GALLIC ACID-BASED DENDRIMERS WITH THIACALIX[4]ARENE CORE: SYNTHESIS, AGGREGATION AND USE FOR Pd NP's STABILIZATION

Aigul M. Fatykhova 1, Elsa D. Sultanova 1, Vladimir A. Burilov 1, Bulat Kh. Gafiatullin 1, Angelina A. Fedoseeva 1, Tatyana A. Veshta 1, Marat A. Ziganshin 1, Sufia A. Ziganshina 1, Vladimir G. Evtugin 2, Daut R. Islamov 3, Konstantin S. Usachev 3, Svetlana E. Solovieva,4, Igor S. Antipin 1
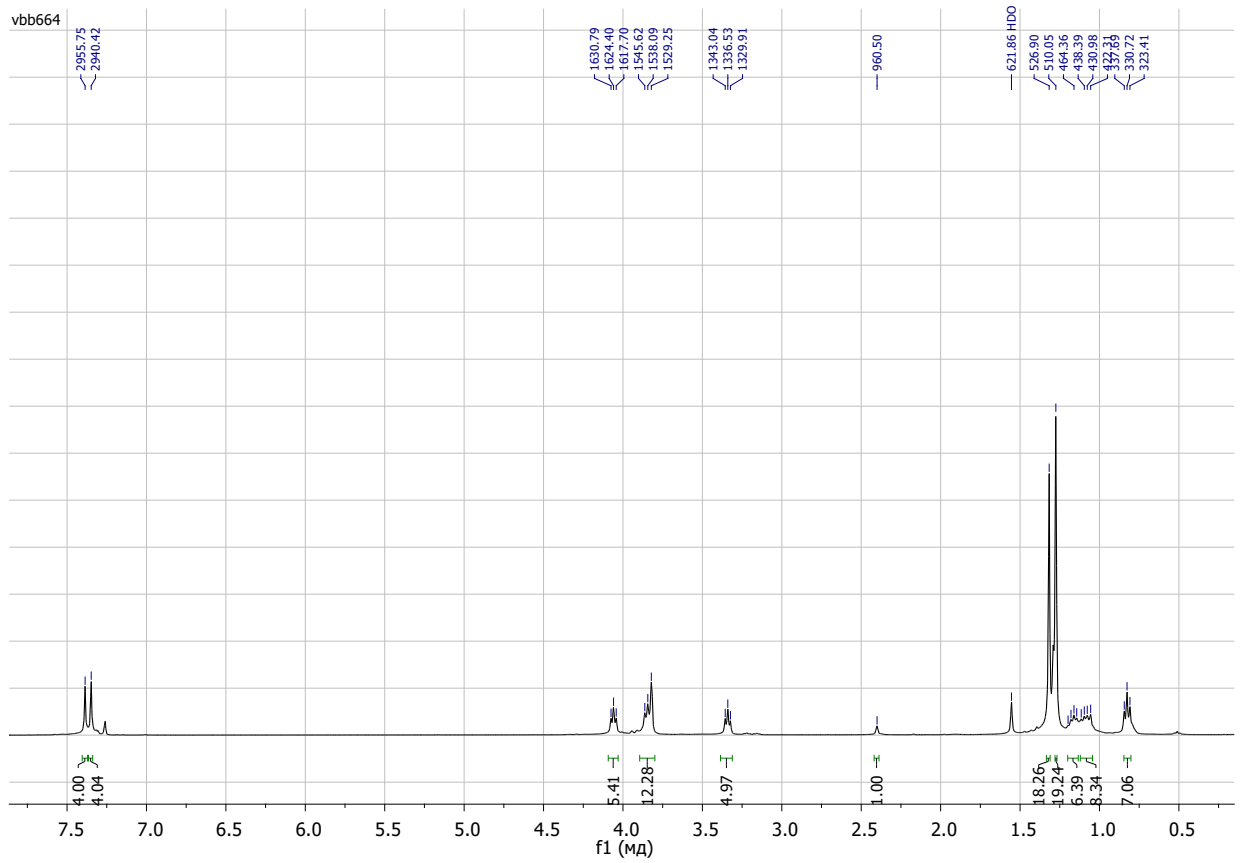
1 Alexander Butlerov Institute of Chemistry, Kazan Federal University, 18 Kremlevskaya Str., 420008 Kazan, Russia

2 Interdisciplinary Center for Analytical Microscopy, Kazan Federal University, 18 Kremlevskaya Str., 420008 Kazan, Russia
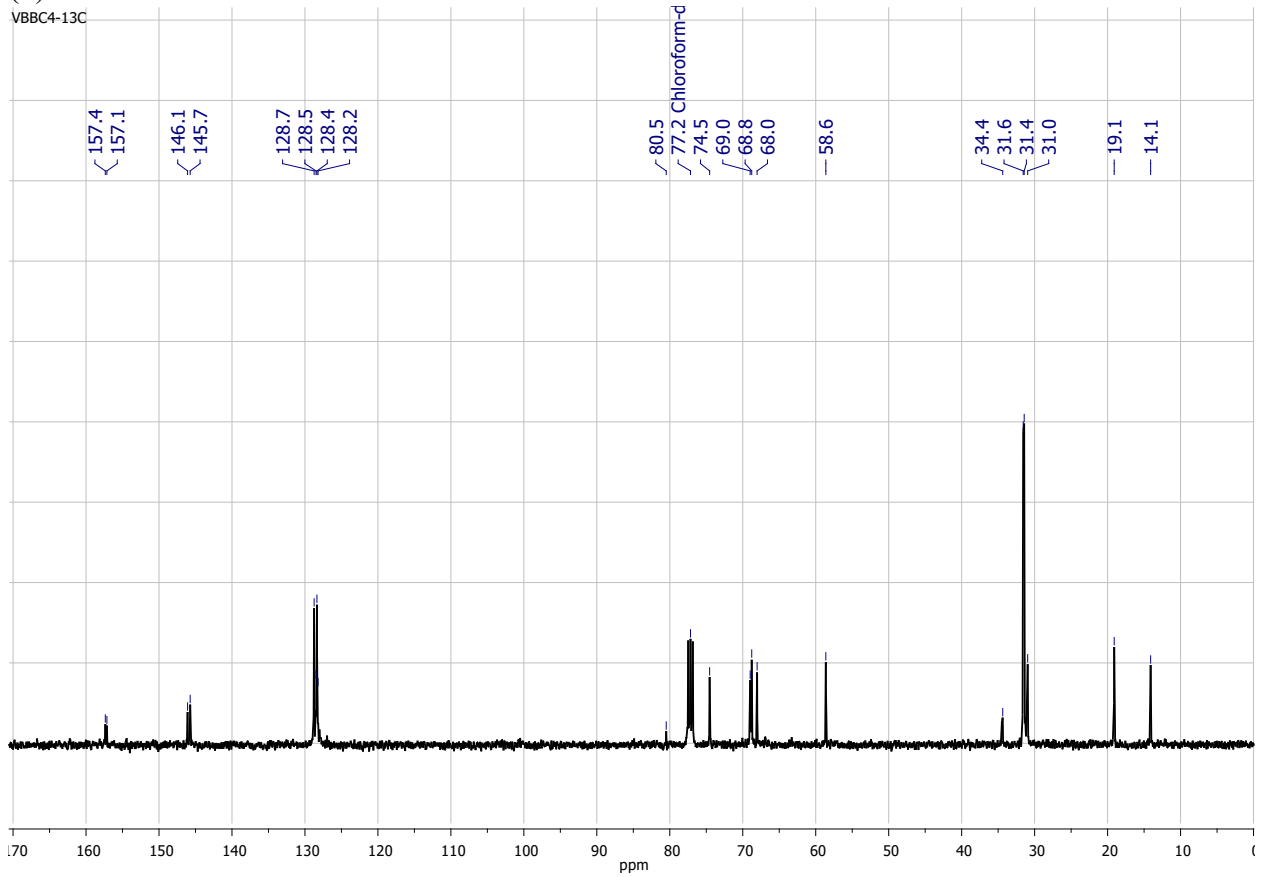
3 Laboratory for Structural Studies of Biomacromolecules, FRC Kazan Scientific Center of RAS, 2/31 Lobachevskogo Str., 420111 Kazan, Russia

4 Arbuzov Institute of Organic and Physical Chemistry, FRC Kazan Scientific Center of RAS, 8 Arbuzov Str., 420088 Kazan, Russia
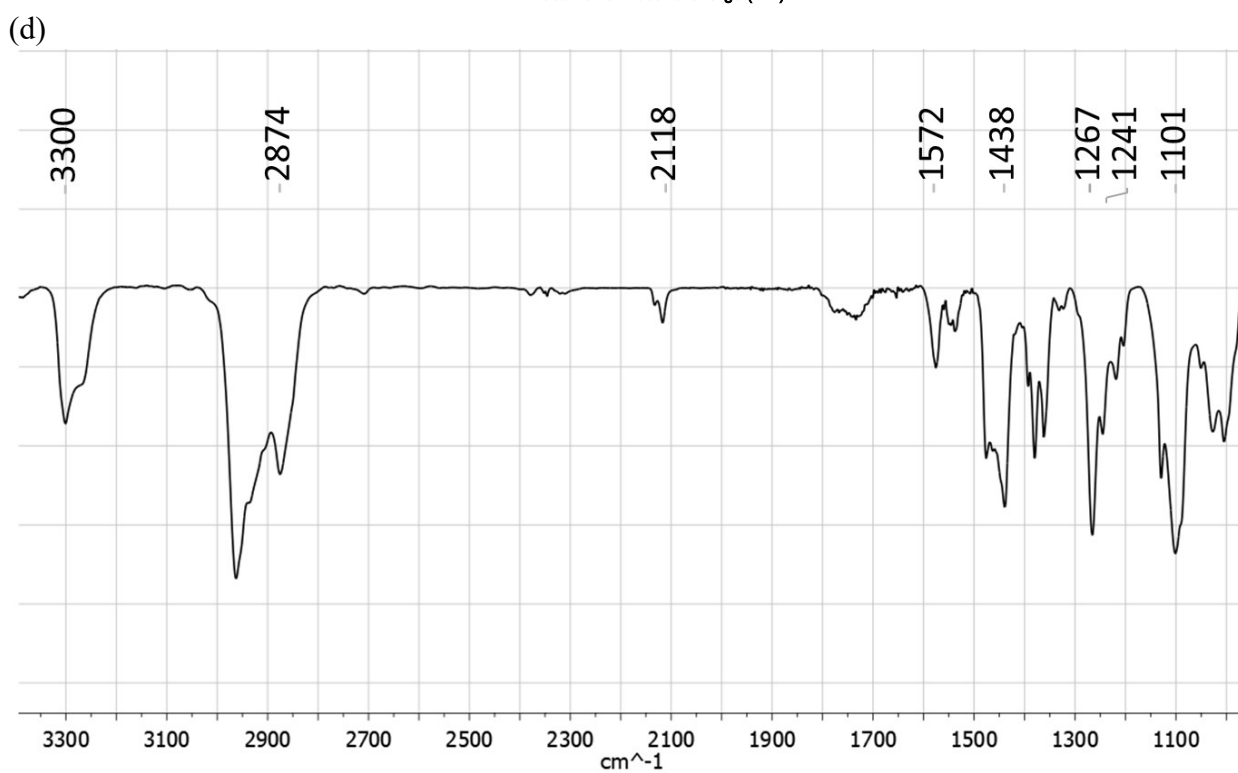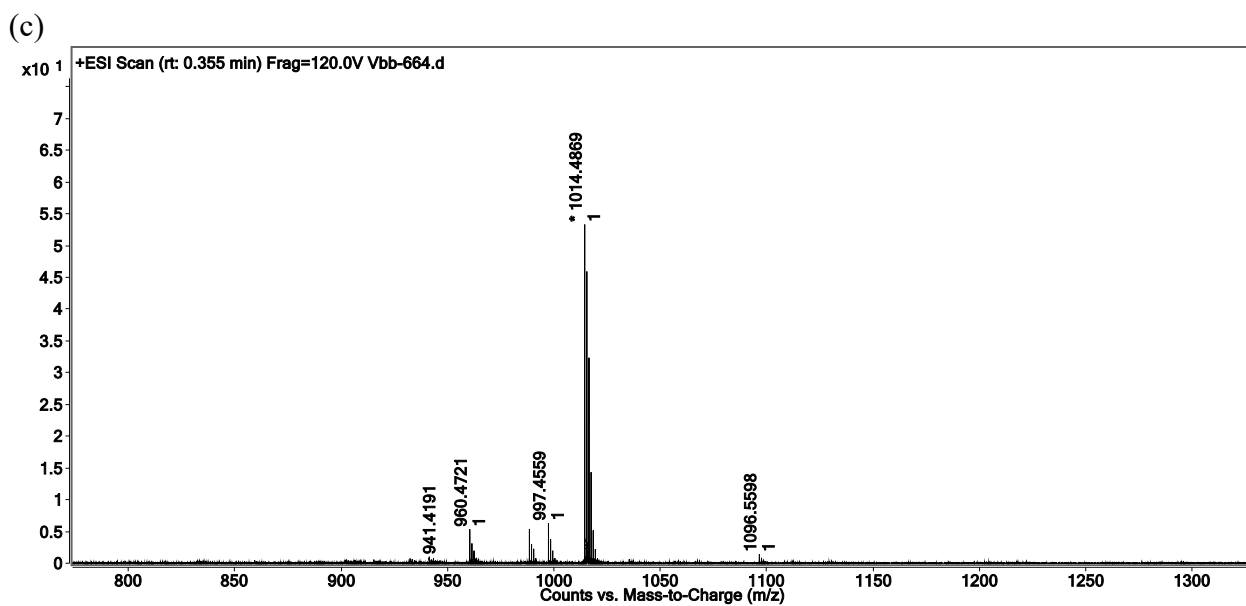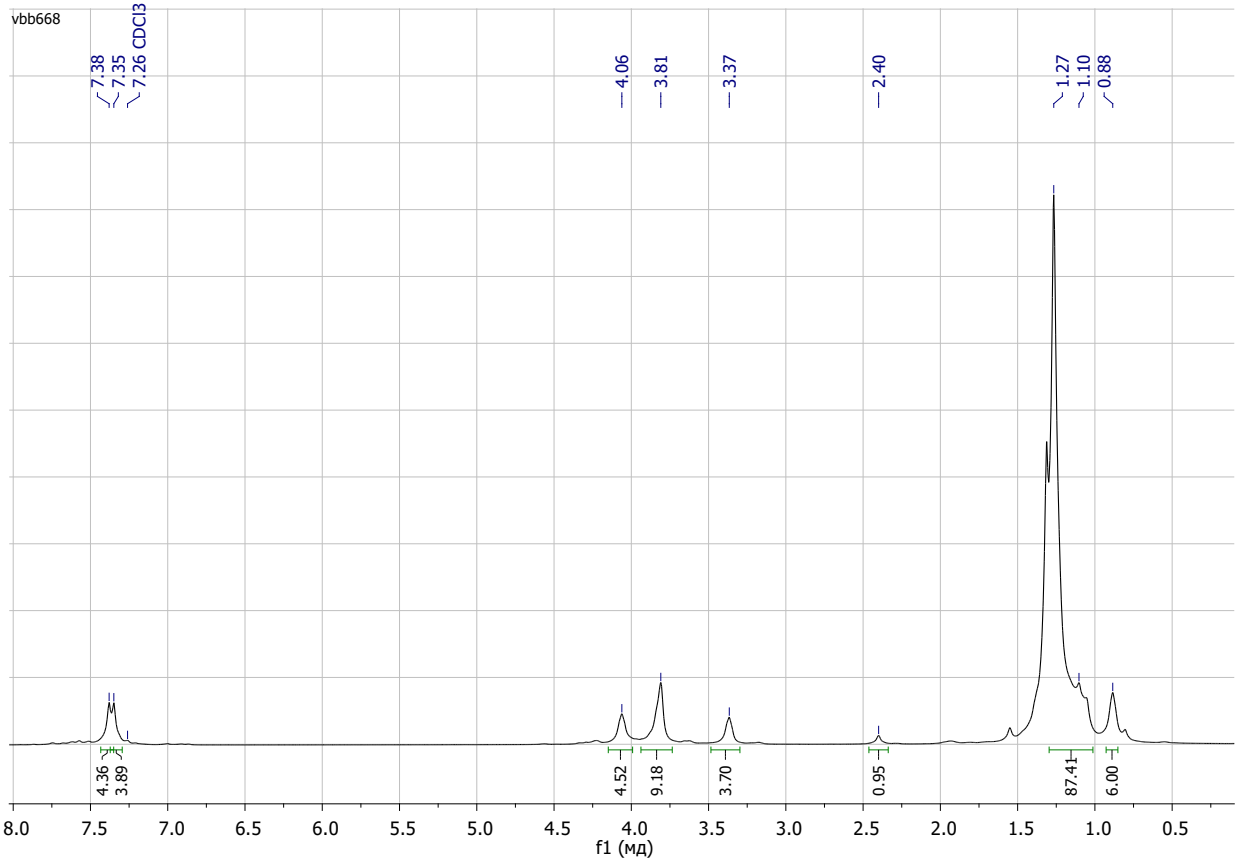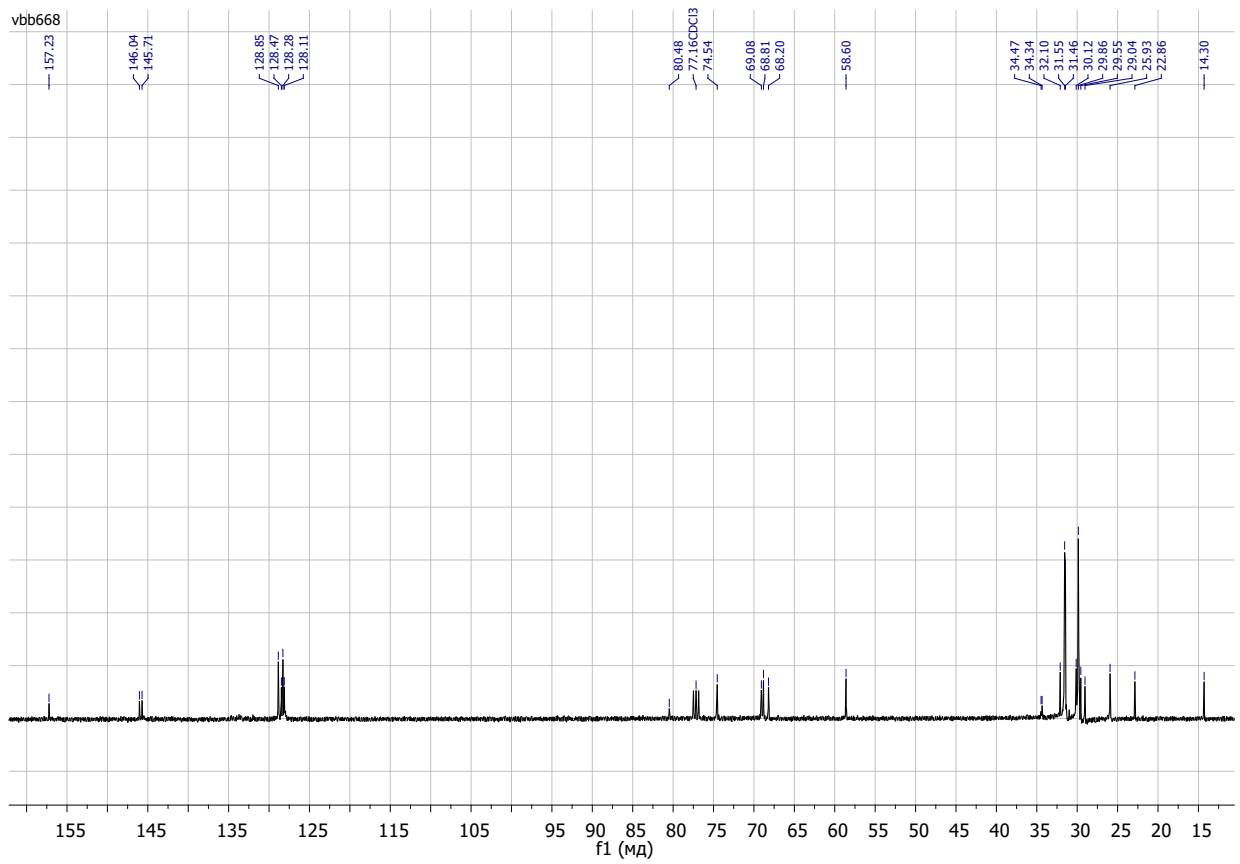
(a)

