Supporting Information

Benzene C-H Etherification via Photocatalytic Hydrogen-Evolution Cross-Coupling Reaction

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Contents

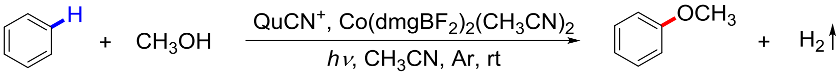
General Information

All commercially available reagents and solvents were used as received. 3-Cyano-1-methylquinolinium perchlorate salt ($QuCN^+ClO_4^-$) and $Co(dmgBF_2)_2(CH_3CN)_2$ were prepared according to published literature procedures[1]. Unless otherwise noted all the reactions were carried out in 10 mL Pyrex tube under Argon atmosphere. 500 W high pressure Hanovia mercury lamp with a glass water cooling jacket ($\lambda > 300$ nm) was used as light source. ^1H NMR spectra were recorded using a Bruker Advance DPX 400 MHz instrument with tetramethylsilane (TMS) as an internal standard. Data 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. 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 Ar 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 He as the carrier gas with capillary column (30 m × 0.25 mm × 0.33 μm) and a flame ionization detector (FID). Conversions and yields that were dertermined by NMR or GC were obtained from the crude reaction mixture by using *n*-tetradecane as an internal standard. The products were isolated by silica column chromatograph (200-300 meshes silica gel). Selectivity = GC yield or NMR yield / conversion.

General Procedure for Optimization

$QuCN^+ClO_4^-$ and $Co(dmgBF_2)_2(CH_3CN)_2$ were dissolved in CH_3CN and the reaction tube was sealed. After degassing by at least three freeze-pump-cycles, benzene (18 uL, 0.2 mmol) and CH_3OH 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 solution was irradiation at room temperature using a 500 W high pressure Hanovia mercury lamp with a glass water cooling jacket ($\lambda > 300$ nm). After 5 h irradiation, yield of H_2 was detected by GC-TCD. The conversion of benzene and yield of anisole were obtained from the crude reaction mixture by GC-FID using *n*-tetradecane as an internal standard. All the reactions were performed at least twice.

Table S1. Optimization for benzene etherification with methanol.



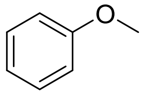
entry	CH_3OH (equiv)	pc (mol %)	cat. (mol %)	conv[a] (%)	select. (%)[b]	
					anisole	H_2
1	10	10	10	77	100	100
2	10	10	8	79	78	88
3	10	5	8	67	87	100
4	10	5	5	75	95	100
5	10	5	3	82	95	100
6	10	5	1	65	93	100
7[c]	10	5	3	80	95	100
8[c]	5	5	3	67	85	100
9[c]	10	0	3	0	0	0
10[c]	10	5	0	7	trace	0
11[d]	10	5	3	0	0	0

Reaction conditions: benzene (0.2 mmol), pc: $QuCN^+$, cat.: $Co(dmgBF_2)_2(CH_3CN)_2$, CH_3CN 8 mL. [a]Based on benzene. [b]Selectivity = GC yield / conversion. [c]CH_3CN 5 mL. [d]CH_3CN 5 mL, no light.

General Procedure for Etherification of Arenes (3a–s)

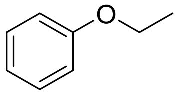
Arene (0.2 mmol, liquid arenes were added after degassing), $QuCN^+ClO_4^-$ (2.7 mg, 0.01 mmol) and $Co(dmgBF_2)_2(CH_3CN)_2$ (2.8 mg, 0.006 mmol) were dissolved in CH_3CN (5 mL) and the reaction tube was sealed. After degassing by at least three freeze-pump-cycles, ROH (2 mmol) was added. Methane (1mL) was then injected as the internal standard for analysis of generated H_2, and the pinholes were sealed by paraffin. The solution was irradiation at room temperature using a 500 W high pressure Hanovia mercury lamp with a glass water cooling jacket ($\lambda > 300$ nm). After 5 h irradiation, yield of H_2 was determined by GC-TCD. The conversion and yields were determined by GC-FID or 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 PE-EtOAc as eluent. The isolated yields were the average yields of parallel reactions.

Anisole (3a)



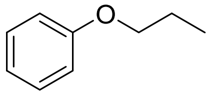
Colorless oil. GC yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.30 (dd, *J* = 8.7, 7.4 Hz, 2H), 6.99 – 6.89 (m, 3H), 3.82 (s, 3H).

Ethoxybenzene[2] (3b)



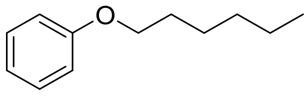
Colorless oil. GC yield: 59%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.33 – 7.25 (m, 2H), 6.93 (m, 3H), 4.05 (q, *J* = 7.0 Hz, 2H), 1.43 (t, *J* = 7.0 Hz, 3H).
MS (EI): *m/z* 122.1[M^+].

Propoxybenzene[3] (3c)



Colorless oil. Isolated yield: 11.2 mg, 41%, petroleum ether/EtOAc = 50/1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.30 – 7.24 (m, 2H), 6.92 (m, 3H), 3.92 (t, *J* = 6.6 Hz, 2H), 1.81 (dd, *J* = 14.1, 7.1 Hz, 2H), 1.04 (t, *J* = 7.4 Hz, 3H).
MS (EI): *m/z* 136.1[M^+].

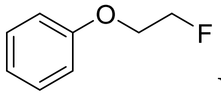
(Hexyloxy)benzene[4] (3d)



Colorless oil. Isolated yield: 16.8 mg, 47%, petroleum ether/EtOAc = 50/1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.29 (dd, *J* = 8.4, 7.5 Hz, 2H), 6.91 (m, 3H), 3.95 (t, J = 6.6 Hz, 2H), 1.82 – 1.73 (m, 2H), 1.51 – 1.41 (m, 2H), 1.38 – 1.30 (m, 4H), 0.91 (dd, *J* = 9.4, 4.5 Hz, 3H).

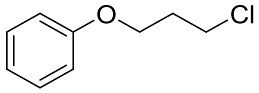
MS (EI): *m/z* 178.1[M$^+$].

(2-Fluoroethoxy)benzene[5] (3e)



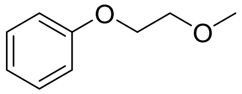
White solid. Isolated yield: 4.6 mg, 16%, petroleum ether/EtOAc = 50/1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.31 (t, *J* = 7.9 Hz, 2H), 6.99 (t, *J* = 7.4 Hz, 1H), 6.94 (d, *J* = 8.5 Hz, 2H), 4.84 – 4.81 (m, 1H), 4.72 – 4.69 (m, 1H), 4.27 – 4.24 (m, 1H), 4.21 – 4.17 (m, 1H).
HR-EI MS: *m/z* calculated for C_8H_9FO[M$^+$] 140.0637, found 140.0636..

(3-Chloropropoxy)benzene[6] (3f)



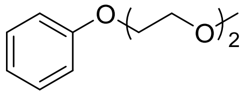
Colorless oil. Isolated yield: 9.7 mg, 28%, petroleum ether/EtOAc = 50/1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.30 (t, *J* = 7.3 Hz, 2H), 6.99 – 6.89 (m, 3H), 4.12 (t, *J* = 5.6 Hz, 2H), 3.76 (t, *J* = 6.1 Hz, 2H), 2.29 – 2.21 (m, 2H).
MS (EI): *m/z* 170.1[M$^+$].

(2-Methoxyethoxy)benzene[7] (3g)



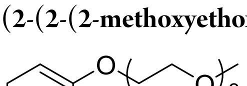
Colorless oil. Isolated yield: 8.0 mg, 26%, petroleum ether/EtOAc = 30/1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.28 (dd, *J* = 11.9, 3.7 Hz, 2H), 6.95 (m, 3H), 4.12 (t, *J* = 4.2 Hz, 2H), 3.76 (t, *J* = 4.1 Hz, 2H), 3.46 (s, 3H).
MS (EI): *m/z* 152.1[M$^+$].

(2-(2-Methoxyethoxy)ethoxy)benzene[7] (3h)



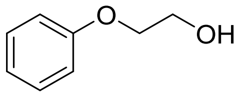
Colorless oil. Isolated yield: 5.6 mg, 14%, petroleum ether/EtOAc = 30/1 - 5/1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.28 (t, *J* = 6.9 Hz, 2H), 6.94 (m, 3H), 4.15 (t, *J* = 4.8 Hz, 2H), 3.87 (t, *J* = 4.7 Hz, 2H), 3.76 – 3.70 (m, 2H), 3.61 – 3.56 (m, 2H), 3.40 (s, 3H).
MS (EI): *m/z* 196.1[M$^+$].

(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)benzene[8] (3i)



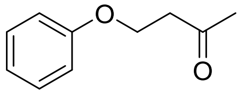
Colorless oil. Isolated yield: 7.3 mg, 15%, petroleum ether/EtOAc = 30/1 - 5/1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.27 (dd, *J* = 9.8, 3.7 Hz, 2H), 6.93 (m, 3H), 4.13 (d, *J* = 4.5 Hz, 2H), 3.87 (d, *J* = 3.8 Hz, 2H), 3.74 (d, *J* = 3.4 Hz, 2H), 3.71 – 3.64 (m, 4H), 3.56 (d, *J* = 3.3 Hz, 2H), 3.38 (s, 3H).
MS (EI): *m/z* 240.1[M$^+$].

2-Phenoxyethan-1-ol[7] (3j)



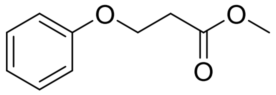
Colorless oil. Isolated yield: 7.5 mg, 27%, petroleum ether/EtOAc = 30/1 - 5/1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.30 (t, *J* = 7.4 Hz, 2H), 7.01 – 6.90 (m, 3H), 4.12 – 4.06 (m, 2H), 3.99 – 3.94 (m, 2H), 2.25 (br, 1H).
MS (EI): *m/z* 138.1$[M^+]$.

4-Phenoxybutan-2-one[9] (3k)

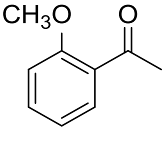


Colorless oil. Isolated yield: 8.6 mg, 26%, petroleum ether/EtOAc = 50/1 - 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.28 (t, *J* = 7.5 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 7.7 Hz, 2H), 4.24 (t, *J* = 6.2 Hz, 2H), 2.91 (t, *J* = 6.2 Hz, 2H), 2.24 (s, 3H).
MS (EI): *m/z* 164.1$[M^+]$.

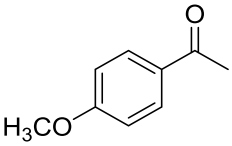
Methyl 3-phenoxypropanoate[10] (3l)



Colorless oil. Isolated yield: 24.6 mg, 68%, petroleum ether/EtOAc = 50/1 - 30/1. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.28 (t, *J* = 7.9 Hz, 2H), 6.98 – 6.88 (m, 3H), 4.25 (t, *J* = 6.4 Hz, 2H), 3.73 (s, 3H), 2.81 (t, *J* = 6.4 Hz, 2H).
MS (EI): *m/z* 180.1$[M^+]$.



3m - *ortho*



3m - *para*

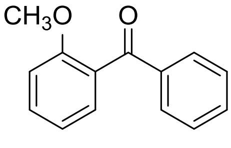
Petroleum ether/EtOAc = 50/1 – 30/1.

1-(2-Methoxyphenyl)ethan-1-one[11] (3m – *ortho*)

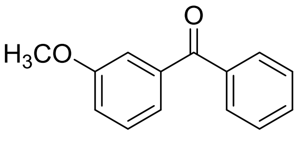
colorless oil. Isolated yield: 10.8 mg, 36%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.73 (d, *J* = 7.7 Hz, 1H), 7.46 (t, *J* = 7.9 Hz, 1H), 6.98 (dd, *J* = 14.6, 7.8 Hz, 2H), 3.91 (s, 3H), 2.61 (s, 3H).

1-(4-Methoxyphenyl)ethan-1-one[11] (3m – *para*)

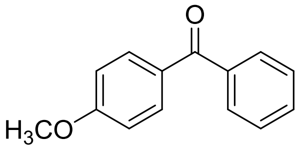
colorless oil. Isolated yield: 4.0 mg, 13%. ^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.94 (d, *J* = 7.7 Hz, 2H), 6.93 (d, *J* = 7.7 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H).
MS (EI): *m/z* 150.1$[M^+]$.



3n - *ortho*



3n - *meta*



3n - *para*

Petroleum ether/EtOAc = 50/1 - 30/1.

(3-methoxyphenyl)(phenyl)methanone[12] (**3n** – ***meta***)

White solid. Isolated yield: 2.1 mg, 5%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.81 (d, J = 7.7 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.48 (t, J = 7.3 Hz, 2H), 7.37 (m, 3H), 7.14 (d, J = 7.8 Hz, 1H), 3.86 (s, 3H).

The mixture of **3n**– ***para*** and **3n** – ***ortho***. White solid. Isolated yield: 16.6 mg, 39%.

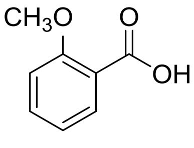
(2-methoxyphenyl)(phenyl)methanone[12] (**3n** – ***ortho***)

Mix with **3n**– ***para***, see the spectrum.

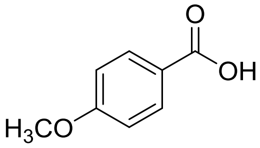
(4-methoxyphenyl)(phenyl)methanone[12] (**3n**– ***para***)

Mix with **3n** – ***ortho***, see the spectrum.

MS (EI): *m/z* 212.1[M$^+$].



3o - *ortho*



3o - *para*

Petroleum ether/EtOAc = 30/1 - 5/1 (with 1% acetic acid).

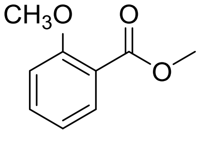
2-Methoxybenzoic acid[13] (**3o** – ***ortho***)

White solid. Isolated yield: 6.7 mg, 22%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 10.53 (br, 1H), 8.18 (d, J = 7.8 Hz, 1H), 7.58 (t, J = 7.9 Hz, 1H), 7.14 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 4.08 (s, 3H).

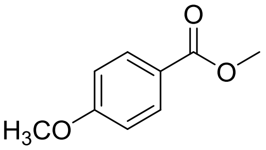
4-Methoxybenzoic acid[13] (**3o** – ***para***)

White solid. Isolated yield: 3.1 mg, 10%. ^{1}H NMR (400 MHz, Acetone, ppm) δ: 10.91 (br, 1H), 8.00 (d, J = 7.9 Hz, 1H), 7.02 (d, J = 7.9 Hz, 1H), 3.88 (s, 2H).

MS (EI): *m/z* 152.0[M$^+$].



3p - *ortho*



3p - *para*

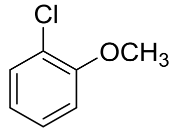
Petroleum ether/EtOAc = 50/1 - 30/1.

Methyl 2-methoxybenzoate[14] (**3p** – ***ortho***)

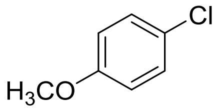
Colorless oil. Isolated yield: 4.1 mg, 12%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.79 (d, J = 7.8 Hz, 1H), 7.47 (t, J = 7.9 Hz, 1H), 7.01 – 6.95 (m, 2H), 3.91 (s, 3H), 3.89 (s, 3H).

Methyl 4-methoxybenzoate[14] **(3p – *para*)**

White solid. Isolated yield: 5.0 mg, 15%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.99 (d, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 7.9 Hz, 2H), 3.88 (s, 3H), 3.86 (s, 3H).
MS (EI): *m/z* 166.1[M$^+$].



