SUPPORTING INFORMATION

Ru-Catalyzed C–H Arylation of Fluoroarenes with Aryl Halides

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General Information

Unless otherwise indicated, all reactions were carried out in Schlenk vials using reagents obtained from commercial sources and used without further purification. All solid reagents were kept under vacuum in a desiccator for 24 h prior to use and stored under vacuum in a desiccator, unless otherwise stated. All other starting materials and solvents were purchased from Acros, Aldrich, Alfa Aesar, Fluorochem, Apollo Scientific and Manchester Organics, and used without further purification unless, otherwise stated. 2,3,5,6-tetrafluoro-N,N-dimethylaniline (1g), 1-bromo-2-phenoxybenzene (2a'), 1-(benzyl oxy)-2-bromobenzene (2e'), 2-phenoxy pyridine (10), 1-benzyl-5-phenyl-1H-tetrazole (12), and 1-(pyrimidin-2-yl)-1H-indole (8) were prepared according to reported methods. Column chromatography was carried out on silica gel, particle size 40-63 μm, using flash techniques. Melting points were obtained using a Stuart SMP11 apparatus and are uncorrected. IR spectra were recorded using a Thermo Scientific Nicolet iS5 FTIR machine, relevant bands are quoted in cm⁻¹. High resolution mass spectra were performed at the EPSRC National Mass Spectrometry Service Centre (Swansea) or by the School of Chemistry Mass Spectrometry Service (University of Manchester) employing a Thermo Finnigan MAT95XP spectrometer. Mass spectra for the characterization of ruthenium complexes were performed by the School of Chemistry Mass Spectrometry Service (University of Manchester) employing a Waters SQD2 spectrometer. Elemental analyses were performed by the School of Chemistry Microanalysis Laboratory (University of Manchester) using a Flash 2000 elemental analyzer machine. ¹H NMR, ¹⁹F NMR and ¹³C NMR spectra were recorded at 400 or 500 MHz on Bruker machines. ¹H NMR are referenced to the residual solvent peak at 7.26 ppm (CDCl₃), 2.05 ppm ((CD₃)₂CO), 5.32 ppm (CD₂Cl₂), 4.79 ppm (D₂O) and quoted in ppm to 2 decimal places with coupling constants (J) to the nearest 0.1 Hz. ¹³C NMR spectra, recorded at 100 MHz or 126 MHz, are referenced to the solvent peak at 77.16 ppm (CDCl₃), 29.84 ppm ((CD₃)₂CO) or 53.84 ppm (CD₂Cl₂) and quoted in ppm to 1 decimal place with coupling constants (J) to the nearest 0.1 Hz. ¹⁹F NMR spectra were recorded at 376 or 471 MHz in CDCl₃, (CD₃)₂CO, CD₂Cl₂ or D₂O, and quoted in ppm to 2 decimal places and with coupling constants (J) to the nearest 0.1 Hz.
General Procedure 1: C–H Arylation of (hetero)aromatic arenes with aryl halides.

[Ru('BuCN)₆](BF₄)₂ (C₅) (15.5 mg, 0.020 mmol), aryl bromide (if solid, 0.50 mmol), arene (if solid, 1.50 mmol), (NMe₄)OC(CF₃)₃ (386.5 mg, 1.250 mmol), (NMe₄)4-fluorobenzoate (37.3 mg, 0.175 mmol) and (NMe₄)OPiv (35.1 mg, 0.20 mmol) were weighed in the open air and placed in a crimp-cap Schlenk microwave vial (10 mL) with a magnetic stirrer bar, unless otherwise stated. The reaction vessel was capped, evacuated and backfilled with N₂ three times, then left under vacuum for 30 min. The vial was then backfilled with N₂ and aryl bromide (if liquid, 0.50 mmol), arene (if liquid, 1.50 mmol) and pivalonitrile (166.3 μL, 1.50 mmol) were added via syringe unless otherwise stated. The vial was resealed with a new cap under a stream of N₂ and the mixture was stirred for 16 h at 115 °C. On completion of the reaction, the mixture was diluted with Et₂O and filtered through a cotton plug. Evaporation of the solvent and purification by silica gel column chromatography afforded the corresponding biaryls.
Procedure 2: D/H scrambling of d$_1$-1a/1a via Ru1a by reversible C–D / C–H activation

