

# Macrocyclic N-Heterocyclic Carbenes: Synthesis and Catalytic Applications

Anibal R. Davalos, Eric Sylvester and Steven T. Diver\*

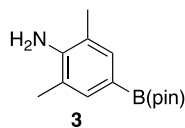
*Department of Chemistry, University at Buffalo, the State University of New York,  
Amherst, NY, 14260-3000*

## SUPPORTING INFORMATION

### *Table of Contents*

<b>A. Synthesis of Macrocyclic Precursors.....</b>	<b>S2</b>
<b>B. Applications</b>	
<b>1. Intramolecular Michael-Stetter Reaction.....</b>	<b>S5</b>
<b>2. Metathesis Applications using Ru1.....</b>	<b>S6</b>
<b>3. Pd-Mediated Cross Coupling Reaction.....</b>	<b>S10</b>
<b>C. NMR Spectra of New Compounds.....</b>	<b>S12</b>
<b>D. References.....</b>	<b>S33</b>

## A. Synthesis of Macrocyclic Precursors



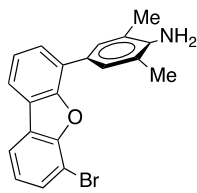
### 2,6-Dimethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)aniline (**3**)

Adapted from a previously published procedure.<sup>1</sup> In an oven-dried Schlenk tube equipped with a stir bar, 2,6-dimethyl-4-bromoaniline (9.3 g, 46.5 mmol, 1 equiv), KOAc (13.7 g, 139.5 mmol, 3 equiv), and bis(pinacolato)diboron (13.0 g, 47.6 mmol, 1.1 equiv) were added followed by dioxane (150 mL). The mixture was sparged with nitrogen for 5 min before adding PdCl<sub>2</sub>(dppf) (1.7 g, 2.3 mmol, 0.05 equiv) and the contents were stirred at 80 °C for 20 h. The reaction was then allowed to cool to room temperature. The crude reaction was added to a separatory funnel containing a benzene/water (75:25) (750 mL) solution. The organic layer was collected, dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. The crude product was purified using silica gel and 10% EtOAc in hexanes as eluent to afford 9.7 g (85%) of the desired boronate as a white solid, mp: 73-74 °C. Analytical tlc R<sub>f</sub> 0.21 (10% EtOAc in hexanes). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ: 7.41 (s, 2H), 3.73 (s, 2H), 2.14 (s, 6H), 1.32 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>, ppm) δ: 146.51, 145.88, 135.07, 120.60, 83.20, 24.80, 17.25. FT-IR (ATR, cm<sup>-1</sup>): 3450, 2974, 1621, 1439, 1321, 1224, 830, 701. HRMS (ESI<sup>+</sup>): *m/z* calculated for C<sub>14</sub>H<sub>22</sub>BNO<sub>2</sub> ([M+H]<sup>+</sup>): 248.1822, found 248.1819, error -1.2 ppm.

### 4,6-Dibromodibenzofuran (**4**)

Following a previously published procedure.<sup>2</sup> In a 2L oven dried round bottom flask, a solution of dibenzofuran (15.4 g, 0.092 mol, 1 equiv), TMEDA (41.0 mL, 0.28 mol, 3 equiv), and 900 mL of Et<sub>2</sub>O was cooled to -78 °C. Then, *sec*-butyllithium (200.0 mL, 0.28 mol, 3 equiv, 1.4 M in hexane) was added dropwise using a syringe, and the reaction mixture was allowed to reach room temperature and stirred for 24 h. The reaction mixture was cooled back to -78 °C before addition of a 1:1 bromine/pentane (14.4 mL, 0.28 mol, 3 equiv/14.4 mL) solution. The reaction mixture was stirred for 24 h at room temperature before

quenching with 300 mL of 30% aqueous NaHSO<sub>3</sub> solution. Extraction with ether (300 mL), followed by washing with 300 mL of 30% aqueous NaHSO<sub>3</sub>, and 600 mL of water afforded the desired product. The crude product was recrystallized using dichloromethane–hexane (70:30) solution to afford 18.4 g, (62%) of white crystalline solid, mp: 144-146 °C. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, ppm) δ: 7.25 (dd, J = 7.9, 2H), 7.65 (d, J = 7.9, 2H), 7.86 (d, J = 7.9, 2H). Data was found to match those previously published in literature.<sup>3</sup>

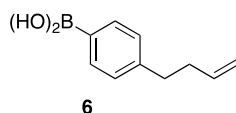


5

#### 4-(6-Bromodibenzofuran-2-yl)-2,6-dimethylaniline (5)

Adapted from a previously published procedure.<sup>3</sup> In a 2L oven-dried round bottom flask, **3** (5.0 g, 20.2 mmol, 1 equiv) and **4** (19.0 g, 58.5 mmol, 2.9 equiv) were added, followed by THF (800 mL) and 2M KOH (aq) solution (30.3 mL, 60.6 mmol, 3 equiv). The mixture was sparged with nitrogen for 5 minutes. Then, Pd(PPh<sub>3</sub>)<sub>4</sub> (1.16 g, 1.0 mmol, 0.05 equiv) was added and the system was stirred and reflux for 24 h. The reaction was allowed to cool to room temperature before transferring to a separatory funnel containing dichloromethane (300 mL). The organic layer was collected, dried over anhydrous magnesium sulfate, filtered and concentrated *in vacuo*. Purification was carried out by first recrystallizing excess starting material **4** using dichloromethane (8.2 g recovered) which can be readily reused. Then, a silica gel column using 10% EtOAc in hexanes as eluent was performed to afford 5.5 g (83%) of the desired product **5** as a white solid, mp: 165-166 °C. Analytical tlc (10% EtOAc in hexanes) R<sub>f</sub> 0.19. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.89 (dd, J = 7.8, 1.0 Hz, 1H), 7.81 (dd, J = 7.6, 1.1 Hz, 1H), 7.65 (s, 2H), 7.64 – 7.57 (m, 2H), 7.40 (dd, J = 7.6, 7.8 Hz, 1H), 7.22 (dd, J = 7.8, 7.6 Hz, 1H), 3.76 (br s, 2H), 2.32 (s, 6H).<sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>, ppm): δ 153.29, 153.13, 142.86, 129.82, 128.66, 126.45, 126.43, 125.82, 125.30, 124.73, 123.80, 123.64, 121.81, 119.58, 118.60, 104.61, 17.86. FT-IR (ATR, cm<sup>-1</sup>): 3464, 3386, 2950, 1621, 1505,

1481, 1421, 1185, 852, 767, 730. HR-MS (ESI):  $m/z$  calculated for  $C_{20}H_{16}BrNO$  ( $[M+H]^+$ ) 366.0494, found 366.0496, error: 0.6 ppm.

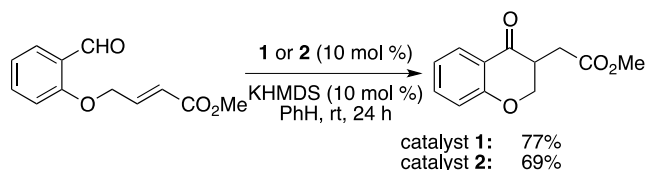


#### 4-(3-Butenyl)phenylboronic acid (**6**)

The synthesis of **6** was carried out following previously published literature procedure.<sup>4</sup> To a stirred solution of 1-bromo-4-(but-3-en-1-yl)benzene (12.0 g, 56.9 mmol, 1 equiv) in THF (800 mL) at  $-78$  °C was added *n*-BuLi (34.1 mL, 68.3 mmol, 1.2 equiv) dropwise. The reaction mixture was stirred at  $-78$  °C for 30 min before adding trimethylborate (19.0 mL, 170.1 mmol, 3 equiv) and the mixture stirred for another 30 min at  $-78$  °C. The reaction was allowed to warm to room temperature for 12 h before being acidified with aqueous 10% HCl (120 mL) to give 9.0 g (90%) of **6** as a white semi-solid that was not further purified.  $^1H$  NMR (300 MHz,  $CDCl_3$ , ppm):  $\delta$  8.16 (d,  $J = 7.2$  Hz, 1H), 8.05 (d,  $J = 7.2$  Hz, 1H), 7.41 – 7.17 (m, 2H), 5.90 (m, 1H), 5.05 (m, 2H), 4.18 – 4.05 (m, 2H), 2.80 (m, 2H). Data was found to match those previously published in literature.<sup>5</sup>

## B. Applications

### 1. NHC-Catalyzed Intramolecular Michael-Stetter Reaction

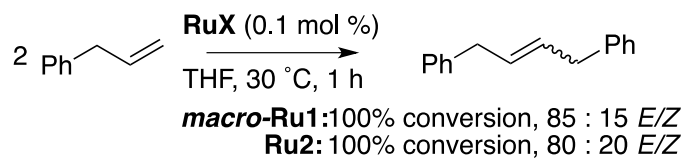


An oven-dried 1 dram vial was charged with **2** (4.2 mg, 4.5  $\mu$ mol, 0.1 equiv), previously dried overnight using a drying pistol, and equipped with a stir bar was placed inside the glovebox. Then, benzene (3.5 mL), followed by KHMDS (1.0 mg, 4.5  $\mu$ mol, 0.1 equiv) were added. Note: Compound **2** was slightly soluble in benzene, but after addition of the base, it dissolved completely giving a persistent orange/yellow solution. The contents were stirred at room temperature for 5 min before the addition of (*E*)-methyl 4-(2-formylphenoxy)but-2-enoate (10 mg, 45.0  $\mu$ mol, 1 equiv). The reaction was left stirring at room temperature and monitored by analytical tlc until the starting material was completely consumed (24 h). The crude reaction was filtered through a silica gel plug and concentrated *in vacuo*. A crude NMR yield was obtained by comparing the phenyl hydrogen (7.86 ppm, d,  $J$ = 7.9 Hz, 1H) ortho to the carbonyl with mesitylene (2.1  $\mu$ L, 1.5  $\mu$ mol, 0.33 equiv) used as internal standard to give 69% yield.

The same procedure was followed, but using **1** (4.0 mg, 4.5  $\mu$ mol, 0.1 equiv) and obtained 77% yield. As control experiments, the same procedure was followed using H<sub>2</sub>IMes (1.8 mg) and IMes (1.6 mg), obtaining 81 and 79% yield, respectively.

## 2. Metathesis Applications of Ru1

### *Allyl Benzene Homodimerization*



Adapted from a previously published procedure.<sup>6</sup> In a glovebox, a one dram vial was charged with **Ru1** (2.4 mg, 2.06  $\mu\text{mol}$ ) catalyst and THF (458  $\mu\text{L}$ ) to prepare a 4.5 mM stock solution. Using a gas tight microliter syringe, the catalyst stock solution (111  $\mu\text{L}$ , *ca.* 1.0  $\mu\text{mol}$ , 0.1 mol %) was transferred to a one dram vial containing allyl benzene (132  $\mu\text{L}$ , 1.0 mmol), THF (111  $\mu\text{L}$ ), tridecane (243  $\mu\text{L}$ , 1.0 mmol) and a stir bar. Then, the reaction was stirred at 30 °C for 1 h. An aliquot was removed and quenched with carboxylate isocyanide  $\text{KO}_2\text{CCH}_2\text{NC}$  in methanol, followed by dilution with ether and filtered through a silica plug before injecting it in the GC and observed 100% conversion, 95% yield with 85:15 *E/Z* ratio. GC response factors for allyl benzene ( $1.86 \pm 0.01$ ) and its dimer Z19 ( $1.05 \pm 0.01$ ) were obtained (E and Z dimers have the same GC response factor) using tridecane as the internal standard.