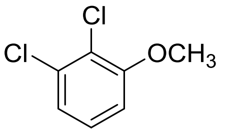
3q - *ortho*



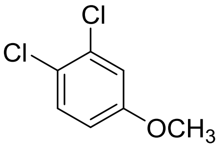
3q - *para*

1-Chloro-2-methoxybenzene[15] **(3q – *ortho*)** and **1-Chloro-4-methoxybenzene**[15] **(3q – *para*)**

Colorless oil (mixture of 3q– ***para*** and 3q – ***ortho***). Isolated yield: 18.0 mg, 63%. Petroleum ether/EtOAc = 50/1 – 30/1.
^{1}H NMR (400 MHz, CDC13, ppm): see the spectrum.
MS (EI): *m/z* 142.0[M$^+$].



3r - 1



3r - 2

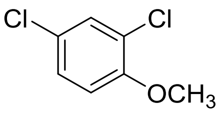
Petroleum ether/EtOAc = 50/1 - 30/1.

1,2-dichloro-3-methoxybenzene[16] **(3r – 1)**

Colorless oil. Isolated yield: 1.9 mg, 5%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.15 (t, *J* = 8.2 Hz, 1H), 7.07 (d, *J* = 8.1 Hz, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 3.90 (s, 3H).

1,2-dichloro-4-methoxybenzene[17] **(3r – 2)**

Colorless oil. Isolated yield: 22.3 mg, 63%. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.31 (d, *J* = 8.9 Hz, 1H), 6.99 (s, 1H), 6.75 (d, *J* = 8.9 Hz, 1H), 3.78 (s, 3H).
MS (EI): *m/z* 176.0[M$^+$].

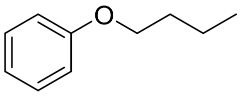


2,4-dichloro-1-methoxybenzene[15] **(3s)**

Colorless oil. Isolated yield: 25.9 mg, 73%, petroleum ether/EtOAc = 50/1 - 30/1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.36 (s, 1H), 7.19 (d, *J* = 8.8 Hz, 1H), 6.84 (d, *J* = 8.8 Hz, 1H), 3.88 (s, 3H).
MS (EI): *m/z* 176.0[M$^+$].

Procedure for Buloxycaine (6) Synthesis

a. Preparation of Butoxybenzene[2-3] (4)



0.2 mmol scale of benzene

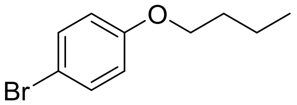
Butoxybenzene was synthesized as the general procedure for etherification of arenes. $QuCN^+ClO_4^-$ (2.7 mg, 0.01 mmol) and $Co(dmgBF_2)_2(CH_3CN)_2$ (2.8 mg, 0.006 mmol) were dissolved in CH_3CN (5 mL) and the reaction tube was sealed. After degassing by at least three freeze-pump-cycles, benzene (18 uL, 0.2 mmol) and 1-butanol (183 uL, 2 mmol) were added. Ten parallel reactions were carried out. After 5 h irradiation with a 500W high pressure Hanovia mercury lamp with a glass water cooling jacket (λ > 300 nm), the solution of ten parallel reactions were combined and isolated by silica column chromatograph using a mixture of petroleum ether/EtOAc (50/1 – 40/1) to afford 4 as colorless oil (169mg, 56% yield).

4 mmol scale of benzene

$QuCN^+ClO_4^-$ (54 mg, 0.2 mmol) and $Co(dmgBF_2)_2(CH_3CN)_2$ (56 mg, 0.12 mmol) were dissolved in CH_3CN (150 mL) in an immersion well apparatus, after degassing by at least three pump-refilled-cycles with argon, benzene (358 uL, 4 mmol) and 1-butanol (3.66 mL, 40 mmol) were added. After 7 h irradiation with a 500W high pressure Hanovia mercury lamp with a glass water cooling jacket (λ > 300 nm), the reaction solution was concentrated and isolated by silica column chromatograph using a mixture of petroleum ether/EtOAc 50/1 – 40/1 to afford 4 as colorless oil (197mg, 33% yield).

^1H NMR (400 MHz, 400 MHz, $CDCl_3$, ppm) δ: 7.29 (t, *J* = 7.9 Hz, 2H), 6.93 (dd, *J* = 14.5, 7.6 Hz, 3H), 3.98 (t, *J* = 6.5 Hz, 2H), 1.83 – 1.74 (m, 2H), 1.57 – 1.46 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

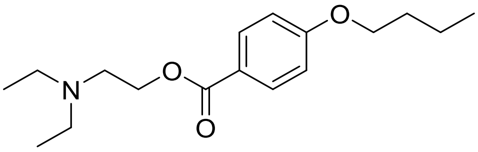
b. Preparation of 1-Bromo-4-butoxybenzene (5)



Bromo-4-butoxybenzene was synthesized according the previous report[18]. Firstly, moist Montmorillonite K10 (ca. 19 wt% loading of water) was prepared. Deionized water (0.24 g) in portions was added to Montmorillonite K10 (1.0 g), and the mixture was vigourously stirred until free-flowing powder was obtained (it should be readily done within a few minutes and was immediately employed for the bromination). 4 (150 mg, 1.0 mmol) and $Mn(acac)_3$ (3.5 mg, 0.01 mmol) was added into dichloromethane (10 mL), and the mixture was stirred. Freshly prepared moist Mont. (1 g), $NaClO_2$ (118 mg, 1.3 mmol) and NaBr (257 mg, 2.5 mmol) were then added. The vial was degassed by three freeze-pump-cycles with argon. After 60 min stirring at room temperature (care should be taken in continuing efficient stirring), the mixture was filtrated and washed with ether (3 × 20 mL). The clear filtrate was condensed and purified by silica column chromatograph (hexane/EtOAc, 10/1) to afford 5 as colorless oil (207mg, 90% yield).

^1H NMR (400 MHz, 400 MHz, $CDCl_3$, ppm) δ: 7.36 (d, *J* = 7.8 Hz, 2H), 6.77 (d, *J* = 7.9 Hz, 2H), 3.92 (t, *J* = 6.5 Hz, 2H), 1.80 – 1.71 (m, 2H), 1.54 – 1.43 (m, 2H), 0.97 (t, *J* = 7.4 Hz, 3H).

c. Preparation of buloxycaine (6)



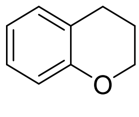
Buloxycaine (**6**) was synthesized according the previous report[19]. In the glovebox, 25-mL round bottom flask was charged with 1-bromo-4- butoxybenzene (115 mg, 0.50 mmol), 2-(diethylamino)ethan-1-ol (266 μL, 2.0 mmol), Pd(dba)$_2$ (15 mg, 0.025 mmol), CataCXium A (18 mg, 0.050 mmol), Na_2CO_3 (160 mg, 1.5 mmol), DMAP (15.3 mg, 0.13 mmol) and toluene (3 mL). The flask was sealed and CO (20 mL) was injected. The mixture was stirred at 100 °C for 18 h. The mixture was filtrated and washed with EtOAc (3 × 5 mL). The filtrate was condensed and purified by silica column chromatograph (EtOAc/MeOH, 20/1) to afford **6** as colorless oil (135mg, 91% yield).

^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.97 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 4.35 (t, *J* = 6.2 Hz, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 2.84 (t, *J* = 6.2 Hz, 2H), 2.62 (q, *J* = 7.1 Hz, 4H), 1.82 – 1.73 (m, 2H), 1.49 (m, *J* = 14.9, 7.5 Hz, 2H), 1.06 (t, *J* = 7.1 Hz, 6H), 0.97 (t, *J* = 7.3 Hz, 3H).

General Procedure for Intramolecular Etherification of Arenes (8a–f')

Arene (0.2 mmol, liquid arenes were added after degassing), $QuCN^+ClO_4^-$ (2.7 mg, 0.01 mmol) and $Co(dmgBF_2)_2(CH_3CN)_2$ (2.8 mg, 0.006 mmol) were dissolved in CH_3CN (5 mL) and the reaction tube was sealed. After degassing by at least three freeze-pump-cycles, methane (1mL) was injected as the internal standard for analysis of generated H_2, and the pinholes were sealed by paraffin. The solution was irradiation at room temperature using a 500 W high pressure Hanovia mercury lamp with a glass water cooling jacket ($\lambda > 300$ nm). Two parallel reactions were carried out. After 5 h irradiation, yield of H_2 was detected by GC-TCD. The conversion and yields were obtained from the crude reaction mixture by ^{1}H NMR using *n*-tetradecane as an internal standard. The solution of parallel reactions were combined. All products were isolated by flash column chromatography on silica gel using a mixture of PE-EtOAc as eluent. The isolated yields were the average yields of two parallel reactions.

Chromane[20] (8a)

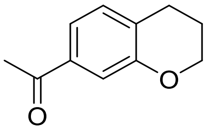


Colorless oil. Isolate yield: 7.1 mg, 21%, petroleum ether/EtOAc = 50/1.

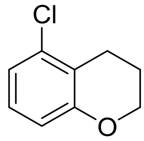
^{1}H NMR (400 MHz, $CDCl_3$, ppm) δ: 7.12 – 7.02 (m, 2H), 6.87 – 6.78 (m, 2H), 4.22 – 4.17 (m, 2H), 2.80 (t, *J* = 6.5 Hz, 2H), 2.06 – 1.98 (m, 2H).

MS (EI): *m/z* 134.1[M$^+$].

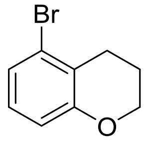
1-(chroman-7-yl)ethan-1-one[21] (8b)


Colorless oil. Isolate yield: 18.4 mg, 52%, petroleum ether/EtOAc = 50/1 - 20/1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.43 (d, *J* = 7.9 Hz, 1H), 7.36 (s, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 4.24 – 4.18 (m, 2H), 2.83 (t, *J* = 6.4 Hz, 2H), 2.54 (s, 3H), 2.02 (dt, *J* = 11.5, 5.9 Hz, 2H).
^{13}C NMR (101 MHz, CDCl$_3$, ppm) δ: 197.69, 154.94, 136.62, 129.96, 127.89, 119.82, 116.89, 66.57, 26.59, 25.12, 21.99.
MS (EI): *m/z* 176.1[M$^+$].

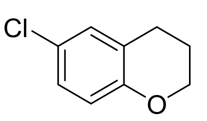
5-chlorochromane[22] (8c)

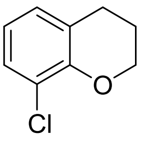

Colorless oil. Isolate yield: 14.5 mg, 43%, petroleum ether/EtOAc = 100/1 - 50/1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.02 (t, *J* = 8.0 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 6.73 (d, *J* = 8.2 Hz, 1H), 4.18 – 4.12 (m, 2H), 2.78 (t, *J* = 6.6 Hz, 2H), 2.07 – 2.00 (m, 2H).
MS (EI): *m/z* 168.0[M$^+$].

5-bromochromane[23] (8d)


Colorless oil. Isolate yield: 17.0 mg, 40%, petroleum ether/EtOAc = 100/1 - 50/1. ^{1}H NMR (400 MHz, CDCl$_3$, ppm) δ: 7.12 (d, *J* = 7.9 Hz, 1H), 6.95 (t, *J* = 8.0 Hz, 1H), 6.77 (d, *J* = 8.2 Hz, 1H), 4.16 – 4.12 (m, 2H), 2.76 (t, *J* = 6.6 Hz, 2H), 2.07 – 2.00 (m, 2H).
MS (EI): *m/z* 212.0[M$^+$].

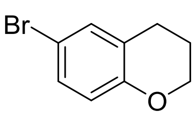
6-chlorochromane[22] (8e) and 8-chlorochromane[24] (8e')


8e

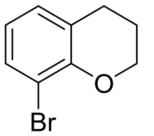

8e'

Colorless oil. Isolate yield: 22.9 mg, 68%, petroleum ether/EtOAc = 50/1.
^{1}H NMR (400 MHz, CDCl$_3$, ppm): see the spectrum.
MS (EI): *m/z* 168.0[M$^+$].

6-bormochromane[25] (8f) and 8-bormochromane[26] (8f')



8f



8f'

Colorless oil. Isolate yield: 26.8 mg, 63%, petroleum ether/EtOAc = 50/1.
^{1}H NMR (400 MHz, $CDCl_3$, ppm): see the spectrum.
MS (EI): *m/z* 212.0[M^+].

