Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supplementary information

Faster Palladium-Catalyzed Arylation of Simple Arenes in the presence of a methylketone: Beneficial effect of an a priori interfering solvent in C-H activation

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1- Experimental details

1.1- General considerations.

^{1}H, $^{13}C\{^{1}H\}$ and ^{19}F NMR spectra were recorded on Bruker AV-400 or Agilent MR-500 spectrometers at the Laboratorio de Técnicas Instrumentales (LTI) of the UVa. Chemical shifts (in δ units, ppm) were referenced to $SiMe_4$ (^{1}H and ^{13}C) and $CFCl_3$ (^{19}F). The spectral data were recorded at 293 K unless otherwise noted. Homonuclear (^{1}H-COSY and ^{1}H-ROESY) and heteronuclear (^{1}H-^{13}C HSQC and HMBC) experiments were used to help with the signal assignments. The GC-MS analyses were performed in a Thermo-Scientific Focus DSQ II GC/MS apparatus. The intensities are reported as percentages relative to the base peak after the corresponding *m/z* value. Elemental analyses were carried out in a Carlo Erba 1108 microanalyser (at the Vigo University, Spain). Infrared spectra were recorded (in the range 4000-200 cm^{-1}) on a Perkin-Elmer FT-IR Spectrum Frontier with an ATR diamond accessory. All catalytic reactions were conducted under N_2 atmosphere. Solvents were dried using a solvent purification system SPS PS-MD-5 (ether, hexane, THF and CH_2Cl_2) or distilled from appropriate drying agents under nitrogen prior to use and stored over 3 Å or 4 Å molecular sieves (pyridine, MeOH, toluene, chlorobenzene, aniline, DMA, DMF, pinacolone, acetone).

4-Iodobenzotrifluoride, 4-bromobenzotrifluoride, 4-iodoanisole, cesium carbonate, potassium carbonate, cesium fluoride, tetrabutylammonium fluoride hydrate, tetrabutylammonium iodide, silver tetrafluoroborate, potassium hydroxide and palladium acetate are commercially available and were purchased from Sigma-Aldrich, Alfa Aesar or Fluorochem.

All commercial reagents and solvents were used as received unless otherwise noted.

[Pd(bipy-6-OH)Br(C_6F_5)] (**1**),[1] [[Pd(bipy-4-OH)Br(C_6F_5)],[1] [Pd(bipy-6-OMe)Br(C_6F_5)],[1] [Pd(bipy)Br(C_6F_5)],[1] [Pd(phen)Br(C_6F_5)],[1,2] [Pd(bipy-6-O)(C_6F_5)(κ-N-py)] (**2**),[1] and (NBu_4)[Pd(bipy-6-O)Br(C_6F_5)] (**6**-NBu_4)[1] were prepared as described elsewhere. $(NBu_4)_2CO_3$,[3] and Tl_2CO_3[4] were prepared according to the procedures in the literature.

1.2- Catalytic reactions

1.2.1. ***General procedure for direct arylation of arenes.***

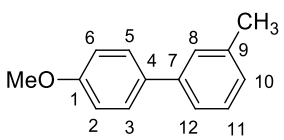
Method A (arene as solvent): [Pd(bipy-6-OH)Br(C_6F_5)] (**1**) (9.0 mg, 0.017 mmol) and cesium carbonate (222 mg, 0.68 mmol) were introduced in a Scklenk flask with a screw

cap in a nitrogen atmosphere. Then, the corresponding arene (3 mL) and the aryl iodide (0.34 mmol) were added. The mixture was kept in a preheated-bath at 130 ˚C for 6 h. After this time, the conversion was checked by ^{19}F (for reactions with *p*-$CF_3C_6H_4I$) or by ^{1}H NMR (OMe region for *p*-$OMeC_6H_4I$) of the crude mixture. Each arene was then removed under vacuum and *n*-hexane (3 mL) and EtOAc (0.3 mL) were added to the residue to extract the organic product. The mixture was filtered off. The filtrate was evaporated to dryness obtaining a yellowish residue. Finally, the product was purified by column chromatography using silica gel and a mixture of *n*-hexane:EtOAc = 2:1. The yields and isomer distribution are collected below as well as in Scheme 3 (main text). The number and ratio of isomers was determined by ^{19}F NMR, available in most cases, or by ^{1}H NMR using distinct signals such as OMe or Me. Then, each isomer was assigned using ^{1}H and ^{13}C NMR and comparison with the literature for the previously reported compounds (see references given for each compound).

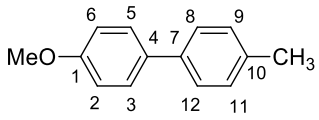
Toluene as arene:

ArI = ***p*-$CF_3C_6H_4I$**. The product is obtained as a colorless oil, mixture of three isomers in a ratio of o:m:p = 1:11:5. Yield: 0.1 g (85 %). The characterization of 3-methyl-4'-(trifluoromethyl)-1,1'-biphenyl,[1,5] 4-methyl-4'-(trifluoromethyl)-1,1'-biphenyl,[1,6] and 2-methyl-4'-(trifluoromethyl)-1,1'-biphenyl,[1,6] has been reported before.

ArI = ***p*-$MeOC_6H_4I$**. The product is obtained as a white solid, mixture of two isomers in a ratio of o:m:p = 0:2:1. Yield: 0.049 g (73 %).



4'-methoxy-3-methyl-1,1'-biphenyl:[7] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.51 (m, 2H, H^3, H^5), 7.36 (m, 1H, H^8), 7.35 (m, 1H, H^{12}), 7.30 (dd, J = 7.0, 7.0 Hz, 1H, H^{11}), 7.12 (d, J = 7.0 Hz, 1H, H^{10}), 6.96 (m, 2H, H^2, H^6), 3.85 (s, 3H, OMe), 2.41 (s, 3H, CH_3). $^{13}C\{^{1}H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 159 (C^1), 140.8 (C^7), 138.3 (C^9), 133.9 (C^4), 128.6 (C^{11}), 128.1 (C^3, C^5), 127.6 (C^8), 127.4 (C^{10}), 123.9 (C^{12}), 114.1 (C^2, C^6), 55.3 (OMe), 21.6 (CH_3). MS (EI, 70 eV): m/z (%) 198 (100) [M^+].

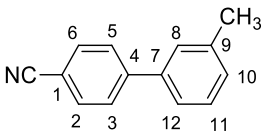


4'-methoxy-4-methyl-1,1'-biphenyl:[7] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.51 (m, 2H, H^3, H^5), 7.44 (m, 2H, H^8, H^{12}), 7.22 (m, 2H, H^9, H^{11}), 6.97 (m, 2H, H^2, H^6), 3.84 (s, 3H, OMe),

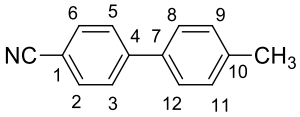
2.38 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 159 (C^1), 136.3 (C^7), 133.8 (C^4), 130.6 (C^{10}), 129.5 (C^9, C^{11}), 128.1 (C^3, C^5), 126.6 (C^8, C^{12}), 114.1 (C^2, C^6), 55.3 (OMe), 21.0 (CH_3). MS (EI, 70 eV): m/z (%) 198 (100) [M^+].

ArI = ***p*-NC-C$_6$H$_4$I**. The product is obtained as a white solid, mixture of two isomers in a ratio of o:m:p = 0:1.7:1. Yield: 0.065 g (98 %).

3'-methyl-[1,1'-biphenyl]-4-carbonitrile:[8] ^1H NMR (499.73 MHz, δ, $CDCl_3$): 7.71 (m, 2H, H^3, H^5), 7.67 (m, 2H, H^2, H^6), 7.40 (m, 1H, H^8), 7.39 (m, 1H, H^{12}), 7.37 (m, 1H, H^{11}), 7.24 (d, J = 7.1 Hz, 1H, H^{10}), 2.44 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 145.8 (C^4), 139.1 (C^7), 138.8 (C^9), 132.5 (C^3, C^5), 129.4 (C^{10}), 129 (C^{11}), 128 (C^8), 127.8 (C^2, C^6), 124.4 (C^{12}), 119 (CN), 110.8 (C^1), 21.5 (CH_3). MS (EI, 70 eV): m/z (%) 193 (100) [M^+].



4'-methyl-[1,1'-biphenyl]-4-carbonitrile:[8] ^1H NMR (499.73 MHz, δ, $CDCl_3$): 7.71 (m, 2H, H^3, H^5), 7.67 (m, 2H, H^2, H^6), 7.49 (m, 2H, H^8, H^{12}), 7.29 (m, 2H, H^9, H^{11}), 2.42 (s, 3H, CH_3). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 145.6 (C^4), 138.7 (C^7), 136.3 (C^{10}), 132.5 (C^3, C^5), 129.9 (C^9, C^{11}), 127.5 (C^2, C^6), 127 (C^8, C^{12}), 119 (CN), 110.5 (C^1), 21.3 (CH_3). MS (EI, 70 eV): m/z (%) 193 (100) [M^+].



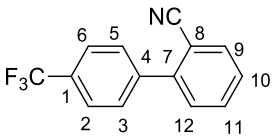
Anisole as arene; ArI = ***p*-CF$_3$C$_6$H$_4$I**: The product is obtained as a colorless oil, mixture of three isomers in a ratio of o:m:p = 2:4:1. Yield: 0.12 g (90 %). The characterization of 3-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl,[1,6] 2-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl,[1,9] and 4-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl,[1,6] has been reported before.

Ethyl benzoate as arene; ArI = ***p*-CF$_3$C$_6$H$_4$I**: The product is obtained as a colorless oil, mixture of three isomers, in a ratio of o:m:p = 1:35:24. Yield: 0.12 g (80 %). The characterization of ethyl 4'-(trifluoromethyl)-[1,1'-biphenyl]-3-carboxylate,[1] ethyl-4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carboxylate,[1,10] and ethyl 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carboxylate,[1] has been reported before.

Fluorobenzene as arene; ArI = ***p*-$CF_3C_6H_4I$**: The product is obtained as a colorless oil, mixture of three isomers in a ratio of o:m:p = 20:5:1. Yield: 0.09 g (74 %). The characterization of 2-fluoro-4'-(trifluoromethyl)-1,1'-biphenyl, 3-fluoro-4'-(trifluoromethyl)-1,1'-biphenyl and 4-fluoro-4'-(trifluoromethyl)-1,1'-biphenyl has been reported before.[1,6]

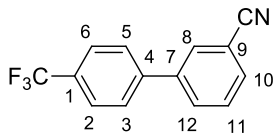
Benzonitrile as arene; ArI = ***p*-$CF_3C_6H_4I$**: The product is obtained as a colorless oil, mixture of three isomers in a ratio of o:m:p = 6:3:1. Yield: 0.09 g (80 %). Signal assignments in the mixture were aided by comparison with authentic samples prepared independently by conventional Suzuki coupling, leading to a more complete assignment than that reported before.[1]

4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile:[11] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$):



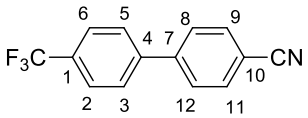
7.81 (d, 1H, J = 7.7 Hz, H^9), 7.76 (m, 2H, H^2, H^6), 7.71-7.67 (m, 3H, H^3, H^5, H^{11}), 7.52 (d, 2H, J = 7.6 Hz, H^{12}), 7.51 (m, H^{10}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 143.9 (C^4), 141.5 (C^7), 133.9 (C^9), 133.1 (C^{11}), 130.8 (q, $^2J_{C-F}$ = 33 Hz, C^1), 130 (C^{12}), 129.2 (C^3, C^5), 128.4 (C^{10}), 125.7 (q, $^3J_{C-F}$ = 3.5 Hz, C^2, C^6), 124 (q, $^1J_{C-F}$ = 270 Hz, CF_3), 118.3 (CN), 111.3 (C^8). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.70 (s, CF_3). MS (EI, 70 eV): m/z (%) 247 (100) [M+].

4'-(Trifluoromethyl)-[1,1'-biphenyl]-3-carbonitrile:[12] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$):



7.87 (m, 1H, H^8), 7.82 (m, 1H, H^{10}), 7.74 (m, H^2, H^6), 7.7-7.66 (m, H^3, H^5, H11), 7.62-7.54 (m, 1H, H^{11}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 142.3 (C^7), 141 (C^4), 131.6 (C^{10}), 130.8 (C^8), 130.8 (q, $^2J_{C-F}$ = 32.5 Hz, C^1), 129.9 (C^{11}), 127.5 (C^3, C^5), 126.1 (q, $^3J_{C-F}$ = 3.5 Hz, C^2, C^6), 124 (q, $^1J_{C-F}$ = 270 Hz, CF_3), 118.5 (CN), 113.3 (C^9). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.64 (s, CF_3). MS (EI, 70 eV): m/z (%) 247 (100) [M^+].

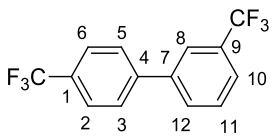
4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile:[13] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$):



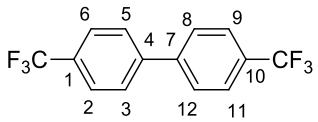
7.77, 7.75 (m, 4H, , H^3, H^5, H^9, H^{11}), 7.7 (m, 4H, H^2, H^6, H^8, H^{12}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, CDCl3): 144.1 (C^7), 142.7 (C^4), 132.8 (C^9, C^{11}), 130.7 (q, $^2J_{C-F}$ = 32.5 Hz, C^1), 127.9 (C^8, C^{12}), 127.6 (C^3, C^5), 126.1 (q, $^3J_{C-F}$ = 3.5 Hz, C^2, C^6), 124 (q, $^1J_{C-F}$ = 270 Hz, CF_3), 118.5 (CN), 112 (C^{10}). ^{19}F NMR (470.17 MHz, δ, CDCl3): -62.67 (s, CF_3). MS (EI, 70 eV): m/z (%) 247 (100) [M^+].

Trifluomethylbenzene as arene; ArI = ***p*-$CF_3C_6H_4I$**: The product is obtained as a colorless oil, mixture of two isomers in a ratio m:p = 2:1. All of them were completely characterized. Yield: 0.093 g (95 %).

3,4'-Bis(trifluoromethyl)-1,1'-biphenyl:[6] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.84 (s, 1H, H^8), 7.78 (d, J = 7.5 Hz, 1H, H^{12}), 7.74 (m, 2H, H^2, H^6), 7.70 (m, 2H, H^3, H^5), 7.67 (d, J = 7.5 Hz, 1H, H^{10}), 7.61 (m, 1H, H^{11}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 143.2 (C^4), 140.6 (C^7), 131.5 (q, $^2J_{C-F}$ = 32.5 Hz, C^9), 130.6 (C^{12}), 130.2 (q, $^2J_{C-F}$ = 32.5 Hz, C^1), 129.5 (C^{11}), 127.6 (C^5), 125.9 (q, $^3J_{C-F}$ = 3.5 Hz, C^2, C^6), 124.8 (q, $^3J_{C-F}$ = 3.5 Hz, C^{10}), 124.2 (q, $^3J_{C-F}$ = 3.5 Hz, C^8), 124.1 (q, $^1J_{C-F}$ = 270 Hz, *p*-CF_3), 124 (q, $^1J_{C-F}$ = 270 Hz, *m*-CF_3). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.70 (s, *p*-CF_3), -62.58 (s, *m*-CF_3). MS (EI, 70 eV): m/z (%) 290 (100) [M^+].

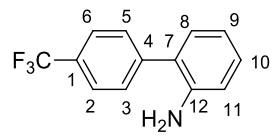


4,4'-Bis(trifluoromethyl)-1,1'-biphenyl:[6] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.74 (m, 4H, H^2, H^6, H^9, H^{11}), 7.70 (m, 4H, H^3, H^5, H^8, H^{12}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 143.2 (C^4, C^7), 130.8 (q, $^2J_{C-F}$ = 32.5 Hz, C^1), 127.6 (C^3, C^5, C^8, C^{12}), 125.9 (q, $^3J_{C-F}$ = 3.5 Hz, C^2, C^6, C^9, C^{11}), 124.1 (q, $^1J_{C-F}$ = 270 Hz, CF_3). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.60 (s, CF_3). MS (EI, 70 eV): m/z (%) 290 (100) [M^+].

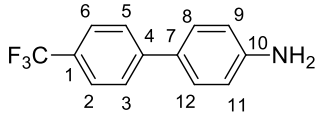


Aniline as arene; ArI = ***p*-$CF_3C_6H_4I$**: The product is obtained as a colorless oil, mixture of three isomers in a ratio of o:m:p = 12:1:2. The major product (ortho) was completely characterized. Yield: 0.077 g (90 %).

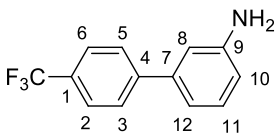
4'-(Trifluoromethyl)-[1,1'-biphenyl]-2-amine:[14] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.70 (m, 2H, H^2, H^6), 7.60 (m, 2H, H^3, H^5), 7.19 (dd, J = 7.5, 7.5 Hz, 1H, H^{10}), 7.11 (d, J = 7.5 Hz, 1H, H^8), 6.85 (dd, J = 7.5 Hz, 1H, H^9), 6.79 (d, J = 7.5 Hz, 1H, H^{11}), 3.8 (br, 2H, NH_2). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 143.6 (C^{12}), 143.3 (C^4, C^7), 130.4 (C^8), 129.5 (C^3, C^5), 129.2 (C^{10}), 125.9 (q, $^2J_{C-F}$ = 33 Hz, C^1), 125.8 (q, $^3J_{C-F}$ = 4 Hz, C^2, C^6), 124.3 (q, $^1J_{C-F}$ = 270 Hz, CF_3), 118.9 (C^9), 115.9 (C^{11}). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.52 (s, CF_3). MS (EI, 70 eV): m/z (%) 237 (100) [M^+].



4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-amine:[15] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.66 (m, 4H, H^2, H^3, H^5, H^6), 7.44 (m, 2H, H^8, H^{12}), 6.99 (m, 2H, H^9, H^{11}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 146.9 (C^{10}), 128.2 (C^8, C^{12}), 127.4 (C^3, C^5), 125.6 (q, $^3J_{C-F}$ = 4 Hz, C^2, C^6), 113.9 (C^9). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.41 (s, CF_3). MS (EI, 70 eV): m/z (%) 237 (100) [M^+].

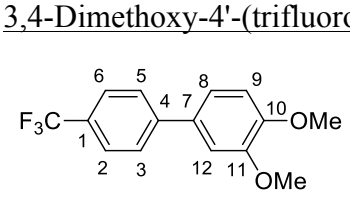


4'-(Trifluoromethyl)-[1,1'-biphenyl]-3-amine:[16] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.63 (m, 4H, H^2, H^3, H^5, H^6). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.28 (s, CF_3). MS (EI, 70 eV): m/z (%) 237 (100) [M^+].

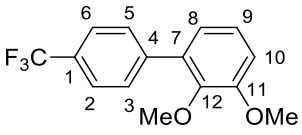


1,2-Dimethoxybenzene as arene; ArI = ***p*-$CF_3C_6H_4I$**: The product is obtained as a colorless oil, mixture of two isomers in a ratio of 3,4:2,3 = 3:1. Both were completely characterized. Yield: 0.086 g (85 %).

3,4-Dimethoxy-4'-(trifluoromethyl)-1,1'-biphenyl:[17] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.66 (m, 4H, H^2, H^3, H^5, H^6), 7.16 (d, J = 8 Hz, 1H, H^8), 7.11 (s, 1H, H^{12}), 6.97 (d, J = 8 Hz, 1H, H^9), 3.96 (s, 3H, OMe^{10}), 3.94 (s, 3H, OMe^{11}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 149.4 (C^{11}, C^{10}), 144.5 (C^4), 141.9 (C^7), 128.8 (q, $^2J_{C-F}$ = 33 Hz, C^1), 127 (C^3, C^5), 125.7 (q, $^3J_{C-F}$ = 4 Hz, C^2, C^6), 123.4 (q, $^1J_{C-F}$ = 270 Hz, CF_3), 119.7 (C^8), 112.3 (C^9), 110.5 (C^{12}), 56 (OMe^{10}, OMe^{11}) ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.36 (s, CF_3). MS (EI, 70 eV): m/z (%) 282 (100) [M^+].



2,3-Dimethoxy-4'-(trifluoromethyl)-1,1'-biphenyl: ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.66 (m, 4H, H^2, H^3, H^5, H^6), 7.13 (m, 1H, H^8), 6.97 (m, 1H, H^9), 6.94 (m, 1H, H^{10}), 3.92 (s, 3H, OMe^{11}), 3.60 (s, 3H, OMe^{12}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 153.2 (C^{12}), 146.6 (C^{11}), 144.5 (C^4), 141.9 (C^7), 129.6 (C^3, C^5), 128.9 (q, $^2J_{C-F}$ = 33 Hz, C^1), 124.9 (q, $^3J_{C-F}$ = 4 Hz, C^2, C^6), 124.3 (C^8), 124 (q, $^1J_{C-F}$ = 270 Hz, CF_3), 122.3 (C^{10}), 111.6 (C^9), 60.7 (OMe^{12}), 55.9 (OMe^{11}). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.42 (s, CF_3). MS (EI, 70 eV): m/z (%) 282 (100) [M^+].



Ethyl phenylacetate as arene; ArI = ***p*-$CF_3C_6H_4I$**: The product is obtained as a colorless oil, mixture of two isomers in a ratio of m:p = 3:2. Both were completely characterized. Yield: 0.09 g (85 %).

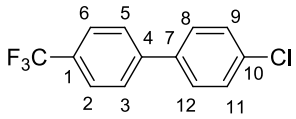
<u>Ethyl 2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetate</u>: ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.69 (m, 4H, H^2, H^3, H^5, H^6), 7.52 (s, 1H, H^8), 7.51 (m, 1H, H^{10}), 7.43 (m, 1H, H^9), 7.33 (m, 1H, H^{12}), 4.18 (q, 2H, CH_2CH_3), 3.69 (s, 2H, CH_2), 1.28 (t, 3H, CH_3). ^{13}C{^{1}H} NMR (125.67 MHz, δ, $CDCl_3$): 171.6 (CO), 144.5 (C^4), 140.1 (C^7), 135 (C^{11}), 129.5 (q, $^2J_{C-F}$ = 33 Hz, C^1), 129.2 (C^9), 129.1 (C^8), 128.3 (C^{12}), 127.3 (C^3, C^5), 126 (C^{10}), 125.7 (q, $^3J_{C-F}$ = 4 Hz, C^2, C^6), 124.3 (q, $^1J_{C-F}$ = 270 Hz, CF_3), 60.8 (CH_2, CH_2-CH_3), 41.4 (CH_2), 14.2 (CH_3). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.44 (s, CF_3). MS (EI, 70 eV): m/z (%) 308 (100) [M^+].

<u>Ethyl 2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl) acetate</u>: ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.69 (m, 4H, H^2, H^3, H^5, H^6), 7.56 (m, 2H, H^8, H^{12}), 7.40 (m, 2H, H^9, H^{11}), 4.18 (q, 2H, CH_2CH_3), 3.69 (s, 2H, CH_2), 1.27 (t, 3H, CH_3). ^{13}C{^{1}H} NMR (125.67 MHz, δ, $CDCl_3$): 171.6 (CO), 144.3 (C^4), 138.5 (C^7), 134.2 (C^{10}), 129.9 (C^9, C^{11}), 129.4 (q, $^2J_{C-F}$ = 33 Hz, C^1), 127.4 (C^8, C^{12}), 127.3 (C^3, C^5), 125.7 (q, $^3J_{C-F}$ = 4 Hz, C^2, C^6), 124.3 (q, $^1J_{C-F}$ = 270 Hz, CF_3), 60.8 (CH_2, CH_2-CH_3), 41 (CH_2), 14.2 (CH_3). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.44 (s, CF_3). MS (EI, 70 eV): m/z (%) 308 (100) [M^+].

Chlorobenzene as arene; ArI = ***p*-$CF_3C_6H_4I$**: The product is obtained as a colorless oil, mixture of three isomers in a ratio of o:m:p = 0:4:1. The major product (meta) was completely characterized. Yield: 0.06 g (65 %).

<u>3-Chloro-4'-(trifluoromethyl)-1,1'-biphenyl</u>:[18] ^{1}H NMR(499.73 MHz, δ, $CDCl_3$): 7.71 (m, 2H, H^2, H^6), 7.66 (m, 2H, H^3, H^5), 7.57 (s, 1H, H^{12}), 7.47 (m, 1H, H^9), 7.41-7.38 (m, 2H, H^8, H^{10}). ^{13}C{^{1}H} NMR (125.67 MHz, δ, $CDCl_3$): 143.3 (C^4), 141.6 (C^7), 135 (C^{11}), 130.2 (C^8), 130.0 (q, $^2J_{C-F}$ = 33 Hz, C^1), 128.2 (C^{10}), 127.4 (C^3, C^5, C^{12}), 125.8 (q, $^3J_{C-F}$ = 4 Hz, C^2, C^6), 125.4 (C^9), 125.2 (q, $^1J_{C-F}$ = 270 Hz, CF_3). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.54 (s, CF_3). MS (EI, 70 eV): m/z (%) 256 (100) [M^+].

4-Chloro-4'-(trifluoromethyl)-1,1'-biphenyl:[19] ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.71 (m, 2H, H^2, H^6), 7.66 (m, 2H, H^3, H^5), 7.57 (m, 2H, H^8, H^{12}), 7.43 (m, 2H, H^9, H^{11}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 139.1 (C^4), 138.1 (C^7), 129.2 (C9), 128.5 (C8), 127.3 (C5), 125.0 (q, $^3J_{C-F}$ = 4 Hz, C^2, C^6). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.51 (s, CF_3). MS (EI, 70 eV): m/z (%) 256 (100) [M^+].



Method B (use of a co-solvent): [Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 9.0 mg, 0.017 mmol) and cesium carbonate (222 mg, 0.68 mmol) were introduced in a Scklenk flask with a screw cap in a nitrogen atmosphere. Then, 4-iodobenzotrifluoride (51 μL, 0.34 mmol), the corresponding arene (1,1 to 40 equivalents), and the amount of pinacolone necessary to reach a total volume of 3 mL, were added. The mixture was kept in a preheated-bath at 130 ˚C. After the specified time the conversion was checked by ^{19}F NMR of the crude mixture. The solvent mixture was then removed under vacuum and the organic product was isolated as described above. The yields and regioselectivities of the different reactions are shown in Table 3 (main text).

The reactions with co-solvents other than pinacolone were carried out in the same way way using toluene as arene to give 3-methyl-4'-(trifluoromethyl)-1,1'-biphenyl (mixture of isomers). Data for these reactions are collected in Table 2 (see main text).

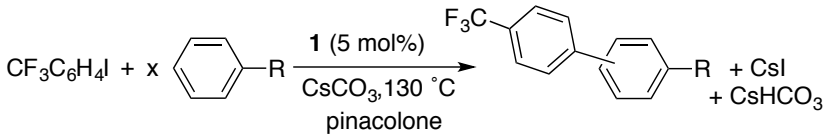
DMA/toluene: reaction time 6 h; isolated yield 90% (o:m:p = 1:4:3).

DMF/toluene: reaction time 1.5 h; isolated yield 77% (o:m:p = 1:2:1.5).

2-Butanone/toluene: reaction time 6 h; isolated yield 80% (o:m:p = 1:4:2).

The lowest amounts of arene that can be used and lead to synthetically useful direct arylation reactions are collected in Table S1.

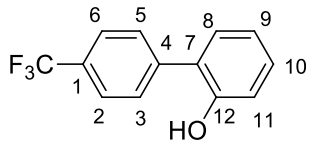
Table S1. Direct arylation reaction of arenes with *p*-$CF_3C_6H_4I$ in pinacolone.[a]



Entry	x	R	time	% Crude yield[b]
1	1.1	NH_2	24 h	60[c]
2	1.1	OH	3 h	45[d]
3	10	CN	24 h	74
4	10	COOEt	4 h	66
5	10	OMe	2 h	84
6	10	Me	6 h	60
7	10	pyridine	24 h	56

[a] Reaction conditions: **1** (9 mg, 0.017 mmol), Cs_2CO_3 (222 mg, 0.68 mmol), *p*-$CF_3C_6H_4I$ (51 μL, 0.34 mmol) and the corresponding amount of arene according to the specified value of x; pinacolone as solvent (total volumen 3 mL). 130 °C [b] Yields and regioselectivities were determined by integration of the CF_3 signals in ^{19}F NMR. In all cases complete conversion was observed with Ar-Ar, ArH and Ar-pinacolone as major byproducts (Ar = $CF_3C_6H_4$). [c] 9% crude yield after 2 h. [d] Isolated yield: 40% (ortho isomer).

Phenol as arene; ArI = ***p*-$CF_3C_6H_4I$**: The product is obtained as a white solid, mixture of the ortho isomer (89 mol %) and two isomers as a result of the double arylation of phenol (11 mol %; checked by GC-MS, m/z = 382). Only the major product could be characterized. Yield (ortho isomer): 0.041 g (40 %).



4'-(trifluoromethyl)-[1,1'-biphenyl]-2-ol:[20] ^1H NMR (499.73 MHz, δ, $CDCl_3$): 7.73 (m, 2H, H^2, H^6), 7.63 (m, 2H, H^3, H^5), 7.29-7.26 (m, 2H, H^8, H^{10}), 7.03 (dd, J = 7.5, 7.5 Hz, 1H, H^9), 6.97 (d, J = 7.5 Hz, 1H, H^{11}), 5.02 (s, 1H, OH). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, $CDCl_3$): 152.3 (C^{12}), 141 (C^4), 130.4 (C^{10}), 129.8 (C^8), 129.5 (C^3, C^5), 129.4 (q, $^2J_{C\text{-}F}$ = 33 Hz, C^1), 126.9 (C^7), 125.9 (q, $^3J_{C\text{-}F}$ = 4 Hz, C^2, C^6), 123.1 (q, $^1J_{C\text{-}F}$ = 270 Hz, CF_3), 121.3 (C^9), 116.2 (C^{11}). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.60 (s, CF_3). MS (EI, 70 eV): m/z (%) 238 (100) [M^+].

1.2.2. ***Additional catalytic experiments.***

Table S2. Arylation of toluene with *p*-$CF_3C_6H_4I$ using **1** as catalyst in the presence of different bases.[a]

Entry	Base:ArI mol ratio	Additive (5 mol %)	%Crude yield Ar-Tol, ArH+Ar-Ar, 6 h[b]	%Crude yield Ar-Tol, ArH+Ar-Ar, 24 h[b]
1	Cs_2CO_3 (2)	-	61, 6+1	90, 8+2[c]
2	Cs_2CO_3 (1)	-	64, 8+2	89, 8+3[c]
3	Cs_2CO_3 (2)	Galvinoxyl	52, 6+3	85, 9+6
4	Tl_2CO_3 (2)	-	24, 2+1	68, 3+1
5	CsF (2)	-	34, 6+1	86, 10+4
6	$NBu_4F.H_2O$ (2)	-	20, 72+8	
7	$(NBu_4)_2CO_3$ (2)	-	12, 2+2	50, 32+18

[a] Reaction conditions: [Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 9 mg, 0.017 mmol), *p*-$CF_3C_6H_4I$ (51 µL, 0.34 mmol), toluene (3 mL), base (0.68 mmol), except for entry 2 (0.34 mmol); 130 ºC. [b] Yields determined by ^{19}F RMN of the crude mixture. [c] Total conversion was observed after 8 h.

1.3- Mechanistic Experiments

1.3.1. ***General procedure for the stoichiometric couplings.***

Complex **2** (1.3 mg, 0.0025 mmol) or complex **4** (2.3 mg, 0.0025 mmol) and the solvent (toluene or benzonitrile, 0.5 mL) were added into an NMR tube along with a sealed glass capillary filled with $(CD_3)_2SO$ as an NMR reference. The mixture was heated at 130 ˚C for 1 h, and the species formed were examined by ^{19}F NMR.

The spectroscopic data for the different species are given below:

C_6F_5H: ^{19}F NMR (470.17 MHz, 298 K, δ, toluene/$(CD_3)_2SO$ capillary): -139.71 (m, 2F, F_{ortho}), -154.65 (t, J = 20.7 Hz, 1F, F_{para}), -162.96 (m, 2F, F_{meta}).

^{19}F NMR (470.17 MHz, 298 K, δ, benzonitrile/$(CD_3)_2SO$ capillary): -139.05 (m, 2F, F_{ortho}), -154.46 (t, J = 20.7 Hz, 1F, F_{para}), -162.15 (m, 2F, F_{meta}).

C_6F_5-Tol: mixture of two isomers (m:p = 2:1). Meta isomer: ^{19}F NMR (470.17 MHz, 298 K, δ, toluene/ $(CD_3)_2SO$ capillary): -144.29 (m, 2F, F_{ortho}), -157.05 (t, J = 20.7 Hz, 1F, F_{para}), -163.39 (m, 2F, F_{meta}). ^{19}F NMR (470.17 MHz, 298 K, δ, $CDCl_3$):[21] -143.05 (m, 2F, F_{ortho}), -155.84 (t, J = 20.7 Hz, 1F, F_{para}), -162.4 (m, 2F, F_{meta}). MS (EI, 70 eV): m/z (%) 258 (100) [M^+]. Para isomer: ^{19}F NMR (470.17 MHz, 298 K, δ, toluene/ $(CD_3)_2SO$ capillary): -144.68 (m, 2F, F_{ortho}), -157.34 (t, J = 20.7 Hz, 1F, F_{para}), -163.39 (m, 2F, F_{meta}). ^{19}F NMR (470.17 MHz, 298 K, δ, $CDCl_3$):[21] -143.3 (m, 2F, F_{ortho}), -156.12 (t, J = 20.7 Hz, 1F, F_{para}), -162.4 (m, 2F, F_{meta}). MS (EI, 70 eV): m/z (%) 258 (100) [M^+].

C_6F_5-benzonitrile: mixture of two isomers (B:A = 1:1.2).[22] A isomer: ^{19}F NMR (470.17 MHz, 298 K, δ, benzonitrile/ $(CD_3)_2SO$ capillary): -143.47 (m, 2F, F_{ortho}), -154.67 (t, J = 20.7 Hz, 1F, F_{para}), -162.58(m, 2F, F_{meta}). ^{19}F NMR (470.17 MHz, 298 K, δ, $CDCl_3$):[23] -142.75 (m, 2F, F_{ortho}), -153.0 (t, J = 20.7 Hz, 1F, F_{para}), -161.0 (m, 2F, F_{meta}). MS (EI, 70 eV): m/z (%) 269 (100) [M^+]. B isomer: ^{19}F NMR (470.17 MHz, 298 K, δ, benzonitrile/$(CD_3)_2SO$ capillary): -143.64 (m, 2F, F_{ortho}), -154.67 (t, J = 20.7 Hz, 1F, F_{para}), -162.58 (m, 2F, F_{meta}). ^{19}F NMR (470.17 MHz, 298 K, δ, $CDCl_3$): -143.0 (m, 2F, F_{ortho}), -153.15 (t, J = 20.7 Hz, 1F, F_{para}), -161.0 (m, 2F, F_{meta}). MS (EI, 70 eV): m/z (%) 269 (100) [M^+].

