Aryl Boronic Acid-Controlled Divergent Ring-Contraction and Ring-Opening/Isomerization Reactions of *tert*-Cyclobutanols Enabled by Nickel Catalysis

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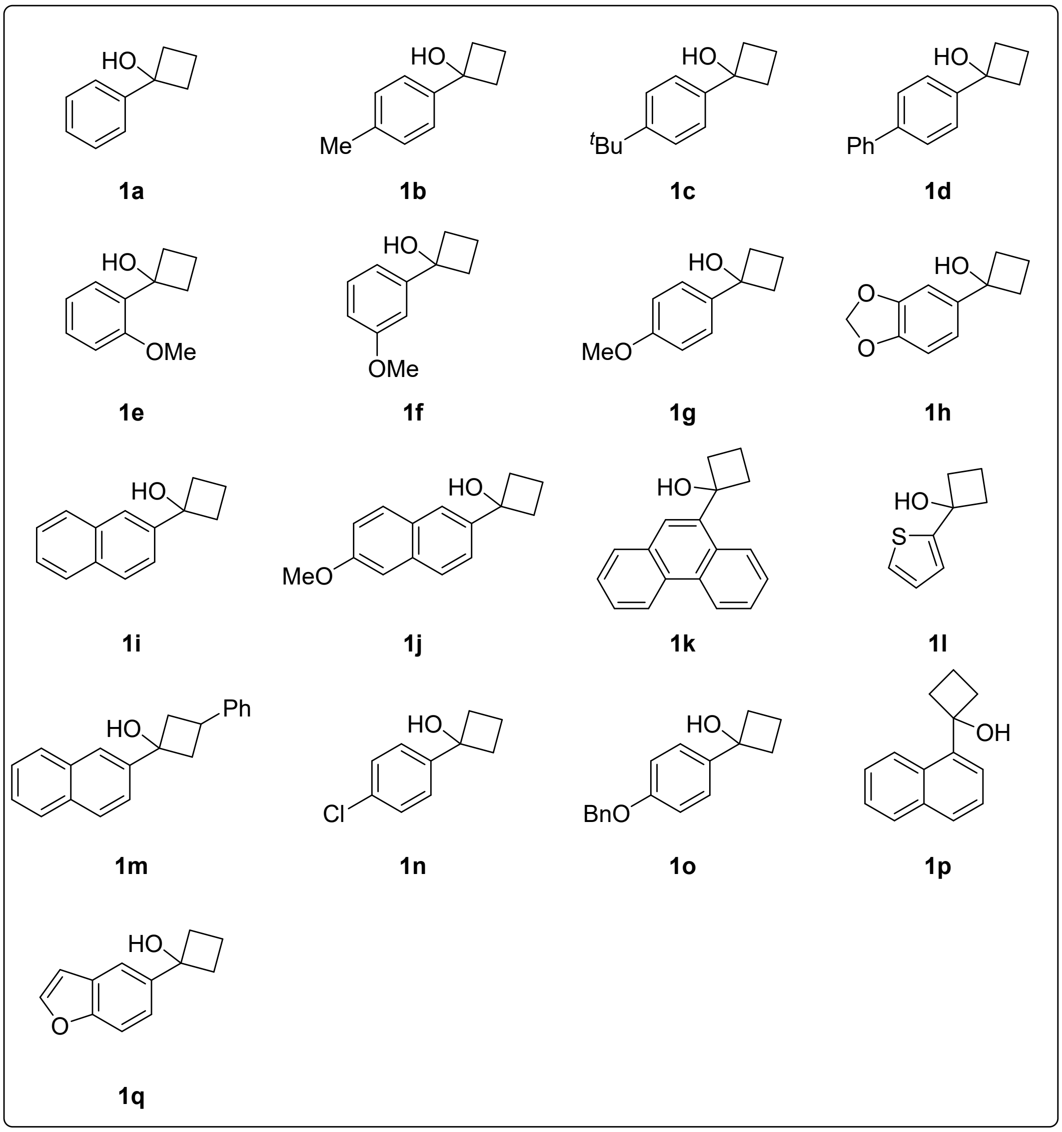
1. General Information

Unless otherwise noted, all reactions were carried out in flame-dried reaction vessels with Teflon screw caps under nitrogen. Solvents were purified and dried according to standard methods prior to use. All commercially available reagents were obtained from chemical suppliers and used after proper purification if necessary. Flash column chromatography was performed on silica gel (200-300 mesh) with the indicated solvent mixtures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 AV or 500 AV spectrometers. Chemical shifts (δ) were reported as parts per million (ppm) downfield from tetramethylsilane and the following abbreviations were used to identify the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, dq = doublet of quartets, br = broad and all combinations thereof can be explained by their integral parts. Coupling constant (J) was reported in hertz unit (Hz).

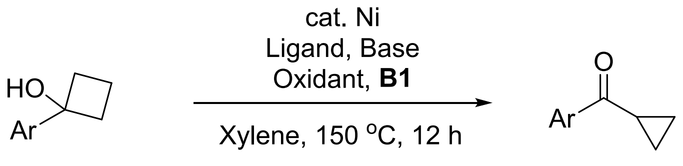
2. Preparation of *tert*-Cyclobutanols



All of the *tert*-cyclobutanols are known compounds and prepared according to the known literature.[1]

3. Nickel-Catalyzed Divergent Ring-Contraction and Ring-Opening/Isomerization Reaction of *tert*-Cyclobutanols

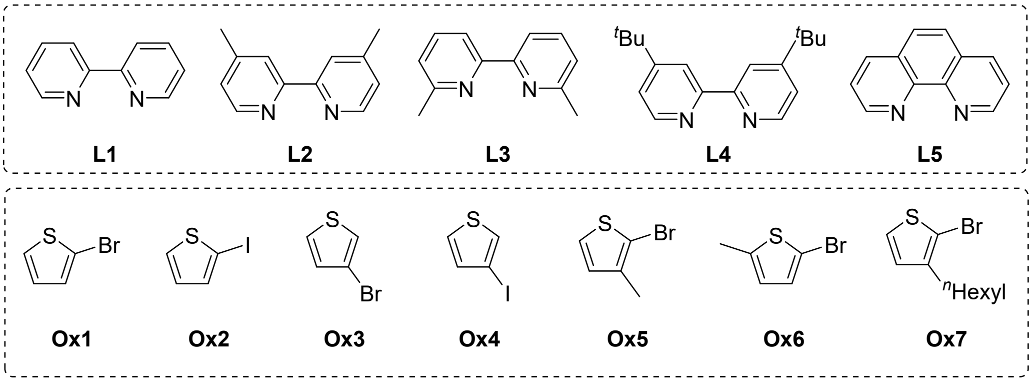
3.1 Optimization of the ring-contraction reaction[a]



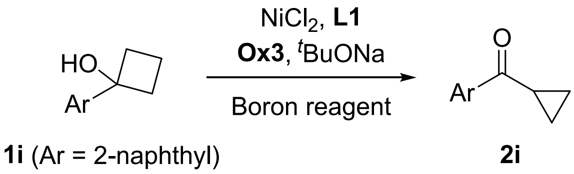
1i (Ar = 2-naphthyl) **2i**

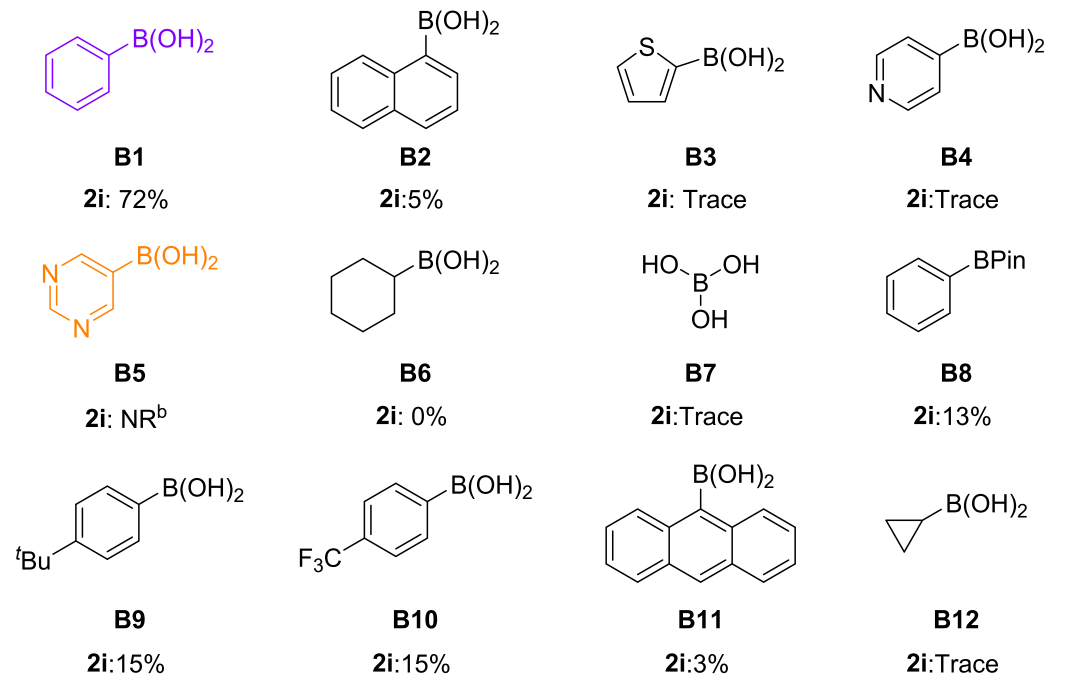
Entry	cat.Ni	Ligand	Base	Oxidant	Yield of **2i**/%
1	$NiBr_2$	**L1**	*t*-BuONa	**Ox1**/1	46
2	$NiBr_2$	**L2**	*t*-BuONa	**Ox1**/1	43
3	$NiBr_2$	**L3**	*t*-BuONa	**Ox1**/1	23
4	$NiBr_2$	**L4**	*t*-BuONa	**Ox1**/1	30
5	$NiBr_2$	**L5**	*t*-BuONa	**Ox1**/1	35
6	$NiBr_2$	dppb	*t*-BuONa	**Ox1**/1	0
7	$NiBr_2$	-	*t*-BuONa	**Ox1**/1	0
8	$NiBr_2$	**L1**	*t*-BuONa	**Ox2**/1	42
9	$NiBr_2$	**L1**	*t*-BuONa	**Ox3**/1	55
10	$NiBr_2$	**L1**	*t*-BuONa	**Ox4**/1	33
11	$NiBr_2$	**L1**	*t*-BuONa	**Ox5**/1	42
12	$NiBr_2$	**L1**	*t*-BuONa	**Ox6**/1	46
13	$NiBr_2$	**L1**	*t*-BuONa	**Ox7**/1	44
14	$NiBr_2$	**L1**	*t*-BuONa	-	0
15	$NiBr_2$	**L1**	*t*-BuONa	**Ox3**/2	50
16	$NiBr_2$	**L1**	*t*-BuONa	**Ox3**/3	67
17	*$NiCl_2$*	***L1***	*t-BuONa*	***Ox3**/3*	*72*
18	$Ni(OAc)_2$	**L1**	*t*-BuONa	**Ox3**/3	43
19	$NiBr_2{\cdot}3H_2O$	**L1**	*t*-BuONa	**Ox3**/3	Trace
20	$Ni(COD)_2$	**L1**	*t*-BuONa	**Ox3**/3	70
21	-	**L1**	*t*-BuONa	**Ox3**/3	0
22	$NiCl_2$	**L1**	*t*-BuOK	**Ox3**/3	63
23	$NiCl_2$	**L1**	*t*-BuOLi	**Ox3**/3	24
24	$NiCl_2$	**L1**	Na_2CO_3	**Ox3**/3	51
25	$NiCl_2$	**L1**	EtONa	**Ox3**/3	47
26	$NiCl_2$	**L1**	-	**Ox3**/3	0

[a]Reaction conditions: **1i** (0.2 mmol), Ni catalyst (20 mol%), Ligand (30 mol%), Base (0.4 mmol), Oxidant, **B1** (0.4 mmol), Xylene (1 mL), 150 °C for 12 h. **B1** = phenylboronic acid. dppb = 1,4-bis(diphenylphosphaneyl)butane



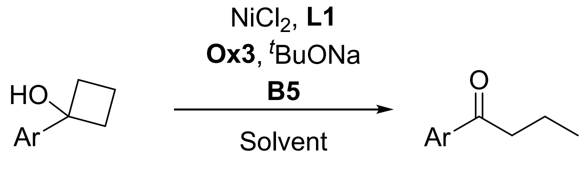
3.2 Examination of boron reagents in the ring-contraction reaction[a]





[a]Reaction conditions: **1i** (0.2 mmol), $NiCl_2$ (20 mol%), **L1** (30 mol%), ^{t}BuONa (0.4 mmol), **Ox3** (0.6 mmol), Boron reagent (0.4 mmol), Xylene (1 mL), 150 °C for 12 h. [b]1-(naphthalen-2-yl)butan-1-one **3c** was isolated in 53% yield.

3.3 Optimization of the ring-opening/isomerization reaction[a]

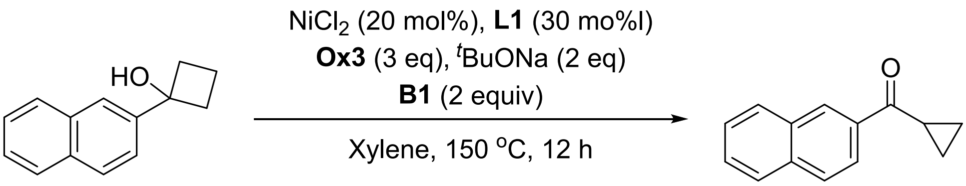


1i (Ar = 2-naphthyl) **3c**

Entry	$NiCl_2$/mol%	L1/mol%	^{t}BuONa	Ox3	Solvent	Yield of 3c/%
1	$NiCl_2$/20	**L1**/30	*t*-BuONa	**Ox3**	Xylene	53
2	$NiCl_2$/10	**L1**/15	*t*-BuONa	**Ox3**	Xylene	55
3	$NiCl_2$/5	**L1**/7.5	*t*-BuONa	**Ox3**	Xylene	34
4	-	-	*t*-BuONa	**Ox3**	Xylene	Trace
5	$NiCl_2$/10	**L1**/15	-	**Ox3**	Xylene	Trace
6	$NiCl_2$/10	**L1**/15	*t*-BuONa	**Ox3**	Xylene	32[b]
7	$NiCl_2$/10	-	*t*-BuONa	-	Xylene	57
8	*$NiCl_2$/10*	-	*t-BuONa*	-	*Toluene*	*75*
9	$NiCl_2$/10	-	*t*-BuONa	-	Toluene	0[c]

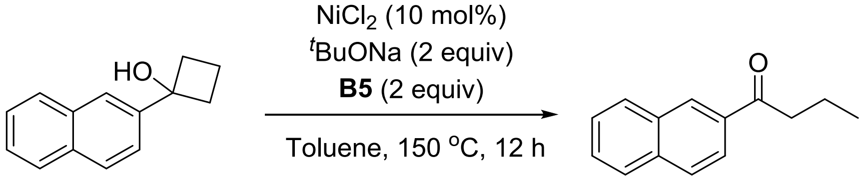
[a]Reaction conditions: **1i** (0.2 mmol), $NiCl_2$, **L1**, ^{t}BuONa (0.4 mmol), **Ox3** (0.6 mmol), **B5** (0.4 mmol), Solvent (1 mL), 150 °C for 12 h. [b]No **B5**. [c]At 100 °C

3.4 Experimental details and characterization of products



1i **2i**

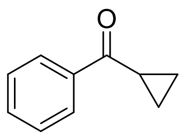
To a 25 ml flame-dried Schlenk tube containing a stirring bar was added 1-(2-naphthalenyl)cyclobutanol **1i** (0.2 mmol, 40 mg), $NiCl_2$ (20 mol%, 0.04 mmol, 5.2 mg), bpy **L1** (30 mol%, 0.06 mmol, 10 mg), phenylboronic acid **B1** (2 eq, 0.4 mmol, 48.8 mg), **Ox3** (0.6 mmol, 97.8 mg), ^{t}BuONa (0.4 mmol, 38.4 mg), xylene (1 mL), sequentially under nitrogen. The tube was sealed and stirred at 150 °C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product **2i** in 72% yield.



1i **3c**

To a 25 ml flame-dried Schlenk tube containing a stirring bar was added 1-(2-Naphthalenyl)cyclobutanol (0.2 mmol, 40 mg), $NiCl_2$ (10 mol%, 0.02 mmol, 2.6 mg), 5-Pyrimidinylboronic acid **B5** (2 eq, 0.4 mmol, 49.6 mg), ^{t}BuONa (0.4 mmol, 38.4 mg), Toluene (1 mL), sequentially under nitrogen. The tube was sealed and stirred at 150 °C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product **3c** in 75% yield.

cyclopropyl(phenyl)methanone (2a) [2]

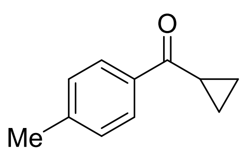


2a

Purified by silica gel column chromatography as yellow oil (18 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 2H), 7.63 – 7.53 (m, 1H), 7.51 – 7.45 (m, 2H), 2.72 – 2.65 (m, 1H), 1.28 – 1.22 (m, 2H), 1.08 – 1.02 (m, 2H).

cyclopropyl(p-tolyl)methanone (2b) [2]

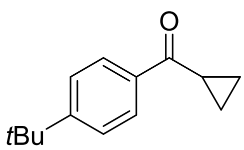


2b

Purified by silica gel column chromatography as yellow oil (20 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.2 Hz, 2H), 7.27 (d, J = 8.2 Hz, 2H), 2.70 – 2.62 (m, 1H), 2.42 (s, 3H), 1.25 – 1.20 (m, 2H), 1.05 – 0.99 (m, 2H).

