Electronic Supplementary Material (ESI) for Polymer Chemistry.

Electronic Supplementary Information

Method for Introducing Organic Functional Groups on Silica Surfaces Using a Functionalized Vinylsilane Containing Polymer

Jung-Woo Park, Dong-Su Kim, Min-Seok Kim, Ji-Hwan Choi and Chul-Ho Jun*

Department of Chemistry, Yonsei University, Seoul 120-749, Korea.

Contents

1. General

Flash column chromatography was performed using E. Merck 230-400 mesh silica gel. Column Chromatography were monitored by analytical thin-layer chromatography(TLC) carried out on 0.25 Merck silica gel plates(60 F-254) using UV light as a visualizing agent and *p*-anisaldehyde solution, and heat as developing agent. ^1H NMR and ^{13}C NMR were recorded on a Bruker Advance II/DPX 400(400 MHz ^1H, 100 MHz ^{13}C) spectrometers with chemical shifts reported relative to residual deuterated solvent peaks. ^1H NMR spectra were referenced to $CDCl_3$ (for ^1H, δ=7.26 ppm) as internal standard, and are reported as chemical shift multiplicity: br=broad, s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet. ^{13}C NMR spectra were referenced to the residual $CDCl_3$ (for ^{13}C, δ =77.26 ppm) as internal standard. Infrared spectra were obtained on a Nicolet Impact 400 spectrometer. Solid state CP-MAS ^{13}C spectra (spin rate= 7 kHz) were provided by the National Instrumentation Center for Environmental Management (NICEM), Seoul National University. GPC analysis was carried out with Futecs NS-4000 series using THF as an eluent at a flow rate of 1.0 ml/min with an Agilent PLgel 20 μm mixed-A (ID.7.8 X L. 300mm) column at 40 °C.

2. Materials

Polubutadiene (**1**) was purchased from Aldrich (CAS No. 9003-17-2) and its molecular weight (*Mw*) is determined as 2,950 with PDI(M_w/M_n) = 1.65. Most reagent grade chemicals [N,N-dimethylacetamide, chlorodimethylsilane, vinylmagnesium chloride (1.6 M solution in THF), 4-pyreneburyric acid, **8b-8e**, **8h**, 4-formylbenzoic acid, 4-formylphenylboronic acid, **10**, **11**, octadecan-1-ol, oxalyl chloride] were purchased from Aldrich and TCI Chemical Company and used as received unless otherwise stated. Silica (**4**, Kromasil, 10 μm, 300 m^2/g) was purchased from RS Tech corporation. $H_2PtCl_6.xH_2O$ was purchased from Pressure Chemical corporation. $[(COE)_2IrCl]_2$ (**5**),[1] $(Ph_3P)_3RhCl$ (**9**),[2] were prepared by using reported procedures. N,N'-Dimethylacetamide hydrochloride (DMA·HCl, **6**) was prepared by treatment of N,N'-dimethylacetamide with 4 M HCl in 1,4-dioxane followed by removal of solvent. Dichloromethane and THF were distilled by using reported procedure prior to their use.[3] Formylphenylboronic acid pinacol ester (**8g**) was prepared by reaction of 4-formylphenylboronic acid and pinacol for 1 h at room temperature. Methyl 4-

---

[1] J. L. Herde, J. C. Lambert, C. V. Senoff, *Inorg. Synth.* 1974, **15**, 18.

[2] J. A. Osborn, G. Wilkinson, *Inorg. Synth.* 1990, **28**, 77.

[3] W. L. F. Armarego, C. L. L. Chai, in Purification of Laboratory Chemicals, Elsevier, 2009, pp.123.

formylbenzoate (**8f**) was prepared by esterification of 4-formylbenzoic acid with methanol. 4-Pyrenylbutanal (**8a**) was prepared by reduction of 4-pyrenylbutyric acid using $LiAlH_4$ followed by Swern oxidation of the resulting alcohol.

3. Experimental

4-(1-Pyrenyl)butyl ketone-incorporated polymer 12a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27-7.81 (br m), 6.16-5.62 (m, 3H), 5.34 (br s, internal -CH=CH-), 3.40 (br s), 3.28 (br s), 2.48 (br s, 2H), 2.30 (br s, 2H), 2.09 (br s, 2H), 1.93 (br s), 1.24 (br m), 0.73 (br s), 0.44-0.39 (br m), 0.04 (br s), -0.01 (br s), -0.05 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 211.9 (CO), 139.3, 136.2, 131.7, 131.1, 130.1, 129.0, 127.6, 127.57, 127.5, 126.8, 126.0, 125.3, 125.2, 125.0, 124.9, 123.6, 41.5, 39.5-36.1, 37.6, 34.9-33.4, 32.9, 28.5-26.3 25.9, 11.8-9.9, 9.0, -3.0, -3.3; IR spectrum ($CDCl_3$) 3667, 3047, 2923, 2853, 1877, 1633, 1456, 1377, 1024, 785, 584 cm^{-1}; $M_w/M_n = 7.27$.

***n*-Butyl ketone-incorporated polymer 12b:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17-5.62 (m, 3H), 5.35 (br s, internal -CH=CH-), 2.38-2.31 (m, 4H), 2.04-1.86 (br m), 1.64-1.25 (m, 2H), 0.91 (t, J = 8.0 Hz, 3H), 0.74 (t, J = 8.0 Hz, 2H), 0.47 (br s), 0.04 (s), -0.04 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.0 (CO), 139.3, 131.7, 44.2, 39.4-35.9, 37.4, 34.9-32.8, 31.4-29.3, 28.1-25.5, 17.6, 14.0, 11.8-9.6, 9.0, -3.1, -3.3; IR spectrum ($CDCl_3$) 3047, 2915, 1899, 1716, 1593, 1407, 1364, 1250, 1179, 1007, 949, 836, 771 cm^{-1}; $M_w/M_n = 2.76$.

***n*-Heptyl ketone-incorporated polymer 12c:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16-5.62 (m, 3H), 5.35 (br s, internal -CH=CH-), 2.38-2.32 (m, 4H), 2.06-1.84 (br m), 1.47-0.96 (br m, 2H), 1.48-0.93 (br m), 0.85 (t, J = 8.0 Hz, 3H), 0.74 (t, J = 8.0 Hz, 2H), 0.45 (br s), 0.04 (s), -0.04 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.1 (CO), 139.3, 131.6, 42.3, 39.5-35.9, 37.4, 34.8-32.7, 31.8, 31.0-29.8, 29.2, 28.2-25.9, 24.1, 22.7, 14.2, 11.7-9.6, 9.0, -3.1, -3.3; IR spectrum ($CDCl_3$) 3047, 2915, 1899, 1718, 1593, 1451, 1405, 1248, 1179, 1066, 966, 837, 770 cm^{-1}; $M_w/M_n = 4.87$.

***n*-Decyl ketone-incorporated incorporated polymer 12d:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.17-5.62 (m, 3H), 5.35 (br s, internal -CH=CH-), 2.40-2.30 (m, 4H), 2.06-1.86 (br m), 1.66-1.50 (br m, 2H), 1.45-0.95 (br m), 0.87 (t, J = 8.0 Hz, 3H), 0.74 (t, J = 8.0 Hz, 2H), 0.46 (br s), 0.05 (s), -0.04 (s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 212.0 (CO), 139.3, 131.6, 42.3, 39.5-35.9, 37.4, 34.9-32.8, 32.1, 30.5-28.9, 29.6, 29.55, 29.5, 28.5-25.5, 24.2, 22.8, 14.3, 11.9-9.8, 9.0, -3.1, -3.3; IR spectrum ($CDCl_3$) 3047, 2914, 1899, 1717, 1593, 1450, 1407, 1248, 1179, 1008, 949, 837, 771 cm^{-1}; $M_w/M_n = 1.54$.

4-Bromophenyl ketone-incorporated polymer 12e: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (br s, 2H), 7.56

(br s, 2H), 6.15-5.61 (m, 3H), 5.33 (br s, internal -CH=CH-), 2.86 (br s, 2H), 2.04-1.77 (br m), 1.66-1.54 (br m), 1.48-0.63 (br m, 2H), 0.87 (br s, 2H), 0.44 (br s), 0.02 (br s), 0.00 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.1 (CO), 139.2, 135.6, 132.0, 131.7, 129.8, 128.1, 39.4-35.6, 34.8-32.4, 33.2, 28.5-25.4, 11.5-8.7, 9.5, -3.1; IR spectrum ($CDCl_3$) 3046, 2952, 1900, 1689, 1585, 1482, 1447, 1404, 1347, 1249, 1175, 1070, 1008, 965, 835, 771, 516 cm^{-1}; $M_w/M_n = 5.80$.

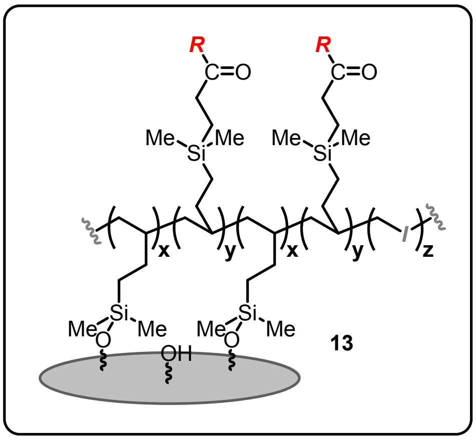
4-Methylbenzoyl ketone-incorporated polymer 12f: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (br s, 2H), 7.96 (br s, 2H), 6.15-5.61 (m, 3H), 5.33 (br s, internal -CH=CH-), 3.92 (br s, 3H), 2.92 (br s, 2H), 2.04-1.75 (br m), 1.66-1.53 (br m), 1.50-1.67 (br m), 0.89 (br s, 2H), 0.45 (br s), 0.02 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6 (CO), 166.4(CO), 140.2, 139.3, 133.8, 131.6, 130.0, 128.1, 52.6, 40.0-35.5, 35.0-32.6, 33.7, 31.1-29.7, 28.1-25.8, 11.8-9.9, 9.5, -3.1; IR spectrum ($CDCl_3$) 1730, 1694, 1436, 1406, 1279, 1248, 1108, 1010, 950, 837, 767, 967 Cm^{-1}; $M_w/M_n = 2.78$.

1-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl) ketone-incorporated polymer 12g: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (br s, 4H), 6.90 (br s), 6.09-5.60 (m, 3H), 5.34 (br s, internal -CH=CH-), 2.91 (br s, 2H), 2.05-1.78 (br m), 1.68-1.53 (br m), 1.52-0.64 (br m), 0.87 (br s, 2H), 0.45 (br s), 0.00 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6 (CO), 139.3, 138.9, 135.1, 133.9, 131.7, 127.2, 84.3, 53.6, 40.2-35.9, 34.9-32.4, 33.5, 31.0-28.9, 28.5-26.3, 25.0, 11.6-9.2, 9.7, -3.1; IR spectrum ($CDCl_3$) 3047, 2918, 1692, 1593, 1557, 1508, 1452, 1403, 1361, 1248, 1145, 1090, 1009, 950, 837 cm^{-1}; $M_w/M_n = 6.74$.