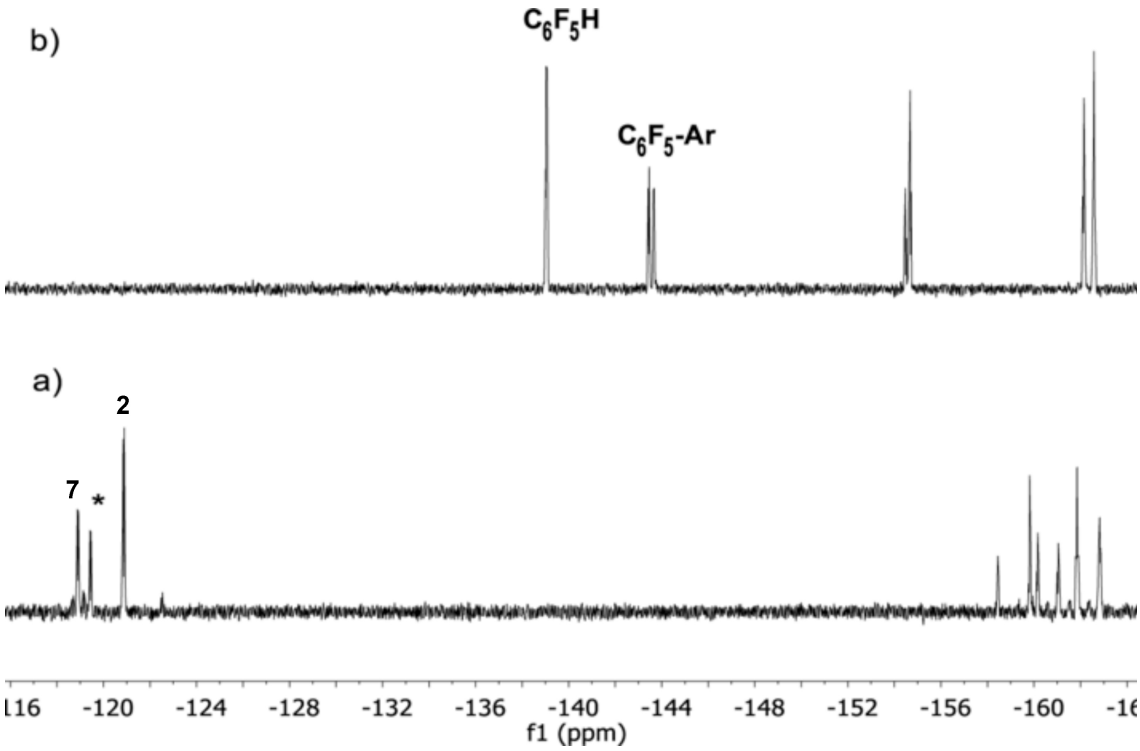


Figure S1. ^{19}F NMR spectra in benzonitrile as solvent using a DMSO-d6 capillary. a) Complex **2** in benzonitrile. * Unknown species. b) Mixture obtained after heating complex **2** for 1 h at 130 ºC (C_6F_5-Ar is a mixture of two isomers). Only the $^{19}F_{ortho}$ region is labeled for clarity (Ar = C_6H_4CN).

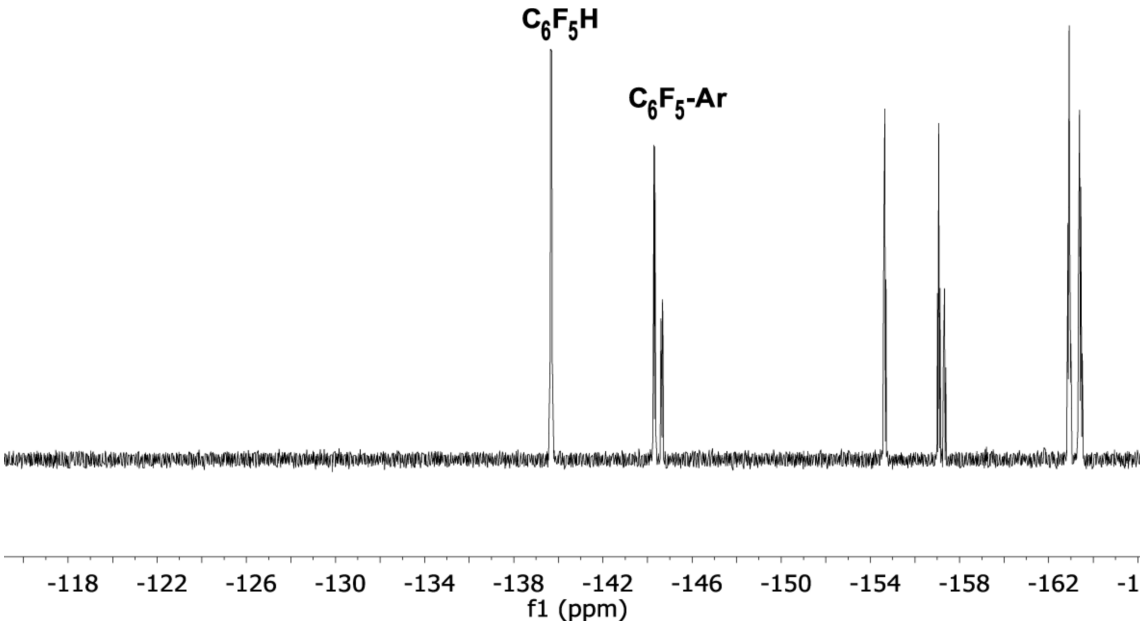


Figure S2. ^{19}F NMR spectrum in toluene as solvent using a DMSO-d6 capillary after heating complex **2** for 1 h at 130 ºC (C_6F_5-Ar is a mixture of two isomers). Only the $^{19}F_{ortho}$ region is labeled for clarity (Ar = Tolyl).

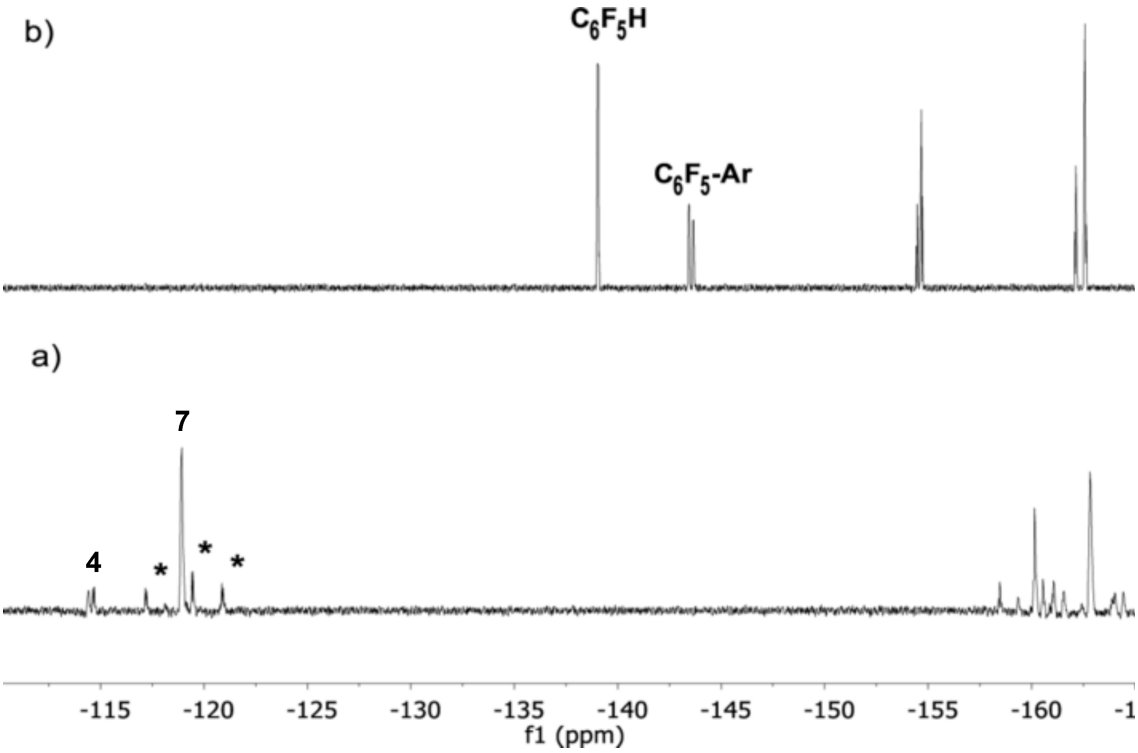


Figure S3. ^{19}F NMR spectra in benzonitrile as solvent using a DMSO-d6 capillary. a) Complex **4** in benzonitrile. * Unknown species. b) Mixture obtained after heating complex **4** for 1 h at 130 ºC (C_6F_5-Ar is a mixture of two isomers). Only the $^{19}F_{ortho}$ region is labeled for clarity (Ar = C_6H_4CN).

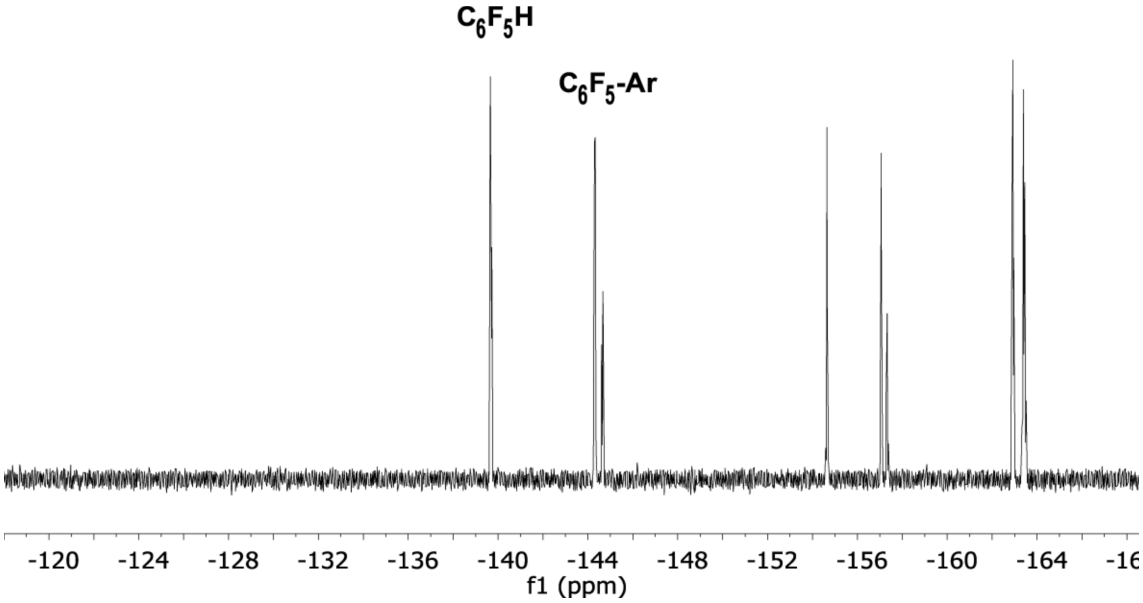


Figure S4. ^{19}F NMR spectrum in toluene as solvent using a DMSO-d6 capillary after heating complex **4** for 1 h at 130 ºC (C_6F_5-Ar is a mixture of two isomers). Only the $^{19}F_{ortho}$ region is labeled for clarity (Ar = Tolyl).

1.3.2. ***Behavior of complex 1 in different solvents and in the presence of base.***

A) Complex **1** in pinacolone/toluene

Complex [Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 1.3 mg, 0.0025 mmol) and solvent (toluene (0.25 mL) and pinacolone, 0.25 mL) were added into an NMR tube along with a sealed glass capillary filled with $(CD_3)_2SO$ as an NMR reference. A yellow solution was observed. The species formed were examined by ^{19}F NMR. Cesium carbonate was added (2.4 mg, 0.0075 mmol) and the species formed were examined again by ^{19}F NMR. The spectroscopic data in toluene/pinacolone of the identified species are given below.

1: ^{19}F NMR (470.17 MHz, 298 K, δ, toluene/pinacolone, $(CD_3)_2SO$ capillary): -118.71 (m, 2F, F_{ortho}), -160.83 (t, J = 22.1 Hz, 1F, F_{para}), -163.55 (m, 2F, F_{meta}).

4: ^{19}F NMR (470.17 MHz, 298 K, δ, toluene/pinacolone, $(CD_3)_2SO$ capillary): -113.54 (m, 2F, F_{ortho}), -113.90 (m, 2F, F_{ortho}), -161.46 (t, J = 22.1 Hz, 2F, F_{para}), -164.55 (m, 2F, F_{meta}), -165.20 (m, 2F, F_{meta}).

3: ^{19}F NMR (470.17 MHz, 298 K, δ, toluene/pinacolone, $(CD_3)_2SO$ capillary): -118.56 (m, 2F, F_{ortho}), -161.11 (t, J = 22.1 Hz, 1F, F_{para}), -163.70 (m, 2F, F_{meta}).

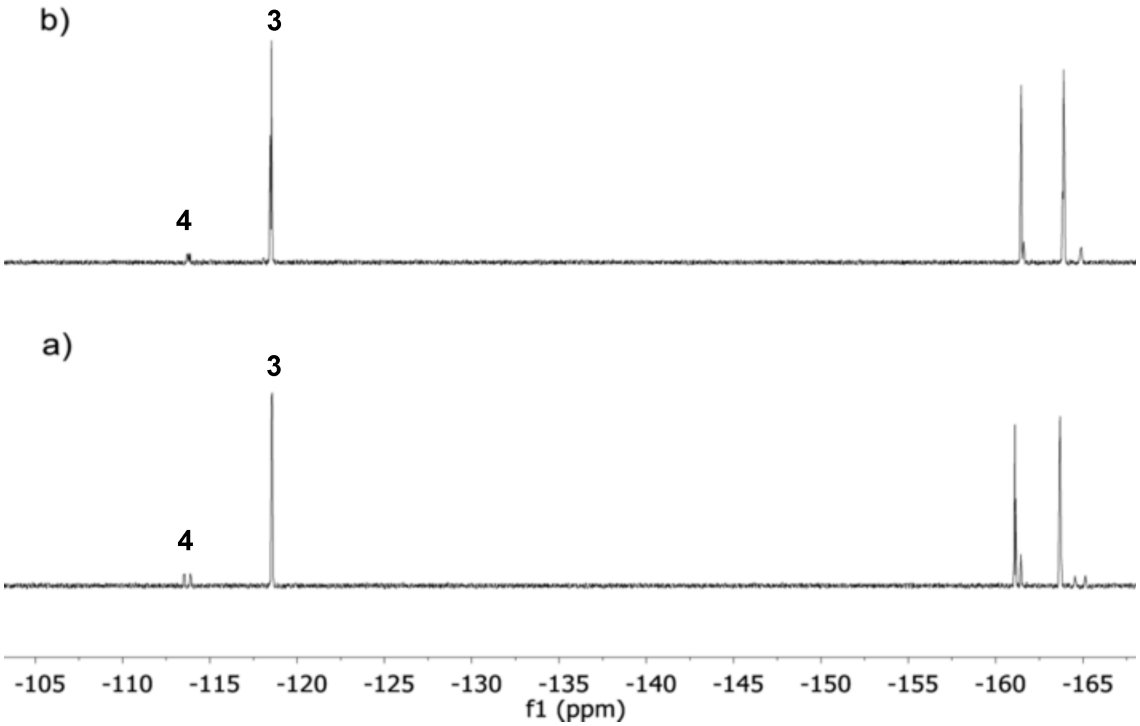


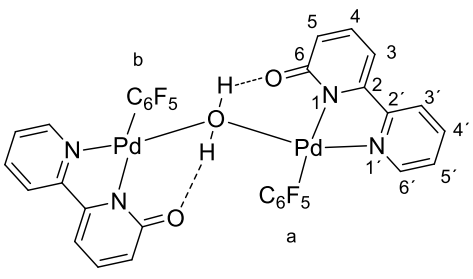
Figure S5. ^{19}F NMR spectra in the indicated solvent using a DMSO-d6 capillary as reference. a) complex **1** and Cs_2CO_3 in a mixture of toluene and pinacolone (1:1) (**3**:**4** = 11:1 mol ratio). b) complex **1** and Cs_2CO_3 in pinacolone (**3**:**4** = 20:1 mol ratio). Only the $^{19}F_{ortho}$ region is labeled for clarity.

B) Synthesis of [Pd_2(bipy-6-O)$_2$(C_6F_5)$_2$μOH_2] (**4**).

Method A: [Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 50 mg, 0.095 mmol) and pinacolone (5 mL) were introduced in a Schlenk flask. When the complex had been dissolved, cesium carbonate (92.8 mg, 0.28mmol) was added into the light yellow solution. The mixture was stirred at room temperature for 6 h. During this time the light yellow solution became an intense yellow one. The solvent was evaporated to dryness. The residue was extracted with 5 mL of CH_2Cl_2 and filtered off to remove the cesium salts. The solvent was evaporated to c.a. 1 mL and *n*-hexane was added to the yellow solution. An intense yellow solid precipitates. The solid was filtered, washed with *n*-hexane and air-dried. Finally, complex **4** was purified by vapor-diffusion crystallization of pentane into a solution of **4** in CH_2Cl_2 at 0 ºC under a nitrogen atmosphere giving yellow crystals. Yield: 30 mg (35 %). When complex **4** is dissolved in pinacolone complex **3** was formed (identical ^{19}F NMR spectrum to Figure S5b).

Method B: [Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 100 mg, 0.19 mmol) and acetone (15 mL) were introduced in a Schlenk flask. When the complex had been dissolved, silver tetrafluoroborate (40.7 mg, 0.20 mmol) was added into the light yellow solution. The mixture was stirred at room temperature for 1 h. After the silver salt (AgBr) was removed by filtration, the solvent was evaporated to c.a. 5 mL. Then, an aqueous solution of KOH (0.23 mL, 0.83 M) was added to the yellow solution. After 5 min with constant stirring, a yellow solid precipitates. The solid was filtered, washed first with water, methanol and it was air-dried. Yield: 75 mg (87 %). The solid contains a water molecule that cannot be eliminated. Anal. Calcd. for (**4**·H_2O) $C_{32}H_{18}F_{10}N_4O_4Pd_2$: C, 41.54 %; H, 1.96 %; N, 6.05 %.; found: C, 41.08 %; H, 1.35 %; N, 6.00 %.

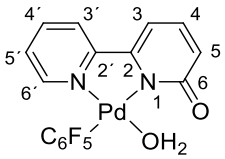
Complex **4** was dissolved in CD_2Cl_2 for its characterization. A small amount of water present is the responsible for the breakdown of the aquo bridge giving a monomeric species in which water is coordinated (**5**). The ratio of the dimeric and monomeric complexes in solution is: 1:1.



4: ^{1}H NMR (499.73 MHz, δ, CD_2Cl_2): 13.54 (s, 2H, H_2O), 7.90 (m, 4H, $H^{3'}$, $H^{4'}$), 7.75 (d, J = 5.8, 2H, $H^{6'}$), 7.53 (dd, J = 8.5, 8,5 Hz, 2H, H^4), 7.17 (m, 2H, $H^{5'}$), 7.12 (d, J = 8.5 Hz, 2H, H^3), 6.40 (d, J = 8.5 Hz, 2H, H^5). ^{13}C {^{1}H} NMR (125.67 MHz, δ, CD_2Cl_2): 170.8 (C^6), 158.9 ($C^{2'}$), 152.2 ($C^{6'}$), 150.2 (C^2), 139.1 ($C^{4'}$), 138.7 (C^4), 125.6 ($C^{5'}$), 122.1 ($C^{3'}$), 118.6

(C^5), 109.2 (C^3). ^{19}F NMR (470.17 MHz, δ, CD_2Cl_2): -114.9 (m, 2F, F_o^a, F_o^b), -115.1 (m, 2F, F_o^a, F_o^b), -160.9 (t, J = 19.5 Hz, 2F, F_p^a, F_p^b), -164.4 (m, 2F, F_m^a, F_m^b), -164.9 (m, 2F, F_m^a, F_m^b).

*The ^{13}C signals for the C_6F_5 group, heavily coupled to ^{19}F, could not be observed due to the low solubility of this complex.

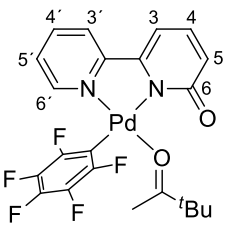


5: ^1H NMR (499.73 MHz, δ, CD_2Cl_2): 8.9 (br, 2H, H_2O), 7.90 (m, 2H, $H^{3'}$, $H^{4'}$), 7.78 (d, J = 5.8, 1H, $H^{6'}$), 7.62 (dd, J = 8.5, 8,5 Hz, 1H, H^4), 7.21 (m, 1H, $H^{5'}$), 7.15 (d, J = 8.5 Hz, 1H, H^3), 6.64 (d, J = 8.5 Hz, 1H, H^5). ^{13}C {^1H} NMR (125.67 MHz, δ, CD_2Cl_2): 168.8 (C^6), 158.9 ($C^{2'}$), 151.5 ($C^{6'}$), 150.2 (C^2), 139.1 ($C^{4'}$), 138.7 (C^4), 126.2 ($C^{5'}$), 122.1 ($C^{3'}$), 118.6 (C^5), 108.8 (C^3). ^{19}F NMR (470.17 MHz, δ, CD_2Cl_2):-120.14 (m, 2F, F_{ortho}), -159.81 (t, J = 19.5 Hz, 1F, F_{para}), -162.86 (m, 2F, F_{meta}).

*The ^{13}C signals for the C_6F_5 group, heavily coupled to ^{19}F, could not be observed due to the low solubility of this complex.

C) Formation of complex **3** from **4**.

Complex **4** (3 mg, 0.0033 mmol) was dissolved in dry CD_2Cl_2 (1 mL) in a 5 mm NMR tube under a nitrogen atmosphere. Different amounts of pinacolone (10 μL and 0.5 mL) were added successively. The evolution of the species were checked by ^{19}F and ^1H NMR. The major complex in the situation shown in Figure S6 (c) (see below) was characterized and assigned to complex **7**.



3: ^1H NMR (499.73 MHz, δ, dry CD_2Cl_2): 8.01 (br, 1H, $H^{3'}$), 7.96 (br, 1H, $H^{4'}$), 7.76 (br 1H, $H^{6'}$), 7.49 (br, 1H, H^4), 7.20 (br, 1H, $H^{5'}$), 7.10 (br, 1H, H^3), 6.49 (d, J = 8.5 Hz, 1H, H^5). ^{13}C {^1H} NMR (125.67 MHz, δ, dry CD_2Cl_2): 152.2 ($C^{6'}$), 139 ($C^{4'}$), 138.6 (C^4), 125.3 ($C^{5'}$), 121.9 ($C^{3'}$), 120.9 (C^5), 107.5 (C^3). ^{19}F NMR (470.17 MHz, δ, dry CD_2Cl_2): -119.61 (m, 2F, F_{ortho}), -160.36 (t, J = 19.5 Hz, 1F, F_{para}), -163.25 (m, 2F, F_{meta}).

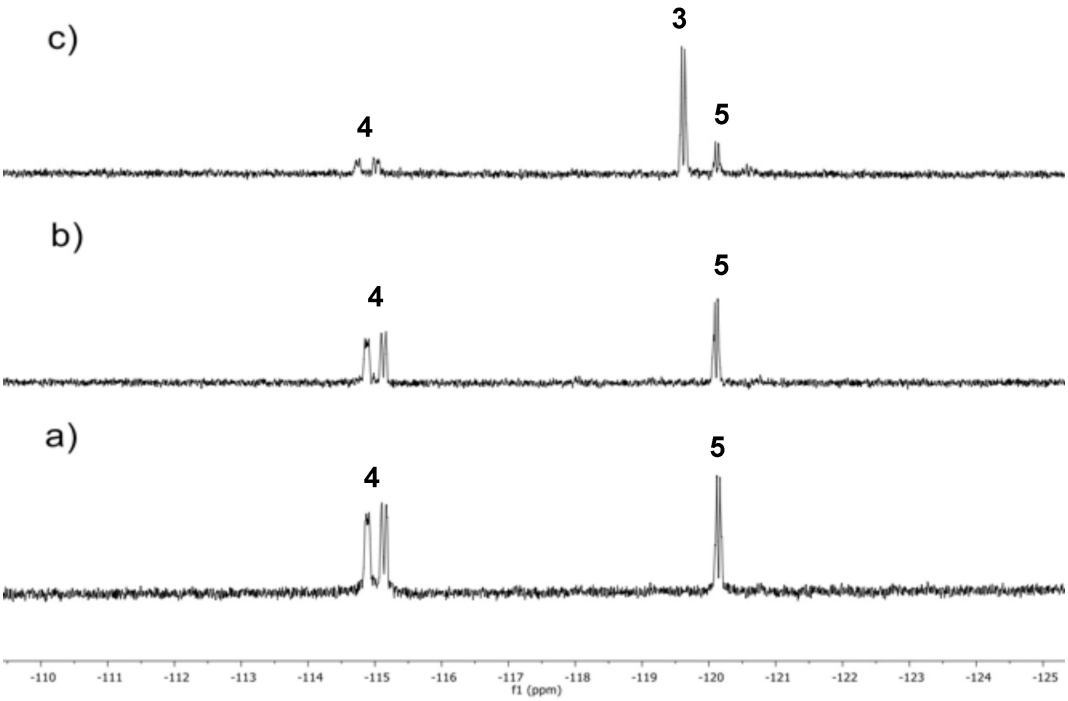


Figure S6. ^{19}F NMR spectra (ortho region) in CD_2Cl_2. a) Complex **4** dissolved in CD_2Cl_2. b) Mixture obtained after adding 10 µL of pinacolone to complex **4** solution in CD_2Cl_2 (ratio Pd:pinacolone = 1:10). c) Mixture obtained after adding 0.5 mL of pinacolone to complex **4** in CD_2Cl_2 (ratio Pd:pinacolone =1:1000).

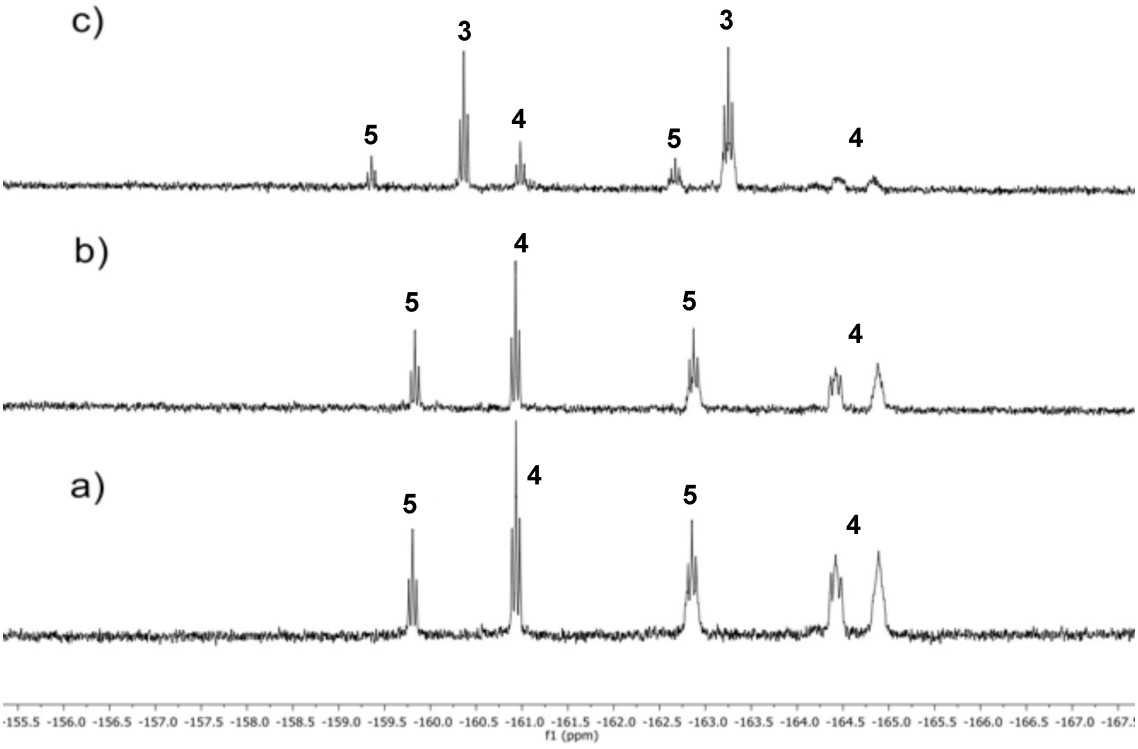


Figure S7. ^{19}F NMR spectra (para and meta region) in CD_2Cl_2. a) Complex **4** dissolved in CD_2Cl_2. b) Mixture obtained after adding 10 µL of pinacolone to complex **4** solution in CD_2Cl_2 (ratio Pd:pinacolone = 1:10). c) Mixture obtained after adding 0.5 mL of pinacolone to complex **4** in CD_2Cl_2 (ratio Pd:pinacolone =1:1000).

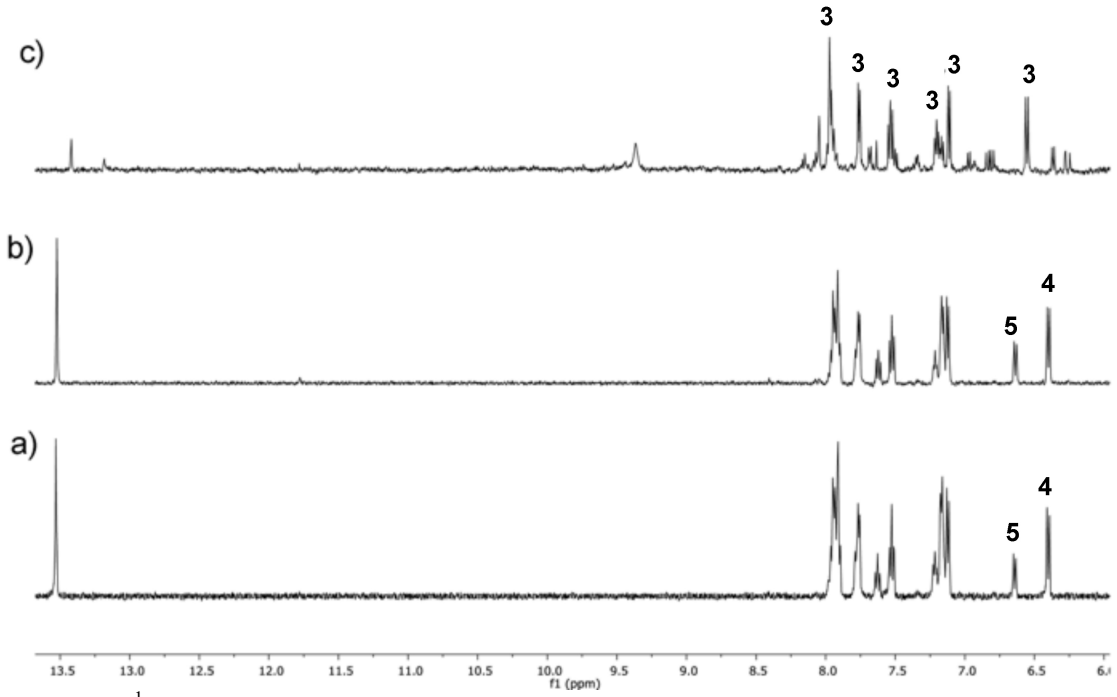


Figure S8. ^{1}H NMR spectra in CD_2Cl_2. a) Complex **4** dissolved in CD_2Cl_2. b) Mixture obtained after adding 10 μL of pinacolone to complex **4** solution in CD_2Cl_2 (ratio Pd:pinacolone = 1:10). c) Mixture obtained after adding 0.5 mL of pinacolone to complex **4** in CD_2Cl_2 (ratio Pd:pinacolone =1:1000).

D) Coordination equilibria between **3** and **6** in toluene/pinacolone

Complex **1** (4 mg, 0.0076 mmol) and solvent (pinacolone, 0.5 mL + toluene, 0.5 mL) were added into a NMR tube along with a sealed glass capillary filled with $(CD_3)_2SO$ as an NMR reference. Then, Cs_2CO_3 (5 mg, 0.015 mmol) was added. The solution was examined by ^{19}F NMR and complexes **3** and **4** were found.

The same experiment was carried out with the soluble $(NBu_4)_2CO_3$ (6.3 mg, 0.11 mmol). The ^{19}F NMR spectrum shows complex **6**. The identity of **6** was checked by comparison with the spectrum of an authentic sample of **6**-NBu_4.[1]

6: ^{19}F RMN (470.17 MHz, 298 K, δ, toluene/pinacolone, $(CD_3)_2SO$ capillary): -117.88 (m, 2F, F_{ortho}), -168.42 (t, J = 22.1 Hz, 1F, F_{para}), -168.84 (m, 2F, F_{meta}).

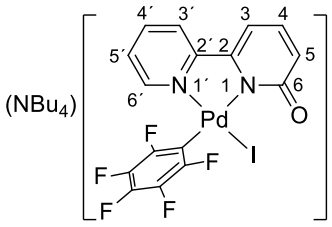
E) Equilibrium constant between **3** and **6-I** in toluene/pinacolone

Complex **1** (13 mg, 0.0247 mmol) and solvent (pinacolone, 1.5 mL + toluene, 1.5 mL) were added into a vial. Then, Cs_2CO_3 (16 mg, 0.0494 mmol) was added and after 15 min stirring the mixture was filtered. The filtrate contained complex **3**, as checked by ^{19}F NMR, and it was transferred to a 5 mL volumetric flask. The exact concentration of the solution of complex **3** was determined by adding 30 μL of an internal standard solution ($C_{12}F_{10}$, 0.0413 M) to 0.4 mL of the solution of **3**. Two aliquots of this solution (1 mL in both; [**7**] = 4.66 mM) were treated with variable amounts of NBu_4I (1.48 mg, 0.004 mmol and 2.19 mg, 0.006 mmol). The ratio of complexes in each solution were determined by ^{19}F NMR using a sealed glass capillary filled with $(CD_3)_2SO$. The mean value of both determination gave $K = 1.6\pm0.1x10^{-4}$ for the equilibrium **6-I** + pinacolone $\rightleftharpoons$ **3** + I^-.

6-I: ^{19}F RMN (470.17 MHz, 298 K, δ, toluene/pinacolone, $(CD_3)_2SO$ capillary): -116.05 (m, 2F, F_{ortho}), -167.83 (t, J = 22.1 Hz, 1F, F_{para}), -168.67 (m, 2F, F_{meta}).