2955.75
2940.42

1630.79
1624.40
1617.70
1545.62
1538.09
1529.25

1343.04
1336.53
1329.91

960.50

621.86 HDO
526.90
510.05
464.36
438.39
430.98
337.39
332.31
330.72
323.41

4.00
4.04

5.41
12.28

4.97

1.00

18.26
19.24
6.39
8.34

7.06

7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5

f1 (мд)

(b)

VBBC4-13C

157.4
157.1

146.1
145.7

128.7
128.5
128.4
128.2

80.5
77.2 Chloroform-d
74.5
69.0
68.8
68.0

58.6

34.4
31.6
31.4
31.0

19.1

14.1

170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

ppm

(c)

x10 1

+ESI Scan (rt: 0.355 min) Frag=120.0V Vbb-664.d

* 1014.4869

941.4191

960.4721

997.4559

1096.5598

Counts vs. Mass-to-Charge (m/z)

(d)

3300

2874

2118

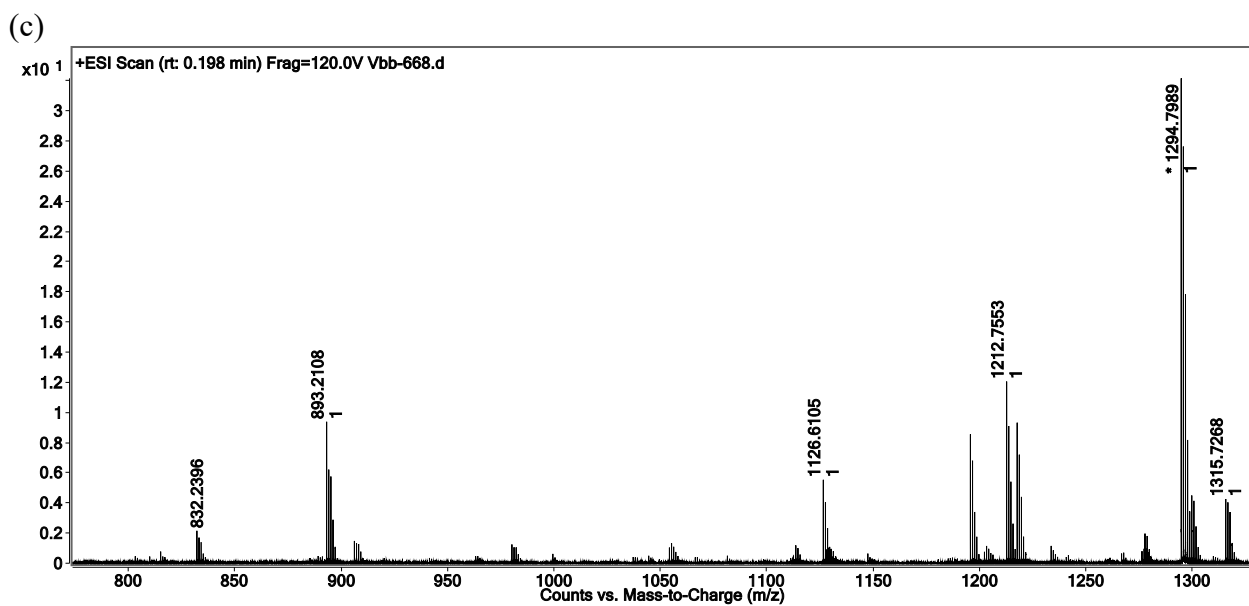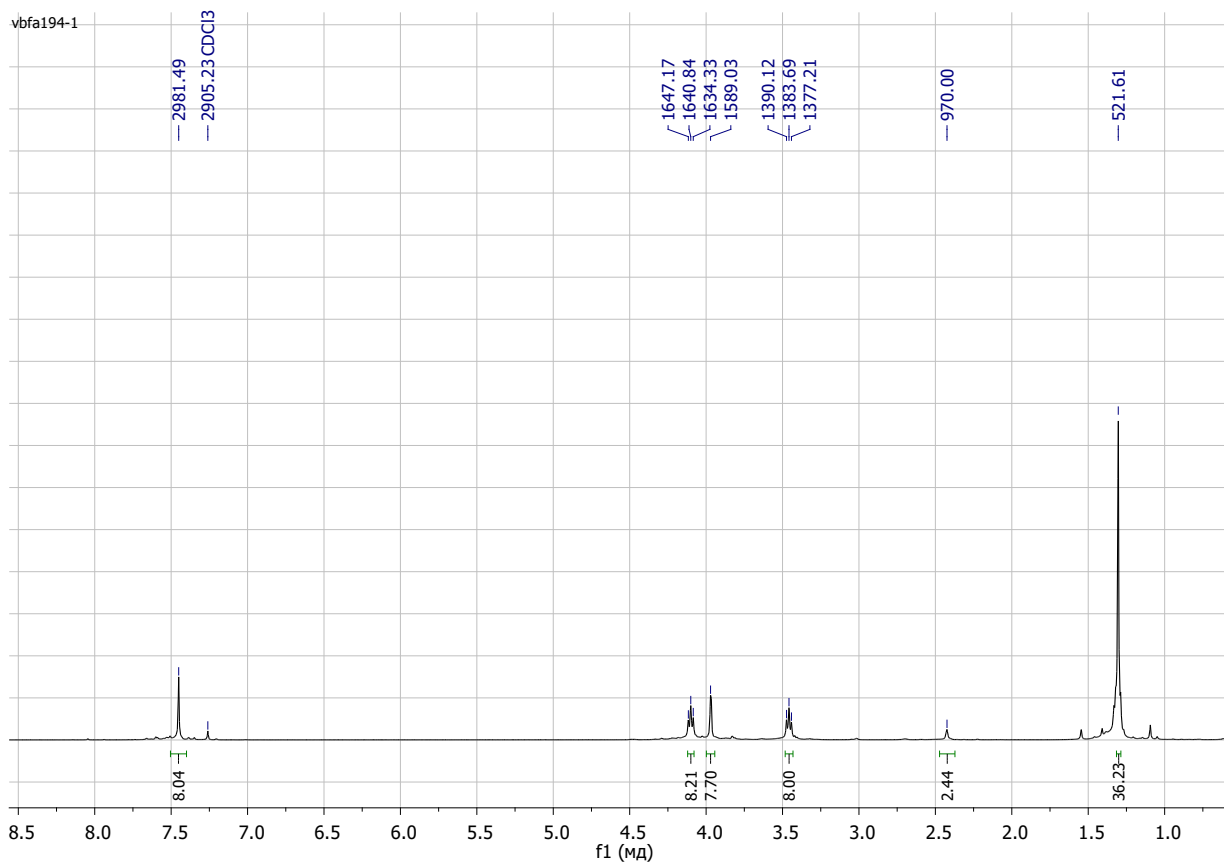1572

1438

1267
1241
1101

cm^-1

Figure S1. NMR ^{1}H (a), ^{13}C (b), and HRESI MS (c), FT IR (d) spectra of *compound (4)*.

vbb668

7.38
7.35
7.26 CDCl3

4.06
3.81
3.37
2.40
1.27
1.10
0.88

4.36
3.89
4.52
9.18
3.70
0.95
87.41
6.00

8.0   7.5   7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0   0.5
f1 (мд)

vbb668

157.23
146.04
145.71
128.85
128.47
128.28
128.11
80.48
77.16 CDCl3
74.54
69.08
68.81
68.20
58.60
34.47
34.34
32.10
31.55
31.46
30.12
29.86
29.55
29.04
25.93
22.86
14.30

155   145   135   125   115   105   95   90   85   80   75   70   65   60   55   50   45   40   35   30   25   20   15
f1 (мд)

(c)