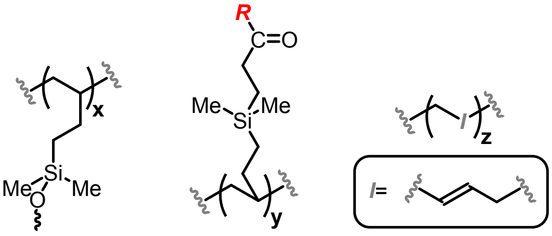
Ferrocenyl ketone-incorporated polymer 12h: ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.16-5.62 (m, 3H), 5.35 (br s, internal -CH=CH-), 4.75 (br s, 2H), 4.46 (br s, 2H), 4.16 (br s, 5H), 2.64 (br s, 2H), 2.10-1.81 (br m), 1.67-1.55 (br m), 1.52-0.95 (br m), 0.88 (br s), 0.46 (br s), 0.03 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 205.3 (CO), 139.2, 131.7, 78.9, 72.2, 69.9, 69.5, 39.4-36.2, 34.8-32.9, 34.2, 32.3-29.6, 28.2-25.6, 11.7-9.5, 10.0, -3.2; IR spectrum ($CDCl_3$) 3096, 3047, 2916, 1670, 1454, 1249, 1171, 835 cm^{-1}; $M_w/M_n = 4.15$.

4-(1-Pyrenyl)phenyl ketone-incorporated polymer 12i (150 °C, 12 h): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29-7.87 (m, 11H), 7.74 (br s, 2H), 6.21-5.67 (m, 3H), 5.40 (br s, internal -CH=CH-), 3.06 (br s, 2H), 1.98 (br s, 2H), 1.67-1.04 (br m), 0.51 (br s), 0.08 (br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1 (CO), 146.1, 139.3, 136.5, 135.7, 135.0, 131.7, 131.2, 131.0, 130.3, 128.4, 128.1, 128.0, 127.56, 127.51, 126.3, 125.6, 125.2, 125.1, 124.96, 124.90, 39.6-36.0, 34.8-32.8, 33.4, 31.1-30.2, 28.3-25.7, 12.1-9.5, 9.8, -3.1; IR spectrum ($CDCl_3$) 3064, 2983, 2862, 2832, 2687, 1603, 1450, 1404, 1247, 837, 772 cm^{-1}; $M_w/M_n = 7.25$.

Calculation of Loading Rate of Functional Group on 13:



13



Number of C	6	9 + $\mathbf{N}_{R}$	4
Molar ratio of each part	0.85-**X**	**X**	0.15

Carbon wt% of functional part ***R***
[C wt%]$_{R}$

$$[\mathbf{C\ wt\%}] \times \frac{[(9 + \mathbf{N}_{R}) \times \mathbf{X}]}{[6 \times (0.85-\mathbf{X})] + [(9 + \mathbf{N}_{R}) \times \mathbf{X}] + [4 \times 0.15]}$$

Calculation of loading rate of ***R*** on **13**

= (**[C wt%]**$_{R}$ x 10^{-2} g of C / 1 g of sample **13**) x (10^{6} μmol of C / 12 g of C) x (1 mmol of **13** / [9 + $\mathbf{N}_{R}$] mmol of C on ***R*** part)

Loading Rate and Elementary Analysis of 13

Functionalized Silica **13**	Loading rate (μmol/g)	Elementary analysis	
		C (wt%)	H (wt%)
13a	264	11.5	1.21
13b	319	9.2	1.2
13c	288	8.9	1.2
13d	246	8.9	1.7
13e	317	9.5	1.4
13f	178	6.7	1.0
13g	262	8.3	1.4
13h	184	6.1	0.7
13i	187	10.8	2.0

Tests for Determining Robustness of the Bonds between Organic Groups and Silica (Figure 3):

To individual slurries of polymer-immobilized silica **7** (50 mg, C (wt %) = 8.7) in THF (0.3 mL) were added aq. 1 M HCl (0.3 ml), aq. 1 M K_2CO_3 (0.3 ml) and aq. 1 M K_2CO_3 (0.3 ml), respectively. The resulting slurries were stirred for 1 or 6 hours at indicated temperature, respectively. After treatment, they were filtered, washed thoroughly with dichloromethane, acetone and methanol, and dried under reduced pressure to give the corresponding silicas. The remaining organic components in the resulting silicas were analyzed by using elemental analysis. In the same manner, individual slurries of dodecyldimethylsilyl group-immobilized silica **14** (50 mg, C (wt %) = 6.5) were treated with aq. 1 M K_2CO_3 (0.3 mL) for 1 h and 6 h at room temperature and 80 °C, and the resulting silicas were analyzed by using elemental analysis. The weight of the resulting silica was not significant changed compared with silica before treatment of base (See below.).

$$\text{Polymer-Grafted Silica } \mathbf{7} \xrightarrow[\text{THF}]{K_2CO_3\ (aq.,\ 1\ M)}$$

room temperature

	before treatment	after treatment
1 h	21.5 mg	19.8 mg
6 h	21.5 mg	18.2 mg

80 °C

	before treatment	after treatment
1 h	50.0 mg	49.0 mg
6 h	50.0 mg	42.8 mg

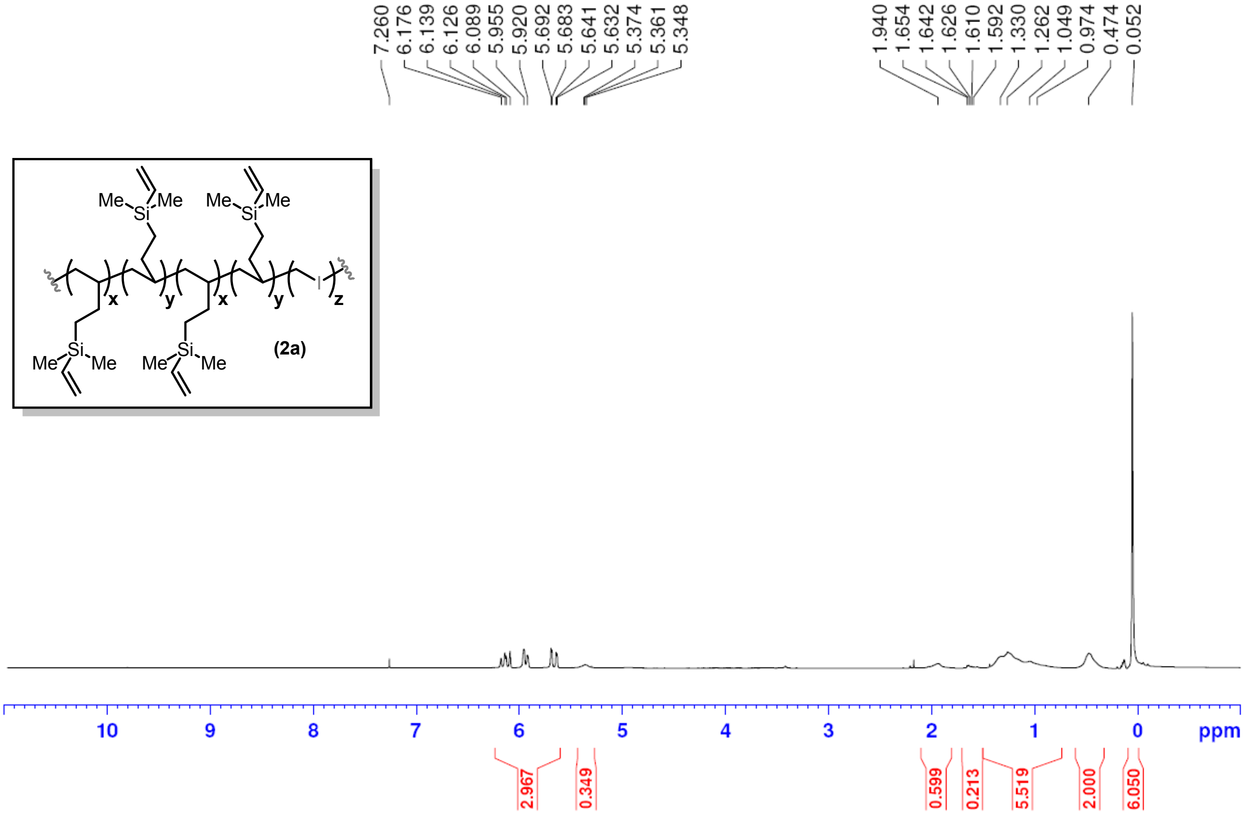
Suzuki Coupling Reaction of Boronic Acid (BA) Group-Covered Silica Surface 15 and 18 with 1-Iodopyrene under Basic Condition (Figure 4):

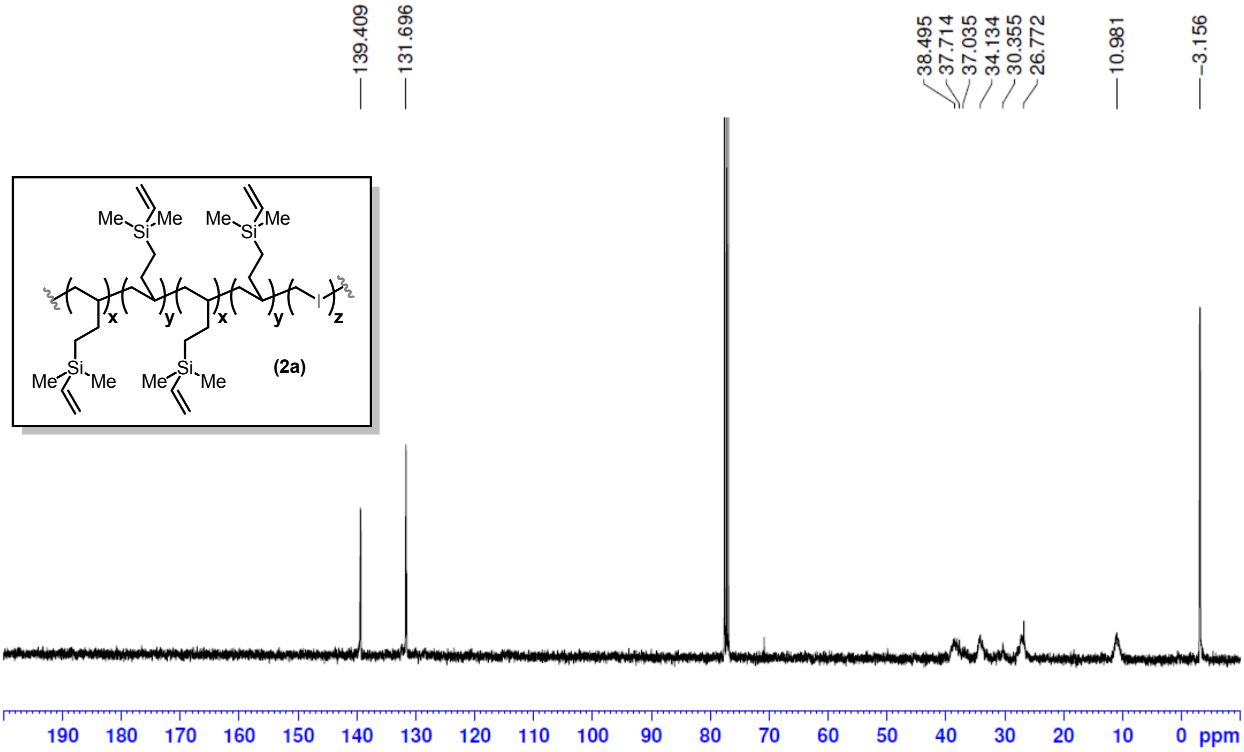
To a suspension of phenylboronic acid-pinacol ester group immobilized silica (**13g**, 250 mg (0.066 mmol phenylboronic acid-pinacol ester group) in THF/H_2O solution (1 ml/1 ml) was added $NaIO_4$ (56.7 mg, 0.265 mmol), and the mixture was stirred for 30 min at ambient temperature. Then, 1 N HCl solution (2 ml, 2 mmol) was added to the mixture, and the resulting mixture was stirred for 12 hours at room temperature. After the reaction, the suspension was filtered, and washed thoroughly with dichloromethane, H_2O, methanol and acetone. Phenylboronic acid group covered silica (**15**, 223 mg) was obtained after drying *in vacuo*.

