Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Ether Cleavage-Triggered Degradation of Benzyl Alkylammonium Cations for Polyethersulfone Anion Exchange Membranes

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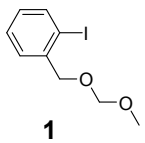
Contents

Synthesis

All reagents were used as received from the provider unless otherwise stated.



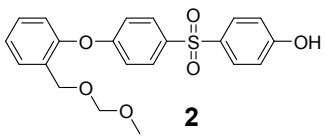
1

1

2-iodobenzylalcohol (11.7 g, 50 mmol) in anhydrous THF (50 ml) was added dropwise to 60 wt% NaH (2.60 g, 65 mmol) in anhydrous THF (100 ml) at 0 °C under nitrogen. The reaction mixture was stirred for 2 h at 25 °C and then MOMCl (4.83 g, 60 mmol) was added dropwise via syringe. The mixture was stirred for 12 h and quenched by adding water. The solution was concentrated on a rotary

evaporator. The residue was extracted with dichloromethane and washed with water three times. Column chromatography of the residue on silica gel (eluent: firstly hexane and then hexane/dichloromethane (3/2 vol)) afforded methoxymethyl-2-iodobenzyl ether (**1**) as a colorless liquid (12.9 g, 46.5 mmol) in 93% yield.

^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84 (d, 1H), δ 7.45 (d, 1H), δ 7.35 (t, 1H), δ 6.99 (t, 1H), δ 4.77 (s, 2H), δ 4.60 (s, 2H), δ 3.44 (s, 3H)



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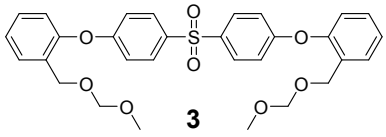


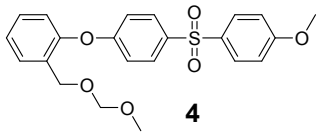
3

2 and 3[1]

1 (13.9 g, 50 mmol), 4,4'-dihydroxydiphenylsulfone (6.26 g, 25 mmol), K_3PO_4 (21.2g, 100 mmol), CuI (952 mg, 5.0 mmol), picolinic acid (1.23 g, 10 mmol) was dissolved into DMSO (100 ml). The mixture was stirred at 105 °C for 48 h and quenched by adding ammonia aqueous. The mixture was extracted with dichloromethane, washed with ammonia aqueous, acidified with $HCl_{(aq)}$ (around pH=6) and washed with water. The solvent was removed on a rotary evaporator. Column chromatography of the residue on silica gel (eluent: $CHCl_3$:hexane = 4:1) afforded **2** (3.61 g) and **3** (6.61 g).

2: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84 (d, 2H), δ 7.82 (d, 2H), δ 7.53 (d, 1H), δ 7.31 (t, 1H), δ 7.25 (t, 1H), δ 6.95 (d, 2H), δ 6.89 (d, 2H), δ 6.89 (d, 1H), δ 5.39 (s, 1H)δ 4.62 (s, 2H), δ 4.54 (s, 2H), δ 3.28 (s, 3H)

3: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.84 (d, 4H), δ 7.54 (d, 2H), δ7.33 (t, 2H), δ7.25 (t, 2H), δ6.98-6.95 (m, 6H), δ 4.62 (s, 2H), δ 4.55 (s, 2H), δ 3.29 (s, 3H)



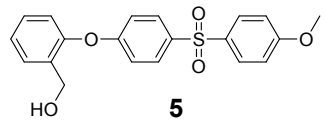
4

4

2 (2.40 g, 6.0 mmol), 2 M bromomethane (6.0 ml, 12 mmol) in THF and 8 M $NaOH_{(aq)}$ (1.0 ml, 8.0

mmol) were dissolved in CH_3CN (30 ml) and THF (10 ml). The reaction mixture was stirred for 6 h and concentrated on a rotary evaporator. The residue was extracted with dichloromethane and washed with water three times. The solvent was removed on a rotary evaporator and the residue was dried under vacuum to obtain **4** (2.40 g, 5.8 mmol) in 97 % yield.

4: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 2H), δ 7.85 (d, 2H), δ 7.55 (d, 1H), δ7.34 (t, 1H), δ 7.27 (t, 1H), δ 6.99 (d, 2H), δ 6.97 (d, 2H),δ 6.97 (d, 1H), δ 4.63 (s, 2H), δ 4.56 (s, 2H), δ 3.87 (s, 3H), δ 3.28 (s, 3H)

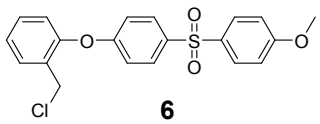


5

5

10 M hydrochloric acid (1.5 ml) was added to **4** (1.24 g, 3.0 mmol) in 2-propanol (15 ml) and THF (15 ml). The mixture was stirred for 6 h at 50 °C and concentrated on a rotary evaporator. The residue was extracted with dichloromethane and washed with water three times. The solvent was removed on a rotary evaporator. Short column chromatography of the residue on silica gel (eluent: $CHCl_3$) afforded **5** (1.0 g, 2.7 mmol) in 90 % yield.

5: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 2H), δ 7.83 (d, 2H), δ 7.52 (d, 1H), δ7.31 (t, 1H), δ 7.24 (t, 1H), δ 6.97 (d, 2H), δ 6.95 (d, 2H), δ 6.92 (d, 2H), δ4.64 (s, 2H), δ3.84 (s, 3H)

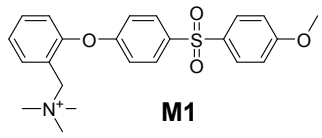


6

6

5 (1.0 g. 2.7 mmol) was dissolved in anhydrous CH_2Cl_2 (20 ml) and $SOCl_2$ (1.0 ml) was added via syringe. The mixture was stirred at 25 ^{o}C under nitrogen for 4 h and dried under vacuum to obtain **6** (1.03 g, 2.65 mmol) in 98 % yield.

6: ^{1}H-NMR (400 MHz, $CDCl_3$): δ7.86 (d, 4H), δ7.51 (d, 1H), δ7.33 (t, 1H), δ7.22 (t, 1H), δ7.01 (d, 2H), δ6.97 (d, 2H), δ6.93 (d, 1H), δ4.58 (s, 2H), δ3.85 (s, 3H)

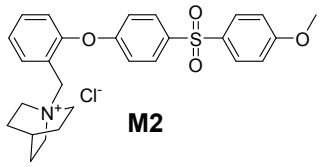


M1

M1

6 (972 mg. 2.5 mmol) was dissolved in THF (10 ml) and 30 wt% trimethylamine aqueous (1 ml) was added. The mixture was stirred for 3 h and dried under vacuum to obtain **M1** (1.10 g, 2.45 mmol) in 98 % yield.

M1: ^{1}H-NMR (400 MHz, $CDCl_3$): δ8.01 (d, 1H), δ7.87 (d, 2H), δ7.85 (d, 4H), δ7.48 (t, 1H), δ7.32 (t, 1H), δ7.01-6.96 (m, 5H), δ4.97 (s, 2H), δ3.85 (s, 3H), δ3.42(s, 9H)

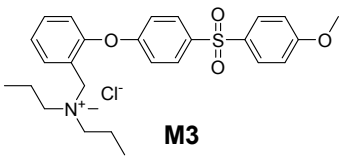


M2

M2

6 (389 mg. 1.0 mmol) was dissolved in THF (10 ml) and qinuclidine (167mg, 1.5 mmol) was added. The mixture was stirred for 12 h and the solvent was removed under reduced pressure. The residue was dried under vacuum at 80 ^{o}C to remove unreacted qinuclidine to obtain **M3** (455 mg, 0.91mmol) in 91% yield.

M2: ^{1}H-NMR (400 MHz, DMSO-d_6): δ7.95 (d, 2H), δ7.88 (d, 2H), δ7.65 (d, 1H), δ7.55 (t, 1H), δ7.36 (t, 1H), δ7.20 (d, 2H), δ7.14 (d, 2H), δ7.10 (d, 1H), δ4.36 (s, 2H), δ3.83(s, 3H), δ3.44 (t, 6H), δ2.23 (t, 1H), δ1.84 (m, 6H)

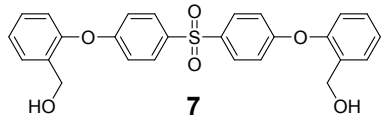


M3

6 (778 mg. 2.0 mmol) was dissolved in THF (10 ml) /CH_3CN (10ml) and *N*-methyldipropylamine (460.9 mg, 4.0 mmol) was added. The mixture was stirred for 6 h at 60 ^{o}C and dried under vacuum to

obtain **M3** (547 mg, 1.8 mmol) in 90 % yield.

M3: ^{1}H-NMR (400 MHz, DMSO-d_6): δ7.97 (d, 2H), δ7.88 (d, 2H), δ7.68 (d, 1H), δ7.57 (t, 1H), δ7.38 (t, 1H), δ7.18 (d, 2H), δ7.14 (d, 1H), δ7.13 (d, 2H), δ4.49 (s, 2H), δ3.83 (s, 3H), δ3.16 (m, 4H), δ2.91 (t,3H), δ1.70 (m, 4H), δ0.83 (t, 6H)

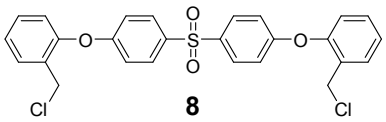


7

Similar procedure to synthesize **5** was applied.

7 (2.66g, 5.76 mmol) was obtained from **3** (3.30g, 6.0 mmol) in 96% yield.

7: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.85 (d, 4H), δ 7.53 (d, 2H), δ7.32 (t, 2H), δ 7.26 (t, 2H), δ 6.98 (d, 4H), δ 6.95 (d, 2H), δ4.65 (4, 2H)

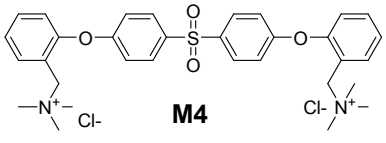


8

Similar procedure to synthesize **6** was applied.

8 (2.40 g, 4.8 mmol) was obtained from **7** (2.31 g, 5.0 mmol) in 96% yield.

12: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 4H), δ 7.51 (d, 2H), δ7.35 (t, 2H), δ7.25 (t, 2H), δ7.03 (d, 4H), δ6.95 (d, 2H), δ4.59 (s, 4H)



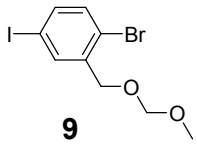
M4

Similar procedure to synthesize **M1** was applied.

M4 (2.29 g, 3.7 mmol) was obtained from **8** (2.0 g, 4.0 mmol) in 93% yield.

M4: ^{1}H-NMR (400 MHz, DMSO-d_6): δ 8.02 (d, 4H), δ 7.75 (d, 1H), δ7.59 (t, 2H), δ7.39 (t, 2H),

δ7.25 (d, 4H), δ7.11 (d, 2H), δ4.60 (s, 4H), 3.11 (s, 9H),

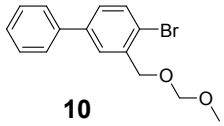


9

Methoxymethyl-2-bromo-5-iodo-benzyl ether (9)

Similar procedure to synthesize **1** was applied. **9** (10.9 g, 30.4 mmol) was obtained from 2-bromo-5-iodo-benzylalcohol (10.0 g. 32 mmol) in 95% yield.

9: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.82 (s, 1H), δ 7.46 (d, 1H), δ 7.25 (d, 1H), δ4.77 (s, 2H), δ4.60 (s, 2H), δ3.43 (s, 3H)



10

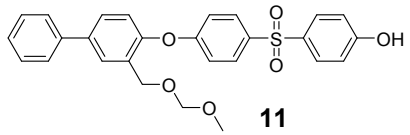
10

Mg (753 mg, 31 mmol) was introduced in tow-necked 100 ml round flask and dried in vacuum by heating. Iodobenzene (6.12 g, 30 mmol) in anhydrous THF (30 ml) was added under nitrogen. The solution was stirred at room temperature and the reaction started. The solution was further stirred for 2 h and 30 min at 40 ^{o}C. Then, methoxymethyl-2-bromo-5-iodo-benzyl ether (10.7 g. 30 mmol) and Ni (dppp)Cl_2 (108 mg, 0.2 mmol) was added in the solution and stirred for 12 h at room temperature.

The reaction was quenched by adding water (2.0 ml) and the solvent was removed under vacuum. The residue was extracted with dichloromethane and washed with water several time. The solvent was removed and column chromatography of the residue on silica gel (eluent: $CHCl_3$: hexane = 1:1) afforded **10** (5.62 g, 18.3 mmol) in 61% yield.

10: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.72 (s, 1H), δ7.62-7.57 (m, 3H), δ 7.44 (t, 2H), δ 7.39-7.34 (m,

2H), δ4.80 (s, 2H), δ4.73 (s, 2H), δ3.45 (s, 3H)



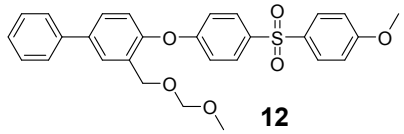
11

11

Similar procedure to synthesize **2** was applied.

11 (5.79 g, 12.2 mmol) was obtained from **10** (4.61 g, 15 mmol), 4,4'-dihydroxyl-diphenyl sulfone (3.75g, 15 mmol) in 81% yield.

11: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.85-7.75 (m, 5H), δ 7.59 (d, 2H), δ7.52 (d, 1H),δ 7.45 (t, 2H), δ7.36 (t, 1H), δ 7.01 (d, 3H), δ 6.89 (d, 2H), δ4.65 (s, 2H), δ4.60 (s, 3H), δ3.30 (s, 3H)



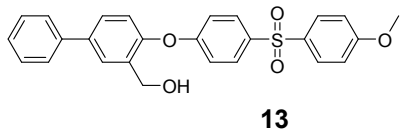
12

12

Similar procedure to synthesize **4** was applied.

12 (4.51 g, 9.2 mmol) was obtained from **11** (4.77 g, 10 mmol) in 92% yield.

12: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.86 (d, 4H), 7.76 (s, 1H), δ 7.59 (d, 2H), δ7.52 (d, 1H), δ7.45 (t, 2H), δ 7.36 (t, 1H), δ 7.03-6.95 (m, 5H), δ4.65 (s, 2H), δ4.60 (s, 3H), δ3.85 (s, 3H), δ3.30 (s, 3H)



13

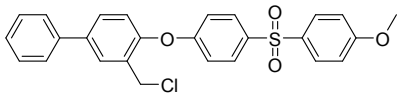
13

Similar procedure to synthesize **5** was applied.

13 (3.78 g, 8.5 mmol) was obtained from **12** (4.42 g, 9.0 mmol) in 94% yield.

13: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.87 (d, 4H), 7.75 (s, 1H), δ 7.59 (d, 2H), δ7.52 (d, 1H), δ7.45 (t,

2H), δ 7.36 (t, 1H), δ 7.03-6.95 (m, 5H), δ4.71 (s, 3H), δ3.85 (s, 3H)



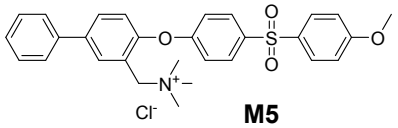
14

14

Similar procedure to synthesize **6** was applied.

14 (3.61 g, 7.76 mmol) was obtained from **13** (3.57 g, 8.0 mmol) in 97% yield.

14: ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.88 (d, 4H), 7.72 (s, 1H), δ 7.57 (d, 2H), δ7.54 (d, 1H), δ7.46 (t, 2H), δ 7.37 (t, 1H), δ 7.07 (d, 2H), δ 7.00-6.96 (m, 3H), δ4.63 (s, 2H), δ3.85 (s, 3H)



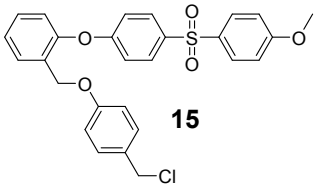
M5

M5

Similar procedure to synthesize **M1** was applied.