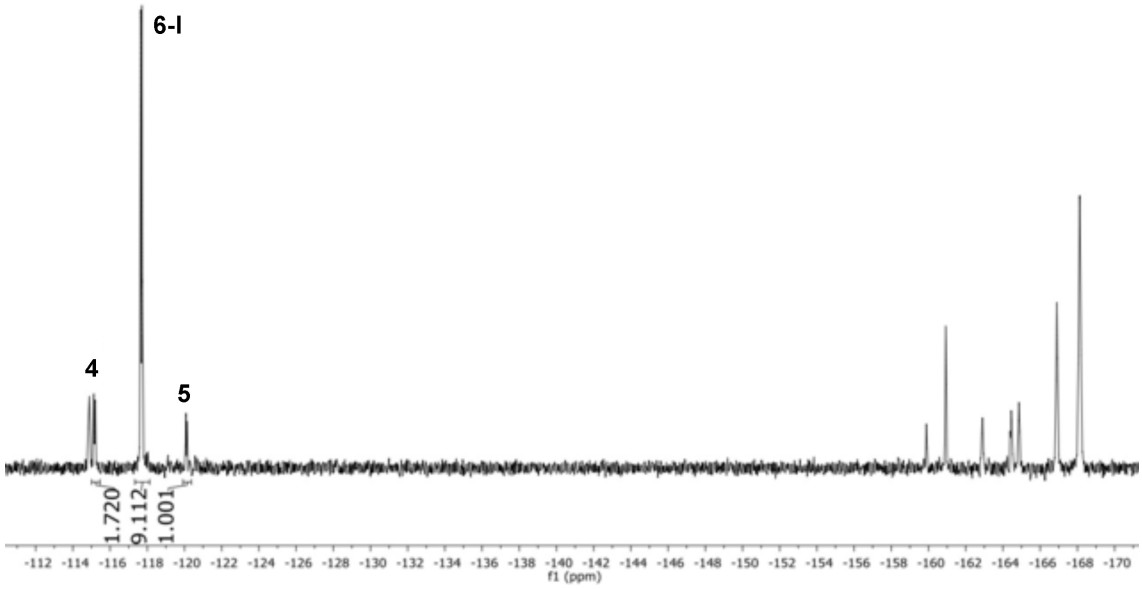
F) Formation of complex (NBu_4)**[6-I]** from **4**.

Complex **4** (1 mg, 0.0011 mmol) was dissolved in dry CD_2Cl_2 (1 mL) in a 5 mm NMR tube under a nitrogen atmosphere. $(NBu_4)I$ (0.8 mg, 0.0022 mmol) was added to the solution and the mixture was checked by ^{19}F and ^1H NMR. It contained a mixture of **4**:**6-I**:**5** = 1.5:9:1 (Figure S9).



6-I: ^1H NMR (499.73 MHz, δ, dry CD_2Cl_2): 9.63 (d, J = 5.9 Hz,1H, $H^{6'}$), 7.83 (m, 2H, $H^{3'}$, $H^{4'}$), 7.25 (ddd, J = 8.7, 5.9, 3.0 Hz, 1H, $H^{5'}$), 7.18 (dd, d, J = 8.1, 6.9 Hz, 1H, H^4), 6.70 (d, J = 6.9 Hz, 1H, H^3), 6.15 (d, J = 8.1 Hz, 1H, H^5), 3.22 (m, 8H, H_{Bu}), 1.64 (m, 8H, H_{Bu}), 1.44 (m, 8H, H_{Bu}), 1.01 (m, 12H, H_{Bu}). $^{13}C\{^1H\}$ NMR (125.67 MHz, δ, dry CD_2Cl_2): 169 (C^6), 159.6 ($C^{2'}$), 153.7 (C^2), 152.6 ($C^{6'}$), 137.7 ($C^{4'}$), 135.8 (C^4), 124 ($C^{5'}$), 121.5 (C^5), 120.8 ($C^{3'}$), 103.9 (C^3), 59.3 (C_{Bu}), 24.1 (C_{Bu}), 20.1 (C_{Bu}), 13.4 (C_{Bu}). ^{19}F NMR (470.17 MHz, δ, dry CD_2Cl_2): -117.55 (m, 2F, F_{ortho}), -166.9 (t, J = 19.5 Hz, 1F, F_{para}), -168.11 (m, 2F, F_{meta}).

a)



b)

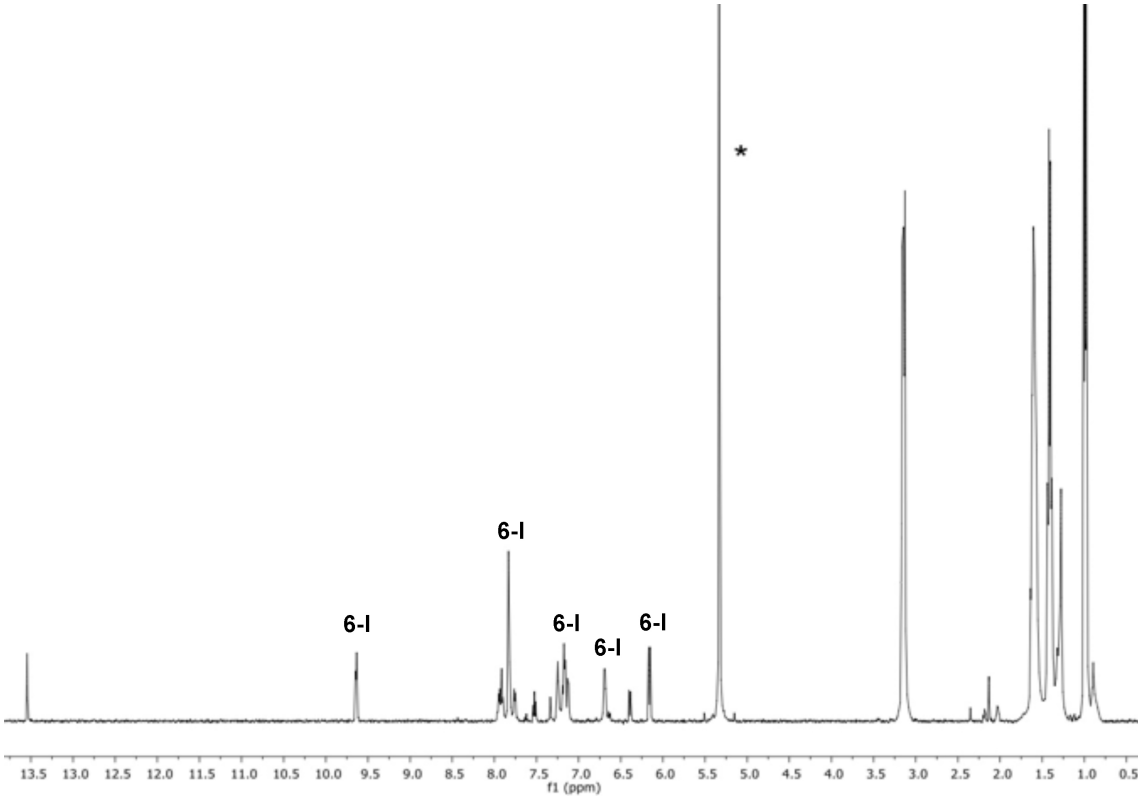


Figure S9. ^{19}F (a) and ^{1}H (b) NMR spectra of the mixture **4**:**6-I**:**5** = 1.5:9:1 in CD_2Cl_2 (only **6-I** is noted for clarity). (*) residual CH_2Cl_2 signal in the solvent.

G) Complex **1** in toluene

Complex [Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 1.3 mg, 0.0025 mmol) and toluene (0.5 mL) were added into an NMR tube along with a sealed glass capillary filled with $(CD_3)_2SO$

as an NMR reference. Almost all the complex remains insoluble at room temperature. Cesium carbonate was added (2.4 mg, 0.0075 mmol) and the suspension was sonicated for 30 min. An intense yellow solid can be observed at the bottom of the NMR tube and the supernatant solution was examined by ^{19}F NMR, showing the presence of some remaining **1** and **4**. When pinacolone was added to the suspension the bright yellow solid was dissolved and the mixture of **3** and **4** was observed (same as Figure S5a).

1: ^{19}F NMR (470.17 MHz, 298 K, δ, toluene, $(CD_3)_2SO$ capillary): -118.95 (m, 2F, F_{ortho}), -159.68 (t, J = 22.1 Hz, 1F, F_{para}), -162.89 (m, 2F, F_{meta}).

4: ^{19}F NMR (470.17 MHz, 298 K, δ, toluene, $(CD_3)_2SO$ capillary): -112.91 (m, 2F, F_{ortho}), -114.16 (m, 2F, F_{ortho}), -161.01 (t, J = 22.1 Hz, 2F, F_{para}), -163.87 (m, 2F, F_{meta}), -165.41 (m, 2F, F_{meta}).

H) Complex **1** in benzonitrile

Complex [Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 1.3 mg, 0.0025 mmol) and benzonitrile (0.5 mL) were added into an NMR tube along with a sealed glass capillary filled with $(CD_3)_2SO$ as an NMR reference. A yellow solution was observed. The species formed were examined by ^{19}F NMR. Cesium carbonate was added (2.4 mg, 0.0075 mmol) and the species formed were examined again by ^{19}F NMR. The spectroscopic data in benzonitrile of the identified species are given below.

The addition of $AgBF_4$ to the mixture formed after adding the base, produces no change in the spectrum and indicates that the species formed do not have a coordinated halide.

1: ^{19}F NMR (470.17 MHz, 298 K, δ, benzonitrile, $(CD_3)_2SO$ capillary): -119.28 (m, 2F, F_{ortho}), -160.23 (t, J = 22.1 Hz, 1F, F_{para}), -162.81 (m, 2F, F_{meta}).

4: ^{19}F NMR (470.17 MHz, 298 K, δ, benzonitrile, $(CD_3)_2SO$ capillary): -114.38 (m, 2F, F_{ortho}), -114.69 (m, 2F, F_{ortho}), -160.54 (t, J = 22.1 Hz, 2F, F_{para}), -164.03 (m, 2F, F_{meta}), -164.42 (m, 2F, F_{meta}).

7: ^{19}F NMR (470.17 MHz, 293 K, δ, benzonitrile, $(CD_3)_2SO$ capillary): -118.91 (m, 2F, F_{ortho}), -160.18 (t, J = 22.1 Hz, 1F, F_{para}), -162.84 (m, 2F, F_{meta}).

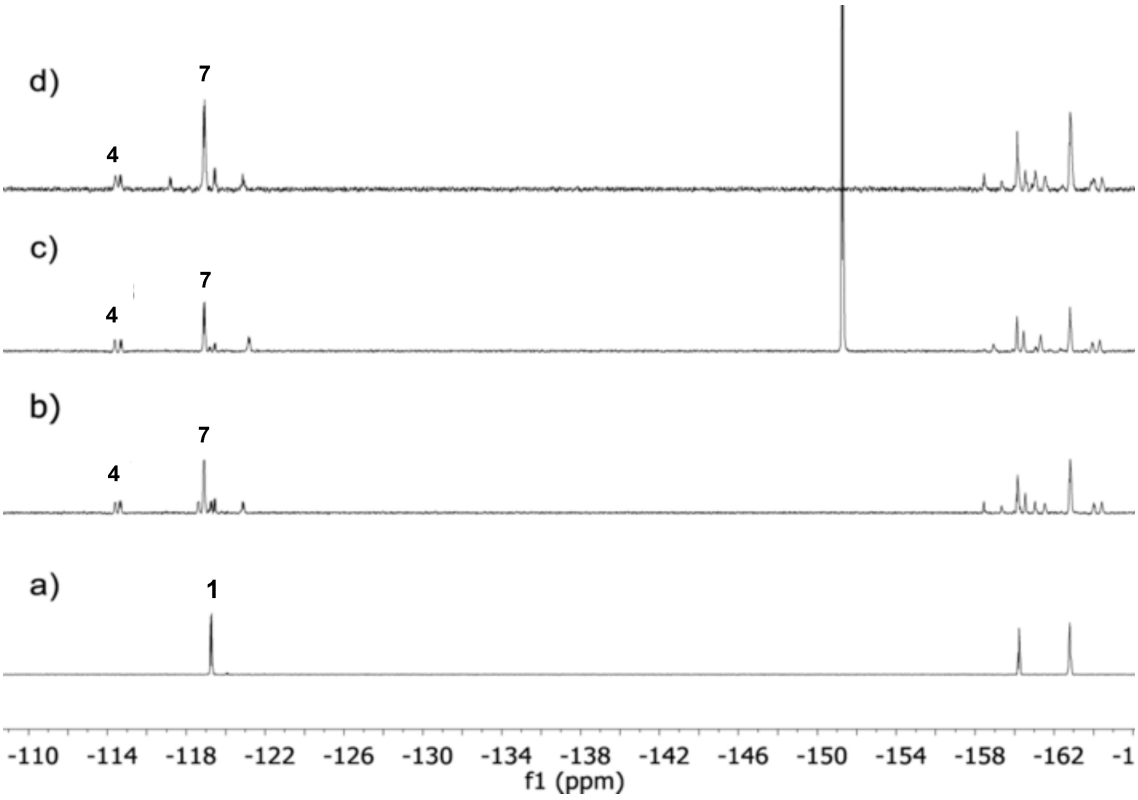
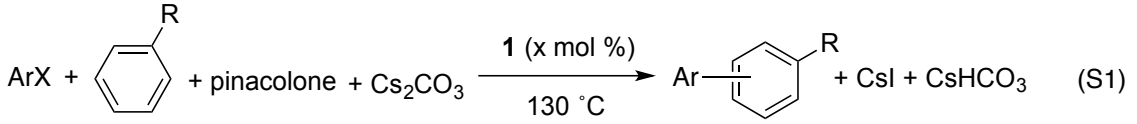


Figure S10. ^{19}F NMR spectra in benzonitrile as solvent using a DMSO-d6 capillary. a) Complex **1** in benzonitrile. b) Complex **1** in benzonitrile after adding Cs_2CO_3. c) mixture b with $AgBF_4$. d) Complex **8** isolated independently and dissolved in benzonitrile. Only the $^{19}F_{ortho}$ region is labeled for clarity.

1.3.3. ***Kinetic Experiments.***

The dependence of the rate of the reaction in Eq. S1 on the different reagents was examined as specified below.



(S1)

Assessment of the kinetic order in aryl halides.

[Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 9 mg, 0.017 mmol) and cesium carbonate (222.0 mg, 0.68 mmol) were introduced in a Schlenk flask with a screw cap equipped with a teflon stirring bar in a nitrogen atmosphere. Then, toluene (3 mL) or a mixture of toluene:pinacolone = 1:1 (total volume 3 mL) and the corresponding amount of 4-iodobenzotrifluoride, 4-iodoanisole or 4-bromobenzotrifluoride were added. Then, the Schlenk flasks were placed in the same pre-heated oil bath at 130 ˚C with constant

stirring. After the allotted time, an aliquot was taken and analyzed by ^{19}F NMR using a sealed glass capillary filled with $(CD_3)_2SO$ as NMR reference. The concentration of the product was determined by integration of the distinct trifluoromethyl signals (^{19}F NMR, Ar = *p*-$CF_3C_6H_4$) of reagent and products or the methoxy group signals (^1H NMR) in the case of 4-iodoanisole.

Table S3. Initial concentrations of ArX and concentrations of the coupling product Ar-PhR formed (Eq. S1) after the allotted time.[a]

Entry	ArX	Arene/solvent	$[ArX]_0$ (M)	[Ar-Tol] (M)
1	*p*-$CF_3C_6H_4I$	Toluene	0.11	0.033[b]
2			0.22	0.020[b]
3		Toluene/pinacolone	0.11	0.046[c]
4			0.22	0.029[c]
5	*p*-$CF_3C_6H_4Br$	Toluene	0.11	0.044[d]
6			0.22	0.045[d]
7		Toluene/pinacolone	0.11	0.090[e]
8			0.22	0.086[e]
9	*p*-$CF_3C_6H_4I$	Benzonitrile/pinacolone	0.11	0.020[f]
10			0.22	0.018[f]
11	*p*-$OMeC_6H_4I$	Toluene	0.11	0.014[g]
12			0.22	0.011[g]

[a] Reaction conditions: **1** (9 mg, 0.017 mmol), Cs_2CO_3 (222 mg, 0.68 mmol); ArX (0.11 M o 0.22 M), solvent: toluene (3 mL) or toluene (1.5 mL) + pinacolone (1.5 mL); 130 ºC. [b] Reaction time: 3h. [c] Reaction time: 30 min. [d] Reaction time: 6 h. [e] Reaction time: 1h. [f] Reaction time: 2 h. [g] Reaction time: 4 h.

As can be seen in Table S3 a distinct inhibition effect upon increase of the initial concentration of *p*-$CF_3C_6H_4I$ is observed in toluene or toluene/pinacolone (entries 1-2 and 3-4, Table S3). This is not observed for the same aryl halide in benzonitrile or for the analogous aryl bromide. We hypothesized that the softer more electron-donating iodide (vs. bromide) substituent could compete with the arene for coordination to the metal. Indeed the DFT calculations of the equilibria depicted in Eq. S2 show that this could be the case for the iodoarene in toluene (Keq = 11.5) whereas this ArI in benzonitrile or the ArBr do not show a higher coordinating ability (Table S4). Nonetheless the situation could be more complex and to ascertain the exact origin of this effect further studies are needed.

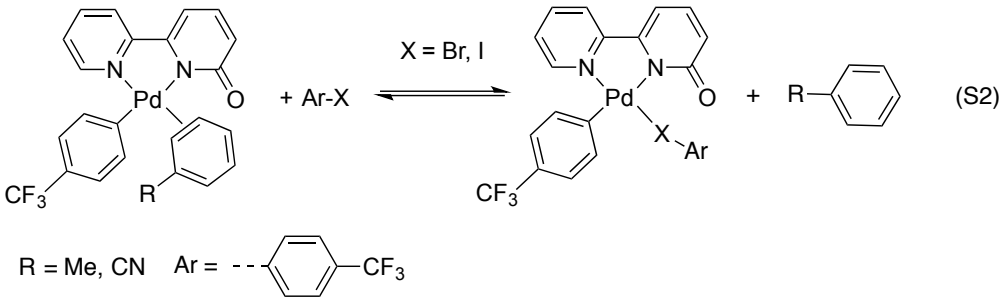


Table S4. Gibbs free energies and Keq for the equilibria shown in Eq. S2 calculated by DFT methods.[a]

Entry	Arene	ArX	ΔG_r (kcal mol^{-1})[a]	K_{eq}
1	toluene	*p*-$CF_3C_6H_4I$	-1.95	11.45
2		*p*-$CF_3C_6H_4Br$	1.34	0.19
3	benzonitrile	*p*-$CF_3C_6H_4I$	4.41	0.0004

[a] All the calculations were carried out at 403.15 K in toluene or benzonitrile solutions (SMD model); see computational methods below for details.

Assessment of the kinetic order in catalyst.

The amount of [Pd(bipy-6-OH)Br(C_6F_5)] (**1**) corresponding to each experiment and cesium carbonate (222.0 mg, 0.68 mmol) were introduced in a Schlenk flask with a screw cap equipped with a teflon stirring bar in a nitrogen atmosphere. Then, toluene (3 mL) or a mixture of toluene:pinacolone = 1:1 (total volume 3 mL) and the corresponding amount of 4-iodobenzotrifluoride or 4-bromobenzotrifluoride were added. Then, the Schlenk flasks were placed in the same pre-heated oil bath at 130 ˚C with constant stirring. After the allotted time, an aliquot was taken and analyzed by ^{19}F NMR using a sealed glass capillary filled with $(CD_3)_2SO$ as NMR reference. The concentration of the product was determined by integration of the distinct trifluoromethyl signals (^{19}F NMR, Ar = *p*-$CF_3C_6H_4$) of reagent and products.

Table S5. Initial concentrations of catalyst **1** and concentrations of the coupling product Ar-Tol formed (Eq. S1) after 3 h at 130 ºC.[a]

Entry	ArX	[Pd] (mM)	[Ar-Tol] (M)[b]
1	*p*-CF_3-C_6H_4I	1.4	0.0055
2		2.8	0.016
3		5.7	0.031

[a] Reaction conditions: *p*-$CF_3C_6H_4I$ (51 µL, 0.34 mmol), Cs_2CO_3 (222.0 mg, 0.34 mmol), toluene (3 mL); 130 ºC. [b] Reaction time: 3 h.

Table S6. Initial concentrations of catalyst **1** and concentrations of the coupling product Ar-Tol formed (Eq. S1) after the alloted time at 130 ºC.[a]

Entry	ArX	Arene/Solvent	[Pd] (mM)	[Ar-Tol] (M)
1	*p*-CF_3-C_6H_4Br	Toluene	1.4	0.013[b]
2			2.8	0.022[b]
3			5.7	0.042[b]
4		Toluene/Pinacolone	1.4	0.012[c]
5			2.8	0.026[c]
6			5.7	0.044[c]

[a] Reaction conditions: *p*-$CF_3C_6H_4Br$ (48 µL, 0.34 mmol), Cs_2CO_3 (222.0 mg, 0.34 mmol), toluene (3 mL) or toluene (1.5 mL) + pinacolone (1.5 mL); 130 ºC. [b] Reaction time: 6 h. [c] Reaction time: 30 min.

Dependence on the toluene concentration

[Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 9 mg, 0.017mmol) and cesium carbonate (222.0 mg, 0.68 mmol) were introduced in a Schlenk flask with a screw cap equipped with a teflon stirring bar in a nitrogen atmosphere. Then, toluene and pinacolone were added to reach the volume ratio 1:1, 1:2, 1:4 and 1:5 in a total of 3 mL for each experiment. Finally, 4-iodobenzotrifluoride (51µL, 0.34 mmol) was added. The Schlenk flasks were placed in the same pre-heated oil bath at 130 ˚C with constant stirring. After the specified time, an aliquot was taken and analyzed by ^{19}F NMR using a sealed glass capillary filled with $(CD_3)_2SO$ as NMR reference. The concentration of the product was determined by integration of the distinct trifluoromethyl signals (^{19}F NMR, Ar = *p*-$CF_3C_6H_4$) of reagent and products (see Table S7).

The data in Table S7 show a linear dependence of the crude yield on the toluene concentration up to 3.1 M (entries 1-2) but a saturation behavior is observed for higher concentrations (cf. entries 3 and 4).

Table S7. Crude yields of Ar-Tol for the reaction shown in Eq S1 (R = Me; ArX = *p*-$CF_3C_6H_4I$) after the allotted time at 130 ºC.

Entry	Toluene/ pinacolone	[toluene] (M)	% Crude yield Ar-Tol (% conversion), 30 min[a]
1	1:9	0.9	31 (47)
2	1:4	1.9	48 (64)
3	1:2	3.1	72 (83)
4	1:1	4.7	69 (78)

[a] The formation of the products ArH and Ar-Ar account for the differences between crude yield and conversion.

Dependence on the free halide concentration

[Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 9 mg, 0.017mmol) and cesium carbonate (222.0 mg, 0.68 mmol) were introduced in a Schlenk flask with a screw cap equipped with a teflon stirring bar in a nitrogen atmosphere. Then, toluene (3 mL) or a mixture of toluene:pinacolone = 1:1 (total of 3 mL), the corresponding amount of 4-iodobenzotrifluoride (51μL, 0.34 mmol) and the indicated amount of NBu_4I were added. Then, the Schlenk flasks were placed in the same pre-heated oil bath at 130 ˚C with constant stirring. After the allotted time, an aliquot was taken and analyzed by ^{19}F NMR using a sealed glass capillary filled with $(CD_3)_2SO$ as NMR reference. The concentration of the product was determined by integration of the distinct trifluoromethyl signals (^{19}F NMR, Ar = *p*-$CF_3C_6H_4$) of reagent and products (see Table S8).

The data in Table S8 show just the qualitative effect of free halide on the reaction: A clear decrease in rate upon halide addition in toluene (cf. entries 2 and 3) vs. no effect in toluene/pinacolone (cf. entries 6 and 7). However the presence of Cs_2CO_3 may lead to ion exchange with NBu_4I and the formation of insoluble CsI. Therefore the actual halide concentration in solution is lower than that calculated based on the halide salt added and this does not allow to determine the halide dependence on the rate law. This also explains the negligible effect upon addition of 5 mol% of the iodide salt (cf. entries 1 and 2).

Table S8. Concentrations of the coupling product Ar-Tol formed (Eq. S1) in the presence of NBu_4I after the alloted time at 130 ºC.

Entry	ArI	Arene/Solvent	Additive (mol%)	[Ar-Tol] (M)
1	*p*-CF_3-C_6H_4I	Toluene	-	6h: 0.070
2	*p*-CF_3-C_6H_4I	Toluene	NBu_4I (5)	6h: 0.073
3	*p*-CF_3-C_6H_4I	Toluene	NBu_4I (10)	6h: 0.047
4	*p*-CF_3-C_6H_4I	Toluene	NBu_4I (200)	6h: 0.004[a]
5	*p*-CF_3-C_6H_4I	Toluene/Pinacolone	-	30min: 0.076
6	*p*-CF_3-C_6H_4I	Toluene/Pinacolone	NBu_4I (5)	30min: 0.072
7	*p*-CF_3-C_6H_4I	Toluene/Pinacolone	NBu_4I (10)	30min: 0.073
8	*p*-CF_3-C_6H_4I	Toluene/Pinacolone	NBu_4I (200)	30min: 0.010[a]

[a] Conversion 100 %; the major products are ArH y Ar-Ar.

General procedure for the determination of the KIE

Two Schlenk flasks equipped with a screw cap and a Teflon stirring bar were charged in a nitrogen atmosphere with [Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 3.0 mg, 0.0057 mmol) and cesium carbonate (74.0 mg, 0.22 mmol). 4-Iodobenzotrifluoride (17μL, 0.11 mmol) was added to each flask. Then, toluene-d8 (1 mL) was added to one flask and toluene (1 mL) to the other. The Schlenk flasks were placed in a pre-heated oil bath at 130 ˚C with constant stirring. After the allotted time, an aliquot was taken and analyzed by ^{19}F NMR using a sealed glass capillary filled with DMSO-d_8 as NMR reference. The concentration of the product was determined by integration of the distinct trifluoromethyl signals of reagent and products. The ratio of product concentrations in these independently experiments determine the ratio of reaction rate constants (k_H/k_D) giving the reported KIE value (see Table S9).

The experiments in the toluene/pinacolone mixture were carried out in the same way adding a mixture of pinacolone (0.5 mL)/toluene-d8 (0.5 mL) to one flask and a mixture of pinacolone (0.5 mL) / toluene (0.5 mL) to the other.

Table S9. KIE values determined in independent experiments.[a]

Entry	Arene/solvent	KIE (Exp A)
1	Toluene	1.5±0.2[b]
2	Toluene/Pinacolone	2.8±0.3[c]

[a] Average of three determinations. [b] Reaction time: 3 h. [c] Reaction time: 30 min.

1.3.4. ***Coupling experiments in the presence acetone-d6.***

Catalytic reaction with acetone-d6 (Eq. 3, main text): [Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 9.0 mg, 0.017 mmol) and cesium carbonate (222 mg, 0.68 mmol) were introduced in a Scklenk flask with a screw cap in a nitrogen atmosphere. Then, toluene (2 mL), acetone-d6 (1 mL) and 4-iodobenzotrifluoride (51 μL, 0.34 mmol) were added. Then, the mixture was kept in a preheated-bath at 130 ˚C for 24 h. After that time, total conversion was observed by ^{19}F NMR of the crude mixture. Finally the solvent mixture was removed under vacuum and the organic products were isolated as described in the general procedure. The GC/MS (EI, 70 eV) spectrum of the organic products shows the coupling products C_6F_5-C_6D_4-CH_3 with a m/z = 262 [M^+] and *p*-CF_3-C_6H_4-C_6H_4-*m*-CH_3, *p*-CF_3-C_6H_4-C_6H_4-*p*-CH_3, *p*-CF_3-C_6H_4-C_6H_4-*o*-CH_3 (Ar-Tol), each of them with a m/z = 236 [M^+].

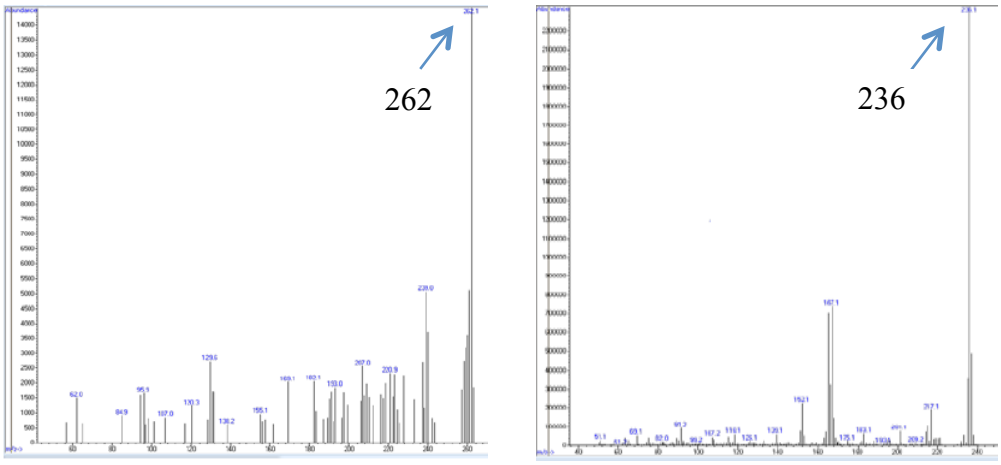


Figure S11. Mass spectra of the organic products obtained in the catalytic reaction shown in Eq. 3 (main text). Left: C_6F_5-C_6D_4-*m*-CH_3. Right: one of the isomers of Ar-Tol, *p*-CF_3-C_6H_4-C_6H_4-*m*-CH_3

Decomposition of **1** in the presence of acetone-d6. [Pd(bipy-6-OH)Br(C_6F_5)] (**1**, 8 mg, 0.015 mmol) and cesium carbonate (15 mg, 0.045 mmol) were introduced in a Schlenk flask with a screw cap in a nitrogen atmosphere. Then, toluene (1 mL) was added. The mixture was kept in constant stirring for two hours. After that, acetone-d6 (0.5 mL) was added and the Schlenk flask was introduced in a preheated-bath at 130 ºC for one hour. The resulting mixture was analyzed by ^{19}F NMR where two isomers of the coupling product, C_6F_5-C_6D_4-CH_3, were observed. Finally, the solvent was removed under vacuum and the organic products were isolated as described in the general procedure. The GC/MS (EI, 70 eV) spectrum of the organic products shows two isomers of the coupling product C_6F_5-C_6D_4-CH_3 both with a m/z = 262 (100) [M^+].

1.3.5. ***Decomposition of ArI in different solvents under catalytic conditions.***

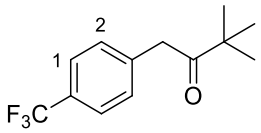
[Pd(bipy-6-OH)Br(C_6F_5)] (**1**) (9.0 mg, 0.017 mmol) and cesium carbonate (222 mg, 0.68 mmol) were introduced in a Scklenk flask with a screw cap in a nitrogen atmosphere. Then, the corresponding solvent (3 mL) and 4-iodobenzotrifluoride (51 µL, 0.34 mmol) were added. The mixture was kept in a preheated-bath at 130 ˚C. After 90 min, 6 h and 24 h, the conversion was checked by ^{19}F NMR of the crude mixture to evaluate the amount of unreacted aryl halide. The results are collected in Table S10.

Table S10. Decomposition of *p*-$CF_3C_6H_4I$ in different solvents under catalytic conditions.

Entry	Solvent	Remaining ArI (%)		
		90 min	6 h	24 h
1	pinacolone	83	21	0
2	DMSO	96	86	64
3	DMA	100	93	80
4	DMF	95	53	0

ArH and Ar-Ar (Ar = *p*-$CF_3C_6H_4$) are observed as well as other unidentified decomposition products. In the case of pinacolone as solvent, the aryl-pinacolone coupling product can be isolated albeit with low yield.

3,3-dimethyl-1-(4-(trifluoromethyl)phenyl)butan-2-one: 12 mg (15% yield). ^{1}H NMR (499.73 MHz, δ, $CDCl_3$): 7.57 (d, 2H, H^1), 7.29 (d, 2H, H^2), 3.86 (s, 2H, CH_2), 1.22 (s, 9H, *t*-Bu). ^{19}F NMR (470.17 MHz, δ, $CDCl_3$): -62.54 (s, CF_3). MS (EI, 70 eV): m/z (%) 244 (15) [M^+], 229 (70) [M^+-CH_3], 159 (100) [M^+-CH_3-CF_3-H].



1.3.6. ***Determination of the solubility of CsI.***

Cesium iodide (60 mg, 0.23 mmol) was added in two Schlenk flasks. Then, toluene (16 mL) was added in one of the flasks and a mixture 1:1 of toluene/pinacolone (total volume 16 mL) was added in the other one. Both Schlenk flasks were introduced in a preheated bath at 90 ºC during 24 h and then worked up independently in the same way: An aliquot of 5 mL was taken and introduced in a vial. The solvent was evaporated and the mass of the solid residue was analyzed by ICP-MS (water solutions diluted to reach a suitable concentration).

Table S11. Determination of the [CsI] in different solvents at 90 ˚C by ICP-MS.

Entry	Solvent	Sample weight (mg)	Mass % CsI (ICP-MS)	[CsI] (M)
1	Toluene	2.17	6.04	10^{-4}
2	Toluene/pinacolone	6.47	4.97	$2.4x10^{-4}$

2- Data for X-ray structure determination

Crystals suitable for X-ray analyses were obtained by slow vapor-diffusion of pentane to a solution of complex $[Pd_2(bipy\text{-}6\text{-}O)_2(C_6F_5)_2(\mu\text{-}OH_2)]$ (**4**) in CH_2Cl_2 at 0 ºC. The crystal was attached to a glass fiber and transferred to an Agilent Supernova diffractometer with an Atlas CCD area detector. Data collection was performed with Mo Kα radiation (0.71073 Å) at 213 K. Data integration, and empirical absorption correction was carried out using the CrysAlisPro program package.[24] The structure was solved using Olex2,[25] with the olex2.solve,[26] and refined with Shelx program.[27] The non-hydrogen atoms were refined anisotropically and hydrogen atoms were constrained to ideal geometries and refined with fixed isotropic displacement parameters except for the hydrogens of the water molecule that were located in the Fourier map. Refinement proceeded smoothly to give the residuals shown in Table S12.

The molecular structure is shown in Figure S12. Selected distances and angles are collected in Table S13.

Table S12. Crystal data and structure refinement for complex **4**.