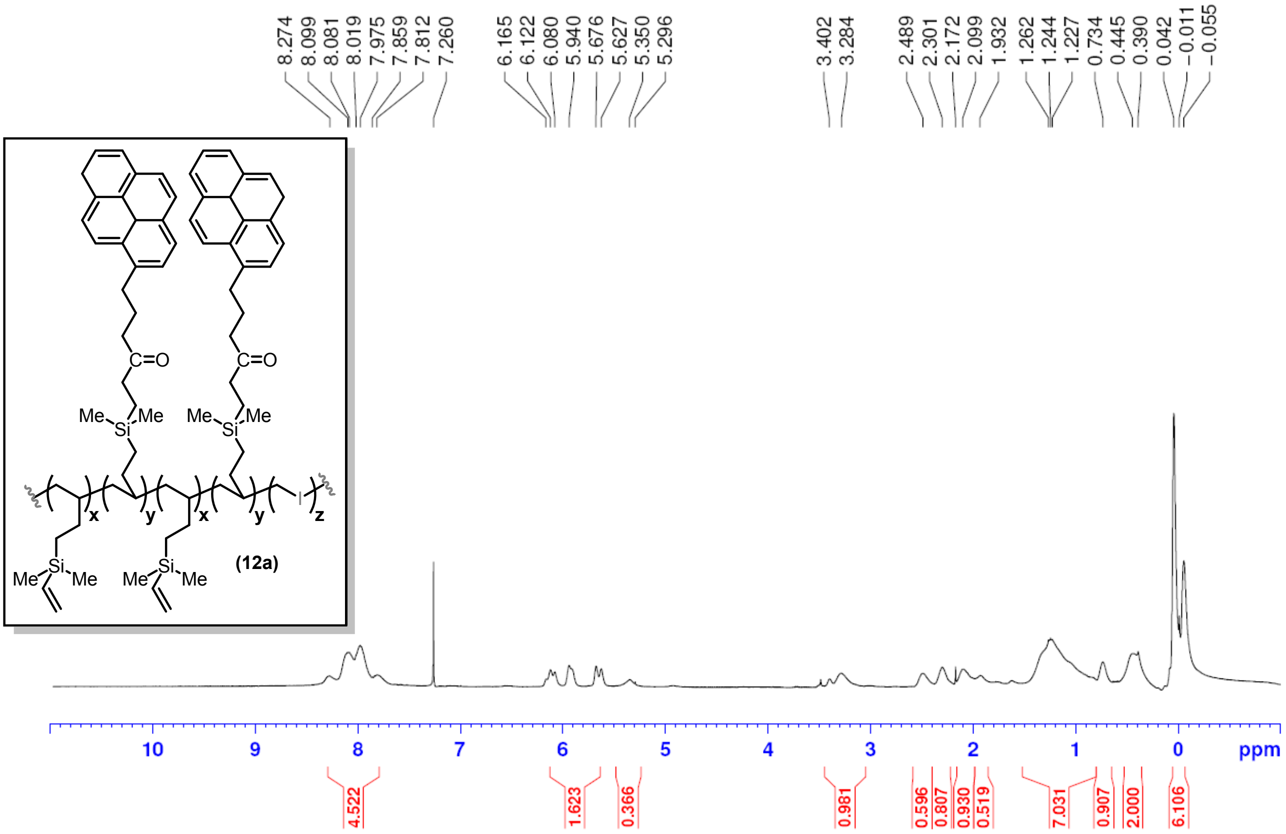
A mixture of silica **15** (20 mg, (0.006 mmol phenylboronic acid group), 1-iodopyrene (5.9 mg (0.018 mmol), $Pd(OAc)_2$ (0.08 mg (0.3 μmol), K_2CO_3 (1.7 mg (0.012 mmol) in diglyme monomethyl ether (DGME, 0.2 ml), dichloromethane (0.2 ml) and H_2O (0.1 ml) was stirred at room temperature for 6 hours. After the reaction, the suspension was filtered, and washed thoroughly with dichloromethane, H_2O, methanol and acetone. Pyrenyl group immobilized silica (**16**, 14 mg) was obtained after drying *in vacuo*.

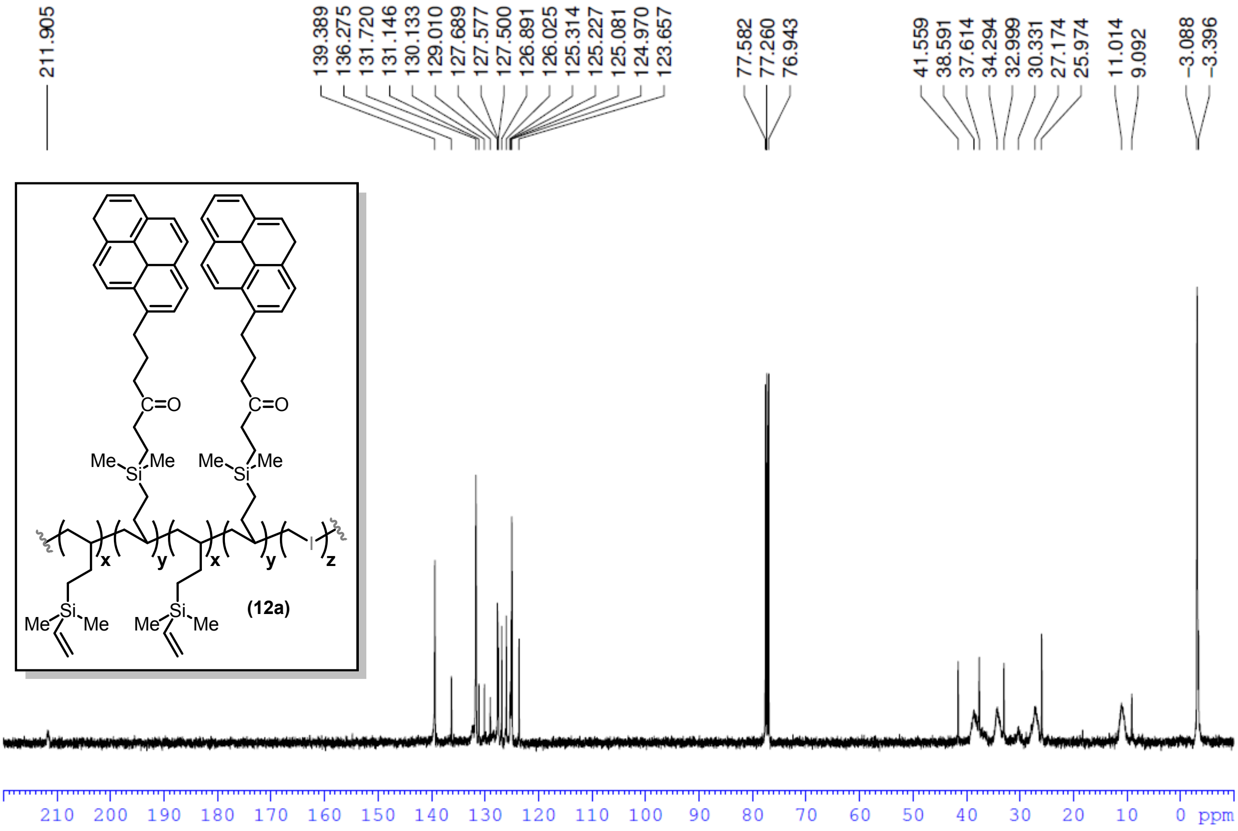
Silica **19** was prepared by identical conditions above from monomeric boronic ester group immobilized silica **17** through phenylboronic acid group covered silica **18**.