PivOH (0.3 equiv, 0.15 mmol), K$_2$CO$_3$ (2.0 equiv, 1.00 mmol) and [RuCl$_2$(p-cymene)]$_2$ (none or 5 mol %, 0.05 mmol) were weighed in a Schlenk microwave vial (10 mL) with a magnetic stirrer bar. The reaction vessel was capped, evacuated and backfilled with N$_2$ three times, then left under vacuum for 30 min. The vial was then backfilled with N$_2$ and 1.0 mL of a 0.5 M solution of a 98:2 mixture of d$_1$-1a : 1a (1.0 equiv, 0.50 mmol) in 1,4-dioxane was then added via syringe. The vial was resealed with a new cap under a stream of N$_2$ and the mixture was heated to 90 °C for 16 h. Upon completion, the reaction mixture was cooled to room temperature diluted with 3 mL of Et$_2$O, filtered through a cotton plug and evaporated in vacuo to give a residue, to which 1,3,5-trimethoxybenzene (0.33 equiv, 0.167 mmol) was added as internal standard in CDCl$_3$.

![Chemical Reaction Diagram]

| entry | [Ru] (mol %) | d$_1$-1a:1a (initial ratio) | d$_1$-1a:1a (final ratio) | Ru1a (%) |
|-------|-------------|----------------------------|--------------------------|----------|
| 1     | none        | 98:2                       | 98:2                     | none     |
| 2     | [Ru(Cl$_2$(p-cymene)]$_2$ (5) | 98:2 | 89:11 | 1 |

Table S1. D/H scrambling of d$_1$-1a/1a via Ru1a by reversible C–D / C–H activation.
1) $^1$H-NMR expansion of $p$-cymene and O-CH$_2$C$_3$H$_7$ region for independently isolated Ru$_1$a. 1#) $^{19}$F-NMR expansion for independently isolated Ru$_1$a. 2) $^1$H-NMR expansion of the reaction described in Table S1 entry 2, showing: $p$-cymene and O-CH$_2$C$_3$H$_7$-regions for Ru$_1$a, and aromatic singlet for internal standard 1,3,5-trimethoxybenzene; relative integration of signals corresponding to Ru$_1$a with respect to the standard gives the yield of Ru$_1$a. 2#) $^{19}$F-NMR expansion of reaction described in Table S1 entry 2, showing Ru$_1$a. 3) $^1$H-NMR expansion of reaction described in Table S1 entry 2, showing the aromatic proton for 1a and O-CH$_2$C$_3$H$_7$-protons for d$_1$-1a and 1a; relative integration of the aromatic proton of 1a with respect to O-CH$_2$C$_3$H$_7$-protons gives the ratio between for d$_1$-1a and for 1a. 3#) $^{19}$F-NMR expansion of the reaction described in Table S1 entry 2, showing d$_1$-1a and 1a. 4) $^1$H-NMR expansion of reaction described in Table S1 entry 2, showing the aromatic proton of 1a and O-CH$_2$C$_3$H$_7$-protons for d$_1$-1a and 1a; relative integration of the aromatic proton of 1a with respect to O-CH$_2$C$_3$H$_7$-protons gives the ratio between d$_1$-1a and 1a.
**General Procedure 3: C–H activation of fluoroarenes with complex C2**

