Supporting Information

α-Oxygenation of N-Aryl/Alky Heterocyclic Compounds via Ruthenium-Photocatalysis

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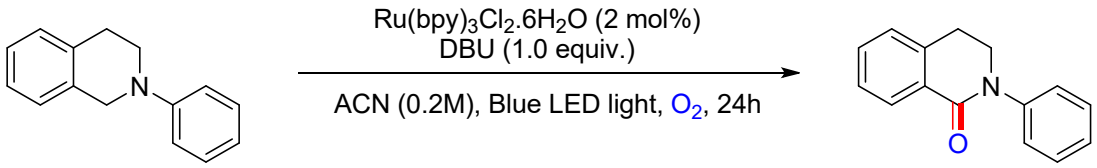
1. General consideration

Reagent Information: Unless otherwise stated, all reactions were carried out under oxygen atmosphere in screw cap reaction vials. All solvents were bought from Sigma Aldrich in sure-seal bottles and used as such. Chemicals were bought from Sigma Aldrich, Alfa-aesar and TCI. For column chromatography, silica gel (230-400 mesh) from Merck was used. A gradient elution using *n*-hexane and ethyl acetate was performed based on Merck aluminium TLC sheets (silica gel $60F_{254}$).

Analytical information: The melting points were recorded on a Barnstead Electro Thermal 9100. All isolated compounds were characterized by ^{1}H NMR, ^{13}C NMR, LC-MS. In addition, all the compounds were further characterized by HRMS. Mass spectra were recorded on Water Q-ToF-Micro Micromass. Copies of ^{1}H, ^{13}C NMR can be found in the NMR supporting information.

Nuclear magnetic resonance spectra were recorded either on a Bruker-Avance 600 or 300MHz instrument. All ^{1}H NMR experiments are reported in units, parts per million (ppm) and were measured relative to the signals for residual chloroform (7.26), acetone (2.05), pyridine (7.22) and methanol (3.31) in the deuterated solvents. All ^{13}C NMR spectra were reported in ppm relative to deuterated chloroform (77.16), acetone (29.84), pyridine (135.91) and methanol (49.00) and all were obtained with ^{1}H decoupling. Optimization studies were done by ^{1}H NMR and NMR yield were calculated by using tetrachloroethane as an internal standard.

2. Photocatalyzed benzylic C-H bond oxidation of N-aryl/alky tetrahydroisoquinolines



2.1. General procedure for the photocatalytic oxidation: To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 2-phenyl-1,2,3,4-tetrahydroisoquinoline (41.8 mg, 0.2 mmol), $Ru(bpy)_3Cl_2.6H_2O$ photocatalyst (3.0 mg, 0.002 mmol) were added. To this MeCN (1.0 mL, 0.2 M) and 1,8-diazabicyclo[5.4.0]undec-7-ene (29.9 µL, 0.2 mmol) were added. The reaction vial was closed with screw cap, purged with oxygen for one minute and kept

for stirring under 34W blue LED light at room temperature for 24 h. After completion, reaction mixture was diluted with ethyl acetate and purified by flash chromatography using silica gel (230-400 mesh size) as stationary phase and *n*-hexane: EtOAc as eluent.

2.2. Experimental setup

Experimental setup used for carrying out iridium photocatalyzed unsymmetrical coupling of 2-methylquinolines is shown in figure S1. Here we used two Kessil LED Photoredox Light PR160 470 nm for photo irradiation. Figure shows only one reaction vial under irradiation, however we used six reaction vials at a time under this setup at 0.2 mmol scale.

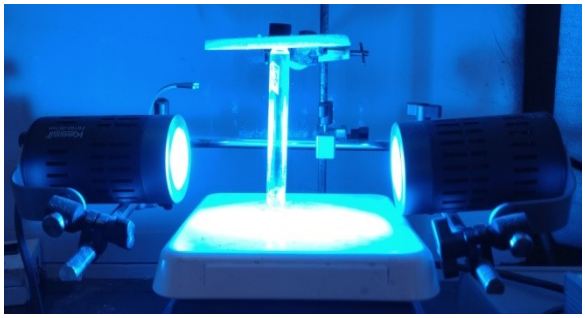


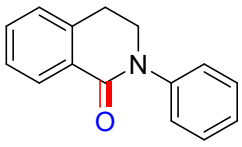
Figure S1: Experimental setup for 0.2 mmol scale reaction.

2.3. Table S1: Optimization study.

Entry	Catalyst (2.0 mol%)	Base (1.0 equiv.)	hv (LED light)	Solvent (0.05 M)	Time (hrs)	NMR Yield[b] (%)
1	$Ru(bpy)_3Cl_2.6H_2O$	DBU	Blue Light	MeOH	24	traces
2	$Ru(bpy)_3Cl_2.6H_2O$	DBU	Blue Light	DCM	24	54
3	$Ru(bpy)_3Cl_2.6H_2O$	DBU	Blue Light	1,4-Dioxane	24	22
4	$Ru(bpy)_3Cl_2.6H_2O$	DBU	Blue Light	$CHCl_3$	24	45
5	$Ru(bpy)_3Cl_2.6H_2O$	DBU	Blue Light	DCE	24	41
6	$Ru(bpy)_3Cl_2.6H_2O$	DBU	Blue Light	H_2O	24	traces
7	$Ru(bpy)_3Cl_2.6H_2O$	DBU	Blue Light	THF	24	78
8	$Ru(bpy)_3Cl_2.6H_2O$	DBU	Blue Light	DMSO	24	74
9	$Ru(bpy)_3Cl_2.6H_2O$	Na_2CO_3	Blue Light	ACN	24	18
10	$Ru(bpy)_3Cl_2.6H_2O$	NaOAc	Blue Light	ACN	24	26
11	$Ru(bpy)_3Cl_2.6H_2O$	DABCO	Blue Light	ACN	24	91
12	$Ru(bpy)_3Cl_2.6H_2O$	-	Blue Light	ACN	24	traces

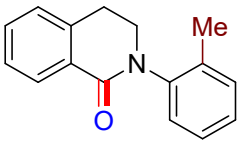
2.4. Characterization data

2-Phenyl-3,4-dihydroisoquinolin-1(2H)-one[1] (Table 2, entry **2a**), White solid (42.3 mg, 95%)



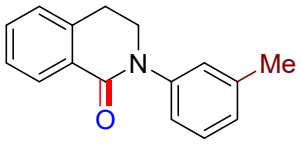
melting point: 94-95°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 7.8 Hz, 1H), 7.46-7.48 (m, 1H), 7.37-7.46 (m, 5H), 7.24-7.27 (m, 2H), 3.99-4.01 (m, 2H), 3.14-3.16 (m, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.3, 143.3, 138.4, 132.2, 129.9, 129.0, 128.9, 127.3, 127.1, 126.4, 125.5, 49.5, 28.8. HRMS (EI) m/z calculated for $C_{15}H_{14}NO$ $[M+H]^+$ 224.1070, found: 224.1075.

2-(o-Tolyl)-3,4-dihydroisoquinolin-1(2H)-one (Table 2, **2b**), Yellow liquid (35.2 mg, 74%), ^{1}H



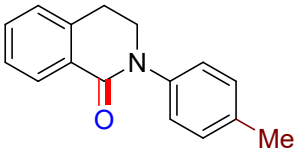
NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz, 1H), 7.46 (t, *J* = 7.2 Hz, 1H), 7.36-7.39 (m, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.22-7.25 (m, 2H), 7.17 (d, *J* = 7.8 Hz, 2H), 7.08 (d, *J* = 7.8 Hz, 1H), 3.97-3.99 (m, 2H), 3.14 (t, *J* = 6.6 Hz, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.4, 143.2, 138.9, 138.4, 132.1, 129.9, 128.9, 128.9, 127.3, 127.3, 127.1, 126.3, 122.4, 49.6, 28.8, 21.5. HRMS (EI) m/z calculated for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1226, found: 238.1216.

2-(m-Tolyl)-3,4-dihydroisoquinolin-1(2H)-one (Table 2, **2c**), Yellow Solid (40.8 mg, 86%),



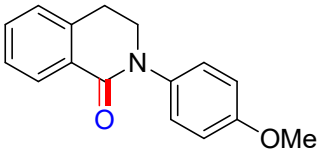
melting point: 96-98°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15-8.17 (m, 1H), 7.45-7.48 (m, 1H), 7.38 (td, *J* = 7.8, 1.2 Hz, 1H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.22-7.25 (m, 2H), 7.16-7.18 (m, 1H), 7.08 (d, *J* = 7.8 Hz, 1H), 3.96-3.98 (m, 2H), 3.13-3.15 (m, 2H), 2.38 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.3, 143.2, 138.9, 138.4, 132.1, 129.9, 128.9, 128.9, 127.29, 127.28, 127.0, 126.3, 49.6, 28.8, 21.5. HRMS (EI) m/z calculated for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1226, found: 238.1218.

2-(p-Tolyl)-3,4-dihydroisoquinolin-1(2H)-one[2] (Table 2, **2d**), Yellow Solid (44.1 mg, 93%)



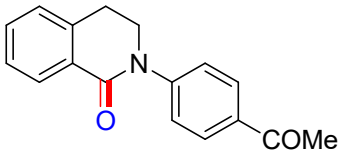
melting point: 84-84°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.2 Hz, 1H), 7.45 – 7.47 (m, 1H), 7.36 – 7.38 (m, 1H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.21 – 7.24 (m, 3H), 3.96 (t, *J* = 6.6 Hz, 2H), 3.12 – 3.14 (m, 2H), 2.37 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.3, 140.7, 138.4, 136.2, 132.0, 129.9, 129.7, 128.8, 127.3, 127.0, 125.3, 49.6, 28.8, 21.2. HRMS (EI) m/z calculated for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1226, found: 238.1211.

2-(4-Methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one[1] (Table 2, **2e**), Yellow solid (44.6 mg,

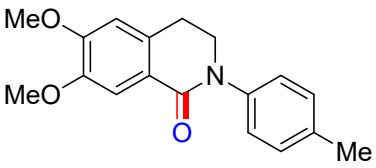


88%), melting point: 98-99°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.2 Hz, 1H), 7.44-7.47 (m, 1H), 7.36-7.38 (m, 1H), 7.28-7.31 (m, 2H), 7.23 (d, *J* = 7.2 Hz, 1H), 6.92-6.95 (m, 2H), 3.94 (t, *J* = 6.6 Hz, 2H), 3.82 (s, 3H), 3.13 (t, *J* = 6.6 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.5, 157.9, 138.4, 136.2, 132.0, 129.9, 128.8, 127.2, 127.0, 126.8, 114.3, 55.6, 49.8, 28.7. HRMS (EI) m/z calculated for $C_{16}H_{16}NO_2$ $[M+H]^+$ 254.1176, found 254.1177.

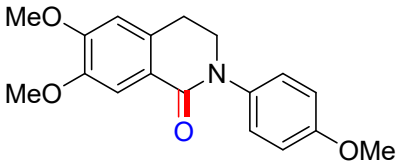
2-(4-Acetylphenyl)-3,4-dihydroisoquinolin-1(2H)-one[2] (Table 2, **2f**), White solid (46.0 mg, 87%), melting point: 156-157°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 7.98 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 9.0 Hz, 2H), 7.45-7.48 (m, 1H), 7.35-7.38 (m, 1H), 7.24 (d, *J* = 7.2 Hz, 1H), 4.00-4.02 (m, 2H), 3.14 (t, *J* = 6.6 Hz, 2H), 2.58 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 197.2, 164.1, 147.3, 138.3, 134.3, 132.5, 129.3, 129.1, 128.9, 127.3, 127.1, 124.6, 49.0, 28.5, 26.6. HRMS (EI) m/z calculated for $C_{17}H_{16}NO_2$ $[M+H]^+$ 266.1176, found: 266.1187.



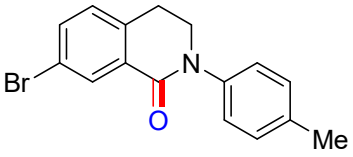
6,7-Dimethoxy-2-(p-tolyl)-3,4-dihydroisoquinolin-1(2H)-one[2] (Table 2, entry **2g**), Yellow solid (49.3 mg, 83%) melting point: 159-160°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.24 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 6.68 (s, 1H), 3.92 (d, *J* = 6.9 Hz, 8H), 3.04 (t, *J* = 6.5 Hz, 2H), 2.35 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.3, 152.1, 148.2, 140.8, 135.9, 132.2, 129.5, 125.3, 122.4, 111.0, 109.3, 56.2, 56.1, 49.8, 28.3, 21.1. HRMS (EI) m/z calculated for $C_{18}H_{20}NO_3$ $[M+H]^+$ 298.1438, found: 298.1440.



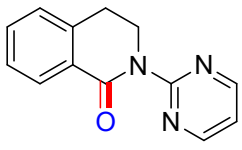
6,7-Dimethoxy-2-(4-methoxyphenyl)-3,4-dihydroisoquinolin-1(2H)-one[3] (Table 2, entry **2h**), Yellow solid (53 mg, 85%) melting point: 166-167°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (s, 1H), 7.25-7.28 (m, 2H), 6.91-6.93 (m, 2H), 6.68 (s, 1H), 3.90-3.93 (m, 8H), 3.81 (s, 3H), 3.05 (t, *J* = 6.6 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.5, 157.8, 152.1, 148.1, 136.4, 132.1, 126.7, 122.4, 114.3, 110.9, 109.3, 56.17, 56.16, 55.6, 50.0, 28.4. HRMS (EI) m/z calculated for $C_{18}H_{20}NO_4$ $[M+H]^+$ 314.1387, found: 314.1384.



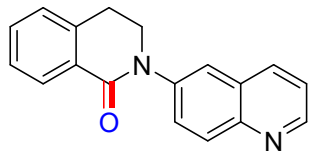
7-Bromo-2-(p-tolyl)-3,4-dihydroisoquinolin-1(2H)-one (Table 2, **2i**), White solid (52.3 mg, 83%) melting point: 108-109°C, ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (d, *J* = 1.8 Hz, 1H), 7.55-7.56 (m, 1H), 7.21-7.25 (m, 4H), 7.12 (d, *J* = 8.4 Hz, 1H), 3.93-3.95 (m, 2H), 3.06-3.08 (m, 2H), 2.36 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 163.0, 140.3, 137.2, 136.4, 134.8, 131.6, 131.6, 129.7, 128.8, 125.2, 121.0, 49.4, 28.2, 21.1. HRMS (EI) m/z **c**alculated for $C_{16}H_{15}BrNO$ $[M+H]^+$ 316.0332, found: 316.0315.



2-(Pyrimidin-2-yl)-3,4-dihydroisoquinolin-1(2H)-one (Table 2, **2j**), Yellow liquid (34.7 mg, 77%), ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.75 (d, *J* = 4.8 Hz, 2H), 8.25 (d, *J* = 7.8 Hz, 1H), 7.48 (td, *J* = 7.5, 1.1 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.11 (t, *J* = 4.8 Hz, 1H), 4.26 (m, 1H), 3.15 (t, *J* = 6.3 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.67, 160.98, 158.08, 139.24, 132.72, 129.54, 129.43, 127.28, 117.54, 46.92, 28.64. HRMS (EI) m/z calculated for $C_{13}H_{12}N_3O$ $[M+H]^+$ 226.0975, found: 226.0978.

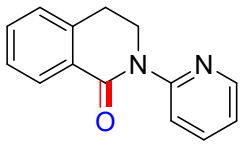


2-(Quinolin-6-yl)-3,4-dihydroisoquinolin-1(2H)-one (Table 2, **2k**), White solid (51 mg, 93%)



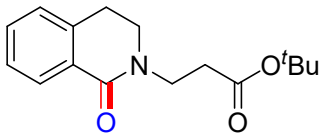
melting point: 145-146°C, ^{1}H NMR (600 MHz, Acetone-d_6) δ 8.88 (dd, J = 4.2, 1.8 Hz, 1H), 8.30 (dd, J = 8.4, 1.2 Hz, 1H), 8.08 (dd, J = 7.8, 1.2 Hz, 1H), 8.05 (d, J = 9.0 Hz, 1H), 7.94 (d, J = 2.4 Hz, 1H), 7.92 (dd, J = 9.0, 2.4 Hz, 1H), 7.53-7.55 (m, 1H), 7.50 (dd, J = 8.4, 4.2 Hz, 1H), 7.40-7.43 (m, 1H), 7.38 (d, J = 7.2 Hz, 1H), 4.19 (t, J = 6.6 Hz, 2H), 3.25 (t, J = 6.6 Hz, 2H). ^{13}C{^{1}H} NMR (151 MHz, Acetone-d_6) δ 164.5, 151.1, 147.4, 142.8, 140.2, 136.44, 133.0, 130.7, 130.1, 129.4, 129.3, 129.1, 128.2, 127.8, 123.1, 122.4, 50.2, 29.2. HRMS (EI) m/z calculated for $C_{18}H_{15}N_2O$ [M+H]$^+$ 275.1179, found: 275.1179.

