Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Analysis of Polyarylene Ether Anion Exchange Membrane Degradation Mechanism for Alkaline Fuel Cell and Water-Splitting Cell Application

Shoji Miyanishi,[†,‡] Takeo Yamaguchi*[,†,‡]

[†]Laboratory for Chemistry and Life Science Institute of Innovative Research Tokyo Institute of Technology, R1-17, 4259, Nagatsuta-tyo, Midori-ku, Yokohama, Kanagawa, 226-8503, Japan

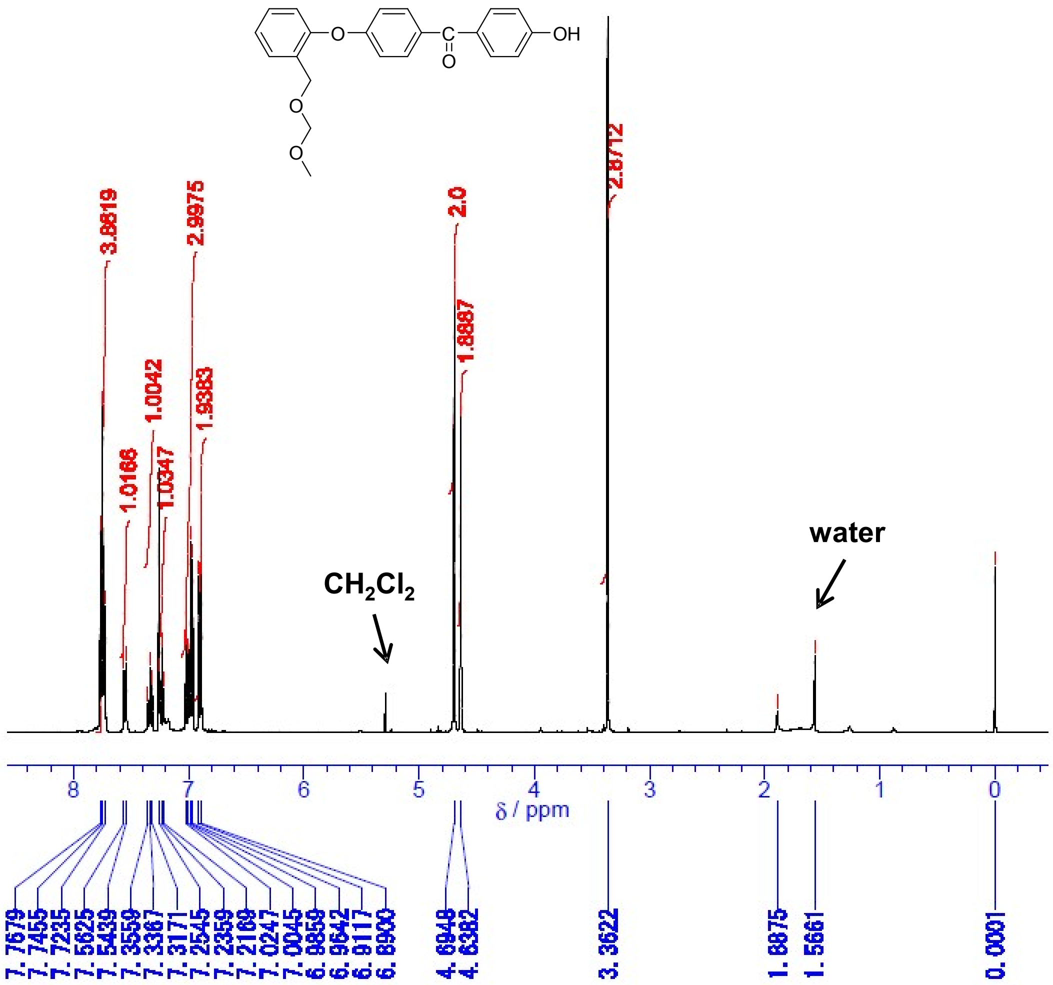
[‡]Core Research for Evolutionary Science and Technology, Japan Science and Technology Agency (JST-CREST)

Corresponding author: yamag@res.titech.ac.jp

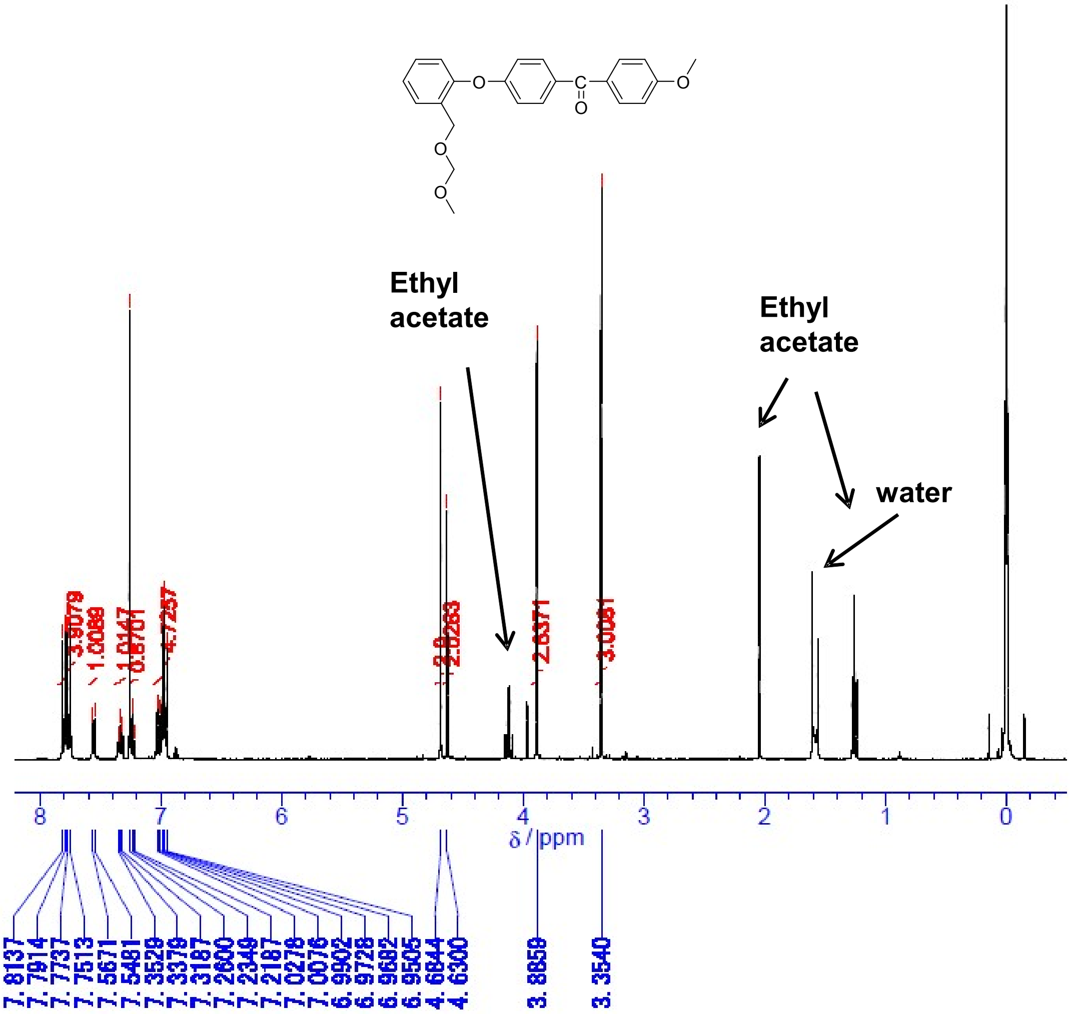
Contents

Figure S1. ^{1}H-NMR spectra of synthetic intermediates of **M2** and **M3**.