M5 (3.49 g, 6.65 mmol) was obtained from **14** (3.25 g, 7.0 mmol) in 95% yield.

M5: ^{1}H-NMR (400 MHz, $CDCl_3$): 8.19 (s, 1H), δ 7.89 (d, 4H), δ 7.70 (d, 1H), δ7.61 (d, 2H), δ7.44 (t, 2H), δ 7.36 (t, 1H), δ 7.05 (m, 3H), δ 6.99 (d, 2H), δ5.05 (s, 2H), δ3.85 (s, 3H), δ3.45 (s, 9H)



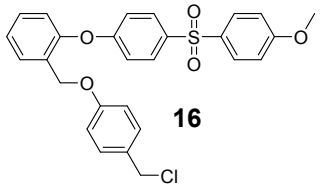
15

15

6 (778 mg, 2.0 mmol) and *p*-hydroxybenzylalcohol (348 mg, 2.8 mmol) and anhydrous K_2CO_3 (415 mg, 3.0 mmol) was dissolved into anhydrous DMF (20 ml). The mixture was stirred for 24 h at 40 ^oC and quenched by adding water. The mixture was extracted with dichloromethane (40 ml x 3) and the combined solution was washed with water (50 ml x 4). The solvent was removed on a rotary

evaporator and dried under vacuum to obtain **9** (820 mg, 1.72 mmol) in 86% yield.

15: ^{1}H-NMR (400 MHz, $CDCl_3$): δ7.85 (d, 4H), δ7.62 (d, 1H), δ7.37 (t, 1H), δ7.27 (t, 1H), δ7.20 (d, 2H), δ7.18-6.96 (m, 5H), δ6.77 (d, 2H), δ5.04 (s, 2H), δ4.58 (s, 2H), δ3.85 (s, 3H)

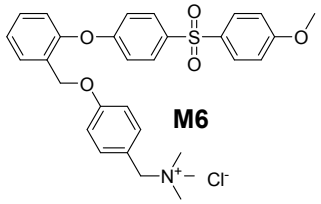


16

Similar procedure to synthesize **6** was applied.

16 (809 mg, 1.63 mmol) was obtained from **15** (820 mg, 1.72 mmol) in 95% yield.

16: ^{1}H-NMR (400 MHz, $CDCl_3$): δ7.85 (d, 4H), δ7.59 (d, 1H), δ7.36 (t, 1H), δ7.26 (t, 1H), δ7.22 (d, 2H), δ7.00-6.96 (m, 5H), δ6.78 (d, 2H), δ5.03 (s, 2H), δ4.52 (s, 2H), δ3.85 (s, 3H)

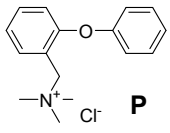


M6

Similar procedure to synthesize **M1** was applied.

M6 (806 mg, 1.46 mmol) was obtained from **10** (743 mg, 1.5 mmol) in 97% yield.

M6: ^{1}H-NMR (400 MHz, DMSO-d_6): δ7.87 (d, 4H), δ7.66 (d, 1H), δ7.49 (t, 1H), δ7.39-7.30 (m, 3H), δ7.15-7.13 (m, 3H), δ7.05 (d, 2H), δ6.94 (d, 2H), δ5.08 (s, 2H), δ4.46 (s, 2H), δ3.82 (s, 3H), δ2.99 (s, 9H



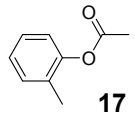
P

Similar procedure to synthesize **M1** was applied.

P (1.07 g, 3.85 mmol) was obtained from 2-phenoxybenzylchloride (855 mg, 4.0 mmol) in 96% yield.

P: ^{1}H-NMR (400 MHz, DMSO-d_6): δ7.52 (t, 1H), δ7.42-7.38 (m, 2H), δ7.36 (d, 1H), δ7.27 (d, 1H),

δ7.16 (t, 2H), δ7.05 (d, 2H), δ4.68 (s, 2H), δ3.10 (s, 9H)

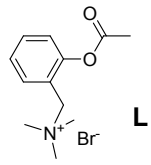


17

17[2]

Acetic anhydride (12.3g, 120 mmol) and triethylamine (30.3 g, 300 mmol) were added to *o*-cresol (10.8 g, 100 mmol) in CH_2Cl_2 (80 ml). The mixture was stirred for 12 h at 25 °C and diluted with ethyl acetate. The mixture was washed with water three times and dried with $MgSO_4$. After filtration, the solvent in the filtrate was removed to obtain **17** (12.9 g, 93 mmol) in 93% yield.

17: ^{1}H-NMR (400 MHz, $CDCl_3$): δ7.23 (t, 1H), δ7.20 (d, 1H), δ7.15 (t, 1H), δ7.00 (d, 1H), δ2.32 (s, 3H), δ2.17 (s, 3H),



L

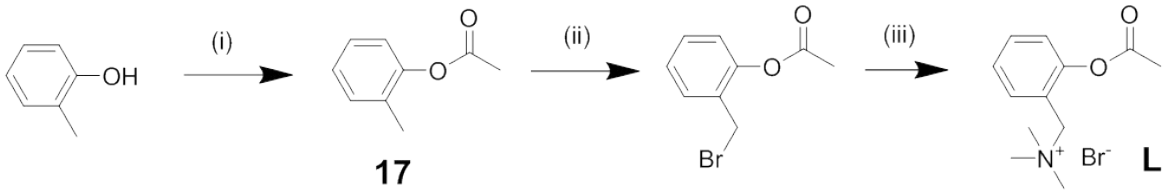
L

N-bromosuccinimide (1.78 g, 10 mml) and azobisisobutyronitrile (10 mg) were added to **17** (1.38 g, 10 mmol) in CCl_4 (30ml). The mixture was stirred at 80 °C for 4 h after flowing nitrogen for 15 min. After the conversion reached to around 80% (checked by H NMR), the mixture was concentrated on a rotary evaporator. Hexane was added to the residue and the resulting solution was filtered to remove succinimide and unreacted *N*-bromosuccinmide. The filtrate was concentrated on a rotary evaporator. The residue was dissolved in THF and stirred for 2 h at 25 °C by adding 30 wt% trimethyl amine aqueous (2.5ml).The mixture was concentrated on a rotary evaporator. The residue was dissolved in water (80 ml) , washed with chloroform (10 ml x 3) to remove unreacted **17** and dried on a rotary evaporator to obtain **L** (1.6 g, 5.6 mmol) in 56% yield.

L: ^{1}H-NMR (400 MHz, $CDCl_3$): δ7.88 (d, 1H), δ7.53 (t, 1H), δ7.35 (t, 1H), δ7.23 (d, 1H), δ5.09 (s,

2H), δ3.44 (s, 9H), δ2.58 (s, 3H),

Scheme S1. Synthesis of **L1**



[a] Reagent and conditions: (i) Ac_2O, TEA, CH_2Cl_2, rt (ii) NBS, AIBN, CCl_4, 80 ^oC (iii) Trimethyl amine $_{(aq)}$, THF, rt

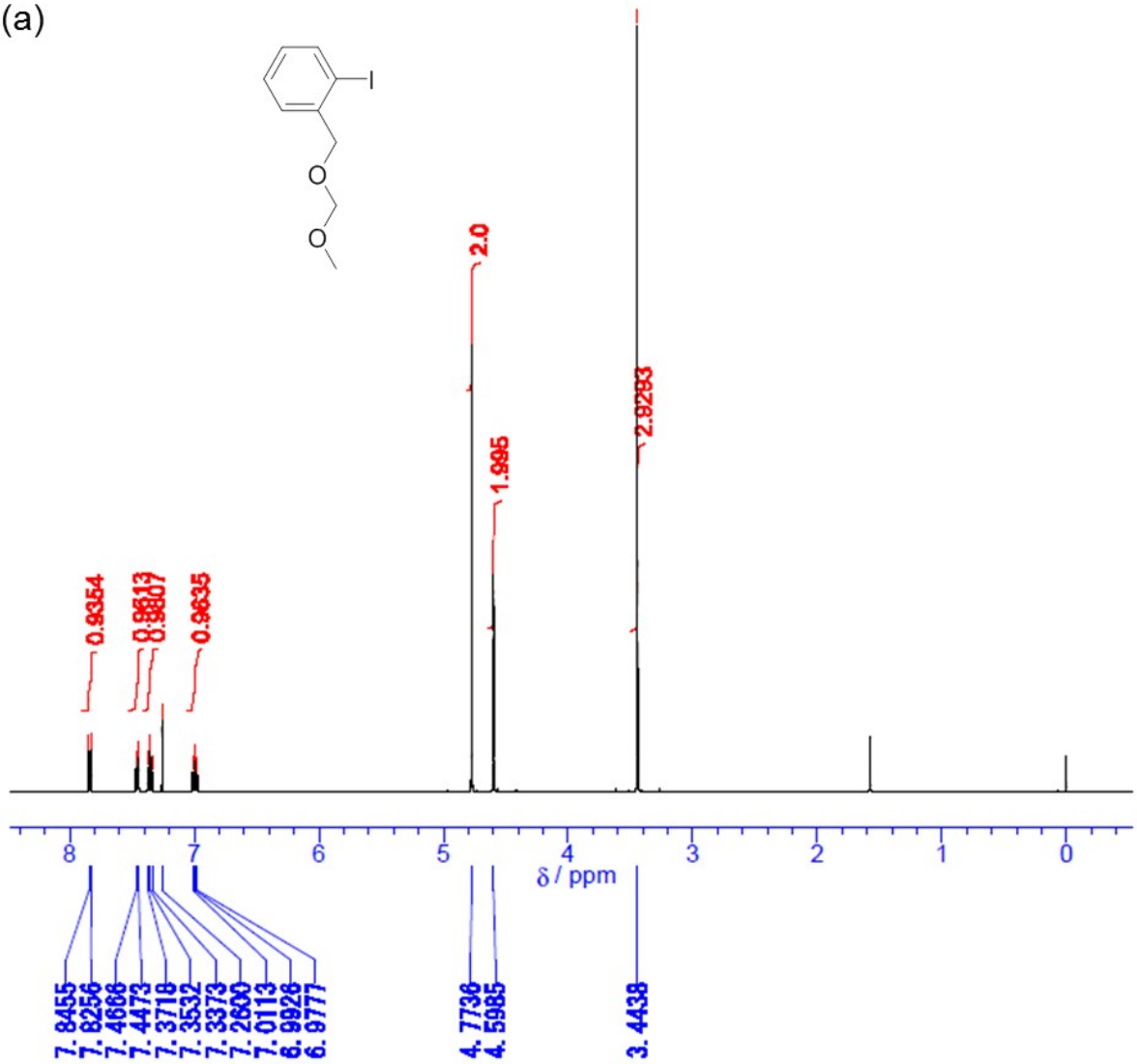
Figure S1. ^{1}H NMR spectra of synthetic intermediate of **M1-M6, P** and **L** in $CDCl_3$

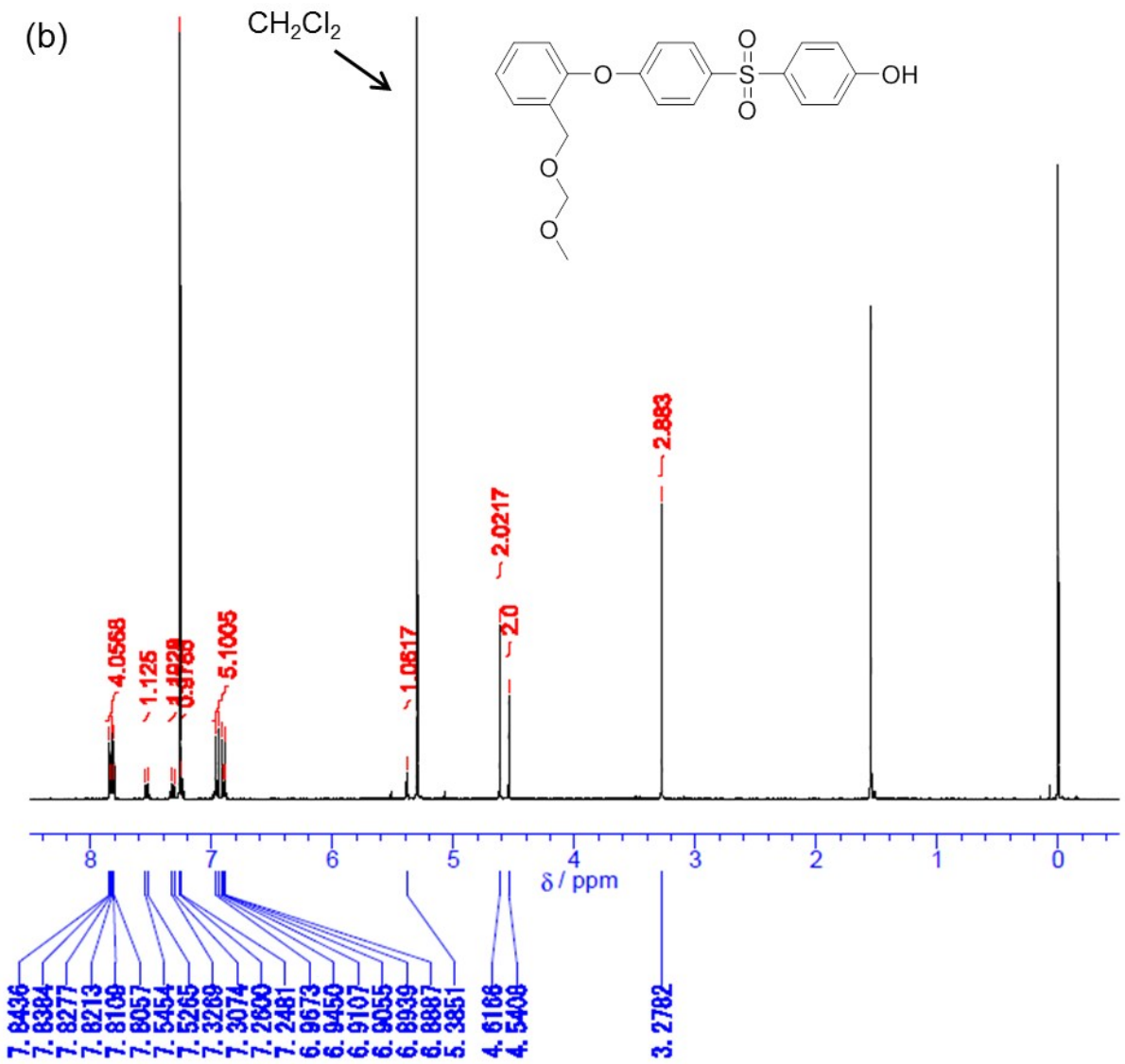
(a) **1** (b) **2** (c) **3** (d) **4** (e) **5** (f) **6** (g) **M1** (h) **M2*** (i) **M3*** (j) **7** (k) **8** (l) **M4*** (m) **9** (n) **10** (o) **11**

