Mechanistic Study on the Reductive Elimination of (Aryl)(fluoroaryl)palladium Complexes: A Key Step in Regiospecific Dehydrogenative Cross-coupling

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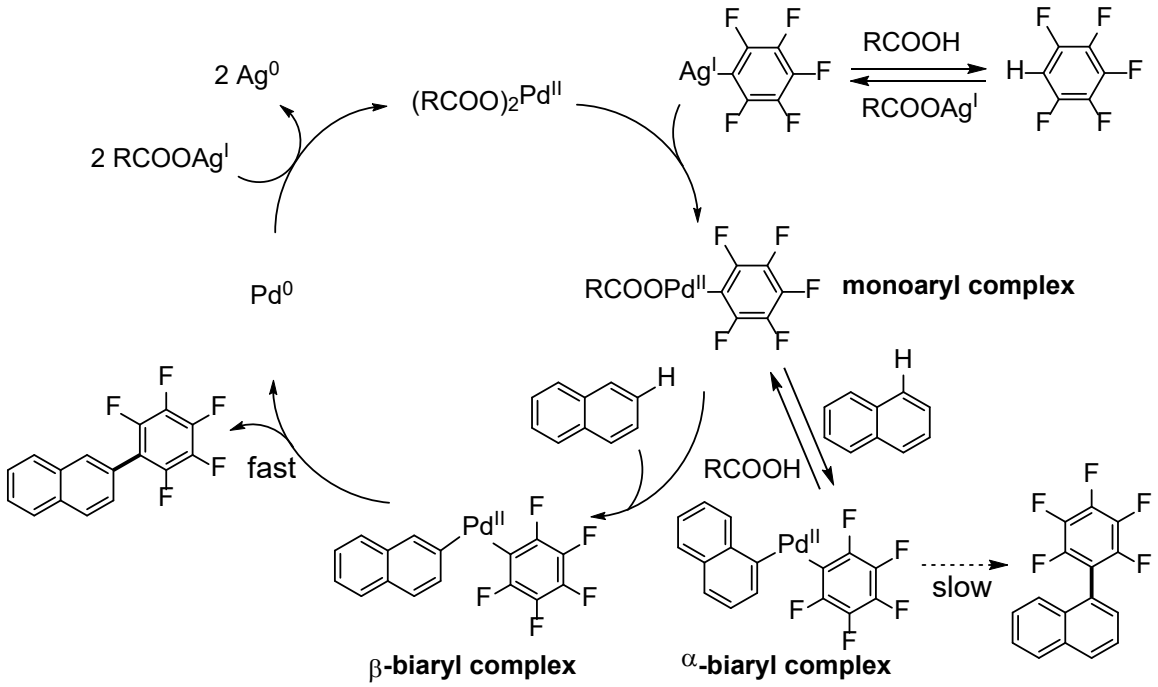
Experimental details

General, Measurement, and Materials.

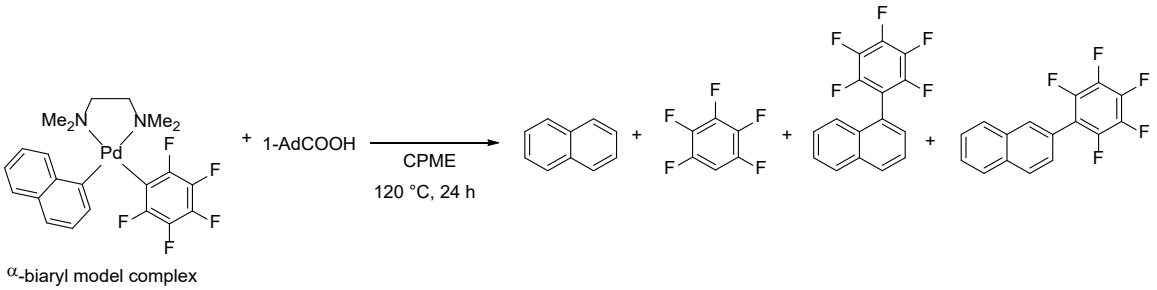
^{1}H, ^{19}F, and $^{13}C\{^{1}H\}$ NMR spectra were recorded using Bruker AVANCE-400 NMR spectrometer and AVANCE-600 NMR spectrometer. APCI TOF/Mass spectra were recorded on Bruker micrOTOF2−kp. Elemental analyses were carried out using Yanaco CHN coder MT-6 or MT-5. Anhydrous CPME (cyclopentylmethylether), THF (tetrahydrofuran), DMAc (*N*,*N*-dimethylacetamide), DMF (*N*,*N*-dimethylformamide), hexane, dichloromethane, methanol were purchased from Kanto Chemical and used as dry solvents. Other compounds were purchased and used without further purification. 2-pentafluorophenylnaphthalene, α-biaryl model complex, and β-biaryl model complex were synthesised according to methods described in the literature.[1]

Crystal structure determination

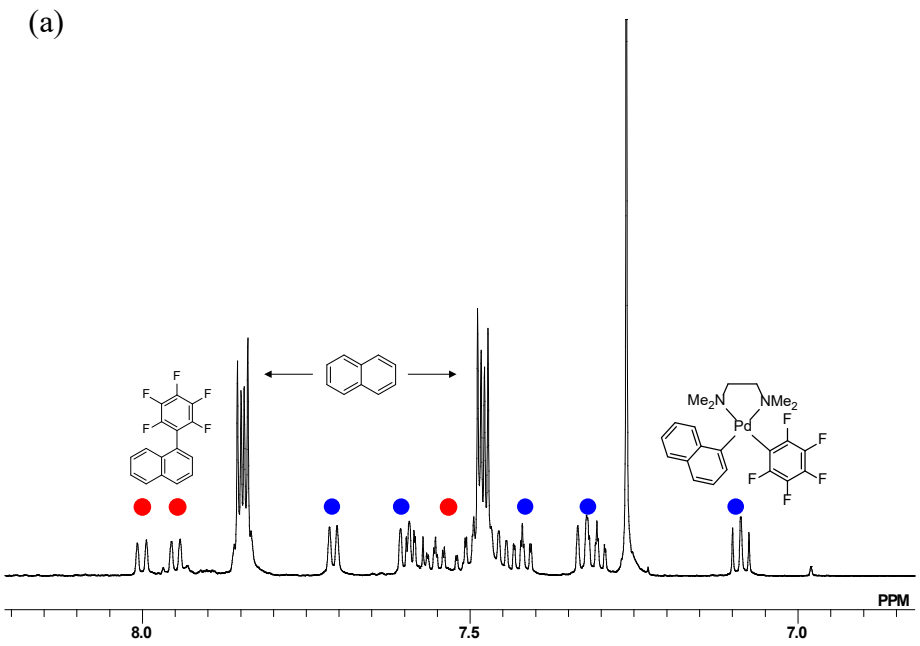
Intensity data were collected on a Bruker SMART APEX II ULTRA with Mo Kα radiation. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters using the SHELXL-97 program. CCDC 2338608-2338611 contain the supplementary crystallo-graphic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

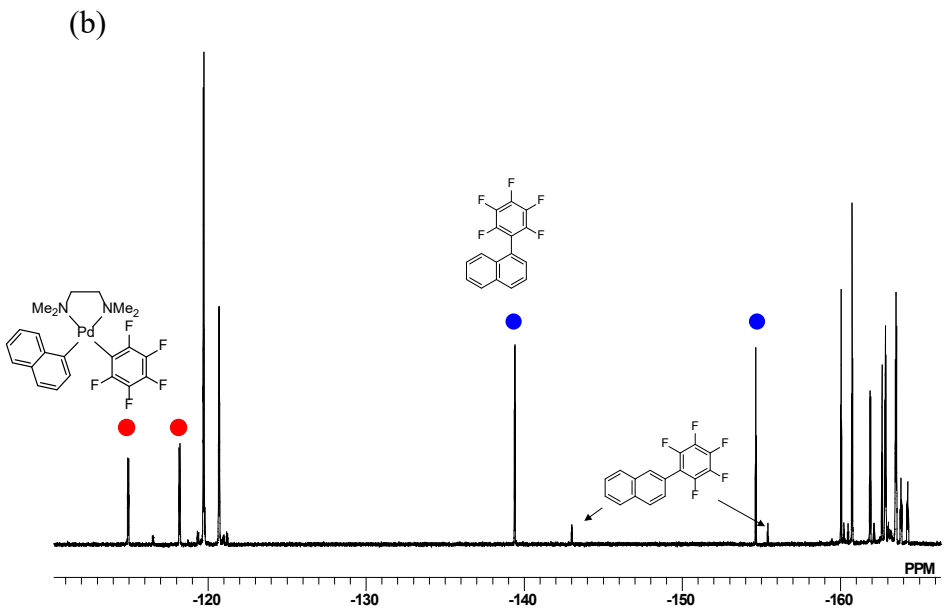


Scheme S1. Possible reaction mechanism.[1]

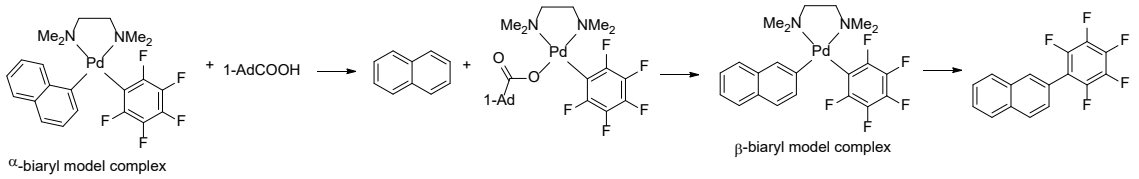


α-biaryl model complex



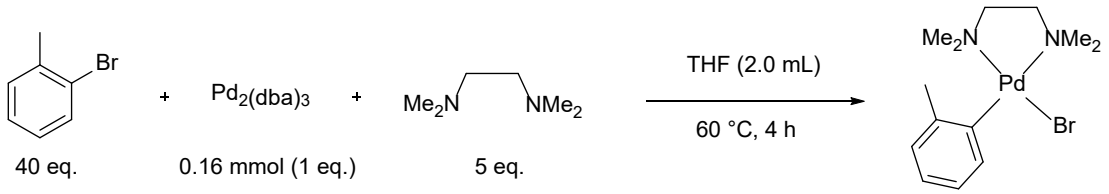


Scheme S2. Reaction of α-biaryl model complex with 1-adamantanecarboxylic acid. (a) ^{1}H NMR spectrum of the products (600 MHz, $CDCl_3$, r.t.) and (b) ^{19}F NMR spectrum of the products (565 MHz, $CDCl_3$, r.t.).



Scheme S3. A proposed reaction pathway from the α-biaryl model complex to the β-substituted product.

Synthesis of PdBr(2-tolyl)(tmeda)

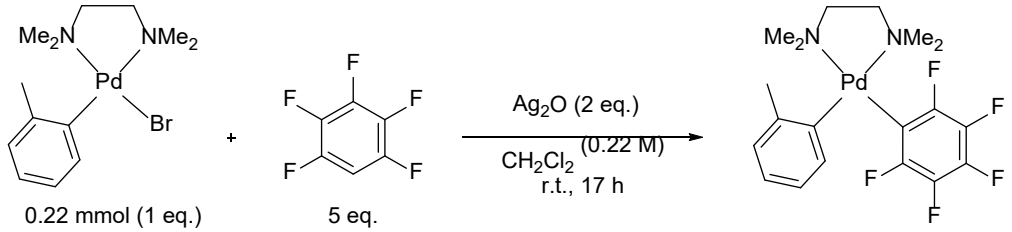


A mixture of $Pd_2(dba)_3$ (146.1 mg, 0.16 mmol), 2-bromotoluene (785.3 μL, 6.4 mmol), and *N,N,N′,N′*-tetramethylethylenediamine (118.9 μL, 0.80 mmol) was stirred in THF (2.0 mL) for 4 h at 60 °C under a nitrogen atmosphere. After removal of the volatiles, residue was extracted with chloroform. Following Celite® filtration, the filtrate was concentrated under reduced pressure. PdBr(2-tolyl)(tmeda) was isolated by washing with hexane (78.0 mg, 69%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.20 (dd, 1H, J = 7.2, 1.6 Hz), 6.85-6.84 (m, 1H), 6.82-6.77 (m, 2H), 2.90-2.86 (m, 1H), 2.80 (s, 3H), 2.70-2.65 (m, 1H), 2.66 (s, 3H), 2.65 (s, 3H), 2.61 (dt, 1H, J = 12.9, 4.4 Hz), 2.55 (s, 3H), 2.50 (ddd, 1H, J = 13.6, 5.3, 3.6 Hz), 2.26 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 147.31, 141.32, 134.06, 128.01, 123.84, 122.87, 62.60, 58.12, 51.06, 49.36, 48.99, 47.46.

Synthesis of Pd(2-tolyl)(pentafluorophenyl)(tmeda)



A mixture of PdBr(2-tolyl)(tmeda) (85.7 mg, 0.22 mmol), Ag_2O (100.9 mg, 0.44 mmol), and pentafluorobenzene (119.6 μL, 1.09 mmol) was stirred in dichloromethane (1.0 mL) for 17 h at room temperature under a nitrogen atmosphere. After removal of the volatiles, residue was extracted with chloroform. Following Celite® filtration, the filtrate was concentrated under reduced pressure. Pd(2-tolyl)(pentafluorophenyl)(tmeda) was isolated by column chromatography on silica gel using a mixture of chloroform and hexane (3:2) as an eluent (77.9 mg, 74%).

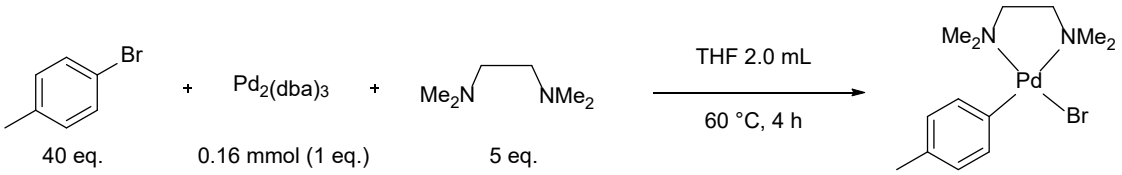
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54-7.53 (m, 1H), 6.84-6.83 (m, 1H), 6.77-6.74 (m, 1H), 2.83-2.79 (m, 1H), 2.74 (s, 1H), 2.74-2.70 (m, 1H), 2.62 (ddd, 1H, J = 13.2, 5.5, 3.2 Hz), 2.52-2.49 (m, 1H), 2.49 (s, 1H), 2.43 (s, 1H), 2.31 (s, 1H), 2.28 (s, 1H).

^{19}F NMR (564 MHz, $CDCl_3$): δ -114.66 (dt, 1F, J = 34.5, 9.3 Hz), -117.56 (dt, 1F, J = 34.7, 9.3 Hz), -163.19 (t, 1F, J = 20.3 Hz), -164.46 to -164.70 (m, 2F).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 153.49, 147.49 (dm, J_F = 223.0 Hz), 141.99, 136.66, 136.38 (dm, J_F = 241.3 Hz), 136.02 (dm, J_F = 250.9 Hz), 127.36, 123.14, 122.28, 121.84 (t, J_F = 57.5 Hz), 60.98, 59.16, 49.43, 49.28, 48.35, 47.90, 26.46.

EA: Found. C 47.18%, H 4.89%, N 5.87%; Calcd. for $C_{19}H_{23}N_2F_5Pd$: C 47.46%, H 4.82%, N 5.83%.

Synthesis of PdBr(4-tolyl)(tmeda)

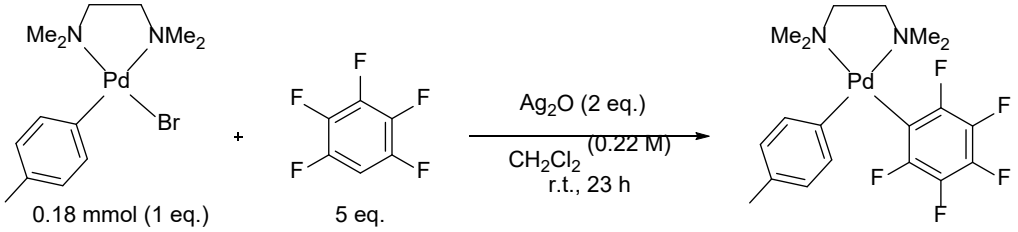


A mixture of $Pd_2(dba)_3$ (143.9 mg, 0.16 mmol), 4-bromotoluene (773.5 μL, 6.3 mmol), and *N,N,N′,N′*-tetramethylethylenediamine (117.1 μL, 0.79 mmol) was stirred in THF (2.0 mL) for 4 h at 60 °C under a nitrogen atmosphere. After removal of the volatiles, residue was extracted with chloroform. Following Celite® filtration, the filtrate was concentrated under reduced pressure. PdBr(4-tolyl)(tmeda) was isolated by washing with hexane (85.1 mg, 69%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.13 (d, 2H, J = 7.8 Hz), 6.79 (dd, 2H, J = 8.2, 0.6 Hz), 2.74 (t, 2H, J = 5.6 Hz), 2.64 (s, 6H), 2.57 (t, 2H, J = 5.5 Hz), 2.43 (s, 6H), 2.22 (s, 3H).

^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 142.36, 134.65, 131.79, 127.68, 62.58, 58.13, 50.51, 48.45, 20.55.

Synthesis of Pd(4-tolyl)(pentafluorophenyl)(tmeda)



A mixture of PdBr(4-tolyl)(tmeda) (70.8 mg, 0.18 mmol), Ag_2O (83.4 mg, 0.36 mmol), and pentafluorobenzene (98.8 μL, 1.09 mmol) was stirred in dichloromethane (0.83 mL) for 23 h at room temperature under a nitrogen atmosphere. After removal of the volatiles, residue was extracted with chloroform. Following Celite® filtration, the filtrate was concentrated under reduced pressure. Pd(4-tolyl)(pentafluorophenyl)(tmeda) was isolated by column chromatography on silica gel using a mixture of chloroform and hexane (3:2) as an eluent (71.9 mg, 83%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.29 (d, 2H, J = 7.8 Hz), 6.73 (dd, 2H, J = 8.0, 0.6 Hz), 2.71 (t, 2H, J = 5.5 Hz), 2.60 (t, 2H, J = 5.5 Hz), 2.39 (s, 6H), 2.38 (s, 6H), 2.16 (s, 3H).

^{19}F NMR (564 MHz, $CDCl_3$): δ -117.96 (d, 2F, J = 24.7 Hz), -162.77 (t, 1F, J = 20.0 Hz), -164.09 to -164.19 (m, 2F).

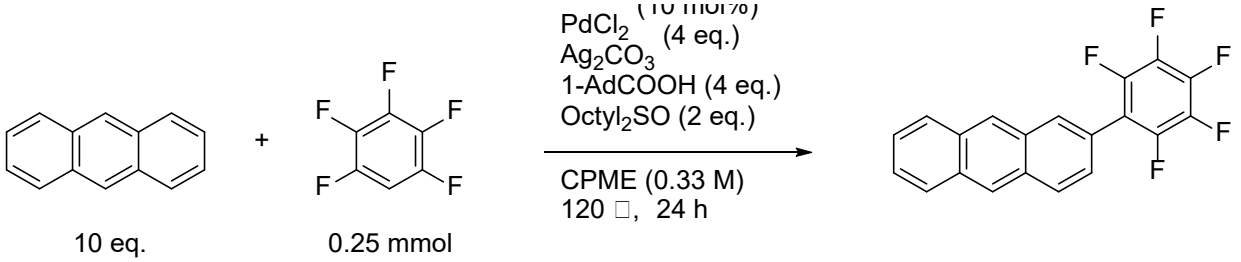
^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 148.70, 147.27 (dm, J_F = 222.2 Hz), 136.33 (dm, J_F = 241.0 Hz), 135.99, 135.99 (dm, J_F = 251.8 Hz), 131.25, 127.38, 123.11 (t, J_F = 57.1 Hz), 60.85, 59.07, 48.87, 48.63, 20.78.

EA: Found. C 47.53%, H 5.03%, N 5.79%; Calcd. for $C_{19}H_{23}N_2F_5Pd$: C 47.46%, H 4.82%, N 5.83%.

Tracing reductive elimination reactions for kinetic analysis

The representative time-course change was tracked as follows. The β-biaryl model complex (4.9 mg, 0.0095 mmol) and 1,3,5-trimethoxybenzene (5.4 mg, 0.032 mmol) as internal standard were dissolved in 0.60 mL of toluene-d_8. The reaction was set to each temperature by VT NMR and followed by ^{1}H NMR.

Synthesis of 2-(pentafluorophenyl)anthracene



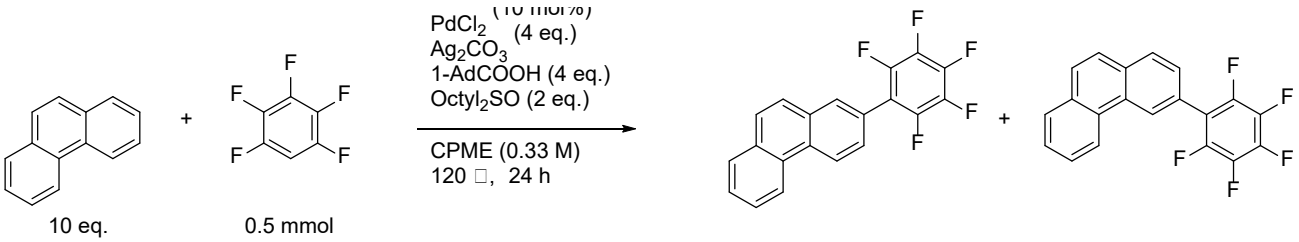
A mixture of $PdCl_2$ (4.4 mg, 0.025 mmol), di-*n*-octylsulfoxide (137.3 mg, 0.5 mmol), 1-adamantanecarboxylic acid (180.3 mg, 1.0 mmol), silver(I) carbonate (275.7 mg, 1.0 mmol), anthracene (445.6 mg, 2.5 mmol), and pentafluorobenzene (27.5 μL, 0.25 mmol) was stirred in CPME (0.75 mL) for 24 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$, and the crude product was analysed by NMR spectroscopy. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using hexane as an eluent and HPLC. The solvents were removed in vacuo to give 2-(pentafluorophenyl)anthracene (14.7 mg, 17%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.49 (d, 2H, J = 3.5 Hz), 8.13-8.12 (m, 2H), 8.04 (dt, 2H, J = 6.9, 2.4 Hz), 7.54-7.50 (m, 2H), 7.47 (dd, 1H, J = 8.7, 1.6 Hz).

^{19}F NMR (376 MHz, $CDCl_3$): δ -146.0 (dd, 2F, J = 23.2, 8.2 Hz), -158.6 (t, 1F, J = 21.1 Hz), -165.2 to -165.3 (m, 2F). The spectral data corresponds to that reported earlier.[2]

EA: Found. C 69.52%, H 2.75%, N 0%; Calcd. for $C_{20}H_9F_5$: C 69.77%, H 2.64%, N 0%.

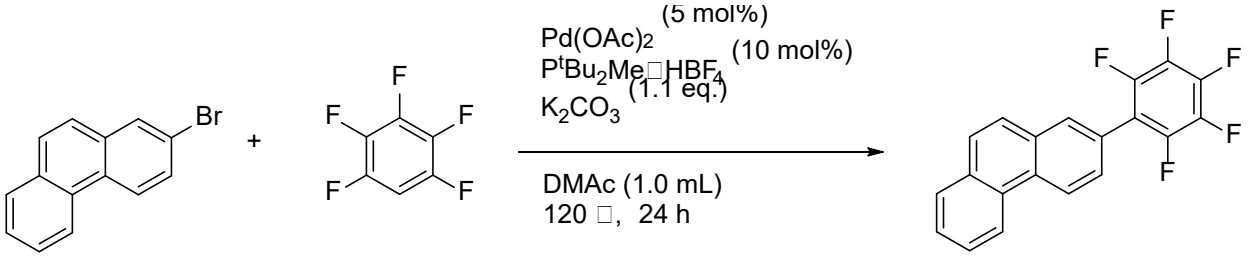
Synthesis of 2-(pentafluorophenyl)phenanthrene and 3-(pentafluorophenyl)phenanthrene by the CDC reaction



A mixture of $PdCl_2$ (8.9 mg, 0.050 mmol), di-*n*-octylsulfoxide (275 mg, 1.0 mmol), 1-adamantanecarboxylic acid (360 mg, 2.0 mmol), silver(I) carbonate (550 mg, 2.0 mmol), phenanthrene (891 mg, 5.0 mmol), and pentafluorobenzene (55 μL, 0.50 mmol) was stirred in CPME (0.75 mL) for 24 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$, and the crude product

was analysed by NMR spectroscopy. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using hexane as an eluent and HPLC. The solvents were removed in vacuo to give a mixture of 2-(pentafluorophenyl)phenanthrene and 3-(pentafluorophenyl)phenanthrene (89.4 mg, 52%). The ratio of the regioisomers was calculated from ^{1}H NMR spectroscopy. The reference samples were prepared by direct arylation (see description below).

Synthesis of 2-(pentafluorophenyl)phenanthrene by direct arylation



0.2 mmol 1.5 eq.

A mixture of $Pd(OAc)_2$ (2.3 mg, 0.010 mmol), $P^tBu_2MeHBF_4$ (5.0 mg, 0.020 mmol), potassium carbonate (30 mg, 0.22 mmol), 2-bromophenanthrene (51 mg, 0.20 mmol), and pentafluorobenzene (33 μL, 0.30 mmol) was stirred in *N*,*N*-dimethylacetamide (0.10 mL) for 5 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using hexane as an eluent. The solvents were removed in vacuo to give 2-(pentafluorophenyl)phenanthrene (23 mg, 33%).

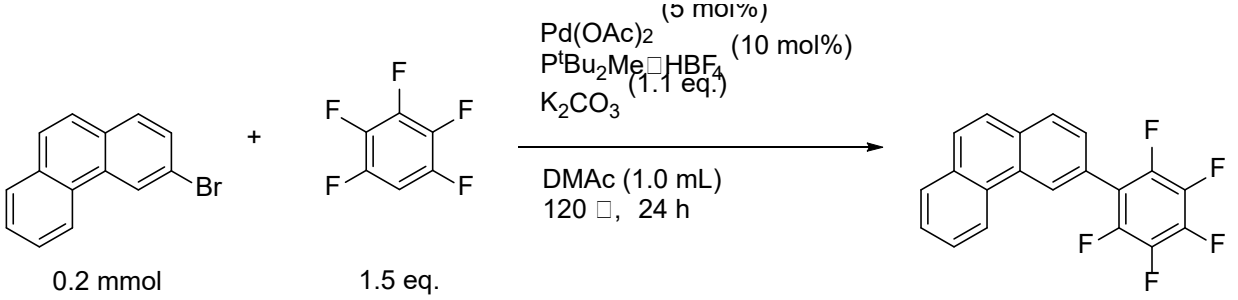
^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 8.80 (d, 1H, J = 8.4 Hz), 8.72 (d, 1H, J = 8.0 Hz), 7.97 (s, 1H), 7.93 (d, 1H, J = 7.8 Hz), 7.82 (d, 1H, 8.8 Hz), 7.77 (d, 1H, 8.8 Hz), 7.72-7.63 (m, 3H).

^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -146.2 (dd, 2F, J_F = 23.2, 8.2 Hz), -158.5 (t, 1F, J_F = 20.4 Hz), -165.3 (dt, 2F, J_F = 21.8, 7.7 Hz).

^{13}C{^{1}H} NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 393 K): δ 132.5, 131.9, 130.7, 130.2, 129.8, 128.5, 127.7, 127.6, 127.1 126.9, 126.4, 124.4, 123.1, 122.7. Several quaternary carbons were not clearly observed due to coupling with F and low solubility.

EA: Found. C 69.74%, H 2.62%; Calcd. for $C_{20}H_9F_5$: C 69.77%, H 2.64%.

Synthesis of 3-(pentafluorophenyl)phenanthrene by direct arylation



A mixture of $Pd(OAc)_2$ (2.3 mg, 0.010 mmol), $P^tBu_2MeHBF_4$ (5.0 mg, 0.020 mmol), potassium carbonate (30 mg, 0.22 mmol), 3-bromophenanthrene (51 mg, 0.20 mmol), and pentafluorobenzene (33 μL, 0.3 mmol) was stirred in *N*,*N*-dimethylacetamide (0.2 mL) for 19 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using hexane as an eluent. The solvents were removed in vacuo to give 3-(pentafluorophenyl)phenanthrene (55 mg, 80%).