(d)
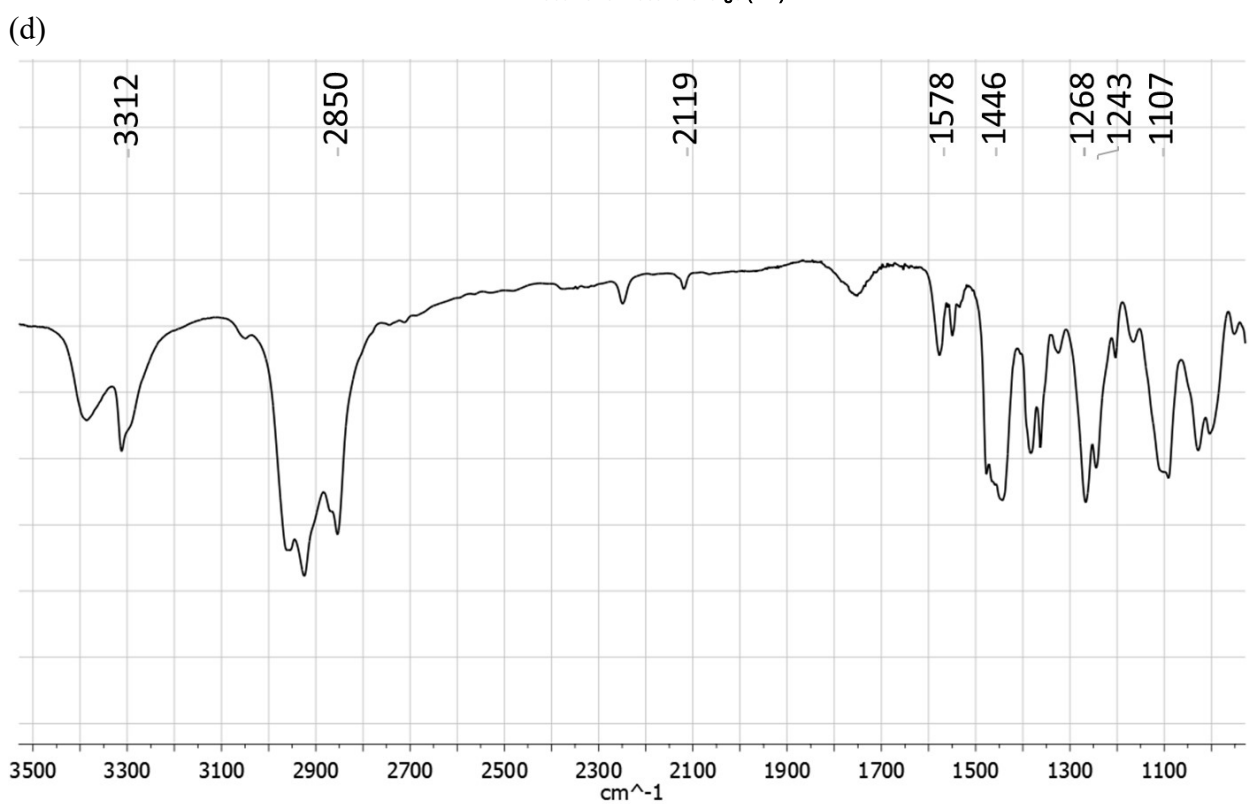
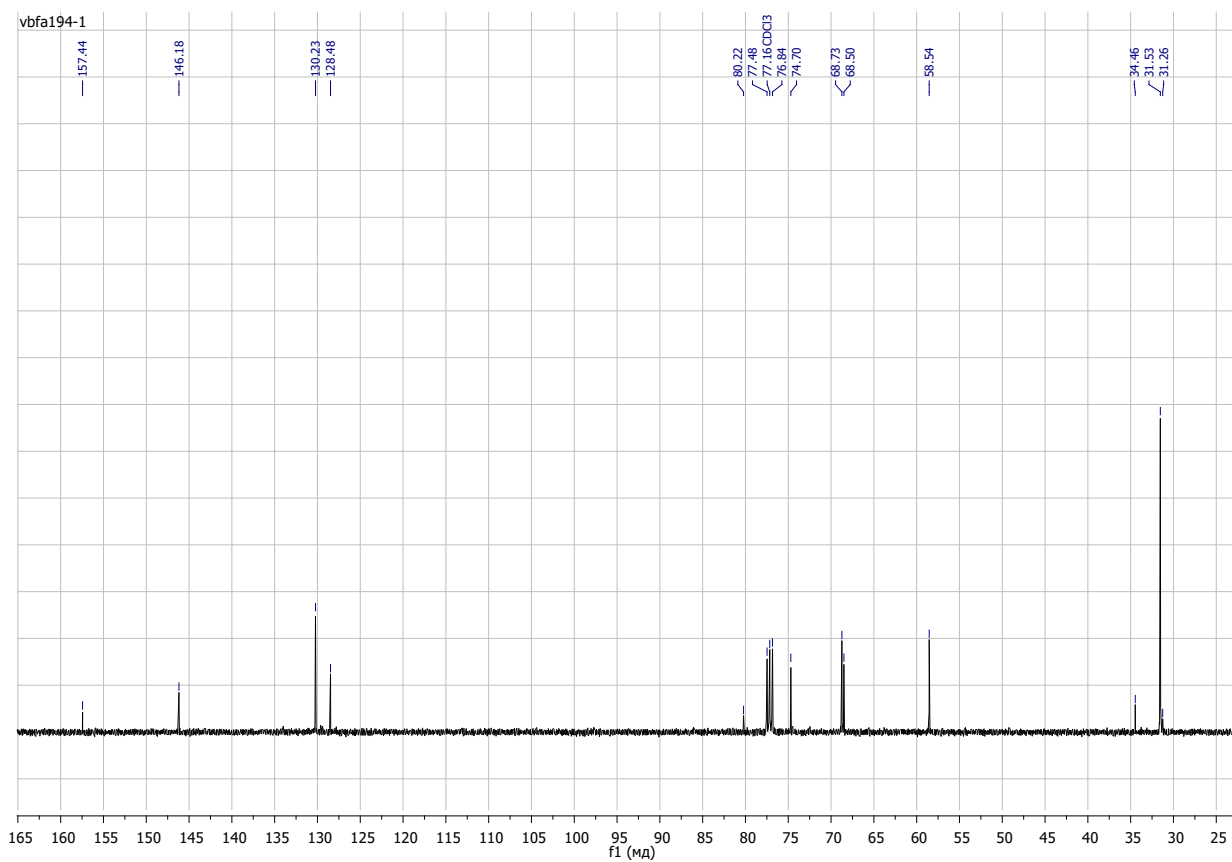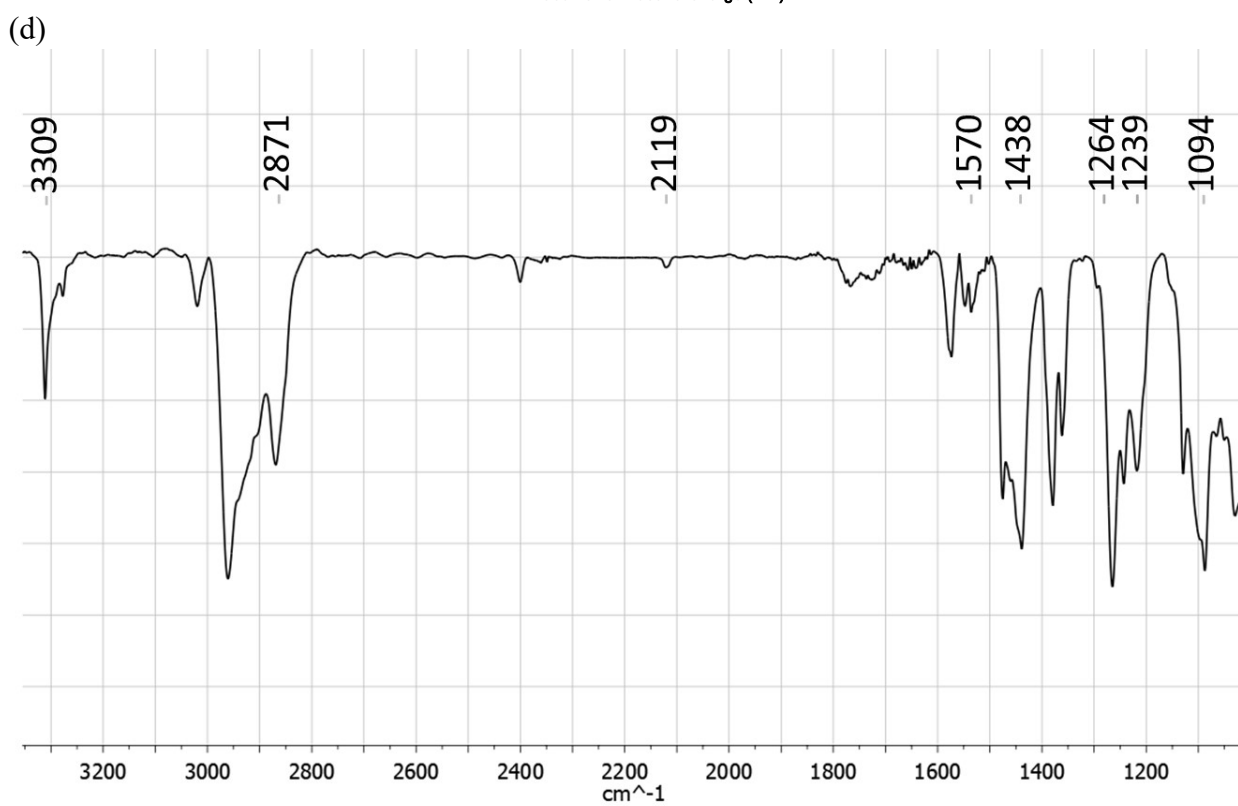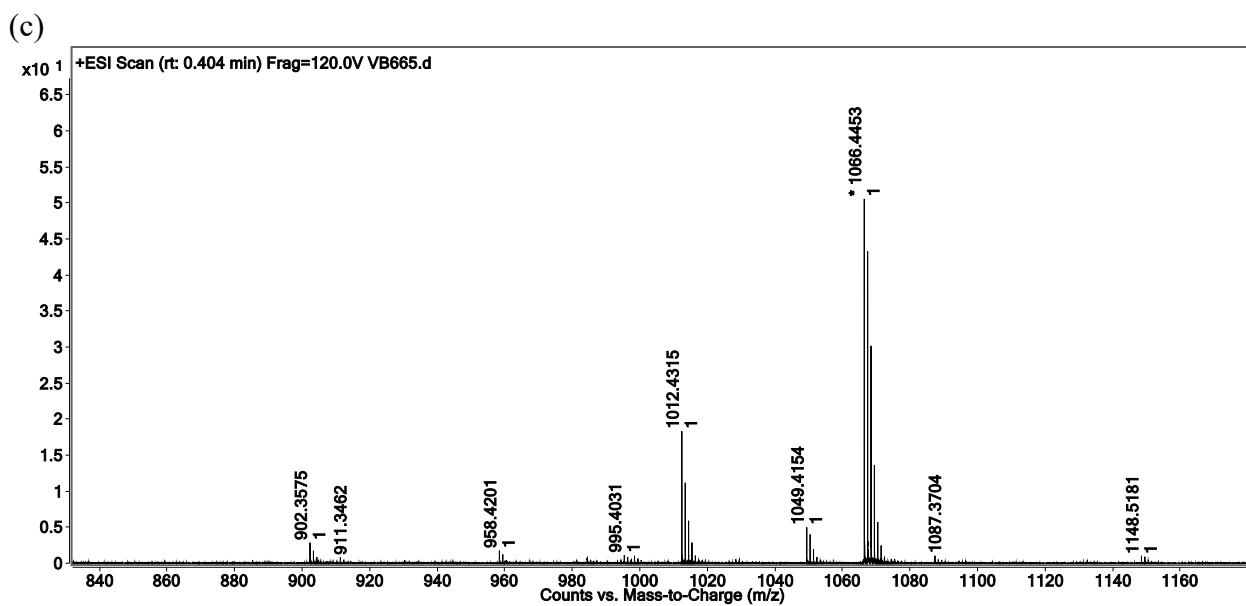Figure S2. NMR ^{1}H (a), ^{13}C (b), and HRESI MS (c), FT IR (d) spectra of *compound (5)*.

(a)

vbfa194-1

2981.49
2905.23 CDCl3
1647.17
1640.84
1634.33
1589.03
1390.12
1383.69
1377.21
970.00
521.61

8.04

8.21
7.70

8.00

2.44

36.23

8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (мд)

(b)

vbfa194-1

157.44

146.18

130.23
128.48

80.22
77.48
77.16 CDCl3
76.84
74.70

68.73
68.50

58.54

34.46
31.53
31.26

165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (мд)

(c)

(d)

Figure S3. NMR ^{1}H (a), ^{13}C (b), and HRESI MS (c), FT IR (d) spectra of *compound (6)*.
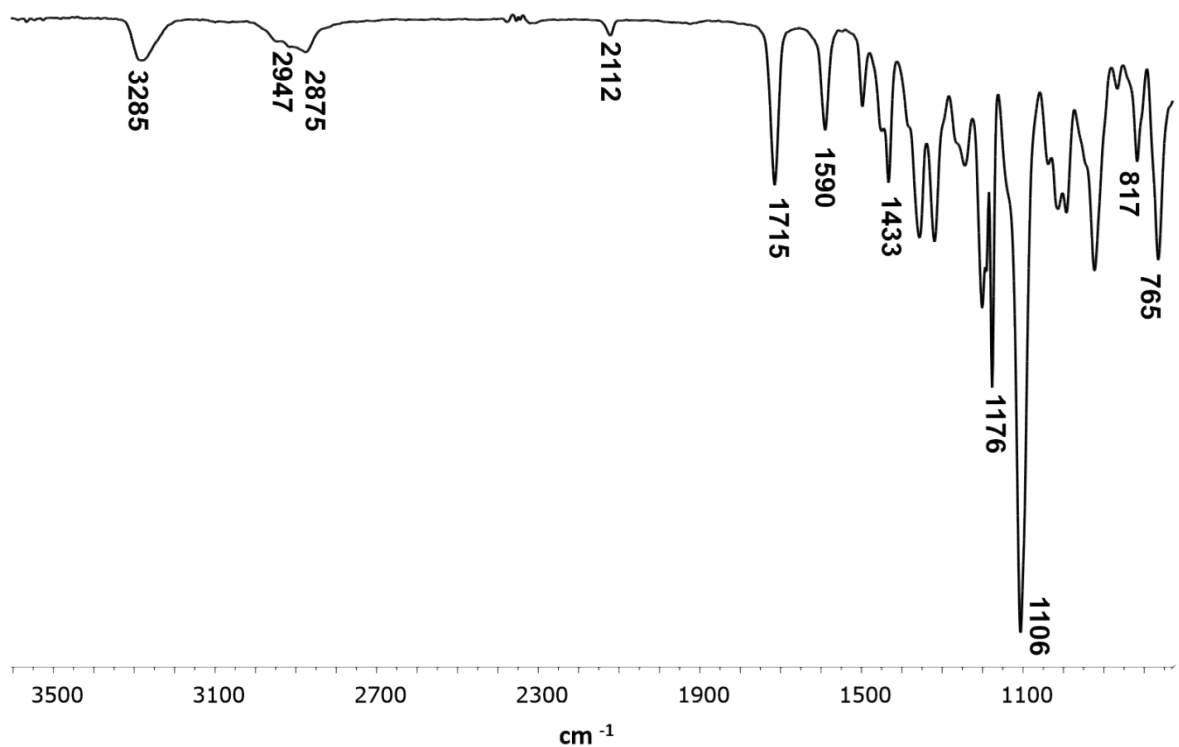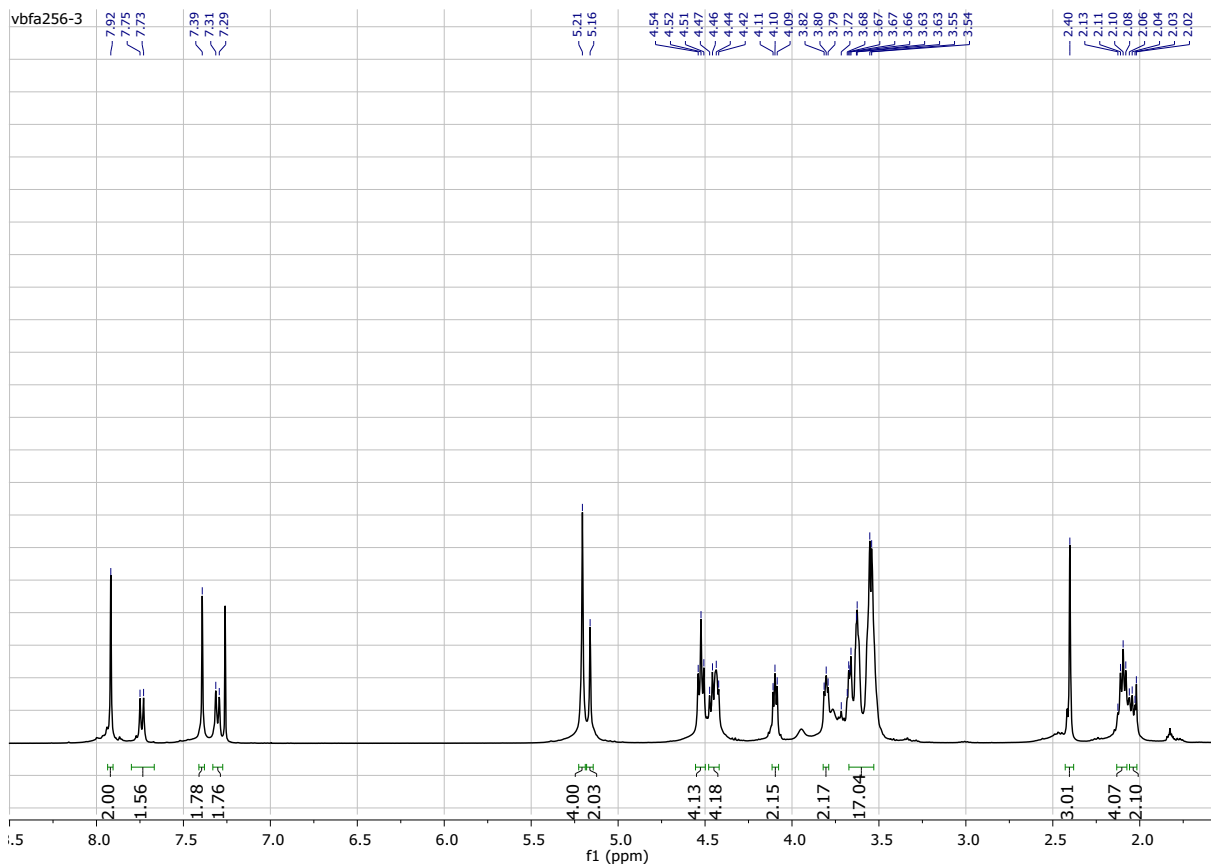
(a)

vbfa246-5.1.fid

7.78
7.76
7.47
7.33
7.31
7.26 CDCl3
4.81
4.80
4.78
4.78
4.46
4.44
4.43
4.14
4.11
3.82
3.79
3.69
3.68
3.67
3.66
3.65
3.64
3.63
3.62
3.61
3.60
3.56
2.55
2.54
2.46
2.45
2.42

