Supporting Information for

Combining oxidative photocatalysis and nucleophilic catalysis: direct *sp*^{3} C-H acroleination of N-aryl-tetrahydroisoquinolines

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1. General Information

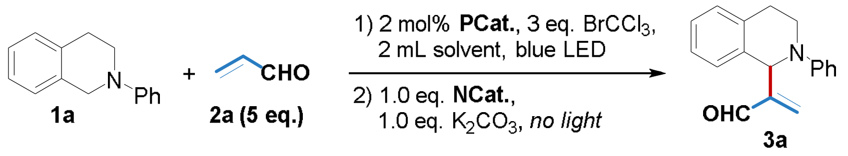
Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. All the solvents were treated according to general methods. Flash column chromatography was performed using 200-300 mesh silica gel.

^{1}H NMR spectra were recorded on 400 MHz or 600 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm). Data are reported as follows: chemical shift, multiplicity ((s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on 100 MHz with complete proton decoupling spectrophotometers. Chemical shifts are reported in ppm relative to the central line of the heptalet at 77.0 ppm for $CDCl_3$. The ee values determination was carried out using chiral high performance liquid chromatography (HPLC) with Daicel Chiracel OD column. Mass spectra were measured on a MS spectrometer.

Substrates **1** were prepared according to previous method[1] and products **3a-3g** and **3m** were known coumpounds.[2] Chiral catalyst *β*-isocupreidine (*β*-ICD) was synthesized according to reported method.[3]

2. Details for Reaction Condition Optimization

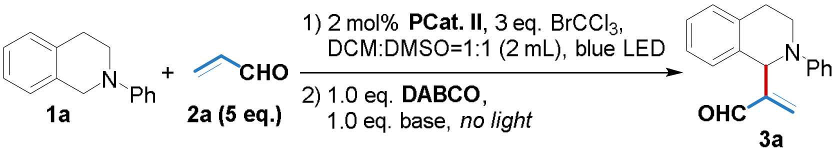
Table S-1. Optimization of reaction conditions[a]



Entry	PCat.[b]	NCat.[c]	Oxidant	Solvent	Yield (%)[d]
1	**$Ru(bpy)_3Cl_2{\cdot}6H_2O$ (I)**	**DABCO**	O_2	DMF	n.d.
2[e]	**$Ru(bpy)_3Cl_2{\cdot}6H_2O$ (I)**	**DABCO**	$BrCCl_3$	DMF	49
3	**$Ru(bpy)_3Cl_2{\cdot}6H_2O$ (I)**	**DABCO**	$BrCCl_3$	DMF	75
4	**$Ru(bpy)_3Cl_2{\cdot}6H_2O$ (I)**	**DBU**	$BrCCl_3$	DMF	trace
5	**$Ru(bpy)_3Cl_2{\cdot}6H_2O$ (I)**	**PPh_3**	$BrCCl_3$	DMF	71
6	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	DMF	79
7	**Esion Y (III)**	**DABCO**	$BrCCl_3$	DMF	11
8	**$Ru(bpy)_3PF_6$(IV)**	**DABCO**	$BrCCl_3$	DMF	73
9	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	MeCN	69
10	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	THF	46
11	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	DMSO	79
12	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	DCM	79
13	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	DMSO:DCM=1:1	83
14	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	DMF:DCM=1:1	76
15	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	DMSO:DMF=1:1	82
16	**2,4,6-Triphenylpyrylium tetrafluoroborate (V)**	**DABCO**	$BrCCl_3$	DMSO:DCM=1:1	77

[a] Reaction conditions: **1a** (0.5 mmol), **PCat.** (2 mol%), $BrCCl_3$ (3.0 equiv) in solvent (2 mL), blue LED irradiation at r.t., 3h, then *no light*, **2a** (5.0 equiv.), **OC** (1.0 equiv.), K_2CO_3 (1.0 equiv.). [b] **PCat.** is photoredox catalyst. [c] **NCat.** is nucleophilic catalyst. [d] Yield of isolated product. [e] Reaction conditions: **1a** (0.5 mmol), **PCat.** (2 mol%), **2a** (5.0 equiv.), **NCat.** (1.0 equiv.), K_2CO_3 (1.0 equiv.) and oxygen (1 atm) or $BrCCl_3$ (3.0 equiv.) in DMF (2 mL) under blue LED irradiation at r.t.

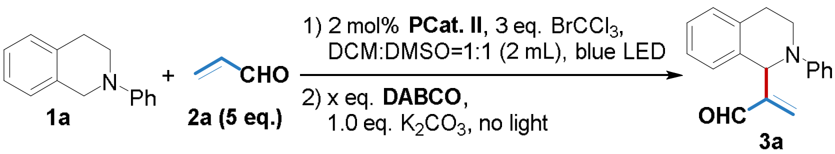
Table S-2. Screening the base[a]



Entry	Base	Yield(%)[b]	Entry	Base	Yield(%)[b]
1	Na_2CO_3	83	4	K_2HPO_4	78
2	Cs_2CO_3	79	5	TMG	68
3	KOH	75	6	Proton Sponge	81

[a] Reaction conditions: **1a** (0.5 mmol), **PCat. II** (2 mol%), $BrCCl_3$ (3.0 equiv) in solvent (2 mL), blue LED irradiation at r.t., 3h, then *no light*, **2a** (5.0 equiv.), **NCat.** (1.0 equiv.), K_2CO_3 (1.0 equiv.). [b] Isolated yield.

Table S-3. Optimization of the loading of nucleophilic catalyst[a]

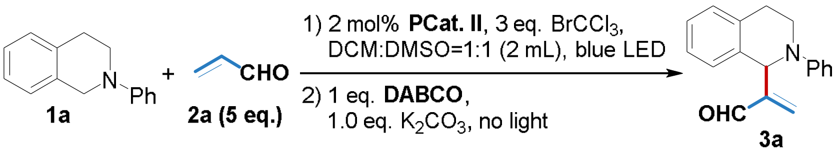


Entry	**Loading of Nucleophilic Catalyst**	Yield (%)[d]
1	**0.5 equiv.**	77
2[e]	**0.2 equiv.**	69

[a] Reaction conditions: **1a** (0.5 mmol), **Photoredox Catalyst** (2 mol%), $BrCCl_3$ (3.0 equiv) in DMSO:DCM=1:1 (2 mL), blue LED irradiation at r.t., 3h, then *no light*, **2a** (5.0 equiv.), **DABCO** (x equiv.), K_2CO_3 (1.0 equiv.). [b] Isolated yield.

3. Details for control experiment

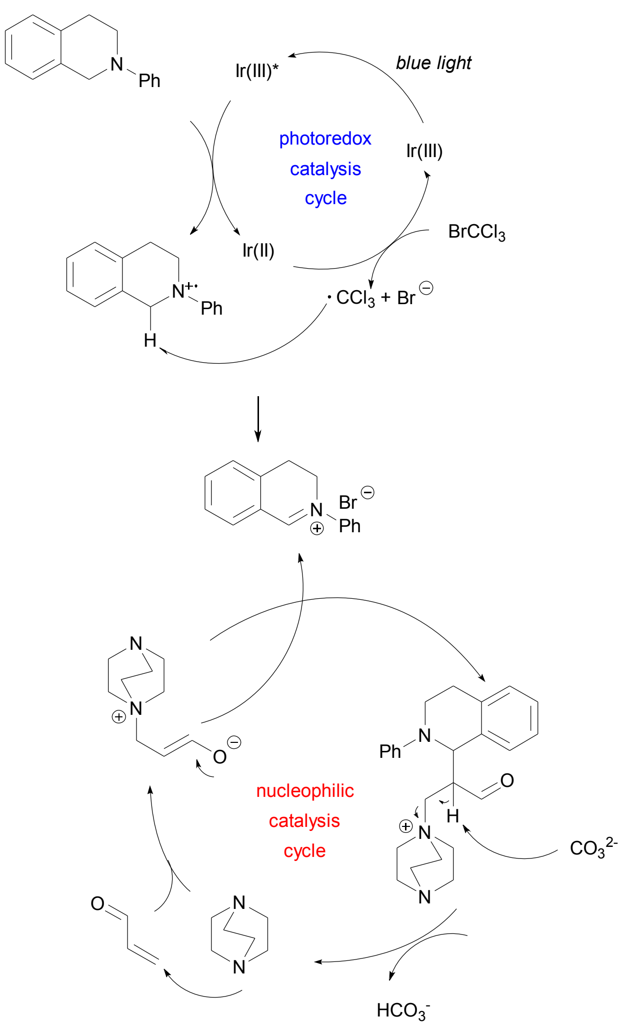
Table S-4. Control experiment.[a]



Entry	PCat.	NCat.	Oxidant	Base	Light source	Yield (%)[b]
1	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	K_2CO_3	Blue LED	83
2	--	**DABCO**	$BrCCl_3$	K_2CO_3	Blue LED	0
3	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	--	$BrCCl_3$	K_2CO_3	Blue LED	0
4	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	--	K_2CO_3	Blue LED	0
5	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	--	Blue LED	13
6	**$Ir(ppy)_2(dtb\text{-}bpy)PF_6$ (II)**	**DABCO**	$BrCCl_3$	K_2CO_3	--	0

[a] Reaction conditions: **1a** (0.5 mmol), **$Ir(ppy)_2(dtbbpy)PF_6$** (2 mol%), $BrCCl_3$ (3.0 equiv) in DMSO:DCM=1:1 (2 mL), blue LED irradiation at r.t., 3h, then *no light*, **2a** (5.0 equiv.), **DABCO** (1.0 equiv.), K_2CO_3 (1.0 equiv.). [b] Isolated yield.

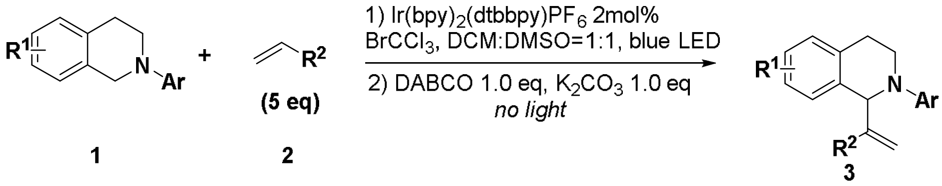
4. The proposed mechanism



Scheme S-1. Proposed Mechanism

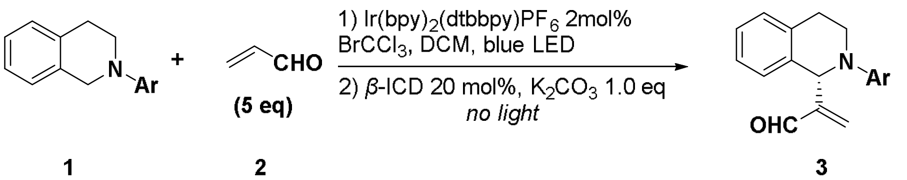
5. Preparation and Spectral Data of Substrates

5.1 General procedure



In a 10 mL dry flask equipped with magnetic bar was charged with **1** (0.5 mmol, 1.0 eq.) and $Ir(bpy)_2(dtbbpy)PF_6$ (2 mol%) and DMSO (1 mL), DCM (1 mL). The mixture was degassed via freeze-pump-thaw method (3 times), after which $BrCCl_3$ (1.5 mmol, 3.0 eq.) was added via a syringe. The resultant mixture was the stirred under the irradiation of blue LED strip at room temperature for 3h. The DABCO (0.5 mmol, 1.0 eq.), K_2CO_3 (0.5 mmol, 1.0 eq.) were added under N_2 protection, **2** (2.5 mmol, 5.0 eq.) was added via a syringe. Then the mixture was stirred without light at room temperature. 24h later, the resultant mixture was transformed to a flask using additional diethyl ether (1 mL) to assure complete transfer. Remoed DCM and diethyl ether under vacuum, the resultant was poured into 10 mL H_2O, extracted with diethyl ether (20 mL* 3 times), the combined organic layer was dried over anhydrous Na_2SO_4. Removed the solvent and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1 or 10:1) to affored the desired product **3**.

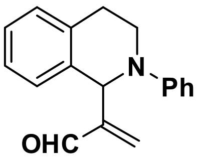
5.2 General procedure for asymmetric version



In a 10 mL dry flask equipped with magnetic bar was charged with **1** (0.2 mmol, 1.0 eq.) and $Ir(bpy)_2(dtbbpy)PF_6$ (2 mol%) and DCM (1 mL). The mixture was degassed via freeze-pump-thaw method (3 times), after which $BrCCl_3$ (0.6 mmol, 3.0 eq.) was added via a syringe. The resultant mixture was the stirred under the irradiation of blue LED strip at room temperature for 3h. The *β*-ICD (0.04 mmol, 0.2 eq.), K_2CO_3 (0.2 mmol, 1.0 eq.) were added under N_2 protection, **2** (1.0 mmol, 5.0 eq.) was added via a syringe. Then the mixture was stirred without light at room temperature. 24h later, the resultant mixture was poured into 5mL H_2O, extracted with DCM (10 mL* 3 times), the combined organic layer was dried over anhydrous Na_2SO_4. Removed the solvent and purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 30:1 or 10:1) to afforded the desired product **3**.

5.3 Spectral Data of Substrates

N-benzyl-*N*-tosylbenzamide (3a)

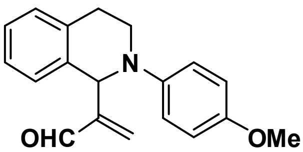


3a

Yellow oil, 83% yield. **^{1}H NMR** δ $_H$ (600 MHz, cdcl3) 9.64 (1 H, s), 7.31 (1 H, d, J 7.0), 7.24 (3 H, dd, *J* 13.5, 4.4), 7.17 (3 H, dd, *J* 14.5, 6.9), 6.83 (1 H, s), 6.82 (1 H, s), 6.77 (1 H, t, *J* 7.1), 6.24 (1 H, s), 6.07 (1 H, s), 5.80 (1 H, s), 3.79 – 3.70 (1 H, m), 3.55 – 3.45 (1 H, m), 3.04 (1 H, dd, *J* 10.8, 4.9), 3.00 – 2.90 (1 H, m).**^{13}C NMR** δ $_C$ (101 MHz, $cdcl_3$) 193.28, 151.04, 148.25, 135.56, 134.78, 134.31, 129.05, 128.17, 127.84, 127.08, 126.25, 117.73, 113.62, 77.32, 77.00, 76.67, 56.68, 43.22, 27.73. **IR** (in KBr thin film): □ = 3447, 3059, 3024, 2915, 2835, 1685, 1596, 1503, 1384, 1326, 940, 750, 691 cm^{-1}. **MS** (EI)**:** m/z = 263.11.

