CHEMISTRY
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# Supporting Information



## Weakly Associated TFPB Anions Are Superior to $PF_6$ Anions When Preparing (Pseudo)Rotaxanes from Crown Ethers and Secondary Dialkylammonium Ions**

Nai-Chia Chen,[a] Chun-Ju Chuang,[a] Liang-Yun Wang,[a] Chien-Chen Lai,[b] and Sheng-Hsien Chiu*[a]

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# Weakly Associated TFPB Anions are Superior to $PF_6$ Anions When Preparing (Pseudo)Rotaxanes from Crown Ethers and Secondary Dialklyammonium Ions

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## Supplementary Material

Data Page Number

Threadlike salt **1**-H•TFPB: **1**-H•$PF_6$ (114 mg, 0.247 mmol) and NaTFPB (222 mg 0.25 mmol) were mixed in MeOH (10 mL) and then the organic solvent was evaporated under reduced pressure. The residue was partitioned between $CH_2Cl_2$ (50 mL) and $H_2O$ (10 mL). The organic layer was collected, washed with $H_2O$ (4 × 10 mL), dried ($MgSO_4$), and concentrated to give the desired product as a pale yellow liquid (275 mg, 93%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.30 (s, 9H), 4.07 (s, 4H), 4.37 (s, 2H), 7.14 (d, $J$ = 8 Hz, 2H), 7.20 (d, $J$ = 8 Hz, 2H), 7.36 (d, $J$ = 8 Hz, 2H), 7.46 (d, $J$ = 8 Hz, 2H), 7.49–7.52 (br, 4H), 7.65–7.72 (br, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 30.9, 35.0, 51.8, 52.3, 53.8, 117.5, 124.5 (q, $^1J_{CF}$ = 272 Hz), 124.9, 127.1, 128.1, 128.8 (q, $^2J_{CF}$ = 31 Hz), 128.8, 129.5, 134.7, 138.8, 154.9, 161.5 (q, $^1J_{CB}$ = 50 Hz) (one signal is missing, possibly because of signal overlap); MS (ESI): $C_{19}H_{25}N_4^+$ ([**1**-H]$^+$) calcd *m*/*z* 309.2079; found *m*/*z* 309.2073.

[2]Rotaxane **2**-H•TFPB: Triethyl phosphite (80 μL, 0.47 mmol) was added dropwise to a solution of **1**-H•TFPB (266 mg, 0.227 mmol) and DA24C8 (243 mg, 0.458 mmol) in $CH_2Cl_2$ (2.3 mL). The mixture was stirred at ambient temperature overnight. The solvent was evaporated and the residue purified chromatographically ($SiO_2$; $CH_3CN/CH_2Cl_2$, 5:95). The product was isolated as a pale yellow oil (284 mg, 69%). $^1$H NMR (800 MHz, $CDCl_3$): δ = 1.27–1.34 (m, 15H), 2.21 (s, 6H), 2.82–2.95 (br, 8H), 3.22–3.34 (br, 8H), 3.49–3.60 (br, 16H), 4.02–4.13 (m, 4H), 4.13–4.20 (m, 2H), 4.51–4.59 (br, 2H), 4.59–4.66 (br, 2H), 6.38 (d, $J$ = 6 Hz, 4H), 6.92 (d, $J$ = 8 Hz, 4H), 7.42 (d, $J$ = 8 Hz, 2H), 7.45–7.48 (br, 4H), 7.48–7.51 (br, 4H), 7.56 (d, $J$ = 7 Hz, 2H), 7.66–7.70 (br, 8H), 7.91–7.99 (br, 2H); $^{13}$C NMR (200 MHz, $CDCl_3$): δ = 16.1 (d, $^3J_{CP}$ = 7 Hz), 20.3, 31.1, 34.9, 44.9, 52.3, 52.8, 53.1, 62.7, 69.9, 71.0, 71.1, 117.2, 117.4, 124.5 (q, $^1J_{CF}$ = 273 Hz), 126.1, 127.7, 127.9, 128.9 (q, $^2J_{CF}$ = 31 Hz), 130.0, 130.3, 130.5, 130.8, 134.8, 142.2, 144.6, 154.1, 161.7 (q, $^1J_{CB}$ = 50 Hz) (one signal is missing, possibly because of signal overlap); MS (ESI): $C_{53}H_{82}N_4O_9P^+$ ([**2**-H]$^+$) calcd *m*/*z* 949.5819; found *m*/*z* 949.5779.

[2]Rotaxane **2**-H•$PF_6$: Amberlite® IRA-402 resin (0.21 g) was added to a solution of the [2]rotaxane **2**-H•TFPB (77 mg, 43 μmol) in MeOH (10 mL). The suspension was stirred at room temperature for 5 min and then filtered. The same resin addition/filtration process was applied to the filtrate for another nine cycles. The organic solution was then treated with 1 N $HCl_{(aq)}$ (0.1 mL, 0.1 mmol) and saturated $NH_4PF_{6(aq)}$ (20 mL). The organic solvent was evaporated under reduced pressure and the residue was partitioned between $CH_2Cl_2$ (50 mL) and $H_2O$ (10 mL). The organic layer was separated, washed with $H_2O$ (4 × 10 mL), dried ($MgSO_4$), and concentrated; the residue was purified chromatographically ($SiO_2$; $CH_3CN/CH_2Cl_2$,

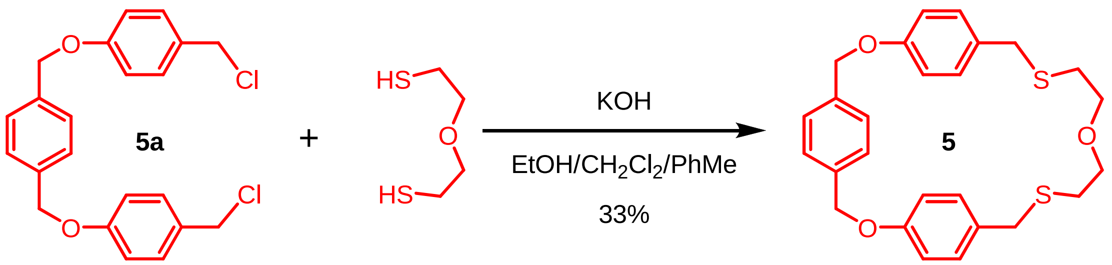
1:9) to give the product as a white solid (43 mg, 92%). M.p. = 182–183 °C; $^1$H NMR (400 MHz, $CD_3CN$): δ = 1.23 (t, *J* = 7 Hz, 6H), 1.33 (s, 9H), 2.19 (s, 6H), 2.89–2.98 (br, 8H), 3.25–3.34 (m, 8H), 3.59–3.66 (m, 16H), 3.92–4.00 (m, 4H), 4.09–4.13 (m, 2H), 4.59–4.67 (m, 4H), 6.47 (d, *J* = 8 Hz, 4H), 6.93 (d, *J* = 8 Hz, 4H), 7.44 (d, *J* = 8 Hz, 2H), 7.52 (d, *J* = 8 Hz, 2H), 7.57 (d, *J* = 8 Hz, 2H), 7.63 (d, *J* = 8 Hz, 2H), 7.95–8.10 (br, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 16.7 ($^3J_{CP}$ = 7 Hz), 20.4, 31.6, 35.5, 45.5, 53.2, 53.4, 53.5, 63.0 ($^2J_{CP}$ = 5 Hz), 70.7, 72.0, 72.1, 117.4, 127.0, 128.9, 129.6, 129.7, 130.8, 131.5, 131.9, 146.6 ($^3J_{CP}$ = 5 Hz), 154.3; MS (ESI): $C_{53}H_{82}N_4O_9P^+$ ([**2**-H]$^+$) calcd *m/z* 949.5819; found *m/z* 949.5788.

*N*-Benzyl-1-(3,5-di-*tert*-butylphenyl)methanamine (**4**): A mixture of benzylamine (0.5 mL, 4.58 mmol), 3,5-di-*tert*-butylbenzaldehyde (1.0 g, 4.58 mmol), and molecular sieves (1.0 g) in dry MeOH (23 mL) was stirred at room temperature for 16 h before being cooled to 0 °C and treated with $NaBH_4$ (0.348 g, 9.16 mmol) in portions. The resulting mixture was stirred at room temperature for 4 h and then the organic solvent was evaporated under reduced pressure. The residue was partitioned between $CH_2Cl_2$ (100 mL) and $H_2O$ (100 mL). The organic phase was collected, washed with $H_2O$ (100 mL), dried ($MgSO_4$), and concentrated; the residue was purified chromatographically ($SiO_2$; MeOH/$CH_2Cl_2$, 2:98) to give the product as a colorless oil (0.73 g, 51%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.32 (s, 18H), 3.79 (s, 2H), 3.82 (s, 2H), 7.15 (d, *J* = 2 Hz, 2H), 7.29–7.34 (m, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 31.6, 34.8, 53.3, 53.7, 120.7, 122.1, 126.6, 128.0, 128.1, 139.1, 140.2, 150.4; MS (ESI): $C_{22}H_{32}N^+$ ([**4**-H]$^+$) calcd *m*/*z* 310.2535; found *m*/*z* 310.2567.

**4**-H·$PF_6$: A solution of the amine **4** (216 mg, 0.704 mmol) in MeCN (10 mL) was treated with 1 N $HCl_{(aq)}$ (5 mL) and saturated $NH_4PF_{6(aq)}$ (10 mL). After evaporating the organic solvent under reduced pressure, the white precipitate was filtered off, washed with water (5 mL) and ether (2 mL), and then dried to give a white solid (232 mg, 72%). M.p. = 173–178 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 18H), 4.12–4.20 (br, 4H), 7.14 (d, *J* = 2 Hz, 2H), 7.29–7.36 (br, 2H), 7.38–7.44 (br, 3H), 7.45–7.49 (br, 1H); $^{13}$C NMR (100 MHz, $CD_3CN$): δ = 31.6, 35.6, 52.4, 52.8, 124.4, 125.2, 129.8, 130.5, 130.5, 131.0, 131.2, 152.5; MS (ESI): $C_{22}H_{32}N^+$ ([**4**-H]$^+$) calcd *m*/*z* 310.2535; found *m*/*z* 310.2562.

**4**-H·TFPB: A solution of the amine **4** (290 mg, 0.945 mmol) in MeOH (10 mL) was treated with 1 N $HCl_{(aq)}$ (10 mL). The organic solvent was evaporated under reduced pressure and then the precipitate was filtered off, dissolved in MeOH (10 mL), and treated with NaTFPB (256 mg, 0.289 mmol). After evaporating the organic solvent under reduced pressure, the residue was partitioned between $CH_2Cl_2$ (50 mL) and $H_2O$ (50 mL). The organic layer was collected, washed with $H_2O$ (4 × 50 mL), dried ($MgSO_4$), and concentrated to give a pale green liquid (194 mg, 57%). M.p. > 66 °C (dec.); $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.29 (s, 18H), 4.08–4.16 (m, 4H), 7.06 (d, $J$ = 2 Hz, 2H), 7.17 (d, $J$ = 7 Hz, 2H), 7.39 (t, $J$ = 7 Hz, 2H), 7.46 (d, $J$ = 7 Hz, 1H), 7.48–7.52 (br, 4H), 7.56 (t, $J$ = 2 Hz, 1H), 7.65–7.72 (br, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 31.2, 35.0, 52.2, 53.0, 117.4, 124.5 (q, $^1J_{CF}$ = 272 Hz), 123.2, 125.1, 127.5, 128.1, 128.8 (q, $^2J_{CF}$ = 32 Hz), 129.0, 129.9, 130.9, 134.7, 153.1, 161.5 (q, $^1J_{CB}$ = 50 Hz); MS (ESI): $C_{22}H_{32}N^+$ ([**4**-H]$^+$) calcd $m/z$ 310.2535; found $m/z$ 310.2525.

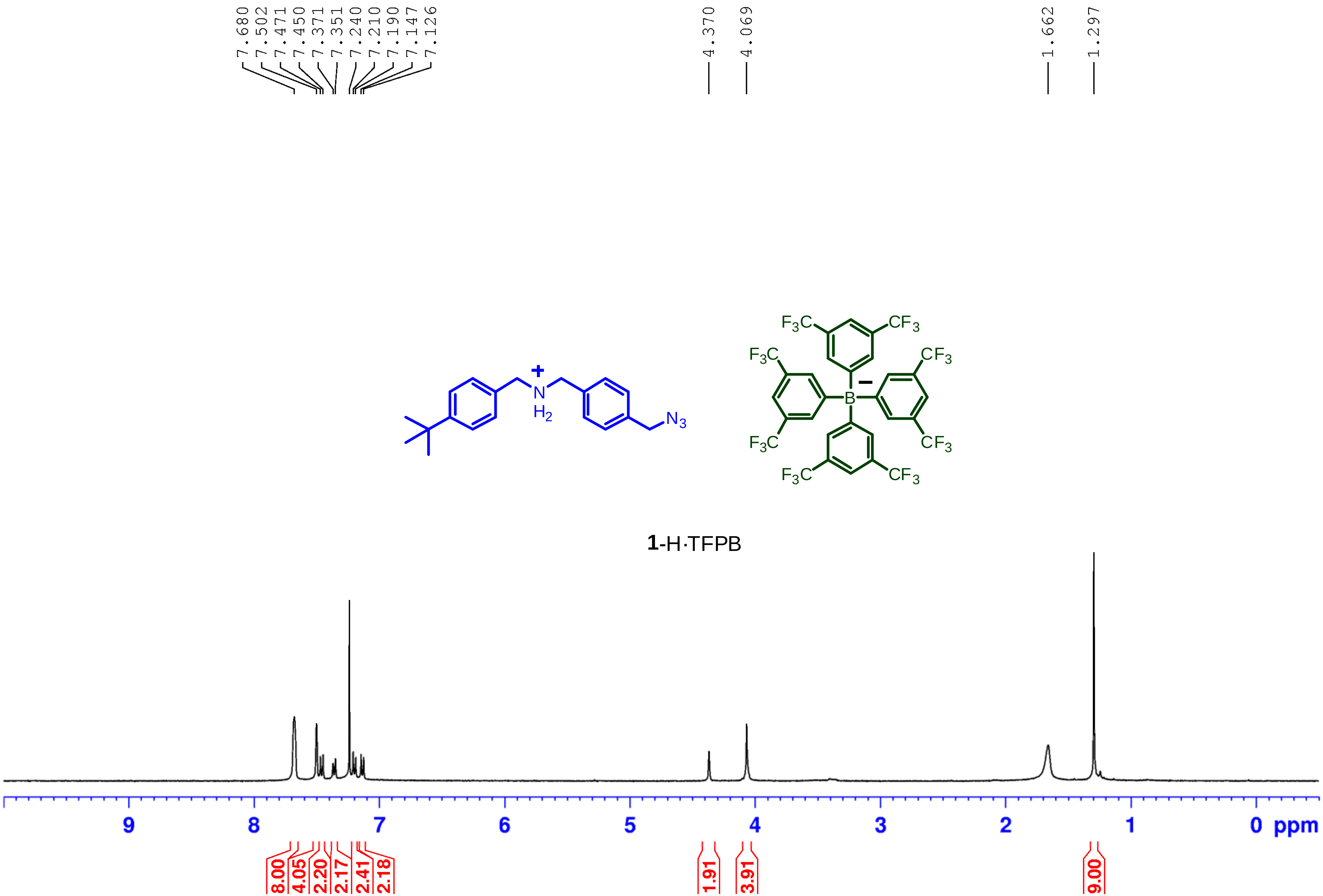
Macrocycle **5**




A solution of the dichloride **5a** (3.12 g, 8 mmol) and bis(2-mercaptoethyl) ether (1 mL, 8 mmol) in a mixture of $CH_2Cl_2$ (100mL) and toluene (700 mL) was added slowly (addition funnel) to a solution of KOH (896 mg, 16.0 mmol) in EtOH (2.4 L). The mixture was then stirred at room temperature for 7 days. The organic solvents were evaporated under reduced pressure and then the residue was purified chromatographically ($SiO_2$; EtOAc/hexanes, 2:8) to give a white solid (1.2 g, 33%). M.p. = 129–130 °C; $^1$H NMR (400 MHz, $CDCl_3$): δ = 2.42 (t, $J$ = 7 Hz, 4H), 3.47 (t, $J$ = 7 Hz, 4H), 3.63 (s, 4H), 5.17 (s, 4H), 6.67 (d, $J$ = 8 Hz, 4H), 7.04 (d, $J$ = 8 Hz, 4H), 7.30 (s, 4H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 29.6, 35.5, 69.5, 70.5, 115.5, 127.0, 129.6, 130.0, 136.9, 156.6; MS (ESI): $C_{26}H_{28}NaO_3S_2^+$ ([**5** + Na]$^+$) calcd $m/z$ 475.1378; found $m/z$ 475.1343.

Threadlike salt **6**-H·TFPB: A solution of **6**-H·$PF_6$ (300 mg, 0.676 mmol) and NaTFPB (599 mg, 0.676 mmol) in MeOH (20 mL) was treated with $H_2O$ (10 mL). The mixture was stirred at room temperature for 5 min and then the organic solvent was evaporated under reduced pressure. The solution was partitioned between $CH_2Cl_2$ (50 mL) and $H_2O$ (150 mL). The organic layer was collected, washed with $H_2O$ (4 × 150 mL), dried ($MgSO_4$), and concentrated to give a deep green oil (707 mg, 90%). $^1$H NMR (400 MHz, $CDCl_3$): δ = 0.60 (q, $J$ = 6 Hz, 1H), 1.13–1.22 (m, 2H), 1.29 (s, 9H), 1.66–1.82 (m, 4H), 2.16–2.34 (m, 2H), 2.91–3.07 (m, 2H), 4.00 (t, $J$ = 6 Hz, 2H), 4.94 (dd, $J$ = 2, 10 Hz, 1H), 5.08 (dd, $J$ = 1, 17 Hz, 1H), 5.16–5.67 (m, 2H), 6.73–6.93 (br, 2H), 7.18 (d, $J$ = 8 Hz, 2H), 7.45 (d, $J$ = 8 Hz, 2H), 7.50–7.53 (br, 4H), 7.67–7.76 (br, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 15.1, 17.1, 22.9, 24.3, 25.1, 31.0, 34.9, 48.1, 52.2, 115.1, 117.4, 124.4 (q, $^1J_{CF}$ = 272 Hz), 125.1, 126.7, 127.0, 128.8 (q, $^2J_{CF}$ = 27 Hz), 132.7, 134.6, 137.4, 154.4, 161.5 (q, $^1J_{CB}$ = 50 Hz); MS (ESI): $C_{21}H_{32}N^+$ ([**6**-H]$^+$) calcd *m*/*z* 298.2535; found *m*/*z* 298.2482.