1.50
1.78
1.56
2.00
4.01
2.00
2.17
2.08
6.08
4.03
1.50
0.64
2.80

f1 (ppm)

(b)

vbfa246-5C13.1.fid

165.75
151.35
144.89
141.23
133.00
129.90
128.03
125.79
110.12
78.81
78.05
77.16 CDCl3
76.40
75.73
70.80
70.74
70.61
69.30
69.27
68.74
64.57
60.39
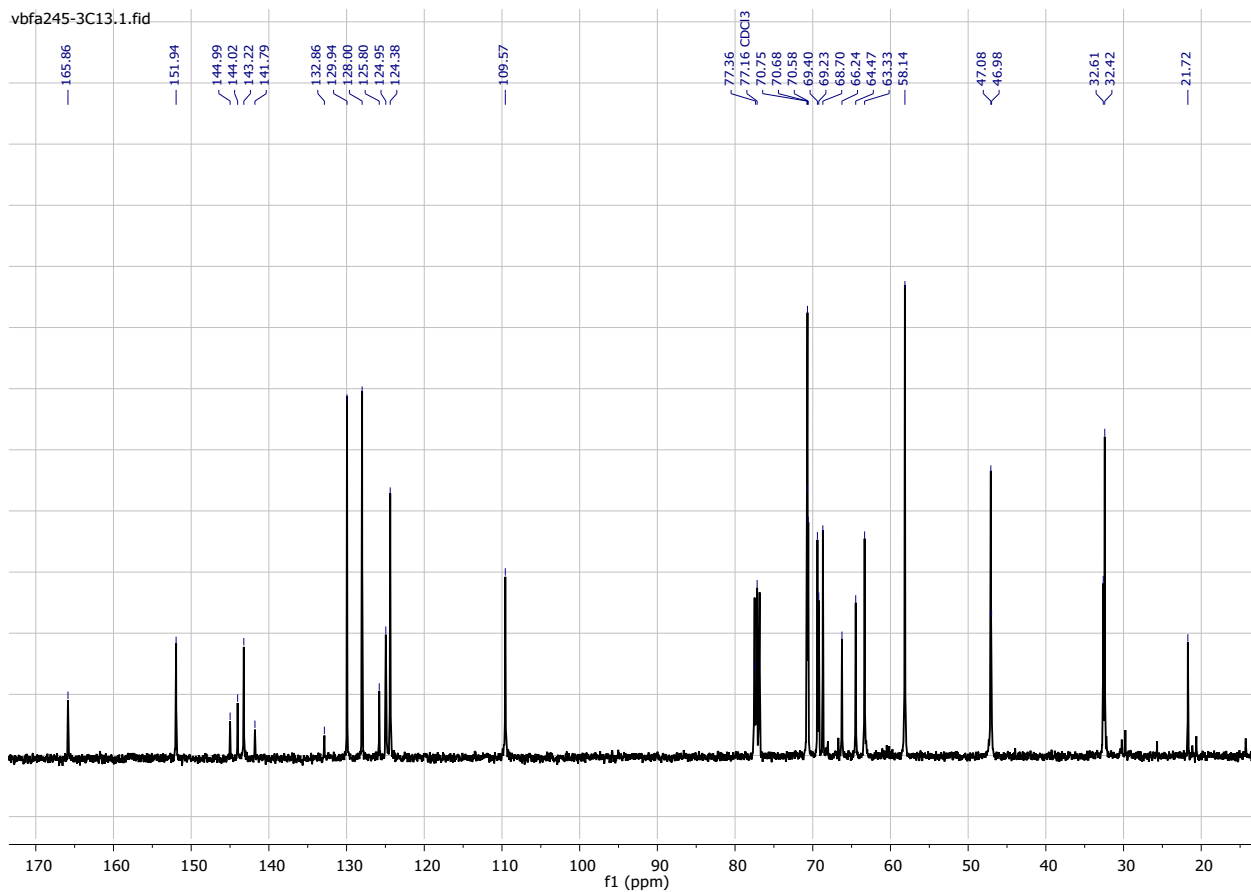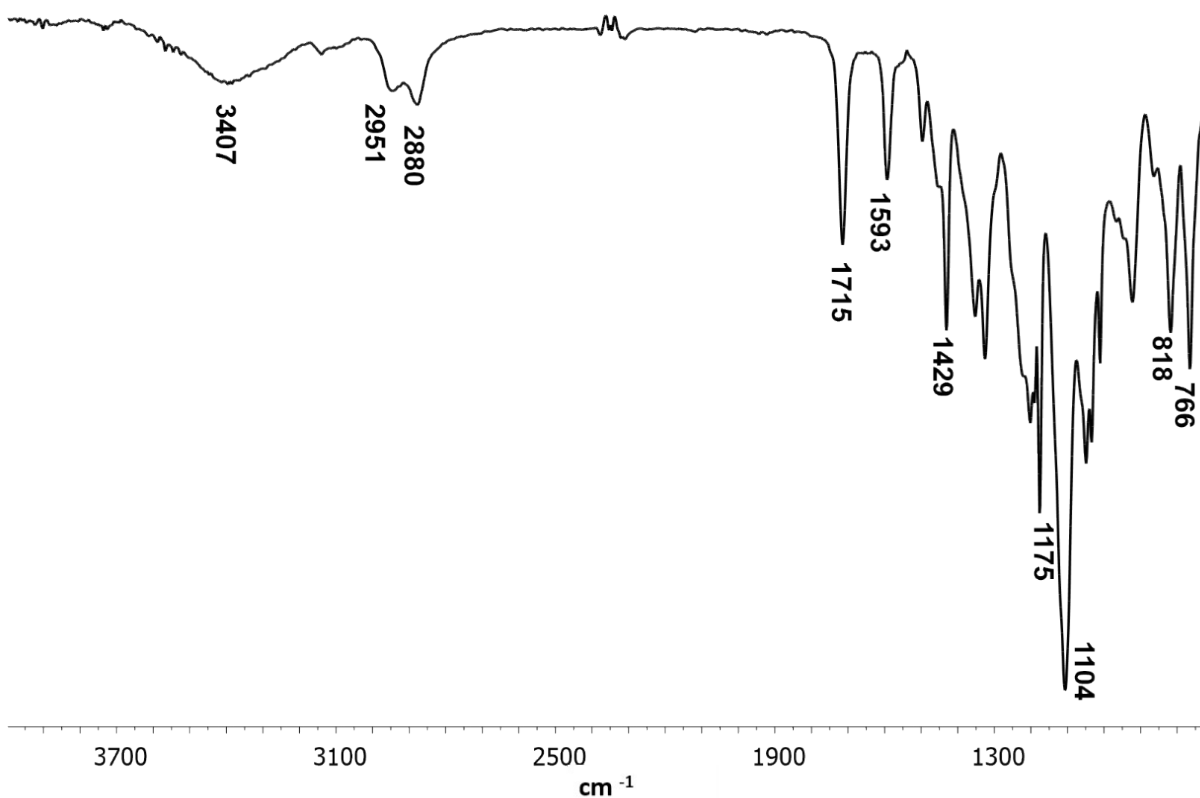57.20
29.76
21.72
21.14
14.28

f1 (ppm)
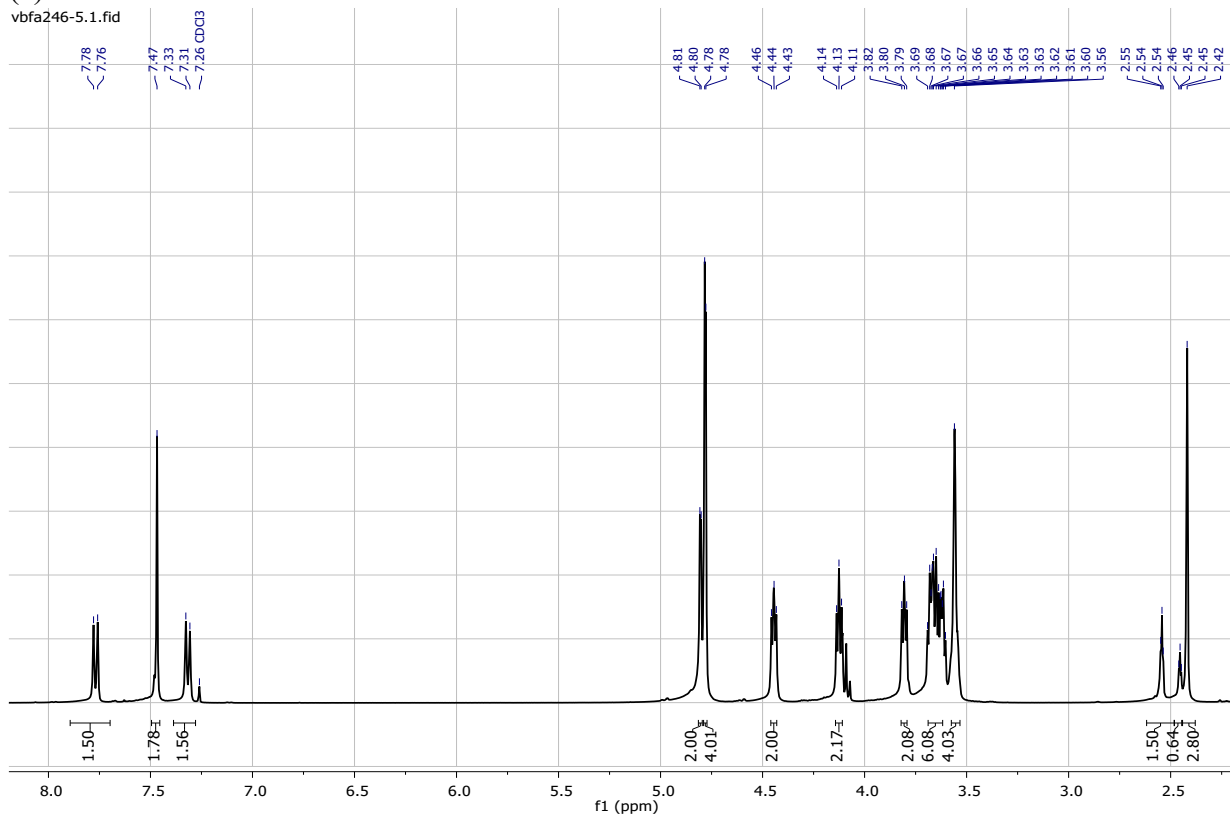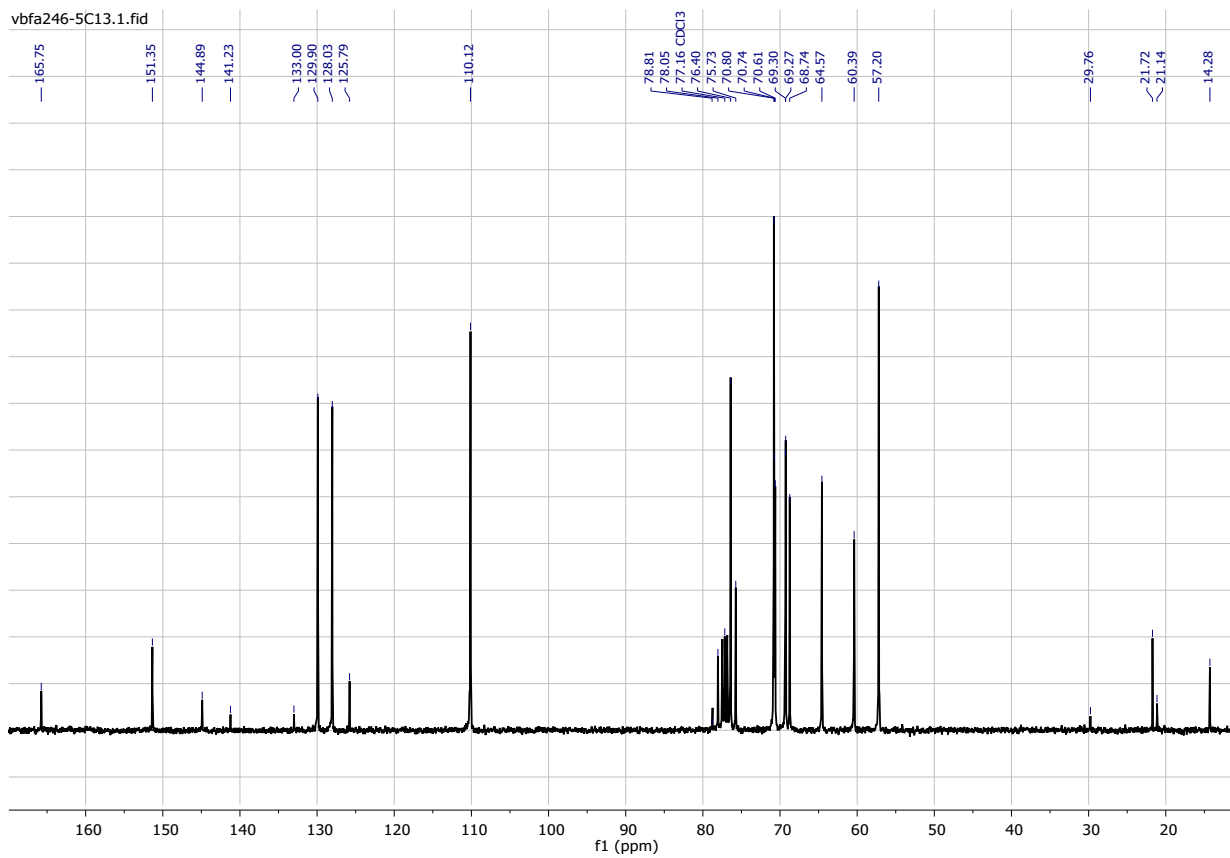
(c)
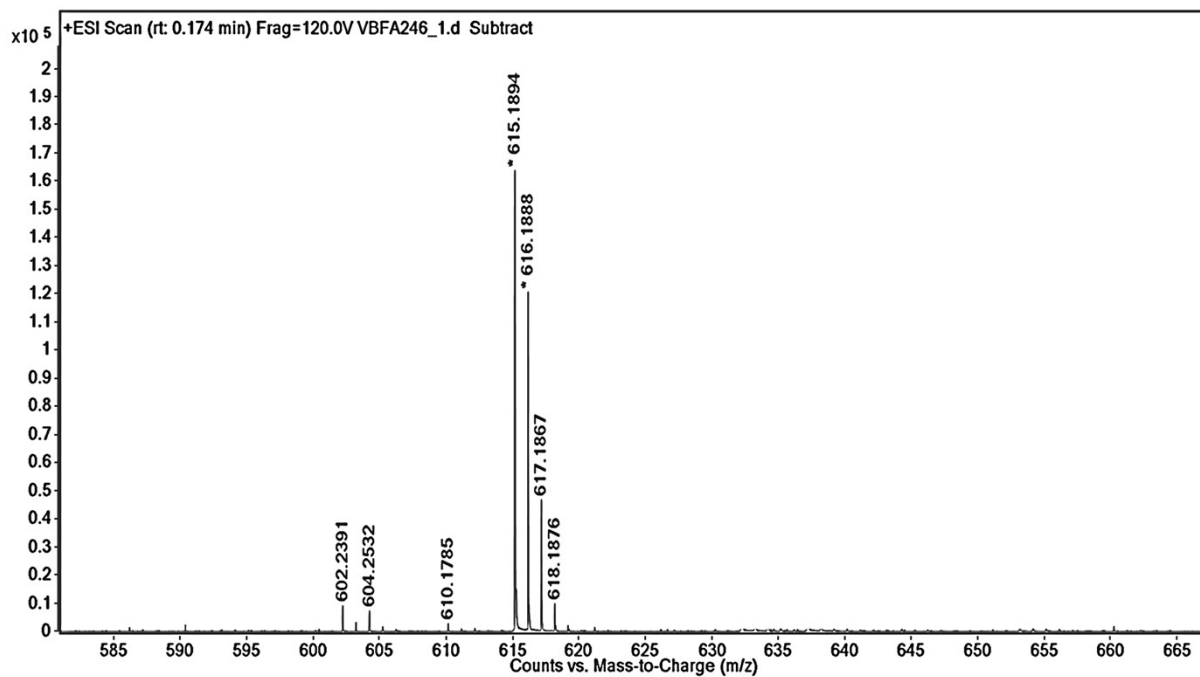
(d)

