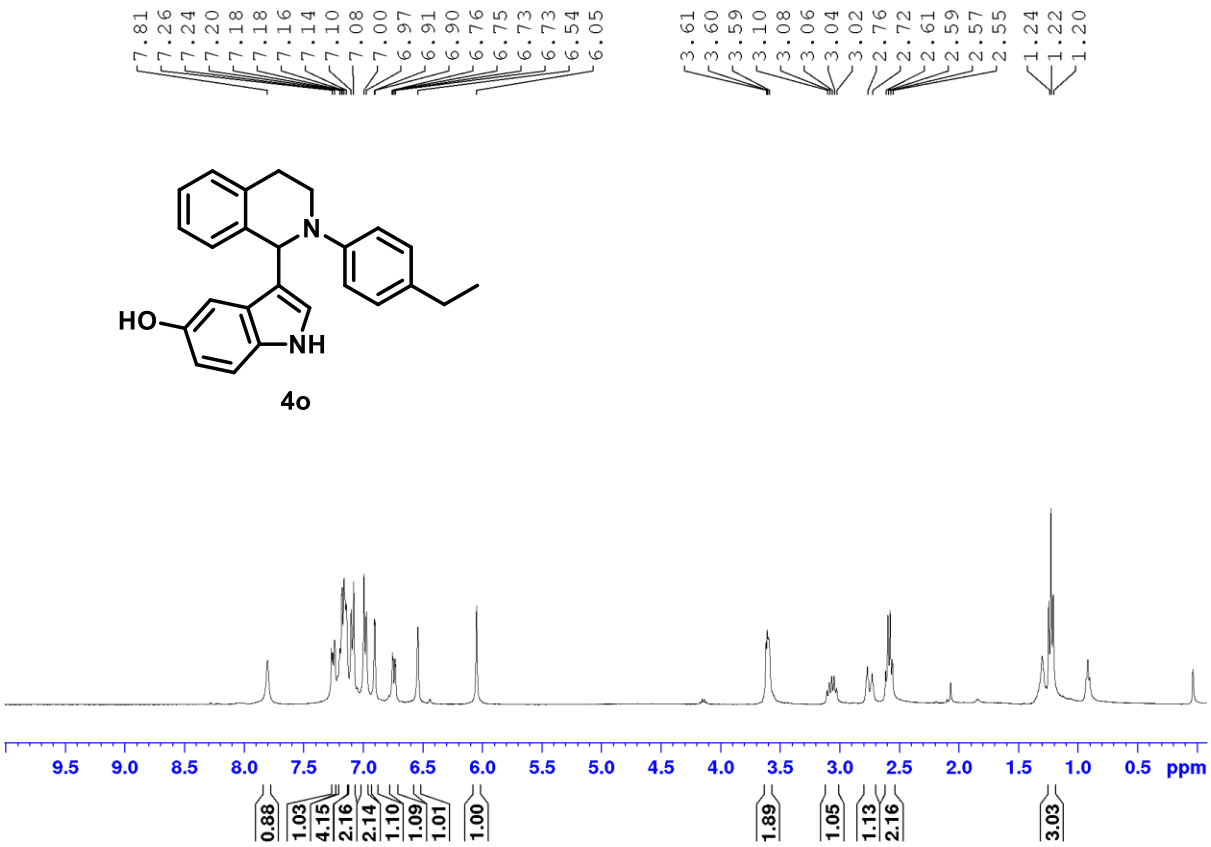
^{1}H NMR (400 MHz, $CDCl_3$) for 4n'



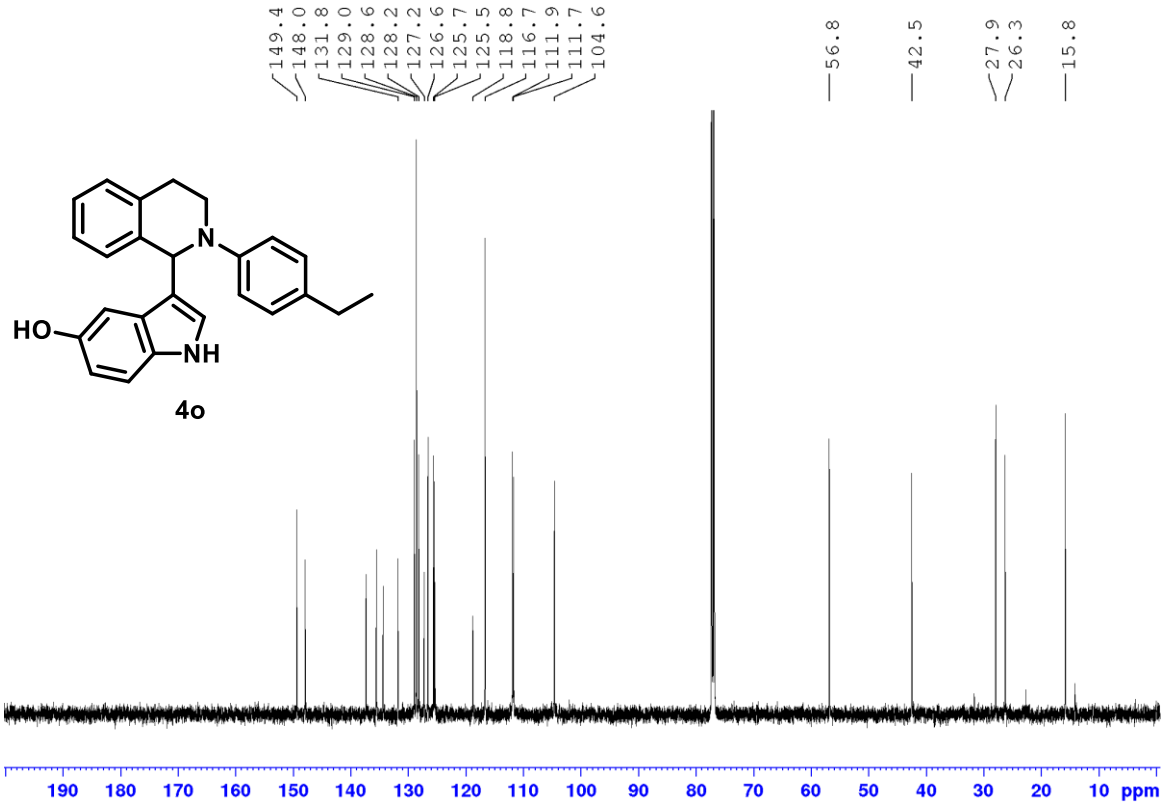
^{13}C NMR (101 MHz, $CDCl_3$) for 4n'



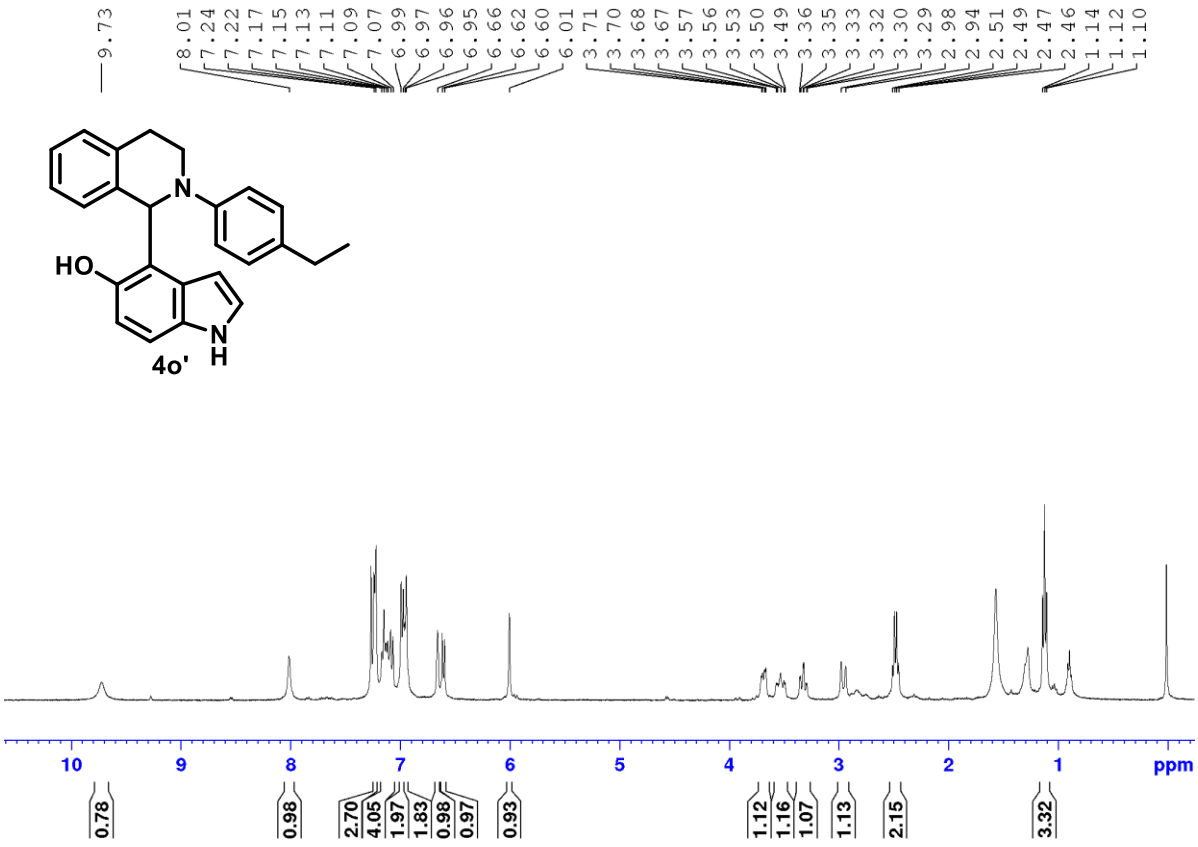
^{1}H NMR (400 MHz, $CDCl_3$) for 4o



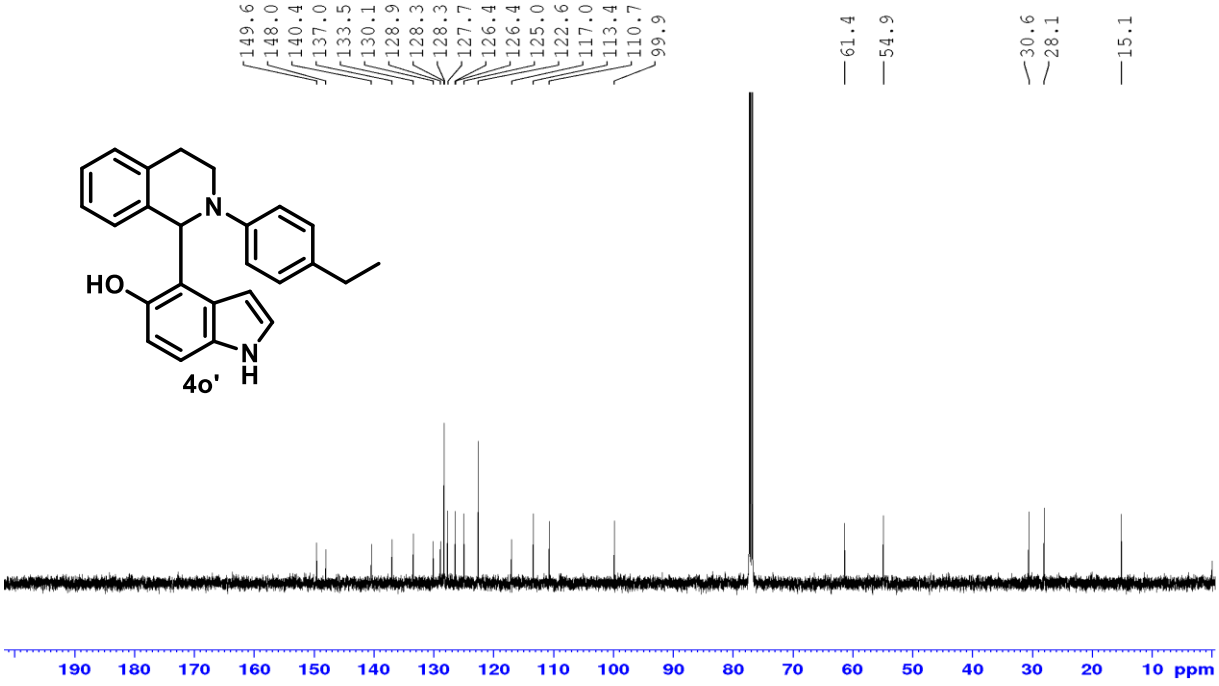
^{13}C NMR (101 MHz, $CDCl_3$) for 4o



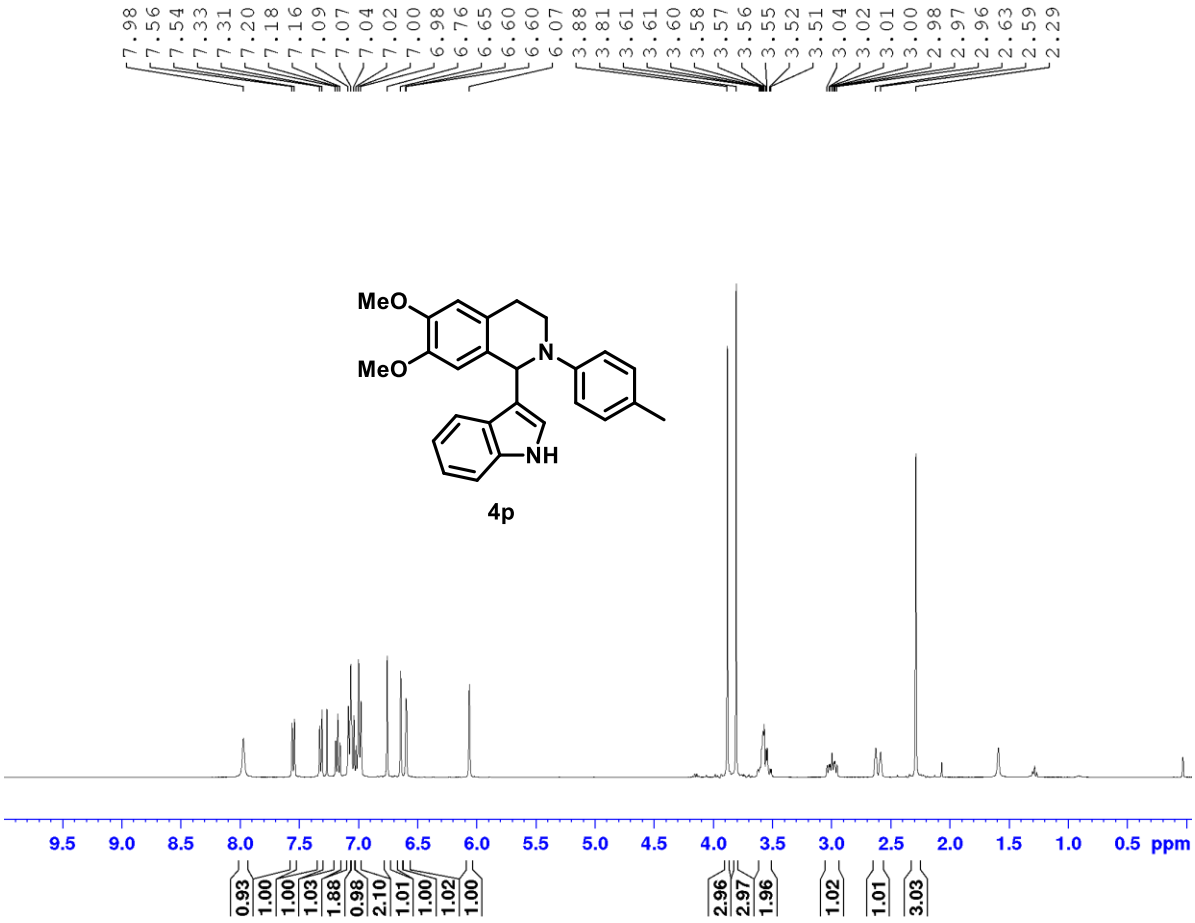
^{1}H NMR (101 MHz, $CDCl_3$) for 4o'



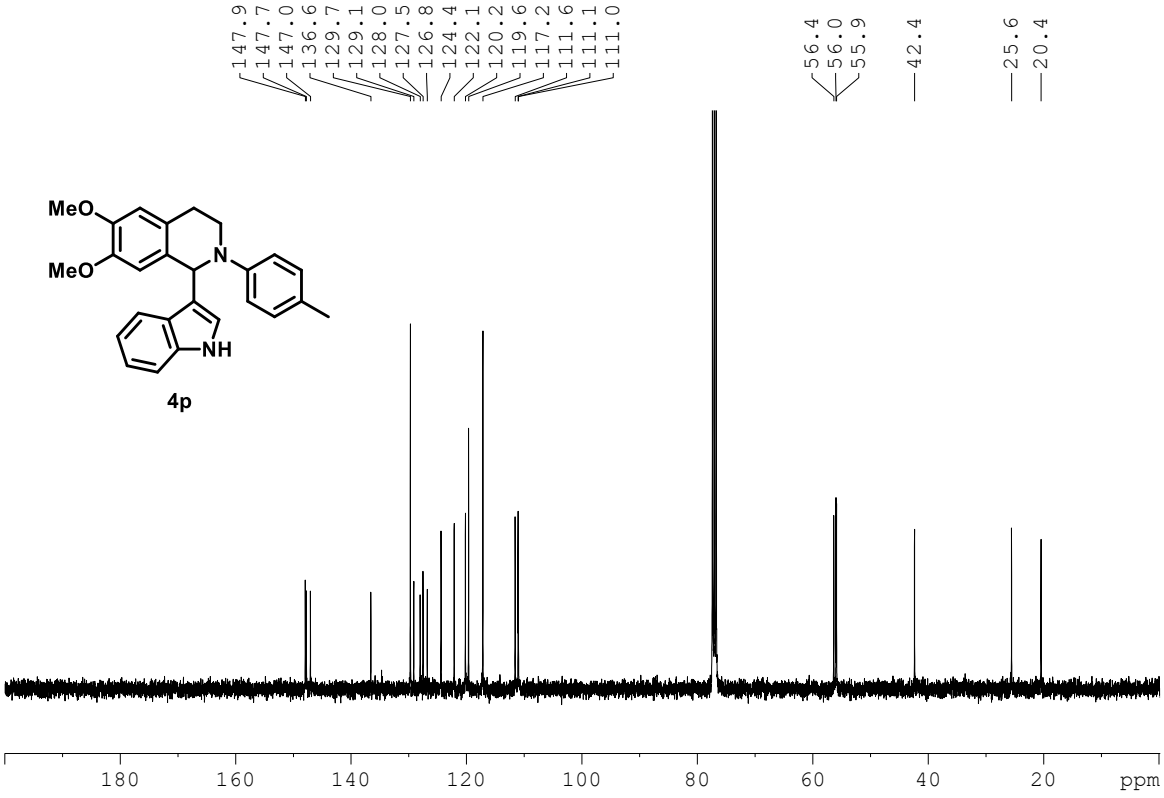
^{13}C NMR (101 MHz, $CDCl_3$) for 4o'



