Supporting Information

Photocatalytic hydrogen-evolution of 1-tetralones to α-naphthols by continuous-flow technology

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Contents

1. General information

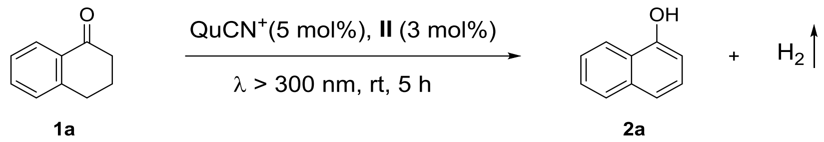
All reagents and solvents were commercial available unless individually noted. $Co(dmgH)_2PyCl$ (**III**) was purchased from Acros. Quinolinium photocatalysts[1] and other cobaloxime catalysts[2] were prepared as previously reported. 500 W medium pressure Hanovia mercury lamp with a glass water cooling jacket (λ > 300 nm) was used as light source (please pay attention to the eye protection). The products were isolated by silica column chromatograph (200-300 meshes silica gel). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded using a Bruker Advance DPX instrument (400, 101 and 377 MHz, respectively) with tetramethylsilane (TMS) as an internal standard. Data for ^{1}H NMR are presented as follows: chemical shift (ppm), multiplicity (s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, br = broad), coupling constant *J* (Hz) and integration. Data for ^{13}C NMR and ^{19}F NMR was reported in terms of chemical shift relative to different deuterium reagents. Mass spectra were recorded using a Trio-2000 GC-MS spectrometer. The generated photoproduct of H_2 was characterized and measured by GC analysis (14B Shimadzu) using argon as the carrier gas with a molecular sieve column (5 Å; 30 m × 0.53 mm) and a thermal conductivity detector (TCD). Methane was used as internal standard for the measurement of the yield of H_2. GC analysis was performed using N_2 as the carrier gas with capillary column (30 m × 0.25 mm × 0.33 μm) and a flame ionization detector (FID) using *n*-tetradecane as internal standard. Conversions and yields that were determined by ^{1}H NMR were obtained from the crude reaction mixture by using *n*-tetradecane as an internal standard. Yields of products were based on the consumed substrates. UV-Vis absorption and luminescent quenching was performed on U-3900, F-4600 and LP-920. Cyclic voltammetry was performed on a CHI660E.

2. Experimental procedures

2.1 The lab-scale experiment conditions

$QuCN^+$ (1×10^{-2} mmol, 2.69 mg) and $Co(dmgBF_2)_2(CH_3CN)_2$ (**II**) (6×10^{-3} mmol. 2.8 mg) were dissolved in different solvents and the reaction tube was sealed. After degassing by the argon, 1-tetralone (0.2 mmol, 27 μL) and $BF_3\cdot Et_2O$ (4×10^{-2} mmol, 5 μL) were added. Methane (1mL) was then injected as the internal standard for analysis of generated H_2, and the pinholes were sealed by paraffin. The reaction mixture was irradiation at room temperature using a 500 W medium pressure Hanovia mercury lamp with a glass water cooling jacket (λ > 300 nm). After 5 h irradiation, yield of H_2 was detected by GC-TCD. The conversion of 1-tetralone and yield of 1-naphathol (based on consumed 1-tetralone) were obtained from the crude reaction mixture by GC-FID using *n*-tetradecane as an internal standard.

Table S1. Optimization of solvents for the reaction condition

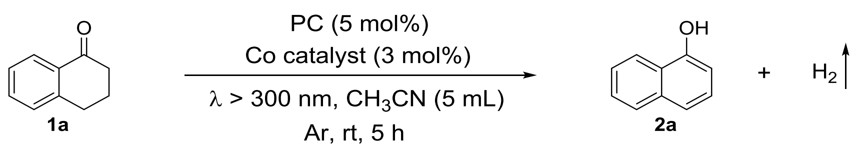


entry	solvent (5 mL)	conv. **1a** (%)	Yield **2a** (%)[a]
1	DCE	54	70
2	DCM	43	46
3	EtOH	n.d.	—
4	Acetone	66	49
5	DMF	n.d.	—
6	DMSO	n.d.	—
7	H_2O	n.d.	—
8	CH_3CN	63	70

[a] Yields of **2a** were based on the consumed **1a**.

Photocatalysts (1×10^{-2} mmol) and cobaloxime complexes (6×10^{-3} mmol. 2.8 mg) were dissolved in CH_3CN and the reaction tube was sealed. After degassing by the argon, 1-tetralone (**1a**, 0.2 mmol, 27 μL) was added. Methane (1mL) was then injected as the internal standard for analysis of generated H_2, and the pinholes were sealed by paraffin. The reaction mixture was irradiation at room temperature using a 500 W medium pressure Hanovia mercury lamp with a glass water cooling jacket (λ > 300 nm). After 5 h irradiation, yield of H_2 was detected by GC-TCD. The conversion of **1a** and yield of 1-naphathol **2a** (based on consumed **1a**) were obtained from the crude reaction mixture by GC-FID using *n*-tetradecane as an internal standard.

Table S2. Optimization of the reaction condition

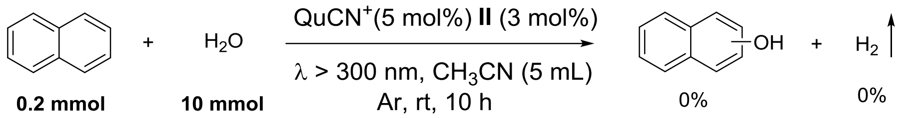


entry	PC	Co	Additives	Conv. **1a** (%)	Yield **2a**. (%)[a]	Yield H_2 (%)
1	QuH^+	**I**	—	48	48	31
2	QuH^+	**II**	—	40	52	25
3	QuH^+	**III**	—	45	62	30
4	QuH^+	**IV**	—	25	60	22
5	$QuCN^+$	**I**	—	30	53	20
6	$QuCN^+$	**II**	—	63	70	50
7	$QuCN^+$	**II**	$BF_3·Et_2O$[b]	78	77	70
8[c]	$QuCN^+$	**II**	$BF_3·Et_2O$[b]	73	76	65
9[d]	$QuCN^+$	**II**	$BF_3·Et_2O$[b]	36	53	0
10[d]	$QuCN^+$	**—**	$BF_3·Et_2O$[b]	19	34	0

[a] Yields of **2a** were based on the consumed **1a**. [b] 20 mol% $BF_3·Et_2O$ was added.[c] Under N_2 atmosphere. [d] Under 1 atm O_2.

2.2 The attempt to hydroxylation of naphthalene with H_2O

The reaction was carried out according the previous report.[1b] After 10 hour's irradiation, H_2 was detected by GC-TCD. The conversion of naphthalene and yield of 1-naphathol and 2-naphthanol were detected from the crude reaction mixture by GC-FID using *n*-tetradecane as an internal standard.



2.3 The continuous-flow reactor

The self-built continuous-flow reactor: a PTFE tube (ID = 612 μm, L= 9 m, V_R = 2.65 mL) is coiled around a glass cooling jacket, and a 500 W medium pressure mercury lamp is put into the jacket. The jacket system is immersed in a cooling water bath. The two ends of the tube are respectively connected with a peristaltic pump to push the solution through the PTFE tube and a conical flask for receiving the reaction mixture (**Fig. S1**).

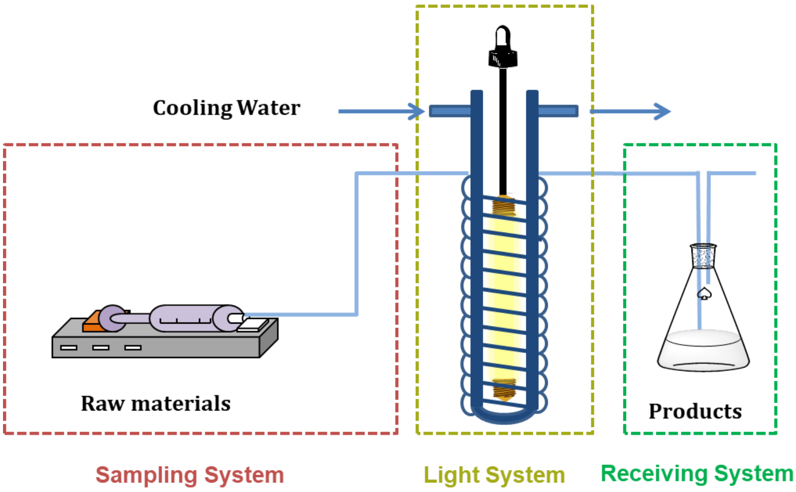
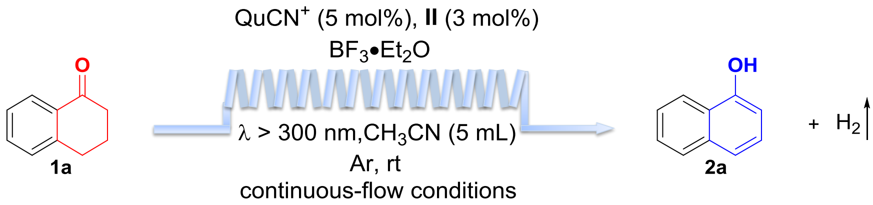


Fig. S1. The continuous-flow reactor

2.4 General Procedure for Continuous-Flow Experiments

1-tetralones (0.2 mmol, liquid 1-tetralone derivatives were added after degassing), $QuCN^+$ (1×10^{-2} mmol, 2.69 mg) and $Co(dmgBF_2)_2(CH_3CN)_2$ (**II**) (6×10^{-3} mmol, 2.8 mg,) were dissolved in CH_3CN (5 mL) and the reaction tube was sealed. After degassing by argon, a 10 mL syringe was used to extract the liquid from the reaction and connected to PTEF tube (ID = 612 μm, L= 9 m, V_R = 2.65 mL) of continuous flow reactor. The solution was irradiation at room temperature using a 500 W high pressure Hanovia mercury lamp with a glass water cooling jacket (λ > 300 nm). The conversion and yields were determined by ^{1}H NMR using *n*-tetradecane as an internal standard. All the reactions were performed at least twice. The reaction mixture of parallel reactions were combined and isolated by flash column chromatography on silica gel using a mixture of petroleum ether-EtOAc as eluent. The isolated yields were the average yields of parallel reactions.

Table S3. Optimization of the continuous-flow reaction condition

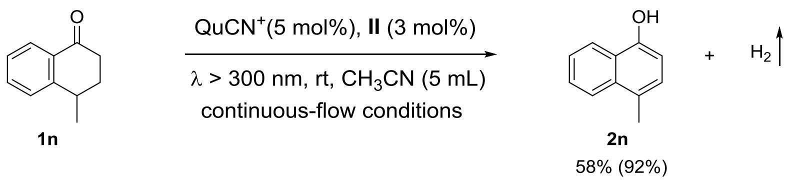


entry	reaction time	$BF_3 \cdot Et_2O$	Conv. **1a** (%)	Yield **2a** (%)[a]
1	30 min	10 mol%	60	97
2	1 h	10 mol%	78	77
3	30 min	20 mol%	66	100
4	1 h	20 mol%	83	48

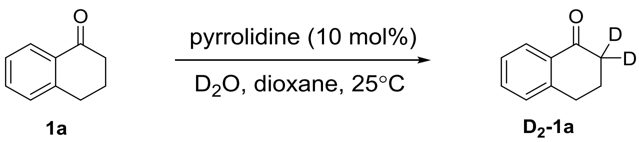
[a] Yields of **2a** were based on the consumed **1a**.

2.5 The scaled-up experiment in continuous-flow conditions

$QuCN^+$ (5×10^{-2} mmol, 13.4 mg), $Co(dmgBF_2)_2(CH_3CN)_2$ (**II**) (3×10^{-2} mmol, 14 mg) and **1n** (1 mmol, 158.2 mg,) were dissolved in CH_3CN (25 mL) and the reactions tube was sealed. After degassing by the argon, $BF_3 \cdot Et_2O$ (0.2 mmol, 25 μL) was added. After that, the reaction mixture was pumped into a 50 mL syringe under argon atmosphere; the syringe was then attached to the peristaltic pump. Continuous flow reactor: PTEF tube (ID = 612 μm, L = 9 m, V_R = 2.65 mL), continuous flowrate was set as 2.65 mL/h and the reaction time was determined to be 1 hour. 500 W medium pressure Hanovia mercury lamp with a glass water cooling jacket (λ > 300 nm) was used as light source. After irradiation for a while, The conversion of 4-methyl-3,4-dihydronaphthalen-1(2*H*)-one and yield of 4-methylnaphthalen-1-ol were determined by ^{1}H NMR from the crude reaction mixture by using *n*-tetradecane as an internal standard. The isolated yield of **1n** and the yield of **2n** (based on consumed **1n**) were given under the product **2n**.



2.6 Preparation of D_2-1a



D_2-1a was synthesized according the previous report.[4] The **D_2-1a** was obtained in 85% yield with 98% D incorporation at C-2 according to spectroscopic analysis. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.38 – 7.20 (m, 2H), 2.97 (t, J = 6.0 Hz, 2H), 2.63 (s, 0.04H), 2.13 (t, J = 5.9 Hz, 2H) (**Fig. S2**).

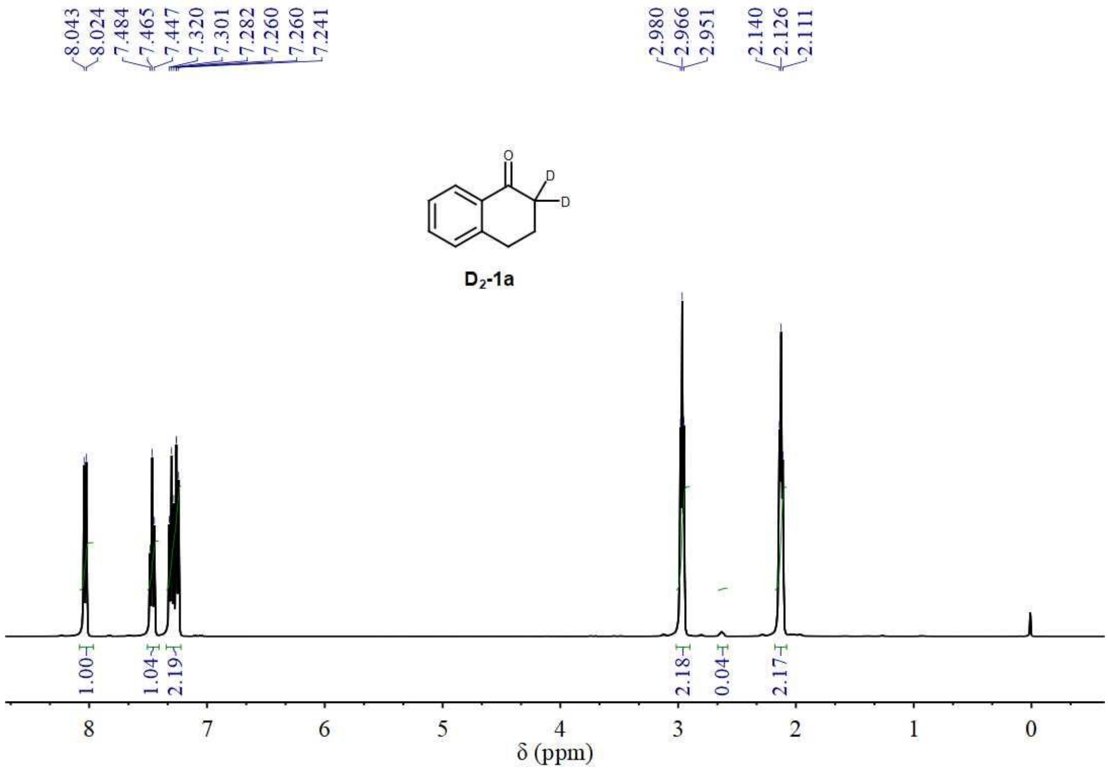


Fig. S2. ^{1}H NMR of a mixture of **D$_2$-1a** and **1a**

2.7 Photocatalysts and cobaloxime complexes:

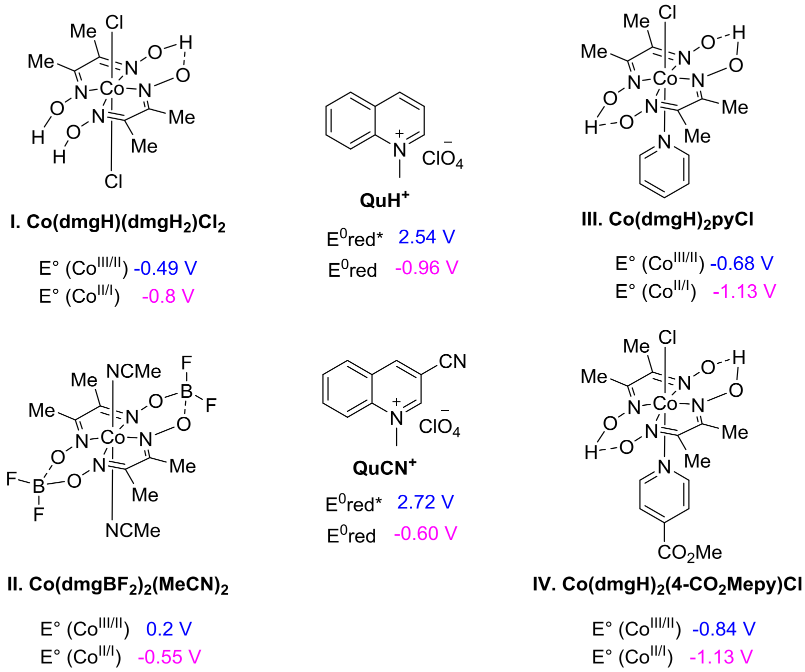


Fig. S3. Photocatalysts and cobaloxime catalysts

3. Mechanism studies

3.1 Cyclic voltammetry (CV) experiments:

A CH_3CN solution (3×10^{-4} M) of **1a** and a CH_3CN solution (3×10^{-4} M) of 1-tetralone **1a** with BF_3•Et_2O (3×10^{-4} M) was prepared with NBu_4PF_6 (0.1 M) as the supporting electrolyte respectively. The cyclic voltammogram was obtained using a glassy carbon as working electrode, a Pt strip as counter electrode, and a saturated calomel electrode as reference electrode. Scan rate = 0.1 V/s, range from 0 V to 3.0 V.

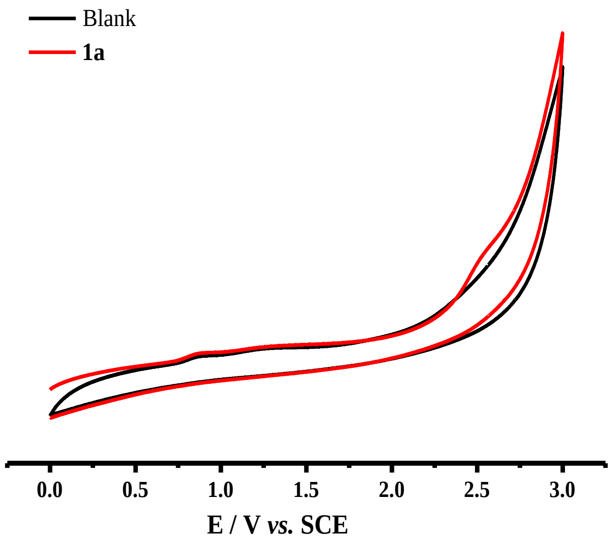


Fig. S4. Cyclic voltammetry spectra of **1a** shows an oxidative potential at 2.51 V vs. SCE in anhydrous CH_3CN.

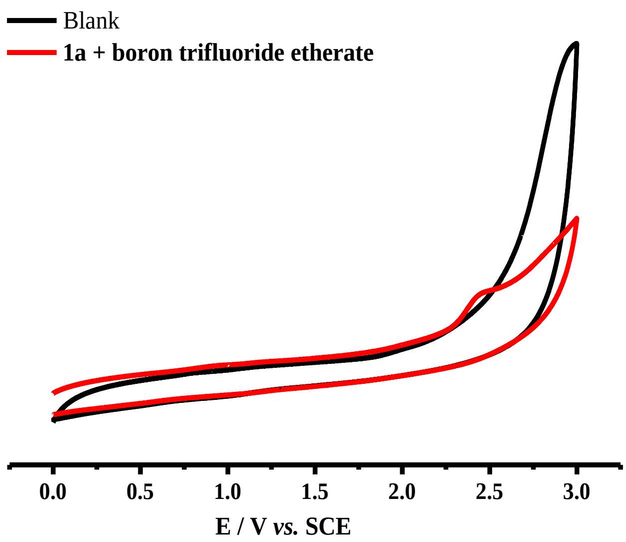


Fig. S5. Cyclic voltammetry spectra of **1a** with BF_3•Et_2O shows an oxidative potential at 2.44 V vs. SCE in anhydrous CH_3CN.

3.2 Spectroscopy experiments

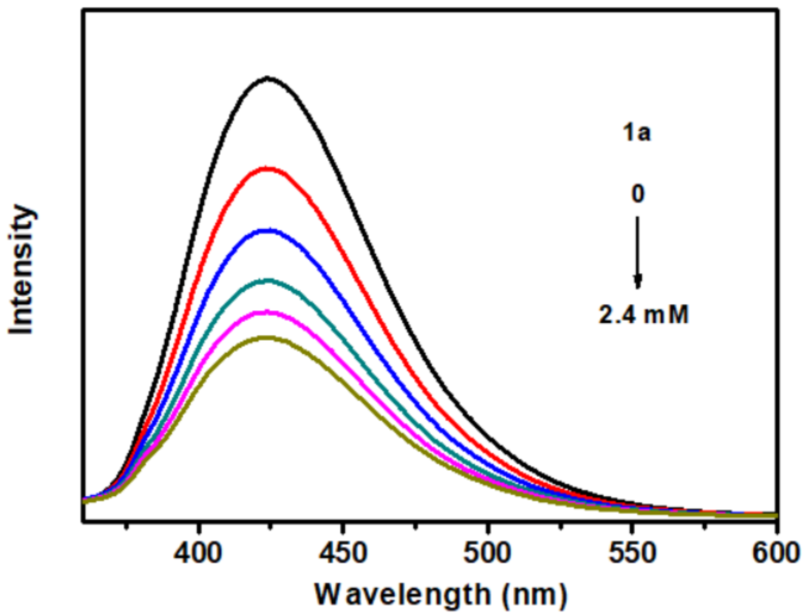


Fig. S6. Fluorescence quenching spectra of $QuCN^+$ (2×10^{-5} M) with different concentrations of **1a** in degassed CH_3CN with excitation at 340 nm.

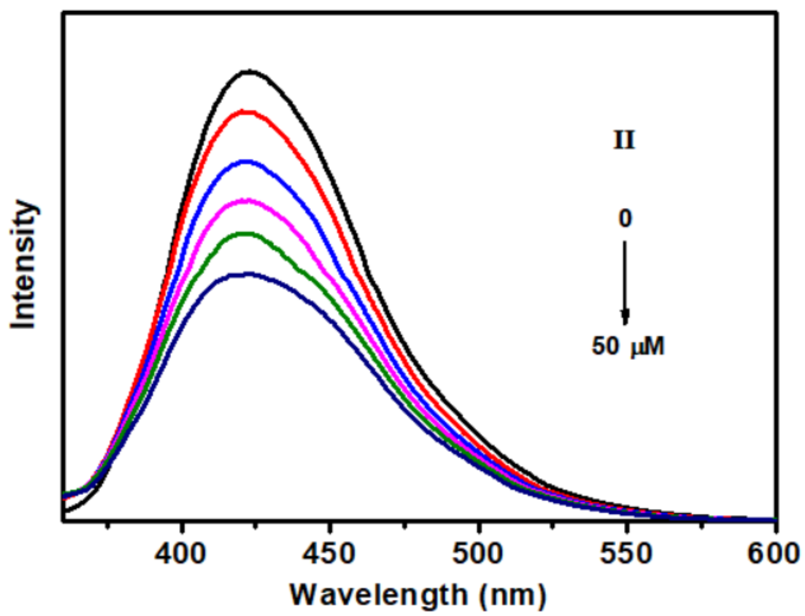


Fig. S7. Fluorescence quenching spectra of $QuCN^+$ (2×10^{-5} M) with different concentrations of $Co(dmgBF_2)_2(MeCN)_2$ (**II**) in degassed CH_3CN with excitation at 340 nm.

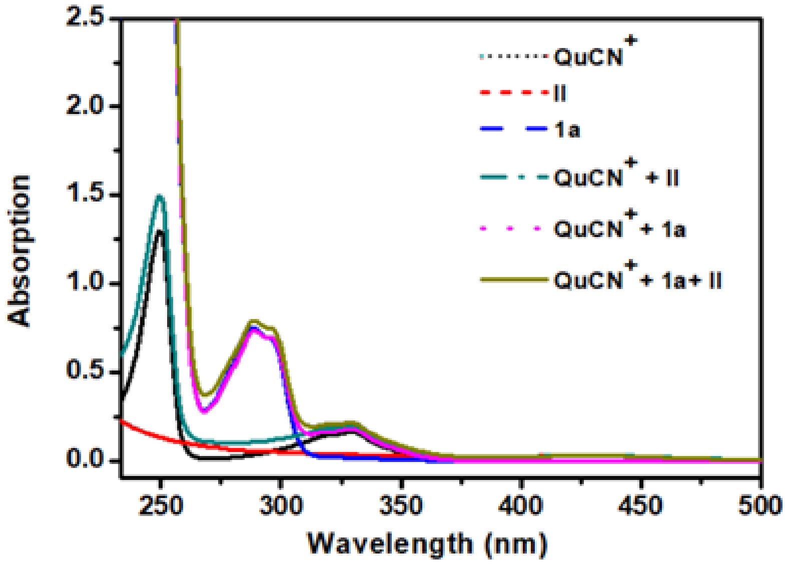


Fig. S8. UV-Vis absorption spectra of $QuCN^+$ (2×10^{-5} M), $Co(dmgBF_2)_2(MeCN)_2$ (**II**) (1.2×10^{-5} M) and **1a** (4×10^{-4} M), respectively in degassed CH_3CN; $QuCN^+$ (2×10^{-5} M) in the presence of $Co(dmgBF_2)_2(MeCN)_2$ (**II**) (1.2×10^{-5} M) or **1a** (4×10^{-4} M), respectively in degassed CH_3CN; $QuCN^+$ (2×10^{-5} M) in conjugation with $Co(dmgBF_2)_2(MeCN)_2$ (**II**) (1.2×10^{-5} M) and **1a** (4×10^{-4} M) in degassed CH_3CN.