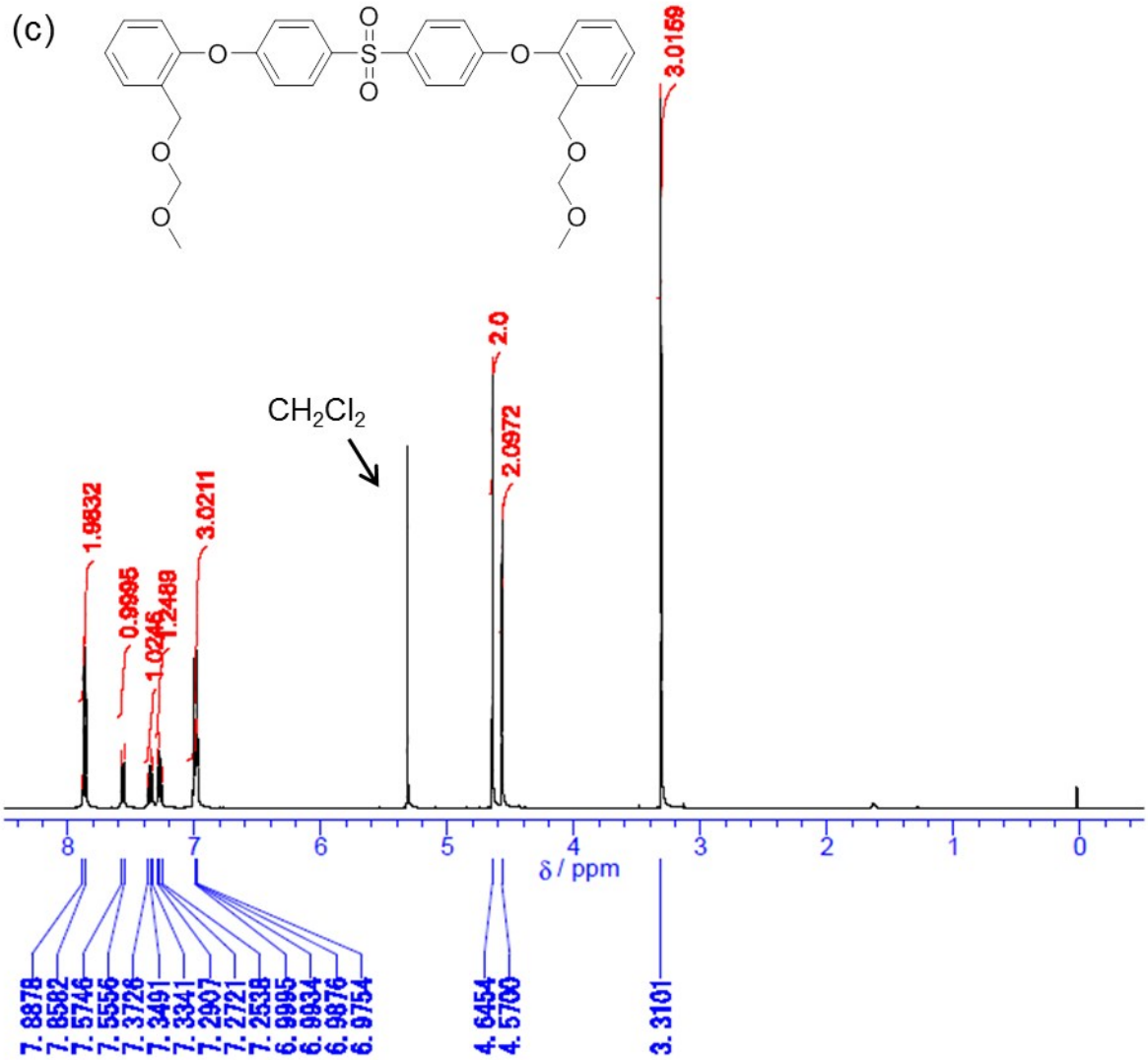
(p) **12** (q) **13** (r) **14**(s) **M5** (t) **15** (u) **16** (v) **M6*** (w) **P*** (x) **17** (y) **L**

* ^{1}H NMR spectra in DMSO-d_6

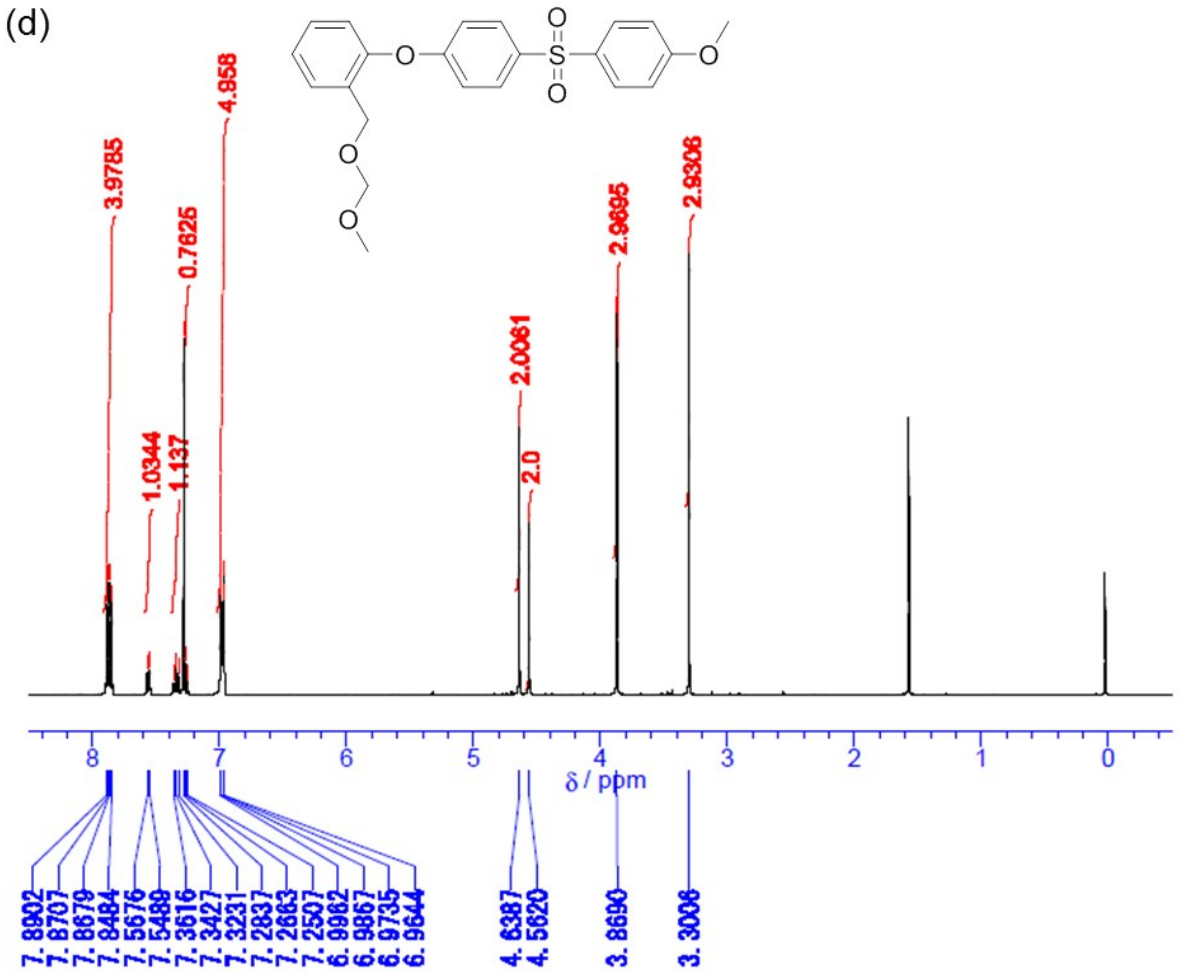
(a)


I
O
O
2.0
1.995
2.8283
0.9354
0.9635
8
7
6
5
4
3
2
1
0
δ / ppm
7.8455
7.8256
7.4666
7.4473
7.3718
7.3532
7.3373
7.2600
7.0113
6.9928
6.9777
4.7730
4.5985
3.4438

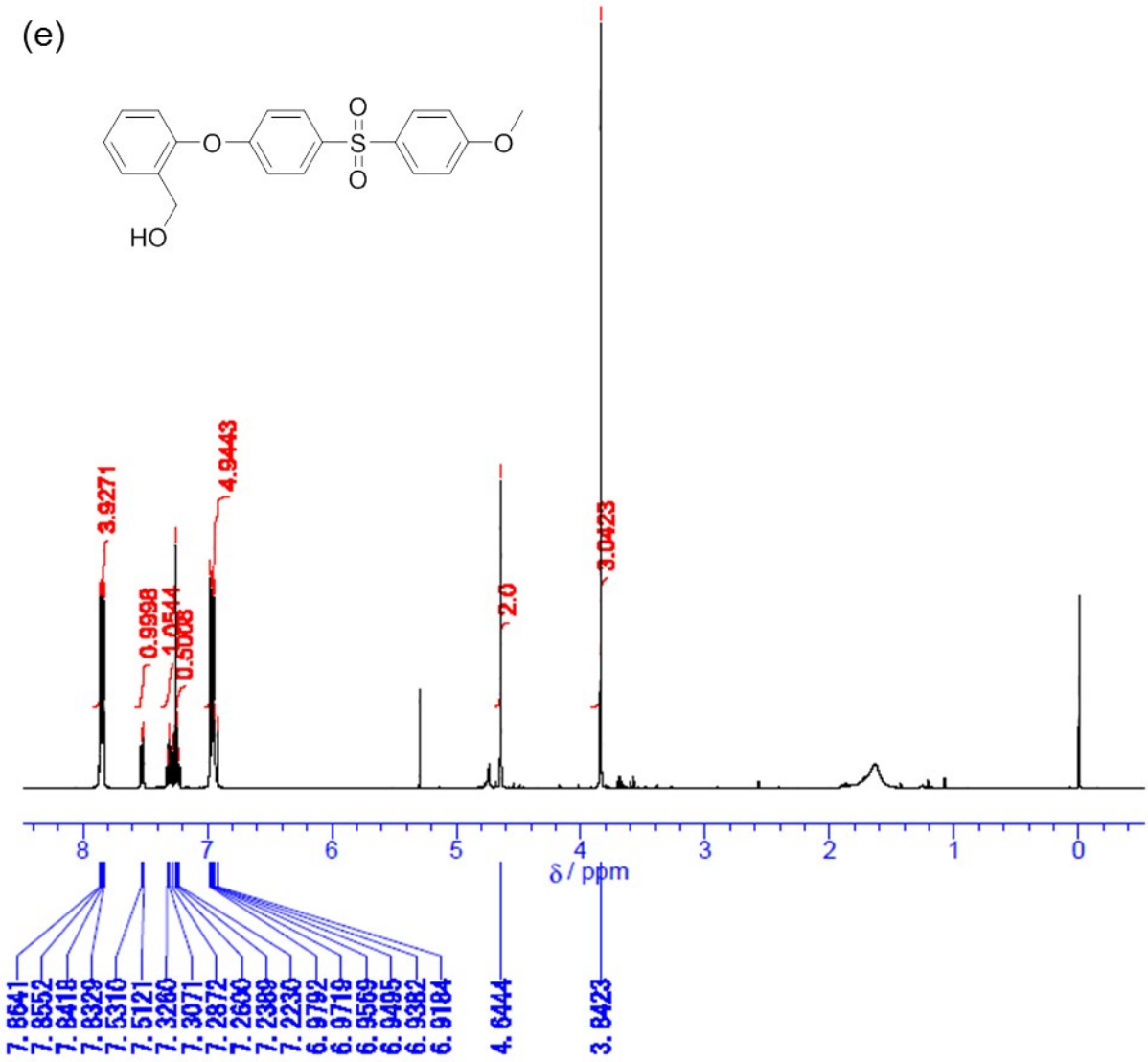

(b)
CH_2Cl_2
O
S
O
O
OH
O
O
4.0588
1.125
5.1005
1.0617
2.0217
2.0
2.883
8
7
6
5
4
3
2
1
0
δ / ppm
7.8436
7.8384
7.8277
7.8213
7.8108
7.8057
7.5454
7.5265
7.3269
7.3074
7.2600
7.2481
6.9673
6.9450
6.9107
6.9055
6.8939
6.8887
5.3851
4.6166
4.5408
3.2782


(c)
O
O
S
O
O
O
O
O
O
O
3.0159
2.0
2.0972
CH2Cl2
1.9832
0.9995
1.0246
1.2489
3.0211
8
7
6
5
4
3
2
1
0
δ / ppm
7.8878
7.8582
7.5746
7.5556
7.3726
7.3491
7.3341
7.2907
7.2721
7.2538
6.9995
6.9834
6.9876
6.9754
4.6454
4.5700
3.3101

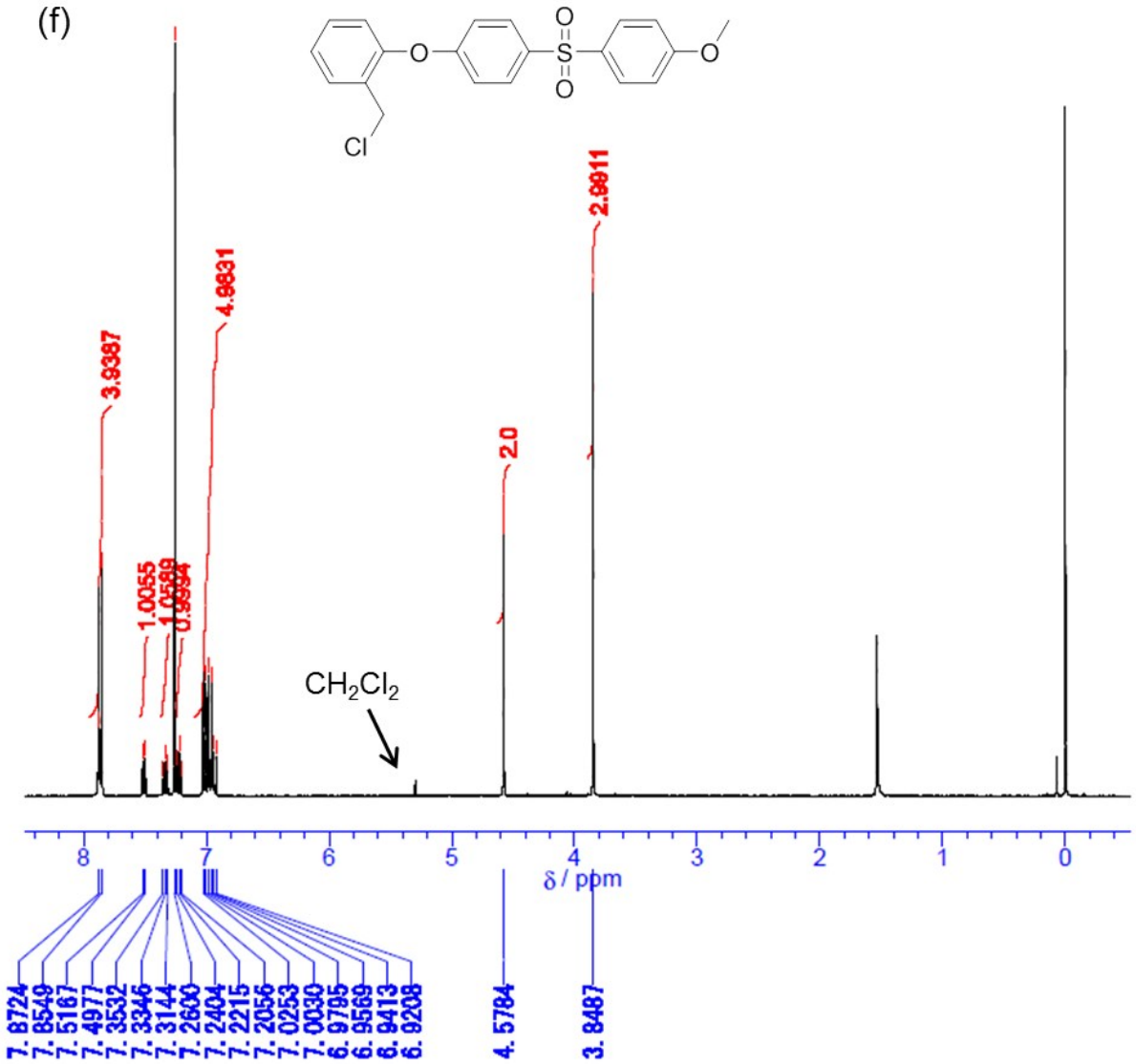
(d)

