Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Pseudorotaxane Orientational Stereoisomerism Driven by π-Electron Density

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GENERAL COMMENTS

ESI(+)-MS measurements were performed on a triple quadrupole mass spectrometer equipped with electrospray ion source, using a mixture of H_2O/CH_3CN (1:1) and 5% HCOOH as solvent. All chemicals were reagent grade and were used without further purification. Anhydrous solvents were purchased from Aldrich. When necessary compounds were dried *in vacuo* over $CaCl_2$. Reaction temperatures were measured externally. Reactions were monitored by TLC on Merck silica gel plates (0.25 mm) and visualized by UV light, or by sprying with H_2SO_4-$Ce(SO_4)_2$.

Derivatives **1**, **2**$^+$, **4a**$^+$, **11c**$^+$, and sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate, were synthesized according to literature procedures.[1]

NMR spectra were recorded on a Bruker Avance-600 spectrometer [600 (^{1}H) and 150 MHz (^{13}C)], Bruker Avance-400 spectrometer [400 (^{1}H) and 100 MHz (^{13}C)], Bruker Avance-300 spectrometer [300 (^{1}H) and 75 MHz (^{13}C)], or Bruker Avance-250 spectrometer [250 (^{1}H) and 63 MHz (^{13}C)]; chemical shifts are reported relative to the residual solvent peak ($C\mathit{H}Cl_3$: δ 7.26, $\mathit{C}DCl_3$: δ 77.23; $CD_3O\mathit{H}$: δ 4.87, $\mathit{C}D_3OD$: δ 49.0). A standard pulse program, provided by the manufacturer, was used for 2D COSY experiments.

Full geometry optimizations have been carried out with the B3LYP density functional with the standard 6-31G(d,p) basis set with the Gaussian 09 package.[2] All calculations included Grimme's dispersion[3] correction, present in Gaussian 09, using IOp(3/124 = 3). Single-point calculations were carried out at M06/6-31+G(d,p) level of theory. GaussianView 5.0.8W was used in the calculation of ESP at the B3LYP/6-31G(d,p) level. The input structures for ESP calculations were optimized at the B3LYP/6-31G(d,p) level of theory.

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[1] a) Gaeta, C.; Troisi, F.; Neri, P. *Org. Lett.* **2010**, *12*, 2092−2095; b) Nishida, H.;Takada, N.; Yoshimura, M.; Sonoda, T.; Kobayashi, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2600−2604; c) Gaeta, C.; Talotta, C.; Farina, F.; Camalli, M.; Campi, G.; Neri, P. *Chem. Eur. J.* **2012**, *18*, 1219−1230; d) Ikeda, A.; Nagasaki, T.; Araki, K.; Shinkai, S. *Tetrahedron* **1992**, *48*, 1059–1070; e) Sutter, M.; Pehlivan, L.; Lafon, R.; Dayoub, W.; Raoul, Y.; Métaya, E.; Lemaire, M. *Gren Chem.*, **2013**, *15*, 3020-3026.

[2] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc.: Wallingford CT, 2009.

[3] Grimme, S. *J. Comput. Chem.* **2006**, *27*, 1787-1799.

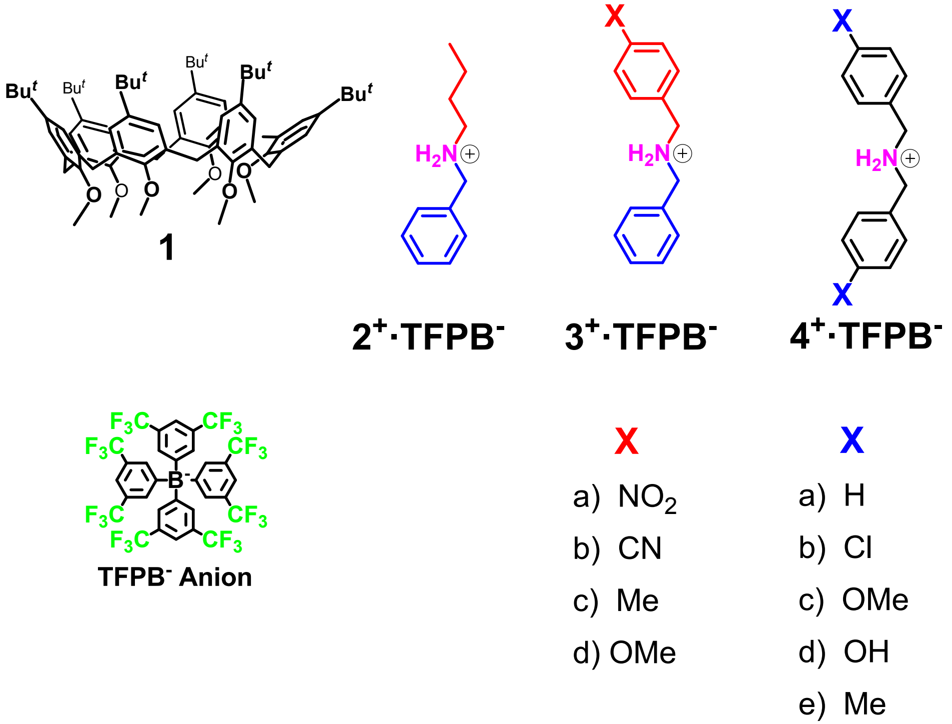
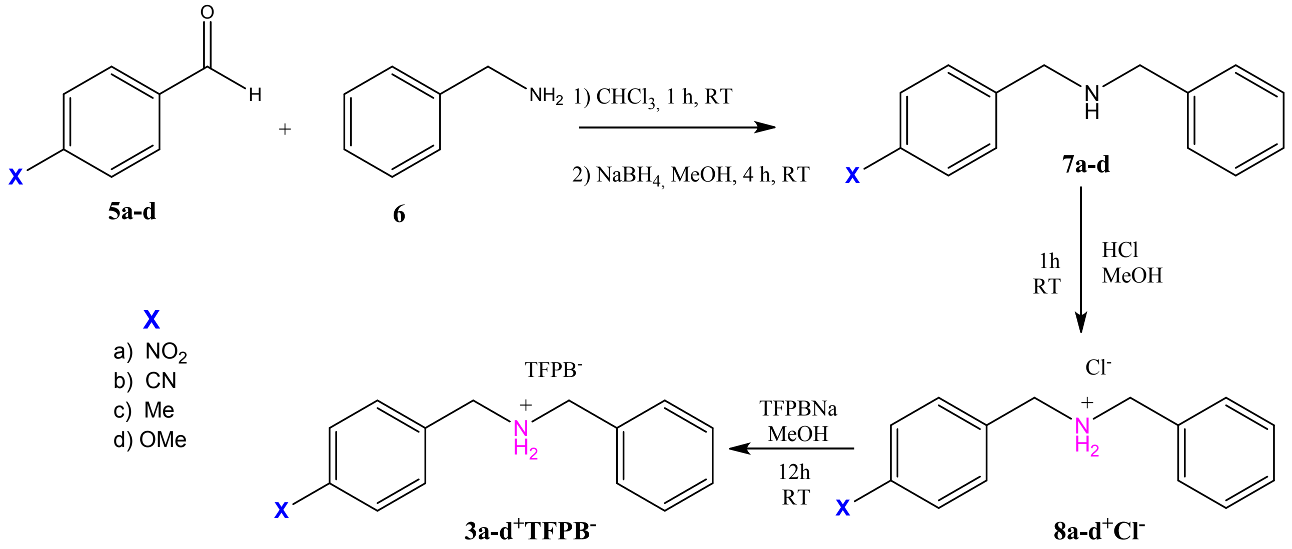
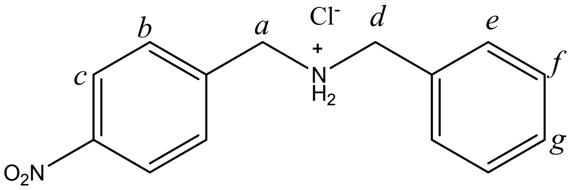

Bu^t
1
$H_2N^{\oplus}$
X
$2^+\cdot$TFPB$^-$
$3^+\cdot$TFPB$^-$
$4^+\cdot$TFPB$^-$
F_3C
CF_3
B^-
TFPB$^-$ Anion
X
a) NO_2
b) CN
c) Me
d) OMe
X
a) H
b) Cl
c) OMe
d) OH
e) Me

Chart S1

General procedure for the synthesis of 3a-d$^+\cdot$TFPB$^-$ salts

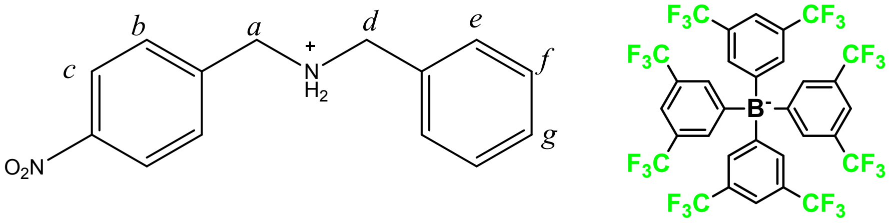


To a solution of aldehyde **5a-d** (5.0 mmol) in $CHCl_3$ (5 mL) was added benzylamine **6** (5.0 mmol). The reaction mixture was stirred at room temperature for 1 h. The solvent was evaporated to give the imine intermediate in quantitative yield as a yellow solid. The solid was used for the next step without further purification. The imine was dissolved in dry MeOH (50 mL) under a nitrogen atmosphere and $NaBH_4$ (50.0 mmol) was added at 0 °C and then the mixture was allowed to warm at room temperature. The solution was kept under stirring for 4 h. The solvent was removed under reduced pressure and the residue partitioned between AcOEt (100 mL) and a saturated aqueous solution of $NaHCO_3$ (100 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure, to give secondary amine **7a-d** as a yellow solid. The solid was used for the next step without further purification. The crude product was dissolved in MeOH at room temperature and an aqueous solution of HCl (37% w/w, 10 mmol) was added dropwise. The mixture was kept under stirring for 1 h, until a white precipitate was formed. The solid was collected by filtration, washed with MeOH (10 mL) and CH_3CN (10 mL), and dried under vacuum to give salt **8a-d**$^+\cdot$Cl$^-$ as a white solid. Derivative **8a-d**$^+\cdot$Cl$^-$ (2.0 mmol) was dissolved in warm dry MeOH (20 mL), then a solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (2.0 mmol) in dry MeOH (10 mL) was added. The mixture was kept under stirring overnight in the dark. The solvent was removed and deionized water was added, obtaining a brown precipitate that was filtered off and dried under vacuum to give salt **3a-d**$^+\cdot$TFPB$^-$.



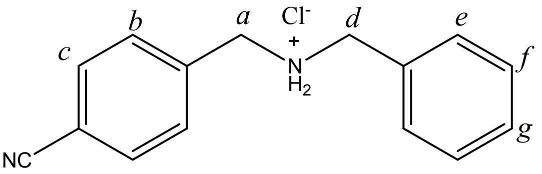
8a$^+$·Cl$^-$

Derivative 8a$^+$·Cl$^-$: (1.19 g, 4.3 mmol, 86%). **ESI(+) MS**: *m*/*z* = 267.2 (M$^+$). **^{1}H NMR** (300 MHz, CD_3OD, 298 K): δ 4.03 (s, 2H, H_d), 4.04 (s, 2H, H_a), 7.45-7.52- (overlapped, 5H, $H_{e\text{-}f\text{-}g}$), 7.76 (d, *J* = 6Hz, 2H, H_b), 8.29 (d, *J* = 6Hz, 2H, H_c); **^{13}C NMR** (75 MHz, CD_3OD, 298 K): δ 49.8, 51.3, 123.8, 129.1, 129.6, 129.9, 130.9, 131.2, 138.2, 148.8. Anal. Calcd for $C_{14}H_{15}ClN_2O_2$: C, 60.33; H, 5.42. Found: C, 60.41; H, 5.33.



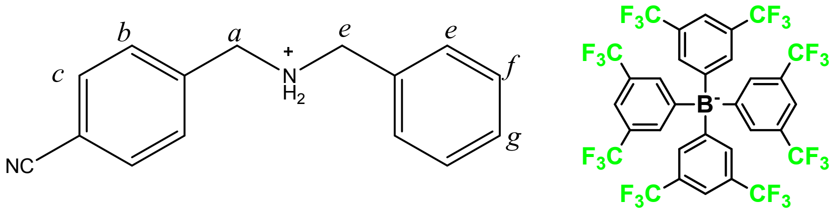
3a$^+$·TFPB$^-$

Derivative 3a$^+$·TFPB$^-$: (1.97 g, 1.78 mmol, 89%). **ESI(+) MS**: *m*/*z* = 267.2 (M$^+$). **^{1}H NMR** (400 MHz, CD_3OD, 298 K): 4.28 (s, 2H, H_d), 4.38 (s, 2H, H_a), 7.47 (overlapped, 5H, $H_{e\text{-}g}$), 7.58 (overlapped, 12H, ArH^{TFPB}), 7.72 (d, *J* = 8.4Hz, 2H, H_b), 8.31 (d, *J* = 8.4Hz, 2H, H_c); **^{13}C NMR** (100 MHz, CD_3OD, 298 K): δ 49.7, 51.2, 117.1, 120.3, 123.0, 123.7, 125.7, 128.4, 128.9, 129.2, 129.2, 129.4, 129.6, 130.8, 130.9, 134.4, 138.1, 148.6, 160.7, 161.2, 161.7, 162.2. Anal. Calcd for $C_{46}H_{27}BF_{24}N_2O_2$: C, 49.93; H, 2.46. Found: C, 50.02; H, 2.39.



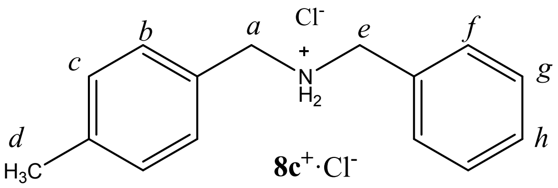
8b$^+$·Cl$^-$

Derivative 8b$^+$·Cl$^-$: (1.19 g, 4.6 mmol, 92%). **ESI(+) MS**: *m*/*z* = 222.6 (M$^+$). **^{1}H NMR** (300 MHz, CD_3OD, 298 K): δ 4.30-4.35 (overlapped, 4H, $H_{a,d}$), 7.45-7.80 (overlapped, 9H, $H_{e\text{-}g}$ H_b+ H_c); **^{13}C NMR** (75 MHz, CD_3OD, 298 K): δ 49.9, 51.2, 113.3, 129.1, 129.6, 129.9, 130.8, 132.7, 136.4. Anal. Calcd for $C_{15}H_{15}ClN_2$: C, 69.63; H, 5.84. Found: C, 69.72; H, 5.75.



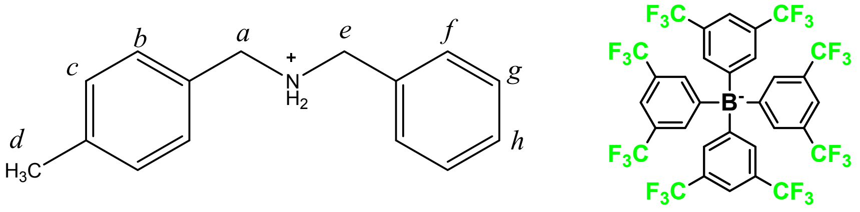
3b$^+$·TFPB$^-$

Derivative 3b$^+$·TFPB$^-$: (2.13 g, 1.96 mmol, 98%). **ESI(+) MS**: *m*/*z* = 222.6 (M$^+$). **^{1}H NMR** (400 MHz, CD_3OD, 298 K): δ 4.24 (s, 2H, H_d), 4.32 (s, 2H, H_a), 7.47 (overlapped, 5H, $H_{e\text{-}g}$), 7.58 (overlapped, 12H, Ar^{TFPB}), 7.64 (d, J = 9.2Hz, 2H, H_b), 7.82 (d, J = 9.2Hz, 2H, H_c); **^{13}C NMR** (100 MHz, CD_3OD, 298 K): δ; 51.4, 52.6, 114.6, 118.4, 118.9, 121.7, 124.4, 127.1, 129.8, 129.9, 130.3, 130.4, 130.6, 130.8, 131.0, 131.9, 132.3, 134.0, 135.8, 137.8, 162.1, 162.6, 163.1, 163.6. Anal. Calcd for $C_{47}H_{27}BF_{24}N_2$: C, 51.96; H, 2.50. Found: C, 52.05; H, 2.42.



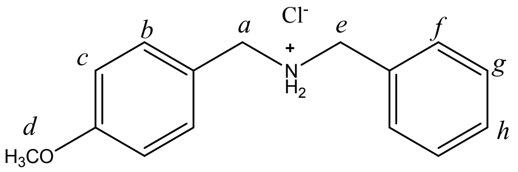
$\mathbf{8c^{+}{\cdot}Cl^{-}}$

Derivative $\mathbf{8c^{+}{\cdot}Cl^{-}}$: (1.00 g, 4.05 mmol, 81%). **ESI(+) MS**: m/z = 211.7 (M^+). ^{1}**H NMR** (400 MHz, CD_3OD, 298 K): δ 2.36 (s, 3H, H_d),4.18 (s, 2H, H_e), 4.20 (s, 2H, H_a), 7.27 (d, J = 8Hz, 2H, H_c), 7.36 (d, J = 8 Hz, 2H, H_b), 7.45-7.46 (overlapped, 5H, $H_{f\text{-}h}$); ^{13}**C NMR** (63 MHz, CD_3OD, 298 K): δ 38.3, 49.9, 50.4, 115.3, 123.9,130.0, 130.4,130.9, 132.3, 132.6. Anal. Calcd for $C_{15}H_{18}ClN$: C, 72.71; H, 7.32. Found: C, 72.80; H, 7.23.



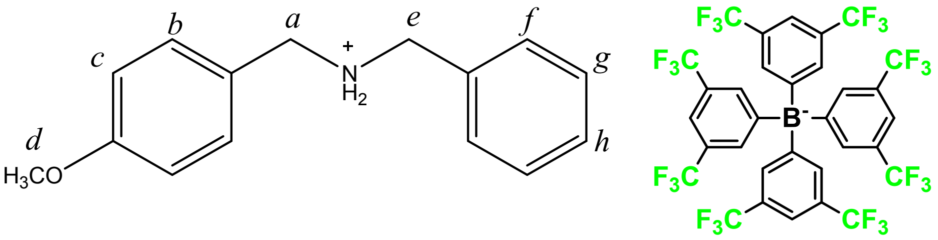
$\mathbf{3c^{+}}{\cdot}\mathrm{TFPB^{-}}$

Derivative $\mathbf{3c^{+}{\cdot}TFPB^{-}}$: (1.85 g, 1.72 mmol, 86%).**ESI(+) MS**: m/z = 211.7 (M^+). ^{1}**H NMR** (250 MHz, CD_3OD, 298 K): δ 2.34 (s, 3H, H_d), 4.16 (s, 2H, H_e), 4.19 (s, 2H, H_a), 7.28-7.36 (overlapped, 4H, $H_{c,b}$), 7.36 (overlapped, 5H, $H_{f\text{-}h}$), 7.59 (overlapped, 12H, Ar^{TFPB}); ^{13}**C NMR** (63 MHz, CD_3OD, 298 K): δ 21.2, 51.8, 51.9, 118.5, 119.3, 123.6, 127.9, 129.4, 129.7, 130.3, 130.7, 130.9, 132.2, 132.6, 135.8, 141.0, 161.6, 162.4, 163.2, 164.0. Anal. Calcd for $C_{47}H_{30}BF_{24}N$: C, 52.49; H, 2.81. Found: C, 52.58; H, 2.73.



8d$^+$·Cl$^-$

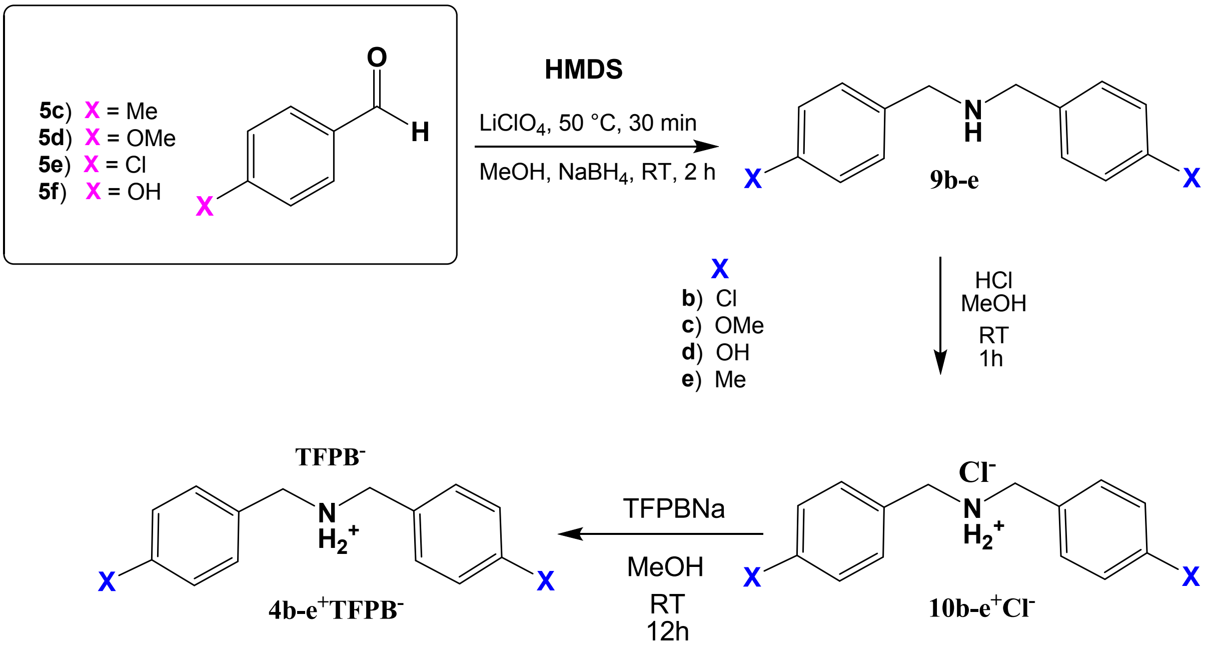
Derivative 8d$^+$·Cl$^-$: (1.10 g, 4.2 mmol, 84%). **ESI(+) MS**: m/z = 227.7 (M$^+$). **^{1}H NMR** (400 MHz, CD$_3$OD, 298 K): δ 3.80 (s, 3H, H$_d$), 4.18 (s, 2H, H$_a$), 4.21 (s, 2H, H$_e$), 6.98 (broad, 2H, H$_b$), 7.44-7.52 (overlapped, 7H, H$_c$+$H_{f\text{-}h}$); **^{13}C NMR** (100 MHz, CD$_3$OD, 298 K): δ 51.6, 51.7, 55.8, 115.5, 124.1, 130.3, 130.6, 131.1, 132.5, 132.7, 162.1. Anal. Calcd for $C_{15}H_{18}ClNO$: C, 68.30; H, 6.88. Found: C, 68.40; H, 6.97.



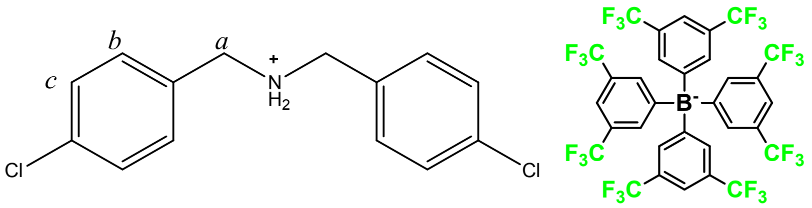
3d$^+$·TFPB$^-$

Derivative 3d$^+$·TFPB$^-$: (2.07 g, 1.90 mmol, 95%). **ESI(+) MS**: m/z = 227.7 (M$^+$). **^{1}H NMR** (250MHz, CD$_3$OD, 298 K): δ 3.66 (s, 3H, H$_d$), 4.20 (s, 2H, H$_e$), 4.22 (s, 2H, H$_a$), 7.48-7.63 (overlapped, 21H, H$_{c,b}$ +H$_{f\text{-}h}$ + Ar^{TFPB});**^{13}C NMR** (63 MHz, CD$_3$OD, 298 K): δ 52.4, 52.5, 55.3, 119.0, 119.8, 124.1, 128.4, 130.0, 130.8, 131.2, 131.39, 131.43, 132.7, 133.1, 136.3, 141.5, 162.1, 162.9, 163.7, 164.5. Anal. Calcd for $C_{47}H_{30}BF_{24}NO$: C, 51.72; H, 2.77. Found: C, 51.81; H, 2.68.

Synthesis of 4b-e$^+$·TFPB$^-$ salts

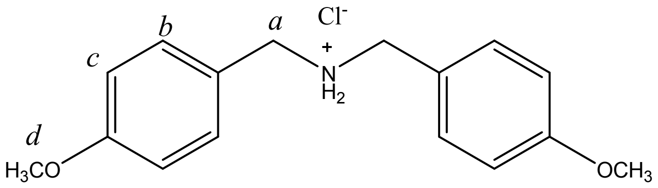


A mixture of appropriate aldehyde **5c-f** (2 mmol), hexamethyldisilazane (HMDS, 4 mmol), and $LiClO_4$ (2 mmol) was heated for 30 min at 50 °C. The reaction mixture was cooled at 0 °C and a solution of $NaBH_4$ (10 mmol) in methanol (5 mL) was slowly added over a period of 15 min. The reaction mixture was allowed to warm at room temperature and then stirred for 2 h. Methanol was removed under reduced pressure, the residue was quenched with a saturated aqueous solution of $NaHCO_3$ (50 mL) and extracted with AcOEt (50 mL). The combined organic extract was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was dissolved in MeOH at room temperature and an aqueous solution of HCl (37% w/w, 3 mmol) was added dropwise. The mixture was kept under stirring for 15 min until a white precipitate was formed. The solid was collected by filtration, washed with MeOH (20 mL) and CH_3CN (20 mL), and dried under vacuum, to give solid salts **10b-e$^+$·Cl$^-$**. Each salt **10b-e$^+$·Cl$^-$** (1.0 mmol) was dissolved in warm dry MeOH (50 mL), then a solution of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1.0 mmol) in dry MeOH (25 mL) was added. The mixture was kept under stirring overnight in the dark. The solvent was removed and deionized water was added, obtaining a brown precipitate that was filtered off and dried under vacuum to give salts **4b-e$^+$·TFPB$^-$** .