[2]Rotaxane **7**-H·TFPB and dumbbell-shaped salt **8**-H·TFPB: A solution of the threadlike salt **6**-H·TFPB (466 mg, 0.401 mmol) and the macrocycle **5** (363 mg, 0.802 mmol) in $CDCl_3$ (2.0 mL) was heated at 50 °C with stirring for 48 h. After evaporating the organic solvent under reduced pressure, the residue was purified chromatographically ($SiO_2$; $CH_2Cl_2$/hexanes, 8:2) to give the [2]rotaxane **7**-H·TFPB, which solidified in hexane to give a white powder (193 mg, 30%). The corresponding dumbbell-shaped salt **8**-H·TFPB was isolated as a colorless liquid (106 mg, 23%) after two sequential chromatographic purification processes ($SiO_2$; $CH_2Cl_2$/MeOH, 9:1 and then $CH_2Cl_2$/MeOH 98:2). Data for **7**-H·TFPB: m.p. = 125–127 °C; $^1$H NMR (500 MHz, $CDCl_3$): δ = 0.25–0.75 (m, 6H), 1.37 (s, 9H), 1.95–2.26 (m, 3H), 2.65–2.85 (m, 5H), 2.92–3.09 (m, 3H), 3.36–3.62 (m, 8H), 5.08–5.25 (m, 4H), 5.38 (dd, $J$= 5, 11 Hz, 1H), 5.64–5.79 (m, 3H), 6.54–6.86 (several overlapping broad peaks, 10H), 6.99 (d, $J$ = 8 Hz, 2H), 7.43 (s, 4H), 7.48–7.52 (br, 4H), 7.56 (d, $J$ = 8 Hz, 2H), 7.65–7.73 (br, 8H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ = 24.2, 29.0, 31.1, 32.1, 32.4, 33.8, 34.9, 36.3, 37.0, 47.1, 51.6, 67.7, 69.0, 117.4, 124.6 (q, $^1J_{CF}$ = 272 Hz), 125.7, 126.4, 128.5, 128.6, 128,7, 128.9 (q, $^2J_{CF}$ = 31 Hz), 129.2, 129.4, 131.3, 134.0, 137.3, 137.4, 154.7, 156.9, 161.7 (q, $^1J_{CB}$ = 50 Hz) (two signals missing, possibly because of signal overlap); MS (ESI): $C_{47}H_{60}NO_3S_2^+$ ([**7**-H]$^+$) calcd *m*/*z* 750.4014; found *m*/*z* 750.3990. Data for **8**-H·TFPB: $^1$H NMR (400 MHz, $CDCl_3$): δ = 1.26–1.40 (m, 11H), 1.50–1.65 (m, 2H), 1.99–2.10 (m, 1H), 2.13–2.24 (m, 1H) 2.35–2.48 (br, 1H), 2.62–2.73 (m, 1H), 2.80 (t, $J$ = 8 Hz 2H), 2.86–2.98 (m, 1H), 3.65–3.80 (br, 2H), 3.83 (s, 2H), 5.39–5.47 (m, 1H), 5.55–5.70 (m, 3H), 7.08 (d, $J$ = 8 Hz, 2H), 7.43 (d, $J$ = 8 Hz, 2H), 7.52 (s, 4H), 7.69 (s, 8H); $^{13}$C NMR (100 MHz, $CDCl_3$): δ = 24.7, 28.6, 31.1, 32.6, 32.6, 34.9, 36.7, 48.4, 52.4, 117.4, 124.4 (q, $^1J_{CF}$ = 271 Hz), 126.8, 127.1, 128.5, 128.6, 128.8 (q, $^2J_{CF}$ = 32 Hz), 129.1, 133.9, 134.7, 154.1, 161.5 (q, $^1J_{CB}$ = 50 Hz) (one signal missing, possibly because of signal overlap); MS (ESI): $C_{21}H_{32}N^+$ ([**8**-H]$^+$) calcd *m*/*z* 298.2535; found *m*/*z* 298.2518.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N
$H_2$
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5
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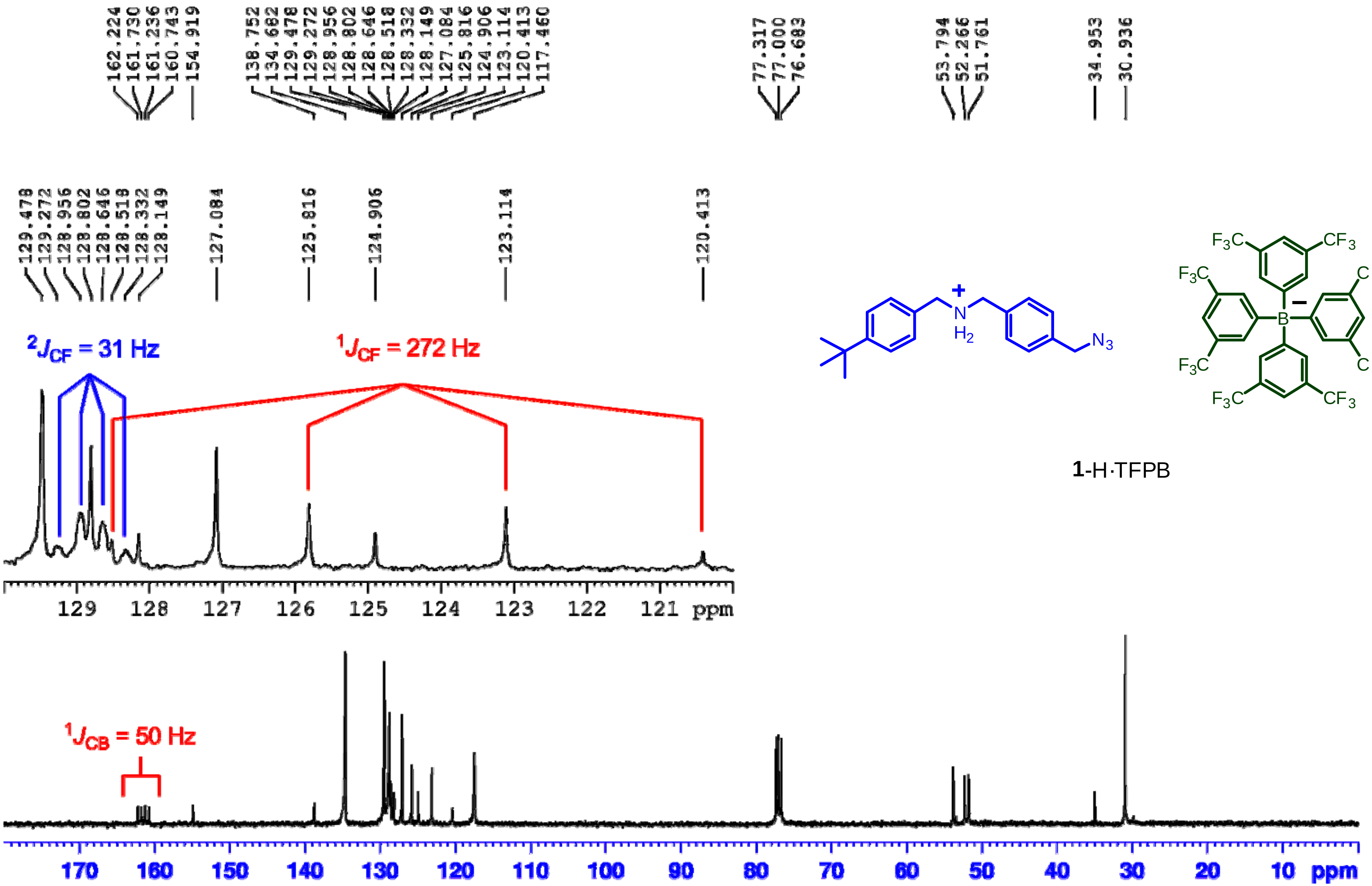
**1**-H·TFPB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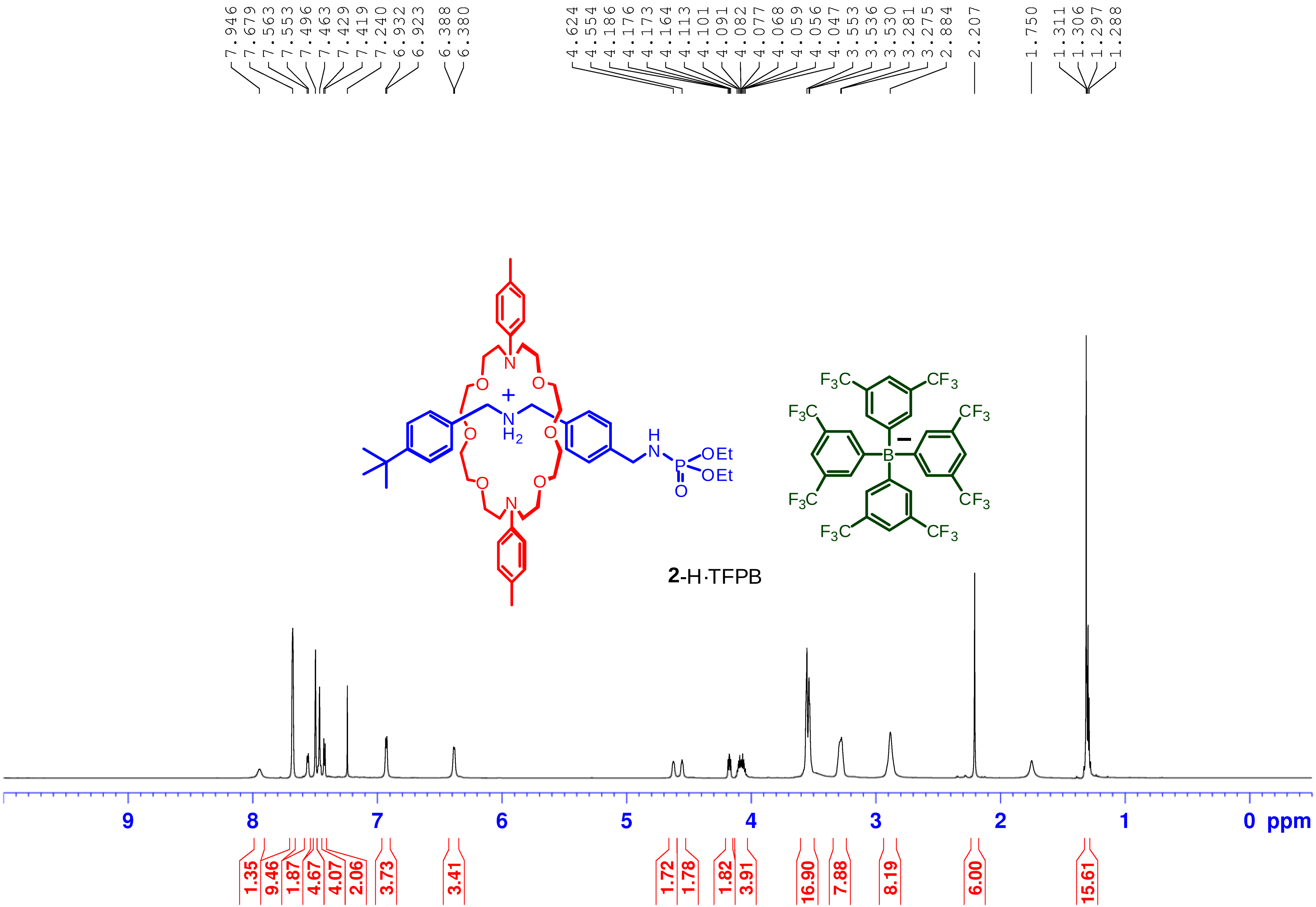
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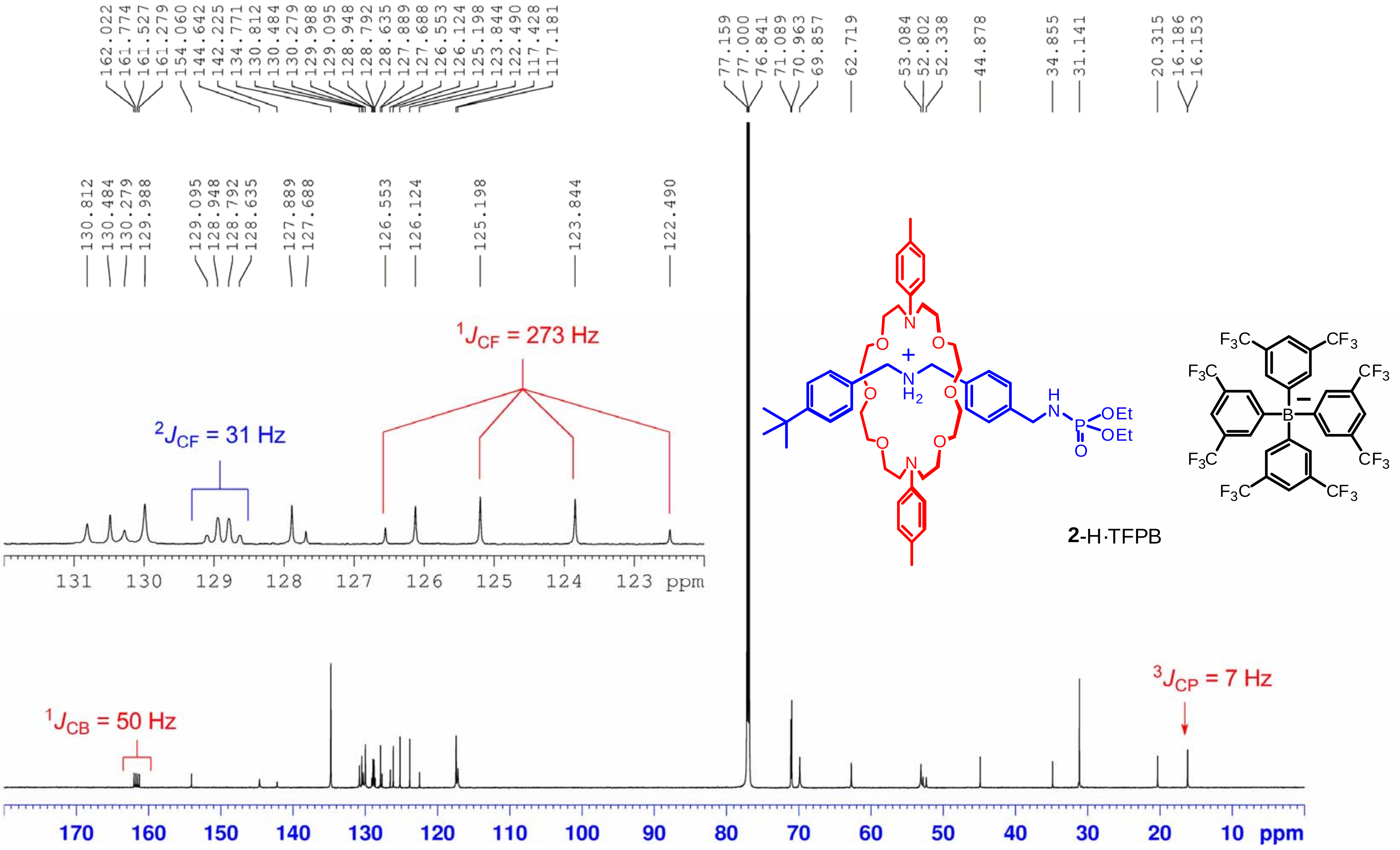

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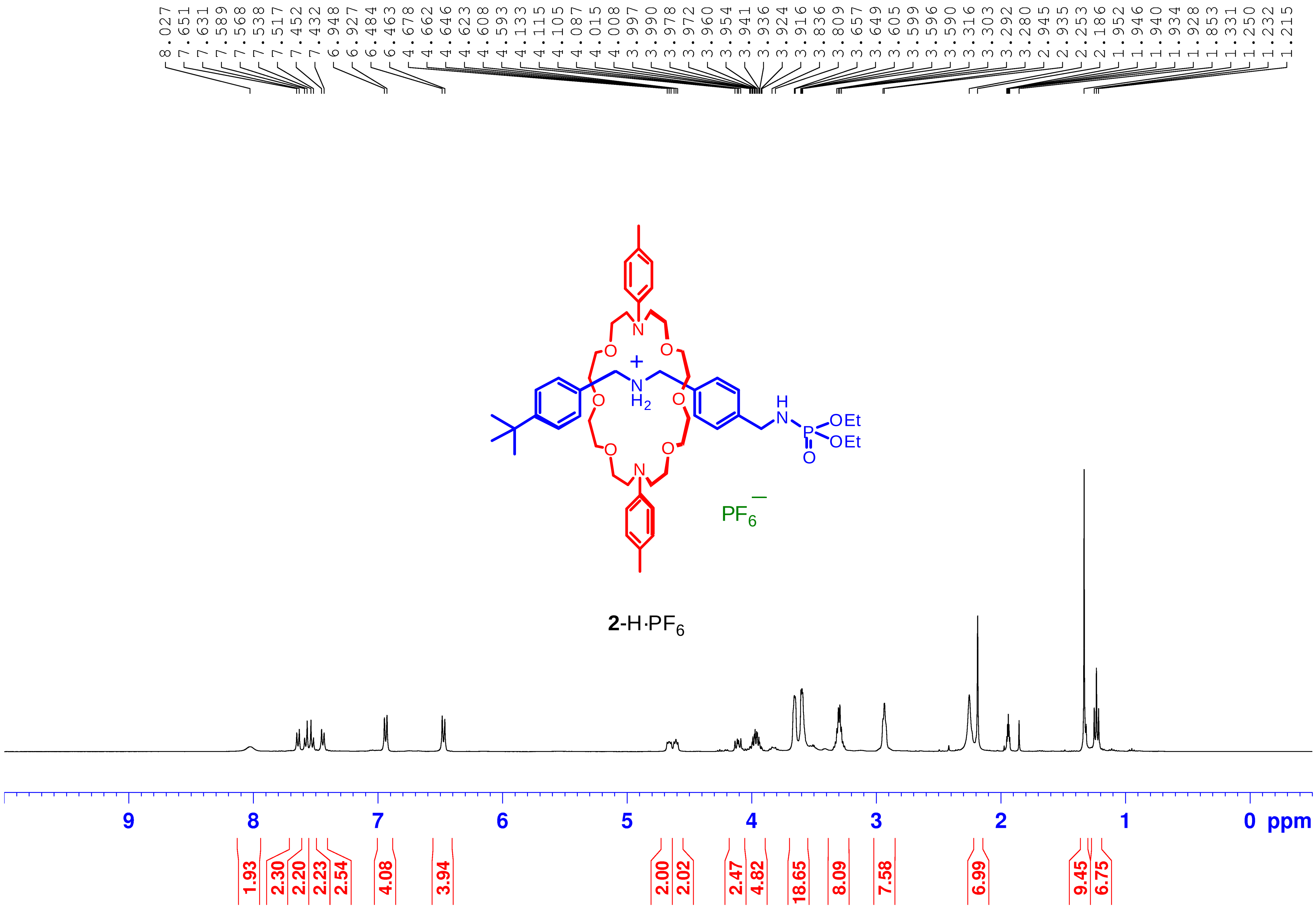