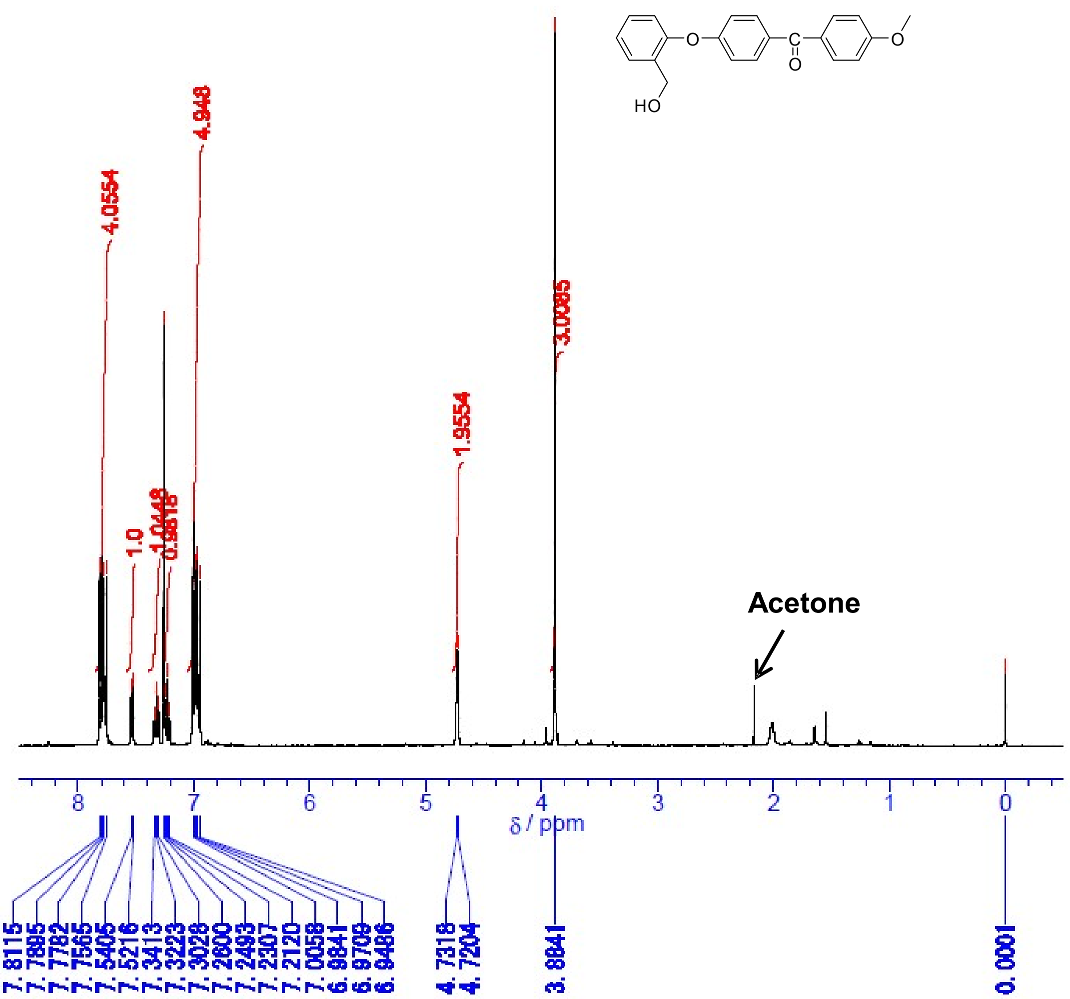
(a) **2**



(b) **3**

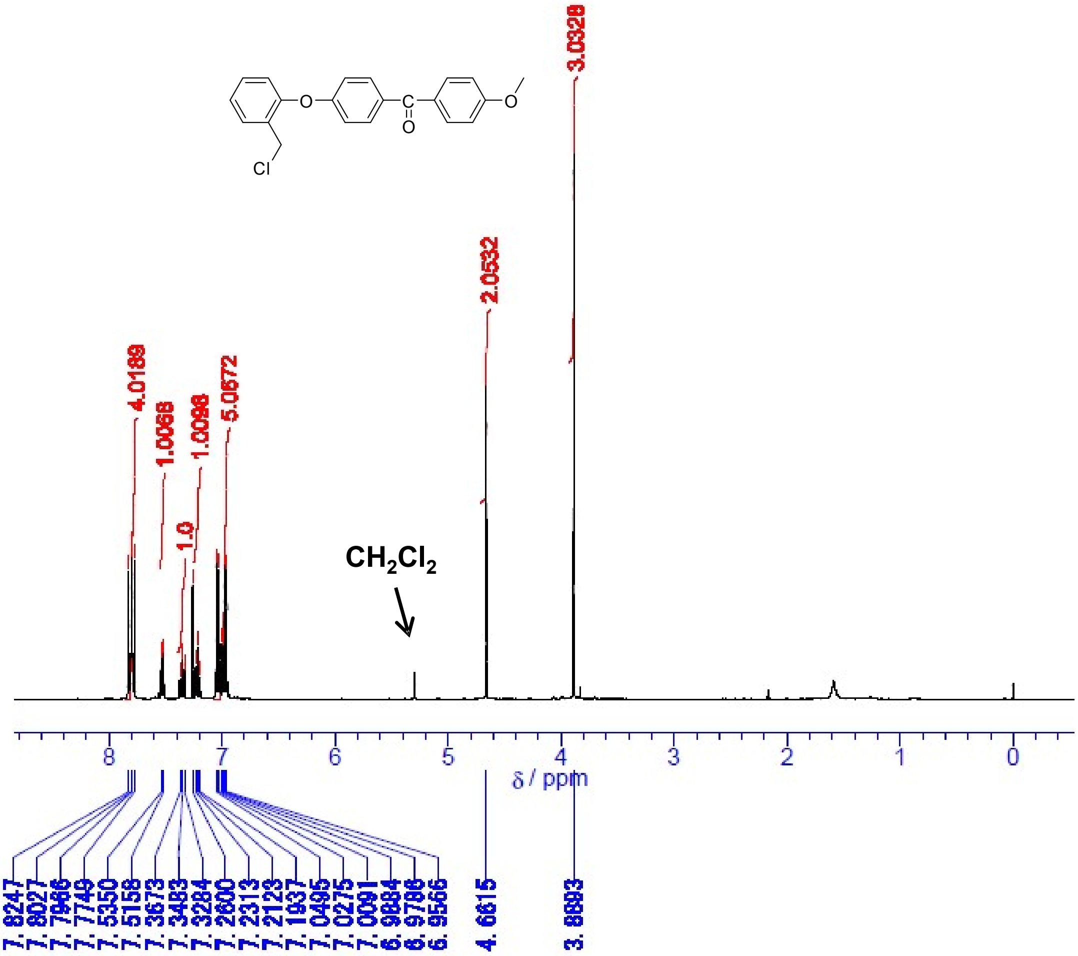


(c) **4**



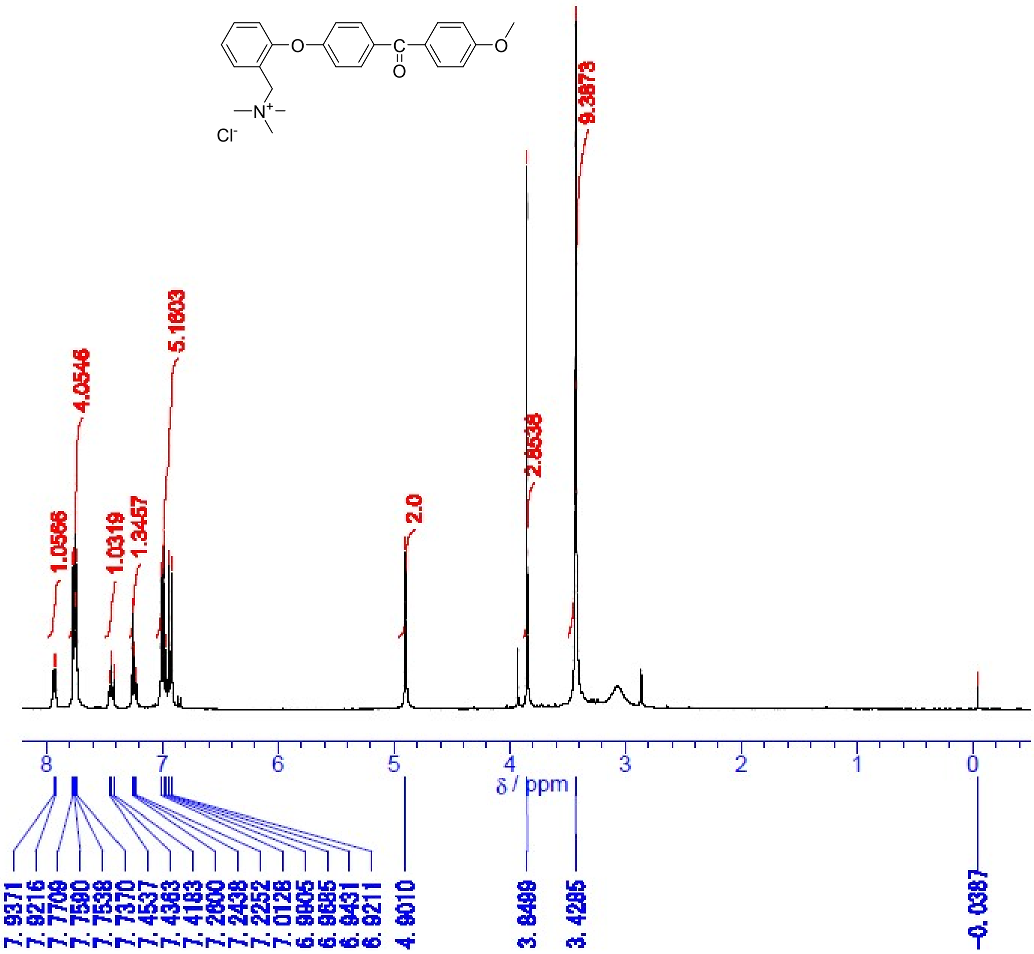
HO
O
C
O
O
Acetone
4.0554
4.948
1.0
1.0448
0.9818
1.9554
3.0085
8
7
6
5
4
3
2
1
0
δ / ppm
7.8115
7.7895
7.7782
7.7565
7.5405
7.5216
7.3413
7.3223
7.3028
7.2600
7.2493
7.2307
7.2120
7.0058
6.9841
6.9709
6.9486
4.7318
4.7204
3.8841
0.0001

(d) **5**



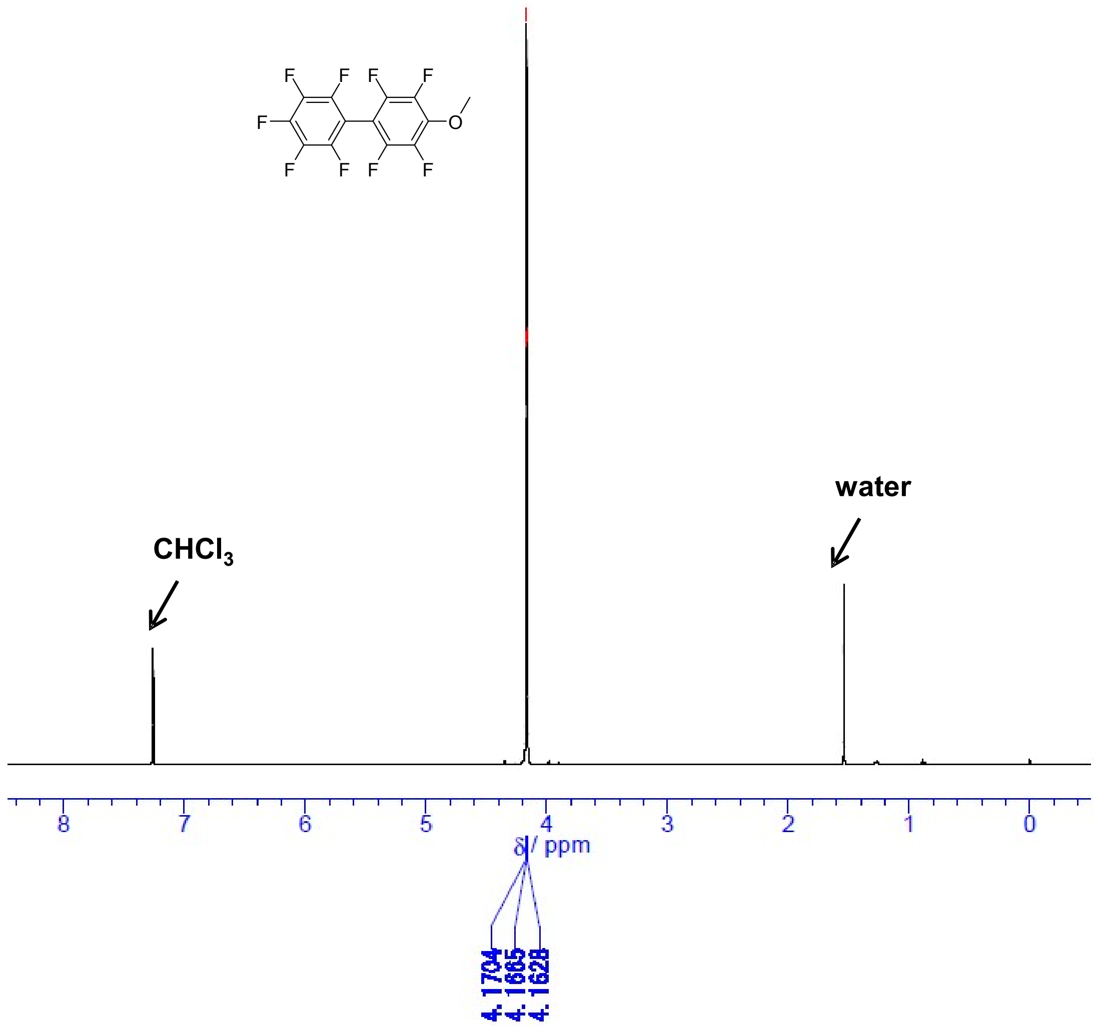
CH2Cl2
δ / ppm
8
7
6
5
4
3
2
1
0
4.0189
1.0068
1.0
1.0098
5.0672
2.0532
3.0328
7.8247
7.8027
7.7966
7.7749
7.5350
7.5158
7.3673
7.3483
7.3284
7.2600
7.2313
7.2123
7.1937
7.0495
7.0275
7.0091
6.9884
6.9786
6.9566
4.6615
3.8893
O
O
Cl

