Supporting Information

Glyoxylic Acid Monohydrate Promoted Reductive Addition of Sodium Sulfinates to Pillar[4]arene[1]quinone

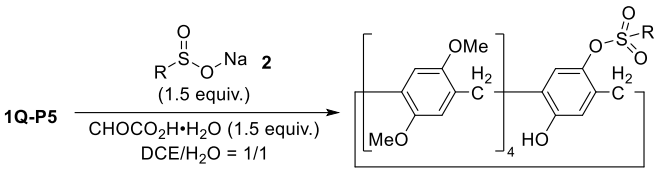
Enfu Zhang, Da Ma* and Chenghao Zhu*
School of Pharmaceutical Engineering & Institute for Advanced Studies, Taizhou University, 1139 Shifu Avenue, Taizhou 318000, Zhejiang, China
E-mail: chhzhu@tzc.edu.cn; dama@tzc.edu.cn

Table of Contents

1. General information

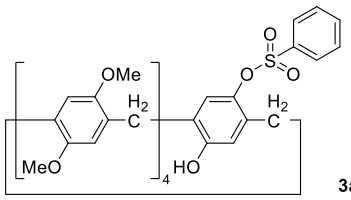
^{1}H NMR spectra, ^{19}F NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 400 MHz spectrometer in $CDCl_3$, CD_2Cl_2 and DMSO-d_6. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet), coupling constant (Hz), and intergration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). DCE = 1,2-dichloroethane, PE = petroleum ether, DCM = dichloromethane, EA = ethyl acetate. Pillar[5]arene (**P5**) and pillar[4]arene[1]quinone (**1Q-P5**) were prepared according to literature[1].

2. General procedure for the synthesis of 3



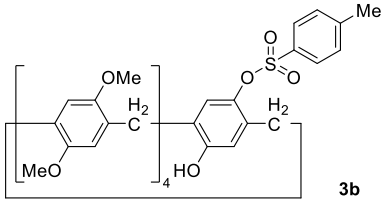
1Q-P5 (0.2 mmol, 1 equiv.), sodium sulfinates **2** (0.3 mmol, 1.5 equiv.), $CHOCO_2H{\cdot}H_2O$ (0.3 mg, 1.5 equiv.), DCE (3 mL) and H_2O (3 mL) were added to a 10 mL sealing tube. Then the mixture was stirred in a heating mantle temperature at 90 °C for 24 h. The solvent was removed and the residue was purified by silica-gel column chromatography (PE/EA/DCM = 10/1/2) to afford the desired product **3**.

1^5-hydroxy-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1^2-yl benzenesulfonate **(3a)**



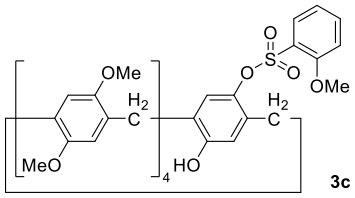
Prepared from the general procedure as a white solid (134.5 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.79 (m, 2H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.48 (t, *J* = 8.0 Hz, 2H), 7.23 (s, 1H), 6.91 (d, *J* = 12.0 Hz, 2H), 6.74-6.72 (m, 3H), 6.66 (s, 1H), 6.57 (s, 1H), 6.52 (d, *J* = 8.0 Hz, 3H), 3.80 (s, 3H), 3.76 (d, *J* = 4.0 Hz, 6H), 3.71 (s, 3H), 3.68 (s, 2H), 3.63-3.59 (m, 16H), 3.42-3.37 (m, 3H), 3.27 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.62, 151.91, 150.96, 150.90, 150.72, 150.71, 150.67, 150.63, 148.08, 140.22, 135.84, 134.08, 133.94, 129.60, 128.98, 128.84, 128.39, 128.14, 128.07, 128.00, 127.58, 126.90, 125.90, 125.59, 123.69, 118.52, 114.56, 114.41, 114.25, 114.19, 113.88, 113.60, 112.81, 56.38, 55.96, 55.92, 55.77, 55.74, 55.72, 55.69, 55.61, 30.39, 29.96, 29.72, 29.32, 29.13. HRMS (ESI) calcd. for $C_{49}H_{50}O_{12}SNa$ $[M+Na]^+$: 885.2921, found: 885.2921.

1^5-hydroxy-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1^2-yl 4-methylbenzenesulfonate **(3b)**



Prepared from the general procedure as a white solid (155.8 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 7.20 (s, 1H), 6.95 (s, 1H), 6.90 (s, 1H), 6.76-6.69 (m, 3H), 6.65 (s, 1H), 6.57 (s, 1H), 6.54 (s, 1H), 6.52 (s, 2H), 3.82 (s, 3H), 3.79-3.73 (m, 6H), 3.71 (s, 3H), 3.69 (s, 2H), 3.64-3.60 (m, 15H), 3.42 (s, 3H), 3.27 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.61, 151.96, 150.98, 150.93, 150.74, 150.71, 150.68, 150.62, 148.03, 145.05, 140.25, 134.18, 132.96, 129.64, 129.62, 128.84, 128.43, 128.13, 128.06, 128.02, 127.56, 127.00, 125.85, 125.60, 123.86, 118.46, 114.60, 114.45, 114.27, 114.19, 113.86, 113.62, 113.59, 112.80, 56.43, 55.99, 55.96, 55.81, 55.77, 55.72, 55.71, 55.66, 30.43, 30.01, 29.78, 29.34, 29.11, 21.63. HRMS (ESI) calcd. for $C_{50}H_{52}O_{12}SNa$ $[M+Na]^+$: 899.3077, found: 899.3078.

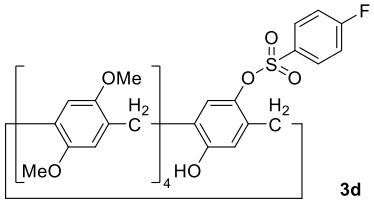
1^5-hydroxy-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1^2-yl 2-methoxybenzenesulfonate **(3c)**



3c

Prepared from the general procedure as a white solid (144.5 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.78 (m, 1H), 7.55-7.47 (m, 1H), 7.05 (s, 1H), 6.97-6.89 (m, 3H), 6.80 (s, 1H), 6.65 (s, 2H), 6.62 (s, 1H), 6.58 (d, *J* = 2.3 Hz, 2H), 6.52 (s, 1H), 6.50 (s, 1H), 6.45 (s, 1H), 3.76 (s, 3H), 3.71-3.69 (m, 9H), 3.62 (s, 3H), 3.59 (s, 2H), 3.56-3.48 (m, 17H), 3.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.64, 152.29, 151.79, 150.96, 150.85, 150.67, 150.61, 150.56, 148.11, 140.40, 135.98, 134.01, 131.67, 129.43, 128.59, 128.02, 127.94, 127.57, 127.32, 125.71, 125.64, 124.08, 123.47, 120.15, 118.32, 114.45, 114.25, 114.06, 113.77, 113.72, 113.51, 112.80, 112.30, 56.33, 56.02, 55.95, 55.84, 55.76, 55.71, 55.65, 55.61, 30.32, 30.00, 29.71, 29.36, 28.76. HRMS (ESI) calcd. for $C_{50}H_{52}O_{13}SNa$ $[M+Na]^+$: 915.3026, found: 915.3032.

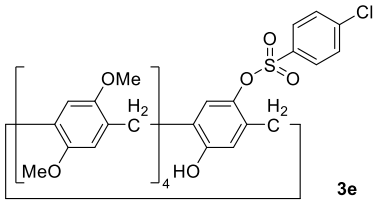
1^5-hydroxy-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1^2-yl 4-fluorobenzenesulfonate **(3d)**



3d

Prepared from the general procedure as a white solid (119.7 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 4.0 Hz, 2H), 7.24 (s, 1H), 7.19 (t, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.76 (d, *J* = 4.0 Hz, 3H), 6.68 (s, 1H), 6.60 (s, 1H), 6.53 (d, *J* = 4.0 Hz, 3H), 3.82 (s, 3H), 3.76 (d, *J* = 4.0 Hz, 6H), 3.72 (s, 3H), 3.69 (s, 2H), 3.67-3.61 (m, 15H), 3.43 (s, 3H), 3.26 (s, 2H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -102.41, -102.42, -102.43, -102.44, -102.45, -102.46, -102.47, -102.48. ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.88 (d, *J* = 257.0 Hz), 152.75, 151.83, 150.85, 150.79, 150.61, 150.55, 150.52, 148.01, 139.98, 134.08, 131.82 (d, *J* = 3.2 Hz), 131.32 (d, *J* = 9.6 Hz), 129.69, 129.01, 128.16, 128.10, 127.98, 127.57, 126.72, 126.07, 125.46, 123.76, 118.43, 116.46, 116.23, 114.47, 114.25, 114.11, 114.04, 113.74, 113.46, 112.73, 56.36, 55.98, 55.87, 55.75, 55.72, 55.69, 55.63, 55.57, 30.37, 29.91, 29.65, 29.25, 29.06. HRMS (ESI) calcd. for $C_{49}H_{49}FO_{12}SNa$ $[M+Na]^+$: 903.2826, found: 903.2830.

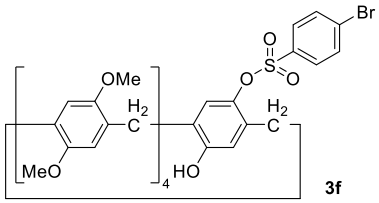
1⁵-hydroxy-3²,3⁵,5²,5⁵,7²,7⁵,9²,9⁵-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1²-yl 4-chlorobenzenesulfonate **(3e)**



3e

Prepared from the general procedure as a white solid (130.8 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.22 (s, 1H), 6.88 (d, *J* = 8.0 Hz, 2H), 6.71 (s, 1H), 6.70 (s, 2H), 6.63 (s, 1H), 6.54 (s, 1H), 6.50 (s, 2H), 6.48 (s, 1H), 3.77 (s, 3H), 3.74-3.73 (m, 6H), 3.67 (s, 3H), 3.65 (s, 2H), 3.63-3.55 (m, 15H), 3.37 (s, 3H), 3.24 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.78, 151.86, 150.89, 150.83, 150.66, 150.61, 150.56, 148.00, 140.65, 140.00, 134.25, 133.97, 129.80, 129.59, 129.29, 128.90, 128.09, 128.03, 127.88, 127.48, 126.64, 125.99, 125.39, 123.65, 118.50, 114.52, 114.32, 114.16, 114.10, 113.81, 113.51, 112.75, 56.34, 55.94, 55.87, 55.72, 55.70, 55.65, 55.63, 55.53, 30.33, 29.92, 29.68, 29.27, 29.14. HRMS (ESI) calcd. for $C_{49}H_{49}ClO_{12}SNa$ $[M+Na]^+$: 919.2531, found: 919.2537.

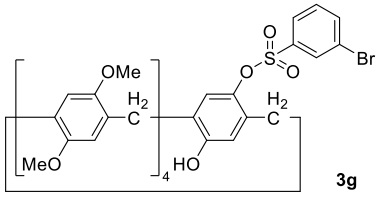
1⁵-hydroxy-3²,3⁵,5²,5⁵,7²,7⁵,9²,9⁵-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1²-yl 4-bromobenzenesulfonate **(3f)**



3f

Prepared from the general procedure as a white solid (137.3 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.24 (s, 1H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.73 (s, 3H), 6.66 (s, 1H), 6.57 (s, 1H), 6.53 (s, 2H), 6.51 (s, 1H), 3.80 (s, 3H), 3.77-3.76 (m, 6H), 3.70 (s, 3H), 3.68 (s, 2H), 3.66-3.58 (m, 15H), 3.40 (s, 3H), 3.29 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.79, 151.88, 150.92, 150.85, 150.69, 150.64, 150.59, 148.07, 140.02, 134.85, 133.98, 132.30, 129.84, 129.63, 129.25, 128.94, 128.14, 128.07, 127.94, 127.54, 126.68, 126.03, 125.45, 123.63, 118.54, 114.54, 114.34, 114.19, 114.14, 113.86, 113.56, 112.79, 56.35, 55.95, 55.89, 55.72, 55.69, 55.66, 55.56, 30.35, 29.93, 29.68, 29.30, 29.18. HRMS (ESI) calcd. for $C_{49}H_{49}BrO_{12}SNa$ $[M+Na]^+$: 963.2026, found: 963.2027.

15-hydroxy-32,35,52,55,72,75,92,95-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-12-yl 3-bromobenzenesulfonate **(3g)**

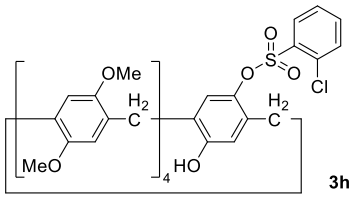


3g

Prepared from the general procedure as a white solid (141.1 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.6 Hz, 1H), 7.78 (dd, *J* = 8.0, 0.9 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 1H), 7.28 (s, 1H), 6.91 (s, 1H), 6.88 (s, 1H), 6.74 (s, 3H), 6.67 (s, 1H), 6.58 (s, 1H), 6.56 (s, 1H), 6.54 (s, 1H), 6.51 (s, 1H), 3.82 (s, 3H), 3.77-3.76 (d, *J* = 2.6 Hz, 6H), 3.72 (s, 3H), 3.69 (s, 2H), 3.67-3.61 (m, 15H), 3.42 (s,

3H), 3.33 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.87, 151.90, 150.93, 150.86, 150.69, 150.65, 150.61, 148.05, 139.98, 137.69, 137.00, 134.02, 131.19, 130.47, 129.63, 128.96, 128.13, 128.07, 127.97, 127.54, 126.95, 126.72, 126.05, 125.44, 123.62, 122.92, 118.65, 114.58, 114.38, 114.21, 114.15, 113.85, 113.56, 112.78, 56.40, 56.01, 55.93, 55.78, 55.75, 55.72, 55.68, 55.59, 30.42, 29.95, 29.72, 29.28, 29.23. HRMS (ESI) calcd. for $C_{49}H_{49}BrO_{12}SNa$ $[M+Na]^+$: 963.2026, found: 963.2032.

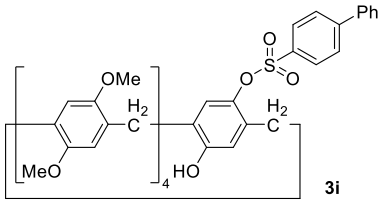
1^5-hydroxy-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1^2-yl 2-chlorobenzenesulfonate **(3h)**



3h

Prepared from the general procedure as a white solid (145.2 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97-7.87 (m, 1H), 7.58-7.45 (m, 2H), 7.30 (t, *J* = 8.0 Hz, 1H), 7.08 (s, 1H), 6.82 (s, 1H), 6.74 (s, 1H), 6.66 (s, 2H), 6.65 (s, 1H), 6.59 (d, *J* = 4.0 Hz, 2H), 6.53 (d, *J* = 2.2 Hz, 2H), 6.43 (s, 1H), 3.73 (s, 3H), 3.70 (s, 6H), 3.64 (s, 3H), 3.57-3.53 (m, 19H), 3.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.69, 151.82, 151.00, 150.89, 150.69, 150.62, 148.15, 140.17, 134.85, 134.56, 134.24, 133.24, 132.07, 129.55, 128.78, 128.14, 128.09, 128.02, 127.57, 127.06, 125.88, 125.53, 123.34, 118.73, 114.49, 114.28, 114.16, 113.80, 113.71, 113.58, 112.81, 56.33, 56.01, 55.92, 55.81, 55.74, 55.72, 55.68, 55.65, 30.37, 29.97, 29.77, 29.68, 29.32. HRMS (ESI) calcd. for $C_{49}H_{49}ClO_{12}SNa$ $[M+Na]^+$: 919.2531, found: 919.2532.

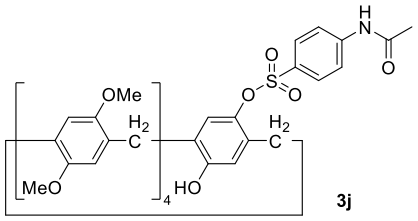
1^5-hydroxy-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1^2-yl [1,1'-biphenyl]-4-sulfonate **(3i)**



3i

Prepared from the general procedure as a white solid (150.1 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.43-7.36 (m, 1H), 7.21 (s, 1H), 6.97 (s, 1H), 6.89 (s, 1H), 6.74 (s, 2H), 6.73 (s, 1H), 6.66 (s, 1H), 6.55 (t, *J* = 12.0 Hz, 4H), 3.78-3.76 (m, 9H), 3.69 (s, 5H), 3.66-3.55 (m, 15H), 3.41 (s, 3H), 3.34 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.60, 151.81, 150.86, 150.80, 150.65, 150.62, 150.59, 150.55, 148.05, 146.72, 140.13, 138.73, 134.33, 134.10, 129.49, 129.02, 128.90, 128.76, 128.69, 128.07, 128.00, 127.94, 127.52, 127.40, 127.21, 126.83, 125.90, 125.55, 123.75, 118.42, 114.43, 114.27, 114.12, 114.08, 113.77, 113.51, 113.48, 112.74, 56.26, 55.83, 55.68, 55.66, 55.60, 55.54, 30.28, 29.89, 29.66, 29.26, 29.18. HRMS (ESI) calcd. for $C_{55}H_{54}O_{12}SNa$ $[M+Na]^+$: 961.3234, found: 961.3233.

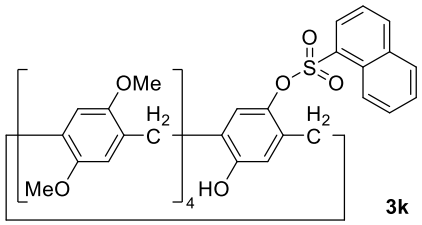
1⁵-hydroxy-3²,3⁵,5²,5⁵,7²,7⁵,9²,9⁵-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1²-yl 4-acetamidobenzenesulfonate **(3j)**



3j

Prepared from the general procedure as a white solid (137.8 mg, 75%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.70 (d, *J* = 8.0 Hz, 3H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.16 (s, 1H), 6.85 (s, 1H), 6.81 (s, 1H), 6.77 (s, 3H), 6.72 (d, *J* = 4.0 Hz, 2H), 6.54 (s, 1H), 6.51 (s, 1H), 6.47 (s, 1H), 3.78-3.43 (m, 32H), 3.22 (s, 2H), 2.06 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 169.24, 153.15, 152.06, 150.89, 150.86, 150.80, 150.70, 148.57, 143.97, 140.18, 134.46, 130.46, 130.17, 129.77, 129.23, 128.62, 128.56, 128.49, 128.05, 127.23, 126.71, 126.22, 124.39, 119.21, 118.64, 114.38, 114.11, 113.89, 113.84, 113.75, 113.32, 113.02, 56.61, 56.08, 55.99, 55.92, 30.53, 30.09, 29.90, 29.72, 29.53, 29.30, 24.92. HRMS (ESI) calcd. for $C_{51}H_{53}NO_{13}SNa$ $[M+Na]^+$: 942.3135, found: 942.3129.

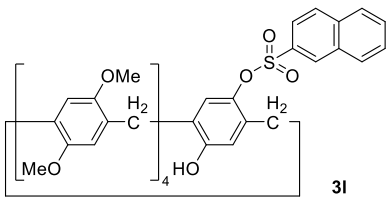
1⁵-hydroxy-3²,3⁵,5²,5⁵,7²,7⁵,9²,9⁵-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1²-yl naphthalene-1-sulfonate **(3k)**



3k

Prepared from the general procedure as a white solid (147.8 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 1H), 7.06 (s, 1H), 6.83 (s, 1H), 6.70 (s, 3H), 6.64 (s, 1H), 6.57 (s, 2H), 6.54 (d, *J* = 4.0 Hz, 2H), 6.30 (s, 1H), 3.76-3.74 (m, 6H), 3.71 (s, 3H), 3.65-3.55 (m, 15H), 3.54 (s, 3H), 3.49 (s, 2H), 3.45 (s, 2H), 3.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.39, 151.70, 150.91, 150.81, 150.66, 150.62, 150.59, 150.55, 148.09, 140.50, 135.32, 134.25, 134.00, 132.03, 130.68, 129.37, 128.80, 128.63, 128.55, 128.09, 128.00, 127.53, 127.09, 127.03, 125.67, 125.57, 125.25, 124.03, 123.17, 118.66, 114.36, 114.17, 114.08, 113.77, 113.58, 113.54, 112.58, 56.20, 55.90, 55.74, 55.70, 55.67, 55.59, 55.55, 30.22, 29.85, 29.69, 29.42, 29.22. HRMS (ESI) calcd. for $C_{53}H_{53}O_{12}SNa$ $[M+Na]^+$: 935.3077, found: 935.3076.