For chiral product: Yellow oil, 82% yield, enantiomer ratio: 83:17 e.r. The enantioselectivity was determined by chiral HPLC: Daicel Chirapak OD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 25 °C, 254 nm, t_R = 7.33 min (minor), t_R = 8.12 min (major); $[\alpha]^{20}_D$= -3.2 (*c*=1.0, $CHCl_3$). Compared optical rotation with the literature (JACS, 2012, 134, 12334), it is the same configuration with literature report.

N-benzyl-4-methyl-*N*-tosylbenzamide (3b)



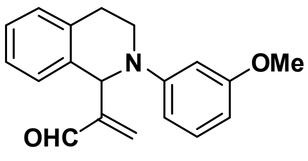
3b

Yellow solid, 78% yield. **^{1}H NMR** δ $_H$ (600 MHz, cdcl3) 9.62 (1 H, s), 7.21 – 7.13 (4 H, m), 6.87 (2 H, d, *J* 9.0), 6.83 (2 H, d, *J* 9.0), 6.10 (2 H, s), 5.71 (1 H, s), 3.76 (3 H, s), 3.65 – 3.59 (1 H, m), 3.48 – 3.41 (1 H, m), 3.06 – 2.98 (1 H, m), 2.95 – 2.87 (1 H, m). **^{13}C NMR** δ $_C$ (101 MHz, $cdcl_3$) 193.29, 152.82, 151.30, 143.18, 135.47, 135.01, 135.00, 134.64, 128.27, 128.00, 126.85, 126.10, 117.03, 114.42, 77.32, 77.00, 76.68, 57.14, 55.52, 43.94, 27.47.

IR (in KBr thin film): □ = 2930, 2832, 1689, 1511, 1244, 1037, 941, 755 cm^{-1}. **MS** (EI)**:** m/z = 293.32.

For chiral product: Yellow oil, 64% yield, enantiomer ratio: 78:22 e.r. The enantioselectivity was determined by chiral HPLC: Daicel Chirapak OD-H, hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 25 ^{o}C, 254 nm, t_R = 6.81 min (major), t_R = 9.06 min (minor).

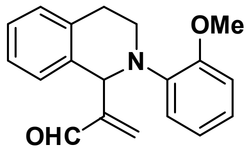
***N*-(4-chlorobenzyl)-*N*-tosylbenzamide (3c)**



3c

Yellow solid, 65% yield. ^{1}**H NMR** δ_H (600 MHz, cdcl3) 9.64 (1 H, s), 7.32 (1 H, d, *J* 7.4), 7.22 – 7.12 (4 H, m), 6.44 (1 H, d, *J* 8.5), 6.39 (1 H, s), 6.34 (1 H, d, *J* 8.3), 6.24 (1 H, s), 6.07 (1 H, s), 5.80 (1 H, s), 3.78 (3 H, s), 3.76 – 3.70 (1 H, m), 3.53 – 3.45 (1 H, m), 3.03 (1 H, dt, J 10.1, 4.8), 3.00 – 2.92 (1 H, m). ^{13}**C NMR** δ_C (101 MHz, $cdcl_3$) 193.18, 160.57, 151.12, 149.74, 135.56, 134.80, 134.22, 129.74, 128.21, 127.85, 127.14, 126.30, 106.59, 102.60, 100.22, 77.32, 77.00, 76.68, 56.81, 55.05, 43.38, 27.80. **IR** (in KBr thin film): □ = 3446, 2910, 2834, 1685, 1607, 1576, 1496,1210, 1168, 816, 751, 686 cm^{-1}. **MS** (EI)**:** m/z = 293.27.

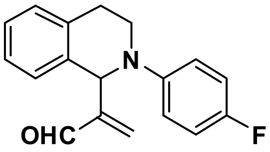
***N*-benzyl-*N*-tosylfuran-2-carboxamide (3d)**



3d

Yellow oil, 83% yield. ^{1}**H NMR** δ_H (600 MHz, $cdcl_3$) 9.37 (1 H, s), 7.15 (3 H, tt, *J* 14.0, 6.9), 6.99 (1 H, ddd, *J* 10.0, 5.2, 2.1), 6.94 (1 H, d, *J* 7.6), 6.87 (1 H, d, *J* 7.8), 6.80 (2 H, d, *J* 3.2), 6.05 (1 H, s), 5.89 (1 H, s), 5.77 (1 H, s), 3.88 (3 H, s), 3.43 – 3.29 (2 H, m), 3.04 – 2.95 (1 H, m), 2.88 (1 H, d, *J* 16.3). ^{13}**C NMR** δ_C (101 MHz, $cdcl_3$) 192.85, 153.51, 150.20, 139.43, 135.68, 135.27, 135.05, 128.81, 127.69, 126.42, 125.79, 123.68, 121.42, 120.60, 111.71, 77.32, 77.00, 76.68, 55.61, 43.57, 28.37. **IR** (in KBr thin film): □ = 3447, 3061, 1694, 1499, 1247, 1027, 747 cm^{-1}. **MS** (EI)**:** m/z = 293.29.

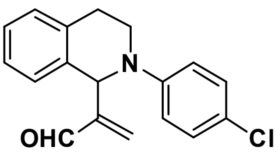
***N*-benzyl-3-chloro-*N*-tosylbenzamide (3e)**



3e

Yellow oil, 89% yield. **^{1}H NMR** δ $_H$ (600 MHz, cdcl$_3$) 9.62 (1 H, s), 7.24 – 7.13 (4 H, m), 6.93 (2 H, t, *J* 8.4), 6.81 (2 H, dd, *J* 7.6, 4.5), 6.13 (1 H, s), 6.10 (1 H, s), 5.72 (1 H, s), 3.64 (1 H, dt, *J* 11.4, 5.5), 3.50 – 3.42 (1 H, m), 3.06 – 2.98 (1 H, m), 2.95 – 2.88 (1 H, m). **^{13}C NMR** (100 MHz, CDCl$_3$) δ $_C$ (101 MHz, cdcl$_3$) 193.17, 157.27, 154.91, 150.97, 145.15, 135.31, 134.70, 134.60, 128.14, 127.99, 127.02, 126.18, 115.81, 115.74, 115.45, 115.24, 56.96, 43.43, 27.28.**IR** (in KBr thin film): □ = 3366, 3054, 2915, 2841, 1694, 1505, 1385, 1231, 1112, 941, 754 cm^{-1}. **MS** (EI)**:** m/z = 281.27.

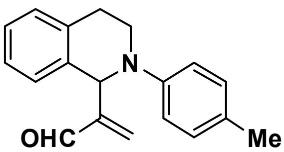
***N*-benzyl-4-fluoro-*N*-tosylbenzamide (3f)**



3f

Yellow oil, 93% yield. **^{1}H NMR**δ $_H$ (400 MHz, cdcl$_3$) 9.63 (1 H, s), 7.29 (1 H, d, *J* 6.4), 7.17 (5 H, d, *J* 8.7), 6.75 (2 H, d, *J* 8.8), 6.19 (1 H, s), 6.09 (1 H, s), 5.75 (1 H, s), 3.77 – 3.57 (1 H, m), 3.54 – 3.36 (1 H, m), 3.11 – 2.82 (2 H, m). **^{13}C NMR** δ $_C$ (101 MHz, cdcl$_3$) 193.17, 150.55, 146.76, 135.25, 134.59, 134.30, 128.74, 128.05, 127.91, 127.18, 126.26, 122.32, 114.70, 56.56, 43.03, 27.34. **IR** (in KBr thin film): □ = 3448, 2916, 2843, 1689, 1594, 1495, 1384, 1330, 940, 752 cm^{-1}. **MS** (EI)**:** m/z = 297.24.

***N*-(4-methylbenzyl)-*N*-tosylbenzamide (3g)**

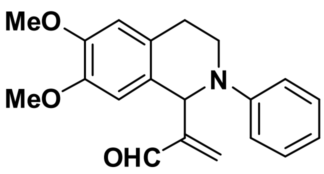


3g

Yellow oil, 82% yield. **^{1}H NMR** δ $_H$ (600 MHz, cdcl$_3$) 9.63 (1 H, s), 7.26 (1 H, d, *J* 8.8), 7.16 (3 H, dt, *J* 12.5, 7.0), 7.04 (2 H, d, *J* 8.3), 6.76 (2 H, d, *J* 8.5), 6.18 (1 H, s), 6.06 (1 H, s), 5.76 (1 H, s), 3.73 – 3.65 (1 H, m), 3.51 – 3.43 (1 H, m), 3.02 (1 H, dt, *J* 11.1, 5.2), 2.93 (1 H, ddd, *J* 16.1, 6.4, 5.0), 2.24 (3 H, s). **^{13}C NMR** δ $_C$ (101 MHz, cdcl$_3$) 193.22, 151.23, 146.28, 135.53, 134.89, 134.26, 129.55, 128.08, 127.97, 127.19, 126.94, 126.14, 114.32, 77.32, 77.00, 76.68, 56.72, 43.35, 27.62, 20.19. **IR** (in KBr thin film): □ = 3447, 3028, 2916, 2834, 1688, 1617, 1518, 1384, 904, 775, 754 cm^{-1}. **MS** (EI)**:** m/z = 277.27.

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

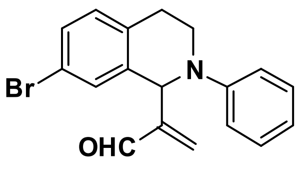
2-(6,7-dimethoxy-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acrylaldehyde(3h)



3h

Yellow oil, 79% yield. **^{1}H NMR** δ_H (600 MHz, cdcl$_3$) 9.66 (1 H, s), 7.24 (2 H, dd, *J* 14.5, 6.0), 6.85 (2 H, d, *J* 8.1), 6.80 (1 H, d, *J* 16.6), 6.77 (1 H, t, *J* 7.2), 6.64 (1 H, s), 6.21 (1 H, s), 6.07 (1 H, s), 5.72 (1 H, s), 3.85 (6 H, d, *J* 9.3), 3.77 – 3.56 (1 H, m), 3.53 – 3.42 (1 H, m), 2.96 (1 H, dd, *J* 10.3, 5.2), 2.87 – 2.76 (1 H, m). **^{13}C NMR** δ_C (101 MHz, cdcl$_3$) 193.43, 151.14, 148.39, 147.88, 147.23, 134.10, 129.00, 127.60, 126.59, 117.82, 113.90, 111.02, 110.69, 77.32, 77.00, 76.68, 56.27, 55.83, 55.74, 42.97, 27.00.**IR** (in KBr thin film): □ = 3482, 2934, 2834, 1689, 1503, 1254, 1220, 1119, 750 cm^{-1}. **HRMS** (MALDI)**:** m/z = 324.1591 ([M+H]+). Calcd for C20H21NO3: ([M+H]+) 324.1594

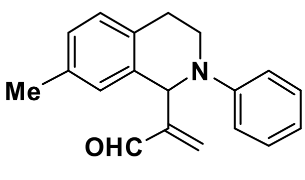
2-(7-bromo-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acrylaldehyde



3i

Yellow oil, 52% yield. **^{1}H NMR** δ_H (600 MHz, cdcl$_3$) 9.64 (1 H, s), 7.42 (1 H, s), 7.31 (1 H, d, *J* 8.2), 7.27 – 7.20 (3 H, m), 7.03 (1 H, d, *J* 8.1), 6.85 (2 H, d, *J* 8.1), 6.79 (1 H, t, *J* 7.3), 6.19 (1 H, s), 6.13 (1 H, s), 5.77 (1 H, s), 3.72 – 3.64 (1 H, m), 3.55 – 3.48 (1 H, m), 2.99 (1 H, dt, *J* 15.4, 5.5), 2.89 – 2.81 (1 H, m). **^{13}C NMR** δ_C (101 MHz, CDCl$_3$) 193.43, 152.81, 151.19, 147.73, 147.16, 143.20, 134.53, 127.51, 126.52, 117.23, 114.32, 110.81, 110.54, 56.67, 55.76, 55.68, 55.42, 43.52, 26.52. **IR** (in KBr thin film): □ = 3445, 3058, 2911, 2836, 1694, 1596, 1504, 1382, 942, 749, 691 cm^{-1}. **HRMS** (MALDI)**:** m/z = 342.04865 ([M+H]+). Calcd for C18H16BrNO: ([M+H]+) 342.0488

2-(7-methyl-2-phenyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acrylaldehyde

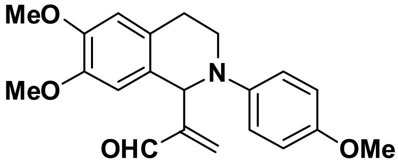


3j

Yellow oil, 91% yield. **^{1}H NMR** δ_H (600 MHz, cdcl$_3$) 9.64 (1 H, s), 7.23 (2 H, dd, *J* 8.6, 7.3), 7.11 (1 H, s), 7.04 (1 H, d, *J* 7.6), 7.00 (1 H, d, *J* 7.6), 6.83 (2 H, d, *J* 8.2), 6.76 (1 H, t, *J* 7.3), 6.22 (1 H, s), 6.06

(1 H, s), 5.76 (1 H, s), 3.72 (1 H, dt, *J* 11.2, 5.5), 3.52 – 3.42 (1 H, m), 3.00 (1 H, dt, *J* 15.4, 5.2), 2.91 (1 H, ddd, *J* 15.0, 6.9, 5.0). ^{13}**C NMR** δ_C (101 MHz, cdcl$_3$) 193.24, 151.17, 148.33, 135.71, 134.60, 134.18, 132.40, 128.99, 128.55, 127.82, 127.72, 117.68, 113.71, 77.32, 77.00, 76.68, 56.54, 43.22, 27.24, 21.00. **IR** (in KBr thin film): □ = 3447, 3023, 2915, 2837, 1689, 1597, 1502, 1382, 943, 749, 691 cm^{-1}. **HRMS** (MALDI)**:** m/z = 278.1546 ([M+H]+). Calcd for C19H19NO: ([M+H]+) 278.1539.