References

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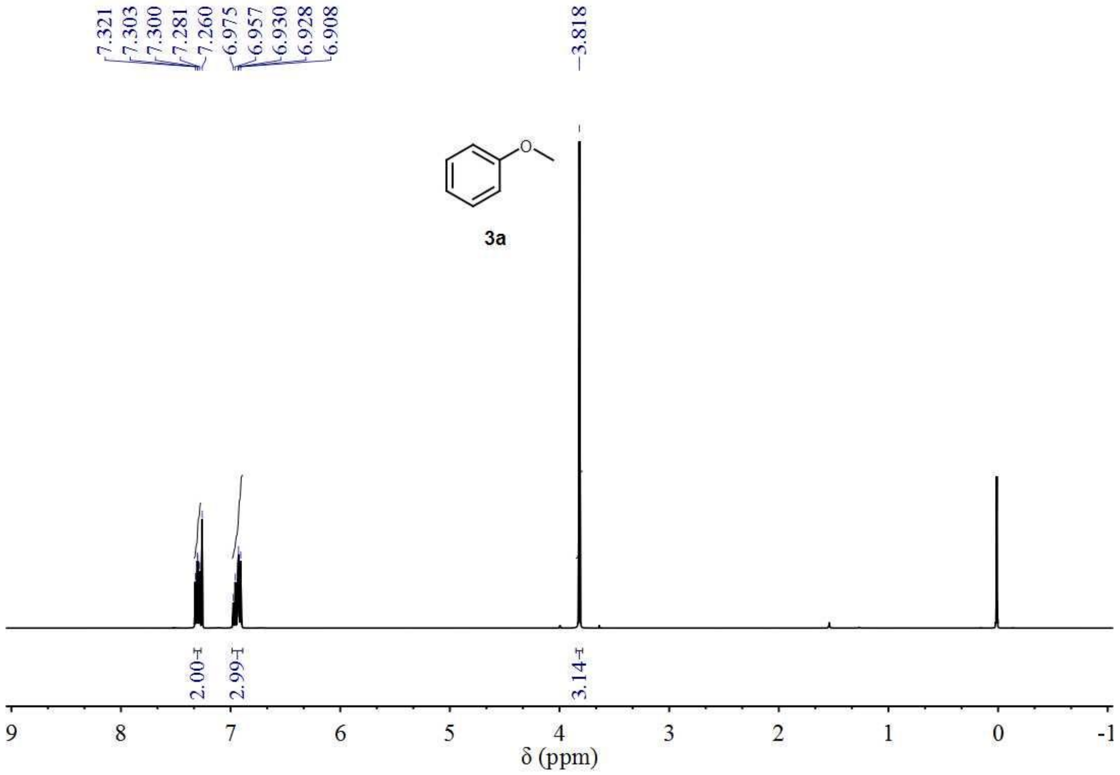
NMR Spectra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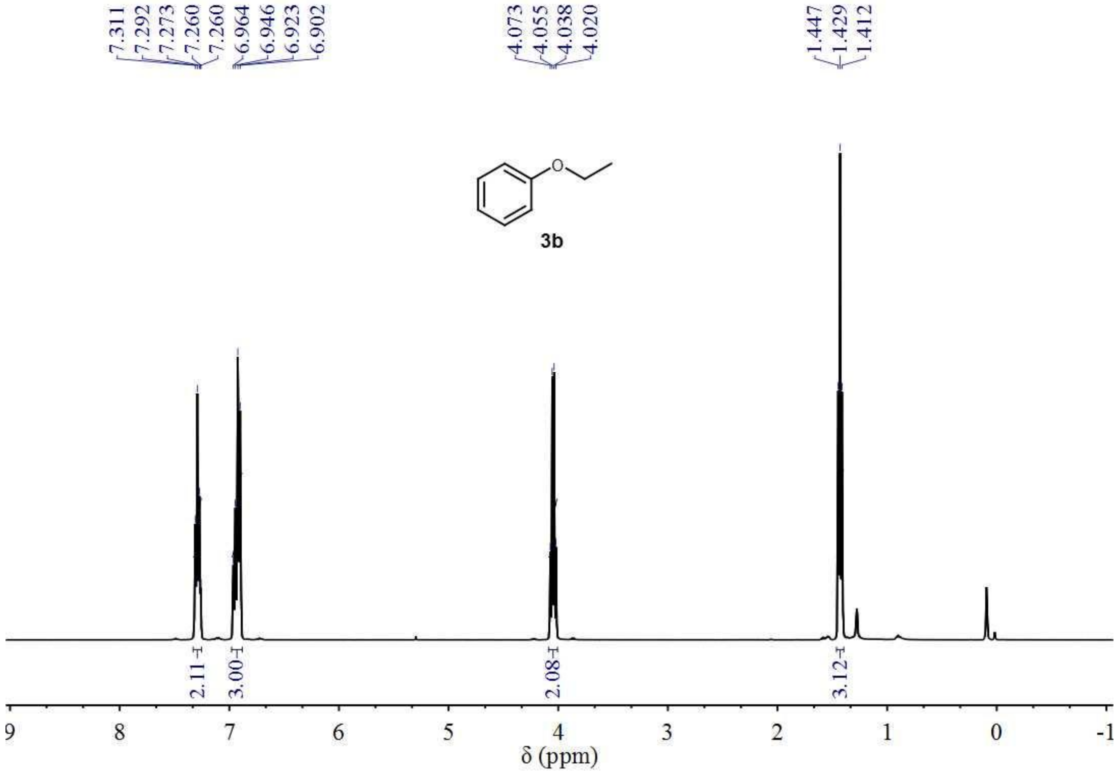
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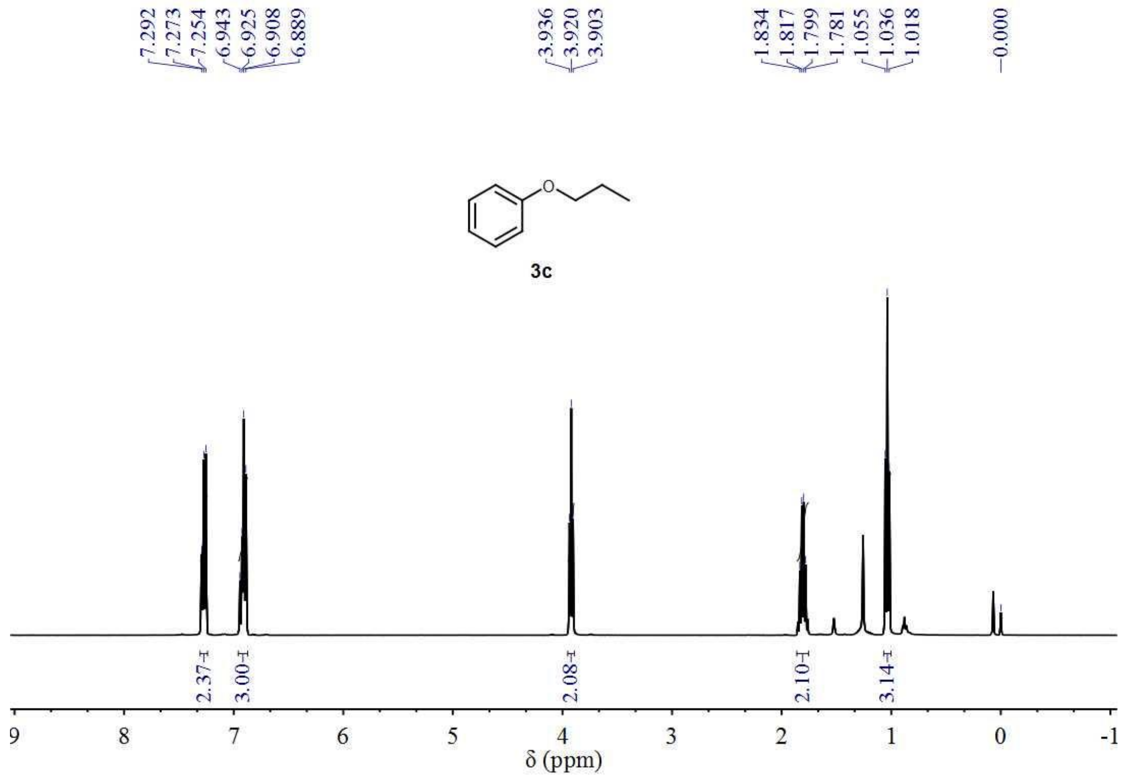
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O
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2
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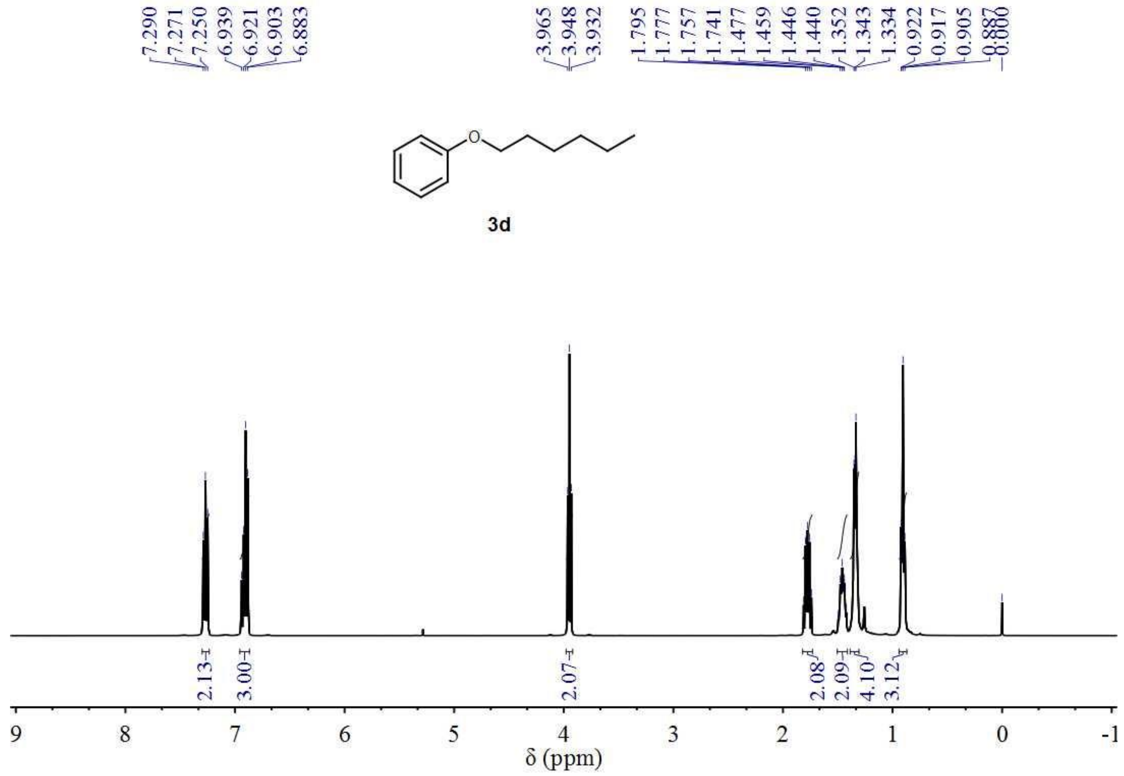
δ (ppm)

3c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0.917
0.905
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2.13
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2.08
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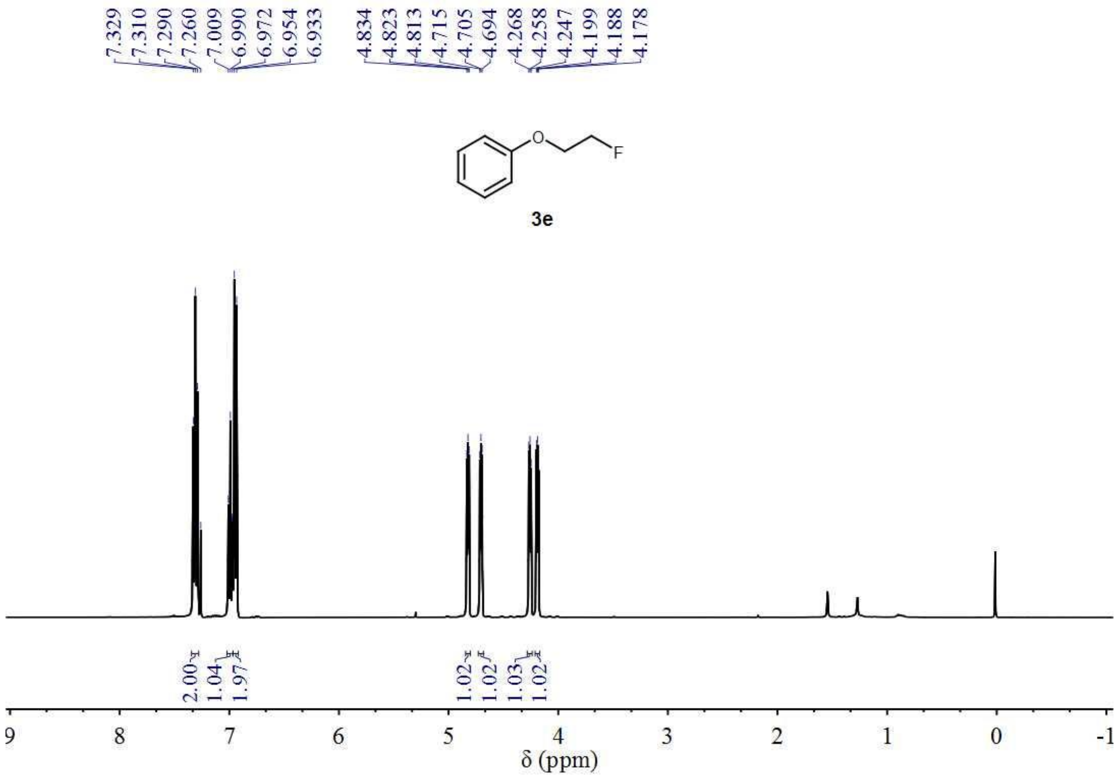
δ (ppm)