Compound	Response Factor	Retention Time (min)
Tridecane	----	8.13
Allyl Benzene	1.86	11.1
Z-Dimer	1.05	13.9
E-Dimer	1.05	14.0

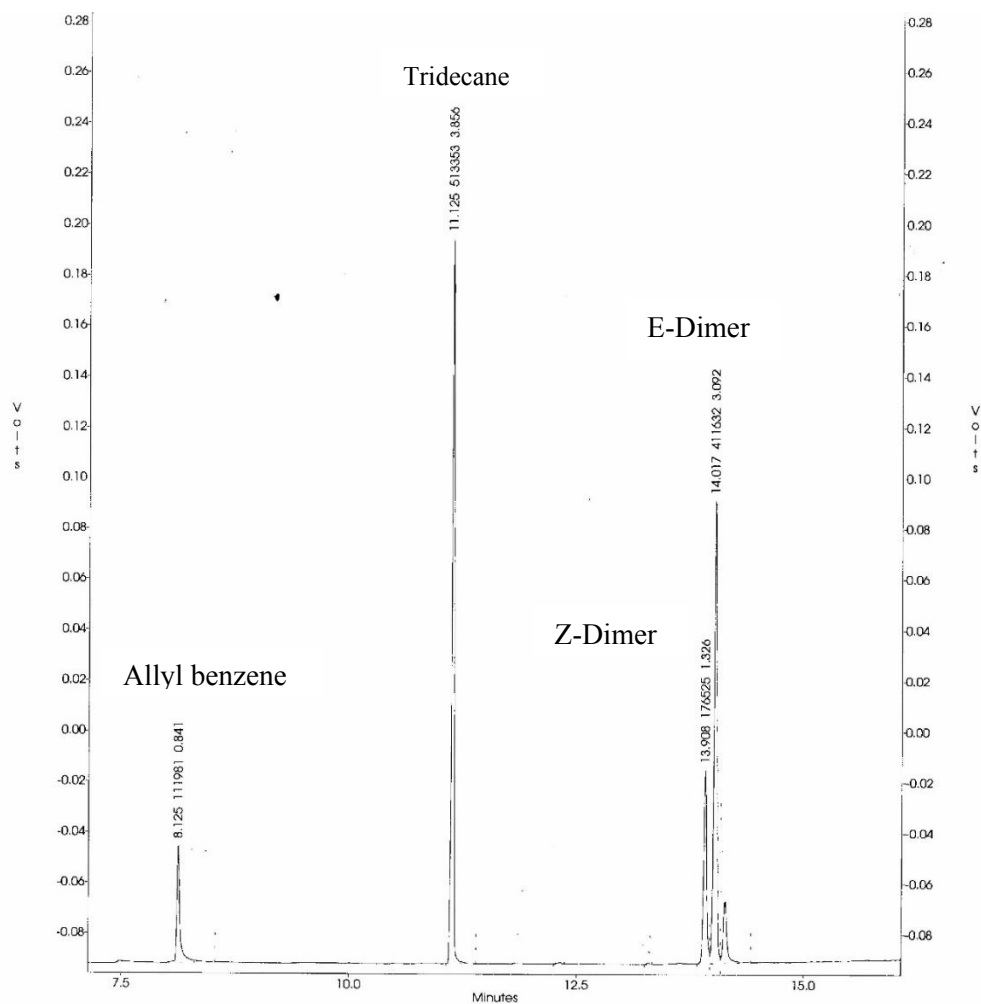
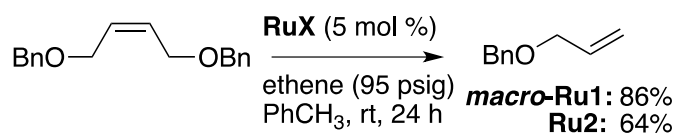


Figure S1. GC-chromatogram of allyl benzene homodimerization.

### Ethenolysis



Inside a glovebox, a Fischer-Porter tube equipped with a stir bar was charged with *cis*-1,4-dibenzoyloxy-2-butene (10 mg, 37.3  $\mu\text{mol}$ , 1 equiv) and **Ru1** (2.2 mg, 1.9  $\mu\text{mol}$ , 0.05 equiv) catalyst followed by  $\text{PhCH}_3$  (100  $\mu\text{L}$ ) before sealing the tube with a regulator. The Fischer-Porter tube was taken outside the glovebox and purged with ethylene before pressurizing to 90 psig. Then, the reaction was left

stirring for 24 h at room temperature. The reaction was vented, the solution was diluted with  $\text{CH}_2\text{Cl}_2$  and quenched with a methanolic carboxylate isocyanide ( $\text{KO}_2\text{CCH}_2\text{NC}$ , 1 mg, 7.6  $\mu\text{mol}$ , 0.2 equiv) solution, before filtration and concentration *in vacuo*. The NMR yield was obtained by comparing the  $\alpha$ -olefin hydrogen (5.21 ppm, d,  $J = 10.0$  Hz, 1 H) with mesitylene (1.95  $\mu\text{L}$ , 0.33 equiv) used as internal standard to give 86% NMR yield. The same procedure was followed, but using the second generation Grubbs-Hoveyda catalyst (1.5 mg, 2.3  $\mu\text{mol}$ , 0.05 equiv) which gave a 64% NMR yield. The small scale of the reaction precluded further purification.

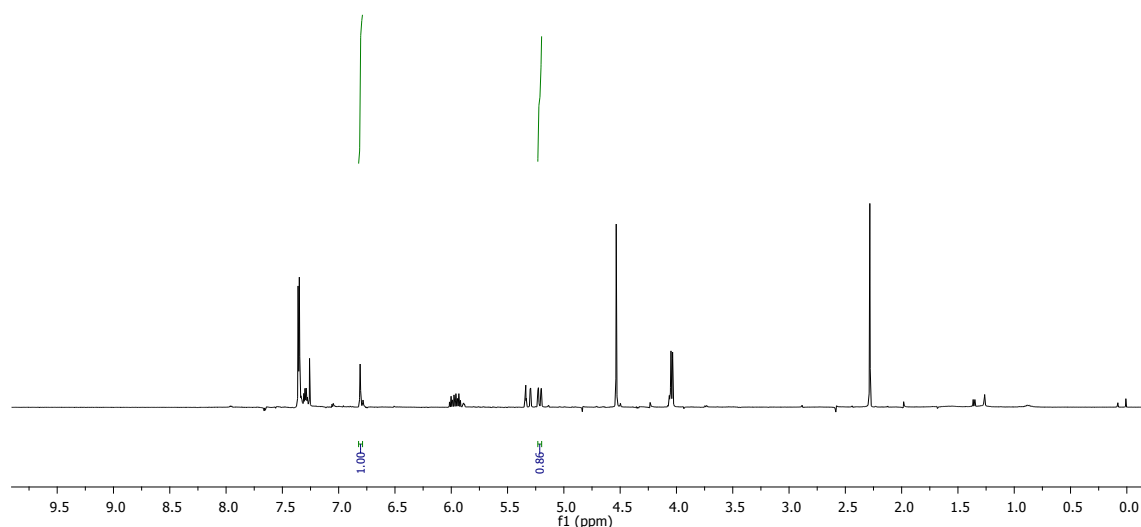
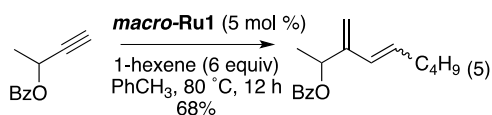


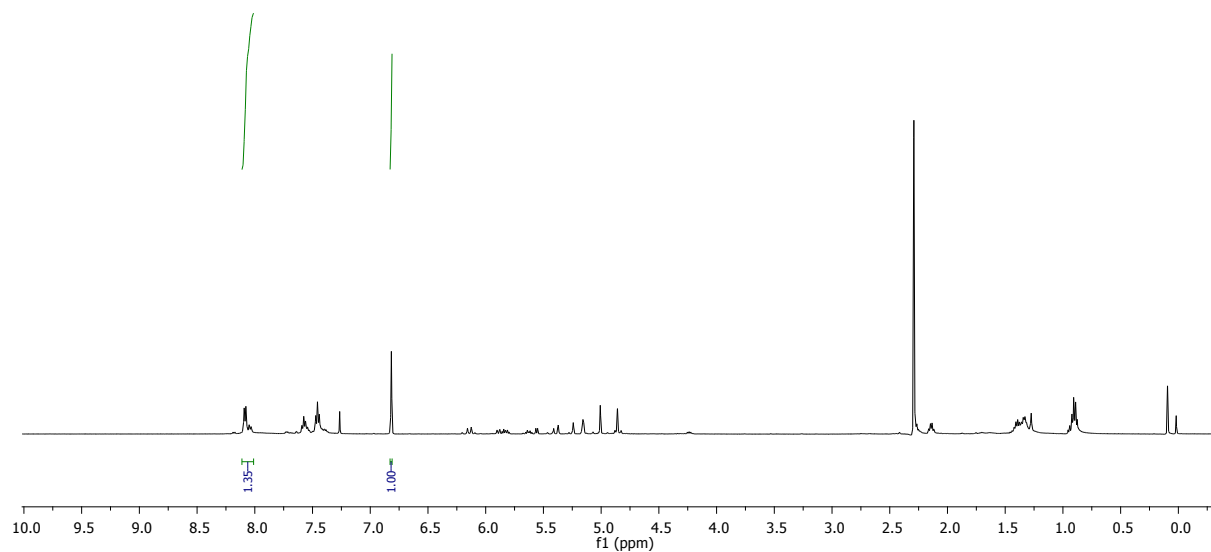
Figure S2.  $^1\text{H}$  NMR spectrum of ethenolysis of cis-1,4-dibenzoyloxy-2-butene. An asterisk marks mesitylene peak.

### Ene-yne Metathesis

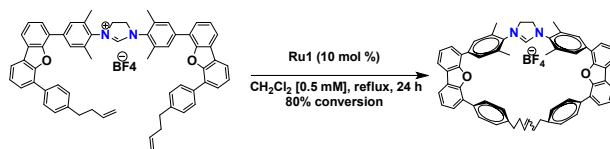


An oven-dried Schlenk tube equipped with a stir bar and connected to a Schlenk line was charged with propargyl benzoate (29.5 mg, 0.18 mmol, 1 equiv), 1-hexene (140  $\mu\text{L}$ , 1.1 mmol, 6 equiv),  $\text{PhCH}_3$  (3.7 mL) and **Ru1** (4.5 mg, 21.5  $\mu\text{mol}$ , 0.025 equiv) catalyst. The reaction was stirred for 12 h at 80  $^\circ\text{C}$ . Then,

a methanolic solution of carboxylate isocyanide ( $\text{KO}_2\text{CCH}_2\text{NC}$ , 10.6 mg, 85.9  $\mu\text{mol}$ , 0.1 equiv, 0.3 mL) quenching agent was added, and allowed to stir for 30 min. The crude product was diluted with  $\text{CH}_2\text{Cl}_2$  and filtered through a silica plug. The NMR yield was determined by comparing the phenyl hydrogens at the ortho-position (8.08 ppm, d,  $J = 8.0$  Hz, 2H) with mesitylene which was used as internal standard to give 68% NMR yield. The E/Z ratio was determined to be 58:42 based on the integration of the vinyl hydrogen at 6.14 (E) and 5.89 (Z) ppm resonances.

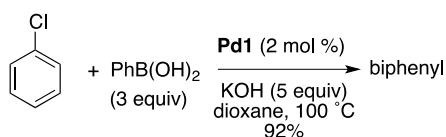


*Figure S3.*  $^1\text{H}$  NMR spectrum of ene-yne metathesis product (5) in  $\text{CDCl}_3$ . An asterisk \* marks the mesitylene peak.

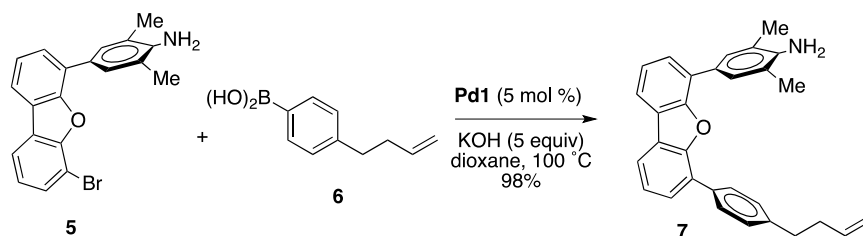


In a 100 mL oven-dried three neck flask equipped with a stir bar and a water condenser under nitrogen atmosphere, a solution of **11** (20 mg, 21.0  $\mu\text{mol}$ , 1 equiv) in  $\text{CH}_2\text{Cl}_2$  (42 mL, 0.5 mM) was prepared. To the solution, **Ru1** catalyst (2.4 mg, 2.1  $\mu\text{mol}$ , 0.1 equiv) was added and kept under nitrogen with an open needle at the top of the condenser as an ethylene exhaust. The reaction was refluxed for 24 h before quenching the catalyst with carboxylate isocyanide  $\text{KO}_2\text{CCH}_2\text{NC}$  (1.0 mg, 8.4  $\mu\text{mol}$ , 0.4 equiv) in methanol. After stirring 30 min, the reaction mixture was filtered through a pad of silica gel and concentrated to obtain 80% conversion, with 69:31 E/Z ratio.

