Supporting information

Computational details

All computations were carried out with the Gaussian 09 package (Frisch et al., 2009). The geometries **1**-**11** in this study were optimized with no symmetry constraints at the hybrid-DFT functional B3LYP (Becke, 1993, Lee et al., 1988) and the basis set 6-31G(d) (Petersson et al, 1988, Petersson et al, 1991). The optimized geometries were found to be true minima based on no imaginary frequencies obtained from frequency calculations. Frontier orbital densities were analysed with GaussSum (O'Boyle et al., 2008) and listed along with Mulliken charges as atomic charges in Table S1. The frontier orbitals for **2** depicted in Figure S1 were generated using GabEdit (Allouche, 2011). The ^{19}F GIAO (Wolinski et al., 1990) NMR shifts at B3LYP (Becke, 1993, Lee et al., 1988) /6-31G(d) were converted to the CFCl$_3$ scale $\delta(^{19}\text{F}) = 171 - [0.95\sigma(^{19}\text{F})]$ in ppm in Table S2.

References

Allouche, A. R., 2011. Gabedit-A graphical user interface for computational chemistry softwares. *J. Comput. Chem.*, 32, 174–182.

Becke, A. D., 1993. Density-functional thermochemistry. 3. The role of exact exchange. *J. Chem. Phys.*, 98, 5648-5652.

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, Jr., J. A., 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, O., Foresman, J. B., Ortiz, J. V., Cioslowski, J. & Fox, D. J., 2009. *Gaussian, Inc.*, Wallingford CT, 2009. Gaussian 09, Revision A.02.

Lee, C., Yang, W. & Parr, R. G., 1988. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron-density. *Phys. Rev. B,* 37, 785-789.

O'Boyle, N. M., Tenderholt, A. L. & Langner, K. M., 2008. cclib: A library for package-independent computational chemistry algorithms. *J. Comput. Chem.*, 29, 839–845.

Petersson, G. A., Bennett, A., Tensfeldt, T. G., Al-Laham, M. A., Shirley, W. A. & Mantzaris, J., 1988. A complete basis set model chemistry. 1. The total energies of closed-shell atoms and hydrides of the 1st-row elements. *J. Chem. Phys.*, 89, 2193-2218.

Petersson, G. A. & Al-Laham, M. A., 1991. A complete basis set model chemistry .2. Open-shell systems and the total energies of the 1st-row atoms. *J. Chem. Phys.*, 94, 6081-6090.

Wolinski, K., Hinton, J. F. & Pulay, P., 1990. Efficient implementation of the gauge-independent atomic orbital method for NMR chemical shift calculations. *J. Am. Chem. Soc.*, 112, 8251-8260.

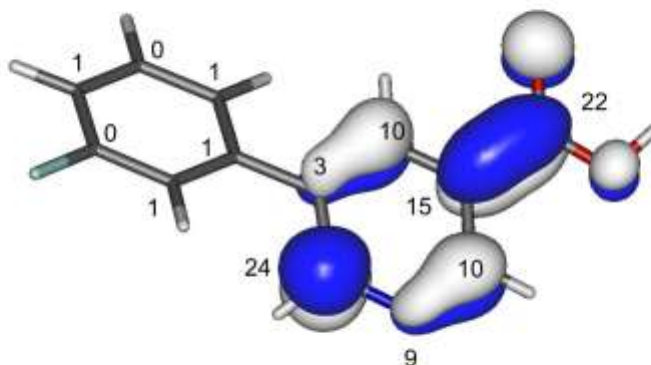Table S1. Calculated frontier orbital densities (%) and atomic charges (a.u.) on aromatic carbons of **1**-**5**.

1	C2	C3	C4	C5	C6	C1'	C2'	C3'	C4'	C5'	C6'
LUMO	17	5	8	17	1	3	4	1	6	1	4
HOMO	11	2	4	8	10	16	8	3	19	4	8
Charge	0.232	-0.149	-0.147	0.074	-0.003	0.085	-0.171	-0.133	-0.123	-0.133	-0.171

2	C2	C3	C4	C5	C6	C1'	C2'	C3'	C4'	C5'	C6'
LUMO	10	15	10	3	24	1	1	0	1	0	1
HOMO	8	2	4	7	7	14	1	10	21	0	19
Charge	0.016	0.046	-0.168	0.059	0.013	0.091	-0.250	0.384	-0.193	-0.135	-0.170

3	C2	C3	C4	C5	C6	C1'	C2'	C3'	C4'	C5'	C6'
LUMO	11	15	10	3	24	1	1	0	1	0	1
HOMO	9	2	4	8	8	17	14	0	15	10	2
Charge	0.017	0.046	-0.166	0.070	0.022	0.014	0.328	-0.194	-0.127	-0.132	-0.176

4	C2	C3	C4	C5	C6	C1'	C2'	C3'	C4'	C5'	C6'
LUMO	9	16	12	3	24	0	1	0	1	0	1
HOMO	8	2	5	7	8	19	7	6	17	6	7
Charge	0.015	0.047	-0.169	0.060	0.010	0.089	-0.174	-0.201	0.386	-0.201	-0.174

5	C2	C3	C4	C5	C6	C1'	C2'	C3'	C4'	C5'	C6'
LUMO	4	14	11	3	18	4	5	1	9	1	6
HOMO	4	12	0	11	6	18	12	0	16	8	3
Charge	0.022	0.051	-0.130	-0.179	0.273	0.038	0.316	-0.196	-0.124	-0.130	-0.168

Table S2. Comparison of computed (GIAO) and observed ^{19}F NMR chemical shifts for **2-5** and **8-11**
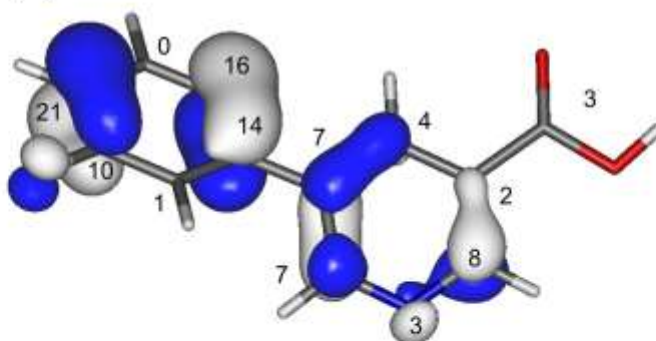
Compound	Calculated [19]F	Observed [19]F
2	-112.1	-112.5
3	-118.6	-118.6
4	-112.7	-113.2
5	-117.4	-116.7
8	-134.4	-135.6
9	-115.9	-116.9
10	-114.4	-114.0
11	-119.7	-117.5

Figure S1. Computed frontier orbitals and atomic charges for **2**.

LUMO densities
heavy atoms only (%)

HOMO densities
heavy atoms only (%)

Atomic charges
heavy atoms only (a.u.)