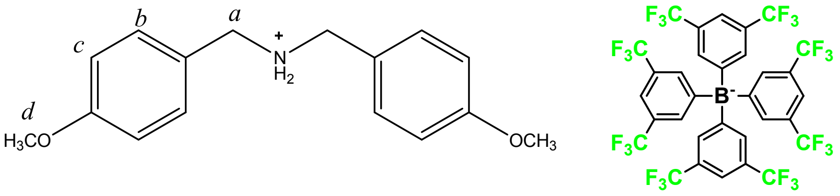
4b$^+$·TFPB$^-$

Derivative 4b$^+$·TFPB$^-$: (1.05 g, 0.93 mmol, 93%). **ESI(+) MS**: m/z = 265.6 (M^+). **^{1}H NMR** (400 MHz, CD_3OD, 298 K): δ 4.23 (s, 4H, H_a), 7.48 (s, 12H, ArH^{TFPB}), 7.60-7.63 (overlapped, 8H, H_{b+c}); **^{13}C NMR** (100 MHz, CD_3OD, 298 K): δ 53.0, 120.0, 123.2, 126.0, 128.6, 131.3, 131.5, 131.8, 132.0, 132.1, 132.1, 132.5, 132.8, 133.9, 134.2, 137.3, 138.4, 163.7, 164.2, 164.7, 165.2. Anal. Calcd for $C_{46}H_{26}BCl_2F_{24}N$: C, 48.88; H, 2.32. Found: C, 48.99; H, 2.23.



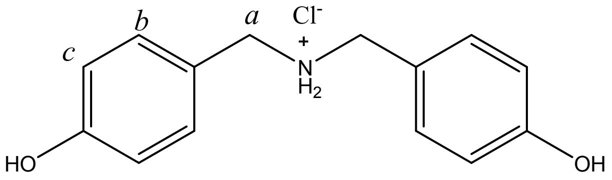
10c$^+$·Cl$^-$

Derivative 10c$^+$·Cl$^-$: (0.37 g, 1.28 mmol, 64%) **ESI(+) MS**: m/z = 257.7 (M^+). **^{1}H NMR** (600 MHz, CD_3OD, 298 K): 3.83 (s, 6H, H_d), 4.17 (s, 4H, H_a), 7.02 (d, J = 7.8Hz, 4H, H_c), 7.43 (d, J = 7.8Hz, 4H, H_b); **^{13}C NMR** (150 MHz, CD_3OD, 298 K): δ 51.3, 55.8, 115.5, 124.2, 132.6, 162.1. Anal. Calcd for $C_{16}H_{20}ClNO_2$: C, 65.41; H, 6.86. Found: C, 65.50; H, 6.78.



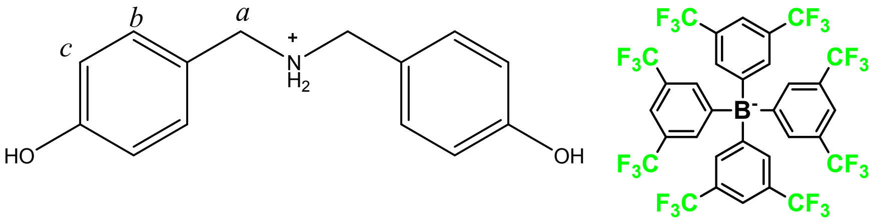
$4c^+$·TFPB$^-$

Derivative $4c^+\cdot$TFPB$^-$: (1.02 g, 0.91 mmol, 91%). **ESI(+) MS**: $m/z = 257.7$ (M^+). **^{1}H NMR** (600 MHz, CD_3OD, 298 K): 3.82 (s, 6H, H_d), 4.15 (s, 4H, H_a), 7.02 (d, J = 9Hz, 4H, H_c), 7.39 (d, J = 9Hz, 4H, H_b), 7.61-7.63 (overlapped, 12H, ArH^{TFPB}); **^{13}C NMR** (150 MHz, CD_3OD, 298 K): δ 55.5, 62.0, 116.5, 117.9, 119.8, 122.0, 123.4, 126.9, 129.4, 130.0, 130.5, 131.8, 135.2, 155.5, 161.4, 162.0, 162.8, 163.4. Anal. Calcd for $C_{48}H_{32}BF_{24}NO_2$: C, 51.40; H, 2.88. Found: C, 51.48; H, 2.79.



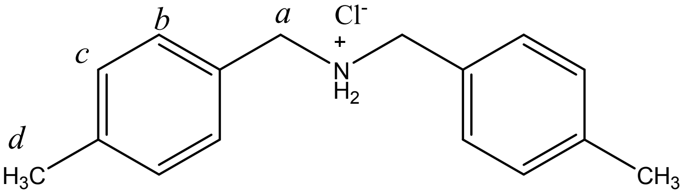
$10d^+$·Cl$^-$

Derivative $10d^+\cdot$Cl$^-$: (0.32 g, 1.20 mmol, 60%). **ESI(+) MS**: $m/z = 229.6$ (M^+). **^{1}H NMR** (400 MHz, CD_3OD, 298 K): 4.11(s, 4H, H_a), 6.87 (d, J = 8.8Hz, 4H, H_c), 7.32 (d, J = 8.8Hz, 4H, H_b); **^{13}C NMR** (100 MHz, CD_3OD, 298 K): δ 51.3, 116.9, 122.9, 132.6, 159.9. Anal. Calcd for $C_{14}H_{16}ClNO_2$: C, 63.28; H, 6.07. Found: C, 63.35; H, 6.15.



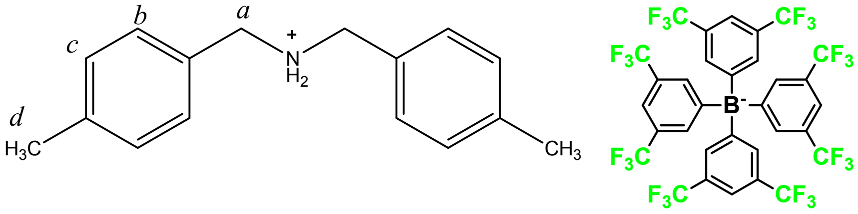
$4d^+ \cdot$TFPB$^-$

Derivative $4d^+ \cdot$TFPB$^–$: (0.96 g, 0.88 mmol, 88%). **ESI(+) MS**: *m*/*z* = 229.6 (M^+). **^{1}H NMR** (300 MHz, CD_3OD, 298 K): 4.10 (s, 4H, H_a), 6.87 (d, *J* = 8.4Hz, 4H, H_c), 7.30 (d, *J* = 8.4 Hz, 4H, H_b), 7.62 (overlapped, 12H, ArH^{TFPB}); **^{13}C NMR** (75 MHz, CD_3OD, 298 K): δ 51.4, 117.0, 118.4, 118.49, 118.54, 120.4, 122.8, 124.0, 127.6, 129.9, 130.24, 130.28, 130.66, 130.69, 130.73, 131.2, 132.6, 135.8, 160.0, 161.9, 162.6, 162.9, 163.2, 163.9. Anal. Calcd for $C_{46}H_{28}BF_{24}NO_2$: C, 50.53; H, 2.58. Found: C, 50.62; H, 2.49.



$10e^+ \cdot$Cl$^-$

Derivative $10e^+ \cdot$Cl$^–$: (0.46 g, 1.76 mmol, 88%).**ESI(+) MS**: *m*/*z* = 225.7 (M^+). **^{1}H NMR** (250 MHz, CD_3OD, 298 K): 2.37 (s, 6H, H_d), 4.17 (s, 4H, H_a), 7.29 (d, *J* = 7.7Hz, 4H, H_b), 7.35 (d, *J* = 7.7 Hz, 4H, H_c); **^{13}C NMR** (63 MHz, $CDCl_3$, 298 K): δ 19.8, 50.2, 127.9, 129.4, 129.6, 139.5. Anal. Calcd for $C_{16}H_{20}ClN$: C, 73.41; H, 7.70. Found: C, 73.50; H, 7.78.



4e$^+$·TFPB$^-$

Derivative 4e$^+$·TFPB$^–$: (1.00 g, 0.92 mmol, 92%)**. ESI(+) MS**: *m*/*z* = 225.7 (M$^+$). **^{1}H NMR** (250 MHz, CD_3OD, 298 K): 2.36 (s, 6H, H_d), 4.14 (s, 4H, H_a), 7.29 (d, *J* = 8.2, 4H, H_b), 7.32 (d, *J* = 8.2Hz, 4H, H_c), 7.59 (overlapped, 12H, ArH^{TFPB}); **^{13}C NMR** (75 MHz, CD_3OD, 298 K): δ 22.6, 53.5, 119.81, 119.86, 119.92, 121.8, 125.4, 128.9, 129.8. 131.2, 131.6, 131.65, 131.69, 132.0, 132.03, 132.07, 132.1, 132.5, 133.3, 134.3, 137.2, 141.5, 163.3, 163.9, 164.6, 165.3. Anal. Calcd for $C_{48}H_{32}BF_{24}N$: C, 52.91; H, 2.96. Found: C, 53.00; H, 2.88.

^{1}H and ^{13}C NMR spectra of 8a-d$^+$·Cl$^-$ salts

Derivative 8a$^+$·Cl$^-$

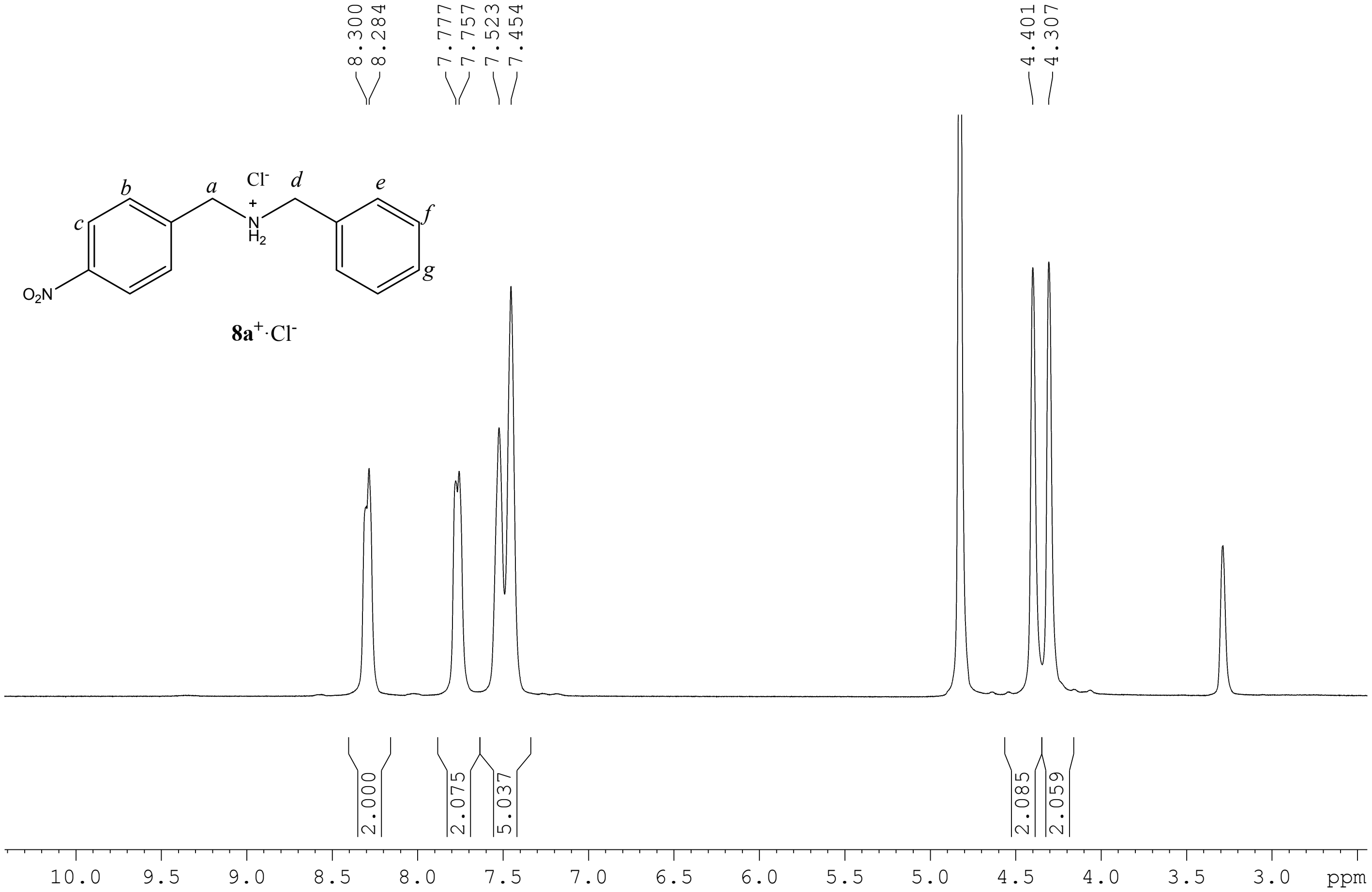


Figure S1. ^{1}H NMR spectrum of derivate **8a$^+$·Cl$^-$** (300 MHz, CD_3OD, 298 K).

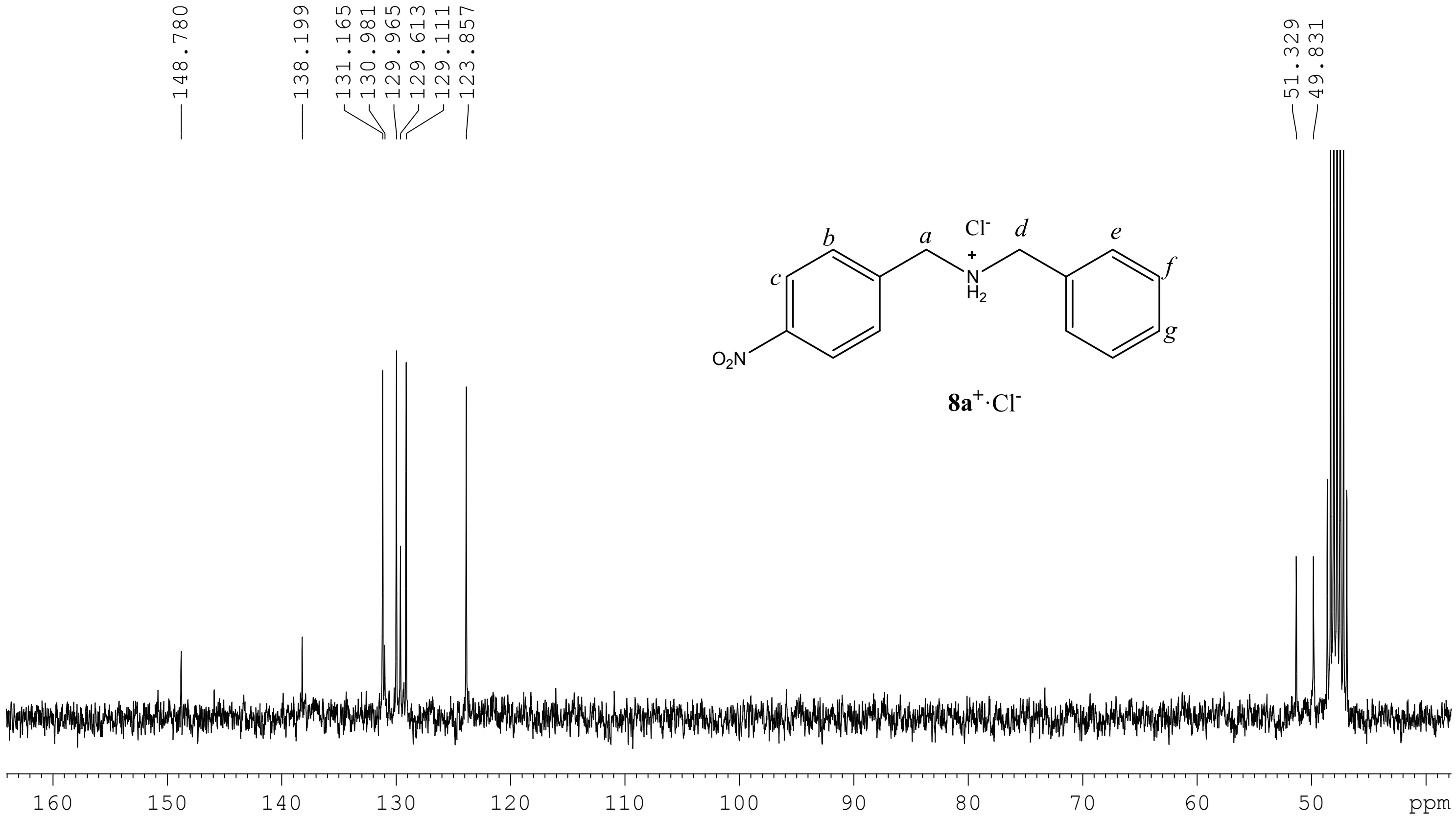
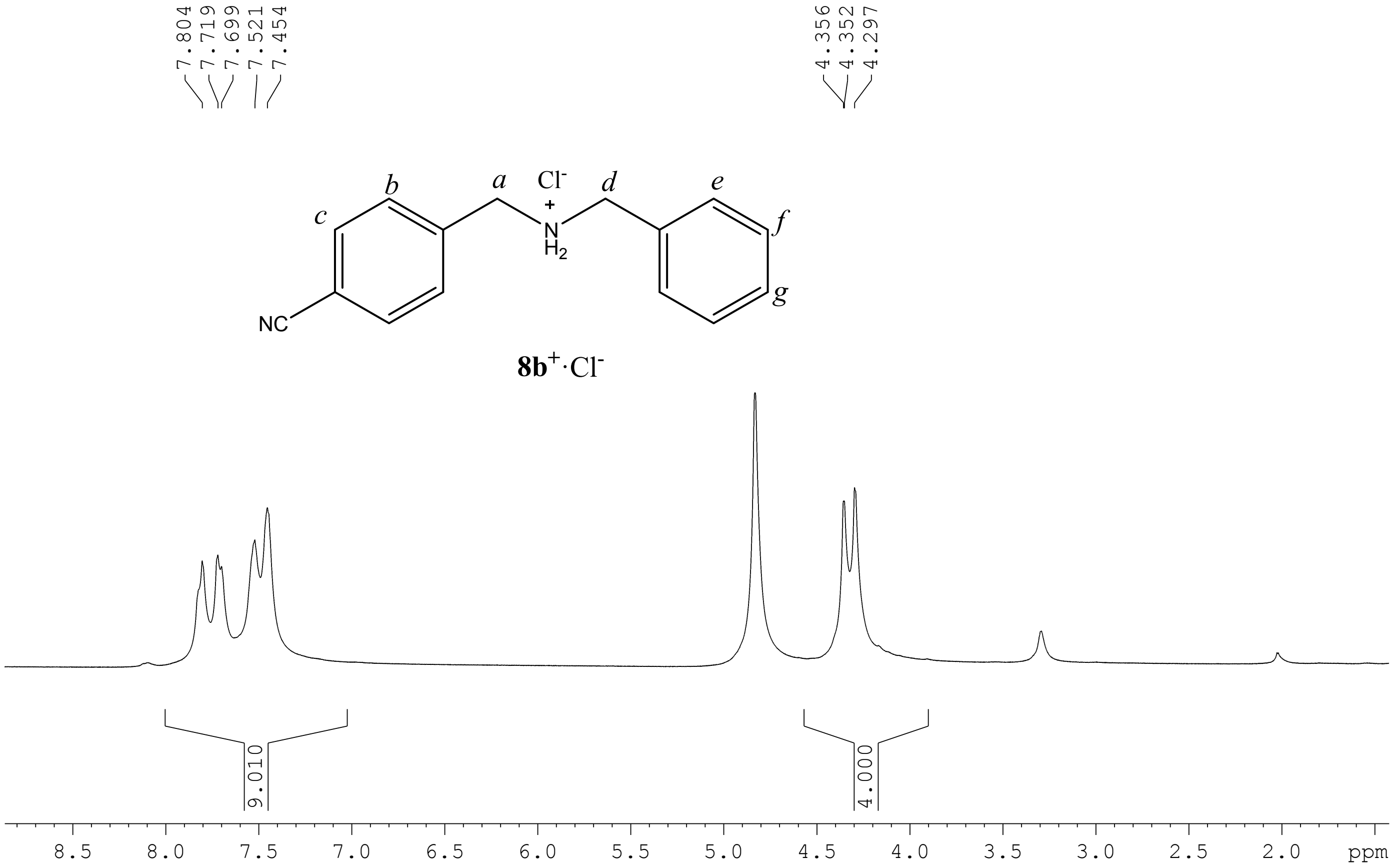


Figure S2. ^{13}C NMR spectrum of derivative **8a^{+}·Cl^{-}** (75 MHz, CD$_3$OD, 298 K).

Derivative $8b^{+}\cdot Cl^{-}$



$8b^{+}\cdot Cl^{-}$

Figure S3. ^{1}H NMR spectrum of derivative **$8b^{+}\cdot Cl^{-}$** (300 MHz, CD_3OD, 298 K).

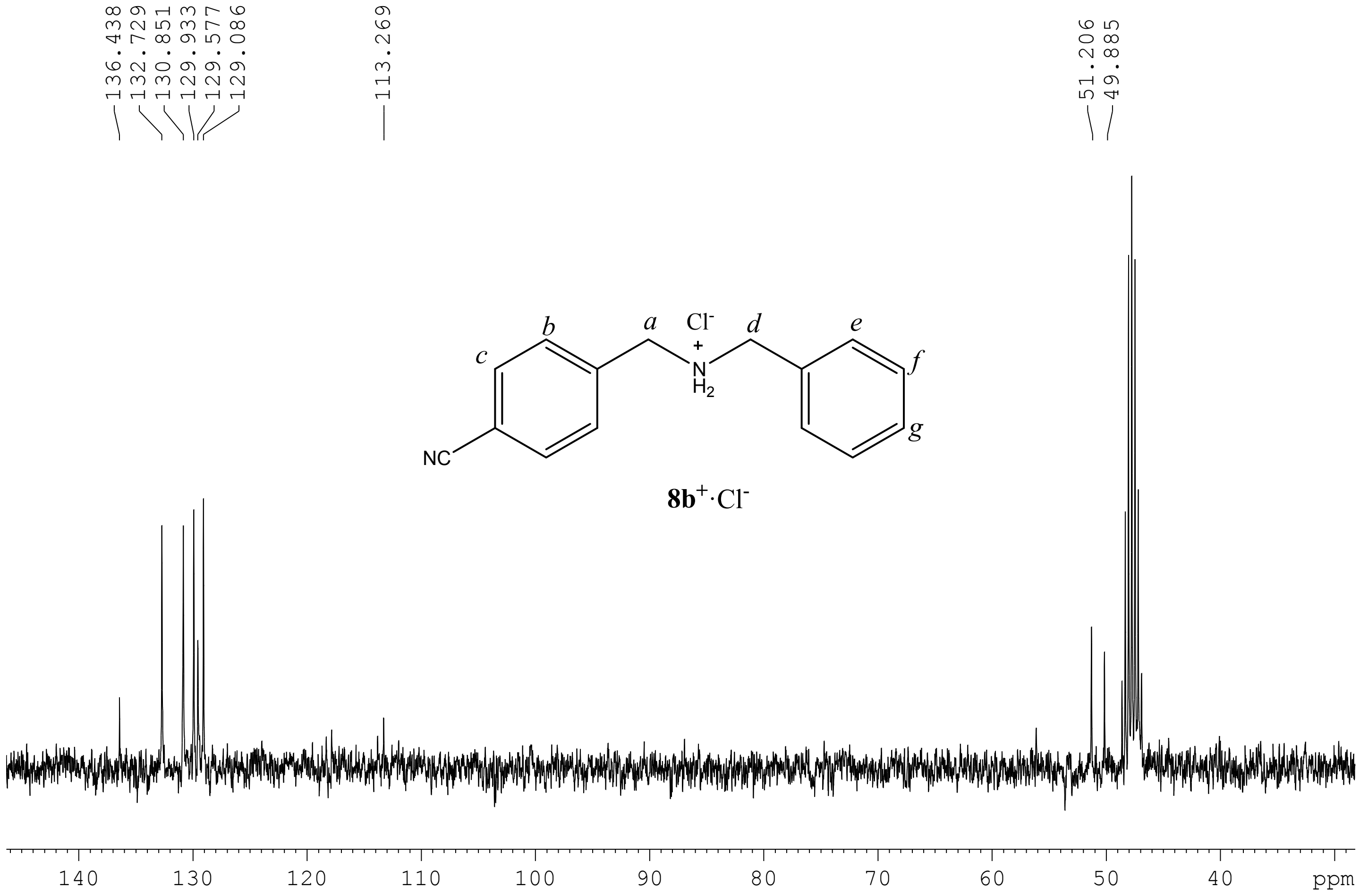


Figure S4. ^{13}C NMR spectrum of derivative **8b^{+}·Cl^{-}** (75 MHz, CD_3OD, 298 K).