Ru(OPiv)$_2$(p-cymene) (C2) (1.0 equiv) and the appropriate base (if any, see Table S2) were weighed in the open air and placed in a crimp-cap Schlenk microwave vial (10 mL) with a magnetic stirrer bar. The reaction vessel was capped, evacuated and backfilled with Ar three times, then left under vacuum for 30 min. The vial was then backfilled with Ar and the appropriate perfluoroarene and 1,4-dioxane (see Table S2) were added via syringe. The vial was resealed with a new cap under a stream of Ar and the reaction was heated at the stated temperature (see Table S2) for 16 h. Upon completion, the reaction mixture was cooled to room temperature and a given amount of 1,3,5-trimethoxybenzene was added as internal standard in CDCl$_3$. The crude mixture was then filtered through a cotton plug directly to an NMR tube. If purification was needed after NMR analysis, the crude was evaporated, dissolved in hexane and loaded on a silica column. The column was flushed with a 0-15% Et$_2$O-hexane gradient using N$_2$ in replacement of compressed air. The yellow band observed was eluted and evaporated *in vacuo* to give the desired aryl ruthenium complex as a yellow/orange solid. The final complexes are stable under air for a few days, but decompose if exposed to oxygen for longer. Storage in a desiccator under vacuum or in a glove box is needed. Suitable crystals of Ru1c for X-ray crystallography (see crystallographic section) were grown by slow evaporation from a concentrated solution of the complex in CDCl$_3$. 

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Table S2. Optimization of the C–H activation of fluoroarenes with complex C2.
Figure S2.

$^1$H-NMR expansion of $p$-cymene ruthenium complexes region of reactions described in Table S2: 1) entry 4; 2) entry 5; 3) entry 6; 4) entry 7.

**Characterization data of Ru1a, Ru1b and Ru1c**

The General Procedure 3 was applied with Ru(OPiv)$_2$(p-cymene) (C2) (1.0 equiv, 87.5 mg, 0.20 mmol), 3-butoxy-1,2,4,5-tetrafluorobenzene (1a) (888.8 mg, 4.00 mmol), Na$_2$CO$_3$ (42.4 mg, 0.4 mmol), 1,4-dioxane (0.4 mL, 0.5 M), 120 °C, 16 h. Column chromatography afforded the title product as a dark yellow/orange solid (66.9 mg, 60%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 5.55 (d, $J = 5.9$ Hz, 2H), 5.22 (d, $J = 5.9$ Hz, 2H), 4.10 (t, $J = 6.8$ Hz, 2H), 2.85 (septet, $J = 6.9$ Hz, 1H), 2.10 (s, 3H), 1.72 (app quintet, $J = 7.0$ Hz, 2H), 1.49 (app sextet, $J = 7.4$ Hz, 2H), 1.34 (d, $J = 6.8$ Hz, 6H), 0.95 (t, $J = 7.4$ Hz, 3H), 0.76 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$): δ 196.0, 148.0 (dm, $J = 224.9$ Hz), 140.3 (dm, $J = 249.3$ Hz), 133.3 - 133.0 (m), 130.6 - 129.5 (m), 106.3, 93.3, 80.6, 78.1, 74.8 (t, $J = 2.6$ Hz), 40.1, 32.1, 27.8, 26.1, 22.6, 19.1, 19.0, 13.9; $^{19}$F NMR (376 MHz, CDCl$_3$) δ -119.2 - -119.3 (m, 2F), -158.7 - -158.8 (m, 2F);
IR (ATR) 2962, 1489, 1439; m.p. 77 - 80 °C. Anal. Calcd. for C\textsubscript{25}H\textsubscript{32}F\textsubscript{4}O\textsubscript{3}Ru: C, 53.85; H, 5.78. Found: C, 53.76; H, 5.84. HRMS (APCI) m/z calcd. C\textsubscript{25}H\textsubscript{32}F\textsubscript{4}O\textsubscript{3}Ru [M]\textsuperscript{+} 558.1331; found [M]\textsuperscript{+} 558.1316.