1⁵-hydroxy-3²,3⁵,5²,5⁵,7²,7⁵,9²,9⁵-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1²-yl naphthalene-2-sulfonate **(3l)**

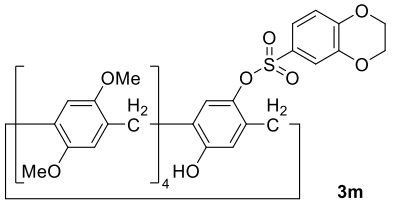


3l

Prepared from the general procedure as a white solid (151.4 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (s, 1H), 7.84-7.68 (m, 4H), 7.51 (t, *J* = 8.0 Hz, 1H), 7.44 (t, *J* = 8.0 Hz, 1H), 6.77 (s, 1H),

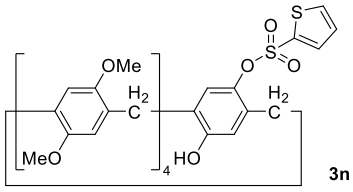
6.73 (s, 1H), 6.57 (s, 3H), 6.49 (s, 1H), 6.40 (s, 1H), 6.36 (s, 2H), 6.33 (s, 1H), 3.63 (s, 3H), 3.61-3.55 (m, 6H), 3.53 (s, 3H), 3.50 (s, 2H), 3.48-3.37 (m, 15H), 3.23 (s, 3H), 3.13 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.64, 151.86, 150.92, 150.85, 150.67, 150.63, 150.58, 148.03, 140.24, 135.26, 134.13, 132.91, 131.80, 130.19, 129.53, 129.41, 129.24, 128.79, 128.10, 128.02, 127.99, 127.92, 127.72, 127.53, 126.89, 125.90, 125.55, 123.76, 123.03, 118.52, 114.51, 114.36, 114.18, 114.12, 113.80, 113.52, 112.74, 56.34, 55.89, 55.75, 55.71, 55.66, 55.59, 30.34, 29.93, 29.72, 29.25. HRMS (ESI) calcd. for $C_{53}H_{53}O_{12}SNa$ $[M+Na]^+$: 935.3077, found: 935.3079.

1^5-hydroxy-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1^2-yl 2,3-dihydrobenzo[b][1,4]dioxine-6-sulfonate **(3m)**



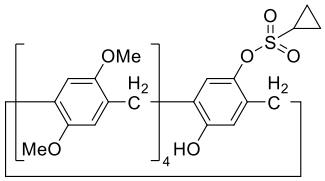
Prepared from the general procedure as a white solid (156.4 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 4.0 Hz, 1H), 7.34 (dd, *J* = 8.0, 4.0 Hz, 1H), 7.22 (s, 1H), 6.96-6.93 (m, 2H), 6.90 (s, 1H), 6.73 (d, *J* = 4.0 Hz, 2H), 6.72 (s, 1H), 6.66 (s, 1H), 6.59 (s, 1H), 6.56 (s, 1H), 6.54 (d, *J* = 4.0 Hz, 2H), 4.27 (d, *J* = 4.0 Hz, 2H), 4.23 (d, *J* = 4.0 Hz, 2H), 3.82 (s, 3H), 3.77-3.76 (d, *J* = 4.0 Hz, 6H), 3.71 (d, *J* = 4.0 Hz, 5H), 3.64-3.60 (m, 15H), 3.44 (s, 3H), 3.35 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.59, 151.95, 150.99, 150.92, 150.73, 150.71, 150.67, 150.63, 148.47, 148.03, 143.46, 140.27, 134.17, 129.57, 128.81, 128.10, 128.04, 127.56, 127.07, 125.83, 125.62, 123.86, 122.24, 118.45, 118.09, 117.71, 114.59, 114.47, 114.28, 114.19, 113.85, 113.66, 113.58, 112.82, 64.55, 64.02, 56.43, 56.00, 55.98, 55.82, 55.78, 55.74, 55.69, 30.44, 30.02, 29.80, 29.34, 29.13. HRMS (ESI) calcd. for $C_{51}H_{52}O_{14}SNa$ $[M+Na]^+$: 943.2975, found: 943.2977.

1^5-hydroxy-3^2,3^5,5^2,5^5,7^2,7^5,9^2,9^5-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1^2-yl thiophene-2-sulfonate **(3n)**



Prepared from the general procedure as a white solid (86.7 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (s, 1H), 7.07 (d, *J* = 2.9 Hz, 1H), 6.97 (s, 1H), 6.92 (d, *J* = 4.0 Hz, 1H), 6.90 (s, 1H), 6.77 (d, *J* = 8.0 Hz, 2H), 6.69 (d, *J* = 4.0 Hz, 2H), 6.65-6.58 (m, 3H), 6.57 (s, 1H), 6.46-6.38 (m, 1H), 3.80-3.73 (m, 12H), 3.67-3.66 (m, 5H), 3.63-3.62 (m, 9H), 3.58 (s, 3H), 3.45 (s, 3H), 3.43 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.14, 151.79, 150.85, 150.80, 150.72, 150.68, 148.35, 140.91, 135.04, 134.13, 133.84, 133.28, 129.43, 128.79, 128.30, 128.10, 128.08, 127.65, 127.25, 126.69, 125.98, 125.90, 122.54, 119.11, 114.48, 114.42, 114.28, 114.21, 113.99, 113.81, 113.73, 113.19, 56.32, 55.87, 55.75, 55.73, 55.68, 30.35, 29.66, 29.61, 29.39. HRMS (ESI) calcd. for $C_{47}H_{48}O_{12}S_2Na$ $[M+Na]^+$: 891.2485, found: 891.2489.

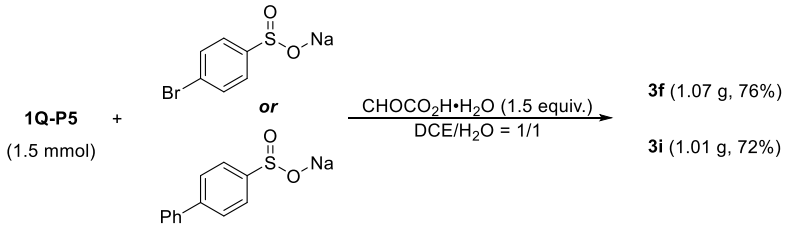
1⁵-hydroxy-3²,3⁵,5²,5⁵,7²,7⁵,9²,9⁵-octamethoxy-1,3,5,7,9(1,4)-pentabenzenacyclodecaphane-1²-yl cyclopropanesulfonate **(3o)**



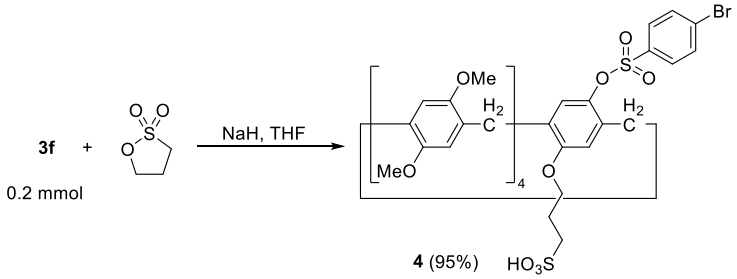
3o

Prepared from the general procedure as a white solid (95.9 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 6.88 (s, 1H), 6.80 (s, 1H), 6.77 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 4H), 6.64 (s, 1H), 6.61 (d, *J* = 4.0 Hz, 2H), 3.76-3.64 (m, 28H), 3.59 (s, 3H), 3.51 (s, 3H), 0.73 (s, 1H), -0.00 (s, 2H), -0.43 (d, *J* = 8.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.90, 151.20, 150.91, 150.80, 150.63, 150.53, 150.49, 150.46, 148.52, 141.96, 132.40, 129.28, 129.17, 128.41, 128.28, 128.21, 127.79, 127.07, 126.50, 126.37, 122.43, 119.62, 114.41, 114.22, 114.07, 113.94, 113.85, 113.66, 112.38, 56.34, 55.95, 55.81, 55.71, 55.68, 55.65, 30.63, 29.96, 29.91, 29.81, 28.92, 25.58, 4.90. HRMS (ESI) calcd. for $C_{46}H_{50}O_{12}SNa$ $[M+Na]^+$: 849.2921, found: 849.2922.

3. Gram scale synthesis and synthetic transformations

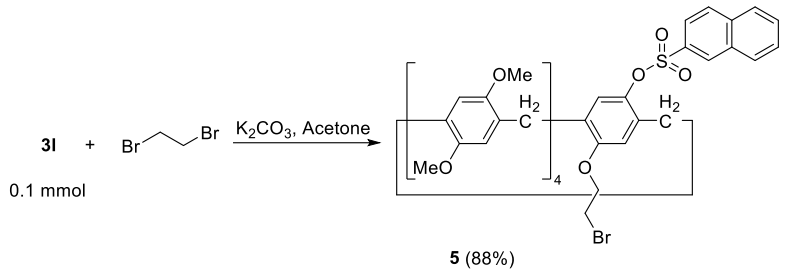


1Q-P5 (1.5 mmol, 1 equiv.), sodium sulfinates (2.25 mmol, 1.5 equiv.), $CHOCO_2H{\cdot}H_2O$ (2.25 mmol, 1.5 equiv.), DCE (30 mL) and H_2O (30 mL) were added to a 250 mL sealing tube. Then the mixture was stirred in a heating mantle temperature at 90 °C for 24 h. The solvent was removed and the residue was purified by silica-gel column chromatography (PE/EA/DCM = 10/1/2) to afford the desired product **3f** (1.07 g, 76%) and **3i** (1.01 g, 72%), respectively.



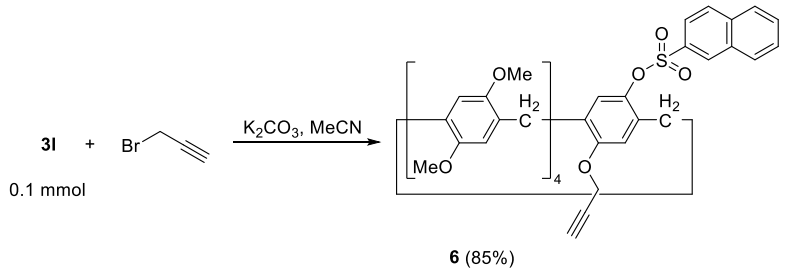
To a solution of **3f** (188 mg, 0.2 mmol, 1 equiv.) in dry THF (4 mL) was added NaH (16.4 mg, 0.41 mmol, 2.05 equiv., 60% dispersion in mineral oil). After stirring for 5 min, 1,3-Propanesultone (51.3 mg, 0.42 mmol, 2.1 equiv.) was added and stirred at room temperature for 3 h. The reaction was quenched with 2d H_2O, and the solvent was removed under vacuum. The residue was crystallized from petroleum ether/dichloromethane solvent system to afford the desired product **4** as a white solid (201.8 mg, 95%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.0 Hz, 2H), 6.84 (s, 1H), 6.81-6.71 (m, 6H), 6.69 (s, 1H), 6.65 (s, 1H), 6.57 (s, 1H), 5.66 (s, 1H), 4.06-3.94 (m, 2H), 3.77-3.43 (m, 34H), 2.70 (t, *J* = 8.0 Hz, 2H), 2.17-2.01 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.41, 150.51, 150.39, 150.29, 150.05, 139.96, 134.83, 133.44, 133.15, 130.68, 129.69, 128.92, 128.79, 128.24, 128.13, 127.99, 127.86, 127.83, 127.40, 126.13, 123.43,

114.43, 114.15, 113.68, 113.24, 67.46, 56.08, 56.06, 55.97, 55.93, 55.89, 55.76, 55.29, 48.76, 30.88, 29.38, 28.94, 28.32, 26.06, 22.19, 14.39. HRMS (ESI) calcd. for $C_{52}H_{55}O_{15}S_2BrNa$ $[M+Na]^+$: 1085.2063, found: 1085.2056.



5 (88%)

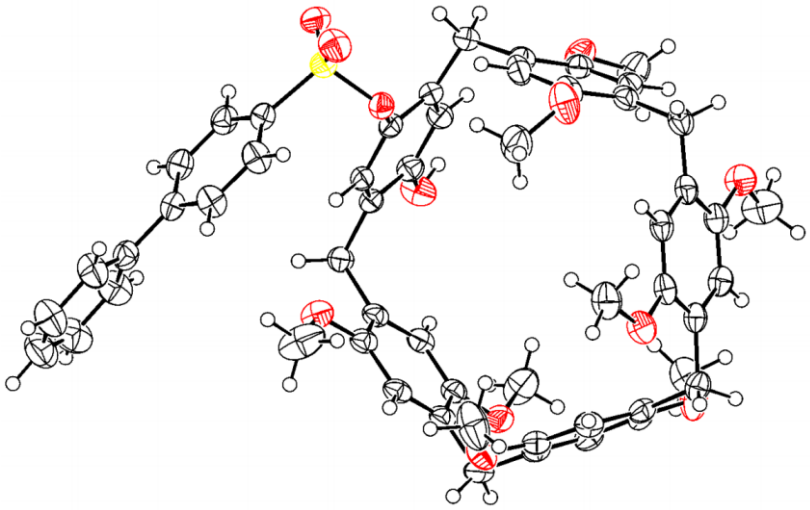
3l (91.2 mg, 0.1 mmol, 1 equiv.), 1,2-dibromoethane (40.9 mg, 0.22 mmol, 2.2 equiv.), K_2CO_3 (22.0 mg, 0.16 mmol, 1.6 equiv.) and acetone (3 mL) were added to a 10 mL sealing tube. Then the mixture was stirred in a heating mantle temperature at 45 °C for 24 h. The solvent was removed and the residue was purified by silica-gel column chromatography (PE/EA = 10/1) to afford the desired product **5** as a white solid (89.6 mg, 88%). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.56 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 8.10-8.03 (m, 2H), 7.97 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.79 (t, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 6.98-6.86 (m, 7H), 6.86-6.78 (m, 3H), 4.28 (t, *J* = 8.0 Hz, 2H), 3.80-3.72 (m, 26H), 3.70 (s, 3H), 3.66 (d, *J* = 4.0 Hz, 4H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 153.76, 150.76, 150.72, 150.66, 150.59, 150.52, 141.44, 135.85, 133.79, 133.75, 132.37, 130.58, 130.02, 129.89, 129.82, 129.26, 128.90, 128.66, 128.52, 128.39, 128.32, 127.57, 126.48, 124.49, 123.34, 114.31, 113.73, 113.68, 113.64, 113.59, 113.53, 113.47, 68.33, 56.04, 55.87, 55.84, 55.81, 55.78, 55.67, 55.59, 31.99, 30.74, 29.53, 29.32, 29.28, 28.64, 23.06. HRMS (ESI) calcd. for $C_{55}H_{55}O_{12}SBrNa$ $[M+Na]^+$: 1041.2495, found: 1041.2493.



6 (85%)

3l (91.2 mg, 0.1 mmol, 1 equiv.), 3-bromoprop-1-yne (23.6 mg, 0.2 mmol, 2 equiv.), K_2CO_3 (41.4.0 mg, 0.3 mmol, 3 equiv.) and MeCN (2 mL) were added to a 10 mL sealing tube. Then the mixture was stirred in a heating mantle temperature at 80 °C for 24 h. The solvent was removed and the residue was purified by silica-gel column chromatography (PE/EA = 10/1) to afford the desired product **6** as a white solid (80.8 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 1.2 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.94 (d, *J* = 4.0 Hz, 1H), 7.92 (d, *J* = 4.0 Hz, 1H), 7.89 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.71-7.64 (m, 1H), 7.64-7.57 (m, 1H), 6.85 (s, 1H), 6.78 (s, 1H), 6.77 (s, 1H), 6.75 (s, 1H), 6.75 (s, 1H), 6.70 (s, 1H), 6.66 (s, 1H), 6.64 (s, 1H), 6.62 (s, 1H), 6.59 (s, 1H), 4.36 (d, *J* = 2.3 Hz, 2H), 3.76-3.75 (M, 6H), 3.71-3.50 (m, 25H), 3.47 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.19, 150.81, 150.72, 150.62, 150.56, 150.52, 150.36, 140.84, 135.30, 133.40, 133.09, 131.83, 130.24, 129.45, 129.40, 129.32, 129.24, 128.69, 128.66, 128.39, 128.21, 127.97, 127.94, 127.89, 127.75, 126.85, 126.67, 124.56, 122.97, 114.26, 114.22, 114.07, 113.99, 113.83, 113.78, 113.72, 113.56, 77.48, 75.06, 55.85, 55.74, 55.73, 55.63, 55.57, 55.49, 55.20, 30.15, 29.66, 29.57, 29.50. HRMS (ESI) calcd. for $C_{56}H_{54}O_{12}SNa$ $[M+Na]^+$: 973.3234, found: 973.3234.

4. Single crystal X-ray diffraction of 3i



CCDC: 2404953

Table S1. Crystal data and structure refinement for platon_sq.