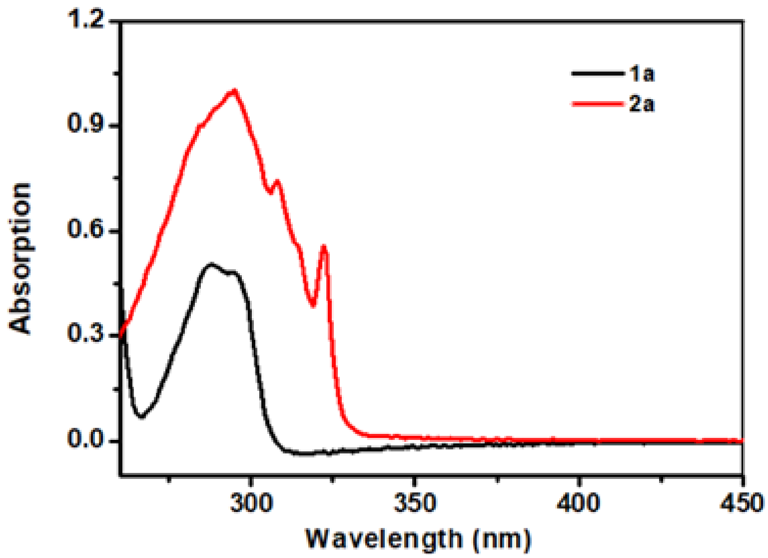


Fig. S9. UV-Vis absorption spectra of **1a** (4×10^{-4} M) and **2a** (2×10^{-4} M) in anhydrous CH_3CN.

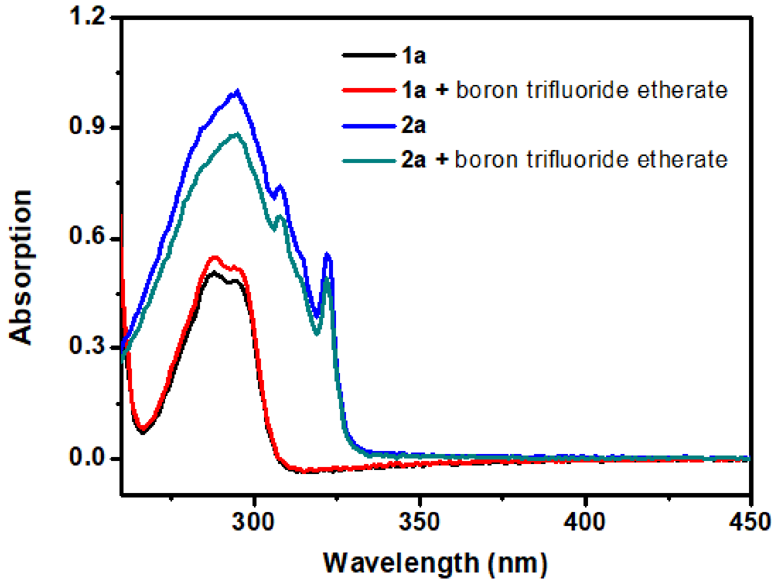


Fig. S10. UV-Vis absorption spectra of **1a** (4×10^{-4} M), **1a** (4×10^{-4} M) with BF_3•Et_2O (8×10^{-5} M), **2a** (2×10^{-4} M) and **2a** (2×10^{-4} M) with BF_3•Et_2O (4×10^{-5} M) in anhydrous CH_3CN.

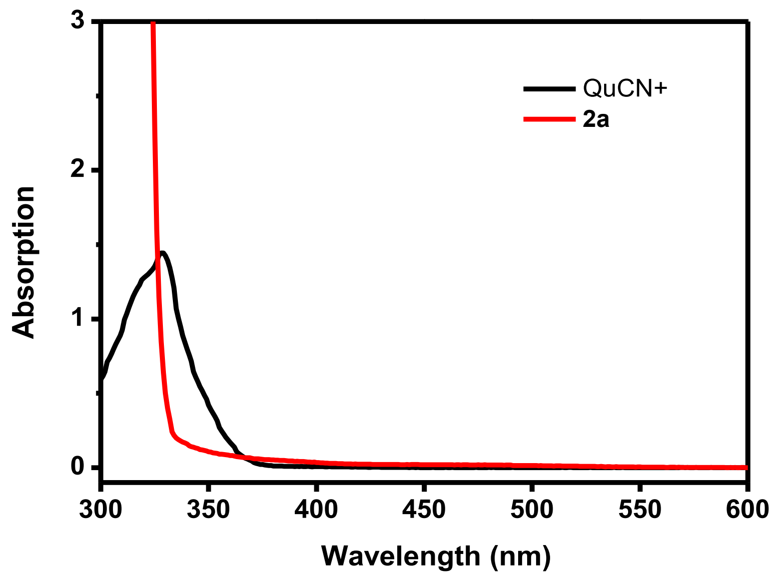
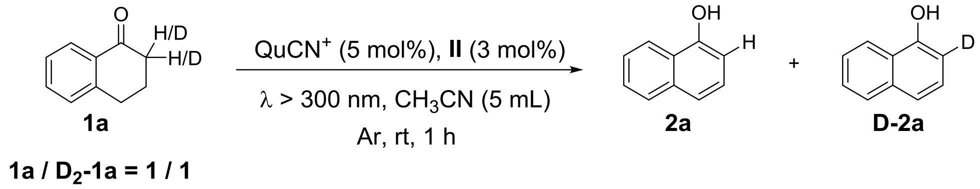


Fig. S11. UV-Vis absorption spectra of $QuCN^+$ (2×10^{-4} M) and **2a** (2×10^{-3} M) in anhydrous CH_3CN.

3.3 Kinetics isotopic effect experiment

A Pyrex tube equipped with a stir-bar was charged with $QuCN^+$ (1×10^{-2} mmol, 2.69 mg), $Co(dmgBF_2)_2(CH_3CN)_2$ (**II**) (6×10^{-3} mmol. 2.8 mg) and CH_3CN (5 mL). After degassing by the argon, **1a** (0.10 mmol, 13.5 μL) and **D_2-1a** (0.1 mmol, 13.5 μL) were added and the pinholes were sealed by paraffin. The reaction mixture was irradiation at room temperature using a 500 W medium pressure Hanovia mercury lamp with a glass water cooling jacket (λ > 300 nm) for 1 h. And then the solvent of the reaction mixture was removed, the pure product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/EtOAc = 20:1) to afford 17% combined products.. Comparing the ^{1}H NMR spectra of **2a** and **D_2-2a,** we found the ratio of **2a: D_2-2a** was 0.55:0.45. So the KIE value (k_H/k_D = 1.2) was determined to be 1.2 (**Fig. S12-S13**).



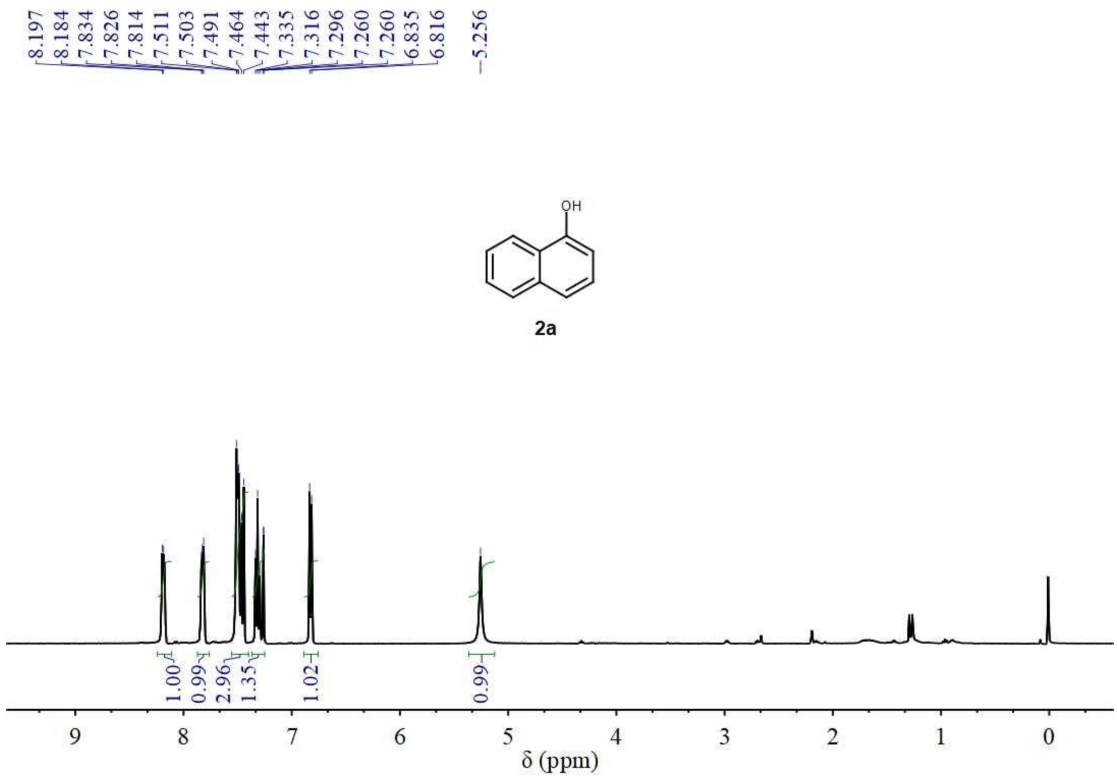


Fig. S12. ^{1}H NMR of **2a**

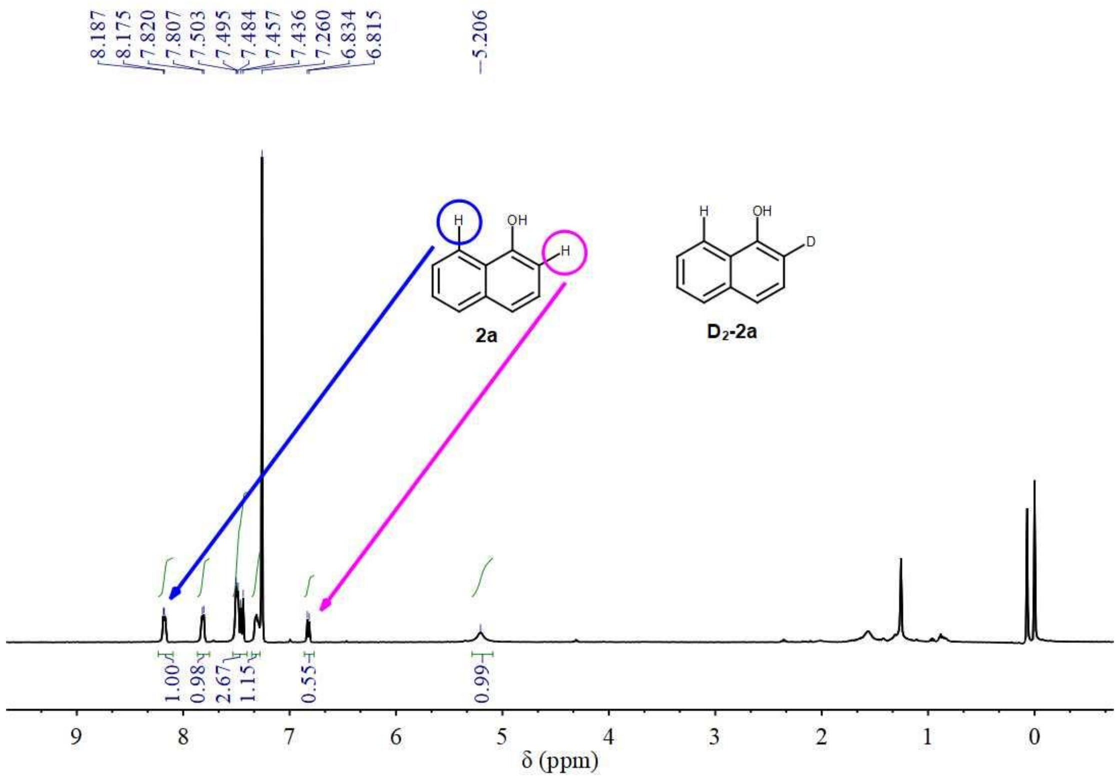
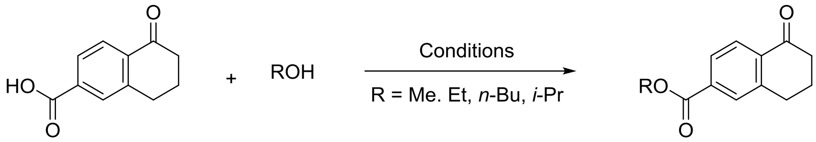


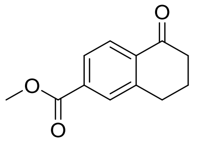
Fig. S13. ^{1}H NMR of a mixture of **D_2-2a** and **2a**

4. Substrate synthesis

General procedures (1)

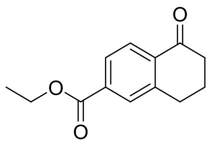


Methyl 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylate (1h)



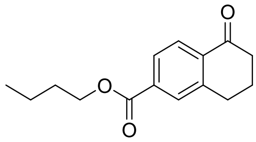
Methyl 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylate was synthesized according the previous report.[5] A 10 mL round-bottom flask was charged with 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (190.2 mg, 1 mmol), oxone (0.3 mmol) and methanol (3 mL). The mixture was stirred at 65 ℃. After completion of the reaction that was confirmed by thin layer chromatography the crude mixture was cooled to room temperature, filtered and purified by column chromatography using silica gel (200-300 meshes silica gel) with ethyl acetate and petroleum ether as an eluent to afford the title compound as a white solid (150.2 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.06 (d, J = 8.0 Hz, 1H), 7.92 (m, 2H), 3.92 (s, 3H), 3.01 (t, J = 6.0 Hz, 2H), 2.72 – 2.64 (t, J = 6.4 Hz, 2H), 2.19 – 2.11 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 197.66, 166.32, 144.35, 135.53, 133.93, 130.19, 127.39, 127.25, 52.41, 39.12, 29.60, 23.07. HRMS (EI): m/z calculated for $C_{12}H_{12}O_3$ $[M]^+$ 204.0786, found 204.0788.

Ethyl 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylate (1i)



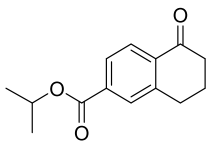
Ethyl 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylate was synthesized according the previous report.[5] A 10 mL round-bottom flask was charged with 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (285.3 mg, 1.5 mmol), oxone (0.45 mmol) and alcohol (5 mL). The mixture was stirred at 65 ℃. After completion of the reaction that was confirmed by thin layer chromatography the crude mixture was cooled to room temperature, filtered and purified by column chromatography using silica gel (200-300 meshes silica gel) with ethyl acetate and petroleum ether as an eluent to afford the title compound as a colorless oil(192.3 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.07 (d, J = 8.6 Hz, 1H), 7.93 (m, 2H), 4.40 (q, J = 7.1 Hz, 2H), 3.02 (t, J = 6.1 Hz, 2H), 2.75 – 2.61 (t, J = 6.4 Hz, 2H), 2.22 – 2.10 (m, 2H), 1.40 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 197.86, 165.99, 144.41, 135.57, 134.43, 130.23, 127.49, 127.35, 61.51, 39.25, 29.72, 23.18, 14.39. HRMS (ESI): m/z calculated for $C_{13}H_{14}O_3$ $[M+H]^+$ 219.1016, found 219.1010.

Butyl 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylate (1j)



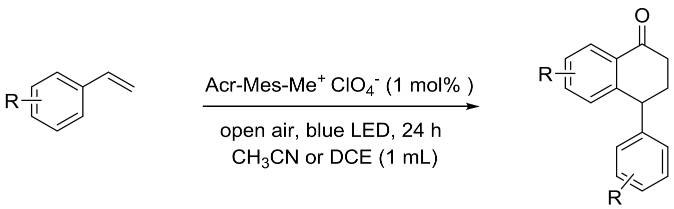
Butyl 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylate was synthesized according the previous report.[5] A 10 mL round-bottom flask was charged with 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (285.3 mg, 1.5 mmol), oxone (0.45 mmol) and *n*-butyl alcohol (5 mL). The mixture was stirred at 65 ℃. After completion of the reaction that was confirmed by thin layer chromatography the crude mixture was cooled to room temperature, filtered and purified by column chromatography using silica gel (200-300 meshes silica gel) with ethyl acetate and petroleum ether as an eluent to afford the title compound as a colorless oil (142.6 mg, 38%).^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, J = 8.5 Hz, 1H), 7.92 (m, 2H), 4.33 (t, J = 6.6 Hz, 2H), 3.02 (t, J = 6.0 Hz, 2H), 2.73 – 2.64 (m, 2H), 2.21 – 2.09 (m, 2H), 1.80 – 1.69 (m, 2H), 1.55 – 1.41 (m, 2H), 0.98 (t, J = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 197.83, 166.04, 144.41, 135.56, 134.45, 130.21, 127.47, 127.35, 65.38, 39.24, 30.82, 29.73, 23.17, 19.35, 13.83. HRMS (EI): m/z calculated for $C_{15}H_{18}O_3$ $[M + H]^+$ 247.1329, found 247.1322.

Isopropyl 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylate (1k)

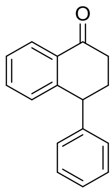


Isopropyl 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylate was synthesized according the previous report.[6] To a 10 mL round-bottom flask, sulfuric acid (98%, 0.94 mmol, 50 µL) was added to a well-stirred mixture of 5-oxo-5,6,7,8-tetrahydronaphthalene-2-carboxylic acid (0.8 mmol, 152.16 mg), isopropanol (137 µL), and acetonitrile (7 mL) at room temperature, and the temperature was maintained at 80–85℃ for 18 h. The reaction mixture was concentrated under reduced pressure and purified over silica gel using ethyl acetate–petroleum ether to afford the title compound as a colorless oil(115 mg, 62%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.07 (d, J = 8.5 Hz, 1H), 7.93 (m, 2H), 5.38 – 5.15 (m, 1H), 3.02 (t, J = 6.0 Hz, 2H), 2.69 (t, J = 6.5 Hz, 2H), 2.23 – 2.07 (m, 2H), 1.38 (d, J = 6.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 197.95, 165.52, 144.40, 135.52, 134.90, 130.20, 127.51, 127.35, 69.09, 39.28, 29.76, 23.22, 22.02. HRMS (EI): m/z calculated for $C_{14}H_{16}O_3$ $[M + H]^+$ 233.1172, found 233.1167.

General procedures (2)

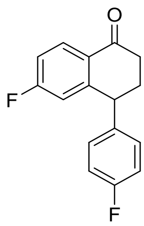


4-Phenyl-3,4-dihydronaphthalen-1(2H)-one (1p)



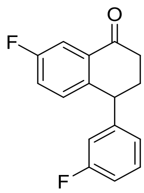
4-phenyl-3,4-dihydronaphthalen-1(2*H*)-one was synthesized according the previous report.[7] ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.12 (d, *J* = 7.7 Hz, 1H), 7.53 – 7.21 (m, 5H), 7.12 (d, *J* = 7.3 Hz, 2H), 6.99 (d, *J* = 7.7 Hz, 1H), 4.31 (dd, *J* = 7.7, 4.6 Hz, 1H), 2.69 (m, 2H), 2.48 (dd, *J* = 8.6, 4.5 Hz, 1H), 2.31 (m, *J* = 13.3, 8.7, 4.5 Hz, 1H).

6-Fluoro-4-(4-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one (1q)



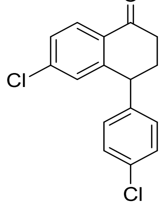
6-fluoro-4-(4-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one was synthesized according the previous report.[7] ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.14 (dd, *J* = 8.7, 6.1 Hz, 1H), 7.20 – 6.95 (m, 5H), 6.60 (dd, *J* = 9.6, 2.1 Hz, 1H), 4.25 (dd, *J* = 8.6, 4.4 Hz, 1H), 2.85 – 2.57 (m, 2H), 2.44 (m, 1H), 2.34 – 2.19 (m, 1H).

7-Fluoro-4-(3-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one (1r)



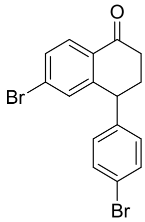
7-fluoro-4-(3-fluorophenyl)-3,4-dihydronaphthalen-1(2H)-one was synthesized according the previous report.[7] ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.70 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.39 – 7.04 (m, 5H), 6.66 (d, *J* = 9.9 Hz, 1H), 4.21 (dd, *J* = 7.4, 4.8 Hz, 1H), 2.62 (m, 2H), 2.40 (m, 1H), 2.21 (m, 1H).

6-Chloro-4-(4-chlorophenyl)-3,4-dihydronaphthalen-1(2H)-one (1s)



6-chloro-4-(4-chlorophenyl)-3,4-dihydronaphthalen-1(2H)-one was synthesized according the previous report.[7] ^{1}H NMR (400 MHz, Acetone, ppm) δ: 8.02 (d, *J* = 8.3 Hz, 1H), 7.53 – 7.35 (m, 3H), 7.28 – 7.20 (d, *J* = 8.0 Hz, 2H), 6.98 (s, 1H), 4.46 (dd, *J* = 7.8, 4.3 Hz, 1H), 2.75 – 2.57 (m, 2H), 2.46 (m, 1H), 2.34 (m, 1H).

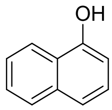
6-Bromo-4-(4-bromophenyl)-3,4-dihydronaphthalen-1(2H)-one (1t)



6-bromo-4-(4-bromophenyl)-3,4-dihydronaphthalen-1(2H)-one was synthesized according the previous report.[7] ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.96 (d, *J* = 8.4 Hz, 1H), 7.53 – 7.41 (m, 3H), 7.10 (s, 1H), 6.99 (d, *J* = 8.2 Hz, 2H), 4.22 (dd, *J* = 8.1, 4.5 Hz, 1H), 2.75 – 2.55 (m, 2H), 2.43 (m, 1H), 2.29 – 2.19 (m, 1H).

5. Characterization of products (2a – 2u)

Naphthalen-1-ol (2a)



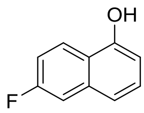
White solid. Isolated yield: 37.5 mg, 65%. Petroleum ether/EtOAc=20/1-10/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.19 (m, 1H), 7.89 – 7.73 (m, 1H), 7.57 – 7.38 (m, 3H), 7.32 (t, J = 7.8 Hz, 1H), 6.83 (d, J = 7.4 Hz, 1H), 5.26 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 151.4, 134.9, 127.8, 126.6, 126.0, 125.4, 124.4, 121.6, 120.9, 108.8.

HRMS (ESI): m/z calculated for $C_{10}H_8O$ $[M -H]^-$ 143.0502 found 143.0498.

6-Fluoronaphthalen-1-ol (2b)



White solid. Isolated yield: 32.3 mg, 50%. Petroleum ether/EtOAc=20/1-15/1.

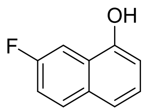
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.79 (m, 2H), 7.43 (d, J = 8.3 Hz, 1H), 7.36 – 7.17 (m, 2H), 6.83 (d, J = 7.4 Hz, 1H), 5.31 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 160.6 (d, J = 245.1 Hz), 151.1 (d, J = 5.4 Hz), 131.9 (s), 130.2 (d, J = 8.8 Hz), 125.3 (d, J = 8.9 Hz), 125.1 (d, J = 2.5 Hz), 120.7 (s), 116.9 (d, J = 25.5 Hz), 109.5 (s), 105.7 (d, J = 22.3 Hz).

^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ: -114.69.

HRMS (ESI): m/z calculated for $C_{10}H_7FO$ $[M -H]^-$161.0408 found 161.0396.

7-Fluoronaphthalen-1-ol (2c)



White solid. Isolated yield: 29.0 mg, 45%. Petroleum ether/EtOAc=15/1-10/1.

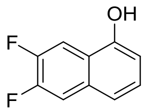
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.84 – 7.74 (m, 2H), 7.43 (d, J = 8.3 Hz, 1H), 7.31 – 7.20 (m, 2H), 6.83 (d, J = 7.4 Hz, 1H), 5.25 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 160.6 (d, J = 245.1 Hz), 151.1 (d, J = 5.4 Hz), 131.9 (s), 130.2 (d, J = 8.8 Hz), 125.3 (d, J = 8.9 Hz), 125.1 (d, J = 2.5 Hz), 120.7 (d, J = 1.0 Hz), 117.0 (d, J = 25.4 Hz), 109.5 (s), 105.7 (d, J = 22.3 Hz).

^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ: -114.68.

HRMS (ESI): m/z calculated for $C_{10}H_7FO$ $[M -H]^-$ 161.0481, found 161.0395.

6,7-Difluoronaphthalen-1-ol (2d)



White solid. Isolated yield: 31.1 mg, 43%. Petroleum ether/EtOAc=20/1-15/1.