(e) **M2**

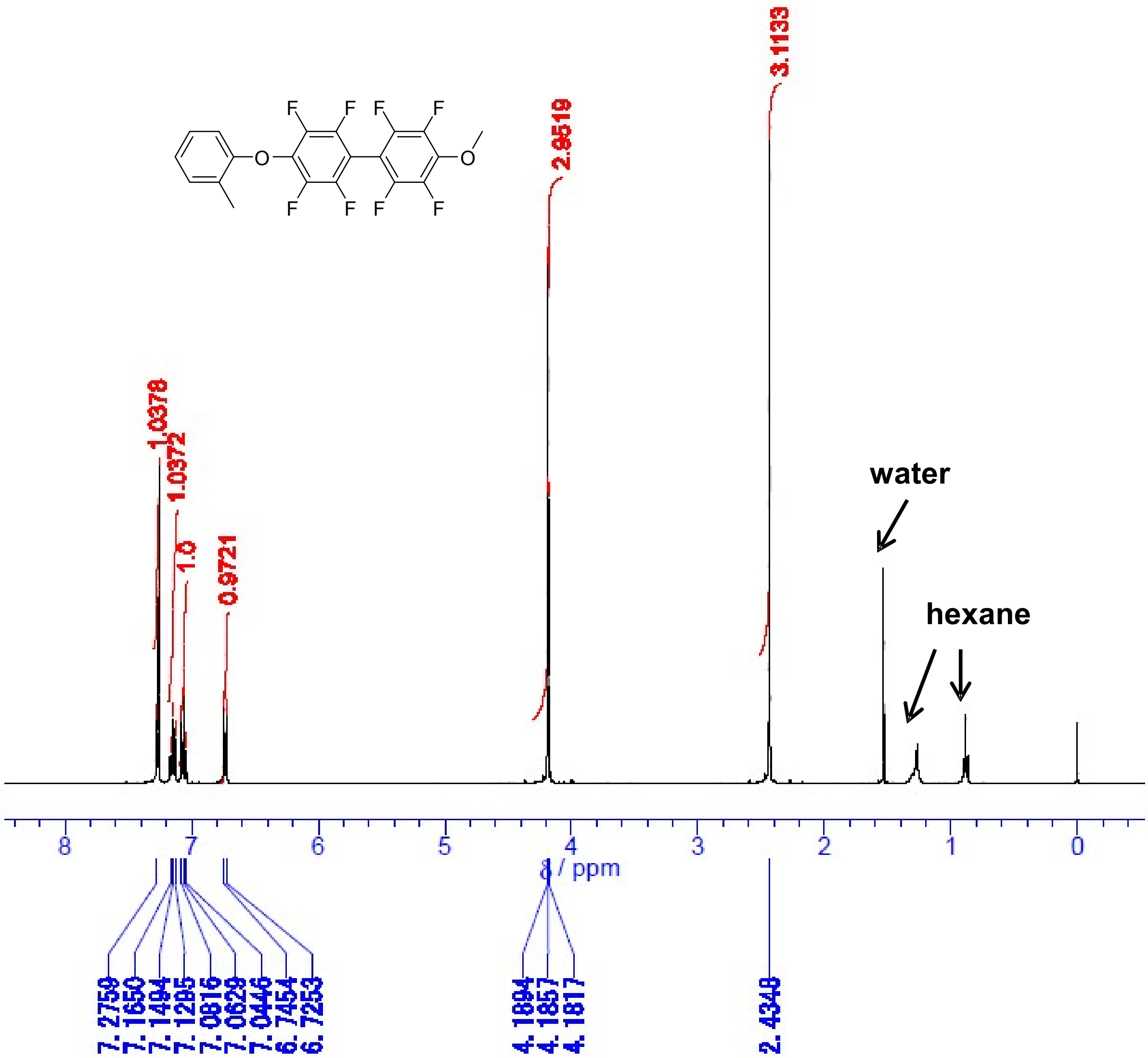


O
O
O
N+
Cl-
9.3873
5.1603
4.0546
2.8538
2.0
1.0566
1.0319
1.3457
8
7
6
5
4
3
2
1
0
δ / ppm
7.9371
7.9216
7.7709
7.7580
7.7538
7.7370
7.4537
7.4363
7.4183
7.2600
7.2438
7.2252
7.0128
6.9805
6.9685
6.9431
6.9211
4.9010
3.8499
3.4285
-0.0387

(f) **7**

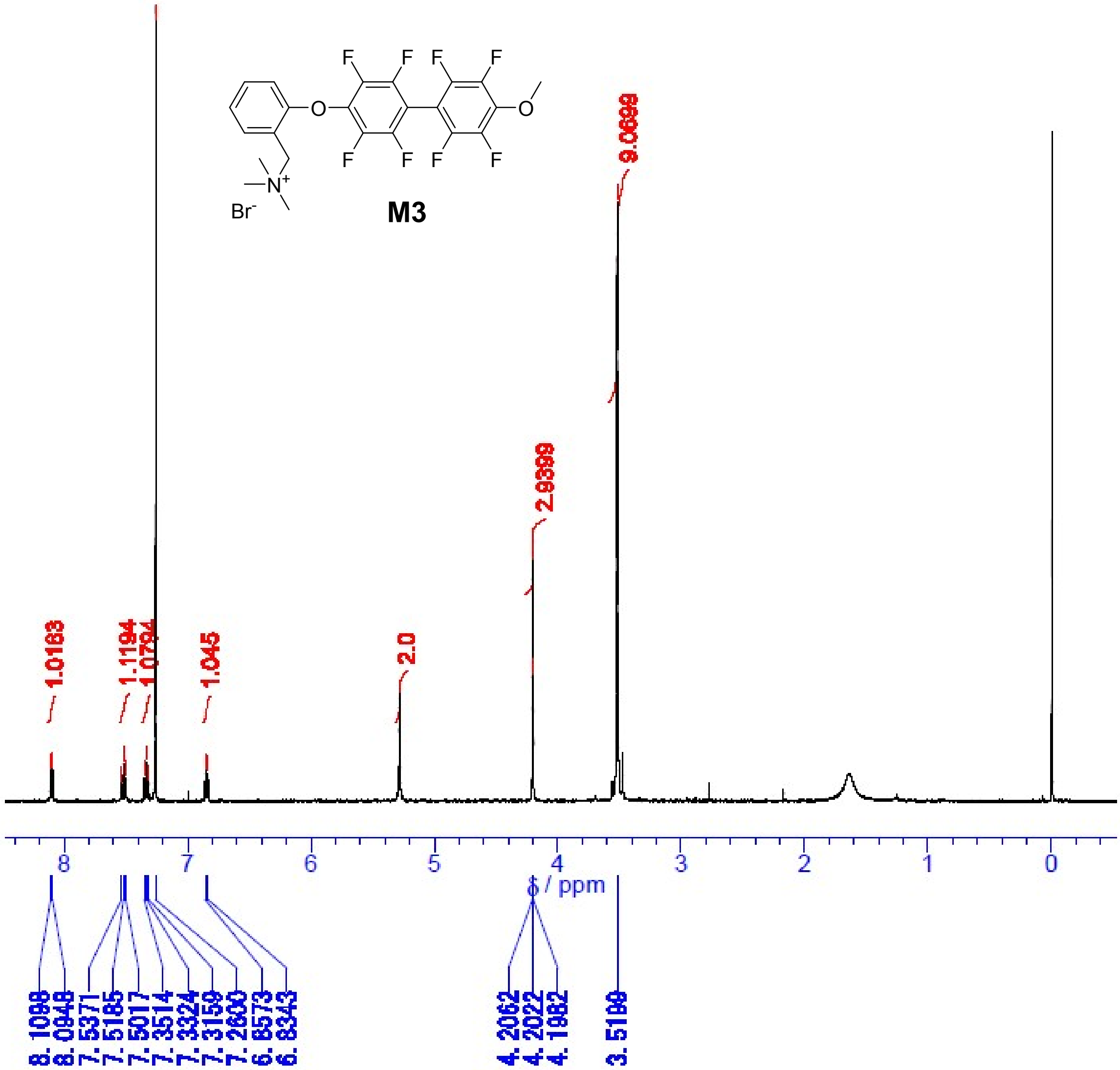


(g) **8**



F
F
F
F
O
O
F
F
F
F
3.1133
2.9519
1.0378
1.0372
1.0
0.9721
water
hexane
8
7
6
5
4
3
2
1
0
δ / ppm
7.2759
7.1650
7.1494
7.1285
7.0816
7.0629
7.0446
6.7454
6.7253
4.1894
4.1857
4.1817
2.4348