3d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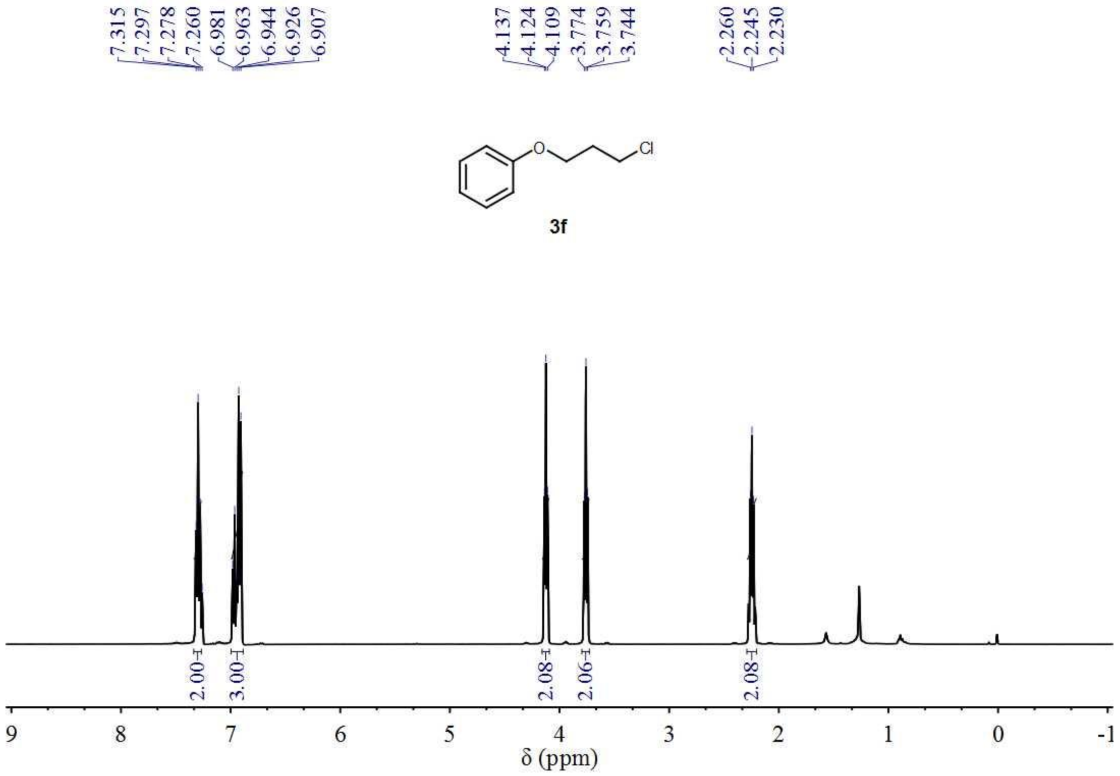
δ (ppm)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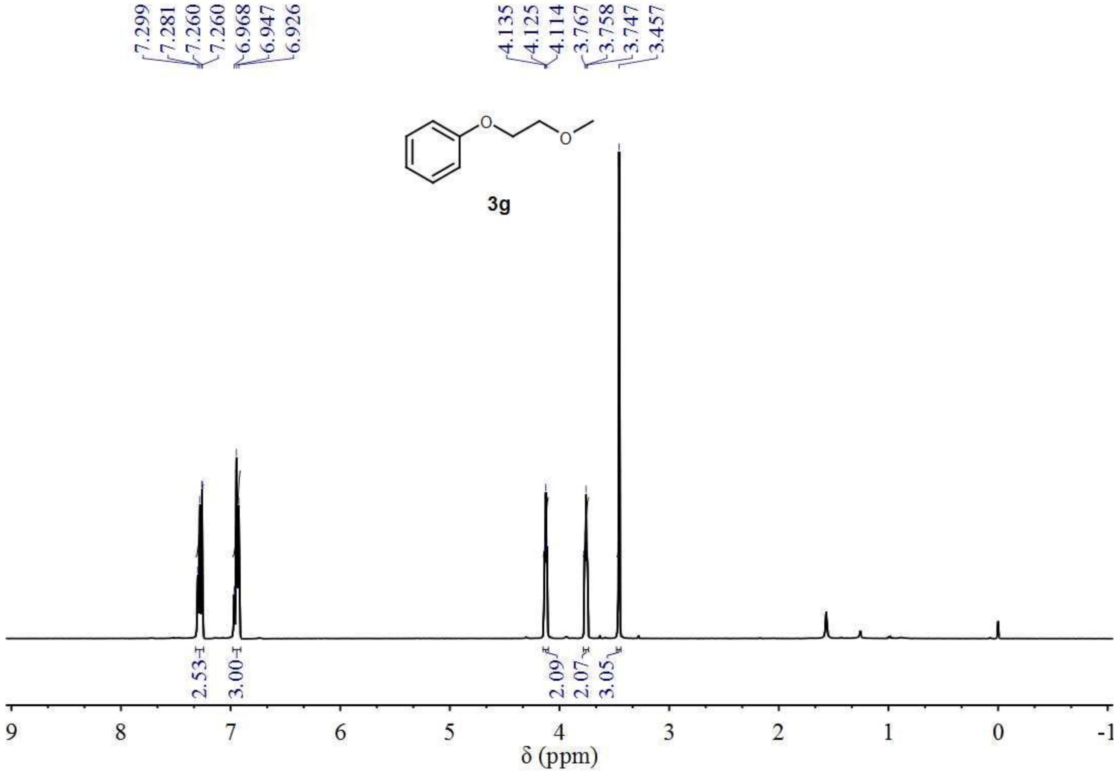
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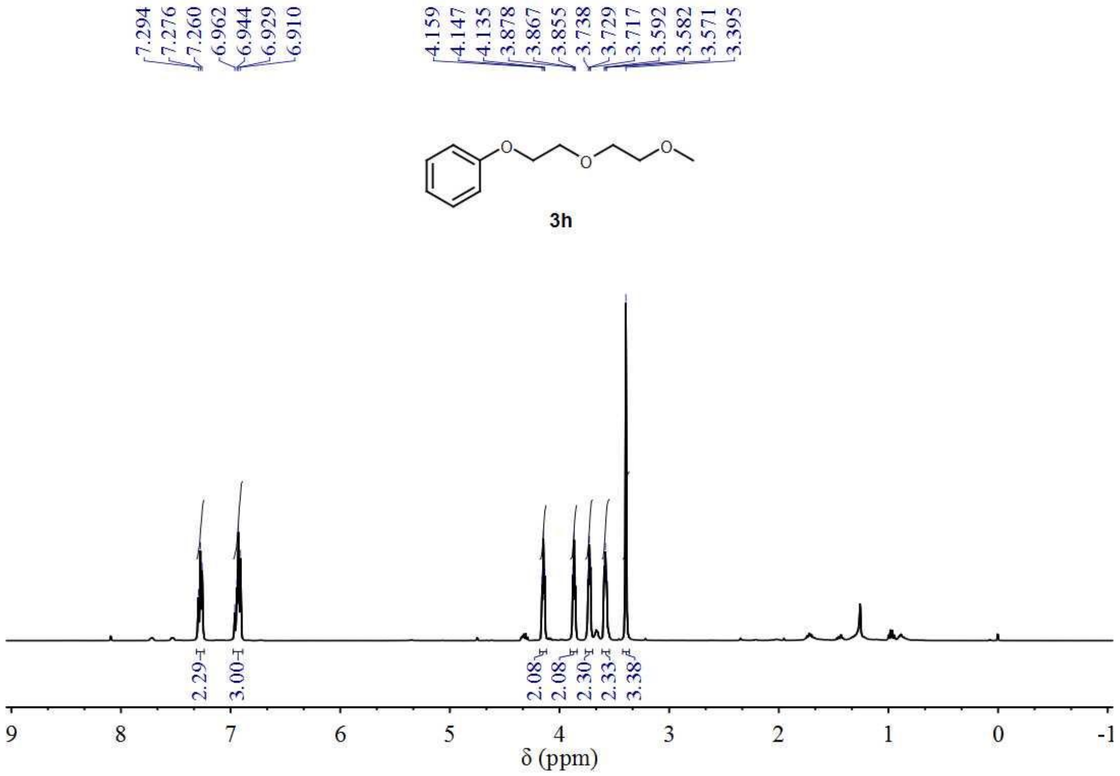
δ (ppm)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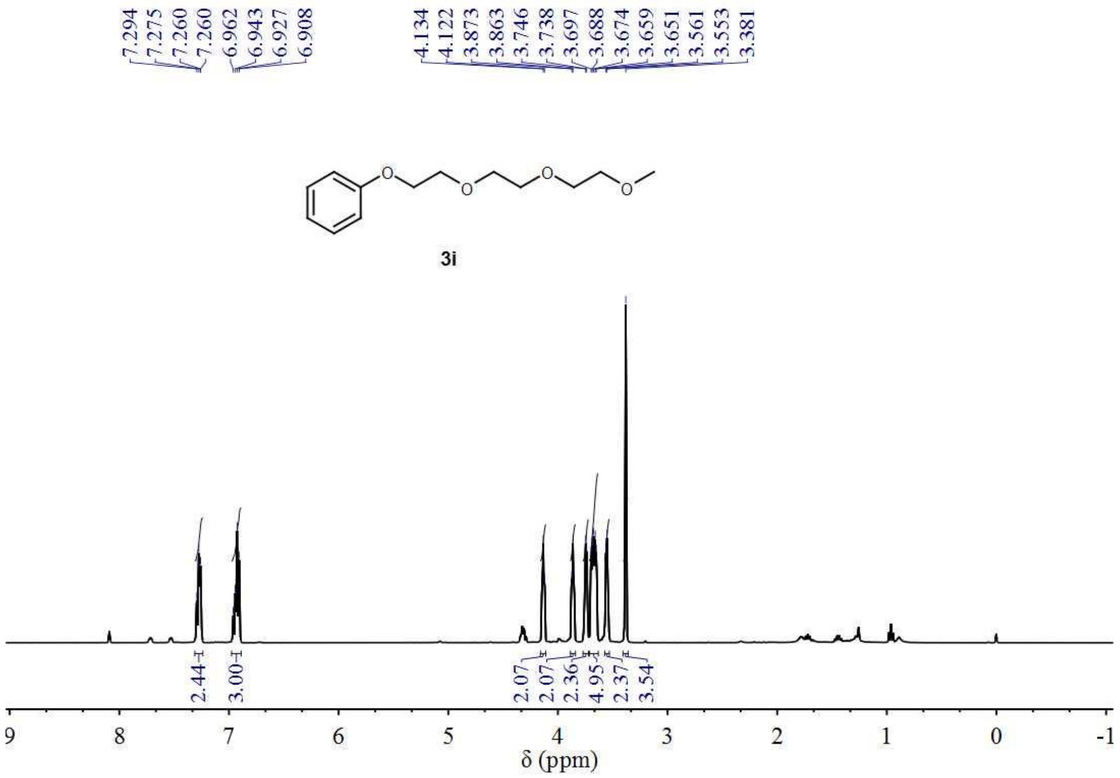
δ (ppm)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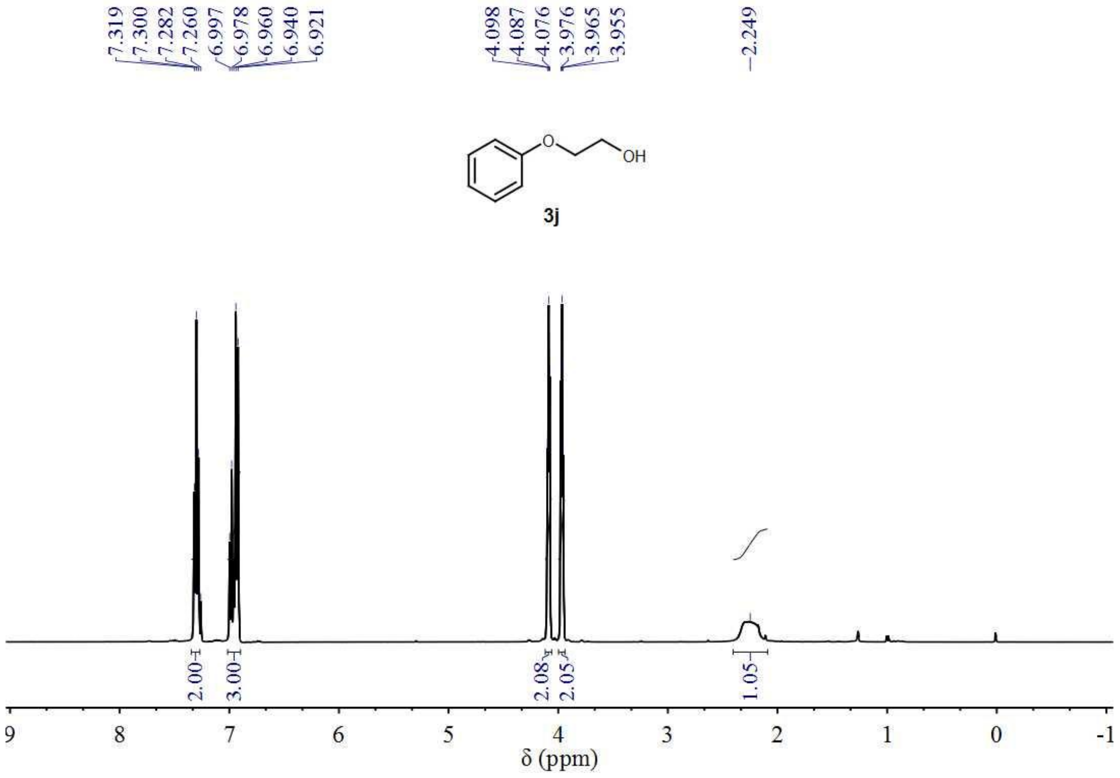
δ (ppm)

3i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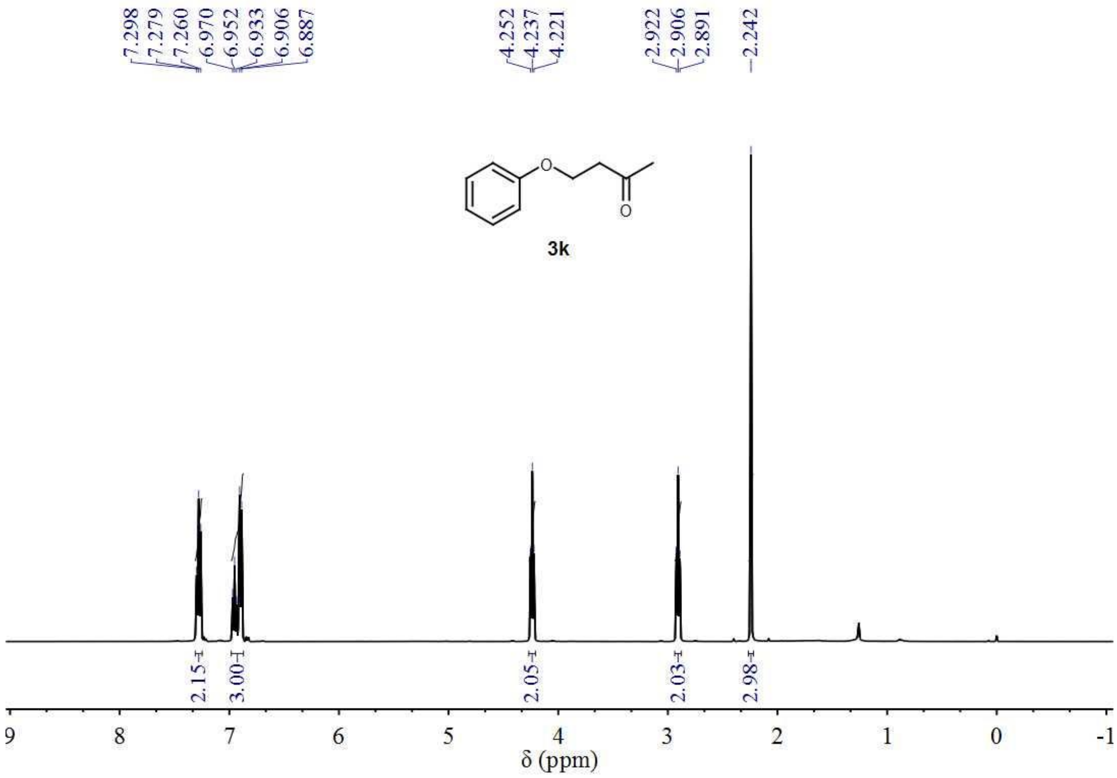
δ (ppm)

3j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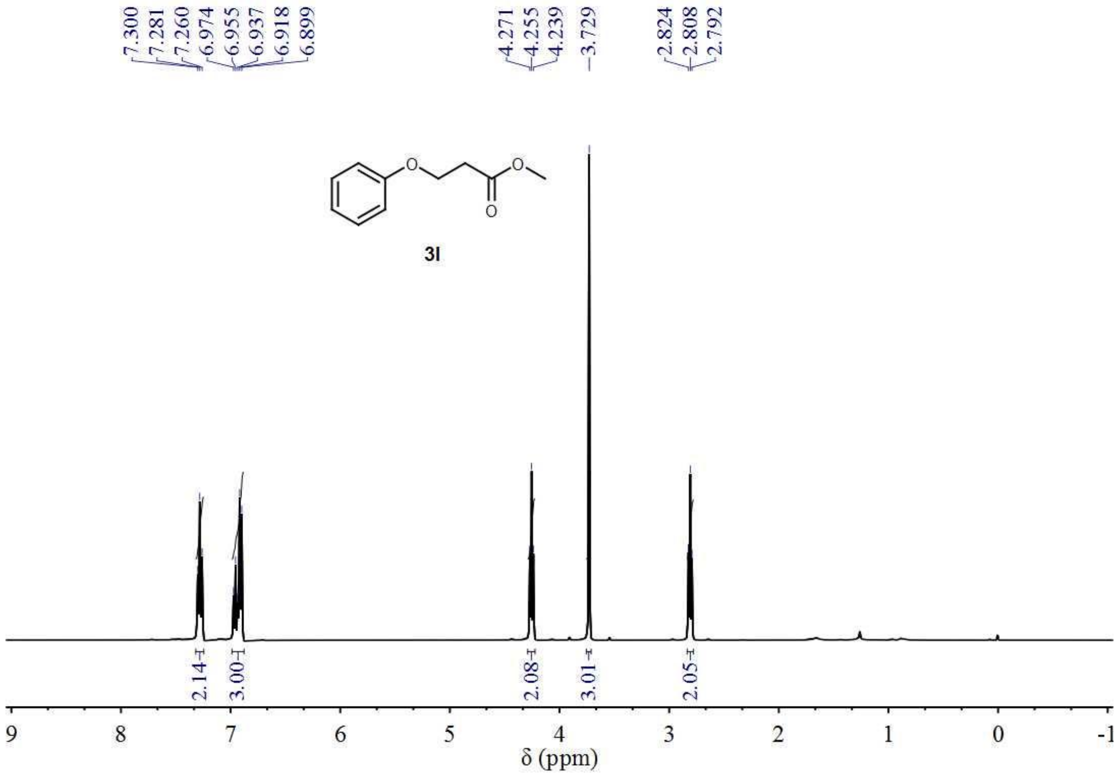
δ (ppm)