Identification code	platon_sq
Empirical formula	$C_{55}H_{54}O_{12}S$
Formula weight	939.04
Temperature/K	170.0
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	25.9910(19)
b/Å	14.3060(11)
c/Å	14.7845(11)
α/°	90
β/°	94.361(2)
γ/°	90
Volume/Å^3	5481.4(7)
Z	4
ρ_{calc}g/cm^3	1.138
μ/mm^{-1}	0.641
F(000)	1984.0
Crystal size/mm^3	0.12 × 0.12 × 0.12
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	7.912 to 105.962
Index ranges	-30 ⩽ h ⩽ 30, -17 ⩽ k ⩽ 16, -17 ⩽ l ⩽ 17
Reflections collected	75666
Independent reflections	9553 [R_{int} = 0.0327, R_{sigma} = 0.0269]
Data/restraints/parameters	9553/0/625
Goodness-of-fit on F^2	1.028

Final R indexes [I>=2σ (I)]	R_1 = 0.0391, wR_2 = 0.1071
Final R indexes [all data]	R_1 = 0.0431, wR_2 = 0.1099
Largest diff. peak/hole / e Å^{-3}	0.24/-0.45

Table S2. Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for platon_sq. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

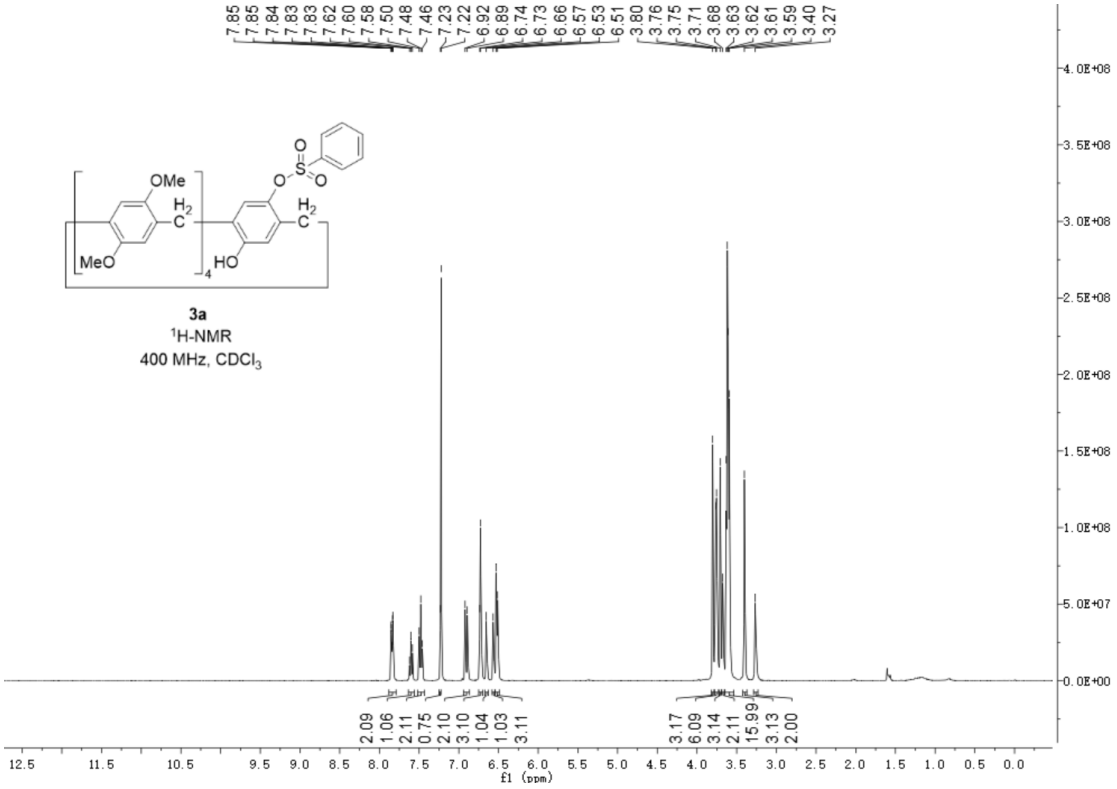
Atom	x	y	z	U(eq)
S(1)	6294.8(2)	5692.8(3)	6918.8(3)	35.78(10)
O(1)	6696.1(4)	5655.2(7)	6157.5(7)	34.1(2)
O(2)	6093.9(5)	6631.3(9)	2610.1(8)	48.4(3)
O(3)	6240.2(5)	3141.4(8)	3991.8(8)	44.3(3)
O(4)	7100.1(4)	4017.6(8)	791.9(8)	41.7(3)
O(5)	7984.0(5)	1682.7(8)	3249.7(8)	44.7(3)
O(6)	8975.3(5)	4514.8(10)	1527.5(9)	54.4(3)
O(7)	9432.9(5)	3380.4(8)	4893.6(8)	44.1(3)
O(8)	9279.5(5)	7082.1(8)	3813.0(8)	44.7(3)
O(9)	8514.4(5)	5853.9(10)	6828.4(9)	57.0(3)
O(10)	7576.7(5)	8390.9(8)	4416.2(8)	47.7(3)
O(11)	5999.2(5)	6535.5(8)	6817.2(8)	44.3(3)
O(12)	6605.5(5)	5523.4(9)	7734.9(8)	50.6(3)
C(1)	6533.7(5)	5932.7(10)	5253.3(10)	30.1(3)
C(2)	6300.6(5)	5275.9(10)	4675.8(10)	30.2(3)
C(3)	6151.6(5)	5506.5(10)	3779.1(10)	31.0(3)
C(4)	6248.6(6)	6414.3(11)	3490.8(11)	35.2(3)
C(5)	6495.9(6)	7059.7(11)	4080.2(11)	36.6(3)
C(6)	6647.3(6)	6832.1(10)	4974.6(11)	32.8(3)
C(7)	5901.0(6)	4783.3(11)	3137.8(11)	34.8(3)
C(8)	6471.6(6)	3347.2(11)	3209(1)	33.9(3)
C(9)	6849.0(6)	2794.5(10)	2860.5(10)	33.8(3)
C(10)	7055.5(6)	3019.4(10)	2047.3(10)	32.2(3)
C(11)	6881.9(6)	3829.7(10)	1592.9(10)	33.2(3)
C(12)	6508.9(6)	4389.1(10)	1947.1(11)	33.8(3)
C(13)	6298.7(6)	4156.8(10)	2750.5(11)	32.8(3)
C(14)	7468.3(6)	2410.4(11)	1679.7(11)	36.5(3)
C(15)	8253.2(6)	2356.4(10)	2810.2(10)	34.0(3)
C(16)	8743.3(6)	2657.1(11)	3115.4(11)	35.0(3)
C(17)	8989.5(6)	3370.5(11)	2680.5(10)	33.8(3)
C(18)	8727.8(6)	3784.5(11)	1926.3(11)	36.8(3)
C(19)	8248.1(6)	3452.7(12)	1597.5(11)	37.8(4)
C(20)	8003.9(6)	2734.9(10)	2025.7(10)	33.0(3)
C(21)	9509.5(6)	3734.8(11)	3065.0(11)	38.1(4)
C(22)	9388.9(6)	4311.1(11)	4652.6(11)	34.8(3)
C(23)	9307.5(6)	5028.9(11)	5256.0(11)	35.4(3)

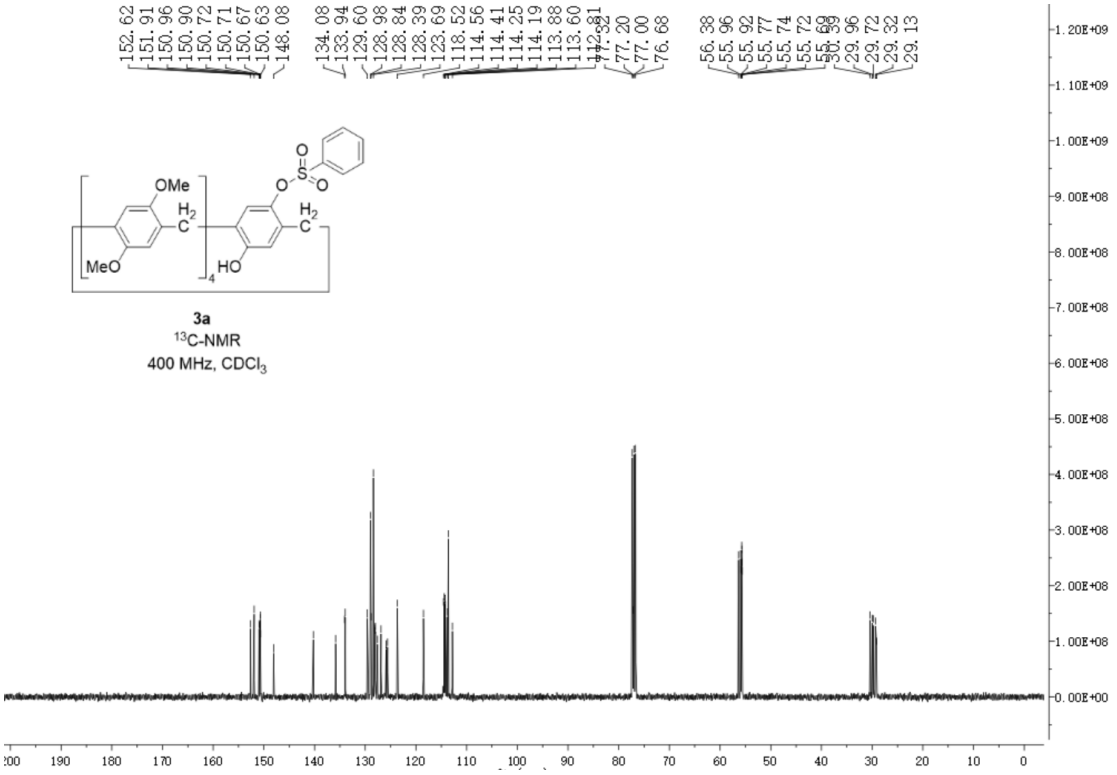
C(24)	9266.5(6)	5955.0(11)	4969.4(10)	34.4(3)
C(25)	9315.7(6)	6149.8(11)	4055.4(11)	35.2(3)
C(26)	9404.5(6)	5436.9(11)	3454.4(11)	35.6(3)
C(27)	9441.0(5)	4507.4(11)	3739.1(11)	34.4(3)
C(28)	9164.5(6)	6728.8(12)	5630.0(11)	38.6(4)
C(29)	8284.3(6)	6495.2(12)	6226.5(11)	39.7(4)
C(30)	7762.3(6)	6703.8(12)	6226.3(11)	40.8(4)
C(31)	7524.7(6)	7339.2(11)	5621.7(10)	35.6(3)
C(32)	7832.1(6)	7781.7(11)	5015.2(10)	35.8(3)
C(33)	8358.3(6)	7601.0(11)	5036.2(10)	36.1(3)
C(34)	8593.9(6)	6951.2(11)	5638.7(10)	35.0(3)
C(35)	6947.8(6)	7518.4(11)	5594.1(11)	38.8(4)
C(36)	5891.8(6)	4733.4(11)	6654.8(10)	33.4(3)
C(37)	5410.1(6)	4850.1(11)	6203.0(11)	38.7(4)
C(38)	5121.9(6)	4068.0(12)	5947.3(12)	40.6(4)
C(39)	5303.4(6)	3168.3(11)	6140.1(11)	34.8(3)
C(40)	5789.2(6)	3073.7(11)	6606.6(12)	41.2(4)
C(41)	6082.1(6)	3847.1(11)	6857.3(12)	41.4(4)
C(42)	5000.7(6)	2321.8(12)	5853.8(11)	39.0(4)
C(43)	4985.4(8)	1552.2(13)	6423.5(14)	53.0(5)
C(44)	4719.3(9)	748.8(15)	6148.4(16)	63.9(6)
C(45)	4467.2(8)	706.1(15)	5295.1(17)	64.6(6)
C(46)	4471.5(8)	1461.7(16)	4729.0(17)	66.9(6)
C(47)	4736.4(7)	2272.0(14)	5003.6(14)	53.9(5)
C(48)	6382.8(11)	2297.9(16)	4441.0(15)	74.7(7)
C(49)	7022.9(9)	4920.7(14)	426.3(16)	63.3(6)
C(50)	8127.9(10)	1538.6(19)	4170.7(15)	74.3(7)
C(51)	8656.1(8)	5209.4(14)	1092.9(14)	55.4(5)
C(52)	9343.7(8)	3135.9(13)	5800.3(13)	52.8(5)
C(53)	9239.1(10)	7298.3(14)	2876.1(13)	61.0(5)
C(54)	8271.8(9)	4960.9(14)	6830.8(16)	63.3(6)
C(55)	7852.6(8)	8763.5(15)	3710.6(13)	55.8(5)

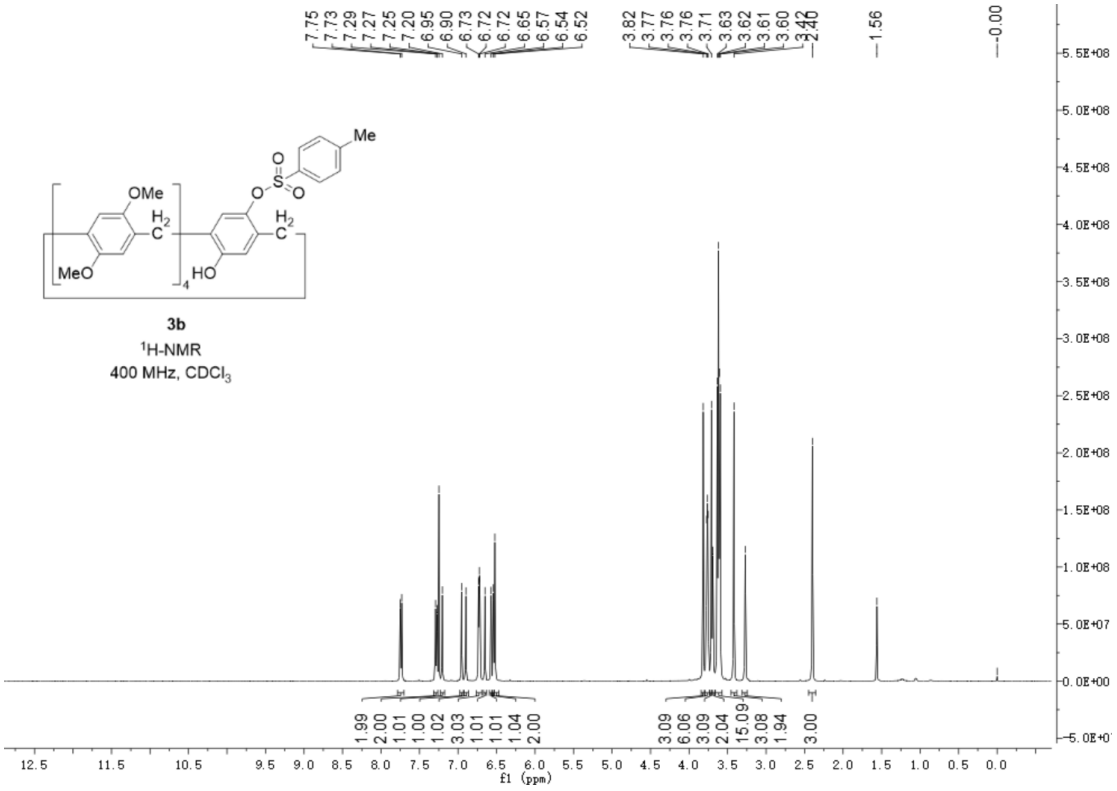
5. References

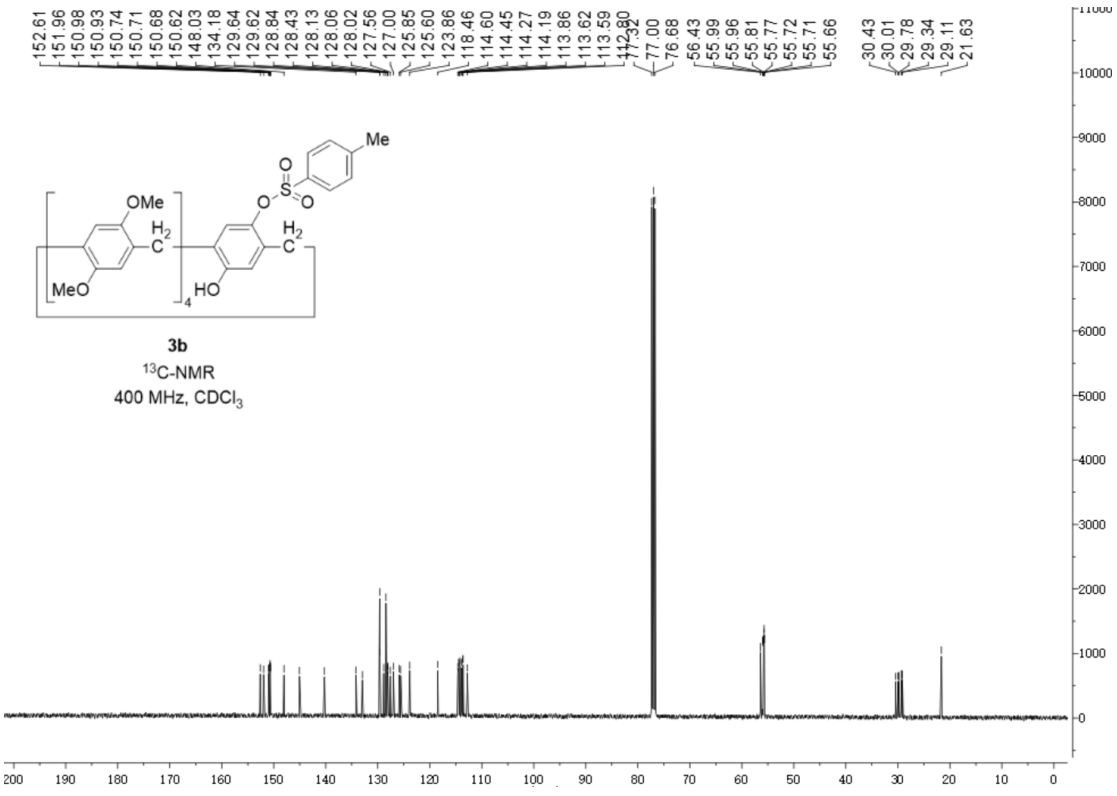
[1] G. Wang, H. Qiang, Y.-Z. Guo, J. Yang, K. Wen, W.-B. Hu, Systematic rim cyano-functionalization of pillar[5]arene and corresponding host-guest property varieties. *Org. Biomol. Chem.* **2019**, *17*, 4600-4604.

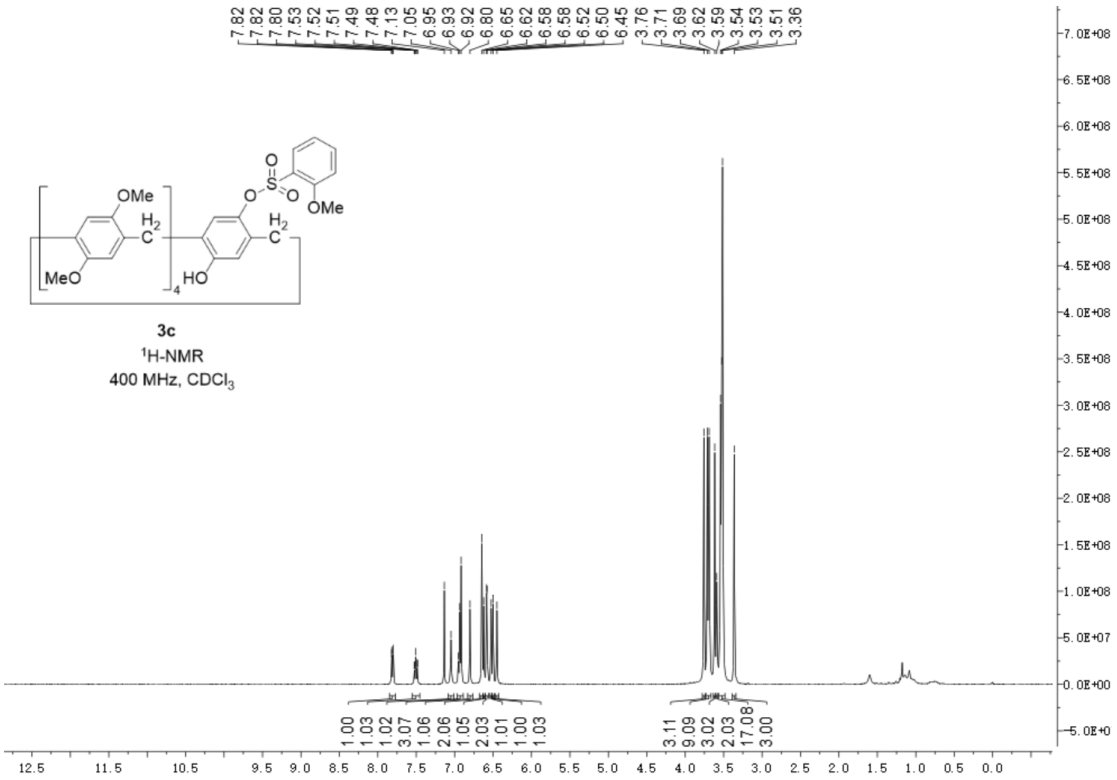
6. ^{1}H, ^{19}F and ^{13}C NMR Spectra of Compounds






7.75
7.73
7.29
7.27
7.25
7.20
6.95
6.90
6.73
6.72
6.72
6.65
6.57
6.54
6.52
3.82
3.77
3.76
3.76
3.71
3.63
3.62
3.61
3.60
2.40
1.56
0.00
Me
O
S
O
O
OMe
H2
C
H2
C
MeO
4
HO
3b
1H-NMR
400 MHz, CDCl3
1.99
2.00
1.01
1.00
1.02
3.03
1.01
1.01
1.04
2.00
3.09
6.06
3.09
2.04
15.09
3.08
1.94
3.00
f1 (ppm)