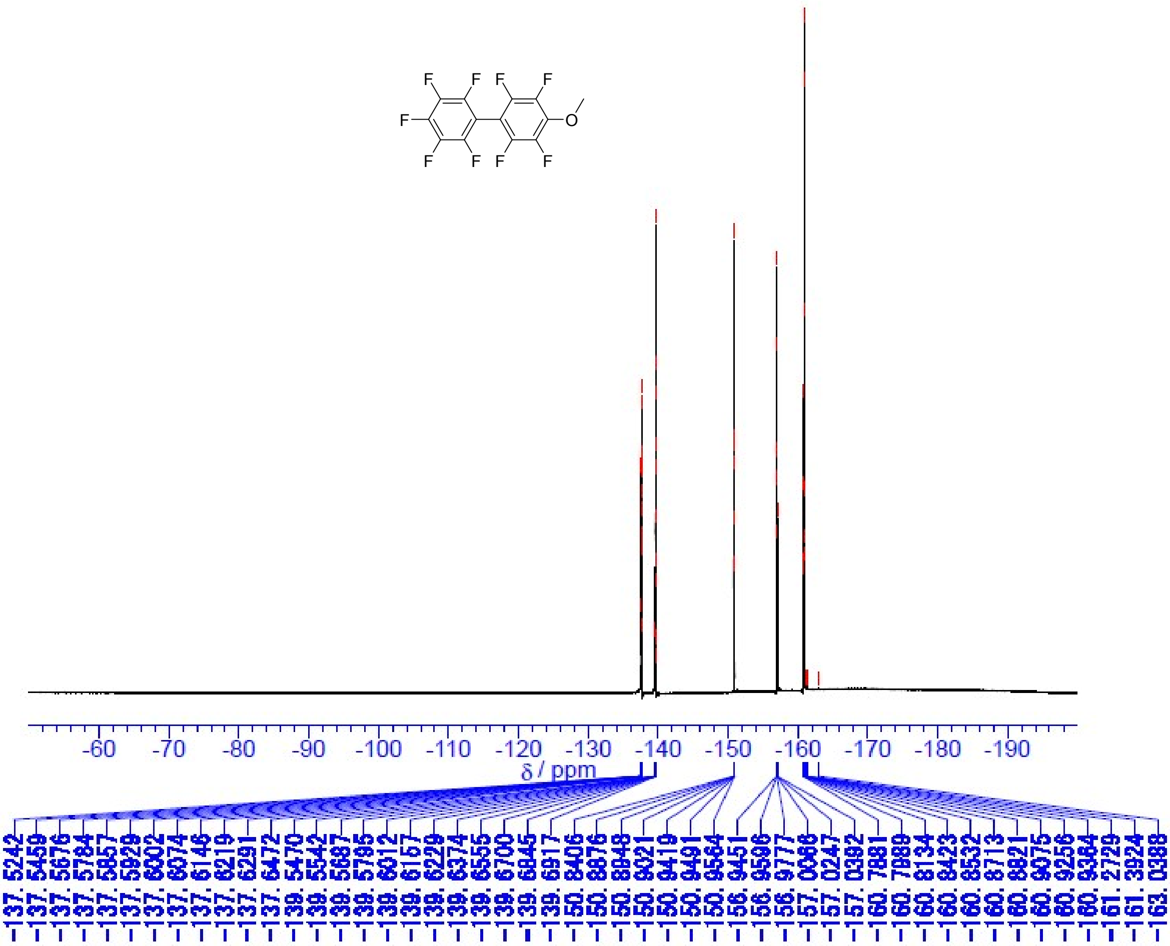
(h) **M3**



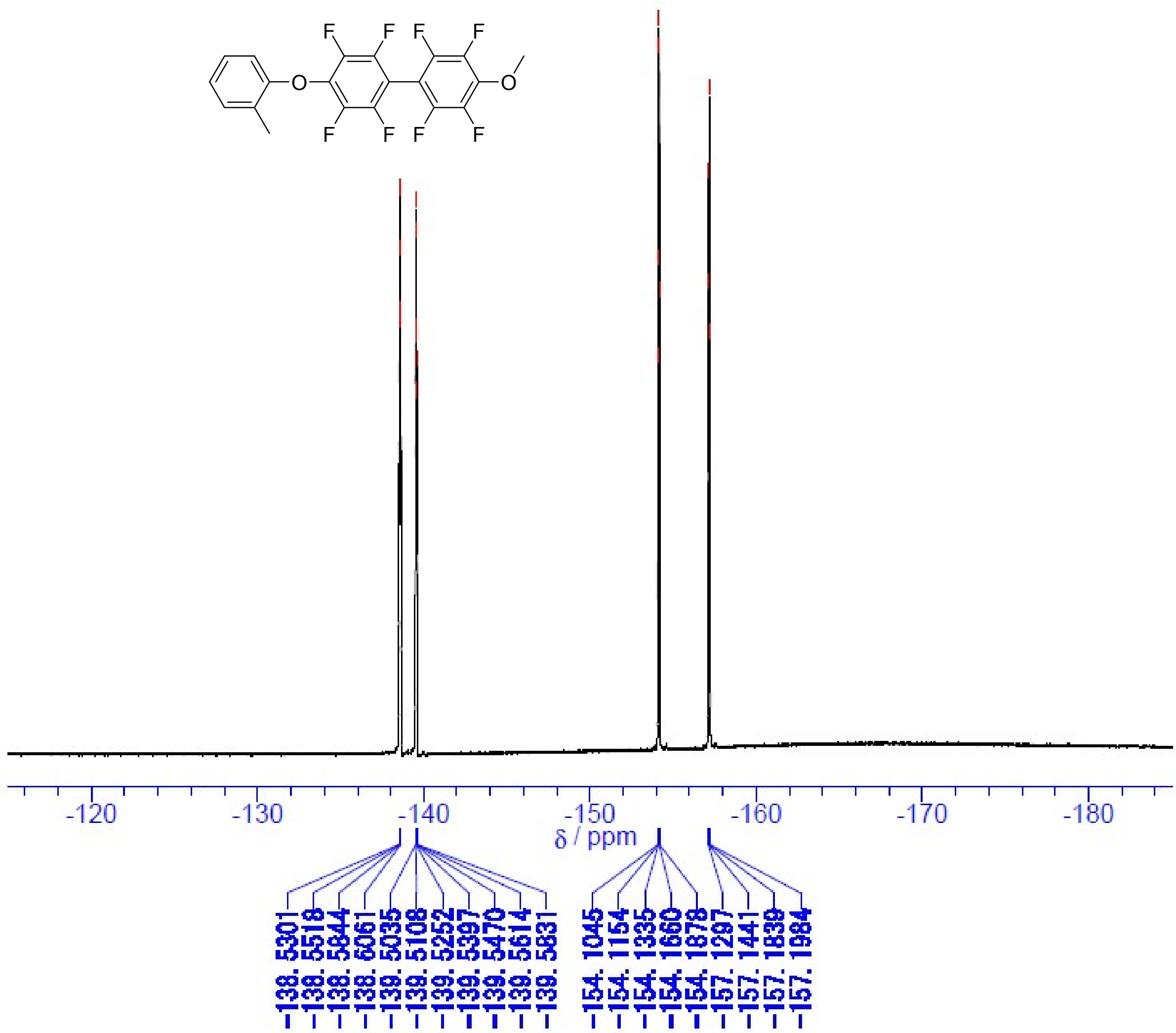
F
F
F
F
O
O
N+
Br-
F
F
F
F
M3
1.0163
1.1194
1.0794
1.045
2.0
2.9399
9.0699
8
7
6
5
4
3
2
1
0
δ / ppm
8.1098
8.0948
7.5371
7.5185
7.5017
7.3514
7.3324
7.3159
7.2600
6.8573
6.8343
4.2062
4.2022
4.1982
3.5198

Figure S2. ^{19}F-NMR spectra of synthetic intermediates of **M3**.

(a) **7**



(b) **8**



F
F
F
F
O
O
F
F
F
F
-120
-130
-140
-150
-160
-170
-180
δ / ppm
-138.5301
-138.5518
-138.5844
-138.6061
-139.5035
-139.5108
-139.5252
-139.5397
-139.5470
-139.5614
-139.5831
-154.1045
-154.1154
-154.1335
-154.1660
-154.1878
-157.1297
-157.1441
-157.1839
-157.1984