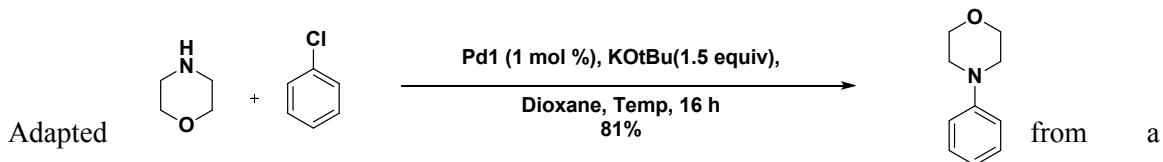
### 3. Pd-Mediated Cross Coupling Applications



A 50 mL Schlenk tube equipped with a stir bar and connected to a Schlenk line was charged with aryl chloride (23  $\mu\text{L}$ , 0.22 mmol, 1 equiv), phenyl boronic acid (82 mg, 0.66 mmol, 3 equiv),  $\text{K}_2\text{CO}_3$  (153 mg, 1.1 mmol, 5 equiv), tridecane (54  $\mu\text{L}$ , 0.22, 1 equiv), dioxane (1.5 mL) and sparged with nitrogen for 5 min before adding the **Pd1** (5.0 mg, 4.44 mmol, 0.02 equiv) catalyst. The Schlenk tube was sealed and the reaction was stirred at 90  $^\circ\text{C}$ . The reaction conversion was monitored by analyzing aliquots by GC. An aliquot was taken at the beginning of the reaction Aliquots (50  $\mu\text{L}$ ) were taken every 4 h and diluted with ether before filtering through a silica plug. After 24 h 100% conversion and 92% yield was determined using tridecane. The reaction crude was diluted with ether and filtered using a silica plug. The product was isolated using silica gel and 2% EtOAc in hexanes as eluent to give 28.5 mg (83%) of a white/yellowish solid.  $^1\text{H}$  NMR data matched that of biphenyl.



A 50 mL Schlenk tube equipped with a stir bar and connected to a Schlenk line was charged with **5** (15 mg, 41.0  $\mu\text{mol}$ , 1 equiv), **6** (22 mg, 123  $\mu\text{mol}$ , 3 equiv), KOH (11 mg, 205  $\mu\text{mol}$ , 5 equiv), and dioxane (240  $\mu\text{L}$ ). The solution was sparged with nitrogen for 5 min before adding the **Pd1** (2.3 mg, 2.05  $\mu\text{mol}$ , 0.05 equiv) catalyst. The Schlenk tube was sealed and the reaction was stirred at 100  $^\circ\text{C}$  until **5** was completely consumed (monitored by tlc, 20% EtOAc in hexanes). After 8 h, 100% conversion was observed and the crude reaction was diluted with  $\text{CH}_2\text{Cl}_2$  before filtering it using a silica plug and concentrated *in vacuo*. NMR yield: 98% (mesitylene as internal standard).



Adapted from a previously published procedure.<sup>7</sup> A 25 mL Schlenk tube equipped with a stir bar and connected to a Schlenk line was charged with aryl chloride (29  $\mu\text{L}$ , 0.28 mmol, 1 equiv), morpholine (30  $\mu\text{L}$ , 0.34 mmol, 1.2 equiv), KOtBu (48 mg, 1. mmol, 1.5 equiv), dioxane (0.5 mL) and sparged with nitrogen for 2 min before adding the **Pd1** (3.0 mg, 2.84  $\mu\text{mol}$ , 0.01 equiv) catalyst. The Schlenk tube was sealed and the reaction was stirred at 100  $^\circ\text{C}$  for 16 h. The reaction conversion was monitored by analyzing aliquots by GC. A 50  $\mu\text{L}$  aliquot was taken at the beginning of the reaction, diluted with  $\text{CH}_2\text{Cl}_2$  and filtered through a silica plug before injecting it in the GC. After 16 h 100% consumption of the aryl chloride was observed. The reaction crude was diluted with  $\text{CH}_2\text{Cl}_2$  and filtered using a silica plug and the product was isolated using silica gel and 2% EtOAc in hexanes as eluent to give 38.0 mg (81%) of a white crystalline solid. The  $^1\text{H}$  NMR spectrum matched those reported in literature.<sup>8</sup>

**C. NMR Spectra for New Compounds (Following Pages)**

A7\_G

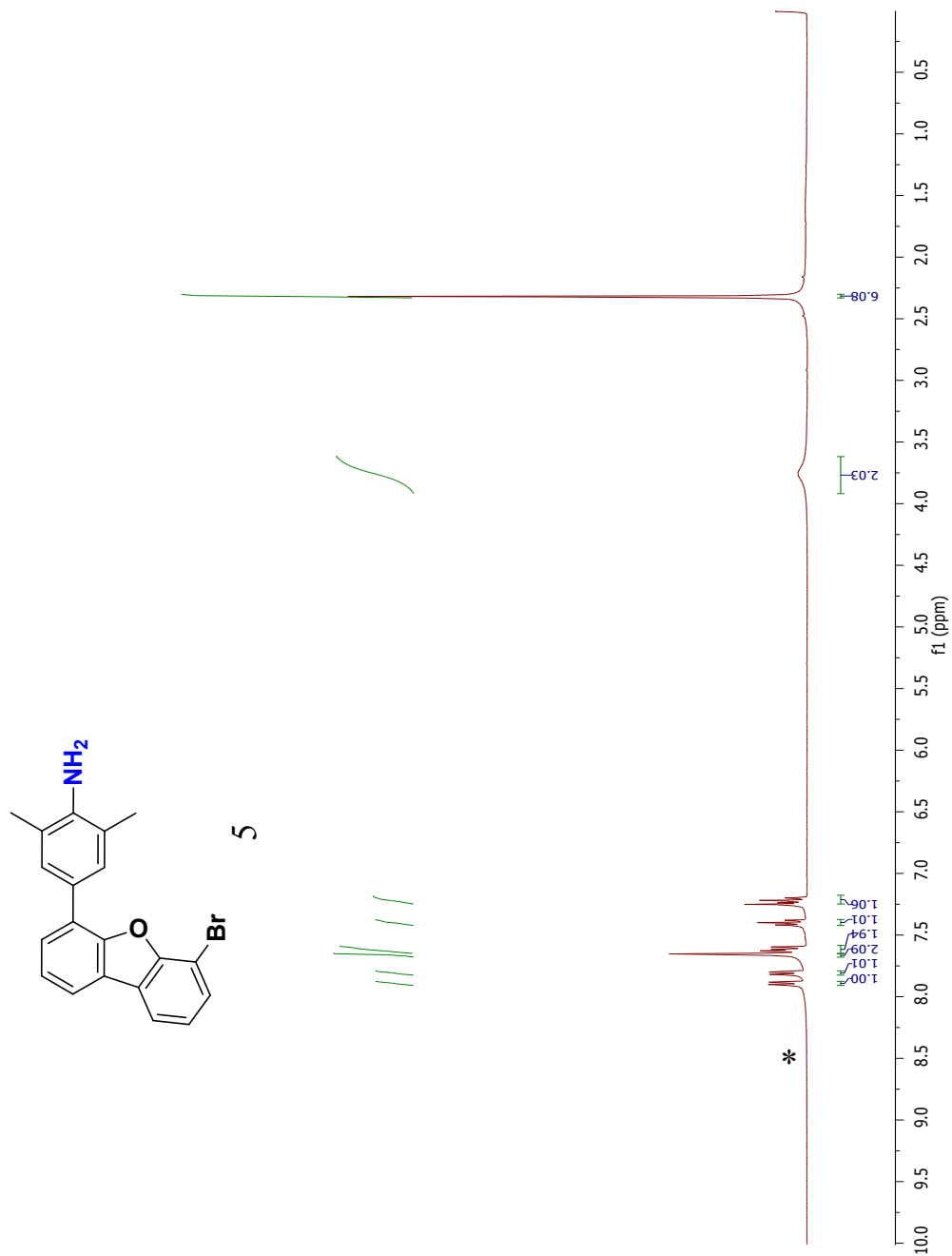


Figure S4. <sup>1</sup>H NMR spectrum of 4-(6-bromodibenzofuranyl)-2,6-dimethylaniline **5** in CDCl<sub>3</sub>. An asterisk \* marks the solvent peak.

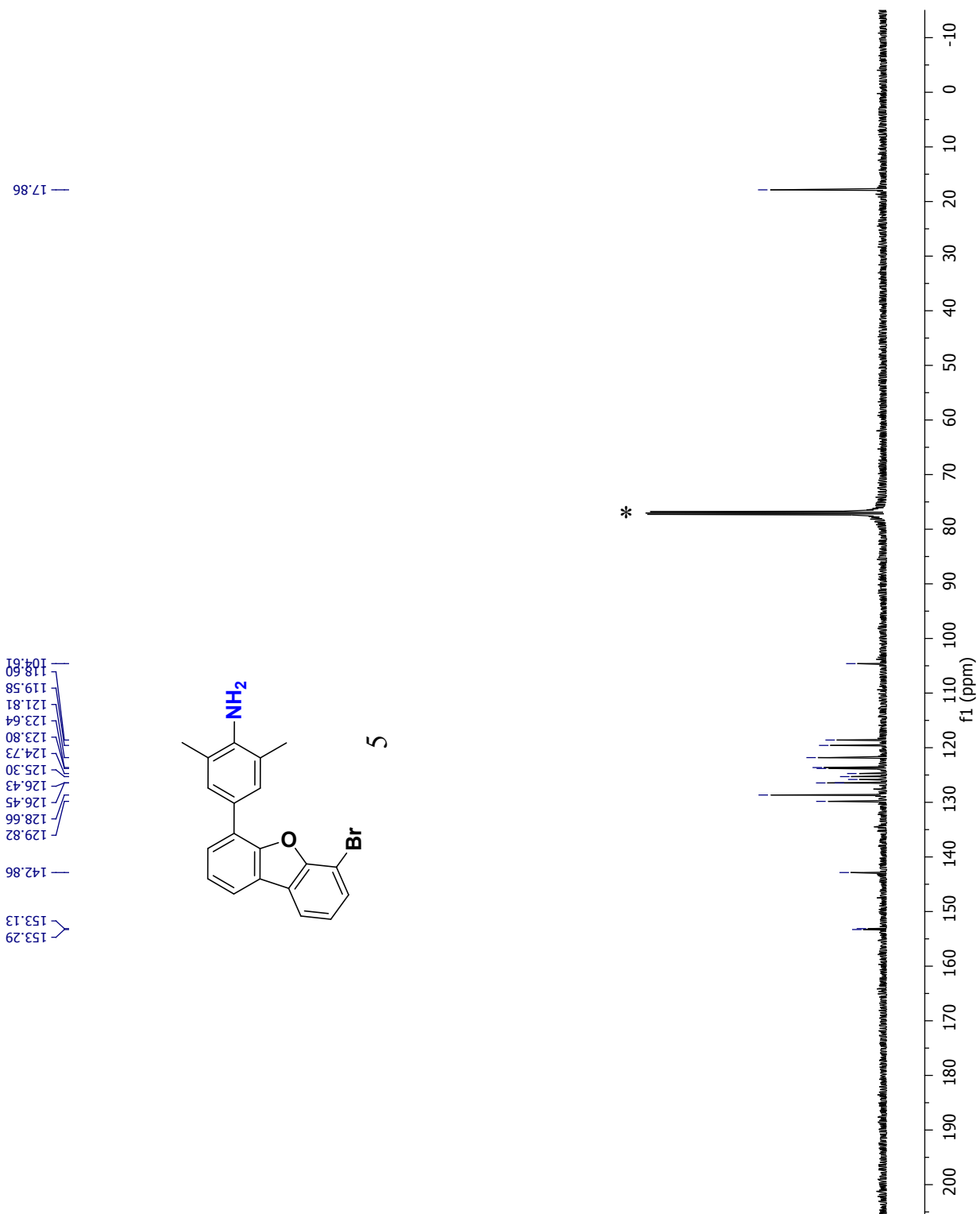


Figure S5. <sup>13</sup>C NMR spectrum of 4-(6-bromodibenzofuranyl)-2,6-dimethylaniline **5** in CDCl<sub>3</sub>. An asterisk \* marks the solvent peak.

homo\_allyl\_G

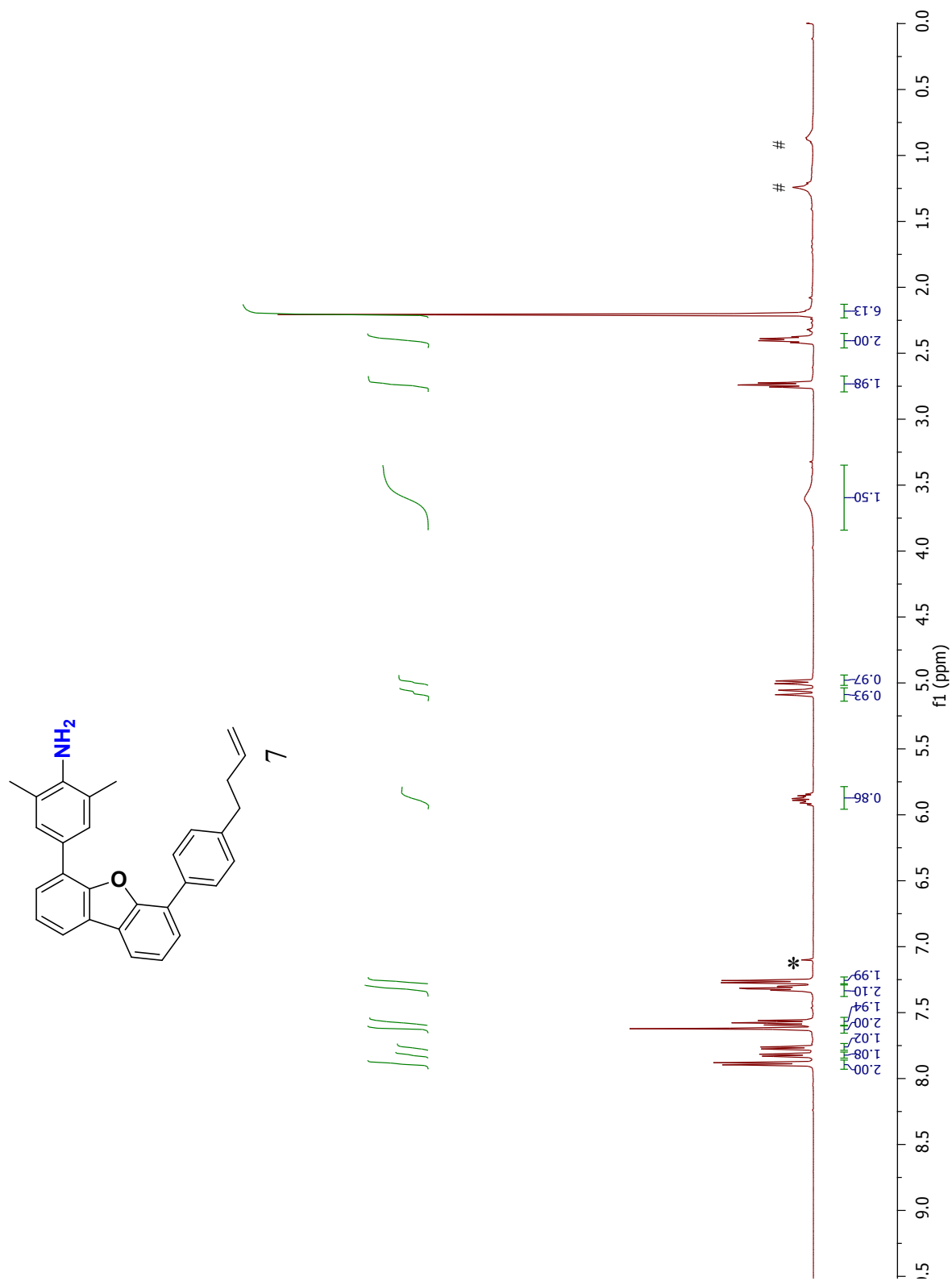


Figure S6. <sup>1</sup>H NMR spectrum of 4-(6-(4-(but-3-en-1-yl)phenyl)dibenzo[b,d]furan-4-yl)-2,6-dimethylaniline **7** in CDCl<sub>3</sub>. An asterisk \* marks the solvent peak and # symbol denotes impurities.

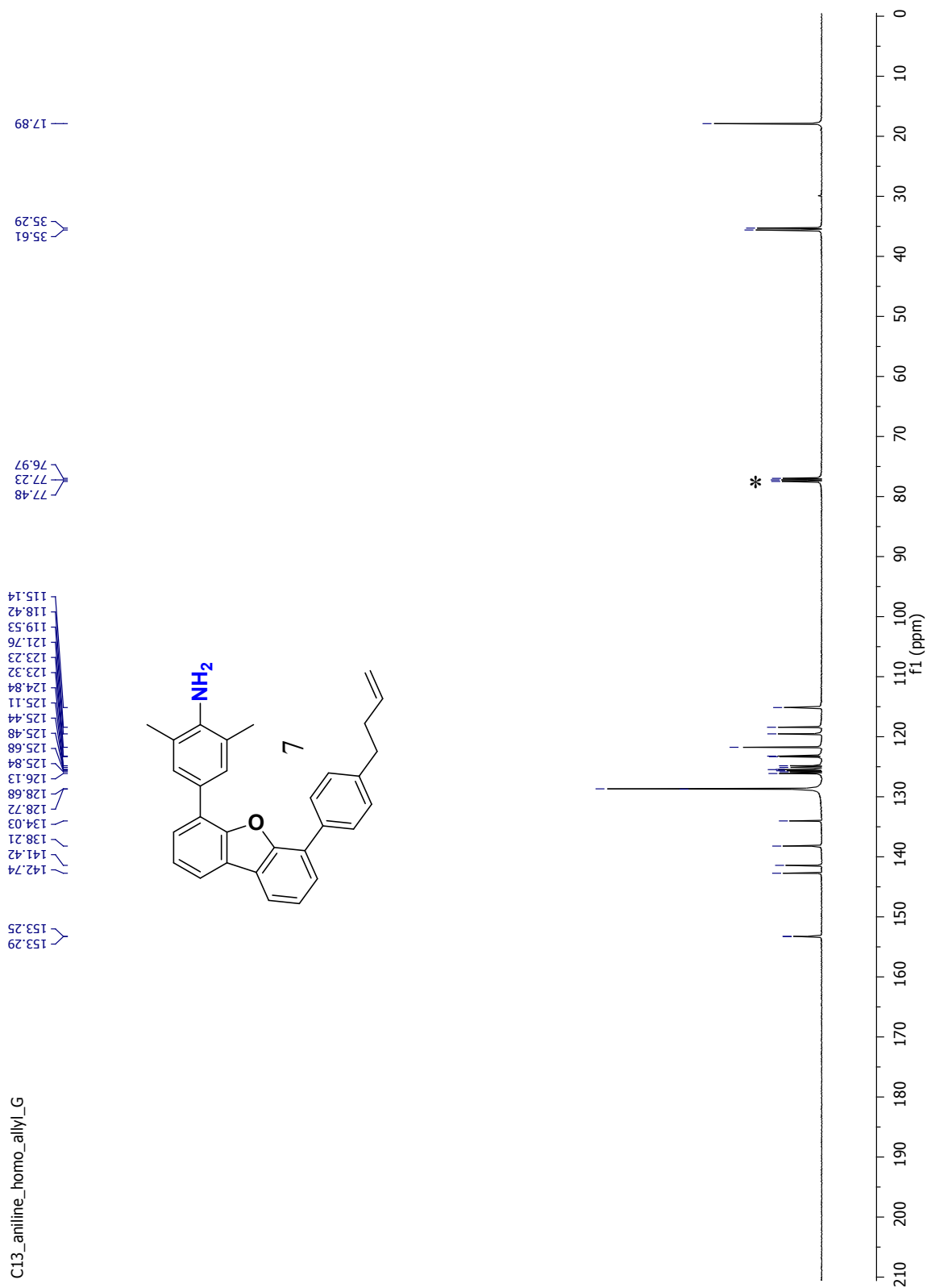


Figure S7. <sup>13</sup>C NMR spectrum of 4-(6-(4-(but-3-en-1-yl)phenyl)dibenzo[b,d]furan-4-yl)-2,6-dimethylaniline **7** in CDCl<sub>3</sub>. An asterisk \* marks the solvent peak.

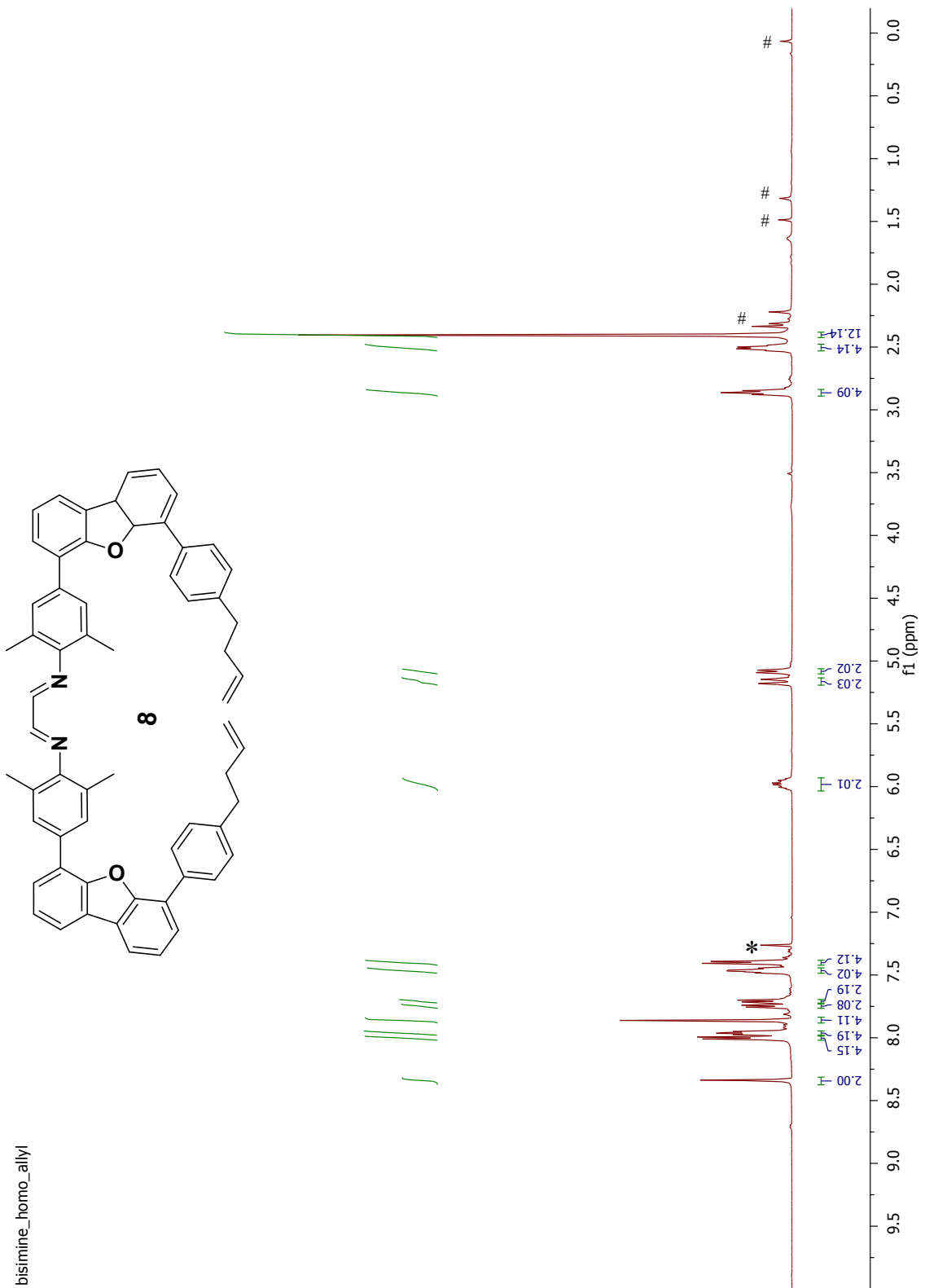


Figure S8.  $^1\text{H}$  NMR spectrum of bisimine **8** in  $\text{CDCl}_3$ . An asterisk \* marks the solvent peak and # symbol denotes impurities.

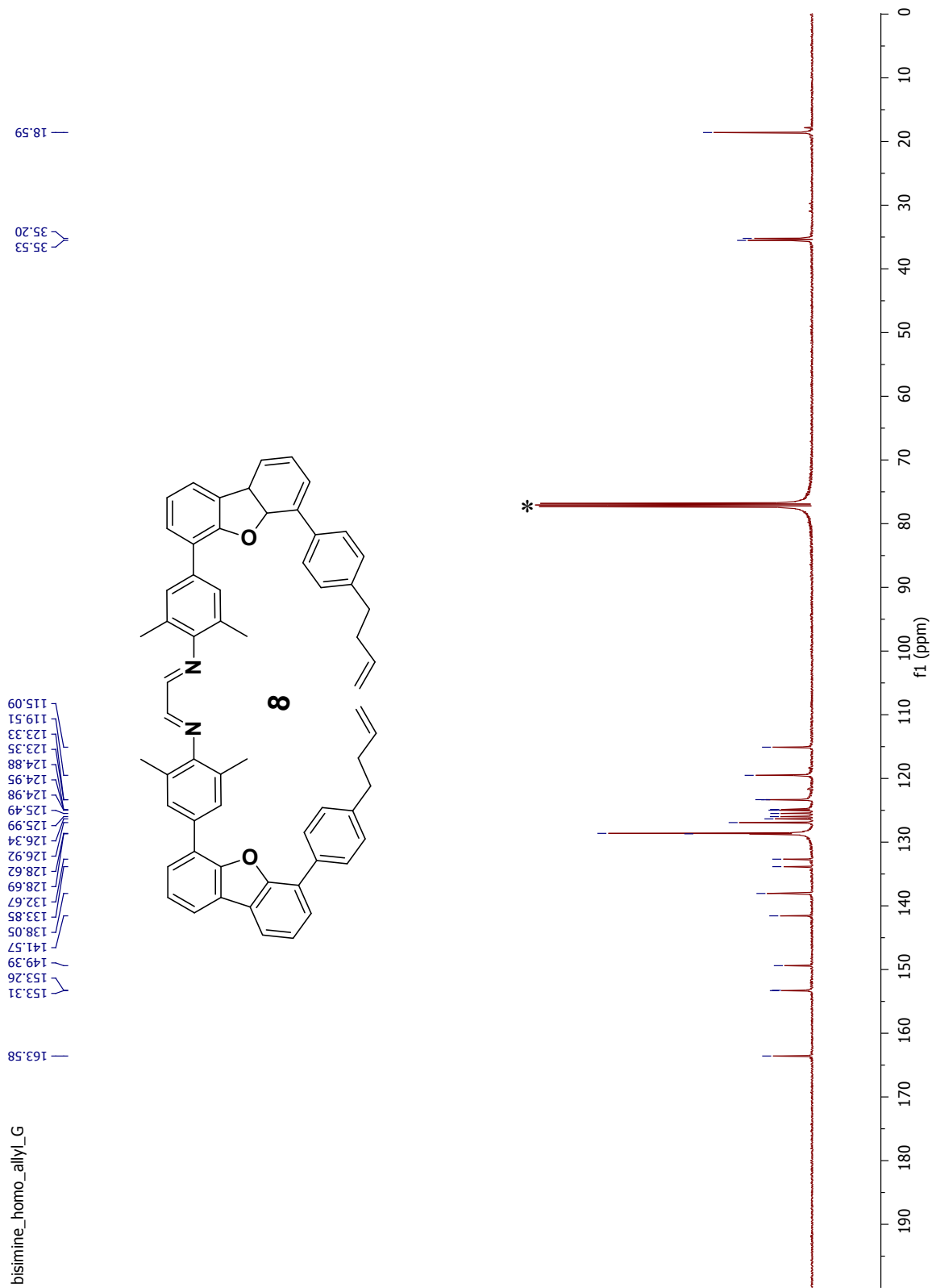


Figure S9.  $^{13}\text{C}$  NMR spectrum of bisimine **8** in  $\text{CDCl}_3$ . An asterisk \* marks the solvent peak.



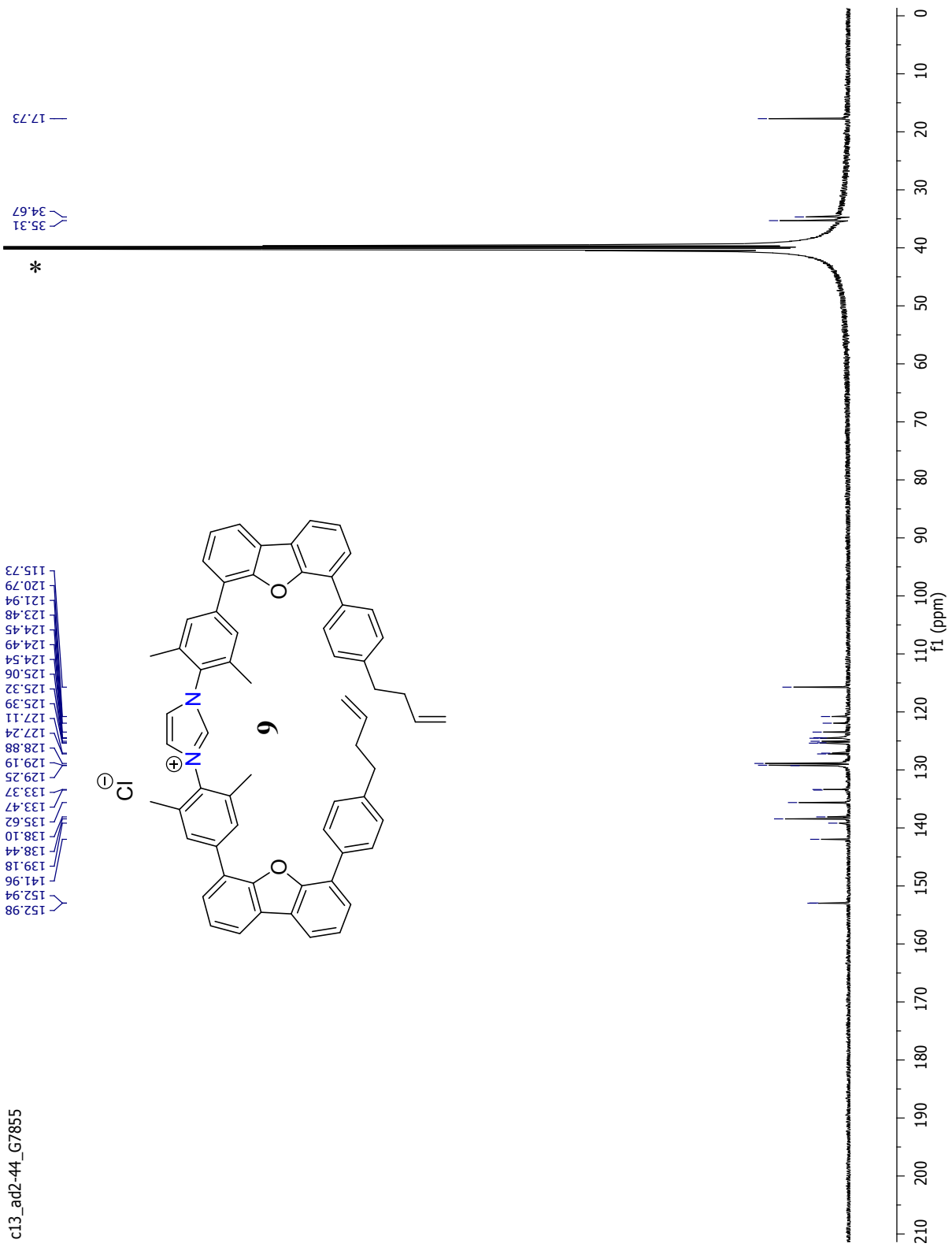


Figure S11.  $^{13}\text{C}$  NMR spectrum of imidazolium chloride **9** in  $(\text{CD}_3)_2\text{SO}$ . An asterisk \* marks the solvent peak.

ad2-48good  
check



Figure S12. <sup>1</sup>H NMR spectrum of macrocyclic imidazolium chloride **1** in (CD<sub>3</sub>)<sub>2</sub>SO. An asterisk \* marks the solvent peak and # symbol denotes impurities.

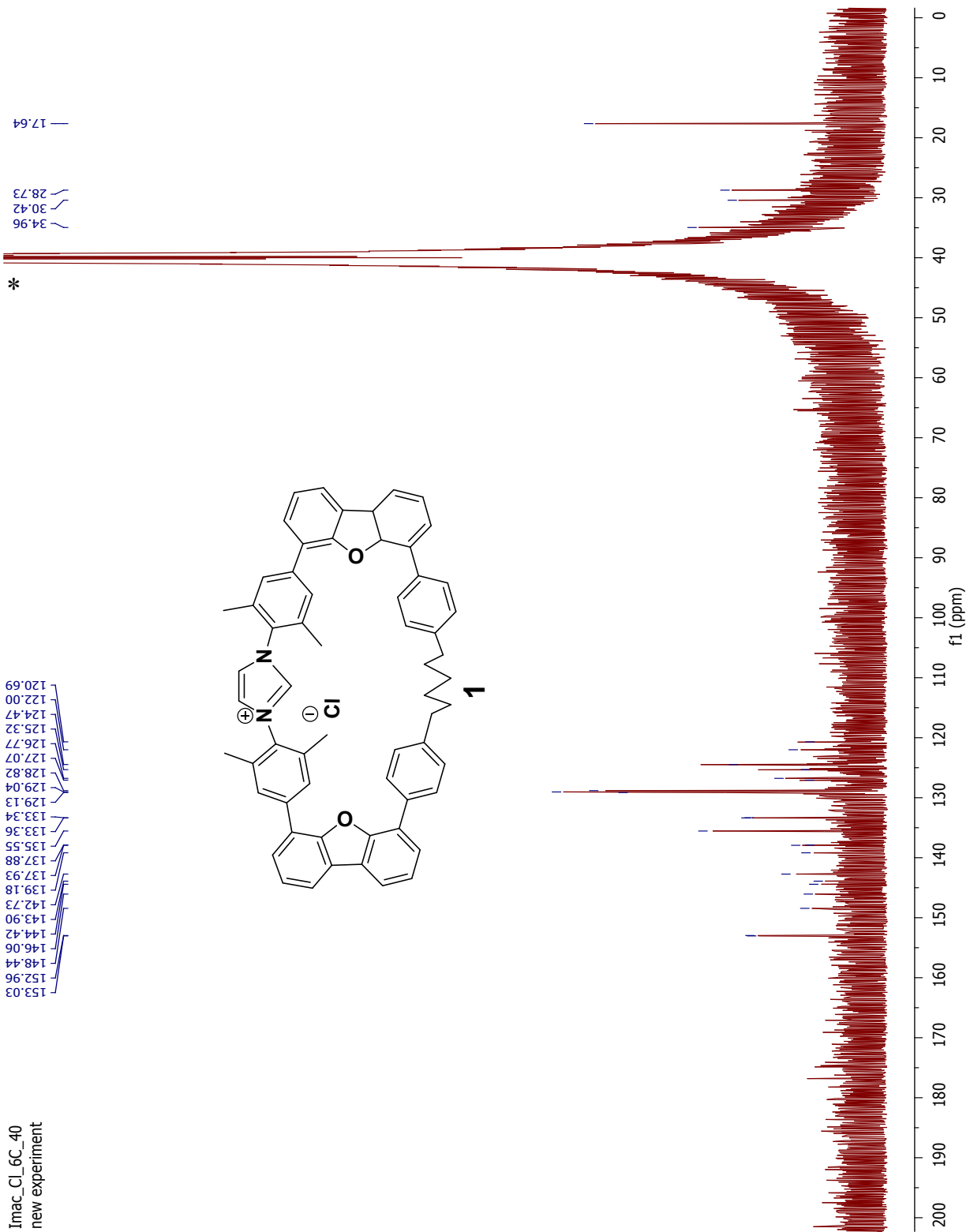


Figure S13. <sup>13</sup>C NMR spectrum of macrocyclic imidazolium chloride **1** in (CD<sub>3</sub>)<sub>2</sub>SO. An asterisk \* marks the solvent peak.

DADHA\_1H~G  
DADHA

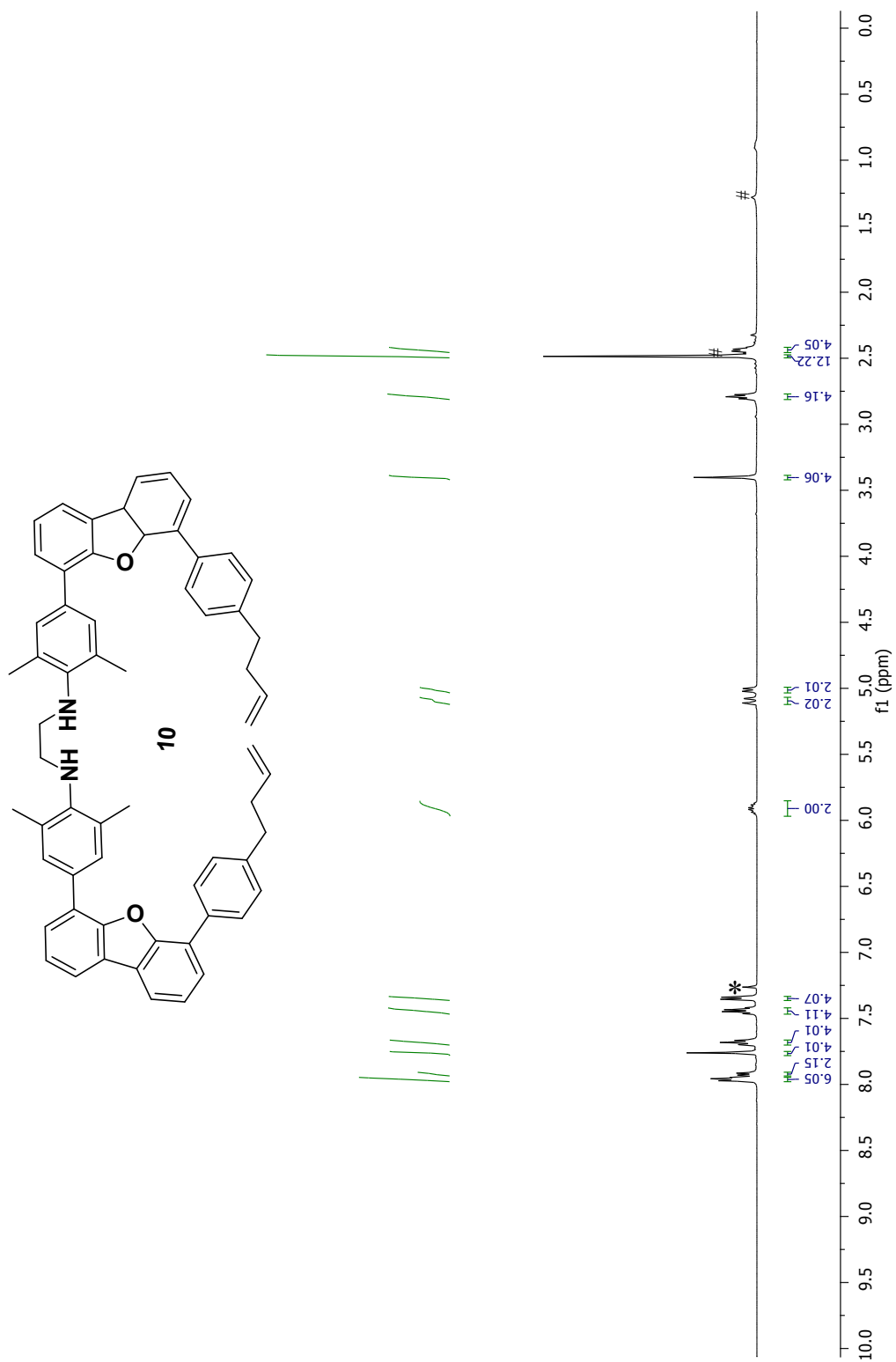


Figure S14.  $^1\text{H}$  NMR spectrum of diamine **10** in  $(\text{CD}_3)_2\text{SO}$ . An asterisk \* marks the solvent peak and # symbol denotes impurities.

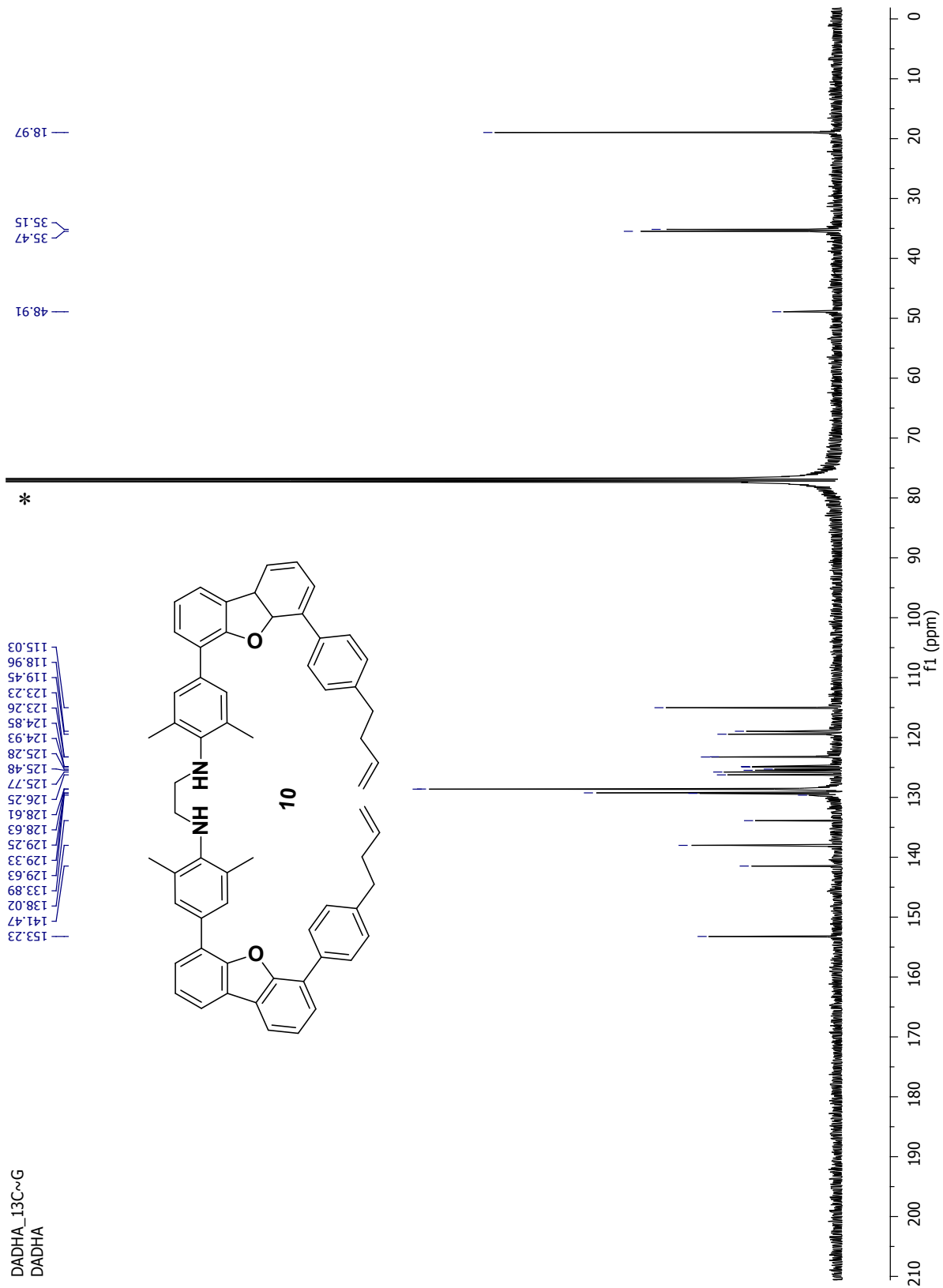


Figure S15.  $^{13}\text{C}$  NMR spectrum of diamine **10** in  $(\text{CD}_3)_2\text{SO}$ . An asterisk \* marks the solvent peak.

H2Imi\_HA\_1H\_G  
H2Imi\_HA

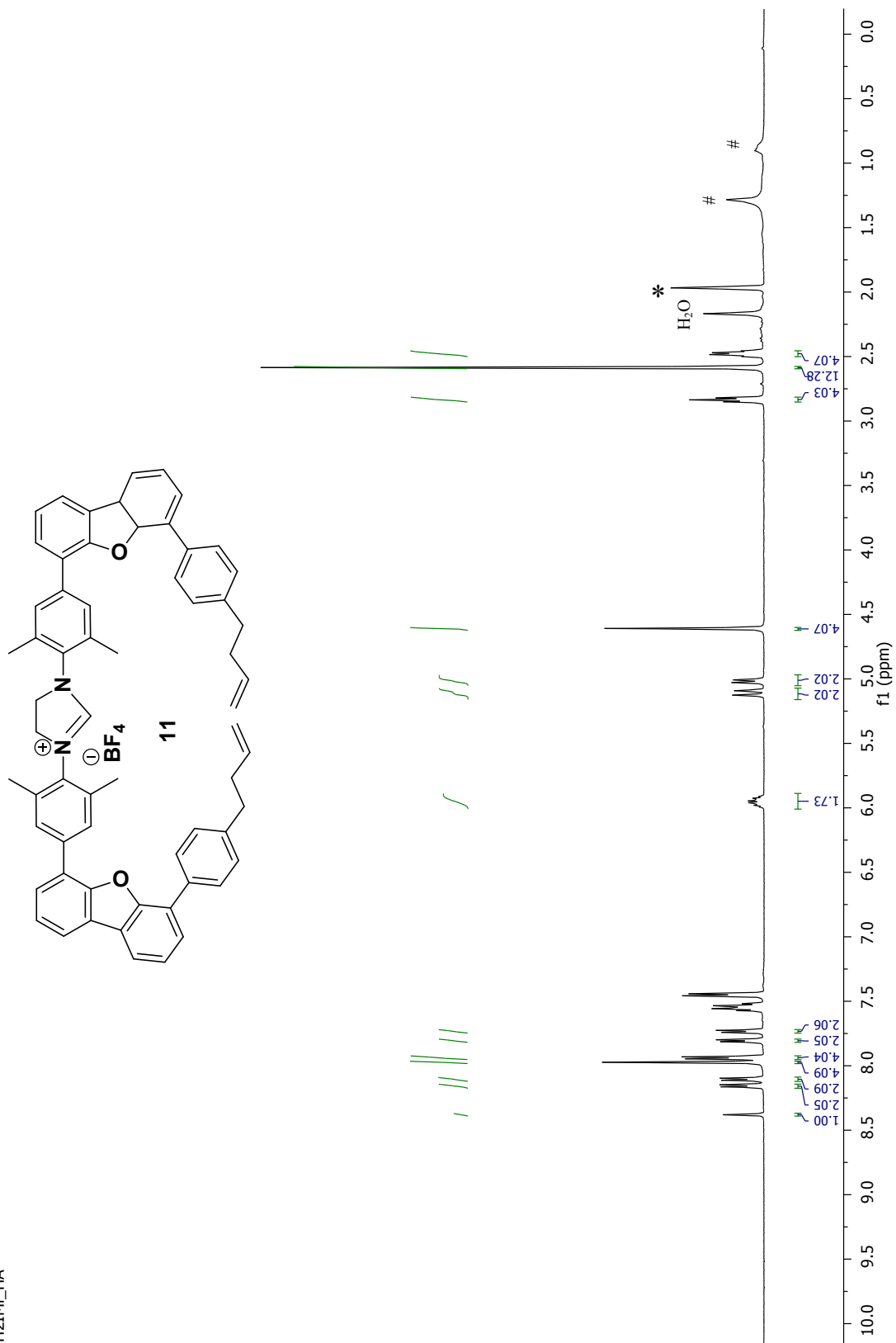


Figure S16. <sup>1</sup>H NMR spectrum of dihydroimidazolium tetrafluoroborate **11** in CD<sub>3</sub>CN. An asterisk \* marks the solvent peak and # symbol denotes impurities.

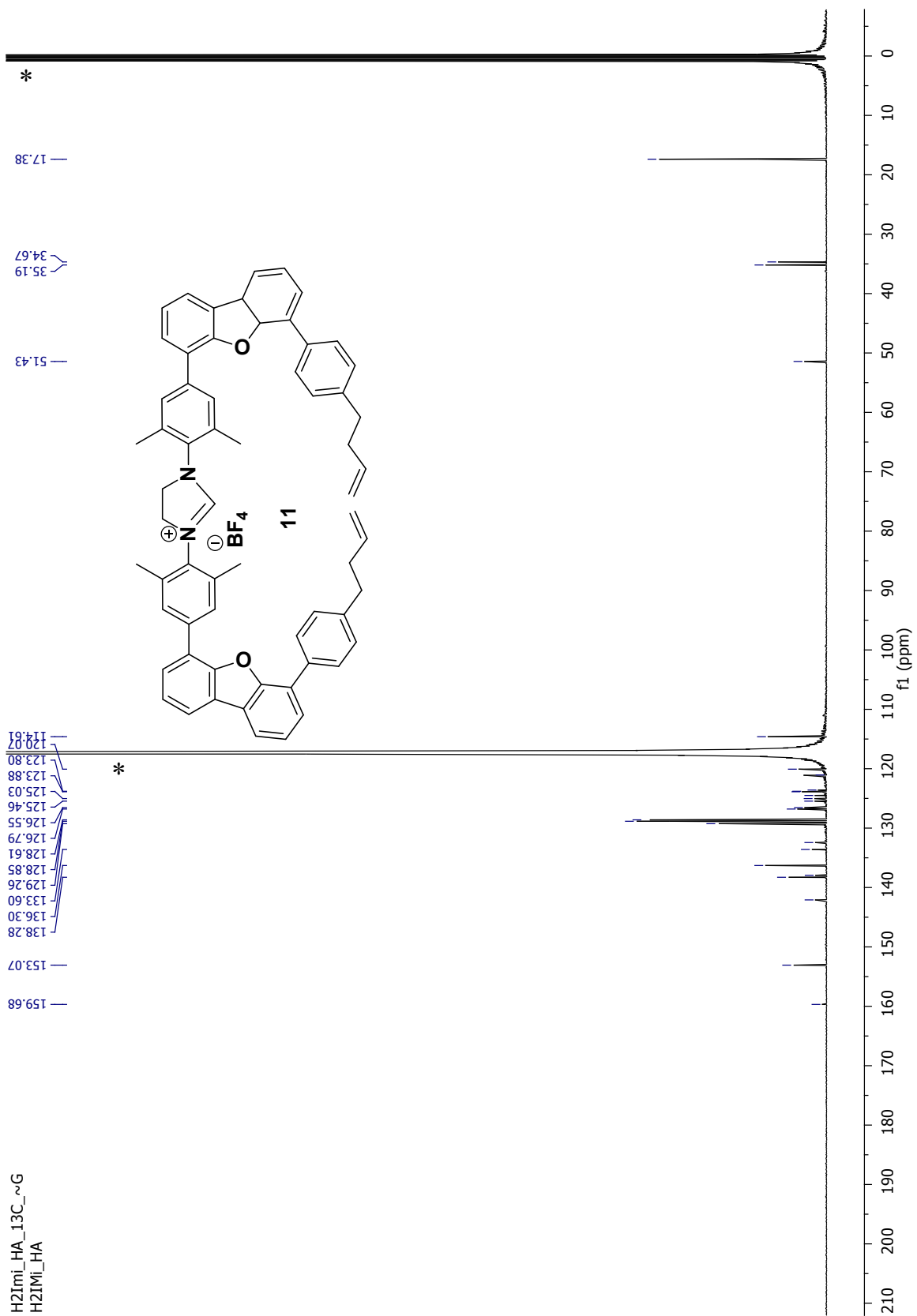


Figure S17.  $^{13}\text{C}$  NMR spectrum of dihydroimidazolium tetrafluoroborate **11** in  $\text{CD}_3\text{CN}$ . An asterisk \* marks the solvent peak.