(4-(tert-butyl)phenyl)(cyclopropyl)methanone (2c) [2]

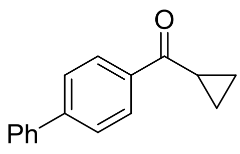


2c

Purified by silica gel column chromatography as yellow oil (30 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.93 (m, 2H), 7.52 – 7.47 (m, 2H), 2.72 – 2.64 (m, 1H), 1.35 (s, 9H), 1.25 – 1.19 (m, 2H), 1.05 – 0.98 (m, 2H).

[1,1'-biphenyl]-4-yl(cyclopropyl)methanone (2d) [2]

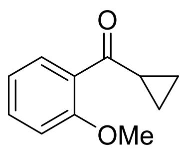


2d

Purified by silica gel column chromatography as yellow oil (24 mg, 54% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.09 (d, J = 8.4 Hz, 2H), 7.69 (d, J = 8.4 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.47 (t, J = 7.4 Hz, 2H), 7.39 (dd, J_1 = 8.4, J_2 = 6.2 Hz, 1H), 2.75 – 2.67 (m, 1H), 1.30 – 1.24 (m, 2H), 1.09 – 1.03 (m, 2H).

cyclopropyl(2-methoxyphenyl)methanone (2e) [2]

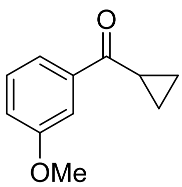


2e

Purified by silica gel column chromatography as yellow oil (15 mg, 42% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.59 (d, J = 7.6 Hz, 1H), 7.44 (t, J = 7.8 Hz, 2H), 6.99 (dd, J_1 = 12.1, J_2 = 6.6 Hz, 2H), 3.91 (s, 3H), 2.78 – 2.68 (m, 1H), 1.22 (s, 2H), 0.98 (d, J = 3.6 Hz, 2H).

cyclopropyl(3-methoxyphenyl)methanone (2f) [3]

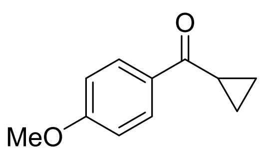


2f

Purified by silica gel column chromatography as yellow oil (20 mg, 58% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.63 (d, J = 7.6 Hz, 1H), 7.52 (dd, J_1 = 2.4, J_2 = 1.6 Hz, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.14 – 7.10 (m, 1H), 3.86 (s, 3H), 2.70 – 2.62 (m, 1H), 1.28 – 1.21 (m, 2H), 1.09 – 1.01 (m, 2H).

cyclopropyl(4-methoxyphenyl)methanone (2g) [2]

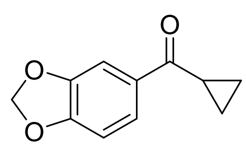


2g

Purified by silica gel column chromatography as yellow oil (22 mg, 62% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, J = 8.8 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 3.88 (s, 3H), 2.68 – 2.60 (m, 1H), 1.23 – 1.18 (m, 2H), 1.03 – 0.97 (m, 2H).

benzo[d][1,3]dioxol-5-yl(cyclopropyl)methanone (2h)[4]

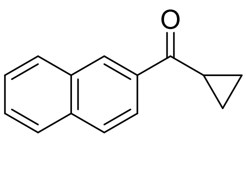


2h

Purified by silica gel column chromatography as yellow oil (18 mg, 47% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.65 (dd, J_1 = 8.2, J_2 = 1.7 Hz, 1H), 7.47 (d, J = 1.7 Hz, 1H), 6.87 (d, J = 8.2 Hz, 1H), 6.04 (s, 2H), 2.64 – 2.52 (m, 1H), 1.23 – 1.17 (m, 2H), 1.03 – 0.97 (m, 2H).

cyclopropyl(naphthalen-2-yl)methanone (2i)[2]

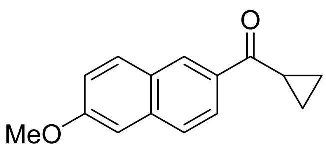


2i

Purified by silica gel column chromatography as yellow oil (28 mg, 72% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.56 (s, 1H), 8.06 (dd, J_1 = 8.6, J_2 = 1.7 Hz, 1H), 7.97 (d, J = 8.0 Hz, 1H), 7.88 (t, J = 8.6 Hz, 2H), 7.61 – 7.52 (m, 2H), 2.87 – 2.80 (m, 1H), 1.33 – 1.28 (m, 2H), 1.12 – 1.06 (m, 2H).

cyclopropyl(6-methoxynaphthalen-2-yl)methanone (2j)



2j

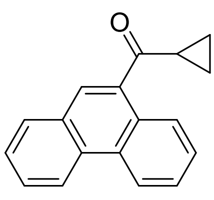
Purified by silica gel column chromatography as yellow oil (26 mg, 58% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.50 (s, 1H), 8.04 (dd, J_1 = 8.6, J_2 = 1.7 Hz, 1H), 7.87 (d, J = 8.9 Hz, 1H), 7.78 (d, J = 8.6 Hz, 1H), 7.20 (dd, J_1 = 8.9, J_2 = 2.5 Hz, 1H), 7.16 (d, J = 2.4 Hz, 1H), 3.95 (s, 3H), 2.86 – 2.78 (m, 1H), 1.32 – 1.26 (m, 2H), 1.11 – 1.04 (m, 2H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 200.19 (s), 159.62 (s), 137.14 (s), 133.41 (s), 131.12 (s), 129.48 (s), 127.91 (s), 127.04 (s), 124.74 (s), 119.66 (s), 105.73 (s), 55.43 (s), 17.01 (s), 11.53 (s).

HRMS(ESI) Calculated for $C_{15}H_{15}O_2^+$ ($[M+H]^+$): 227.10720, found: 227.10711.

cyclopropyl(phenanthren-9-yl)methanone (2k) [5]

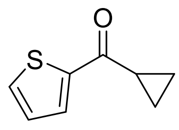


2k

Purified by silica gel column chromatography as yellow oil (16 mg, 33% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.73 – 8.64 (m, 2H), 8.47 – 8.43 (m, 1H), 8.17 (s, 1H), 7.97 – 7.93 (m, 1H), 7.75 – 7.61 (m, 4H), 2.68 – 2.60 (m, 1H), 1.46 – 1.40 (m, 2H), 1.19 – 1.11 (m, 2H).

cyclopropyl(thiophen-2-yl)methanone (2l) [6]

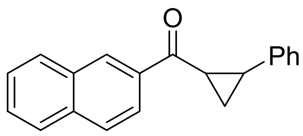


2l

Purified by silica gel column chromatography as yellow oil (16 mg, 52% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.83 (dd, J_1 = 3.8, J_2 = 1.0 Hz, 1H), 7.63 (dd, J_1 = 4.9, J_2 = 1.0 Hz, 1H), 7.16 (dd, J_1 = 4.9, J_2 = 3.8 Hz, 1H), 2.58 – 2.52 (m, 1H), 1.27 – 1.23 (m, 2H), 1.05 – 1.00 (m, 2H).

naphthalen-2-yl(2-phenylcyclopropyl)methanone (2m) [7]

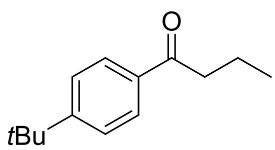


2n

Purified by silica gel column chromatography as yellow oil (21 mg, 61% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.52 (s, 1H), 8.05 (dd, J_1 = 8.6, J_2 = 1.7 Hz, 1H), 7.94 (d, J = 8.1 Hz, 1H), 7.88 (dd, J_1 = 11.6, J_2 = 8.5 Hz, 2H), 7.60 – 7.51 (m, 2H), 7.36 – 7.30 (m, 2H), 7.27 – 7.21 (m, 3H), 3.11 – 2.95 (m, 1H), 2.88 – 2.71 (m, 1H), 2.07 – 1.88 (m, 1H), 1.66 – 1.52 (m, 1H).

1-(4-(tert-butyl)phenyl)butan-1-one (3a) [8]

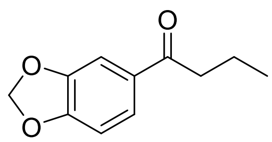


3a

Purified by silica gel column chromatography as purple liquid (27 mg, 67% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.91 (d, J = 8.5 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 2.92 (t, J = 7.3 Hz, 2H), 1.84 – 1.70 (m, 2H), 1.34 (s, 9H), 1.00 (t, J = 7.4 Hz, 3H).

1-(benzo[d][1,3]dioxol-5-yl)butan-1-one (3b) [9]

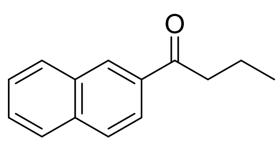


3b

Purified by silica gel column chromatography as purple liquid (30 mg, 78% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.56 (dd, J_1 = 8.2, J_2 = 1.7 Hz, 1H), 7.44 (d, J = 1.7 Hz, 1H), 6.84 (d, J = 8.2 Hz, 1H), 6.03 (s, 2H), 2.86 (t, J = 7.3 Hz, 2H), 1.84 – 1.60 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).

1-(naphthalen-2-yl)butan-1-one (3c) [9]



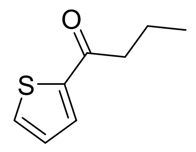
3c

Purified by silica gel column chromatography as colorless liquid (29.7 mg, 75% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 8.44 (s, 1H), 8.02 (dd, J_1 = 8.6, J_2 = 1.7 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.85 (t, J =

8.2 Hz, 2H), 7.60 – 7.49 (m, 2H), 3.05 (t, J = 7.3 Hz, 2H), 1.89 – 1.75 (m, 2H), 1.04 (t, J = 7.4 Hz, 3H).

1-(thiophen-2-yl)butan-1-one (3d) [10]

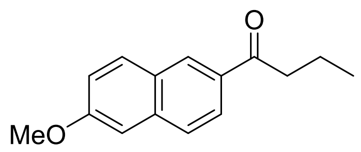


3d

Purified by silica gel column chromatography as yellow oil (22.5 mg, 75% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.71 (dd, J_1 = 3.8, J_2 = 1.1 Hz, 1H), 7.62 (dd, J_1 = 4.9, J_2 = 1.0 Hz, 1H), 7.12 (dd, J_1 = 4.9, J_2 = 3.8 Hz, 1H), 2.88 (t, J = 7.3 Hz, 2H), 1.86 – 1.71 (m, 2H), 1.01 (t, J = 7.4 Hz, 3H).

1-(6-methoxynaphthalen-2-yl)butan-1-one (3e) [11]

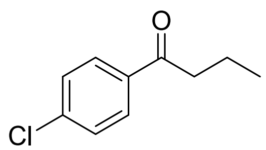


3e

Purified by silica gel column chromatography as white solid (32 mg, 71% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.37 (s, 1H), 7.99 (dd, J_1 = 8.6, J_2 = 1.5 Hz, 1H), 7.81 (d, J = 8.9 Hz, 1H), 7.73 (d, J = 8.6 Hz, 1H), 7.18 (dd, J_1 = 8.9, J_2 =2.4 Hz, 1H), 7.12 (s, 1H), 3.91 (s, 3H), 3.02 (t, J = 7.3 Hz, 2H), 1.89 – 1.75 (m, 2H), 1.03 (t, J = 7.4 Hz, 3H).

1-(4-chlorophenyl)butan-1-one (3f) [9]

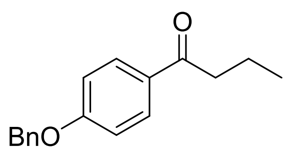


3f

Purified by silica gel column chromatography as yellow oil (22 mg, 60% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90 (d, J = 8.6 Hz, 2H), 7.43 (d, J = 8.6 Hz, 2H), 2.92 (t, J = 7.3 Hz, 2H), 1.82 – 1.71 (m, 2H), 1.00 (t, J = 7.4 Hz, 3H).

1-(4-(benzyloxy)phenyl)butan-1-one (3g) [9]

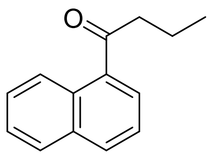


3g

Purified by silica gel column chromatography as yellow oil (37 mg, 73% yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.97 – 7.92 (m, 2H), 7.47 – 7.37 (m, 4H), 7.37 – 7.31 (m, 1H), 7.05 – 6.97 (m, 2H), 5.13 (s, 2H), 2.89 (t, J = 7.3 Hz, 2H), 1.81 – 1.70 (m, 2H), 0.99 (t, J = 7.4 Hz, 3H).

1-(naphthalen-1-yl)butan-1-one (3h) [12]

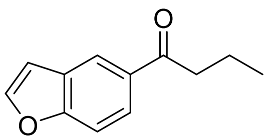


3h

Purified by silica gel column chromatography as colorless liquid (35 mg, 87% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.5 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.82 (dd, J_1 = 15.0, J_2 = 7.4 Hz, 2H), 7.61 – 7.40 (m, 3H), 3.00 (t, *J* = 7.3 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.01 (t, *J* = 7.4 Hz, 3H).

1-(benzofuran-5-yl)butan-1-one (3i) [13]

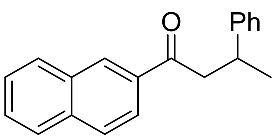


3i

Purified by silica gel column chromatography as purple liquid (27 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 1.6 Hz, 1H), 7.97 (dd, J_1 = 8.7, J_2 = 1.7 Hz, 1H), 7.68 (d, *J* = 2.2 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 6.89 – 6.82 (m, 1H), 3.01 (t, *J* = 7.3 Hz, 2H), 1.87 – 1.75 (m, 2H), 1.02 (t, *J* = 7.4 Hz, 3H).

1-(naphthalen-2-yl)-3-phenylbutan-1-one (3j)[14]

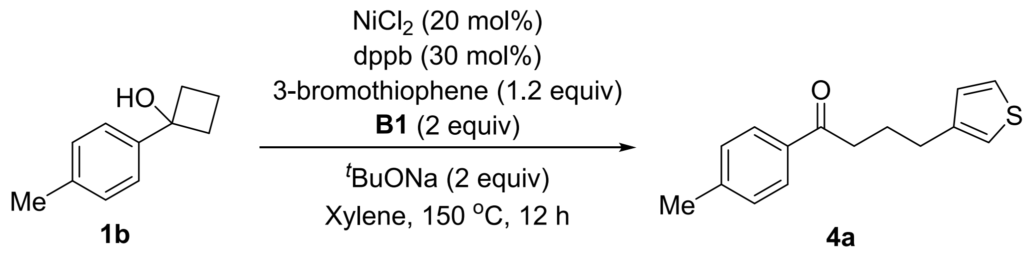


3j

Purified by silica gel column chromatography as colorless liquid (31 mg, 56% yield).

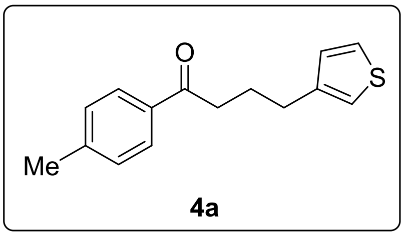
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.01 – 7.98 (m, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.88 – 7.83 (m, 2H), 7.60 – 7.51 (m, 2H), 7.31 (d, *J* = 4.5 Hz, 4H), 7.22 – 7.17 (m, 1H), 3.61 – 3.53 (m, 1H), 3.45 – 3.39 (m, 1H), 3.35 – 3.27 (m, 1H), 1.38 (d, *J* = 7.0 Hz, 3H).

4. Investigation of Possible Intermediates



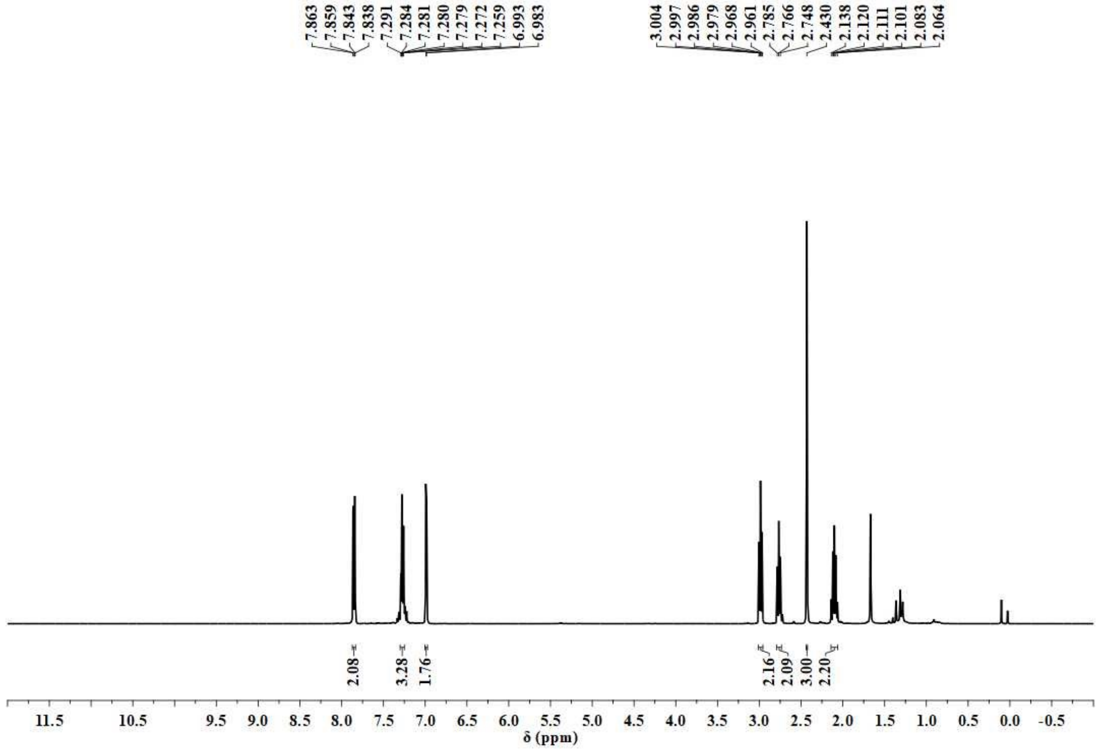
To a 25 ml flame-dried Schlenk tube containing a stirring bar was added 1-(2-naphthalenyl)cyclobutanol **1i** (0.2 mmol, 40 mg), $NiCl_2$ (20 mol%, 0.04 mmol, 5.2 mg), dppb (30 mol%, 0.06 mmol, 25.6 mg), phenylboronic acid **B1** (2 eq, 0.4 mmol, 48.8 mg), **Ox3** (0.6 mmol, 97.8 mg), ^{t}BuONa (0.4 mmol, 38.4 mg), xylene (2 mL), sequentially under nitrogen. The tube was sealed and stirred at 50 ^{o}C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product **4a** in 25% yield.

