Supporting Information

Jonas R. Schmid, Anja Wiesner, Patrick Voßnacker, Martin Jansen*, Sebastian Riedel*

$[Me_3N(C_6H_3(CF_3)_2)][BF_4]$ and $[Me_3N(C_6H_3(CH_3)_2)][BF_4]$, as potential synthons for non-covalent supramolecular assembly

https://doi.org/10.1515/znb-2023-0095.

Received November 1, 2023; accepted November 6, 2023

*** Corresponding authors: Prof. Dr. Dr. h.c. Martin Jansen,** Max-Planck-Institut für Festkörperforschung, Heisenbergstraße 1, 70569 Stuttgart, Germany; E-mail: m.jansen@fkf.mpg.de, and **Prof. Dr. Sebastian Riedel,** Anorganische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34/36, 14195 Berlin, Germany; E-mail: s.riedel@fu-berlin.de

Jonas R. Schmid, Anja Wiesner, Patrick Voßnacker: Anorganische Chemie, Institut für Chemie und Biochemie, Freie Universität Berlin, Fabeckstraße 34/36, 14195 Berlin, Germany

Table of content

Vibrational spectroscopy

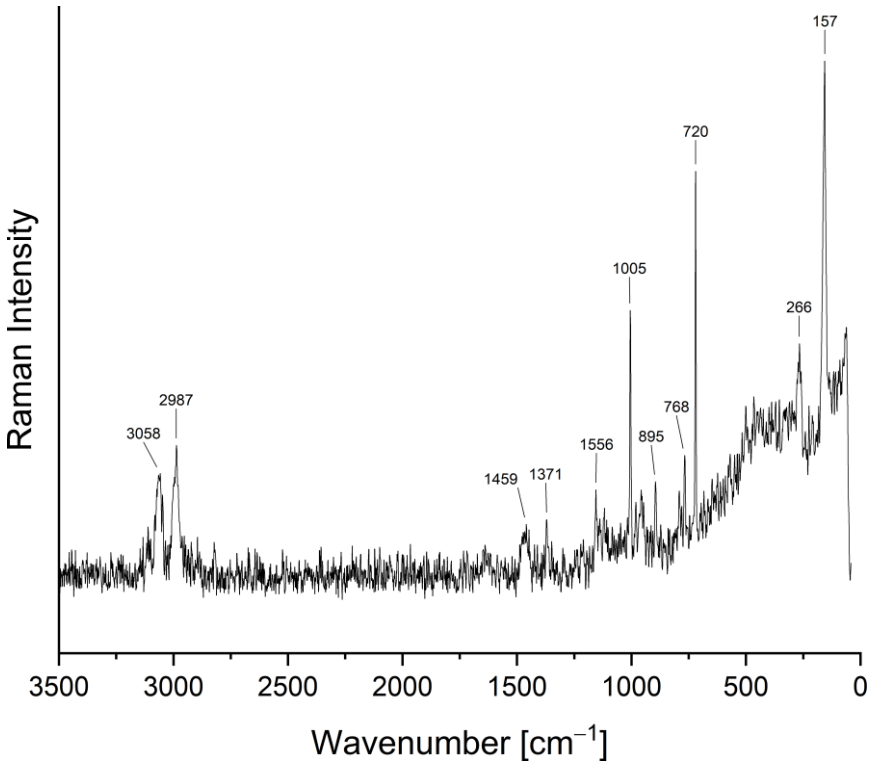


Figure S1: Full Raman spectrum of $[Me_3N(C_6H_3(CF_3)_2)][BF_4]$ at r.t.

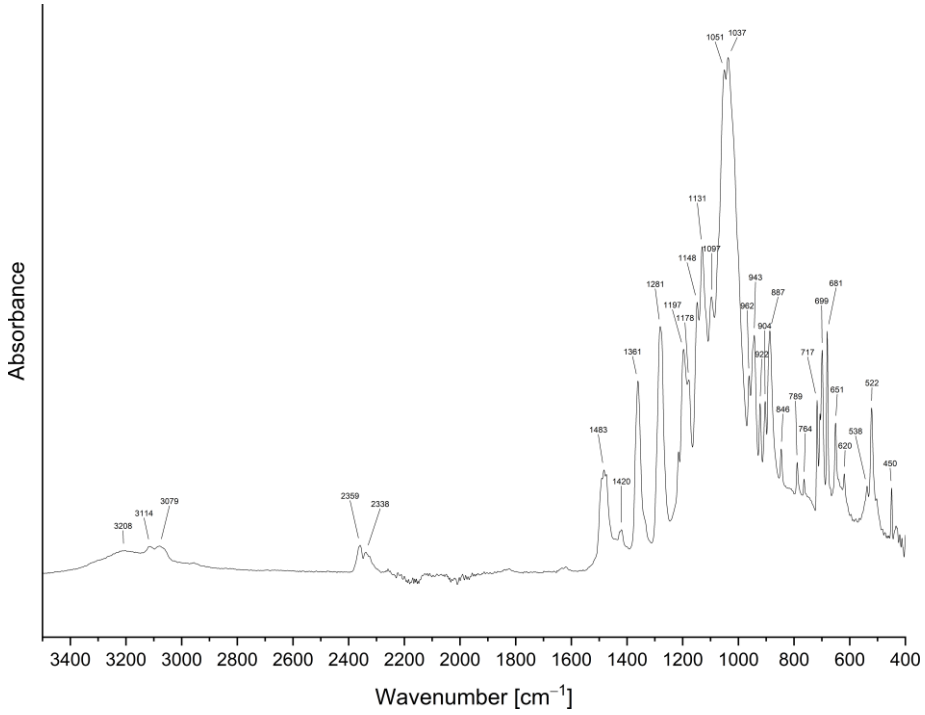


Figure S2: Full IR spectrum of $[Me_3N(C_6H_3(CF_3)_2)][BF_4]$ at r.t.