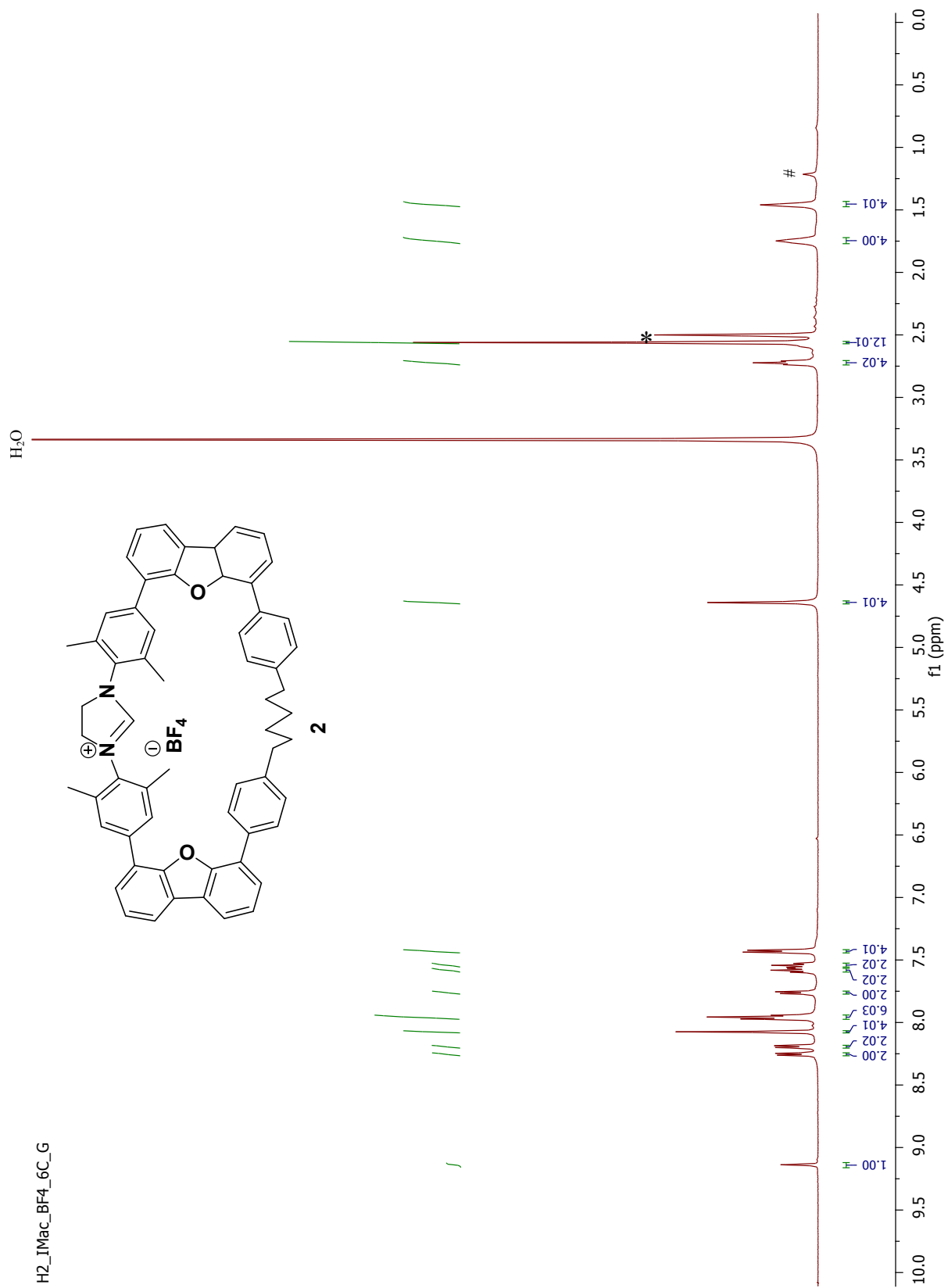


Figure S18.  $^1\text{H}$  NMR spectrum of macrocyclic dihydroimidazolium tetrafluoroborate **2** in  $(\text{CD}_3)_2\text{SO}$ . An asterisk \* marks the solvent peak and # symbol denotes impurities.

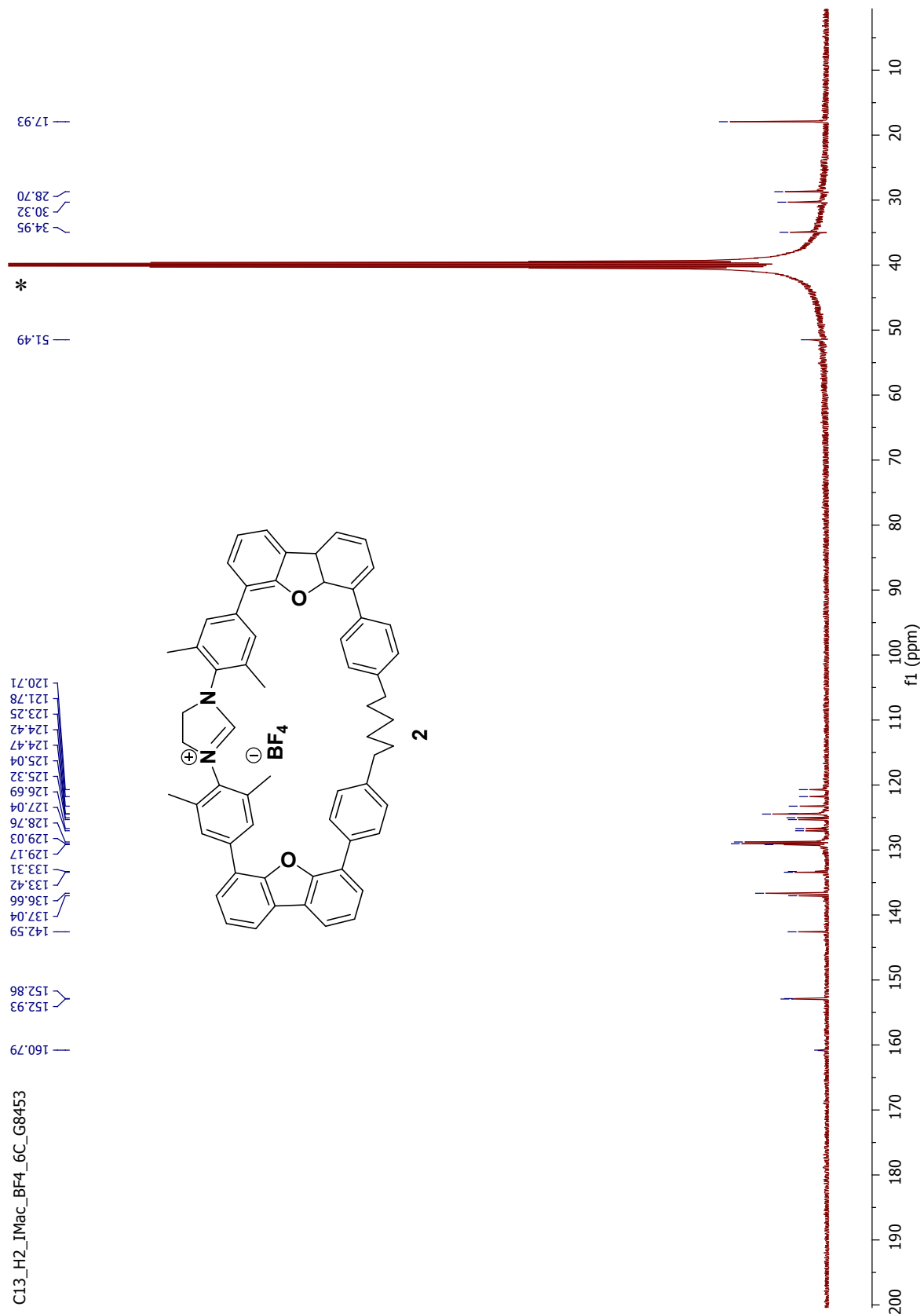


Figure S19. <sup>13</sup>C NMR spectrum of macrocyclic dihydroimidazolium tetrafluoroborate **2** in (CD<sub>3</sub>)<sub>2</sub>SO. An asterisk \* marks the solvent peak.

pmc6\_h1~9

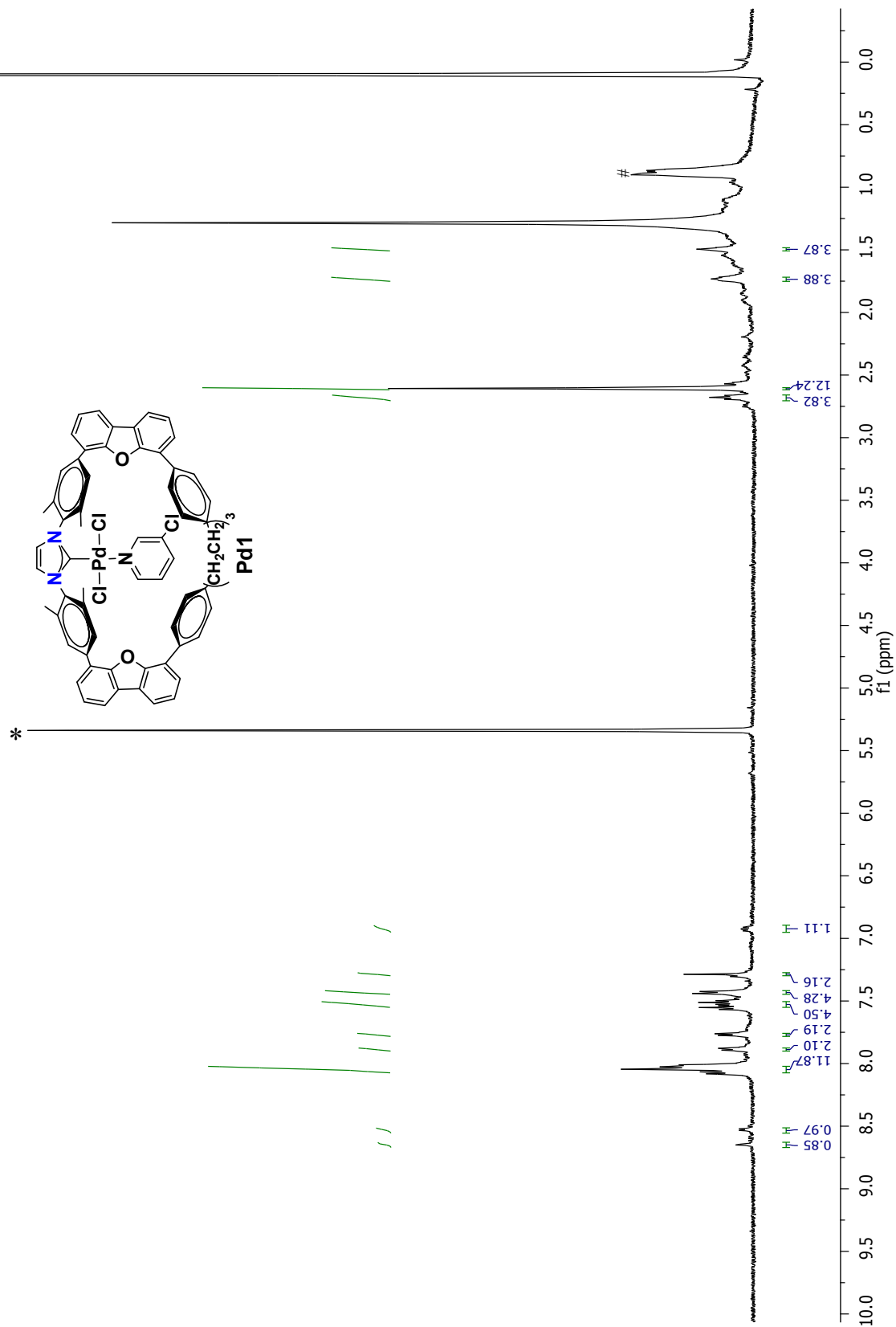


Figure S20. <sup>1</sup>H NMR spectrum of **Pd1** in CD<sub>2</sub>Cl<sub>2</sub>. An asterisk \* marks the solvent peak and # symbol denotes impurities.