(c) **M3**

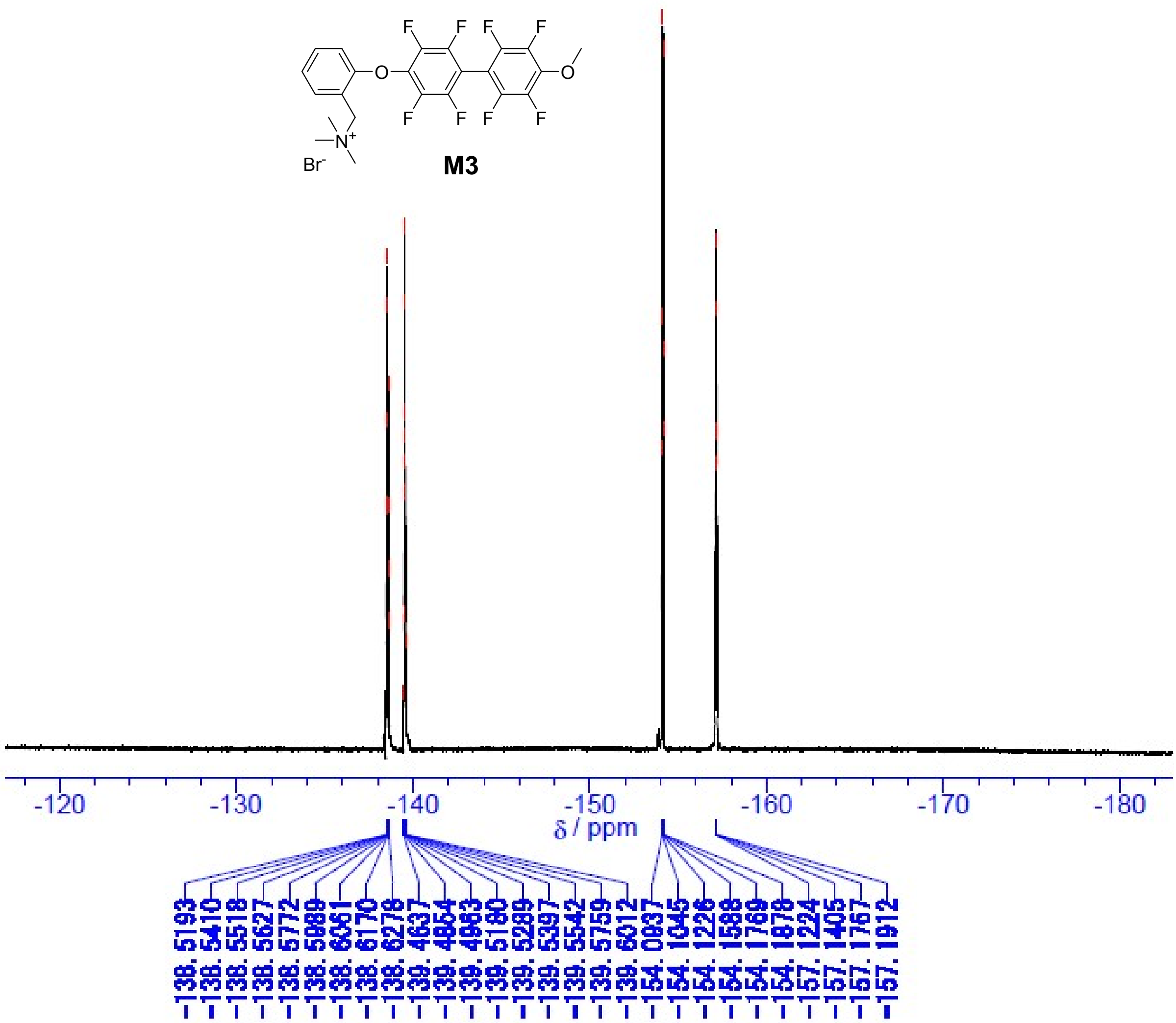
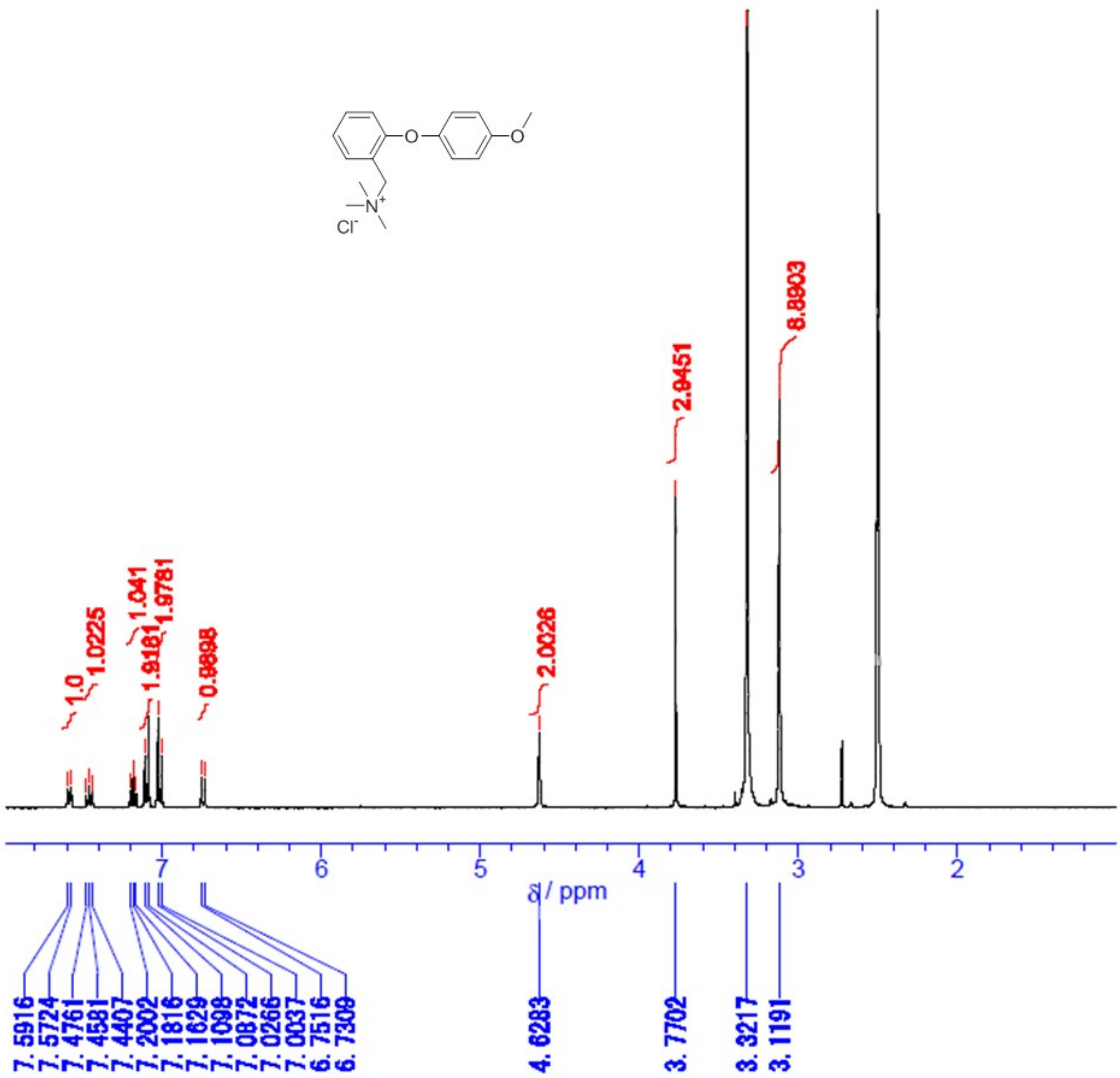
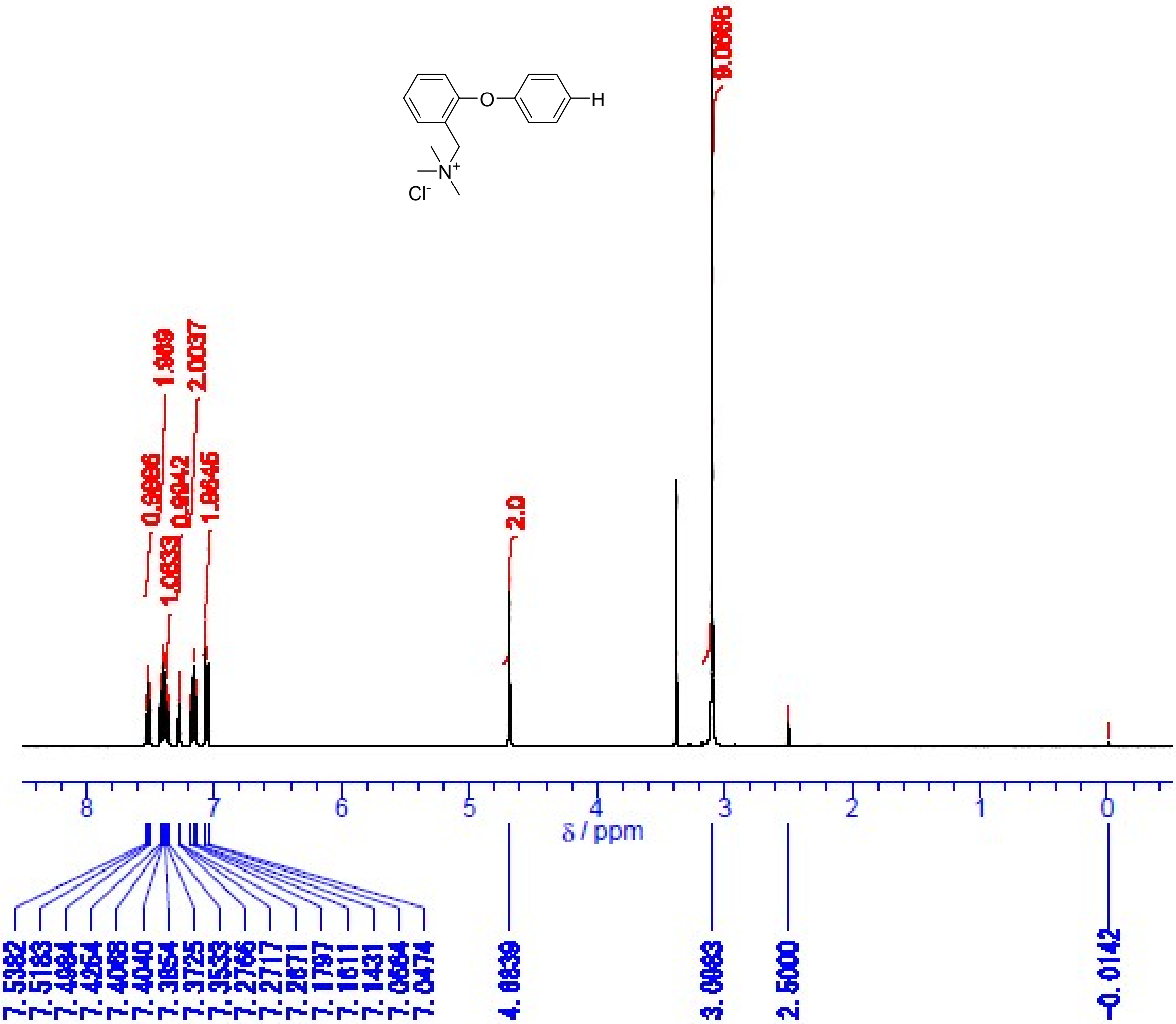


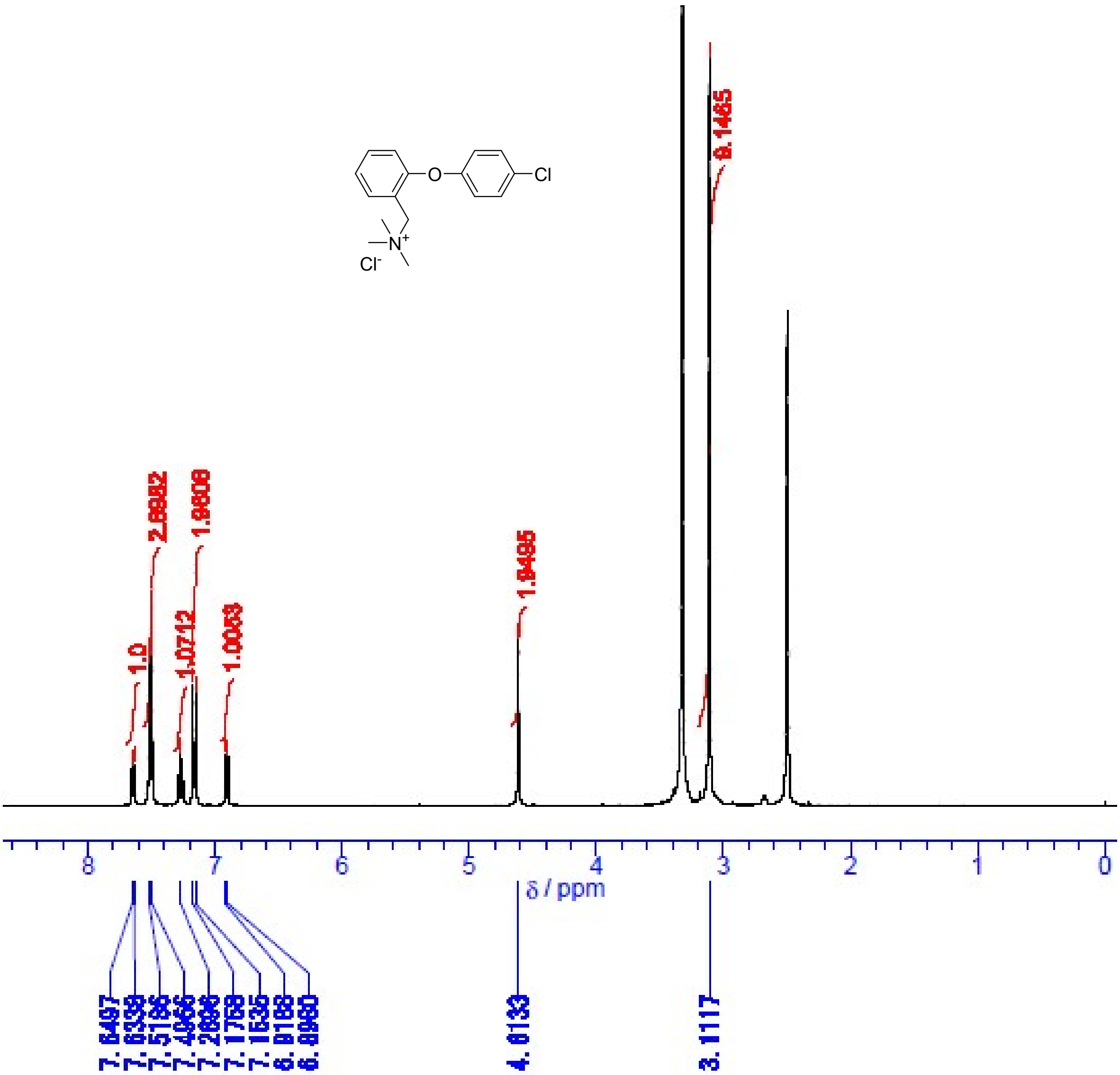
Figure S3. ¹H-NMR spectra of **L1–L4** in DMSO-d_6.