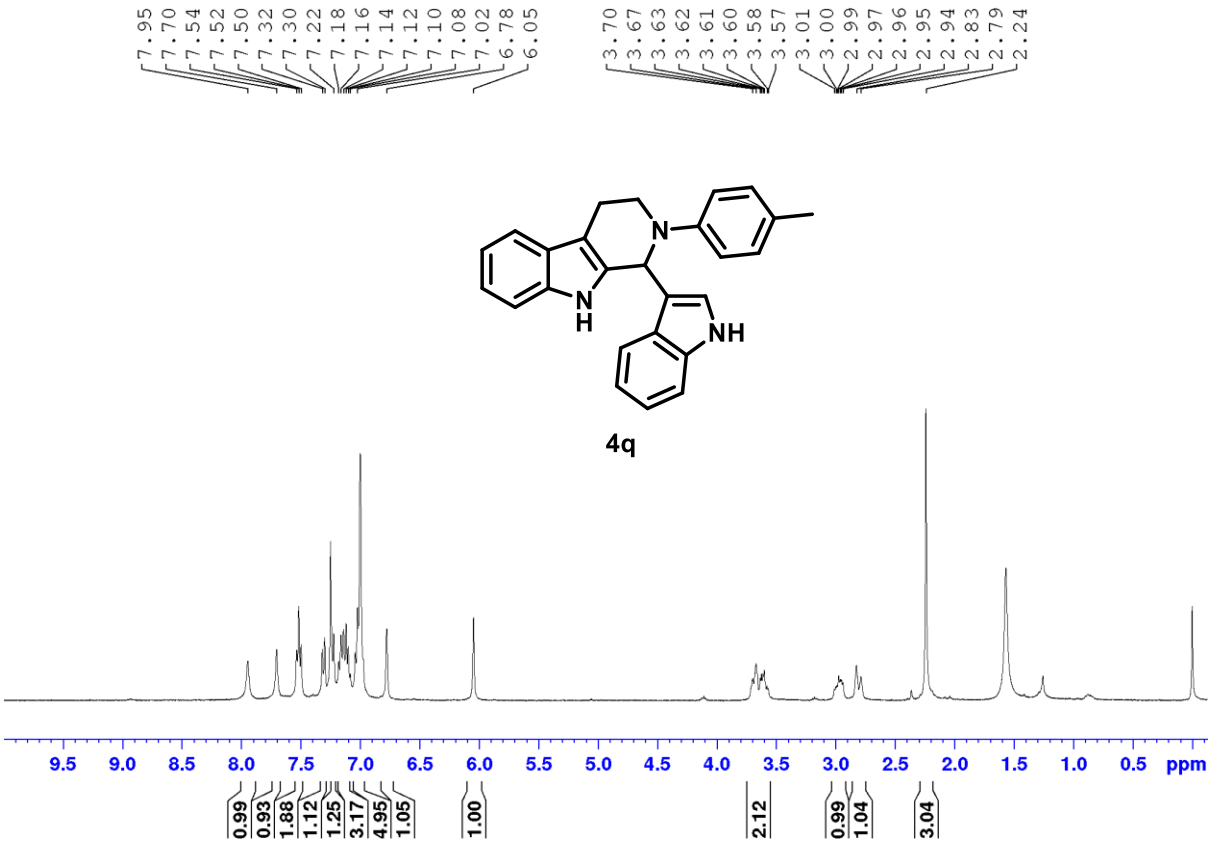
^{1}H NMR (400 MHz, $CDCl_3$) for 4p



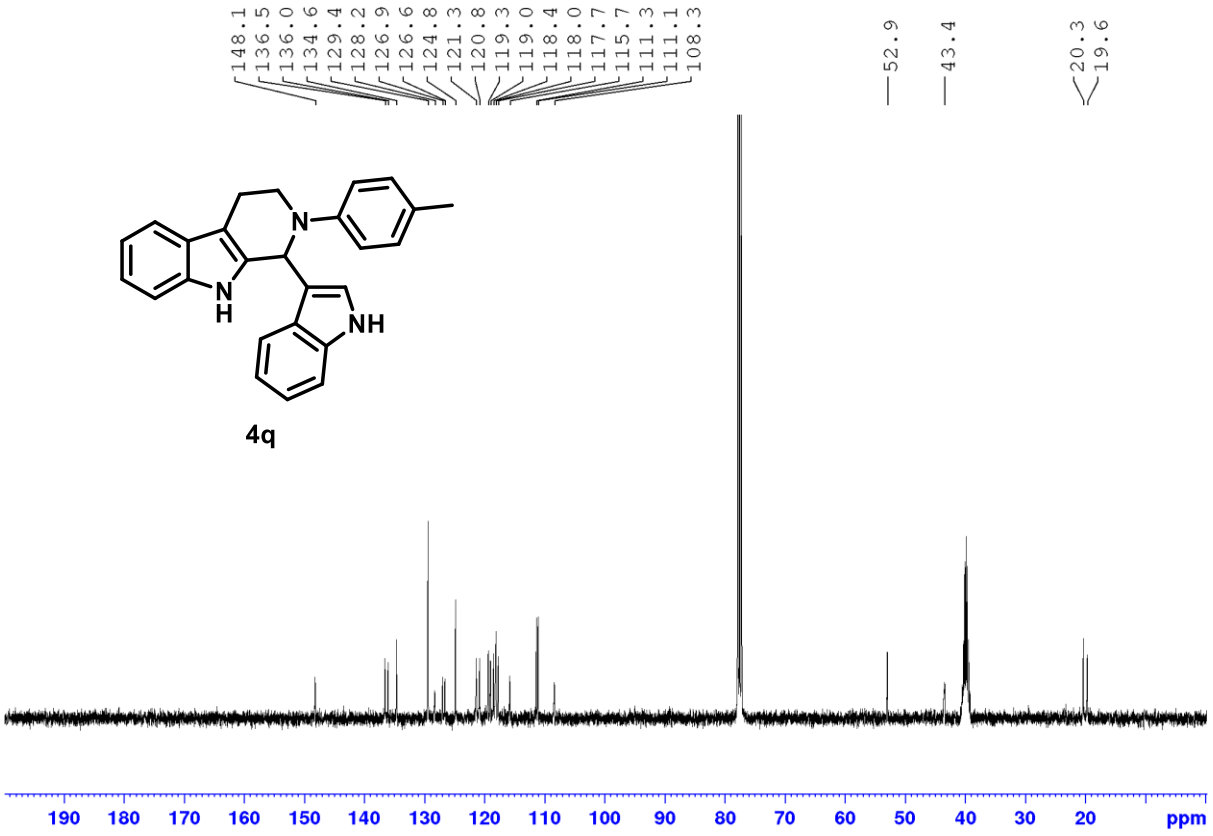
^{13}C NMR (101 MHz, $CDCl_3$) for 4p



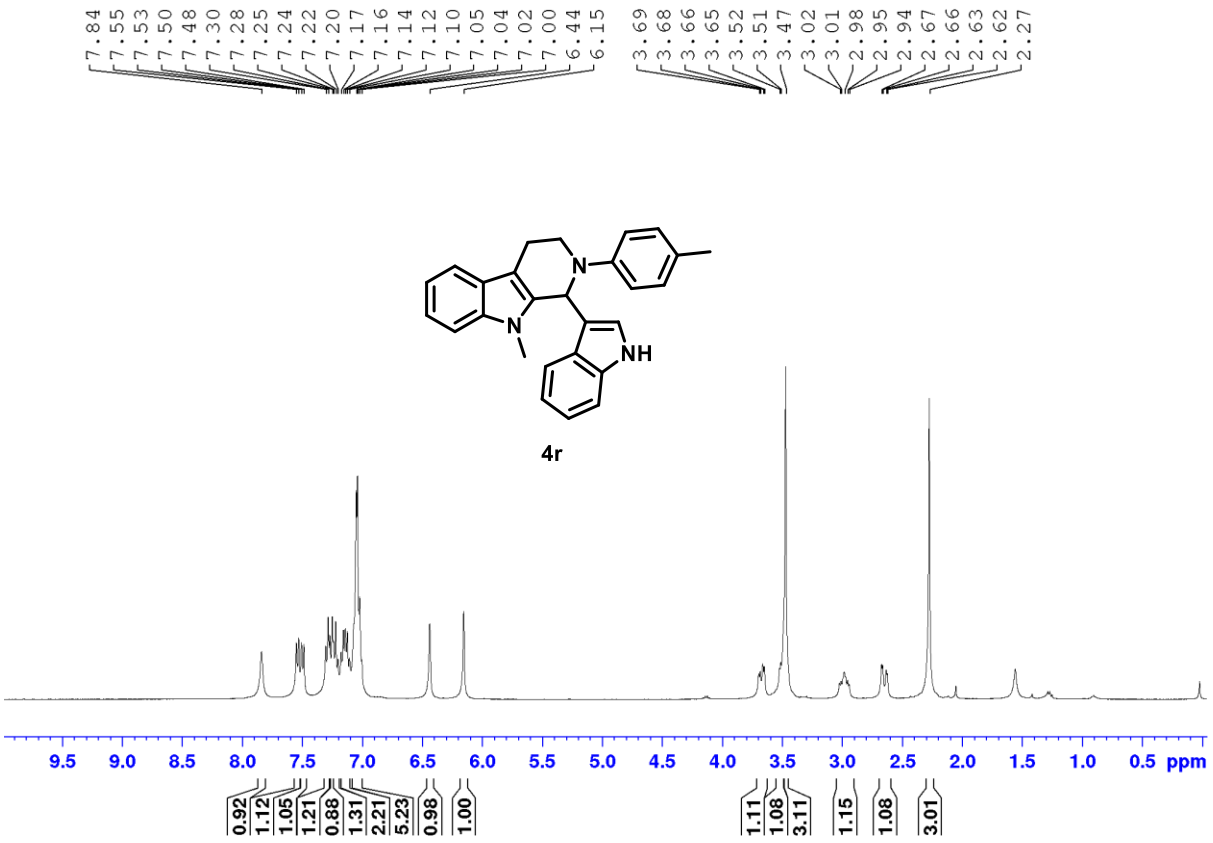
^{1}H NMR (400 MHz, $CDCl_3$) for 4q



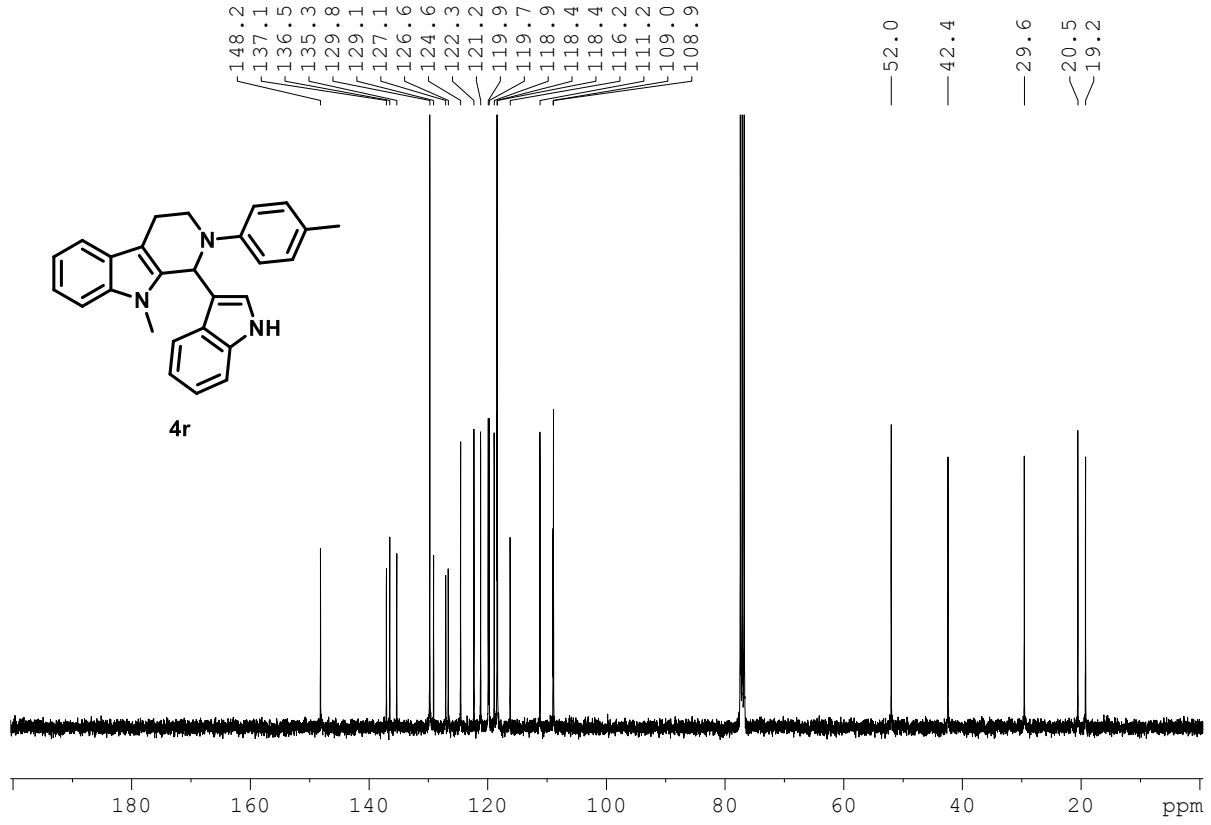
^{13}C NMR (101 MHz, $CDCl_3$) for 4q



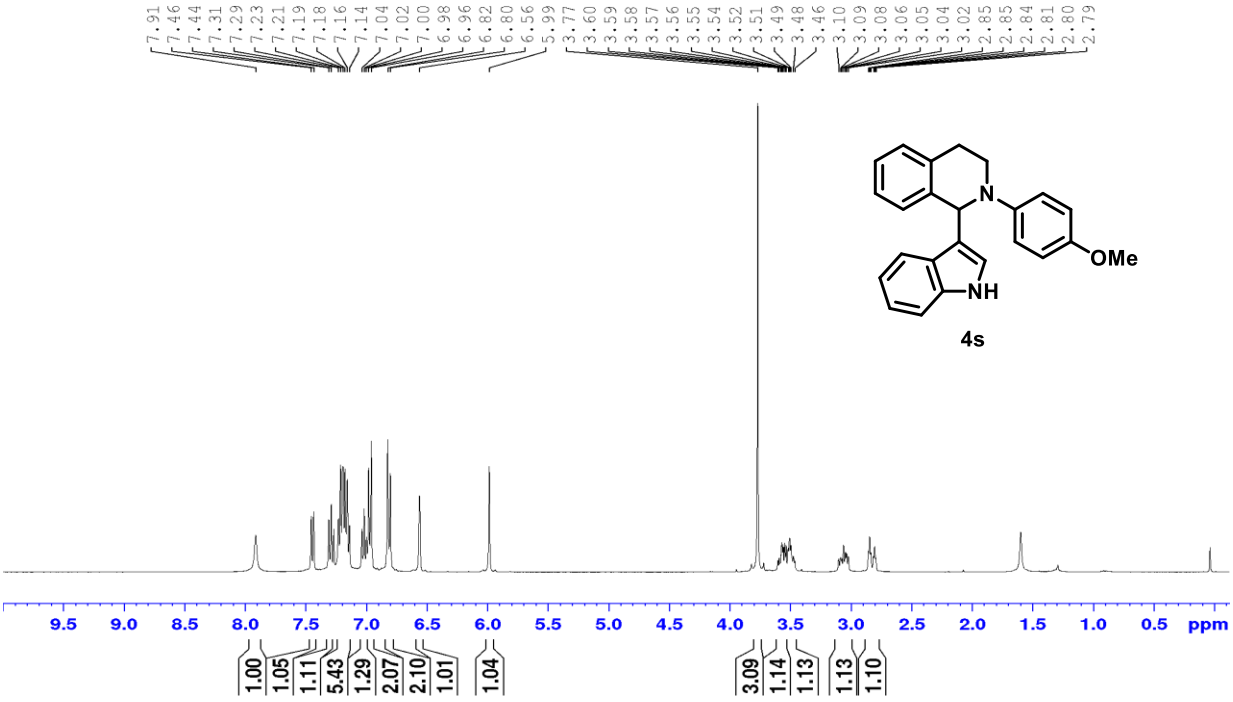
^{1}H NMR (400 MHz, $CDCl_3$) for 4r



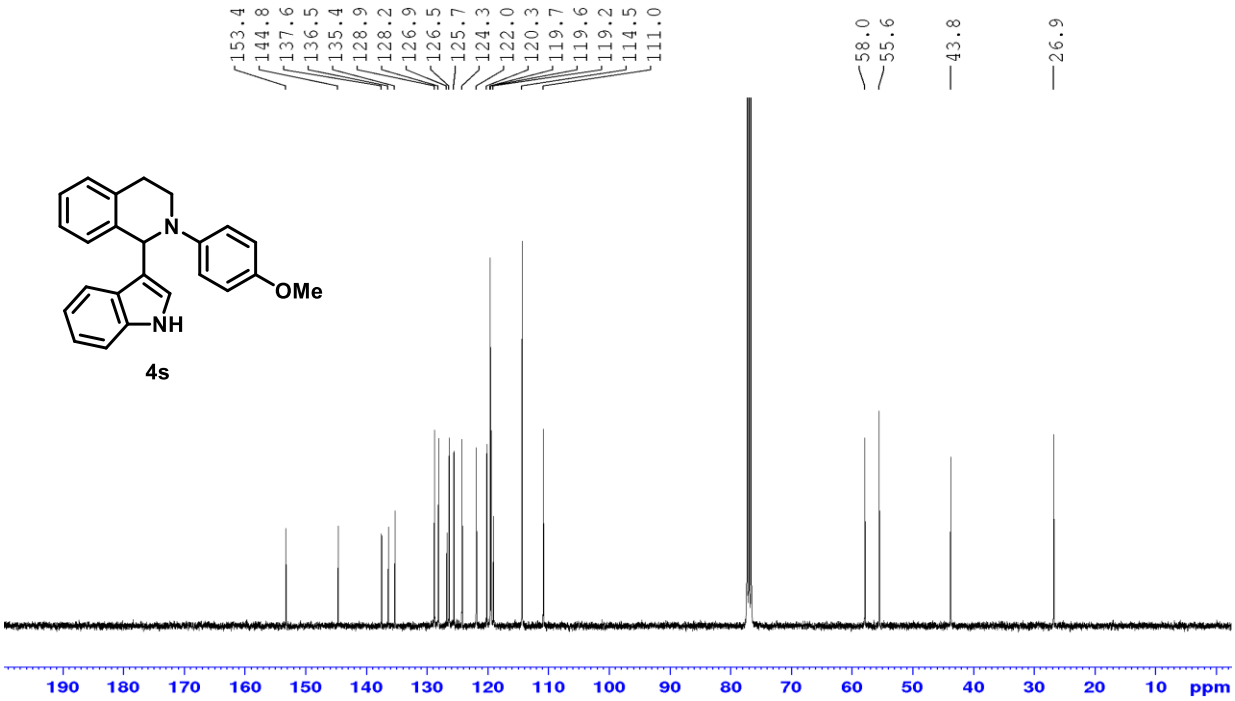
^{13}C NMR (101 MHz, $CDCl_3$) for 4r



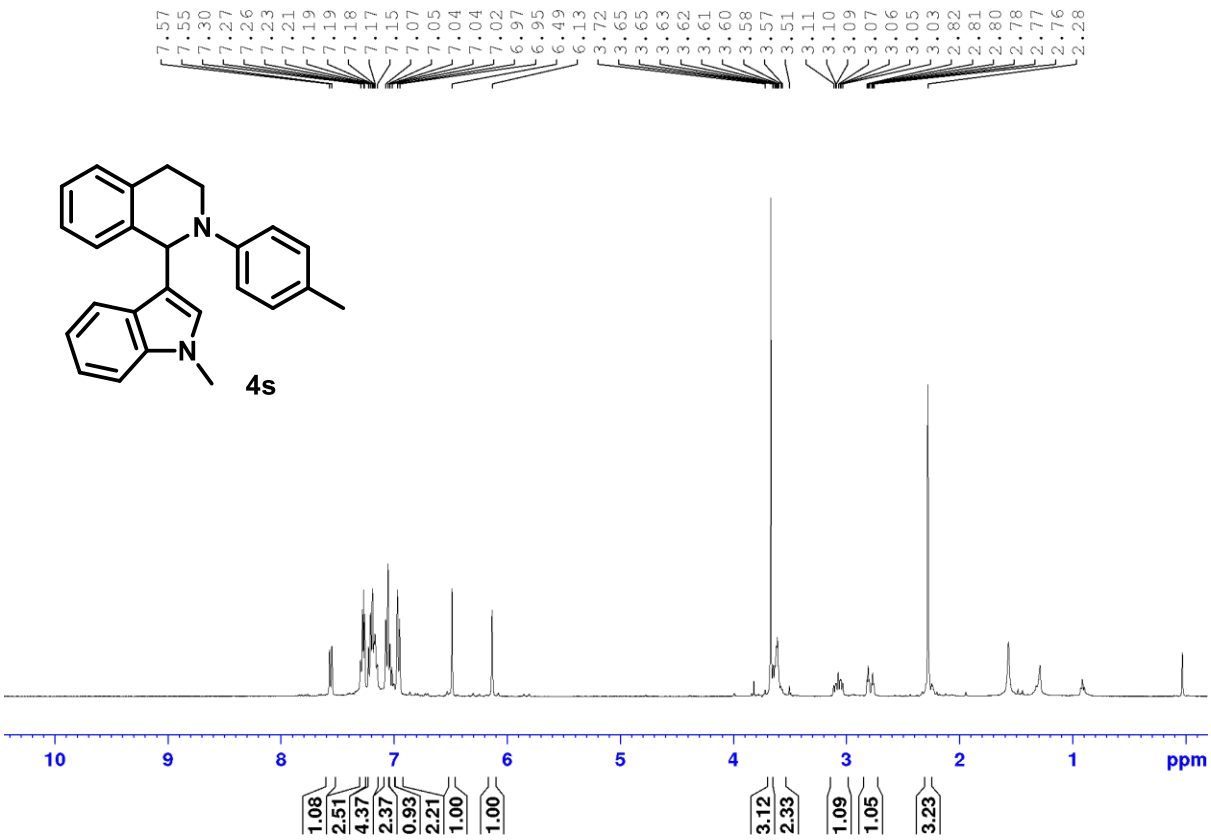
^{1}H NMR (400 MHz, $CDCl_3$) for 4s



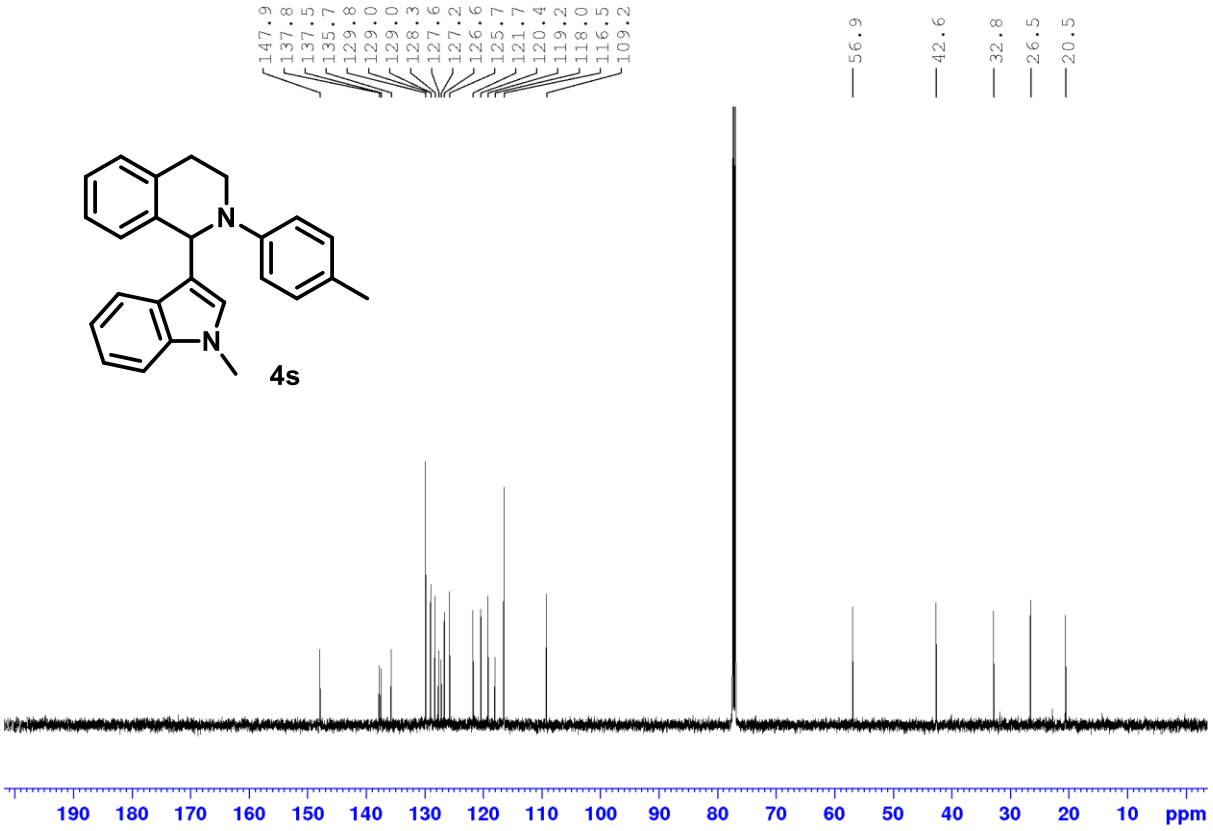
^{13}C NMR (101 MHz, $CDCl_3$) for 4s



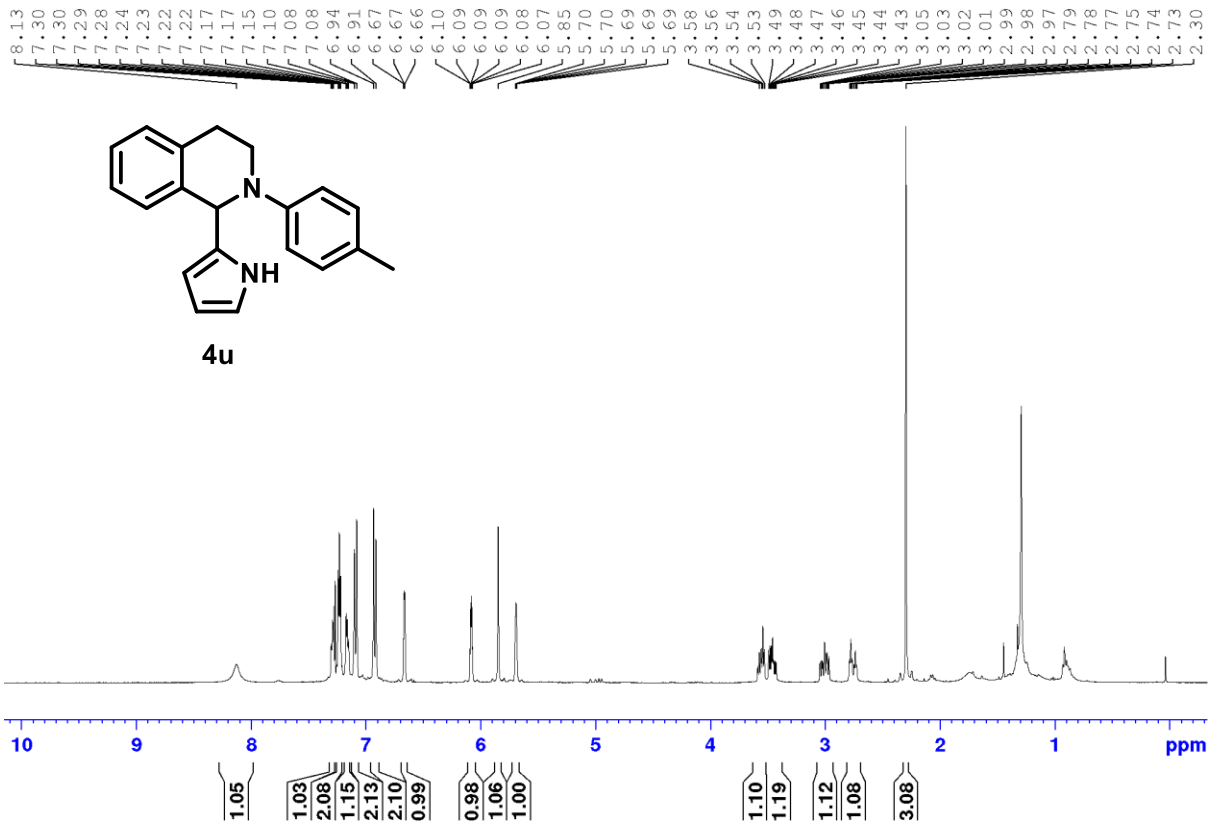
^{1}H NMR (400 MHz, $CDCl_3$) for 4t



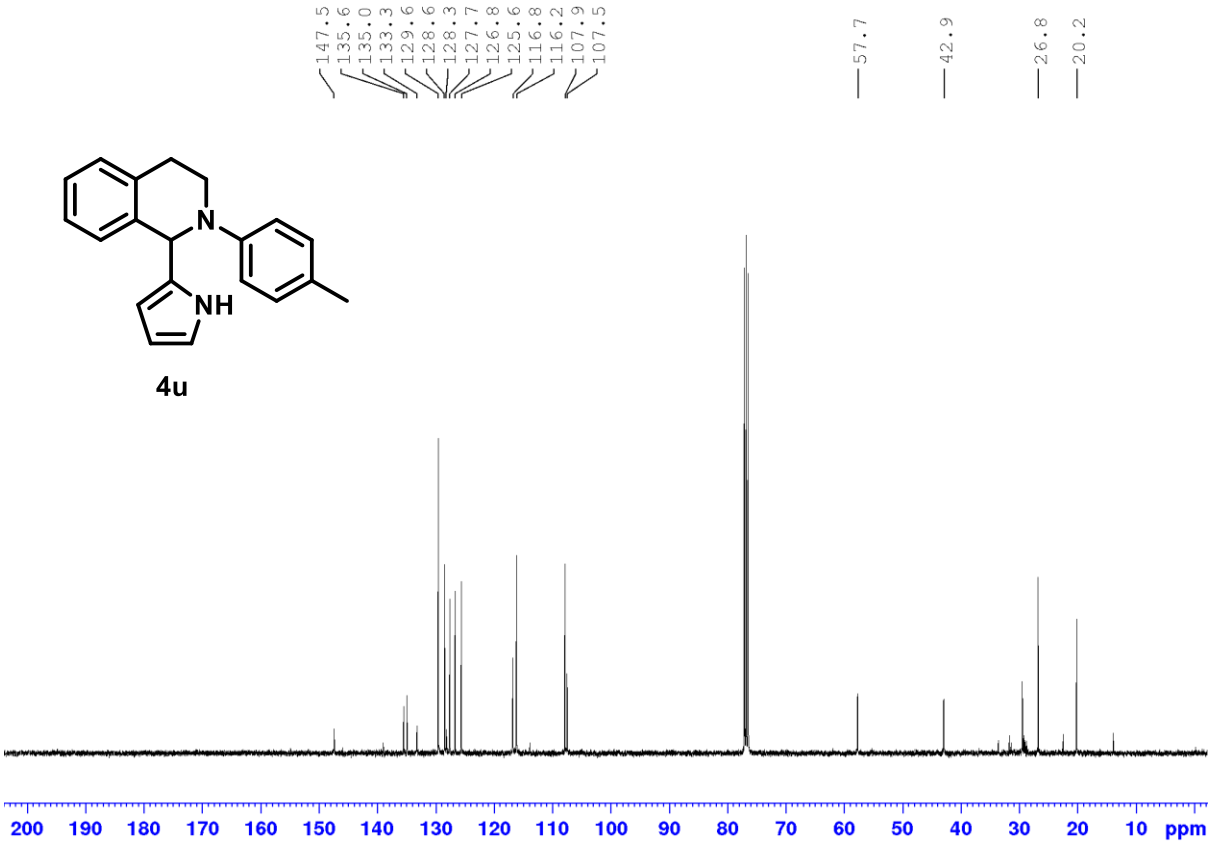
^{13}C NMR (101 MHz, $CDCl_3$) for 4t



