Chemical Communications

Host–Guest Association Prior to Threading in the Formation of Pseudorotaxanes from Bis(dialkylammonium ion)s and a Molecular Cage

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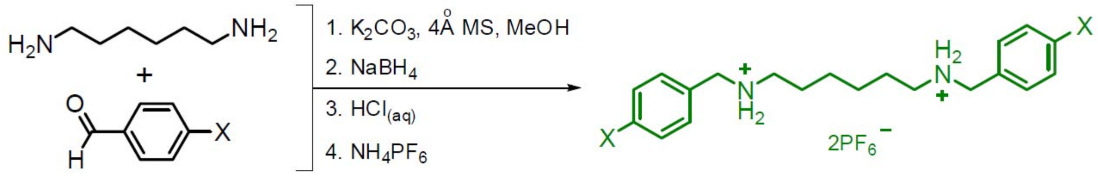
SUPPORTING INFORMATION

Experimental Section

General synthetic procedure for the threadlike salts [**2**–**6**-H_2][2PF_6]



Scheme S1. Synthesis of the threadlike salts [**2**–**6**-H_2][2PF_6].

4-Å Molecular sieves (0.3 g $mmol^{-1}$ of diamine), K_2CO_3 (2.4 equiv), and the pertinent para-substituted benzaldehyde (2.1 equiv) were added to a solution of 1,6-diaminohexane (0.1 M) in MeOH. The mixture was heated under reflux for 16 h, before being cooled to room temperature and filtered. $NaBH_4$ (5 equiv) was added to the filtrate and then the mixture was heated under reflux for 6 h. After concentration, the residue was taken up in CH_2Cl_2 (100 mL) and washed with water (2 × 50 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was dissolved in MeOH (15 mL) and the solution acidified using 6 N $HCl_{(aq)}$. The white precipitate was filtered, washed with CH_2Cl_2 (10 mL), dissolved in MeOH (15 mL), and treated with saturated $NH_4PF_{6(aq)}$ (20 mL). The organic solvent was evaporated under reduced pressure; the precipitate was filtered, washed with water (5 mL), and dried.

[**2**-H_2][2PF_6]: 22 %; mp 260 °C (dec); ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ =1.31–1.37 (m, 4H), 1.59–1.67 (m, 4H), 3.00 (t, *J* = 8 Hz, 4H), 4.13 (s, 4H), 7.38 (d, *J* = 8 Hz, 4H), 7.64 (d, *J* = 8 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): δ = 26.8, 49.2, 52.3, 125.0, 131.3, 133.6, 133.7 (one aliphatic carbon signal was missing possibly because of signals overlapping); HRMS (ESI): *m/z* calcd for [**2**-H_2][PF_6]$^+$ $C_{20}H_{28}Br_2F_6N_2P^+$ 599.0261, found *m/z* 599.0295.

[**3**-H_2][2PF_6]: 80 %; mp 237–239 °C; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ = 1.31–1.38 (m, 4H), 1.58–1.68 (m, 4H), 2.36 (s, 6H), 2.99 (t, *J* = 8 Hz, 4H), 4.10 (s, 4H), 7.27 (d, *J* = 8 Hz, 4H), 7.33 (d, *J* = 8 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): δ =21.3, 26.3, 26.4, 48.7, 52.4, 128.6, 130.7, 131.1, 141.0; HRMS (ESI): *m/z* calcd for [**3**-H_2][PF_6]$^+$ $C_{22}H_{34}F_6N_2P^+$ 471.2364, found *m/z* 471.2391.

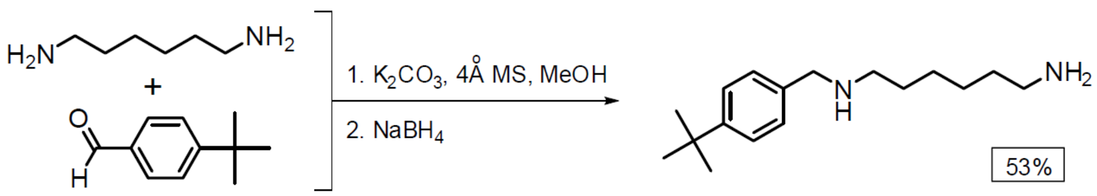
[**4**-H_2][2PF_6]: 60 %; mp 240–241 °C; ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ =

1.29–1.42 (m, 4H), 1.58–1.70 (m, 4H), 2.98 (t, J = 7 Hz, 4H), 3.81 (s, 6H), 4.09 (s, 4H), 6.44–6.81 (br, 4H), 6.98 (d, J = 9 Hz, 4H), 7.37 (d, J = 9 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): δ = 26.7, 26.7, 48.8, 52.5, 56.4, 115.6, 123.5, 132.9, 161.8; HRMS (ESI): *m/z* calcd for [**4**-H_2][PF_6]$^+$ $C_{22}H_{34}F_6N_2O_2P^+$ 503.2262, found *m/z* 503.2288.

[**5**-H_2][2PF_6]: 64 %; mp 250 °C (dec); ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ = 1.31–1.37 (m, 4H), 1.58–1.67 (m, 4H), 2.96–3.05 (m, 4H), 4.15 (t, J = 6 Hz, 4H), 6.55–6.86 (br, 4H), 7.22 (dd, J = 9, 9 Hz, 4H), 7.50 (dd, J = 6, 9 Hz, 4H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): δ = 26.8, 26.8, 49.2, 52.3, 117.4 ($^3J_{CF}$ = 22 Hz), 128.2 ($^4J_{CF}$ = 3 Hz), 134.0 ($^2J_{CF}$ = 9 Hz), 164.9 ($^1J_{CF}$ = 246 Hz); HRMS (ESI): *m/z* calcd for [**5**-H_2][PF_6]$^+$ $C_{20}H_{28}F_8N_2P^+$ 479.1862, found *m/z* 479.1844.

[**6**-H_2][2PF_6]: 6 %; mp 257 °C (dec); ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ = 1.28–1.43 (m, 4H), 1.57–1.72 (m, 4H), 3.00 (t, J = 8 Hz, 4H), 4.15 (s, 4H), 7.40–7.57 (m, 10H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): δ = 26.8, 26.8, 49.2, 53.1, 130.6, 131.2, 131.5, 132.1; HRMS (ESI): *m/z* calcd for [**6**-H_2][PF_6]$^+$ $C_{20}H_{30}F_6N_2P^+$ 443.2045, found *m/z* 443.2050.

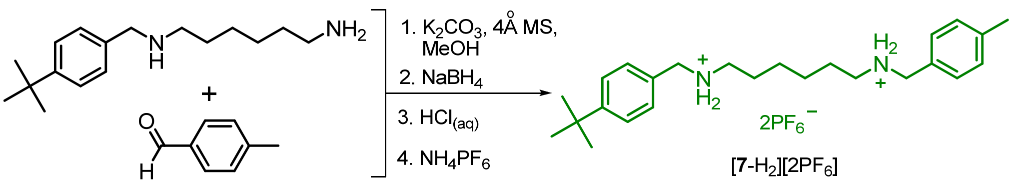
N-(4-*tert*-Butylbenzyl)-1,6-diaminohexane (**S1**)



Scheme S2. Synthesis of *N*-(4-*tert*-butylbenzyl)-1,6-diaminohexane

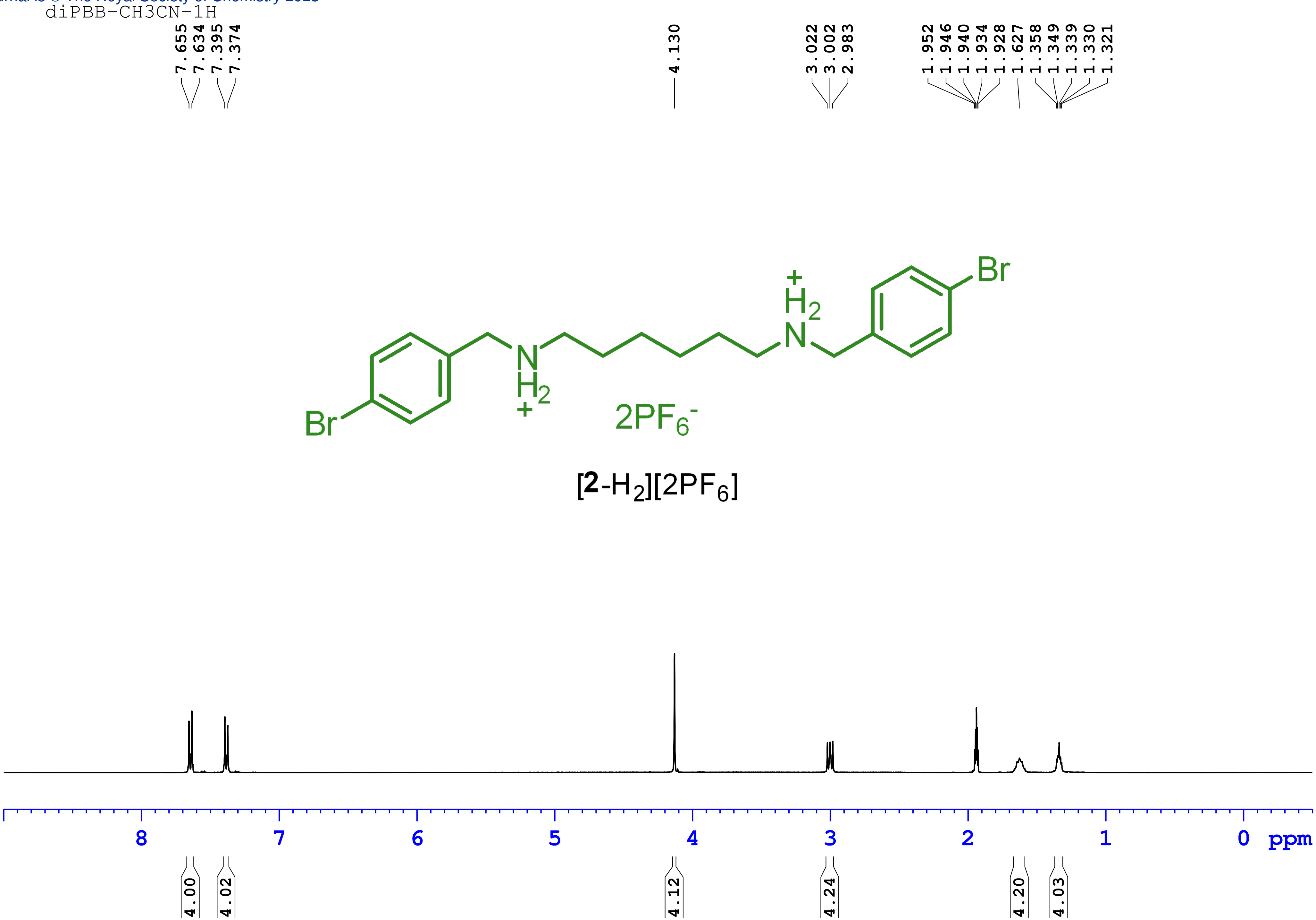
4-Å Molecular sieves (0.3 g), K_2CO_3 (0.3 g), and 4-*tert*-butylbenzaldehyde (0.14 g, 0.9 mmol) were added to a solution of 1,6-diaminohexane (0.50 g, 4.3 mmol) in MeOH (50 mL) and the mixture was heated under reflux for 16 h, before being cooled to room temperature and filtered. $NaBH_4$ (43 mg, 1.12 mmol) was added to the filtrate and then the mixture was heated under reflux for 6 h. After concentration, the residue was partitioned between CH_2Cl_2 (30 mL) and water (100 mL) and then the aqueous layer was extracted with CH_2Cl_2 (2 × 30 mL). The combined organic phases were dried ($MgSO_4$) and concentrated. The residue was purified chromatographically (SiO_2; MeOH/CH_2Cl_2, 5:95 to 10:90) to afford a yellow liquid (0.12 g, 53%); ^{1}H NMR (400 MHz, $CDCl_3$, 298 K): δ 1.09–1.67 (m, 17H), 2.62 (t, J = 7 Hz, 2H), 2.66 (t, J = 7 Hz, 2H), 3.73 (s, 2H), 7.22 (d, J = 8 Hz, 2H), 7.32 (d, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, 298 K): δ 26.8, 27.2, 30.0, 31.4, 33.7, 34.4, 42.1, 49.5, 53.7, 125.3, 127.8, 137.4, 149.8; HRMS (ESI): calcd for [**S1** + H]$^+$ $C_{17}H_{31}N_2^+$ m/z 263.2487, found m/z 263.2466.

The synthesis of threadlike salt [**7**-H_2][2PF_6]

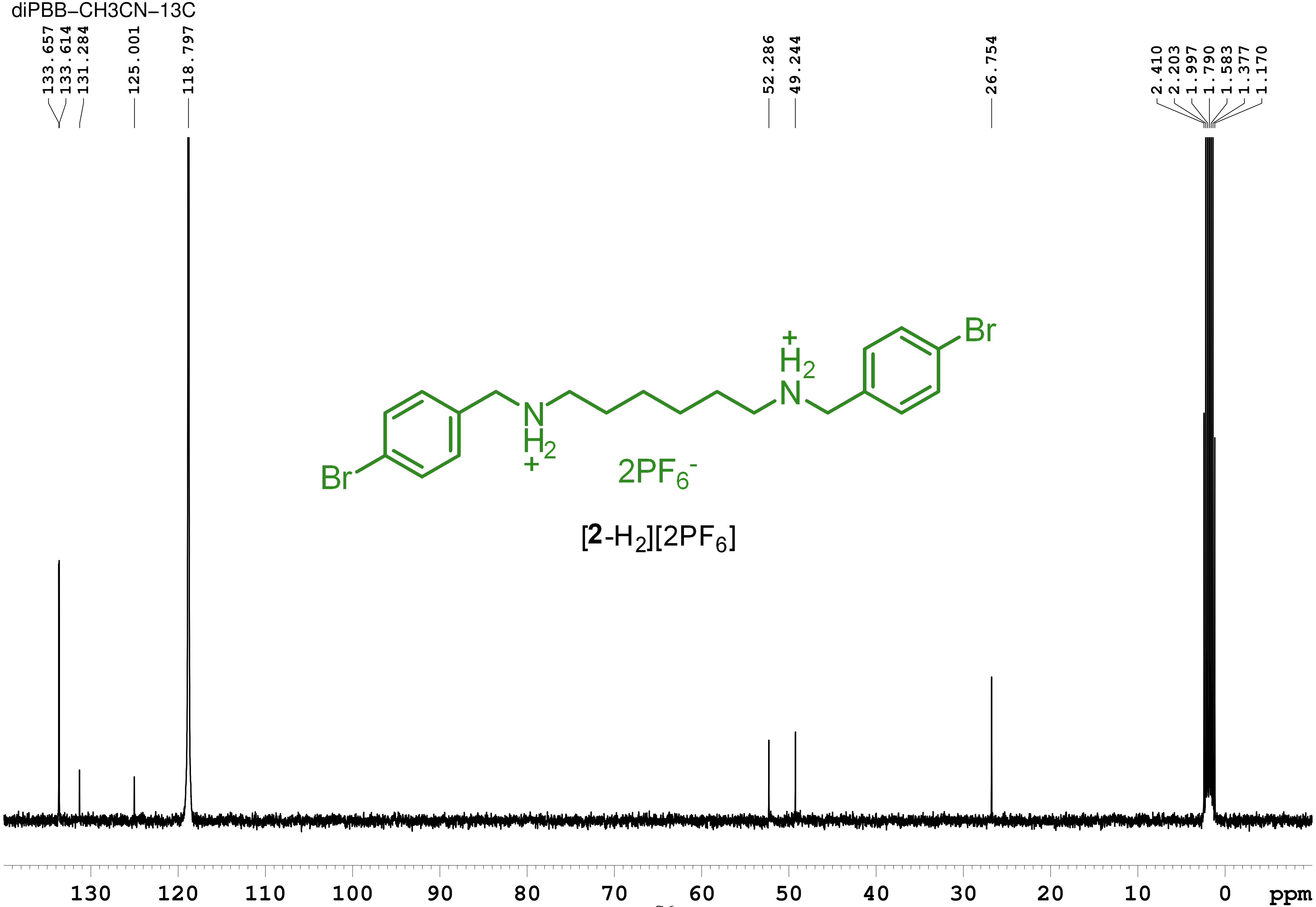


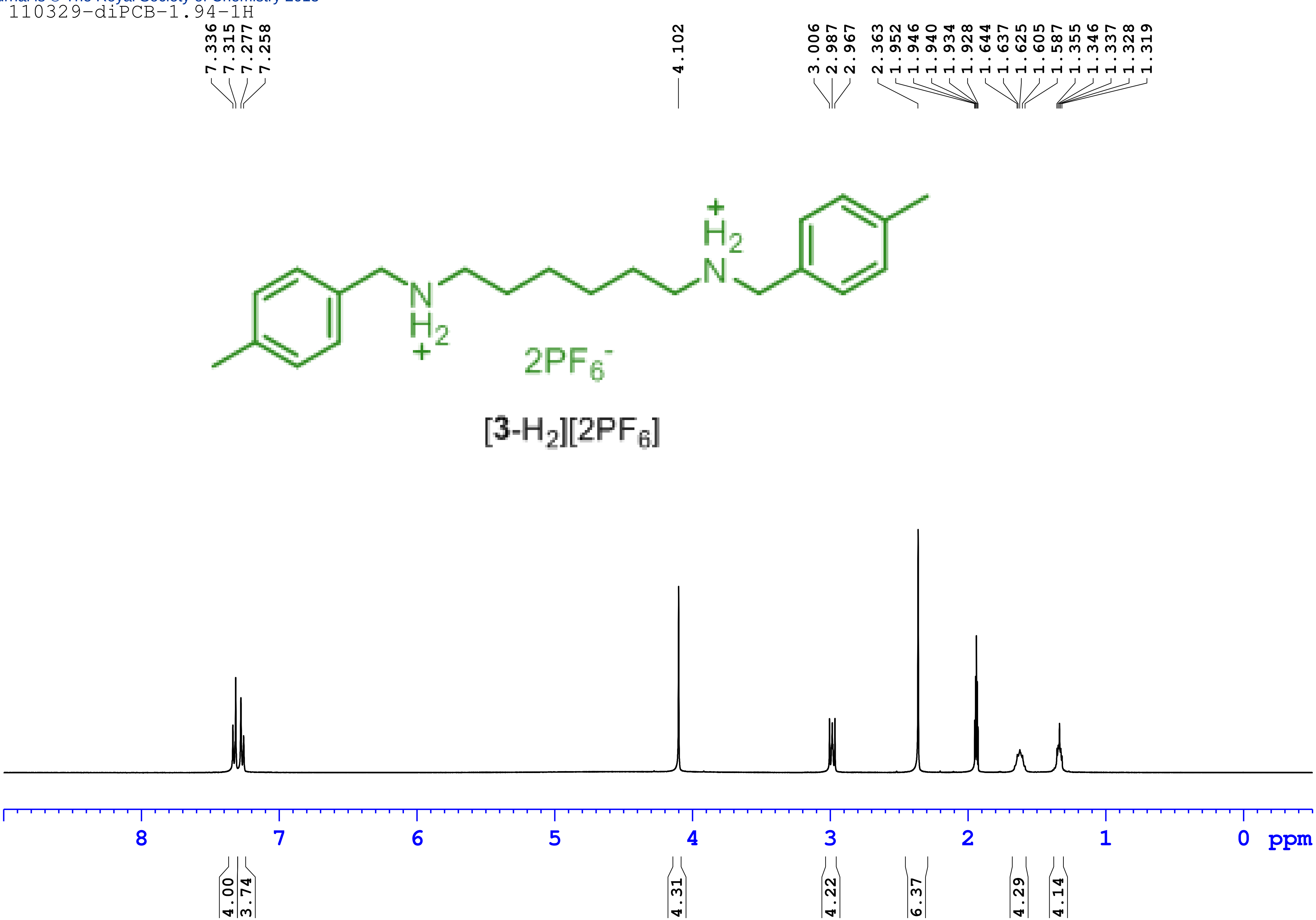
Scheme S4. Synthesis of [**7**-H_2][2PF_6]