Derivative $8c^+ \cdot Cl^-$

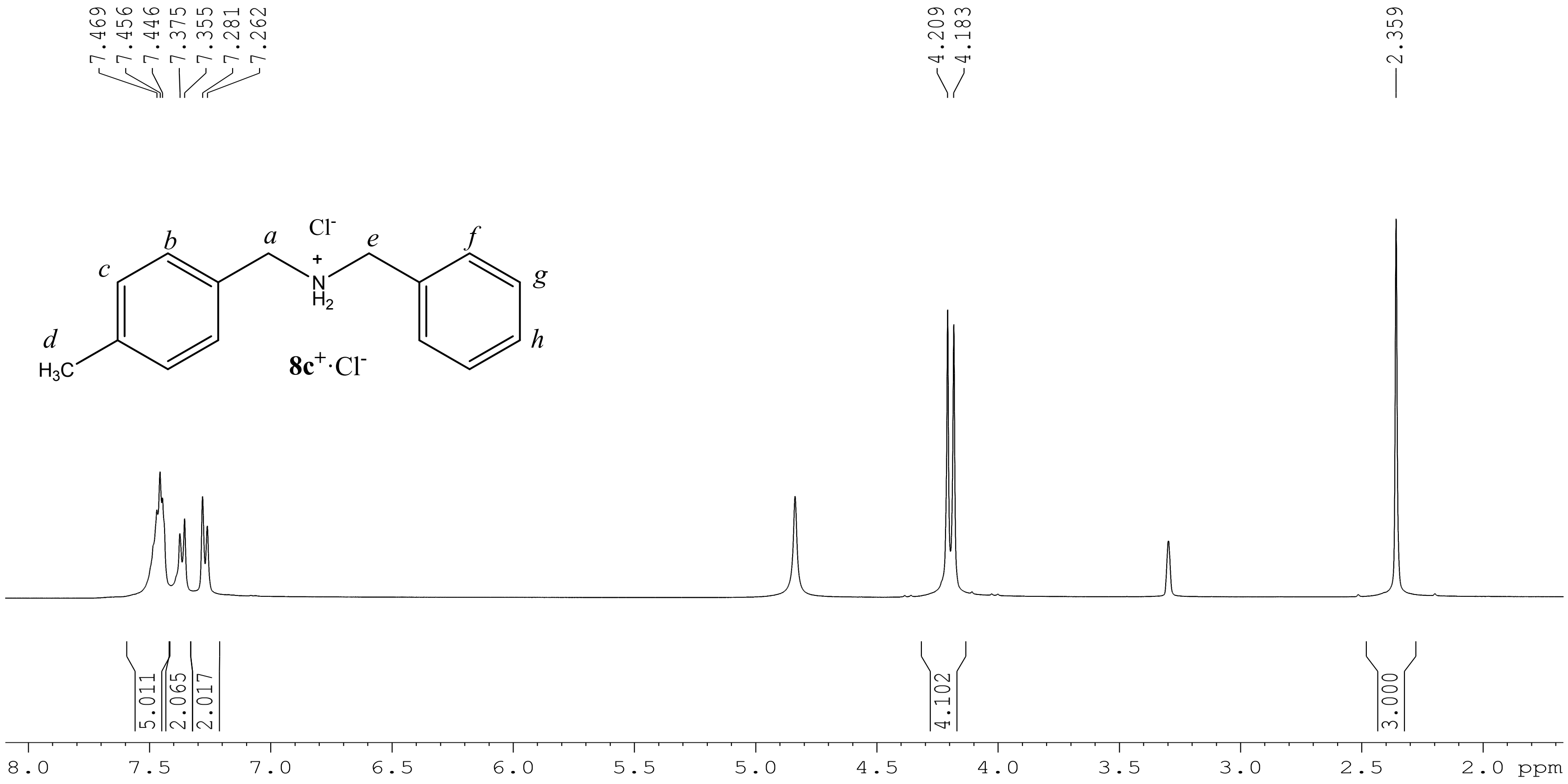


Figure S5. ^1H NMR spectrum of derivative **$8c^+ \cdot Cl^-$** (400 MHz, CD_3OD, 298 K).

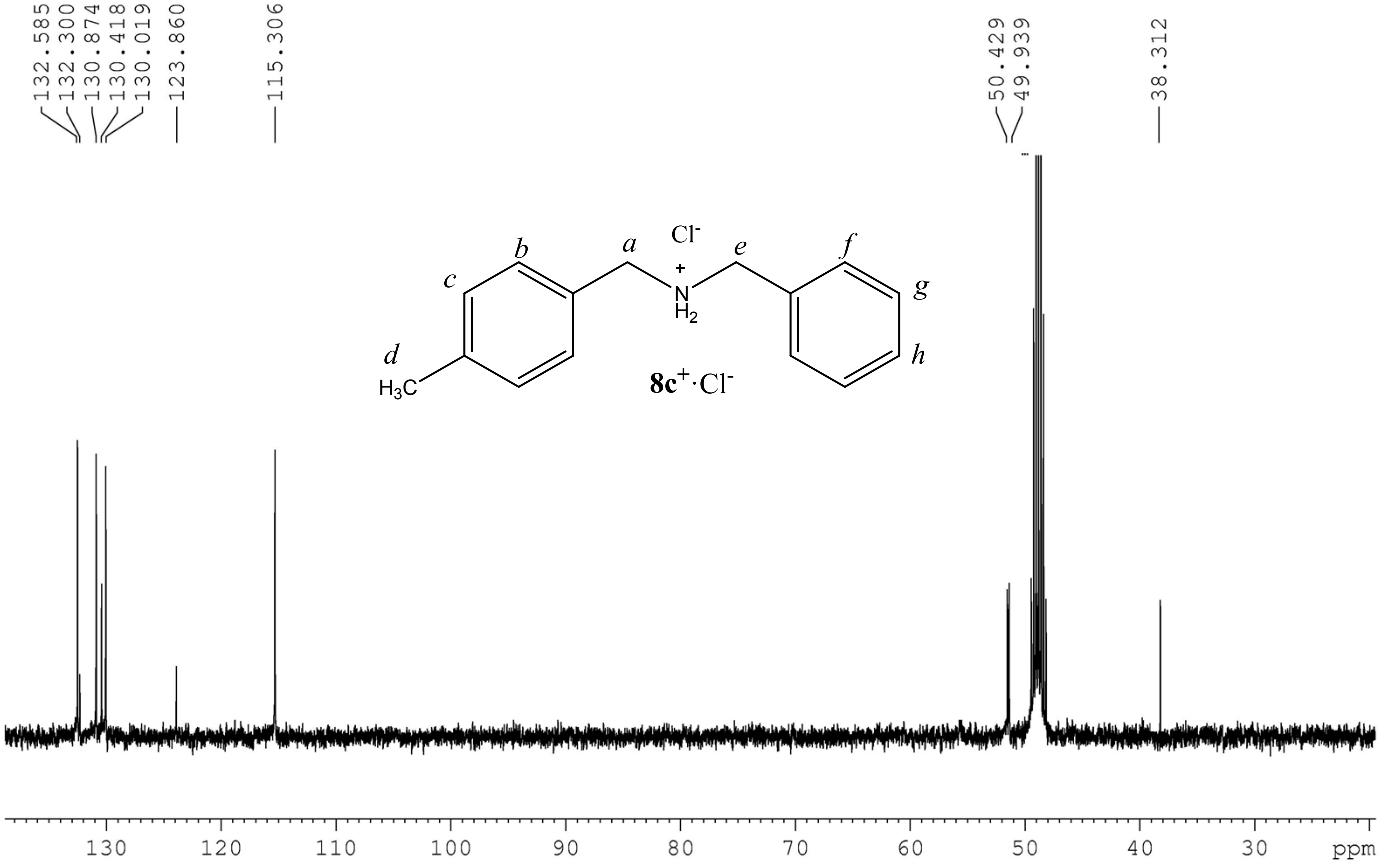


Figure S6. ^{13}C NMR spectrum of derivative **8c^{+}·Cl$^{–}$** (100 MHz, CDCl$_3$, 298 K).

Derivative $8d^{+}\cdot Cl^{-}$

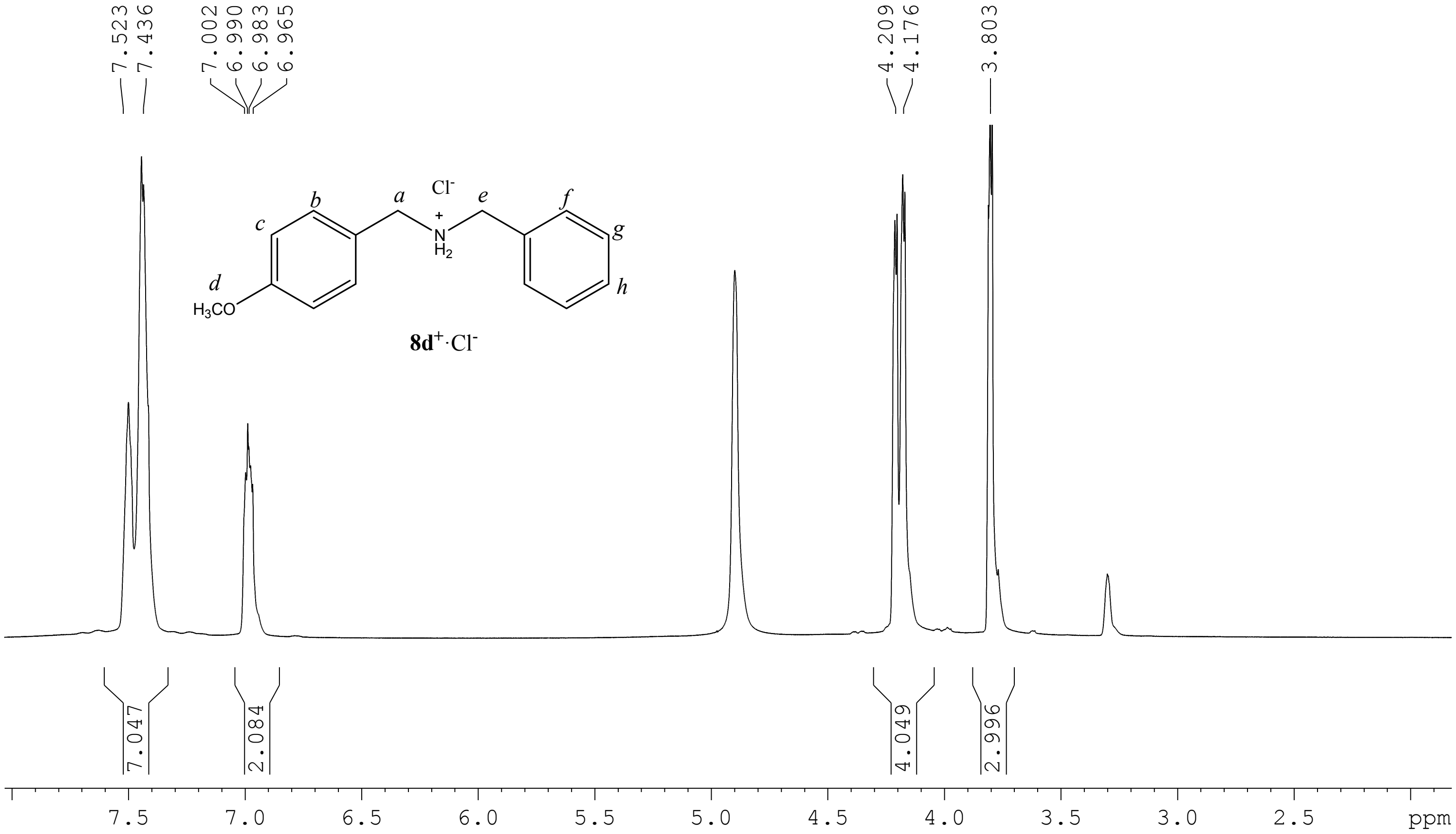


Figure S7. ^{1}H NMR spectrum of derivative **$8d^{+}\cdot Cl^{-}$** (400 MHz, CD_3OD, 298 K).

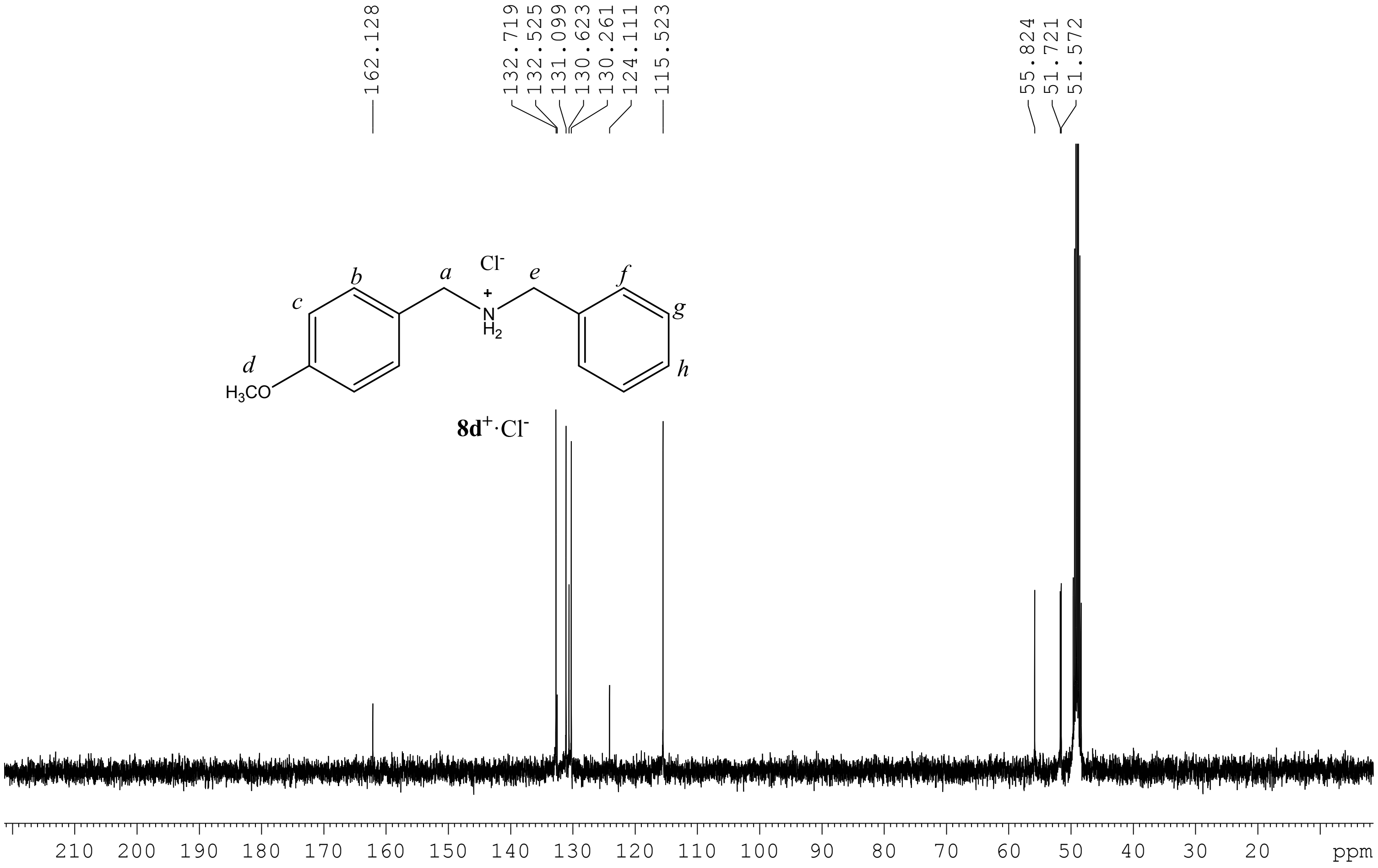


Figure S8. ^{13}C NMR spectrum of derivative **$8d^{+}$·Cl^{-}** (100 MHz, CD_3OD, 298 K).

^{1}H and ^{13}C NMR spectra of 3a-d$^{+}\cdot$TFPB$^{–}$ salts

Derivative 3a$^{+}\cdot$TFPB^{-}

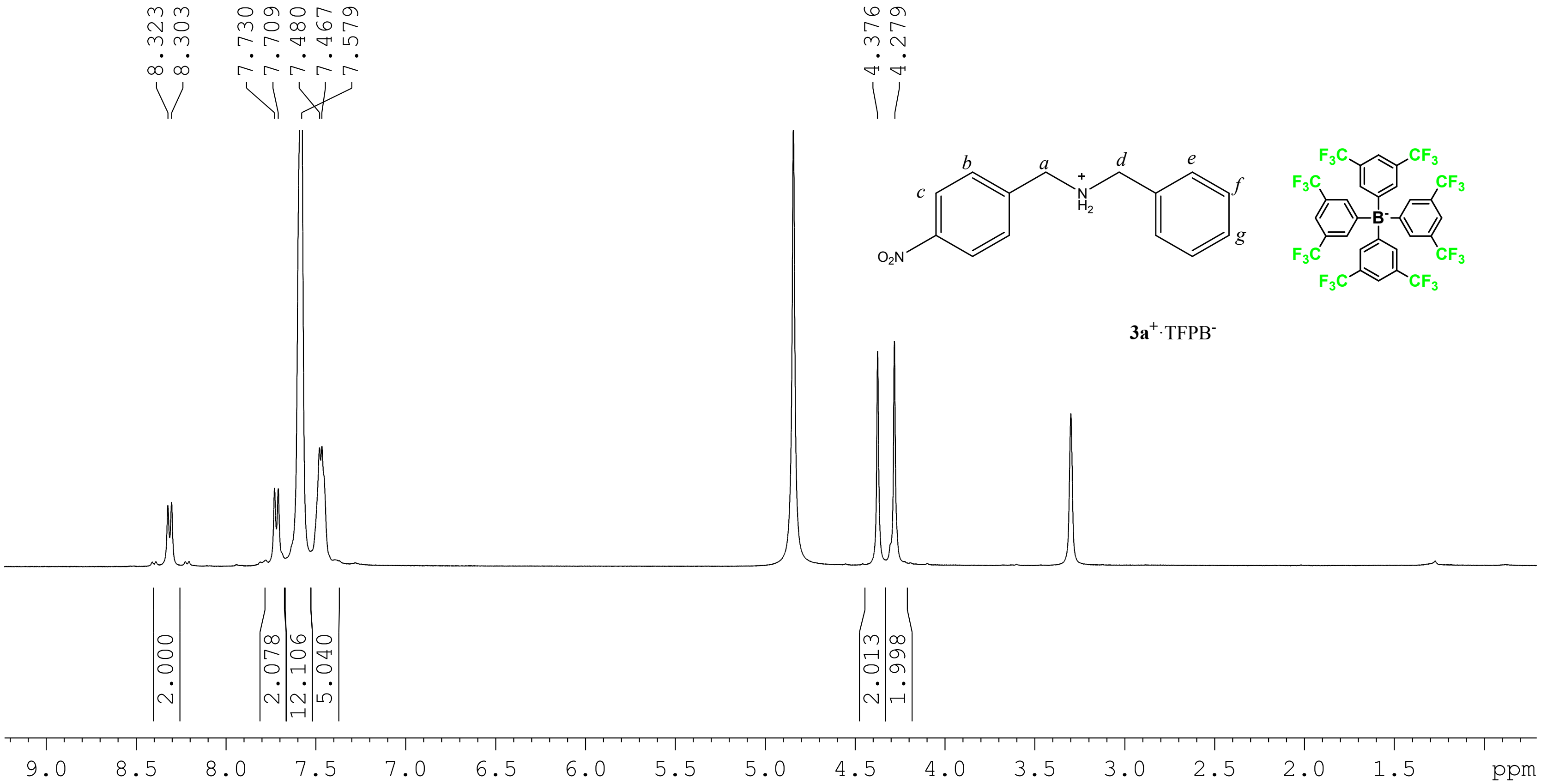


Figure S9. ^{1}H NMR spectrum of derivate **3a$^{+}\cdot$TFPB$^{–}$** (400 MHz, CD$_3$OD, 298 K).

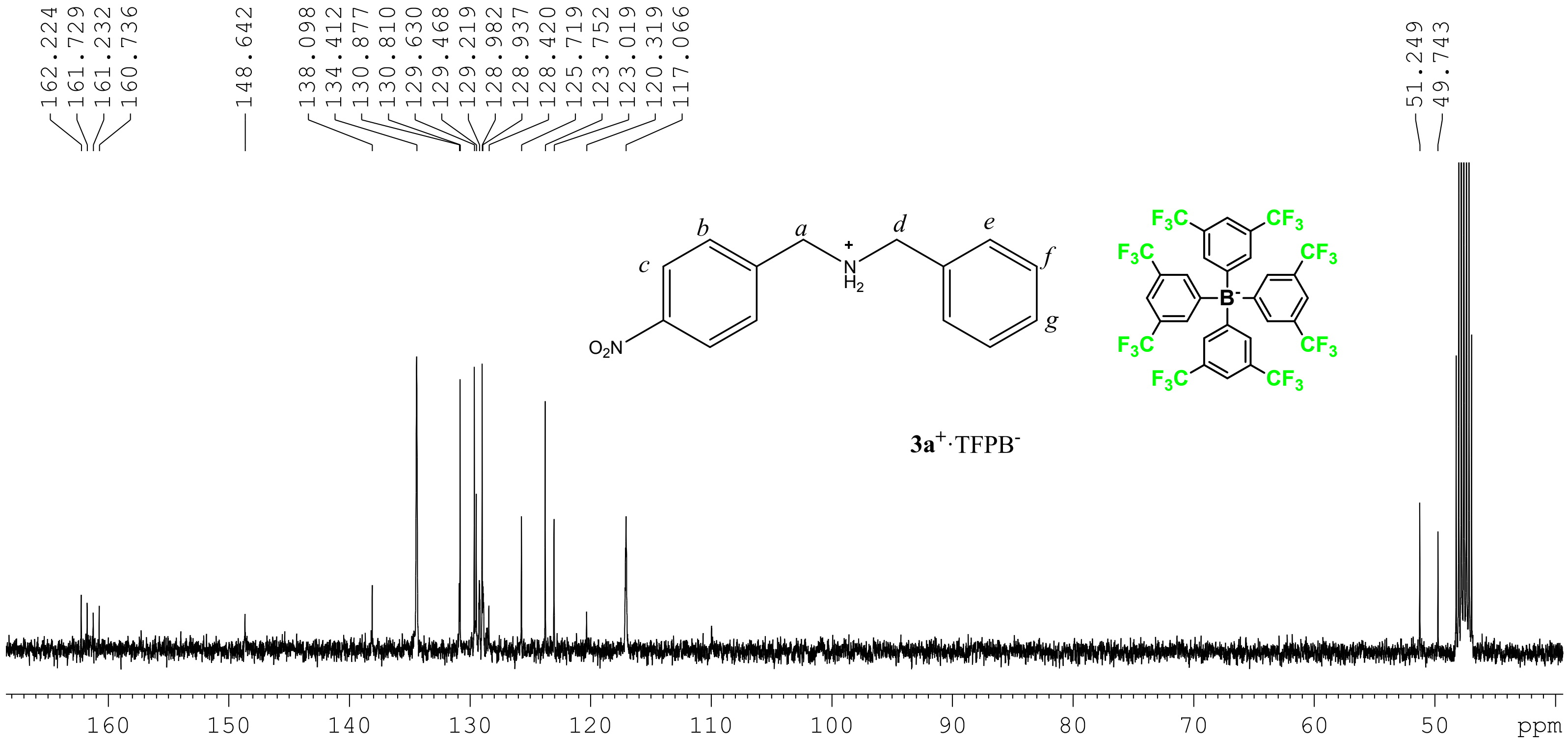


Figure S10. ^{13}C NMR spectrum of derivative **3a^{+}·TFPB^{-}** (100 MHz, CD$_3$OD, 298 K).