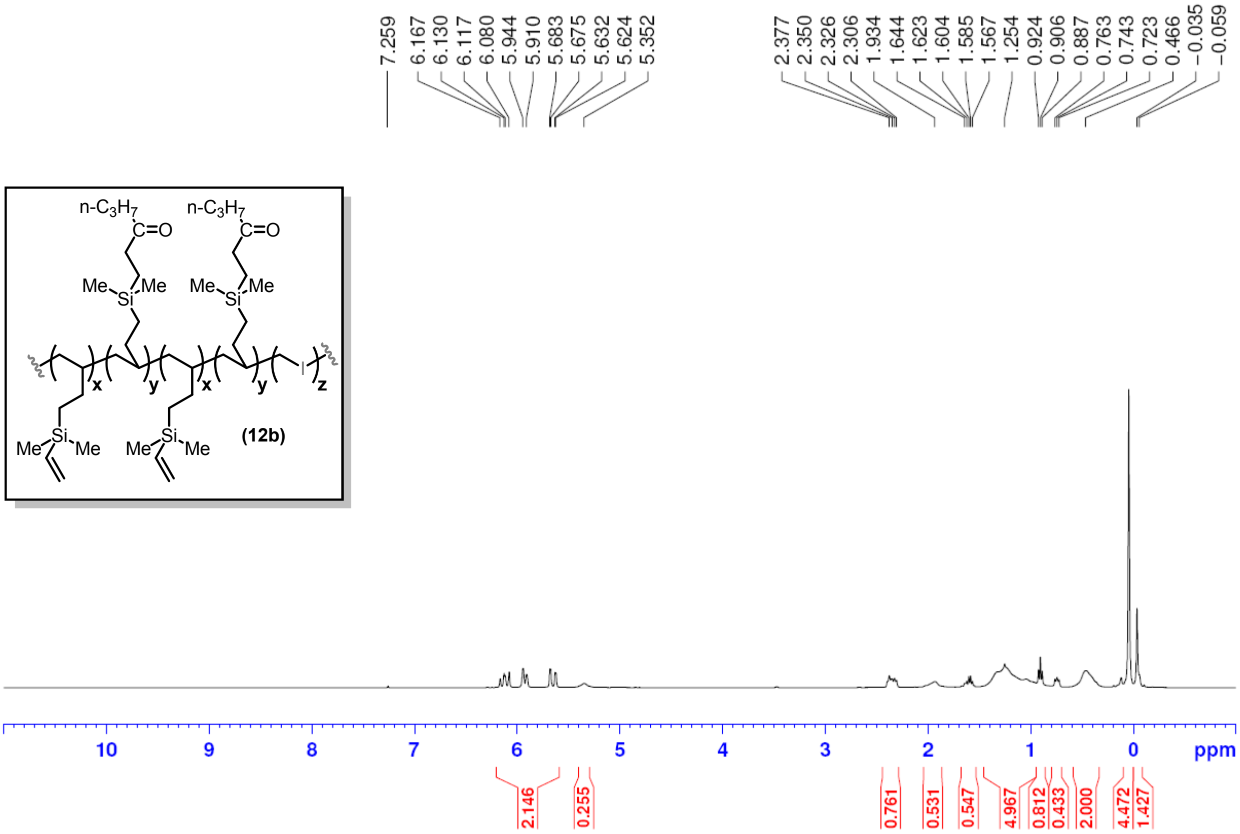
^{1}H and ^{13}C NMR spectra

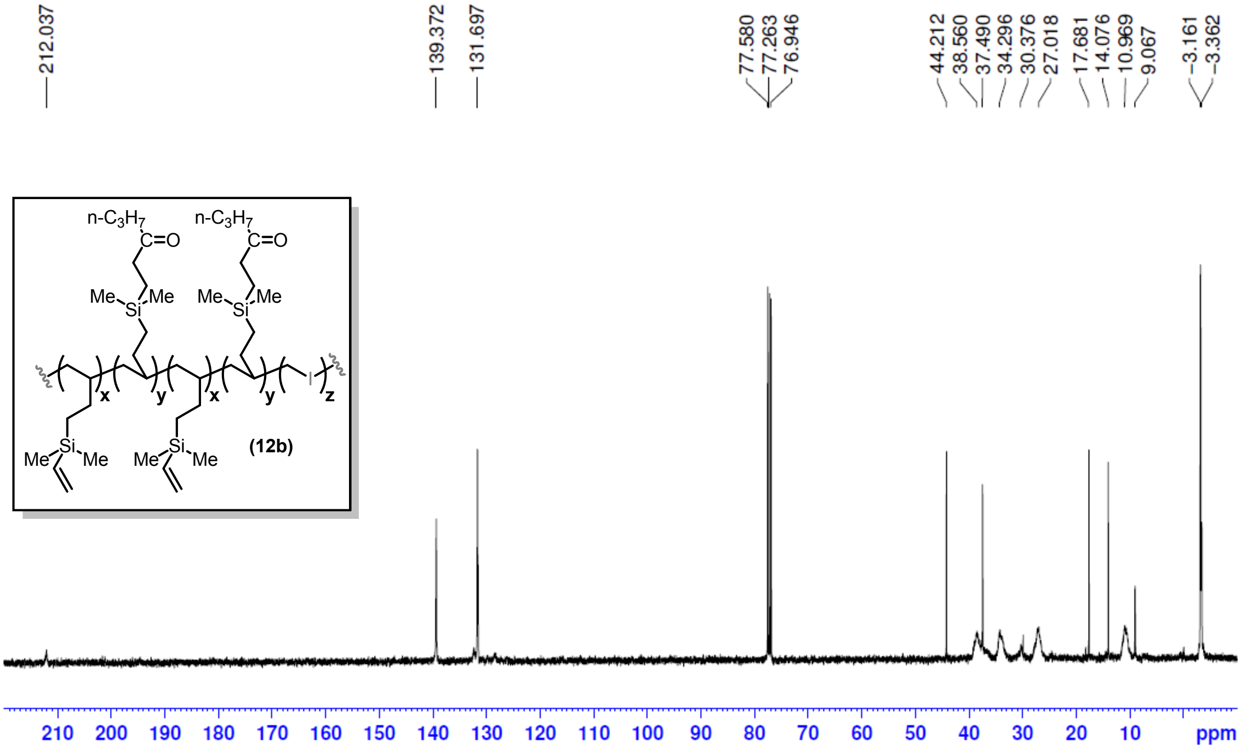


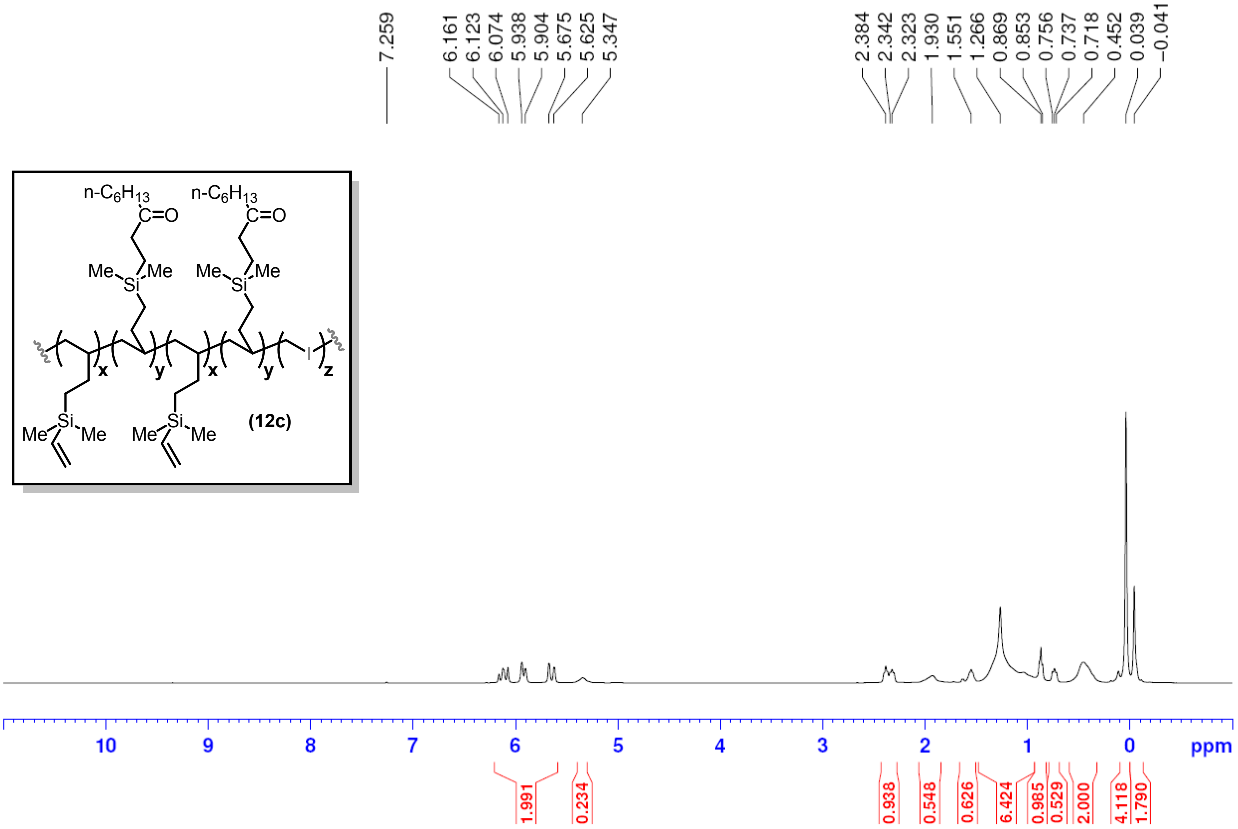


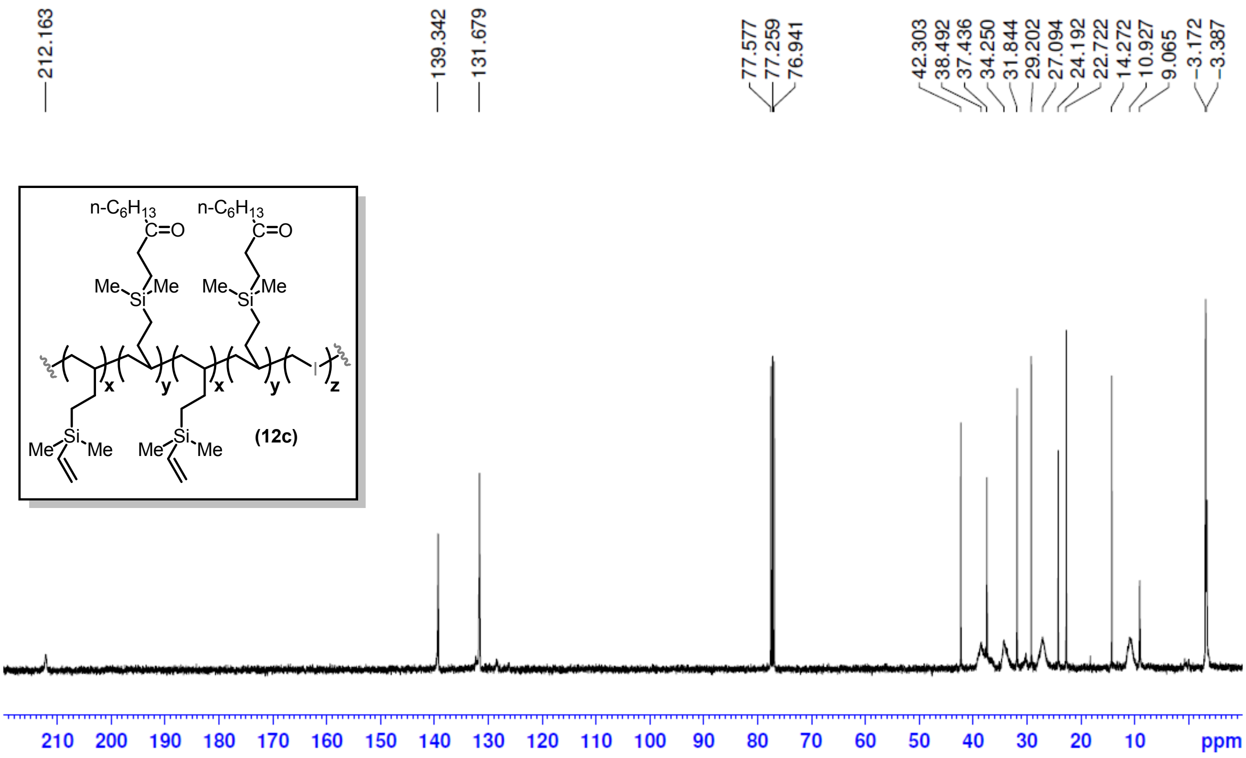

8.274
8.099
8.081
8.019
7.975
7.859
7.812
7.260
6.165
6.122
6.080
5.940
5.676
5.627
5.350
5.296
3.402
3.284
2.489
2.301
2.172
2.099
1.932
1.262
1.244
1.227
0.734
0.445
0.390
0.042
−0.011
−0.055
C=O
C=O
Me
Si
Me
Me
Si
Me
x
y
x
y
z
Me
Si
Me
Me
Si
Me
(12a)
10
9
8
7
6
5
4
3
2
1
0
ppm
4.522
1.623
0.366
0.981
0.596
0.807
0.930
0.519
7.031
0.907
2.000
6.106