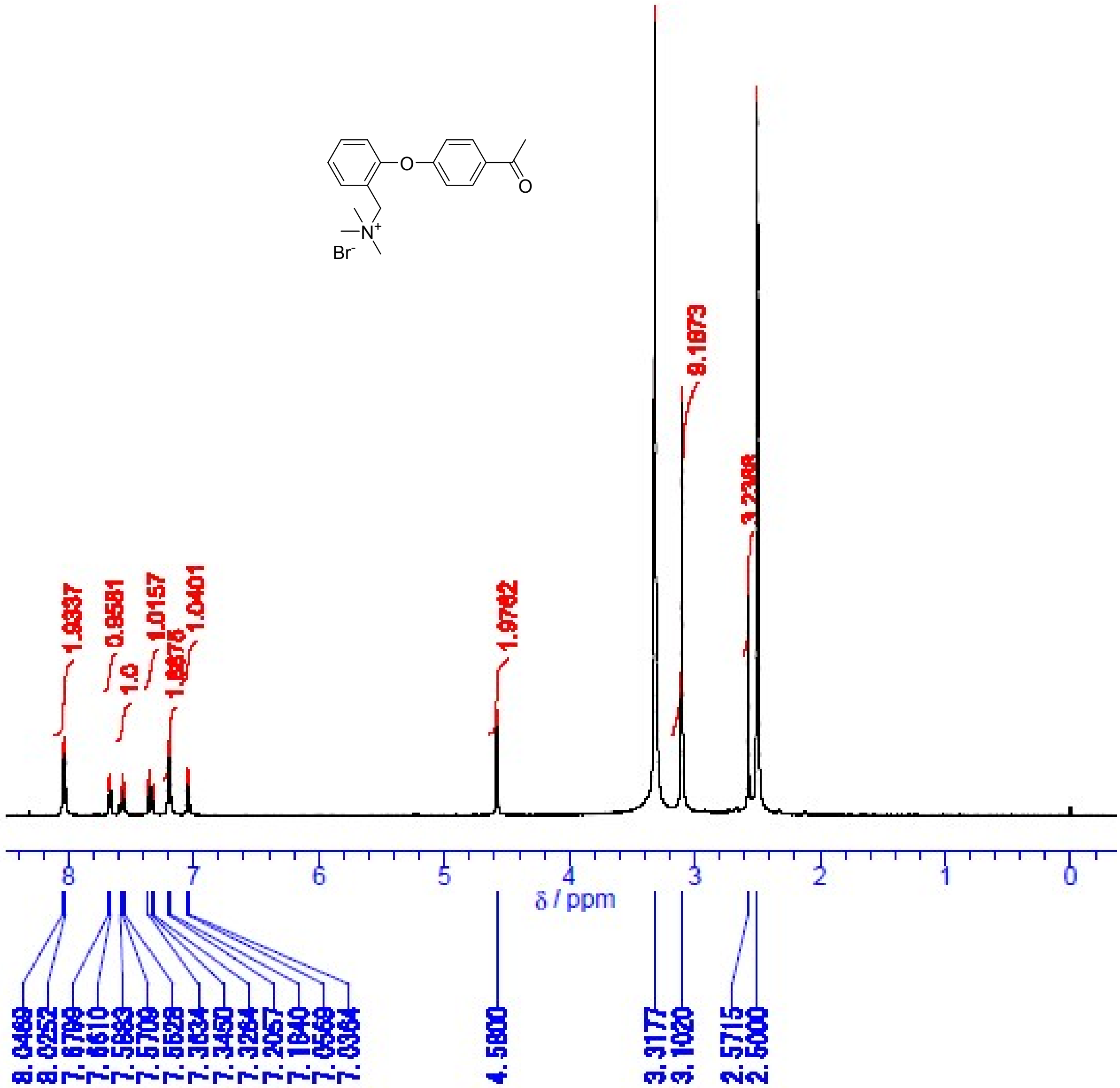
L1:¹H-NMR (400 MHz, DMSO-d_6): δ 7.58 (d, 1H), δ 7.46 (t, 1H), δ 7.18 (t, 1H), δ 7.09 (d, 2H), δ 7.01 (d, 2H), δ 6.74 (d, 1H), δ 4.63 (s, 2H), δ3.77 (s, 3H), δ 3.12 (s, 9H).



L2:^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.52 (t, 1H), δ 7.50-7.35 (m, 3H), δ 7.27 (s, 1H), δ 7.18-7.14

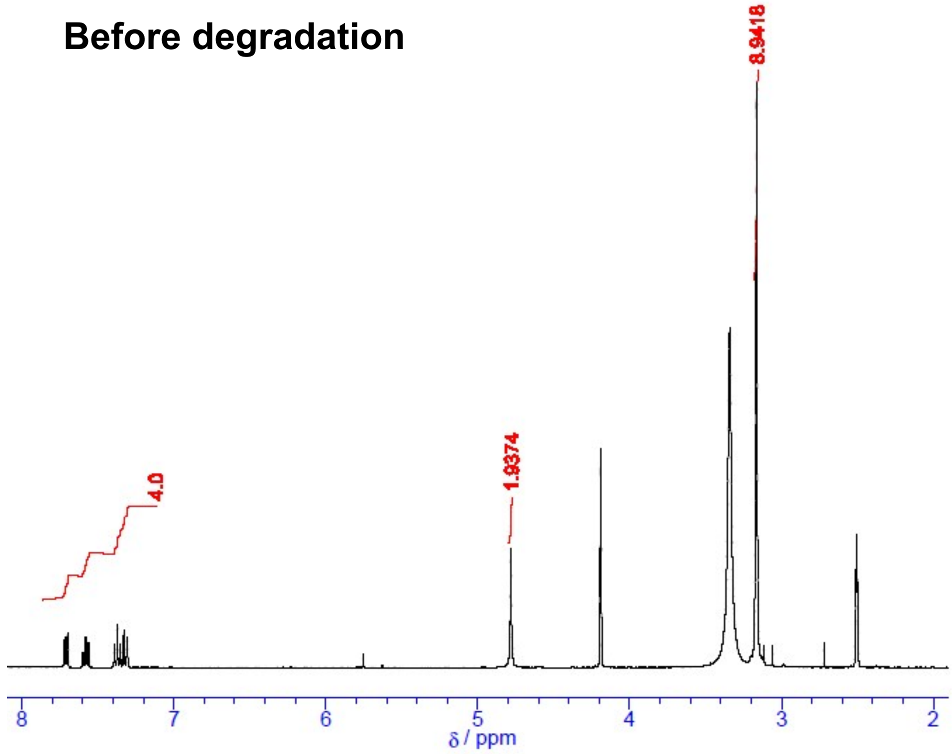


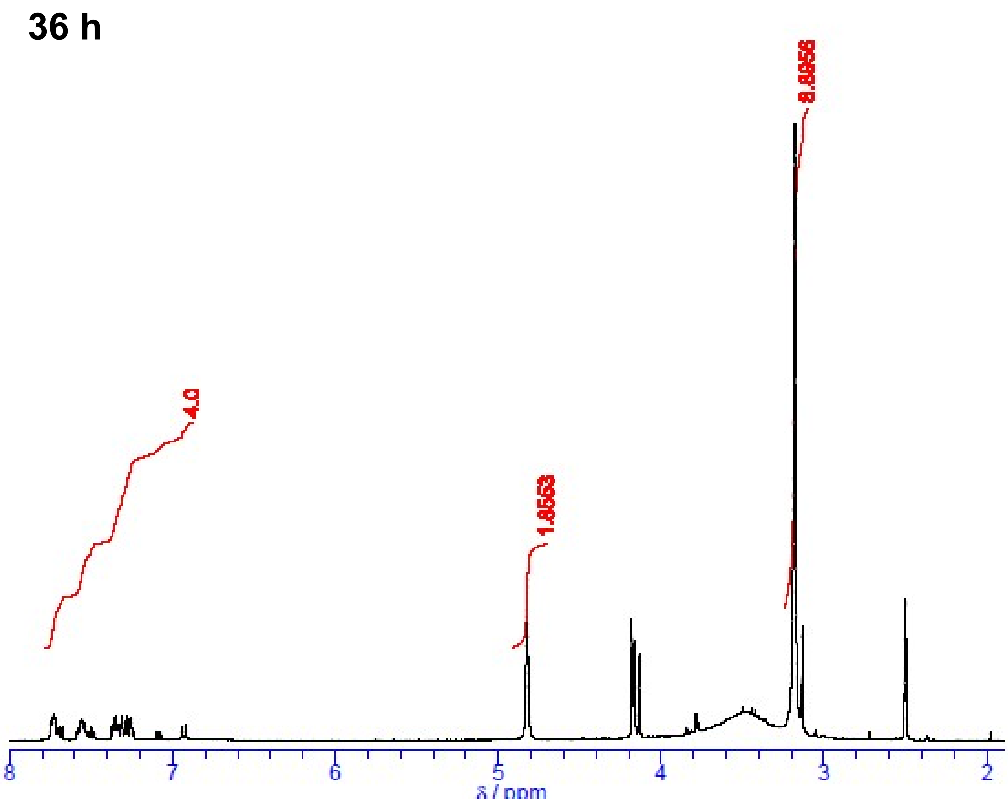
L3:^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.64 (d, 1H), δ 7.51 (t, 1H), δ 7.50 (d, 2H), δ 7.27 (t, 1H), δ 7.16 (d, 2H), δ 6.90 (d, 1H), δ 4.61 (s, 2H), δ 3.11 (s, 9H).