4-(thiophen-3-yl)-1-(p-tolyl)butan-1-one (**4a**)



Purified by silica gel column chromatography as White solid (12.7 mg, 25% yield)

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.85 (dd, J = 8.3, 1.8 Hz, 2H), 7.30 – 7.25 (m, 3H), 6.99 (d, J = 4.0 Hz, 2H), 3.01 – 2.96 (m, J = 7.3, 2.9 Hz, 2H), 2.77 (t, J = 7.5 Hz, 2H), 2.43 (s, 3H), 2.10 (dt, J = 18.7, 7.4 Hz, 2H). **^{13}C NMR (100 MHz, CDCl$_3$)** δ 199.78 (s), 143.71 (s), 142.05 (s), 134.48 (s), 129.21 (s), 128.15 (s), 128.12 (s), 125.39 (s), 120.37 (s), 37.58 (s), 29.58 (s), 24.98 (s), 21.59 (s).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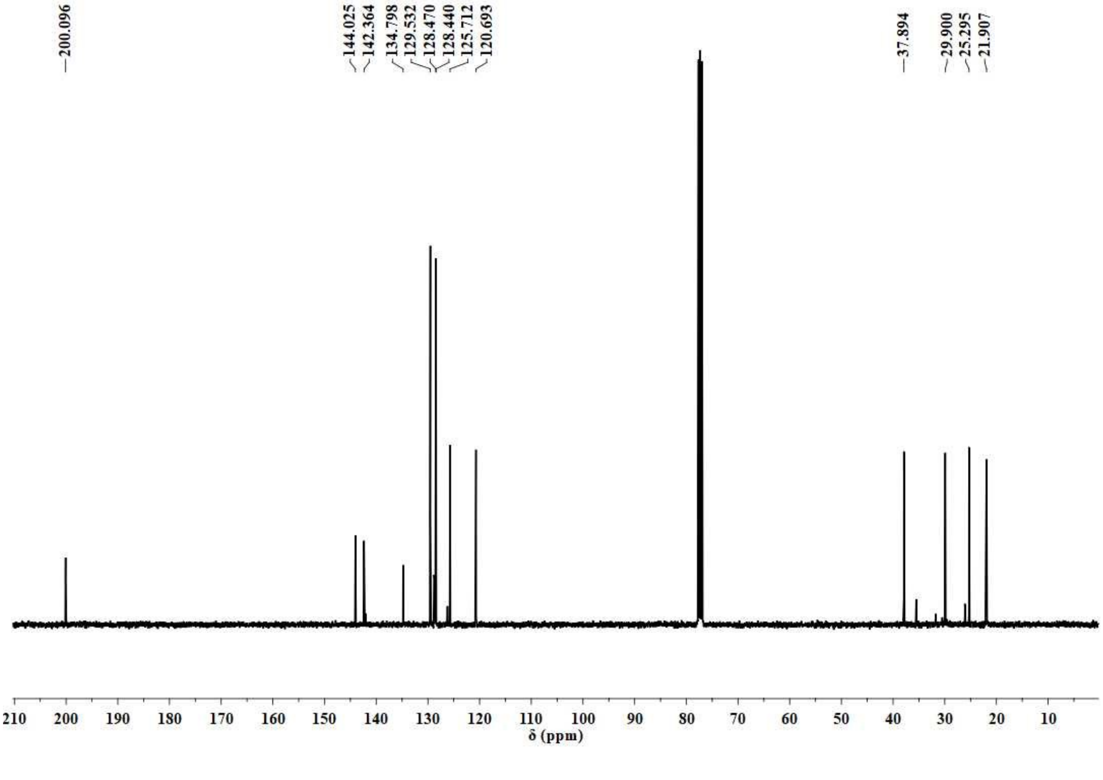
7.859
7.843
7.838
7.291
7.284
7.281
7.280
7.279
7.272
7.259
6.993
6.983
3.004
2.997
2.986
2.979
2.968
2.961
2.785
2.766
2.748
2.430
2.138
2.120
2.111
2.101
2.083
2.064
2.08
3.28
1.76
2.16
2.09
3.00
2.20
δ (ppm)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134.798
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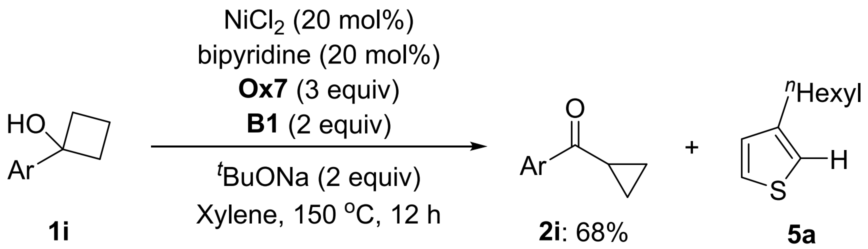
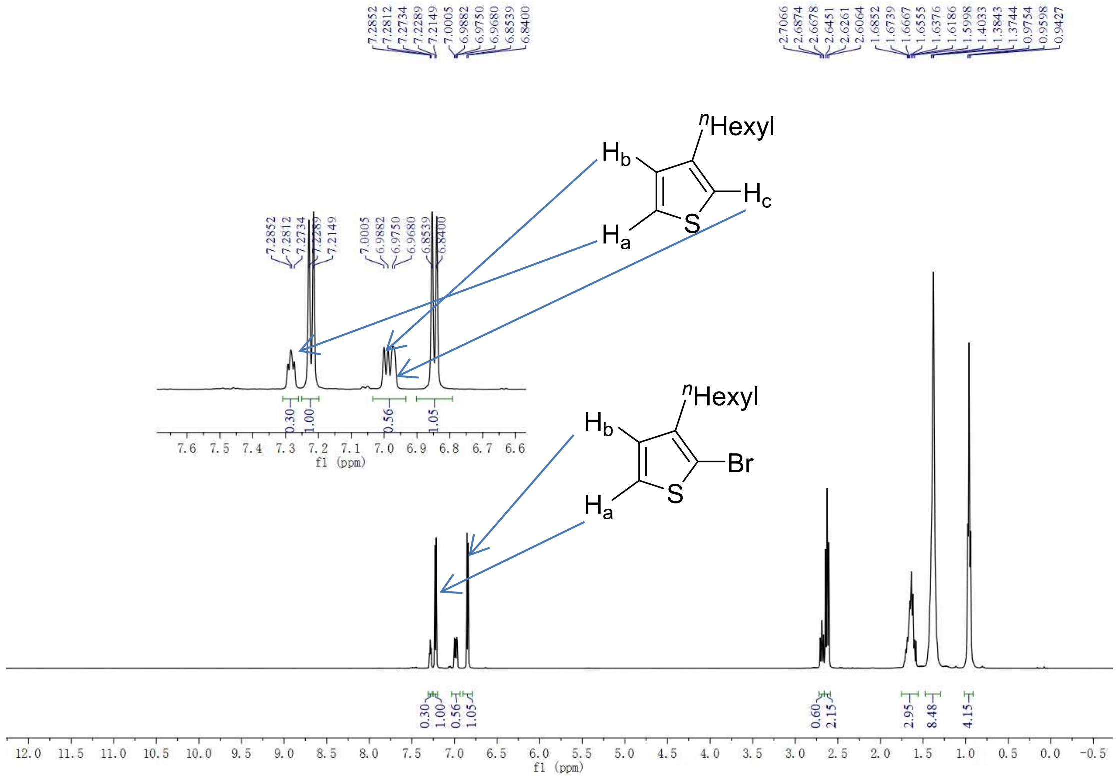
128.470
128.440
125.712
120.693
37.894
29.900
25.295
21.907
δ (ppm)



To a 25 ml flame-dried Schlenk tube containing a stirring bar was added 1-(2-naphthalenyl)cyclobutanol **1i** (0.2 mmol, 40 mg), $NiCl_2$ (20 mol%, 0.04 mmol, 5.2 mg), bipyridine (30 mol%, 0.06 mmol, 9.38mg), phenylboronic acid **B1** (2 eq, 0.4 mmol, 48.8 mg), 2-bromo-3-hexylthiophene **Ox7** (0.6 mmol, 148.2 mg), ^{t}BuONa (0.4 mmol, 38.4 mg), xylene (1 mL), sequentially under nitrogen. The tube was sealed and stirred at 150 °C for 12 h. After completion, the reaction mixture was concentrated and purified by silica gel column chromatography to provide the product **2i** in 68% yield. In addition, the **5a** was also isolated as mixture with **Ox7**.



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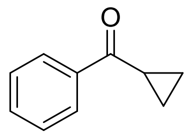
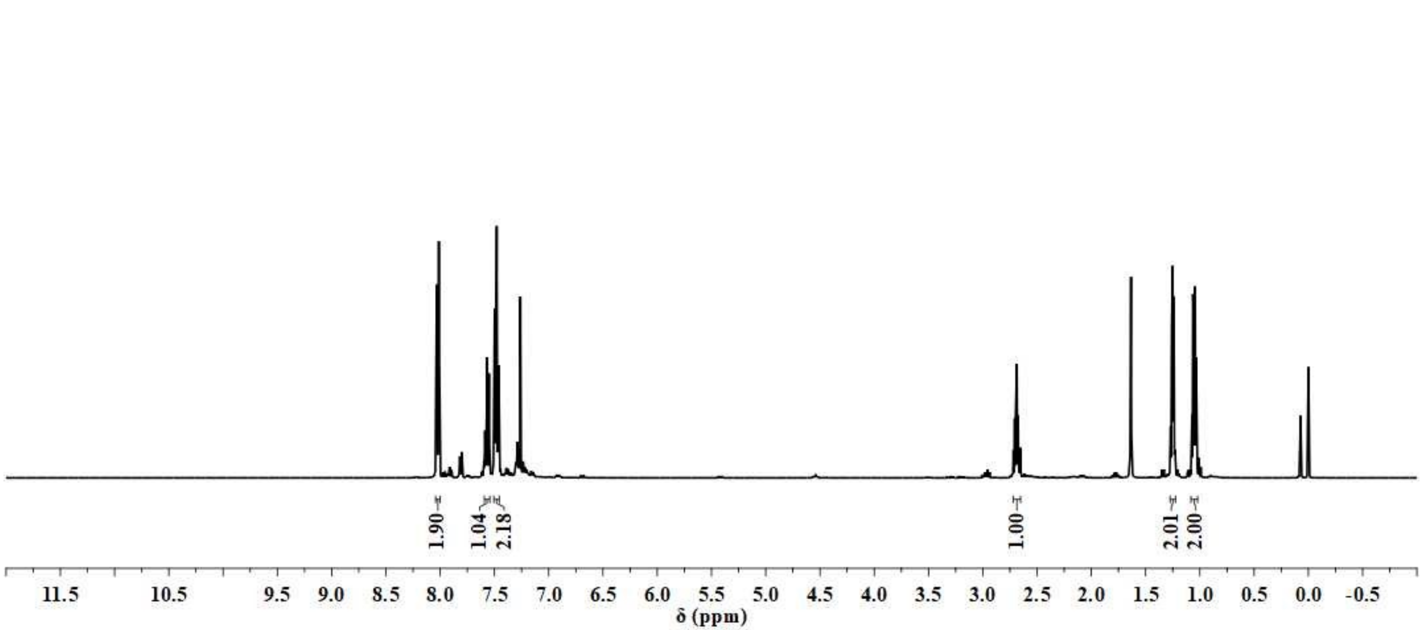
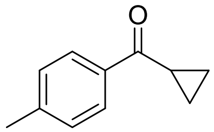
6. ^{1}H NMR and ^{13}C NMR Spectra

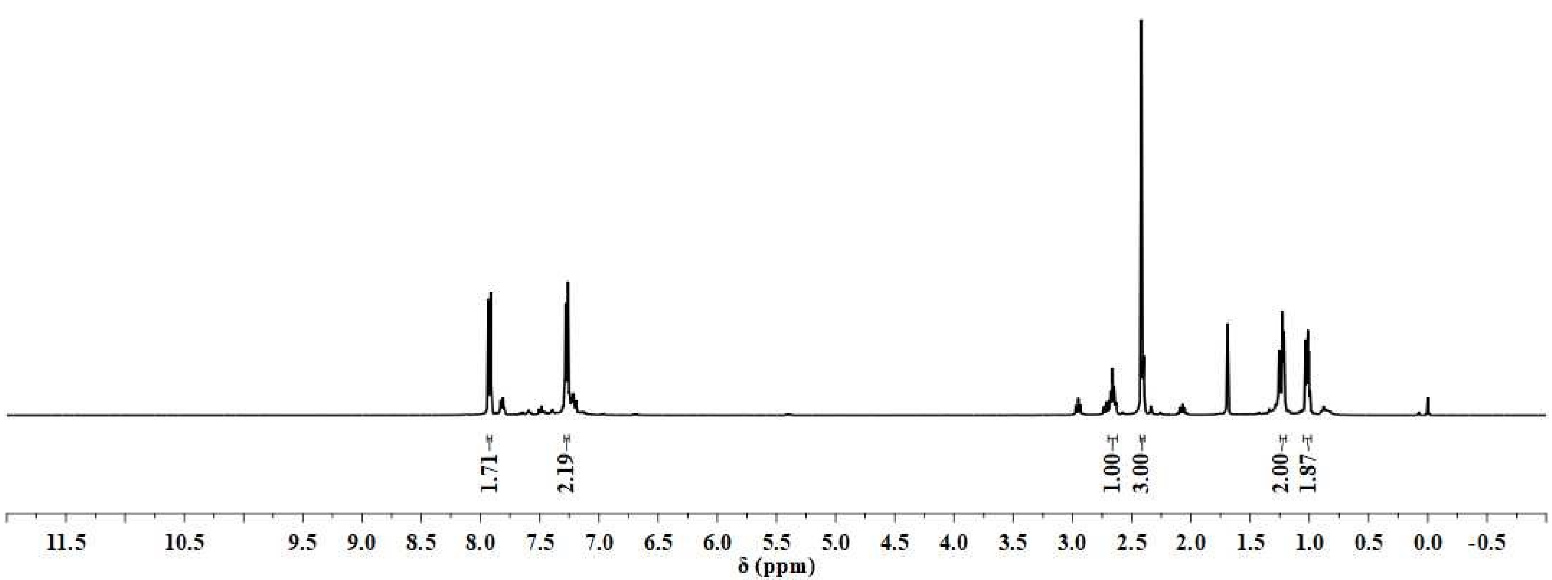


2a




O

2b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7.281
7.260
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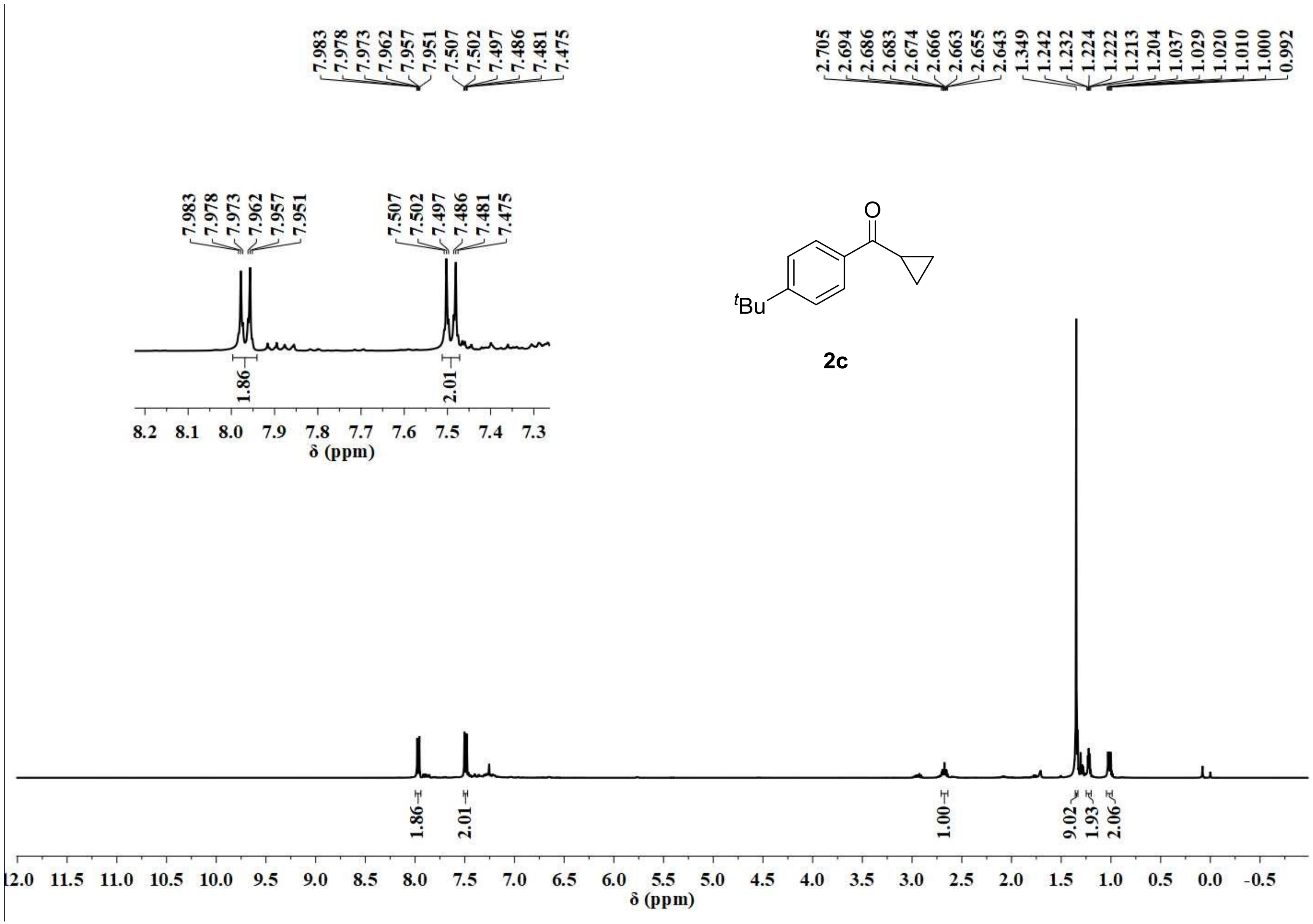
2.680
2.672
2.661
2.649
2.641
2.630
2.418
1.243
1.234
1.225
1.214
1.206
1.040
1.031
1.022
1.012
1.003
0.994
1.71
2.19
1.00
3.00
2.00
1.87
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
δ (ppm)