2-(Pyridin-2-yl)-3,4-dihydroisoquinolin-1(2H)-one[1] (Table 2, entry **2l**), Yellow solid (40.8 mg, 91%)



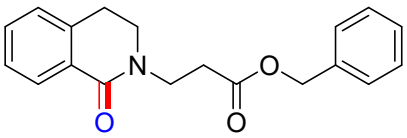
melting point: 62-63°C,^{1}H NMR (600 MHz, $CDCl_3$) δ 8.43-8.44 (m, 1H), 8.18 (d, J = 7.8 Hz, 1H), 8.01 (d, J = 8.4 Hz, 1H), 7.69-7.72 (m, 1H), 7.45-7.49 (m, 1H), 7.37 (t, J = 7.2 Hz, 1H), 7.24 (d, J = 7.2 Hz, 1H), 7.07-7.09 (m, 1H), 4.29 (t, J = 6.6 Hz, 1H), 3.10 (t, J = 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 164.8, 154.2, 147.7, 139.2, 137.0, 132.5, 129.8, 129.0, 127.2, 127.1, 120.3, 45.8, 28.6. HRMS (EI) m/z calculated for $C_{14}H_{13}N_2O$ [M+H]$^+$ 225.1022, found: 225.1004.

Tert-butyl 3-(1-oxo-3,4-dihydroisoquinolin-2(1H)-yl)propanoate (Table 2, entry **2m**), Colourless liquid (33.7 mg, 61%),



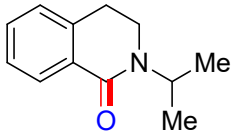
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04-8.05 (m, 1H), 7.38-7.41 (m, 1H), 7.30-7.33 (m, 1H), 7.15 (d, J = 7.2 Hz, 1H), 3.78 (t, J = 6.6 Hz, 2H), 3.62-3.64 (m, 2H), 2.96 (t, J = 6.6 Hz, 2H), 2.62 (t, J = 6.6 Hz, 2H), 1.42 (s, 9H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 171.6, 164.6, 138.3, 131.7, 129.6, 128.2, 127.1, 127.0, 80.9, 47.4, 44.4, 34.5, 28.4, 28.2. HRMS (EI) m/z calculated for $C_{16}H_{22}NO_3$ [M+H]$^+$ 276.1594, found: 276.1595.

Benzyl 3-(1-oxo-3,4-dihydroisoquinolin-2(1H)-yl)propanoate (Table 2, entry **2n**), Colourless liquid (52.5 mg, 85%),



^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04-8.06 (m, 1H), 7.37-7.41 (m, 1H), 7.29-7.33 (m, 6H), 7.14 (d, J = 7.8 Hz, 1H), 5.12 (s, 1H), 3.83 (t, J = 6.6 Hz, 1H), 3.57 (t, J = 6.6 Hz, 2H), 2.88 (t, J = 6.6 Hz, 2H), 2.78 (t, J = 6.6 Hz, 1H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 172.1, 164.7, 138.3, 135.8, 131.8, 129.4, 128.6, 128.41, 128.38, 128.2, 127.1, 127.0, 66.9, 47.5, 44.5, 33.3, 28.3. HRMS (EI) m/z calculated for $C_{19}H_{20}NO_3$ [M+H]$^+$ 310.1438, found: 310.1440.

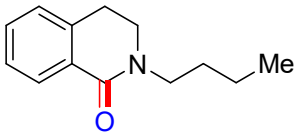
2-Isopropyl-3,4-dihydroisoquinolin-1(2H)-one[4] (Table 2, entry **2o**), Yellow resin (31 mg, 82%),



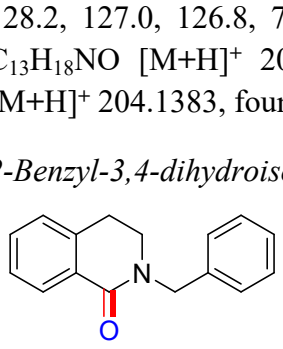
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, J = 7.8 Hz, 1H), 7.38 (td, J = 7.2, 1.2 Hz, 1H), 7.30-7.33 (m, 1H), 7.15 (d, J = 7.2 Hz, 1H), 5.05-5.12 (m, 1H), 3.42 (t, J = 6.6 Hz, 2H), 2.91-2.93 (m, 2H), 1.19 (s, 3H), 1.18 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 163.8, 137.8, 131.4, 130.1, 128.4,

127.0, 126.7, 43.7, 38.8, 28.5, 19.8. HRMS (EI) m/z calculated for $C_{12}H_{16}NO$ $[M+H]^+$ 190.1226, found: 190.1221.

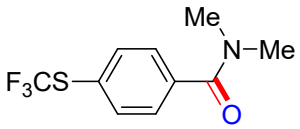
2-Butyl-3,4-dihydroisoquinolin-1(2H)-one[5] (Table 2, entry **2p**), Yellow liquid (40 mg, 91%), ^1H NMR (600 MHz, $CDCl_3$) δ 8.04-8.06 (m, 1H), 7.37 (td, J = 7.2, 1.2 Hz, 1H), 7.28-7.31 (m, 1H), 7.13 (d, J = 7.2 Hz, 1H), 3.50-3.55 (m, 4H), 2.93-2.96 (m, 2H), 1.56-1.61 (m, 2H), 1.33-1.39 (m, 2H), 0.92-0.94 (m, 3H).$^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 164.3, 138.0, 131.4, 129.8, 128.2, 127.0, 126.8, 77.2, 47.2, 46.1, 29.9, 28.2, 20.2, 13.9. HRMS (EI) m/z calculated for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1383, found: 204.1386. HRMS (EI) m/z calculated for $C_{13}H_{18}NO$ $[M+H]^+$ 204.1383, found: 204.1386.



2-Benzyl-3,4-dihydroisoquinolin-1(2H)-one[1] (Table 2, entry **2q**), Yellow resin (40.8 mg, 86%), ^1H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 7.8 Hz, 1H), 7.39-7.42 (m, 1H), 7.31-7.36 (m, 5H), 7.27 (t, J = 7.2 Hz, 1H), 7.15 (d, J = 7.8 Hz, 1H), 4.80 (s, 2H), 3.46-3.48 (m, 2H), 2.91-2.93 (m, 2H). $^{13}C\{^1H\}$ NMR (151 MHz, $CDCl_3$) δ 164.6, 138.1, 137.5, 131.7, 129.4, 128.6, 128.4, 128.0, 127.4, 127.0, 126.9, 50.4, 45.4, 28.1. HRMS (EI) m/z calculated for $C_{16}H_{16}NO$ $[M+H]^+$ 238.1226, found: 238.1210.



N,N-dimethyl-4-((trifluoromethyl)thio)benzamide (Table 2, entry **2r**) Colourless resin (26.8 mg, 54% yield),1H NMR (600 MHz, CDCl3) δ 7.69 (d, J = 7.8 Hz, 2H), 7.46 (d, J = 7.8 Hz, 2H), 3.12 (s, 3H), 2.97 (s, 3H). 13C{1H} NMR (151 MHz, $CDCl_3$) δ 170.4, 138.9, 136.3, 130.6, 128.5, 128.2, 128.0, 126.0, 124.8, 39.6, 35.5. HRMS (EI) m/z calculated for $C_{10}H_{11}F_3NOS$ $[M+H]^+$ 250.0508, found: 250.0496.



3. Mechanistic Study

3.1 Radical Quenching Experiments

To three oven-dried screw cap reaction vials charged with a spin vane magnetic stir-bar, 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol), $Ru(bpy)_3Cl_2.6H_2O$ photocatalyst (1.5 mg, 0.002 mmol) were added. To this MeCN (0.5 mL, 0.2 M) and 1,8-diazabicyclo[5.4.0]undec-7-ene (14.9 µL, 0.1 mmol) were added. After this, TEMPO (2, 2, 6, 6-tetramethylpiperidine N-oxide), BHT (bultylated hydroxytoluene) and benzoquinone (2.0 equivalents of each) were added to these reaction vials separately. The reaction vial was closed with screw cap, purged with oxygen for one minute and kept for stirring under 34W blue LED light at room temperature for 24 h. After completion, the reactions were dried over rotary evaporator and crude reactions were analyzed with the help of NMR using tetrachloroethane as an internal standard.

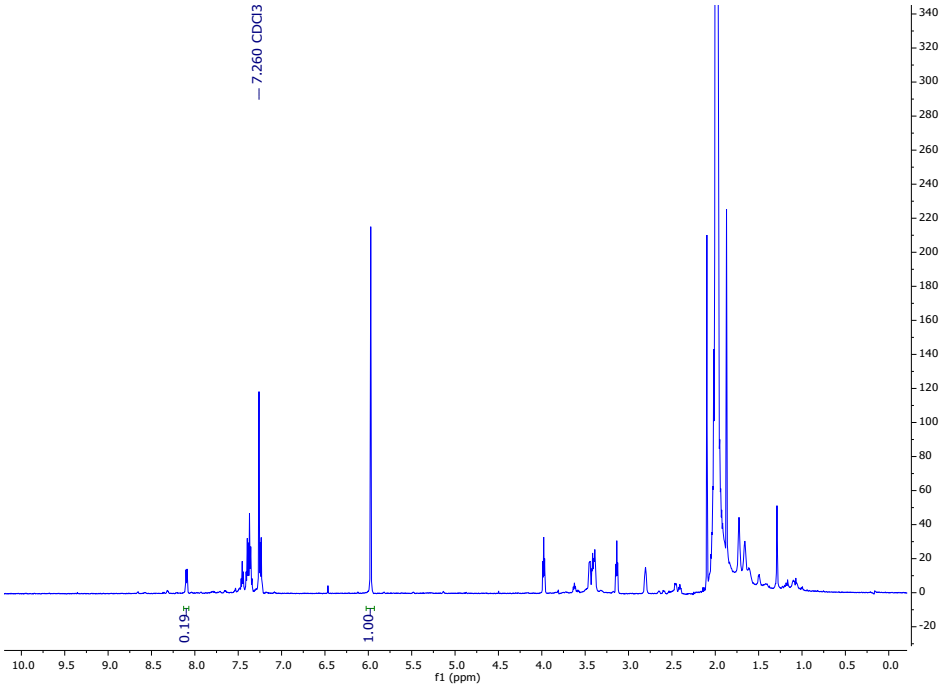


Figure S2. Radical quenching experiment with TEMPO (2,2,6,6-tetramethylpiperidine *N*-oxide)

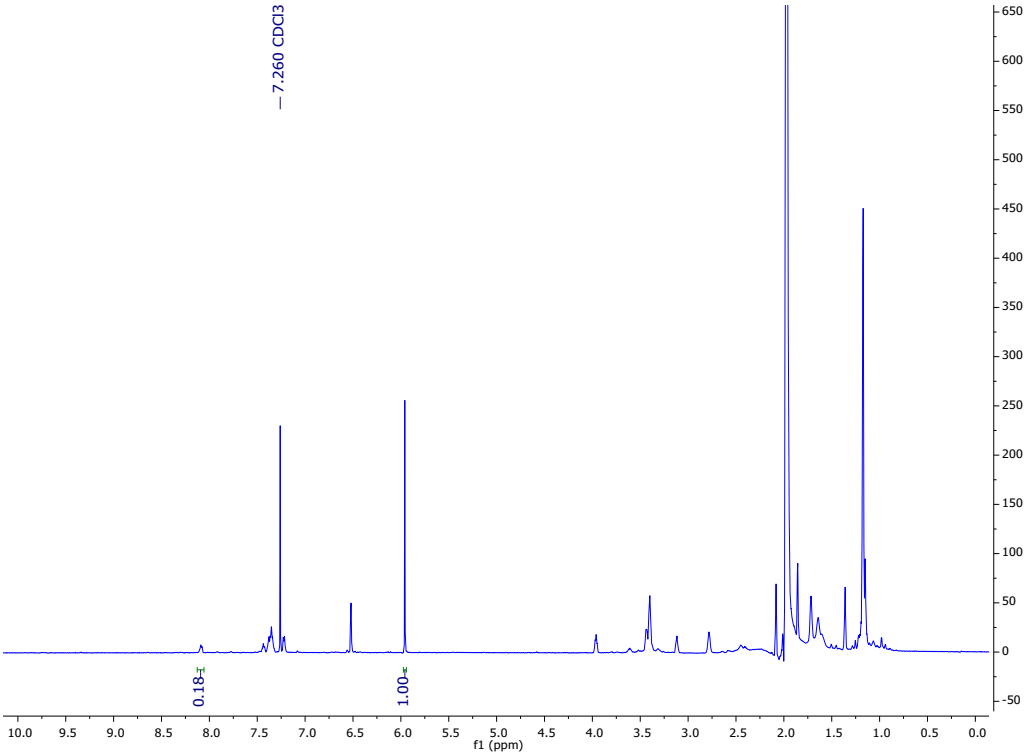


Figure S3. Radical quenching experiment with BHT (butylated hydroxy toluene)

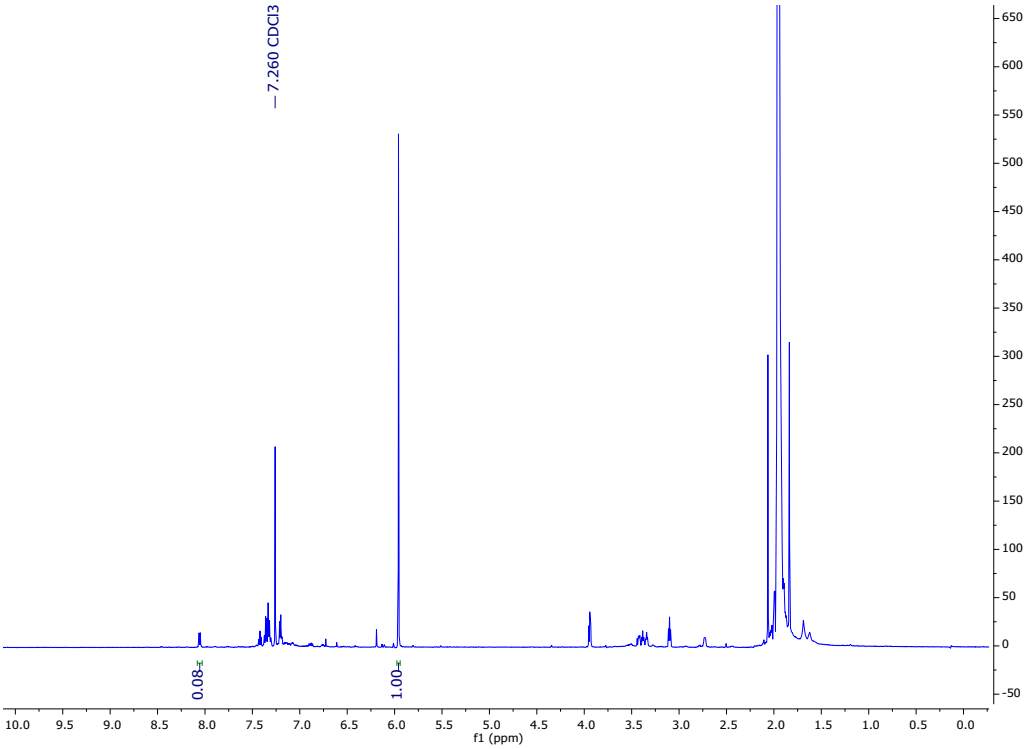


Figure S4. Radical quenching experiment with benzoquinone

3.2 ^{18}O-Labelling Experiment

To an oven-dried screw cap reaction vial charged with a spin vane magnetic stir-bar, 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol), $Ru(bpy)_3Cl_2.6H_2O$ photocatalyst (1.5 mg, 0.002 mmol) were added. To this MeCN (0.5 mL, 0.2 M) and 1,8-diazabicyclo[5.4.0]undec-7-ene (14.9 µL, 0.1 mmol) were added. The reaction vial was closed with screw cap, purged with ^{18}O-oxygen three times using freeze-thaw technique and kept for stirring under 34W blue LED light at room temperature for 24 h. After completion, the crude reaction was analyzed with the LC-MS.

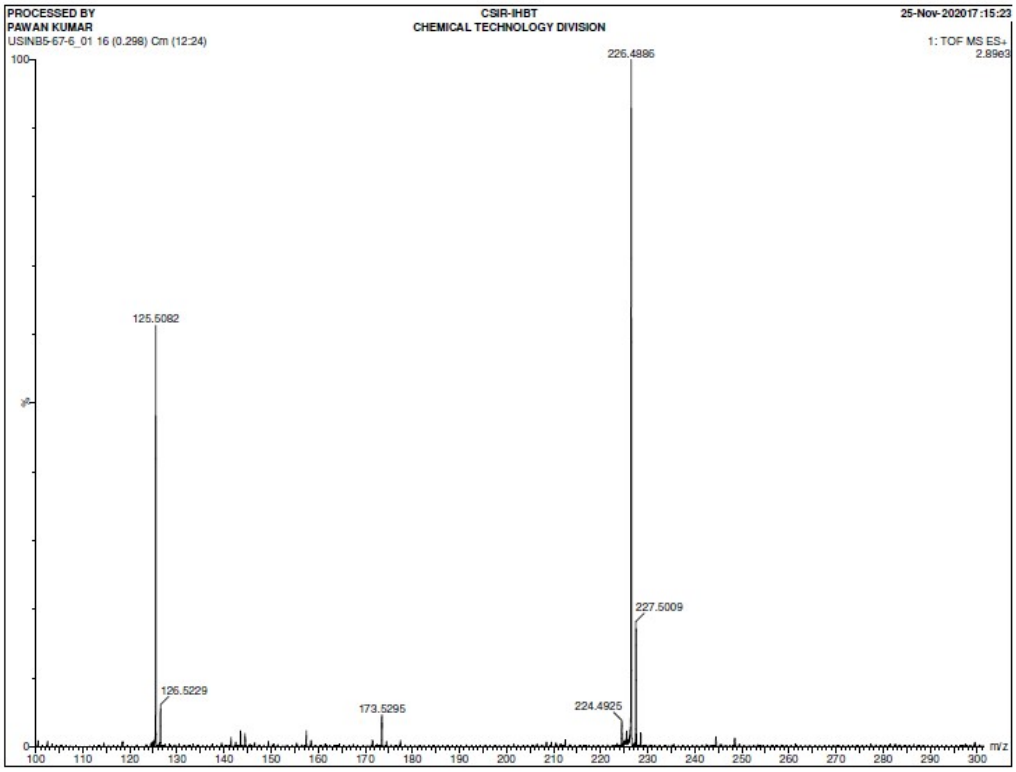


Figure S5. LC-MS chromatogram of crude reaction performed under labeled oxygen i.e. $^{18}O_2$.

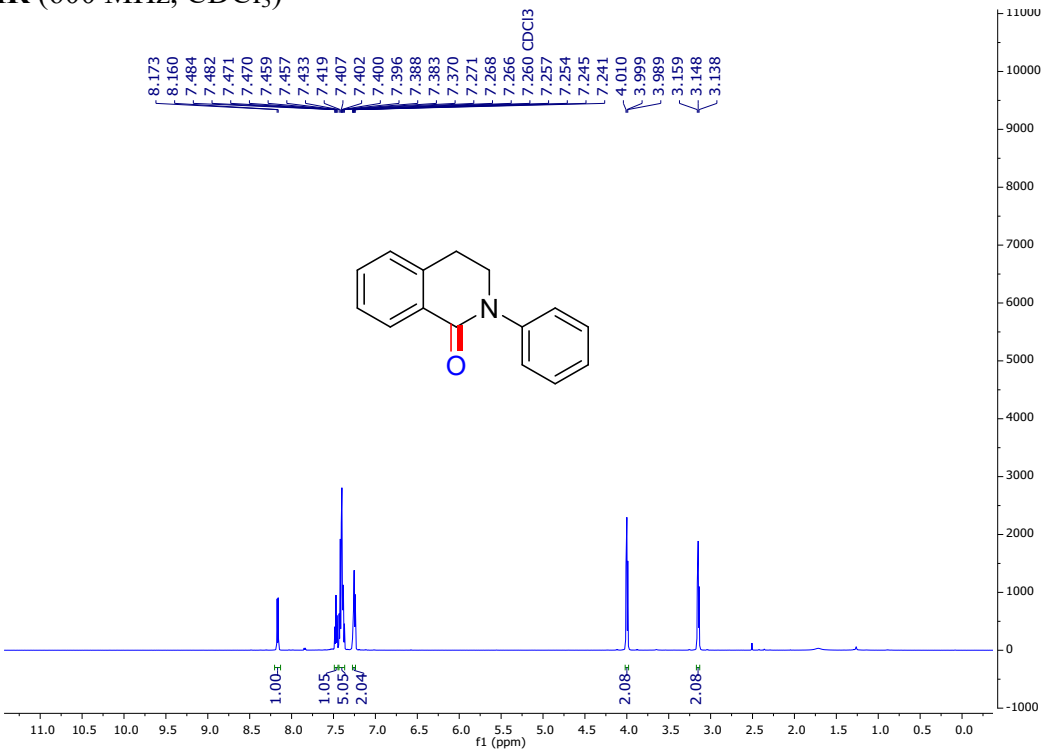
3.3 Light On-Off Experiments.

To four oven-dried screw cap reaction vials charged with a spin vane magnetic stir-bar, 2-phenyl-1,2,3,4-tetrahydroisoquinoline (20.9 mg, 0.1 mmol), $Ru(bpy)_3Cl_2.6H_2O$ photocatalyst (1.5 mg, 0.002 mmol) were added. To this MeCN (0.5 mL, 0.2 M) and 1,8-diazabicyclo[5.4.0]undec-7-ene (14.9 µL, 0.1 mmol) were added. The reaction vials were closed with screw cap, purged with oxygen for one minute and kept for stirring under 34W blue LED light. Firstly the reactions were irradiated for two hours, LED light was turned off, and NMR yield of one reaction was calculated. Second reaction was analyzed after four hours and light was turned on. Again light was turned off after six hours and third reaction was analyzed with NMR. Fourth raction was analyzed after eight hours.

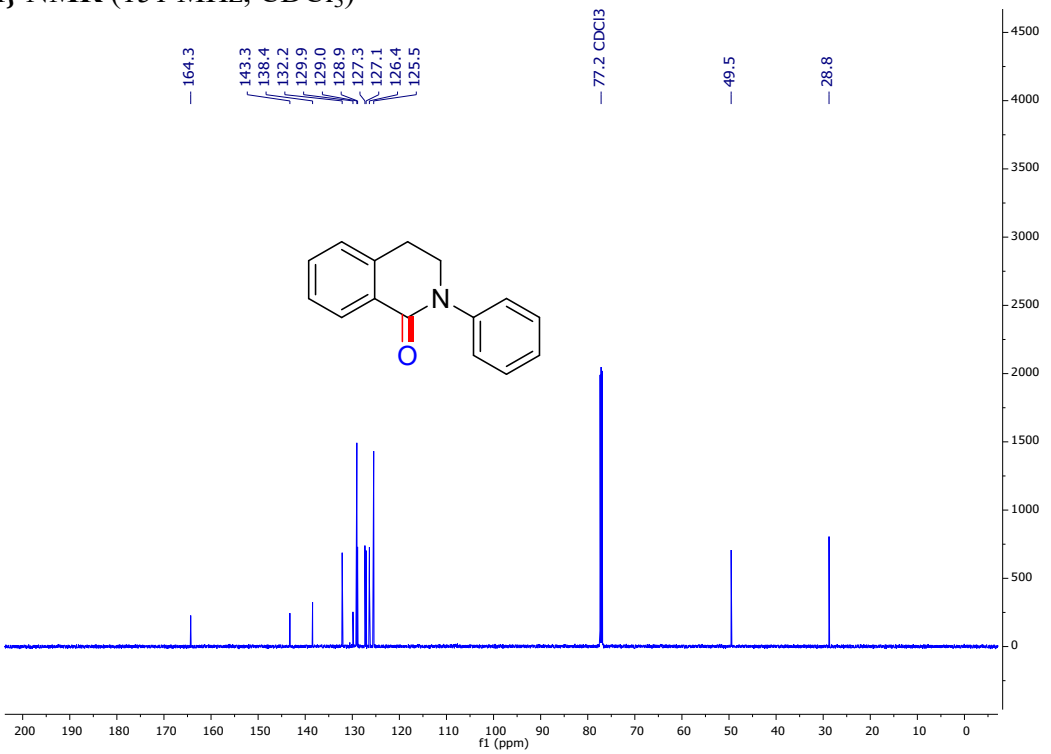
4. NMR Spectra of synthesized compounds

*3,4-Dihydroisoquinolin-1(2H)-one (Table 2, entry **2a**)*

^{1}H NMR (600 MHz, $CDCl_3$)

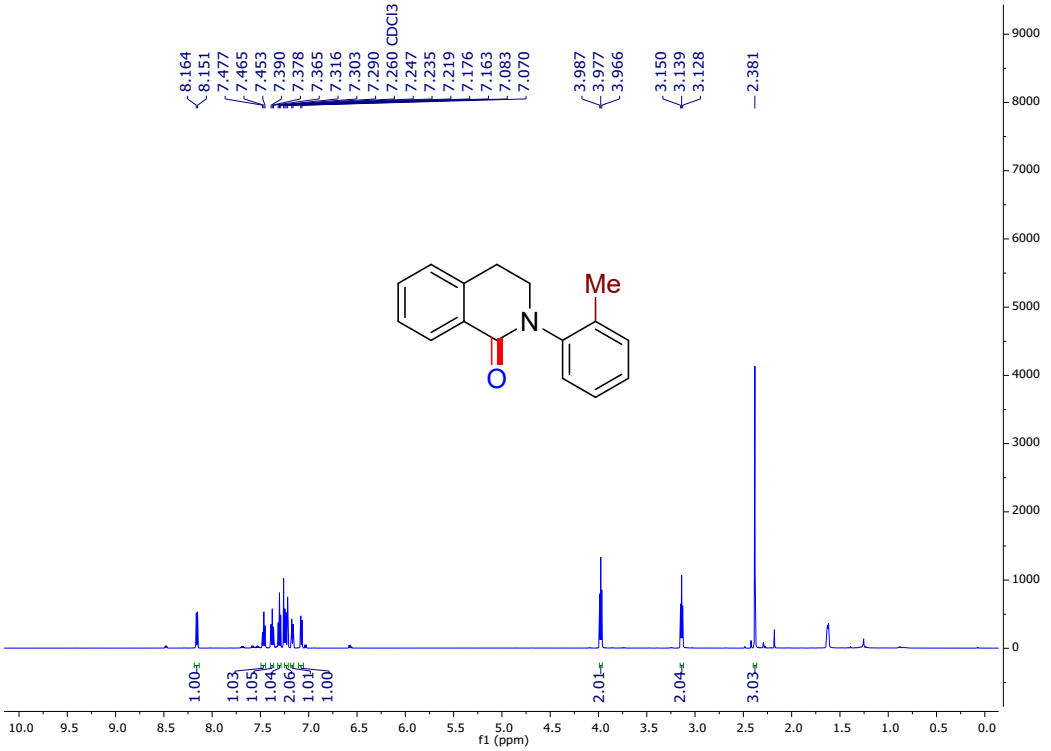


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

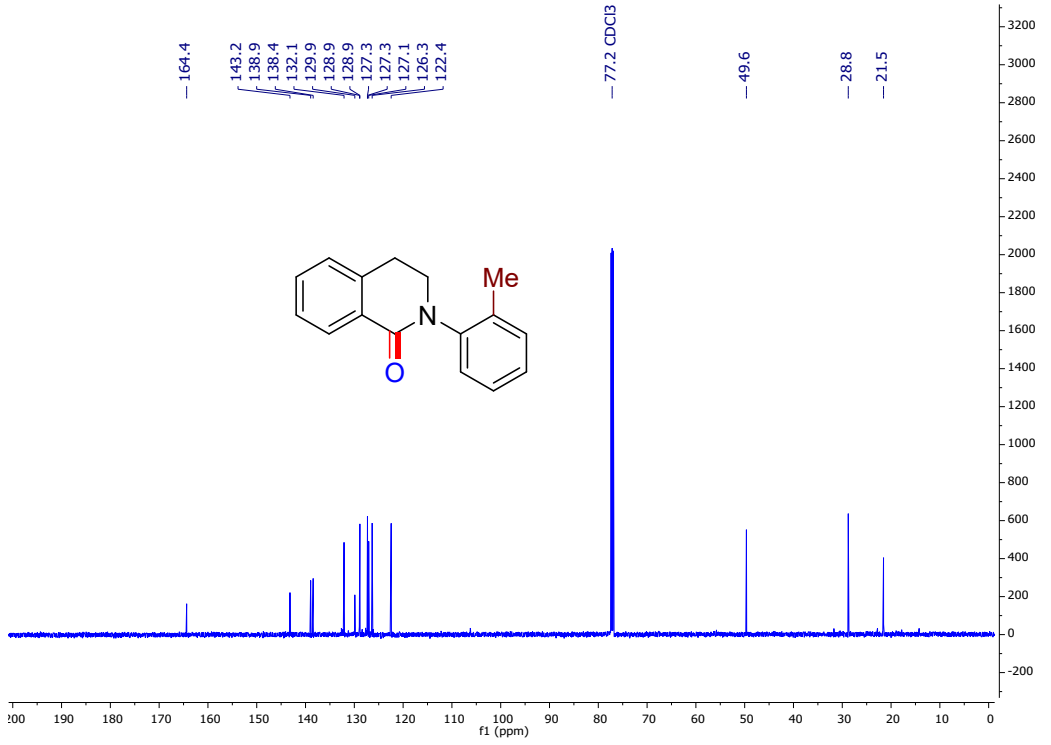


2-(o-Tolyl)-3,4-dihydroisoquinolin-1(2H)-one (Table 2, **2b**)

^{1}H NMR (600 MHz, $CDCl_3$)

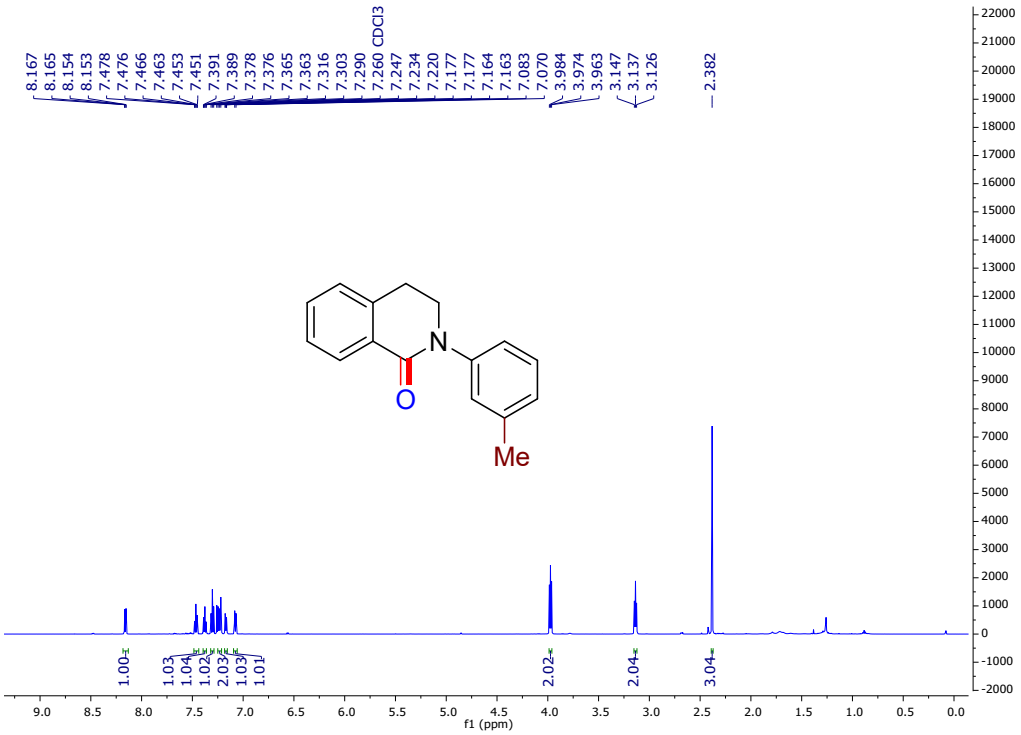


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

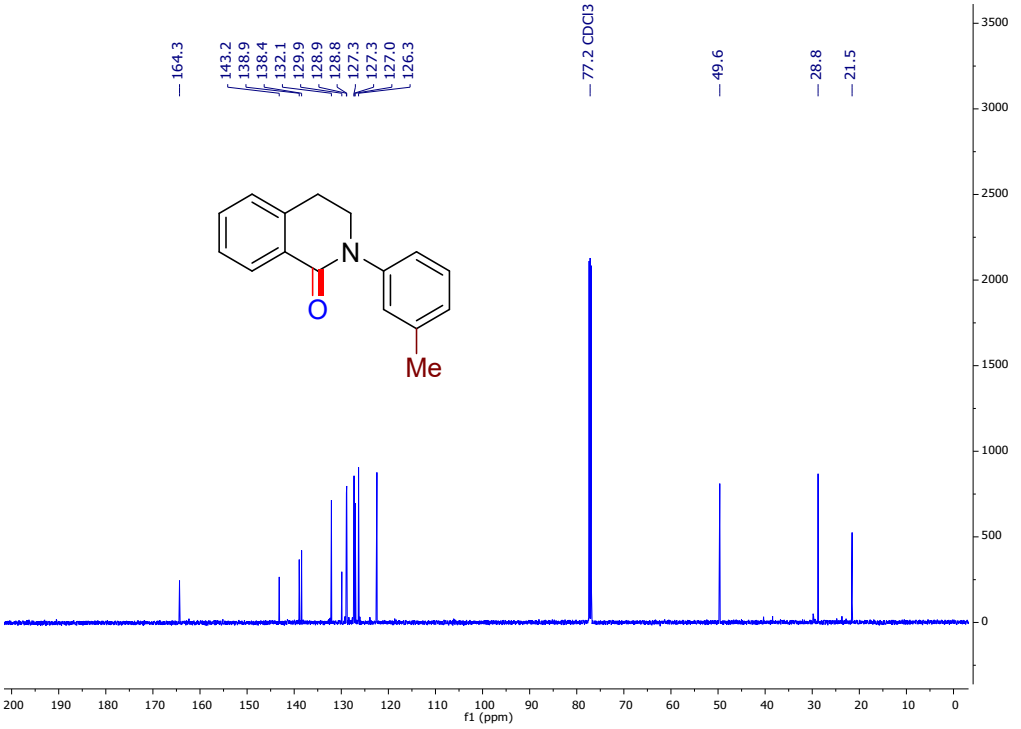


*2-(m-Tolyl)-3,4-dihydroisoquinolin-1(2H)-one (Table 2, **2c**)*

^{1}H NMR (600 MHz, $CDCl_3$)

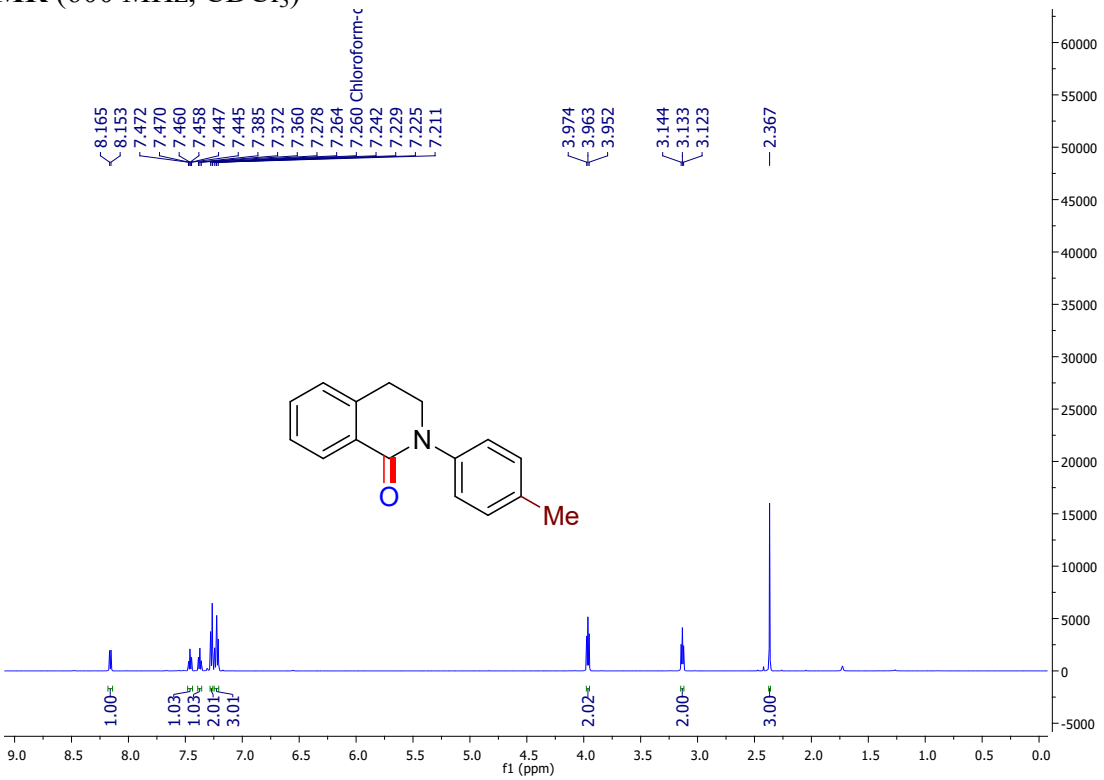


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

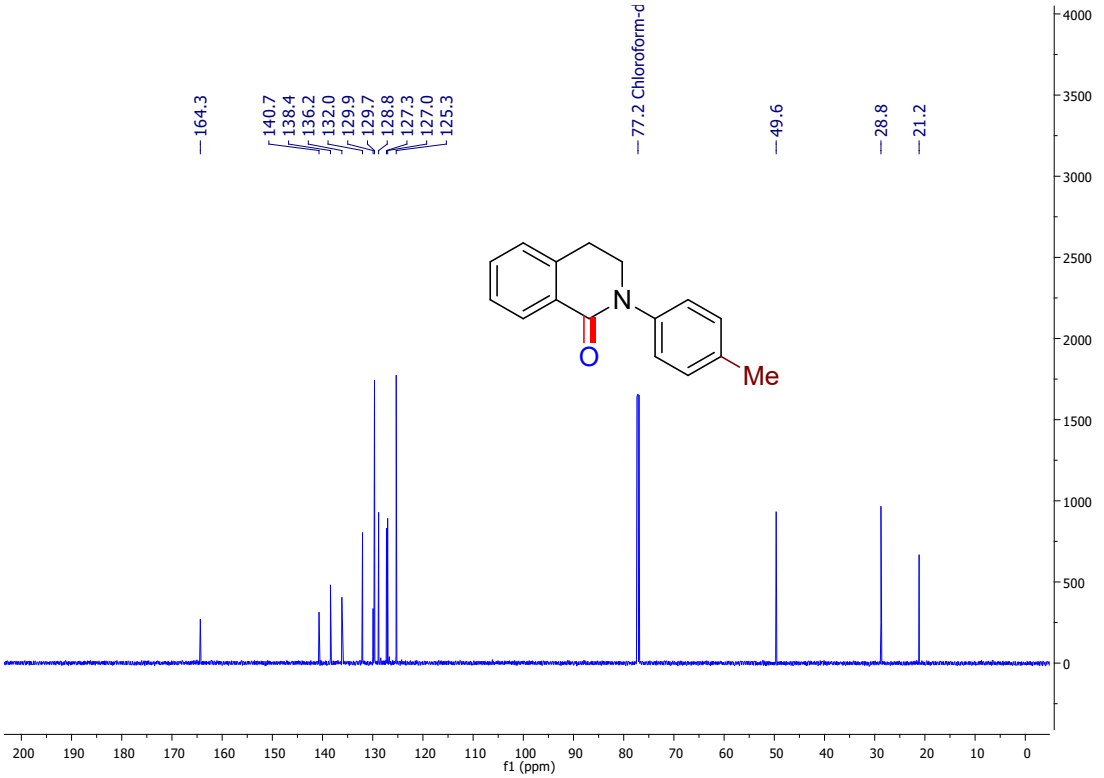


*2)-p-tolyl-(3,4-dihydroisoquinolin-1)2H-(one) (Table 2, entry **2d**)*

^{1}H NMR (600 MHz, $CDCl_3$)

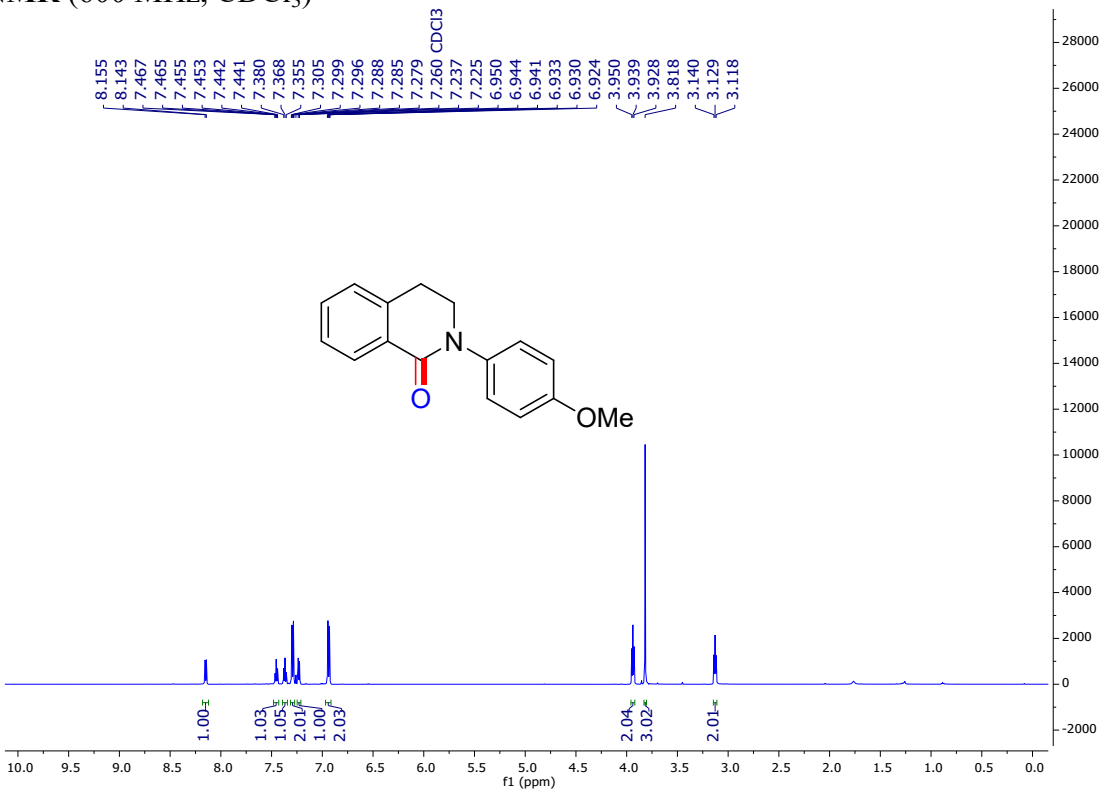


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

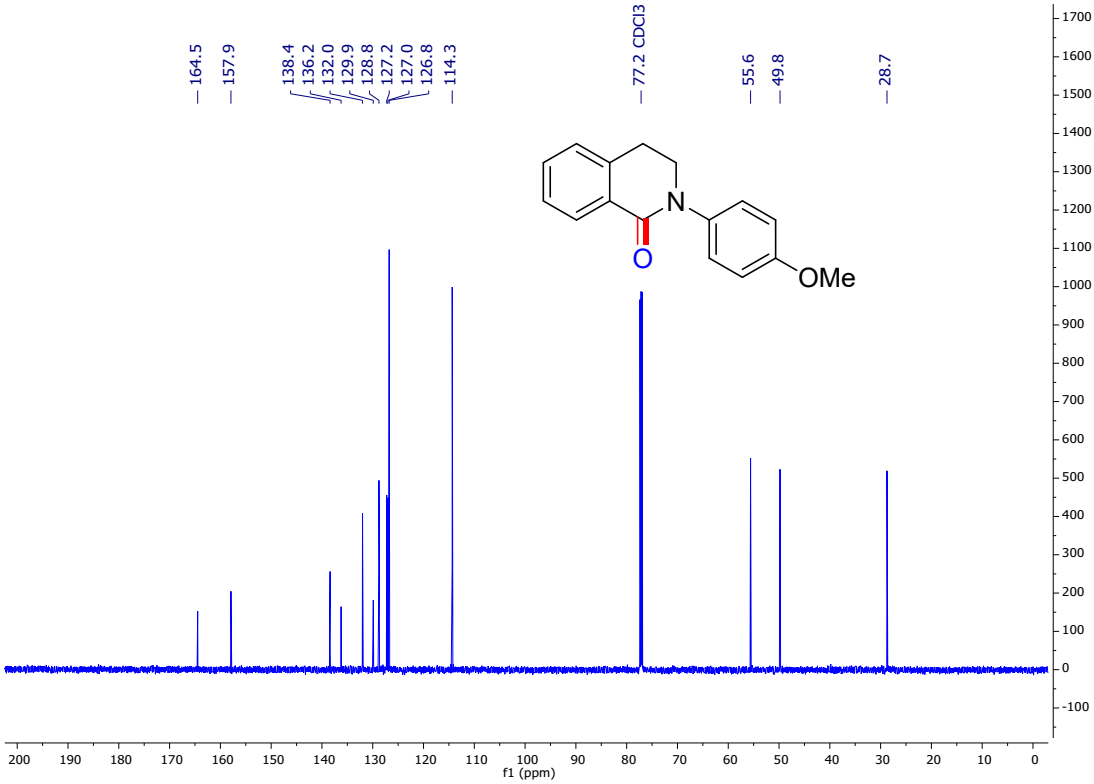


*2)-4-methoxyphenyl-(3,4-dihydroisoquinolin-1)2H-(one) (Table 2, entry **2e**)*

^{1}H NMR (600 MHz, $CDCl_3$)

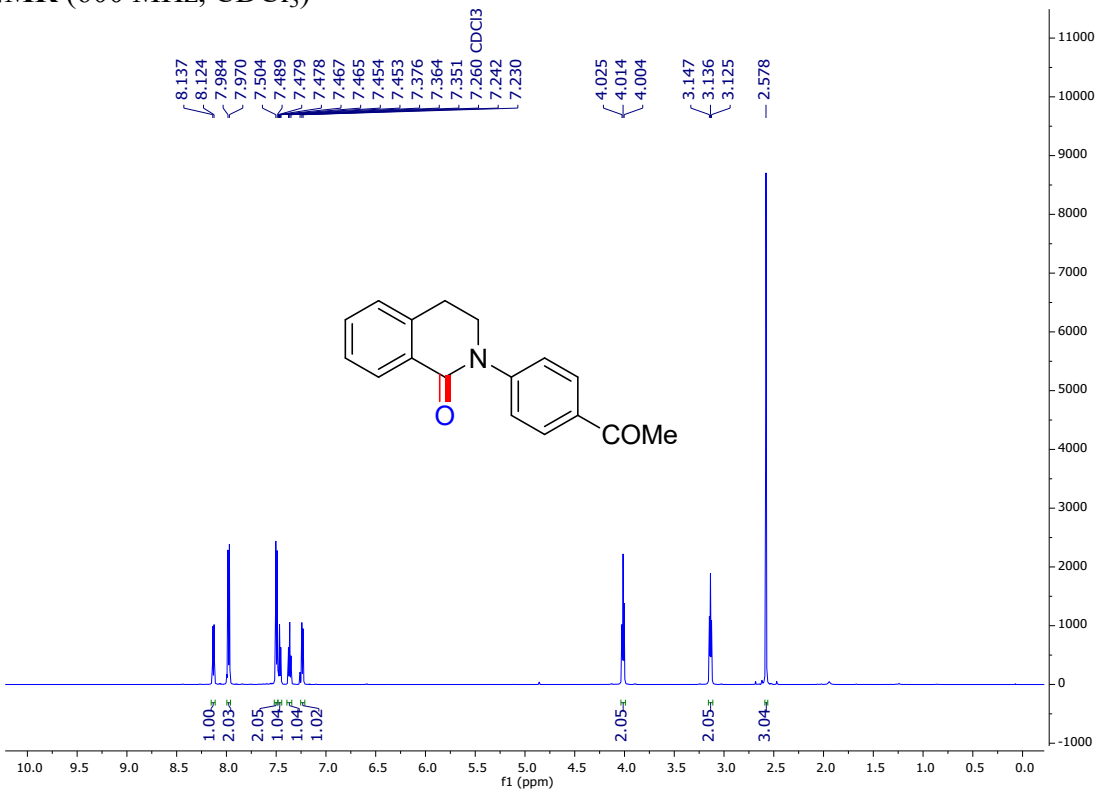


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

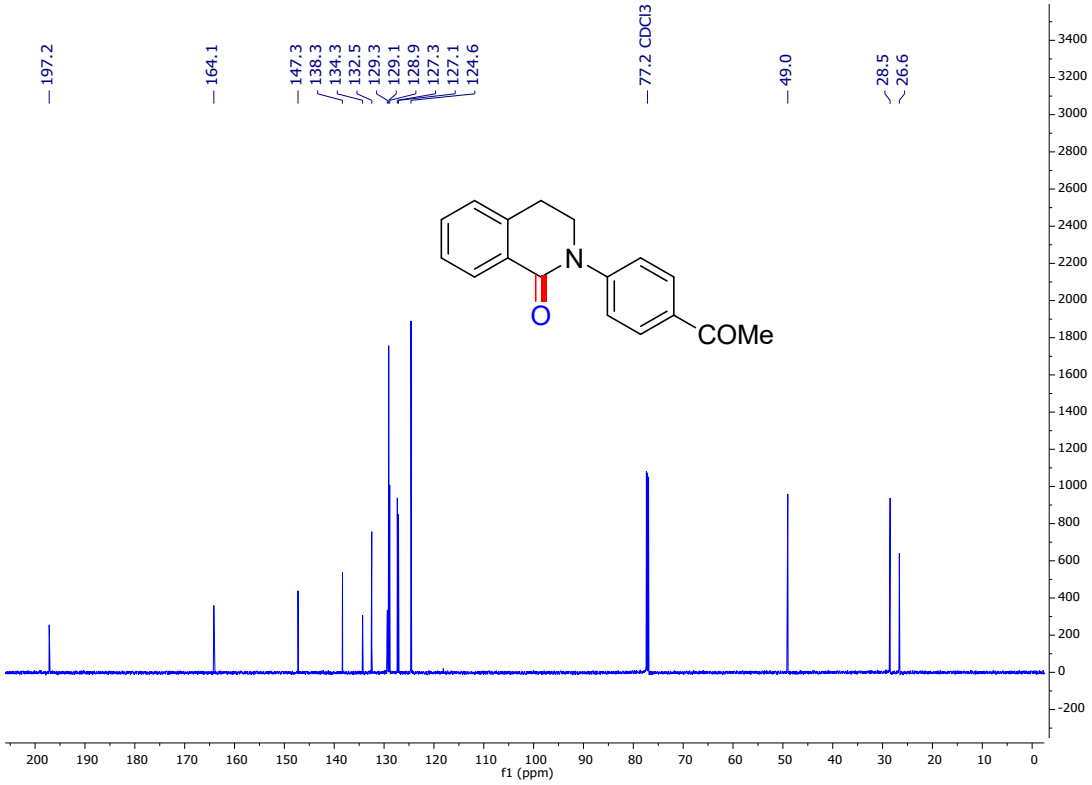


*2)-4-acetylphenyl-(3,4-dihydroisoquinolin-1)2H-(one) (Table 2, entry **2f**)*

^{1}H NMR (600 MHz, $CDCl_3$)

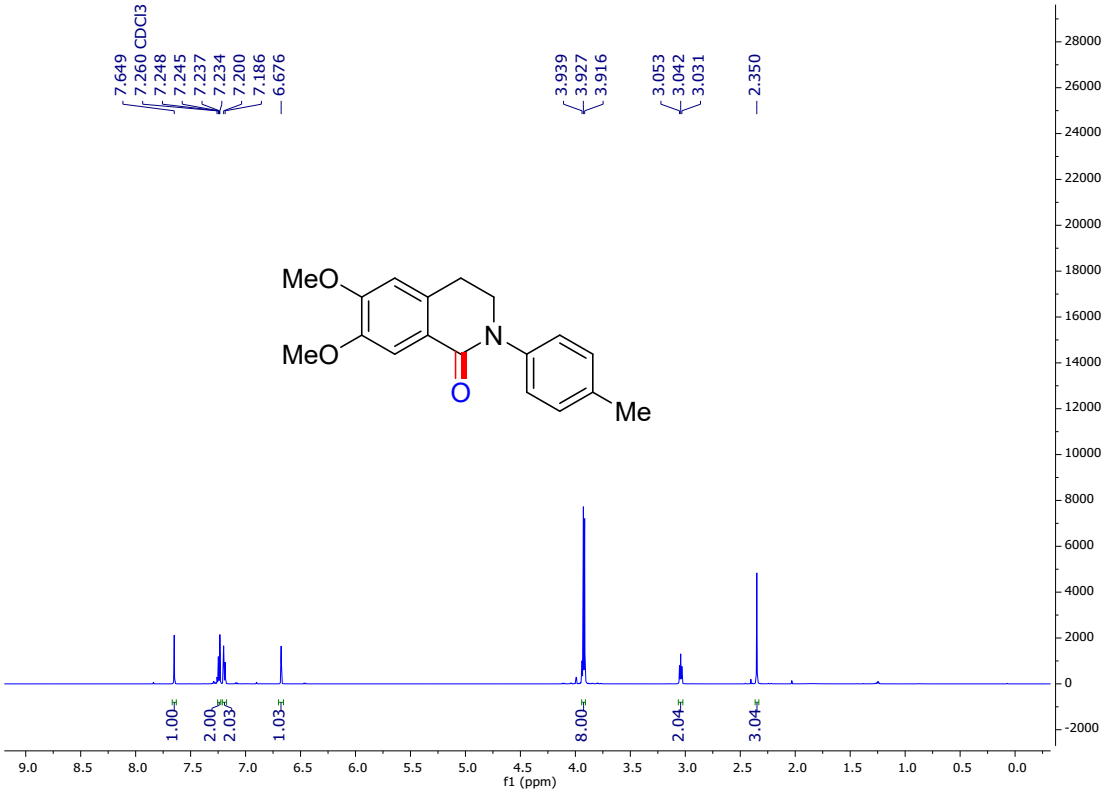


^{13}C{^{1}H} NMR) (151 MHz, $CDCl_3$)

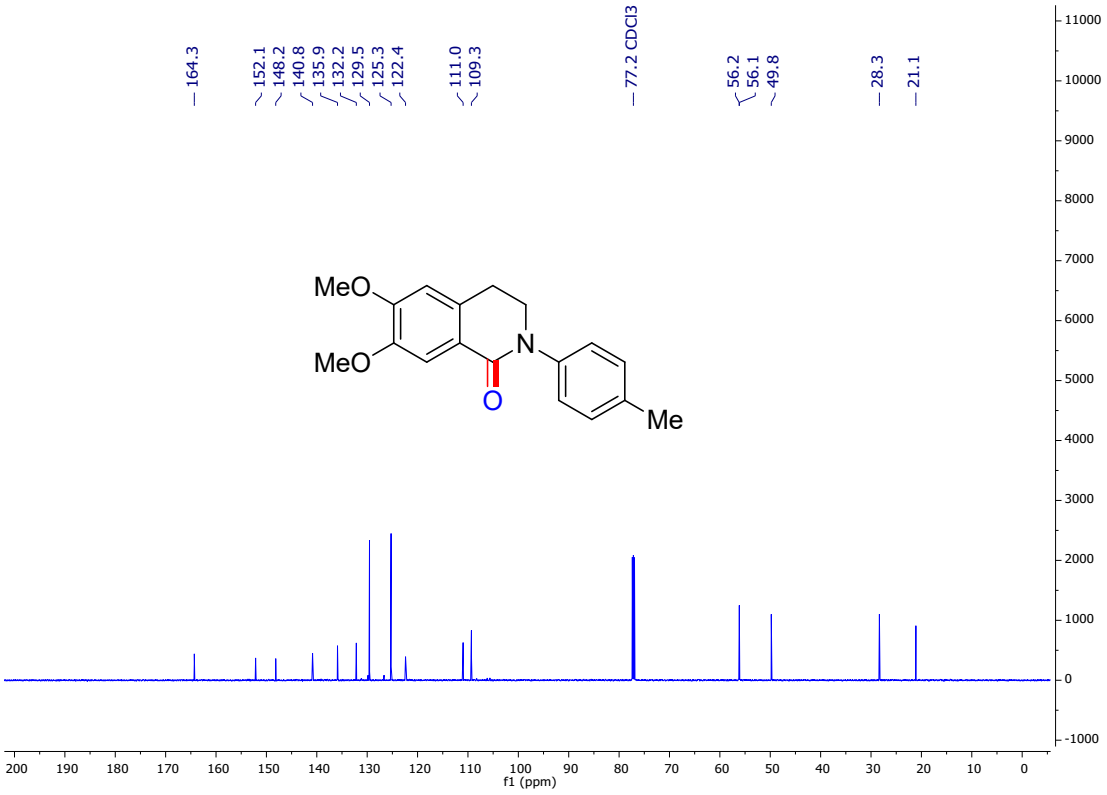


*6,7-dimethoxy-2)-p-tolyl-(3,4-dihydroisoquinolin-1)2H-(one) (Table 2, entry **2g**)*

^{1}H NMR (600 MHz, $CDCl_3$)

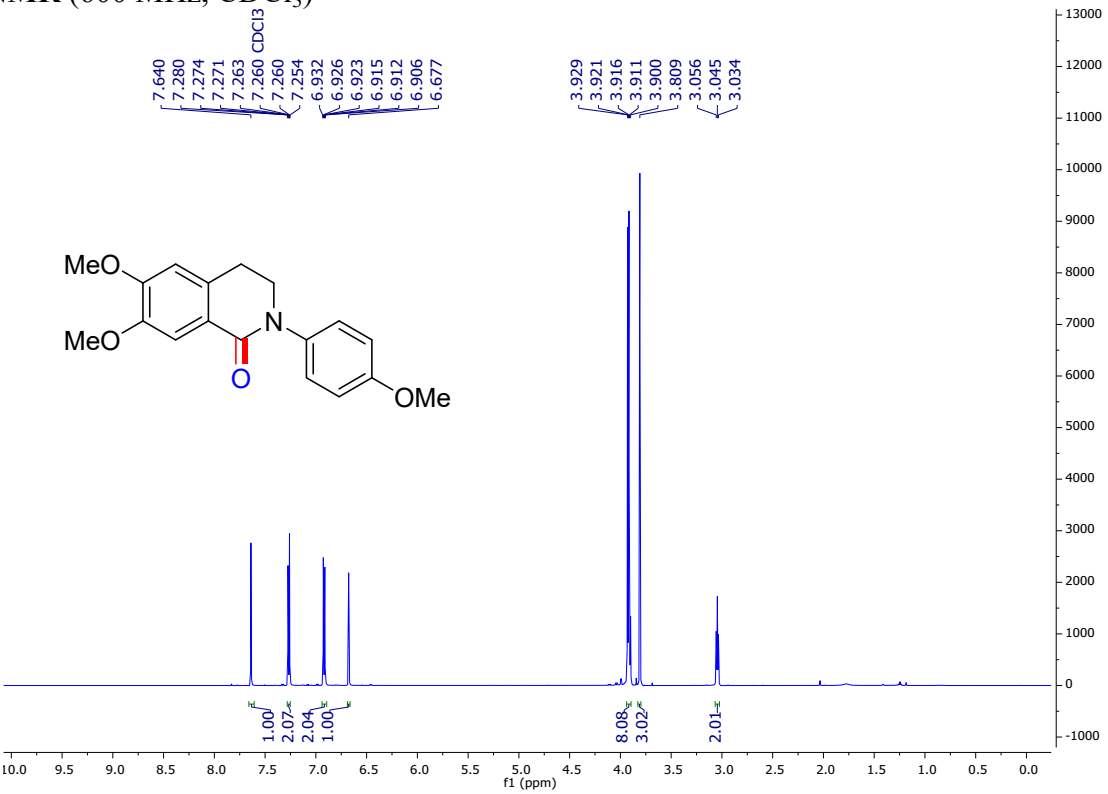


^{13}C{^{1}H} NMR) (151 MHz, $CDCl_3$)

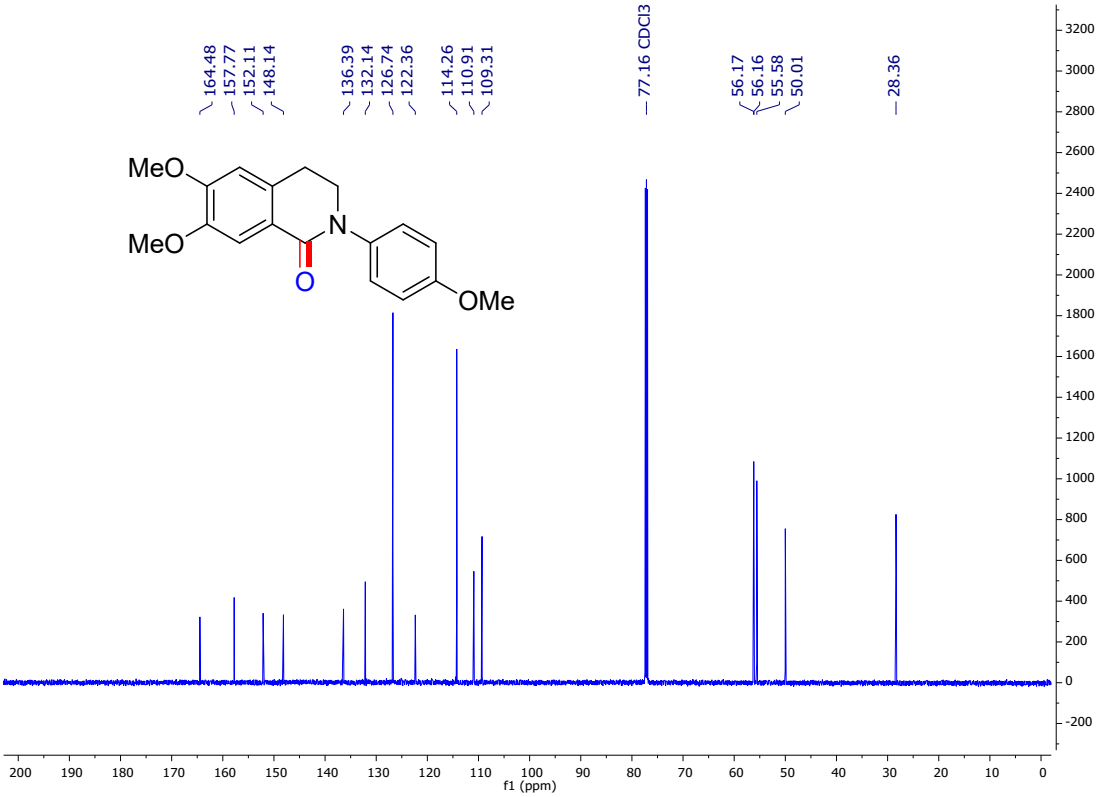


6,7-dimethoxy-2)-4-methoxyphenyl-(3,4-dihydroisoquinolin-1)2H-(one *)(Table 2, entry **2h**)*

^{1}H NMR (600 MHz, $CDCl_3$)

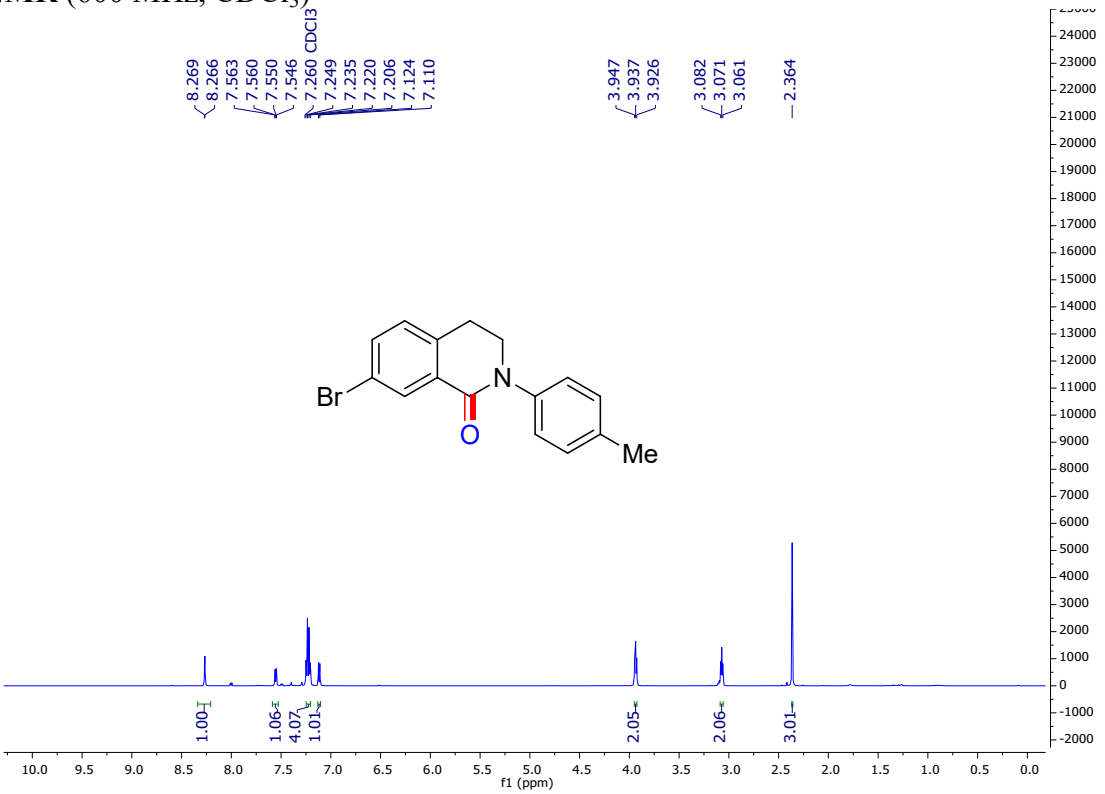


^{13}C{^{1}H} NMR) (151 MHz, $CDCl_3$)

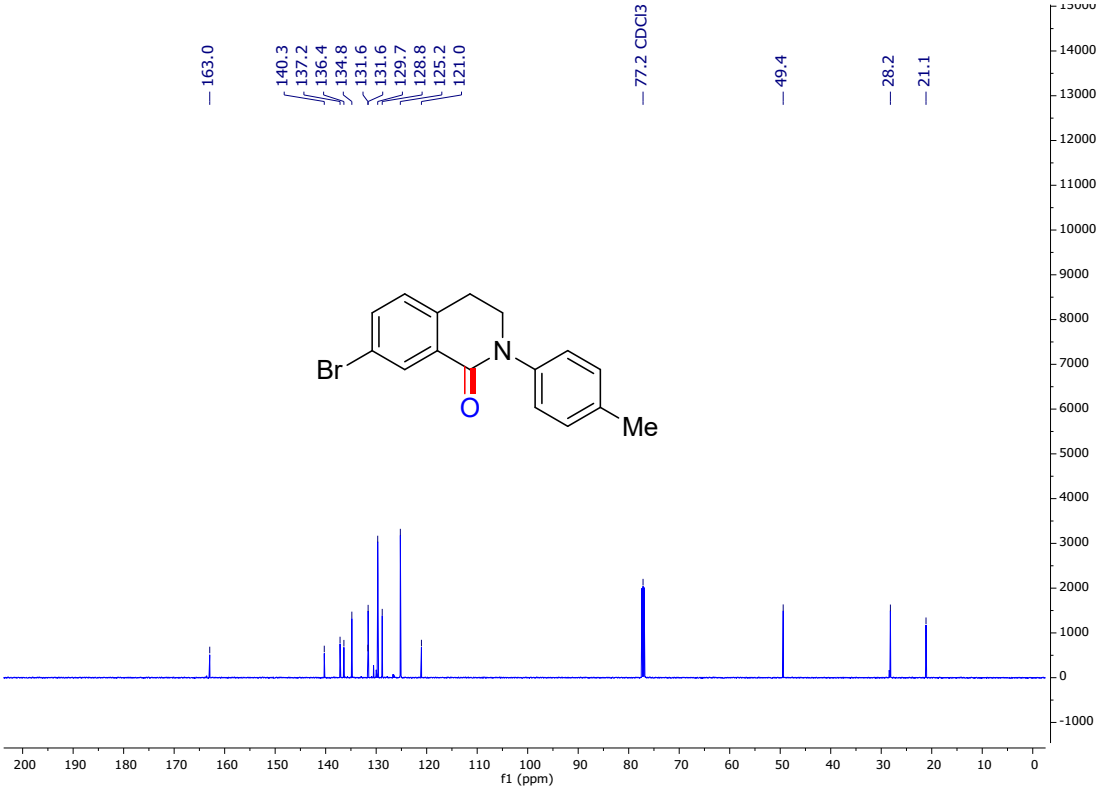


*7-bromo-2)-p-tolyl-(3,4-dihydroisoquinolin-1)2H-(one) (Table 2, entry **2i**)*

^{1}H NMR (600 MHz, $CDCl_3$)

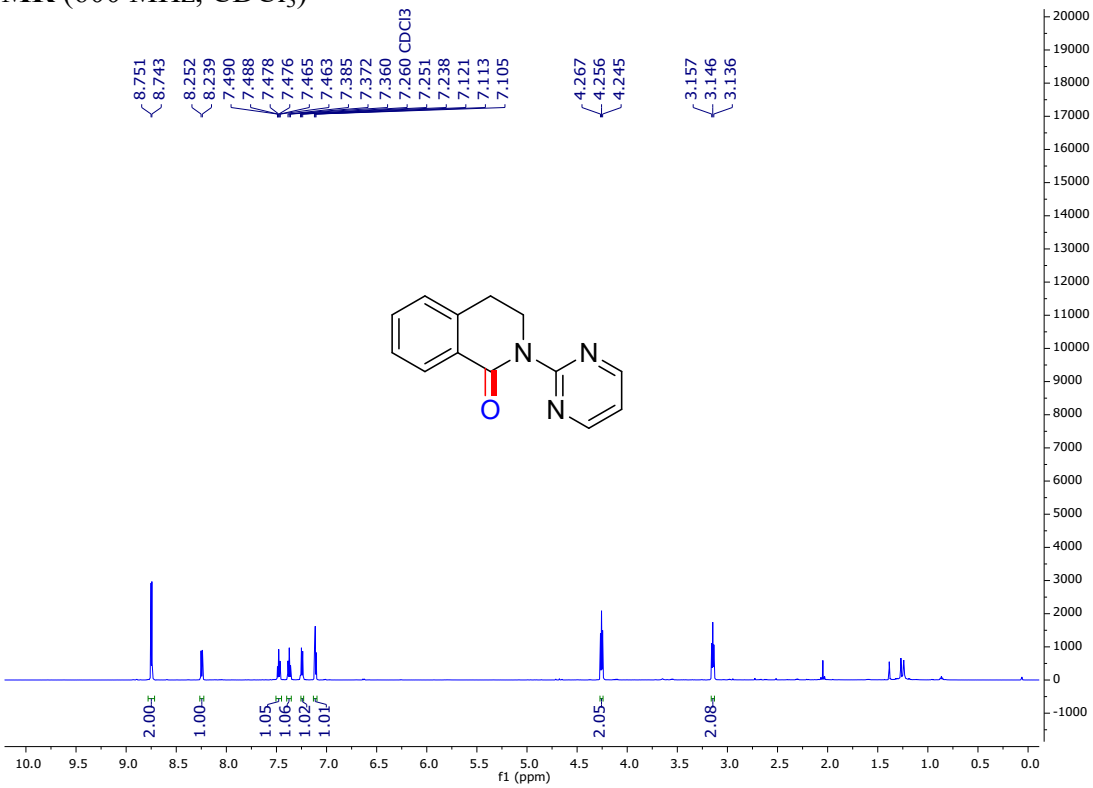


^{13}C{^{1}H} NMR) (151 MHz, $CDCl_3$)

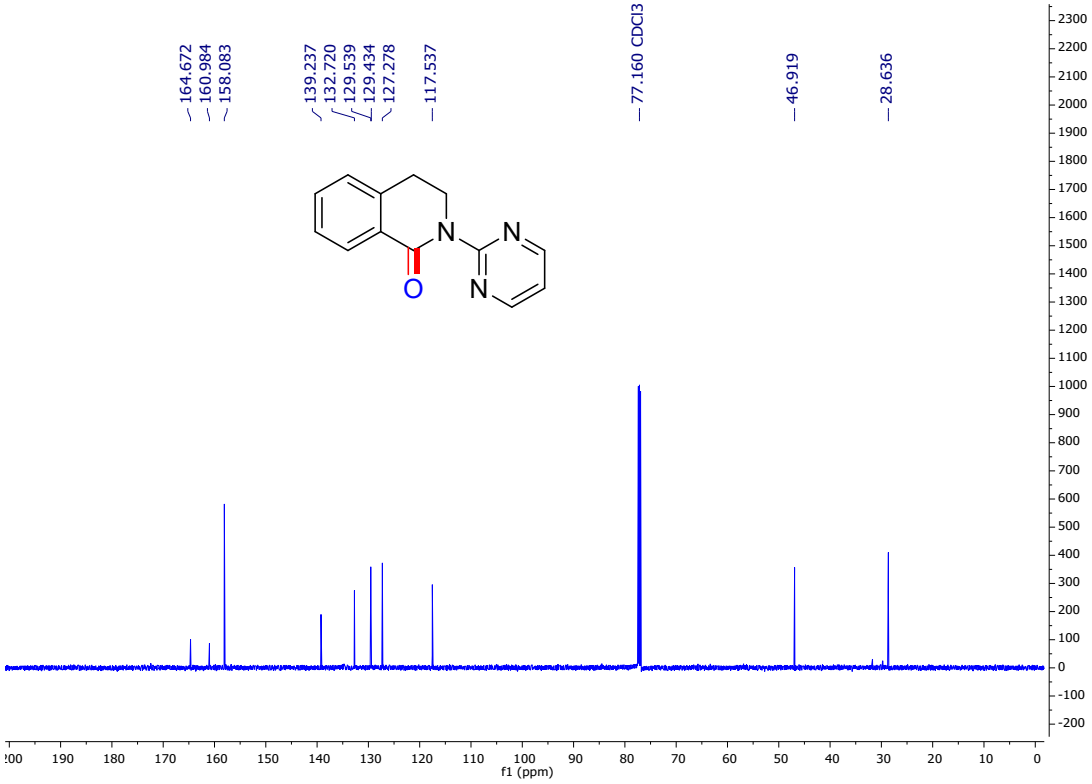


*2)-pyrimidin-2-yl-(3,4-dihydroisoquinolin-1)2H-(one) (Table 2, entry **2j**)*

^{1}H NMR (600 MHz, $CDCl_3$)

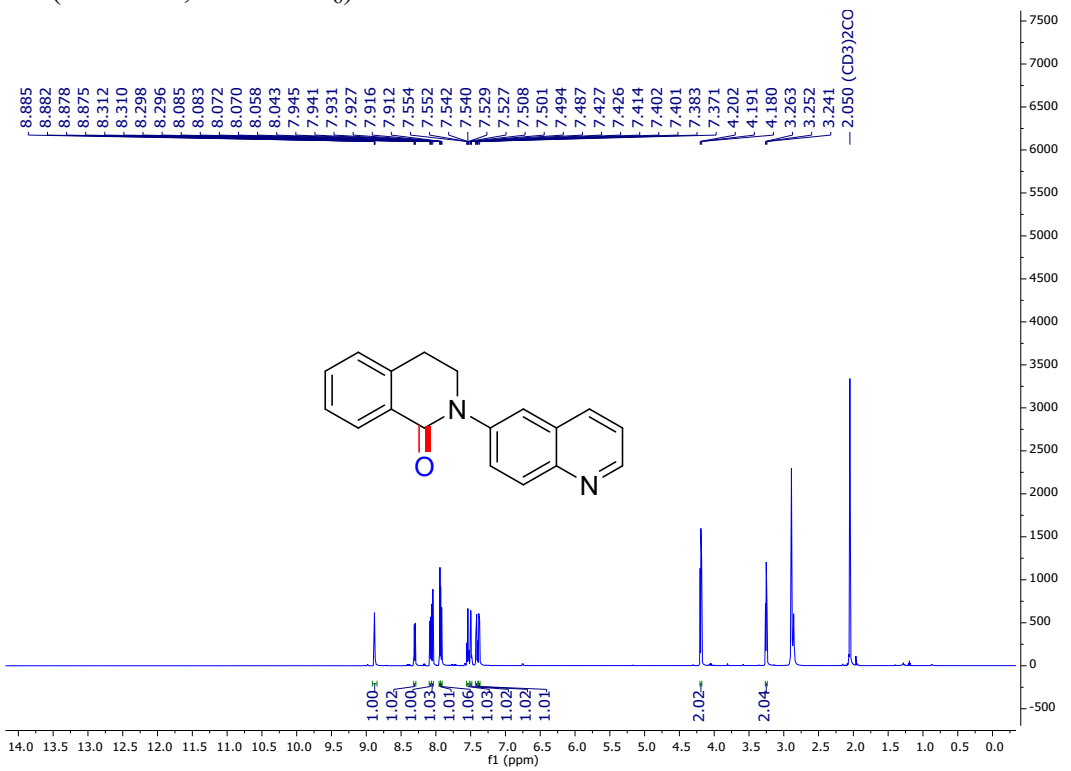


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

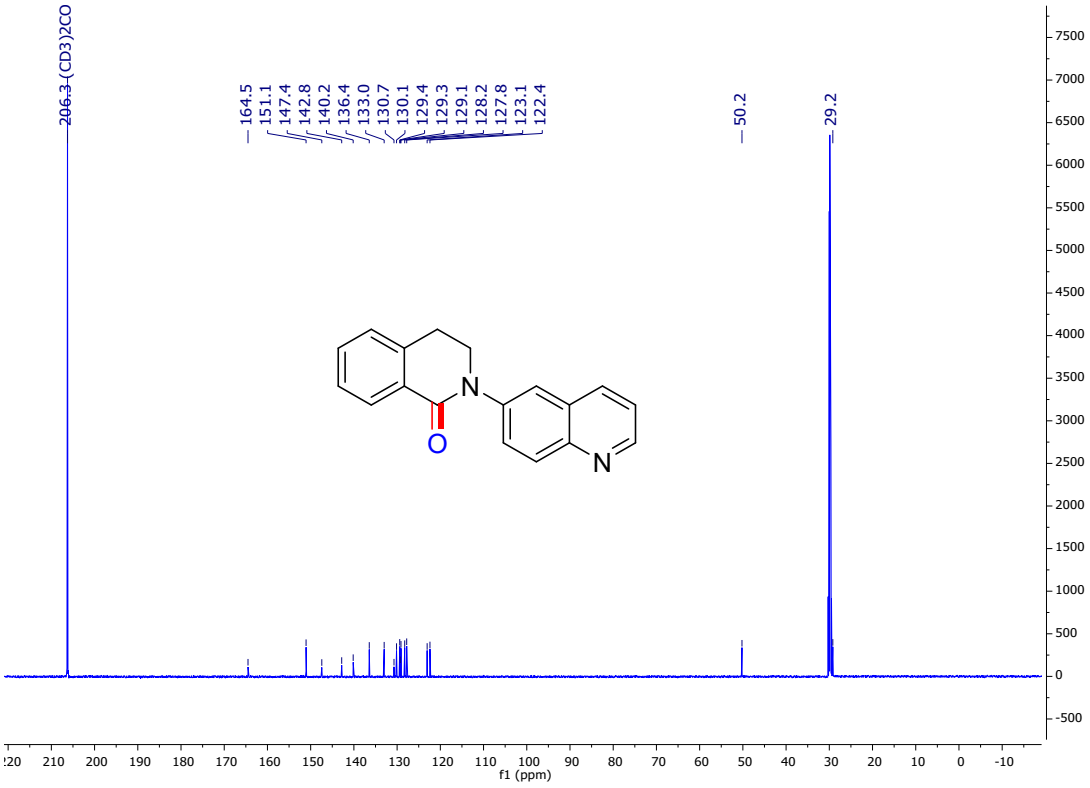


*2)-quinolin-6-yl-(3,4-dihydroisoquinolin-1)2H-(one) (Table 2, entry **2k**)*

^{1}H NMR (600 MHz, Acetone-d_6)

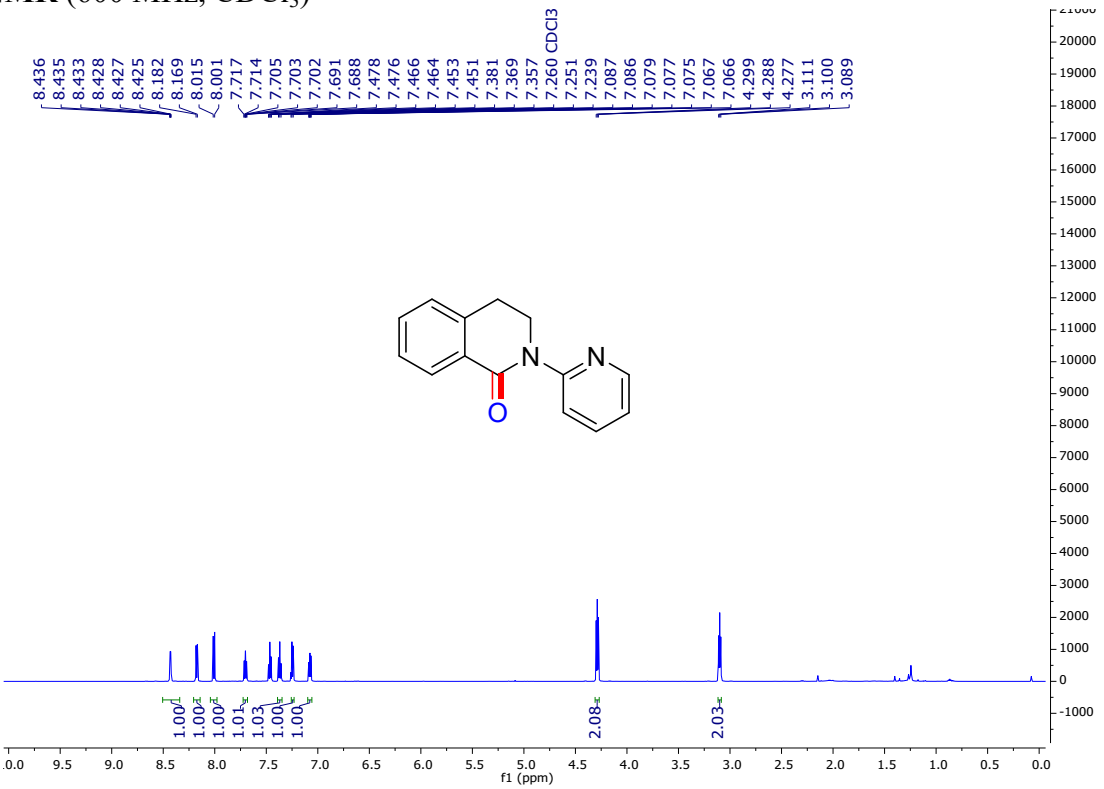


^{13}C{^{1}H} NMR (151 MHz, Acetone-d_6)

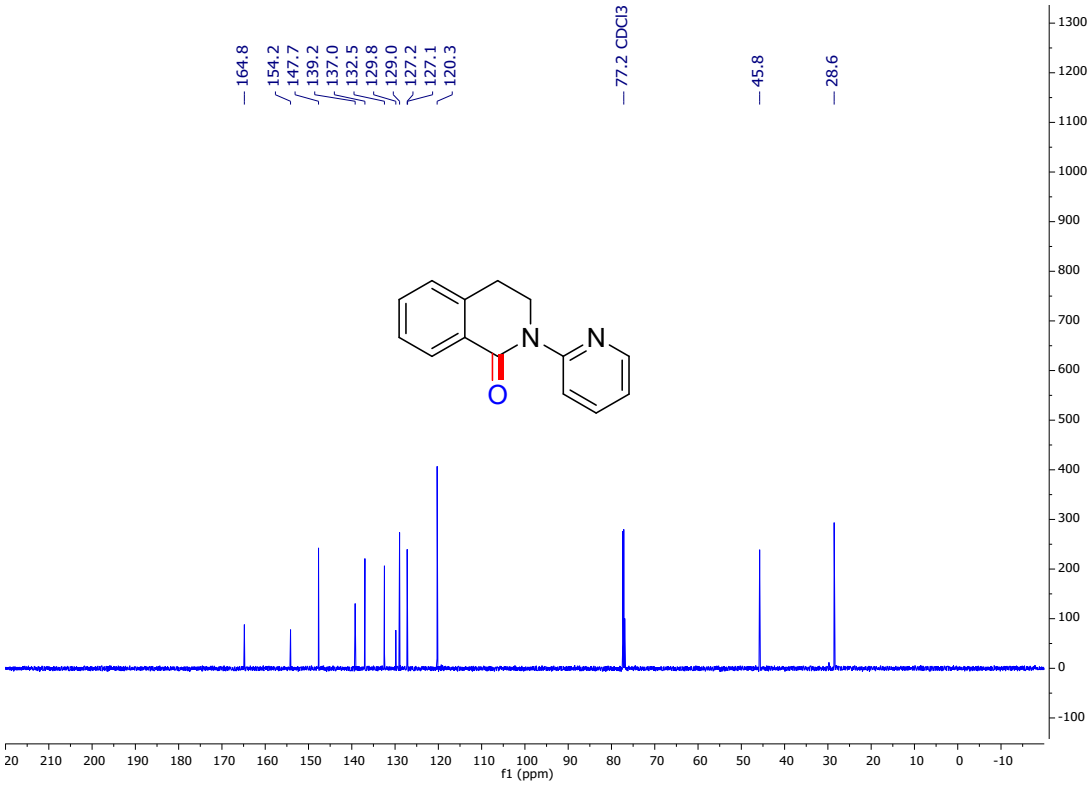


*2)-pyridin-2-yl-(3,4-dihydroisoquinolin-1)2H-(one) (Table 2, entry **2l**)*

^{1}H NMR (600 MHz, $CDCl_3$)

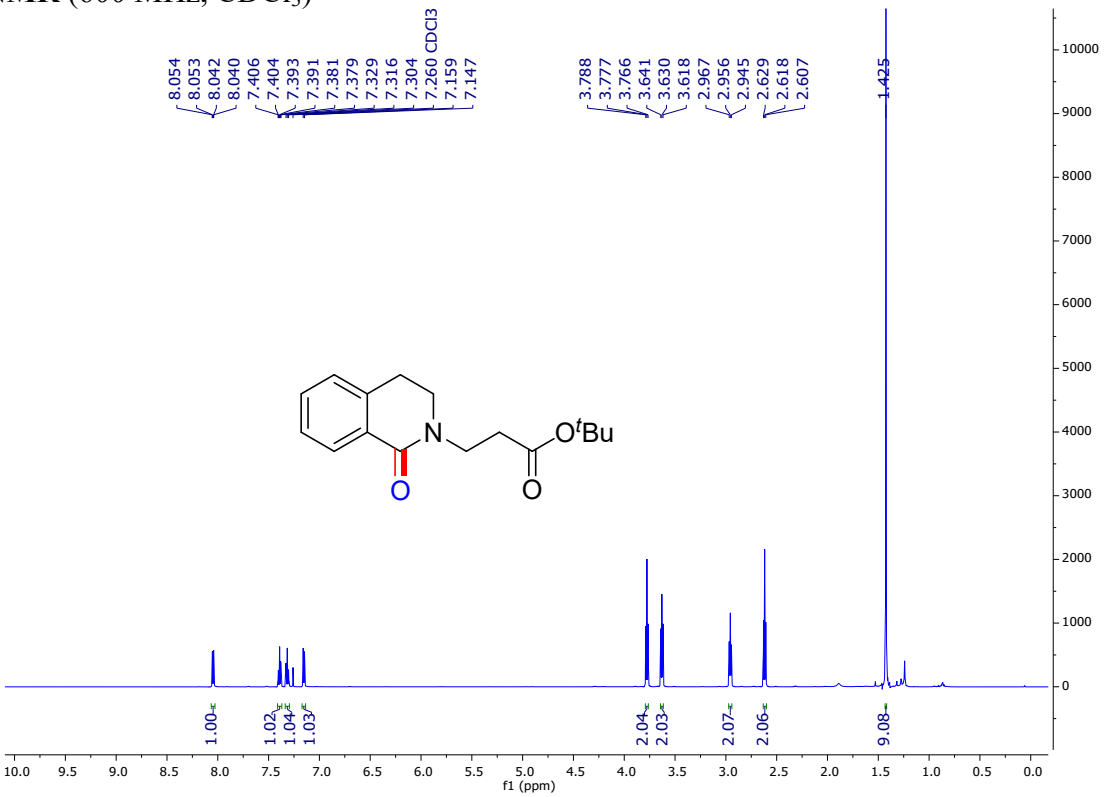


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

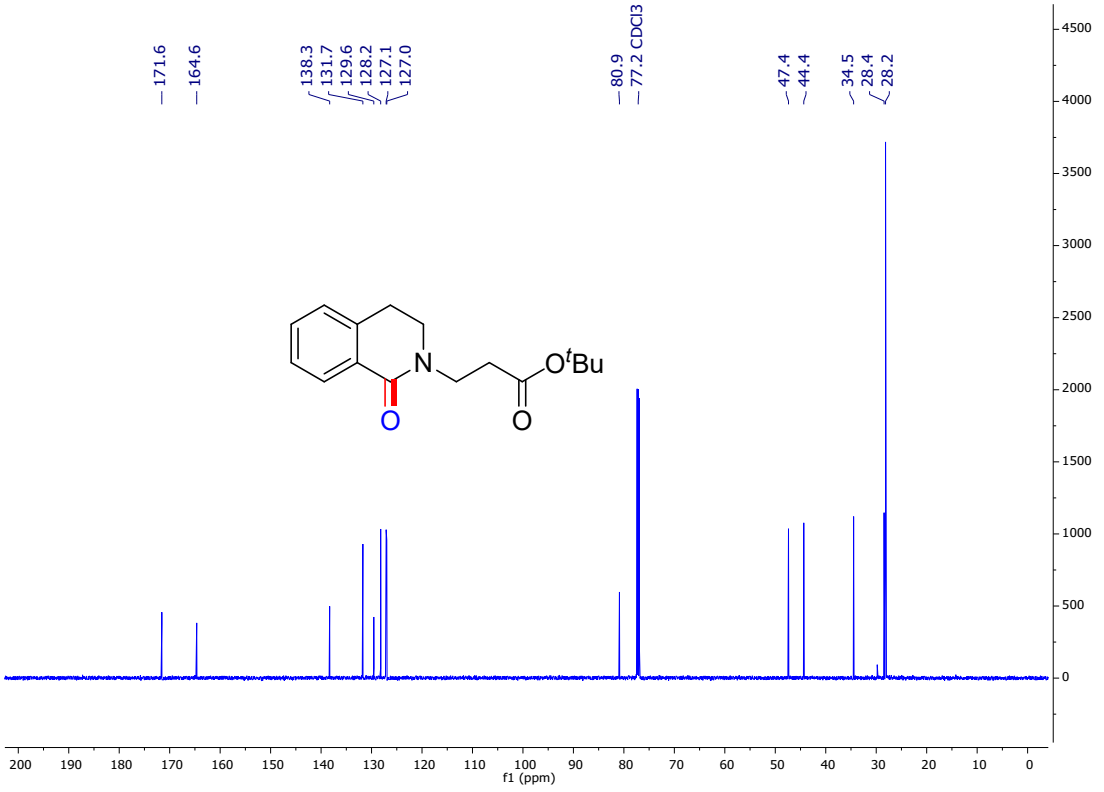


*tert-butyl 3)-1-oxo-3,4-dihydroisoquinolin-2)1H-(yl(propanoate) (Table 2, entry **2m**)*

^{1}H NMR (600 MHz, $CDCl_3$)

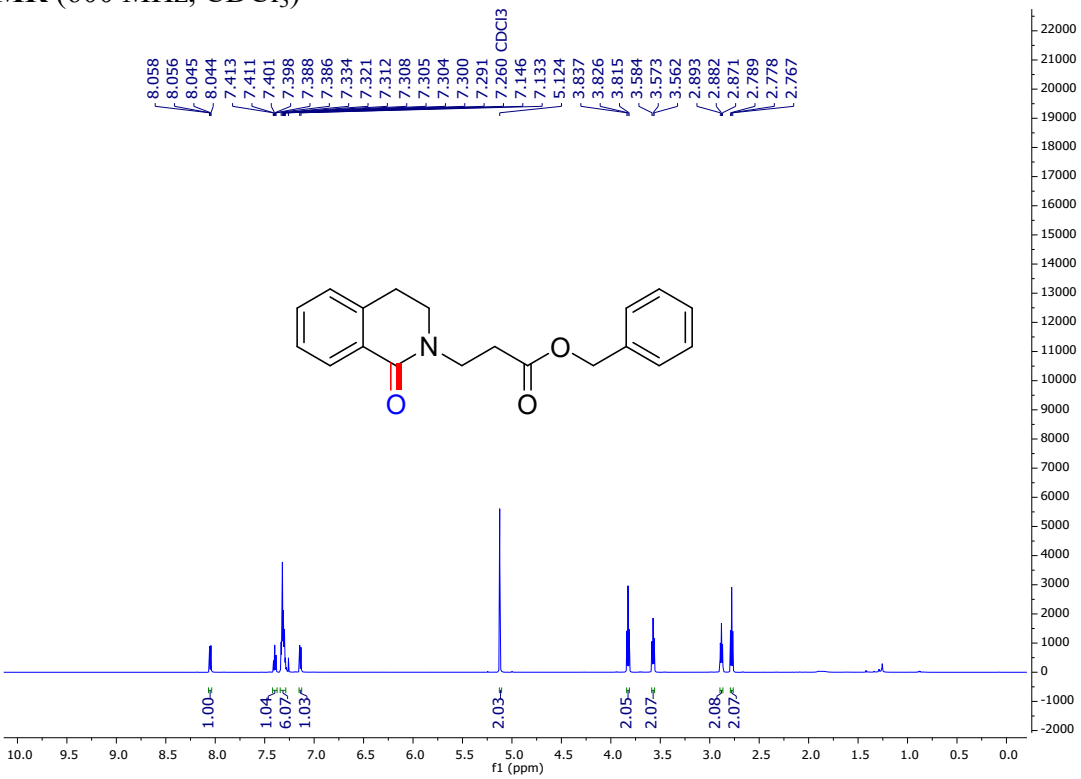


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

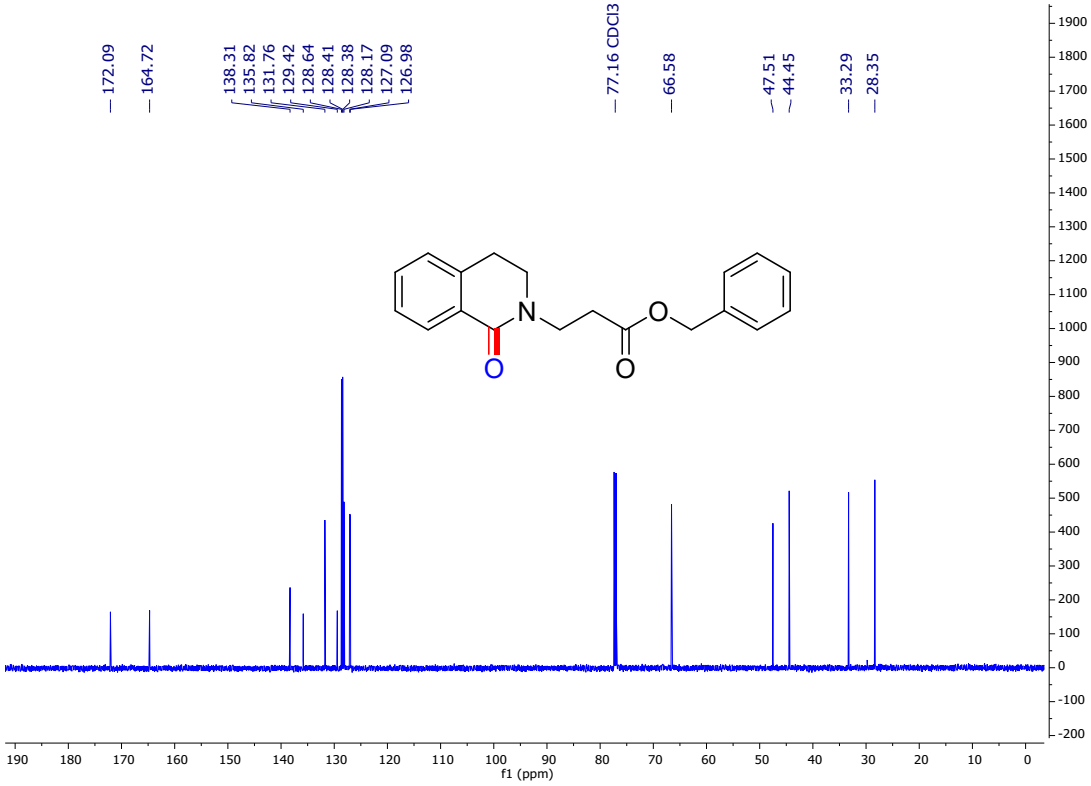


*benzyl 3)-1-oxo-3,4-dihydroisoquinolin-2)1H-(yl(propanoate) (Table 2, entry **2n**)*

^{1}H NMR (600 MHz, $CDCl_3$)

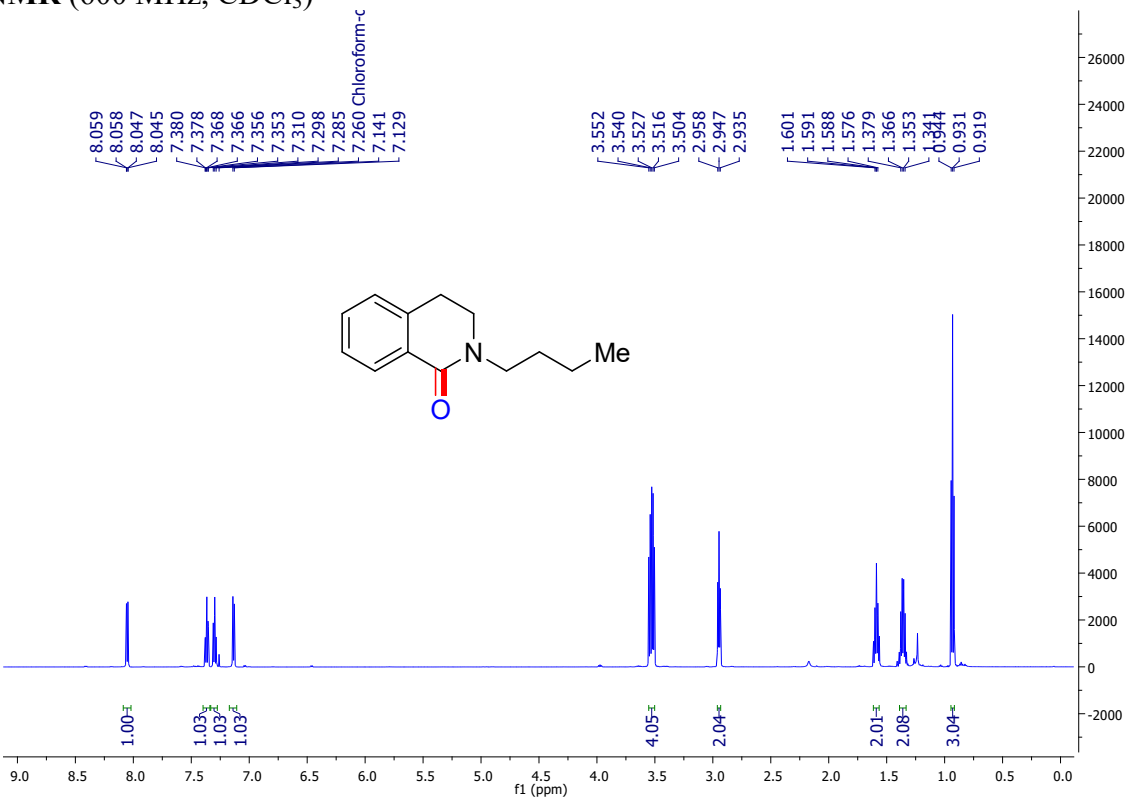


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

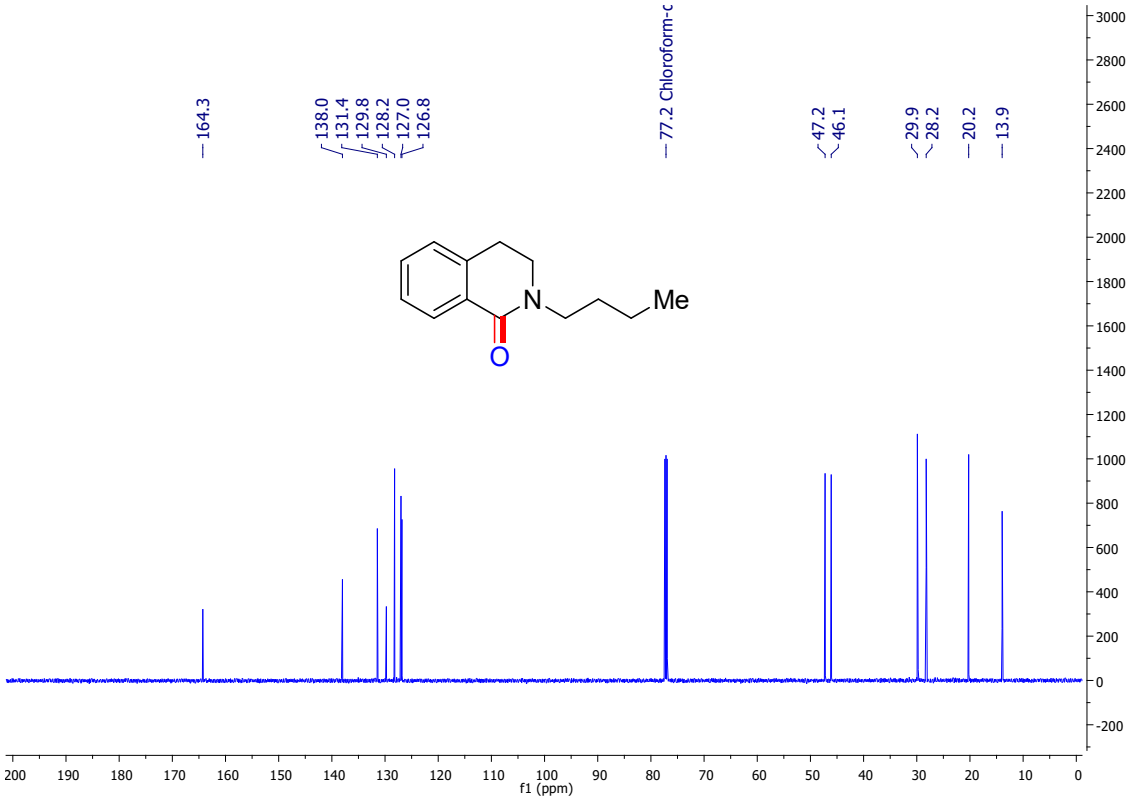


*2-butyl-3,4-dihydroisoquinolin-1)2H-(one) (Table 2, entry **2o**)*

^{1}H NMR (600 MHz, $CDCl_3$)