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H2
O
O
H
N
P
OEt
OEt
O
O
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N
PF6
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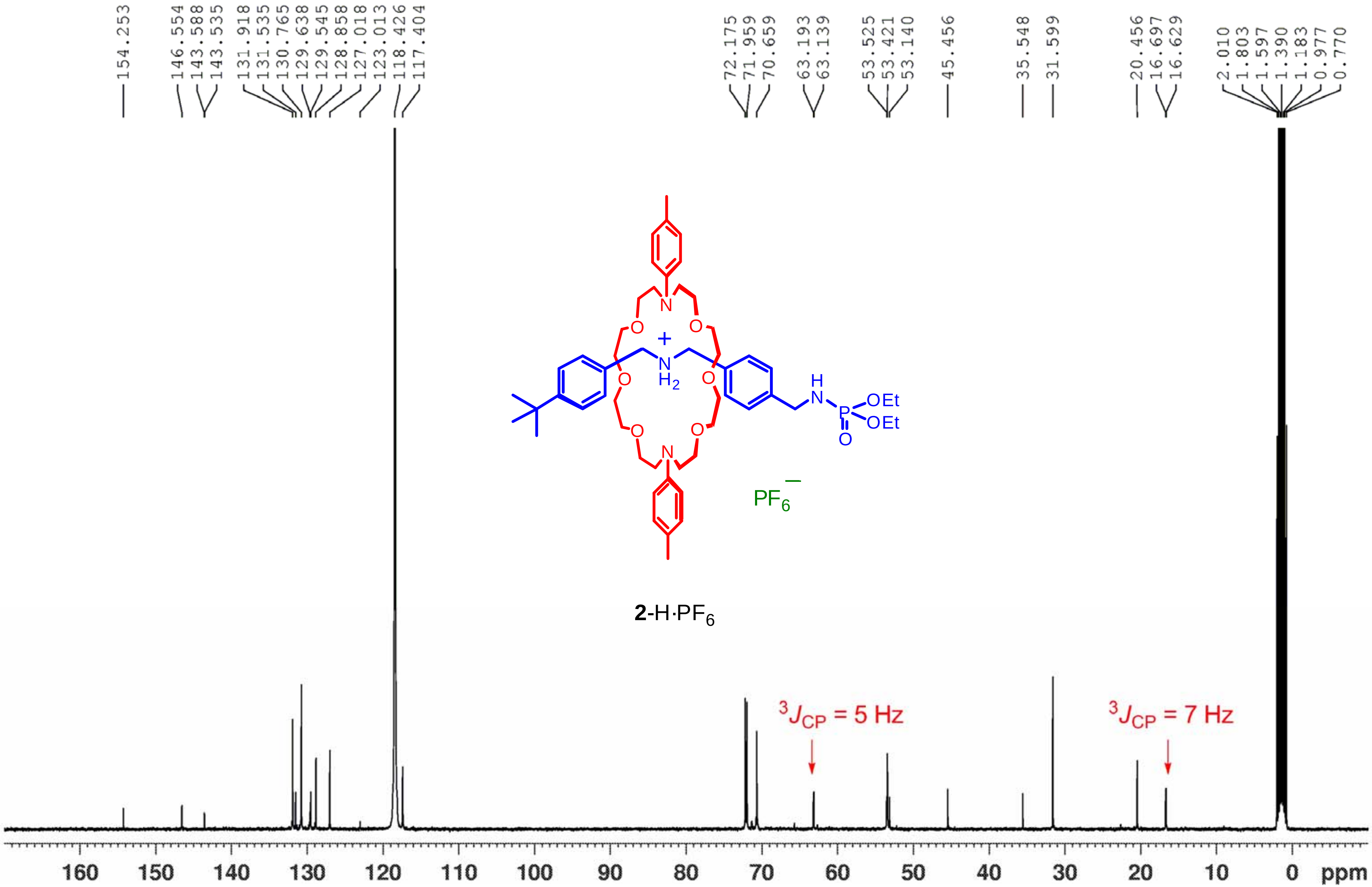
**2**-H·$PF_6$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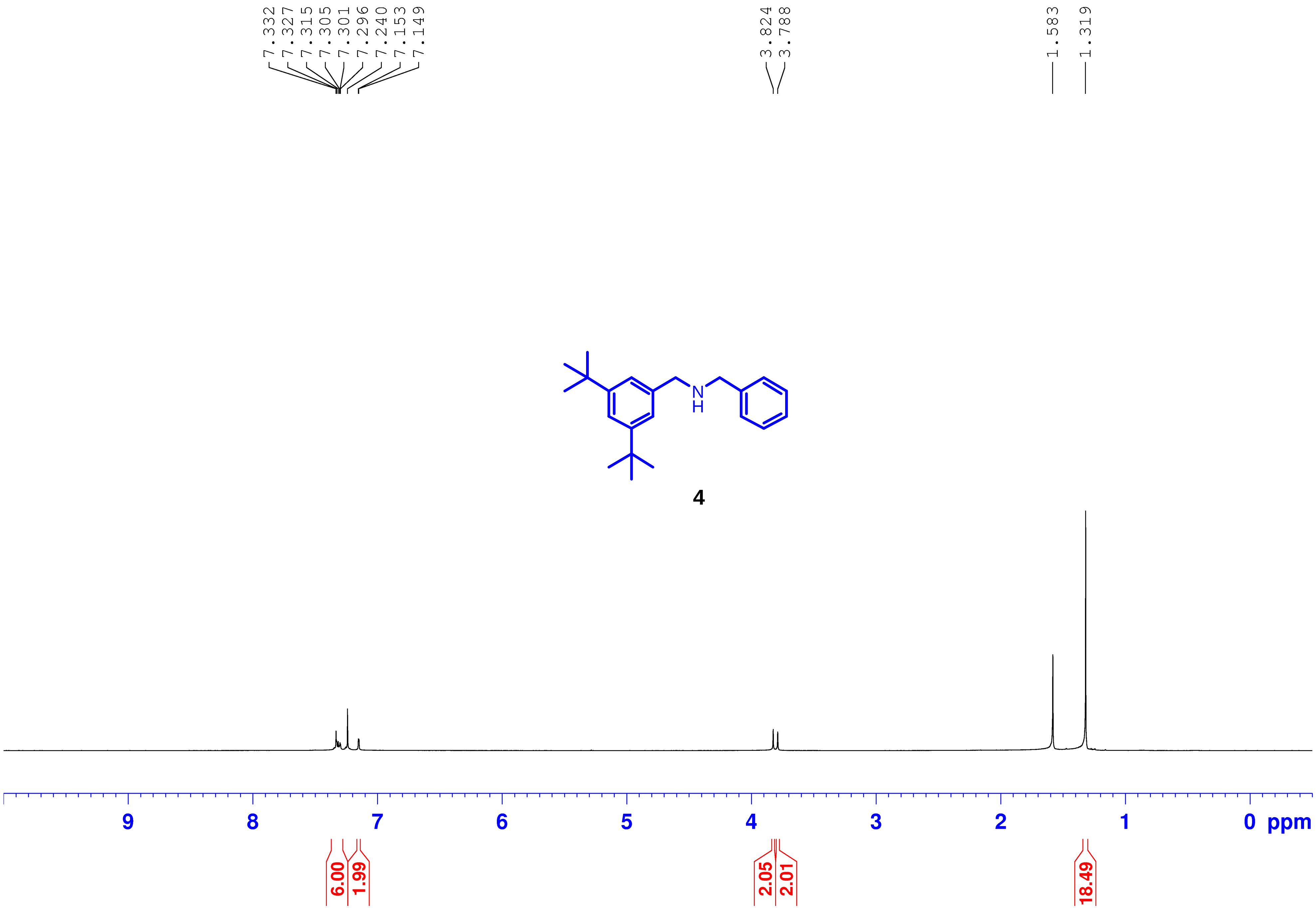
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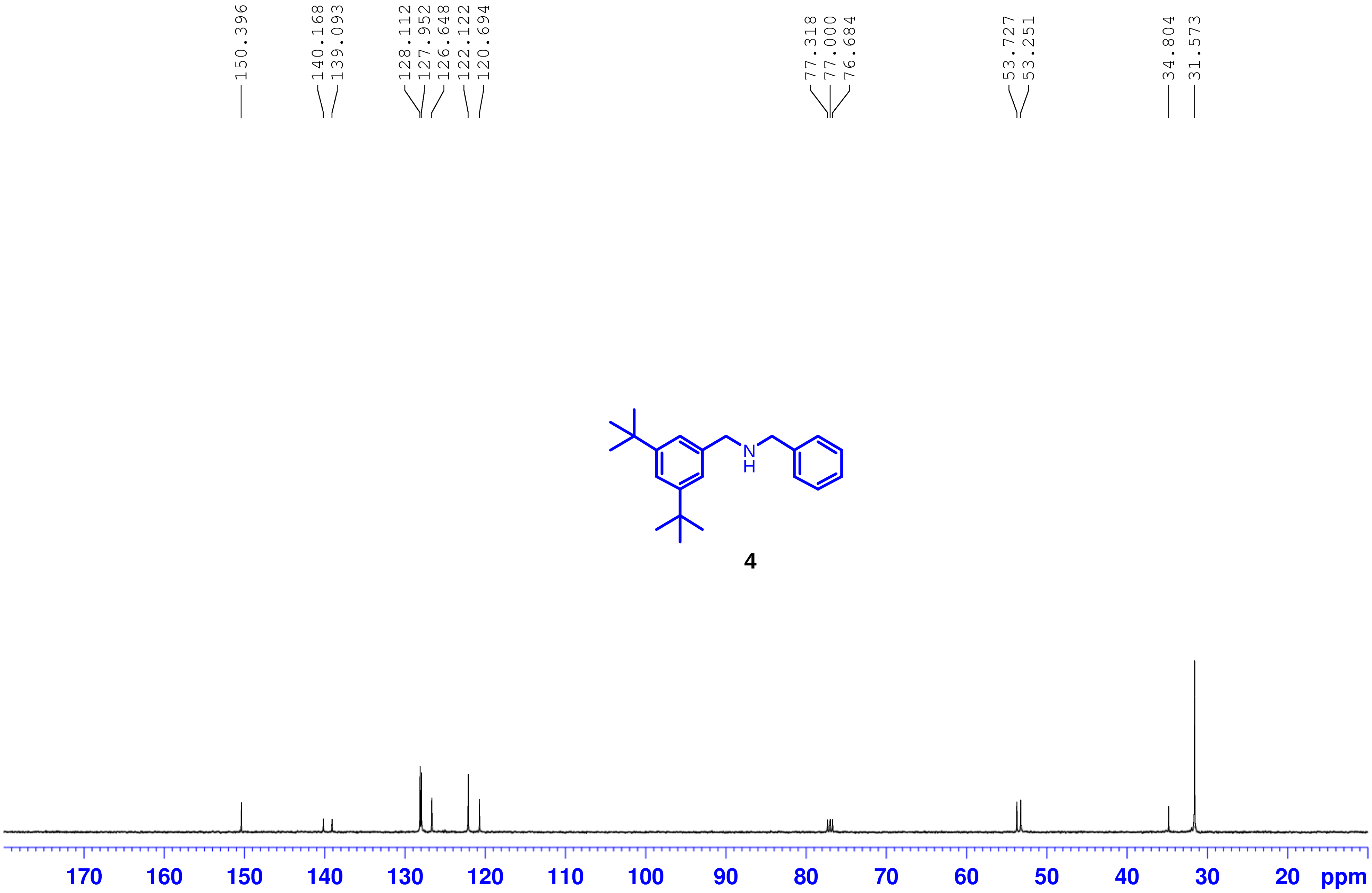
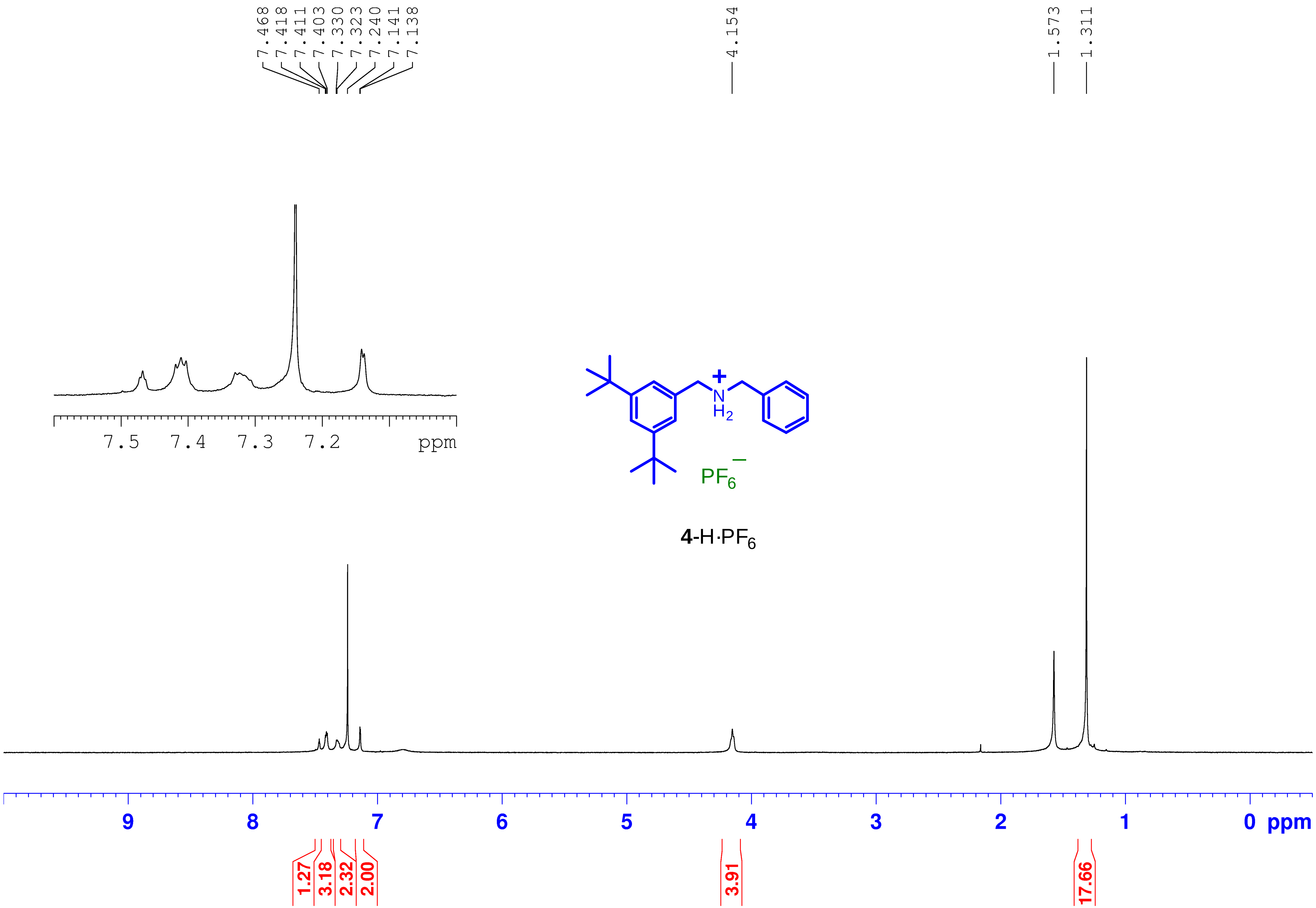
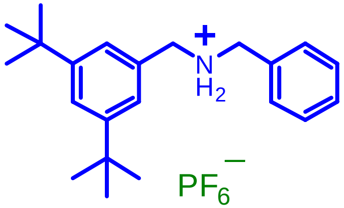
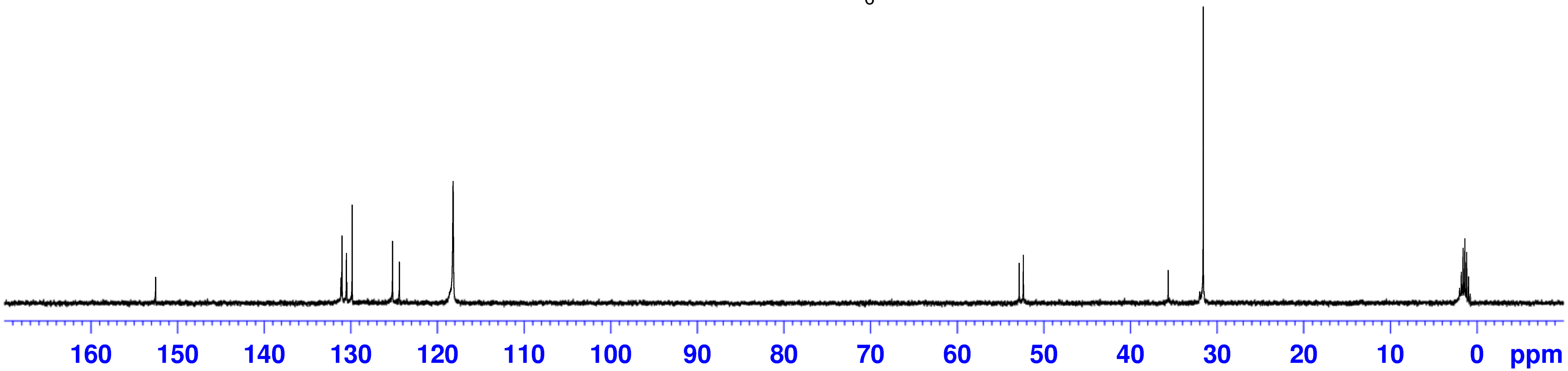
2.01
18.49

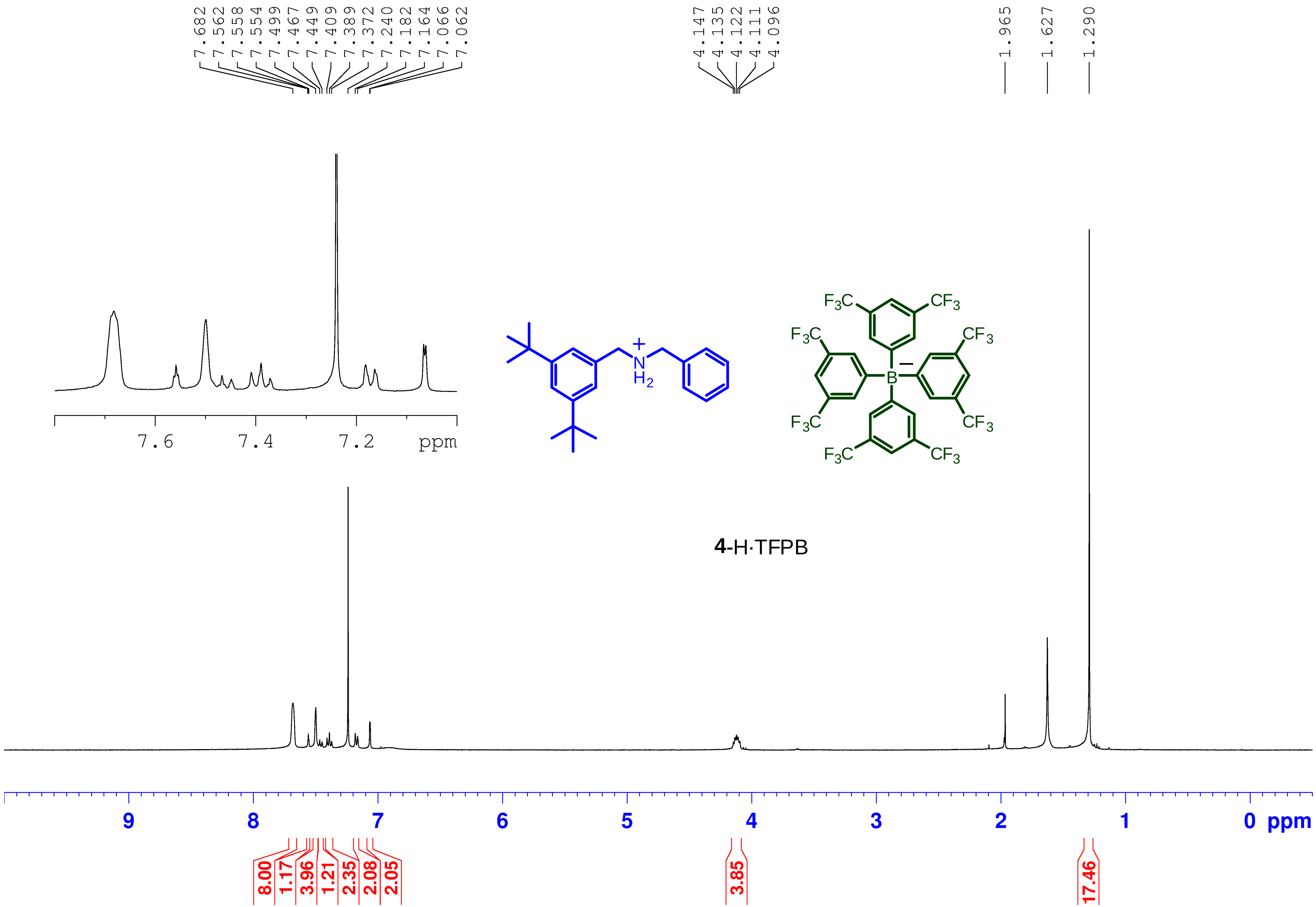

150.396
140.168
139.093
128.112
127.952
126.648
122.122
120.694
77.318
77.000
76.684
53.727
53.251
34.804
31.573
N
H
4
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm


7.468
7.418
7.411
7.403
7.330
7.323
7.240
7.141
7.138
4.154
1.573
1.311
7.5
7.4
7.3
7.2
ppm
N
H2
PF6
4-H·PF6
9
8
7
6
5
4
3
2
1
0
ppm
1.27
3.18
2.32
2.00
3.91
17.66

