Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Material

Intramolecular C–H Insertion vs Friedel-Crafts Coupling Induced by Silyl Cation-promoted C–F Activation

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(21 pages)

1 Materials and Methods

1.1 Reaction Conditions and Chemicals

The C–F/C–H activation cascade reactions were set up in an MBraun glovebox under a nitrogen atmosphere with O_2, H_2O < 0.1 ppm. The reaction mixture was prepared in a microwave tube. The tube was equipped with a regular cap and heated using a CEM Discover microwave reactor. All glassware involved was dried at 150 °C for at least 12 h and allowed to cool *in vacuo*.

The substrates and reagents used for the C–F activation reactions were synthesized and purified in our group (exceptions in Table S.1). Chlorobenzene was passed through activated alumina and stored over molecular sieves. For work-up and purification outside the glovebox, distilled solvents of technical grade were used.

Table S.1. Suppliers and grade of used chemicals.

Compound	**Quality**	**Supplier**
2-Bromo-1-fluorobenzene	99%	Alfa Aesar
1-Bromo-2-iodobenzene	99%	Fluorochem
1-Bromo-2-methylnaphthalene	~90%	Acros
2-*tert*-Butylaniline	98%	Acros
Chlorobenzene	puriss.	Fluka
1-Fluoro-2-iodobenzene	99 %	Alfa Aesar
2-Fluorophenylboronic acid	97%	Apollo
Iodomethane-d3	99.5 atom % D	Aldrich
2-Isopropylnaphthalene	99%	Acros

1.2 Instruments

Melting points were measured with a Büchi Melting Point P-540 apparatus and are uncorrected.

Infrared spectra were recorded on a Jasco FT/IR-410 spectrophotometer. Compounds were measured as solids or oils (neat). Absorption bands are given in wave numbers (cm^{-1}); the intensities are characterized as follows: s = strong (0–33% transmission), m = medium (34–66% transmission), w = weak (67–100% transmission).

NMR spectra were recorded on Bruker AV-400 (^{1}H, ^{13}C, ^{19}F), and Bruker AV-500 (^{1}H, ^{13}C) instruments. ^{13}C-NMR spectra are proton decoupled. Data are reported as follows: chemical shift in ppm, multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, etc.), coupling constant ^{n}J in Hz, and integration. The signals were referenced against solvent peaks (^{1}H: residual $CHCl_3$ 7.26 ppm; ^{13}C: $CDCl_3$ 77.16 ppm) or external standards (^{19}F: CCl_3F in $CDCl_3$ 0 ppm).

Mass spectra were recorded on a Finnigan MAT95 instrument for high resolution mass (measured by the Laboratory for Mass Spectroscopy of the Organic Chemistry Institute of the University of Zurich) or on a Finnigan Trace DSQ GC-MS. Data are reported as follows: m/z (% relative intensity).

1.3 Computational Methods and Computed Structures

The conformational analyses of the molecular systems described in this study were carried out using the GAMESS[1] and the GAUSSIAN09[2] software packages, using several density functionals to check for consistency in structure and energetic results. Reported here are results using the M06-2X density functional,[3] with an ultrafine grid, together with the Def2-TZVPP basis set.[4] Effects of solvent were included by the continuum solvation model based on the original COSMO theory of Klamt modified by us for *ab initio* theory,[5] with a dielectric for chlorobenzene and water and solvent radii from Klamt.[6] Full geometry optimizations were performed and uniquely characterized via second derivative (Hessian) analysis at standard temperature and pressure (298.15 K, 1 atm) to establish stationary points and effects of zero point energy and thermal corrections. Free energies are reported. Visualization and analysis of structural results was carried out using Avogadro.[7]

TS(8,9a)
TS mode: -134.6934 cm^{-1}
G = -1164.184692

C	6.0	-2.5854928796	-0.8051303202	1.7647333151
C	6.0	-2.2546136712	0.4184352228	2.2638191199
C	6.0	-1.4691618243	1.3437662174	1.5307722001
C	6.0	-1.0560263985	0.9884523979	0.2611838169
C	6.0	-1.3591796516	-0.3032327287	-0.2813106489
C	6.0	-2.1373826257	-1.2073164831	0.4840314644
C	6.0	-0.9087100475	-0.7413484634	-1.5425115943
C	6.0	-2.4386879001	-2.4880775057	-0.0357222085
C	6.0	-1.9774308158	-2.8752980569	-1.2635937599
C	6.0	-1.1885554991	-1.9903074152	-2.025856175
C	6.0	-0.2449319706	1.8638216945	-0.5905527572
C	6.0	-0.1524421487	3.2920882513	-0.6215954893
C	6.0	0.6428287494	3.978012125	-1.5252965973
C	6.0	1.394016859	3.3137566697	-2.4851084254
C	6.0	1.347751709	1.9037499752	-2.573681768
C	6.0	0.5292029629	1.5002821926	-1.6122579849

F	9.0	1.9480274454	-0.4371152809	-0.6028456913
Si	14.0	2.2370914659	-1.3900701299	0.6938128979
C	6.0	4.0827200847	-1.5008567031	0.8337255398
C	6.0	1.4433843224	-3.0266958401	0.3410582314
C	6.0	1.4659619647	-0.5565200734	2.1620327753
H	1.0	-3.1810036219	-1.4953775536	2.3487927213
H	1.0	-2.5778284553	0.7015473811	3.2569566409
C	6.0	-1.0949108179	2.6250351025	2.2205856676
H	1.0	-0.3498342867	-0.0736796262	-2.2100884197
H	1.0	-3.0384103331	-3.1586587024	0.5665816359
H	1.0	-2.2106383298	-3.8560209603	-1.6545564274
H	1.0	-0.8195340815	-2.2914167873	-2.9964135897
H	1.0	-0.7778079292	3.8298923302	0.0750351015
H	1.0	0.6665430713	5.0571703766	-1.4832771949
H	1.0	2.035071504	3.8334363781	-3.1841457742
H	1.0	1.9052267212	1.3058226445	-3.2783833918
H	1.0	4.5172918949	-1.9283767157	-0.0709366397
H	1.0	4.5221010136	-0.5156287587	0.9962823593
H	1.0	4.3578456784	-2.137994264	1.676030999
H	1.0	1.6617048814	-3.7282281189	1.1486050294
H	1.0	0.35930994	-2.9200491074	0.2687245833
H	1.0	1.8128403161	-3.4552953031	-0.5917771705
H	1.0	1.7092710942	0.5075652622	2.1869956626
H	1.0	0.380073234	-0.6645601929	2.1496654673
H	1.0	1.8395629642	-1.0112637464	3.0816511339
H	1.0	-1.1807309499	2.4937106308	3.2968825533
H	1.0	-1.7633000345	3.44085023	1.9379870224
H	1.0	-0.0734776041	2.926767755	1.9933387696