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7.978
7.973
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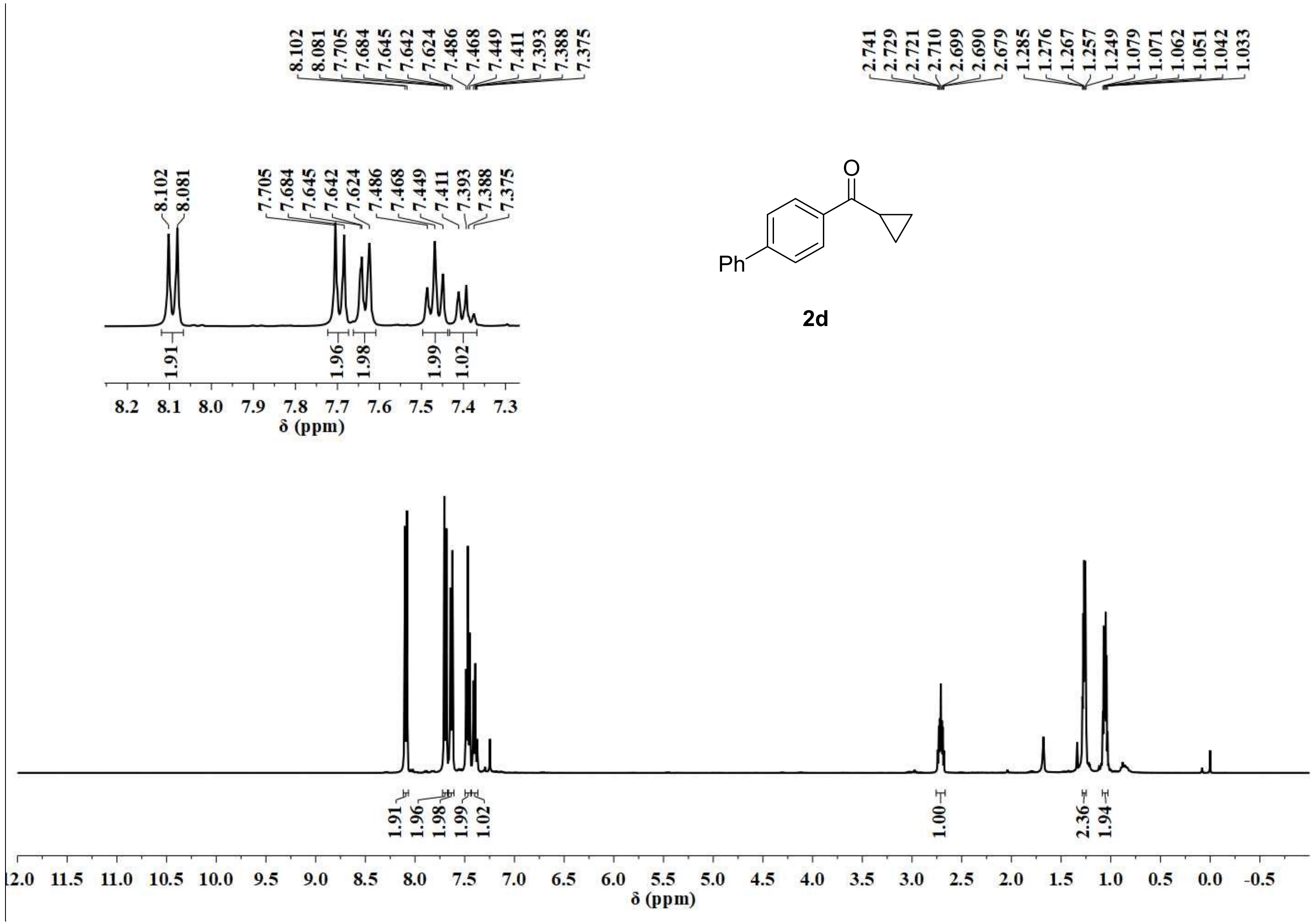
7.957
7.951
7.507
7.502
7.497
7.486
7.481
7.475
2.705
2.694
2.686
2.683
2.674
2.666
2.663
2.655
2.643
1.349
1.242
1.232
1.224
1.222
1.213
1.204
1.037
1.029
1.020
1.010
1.000
0.992
1.86
2.01
δ (ppm)
O
tBu
1.00
9.02
1.93
2.06

2c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7.388
7.375
2.741
2.729
2.721
2.710
2.699
2.690
2.679
1.285
1.276
1.267
1.257
1.249
1.079
1.071
1.062
1.051
1.042
1.033
Ph
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1.99
1.02
1.00
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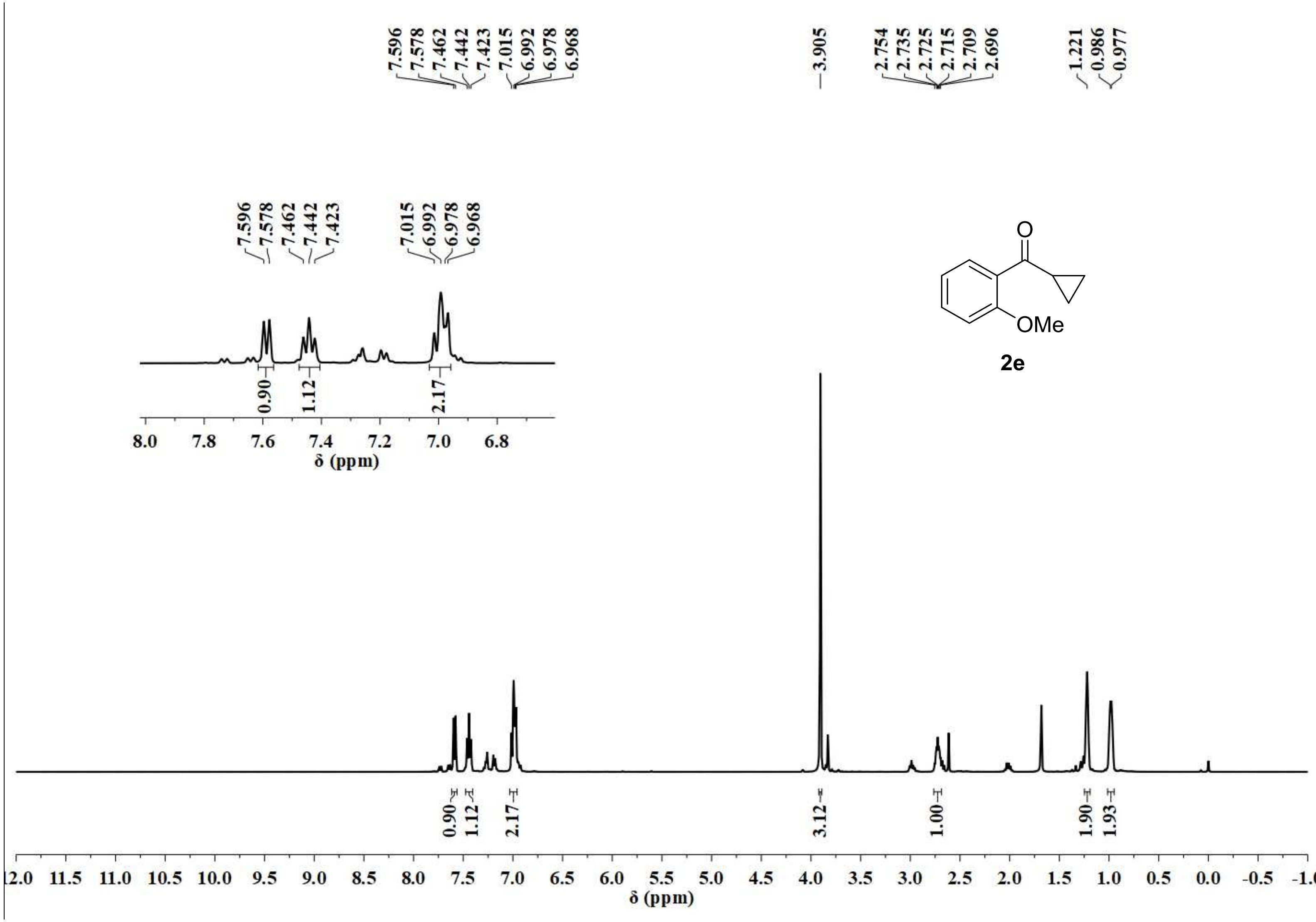
1.94
δ (ppm)

2d



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7.015
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6.978
6.968
3.905
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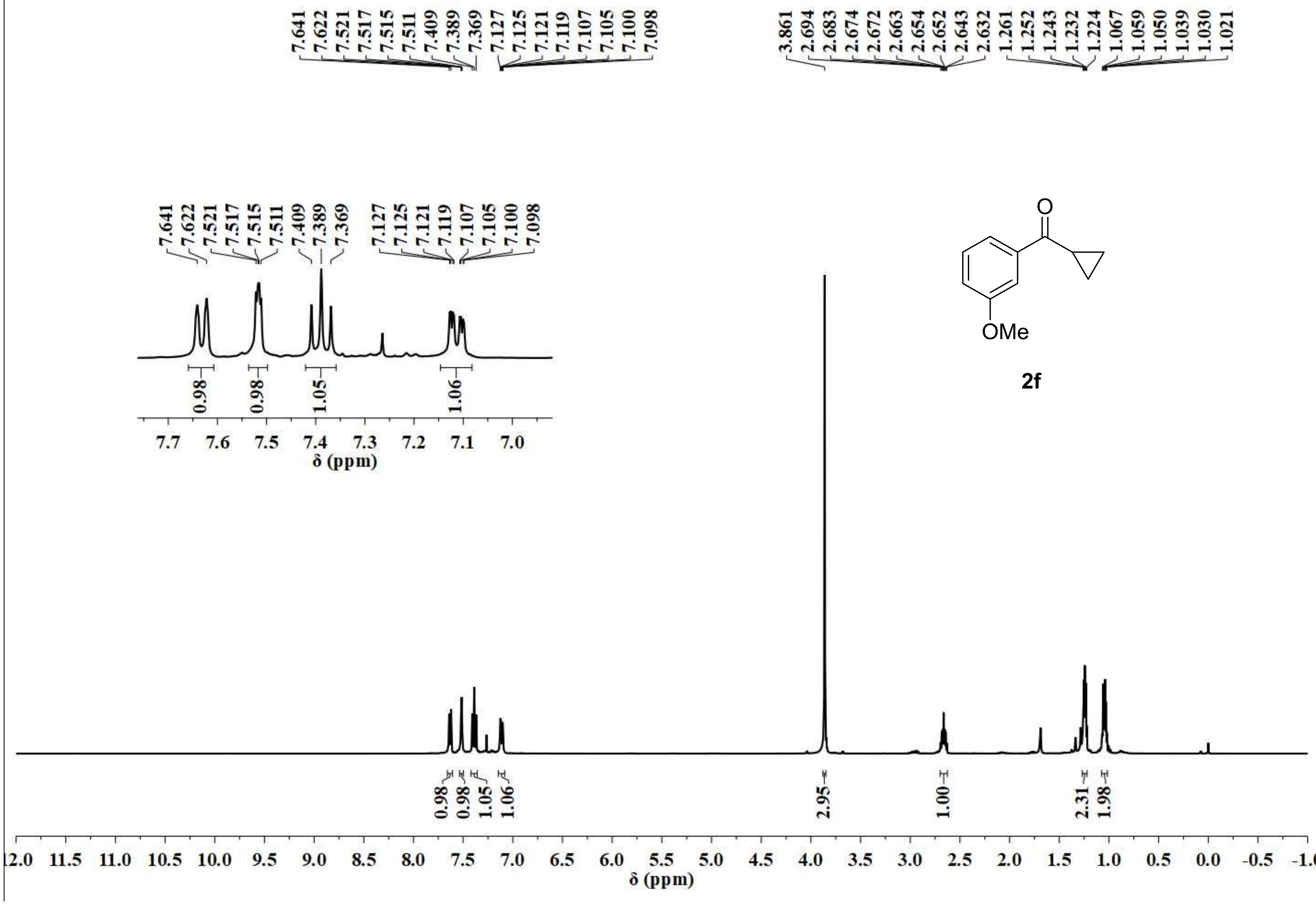
2.735
2.725
2.715
2.709
2.696
1.221
0.986
0.977
O
OMe
2e
0.90
1.12
2.17
8.0 7.8 7.6 7.4 7.2 7.0 6.8
δ (ppm)
3.12
1.00
1.90
1.93
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)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1.039
1.030
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0.98
0.98
1.05
1.06
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
δ (ppm)
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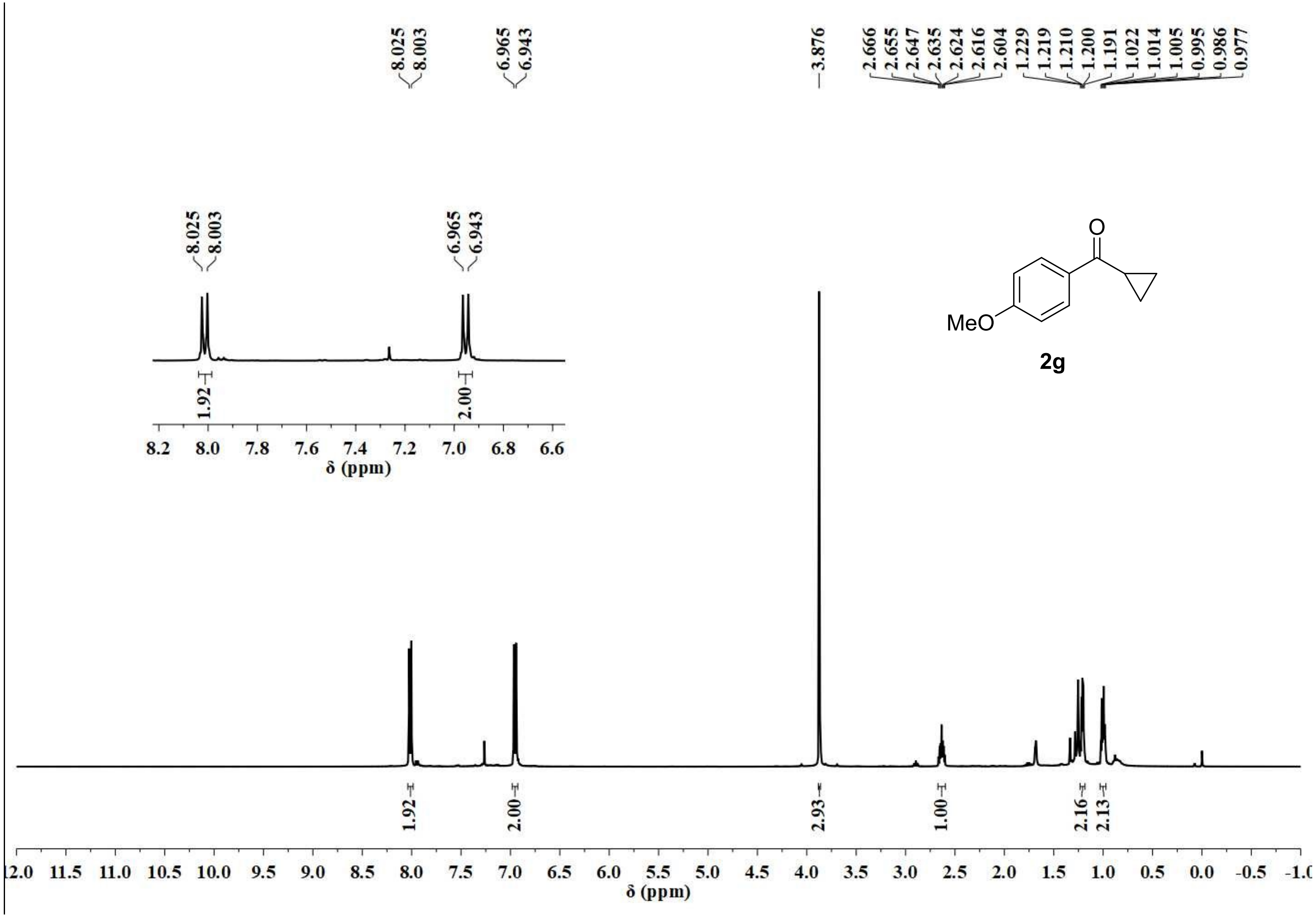
0.98
1.05
1.06
2.95
1.00
2.31
1.98
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)
O
OMe