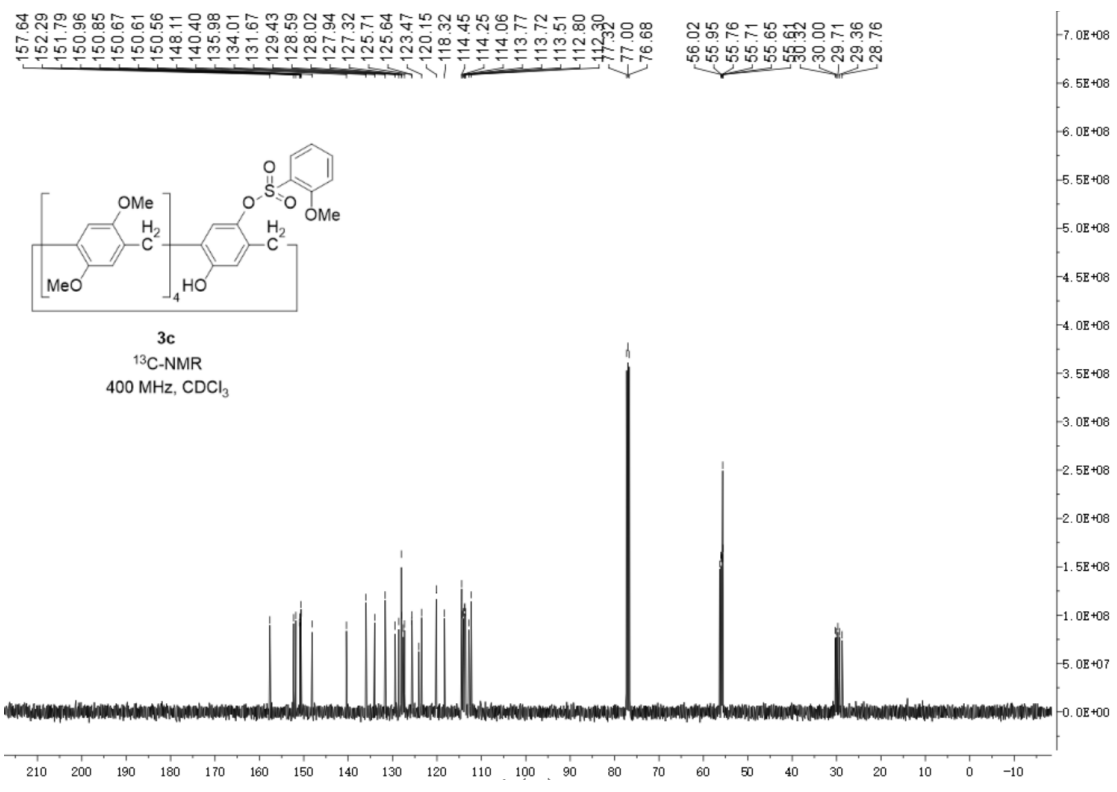

152.61
151.96
150.98
150.93
150.74
150.71
150.68
150.62
148.03
134.18
129.64
129.62
128.84
128.43
128.13
128.06
128.02
127.56
127.00
125.85
125.60
123.86
118.46
114.60
114.45
114.27
114.19
113.86
113.62
113.59
77.32
77.00
76.68
56.43
55.99
55.96
55.81
55.77
55.72
55.71
55.66
30.43
30.01
29.78
29.34
29.11
21.63
Me
O
S
O
O
OMe
H2
C
H2
C
MeO
4
HO
3b
13C-NMR
400 MHz, CDCl3



3c

^{1}H-NMR

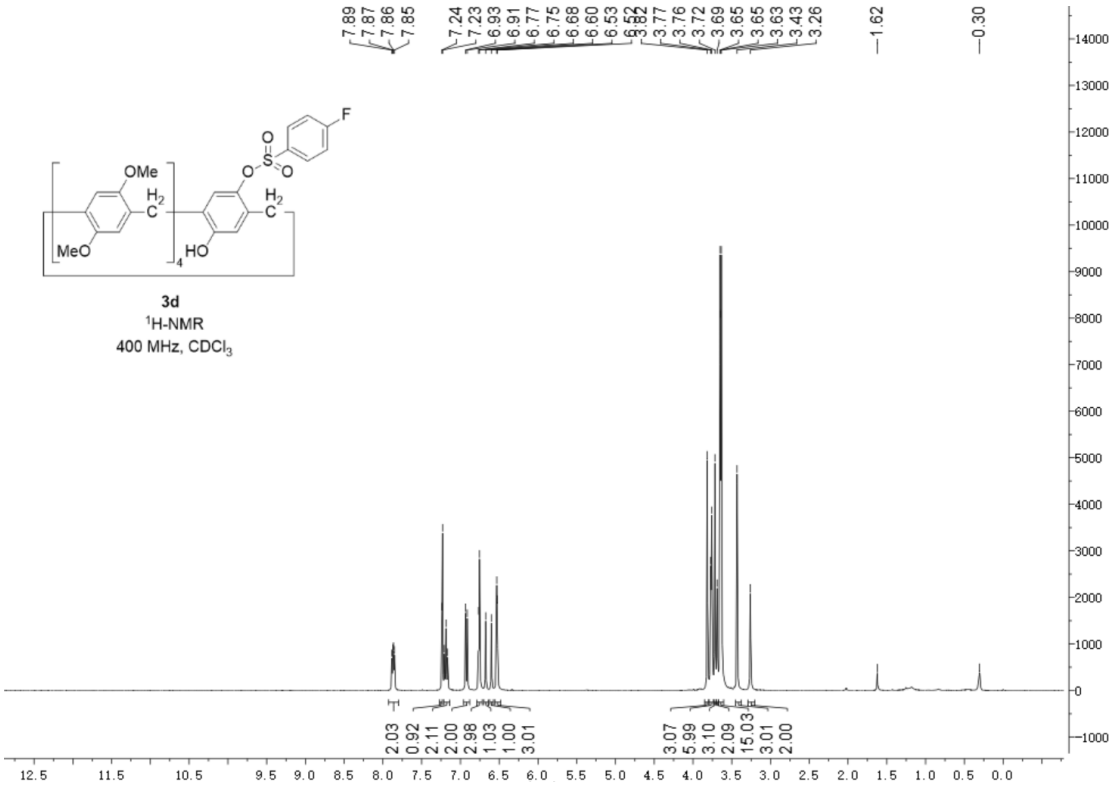
400 MHz, $CDCl_3$



3c

^{13}C-NMR

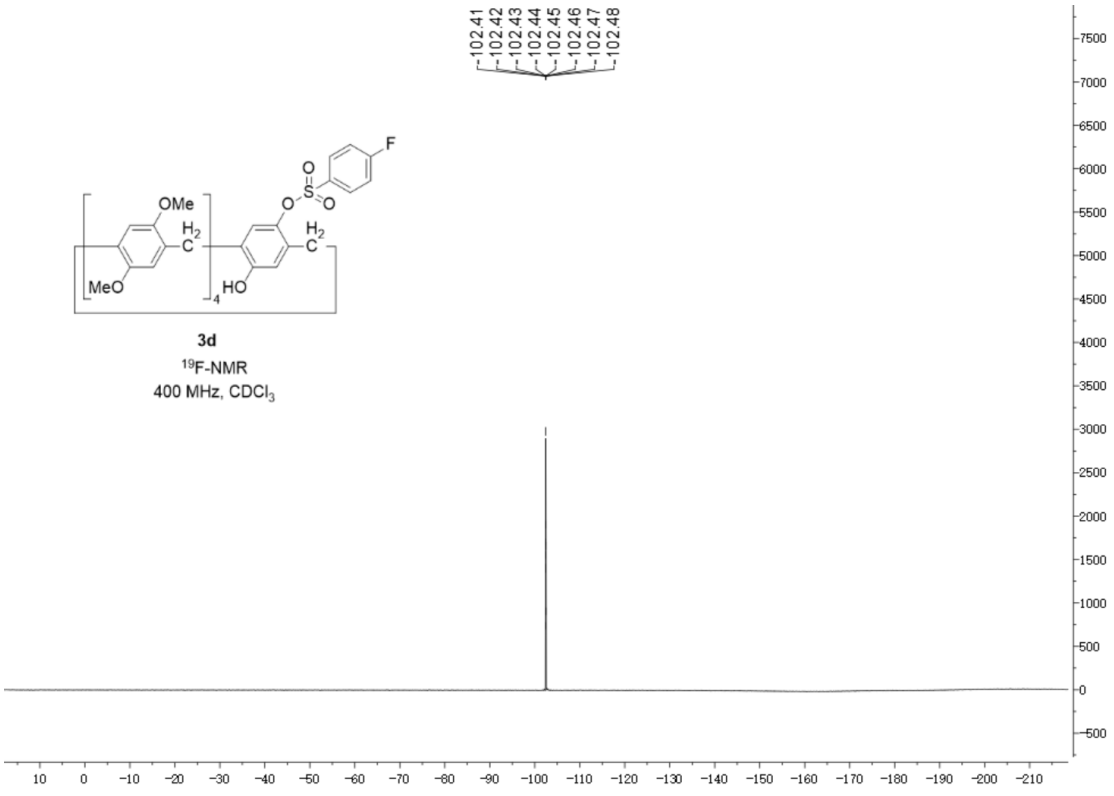
400 MHz, $CDCl_3$



3d

^{1}H-NMR

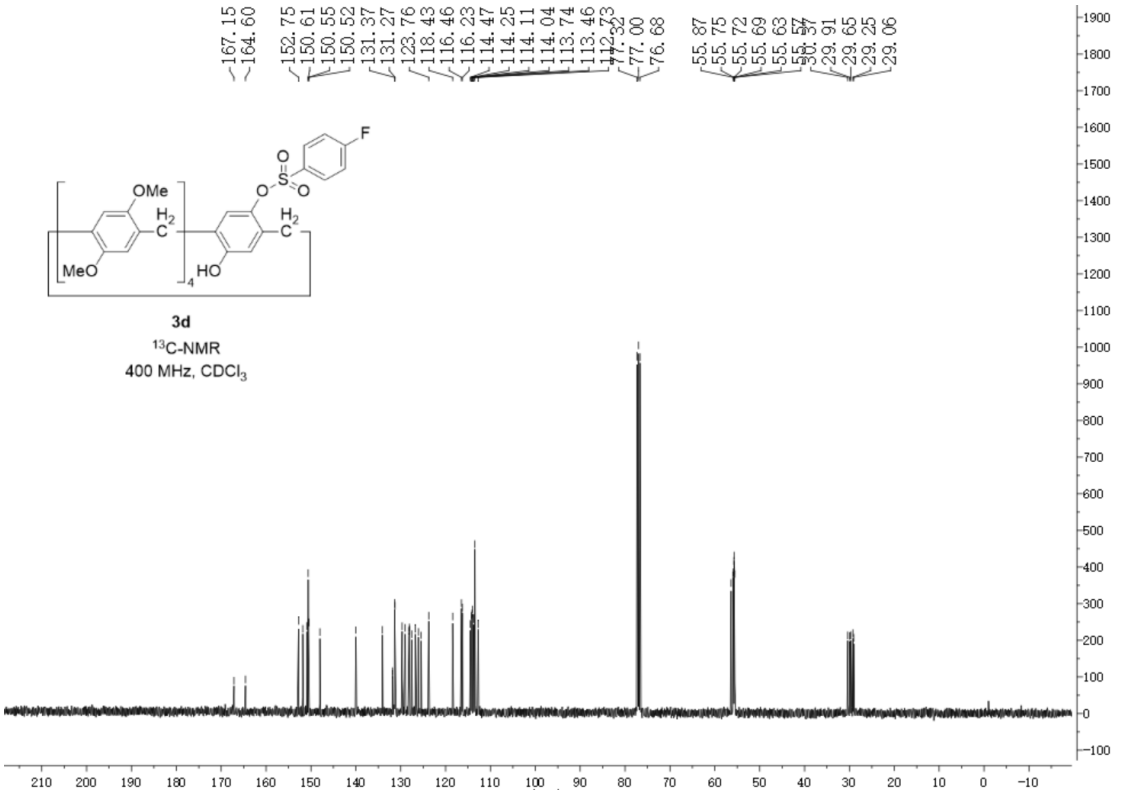
400 MHz, $CDCl_3$

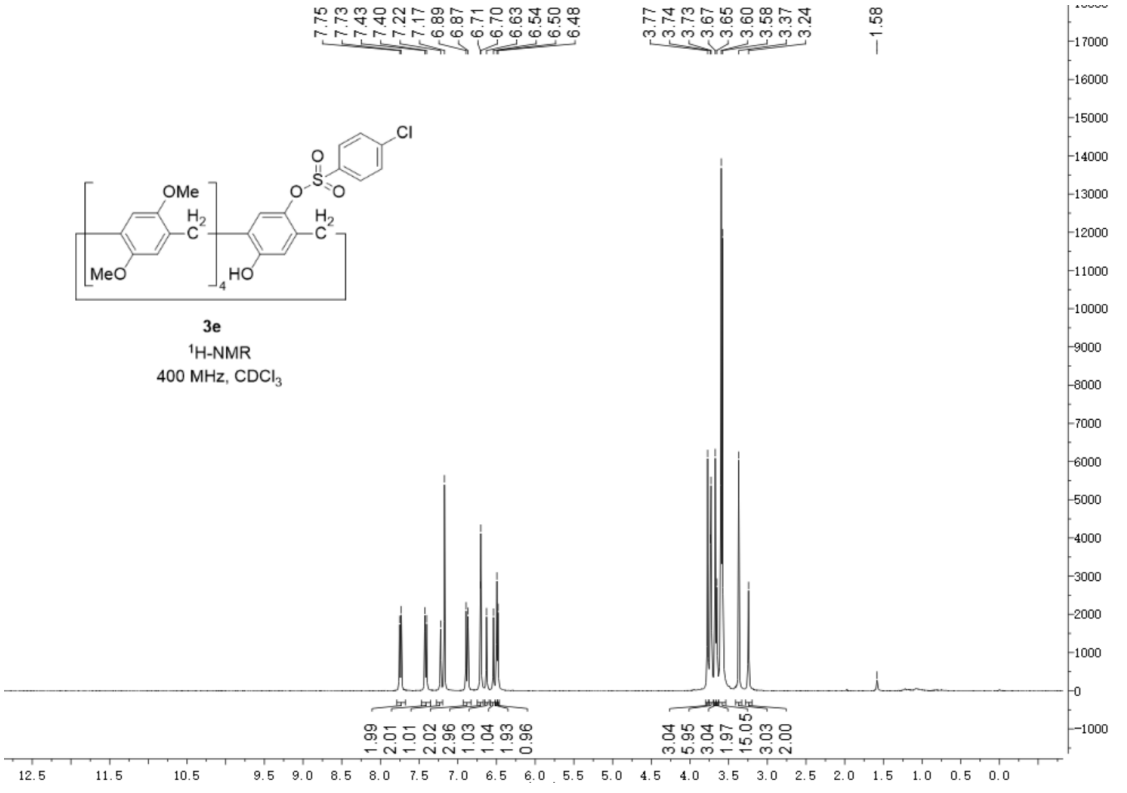


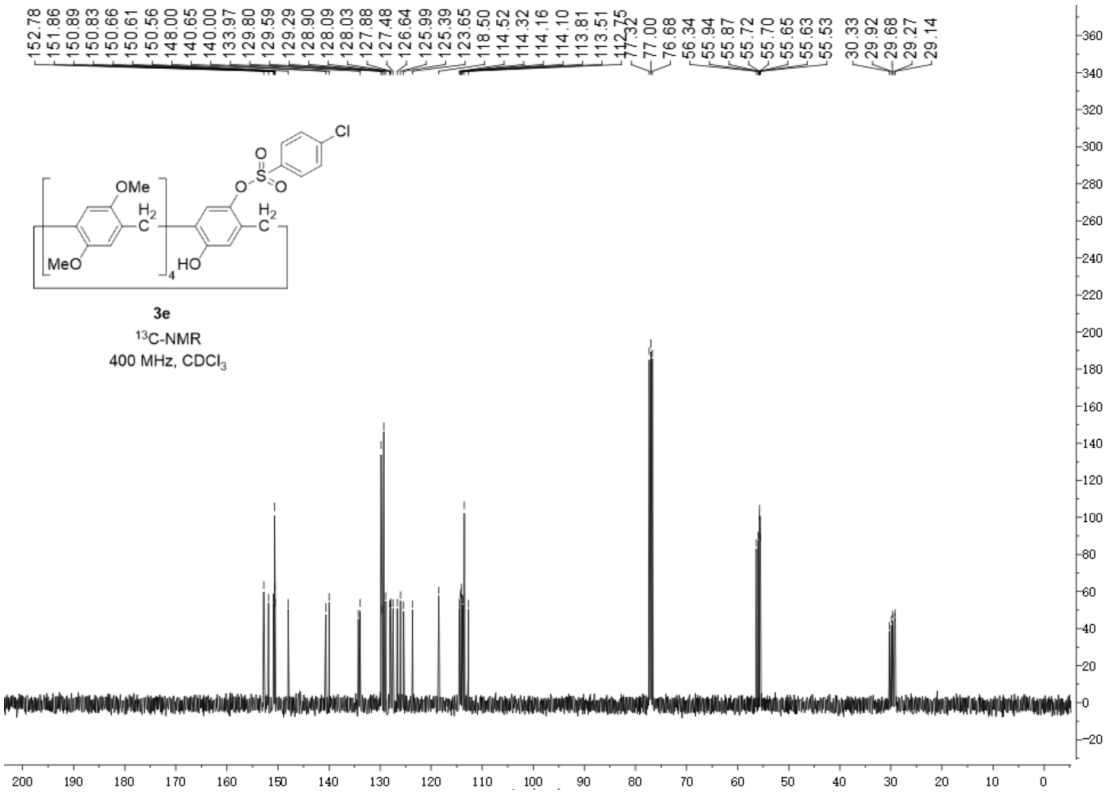
3d

^{19}F-NMR

400 MHz, $CDCl_3$


167.15
164.60
152.75
150.61
150.55
150.52
131.37
131.27
123.76
118.43
116.46
116.23
114.47
114.25
114.11
114.04
113.74
113.46
77.32
77.00
76.68
55.87
55.75
55.72
55.69
55.63
55.57
30.37
29.91
29.65
29.25
29.06
OMe
MeO
HO
F
3d
13C-NMR
400 MHz, CDCl3