Empirical formula	$C_{34}H_{17}Cl_{3.5}F_{10}N_4O_3Pd_2$	ρ_{calc}g/cm^3	2.000
Formula weight	1056.39	μ/mm^{-1}	1.389
Crystal color and habit	Yellow prism	F(000)	1029.0
Temperature/K	213.00(14)	Crystal size/mm^3	0.33 × 0.211 × 0.103
Crystal system	triclinic	Radiation	MoKα (λ = 0.71073)
Space group	P-1	2θ range for data collection/°	6.656 to 59.002
a/Å	11.4134(5)	Index ranges	-10 ≤ h ≤ 15, -14 ≤ k ≤ 16, -16 ≤ l ≤ 17
b/Å	11.7795(5)	Reflections collected	12293
c/Å	14.2283(6)	Independent reflections	7994 [R_{int} = 0.0292, R_{sigma} = 0.0675]
α/°	112.372(4)	Data/restraints/parameters	7994/0/519
β/°	96.046(3)	Goodness-of-fit on F^2	1.056
γ/°	91.729(3)	Final R indexes [I>=2σ (I)]	R_1 = 0.0528, wR_2 = 0.1140
Volume/Å^3	1753.95(14)	Final R indexes [all data]	R_1 = 0.0789, wR_2 = 0.1353
Z	2	Largest diff. peak/hole / e Å^{-3}	1.62/-1.31

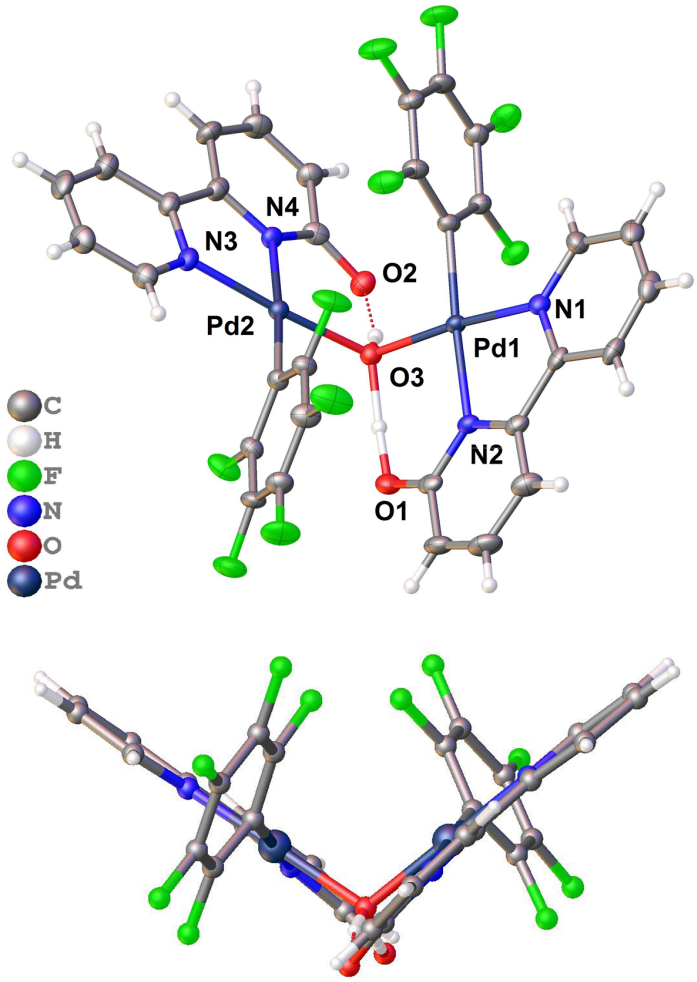


Figure S12. X-ray molecular structure of $[Pd_2(bipy\text{-}6\text{-}O)_2(C_6F_5)_2(\mu\text{-}OH_2)]$ (**4**). ORTEP plots (30% probability ellipsoids) are shown. Hydrogen atoms are omitted for clarity except those of the bridging water molecule. The complex crystallizes with two CH_2Cl_2 molecules that have also been omitted.

Table S13. Selected distances (Å) and angles for $[Pd_2(bipy\text{-}6\text{-}O)_2(C_6F_5)_2(\mu\text{-}OH_2)]$ (**4**).

Pd1-N1	2.002	O3-H2A	1.768
Pd1-N2	2.064	O2-H2A	0.790
Pd1-C11	2.010	Pd1-N1-N2	80.50(18)
Pd1-O2	2.033	Pd1-N1-C11	94.7(2)
C10-O1	1.280	Pd1-C11-O2	91.0(2)
O1-H2B	1.199	Pd1-N2-O2	93.71(17)
O2-H2B	1.371	N2-C10-O1	120.2(5)
Pd2-N3	2.011	Pd2-N3-N4	80.70(19)
Pd2-N4	2.071	Pd2-N3-C27	96.0(2)
Pd2-C27	2.006	Pd2-C27-O2	89.5(2)
Pd2-O2	2.031	Pd2-N4-O2	93.81(18)
C26-O3	1.298	N4-C26-O3	119.4 (5)

3- Selected Spectra

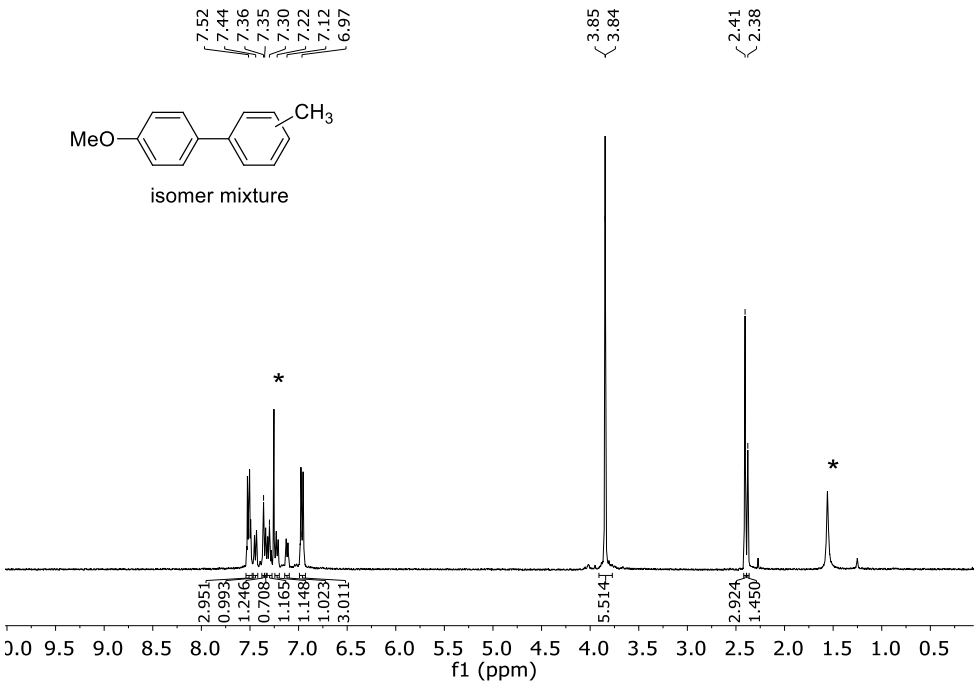


Figure S13. ^{1}H NMR (499.73, $CDCl_3$) of an isomer mixture of 4'-methoxy-3-methyl-1,1'-biphenyl and 4'-methoxy-4-methyl-1,1'-biphenyl (2:1) at 298 K. * Signal corresponding to the solvent (chloroform and H_2O).

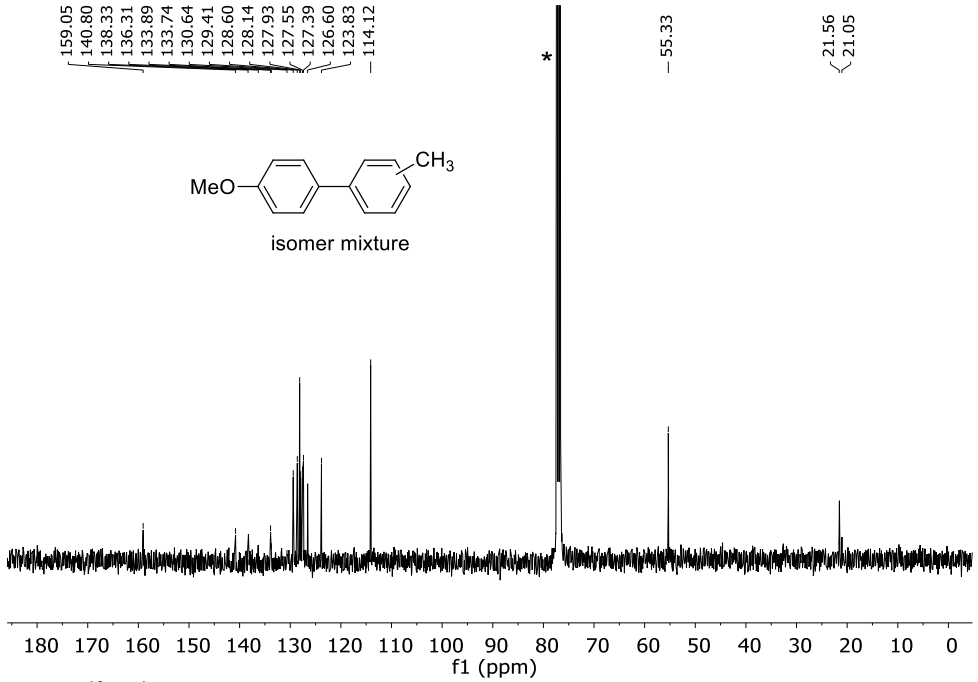


Figure S14. $^{13}C\{^{1}H\}$ NMR (125.67 MHz, $CDCl_3$) of an isomer mixture of 4'-methoxy-3-methyl-1,1'-biphenyl and 4'-methoxy-4-methyl-1,1'-biphenyl (2:1) at 298 K. * Signal corresponding to the solvent (chloroform).

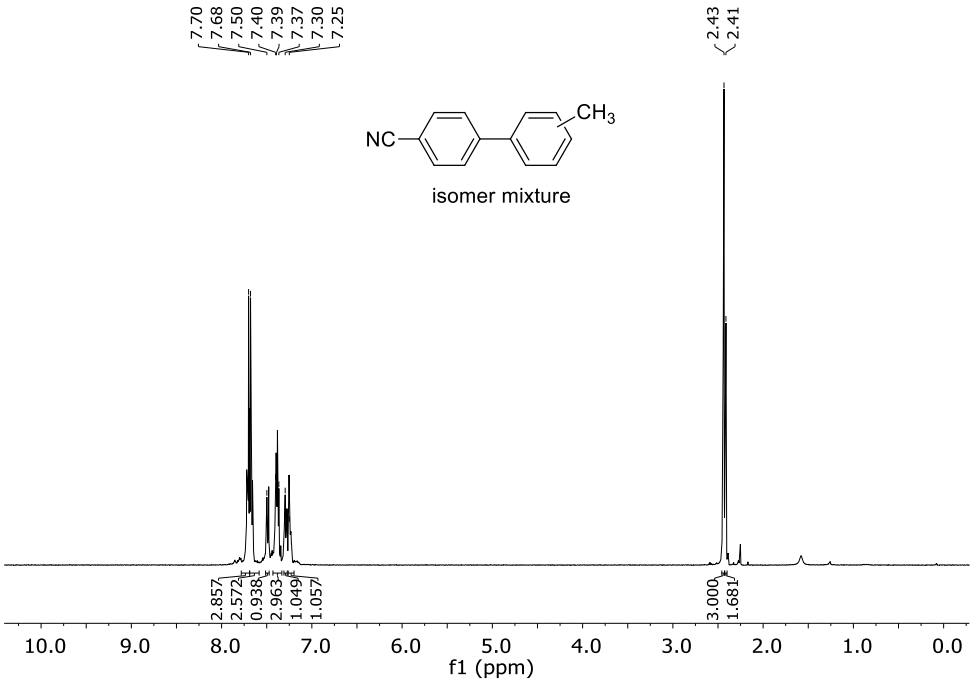


Figure S15. ^{1}H NMR (499.73, $CDCl_3$) of an isomer mixture of 3'-methyl-[1,1'-biphenyl]-4-carbonitrile and 4'-methyl-[1,1'-biphenyl]-4-carbonitrile (1.7:1) at 298 K.

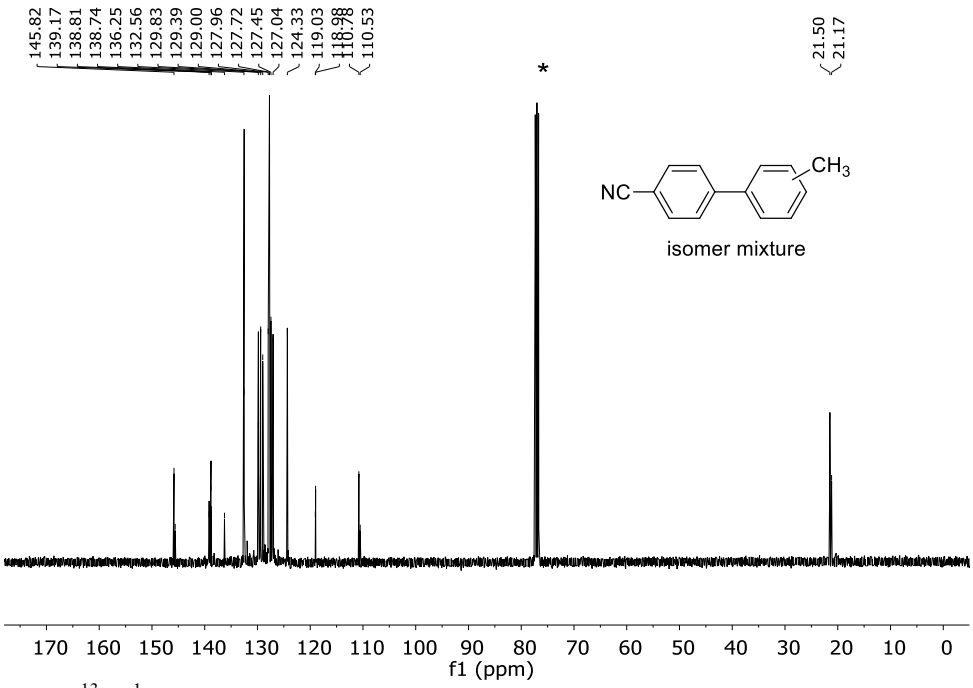


Figure S16. $^{13}C\{^{1}H\}$ NMR (125.67 MHz, $CDCl_3$) of an isomer mixture of 3'-methyl-[1,1'-biphenyl]-4-carbonitrile and 4'-methyl-[1,1'-biphenyl]-4-carbonitrile (1.7:1) at 298 K. * Signal corresponding to the solvent (chloroform).

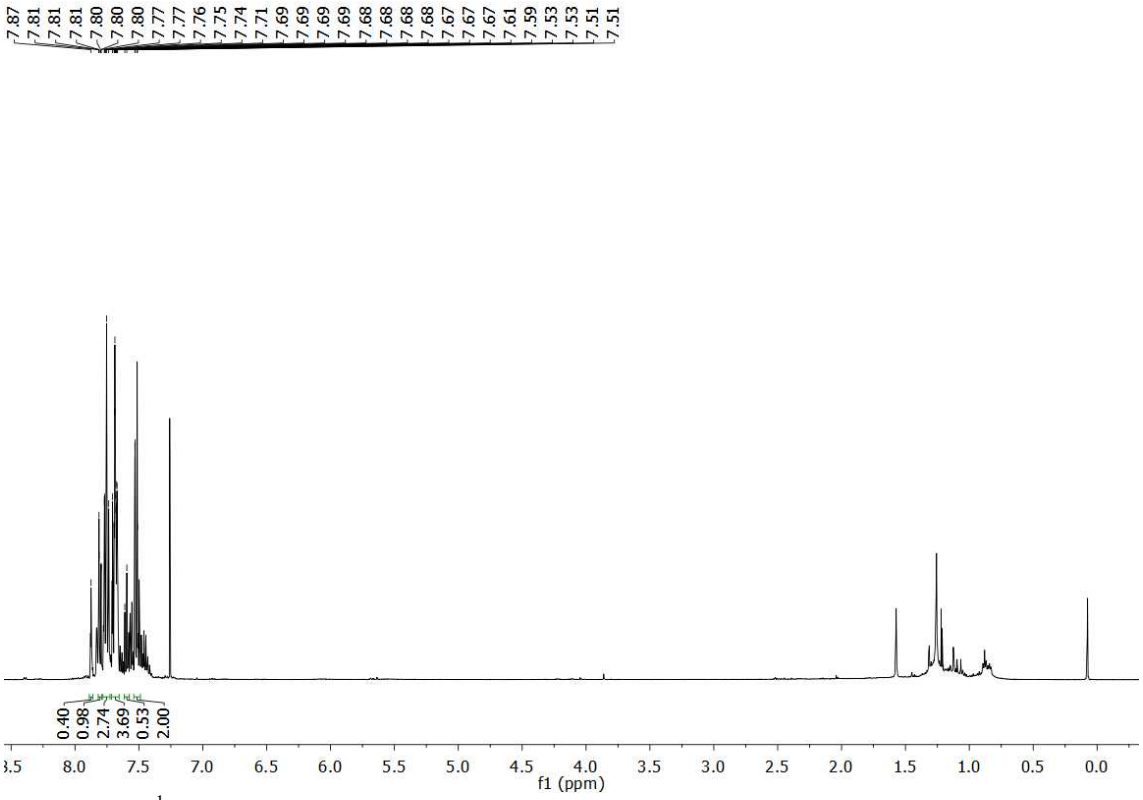


Figure S17. ^{1}H NMR (499.73, $CDCl_3$) of an isomer mixture of 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile, 4'-(trifluoromethyl)-[1,1'-biphenyl]-3-carbonitrile and 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile (6:3:1) at 298 K.

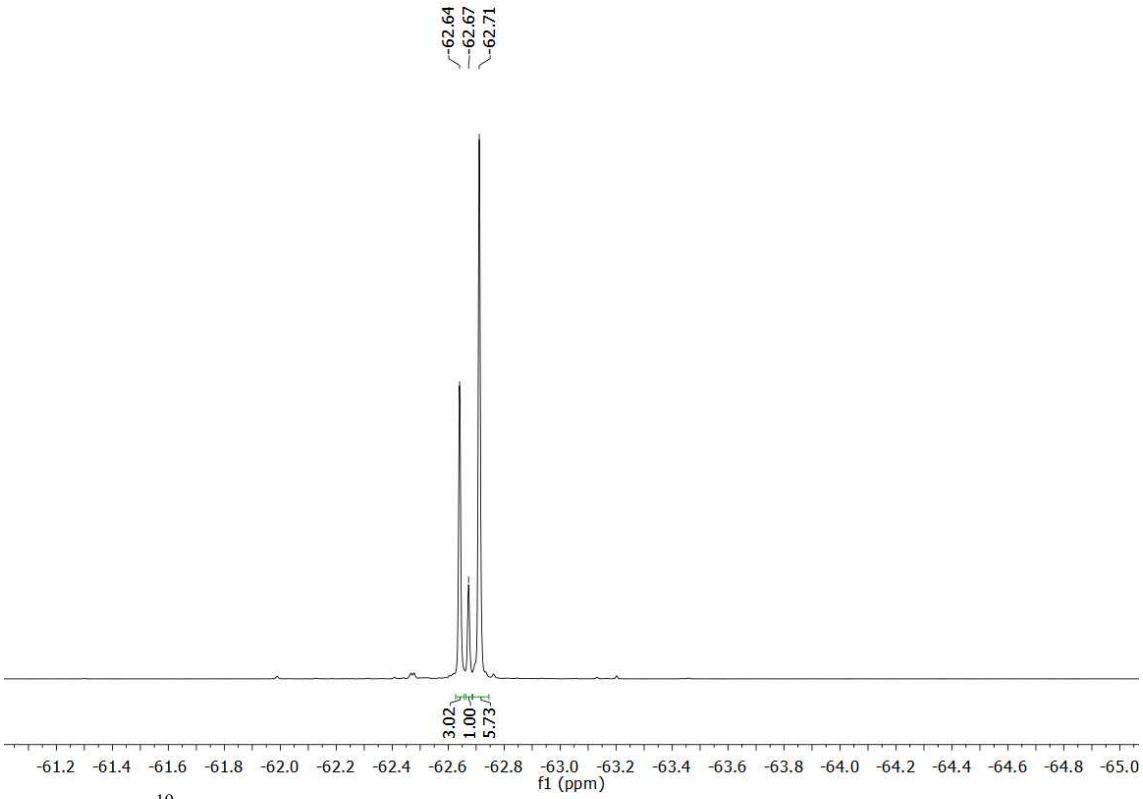


Figure S18. ^{19}F NMR (470.17 MHz, $CDCl_3$) of an isomer mixture of 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile, 4'-(trifluoromethyl)-[1,1'-biphenyl]-3-carbonitrile and 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile (6:3:1) at 298 K.

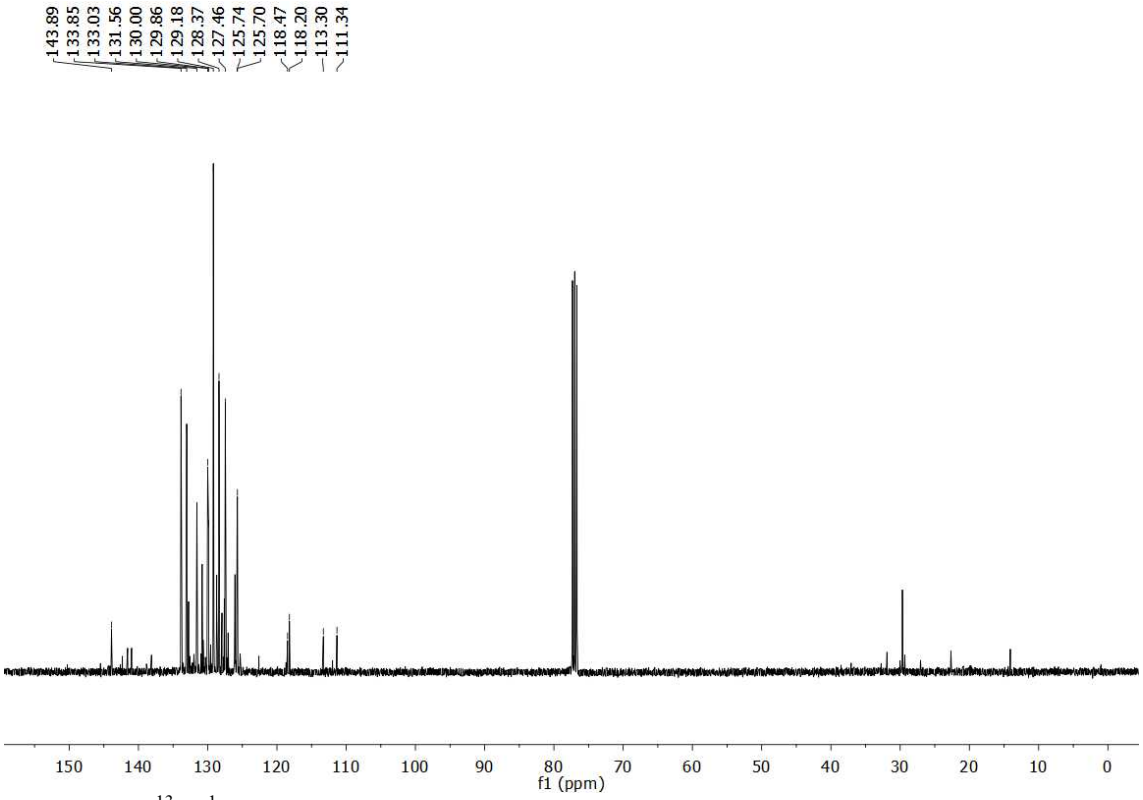


Figure S19. $^{13}C\{^{1}H\}$ NMR (125.67 MHz, $CDCl_3$) of an isomer mixture of 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-carbonitrile, 4'-(trifluoromethyl)-[1,1'-biphenyl]-3-carbonitrile and 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile (6:3:1) at 298 K.

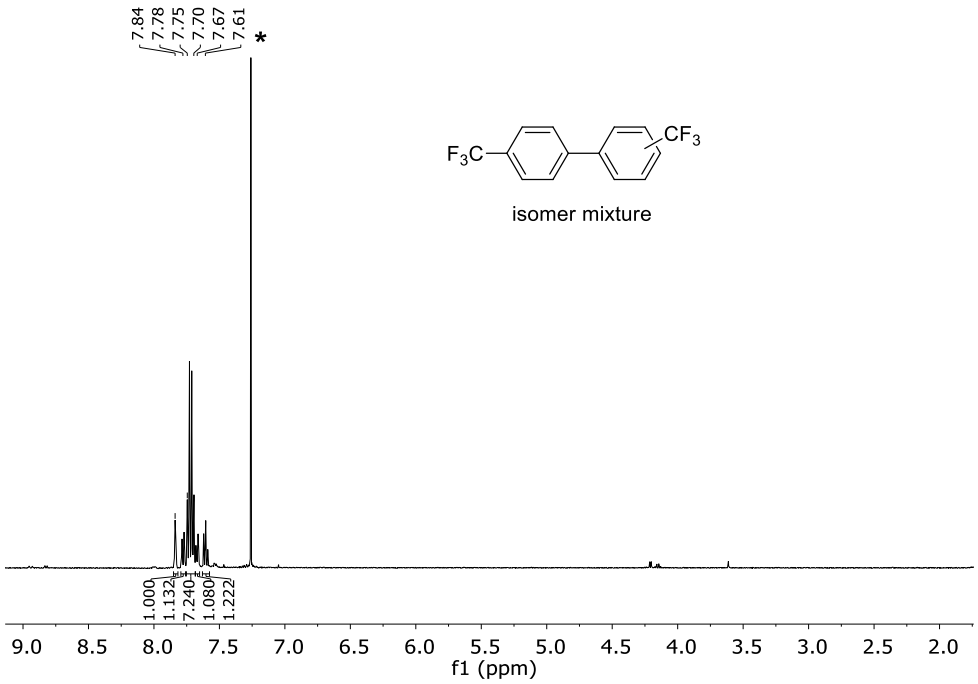


Figure S20. ^{1}H NMR (499.73, $CDCl_3$) of an isomer mixture of 3,4'-bis(trifluoromethyl)-1,1'-biphenyl, and 4,4'-bis(trifluoromethyl)-1,1'-biphenyl (2:1) at 298 K. * Signal corresponding to the solvent (chloroform).

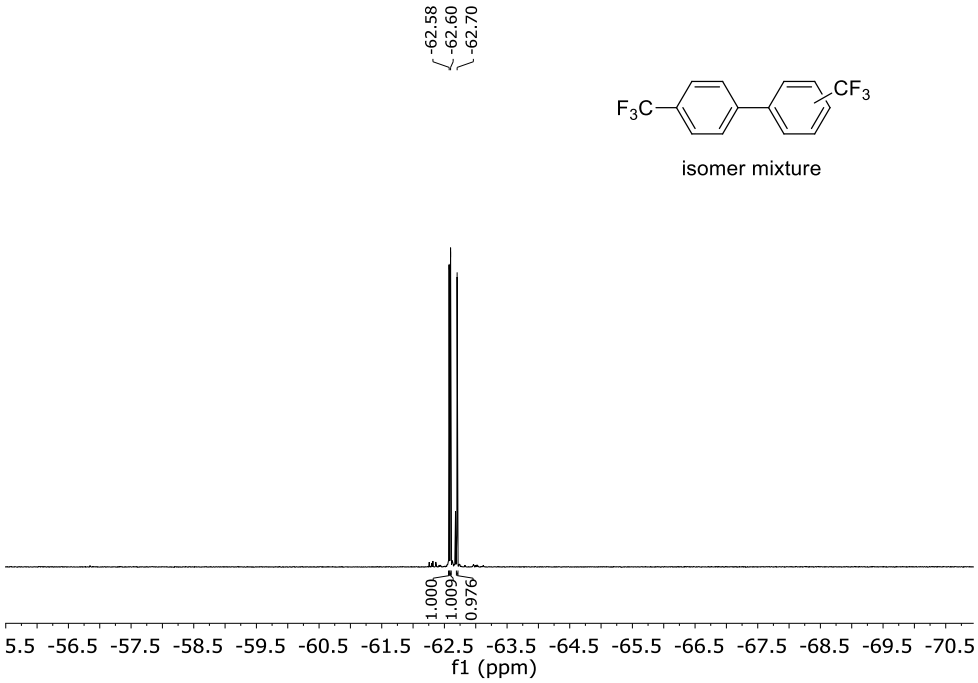


Figure S21. ^{19}F NMR (470.17 MHz, $CDCl_3$) of an isomer mixture of 3,4'-bis(trifluoromethyl)-1,1'-biphenyl, and 4,4'-bis(trifluoromethyl)-1,1'-biphenyl (2:1) at 298 K.

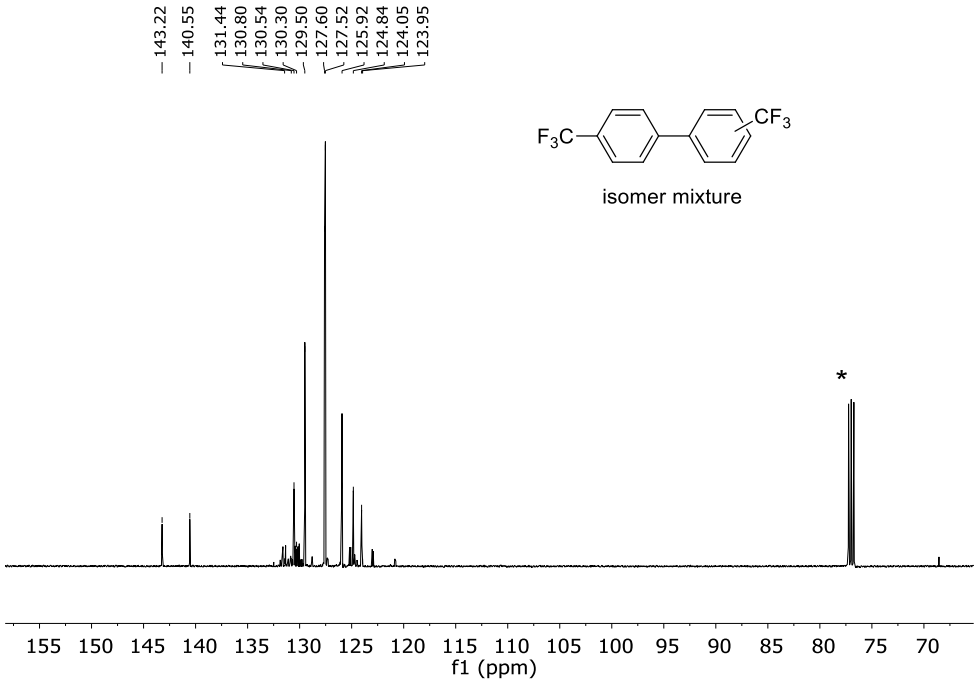


Figure S22. $^{13}C\{^1H\}$ NMR (125.67 MHz, $CDCl_3$) of an isomer mixture of 3,4'-bis(trifluoromethyl)-1,1'-biphenyl, and 4,4'-bis(trifluoromethyl)-1,1'-biphenyl (2:1) at 298 K. * Signal corresponding to the solvent (chloroform).

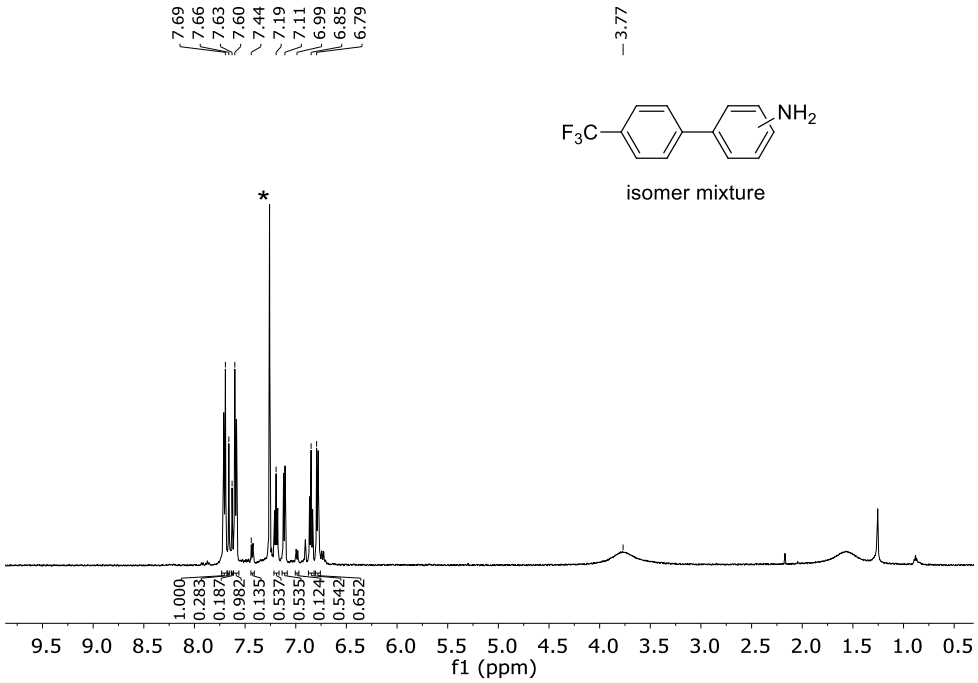


Figure S23. ^{1}H NMR (499.73, $CDCl_3$) of an isomer mixture of 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine, 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-amine and 4'-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (12:1:2) at 298 K. * Signal corresponding to the solvent (chloroform).

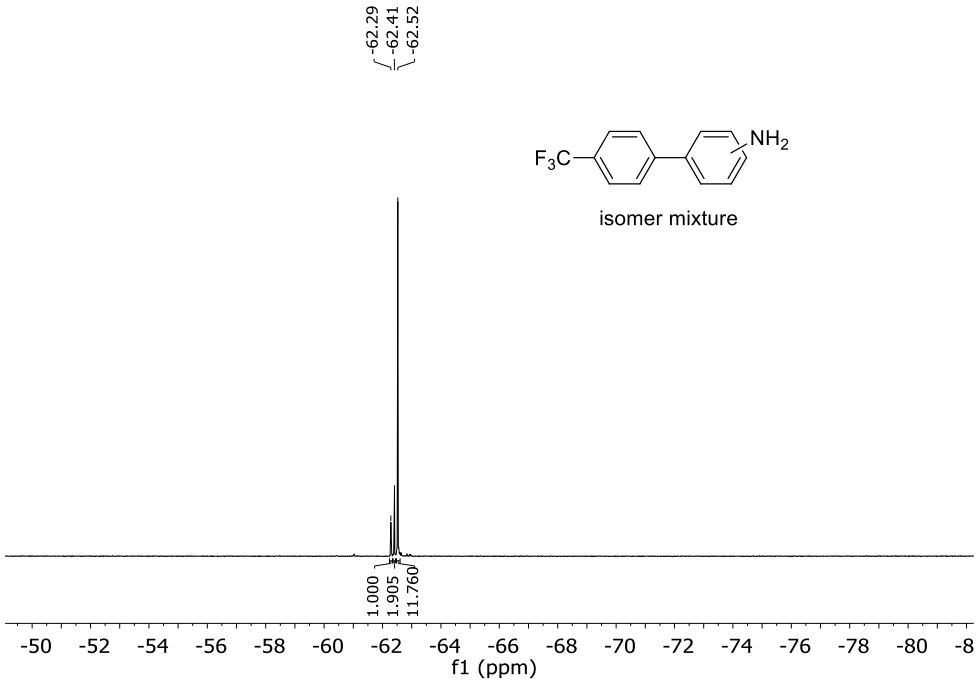


Figure S24. ^{19}F NMR (470.17 MHz, $CDCl_3$) of an isomer mixture of 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine, 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-amine and 4'-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (12:1:2) at 298 K.