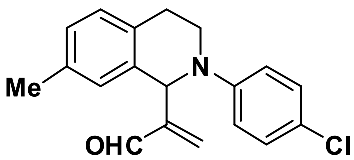
2-(6,7-dimethoxy-2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acrylaldehyde



3k

Yellow oil, 61% yield. ^{1}**H NMR**δ_H (400 MHz, CDCl$_3$) 9.62 (1 H, s), 6.97 – 6.75 (4 H, m), 6.63 (2 H, d, *J* 9.7), 6.08 (2 H, d, *J* 12.3), 5.61 (1 H, s), 3.86 (3 H, s), 3.82 (3 H, s), 3.75 (3 H, s), 3.55 (1 H, ddd, *J* 12.5, 7.8, 4.8), 3.47 – 3.35 (1 H, m), 2.93 (1 H, ddd, *J* 15.7, 7.8, 5.0), 2.75 (1 H, dt, *J* 15.8, 5.4). ^{13}**C NMR** δ_C (101 MHz, CDCl$_3$) 193.43, 152.81, 151.19, 147.73, 147.16, 143.20, 134.53, 127.51, 126.52, 117.23, 114.32, 110.81, 110.54, 56.67, 55.76, 55.68, 55.42, 43.52, 26.52. **IR** (in KBr thin film): □ = 3440, 2934, 2833, 1689, 1510, 1248, 1116, 1035, 785 cm^{-1}. **HRMS** (MALDI)**:** m/z = 354.1701 ([M+H]+). Calcd for C20H21NO3: ([M+H]+) 354.1700.

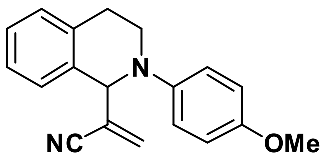
2-(2-(4-chlorophenyl)-7-methyl-1,2,3,4-tetrahydroisoquinolin-1-yl)acrylaldehyde



3l

Yellow oil, 81% yield. ^{1}**H NMR** δ_H (400 MHz, CDCl$_3$) 9.64 (1 H, s), 7.16 (2 H, d, *J* 8.9), 7.08 (1 H, s), 7.03 (2 H, q, *J* 7.8), 6.75 (2 H, d, *J* 9.0), 6.18 (1 H, s), 6.08 (1 H, s), 5.71 (1 H, s), 3.67 (1 H, dt, *J* 11.5, 5.7), 3.52 – 3.39 (1 H, m), 2.99 (1 H, dt, *J* 15.4, 5.3), 2.93 – 2.81 (1 H, m), 2.29 (3 H, s). ^{13}**C NMR**δ_C (101 MHz, CDCl$_3$) 193.22, 150.86, 146.96, 135.89, 134.52, 134.22, 132.18, 128.79, 128.55, 128.02, 127.87, 122.46, 114.92, 56.56, 43.18, 26.98, 21.03. **IR** (in KBr thin film): □ = 3447, 3045, 2916, 2839, 1690, 1594, 1496, 1383, 944, 812 cm^{-1}. **HRMS** (MALDI)**:** m/z = 312.1149 ([M+H]+). Calcd for C19H18ClNO: ([M+H]+) 312.1150.

2-(2-(4-methoxyphenyl)-1,2,3,4-tetrahydroisoquinolin-1-yl)acrylonitrile



3m

Yellow oil, 65% yield. ^{1}**H NMR**δ_H (400 MHz, cdcl$_3$) 7.33 – 7.22 (1 H, m), 7.20 (1 H, s), 6.91 (1 H, d, *J* 9.1), 6.85 (1 H, d, *J* 9.1), 5.95 (1 H, s), 5.74 (0 H, s), 5.14 (1 H, s), 3.77 (2 H, s), 3.69 – 3.56 (1 H, m), 3.42 (1 H, dt, *J* 11.9, 5.9), 2.96 (1 H, d, *J* 4.9). ^{13}**C NMR** δ_C (101 MHz, cdcl$_3$) 153.68, 143.02, 135.66, 132.45, 130.97, 128.62, 127.79, 127.69, 126.32, 125.59, 118.35, 117.95, 114.49, 77.31, 77.00, 76.68, 63.68, 55.46, 44.69, 27.91. **IR** (in KBr thin film): □ = 2932, 2833, 2221, 1616, 1511, 1464, 1244, 1036, 945, 815, 756 cm^{-1}. **MS** (EI)**:** m/z = 290.27.

Reference:

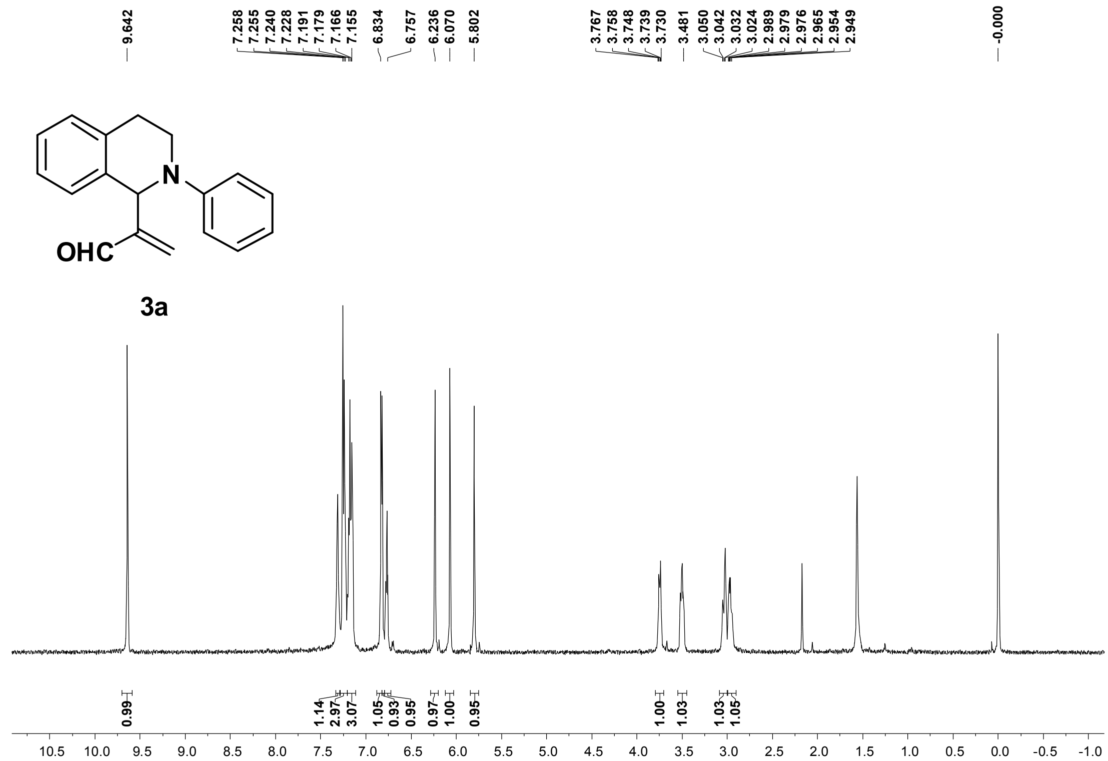
1. Z. Li, D. S. Bohle and C.-J. Li, *P. N. A. S.,* 2006, **103**, 8928.

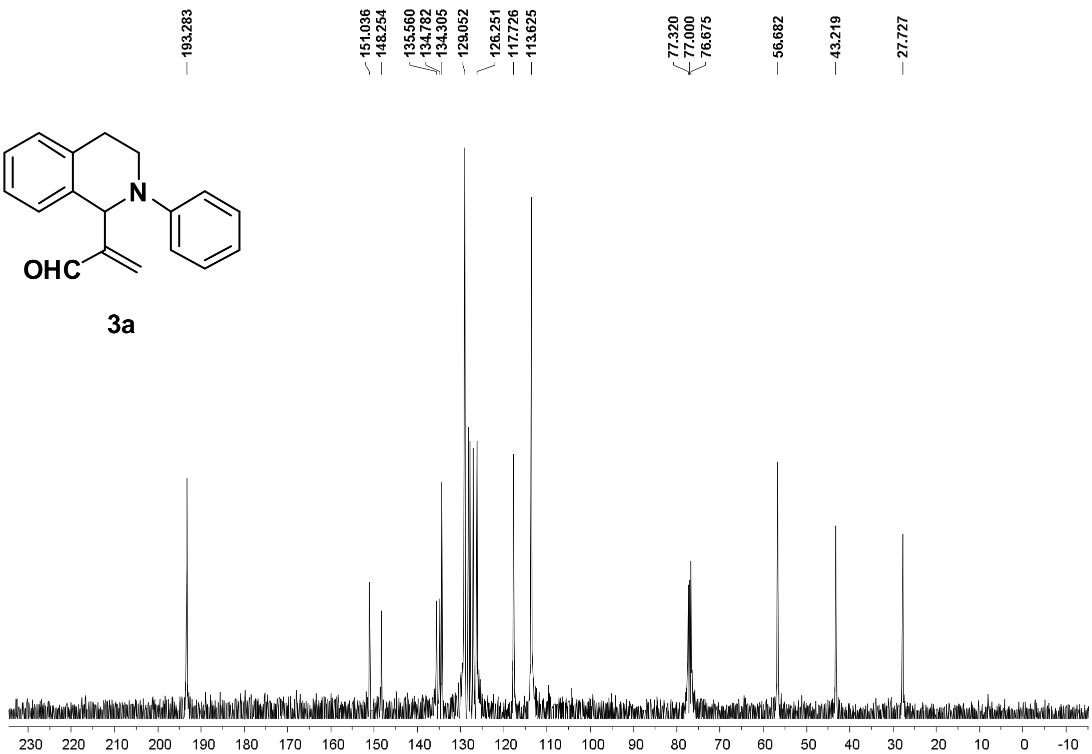
2. G. Zhang, Y. Ma, S. Wang, Y. Zhang and R. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 12334.

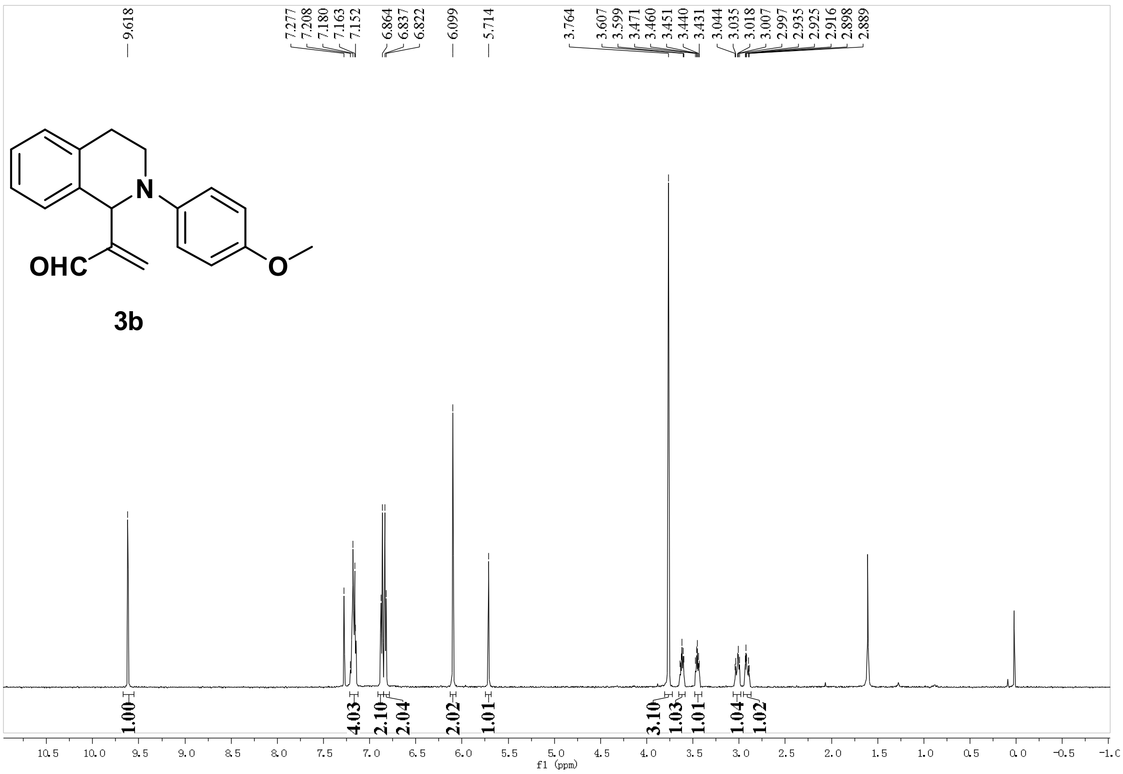
3. Y. Iwabuchi, M.i Nakatani, N. Yokoyama and S. Hatakeyama, *J. Am. Chem. Soc.*, 1999, **121**, 10219.