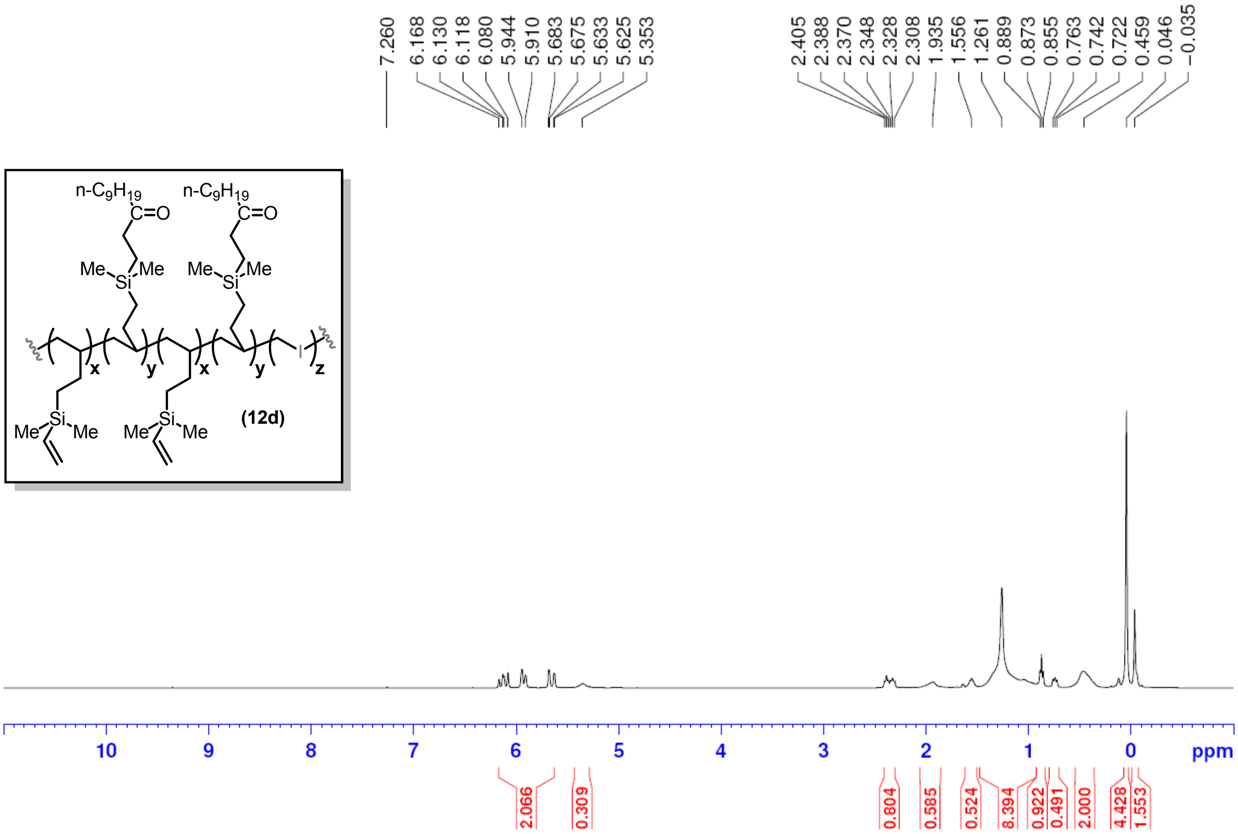

211.905
139.389
136.275
131.720
131.146
130.133
129.010
127.689
127.577
127.500
126.891
126.025
125.314
125.227
125.081
124.970
123.657
77.582
77.260
76.943
41.559
38.591
37.614
34.294
32.999
30.331
27.174
25.974
11.014
9.092
−3.088
−3.396
C=O
C=O
Me
Si
Me
Me
Si
Me
x
y
x
y
z
Me
Si
Me
Me
Si
Me
(12a)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

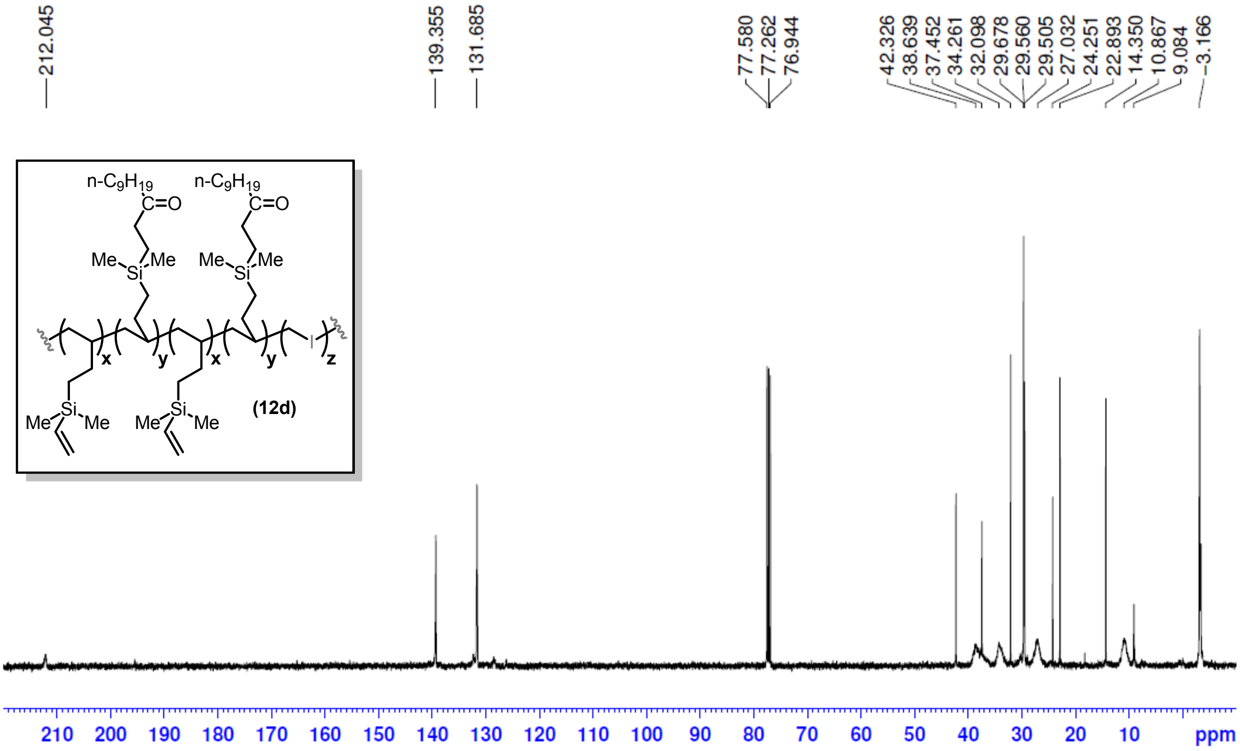

7.259
6.167
6.130
6.117
6.080
5.944
5.910
5.683
5.675
5.632
5.624
5.352
2.377
2.350
2.326
2.306
1.934
1.644
1.623
1.604
1.585
1.567
1.254
0.924
0.906
0.887
0.763
0.743
0.723
0.466
-0.035
-0.059
n-C3H7
C=O
Me
Si
x
y
z
(12b)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.146
0.255
0.761
0.531
0.547
4.967
0.812
0.433
2.000
4.472
1.427

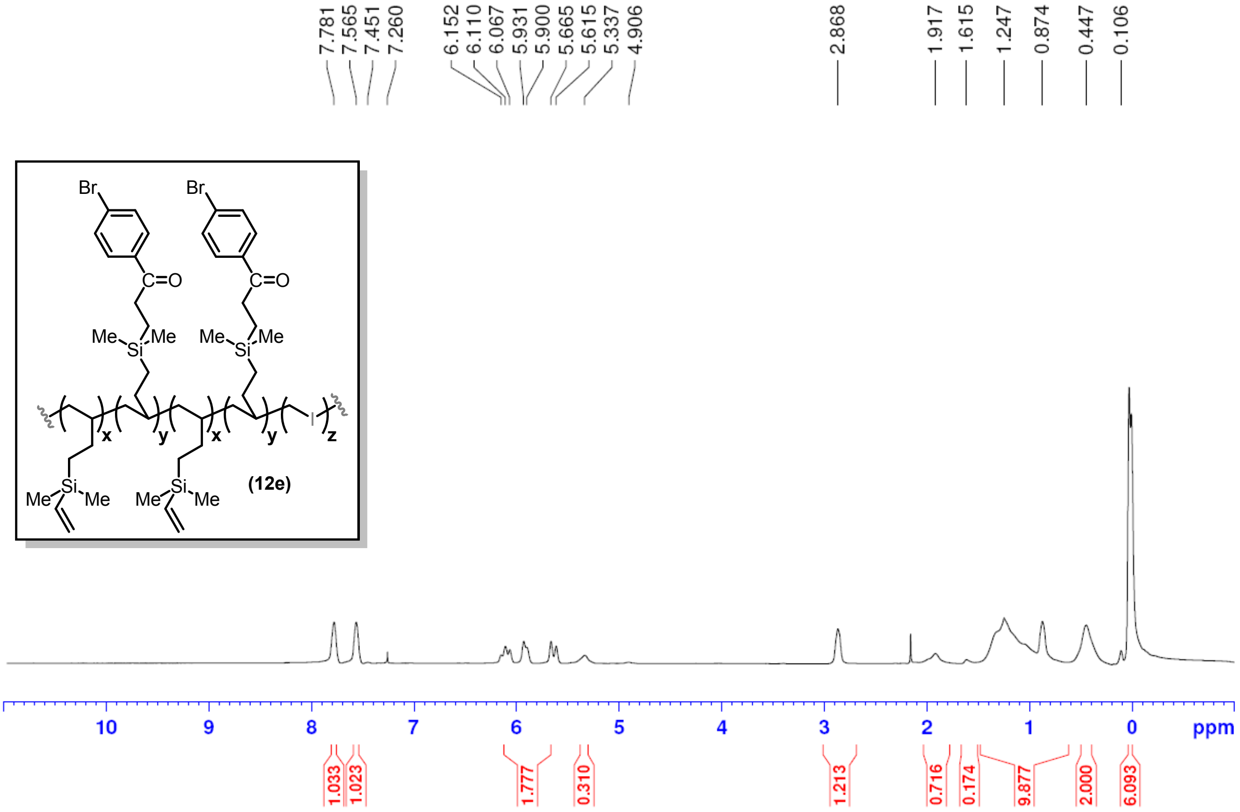

212.037
139.372
131.697
77.580
77.263
76.946
44.212
38.560
37.490
34.296
30.376
27.018
17.681
14.076
10.969
9.067
-3.161
-3.362
n-C3H7
C=O
Me
Si
x
y
z
(12b)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