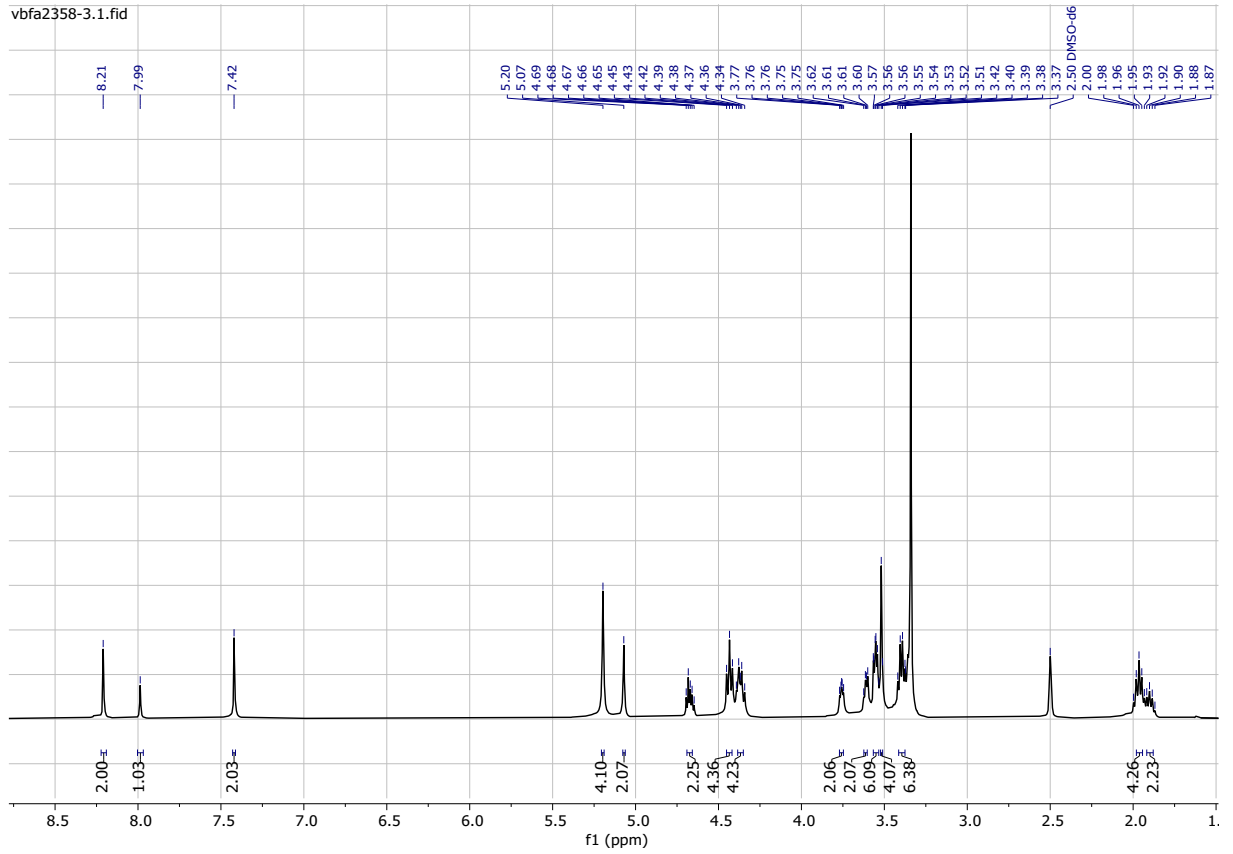
Figure S4. NMR ^{1}H (a), ^{13}C (b), and HRESI MS (c), FT IR (d) spectra of *compound (12)*

(a)

vbfa256-3

7.92
7.75
7.73
7.39
7.31
7.29
5.21
5.16
4.54
4.52
4.51
4.47
4.46
4.44
4.42
4.11
4.10
4.09
3.82
3.80
3.79
3.72
3.68
3.67
3.66
3.63
3.63
3.55
3.54
2.40
2.13
2.11
2.10
2.08
2.06
2.04
2.03
2.02

2.00
1.56
1.78
1.76
4.00
2.03
4.13
4.18
2.15
2.17
17.04
3.01
4.07
2.10

f1 (ppm)

(b)

vbfa245-3C13.1.fid

165.86
151.94
144.99
144.02
143.22
141.79
132.86
129.94
128.00
125.80
124.95
124.38
109.57
77.36
77.16 CDCl3
70.75
70.68
70.58
69.40
69.23
68.70
66.24
64.47
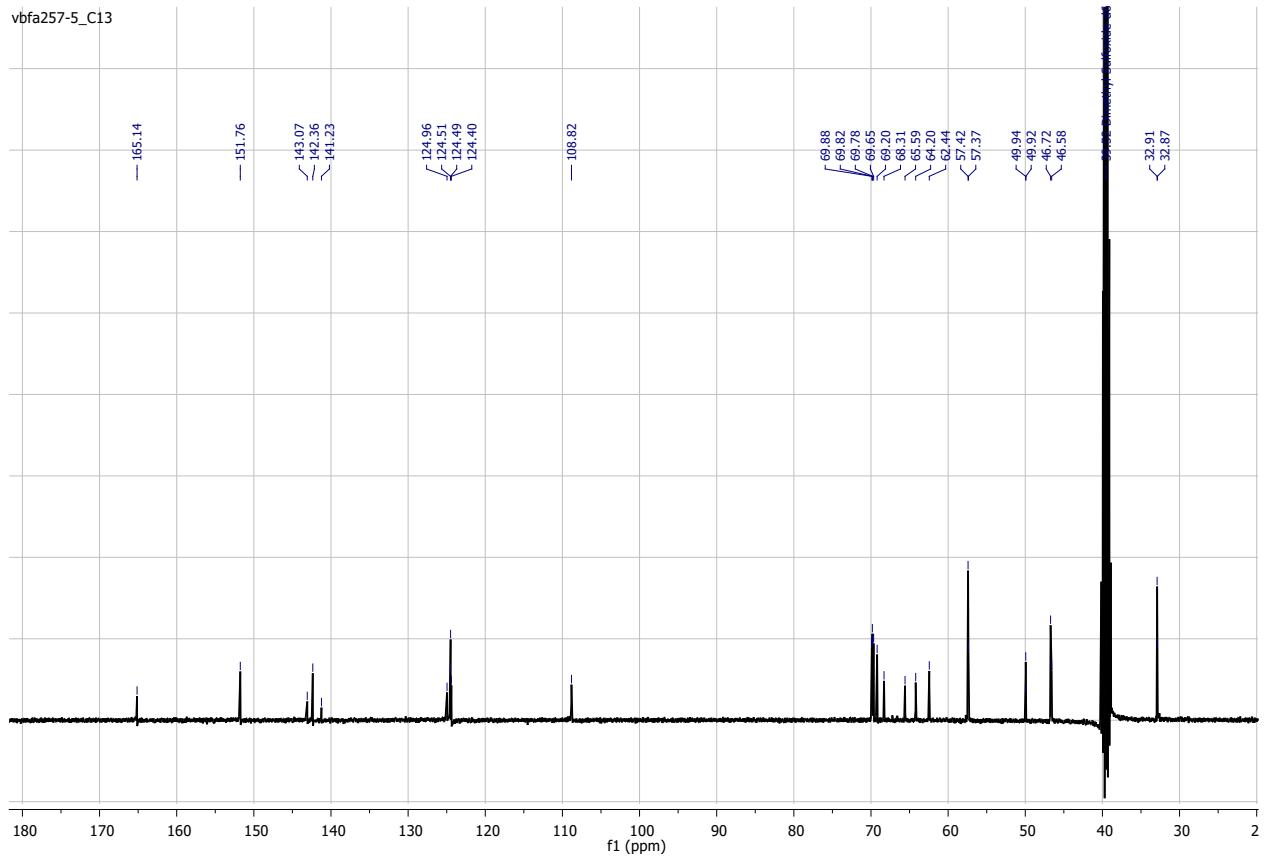63.33
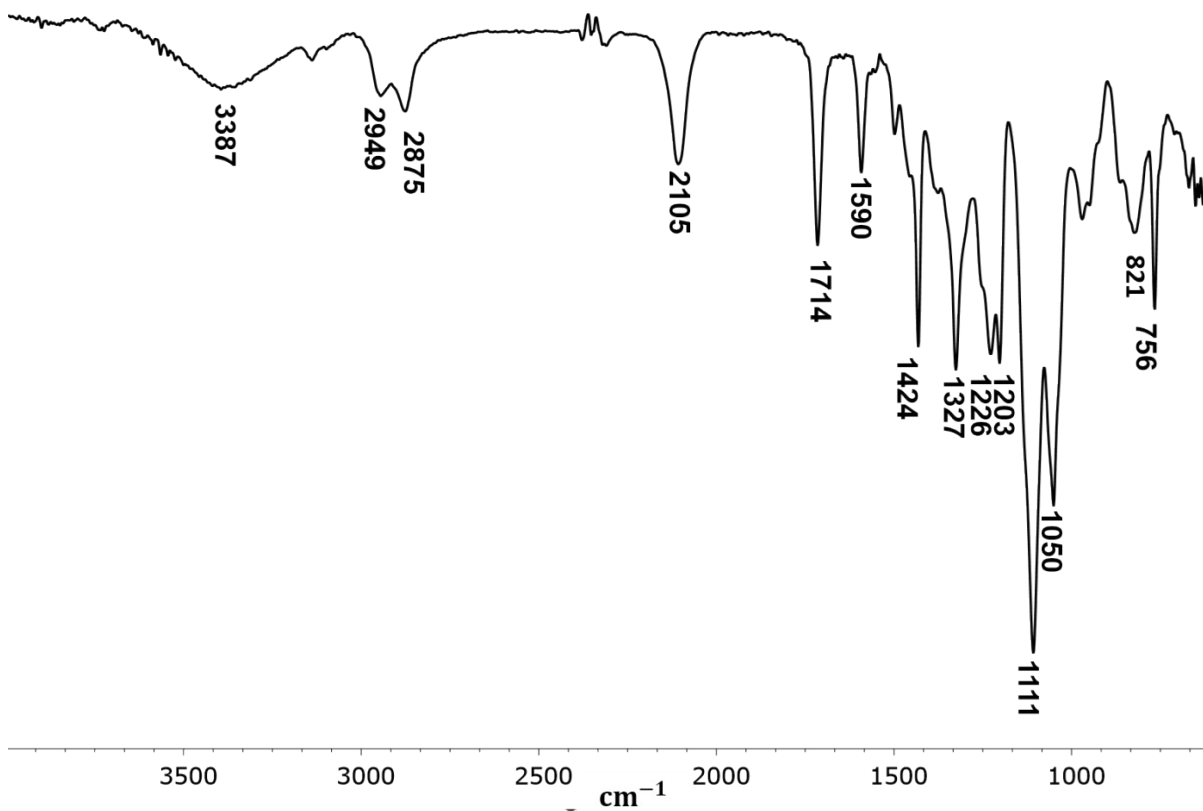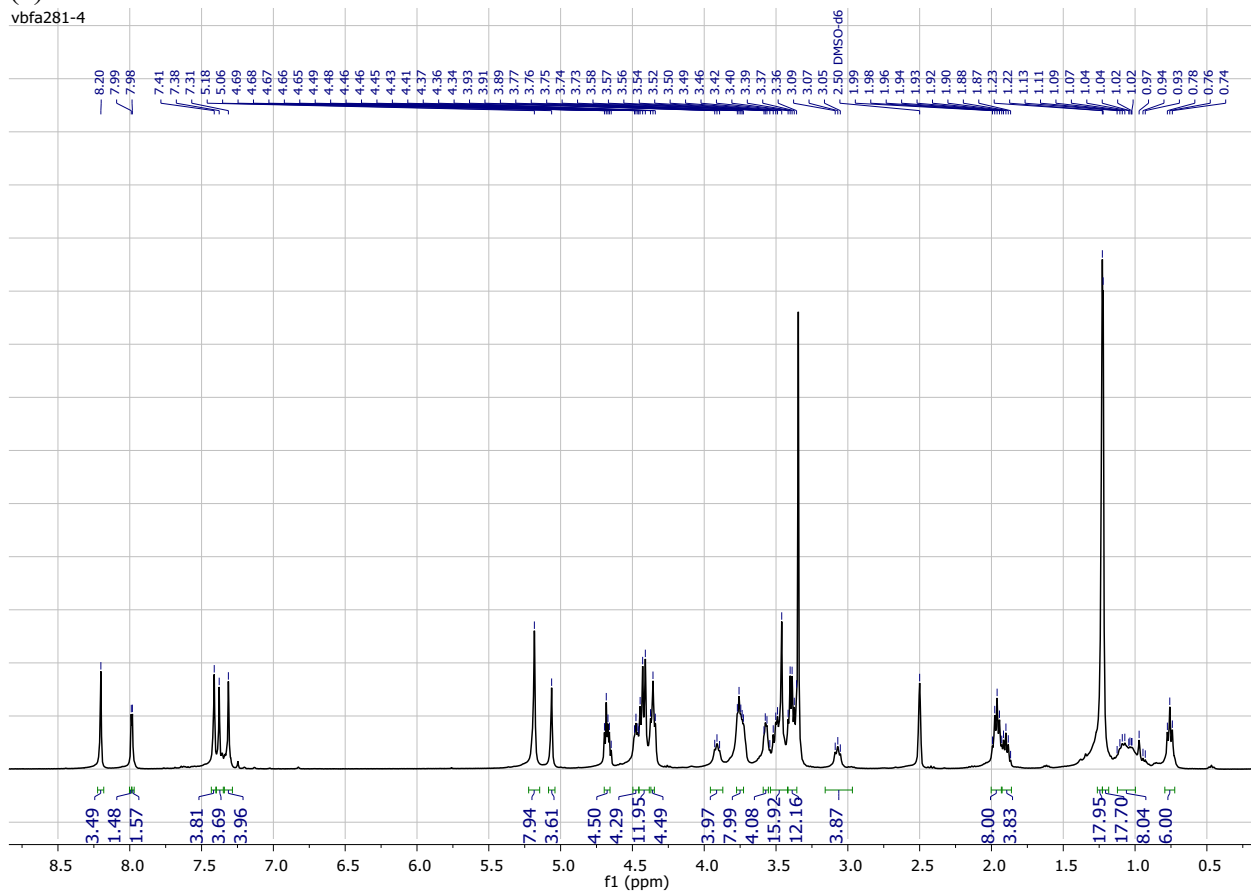58.14
47.08
46.98
32.61
32.42
21.72

f1 (ppm)

(c)

(d)