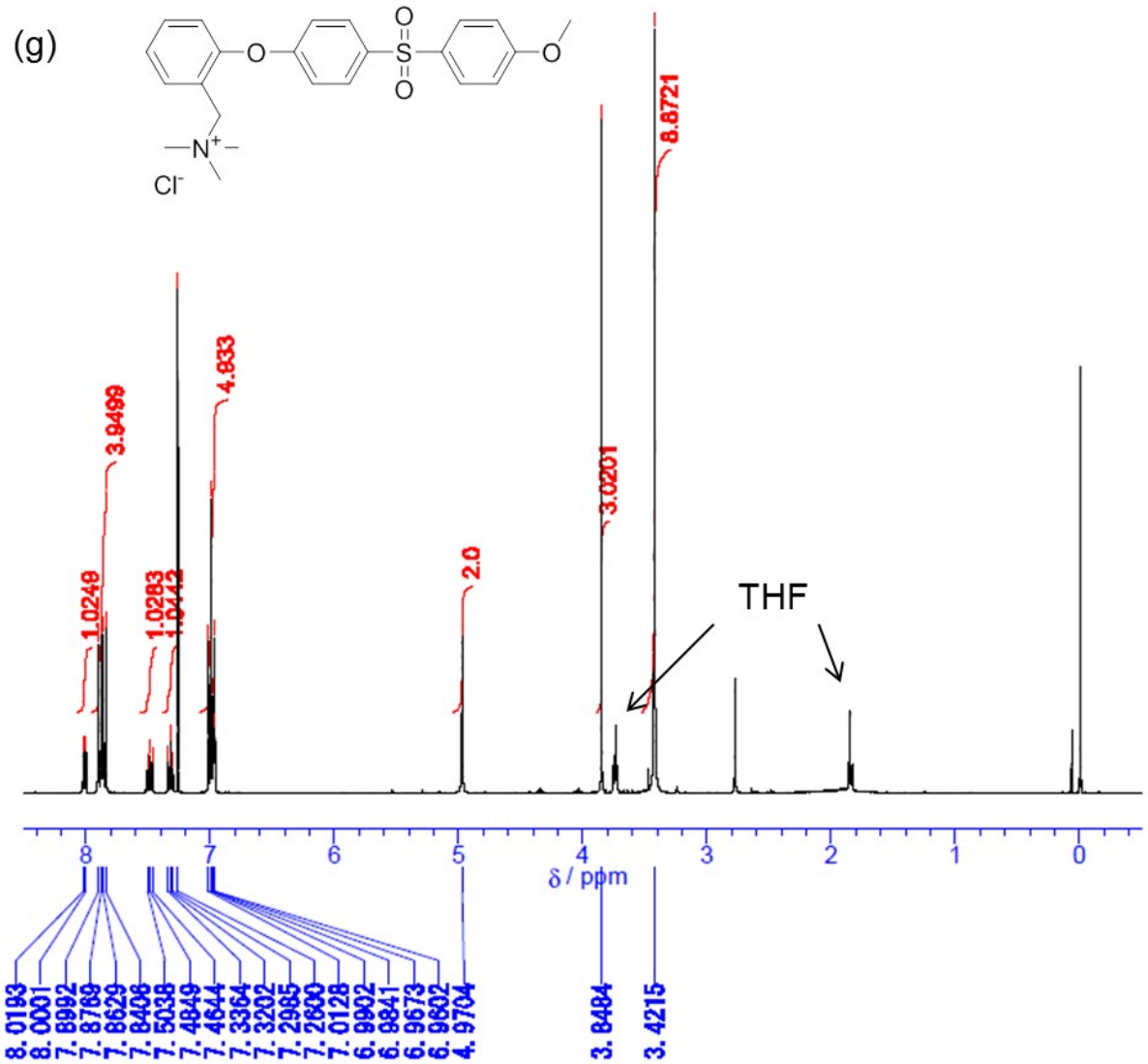

3.9785
1.0344
1.137
0.7625
4.858
2.0061
2.0
2.9695
2.9306
8
7
6
5
4
3
2
1
0
δ / ppm
7.8902
7.8707
7.8679
7.8484
7.5676
7.5489
7.3616
7.3427
7.3231
7.2837
7.2663
7.2507
6.9962
6.9867
6.9735
6.9644
4.6387
4.5620
3.8690
3.3006

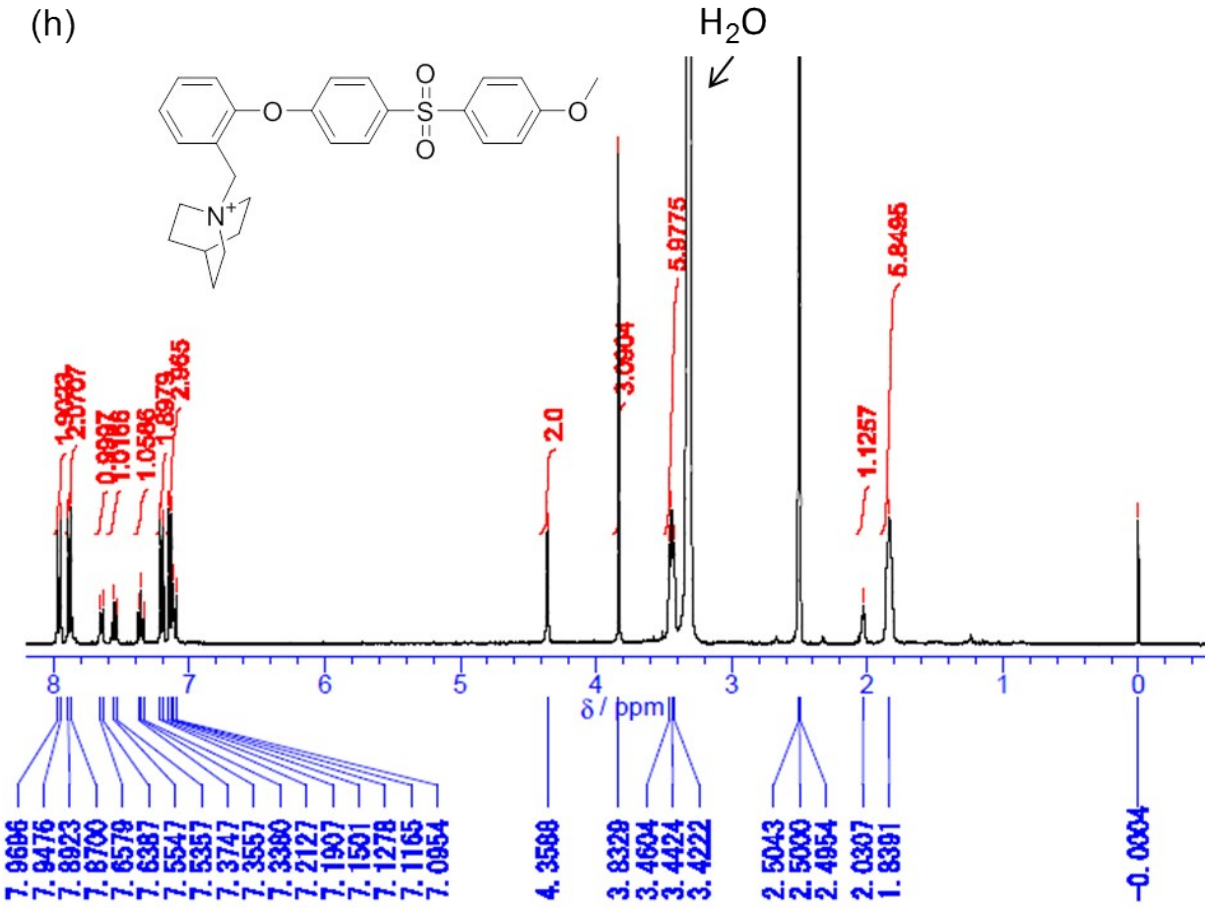
(e)


O
S
O
O
O
HO
3.9271
0.9998
1.0544
0.5008
4.9443
2.0
3.0423
8
7
6
5
4
3
2
1
0
δ / ppm
7.8641
7.8552
7.8418
7.8329
7.5310
7.5121
7.3260
7.3071
7.2872
7.2600
7.2389
7.2230
6.9792
6.9719
6.9569
6.9485
6.9382
6.9184
4.6444
3.8423

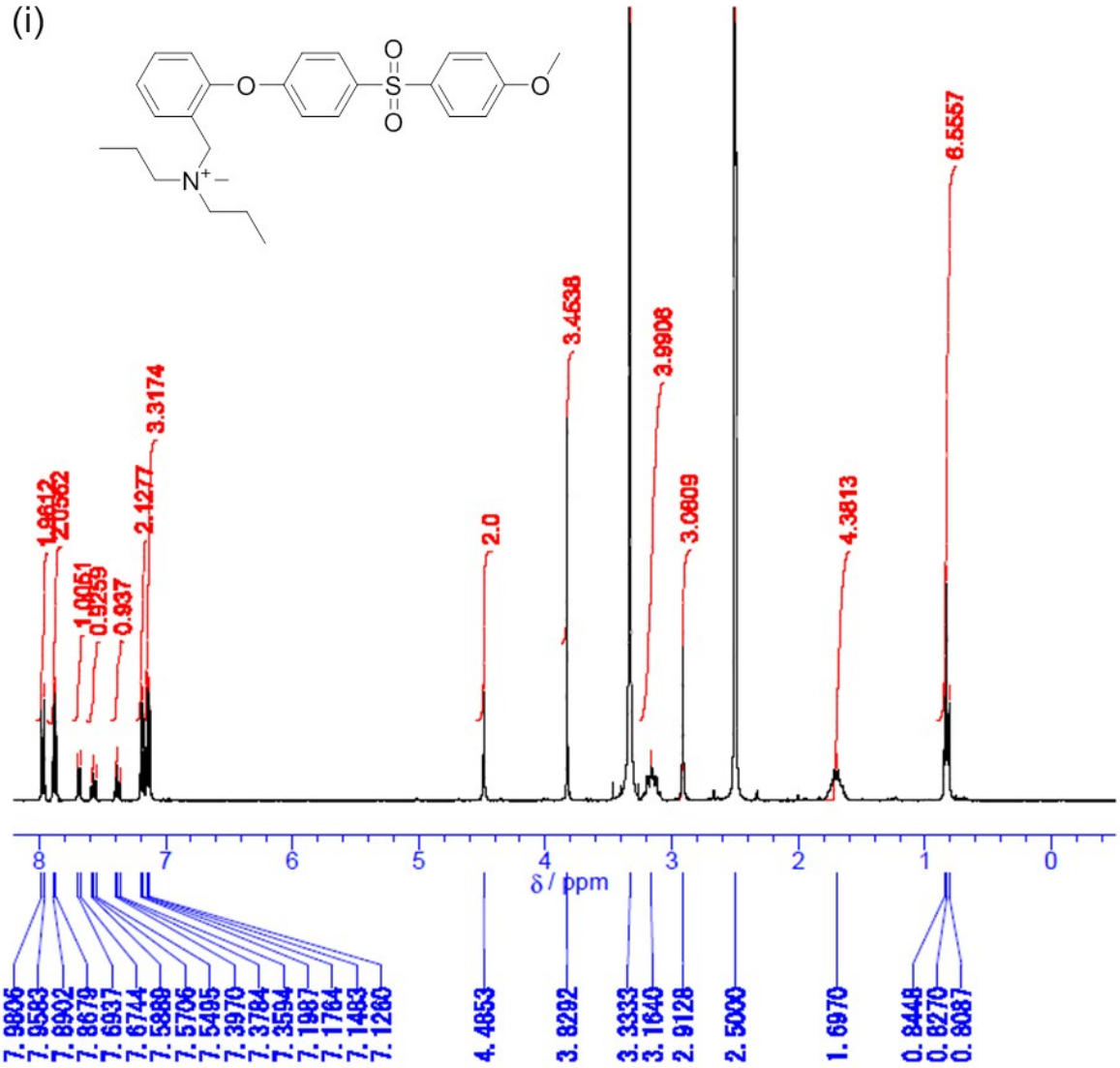
(f)


O
S
O
O
O
Cl
3.9387
4.9831
2.9911
2.0
1.0055
CH2Cl2
8
7
6
5
4
3
2
1
0
δ / ppm
7.8724
7.8549
7.5167
7.4977
7.3532
7.3346
7.3144
7.2600
7.2404
7.2215
7.2056
7.0253
7.0030
6.9795
6.9569
6.9413
6.9208
4.5784
3.8487

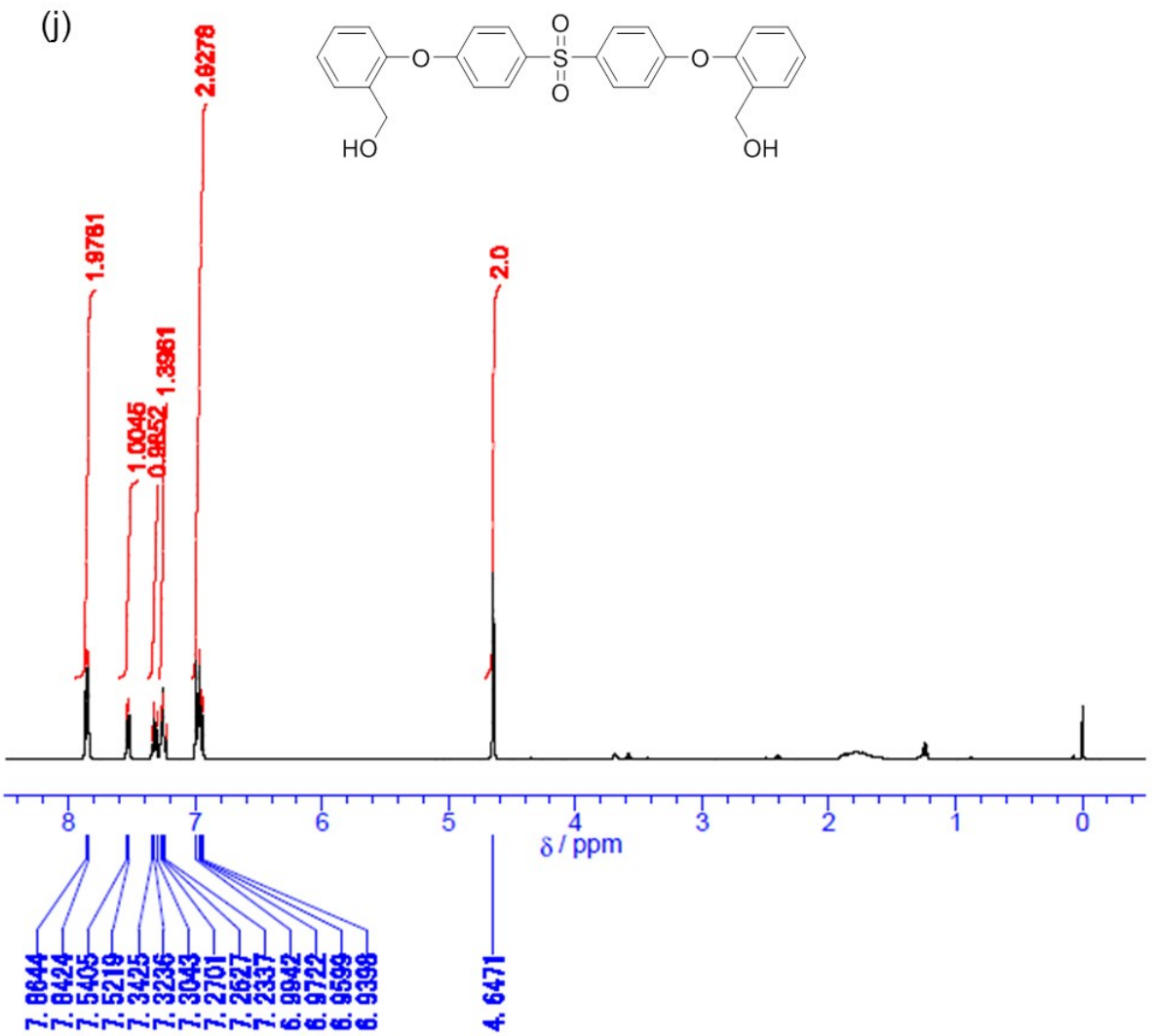

(g)
O
S
O
O
O
N+
Cl-
8.8721
4.833
3.9499
3.0201
2.0
1.0249
1.0283
1.0442
THF
8
7
6
5
4
3
2
1
0
δ / ppm
8.0183
8.0001
7.8992
7.8769
7.8629
7.8406
7.5038
7.4849
7.4644
7.3364
7.3202
7.2985
7.2600
7.0128
6.9902
6.9841
6.9673
6.9602
4.9704
3.8484
3.4215


(h)
H_2O
δ / ppm

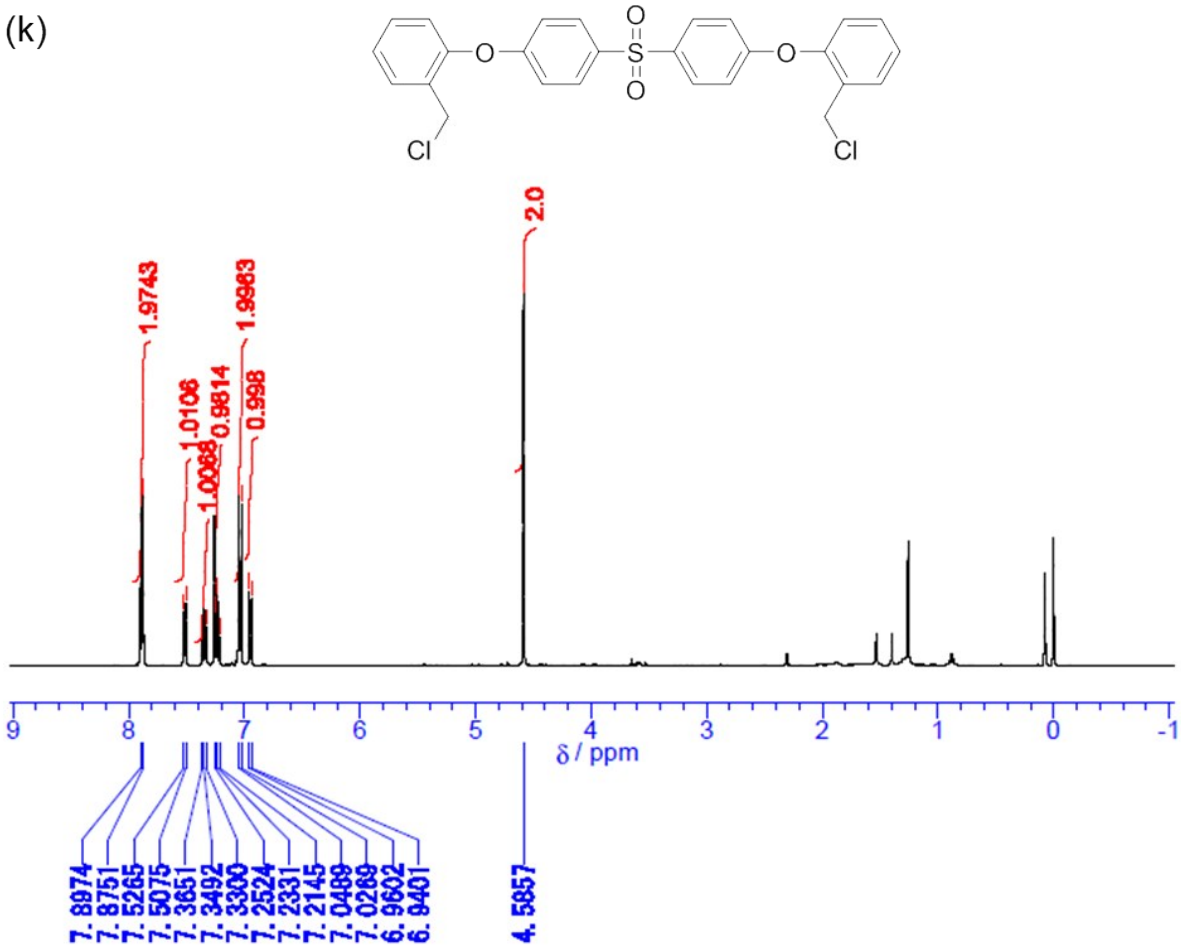
(i)


O
S
O
O
O
N+
6.5557
3.4538
3.9906
3.3174
2.1277
2.0
3.0809
4.3813
0.937
δ / ppm
8
7
6
5
4
3
2
1
0
7.9806
7.9583
7.8902
7.8679
7.6937
7.6744
7.5888
7.5706
7.5495
7.3970
7.3784
7.3594
7.1987
7.1764
7.1483
7.1260
4.4853
3.8292
3.3333
3.1640
2.9128
2.5000
1.6970
0.8448
0.8270
0.8087

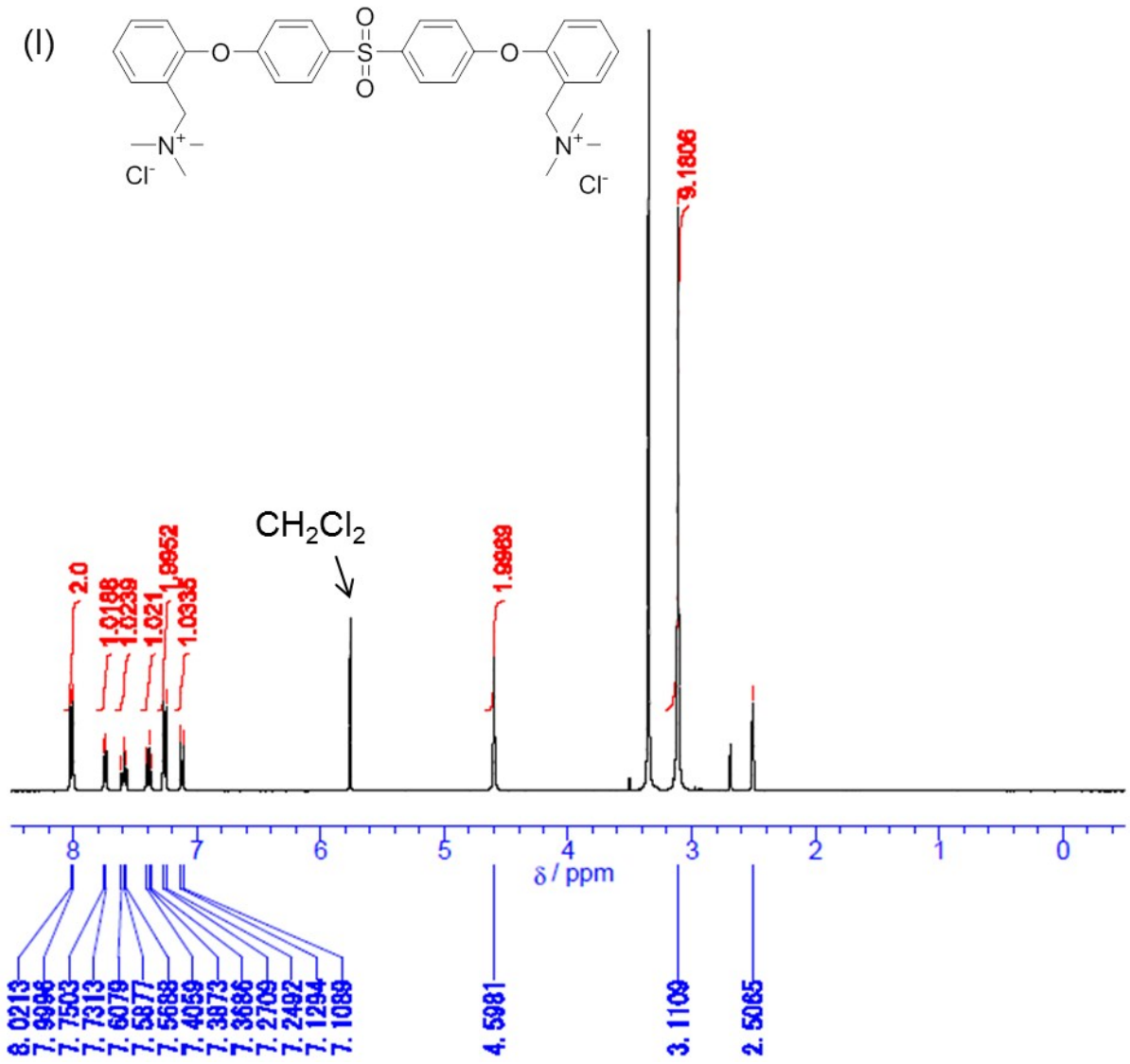
(j)


HO
OH
2.0278
1.9761
2.0
1.3961
1.0046
0.9852
8
7
6
5
4
3
2
1
0
δ / ppm
7.8644
7.8424
7.5405
7.5219
7.3425
7.3236
7.3043
7.2701
7.2627
7.2337
6.9942
6.9722
6.9599
6.9398
4.6471

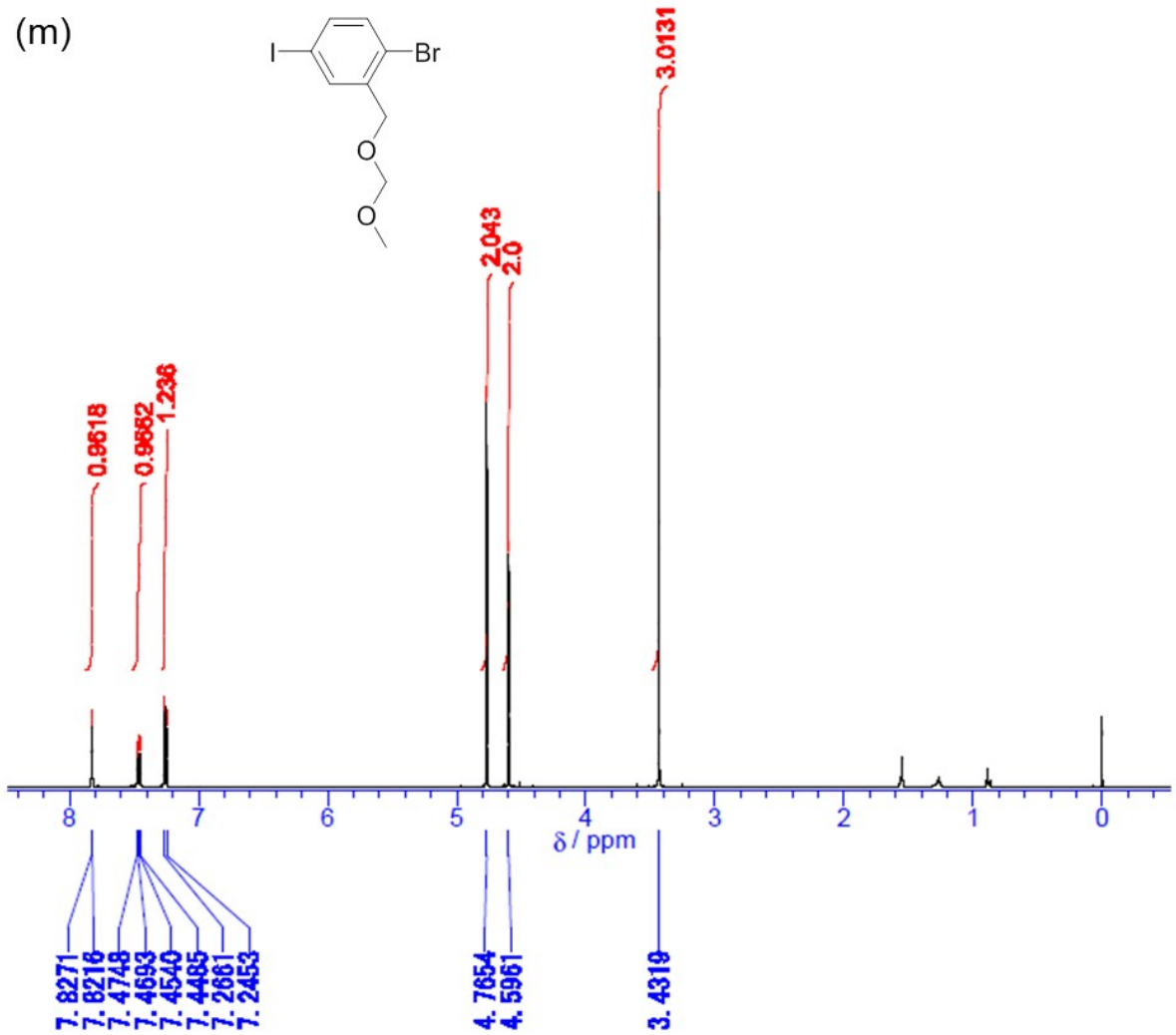
(k)

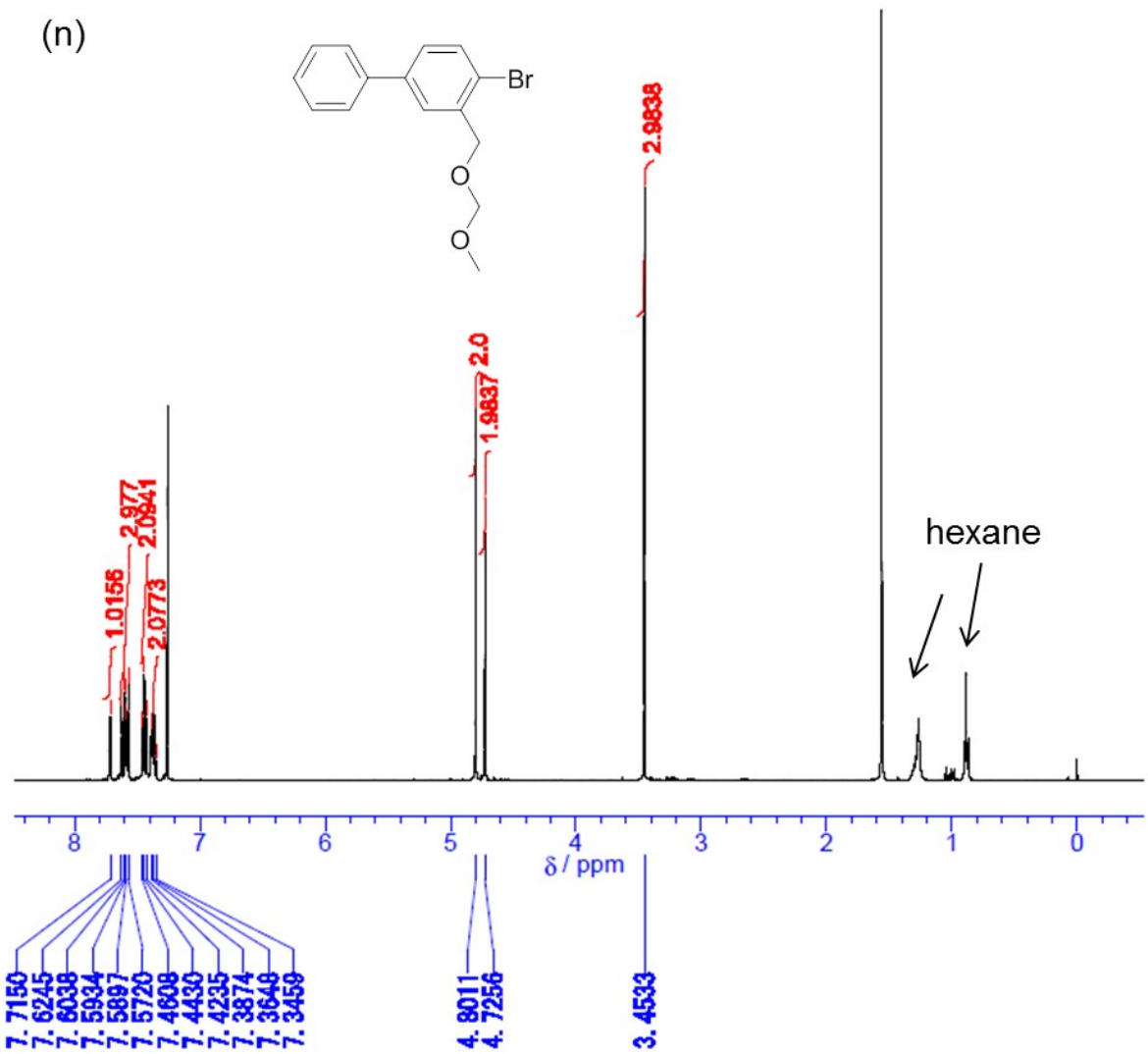

O
S
O
O
O
Cl
Cl
2.0
1.9743
1.9963
1.0106
0.9814
0.998
9
8
7
6
5
4
3
2
1
0
-1
δ / ppm
7.8974
7.8751
7.5265
7.5075
7.3651
7.3492
7.3300
7.2524
7.2331
7.2145
7.0489
7.0269
6.9602
6.9401
4.5857

(I)

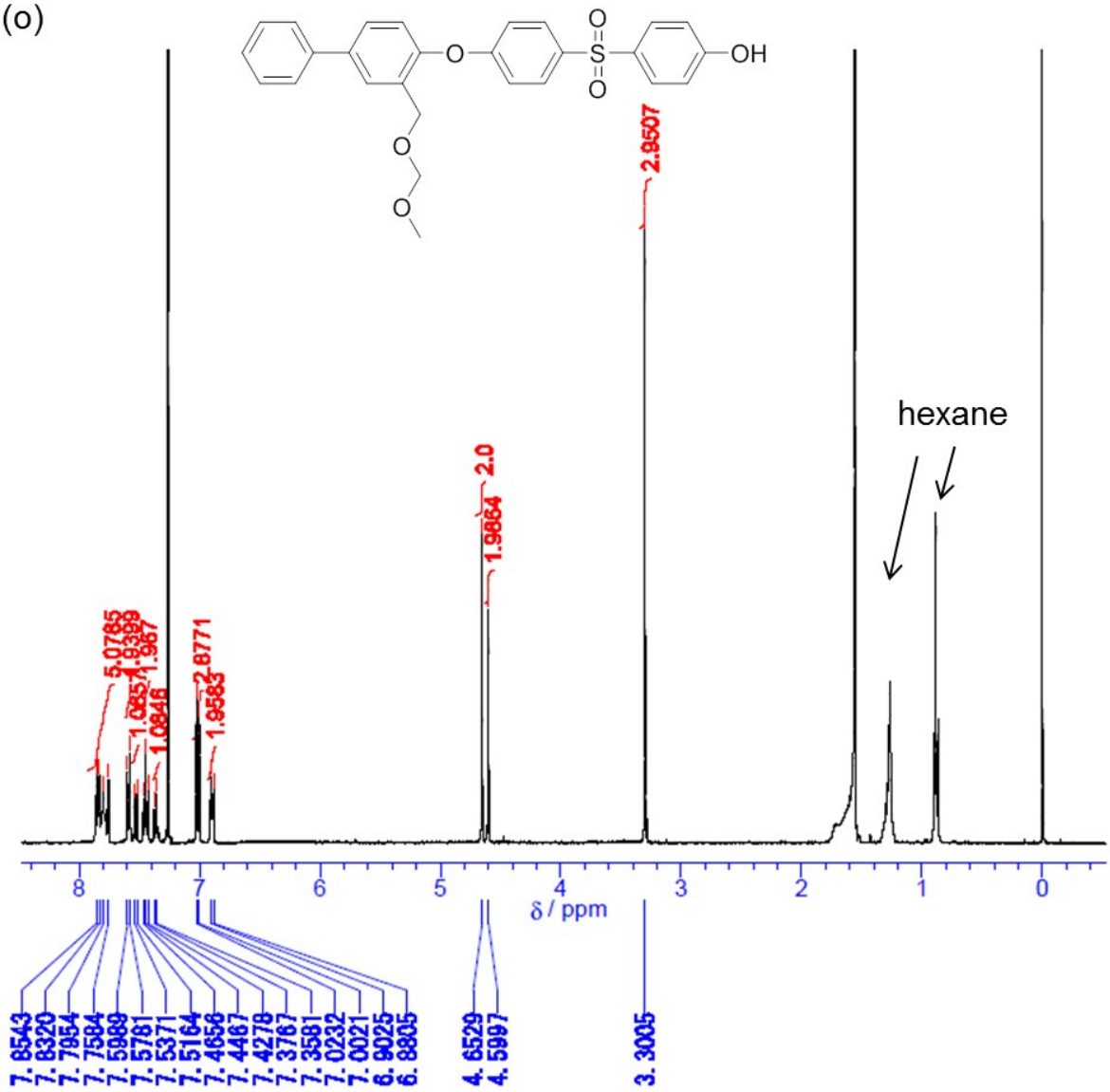

O
S
O
O
O
N+
Cl-
N+
Cl-
CH2Cl2
9.1806
2.0
1.0188
1.0239
1.021
1.9652
1.0335
1.9988
8
7
6
5
4
3
2
1
0
δ / ppm
8.0213
7.9996
7.7503
7.7313
7.6079
7.5877
7.5688
7.4059
7.3873
7.3686
7.2709
7.2492
7.1294
7.1089
4.5981
3.1109
2.5065

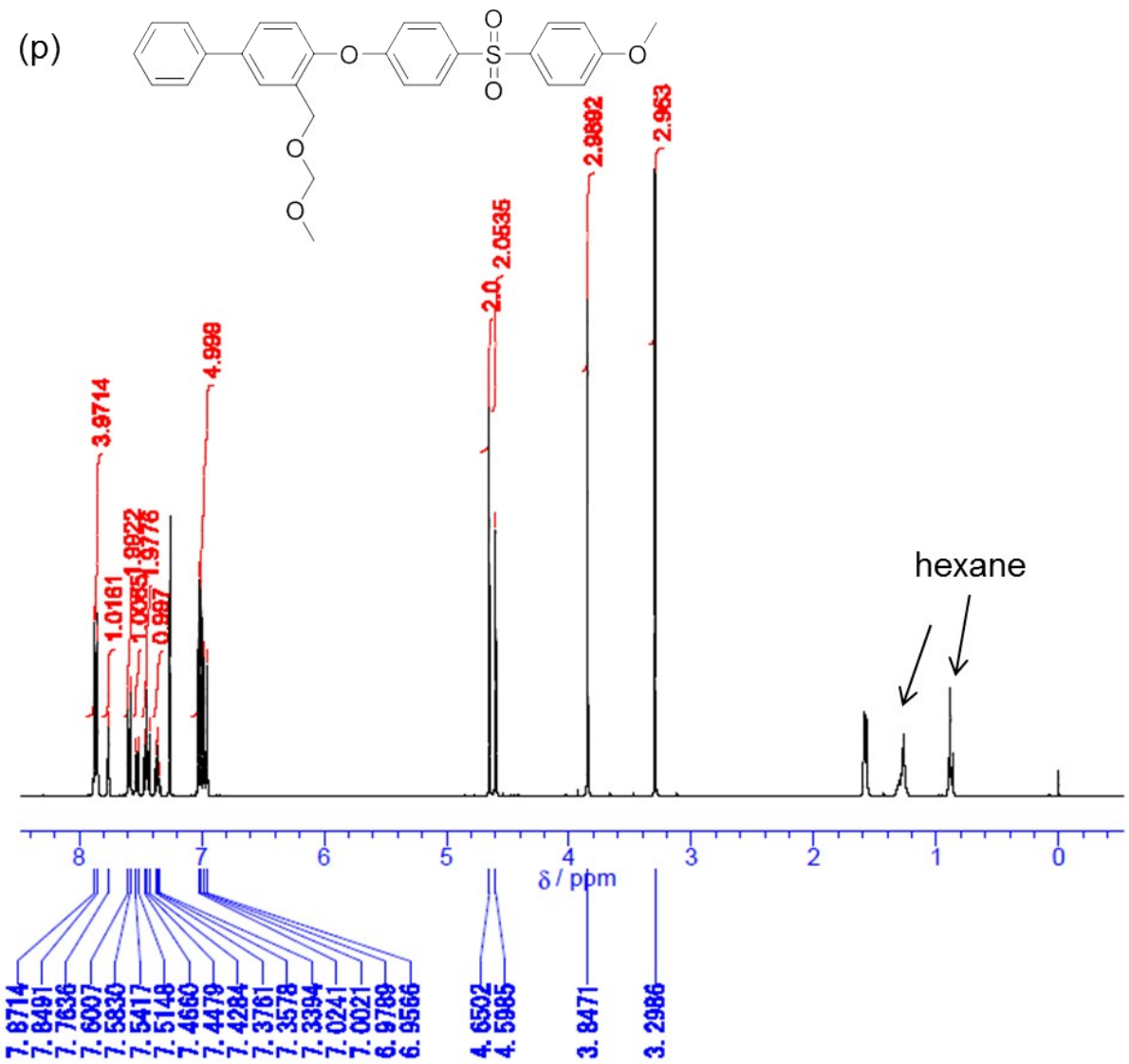
(m)

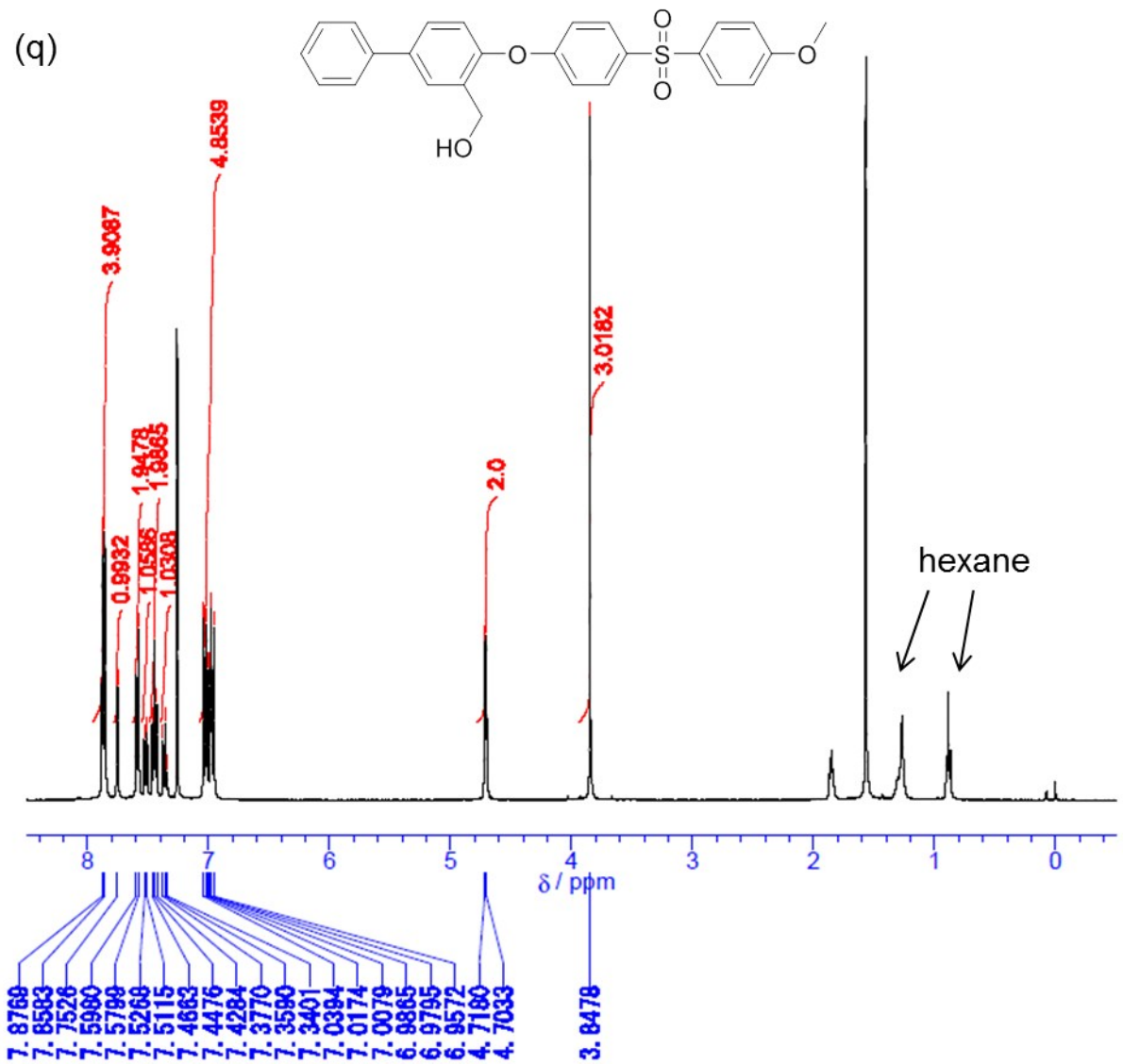

I
Br
O
O
3.0131
2.043
2.0
0.9618
0.9562
1.236
8
7
6
5
4
3
2
1
0
δ / ppm
7.8271
7.8216
7.4748
7.4693
7.4540
7.4485
7.2661
7.2453
4.7654
4.5961
3.4319


(n)
Br
O
O
2.9838
2.0
1.9837
2.977
2.0941
1.0156
2.0773
hexane
8
7
6
5
4
3
2
1
0
δ / ppm
7.7150
7.6245
7.6038
7.5934
7.5897
7.5720
7.4608
7.4430
7.4235
7.3874
7.3640
7.3459
4.8011
4.7256
3.4533

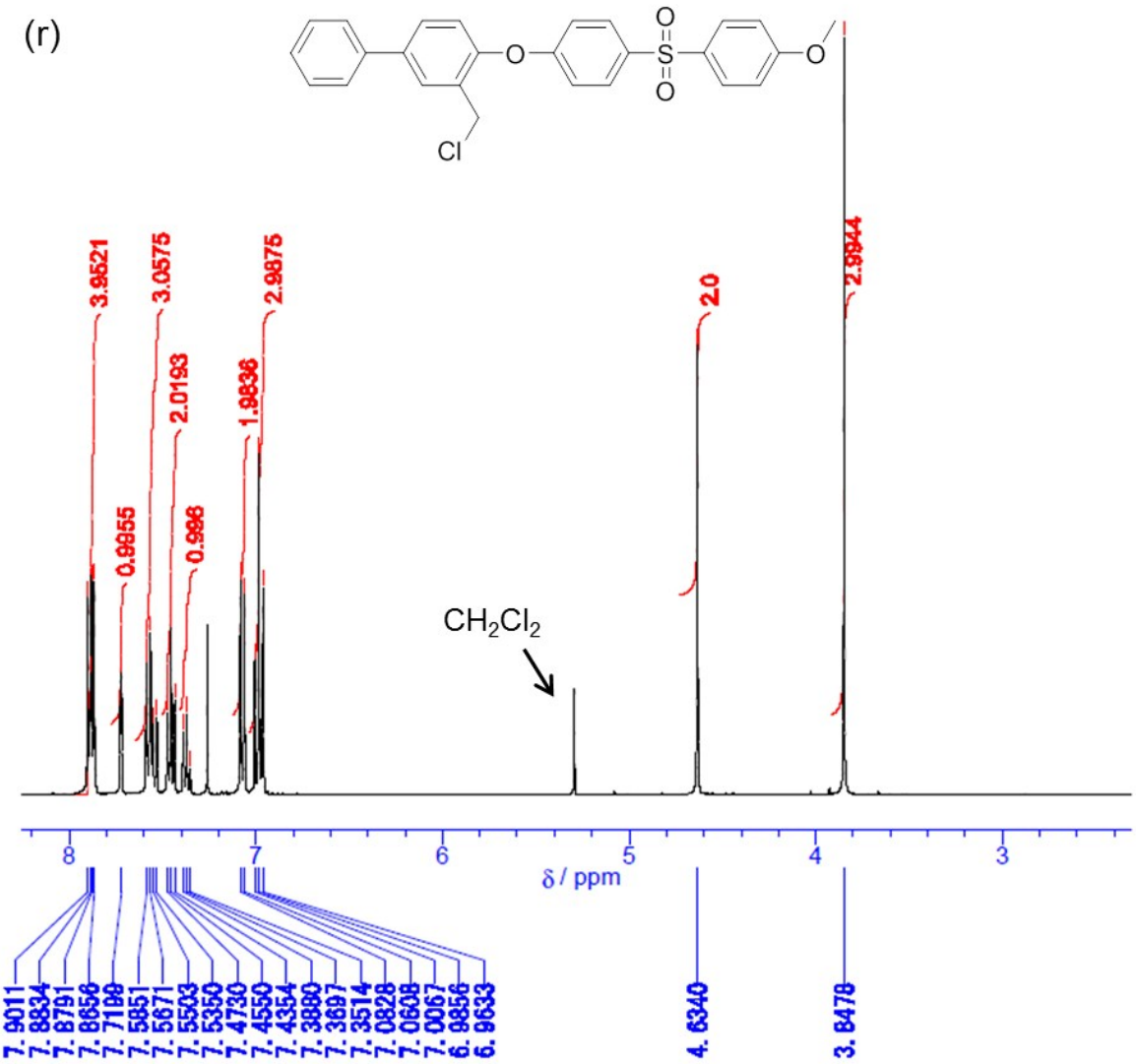
(o)