4-Å Molecular sieves (0.21 g), K_2CO_3 (0.21 g), and 4-methylbenzaldehyde (0.09 g, 0.8 mmol) were added to a solution of **S1** (0.18 g, 0.7 mmol) in MeOH (4 mL) and the mixture was heated under reflux for 16 h, before being cooled to room temperature and filtered. $NaBH_4$ (0.03 g, 0.8 mmol) was added to the filtrate and then the mixture was heated under reflux for 6 h. After concentration, the residue was taken up in CH_2Cl_2 (100 mL) and washed with water (2 × 50 mL). The organic phase was dried ($MgSO_4$) and concentrated. The residue was dissolved in MeOH (15 mL) and the solution acidified using 6N $HCl_{(aq)}$. The white precipitate was filtered, washed with CH_2Cl_2 (10 mL), dissolved in MeOH (15 mL), and treated with saturated $NH_4PF_{6(aq)}$ (20 mL). The organic solvent was evaporated under reduced pressure; the precipitate was filtered, washed with water (5 mL), and dried to afford thread [**7**-H_2][2PF_6] as a white solid (0.32 g, 70 %). mp 241 °C (dec); ^{1}H NMR (400 MHz, CD_3CN, 298 K): δ = 1.29–1.42 (m, 13H), 1.57–1.72 (m, 4H), 2.37 (s, 3H), 2.93–3.11 (m, 4H), 4.12 (s, 2H), 4.13 (s, 2H), 6.48–6.87 (br, 4H), 7.28 (d, J = 8 Hz, 2H), 7.35 (d, J = 8 Hz, 2H), 7.39 (d, J = 8 Hz, 2H), 7.52 (d, J = 8 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN, 298 K): δ =21.7, 26.7, 26.8, 31.9, 35.9, 49.1, 49.2, 52.7, 52.8, 127.5, 129.0, 129.0, 131.2, 131.3, 131.5, 141.5, 154.4 (two aliphatic signals are missing possibly because of signals overlapping); HRMS (ESI): m/z calcd for [**7**-H_2][PF_6]$^+$ $C_{25}H_{40}F_6N_2P^+$ 513.2833, found m/z 513.2869.


diPBB-CH3CN-1H
7.655
7.634
7.395
7.374
4.130
3.022
3.002
2.983
1.952
1.946
1.940
1.934
1.928
1.627
1.358
1.349
1.339
1.330
1.321
8
7
6
5
4
3
2
1
0
ppm
4.00
4.02
4.12
4.24
4.20
4.03
Br
H2
N
2PF6-
Br

[**2**-H_2][$2PF_6$]


diPBB–CH3CN–13C
133.657
133.614
131.284
125.001
118.797
52.286
49.244
26.754
2.410
2.203
1.997
1.790
1.583
1.377
1.170
Br
Br
N
H2
+
N
H2
+
2PF6-
[2-H2][2PF6]
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm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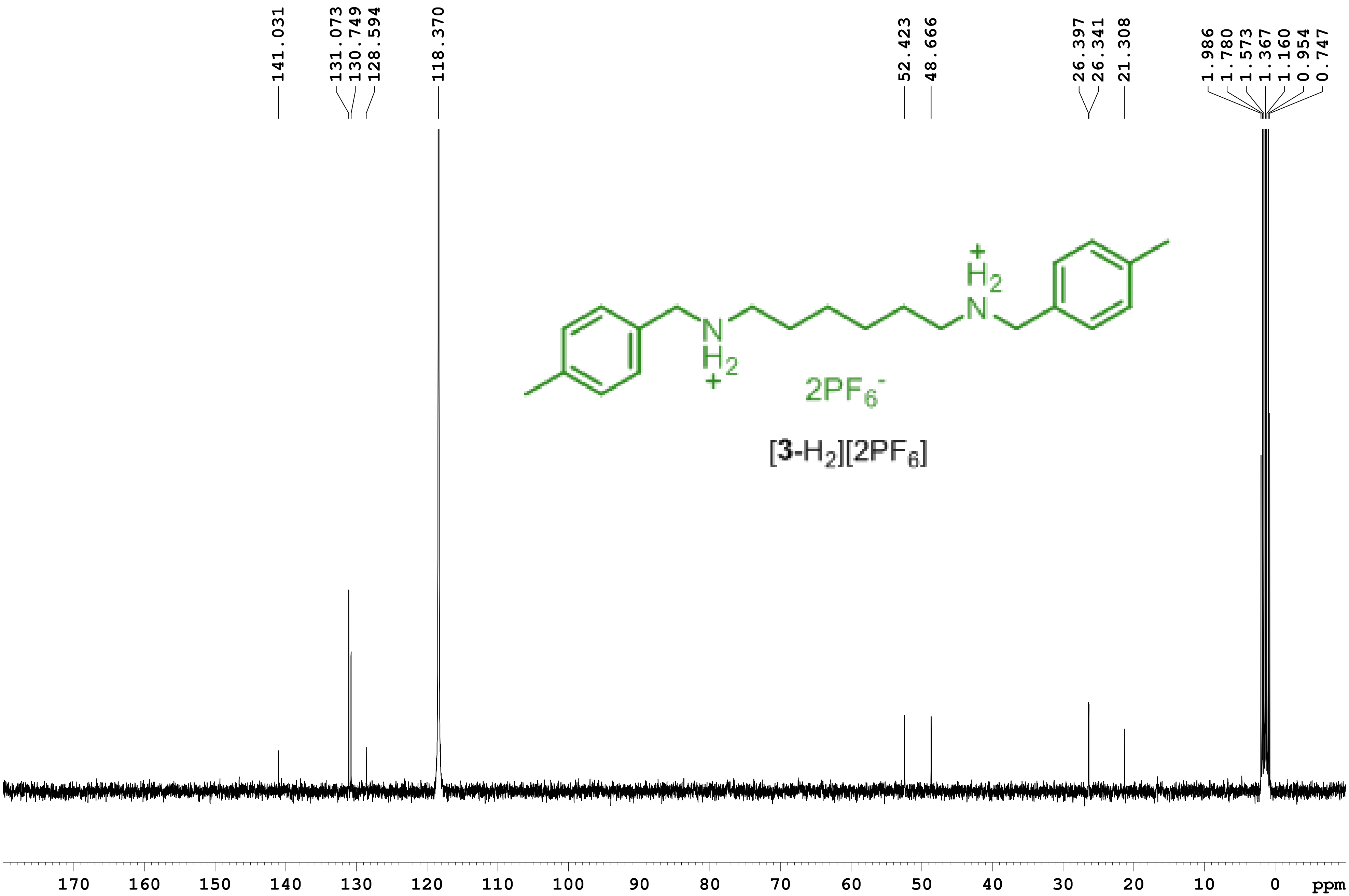
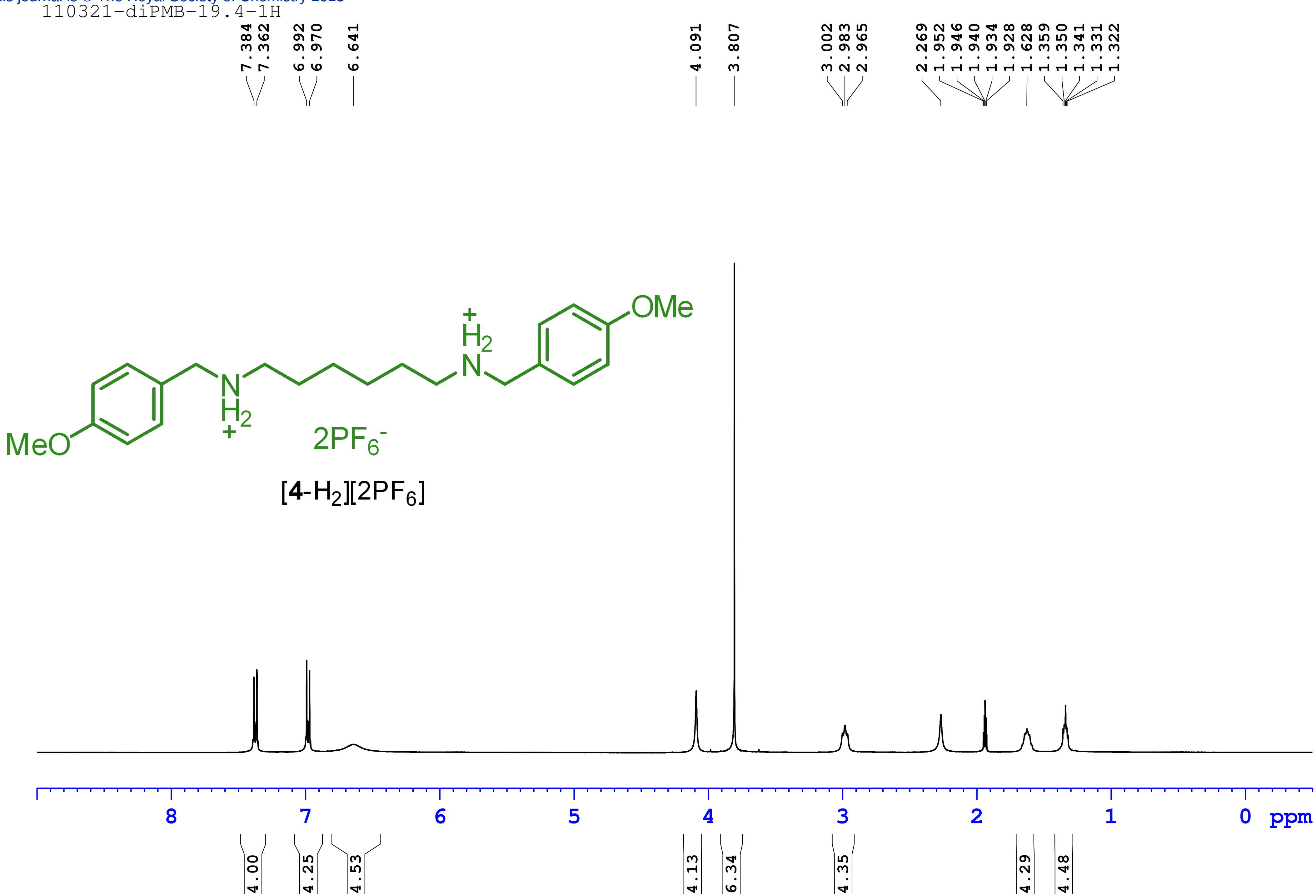
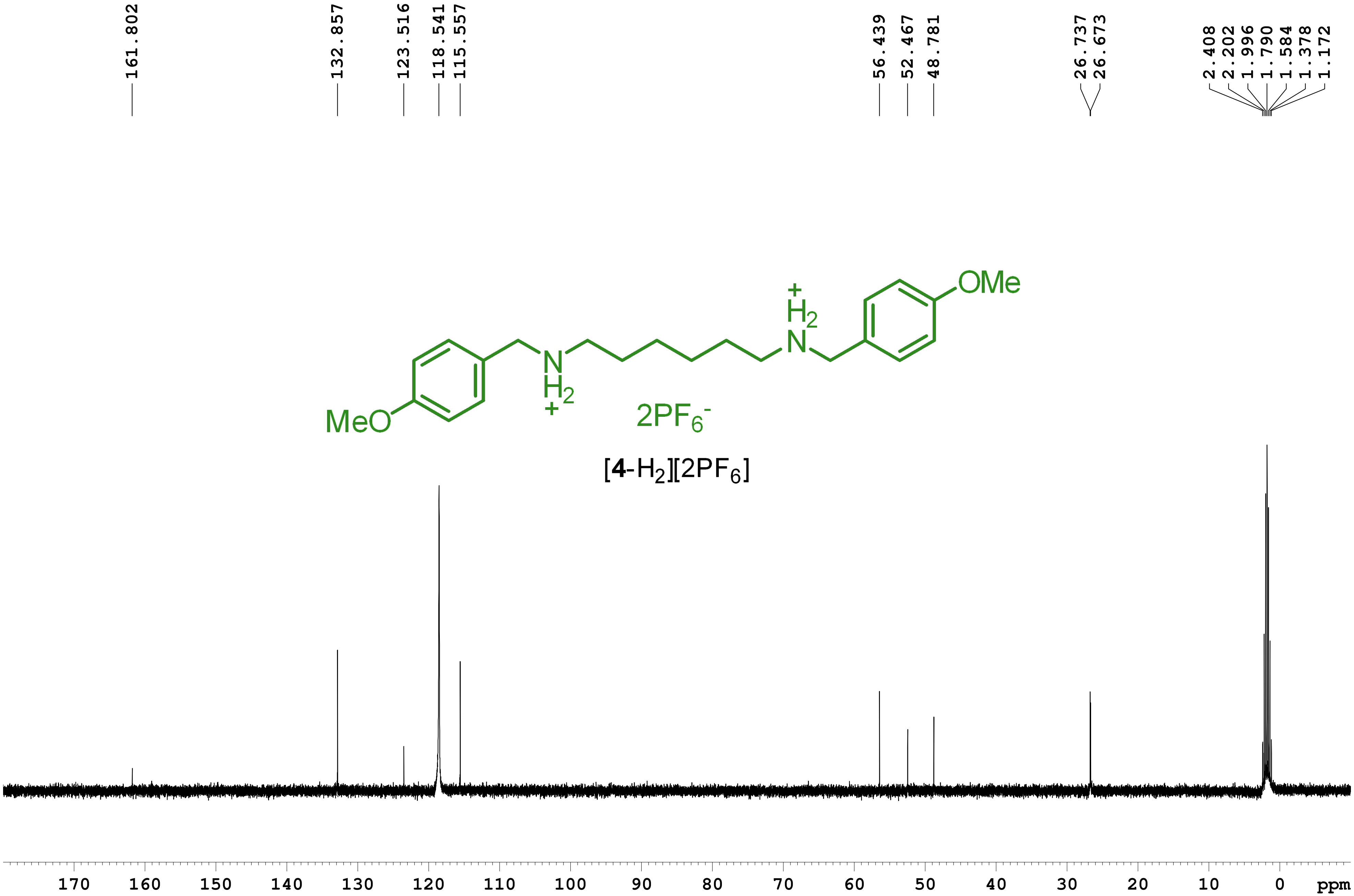
7.336
7.315
7.277
7.258
4.102
3.006
2.987
2.967
2.363
1.952
1.946
1.940
1.934
1.928
1.644
1.637
1.625
1.605
1.587
1.355
1.346
1.337
1.328
1.319
N
H2
+
2PF6-
[3-H2][2PF6]
8
7
6
5
4
3
2
1
0
ppm
4.00
3.74
4.31
4.22
6.37
4.29
4.14

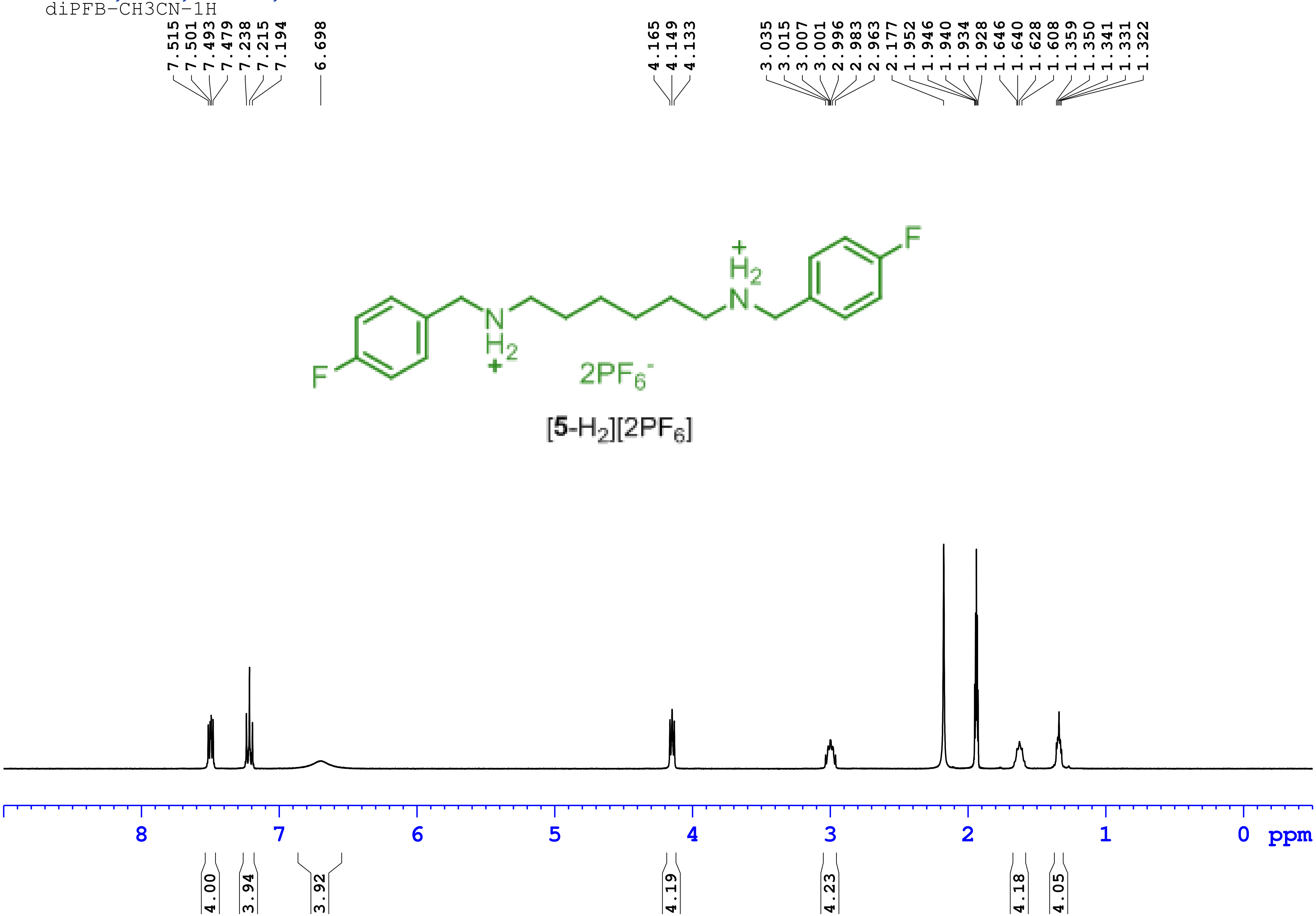
29–diPCB–1.94-

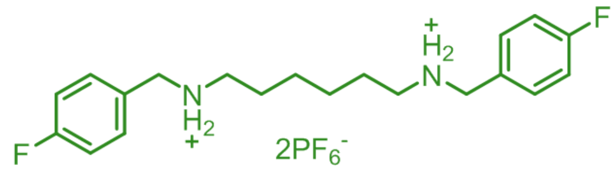

141.031
131.073
130.749
128.594
118.370
52.423
48.666
26.397
26.341
21.308
1.986
1.780
1.573
1.367
1.160
0.954
0.747
2PF6-
[3-H2][2PF6]
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