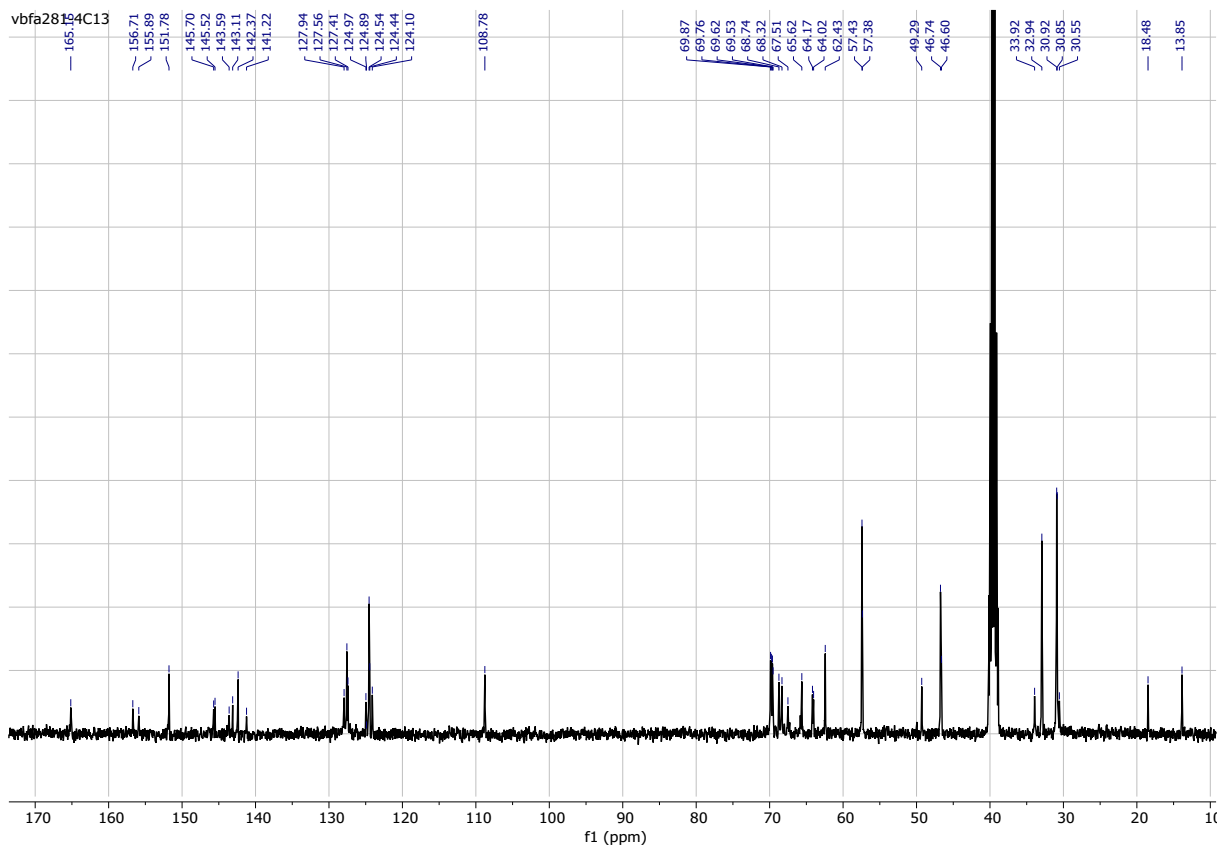Figure S5. NMR ¹H (a), ¹³C (b), and HRESI MS (c), FT IR (d) spectra of *compound (13)*

(a)

vbfa2358-3.1.fid

8.21
7.99
7.42
5.20
5.07
4.69
4.68
4.67
4.66
4.65
4.45
4.43
4.42
4.39
4.38
4.37
4.36
4.34
3.77
3.76
3.76
3.75
3.62
3.61
3.60
3.57
3.56
3.56
3.55
3.54
3.53
3.52
3.51
3.42
3.40
3.39
3.38
3.37
2.50 DMSO-d6
2.00
1.98
1.96
1.95
1.93
1.92
1.90
1.88
1.87

2.00
1.03
2.03
4.10
2.07
2.25
4.36
4.23
2.06
2.07
6.09
4.07
6.38
4.26
2.23

8.5   8.0   7.5   7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.

f1 (ppm)

(b)

vbfa257-5_C13

165.14
151.76
143.07
142.36
141.23
124.96
124.51
124.49
124.40
108.82
69.88
69.82
69.78
69.65
69.20
68.31
65.59
64.20
62.44
57.42
57.37
49.94
49.92
46.72
46.58
32.91
32.87

180   170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   2

f1 (ppm)

(c)

+ESI Scan (rt: 0.137 min) Frag=120.0V VBFA257.d Subtract

x10 5

* 789.3635

* 811.3397

Counts vs. Mass-to-Charge (m/z)

(d)

3387
2949
2875
2105
1714
1590
1424
1327
1226
1203
1111
1050
821
756

cm^{-1}

Figure S6. NMR ^{1}H (a), ^{13}C (b), and HRESI MS (c), FT IR (d) spectra of *compound (14)*
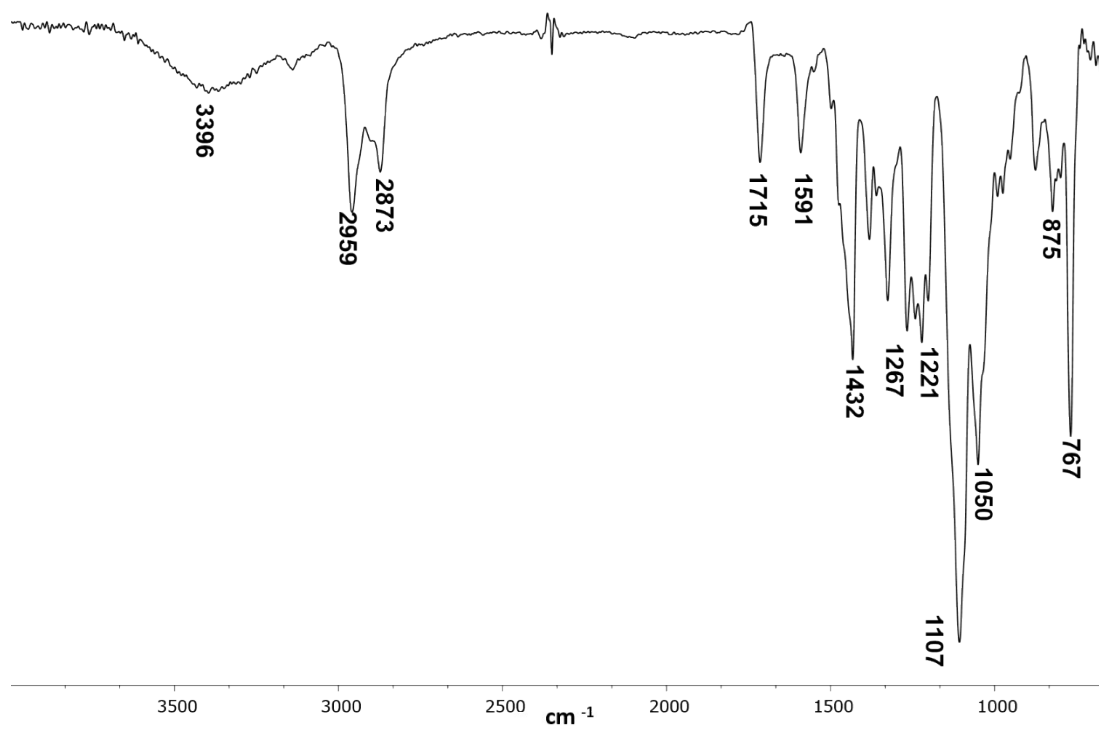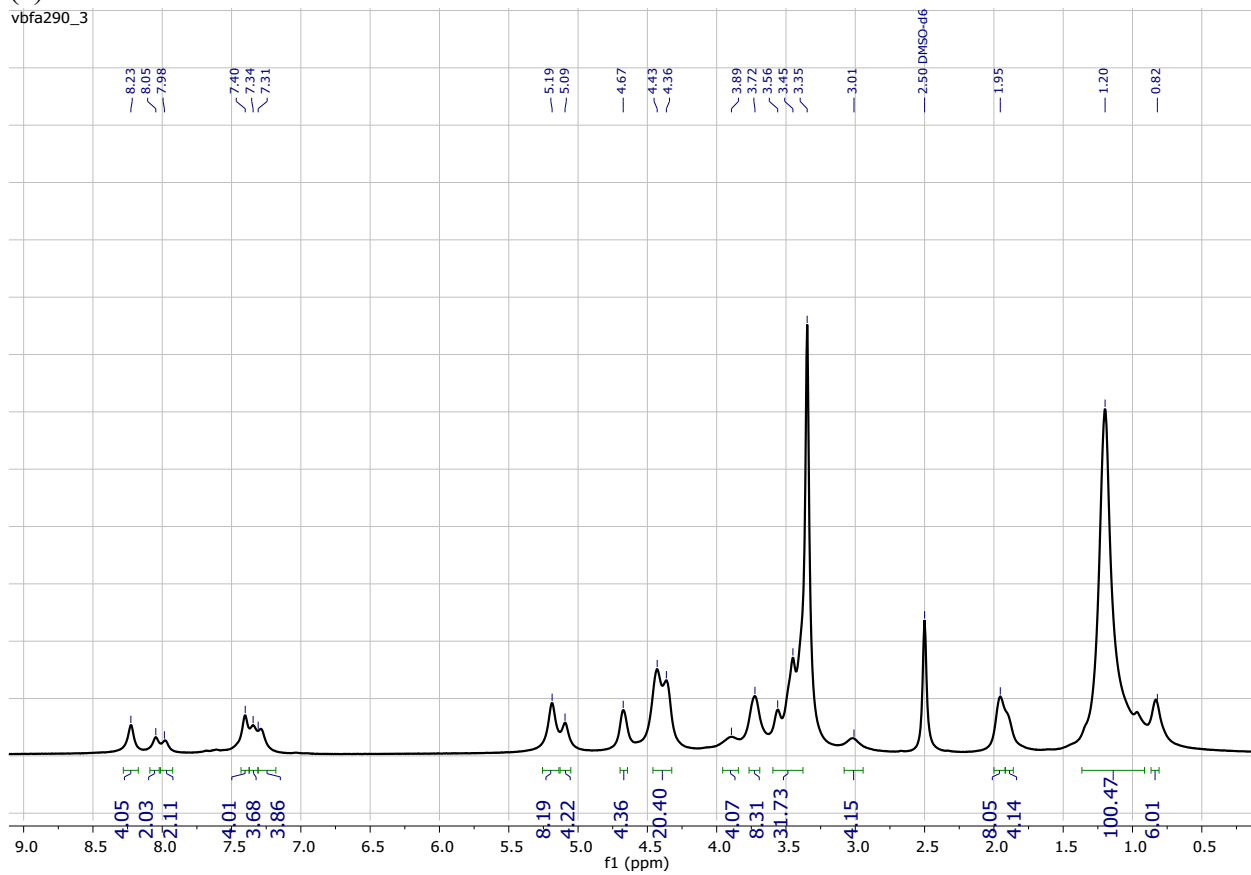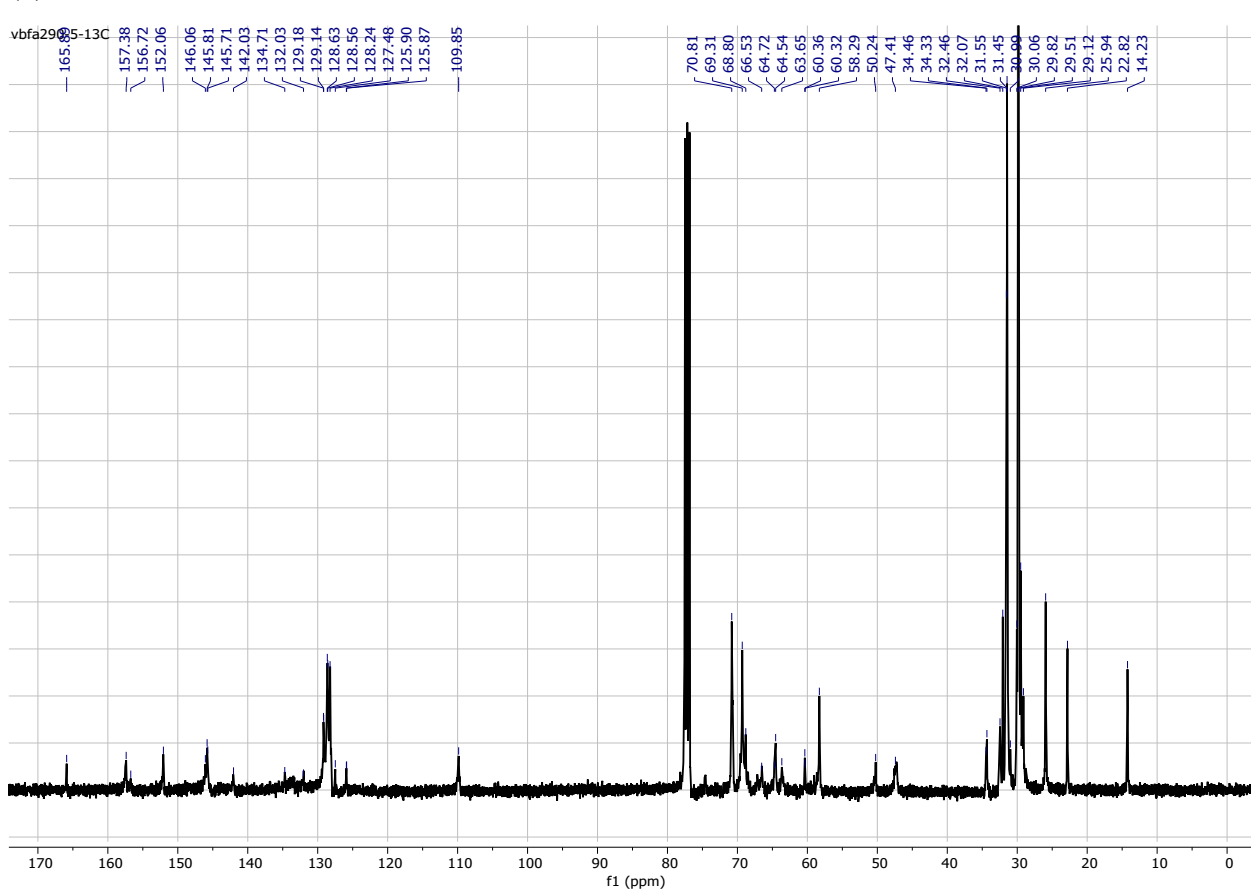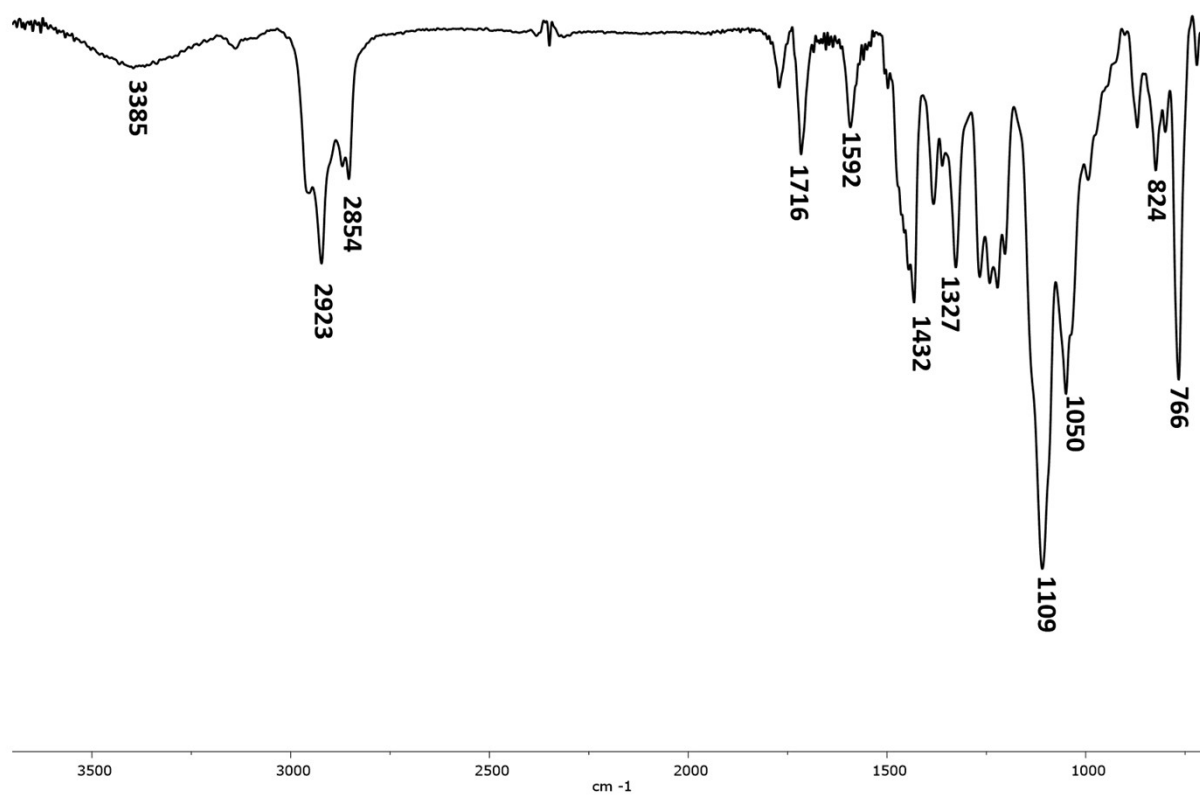
(a) vbfa281-4