O
S
O
O
OH
O
O
2.9507
2.0
1.9864
hexane
5.0785
1.9399
1.9670
1.0857
1.0846
2.8771
1.9583
8
7
6
5
4
3
2
1
0
δ / ppm
7.8543
7.8320
7.7954
7.7584
7.5989
7.5781
7.5371
7.5164
7.4656
7.4467
7.4278
7.3767
7.3581
7.0232
7.0021
6.9025
6.8805
4.6529
4.5997
3.3005

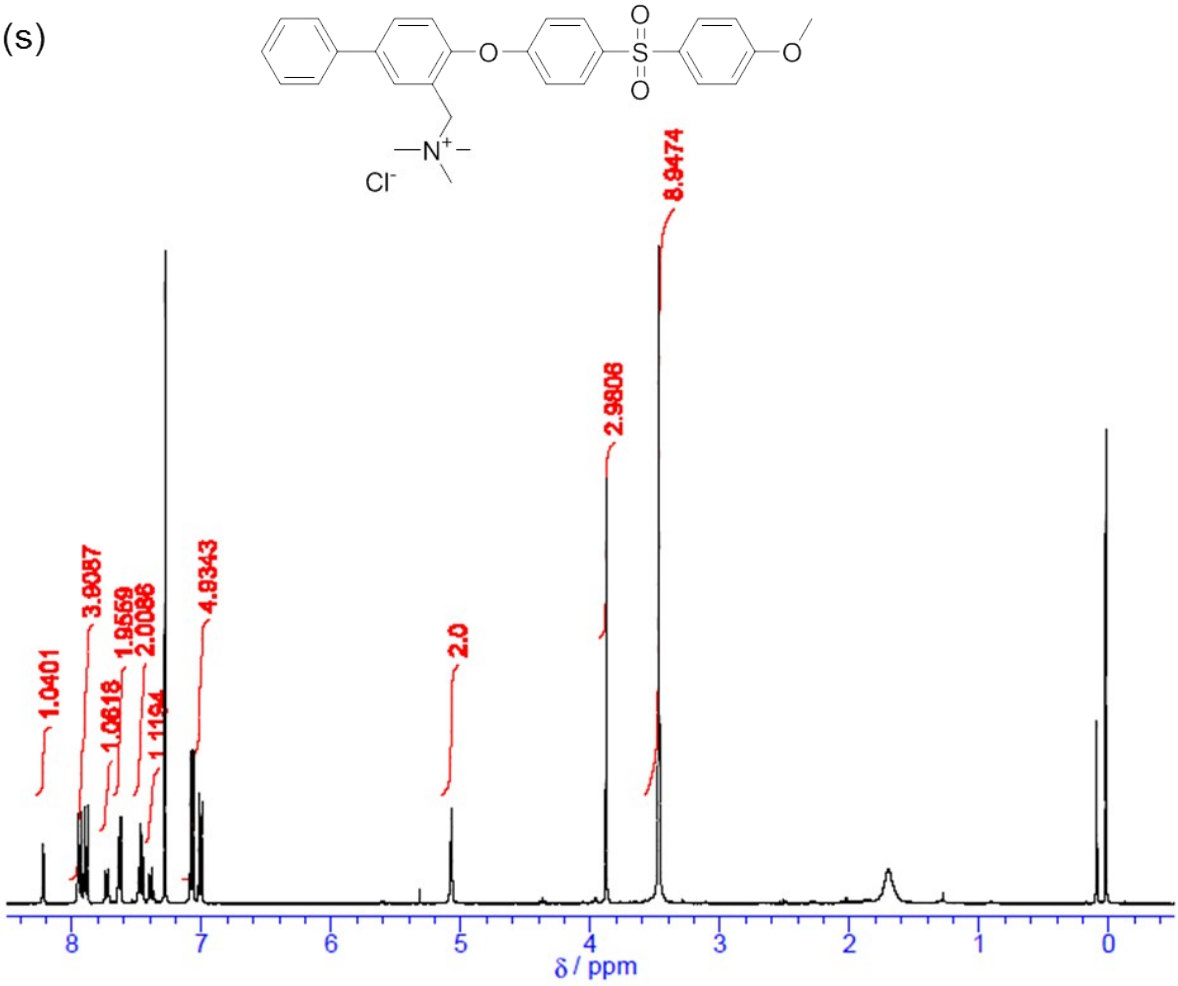

(p)
O
O
S
O
O
O
O
3.9714
4.998
2.0535
2.0
2.9892
2.963
1.0161
hexane
8
7
6
5
4
3
2
1
0
δ / ppm
7.8714
7.8491
7.7636
7.6007
7.5830
7.5417
7.5148
7.4660
7.4479
7.4284
7.3761
7.3578
7.3394
7.0241
7.0021
6.9789
6.9566
4.6502
4.5985
3.8471
3.2986


(q)
HO
O
S
O
O
O
3.9087
4.8539
3.0182
2.0
0.9932
hexane
δ / ppm
7.8769
7.8583
7.7526
7.5980
7.5798
7.5268
7.5115
7.4663
7.4476
7.4284
7.3770
7.3590
7.3401
7.0394
7.0174
7.0079
6.9865
6.9795
6.9572
4.7180
4.7033
3.8478

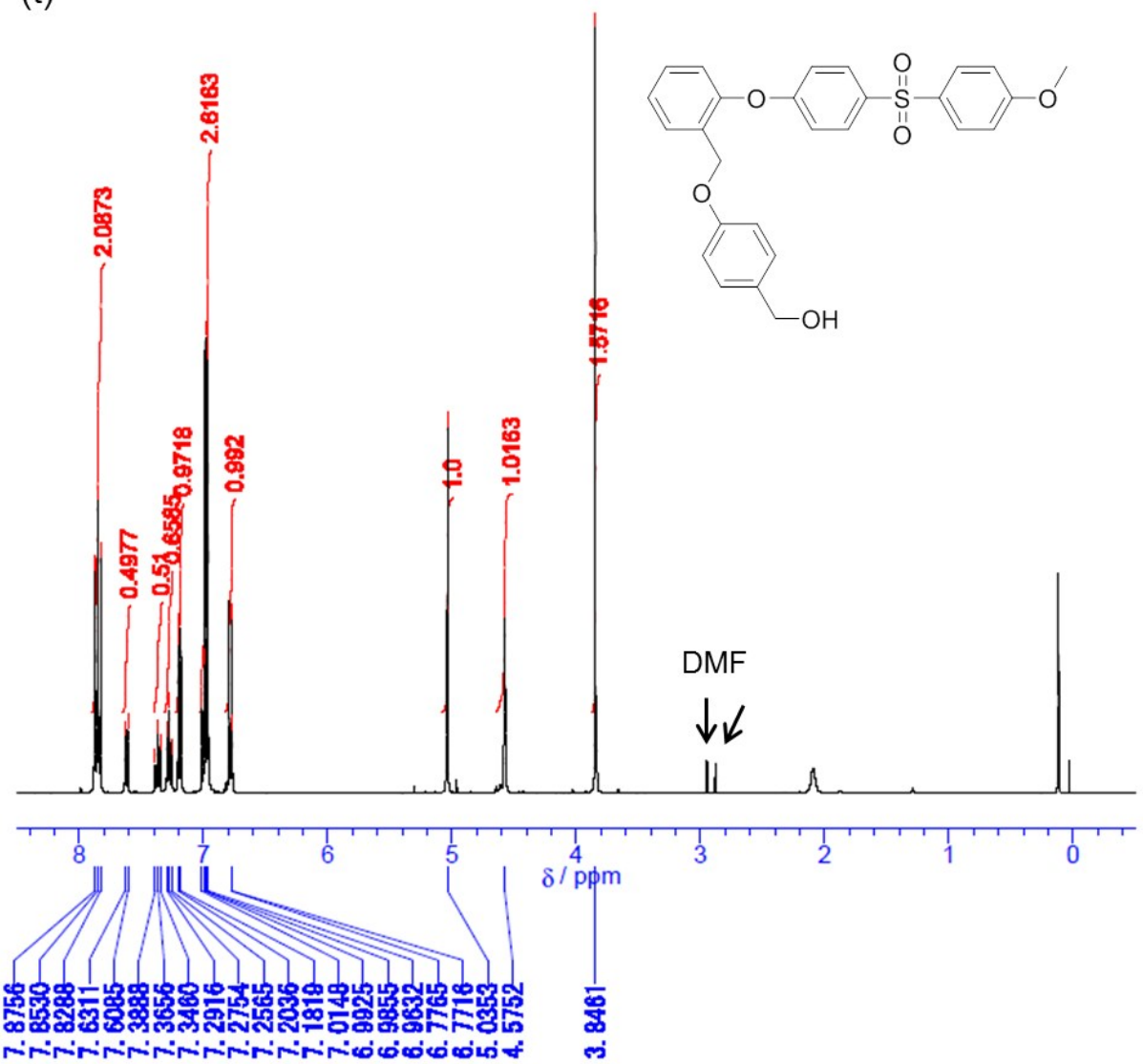
(r)


O
S
O
O
O
Cl
3.9521
3.0575
2.0193
1.9836
2.9875
0.9855
0.998
2.0
2.9944
CH2Cl2
8
7
6
5
4
3
δ / ppm
7.9011
7.8834
7.8791
7.8656
7.7198
7.5851
7.5671
7.5503
7.5350
7.4730
7.4550
7.4354
7.3880
7.3697
7.3514
7.0828
7.0608
7.0067
6.9856
6.9633
4.6340
3.8478

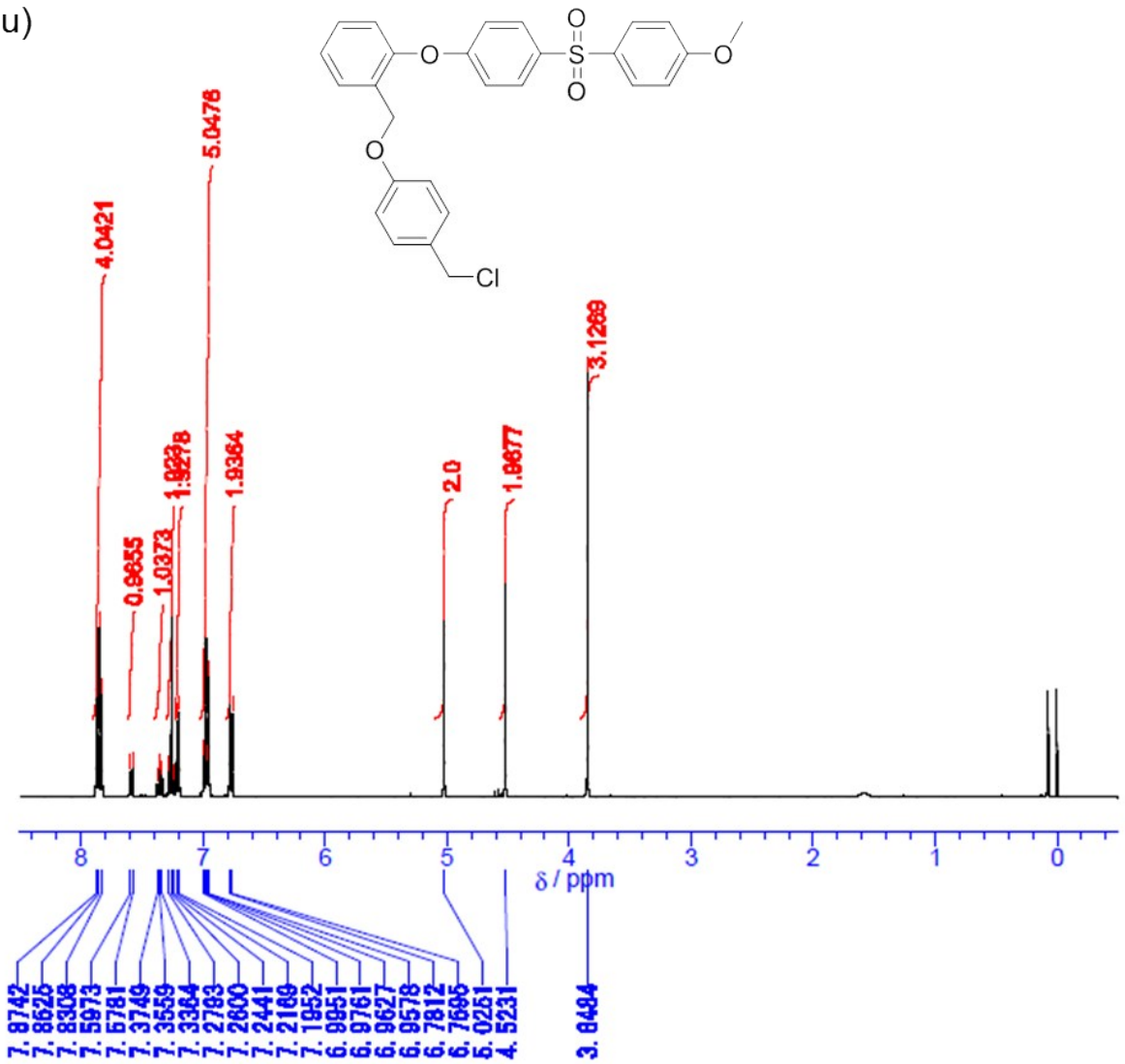
(s)


O
S
O
O
O
N+
Cl-
8.9474
2.9808
4.8343
3.8087
1.9559
2.0086
1.0618
1.1194
1.0401
2.0
8
7
6
5
4
3
2
1
0
δ / ppm