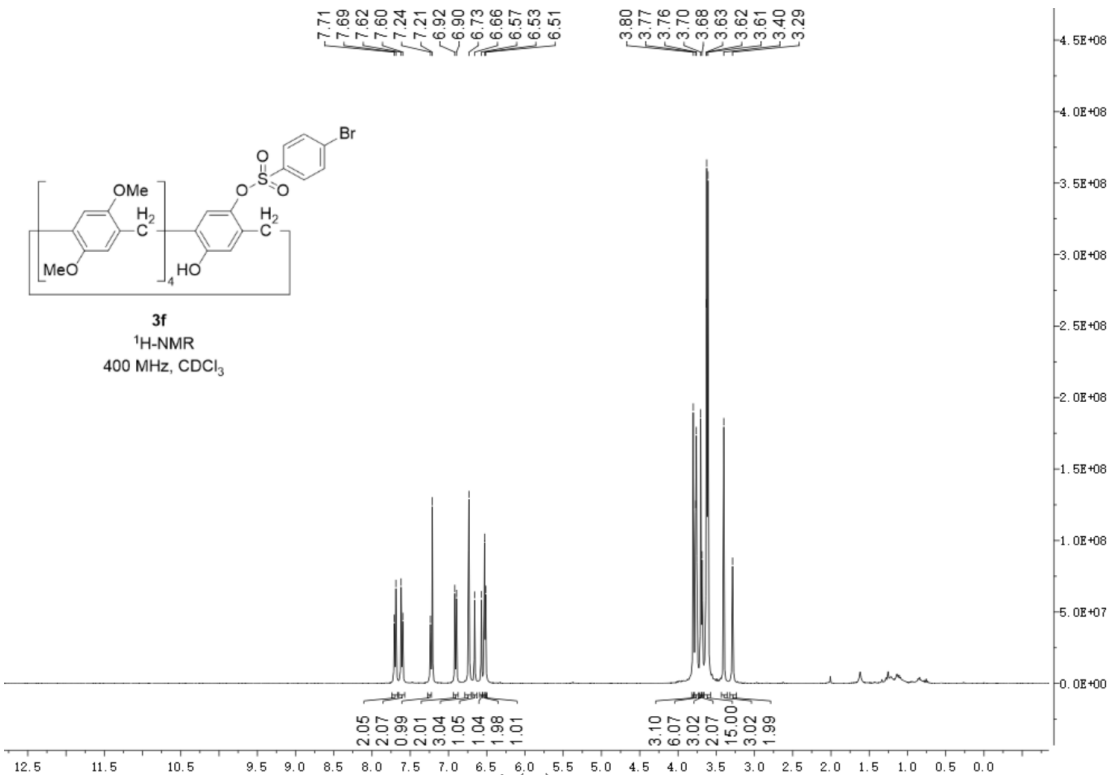

7.75
7.73
7.43
7.40
7.22
7.17
6.89
6.87
6.71
6.70
6.63
6.54
6.50
6.48
3.77
3.74
3.73
3.67
3.65
3.60
3.58
3.37
3.24
1.58
1.99
2.01
1.01
2.02
2.96
1.03
1.04
1.93
0.96
3.04
5.95
3.04
1.97
15.05
3.03
2.00
OMe
MeO
HO
Cl
3e
1H-NMR
400 MHz, CDCl3



3e

^{13}C-NMR

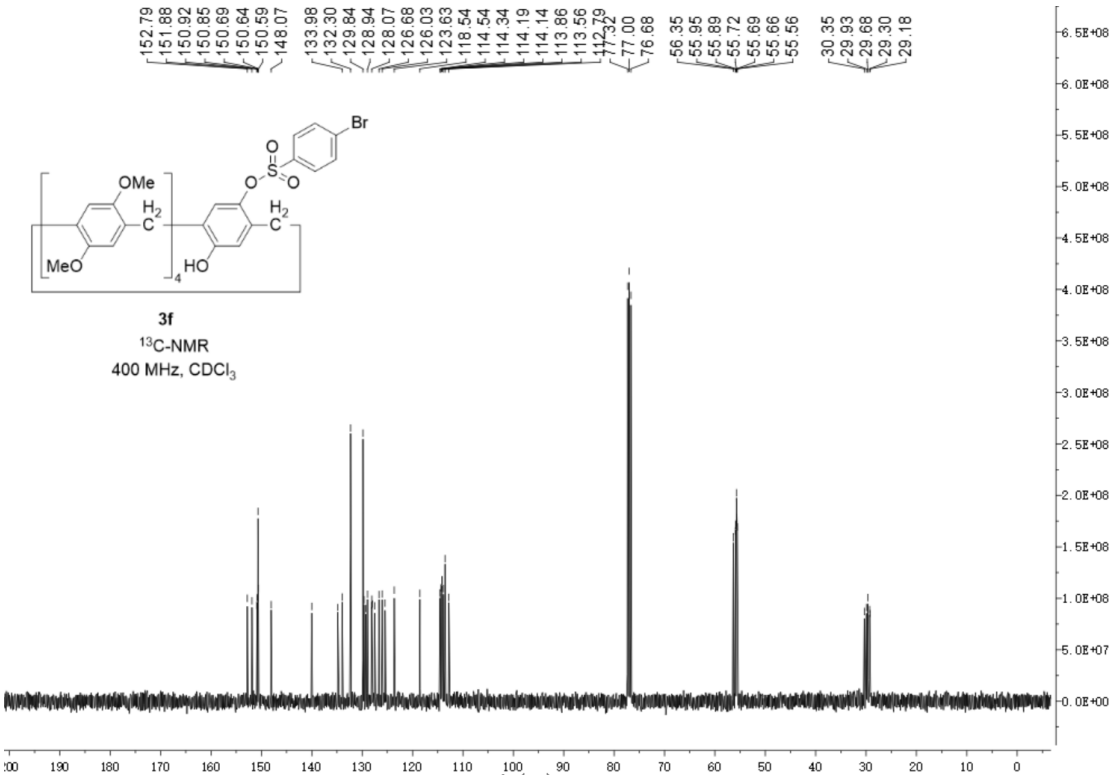
400 MHz, $CDCl_3$

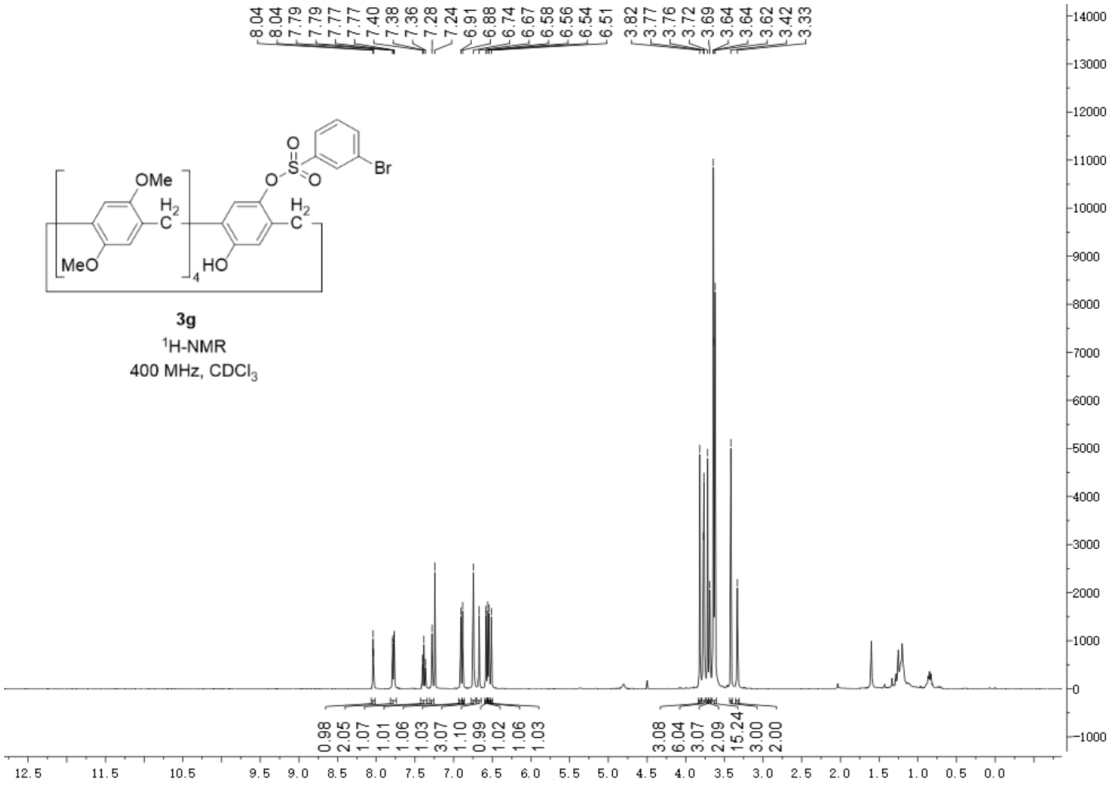


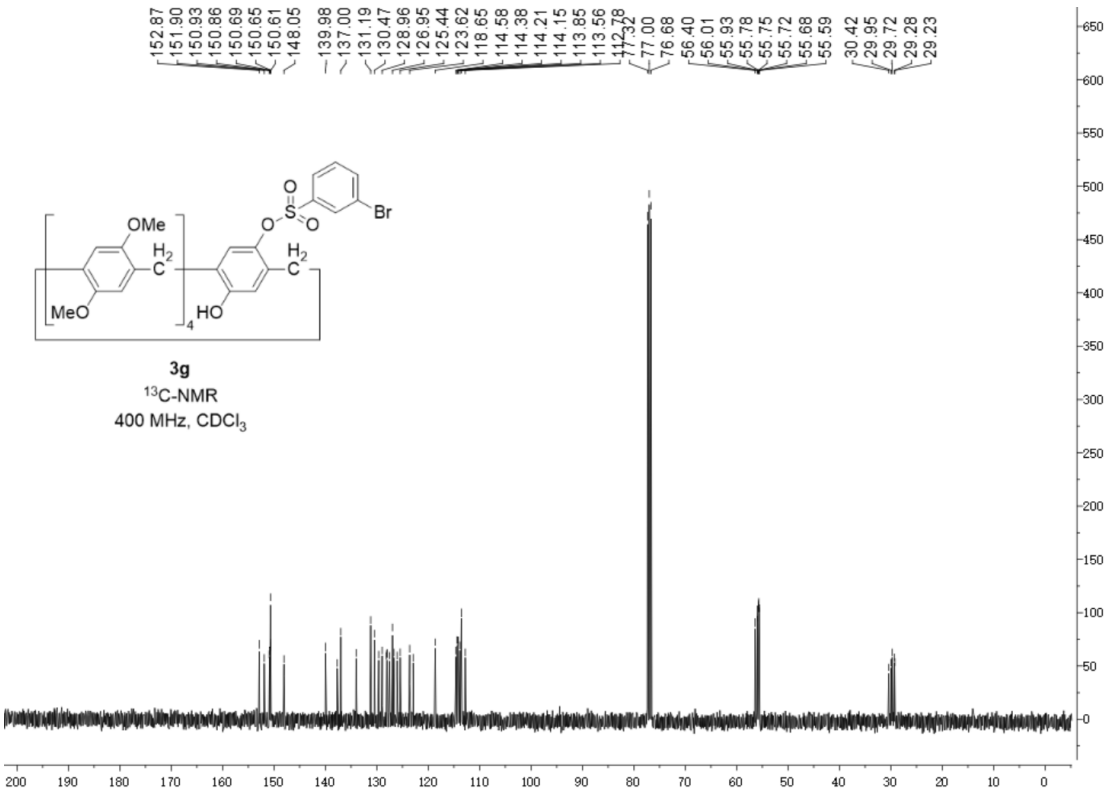
3f

^{1}H-NMR

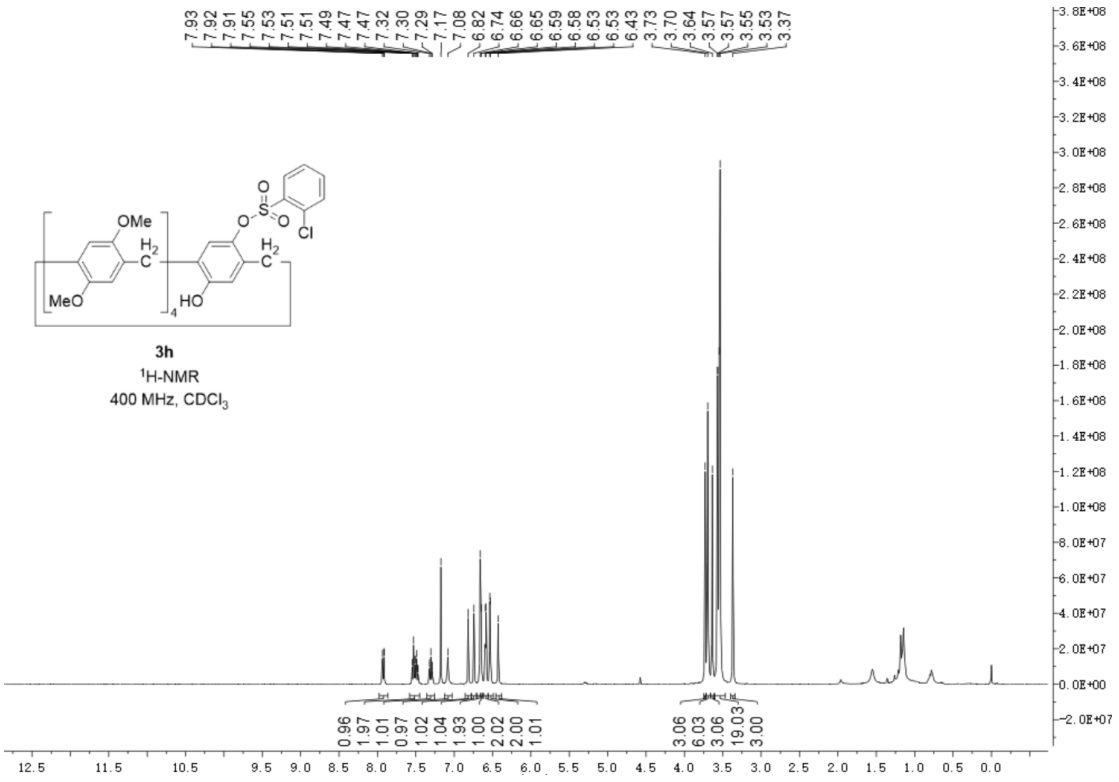
400 MHz, $CDCl_3$


152.79
151.88
150.92
150.85
150.69
150.64
150.59
148.07
133.98
132.30
129.84
128.94
128.07
126.68
126.03
123.63
118.54
114.54
114.34
114.19
114.14
113.86
113.56
112.79
77.32
77.00
76.68
56.35
55.95
55.89
55.72
55.69
55.66
55.56
30.35
29.93
29.68
29.30
29.18
Br
OMe
MeO
HO
4
3f
13C-NMR
400 MHz, CDCl3

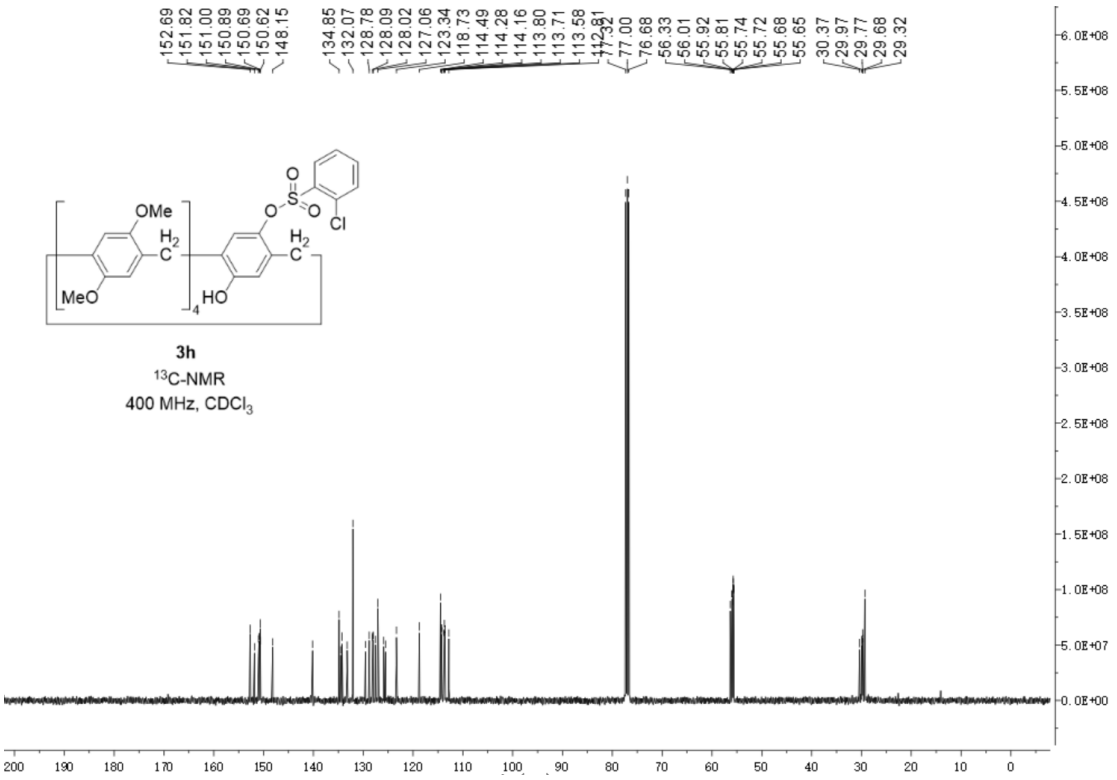

8.04
8.04
7.79
7.79
7.77
7.77
7.40
7.38
7.36
7.28
7.24
6.91
6.88
6.74
6.67
6.58
6.56
6.54
6.51
3.82
3.77
3.76
3.72
3.69
3.64
3.64
3.62
3.42
3.33
Br
OMe
MeO
HO
4
3g
1H-NMR
400 MHz, CDCl3
0.98
2.05
1.07
1.01
1.06
1.03
3.07
1.10
0.99
1.02
1.06
1.03
3.08
6.04
3.07
2.09
15.24
3.00
2.00

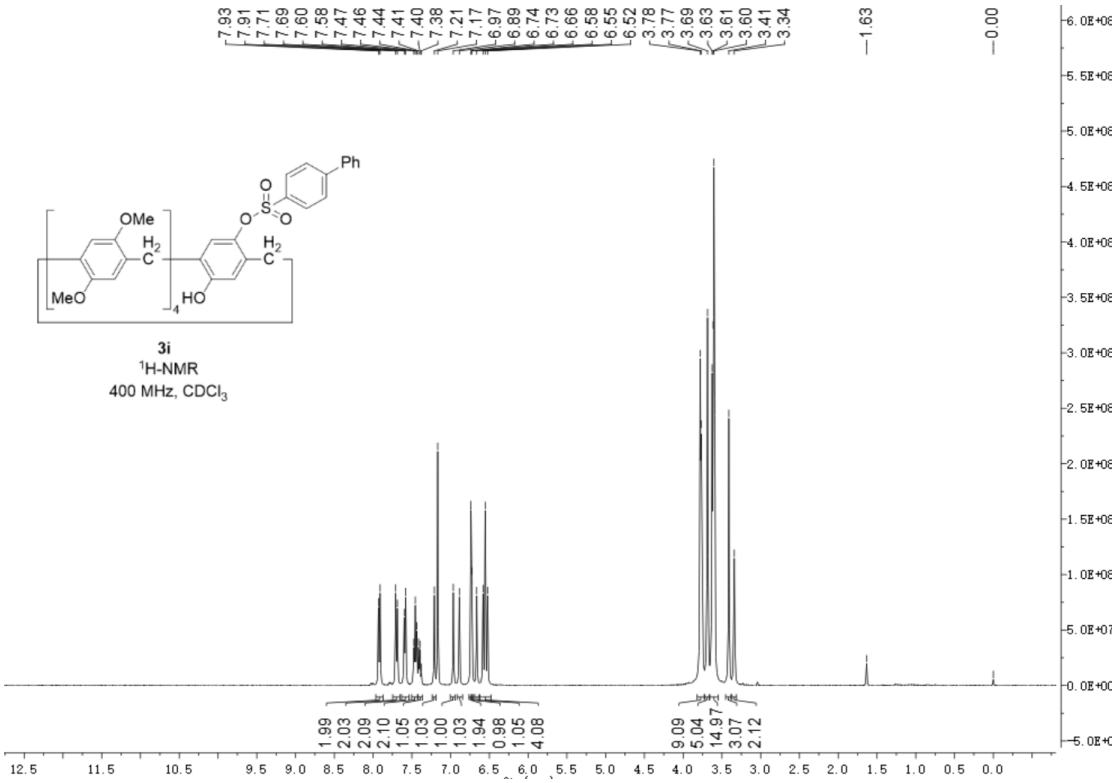


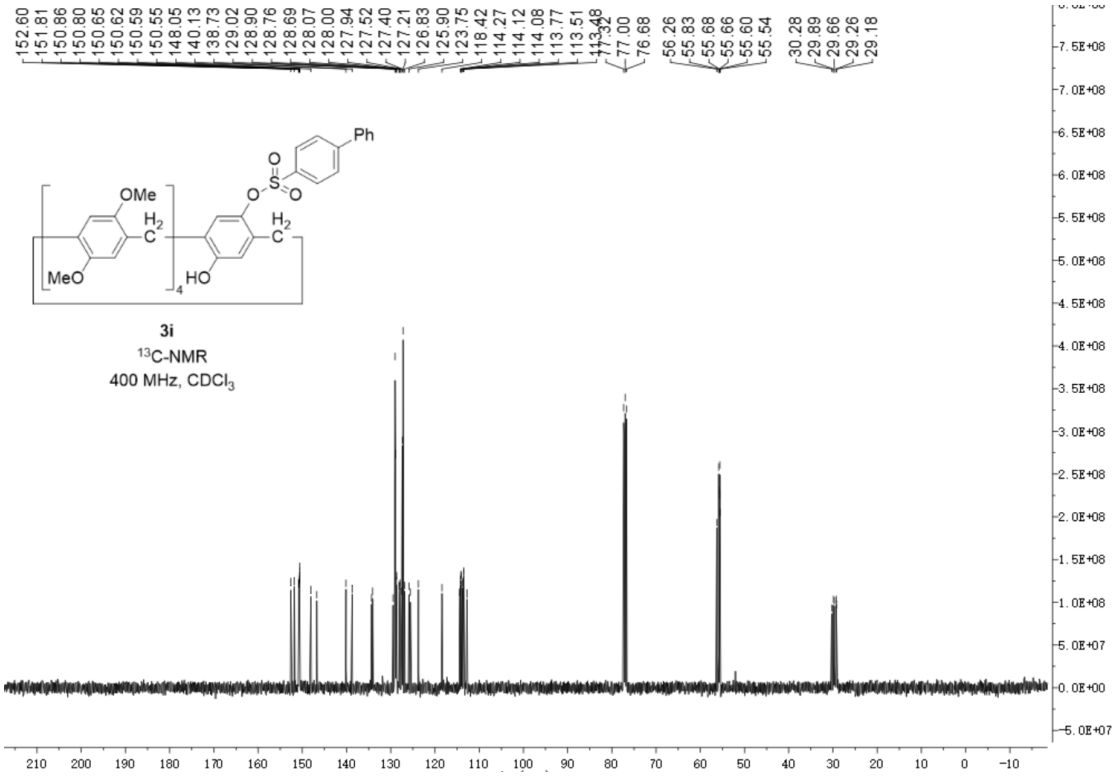
3g
^{13}C-NMR
400 MHz, $CDCl_3$

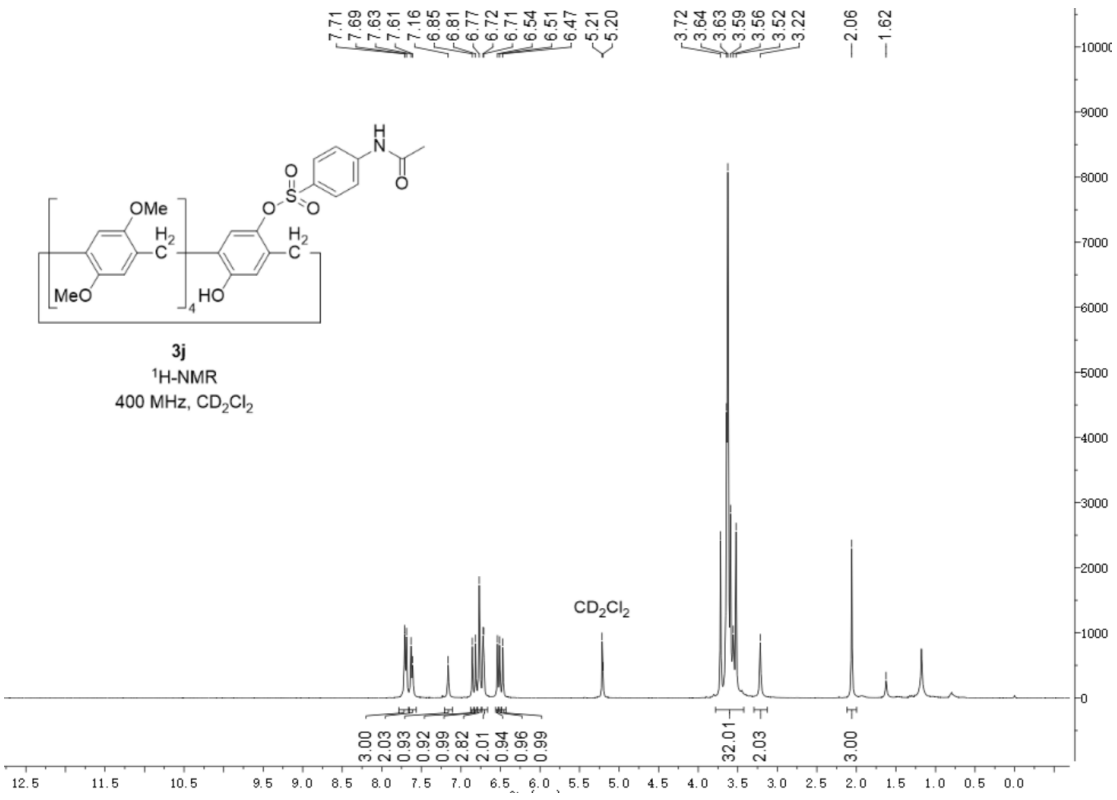


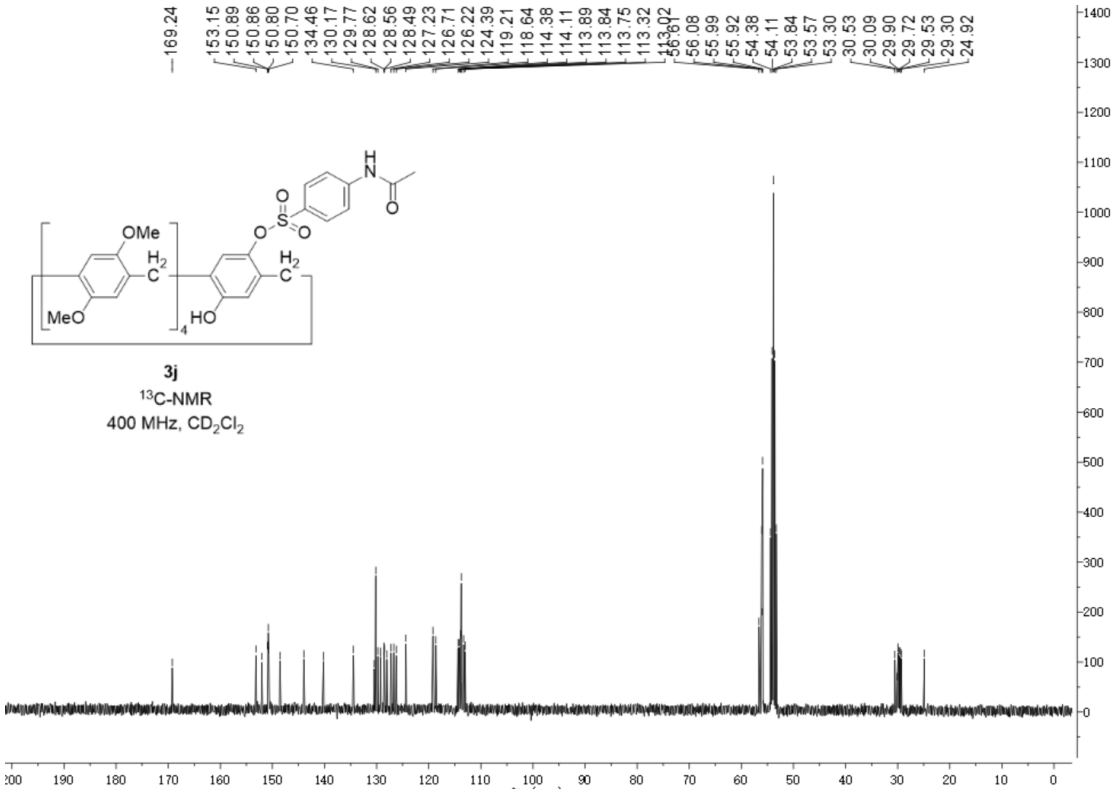
3h
^{1}H-NMR
400 MHz, $CDCl_3$


152.69
151.82
151.00
150.89
150.69
150.62
148.15
134.85
132.07
128.78
128.09
128.02
127.06
123.34
118.73
114.49
114.28
114.16
113.80
113.71
113.58
112.81
77.32
77.00
76.68
56.33
56.01
55.92
55.81
55.74
55.72
55.68
55.65
30.37
29.97
29.77
29.68
29.32
OMe
MeO
HO
Cl
4
3h
13C-NMR
400 MHz, CDCl3


7.93
7.91
7.71
7.69
7.60
7.58
7.47
7.46
7.44
7.41
7.40
7.38
7.21
7.17
6.97
6.89
6.74
6.73
6.66
6.58
6.55
6.52
3.78
3.77
3.69
3.63
3.61
3.60
3.41
3.34
1.63
0.00
Ph
OMe
MeO
HO
4
1.99
2.03
2.09
2.10
1.05
1.03
1.00
1.03
1.94
0.98
1.05
4.08
9.09
5.04
14.97
3.07
2.12
3i
1H-NMR
400 MHz, CDCl3


152.60
151.81
150.86
150.80
150.65
150.62
150.59
150.55
148.05
140.13
138.73
129.02
128.90
128.76
128.69
128.07
128.00
127.94
127.52
127.40
127.21
126.83
125.90
123.75
118.42
114.27
114.12
114.08
113.77
113.51
113.48
77.32
77.00
76.68
56.26
55.83
55.68
55.66
55.60
55.54
30.28
29.89
29.66
29.26
29.18
Ph
O
S
O
O
OMe
H2
C
H2
C
MeO
HO
4
3i
13C-NMR
400 MHz, CDCl3

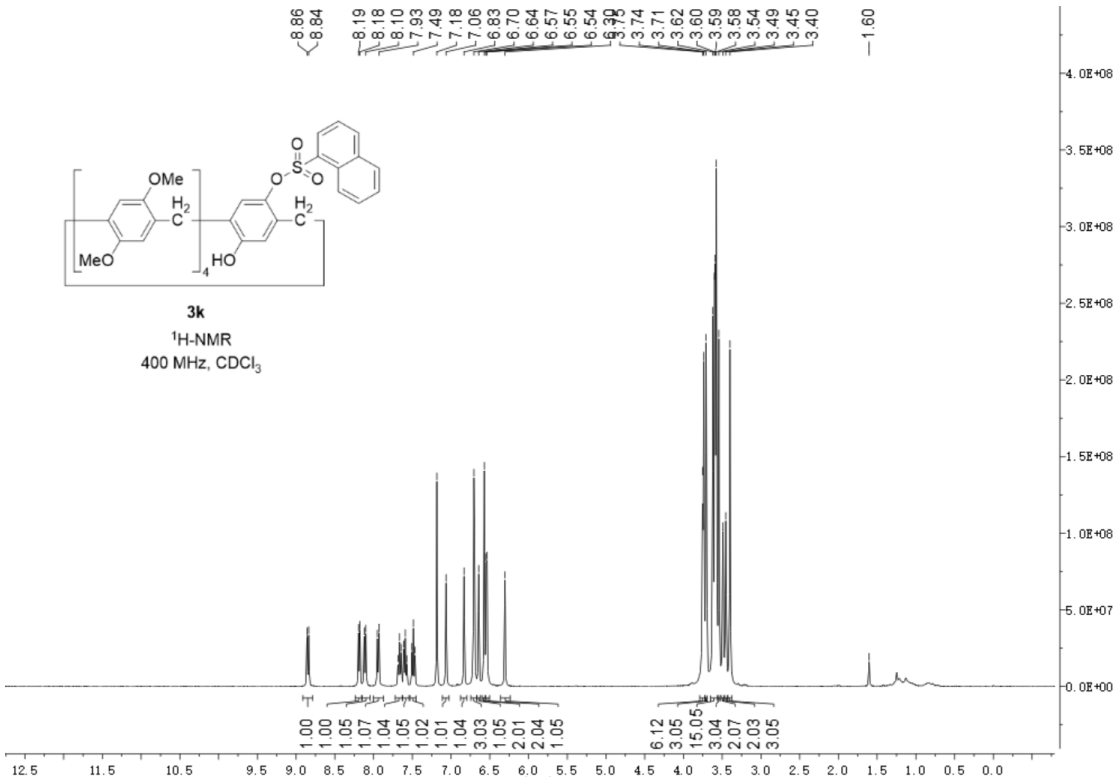

7.71
7.69
7.63
7.61
7.16
6.85
6.81
6.77
6.72
6.71
6.54
6.51
6.47
5.21
5.20
3.72
3.64
3.63
3.59
3.56
3.52
3.22
2.06
1.62
H
N
O
O
S
O
O
OMe
H2
C
H2
C
MeO
HO
4
CD2Cl2
3.00
2.03
0.93
0.92
0.99
2.82
2.01
0.94
0.96
0.99
32.01
2.03
3.00
3j
1H-NMR
400 MHz, CD2Cl2



3j

^{13}C-NMR

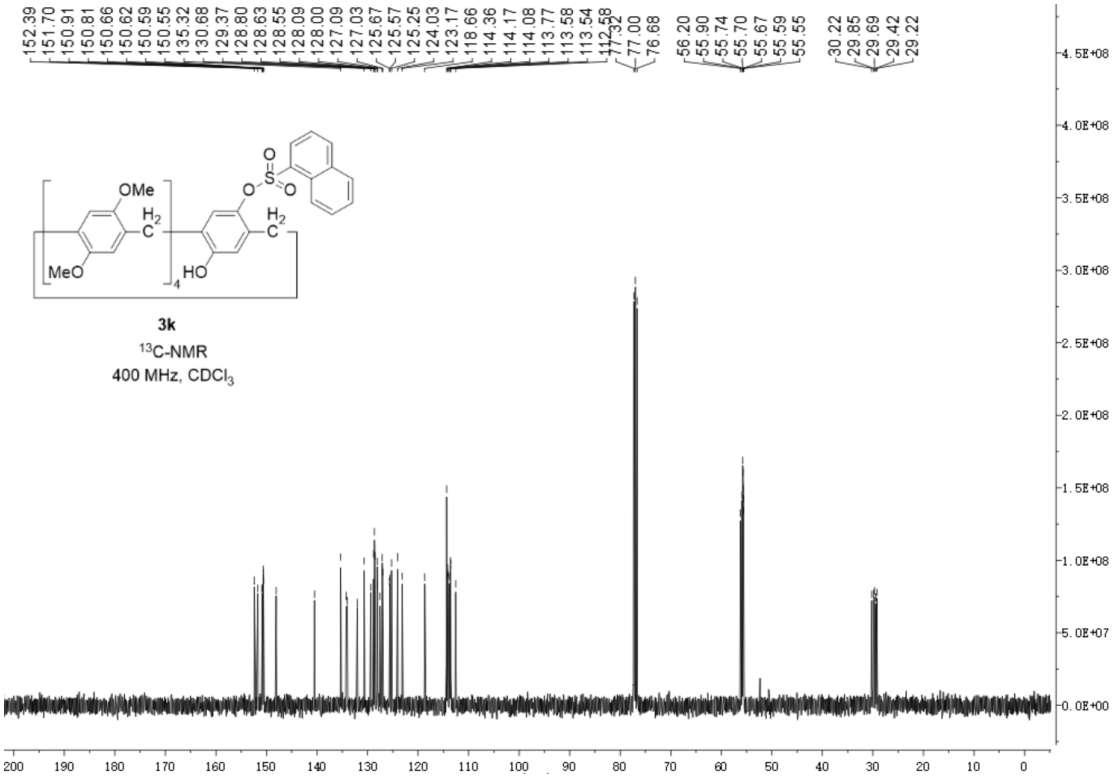
400 MHz, CD_2Cl_2

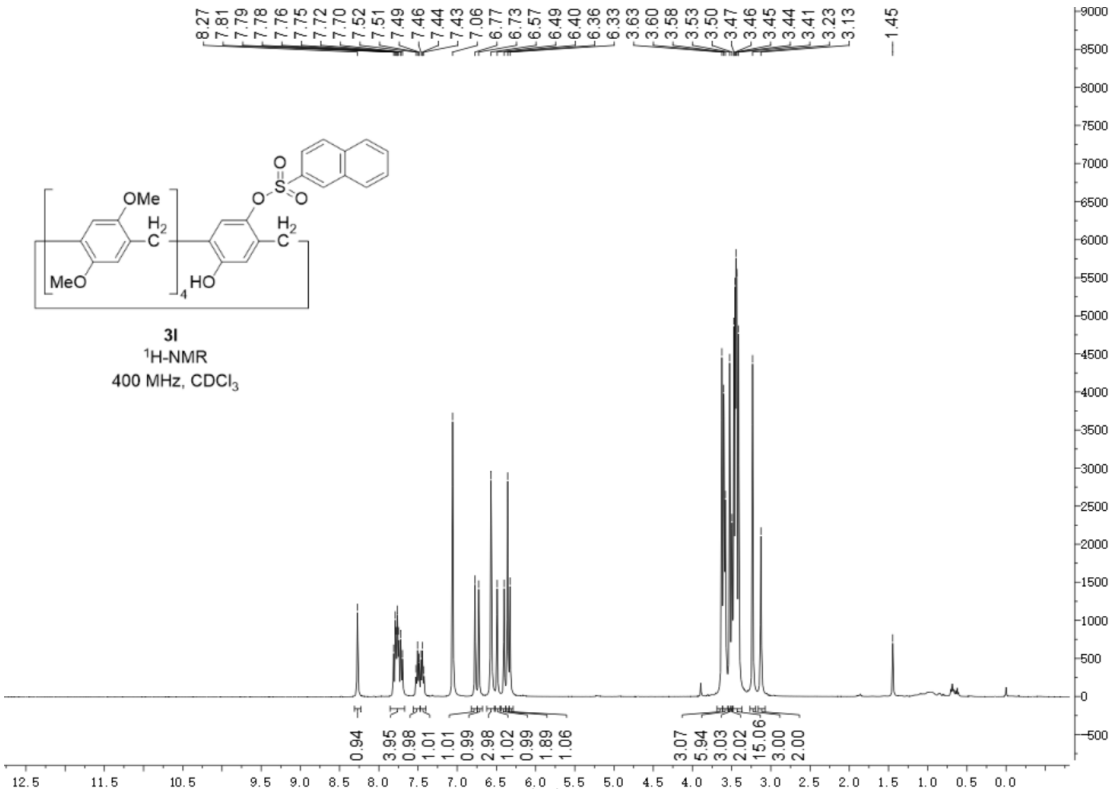


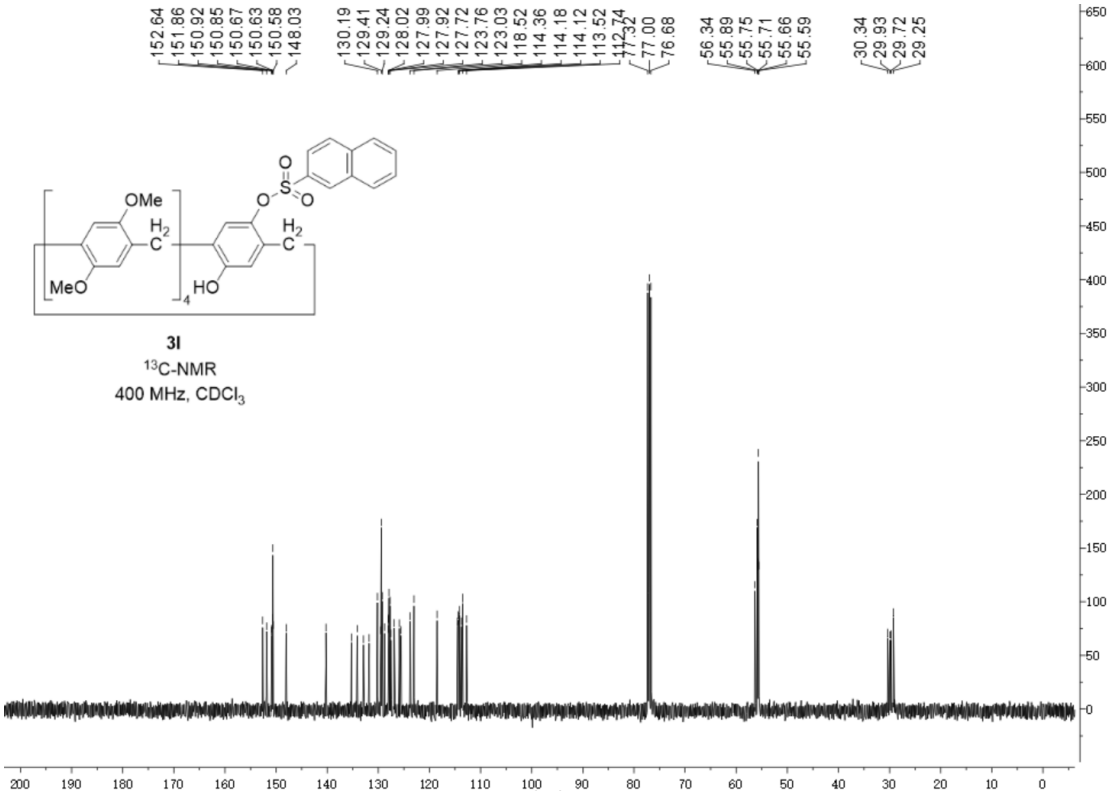
3k

^{1}H-NMR

400 MHz, $CDCl_3$


152.39
151.70
150.91
150.81
150.66
150.62
150.59
150.55
135.32
130.68
129.37
128.80
128.63
128.55
128.09
128.00
127.09
127.03
125.67
125.57
125.25
124.03
123.17
118.66
114.36
114.17
114.08
113.77
113.58
113.54
112.58
77.32
77.00
76.68
56.20
55.90
55.74
55.70
55.67
55.59
55.55
30.22
29.85
29.69
29.42
29.22
OMe
MeO
HO
4
3k
13C-NMR
400 MHz, CDCl3

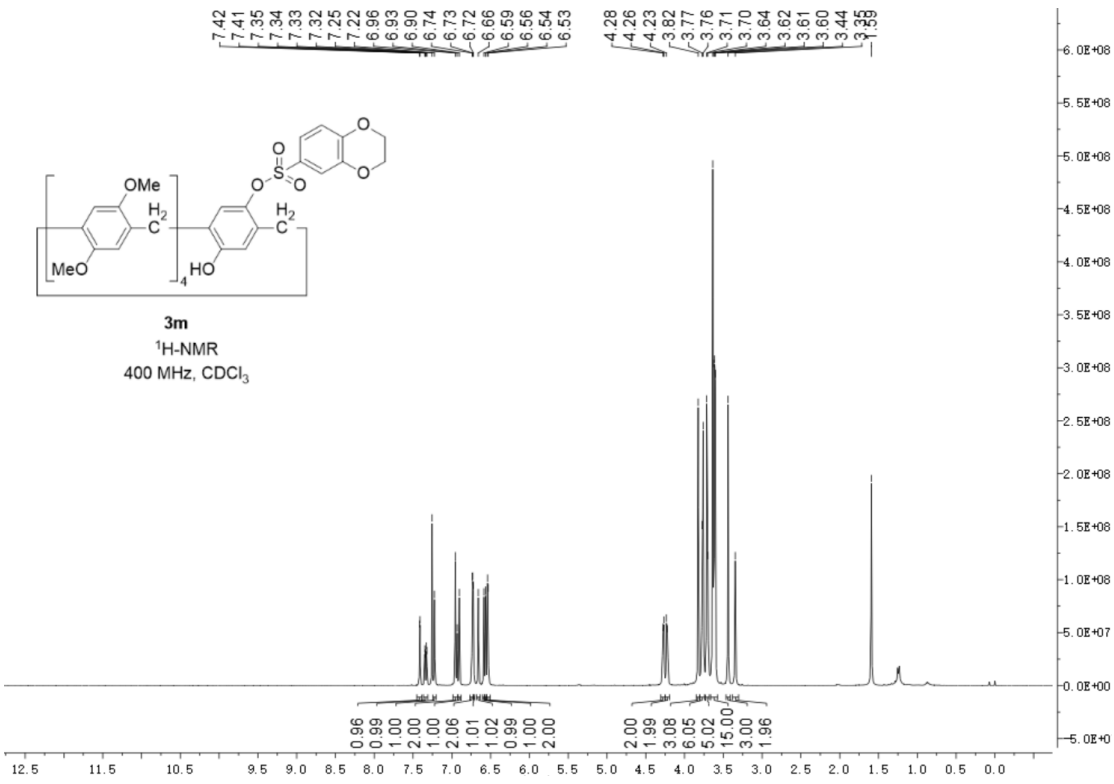

8.27
7.81
7.79
7.78
7.76
7.75
7.72
7.70
7.52
7.51
7.49
7.46
7.44
7.43
7.06
6.77
6.73
6.57
6.49
6.40
6.36
6.33
3.63
3.60
3.58
3.53
3.50
3.47
3.46
3.45
3.44
3.41
3.23
3.13
1.45
OMe
MeO
HO
4
3l
1H-NMR
400 MHz, CDCl3
0.94
3.95
0.98
1.01
1.01
0.99
2.98
1.02
0.99
1.89
1.06
3.07
5.94
3.03
2.02
15.06
3.00
2.00