(b) vbfa281-4C13

(c)
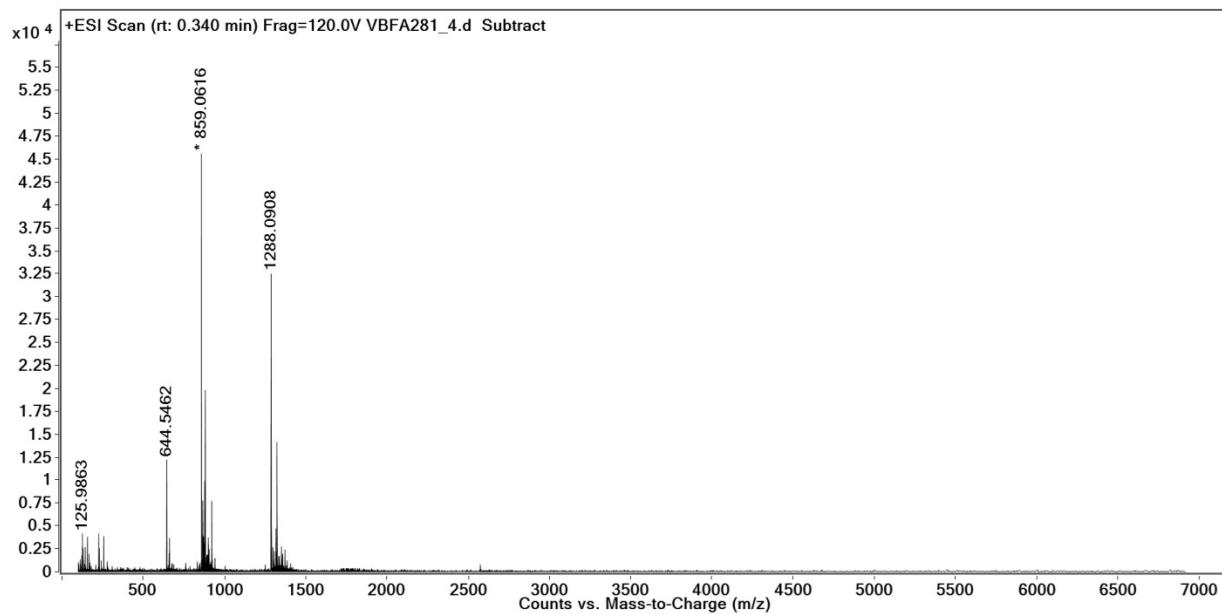
(d)

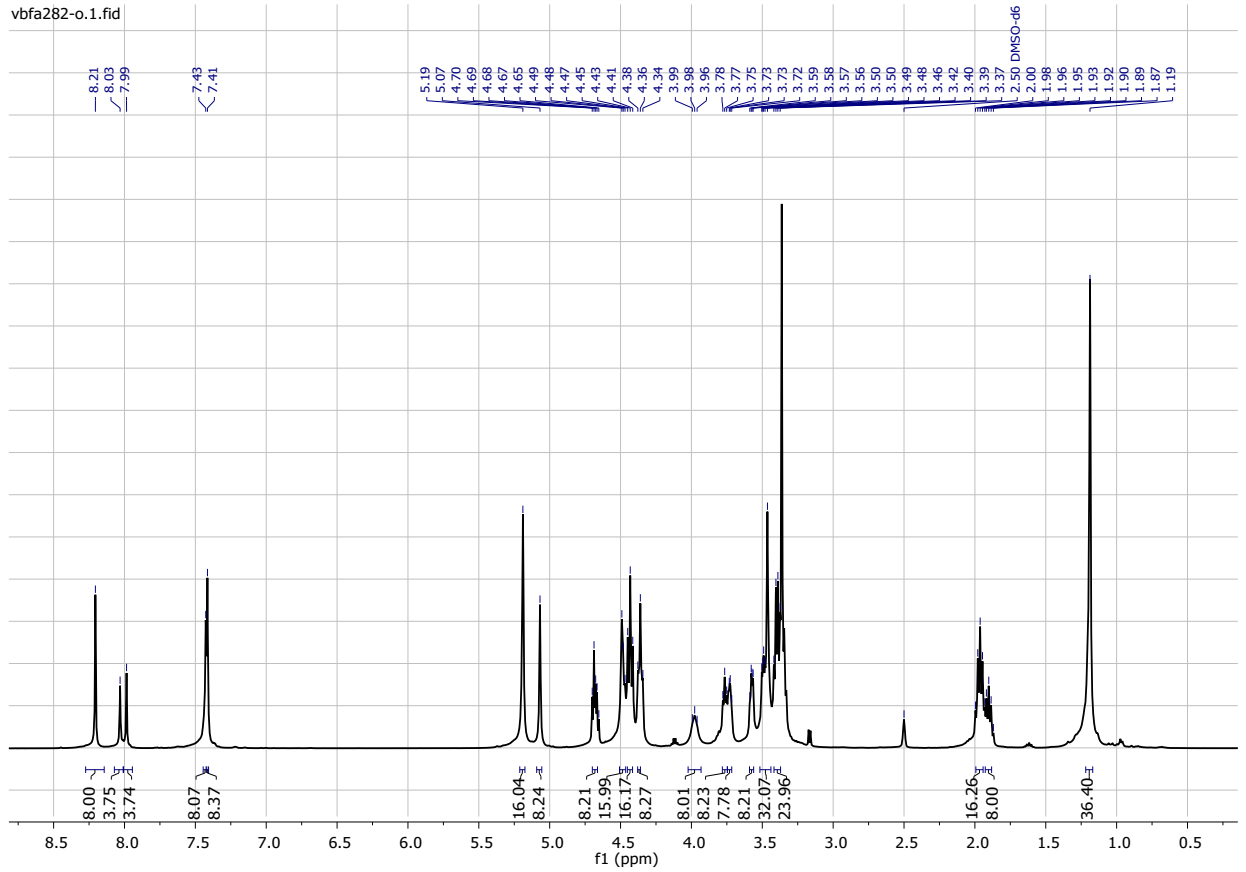
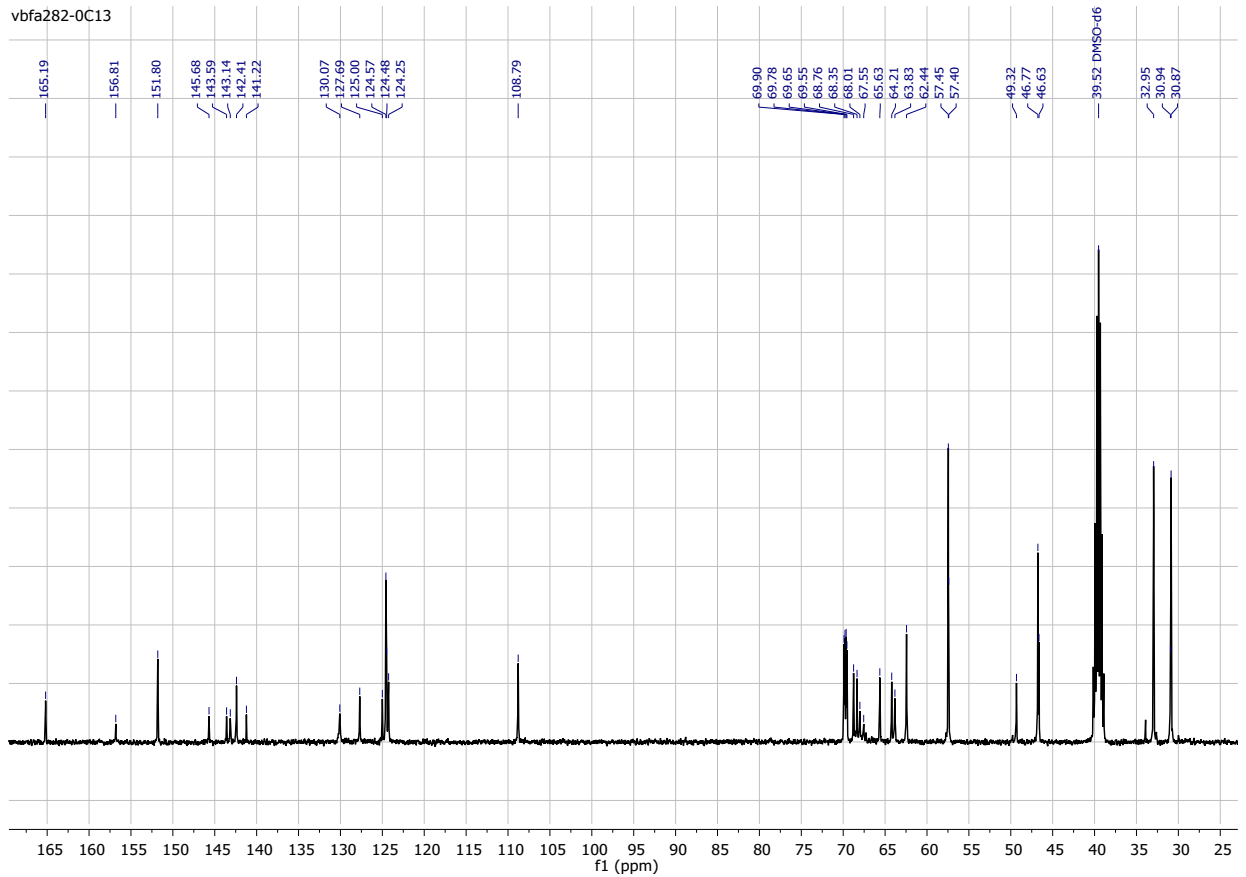Figure S7. NMR ^{1}H (a), ^{13}C (b), and HRESI MS (c), FT IR (d) spectra of *compound (15)*

(a)

vbfa290_3

8.23
8.05
7.98
7.40
7.34
7.31
5.19
5.09
4.67
4.43
4.36
3.89
3.72
3.56
3.45
3.35
3.01
2.50 DMSO-d6
1.95
1.20
0.82

4.05
2.03
2.11
4.01
3.68
3.86
8.19
4.22
4.36
20.40
4.07
8.31
31.73
4.15
8.05
4.14
100.47
6.01

9.0   8.5   8.0   7.5   7.0   6.5   6.0   5.5   5.0   4.5   4.0   3.5   3.0   2.5   2.0   1.5   1.0   0.5
f1 (ppm)

(b)

vbfa290_5-13C

165.38
157.38
156.72
152.06
146.06
145.81
145.71
142.03
134.71
132.03
129.18
129.14
128.63
128.56
128.24
127.48
125.90
125.87
109.85
70.81
69.31
68.80
66.53
64.72
64.54
63.65
60.36
60.32
58.29
50.24
47.41
34.46
34.33
32.46
32.07
31.55
31.45
30.90
30.06
29.82
29.51
29.12
25.94
22.82
14.23

170   160   150   140   130   120   110   100   90   80   70   60   50   40   30   20   10   0
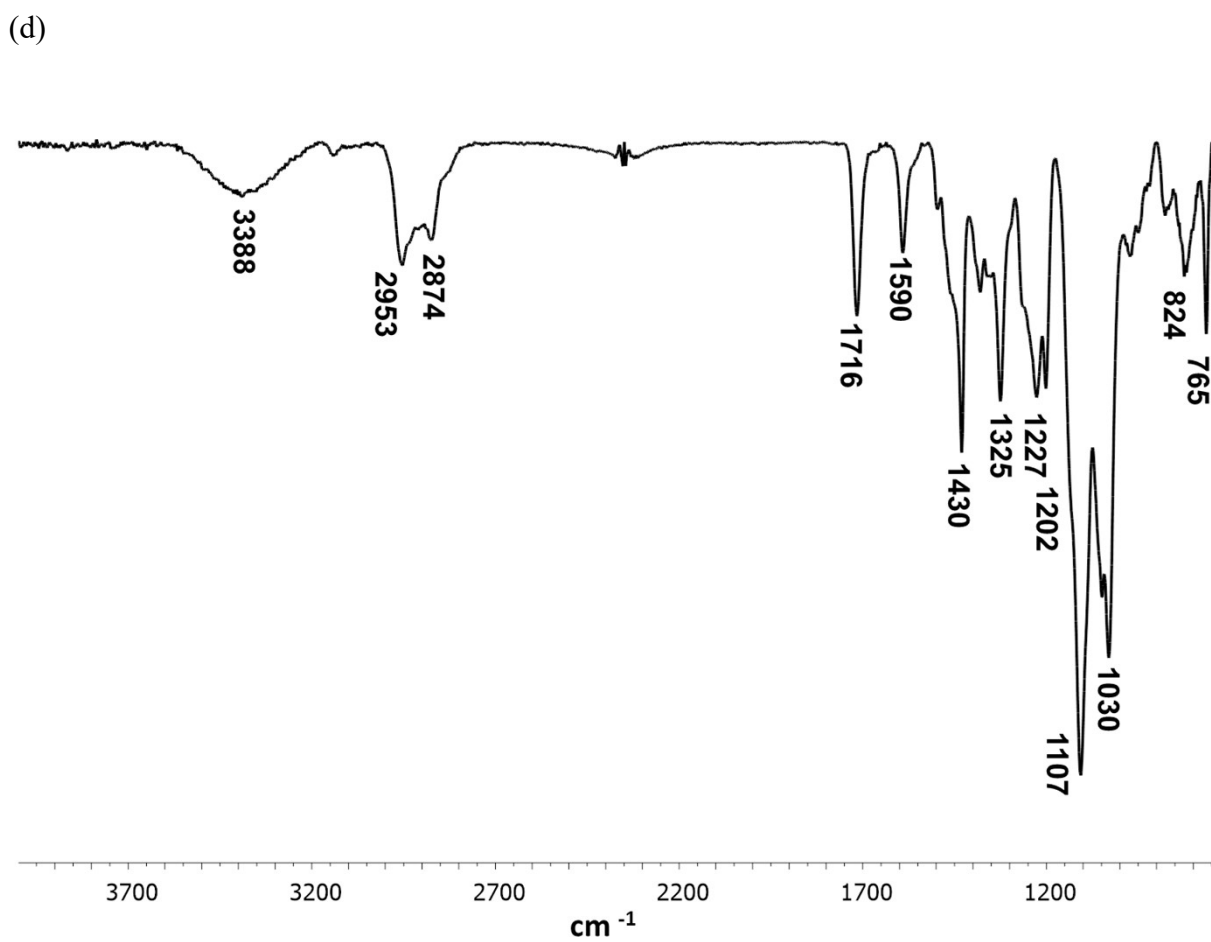f1 (ppm)