110321-diPMB-19.4-1H
7.384
7.362
6.992
6.970
6.641
4.091
3.807
3.002
2.983
2.965
2.269
1.952
1.946
1.940
1.934
1.928
1.628
1.359
1.350
1.341
1.331
1.322
OMe
MeO
2PF6-
[4-H2][2PF6]
8
7
6
5
4
3
2
1
0
ppm
4.00
4.25
4.53
4.13
6.34
4.35
4.29
4.48

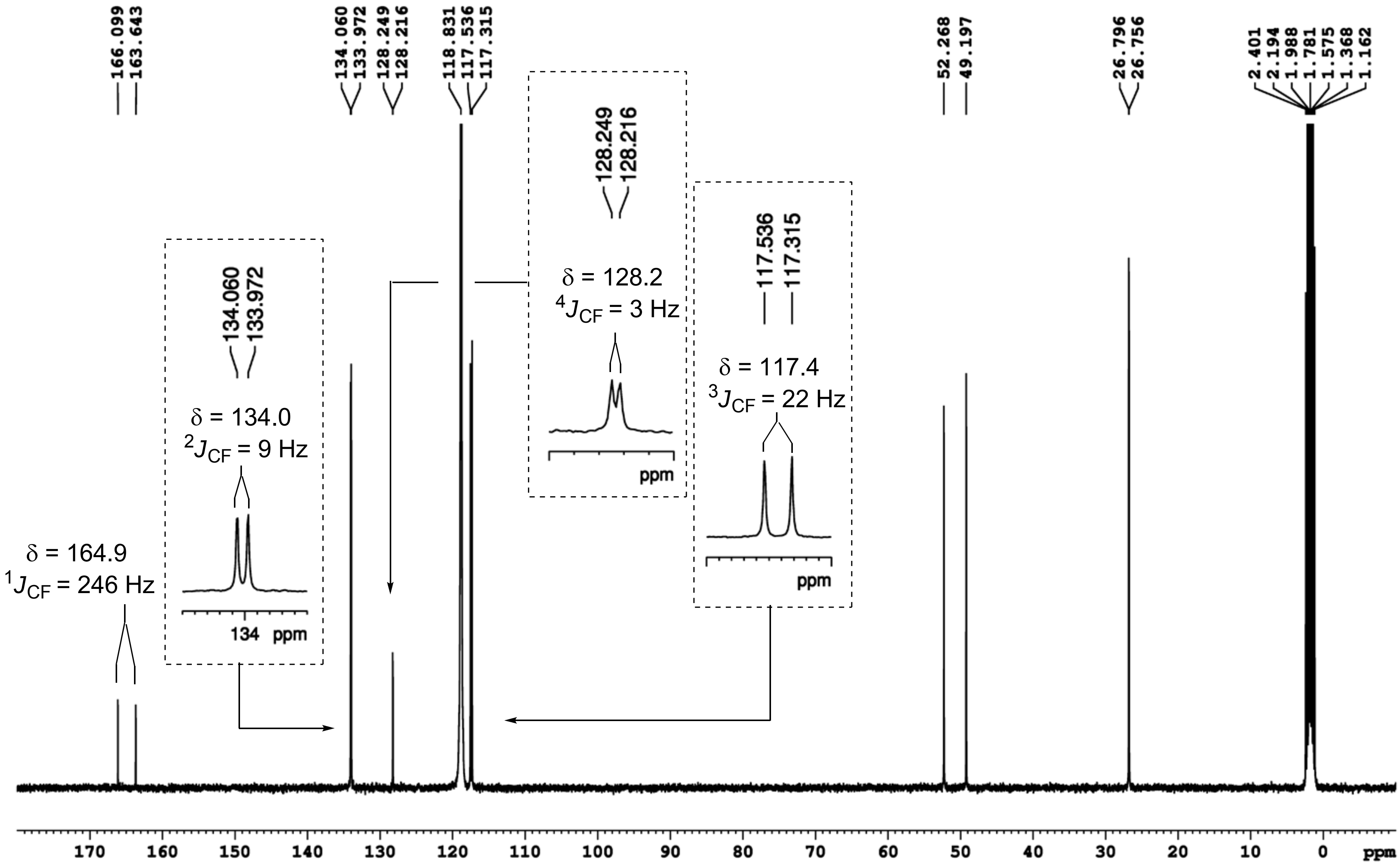
21–diPMB–1.94


161.802
132.857
123.516
118.541
115.557
56.439
52.467
48.781
26.737
26.673
2.408
2.202
1.996
1.790
1.584
1.378
1.172
OMe
MeO
2PF6-
[4-H2][2PF6]
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


diPFB-CH3CN-1H
7.515
7.501
7.493
7.479
7.238
7.215
7.194
6.698
4.165
4.149
4.133
3.035
3.015
3.007
3.001
2.996
2.983
2.963
2.177
1.952
1.946
1.940
1.934
1.928
1.646
1.640
1.628
1.608
1.359
1.350
1.341
1.331
1.322
$2PF_6^-$
$[\mathbf{5}\text{-}H_2][2PF_6]$
8
7
6
5
4
3
2
1
0
ppm
4.00
3.94
3.92
4.19
4.23
4.18
4.05


2PF6-

[5-H_2][2PF_6]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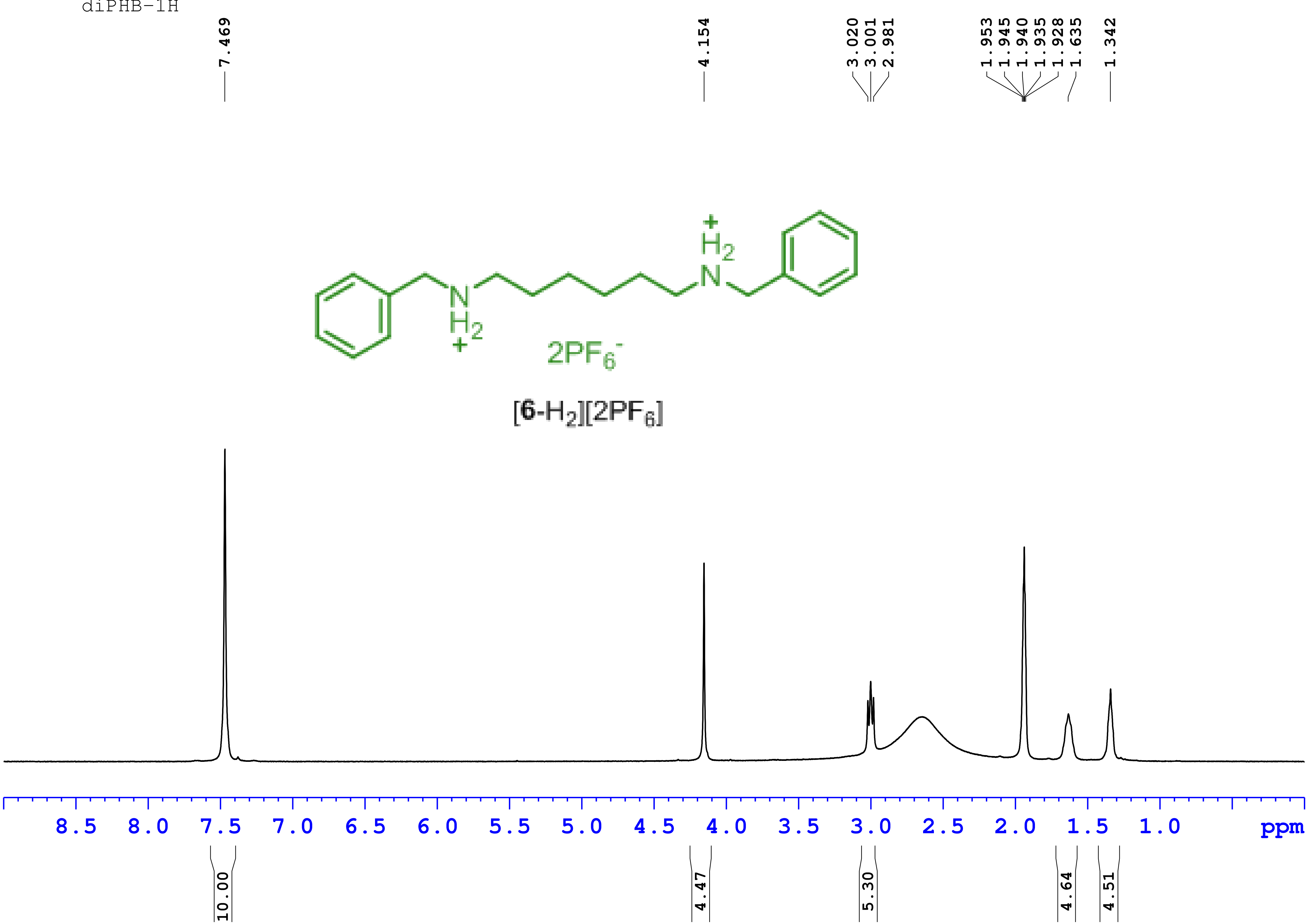
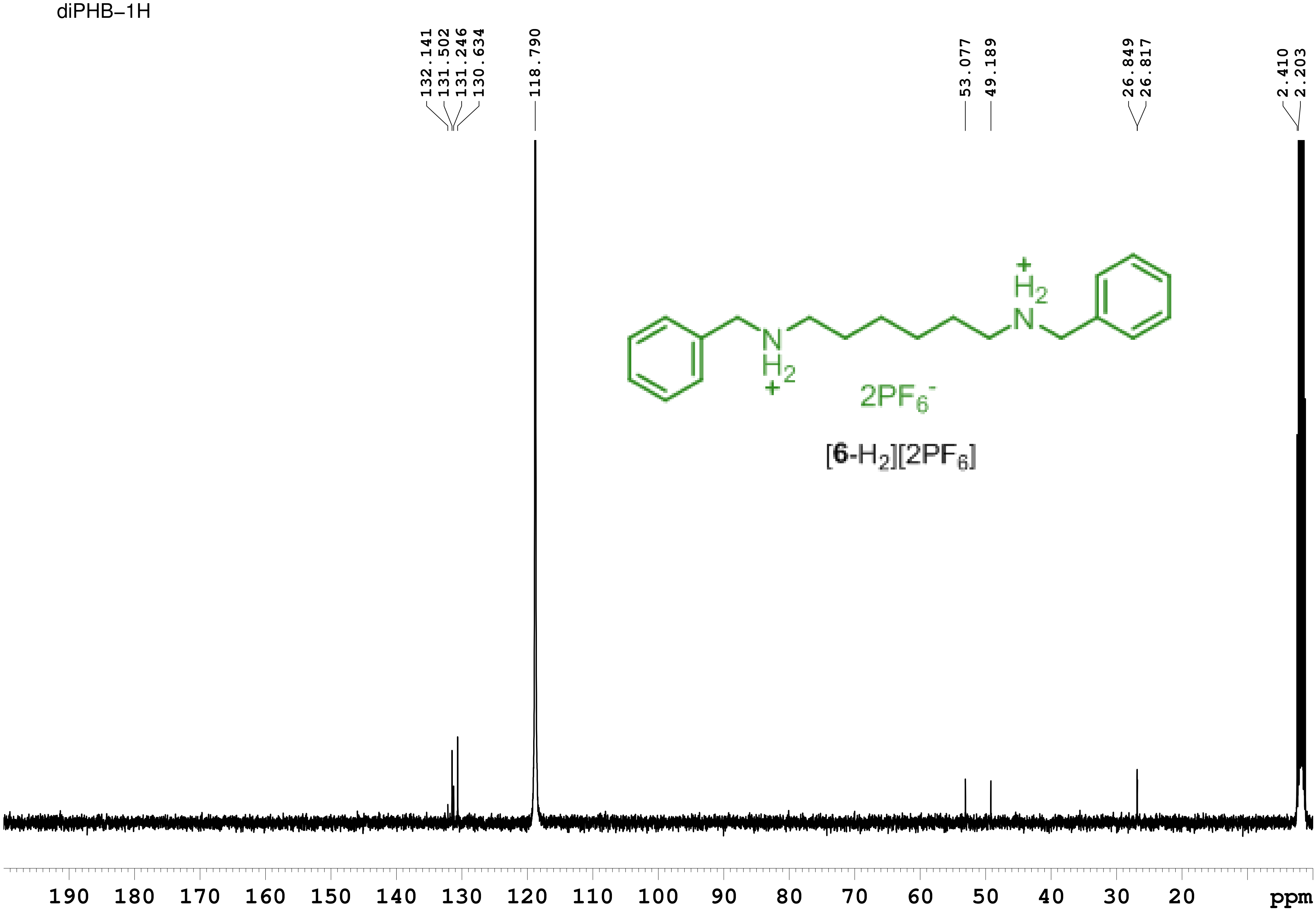
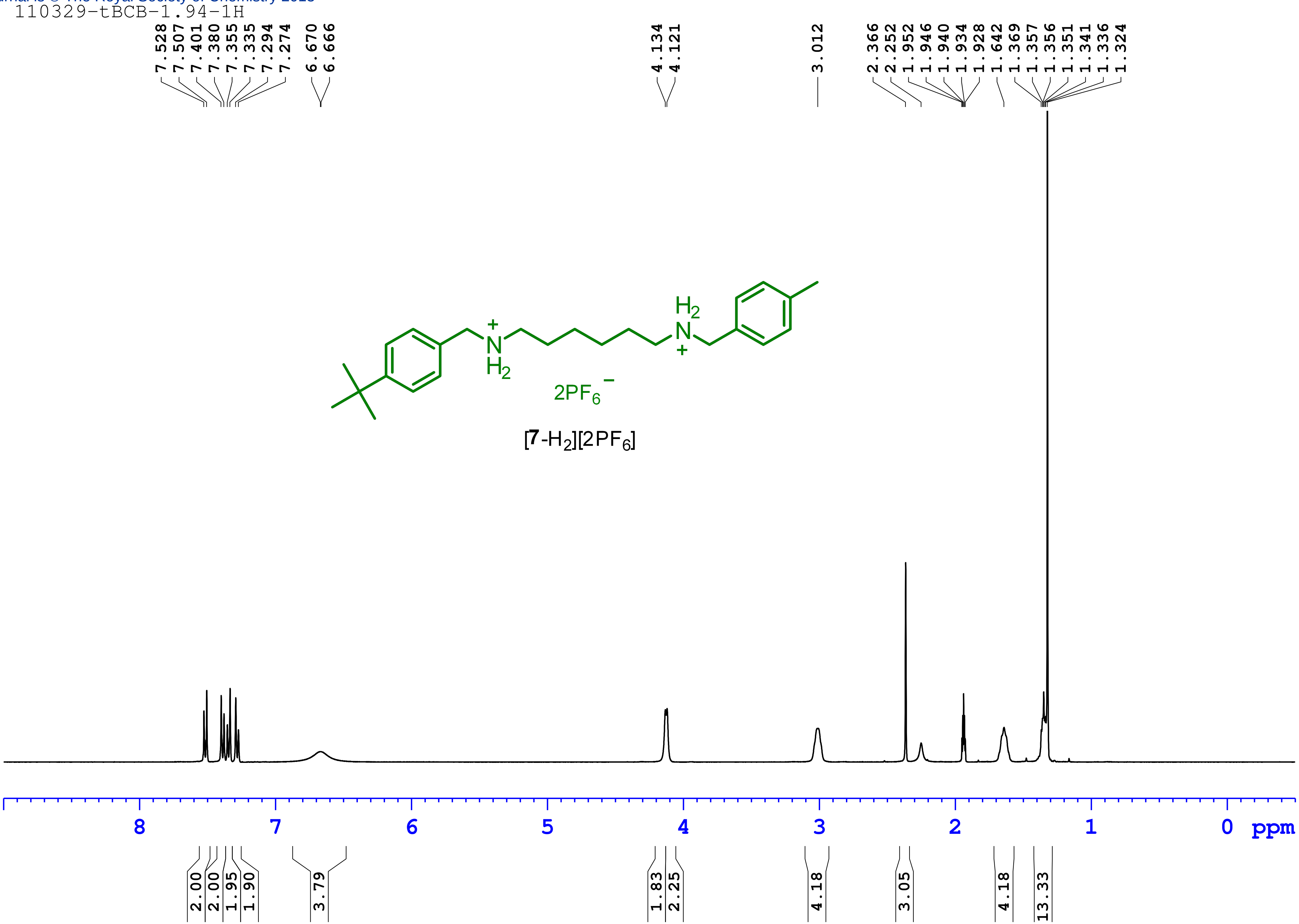
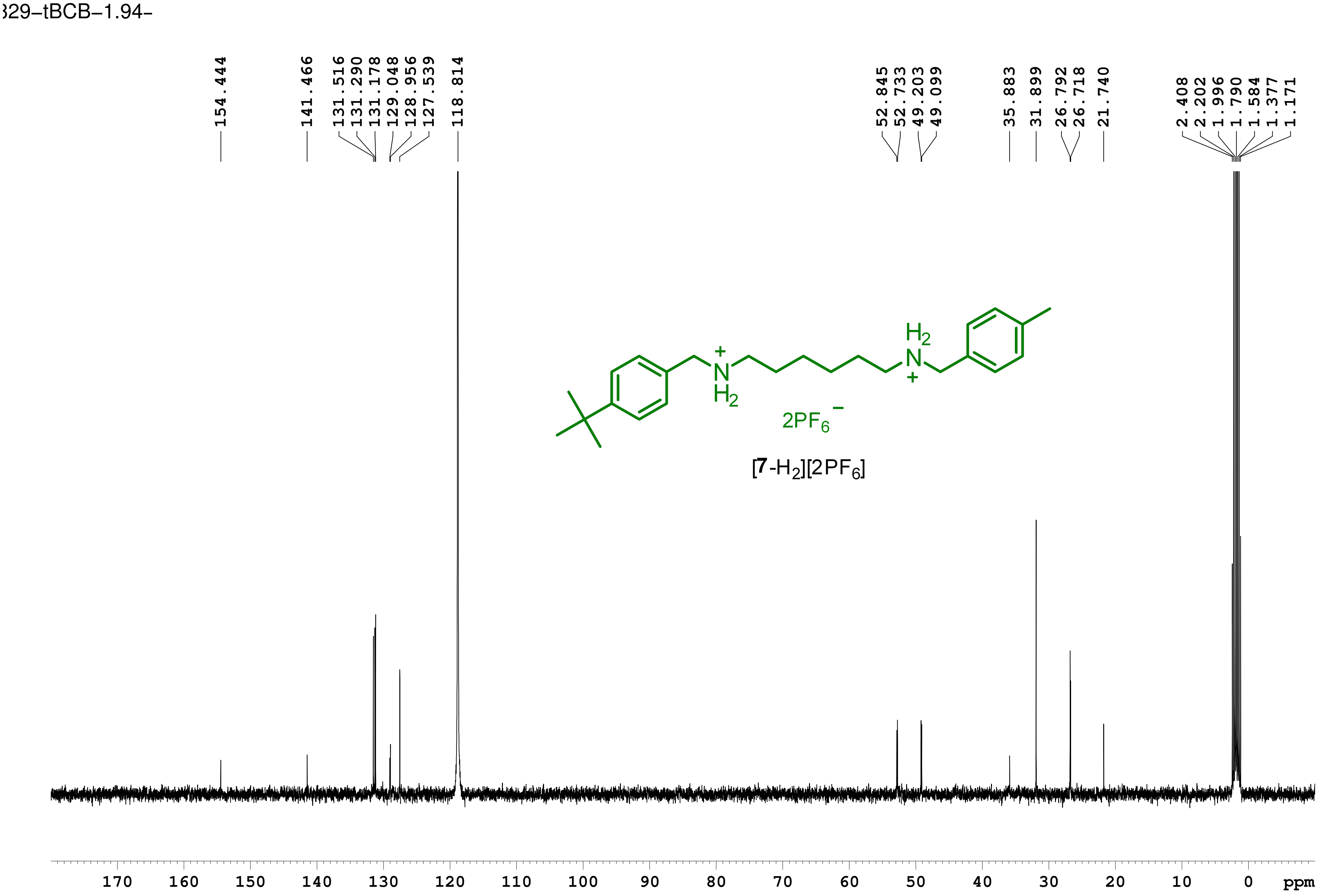
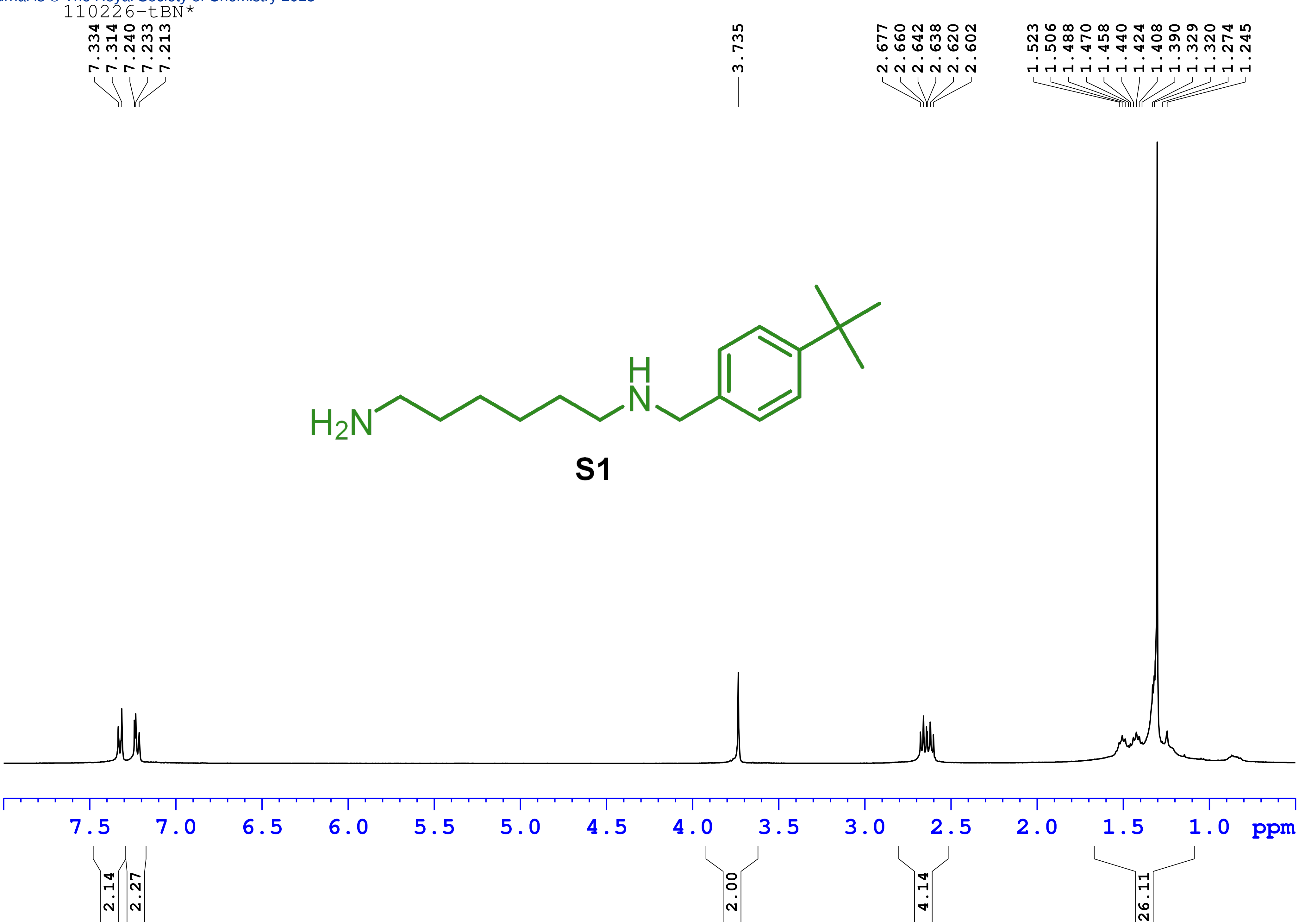
163.643
134.060
133.972
128.249
128.216
118.831
117.536
117.315
52.268
49.197
26.796
26.756
2.401
2.194
1.988
1.781
1.575
1.368
1.162
δ = 164.9
1JCF = 246 Hz
δ = 134.0
2JCF = 9 Hz
134 ppm
δ = 128.2
4JCF = 3 Hz
ppm
δ = 117.4
3JCF = 22 Hz
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm


diPHB-1H
7.469
4.154
3.020
3.001
2.981
1.953
1.945
1.940
1.935
1.928
1.635
1.342
2PF6-
[6-H2][2PF6]
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
ppm
10.00
4.47
5.30
4.64
4.51


diPHB–1H
132.141
131.502
131.246
130.634
118.790
53.077
49.189
26.849
26.817
2.410
2.203
2PF6-
[6-H2][2PF6]
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


110329-tBCB-1.94-1H
7.528
7.507
7.401
7.380
7.355
7.335
7.294
7.274
6.670
6.666
4.134
4.121
3.012
2.366
2.252
1.952
1.946
1.940
1.934
1.928
1.642
1.369
1.357
1.356
1.351
1.341
1.336
1.324
2PF6
[7-H2][2PF6]
8
7
6
5
4
3
2
1
0
ppm
2.00
2.00
1.95
1.90
3.79
1.83
2.25
4.18
3.05
4.18
13.33


329–tBCB–1.94–
154.444
141.466
131.516
131.290
131.178
129.048
128.956
127.539
118.814
52.845
52.733
49.203
49.099
35.883
31.899
26.792
26.718
21.740
2.408
2.202
1.996
1.790
1.584
1.377
1.171
2PF6−
[7-H2][2PF6]
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm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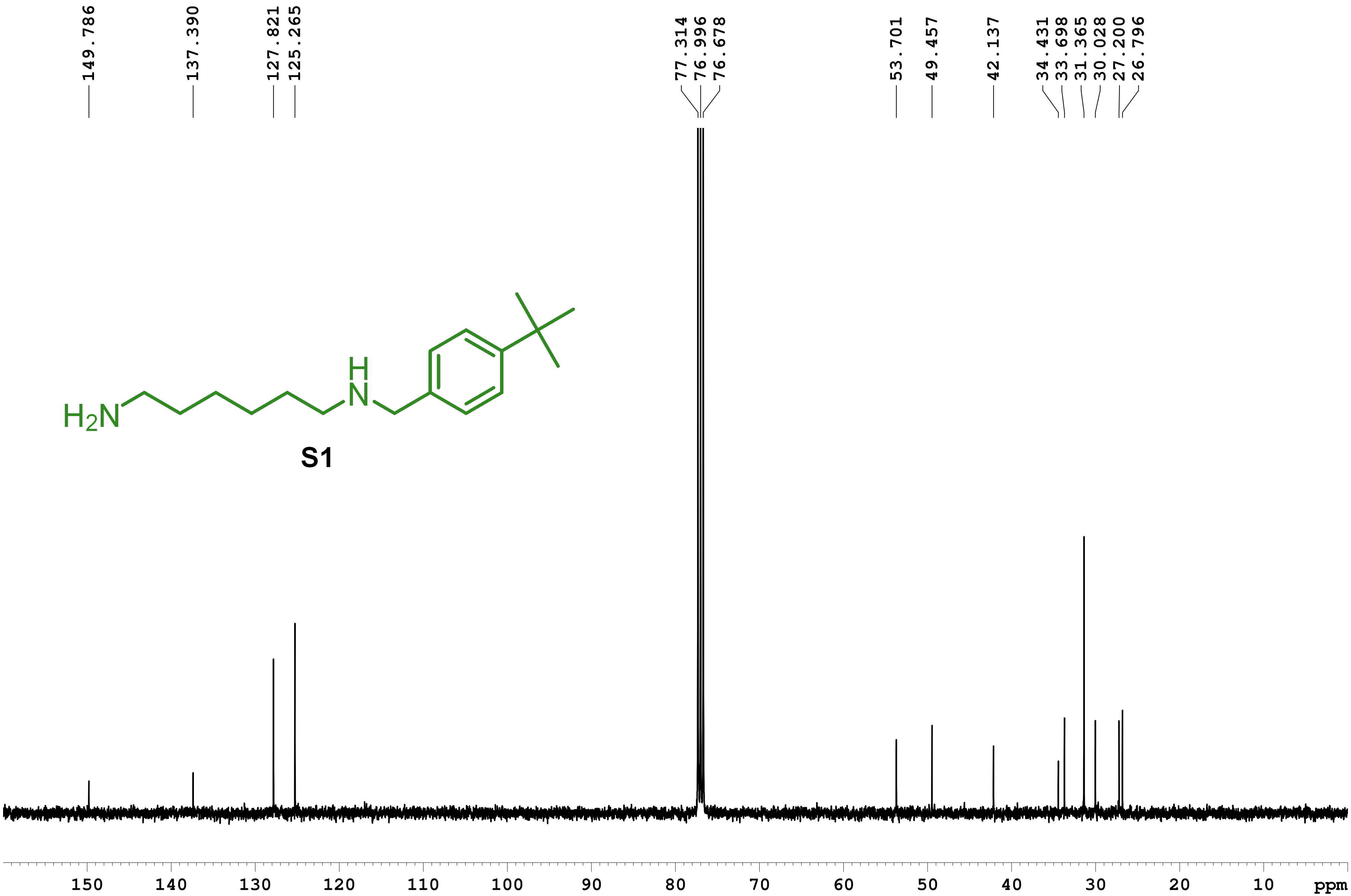
7.314
7.240
7.233
7.213
3.735
2.677
2.660
2.642
2.638
2.620
2.602
1.523
1.506
1.488
1.470
1.458
1.440
1.424
1.408
1.390
1.329
1.320
1.274
1.245
H2N
H
N
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.14
2.27
2.00
4.14
26.11

S1


149.786
137.390
127.821
125.265
77.314
76.996
76.678
53.701
49.457
42.137
34.431
33.698
31.365
30.028
27.200
26.796
H2N
H
N
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40
30
20
10
ppm

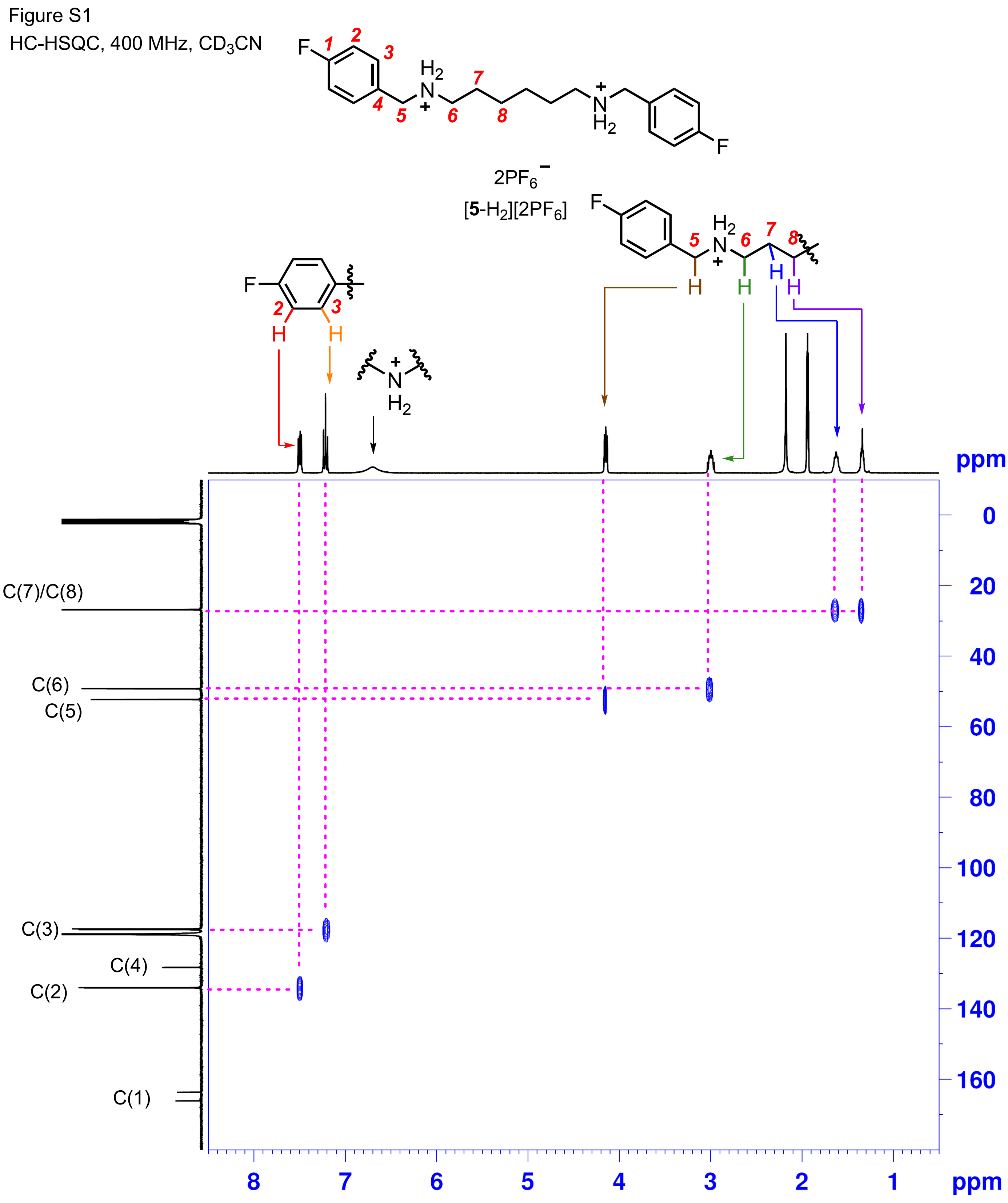
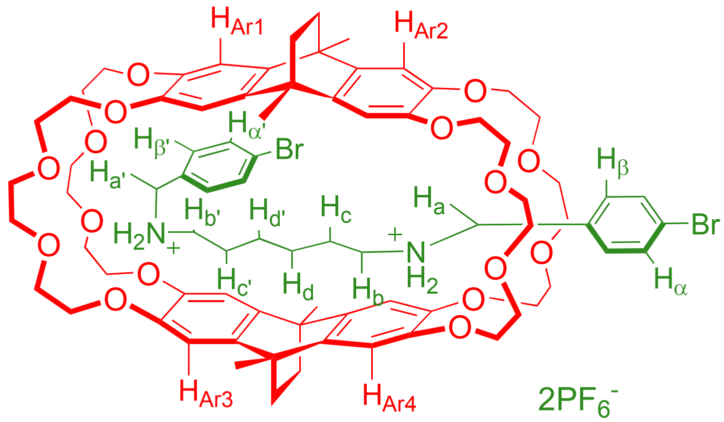


Figure S1. HSQC spectrum (400 MHz, CD_3CN, 298 K) of the threadlike salt [**5**-H][$2PF_6$].

The aromatic carbon signals of the threadlike salt [**5**-H][$2PF_6$] were identified based on the C–F couplings and cross signals appeared in ^{13}C NMR and HSQC spectra, respectively. The signals of the aliphatic protons were identified from their chemical shifts and cross signals appeared in HSQC spectra.

Figure S2

COSY of [**1**⊃·**2**-H_2][2PF_6]



[**1**⊃·**2**-H_2][2PF_6]

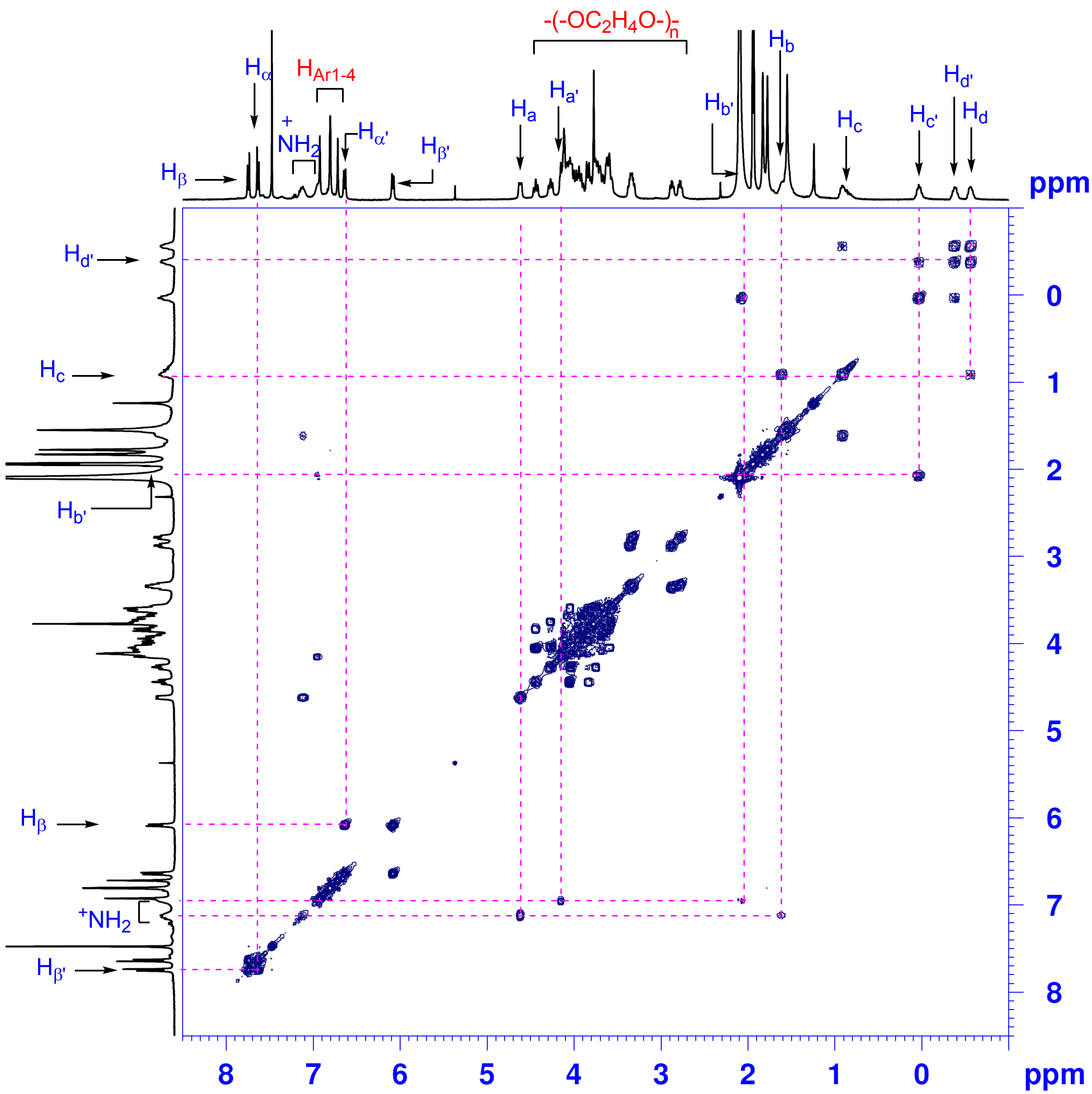
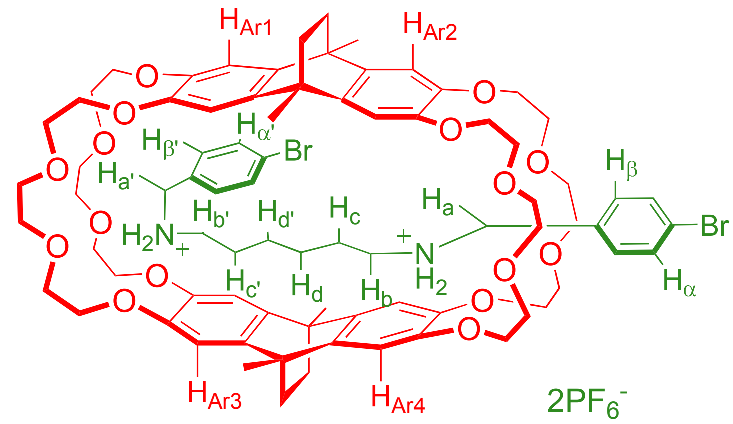


Figure S2. COSY spectrum [400 MHz, $CDCl_3$/CD_3CN (1:1), 298 K] of the complex [**1**⊃·**2**-H_2][2PF_6], recorded after mixing the molecular cage **1** and the threadlike salt [**2**-H_2][2PF_6] at 298 K for 13 h.