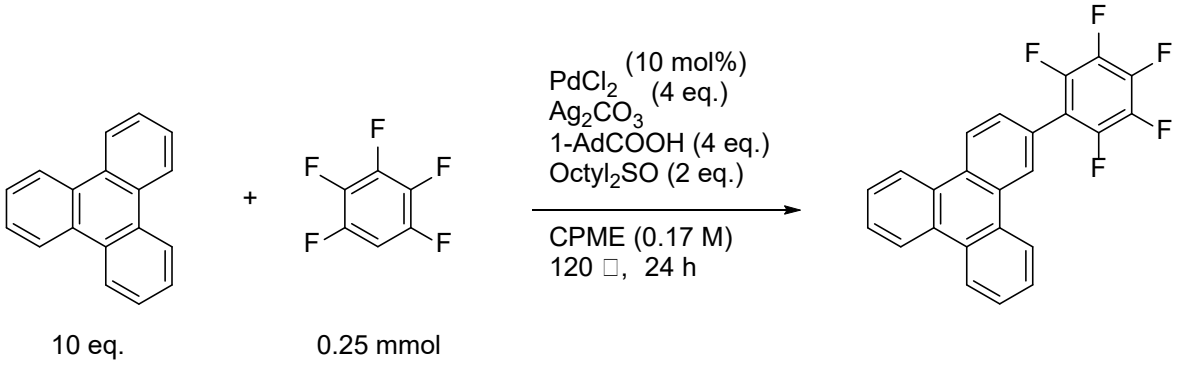
^{1}H NMR (400 MHz, $CDCl_3$, room temperature): δ 8.75 (s, 1H), 8.67 (d, 1H, J = 8.1 Hz), 8.01 (d, 1H, J = 8.2 Hz), 7.94 (d, 1H, J = 8.0 Hz), 7.84 (d, 1H, J = 8.9 Hz), 7.79 (d, 1H, J = 8.8 Hz), 7.71-7.61 (m, 3H).

^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -146.1 (dd, 2F, J = 23.2, 8.2 Hz), -158.5 (t, 1F, J = 20.4 Hz), -165.2 (dt, 2F, J = 22.5, 7.7 Hz).

^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, room temperature): δ 144.4 (dm, J_F = 243.6 Hz), 141.9-141.7 (m), 138.0 (dm, J_F = 254.6 Hz), 132.3, 130.3, 130.1, 129.0, 128.8, 128.4, 127.9, 127.1, 127.0, 126.3, 124.9, 124.4, 124.4, 122.6, 116.3-116.1 (m).

EA: Found. C 69.93%, H 2.79%; Calcd. for $C_{20}H_9F_5$: C 69.77%, H 2.64%.

Synthesis of 2-(pentafluorophenyl)triphenylene by the CDC reaction



A mixture of $PdCl_2$ (4.4 mg, 0.025 mmol), di-*n*-octylsulfoxide (137.3 mg, 0.5 mmol), 1-adamantanecarboxylic acid (180.3 mg, 1.0 mmol), silver(I) carbonate (275.7 mg, 1.0 mmol), triphenylene (570.7 mg, 2.5 mmol), and pentafluorobenzene (27.5 μL, 0.25 mmol) was stirred in CPME (1.5 mL) for 24 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$, and the crude product was evaluated by NMR spectroscopy. Following Celite® filtration, the filtrate was concentrated under reduced

pressure. The product was isolated by column chromatography on silica gel using hexane as an eluent and HPLC. The solvents were removed in vacuo to give 2-(pentafluorophenyl)triphenylene (40.6 mg, 21%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.77 (d, 1H, J = 8.5 Hz), 8.73 (s, 1H), 8.69 (dd, 3H, J = 7.5, 1.9 Hz), 8.63 (dd, 1H, J = 7.8, 1.8 Hz), 7.74-7.67 (m, 5H).

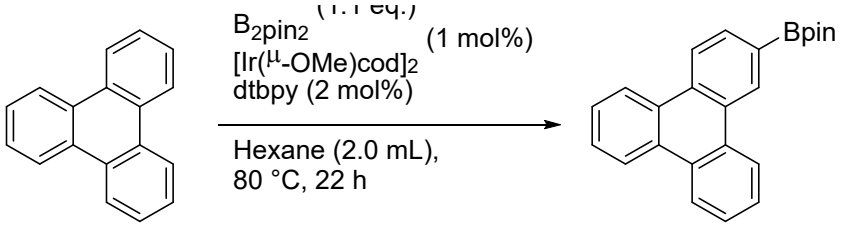
^{19}F NMR (564 MHz, $CDCl_3$): δ -143.28 (dd, 2F, J = 23.0, 8.2 Hz), -155.55 (t, 1F, J = 20.8 Hz), -162.27 to -162.36 (m, 2F).

^{13}C{^{1}H} NMR (151 MHz, 1,1,2,2-tetrachloroethane-d_2, 373K): δ 144.37 (dm, J_F = 248.7 Hz), 140.51 (dm, J_F = 253.2 Hz), 137.92 (dm, J_F = 246.6 Hz), 130.35, 130.20, 130.07, 129.19, 129.07, 128.31, 127.79, 127.64, 127.35, 125.23, 125.04, 123.70, 123.39, 123.31, 123.14, 120.23, 116.00 (t, J_F = 17.1 Hz).

EA: Found. C 72.88%, H 2.81%, N 0%; Calcd. for $C_{24}H_{11}F_5$: C 73.10%, H 2.81%, N 0%.

To confirm the substituted position, the reference compound was synthesised separately as follows. The spectra of the reference compound were consistent with that of the product of the CDC reaction.

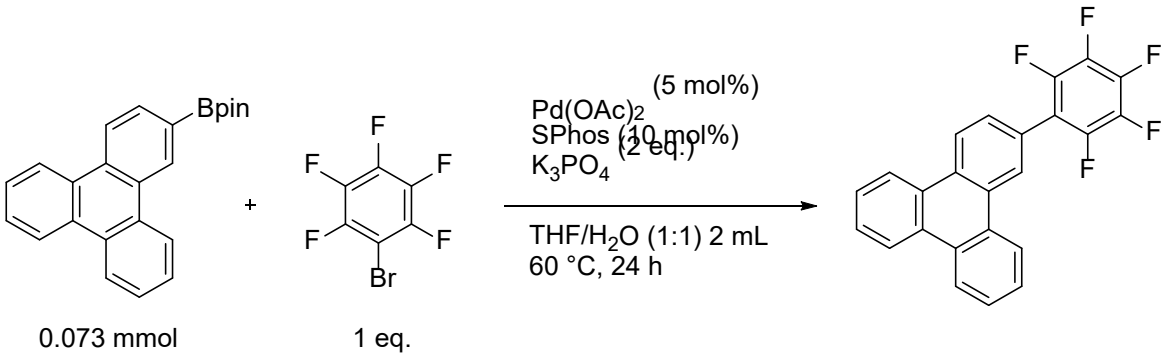
Synthesis of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene[3]



Triphenylene (114.1 mg, 0.5 mmol), bis(pinacolato)diboron (139.7 mg, 0.55 mmol) and hexane (1.0 mL) were added in a Schlenk tube. To the mixture, a solution of [Ir(μ-OMe)cod]$_2$ (3.3 mg, 0.0050 mmol), 4,4'-di-tert-butyl-2,2'-bipyridyl (2.7 mg, 0.010 mmol) in hexane (1.0 mL) was added in a dropwise manner. The mixture was stirred at 80 °C for 24 h under a nitrogen atmosphere. The product was isolated by column chromatography on silica gel using a mixture of chloroform and hexane (1:1) as an eluent. The solvents were removed in vacuo to give 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene (26.0 mg, 14%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.14 (s, 1H), 8.83-8.81 (m, 1H), 8.70-8.64 (m, 4H), 8.06 (dd, 1H, J = 8.1, 1.2 Hz), 7.69-7.64 (m, 4H), 1.43 (s, 12H). The spectral data corresponds to that reported earlier.[3]

Synthesis of 2-(pentafluorophenyl)triphenylene by the Suzuki-Miyaura cross coupling

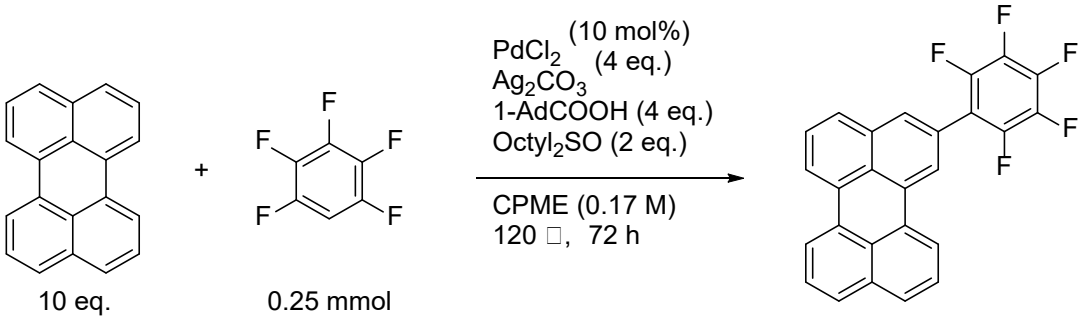


A mixture of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene (26.0 mg, 0.073 mmol), palladium(II) diacetate (0.8 mg, 0.0037 mmol) , 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 2.8 mg, 0.0073 mmol), tripotassium phosphate (29.2 mg, 0.15 mmol), and bromopentafluorobenzene (8.7 μL, 0.073 mmol) was stirred in tetrahydrofuran/H_2O (2.0 mL, 1/1 (v/v)) at 60 °C for 24 h under a nitrogen atmosphere. The product was isolated by column chromatography on silica gel using hexane as an eluent and HPLC. The solvents were removed in vacuo to give 2-(pentafluorophenyl)triphenylene (5.4 mg, 19%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.77 (d, 1H, J = 8.6 Hz), 8.72 (s, 1H), 8.70-8.69 (m, 3H), 8.64-8.62 (m, 1H), 7.74-7.67 (m, 5H)

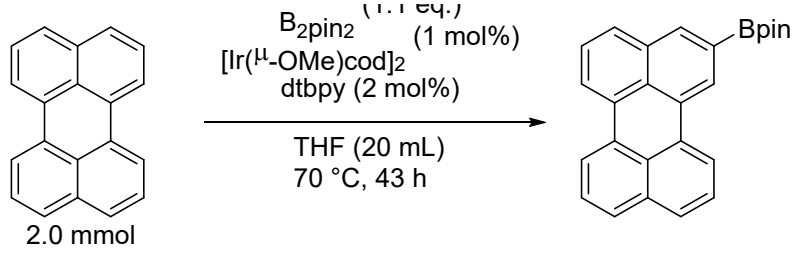
^{19}F NMR (564 MHz, $CDCl_3$): δ -143.28 (dd, 2F, J = 23.0, 8.2 Hz), -155.55 (t, 1F, J = 21.1 Hz), -162.27 to -162.36 (m, 2F).

Synthesis of 2-(pentafluorophenyl)perylene by the CDC reaction



A mixture of $PdCl_2$ (4.4 mg, 0.025 mmol), di-*n*-octylsulfoxide (137.3 mg, 0.5 mmol), 1-adamantanecarboxylic acid (180.3 mg, 1.0 mmol), silver(I) carbonate (275.7 mg, 1.0 mmol), perylene (631 mg, 2.5 mmol), and pentafluorobenzene (27.5 μL, 0.25 mmol) was stirred in CPME (1.5 mL) for 72 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$, and the crude product was analysed by ^{19}F NMR spectroscopy. The crude product contained three kinds of isomers. The two of isomers were assigned by comparison with the reference compound, 2-(pentafluorophenyl)perylene and 3-(pentafluorophenyl)perylene, which were prepared by the following method. The remaining isomer was assigned to the 1-position substituted isomer by process of elimination. The ratio of the regioisomers was calculated from ^{19}F NMR spectroscopy.

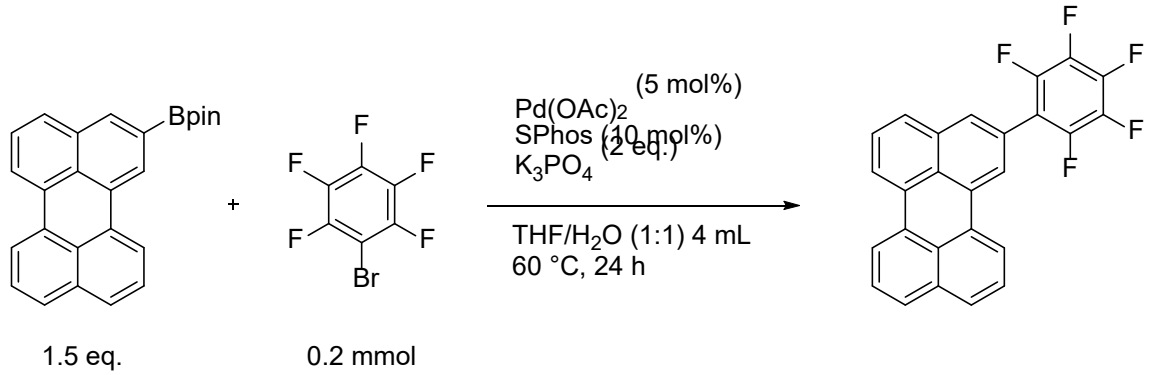
Synthesis of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)perylene[4]



A mixture of [Ir(μ-OMe)cod]$_2$ (19.9 mg, 0.030 mmol), 4,4'-di-tert-butyl-2,2'-bipyridyl (16.1 mg, 0.060 mmol), bis(pinacolato)diboron (507.9 mg, 2.0 mmol) and perylene (504.6 mg, 2.0 mmol) was stirred in tetrahydrofuran (20 mL) for 43 h at 70 °C under a nitrogen atmosphere. The product was isolated by column chromatography on silica gel using a mixture of chloroform and hexane (9:11) as an eluent. The solvents were removed in vacuo to give 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)perylene (182.4 mg, 24%). The spectral data corresponds to that reported earlier.[4]

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.33 (d, 1H, J = 7.0 Hz), 8.21 (d, 1H, J = 6.7 Hz), 8.18 (s, 1H), 8.16 (d, 1H, J = 7.3 Hz), 7.72 (d, 1H, J = 7.9 Hz), 7.67 (d, 1H, J = 3.5 Hz), 7.66 (d, 1H, J = 3.5 Hz), 7.49-7.45 (m, 3H), 1.42 (s, 12H).

Synthesis of 2-(pentafluorophenyl)perylene by the Suzuki-Miyaura cross coupling



A mixture of 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)perylene (113.5 mg, 0.30 mmol), palladium(II) diacetate (2.2 mg, 0.010 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (SPhos, 8.2 mg, 0.020 mmol), tripotassium Phosphate (84.9 mg, 0.40 mmol), and bromopentafluorobenzene (25.3 μL, 0.2 mmol) was stirred in tetrahydrofuran/H_2O (4.0 mL, 1/1 (v/v)) for 24 h at 60 °C under a nitrogen atmosphere. The product was isolated by column chromatography on silica gel using hexane as an eluent and HPLC. The solvents were removed in vacuo to give 2-(pentafluorophenyl)perylene (9.4 mg, 11%).

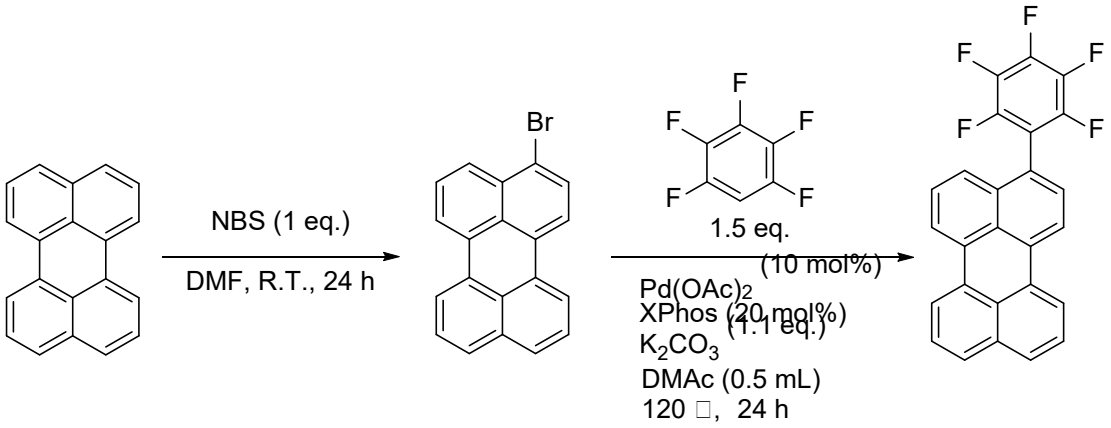
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.26 (dd, 1H, J = 7.6, 0.8 Hz), 8.23 (d, 1H, J = 6.8 Hz), 8.19 (d, 1H, J = 7.2 Hz), 8.17 (d, 1H, J = 1.3 Hz), 7.74-7.72 (m, 4H), 7.57-7.49 (m, 3H).

^{19}F NMR (564 MHz, $CDCl_3$): δ -142.92 (dd, 2F, J = 23.3. 7.9 Hz), -154.47 (t, 1F, J = 21.1 Hz), -162.23 to -162.32 (m, 2F).

^{13}C{^{1}H} NMR spectrum could not be obtained due to the low solubility of this compound.

HRMS (APCI): *m/z* calcd For $C_{26}H_{11}F_5$: 418.0781. Found: 418.0801 (error 4.8ppm).

Synthesis of 3-(pentafluorophenyl)perylene by direct arylation



Perylene (132.9 mg, 0.53 mmol) and DMF (2.53 mL) were added in a Schlenk tube. To the mixture, NBS (93.7 mg, 0.53 mmol) in DMF (1.9 mL) was added in a dropwise manner. The mixture was stirred at room temperature for 24 h, and then poured into water. The precipitate was filtered and washed with water several times. The solid contained 3-bromoperylene[5] and a small amount of perylene (77:23). This mixture was used for the following reaction without further purification. The mixture (51.3 mg, 0.13 mmol of 3-bromoperylene), $Pd(OAc)_2$ (2.8 mg, 0.013 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropylbiphenyl (XPhos, 12.1 mg, 0.025 mmol), potassium carbonate (19.2 mg, 0.14 mmol), and pentafluorobenzene (20.8 μL, 0.55 mmol), *N*,*N*-dimethylacetamide (0.5 mL) were added in a Schlenk tube. The mixture was stirred for 24 h at 120 °C under a nitrogen atmosphere. The product was isolated by column chromatography on silica gel using hexane as an eluent and HPLC. The solvents were removed in vacuo to give 3-(pentafluorophenyl)perylene (3.4 mg, 6%).

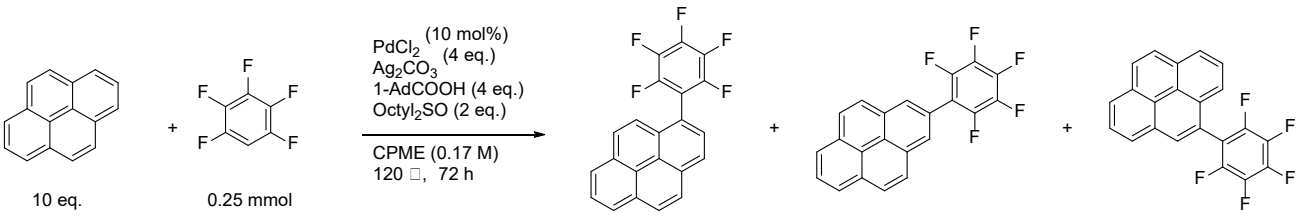
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28-8.23 (m, 4H), 7.74 (2H, dd, *J* = 10.8, 8.0 Hz), 7.54-7.49 (m, 3H), 7.44 (d, 1H, *J* = 7.7 Hz), 7.31 (d, 1H, *J* = 7.8 Hz).

^{19}F NMR (564 MHz, CDCl3): δ -139.56 (dd, 2F, *J* = 23.3, 7.9 Hz), -154.93 (t, 1F, *J* = 20.8 Hz), -162.01 to -162.10 (m, 2F).

^{13}C{^{1}H} NMR spectrum could not be obtained due to the low solubility of this compound.

HRMS (APCI): *m/z* calculated for $C_{26}H_{12}F_5^+$ [M+H$^+$]: 419.0854, found: 419.0873 (error 4.5 ppm).

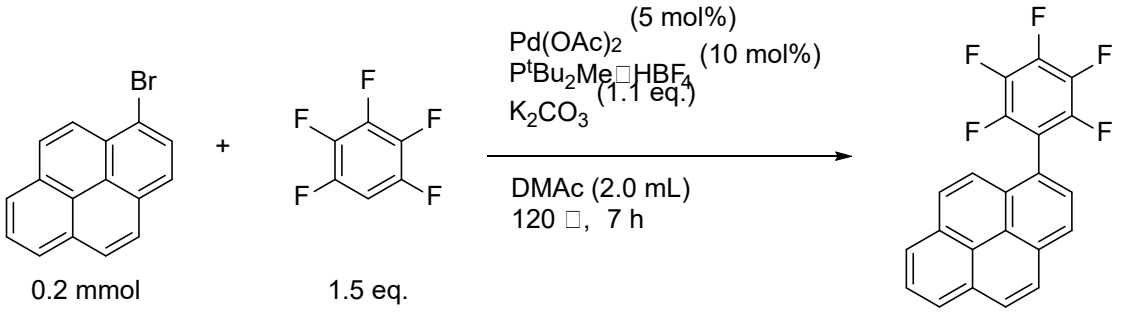
Synthesis of (pentafluorophenyl)pyrenes by the CDC reaction



A mixture of $PdCl_2$ (4.4 mg, 0.025 mmol), di-*n*-octylsulfoxide (137.3 mg, 0.5 mmol), 1-adamantanecarboxylic acid (180.3 mg, 1.0 mmol), silver(I) carbonate (275.7 mg, 1.0 mmol), pyrene (506 mg, 2.5 mmol), and pentafluorobenzene (27.5 μL, 0.25 mmol) was stirred in CPME (1.5 mL) for 72 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$, and the crude product was analysed by ^{19}F NMR

spectroscopy. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane as an eluent and HPLC. The solvents were removed in vacuo to give a mixture of regioisomers of (pentafluorophenyl)pyrene (56.1 mg, 30%). The crude product contained three kinds of isomers. The two of isomers were assigned by comparison with the spectra of the known compound, 1-(pentafluorophenyl)pyrene[6], and the reference sample, 2-(pentafluorophenyl)pyrene, which was prepared by the following method. The remaining isomer was assigned to the 4-position substituted isomer by process of elimination. The ratio of the regioisomers was calculated from ^{19}F NMR spectroscopy.

Synthesis of 1-(pentafluorophenyl)pyrene[6]



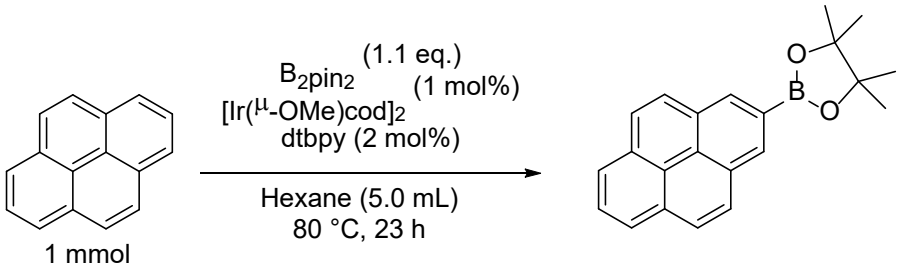
A mixture of $Pd(OAc)_2$ (3.4 mg, 0.015 mmol), $P^tBu_2MeHBF_4$ (7.5 mg, 0.030 mmol), potassium carbonate (46.1 mg, 0.33 mmol), 1-bromopyrene (85.3 mg, 0.30 mmol), and pentafluorobenzene (76.5 μL, 0.46 mmol) was stirred in *N*,*N*-dimethylacetamide (2.0 mL) for 7 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using a hexane as an eluent and HPLC. The solvents were removed in vacuo to give 1-(pentafluorophenyl)pyrene (1.8 mg, 2%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.29-8.24 (m, 3H), 8.20-8.12 (m, 3H), 8.07 (t, 1H, J = 7.6 Hz), 7.93 (d, 1H, J = 7.8 Hz), 7.74 (1H, dt, J = 9.2, 1.8 Hz).

^{19}F NMR (564 MHz, CDCl3): δ -139.79 (dd, 2F, J = 23.3, 8.5 Hz), -154.87 (t, 1F, J = 21.1 Hz), -162.09 to -162.18 (m, 2F).

The spectral data corresponds to that reported earlier.

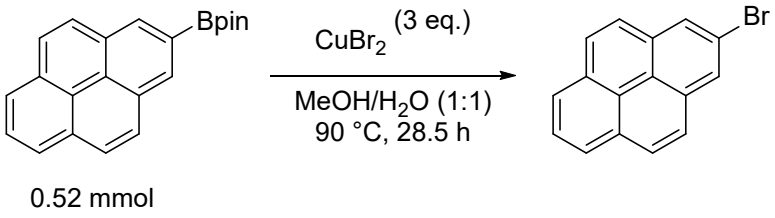
Synthesis of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene[7]



Pyrene (202.3 mg, 1.0 mmol), bis(pinacolato)diboron (253.9 mg, 1.0 mmol), [Ir(μ-OMe)cod]$_2$ (6.6 mg, 0.010 mmol), 4,4'-di-tert-butyl-2,2'-bipyridyl (5.4 mg, 0.020 mmol), and hexane (5.0 mL) were added in a Schlenk tube. The mixture was stirred at 80 °C for 24 h under a nitrogen atmosphere. The product was isolated by column chromatography on silica gel using a mixture of dichloromethane and hexane (1:1) as an eluent. The solvents were removed in vacuo to give 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (170.1 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.64 (s, 2H), 8.17 (d, 2H, *J* = 7.6 Hz), 8.10 (d, 2H, *J* = 8.9 Hz), 8.06 (d, 2H, *J* = 8.9 Hz), 8.01 (dd, 1H, *J* = 7.8, 7.3 Hz).

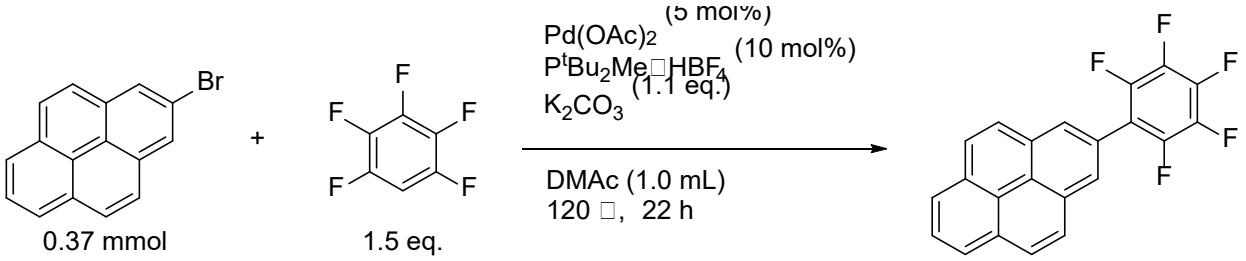
Synthesis of 2-bromopyrene[7]



A mixture of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (170.1 mg, 0.52 mmol) and $CuBr_2$ (347.3 mg, 1.55 mmol) was stirred in methanol/H_2O (10 mL, 1:1) at 90 °C for 28.5 h under a nitrogen atmosphere. After the reaction, H_2O was added and a white precipitate was collected by filtration and washed with H_2O. 2-bromopyrene was obtained (113.5 mg, 48%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.28 (s, 2H), 8.20 (d, 2H, *J* = 7.5 Hz), 8.10 (d, 2H, *J* = 9.0 Hz), 8.03 (t, 1H, *J* = 7.6 Hz), 7.98 (d, 2H, *J* = 9.0 Hz).

Synthesis of 2-(pentafluorophenyl)pyrene by direct arylation



A mixture of $Pd(OAc)_2$ (4.1 mg, 0.018 mmol), P^{t}Bu$_2$MeHBF$_4$ (9.1 mg, 0.037 mmol), potassium carbonate (55.5 mg, 0.40 mmol), 2-bromopyrene (102.7 mg, 0.37 mmol), and pentafluorobenzene (53.7 μL, 0.55 mmol) was stirred in *N*,*N*-dimethylacetamide (1.0 mL) for 22 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room

temperature and diluted with $CHCl_3$. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using a hexane as an eluent and HPLC. The solvents were removed in vacuo to give 2-(pentafluorophenyl)pyrene (28.1 mg, 21%).