The General Procedure 3 was applied with Ru(OPiv)\textsubscript{2}(p-cymene) (C\textsubscript{2}) (1.0 equiv, 87.5 mg, 0.20 mmol), pentafluorobenzene (1b) (444.0 µL, 4.00 mmol), Na\textsubscript{2}CO\textsubscript{3} (42.4 mg, 0.4 mmol), 1,4-dioxane (0.4 mL, 0.5 M), 120 °C, 16 h. Column chromatography afforded the title product as a yellow solid (75.5 mg, 75%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 5.56 (d, J = 5.8 Hz, 2H), 5.22 (d, J = 5.8 Hz, 2H), 2.84 (septet, J = 6.9 Hz, 1H), 2.09 (s, 3H), 1.34 (d, J = 6.9 Hz, 6H), 0.77 (s, 9H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): δ 196.3, 147.5 (dm, J = 225.3 Hz), 137.3 (dm, J = 240.3 Hz), 136.1 (dm, J = 251.8 Hz), 131.0 - 130.0 (m), 106.6, 93.5, 80.8, 78.1, 40.1, 32.1, 26.1, 22.6, 19.1; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) δ -117.1 - -117.3 (m, 2F), 160.9 (t, J = 19.8 Hz, 1F), -164.0 - -164.2 (m, 2F); IR (ATR) 2966, 1489, 1438, 1443, 729; m.p. 139 -142 °C. Anal. Calcd for C\textsubscript{21}H\textsubscript{23}F\textsubscript{5}O\textsubscript{2}Ru: C, 50.10; H, 4.60. Found: C, 50.21; H, 4.60. HRMS (APCI) m/z calcd. C\textsubscript{21}H\textsubscript{23}F\textsubscript{5}O\textsubscript{2}Ru [M]\textsuperscript{+} 504.0662; found [M]\textsuperscript{+} 504.0656.

The General Procedure 3 was applied with Ru(OPiv)\textsubscript{2}(p-cymene) (C\textsubscript{2}) (1.0 equiv, 87.5 mg, 0.20 mmol), 1,2,4,5-tetrafluorobenzene (1c) (446.6 µL, 4.00 mmol), Na\textsubscript{2}CO\textsubscript{3} (42.4 mg, 0.4 mmol), 1,4-dioxane (0.4 mL, 0.5 M), 120 °C, 16 h. Column chromatography afforded the title product as a yellow/orange solid (74.9 mg, 77%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 6.64 (tt, J = 9.5, 6.9 Hz, 1H), 5.56 (d, J = 6.0 Hz, 2H), 5.22 (d, J = 6.0 Hz, 2H), 2.85 (septet, J = 6.9 Hz, 1H), 2.10 (s, 3H), 1.34 (d, J = 6.9 Hz, 6H), 0.76 (s, 9H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}): δ 196.1, 148.0 (dm, J = 225.2 Hz), 144.9 (dm, J = 248.7 Hz), 141.2 - 140.1 (m), 106.5, 101.4 (t, J = 23.5 Hz), 93.4, 80.8, 78.1, 40.1, 32.0, 26.1, 22.6, 19.1; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) δ -119.3 - -119.4 (m, 2F), -142.3 - -142.4 (m, 2F); IR (ATR) 2966, 1489, 1443, 729; m.p. 139 -142 °C. Anal. Calcd for C\textsubscript{21}H\textsubscript{24}F\textsubscript{4}O\textsubscript{2}Ru: C, 51.95; H, 4.98. Found: C, 51.86; H, 5.03. HRMS (APCI) m/z calcd. C\textsubscript{21}H\textsubscript{24}F\textsubscript{4}O\textsubscript{2}Ru [M]\textsuperscript{+} 486.0756; found [M]\textsuperscript{+} 486.0745.
General Procedure 4: C−H activation of fluoroarenes 1a and d1-1a with complex C2 for the KIE experiment