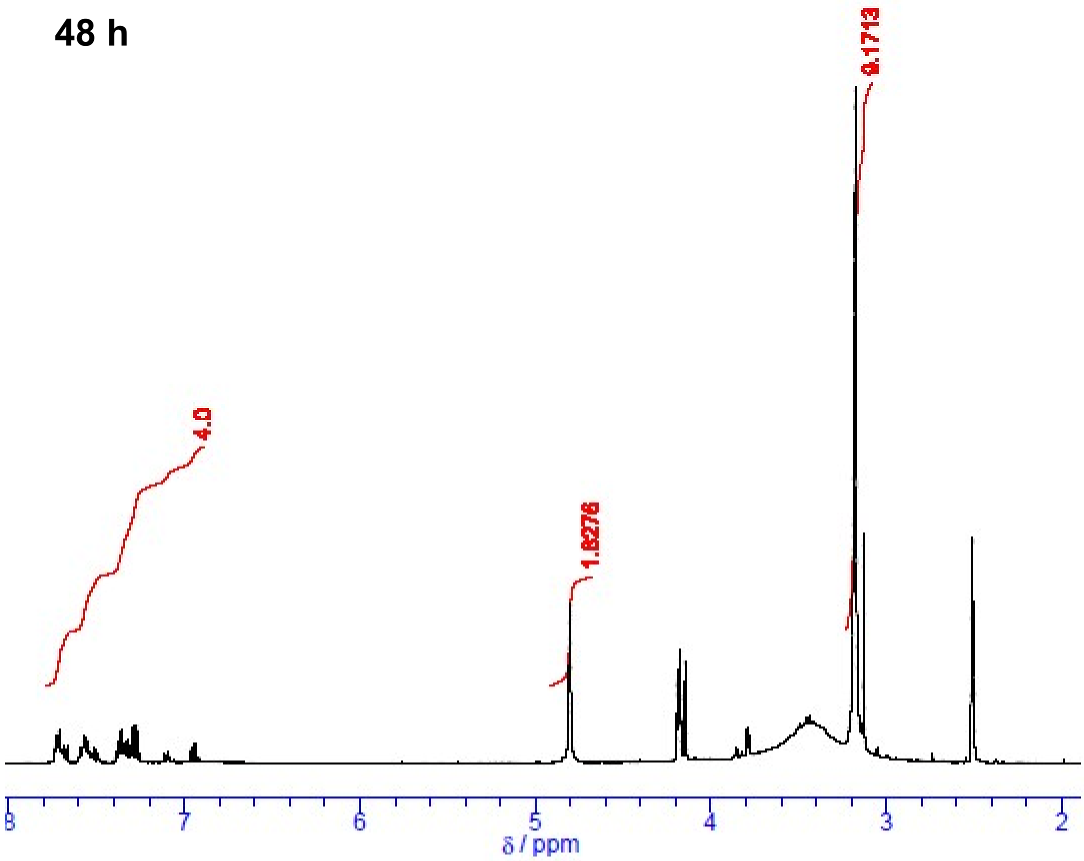
L4:^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.03 (d, 2H), δ 7.87 (d, 1H), δ 7.57 (t, 1H), δ 7.35 (t, 1H), δ 7.19 (d, 2H), δ 7.04 (d, 1H), δ 4.58 (s, 2H), δ3.10 (s, 3H), δ 2.57 (s, 3H).

Figure S4. [1]H-NMR spectral change of **M3** before and after 30-, 48-, and 168-h degradation in aqueous 8-M NaOH. The integration ratio between aromatic protons (6.8–7.8 ppm), benzyl protons (4.81 ppm), and trimethylammonium group (3.16 and 3.14 ppm) does not change significantly.





48 h



168 h

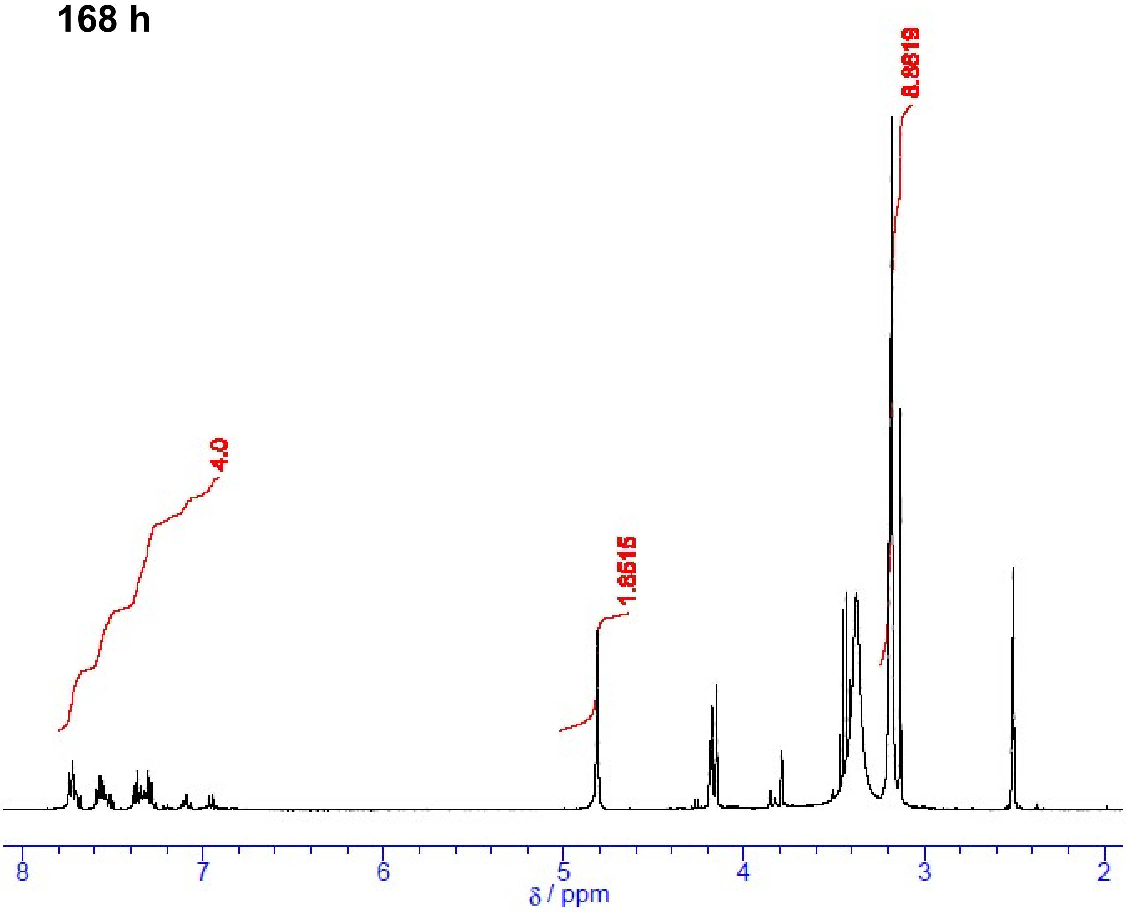
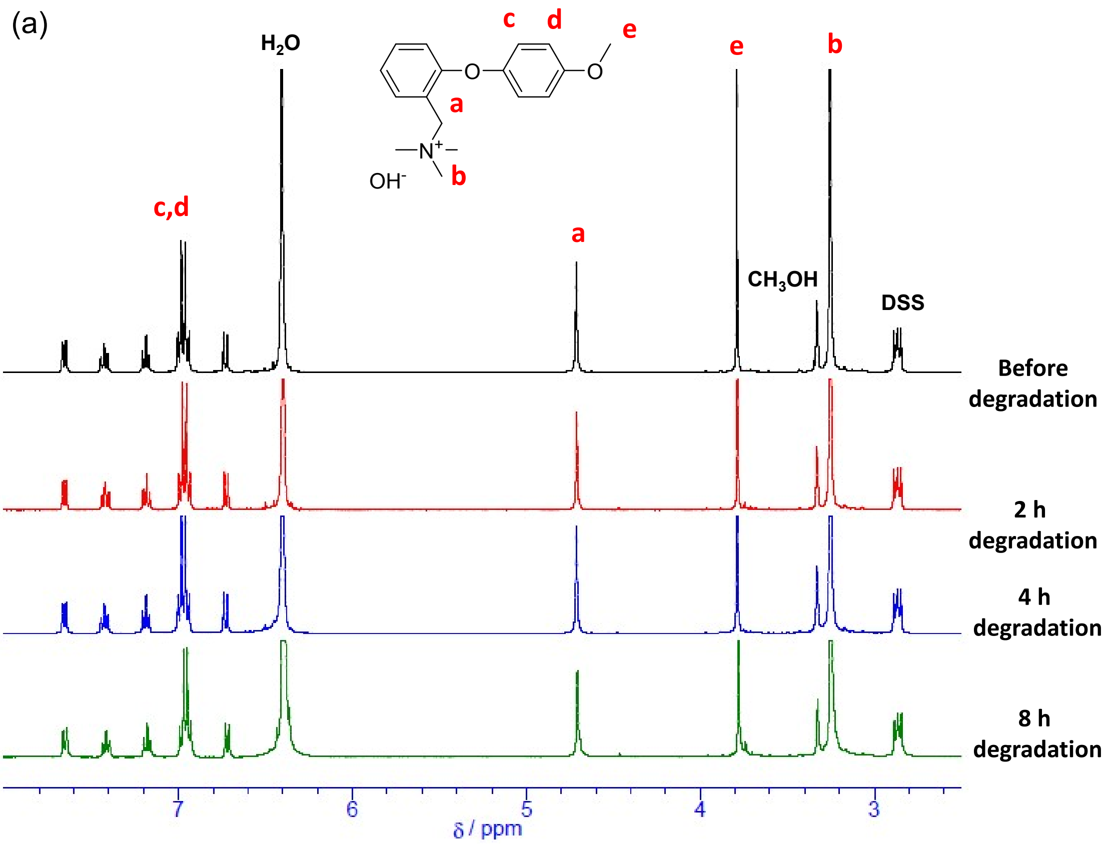
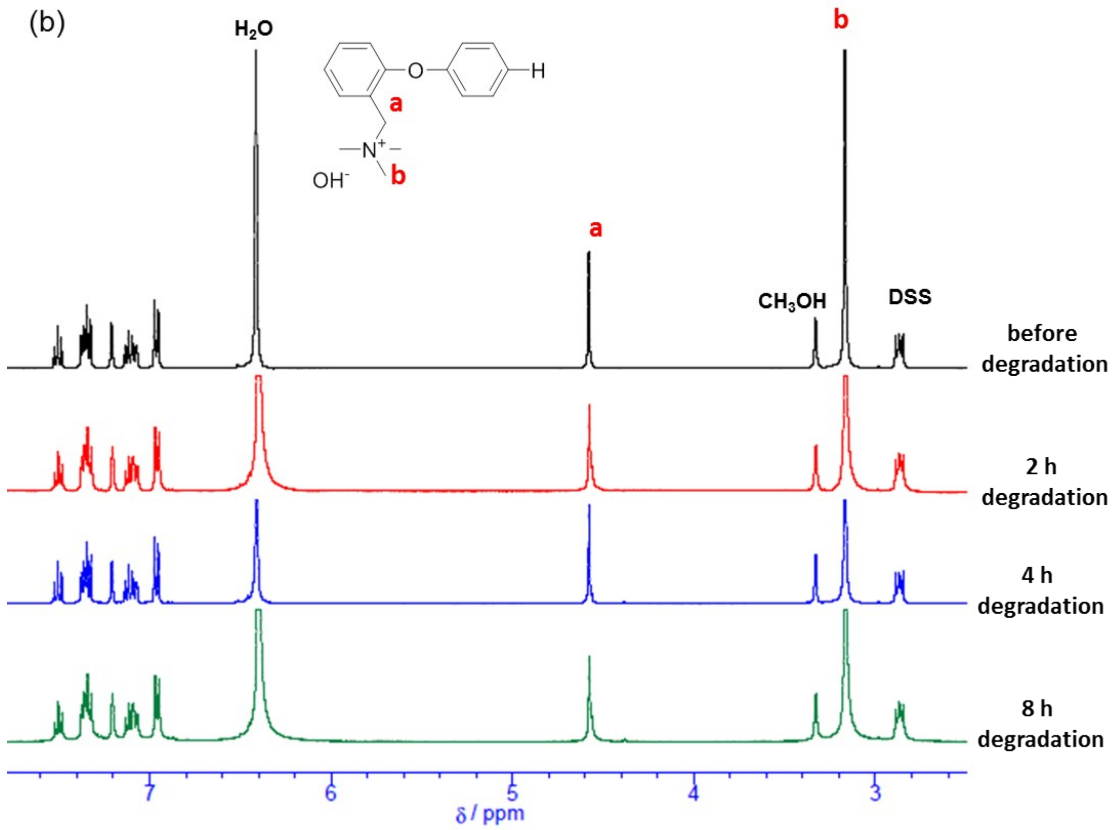
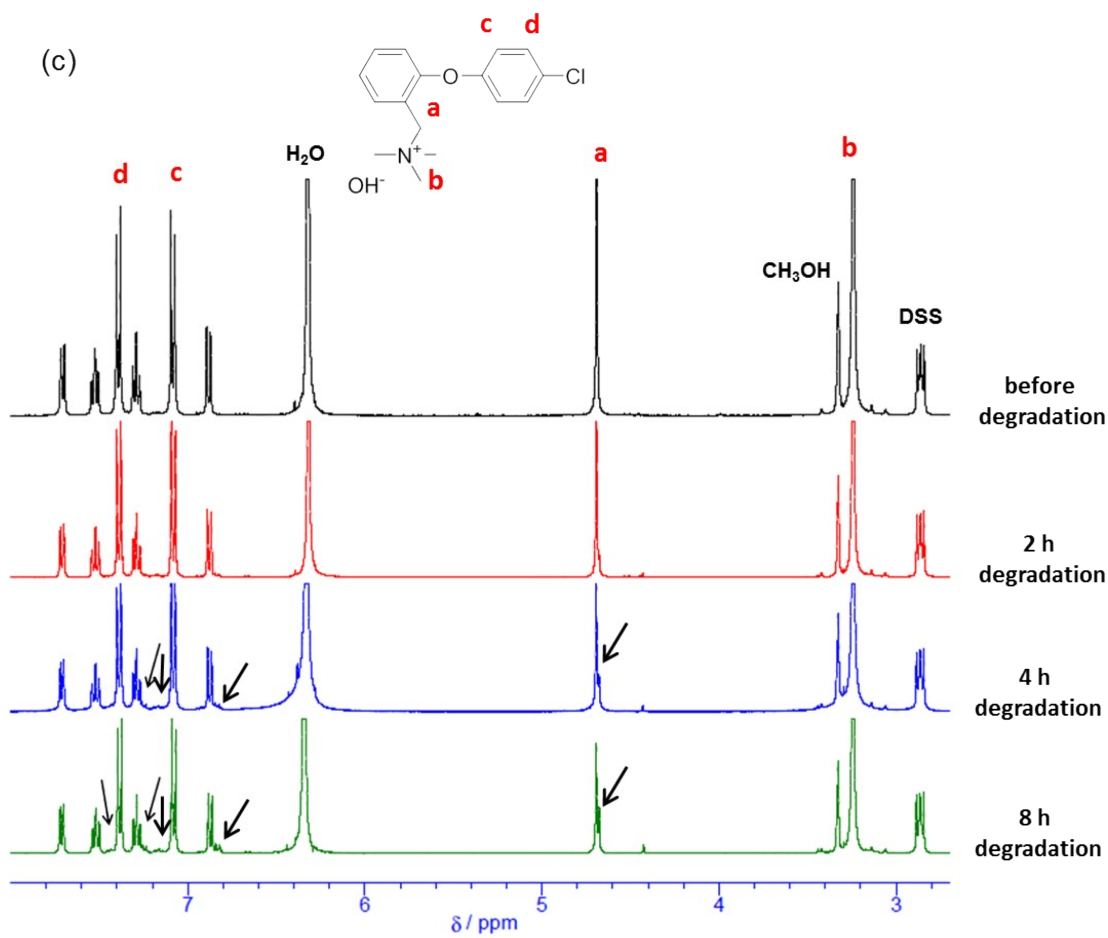


Figure S5. ^{1}H-NMR spectral change of (a) **L1** (b) **L2** (c) **L3** and (d) **L4** in 2-M $CD_3ONa/NaOD$ ($CD_3OD:D_2O$=4:1). The peak intensity of these NMR spectra was normalized by **DSS** peak at around 0 ppm. Arrows indicate peaks derived from the decomposed product. The degradation rate was estimated by change of the relative peak intensity derived from aromatic protons of **L1-L4** (6.5-8.2 ppm) because other peak intensity derived from benzyl protons (-4.7 ppm) or trimethyl ammonium (3.2 ppm) protons is not reliable due to D/H exchange.

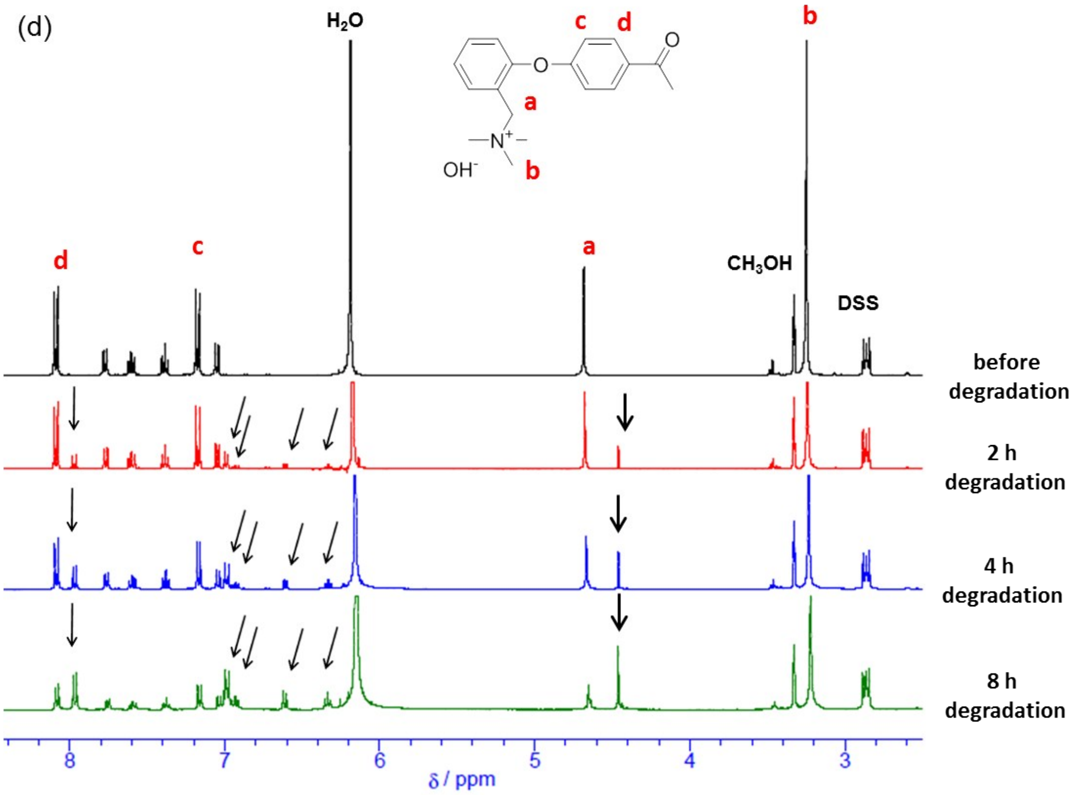
(a)




(b)
H2O
a
b
a
b
OH-
H
CH3OH
DSS
before degradation
2 h degradation
4 h degradation
8 h degradation
7
6
5
4
3
δ / ppm


(c)
c
d
Cl
a
b
OH-
d
c
H2O
a
b
CH3OH
DSS
before degradation
2 h degradation
4 h degradation
8 h degradation
7
6
5
4
3
δ / ppm

(d)


H2O
c d
a
OH-
b
d
c
a
CH3OH
b
DSS
before degradation
2 h degradation
4 h degradation
8 h degradation
8
7
6
5
4
3
δ / ppm