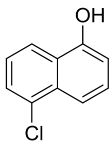
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.92 (dd, *J* = 11.5, 8.2 Hz, 1H), 7.51 (dd, *J* = 11.0, 7.9 Hz, 1H), 7.37 – 7.21 (m, 2H), 6.78 (d, *J* = 7.3 Hz, 1H), 5.36 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 151.2 (dd, *J* = 5.2, 1.9 Hz), 150.7 (dd, *J* = 250.2, 14.8 Hz), 149.7 ((dd, *J* = 249.4, 15.2 Hz) 131.9 (d, *J* = 7.6 Hz), 126.5 (d, *J* = 2.4 Hz), 121.3 (d, *J* = 7.1 Hz), 120.0 (dd, *J* = 4.9, 1.9 Hz), 113.5 (d, *J* = 16.7 Hz), 108.8 (d, *J* = 18.3 Hz), 108.8 (d, *J* = 2.2 Hz).

^{19}F NMR (377 MHz, $CDCl_3$, ppm) δ: -136.91 (d, *J* = 20.7 Hz), -137.51 (d, *J* = 20.7 Hz).

HRMS (ESI): m/z calculated for $C_{10}H_6F_2O$ $[M -H]^-$179.0314 found 179.0305.

5-Chloronaphthalen-1-ol (2e)



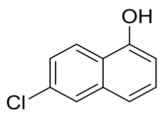
White solid. Isolated yield: 20.3 mg, 28%. Petroleum ether/EtOAc=15/1-10/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.15 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.59 (d, *J* = 7.4 Hz, 1H), 7.47 – 7.33 (m, 2H), 6.88 (d, *J* = 7.5 Hz, 1H), 5.35 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 151.8, 132.4, 132.1, 127.1, 127.0, 125.9, 125.1, 121.1, 117.4, 109.7.

HRMS (ESI): m/z calculated for $C_{10}H_7ClO$ $[M -H]^-$ 177.0113, found 177.0103.

6-Chloronaphthalen-1-ol (2f)



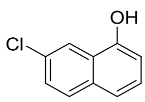
White solid. Isolated yield: 23.9 mg, 34%. Petroleum ether/EtOAc=20/1-10/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 8.14 (d, *J* = 9.0 Hz, 1H), 7.79 (s, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.37 – 7.29 (m, 2H), 6.80 (d, *J* = 6.5 Hz, 1H), 5.27 (br, 1H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 151.6, 135.6, 132.6, 127.3, 126.4, 126.2, 123.8, 122.8, 120.0, 109.0.

HRMS (ESI): m/z calculated for $C_{10}H_7ClO$ $[M -H]^-$ 177.0113, found 177.0101.

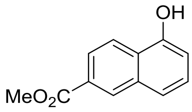
7-Chloronaphthalen-1-ol (2g)



White solid. Isolated yield: 16.5 mg, 22%. Petroleum ether/EtOAc=15/1-10/1.

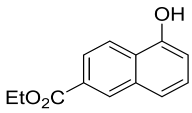
^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ*: 8.17 (s, 1H), 7.72 (d, *J* = 8.8 Hz, 1H), 7.41 (m, 2H), 7.35 – 7.19 (m, 1H), 6.81 (d, *J* = 7.4 Hz, 1H), 5.23 (br, 1H).
^{13}C NMR (101 MHz, $CDCl_3$, ppm) *δ:* 150.7, 133.1, 131.3, 129.4, 127.5, 126.2, 125.2, 121.2, 120.7, 109.6.
HRMS (ESI): m/z calculated for $C_{10}H_7ClO$ $[M -H]^-$ 177.0113, found177.0099

Methyl- 5-hydroxy-2-naphthoate (2h)



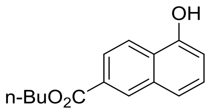
White solid. Isolated yield: 38.5 mg, 48%. Petroleum ether/EtOAc=20/1-10/1.
^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ*: 8.58 (s, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 8.06 (dd, *J* = 8.8, 1.4 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.04 (br, 1H), 4.00 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$, ppm) *δ*: 167.6, 151.6, 134.0, 130.9, 128.0, 126.89, 126.6, 124.7, 122.4, 122.1, 111.1, 52.5.
HRMS (ESI): m/z calculated for $C_{12}H_{10}O_3$ $[M -H]^-$ 201.0557, found 201.0548.

Ethyl 5-hydroxy-2-naphthoate (2i)



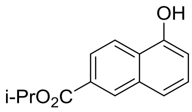
White solid. Isolated yield: 32.2 mg, 37%. Petroleum ether/EtOAc=20/1-15/1.
^{1}H NMR (400 MHz, CD_3COCD_3, ppm) *δ*: 9.26 (br, 1H), 8.55 (s, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 8.00 (d, *J* = 8.8 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.41 (t, *J* = 7.9 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H)., 7.07 (d, *J* = 7.5 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, CD_3COCD_3, ppm) *δ*: 167.0, 154.1, 135.0, 131.1, 129.1, 128.2, 127.8, 124.7, 123.5, 121.4, 111.4, 61.6, 14.7.
HRMS (ESI): m/z calculated for $C_{13}H_{12}O_3$ $[M -H]^-$ 215.0714, found 215.0706.

Butyl 5-hydroxy-2-naphthoate (2j)



White solid. Isolated yield: 49.1 mg, 50%. Petroleum ether/EtOAc=20/1-10/1.
^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ*: 8.58 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.47 (br, 1H), 4.42 (t, *J* = 6.6 Hz, 2H), 1.90 – 1.72 (m, 2H), 1.62 – 1.42 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$, ppm) *δ*: 167.5, 151.8, 134.0, 130.8, 128.2, 126.9, 126.7, 124.4, 122.4, 121.9, 111.0, 65.4, 30.9, 19.4, 13.9.
HRMS (ESI): m/z calculated for $C_{15}H_{16}O_3$ $[M -H]^-$ 243.1027, found 243.1022.

Isopropyl 5-hydroxy-2-naphthoate (2k)



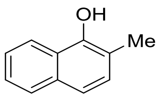
White solid. Isolated yield: 36.5 mg, 40%. Petroleum ether/EtOAc=20/1-10/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ*: 8.57 (s, 1H), 8.28 (d, *J* = 8.8 Hz, 1H), 8.07 (d, *J* = 8.8 Hz, 1H), 7.53 (d, *J* = 8.2 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 1H), 6.47 (br, 1H), 5.45 – 5.27 (m, 1H), 1.44 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) *δ*: 167.1, 151.9, 134.0, 130.8, 128.5, 126.9, 126.7, 124.5, 122.4, 121.8, 111.0, 69.1, 22.1.

HRMS (ESI): m/z calculated for $C_{14}H_{14}O_3$ $[M -H]^-$ 229.0870 found 229.0864.

2-Methylnaphthalen-1-ol (2m)



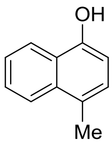
Colorless oil. Isolated yield: 30.5 mg, 48%. Petroleum ether/EtOAc=20/1-10/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ*: 8.13 (d, *J* = 8.2 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.35 (m, 3H), 7.25 (d, *J* = 8.1 Hz, 1H), 5.10 (br, 1H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) *δ*: 148.7, 133.5, 129.1, 127.8, 125.5, 125.4, 124.4, 121.0, 120.3, 116.4, 15.8.

HRMS (ESI): m/z calculated for $C_{11}H_{10}O$ $[M -H]^-$ 157.0659, found 157.0648.

4-Methylnaphthalen-1-ol (2n)



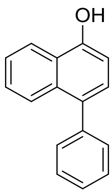
White solid. Isolated yield: 45.0 mg, 71%. Petroleum ether/EtOAc=20/1-10/1.

^{1}H NMR (400 MHz, $CDCl_3$, ppm) *δ*: 8.23 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.5 Hz, 1H), 7.60 –7.44 (m, 2H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.73 (d, *J* = 7.5 Hz, 1H), 5.16 (br, 1H), 2.63 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$, ppm) *δ*: 150.0, 133.7, 126.8, 126.4, 126.2, 125.1, 124.8, 124.4, 122.2, 18.9.

HRMS (ESI): m/z calculated for $C_{11}H_{10}O$ $[M -H]^-$ 157.0659, found 157.0656.

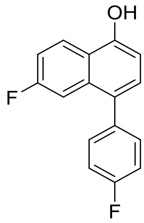
4-Phenylnaphthalen-1-ol (2p)



White solid. Isolated yield: 51.0 mg, 58%. Petroleum ether/EtOAc=50/1-20/1.

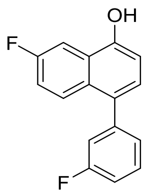
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.57 – 7.35 (m, 7H), 7.25 (d, *J* = 7.7 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 5.32 (br, 1H).
^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 151.1, 140.9, 133.4, 132.8, 130.4, 128.4, 127.1, 127.0, 126.7, 126.1, 125.3, 124.0, 122.0, 108.3.
HRMS (ESI): m/z calculated for $C_{16}H_{12}O$ $[M -H]^{-}$ 219.0815, found 219.0807.

6-Fluoro-4-(4-fluorophenyl)naphthalen-1-ol (2q)



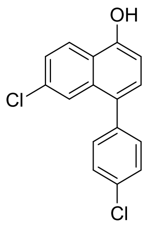
White solid. Isolated yield: 20.5 mg, 40%. Petroleum ether/EtOAc=100/1-70/1.
^{1}H NMR (400 MHz, CD_3COCD_3, ppm) δ: 9.35 (br, 1H), 8.39 (dd, *J* = 9.1, 6.2 Hz, 1H), 7.48 (dd, *J* = 8.1, 5.8 Hz, 2H), 7.41 – 7.23 (m, 5H), 6.98 (d, *J* = 7.8 Hz, 1H).
^{13}C NMR (101 MHz, CD_3COCD_3, ppm) δ: 162.9 (d, *J* = 244.9 Hz), 162.2 (d, *J* = 243.9 Hz), 154.0, 137.6 (d, *J* = 3.3 Hz), 134.7 (d, *J* = 8.7 Hz), 132.6 (d, *J* = 8.0 Hz), 130.7 (d, *J* = 5.3 Hz), 129.7, 126.5 (d, *J* = 9.3 Hz), 123.0, 116.0 (d, *J* = 21.5 Hz), 115.3 (d, *J* = 25.3 Hz), 109.2 (d, *J* = 22.1 Hz), 108.1 (d, *J* = 2.1 Hz).
^{19}F NMR (377 MHz, CD_3COCD_3, ppm) δ: -115.10, -117.29.
HRMS (ESI): m/z calculated for $C_{16}H_{10}F_2O$ $[M -H]^{-}$ 255.0627, found 255.0622.

7-Fluoro-4-(3-fluorophenyl)naphthalen-1-ol (2r)



White solid. Isolated yield: 12.8 mg, 25%. Petroleum ether/EtOAc=100/1-50/1.
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.89 (dd, *J* = 10.3, 2.4 Hz, 1H), 7.84 (dd, *J* = 9.3, 5.5 Hz, 1H), 7.43 (dd, *J* = 14.3, 7.5 Hz, 1H), 7.30 – 7.04 (m, 5H), 6.89 (d, *J* = 7.7 Hz, 1H), 5.52 (br, 1H).
^{13}C NMR (101 MHz, $CDCl_3$, ppm) δ: 162.9 (d, *J* = 236.1 Hz), 160.5 (d, *J* = 235.9 Hz), 151.0 (d, *J* = 5.3 Hz), 142.9 (d, *J* = 7.8 Hz), 132.2, 129.9 (d, *J* = 8.5 Hz), 129.7, 128.5 (d, *J* = 8.7 Hz), 126.2 (d, *J* = 2.4 Hz), 126.1 (d, *J* = 2.9 Hz), 125.7 (d, *J* = 8.9 Hz), 117.3 (d, *J* = 12.4 Hz), 117.0 (d, *J* = 16.2 Hz), 114.2 (d, *J* = 21.0 Hz), 109.1, 106.2 (d, *J* = 22.2 Hz).
^{19}F NMR (377 MHz, CD_3COCD_3, ppm) δ: -114.89, -117.16.
HRMS (ESI): m/z calculated for $C_{16}H_{10}F_2O$ $[M -H]^{-}$ 255.0627, found 255.0618.

6-Chloro-4-(4-chlorophenyl)naphthalen-1-ol (2s)



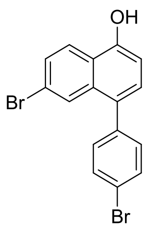
White solid. Isolated yield: 25.9 mg, 45%. Petroleum ether/EtOAc=100/1-80/1.

^{1}H NMR (400 MHz, CD_3COCD_3, ppm) δ: 9.45 (br, 1H), 8.34 (d, *J* = 9.0 Hz, 1H), 7.74 (s, 1H), 7.51 (m, 5H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, CD_3COCD_3, ppm) δ: 154.3, 140.1, 134.3, 133.7, 133.3, 132.7, 130.4, 130.0, 129.6, 126.3, 125.9, 124.8, 124.4, 109.3.

HRMS (ESI): m/z calculated for $C_{16}H_{10}Cl_2O$ $[M -H]^-$ 287.0036, found 287.0035.

6-Bromo-4-(4-bromophenyl)naphthalen-1-ol (2t)



White solid. Isolated yield: 26.5 mg, 35%. Petroleum ether/EtOAc=100/1-80/1.

^{1}H NMR (400 MHz, CD_3COCD_3, ppm) δ: 9.45 (br, 1H), 8.27 (d, *J* = 9.0 Hz, 1H), 7.91 (s, 1H), 7.70 (d, *J* = 8.2 Hz, 2H), 7.61 (d, *J* = 9.0 Hz, 1H), 7.41 (d, J = 8.2 Hz, 2H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, CD_3COCD_3, ppm) δ: 154.3, 140.5, 134.6, 133.0, 132.6, 130.4, 129.9, 128.9, 128.1, 126.0, 124.6, 121.8, 121.8, 109.5.

HRMS (ESI): m/z calculated for $C_{16}H_{10}Br_2O$ $[M -H]^-$ 376.9005, found 376.9004.

6. Reference

1 (a) K. Ohkubo, T. Kobayashi, S. Fukuzumi, *Angew. Chem. Int. Ed.* **2011,** *50*, 8652-8655; (b) Y.-W. Zheng, B. Chen, P. Ye, K. Feng, W. Wang, Q.-Y. Meng, L.-Z. Wu, C.-H. Tung, *J. Am. Chem. Soc.* 2016**, 138**, 10080-10083.

2 (a) J. L. Dempsey, B. S. Brunschwig, J. R. Winkler, H. B. Gray, *Acc. Chem. Res.* 2009**, 42**, 1995-2004; (b) V. Artero, M. Chavarot-Kerlidou, M. Fontecave, *Angew. Chem. Int. Ed.* 2011**, 50**, 7238-7266.

3 (a) B. P. Mason, K. E. Price, J. L. Steinbacher, A. R. Bogdan, D. T. McQuade, *Chem. Rev.* 2007**, 107**, 2300-2318; (b) J. P. Knowles, L. D. Elliott, K. I. Booker-Milburn, *Beilstein J. Org. Chem.* 2012**, 8**, 2025-2052; (c) K. G. Maskill, J. P. Knowles, L. D. Elliott, R. W. Alder, K. I. Booker-Milburn, *Angew. Chem. Int. Ed.* 2013**, 52**, 1499-1502; (d) Z. J. Garlets, J. D. Nguyen, C. R. J. Stephenson, *Isr. J. Chem.* 2014**, 54**, 351-360; (e) E. M. Schuster, P. Wipf, *Isr. J. Chem.* 2014**, 54**, 361-370; (g) Y. Su, N. J. W. Straathof, V. Hessel, T. Noël, *Chem. Eur. J.* 2014**, 20**, 10562-10589;

4 F.-L. Yang, Y. Gui, B.-K. Yu, Y.-X. Jin, S.-K. Tian, *Adv. Synth. Catal.* 2016**, 358**, 3368-3372.

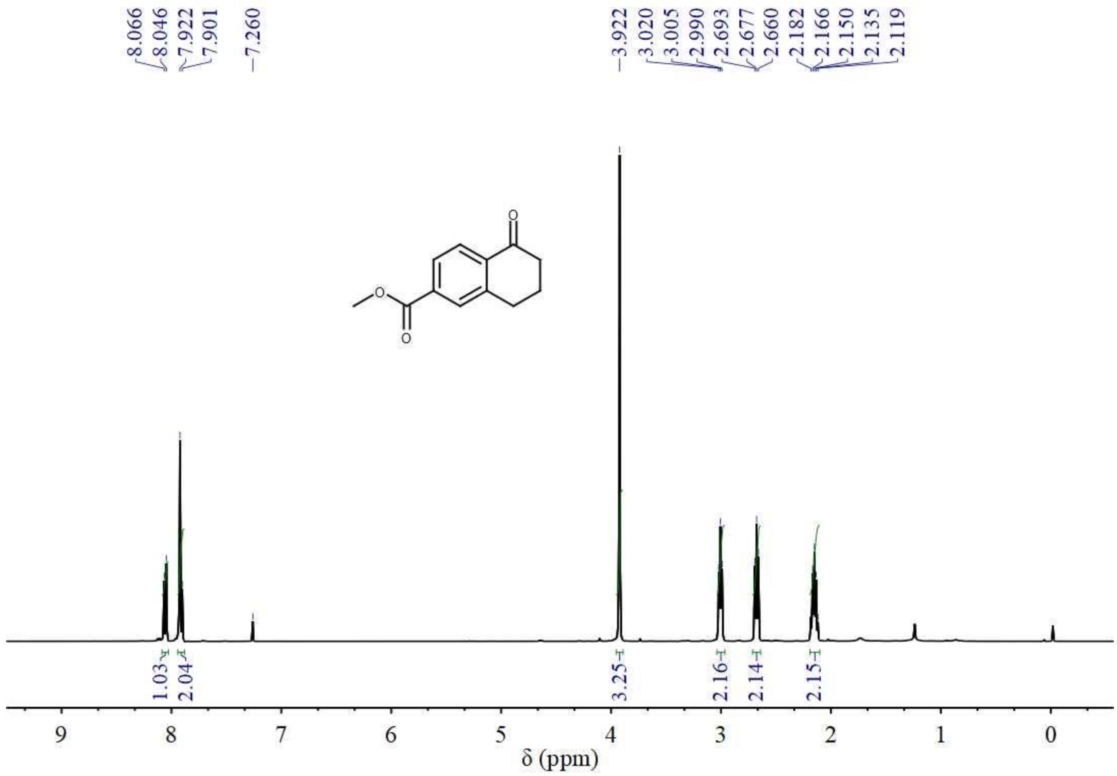
5 A. K. Padala, V. Saikam, A. Ali, Q. N. Ahmed, *Tetrahedron* 2015**, 71**, 9388-9395.

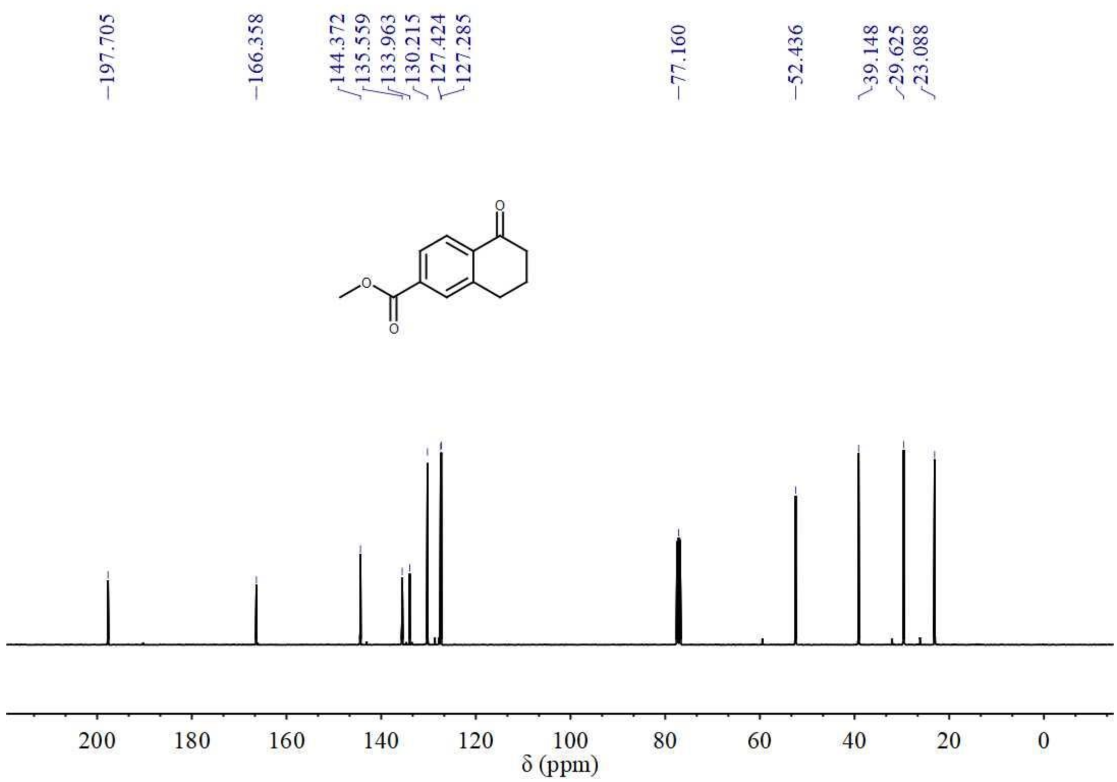
6 S. W. Wright, D. L. Hageman, A. S. Wright, L. D. McClure, *Tetrahedron Lett.* 1997**, 38**, 7345-7348.

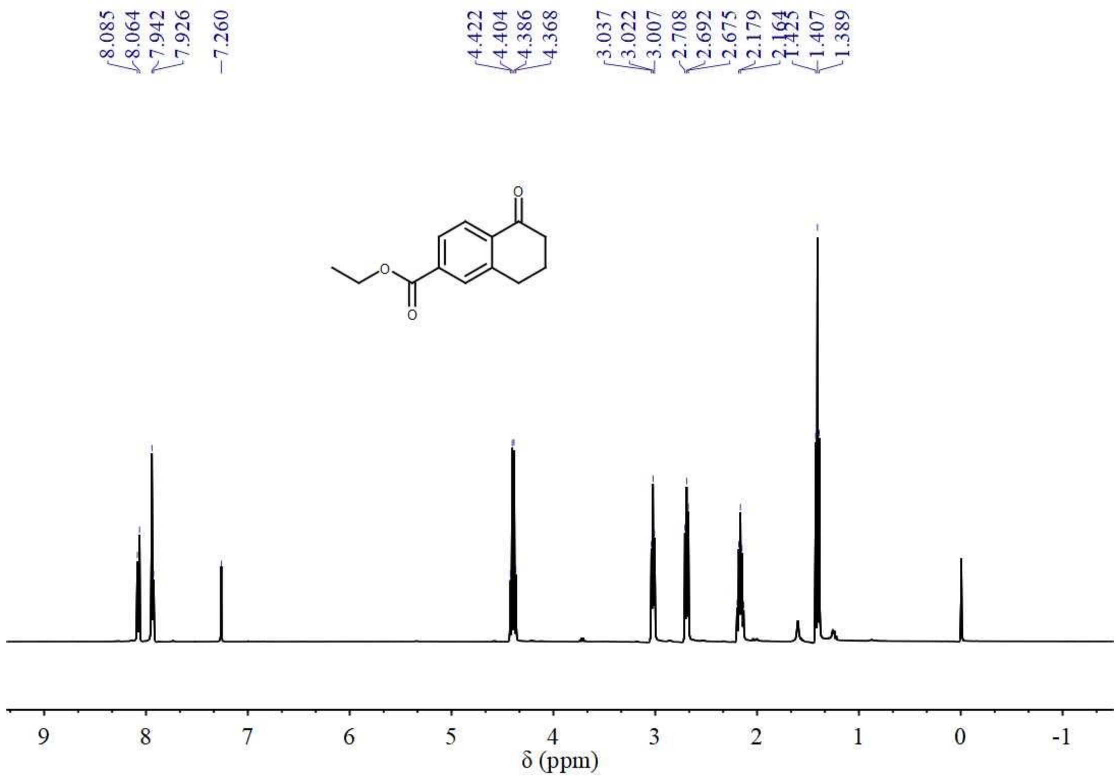
7 D. Wei, Y. Li, F. Liang, *Adv. Synth. Catal.* 2016**, 358**, 3887-3896.

8 A. Odedra, C.-J. Wu, T. B. Pratap, C.-W. Huang, Y.-F. Ran, R.-S. Liu, *J. Am. Chem. Soc.* 2005**, 127,** 3406-3412.

7. NMR spectra for substrates



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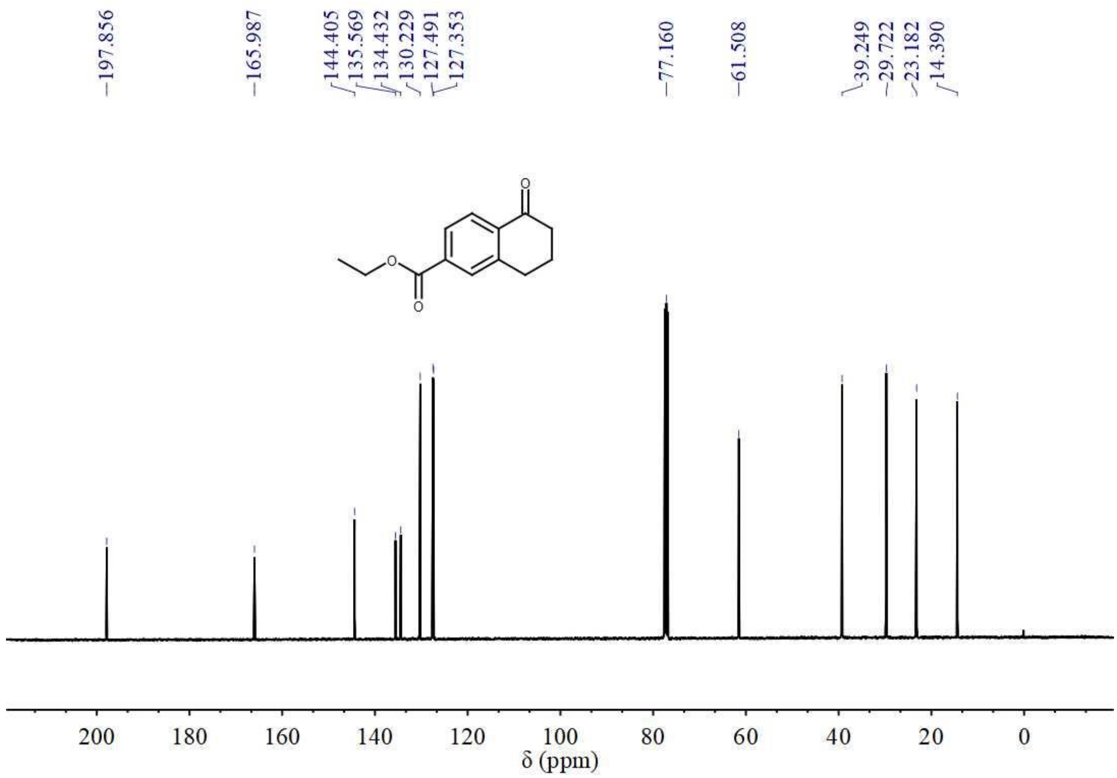
8.064
7.942
7.926
7.260
4.422
4.404
4.386
4.368
3.037
3.022
3.007
2.708
2.692
2.675
2.179
1.407
1.389
O
O
O
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)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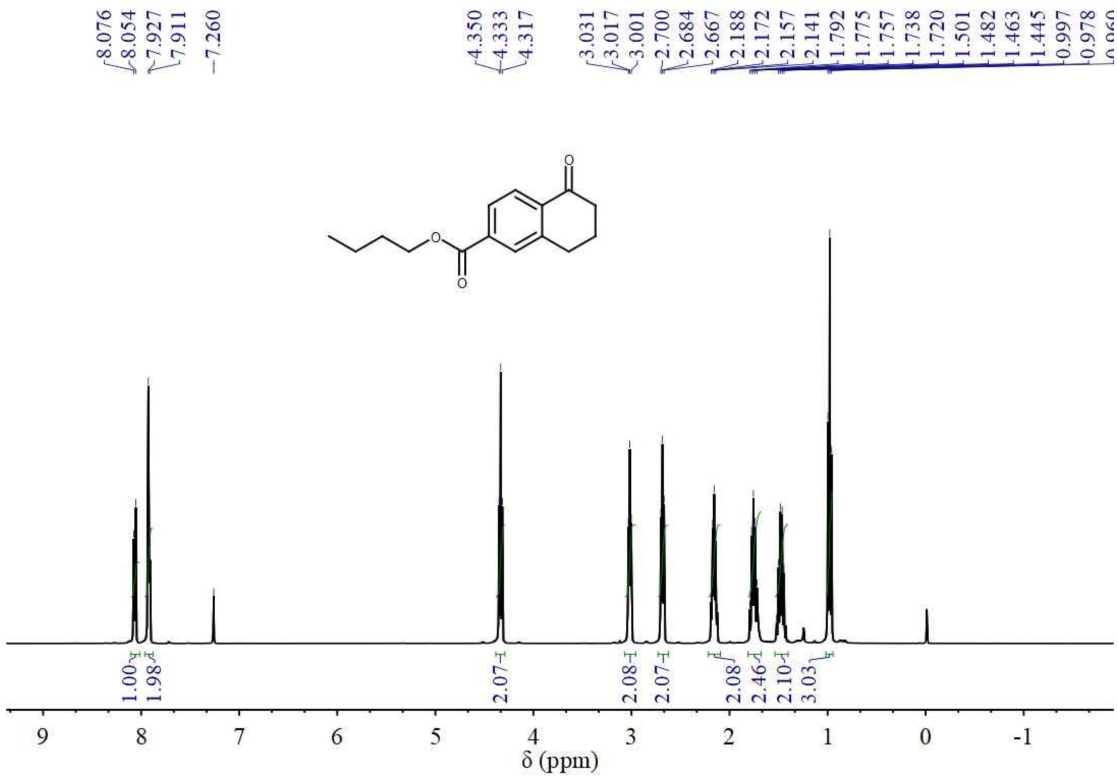
165.987
144.405
135.569
134.432
130.229
127.491
127.353
77.160
61.508
39.249
29.722
23.182
14.390
O
O
O
200
180
160
140
120
100
80
60
40
20
0
δ (ppm)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8.054
7.927
7.911
7.260
4.350
4.333
4.317
3.031
3.017
3.001
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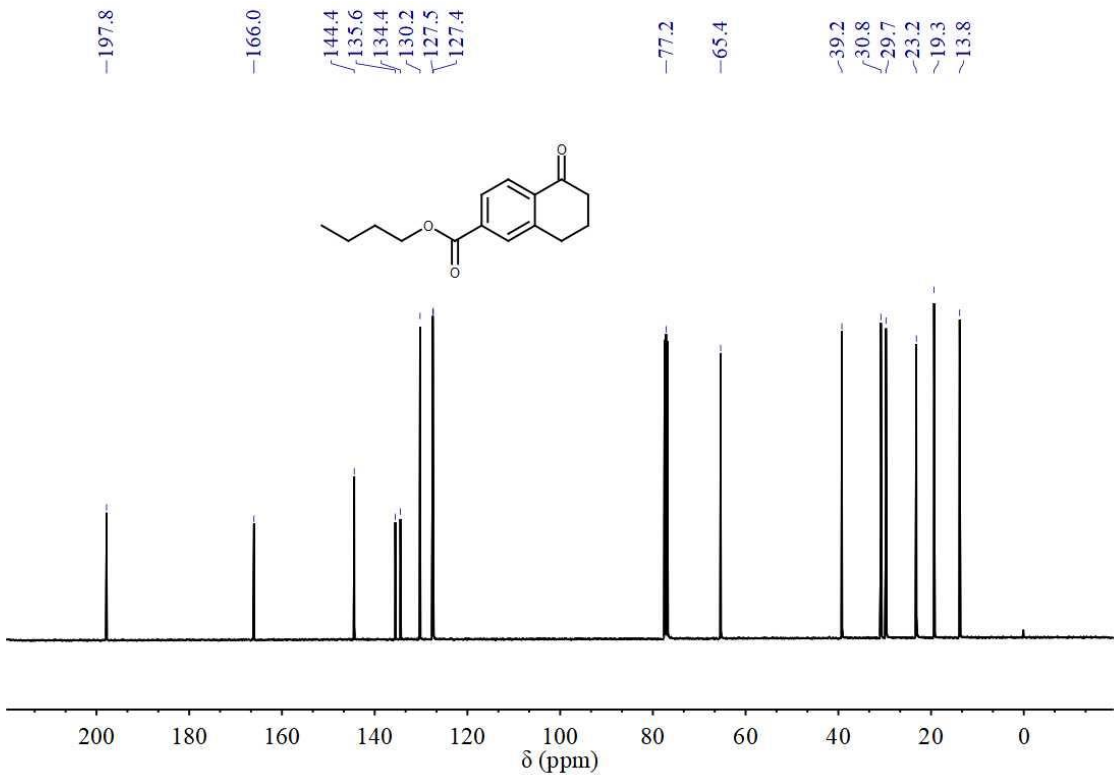
2.684
2.667
2.188
2.172
2.157
2.141
1.792
1.775
1.757
1.738
1.720
1.501
1.482
1.463
1.445
0.997
0.978
1.00
1.98
2.07
2.08
2.07
2.08
2.46
2.10
3.03
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)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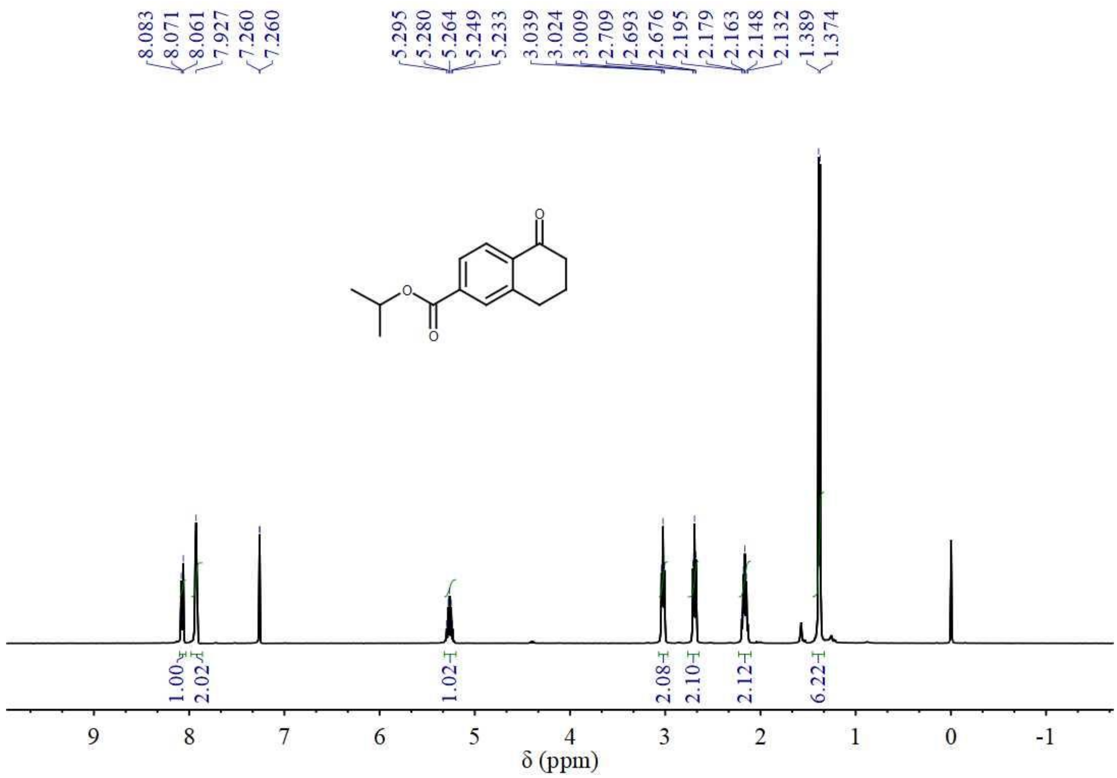
166.0
144.4
135.6
134.4
130.2
127.5
127.4
77.2
65.4
39.2
30.8
29.7
23.2
19.3
13.8
200
180
160
140
120
100
80
60
40
20
0
δ (ppm)



8.083
8.071
8.061
7.927
7.260
7.260
5.295
5.280
5.264
5.249
5.233
3.039
3.024
3.009
2.709
2.693
2.676
2.195
2.179
2.163
2.148
2.132
1.389
1.374
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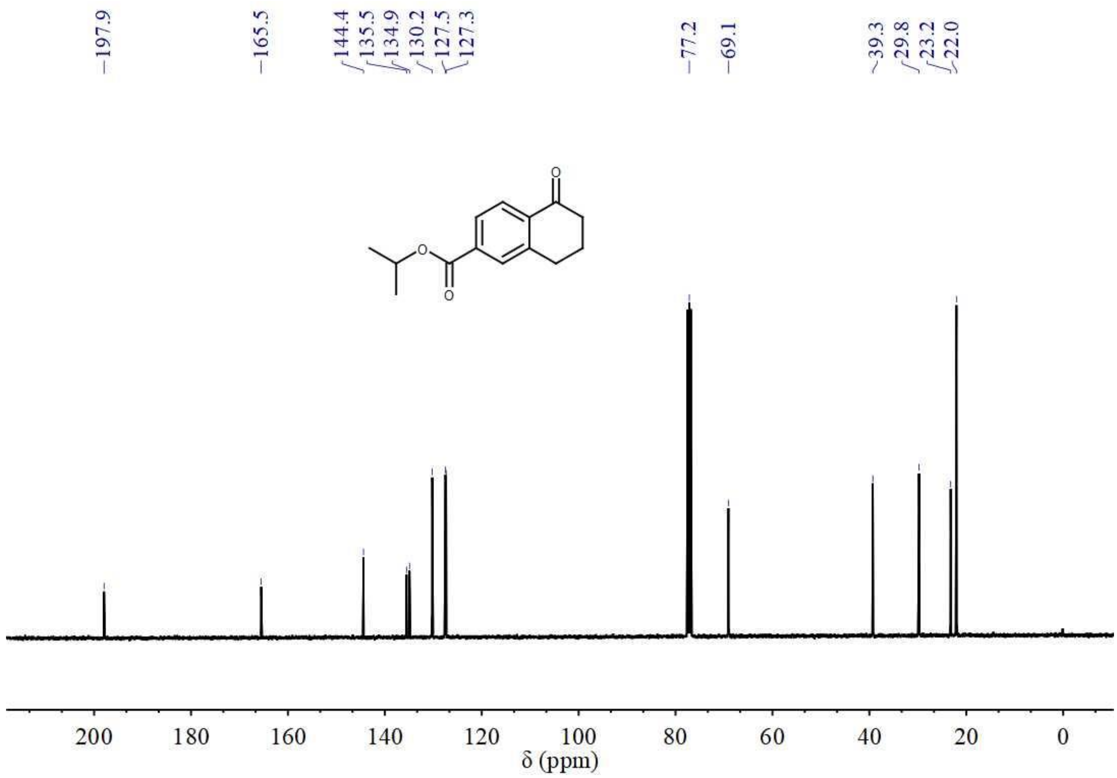
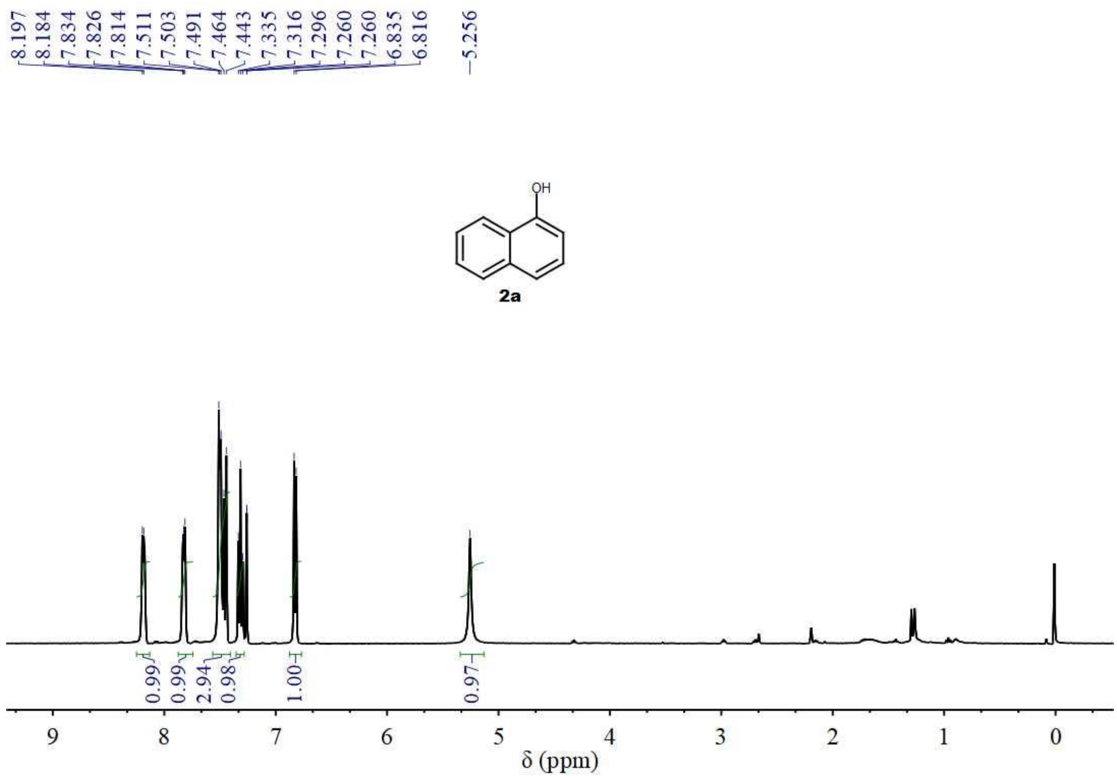
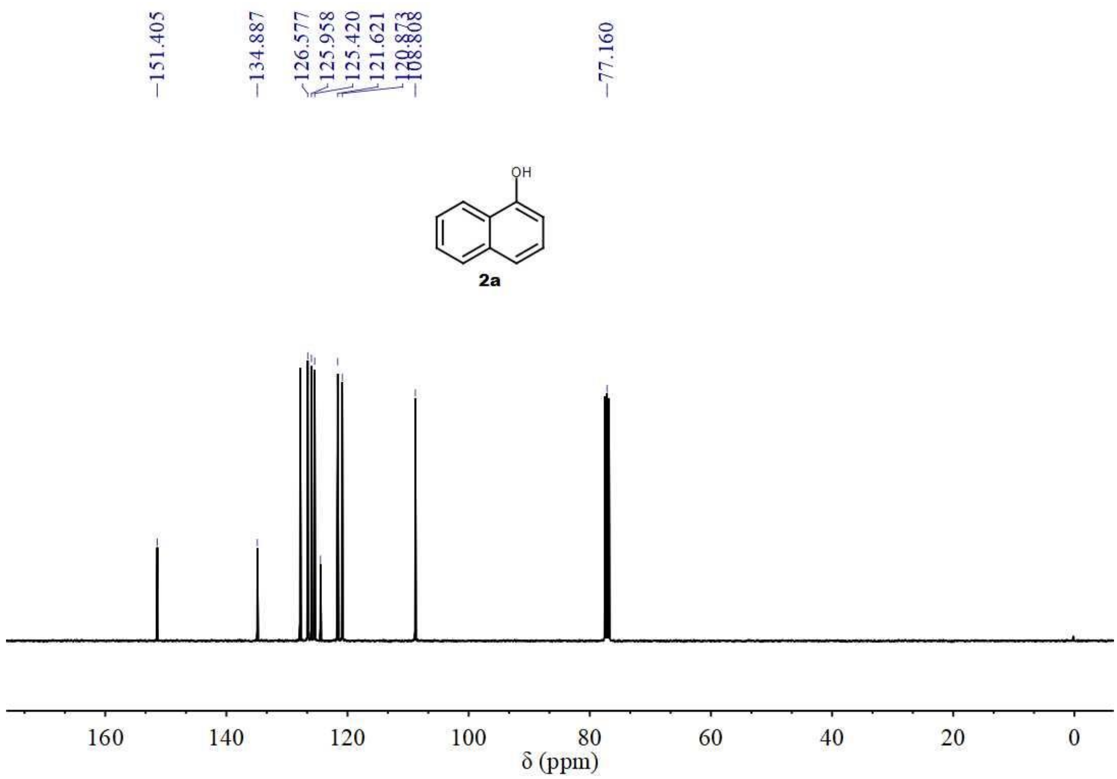
2.02
1.02
2.08
2.10
2.12
6.22
δ (ppm)

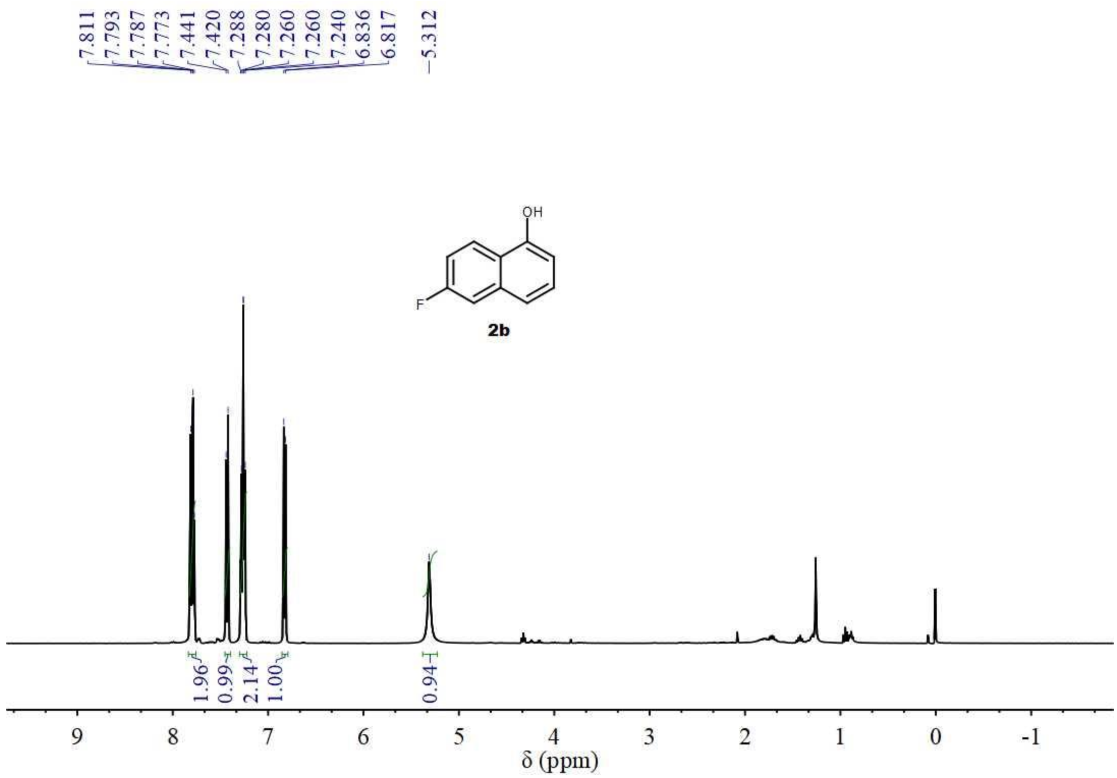


197.9
165.5
144.4
135.5
134.9
130.2
127.5
127.3
77.2
69.1
39.3
29.8
23.2
22.0
δ (ppm)

8. NMR spectra for products



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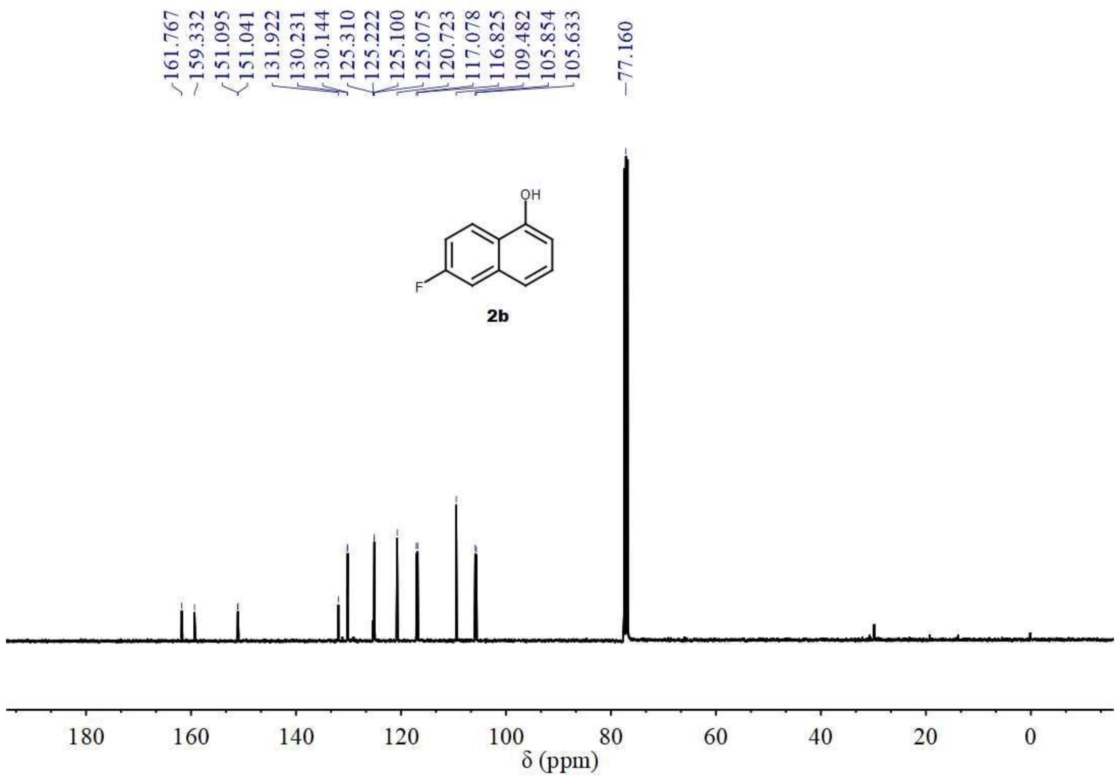
7.793
7.787
7.773
7.441
7.420
7.288
7.280
7.260
7.260
7.240
6.836
6.817
5.312
OH
F
2b
1.96
0.99
2.14
1.00
0.94
9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)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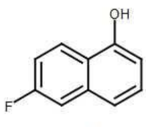
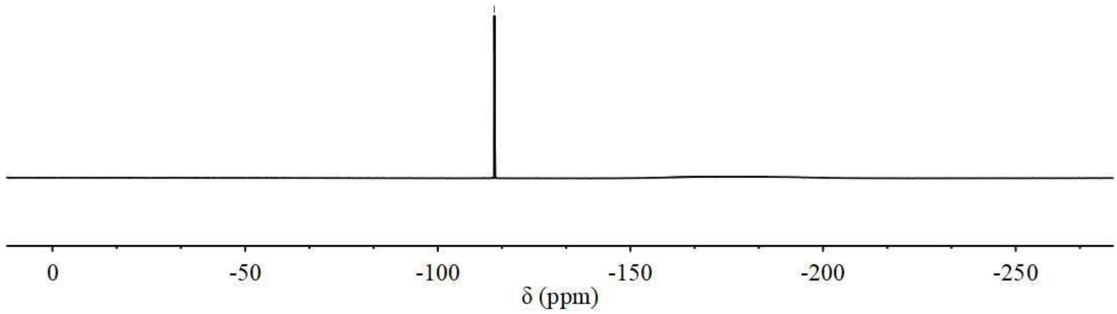
159.332
151.095
151.041
131.922
130.231
130.144
125.310
125.222
125.100
125.075
120.723
117.078
116.825
109.482
105.854
105.633
77.160
OH
F
2b
180 160 140 120 100 80 60 40 20 0
δ (ppm)

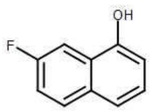
—114.692



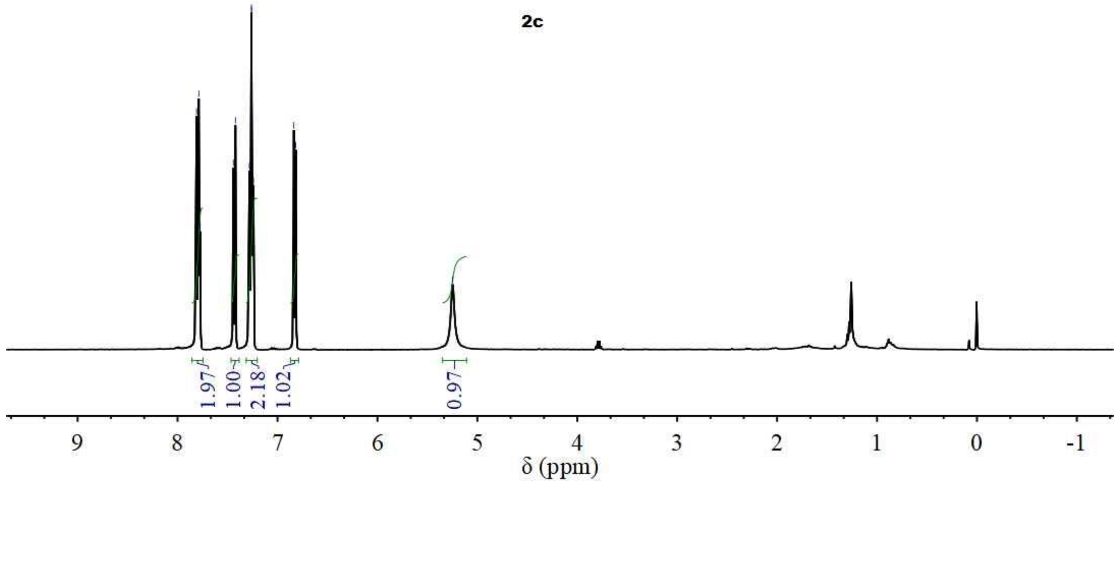
2b

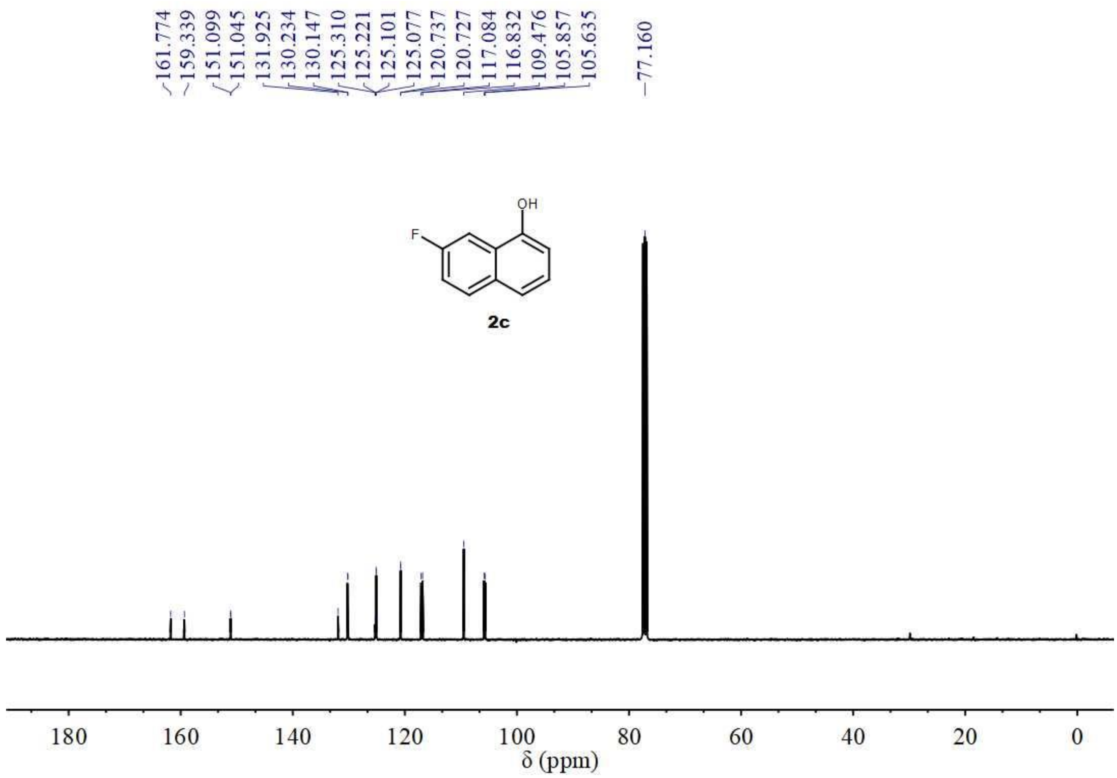


7.810
7.787
7.773
7.441
7.421
7.281
7.260
7.260
7.251
7.240
6.836
6.817
—5.247



2c

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125.101
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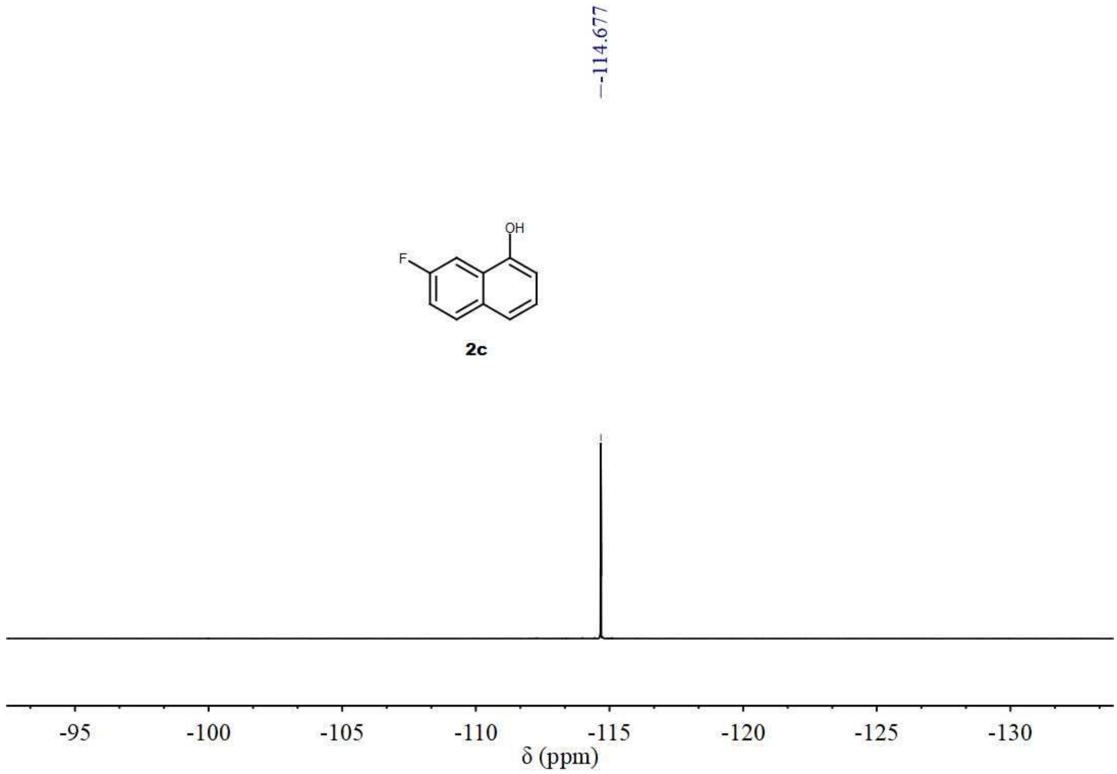
120.727
117.084
116.832
109.476
105.857
105.635
77.160
OH
F
2c
180 160 140 120 100 80 60 40 20 0
δ (ppm)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2c
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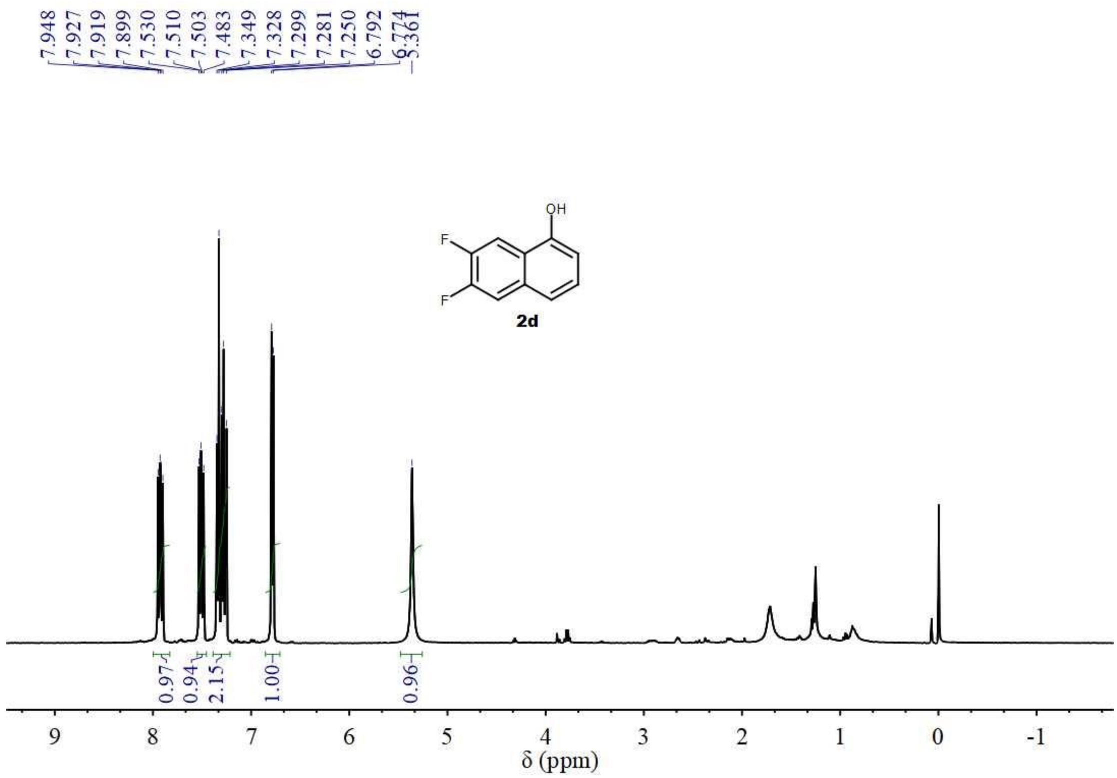
δ (ppm)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7.349
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7.281
7.250
6.792
6.774
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F
F
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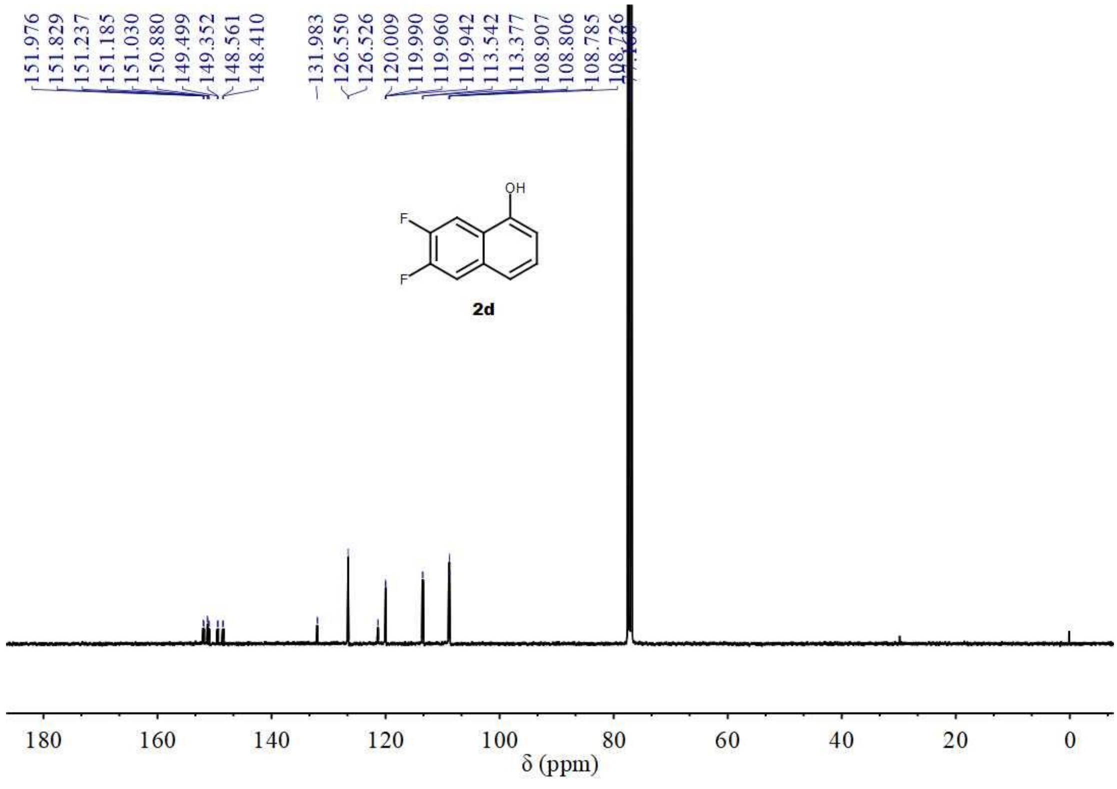
1.00
0.96
9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)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149.352
148.561
148.410
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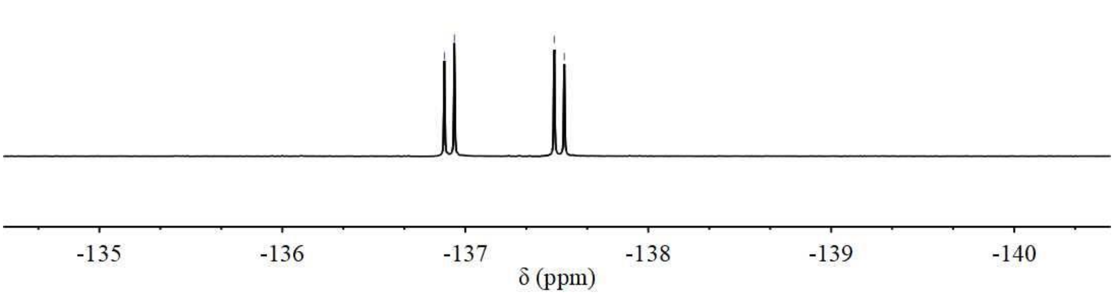
126.526
120.009
119.990
119.960
119.942
113.542
113.377
108.907
108.806
108.785
108.726
OH
F
F
2d
180 160 140 120 100 80 60 40 20 0
δ (ppm)



-136.886
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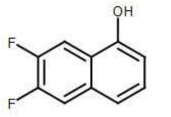
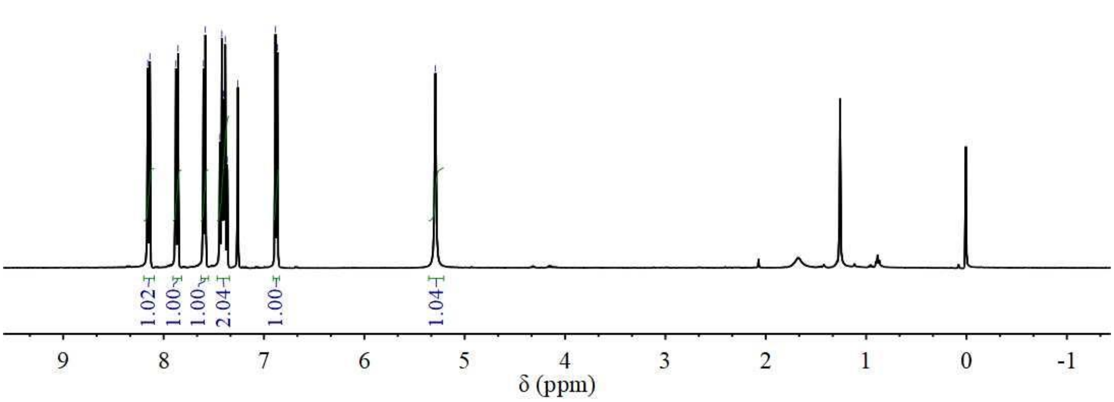
-137.486
-137.541
-135
-136
-137
-138
-139
-140
δ (ppm)



2d



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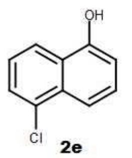
7.585
7.440
7.420
7.404
7.386
7.367
7.260
6.885
6.867
5.292
1.02
1.00
1.00
2.04
1.00
1.04
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)



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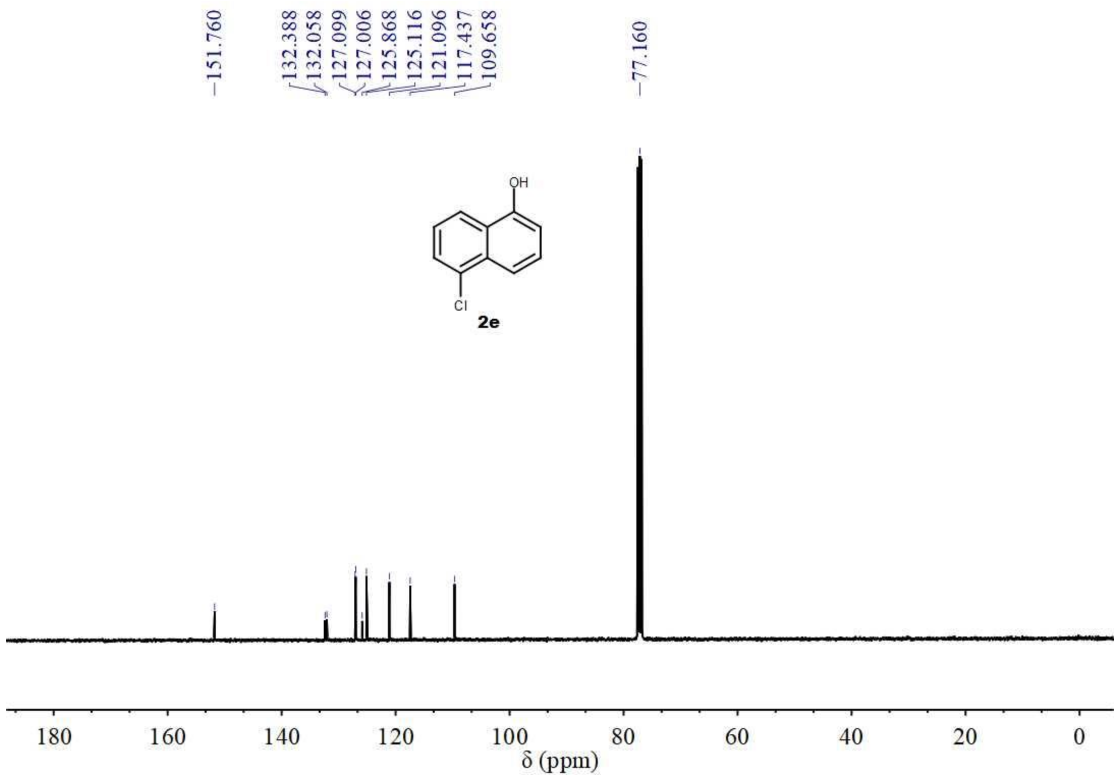
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127.006
125.868
125.116
121.096
117.437
109.658
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OH
Cl
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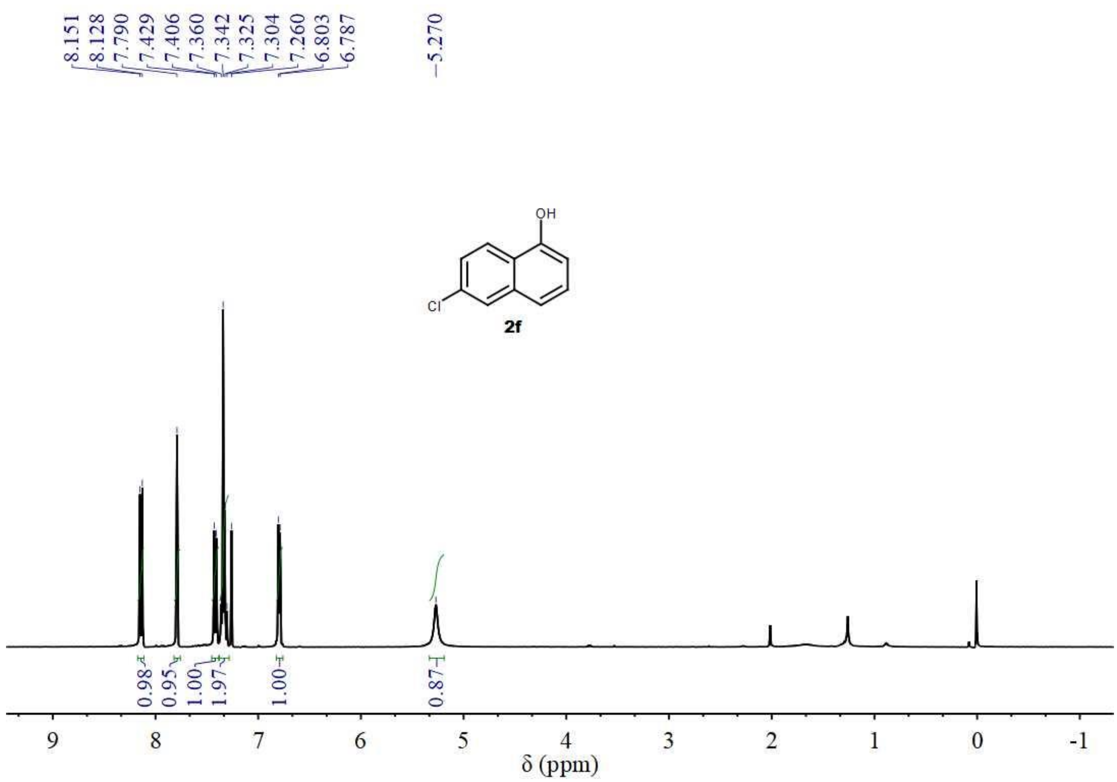
180
160
140
120
100
80
60
40
20
0
δ (ppm)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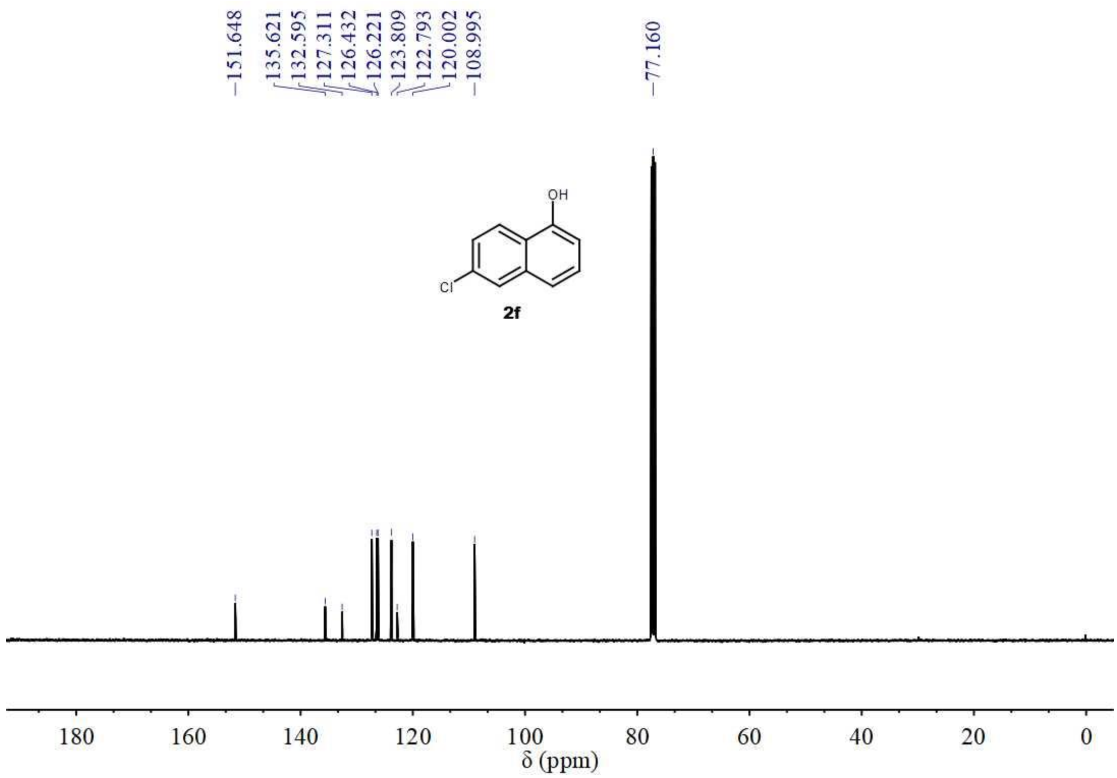
7.790
7.429
7.406
7.360
7.342
7.325
7.304
7.260
6.803
6.787
5.270
OH
Cl
2f
0.98
0.95
1.00
1.97
1.00
0.87
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)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OH
Cl
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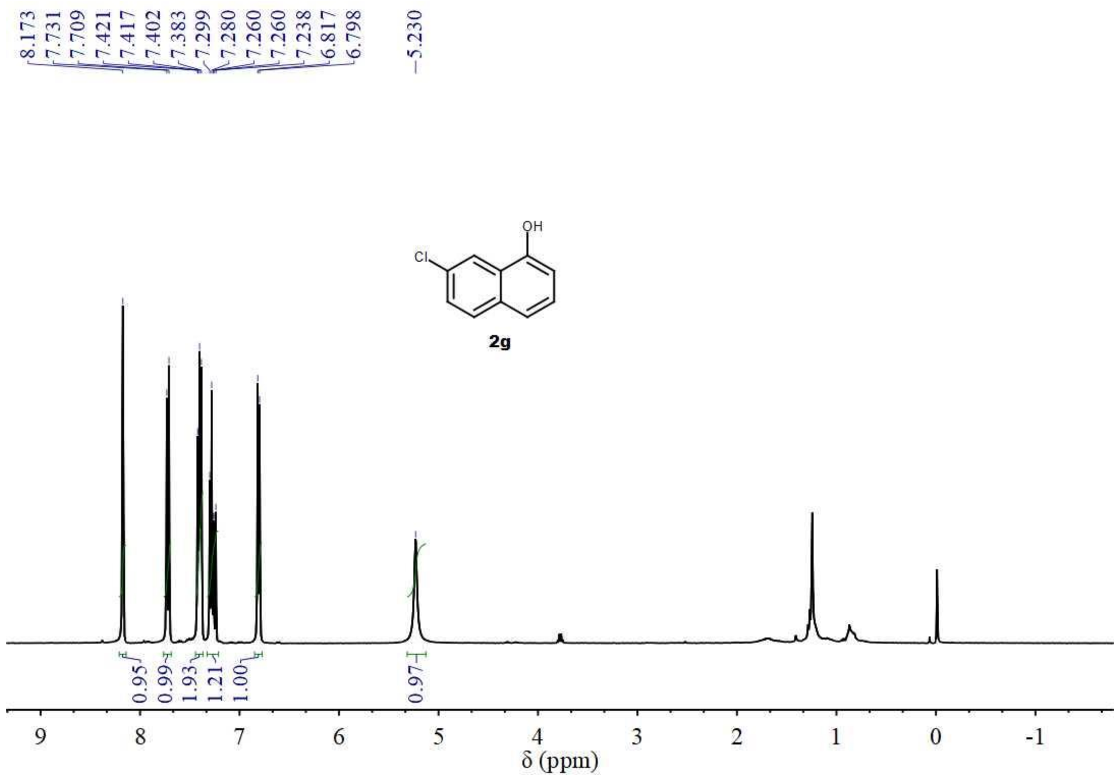
140
120
100
80
60
40
20
0
δ (ppm)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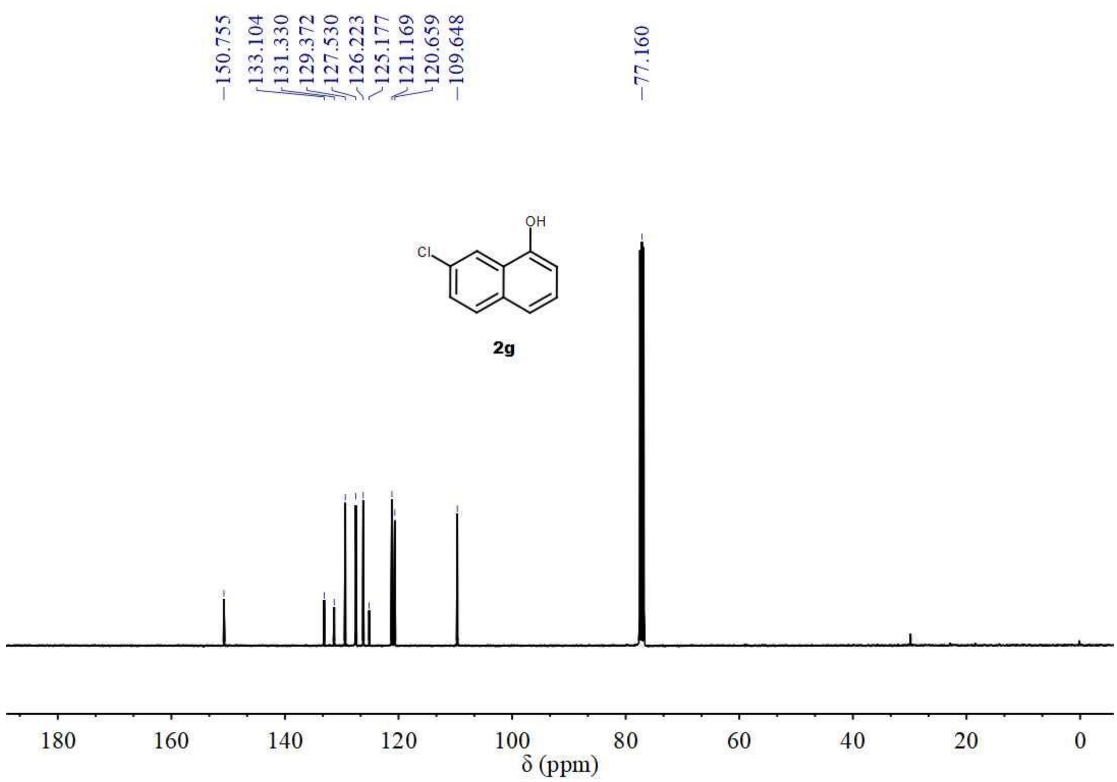
6.817
6.798
5.230
OH
Cl
2g
0.95
0.99
1.93
1.21
1.00
0.97
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)



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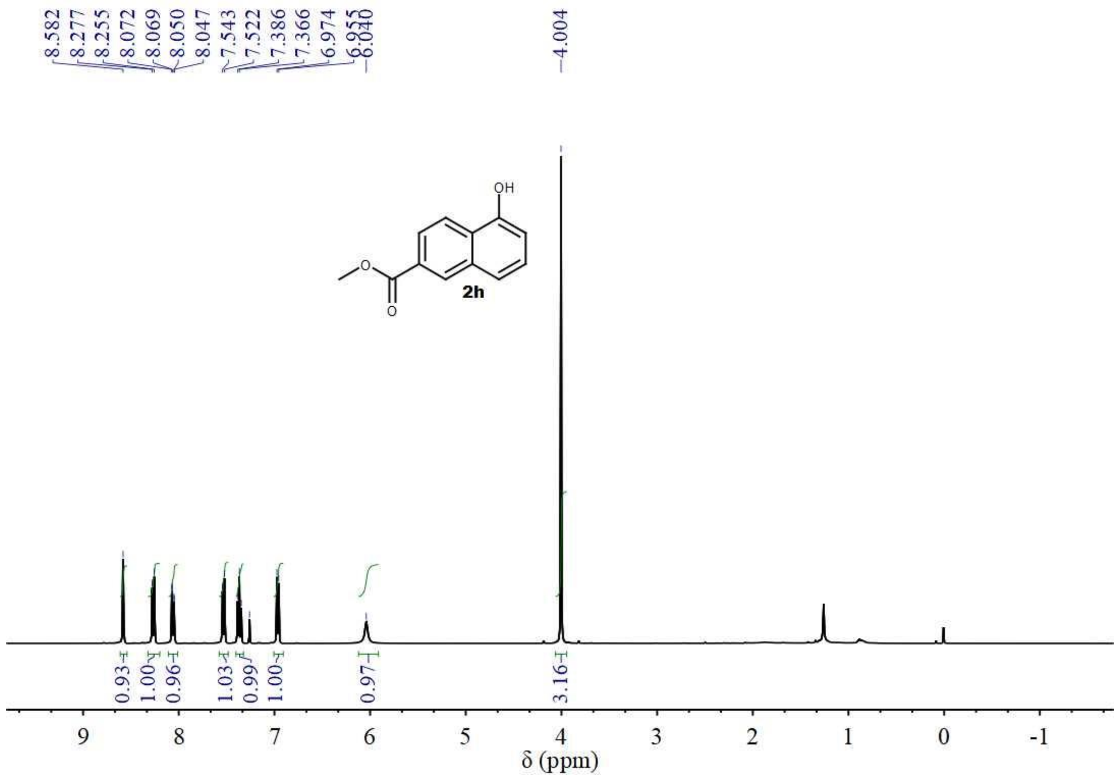
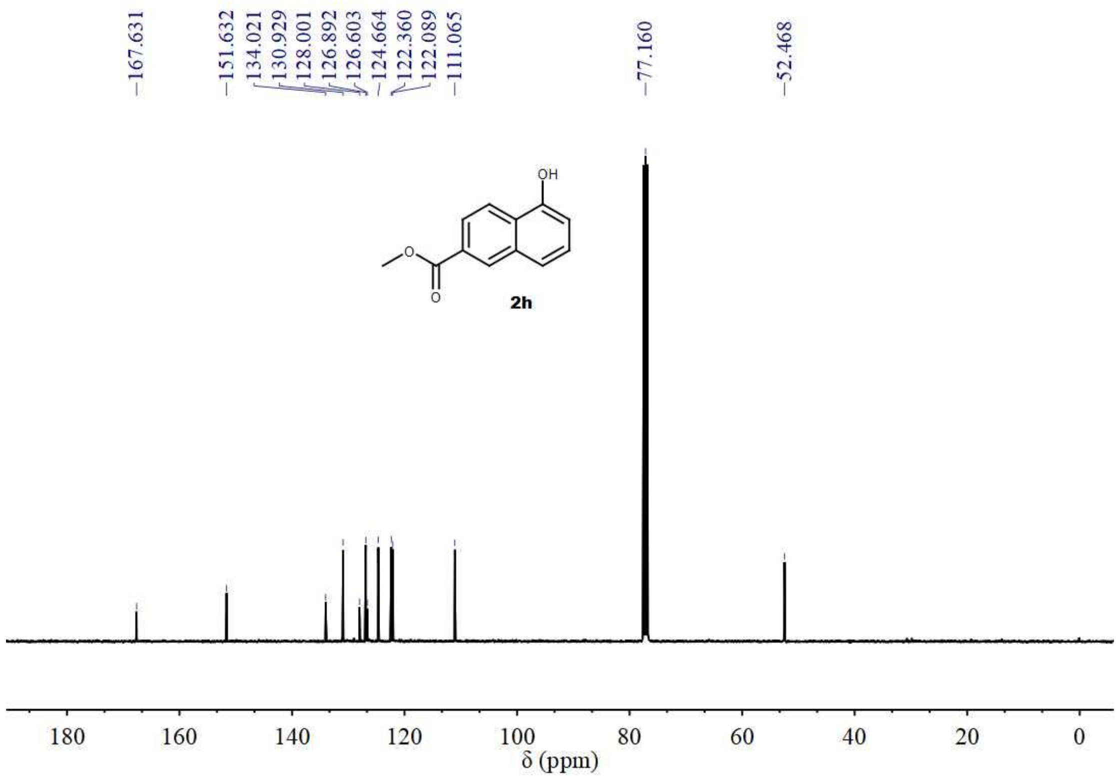
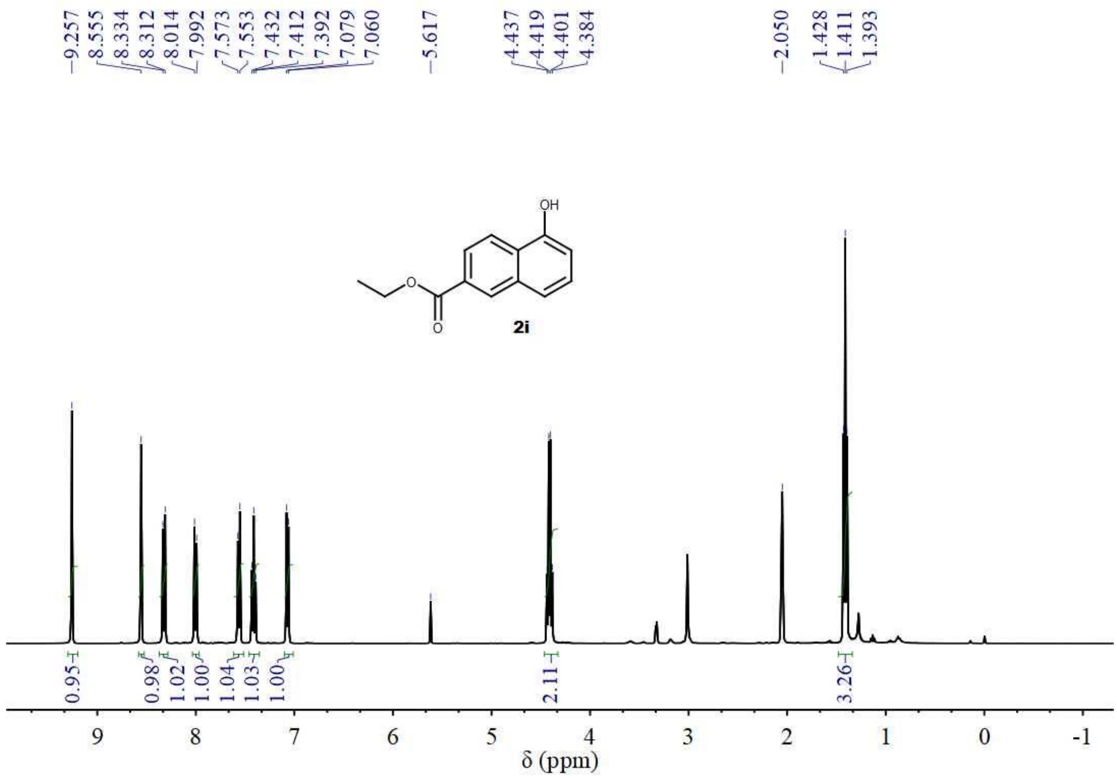
109.648
77.160
OH
Cl
2g
180
160
140
120
100
80
60
40
20
0
δ (ppm)



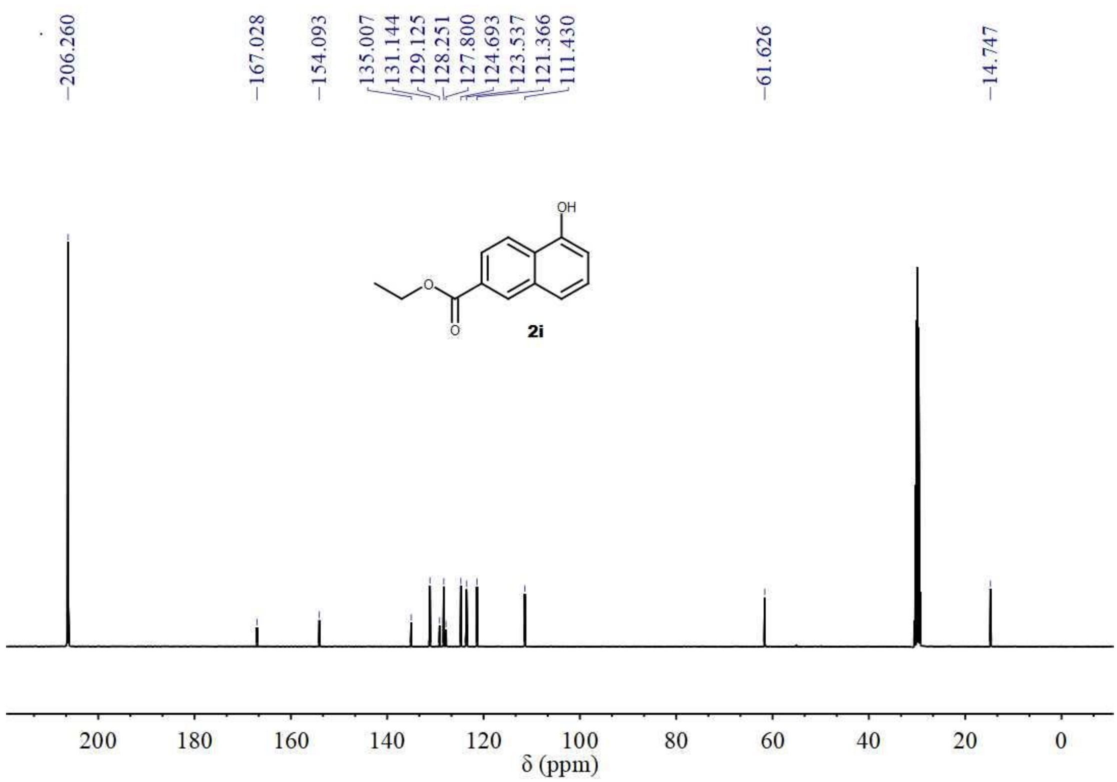
8.582
8.277
8.255
8.072
8.069
8.050
8.047
7.543
7.522
7.386
7.366
6.974
6.955
6.040
4.004
OH
O
O
2h
0.93
1.00
0.96
1.03
0.99
1.00
0.97
3.16
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

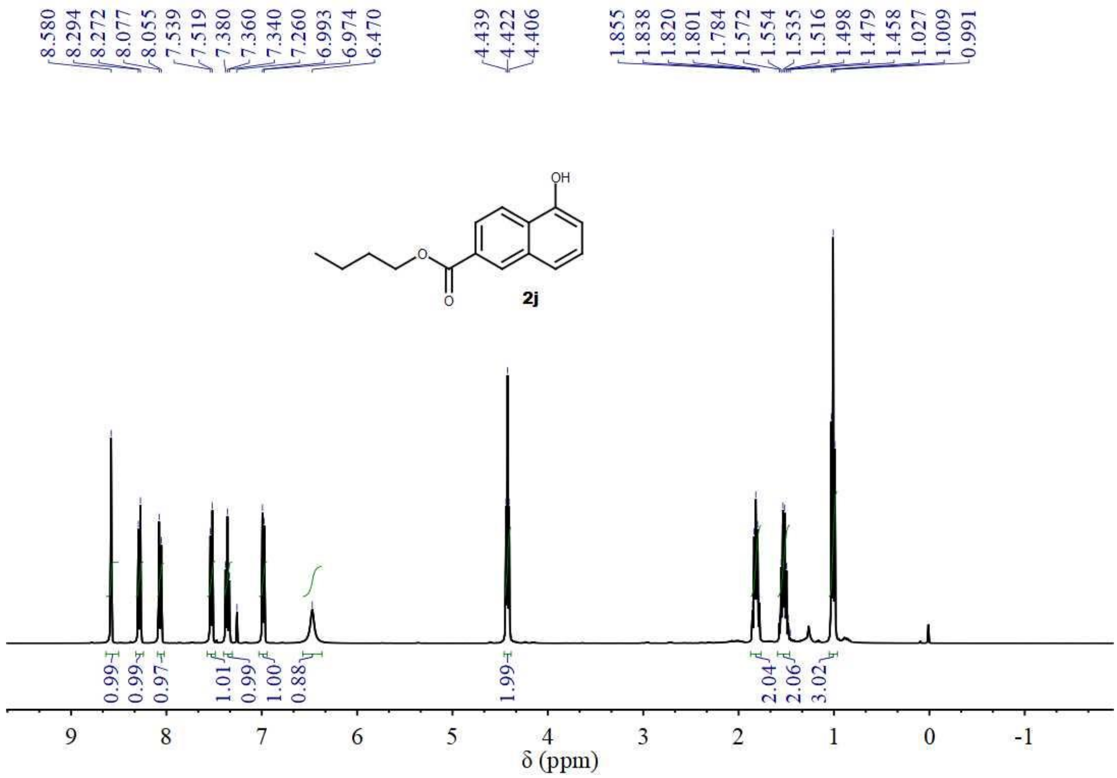


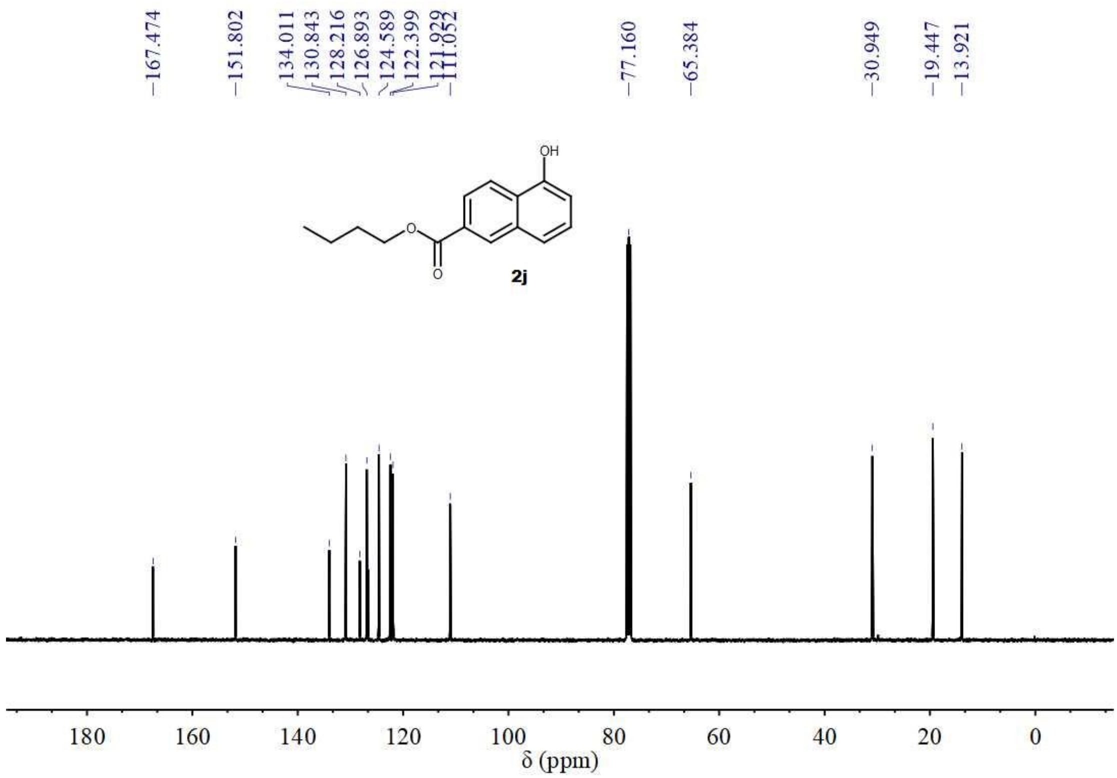
167.631
151.632
134.021
130.929
128.001
126.892
126.603
124.664
122.360
122.089
111.065
77.160
52.468
OH
O
O
2h
180
160
140
120
100
80
60
40
20
0
δ (ppm)



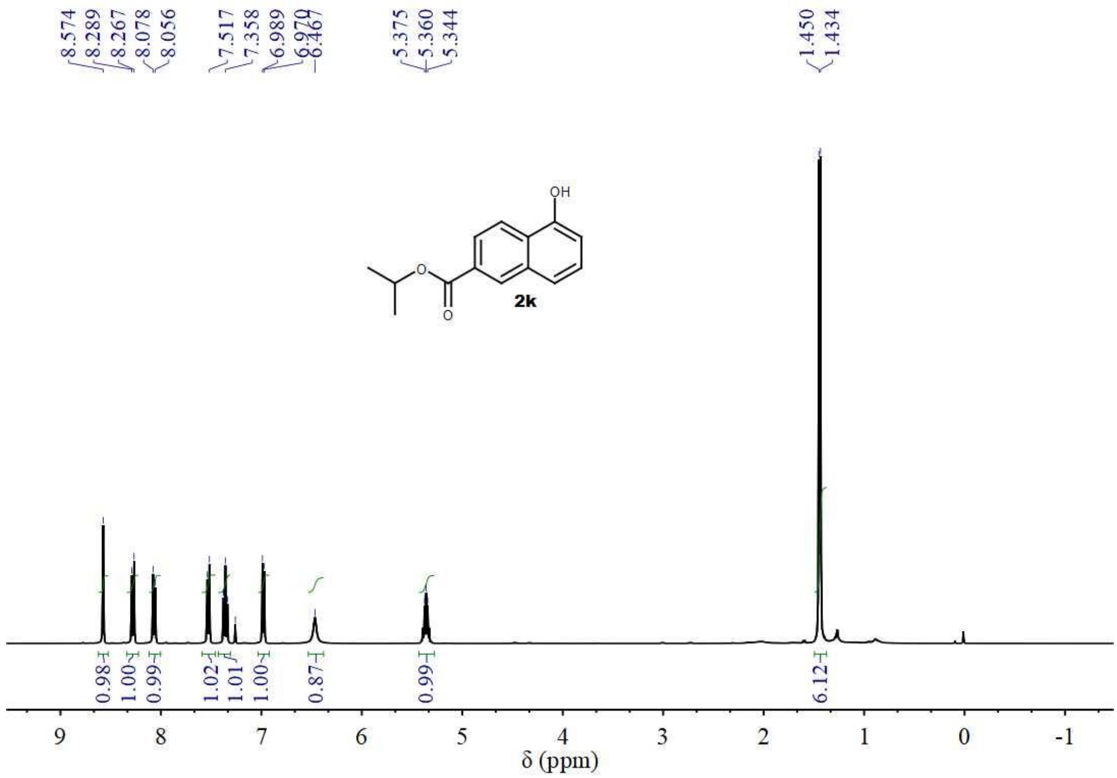
9.257
8.555
8.334
8.312
8.014
7.992
7.573
7.553
7.432
7.412
7.392
7.079
7.060
5.617
4.437
4.419
4.401
4.384
2.050
1.428
1.411
1.393
OH
O
O
2i
0.95
0.98
1.02
1.00
1.04
1.03
1.00
2.11
3.26
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


206.260
167.028
154.093
135.007
131.144
129.125
128.251
127.800
124.693
123.537
121.366
111.430
61.626
14.747
OH
O
O
2i
200
180
160
140
120
100
80
60
40
20
0
δ (ppm)

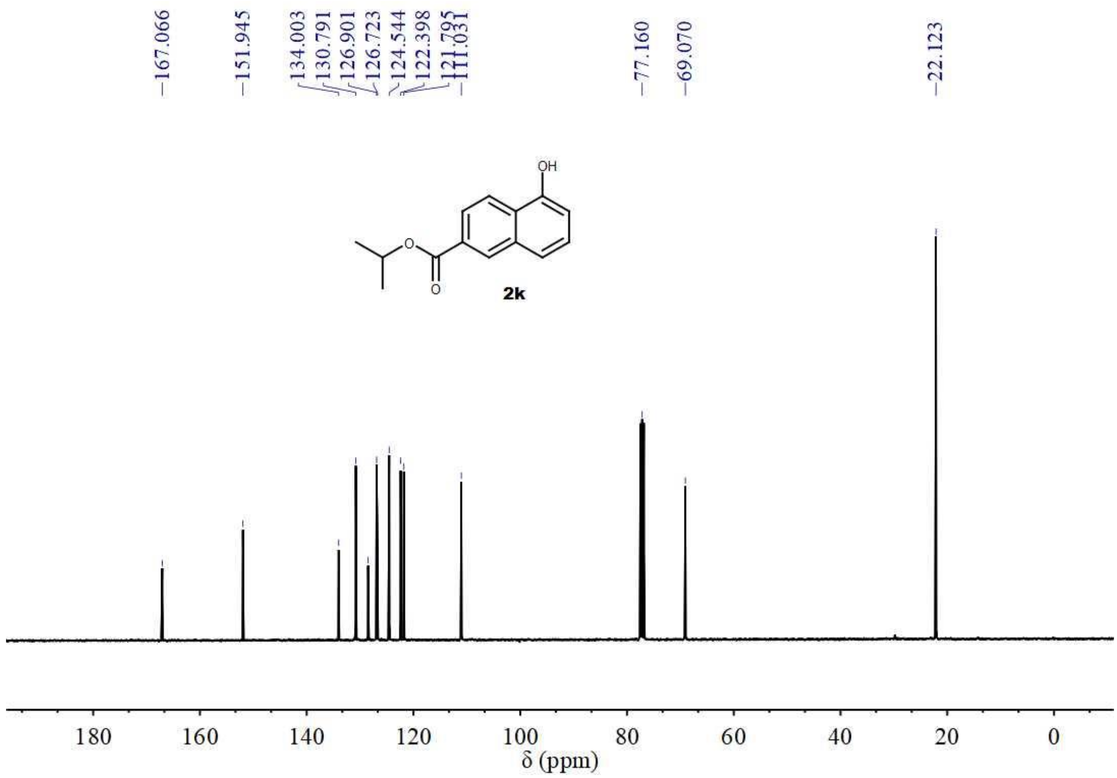

8.580
8.294
8.272
8.077
8.055
7.539
7.519
7.380
7.360
7.340
7.260
6.993
6.974
6.470
4.439
4.422
4.406
1.855
1.838
1.820
1.801
1.784
1.572
1.554
1.535
1.516
1.498
1.479
1.458
1.027
1.009
0.991
OH
O
O
2j
0.99
0.99
0.97
1.01
0.99
1.00
0.88
1.99
2.04
2.06
3.02
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

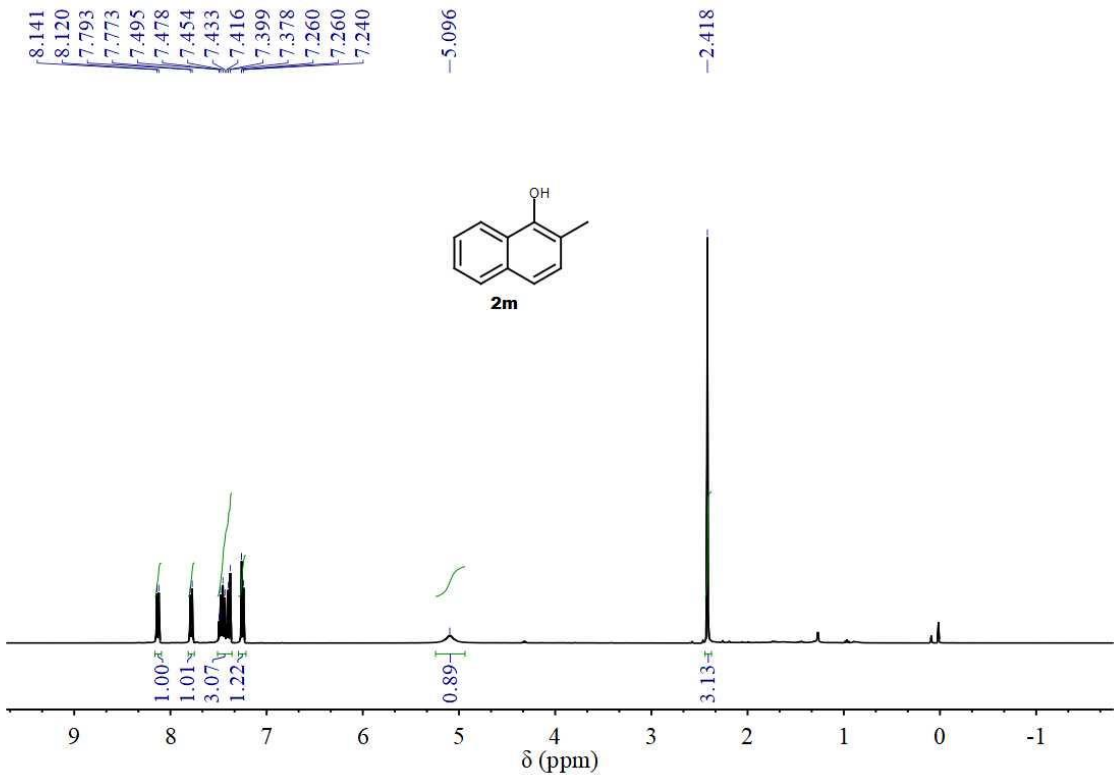


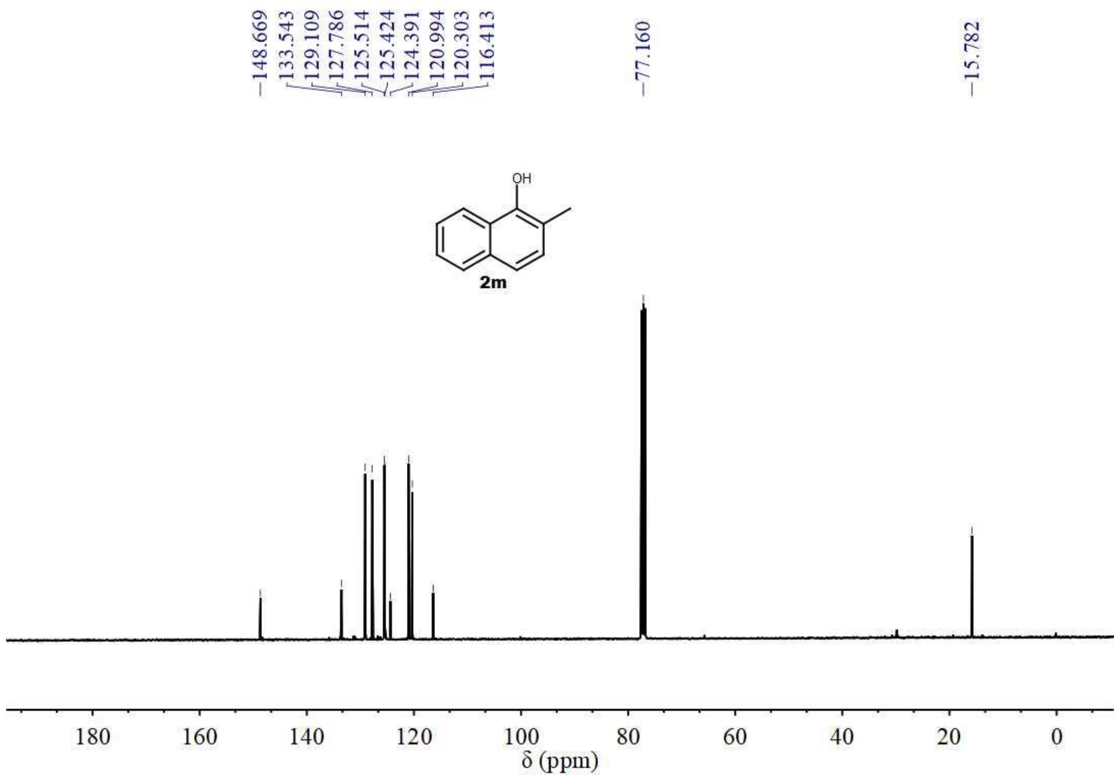
167.474
151.802
134.011
130.843
128.216
126.893
124.589
122.399
121.929
111.052
77.160
65.384
30.949
19.447
13.921
OH
O
O
2j
180
160
140
120
100
80
60
40
20
0
δ (ppm)

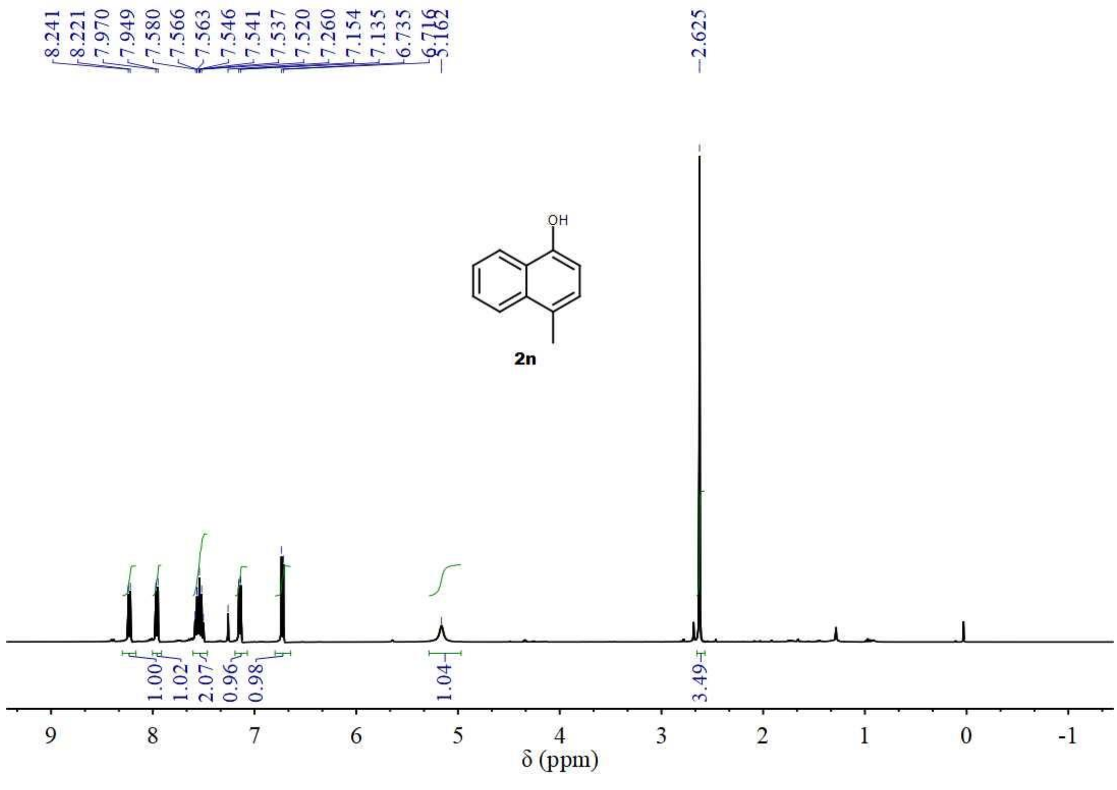


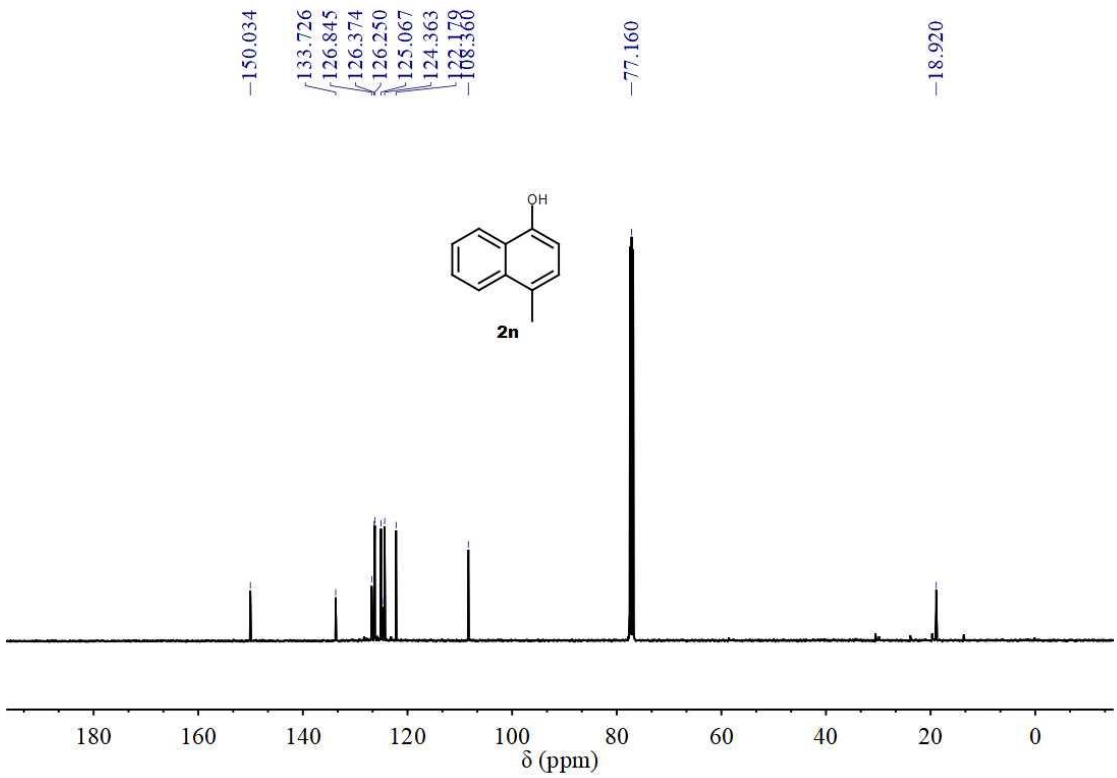
8.574
8.289
8.267
8.078
8.056
7.517
7.358
6.989
6.970
6.467
5.375
5.360
5.344
1.450
1.434
OH
O
O
2k
0.98
1.00
0.99
1.02
1.01
1.00
0.87
0.99
6.12
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

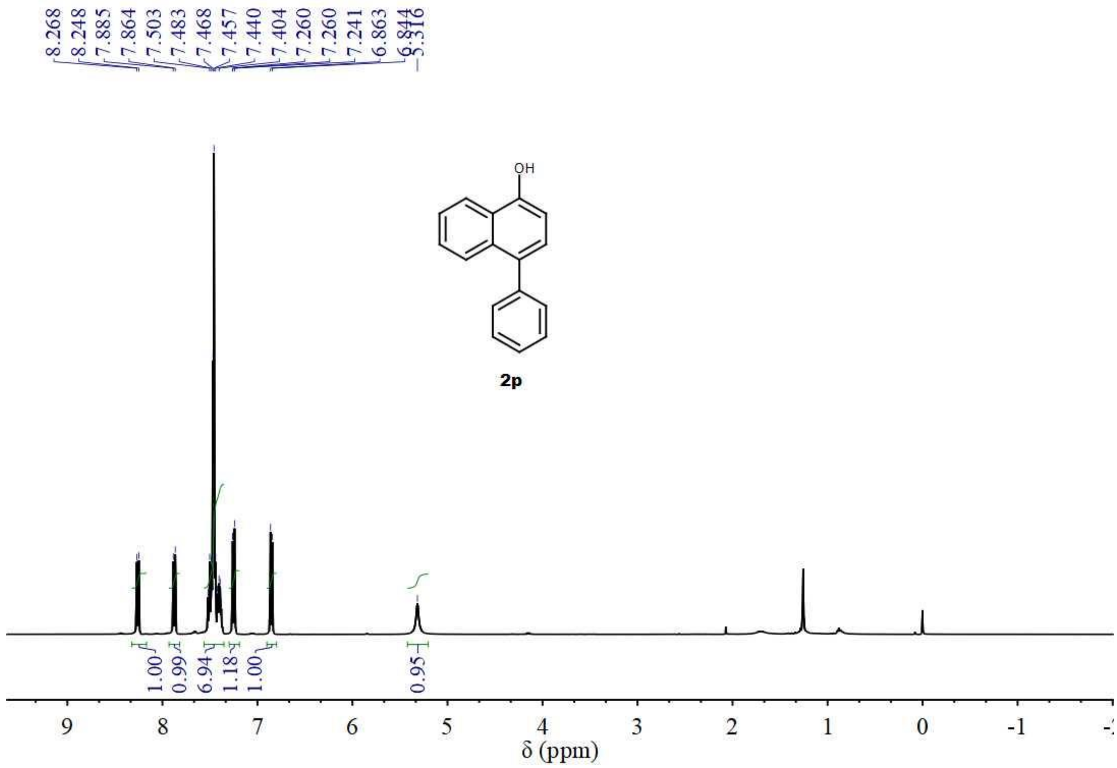

167.066
151.945
134.003
130.791
126.901
126.723
124.544
122.398
121.795
111.031
77.160
69.070
22.123
OH
O
O
2k
180
160
140
120
100
80
60
40
20
0
δ (ppm)

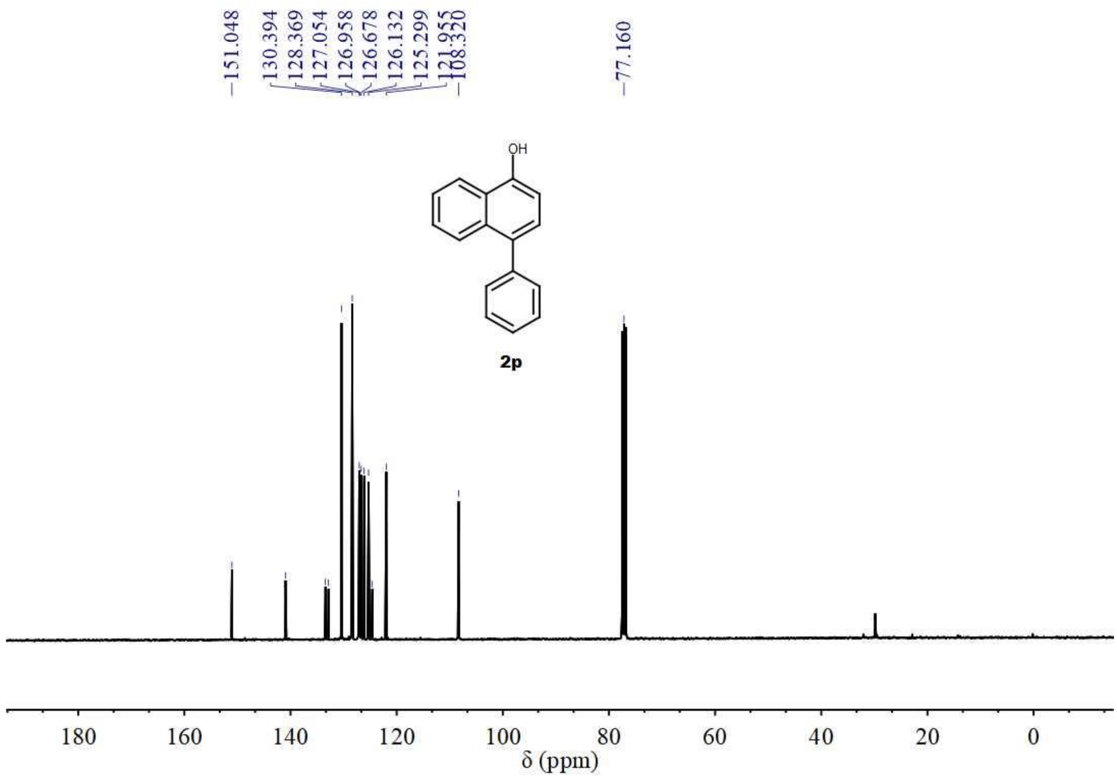

8.141
8.120
7.793
7.773
7.495
7.478
7.454
7.433
7.416
7.399
7.378
7.260
7.260
7.240
5.096
2.418
OH
2m
1.00
1.01
3.07
1.22
0.89
3.13
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


148.669
133.543
129.109
127.786
125.514
125.424
124.391
120.994
120.303
116.413
77.160
15.782
OH
2m
180
160
140
120
100
80
60
40
20
0
δ (ppm)

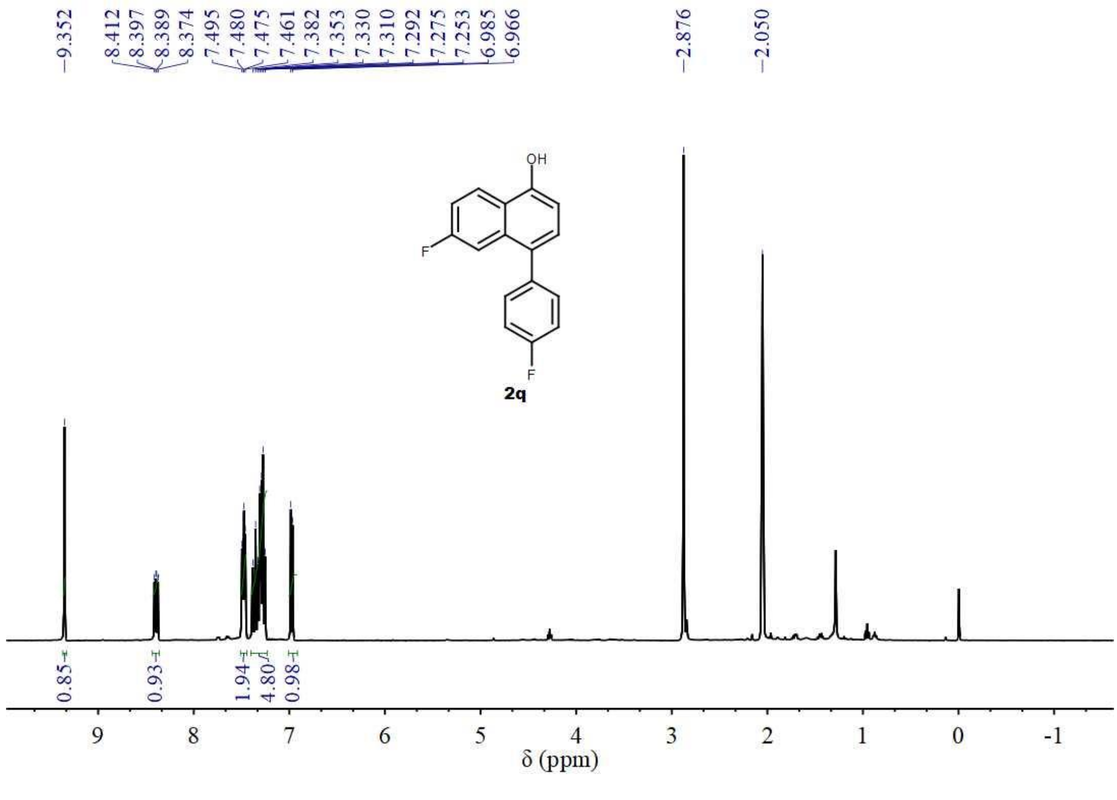

8.241
8.221
7.970
7.949
7.580
7.566
7.563
7.546
7.541
7.537
7.520
7.260
7.154
7.135
6.735
6.716
5.162
2.625
OH
2n
1.00
1.02
2.07
0.96
0.98
1.04
3.49
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


150.034
133.726
126.845
126.374
126.250
125.067
124.363
122.179
108.360
77.160
18.920
OH
2n
180
160
140
120
100
80
60
40
20
0
δ (ppm)

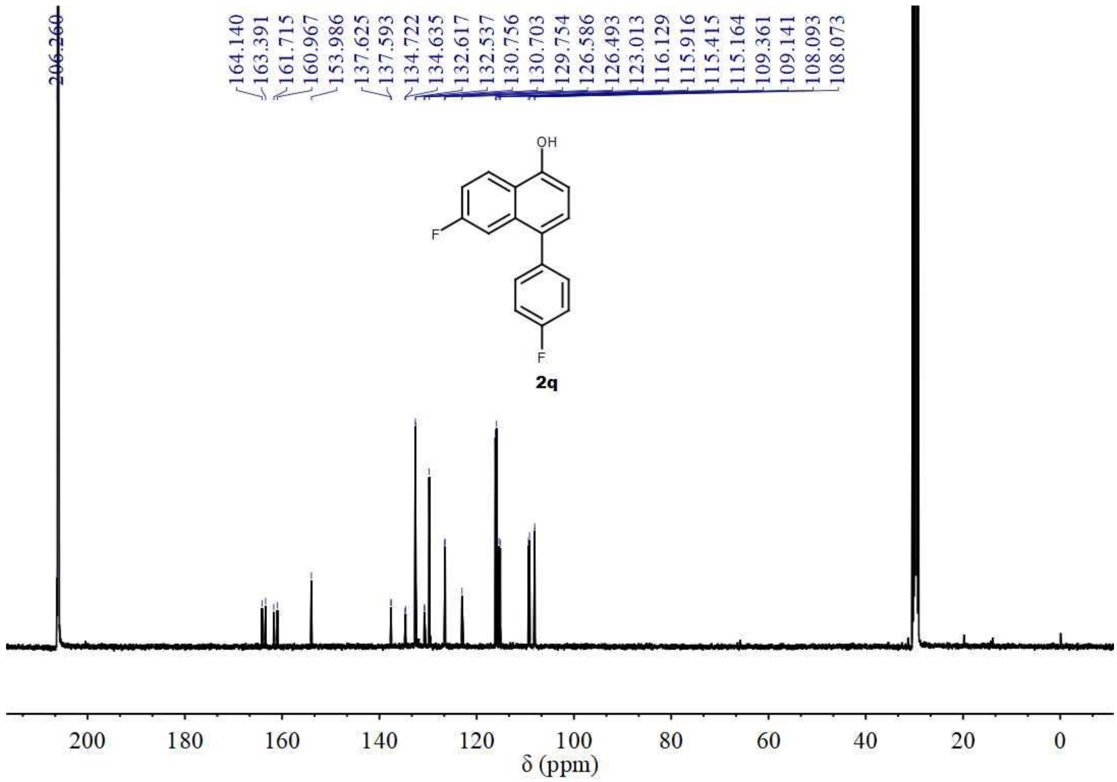

8.268
8.248
7.885
7.864
7.503
7.483
7.468
7.457
7.440
7.404
7.260
7.260
7.241
6.863
6.844
5.316
OH
2p
1.00
0.99
6.94
1.18
1.00
0.95
9
8
7
6
5
4
3
2
1
0
-1
-
δ (ppm)

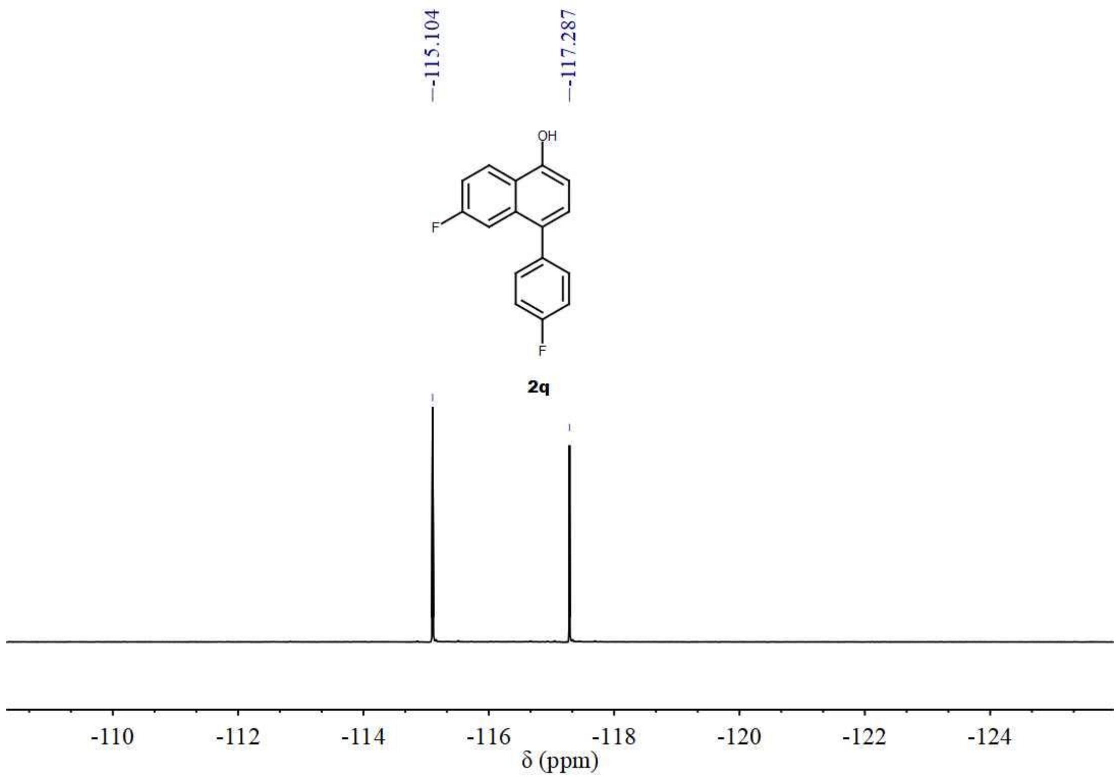


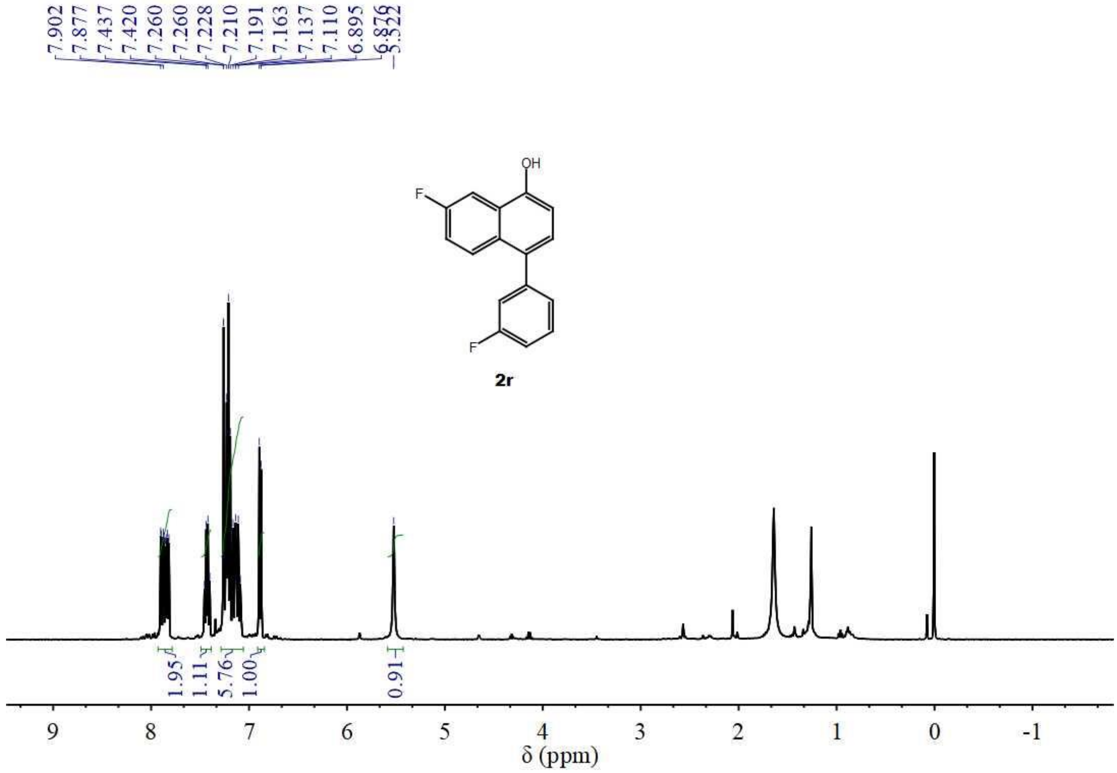
151.048
130.394
128.369
127.054
126.958
126.678
126.132
125.299
121.955
108.320
77.160
OH
2p
180 160 140 120 100 80 60 40 20 0
δ (ppm)

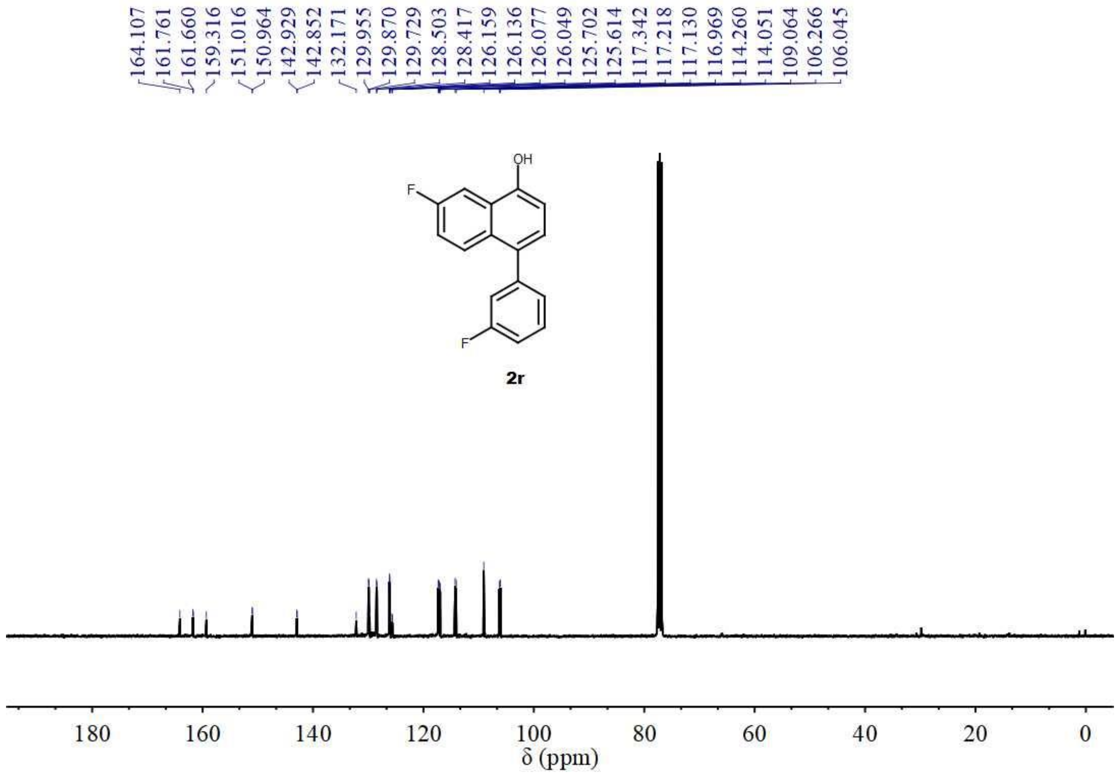


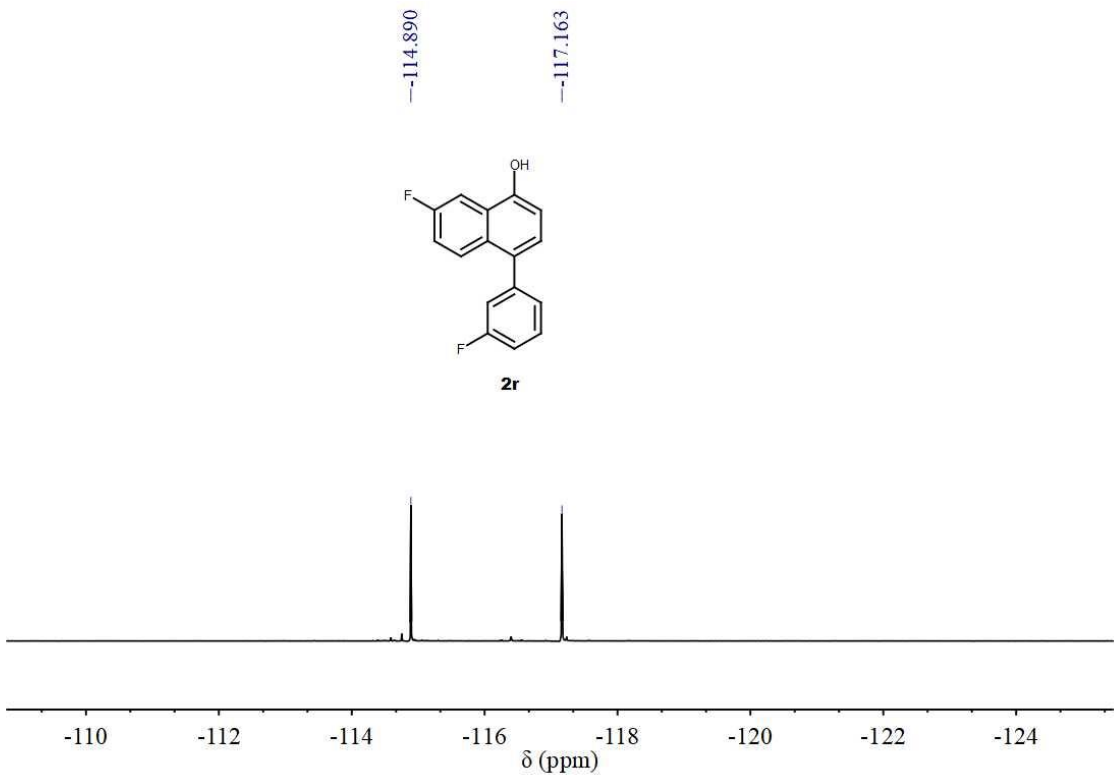
9.352
8.412
8.397
8.389
8.374
7.495
7.480
7.475
7.461
7.382
7.353
7.330
7.310
7.292
7.275
7.253
6.985
6.966
2.876
2.050
OH
F
F
2q
0.85
0.93
1.94
4.80
0.98
9 8 7 6 5 4 3 2 1 0 -1
δ (ppm)


206.260
164.140
163.391
161.715
160.967
153.986
137.625
137.593
134.722
134.635
132.617
132.537
130.756
130.703
129.754
126.586
126.493
123.013
116.129
115.916
115.415
115.164
109.361
109.141
108.093
108.073
OH
F
F
2q
200
180
160
140
120
100
80
60
40
20
0
δ (ppm)

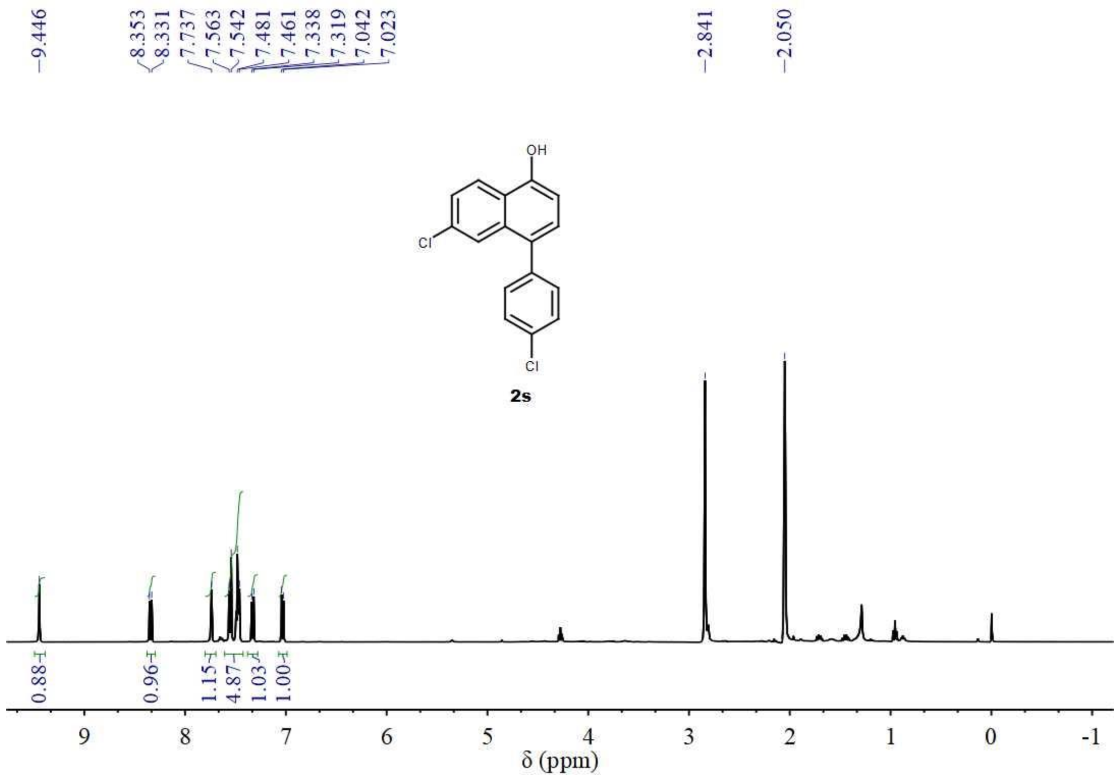

-115.104
-117.287
OH
F
F
2q
-110
-112
-114
-116
-118
-120
-122
-124
δ (ppm)


7.902
7.877
7.437
7.420
7.260
7.260
7.228
7.210
7.191
7.163
7.137
7.110
6.895
6.876
5.522
OH
F
F
2r
1.95
1.11
5.76
1.00
0.91
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

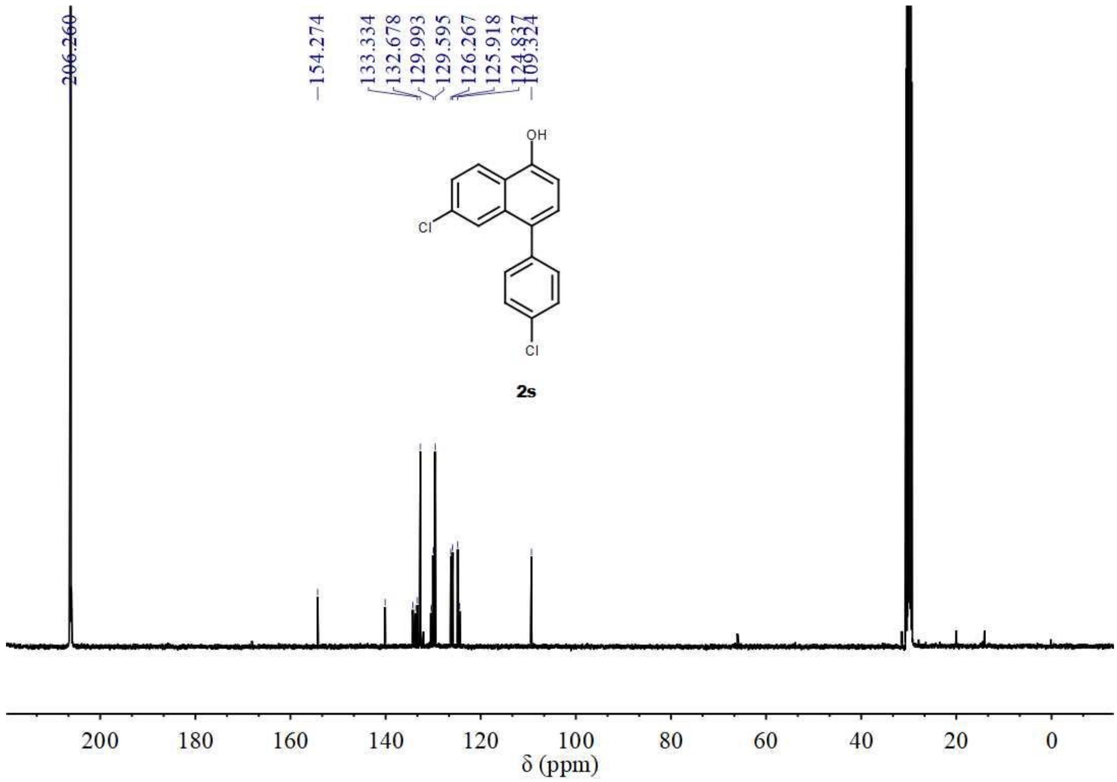

164.107
161.761
161.660
159.316
151.016
150.964
142.929
142.852
132.171
129.955
129.870
129.729
128.503
128.417
126.159
126.136
126.077
126.049
125.702
125.614
117.342
117.218
117.130
116.969
114.260
114.051
109.064
106.266
106.045
OH
F
F
2r
180
160
140
120
100
80
60
40
20
0
δ (ppm)

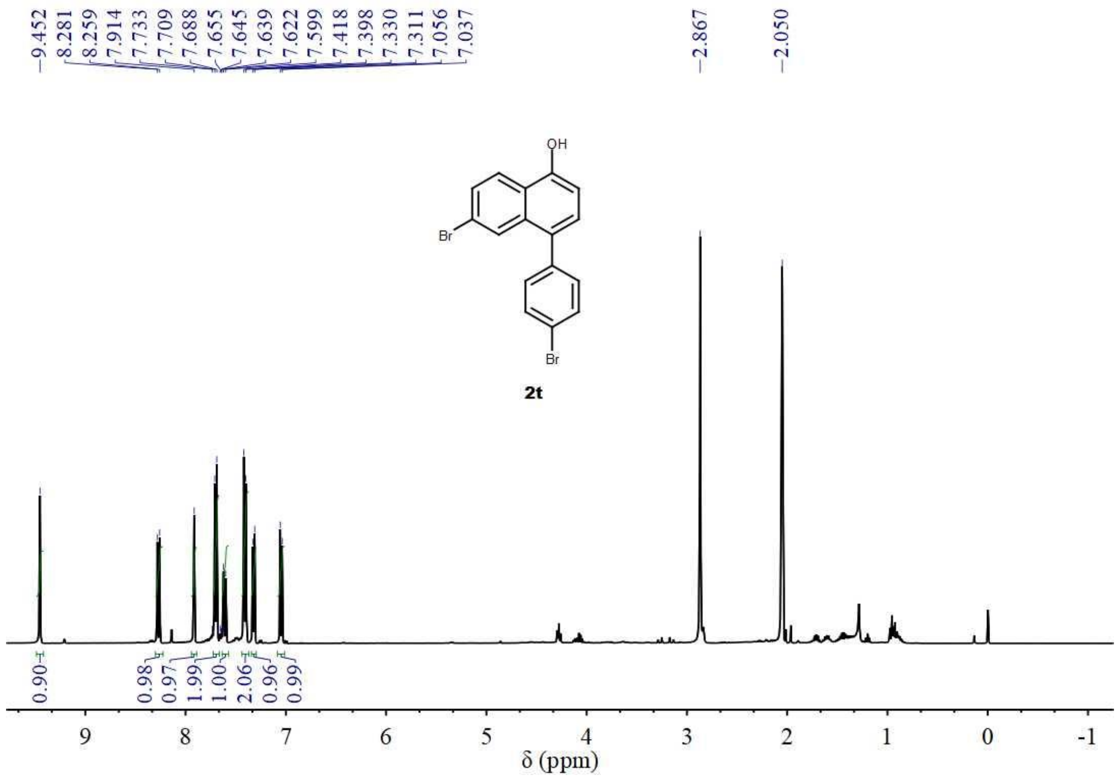


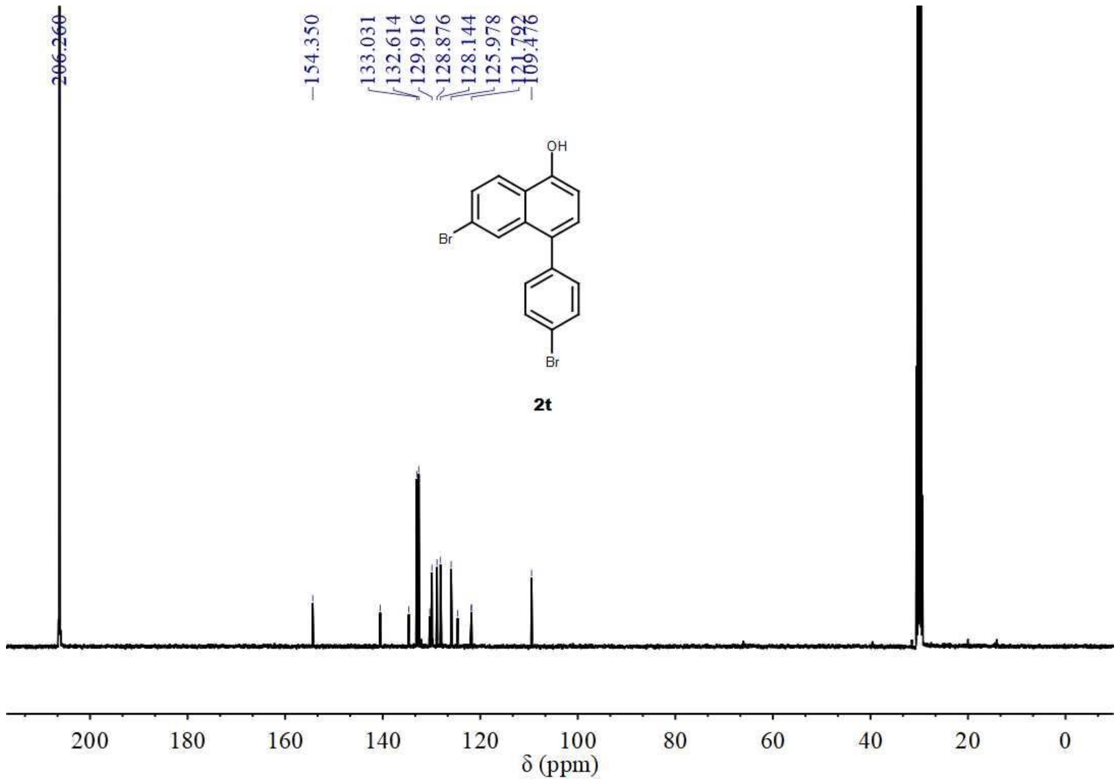
-114.890
-117.163
OH
F
F
2r
-110
-112
-114
-116
-118
-120
-122
-124
δ (ppm)



9.446
8.353
8.331
7.737
7.563
7.542
7.481
7.461
7.338
7.319
7.042
7.023
2.841
2.050
OH
Cl
Cl
2s
0.88
0.96
1.15
4.87
1.03
1.00
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


206.260
154.274
133.334
132.678
129.993
129.595
126.267
125.918
124.837
109.324
OH
Cl
Cl
2s
200
180
160
140
120
100
80
60
40
20
0
δ (ppm)


9.452
8.281
8.259
7.914
7.733
7.709
7.688
7.655
7.645
7.639
7.622
7.599
7.418
7.398
7.330
7.311
7.056
7.037
2.867
2.050
OH
Br
Br
2t
0.90
0.98
0.97
1.99
1.00
2.06
0.96
0.99
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


206.260
154.350
133.031
132.614
129.916
128.876
128.144
125.978
121.792
109.476
OH
Br
Br
2t
200
180
160
140
120
100
80
60
40
20
0
δ (ppm)