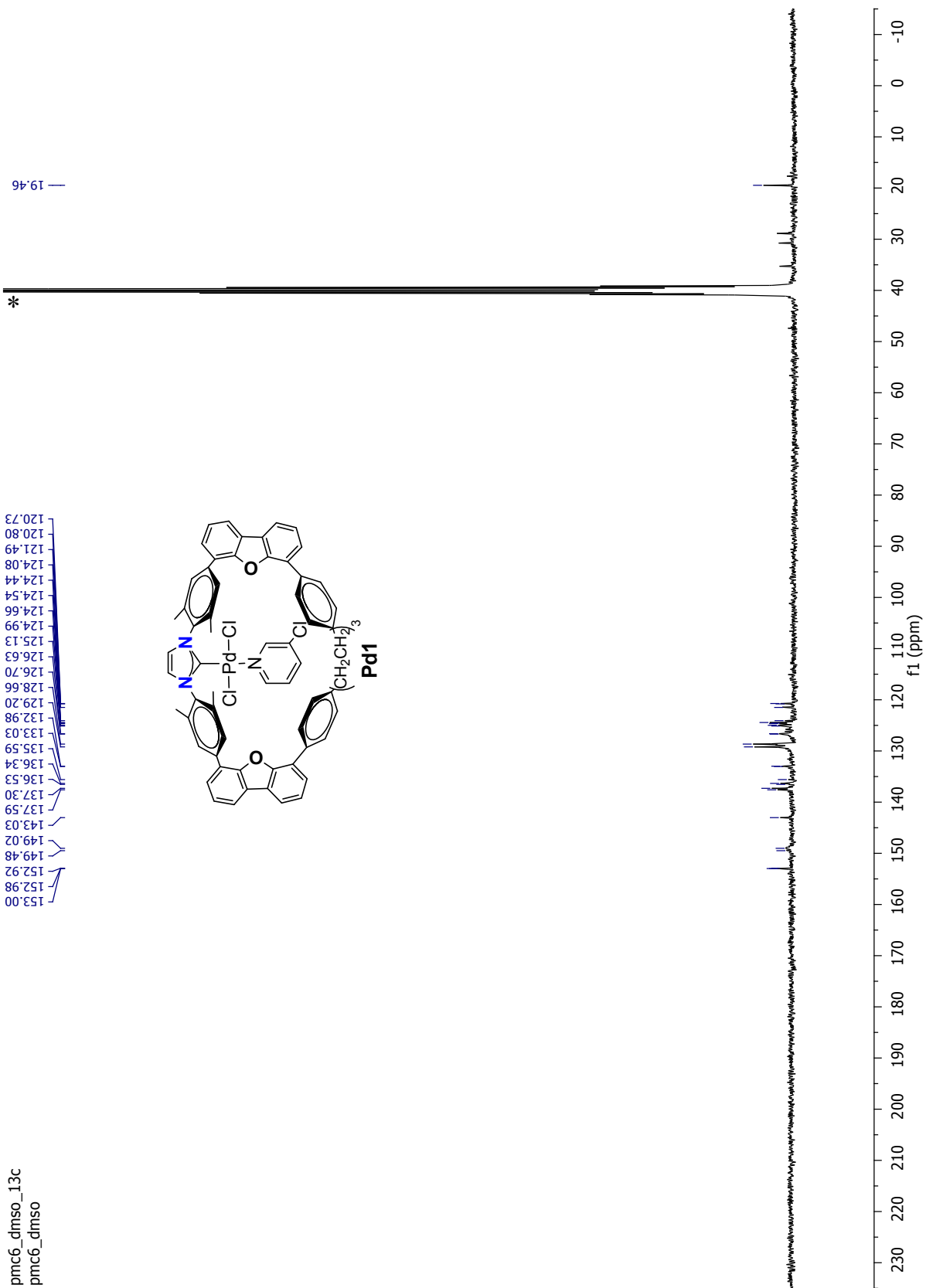


Figure S21.  $^{13}\text{C}$  NMR spectrum of **Pd1** in  $\text{CD}_2\text{Cl}_2$ . An asterisk \* marks the solvent peak.

HZIMachHov\_C6\_1H

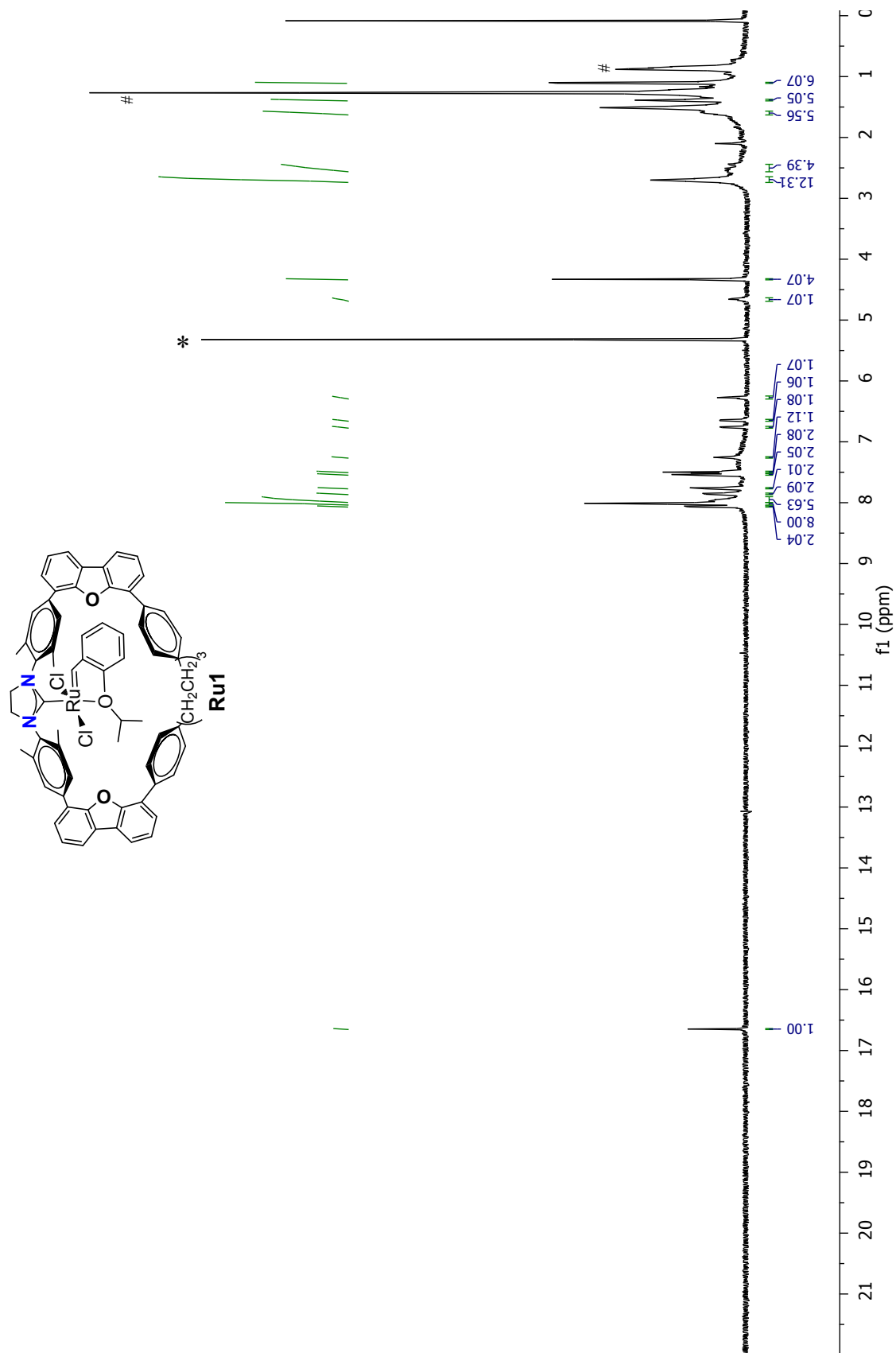


Figure S22. <sup>1</sup>H NMR spectrum of **Ru1** in CD<sub>2</sub>Cl<sub>2</sub>. An asterisk \* marks the solvent peak and # symbol denotes impurities.

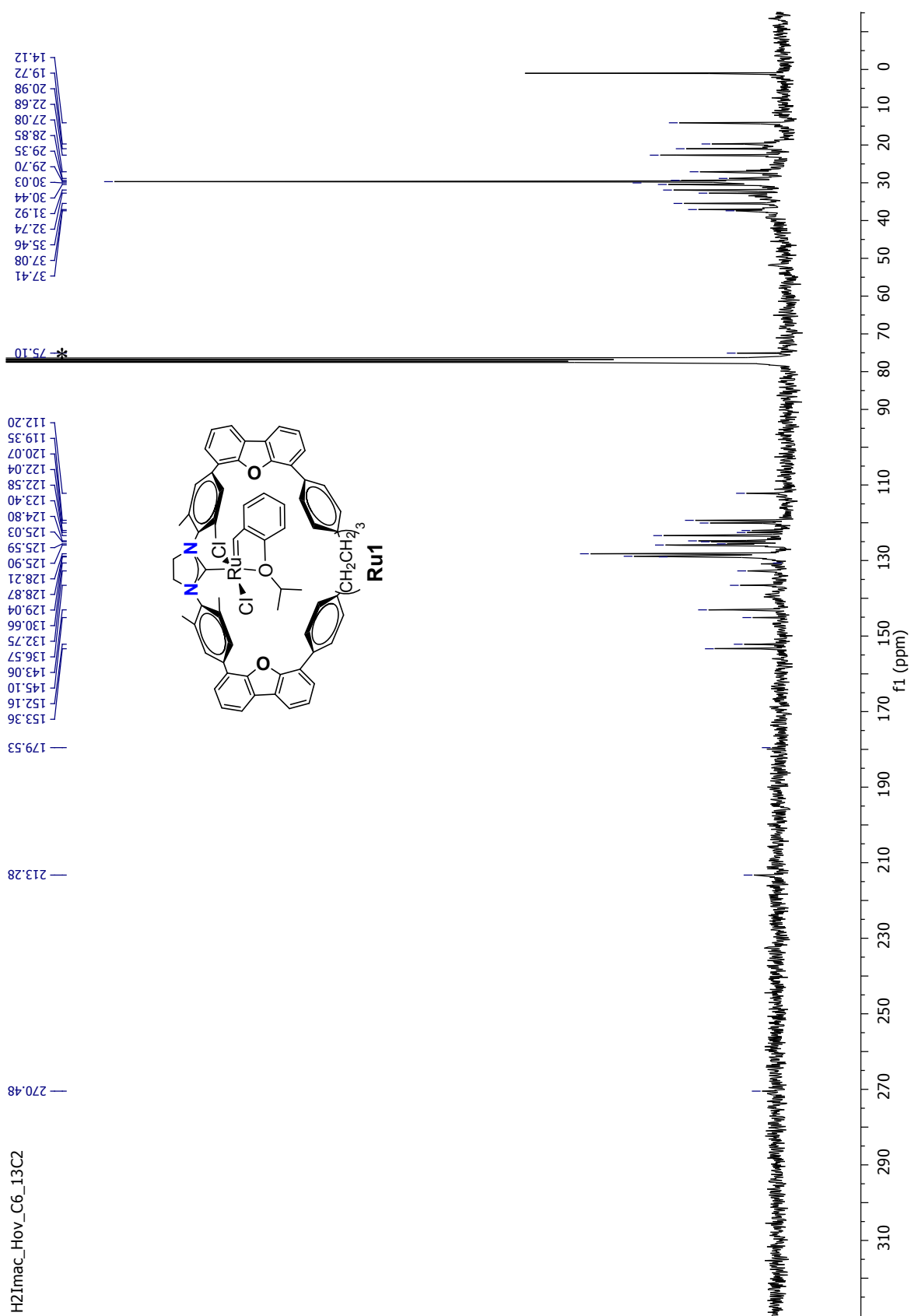


Figure S23.  $^{13}\text{C}$  NMR spectrum of **Ru1** in  $\text{CDCl}_3$ . An asterisk \* marks the solvent peak.

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