TS(8,10a)

TS mode = -120.7922 cm^{-1}

G = -1164.184281

C	6.0	2.46015	0.11743	1.71639
C	6.0	1.84809	-0.79976	2.60304
C	6.0	0.76811	-1.60076	2.14534
C	6.0	0.38621	-1.48082	0.77505
C	6.0	0.95805	-0.53628	-0.05854
C	6.0	2.00776	0.26843	0.43745
C	6.0	0.50056	-0.37542	-1.47552
C	6.0	-0.62025	-2.35663	0.16708
C	6.0	-0.85184	-3.75097	0.40189
C	6.0	-1.76133	-4.50244	-0.3237
C	6.0	-2.49952	-3.94424	-1.35821
C	6.0	-2.32362	-2.58343	-1.70906
C	6.0	-1.42386	-2.1112	-0.86262
F	9.0	-2.25134	0.21224	0.08027
Si	14.0	-2.05543	1.66915	0.79906
C	6.0	-3.7587	2.37743	0.9789
C	6.0	-0.98897	2.67806	-0.33645
C	6.0	-1.23418	1.35605	2.43114
H	1.0	3.28091	0.72183	2.0816
C	6.0	0.08751	-2.40873	3.09075
H	1.0	-0.21925	-4.20773	1.15245
H	1.0	-1.8841	-5.54857	-0.08399
H	1.0	-3.23677	-4.50513	-1.91669
H	1.0	-2.87447	-2.0639	-2.47837
H	1.0	-4.2387	2.49179	0.00599
H	1.0	-4.38462	1.73566	1.60045
H	1.0	-3.70819	3.36063	1.44994
H	1.0	-1.40043	2.70132	-1.34686
H	1.0	-0.93301	3.70528	0.02926
H	1.0	0.02795	2.28494	-0.38149
H	1.0	-1.7682	0.5956	3.00355
H	1.0	-0.20321	1.02642	2.29218
H	1.0	-1.21794	2.2755	3.01968
H	1.0	0.90189	0.53252	-1.92205
H	1.0	-0.59824	-0.26341	-1.52406
H	1.0	0.79109	-1.2245	-2.09591
H	1.0	2.46208	0.99663	-0.22146
C	6.0	0.5006	-2.45993	4.39425
C	6.0	1.61295	-1.71022	4.83092
C	6.0	2.26295	-0.88949	3.95398
H	1.0	-0.79369	-2.96103	2.80012
H	1.0	-0.04105	-3.07291	5.10206
H	1.0	1.93003	-1.77043	5.86302

H 1.0 3.09604 -0.27854 4.27812

TS(1,2)
TS mode = -477.4174 cm^{-1}
G = -501.584797
C 6.0 -0.6750161876 -0.8786474905 0.4628052117
C 6.0 -1.9258793796 -1.3835141323 0.9342552744
C 6.0 -3.0969506988 -0.6270318873 0.6935753749
C 6.0 -3.0143565742 0.5756067973 0.0322022909
C 6.0 -1.7881003875 1.0875143551 -0.4257931344
C 6.0 -0.6305443167 0.3745393699 -0.2191828749
C 6.0 0.7537769637 0.6163084279 -0.6097659757
C 6.0 1.3146629678 1.6935030578 -1.2867655917
C 6.0 2.6776428979 1.6707780848 -1.536422144
C 6.0 1.5351699679 -0.4668605706 -0.1908081914
C 6.0 2.8956589619 -0.4845717376 -0.4437922549
C 6.0 3.4587663458 0.5927566947 -1.1183516496
C 6.0 0.6933035178 -1.5080634921 0.5040150576
H 1.0 -1.1580526161 -0.6325777748 1.6613759576
H 1.0 -4.0450151911 -1.0102214617 1.0403012532
H 1.0 -3.9164870922 1.1462284326 -0.1406828261
H 1.0 -1.7630735726 2.0355395682 -0.9467549618
H 1.0 0.7044036869 2.5268349145 -1.6094129439
H 1.0 3.1420373336 2.4951861349 -2.0597876621
H 1.0 3.5096314306 -1.3167175369 -0.1255697704
H 1.0 4.520838542 0.5958093305 -1.3237461664
H 1.0 0.6814752152 -2.4571127791 -0.0354452832
H 1.0 1.0245897738 -1.7142177388 1.5223023782
H 1.0 -1.9568315885 -2.3419285668 1.4354786321

TS(2,3)
TS mode = -602.0062 cm^{-1}
G = -501.586463
C 6.0 -0.6926177768 -0.887597502 0.4443065127
C 6.0 -1.9216044332 -1.3785783427 0.9325358807
C 6.0 -3.110989334 -0.5987349452 0.6954350387
C 6.0 -3.0226923598 0.6363186908 0.0342795294
C 6.0 -1.8062910712 1.0946019336 -0.4183977184
C 6.0 -0.6427929919 0.3354781948 -0.2101706603
C 6.0 0.7406903505 0.5963824653 -0.6038001588
C 6.0 1.2997111147 1.6749464132 -1.278603156
C 6.0 2.662673019 1.6504447195 -1.5325489101
C 6.0 1.5217979207 -0.4884496646 -0.186713875
C 6.0 2.8815467884 -0.5078411177 -0.4455669253
C 6.0 3.4435755229 0.5701981941 -1.1203188889
C 6.0 0.6664169771 -1.5109004825 0.5144142342
H 1.0 -2.2913654819 -0.5773156586 1.8113233038
H 1.0 -4.0541328365 -0.980798107 1.0601212779
H 1.0 -3.9241829381 1.2102145864 -0.1218229121
H 1.0 -1.7471149085 2.0444125033 -0.9343331114
H 1.0 0.6910715758 2.5106403505 -1.5986533635
H 1.0 3.1266254013 2.4752700942 -2.0558566398
H 1.0 3.4963235089 -1.3409205957 -0.1309522046
H 1.0 4.5048745753 0.5725148393 -1.3299756364
H 1.0 0.6844036377 -2.4845796542 0.0182237688
H 1.0 0.9730513962 -1.6760927472 1.5504375746
H 1.0 -2.0123776565 -2.3569941675 1.3853370403