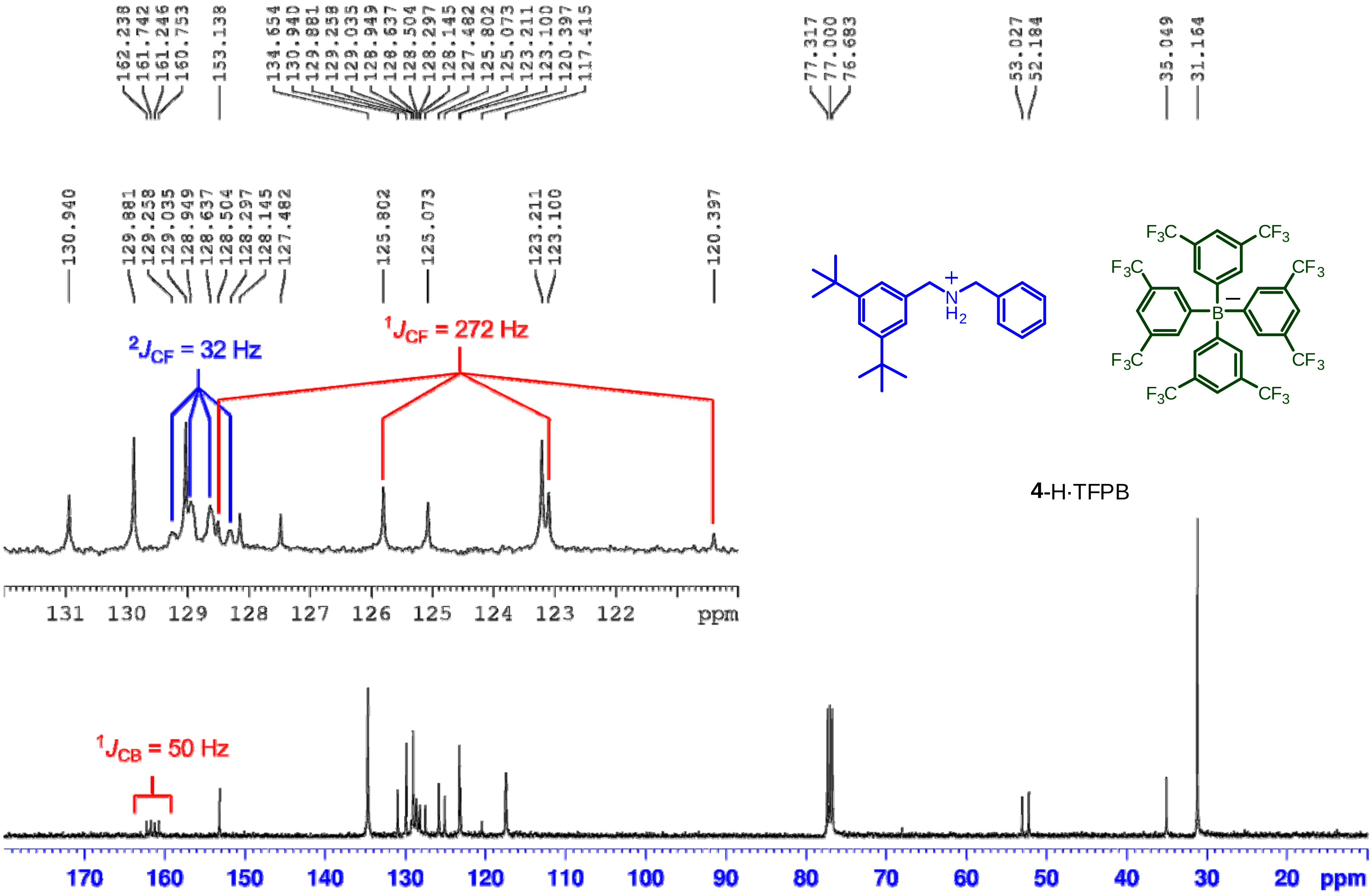

N
H2
PF6

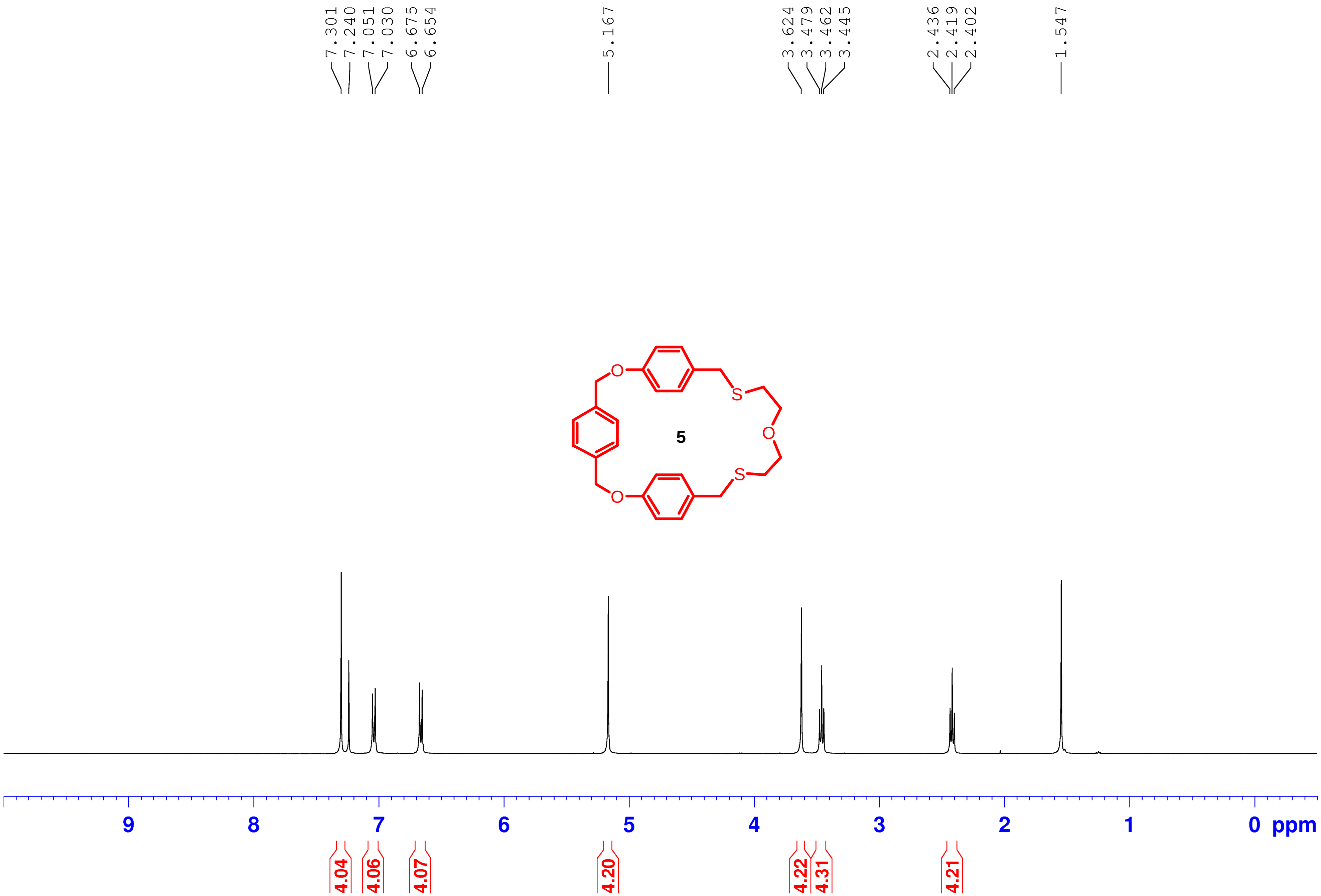
**4**-H·$PF_6$

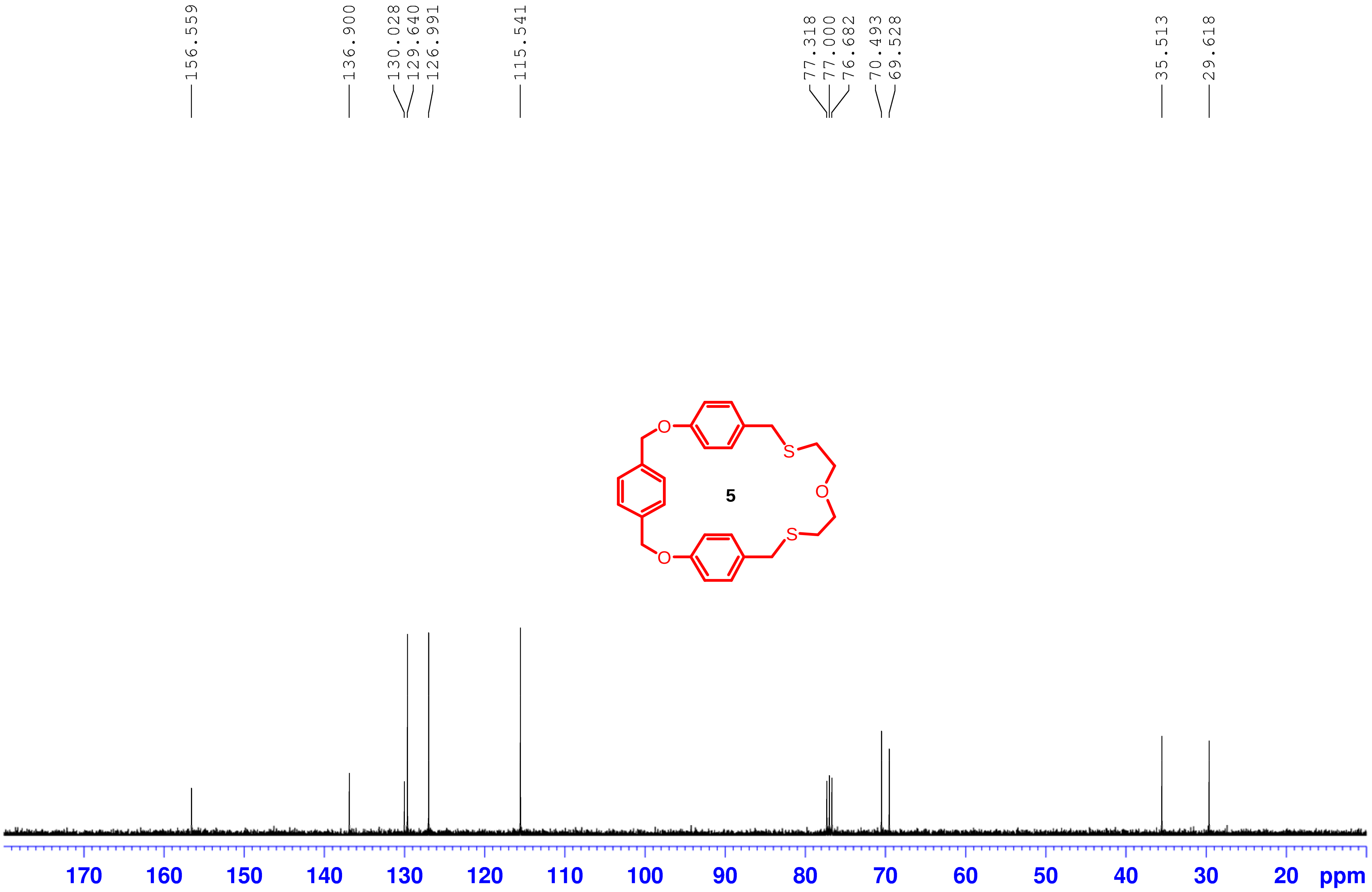

152.519
131.152
131.031
130.517
130.471
129.848
125.187
124.404
118.199
52.846
52.363
35.647
31.595
2.007
1.802
1.593
1.390
1.184
0.976
0.774
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

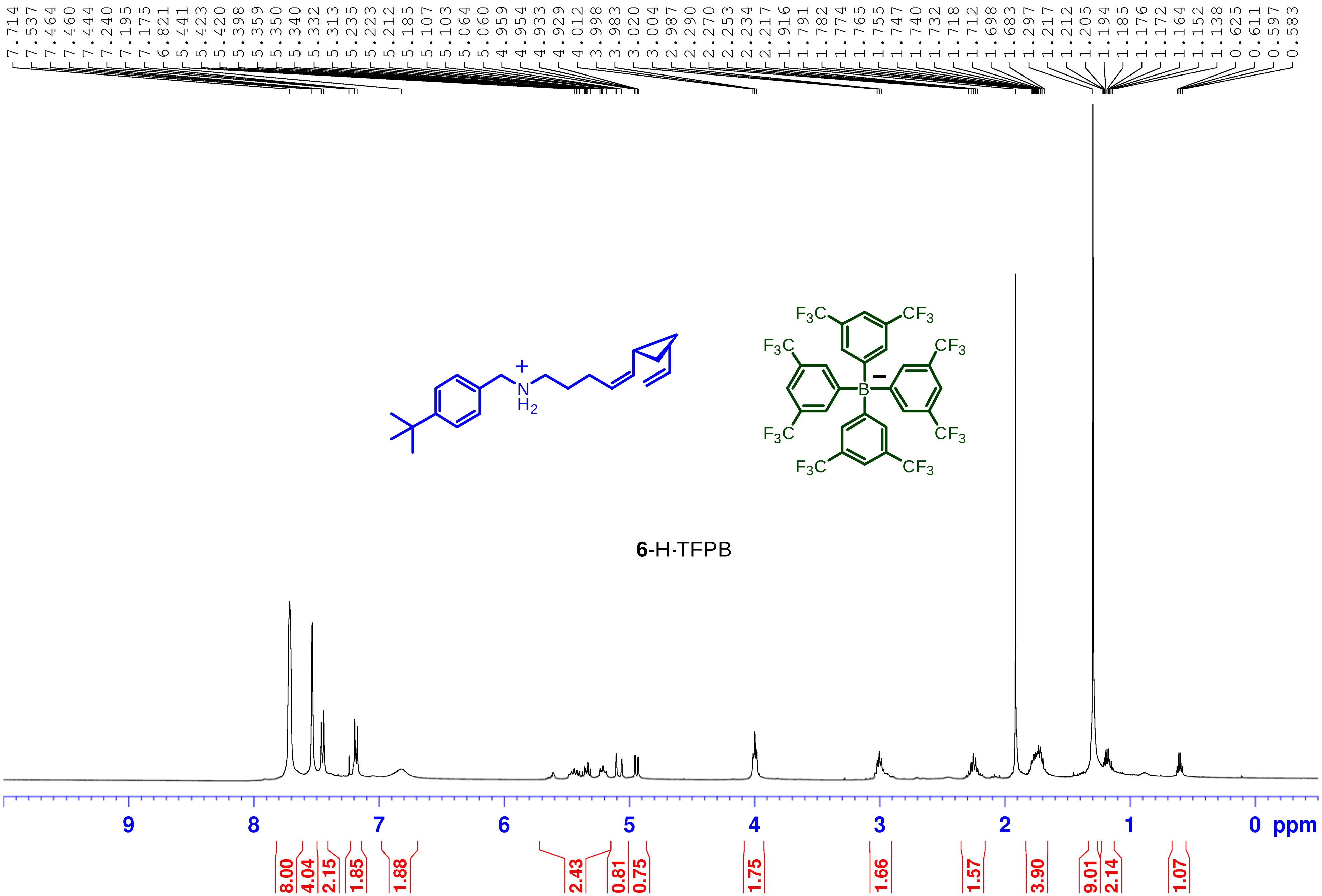

7.682
7.562
7.558
7.554
7.499
7.467
7.449
7.409
7.389
7.372
7.240
7.182
7.164
7.066
7.062
4.147
4.135
4.122
4.111
4.096
1.965
1.627
1.290
8.00
1.17
3.96
1.21
2.35
2.08
2.05
3.85
17.46
ppm

**4**-H·TFPB

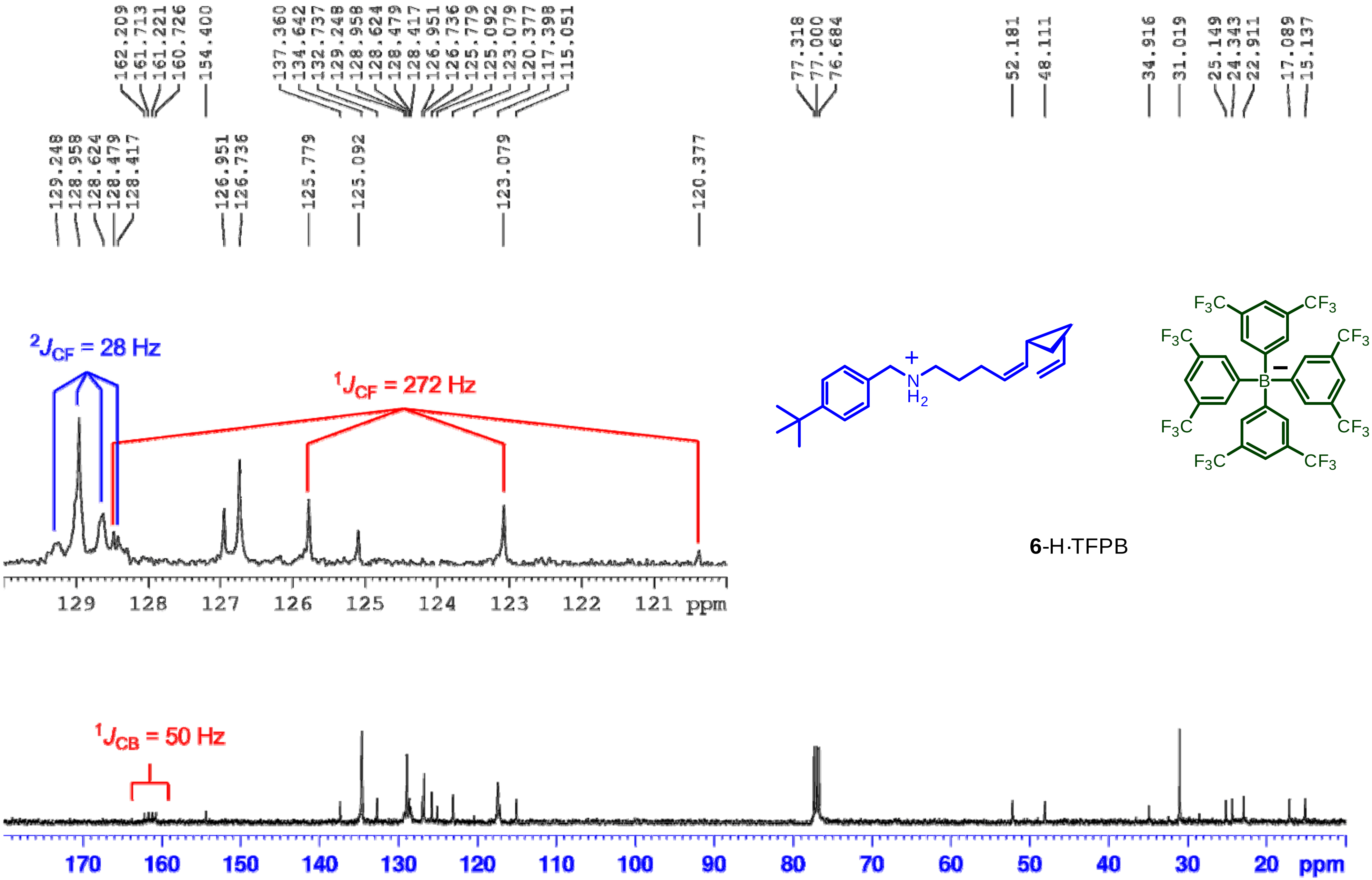

162.238
161.742
161.246
160.753
153.138
134.654
130.940
129.881
129.258
129.035
128.949
128.637
128.504
128.297
128.145
127.482
125.802
125.073
123.211
123.100
120.397
117.415
77.317
77.000
76.683
53.027
52.184
35.049
31.164
$^{2}J_{CF}$ = 32 Hz
$^{1}J_{CF}$ = 272 Hz
$^{1}J_{CB}$ = 50 Hz
ppm
4-H·TFPB


7.301
7.240
7.051
7.030
6.675
6.654
5.167
3.624
3.479
3.462
3.445
2.436
2.419
2.402
1.547
O
S
O
S
O
5
9
8
7
6
5
4
3
2
1
0 ppm
4.04
4.06
4.07
4.20
4.22
4.31
4.21


156.559
136.900
130.028
129.640
126.991
115.541
77.318
77.000
76.682
70.493
69.528
35.513
29.618
5
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

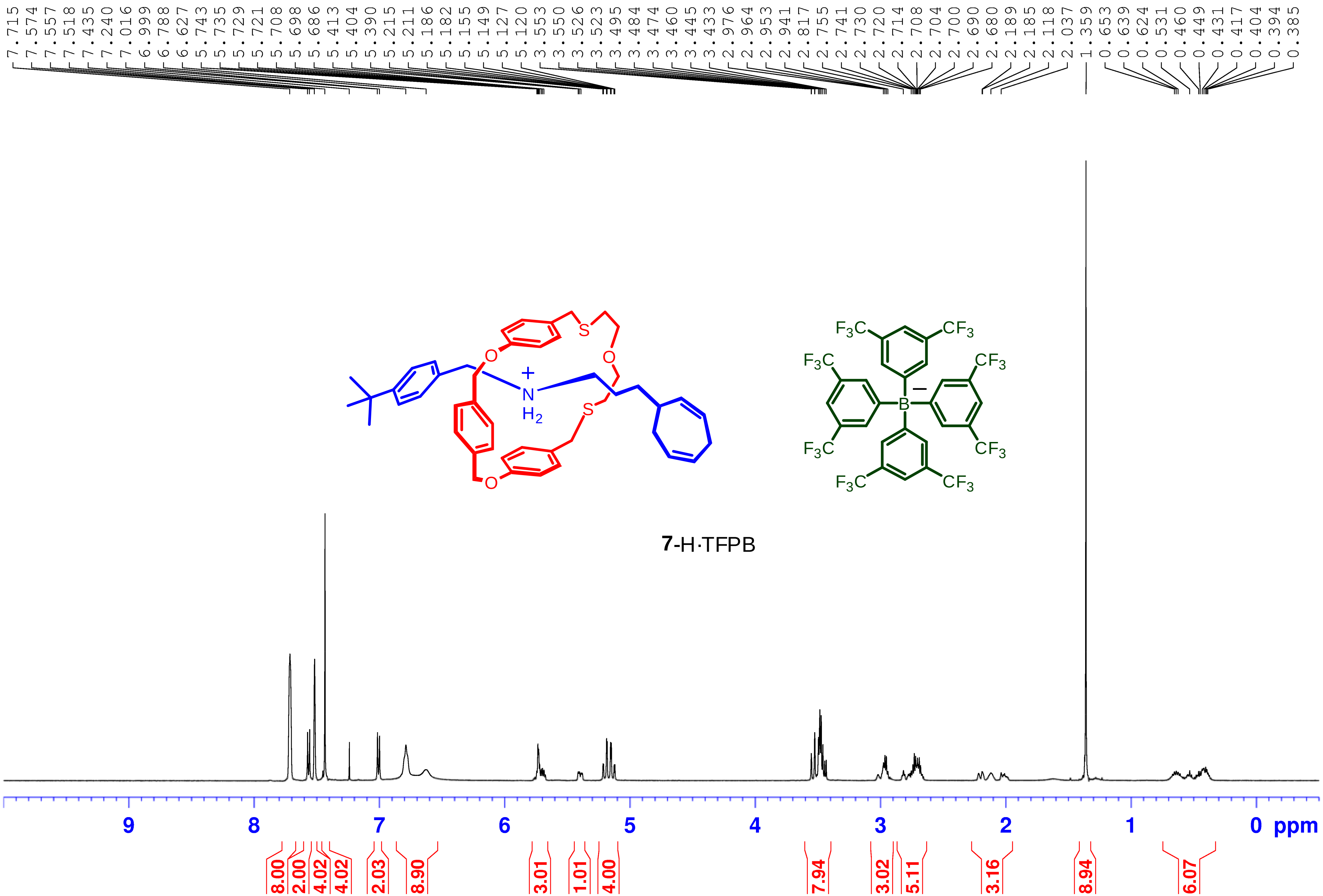

7.714
7.537
7.464
7.460
7.444
7.240
7.195
7.175
6.821
5.441
5.423
5.420
5.398
5.359
5.350
5.340
5.332
5.313
5.235
5.223
5.212
5.185
5.107
5.103
5.064
5.060
4.959
4.954
4.933
4.929
4.012
3.998
3.983
3.020
3.004
2.987
2.290
2.270
2.253
2.234
2.217
1.916
1.791
1.782
1.774
1.765
1.755
1.747
1.740
1.732
1.718
1.712
1.698
1.683
1.297
1.217
1.212
1.205
1.194
1.185
1.176
1.172
1.164
1.152
1.138
0.625
0.611
0.597
0.583
F3C
CF3
N
H2
B
9
8
7
6
5
4
3
2
1
0
ppm
8.00
4.04
2.15
1.85
1.88
2.43
0.81
0.75
1.75
1.66
1.57
3.90
9.01
2.14
1.07

**6**-H·TFPB

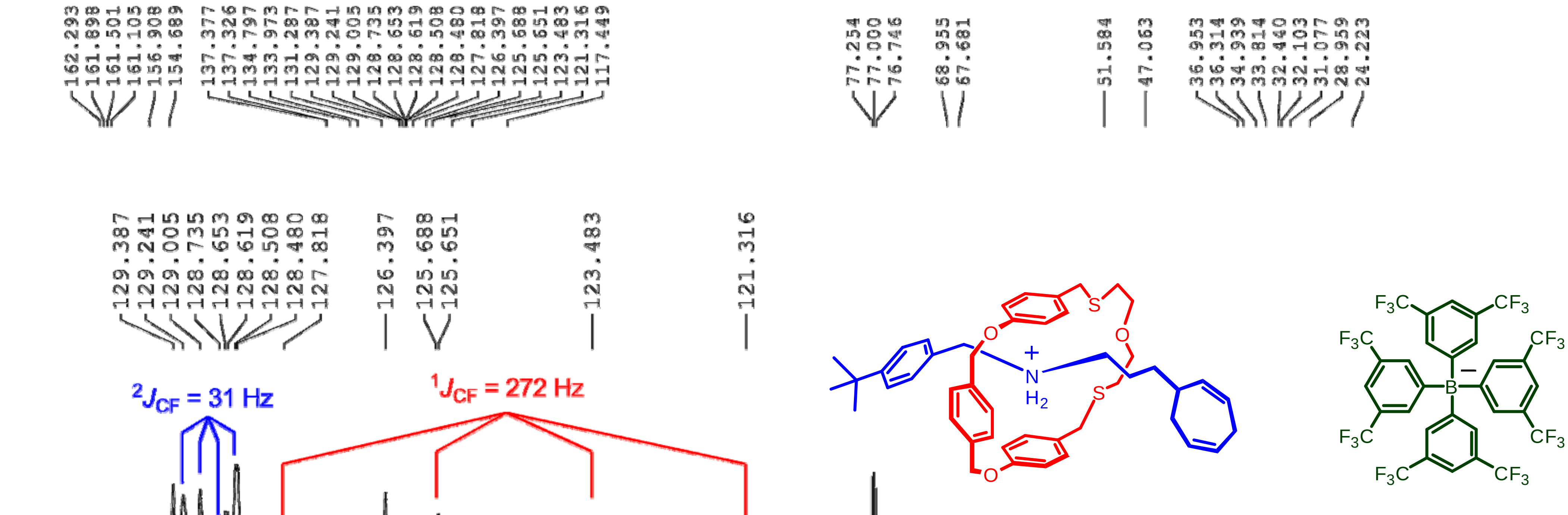


162.209
161.713
161.221
160.726
154.400
137.360
134.642
132.737
129.248
128.958
128.624
128.479
128.417
126.951
126.736
125.779
125.092
123.079
120.377
117.398
115.051
77.318
77.000
76.684
52.181
48.111
34.916
31.019
25.149
24.343
22.911
17.089
15.137
$^2J_{CF}$ = 28 Hz
$^1J_{CF}$ = 272 Hz
$^1J_{CB}$ = 50 Hz
ppm

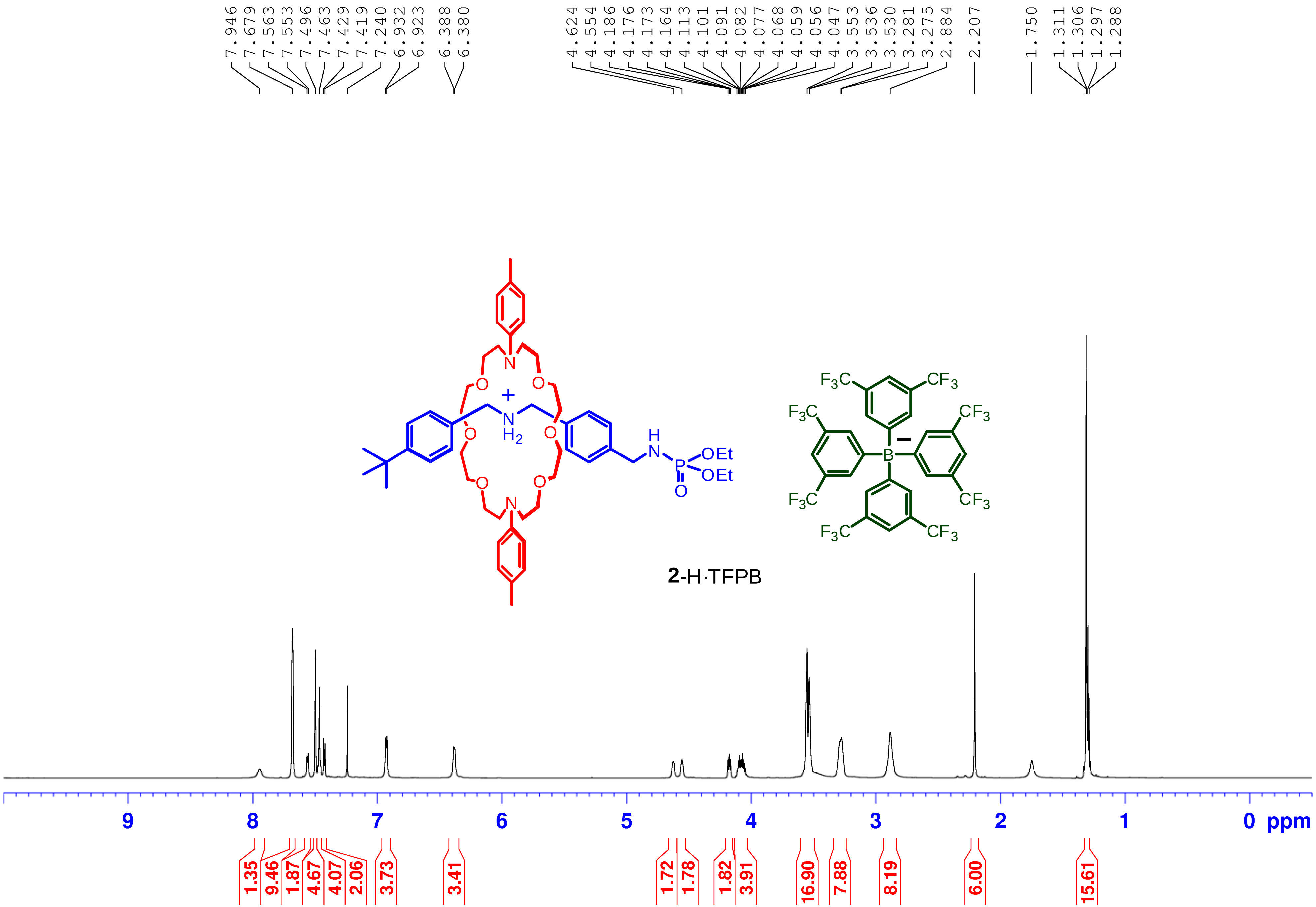

**6**-H·TFPB

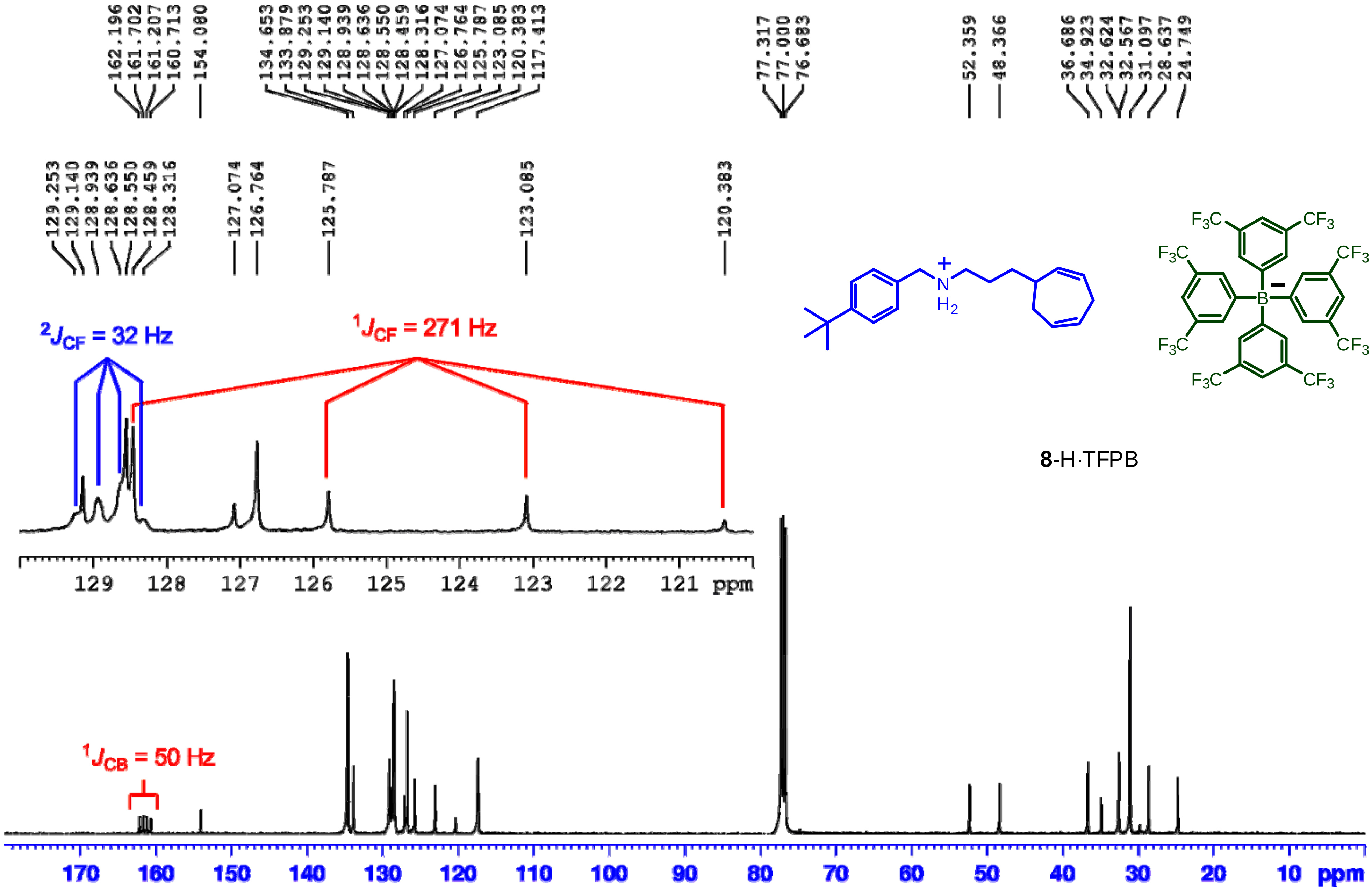

7.715
7.574
7.557
7.518
7.435
7.240
7.016
6.999
6.788
6.627
5.743
5.735
5.729
5.721
5.708
5.698
5.686
5.413
5.404
5.390
5.215
5.211
5.186
5.182
5.155
5.149
5.127
5.120
3.553
3.550
3.526
3.523
3.495
3.484
3.474
3.460
3.445
3.433
2.976
2.964
2.953
2.941
2.817
2.755
2.741
2.730
2.720
2.714
2.708
2.704
2.700
2.690
2.680
2.189
2.185
2.118
2.037
1.359
0.653
0.639
0.624
0.531
0.460
0.449
0.431
0.417
0.404
0.394
0.385
9
8
7
6
5
4
3
2
1
0 ppm
8.00
2.00
4.02
4.02
2.03
8.90
3.01
1.01
4.00
7.94
3.02
5.11
3.16
8.94
6.07
O
S
O
S
O
N
H2
F3C
CF3
B

**7**-H·TFPB


162.293
161.898
161.501
161.105
156.908
154.689
137.377
137.326
134.797
133.973
131.287
129.387
129.241
129.005
128.735
128.653
128.619
128.508
128.480
127.818
126.397
125.688
125.651
123.483
121.316
117.449
77.254
77.000
76.746
68.955
67.681
51.584
47.063
36.953
36.314
34.939
33.814
32.440
32.103
31.077
28.959
24.223
129.387
129.241
129.005
128.735
128.653
128.619
128.508
128.480
127.818
126.397
125.688
125.651
123.483
121.316
²J_CF = 31 Hz
¹J_CF = 272 Hz
130 129 128 127 126 125 124 123 122 ppm
¹J_CB = 50 Hz
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 ppm
O
S
O
N
H2
S
O
F3C
CF3
F3C
CF3
B
F3C
CF3
F3C
CF3

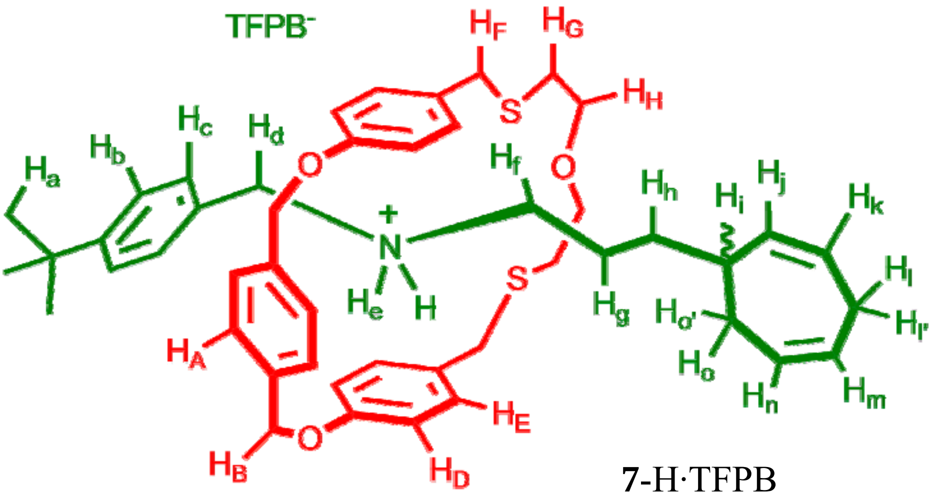
**7**-H·TFPB


7.946 7.679 7.563 7.553 7.496 7.463 7.429 7.419 7.240 6.932 6.923 6.388 6.380
4.624 4.554 4.186 4.176 4.173 4.164 4.113 4.101 4.091 4.082 4.077 4.068 4.059 4.056 4.047 3.553 3.536 3.530 3.281 3.275 2.884 2.207
1.750 1.311 1.306 1.297 1.288
N
O
O
+
N
H2
O
O
H
N
P
OEt
OEt
O
O
O
N
F3C
CF3
F3C
CF3
B
F3C
CF3
F3C
CF3
2-H·TFPB
9 8 7 6 5 4 3 2 1 0 ppm
1.35 9.46 1.87 4.67 4.07 2.06 3.73 3.41 1.72 1.78 1.82 3.91 16.90 7.88 8.19 6.00 15.61

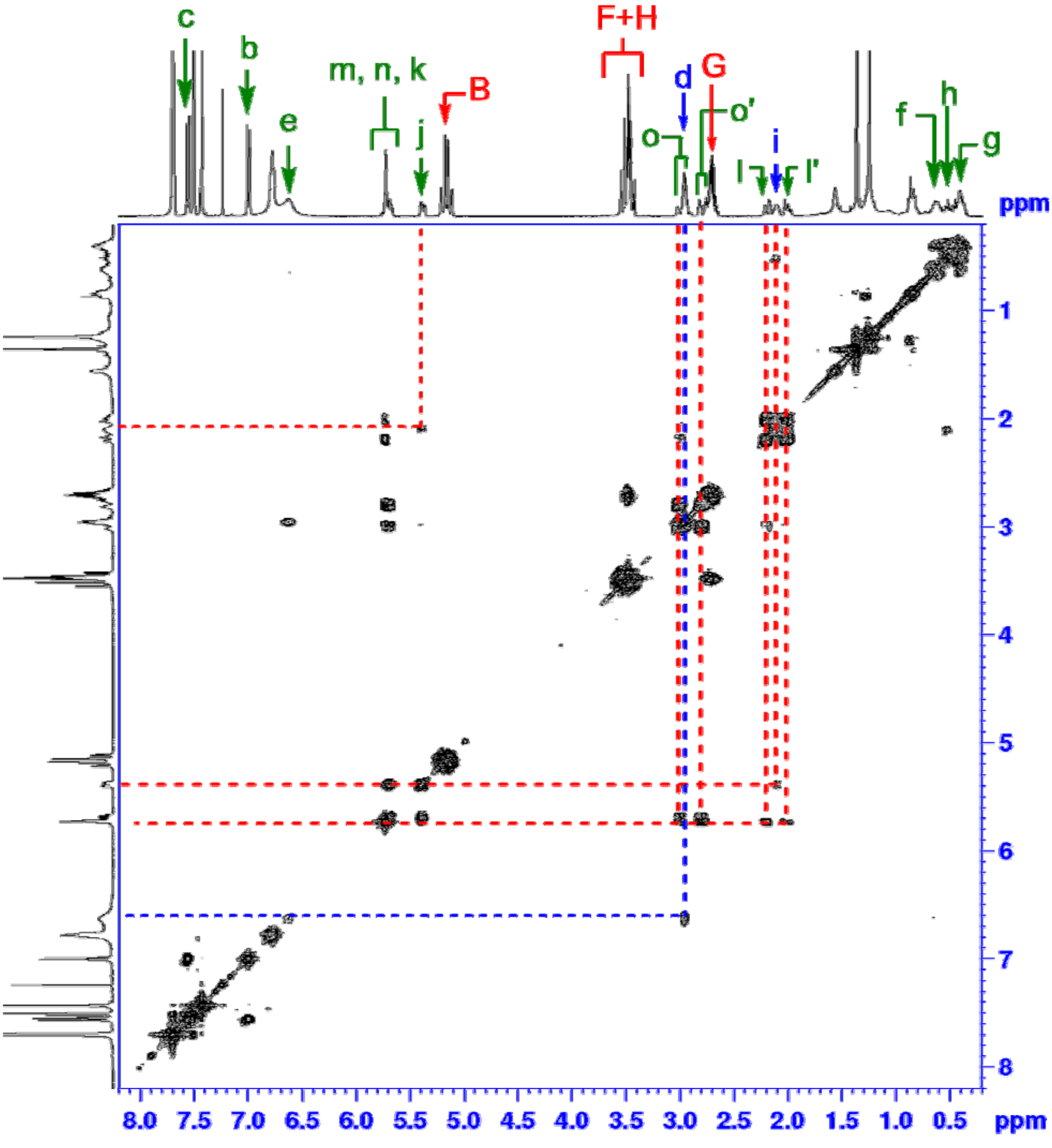

162.196
161.702
161.207
160.713
154.080
134.653
133.879
129.253
129.140
128.939
128.636
128.550
128.459
128.316
127.074
126.764
125.787
123.085
120.383
117.413
77.317
77.000
76.683
52.359
48.366
36.686
34.923
32.624
32.567
31.097
28.637
24.749
$^2J_{CF}$ = 32 Hz
$^1J_{CF}$ = 271 Hz
$^1J_{CB}$ = 50 Hz
129 128 127 126 125 124 123 122 121 ppm
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
$F_3C$
$CF_3$
B
N
$H_2$

**8**-H·TFPB

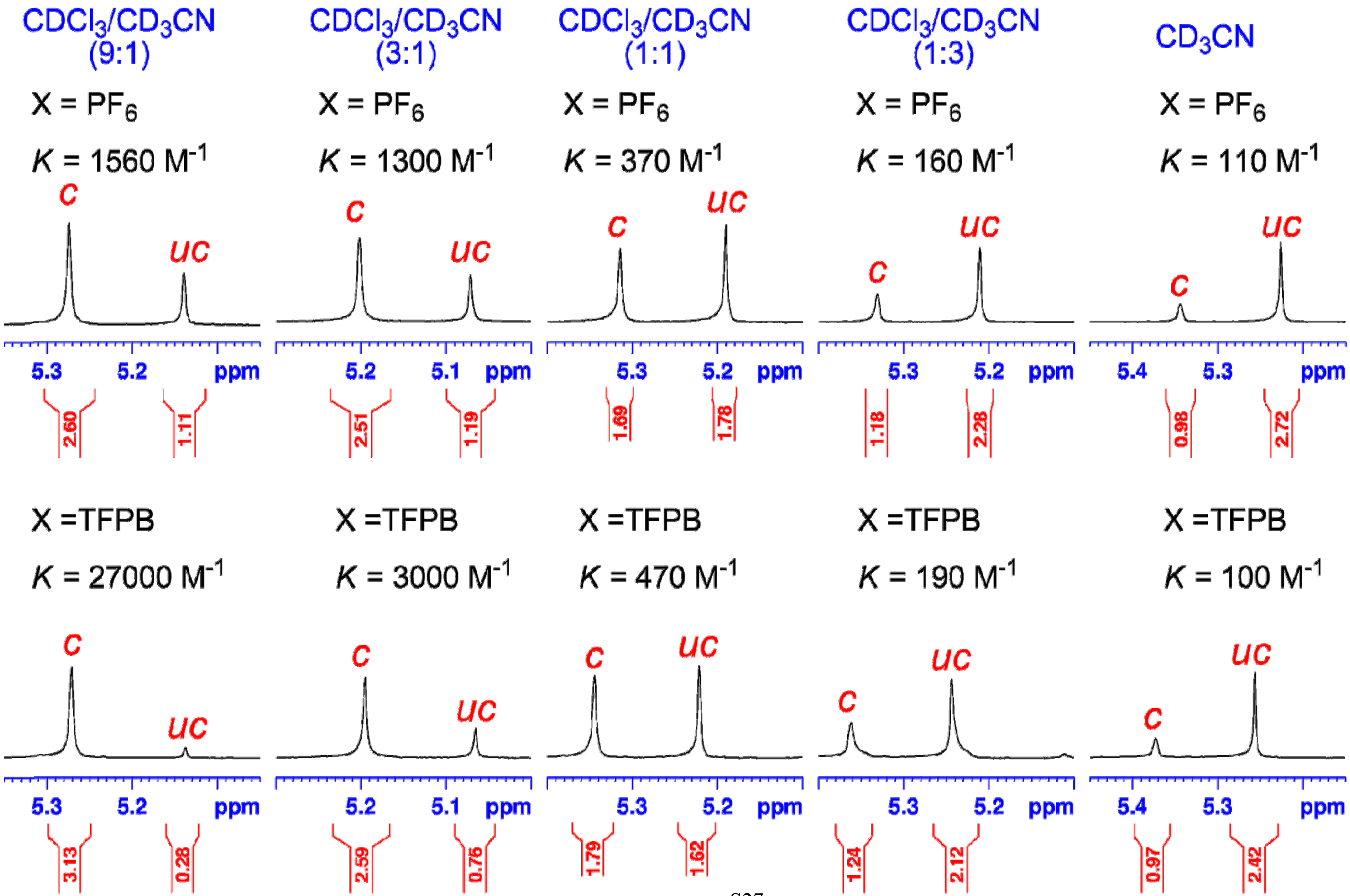
400 MHz NMR COSY CDCl3 298 K



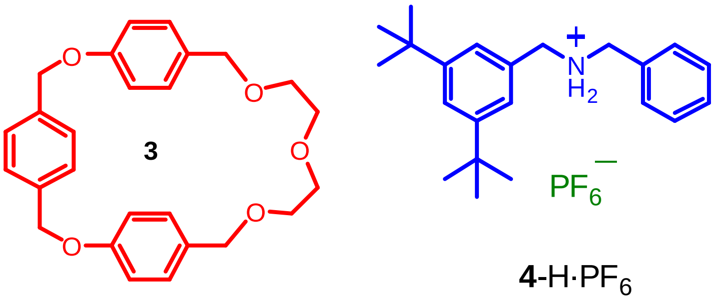

**7**-H·TFPB



Partial $^{1}H$ NMR spectra for the complexation of macrocycle **3** to threadlike salts [**4**-H]$^{+}$ in Various Solvents (400 MHz, 298K, 5mM)

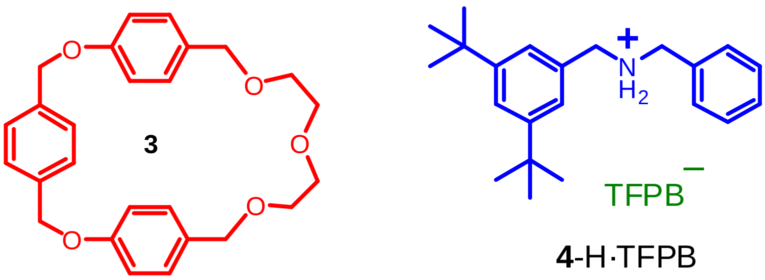


ITC measurements were performed using a Microcal MCS calorimeter interfaced with a microcomputer. All sample solutions were carefully degassed prior to titration using the equipment provided with the instrument. The host molecule in solution ($CHCl_3$) was titrated into the guest solution ($CHCl_3$) using a 280-μL syringe. Each titration consisted of a preliminary 3-μL injection followed by 27 subsequent additions of 10 μL. The entropy of complexation was determined by subtracting the heat of dilution for each titration from the enthalpy of the titration. All experiments were performed at 25 °C. Microcal LLC software was used to compute the thermodynamic parameters of the titration based on the one-site binding model or competitive binding model.




**4**-H·$PF_6$

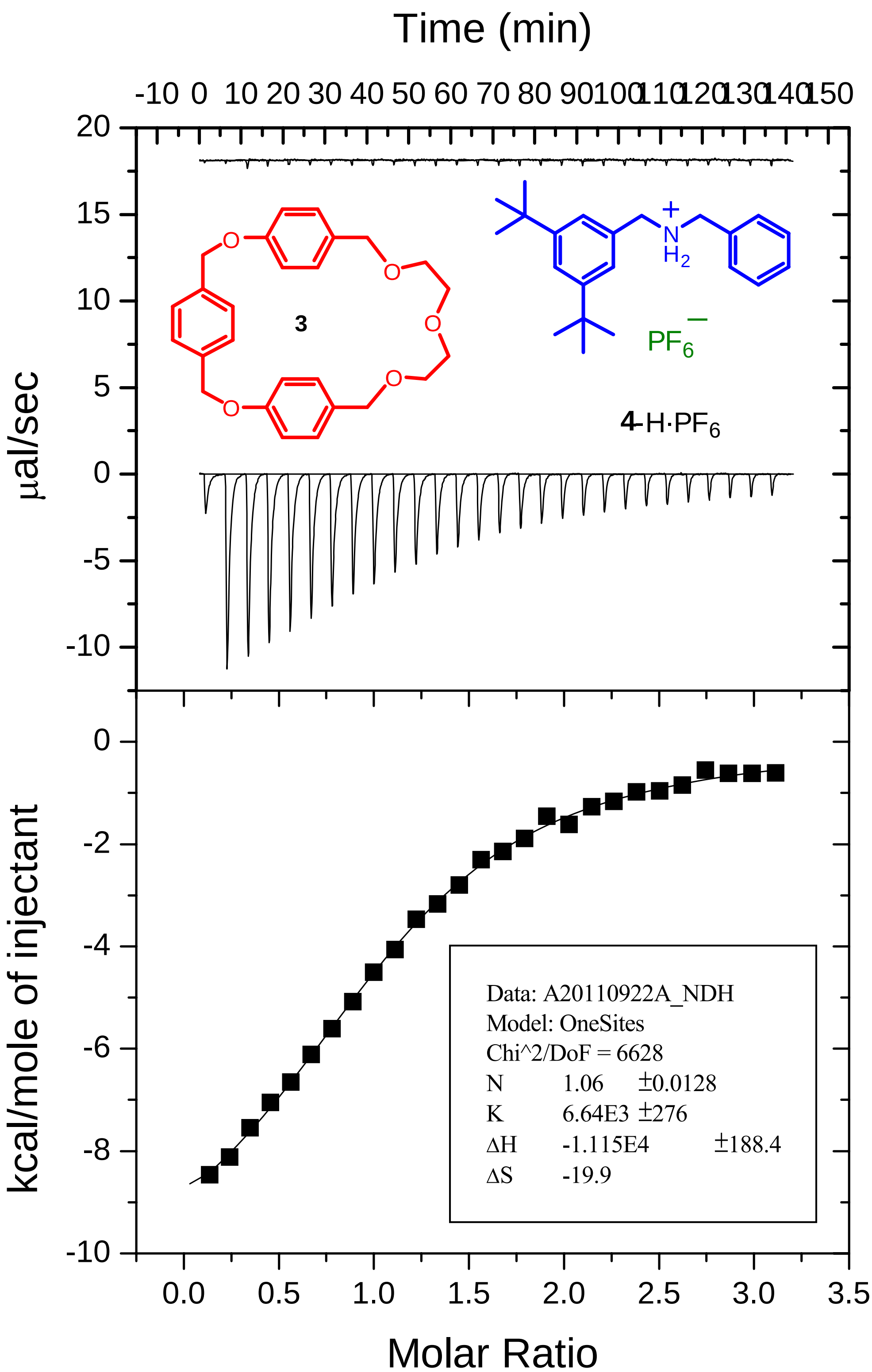
| entry | N | *K* | ΔH | ΔS |
|---|---|---|---|---|
| 1 | 1.060 ± 0.0128 | 6.64E+03 ± 276 | -11150 ± 188.4 | -19.9 |
| 2 | 1.040 ± 0.0141 | 7.17E+03 ± 344 | -11690 ± 220.7 | -21.6 |
| average | 1.050 ± 0.0141 | 6.91E+03 ± 375 | -11420 ± 382 | -20.8 ± 1.2 |



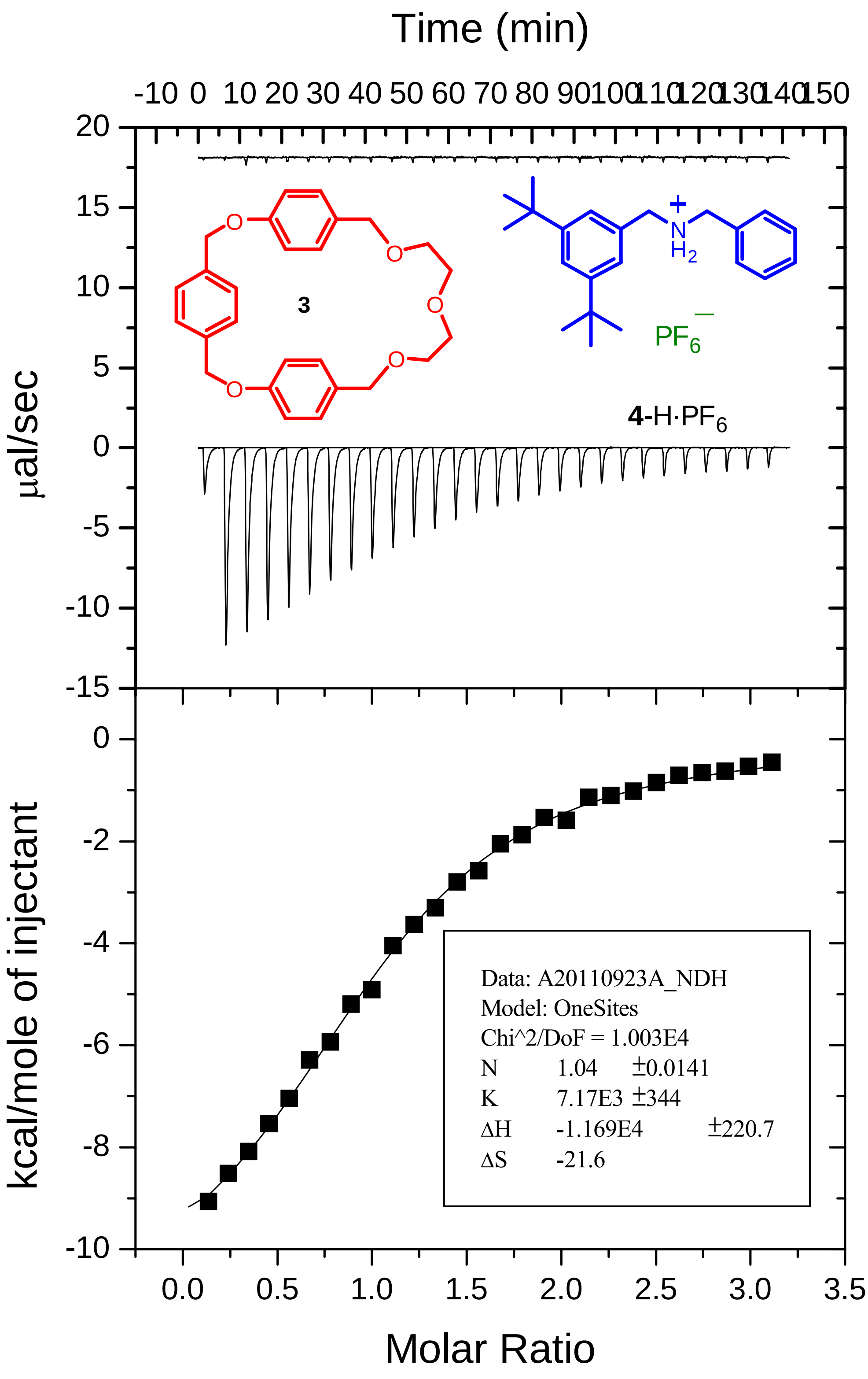

**4**-H·TFPB

| entry | N | *K* | ΔH | ΔS |
|---|---|---|---|---|
| 1 | 1.050 ± 0.00188 | 7.36E+06 ± 1.27E+06 | -10010 ± 44.81 | -2.15 |
| 2 | 0.998 ± 0.00261 | 5.21E+06 ± 1.59E+06 | -10790 ± 75.36 | -5.45 |
| average | 1.024 ± 0.03677 | 6.29E+06 ± 1.52E+06 | -10400 ± 552 | -3.80 ± 2.33 |

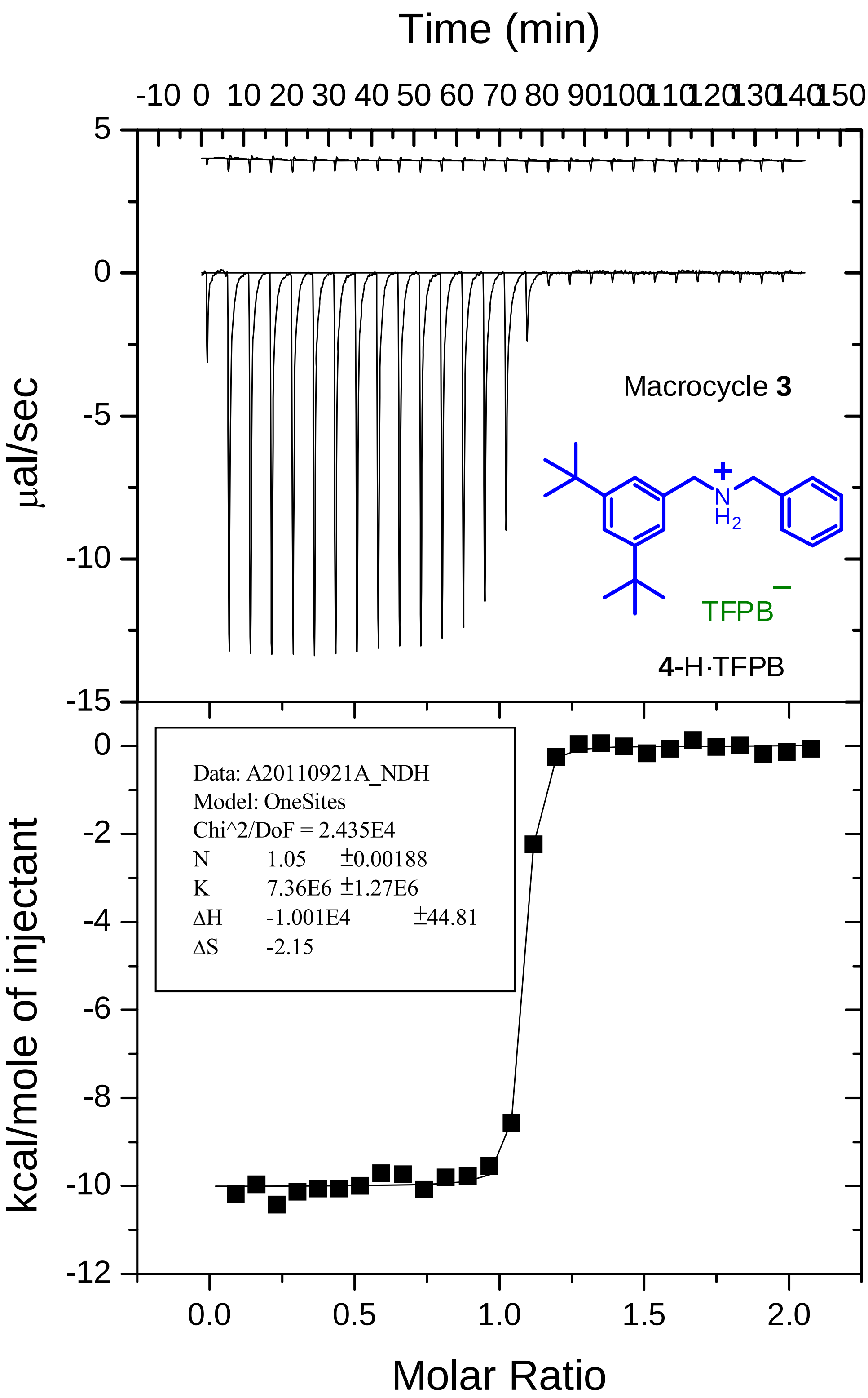
Using a Microcal VP-ITC titration microcalorimeter, aliquouts (10 μL, 7.5 mM) of degassed $CHCl_3$ solution of macrocycle **3** were titrated into stirring $CHCl_3$ solution of **4**-H·$PF_6$ (0.5 mM) at 298 K. The entropy of complexation was determined by subtracting the heat of dilution for each titration from the enthalpy of the titration. Microcal LLC software was used to compute the thermodynamic parameters of the titration based on the one-site binding model.



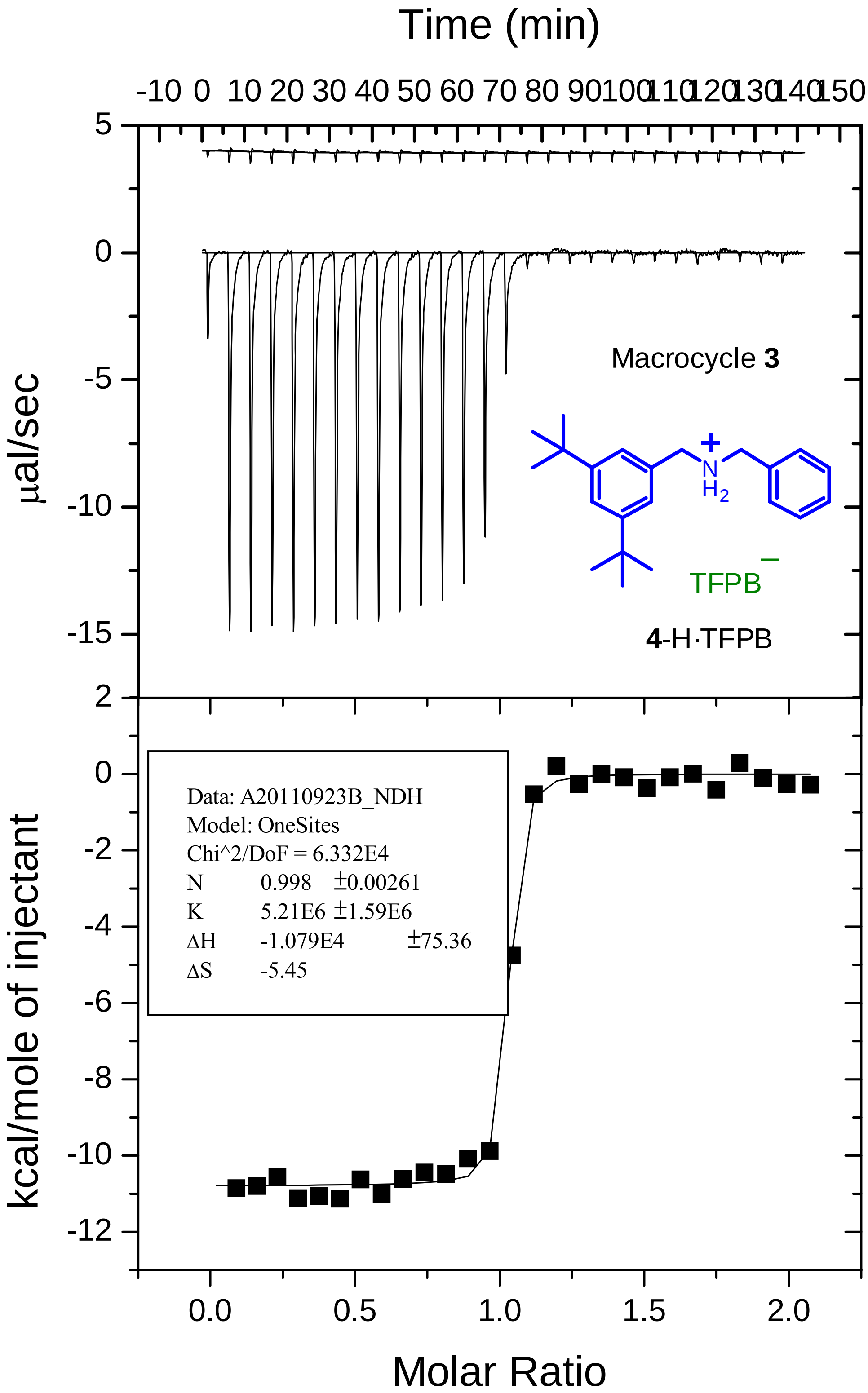
Using a Microcal VP-ITC titration microcalorimeter, aliquouts (10 μL, 7.5 mM) of degassed $CHCl_3$ solution of macrocycle **3** were titrated into stirring $CHCl_3$ solution of **4**-H·$PF_6$ (0.5 mM) at 298 K. The entropy of complexation was determined by subtracting the heat of dilution for each titration from the enthalpy of the titration. Microcal LLC software was used to compute the thermodynamic parameters of the titration based on the one-site binding model.