3k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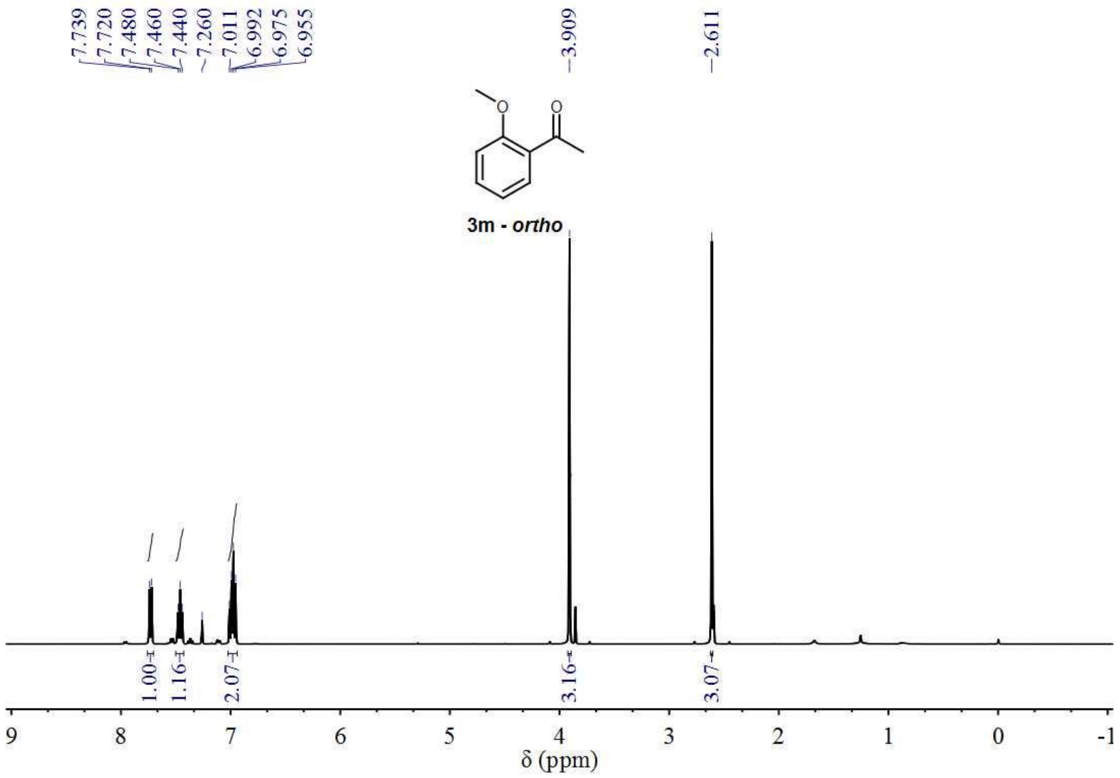
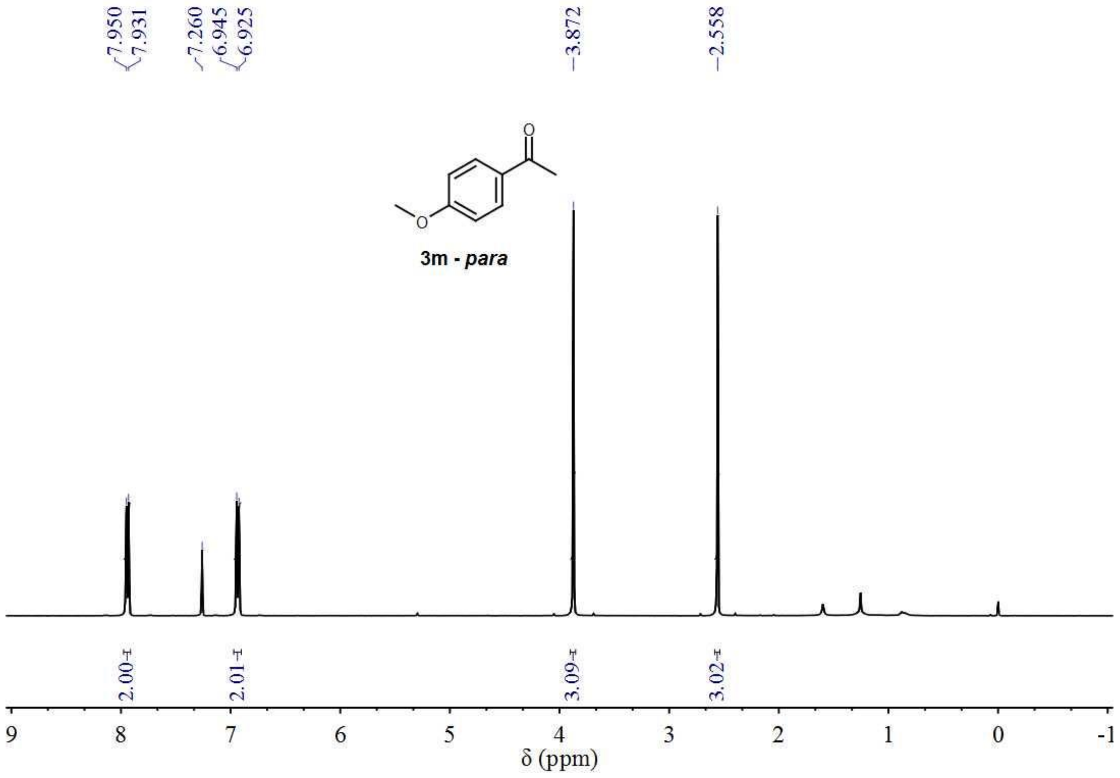
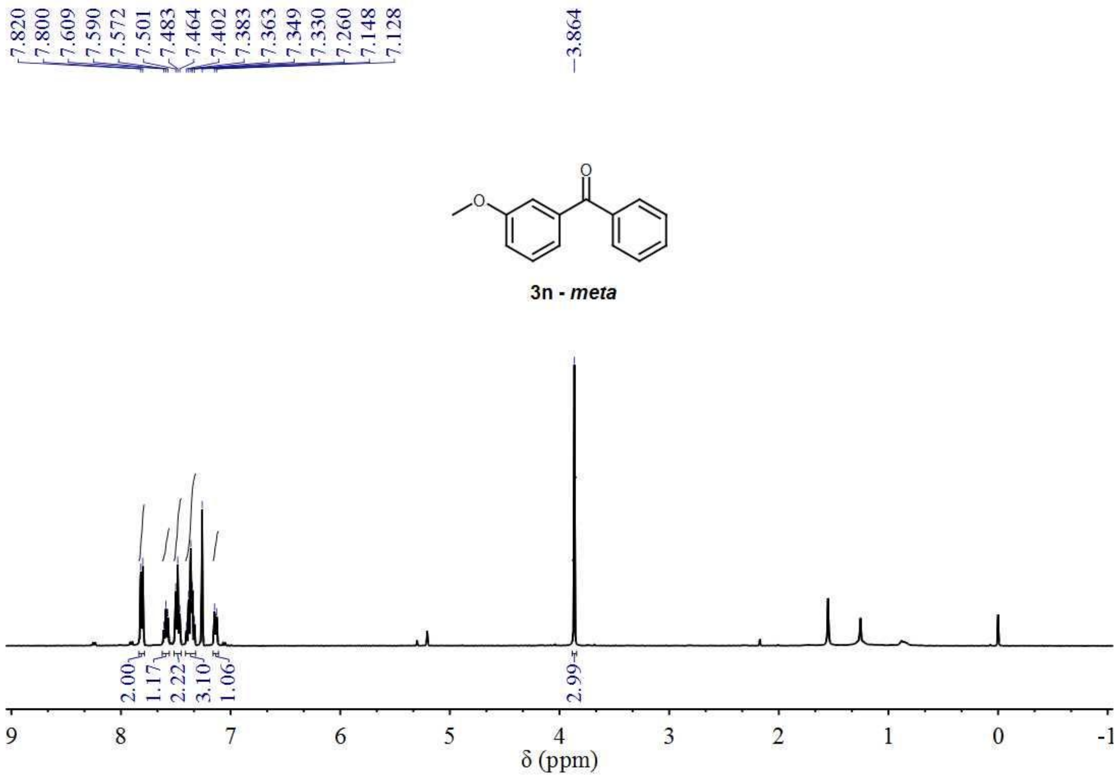
δ (ppm)

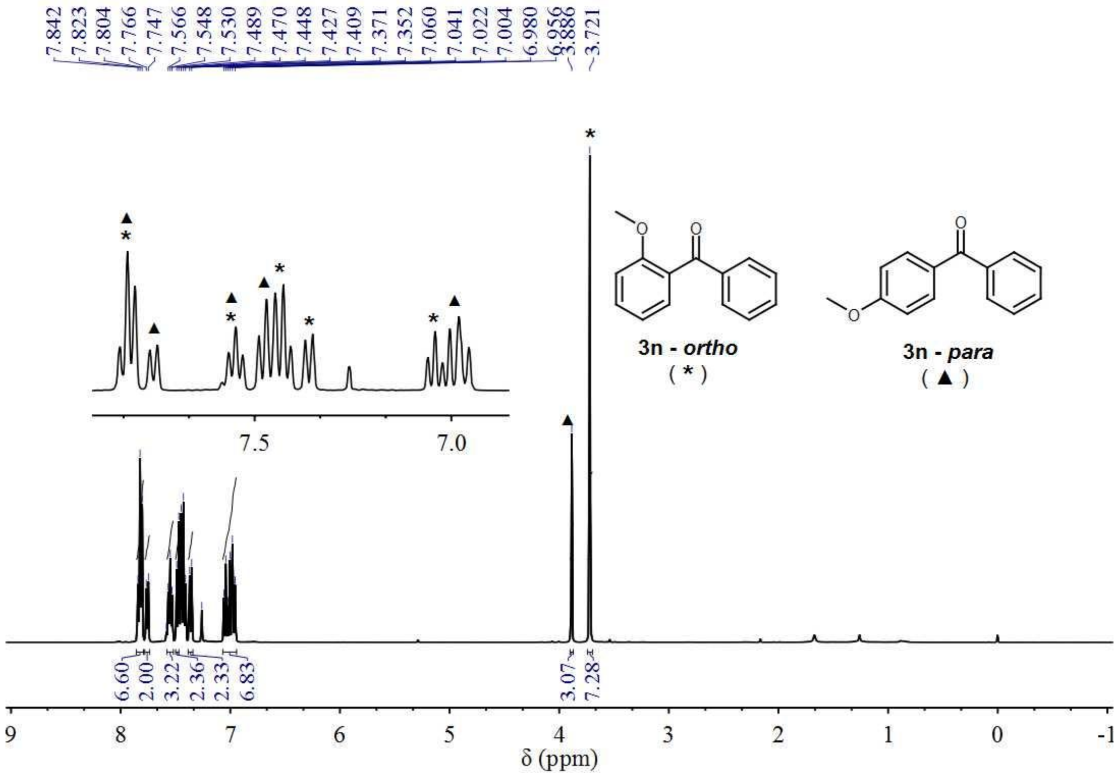
3l


7.739
7.720
7.480
7.460
7.440
7.260
7.011
6.992
6.975
6.955
3.909
2.611
O
O
3m - *ortho*
1.00
1.16
2.07
3.16
3.07
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


7.950
7.931
7.260
6.945
6.925
3.872
2.558
O
O
3m - *para*
2.00
2.01
3.09
3.02
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

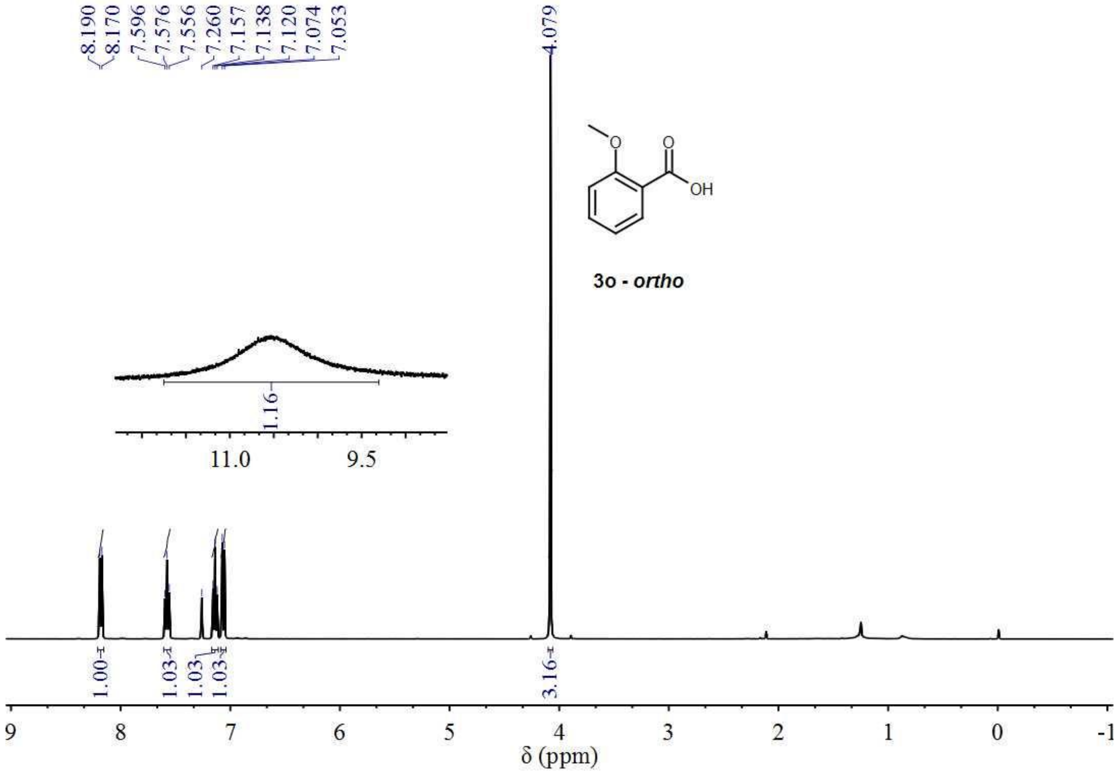


3n - *meta*

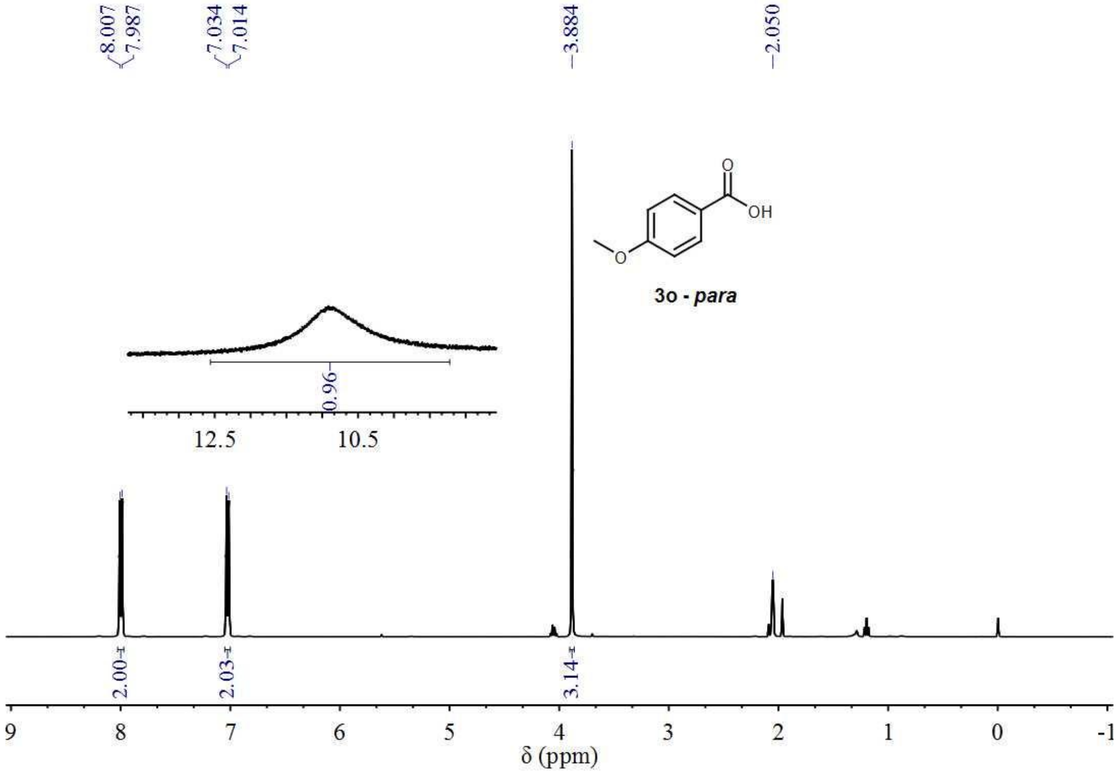


3n - *ortho*
(*)