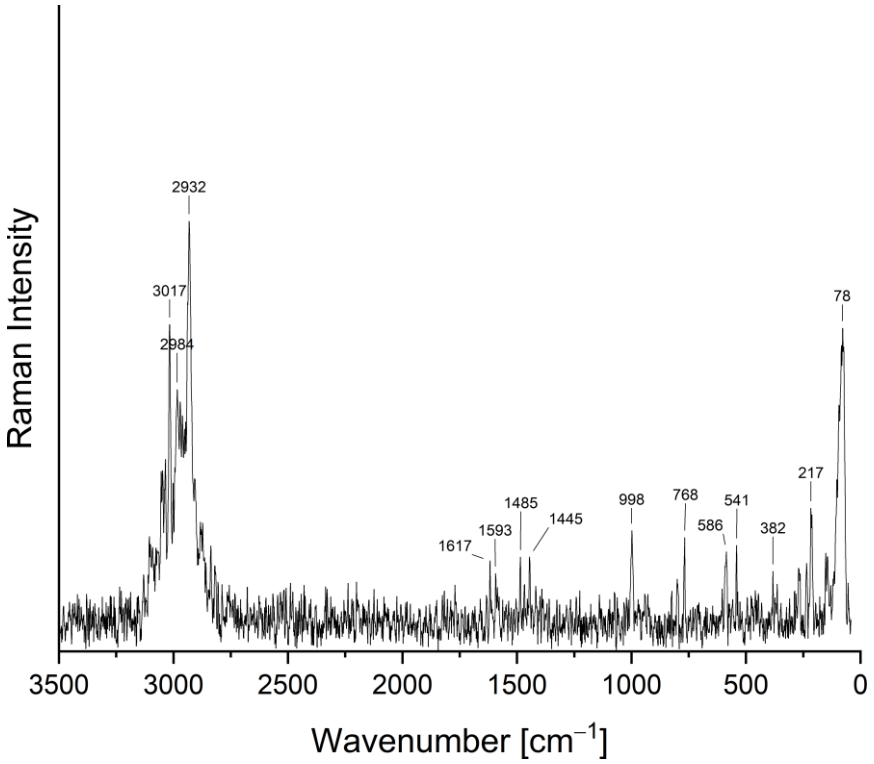


Figure S3: Full Raman spectrum of $[Me_3N(C_6H_3(CH_3)_2)][BF_4]$ at r.t.

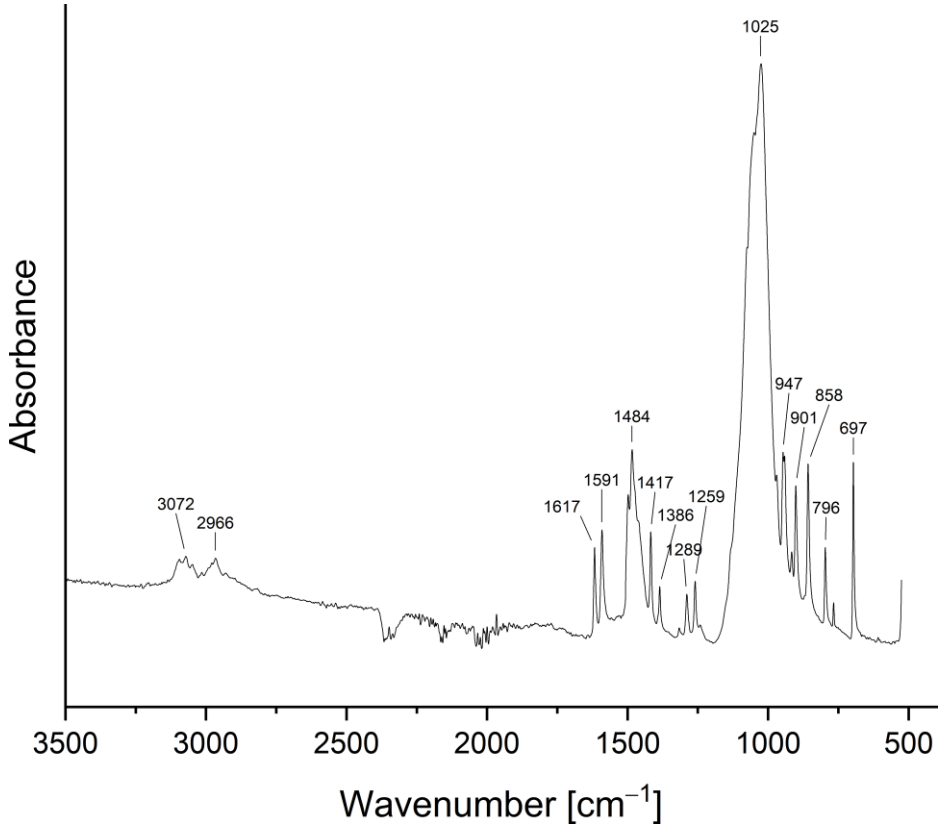


Figure S4: Full IR spectrum of $[Me_3N(C_6H_3(CH_3)_2)][BF_4]$ at r.t.