Using a Microcal VP-ITC titration microcalorimeter, aliquouts (10 μL, 5.0 mM) of degassed $CHCl_3$ solution of macrocycle **3** were titrated into stirring $CHCl_3$ solution of **4**-H·TFPB (0.5 mM) at 298 K. The entropy of complexation was determined by subtracting the heat of dilution for each titration from the enthalpy of the titration. Microcal LLC software was used to compute the thermodynamic parameters of the titration based on the one-site binding model.



Using a Microcal VP-ITC titration microcalorimeter, aliquouts (10 μL, 5.0 mM) of degassed $CHCl_3$ solution of macrocycle **3** were titrated into stirring $CHCl_3$ solution of **4**-H·TFPB (0.5 mM) at 298 K. The entropy of complexation was determined by subtracting the heat of dilution for each titration from the enthalpy of the titration. Microcal LLC software was used to compute the thermodynamic parameters of the titration based on the one-site binding model.



## Kinetic Data for the Dissociation of **7**-H•TFPB into Its Components

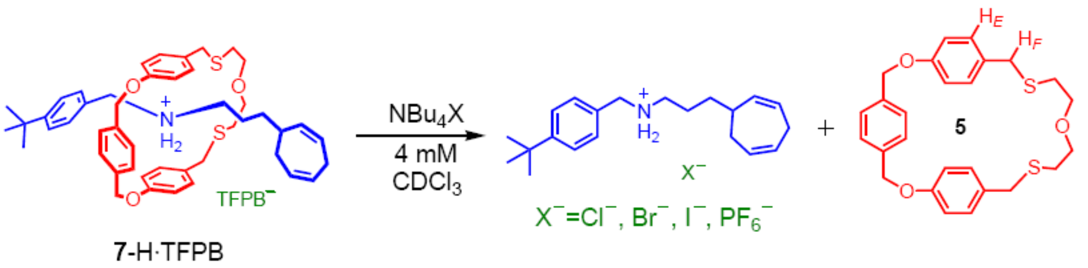



Figure S1. Dethreading of the macrocycle **5** from the dumbbell-shaped component after adding a tetra-*n*-butylammonium salt ($NBu_4X$; X was chloride, bromide, iodide, or hexafluorophosphate) to a $CDCl_3$ solution of the [2]rotaxane **7**-H•TFPB.

Experiments were performed in $CDCl_3$ with an initial concentration of **7**-H•TFPB of 4 mM, followed by the addition of 1 equiv of $NBu_4X$ [X = Cl (Part A), Br (Part B), or I (Part C)] or 6 equiv of $NBu_4PF_6$ (Part D). The values of $k_d$ ($s^{-1}$) were obtained from the slopes of the straight line in the plots of $\ln([A_0]/[A_t])$ against $t$ (s) at five temperatures. The values of $[A_t]$ were determined based on the standard signal at δ 7.69 (br, 8H; the aromatic protons of TFPB) and by integration of the signals of the macrocycle **5** ($H_E$ or $H_F$) over a period of time. The values of $\Delta G^{\ddagger}$ (kcal $mol^{-1}$) were calculated using the relationship $\Delta G^{\ddagger} = -RT \ln(k_d h/k_B T)$, where $R$, $h$, and $k_B$ correspond to the gas, Planck, and Boltzmann constants, respectively. The values of $\Delta H^{\ddagger}$ (kcal $mol^{-1}$) and $\Delta S^{\ddagger}$ (cal $mol^{-1}$ $K^{-1}$) were obtained from the intercepts and slopes, respectively, of the straight lines in the plots of $\Delta G^{\ddagger}$ against $T$, using the relationship $\Delta G^{\ddagger} = \Delta H^{\ddagger} - T\Delta S^{\ddagger}$.

Part A

In the chloride experiments, the $k_d$ ($s^{-1}$) were obtained at 258 K, 268 K, 278 K, 288 K and 298 K. $[A]_t$ were determined by integration of the signals of macrocycle **5** at δ 6.66 ($H_E$, d, *J* = 9 Hz, 4H).

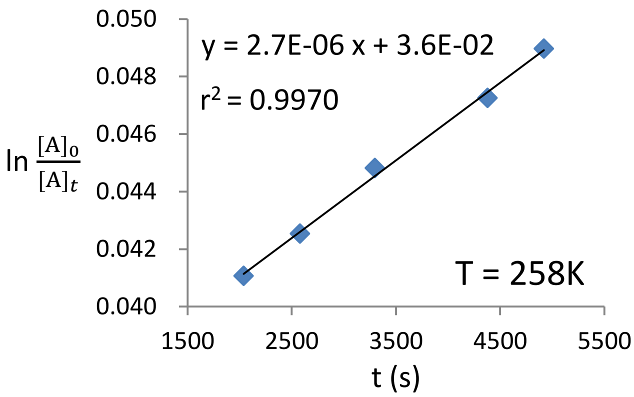



Figure S2.

$k_d$ = Slope = $2.7 \times 10^{-6}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 21.6 (kcal/mol)

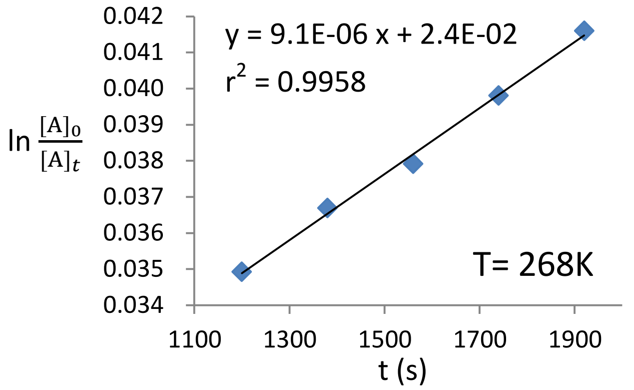



Figure S3.

$k_d$ = Slope = $9.1 \times 10^{-6}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 21.8 (kcal/mol)

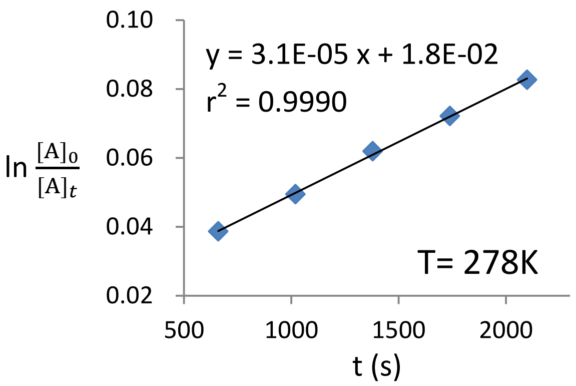



Figure S4.

$k_d$ = Slope = $3.1 \times 10^{-5}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 22.0 (kcal/mol)

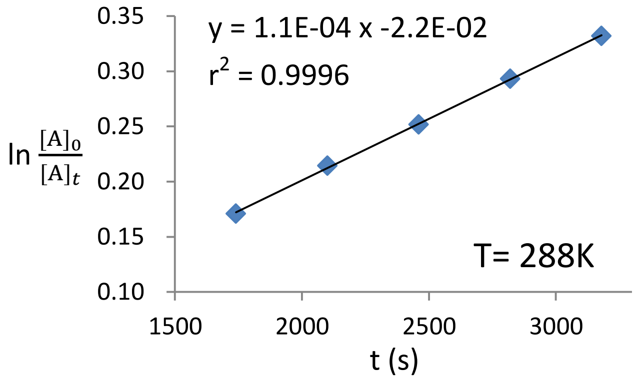



Figure S5.

$k_d$ = Slope = $1.1 \times 10^{-4}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 22.0 (kcal/mol)

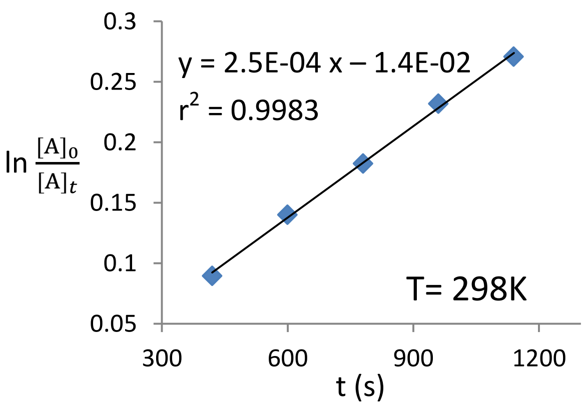



Figure S6.

$k_d$ = Slope = $2.5 \times 10^{-4}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 22.3 (kcal/mol)

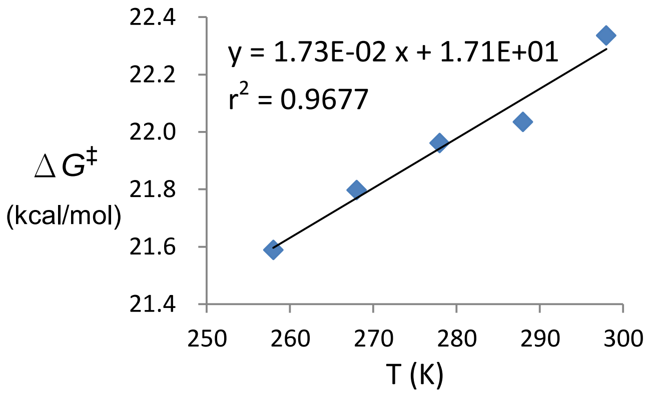



Figure S7.

$\Delta H^{\ddagger}$ = intercept = 17.1 (kcal/mol),

$\Delta S^{\ddagger}$ = - slope = - 17.3 (cal/mol)

Part B

In the bromide experiments, the $k_d$ ($s^{-1}$) were obtained at 268 K, 278 K, 288 K, 298 K and 308 K. $[A]_t$ were determined by integration of the signals of macrocycle 5 at δ 6.66 ($H_E$, d, $J$ = 9 Hz, 4H).

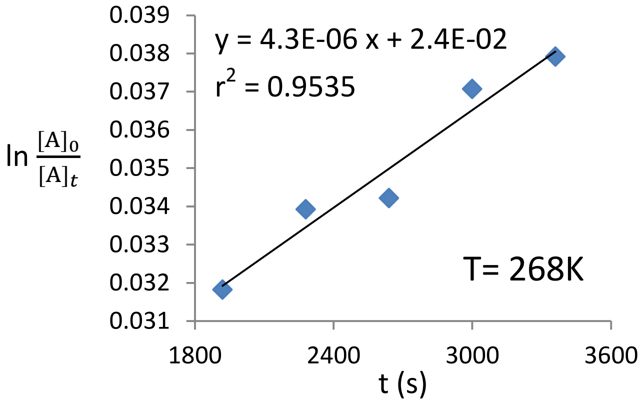



Figure S8.

$k_d$ = Slope = 4.3x10$^{-6}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 22.2 (kcal/mol)

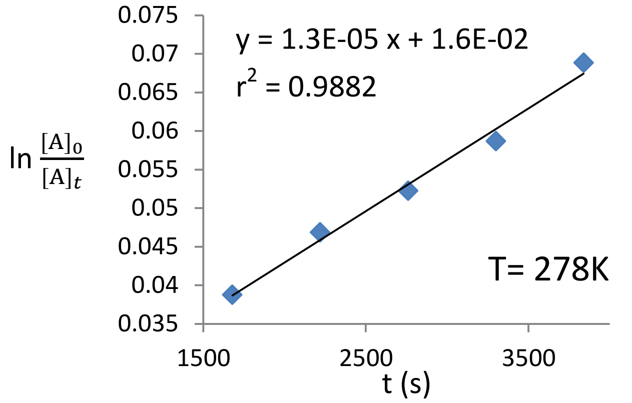



Figure S9.

$k_d$ = Slope = 1.3x10$^{-5}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 22.4 (kcal/mol)

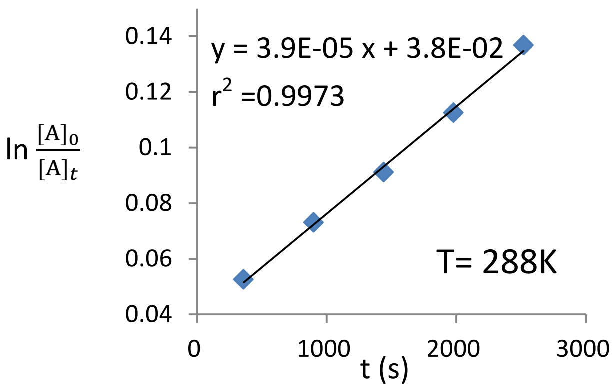



Figure S10.

$k_d$ = Slope = 3.9x10$^{-5}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 22.6 (kcal/mol)

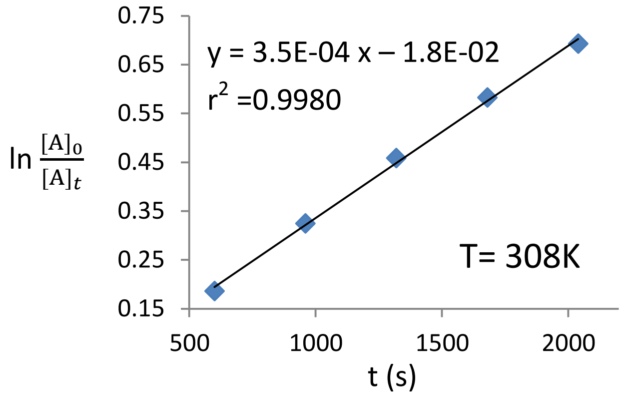



Figure S11.

$k_d$ = Slope = 3.5x10$^{-4}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 22.9 (kcal/mol)

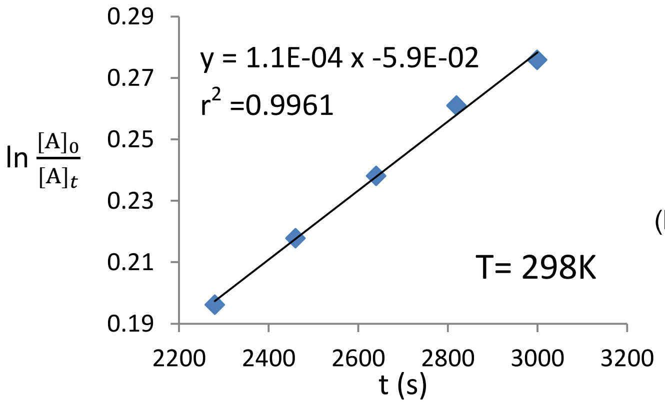



Figure S12.

$k_d$ = Slope = 1.1x10$^{-4}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 22.8 (kcal/mol)

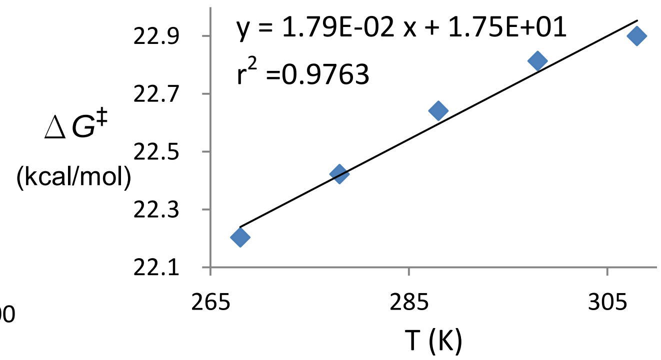



Figure S13.

$\Delta H^{\ddagger}$ = intercept = 17.5 (kcal/mol),

$\Delta S^{\ddagger}$ = - slope = - 17.9 (cal/mol)

Part C

In the iodide experiments, the $k_d$ ($s^{-1}$) were obtained at 288 K, 293 K, 298 K, 303 K and 308 K. $[A]_t$ were determined by integration of the signals of macrocycle **5** at δ 6.66 ($H_E$, d, *J* = 9 Hz, 4H).

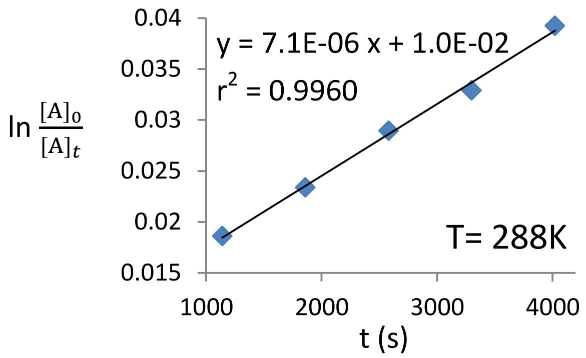



Figure S14.

$k_d$ = Slope = 7.1x$10^{-6}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 23.6 (kcal/mol)

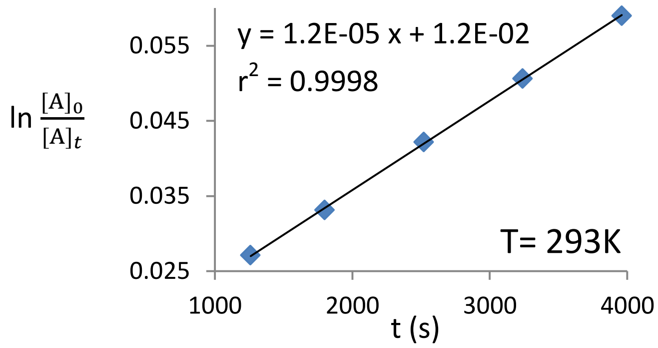



Figure S15.

$k_d$ = Slope = 1.2x$10^{-5}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 23.7 (kcal/mol)

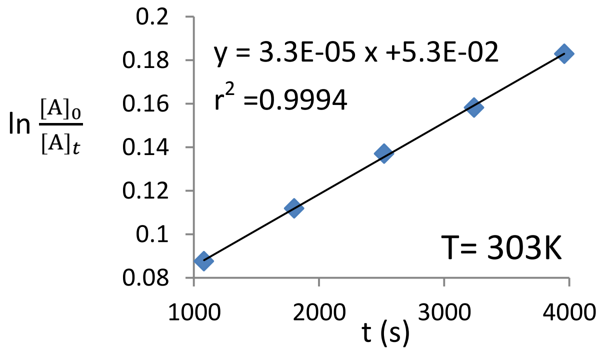



Figure S16.

$k_d$ = Slope = 3.3x$10^{-5}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 23.9 (kcal/mol)

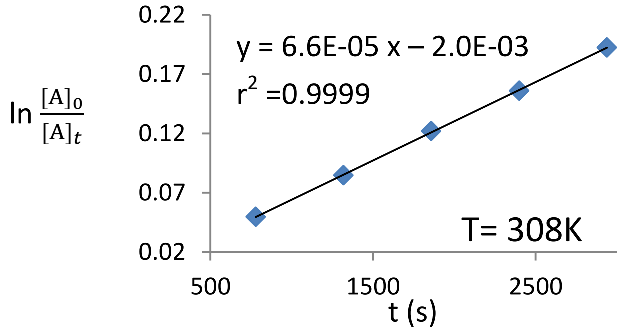



Figure S17.

$k_d$ = Slope = 6.6x$10^{-5}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 23.9 (kcal/mol)

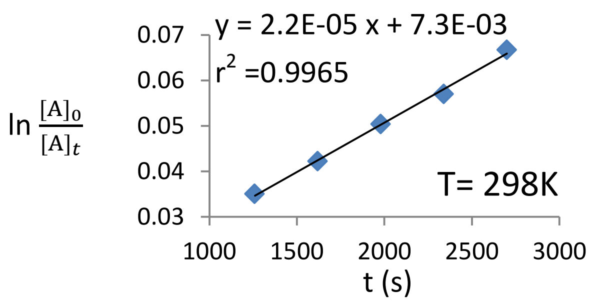



Figure S18.

$k_d$ = Slope = 2.2x$10^{-5}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 23.8 (kcal/mol)

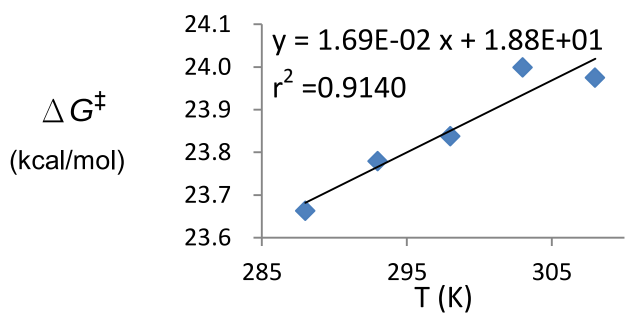



Figure S19.

$\Delta H^{\ddagger}$ = intercept = 18.8 (kcal/mol),

$\Delta S^{\ddagger}$ = - slope = - 16.9 (cal/mol)

Part D

In the hexafluorophosphate experiments, the $k_d$ ($s^{-1}$) were obtained at 298 K, 303 K, 308 K, 313 K and 318 K. $[A]_t$ were determined by integration of the signals of macrocycle 5 at δ 3.62 ($H_F$, s, 4H).