Ru(OPiv)2(p-cymene) (C2) (43.8 mg, 0.10 mmol), Na2CO3 (21.2 mg, 0.20 mmol) were weighed in a crimp-cap Schlenk microwave vial (10 mL) with a magnetic stirrer bar. The reaction vessel was capped, evacuated and backfilled with Ar three times, then left under vacuum for 30 min. The vial was backfilled with Ar then 1a or d1-1a (111.1 or 111.6 mg, 0.50 mmol) and 1,4-dioxane (1.0 mL, 0.1 M with respect to C2) were added via syringe. The vial was resealed with a new cap under a stream of Ar and the mixture was stirred for 5 min at room temperature. The vial was then heated at 120 °C for the appropriate time (see Table S3). Upon completion, the vial was quickly cooled in a dry ice/acetone bath and a given amount of 1,3,5-trimethoxybenzene was added as internal standard in CDCl3. The crude was then filtered through a cotton plug directly into an NMR tube for analysis.

![](image)

| entry | fluoroarene (1a or d1-1a) | time (min) | Ru1a (%) |
|-------|--------------------------|------------|----------|
| 1     | 1a                       | 5          | 3.3      |
| 2     | 1a                       | 10         | 4.9      |
| 3     | 1a                       | 15         | 6.4      |
| 4     | 1a                       | 20         | 8.9      |
| 5     | d1-1a                    | 5          | 0.9      |
| 6     | d1-1a                    | 10         | 2.0      |
| 7     | d1-1a                    | 15         | 2.6      |
| 8     | d1-1a                    | 20         | 3.2      |

*Reaction conditions: C2 (1.0 equiv, 0.1 mmol), 1a (5.0 equiv, 0.5 mmol), Na2CO3 (2.0 equiv, 0.2 mmol), 1,4-dioxane (1.0 mL, 0.1 M) were stirred under Ar in a closed vessel at 120 °C for the appropriate time; yield is evaluated by 1H-NMR using 1,3,5-trimethoxybenzene as internal standard.*

**Table S3.** KIE experiment for the C−H activation of 1a and d1-1a with complex C2.
Graph S1.

Rate of formation of Ru1a for C−H activation of 1a and d1-1a with complex C2 (%/min).

\[
\text{KIE} = \frac{k_H}{k_D} = \frac{0.366}{0.150} = 2.4
\]

General Procedure 5: C−H arylation of 1a with catalysts C2-C4
The appropriate ruthenium catalyst (C2-C4) (10 mol), base and additive(s) (if any, see Table S4) were weighed in a crimp-cap Schlenk microwave vial (10 mL) with a magnetic stirrer bar. The reaction vessel was capped, evacuated and backfilled with N₂ three times, then left under vacuum for 30 min. The vial was backfilled with N₂ then 1a (111.1 mg, 0.5 mmol, 5.0 equiv), 2a or 2b (0.1 mmol, 1.0 equiv, 12.6 μL or 10.5 μL) and the appropriate solvent (see Table S4, concentration or equivalents with respect to the limiting reagent 2a or 2b) were added via syringe. The vial was resealed with a new cap under a stream of N₂ and the reaction was heated at 120 °C for 16 h. Upon completion, the reaction mixture was cooled to room temperature and a given amount of 1,3-dinitrobenzene was added as internal standard in CDCl₃. The crude was then filtered through a cotton plug directly into an NMR tube.
Table S4. Optimization of the Ru-catalyzed C–H arylation of 1a with catalysts C2–C4.
General Procedure 6: screening of benzoic acids with catalyst C2