4. G. Zhang, Y. Ma, S. Wang, Y. Zhang, and R. Wang, *J. Am. Chem. Soc*., 2012, **134**, 12334.

6. Copies of ^{1}H NMR, ^{13}C NMR Spectra



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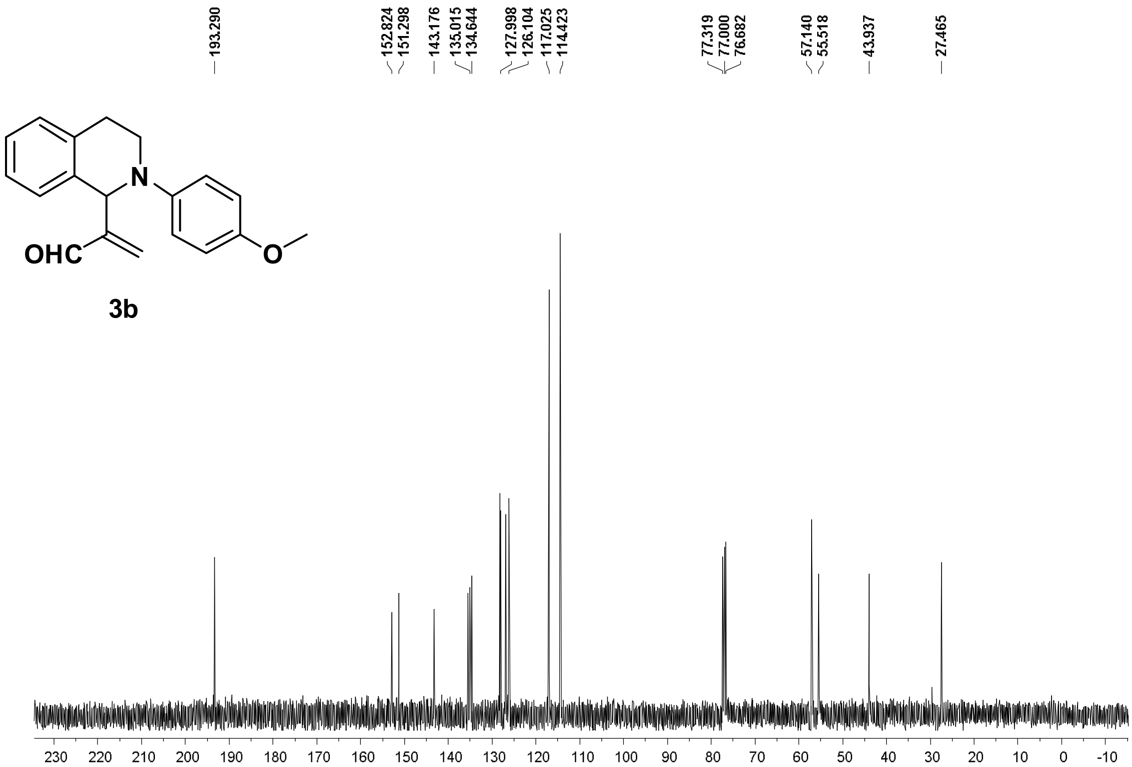
f1 (ppm)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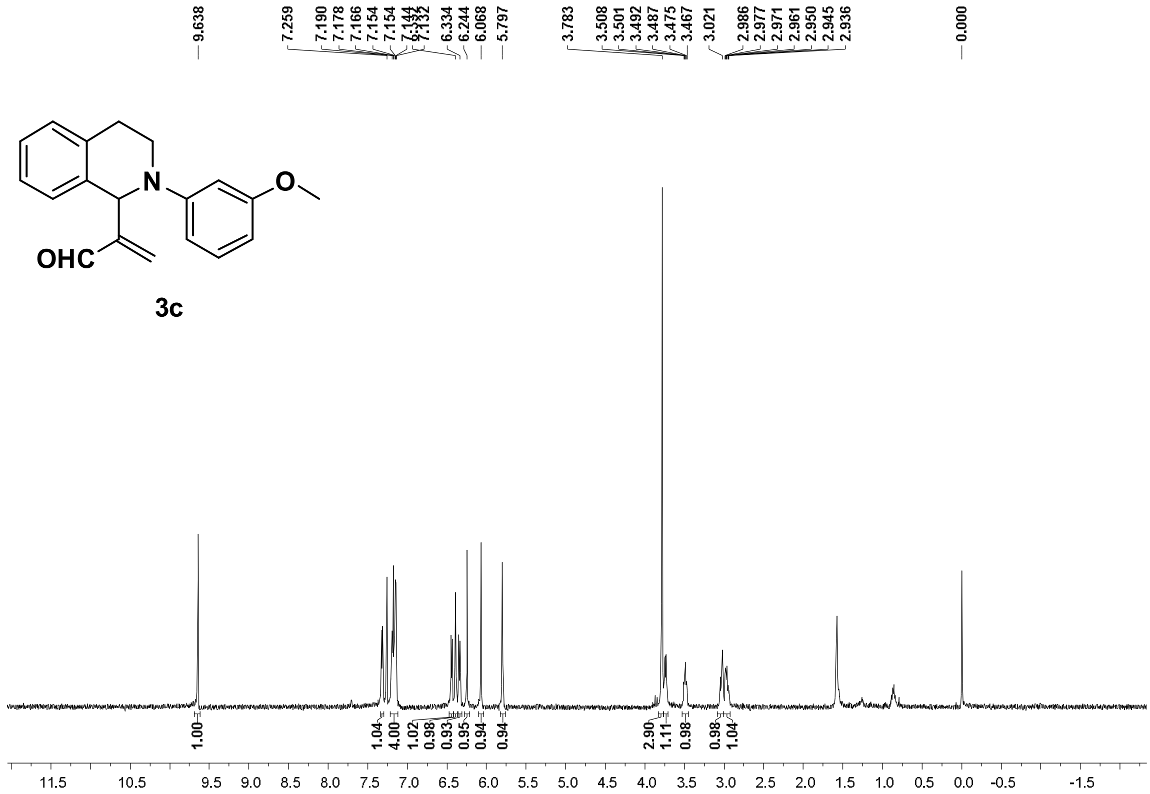
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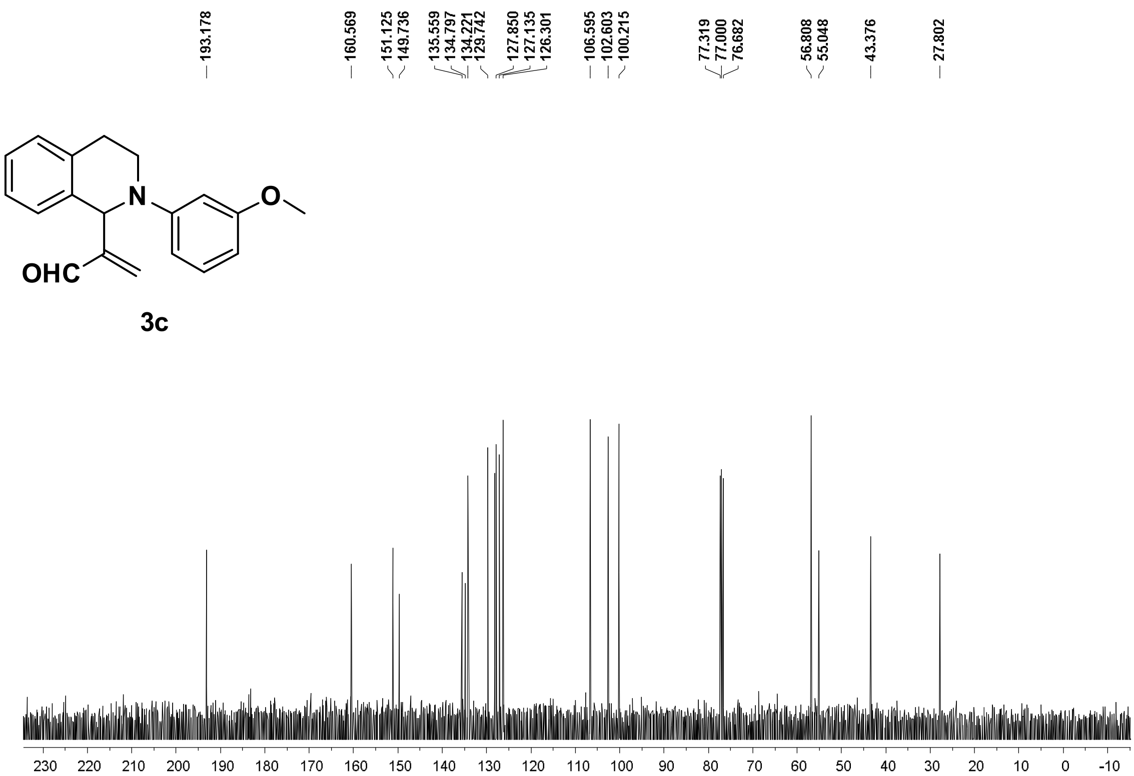
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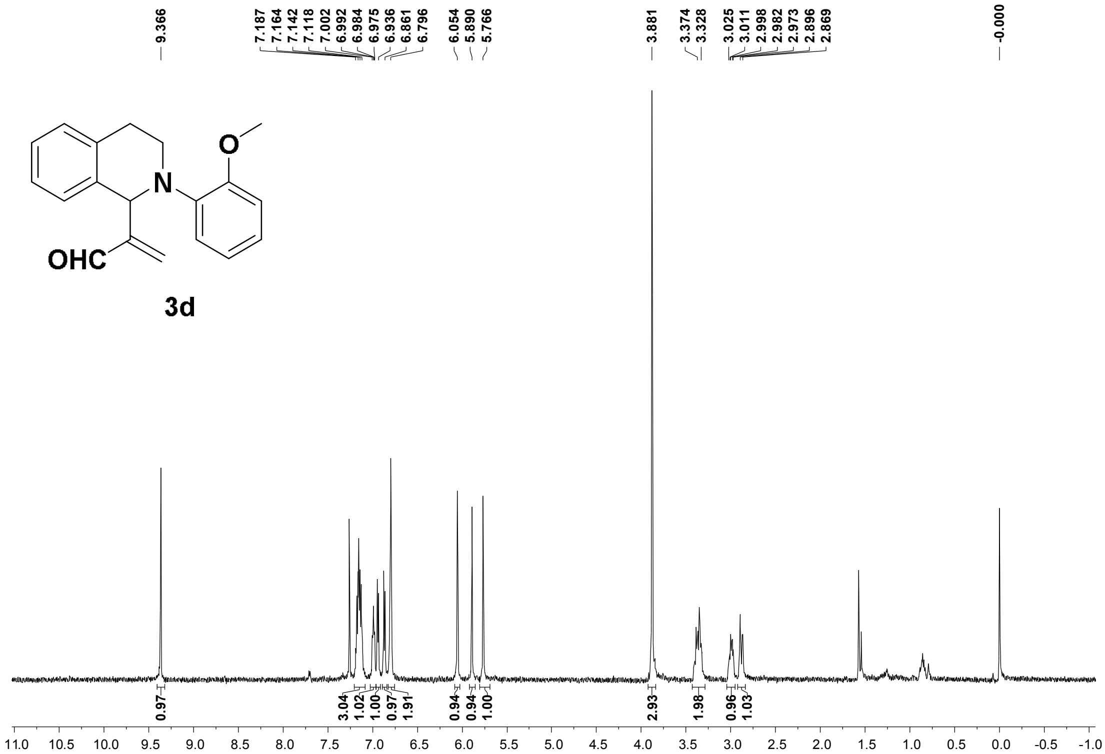
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1.03
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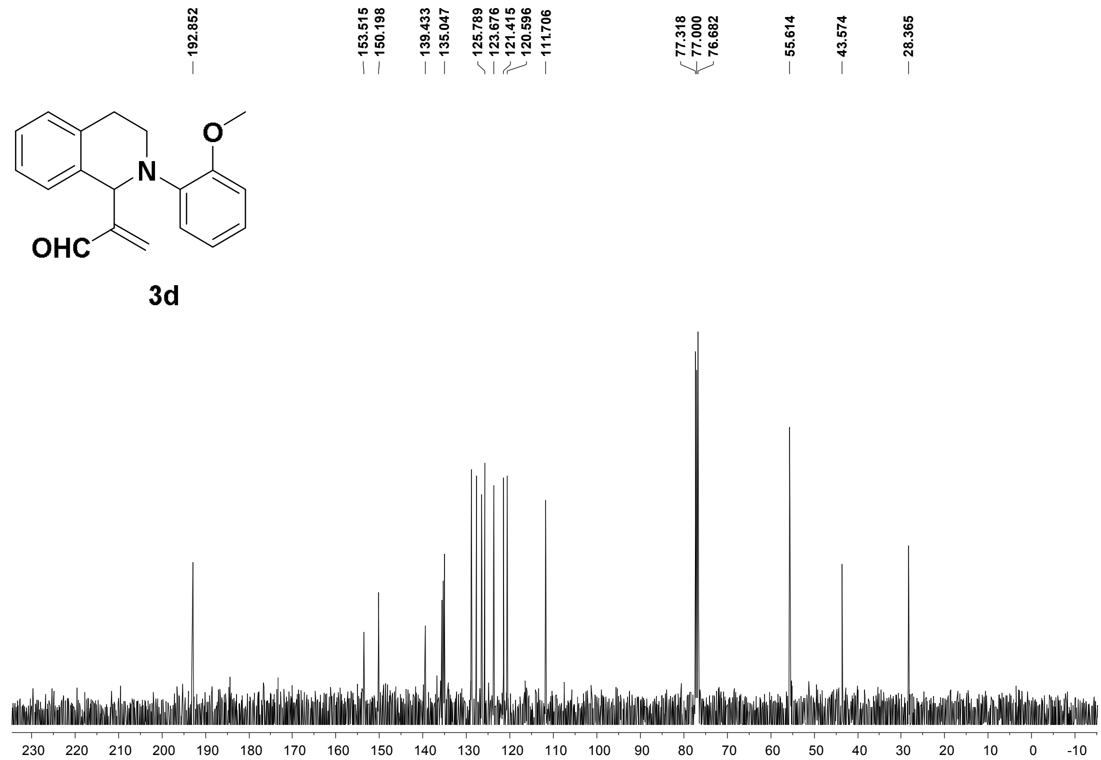
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43.574
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3d
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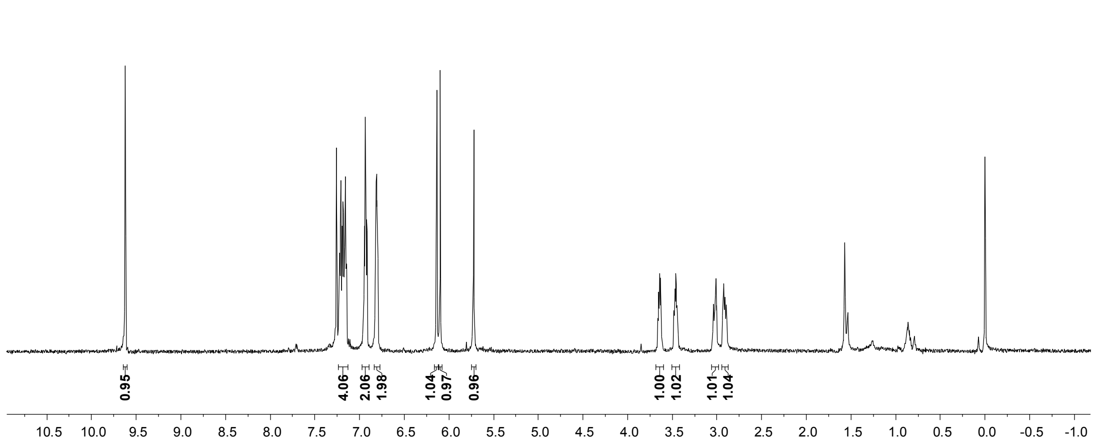
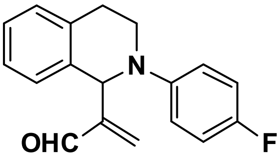
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry





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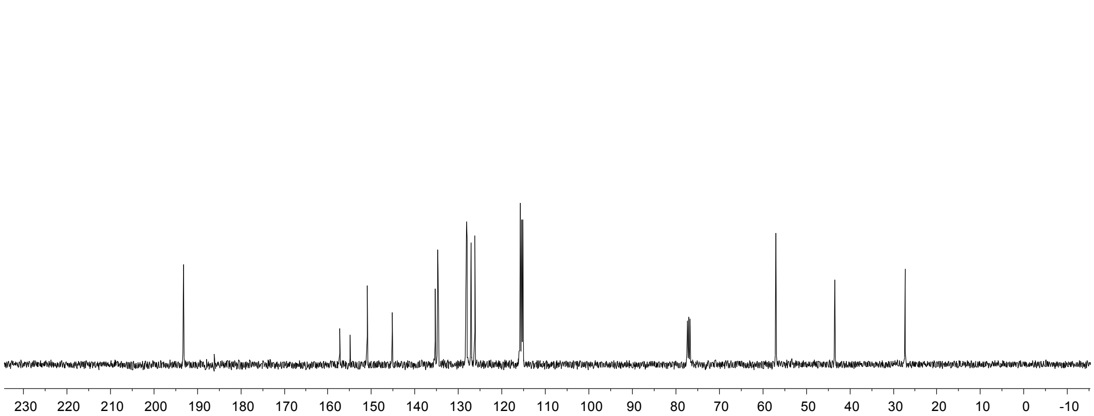

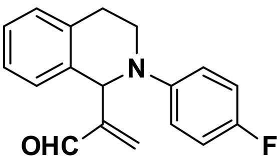

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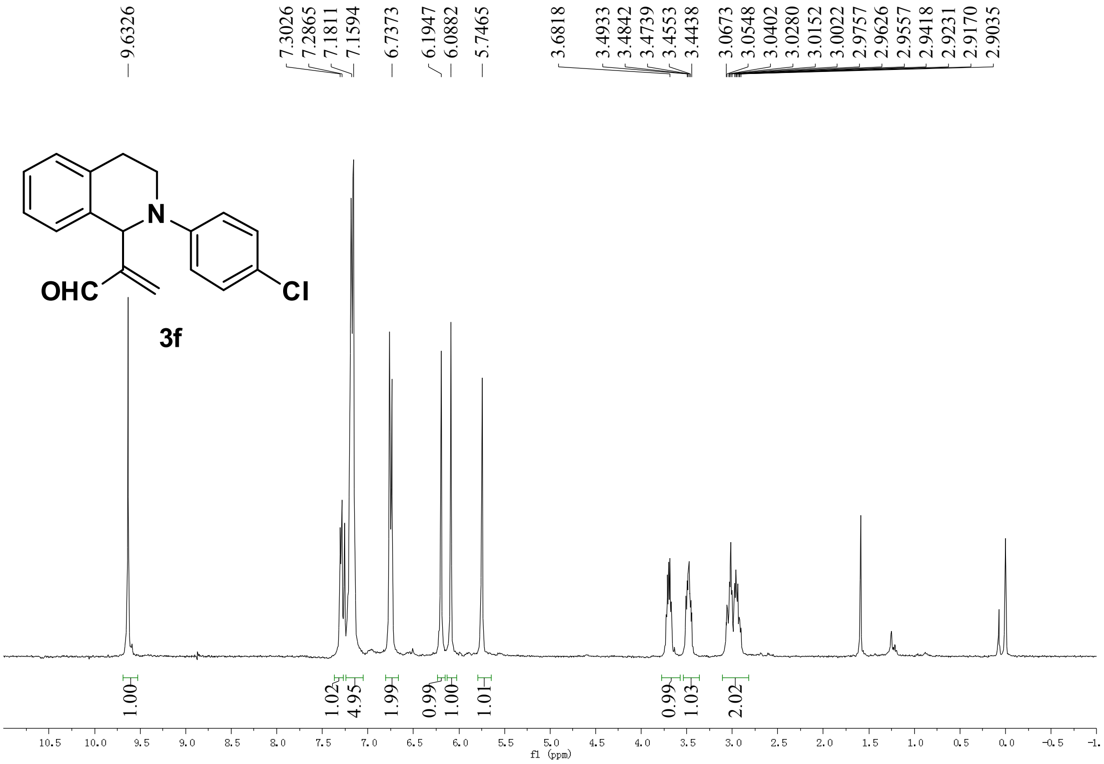
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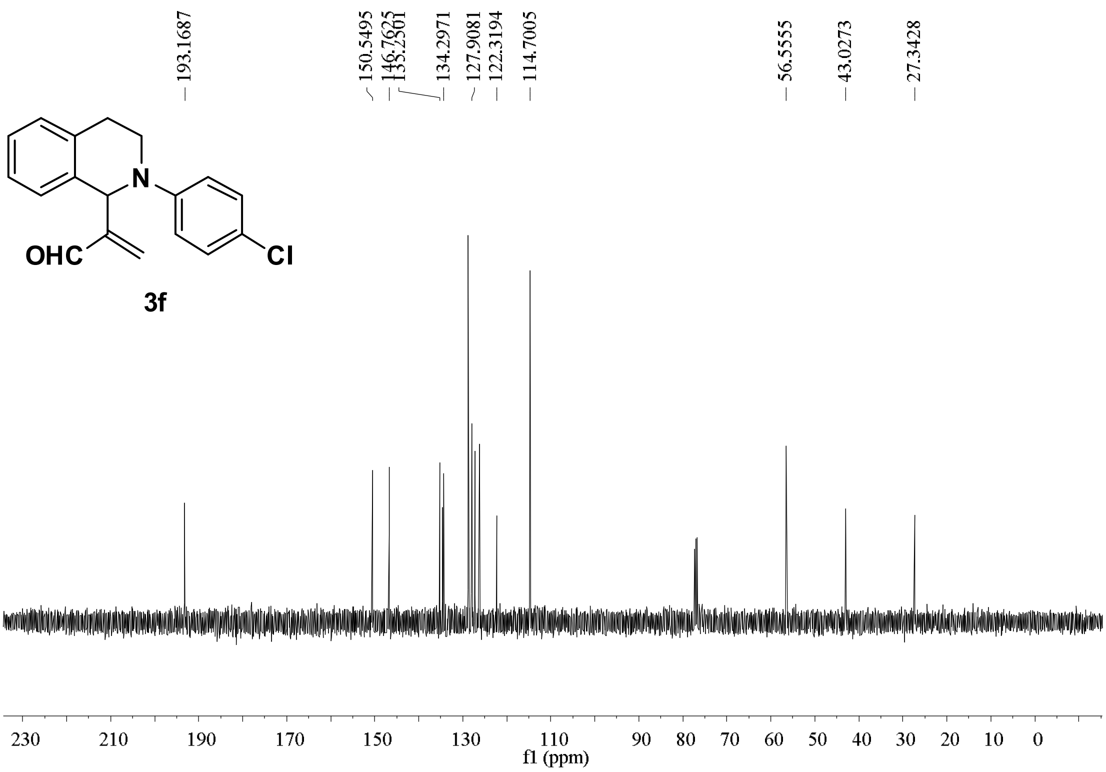
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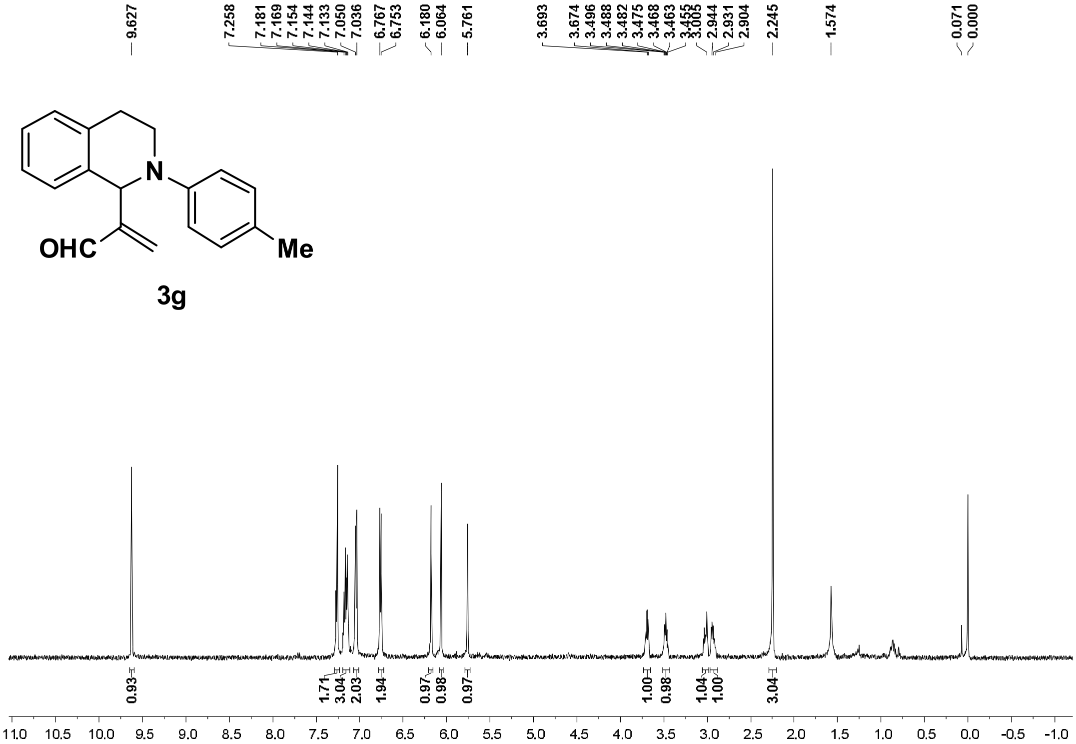
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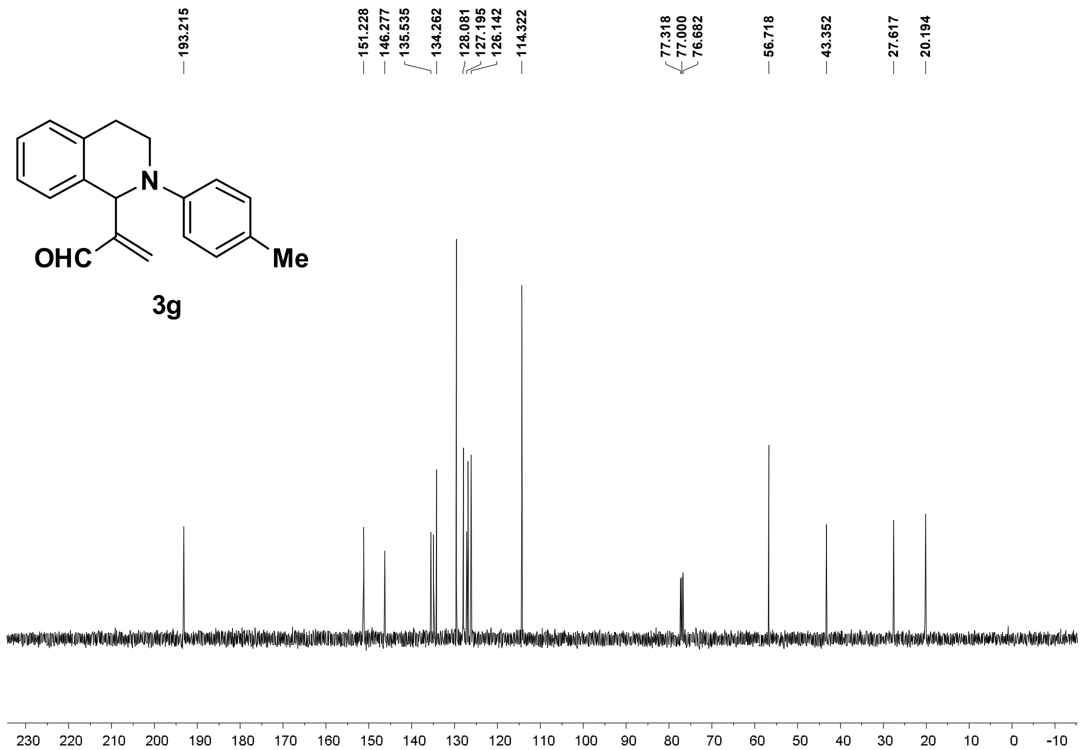
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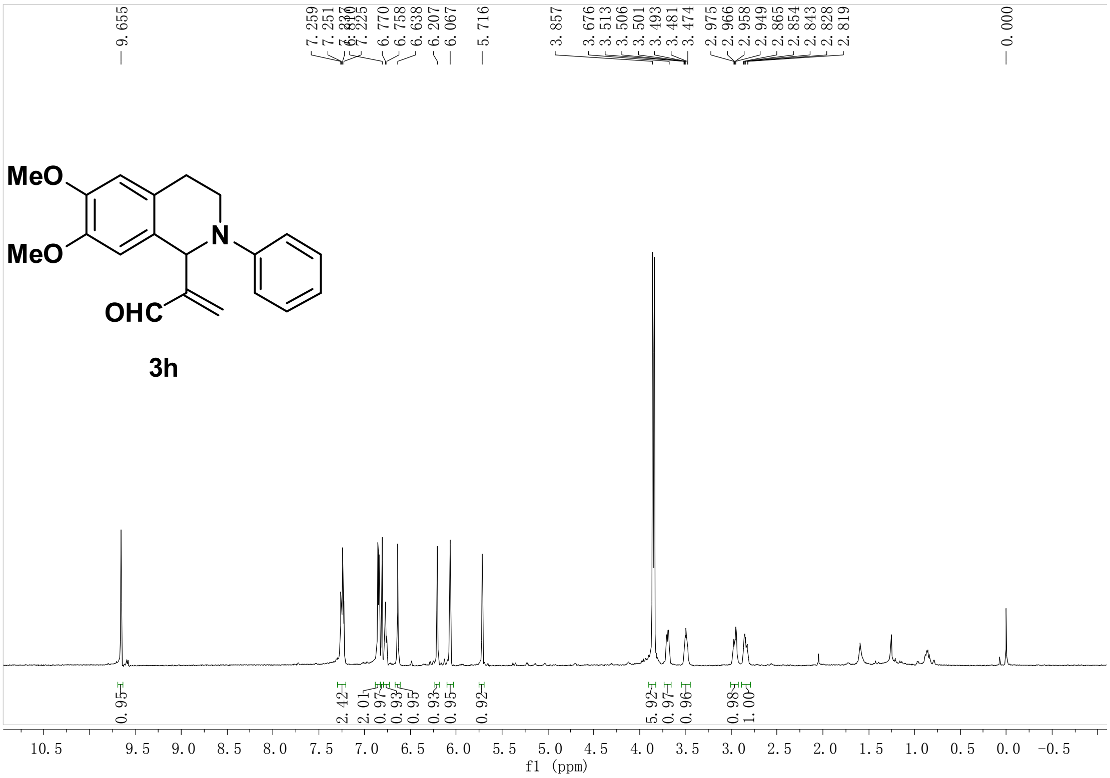
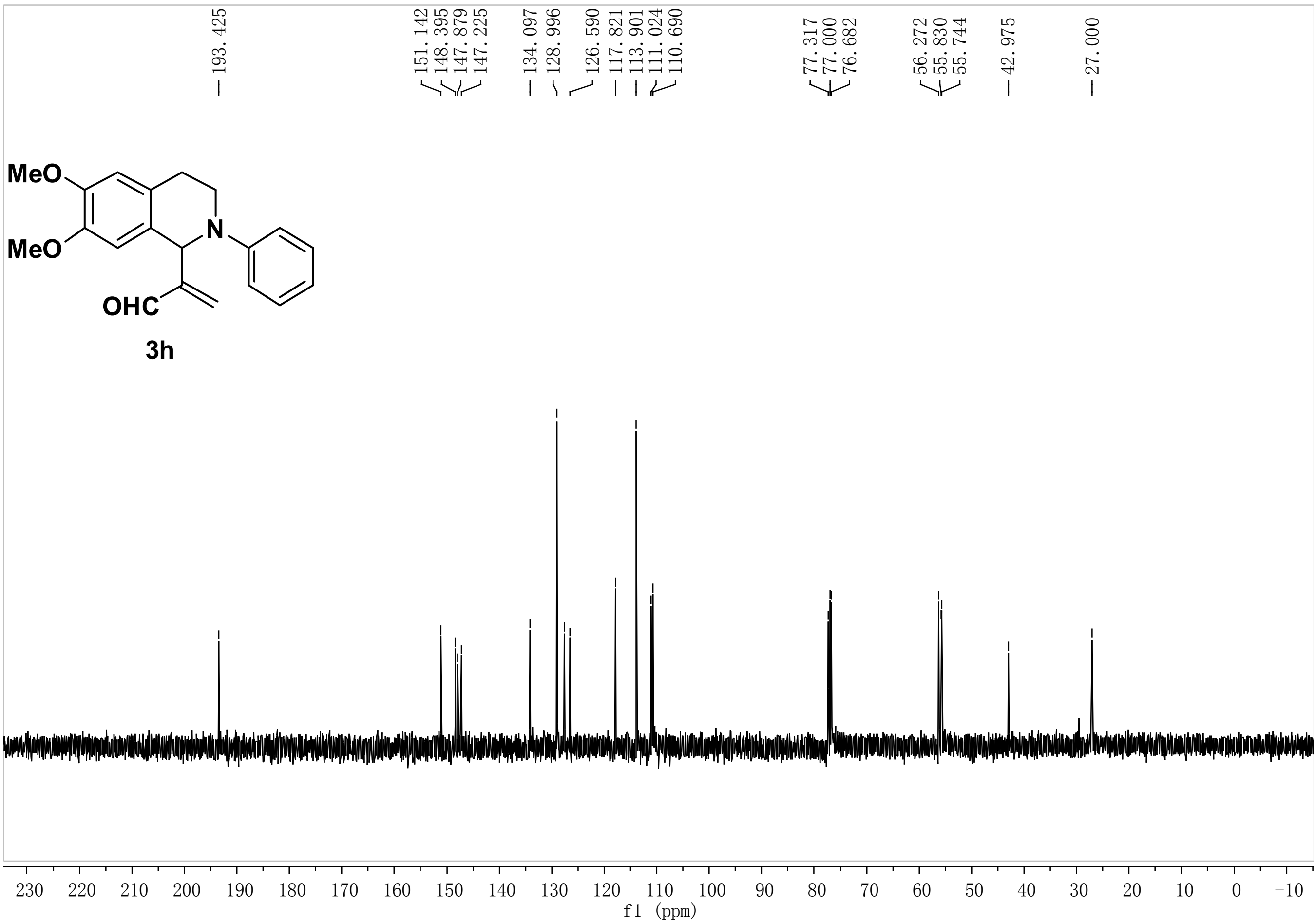
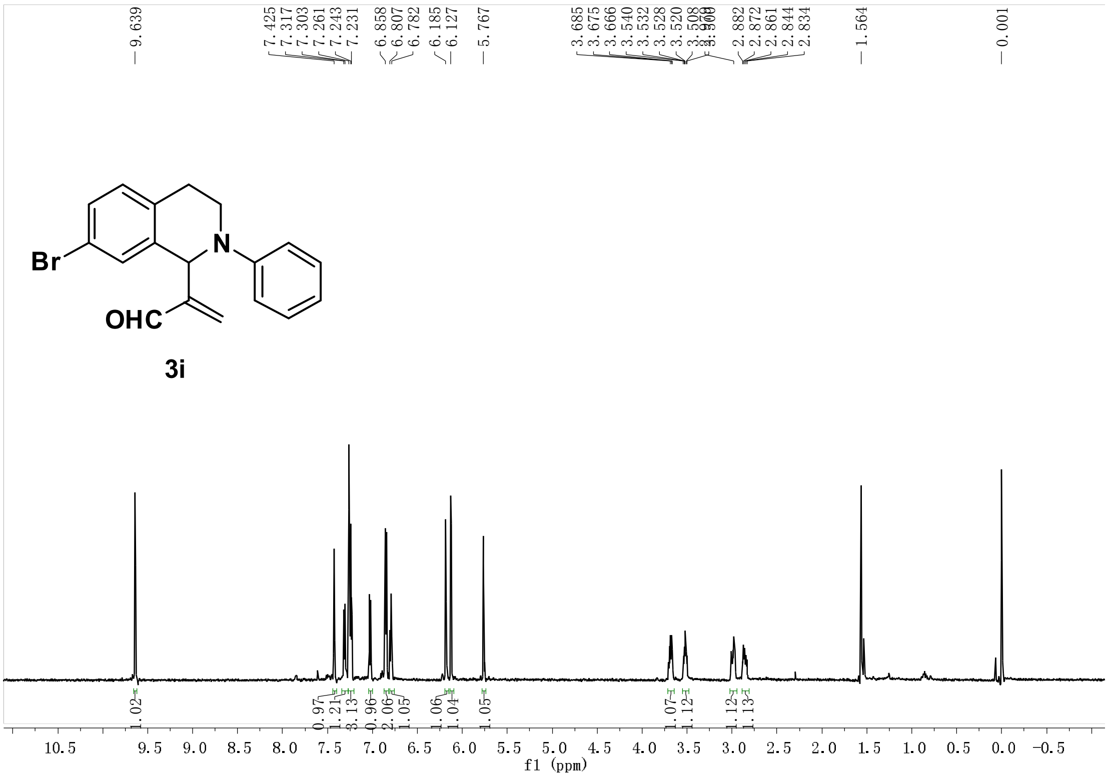
Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