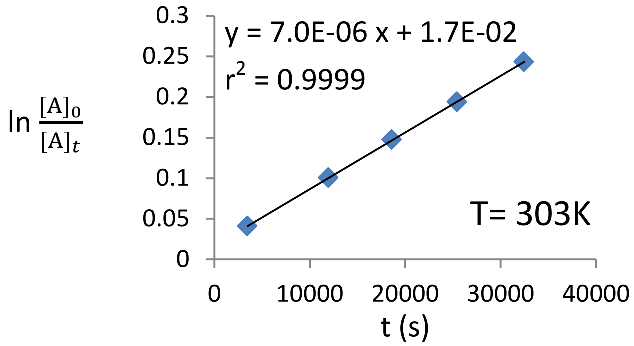



Figure S20.

$k_d$ = Slope = 7.0x10$^{-6}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 24.9 (kcal/mol)

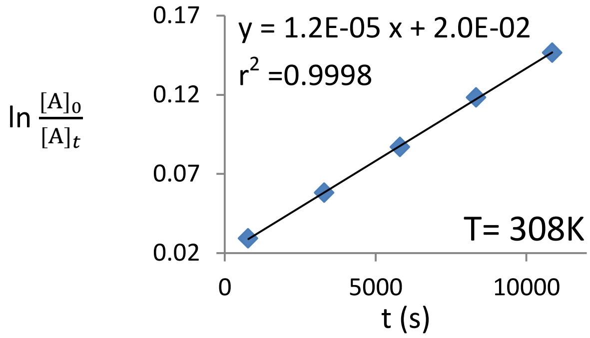



Figure S21.

$k_d$ = Slope = 1.2x10$^{-5}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 25.0 (kcal/mol)

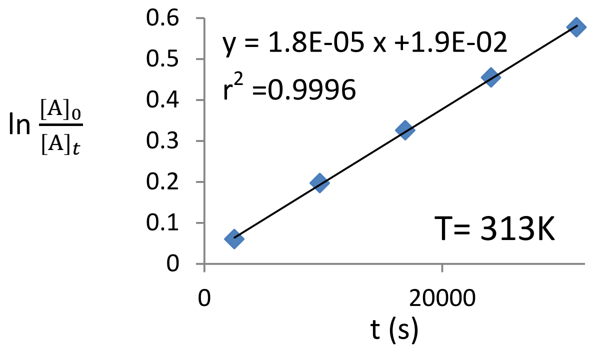



Figure S22.

$k_d$ = Slope = 1.8x10$^{-5}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 25.1 (kcal/mol)

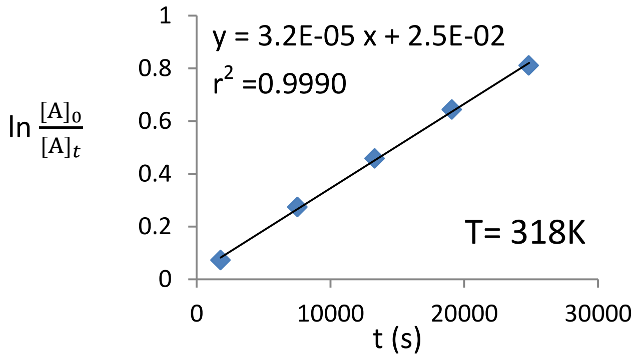



Figure S23.

$k_d$ = Slope = 3.2x10$^{-5}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 25.2 (kcal/mol)

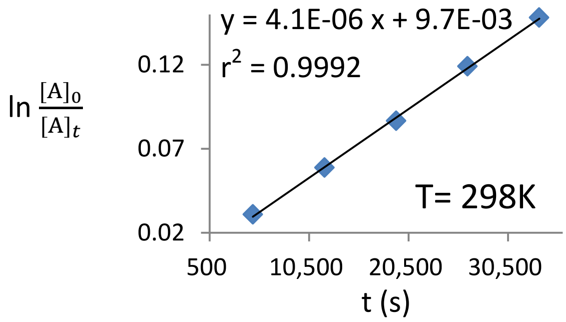



Figure S24.

$k_d$ = Slope = 4.1x10$^{-6}$ ($s^{-1}$), $\Delta G^{\ddagger}$ = 24.8 (kcal/mol)

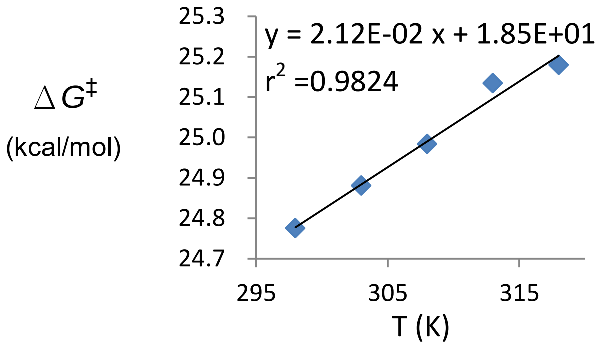



Figure S25.

$\Delta H^{\ddagger}$ = intercept = 18.5 (kcal/mol),

$\Delta S^{\ddagger}$ = - slope = - 21.2 (cal/mol)

**7**-H• TPFB + $Bu_4NCl$

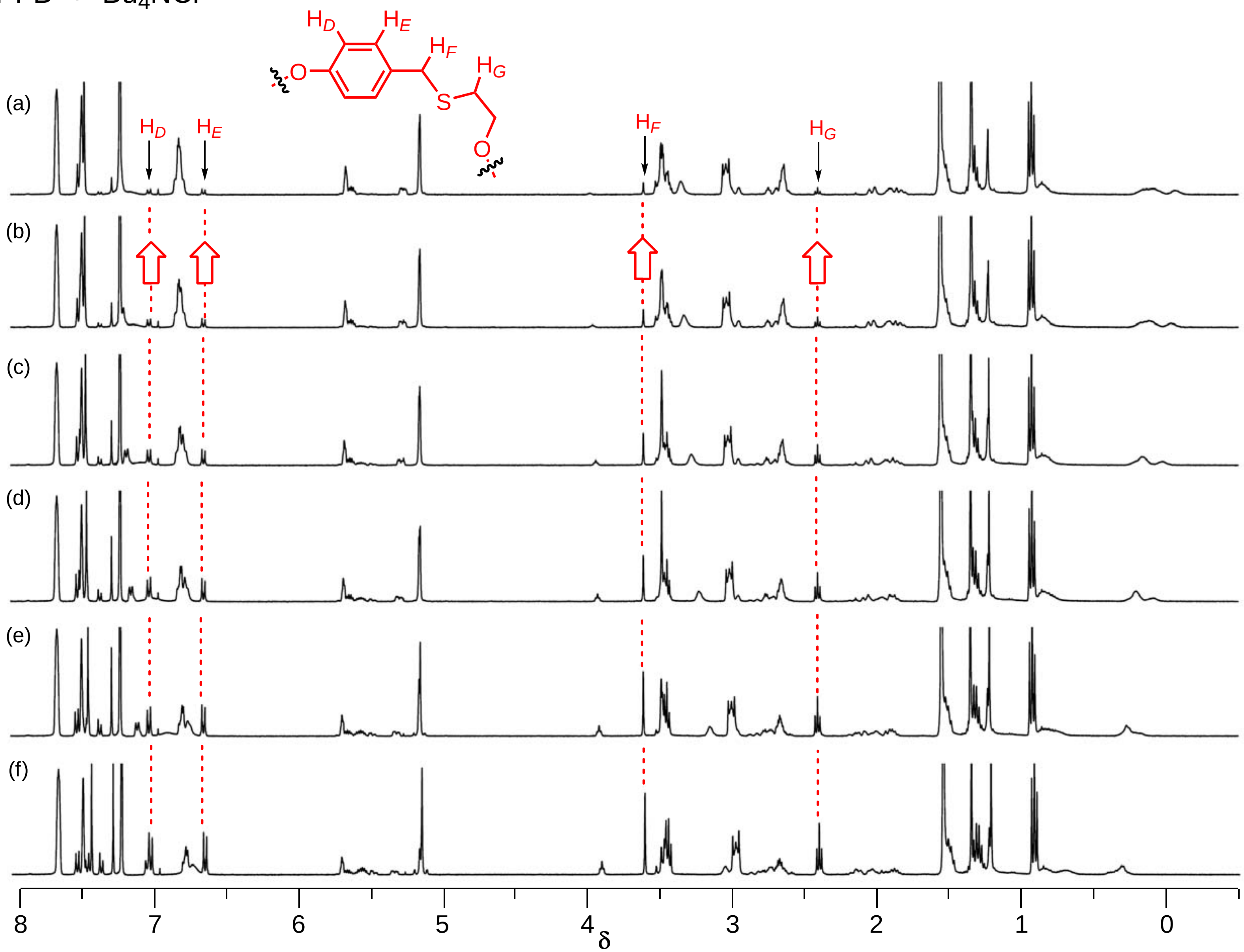



Fig. [1]H NMR spectra (400 MHz, $CDCl_3$, 298 K) revealing the disociation ofthe macrocycle **5** from an equimolar mixture of $Bu_4NCl$ and **7**-H• TPFB (4 mM) over time; a) 4, b) 7, c) 13, d) 19, e) 28, f) 43 min.

**7**-H• TPFB + $Bu_4NBr$

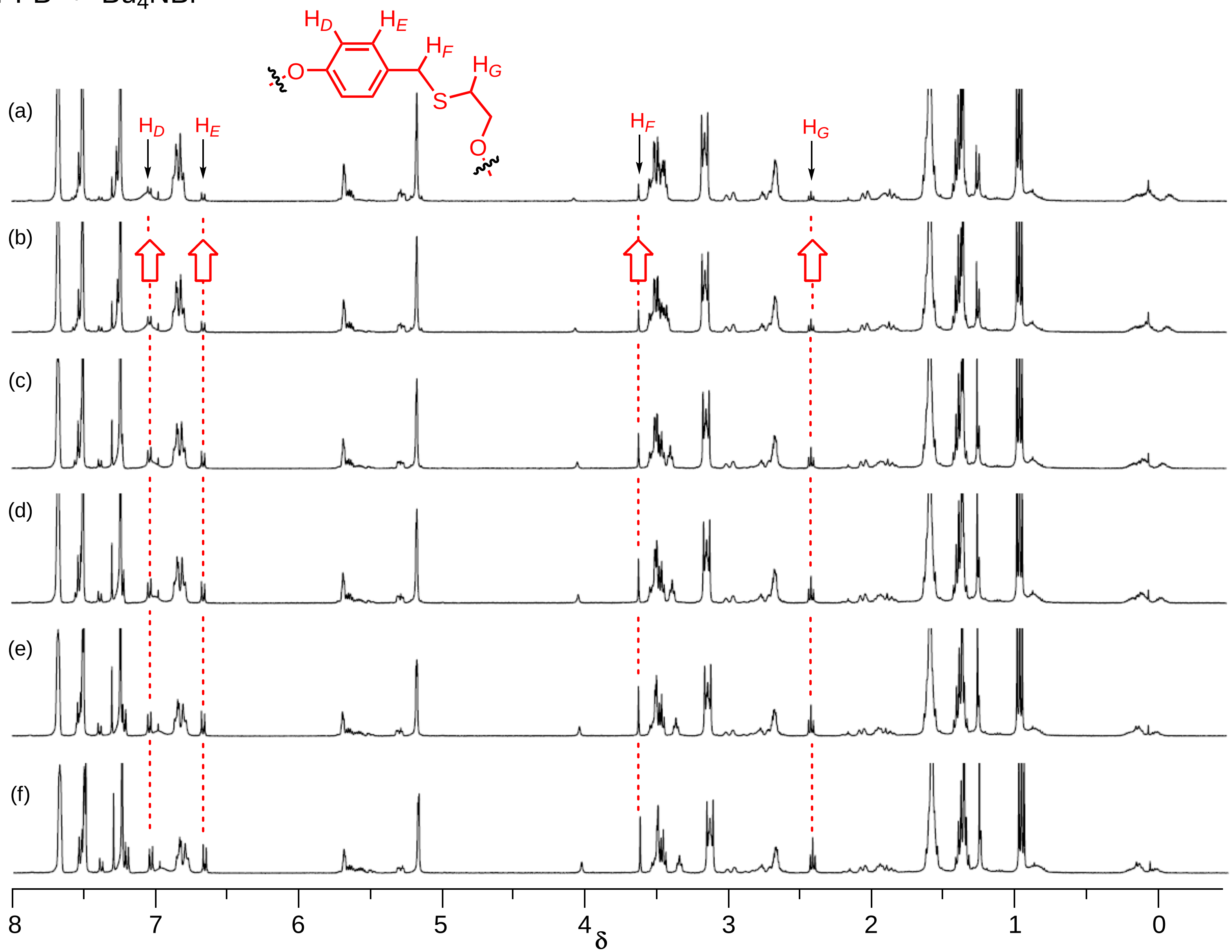



Fig. [1]H NMR spectra (400 MHz, $CDCl_3$, 298 K) revealing the dissociation of the macrocycle **5** from an equimolar mixture of $Bu_4NBr$ and **7**-H• TPFB (4 mM) over time; a) 14, b) 20, c) 32, d) 38, e) 50, and f) 56 min.

**7**-H• TPFB + $Bu_4NI$

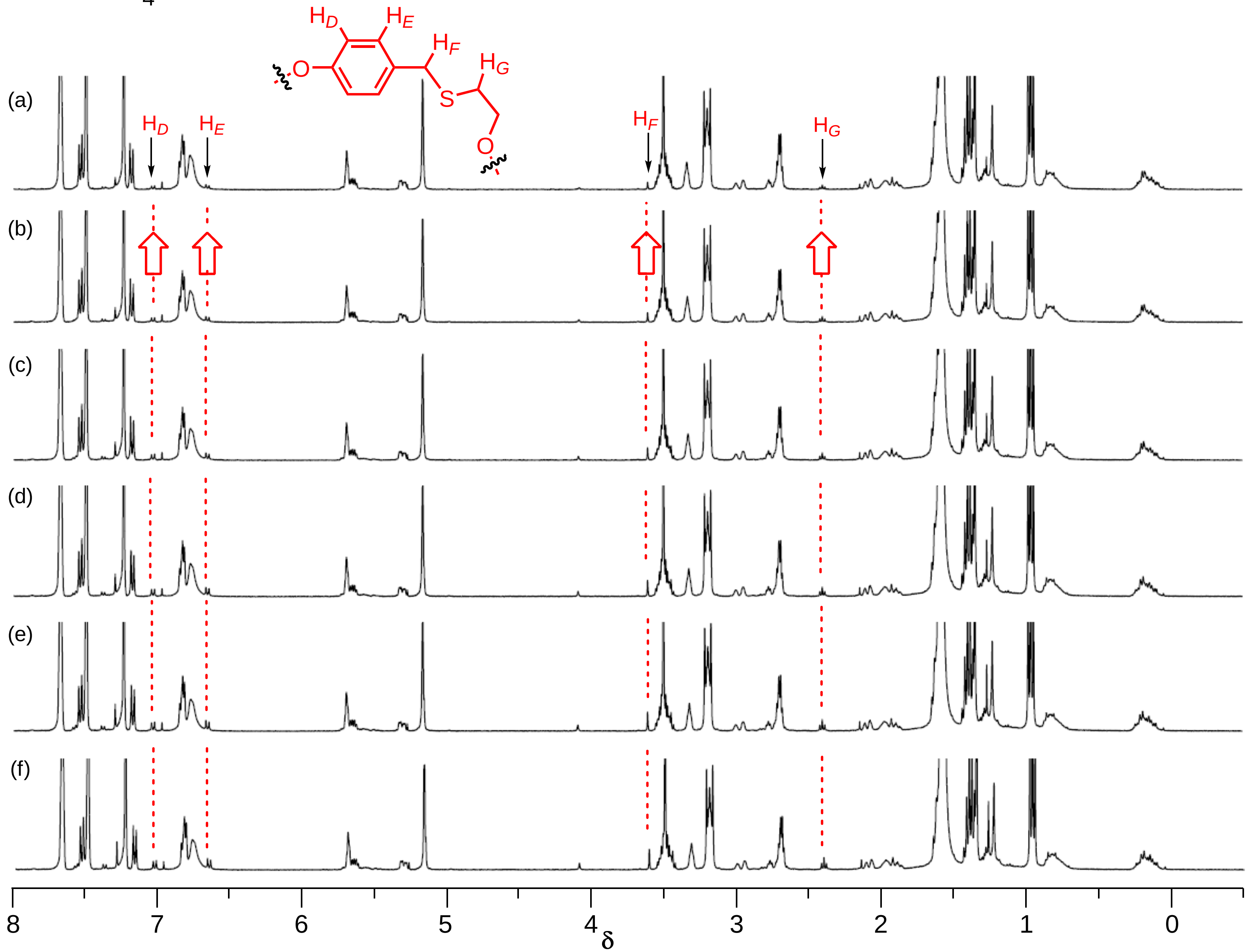



Fig. [1]H NMR spectra (400 MHz, $CDCl_3$, 298 K) revealing the dissociation of the macrocycle **5** from an equimolar mixture of $Bu_4NI$ and **7**-H• TPFB (4 mM) over time; a) 21, b) 30, c) 39, d) 48, e) 57, and f) 63 min.

**7**-H• TPFB + $Bu_4NPF_6$

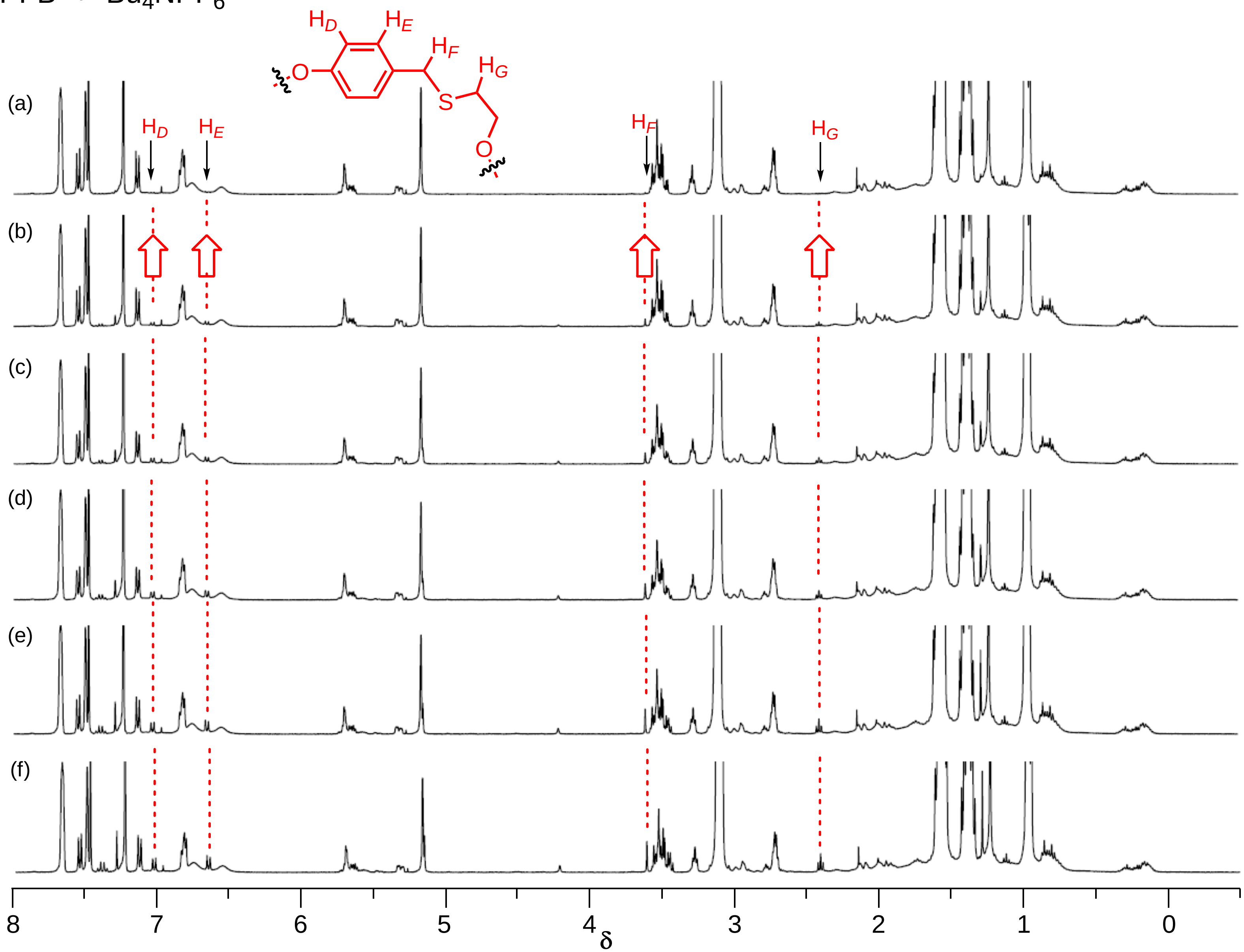



Fig. [1]H NMR spectra (400 MHz, $CDCl_3$, 298 K) revealing the dissociation of the macrocycle **5** from a mixture of $Bu_4NPF_6$ (24 mM) and **7**-H• TPFB (4 mM) over time; a) 0.4, b) 2.5, c) 4.6, d) 6.7, e) 8.8, and f) 10.9 h.