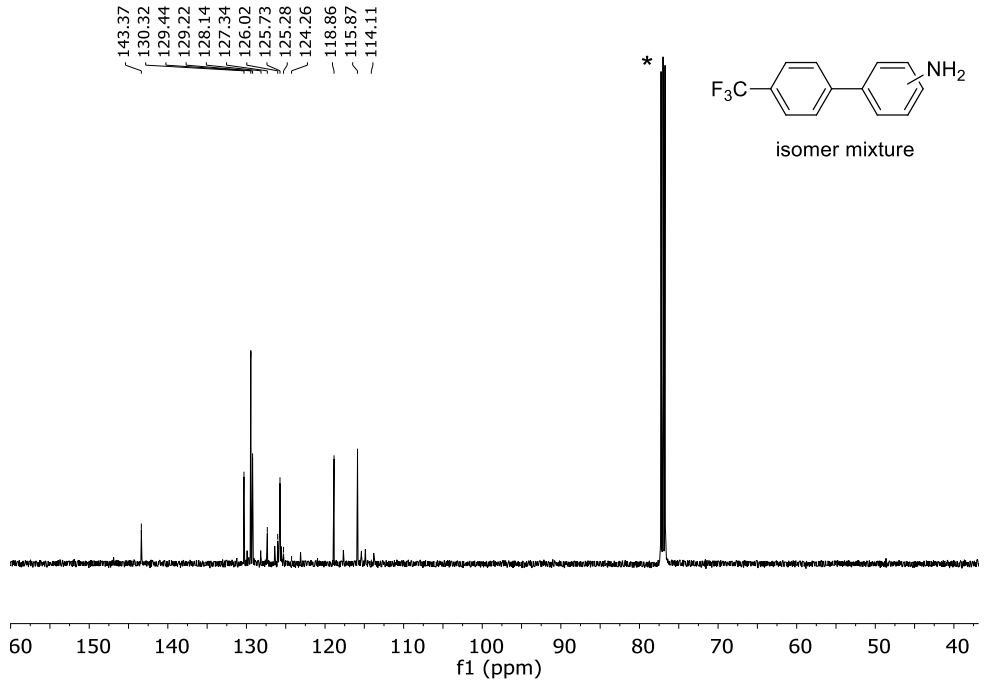


Figure S25. $^{13}C\{^{1}H\}$ NMR (125.67 MHz, $CDCl_3$) of an isomer mixture of 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-amine, 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-amine and 4'-(trifluoromethyl)-[1,1'-biphenyl]-3-amine (12:1:2) at 298 K. * Signal corresponding to the solvent (chloroform).

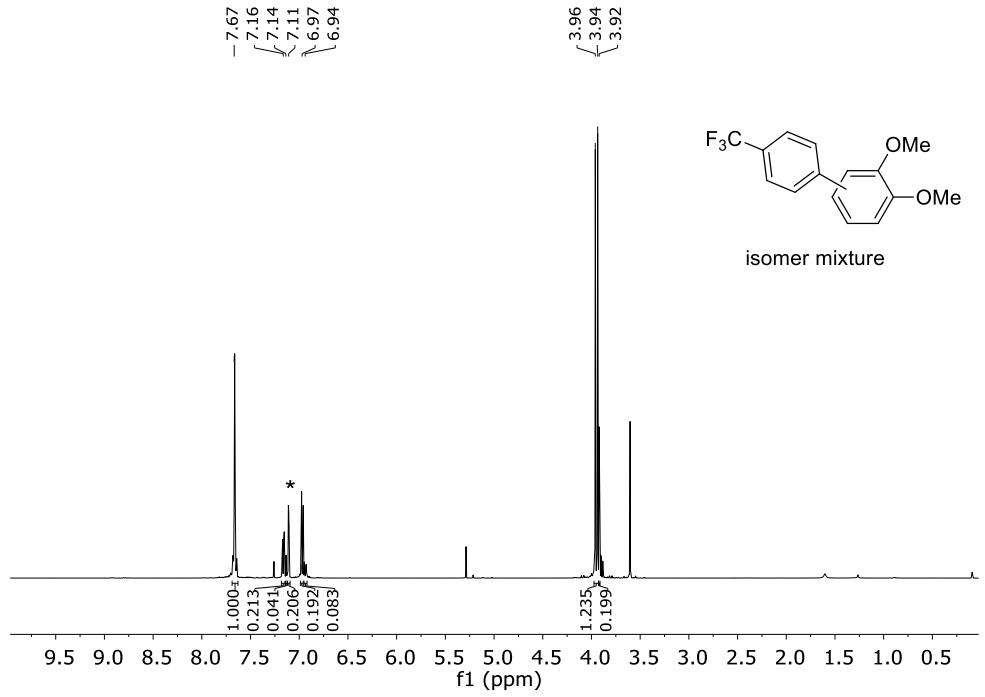


Figure S26. ^{1}H NMR (499.73, $CDCl_3$) of an isomer mixture of 3,4-dimethoxy-4'-(trifluoromethyl)-1,1'-biphenyl and 2,3-dimethoxy-4'-(trifluoromethyl)-1,1'-biphenyl (3:1) at 298 K. * Signal corresponding to the solvent (chloroform).

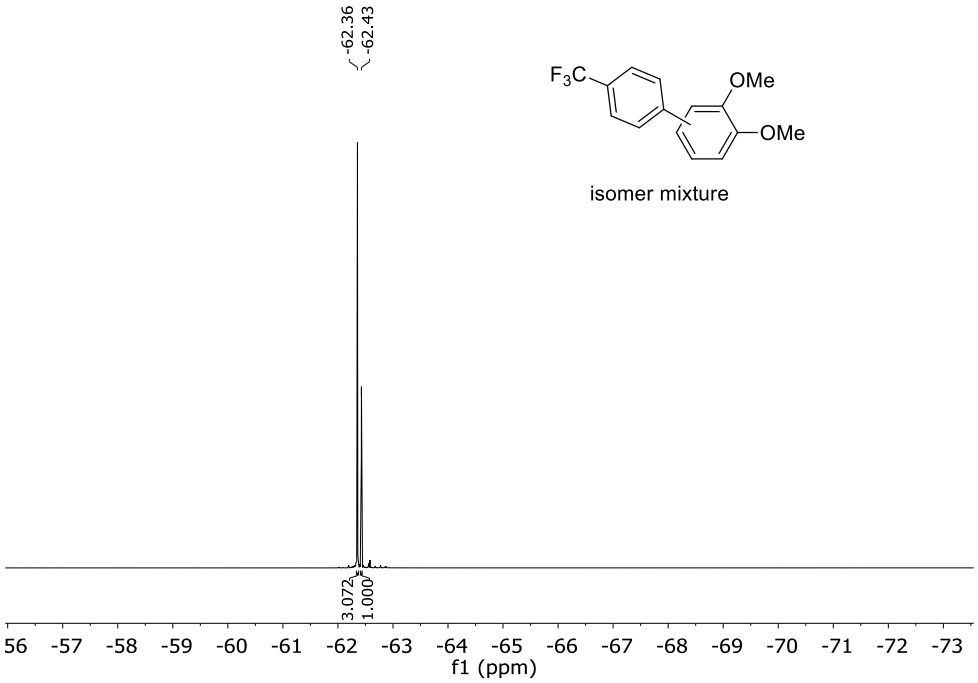


Figure S27. ^{19}F NMR (470.17 MHz, $CDCl_3$) of an isomer mixture of 3,4-dimethoxy-4'-(trifluoromethyl)-1,1'-biphenyl and 2,3-dimethoxy-4'-(trifluoromethyl)-1,1'-biphenyl (3:1) at 298 K.

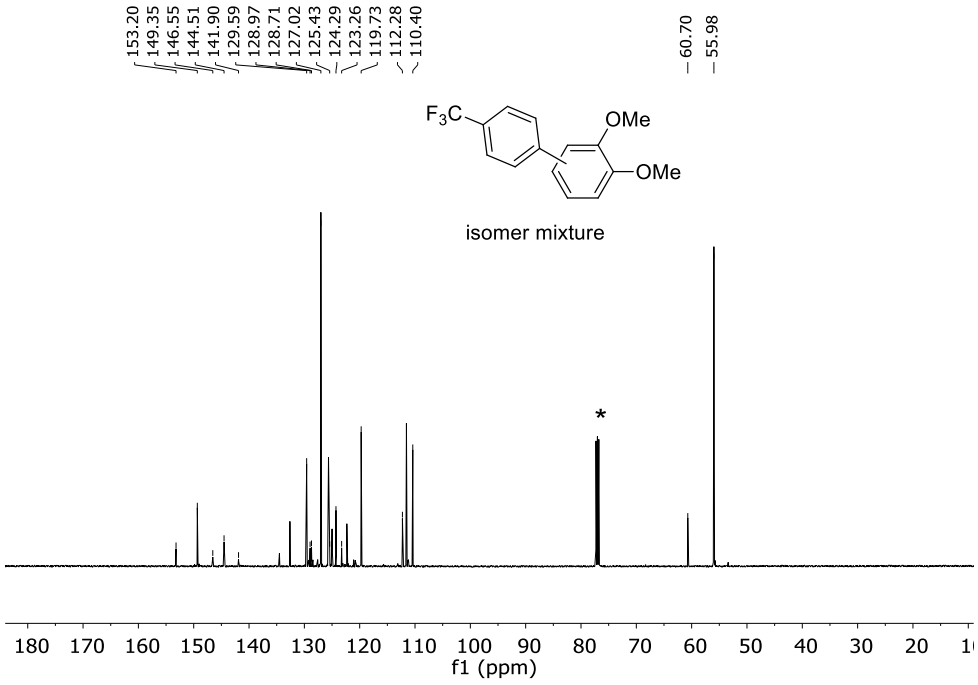


Figure S28. $^{13}C\{^1H\}$ NMR (125.67 MHz, $CDCl_3$) of an isomer mixture of 3,4-dimethoxy-4'-(trifluoromethyl)-1,1'-biphenyl and 2,3-dimethoxy-4'-(trifluoromethyl)-1,1'-biphenyl (3:1) at 298 K. * Signal corresponding to the solvent (chloroform).

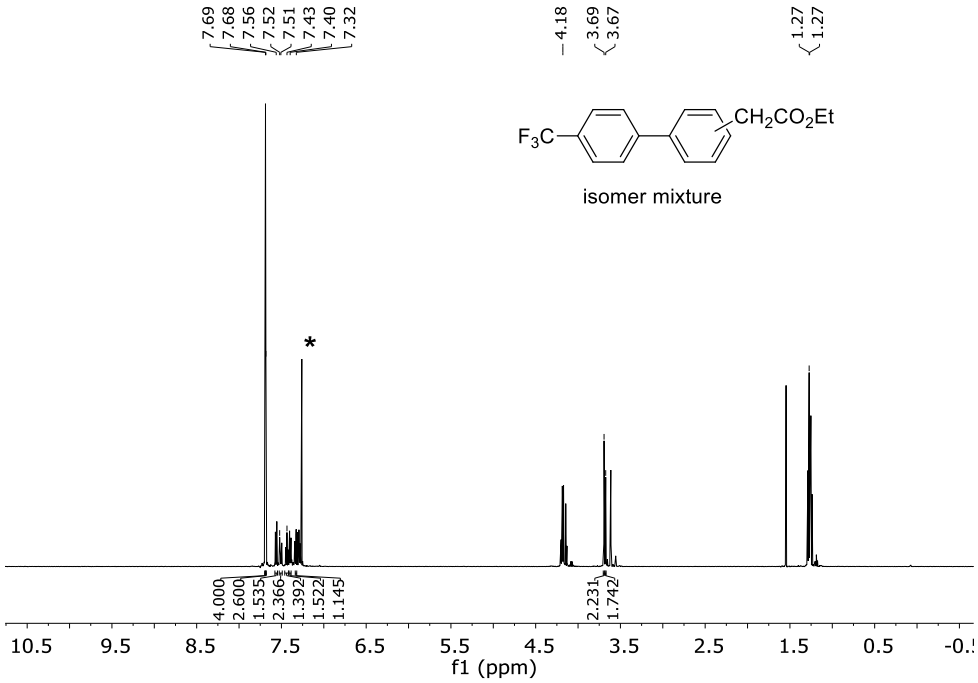


Figure S29. ^{1}H NMR (499.73, $CDCl_3$) of an isomer mixture of ethyl 2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetate and ethyl 2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)acetate (3:2) at 298 K. * Signal corresponding to the solvent (chloroform).

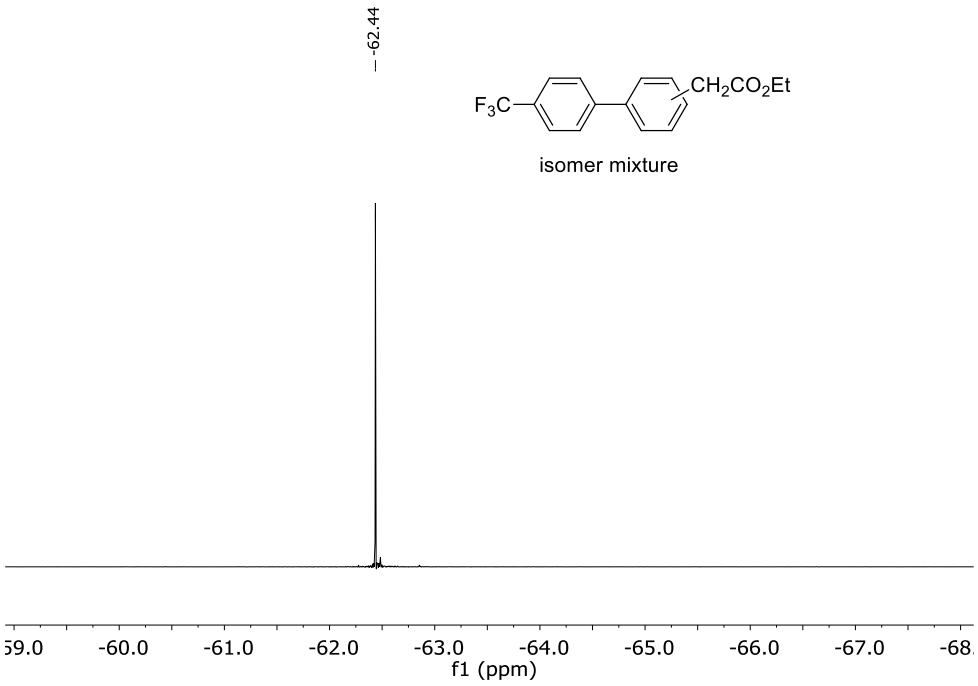


Figure S30. ^{19}F NMR (470.17 MHz, $CDCl_3$) of an isomer mixture of ethyl 2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetate and ethyl 2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)acetate (3:2) at 298 K.

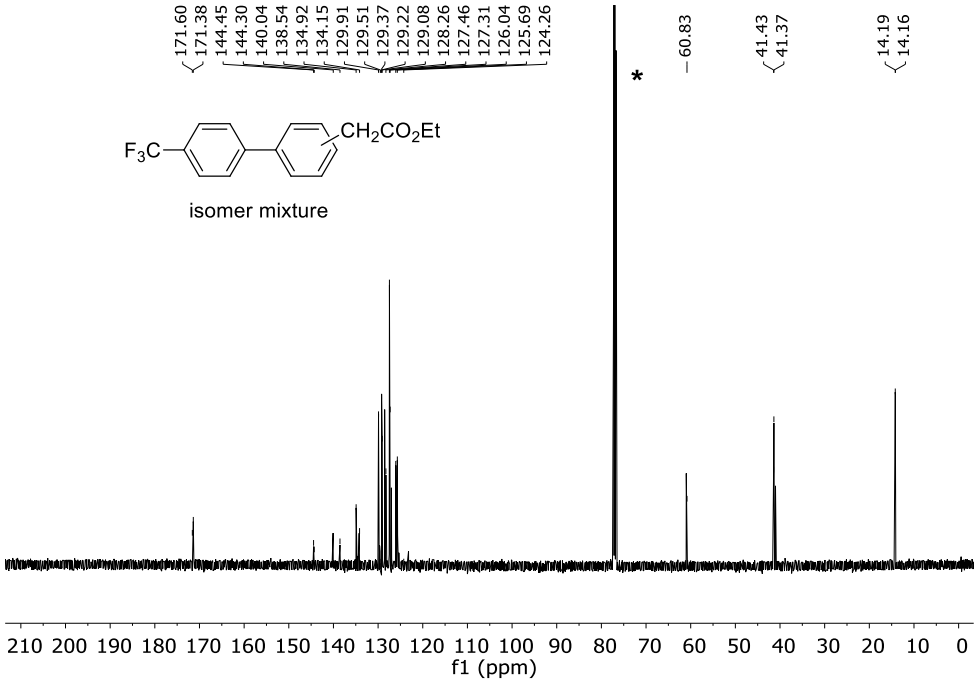


Figure S31. $^{13}C\{^{1}H\}$ NMR (125.67 MHz, $CDCl_3$) of an isomer mixture of ethyl 2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-3-yl)acetate and ethyl 2-(4'-(trifluoromethyl)-[1,1'-biphenyl]-4-yl)acetate (3:2) at 298 K.* Signal corresponding to the solvent (chloroform).

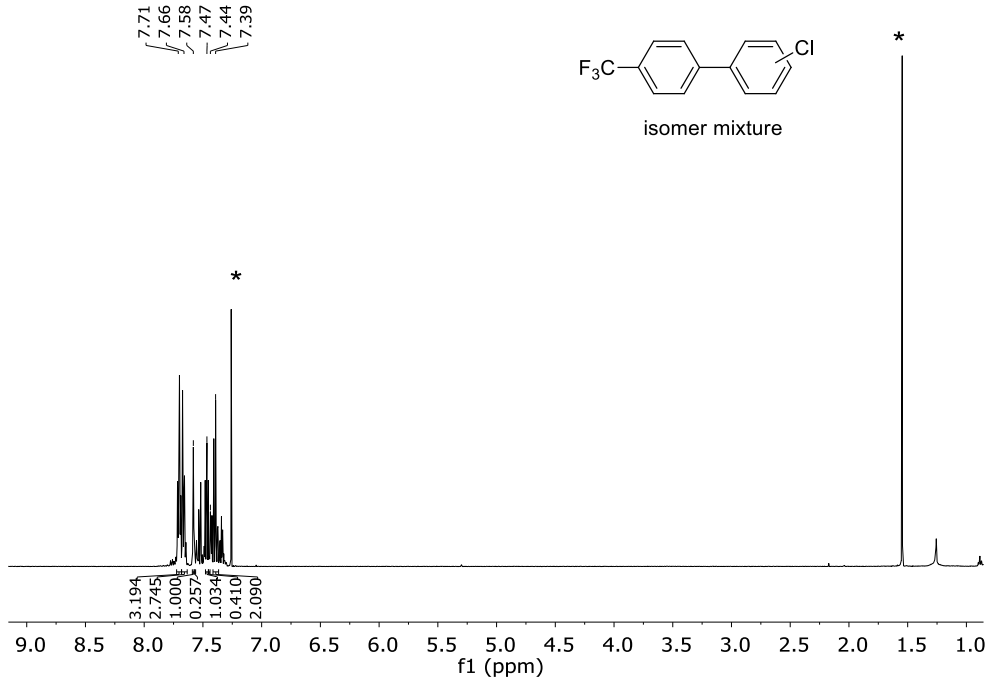


Figure S32. ^{1}H NMR (499.73, $CDCl_3$) of an isomer mixture of 3-chloro-4'-(trifluoromethyl)-1,1'-biphenyl and 4-chloro-4'-(trifluoromethyl)-1,1'-biphenyl (4:1) at 298 K. * Signal corresponding to the solvent (chloroform and H_2O).

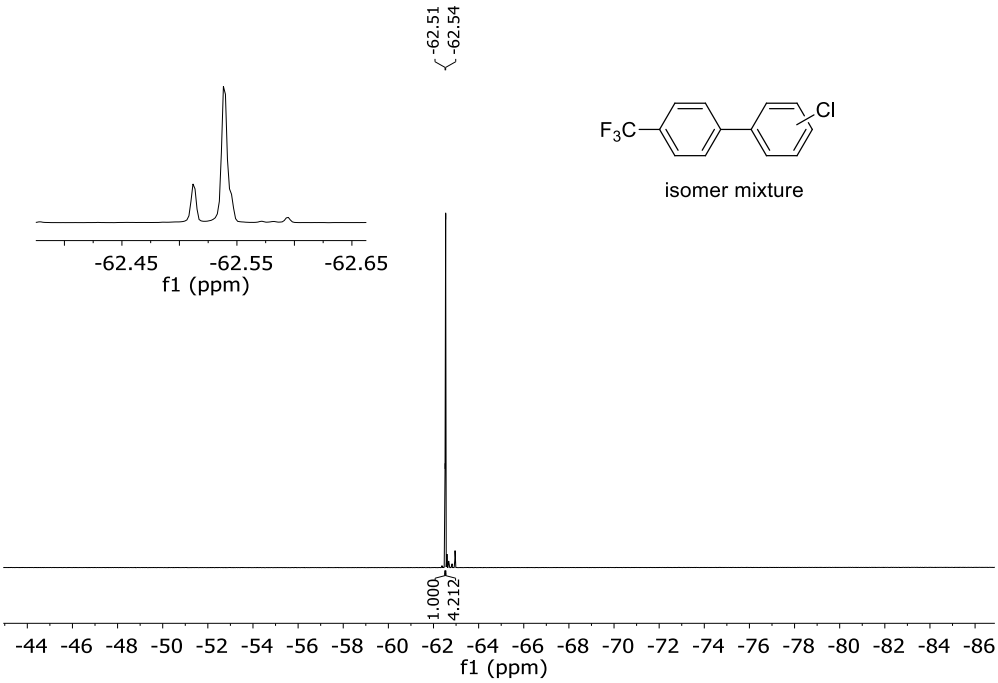


Figure S33. ^{19}F NMR (470.17 MHz, $CDCl_3$) of an isomer mixture of 3-chloro-4'-(trifluoromethyl)-1,1'-biphenyl and 4-chloro-4'-(trifluoromethyl)-1,1'-biphenyl (4:1) at 298 K.

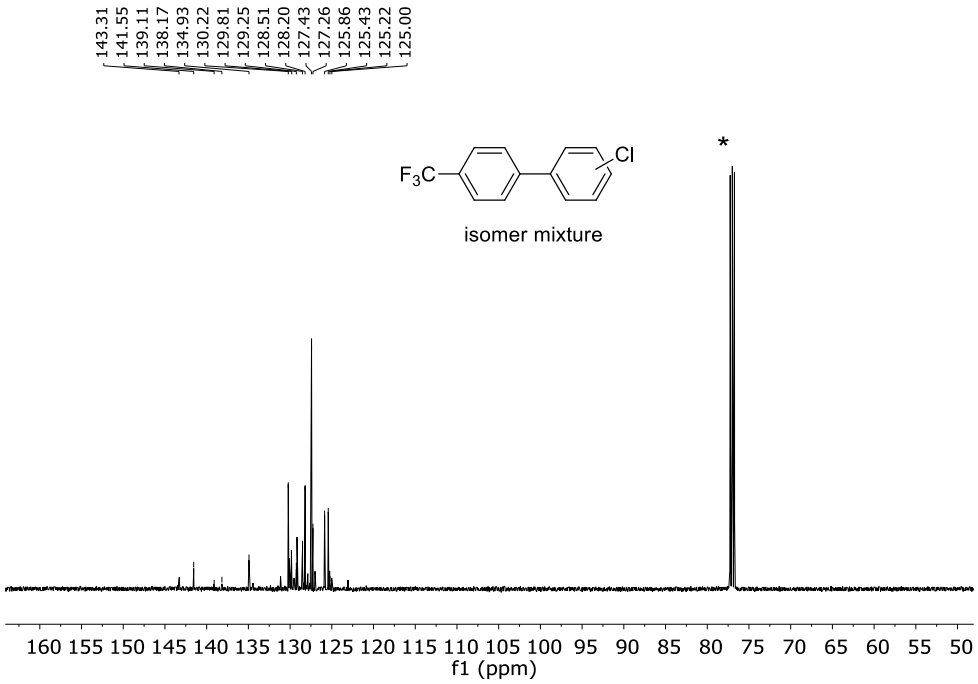


Figure S34. $^{13}C\{^1H\}$ NMR (125.67 MHz, $CDCl_3$) of an isomer mixture of 3-chloro-4'-(trifluoromethyl)-1,1'-biphenyl and 4-chloro-4'-(trifluoromethyl)-1,1'-biphenyl (4:1) at 298 K. * Signal corresponding to the solvent (chloroform).

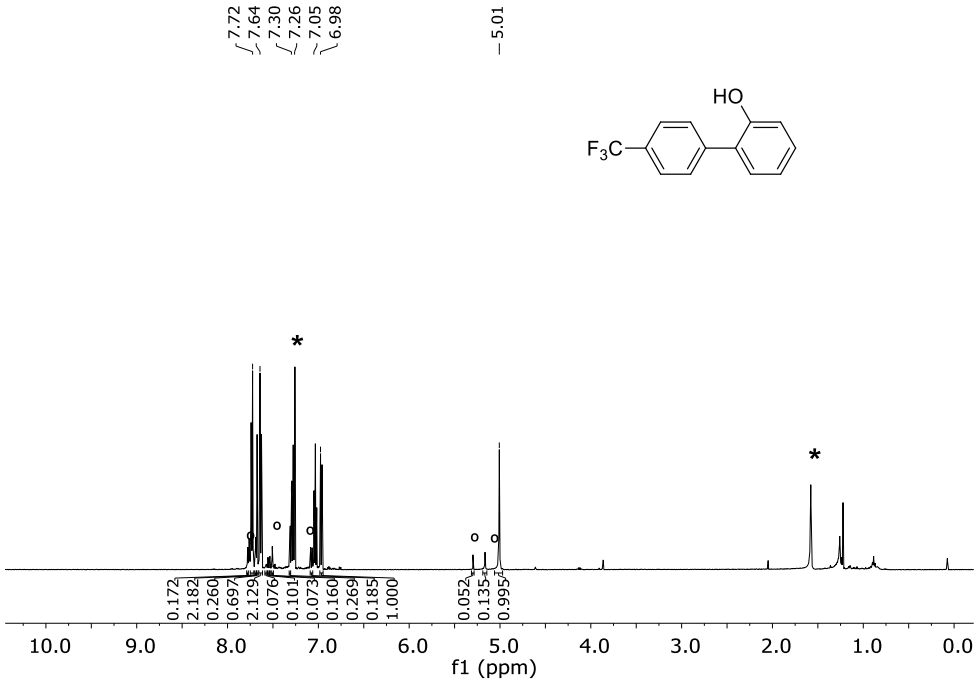


Figure S35. ^{1}H NMR (499.73, $CDCl_3$) of 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-ol (80 % pure) at 298 K. * Signal corresponding to the solvent (chloroform and H_2O). º Signals corresponding to the doble arylation of phenol products (m/z = 382).

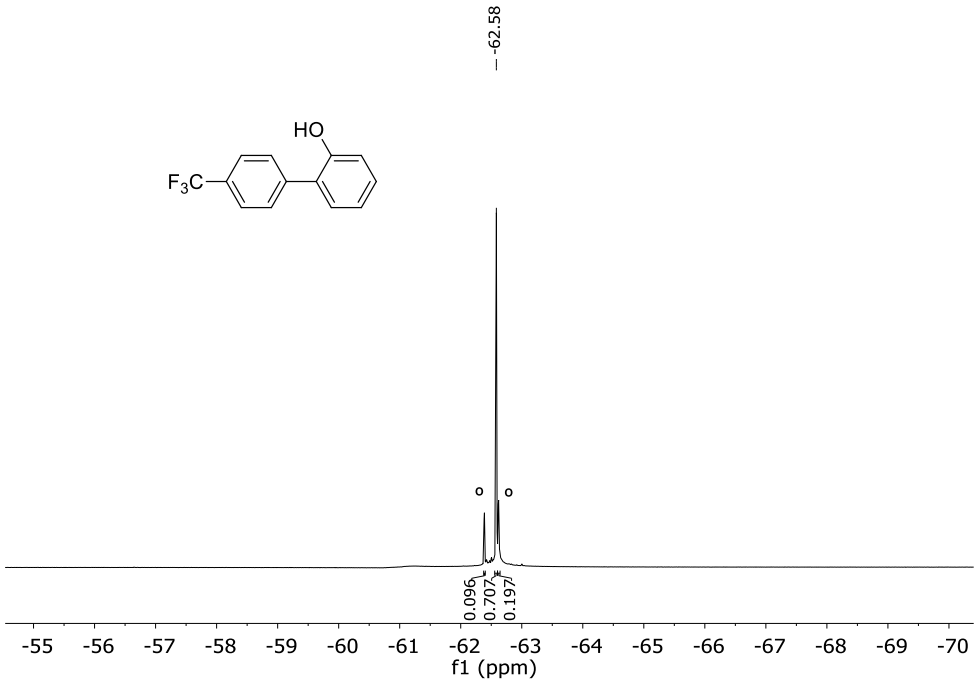


Figure S36. ^{19}F NMR (470.17 MHz, $CDCl_3$) of 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-ol (80 % pure) at 298 K. º Signals corresponding to the doble arylation of phenol products (m/z = 382).

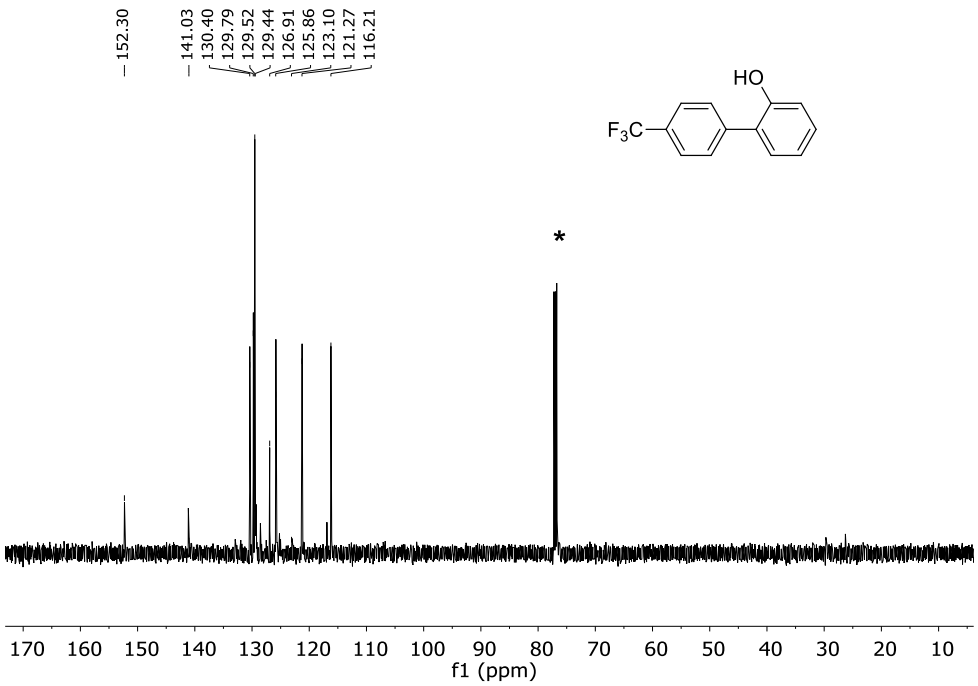


Figure S37. $^{13}C\{^{1}H\}$ NMR (125.67 MHz, $CDCl_3$) of an isomer mixture of 4'-(trifluoromethyl)-[1,1'-biphenyl]-2-ol (80 % pure) at 298 K * Signal corresponding to the solvent (chloroform).

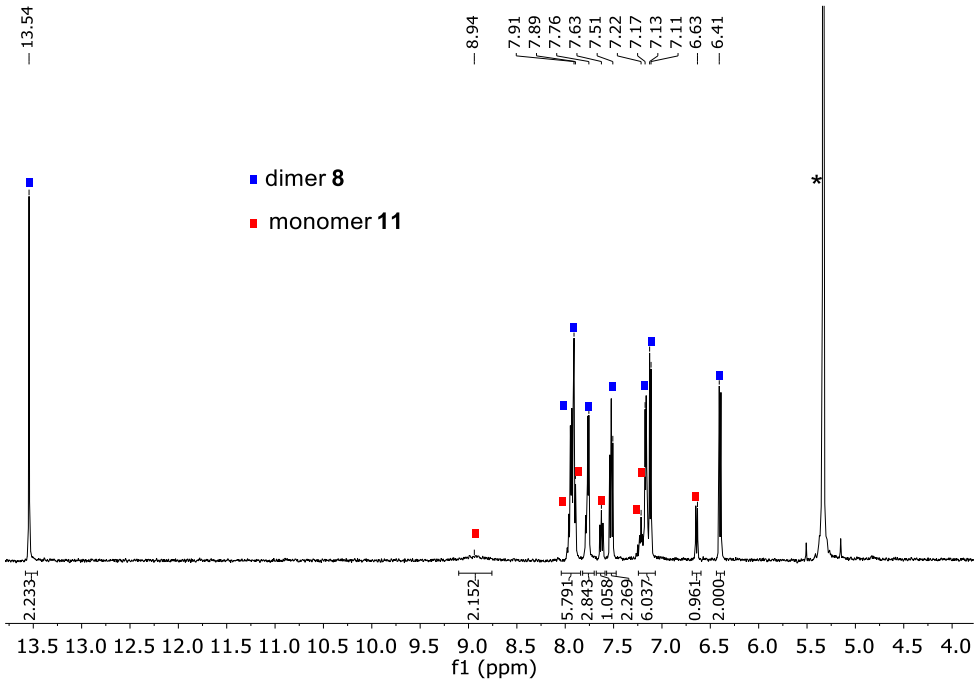


Figure S38. ^{1}H NMR (499.73 MHz, CD_2Cl_2) of the mixture formed after complex $[Pd_2(bipy\text{-}6\text{-}O)_2(C_6F_5)_2\mu OH_2]$ (**8**) is dissolved in CD_2Cl_2. The red species corresponds to the monomer species $[Pd(bipy\text{-}6\text{-}O)(C_6F_5)(H_2O)]$. Ratio dimer **8**:**11** = 1:1. * Signal corresponding to the solvent.