2f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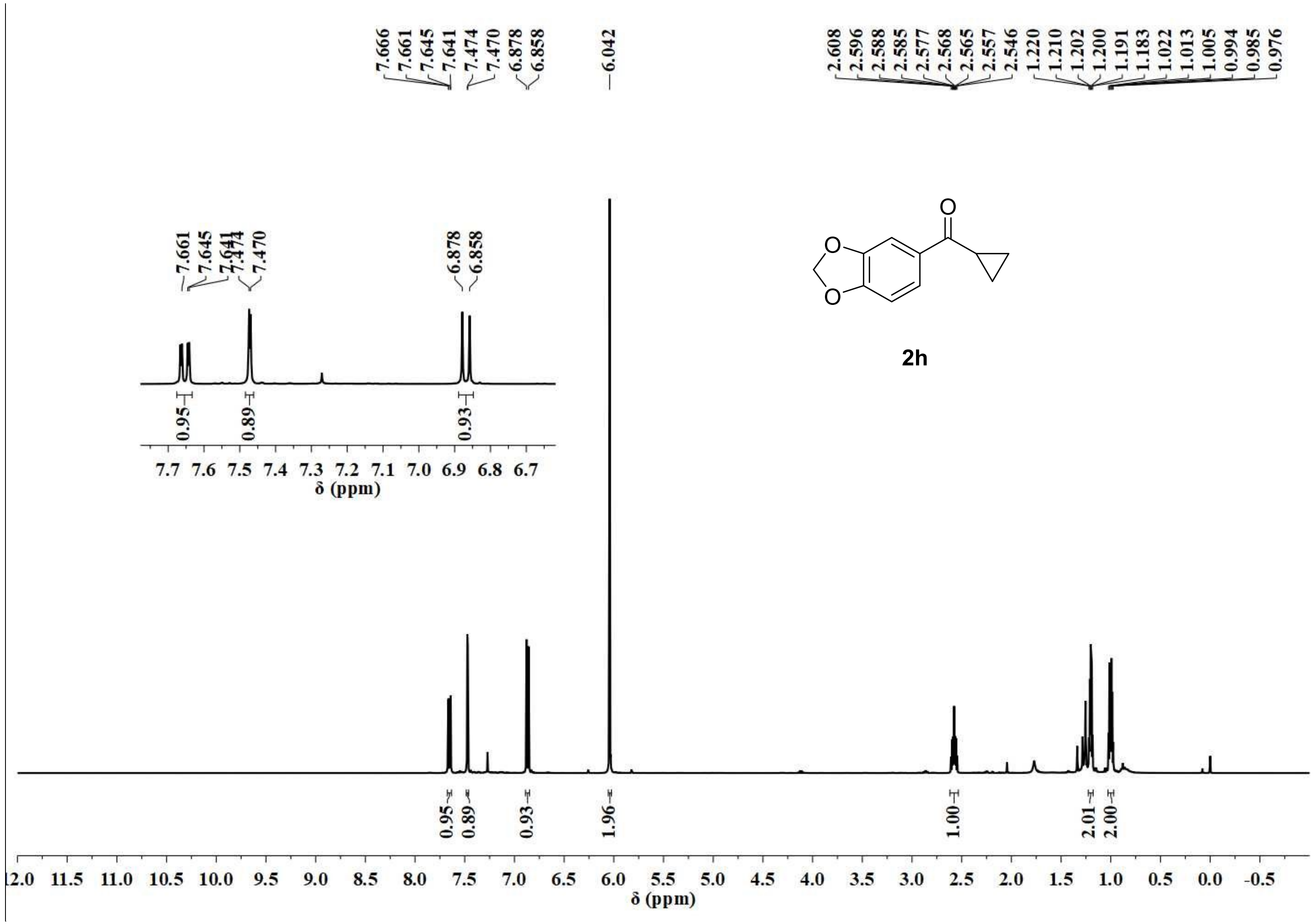
1.219
1.210
1.200
1.191
1.022
1.014
1.005
0.995
0.986
0.977
1.92
2.00
8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6
δ (ppm)
MeO
O
2g
1.92
2.00
2.93
1.00
2.16
2.13
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)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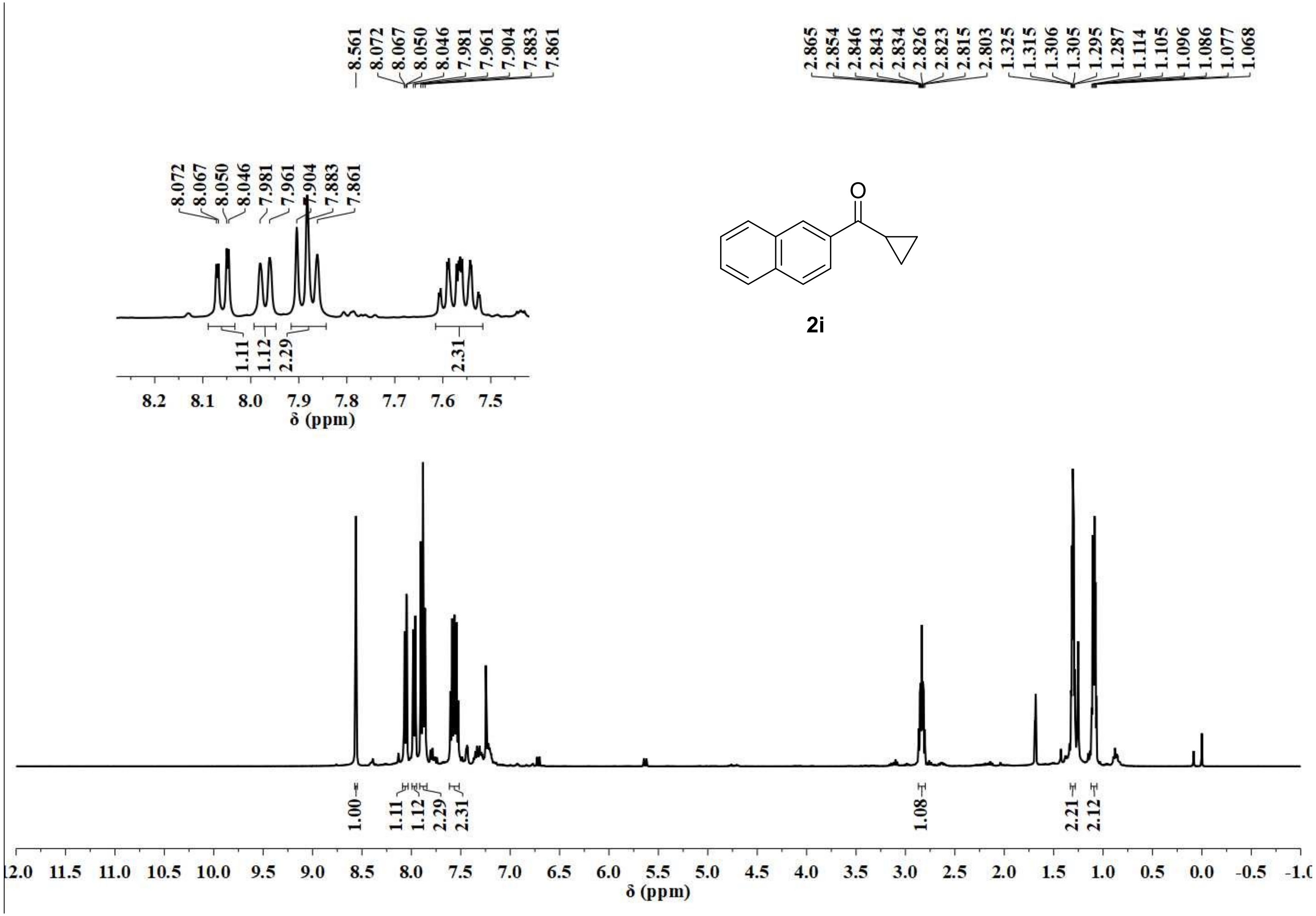
0.976
0.95
0.89
0.93
1.96
1.00
2.01
2.00
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0 6.9 6.8 6.7
δ (ppm)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)
O
O
O

2h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2.826
2.823
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2.803
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1.315
1.306
1.305
1.295
1.287
1.114
1.105
1.096
1.086
1.077
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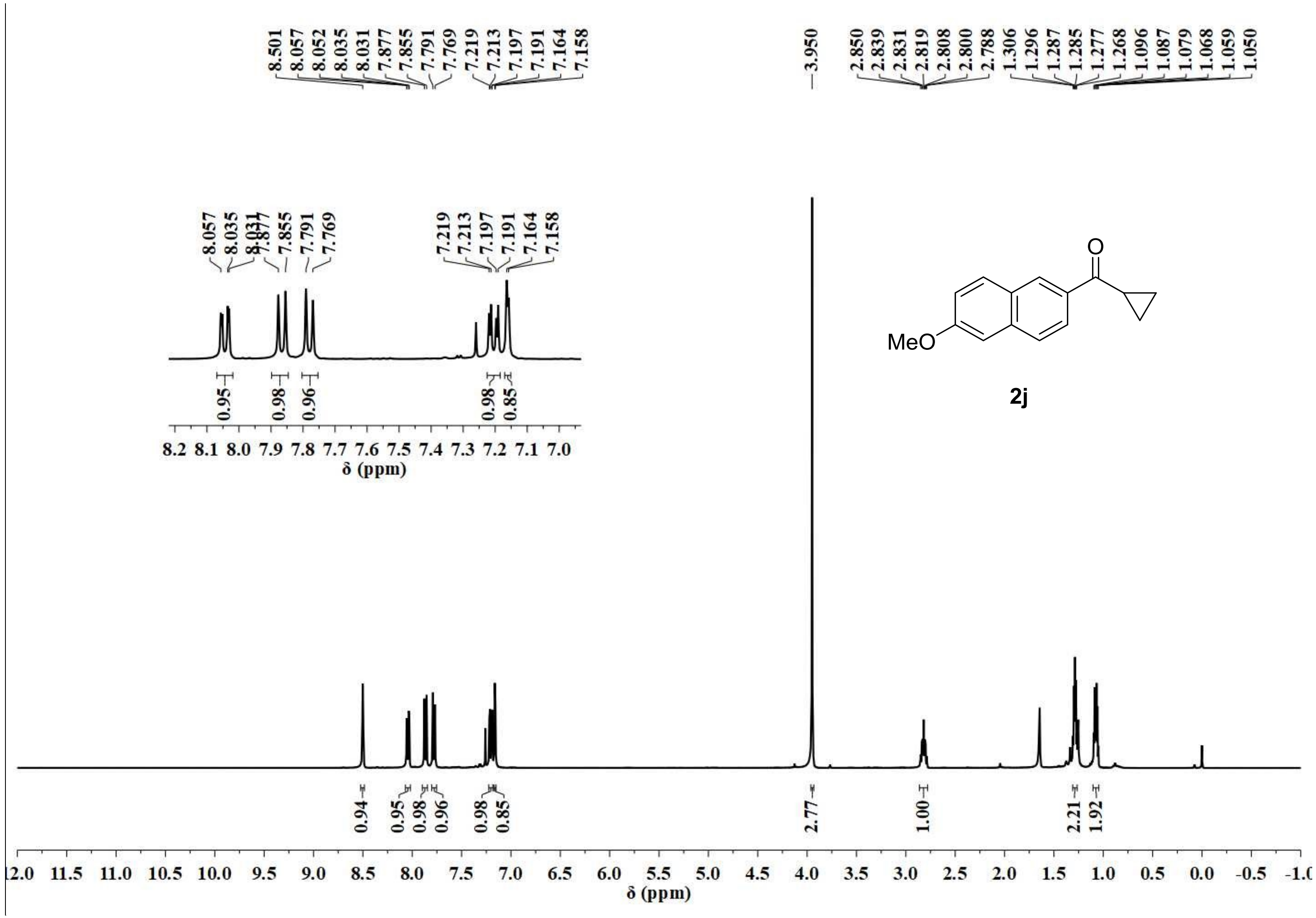
O
2i
1.00
1.11
1.12
2.29
2.31
1.08
2.21
2.12
δ (ppm)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7.158
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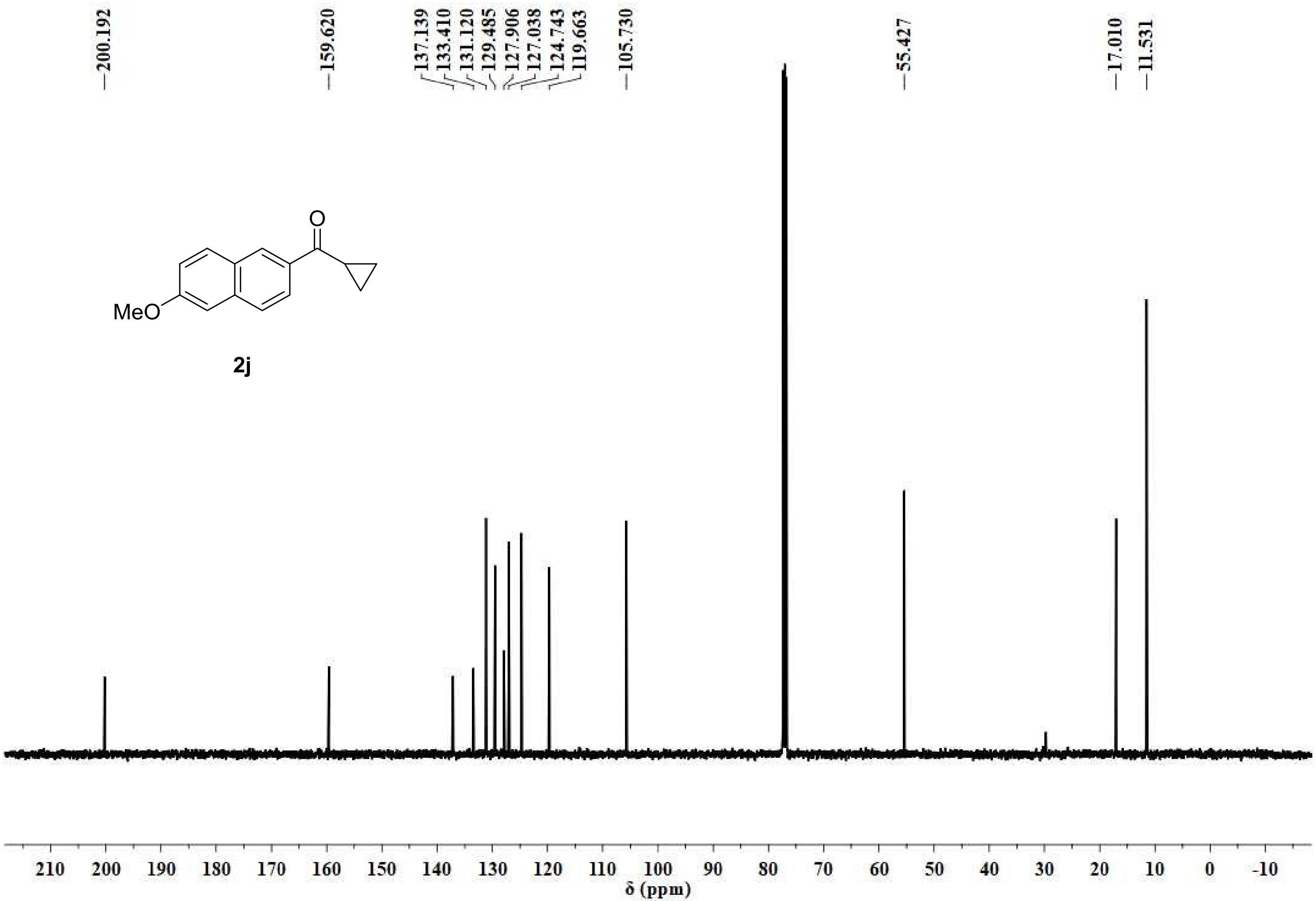
2.831
2.819
2.808
2.800
2.788
1.306
1.296
1.287
1.285
1.277
1.268
1.096
1.087
1.079
1.068
1.059
1.050
0.95
0.98
0.96
0.98
0.85
8.2 8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
δ (ppm)
MeO
O
0.94
0.95
0.98
0.96
0.98
0.85
2.77
1.00
2.21
1.92
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)