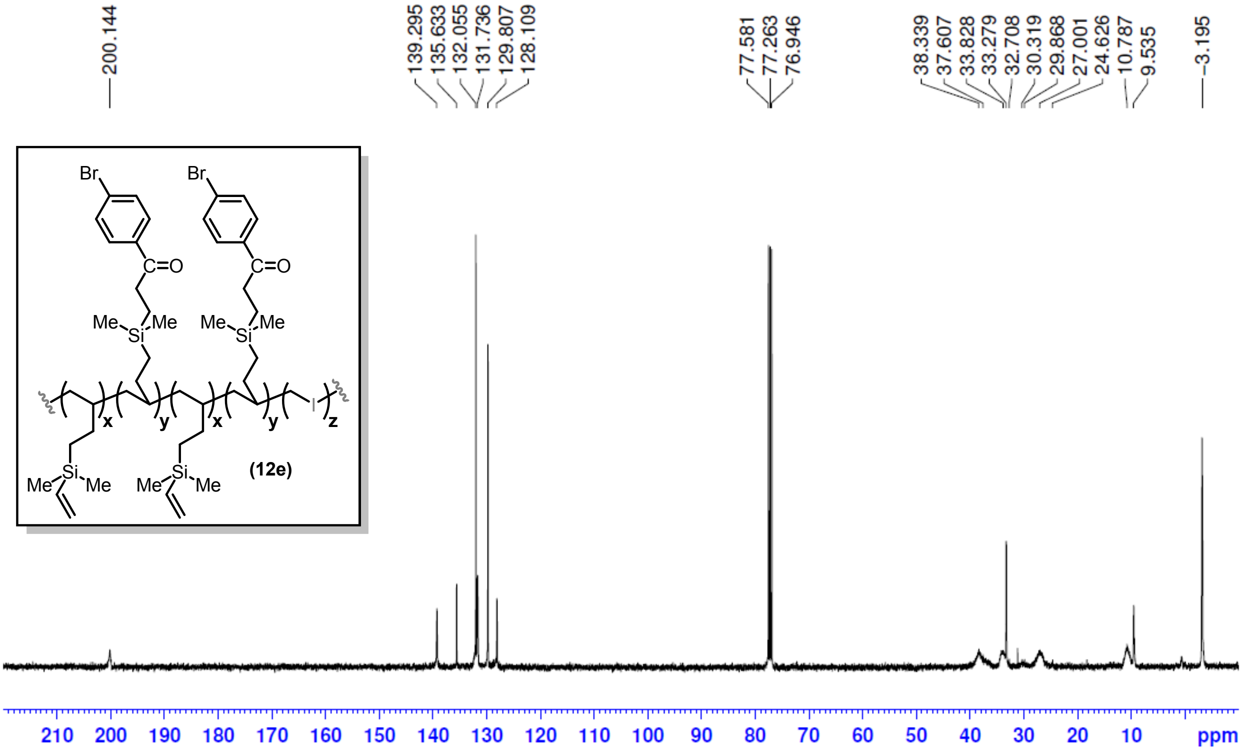

7.259
6.161
6.123
6.074
5.938
5.904
5.675
5.625
5.347
2.384
2.342
2.323
1.930
1.551
1.266
0.869
0.853
0.756
0.737
0.718
0.452
0.039
-0.041
n-C6H13
C=O
Me
Si
Me
x
y
z
(12c)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.991
0.234
0.938
0.548
0.626
6.424
0.985
0.529
2.000
4.118
1.790

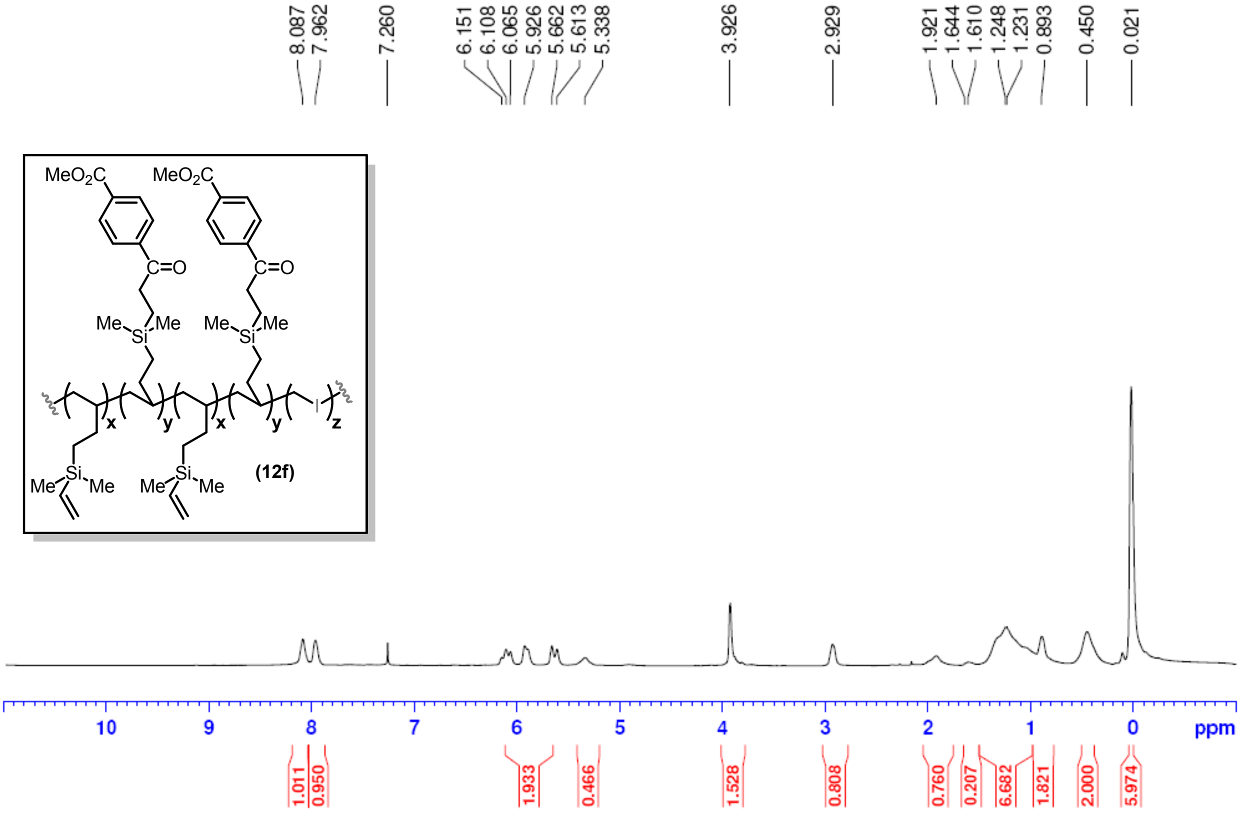

212.163
139.342
131.679
77.577
77.259
76.941
42.303
38.492
37.436
34.250
31.844
29.202
27.094
24.192
22.722
14.272
10.927
9.065
-3.172
-3.387
n-C6H13
C=O
Me
Si
Me
x
y
z
(12c)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

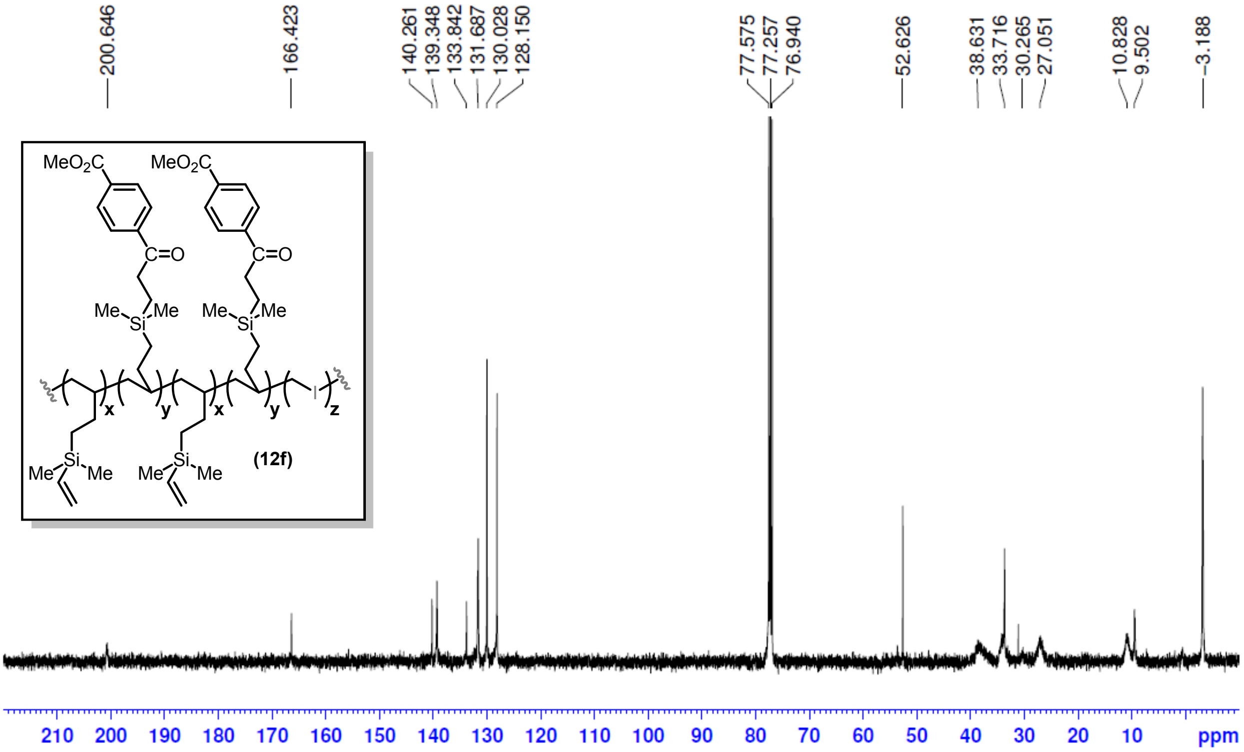

7.260
6.168
6.130
6.118
6.080
5.944
5.910
5.683
5.675
5.633
5.625
5.353
2.405
2.388
2.370
2.348
2.328
2.308
1.935
1.556
1.261
0.889
0.873
0.855
0.763
0.742
0.722
0.459
0.046
−0.035
n-C9H19
C=O
Me
Si
Me
x
y
z
(12d)
10
9
8
7
6
5
4
3
2
1
0
ppm
2.066
0.309
0.804
0.585
0.524
8.394
0.922
0.491
2.000
4.428
1.553