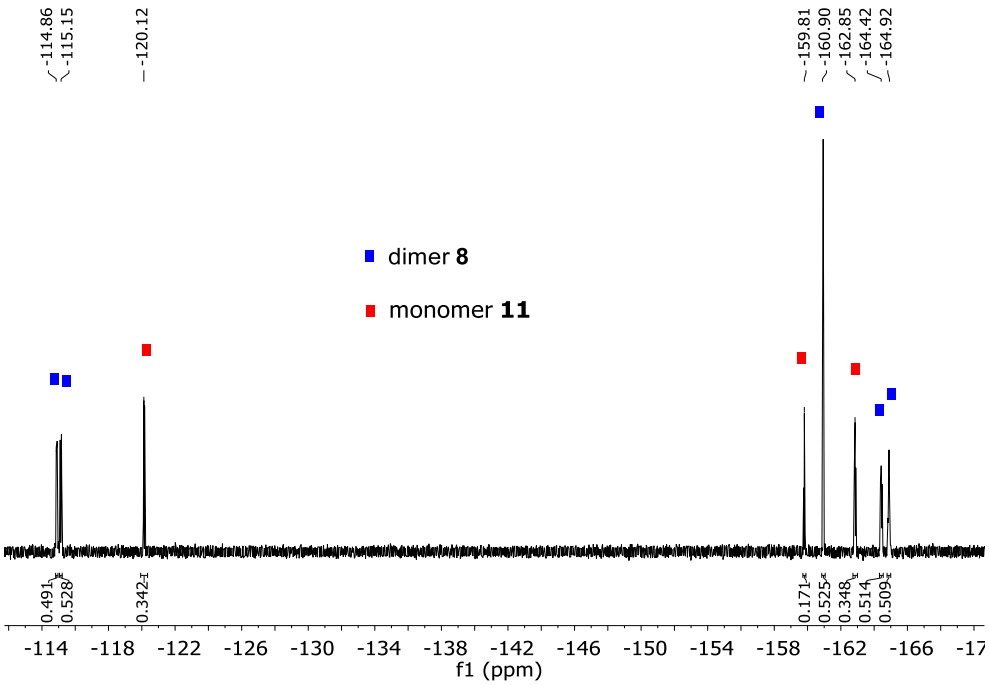


Figure S39. ^{19}F NMR (470.17 MHz, CD_2Cl_2) of the mixture formed after complex [Pd_2(bipy-6-O)$_2$(C_6F_5)$_2$μOH_2] (**8**) is dissolved in CD_2Cl_2. The red species corresponds to the monomer species [Pd(bipy-6-O)(C_6F_5)(H_2O)]. Ratio dimer **8**:**11** = 1:1.

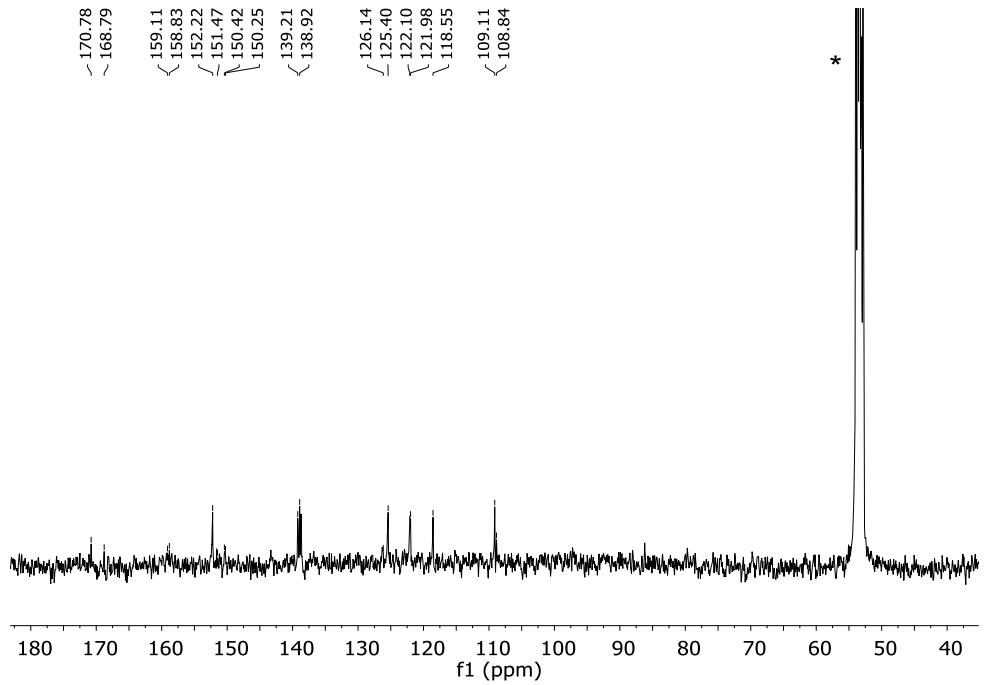
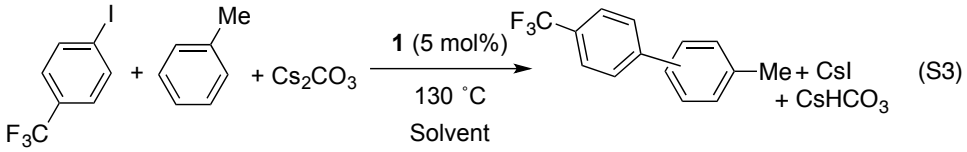


Figure S40. $^{13}C\{^1H\}$ NMR (125.67 MHz, CD_2Cl_2) of the mixture formed after complex [Pd_2(bipy-6-O)$_2$(C_6F_5)$_2$μOH_2] (**8**) is dissolved in CD_2Cl_2. Ratio dimer **8**:**11** = 1:1.

4- Microkinetic modeling

Kinetic simulations of the reaction shown in Eq. S3 in two different solvents (toluene or the 1:1 v/v mixture of toluene/pinacolone) were carried out using the COPASI software.[28]

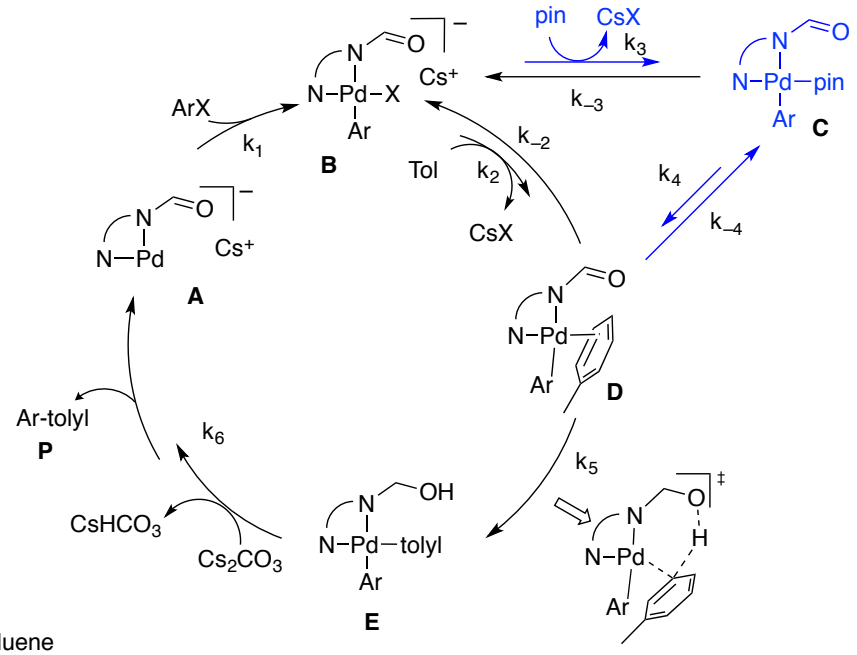


(S3)

The kinetic models used and the nomenclature for the different species are depicted in Scheme S1 where all the intermediates proposed are supported by experimental data (**B** and **C**) or calculations for this system in toluene (**D**, **E**, analogous to the previously reported intermediates in the arylation of pyridine).[1] Simple kinetic probing of the reaction, allows to find out the steps that are fast (those where ArX is involved) and those which are relevant to determine the overall rate, i.e ligand substitution (arene dependence of the rate) and the C-H activation (positive KIE).

Experimental concentrations were used. Equilibrium and rate constants for the kinetic model were calculated from the energy differences (DFT) between intermediates (ΔG) or intermediates and transition states ($\Delta G^{\ddagger}$) according to the following equations.

Equilibrium constants: $K = e^{-\Delta G/RT}$ Rate constants: $k = (k_B T/h)e^{-\Delta G^{\ddagger}/RT}$



Tol = toluene
pin = pinacolone (MeC(O)^{t}Bu)
X = iodide

Scheme S1.

Solvent: Toluene

Kinetic model and rate constants.

A + ArI → B	$k_1 = 10^6\ M^{-1}\ s^{-1}$
B + Tol = D + X	$k_2 = 7x10^{-5}\ M^{-1}\ s^{-1}$, $k_{-2} = 1.45x10^{10}\ M^{-1}\ s^{-1}$; $K_2 = 4.8x10^{-15}$, ΔG = 26.4 kcal mol^{-1}
D → E	$k_5 = 6.3x10^6\ s^{-1}$
E → P + A	$k_6 = 2x10^8\ s^{-1}$

For the reactions that are fast in the catalytic cycle, arbitrary large values for $k_1 = 10^6$ (oxidative addition) and $k_6 = 2x10^8$ (reactions leading to product from **E**) were used. Rate constant k_5 was calculated from the energy difference between **D** and the TS for the C-H activation (11.3 kcal mol^{-1}). Rate constants k_2, k_{-2} (K_2) were fitted to conform to the experimental observed conversion and KIE. The value of K_2 used accounts for only 1.3 kcal mol^{-1} energy difference between intermediates **B** and **D** (26.4 kcal mol^{-1}) when compared to the DFT calculated value (25.1 kcal mol^{-1}).

Initial concentrations:

$[A]_0 = 0.0057$ M

$[ArX]_0 = 0.11$ M

$[Tol]_0 = 9.4$ M

[X] = 0.0001 M; this concentration is considered constant since it is controlled by the solubility of CsI in toluene. The value was determined experimentally (see above).

$[P]_0 = [B]_0 = [D]_0 = [E]_0 = 0$

The simulation of the KIE in experiments run in separate flasks was carried modeling the reactions with toluene or toluene-d8, using the same kinetic constants listed above in both cases except k_5: $k_{5H} = 6.3x10^6\ s^{-1}$ (for toluene) and $k_{5D} = 1.73x10^6\ s^{-1}$ (for toluene-d8) according to the DFT calculated KIE = 3.64.

This model reproduces the experimental conversions (see Figure S41) and observed KIE (KIE = 1.5, Figure S42).

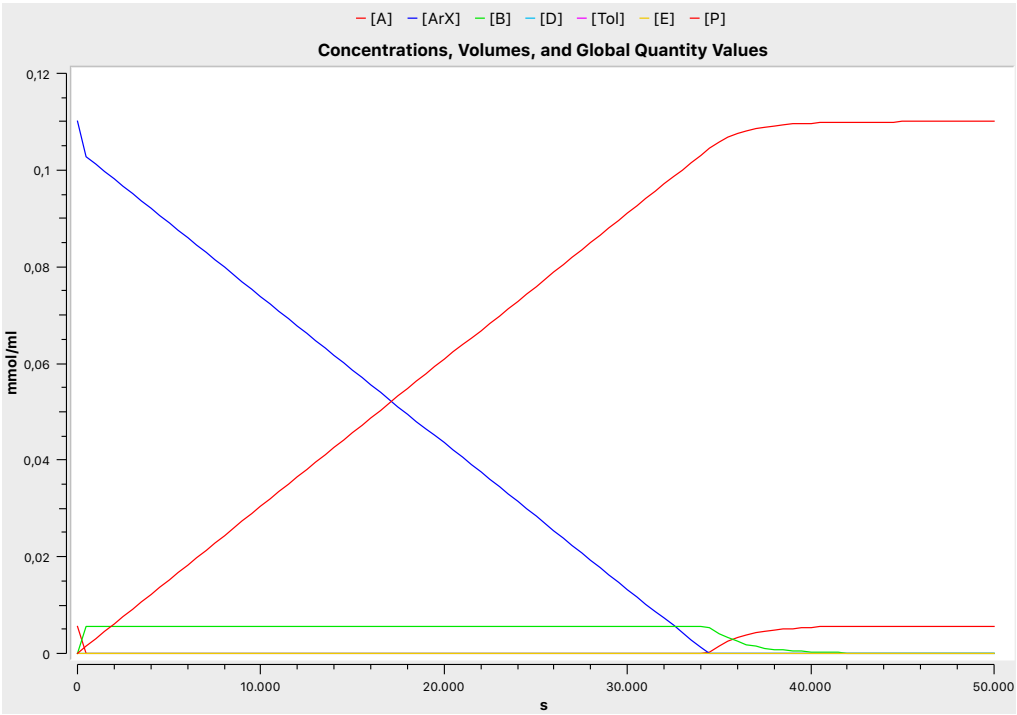


Figure S41. Evolution of concentration (M) over time (s) for the reaction in Eq. S3 in toluene. Experimental product formation: 0.033 M of product after 3 h (10800 s). The concentration of toluene remains constant and has been omitted for clarity.

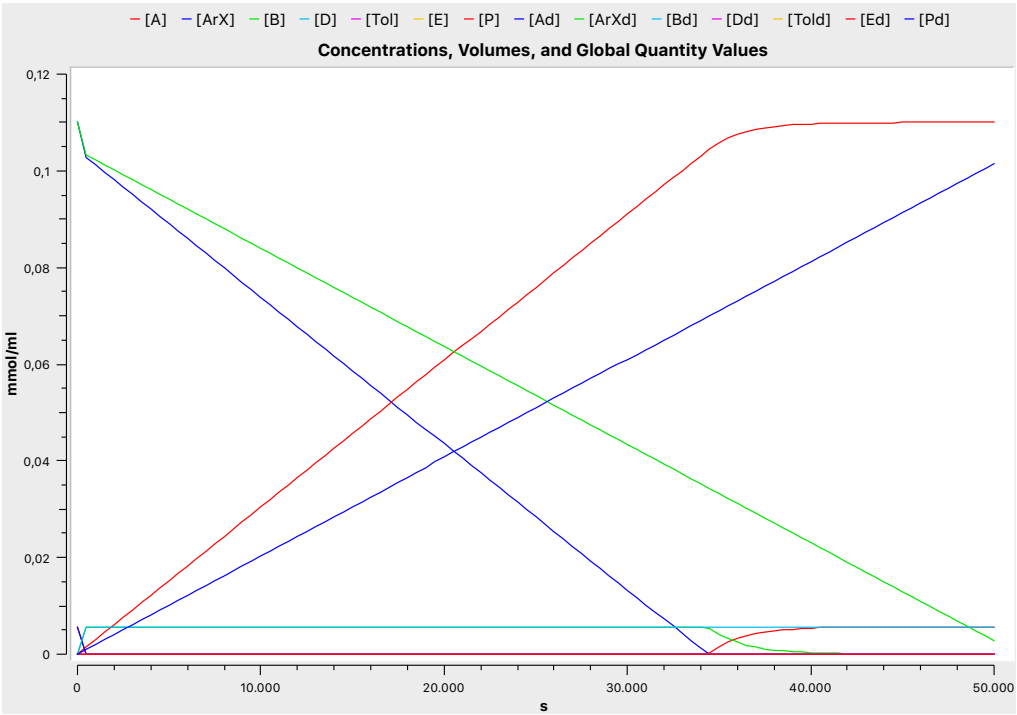


Figure S42. Kinetic simulation of the KIE in separate flasks. It shows the evolution of concentration (M) over time (s) for the reaction in Eq. S3 in toluene (product P, red) or toluene-d8 (product Pd, blue). The concentrations of toluene and toluene-d_8 remain constant and have been omitted for clarity.

Solvent: Toluene/pinacolone (1/1)

Kinetic model and rate constants.

A + ArI → B	$k_1 = 10^6\ M^{-1}\ s^{-1}$
B + Tol = D + X	$k_2 = 7x10^{-5}\ M^{-1}\ s^{-1}$, $k_{-2} = 8.75x10^7\ M^{-1}\ s^{-1}$; $K_2 = 8x10^{-13}$, ΔG = 22.3 kcal mol^{-1}
B + pin = C + X	$k_3 = 10^7\ M^{-1}\ s^{-1}$, $k_{-3} = 6.67x10^9\ M^{-1}\ s^{-1}$; $K_3 = 1.5x10^{-3}$, ΔG = 5.2 kcal mol^{-1}
C + Tol = D + pin	$k_4 = 4.4x10^{-3}\ M^{-1}\ s^{-1}$, $k_{-4} = 8.3x10^6\ M^{-1}\ s^{-1}$; $K_4 = 5.3x10^{-10}$, ΔG = 17.1 kcal mol^{-1}
D → E	$k_5 = 6.3\ x10^6\ s^{-1}$
E → P + A	$k_6 = 2x10^8\ s^{-1}$

As above, for the reactions that are fast in the catalytic cycle, arbitrary large values for $k_1 = 10^6$ (oxidative addition) and $k_6 = 2x10^8$ (reactions leading to product from **E**) were used. Rate constant k_5 was calculated from the energy difference between **D** and the TS for the C-H activation (11.3 kcal mol^{-1}), which is almost insensitive to the solvent used for the calculations. K_3 was estimated according to the ΔG value (5.2 kcal mol^{-1}) calculated from the experimental K_3 at 298 K ($1.6x10^{-4}$), assuming a small entropy change in this equilibrium. Rate constatnts k_3 and k_{-3} have arbitrary values. K_2 and K_4, k_4, k_{-4} were fitted to reach the experimental observed conversion. Rate constant k_2 has the same value used for the reaction in toluene ($\Delta G^{\ddagger}$ for halide-toluene substitution 31.5 kcal/mol) but it is not kinetically relevant.

Initial concentrations:

$[A]_0 = 0.0057$ M

$[ArX]_0 = 0.11$ M

$[Tol]_0 = 4.7$ M

$[pin]_0 = 4$ M

[X] = 0.00024 M; this concentration is considered constant since it is controlled by the solubility of CsI in the mixture toluene/pinacolone. The value was determined experimentally (see above).

$[P]_0 = [B]_0 = [D]_0 = [E]_0 = 0$

The simulation of the KIE in experiments run in separate flasks was carried out modeling the reactions with toluene or toluene-d8, using the same kinetic constants

listed above in both cases except k_5: k_{5H} = 6.3x10^6 s^{-1} (for toluene) and k_{5D} = 1.73x10^6 s^{-1} (for toluene-d8) according to the DFT calculated KIE = 3.64.

This model reproduces the experimental conversions (see Figure S43) and shows that a KIE higher than the reaction in toluene (KIE = 3.2, Figure S44), as observed experimentally (KIE = 2.8).

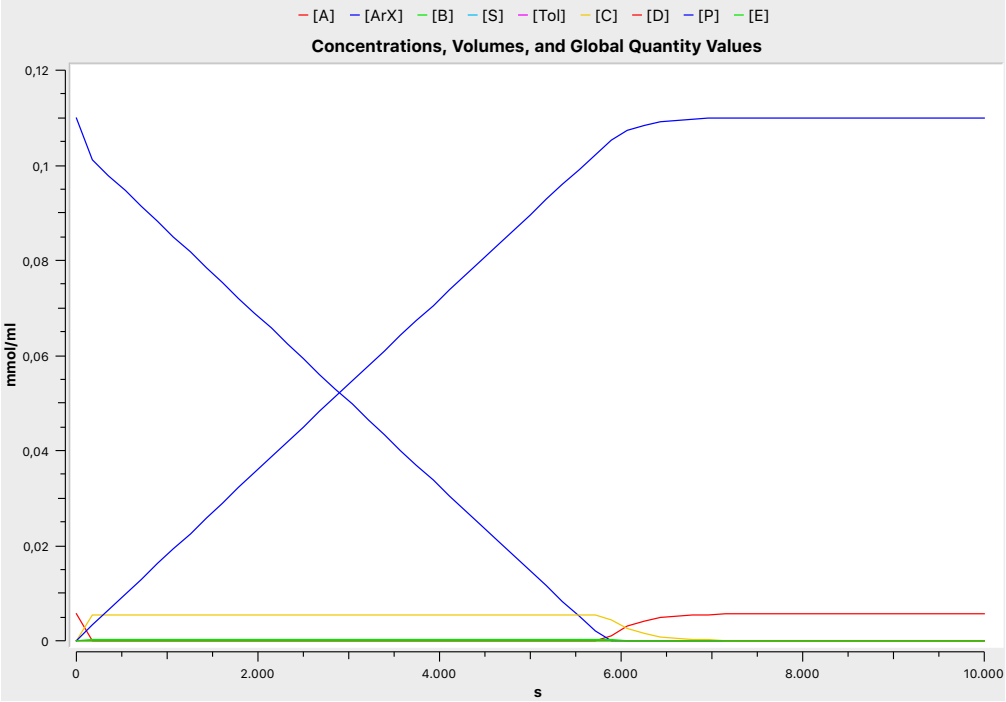


Figure S43. Evolution of concentration (M) over time (s) for the reaction in Eq. S3 in toluene/pinacolone. Experimental product formation: 0.09 M of product after 1.5 h (5400 s). The concentration of toluene and pinacolone remain constant and has been omitted for clarity.

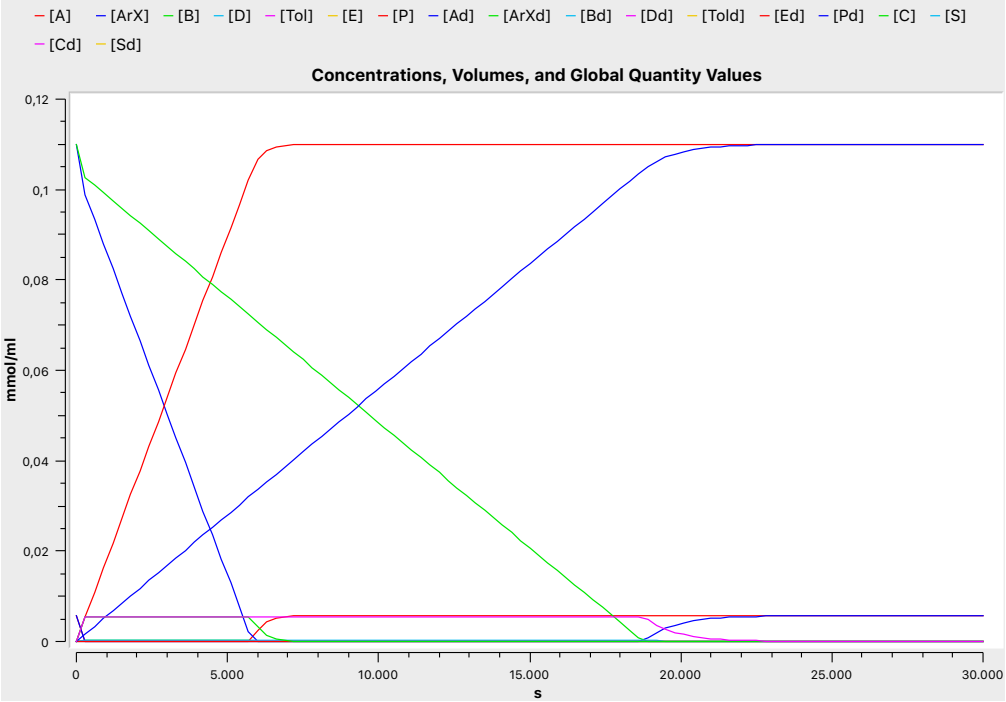


Figure S44. Kinetic simulation of the KIE in separate flasks. It shows the evolution of concentration (M) over time (s) for the reaction in Eq. S3 in toluene/pinacolone (product P, red) or toluene-d8/pinacolone (product Pd, blue). The concentration of toluene and pinacolone remain constant and have been omitted for clarity.

Simulation of differences in the base solubility (solvent: toluene).

A microkinetic simulation was carried out in toluene with the deprotonation of intermediate **E** to give **F** (see Scheme 6 in the text) as an additional step of the model above. This is in order to test any possible influence of the solubility of the base in the reaction rate. The rate and equilibrium constants are the same as above (solvent, toluene) and the value of k_7 was calculated form the DFT energy barrier for protonation ($\Delta G^{\ddagger}$ = 5.8 kcal mol^{-1}, Figure 4 in the text).

Kinetic model and rate constants.

A + ArI → B	$k_1 = 10^6\ M^{-1}\ s^{-1}$
B + Tol = D + X	$k_2 = 7x10^{-5}\ M^{-1}\ s^{-1}$, $k_{-2} = 1.45x10^{10}\ M^{-1}\ s^{-1}$; $K_2 = 4.8x10^{-15}$, ΔG = 26.4 kcal mol^{-1}
D → E	$k_5 = 6.3x10^6\ s^{-1}$
E + Cs_2CO_3 → F	$k_6 = 6x10^9\ M^{-1}\ s^{-1}$
F → P + A	$k_7 = 2x10^8\ s^{-1}$

Initial concentrations:

$[A]_0 = 0.0057$ M

$[ArX]_0 = 0.11$ M

$[Tol]_0 = 9.4$ M

[X] = 0.0001 M; this concentration is considered constant since it is controlled by the solubility of CsI in toluene. The value was determined experimentally (see above).

$[Cs_2CO_3] = 0.0015$ M; this concentration is considered constant since it is controlled by the solubility of cesium carbonate in toluene. The value was roughly estimated experimentally by taking an aliquot of a saturated solution of Cs_2CO_3 in toluene at 90 ˚C, evaporating the solvent and weighting the residue.

$[P]_0 = [B]_0 = [D]_0 = [E]_0 = [F]_0 = 0$

As can be seen in Figure S45, the concentration-time plots do not change upon changing the amount of dissolved carbonate tenfold and are the same as that shown in Figure S41. The deprotonation of complex **F**, the step where the base is involved, is kinetically non-relevant.

a) b)

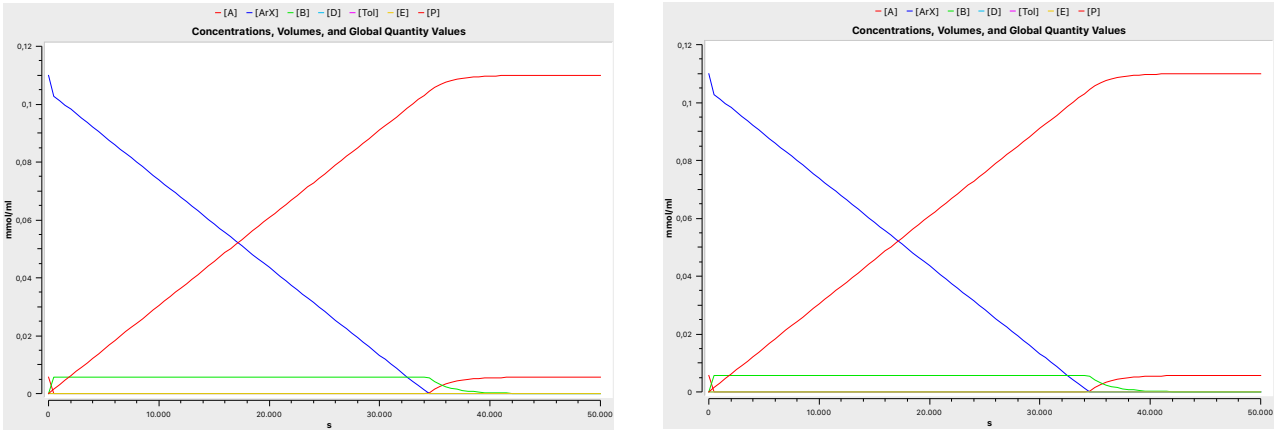


Figure S45. Evolution of concentration (M) over time (s) for the reaction in Eq. S3 in toluene using a fixed concentration of cesium carbonate: a) $[Cs_2CO_3] = 0.0015$ M and b) $[Cs_2CO_3] = 0.015$ M**.**

5- Computational details

5.1. Computational methods.

The DFT studies have been performed with the M06 functional,[29,30] as implemented in the Gaussian09 program package.[31] The 6-31+G(d) basis set was used for C, O, N and H,[32,33] and LANL2TZ(f) for Pd, Cs, Br and I,[34,35] (Basis set I). Solvent effects have been considered trough the continuum model SMD for the experimental solvent, toluene (ε = 2.37 at 25 ºC), which was introduced in all the optimizations, frequency calculations and potential energy refinement. In a few cases, for comparison purposes, the solvent used was acetone (ε = 20.49 at 25 ºC). All structure optimizations were carried out in solvent phase with no symmetry restrictions. Free energy corrections were calculated at 413.15 K (the experimental temperature) and 10^5 Pa pressure, including zero point energy corrections (ZPE), and the energies were converted to 1M standard state in solution (adding/subtracting 2.8 kcal mol^{-1} for non-unimolecular processes). Vibrational frequency calculations were performed in order to confirm that the stationary points were minima (without imaginary frequencies) or transition states (with one imaginary frequency). Connectivity of the transition state structures was confirmed by relaxing the transition state geometry towards both the reactant and the product. Final potential energies were refined by performing additional single-point energy calculations (also in solution); Pd, Cs, Br and I were still described with LANL2TZ(f) basis set, and the remaining atoms were treated with 6-311++G(d,p) basis set (Basis set II). All energies presented correspond to free energies in solution, obtained from potential energies (including solvation) with basis set II plus Gibbs energy corrections with basis set I and are given in kcal mol^{-1}.

5.2. Additional free energy profiles

Reductive elimination from complexes **c3**.

All the energy barriers for the reductive elimination of Ar-Tol, Ar-pin and C_6F_5-Tol (Ar = *p*-CF_3-C_6H_4) were calculated in solution of toluene (SMD model) for their comparison.

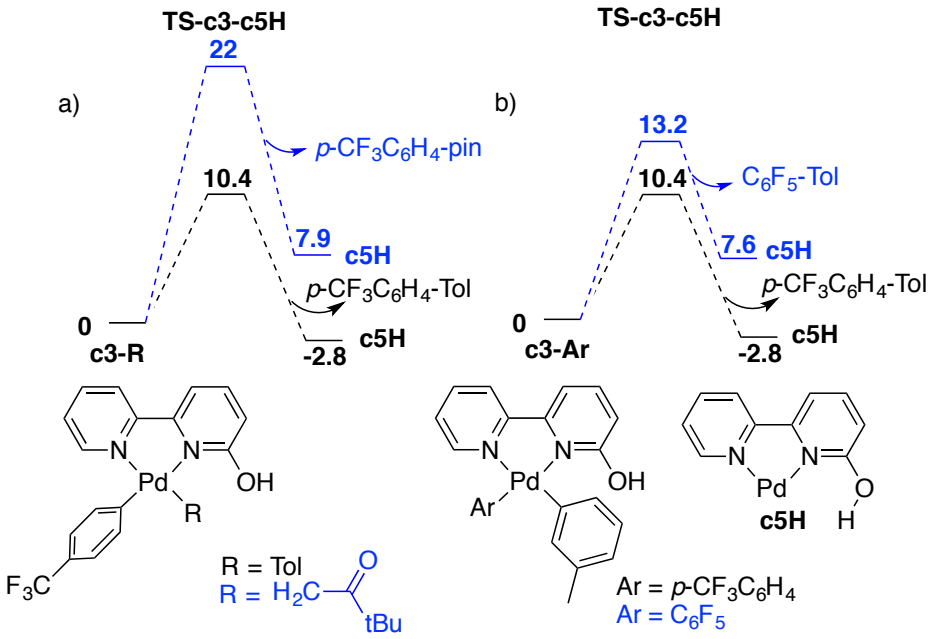


Figure S46. Free energy barriers for the reductive elimination step starting from a neutral complex (protonated ligand). Energies in kcal mol^{-1}

5.3. Theoretical analysis of KIE.

The deuterated structures of **c2** and **TS-c2-c3** were calculated with the substitution of one of the H_{meta} in the toluene ring for deuterium.

The theoretical KIE can be calculated according to the formula:

$$KIE = e^{\frac{\Delta G_D^{\neq} - \Delta G_H^{\neq}}{RT}}$$

$\Delta G_D^{\neq}$ = Activation energy from deuterated structures of **c2** to **TS-c2-c3**

$\Delta G_H^{\neq}$ = Activation energy from **c2** to **TS-c2-c3**

R = 1.987207 cal $mol^{-1}.K^{-1}$

T = 403.15 K

$\Delta G_D^{\neq}$ = 12.34 kcal mol^{-1} and $\Delta G_H^{\neq}$ = 11.3 kcal mol^{-1}. The theoretical KIE calculated is 3.64.

5.4. Optimized structures.

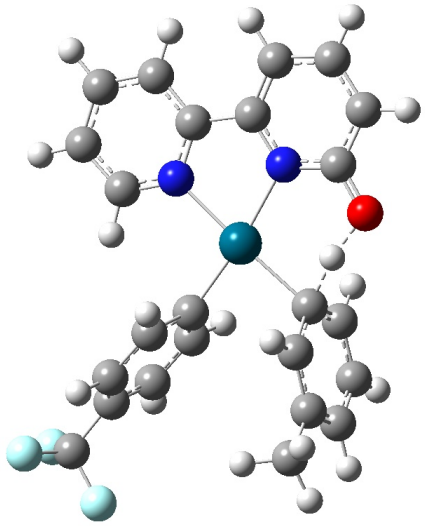


Figure S47. Optimized structure for TS-**c2-c3** with bond lengths (Å): Pd-C, 2.159; C-H, 1.329; H-O, 1.331.

5.5. Cartesian coordinates (Å) and calculated potential energies (atomic units)

SCF energy at high basis set level (Basis set II) and free energy correction at low basis set level (Basis set I). Then sum of both energies provides the final free energy of each compound used in the manuscript. Solvent = toluene (SMD model) unless otherwise noted.

Toluene

SCF Energy = -271,416038973
Thermal Correction to Gibbs Free Energy = 0,083956

C	0.70526200	1.77501300	0.01444900
C	2.09672100	1.77682100	0.02700500
C	2.81401100	2.97483400	0.01311600
C	2.09848500	4.17522200	-0.00820500
C	0.70815300	4.17917400	-0.02123300
C	0.00518700	2.97722000	-0.01000700
H	0.16553500	0.82883300	0.02884700
H	2.64136600	0.83173100	0.05079100
H	2.64511800	5.11964400	-0.01413600
H	0.16980600	5.12615100	-0.03634400
H	-1.08373000	2.97843500	-0.01652500
C	4.31327900	2.97716200	-0.00072000
H	4.70599000	3.10043500	-1.02056200
H	4.72279400	3.80005600	0.59961000
H	4.72270400	2.03762400	0.39153700

Pinacolone

SCF Energy = -310,963631829
Thermal Correction to Gibbs Free Energy = 0,120813

C	0.36792200	1.73655300	1.79751300
O	0.98385000	2.71466700	2.17362900
C	1.08859800	0.44383000	1.50738100
H	2.08805500	0.47897100	1.95193900
H	0.54868200	-0.43784900	1.87398600
H	1.20032300	0.32048100	0.42057600
C	-1.15253400	1.76791600	1.62948900
C	-1.63401100	3.21178200	1.56275700
H	-1.20829900	3.73462400	0.69556100
H	-2.72898600	3.24094700	1.47318800
H	-1.34641300	3.77351000	2.45912600
C	-1.59171600	1.01795900	0.37233600
H	-1.33686800	-0.04949800	0.40497300
H	-2.68326600	1.08720000	0.26274500
H	-1.14250700	1.44824300	-0.53455000
C	-1.74861100	1.09080800	2.87103100
H	-1.44861500	1.61537700	3.78889500
H	-2.84644000	1.11143700	2.81497500
H	-1.44156300	0.03972900	2.96246400

C_6F_5-Tol

SCF Energy = -998,516472761
Thermal Correction to Gibbs Free Energy = 0,102508

C	-4.07976000	-2.50184000	-0.11120500
C	-5.46860800	-2.58432300	-0.15989400
C	-5.34421000	-4.97067000	-0.24459400
C	-3.95852300	-4.90112100	-0.19542000
C	-3.32190900	-3.67273000	-0.12775000
C	-3.41927900	-1.17934600	-0.05166000
C	-3.68430800	-0.18816100	-0.99165700
C	-3.08166400	1.05683300	-0.94528200
C	-2.17831100	1.34272600	0.06241300
C	-1.88895100	0.38095900	1.01358600
C	-2.50378800	-0.85736500	0.94565400
H	-6.06396200	-1.67379500	-0.13754700
H	-5.83521300	-5.93921600	-0.30230400
H	-3.36912000	-5.81278600	-0.21684100
H	-2.23758500	-3.61922300	-0.10496400
C	-6.11849400	-3.81424600	-0.22466900
C	-7.61315100	-3.87748200	-0.25762700
H	-8.04103700	-3.62359000	0.71914700
H	-8.02785300	-3.16966900	-0.98287800
H	-7.96549000	-4.87823900	-0.52214600
F	-1.59733700	2.52842000	0.11807500
F	-3.35561300	1.97254200	-1.86205600
F	-4.52605400	-0.42386100	-1.99281300
F	-2.21005700	-1.73901100	1.89538700
F	-1.03474700	0.65601900	1.98753700

***p*-$CF_3C_6H_4$-Tol**

SCF Energy = -839,385967585
Thermal Correction to Gibbs Free Energy = 0,146873

C	-4.07511900	-2.48696500	-0.07964600
C	-5.45746500	-2.57803700	-0.24455600
C	-5.34895400	-4.96619600	-0.16489200
C	-3.97235200	-4.89479700	-0.00283000
C	-3.33542800	-3.66466300	0.04382400
C	-3.41183400	-1.16871000	-0.04186400
C	-3.81993500	-0.13936600	-0.89606400
C	-3.21005100	1.10010800	-0.85459400
C	-2.18127500	1.33532600	0.05152600
C	-1.75645000	0.32484600	0.90222100
C	-2.37090800	-0.91649600	0.85261900

H	-6.04677700	-1.66588600	-0.32016600
H	-5.84143700	-5.93520500	-0.20156700
H	-3.38926700	-5.80758900	0.07797700
H	-2.25486900	-3.61378800	0.14596100
H	-4.61100400	-0.32309900	-1.61693300
H	-3.52930200	1.88999600	-1.52860600
H	-0.95811400	0.50953900	1.61301600
H	-2.05460100	-1.69697600	1.53857300
C	-1.53057700	2.67898500	0.05579600
F	-2.43363800	3.67222400	0.07693900
F	-0.72245300	2.86296900	1.10334800
F	-0.78680200	2.87694000	-1.04759400
C	-6.11139100	-3.80629400	-0.28199600
C	-7.60092700	-3.87214400	-0.41350400
H	-8.08797000	-3.76118300	0.56288400
H	-7.98453900	-3.07432500	-1.05698300
H	-7.92436500	-4.83021200	-0.83083400

_p_-$CF_3C_6H_4$-$CH_2C(O)^tBu$)

SCF Energy = -878,925998086
Thermal Correction to Gibbs Free Energy = 0,186007

C	-3.40366500	-0.84762700	-0.21370100
C	-3.65215700	0.32105100	-0.93079800
C	-2.76938600	1.38535500	-0.87458100
C	-1.62261800	1.28968200	-0.09414000
C	-1.35235700	0.12625700	0.61354900
C	-2.24047400	-0.93520600	0.54829400
H	-4.54951200	0.39825000	-1.53900100
H	-2.97013000	2.29326000	-1.43696600
H	-0.45266500	0.05059600	1.21493000
H	-2.03500800	-1.84436200	1.10799700
C	-0.69434800	2.45898100	-0.05522200
F	-1.31340300	3.57273700	0.37073200
F	0.35424800	2.26470500	0.74780400
F	-0.20635400	2.74756400	-1.27355500
C	-4.37967100	-1.99491500	-0.22385800
H	-5.20235300	-1.78077000	-0.91209500
H	-3.87892400	-2.90857200	-0.56061400
C	-4.89565000	-2.28278800	1.18177200
C	-5.94202700	-1.36058000	1.81802000
C	-6.77431000	-2.16857700	2.80867200
H	-7.51424300	-1.51573100	3.28527500
H	-7.31335300	-2.98254600	2.31038200
H	-6.15097700	-2.60955900	3.59042100
C	-5.17722800	-0.27232300	2.58468900
H	-4.60601500	0.38628000	1.92115900
H	-5.89307500	0.34879800	3.13638200
H	-4.48456500	-0.71457800	3.30957500
C	-6.86534900	-0.71114300	0.79271300
H	-7.40700900	-1.45834300	0.20046000
H	-7.61377700	-0.10184200	1.31227700
H	-6.33111300	-0.04641000	0.10630900
O	-4.42587200	-3.20703400	1.80402500

CsI

SCF Energy = -31,3110044211
Thermal Correction to Gibbs Free Energy = -0,039096

Cs	-1.40258700	1.00490200	0.00000000
I	2.39180300	1.00490200	0.00000000

Cs_2CO_3

SCF Energy = -303,576992759
Thermal Correction to Gibbs Free Energy = -0,038302

C	-3.65144200	3.24263300	1.10882700
O	-2.34917100	3.16691300	0.93101800
O	-4.14391100	4.28644500	1.66208000
Cs	-1.85213700	6.10390800	1.46071900
O	-4.39101000	2.27179600	0.72156000
Cs	-2.33338700	0.24795100	0.15408600

$CsHCO_3$

SCF Energy = -284,303879453
Thermal Correction to Gibbs Free Energy = -0,017961

C	-1.67865200	2.40073700	0.03576900
O	-0.54308000	2.86313000	-0.21320400
O	-2.66122800	2.96993900	0.52897500
Cs	-1.27501900	5.70231900	0.70963500
O	-1.86815200	1.06770700	-0.28311900
H	-1.02563800	0.77219000	-0.64463800

c1

SCF Energy = -1296,46154653
Thermal Correction to Gibbs Free Energy = 0,152674

C	3.83950300	0.69448500	0.04463500
H	2.76280100	0.83128600	0.01781700
C	4.69720500	1.63544800	-0.43780300
H	4.31683100	2.56270500	-0.85907000
C	4.32430300	-0.54968800	0.58466600
C	6.07959000	1.39896400	-0.40468200
H	6.76904200	2.12626200	-0.81301900
C	6.52049900	0.23121200	0.18376100
C	7.95933300	-0.10437300	0.22302100
C	8.92029200	0.60228700	-0.50003300
H	8.62963100	1.45235500	-1.10449300
C	10.24198800	0.20539200	-0.46227300
H	10.99095700	0.75117800	-1.02745200
C	10.59399400	-0.90099300	0.29648300
H	11.61692300	-1.25478400	0.35201300
C	9.59943200	-1.55670400	0.99400900
H	9.82637800	-2.42305100	1.60929700
C	8.02370000	-3.07785300	3.23209600
C	8.71409700	-2.42804100	4.25420500
C	9.76827700	-3.05203600	4.90900600
C	10.13315600	-4.34426600	4.55350400
C	9.43077400	-5.01703500	3.55619800
C	8.37908800	-4.38913300	2.90750900
N	5.68728500	-0.68709900	0.72523800

N	8.31924500	-1.17331100	0.96112800
O	3.54899800	-1.46972200	0.90009200
Pd	6.74485300	-2.05428900	2.10054600
C	11.25991000	-5.05027600	5.22314600
F	12.21138500	-5.43194700	4.34641100
F	11.87249900	-4.30584000	6.14967400
F	10.86120600	-6.18029200	5.83670600
H	7.83434700	-4.92544200	2.13425500
H	9.70801000	-6.03502100	3.29128200
H	10.30329600	-2.53076300	5.69685700
H	8.43419300	-1.41762800	4.54241000
I	4.95927200	-2.99973600	3.81964100
Cs	2.48215000	-4.17477800	1.07034600

c2

SCF Energy = -1536,53353854
Thermal Correction to Gibbs Free Energy = 0,282725

C	4.88788800	-1.37526400	0.33445300
H	5.50562500	-2.26703000	0.39200800
C	5.40144500	-0.10224600	0.41797200
H	6.47065700	0.04949400	0.55066800
C	3.50039300	-1.51928900	0.17023700
C	4.54578800	0.99847400	0.33399700
H	4.95141000	2.00234400	0.40765200
C	3.18778600	0.78075600	0.16427800
C	2.21813900	1.89429400	0.06347500
C	2.60882100	3.23359600	0.05311700
H	3.65799600	3.50855700	0.10943100
C	1.64473200	4.22667500	-0.03968500
H	1.94078400	5.27353800	-0.05050300
C	0.30606200	3.86701400	-0.11722300
H	-0.48227700	4.61154200	-0.18990900
C	-0.01144900	2.51651000	-0.10484900
H	-1.04468600	2.17490000	-0.16450300
C	-1.53165700	-0.40603400	-0.19932700
C	-2.19474100	-0.33498800	-1.43382500
C	-3.54460800	-0.01397700	-1.50498200
C	-4.26628900	0.22891900	-0.33586800
C	-3.63430600	0.14256200	0.90079800
C	-2.28060200	-0.17925100	0.96319900
N	2.67533200	-0.47399900	0.08650400
N	0.91487800	1.55805200	-0.01903000
O	3.01622800	-2.74800800	0.10059200
Pd	0.45682600	-0.57554200	-0.08613900
C	-5.70160100	0.61122400	-0.45586900
F	-6.32747000	0.66394000	0.72680200
F	-5.84797700	1.82167000	-1.02748000
F	-6.38829100	-0.24522400	-1.22938700
H	-1.80172100	-0.24666000	1.94157800
H	-4.19975400	0.32313400	1.81360700
H	-4.04742200	0.04645000	-2.47086800
H	-1.64843200	-0.53161600	-2.35743100
C	-0.27408300	-3.30109400	0.96001300
C	0.08440900	-3.24022500	-1.41335100
C	-0.42459900	-5.33128600	-0.31631600
C	-0.50023700	-4.67921300	0.91793600
H	-0.33715000	-2.79767700	1.92877400
H	0.31239700	-2.69652000	-2.33247700
H	-0.59473800	-6.40820400	-0.36525500
C	0.02641200	-2.55483400	-0.19002900
H	2.03575900	-2.71913900	-0.00991500
C	-0.13485600	-4.61664500	-1.47198700
H	-0.07668000	-5.13360000	-2.43031800
C	-0.84146900	-5.44467300	2.16186700
H	-1.91014700	-5.70224100	2.19266900
H	-0.28459900	-6.38977700	2.22175100
H	-0.61893700	-4.86500300	3.06667900

c2_D

SCF Energy = -1536,53353901
Thermal Correction to Gibbs Free Energy = 0,279184

C	4.98881300	-1.37618100	0.29559200
H	5.65168200	-2.23631300	0.36546800
C	5.45794400	-0.09714200	0.30370100
H	6.52677200	0.10075500	0.38268000
C	3.57470500	-1.66369900	0.19423900
C	4.55507500	0.97933200	0.21155300
H	4.92409900	1.99957400	0.22756100
C	3.20728900	0.69268800	0.11121800
C	2.20999300	1.77441000	0.02145400
C	2.55865300	3.12718100	-0.03562400
H	3.60414700	3.41835000	-0.02600700
C	1.57773600	4.09906000	-0.11168600
H	1.85423100	5.15041400	-0.15669700
C	0.24260000	3.71263000	-0.12766000
H	-0.56500900	4.43729300	-0.18479500
C	-0.04788600	2.36216500	-0.07216700
H	-1.07685300	2.01233500	-0.08349500
C	-1.42235000	-0.37862900	0.01143100
C	-2.14429300	-0.26123700	-1.18096700
C	-3.50398000	0.02662200	-1.15385000
C	-4.15612400	0.20373100	0.06661900
C	-3.44317600	0.11293400	1.25830200
C	-2.08021700	-0.17279200	1.22657600
N	2.71775700	-0.57506600	0.09635200
N	0.90201900	1.41595400	-0.00128200
O	3.14424000	-2.82823800	0.19174800
Pd	0.55164000	-0.66358300	0.00515700
C	-5.60826900	0.54664300	0.04971900
F	-6.16650600	0.50096100	1.26493400
F	-5.81938400	1.78384700	-0.43237900
F	-6.30661800	-0.28427600	-0.74010600
H	-1.53235100	-0.24432900	2.16779200
H	-3.94930600	0.26027700	2.21057500
H	-4.06646600	0.11497400	-2.08372700
H	-1.64730100	-0.39607700	-2.14197000
C	-1.87859300	-3.50202100	-1.41359900
C	-1.05702400	-3.27865000	0.85665100
C	0.22005000	-2.95043700	0.33158300
C	0.42530100	-2.91178300	-1.06251900
H	-2.70889500	-3.72387800	-2.08316300
H	1.10455500	-2.95839000	0.97295400
H(Iso=2)	1.44609400	-2.79818200	-1.42328500
C	-2.08574400	-3.55352900	-0.02844200
H	-3.07193300	-3.81088200	0.36032100
C	-0.64004700	-3.17239300	-1.93600900

H	-0.48186000	-3.14720500	-3.01266000
C	-1.25319300	-3.36750400	2.33675200
H	-2.28784000	-3.13730800	2.62203400
H	-1.03067700	-4.38109900	2.70137900
H	-0.58401600	-2.68259600	2.87385300

c2 (smd acetone)

SCF Energy = -1536,54101573
Thermal Correction to Gibbs Free Energy = 0,282569

C	4.99575800	-1.37889400	0.28532500
H	5.66232200	-2.23702100	0.35423600
C	5.46659700	-0.09841900	0.28300500
H	6.53628400	0.09899700	0.35145700
C	3.58180000	-1.66307900	0.20002800
C	4.56488600	0.97832800	0.19439400
H	4.93515500	1.99813400	0.20374600
C	3.21518300	0.69279200	0.10597600
C	2.21804800	1.77758000	0.01974300
C	2.57396200	3.12701000	-0.04079800
H	3.62015900	3.41594700	-0.03785400
C	1.59597600	4.10412100	-0.11115600
H	1.87696100	5.15396300	-0.15832000
C	0.25982600	3.72300800	-0.11979900
H	-0.54520500	4.45084600	-0.17341400
C	-0.03745800	2.37346000	-0.06252800
H	-1.06934500	2.03286200	-0.06919700
C	-1.42133200	-0.36525200	0.01046000
C	-2.13321200	-0.24286300	-1.18734100
C	-3.49539800	0.03552100	-1.16786200
C	-4.15660800	0.19619900	0.05058300
C	-3.45190400	0.10330600	1.24779200
C	-2.08628600	-0.17151100	1.22360200
N	2.72497600	-0.57580800	0.10110100
N	0.90857100	1.42234900	0.00445400
O	3.14774200	-2.83006200	0.21261500
Pd	0.54900500	-0.65604100	0.01204200
C	-5.61089100	0.52429200	0.02604000
F	-6.17983800	0.46847900	1.23626900
F	-5.83490600	1.76189600	-0.45284300
F	-6.29893700	-0.30987300	-0.77184600
H	-1.54484000	-0.24173200	2.16854000
H	-3.96314000	0.24060200	2.19884300
H	-4.04943900	0.12860500	-2.10240200
H	-1.62989700	-0.36491300	-2.14682300
C	-1.90057100	-3.49940600	-1.39559900
C	-1.07110800	-3.28255600	0.87398200
C	0.20276500	-2.94587600	0.34491500
C	0.40246200	-2.90028100	-1.04957200
H	-2.73142600	-3.72543300	-2.06316300
H	1.08557500	-2.95007500	0.98850000
H	1.41937900	-2.78264300	-1.42041100
C	-2.10170800	-3.55878900	-0.00845800
H	-3.08285500	-3.83057400	0.38326900
C	-0.66564400	-3.16192900	-1.92127000
H	-0.51160600	-3.13079700	-2.99839500
C	-1.25442200	-3.38151700	2.35443900
H	-2.31490600	-3.34712300	2.63400700
H	-0.84083800	-4.32624800	2.73744900
H	-0.73019000	-2.57087000	2.87834400

c3

SCF Energy = -1536,5368422
Thermal Correction to Gibbs Free Energy = 0,278941

C	4.88788800	-1.37526400	0.33445300
H	5.50562500	-2.26703000	0.39200800
C	5.40144500	-0.10224600	0.41797200
H	6.47065700	0.04949400	0.55066800
C	3.50039300	-1.51928900	0.17023700
C	4.54578800	0.99847400	0.33399700
H	4.95141000	2.00234400	0.40765200
C	3.18778600	0.78075600	0.16427800
C	2.21813900	1.89429400	0.06347500
C	2.60882100	3.23359600	0.05311700
H	3.65799600	3.50855700	0.10943100
C	1.64473200	4.22667500	-0.03968500
H	1.94078400	5.27353800	-0.05050300
C	0.30606200	3.86701400	-0.11722300
H	-0.48227700	4.61154200	-0.18990900
C	-0.01144900	2.51651000	-0.10484900
H	-1.04468600	2.17490000	-0.16450300
C	-1.53165700	-0.40603400	-0.19932700
C	-2.19474100	-0.33498800	-1.43382500
C	-3.54460800	-0.01397700	-1.50498200
C	-4.26628900	0.22891900	-0.33586800
C	-3.63430600	0.14256200	0.90079800
C	-2.28060200	-0.17925100	0.96319900
N	2.67533200	-0.47399900	0.08650400
N	0.91487800	1.55805200	-0.01903000
O	3.01622800	-2.74800800	0.10059200
Pd	0.45682600	-0.57554200	-0.08613900
C	-5.70160100	0.61122400	-0.45586900
F	-6.32747000	0.66394000	0.72680200
F	-5.84797700	1.82167000	-1.02748000
F	-6.38829100	-0.24522400	-1.22938700
H	-1.80172100	-0.24666000	1.94157800
H	-4.19975400	0.32313400	1.81360700
H	-4.04742200	0.04645000	-2.47086800
H	-1.64843200	-0.53161600	-2.35743100
C	-0.27408300	-3.30109400	0.96001300
C	0.08440900	-3.24022500	-1.41335100
C	-0.42459900	-5.33128600	-0.31631600
C	-0.50023700	-4.67921300	0.91793600
H	-0.33715000	-2.79767700	1.92877400
H	0.31239700	-2.69652000	-2.33247700
H	-0.59473800	-6.40820400	-0.36525500
C	0.02641200	-2.55483400	-0.19002900
H	2.03575900	-2.71913900	-0.00991500
C	-0.13485600	-4.61664500	-1.47198700
H	-0.07668000	-5.13360000	-2.43031800
C	-0.84146900	-5.44467300	2.16186700
H	-1.91014700	-5.70224100	2.19266900
H	-0.28459900	-6.38977700	2.22175100
H	-0.61893700	-4.86500300	3.06667900

c3-R (R = $CH_2C(O)^tBu$)

SCF Energy = -1576,09799283
Thermal Correction to Gibbs Free Energy = 0,322148

C	5.11174800	-1.05909500	-0.20681800
H	5.83754500	-1.84949800	-0.37730600
C	5.43680200	0.27246300	-0.25301300
H	6.45298300	0.58539500	-0.48460200
C	3.78348100	-1.42926200	0.09200700
C	4.45002600	1.22494100	0.01431500
H	4.69155800	2.28241100	-0.02279100
C	3.16285100	0.79497000	0.28879100
C	2.09074300	1.77200600	0.57314800
C	2.37205500	3.09017200	0.93760800
H	3.40028500	3.41831100	1.05736500
C	1.33218200	3.97590300	1.17177200
H	1.54458700	5.00411300	1.45717600
C	0.02482900	3.52765800	1.04194800
H	-0.82473900	4.18335600	1.21233700
C	-0.18331900	2.20153000	0.69627400
H	-1.18917500	1.79957800	0.58782500
C	-1.38878100	-0.63636900	-0.37668800
C	-1.89024400	-0.71431300	-1.68429600
C	-3.24163800	-0.52402400	-1.94479700
C	-4.12777500	-0.26788800	-0.89772800
C	-3.65359400	-0.19125600	0.40737600
C	-2.29473400	-0.37155400	0.65976100
N	2.81675900	-0.52082500	0.29110200
N	0.81648800	1.34111100	0.47549100
O	3.53768800	-2.71637600	0.15933400
Pd	0.56023600	-0.75966100	0.00592200
C	-5.56783100	-0.06002300	-1.22657100
F	-6.33139700	0.10721300	-0.14010200
F	-5.74749400	1.02266500	-2.00378100
F	-6.07792100	-1.09586200	-1.91236100
H	-1.93939600	-0.30058200	1.68981300
H	-4.34091000	0.00607800	1.22797200
H	-3.61689200	-0.57852100	-2.96725500
H	-1.21721500	-0.93334500	-2.51354800
H	2.67799200	-2.95925600	0.64930800
C	0.40855200	-2.78907900	-0.53543200
H	-0.45989800	-2.98886700	-1.16438800
H	1.34653800	-2.93060400	-1.08815100
C	0.41944900	-3.47758400	0.74726700
O	1.46993500	-3.58434100	1.41210700
C	-0.83925500	-4.10246800	1.36381600
C	-0.50315600	-5.56779100	1.66341300
H	-1.36030000	-6.05658700	2.14818600
H	-0.27928500	-6.12409300	0.74132600
H	0.36581700	-5.64775300	2.32642200
C	-2.07110100	-4.05654300	0.46720300
H	-2.91548800	-4.53531400	0.98399500
H	-2.37496100	-3.03064600	0.22255700
H	-1.91445600	-4.60253100	-0.47387800
C	-1.12921600	-3.37424300	2.67862000
H	-0.26132200	-3.40847400	3.34860000
H	-1.38253400	-2.31978400	2.49856800
H	-1.98168100	-3.84354500	3.19077000

c5H

SCF Energy = -697,130432563
Thermal Correction to Gibbs Free Energy = 0,102794

C	3.81274300	0.49228400	-0.08329900
H	2.72928600	0.54991500	-0.14051700
C	4.63483100	1.54195000	-0.44524500
H	4.20162300	2.47709400	-0.79515400
C	4.41881700	-0.67689500	0.38797600
C	6.02031500	1.40533400	-0.35512900
H	6.67638200	2.23458100	-0.60664000
C	6.54536700	0.19927900	0.09346700
C	8.00509700	-0.03734100	0.18260900
C	8.89215300	0.62597000	-0.66824000
H	8.51859900	1.31338400	-1.42434200
C	10.25181800	0.36748100	-0.56058400
H	10.95920800	0.86612900	-1.22055400
C	10.68888300	-0.54592300	0.39067800
H	11.74423100	-0.77888800	0.51228700
C	9.73577200	-1.16470300	1.19187800
H	10.03629200	-1.88418500	1.95451300
N	5.74319500	-0.82047700	0.46451700
N	8.42734200	-0.92664700	1.09705900
Pd	6.55085800	-2.58728800	1.42872200
O	3.66470600	-1.69916800	0.77934200
H	4.30561600	-2.40389400	1.08015900

c3-C_6F_5

SCF Energy = -1695,68596435
Thermal Correction to Gibbs Free Energy = 0,236681

C	4.82268500	-1.42518100	0.33929300
H	5.41682600	-2.33253000	0.40033400
C	5.36498000	-0.16631600	0.43594100
H	6.43537600	-0.03914400	0.58325200
C	3.43365700	-1.53875800	0.15997400
C	4.53393100	0.95286200	0.34734300
H	4.95866800	1.94734300	0.43634800
C	3.17462300	0.76856800	0.15851600
C	2.23869200	1.90835600	0.05124700
C	2.66536200	3.23639800	0.03974800
H	3.72151300	3.48316400	0.09648200
C	1.72810400	4.25424500	-0.05737300
H	2.05152300	5.29287800	-0.06880400
C	0.38040300	3.93066800	-0.14011900
H	-0.38739000	4.69588900	-0.21675700
C	0.02716400	2.58937700	-0.12940900
H	-1.01354600	2.27433100	-0.19504100
C	-1.56974000	-0.33897500	-0.21196300
C	-2.24531000	-0.24083000	-1.41840100
C	-3.62202500	-0.06374800	-1.49741700
C	-3.72337600	-0.08392700	0.90076800
C	-2.34571700	-0.25990600	0.93422600
N	2.63041000	-0.47524600	0.07003300
N	0.92782600	1.60770000	-0.03854700
O	2.93273100	-2.75880600	0.08310200
Pd	0.43324300	-0.50359000	-0.10464400
C	-0.33243000	-3.19693200	0.95555500

C	0.03246900	-3.15465600	-1.42420300
C	-0.49685300	-5.23320700	-0.31093000
C	-0.57022100	-4.57332900	0.91958700
H	-0.40270300	-2.68036700	1.91551900
H	0.26437400	-2.61679100	-2.34425200
H	-0.67619600	-6.30881500	-0.35303200
C	-0.01636700	-2.47003900	-0.20179900
H	1.95425300	-2.71943600	-0.03437000
C	-0.20089900	-4.52963000	-1.47156300
H	-0.14907700	-5.05297400	-2.42649200
C	-0.92040700	-5.32819000	2.16735200
H	-1.98875000	-5.58750100	2.19130300
H	-0.36223100	-6.27161700	2.23921000
H	-0.70619100	-4.74019700	3.06850700
C	-4.36414200	0.01185800	-0.32692800
F	-1.57184900	-0.31161300	-2.57758900
F	-1.77255200	-0.34801200	2.14699000
F	-4.43768800	-0.00155100	2.02237500
F	-5.68243900	0.18381900	-0.37981400
F	-4.24037400	0.03497100	-2.67369400

c4

SCF Energy = -1555,85735928
Thermal Correction to Gibbs Free Energy = 0,262473

C	5.08439100	-1.19972600	0.42145900
H	5.76514200	-2.04425300	0.51744800
C	5.53756800	0.08424200	0.33119700
H	6.60610000	0.30026600	0.35277700
C	3.67318000	-1.50095600	0.41672700
C	4.61495100	1.13536700	0.21348000
H	4.96505300	2.16095000	0.15985900
C	3.26664200	0.82050900	0.16917100
C	2.25579500	1.89476500	0.03956800
C	2.59110200	3.24776700	-0.08079400
H	3.63093000	3.55959000	-0.09280100
C	1.59253800	4.20065500	-0.19091800
H	1.85238400	5.25344700	-0.28535100
C	0.26372300	3.79412600	-0.17955600
H	-0.55403900	4.50513200	-0.26421000
C	-0.00046700	2.43988600	-0.06087800
H	-1.02317200	2.06499600	-0.05057800
C	-1.40954800	-0.44017500	-0.06571900
C	-2.11010200	-0.52286000	-1.28068600
C	-3.46660800	-0.23142300	-1.35575300
C	-4.16738500	0.13983900	-0.20731600
C	-3.50288300	0.20664200	1.01471800
C	-2.14212200	-0.07941900	1.07689300
N	2.79317300	-0.44859400	0.24568900
N	0.96157500	1.51607300	0.04762100
O	3.26821200	-2.67127200	0.56850700
Pd	0.58098600	-0.63152100	0.06807100
C	-5.62994800	0.39972800	-0.30929800
F	-6.12208700	1.02658800	0.76907800
F	-5.93383500	1.15799200	-1.37708200
F	-6.33974700	-0.73527800	-0.45019000
H	-1.63630300	-0.00520800	2.04221000
H	-4.04758300	0.49102400	1.91393400
H	-3.99050100	-0.29051100	-2.31045100
H	-1.58317100	-0.82242000	-2.18780600
C	-0.75641000	-3.29555700	0.72658800
C	0.64368000	-3.31100300	-1.21037600
C	-0.63309300	-5.28561400	-0.62411900
C	-1.15169200	-4.62060200	0.48841700
H	-1.20696100	-2.78007900	1.57981900
H	1.35343900	-2.82342100	-1.88062500
H	-0.94972500	-6.30762500	-0.84318700
C	0.13191700	-2.60155400	-0.10755900
Cs	2.26272900	-5.15834400	1.58950700
C	0.26083900	-4.62462300	-1.47115500
H	0.65828300	-5.14092200	-2.34697400
C	-2.14539700	-5.28612100	1.39756700
H	-3.15427000	-4.87319200	1.25369500
H	-2.20825500	-6.36718300	1.21385300
H	-1.89958700	-5.13545100	2.45889100

c4-R (R = $CH_2C(O)^tBu$)
SCF Energy = -1595,41117175
Thermal Correction to Gibbs Free Energy = 0,304524

C	4.28801600	-1.99611400	0.29657300
H	4.78198200	-2.94818200	0.48347700
C	4.93515100	-0.94974100	-0.29982400
H	5.97321000	-1.05367000	-0.61609700
C	2.92247700	-1.86499000	0.74072000
C	4.27064700	0.27643000	-0.48945800
H	4.79106400	1.11899700	-0.93501700
C	2.93959700	0.35103100	-0.12104600
C	2.17234800	1.61334100	-0.22482600
C	2.77068400	2.84079800	-0.52264900
H	3.83697500	2.89577100	-0.72269800
C	2.00251200	3.99371400	-0.54558800
H	2.46500000	4.95270400	-0.77175000
C	0.64236900	3.90854000	-0.26910200
H	0.00159900	4.78658500	-0.27193000
C	0.11107500	2.65960700	0.01229500
H	-0.95170600	2.52829900	0.21472000
C	-1.87266400	-0.07390500	0.07472300
C	-2.35549100	0.68837300	-1.00518600
C	-3.67949800	1.10702900	-1.06678800
C	-4.56266200	0.77578700	-0.03887300
C	-4.11844000	0.00532800	1.03237200
C	-2.79447400	-0.42365900	1.07518300
N	2.26295200	-0.69803600	0.40798700
N	0.84822900	1.54403300	0.03802200
O	2.35054500	-2.74165000	1.42559600
Pd	0.07912200	-0.49803000	0.22911700
C	-5.96909200	1.25774600	-0.12936600
F	-6.71849000	0.87984500	0.91452400
F	-6.03453600	2.60159400	-0.19053100
F	-6.58636200	0.81246400	-1.23738800
H	-2.46760300	-1.06666600	1.89425500
H	-4.81134900	-0.26793200	1.82690800
H	-4.03273200	1.69611900	-1.91449200
H	-1.67893500	0.96987800	-1.81458800
C	-0.49252300	-2.49150700	0.08272200
H	-1.54696900	-2.53196000	-0.23398500
H	0.11234000	-2.89551800	-0.73834500
C	-0.40255600	-3.32349600	1.31357900

O	-0.80343700	-2.91523100	2.40441200
C	-0.01367700	-4.81393600	1.21347600
C	0.65250800	-5.26038900	2.51247200
H	0.83559300	-6.34489500	2.49162700
H	1.61761000	-4.75131300	2.63683300
H	0.01939800	-5.03764000	3.37979600
C	0.89263100	-5.16439700	0.03722600
H	1.15659900	-6.23189500	0.08535800
H	0.40286000	-4.99972000	-0.93214100
H	1.81939600	-4.57805900	0.07111300
C	-1.35245300	-5.54960300	1.05133600
H	-2.01921500	-5.34993900	1.90126600
H	-1.87194100	-5.24439100	0.13103400
H	-1.18236100	-6.63500300	0.99458600
Cs	1.05049500	-0.99851100	3.67150900

c4-C_6F_5

SCF Energy = -1715,00887929
Thermal Correction to Gibbs Free Energy = 0,217936

C	4.95603200	-1.30593500	0.00281600
H	5.61173200	-2.17505100	-0.00106700
C	5.41675200	-0.05165700	-0.27133000
H	6.46703500	0.11470800	-0.51164500
C	3.57169200	-1.54446100	0.33592500
C	4.52737100	1.03508500	-0.23093800
H	4.88061200	2.04098700	-0.43450600
C	3.19531700	0.77873500	0.03903400
C	2.22473200	1.89075100	0.11682100
C	2.60264200	3.23673900	0.13224200
H	3.65171000	3.51409200	0.08839100
C	1.63408200	4.22198000	0.22845600
H	1.92365600	5.27096400	0.24480500
C	0.29560800	3.85430700	0.30818000
H	-0.49735200	4.59347000	0.38664500
C	-0.00977600	2.50352500	0.29141700
H	-1.04064200	2.15594400	0.34625300
C	-1.47423900	-0.37698900	-0.13613300
C	-2.01433000	-0.36675200	-1.41360800
C	-3.36475600	-0.15517400	-1.66422400
C	-4.23059200	0.05011300	-0.59897000
C	-3.73281300	0.04148500	0.69615100
C	-2.37394100	-0.17161300	0.89827500
N	2.70375500	-0.46850400	0.26609000
N	0.92344300	1.55040000	0.20196500
O	3.17829200	-2.67651600	0.67822700
Pd	0.51633000	-0.57476300	0.15044400
C	-0.82401500	-3.21207400	0.80489400
C	0.68812300	-3.28009800	-1.04876200
C	-0.55629900	-5.26341600	-0.42672100
C	-1.16104900	-4.56117300	0.61558000
H	-1.32162900	-2.67307800	1.61560300
H	1.42311400	-2.80183700	-1.69674500
H	-0.82122600	-6.30769000	-0.60413300
C	0.09448400	-2.54119500	-0.01210900
Cs	1.92041200	-4.78081500	2.20213800
C	0.36761200	-4.61847400	-1.25319800
H	0.83475700	-5.16649200	-2.07284200
C	-2.16255000	-5.21957200	1.52159400
H	-3.16046700	-4.77232300	1.40947100
H	-2.26015500	-6.29256000	1.30983500
H	-1.89632500	-5.10952100	2.58446300
F	-1.94775200	-0.16751900	2.17728900
F	-4.56333500	0.24074500	1.72187000
F	-3.84452400	-0.14531300	-2.90837700
F	-1.22679300	-0.56349400	-2.48308400
F	-5.52837200	0.25693400	-0.81848000

c5Cs

SCF Energy = -716,4419448
Thermal Correction to Gibbs Free Energy = 0,081605

C	3.72818600	0.74314000	-0.36926500
H	2.66121900	0.89584800	-0.52793000
C	4.61429200	1.78918400	-0.37988400
H	4.25620800	2.80821800	-0.53404400
C	4.17150700	-0.60885700	-0.13912100
C	5.98547400	1.55203600	-0.19074900
H	6.70460700	2.36740600	-0.16081400
C	6.38656000	0.23474900	-0.01407400
C	7.82477300	-0.09708100	0.15284400
C	8.81184900	0.60896700	-0.53592000
H	8.52674400	1.42004600	-1.20300400
C	10.14402100	0.23959200	-0.39532400
H	10.92296900	0.76824600	-0.94218800
C	10.45904500	-0.82317700	0.44309400
H	11.48714000	-1.14882600	0.58713100
C	9.42106900	-1.46325800	1.10982400
H	9.62773700	-2.27893900	1.80417200
N	5.53098400	-0.80545500	0.00757600
N	8.13060300	-1.12898400	0.97182900
O	3.37611700	-1.57355600	-0.05770300
Pd	6.59291800	-2.76820400	0.34689700
Cs	3.84017600	-2.95744900	2.50818000