Derivative 3b^{+}·TFPB^{-}

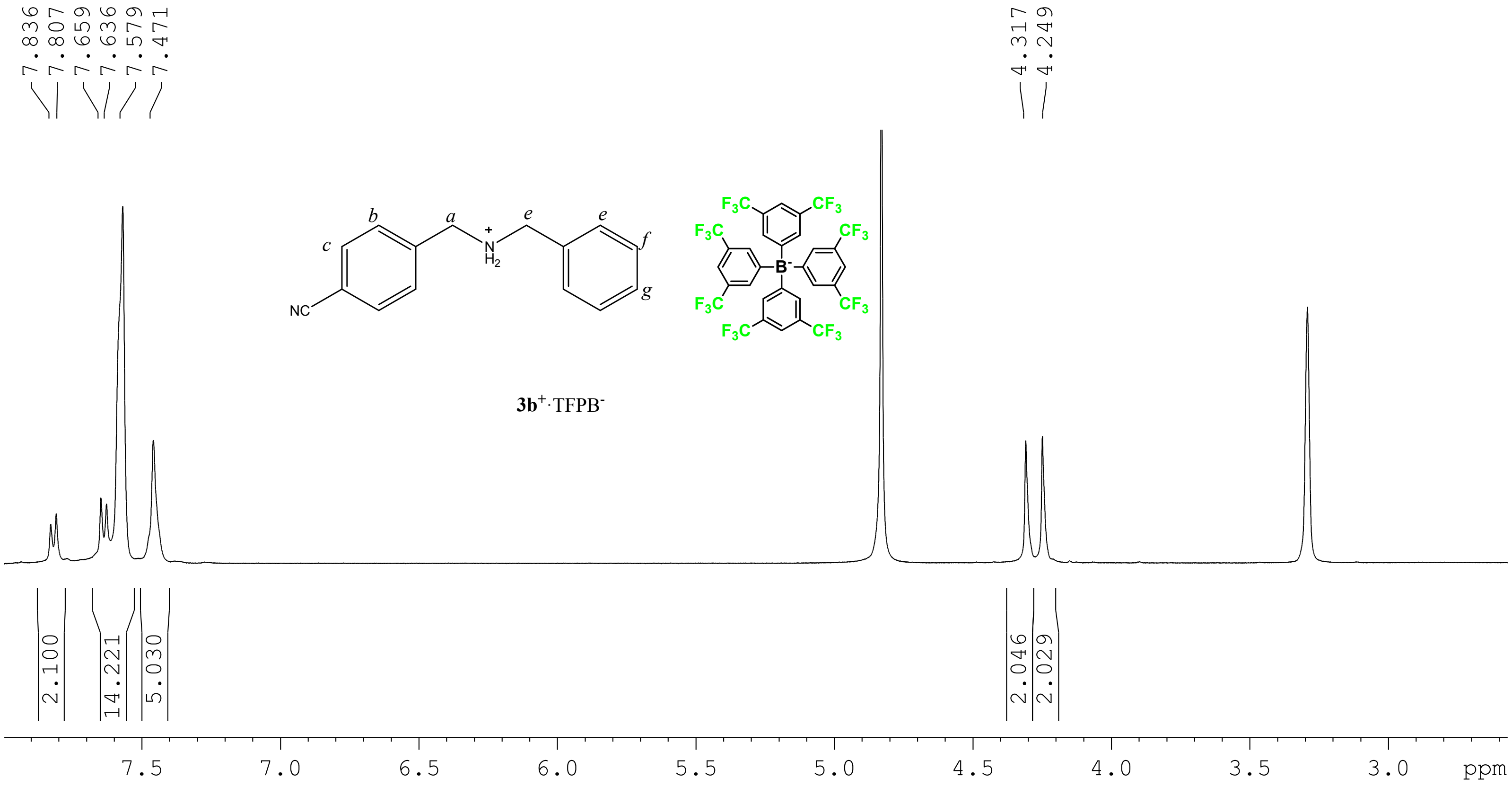


Figure S11. ^{1}H NMR spectrum of derivate **3b^{+}·TFPB$^{–}$** (400 MHz, CD$_3$OD, 298 K).

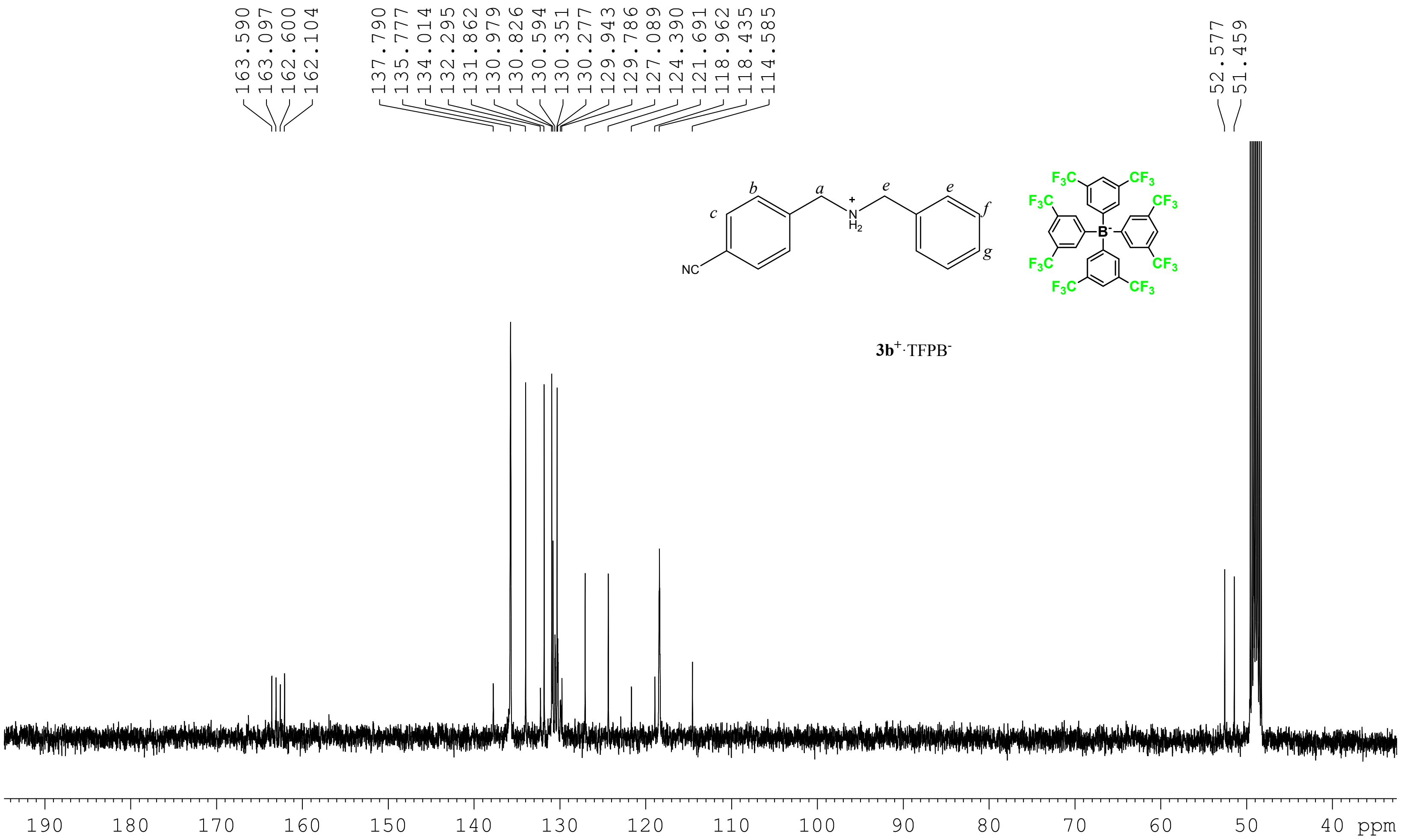


Figure S12. ^{13}C NMR spectrum of derivative **3b$^+$·TFPB$^-$** (100 MHz, CD$_3$OD, 298 K).

Derivative 3c$^+$·TFPB$^-$

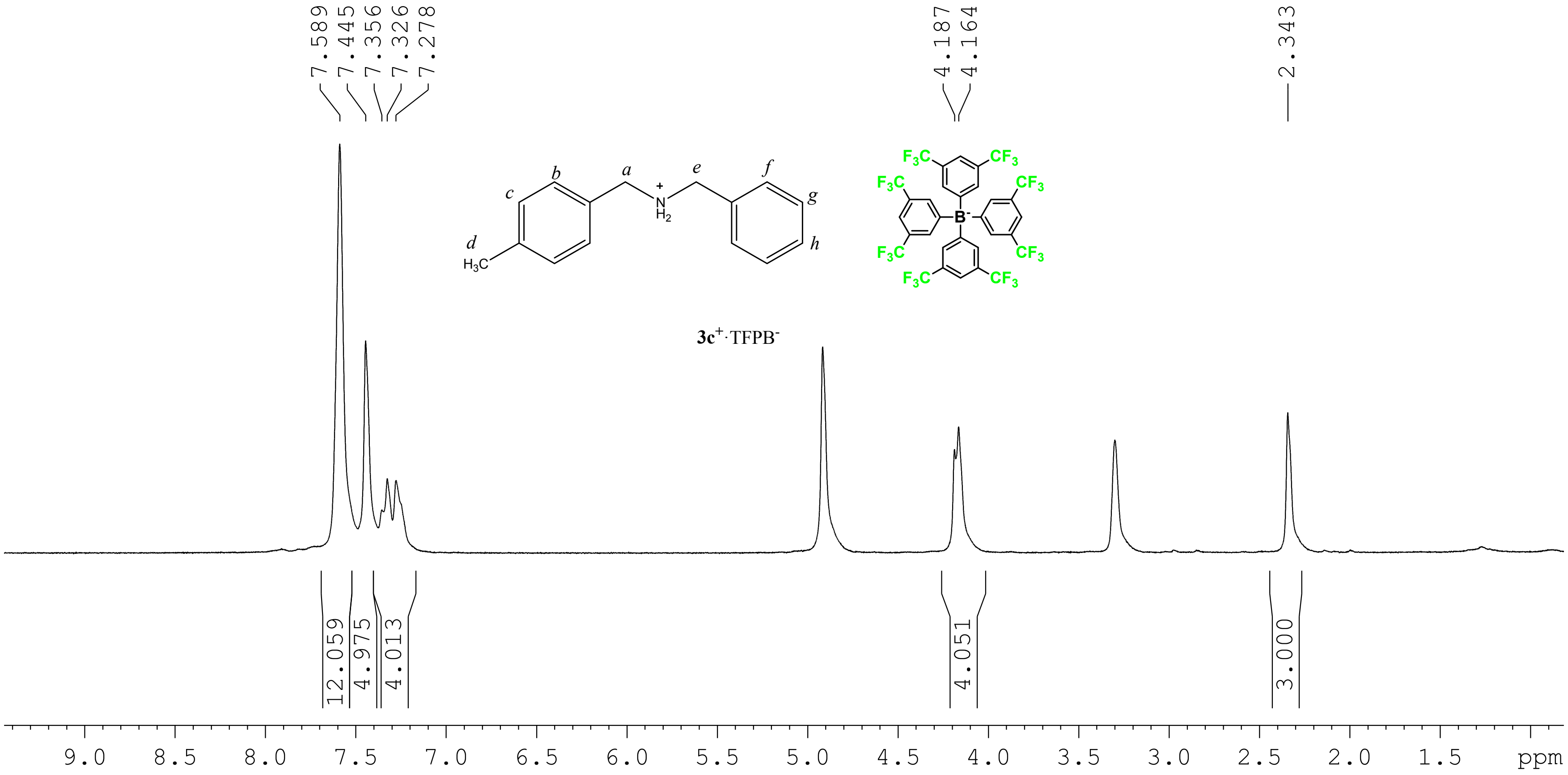


Figure S13. ^{1}H NMR spectrum of derivate **3c$^+$·TFPB$^-$** (250 MHz, CD$_3$OD, 298 K).

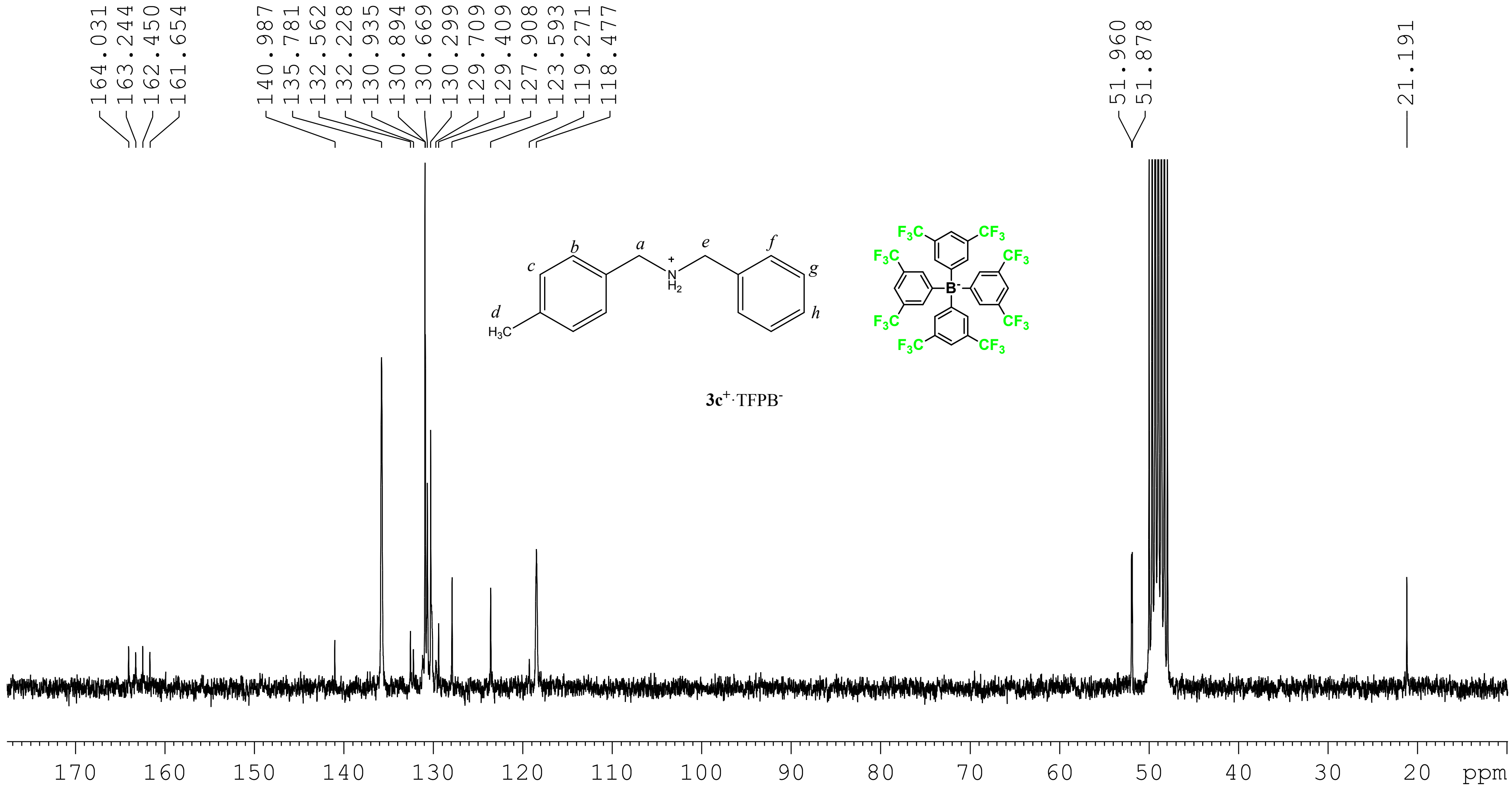


Figure S14. ^{13}C NMR spectrum of derivative **$3c^+ \cdot$TFPB$^-$** (63 MHz, CD_3OD, 298 K).

Derivative 3d$^+$·TFPB$^-$

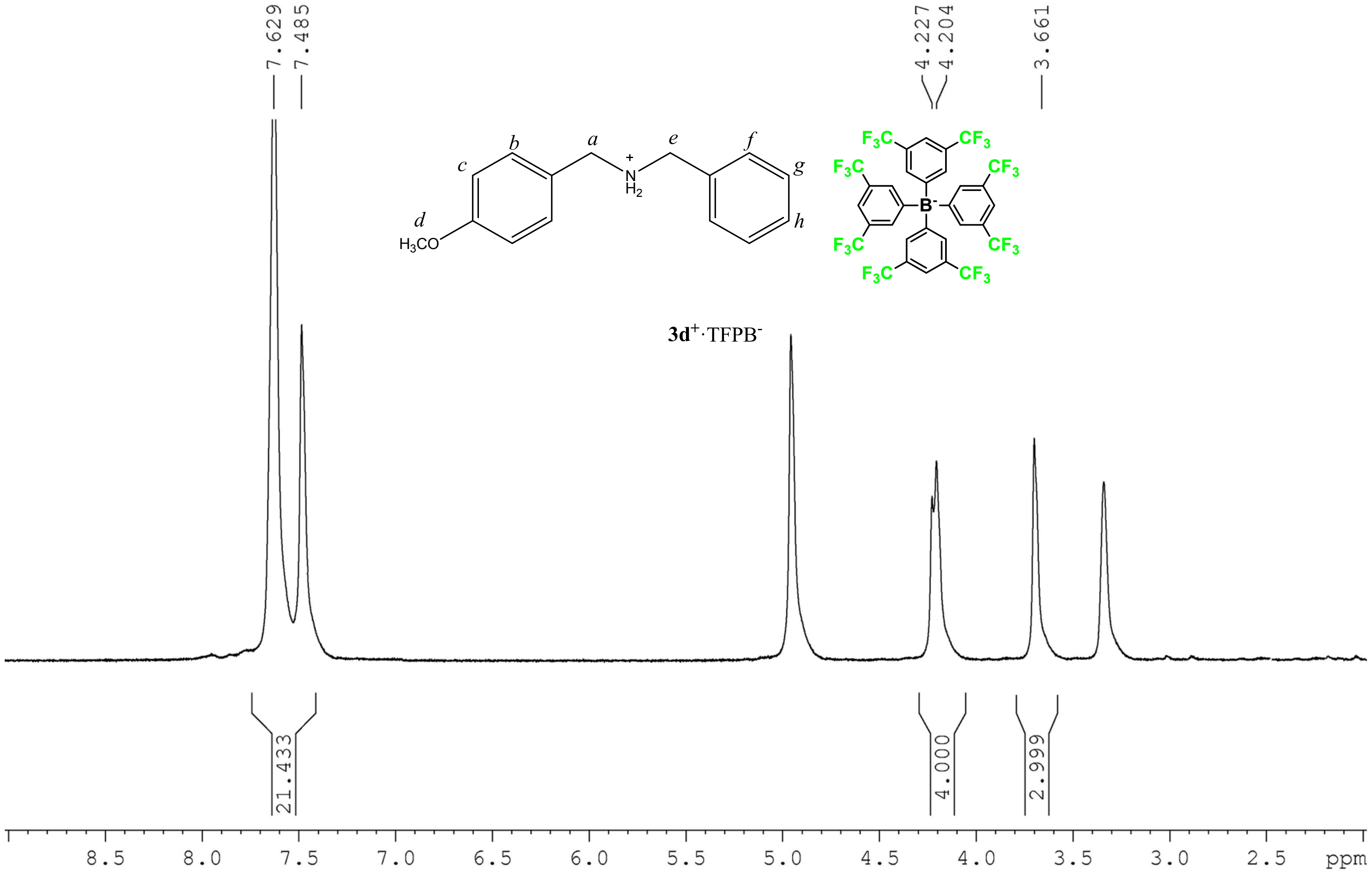


Figure S15. ^{1}H NMR spectrum of derivate **3d$^+$·TFPB$^–$** (250 MHz, CD_3OD, 298 K).

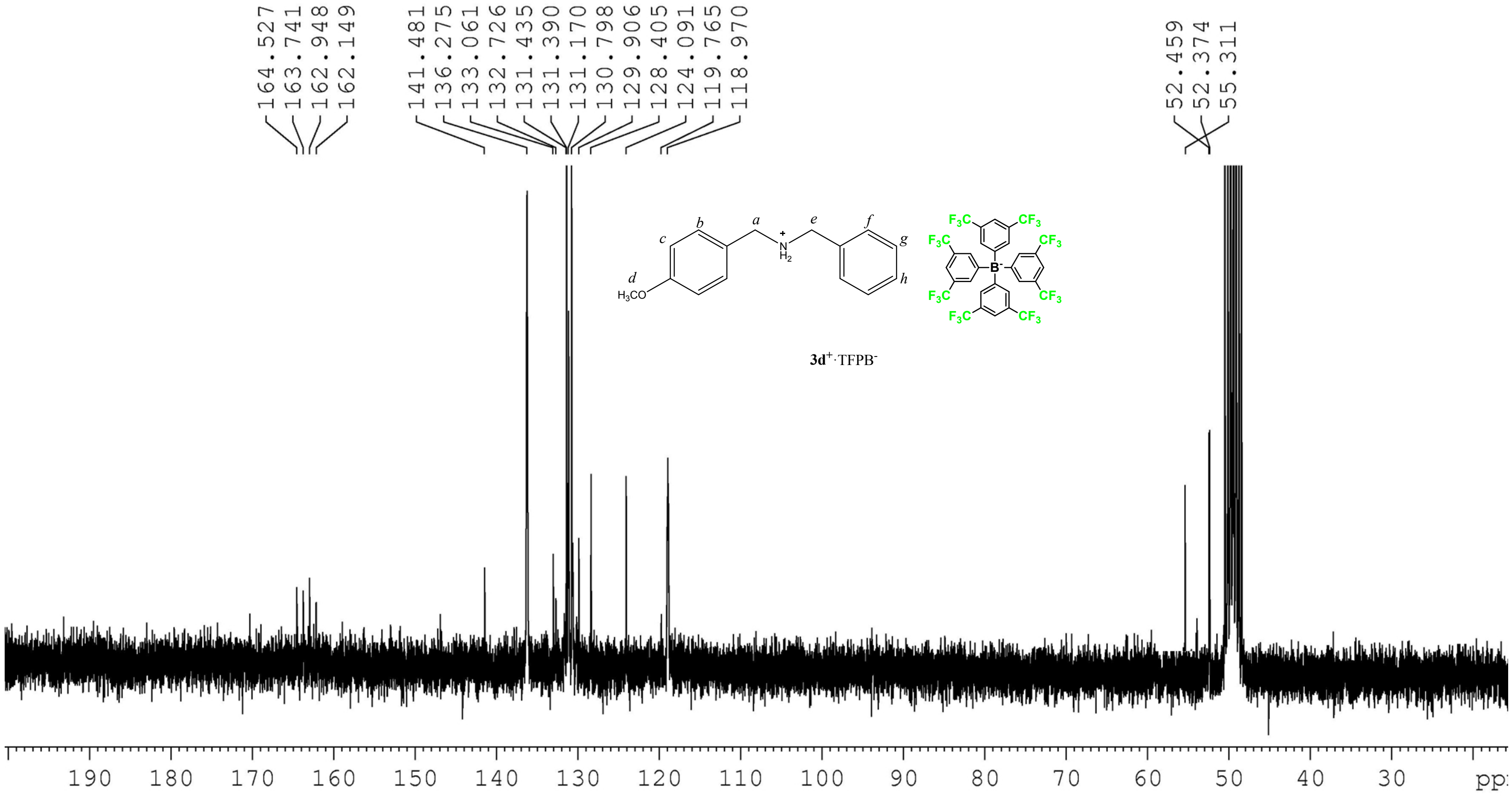


Figure S16. ^{13}C NMR spectrum of derivative **3d^{+}·TFPB^{-}** (63 MHz, CD$_3$OD, 298 K).

^{1}H and ^{13}C NMR spectra of 10c-e^{+}·Cl$^{–}$ salts

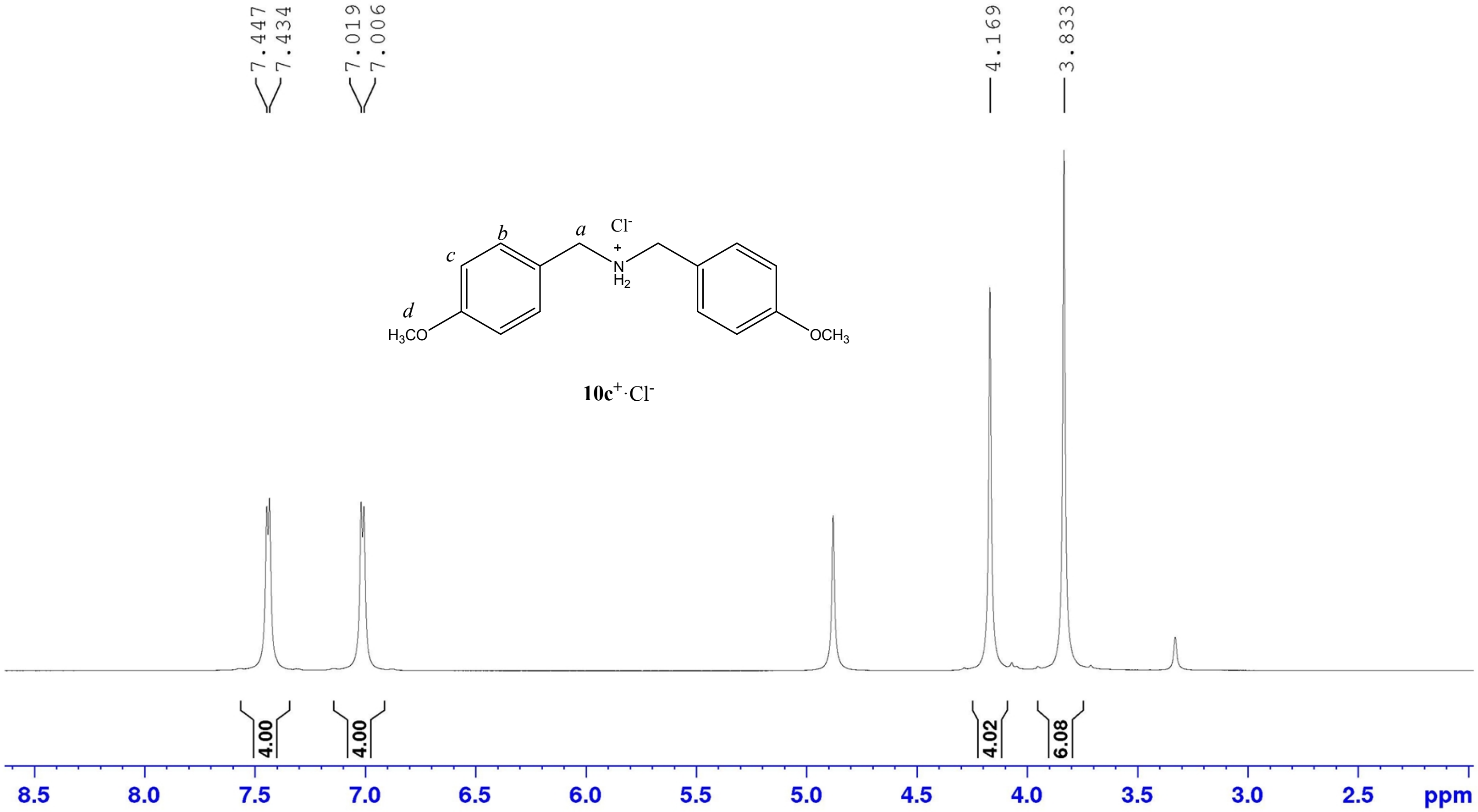


Figure S17. ^{1}H NMR spectrum of derivative **10c^{+}·Cl$^{–}$** (600 MHz, CD_3OD, 298 K).