8a
G = -755.269231
C 6.0 1.3345685527 1.8856988925 1.0415123894
C 6.0 0.6420040915 1.284399986 -0.0085889109
C 6.0 -0.0203665769 2.1293911062 -0.8872884132
C 6.0 -0.0190022575 3.5049161722 -0.7635310936
C 6.0 -1.7859717613 -0.2834632044 0.4631506768
C 6.0 -0.5839192702 -0.9175108792 0.0539424511
C 6.0 0.6232769035 -0.1926889766 -0.1875406175
C 6.0 -2.9238993166 -1.0091792282 0.6854257598
C 6.0 -2.927670148 -2.4112075737 0.5149055122
C 6.0 -1.7842698793 -3.0524240888 0.129464214
C 6.0 -0.5901855123 -2.3274003584 -0.1066658513
C 6.0 0.6031814874 -2.97854381 -0.4999597943
C 6.0 1.7411813554 -2.2612325189 -0.7224210413
C 6.0 1.7714282634 -0.8514211435 -0.5717941555
C 6.0 0.6781190915 4.0746483304 0.292630467

C	6.0	1.3551456609	3.264717941	1.1960340711
H	1.0	-3.8355767265	-2.9717426258	0.6934245797
H	1.0	-1.769428311	-4.1276266681	-0.0011865848
H	1.0	0.5947305283	-4.0544642005	-0.6245560089
H	1.0	2.6479709484	-2.7668257899	-1.0305372305
H	1.0	1.8598535125	1.2511384151	1.7442728805
H	1.0	-0.5554584454	4.1042201997	-1.4861708966
H	1.0	-3.829963985	-0.5067497624	0.9974905042
C	6.0	3.0598310146	-0.120677037	-0.8432941226
H	1.0	0.6902874986	5.1500235495	0.4066494194
H	1.0	1.8974135469	3.7061779838	2.0208516185
H	1.0	-1.798760472	0.7889617701	0.606118549
F	9.0	-0.6977947389	1.5832176491	-1.915774911
H	1.0	3.7291475676	-0.7398968051	-1.4377891931
H	1.0	3.5730971485	0.1276129703	0.0877969067
H	1.0	2.8843202294	0.8142597043	-1.3743411742

10a

G = -654.830540

C	6.0	1.01567506	0.4757125519	-0.1172153225
C	6.0	2.1987209161	-0.2381693588	-0.0423932633
C	6.0	2.2181863051	-1.6400327158	0.0587864787
C	6.0	1.0344108532	-2.3216484686	0.0843123362
C	6.0	-0.2047513542	-1.6340433056	0.0102489759
C	6.0	-0.2337234268	-0.2125464893	-0.0925805196
C	6.0	-1.4991054593	0.4221542014	-0.163480291
C	6.0	-2.6602245582	-0.3029112692	-0.1344296562
C	6.0	-2.6269786376	-1.7091321866	-0.0325493092
C	6.0	-1.4240956994	-2.3544772018	0.0378261624
H	1.0	-3.6125403981	0.2077791104	-0.1901835766
H	1.0	-3.5515162735	-2.2704471351	-0.0105532877
H	1.0	-1.3813510542	-3.4340986399	0.1163549934
H	1.0	3.1626134753	-2.1665478378	0.1153722757
H	1.0	1.0200047676	-3.40185117	0.1617011765
C	6.0	3.3884915365	0.6754130377	-0.084398174
H	1.0	-1.5581444092	1.494767915	-0.2419129875
C	6.0	1.3514545062	1.9132220611	-0.2139076666
C	6.0	2.7531588832	2.0309357632	-0.1946434498
H	1.0	4.0374395025	0.4565773688	-0.9361783057
H	1.0	4.0020688644	0.582778368	0.8153491727
C	6.0	3.3747373434	3.2634454471	-0.2710352277
C	6.0	2.5929177026	4.4101197842	-0.3689664965
C	6.0	1.2065156083	4.3069226957	-0.3888847319
C	6.0	0.5774034118	3.0689773381	-0.3122679695
H	1.0	0.603283437	5.2020499084	-0.4651492328
H	1.0	-0.5001506954	3.0404098717	-0.3314215016
H	1.0	4.4553550638	3.3340143856	-0.254760283
H	1.0	3.0627847261	5.382805981	-0.4296801689

9a

G = -654.832774

C	6.0	-1.2430880219	4.0935669877	-0.0379146555
C	6.0	0.1452215946	4.1712396696	-0.0315127423
C	6.0	0.9284503416	3.0175124023	-0.0168104914
C	6.0	-1.884932086	2.8564042717	-0.0297383565
C	6.0	0.3011542835	1.780775343	-0.0085852422
C	6.0	-1.1165867891	1.7062742899	-0.0151410563
H	1.0	-1.8305160101	5.0020642585	-0.0493383844
H	1.0	-2.9662511464	2.7987605889	-0.0347458633
H	1.0	0.6260924322	5.1404909285	-0.0380143028
H	1.0	2.0065323208	3.098711182	-0.0120242553
C	6.0	0.8315552939	0.4032680489	0.0069008306
C	6.0	2.090590202	-0.1523119299	0.0185696789
C	6.0	2.1714874183	-1.5760788956	0.0323488575
C	6.0	1.0714416745	-2.3990570565	0.0344290902
C	6.0	-0.2329566341	-1.8392068627	0.0224721053
C	6.0	-0.2957725987	-0.4487560772	0.0090895381
C	6.0	-1.5030565469	0.284814045	-0.0039025349
C	6.0	-2.6894414322	-0.4008233027	-0.0034607979
C	6.0	-2.6543876357	-1.8208018538	0.0100310928
C	6.0	-1.4745936711	-2.5278381393	0.0226372256
H	1.0	-3.6439695655	0.1103790026	-0.0130500254
H	1.0	-3.5924645967	-2.3601116649	0.0103564866
H	1.0	-1.4886320435	-3.6107271538	0.0327310835
H	1.0	3.1587935143	-2.02185322	0.0415922875

H 1.0 1.1980248778 -3.4746487612 0.0451671644
C 6.0 3.3421112545 0.6758985162 0.0172734393
H 1.0 3.375900781 1.3298722678 0.8905122978
H 1.0 3.3847201625 1.3138240154 -0.8673684909
H 1.0 4.228622627 0.0447290998 0.0274808363