NMR spectroscopy

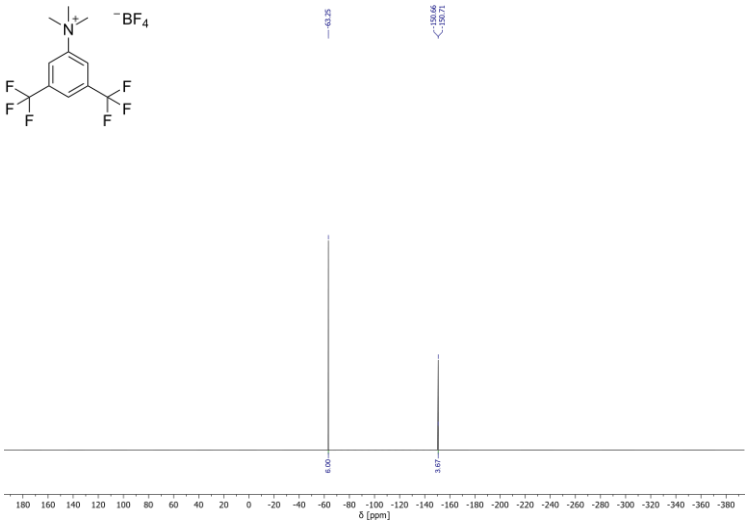


Figure S5: ^{19}F NMR (565 MHz, MeCN-d_3).

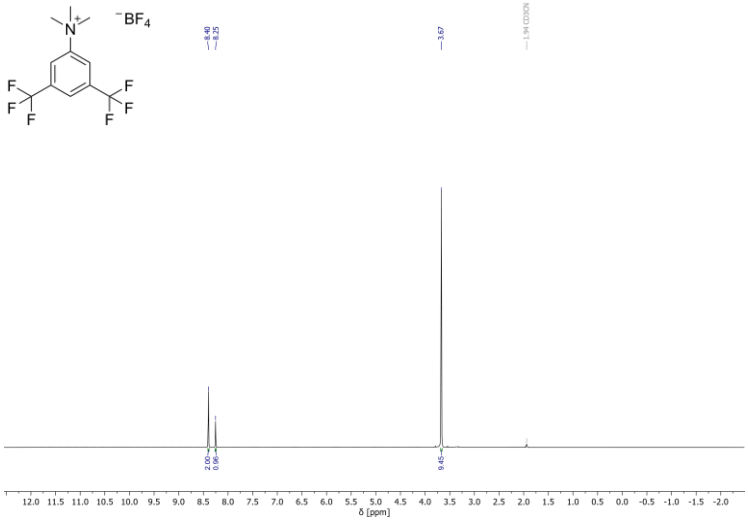


Figure S6: ^{1}H NMR (600 MHz, MeCN-d_3).

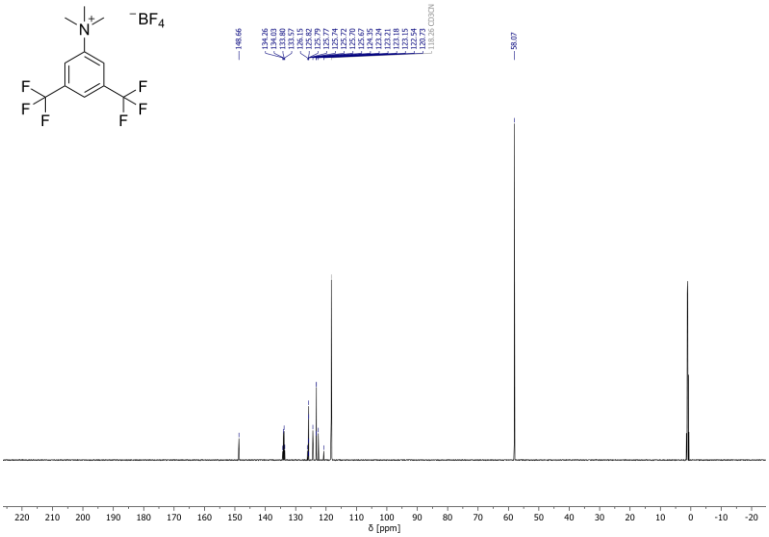


Figure S7: ^{13}C NMR (151 MHz, MeCN-d_3).

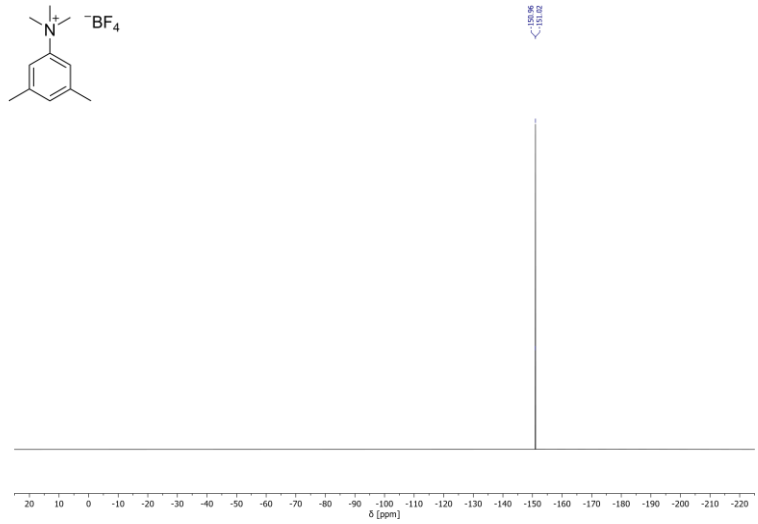


Figure S8: ^{19}F NMR (377 MHz, MeCN-d_3).

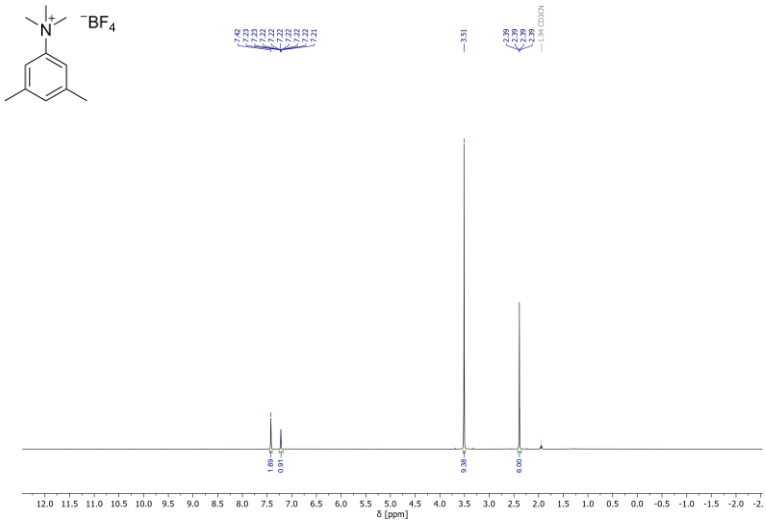


Figure S9: ^{1}H NMR (401 MHz, MeCN-d_3).

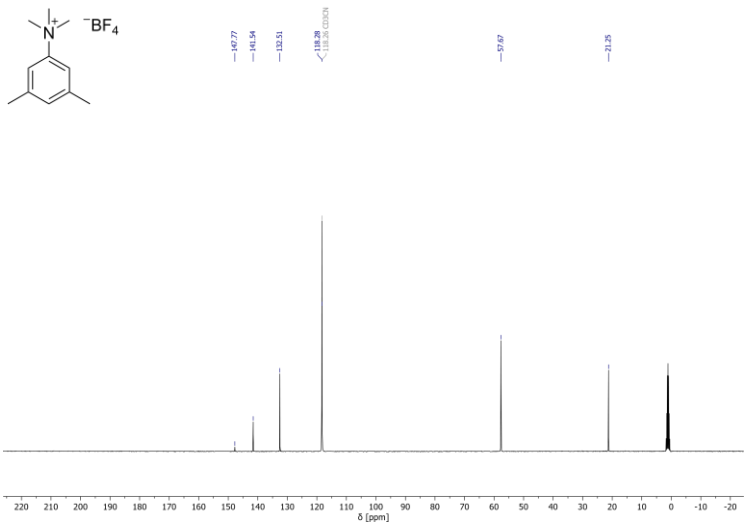


Figure S10: ^{13}C NMR (101 MHz, MeCN-d_3).

Atom parameters for $[Me_3N(C_6H_3(CF_3)_2)][BF_4]$

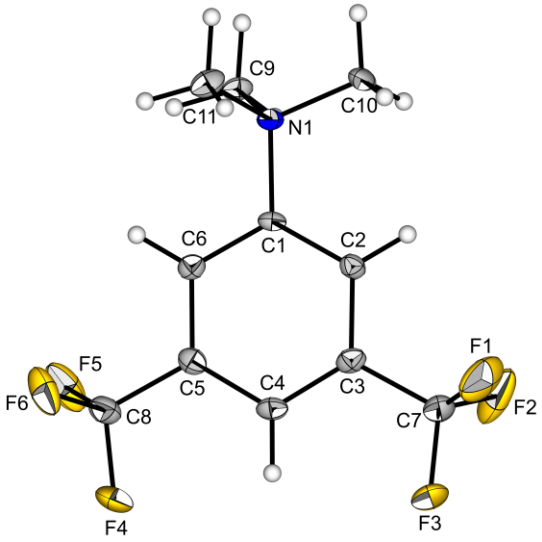


Figure S11: Molecular structure of the cation of $[Me_3N(C_6H_3(CF_3)_2)][BF_4]$ in the crystal and atom numbering adopted.

Table S1: Fractional atomic coordinates ($\times10^4$) and equivalent isotropic displacement parameters ($Å^2\times10^3$) for $[Me_3N(C_6H_3(CF_3)_2)][BF_4]$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}
B1	1219(5)	7662(4)	1836.4(9)	16.0(6)
F7	–336(3)	7605(3)	2165.1(5)	30.5(4)
F8	3316(3)	7352(2)	2005.6(5)	25.4(4)
F9	1184(3)	9347(2)	1648.1(6)	30.3(4)
F10	728(3)	6378(2)	1530.5(5)	23.8(4)
C11	–3638(5)	991(4)	1740.7(9)	21.6(6)
C10	–2715(5)	3982(4)	1987.5(9)	22.5(7)
C9	–6436(5)	2861(4)	2094.1(8)	16.8(6)
N1	–4498(4)	2870(3)	1789.0(6)	14.7(5)
C1	–5213(4)	3581(3)	1359.5(8)	12.7(5)
C2	–4265(5)	5111(3)	1194.6(8)	15.2(6)
C3	–5014(5)	5738(4)	799.7(8)	17.1(6)
C4	–6665(5)	4877(4)	574.2(8)	17.4(6)
C5	–7563(5)	3335(3)	746.4(8)	17.2(6)
C6	–6846(4)	2673(4)	1140.4(8)	15.4(5)
C7	–3963(5)	7397(4)	626.1(8)	25.5(7)
F1	–1773(4)	7286(3)	617.0(8)	56.2(7)
F2	–4423(5)	8810(2)	865.0(7)	60.3(8)
F3	–4582(4)	7778(3)	229.1(6)	46.7(6)
C8	–9343(5)	2350(4)	513.6(8)	22.5(6)
F4	–9922(4)	3123(3)	148.0(6)	50.5(6)
F5	–11164(3)	2175(3)	752.3(6)	42.1(5)
F6	–8744(3)	689(3)	411.2(6)	39.9(5)

Table S2: Anisotropic displacement parameters ($Å^2 \times 10^3$) for $[Me_3N(C_6H_3(CF_3)_2)][BF_4]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	15.5(14)	14.8(13)	17.5(14)	–1.5(12)	1.6(12)	–4.0(13)
F7	29.0(9)	39.9(10)	22.7(8)	–10.0(8)	11.7(7)	–10.8(9)
F8	22.7(9)	28.3(9)	25.3(8)	–1.3(7)	–8.3(7)	2.1(8)
F9	26.5(9)	18.6(8)	45.9(11)	9.1(8)	–3.7(9)	–0.7(8)
F10	25.2(9)	26.6(8)	19.5(8)	–7.1(7)	0.7(7)	–7.6(8)
C11	21.6(15)	19.3(14)	24.0(15)	5.4(11)	1.7(13)	6.6(12)
C10	23.2(16)	29.4(15)	14.7(14)	5.5(12)	–7.1(12)	–10.5(13)
C9	17.8(14)	21.3(13)	11.4(12)	2.9(10)	3.4(10)	0.4(12)
N1	14.3(11)	17.7(10)	12.0(10)	3.0(9)	–1.6(9)	0.3(10)
C1	13.0(13)	16.1(11)	8.9(12)	0.8(10)	–0.3(10)	3.0(11)
C2	16.0(14)	17.6(12)	12.0(12)	–1.6(10)	0.4(10)	–1.1(11)
C3	21.3(15)	18.0(12)	12.0(13)	0.8(10)	3.9(11)	1.0(12)
C4	20.8(14)	20.9(13)	10.4(12)	0.9(11)	1.1(11)	2.1(12)
C5	17.4(14)	18.9(13)	15.3(13)	–2.8(11)	0.1(11)	1.7(12)
C6	16.7(13)	15.8(12)	13.7(12)	–0.1(10)	2.5(10)	0.8(12)
C7	33.5(17)	26.5(16)	16.3(13)	4.5(12)	–1.2(12)	–6.8(15)
F1	35.2(13)	59.9(14)	73.5(15)	37.6(13)	–1.1(10)	–18.4(11)
F2	118(2)	21.7(9)	41.4(12)	–4.9(9)	28.9(14)	–19.8(13)
F3	72.8(15)	44.5(11)	22.8(9)	19.6(9)	–13.5(10)	–25.6(12)
C8	24.0(16)	27.6(15)	15.8(13)	–1.5(12)	–2.1(11)	–0.9(14)
F4	62.9(15)	55.2(13)	33.5(11)	16.8(10)	–32.8(11)	–25.4(12)
F5	22.6(10)	68.7(14)	35.0(10)	–18.4(10)	5.0(8)	–14.4(11)
F6	36.9(11)	33.0(10)	49.6(12)	–19.8(9)	–9.0(10)	–4.4(10)

Table S3: Bond lengths for $[Me_3N(C_6H_3(CF_3)_2)][BF_4]$.

Atom	Atom	Length in pm
F7	B1	139.0(3)
F8	B1	139.4(4)
F9	B1	139.2(3)
F10	B1	138.6(3)
N1	C11	151.0(3)
N1	C10	149.8(3)
N1	C9	150.9(3)
N1	C1	150.1(3)
C1	C2	138.1(4)
C3	C2	139.1(4)
C3	C4	138.1(4)
C4	C5	138.5(4)
C6	C5	139.1(4)
C1	C6	138.1(4)

C7	C3	149.8(4)
F1	C7	132.9(4)
F2	C7	132.3(4)
F3	C7	132.1(3)
C5	C8	149.4(4)
C8	F4	132.3(3)
C8	F5	133.6(3)
C8	F6	133.6(4)

Table S4: Bond angles for $[Me_3N(C_6H_3(CF_3)_2)][BF_4]$.

Atom	Atom	Atom	Angle in deg
C1	N1	C9	109.65(19)
C1	N1	C11	110.0(2)
C9	N1	C11	109.1(2)
C10	N1	C1	112.1(2)
C10	N1	C9	107.7(2)
C10	N1	C11	108.2(2)
F7	B1	F8	109.5(2)
F7	B1	F9	109.1(2)
F9	B1	F8	108.9(2)
F10	B1	F8	109.8(2)
F10	B1	F7	109.7(2)
F10	B1	F9	109.8(2)
F3	C7	F1	106.1(2)
F3	C7	F2	107.0(3)
F3	C7	C3	113.3(2)
F1	C7	C3	112.3(3)
F2	C7	F1	105.8(3)
F2	C7	C3	111.9(2)
C4	C3	C7	120.9(2)
C4	C3	C2	121.8(3)
C2	C3	C7	117.4(3)
C3	C4	C5	118.6(2)
C2	C1	N1	120.3(2)
C6	C1	N1	118.0(2)
C6	C1	C2	121.6(2)
C1	C2	C3	118.2(3)
C1	C6	C5	118.8(2)
C4	C5	C6	121.1(3)
C4	C5	C8	120.6(2)
C6	C5	C8	118.4(2)
F5	C8	C5	112.1(2)
F6	C8	C5	112.4(2)
F6	C8	F5	105.4(2)
F4	C8	C5	113.0(2)
F4	C8	F5	107.5(3)
F4	C8	F6	106.0(2)

Atom parameters for $[Me_3N(C_6H_3(CH_3)_2)][BF_4]$

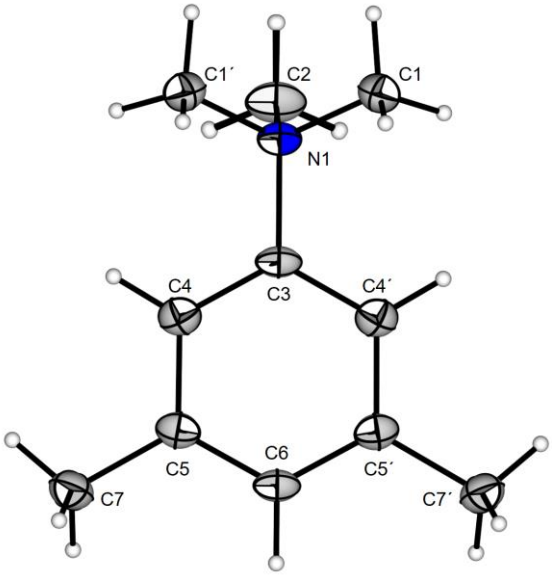


Figure S12: Molecular structure of the cation of $[Me_3N(C_6H_3(CH_3)_2)][BF_4]$ in the crystal and atom numbering adopted.

Table S5: Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for $[Me_3N(C_6H_3(CH_3)_2)][BF_4]$. U_{eq} is defined as 1/3 of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}
B1	7842(4)	7500	5986.5(17)	26.3(7)
F3	8921.2(18)	8725.7(14)	6107.7(7)	38.5(4)
F1	6288(3)	7500	6423.1(12)	50.8(6)
F2	7253(3)	7500	5276.2(10)	46.3(6)
C1	2696(3)	8788(2)	4984.5(11)	31.5(5)
C2	802(4)	7500	4089.8(17)	36.9(8)
N1	2621(3)	7500	4497.5(12)	23.9(5)
C3	4216(4)	7500	3966.0(14)	22.0(6)
C4	4894(3)	6200(2)	3711.6(10)	23.6(5)
C5	6335(2)	6190(2)	3200.6(10)	23.2(5)
C6	7029(4)	7500	2959.0(14)	23.2(6)
C7	7095(3)	4786(2)	2925.7(11)	29.5(5)

Table S6: Anisotropic displacement parameters (Å^2×10^3) for $[Me_3N(C_6H_3(CH_3)_2)][BF_4]$. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
B1	22.2(15)	27.0(16)	29.7(16)	0	3.7(13)	0
F3	33.4(7)	35.8(7)	46.4(8)	1.1(6)	–3.5(5)	–8.9(6)
F1	38.1(11)	43.7(12)	70.6(14)	0	29.2(10)	0
F2	47.4(12)	52.3(12)	39.3(11)	0	–14.0(9)	0
C1	32.5(11)	30.0(11)	32.1(10)	–5.0(9)	9.7(9)	–1.9(9)
C2	16.5(14)	55(2)	38.8(17)	0	–0.5(12)	0
N1	18.7(11)	29.0(12)	24.0(11)	0	3.2(9)	0
C3	14.6(12)	31.8(15)	19.7(12)	0	1.1(10)	0
C4	19.0(9)	27.2(11)	24.8(9)	1.7(8)	–2.4(7)	0.6(8)
C5	16.7(8)	29.6(11)	23.3(9)	–0.2(8)	–1.6(7)	2.2(8)
C6	14.7(12)	33.0(15)	22.0(13)	0	1.3(10)	0
C7	24.9(10)	32.0(12)	31.5(10)	–2.1(9)	4.3(8)	3.7(9)

Table S7: Bond lengths for $[Me_3N(C_6H_3(CH_3)_2)][BF_4]$.

Atom	Atom	Length in pm
F3	B1	1.394(2)
F1	B1	1.374(4)
F2	B1	1.392(4)
N1	C1	1.507(2)
N1	C11	1.507(2)
N1	C2	1.501(4)
N1	C3	1.508(3)
C3	C4	1.387(2)
C3	C41	1.387(2)
C4	C5	1.401(3)
C5	C6	1.392(2)
C5	C7	1.506(3)

Table S8: Bond angles for $[Me_3N(C_6H_3(CH_3)_2)][BF_4]$.

Atom	Atom	Atom	Angle in deg
C11	N1	C3	111.76(13)
C1	N1	C3	111.76(13)
C1	N1	C1´	105.6(2)
C2	N1	C3	108.3(2)
C2	N1	C1	109.71(15)
C2	N1	C1´	109.71(15)
C4	C3	N1	119.16(12)
C4´	C3	N1	119.16(12)
C4´	C3	C4	121.6(2)

C3	C4	C5	119.58(19)
C4	C5	C7	120.07(18)
C6	C5	C4	118.37(18)
C6	C5	C7	121.56(17)
C5´	C6	C5	122.5(2)
F3	B1	F3´	109.9(2)
F2	B1	F3´	108.70(17)
F2	B1	F3	108.70(17)
F1	B1	F3	110.28(17)
F1	B1	F3´	110.28(17)
F1	B1	F2	108.9(3)

Quantum chemistry

The strong influence of the fluorinated groups can be visualized by the lowering of the orbital energies, as shown in Figure S13.

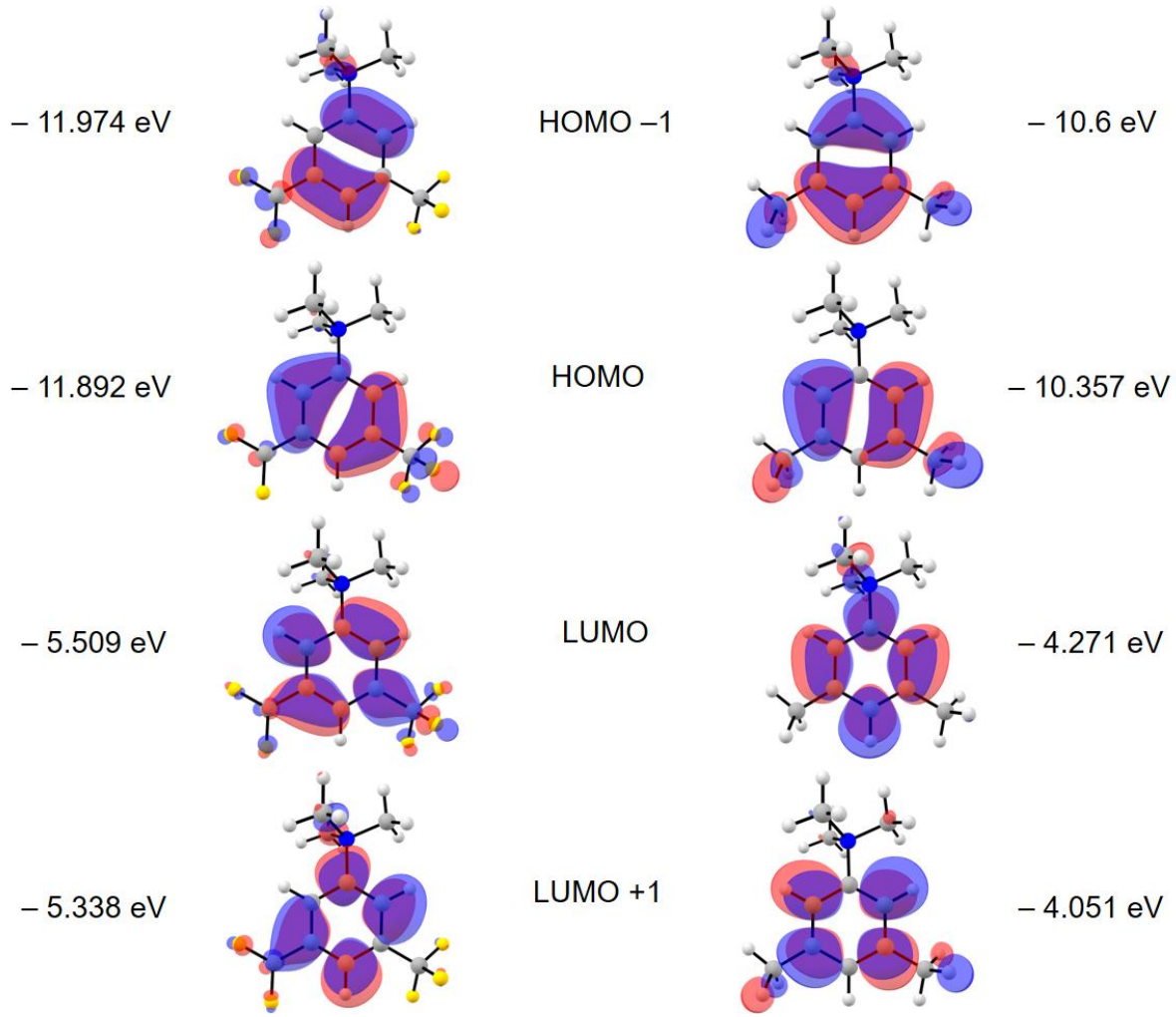
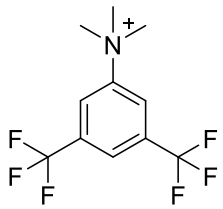


Figure S13: Frontier orbitals of $[Me_3N(C_6H_3(CF_3)_2)][BF_4]$ (right) and $[Me_3N(C_6H_3(CH_3)_2)][BF_4]$ (left) at B3LYP-D3(BJ)/aug-cc-pVTZ (ORCA 5.03) level of theory. The contour value is set to 0.03 in CHEMCRAFT 1.8.