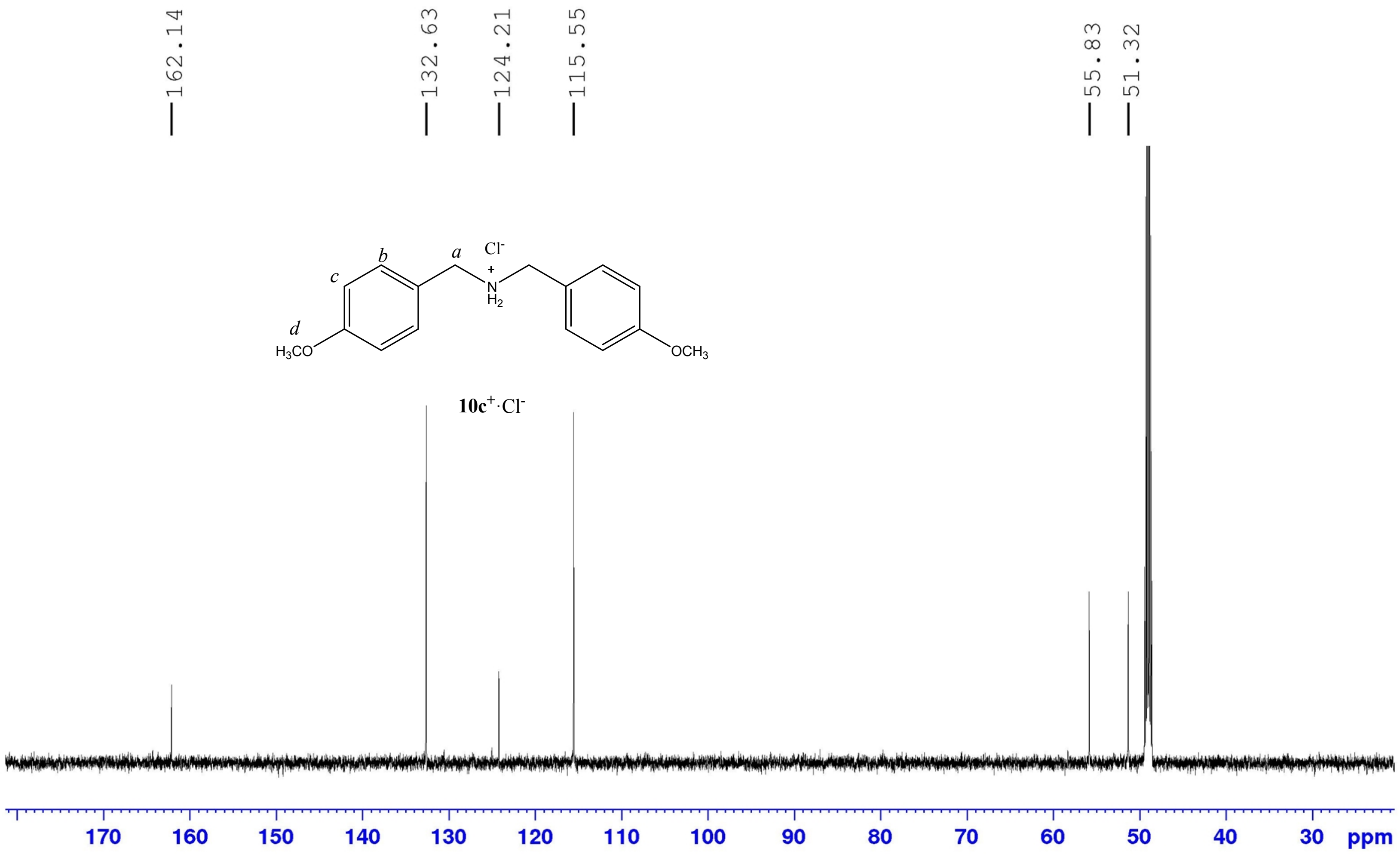


Figure S18. ^{13}C NMR spectrum of derivative **$10c^{+}·Cl^{–}$** (150 MHz, CD_3OD, 298 K).

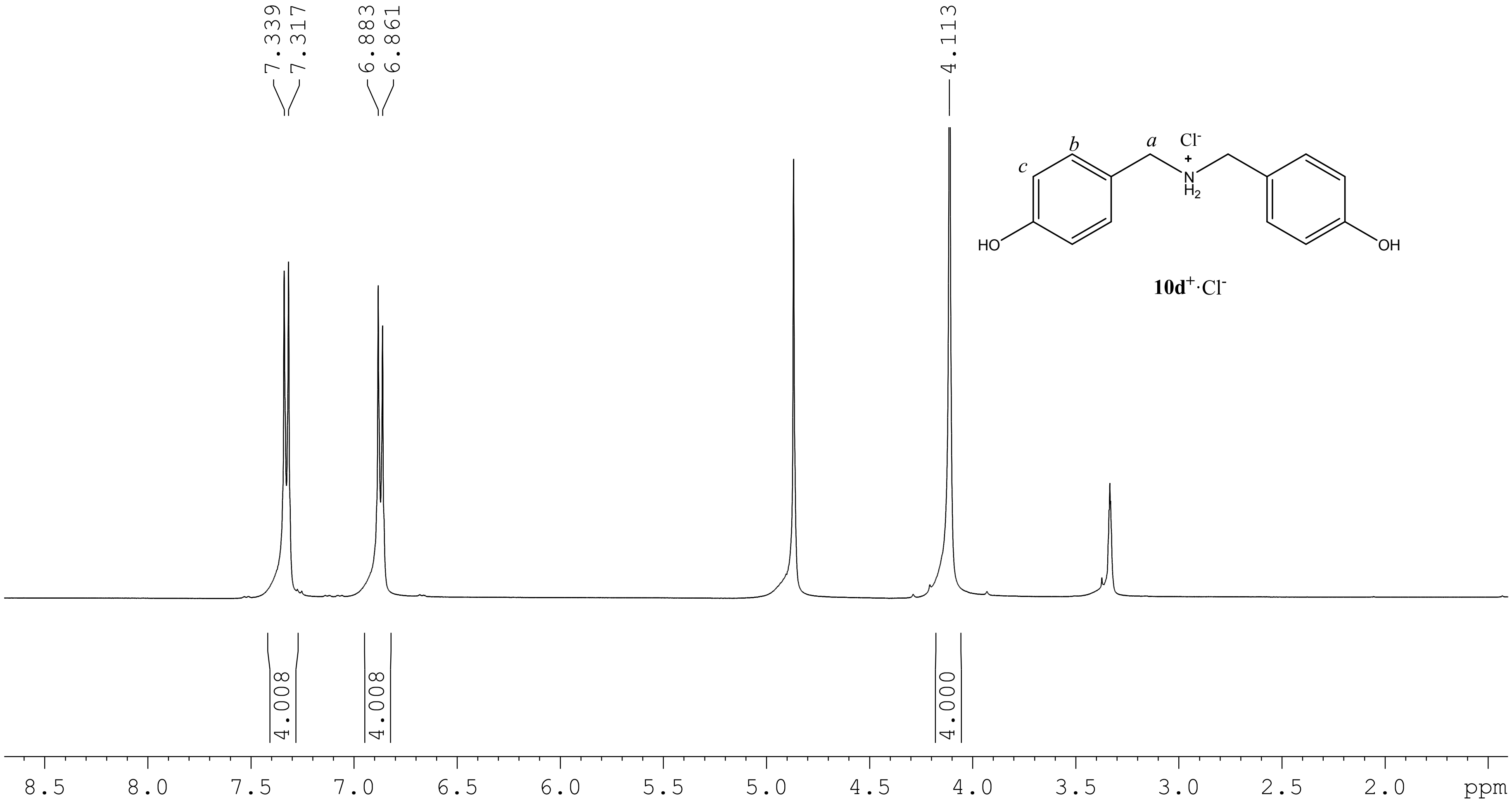


Figure S19. ^{1}H NMR spectrum of derivative **10d$^+$·Cl$^–$** (400 MHz, CD_3OD, 298 K).

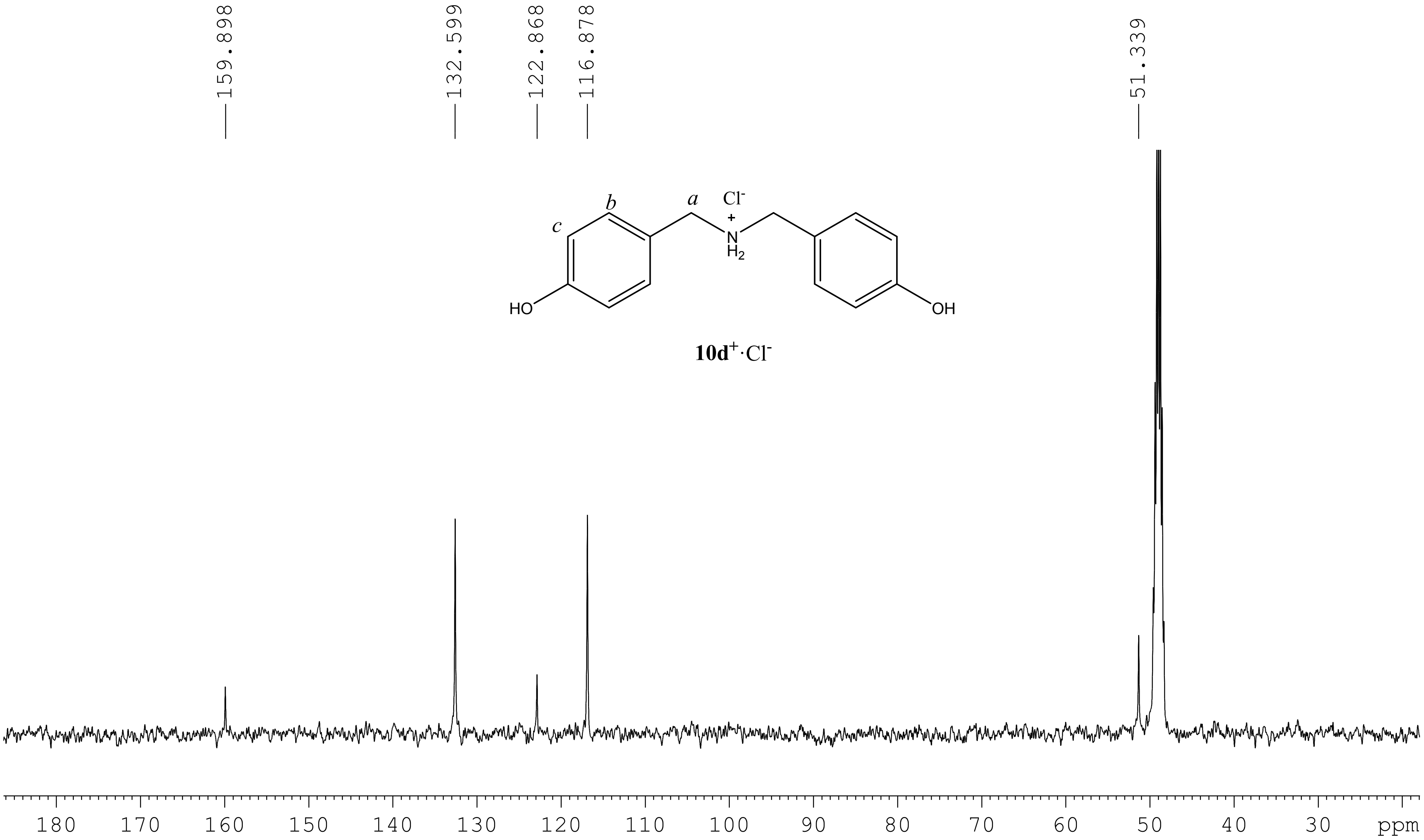


Figure S20. ^{13}C NMR spectrum of derivative **10d^{+}·Cl^{-}** (100 MHz, CD_3OD, 298 K).

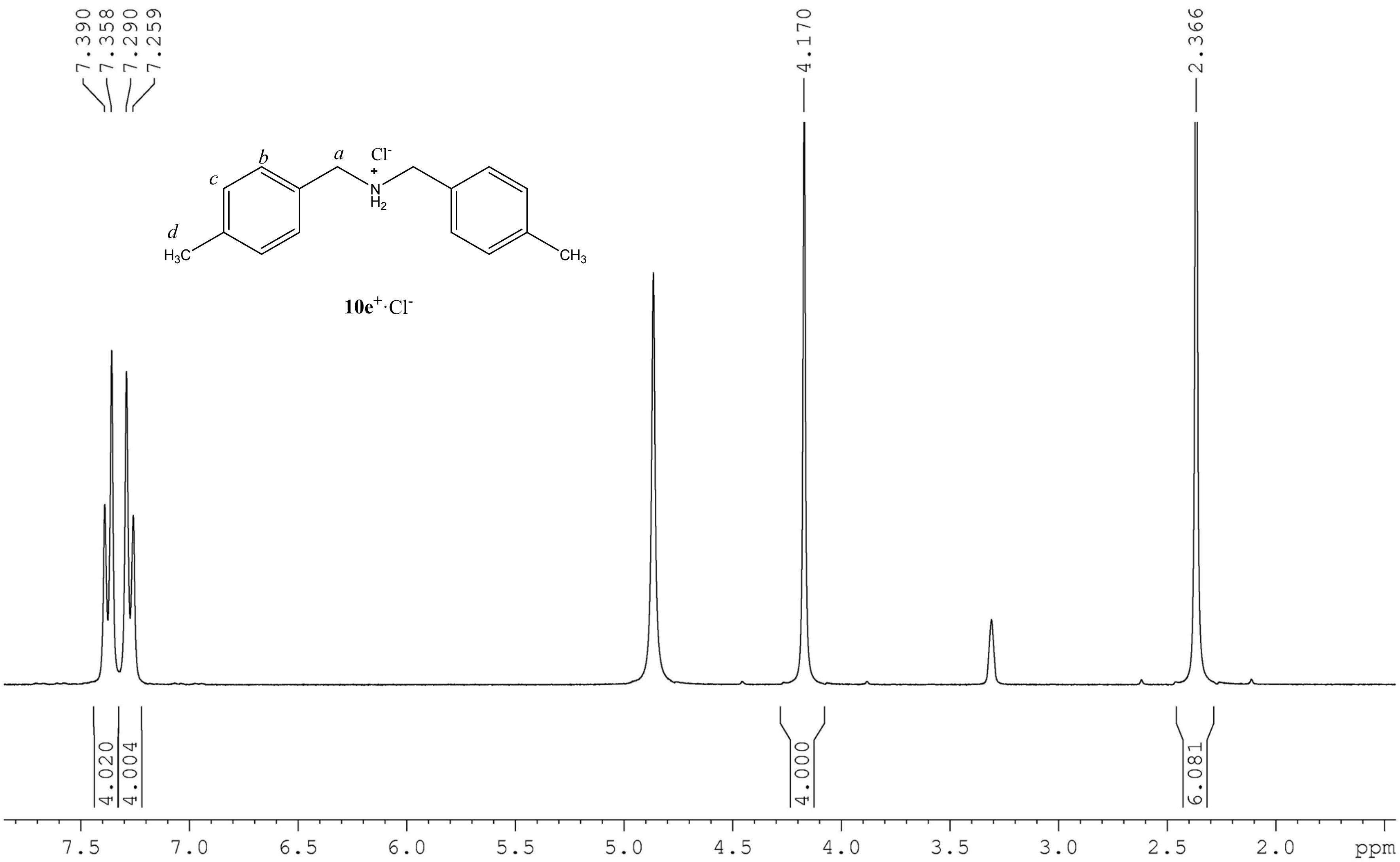


Figure S21. ^{1}H NMR spectrum of derivative **10e$^+$·Cl$^-$** (250 MHz, CD_3OD, 298 K).

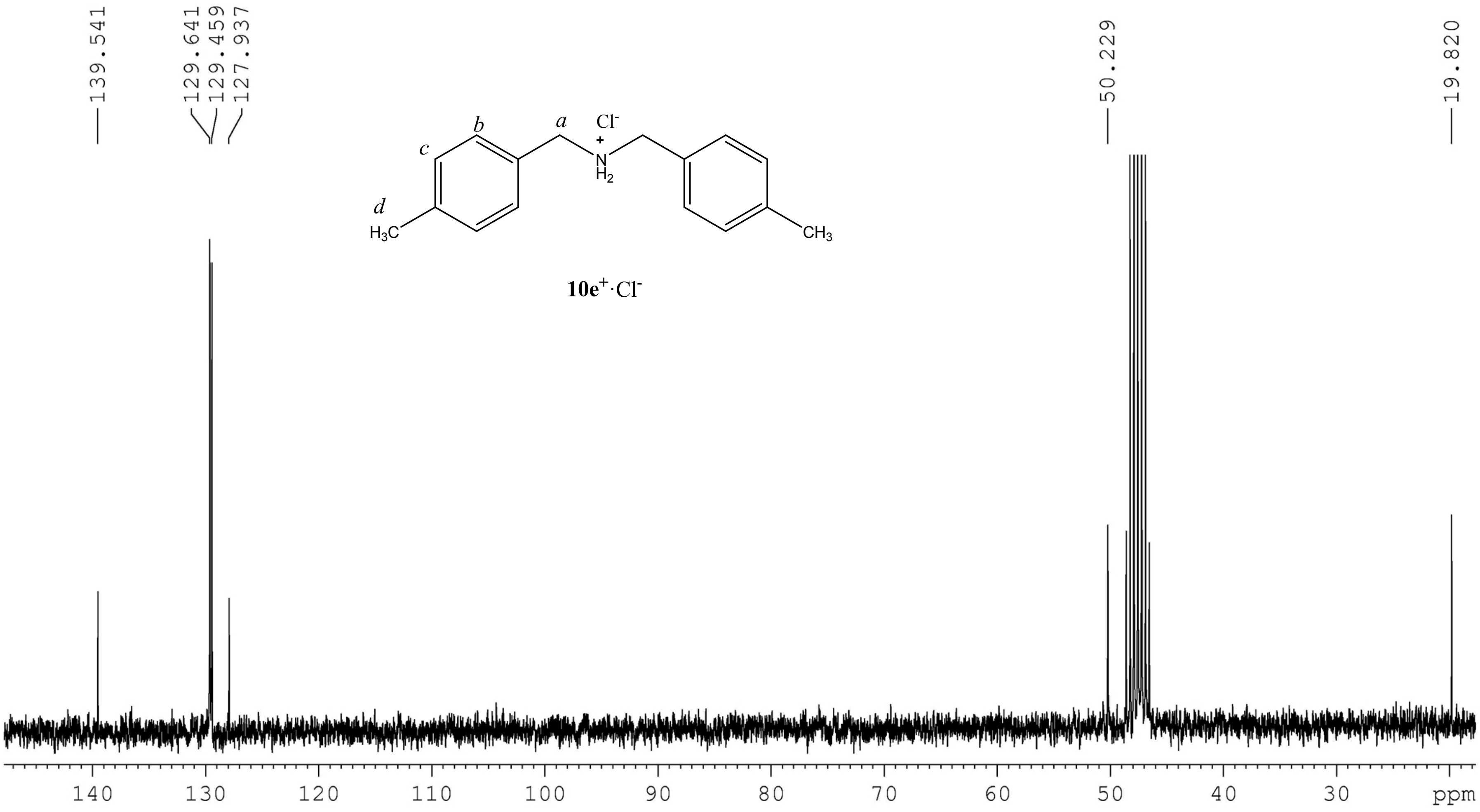


Figure S22. ^{13}C NMR spectrum of derivative **10e$^+$·Cl$^-$** (63 MHz, CD_3OD, 298 K).

^{1}H and ^{13}C NMR spectra of 4b-f^{+}·TFPB^{-} salts

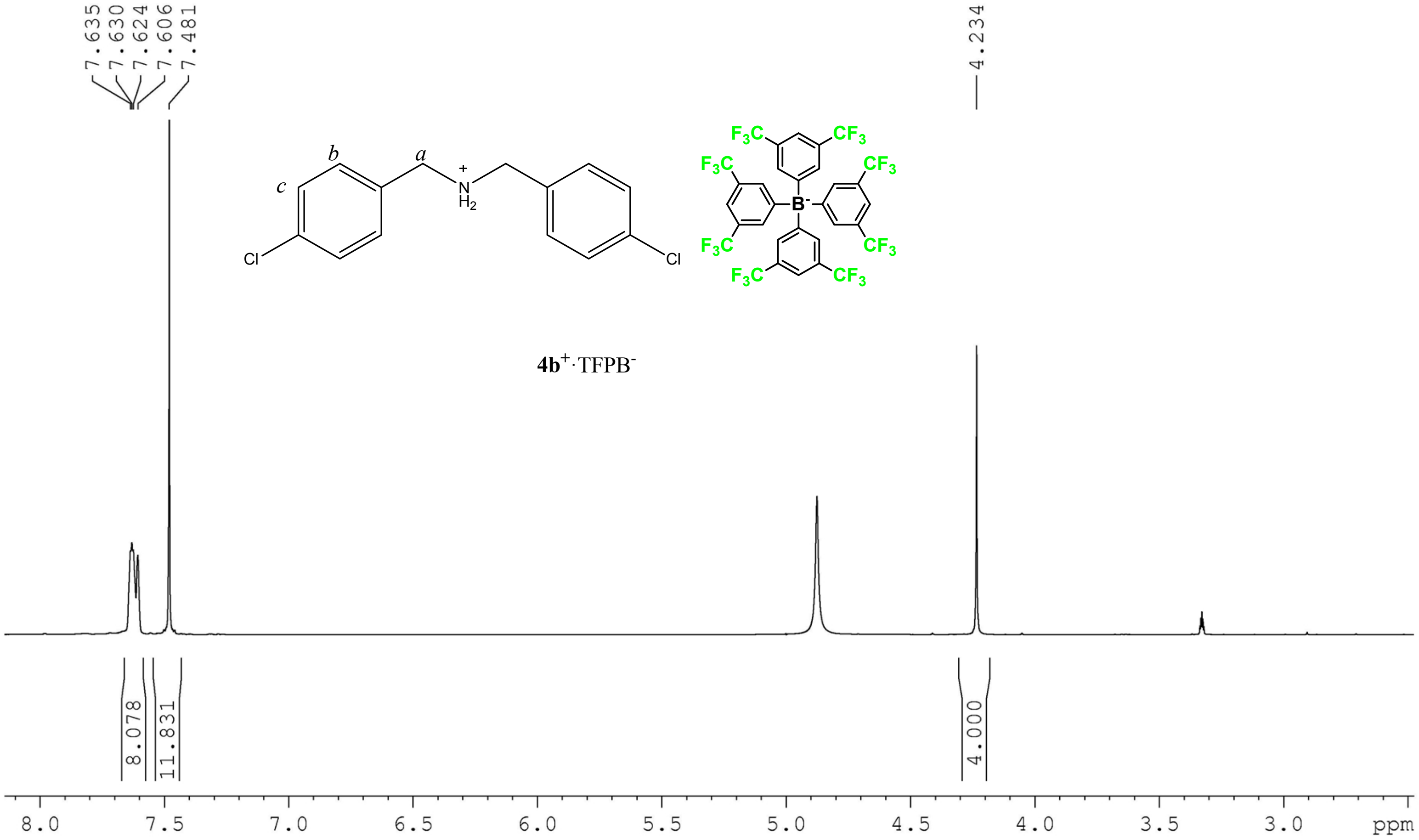


Figure S23. ^{1}H NMR spectrum of derivative **4b^{+}·TFPB$^{–}$** (400 MHz, CD_3OD, 298 K).

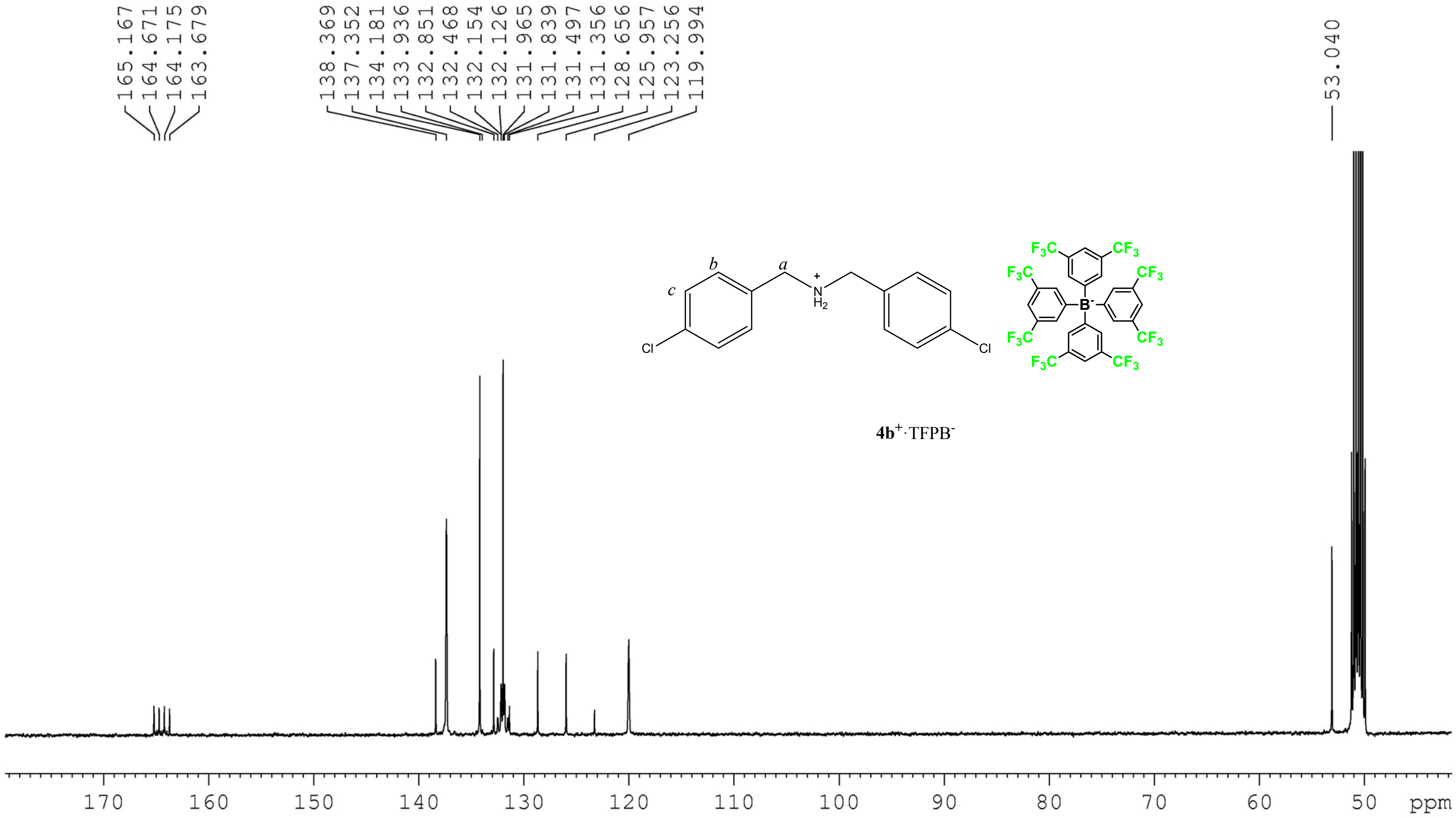


Figure S24. ^{13}C NMR spectrum of derivative **4b^{+}·TFPB$^{–}$** (100 MHz, CD$_3$OD, 298 K).