2j



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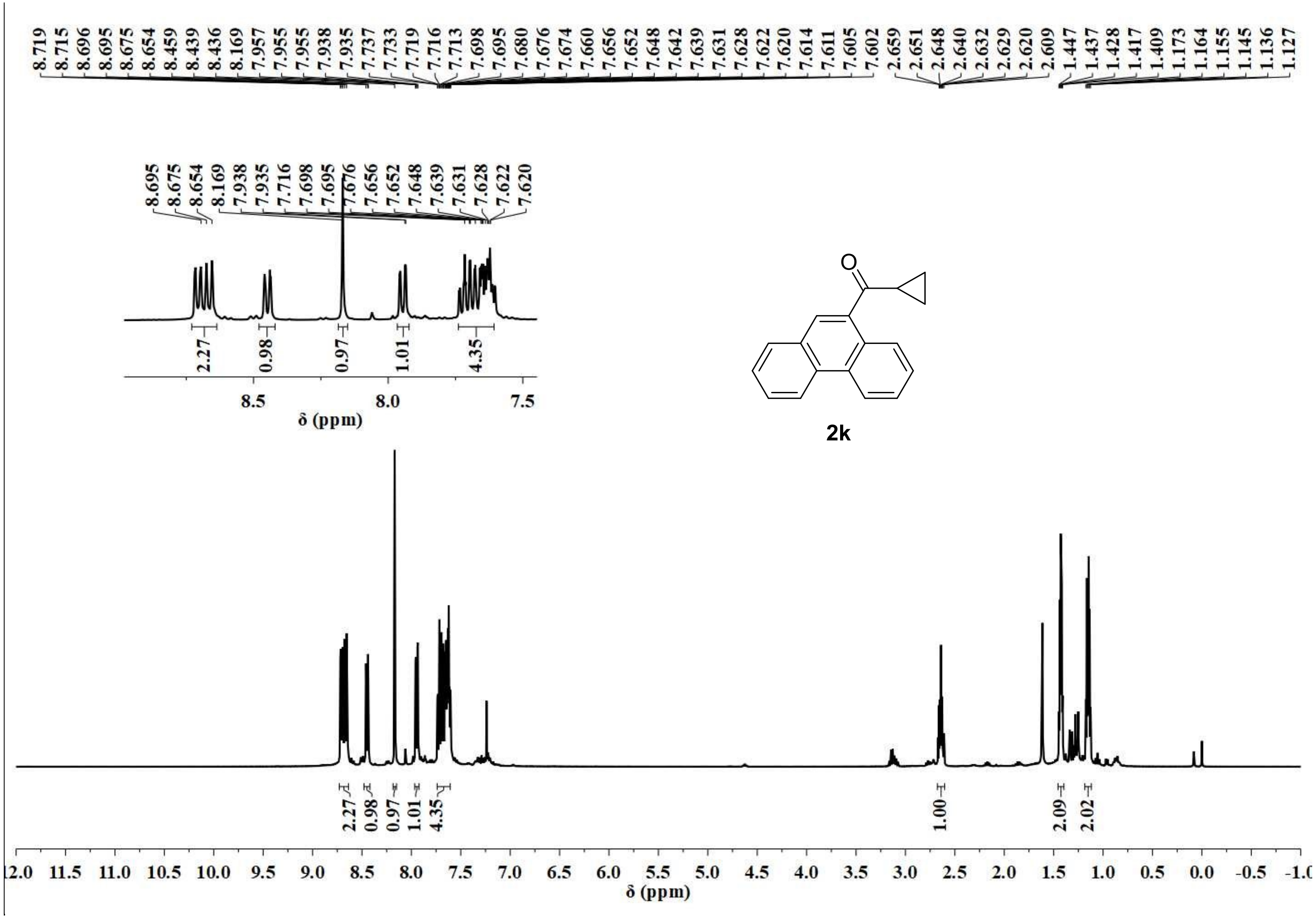
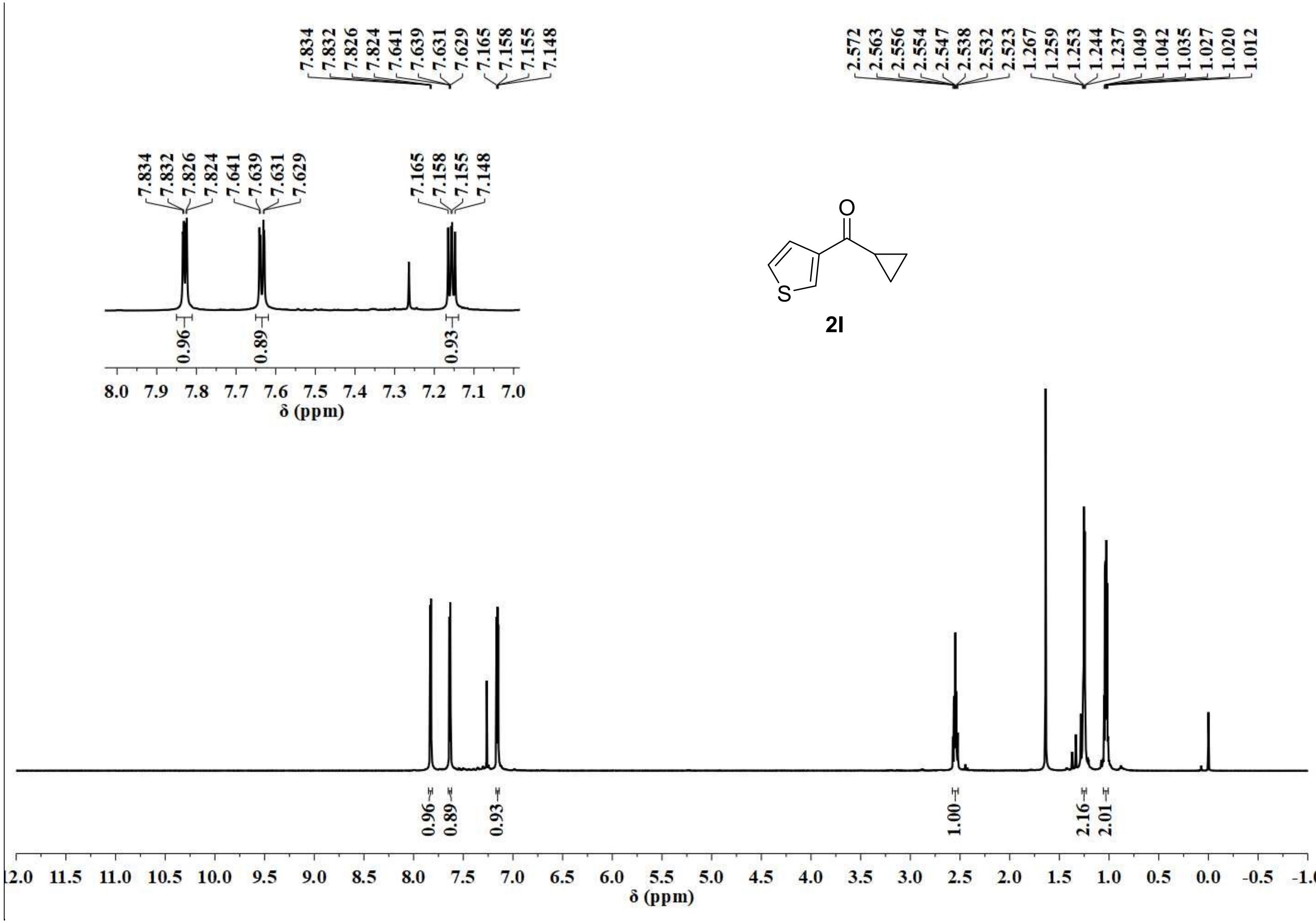
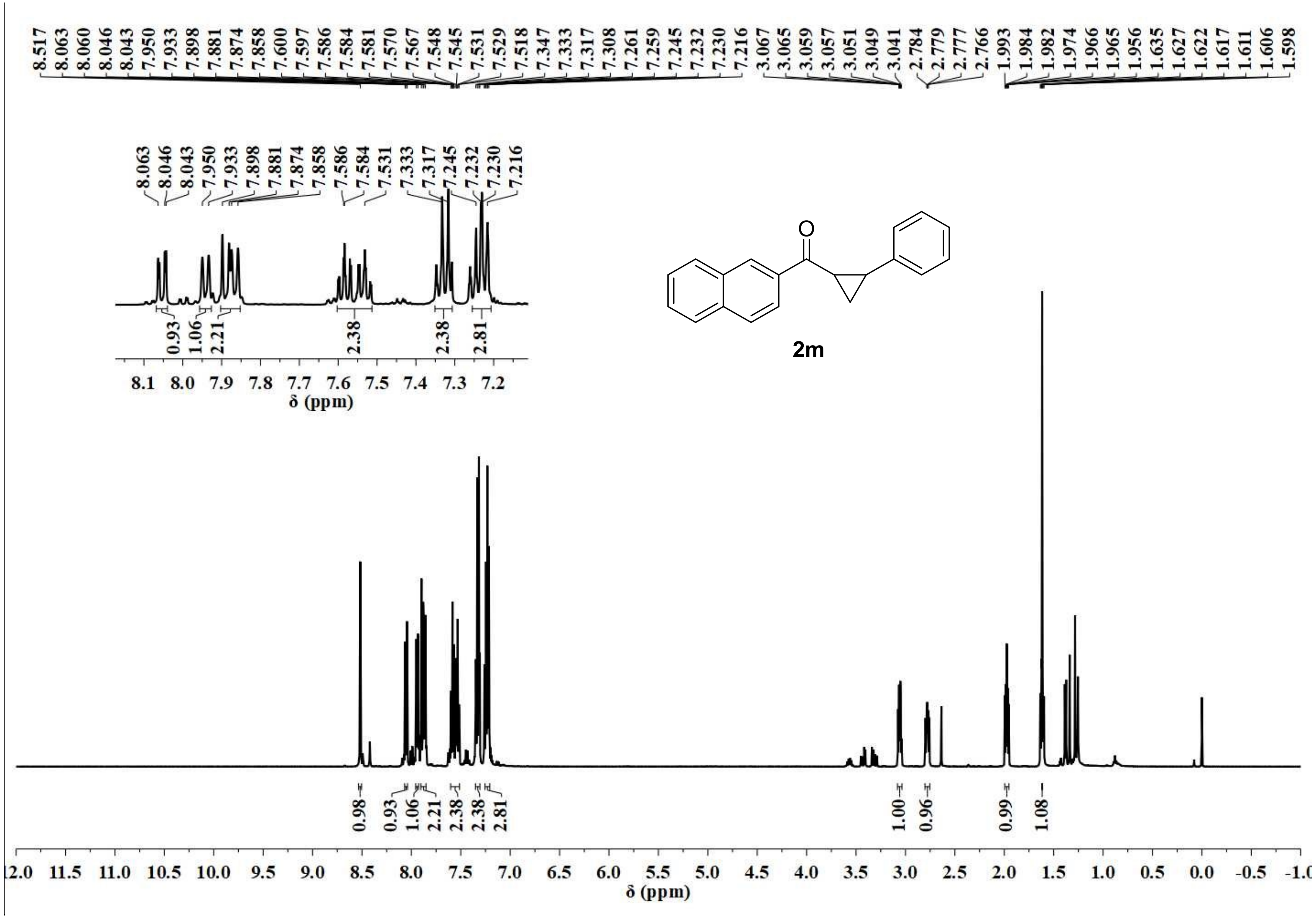
133.410
131.120
129.485
127.906
127.038
124.743
119.663
105.730
55.427
17.010
11.531
O
MeO
2j
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
δ (ppm)

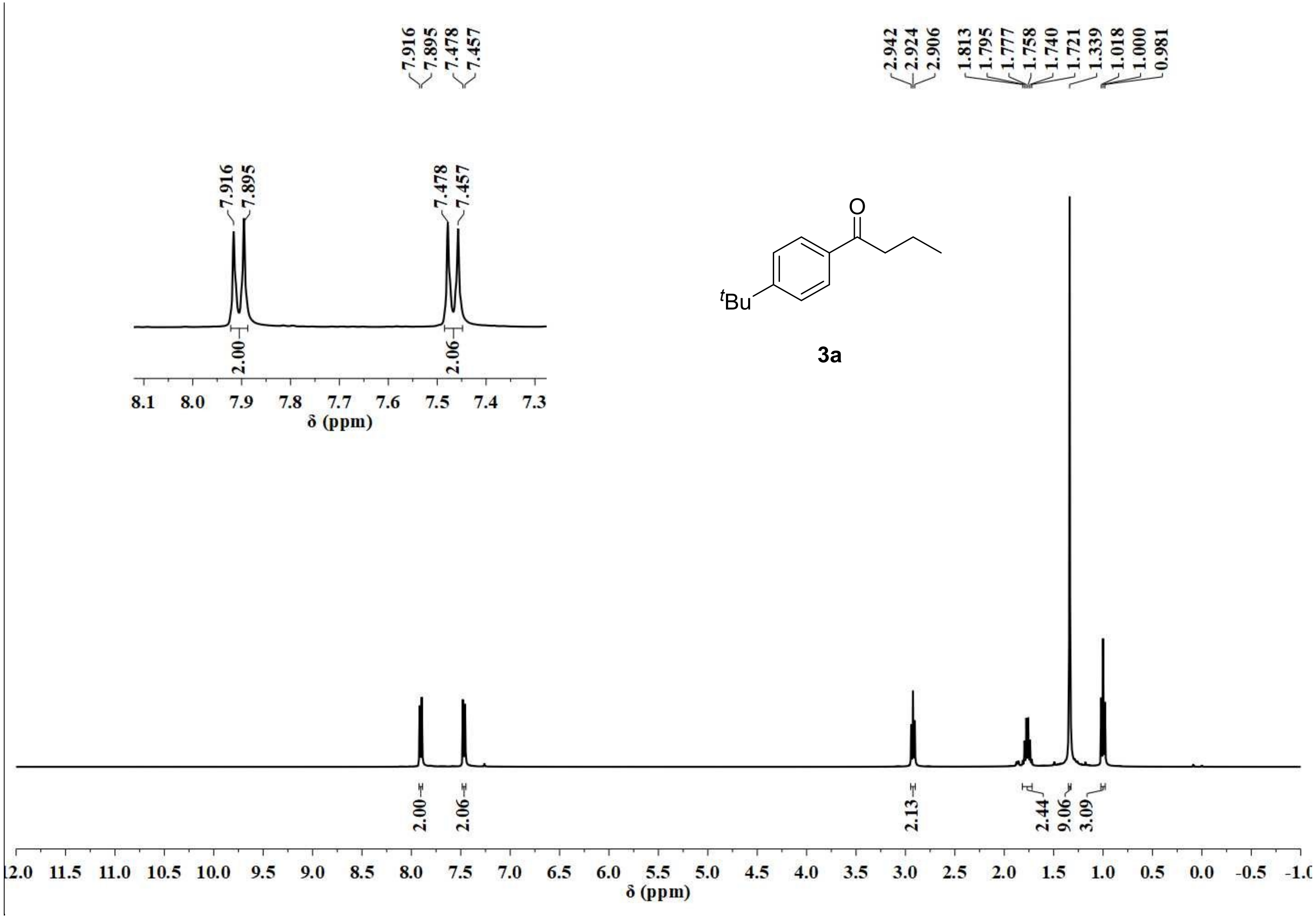

8.719 8.715 8.696 8.695 8.675 8.654 8.459 8.439 8.436 8.169 7.957 7.955 7.955 7.938 7.935 7.737 7.733 7.719 7.716 7.713 7.698 7.695 7.680 7.676 7.674 7.660 7.656 7.652 7.648 7.642 7.639 7.631 7.628 7.622 7.620 7.614 7.611 7.605 7.602 2.659 2.651 2.648 2.640 2.632 2.629 2.620 2.609 1.447 1.437 1.428 1.417 1.409 1.173 1.164 1.155 1.145 1.136 1.127
8.695 8.675 8.654 8.169 7.938 7.935 7.716 7.698 7.695 7.676 7.656 7.652 7.648 7.639 7.631 7.628 7.622 7.620
2.27 0.98 0.97 1.01 4.35
8.5 8.0 7.5
δ (ppm)
O
2.27 0.98 0.97 1.01 4.35 1.00 2.09 2.02
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)