TS-c2-c3

SCF Energy = -1536,5093548
Thermal Correction to Gibbs Free Energy = 0,276496

C	5.01328800	-1.25071100	0.45902400
H	5.64795000	-2.12554400	0.57513900
C	5.51762300	0.02462300	0.45182500
H	6.58899300	0.18473200	0.56373900
C	3.60949800	-1.45629100	0.31732000
C	4.66379700	1.13065900	0.30896600
H	5.06545600	2.13934800	0.31613400
C	3.31073600	0.88803300	0.16760700
C	2.30160300	1.95784600	0.02948900
C	2.63010700	3.31141200	-0.02791700
H	3.66945000	3.62451500	0.01807600
C	1.62518100	4.25929500	-0.14754300
H	1.87707700	5.31678000	-0.19315000
C	0.30173000	3.84219900	-0.20615200
H	-0.51675400	4.55087600	-0.29876800
C	0.03770900	2.48264400	-0.14597600
H	-0.98006800	2.09790500	-0.18870900
C	-1.29488600	-0.47980100	-0.11098200

C	-1.99779400	-0.56719800	-1.31996900
C	-3.37633600	-0.38695300	-1.36043600
C	-4.08000900	-0.11864100	-0.18706100
C	-3.40139300	-0.04318200	1.02736000
C	-2.02158200	-0.22148100	1.05945400
N	2.81297600	-0.36983400	0.16042200
N	1.00453700	1.56572700	-0.03141600
O	3.09148800	-2.62206800	0.33781800
Pd	0.70717100	-0.54151200	-0.01766300
C	-5.56491500	0.00783900	-0.23911500
F	-6.06248300	0.64780400	0.82820800
F	-5.97617000	0.67712900	-1.32777700
F	-6.17201400	-1.19128200	-0.28581700
H	-1.50433300	-0.15094200	2.01856200
H	-3.95116400	0.16269200	1.94460500
H	-3.90873700	-0.45102500	-2.30933700
H	-1.46596700	-0.77568700	-2.24880500
C	-0.36792600	-3.23923800	0.85245700
C	0.36699800	-3.16841100	-1.44014600
C	-1.42146100	-4.63411000	-0.77937800
C	-1.33172800	-4.19883600	0.54509100
H	-0.29231900	-2.89110300	1.88626000
H	1.04244700	-2.78317900	-2.20673100
H	-2.16815400	-5.38643000	-1.03896100
C	0.48635900	-2.68734800	-0.11907800
H	1.77109800	-2.54385000	0.19054900
C	-0.57447500	-4.13290100	-1.76791300
H	-0.65637700	-4.50454100	-2.78882400
C	-2.26371900	-4.70903300	1.60276100
H	-2.98047400	-3.93061900	1.90312700
H	-2.84306300	-5.57293800	1.25427200
H	-1.72090500	-5.01089800	2.50871300

TS-c2-c3_D

SCF Energy = -1536,5093548
Thermal Correction to Gibbs Free Energy = 0,274663

C	5.01328800	-1.25071100	0.45902400
H	5.64795000	-2.12554400	0.57513900
C	5.51762300	0.02462300	0.45182500
H	6.58899300	0.18473200	0.56373900
C	3.60949800	-1.45629100	0.31732000
C	4.66379700	1.13065900	0.30896600
H	5.06545600	2.13934800	0.31613400
C	3.31073600	0.88803300	0.16760700
C	2.30160300	1.95784600	0.02948900
C	2.63010700	3.31141200	-0.02791700
H	3.66945000	3.62451500	0.01807600
C	1.62518100	4.25929500	-0.14754300
H	1.87707700	5.31678000	-0.19315000
C	0.30173000	3.84219900	-0.20615200
H	-0.51675400	4.55087600	-0.29876800
C	0.03770900	2.48264400	-0.14597600
H	-0.98006800	2.09790500	-0.18870900
C	-1.29488600	-0.47980100	-0.11098200
C	-1.99779400	-0.56719800	-1.31996900
C	-3.37633600	-0.38695300	-1.36043600
C	-4.08000900	-0.11864100	-0.18706100
C	-3.40139300	-0.04318200	1.02736000
C	-2.02158200	-0.22148100	1.05945400
N	2.81297600	-0.36983400	0.16042200
N	1.00453700	1.56572700	-0.03141600
O	3.09148800	-2.62206800	0.33781800
Pd	0.70717100	-0.54151200	-0.01766300
C	-5.56491500	0.00783900	-0.23911500
F	-6.06248300	0.64780400	0.82820800
F	-5.97617000	0.67712900	-1.32777700
F	-6.17201400	-1.19128200	-0.28581700
H	-1.50433300	-0.15094200	2.01856200
H	-3.95116400	0.16269200	1.94460500
H	-3.90873700	-0.45102500	-2.30933700
H	-1.46596700	-0.77568700	-2.24880500
C	-0.36792600	-3.23923800	0.85245700
C	0.36699800	-3.16841100	-1.44014600
C	-1.42146100	-4.63411000	-0.77937800
C	-1.33172800	-4.19883600	0.54509100
H	-0.29231900	-2.89110300	1.88626000
H	1.04244700	-2.78317900	-2.20673100
H	-2.16815400	-5.38643000	-1.03896100
C	0.48635900	-2.68734800	-0.11907800
H(Iso=2)	1.77109800	-2.54385000	0.19054900
C	-0.57447500	-4.13290100	-1.76791300
H	-0.65637700	-4.50454100	-2.78882400
C	-2.26371900	-4.70903300	1.60276100
H	-2.98047400	-3.93061900	1.90312700
H	-2.84306300	-5.57293800	1.25427200
H	-1.72090500	-5.01089800	2.50871300

TS-c2-c3 (smd acetone)

SCF Energy = -1536,51569994
Thermal Correction to Gibbs Free Energy = 0,275187

C	5.01619500	-1.25538400	0.44488900
H	5.65339700	-2.12939700	0.55681300
C	5.52264700	0.02091000	0.44151700
H	6.59430900	0.17941600	0.55206600
C	3.61387600	-1.45578700	0.30374600
C	4.67092000	1.12864900	0.30415100
H	5.07426800	2.13662800	0.31309700
C	3.31673800	0.88985500	0.16492900
C	2.30854500	1.96118100	0.03595600
C	2.63940800	3.31404700	0.00118600
H	3.67839000	3.62637200	0.05858500
C	1.63525200	4.26516100	-0.10777600
H	1.88851500	5.32273800	-0.13474800
C	0.31183400	3.85009700	-0.17934100
H	-0.50585800	4.56065100	-0.26438400
C	0.04513500	2.49021600	-0.14183300
H	-0.97453800	2.11279400	-0.19538100
C	-1.28850300	-0.46956200	-0.13667100
C	-1.98740500	-0.54388900	-1.34966400
C	-3.36900500	-0.38151900	-1.39189800
C	-4.07865100	-0.14277100	-0.21520100
C	-3.40436200	-0.07774000	1.00326100
C	-2.02232500	-0.23919200	1.03598300
N	2.81766700	-0.36950400	0.15332000
N	1.01046700	1.56912200	-0.03673400
O	3.08937700	-2.62376500	0.31904500

Pd	0.71395700	-0.53356000	-0.03361200
C	-5.56412500	-0.03462800	-0.26709700
F	-6.07249700	0.59343800	0.80219200
F	-5.98715700	0.63300700	-1.35269700
F	-6.15823100	-1.24247000	-0.31836100
H	-1.51061900	-0.17728800	1.99862900
H	-3.95661700	0.10530000	1.92396200
H	-3.89591300	-0.43717500	-2.34451300
H	-1.45263400	-0.72449300	-2.28324100
C	-0.35756600	-3.22970100	0.86089100
C	0.33778300	-3.17007600	-1.44510100
C	-1.45500700	-4.61827700	-0.75056500
C	-1.33646700	-4.18136300	0.57218000
H	-0.26119000	-2.88123700	1.89313100
H	0.99852000	-2.79086500	-2.22760300
H	-2.21307700	-5.36421000	-0.99486900
C	0.48345800	-2.68639300	-0.12757200
H	1.77205800	-2.53268000	0.16813700
C	-0.61987700	-4.12624700	-1.75480900
H	-0.72411800	-4.49751500	-2.77394100
C	-2.25261100	-4.68443300	1.64700400
H	-2.95663700	-3.90002600	1.96239600
H	-2.84497900	-5.54290400	1.30709300
H	-1.69468100	-4.98906200	2.54280600

TS-c3-c5H

SCF Energy = -1536,52202378
Thermal Correction to Gibbs Free Energy = 0,280772

C	4.84589100	-1.39287700	0.34388300
H	5.43538500	-2.30390100	0.39726900
C	5.40063400	-0.13547700	0.45236100
H	6.47310300	-0.02462700	0.60008000
C	3.45785300	-1.47767800	0.16221600
C	4.58910400	0.99902300	0.37561700
H	5.02983600	1.98704400	0.46901300
C	3.22501600	0.82906700	0.18618100
C	2.27475700	1.96264400	0.08354000
C	2.68535000	3.29603700	0.09975800
H	3.73700500	3.55578000	0.18655700
C	1.73338700	4.30051000	-0.00525800
H	2.03974900	5.34460500	0.00318300
C	0.39229900	3.95714000	-0.12113900
H	-0.38443100	4.71288000	-0.20551900
C	0.06127200	2.60842800	-0.12992700
H	-0.97483400	2.27733700	-0.21928700
C	-1.57310400	-0.83187100	-0.24606700
C	-2.19600700	-0.56302900	-1.48079000
C	-3.49122100	-0.06984100	-1.54615900
C	-4.21061000	0.16474400	-0.37452900
C	-3.62420700	-0.11515100	0.86094300
C	-2.33108300	-0.61180200	0.92166100
N	2.68035700	-0.40171400	0.08449800
N	0.97388200	1.64139800	-0.03212900
O	2.90114200	-2.67989100	0.06534100
Pd	0.42692800	-0.54934500	-0.11107700
C	-5.61944500	0.64348900	-0.43745100
F	-5.93299700	1.43047800	0.60454700
F	-5.86735500	1.34857400	-1.55178500
F	-6.50604600	-0.36779700	-0.42328700
H	-1.89368800	-0.82283300	1.89783300
H	-4.18144100	0.06713200	1.77924800
H	-3.94438400	0.14689100	-2.51256700
H	-1.65167100	-0.73374100	-2.40975600
C	-0.43011300	-3.18563900	0.96963500
C	-0.29470100	-3.12628800	-1.43180600
C	-0.22363600	-5.23892500	-0.26127800
C	-0.34063600	-4.57946000	0.96451100
H	-0.52030600	-2.67690400	1.93261400
H	-0.27428100	-2.57722900	-2.37389600
H	-0.15002100	-6.32679600	-0.28107100
C	-0.39744100	-2.42680000	-0.21383900
H	1.92857100	-2.56293800	-0.03987500
C	-0.20279900	-4.51330100	-1.44917500
H	-0.10564200	-5.03463000	-2.40153200
C	-0.38628600	-5.35115300	2.24968800
H	-1.42191500	-5.52372800	2.57710200
H	0.08816600	-6.33538900	2.14550400
H	0.12190500	-4.81618800	3.06258500

TS-c3R-c5H (R = $CH_2C(O)^tBu$)

SCF Energy = -1576,06483579
Thermal Correction to Gibbs Free Energy = 0.04798400

C	4.72497400	-1.67309400	-1.75150700
H	5.34236800	-2.35205900	-2.33335400
C	5.23693900	-0.60104400	-1.06655000
H	6.30399500	-0.38834000	-1.08667700
C	3.33375500	-1.90395500	-1.71401000
C	4.36595700	0.22820700	-0.35678400
H	4.74415100	1.11209300	0.14736900
C	3.01188500	-0.06765800	-0.35360600
C	2.06669400	0.83761200	0.33891200
C	2.48063700	1.73019200	1.33227400
H	3.50513400	1.71782400	1.69457400
C	1.56387300	2.62013600	1.87050200
H	1.87337200	3.31986700	2.64434000
C	0.25176200	2.60191800	1.41294200
H	-0.49597600	3.29126100	1.79659600
C	-0.09293600	1.65591600	0.45892200
H	-1.11727500	1.56723800	0.09462500
C	-1.90436500	-0.78699700	-1.13679300
C	-2.28903200	-0.01985700	-2.25219200
C	-3.32000000	0.90637600	-2.16314000
C	-4.01122700	1.07225300	-0.96445400
C	-3.66333100	0.29968000	0.14596700
C	-2.62908700	-0.61915200	0.06153400
N	2.49001800	-1.13087400	-1.01858000
N	0.78533900	0.79357200	-0.05744300
Pd	0.08617600	-1.13982700	-1.00656600
C	-5.16768400	2.00560900	-0.86245800
F	-5.15681800	2.69259100	0.29217400
F	-5.19186000	2.90275200	-1.85646100
F	-6.34504100	1.35684800	-0.89652500
H	-2.37393300	-1.21897600	0.93580000
H	-4.20533900	0.42352000	1.08337600
H	-3.59189900	1.50257200	-3.03252300
H	-1.77053500	-0.15707200	-3.20111800

C	-0.29905200	-3.45607500	-1.46635000
O	0.42889300	-3.70472700	-2.45541500
C	-0.09419900	-4.27023900	-0.17614100
C	-0.74255900	-3.65823700	1.06147400
H	-0.35032700	-2.64961500	1.26401900
H	-1.83652700	-3.59440100	0.97997700
H	-0.52330100	-4.28326600	1.93929500
C	-0.74089400	-5.63280100	-0.46709800
H	-0.27124200	-6.10946200	-1.33714500
H	-0.62231400	-6.30152500	0.39773900
H	-1.81766500	-5.53619300	-0.67011300
C	1.39429700	-4.47548700	0.08988400
H	1.53122500	-5.15895000	0.93971400
H	1.90135600	-4.90850800	-0.77999200
H	1.89009500	-3.52632400	0.34177200
C	-1.50266400	-2.62327500	-1.62252900
H	-1.77322600	-2.55072800	-2.67816600
H	-2.33897600	-2.96381400	-1.00975300
O	2.91576900	-2.93812900	-2.41308400
H	1.93727300	-3.13280500	-2.35244400

TS-c3Pf-c5H

SCF Energy = -1695,66275554
Thermal Correction to Gibbs Free Energy = 0,234487

C	4.80424800	-1.47516300	0.25849200
H	5.37044300	-2.40190800	0.28596300
C	5.39520500	-0.23434000	0.36241000
H	6.47414200	-0.15243600	0.47805000
C	3.41049800	-1.52007200	0.11231900
C	4.61190200	0.92138900	0.32003600
H	5.08294800	1.89615200	0.40313800
C	3.23829400	0.78956500	0.17199600
C	2.31742300	1.95030000	0.10885100
C	2.76321600	3.26980000	0.19567200
H	3.81835000	3.49480400	0.32538200
C	1.84314200	4.30511800	0.11382900
H	2.17796900	5.33849600	0.17704800
C	0.49661600	4.00551400	-0.04912200
H	-0.25757500	4.78511300	-0.11955500
C	0.12906100	2.66848400	-0.12000000
H	-0.91401000	2.37355100	-0.24272800
C	-1.61449600	-0.87257800	-0.26595900
C	-2.26032800	-0.59415600	-1.48390100
C	-3.57884400	-0.18171400	-1.58170400
C	-4.32950800	0.00977700	-0.42975600
C	-3.72877200	-0.20173700	0.80373800
C	-2.40816300	-0.61448000	0.86627700
N	2.65894400	-0.42486000	0.07042700
N	1.01059600	1.67055600	-0.04413200
O	2.82148400	-2.70694700	0.01218400
Pd	0.38883100	-0.49913500	-0.12149500
C	-0.50840400	-3.10670600	0.98961100
C	-0.34035700	-3.07186800	-1.41875900
C	-0.14207600	-5.15820700	-0.21183900
C	-0.32183900	-4.48745800	1.00273200
H	-0.65126800	-2.59376300	1.93841400
H	-0.35008600	-2.54109700	-2.36626500
H	0.00783400	-6.23862300	-0.21264000
C	-0.51636700	-2.36120000	-0.21161100
H	1.85242800	-2.56314500	-0.07691600
C	-0.15305800	-4.45011800	-1.40763900
H	-0.00553300	-4.97462200	-2.35145200
C	-0.29776700	-5.24741500	2.29554200
H	-1.07335400	-6.02561700	2.31684400
H	0.66559000	-5.75496700	2.44469800
H	-0.46348400	-4.58775800	3.15575300
F	-1.58803400	-0.70874700	-2.63924500
F	-4.12749900	0.06012200	-2.77055300
F	-5.59557200	0.40785700	-0.50583900
F	-4.42372000	0.01959200	1.91767800
F	-1.88742300	-0.75059600	2.09580700

TS-c3-c4

SCF Energy = -1840,1341972
Thermal Correction to Gibbs Free Energy = 0,274761

C	4.88158300	-1.59342000	0.82508900
H	5.45677400	-2.49430500	1.02572200
C	5.44516700	-0.33425300	0.82275300
H	6.50513700	-0.20629300	1.03432800
C	3.50861100	-1.69792400	0.56997900
C	4.64441400	0.77706900	0.57174800
H	5.06939700	1.77455200	0.62347200
C	3.29587800	0.58299100	0.29298400
C	2.37797800	1.71361800	0.04810100
C	2.84483400	3.00770900	-0.18774800
H	3.91118100	3.20859500	-0.24300900
C	1.93726700	4.03965400	-0.36942200
H	2.28934000	5.05269100	-0.55386300
C	0.57983200	3.75584700	-0.31650000
H	-0.17215300	4.52965600	-0.44836200
C	0.18974300	2.44125800	-0.10335900
H	-0.86378000	2.16730600	-0.06752600
C	-1.48266300	-0.45858200	-0.05447200
C	-2.35707600	-0.88637200	-1.06302300
C	-3.72139000	-0.60169500	-1.01772500
C	-4.23944200	0.14162900	0.03969200
C	-3.38642700	0.59563600	1.04954200
C	-2.03078500	0.28775400	1.01084900
N	2.74699700	-0.64924600	0.26673100
N	1.05742300	1.44115800	0.07149400
O	2.94886900	-2.90202000	0.62897700
Pd	0.50572900	-0.70801300	0.06354600
C	-5.70057900	0.37150600	0.19166500
F	-5.99576400	1.65134600	0.46565600
F	-6.40564800	0.02324700	-0.89105400
F	-6.20422800	-0.34663400	1.22482200
H	-1.38833300	0.54040900	1.86215700
H	-3.79557500	1.16570600	1.88668000
H	-4.38369900	-0.95978900	-1.80494500
H	-1.97933100	-1.47741600	-1.89750200
C	-0.14772500	-3.60377600	0.71193700
C	0.11957300	-3.13972900	-1.62789000
C	-0.31452800	-5.39595600	-0.91779100
H	-0.13538800	-3.30056700	1.76780500
H	0.30132400	-2.43646000	-2.44577600
H	-0.47195300	-6.45036500	-1.15504200

C	0.09537600	-2.66457100	-0.30481900
H	1.96953600	-2.76808300	0.63067200
C	-0.07725800	-4.48416500	-1.95221800
O	-0.11406800	-2.75123900	3.80490000
O	-0.58195400	-0.57889800	3.53197600
C	0.21552000	-1.56225200	3.35878900
O	1.33512800	-1.43587900	2.71583800
Cs	2.53338800	-3.97489400	3.63128100
Cs	-2.91180900	-2.40759800	2.91006300
C	-0.34640700	-4.95400100	0.39910200
H	-0.53096200	-5.67094200	1.20412900
C	-0.03732200	-4.95048300	-3.37806900
H	0.71923800	-5.73401800	-3.52813600
H	-1.00080200	-5.37768700	-3.69214700
H	0.19830300	-4.12723300	-4.06430300

TS-c4-c5Cs

SCF Energy = -1555,83754879
Thermal Correction to Gibbs Free Energy = 0,262219

C	4.71686900	-1.29053900	1.39140300
H	5.29386500	-2.12301200	1.79122700
C	5.12216400	0.00578300	1.53770200
H	6.04567100	0.24050500	2.06820400
C	3.48701800	-1.62208600	0.71017400
C	4.33259200	1.04279000	1.01231300
H	4.60895500	2.08283900	1.16245800
C	3.15710700	0.69703200	0.36515400
C	2.26466800	1.76400400	-0.14630500
C	2.70939000	3.06299600	-0.41449900
H	3.76056200	3.31572600	-0.29977000
C	1.80336600	4.01704200	-0.85106700
H	2.13781300	5.03088200	-1.06447300
C	0.46812500	3.66307400	-1.01812100
H	-0.27550500	4.38205900	-1.35297100
C	0.10642200	2.35020200	-0.75604700
H	-0.92291600	2.00564800	-0.87943300
C	-1.54966600	-0.90209500	-0.27856000
C	-2.23993100	-0.50782700	-1.44360600
C	-3.50287400	0.06747100	-1.38541600
C	-4.12386300	0.26327400	-0.15383600
C	-3.46689700	-0.12627000	1.01642500
C	-2.21149900	-0.70654800	0.95341000
N	2.73104600	-0.57694600	0.20133300
N	0.97857500	1.42884600	-0.34032600
O	3.12855000	-2.80988500	0.55846800
Pd	0.46263200	-0.75265700	-0.26022500
C	-0.33761200	-3.34688000	0.80315700
C	-0.82325200	-3.26661700	-1.54391500
C	-0.61754700	-5.39746200	-0.42207000
C	-0.34634800	-4.74245300	0.78253300
H	-0.11834300	-2.85044300	1.75177700
H	-1.04085400	-2.70904200	-2.45780500
H	-0.65491200	-6.48750300	-0.44683800
C	-0.53234400	-2.57180800	-0.35314100
Cs	2.52694600	-3.22162400	-2.26646000
C	-0.87022200	-4.65689000	-1.57622000
H	-1.11928100	-5.17055400	-2.50650600
C	-0.03864300	-5.50975600	2.03383800
H	-0.70262400	-5.21982000	2.85983500
H	-0.14331900	-6.59191300	1.88443500
H	0.98976600	-5.31479000	2.36981100
H	-1.77107400	-0.63996700	-2.41981200
H	-1.72329600	-1.01685900	1.87740100
H	-4.00473900	0.37502900	-2.30137400
H	-3.94990200	0.02681300	1.98224300
C	-5.47367000	0.87822500	-0.03818100
F	-5.45709000	1.97975700	0.73459500
F	-5.98422500	1.24164300	-1.22251700
F	-6.36333700	0.04622700	0.53245400

TS-c4R-c5Cs (R = $CH_2C(O)^tBu$)

SCF Energy = -1595,38385434
Thermal Correction to Gibbs Free Energy = 0,303469

C	4.61209200	-1.75489200	-0.72344400
H	5.24098200	-2.57511400	-1.06553400
C	5.12128900	-0.68864700	-0.03472600
H	6.18671000	-0.63537000	0.19103800
C	3.21340900	-1.81536800	-1.06084900
C	4.26979500	0.35355900	0.36720000
H	4.67278000	1.23593400	0.85562400
C	2.91691100	0.22799100	0.09351700
C	1.97151100	1.31322900	0.44945000
C	2.31283300	2.37539900	1.29394600
H	3.27843800	2.39824400	1.79183300
C	1.39876900	3.39450200	1.50991200
H	1.65502100	4.22805700	2.16155000
C	0.15491500	3.33747100	0.88893600
H	-0.58831100	4.11951400	1.02424600
C	-0.12566400	2.23086400	0.10162400
H	-1.09999700	2.10827800	-0.37560600
C	-1.86602700	-0.72419400	-0.77334300
C	-2.38147200	-0.42654200	-2.05644000
C	-3.44793600	0.44234000	-2.21587600
C	-4.06638300	1.01690300	-1.10133100
C	-3.60574800	0.69735600	0.17722400
C	-2.52846000	-0.16075700	0.33980200
N	2.38804400	-0.83331800	-0.55523900
N	0.75176000	1.24889100	-0.11117400
O	2.74640600	-2.71644800	-1.79611300
Pd	0.12036400	-0.93207700	-0.65603300
C	-5.25480300	1.88901000	-1.29592400
F	-5.50145100	2.66694900	-0.23196900
F	-5.11549000	2.70399600	-2.35652600
F	-6.37917000	1.18234800	-1.52071300
H	-2.17292400	-0.39318400	1.34440500
H	-4.08599500	1.13653900	1.05063400
H	-3.81574000	0.67484800	-3.21554400
H	-1.94994200	-0.92031400	-2.92688300
Cs	1.13522800	-1.69983500	-4.07395800
C	-0.67936600	-3.49855800	-1.38792300
O	-0.85471300	-3.43290500	-2.60813600
C	0.07581700	-4.69221200	-0.78322000
C	0.91983600	-4.34938100	0.44128000
H	1.73583400	-3.66860000	0.17093500
H	0.33624100	-3.89563600	1.25344200
H	1.36467700	-5.27257400	0.84270400

C	-1.03323700	-5.68032400	-0.38035300
H	-1.66406100	-5.94332300	-1.24195100
H	-0.58372100	-6.60802000	0.00265400
H	-1.68458800	-5.27568400	0.40750600
C	0.96270700	-5.34719600	-1.83741200
H	1.40677400	-6.26598700	-1.42651300
H	0.38818100	-5.61955100	-2.73158200
H	1.77972700	-4.67040000	-2.12013300
C	-1.40805000	-2.57762500	-0.47680100
H	-2.47280300	-2.71018400	-0.69429600
H	-1.26402200	-2.76191800	0.59309800

TS-c4C_6F_5-c5Cs

SCF Energy = -1714,97976621
Thermal Correction to Gibbs Free Energy = 0,216479

C	4.73824200	-1.34129100	1.35455700
H	5.30798300	-2.18048200	1.75059900
C	5.17168900	-0.05167800	1.47638600
H	6.11158000	0.17063000	1.98283300
C	3.48774400	-1.65643200	0.70352400
C	4.38942800	0.99485700	0.95802900
H	4.68658700	2.03156200	1.09106400
C	3.19219700	0.66423800	0.34452100
C	2.30477900	1.74406600	-0.14588600
C	2.77095100	3.02464100	-0.46209500
H	3.83359800	3.24760100	-0.40467400
C	1.87090700	3.99532900	-0.87294500
H	2.22158300	4.99459900	-1.12512000
C	0.51933200	3.67665400	-0.96426200
H	-0.22024300	4.40979300	-1.27635900
C	0.13589000	2.38030000	-0.65692300
H	-0.90817300	2.06503400	-0.71658400
C	-1.56757900	-0.93103800	-0.22935500
C	-2.23524600	-0.46878600	-1.38013900
C	-3.50882400	0.07415100	-1.37161300
C	-4.19337400	0.20964800	-0.17067400
C	-3.56901400	-0.19065800	1.00228400
C	-2.29305100	-0.72859400	0.95885300
N	2.74003000	-0.60319500	0.19999100
N	1.00174300	1.44170400	-0.26682700
O	3.10474900	-2.83807000	0.56710700
Pd	0.44944700	-0.72338600	-0.19572400
C	-0.38312700	-3.29002000	0.84361700
C	-0.90642900	-3.22557200	-1.50536100
C	-0.58059900	-5.34673600	-0.39041600
C	-0.31879700	-4.68430900	0.81042100
H	-0.18011300	-2.78991000	1.78934800
H	-1.15257700	-2.67896600	-2.41404900
H	-0.56099000	-6.43695400	-0.42101400
C	-0.63652700	-2.52141500	-0.30917800
Cs	2.43825400	-3.12193600	-2.26781700
C	-0.88922700	-4.61428900	-1.53652600
H	-1.12639700	-5.13485800	-2.46582100
C	0.05845300	-5.43820300	2.05042300
H	-0.58422900	-5.16837800	2.89954100
H	-0.01387600	-6.52342400	1.90472700
H	1.09121400	-5.20648100	2.34734100
F	-5.41804500	0.72951400	-0.14352900
F	-4.07512100	0.49932600	-2.50112000
F	-1.62092700	-0.52142100	-2.57929500
F	-4.20044400	-0.03993500	2.16482500
F	-1.74997200	-1.07069700	2.13421900

4- References

(1) V. Salamanca, A. Toledo, A. C. Albéniz, *J. Am. Chem. Soc.* **2018**, *140*, 17851-17856.

(2) G. B. Deacon, I. L. Grayson, *Trans. Met. Chem*. **1983**. *8*, 131-139.

(3) C. –T. Yang, Y. Fu, Y. –B. Huang, J. Yi, Q. –X. Guo, L. Liu, *Angew. Chem. Int. Ed*. **2009**, *48*, 7398–7401.

(4) K. Freudenberg, G. Uthemann, *Ber. Dtsch. Chem. Ges*. **1919**, *52*, 1509-1513.

(5) Z. -Y.Lian, J. Yuan, M. –Q. Yan,; Y. Liu, X. Luo, Q. –G. Wu,; S. –H. Liu, J. Chen, X. –L. Zhu, G. –A. Yu, *Org. Biomol. Chem*. **2016**, *14*, 10090-10094.

(6) S. Shi, G. Meng, M. Szostak, *Angew. Chem. Int. Ed*. **2016**, *55*, 6959-6963.

(7) X. Gong, J. Wu, Y. Meng, Y. Zhang, L.-W. Ye, C. Zhu, *Green Chem*. **2019**, *21*, 995-999.

(8) X. Li, Y. Ma, Q. Hu, B. Jiang, Q. Wu, Z. Yuan, *Catal. Commun.* **2018**, *117*, 57-62.

(9) S. Thapa, A. S. Vangala, R. Giri, *Synthesis*, **2016**, *48*, 504-511.

(10) X. –Q. Zhang, Z. –X. Wang, *J. Org. Chem*. **2012**, *77*, 3658-3663.

(11) F. M. Piller, A. Metzger, M. A. Schade, B. A.; Haag, A. Gavryushin, P. Knochel, *Chem. Eur. J*. **2009**, *15*, 7192-7202.

(12) S. Sase, M. Jaric, A. Metzger, V. Malakhov, P. Knochel, *J. Org. Chem*. **2008**, *73*, 7380-7382.

(13) N Kataoka, Q. Shelby, J. P. Stambuli, J. F. Hartwig, *J. Org. Chem*. **2002**, *67*, 5553-5566.

(14) Z. Liang, J. Zhang, Z. Liu, K. Wang, Y. Zhang, *Tetrahedron* **2013**, *69*, 6519-6526.

(15) C. A. Contreras-Celedón, D. Mendoza-Rayo, J. A. Rincón-Medina, L. Chacón-García, L. *J. Org. Chem*. **2014**, *10*, 2821-2826.

(16) W. P. Hong, A. V. Iosub, S. S. Stahl, *J. Am. Chem. Soc*. **2013**, *135*, 13664-13667.

(17) M. Wang, X. Yuan, H. Li, L. Ren, Z. Sun, Y. Hou, W. Chu, *Catal. Commun.* **2015**, *58*, 154-157.

(18) K.-X. Sun, Q. -W. He, B. -B. Xu, X. -T. Wu, J. -M. Lu, *Asian J. Org. Chem*. **2018**, *7*, 781-787.

(19) L. Liu, Y. Zhang, B. Xin, *J. Org. Chem*. **2006**, *71*, 3994-3997.

(20) L. -C. Xu, K. –M. Liu, X. -F. Duan, *Adv. Synth. Catal*. **2019**, *361*, 5421-5427.

(21) Y. Budiman, A. Friedrich, U. Radius, T. B. Marder, *ChemCatChem*. **2019**, *11*, 5387-5396.

(22) Y. Song, Z. Fu, Q. Xiong, Z. Li, J. Li, H. Cai, H. *J. Iran Chem. Soc*. **2016**, *13*, 1931-1936.

(23) Q. Chen, A. Wu, S. Qin, M. Zeng, Z. Le, Z. Yan, H. Zhang, *Adv. Synth. Catal*. **2018**, *360*, 3239-3244.

(24) CrysAlisPro Software system, version 1.171.33.51, 2009, Oxford Diffraction Ltd, Oxford, UK.

(25) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 339-341.

(26) L. J. Bourhis, O. V. Dolomanoy, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Cryst.*, **2015**, A71, 59-75.

(27) G. M. Sheldrick, M. George, *Acta Cryst.* **2015**, *C71*, 3-8.

(28) COmplex PAthway SImulator. S. Hoops, S. Sahle, R. Gauges, C. Lee, J. Pahle, N. Simus, M. Singhal, L. Xu, P. Mendes, U. Kummer, *Bioinformatics,* **2006**, *22*, 3067-3074.

(29) Y. Zhao, D. G. J. Truhlar, *Chem. Phys.* **2006,** 125, 194101−194118.

(30) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2006**, *120*, 215-241.

(31) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

(32) M. M. Francl, W. J. Petro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, J. A. Pople, *J. Chem. Phys*. **1982**, *77*, 3654−3665.

(33) T. Clark, J. Chandrasekhar, P. V. R. J. Schleyer, *Comput. Chem*. **1983**, *4*, 294−301.

(34) A. W. Ehlers, M. Böhme, S. Dapprich, A. Gobbi, A. Höllwarth, V. Jonas, K. F. Köhler, R. Stegmann, A. Veldkamp, G. Frenking, *Chem. Phys. Lett*. **1993**, *208*, 111−114.

(35) L. E. Roy, P. J. Hay, R. L. J. Martin, *Chem. Theory Comput.* **2008**, *4*, 1029−1031.