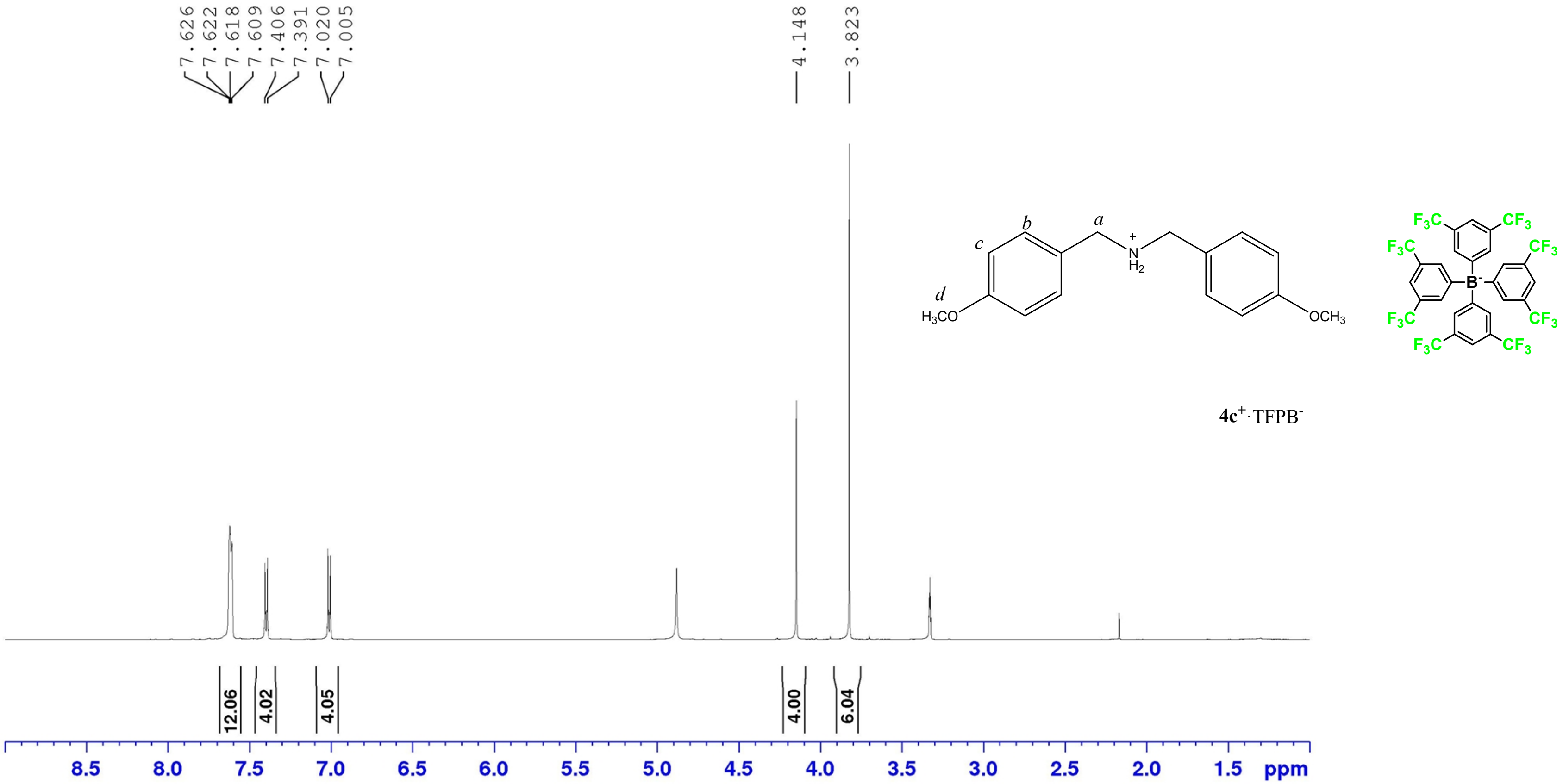


Figure S25. ^{1}H NMR spectrum of derivative **4c^{+}·TFPB^{-}** (600 MHz, CD_3OD, 298 K).

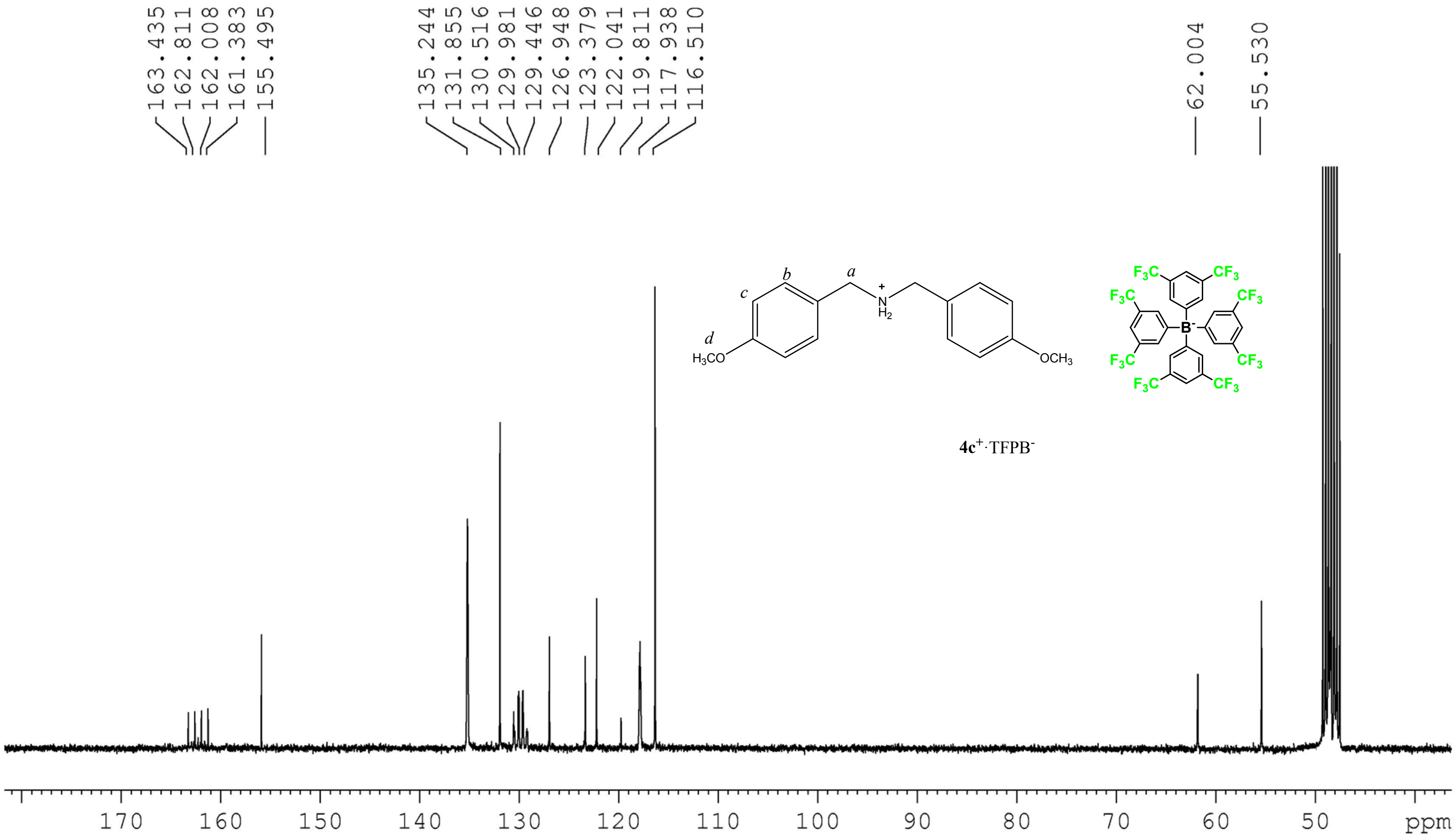


Figure S26. ^{13}C NMR spectrum of derivative **4c^{+}·TFPB^{-}** (100 MHz, CD$_3$OD, 298 K).

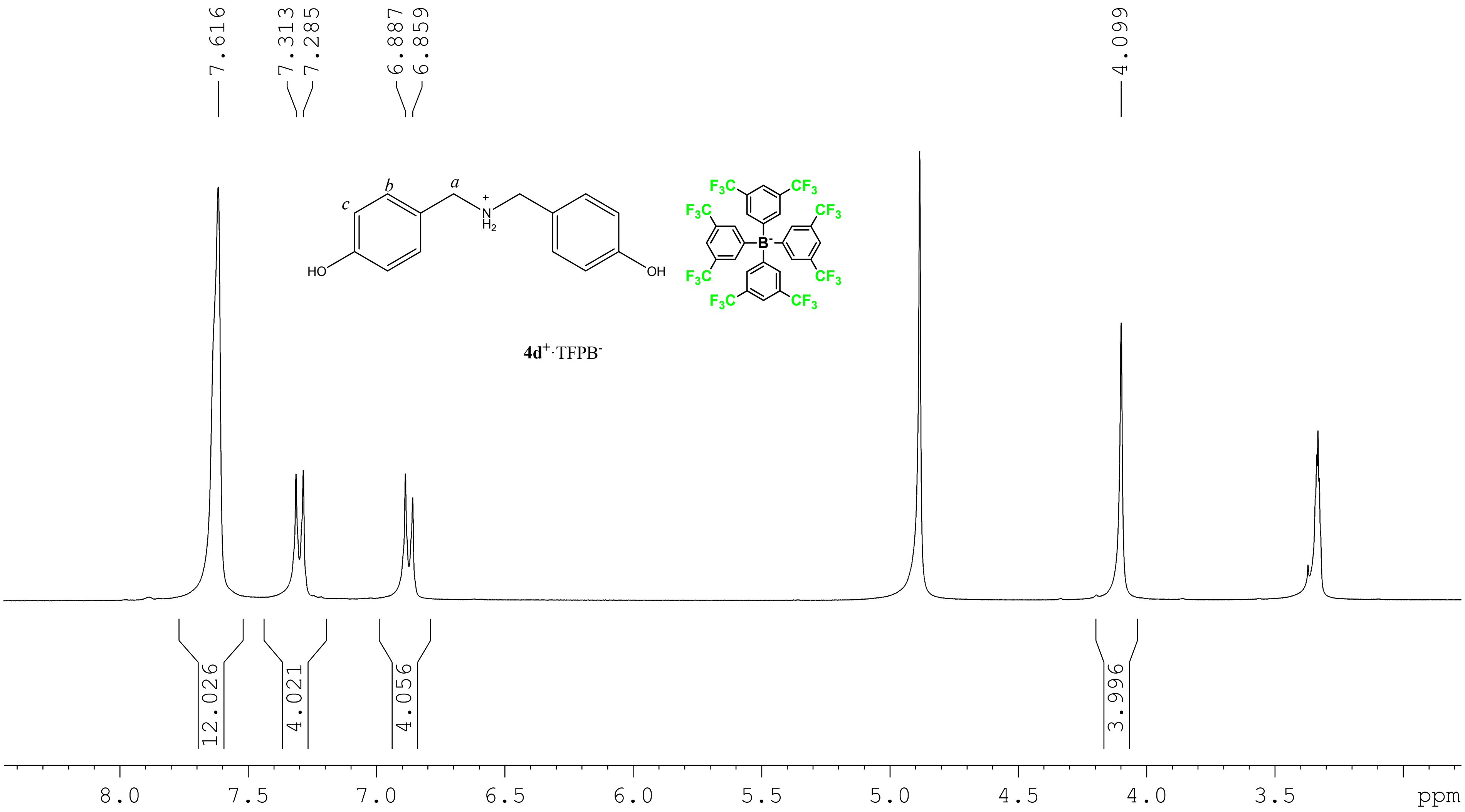


Figure S27. ^{1}H NMR spectrum of derivative **$4d^+$·TFPB$^-$** (300 MHz, CD_3OD, 298 K).

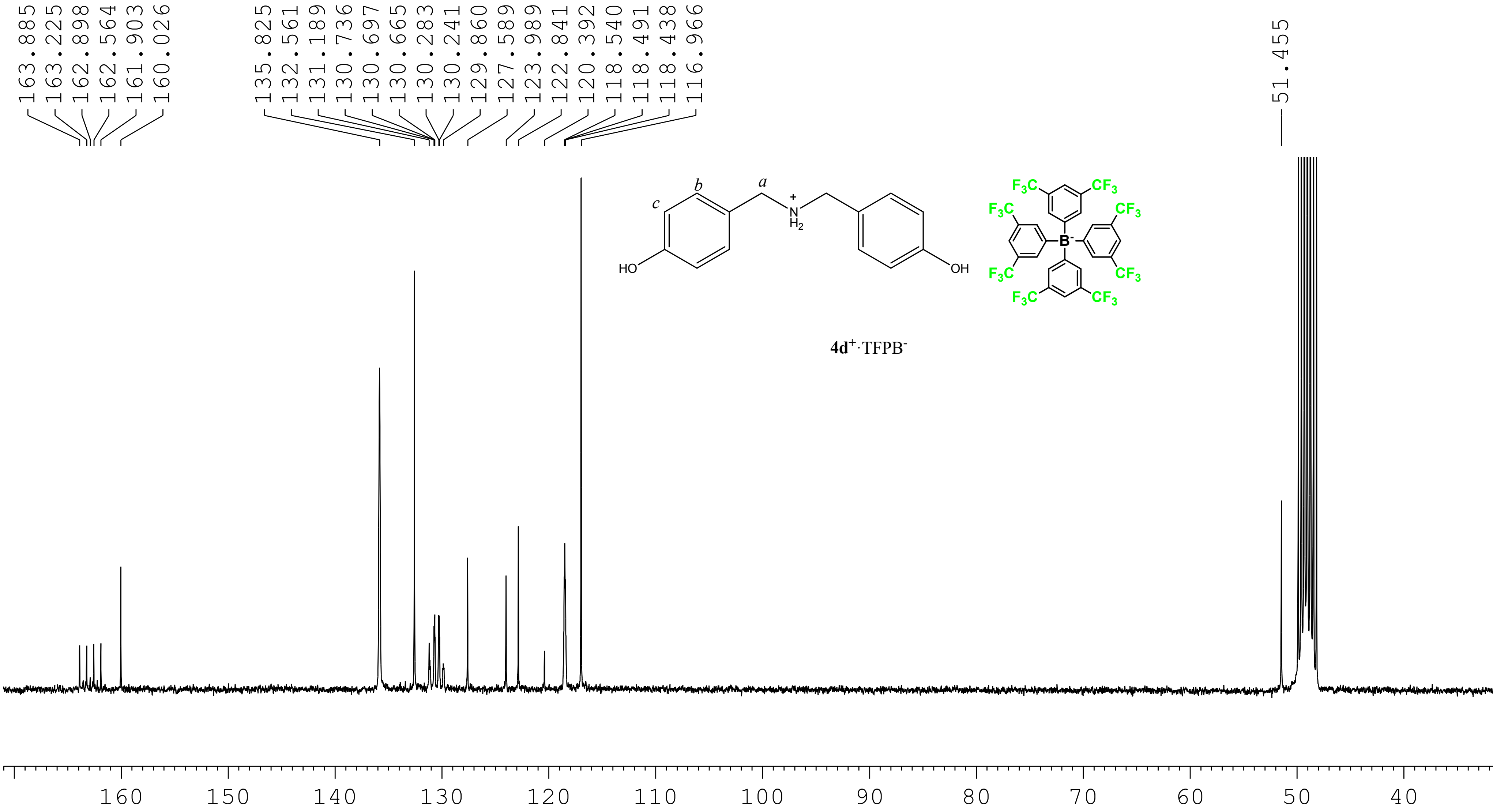


Figure S28. ^{13}C NMR spectrum of derivative **4d$^+$·TFPB$^-$** (75 MHz, CD$_3$OD, 298 K).

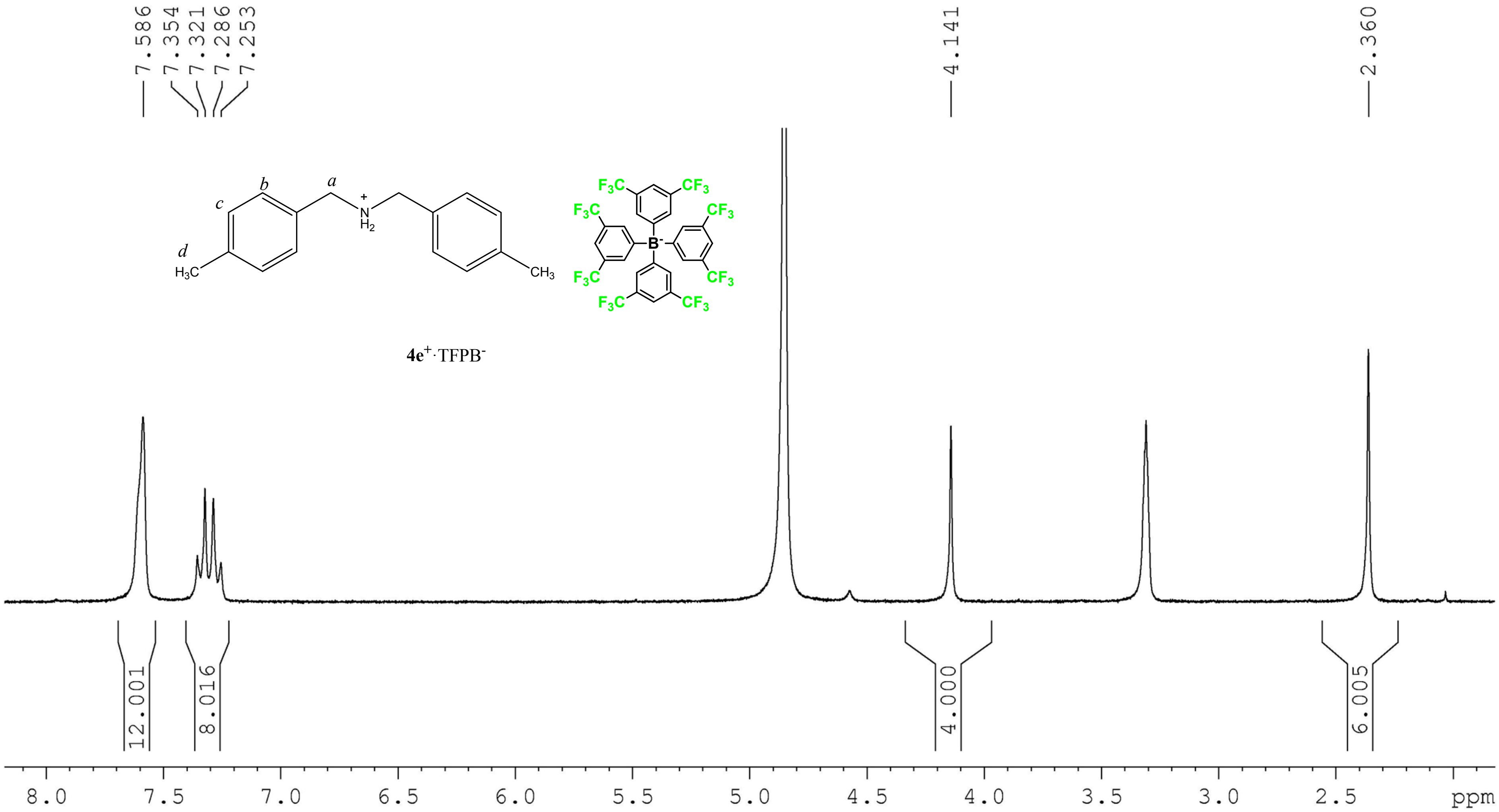


Figure S29. ^{1}H NMR spectrum of derivative **4e$^+$·TFPB$^-$** (250 MHz, CD_3OD, 298 K).

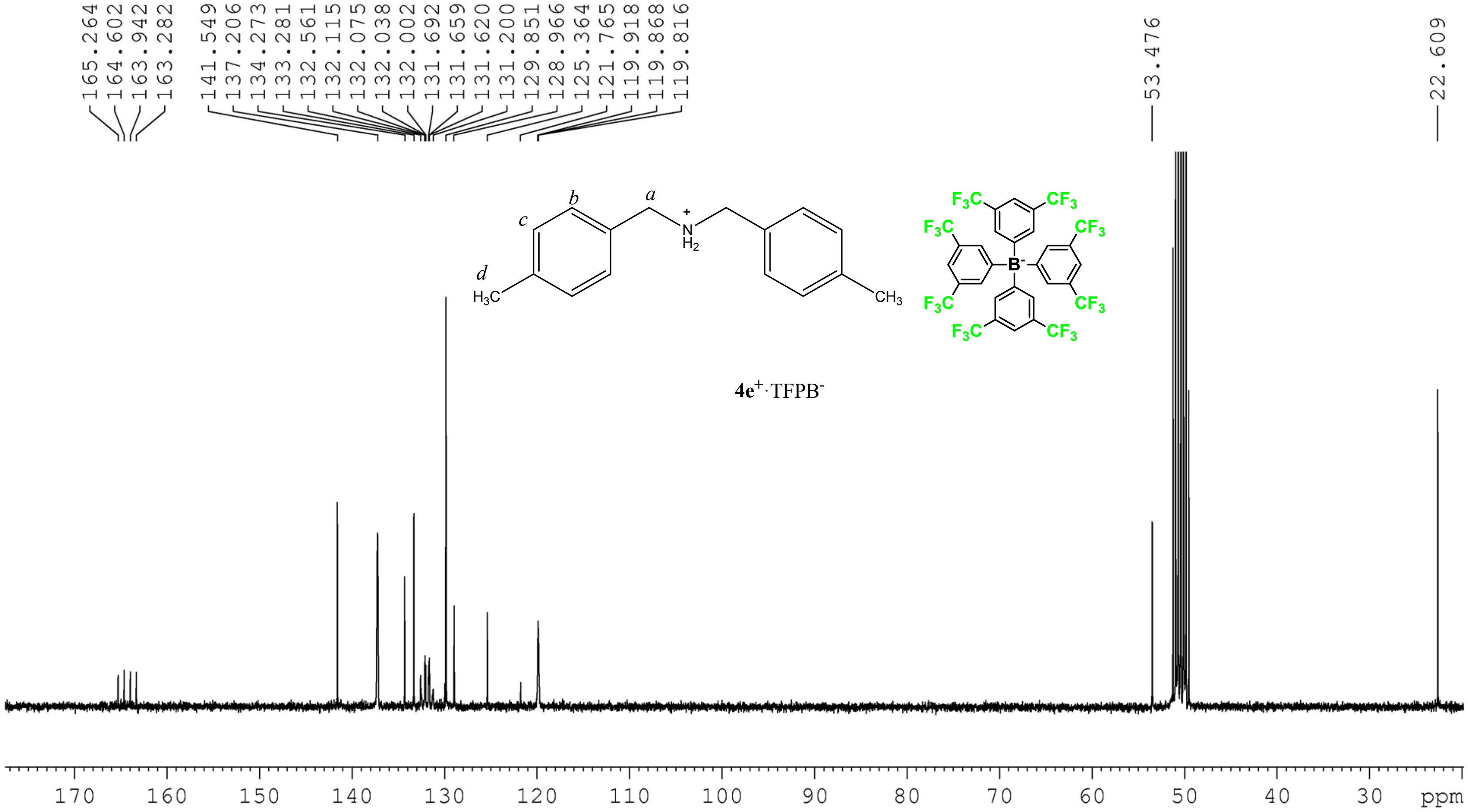


Figure S30. ^{13}C NMR spectrum of derivative **4e^{+}·TFPB^{-}** (75 MHz, CD$_3$OD, 298 K).