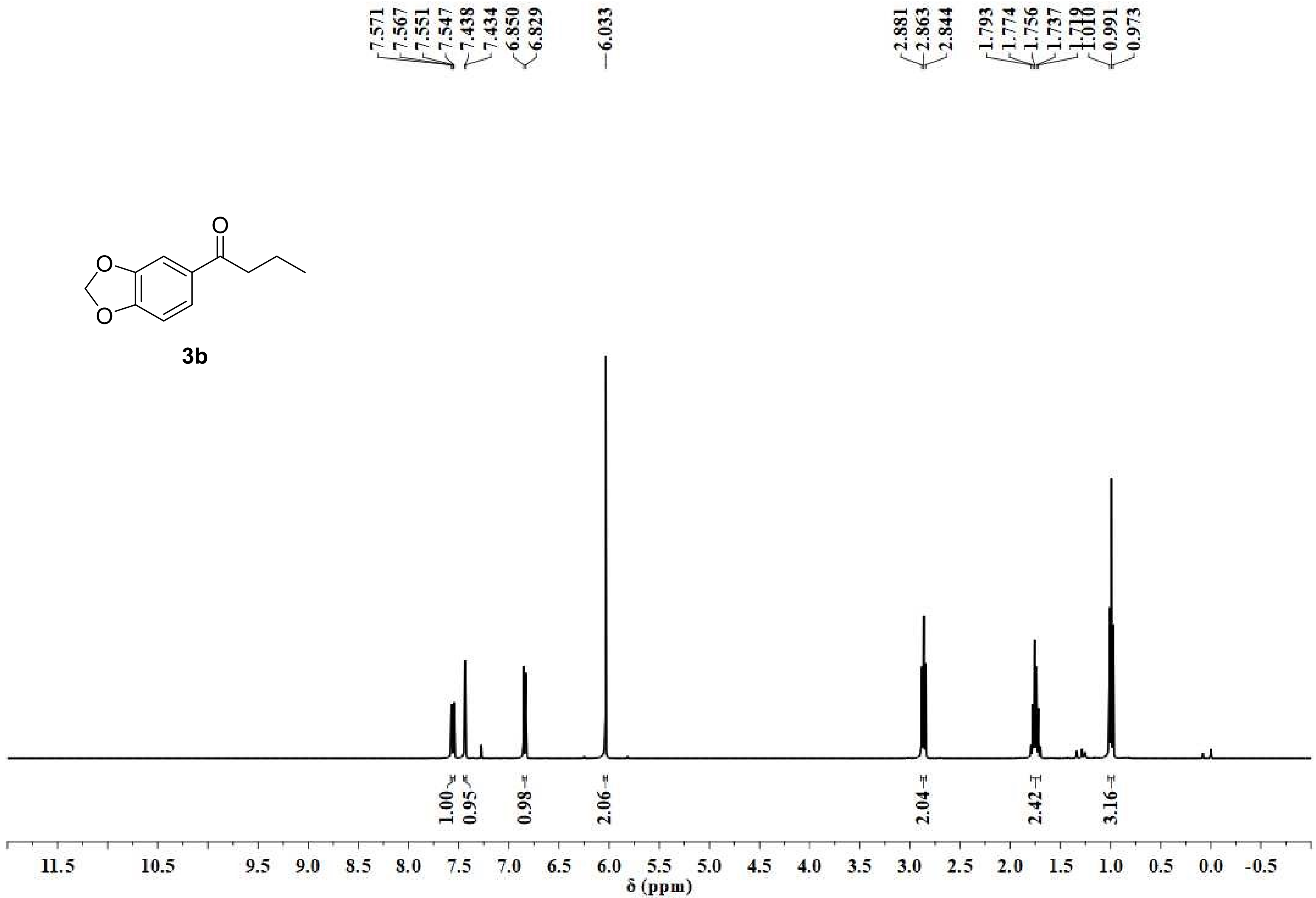
2k

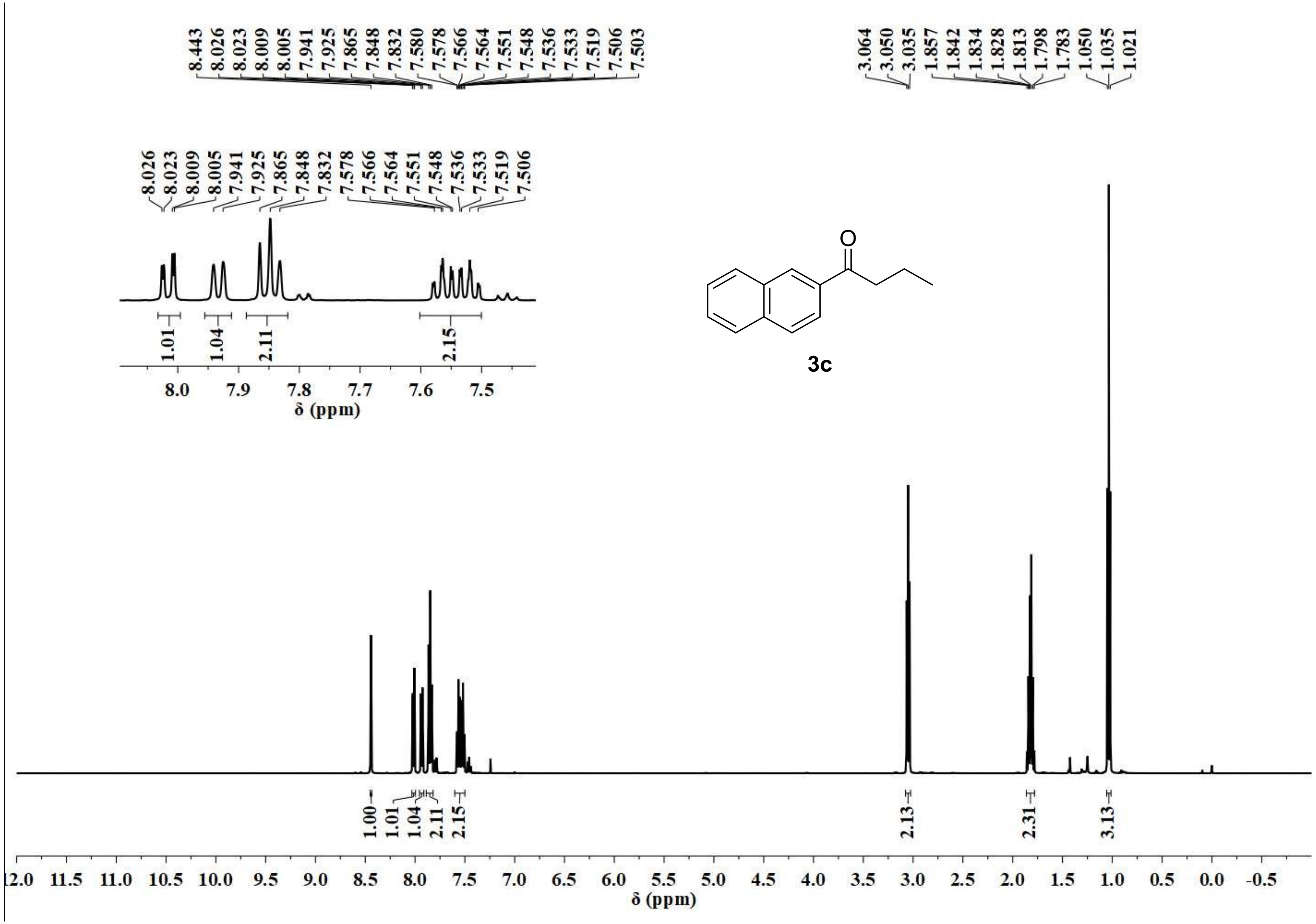

7.834
7.832
7.826
7.824
7.641
7.639
7.631
7.629
7.165
7.158
7.155
7.148
2.572
2.563
2.556
2.554
2.547
2.538
2.532
2.523
1.267
1.259
1.253
1.244
1.237
1.049
1.042
1.035
1.027
1.020
1.012
0.96
0.89
0.93
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
δ (ppm)
O
S
2l
0.96
0.89
0.93
1.00
2.16
2.01
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)

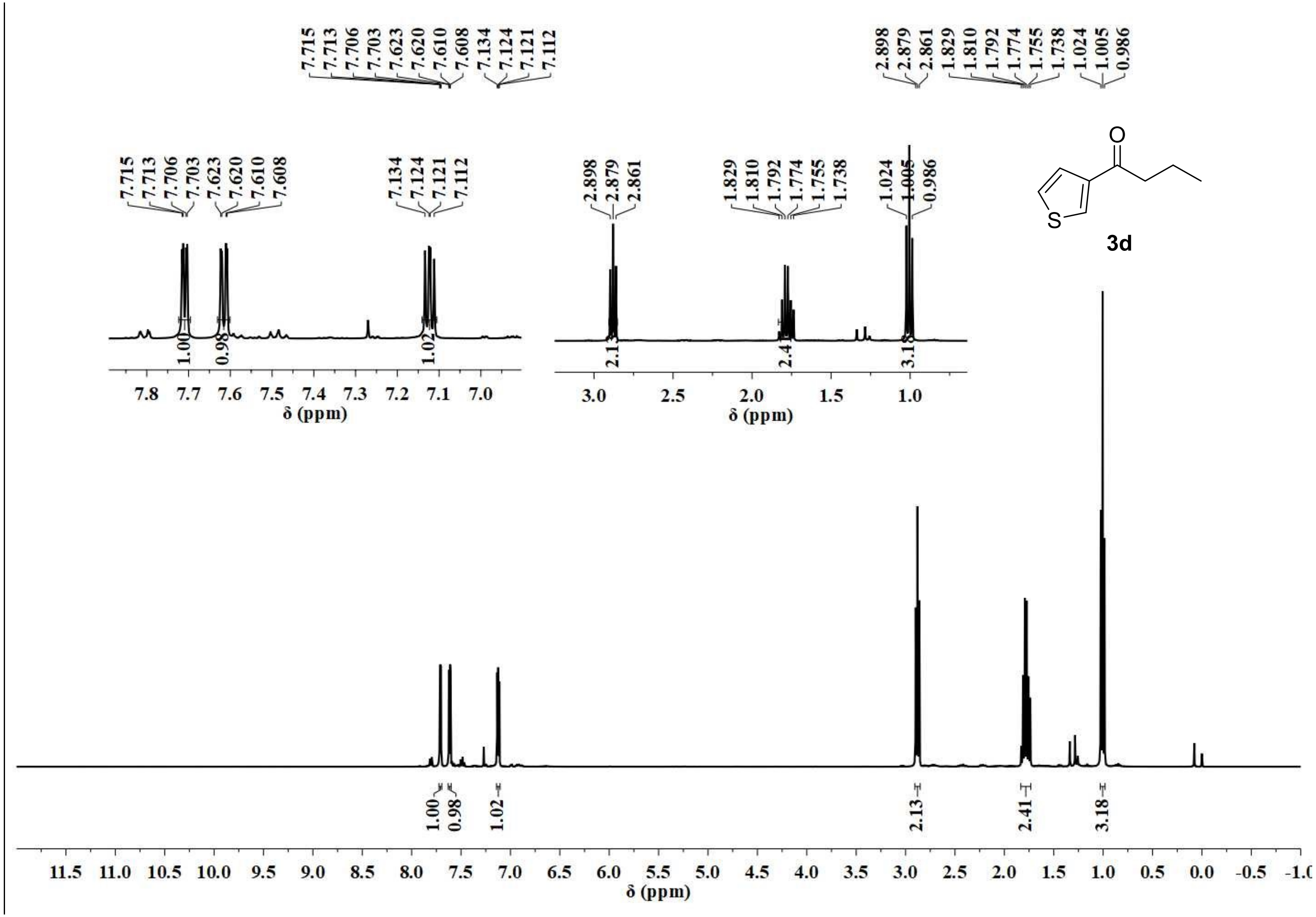


2m

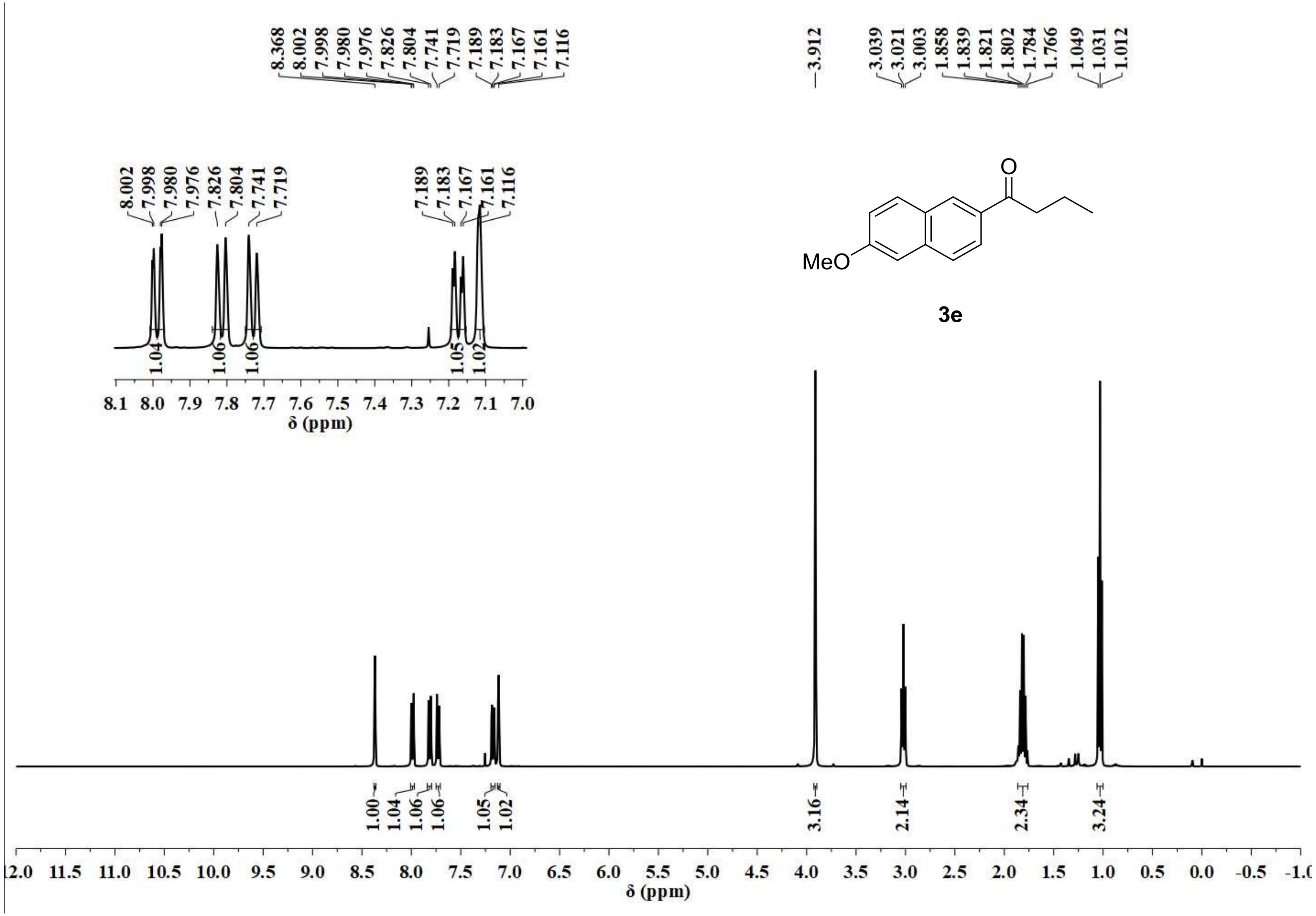

7.916
7.895
7.478
7.457
2.942
2.924
2.906
1.813
1.795
1.777
1.758
1.740
1.721
1.339
1.018
1.000
0.981
O
tBu
3a
2.00
2.06
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3
δ (ppm)
2.00
2.06
2.13
2.44
9.06
3.09
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)

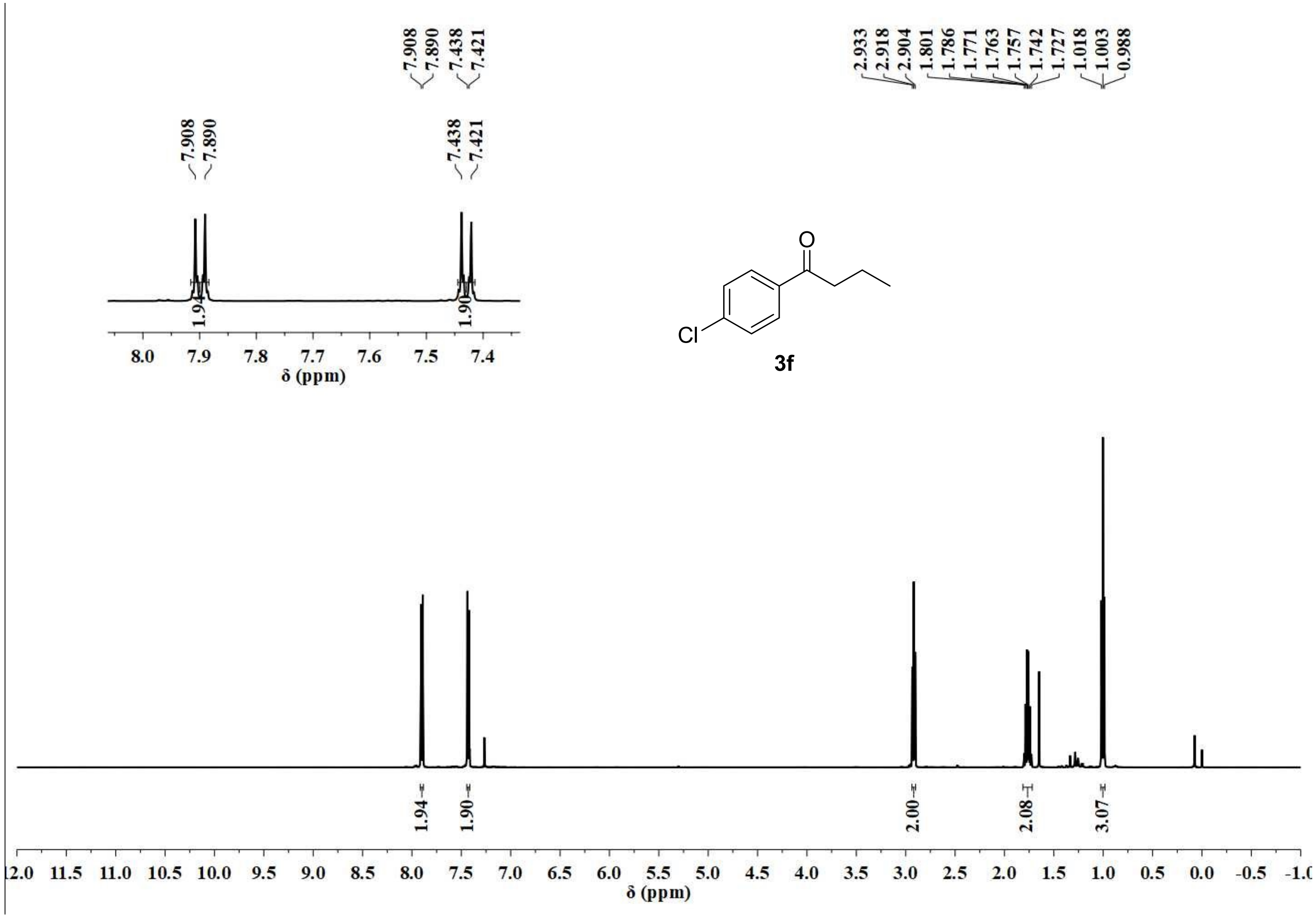

7.571
7.567
7.551
7.547
7.438
7.434
6.850
6.829
6.033
2.881
2.863
2.844
1.793
1.774
1.756
1.737
1.719
1.010
0.991
0.973
O
O
O
3b
1.00
0.95
0.98
2.06
2.04
2.42
3.16
11.5 10.5 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
δ (ppm)


8.443
8.026
8.023
8.009
8.005
7.941
7.925
7.865
7.848
7.832
7.580
7.578
7.566
7.564
7.551
7.548
7.536
7.533
7.519
7.506
7.503
3.064
3.050
3.035
1.857
1.842
1.834
1.828
1.813
1.798
1.783
1.050
1.035
1.021
O
3c
1.00
1.01
1.04
2.11
2.15
2.13
2.31
3.13
δ (ppm)


7.715
7.713
7.706
7.703
7.623
7.620
7.610
7.608
7.134
7.124
7.121
7.112
2.898
2.879
2.861
1.829
1.810
1.792
1.774
1.755
1.738
1.024
1.005
0.986
O
S
1.00
0.98
1.02
2.13
2.41
3.18
δ (ppm)