8a,$Si(CH_3)_3$ cation complex
G = -1164.221069
C -2.4780376011 -2.1712523181 0.8980228589
C -2.6334332821 -1.0897336781 1.7124065349
C -2.0764701413 0.1728422048 1.3871518454
C -1.3866540462 0.3120655834 0.1991271417
C -1.2545621774 -0.7912353256 -0.7037327569
C -1.783398356 -2.0536441043 -0.3292380174
C -0.625481761 -0.6813266048 -1.9714954075
C -1.6163695539 -3.1671092036 -1.1890322295
C -0.9725395482 -3.0352397925 -2.3870603357
C -0.4861202189 -1.7713357968 -2.7859773071
C -0.7313632068 1.6064074127 -0.1175806259
C -1.427758243 2.8162646546 -0.1931491169
C -0.7757601743 4.0154259039 -0.4403062967
C 0.6014723011 4.0528603534 -0.6203528962
C 1.3367912663 2.8756329282 -0.5649822591
C 0.6261292706 1.7319726232 -0.31777494
F 1.3924906836 0.5162609929 -0.3303365983
Si 2.192083594 -0.5651681573 0.9549821638
C 3.7898174231 0.3224581248 1.1122232739
C 2.1613951436 -2.1204120074 -0.014450835
C 1.0597516705 -0.4391364174 2.3915875294
H -2.8857058594 -3.1351103134 1.1764789969
H -3.166325421 -1.1901034108 2.6494668881
C -2.2260617111 1.2834105985 2.3925348796
H -0.2634181437 0.280808638 -2.3094539272
H -2.0174697856 -4.1235779312 -0.8774495434
H -0.8488748452 -3.8892116535 -3.0391584138
H -0.0055343031 -1.6634730101 -3.7492111375
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H -1.3491543388 4.9302199837 -0.4951677943
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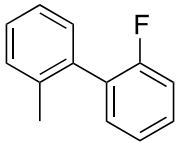
H	1.0	-3.5932075544	-2.1138814866	0.015526782
H	1.0	-2.8225149459	2.1824913243	0.1504474799

2 Synthetic Procedures and Analyses

General procedure for the C–F/C–H activation cascade

In the glove box, a microwave tube was charged with fluoroarene (1 equiv.), [*i*Pr_3Si][$CHB_{11}H_5Cl_6$] (0.05 equiv., for synthesis see reference[8]) and Me_2SiMes_2 (1.1 equiv.) that were dissolved in PhCl (~1 mL per 0.1 mmol of fluoroarene). The cap was put on the tube and without further precautions the tube was placed in the microwave reactor. After stirring at 200 W with switched-on cooling (usually a temperature of 90 °C was reached) for 70 min, the reaction mixture was quenched by adding wet EtOAc. The solvents were evaporated and the residue was subjected to flash column chromatography. For reaction control, the tube was transferred back into the glove box, a sample was taken and analyzed by GC-MS or TLC.

2-Fluoro-2'-methyl-1,1'-biphenyl (2)



1-Fluoro-2-iodobenzene (680 mg, 3.1 mmol), 2-tolylboronic acid (650 mg, 4.8 mmol), $Pd(PPh_3)_4$ (85 mg, 0.07 mmol) and K_2CO_3 (1.62 g, 9.1 mmol) were dissolved in THF (10 mL, degassed) and water (1.2 mL, degassed), heated to 70 °C and stirred for 35 h. The reaction mixture was cooled to room temperature, diluted with CH_2Cl_2 (30 mL) and washed with a saturated aqueous solution of $NaHCO_3$. The inorganic layer was extracted with CH_2Cl_2 (2x40 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography (pure hex to hex/DCM 95:5) to give the product as colorless

oil (510 mg, 89 %). Product has to be handled with care due to low boiling point. From ^{1}H-NMR 2.5 % of impurity was determined. Spectroscopical data matches report in literature.[9]

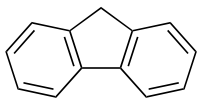
R_f (Hexane)= 0.21.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38–7.09 (m, 8H), 2.22 (d, J = 4 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ = 159.76 (d, $^1J_{C–F}$ = 245.3 Hz), 136.79, 135.87, 131.69 (d, $^3J_{C–F}$ = 3.8 Hz), 130.19, 130.08, 129.36 (d, $^2J_{C–F}$ = 17.6 Hz), 129.16 (d, $^3J_{C–F}$ = 8.8 Hz), 128.09, 125.76, 124.10 (d, $^4J_{C–F}$ = 3.8 Hz), 115.64 (d, $^2J_{C–F}$ = 22.6 Hz), 20.08 (d, $J_{C–F}$ = 2.8 Hz).

MS (EI): *m/z* (%): 186.1 (100), 185.1 (64), 184.1 (27), 171.1 (22), 166.1 (23), 165.1 (62).

Fluorene (3)



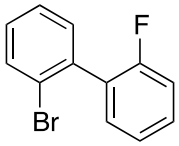
2 (37 mg, 0.20) was treated according to the general procedure using [*i*Pr$_3$Si][$CHB_{11}H_5Cl_6$] (5 mg, 0.01 mmol) and DMDMS (77 mg, 0.26 mmol). Flash column chromatography (pure hex to hex/DCM 99:1) gave the product as white solid (24 mg, 73 %). Product tends to sublime under HV.

R_f (Hexane)= 0.22.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.80 (broad doublet, *J* = 7.5 Hz, 2H), 7.55 (ddd, *J* = 7.4, 0.8, 0.8 Hz, 2H), 7.41–7.35 (m, 2H), 7.30 (ddd, *J* = 7.4, 7.4, 1.2 Hz, 2H), 3.91 (s, 2H). NMR signals match reports in literature.[10]

MS (EI): *m/z* (%): 166.1 (100), 165.1 (93), 139.1 (12), 82.0 (23).

2'-Bromo-2-fluoro-1,1'-biphenyl



To a solution of 1-bromo-2-fluorobenzene (1.12 g, 6.4 mmol) in THF at –78 °C *n*-BuLi (2.7 mL, 2.5 M in hexanes) was added slowly. The solution turned slightly yellow. After stirring for 30 min, $ZnCl_2$ (950 mg, 7.0 mmol) in THF (8 mL) was added and the reaction mixture turned colorless. In another flask 1-bromo-2-iodobenzene (1.65 g, 5.8 mmol) and $Pd(PPh_3)_4$ (67 mg, 0.06 mmol) were dissolved in THF (10 mL). Thereto the solution containing the zincate was transferred and the mixture was stirred at 50 °C for 12 h. Water (50 mL) was added and the aqueous phase was

extracted with CH_2Cl_2 (3x50 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography (hex/DCM 99:1), which afforded the product as colorless oil (1.32 g, 90 %).

R_f (Hexane)= 0.26.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.69 (dd, J = 8.0, 1.5 Hz, 1H), 7.41–7.35 (m, 2H), 7.33–7.24 (m, 3H), 7.22 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 7.15 (ddd, J = 10.0, 8.5, 1.5 Hz, 1H).

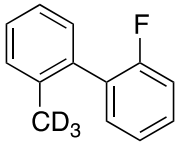
^{13}C-NMR (125.8 MHz, $CDCl_3$): δ = 159.70 (d, $^1J_{C–F}$ = 247.3 Hz), 137.35, 133.01, 131.76, 131.71 (d, $^3J_{C–F}$ = 3.1 Hz), 129.97 (d, $^3J_{C–F}$ = 8.0 Hz), 129.55, 129.03 (d, $^2J_{C–F}$ = 16.1 Hz), 127.31, 123.99, 123.3 (d, $^4J_{C–F}$ = 3.6 Hz), 115.78 (d, $^2J_{C–F}$ = 22.1 Hz).