(c)

(d)

Figure S8. NMR ^{1}H (a), ^{13}C (b), and HRESI MS (c), FT IR (d) spectra of *compound (16)*

vbfa282-o.1.fid

vbfa282-0C13

(c)

(d)
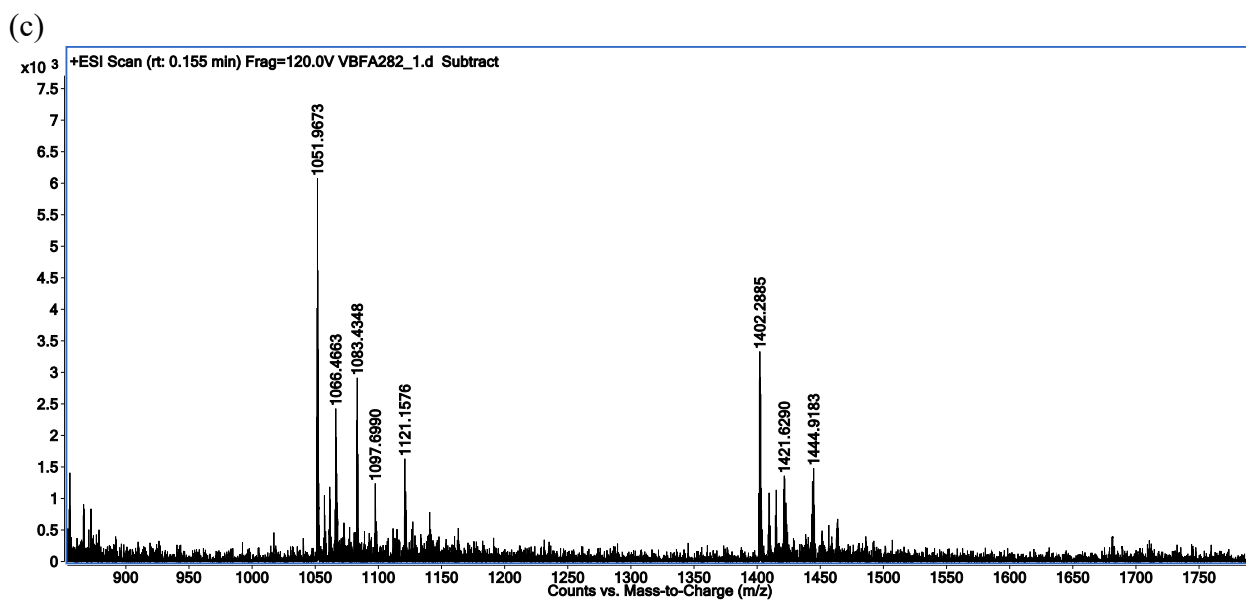
Figure S9. NMR ^{1}H (a), ^{13}C (b), and HRESI MS (c), FT IR (d) spectra of *compound (17)*

Figure S10. NMR ¹H of *compound 10a* (a) and of *mixture 10a, b* (b) (DMSO$_{d6}$, 400 MHz, 25 °C)
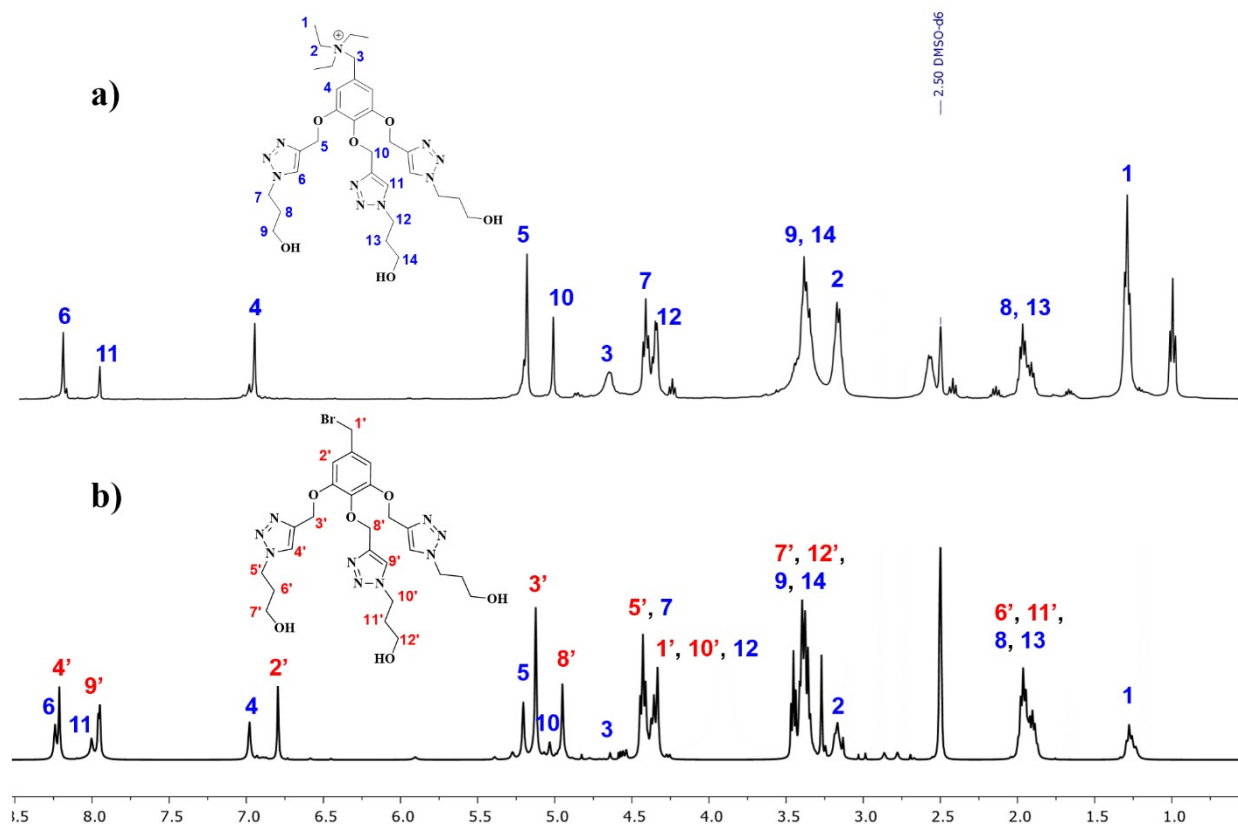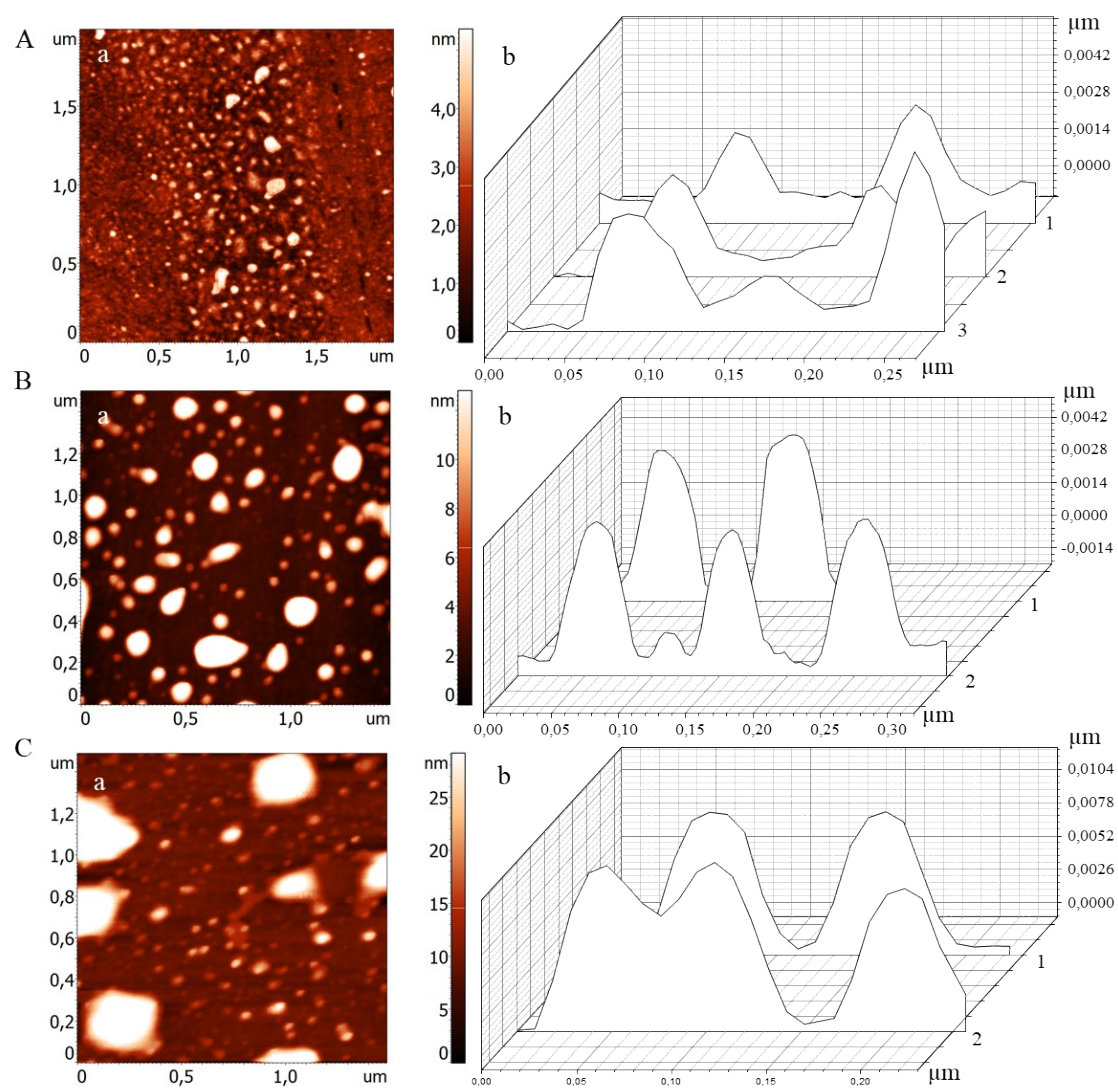
Figure S11 AFM evaluation of the dendrimers: A) **15**, B) **16**, C) **17**, where (a) AFM images and (b) cross-section view of dendrimers showing a diameters and heights; C(macrocycles) = 0.1 mM in 5% THF – water

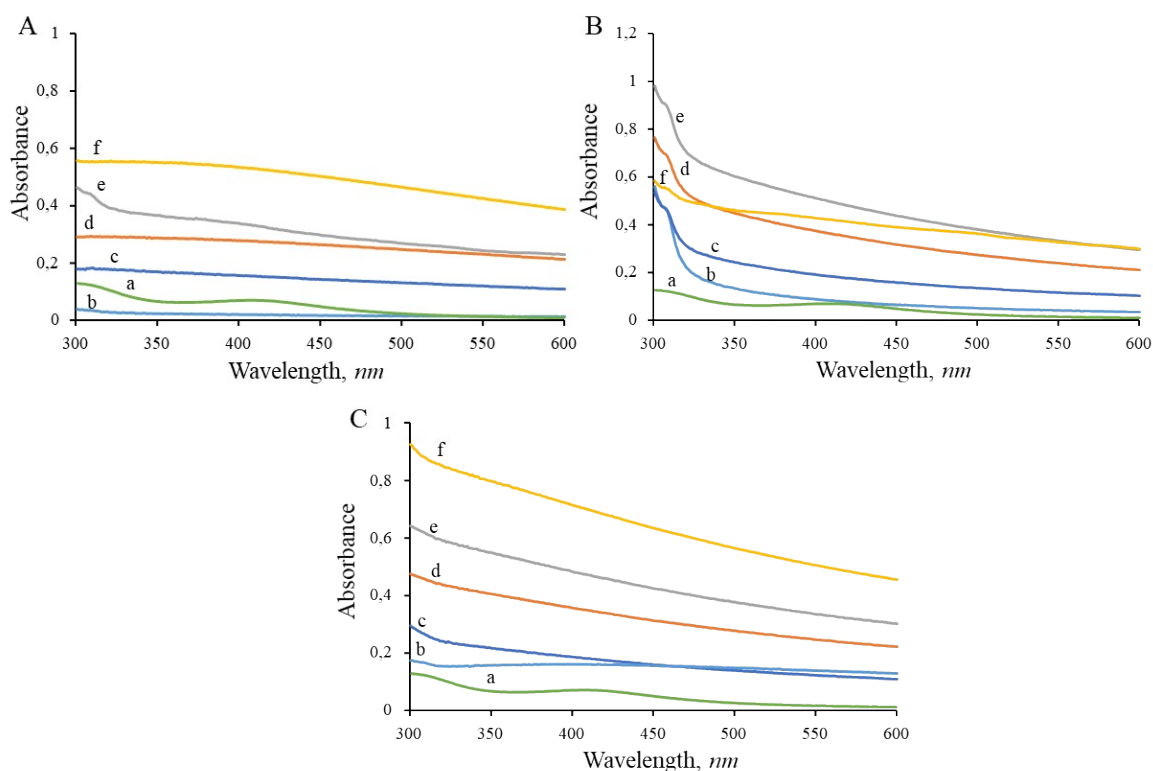Figure S12 UV-Vis spectra of $PdCl_4^{2-}$, dendrimer and double $PdCl_4^{2-}$ -dendrimer systems for A) **15**, B) **16** and C) **17**, where (a) $PdCl_4^{2-}$ (0.2 mM), (b) dendrimer (0.1 mM) and dendrimer (0.1 mM) in the presence of different amounts of palladium after reduction during 1 hour (0.1 mM) (c) 0.05mM, (d) 0.1 mM, (e) 0.15 mM, (f) 0.2 mM; water with 5% THF, l = 1 cm^{-1}.
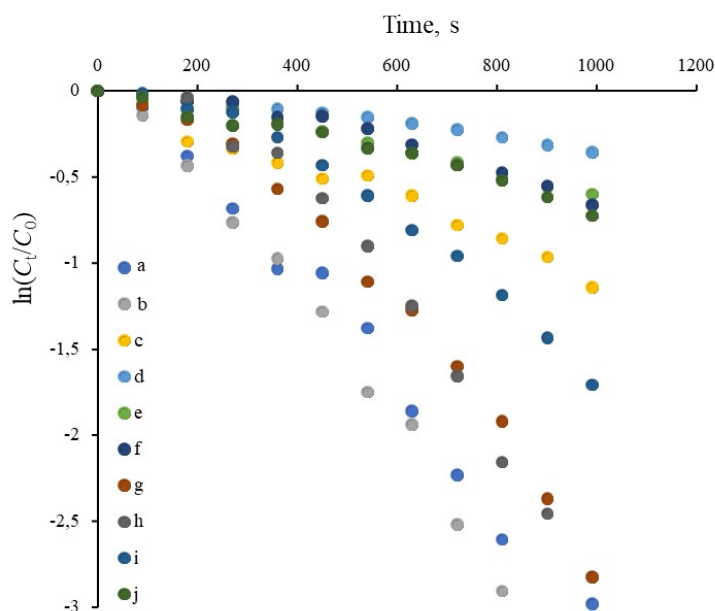

Figure S13 Plots of $\ln(C_t/C_0)$ *vs* time in the presence of (a) 0.5Pd&**15**, (b) 1.5Pd&**15**, (c) 2Pd&**15**; (d) 0.5Pd&**17**; (e) 1Pd&**17**; (f) 1.5Pd&**17** (g) 0.5Pd&**16** (h) 1Pd&**16** (i) 1.5Pd&**16** (j) Pd^0; (C(*p*-nitrophenol) = 0.1 mM, C(NaBH$_4$) = 5 mM, n(Pd) in metal-dendrimer = 5 nanomole, 5 % THF - water, 20 ºC, l = 1 cm.