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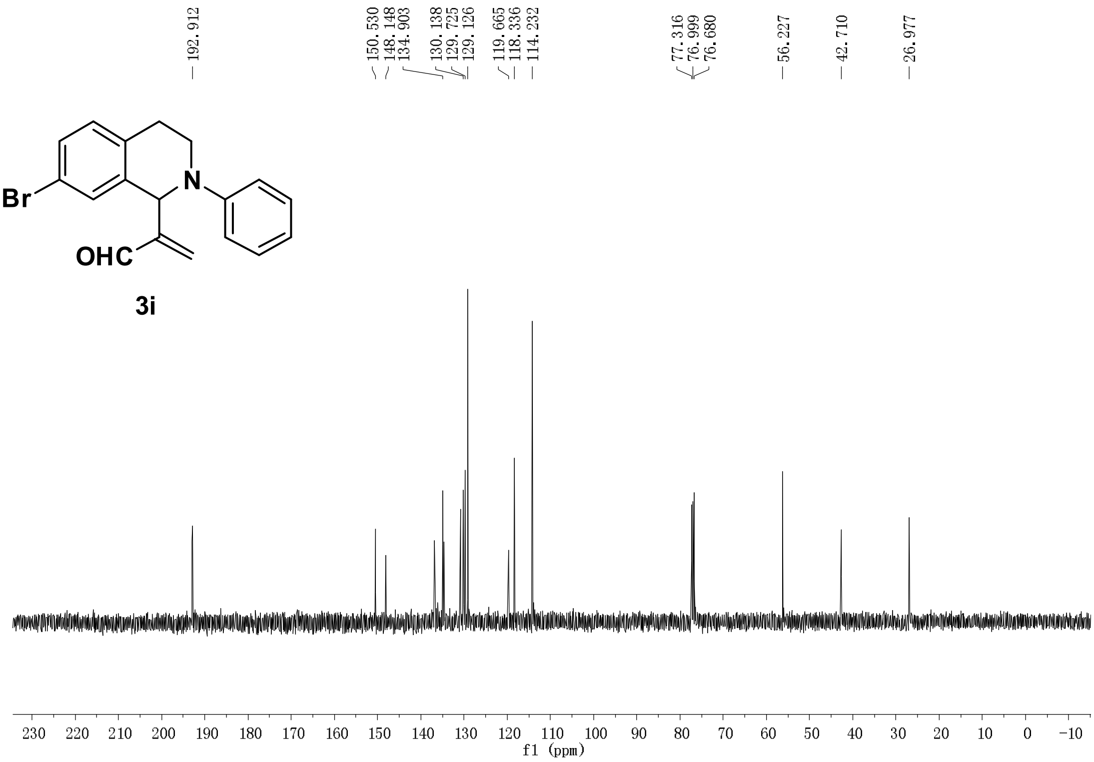
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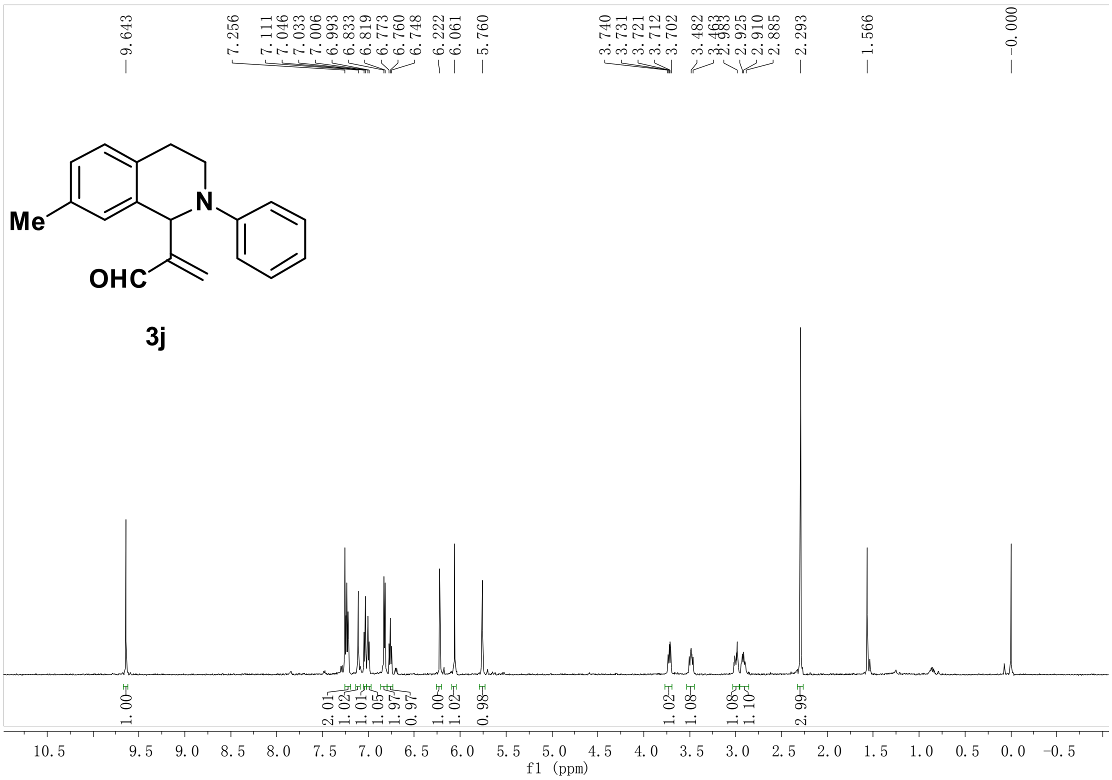
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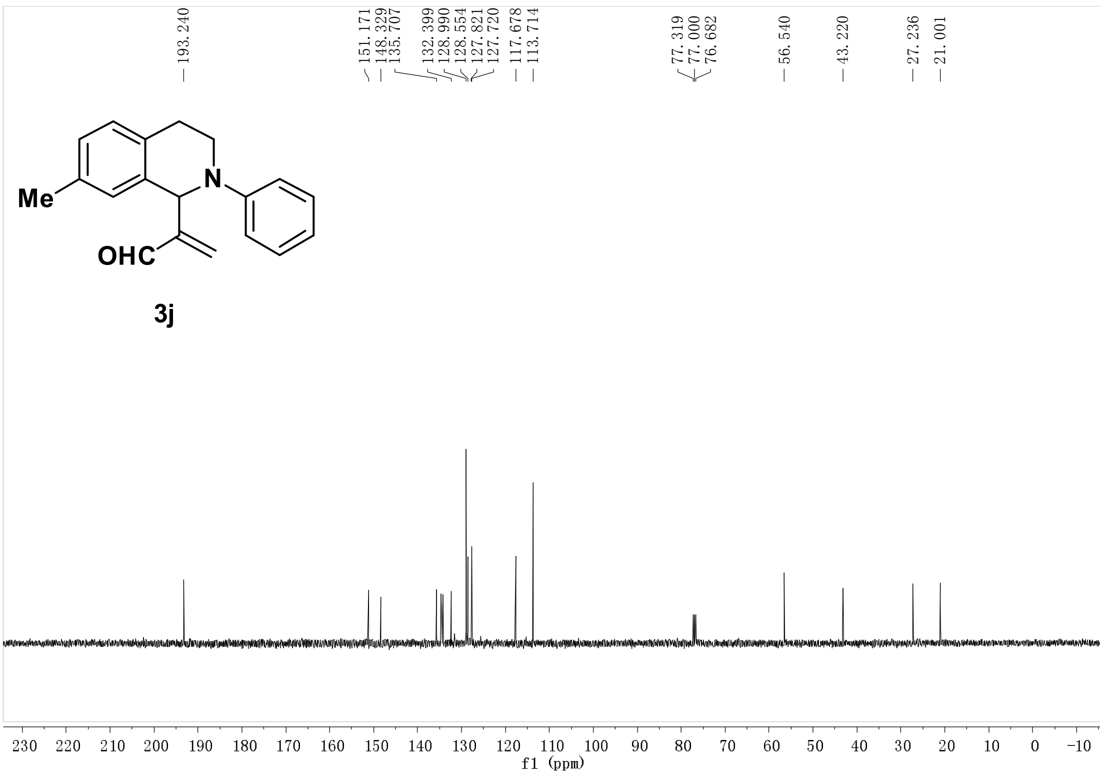
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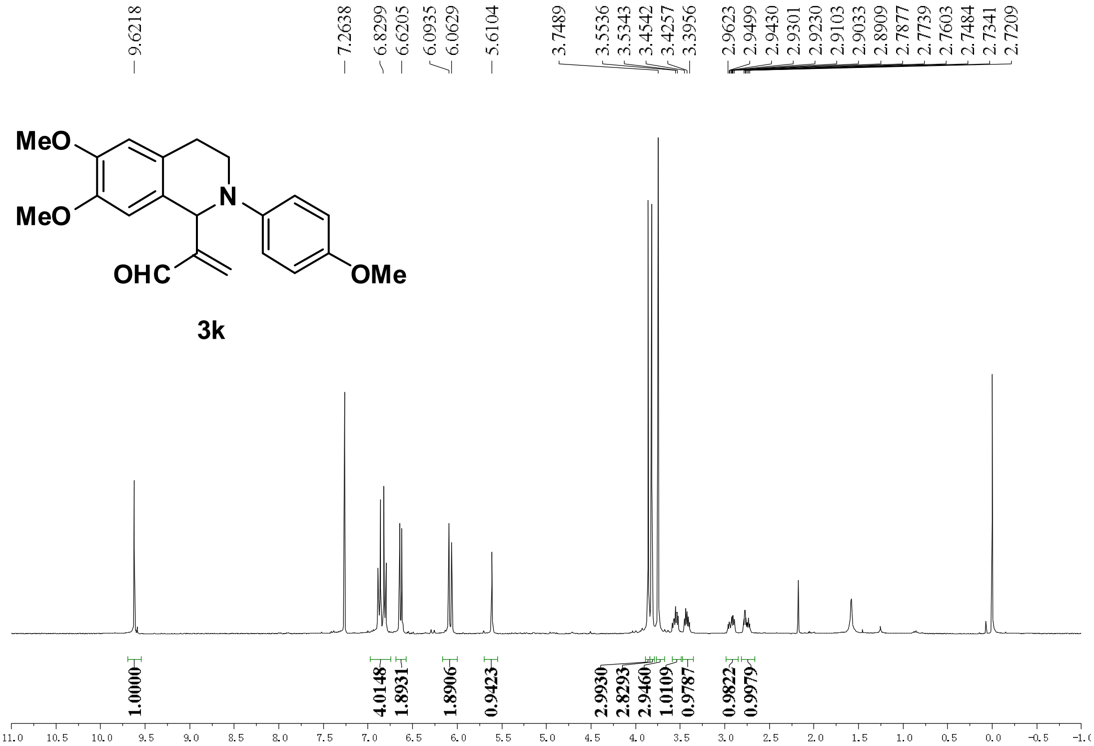