Preparation of pseudorotaxanes $6a\text{-}e^+$ and $7a\text{-}d^+$

Calixarene derivative **1** ($2.0\cdot10^{-3}$ mmol) was dissolved in 0.4 mL of $CDCl_3$ ($5.0\cdot10^{-3}$ M solution), then tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salt **3a-d**$^+$ or **4a-e**$^+$ ($2.0\cdot10^{-3}$ mmol, $5\cdot10^{-3}$ M) was added and the mixture was stirred for 15 min at 40 °C. After cooling, the solution was transferred in a NMR tube for 1D and 2D NMR spectra acquisition.

Determination of pseudorotaxane K_{ass} values by quantitative NMR analysis

Each sample was prepared by dissolving **1** (2.45×10^{-3} mmol) and tetrakis[3,5-bis(trifluoromethyl)phenyl]borate salt **3a-d**$^+$ or **4a-e**$^+$ (2.45×10^{-3} mmol) in $CDCl_3$ (0.4 mL) containing 2 μL of 1,1,2,2-tetrachloroethane (d = 1.59 g/mL) as internal standard. The complex concentration [complex] was evaluated by integration of the ^{1}H NMR signal of $CHCl_2CHCl_2$ *vs* the $ArCH_2Ar$ signals of the complex. The following equation was used to obtain the moles of the complex:

$$\frac{G_a}{G_b} = \frac{F_a}{F_b} \times \frac{N_a}{N_b} \times \frac{M_a}{M_b}$$

where

G_a = grams of 1,1,2,2-tetrachloroethane;

G_b = grams of complex

F_a and F_b = areas of the signals of 1,1,2,2-tetrachloroethane and $ArCH_2Ar$ signal of the complex.

N_a and N_b = numbers of nuclei which cause the signals (N_a for 1,1,2,2-tetrachloroethane; N_b for complex)

M_a and M_b = molecular masses of 1,1,2,2-tetrachloroethane (a) and complex (b)

^{1}H NMR spectrum of pseudorotaxane 6b$^+$·TFPB$^-$

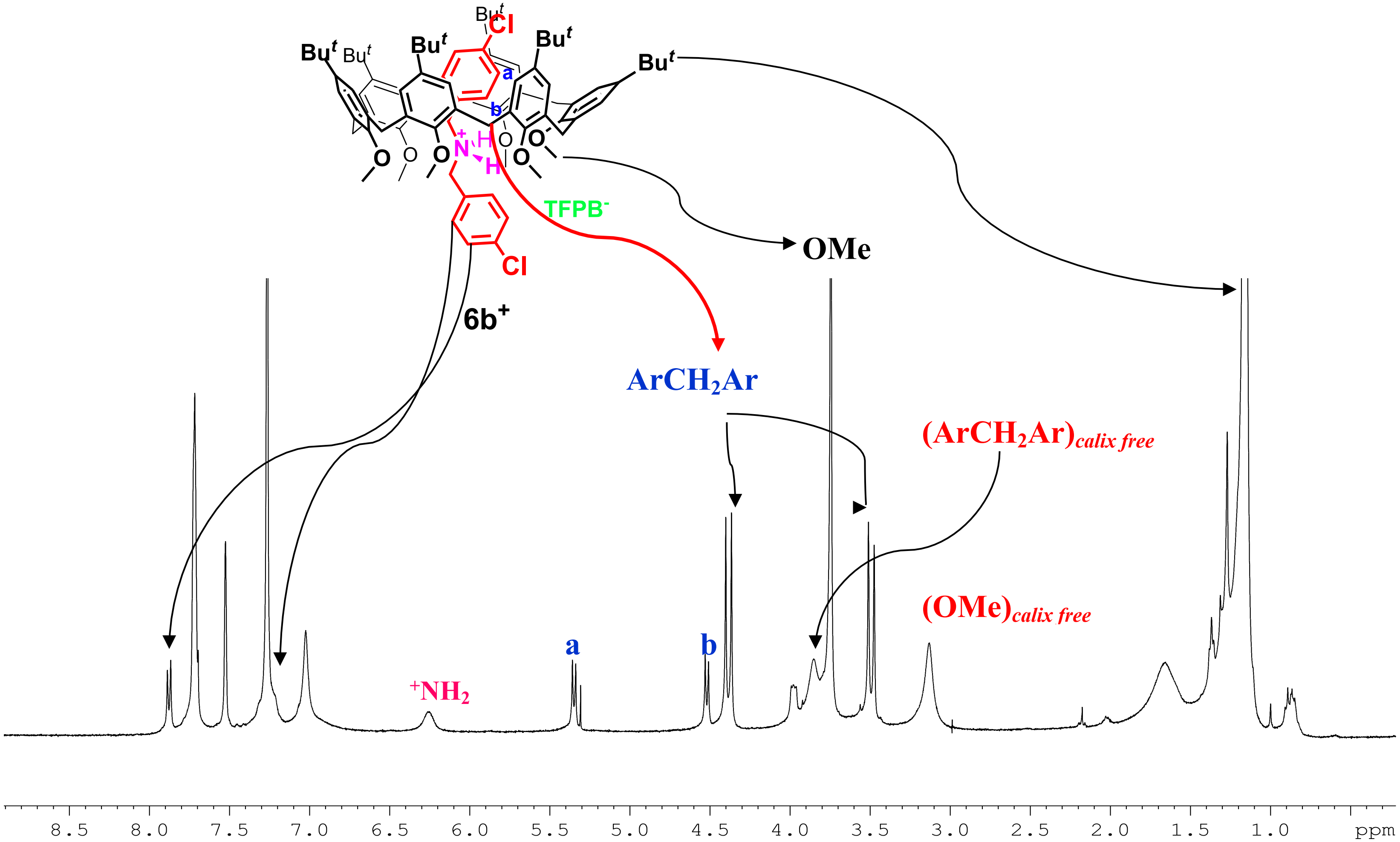


Figure S31. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of an equimolar solution of **4b$^+$·TFPB$^-$** and **1** (5.0·10^{-3} M).

^{1}H NMR spectrum of pseudorotaxane 6c$^+$·TFPB$^-$

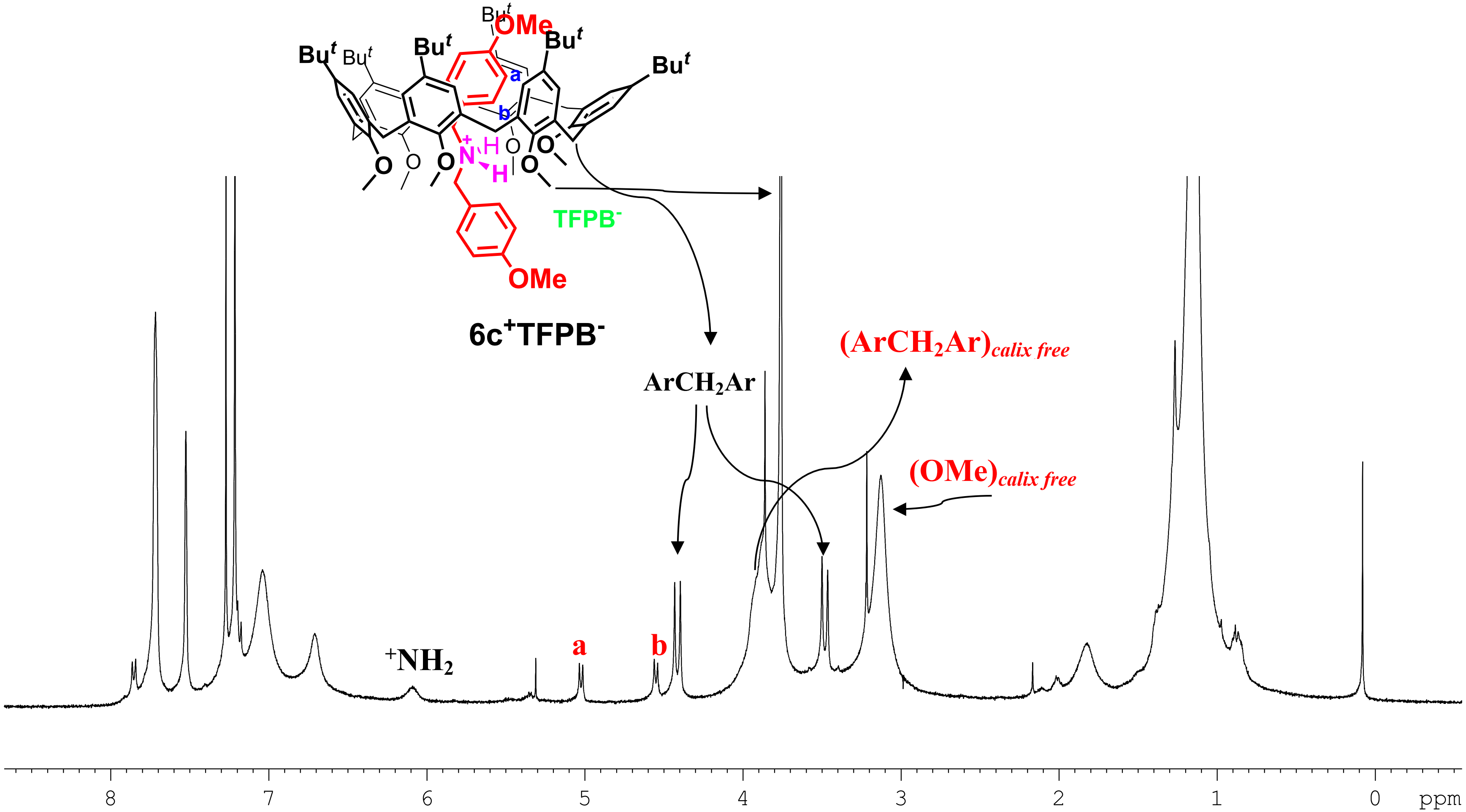


Figure S32. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of an equimolar solution of **4c$^+$·TFPB$^-$** and **1** ($5.0 \cdot 10^{-3}$ M).

^{1}H NMR spectrum of pseudorotaxane 6d$^+$·TFPB$^-$

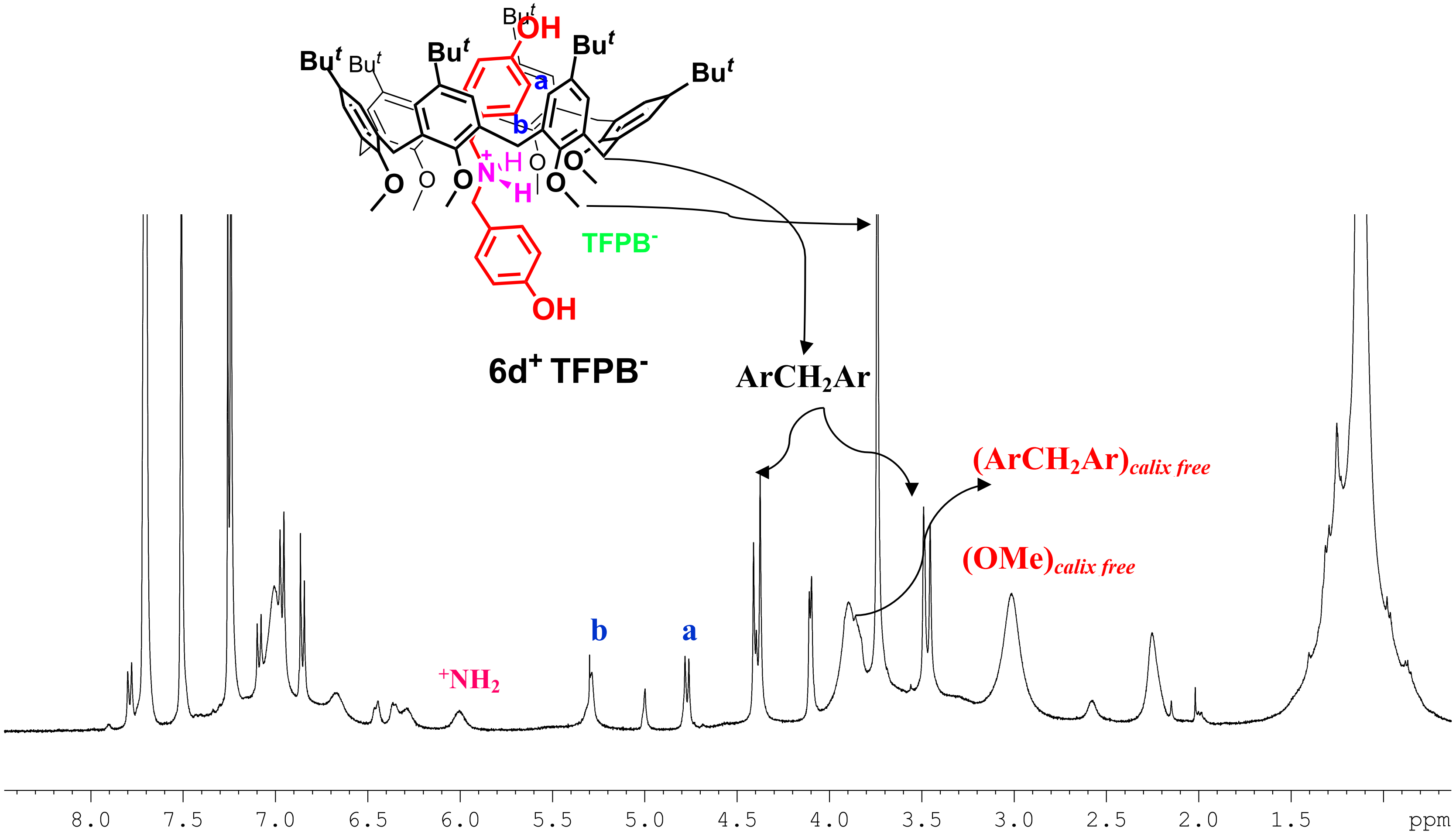


Figure S33. ^{1}H NMR spectrum (400 MHz, CDCl$_3$, 298 K) of an equimolar solution of **4d**$^+$ and **1** ($5.0 \cdot 10^{-3}$ M).

^{1}H NMR spectrum of pseudorotaxane 6e^{+}·TFPB^{-}

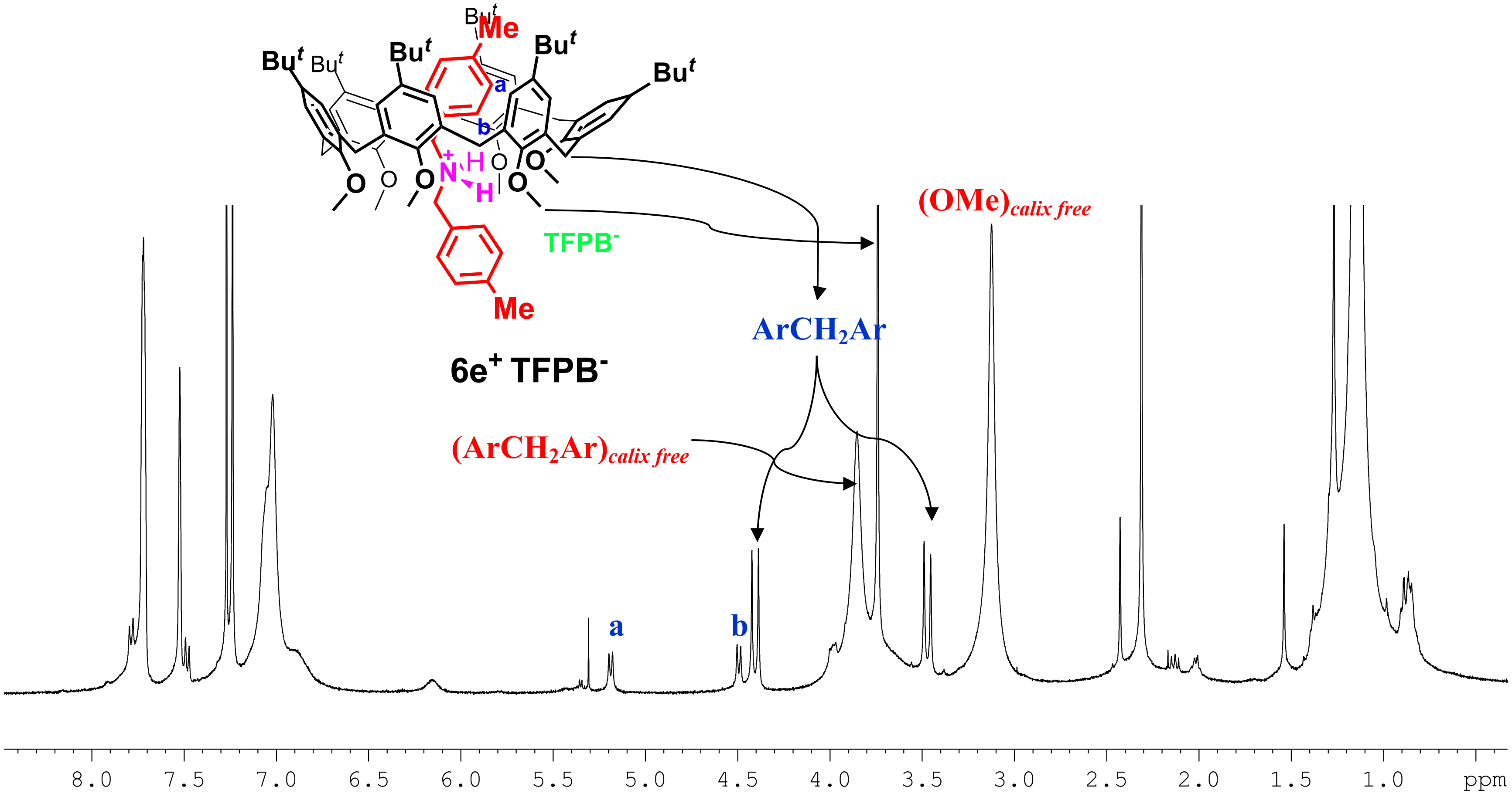


Figure S34. ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of an equimolar solution of **4e**$^{+}$ and **1** ($5.0 \cdot 10^{-3}$ M).

2D COSY spectrum of an equimolar mixture of 1 and $3a^+$

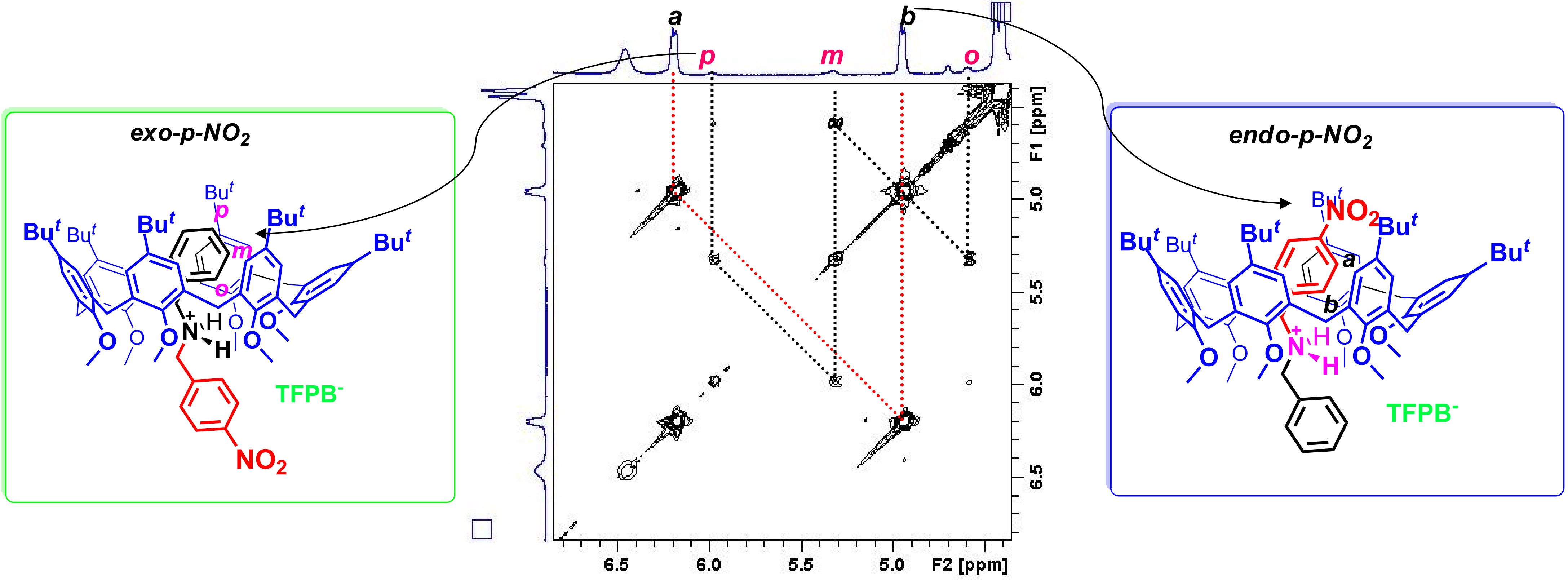


Figure S35. 2D COSY-45 spectrum (400 MHz, CDCl$_3$, 298 K) of an equimolar mixture of **$3a^+$·TFPB$^-$** and **1** (5.0×10^{-3} M).

2D COSY spectrum of an equimolar mixture of 1 and 3b$^+$

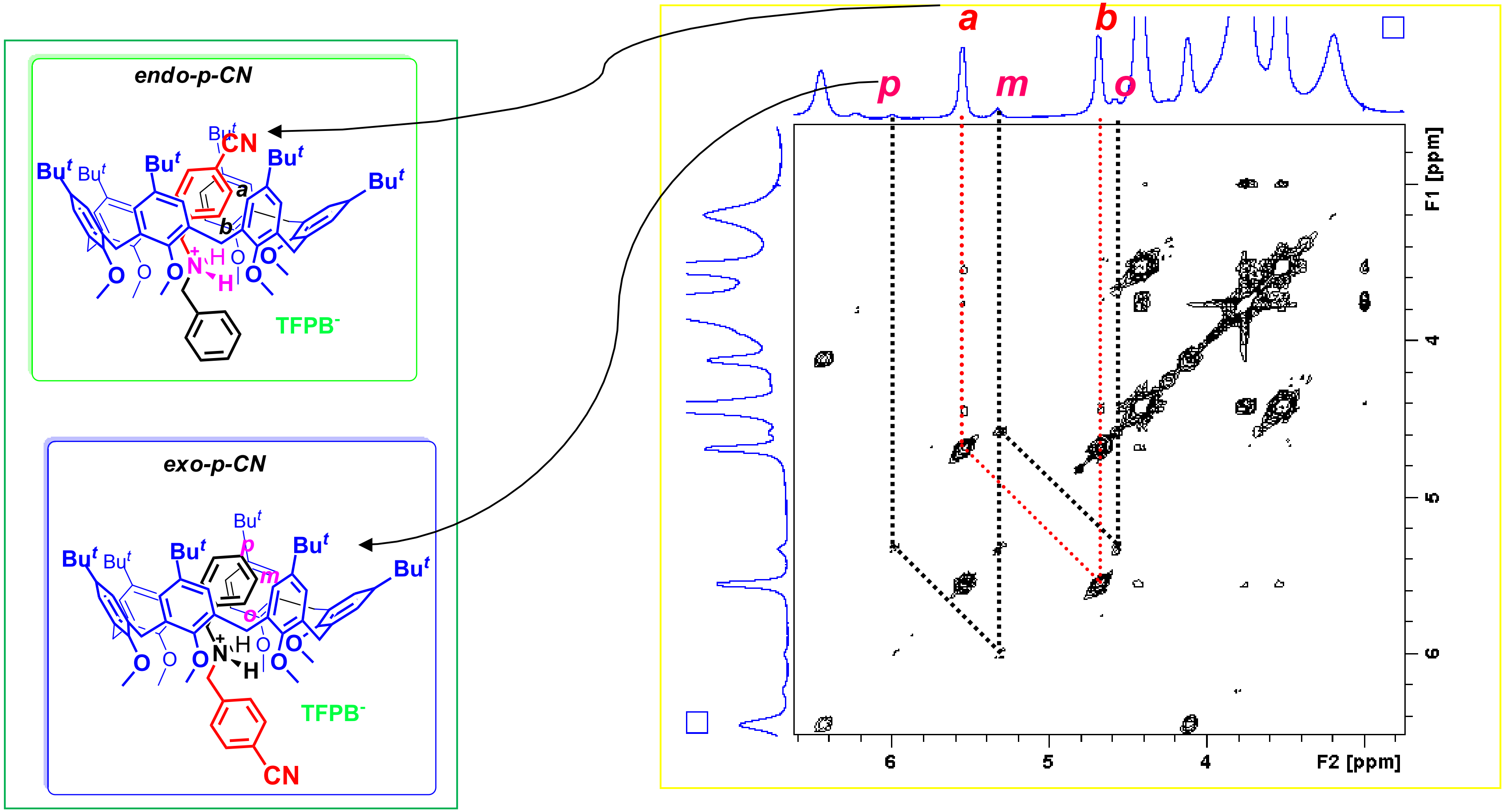


Figure S36. Portion of 2D COSY-45 spectrum (400 MHz, $CDCl_3$, 298 K) of an equimolar mixture of **$3b^+ \cdot TFPB^-$** and **1** (5.0×10^{-3} M).