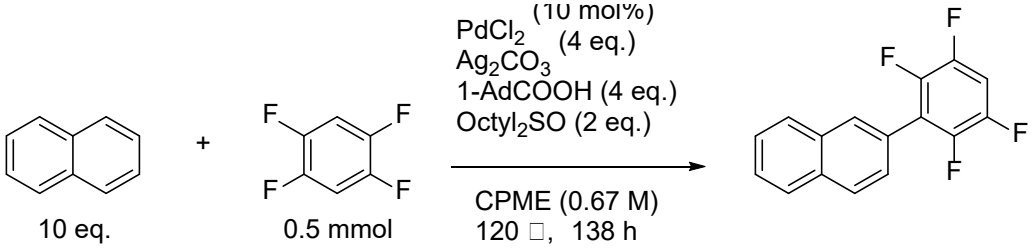
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.24 (d, 2H, J = 7.6 Hz), 8.22 (s, 2H), 8.15 (d, 2H, J = 8.9 Hz), 8.11 (d, 2H, J = 8.9 Hz), 8.07 (t, 1H, J = 7.6 Hz).

^{19}F NMR (564 MHz, $CDCl_3$): δ -143.50 (dd, 2F, J = 23.0, 8.2 Hz), -155.48 (t, 1F, J = 20.8 Hz), -162.33 to -162.43 (m, 2F).

^{13}C{^{1}H} NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 393K): δ 144.44 (d, J_F = 244.2 Hz), 140.57 (d, J_F = 254.3 Hz), 137.95 (d, J_F = 251.1 Hz), 131.32, 128.14, 126.94, 126.40, 125.97, 125.36, 124.64, 124.24, 123.75, 116.42 (t, J_F = 17.6 Hz).

HRMS (APCI): *m/z* calculated for $C_{22}H_{10}F_5^+$ [M+H$^+$]: 369.0697, found: 369.0714 (error 4.6 ppm).

Synthesis of 2-(2,3,5,6-tetrafluorophenyl)naphthalene

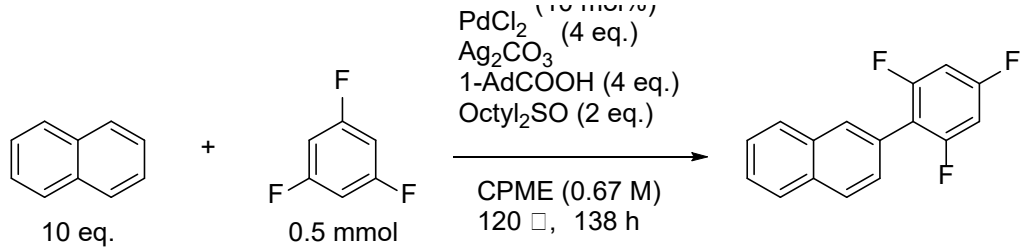


A mixture of $PdCl_2$ (8.9 mg, 0.050 mmol), di-*n*-octylsulfoxide (275 mg, 1.0 mmol), 1-adamantanecarboxylic acid (360 mg, 2.0 mmol), silver(I) carbonate (550 mg, 2.0 mmol), naphthalene (641.0 mg, 5.0 mmol), and 1,2,4,5-tetrafluorobenzene (52.5 µL, 0.50 mmol) was stirred in CPME (0.75 mL) for 138 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$, and the crude product was analysed by NMR spectroscopy. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using a hexane as an eluent. The solvents were removed in vacuo to give 2-(2,3,5,6-tetrafluorophenyl)naphthalene (20.3 mg, 15%). The spectral data corresponds to that reported earlier.[8]

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96 (d, 2H, J = 9.2 Hz), 7.90 (dd, 2H, J = 8.3, 1.1 Hz), 7.58-7.53 (m, 3H), 7.14-7.08 (m, 1H).

^{19}F NMR (564 MHz, $CDCl_3$): δ -139.43 to -139.50 (m, 2F), -144.06 to -144.13 (m, 2F).

Synthesis of 2-(2,4,6-trifluorophenyl)naphthalene

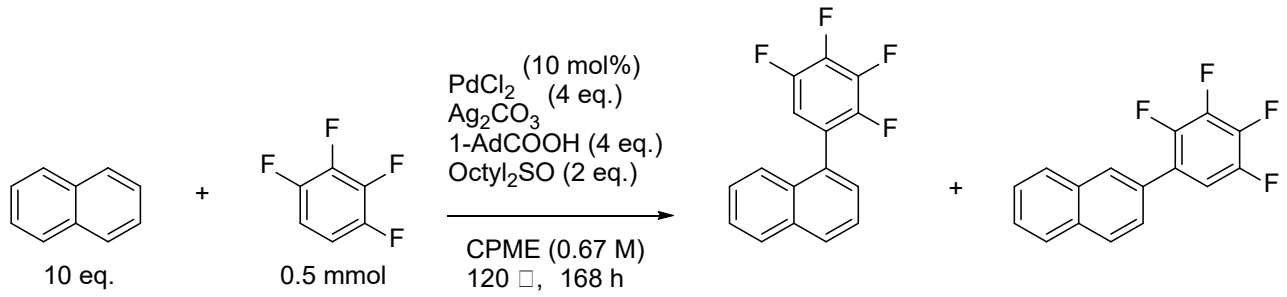


A mixture of $PdCl_2$ (8.9 mg, 0.050 mmol), di-*n*-octylsulfoxide (275 mg, 1.0 mmol), 1-adamantanecarboxylic acid (360 mg, 2.0 mmol), silver(I) carbonate (550 mg, 2.0 mmol), naphthalene (641.0 mg, 5.0 mmol), and 1,3,5-trifluorobenzene (51.6 µL, 0.50 mmol) was stirred in CPME (0.75 mL) for 138 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$, and the crude product was analysed by NMR spectroscopy. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using hexane as an eluent. The solvents were removed in vacuo to give 2-(2,4,6-trifluorophenyl)naphthalene (13.3 mg, 10%). The spectral data corresponds to that reported earlier.[8]

^{1}H NMR (600 MHz, $CDCl_3$): δ: 7.92 (d, 2H, *J* = 8.1 Hz), 7.88 (dt, 2H, *J* = 6.8, 2.8 Hz), 7.54-7.50 (m, 3H), 6.80 (tt, 2H, *J* = 12.2, 3.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$): δ = -108.91 (td, 1F, *J* = 9.9, 5.4 Hz), -111.09 (t, 2F, *J* = 7.2 Hz).

Synthesis of (2,3,4,5-tetrafluorophenyl)naphthalenes



A mixture of $PdCl_2$ (8.9 mg, 0.050 mmol), di-*n*-octylsulfoxide (275 mg, 1.0 mmol), 1-adamantanecarboxylic acid (360 mg, 2.0 mmol), silver(I) carbonate (550 mg, 2.0 mmol), naphthalene (641.0 mg, 5.0 mmol), and 1,2,3,4-tetrafluorobenzene (52.5 µL, 0.50 mmol) was stirred in CPME (0.75 mL) for 168 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$, and the crude product was analysed by NMR spectroscopy. Following Celite® filtration, the filtrate was concentrated under reduced pressure. The product was isolated by column chromatography on silica gel using hexane as an eluent. The solvents were removed in vacuo to give a mixture of 1-(2,3,4,5-tetrafluorophenyl)naphthalene and 2-(2,3,4,5-tetrafluorophenyl)naphthalene in 45:55 ratio (10.4 mg, 8%). The spectral data corresponds to that reported earlier.[8,9]

1-(2,3,4,5-tetrafluorophenyl)naphthalene[9]

^{1}H NMR (600 MHz, $CDCl_3$): 7.96-7.93 (m, 2H), 7.60-7.48 (m, 4H), 7.41 (dd, 1H, *J* = 7.0, 1.0 Hz), 7.08-7.03 (m,

1H).

^{19}F NMR (564 MHz, $CDCl_3$): -139.25 to -139.33 (m, 1F), -140.01 to -140.09 (m, 1F), -155.48 to -155.57 (m, 1F), -156.78 (1F, tdd, J = 20.6, 8.2, 3.1 Hz).

2-(2,3,4,5-tetrafluorophenyl)naphthalene[8]

^{1}H NMR (600 MHz, $CDCl_3$): 7.96 (s, 1H), 7.93 (d, 1H, J = 8.4 Hz), 7.89 (dd, 2H, J = 8.9, 5.6 Hz), 7.58 (dt, 1H, J = 8.4, 1.8 Hz), 7.56-7.53 (m, 2H), 7.20-7.15 (m, 1H).

^{19}F NMR (564 MHz, $CDCl_3$): -139.85 to -139.93 (m, 1F), -143.88 to -143.95 (m, 1F), -155.43 to -155.51 (m, 1F), -157.31 to -157.40 (m, 1F).

Table S1. Rate constants at various temperatures in toluene-d_8

Temperature (°C)	Rate constant (s^{-1})
70	1.6×10^{-4}
75	4.2×10^{-4}
80	6.1×10^{-4}
85	1.6×10^{-3}
90	2.2×10^{-3}

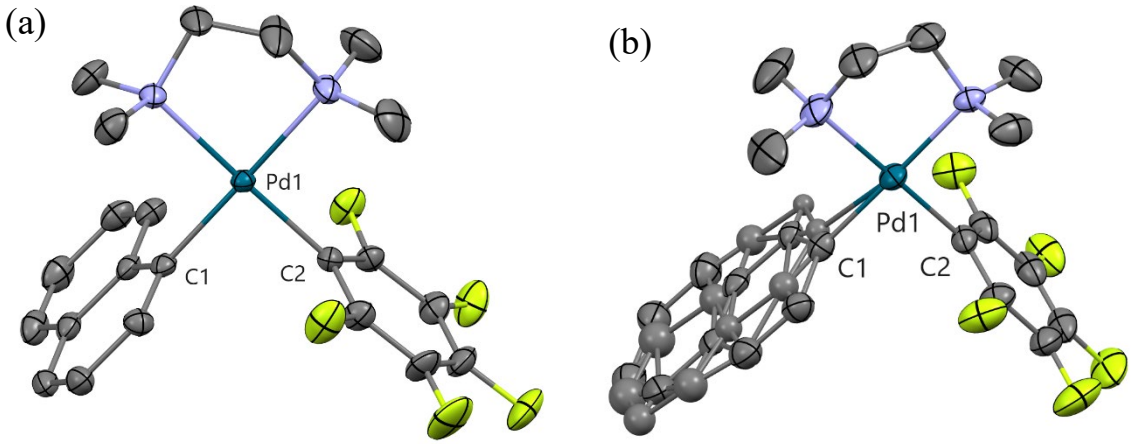


Figure S1(a) Thermal ellipsoid plots (50% probability level) of the molecular structure of **α-biaryl model complex**. A representative molecule is drawn among crystallographically independent molecules. Pd1-C2: 2.006(4) Å.
(b) Thermal ellipsoid plots (50% probability level) of the molecular structure of **β-biaryl model complex**. 2-Naphthyl group is disordered. Pd1-C2: 2.012(3) Å.

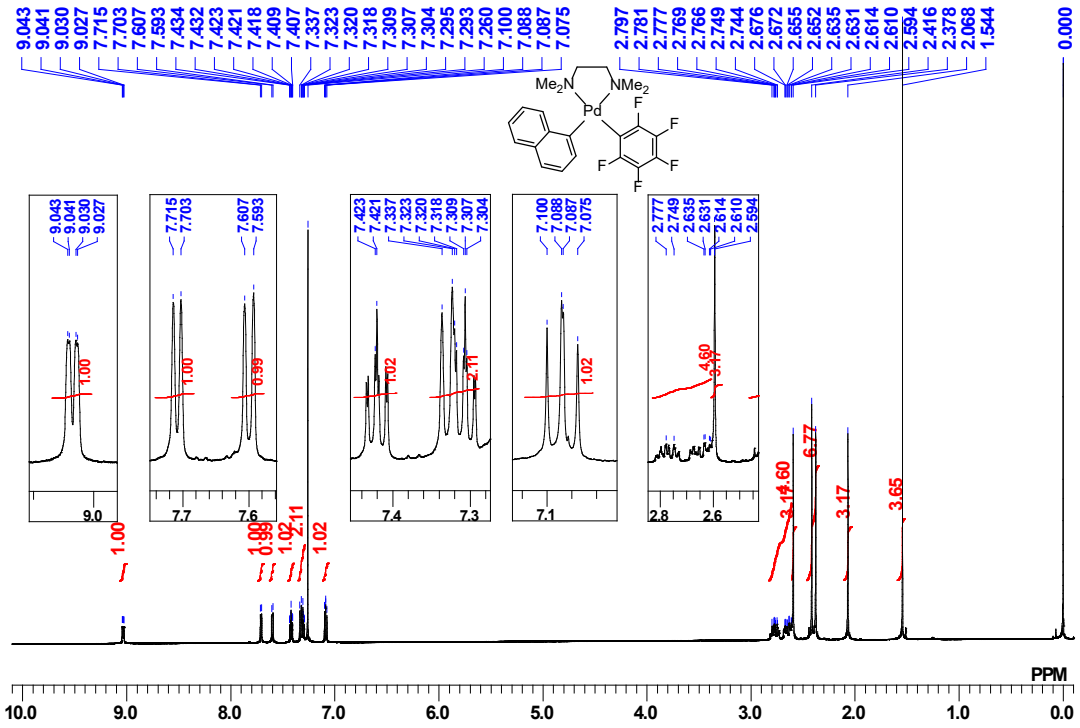


Figure S2. ^{1}H NMR spectrum of the α-biaryl model complex ($CDCl_3$, 600 MHz).

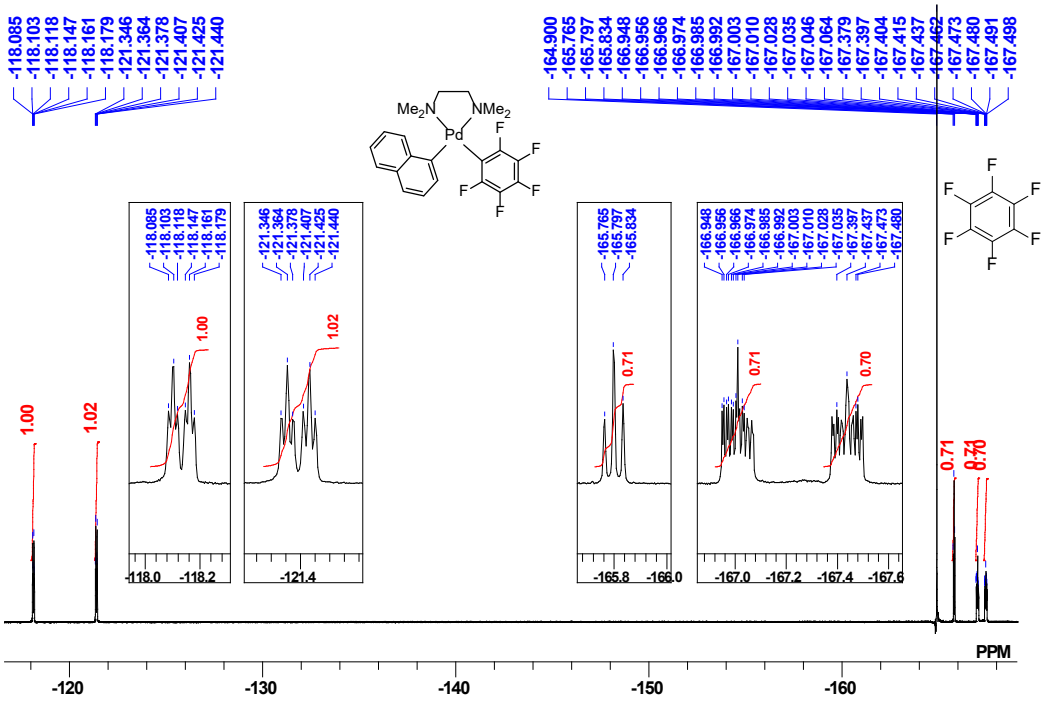


Figure S3. ^{19}F NMR spectrum of the α-biaryl model complex ($CDCl_3$, 565 MHz).

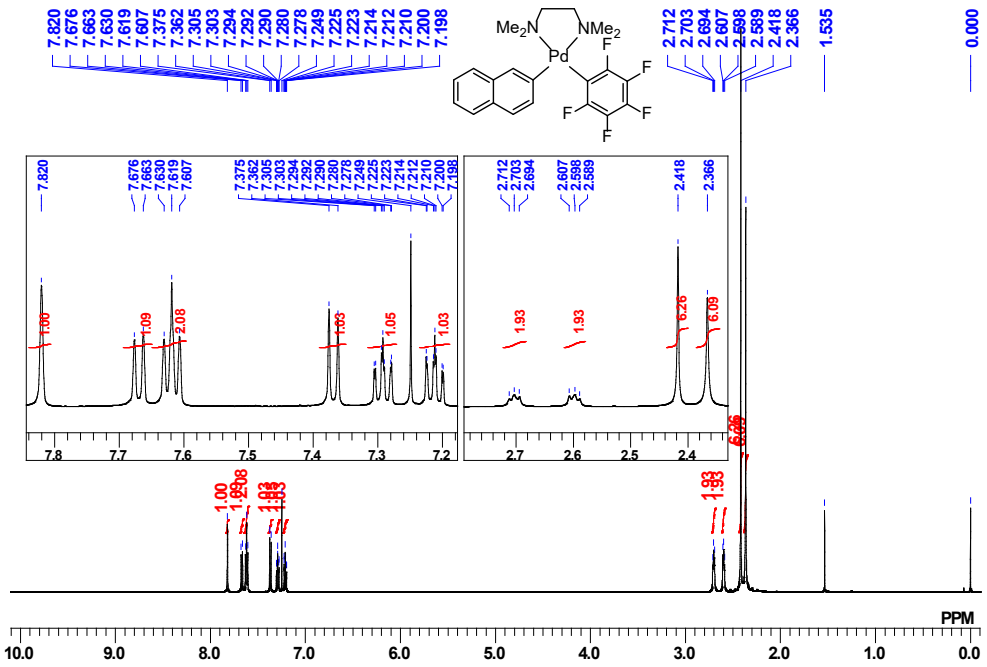


Figure S4. ^{1}H NMR spectrum of the β-biaryl model complex ($CDCl_3$, 600 MHz).

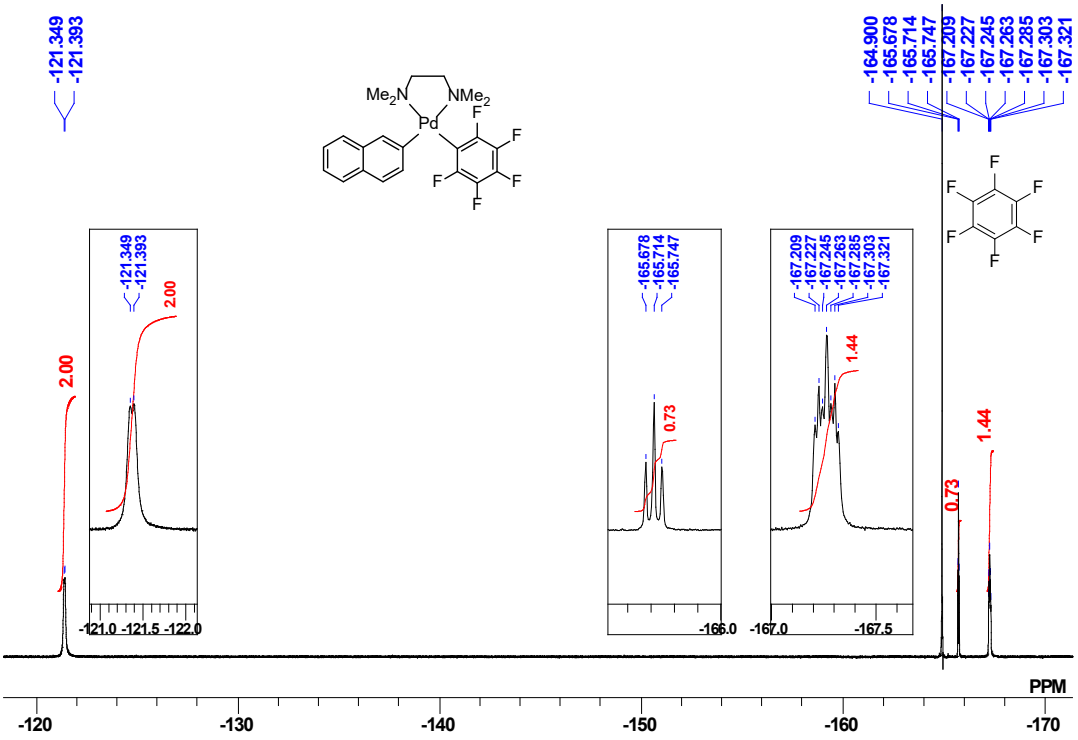


Figure S5. ^{19}F NMR spectrum of the β-biaryl model complex ($CDCl_3$, 376 MHz).

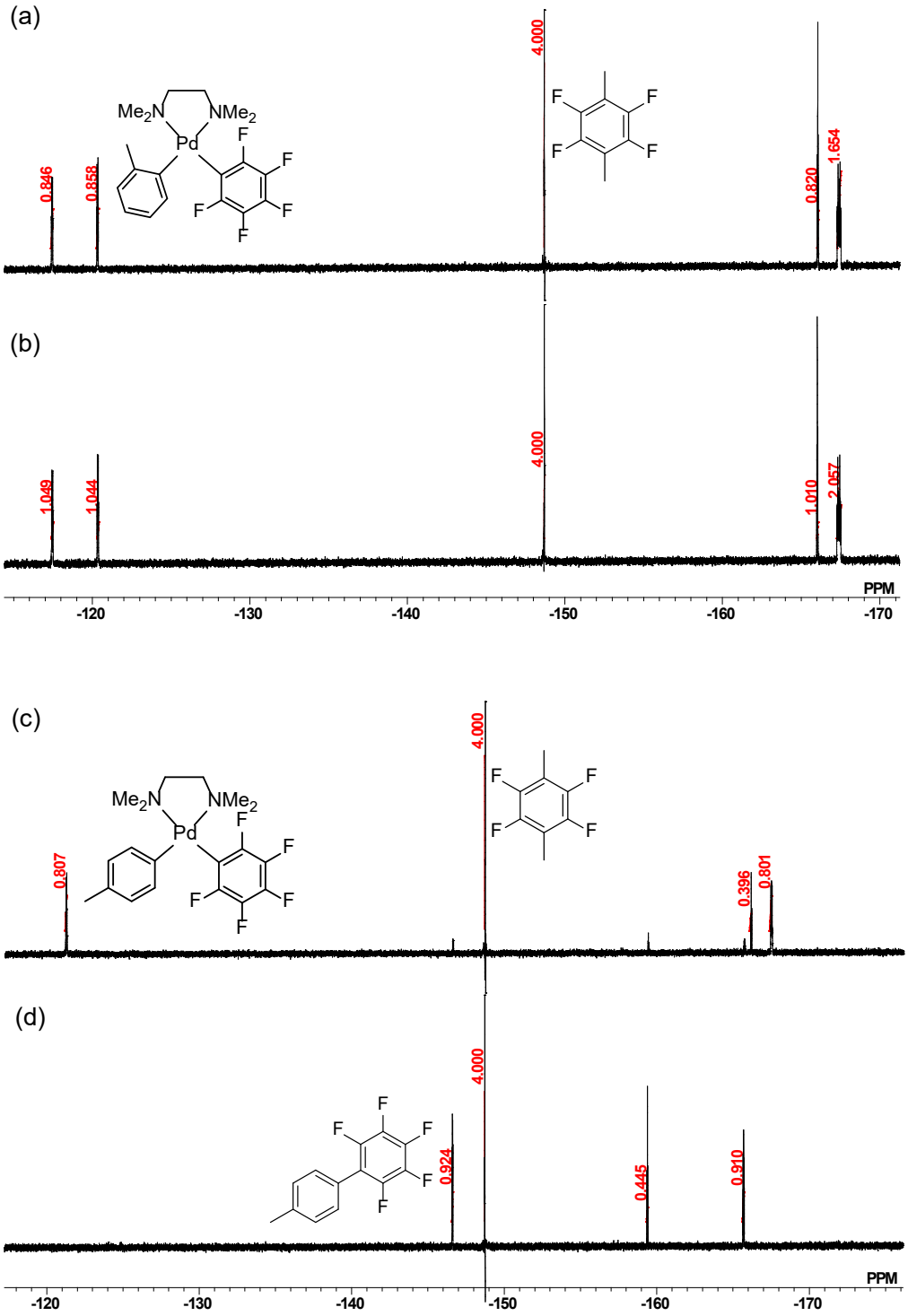


Figure S6. Tracing the reactions in Scheme 4 using ^{19}F NMR spectroscopy (564 MHz, $CDCl_3$, r.t.). 2,3,5,6-tetrafluoro-*p*-xylene was used as internal standard.

(a) Pd(2-tolyl)(pentafluorophenyl)(tmeda), (b) the product after heating at 120 °C for 10 min,

(c) Pd(4-tolyl)(pentafluorophenyl)(tmeda), (d) the product after heating at 120 °C for 10 min.

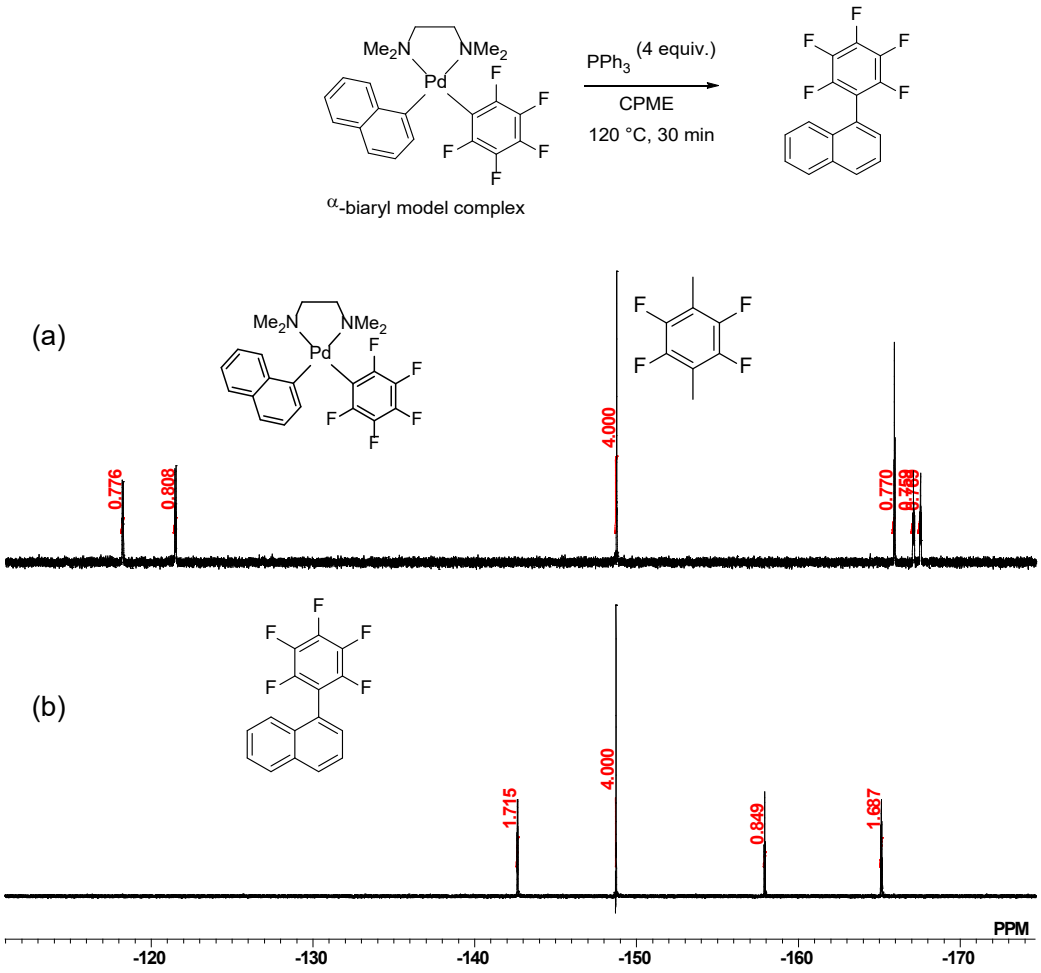


Figure S7. ^{19}F NMR spectra of (a) the α-biaryl model complex and (b) the product after reductive elimination in the presence of PPh_3 shown in Scheme 3 (564 MHz, $CDCl_3$, r.t.).

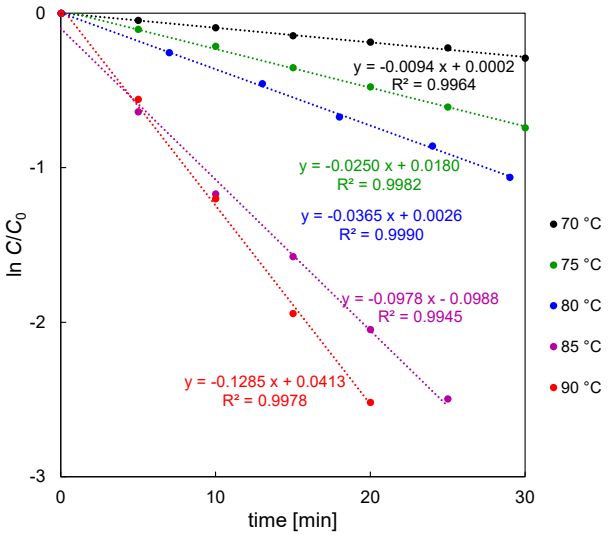


Figure S8. Slope and mean squared error of the first-order plot of reductive elimination of the β-biaryl model complex in toluene-d_8 shown in Figure 1.

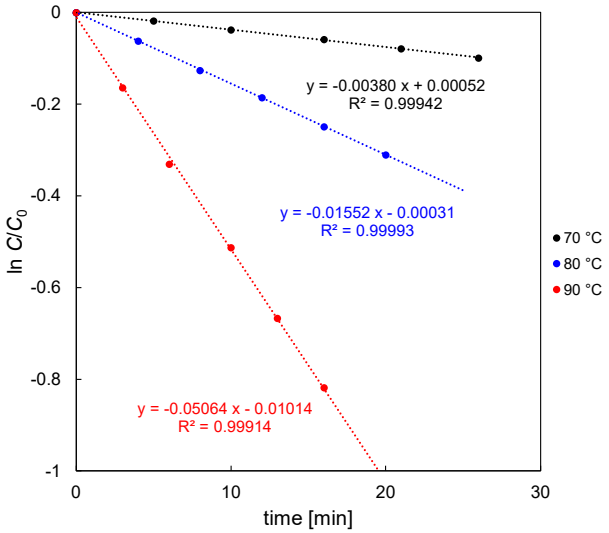


Figure S9. First-order plot of reductive elimination of the β-biaryl model complex in dioxane-d_8.

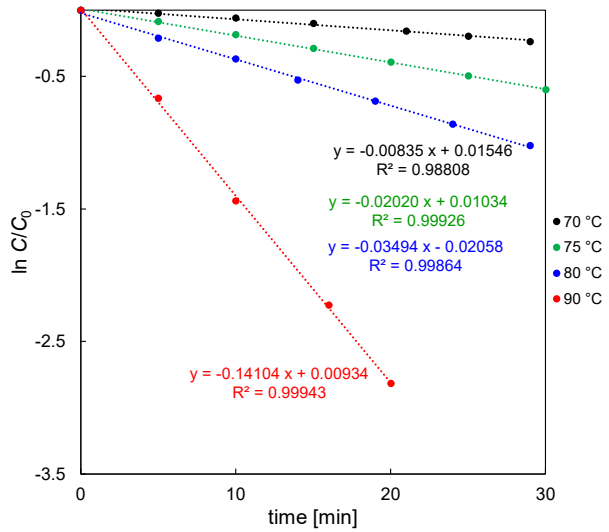


Figure S10. First-order plot of reductive elimination of the β-biaryl model complex in tetrachloroethane-d_2.

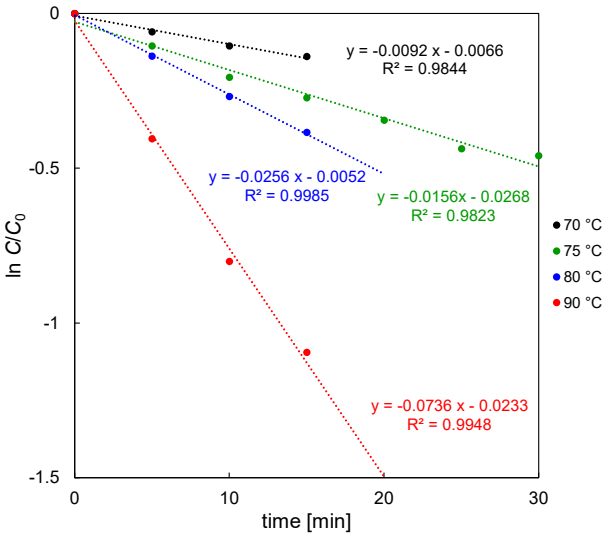


Figure S11. First-order plot of reductive elimination of the β-biaryl model complex in DMSO-d_6.

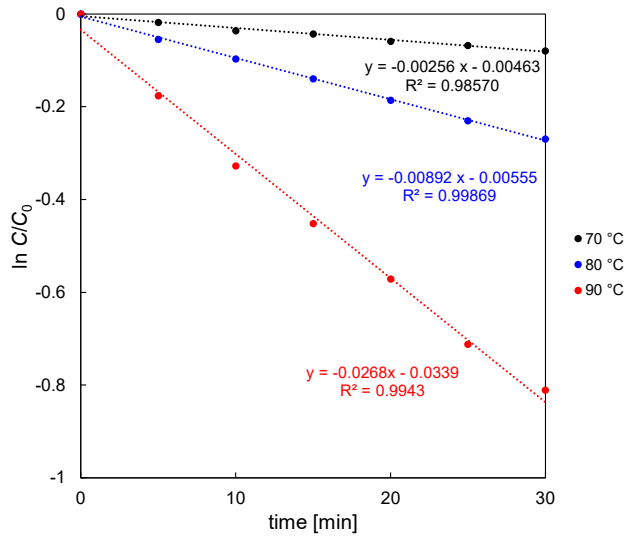


Figure S12. First-order plot of reductive elimination of the β-biaryl model complex in CD_3NO_2**.**

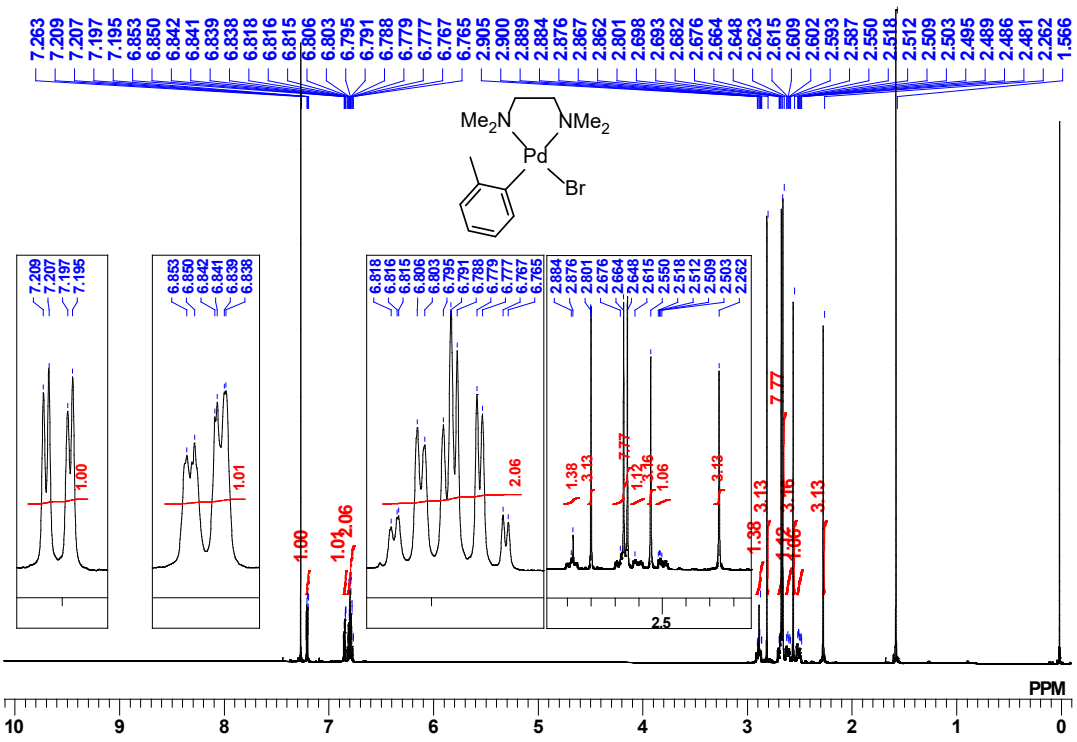


Figure S13. ^{1}H NMR spectrum of PdBr(2-tolyl)(tmeda) (600 MHz, $CDCl_3$, r.t.).

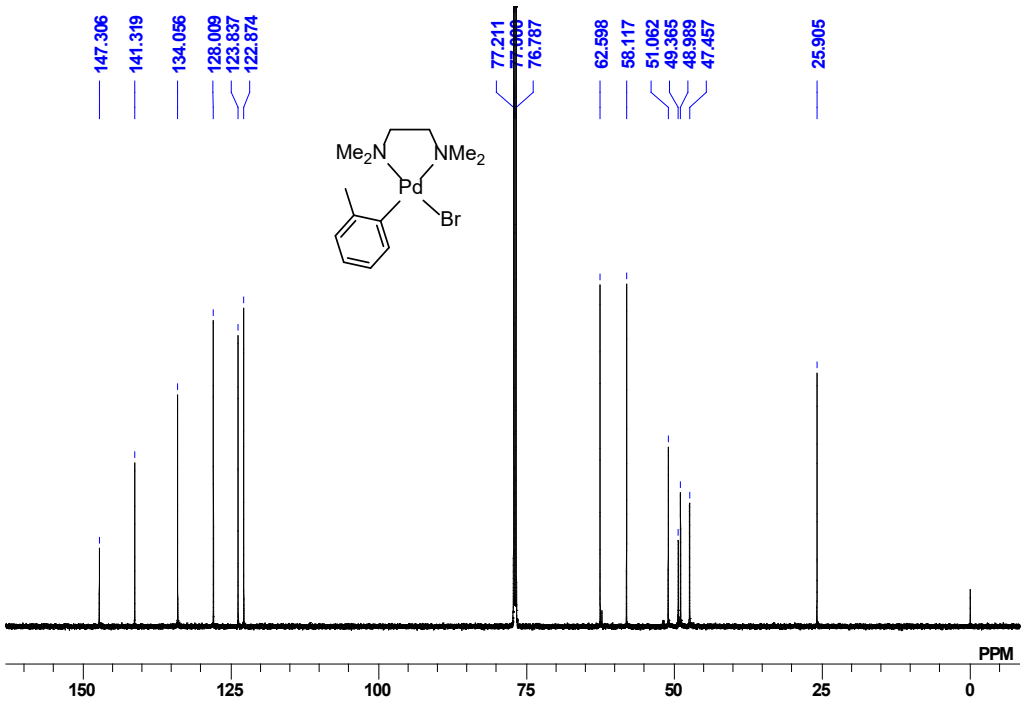


Figure S14. $^{13}C\{^{1}H\}$ spectrum of PdBr(2-tolyl)(tmeda) (150 MHz, $CDCl_3$, r.t.).

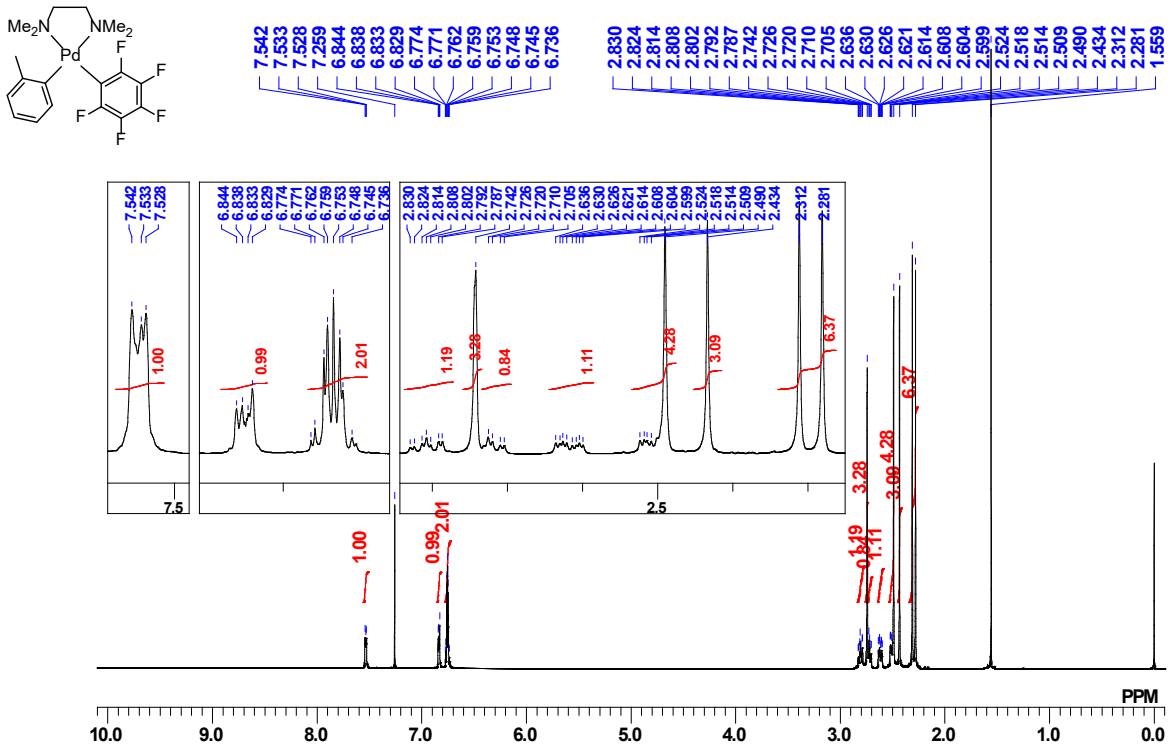


Figure S15. ^{1}H NMR spectrum of Pd(2-tolyl)(pentafluorophenyl)(tmeda) (600 MHz, $CDCl_3$, r.t.).

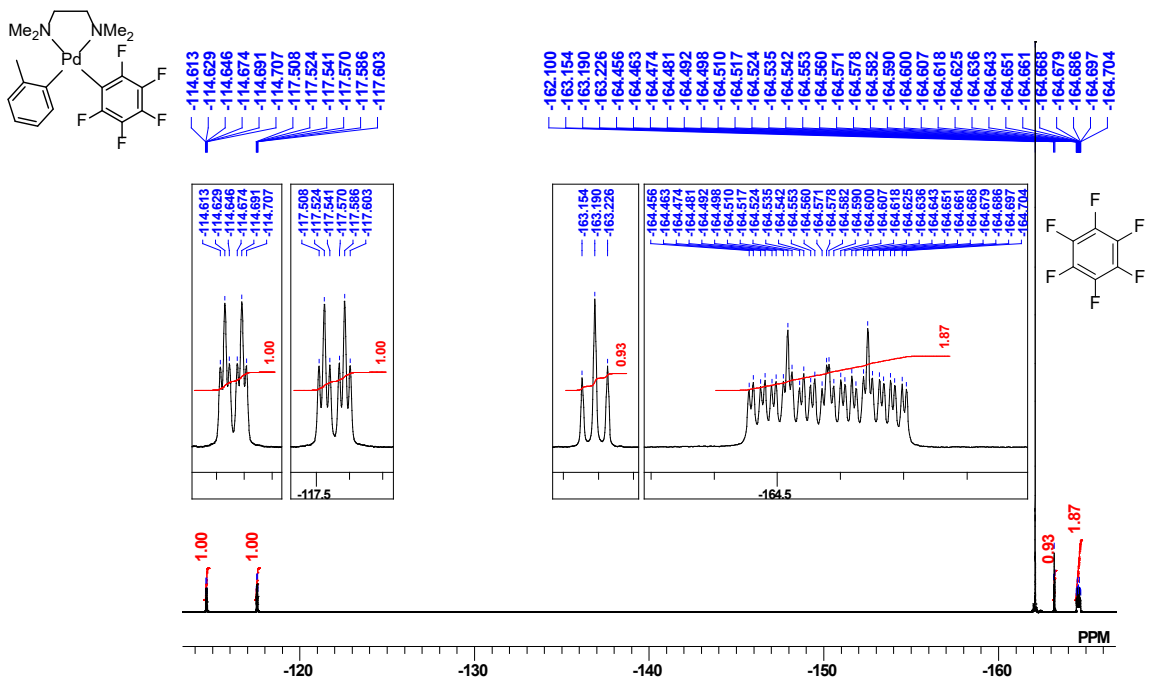


Figure S16. ^{19}F NMR spectrum of Pd(2-tolyl)(pentafluorophenyl)(tmeda) (564 MHz, $CDCl_3$, r.t.).

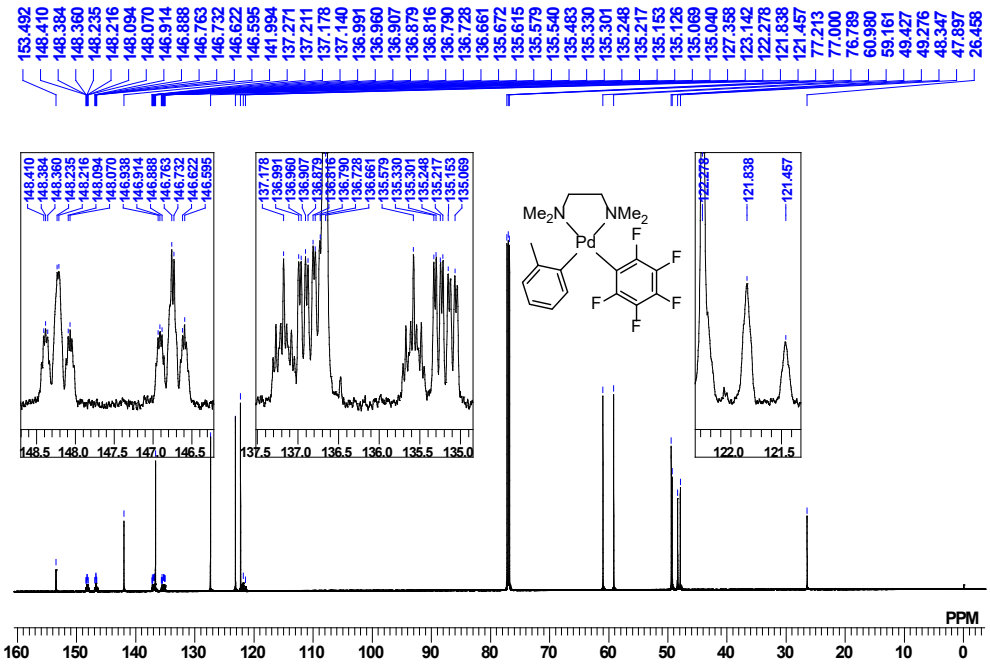


Figure S17. $^{13}C\{^1H\}$ NMR spectrum of Pd(2-tolyl)(pentafluorophenyl)(tmeda) (150 MHz, $CDCl_3$, r.t.).

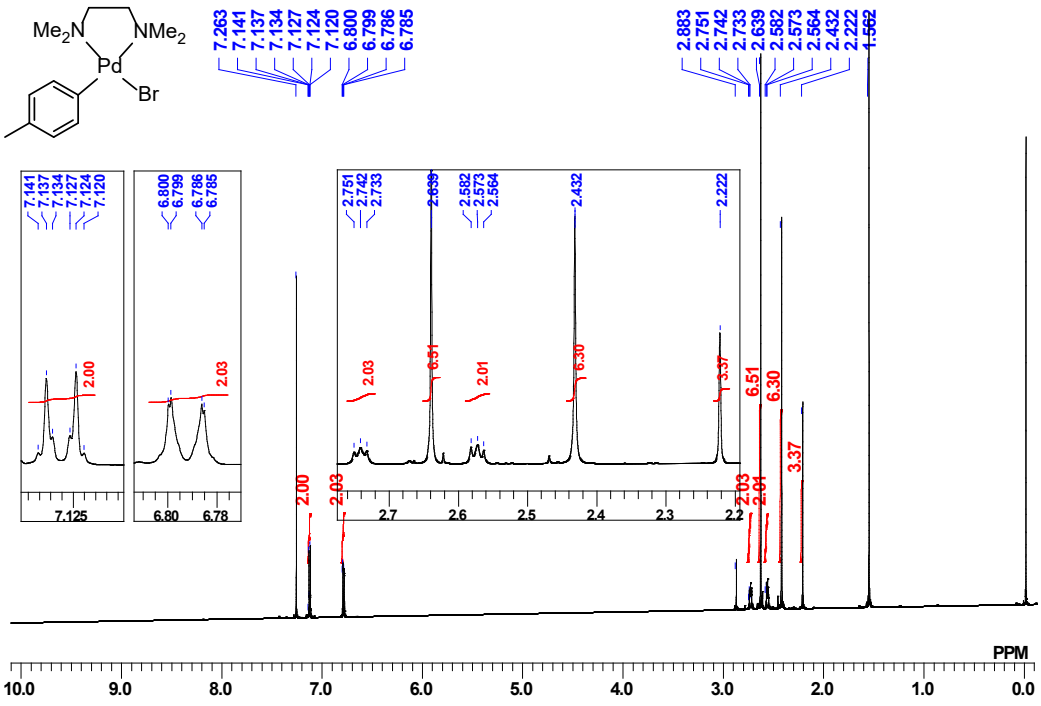


Figure S18. ^{1}H NMR spectrum of PdBr(4-tolyl)(tmeda) (600 MHz, $CDCl_3$, r.t.).

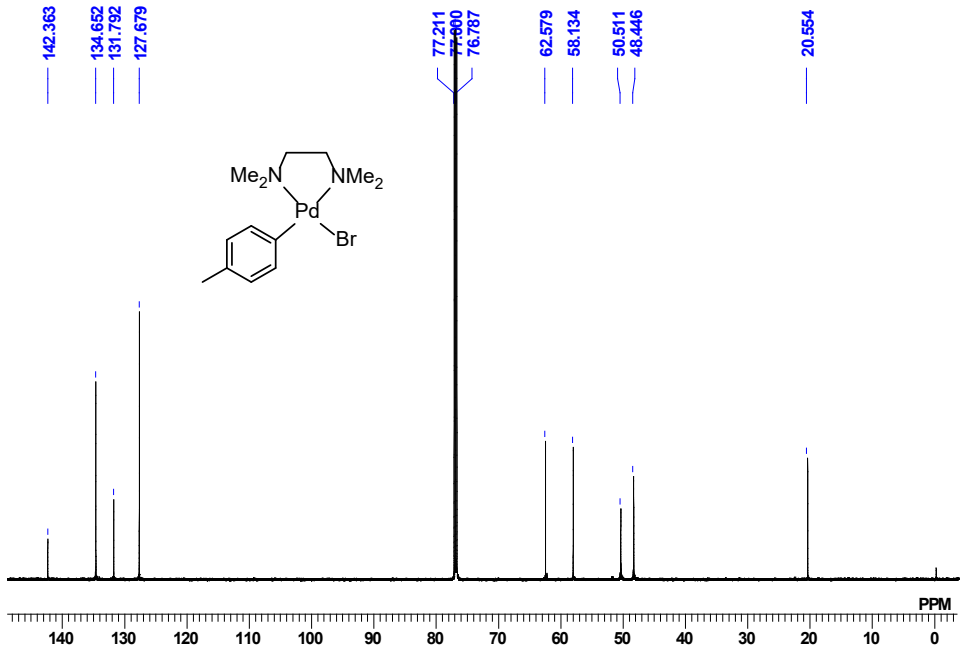


Figure S19. $^{13}C\{^{1}H\}$ NMR spectrum of PdBr(4-tolyl)(tmeda) (150 MHz, $CDCl_3$, r.t.).

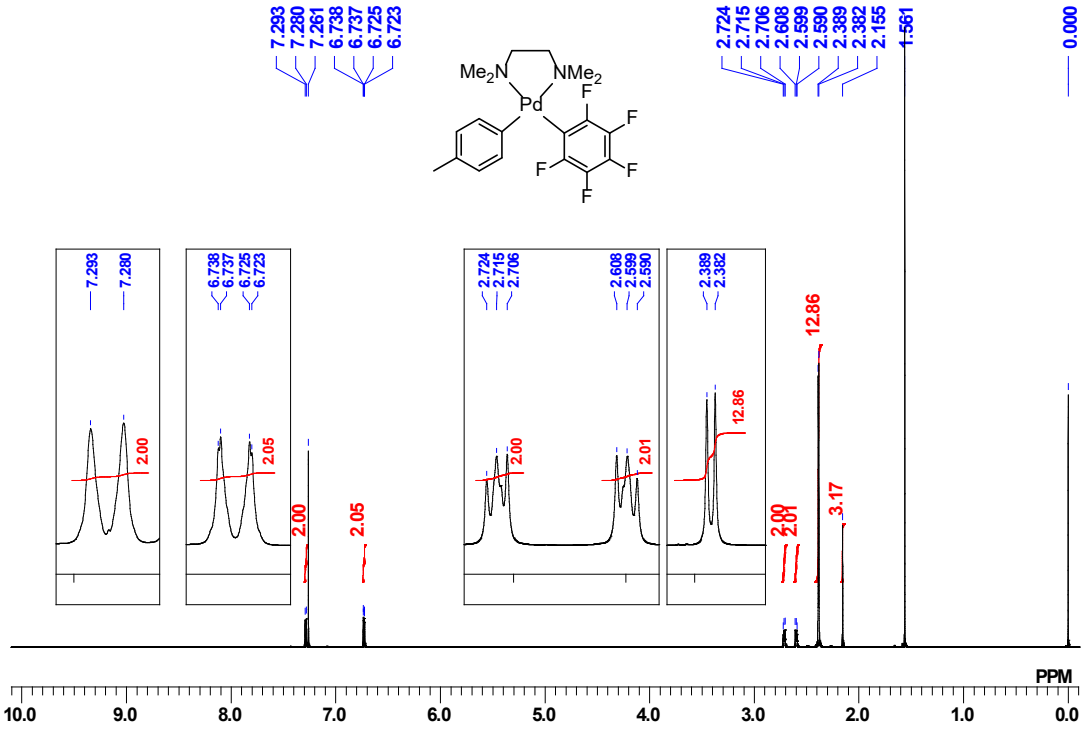


Figure S20. ^{1}H NMR spectrum of Pd(4-tolyl)(pentafluorophenyl)(tmeda) (600 MHz, $CDCl_3$, r.t.).

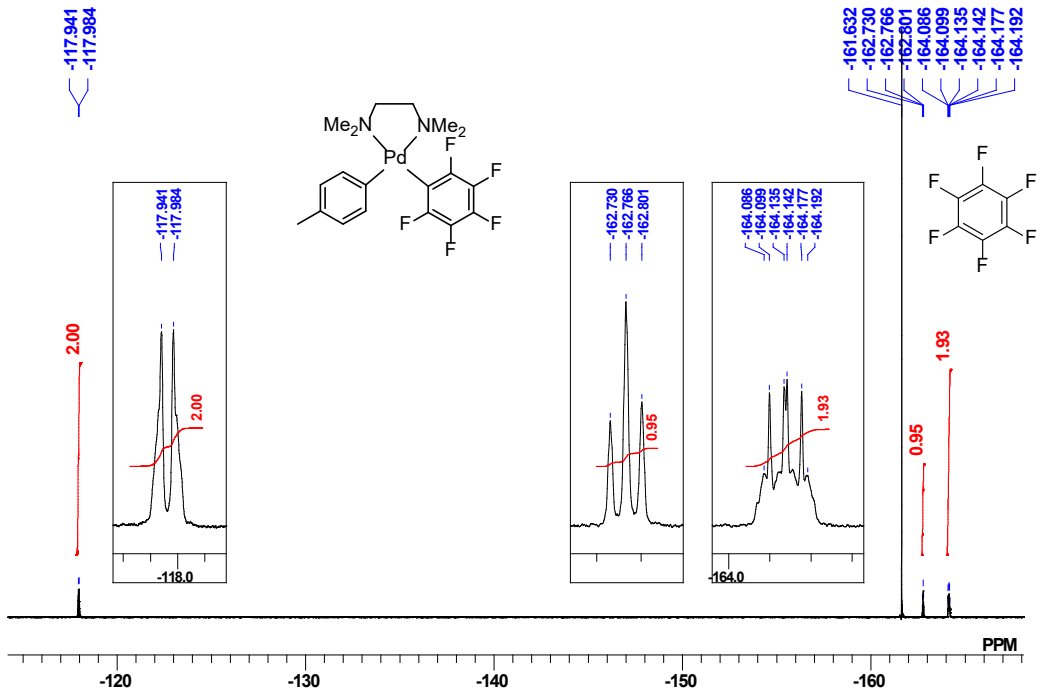


Figure S21. ^{19}F NMR spectrum of Pd(4-tolyl)(pentafluorophenyl)(tmeda) (564 MHz, $CDCl_3$, r.t.).

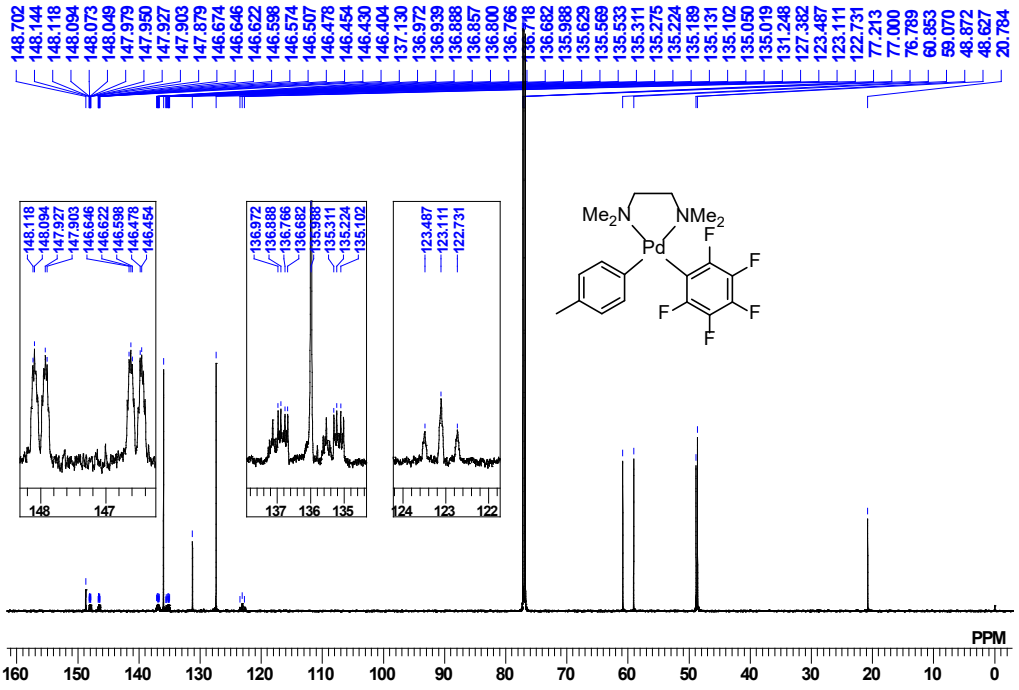


Figure S22. $^{13}C\{^{1}H\}$ NMR spectrum of Pd(4-tolyl)(pentafluorophenyl)(tmeda) (150 MHz, $CDCl_3$, r.t.).

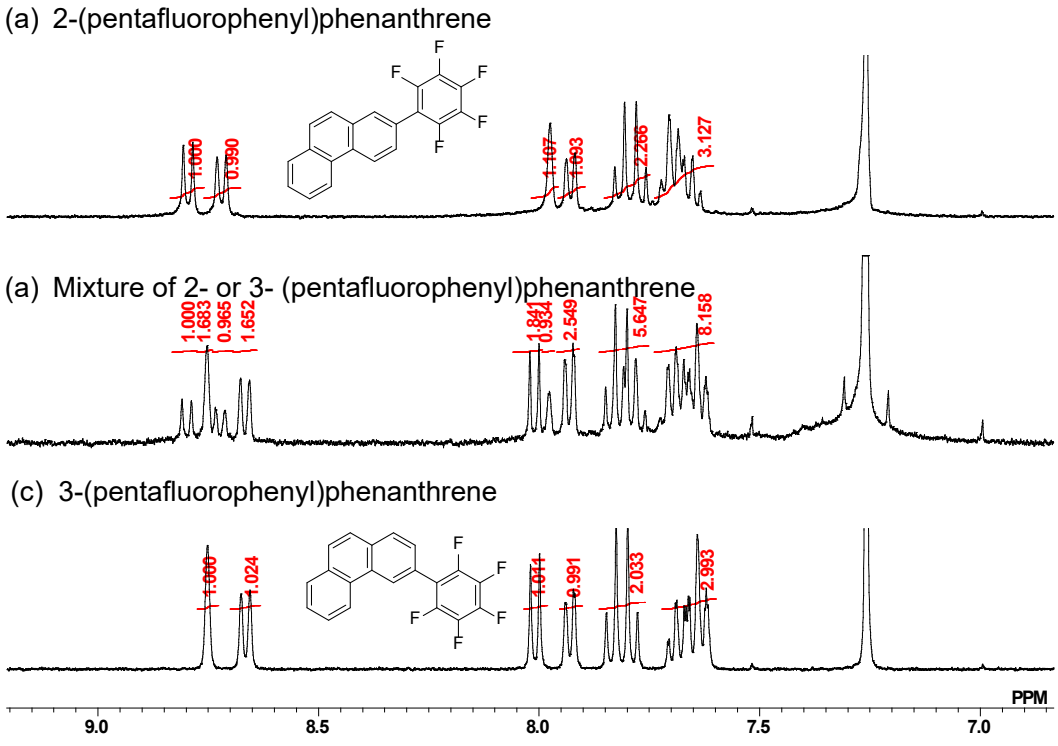


Figure S23. ^{1}H NMR spectra of (pentafluorophenyl)phenanthrenes (a) 2-(pentafluorophenyl)phenanthrene synthesised by direct arylation (b) the products synthesised by the CDC reaction (c) 3-(pentafluorophenyl)phenanthrene synthesised by direct arylation.

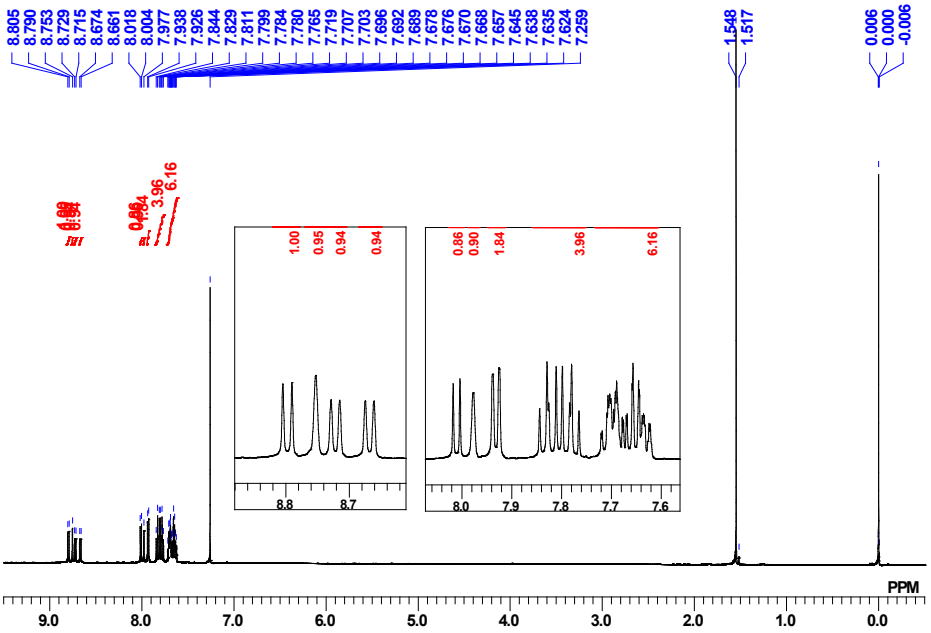


Figure S24. ^{1}H NMR spectrum of a mixture of 2-(pentafluorophenyl)phenanthrene and 3-(pentafluorophenyl)phenanthrene synthesised by the CDC reaction (600 MHz, $CDCl_3$, r.t.).

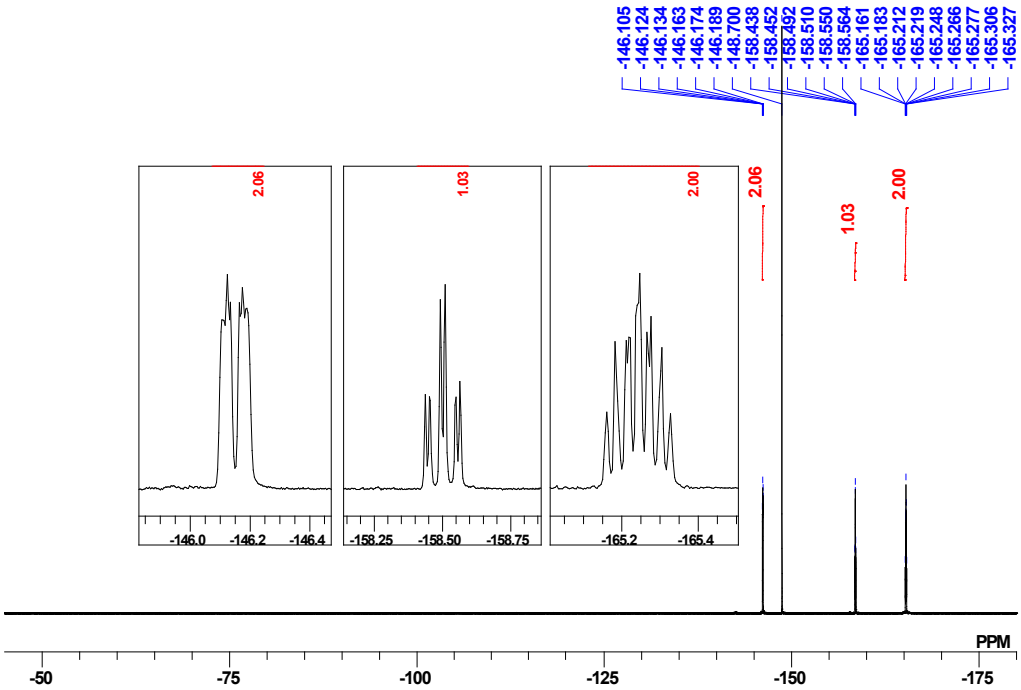


Figure S25. ^{19}F NMR spectra of a mixture of 2-(pentafluorophenyl)phenanthrene and 3-(pentafluorophenyl)phenanthrene synthesised by the CDC reaction (376 MHz, $CDCl_3$, r.t.).

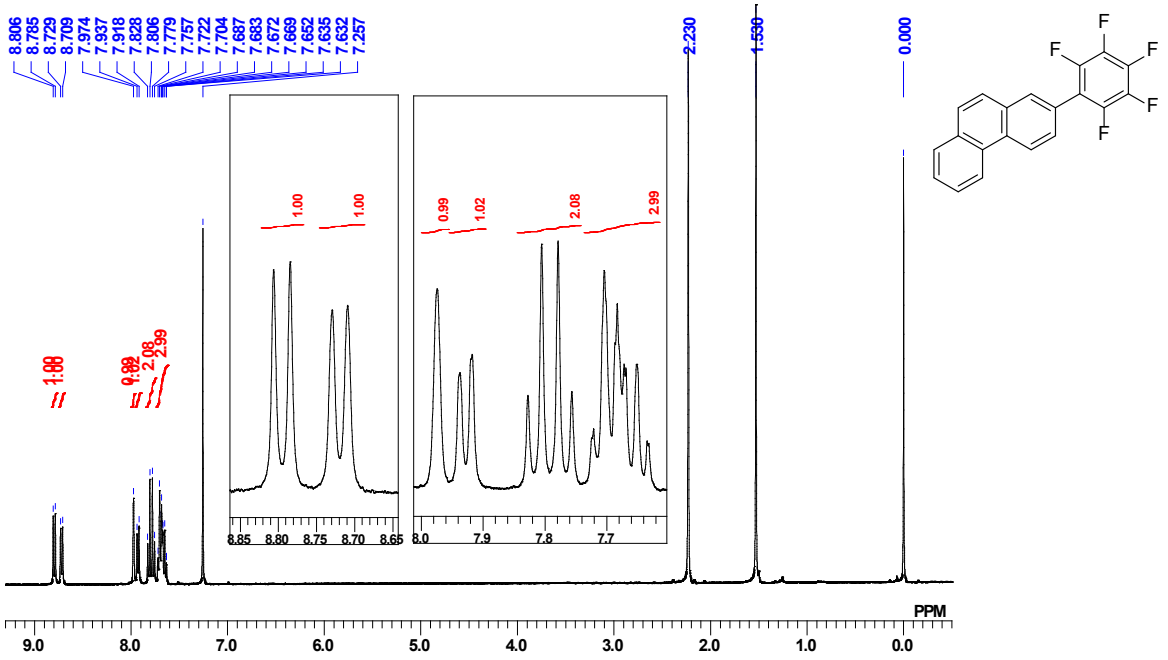


Figure S26. ^{1}H NMR spectrum of 2-(pentafluorophenyl)phenanthrene synthesised by direct arylation (400 MHz, $CDCl_3$, r.t.).

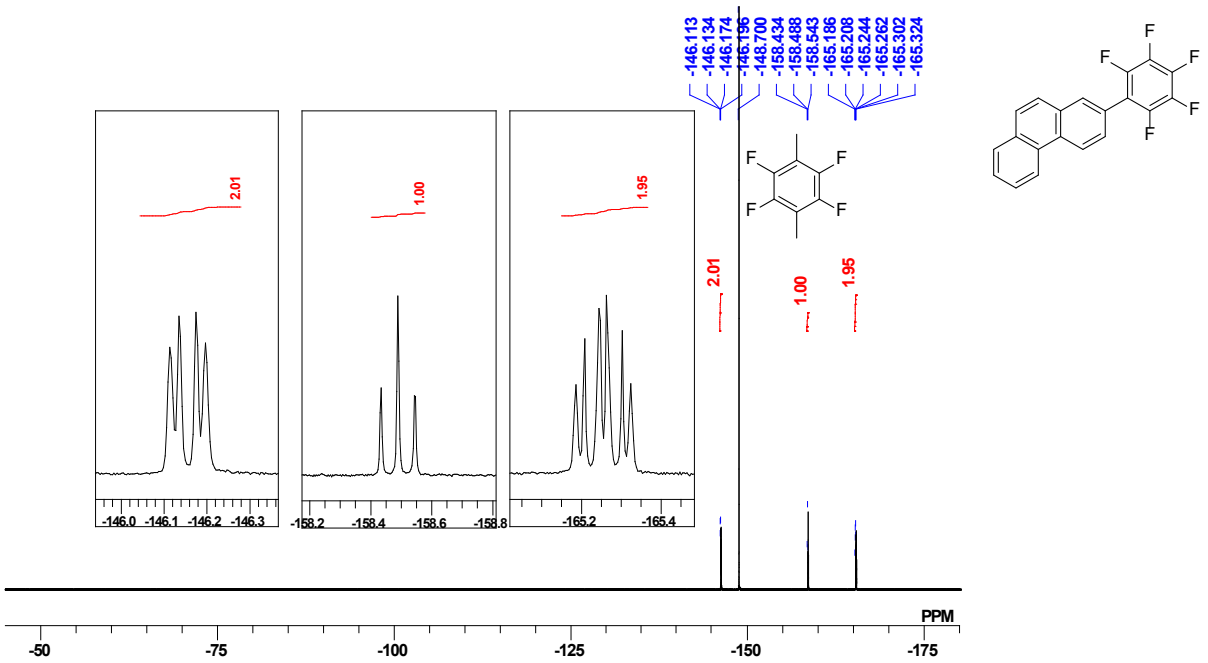


Figure S27. ^{19}F NMR spectrum of 2-(pentafluorophenyl)phenanthrene synthesised by direct arylation (376 MHz, $CDCl_3$, r.t.).

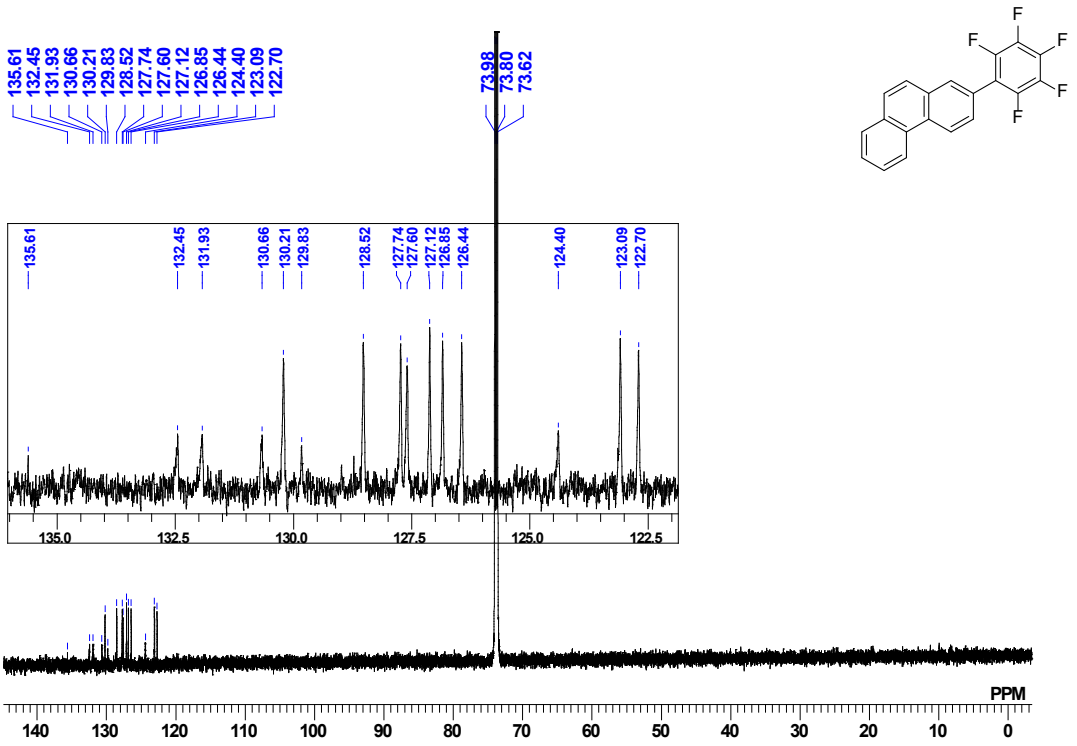


Figure S28. $^{13}C\{^{1}H\}$ NMR spectrum of 2-(pentafluorophenyl)phenanthrene synthesised by direct arylation (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 393 K)

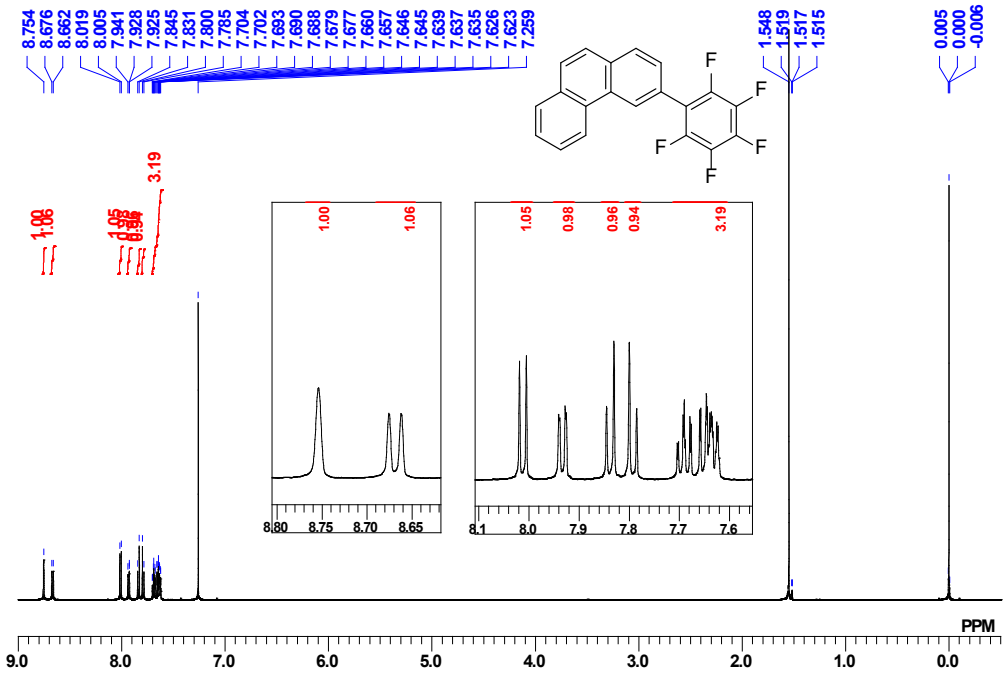


Figure S29. ^{1}H NMR spectrum of 3-(pentafluorophenyl)phenanthrene synthesised by direct arylation (600 MHz, $CDCl_3$, r.t.).

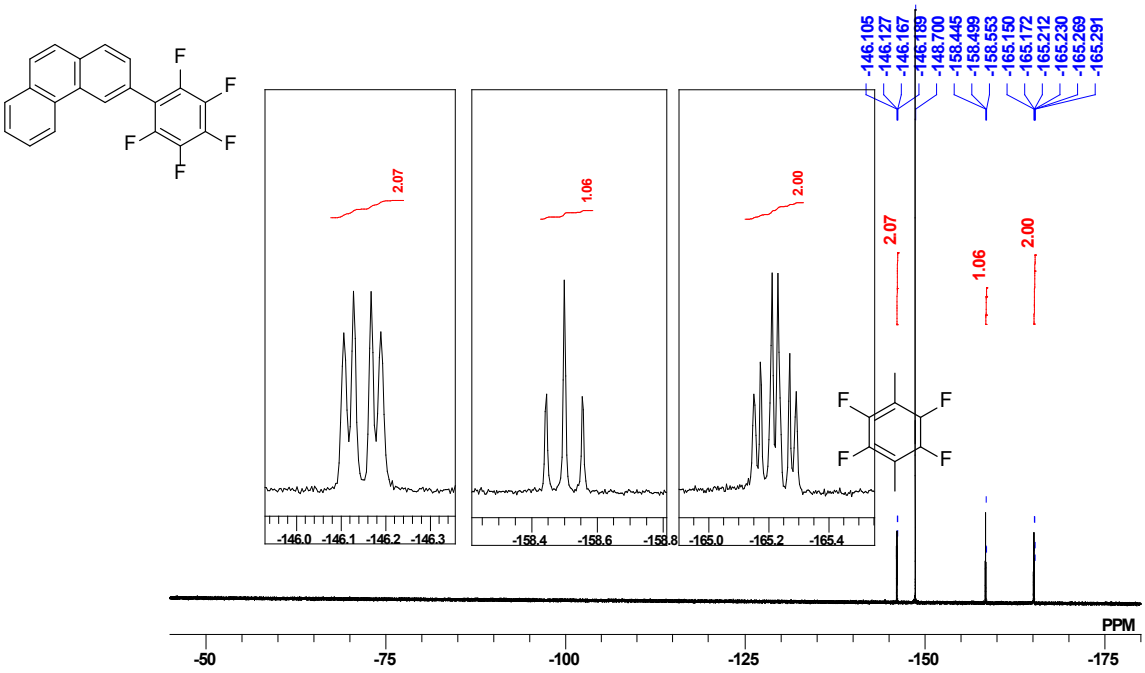


Figure S30. ^{19}F NMR spectrum of 3-(pentafluorophenyl)phenanthrene synthesised by direct arylation (376 MHz, $CDCl_3$, r.t.).

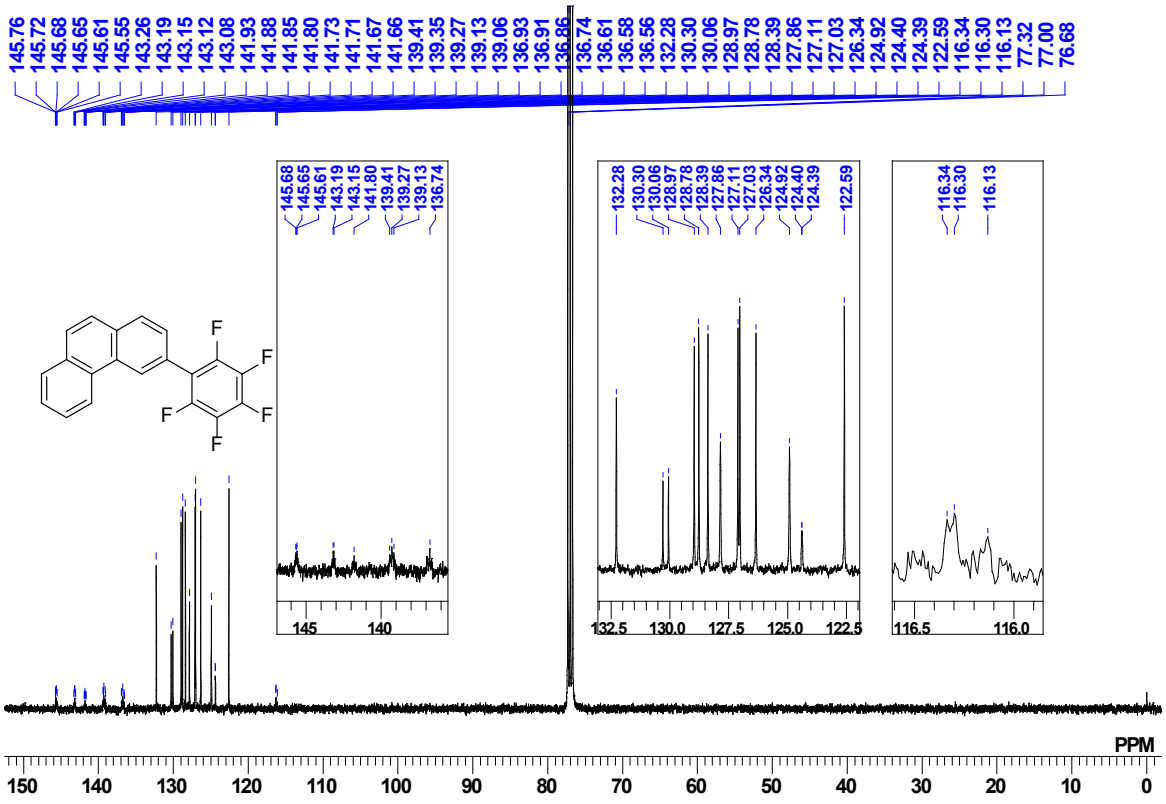


Figure S31. $^{13}C\{^1H\}$ NMR spectrum of 3-(pentafluorophenyl)phenanthrene synthesised by direct arylation (100 MHz, $CDCl_3$, r.t.).

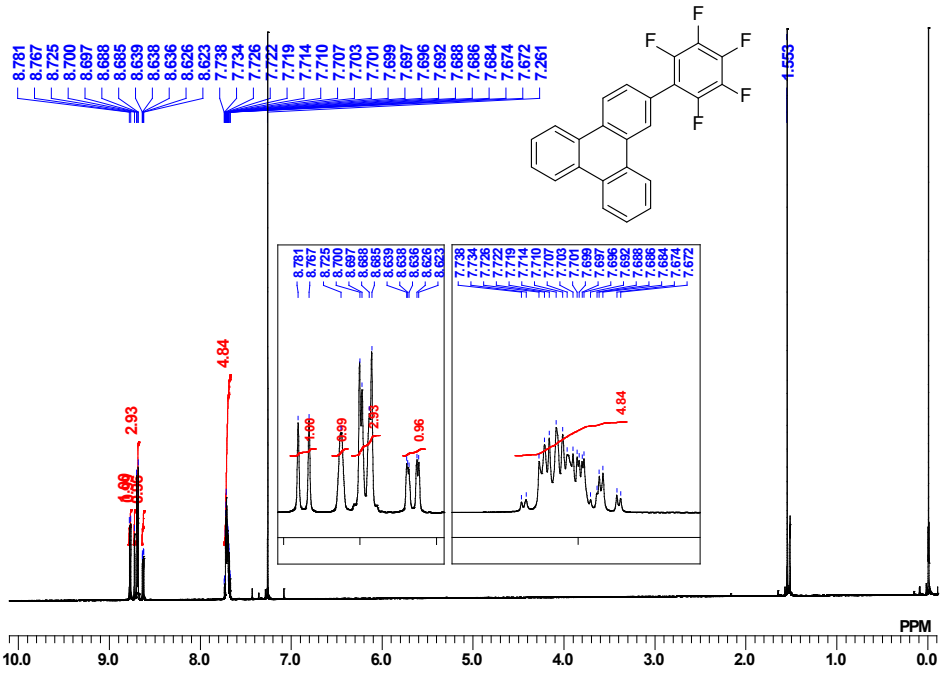


Figure S32. ^{1}H NMR spectrum of 2-(pentafluorophenyl)triphenylene synthesised by the CDC reaction (600 MHz, $CDCl_3$, r.t.).

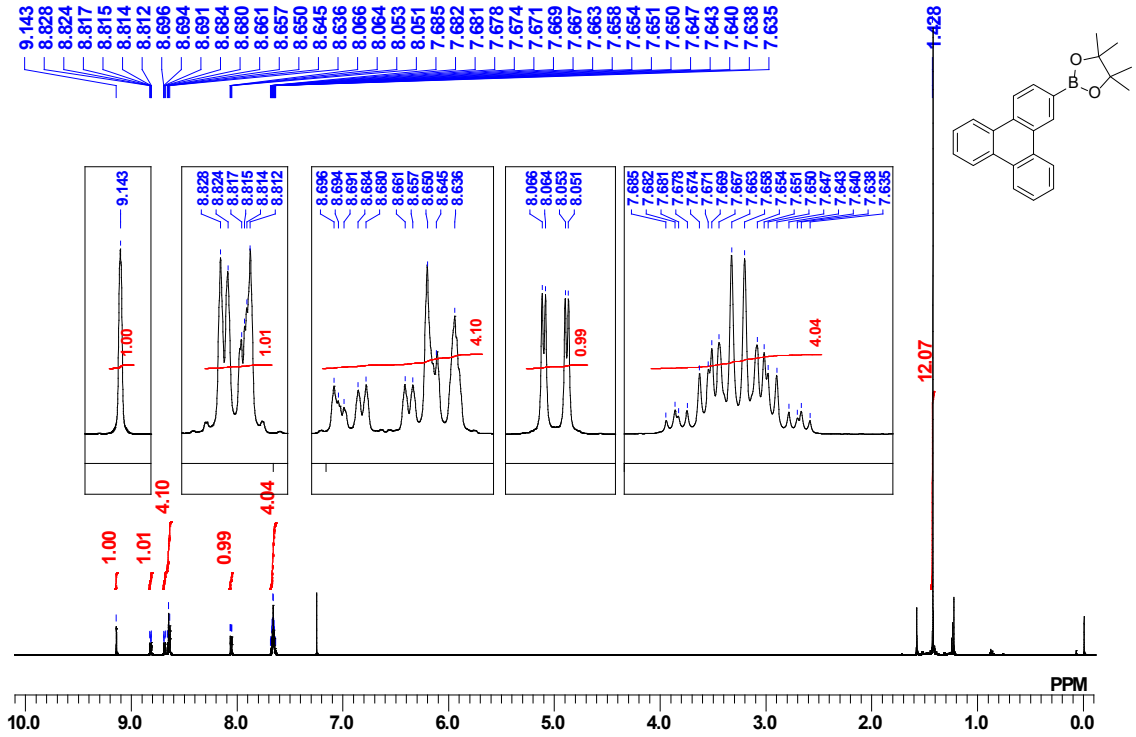


Figure S33. ^{1}H NMR spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylene (600 MHz, $CDCl_3$, r.t.).

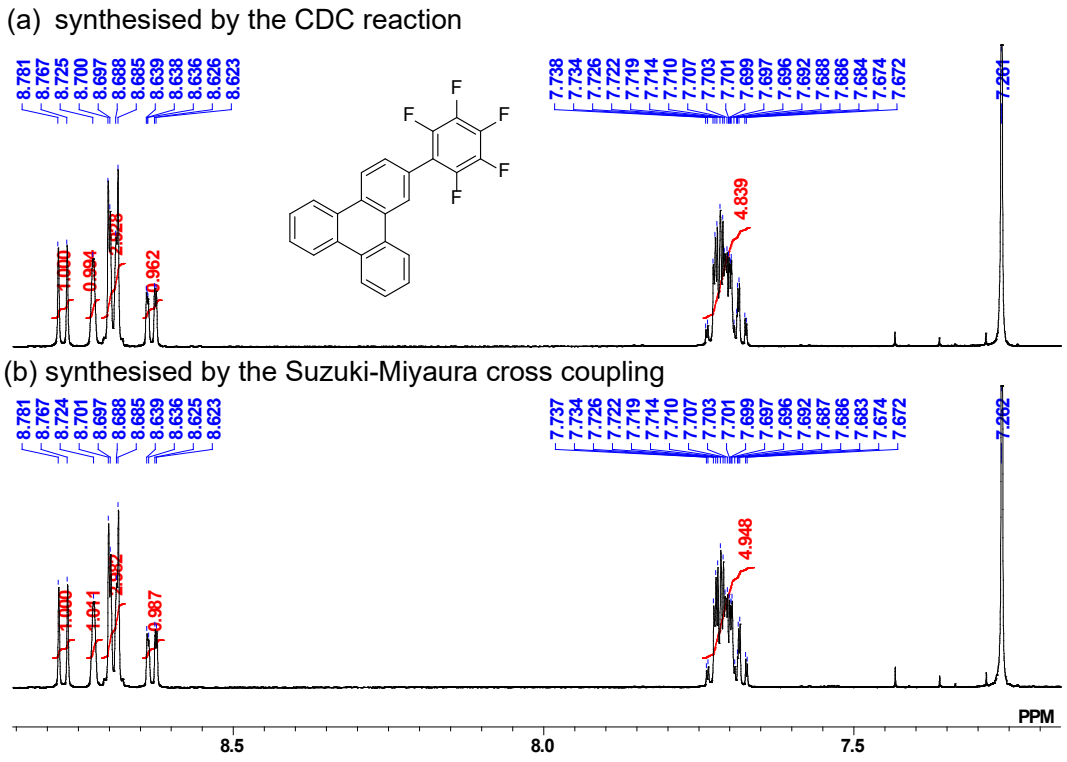


Figure S34. ^{1}H NMR spectra of 2-(pentafluorophenyl)triphenylene (a) synthesised by the CDC reaction (b) synthesised by the Suzuki-Miyaura cross coupling reaction (600 MHz, $CDCl_3$, r.t.).

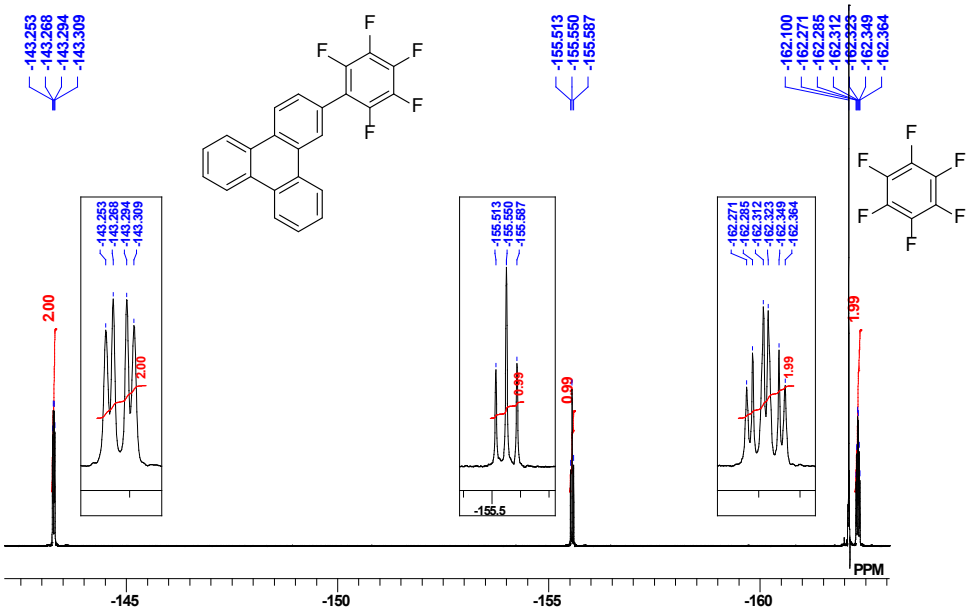


Figure S35. ^{19}F NMR spectrum of 2-(pentafluorophenyl)triphenylene synthesised by the CDC reaction (564 MHz, $CDCl_3$, r.t.).

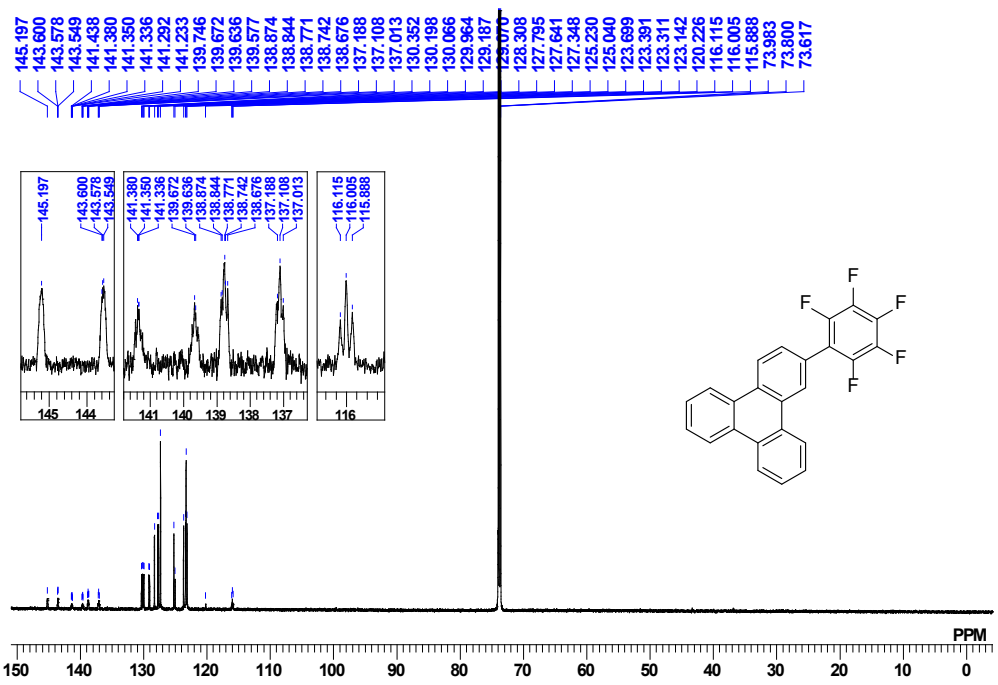


Figure S36. $^{13}C\{^{1}H\}$ NMR spectrum of 2-(pentafluorophenyl)triphenylene synthesised by the CDC reaction (151 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

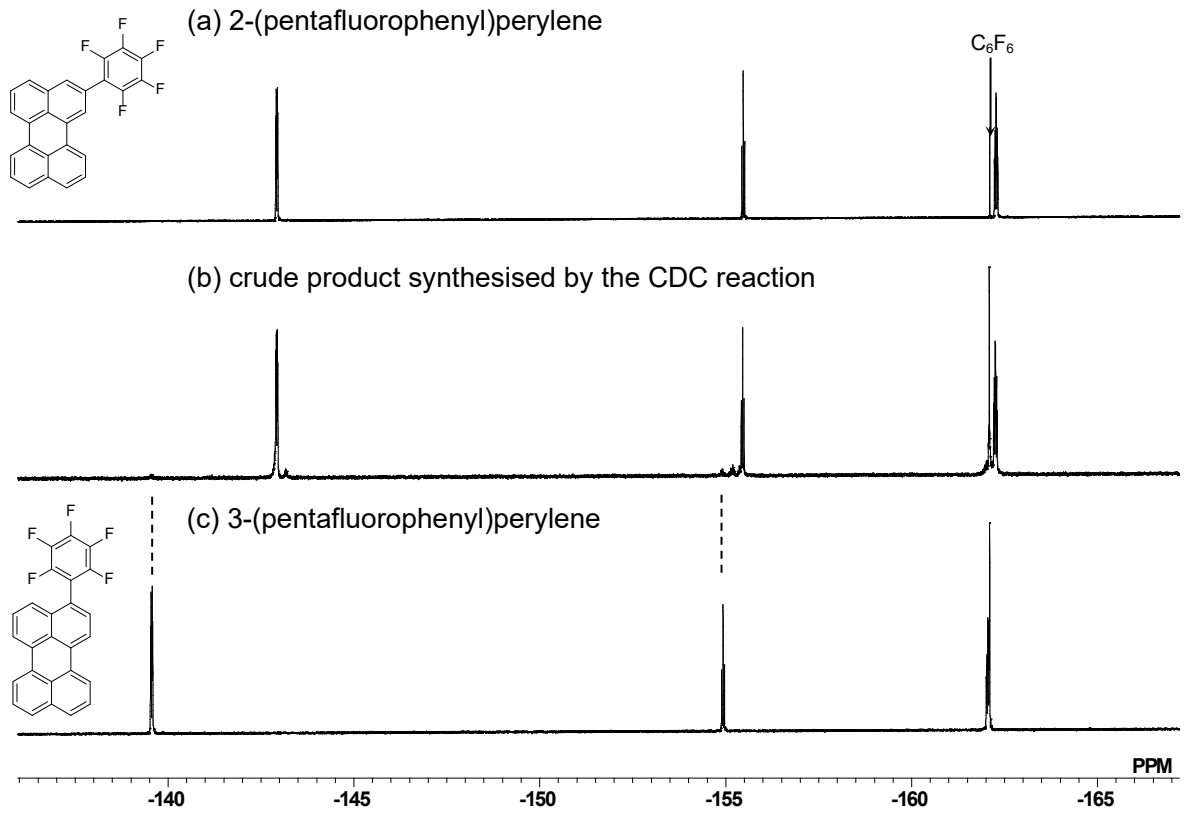


Figure S37. ^{19}F NMR spectra of (a) 2-(pentafluorophenyl)perylene synthesised by the Suzuki-Miyaura coupling reaction, (b) crude product synthesised by the CDC reaction, (c) 3-(pentafluorophenyl)perylene synthesised by direct arylation reaction (564 MHz, $CDCl_3$, r.t.).

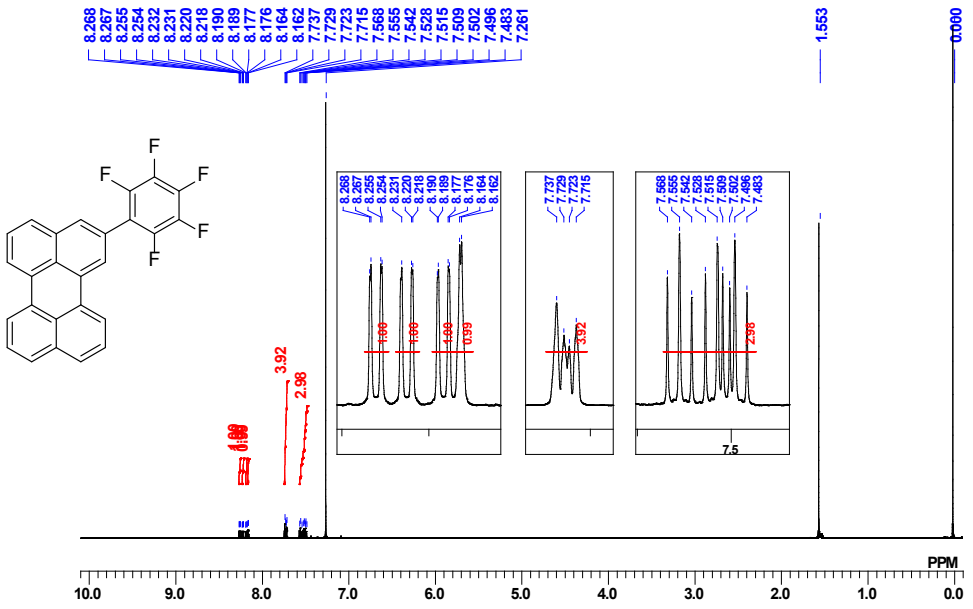


Figure S38. ^{1}H NMR spectrum of 2-(pentafluorophenyl)perylene synthesised by the Suzuki-Miyaura cross coupling (600 MHz, $CDCl_3$, r.t.).

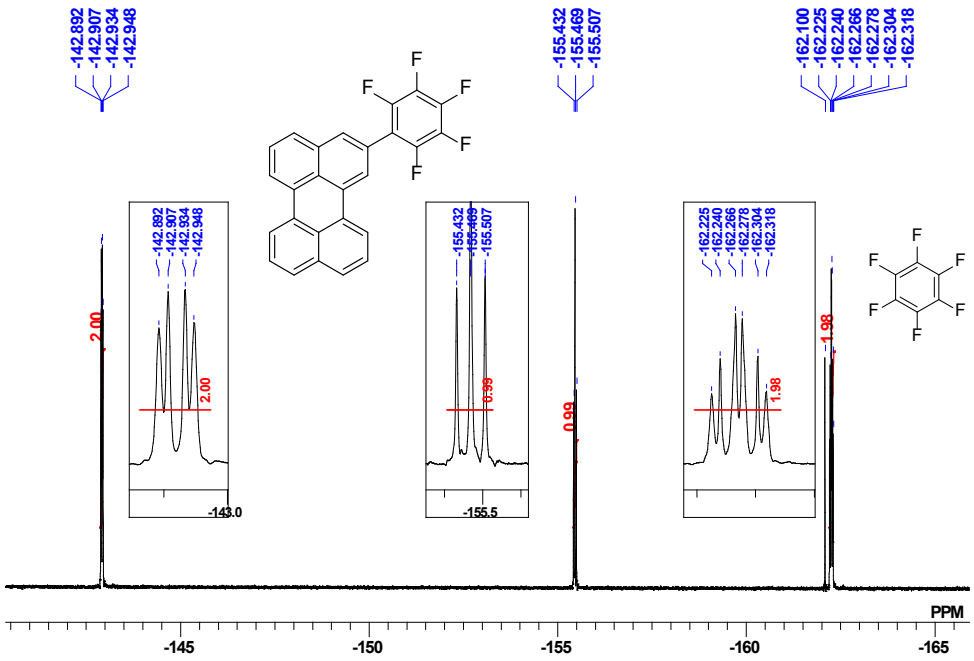


Figure S39. ^{19}F NMR spectrum of 2-(pentafluorophenyl)perylene synthesised by the Suzuki-Miyaura cross coupling (565 MHz, $CDCl_3$, r.t.).

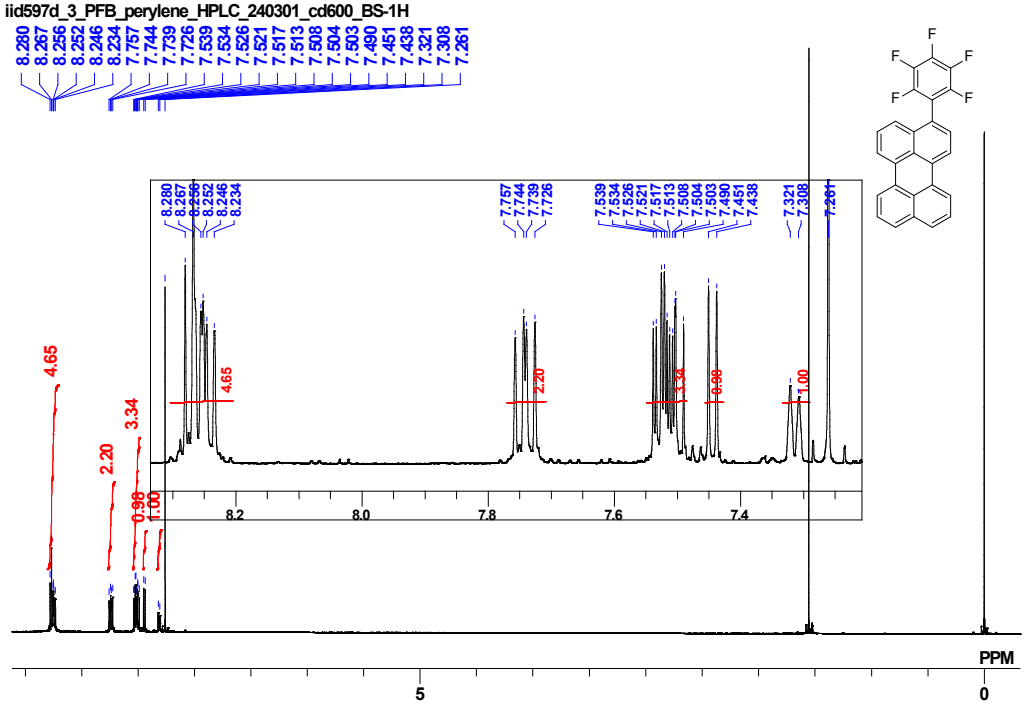


Figure S40. ^{1}H NMR spectrum of 3-(pentafluorophenyl)perylene synthesised by direct arylation (600 MHz, $CDCl_3$, r.t.).

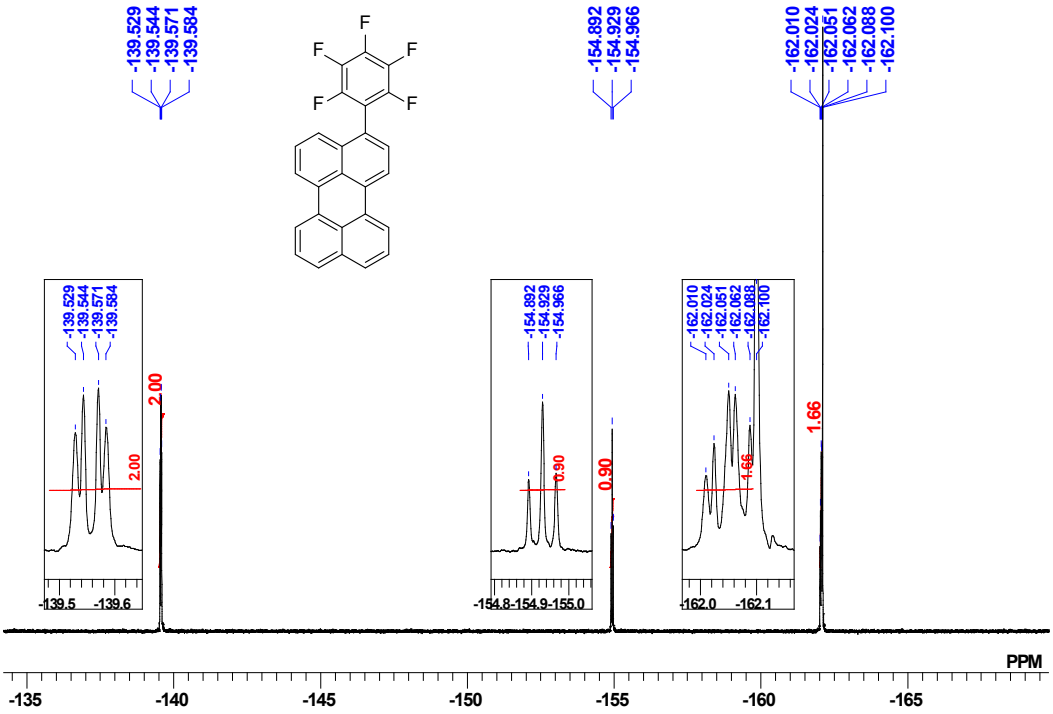


Figure S41. ^{19}F NMR spectrum of 3-(pentafluorophenyl)perylene synthesised by direct arylation (565 MHz, $CDCl_3$, r.t.).

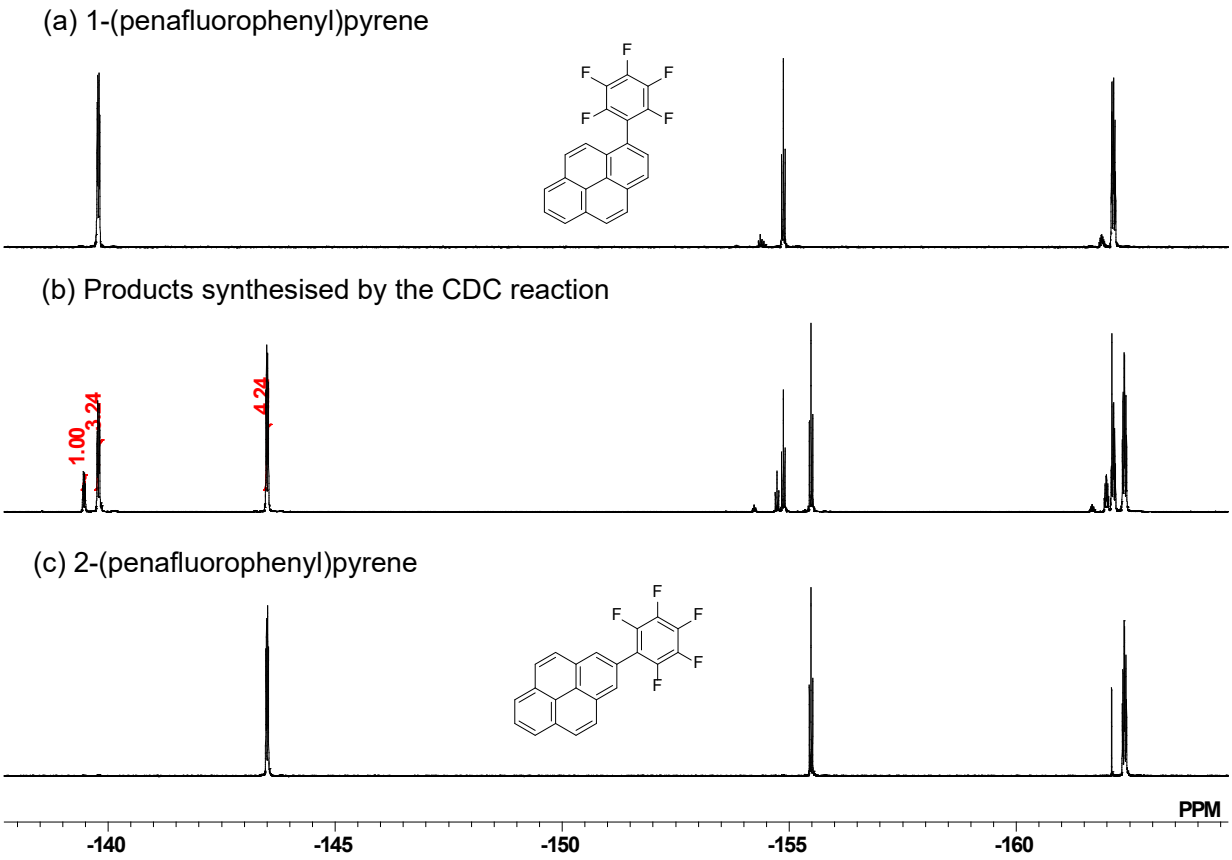


Figure S42. ^{19}F NMR spectra of (a) 1-(pentafluorophenyl)pyrene synthesised by direct arylation (b) products synthesised by the CDC reaction (c) 2-(pentafluorophenyl)pyrene synthesised by the Suzuki-Miyaura coupling reaction (565 MHz, $CDCl_3$, r.t.)

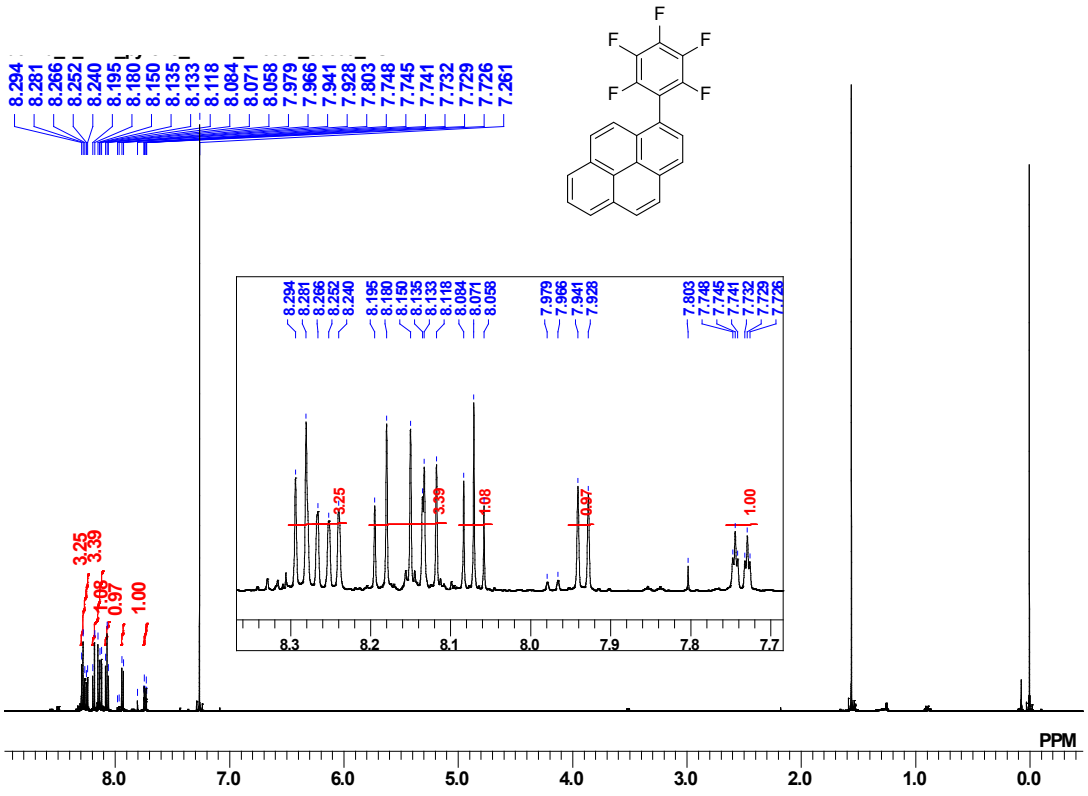


Figure S43. ^{1}H NMR spectrum of 1-(pentafluorophenyl)pyrene (600 MHz, $CDCl_3$, r.t.)

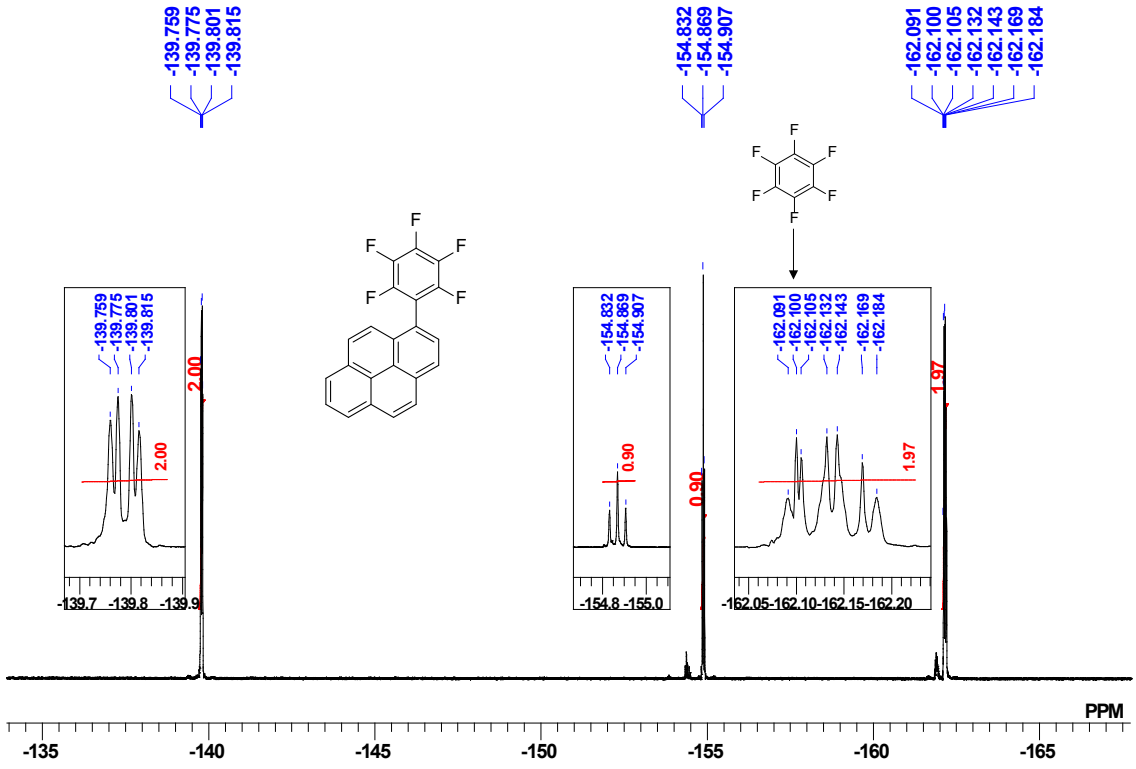


Figure S44. ^{19}F NMR spectrum of 1-(pentafluorophenyl)pyrene (564 MHz, $CDCl_3$, r.t.)

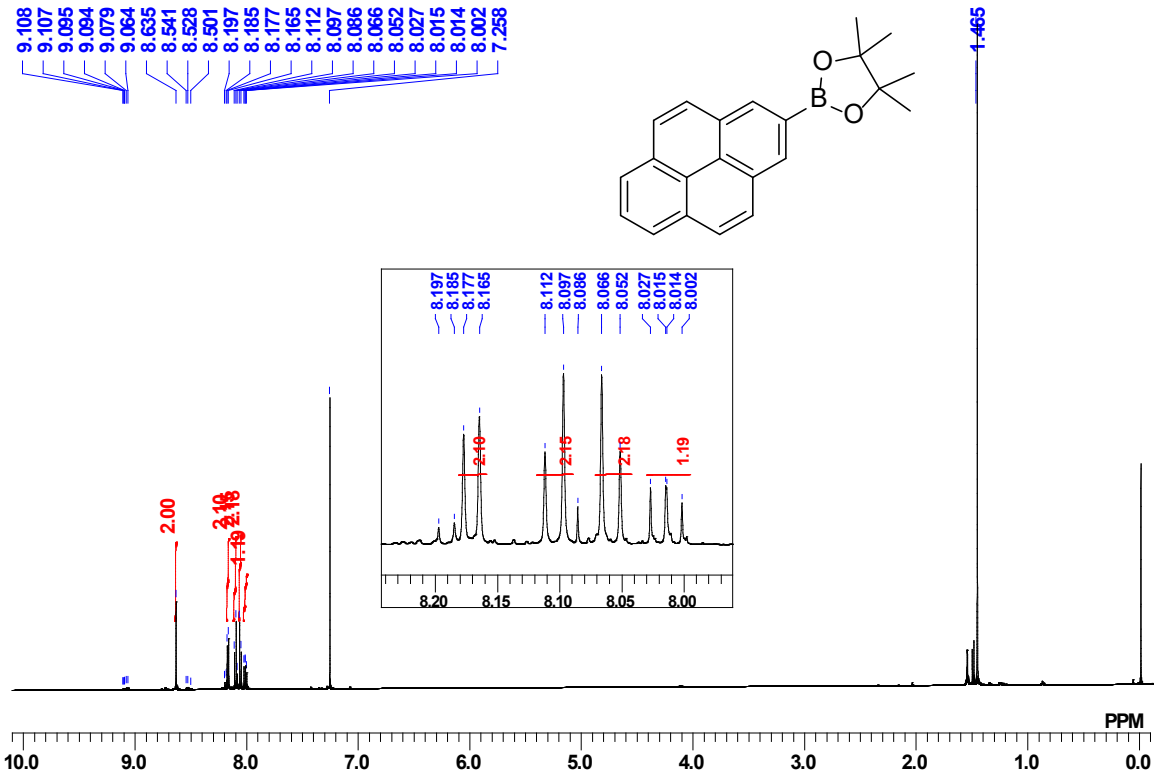


Figure S45. ^{1}H NMR spectrum of 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene (600 MHz, $CDCl_3$, r.t.)

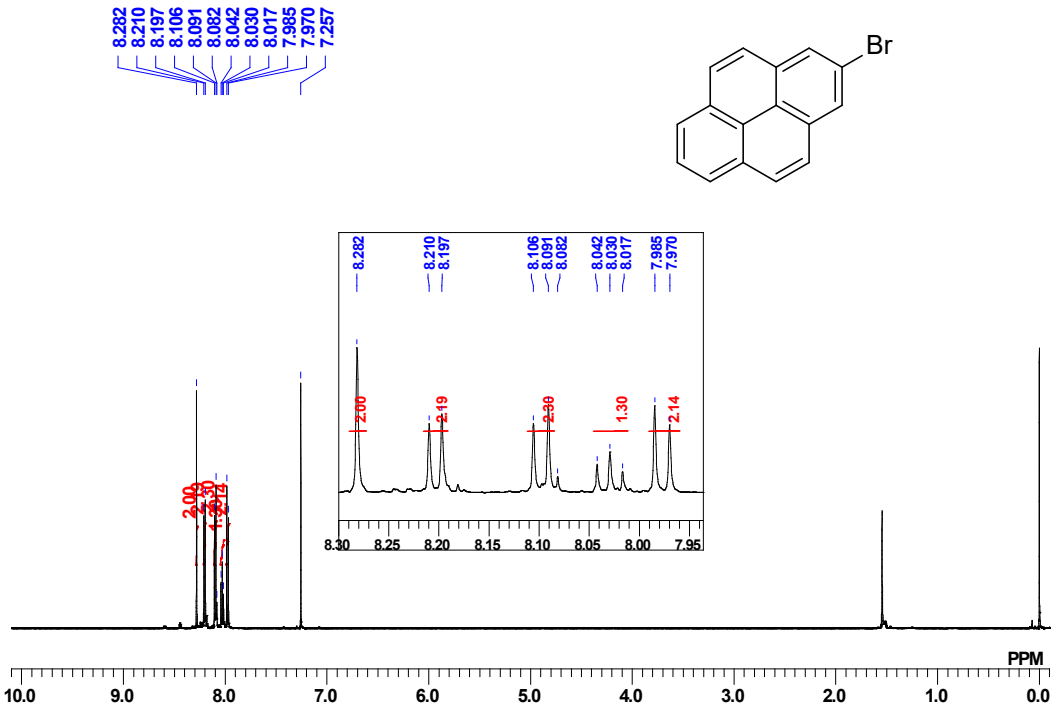


Figure S46. ^{1}H NMR spectrum of 2-bromopyrene (600 MHz, $CDCl_3$, r.t.)

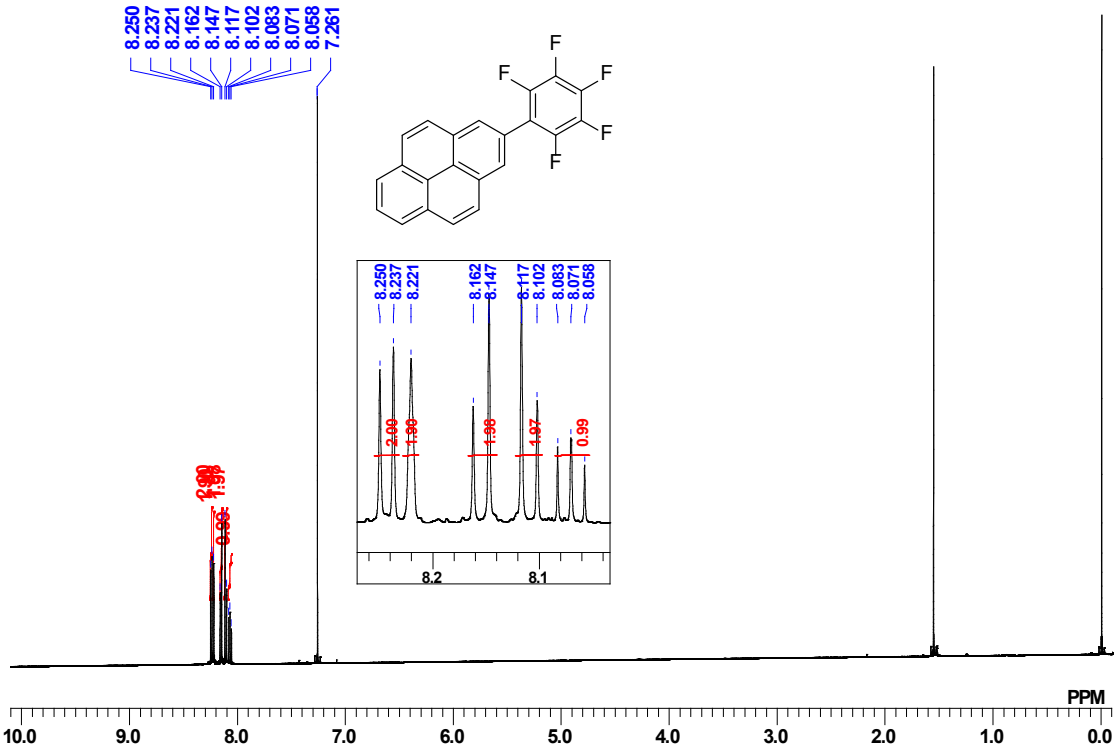


Figure S47. ^{1}H NMR spectrum of 2-(pentafluorophenyl)pyrene (600 MHz, $CDCl_3$, r.t.)

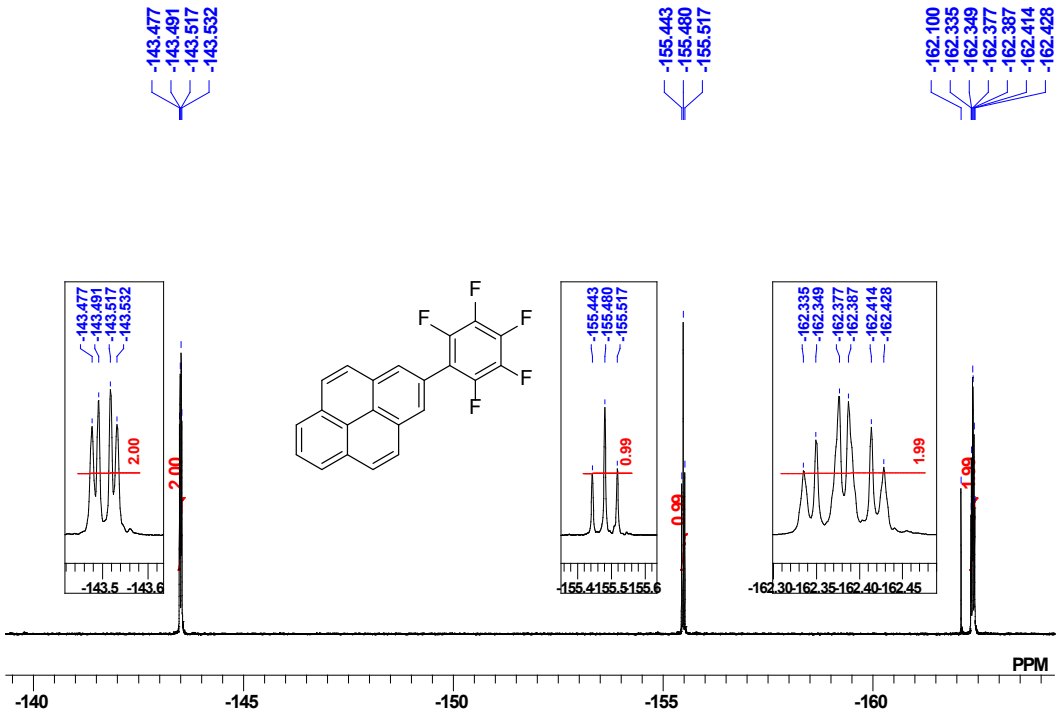


Figure S48. ^{19}F NMR spectrum of 2-(pentafluorophenyl)pyrene (564 MHz, $CDCl_3$, r.t.)

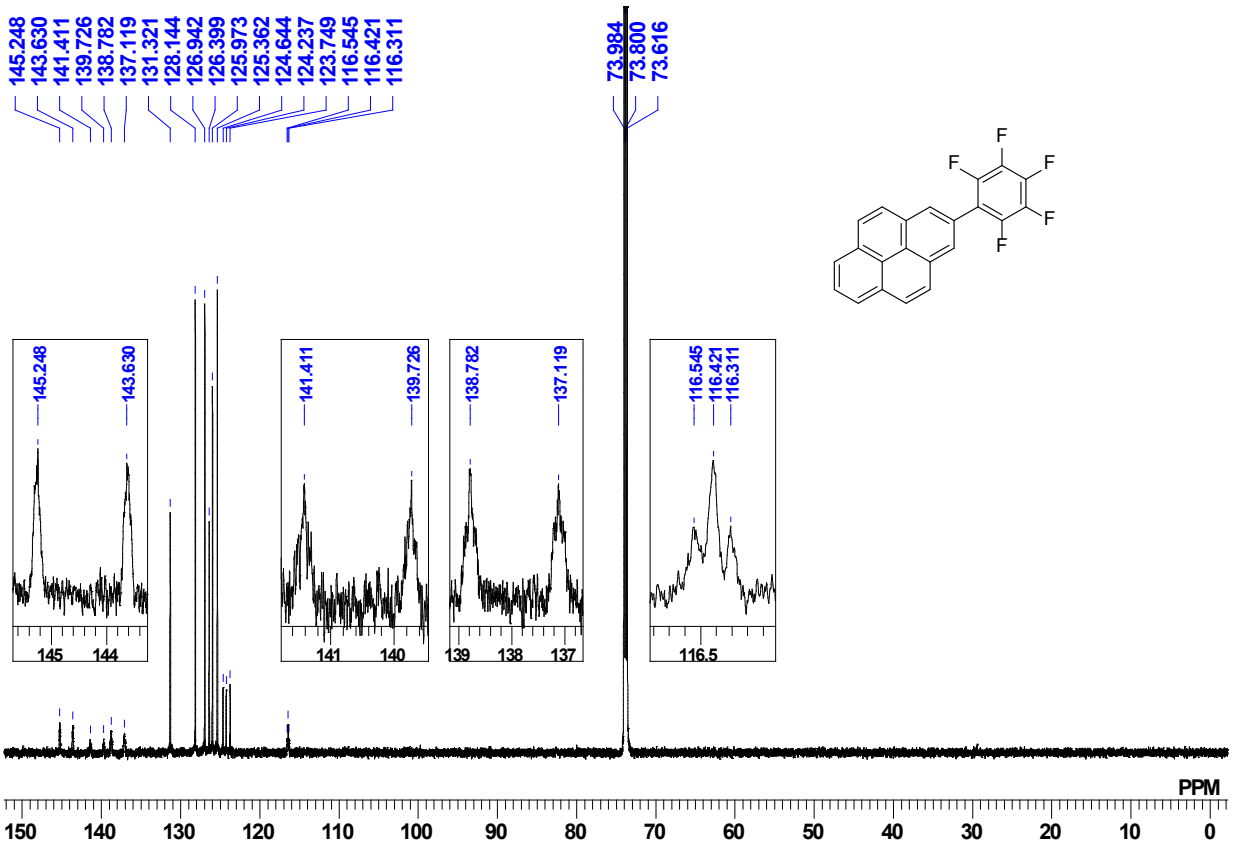


Figure S49. $^{13}C\{^{1}H\}$ NMR spectrum of 2-(pentafluorophenyl)pyrene (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 393K).

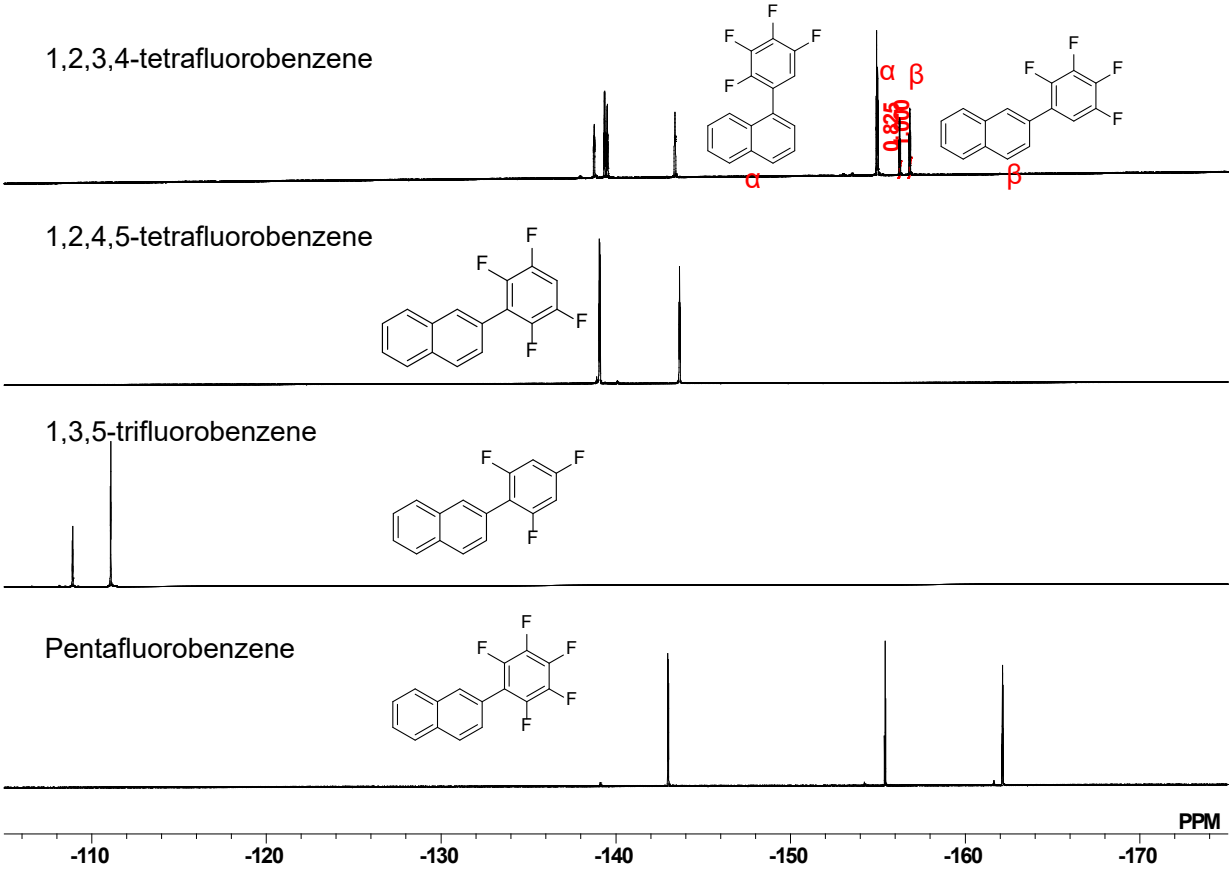


Figure S50. ^{19}F NMR spectra of the products of the CDC reaction with various fluorobenzenes (565 MHz, $CDCl_3$, r.t.). The products from the reaction with 1,2,3,4-tetrafluorobenzene contains the α-substituted compound and β-substituted compound.

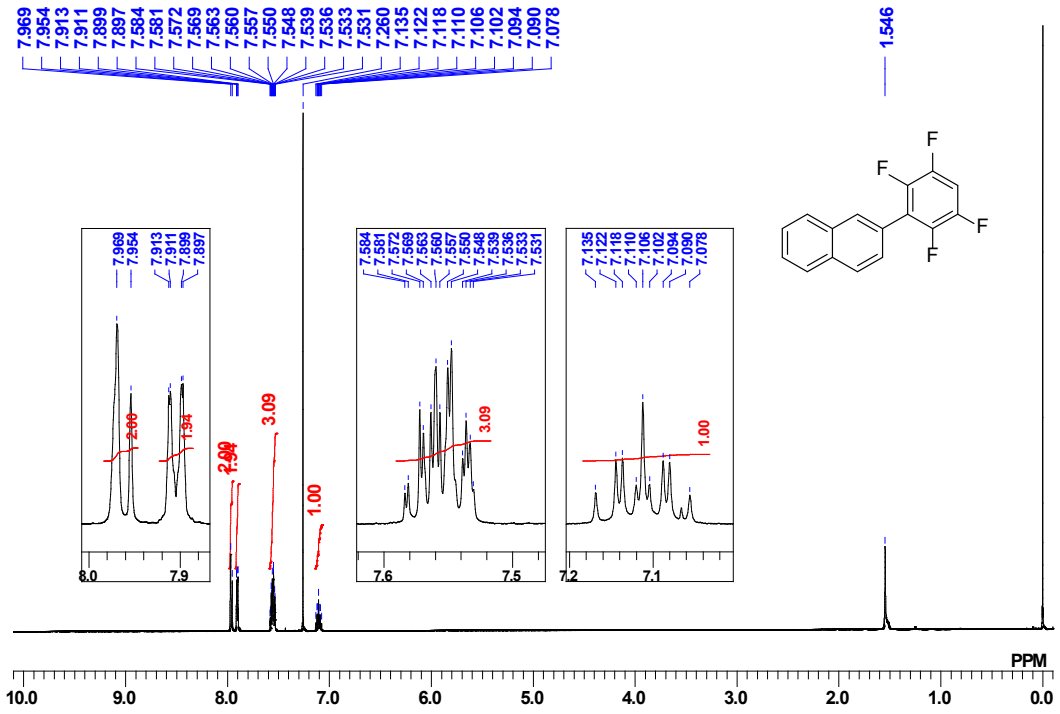


Figure S51. ^{1}H NMR spectrum of 2-(2,3,5,6-tetrafluorophenyl)naphthalene (600 MHz, $CDCl_3$, r.t.).

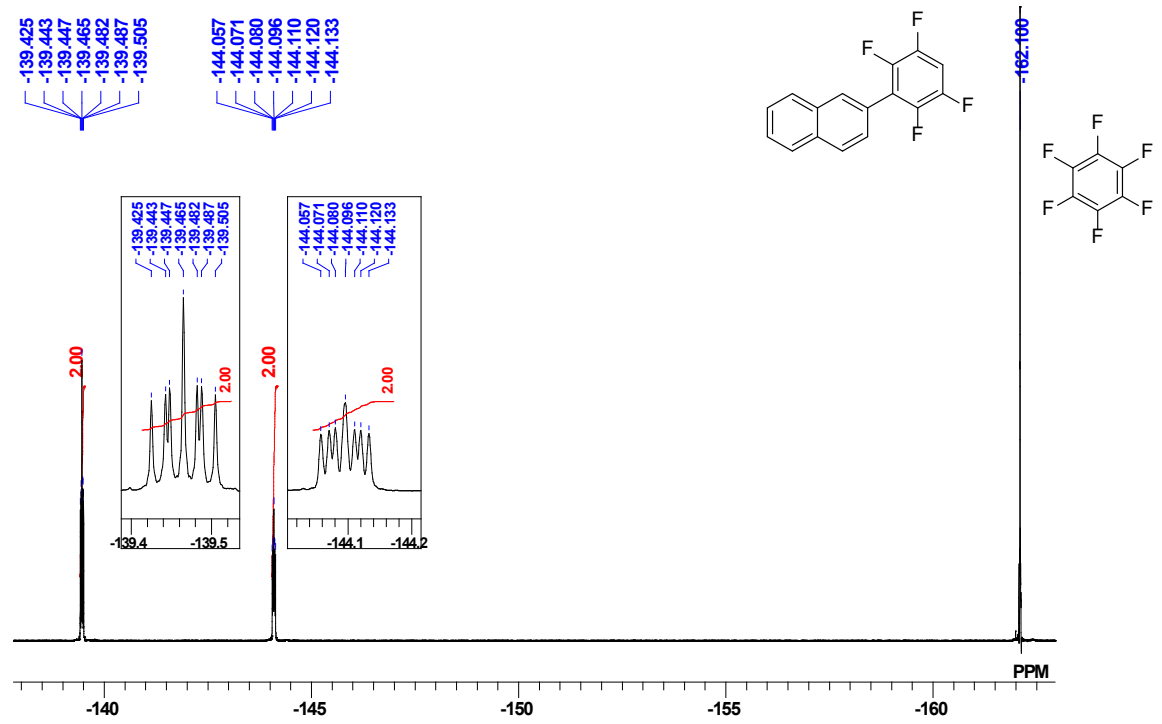


Figure S52. ^{19}F NMR spectrum of 2-(2,3,5,6-tetrafluorophenyl)naphthalene (565 MHz, $CDCl_3$, r.t.).

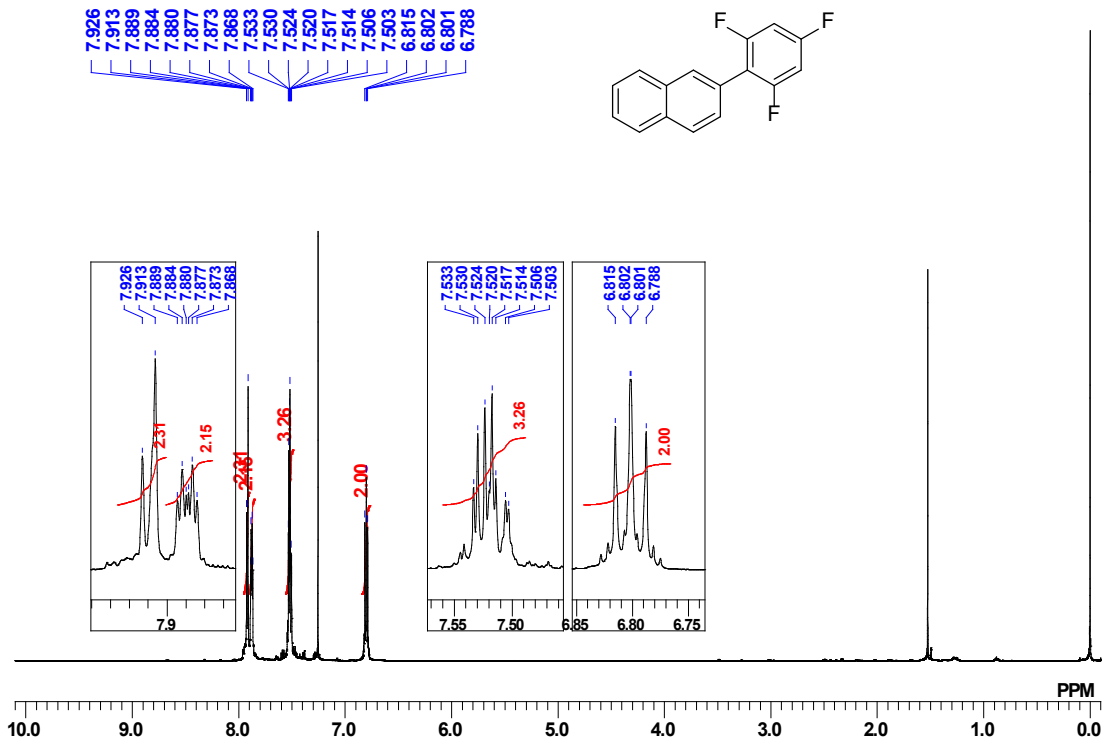


Figure S53. ^{1}H NMR spectrum of 2-(2,4,6-trifluorophenyl)naphthalene (600 MHz, $CDCl_3$, r.t.).

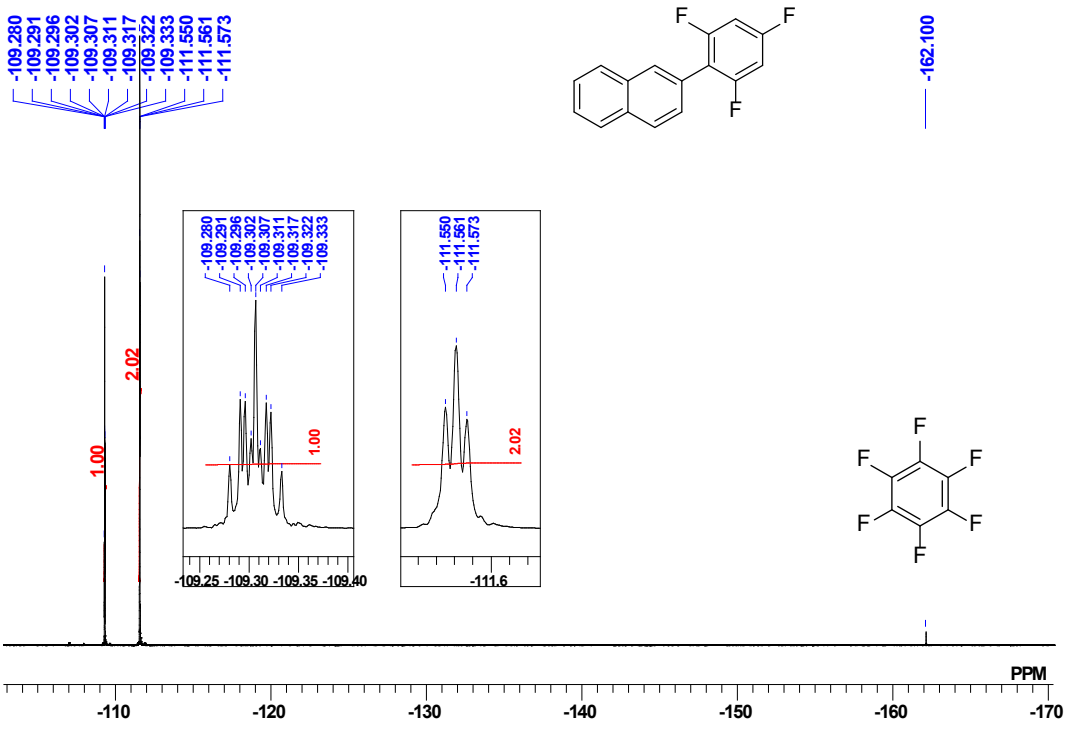


Figure S54. ^{19}F NMR spectrum of 2-(2,4,6-trifluorophenyl)naphthalene (565 MHz, $CDCl_3$, r.t.).

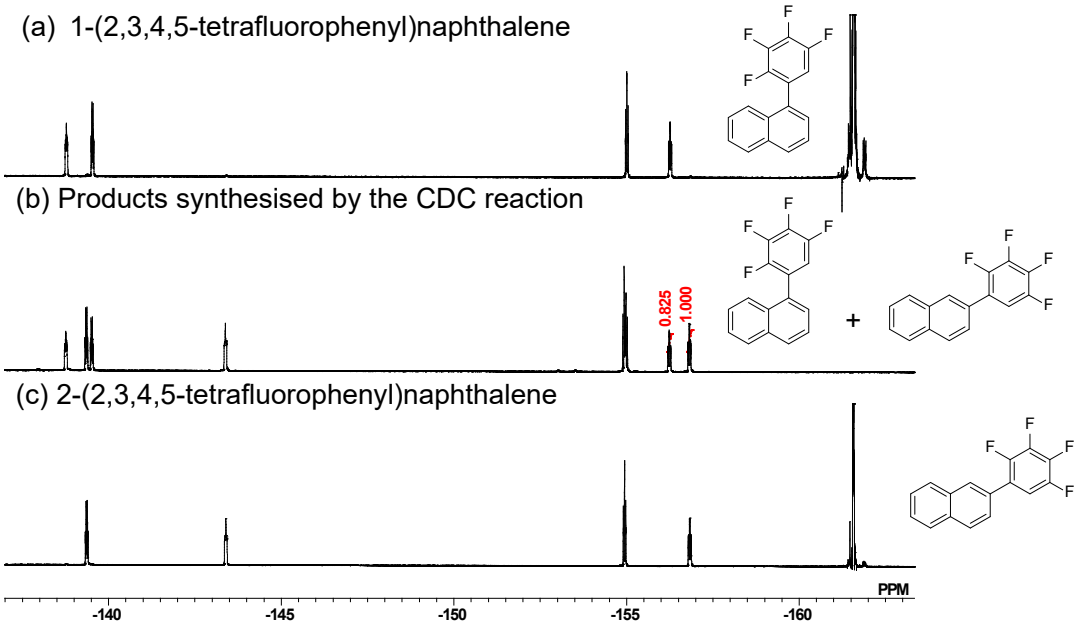


Figure S55. (a) ^{19}F NMR spectra of (a) 1-(2,3,4,5-tetrafluorophenyl)naphthalene (b) products synthesised by the CDC reaction (c) 2-(2,3,4,5-tetrafluorophenyl)naphthalene (565 MHz, $CDCl_3$, r.t.).

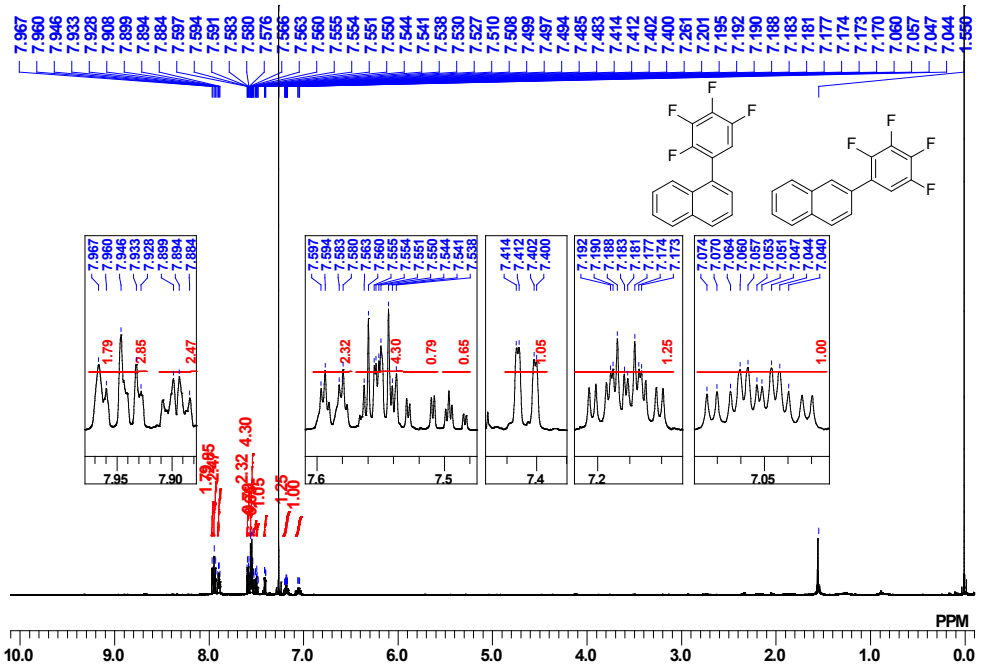


Figure S56. ^{1}H NMR spectrum of products synthesised by the CDC reaction (600 MHz, $CDCl_3$, r.t.).

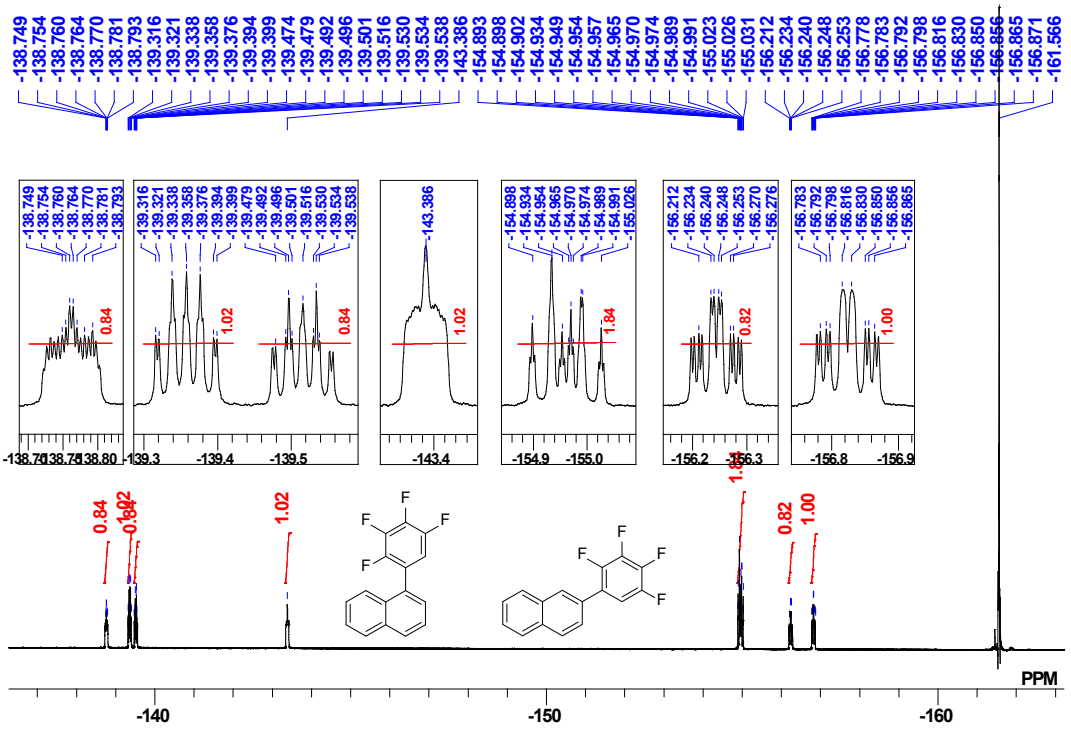


Figure S57. ^{19}F NMR spectrum of the products synthesised by the CDC reaction (565 MHz, $CDCl_3$, r.t.).

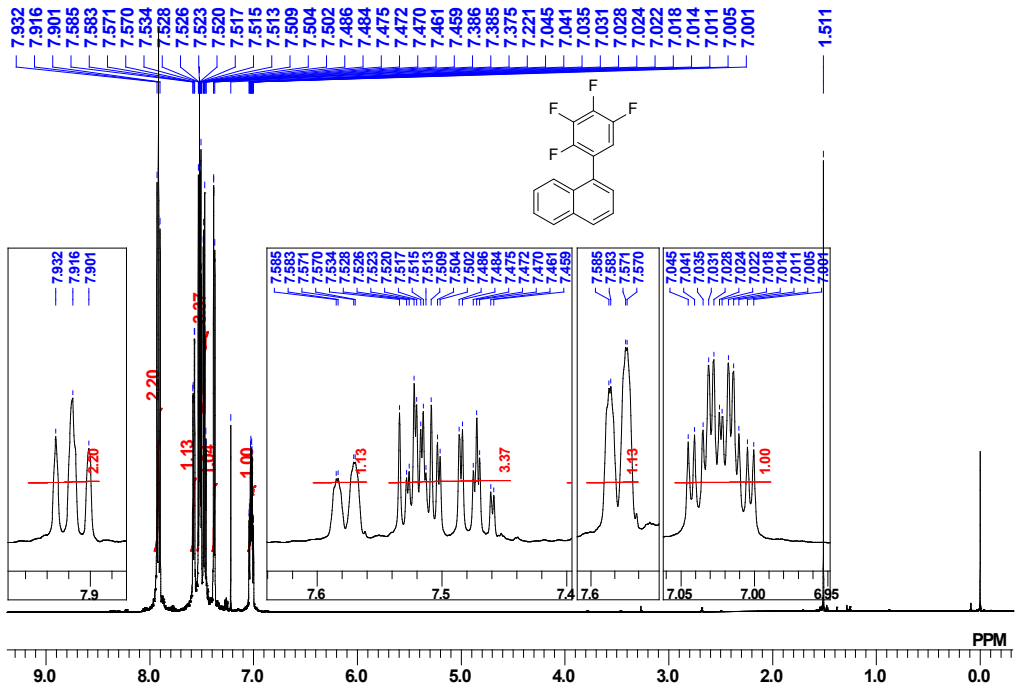


Figure S58. ^{1}H NMR spectrum of 1-(2,3,4,5-tetrafluorophenyl)naphthalene (600 MHz, $CDCl_3$, r.t.).
The compound was isolated from the products synthesised by direct arylation.

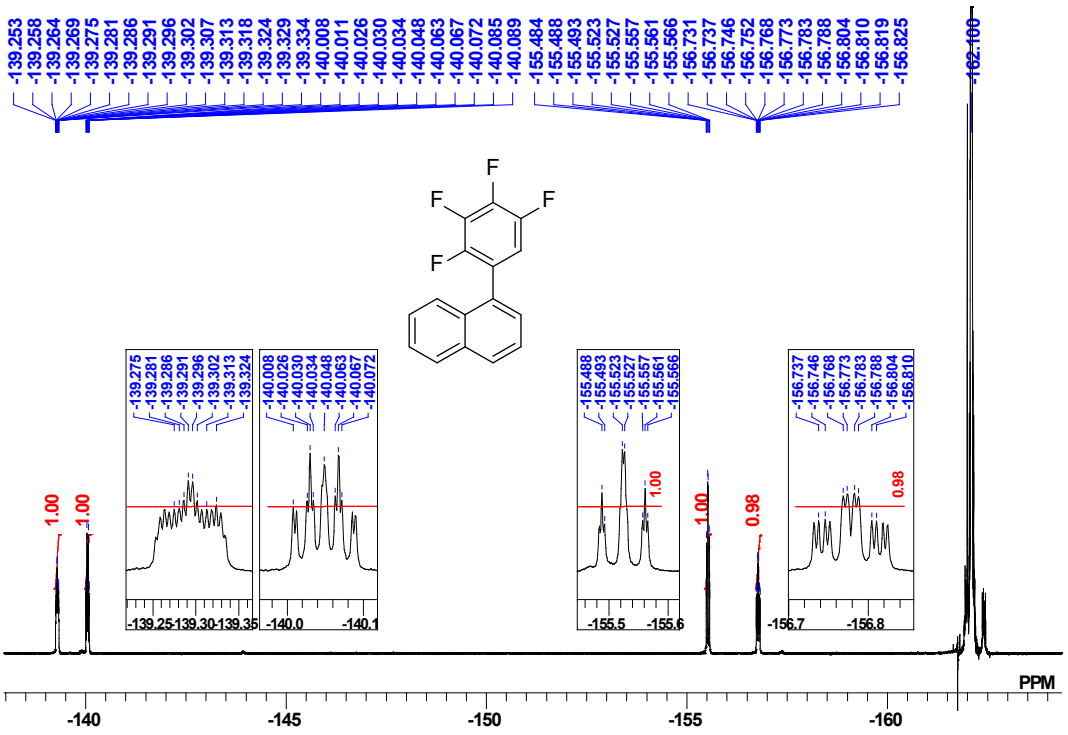


Figure S59. ^{19}F NMR spectrum of 1-(2,3,4,5-tetrafluorophenyl)naphthalene (565 MHz, $CDCl_3$, r.t.)
The compound was isolated from the products synthesised by direct arylation.

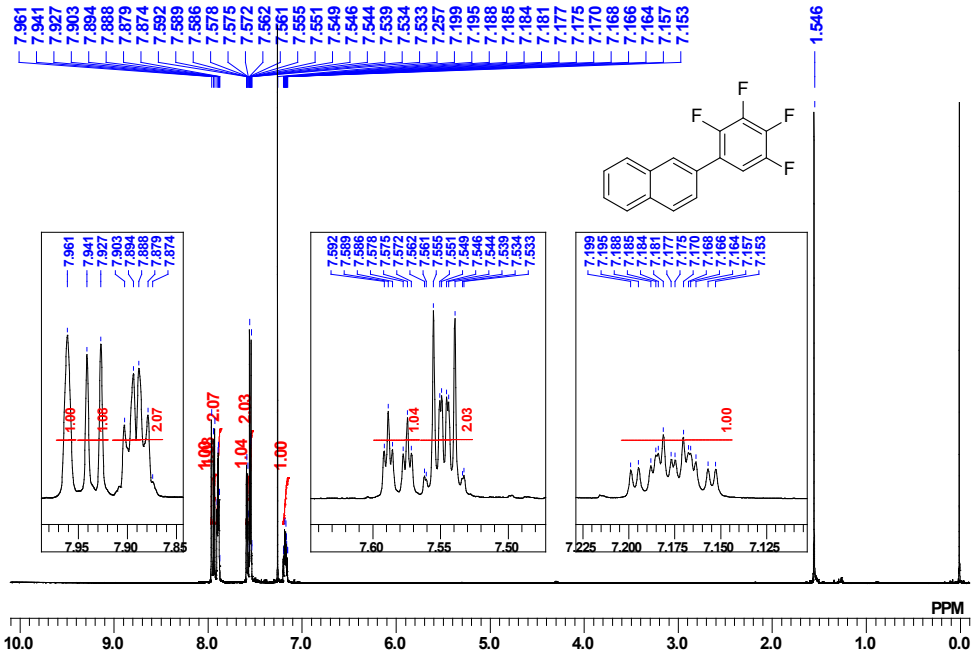


Figure S60. ^{1}H NMR spectrum of 2-(2,3,4,5-tetrafluorophenyl)naphthalene (600 MHz, $CDCl_3$, r.t.)
The compound was isolated from the products synthesised by the CDC reaction.

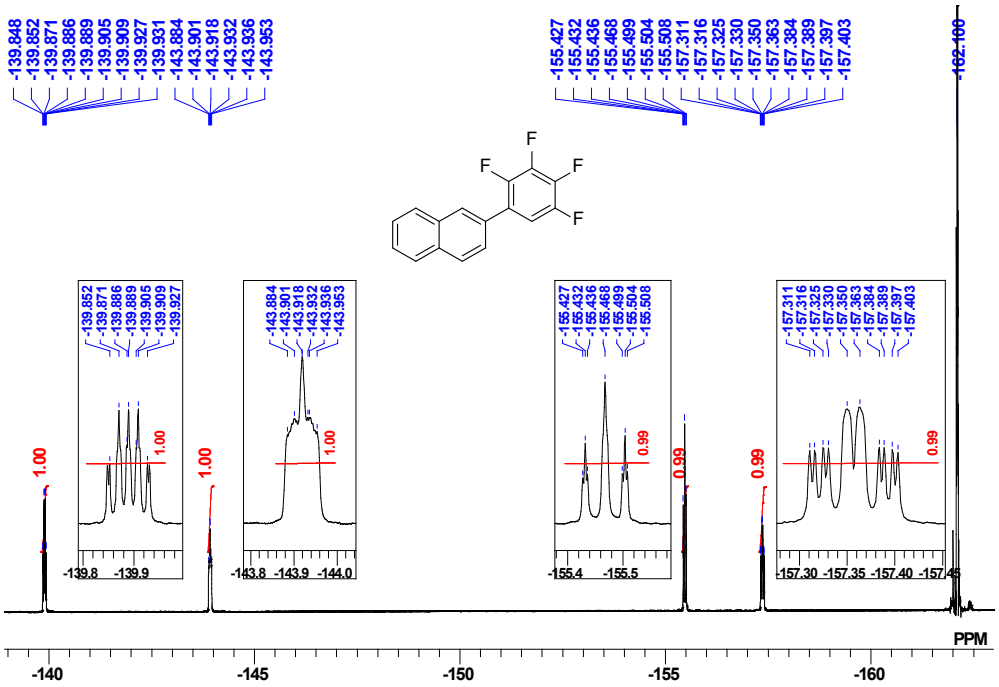


Figure S61. ^{19}F NMR spectra of 2-(2,3,4,5-tetrafluorophenyl)naphthalene (565 MHz, $CDCl_3$, r.t.)
The compound was isolated from the products synthesised by the CDC reaction.

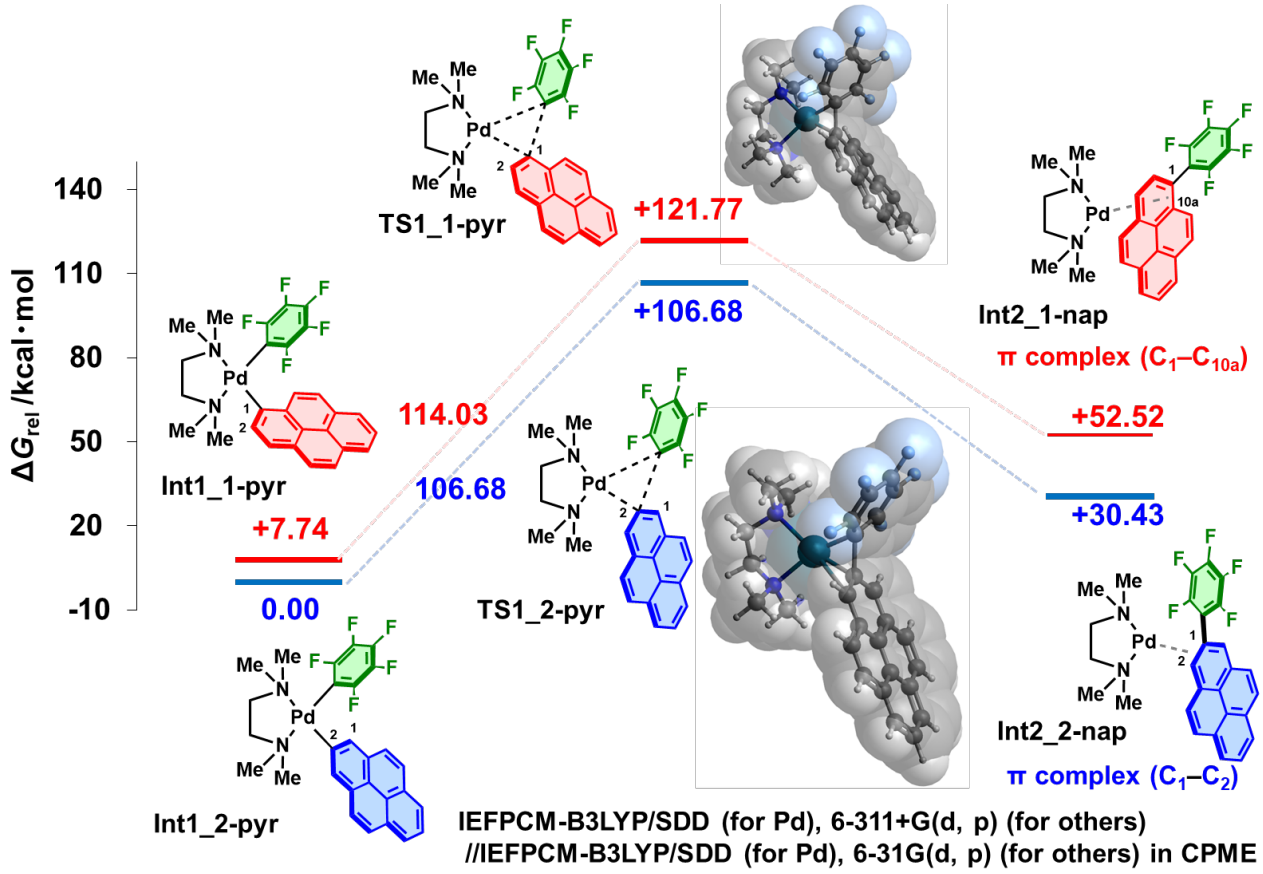


Figure S62. Free-energy profiles of the modeled reaction pathways for the reductive elimination of Pd(1-pyrenyl)C_6F_5(tmeda) and Pd(2-pyrenyl)C_6F_5(tmeda) complexes at the B3LYP/6-311+G(d,p) (with SDD for Pd) level in CPME (ε = 4.76) solution. All ΔG_{rel} values represent the relative Gibbs energy for the complex compared to the Gibbs energy for **Int1_2-pyr**. (ΔG_{rel} = (*G* of any complex) - (*G* of **Int1_2-pyr**). Transition energies, $\Delta G^{\ddagger} = \Delta G_{rel}$ (TS) − ΔG_{rel} (int1), were calculated to be 114 and 107 kJ·mol^{-1} for the Pd(1-pyrenyl)C_6F_5(tmeda) and Pd(2-pyrenyl)C_6F_5(tmeda), respectively.

Table S2. Crystallographic data

	α-biaryl model complex	β-biaryl model complex
CCDC Number	2338608	2338609
Empirical Formula	$C_{66}H_{69}F_{15}N_6Pd_3$	$C_{22}H_{23}F_5N_2Pd$
Formula Weight	1550.49	516.83
Crystal Color	colorless	colorless
Crystal Dimensions / mm	0.346 x 0.176 x 0.050	0.102 x 0.091 x 0.020
Crystal System	triclinic	monoclinic
a / Å	10.6657(12)	9.3955(19)
b / Å	15.3472(17)	14.564(3)
c / Å	20.4601(20)	16.547(4)
α / deg.	79.1470(10)	90.0000
β / deg.	88.9540(10)	106.037(3)
γ / deg.	76.4020(10)	90.0000
V / Å^3	3195.8(6)	2176.2(8)
Space Group	*P*-1	$P2_1/c$
Z	2	4
D / gcm^{-3}	1.611	1.577
*F*000	1560.00	1040.00
μ(MoKα) / cm^{-1}	9.25	9.06
Reflection/Parameter Ratio	17.71	15.49
*R*1 (*I* > 2.00σ(*I*))	0.0470	0.0408
R (All reflections)	0.0490	0.0550
*wR*2 (All reflections)	0.1030	0.1045
GOF	1.338	1.065

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