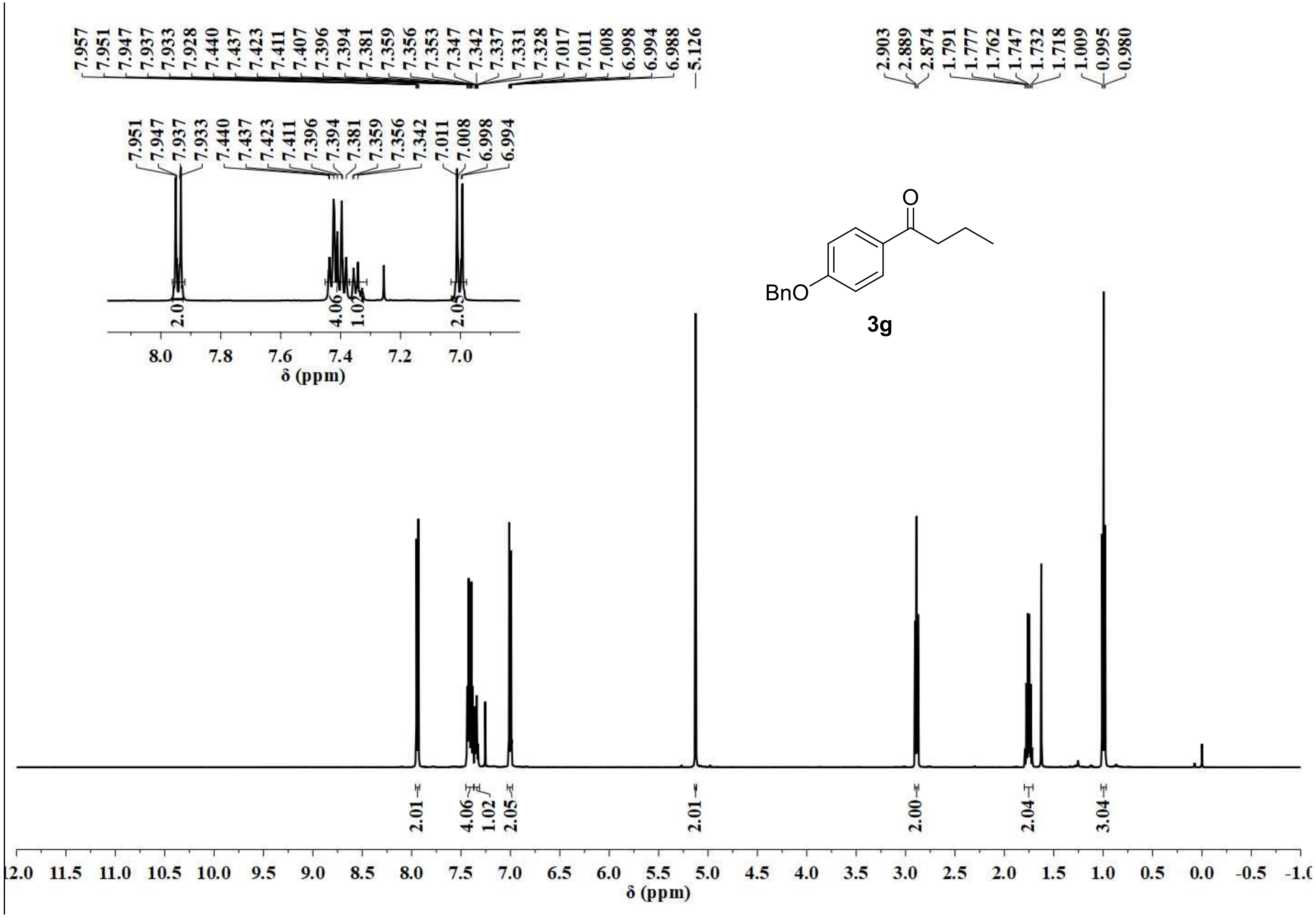
3d

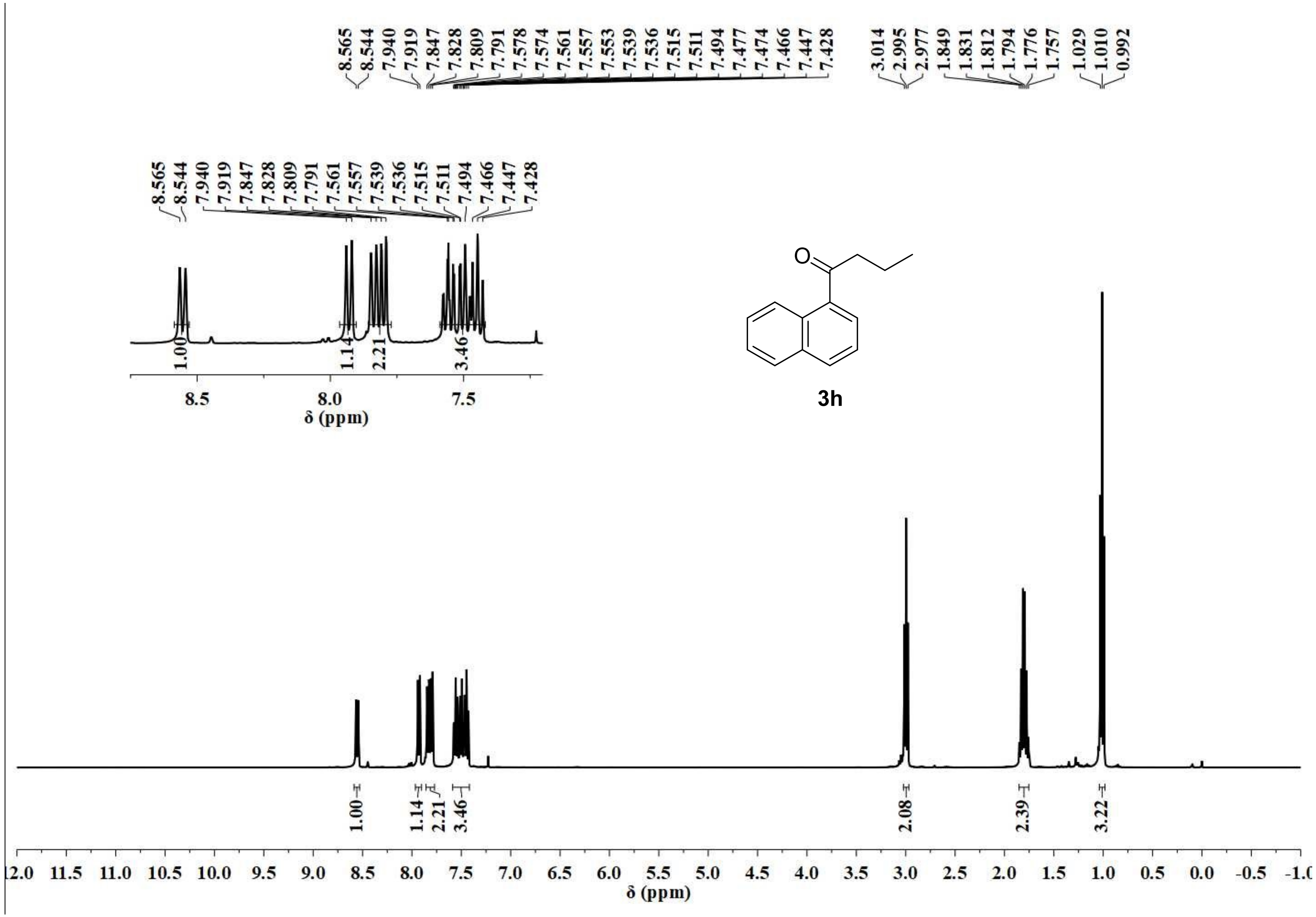

8.368
8.002
7.998
7.980
7.976
7.826
7.804
7.741
7.719
7.189
7.183
7.167
7.161
7.116
3.912
3.039
3.021
3.003
1.858
1.839
1.821
1.802
1.784
1.766
1.049
1.031
1.012
MeO
O
3e
1.00
1.04
1.06
1.06
1.05
1.02
3.16
2.14
2.34
3.24
δ (ppm)

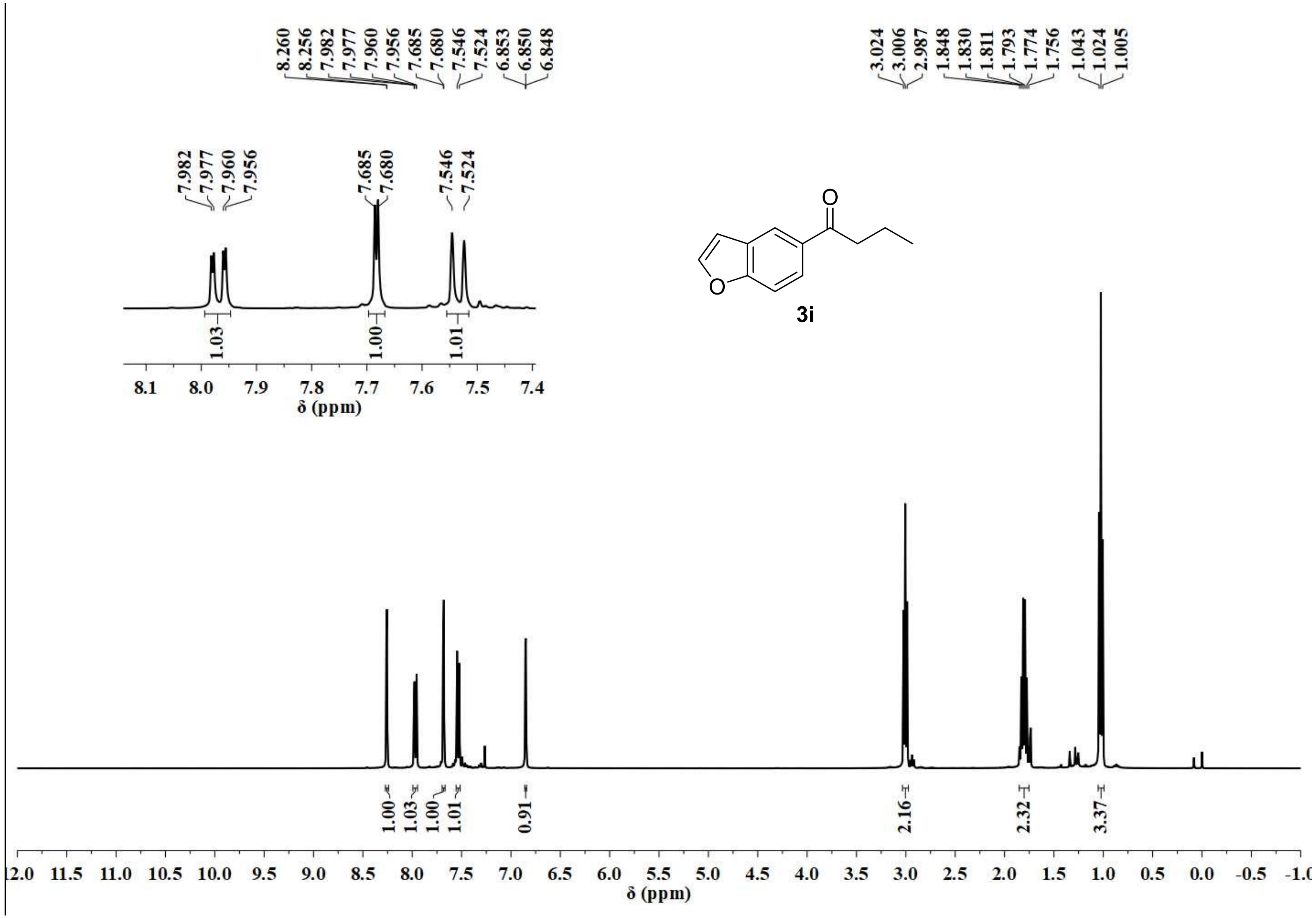


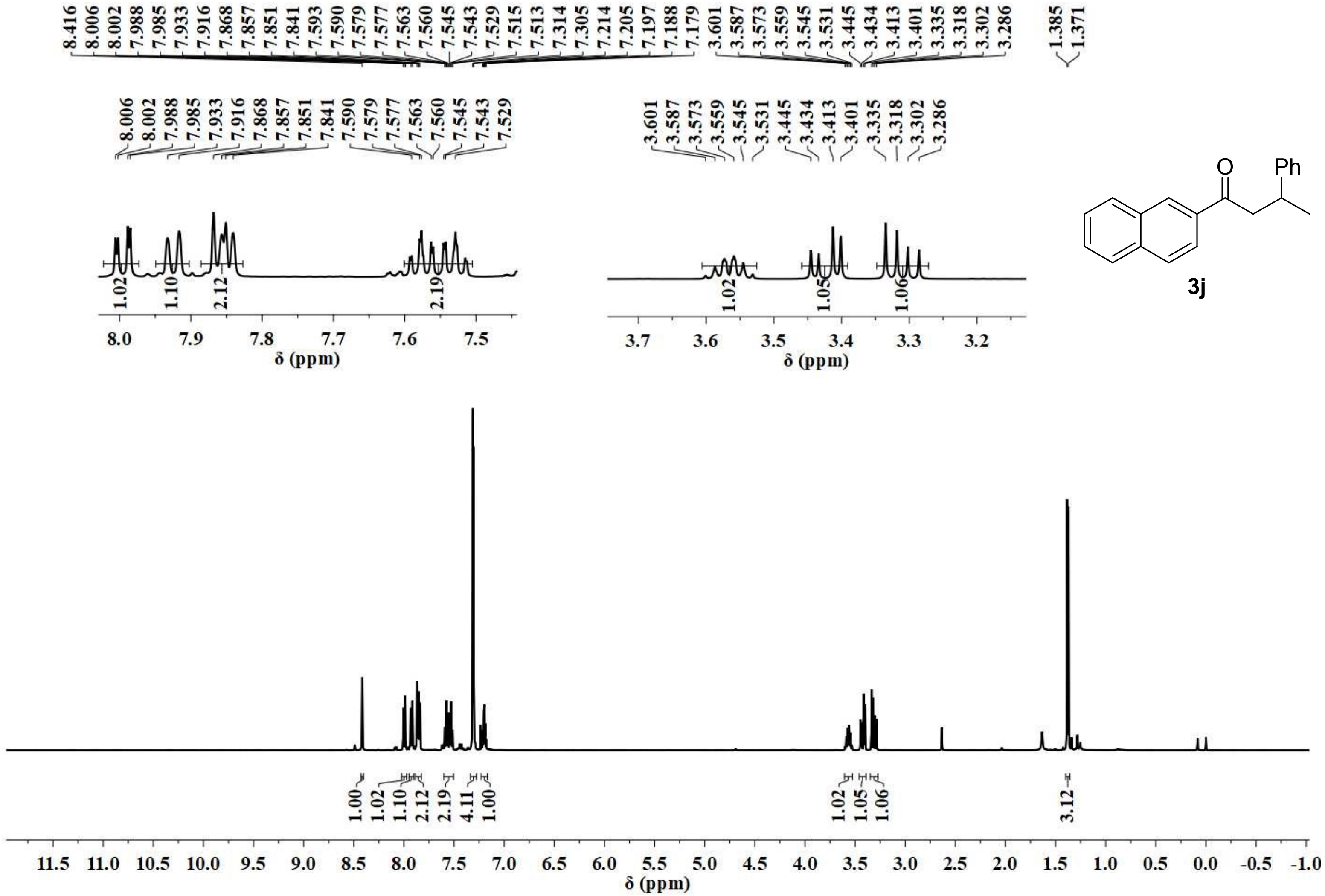
7.908
7.890
7.438
7.421
2.933
2.918
2.904
1.801
1.786
1.771
1.763
1.757
1.742
1.727
1.018
1.003
0.988
1.94
1.90
8.0 7.9 7.8 7.7 7.6 7.5 7.4
δ (ppm)
O
Cl
1.94
1.90
2.00
2.08
3.07
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)

3f


7.957 7.951 7.947 7.937 7.933 7.928 7.440 7.437 7.423 7.411 7.407 7.396 7.394 7.381 7.359 7.356 7.353 7.347 7.342 7.337 7.331 7.328 7.017 7.011 7.008 6.998 6.994 6.988
5.126
2.903 2.889 2.874 1.791 1.777 1.762 1.747 1.732 1.718 1.009 0.995 0.980
7.951 7.947 7.937 7.933 7.440 7.437 7.423 7.411 7.396 7.394 7.381 7.359 7.356 7.342 7.011 7.008 6.998 6.994
2.0
4.06
1.02
2.05
8.0 7.8 7.6 7.4 7.2 7.0
δ (ppm)
O
BnO
3g
2.01 4.06 1.02 2.05 2.01 2.00 2.04 3.04
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)


8.565 8.544 7.940 7.919 7.847 7.828 7.809 7.791 7.578 7.574 7.561 7.557 7.553 7.539 7.536 7.515 7.511 7.494 7.477 7.474 7.466 7.447 7.428
3.014 2.995 2.977 1.849 1.831 1.812 1.794 1.776 1.757 1.029 1.010 0.992
8.565 8.544 7.940 7.919 7.847 7.828 7.809 7.791 7.561 7.557 7.539 7.536 7.515 7.511 7.494 7.466 7.447 7.428
1.00 1.14 2.21 3.46
8.5 8.0 7.5
δ (ppm)
O
3h
1.00 1.14 2.21 3.46 2.08 2.39 3.22
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)


8.260
8.256
7.982
7.977
7.960
7.956
7.685
7.680
7.546
7.524
6.853
6.850
6.848
3.024
3.006
2.987
1.848
1.830
1.811
1.793
1.774
1.756
1.043
1.024
1.005
7.982
7.977
7.960
7.956
7.685
7.680
7.546
7.524
1.03
1.00
1.01
8.1 8.0 7.9 7.8 7.7 7.6 7.5 7.4
δ (ppm)
O
O
3i
1.00
1.03
1.00
1.01
0.91
2.16
2.32
3.37
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
δ (ppm)


8.416 8.006 8.002 7.988 7.985 7.933 7.916 7.868 7.857 7.851 7.841 7.593 7.590 7.579 7.577 7.563 7.560 7.545 7.543 7.529 7.515 7.513 7.314 7.305 7.214 7.205 7.197 7.188 7.179 3.601 3.587 3.573 3.559 3.545 3.531 3.445 3.434 3.413 3.401 3.335 3.318 3.302 3.286 1.385 1.371
O
Ph
3j
1.02
1.10
2.12
2.19
δ (ppm)
1.05
1.06
1.00
4.11
3.12