2D COSY spectrum of an equimolar mixture of 1 and 3c$^+$

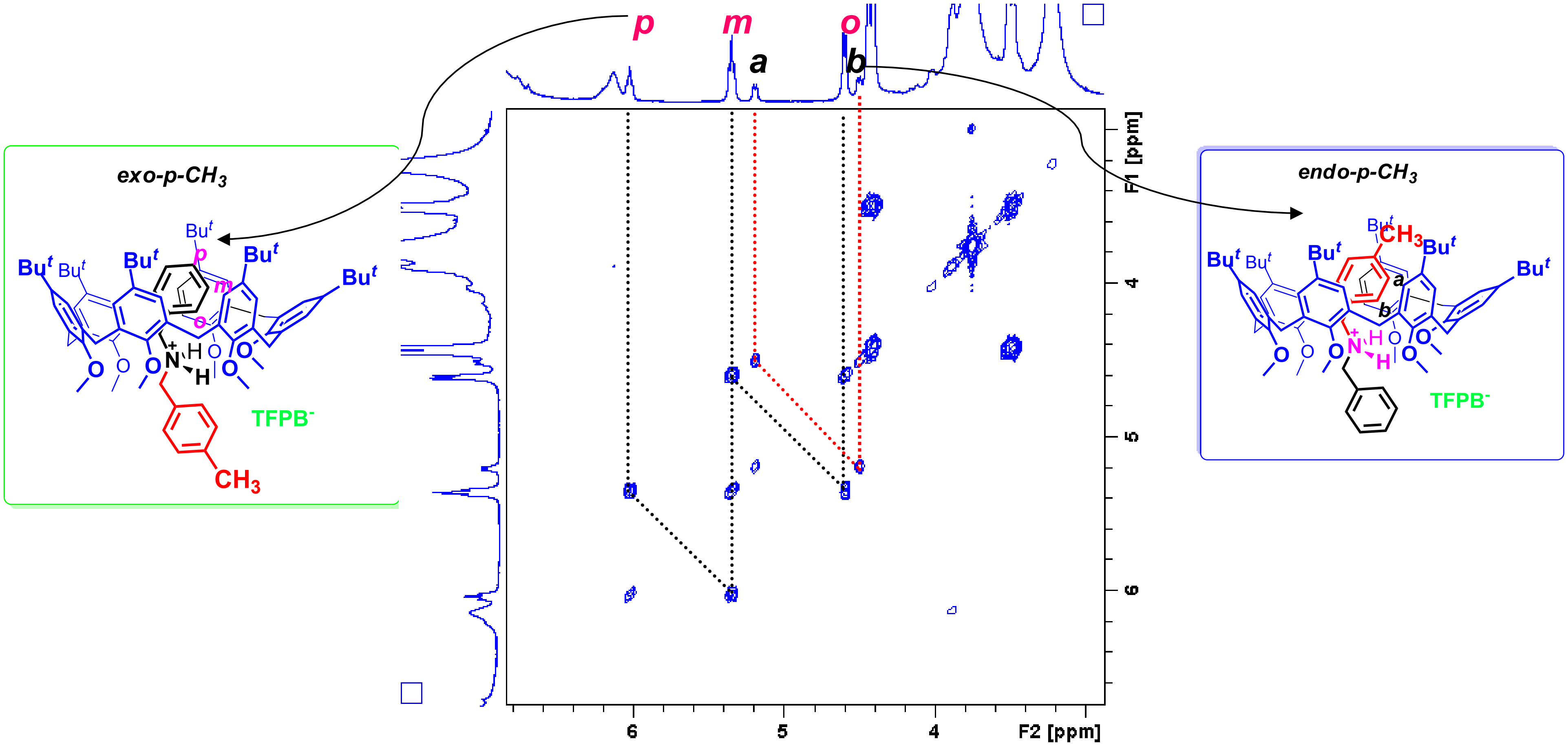


Figure S37. Portion of 2D COSY-45 spectrum (400 MHz, $CDCl_3$, 298 K) of an equimolar mixture of **3c$^+$·TFPB$^-$** and **1** (5.0×10^{-3} M).

2D COSY spectrum of an equimolar mixture of 1 and 3d$^+$

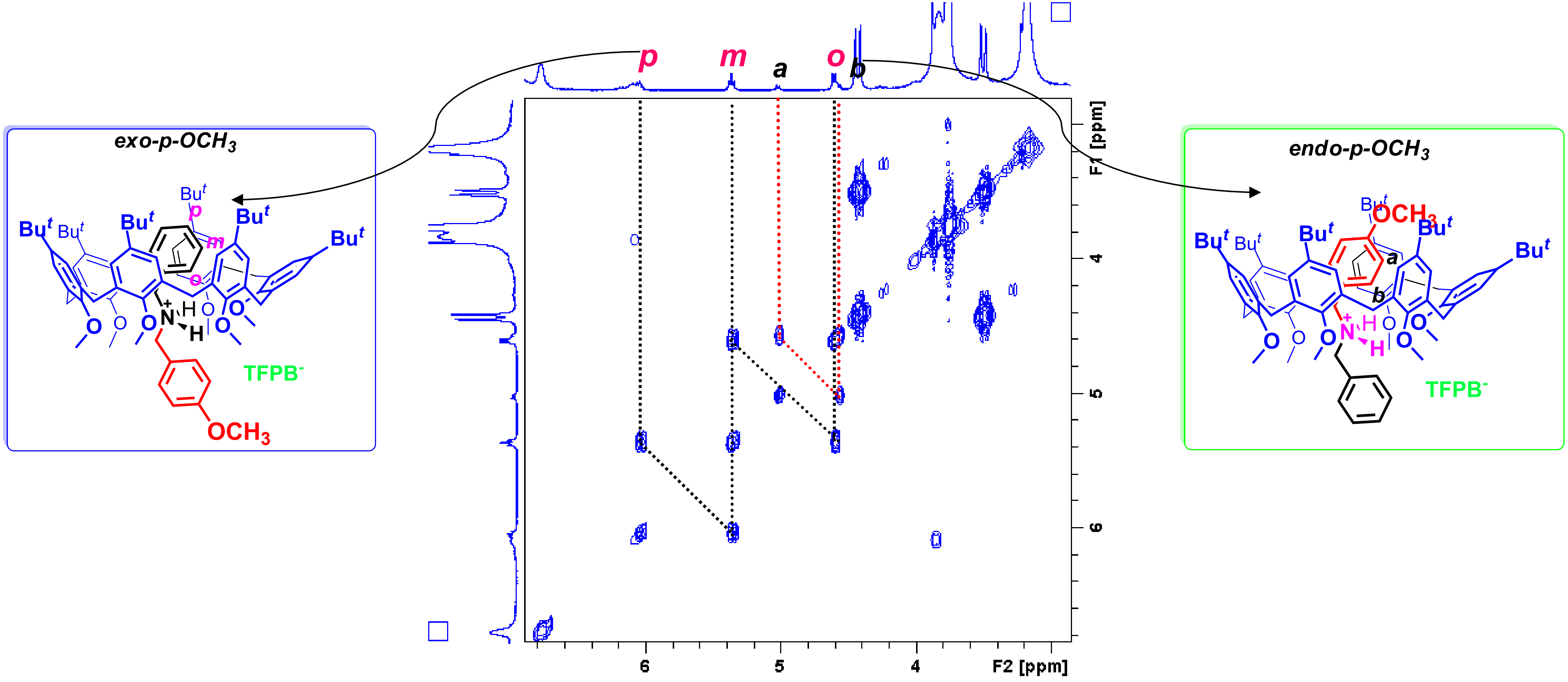
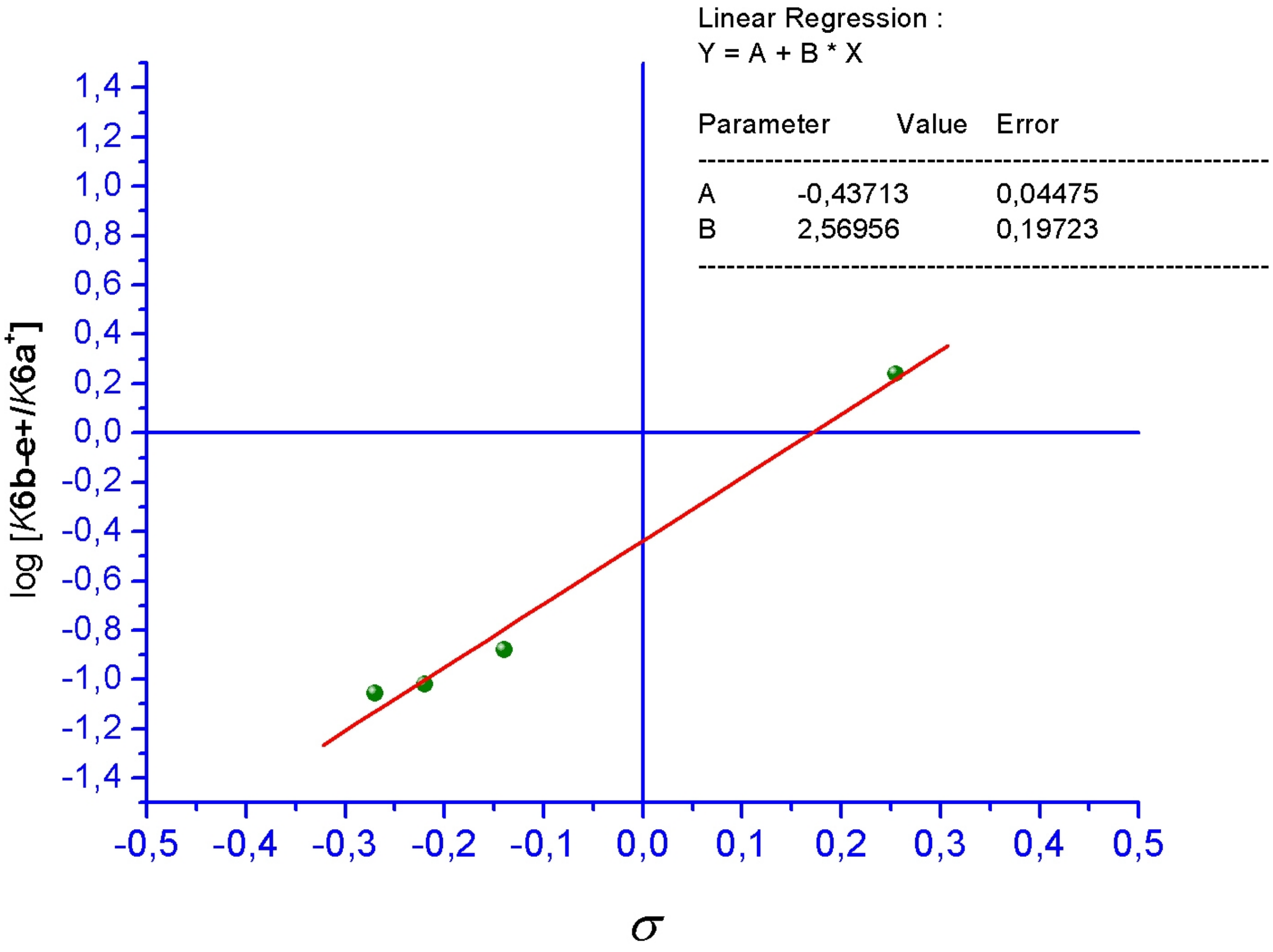


Figure S38. Portion of 2D COSY-45 spectrum (400 MHz, CDCl$_3$, 298 K) of of an equimolar mixture of **3d**$^+$·**TFPB**$^-$ and **1** (5.0×10^{-3} M).

Hammett-type plot



```
Linear Regression :
Y = A + B * X

Parameter        Value    Error
------------------------------------------------------------
A          -0,43713          0,04475
B          2,56956           0,19723
------------------------------------------------------------
```

Figure S39. Hammett correlations between log [K_a(**6b-e**)/K_a(**6a**)] and σ .

Details of the optimized structure of *endo-p*-NO_2-benzyl-7a^{+} complex

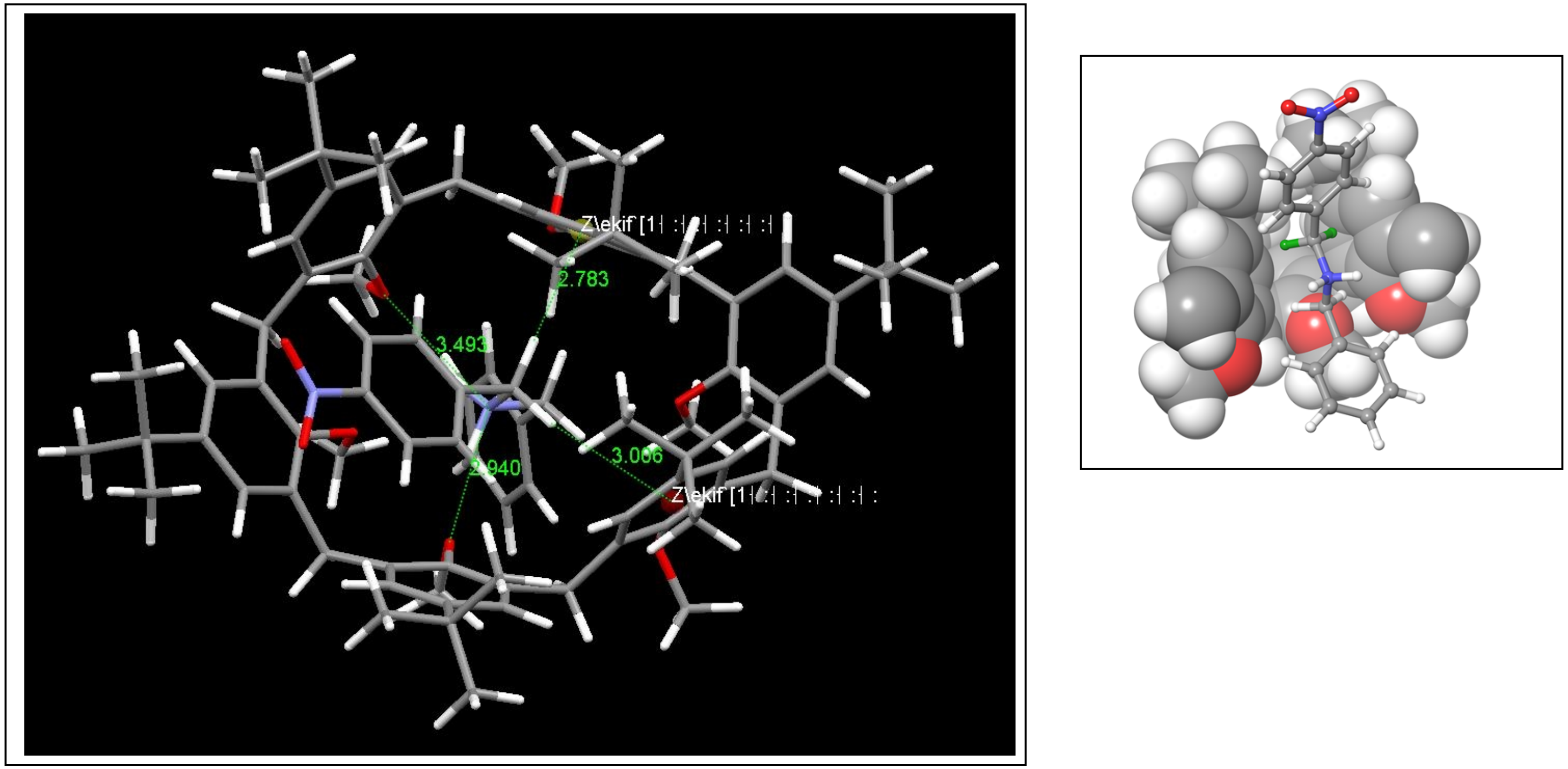


Figure S40. (Left) Details of the optimized structure of *endo*-*p*-NO_2-benzyl-**7a**$^{+}$ complex at the B3LYP/6-31G(d,p) level of theory, indicating the $N^{+}\cdots O^{calix}$ and $^{+}NH_2C\text{-}H\cdots centroids^{calix}$ distances (Å). (Right) Particular showing C-H···π interactions between methylene $PhCH_2{}^{+}NH_2C\boldsymbol{H}_2Ph$-*p*-$NO_2$ hydrogen atoms of **3a**$^{+}$ (in green) and two anisole rings of **1.**

Details of the optimized structure of *endo*-benzyl-7a$^+$ complex

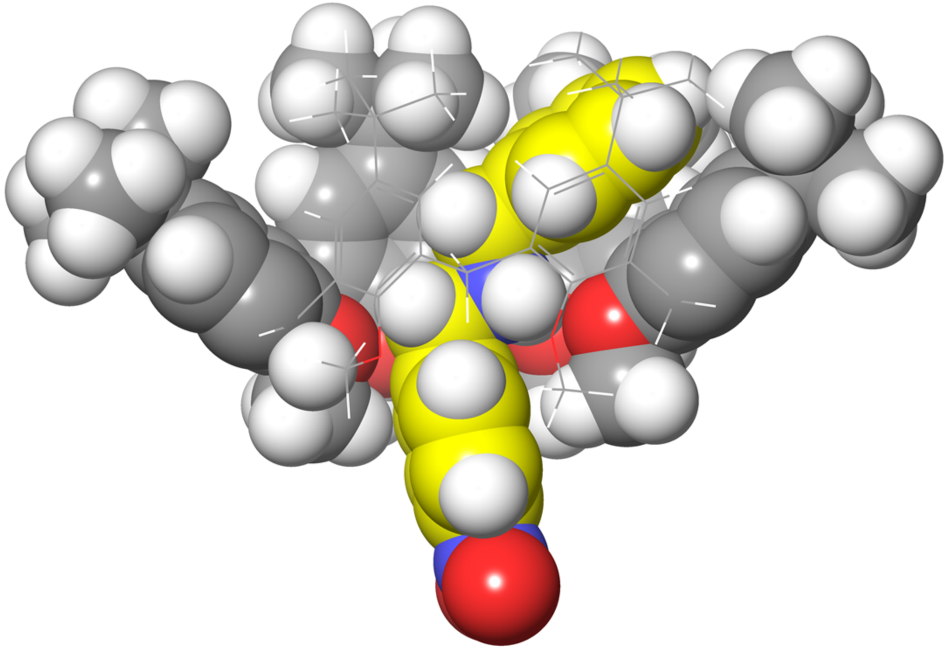


Figure S41. Side view of the optimized structures of the *endo*-benzyl-**7a**$^+$ complex at the B3LYP/6-31G(d,p) level of theory. A mixed CPK/wireframe representation was used for clarity.

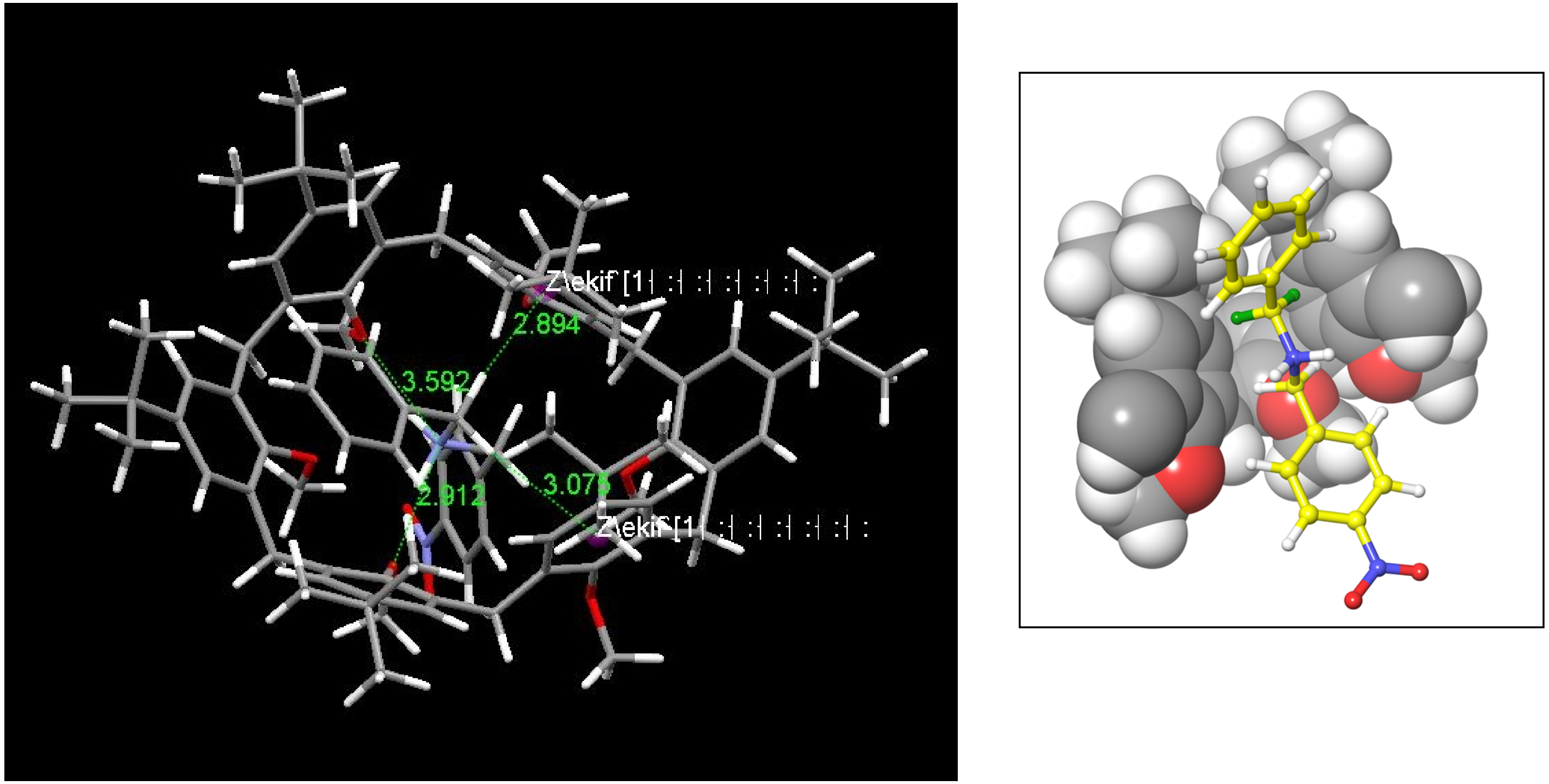


Figure S42. (Left) Details of the optimized structure of the *endo*-benzyl-**7a**$^+$ complex at the B3LYP/6-31G(d,p) level of theory, indicating the $N^+\cdots O^{calix}$ and $^+NH_2C\text{-}H\cdots$centroids^{calix} distances (Å). (Right) Particular showing C-H···π interactions between methylene $PhC\boldsymbol{H}_2{}^+NH_2CH_2Ph$-*p*-$NO_2$ hydrogen atoms of **3a**$^+$ (in green) and two anisole rings of **1.**

^1H NMR titration of hexamethoxy-*p*-NO_2-calix[6]arene with **4a**$^+$•TFPB$^-$

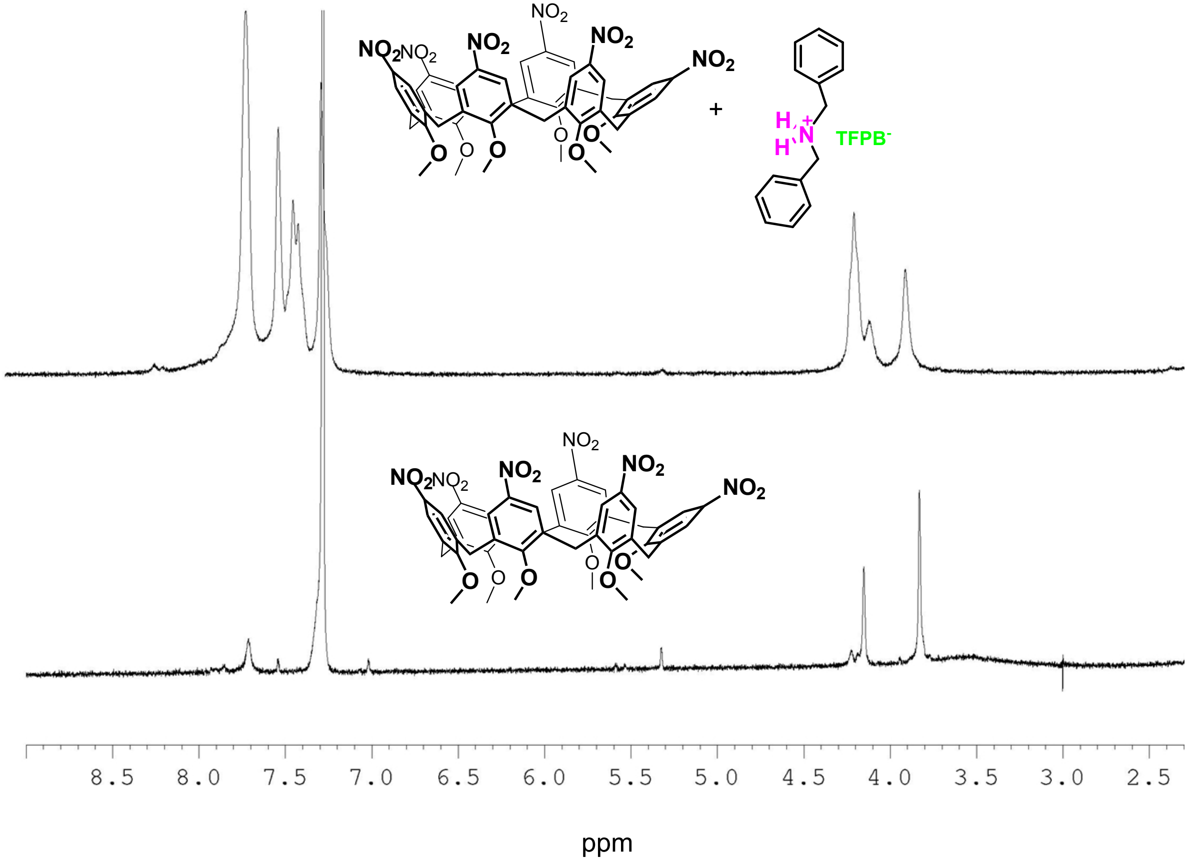


Figure S43. Significant portion of the ^1H NMR spectra (400 MHz, $CDCl_3$, 298 K) of: (bottom) hexamethoxy-*p*-NO_2-calix[6]arene; (top) 1:1 mixture of hexamethoxy-*p*-NO_2-calix[6]arene and **4a$^+$•TFPB$^-$**.