Figure S3

NOESY of [**1**⊃·**2**-H_2][2PF_6]



[**1**⊃·**2**-H_2][2PF_6]

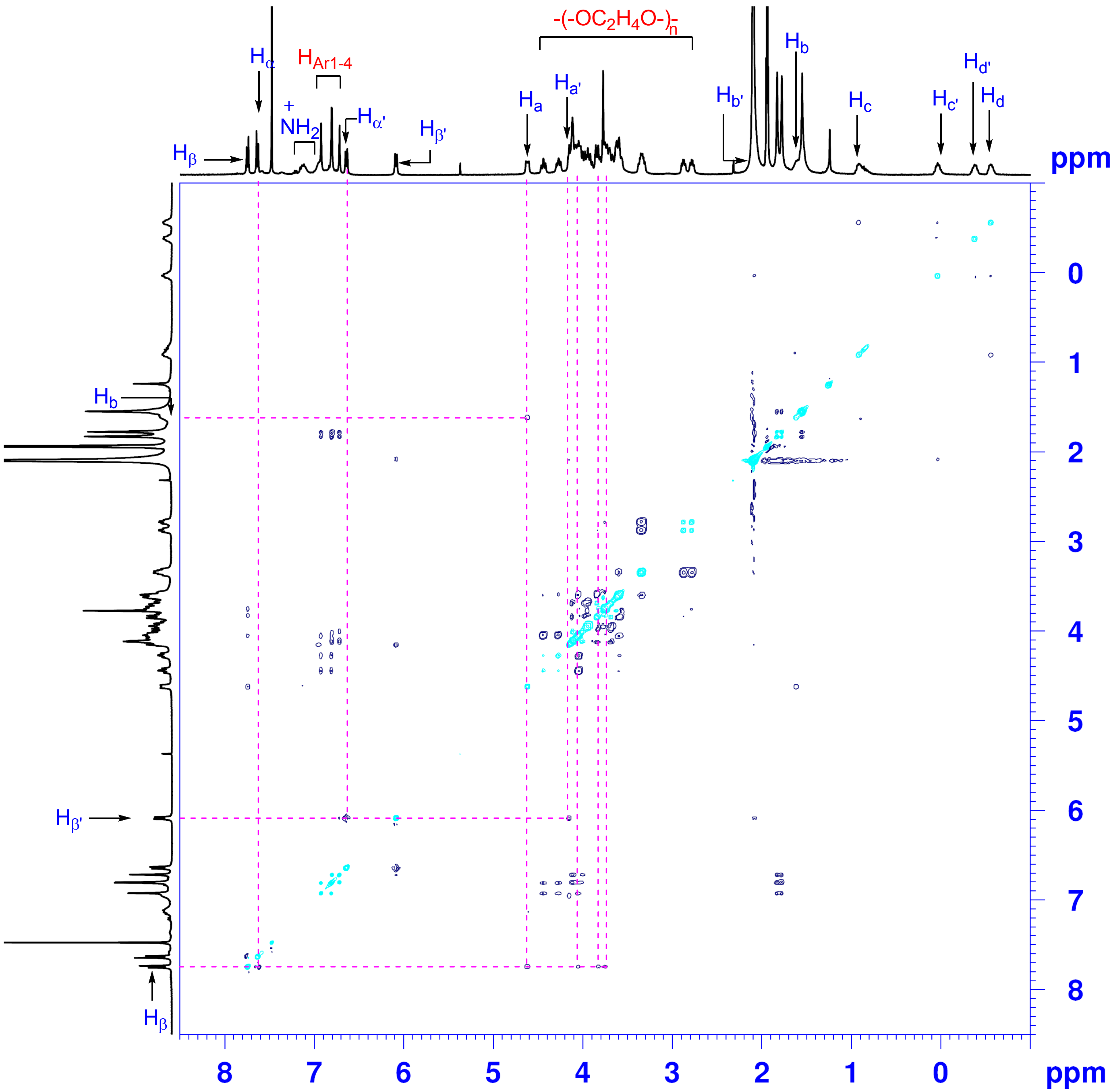


Figure S3. NOESY spectrum [400 MHz, $CDCl_3/CD_3CN$ (1:1), 298 K] of the complex [**1**⊃·**2**-H_2][2PF_6], recorded after mixing the molecular cage **1** and the threadlike salt [**2**-H_2][2PF_6] at 298 K for 13.5 h.

Assignment of Signals in ^{1}H NMR Spectra of the Complex $[1{\supset}\cdot 2\text{-}H_2][2PF_6]$ Based on Its 2D COSY and NOESY Spectra

From NOESY

H_a (δ = 4.62) → H_β (δ = 7.74) → H_α (δ = 7.63) and –(OCH_2CH_2O)– [protons of the tri(ethylene glycol) chains of host **1**; δ = 3.54–4.19]

$H_{\beta'}$ (δ = 6.08) → $H_{\alpha'}$ (δ = 6.64) and $H_{a'}$ [δ = 4.14–4.19, overlapped with –(OCH_2CH_2O)–]

H_a was the characteristic signal for benzylic protons adjacent to an $^+NH_2$ center threaded through the cavity of DB24C8.

$H_{\beta'}$ was shielded strongly by the aromatic moiety of the molecular cage and shifted upfield significantly.

From COSY

H_β (δ = 7.74) → H_α (δ = 7.63)

$H_{\beta'}$ (δ = 6.08) → $H_{\alpha'}$ (δ = 6.64)

H_a (δ = 4.62) → $^+NH_2$ (δ = 7.05–7.18, threaded) → H_b (δ = 1.59–1.67)

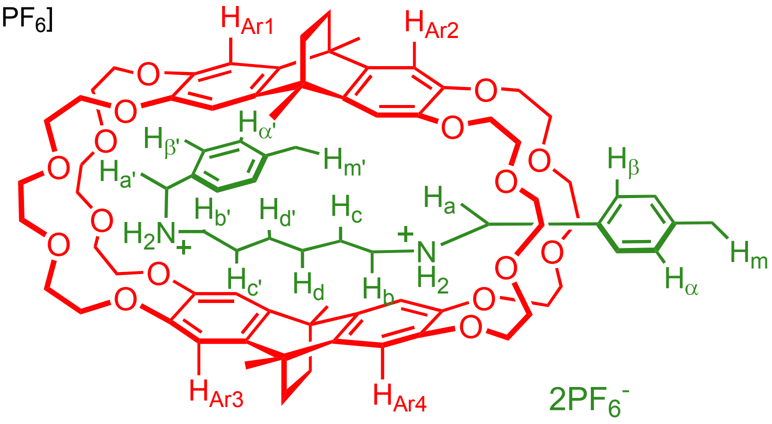
$^+NH_2$ (δ = 6.90–7.01, face-to-face complexed) → $H_{a'}$ (δ = 4.14–4.19) and $H_{b'}$ (δ = 2.00–2.08)

The threaded $^+NH_2$ center may experience stronger [$^+$N–H···O] hydrogen bonding interactions, thereby shifting it further downfield relative to the face-to-face complexes one.

H_b (δ = 1.59–1.67) → H_c (δ = 0.87–0.97) → H_d (δ = –0.62 to –0.50) → $H_{d'}$ (δ = –0.44 to –0.33) → $H_{c'}$ (δ = –0.04 to +0.11) → $H_{b'}$ (δ = 2.00–2.08)

Figure S4

COSY of [1⊃·3-H_2][$2PF_6$]



[1⊃·3-H_2][$2PF_6$]

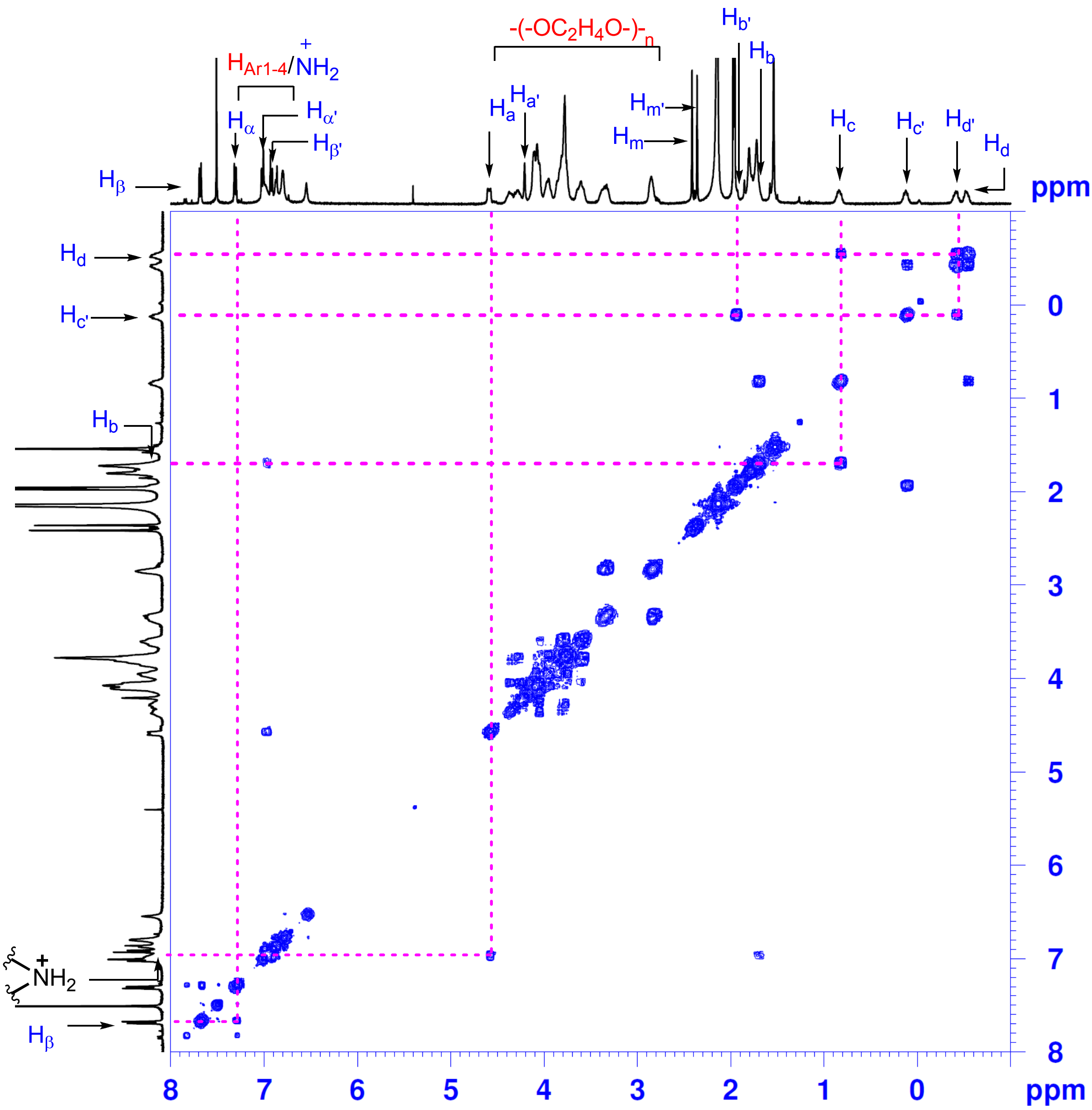
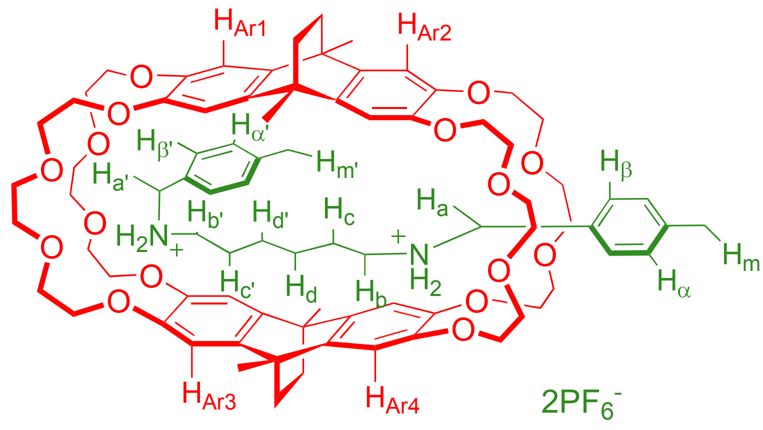


Figure S4. COSY spectrum [400 MHz, $CDCl_3$/CD_3CN (1:1), 298 K] of the complex [**1**⊃·**3**-H_2][$2PF_6$], recorded after mixing the molecular cage **1** and the threadlike salt [**3**-H_2][$2PF_6$] at 298 K for 3.3 days.

Figure S5
NOESY of [**1**⊃·**3**-H_2][2PF_6]



[**1**⊃·**3**-H_2][2PF_6]

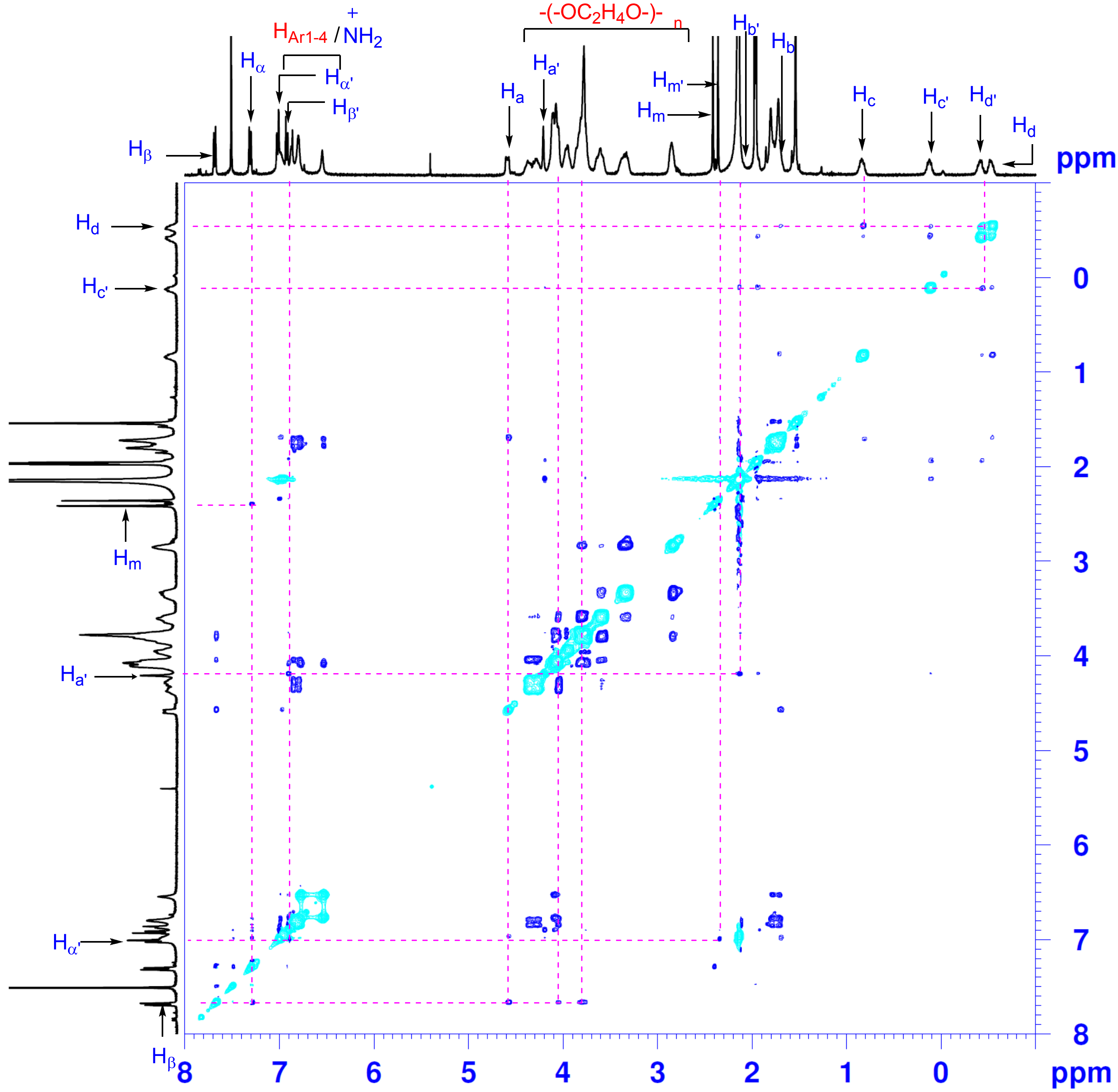


Figure S5. NOESY spectrum [400 MHz, $CDCl_3$/CD_3CN (1:1), 298 K] of the complex [**1**⊃·**3**-H_2][2PF_6], recorded after mixing the molecular cage **1** and the threadlike salt [**3**-H_2][2PF_6] at 298 K for 3.3 days.

Assignment of Signals in ^{1}H NMR Spectra of the Complex $[1{\supset}3\text{-}H_2][2PF_6]$ Based on Its 2D COSY and NOESY Spectra

From NOESY

H_a (δ = 4.56) → H_β (δ = 7.66) → H_α (δ = 7.28) and –(OCH_2CH_2O)– [protons of the tri(ethylene glycol) chains of host **1**; δ = 3.51–4.42, overlapped with $H_{a'}$]

H_α (δ = 7.28) → H_m (δ = 2.39); (so $H_{m'}$ was known)

H_a was the characteristic signal for benzylic protons adjacent to an $^{+}NH_2$ center threaded through the cavity of DB24C8.