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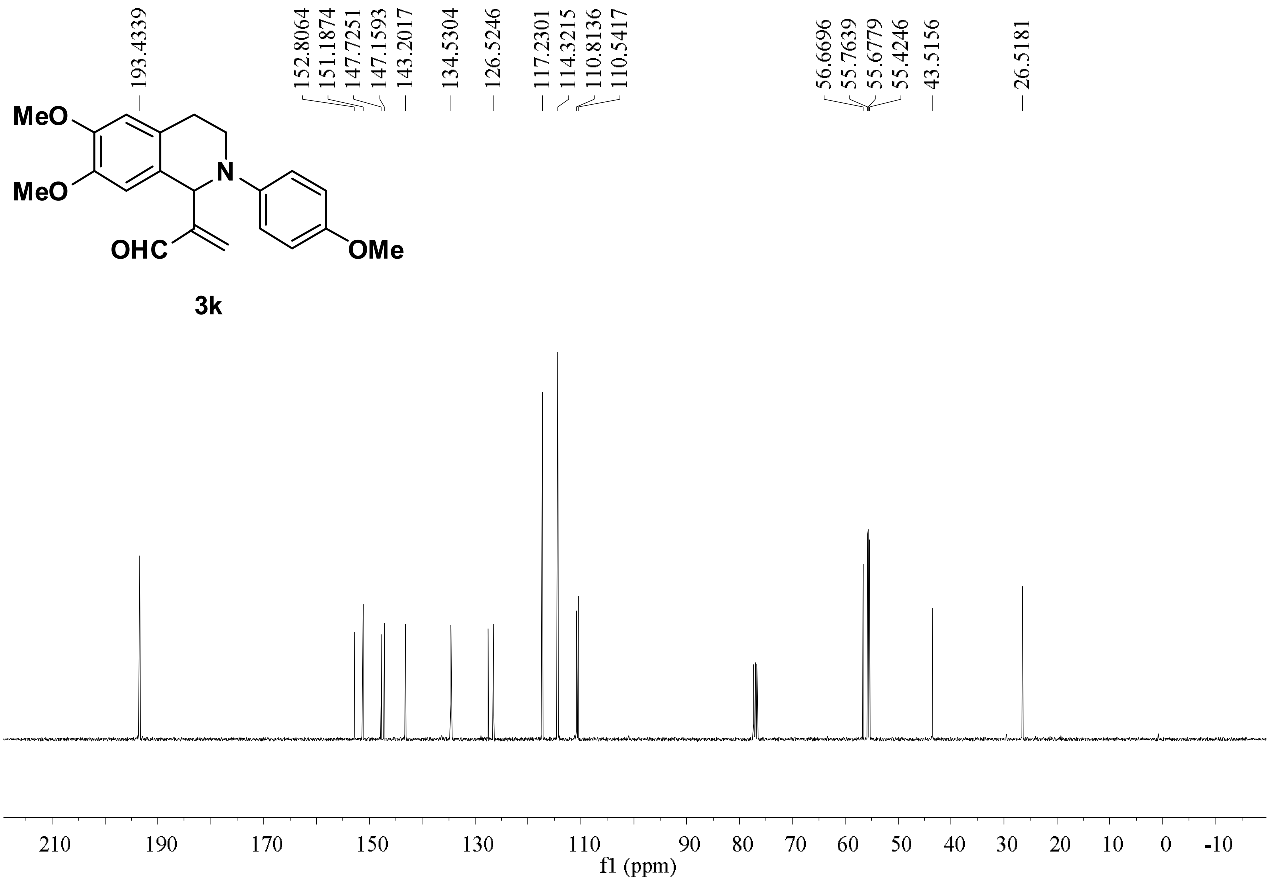
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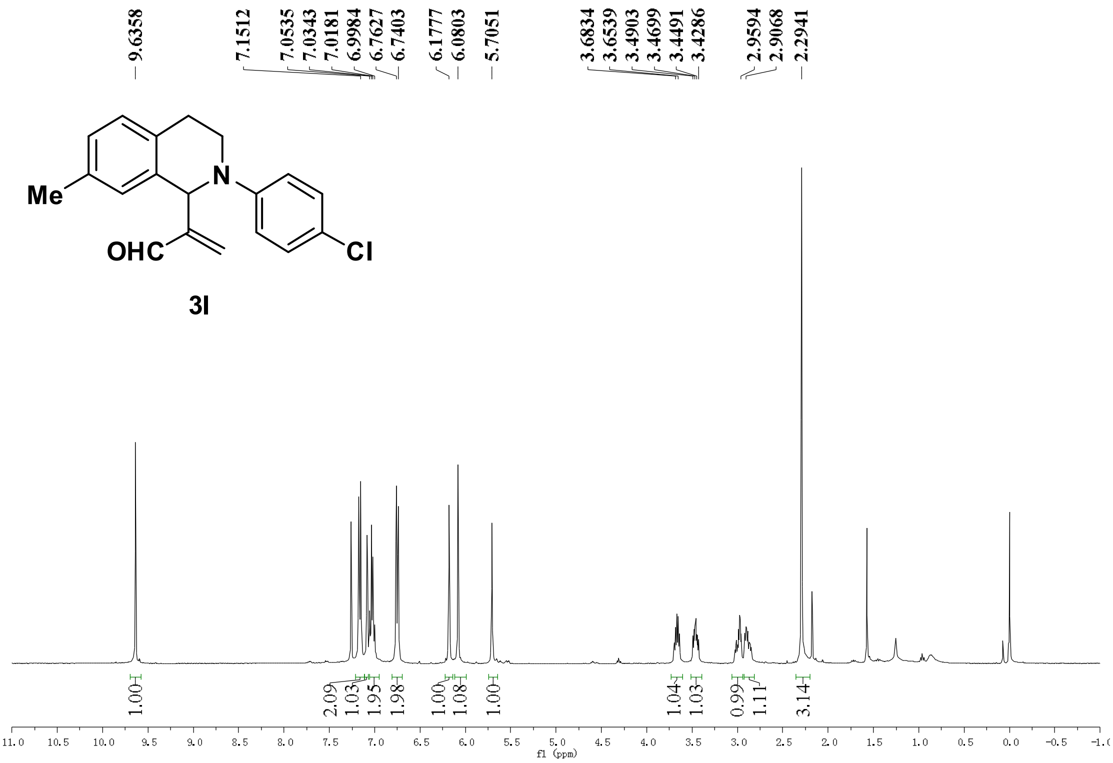
f1 (ppm)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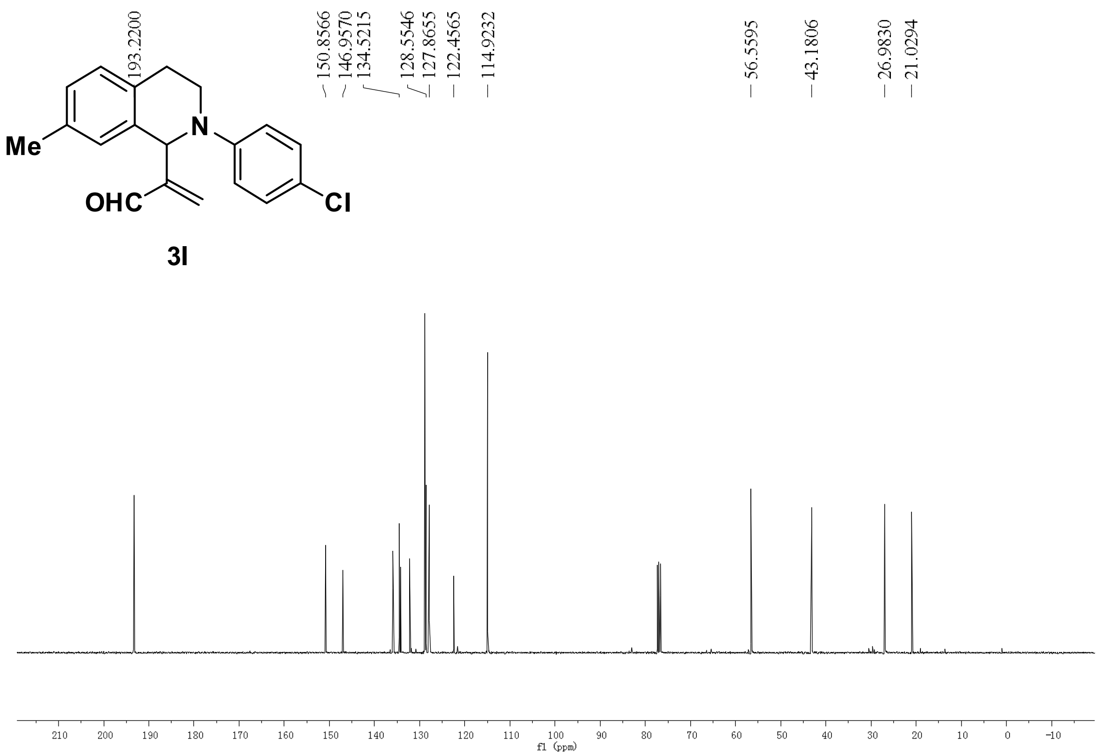
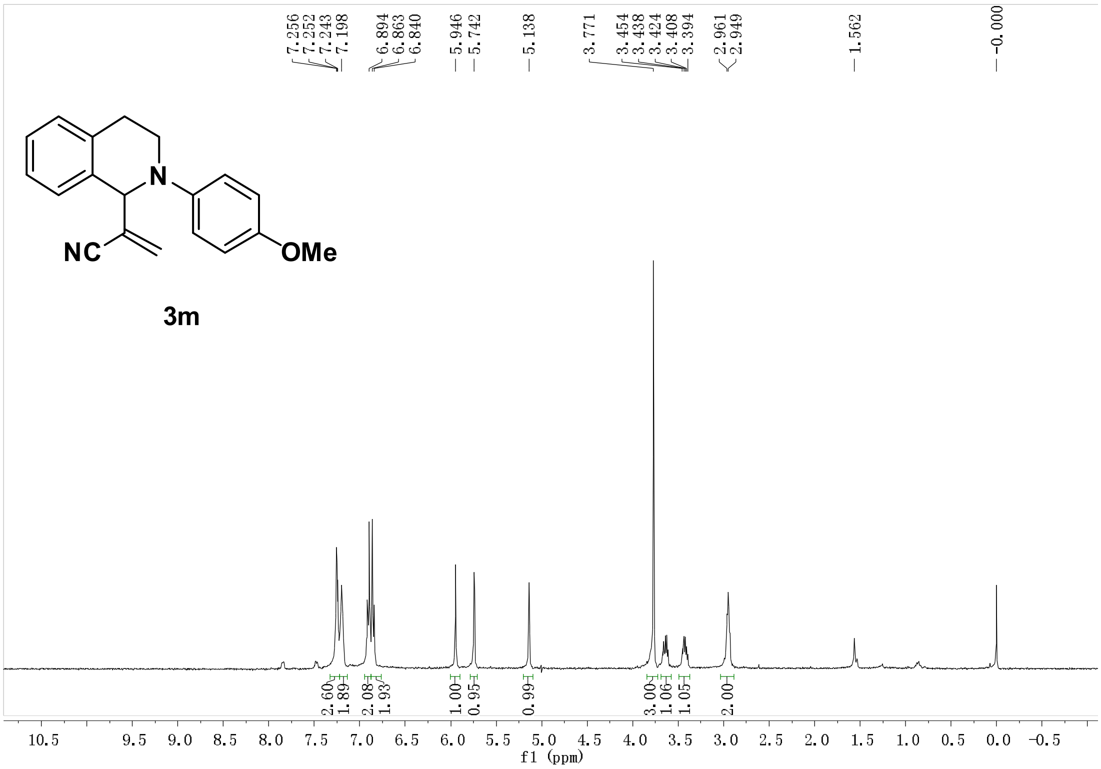
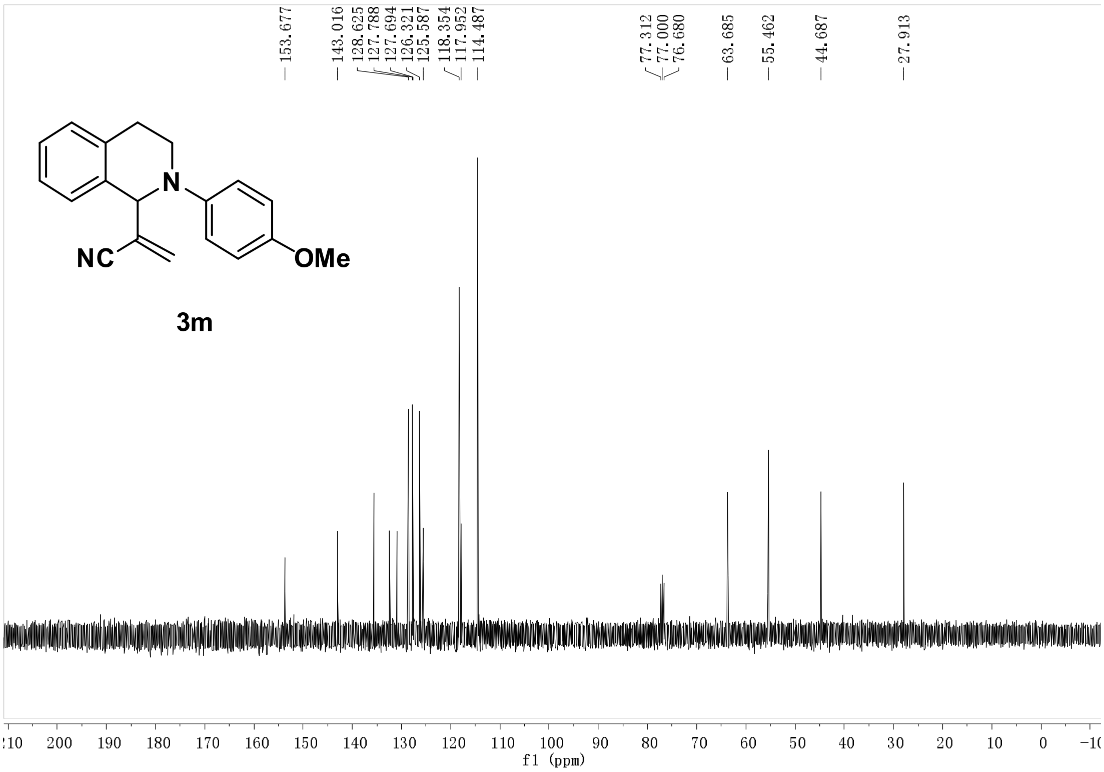
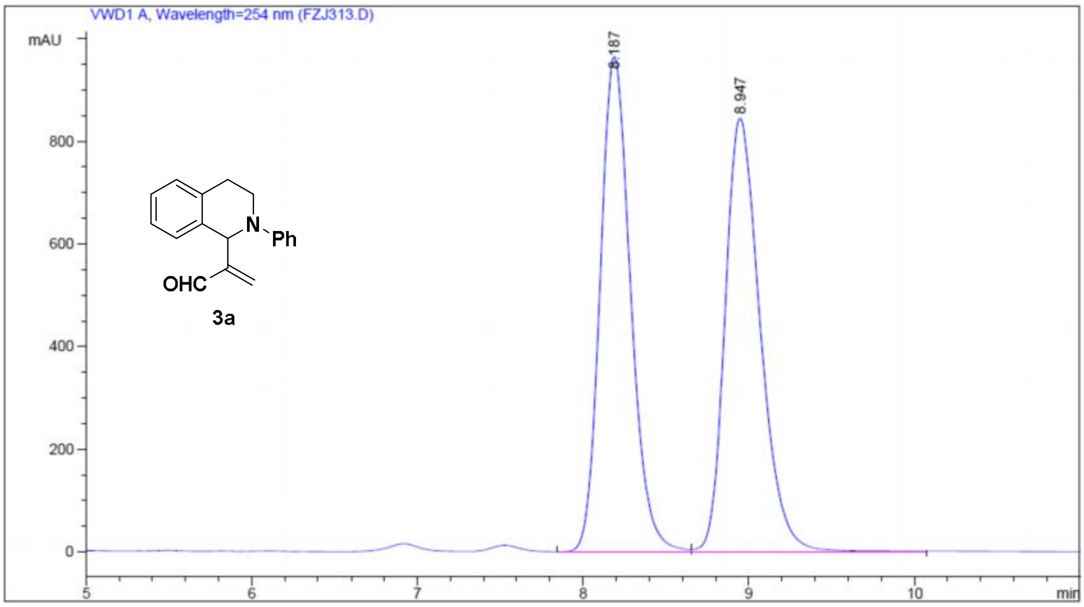
1.03
0.99
1.11
3.14
f1 (ppm)


193.2200
150.8566
146.9570
134.5215
128.5546
127.8655
122.4565
114.9232
56.5595
43.1806
26.9830
21.0294
Me
N
OHC
Cl
3l
f1 (ppm)

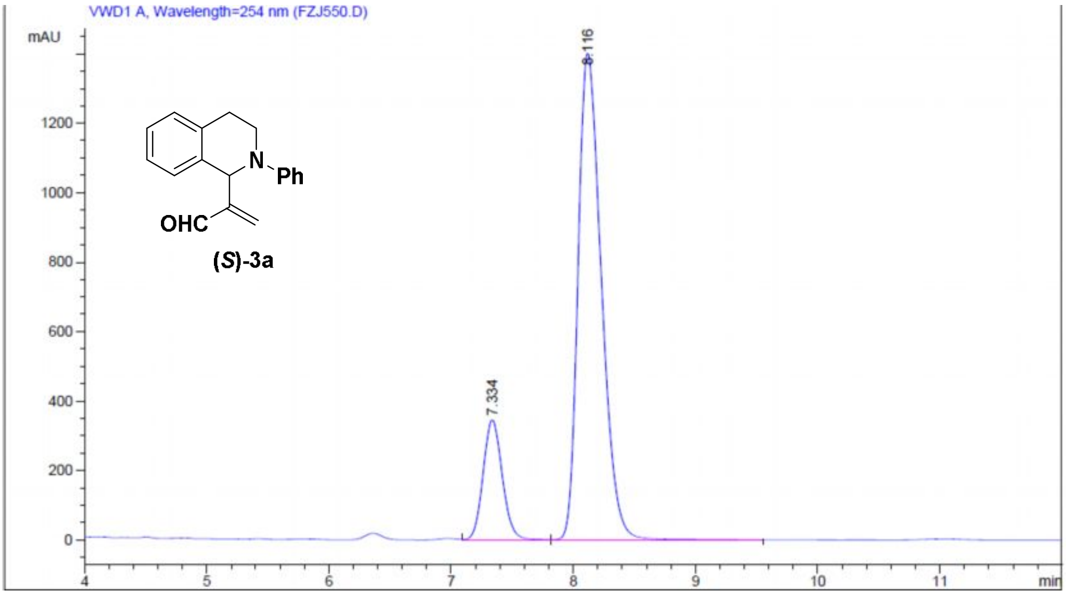

3m
7.256
7.252
7.243
7.198
6.894
6.863
6.840
5.946
5.742
5.138
3.771
3.454
3.438
3.424
3.408
3.394
2.961
2.949
1.562
-0.000
2.60
1.89
2.08
1.93
1.00
0.95
0.99
3.00
1.06
1.05
2.00
f1 (ppm)


3m
153.677
143.016
128.625
127.788
127.694
126.321
125.587
118.354
117.952
114.487
77.312
77.000
76.680
63.685
55.462
44.687
27.913
f1 (ppm)

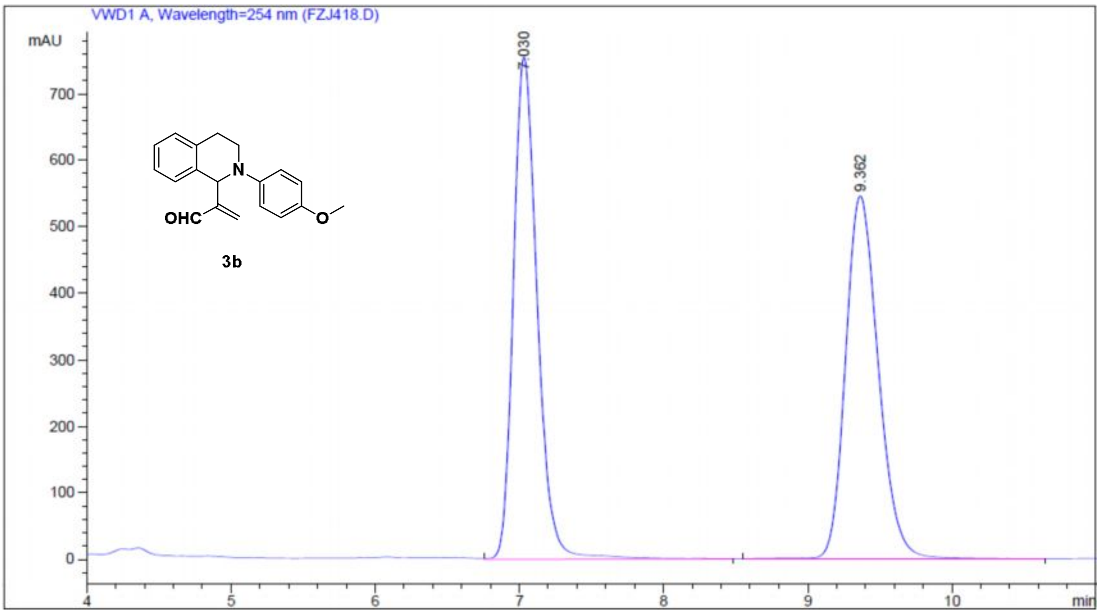
7. HPLC Data of Products 3a and 3b



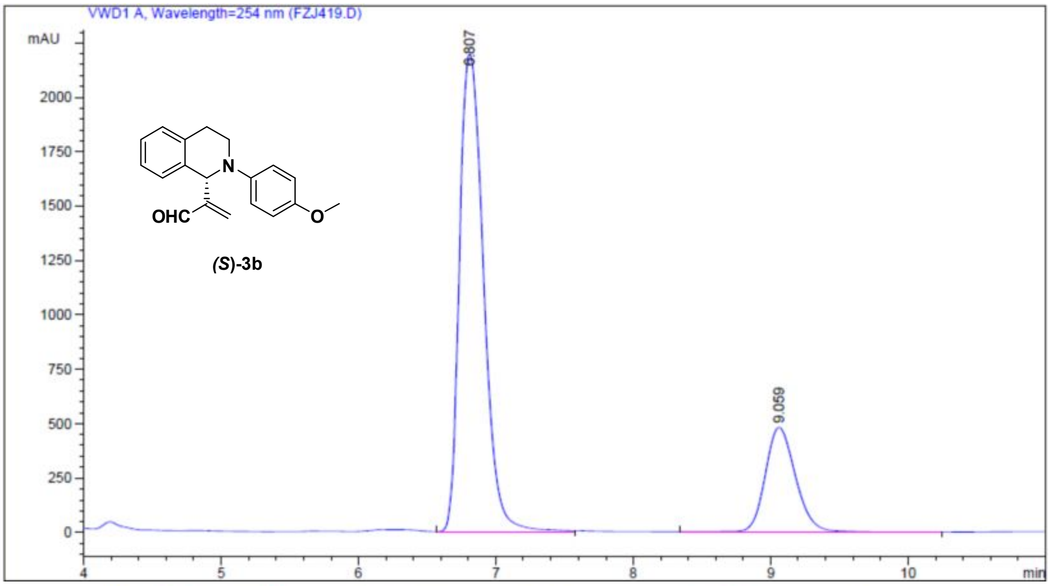
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	8.187	VV	0.1985	1.23172e4	964.14807	49.7078
2	8.947	VB	0.2274	1.24620e4	844.69696	50.2922



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.334	VV	0.1725	3825.25098	346.55032	17.0014
2	8.116	VB	0.2049	1.86743e4	1402.23975	82.9986



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.091	BV	0.1490	3354.80762	352.29385	49.9402
2	8.912	BV	0.2435	3362.84131	215.17610	50.0598



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.807	VV	0.1945	2.70648e4	2199.86597	77.7128
2	9.059	VV	0.2454	7761.90088	483.92703	22.2872