NMR signals match the ones reported in literature.[13]

^{19}F-NMR (376.5 MHz, $CDCl_3$): δ = –114.68.

MS (EI): *m/z* (%): 251.9 (80), 249.9 (84), 171.0 (42), 170.0 (100), 151.0 (20), 85.0 (24), 75.0 (20).

2-Fluoro-2'-methyl-1,1'-biphenyl (2-d_3)



To a solution of 2'-bromo-2-fluoro-1,1'-biphenyl (187 mg, 0.64 mmol) in THF (5 mL) at –78 °C, *n*-BuLi (0.5 mL, 1.6 M in hexanes) was added dropwise. The reaction mixture turned orange and after stirring for 15 min, MeI-d3 (0.1 mL, 1.64 mmol) was added. The solution turned light yellow and after stirring over night the reaction mixture was poured into water (15 mL). The inorganic phase was extracted with CH_2Cl_2 (3x20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography (hex), which afforded the product as colorless oil (123 mg, 87 %). GC-MS showed a small amount of debrominated starting material. Part of the product was lost during evaporation of solvent. ^{1}H-NMR and ^{13}C-NMR spectra match the ones of **2**, except for the missing CH_3 proton signal and the splitting of the CD_3 carbon signal.

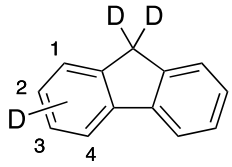
R_f (Hexane)= 0.21.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.38–7.09 (m, 8H).

^{13}C-NMR (151 MHz, $CDCl_3$) δ = 159.83 (d, $^1J_{C–F}$ = 245.9 Hz), 136.68, 135.95, 131.72 (d, $^3J_{C–F}$ = 3.8 Hz), 130.21, 130.09, 129.46 (d, $^2J_{C–F}$ = 16.8 Hz), 129.15 (d, $^3J_{C–F}$ = 8.2

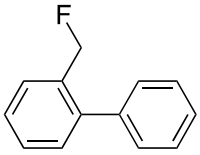
Hz), 128.09, 125.78, 124.09 (d, $^4J_{C-F}$ = 3.7 Hz), 115.65 (d, $^2J_{C-F}$ = 22.6 Hz), 19.24 (quintet of doublets, J_{C-D} = 19.4 Hz, J_{C-F} = 2.8 Hz; septet would be expected for CD_3, but the signal was too weak to see the smallest peaks).
MS (EI): *m/z* (%): 189.1 (100), 168.1 (54), 83.1 (13).

Fluorene-d_3



2-Fluoro-2'-methyl-1,1'-biphenyl-d3 was treated according to the general procedure using 2-fluoro-2'-methyl-1,1'-biphenyl-d3 (27 mg) and a slightly longer reaction time (120 min) to result in deuterated fluorene (19.5 mg, 82%). The ratio of the different isomers (deuteration of the varying aromatic positions) was determined by analyzing ^{1}H- and ^{2}H-NMR spectra. From the ^{2}H-NMR spectrum the amount of deuteration in position 1 was calculated by comparing the integrals of C(1)D to the CD_2 signal. The fractions of deuteration of positions 2 to 4 was then derived from the difference in integration to position 1 in the ^{1}H-NMR spectrum. The resulting ratio was: C(1)D: 60 %, C(2)D: 18 %, C(3)D: 2 %, C(4)D: 5%, no deuteration at the aromatic ring: 15 %.

(1,1'-Biphenyl-2-yl)fluoromethane (4)



2-Bromophenylfluoromethane (750 mg, 3.97 mmol, synthesized from 2-bromophenylmethanol according to a literature procedure[11]), 2-fluorophenylboronic acid (605 mg, 4.96 mmol), $Pd(PPh_3)_4$ (92 mg, 0.08 mmol), and K_2CO_3 (1.65 g, 11.90 mmol) were dissolved in THF (10 mL, degassed) and H_2O (1.5 mL, degassed). The reaction mixture was heated to 70 °C and stirred for 20 h. GC-MS revealed conversion of all starting material. A sat. aq. solution of $NaHCO_3$ (20 mL) was added and the aqueous phase was extracted with DCM (3 x 20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. Flash column chromatography (SiO_2, pentane to pentane/DCM 97:3) afforded the desired product as colorless oil (628 mg, 85%).

R_f (Hexane)= 0.18.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.60–7.56 (m, 1H), 7.47–7.34 (m, 8H), 5.30 (d, J = 48.1 Hz, 2H).

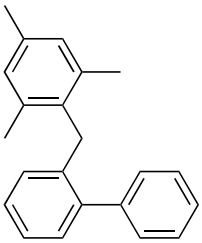
^{13}C-NMR (101 MHz, $CDCl_3$): δ = 142.38 (d, $J_{C–F}$ = 4.5 Hz), 140.15, 133.33 (d, $J_{C–F}$ = 16.0 Hz), 130.28 (d, $J_{C–F}$ = 1.7 Hz), 129.84 (d, $J_{C–F}$ = 6.6 Hz), 129.41 (d, $J_{C–F}$ = 1.8 Hz, 2C), 129.12 (d, $J_{C–F}$ = 3.5 Hz), 128.40 (2C), 127.79 (d, $J_{C–F}$ = 1.9 Hz), 127.61, 82.93 (d, $J_{C–F}$ = 164.6 Hz).

^{19}F-NMR (376.5 MHz, $CDCl_3$): δ = –200.42.

MS (EI): *m/z* (%): 186.1 (98), 165.1 (100), 109.1 (12), 83.0 (16), 51.1 (22).

HR-MS (EI): *m/z*: Calculated for $C_{13}H_{11}F$: 186.08393; measured: 186.08348.

(1,1'-Biphenyl-2-yl)mesitylmethane (5)



Under inert atmosphere (1,1'-biphenyl-2-yl)fluoromethane (33 mg, 0.18 mmol) was dissolved in PhCl (0.75 mL) and added to a solution of [*i*Pr$_3$Si][$CHB_{11}H_5Cl_6$] (4.5 mg, 0.009 mmol) and DMDMS (20 mg, 0.20 mmol) in PhCl (0.25 mL). The mixture was stirred for 5 min, after which all the starting material had been consumed (verified by GC-MS). Wet EtOAc was added to quench the reaction, the solvents were evaporated and the residue was subjected to flash column chromatography, which afforded three different products. The major fraction was coupling of the starting material with mesitylene either once (**5**, 40%) or twice (**6**, 25 %), a small amount had reacted with the solvent (**7**, 9 %).