From COSY

H_a (δ = 4.56, t, J = 7 Hz, 2H) → $^{+}NH_2$ (δ = 6.74–7.03; overlapped with $H_{\alpha'}$, $H_{\beta'}$, and $H_{Ar1–4}$)

From NOESY

$H_{m'}$ (δ = 2.31) → $H_{\alpha'}$ (δ = 6.99)

From COSY

$H_{\alpha'}$ (δ = 6.99) → $H_{\beta'}$ (δ = 6.89)

From NOESY

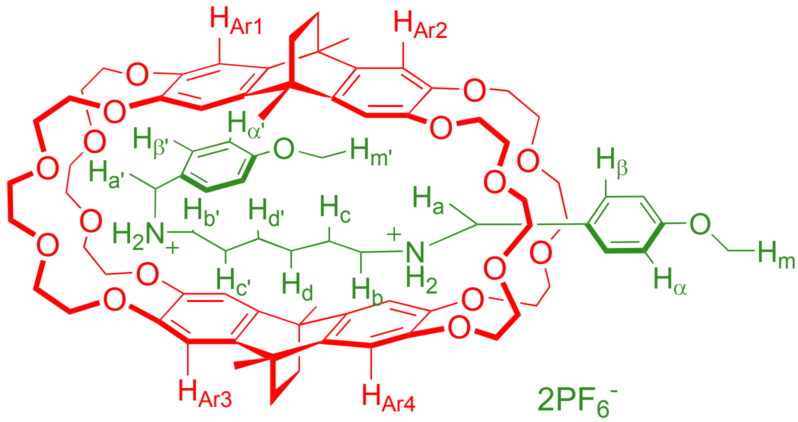
$H_{\beta'}$ (δ = 6.89) → $H_{a'}$ (δ = 4.56) → $H_{b'}$ (δ = 2.04–2.22, overlapped with signal for water)

$H_{\alpha'}$ and $H_{\beta'}$ were shielded strongly by the aromatic moiety of the molecular cage and shifted upfield significantly.

From COSY

$H_{b'}$ (δ = 2.04–2.22, overlapped with signal for water) → $H_{c'}$ (δ = 0.75–0.88) → $H_{d'}$ (δ = –0.50 to –0.36) → H_d (δ = –0.63 to –0.50) → H_c (δ = 1.49–1.55) → H_b (δ = 1.64–1.81; overlapped with the signals for the aliphatic protons of the molecular cage)

Figure S6
COSY of [**1**⊃·**4**-H_2][2PF_6]



[**1**⊃·**4**-H_2][2PF_6]

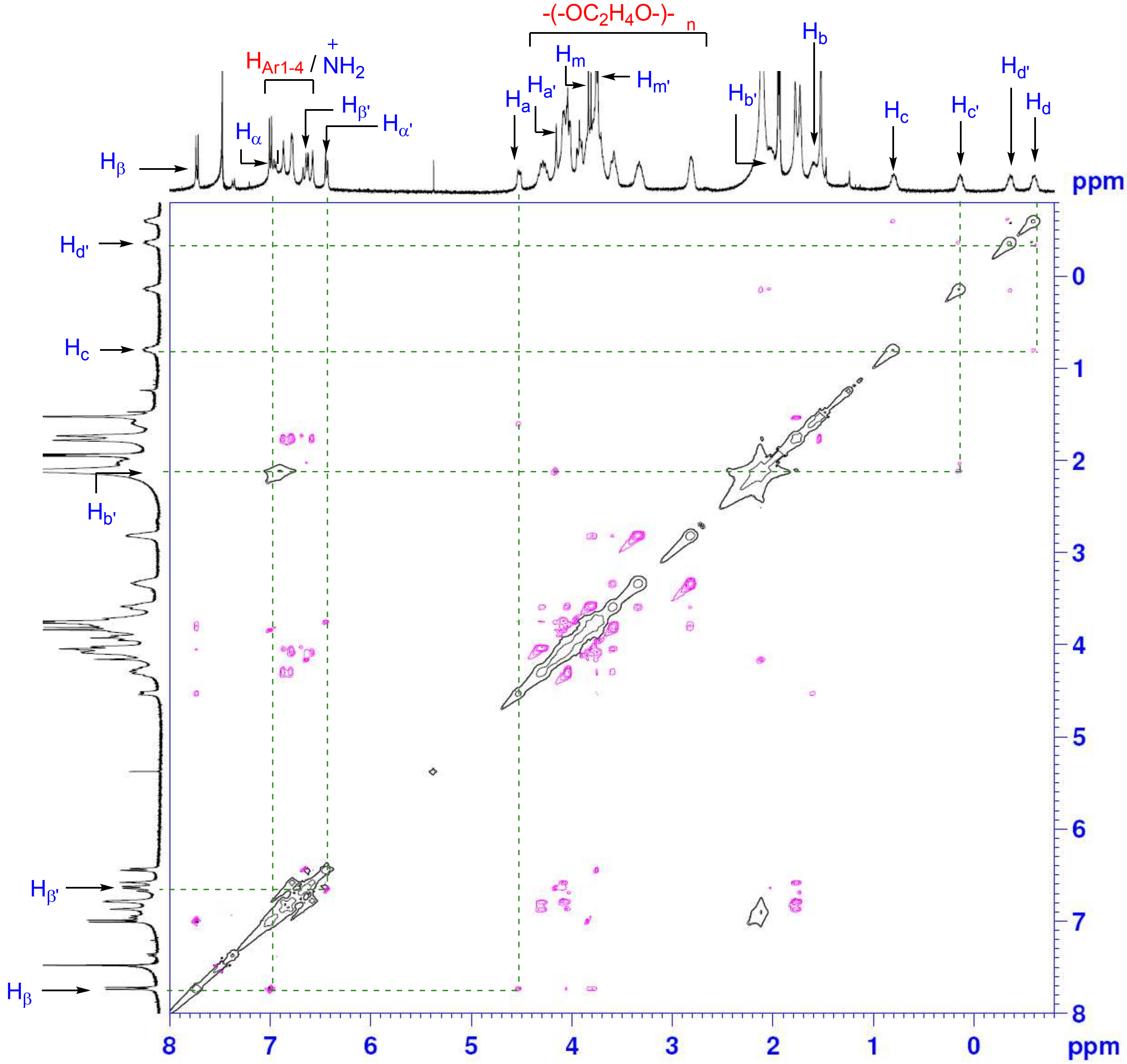
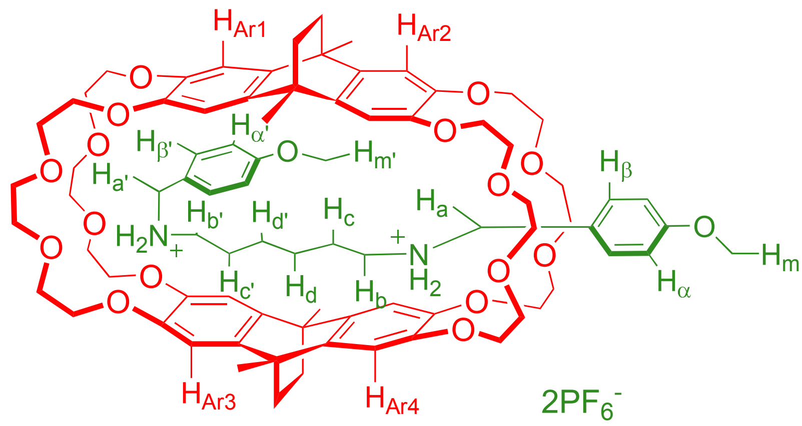


Figure S6. COSY spectrum [400 MHz, $CDCl_3$/CD_3CN (1:1), 298 K] of the complex [**1**⊃·**4**-H_2][2PF_6], recorded after mixing the molecular cage **1** and the threadlike salt [**4**-H_2][2PF_6] at 298 K for 2.4 days.

Figure S7

NOESY of [**1**⊃·**4**-H_2][2PF_6]



[**1**⊃·**4**-H_2][2PF_6]

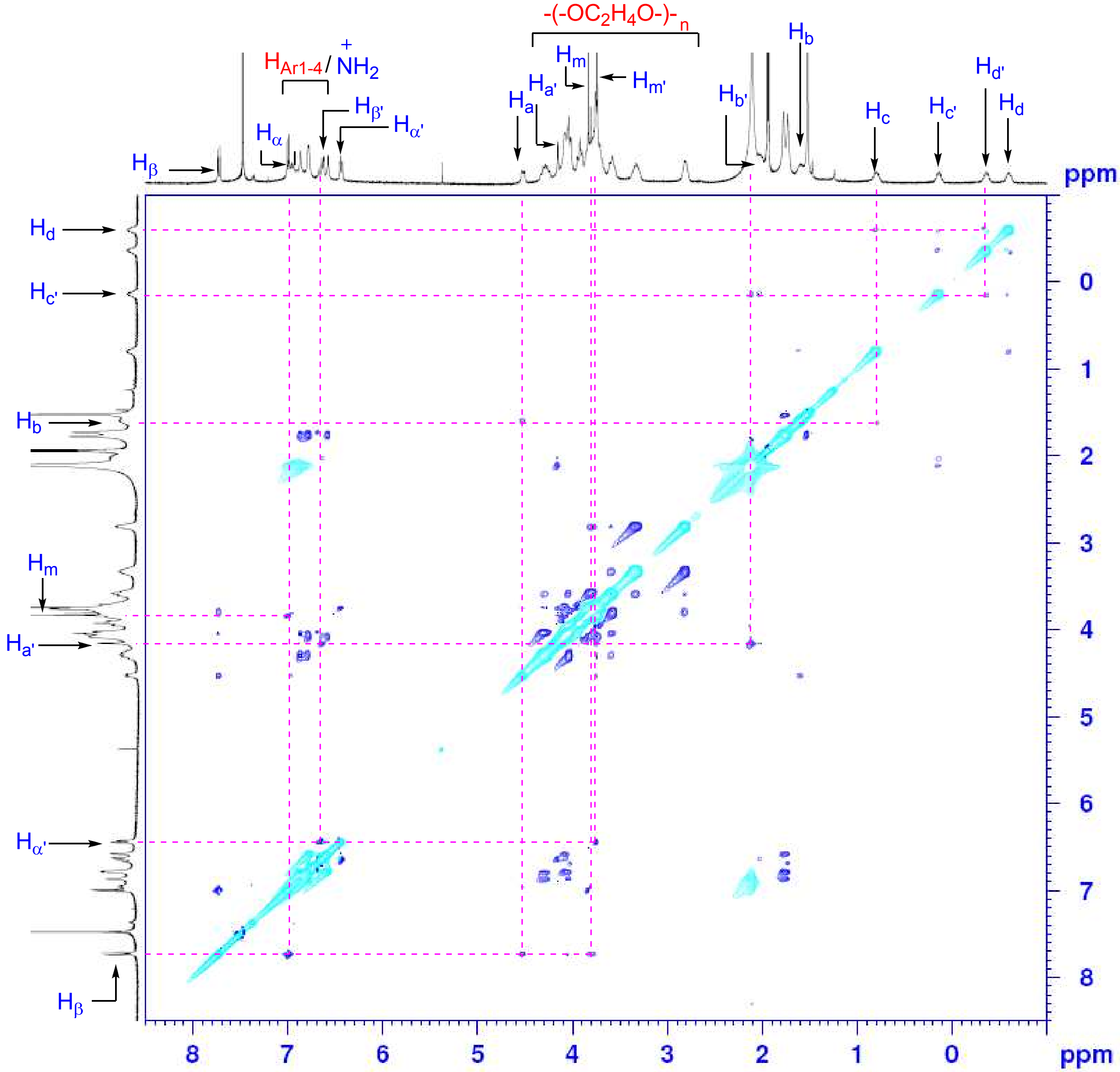


Figure S7. NOESY spectrum [400 MHz, $CDCl_3$/CD_3CN (1:1), 298 K] of the complex [**1**⊃·**4**-H_2][2PF_6], recorded after mixing the molecular cage **1** and the threadlike salt [**4**-H_2][2PF_6] at 298 K for 2.4 days.

Assignment of Signals in ^{1}H NMR Spectra of the Complex [1⊃·4-H_2][2PF_6] Based on Its 2D COSY and NOESY Spectra

From NOESY

H_a (δ = 4.52) → H_β (δ = 7.73) → H_α (δ = 7.00), and –(OCH_2CH_2O)– [protons of the tri(ethylene glycol) chains of host **1**; δ = 3.50–4.40]

H_α (δ = 7.00) → H_m (δ = 3.84)

H_a (δ = 4.52, t, *J* = 7 Hz, 2H) → H_b (δ = 1.57–1.66) → H_c (δ = 0.73–0.88)

H_a was the characteristic signal for benzylic protons adjacent to an $^+NH_2$ center threaded through the cavity of DB24C8.

From COSY

H_c (δ = 0.73–0.88) → H_d (δ = –0.67 to –0.52) → $H_{d'}$ (δ = –0.43 to –0.26) → $H_{c'}$ (δ = 0.07–0.23) → $H_{b'}$ (δ = 1.99–2.06)

From NOESY

$H_{b'}$ (δ = 1.99–2.06) → $H_{a'}$ (δ = 4.16) → $H_{\beta'}$ (δ = 6.63)

From COSY

$H_{\beta'}$ (δ = 6.63) → $H_{\alpha'}$ (δ = 6.44)

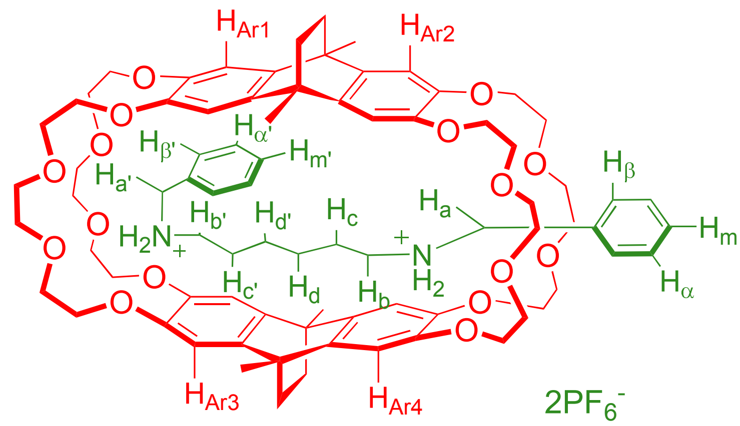
$H_{\alpha'}$ and $H_{\beta'}$ were shielded strongly by the aromatic moiety of the molecular cage and shifted upfield significantly.

From NOESY

$H_{\alpha'}$ (δ = 6.44, d, *J* = 9 Hz, 2H) → $H_{m'}$ (δ = 3.74)

$H_{m'}$ was shielded by the aromatic moiety of the molecular cage and shifted upfield to a greater extent than was H_m).

Figure S8
COSY of [**1**⊃·**6**-H_2][2PF_6]



[**1**⊃·**6**-H_2][2PF_6]

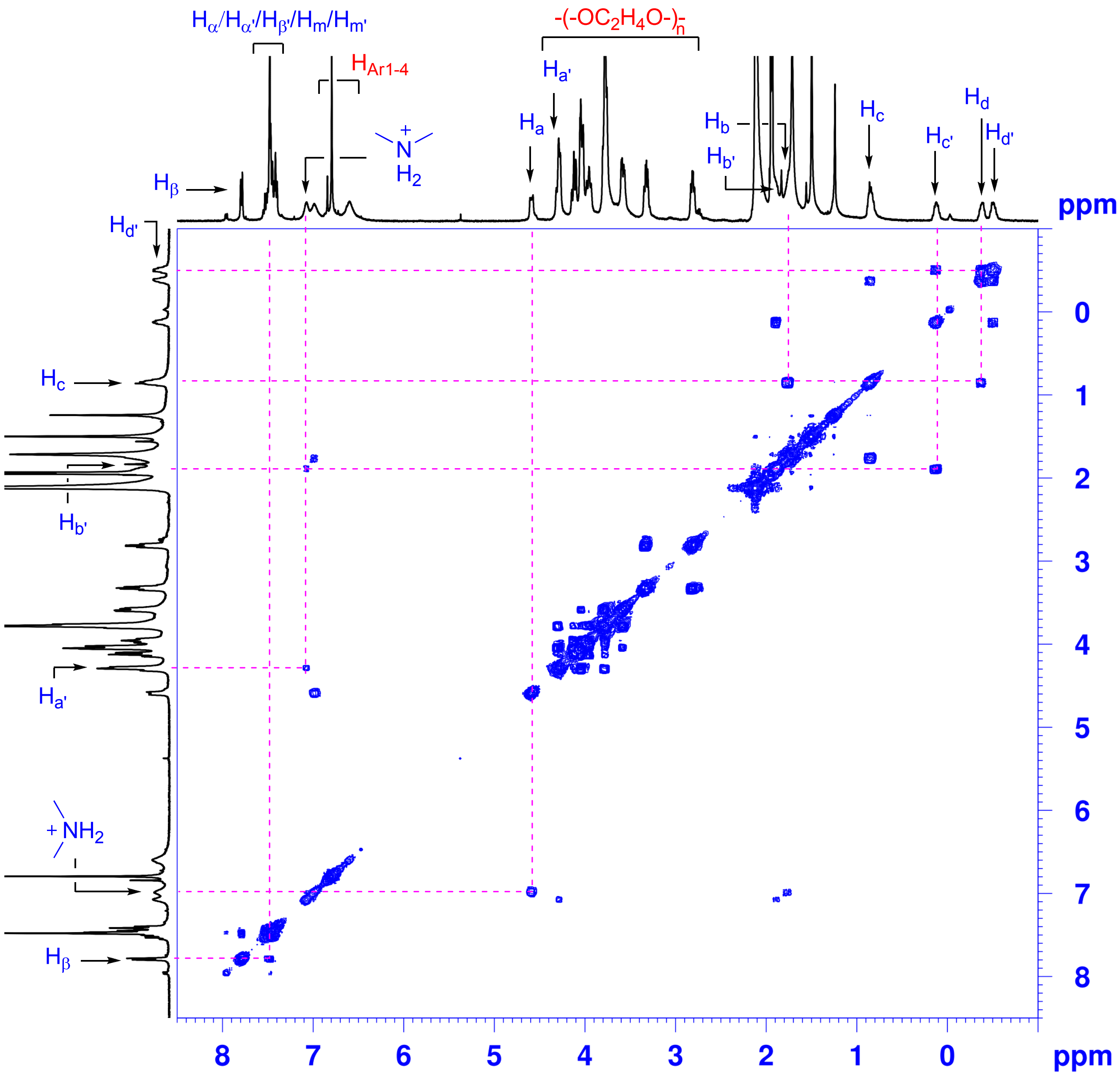
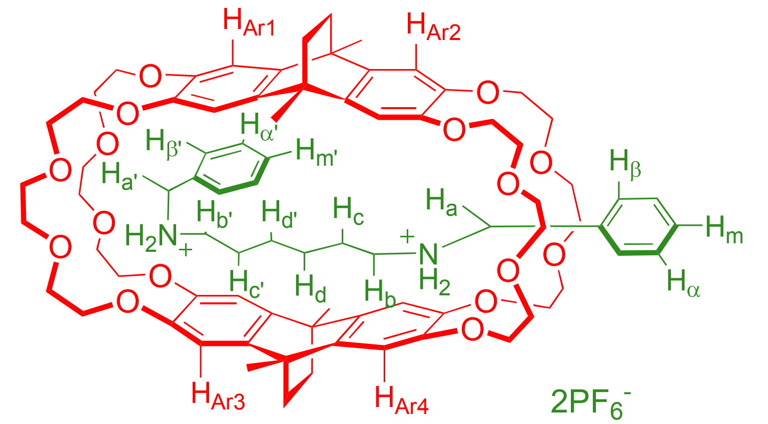


Figure S8. COSY spectrum [400 MHz, $CDCl_3$/CD_3CN (1:1), 298 K] of the complex [**1**⊃·**6**-H_2][2PF_6], recorded after mixing the molecular cage **1** and the threadlike salt [**6**-H_2][2PF_6] at 298 K for 8 h.