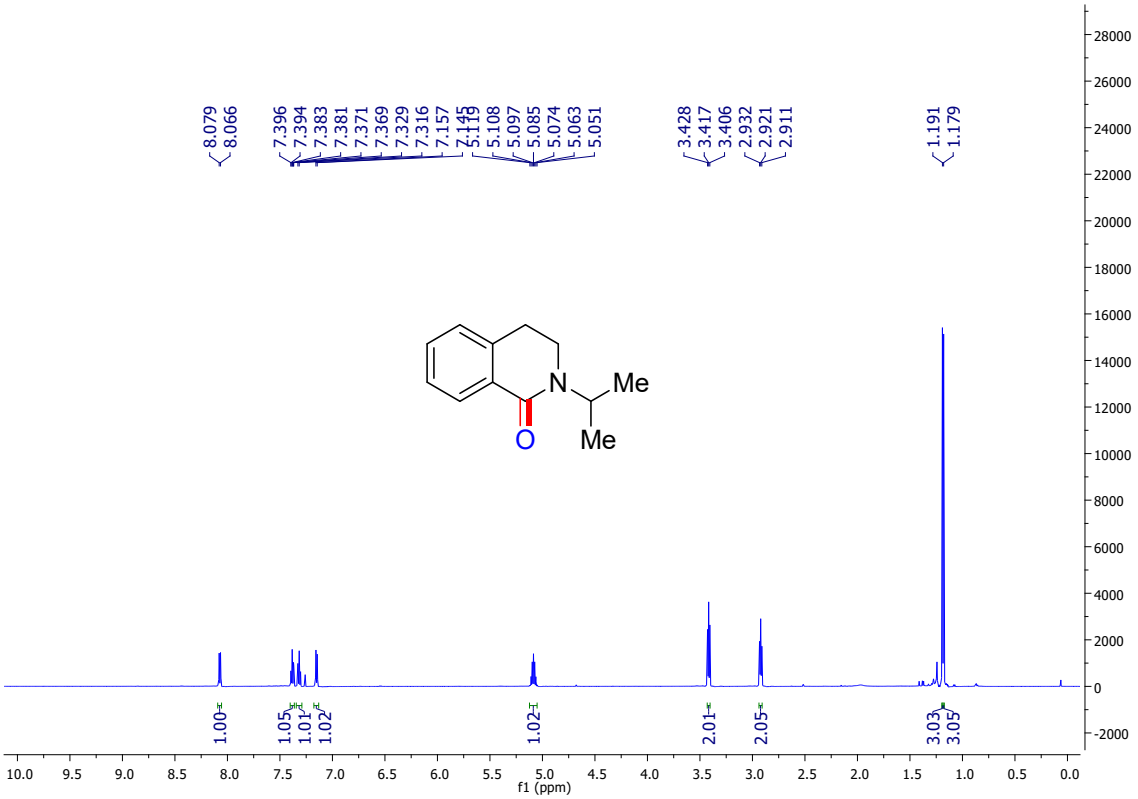


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

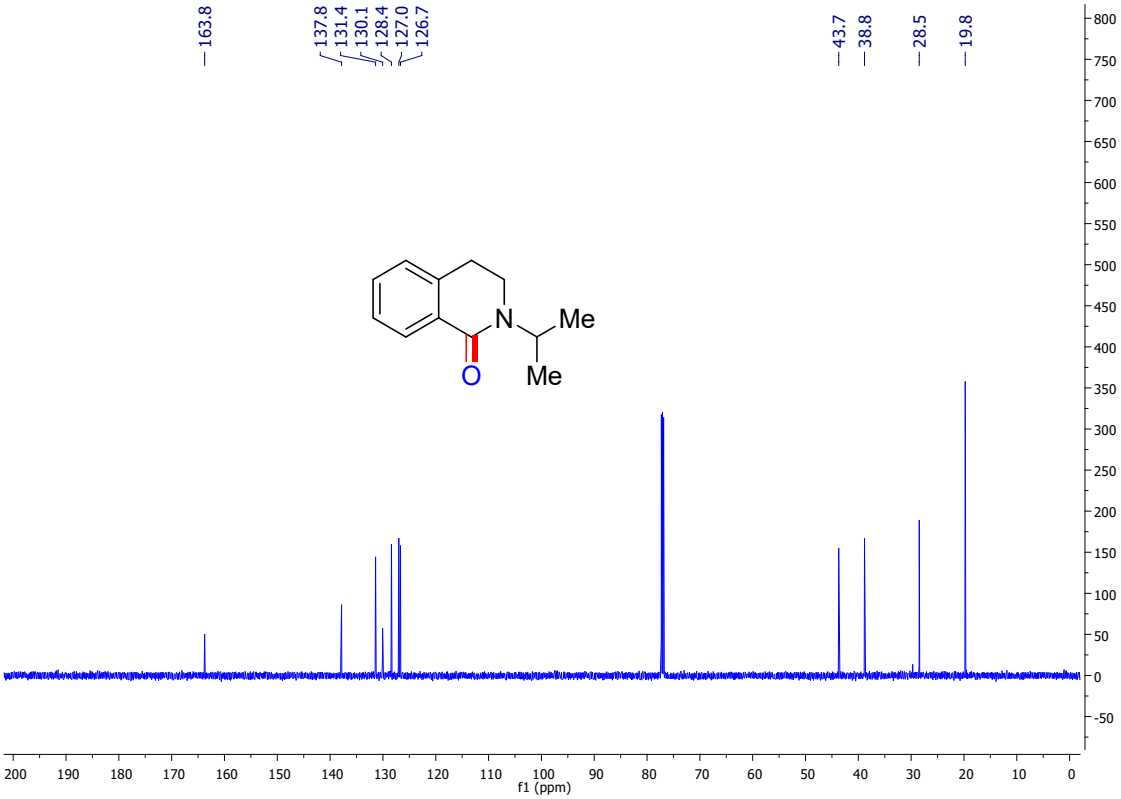


*2-isopropyl-3,4-dihydroisoquinolin-1)2H-(one) (Table 2, entry **2p**)*

^{1}H NMR (600 MHz, $CDCl_3$)

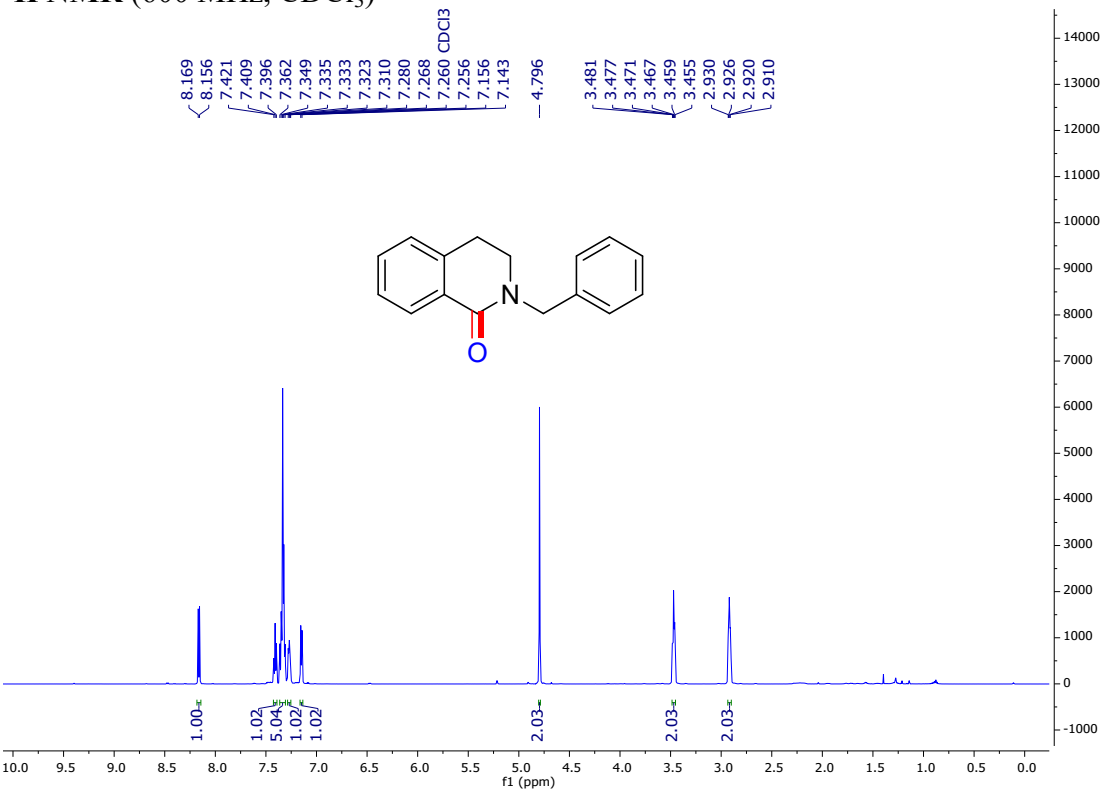


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

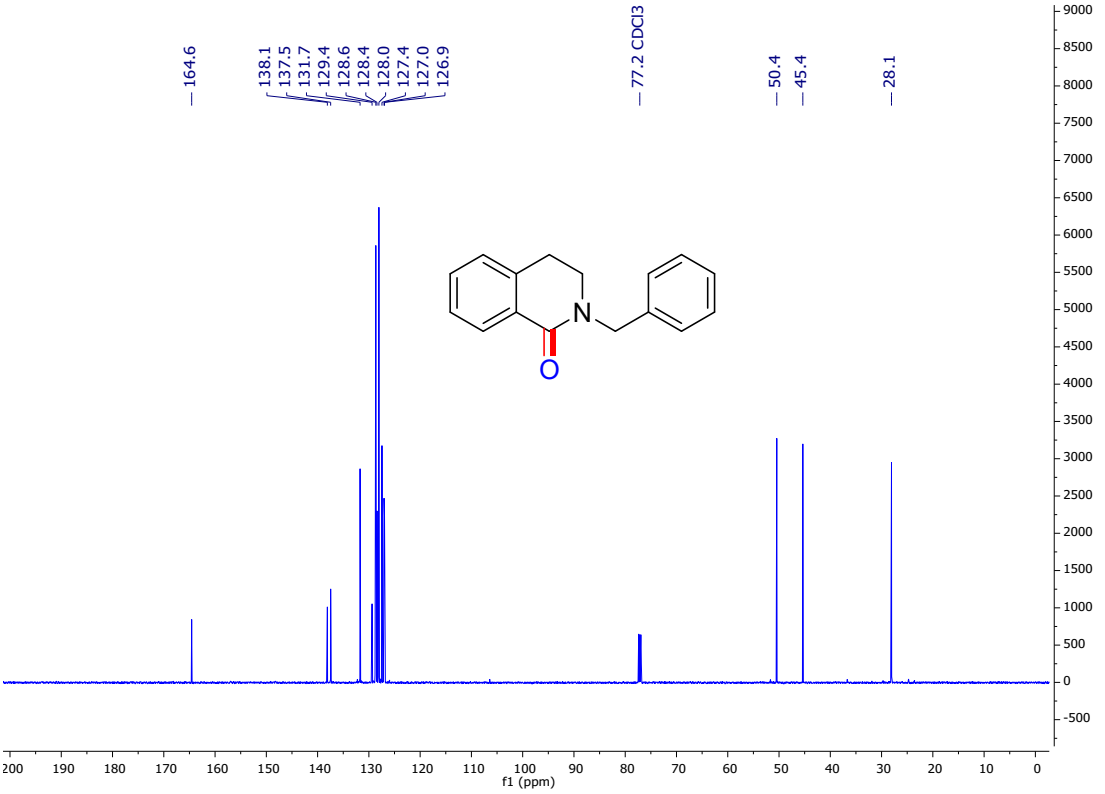


*2-Benzyl-3,4-dihydroisoquinolin-1(2H)-one (Table 2, entry **2q**)*

^{1}H NMR (600 MHz, $CDCl_3$)

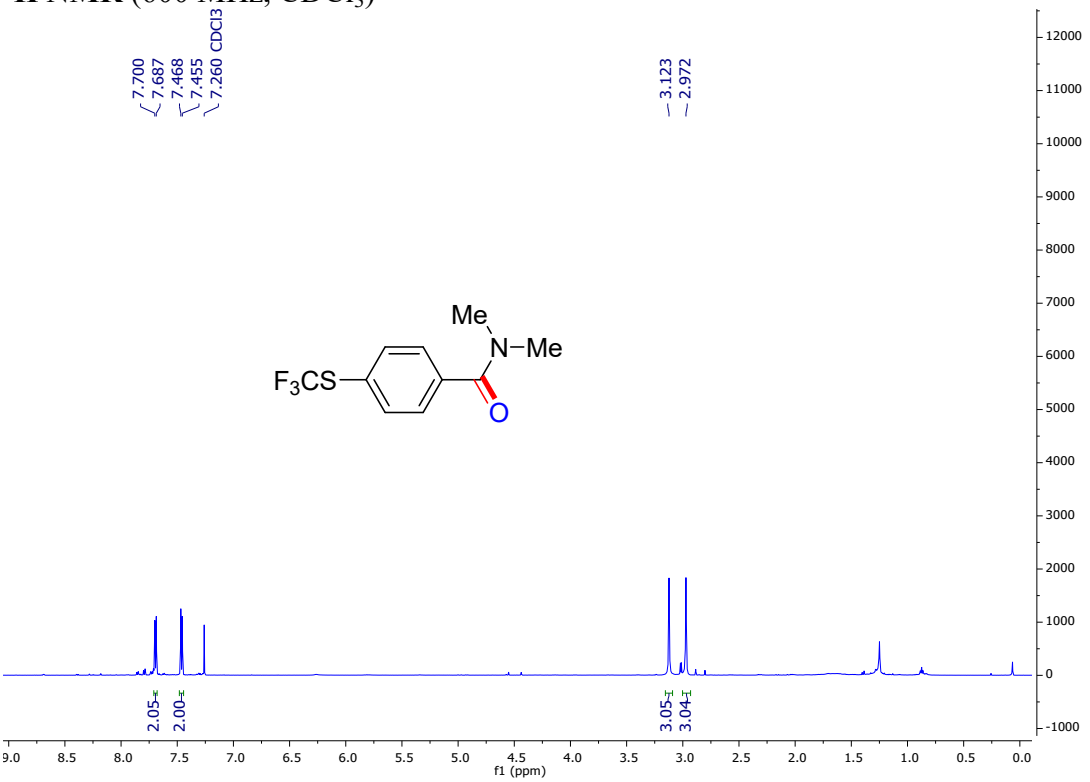


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)

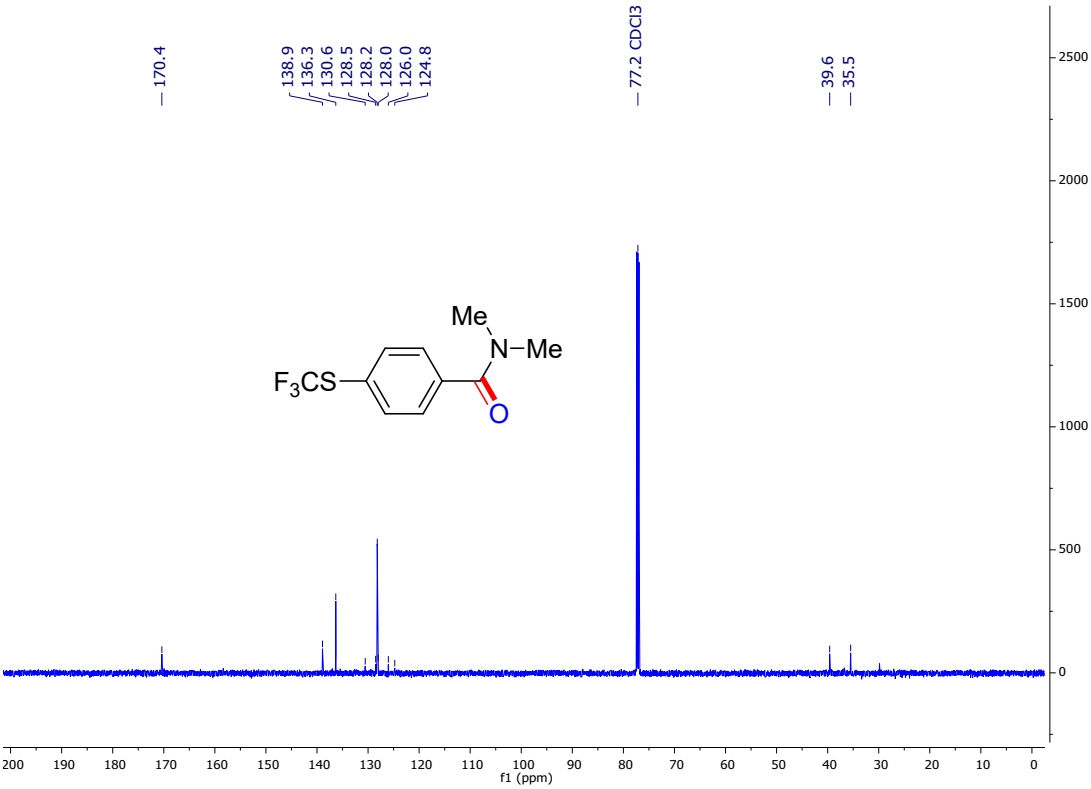


*N,N-dimethyl-4-((trifluoromethyl)thio)benzamide (Table 2, entry **2r**)*

^{1}H NMR (600 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$)



5. References

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