R_f (Hexane)= 0.21.

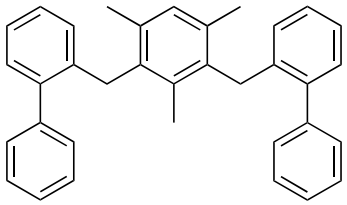
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.51–7.37 (m, 5H), 7.28–7.20 (m, 2H), 7.16 (ddd, J = 7.6, 6.9, 2.0 Hz, 1H), 6.87 (s, 2H), 6.71 (ddq, J = 7.7, 1.4, 0.8 Hz, 1H), 3.86 (s, 2H), 2.29 (s, 3H), 2.12 (s, 6H).

^{13}C-NMR (101 MHz, $CDCl_3$): δ = 142.24, 142.04, 137.48, 137.08 (2C), 135.62, 134.43, 129.73, 129.32 (2C), 128.92 (2C), 128.35 (2C), 127.72, 127.20, 127.11, 125.77, 33.00, 21.05, 20.15 (2C). NMR signals match reports in literature.[12]

MS (EI): *m/z* (%): 286.2 (37), 271.2 (8), 165.1 (100), 132.1 (15).

HR-MS (EI): *m/z*: Calculated for $C_{22}H_{22}$: 286.17160; measured: 286.17148.

Compound 6



R_f (Hexane)= 0.06.

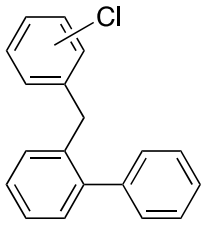
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.48–7.43 (m, 4H), 7.42–7.35 (m, 6H), 7.25–7.18 (m, 4H), 7.13 (ddd, *J* = 7.6, 6.9, 1.9 Hz, 2H), 6.91 (s, 1H), 6.67 (dd, *J* = 7.7, 0.6 Hz, 2H), 3.86 (s, 4H), 2.16 (s, 6H), 1.82 (s, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$): δ = 142.12 (2C), 141.97 (2C), 137.67 (2C), 136.28, 135.39 (2C), 135.05 (2C), 129.86, 129.67 (2C), 129.28 (4C), 128.33 (4C), 127.67 (2C), 127.23 (2C), 127.10 (2C), 125.74 (2C), 33.86 (2C), 20.36 (2C), 16.18.

MS (EI): *m/z* (%): 452.2 (12), 207.1 (26), 165.1 (100).

HR-MS (EI): *m/z*: Calculated for $C_{35}H_{32}$: 542.24985; measured: 542.24936.

Compound 7



Mixture of two different isomers in a ratio of 4:1 was observed (presumably *o*- and *p*-chloro isomers).

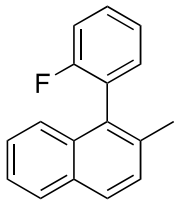
R_f (Hexane)= 0.25.

^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.40–7.05 (m, 11H + 12H(x0.25)), 6.97–6.93 (m, 1H(x0.25)), 6.90–6.85 (m, 2H), 4.05 (s, 2H(x0.25)), 3.92 (s, 2H).

MS (EI): *m/z* (%): 278.1 (53), 243.2 (15), 165.1 (100), 152.1 (12).

HR-MS (EI): *m/z*: Calculated for $C_{19}H_{15}Cl$: 278.08568; measured: 278.08547.

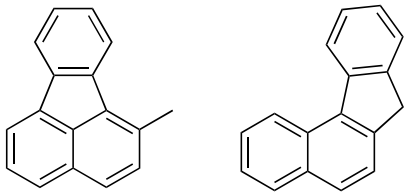
1-(2-Fluorophenyl)-2-methylnaphthalene (8a)



1-Bromo-2-methylnaphthalene (319 mg, 1.36 mmol), 2-fluorophenylboronic acid (286 mg, 2.04 mmol), K_2CO_3 (563 mg, 4.07 mmol) and Pd-PEPPSI-iPr (18 mg, 0.027 mmol) were dissolved in a mixture of THF (degassed, 9 mL) and water (degassed, 1 mL). After stirring at 70 °C for 15 h, GC-MS showed full conversion and the reaction mixture was treated with a sat. aq. solution of $NaHCO_3$ (10 mL), then extracted with DCM (3x20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. FC chromatography (hex/DCM 99:1 to 85:5) afforded the product as colorless oil (289 mg, 85 %).

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.86 (d, J = 8.0 Hz, 1H), 7.83 (d, J = 8.5 Hz, 1H), 7.48–7.34 (m, 5H), 7.32–7.21 (m, 3H), 2.28 (s, 3H).
^{13}C-NMR (100 MHz, $CDCl_3$) δ = 160.38 (d, $^1J_{C–F}$ = 243.9 Hz), 134.45, 132.89, 132.58 (d, $^3J_{C–F}$ = 3.7 Hz), 132.12, 131.70, 129.54 (d, $^3J_{C–F}$ = 7.8 Hz), 128.62, 128.12, 128.06, 126.96 (d, $^2J_{C–F}$ = 17.6 Hz), 126.26, 125.62, 125.03, 124.28 (d, $^4J_{C–F}$ = 3.6 Hz), 115.98 (d, $^2J_{C–F}$ = 22.2 Hz), 20.65.
^{19}F-NMR (376.5 MHz, $CDCl_3$): δ = –114.76.
IR (neat, cm^{-1}): 3054*w*, 2922*w*, 2859*w*, 1508*w*, 1492*m*, 1447*m*, 1382*w*, 1242*w*, 1220*m*, 1099*w*, 1031*w*, 842*w*, 828*w*, 811*s*, 784*m*, 757*s*, 744*s*, 666*w*, 619*w*, 537*w*, 521*w*, 467*w*, 419*w*.
MS (EI): *m/z* (%): 306.1
HR-MS (EI): *m/z*: Calculated for $C_{17}H_{13}F$: 236.09958; measured: 236.09948.

Mixture of 1-methylfluoranthene (9a) and 7*H*-benzo[c]fluorene (10a)

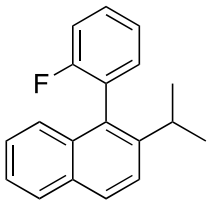


8a (19 mg) was treated according to the general procedure using 0.1 equiv. of [*i*Pr$_3$Si][$CHB_{11}H_5Cl_6$] and a reaction time of 120 min. Flash column chromatography (pure hex to hex/DCM 4:1) gave a mixture of products as slightly yellow oil (11 mg, 65 %). Additionally a substantial amount of intermolecular coupling product with mesitylene (similar to **5**). The ratio of the products was determined by comparing

integrals in the ^{1}H-NMR spectrum. Therefore the integrated signal of the methyl group of **9a** (2.89 ppm) was compared to the integral of the CH_2-signal of **10a** (4.01 ppm). This analysis gave a ratio of 1.6 to 1.0 in favor of the product of the intramolecular arylation (**9a**). The signals were compared to the corresponding compounds, which are already reported in the literature.[14]

MS (EI): *m/z* (%): **9a**: 216.1 (100), 215.1 (90), 214.1 (26), 189.1 (15), 107.7 (20), 106.7 (20), 95.6 (30). **10a**: 216.1 (100), 215.1 (72), 214.1 (24), 189.1 (12), 107.7 (22), 106.7 (21), 95.6 (25).