Figure S9
NOESY of [**1**⊃·**6**-H_2][2PF_6]



[**1**⊃·**6**-H_2][2PF_6]

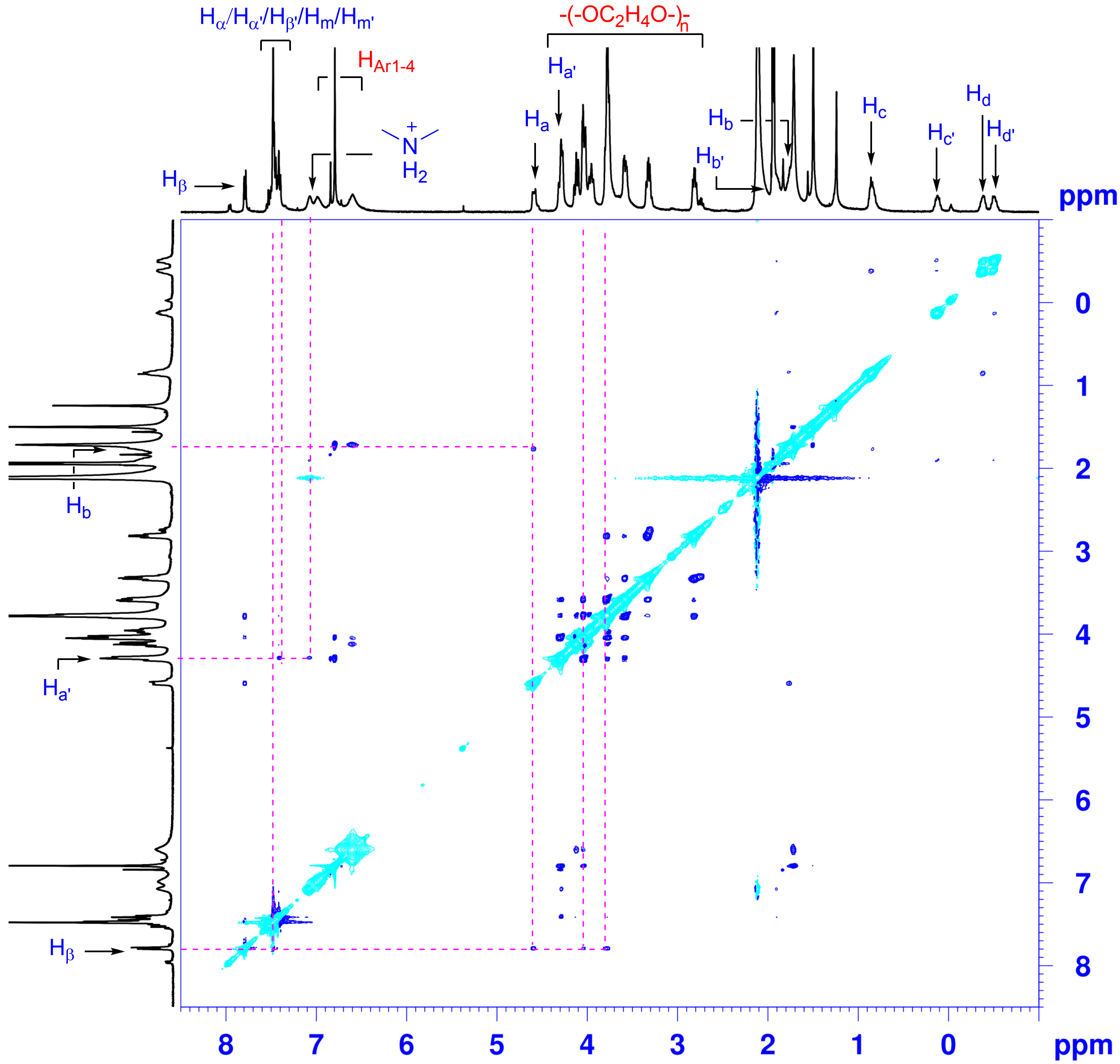


Figure S9. NOESY spectrum [400 MHz, $CDCl_3/CD_3CN$ (1:1), 298 K] of the complex [**1**⊃·**6**-H_2][2PF_6], recorded after mixing the molecular cage **1** and the threadlike salt [**6**-H_2][2PF_6] at 298 K for 8 h.

Assignment of Signals in ^{1}H NMR Spectra of the Complex [1⊃·6-H_2][2PF_6] Based on Its 2D COSY and NOESY Spectra

From NOESY

H_a (δ = 4.59) → H_β (δ = 7.79) → H_α (δ = 7.32–7.58, overlapped with $H_{\alpha'}$, $H_{\beta'}$, H_m, and $H_{m'}$) and –(OCH_2CH_2O)– [protons of the tri(ethylene glycol) chains of host **1**; δ = 3.40–4.19]

H_a (δ = 4.59) → H_b (δ = 1.75–1.81; overlapped with the aliphatic signals of the molecular cage **1**)

H_a was the characteristic signal for benzylic protons adjacent to an $^+NH_2$ center threaded through the cavity of DB24C8.

From COSY

H_b (δ = 1.75–1.81, overlapped with the aliphatic signals of the molecular cage **1**) → H_c (δ = 0.73–0.92) → H_d (δ = –0.44 to –0.32) → $H_{d'}$ (δ = –0.58 to –0.44) → $H_{c'}$ (δ = 0.07–0.20) → $H_{b'}$ (δ = 1.86–1.92, overlapped with the aliphatic signals of the molecular cage **1**)

From NOESY

$H_{b'}$ (δ = 1.86–1.92) → $^+NH_2$ (δ = 6.43–6.69) → $H_{a'}$ [δ = 4.55–4.65, overlapped with the tri(ethylene glycol) signals of the molecular cage **1**] → $H_{\beta'}$ (δ = 7.32–7.58, overlapped with H_α, $H_{\alpha'}$, H_m, and $H_{m'}$)

$H_{\alpha'}$ and $H_{\beta'}$ were shielded by the aromatic moiety of the molecular cage and shifted upfield.

Table S1. Kinetic data for threading of the face-to-face–complexed aromatic termini of [**1**⊃·**x**-H_2][2PF_6] into the DB24C8-like opening of the molecular cage **1** to form completely threaded complexes [**1**⊃⊃**x**-H_2][2PF_6]

Complex formed[a]	Terminal substituent	k (s^{-1})[b,c]	$\Delta G^{\ddagger}$[c,d] (kcal mol^{-1})	$\Delta H^{\ddagger}$[e] (kcal mol^{-1})	$\Delta S^{\ddagger}$[e] (cal mol^{-1} K^{-1})
[**1**⊃⊃**2**-H_2][2PF_6]	Br	(2.2 ±0.2) x 10^{-7}	26.5 ±0.1	11.4 ±6.1	-50.2 ±19.6
[**1**⊃⊃**3**-H_2][2PF_6]	CH_3	(8.6 ±0.9) x 10^{-8}	27.1 ±0.1	19.7 ±0.8	-24.6 ±2.6
[**1**⊃⊃**4**-H_2][2PF_6]	OCH_3	(1.4 ±0.1) x 10^{-7}	26.8 ±0.1	18.3 ±1.9	-28.6 ±6.1
[**1**⊃⊃**5**-H_2][2PF_6]	F	(6.2 ±0.9) x 10^{-6}	24.5 ±0.1	9.2 ±3.9	-51.6 ±12.6
[**1**⊃⊃**6**-H_2][2PF_6]	H	(1.7 ±0.3) x 10^{-6}	25.3 ±0.1	20.3 ±1.2	-16.6 ±3.8

[a] Experiments were performed using an equimolar mixture (4.00 mM) of the molecular cage **1** and the threadlike salt. The 90% confidence limits for k, $\Delta G^{\ddagger}$, $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were evaluated by the least-squarets method. [b] Value of k were obtained either from the slope of the straight line in the plot of $\ln([A_0]/[A_t])$ against t {using the relationship of $\ln([A_0]/[A_t]) = kt$}. [c] Calculated at 298 K. [d] Value of $\Delta G^{\ddagger}$ were calculated using the relationship $\Delta G^{\ddagger} = -RT \ln(kh/k_B T)$, where R, h, and k_B correspond to the gas, Plank, and Boltzmann constants, respectively. [e] Value of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were obtained from the intercept and slope of the straight line in the plot of $\Delta G^{\ddagger}$ against T (using the relationship $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$).

Experiments were performed using an equimolar (4 mM) mixture of molecular cage **1** and the threadlike salt in $CDCl_3$[S-a] / CD_3CN (1:1) The rate constant (k) for the threading process were determined from the slope of the straight line in the plot of $\ln([A_0]/[A_t])$ against t, measured at five temperatures. The value of $[A_0] = [A_t]+[P_t]$ and $[A_t]$ were determined from the reciprocal of the molar ratio of the face-to-face complex to the completely threaded pseudorotaxane in the solution, measured from the integrated signals in ^{1}H NMR spectra: [1/4 integral of $H_{\beta''}$ (4H) + 1/2 integral of $H_{\beta'}$ (2H)] / [1/2 integral of $H_{\beta'}$ (2H)]. The value of $\Delta G^{\ddagger}$ (kcal mol^{-1}) were calculated using the relationship

$$\Delta G^{\ddagger} = -RT \ln(kh/k_B T)$$

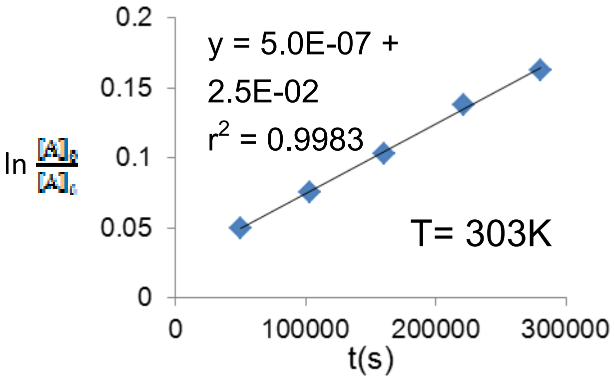
where R, h and k_B correspond to the gas, Plank and Boltzmann constants, respectively. The value of $\Delta H^{\ddagger}$ (kcal mol^{-1}) and $\Delta S^{\ddagger}$ (cal mol^{-1}) were obtained from the intercept and slope, respectively, of the straight lines in the plots of $\Delta G^{\ddagger}$ against T, using the relationship

$$\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$$

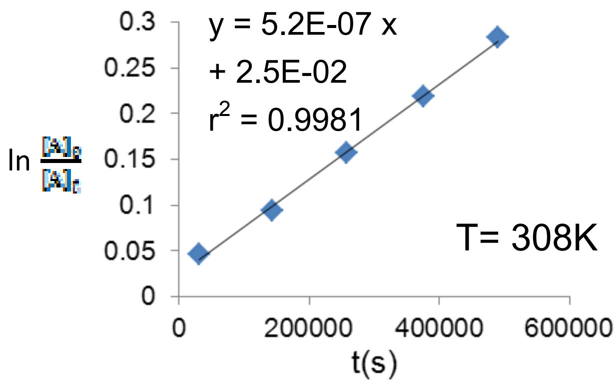
[S-a] To avoid possible disruptive effects caused by Cl^- anion or by the decomposition of PF_6^- into PF_5 and F^- in $CDCl_3$, the deuterated solvent used in kinetic experiments was treated with K_2CO_3 and $Na_2S_2O_3$ and distilled prior to performing these studies.

X = Br and [**1**⊃⊃**2**-H_2][2PF_6] was the product formed.

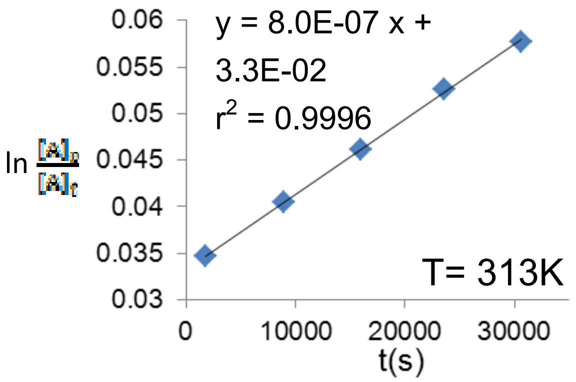
In these experiments,. [A_t] and [P_t] were determined by integration of the signals at δ 7.73 (d, J = 8 Hz, 2H) and δ 7.86 (d, J = 5 Hz, 4H), respectively.



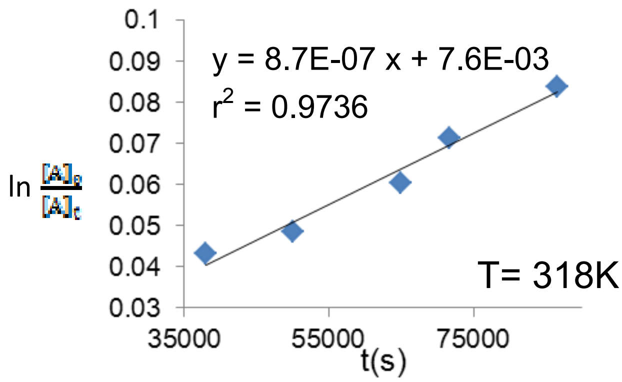
k = (5.0±0.3) x10^{-7} (s^{-1}), $\Delta G^{\ddagger}$ = 26.5±0.1 (kcal mol^{-1})



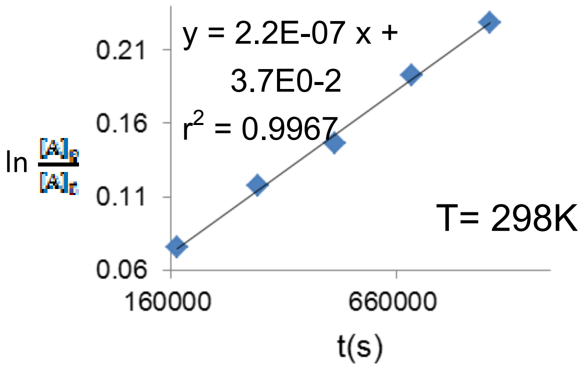
k = (5.2±0.4) x10^{-7} (s^{-1}), $\Delta G^{\ddagger}$ = 26.9±0.1 (kcal mol^{-1})



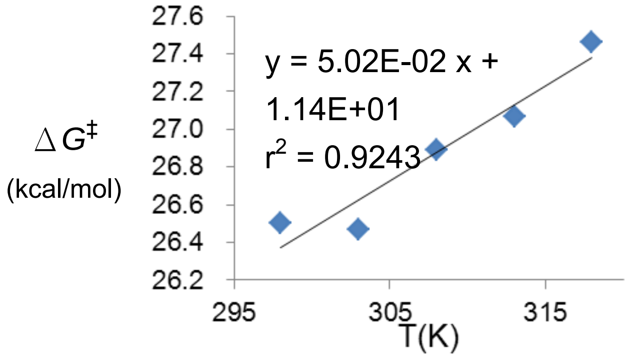
k = (8.0±0.3) x10^{-7} (s^{-1}), $\Delta G^{\ddagger}$ = 27.1±0.1 (kcal mol^{-1})



k = (8.7±2.0) x10^{-7} (s^{-1}), $\Delta G^{\ddagger}$ = 27.5±0.1 (kcal mol^{-1})



k = (2.2±0.2) x10^{-7} (s^{-1}), $\Delta G^{\ddagger}$ = 26.5±0.1 (kcal mol^{-1})

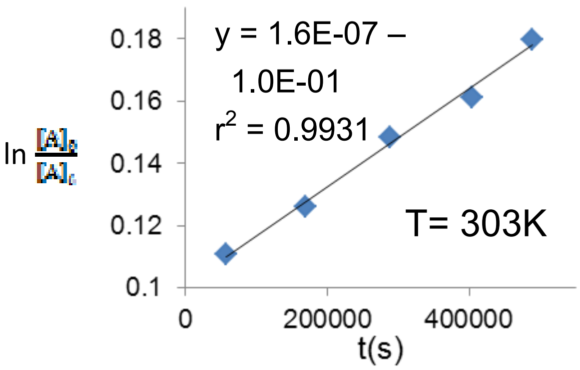


$\Delta H^{\ddagger}$ = intercept = 11.4±6.1 (kcal mol^{-1}),

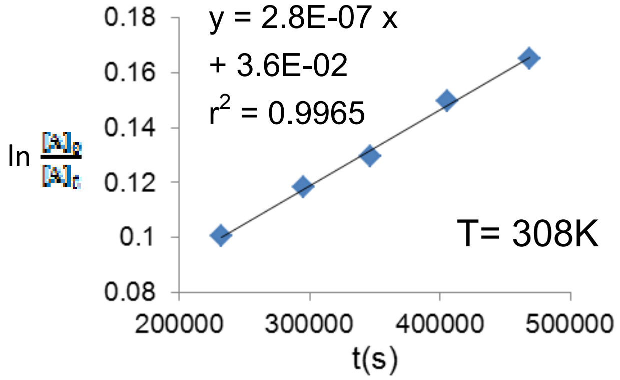
$\Delta S^{\ddagger}$ = - slope = - 50.2±19.6 (cal mol^{-1} K^{-1})

X = CH_3 and [**1**⊃⊃**3**-H_2][2PF_6] was the product formed.

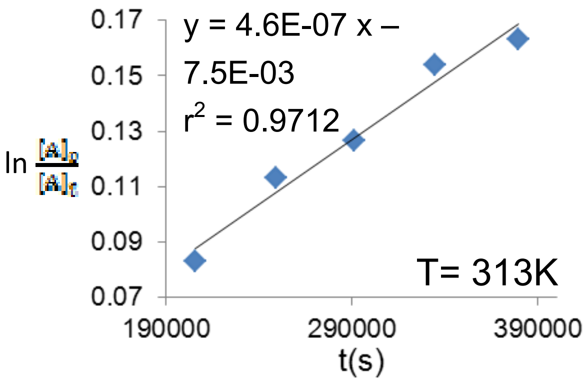
In these experiments,. [A_t] and [P_t] were determined by integration of the signals at δ 7.64 (d, J = 8 Hz, 2H) and δ 7.81 (d, J = 8 Hz, 4H), respectively.



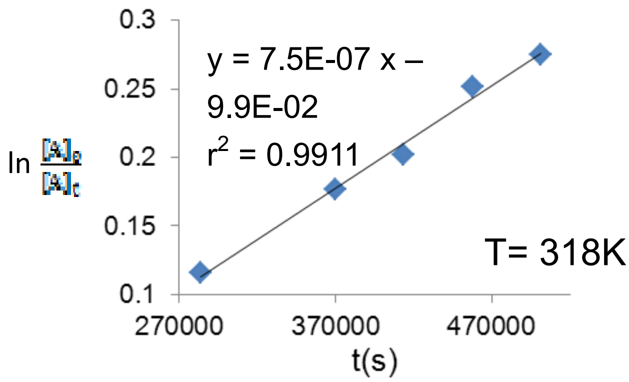
k = (1.6±0.2) x10^{-7} (s^{-1}), $\Delta G^{\ddagger}$ = 27.2±0.1 (kcal mol^{-1})



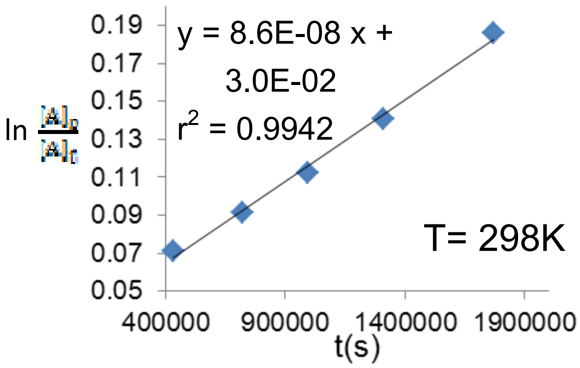
k = (2.8±0.3) x10^{-7} (s^{-1}), $\Delta G^{\ddagger}$ = 27.3±0.1 (kcal mol^{-1})



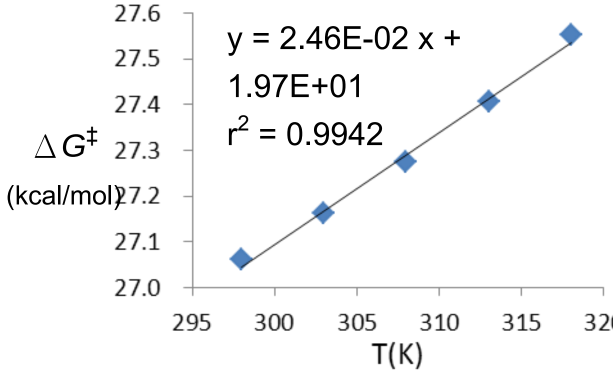
k = (4.6±1.1) x10^{-7} (s^{-1}), $\Delta G^{\ddagger}$ = 27.4±0.1 (kcal mol^{-1})



k = (7.5±1.0) x10^{-7} (s^{-1}), $\Delta G^{\ddagger}$ = 27.6±0.1 (kcal mol^{-1})



k = (8.6±0.9) x10^{-8} (s^{-1}), $\Delta G^{\ddagger}$ = 27.1±0.1 (kcal mol^{-1})

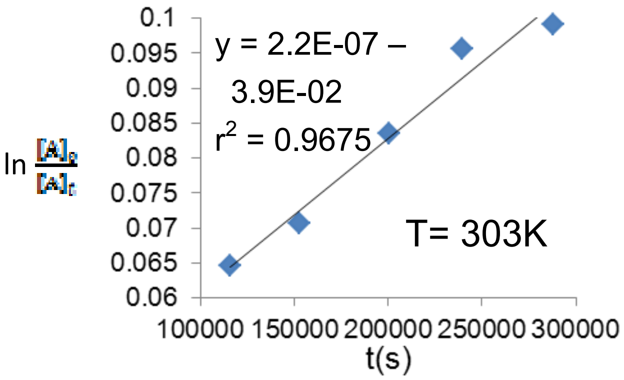


$\Delta H^{\ddagger}$ = intercept = 19.7±0.8 (kcal mol^{-1}),

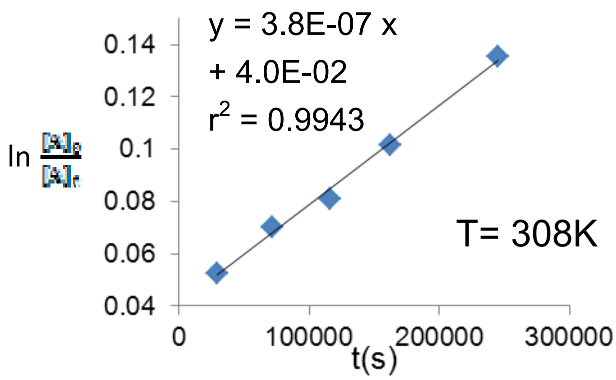
$\Delta S^{\ddagger}$ = - slope = - 24.6±2.6 (cal mol^{-1} K^{-1})

X = OCH_3 and [**1**⊃⊃**4**-H_2][2PF_6] was the product formed.

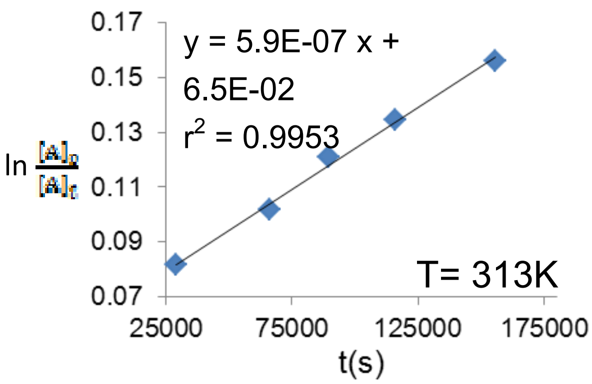
In these experiments,. [A_t] and [P_t] were determined by integration of the signals at δ 7.70 (d, *J* = 9 Hz, 2H) and δ 7.86 (d, *J* = 9 Hz, 4H), respectively.



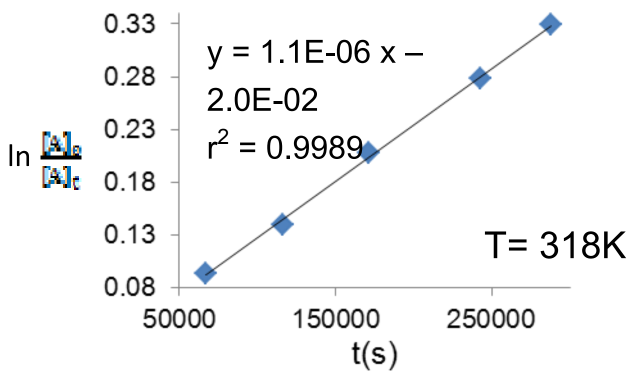
k = (2.2±0.6) x10^{-7} (s^{-1}), Δ$G^‡$ = 27.0±0.1 (kcal mol^{-1})



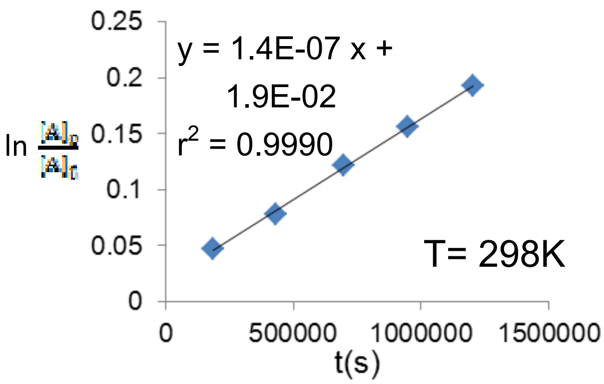
k = (3.8±0.4) x10^{-7} (s^{-1}), Δ$G^‡$ = 27.1±0.1 (kcal mol^{-1})



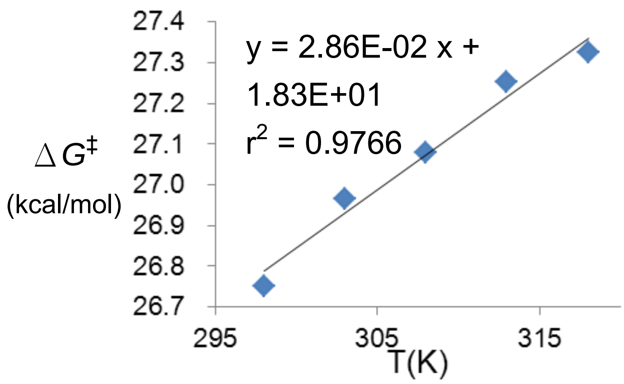
k = (5.9±0.6) x10^{-7} (s^{-1}), Δ$G^‡$ = 27.3±0.1 (kcal mol^{-1})



k = (1.1±0.1) x10^{-6} (s^{-1}), Δ$G^‡$ = 27.3±0.1 (kcal mol^{-1})



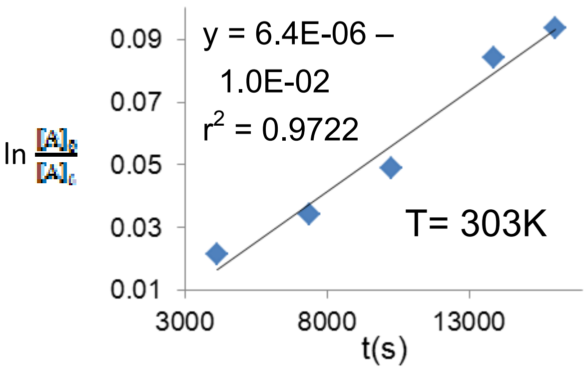
k = (1.4±0.1) x10^{-7} (s^{-1}), Δ$G^‡$ = 26.8±0.1 (kcal mol^{-1})



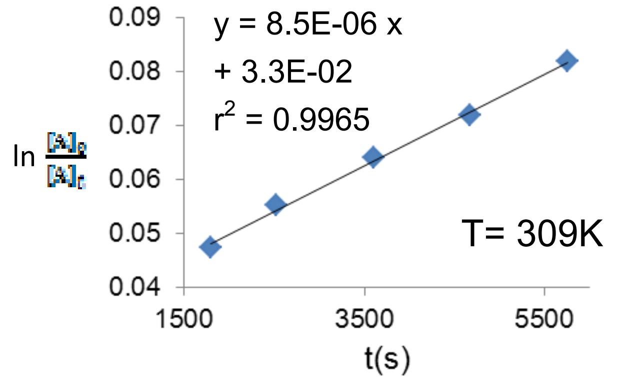
Δ$H^‡$ = intercept = 18.3±1.9 (kcal mol^{-1}),
Δ$S^‡$ = - slope = - 28.6±6.1 (cal mol^{-1} K^{-1})

X = F and [**1**⊃⊃**5**-H_2][2PF_6] was the product formed.

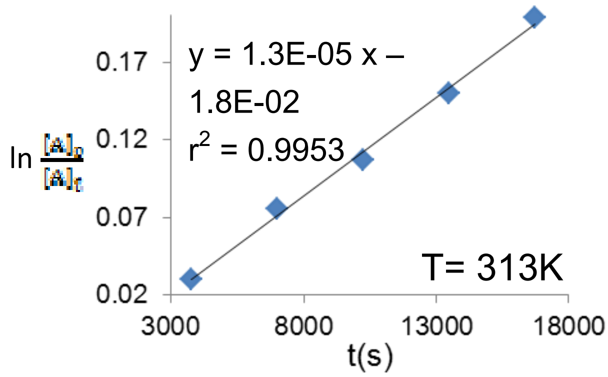
In these experiments,. [A_t] and [P_t] were determined by integration of the signals at δ 7.82 (dd, J = 6, 8 Hz, 2H) and δ 7.96 (dd, J = 6, 8 Hz, 4H), respectively.



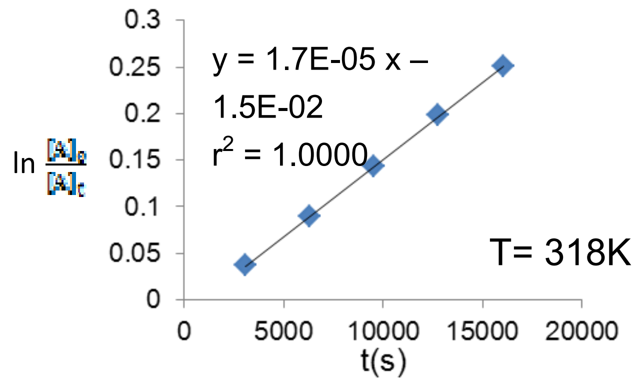
k = (6.4±1.5) x10^{-6} (s^{-1}), Δ$G^‡$ = 24.9±0.1 (kcal mol^{-1})



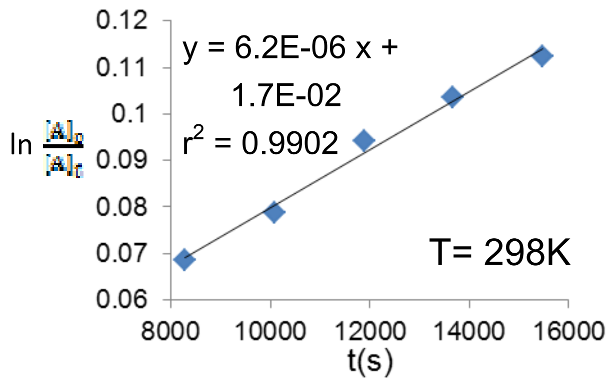
k = (8.5±0.7) x10^{-6} (s^{-1}), Δ$G^‡$ = 25.3±0.1 (kcal mol^{-1})



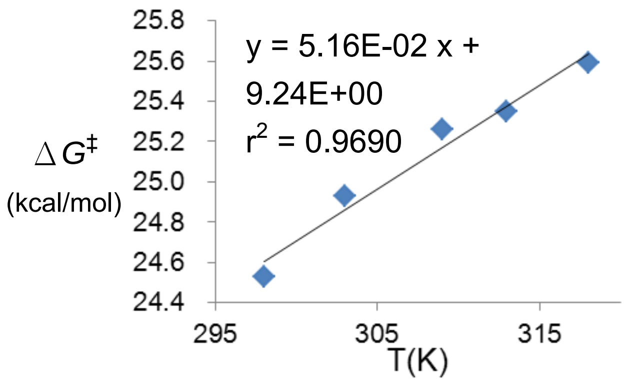
k = (1.3±0.2) x10^{-5} (s^{-1}), Δ$G^‡$ = 25.3±0.1 (kcal mol^{-1})



k = (1.7±0.1) x10^{-5} (s^{-1}), Δ$G^‡$ = 25.6±0.1 (kcal mol^{-1})



k = (6.2±0.9) x10^{-6} (s^{-1}), Δ$G^‡$ = 24.5±0.1 (kcal mol^{-1})

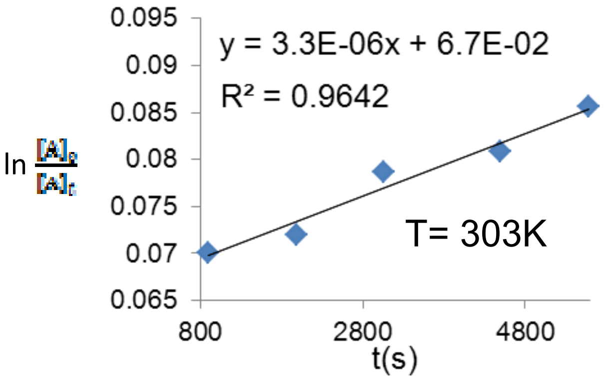


Δ$H^‡$ = intercept = 9.2±3.9 (kcal mol^{-1}),

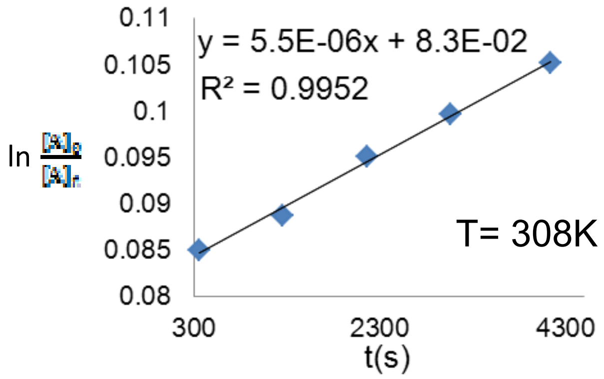
Δ$S^‡$ = - slope = - 51.6±12.6 (cal mol^{-1} K^{-1})

X = H and [**1**⊃⊃**6**-H_2][2PF_6] was the product formed.

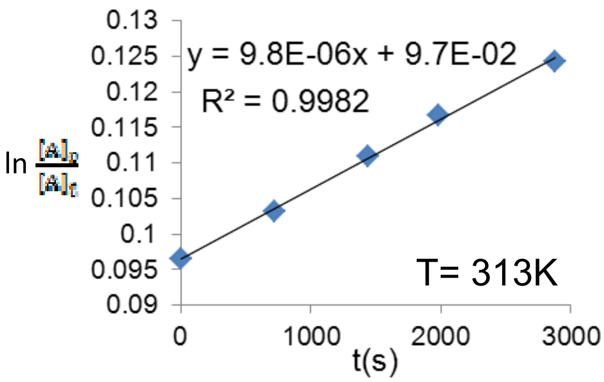
In these experiments,. [A_t] and [P_t] were determined by integration of the signals at δ 7.79 (d, *J* = 7 Hz, 2H) and δ 7.96 (d, *J* = 7 Hz, 4H), respectively.



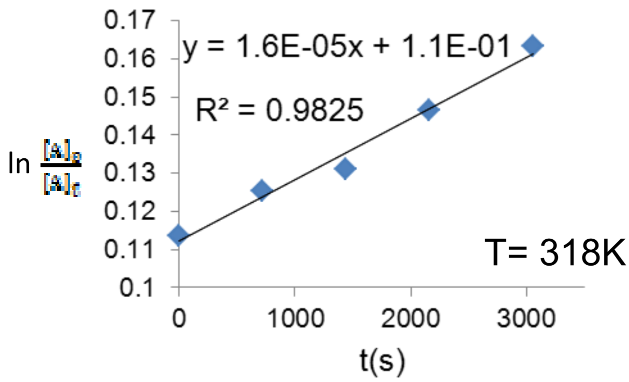
k = (3.3±0.9) x10^{-6} (s^{-1}), $\Delta G^{\ddagger}$ = 25.3±0.1 (kcal mol^{-1})



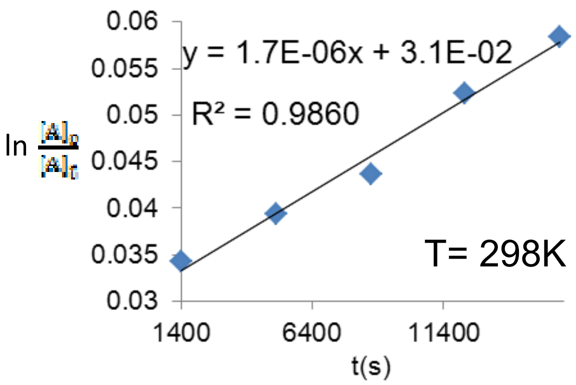
k = (5.5±0.6) x10^{-6} (s^{-1}), $\Delta G^{\ddagger}$ = 25.4±0.1 (kcal mol^{-1})



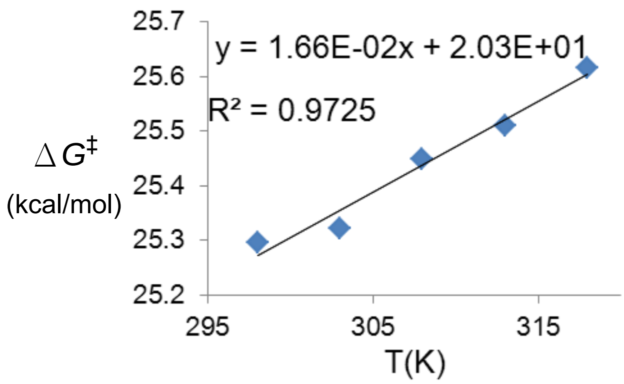
k = (9.8±0.6) x10^{-6} (s^{-1}), $\Delta G^{\ddagger}$ = 25.5±0.1 (kcal mol^{-1})



k = (1.6±0.3) x10^{-5} (s^{-1}), $\Delta G^{\ddagger}$ = 25.6±0.1 (kcal mol^{-1})



k = (1.7±0.3) x10^{-6} (s^{-1}), $\Delta G^{\ddagger}$ = 25.3±0.1 (kcal mol^{-1})



$\Delta H^{\ddagger}$ = intercept = 20.3±1.2 (kcal mol^{-1}),
$\Delta S^{\ddagger}$ = - slope = - 16.6±3.8 (cal mol^{-1} K^{-1})