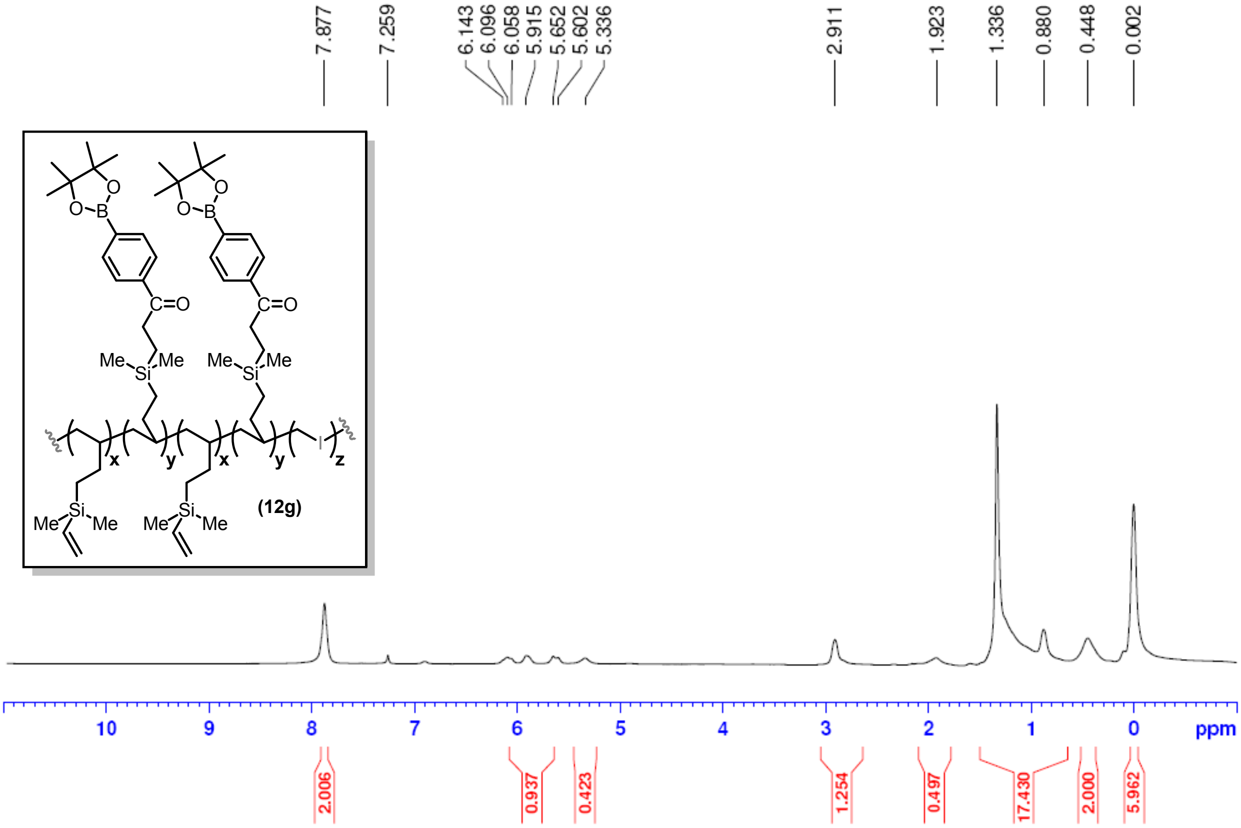

212.045
139.355
131.685
77.580
77.262
76.944
42.326
38.639
37.452
34.261
32.098
29.678
29.560
29.505
27.032
24.251
22.893
14.350
10.867
9.084
−3.166
n-C9H19
C=O
Me
Si
Me
x
y
z
(12d)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

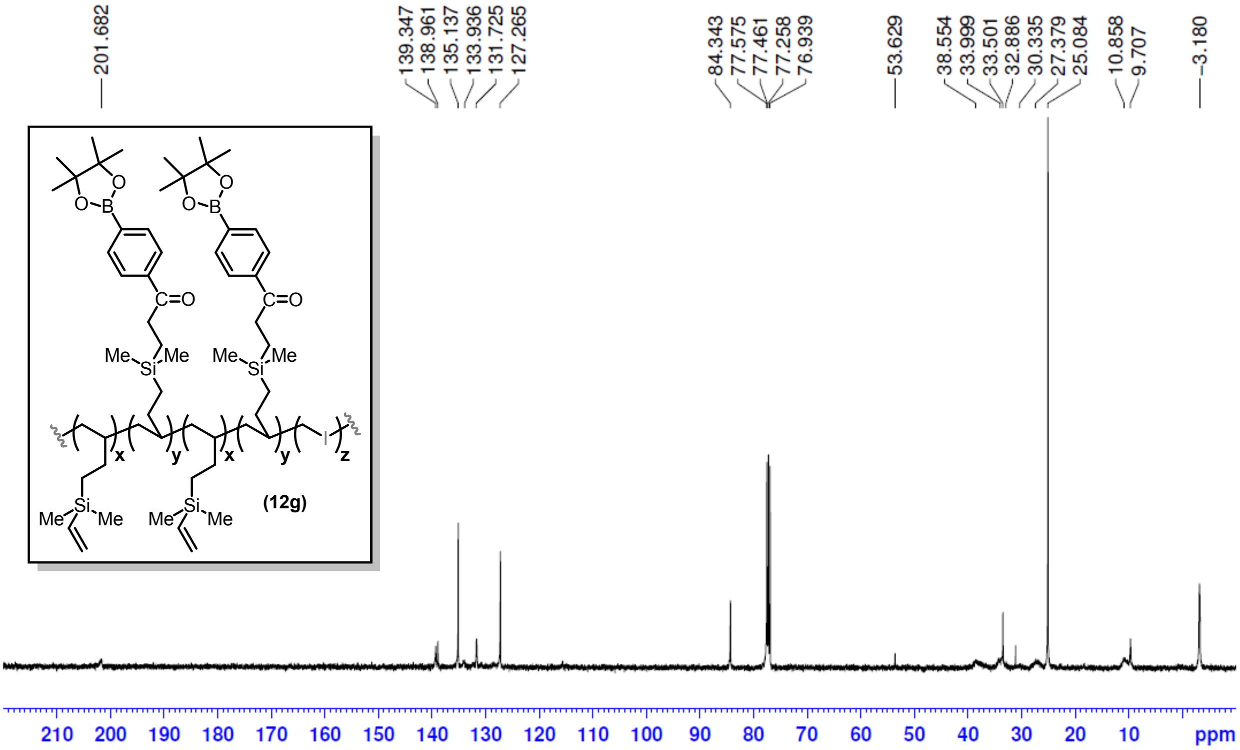

7.781
7.565
7.451
7.260
6.152
6.110
6.067
5.931
5.900
5.665
5.615
5.337
4.906
2.868
1.917
1.615
1.247
0.874
0.447
0.106
Br
Br
C=O
C=O
Me
Si
Me
Me
Si
Me
x
y
x
y
z
Si
Me
Me
Si
Me
Me
(12e)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.033
1.023
1.777
0.310
1.213
0.716
0.174
9.877
2.000
6.093

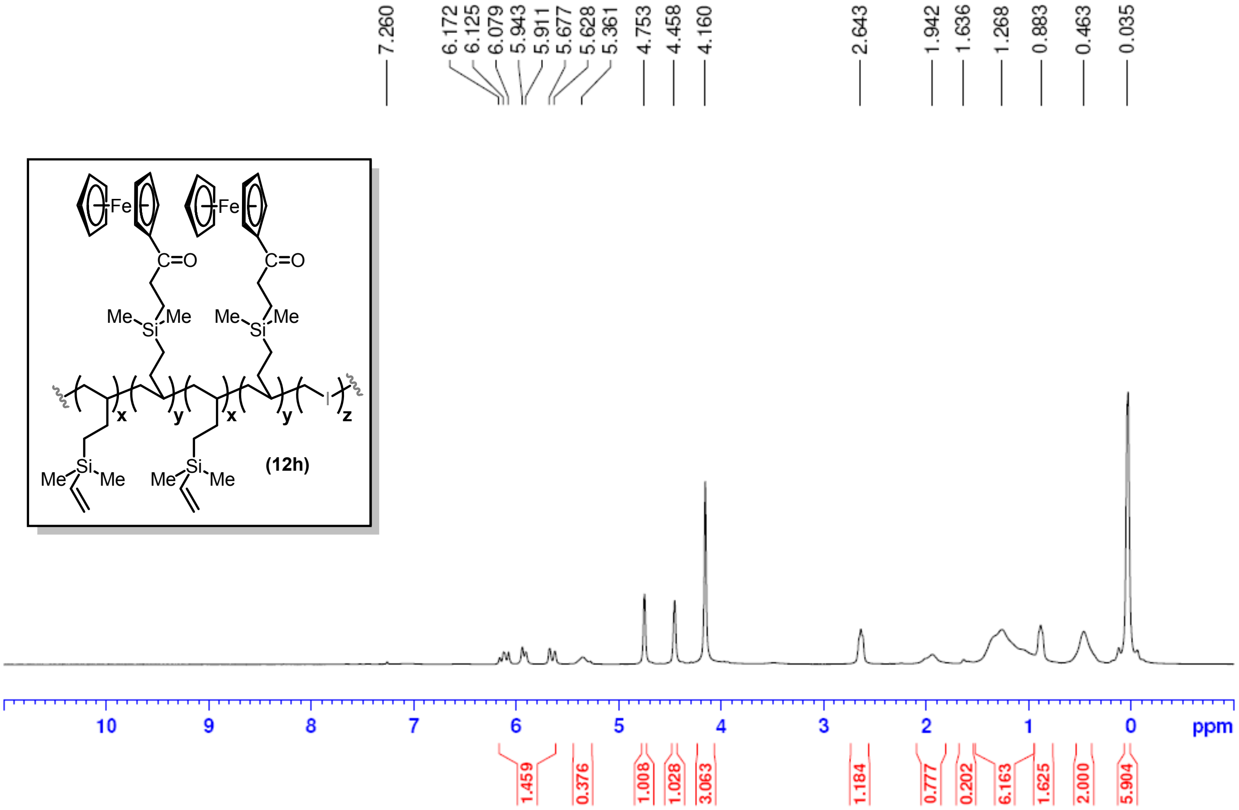

200.144
139.295
135.633
132.055
131.736
129.807
128.109
77.581
77.263
76.946
38.339
37.607
33.828
33.279
32.708
30.319
29.868
27.001
24.626
10.787
9.535
-3.195
Br
Br
C=O
C=O
Me
Si
Me
Me
Si
Me
x
y
x
y
z
Si
Me
Me
Si
Me
Me
(12e)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