1-(2-Fluorophenyl)-2-isopropylnaphthalene (8b)



The starting material (1-bromo-2-isopropylnaphthalene) was synthesized from methyl-2-naphtylketone according to literature procedures[15] and contained a substantial amount of regioisomers. For the synthesis of **8b**, 1-bromo-2-isopropylnaphthalene (540 mg, 2.17 mmol), 2-fluorophenylboronic acid (379 mg, 2.71 mmol), K_2CO_3 (899 mg, 6.50 mmol) and Pd-PEPPSI-iPr (50 mg, 2 mol-%) were dissolved in a mixture of THF (degassed, 10 mL) and water (degassed, 1 mL). After stirring at 70 °C for 13 h, GC-MS showed full conversion and the reaction mixture was treated with a sat. aq. solution of $NaHCO_3$ (10 mL), then extracted with DCM (3x20 mL). The combined organic phases were dried over $MgSO_4$, filtered and concentrated *in vacuo*. FC chromatography afforded the product as colorless oily crystaline needles (97 mg, 65 %).

R_f (Hexane)= 0.22.

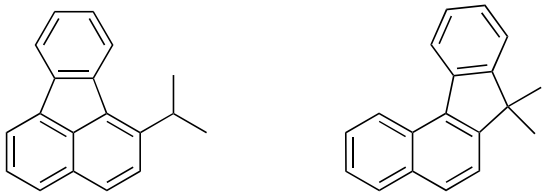
^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.91 (d, J = 8.6 Hz, 1H), 7.85 (d, J = 7.9 Hz, 1H), 7.56 (d, J = 8.7 Hz, 1H), 7.49–7.40 (m, 3H), 7.37–7.32 (m, 1H), 7.31–7.20 (m, 3H), 2.88 (hept, J = 6.9 Hz, 1H), 1.23 (d, J = 6.9 Hz, 3H), 1.19 (d, J = 6.9 Hz, 3H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ = 160.61 (d, $^1J_{C–F}$ = 244.7 Hz), 144.73, 132.92, 132.74 (d, $^3J_{C–F}$ = 3.6 Hz), 132.07, 130.15, 129.49 (d, $^3J_{C–F}$ = 7.8 Hz), 128.75, 127.98, 126.86 (d, $^2J_{C–F}$ = 17.8 Hz), 126.21, 126.11, 125.18, 124.17 (d, $^4J_{C–F}$ = 3.6 Hz), 123.77, 115.85 (d, $^2J_{C–F}$ = 22.3 Hz), 31.09, 24.13, 23.60.

MS (EI): *m/z* (%): 264.1 (76), 249.1 (100), 234.1 (60), 233.1 (71), 220.1 (15), 202.1 (11), 152.1 (10), 116.7 (16), 96.0 (15).

HR-MS (EI): *m/z*: Calculated for $C_{19}H_{17}F$: 264.13088; measured: 264.13074.

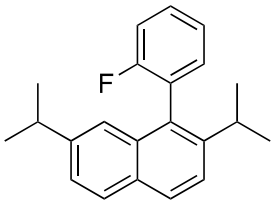
1-isopropylfluoranthene(9b) and 5,5-dimethylbenzo[*c*]-fluorene (10b)



8b (15 mg) was treated according to the general procedure using 0.1 equiv. of [*i*Pr_3Si][$CHB_{11}H_5Cl_6$] and a reaction time of 120 min. Flash column chromatography (pure hex to hex/DCM 4:1) gave a mixture of products as slightly yellow oil (11 mg, 78 %). The ratio of the products was determined by comparing integrals in the ^{1}H-NMR spectrum. Therefore the integrated signal of the isopropyl group of **9b** (at 1.51 ppm) was compared to the integral of the CH_3-signal of **10b** (at 1.56 ppm). This analysis gave a ratio of 1.0 to 1.9 in favor of the product of the C–H insertion (**10b**) (average from five reactions).

MS (EI): *m/z* (%): **9b**: 244.3 (34), 229.1 (100), 202.1 (44), 201.3 (33), 200.2 (24). **10b**: 244.1 (34), 229.1 (100), 202.1 (14), 113.0 (21).

1-(2-Fluorophenyl)2,7-diisopropylnaphthalene (8c)



1-Bromo-2,7-diisopropylnaphthalene (487 mg, 1.67 mmol), 2-fluorophenylboronic acid (416 mg, 2.99 mmol), K_2CO_3 (0.69 g, 2.0 mmol) and $Pd(PPh_3)_4$ (39 mg, 0.02 mmol) were suspended in a mixture of THF/water (15:1, 16 mL, degassed). The reaction mixture was heated to 70 °C and the clear solution was stirred for 77 h. Although the conversion was only about 50 %, a saturated aq. solution of $NaHCO_3$ (20 mL) was added. The inorganic phase was extracted with DCM (3x20 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography (hex/DCM 99:1 to 95:5) to afford the product as colorless crystals (130 mg, 25 %).

M.p.: 58–60 °C.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.85 (d, *J* = 8.6 Hz, 1H), 7.78 (d, *J* = 8.4 Hz, 1H), 7.49 (d, *J* = 8.6 Hz, 1H), 7.49–7.39 (m, 1H), 7.34 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.31–7.19

(m, 3H), 7.06 (broad singlet, 1H), 2.89 (hept, J = 6.9 Hz, 1H), 2.85 (hept, J = 6.9 Hz, 1H), 1.27–1.11 (m, 12H).

^{13}C-NMR (126 MHz, $CDCl_3$) δ = 160.61 (d, $^1J_{C-F}$ = 244.9 Hz), 146.72, 144.71, 132.99, 132.78 (d, $^3J_{C-F}$ = 3.7 Hz), 130.69, 129.80, 129.38 (d, $^3J_{C-F}$ = 7.7 Hz), 128.43, 128.00, 126.99 (d, $^2J_{C-F}$ = 18.0 Hz), 124.55, 124.12 (d, $^4J_{C-F}$ = 3.7 Hz), 122.92, 122.70, 115.78 (d, $^2J_{C-F}$ = 22.4 Hz), 34.56, 31.07, 24.14, 24.06, 24.03, 23.61.

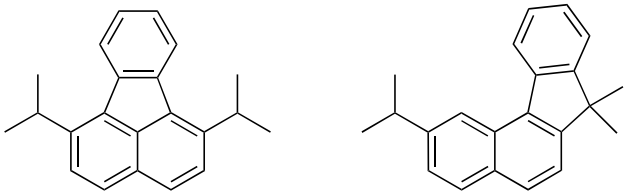
^{19}F-NMR (376.5 MHz, $CDCl_3$): δ = –114.04.

IR (neat, cm^{-1}): 3052*w*, 2960*m*, 2928*w*, 2868*w*, 1625*w*, 1508*w*, 1489*m*, 1446*m*, 1386*w*, 1363*w*, 1243*w*, 1227*w*, 1205*w*, 1096*w*, 1042*w*, 841*s*, 807*m*, 758*s*, 620*w*, 530*w*, 470*w*.

MS (EI): *m/z* (%): 306.1 (94), 291.1 (63), 249.1 (100), 234.1 (48), 233.1 (66).

HR-MS (EI): *m/z*: Calculated for $C_{22}H_{23}F$: 306.17783; measured: 306.17783.

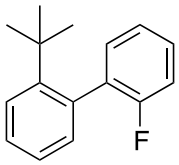
1,6-Diisopropylfluoranthene (9c) and 2-isopropyl-7,7-dimethylbenzo[*c*]fluorene (10c)



8c (14 mg) was treated according to the general procedure using 0.1 equiv. of [*i*Pr$_3$Si][CHB$_{11}$H$_5$Cl$_6$] and a reaction time of 120 min. Flash column chromatography (pure hex to hex/DCM 4:1) gave a mixture of products as slightly yellow oil (11 mg, 85 %). The ratio of the products was determined by comparing integrals in the ^{1}H-NMR spectrum. Therefore the integrated signal of the isopropyl groups of **9c** (at 1.51 ppm) was compared to the integral of the CH_3-signal of **10c** (at 1.55 ppm). This analysis gave a ratio of 1.0 to 2.1 in favor of the product of the C–H insertion (**10c**) (average of 3 reactions).

MS (EI): *m/z* (%): **9c**: 286.2 (100), 271.2 (78), 229.1 (91), 228.2 (84), 226.2 (76), 202.1 (36). **10c**: 286.3 (84), 271.2 (100), 239.1 (25), 229.1 (49), 226.2 (25).

2-*tert*-Butyl-2'-fluoro-1,1'-biphenyl (11)



2-*tert*-Butyl-1-iodobenzene (1.00 g, 3.84 mmol) (synthesized from 2-*tert*-butylaniline according to literature procedure[16]), 2-fluorophenylboronic acid (807 mg, 5.77 mmol), K_2CO_3 (1.59 g, 11.53 mmol) and $Pd(PPh_3)_4$ (60 mg, 0.052 mmol) were dissolved in a mixture of THF/water (10:1, 22 mL, degassed). The reaction mixture was heated to 70 °C and the clear solution was stirred for 16 h. After cooling down, a saturated aq. solution of $NaHCO_3$ (20 mL) was added. The inorganic phase was extracted with DCM (3x25 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was subjected to flash column chromatography (SiO_2, pure hexane) to afford starting material (0.50 g, 50 %) and a mixture of 2,2'-difluoro-1,1'-biphenyl and product as colorless oil. The product was further purified by recrystallization from hexane (byproduct crystallized) to result in a colorless oil (110 mg, 13 %).

R_f (Hexane)= 0.32.

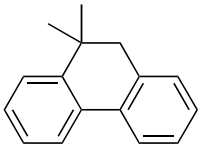
^{1}H-NMR (400 MHz, $CDCl_3$): δ = 7.56 (dd, J = 8.1, 1.3 Hz, 1H), 7.38–7.29 (m, 2H), 7.26 (ddd, J = 7.6, 7.3, 1.8 Hz, 1H), 7.20 (ddd, J = 7.4, 7.4, 1.3 Hz, 1H), 7.13 (ddd, J = 7.5, 7.5, 1.2 Hz, 1H), 7.08 (ddd, J = 8.3, 8.2, 1.1 Hz, 1H), 7.01 (dd, J = 7.6, 1.7 Hz, 1H).

^{13}C-NMR (100 MHz, $CDCl_3$) δ = 159.89 (d, $^1J_{C–F}$ = 242.3 Hz), 148.64, 134.83, 132.77 (d, $^2J_{C–F}$ = 17.3 Hz), 132.57, 132.50 (d, $^3J_{C–F}$ = 3.2 Hz), 129.01 (d, $^3J_{C–F}$ = 7.9 Hz), 128.06, 127.08, 125.33, 123.12 (d, $^4J_{C–F}$ = 3.6 Hz), 115.39 (d, $^2J_{C–F}$ = 22.4 Hz), 36.50, 32.08. ^{19}F-NMR (376.5 MHz, $CDCl_3$): δ = –111.94.

MS (EI): *m/z* (%): 228.1 (33), 213.1 (100), 193.1 (22), 185.1 (38), 183.1 (31), 165.1 (21).

HR-MS (EI): *m/z*: Calculated for $C_{16}H_{17}F$: 228.13088; measured: 228.13098.

10,10-Dihydro-9,9-dimethylphenanthrene (12)



12 was synthesized according to the general procedure, using **11** (41 mg, 0.180 mmol), $[^iPr_3Si][CHB_{11}H_5Cl_6]$ (4.5 mg, 0.009 mmol), and DMDMS (60 mg, 0.205 mmol). Flash column chromatography (pure hex to hex/DCM 98:2) gave the product as colorless crystals (29 mg, 79 %).

R_f (Hexane)= 0.30.

^{1}H-NMR (500 MHz, $CDCl_3$): δ = 7.81–7.73 (m, 2H), 7.44–7.39 (m, 1H), 7.34–7.28 (m, 3H), 7.23 (ddd, *J* = 7.3, 7.3, 1.2 Hz, 1H), 7.19 (d, *J* = 7.3 Hz, 1H), 2.79 (s, 2H), 1.27 (s, 6H).

^{13}C-NMR (125 MHz, $CDCl_3$) δ = 145.57, 136.17, 134.34, 133.40, 128.77, 128.08, 127.56, 126.98, 126.68, 124.39, 124.22, 123.64, 44.22, 34.30, 28.07.

MS (EI): *m/z* (%): 208.1 (31), 193.1 (100), 178.1 (68), 165.2 (17), 89.1 (13).

HR-MS (EI): *m/z*: Calculated for $C_{22}H_{23}F$: 208.12465; measured: 208.12470.

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