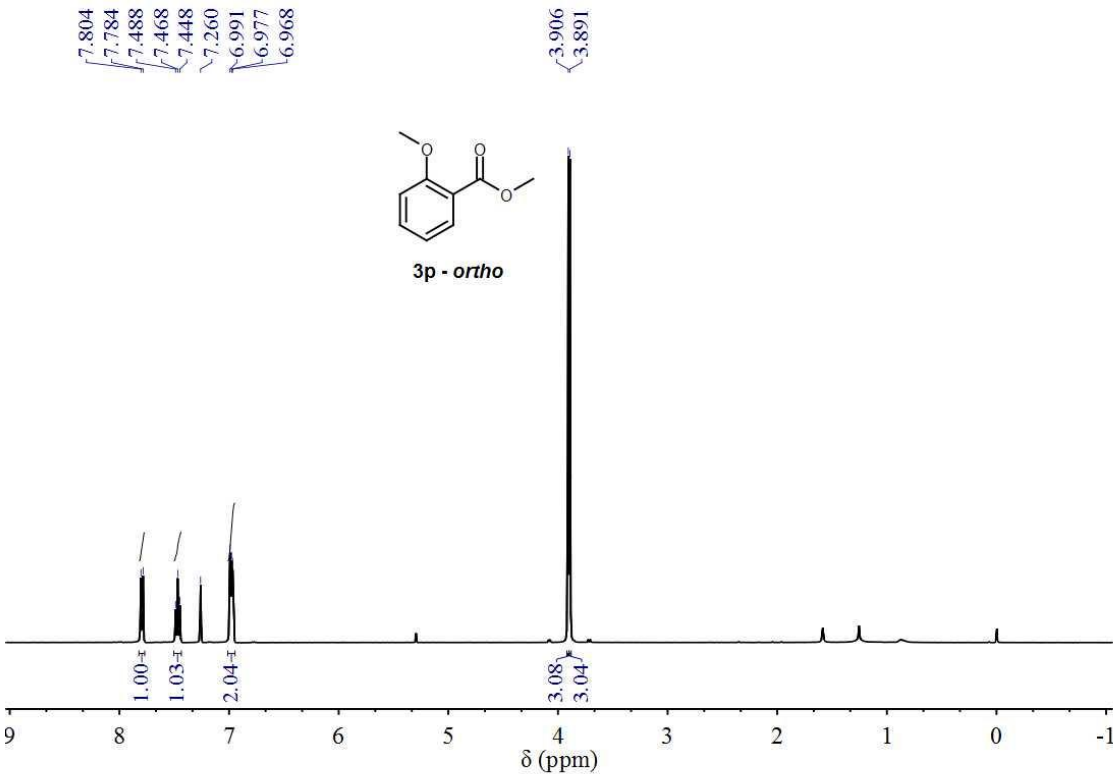
3n - *para*
(▲)