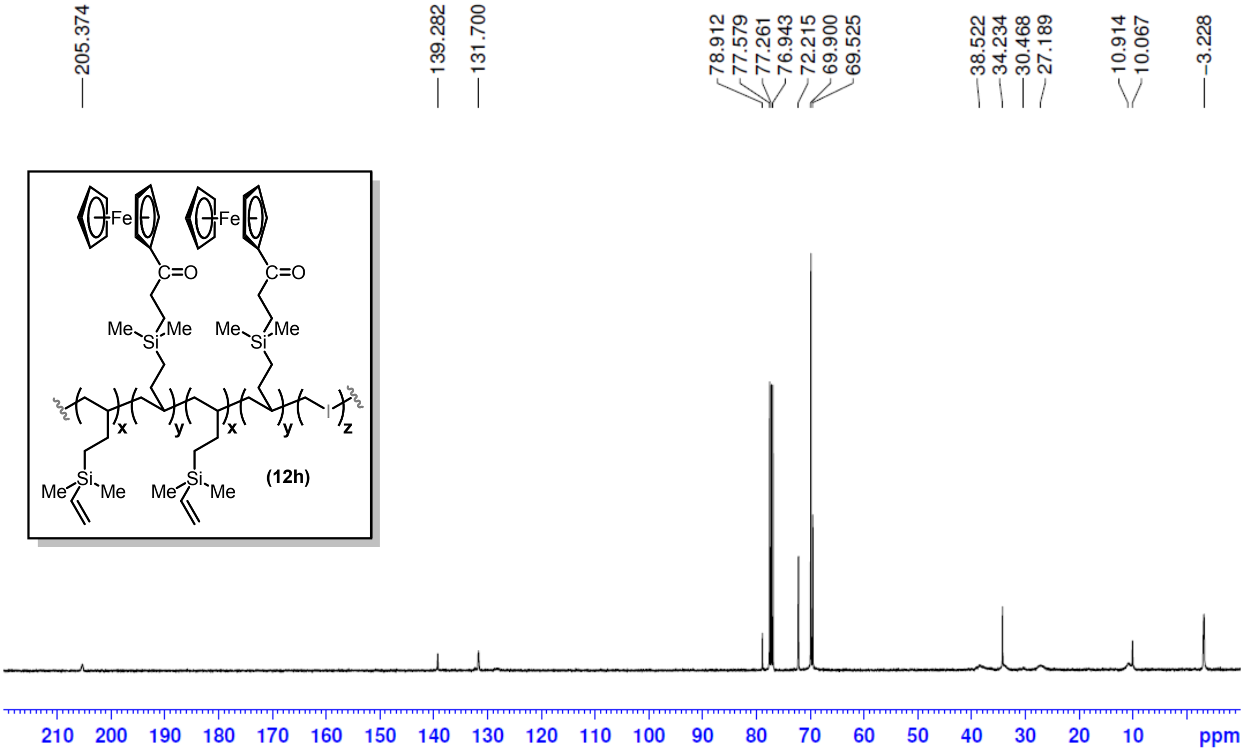

8.087
7.962
7.260
6.151
6.108
6.065
5.926
5.662
5.613
5.338
3.926
2.929
1.921
1.644
1.610
1.248
1.231
0.893
0.450
0.021
MeO2C
MeO2C
C=O
C=O
Me
Si
Me
Me
Si
Me
x
y
x
y
z
Me
Si
Me
Me
Si
Me
(12f)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.011
0.950
1.933
0.466
1.528
0.808
0.760
0.207
6.682
1.821
2.000
5.974

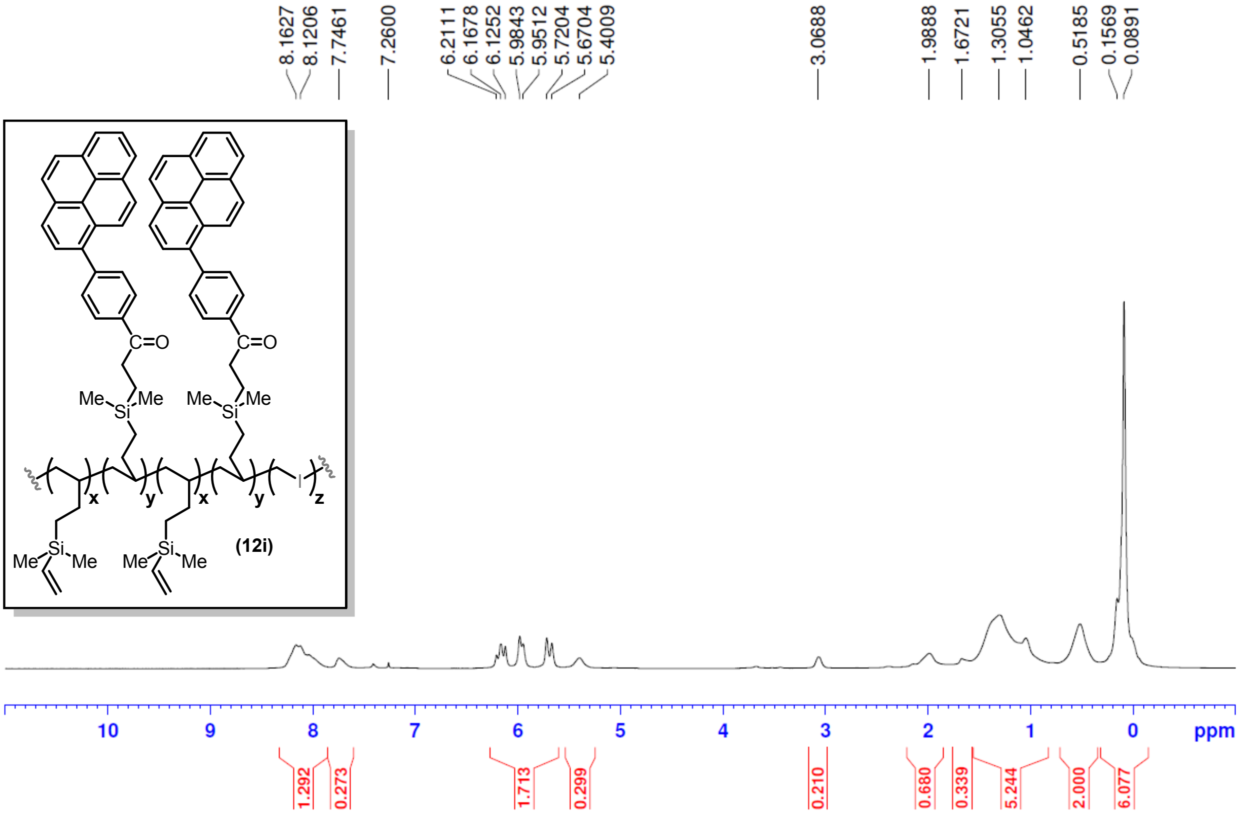

200.646
166.423
140.261
139.348
133.842
131.687
130.028
128.150
77.575
77.257
76.940
52.626
38.631
33.716
30.265
27.051
10.828
9.502
-3.188
MeO2C
MeO2C
C=O
C=O
Me
Si
Me
Me
Si
Me
x
y
x
y
z
Me
Si
Me
Me
Si
Me
(12f)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

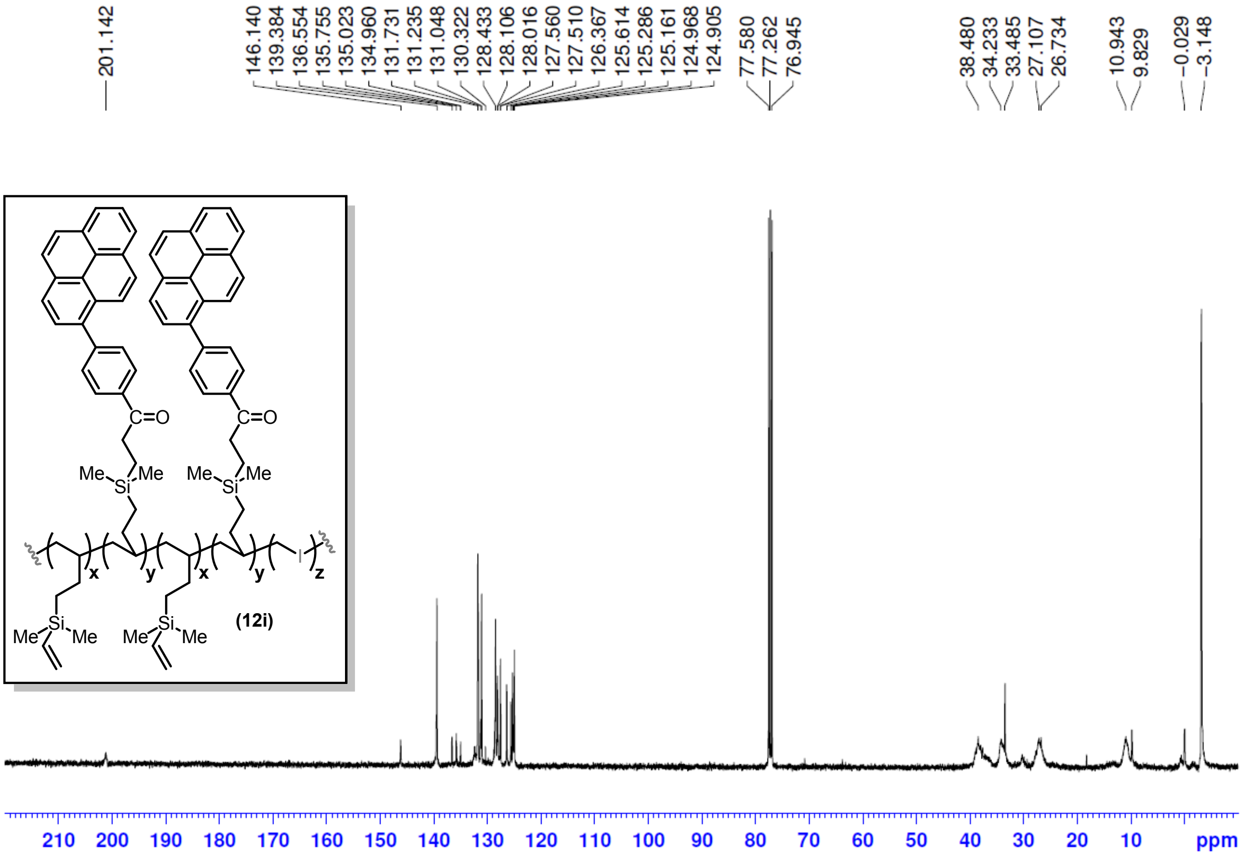

7.877
7.259
6.143
6.096
6.058
5.915
5.652
5.602
5.336
2.911
1.923
1.336
0.880
0.448
0.002
(12g)
Me
Si
O
B
C=O
x
y
z
10
9
8
7
6
5
4
3
2
1
0
ppm
2.006
0.937
0.423
1.254
0.497
17.430
2.000
5.962


201.682
139.347
138.961
135.137
133.936
131.725
127.265
84.343
77.575
77.461
77.258
76.939
53.629
38.554
33.999
33.501
32.886
30.335
27.379
25.084
10.858
9.707
-3.180
(12g)
Me
Si
O
B
C=O
x
y
z
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


7.260
6.172
6.125
6.079
5.943
5.911
5.677
5.628
5.361
4.753
4.458
4.160
2.643
1.942
1.636
1.268
0.883
0.463
0.035
Fe
Fe
C=O
C=O
Me
Si
Me
Me
Si
Me
x
y
x
y
z
Me
Si
Me
Me
Si
Me
(12h)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.459
0.376
1.008
1.028
3.063
1.184
0.777
0.202
6.163
1.625
2.000
5.904


205.374
139.282
131.700
78.912
77.579
77.261
76.943
72.215
69.900
69.525
38.522
34.234
30.468
27.189
10.914
10.067
-3.228
Fe
Fe
C=O
C=O
Me
Si
Me
Me
Si
Me
x
y
x
y
z
Me
Si
Me
Me
Si
Me
(12h)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.1627
8.1206
7.7461
7.2600
6.2111
6.1678
6.1252
5.9843
5.9512
5.7204
5.6704
5.4009
3.0688
1.9888
1.6721
1.3055
1.0462
0.5185
0.1569
0.0891
C=O
Me
Si
Me
x
y
z
(12i)
10
9
8
7
6
5
4
3
2
1
0
ppm
1.292
0.273
1.713
0.299
0.210
0.680
0.339
5.244
2.000
6.077


201.142
146.140
139.384
136.554
135.755
135.023
134.960
131.731
131.235
131.048
130.322
128.433
128.106
128.016
127.560
127.510
126.367
125.614
125.286
125.161
124.968
124.905
77.580
77.262
76.945
38.480
34.233
33.485
27.107
26.734
10.943
9.829
−0.029
−3.148
C=O
Me
Si
Me
x
y
z
(12i)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm