Supporting information of

Unique Regioselectivity of the Pd-Catalysed Cross-Dehydrogenative Coupling Reaction of Simple Polyaromatic Hydrocarbons with Polyfluoroarenes

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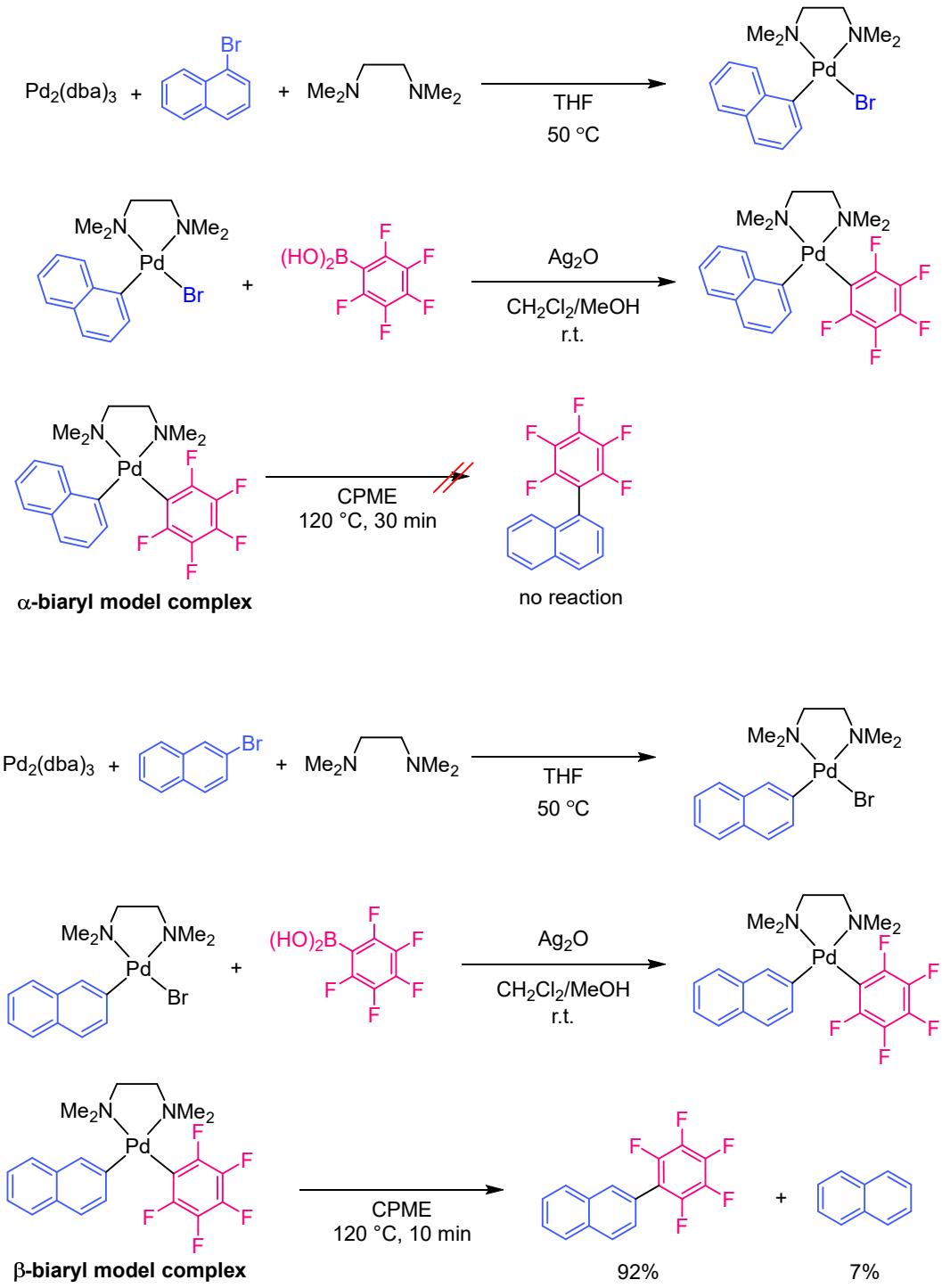


Scheme S1. Syntheses of the model complexes and comparison of reactivity in reductive elimination reactions.

Experimental details

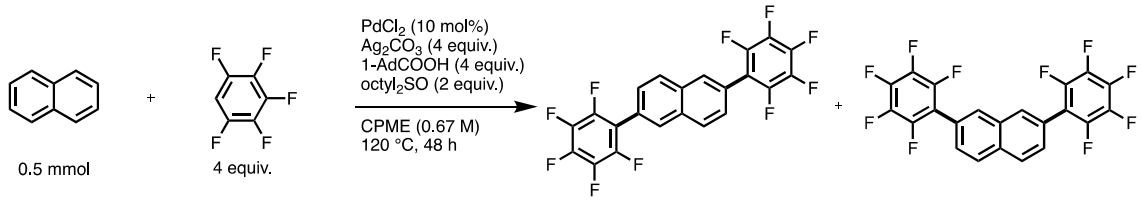
General, Measurement, and Materials.

^{1}H, ^{19}F, and $^{13}C\{^{1}H\}$ NMR spectra were recorded using Bruker AVANCE-400 NMR spectrometer and AVANCE-600 NMR spectrometer. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN elemental analyzer and Yanaco CHN coder MT-6 or MT-5. Anhydrous CPME (cyclopentylmethylether) was purchased from Kanto Chemical and used as dry solvents. Crystal Structure Determination Intensity data were collected on a Bruker SMART APEX II ULTRA with Mo Kα radiation. UV−vis absorption spectra were recorded on a Hitachi U-3900H spectrophotometer. Excitation and emission spectra were recorded on a Hitachi F-2700 fluorescence spectrophotometer.

Synthetic methods

General procedure of CDC reaction bis-polyfluoroaryl substituted naphthalenes and anthracenes.

Synthesis of bis-(pentafluorophenyl)naphthalene (Table 1, entry 4)



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 (64 mg, 0.5 mmol), and pentafluorobenzene (220 μL, 2.0 mmol) was stirred in CPME (0.75 mL) for 48 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 a mixture of bis-(pentafluorophenyl)naphthalene (91.6 mg, 40%). The ratio of regio-isomers was calculated from the ^{1}H NMR spectrum. The authentic samples were prepared by direct arylation (see description below).

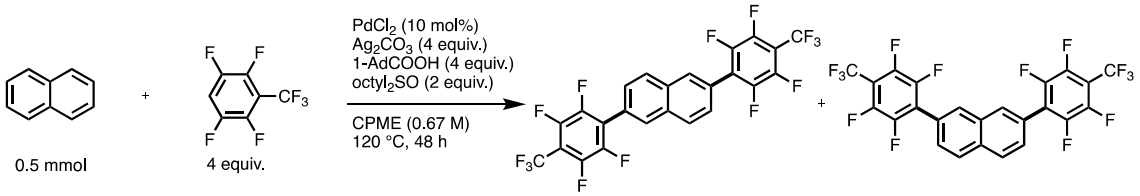
The mixture (91.6 mg) was washed with toluene. Remaining white powder was 2,6-bis(pentafluorophenyl)naphthalene (14.8 mg, 6.4% yield from naphthalene).

The solvents of the toluene-soluble fraction were removed in vacuo. The residual product was washed with a small amount of hexane. Remaining off-white powder was 2,7-bis(pentafluorophenyl)naphthalene (35.8 mg, 15.4% yield from naphthalene).

2,6-bis(pentafluorophenyl)naphthalene: ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.02 (d, 2 H, J = 8.4 Hz), 8.00 (s, 2 H), 7.58 (d, 2 H, J = 8.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -146.1 (dd, 4 F, J_F = 21.8, 8.2 Hz), -158.0 (t, 2 F, J_F = 21.1 Hz), -165.0 (dt, 4 F, J_F = 21.8, 7.7 Hz).

2,7-bis(pentafluorophenyl)naphthalene: ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.03 (d, 2 H, J = 8.6 Hz), 7.99 (s, 2 H), 7.59 (d, 2 H, J = 8.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -146.1 (dd, 4 F, J_F = 22.5, 7.5 Hz), -158.0 (t, 2 F, J_F = 20.4 Hz), -165.0 (dt, 4 F, J_F = 21.8, 7.7 Hz).

Synthesis of bis-((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene (Table 1, entry 5)

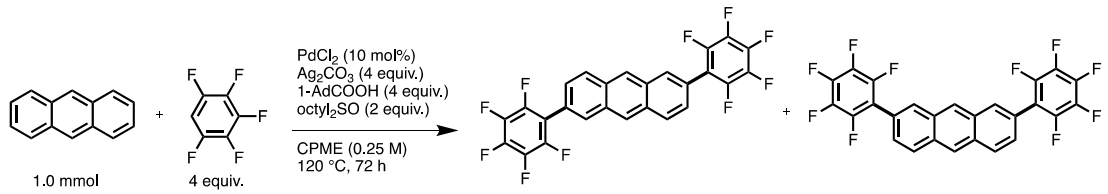


The product was isolated by column chromatography on silica gel using a hexane as an eluent. The solvents were removed in vacuo to give a mixture of bis-((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene (178 mg, 64%). The mixture was washed with toluene, remining solid was 2,6-((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene. The toluene-soluble fraction was evaporated and washed with hexane, remining solid was 2,7-((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene. The ratio of regio-isomers was calculated from the ^{1}H NMR spectrum of the mixture. The authentic sample of 2,7-isomer was prepared by direct arylation (see description below).

2,6-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene: ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.11-8.09 (m, 4 H), 7.67 (dd, 2 H, J = 8.6, 1.3 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -59.3 (t, 6 F, J_F = 21.8 Hz), -143.2- -143.5 (m, 4 F), -144.3 (td, 4 F, J_F = 17.4, 7.3 Hz). Elemental analysis: Calcd.: C 51.45%, H 1.08%; Found: C 51.65%, H 1.16%.

2,7-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene: ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.08-8.06 (m, 4 H), 7.65 (dd, 2 H, J = 8.4, 1.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -59.3 (t, 6 F, J_F = 21.1 Hz), -143.2- -143.5 (m, 4 F), -144.3 (dt, 4 F, J_F = 26.8, 7.8 Hz).

Synthesis of bis-(pentafluorophenyl)anthracene (Scheme 2)



A mixture of $PdCl_2$ (17.8 mg, 0.10 mmol), di-*n*-octylsulfoxide (550 mg, 2.0 mmol), 1-adamantanecarboxylic acid (720 mg, 4.0 mmol), silver(I) carbonate (1.10 g, 4.0 mmol), anthracene (178 mg, 1.0 mmol), and pentafluorobenzene (440 μL, 4.0 mmol) was stirred in CPME (4.0 mL) for 72 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 a mixture of bis-(pentafluorophenyl)anthracene (214 mg, 42%). The authentic samples were prepared by direct arylation (see description below).

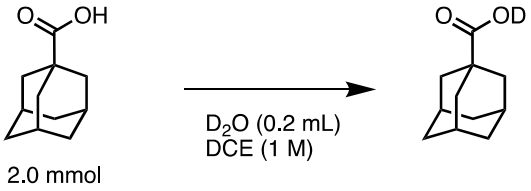
The mixture (203 mg) was washed with $CHCl_3$. Remaining pale yellow powder was 2,6-bis(pentafluorophenyl)anthracene (47 mg, 9.2% yield from anthracene).

The solvents of the $CHCl_3$-soluble fraction were removed in vacuo. The residual product was washed with small amount of hexane and pentane. Remaining pale yellow powder was 2,7-bis(pentafluorophenyl)anthracene (54.9 mg, 10.6% yield from anthracene).

2,6-bis(pentafluorophenyl)anthracene: ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.55 (s, 2 H), 8.15-8.14 (m, 4 H), 7.51 (d, 2 H, J = 9.0). ^{19}F NMR (565 MHz, $CDCl_3$, room temperature): δ -146.0 (dd, 4 F, J_F = 22.5, 8.2 Hz), -158.1 (t, 2 F, J_F = 21.5 Hz), -165.0 (dt, 4 F, J_F = 22.5, 8.2 Hz).

2,7-bis(pentafluorophenyl)anthracene: ^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.55 (d, 2 H, J = 6.6 Hz), 8.16-8.14 (m, 4 H), 7.52 (d, 2 H, J = 9.0 Hz). ^{19}F NMR (565 MHz, $CDCl_3$, room temperature): δ -146.0 (dd, 4 F, J_F = 22.5, 8.2 Hz), -158.1 (t, 2 F, J_F = 21.5 Hz), -165.0 (dt, 4 F, J_F = 21.5, 7.5 Hz). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, RT): δ 144.4 (dm, J_F = 248.8 Hz), 140.6 (dm, J_F = 254.3 Hz), 138.0 (dm, J_F = 249.9 Hz), 131.7, 131.3, 130.7, 128.8, 128.0, 127.0, 126.4, 123.8, 115.8 (td, J = 16.9, 4.1 Hz). Elemental analysis: Calcd.: C 61.19%, H 1.58%; Found: C 61.22%, H 1.61%.

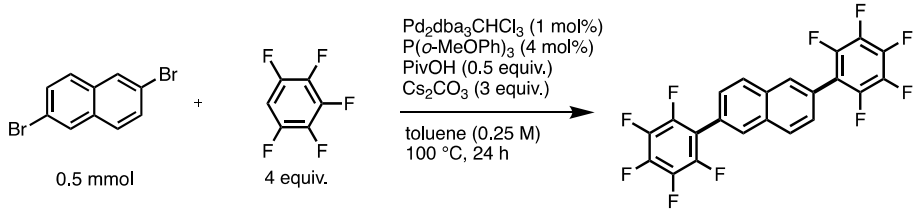
Synthesis of 1-AdCOOD[S1]



1-Adamantanecarboxylic acid (360 mg, 2.0 mmol) was stirred in DCE (2 mL), and then D_2O (0.2 mL) was added and stirred at rt for 2 h. The deuterated 1-adamantanecarboxylic acid was removed the solvent by vacuum and directly used for the reaction.

General procedure of direct C-H arylation reaction for preparation of authentic samples of bis-polyfluoroaryl substituted naphthalenes and anthracene.

Synthesis of 2,6-bis(pentafluorophenyl)naphthalene[S2]

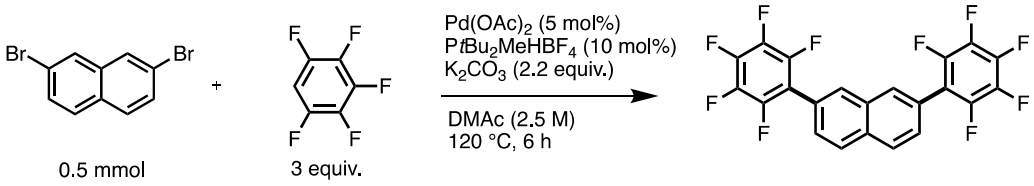


A mixture of $Pd_2(dba)_3CHCl_3$ (5.2 mg, 0.0050 mmol), tris(*o*-methoxyphenyl)phosphine (7.0 mg, 0.020 mmol), pivalic acid (28 μL, 0.25 mmol), cesium carbonate (490 mg, 1.5 mmol), 2,6-dibromonaphthalene (143 mg, 0.50 mmol), and pentafluorobenzene (220 μL, 2.0 mmol) was stirred in toluene (2.0 mL) for 24 h at 100 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with toluene (100 °C). Following filtration, the filtrate was cooled to -20 °C. The precipitates were collected by filtration, and washed with water, and dissolved in $CHCl_3$. The solution was passed through a short silica pad and the silica pad was rinsed with

hot toluene (100 °C). The solvents were removed in vacuo to give 2,6-bis(pentafluorophenyl)naphthalene (223 mg, 97%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.02 (d, 2 H, J = 8.4 Hz), 8.00 (br, 2 H), 7.58 (d, 2 H, J = 8.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -146.1 (dd, 4 F, J_F = 23.2, 8.2 Hz), -158.0 (t, 2 F, J_F = 21.1 Hz), -165.0 (dt, 4 F, J_F = 21.8, 7.7 Hz). ^{13}C{^{1}H} NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K): δ 147.7 (dm, J_F = 247.7 Hz), 143.8 (dm, J_F = 193.5 Hz), 141.3 (dm, J_F = 249.9 Hz), 136.2, 133.1, 132.0, 131.1, 128.5, 119.0 (dt, J = 23.6, 8.6 Hz). Elemental analysis: Calcd.: C 57.41%, H 1.31%; Found: C 57.65%, H 1.67%.

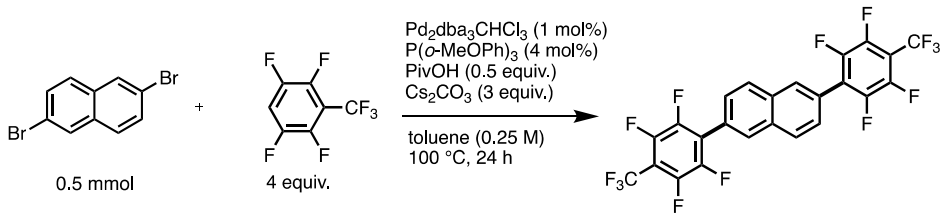
Synthesis of 2,7-bis(pentafluorophenyl)naphthalene[S3]



A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), P*t*Bu_2MeHBF_4 (12.4 mg, 0.050 mmol), potassium carbonate (152 mg, 1.1 mmol), 2,7-dibromonaphthalene (143 mg, 0.50 mmol), and pentafluorobenzene (164 μL, 1.5 mmol) was stirred in DMAc (0.20 mL) for 6 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. After 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 2,7-bis(pentafluorophenyl)naphthalene (187 mg, 68%).[S4]

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.02 (d, 2 H, J = 8.6 Hz), 7.98 (br, 2 H), 7.59 (d, 2 H, J = 8.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -146.1 (dd, 4 F, J_F = 23.2, 8.2 Hz), -158.0 (t, 2 F, J_F = 21.1 Hz), -165.0 (dt, 4 F, J_F = 22.1, 8.2 Hz).

Synthesis of 2,6- bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene [S2]

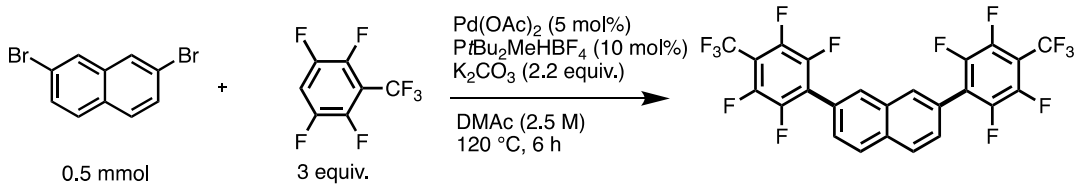


A mixture of $Pd_2(dba)_3CHCl_3$ (5.2 mg, 0.0050 mmol), tris(*o*-methoxyphenyl)phosphine (7.0 mg, 0.020 mmol), pivalic acid (28 μL, 0.25 mmol), cesium carbonate (490 mg, 1.5 mmol), 2,6-dibromonaphthalene (143 mg, 0.50 mmol), and (2,3,5,6-tetrafluoro-4-trifluoromethyl)benzene (273 μL, 2.0 mmol) was stirred in toluene (2.0 mL) for 24 h at 100 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with toluene (100 °C). Following filtration, the filtrate was cooled to -50 °C. The precipitates were collected by filtration and washed with water. The solid was dissolved in hot toluene (100 °C) and passed through a short silica pad. The

silica pad was rinsed with hot toluene (100 °C). The solvents were removed in vacuo to give 2,6-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene (89.6 mg, 32%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.07-8.06 (m, 4 H), 7.63 (d, 2 H, J = 8.3 Hz). ^{19}F NMR (565 MHz, $CDCl_3$, room temperature): δ -59.4 (t, 6 F, J_F = 21.5 Hz), -143.3 - -143.5 (m, 4 F), -144.3 (m, 4 F). ^{13}C{^{1}H} NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K): δ 144.5 (dm, J_F = 260.9 Hz), 144.3 (dm, J_F = 253.2 Hz), 133.0, 129.9, 129.0, 127.4, 125.1, 124.4 (t, J = 16.6 Hz), 120.7 (q, J_F = 274.2 Hz), 109.0 (m).

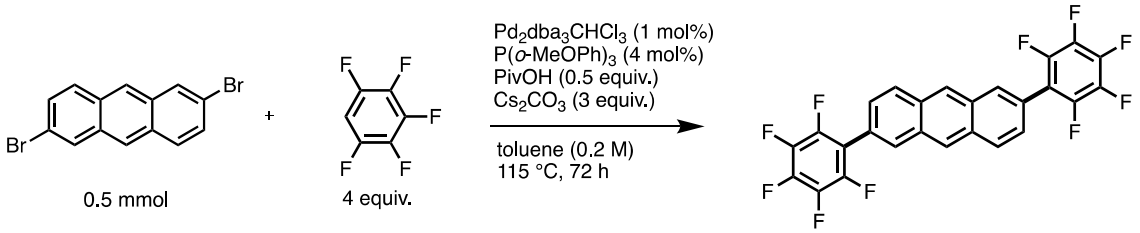
Synthesis of 2,7-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene[S3]



A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PtBu$_2$MeHBF$_4$ (12.4 mg, 0.050 mmol), potassium carbonate (152 mg, 1.1 mmol), 2,7-dibromonaphthalene (143 mg, 0.50 mmol), and (2,3,5,6-tetrafluoro-4-trifluoromethyl)benzene (203 μL, 1.5 mmol) was stirred in DMAc (0.20 mL) for 6 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. After 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 2,7-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene (173 mg, 62%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.07-8.06 (m, 4 H), 7.65 (dd, 2 H, J = 8.4, 1.5 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -59.4 (t, 6 F, J_F = 21.8 Hz), -143.3- -143.6 (m, 4 F), -144.4 (td, 4 F, J_F = 17.4, 7.3 Hz). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, RT): δ 144.6 (dm, J_F = 250.2 Hz), 144.4 (dm, J_F = 252.4 Hz), 133.7, 132.6, 130.7, 128.6, 128.2, 124.7, 124.4 (t J = 16.5 Hz), 120.9 (q, J_F = 274 Hz), 109.4-108.9 (m). Elemental analysis: Calcd.: C 51.45%, H 1.08%; Found: C 51.26%, H 1.05%.

Synthesis of 2,6-bis(pentafluorophenyl)anthracene[S2]



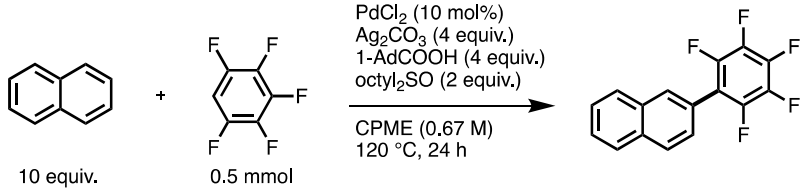
A mixture of $Pd_2(dba)_3CHCl_3$ (5.2 mg, 0.0050 mmol), tris(*o*-methoxyphenyl)phosphine (7.0 mg, 0.020 mmol), pivalic acid (28 μL, 0.25 mmol), cesium carbonate (490 mg, 1.5 mmol), 2,6-dibromoanthracene (168 mg, 0.50 mmol), and pentafluorobenzene (220 μL, 2.0 mmol) was stirred in toluene (2.5 mL) for 72 h at 115 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and poured into a cylindrical filter paper for Soxhlet extraction. The mixture was washed with MeOH and hexane, and extracted with $CHCl_3$ and toluene by

Soxhlet extraction. Solvents of the extracts with $CHCl_3$ and toluene were removed in vacuo to give 2,6-bis(pentafluorophenyl)anthracene (203 mg, 80%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.55 (s, 2 H), 8.15-8.14 (m, 4 H), 7.52 (d, 2 H, J = 8.8 Hz). ^{19}F NMR (565 MHz, $CDCl_3$, room temperature): δ -145.9 (dd, 4 F, J_F = 22.5, 8.2 Hz), -158.1 (t, 2 F, J_F = 20.4 Hz), -165.2 (dt, 4 F, J_F = 22.5, 7.5 Hz). ^{13}C{^{1}H} NMR (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K): δ 144.4 (dm, J_F = 242.2 Hz), 140.6 (dm, J_F = 258.7 Hz), 137.9 (dm, J_F = 256.5 Hz), 131.7, 131.4, 130.4, 128.6, 127.0, 126.7, 124.0, 115.8 (td, J = 16.6, 2.9 Hz). Elemental analysis: Calcd.: C 61.19%, H 1.58%; Found: C 61.37%, H 1.35%.

General procedure of CDC reaction mono-polyfluoroaryl substituted compounds.

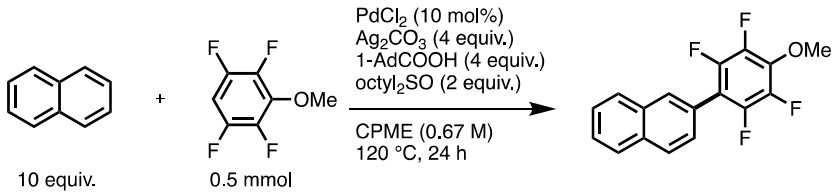
Synthesis of 2-pentafluorophenylnaphthalene (Table 2, entry 1)



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 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 products were 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-pentafluorophenylnaphthalene (100 mg, 68%).[S5]

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.96 (d, 1 H, J = 8.4 Hz), 7.93 (s, 1 H), 7.91-7.89 (m, 2 H), 7.59-7.54 (m, 2 H), 7.50-7.49 (m, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -146.2 (dd, 2 F, J_F = 23.2, 8.2 Hz), -158.6 (t, 1 F, J_F = 21.1 Hz), -165.3 (dt, 2 F, J_F = 22.5, 7.7 Hz).

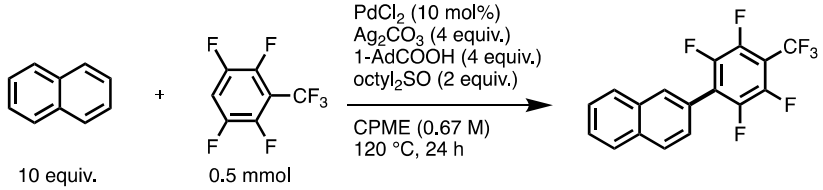
Synthesis of 2-(2,3,5,6-tetrafluoro-4-methoxy)phenylnaphthalene (Table 2, entry 2)



The product was isolated by column chromatography on silica gel using a mixture of hexane as an eluent. The solvents were removed in vacuo to give 2-(2,3,5,6-tetrafluoro-4-methoxy)phenylnaphthalene (107 mg, 70%).[S5]

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.94-7.93 (m, 2 H), 7.90-7.88 (m, 2 H), 7.56-7.51 (m, 3 H), 4.15-4.14 (m, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -148.0 (dd, 2 F, J_F = 22.5, 8.9 Hz), -161.3 (dd, 2 F, J_F = 21.8, 8.2 Hz).

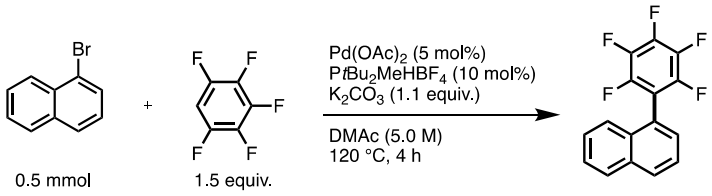
Synthesis of 2-(2,3,5,6-tetrafluoro-4-trifluoromethyl)phenylnaphthalene (Table 2, entry 3)



After Celite® filtration, naphthalene was removed by distillation and the remaining residue was purified by column chromatography on silica gel using a hexane as an eluent and HPLC. The solvents were removed in vacuo to give 2-(2,3,5,6-tetrafluoro-4-trifluoromethyl)phenylnaphthalene (118 mg, 69%).[S5]

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.99-7.98 (m, 2 H), 7.92 (d, 2 H, J = 8.4 Hz), 7.61-7.56 (m, 2 H), 7.54-7.52 (m, 1 H). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -59.3 (t, 3 F, J_F = 21.8 Hz), -143.7- -143.9 (m, 2 F), -144.4 (dt, 2 F, J_F = 17.4, 7.3 Hz).

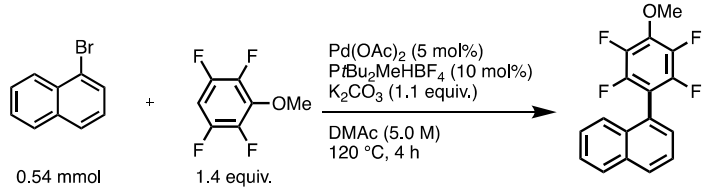
Synthesis of 1-pentafluorophenylnaphthalene



A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PtBu$_2$MeHBF$_4$ (12.4 mg, 0.050 mmol), potassium carbonate (76 mg, 0.55 mmol), 1-bromonaphthalene (70 μL, 0.50 mmol), and pentafluorobenzene (82 μL, 0.75 mmol) was stirred in DMAc (0.10 mL) for 4 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. After 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 1-pentafluorophenylphenanthrene (46 mg, 31%).[S6]

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.00 (d, 1 H, J = 8.4 Hz), 7.95 (d, 1 H, J = 7.8 Hz), 7.59-7.54 (m, 2 H), 7.52-7.47 (m, 2 H), 7.45 (d, 1 H, J = 6.6 Hz). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -142.6 (dd, 2 F, J_F = 23.2, 8.2 Hz), -158.5 (m, 1 F), -165.3 (m, 2 F).

Synthesis of 1-(2,3,5,6-tetrafluoro-4-methoxy)phenylnaphthalene



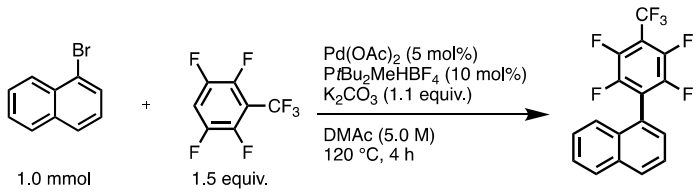
A mixture of $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), PtBu$_2$MeHBF$_4$ (12.4 mg, 0.050 mmol), potassium carbonate (76 mg, 0.55 mmol), 1-bromonaphthalene (76 μL, 0.54 mmol), and 2,3,5,6-tetrafluoro-4-anisole (104 μL, 0.75 mmol) was stirred in DMAc (0.10 mL) for 4 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. Following 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 1-(2,3,5,6-tetrafluoro-4-methoxy)phenylnaphthalene (43 mg, 28%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 7.97 (d, 1 H, J = 8.3 Hz), 7.94-7.93 (m, 1 H), 7.58-7.49 (m, 4 H), 7.45 (d, 1 H, J = 6.8 Hz), 4.18 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -144.5 (dd, 2 F, J_F = 21.8, 8.2 Hz), -161.1 (dd, 2 F, J_F = 22.5, 8.9 Hz). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, RT): δ 144.7 (dm, J_F = 245.5 Hz) 141.1 (dtd, J_F = 247.5, 10.0, 5.3 Hz), 138.0 (tt, J_F = 11.6, 3.3 Hz), 133.7, 131.8, 129.8, 129.0, 128.5, 126.8, 126.2, 125.2, 124.9, 124.7, 112.6 (t, J = 72.6 Hz), 62.2 (t, J = 3.9 Hz).

Elemental analysis: Calcd.: C 66.67%, H 3.29%; Found: C 65.51%, H 3.33%.

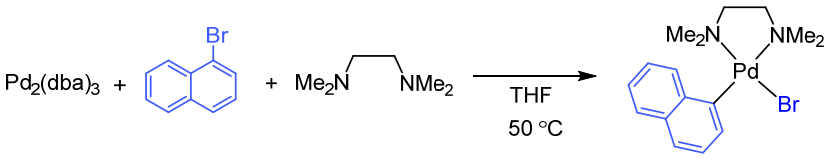
Synthesis of 1-(2,3,5,6-tetrafluoro-4-trifluoromethyl)phenylnaphthalene



A mixture of $Pd(OAc)_2$ (11.2 mg, 0.050 mmol), PtBu$_2$MeHBF$_4$ (24.8 mg, 0.10 mmol), potassium carbonate (152 mg, 1.1 mmol), 1-bromonaphthalene (140 μL, 1.0 mmol), and (2,3,5,6-tetrafluoro-4-trifluoromethyl)benzene (204 μL, 1.5 mmol) was stirred in DMAc (0.20 mL) for 4 h at 120 °C under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with $CHCl_3$. After 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 1-(2,3,5,6-tetrafluoro-4-trifluoromethyl)phenylnaphthalene (108 mg, 31%).

^{1}H NMR (600 MHz, $CDCl_3$, room temperature): δ 8.03 (d, 1 H, J = 8.3 Hz), 7.96 (d, 1 H, J = 8.1 Hz), 7.62-7.52 (m, 3 H), 7.48-7.46 (m, 2 H). ^{19}F NMR (376 MHz, $CDCl_3$, room temperature): δ -59.3 (m, 3 F), -140.6 (dt, 2 F, J_F = 26.8, 7.8 Hz), -143.5- -143.6 (m, 2 F). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, RT): δ 144.7 (dtd, J_F = 249.5, 9.0, 4.4 Hz), 144.3 (dd, J_F = 260.9, 16.6 Hz), 133.7, 131.0, 130.6, 128.7, 128.6, 127.3, 126.6, 125.2, 124.4, 123.8 (t, J = 19.3 Hz), 123.4, 120.9 (q, J_F = 274 Hz), 109.3 (m). Elemental analysis: Calcd.: C 59.32%, H 2.05%; Found: C 59.26%, H 2.01%.

Synthesis of PdBr(1-Naphthyl)(tmeda)

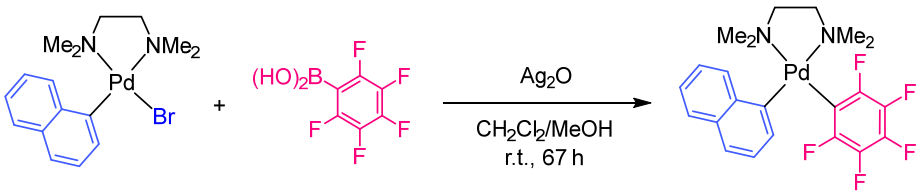


A mixture of $Pd_2(dba)_3$ (120 mg, 0.13 mmol), 1-bromonaphthalene (734 µL, 5.2 mmol), and *N*,*N*,*N*,*N*-tetramethylethylenediamine (97.7 µL, 0.66 mmol) was stirred in THF (2.0 mL) for 20 h at 50 °C under a nitrogen atmosphere. After removal of the volatiles, residue was extracted with chloroform. Following Celite® filtration, the filtrate was concentrated under reduced pressure. PdBr(1-Naphthyl)(tmeda) was isolated by washing with hexane (78.0 mg, 69%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.03 (d, 1H, *J* = 8.4 Hz), 7.63 (d, 1H, *J* = 8.1 Hz), 7.44 (ddd, 1H, *J* = 7.8, 6.6, 1.2 Hz), 7.39 (dd, 1H, *J* = 7.0, 0.9 Hz), 7.37-7.32 (m, 2H), 7.13 (dd, 1H, *J* = 7.9, 7.0 Hz), 2.93-2.89 (m, 1H), 2.79 (s, 3H), 2.76-2.71 (m, 1H), 2.73 (s, 3H), 2.63-2.54 (m, 2H), 2.52 (s, 3H), 2.04 (s, 3H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 149.5, 139.1, 133.9, 133.0, 131.3, 127.7, 124.5, 124.4, 123.9, 122.8, 62.5, 58.2, 51.9, 49.1, 47.7.

EA: Found. C 44.25%, H 5.45%, N 6.75%; Calcd. for $C_{16}H_{23}N_2BrPd$: C 44.72%, H 5.40%, N 6.52%.

Synthesis of Pd(1-Naphthyl)(pentafluorophenyl)(tmeda) (α-biaryl model complex)



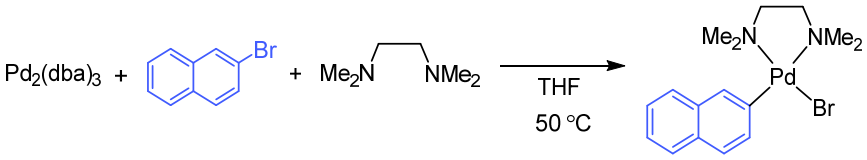
α-biaryl model complex

A mixture of PdBr(1-Naphthyl)(tmeda) (23.2 mg, 0.054 mmol), Ag_2O (25.8 mg, 0.11 mmol), and pentafluorophenylboronic acid (56.0 mg, 0.26 mmol) was stirred in dichloromethane/methanol (1.5 mL 1/1(v/v)) for 67 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. α-Biaryl model complex was isolated by column chromatography on silica gel using a mixture of chloroform and hexane (3:2) as an eluent (14.1 mg, 51%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.04 (dd, 1H, *J* = 8.3, 1.7 Hz), 7.71 (d, 1H, *J* = 7.0 Hz), 7.60 (d, 1H, *J* = 8.1 Hz), 7.42 (ddd, 1H, *J* = 7.8, 6.6, 1.2 Hz), 7.34-7.29 (m, 2H), 7.09 (dd, 1H, *J* = 7.9, 7.2 Hz), 2.82-2.61 (m, 4H), 2.59 (s, 3H), 2.42 (s, 3H), 2.38 (s, 3H), 2.07 (s, 3H). ^{19}F NMR (565 MHz, $CDCl_3$): δ -118.1 (td, 1F, *J* = 17.7, 12.3 Hz), -121.4 (td, 1F, *J* = 34.7, 9.2 Hz), -165.8 (t, 1F, *J* = 19.4 Hz), -167.0 to -167.1 (m, 1F), -167.4 to -167.5 (m, 1F). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): 156.3, 147.6 (dm, J_F = 222.2 Hz), 139.4, 136.5 (dm, J_F = 242.4 Hz), 136.0 (dm, J_F = 242.4 Hz), 133.7, 133.3, 127.6, 124.6, 124.3, 123.3, 122.2, 121.4 (t, *J* = 55.8 Hz), 61.0, 59.4, 50.4, 49.3, 48.5, 48.4.

EA: Found. C 50.94%, H 4.35%, N 5.28%; Calcd. for $C_{22}H_{23}N_2F_5Pd$: C 51.13%, H 4.49%, N 5.42%.

Synthesis of PdBr(2-Naphthyl)(tmeda)

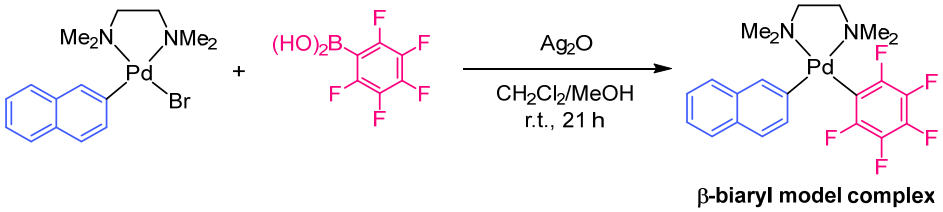


A mixture of $Pd_2(dba)_3$ (142 mg, 0.155 mmol), 2-bromonaphthalene (1.28 g, 6.19 mmol), and *N*,*N*,*N*,*N*-tetramethylethylenediamine (115.4 μL, 0.775 mmol) was stirred in THF (2.0 mL) for 23 h at 50 °C under a nitrogen atmosphere. After removal of the volatiles, residue was extracted with chloroform. Following Celite® filtration, the filtrate was concentrated under reduced pressure. PdBr(2-Naphthyl)(tmeda) was isolated by washing with hexane (95.4 mg, 72%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 (d, 1H, *J* = 8.1 Hz), 7.67 (s, 1H), 7.64 (d, 1H, *J* = 8.1 Hz), 7.55 (dd, 1H, *J* = 8.4, 1.5 Hz), 7.45 (d, 1H, *J* = 8.4 Hz), 7.33 (ddd, 1H, *J* = 7.8, 7.2, 1.2 Hz), 7.27-7.24 (m, 1H), 2.80-2.70 (br, 2H), 2.68 (s, 6H), 2.65-2.55 (br, 2H), 2.45-2.41 (br, 6H). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 146.0, 134.2, 133.0, 132.4, 131.1, 127.4, 126.2, 124.7, 124.6, 123.4, 77.2, 77.0, 76.8, 62.5, 58.1, 50.9, 50.0, 48.4.

EA: Found. C 44.22%, H 5.32%, N 6.56%; Calcd. for $C_{16}H_{23}N_2BrPd$: C 44.72%, H 5.40%, N 6.52%.

Synthesis of Pd(2-Naphthyl)(pentafluorophenyl)(tmeda) (β-biaryl model complex)



β-biaryl model complex

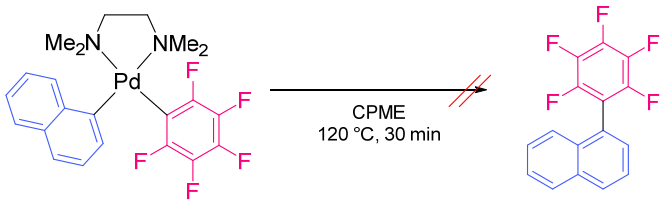
A mixture of PdBr(2-Naphthyl)(tmeda) (28.1 mg, 0.065 mmol), Ag_2O (30.3 mg, 0.13 mmol), and pentafluorophenylboronic acid (69.2 mg, 0.33 mmol) was stirred in dichloromethane/methanol (1.5 mL 1/1(v/v)) for 21 h at room temperature under a nitrogen atmosphere. After removal of the volatiles, residue was extracted with chloroform. Following Celite® filtration, the filtrate was concentrated under reduced pressure. β-biaryl model complex was isolated by column chromatography on silica gel using a mixture of chloroform and hexane (3:2) as an eluent (20.2 mg, 60%).

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82 (s, 1H), 7.67 (d, 1H, *J* = 8.3 Hz), 7.63 (d, 1H, *J* = 6.6 Hz), 7.61 (d, 1H, *J* = 7.2 Hz), 7.37 (d, 1H, *J* = 8.3 Hz), 7.29 (ddd, 1H, *J* = 7.8, 7.2, 1.2 Hz), 7.21 (ddd, 1H, *J* = 7.8, 7.2, 1.2 Hz), 2.70 (t, 2H, *J* = 5.3 Hz), 2.60 (t, 2H, *J* = 5.4 Hz), 2.42 (s, 6H), 2.37 (s, 6H). ^{19}F NMR (565 MHz, $CDCl_3$): δ -121.4 (d, 2F, *J* = 16.5 Hz), -165.7 (t, 1F, *J* = 12.4 Hz), -167.2 to -167.3 (m, 2F).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 152.3, 147.2 (dm, J_F = 220.7 Hz), 136.2 (dm, J_F = 255.5 Hz), 135.9 (dm, J_F = 251.1 Hz), 135.5, 133.6, 133.0, 130.7, 127.5, 126.2, 124.5, 124.4, 123.0, 122.8 (t, J_F = 58.7 Hz), 60.8, 59.0, 48.9, 48.7.

EA: Found. C 50.86%, H 4.46%, N 5.28%; Calcd. for $C_{22}H_{23}N_2F_5Pd$: C 51.13%, H 4.49%, N 5.42%.

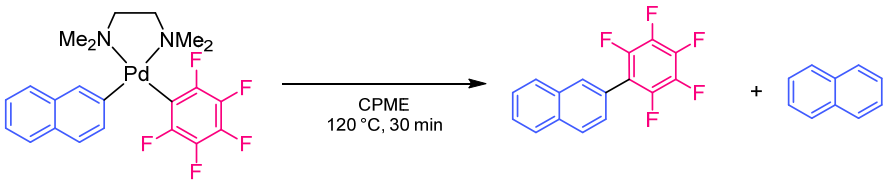
Test for reductive elimination of α-biaryl model complex



α-biaryl complex

α-Biaryl model complex (4.6 mg, 8.9 μmol) was heated at 120 °C under a nitrogen atmosphere in CPME (0.91 mL) with 1,3,5-trimethoxylbenzene (18 μmol) and 1,4-bis(*tert*-butoxy)tetrafluorobenzene (15 μmol) as internal standards. A small portion of the sample was taken out at 0, 10, 20, and 30 min, and ^{1}H and ^{19}F NMR spectra were measured.

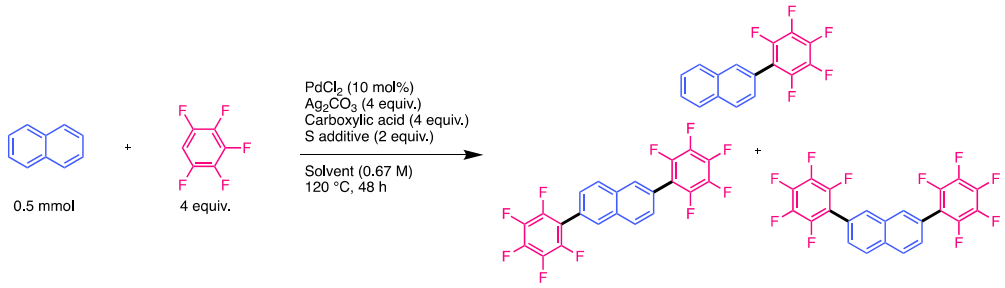
Test for reductive elimination of β-biaryl model complex



β-biaryl complex

β-Biaryl model complex (4.4 mg, 8.5 μmol) was heated at 120 °C under a nitrogen atmosphere in CPME (0.91 mL) with 1,3,5-trimethoxylbenzene (17 μmol) and 1,4-bis(*tert*-butoxy)tetrafluorobenzene (14 μmol) as internal standards. A small portion of the sample was taken out at 0, 10, 20, and 30 min, and ^{1}H and ^{19}F NMR spectra were measured. β-Biaryl model complex reacted in 10 min, giving 2-pentafluorophenylnaphthalene (92 %) and naphthalene (7%).

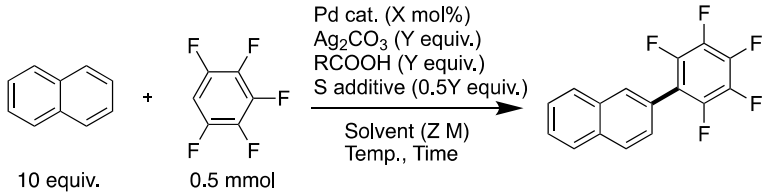
Table S1. Additional data of Table 1.



Entry	RCOOH	S additive	Solvent	Yield of mono-arylated compounds[a] (%)	Yield of di-arylated compounds[a] (%)	Ratio of 2,6-:2,7-[d]
1	PivOH	DMSO	DMF	26	2	-[e]
2	1-AdCOOH	DMSO	DMF	17	7	-[e]
3	1-AdCOOH	octyl$_2$SO	DMF	39	22	-[e]
4	1-AdCOOH	octyl$_2$SO	CPME	37[b]	40[c]	1.0 : 3.0

[a]The yield of 2-, 2,6- and 2,7-substituted compounds was determined by ^{19}F NMR analyses of a crude product with hexafluorobenzene as an internal standard. [b]Isolated yield. [c]Yields of a mixture of 2,6-, 2,7- and other bis(pentafluorophenyl)naphthalenes after purification by column chromatography. [d]The ratio calculated from ^{1}H NMR spectra of the mixture. [e]Not calculated.

Table S2. Optimization of reaction conditions for synthesis of 2-pentafluorophenylnaphthalene.



entry	Pd	X	R	S additive	Y	Solv.	Z	Temp. (°C)	Time (h)	NMR yield (%)[a]
S1	$PdCl_2$	10	1-Ad	octyl$_2$SO	4	CPME	0.67	120	24	74 (68)[b,c]
S2	$Pd(OAc)_2$	10	Me	*i*Pr$_2$S	4	CPME	0.67	120	24	60
S3	$Pd(OAc)_2$	10	1-Ad	*i*Pr$_2$S	4	CPME	0.67	120	24	71
S4	$PdCl_2$	10	1-Ad	DMSO	4	CPME	0.67	120	24	66
S5	$PdCl_2$	10	1-Ad	octyl$_2$SO	4	DMF	0.67	120	24	72
S6	$PdCl_2$	5	1-Ad	octyl$_2$SO	2	CPME	0.67	120	24	52
S7	$PdCl_2$	10	1-Ad	octyl$_2$SO	4	CPME	0.25	120	24	66
S8	$Pd(OAc)_2$	10	1-Ad	octyl$_2$SO	4	CPME	0.67	120	24	62
S9	$PdCl_2$	10	1-Ad	DMSO	4	DMF	0.67	120	24	68
S10	$PdCl_2$	10	1-Ad	*i*Pr$_2$S	4	CPME	0.67	120	24	63
S11	$PdCl_2$	10	1-Ad	octyl$_2$SO	4	CPME	0.67	100	24	69

[a]The yield was determined by ^{19}F NMR analyses of a crude product with hexafluorobenzene as an internal standard. [b]Isolated yield. [c]2-position selectivity = 97%

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 2099539 and 2114882 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.

Table S3. Crystallographic data of the 2,6-bis(pentafluorophenyl)naphthalene and anthracene

	2,6-bis(pentafluorophenyl) naphthalene	2,6-bis(pentafluorophenyl) anthracene
Empirical Formula	$C_{22}H_6F_{10}$	$C_{13}H_4F_5$
Formula Weight	460.27	255.17
Crystal Color	colorless	colorless
Crystal Dimensions / mm	0.134 x 0.069 x 0.010	0.037 x 0.037 x 0.009
Crystal System	monoclinic	monoclinic
Lattice Parameters		
a / Å	19.990(3)	22.572(5)
b / Å	6.2622(10)	6.5859(15)
c / Å	13.262(2)	13.304(3)
β / deg.	95.966(2)	106.248(3)
V / Å^3	1651.1(5)	1898.7(8)
Space Group	C2/c (#15)	C2/c (#15)
Z	4	8
D / gcm^{-3}	1.851	1.785
*F*000	912.00	1016.00
μ(MoKα) / cm^{-1}	1.867	1.723
Reflection/Parameter Ratio	12.53	9.34
*R*1 ($I > 2.00\sigma(I)$)	0.0510	0.0371
R (All reflections)	0.0609	0.0496
*wR*2 (All reflections)	0.1361	0.0934
Goodness of Fit Indicator	1.056	1.035

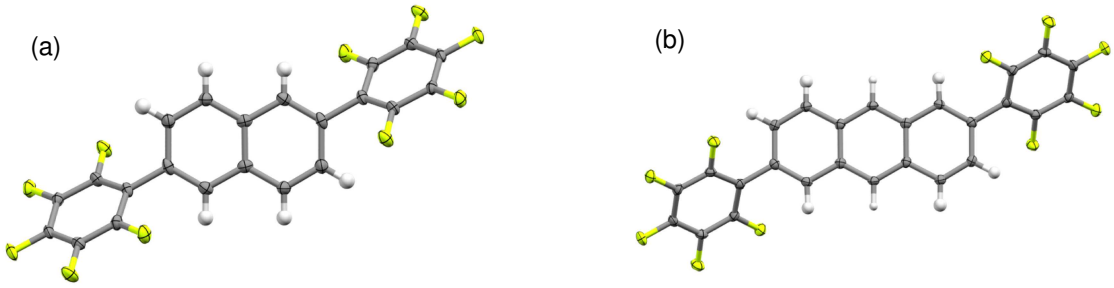


Figure S1. ORTEP drawing of 2,6-bis(pentafluorophenyl)naphthalene synthesised by direct arylation (a) and 2,6-bis(pentafluorophenyl)anthracene synthesised by direct arylation (b) with thermal ellipsoids at the 50% probability level.

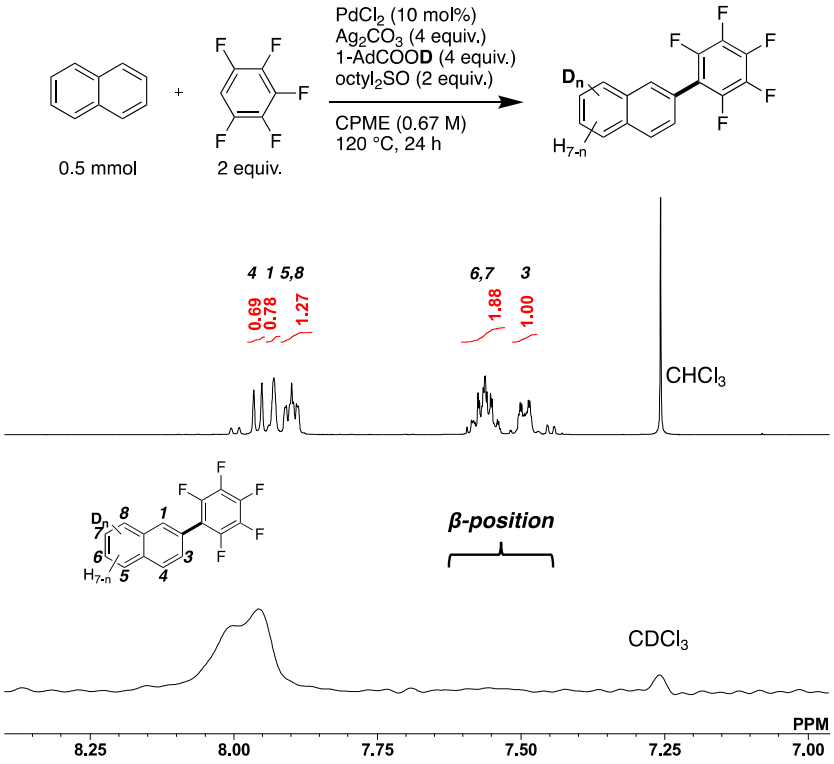


Figure S2. The reaction scheme and ^{1}H NMR spectrum of the products (600 MHz, $CDCl_3$, r.t., top), ^{2}H NMR spectrum of the products (92 MHz, $CHCl_3$, r.t., bottom).

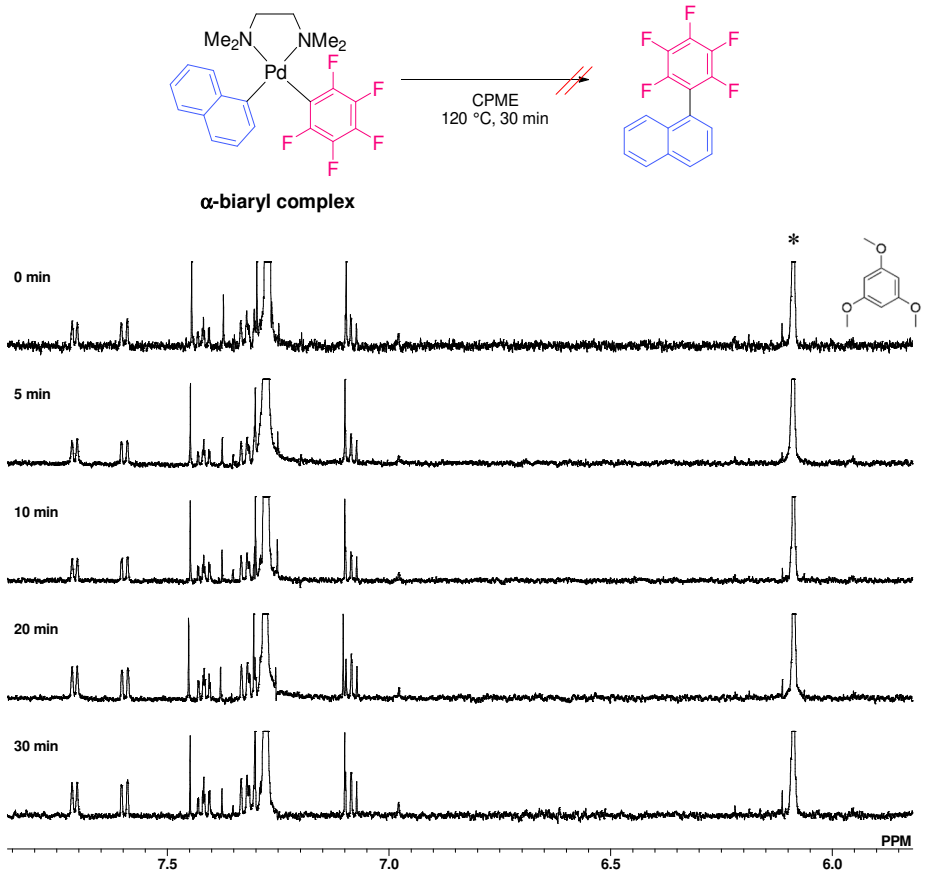


Figure S3. Time-course changes of ^{1}H NMR spectrum of α-biaryl model complex heated at 120 °C in CPME ($CDCl_3$, 600 MHz). Trimethoxybenzene (*) was used as internal standard. There was no essential spectral change.

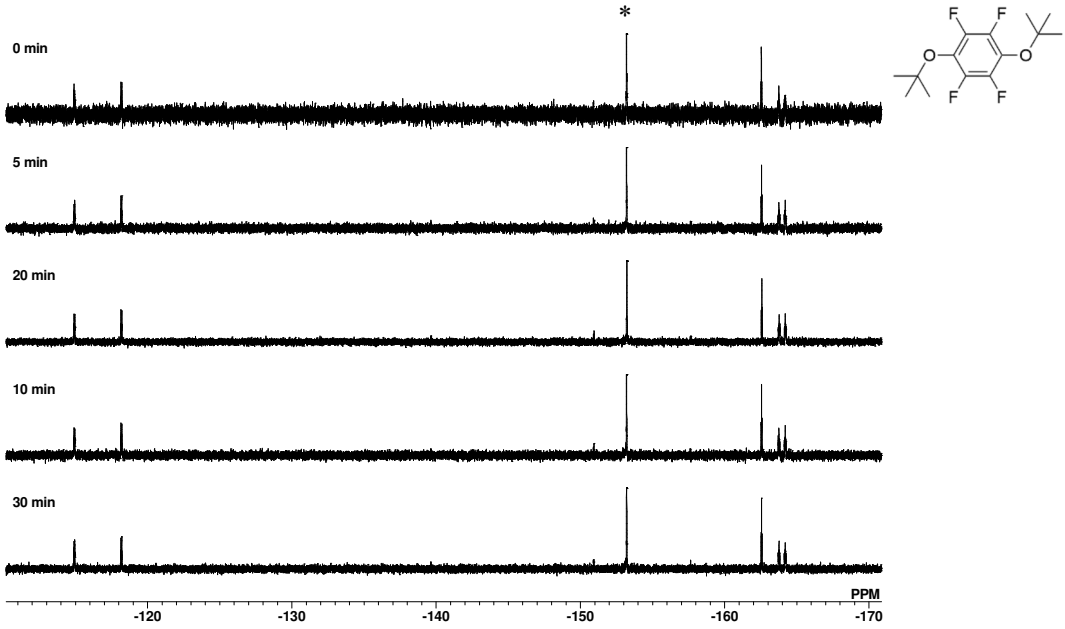


Figure S4. Time-course changes of ^{19}F NMR spectrum of α-biaryl model complex heated at 120 °C in CPME ($CDCl_3$, 565 MHz). 1,4-Bis(*tert*-butoxy)tetrafluorobenzene (*) was used as internal standard. There was no essential spectral change.

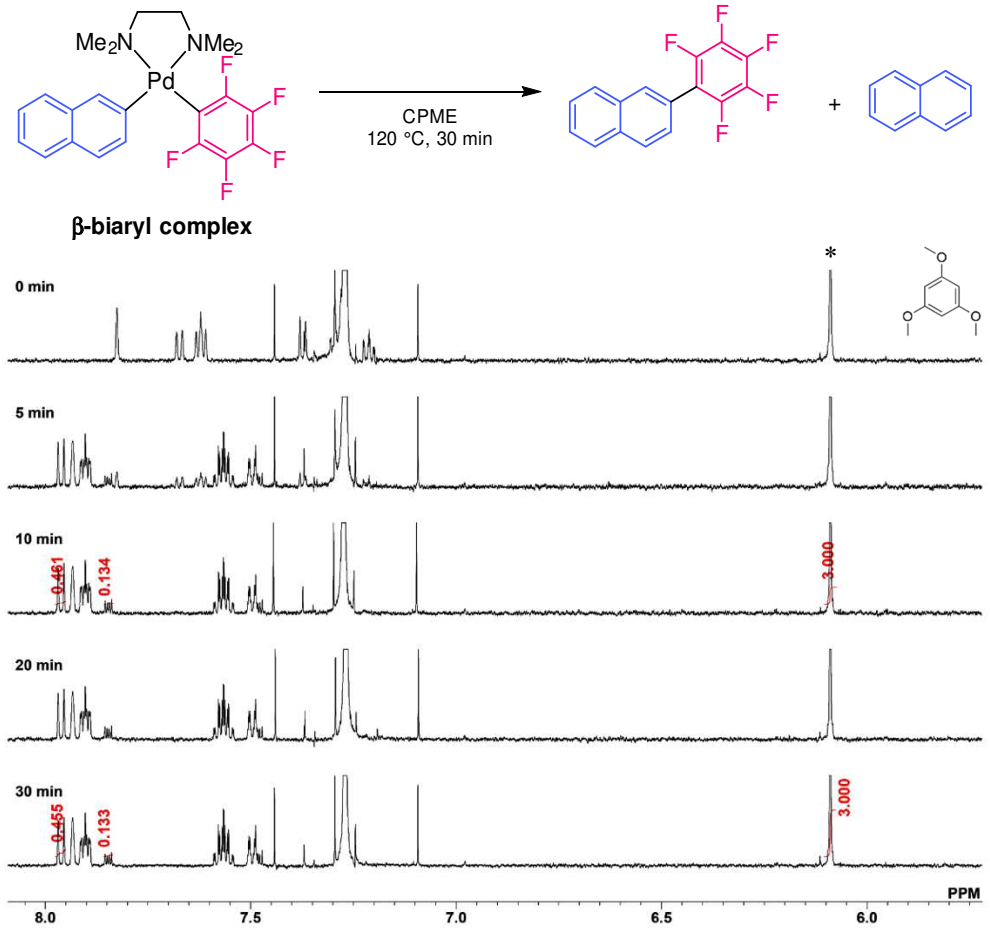


Figure S5. Time-course changes of ^{1}H NMR spectrum of β-biaryl model complex heated at 120 °C in CPME ($CDCl_3$, 600 MHz). Trimethoxybenzene (*) was used as internal standard.

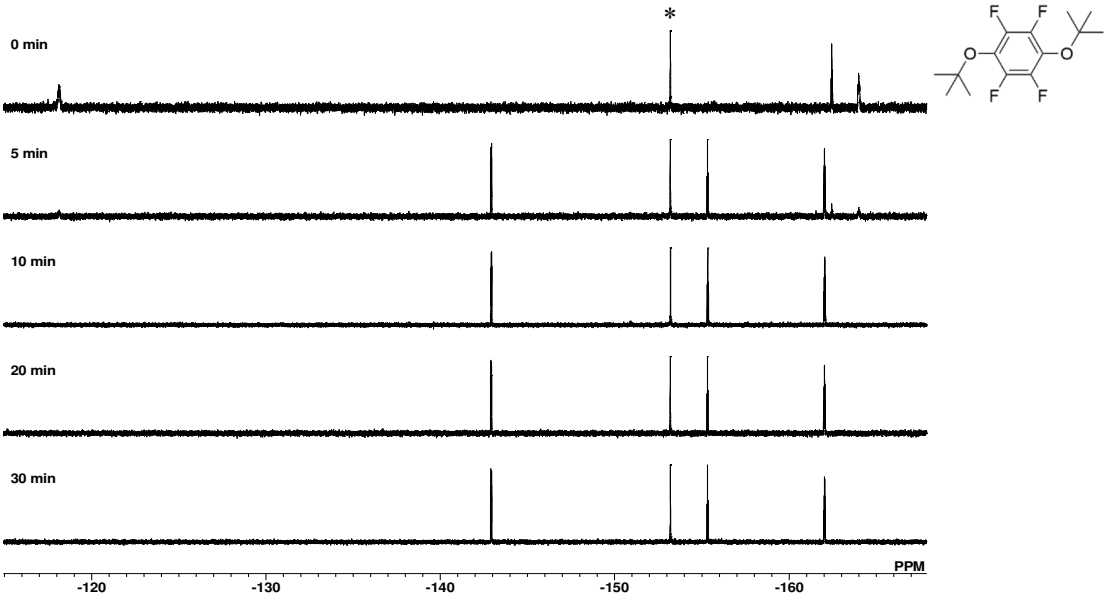


Figure S6. Time-course changes of ^{19}F NMR spectrum of β-biaryl model complex heated at 120 °C in CPME ($CDCl_3$, 565 MHz). 1,4-Bis(*tert*-butoxy)tetrafluorobenzene (*) was used as internal standard.

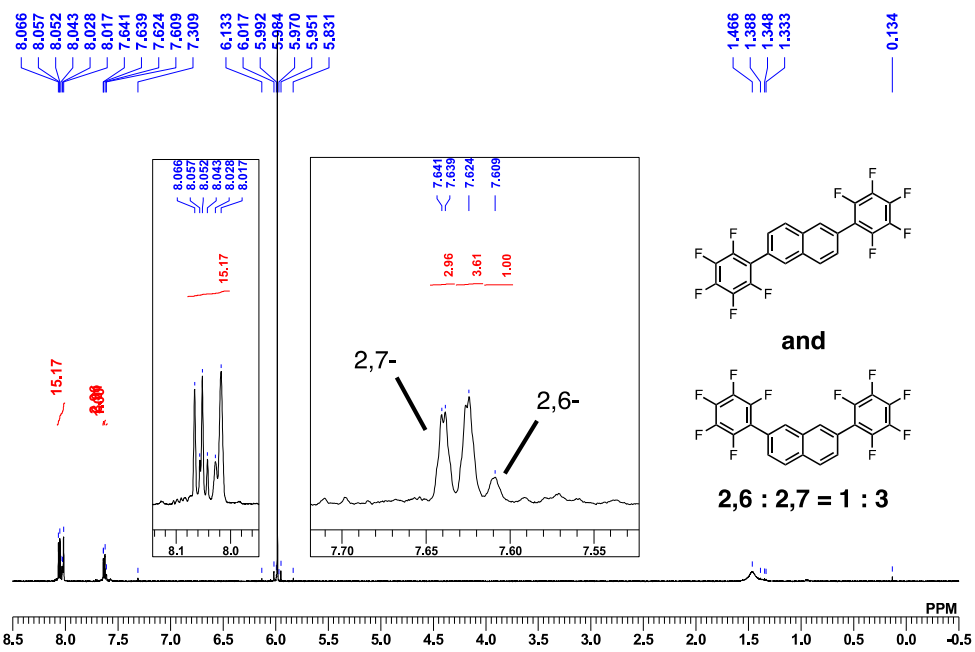


Figure S7. ^{1}H NMR spectrum of a mixture of bis(pentafluorophenyl)naphthalene synthesised by the CDC reaction (600 MHz, 1,1,2,2,-tetrachloroethane-d_2, 373 K).

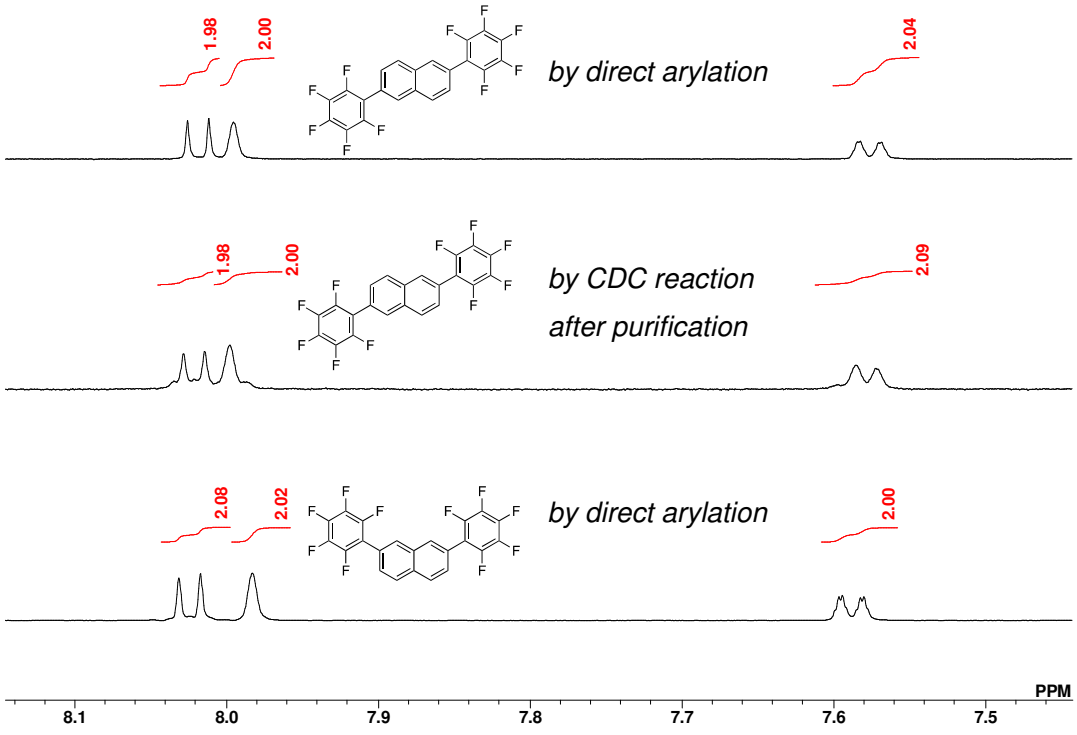


Figure S8. ^{1}H NMR spectra of 2,6-bis(pentafluorophenyl)naphthalene synthesised by the direct arylation reaction (top), 2,6-bis(pentafluorophenyl)naphthalene synthesised by the CDC reaction (middle), 2,7-bis(pentafluorophenyl)naphthalene synthesised by the direct arylation reaction (bottom) (600 MHz, $CDCl_3$, r.t.).

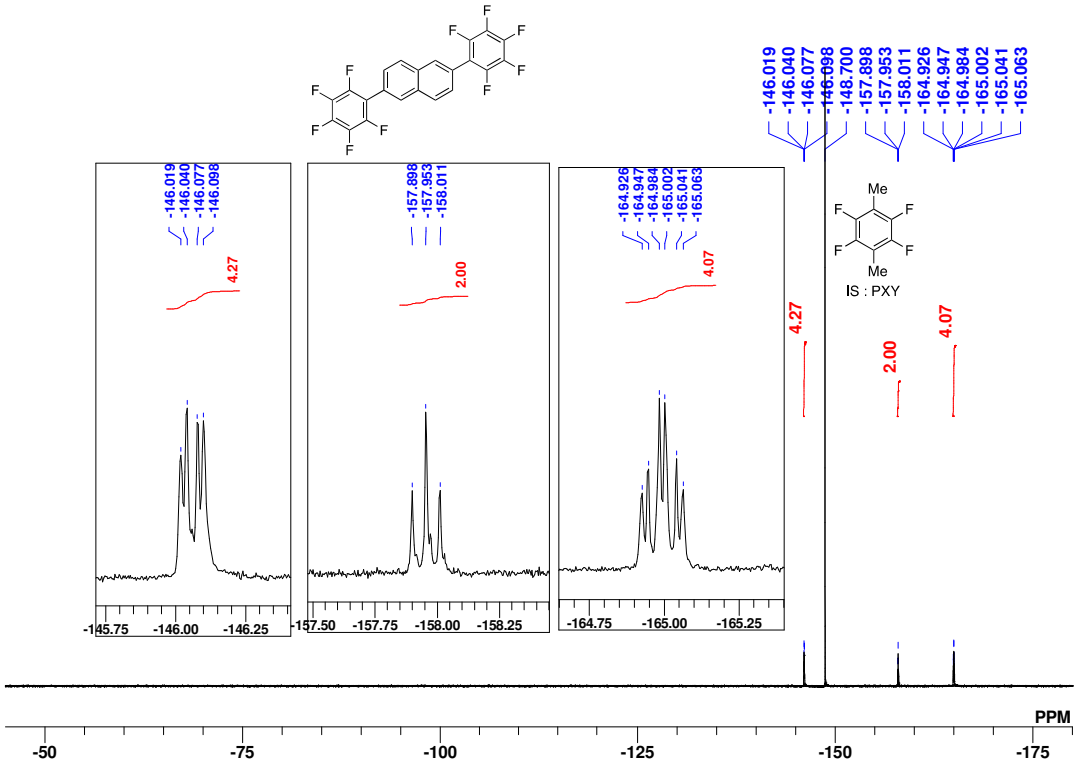


Figure S9. ^{19}F NMR spectrum of 2,6-bis(pentafluorophenyl)naphthalene synthesised by the CDC reaction (376 MHz, $CDCl_3$, r.t.).

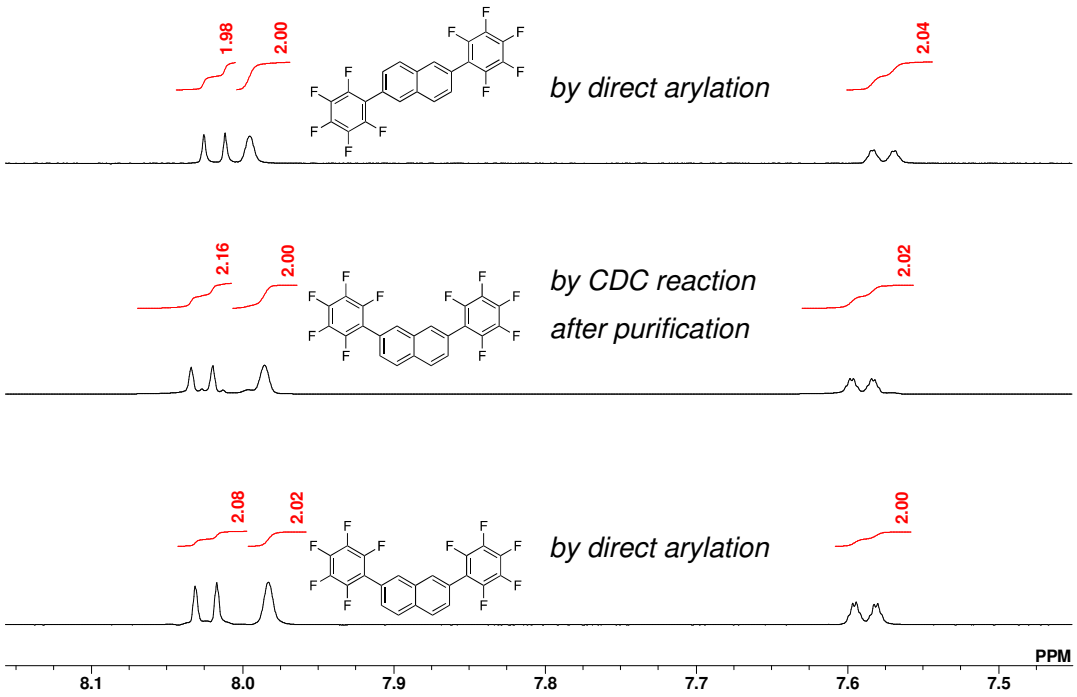


Figure S10. ^{1}H NMR spectra of 2,6-bis(pentafluorophenyl)naphthalene synthesised by the direct arylation reaction (top), 2,7-bis(pentafluorophenyl)naphthalene synthesised by the CDC reaction (middle), 2,7-bis(pentafluorophenyl)naphthalene synthesised by the direct arylation reaction (bottom) (600 MHz, $CDCl_3$, r.t.).

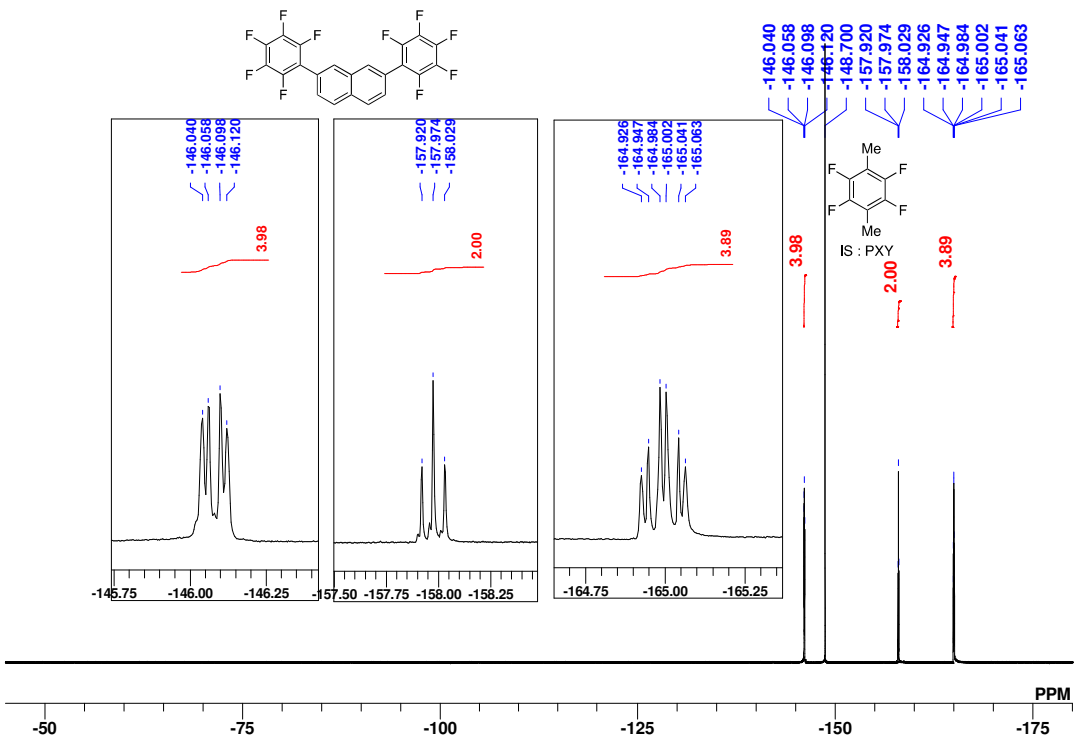


Figure S11. ^{19}F NMR spectrum of 2,7-bis(pentafluorophenyl)naphthalene synthesised by the CDC reaction (376 MHz, $CDCl_3$, r.t.).

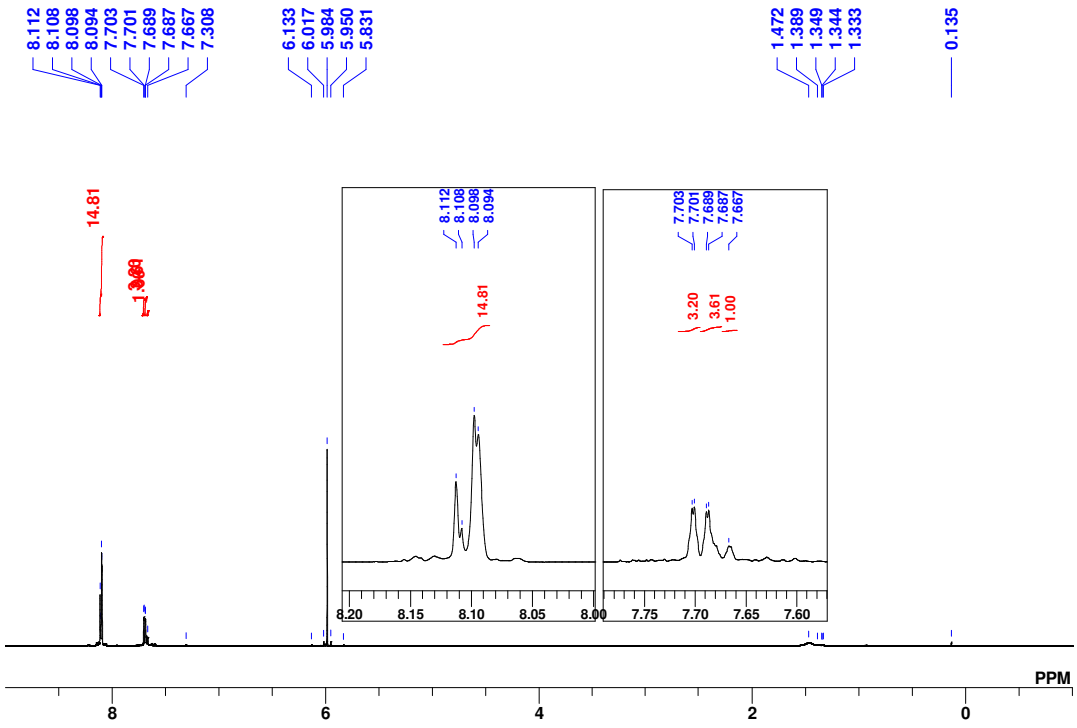


Figure S12. ^{1}H NMR spectrum of a mixture of bis(2,3,5,6-tetrafluoro-4-trifluoromethyl)naphthalene synthesised by the CDC reaction (600 MHz, 1,1,2,2,-tetrachloroethane-d_2, 373 K).

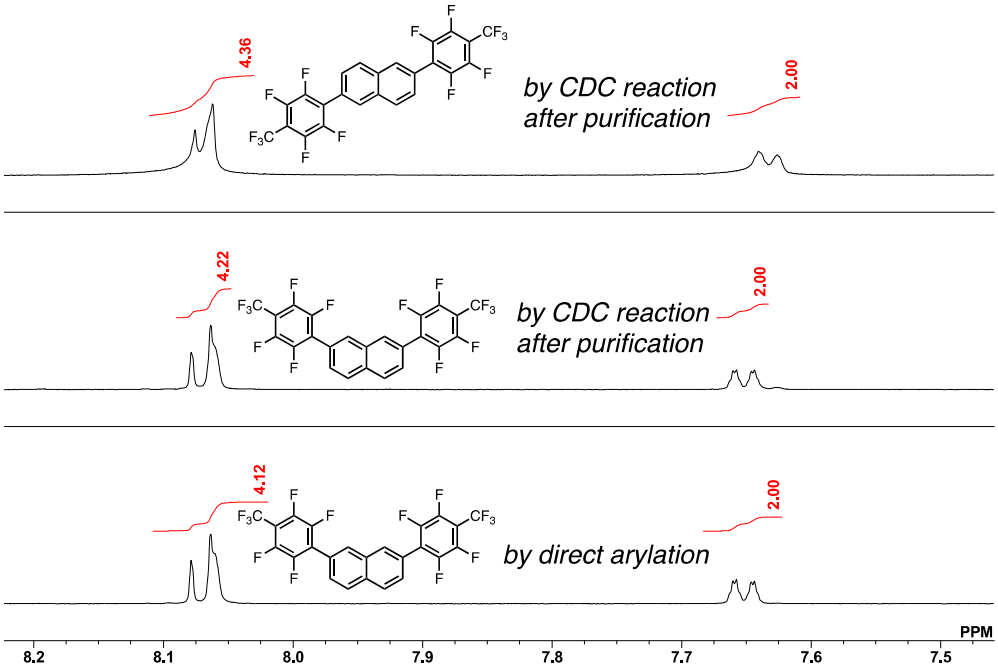


Figure S13. ^{1}H NMR spectra of 2,6-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the CDC reaction (top), 2,7-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the CDC reaction (middle), 2,7-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the direct arylation reaction (bottom) (600 MHz, $CDCl_3$, r.t.).

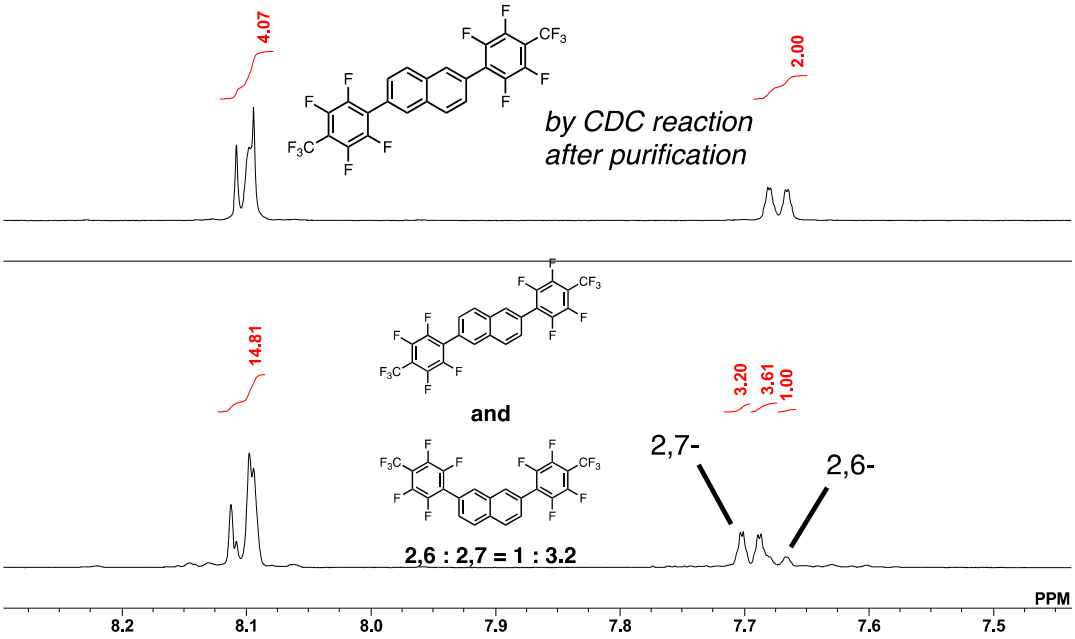


Figure S14. ^{1}H NMR spectra of isolated 2,6-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the CDC reaction (top) and a mixture of bis(2,3,5,6-tetrafluoro-4-trifluoromethyl)naphthalene synthesised by the CDC reaction (600 MHz, 1,1,2,2,-tetrachloroethane-d_2, 373 K).

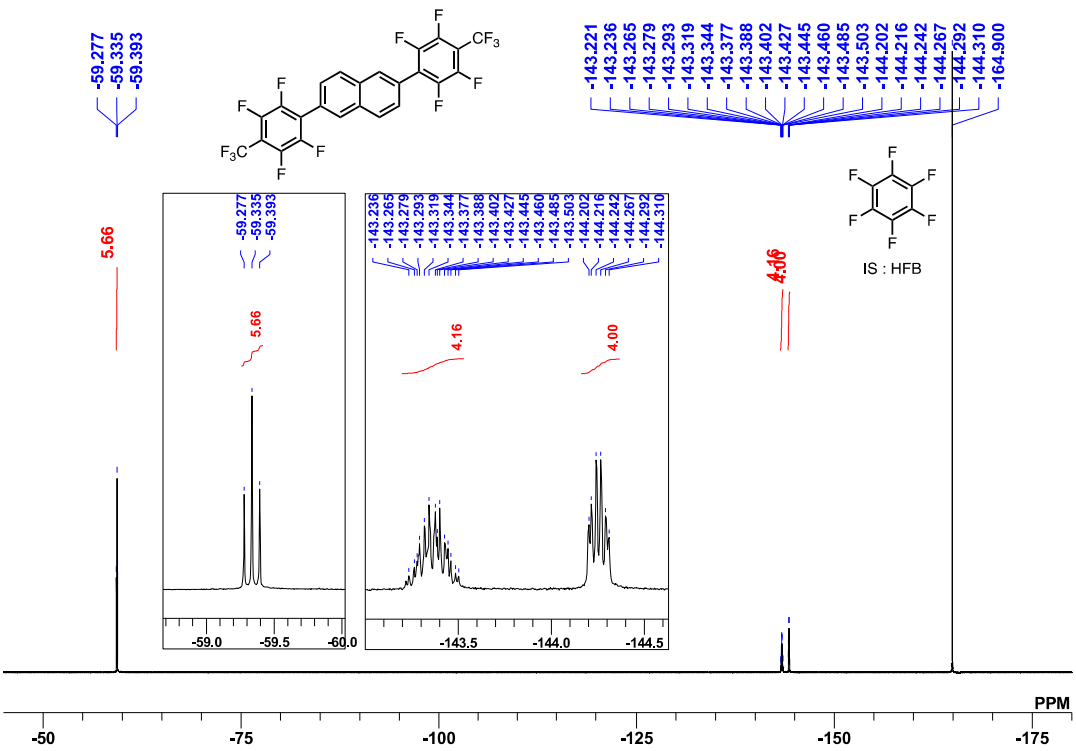


Figure S15. ^{19}F NMR spectrum of 2,6-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the CDC reaction (376 MHz, $CDCl_3$, r.t.).

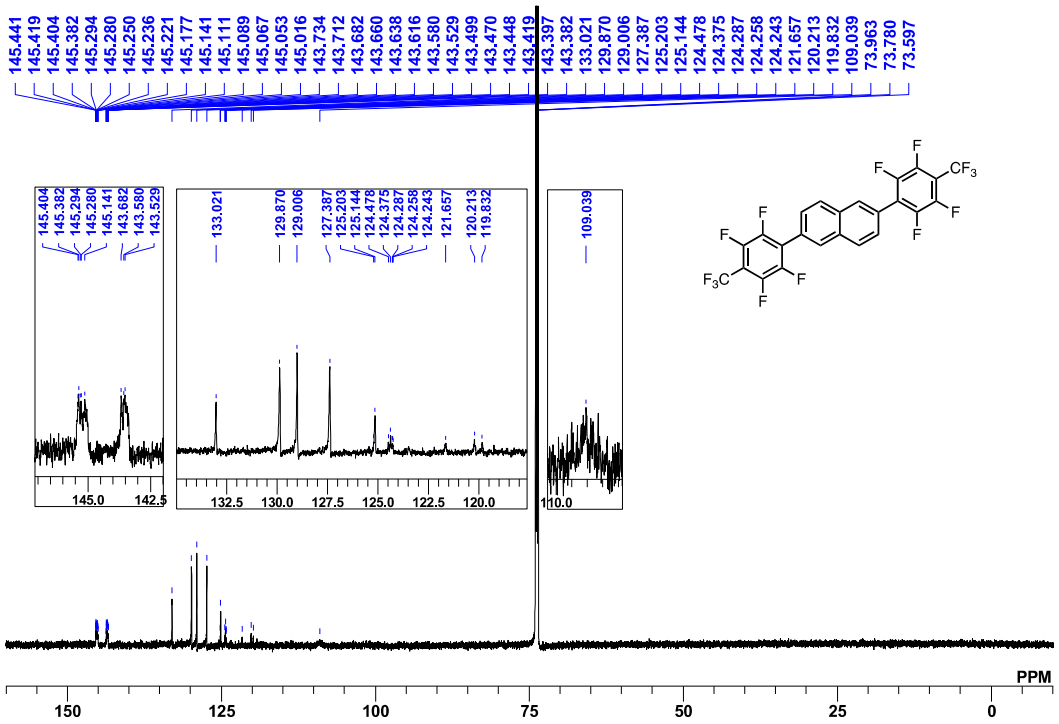


Figure S16. $^{13}C\{^1H\}$ NMR spectrum of 2,6- bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the CDC reaction (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

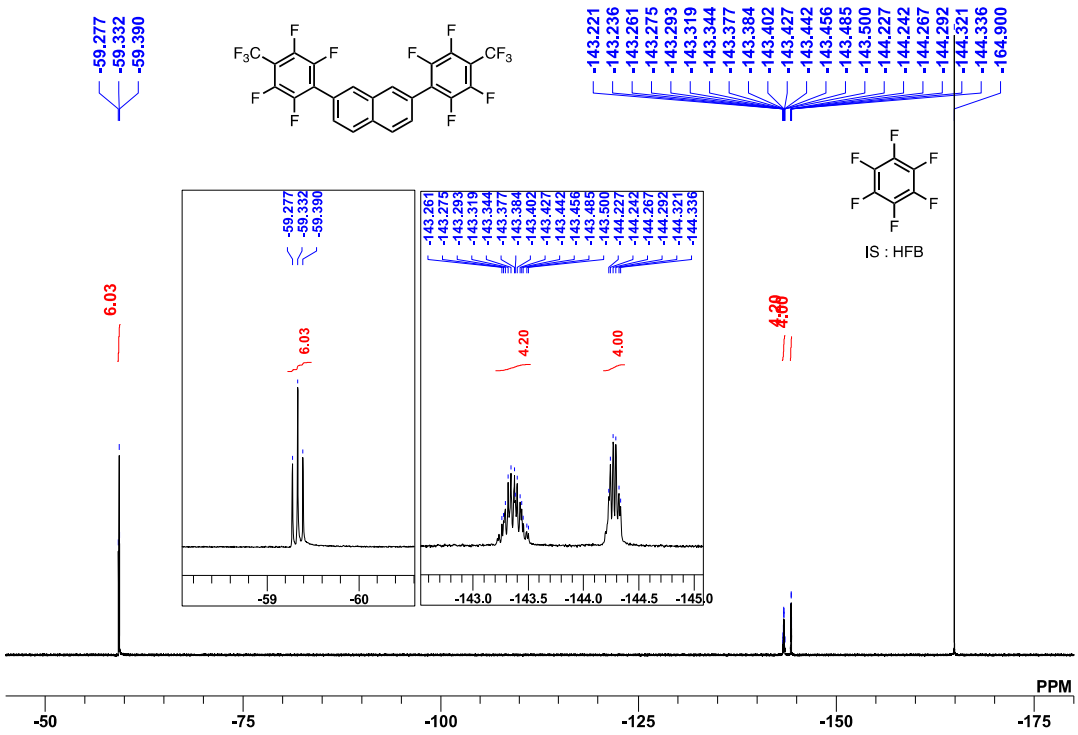


Figure S17. ^{19}F NMR spectrum of 2,7-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the CDC reaction (376 MHz, $CDCl_3$, r.t.).

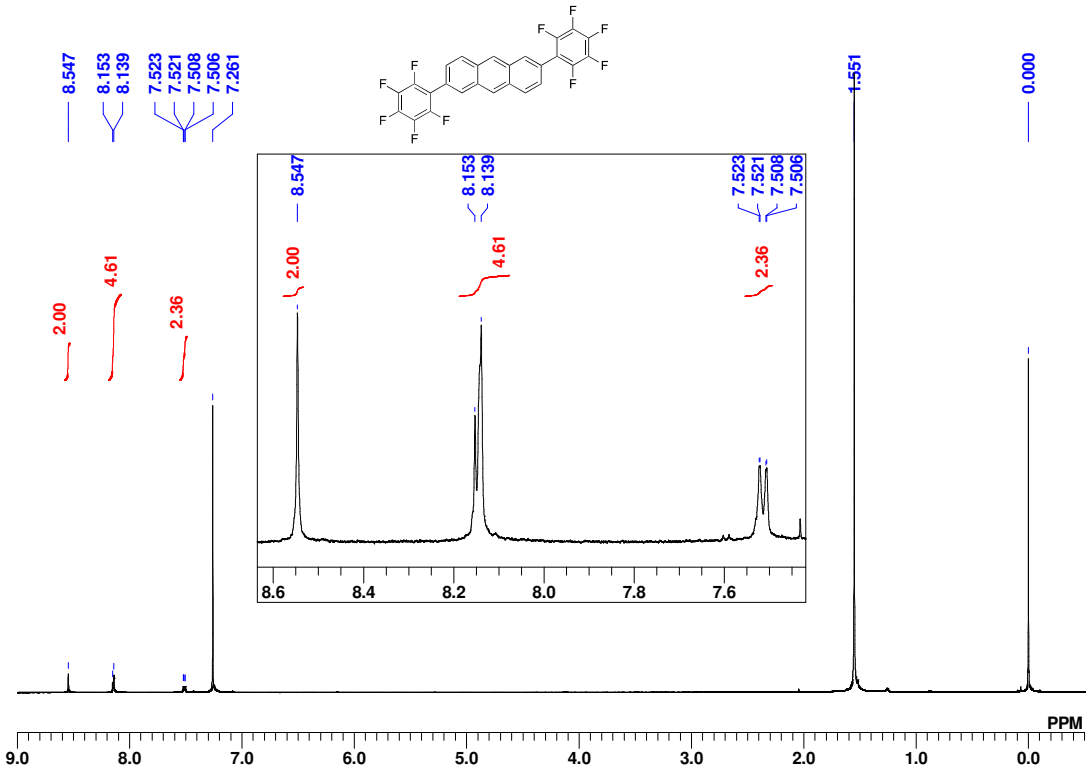


Figure S18. ^{1}H NMR spectrum of 2,6-bis(pentafluorophenyl)anthracene synthesised by the CDC reaction (600 MHz, $CDCl_3$, r.t.).

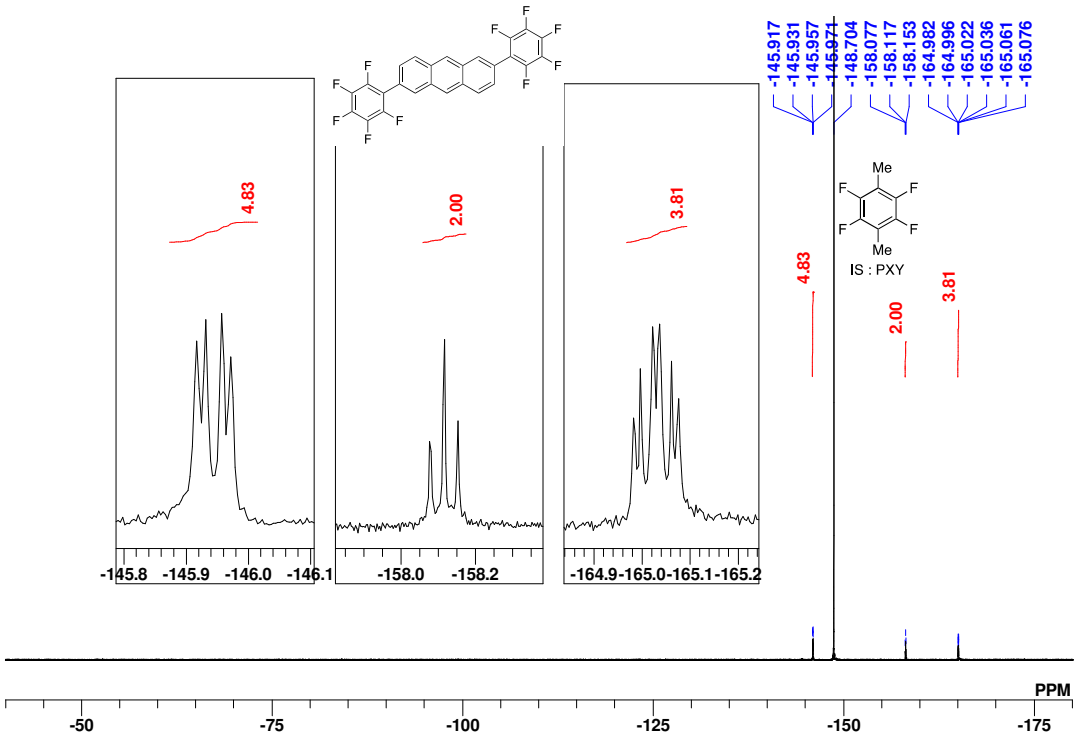


Figure S19. ^{19}F NMR spectrum of 2,6-bis(pentafluorophenyl)anthracene synthesised by the CDC reaction (565 MHz, $CDCl_3$, r.t.).

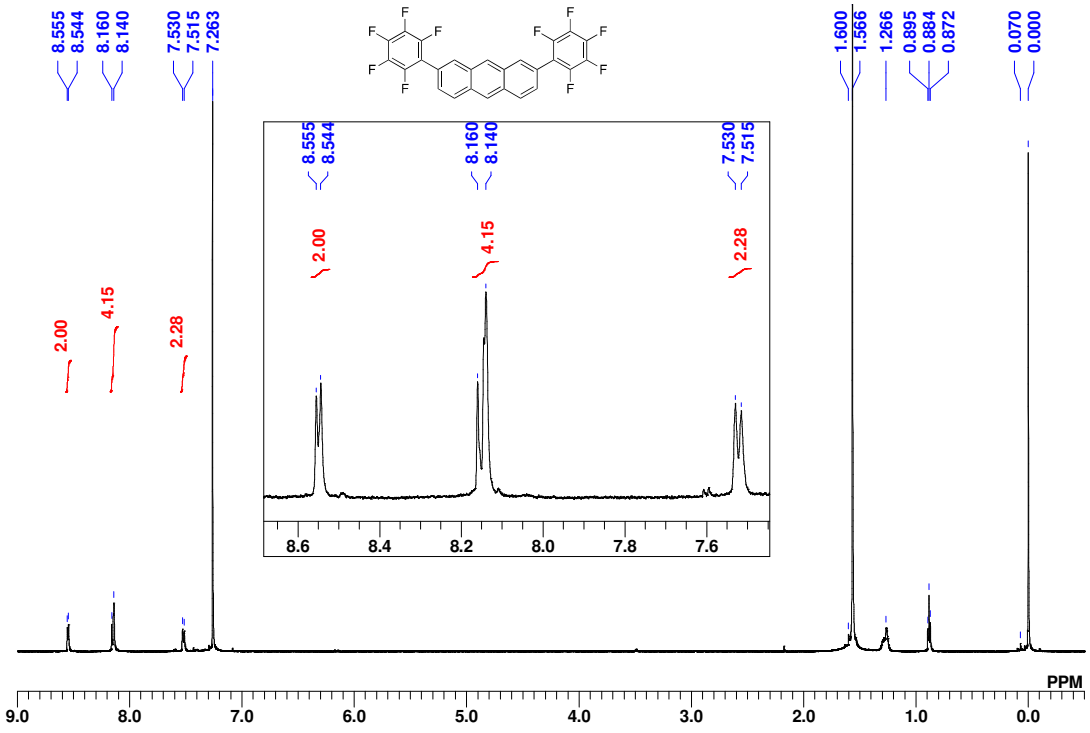


Figure S20. ^{1}H NMR spectrum of 2,7-bis(pentafluorophenyl)anthracene synthesised by the CDC reaction (600 MHz, $CDCl_3$, r.t.).

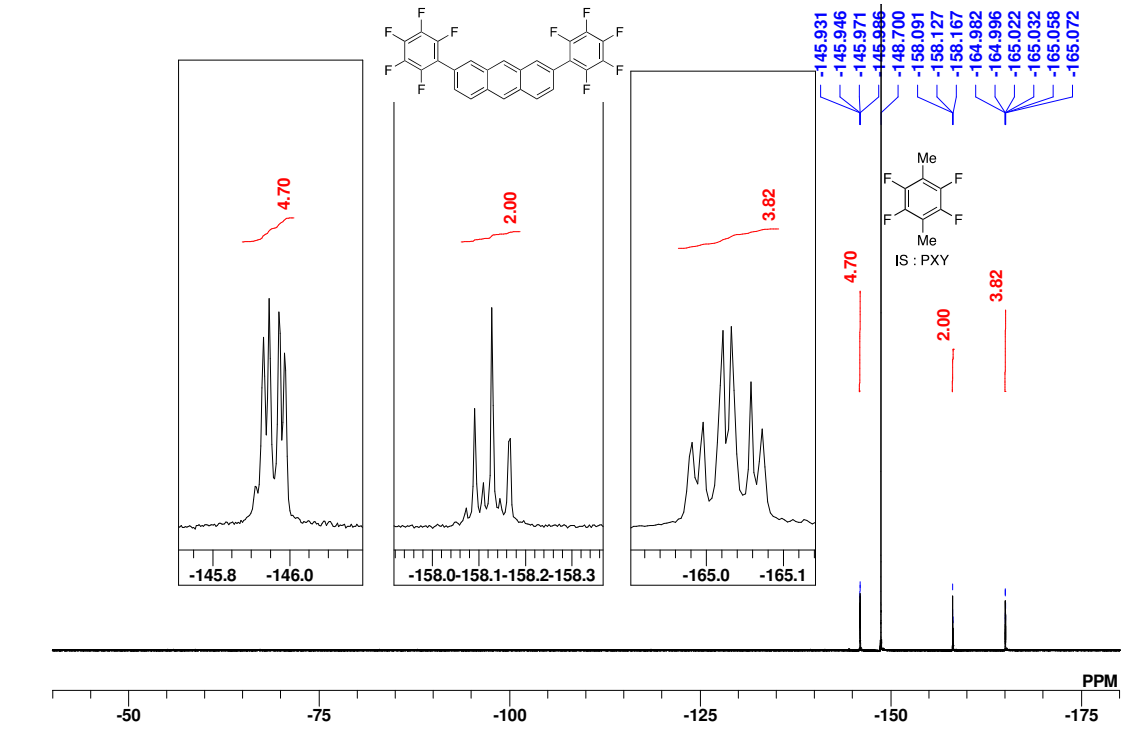


Figure S21. ^{19}F NMR spectrum of 2,7-bis(pentafluorophenyl)anthracene synthesised by the CDC reaction (565 MHz, $CDCl_3$, r.t.).

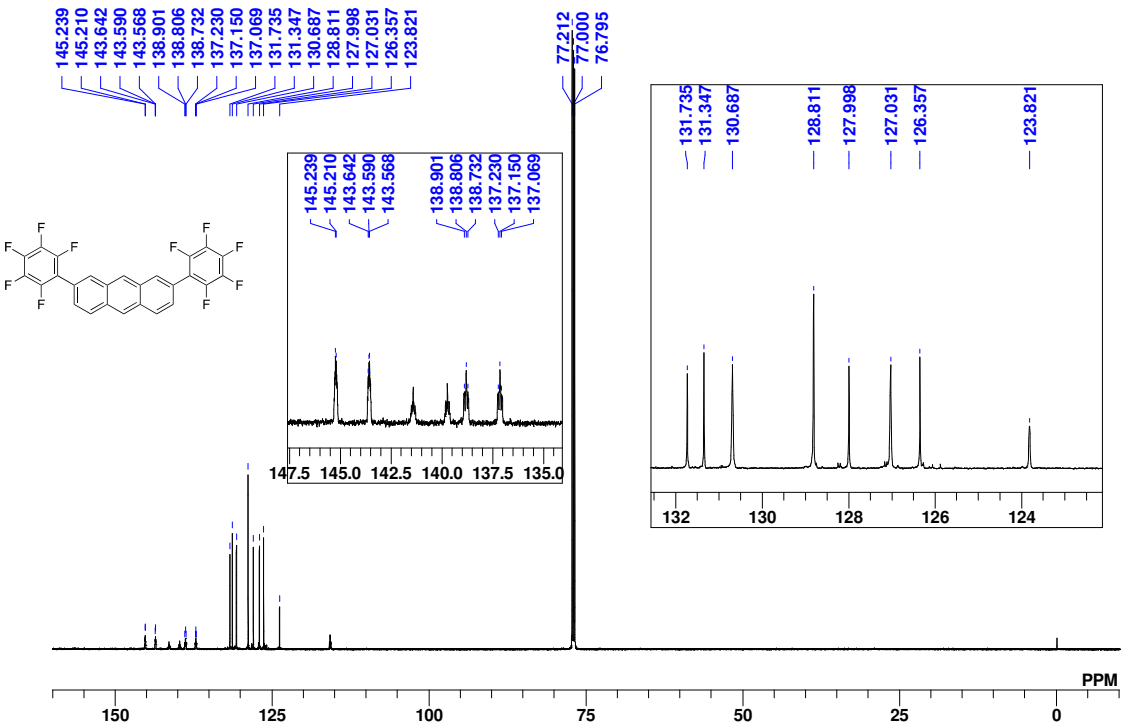


Figure S22. ^{13}C{^{1}H} NMR spectrum of 2,7-bis(pentafluorophenyl)anthracene synthesised by the CDC reaction (150 MHz, $CDCl_3$, r.t.).

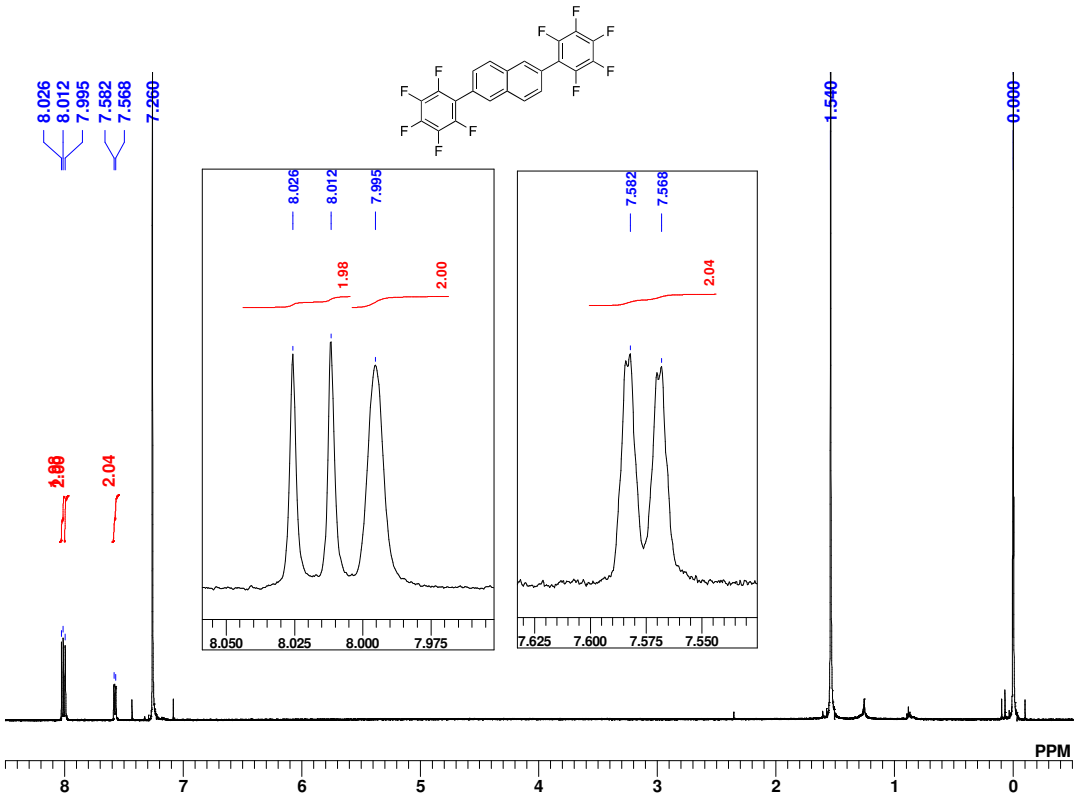


Figure S23. ^{1}H NMR spectrum of 2,6-bis(pentafluorophenyl)naphthalene synthesised by the direct C-H arylation reaction (600 MHz, $CDCl_3$, r.t.).

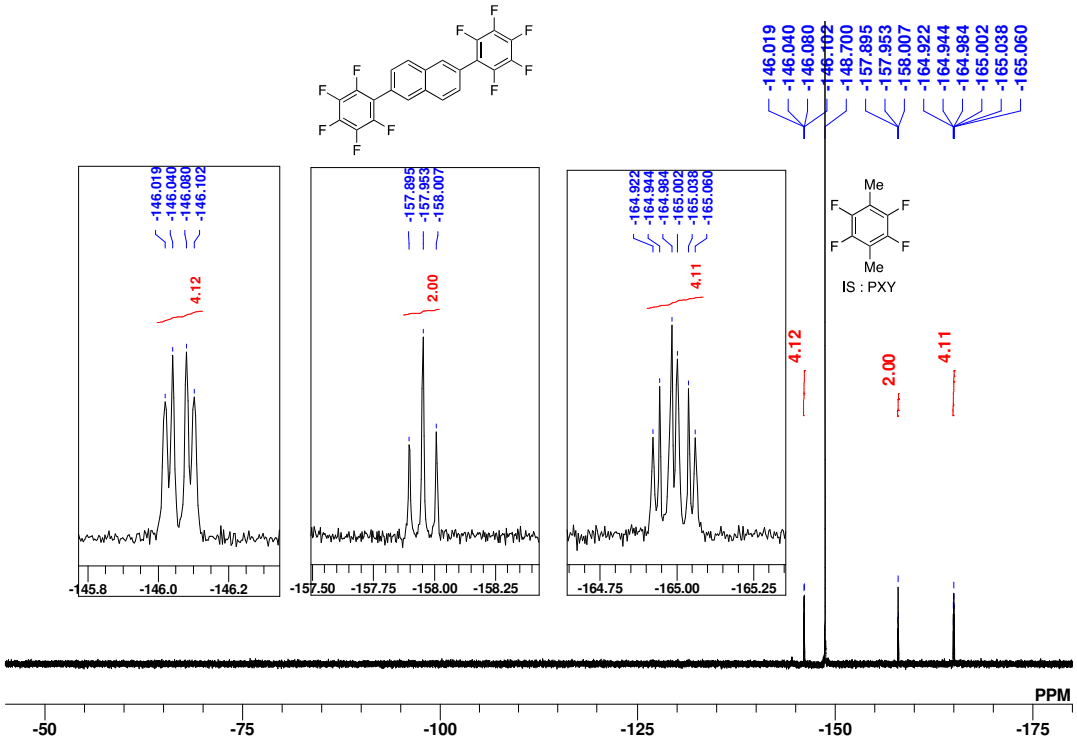


Figure S24. ^{19}F NMR spectrum of 2,6-bis(pentafluorophenyl)naphthalene synthesised by the direct C-H arylation reaction (376 MHz, $CDCl_3$, r.t.).

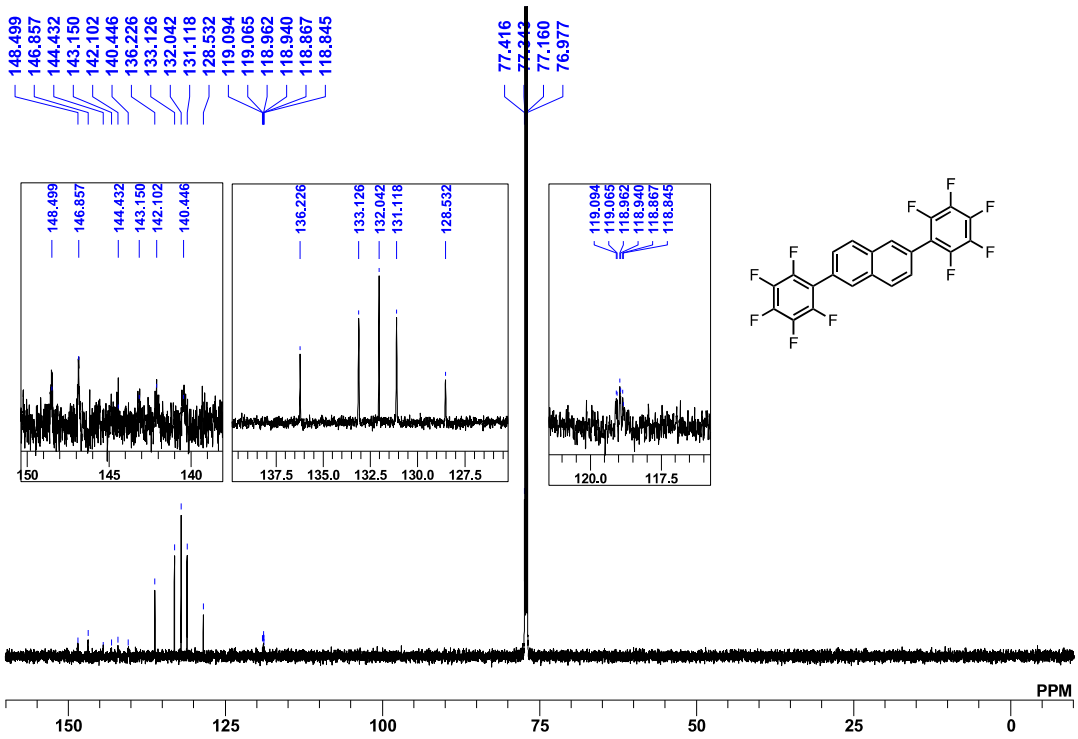


Figure S25. $^{13}C\{^{1}H\}$ NMR spectrum of 2,6-bis(pentafluorophenyl)naphthalene synthesised by the direct C-H arylation reaction (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

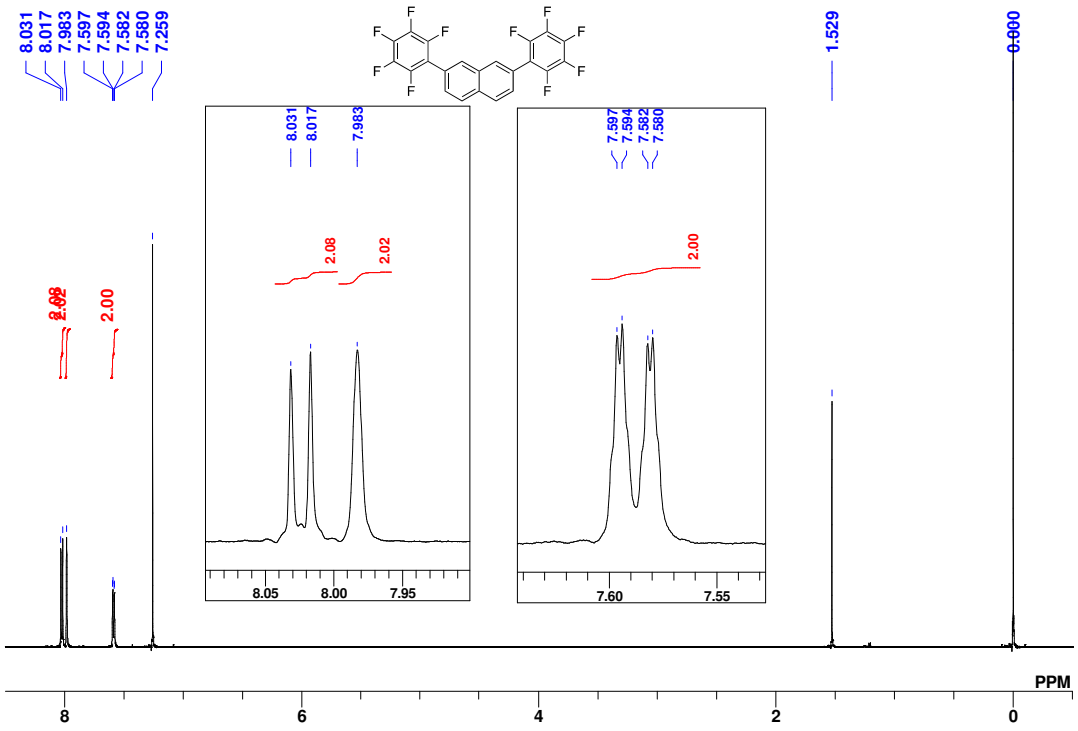


Figure S26. ^{1}H NMR spectrum of 2,7-bis(pentafluorophenyl)naphthalene synthesised by the direct C-H arylation reaction (600 MHz, $CDCl_3$, r.t.).

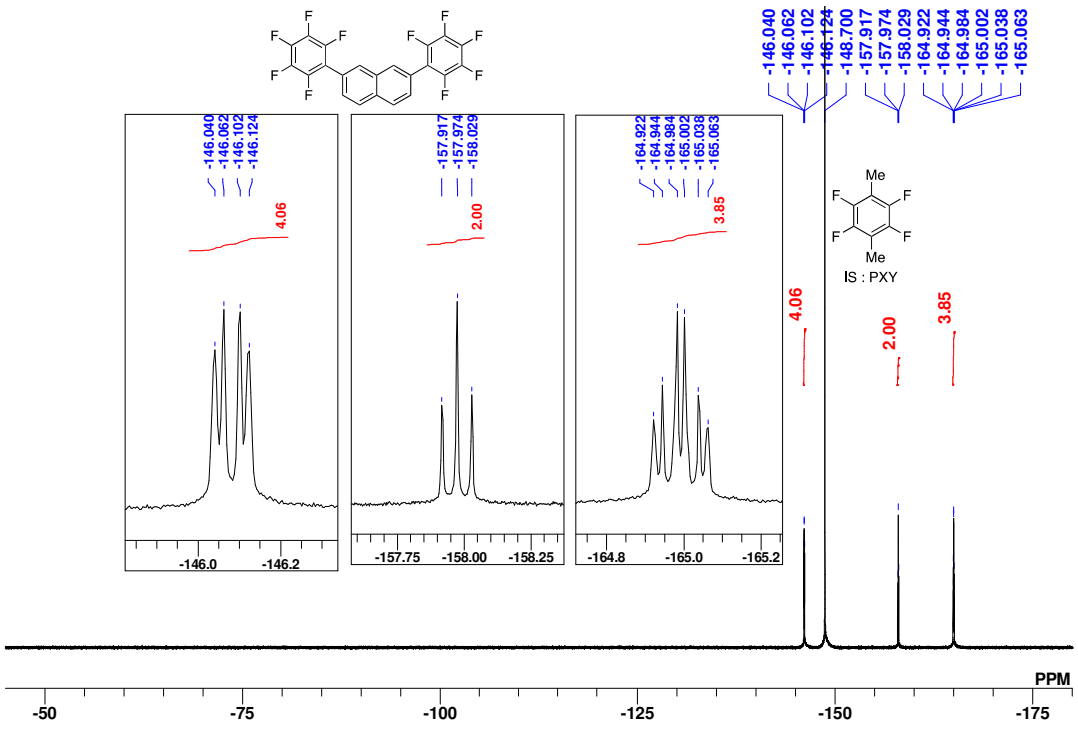


Figure S27. ^{19}F NMR spectrum of 2,7-bis(pentafluorophenyl)naphthalene synthesised by the direct C-H arylation reaction (376 MHz, $CDCl_3$, r.t.).

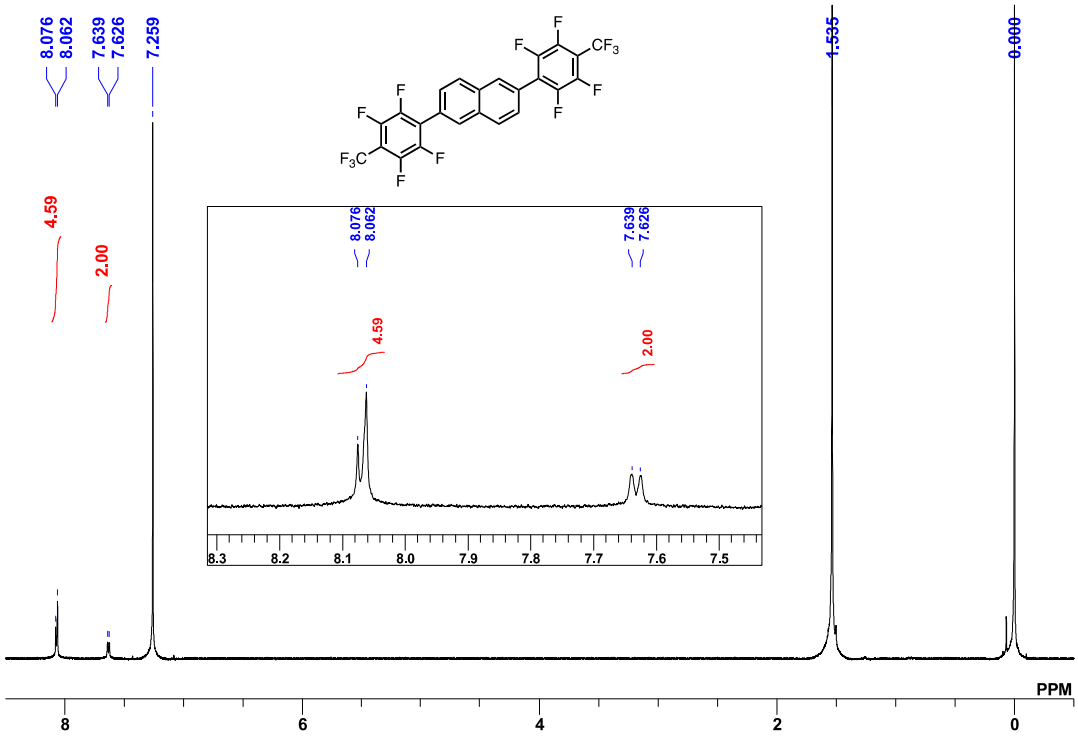


Figure S28. ^{1}H NMR spectra of 2,6-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the direct C-H arylation reaction (600 MHz, $CDCl_3$, r.t.).

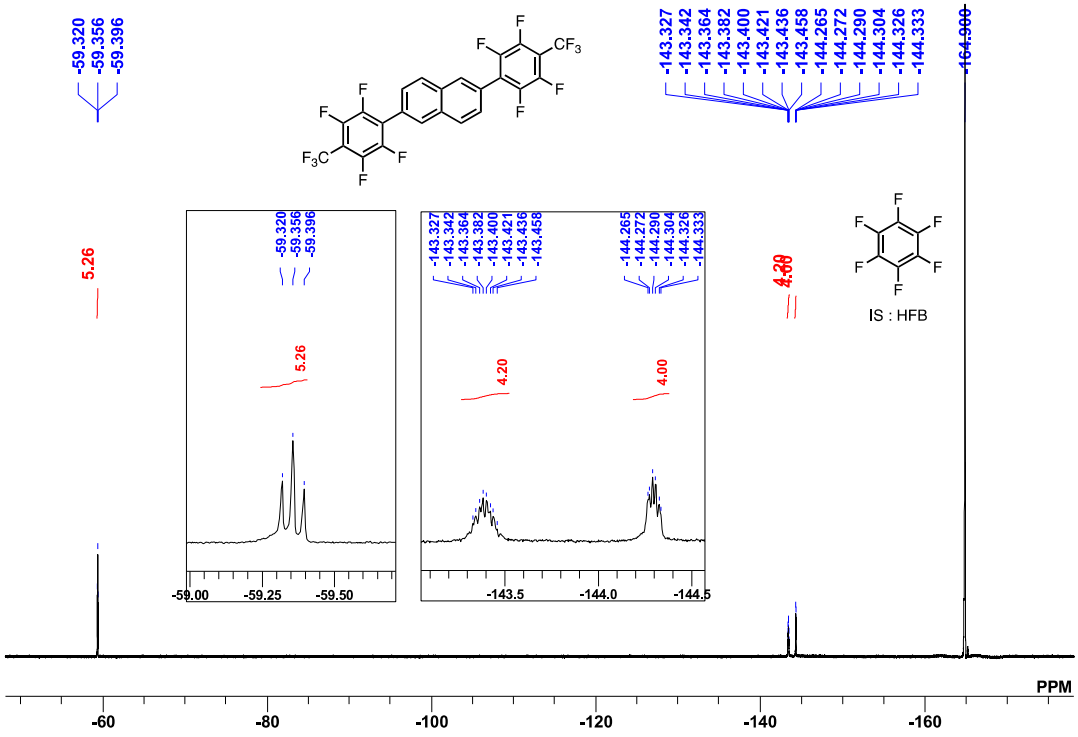


Figure S29. ^{19}F NMR spectrum of 2,6-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the direct C-H arylation reaction (565 MHz, $CDCl_3$, r.t.).

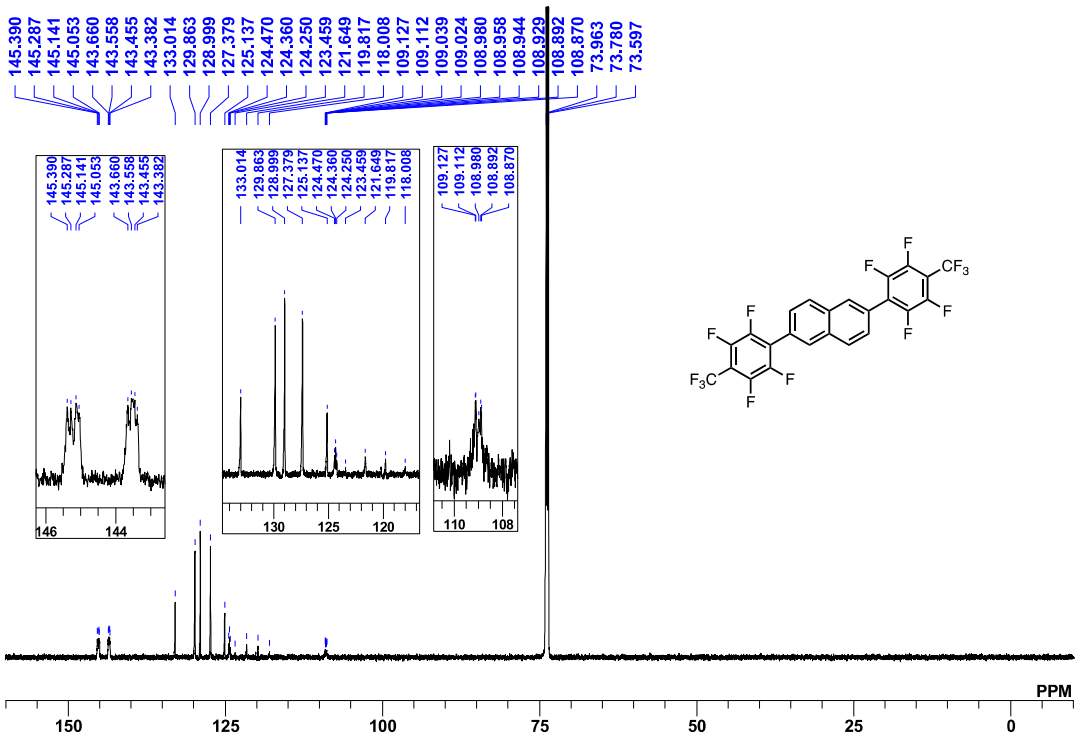


Figure S30. ^{13}C NMR spectra of 2,6-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the direct C-H arylation reaction (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

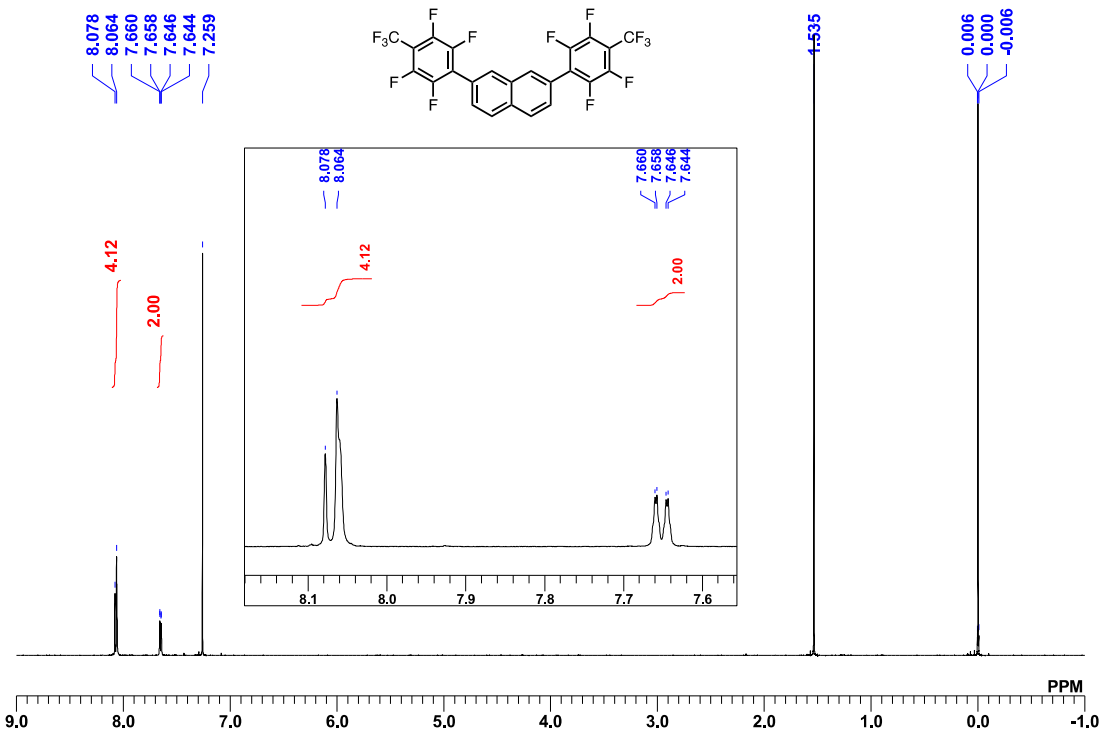


Figure S31. ^{1}H NMR spectra of 2,7-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the direct C-H arylation reaction (400 MHz, $CDCl_3$, r.t.).

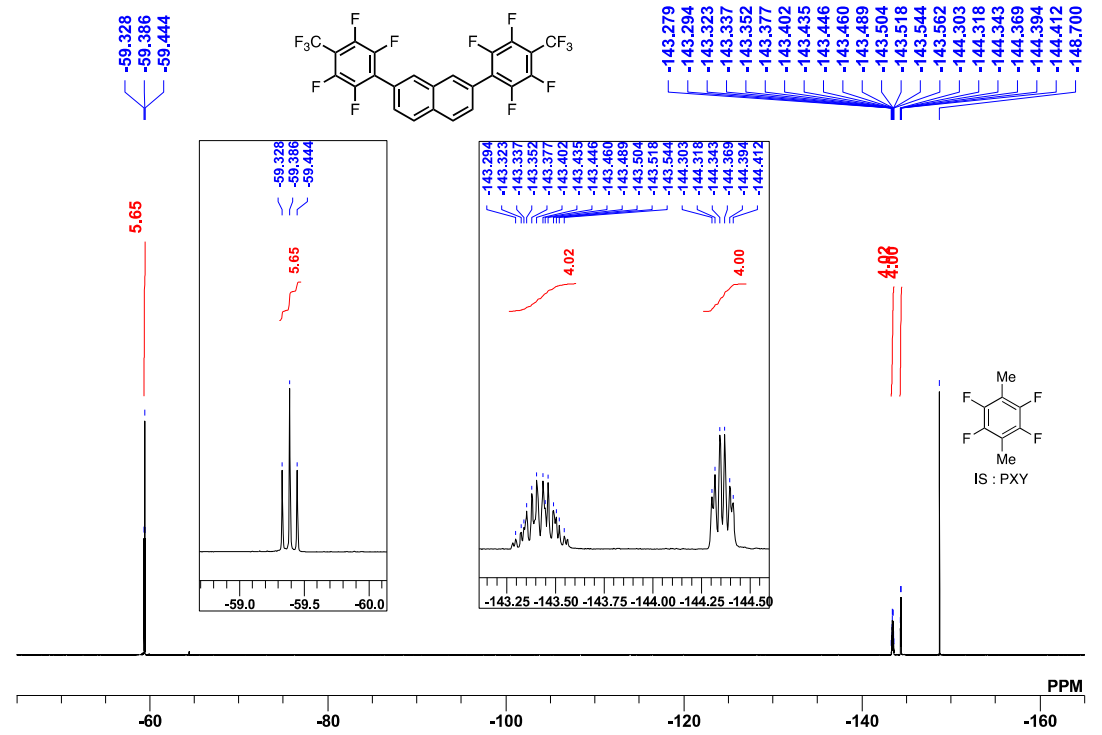


Figure S32. ^{19}F NMR spectra of 2,7-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the direct C-H arylation reaction (376 MHz, $CDCl_3$, r.t.).

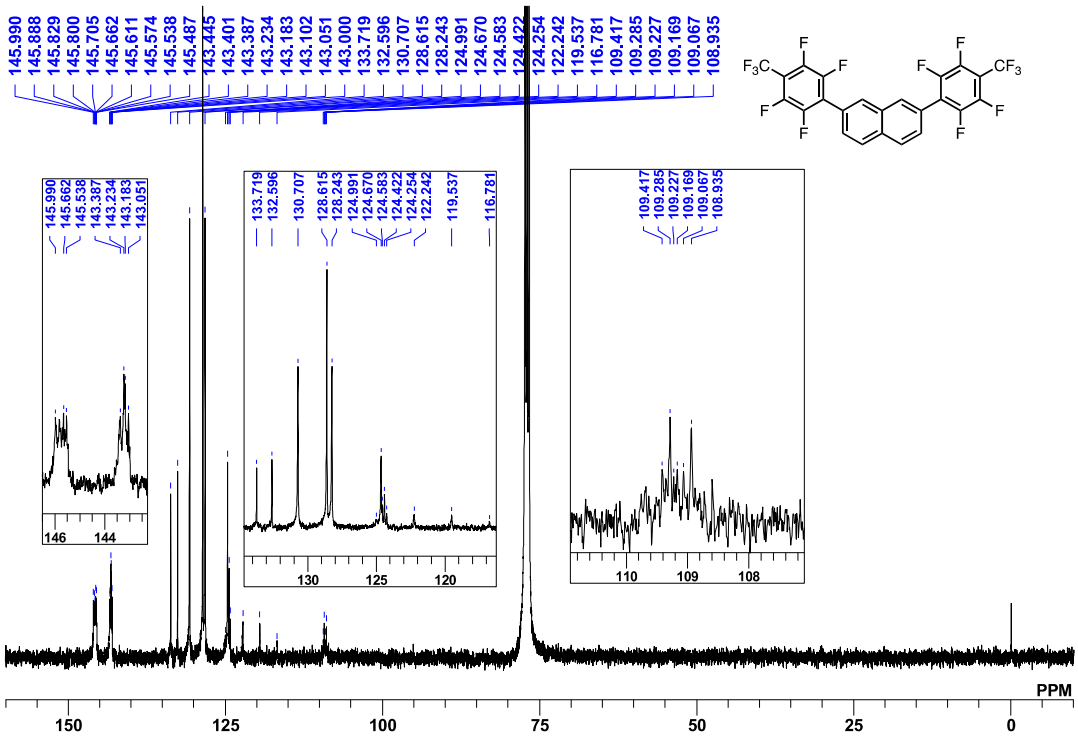


Figure S33. ^{13}C NMR spectrum of 2,7-bis((2,3,5,6-tetrafluoro-4-trifluoromethyl)phenyl)naphthalene synthesised by the direct C-H arylation reaction (100 MHz, $CDCl_3$, r.t.).

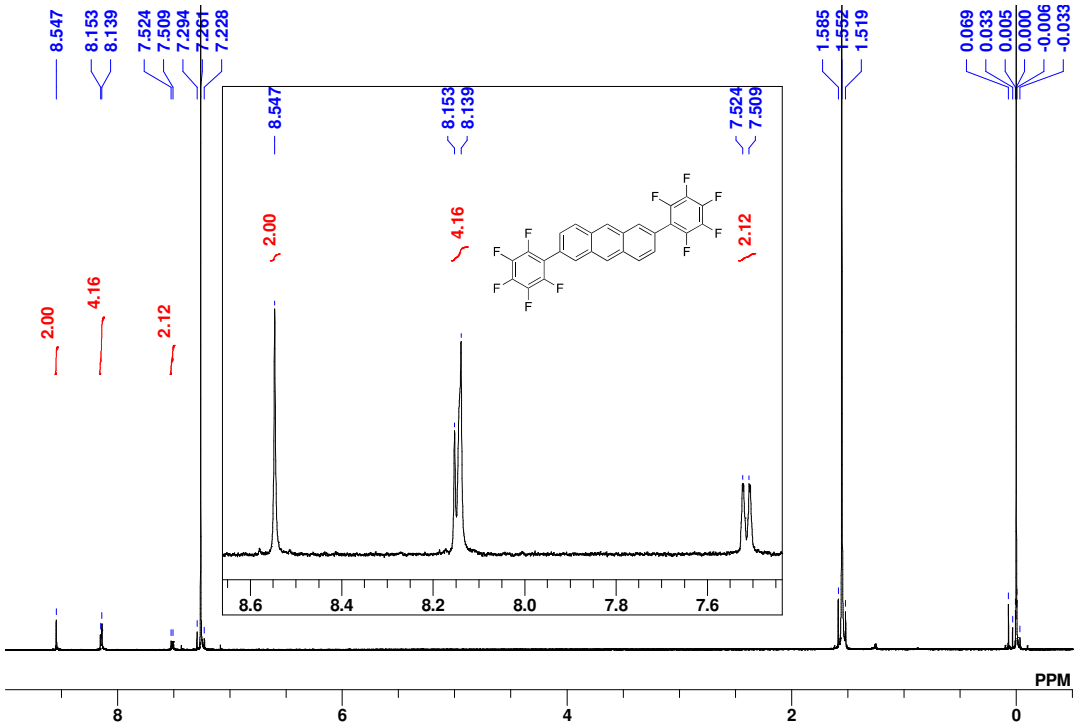


Figure S34. ^{1}H NMR spectrum of 2,6-bis(pentafluorophenyl)anthracene synthesised by the direct C-H arylation reaction (600 MHz, $CDCl_3$, r.t.).

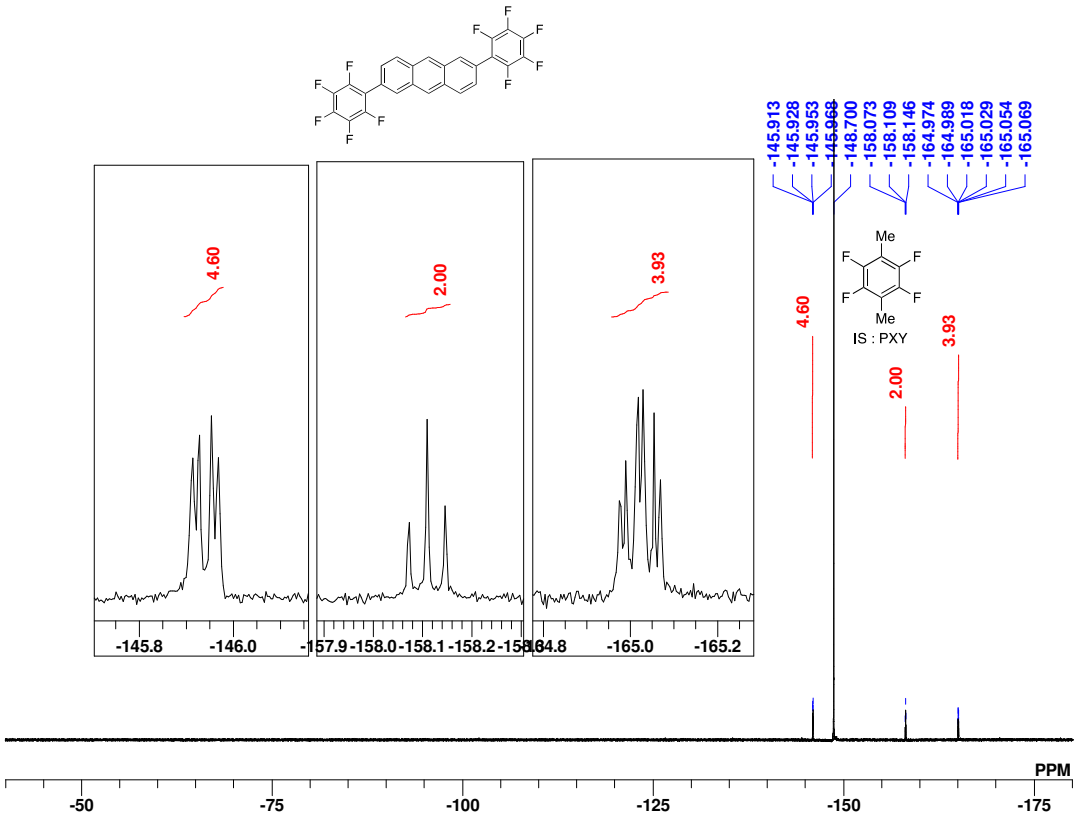


Figure S35. ^{19}F NMR spectrum of 2,6-bis(pentafluorophenyl)anthracene synthesised by the direct C-H arylation reaction (565 MHz, $CDCl_3$, r.t.).

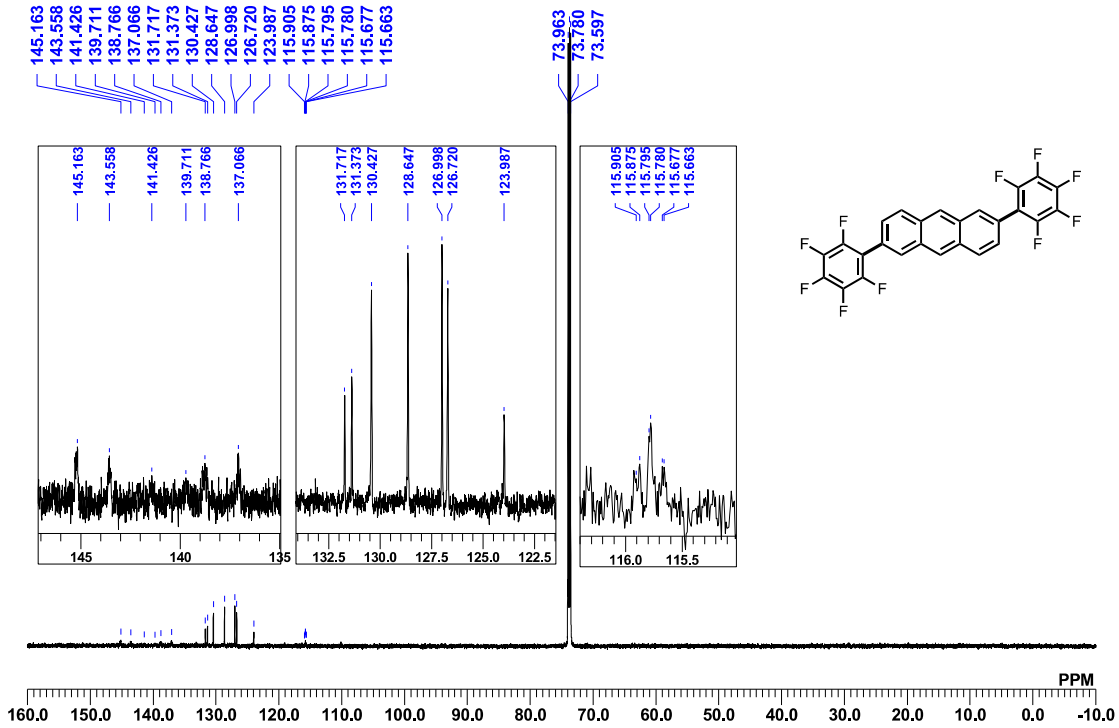


Figure S36. $^{13}C\{^1H\}$ NMR spectrum of 2,6-bis(pentafluorophenyl)anthracene synthesised by the direct C-H arylation reaction (150 MHz, 1,1,2,2-tetrachloroethane-d_2, 373 K).

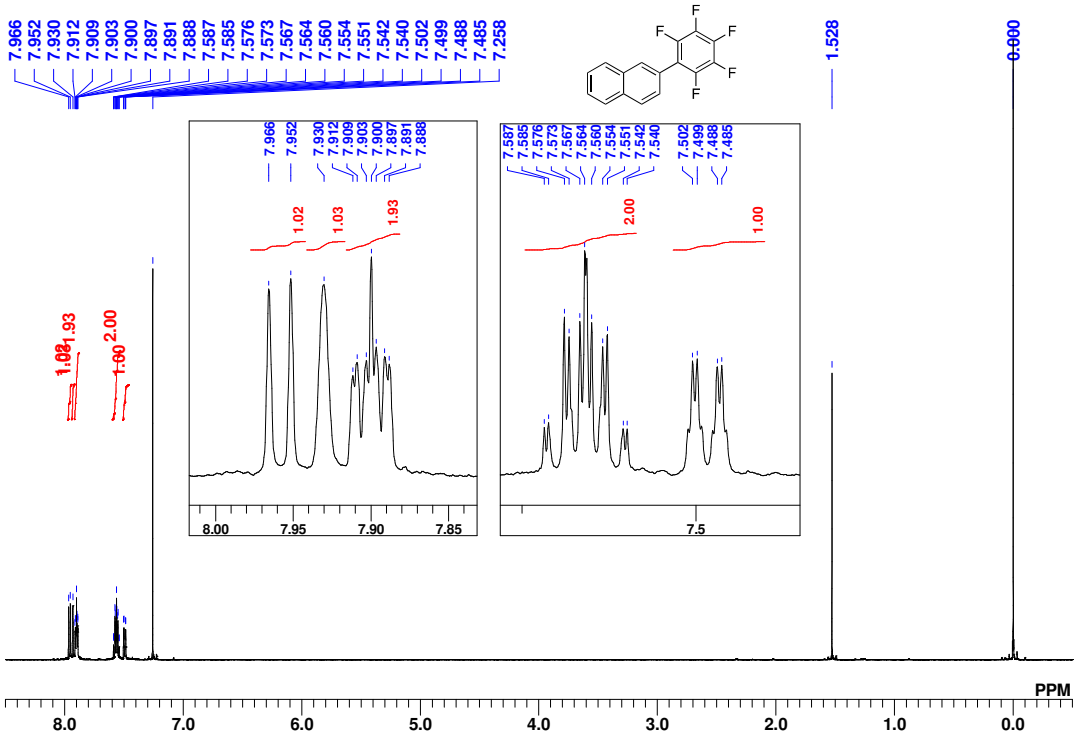


Figure S37. ^{1}H NMR spectrum of 2-pentafluorophenylnaphthalene synthesised by the CDC reaction (600 MHz, $CDCl_3$, r.t.).

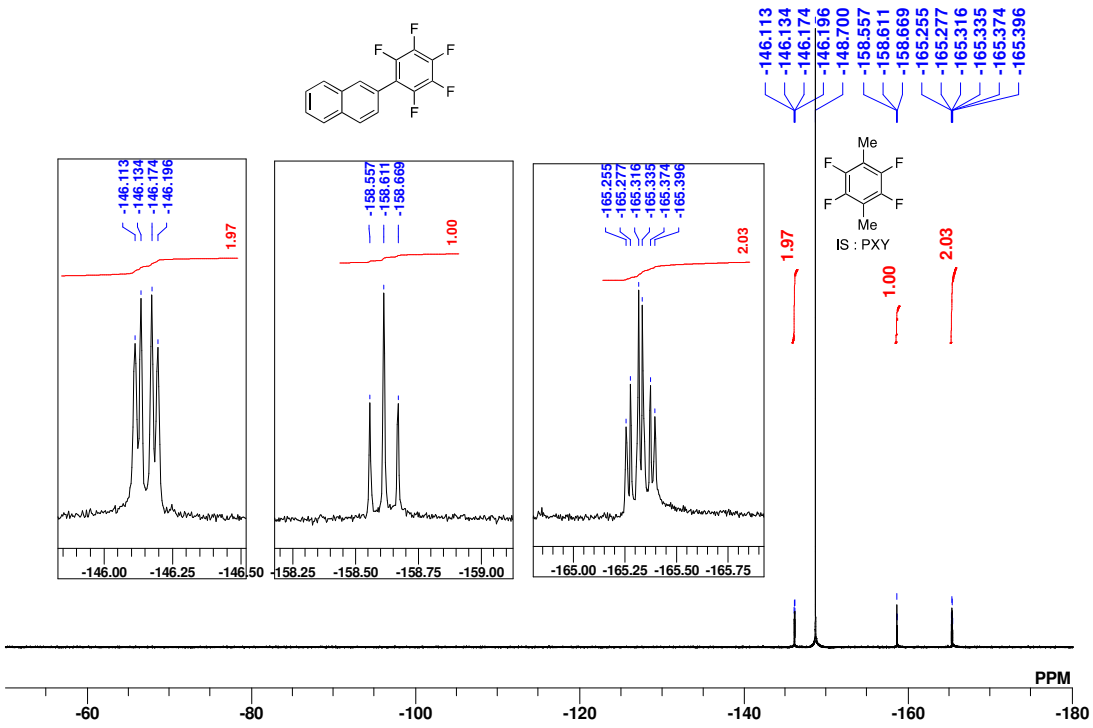


Figure S38. ^{19}F NMR spectrum of 2-pentafluorophenylnaphthalene synthesised by the CDC reaction (376 MHz, $CDCl_3$, r.t.).

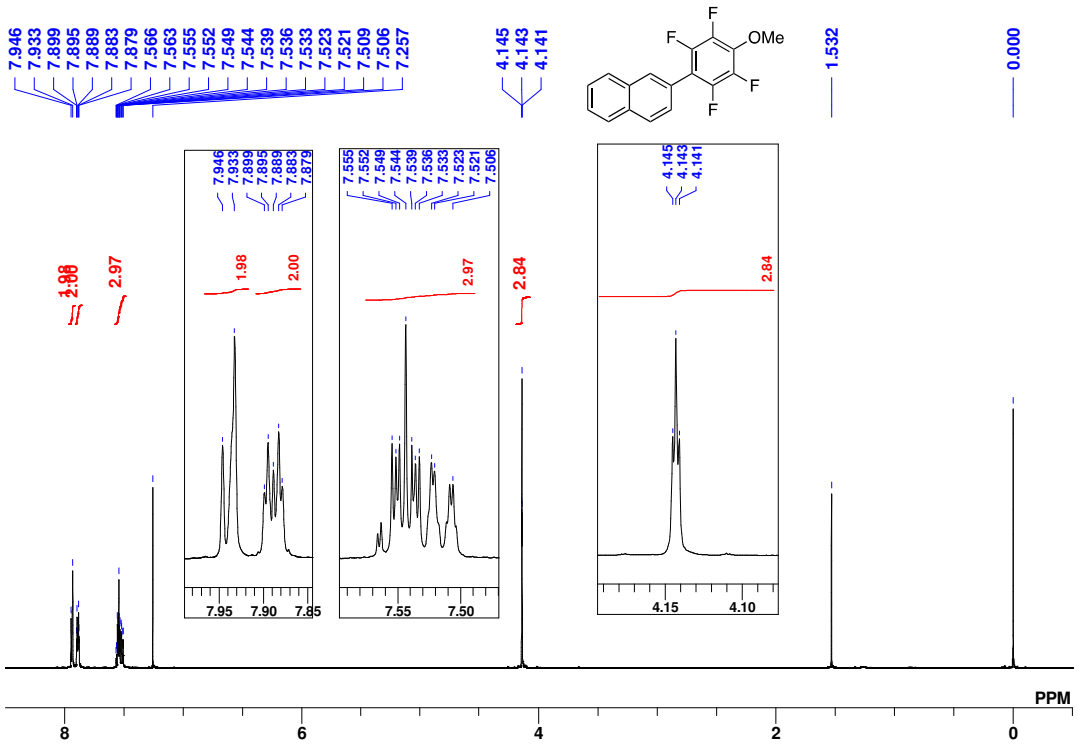


Figure S39. ^{1}H NMR spectrum of 2-(2,3,5,6-tetrafluoro-4-methoxy)phenylnaphthalene synthesised by the CDC reaction (600 MHz, $CDCl_3$, r.t.).

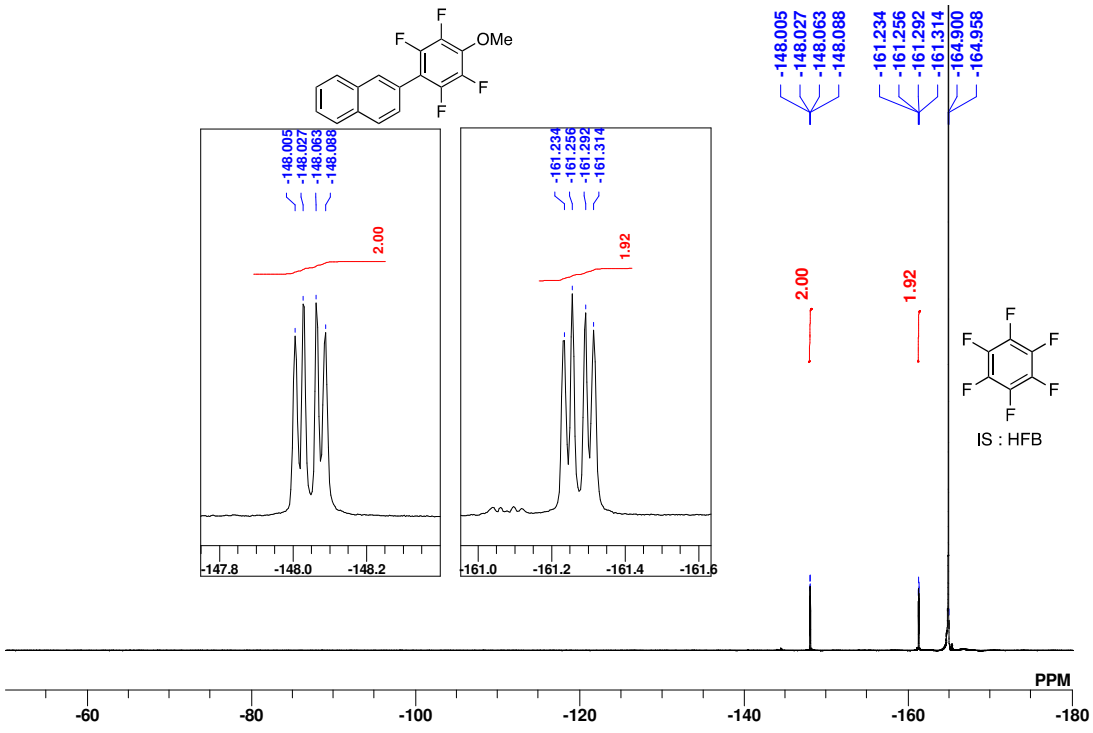


Figure S40. ^{19}F NMR spectrum of 2-(2,3,5,6-tetrafluoro-4-methoxy)phenylnaphthalene synthesised by the CDC reaction (376 MHz, $CDCl_3$, r.t.).

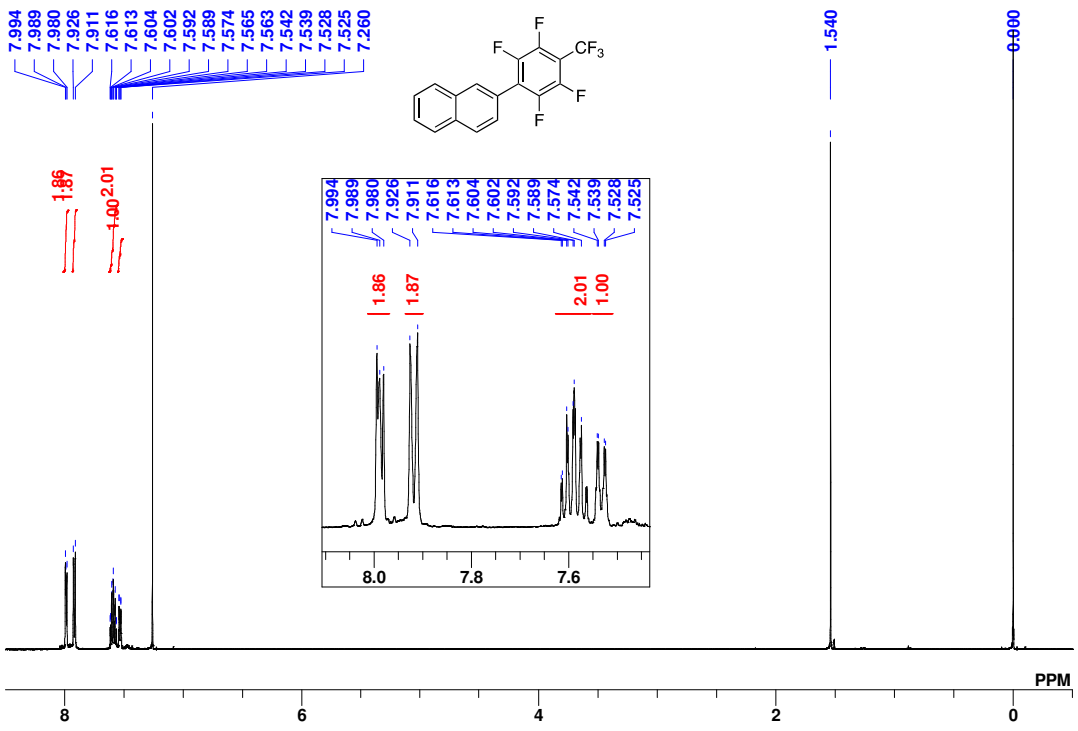


Figure S41. ^{1}H NMR spectrum of 2-(2,3,5,6-tetrafluoro-4-trifluoromethyl)phenylnaphthalene synthesised by the CDC reaction (600 MHz, $CDCl_3$, r.t.).

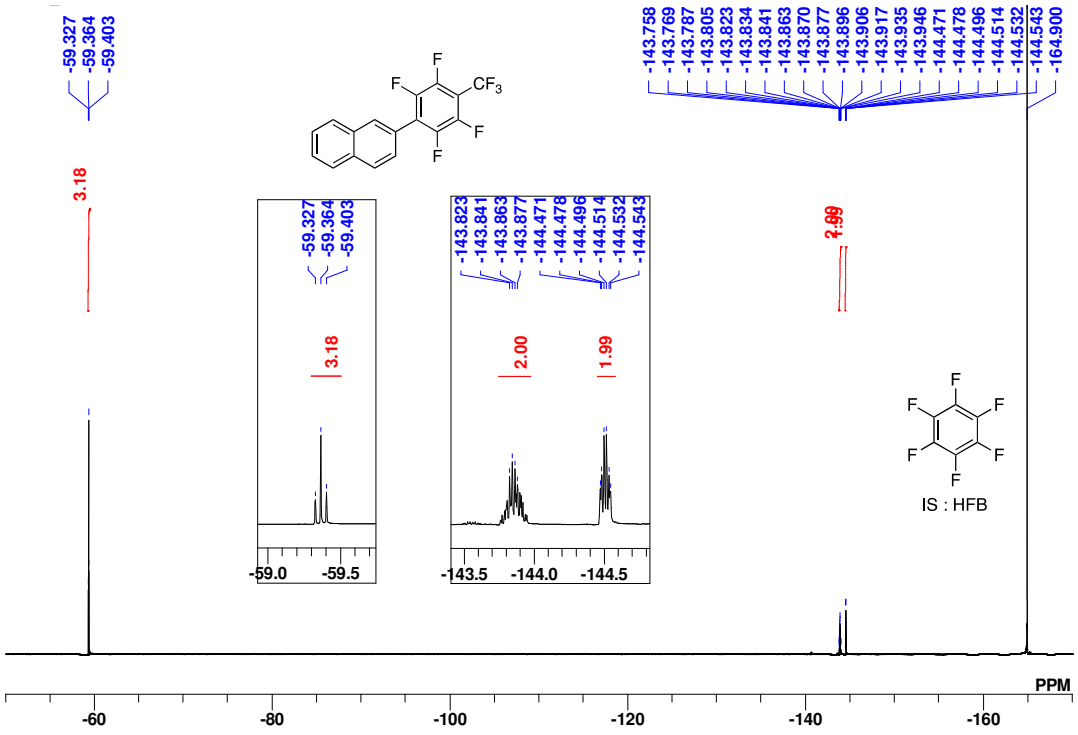


Figure S42. ^{19}F NMR spectrum of 2-(2,3,5,6-tetrafluoro-4-trifluoromethyl)phenylnaphthalene synthesised by the CDC reaction (376 MHz, $CDCl_3$, r.t.).

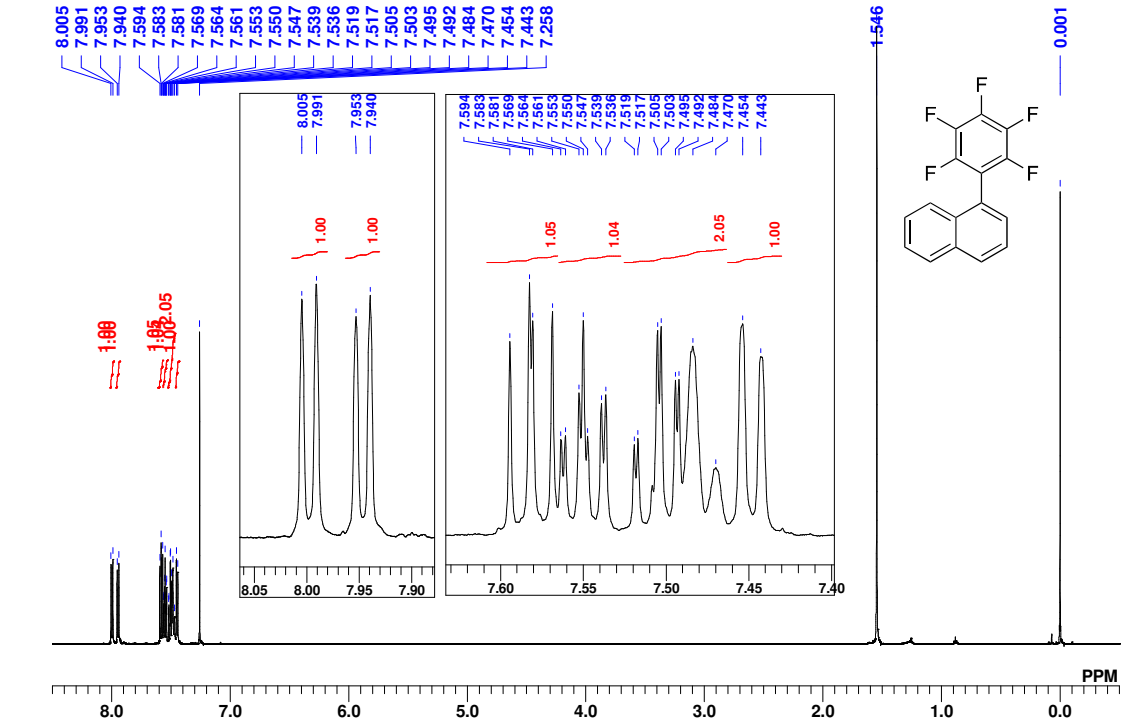


Figure S43. ^{1}H NMR spectrum of 1-(pentafluorophenyl)naphthalene synthesised by the direct C-H arylation reaction (600 MHz, $CDCl_3$, r.t.).

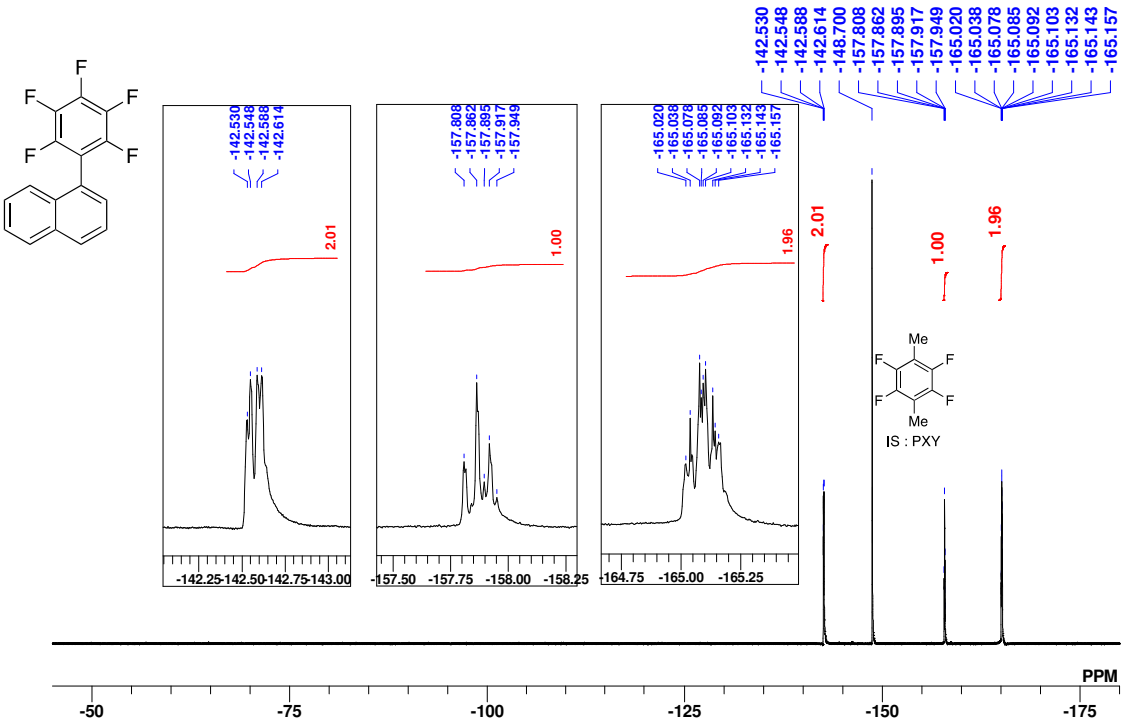


Figure S44. ^{19}F NMR spectrum of 1-(pentafluorophenyl)naphthalene synthesised by the direct C-H arylation reaction (376 MHz, $CDCl_3$, r.t.).

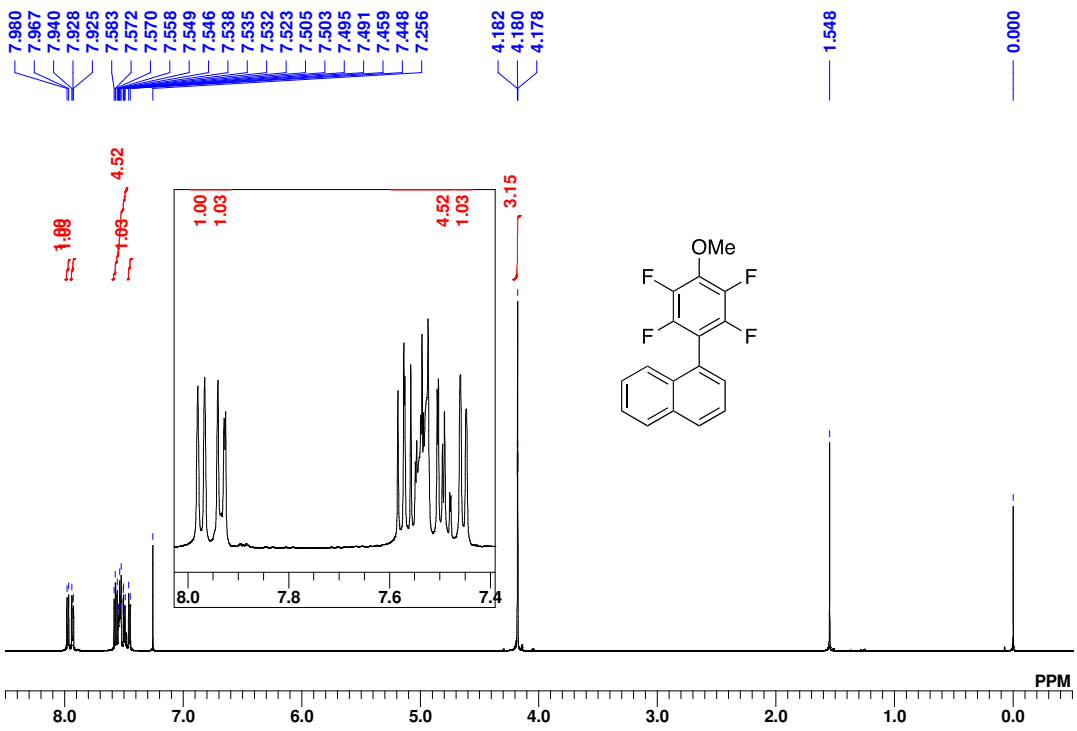


Figure S45. ^{1}H NMR spectrum of 1-(2,3,5,6-tetrafluoro-4-methoxy)phenylnaphthalene synthesised by the direct C-H arylation reaction (600 MHz, $CDCl_3$, r.t.).

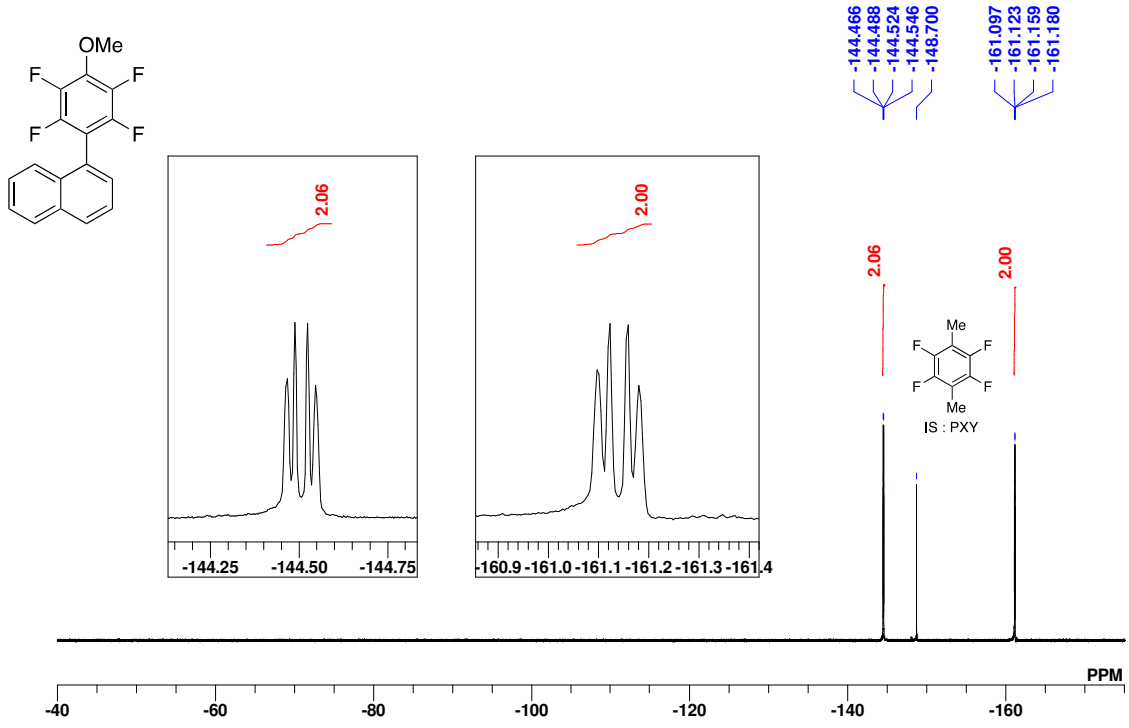


Figure S46. ^{19}F NMR spectrum of 1-(2,3,5,6-tetrafluoro-4-methoxy)phenylnaphthalene synthesised by the direct C-H arylation reaction (376 MHz, $CDCl_3$, r.t.).

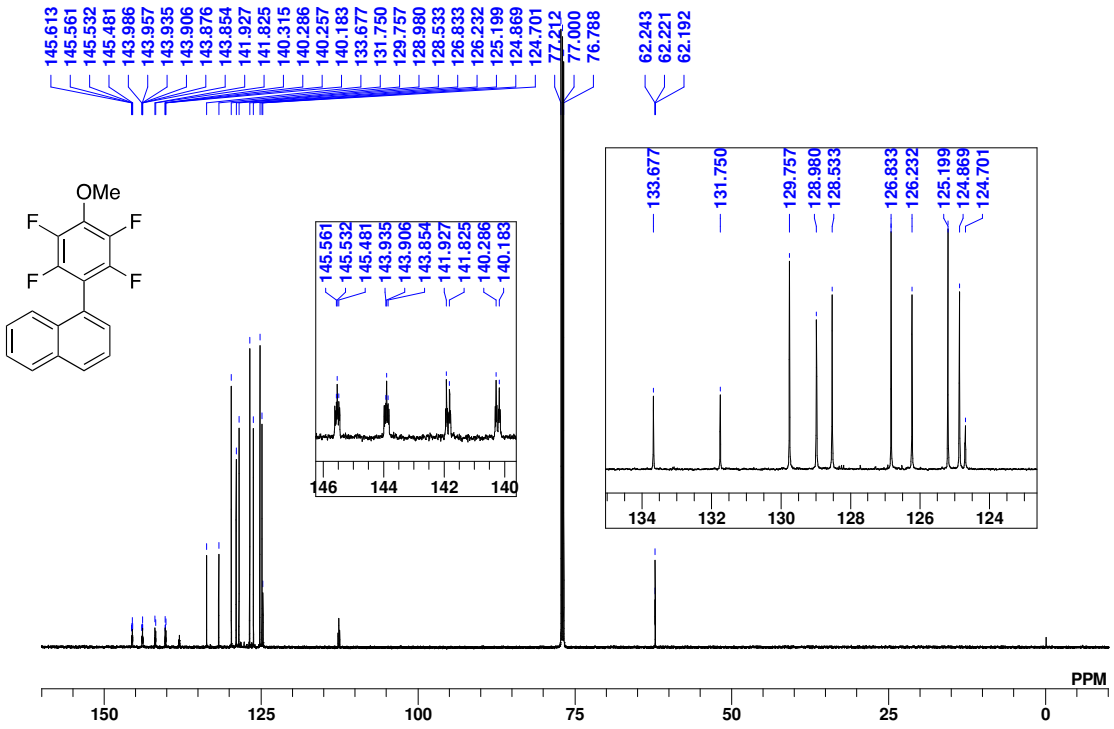


Figure S47. $^{13}C\{^{1}H\}$ NMR spectrum of 1-(2,3,5,6-tetrafluoro-4-methoxy)phenylnaphthalene synthesised by the direct C-H arylation reaction (150 MHz, $CDCl_3$, r.t.).

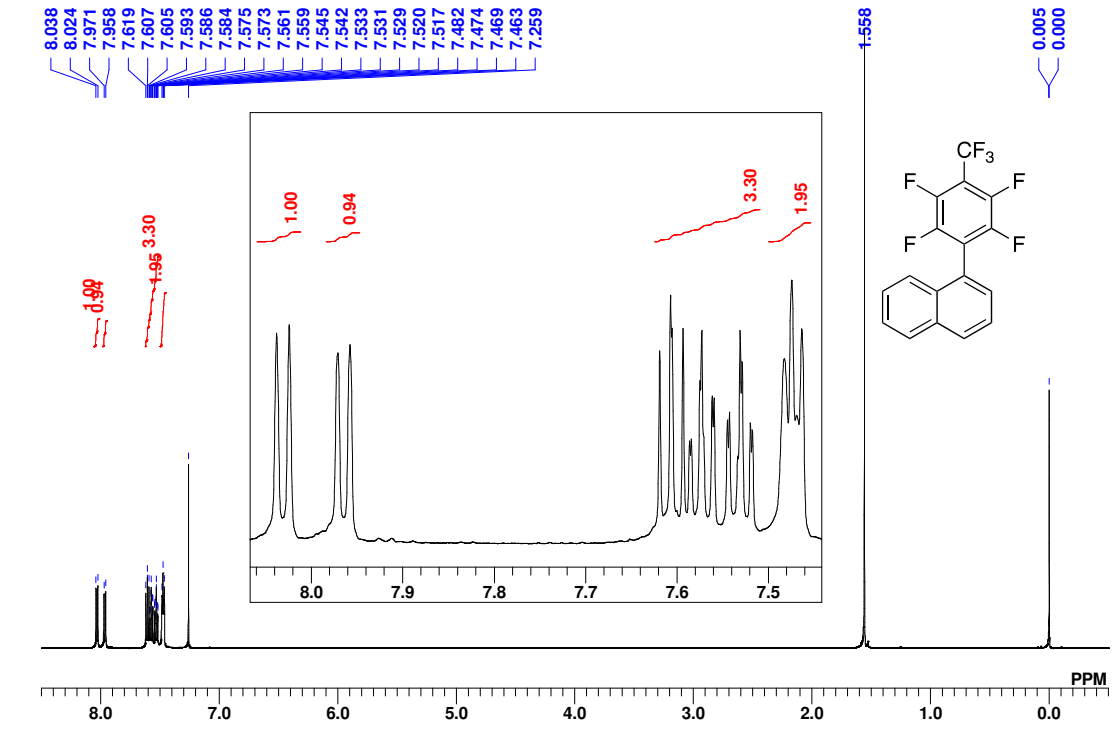


Figure S48. ^{1}H NMR spectrum of 1-(2,3,5,6-tetrafluoro-4-trifluoromethyl)phenylnaphthalene synthesised by the direct C-H arylation reaction (600 MHz, $CDCl_3$, r.t.).

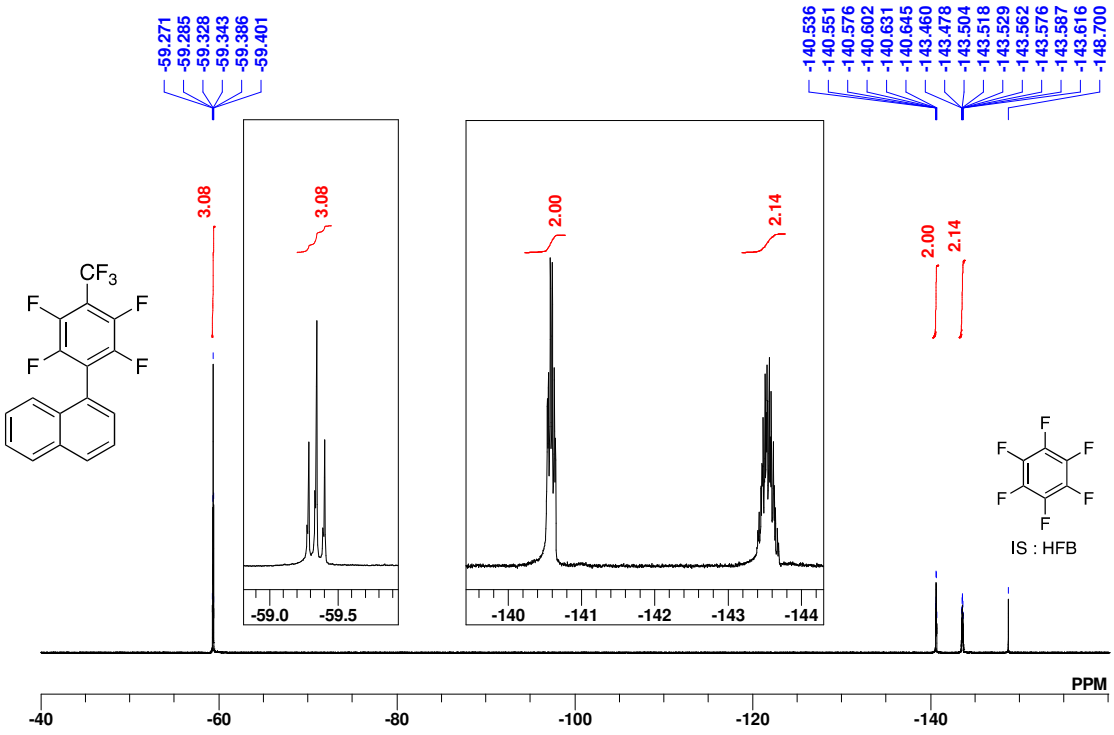


Figure S49. ^{19}F NMR spectrum of 1-(2,3,5,6-tetrafluoro-4-trifluoromethyl)phenylnaphthalene synthesised by the direct C-H arylation reaction (376 MHz, $CDCl_3$, r.t.).

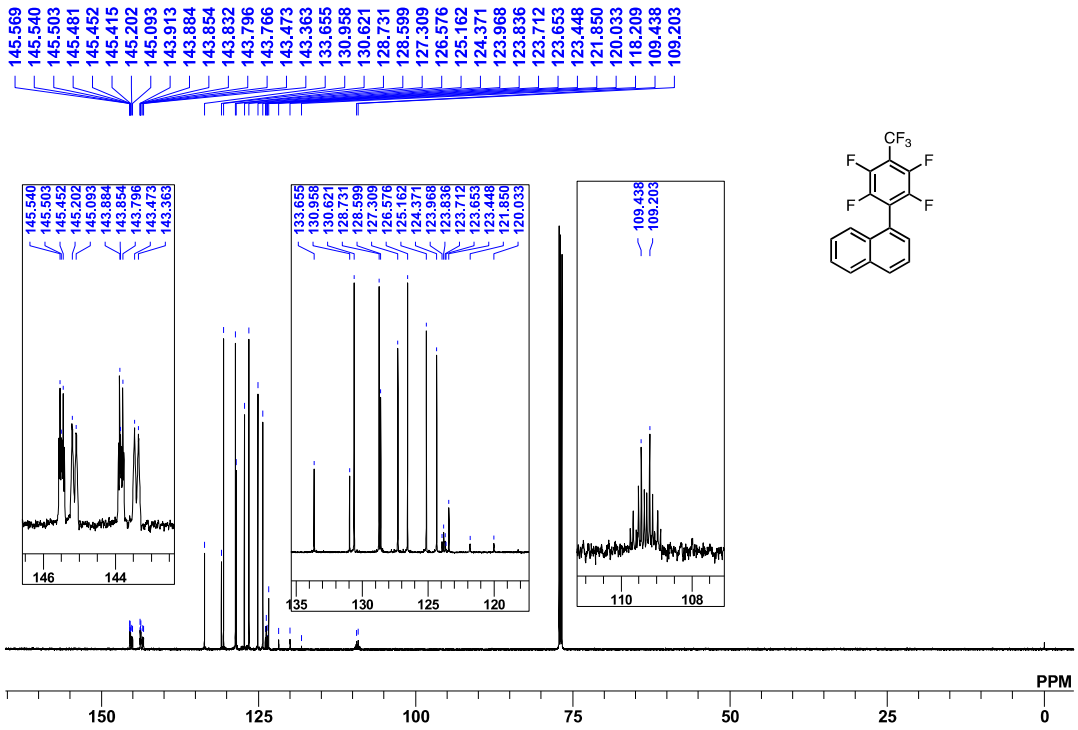


Figure S50. $^{13}C\{^1H\}$ NMR spectrum of 1-(2,3,5,6-tetrafluoro-4-trifluoromethyl)phenylnaphthalene synthesised by the direct C-H arylation reaction (150 MHz, $CDCl_3$, r.t.).

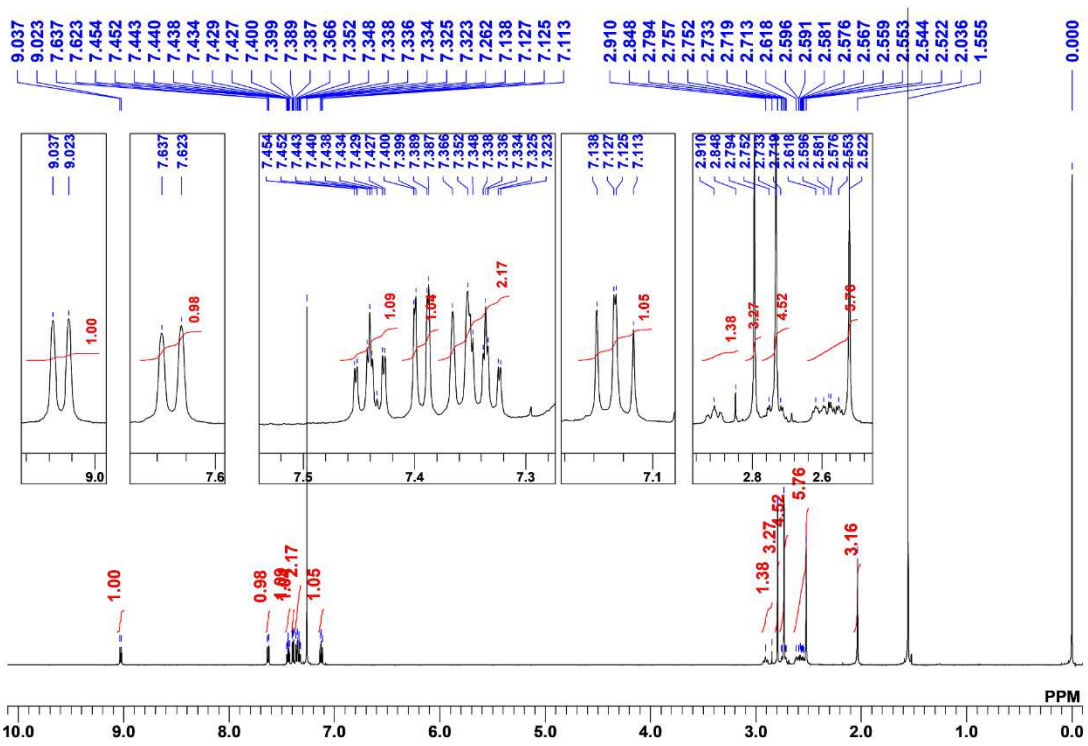


Figure S51. ^{1}H NMR spectrum of PdBr(1-naphthyl)(tmeda) ($CDCl_3$, 600 MHz).

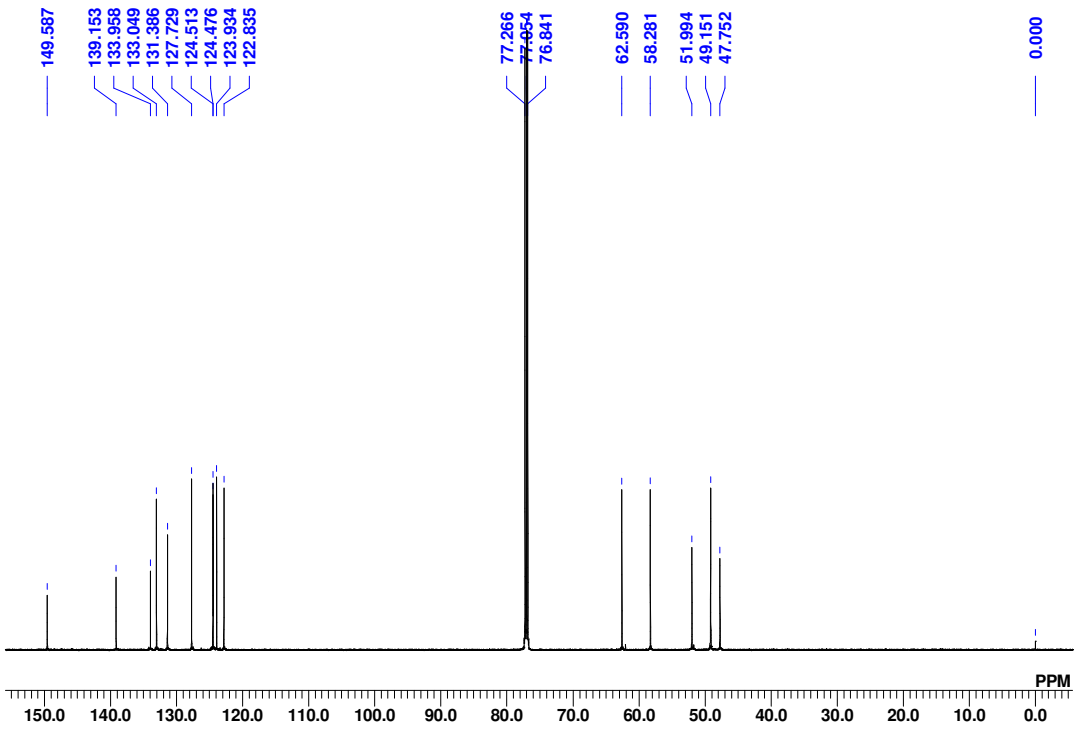


Figure S52. $^{13}C\{^{1}H\}$ NMR spectrum of PdBr(1-naphthyl)(tmeda) ($CDCl_3$, 151 MHz).

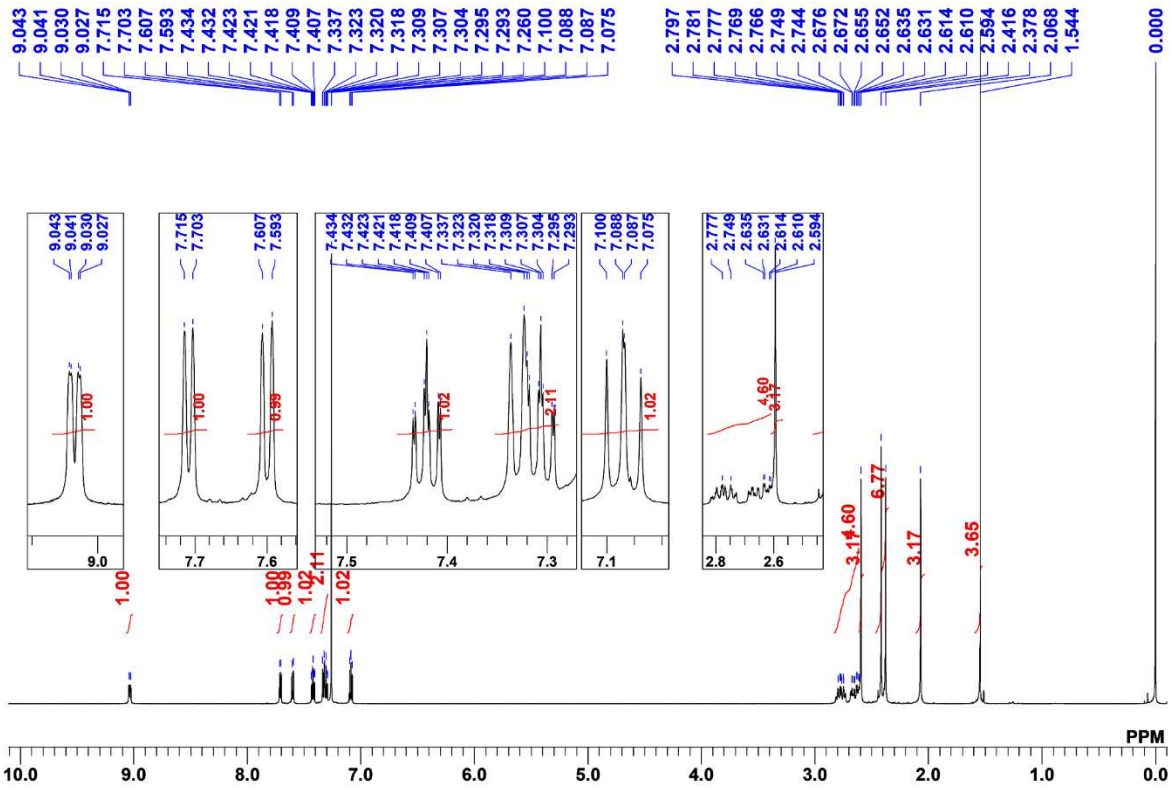


Figure S53. ^{1}H NMR spectrum of α-biaryl model complex ($CDCl_3$, 600 MHz).

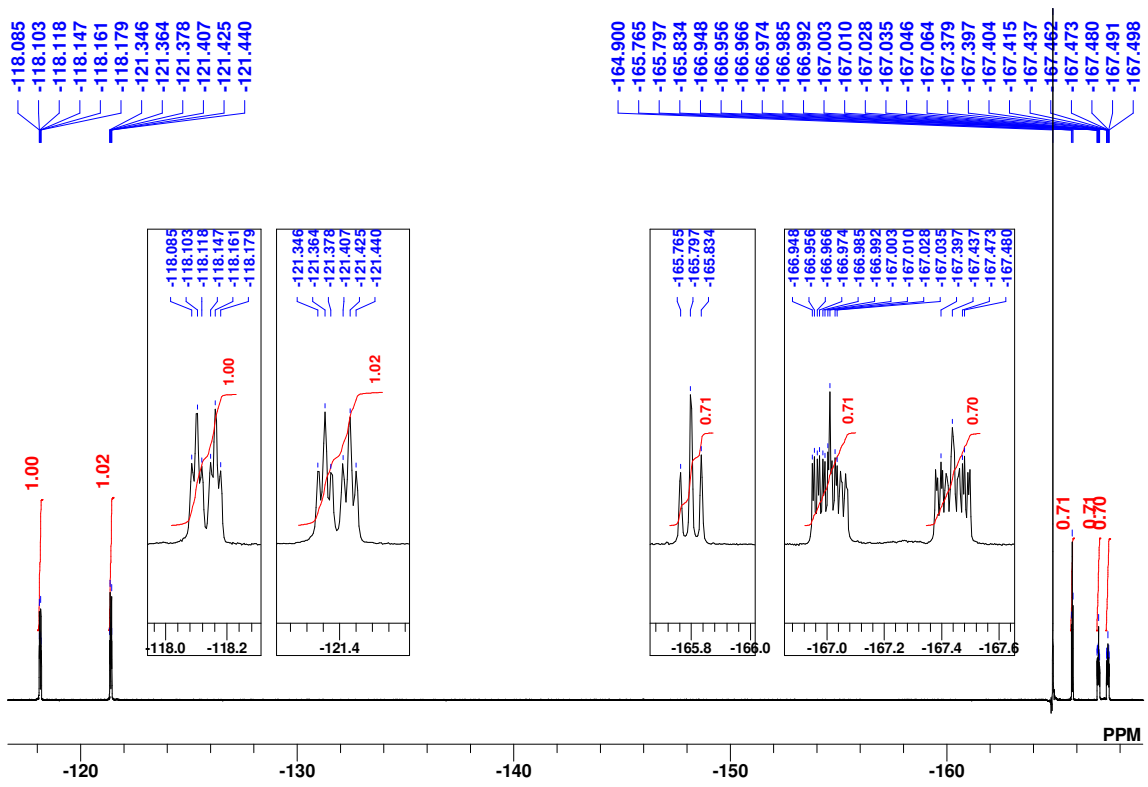


Figure S54. ^{19}F NMR spectrum of α-biaryl model complex ($CDCl_3$, 565 MHz).

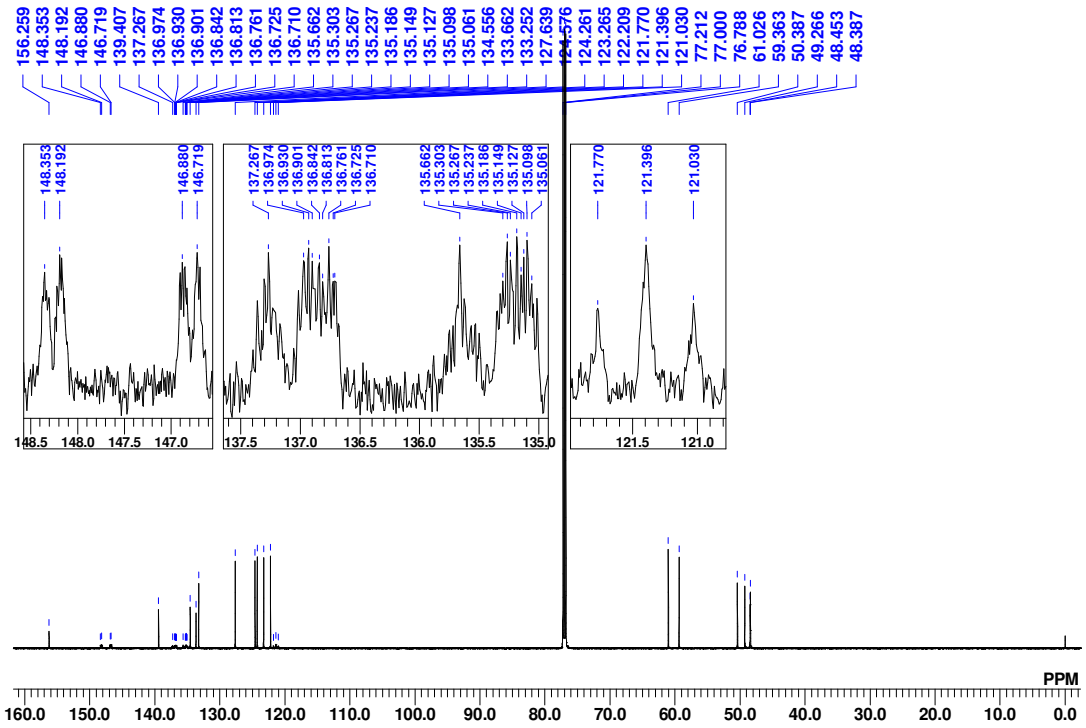


Figure S55. $^{13}C\{^{1}H\}$ NMR spectrum of α-biaryl model complex ($CDCl_3$, 151 MHz).

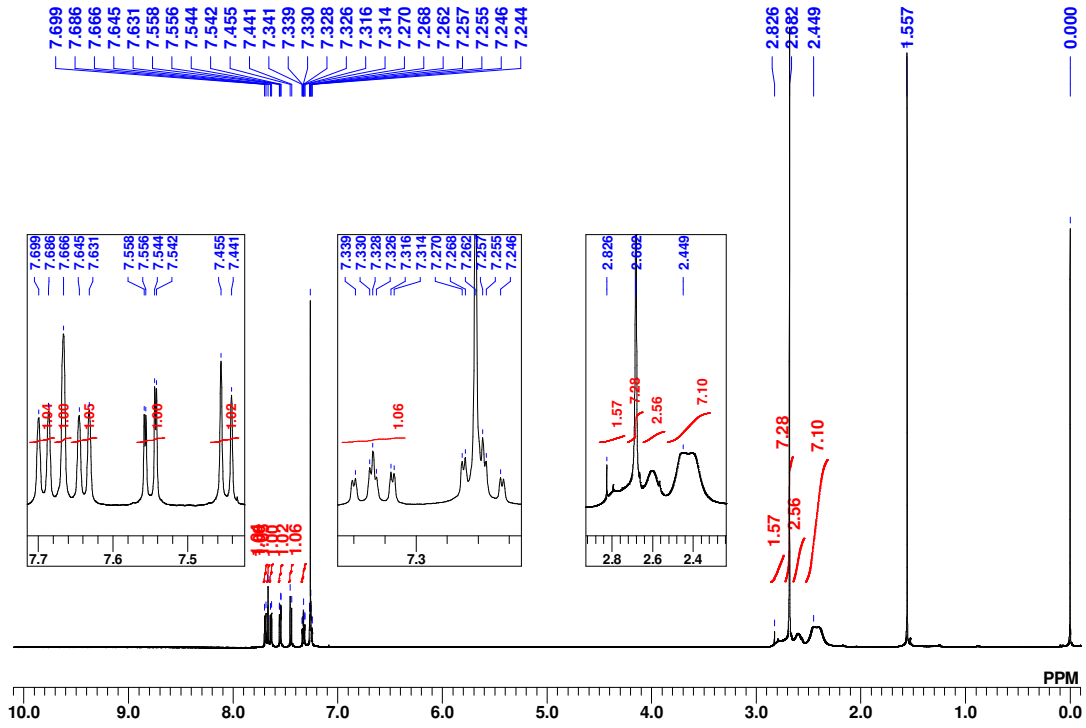


Figure S56. ^{1}H NMR spectrum of PdBr(2-naphthyl)(tmeda) ($CDCl_3$, 600 MHz).

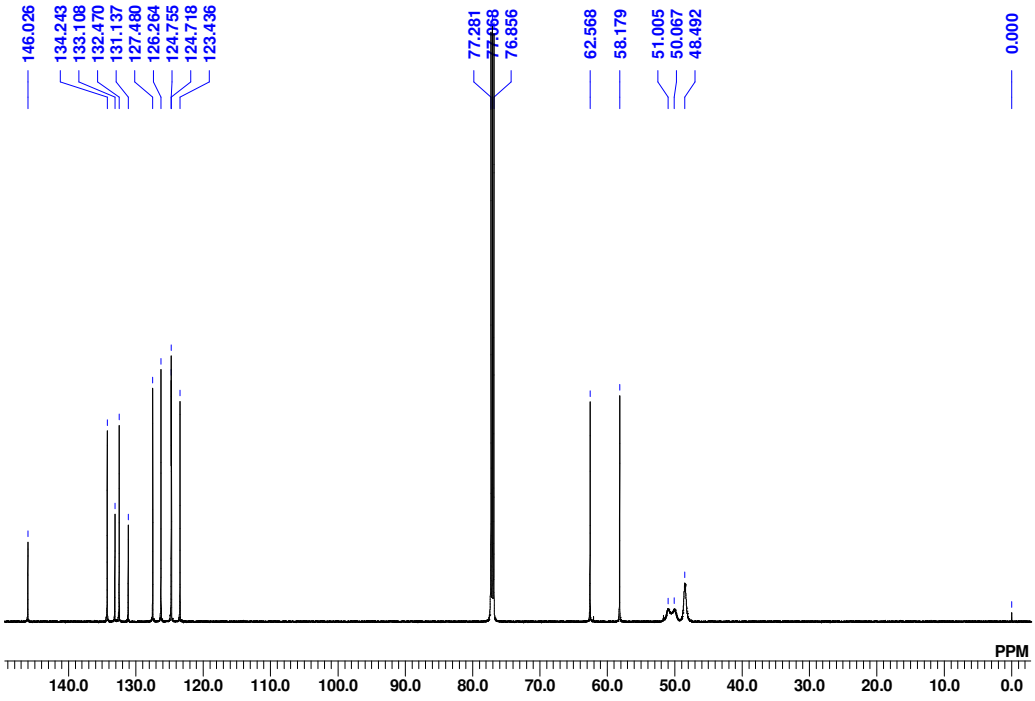


Figure S57. $^{13}C\{^{1}H\}$ NMR spectrum of PdBr(2-naphthyl)(tmeda) ($CDCl_3$, 151 MHz).

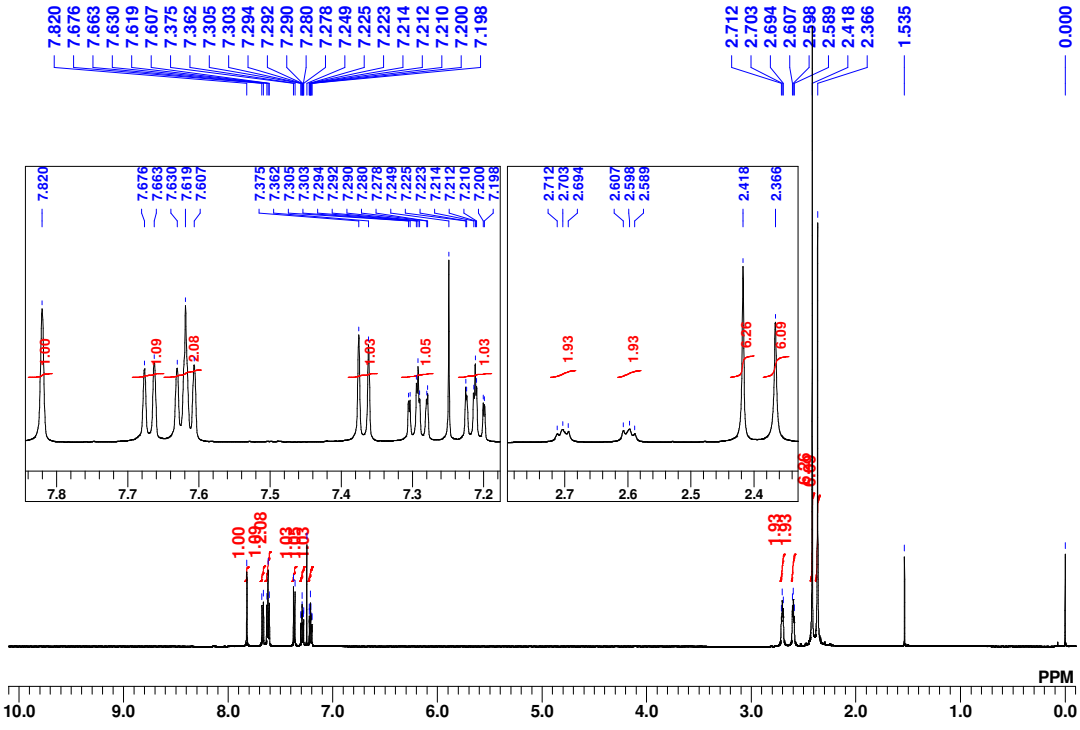


Figure S58. ^{1}H NMR spectrum of β-biaryl model complex ($CDCl_3$, 600 MHz).

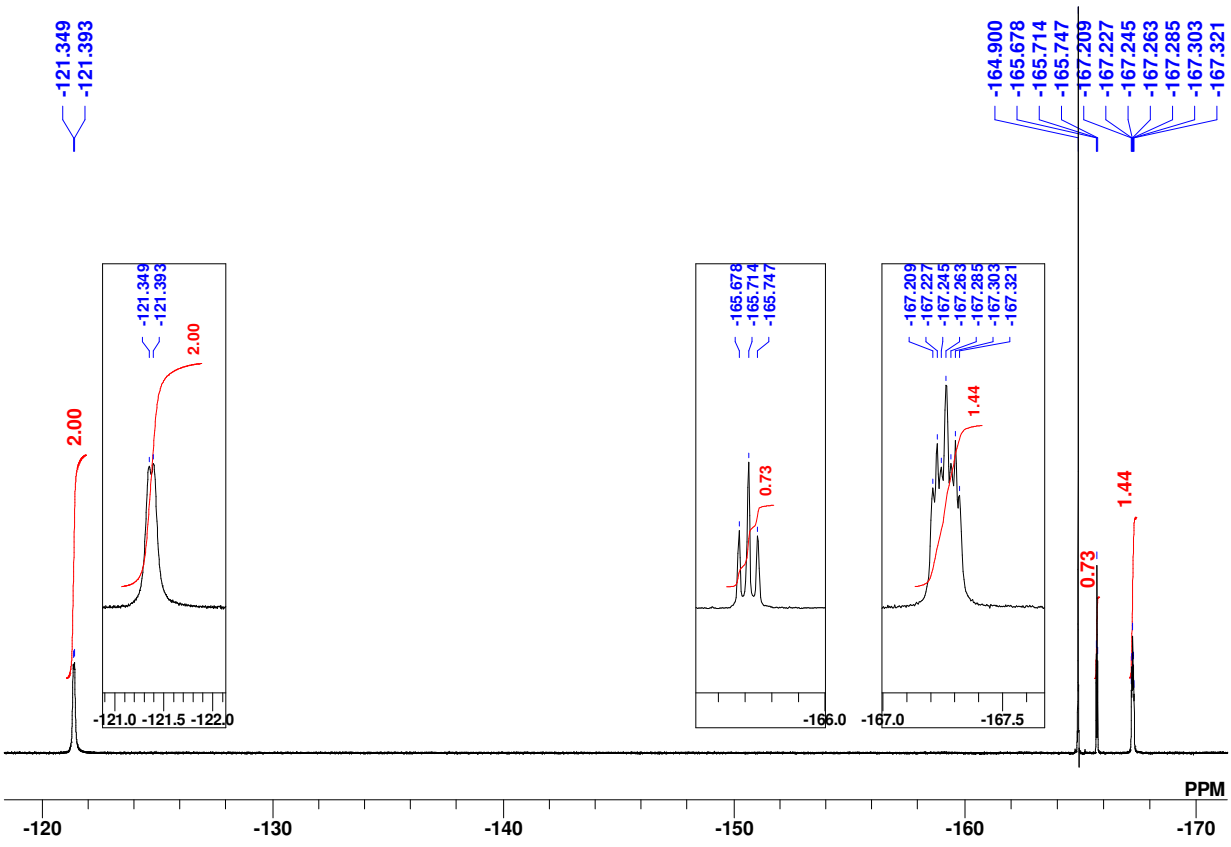


Figure S59. ^{19}F NMR spectrum of β-biaryl model complex ($CDCl_3$, 376 MHz).

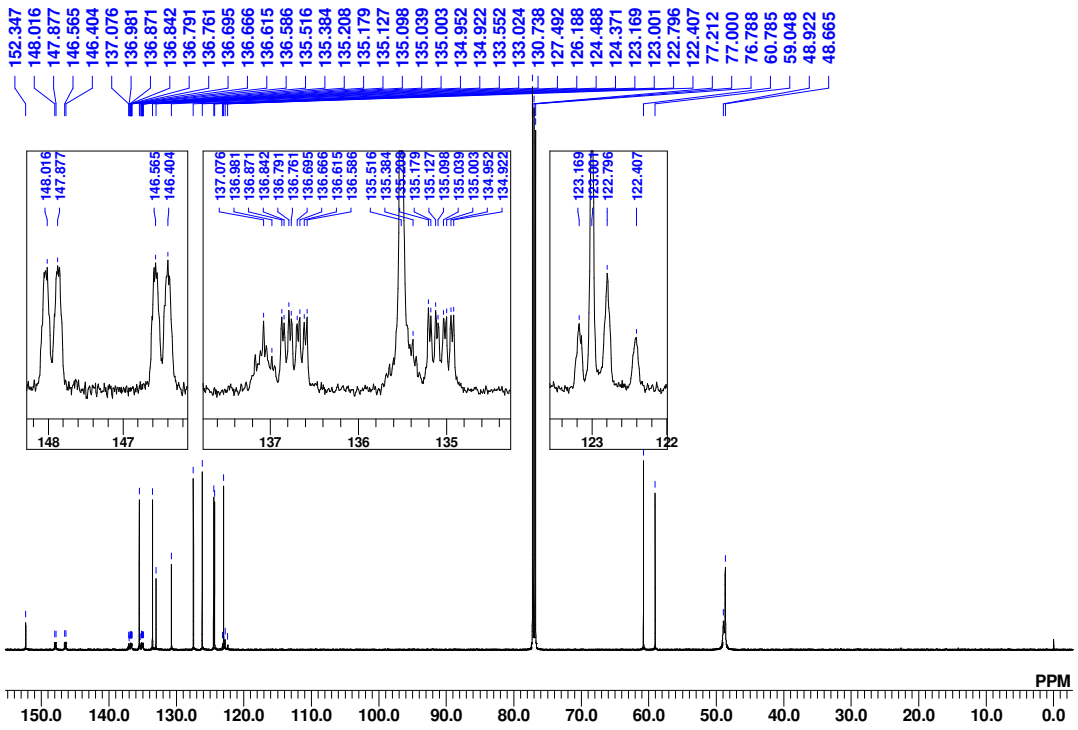


Figure S60. $^{13}C\{^1H\}$ NMR spectrum of β-biaryl model complex ($CDCl_3$, 151 MHz).

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