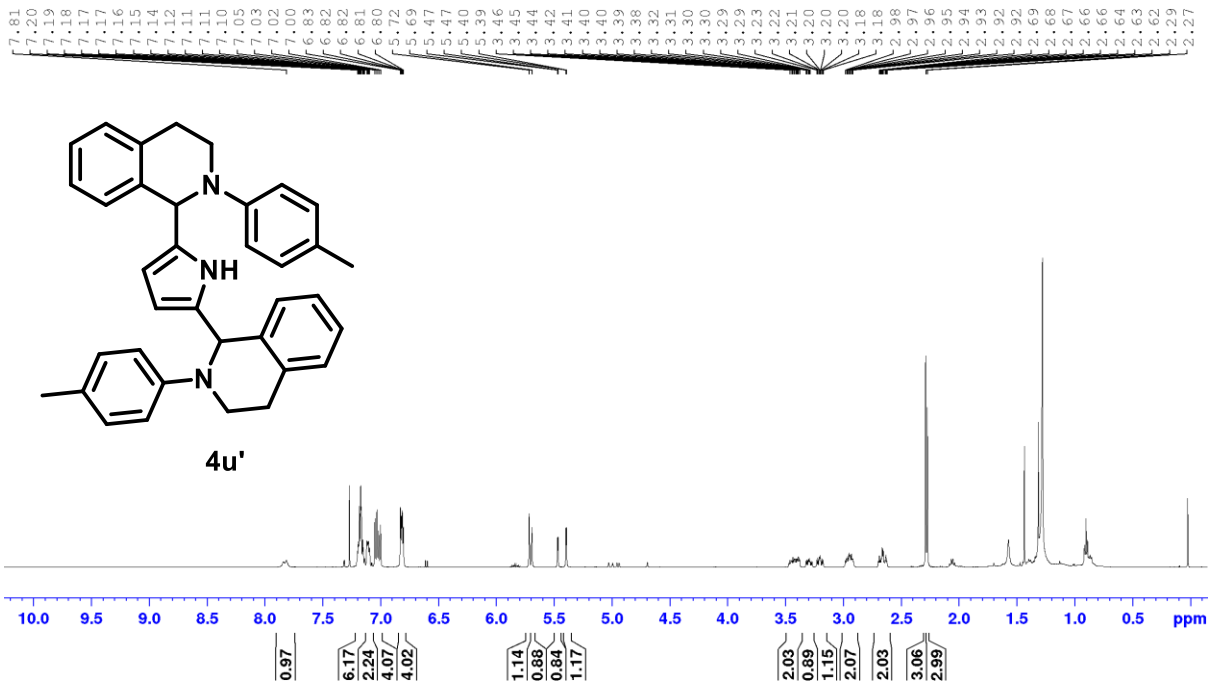
^{1}H NMR (400 MHz, $CDCl_3$) for 4u



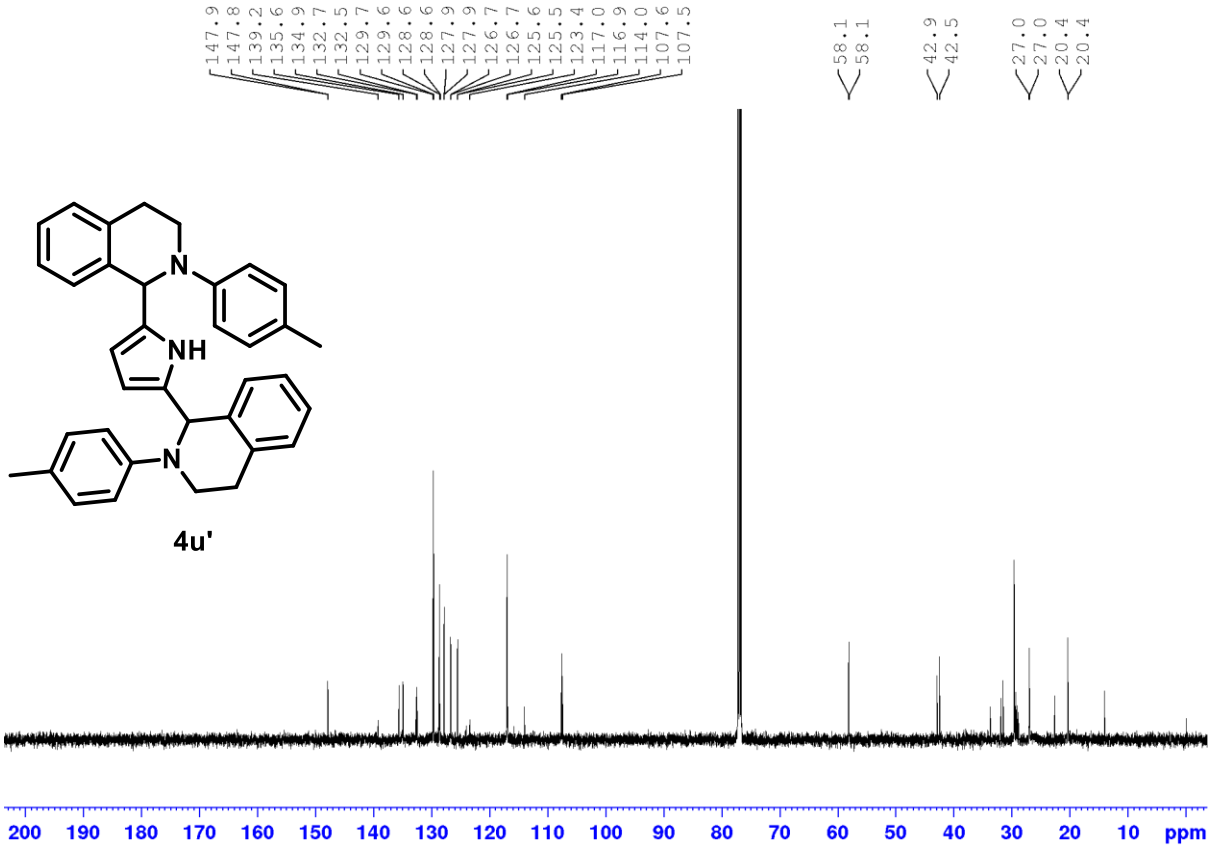
^{13}C NMR (101 MHz, $CDCl_3$) for 4u



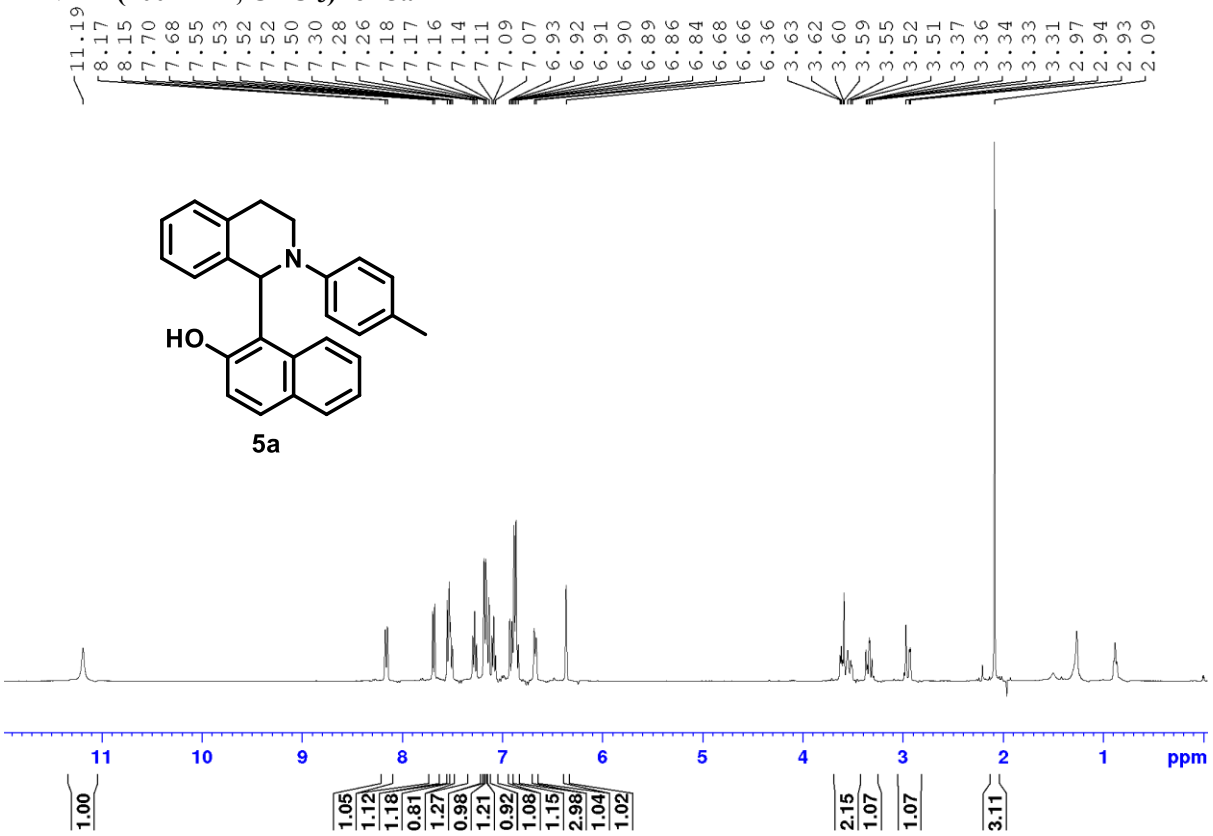
^{1}H NMR (400 MHz, $CDCl_3$) for 4u'



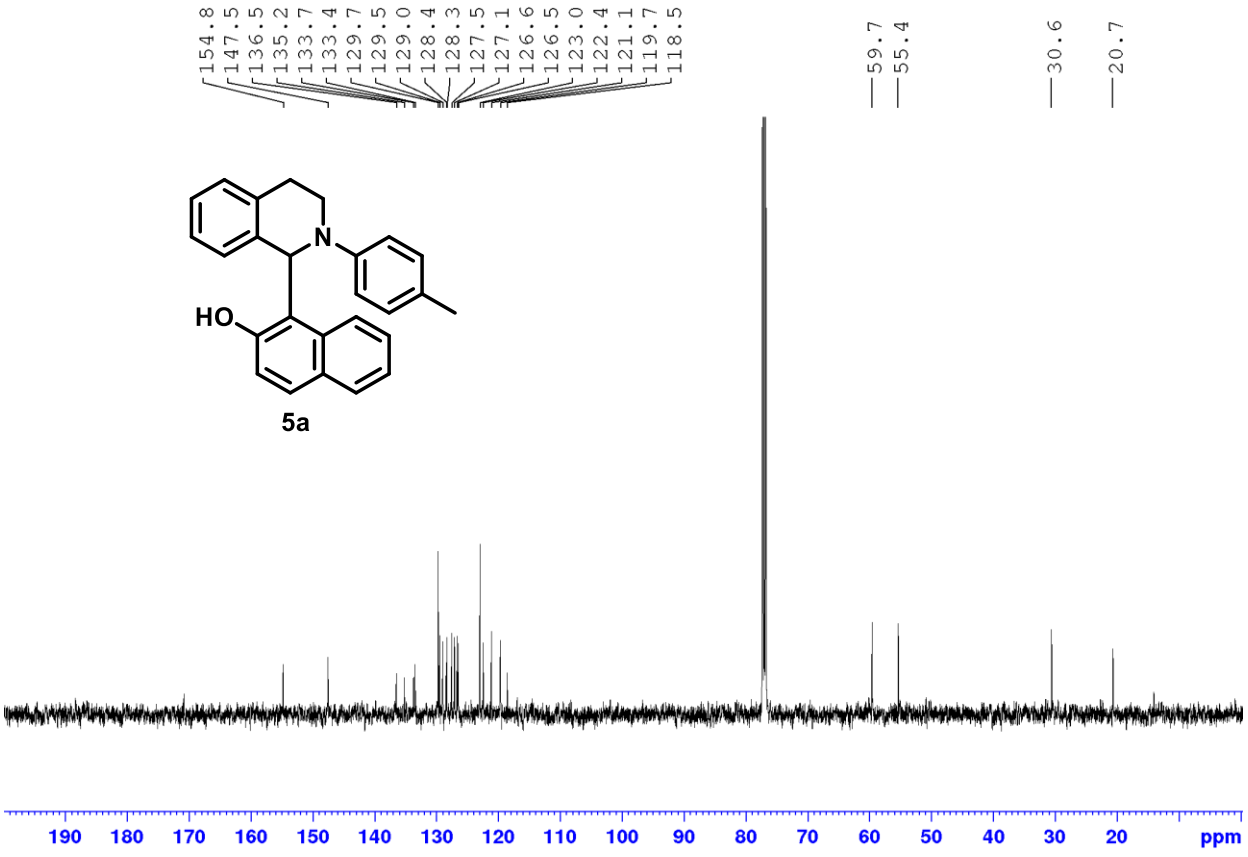
^{13}C NMR (101 MHz, $CDCl_3$) for 4u'



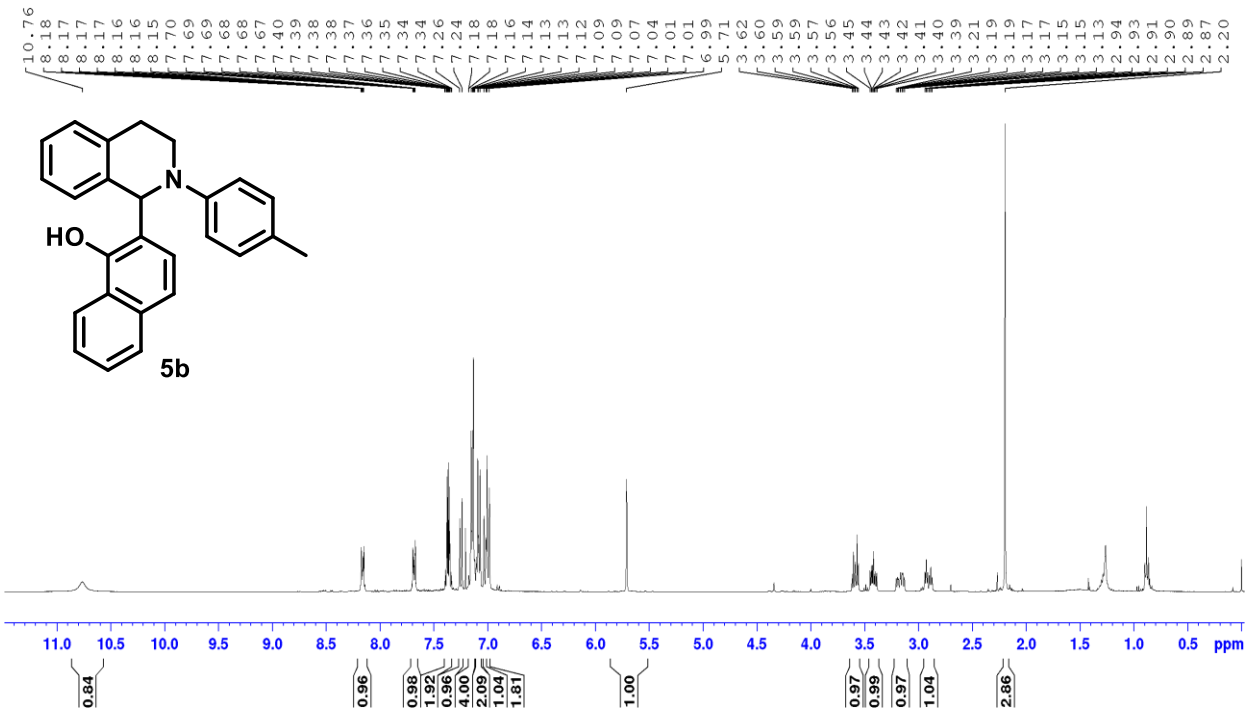
^{1}H NMR (400 MHz, $CDCl_3$) for 5a



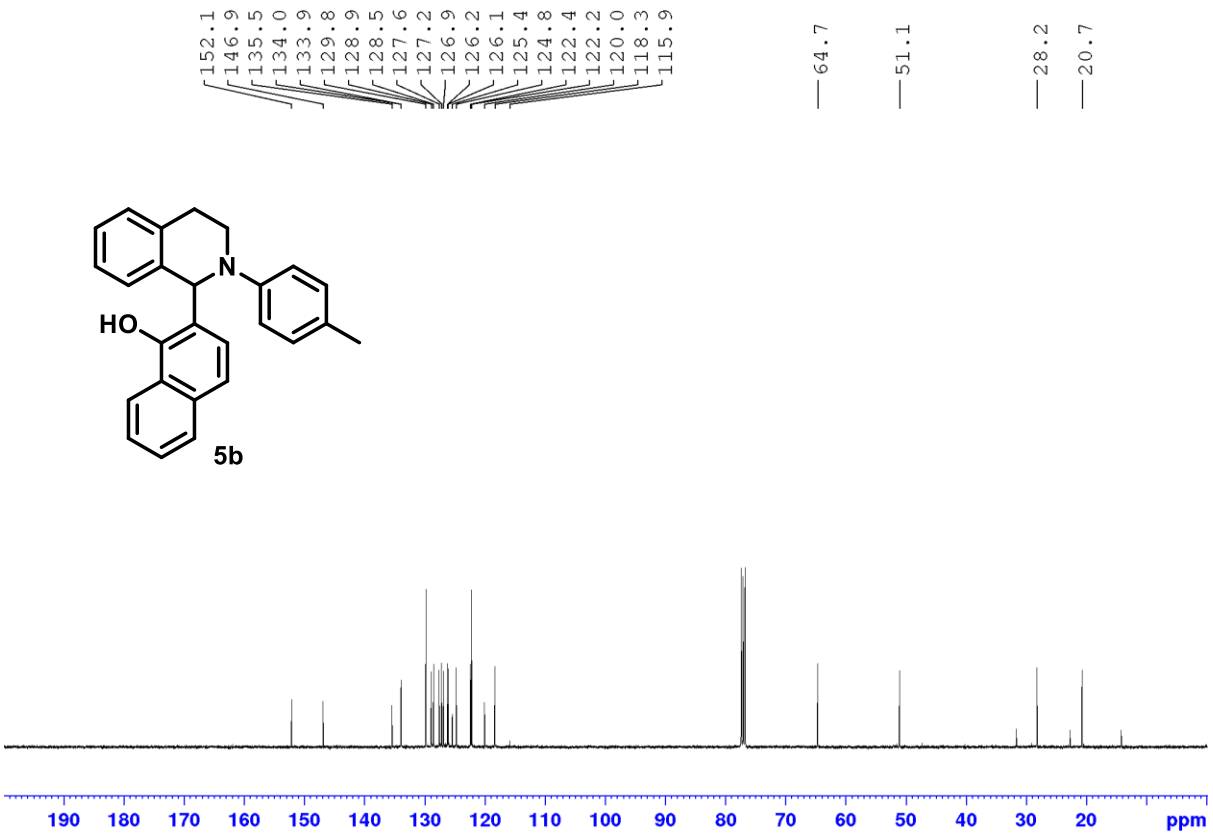
^{13}C NMR (101 MHz, $CDCl_3$) for 5a



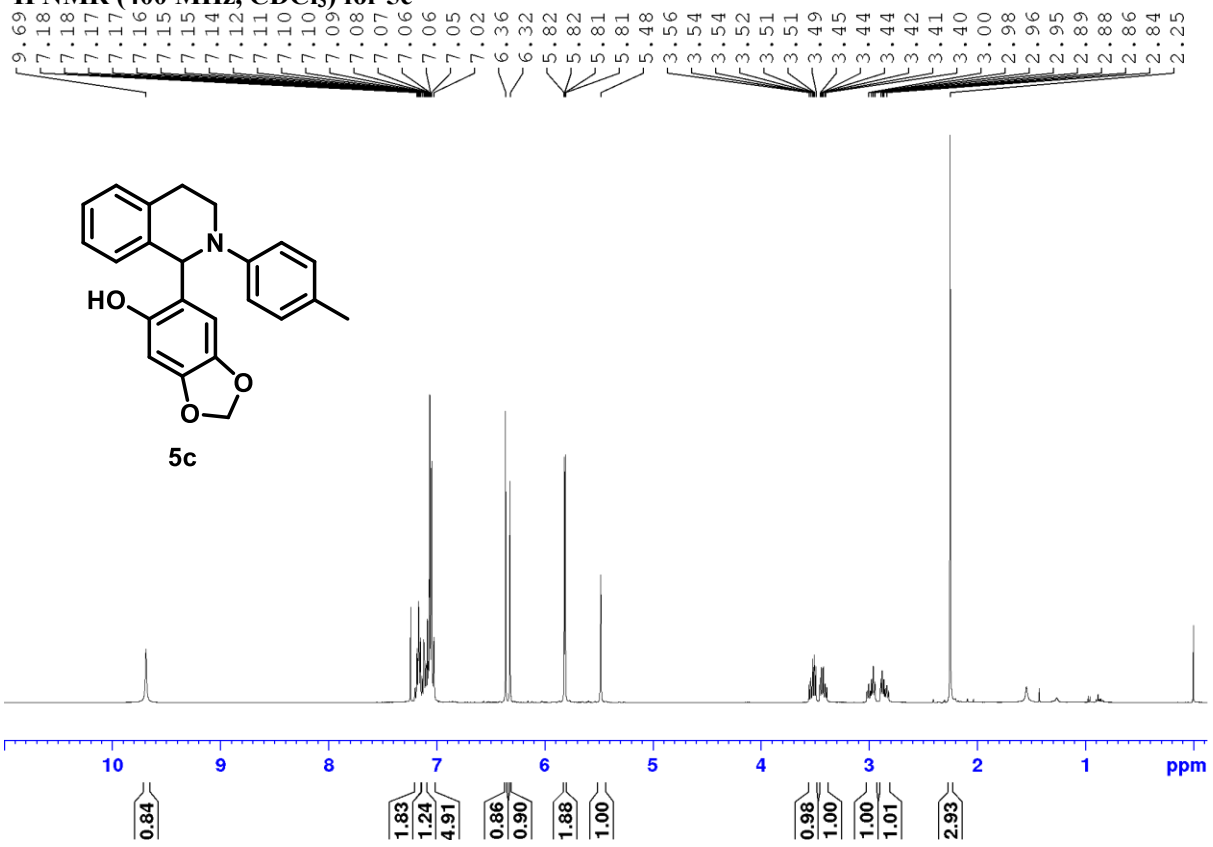
^{1}H NMR (400 MHz, $CDCl_3$) for 5b



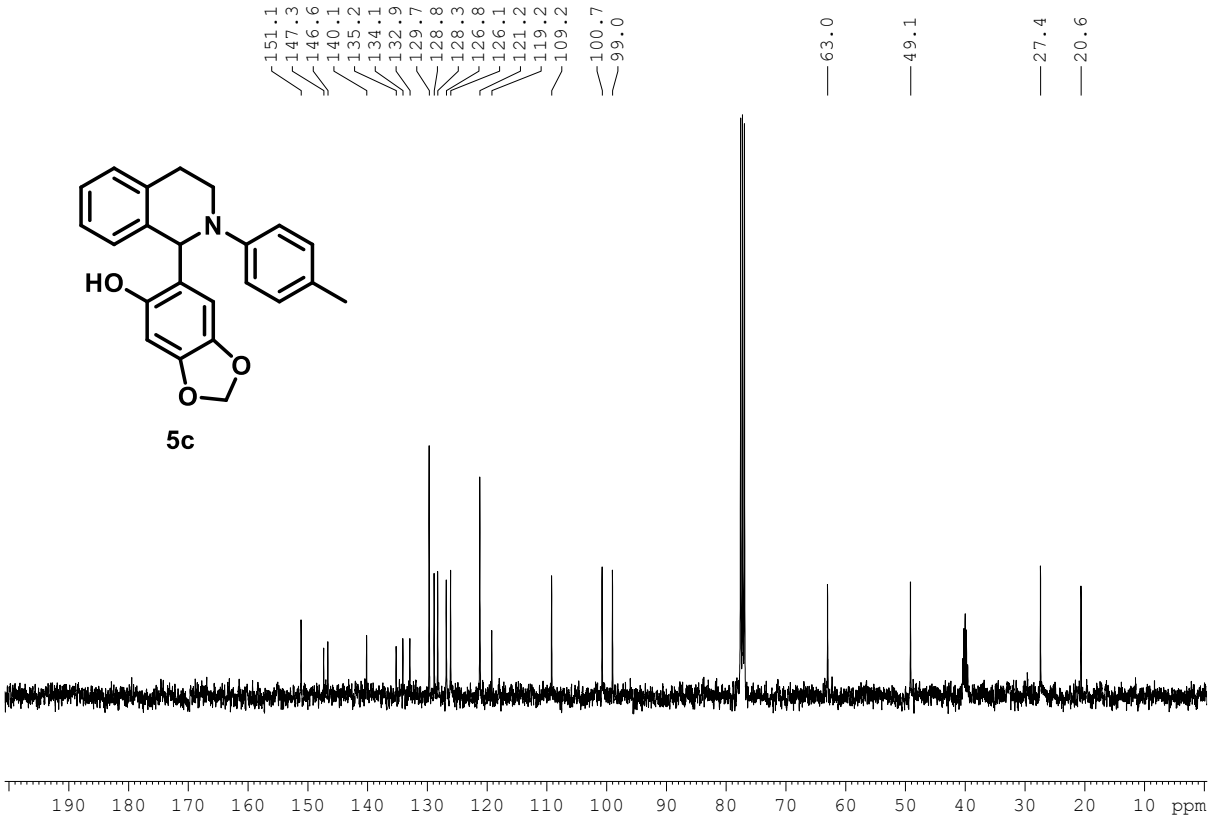
^{13}C NMR (101 MHz, $CDCl_3$) for 5b



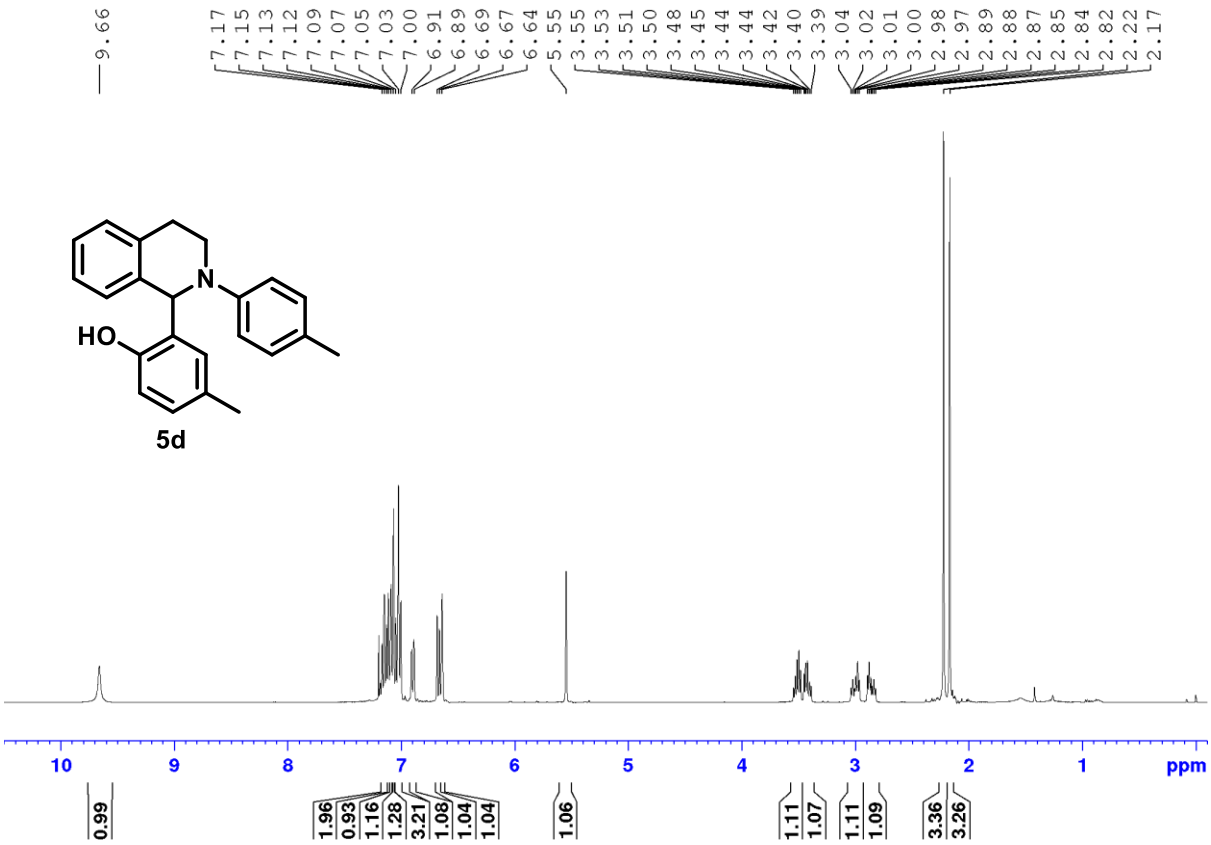
^{1}H NMR (400 MHz, $CDCl_3$) for 5c



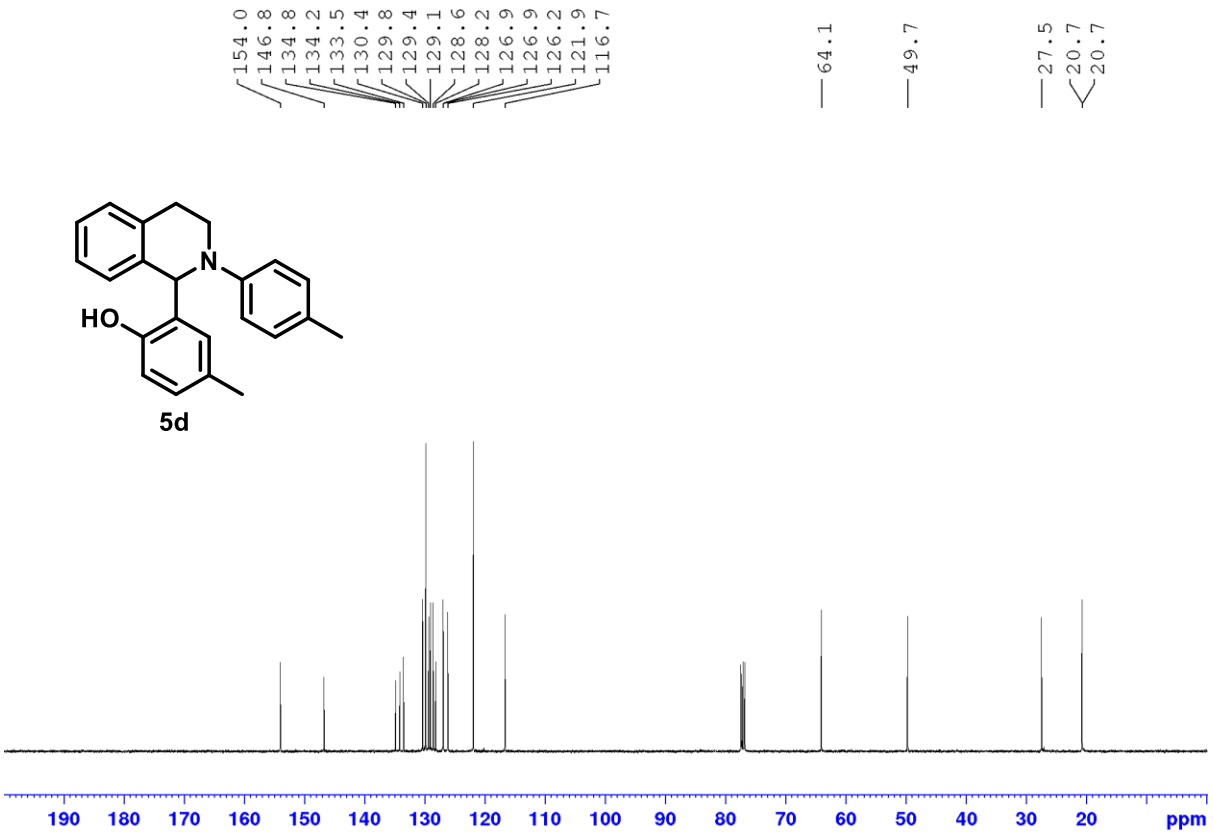
^{13}C NMR (101 MHz, $CDCl_3$ and 3 drops DMSO-d_6) for 5c



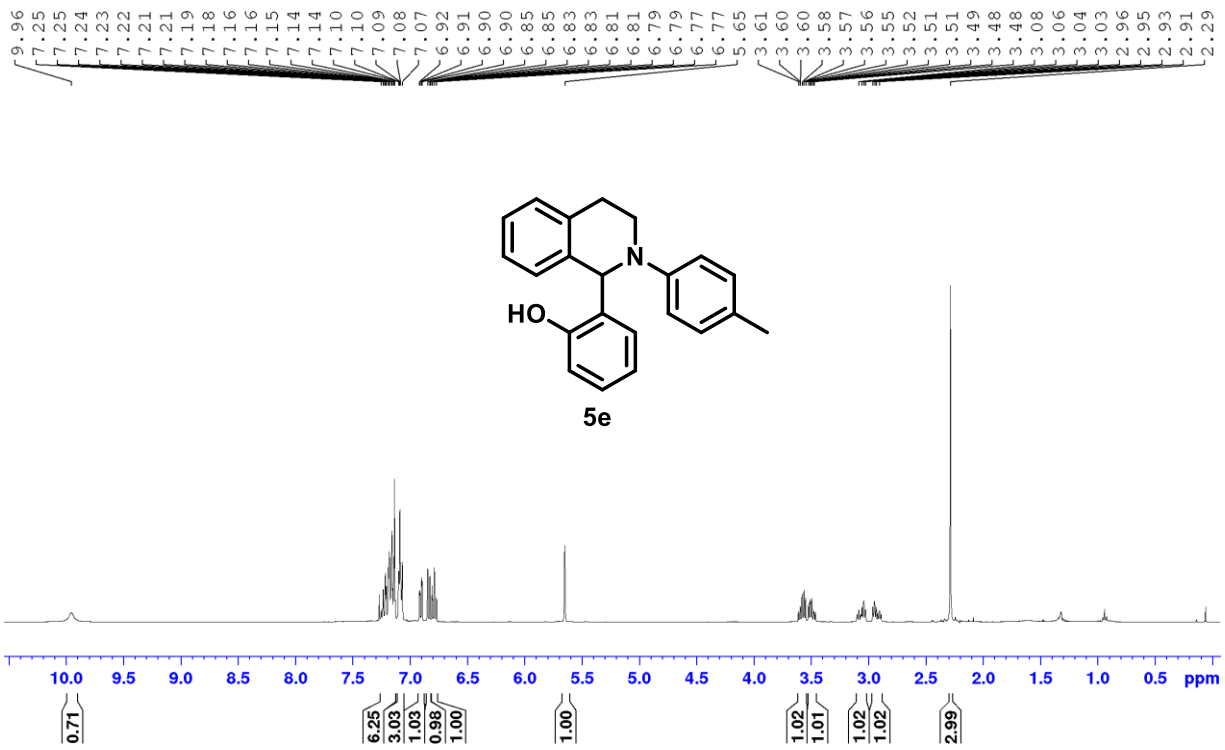
^{1}H NMR (400 MHz, $CDCl_3$) for 5d



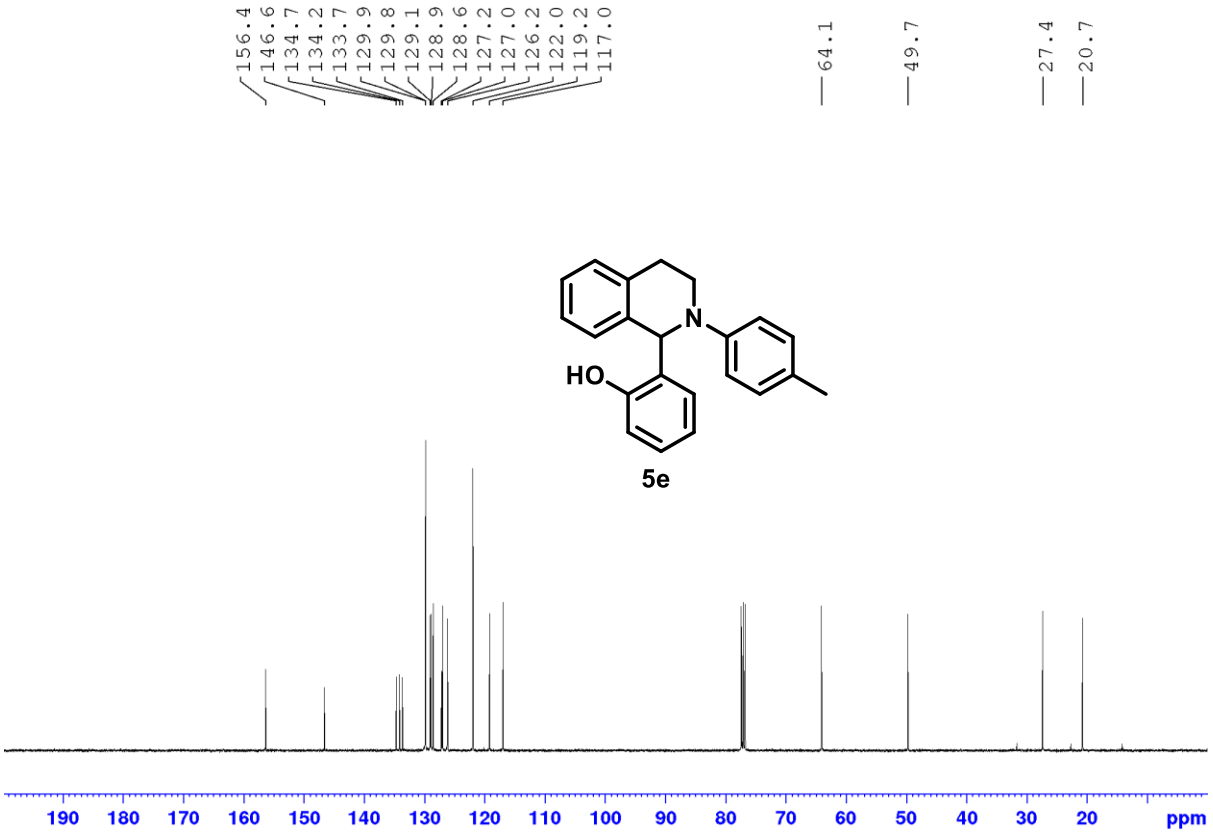
^{13}C NMR (101 MHz, $CDCl_3$) for 5d



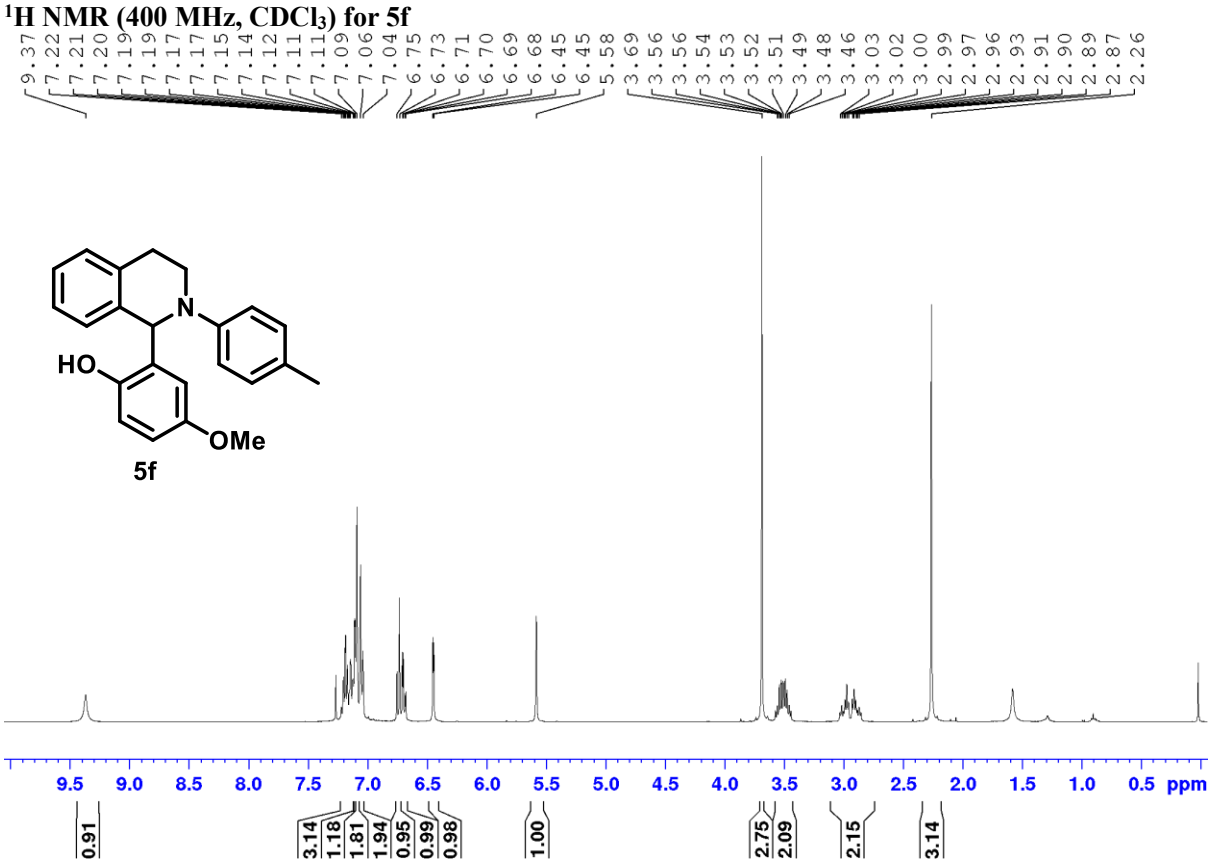
^{1}H NMR (400 MHz, $CDCl_3$) for 5e



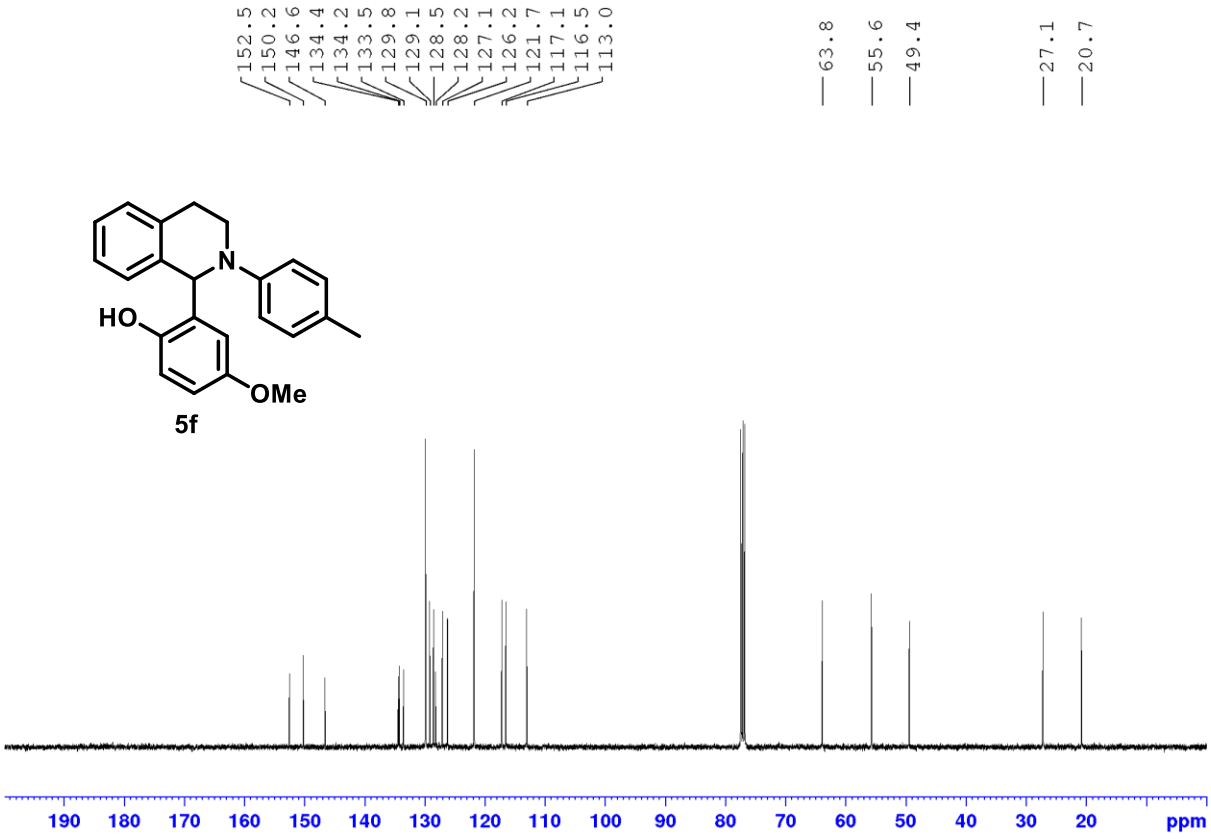
^{13}C NMR (101 MHz, $CDCl_3$) for 5e



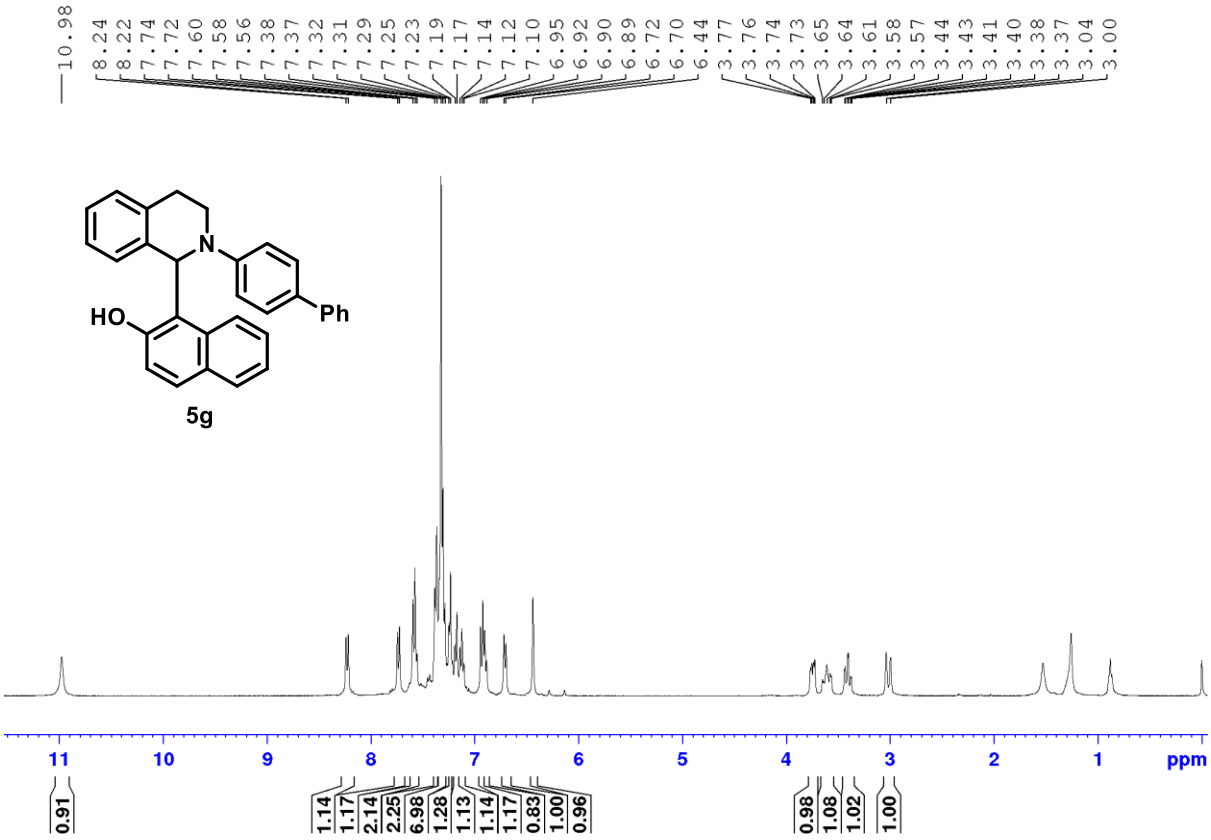
^{1}H NMR (400 MHz, $CDCl_3$) for 5f



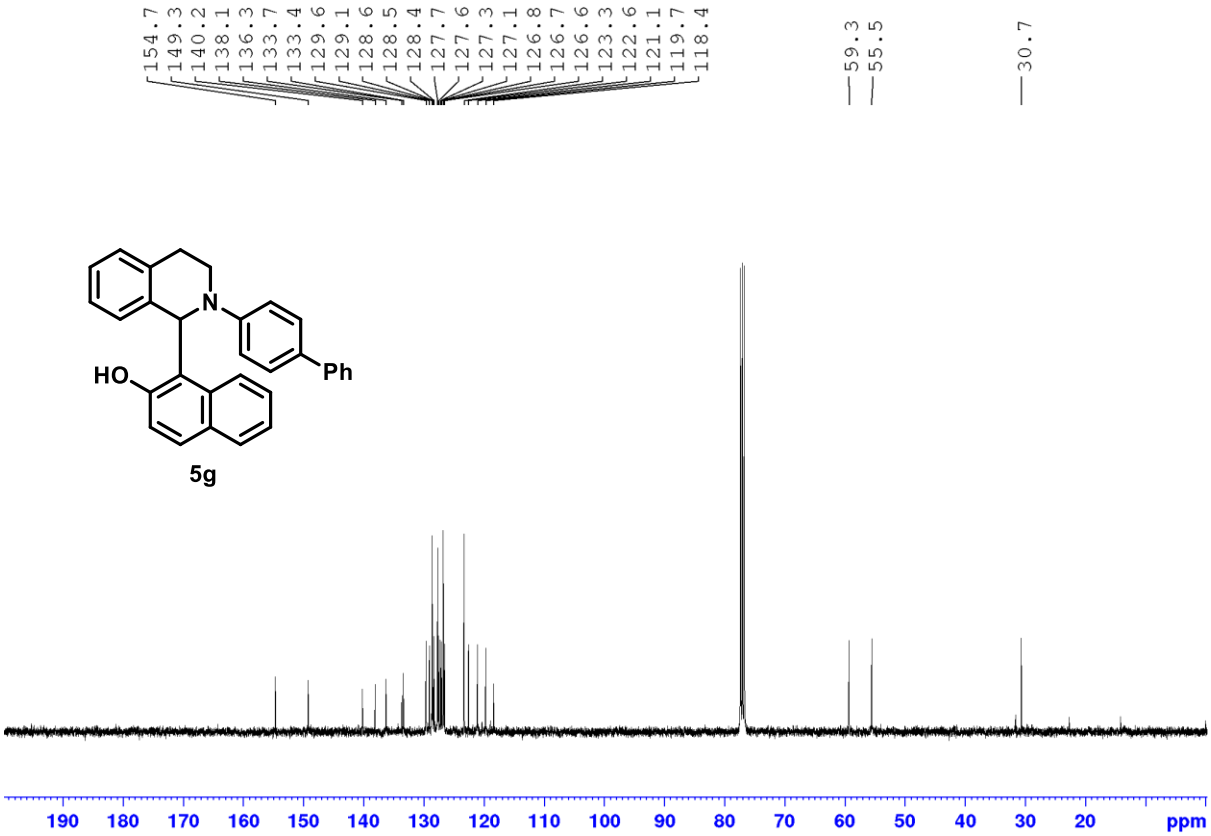
^{13}C NMR (101 MHz, $CDCl_3$) for 5f



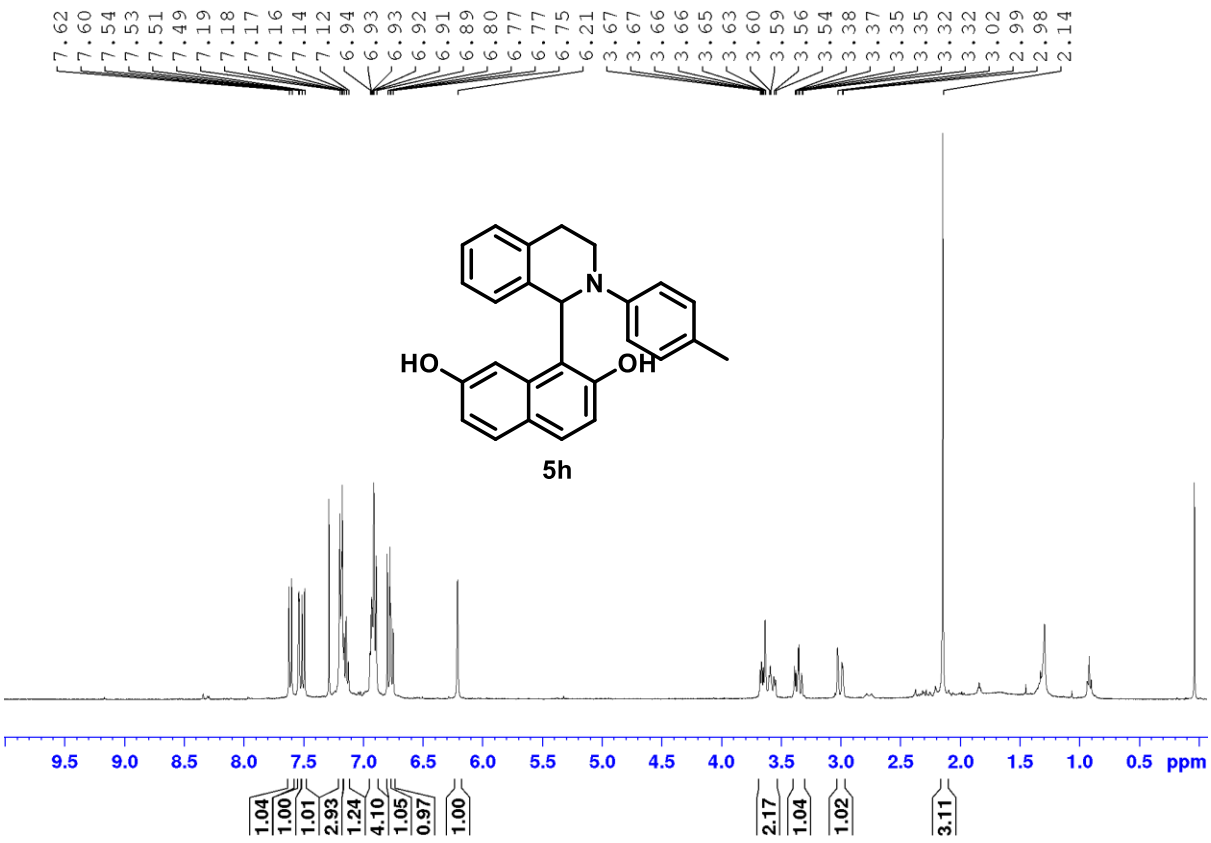
^{1}H NMR (400 MHz, $CDCl_3$) for 5g



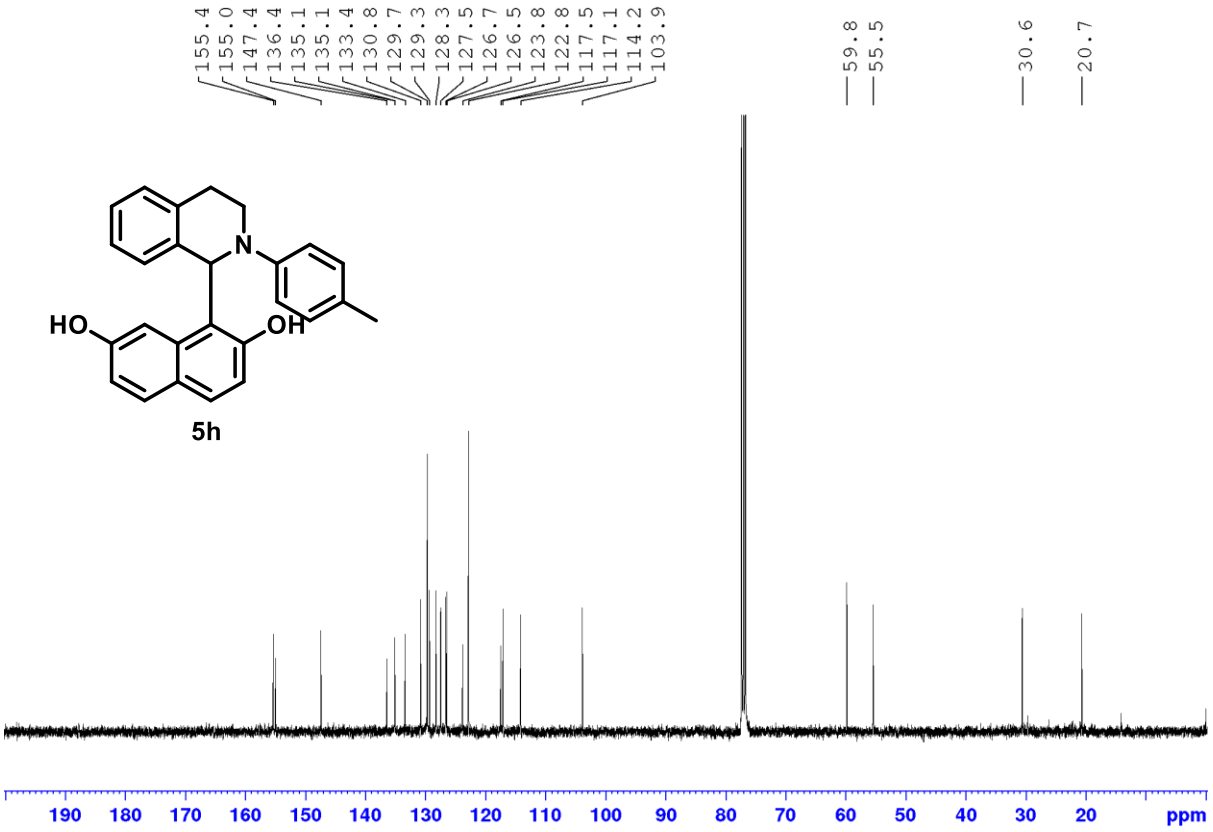
^{13}C NMR (101 MHz, $CDCl_3$) for 5g



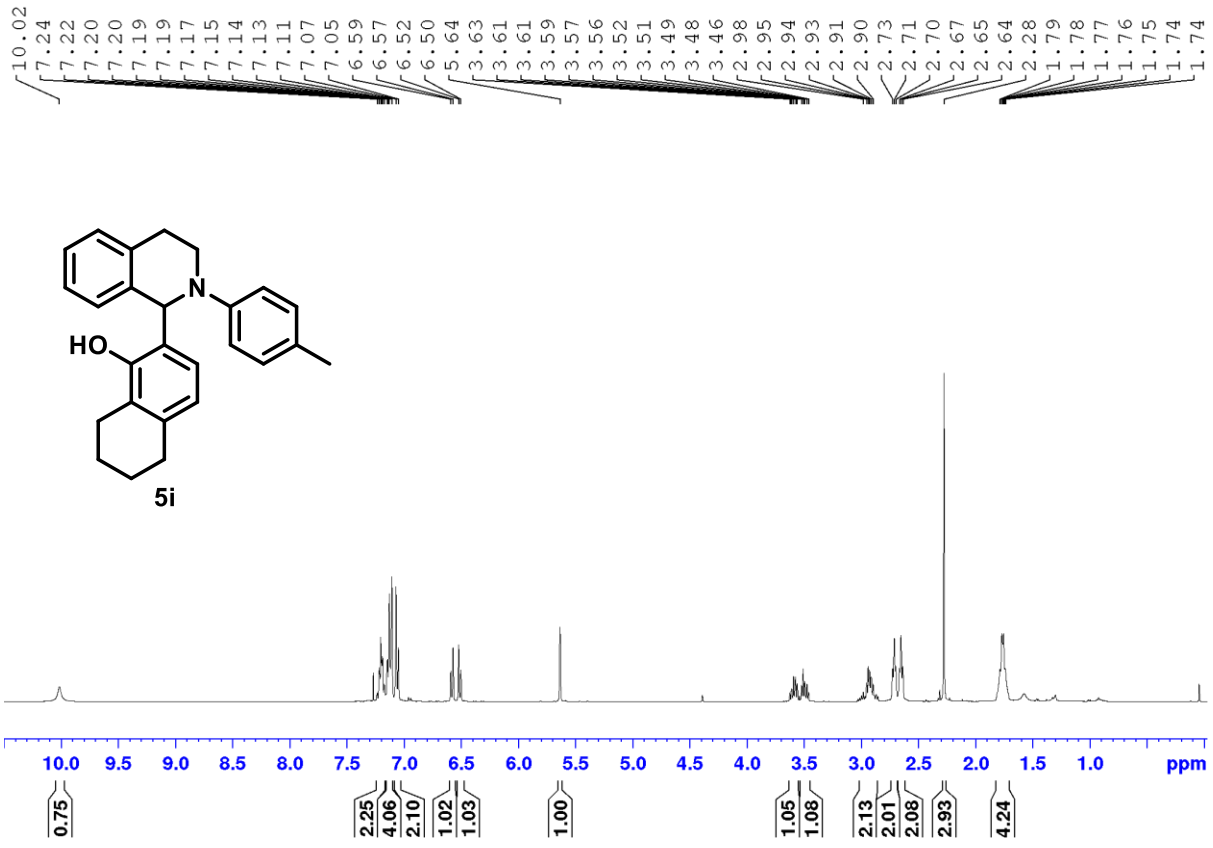
^{1}H NMR (400 MHz, $CDCl_3$) for 5h



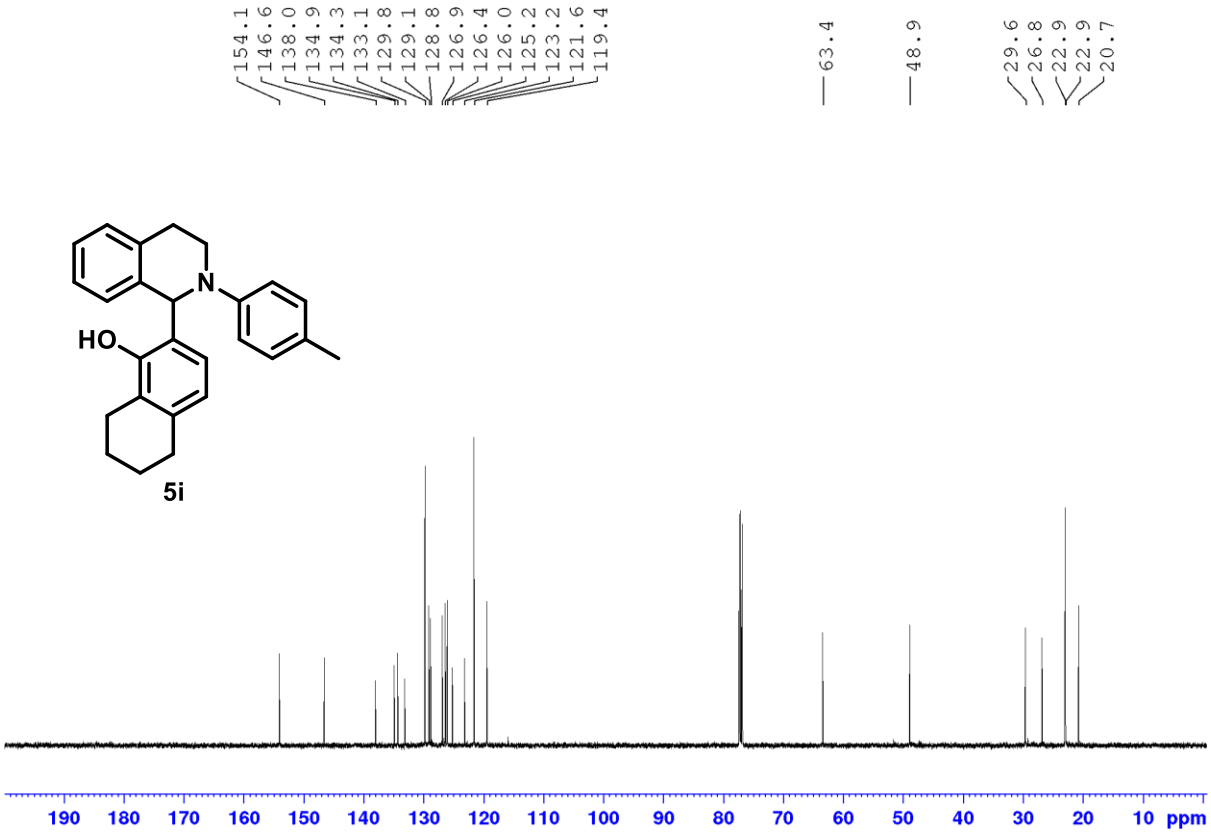
^{13}C NMR (101 MHz, $CDCl_3$) for 5h



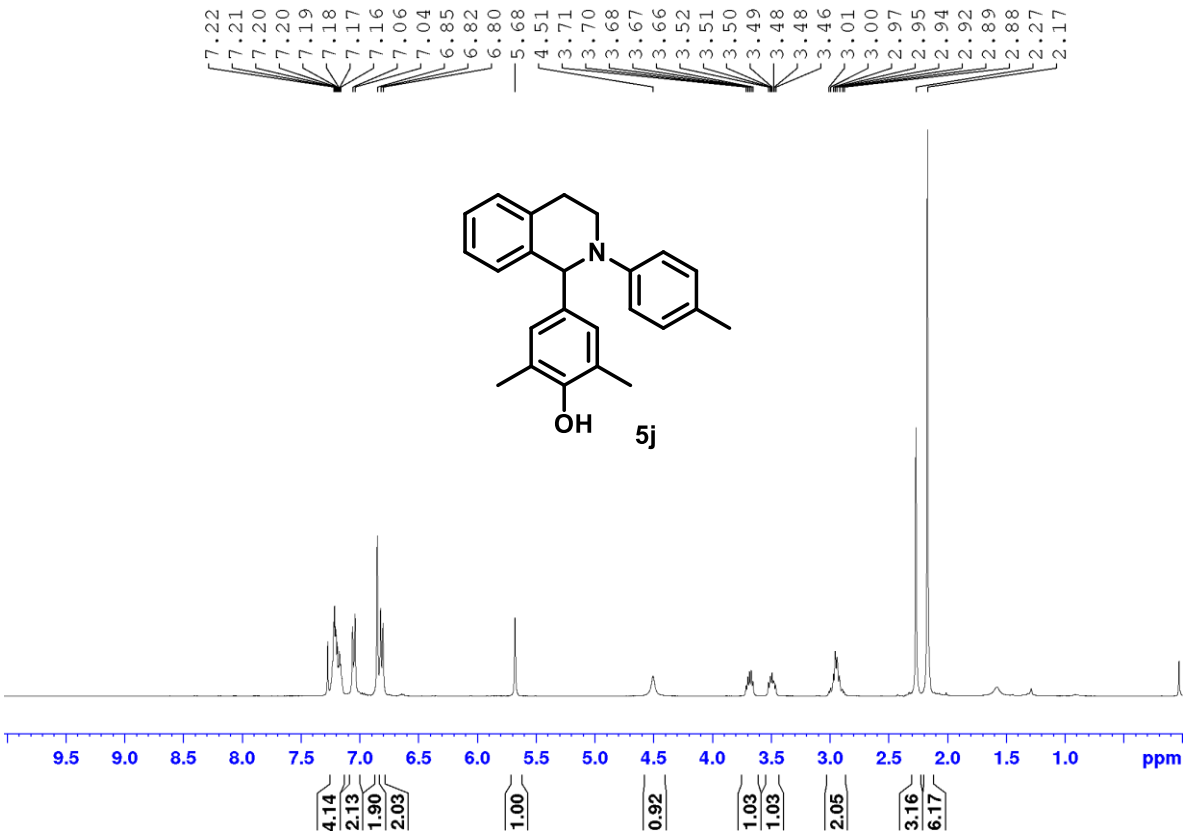
^{1}H NMR (400 MHz, $CDCl_3$) for 5i



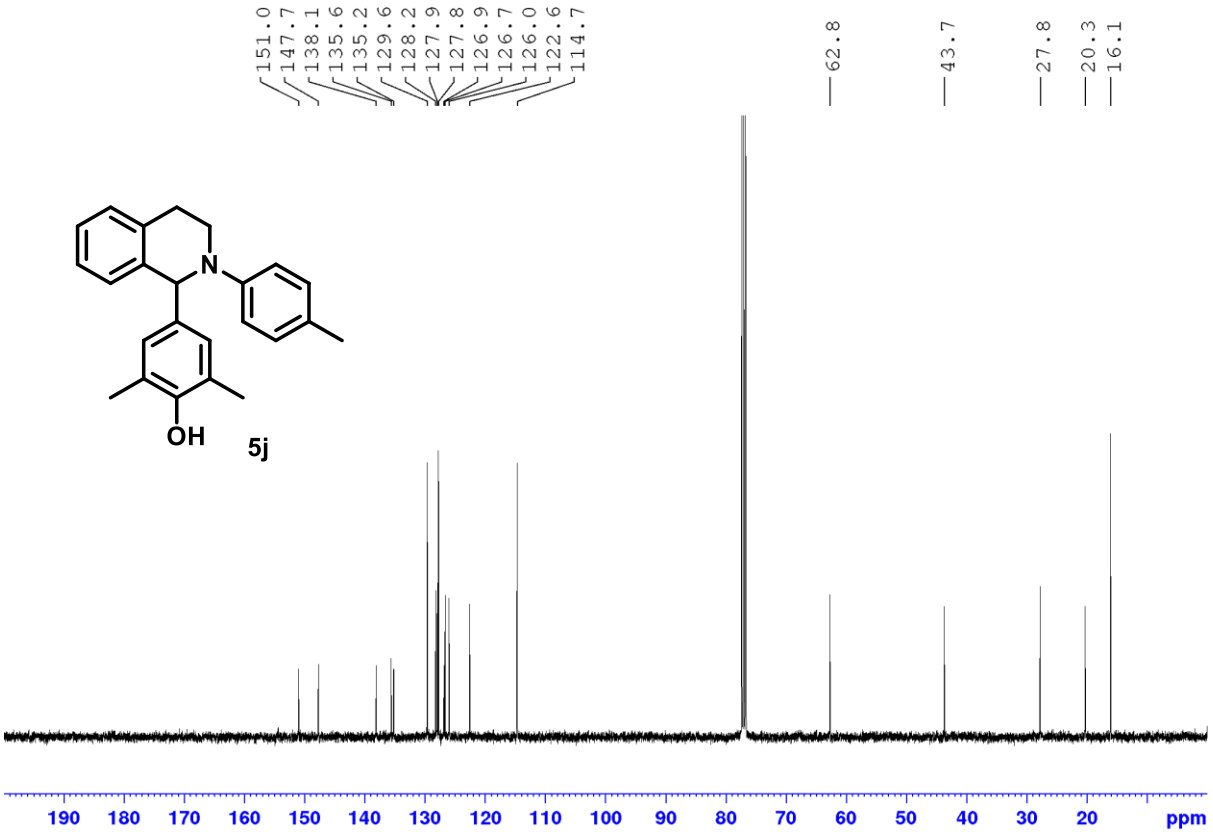
^{13}C NMR (101 MHz, $CDCl_3$) for 5i



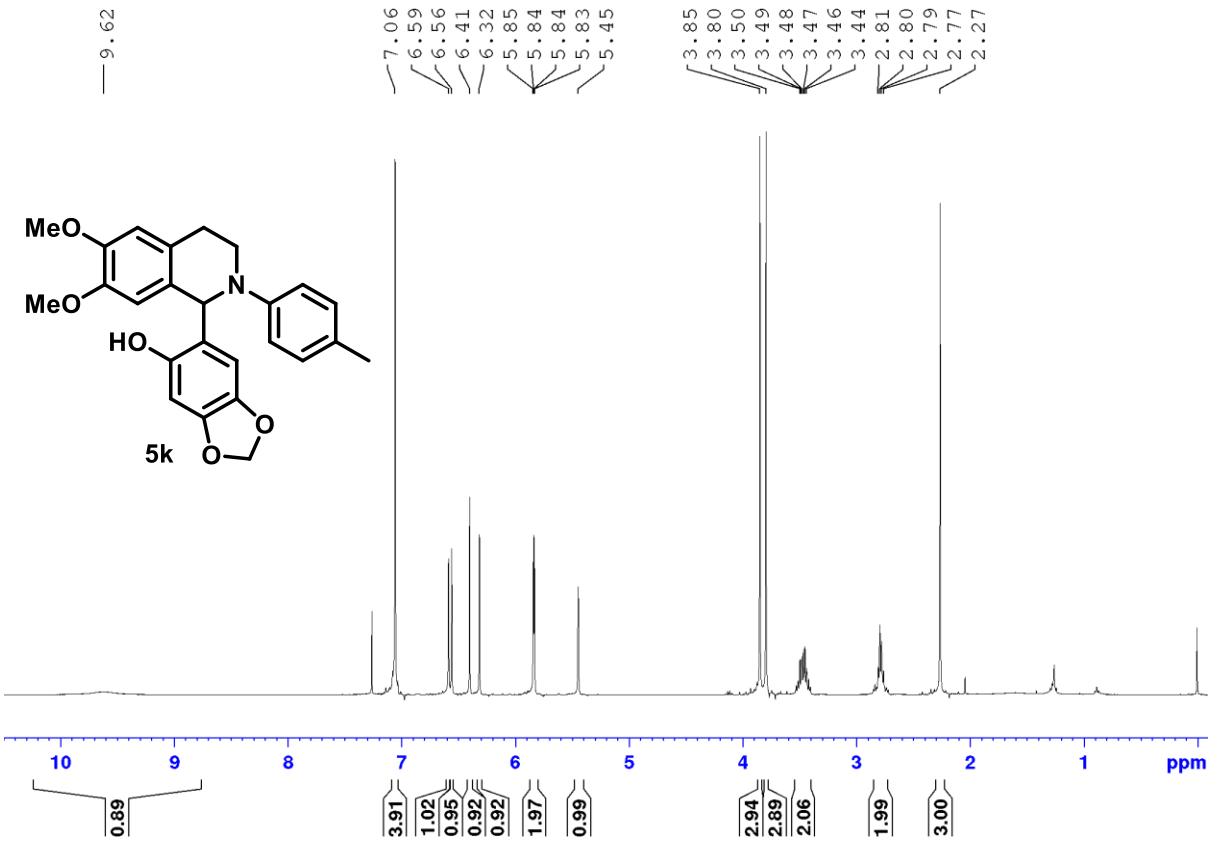
^{1}H NMR (400 MHz, $CDCl_3$) for 5j



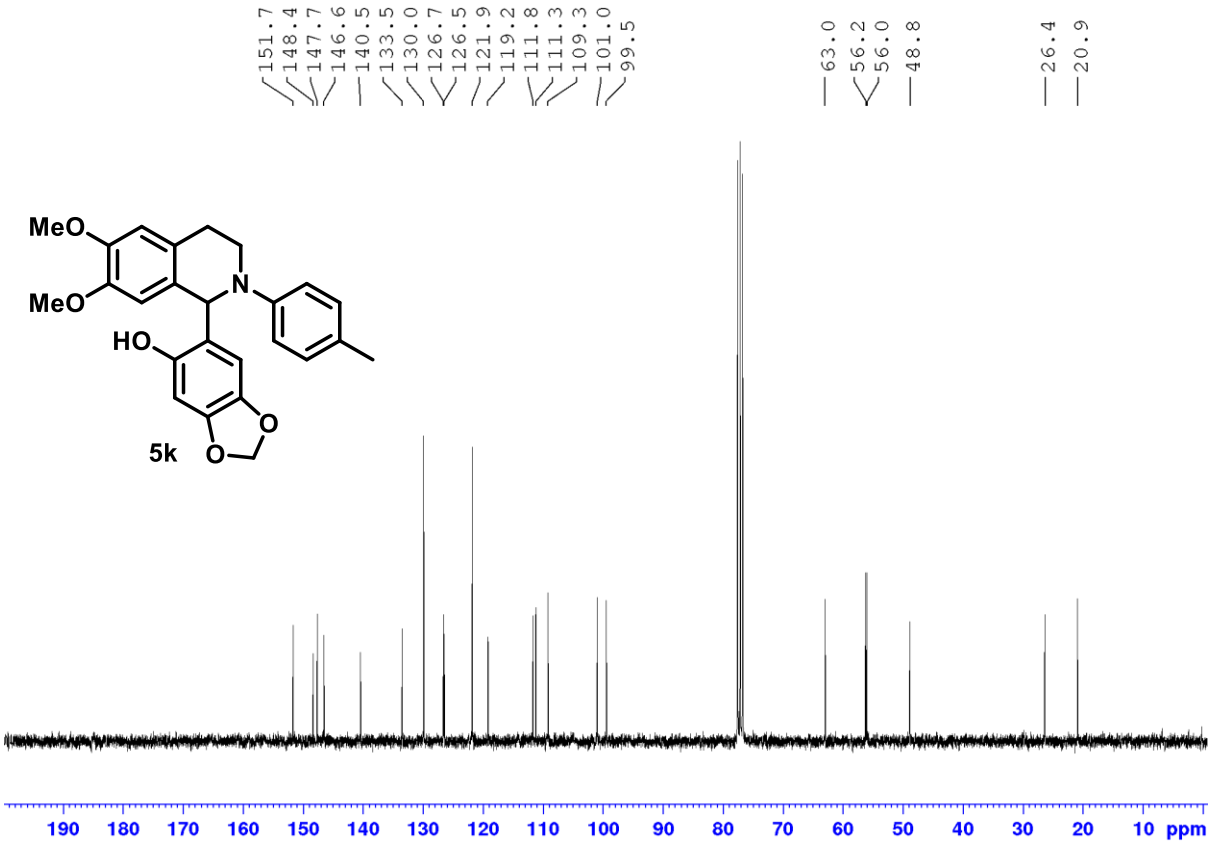
^{13}C NMR (101 MHz, $CDCl_3$) for 5j



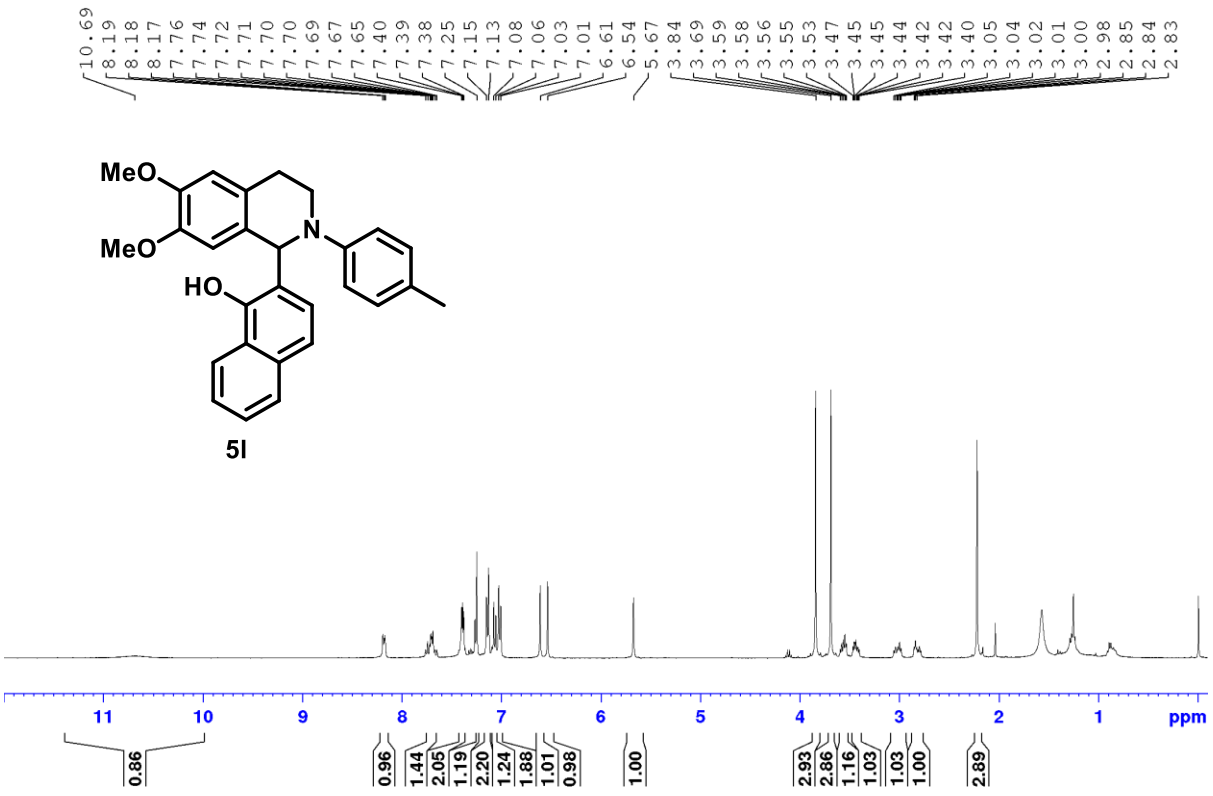
^{1}H NMR (400 MHz, $CDCl_3$) for 5k



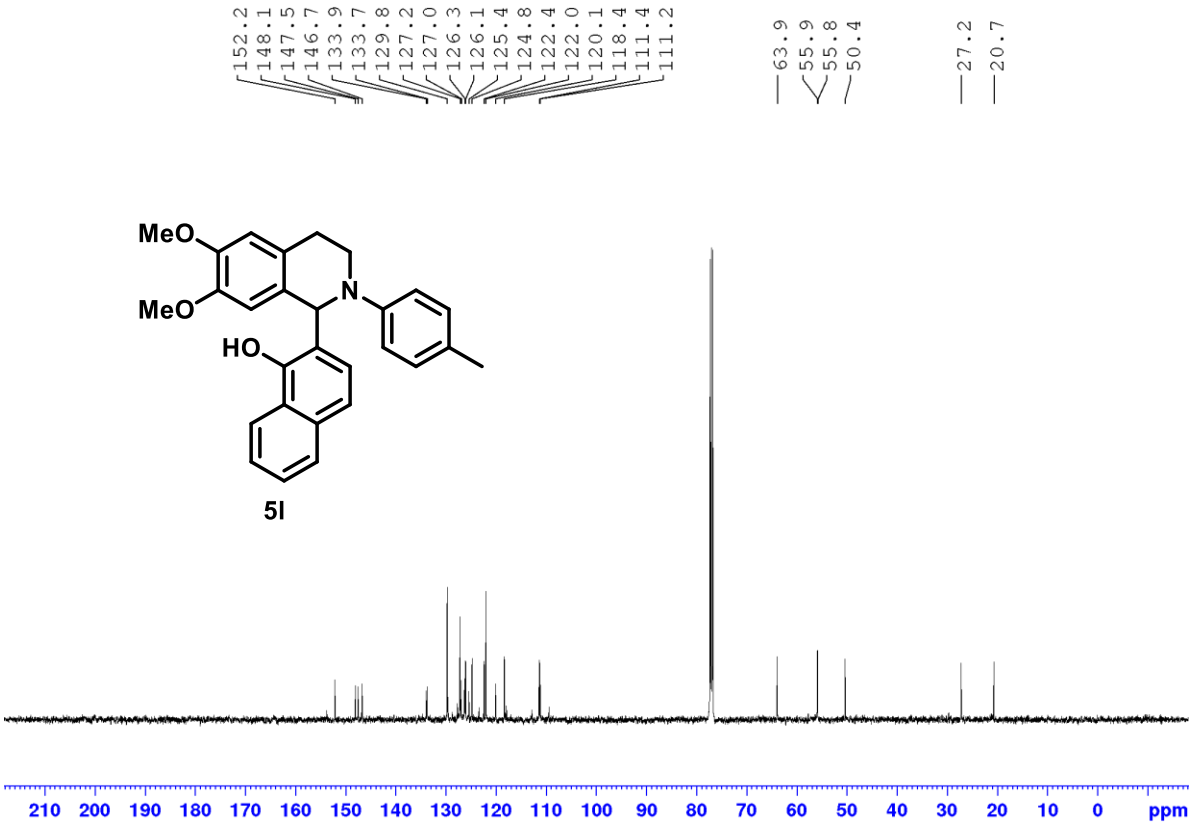
^{13}C NMR (101 MHz, $CDCl_3$) for 5k



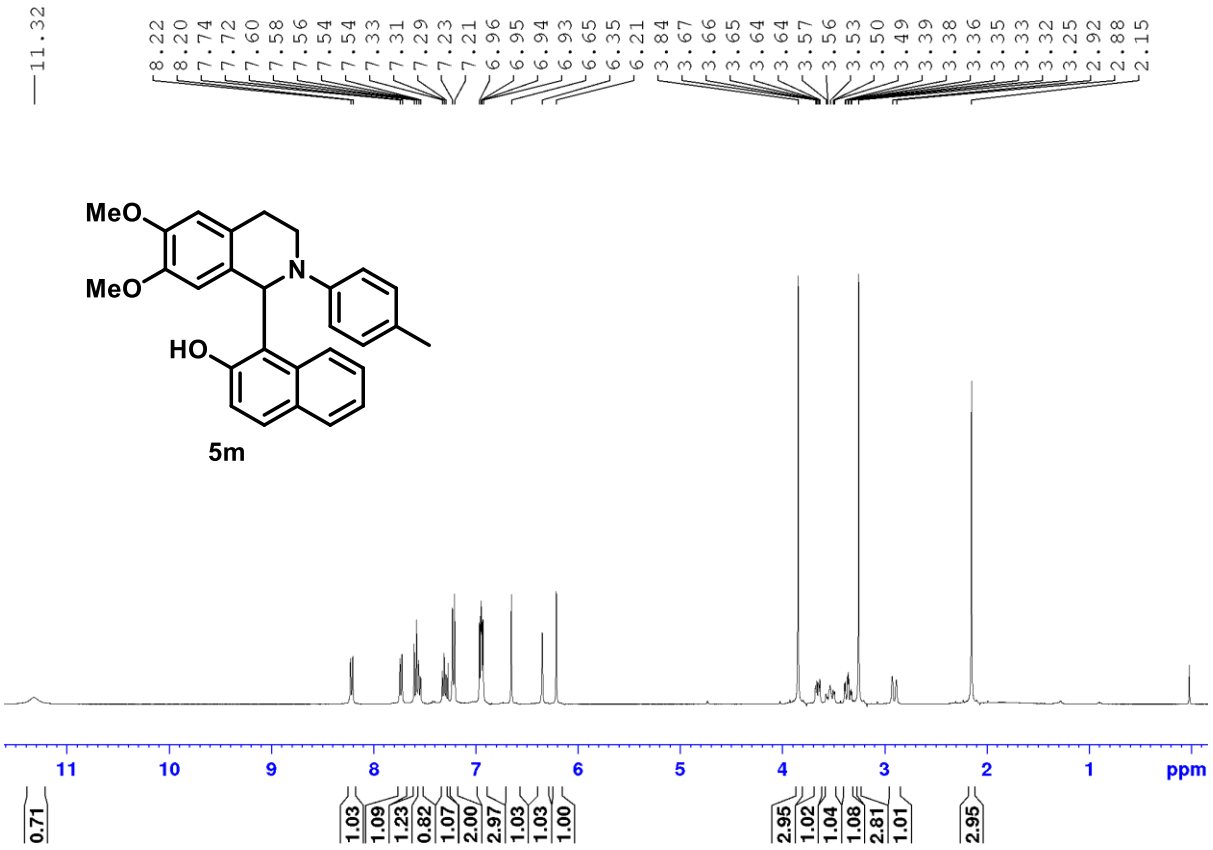
^{1}H NMR (400 MHz, $CDCl_3$) for 5l



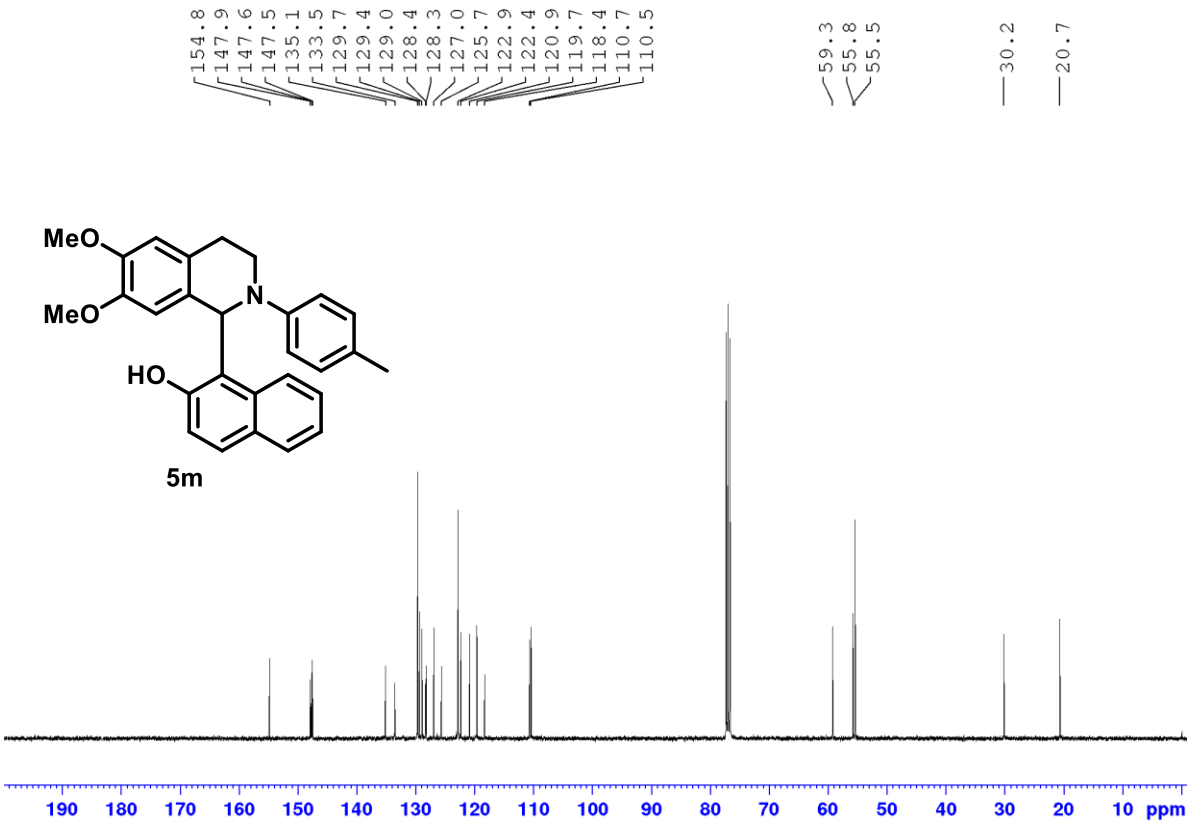
^{13}C NMR (100 MHz, $CDCl_3$) for 5l



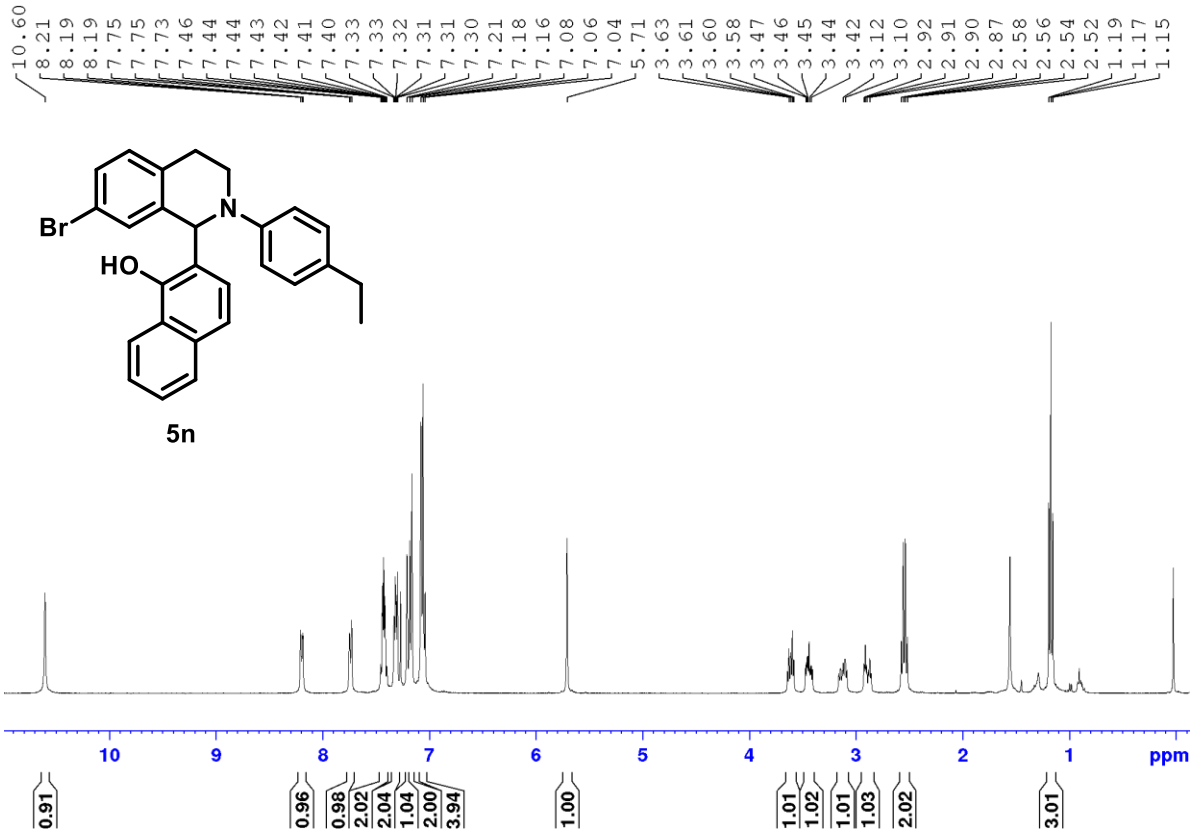
^{1}H NMR (400 MHz, $CDCl_3$) for 5m



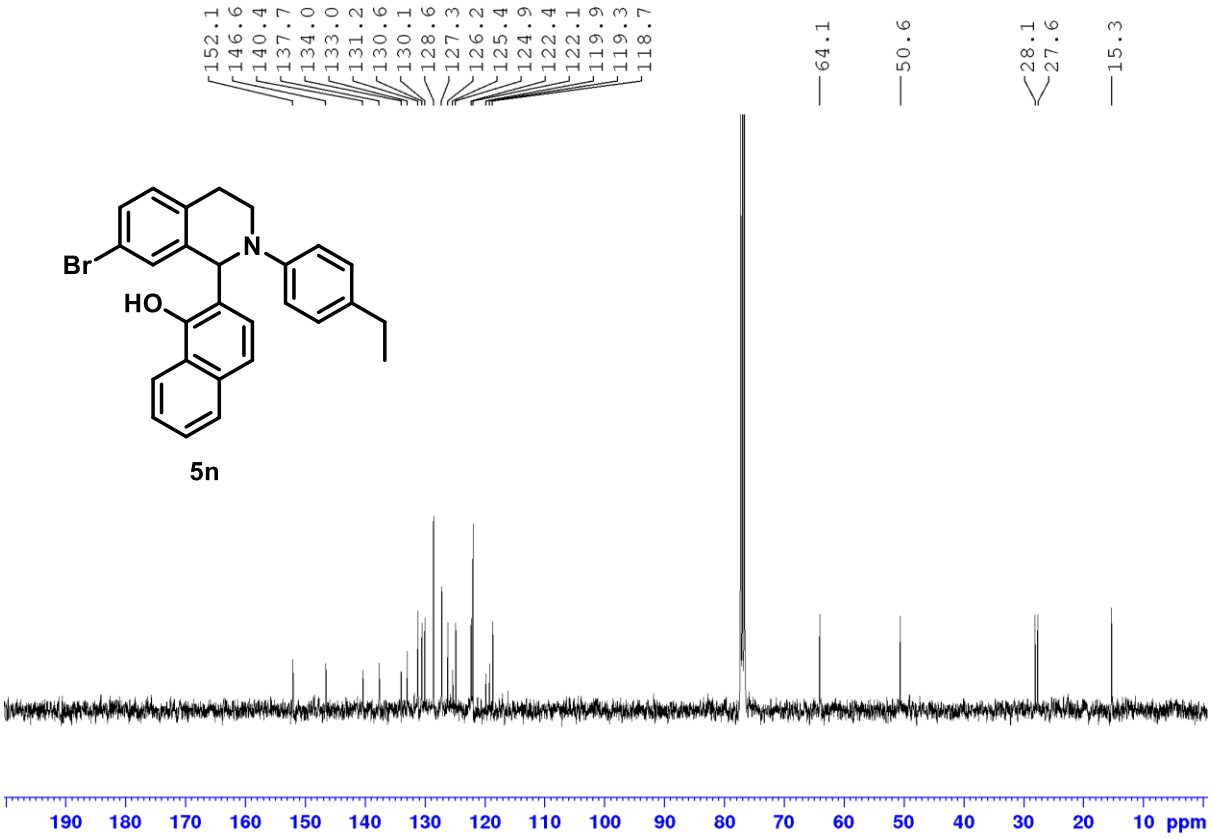
^{13}C NMR (101 MHz, $CDCl_3$) for 5m



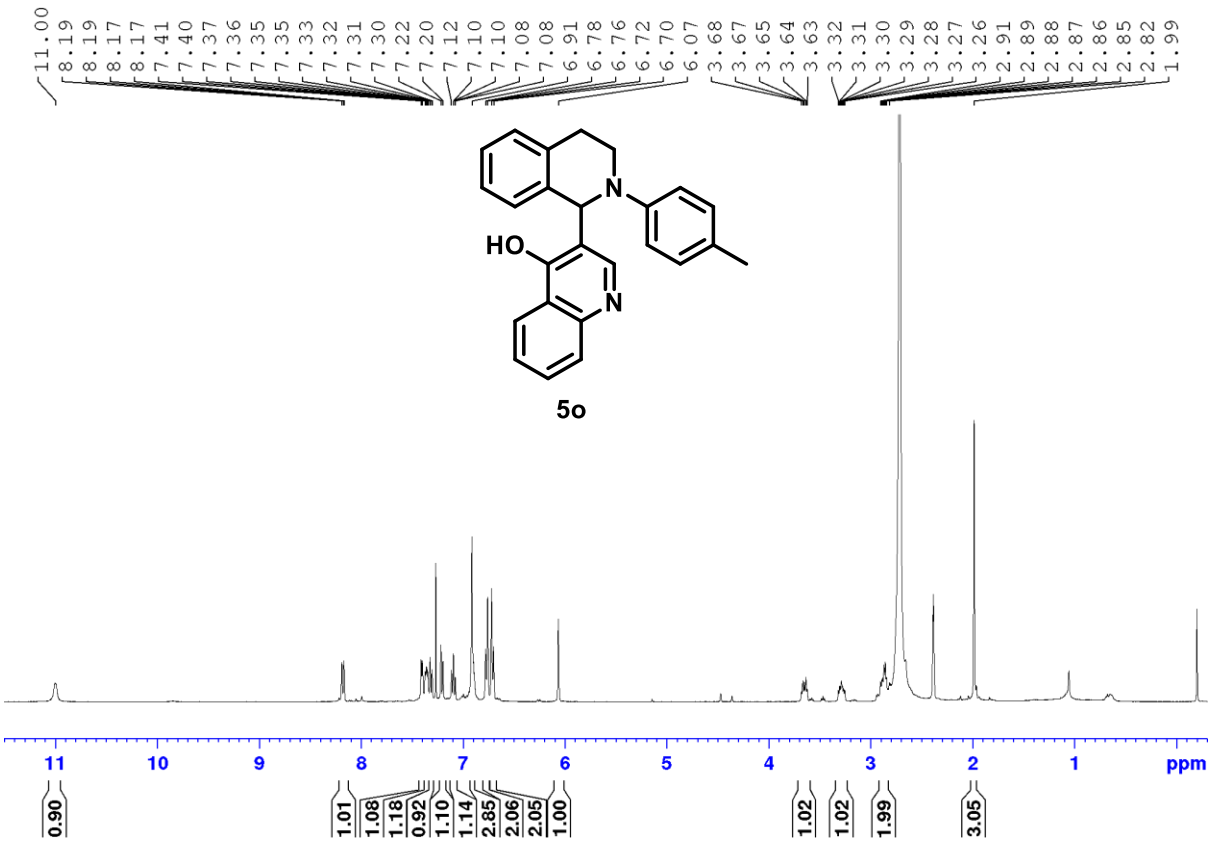
^{1}H NMR (400 MHz, $CDCl_3$) for 5n



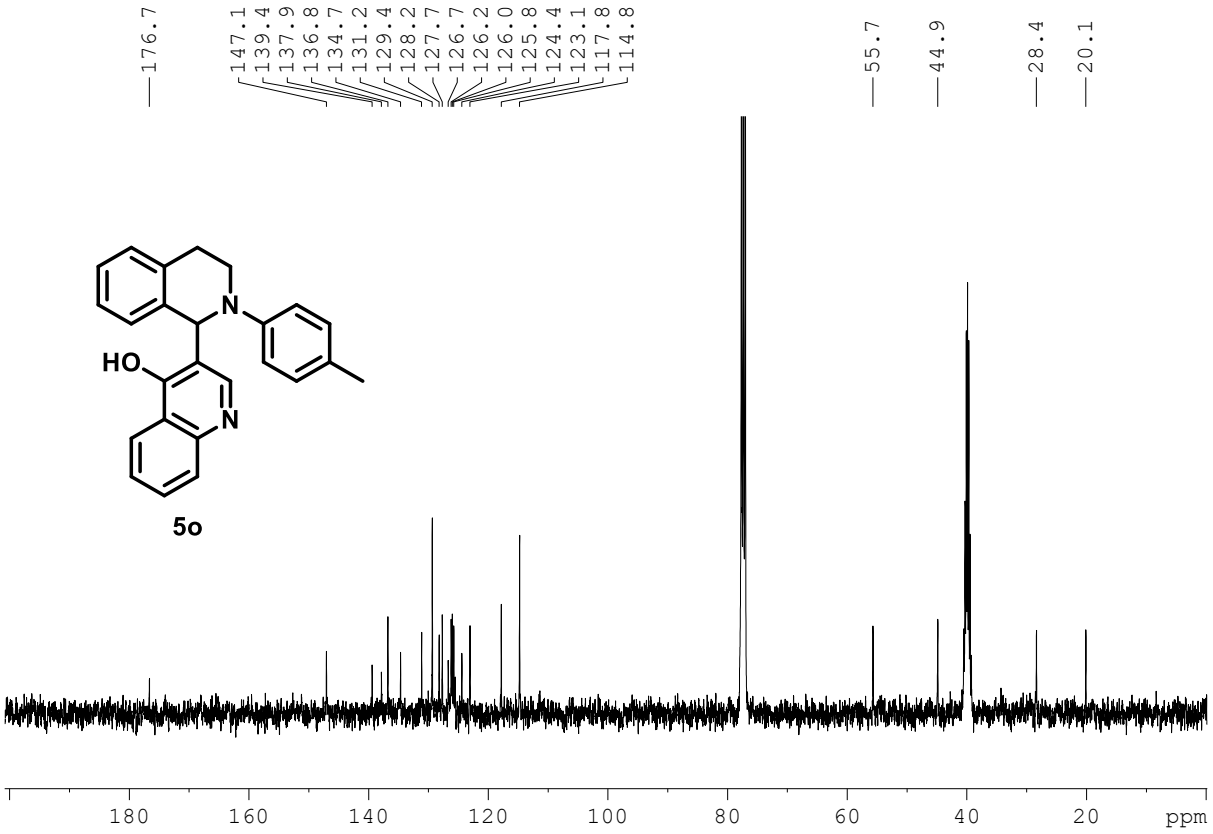
^{13}C NMR (101 MHz, $CDCl_3$) for 5n



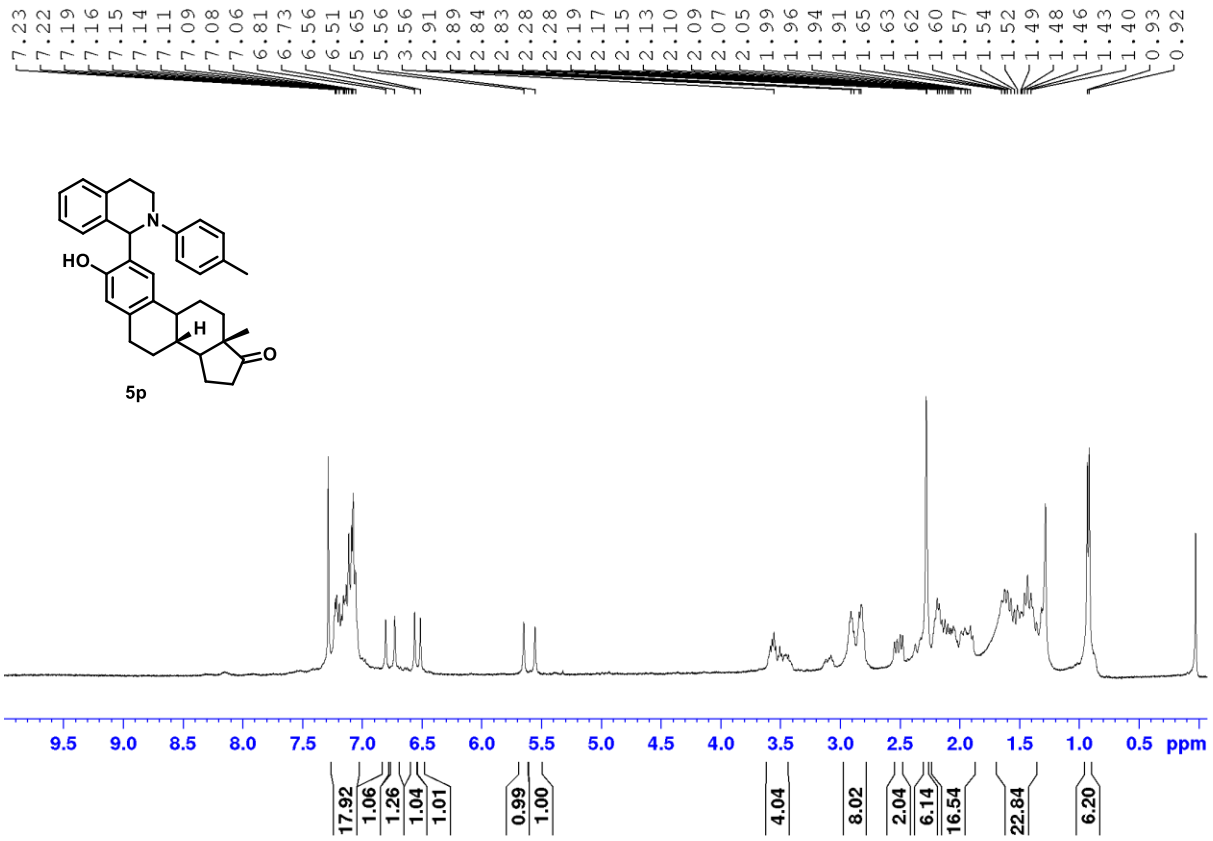
^{1}H NMR (400 MHz, $CDCl_3$ and 3 Drops DMSO-d_6) for 5o



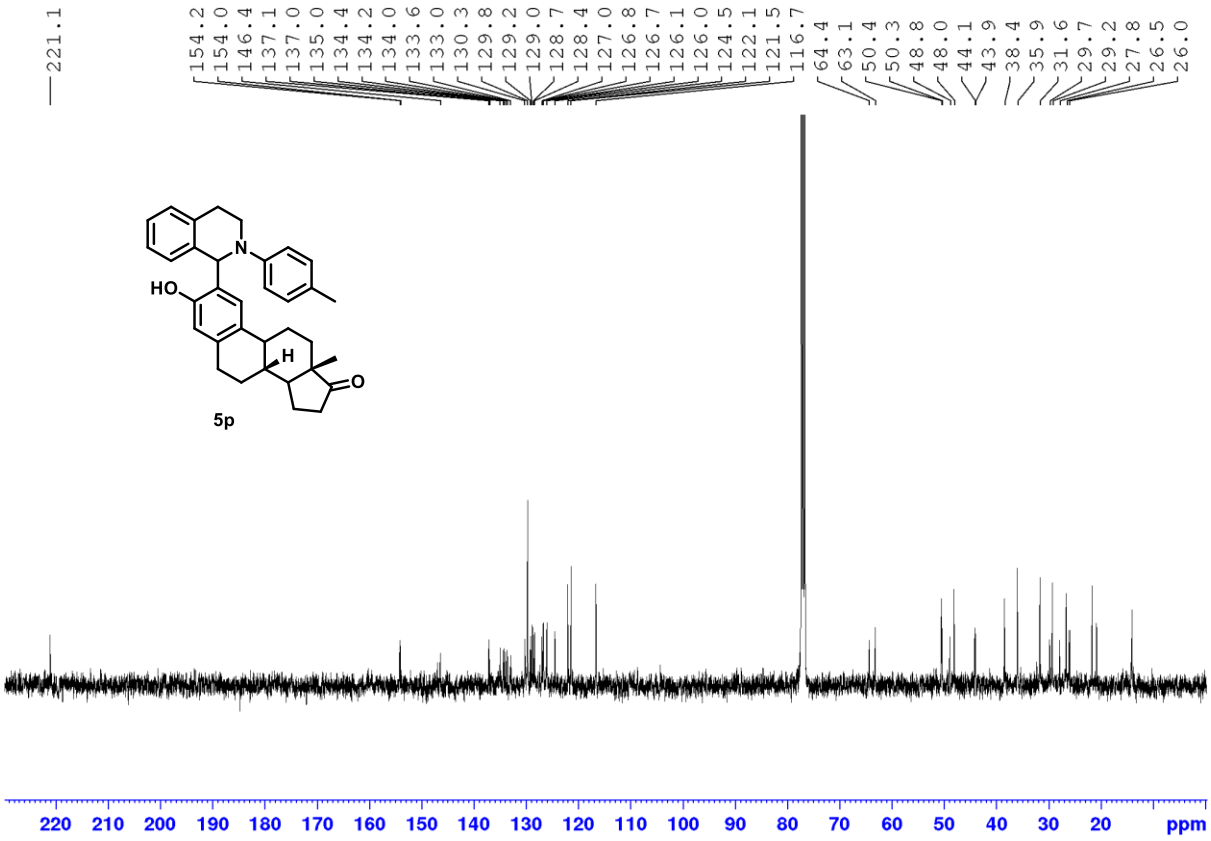
^{13}C NMR (101 MHz, $CDCl_3$ and 3 Drops DMSO-d_6) for 5o



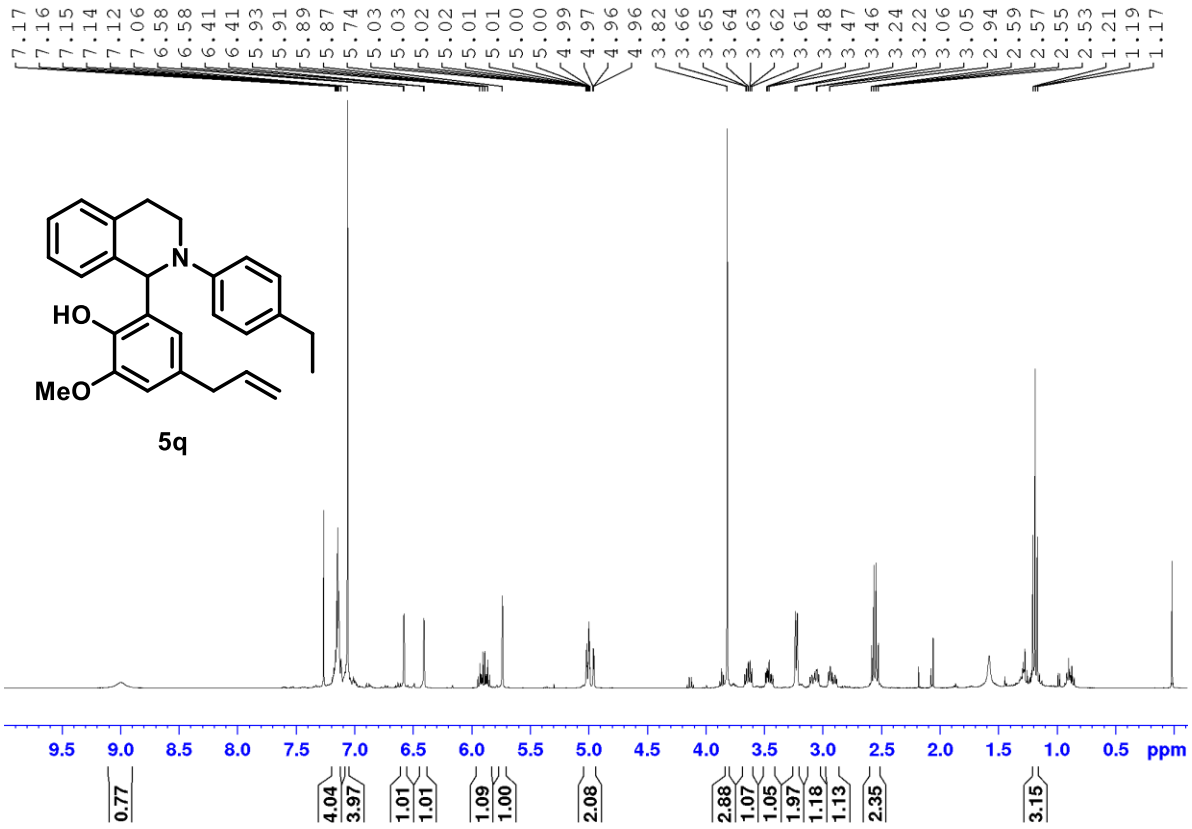
^{1}H NMR (400 MHz, $CDCl_3$) for 5p



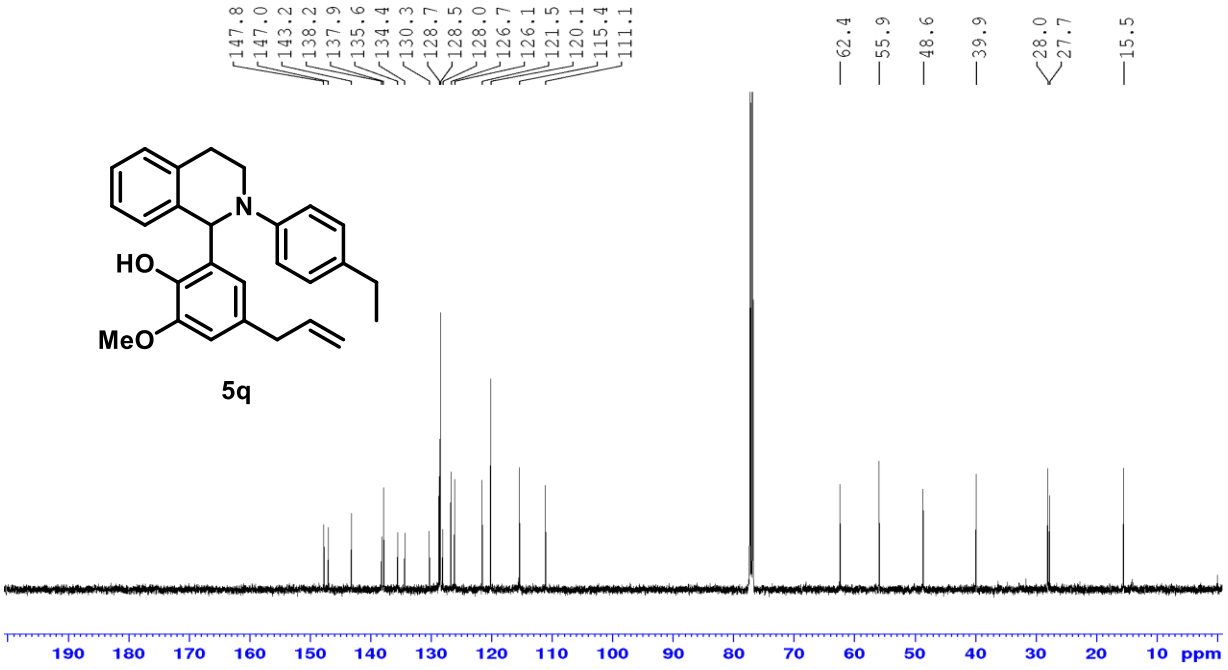
^{13}C NMR (101 MHz, $CDCl_3$) for 5p



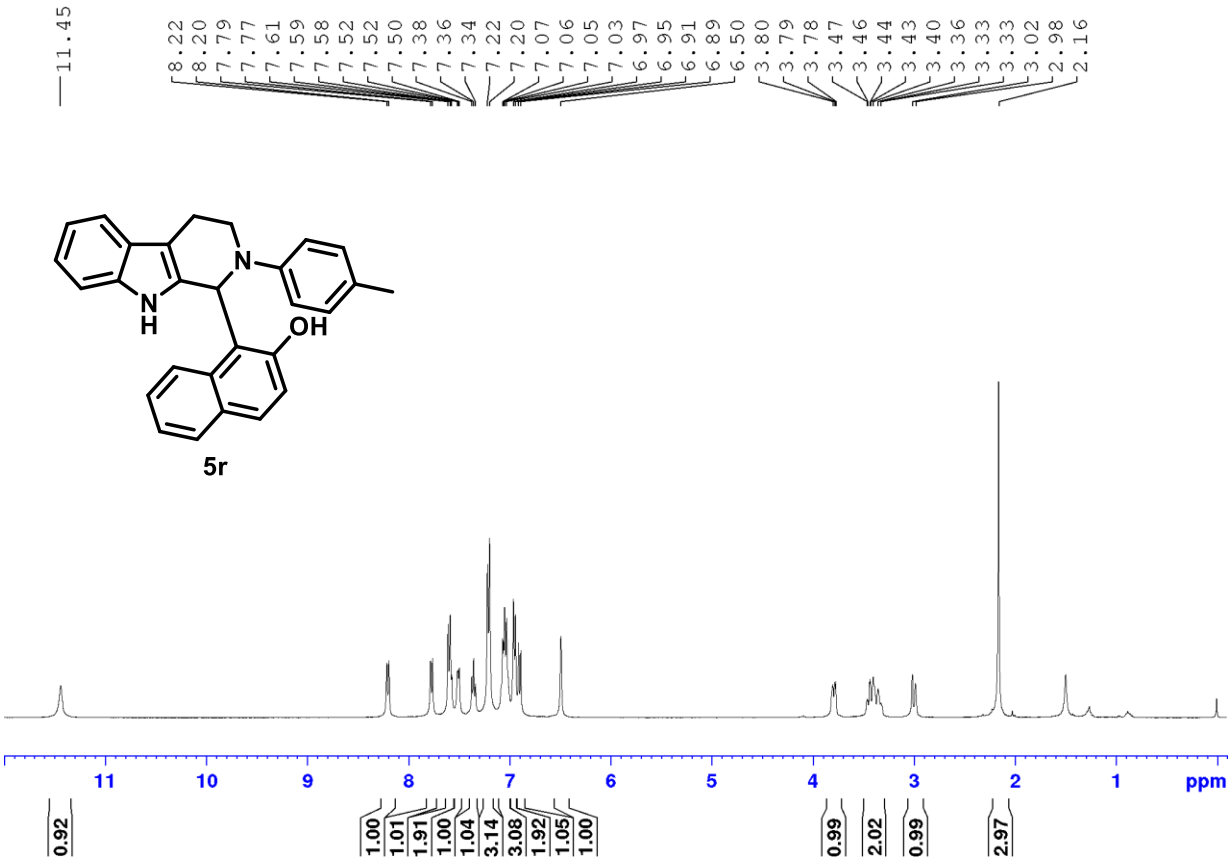
^{1}H NMR (400 MHz, $CDCl_3$) for 5q



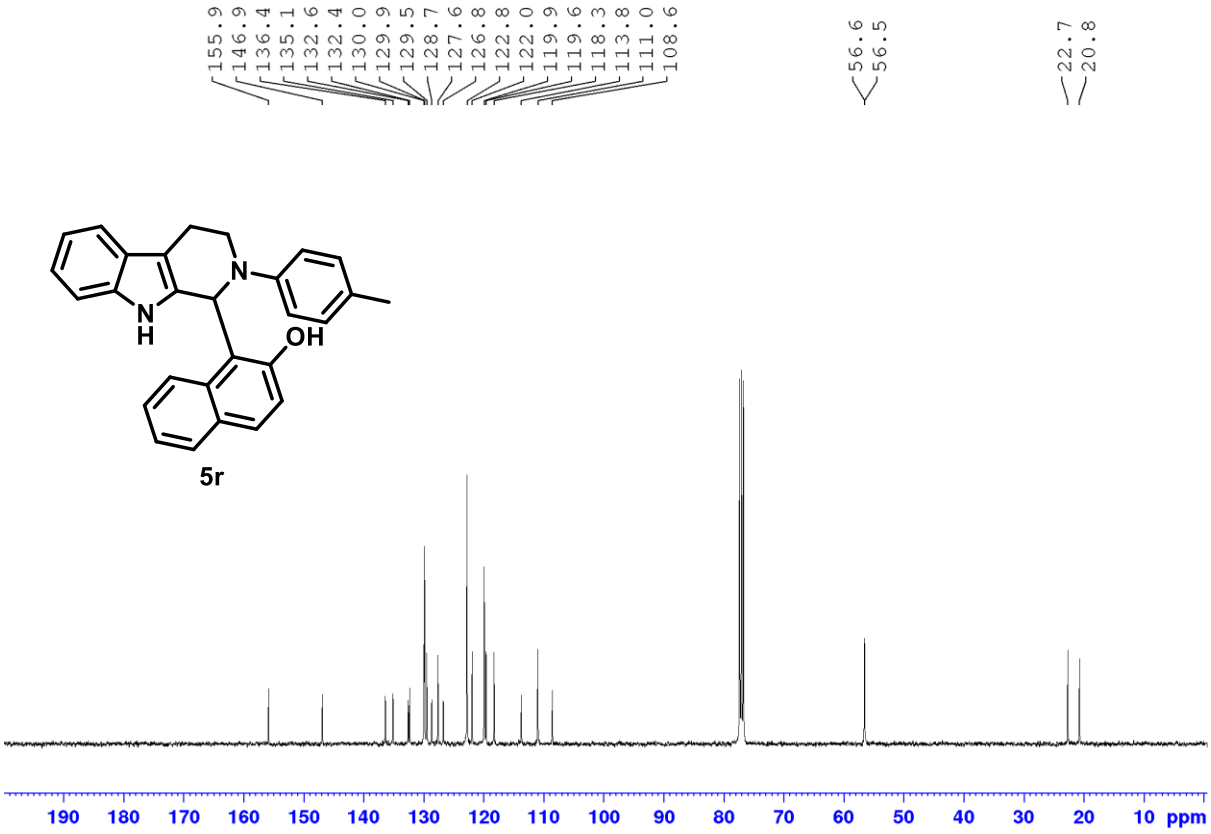
^{13}C NMR (101 MHz, $CDCl_3$) for 5q



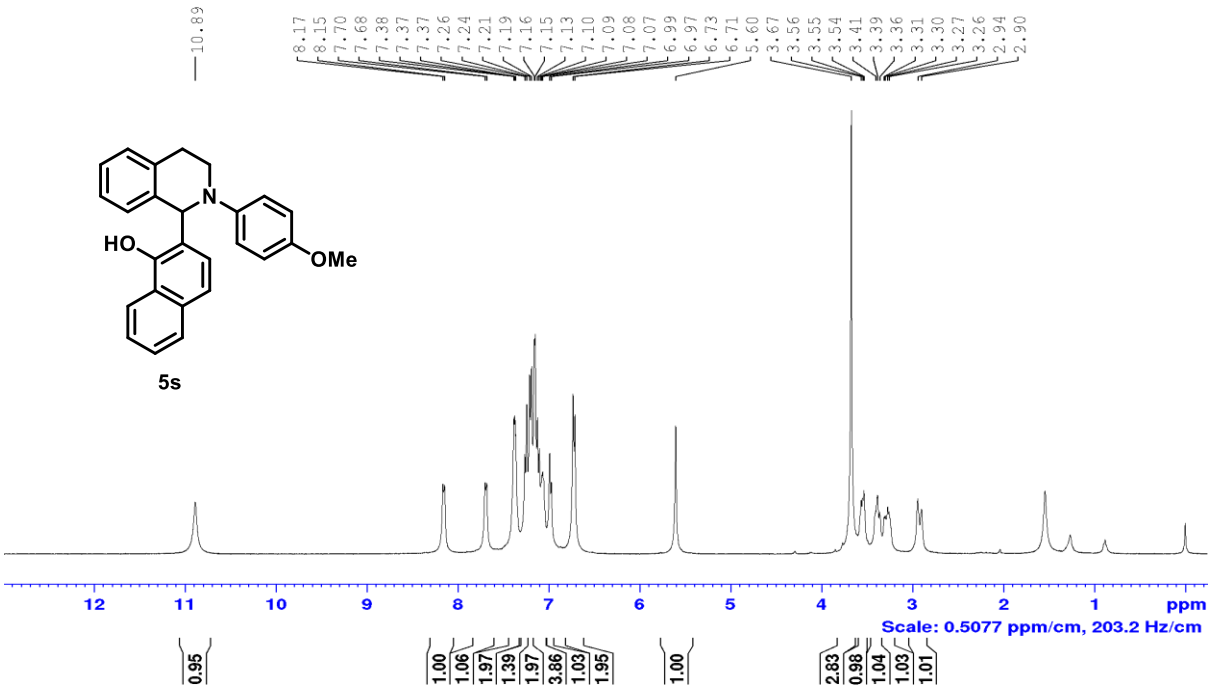
^{1}H NMR (400 MHz, $CDCl_3$) for 5r



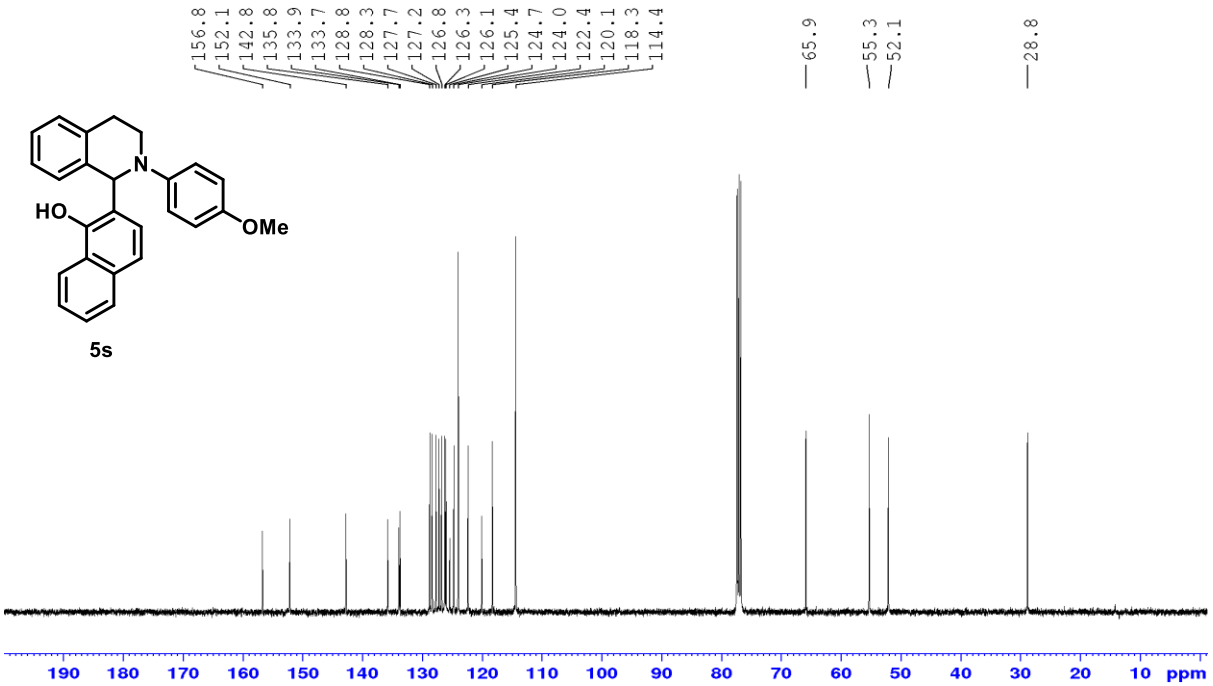
^{13}C NMR (101 MHz, $CDCl_3$) for 5r



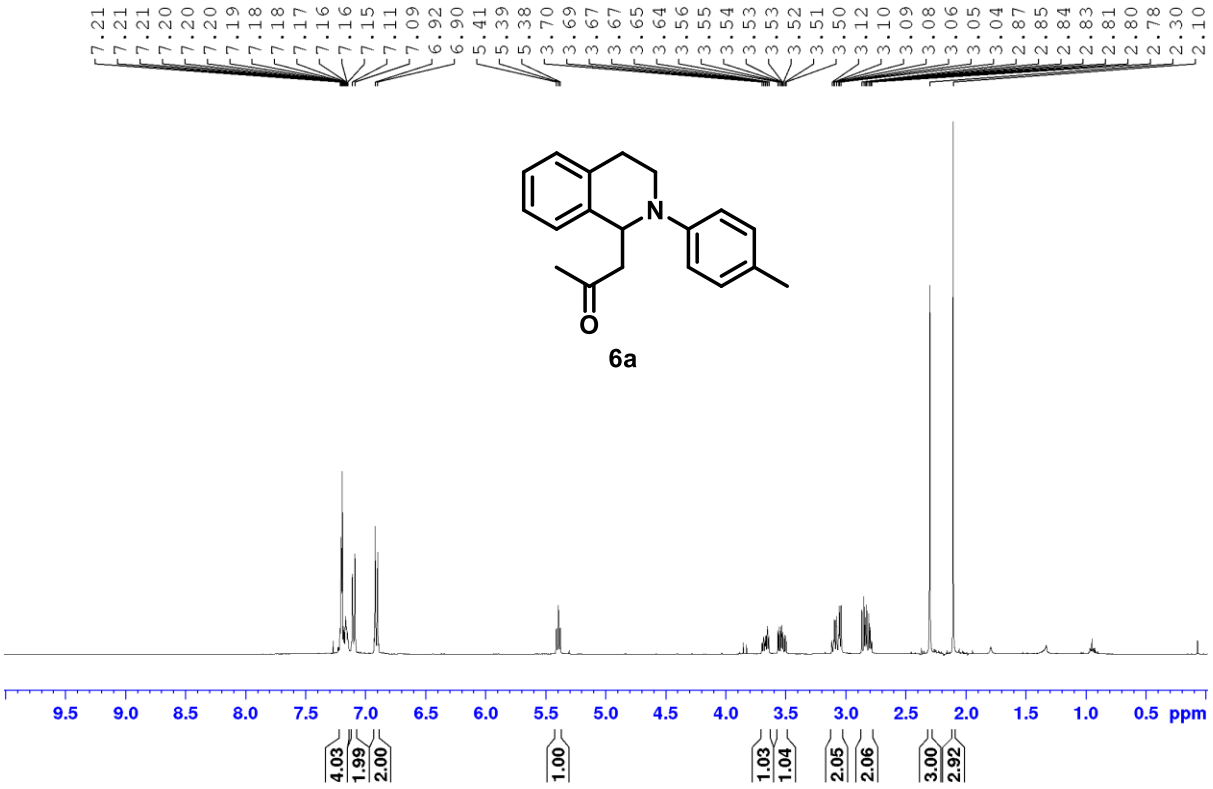
^{1}H NMR (400 MHz, $CDCl_3$) for 5s



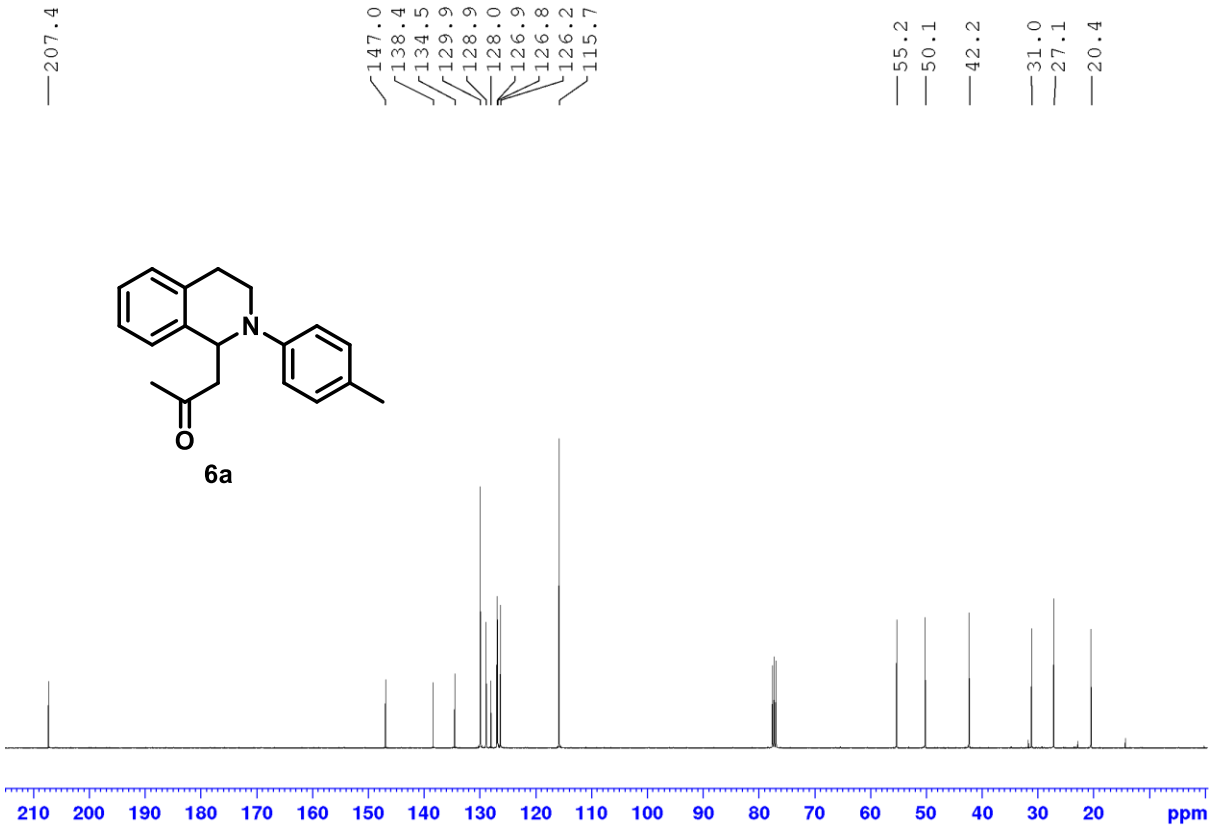
^{13}C NMR (101 MHz, $CDCl_3$) for 5s



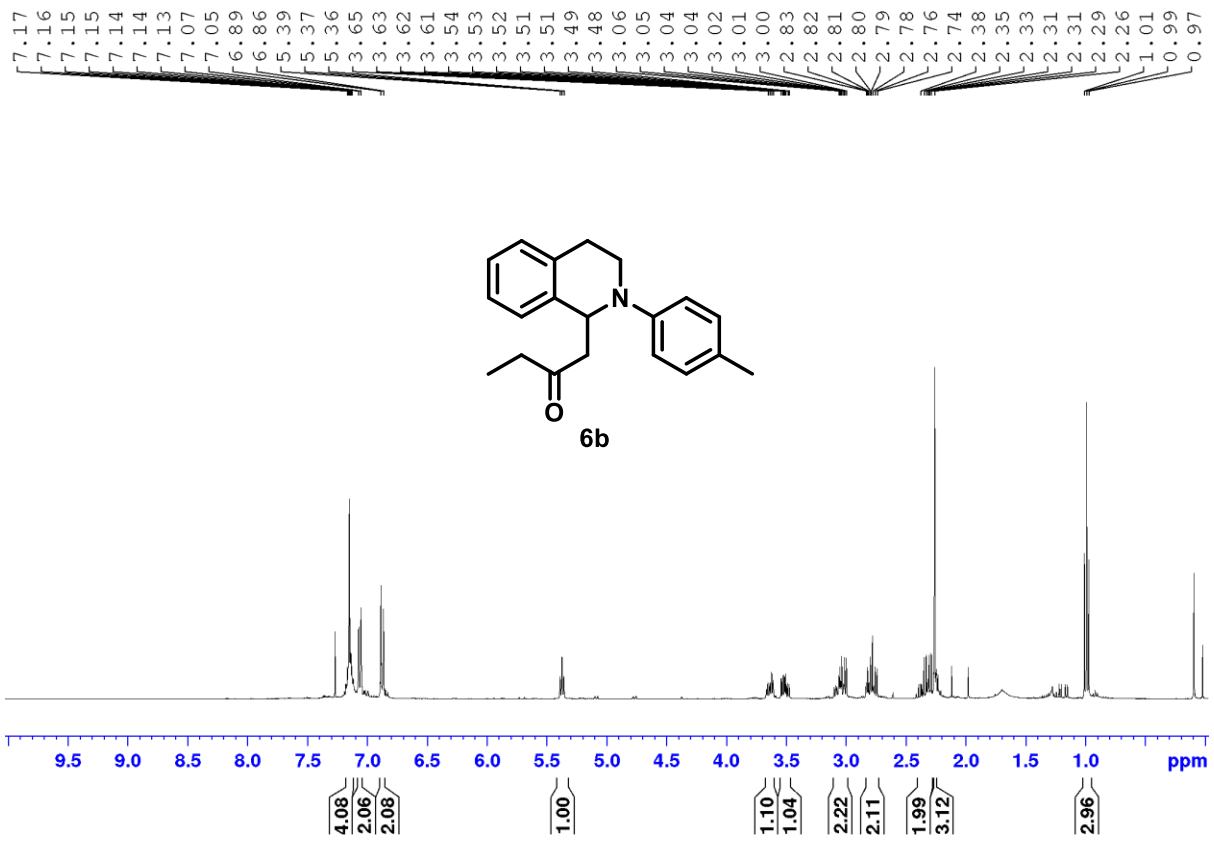
^{1}H NMR (400 MHz, $CDCl_3$) for 6a