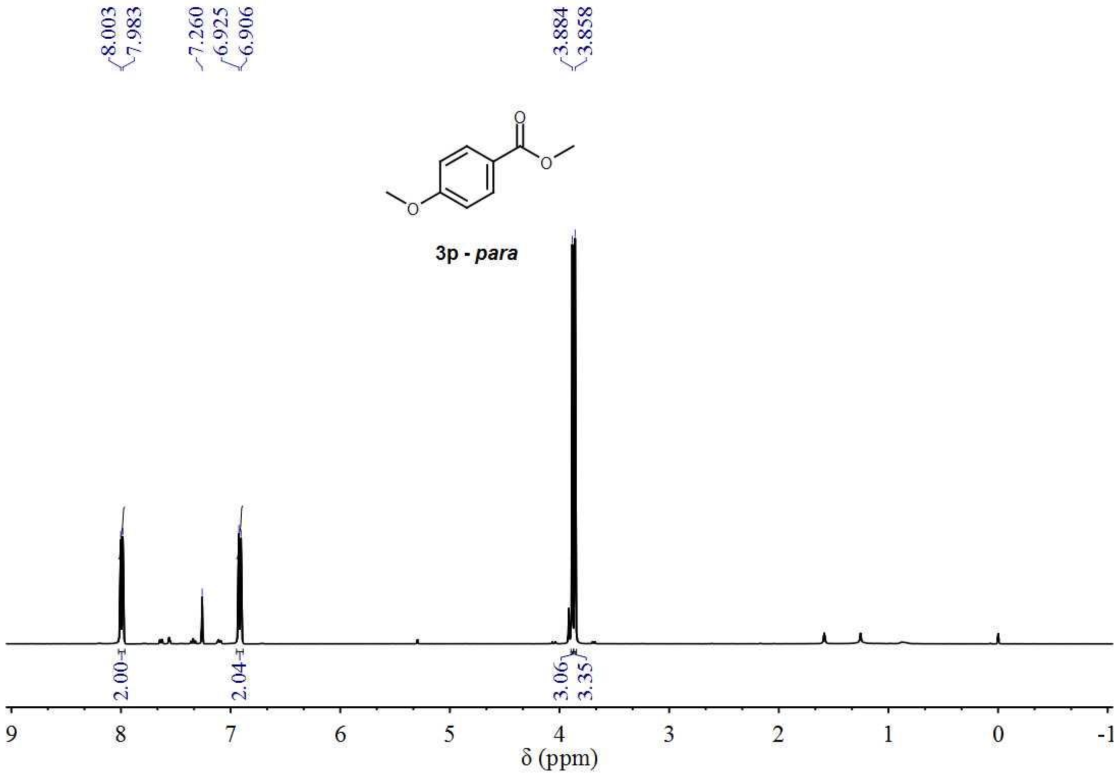


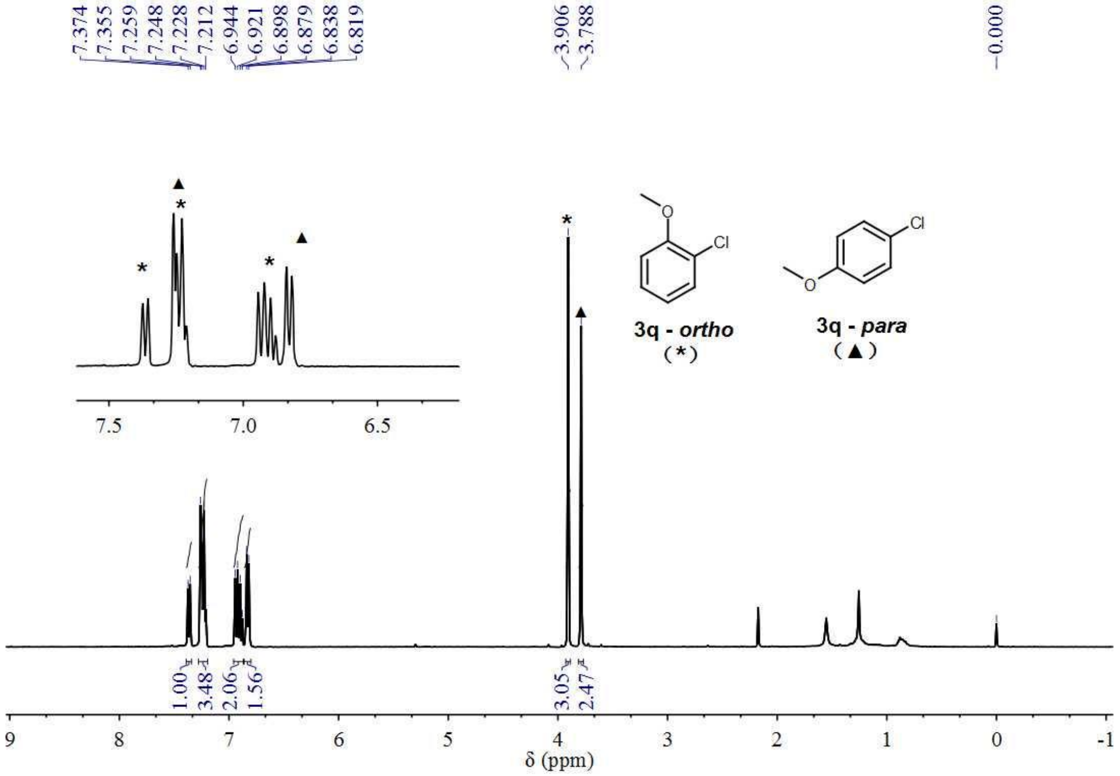
3o - *ortho*

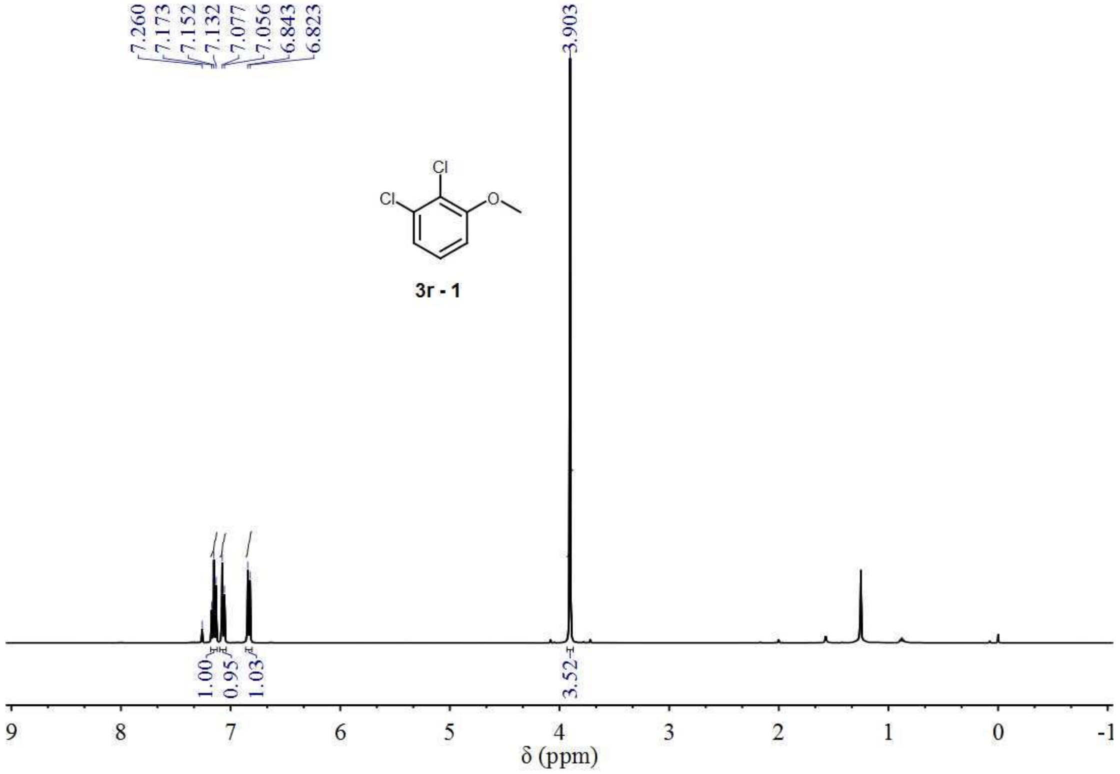


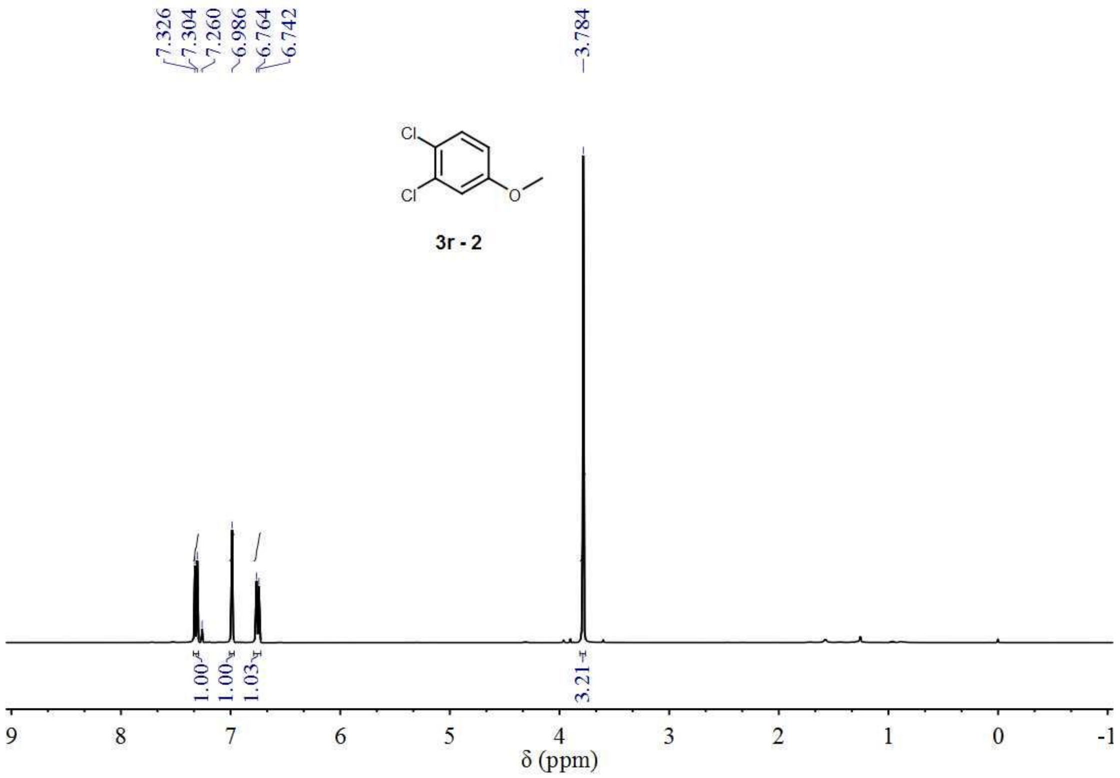
3o - *para*

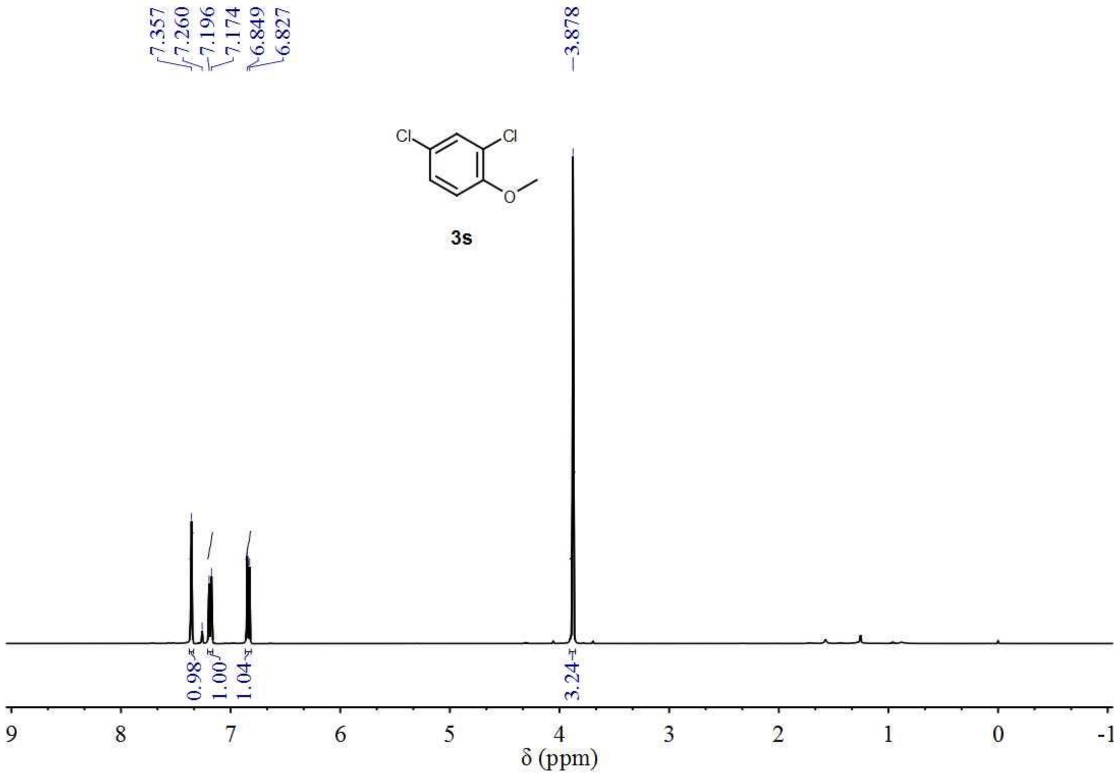

3p - *ortho*

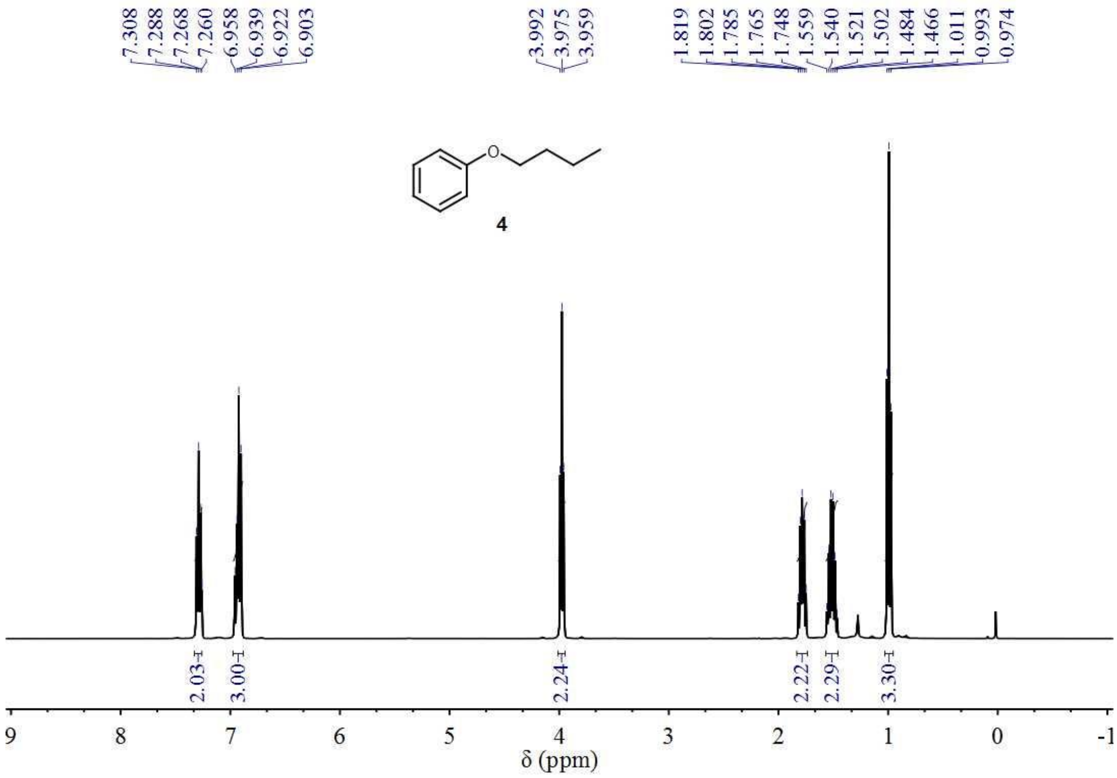

3p - *para*

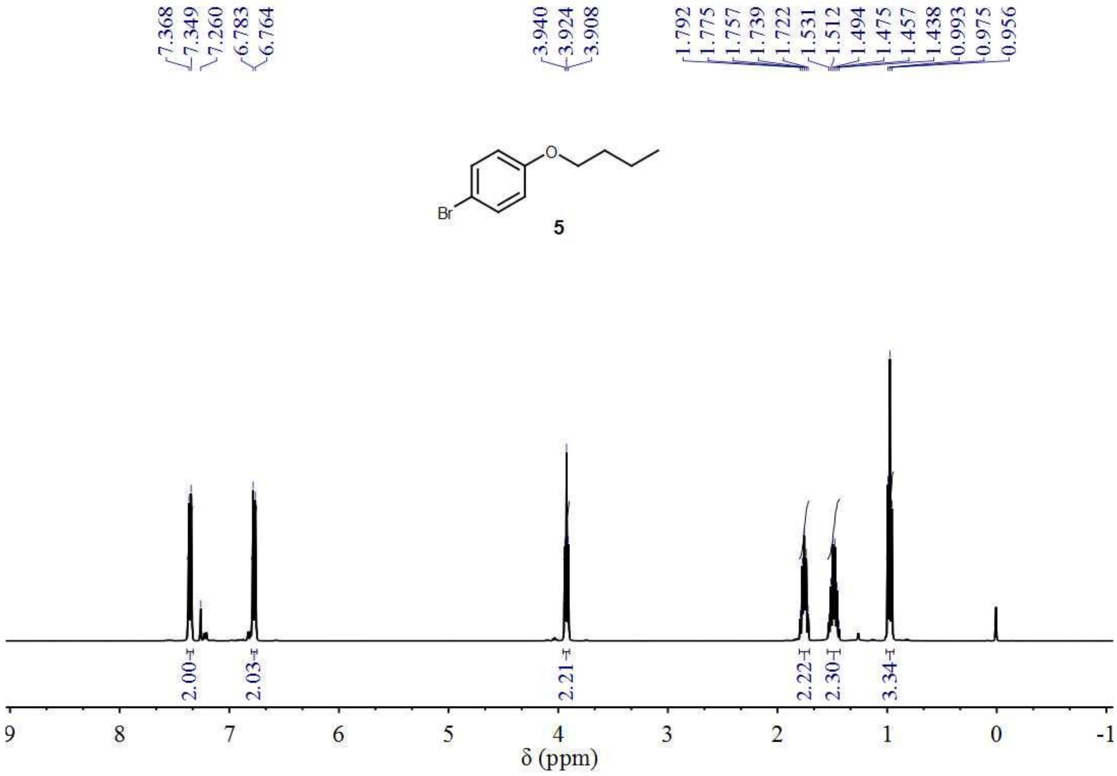

7.374
7.355
7.259
7.248
7.228
7.212
6.944
6.921
6.898
6.879
6.838
6.819
3.906
3.788
-0.000
*
▲
7.5
7.0
6.5
O
Cl
3q - ortho
(*)
3q - para
(▲)
1.00
3.48
2.06
1.56
3.05
2.47
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

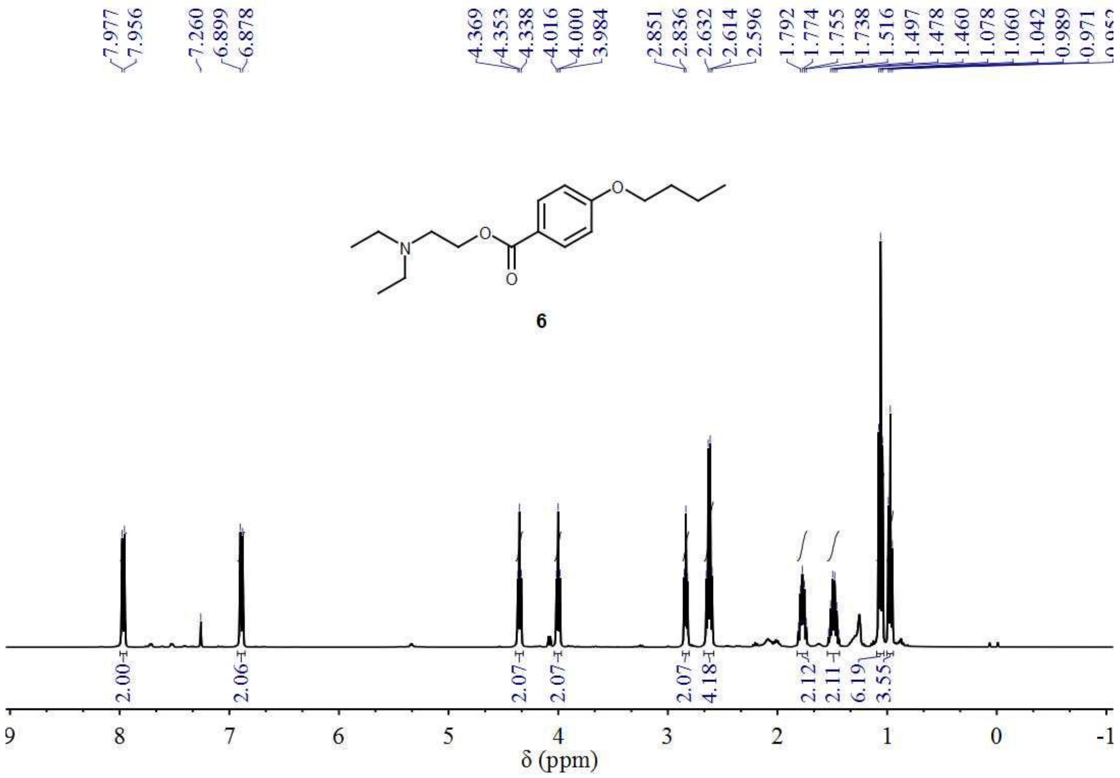

7.260
7.173
7.152
7.132
7.077
7.056
6.843
6.823
3.903
Cl
Cl
O
3r - 1
1.00
0.95
1.03
3.52
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


7.326
7.304
7.260
6.986
6.764
6.742
3.784
Cl
Cl
O
3r - 2
1.00
1.00
1.03
3.21
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


7.357
7.260
7.196
7.174
6.849
6.827
3.878
Cl
Cl
O
3s
0.98
1.00
1.04
3.24
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

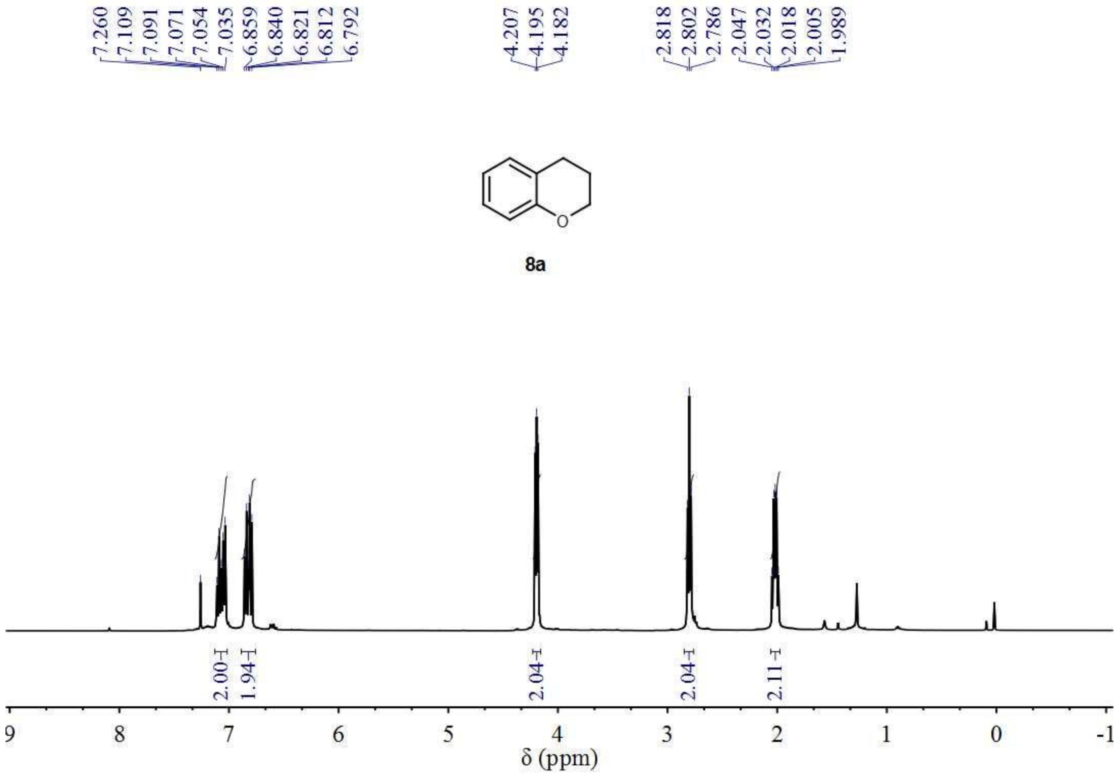

7.308
7.288
7.268
7.260
6.958
6.939
6.922
6.903
3.992
3.975
3.959
1.819
1.802
1.785
1.765
1.748
1.559
1.540
1.521
1.502
1.484
1.466
1.011
0.993
0.974
O
4
2.03
3.00
2.24
2.22
2.29
3.30
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


7.368
7.349
7.260
6.783
6.764
3.940
3.924
3.908
1.792
1.775
1.757
1.739
1.722
1.531
1.512
1.494
1.475
1.457
1.438
0.993
0.975
0.956
O
Br
5
2.00
2.03
2.21
2.22
2.30
3.34
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)



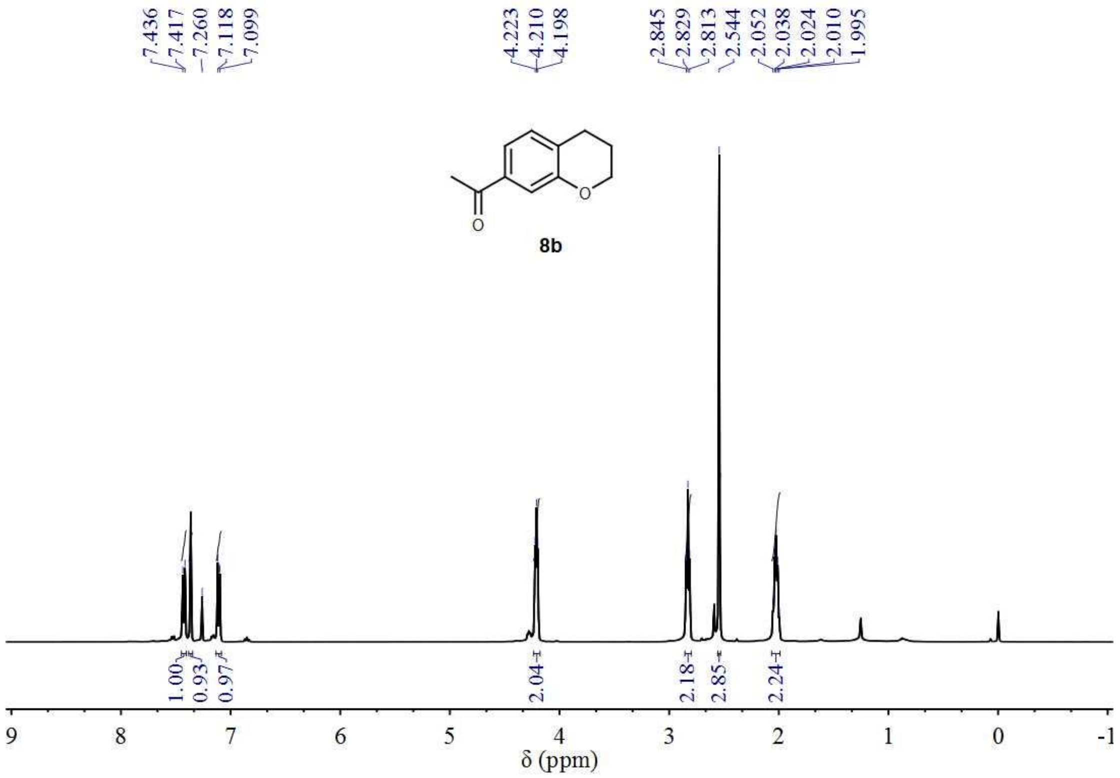
6

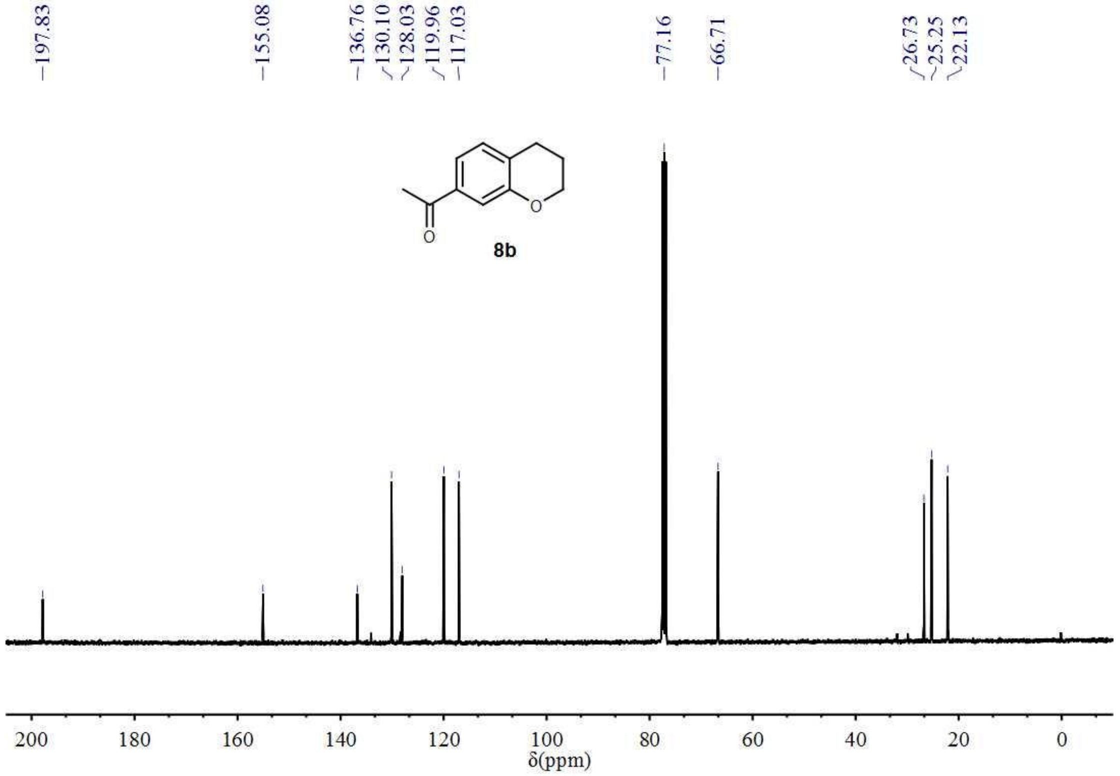
7.977
7.956
7.260
6.899
6.878
4.369
4.353
4.338
4.016
4.000
3.984
2.851
2.836
2.632
2.614
2.596
1.792
1.774
1.755
1.738
1.516
1.497
1.478
1.460
1.078
1.060
1.042
0.989
0.971
0.952
O
N
O
O
2.00
2.06
2.07
2.07
2.07
4.18
2.12
2.11
6.19
3.55
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

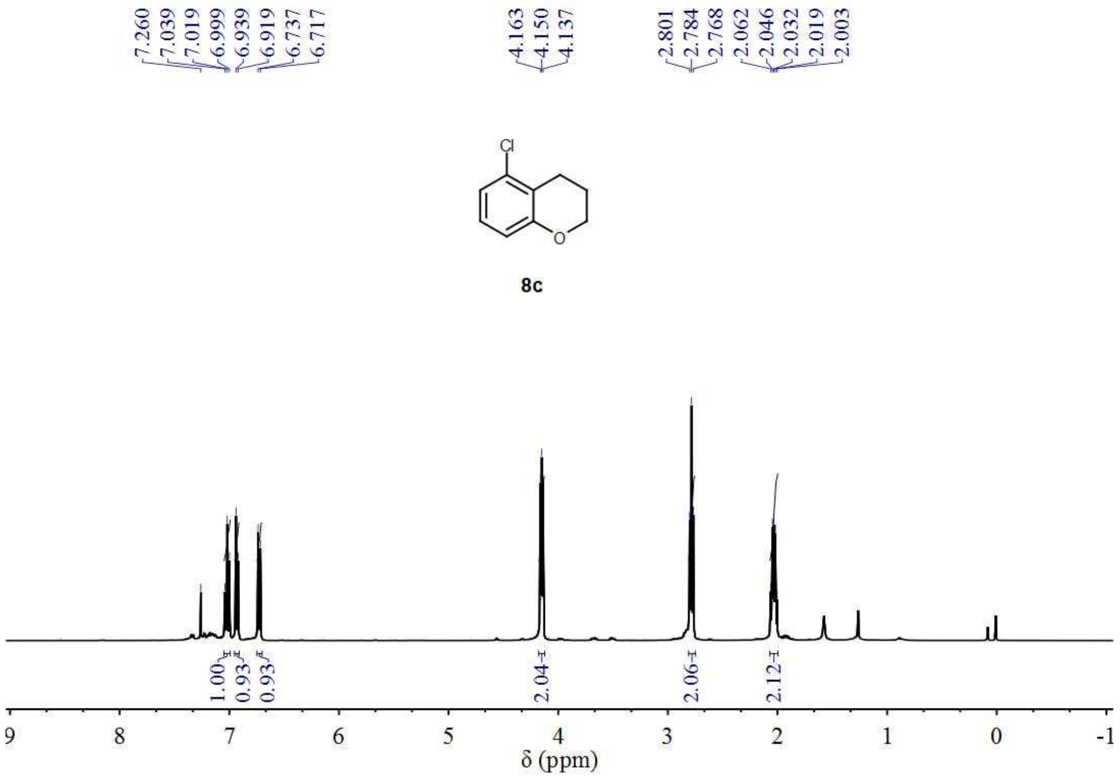


8a

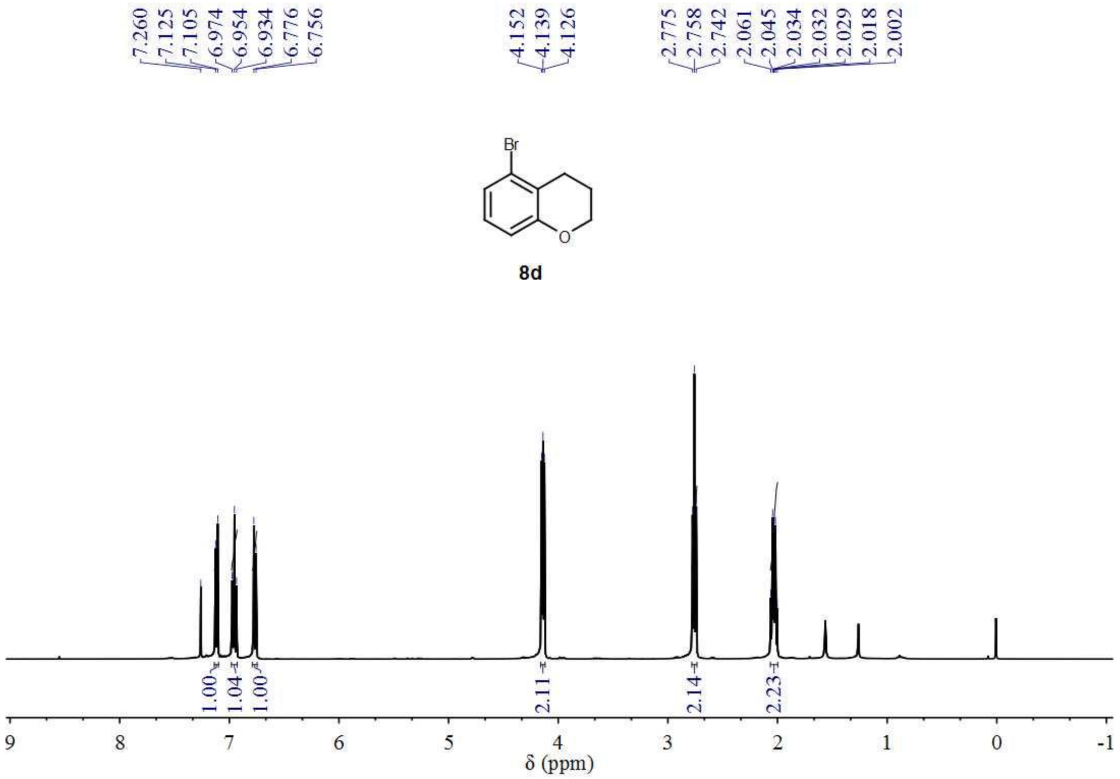
7.260
7.109
7.091
7.071
7.054
7.035
6.859
6.840
6.821
6.812
6.792
4.207
4.195
4.182
2.818
2.802
2.786
2.047
2.032
2.018
2.005
1.989
O
2.00
1.94
2.04
2.04
2.11
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


7.436
7.417
7.260
7.118
7.099
4.223
4.210
4.198
2.845
2.829
2.813
2.544
2.052
2.038
2.024
2.010
1.995
O
O
8b
1.00
0.93
0.97
2.04
2.18
2.85
2.24
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)

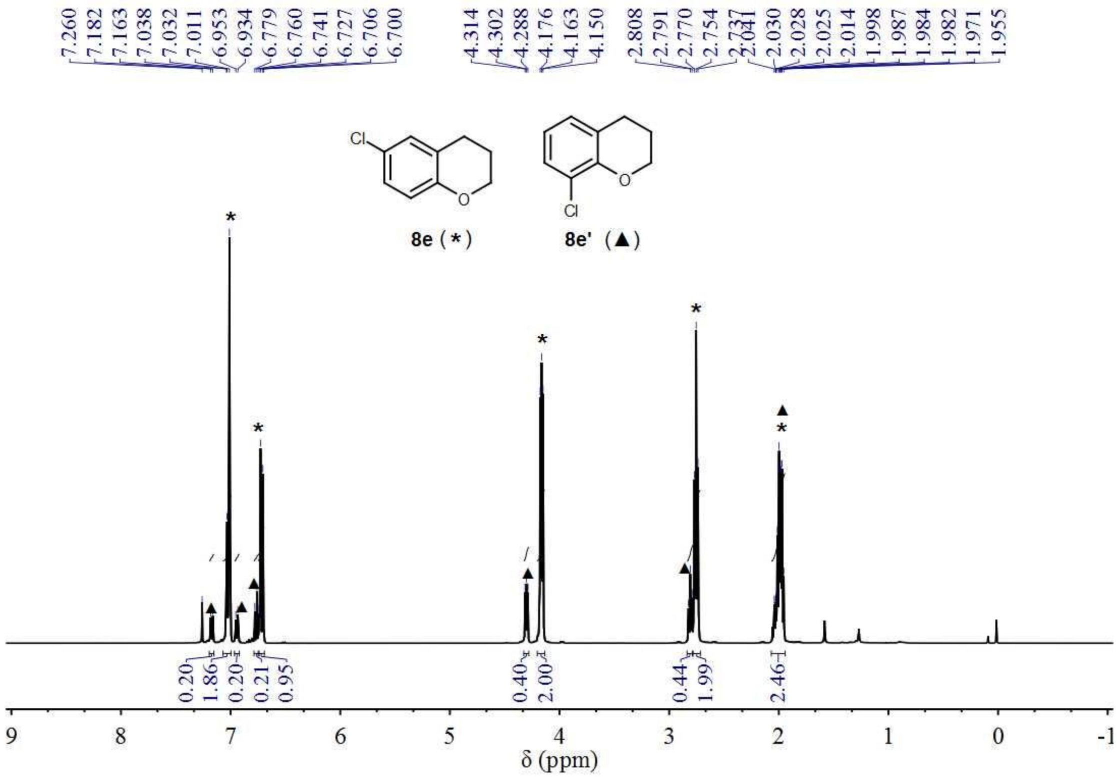

197.83
155.08
136.76
130.10
128.03
119.96
117.03
77.16
66.71
26.73
25.25
22.13
O
O
8b
200
180
160
140
120
100
80
60
40
20
0
δ(ppm)

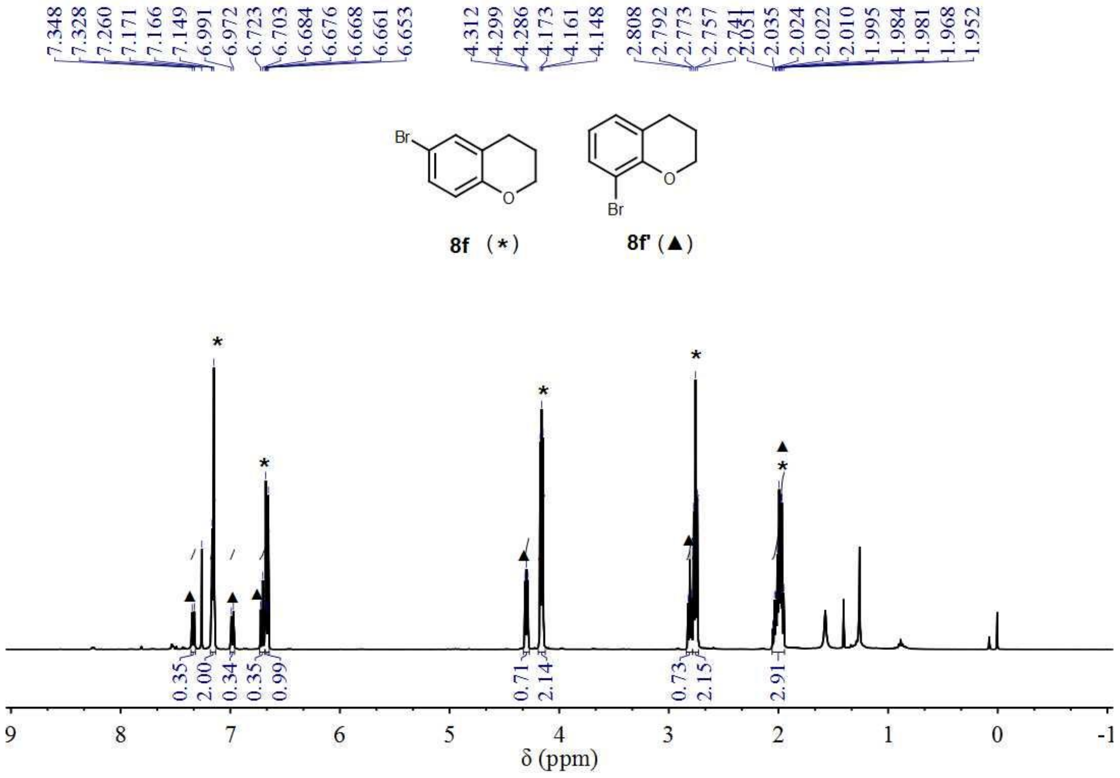

8c

7.260
7.039
7.019
6.999
6.939
6.919
6.737
6.717
4.163
4.150
4.137
2.801
2.784
2.768
2.062
2.046
2.032
2.019
2.003
Cl
O
1.00
0.93
0.93
2.04
2.06
2.12
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


8d

7.260
7.125
7.105
6.974
6.954
6.934
6.776
6.756
4.152
4.139
4.126
2.775
2.758
2.742
2.061
2.045
2.034
2.032
2.029
2.018
2.002
Br
O
1.00
1.04
1.00
2.11
2.14
2.23
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


7.260
7.182
7.163
7.038
7.032
7.011
6.953
6.934
6.779
6.760
6.741
6.727
6.706
6.700
4.314
4.302
4.288
4.176
4.163
4.150
2.808
2.791
2.770
2.754
2.737
2.041
2.030
2.028
2.025
2.014
1.998
1.987
1.984
1.982
1.971
1.955
Cl
O
Cl
O
8e (*)
8e' (▲)
0.20
1.86
0.20
0.21
0.95
0.40
2.00
0.44
1.99
2.46
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)


7.348
7.328
7.260
7.171
7.166
7.149
6.991
6.972
6.723
6.703
6.684
6.676
6.668
6.661
6.653
4.312
4.299
4.286
4.173
4.161
4.148
2.808
2.792
2.773
2.757
2.741
2.051
2.035
2.024
2.022
2.010
1.995
1.984
1.981
1.968
1.952
Br
O
Br
O
8f (*)
8f' (▲)
0.35
2.00
0.34
0.35
0.99
0.71
2.14
0.73
2.15
2.91
9
8
7
6
5
4
3
2
1
0
-1
δ (ppm)