3l

^{13}C-NMR

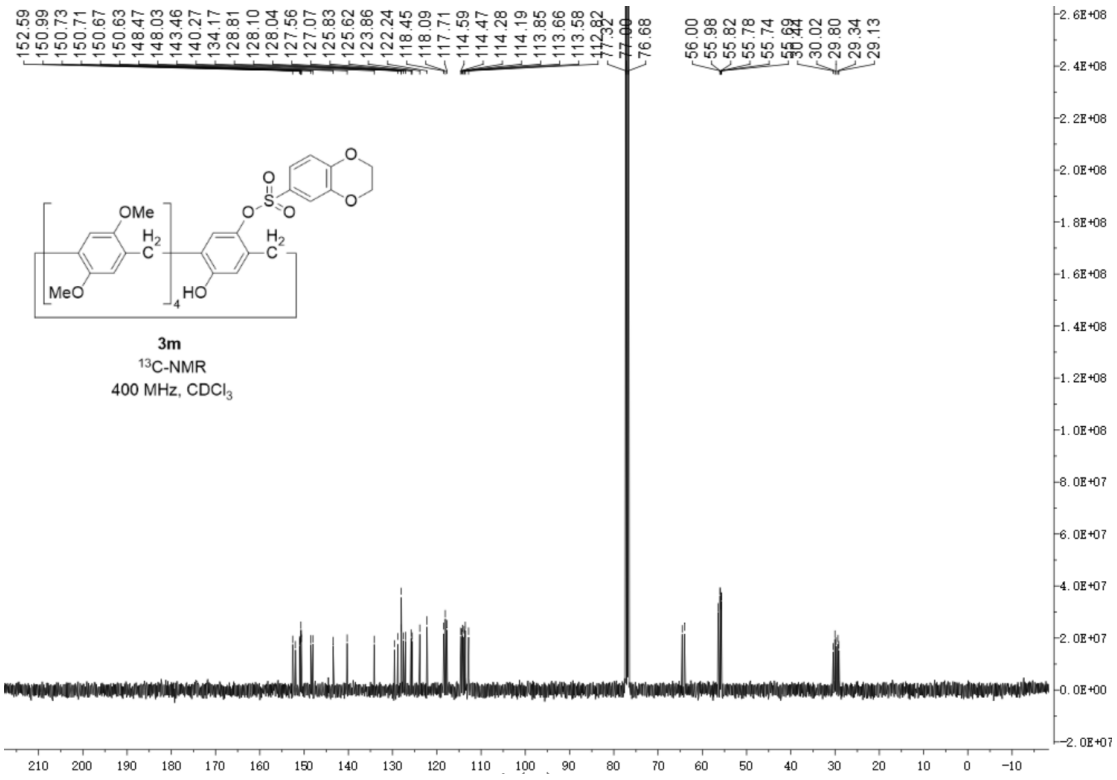
400 MHz, $CDCl_3$



3m

^{1}H-NMR

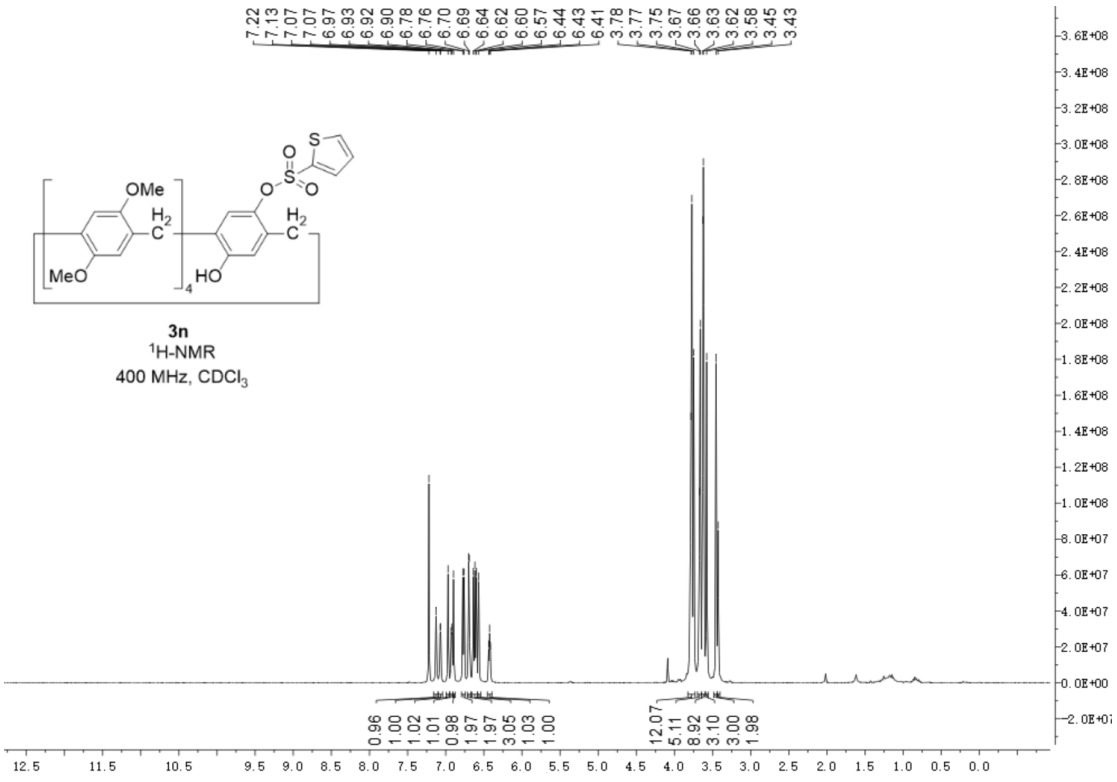
400 MHz, $CDCl_3$



3m

^{13}C-NMR

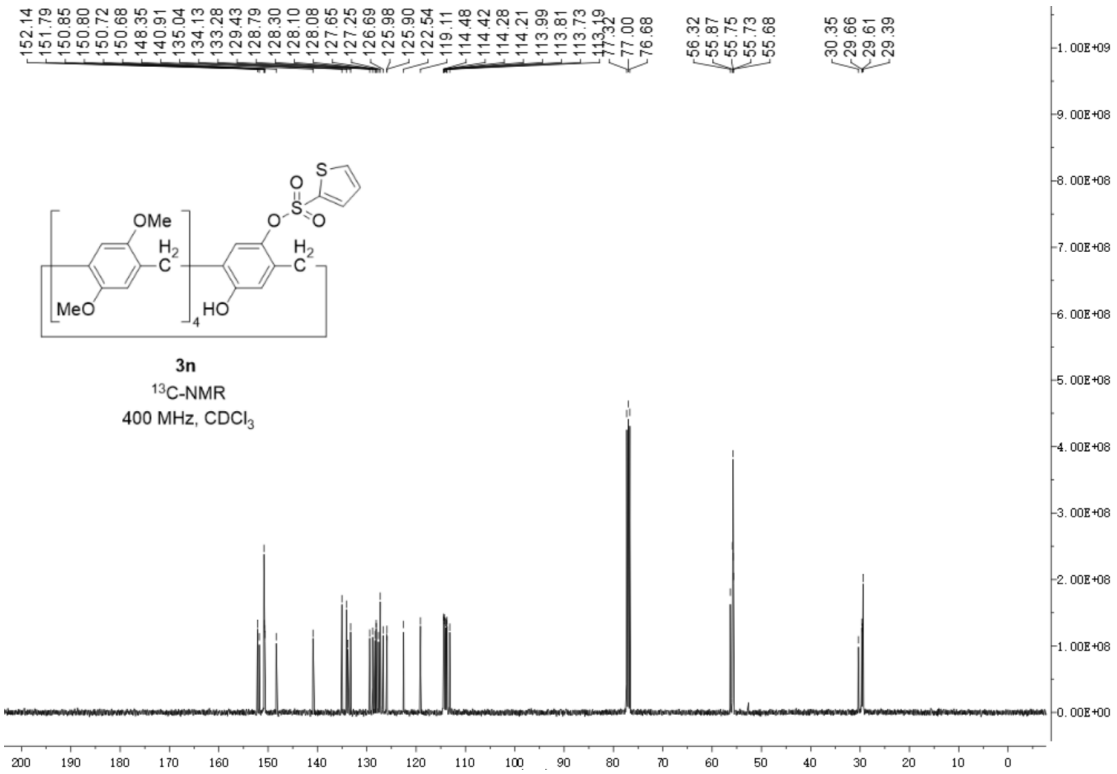
400 MHz, $CDCl_3$



3n

^{1}H-NMR

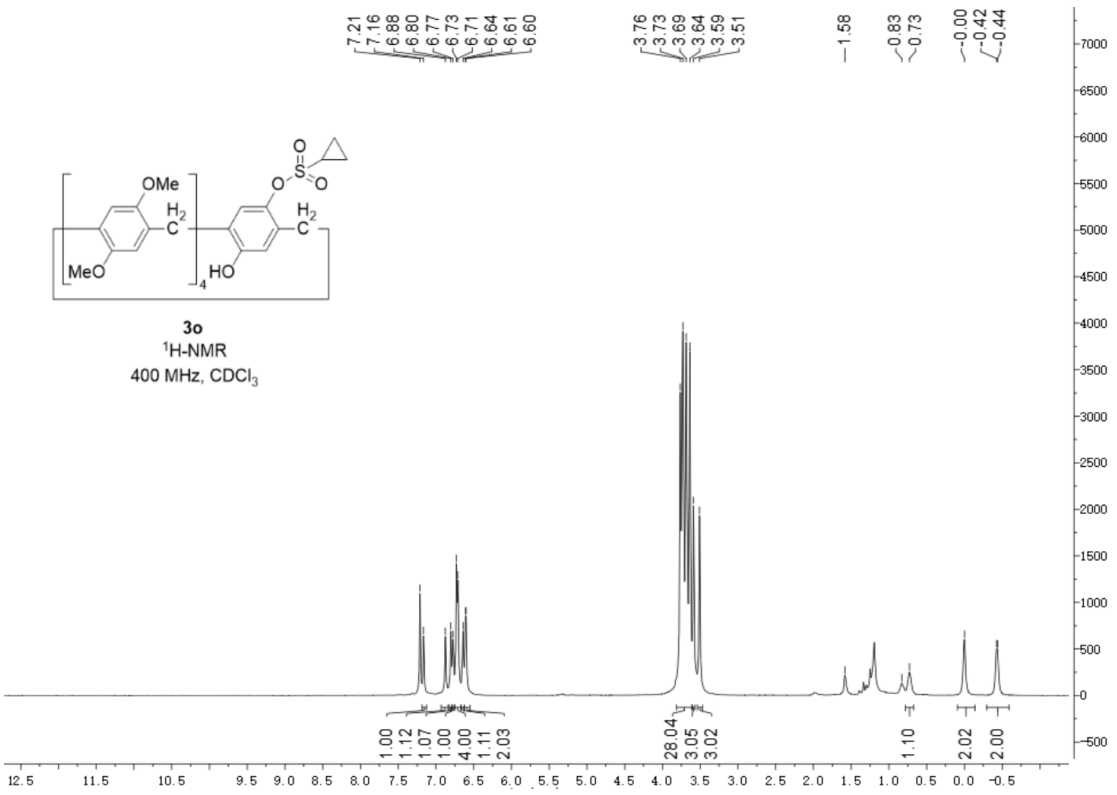
400 MHz, $CDCl_3$



3n

^{13}C-NMR

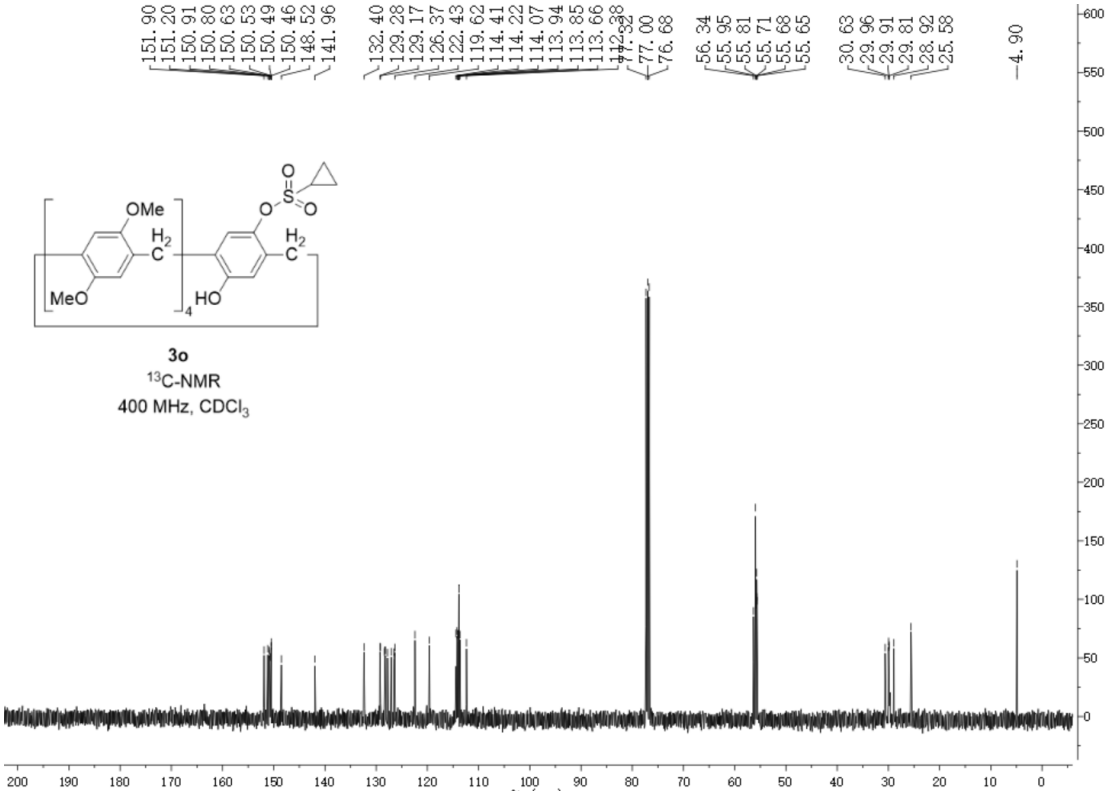
400 MHz, $CDCl_3$

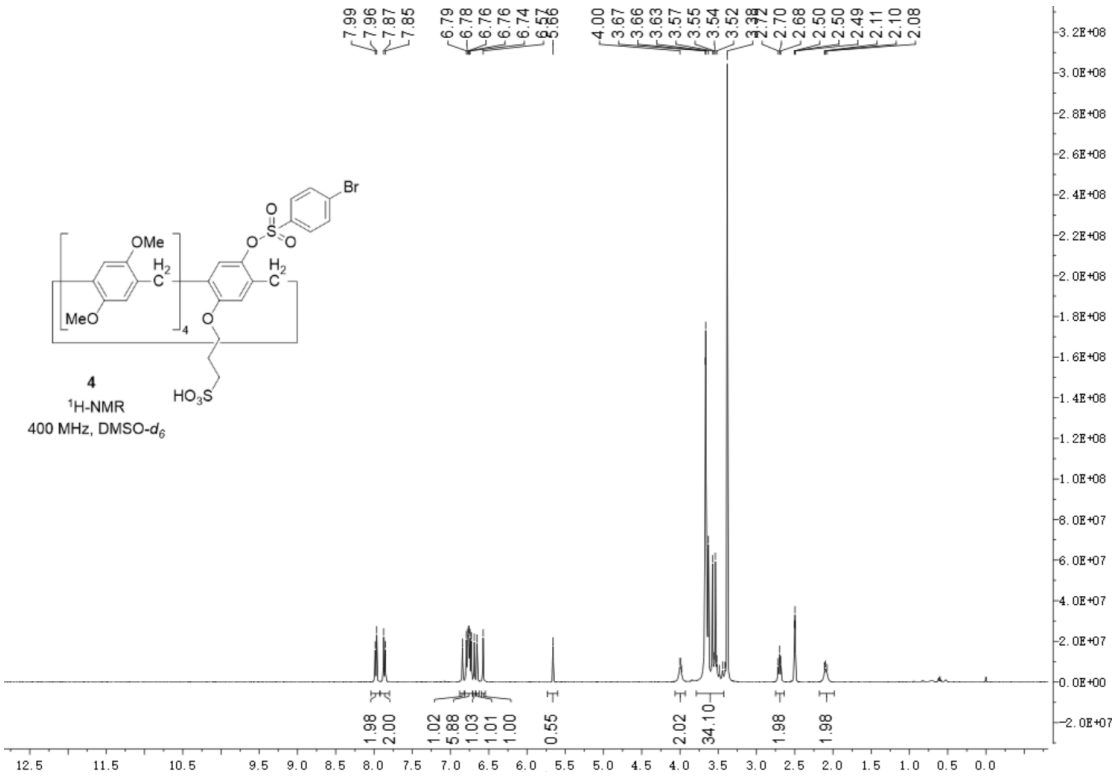


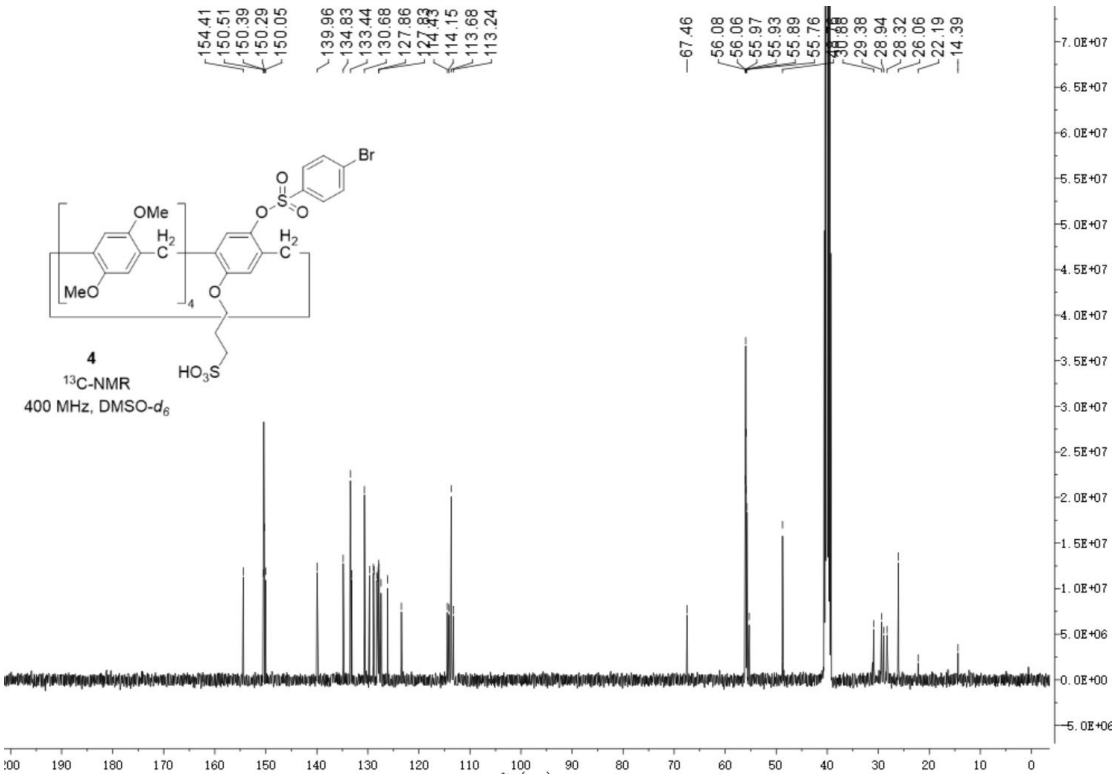
3o

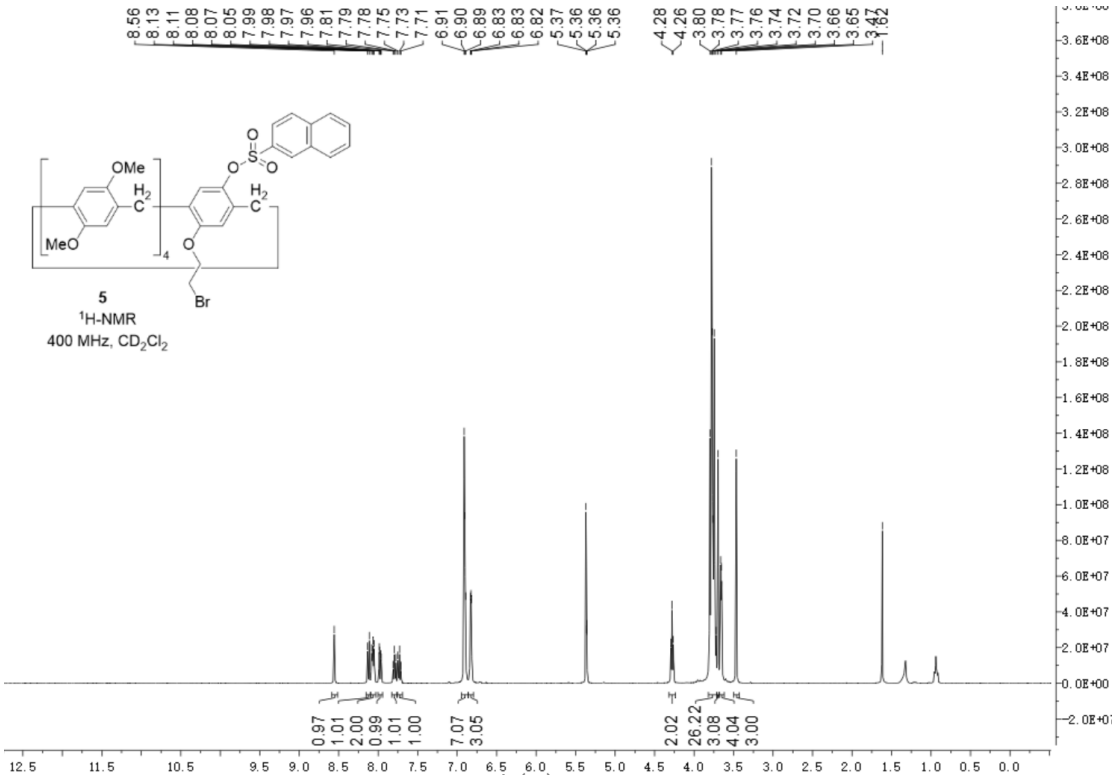
^{1}H-NMR

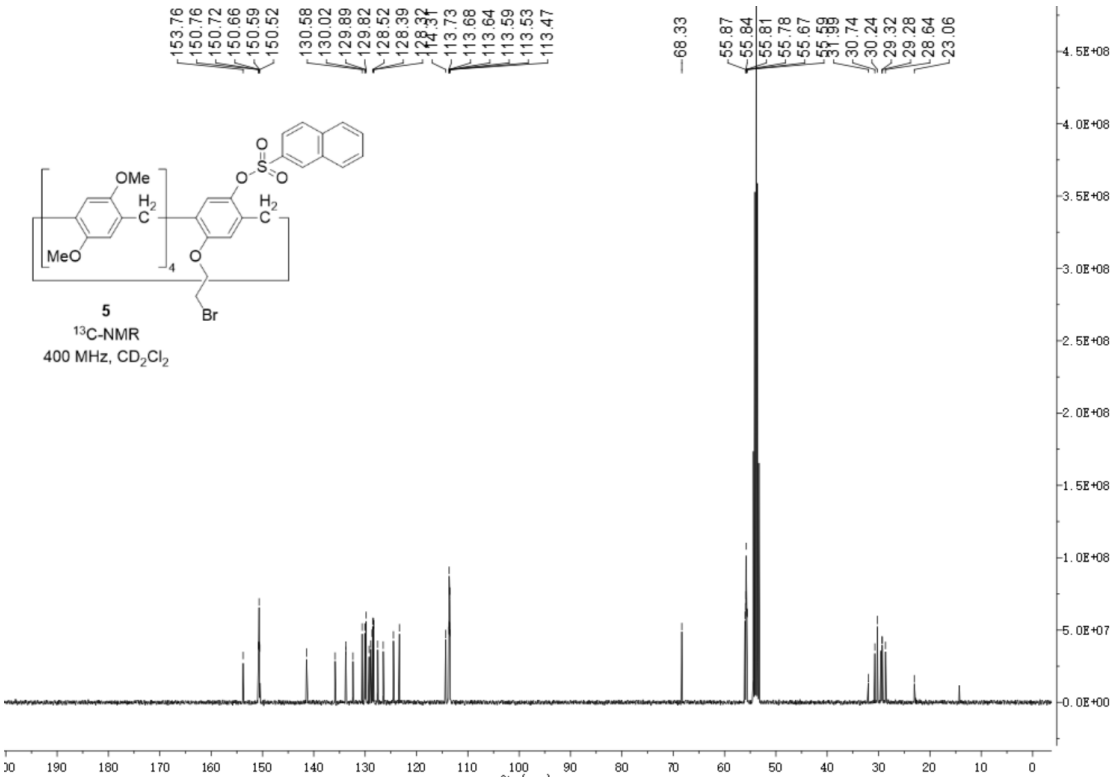
400 MHz, $CDCl_3$

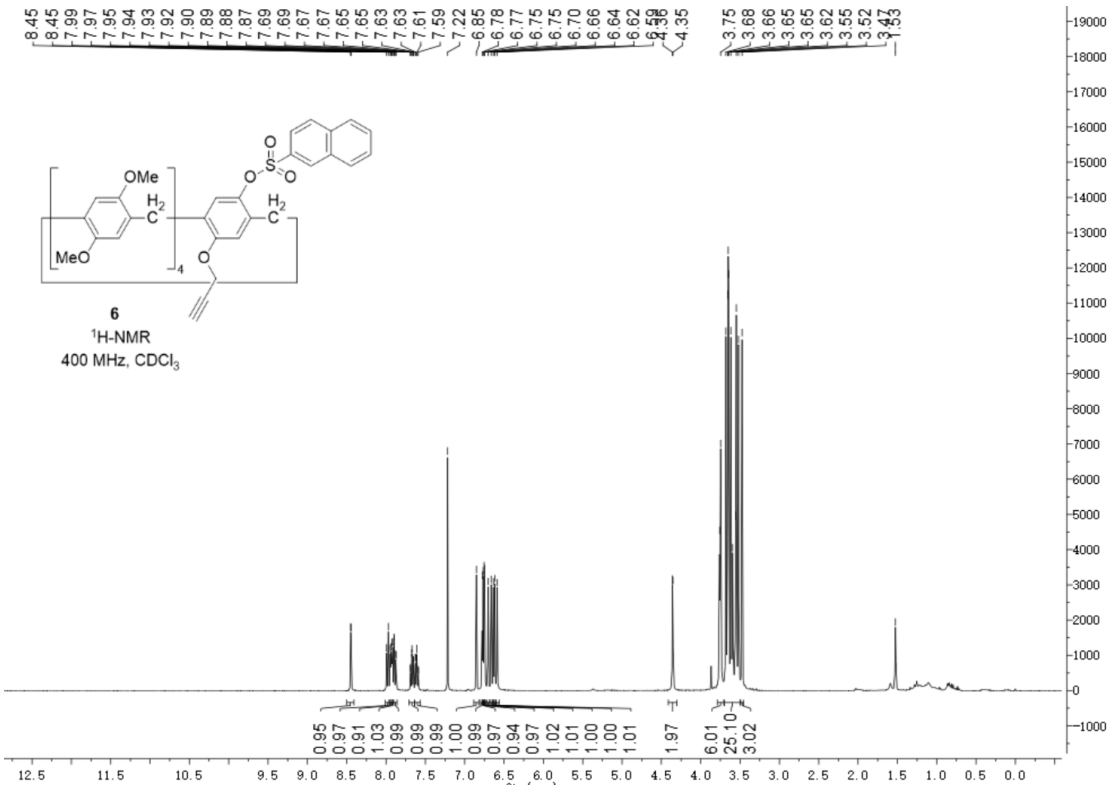

151.90
151.20
150.91
150.80
150.63
150.53
150.49
150.46
148.52
141.96
132.40
129.28
129.17
126.37
122.43
119.62
114.41
114.22
114.07
113.94
113.85
113.66
77.00
76.68
56.34
55.95
55.81
55.71
55.68
55.65
30.63
29.96
29.91
29.81
28.92
25.58
4.90
OMe
MeO
HO
4
3o
13C-NMR
400 MHz, CDCl3

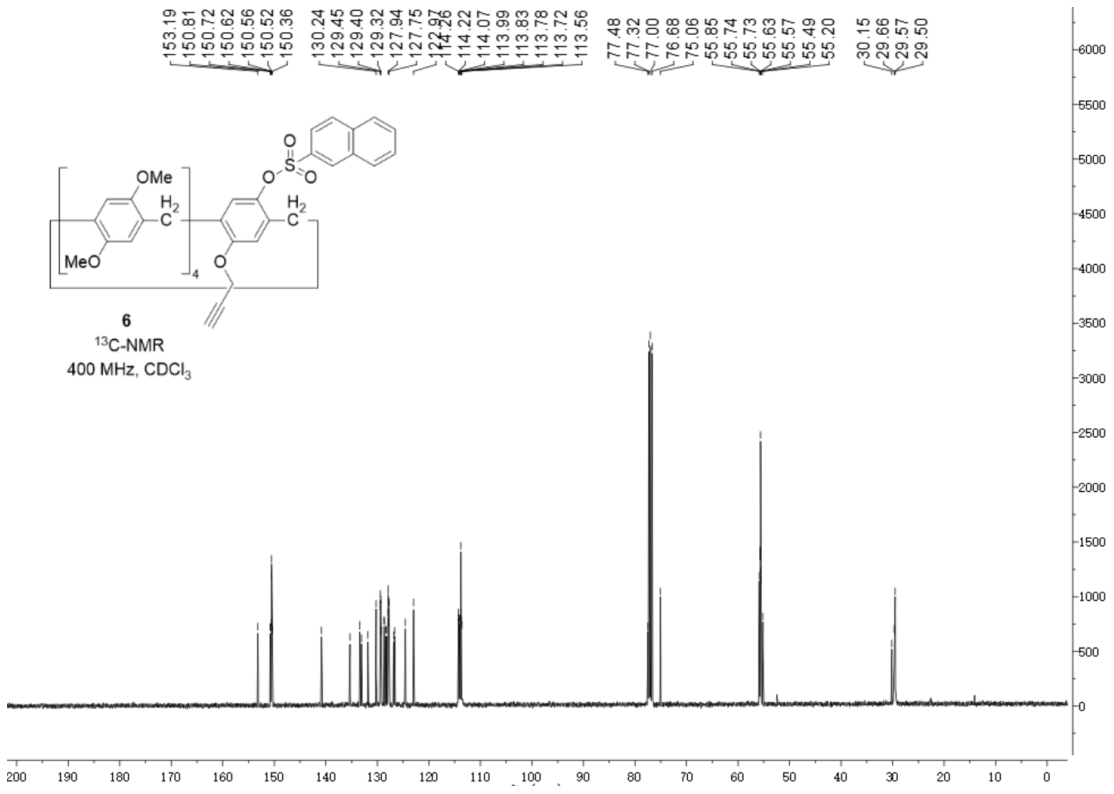

7.99
7.96
7.87
7.85
6.79
6.78
6.76
6.76
6.74
4.00
3.67
3.66
3.63
3.57
3.55
3.54
3.52
2.72
2.70
2.68
2.50
2.50
2.49
2.11
2.10
2.08
Br
OMe
MeO
HO3S
4
1H-NMR
400 MHz, DMSO-d6
1.98
2.00
1.02
5.88
1.03
1.01
1.00
0.55
2.02
34.10
1.98
1.98


154.41
150.51
150.39
150.29
150.05
139.96
134.83
133.44
130.68
127.86
114.15
113.68
113.24
67.46
56.08
56.06
55.97
55.93
55.89
55.76
29.38
28.94
28.32
26.06
22.19
14.39
Br
OMe
MeO
4
13C-NMR
400 MHz, DMSO-d6
HO3S


8.56
8.13
8.11
8.08
8.07
8.05
7.99
7.98
7.97
7.96
7.81
7.79
7.78
7.75
7.73
7.71
6.91
6.90
6.89
6.83
6.83
6.82
5.37
5.36
5.36
5.36
4.28
4.26
3.80
3.78
3.77
3.76
3.74
3.72
3.70
3.66
3.65
1.62
OMe
MeO
5
1H-NMR
400 MHz, CD2Cl2
Br
0.97
1.01
2.00
0.99
1.01
1.00
7.07
3.05
2.02
26.22
3.08
4.04
3.00


153.76
150.76
150.72
150.66
150.59
150.52
130.58
130.02
129.89
129.82
128.52
128.39
113.73
113.68
113.64
113.59
113.53
113.47
68.33
55.87
55.84
55.81
55.78
55.67
31.99
30.74
30.24
29.32
29.28
28.64
23.06
OMe
MeO
Br
5
13C-NMR
400 MHz, CD2Cl2


8.45
8.45
7.99
7.97
7.95
7.94
7.93
7.92
7.90
7.89
7.88
7.87
7.69
7.69
7.67
7.67
7.65
7.65
7.63
7.63
7.61
7.59
7.22
6.85
6.78
6.77
6.75
6.75
6.70
6.66
6.64
6.62
4.35
3.75
3.68
3.66
3.65
3.65
3.62
3.55
3.52
3.47
3.43
OMe
MeO
6
1H-NMR
400 MHz, CDCl3


153.19
150.81
150.72
150.62
150.56
150.52
150.36
130.24
129.45
129.40
129.32
127.94
127.75
122.97
114.26
114.22
114.07
113.99
113.83
113.78
113.72
113.56
77.48
77.32
77.00
76.68
75.06
55.85
55.74
55.73
55.63
55.57
55.49
55.20
30.15
29.66
29.57
29.50
OMe
MeO
O
S
O
O
H2
C
4
6
13C-NMR
400 MHz, CDCl3