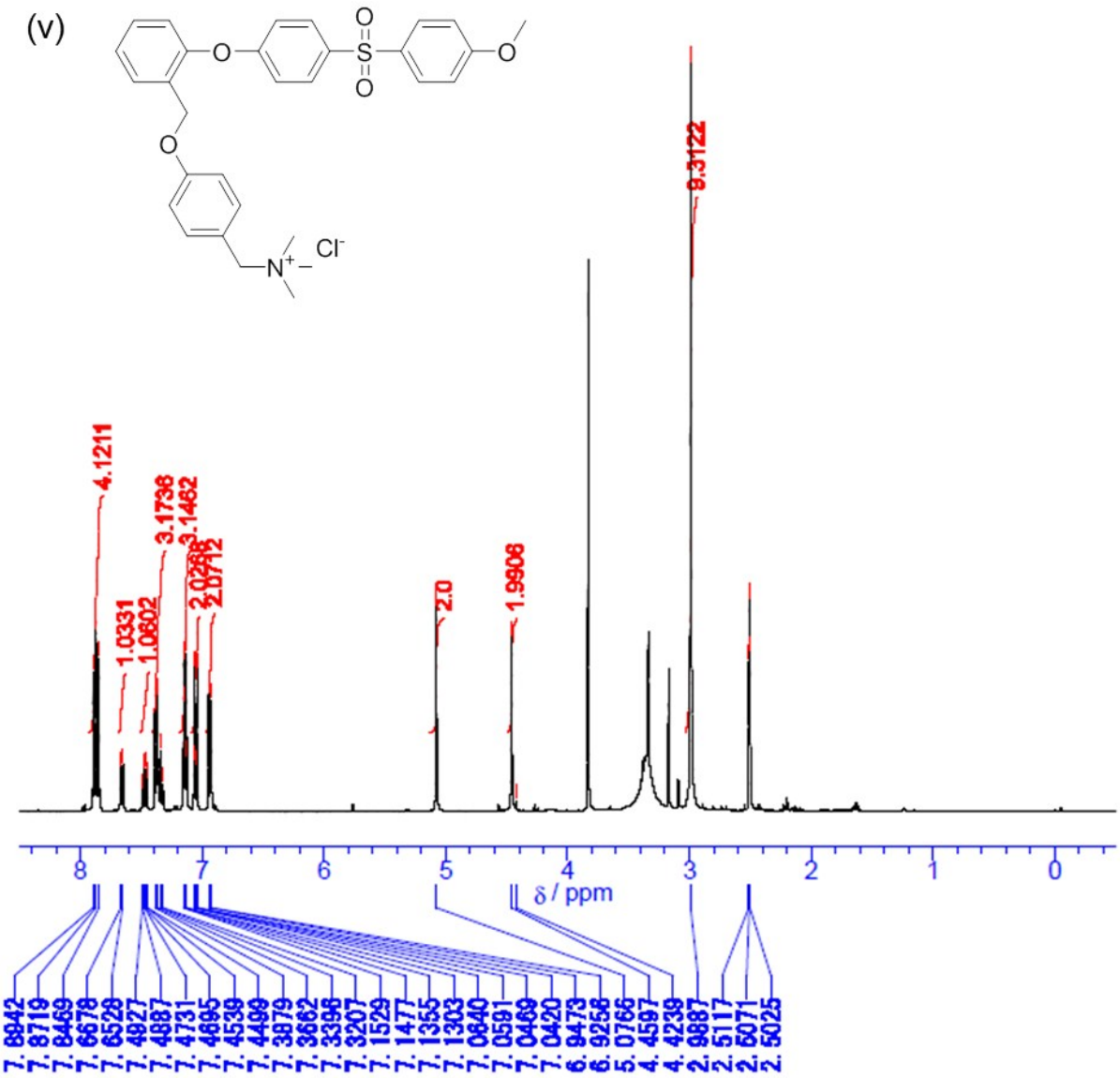
(t)


2.0873
2.6183
0.4977
0.51
0.9718
0.992
1.0
1.0163
1.5716
DMF
O
S
O
O
O
OH
8
7
6
5
4
3
2
1
0
δ / ppm
7.8756
7.8530
7.8288
7.6311
7.6085
7.3888
7.3656
7.3460
7.2916
7.2754
7.2565
7.2036
7.1819
7.0148
6.9925
6.9855
6.9632
6.7765
6.7718
5.0353
4.5752
3.8461

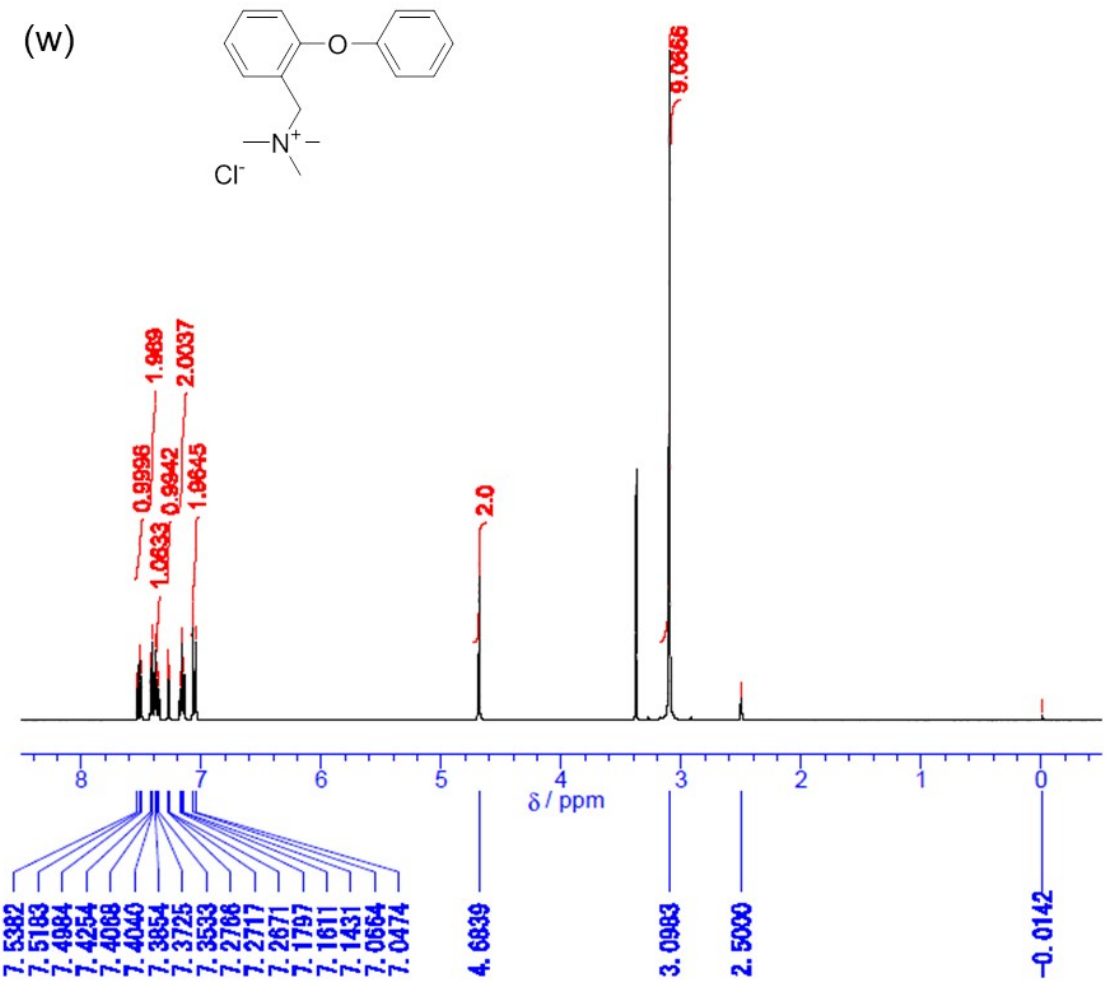
(u)


O
O
S
O
O
O
Cl
4.0421
0.9855
1.0373
1.9364
5.0476
2.0
1.8677
3.1269
8
7
6
5
4
3
2
1
0
δ / ppm
7.8742
7.8625
7.8308
7.5973
7.5781
7.3749
7.3559
7.3364
7.2783
7.2600
7.2441
7.2169
7.1952
6.9951
6.9761
6.9627
6.9578
6.7812
6.7695
6.0251
4.5231
3.8484

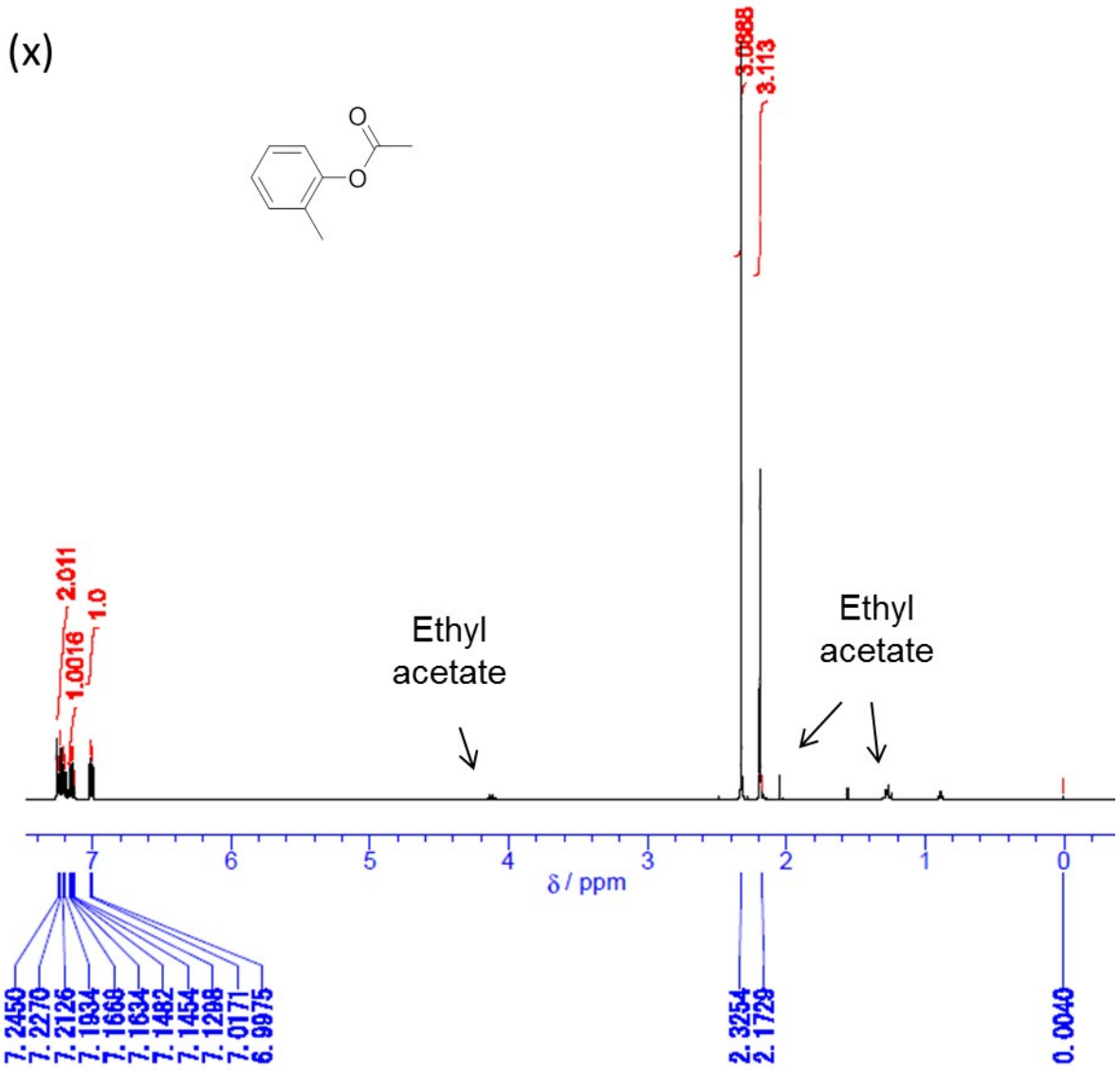
(v)


O
S
O
O
O
O
N+
Cl-
4.1211
1.0331
1.0802
3.1736
2.1462
2.0
1.9906
9.3122
8
7
6
5
4
3
2
1
0
δ / ppm

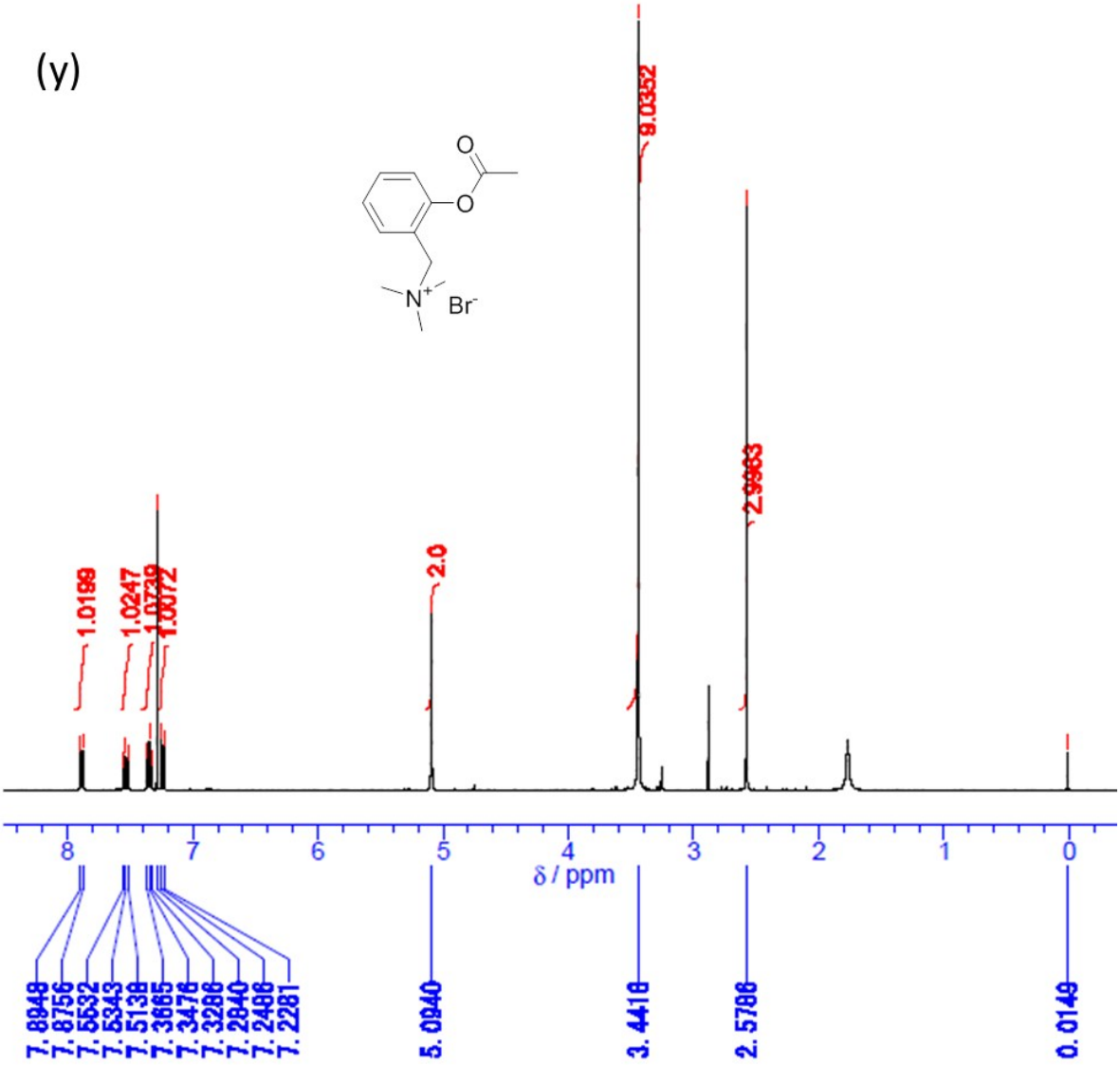
(w)


O
N+
Cl-
9.0666
1.989
2.0037
0.9996
0.9942
1.0633
1.9645
2.0
8
7
6
5
4
3
2
1
0
δ / ppm
7.5382
7.5183
7.4984
7.4254
7.4068
7.4040
7.3854
7.3725
7.3533
7.2766
7.2717
7.2671
7.1797
7.1611
7.1431
7.0664
7.0474
4.6839
3.0983
2.5000
-0.0142

(x)


3.0888
3.113
2.011
1.0016
1.0
Ethyl acetate
Ethyl acetate
7
6
5
4
3
2
1
0
δ / ppm
7.2450
7.2270
7.2126
7.1934
7.1668
7.1634
7.1482
7.1454
7.1208
7.0171
6.9975
2.3254
2.1729
0.0040

(y)


O
O
N+
Br-
9.0352
2.9963
2.0
1.0189
1.0247
1.0739
1.0072
8
7
6
5
4
3
2
1
0
δ / ppm
7.8948
7.8756
7.5532
7.5343
7.5138
7.3665
7.3476
7.3286
7.2840
7.2486
7.2281
5.0940
3.4418
2.5786
0.0149

Reference

(1) Maiti, D.; Buchwald, S. L. *J. Org. Chem.* **2010**, *75*, 1791.
(2) Bakke, B. A.; McIntosh, M. C.; Turnbull, K. D. *J. Org. Chem.* **2005**, *70*, 5771.