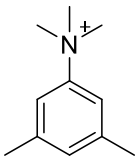
XYZ Files



Final Gibbs free energy: –1079.74236651 Eh

C	–5.42106470140099	0.56069822492959	–0.09573727742072
C	–5.42245374183390	–0.83040955428089	–0.13942275840395
C	–4.23624405115097	–1.54219354874894	–0.20804248918683
C	–3.03250279983292	–0.84881690523408	–0.23381244043588
C	–3.01252696818647	0.53664873284883	–0.19117058143461
C	–4.21195536543233	1.23259885865897	–0.12164874919593
N	–4.15640178474134	2.73367301122591	–0.07260955974174
H	–2.05894034080998	1.04054636208052	–0.21645561771109
H	–4.24593974924030	–2.62134869575229	–0.24113196541607
H	–6.36721930621032	1.07034279593216	–0.03786714597688
C	–5.52059388807464	3.36430098338269	0.00273113206231
H	–6.09195695595490	3.09405762402923	–0.87886451640061
H	–5.38150510433315	4.43994659986173	0.03465348063589
H	–6.02216213731460	3.03218747563657	0.90546324413683
C	–3.47790483052386	3.25686387591635	–1.31860985318452
H	–4.04452848212844	2.92154556648413	–2.18156551835801
H	–2.46600969816578	2.87262858312457	–1.36543459576196
H	–3.46234429178275	4.34161148737326	–1.26833007966883
C	–3.38142550812665	3.17181420236959	1.14983683589975
H	–3.87869135553065	2.77424019837690	2.02897393574432
H	–3.36883303865257	4.25745729132399	1.17478326115388
H	–2.36935755088693	2.78985672006722	1.08989898987828
C	–1.72016680614561	–1.60468424511704	–0.25610988336247
F	–1.84220408785424	–2.78328731435342	–0.87544130540832
F	–1.29079461157177	–1.83650344179156	0.99823266821287
F	–0.76395094727145	–0.89596660882155	–0.88596498761111

C	–6.75027328451381	–1.55875479624524	–0.15882743176785
F	–7.68831933554673	–0.87118027604055	0.51995525920377
F	–6.65124109301263	–2.77642712796263	0.38440796033033
F	–7.19037818376913	–1.70157607927406	–1.42261001081084



Final Gibbs free energy: –484.20102753 Eh

C	–5.47682120322968	0.54388190270084	–0.09024431269994
C	–5.42351360662755	–0.85600348100723	–0.05557672043057
C	–4.18431075780483	–1.47708441311247	–0.10859211173262
C	–2.99411002597645	–0.75076345889781	–0.19884974622383
C	–3.06560493713467	0.63688555034427	–0.23376598899817
C	–4.30401133423817	1.26752847982283	–0.17918299401607
N	–4.32377158086493	2.77586179445019	–0.21470685240011
H	–2.14638882732780	1.19987778411985	–0.30040709661931
H	–4.13659249749864	–2.55802121916598	–0.07776234533874
H	–6.44349431446394	1.01747770168922	–0.04418978596031
C	–5.71283559036329	3.34355498003599	–0.15595233636877
H	–6.28122097662655	2.99177283040276	–1.00986531972903
H	–5.62795256748291	4.42506234844404	–0.18945990000329
H	–6.18653478622773	3.04000376830884	0.77108807065574
C	–3.68849653519394	3.26061413517255	–1.49495576187304
H	–4.24781181809728	2.84786741934484	–2.32841958798641
H	–2.66105535312243	2.92100665372681	–1.53580260977106
H	–3.72476608752974	4.34630340484108	–1.50847213510976
C	–3.55930949775035	3.31960229138398	0.96753141210971
H	–4.02769479382985	2.94860930202575	1.87354232729226
H	–3.59623170326450	4.40482977413000	0.93301410301899
H	–2.53259113931753	2.97888414000368	0.91697484120830
C	–1.67066277388086	–1.45914247431209	–0.25601827726410
H	–1.61819021635678	–2.10774118295652	–1.13156380723355

H	–1.53290043328954	–2.09160300634117	0.62182014713252
H	–0.83887852175607	–0.75901088147170	–0.30341574634769
C	–6.69659495002166	–1.65091551275215	0.02067317645341
H	–7.37203221687326	–1.24596708962072	0.77447489258933
H	–6.49792381554937	–2.69187780536622	0.26538950097069
H	–7.22285999190991	–1.62811280143770	–0.93580587722851

Literature

Becke A. D. *Phys. Rev. A Gen. Phys.* 1988, *38*, 3098–3100.

Lee C., Yang W., Parr R. G. *Phys. Rev. B* 1988, *37*, 785–789.

Grimme S., Ehrlich S., Goerigk L. *J. Comput. Chem.* 2011, *32*, 1456–1465.

Grimme S., Antony J., Ehrlich S., Krieg H. *J. Chem. Phys.* 2010, *132*, 154104–145123.

Kendall R. A., Dunning Jr. T. H., Harrison R. J. *J. Chem. Phys.* 1992, *96*, 6796–6806.

Neese F. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2012, *2*, 73–78.

Neese F. *Wiley Interdiscip. Rev.: Comput. Mol. Sci.* 2022, *12*, e1606 (15 pages).

Zhurko G. A. CHEMCRAFT (version 1.8), *Graphical Software for Visualization of Quantum Chemistry Computations*, Ivanovo (Russia), 2005.