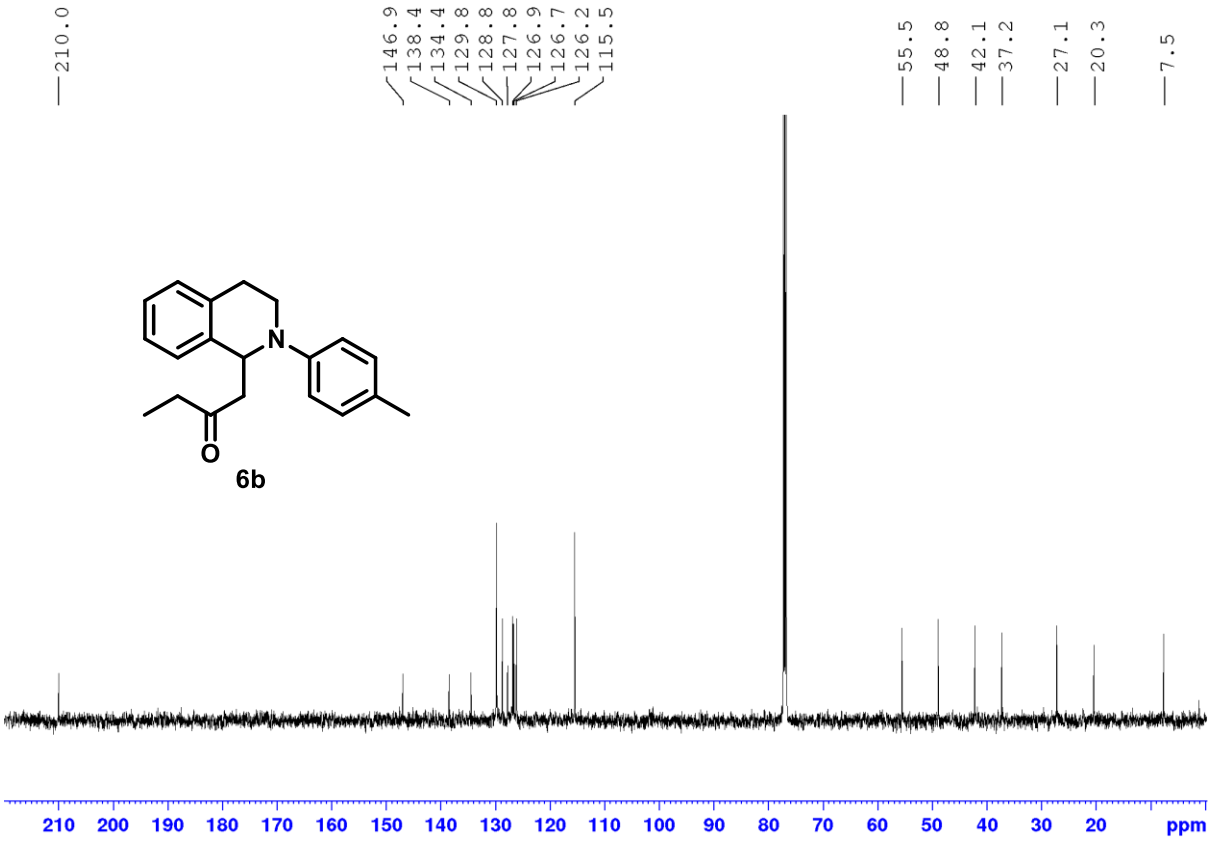
^{13}C NMR (101 MHz, $CDCl_3$) for 6a



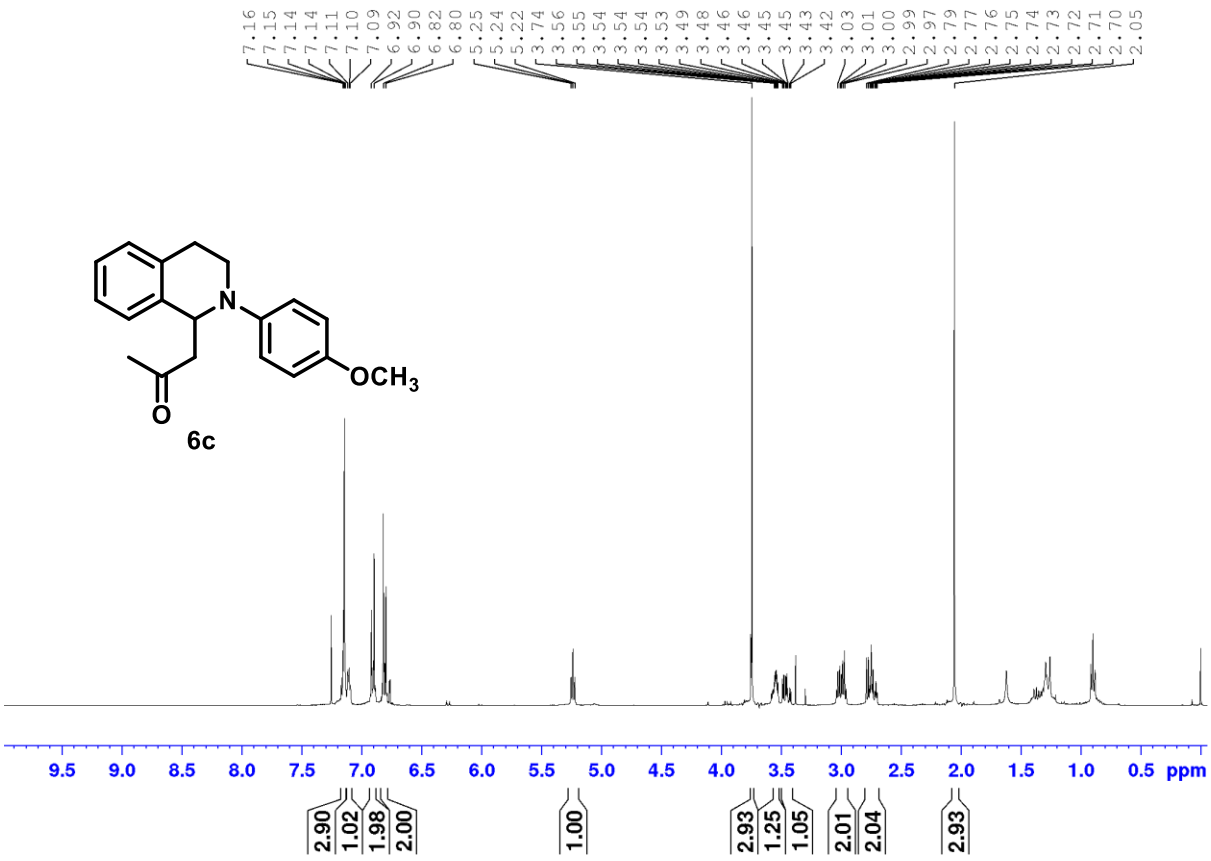
^{1}H NMR (400 MHz, $CDCl_3$) for 6b



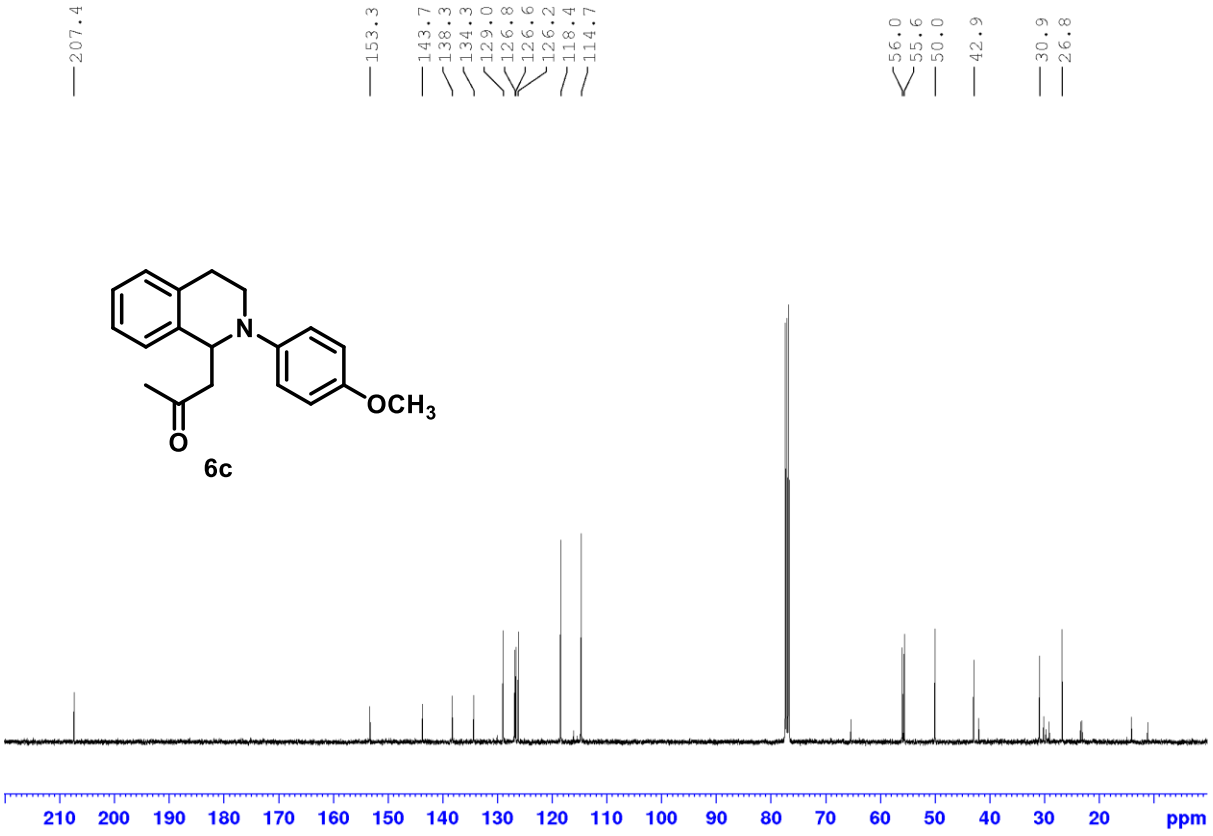
^{13}C NMR (101 MHz, $CDCl_3$) for 6b



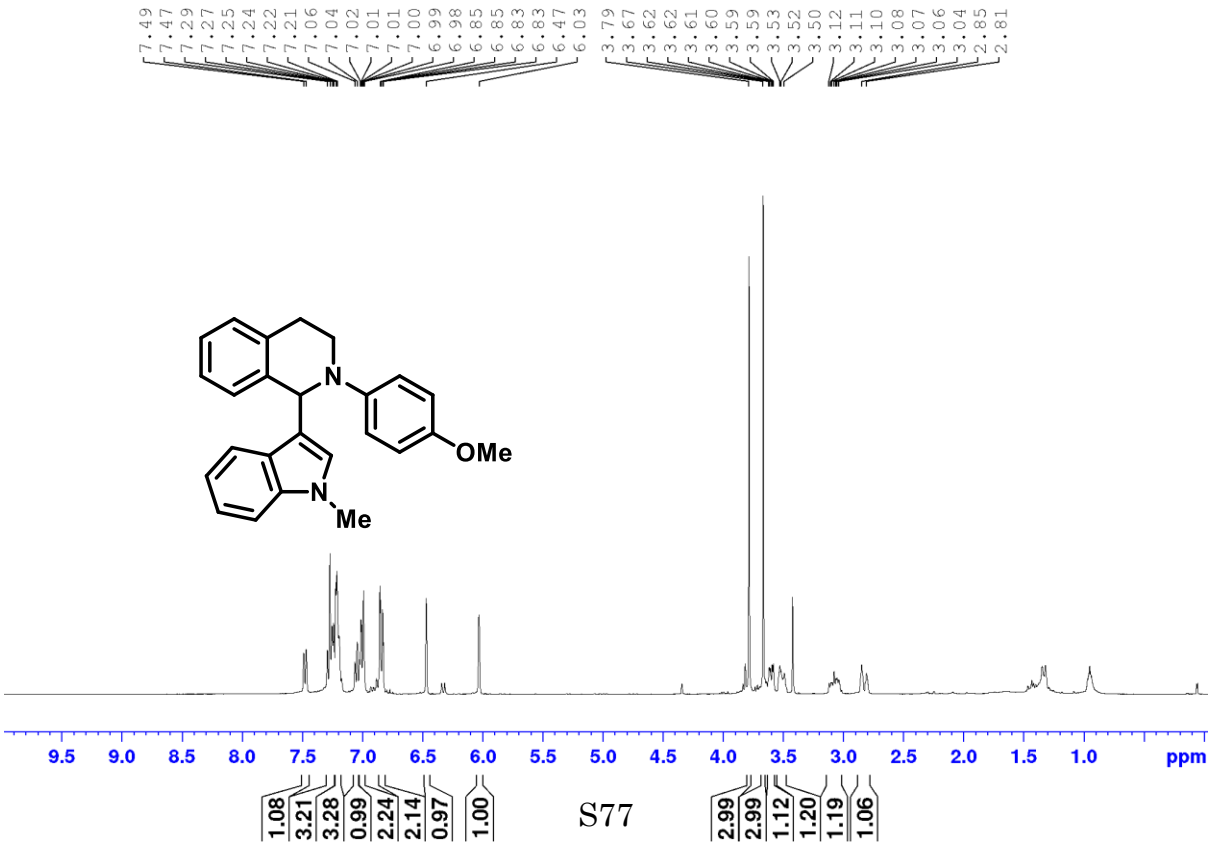
^{1}H NMR (400 MHz, $CDCl_3$) for 6c



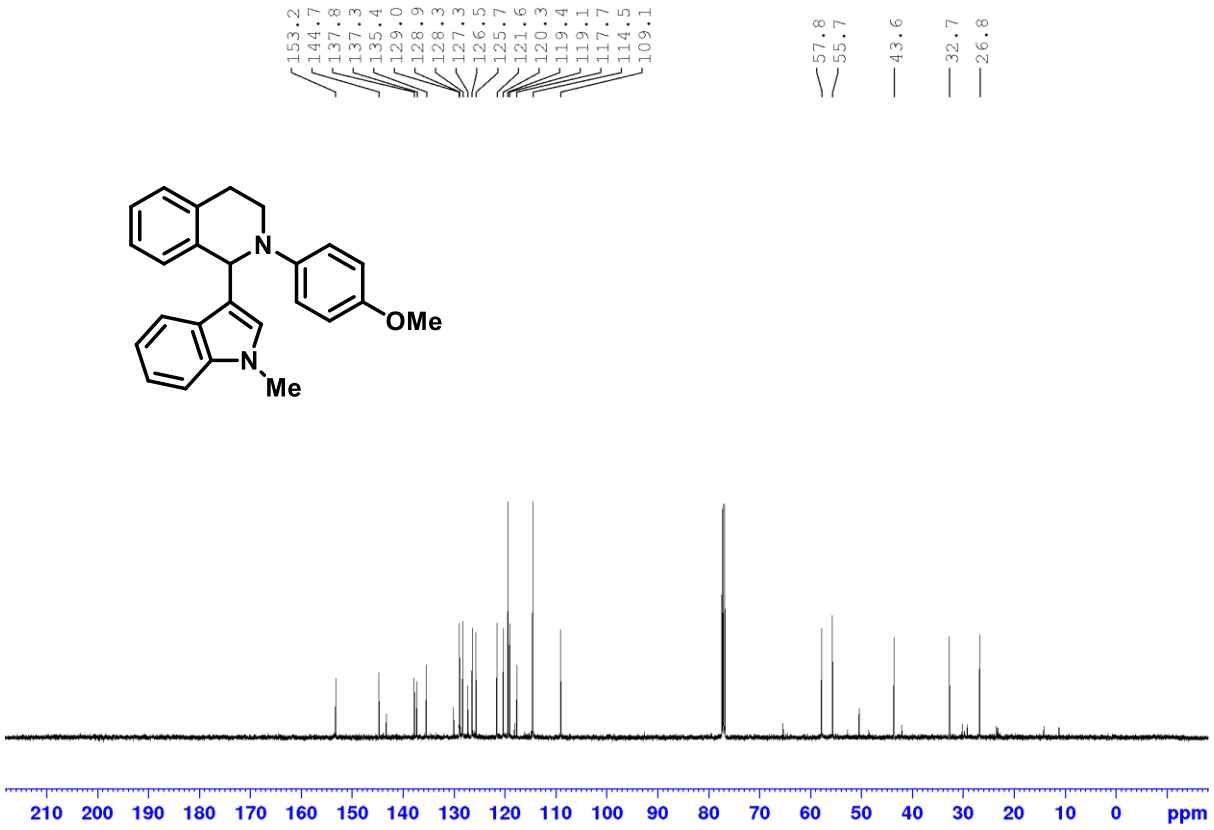
^{13}C NMR (101 MHz, $CDCl_3$) for 6c



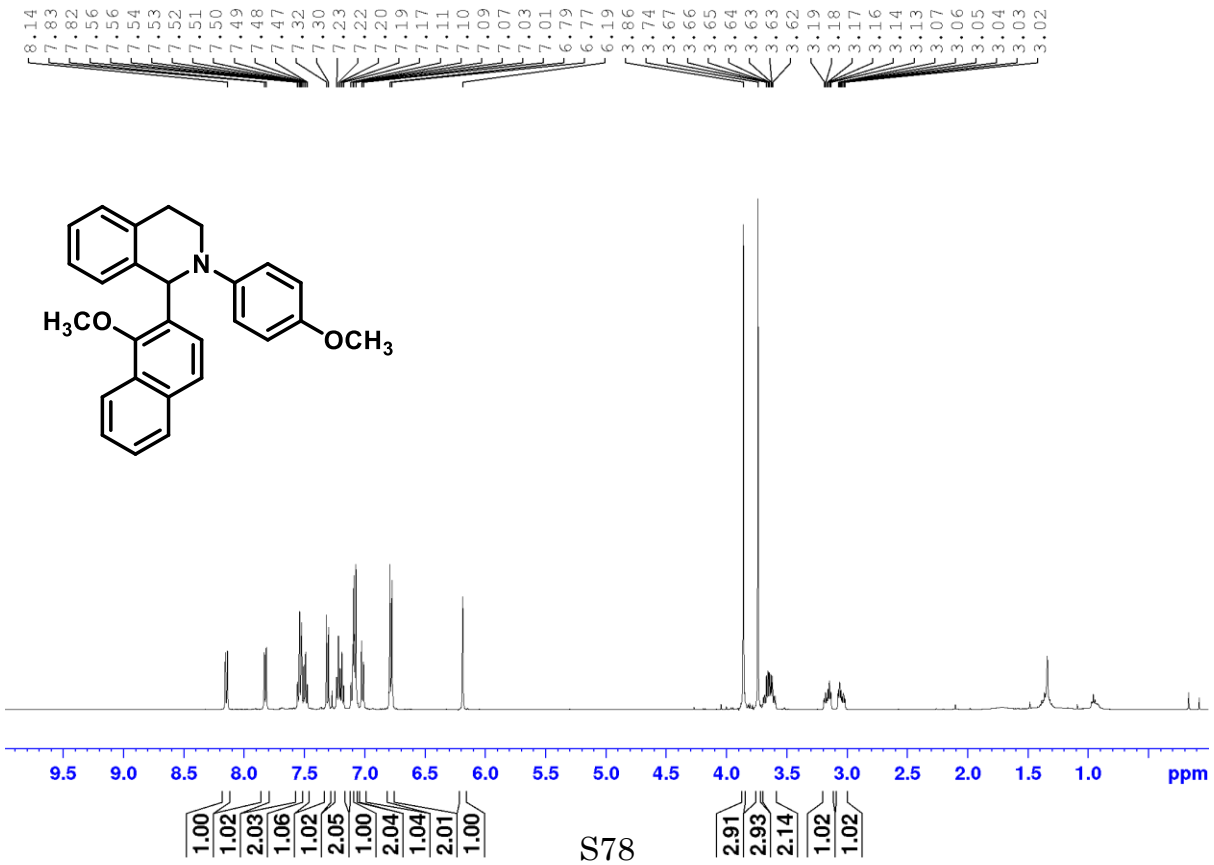
^{1}H NMR (400 MHz, $CDCl_3$)



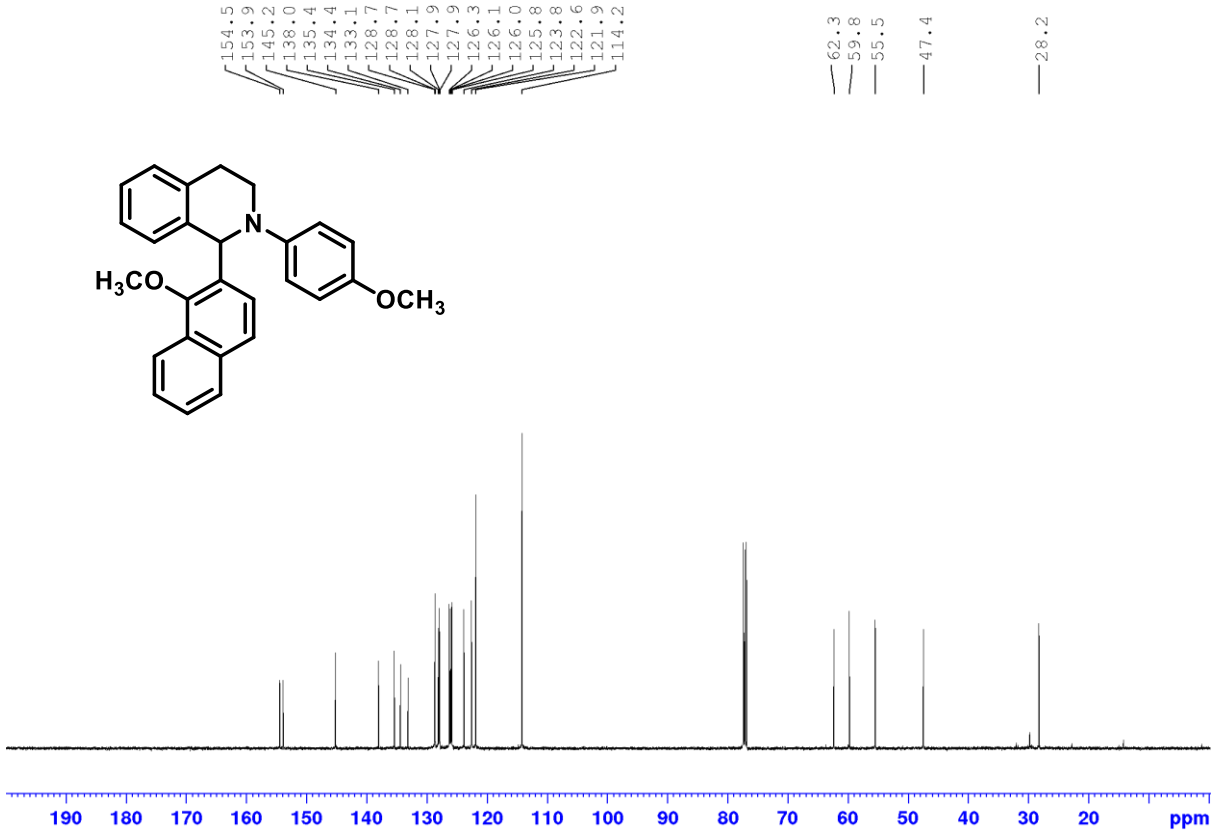
^{13}C NMR (101 MHz, $CDCl_3$)



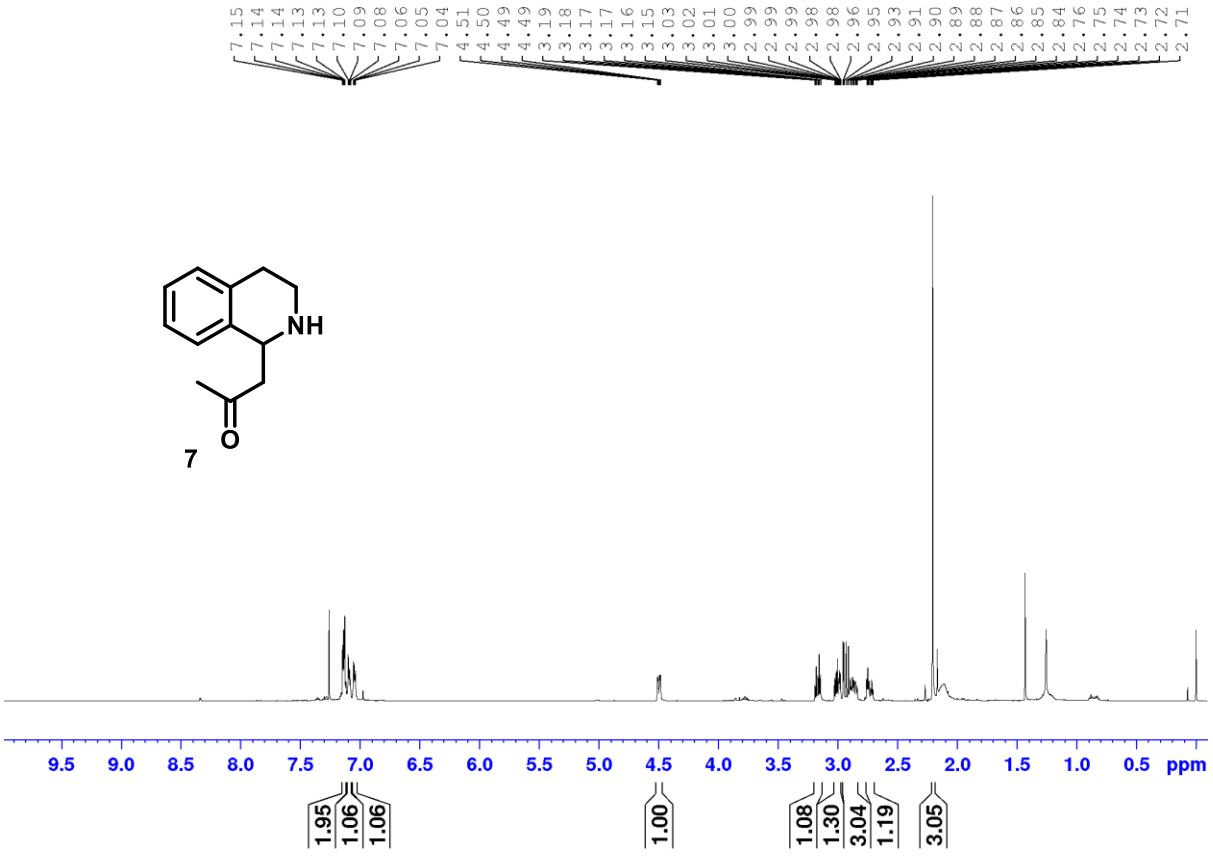
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$) for 7



^{13}C NMR (101 MHz, $CDCl_3$) for 7