The General Procedure 5 was followed, with the reaction conditions stated in Table S5.
| entry | CA-1-30 | 3aa (%) | entry | CA-31-59 | 3aa (%) |
|--------|---------|---------|--------|----------|---------|
| 1      | CA-1   | 0       | 31     | CA-31   | 18      |
| 2      | CA-2   | 0       | 32     | CA-32   | 21      |
| 3      | CA-3   | 0       | 33     | CA-33   | 25      |
| 4      | CA-4   | 0       | 34     | CA-34   | 26      |
| 5      | CA-5   | 0       | 35     | CA-35   | 29      |
| 6      | CA-6   | 0       | 36     | CA-36   | 29      |
| 7      | CA-7   | 0       | 37     | CA-37   | 31      |
| 8      | CA-8   | 0       | 38     | CA-38   | 33.5    |
| 9      | CA-9   | <1      | 39     | CA-39   | 46      |
| 10     | CA-10  | <2      | 40     | CA-40   | 49      |
| 11     | CA-11  | <3      | 41     | CA-41   | 49      |
| 12     | CA-12  | 3.5     | 42     | CA-42   | 49      |
| 13     | CA-13  | 3.5     | 43     | CA-43   | 49      |
| 14     | CA-14  | 3.5     | 44     | CA-44   | 50      |
| 15     | CA-15  | 4       | 45     | CA-45   | 50      |
| 16     | CA-16  | 4       | 46     | CA-46   | 51      |
| 17     | CA-17  | 4       | 47     | CA-47   | 51      |
| 18     | CA-18  | 5.5     | 48     | CA-48   | 54      |
| 19     | CA-19  | 5.5     | 49     | CA-49   | 54.5    |
| 20     | CA-20  | 6       | 50     | CA-50   | 55      |
| 21     | CA-21  | 6.5     | 51     | CA-51   | 58      |
| 22     | CA-22  | 8.5     | 52     | CA-52   | 59      |
| 23     | CA-23  | 8.5     | 53     | CA-53   | 60      |
| 24     | CA-24  | 9.5     | 54     | CA-54   | 63      |
| 25     | CA-25  | 11.5    | 55     | CA-55   | 63.5    |
| 26     | CA-26  | 12      | 56     | CA-56   | 67      |
| 27     | CA-27  | 13      | 57     | CA-57   | 67      |
| 28     | CA-28  | 16      | 58     | CA-58   | 68      |
| 29     | CA-29  | 18      | 59     | CA-59   | 68.5    |
| 30     | CA-30  | 18      |        |          |         |

* Reaction conditions: 2a (0.1 mmol, 1.0 equiv), 1a (5.0 equiv), C2 (10 mol %), CA-1-30 (20 mol %), (NMe₂)OC(CF₃)₃ (2.2 equiv), tBuCN (8.0 equiv) were stirred under N₂ in a closed vessel at 120 °C for 16 h; yield is evaluated by ¹H-NMR using 1,3-dinitrobenzene as internal standard.

**Table S5.** Screening of benzoic acids with catalyst C2, fluoroarene 1a and 4-bromoanisole 2a.
General Procedure 7: C–H arylation of 1a with catalysts C5
C5, base and additive(s) (see Table S6) were weighed in a crimp-cap Schlenk microwave vial (10 mL) with a magnetic stirrer bar. The reaction vessel was capped, evacuated and backfilled with N2 three times, then left under vacuum for 30 min. The vial was backfilled with N2 then 1a (5.0 or 3.0 equiv), 2a or 2b (1.0 equiv, 0.1 mmol or 0.5 mmol) and pivalonitrile (3.0 or 5.0 equiv) were added via syringe. The vial was resealed with a new cap under a stream of N2 and the reaction was stirred at the specified temperature (see Table S6) for 16 h. Upon completion, the reaction mixture was cooled to room temperature and a given amount of 1,3-dinitrobenzene was added as internal standard in CDCl3. The crude was then filtered through a cotton plug directly into an NMR tube. If purification was needed after NMR analysis, the crude was evaporated, dissolved in hexane and loaded on a silica column for flash chromatography to afford the corresponding biaryls.

Procedure 8: C–H arylation of 1a with catalyst C5 (glove box)
All solid reagents, except C5, were dried at 70 °C in a vacuum oven over night. All liquid reagents were dried over 4 Å molecular sieves and degassed with 3 freeze-pump-thaw cycles. In a glove box, C5 (0.02 mmol, 15.5 mg), (NMe4)4-fluorobenzoate (0.175 mmol, 37.3 mg), (NMe4)OPiv (0.2 mmol, 35.1 mg), (NMe4)OC(CF3)3 (1.25 mmol, 386.5 mg), bromobenzene (0.5 mmol, 53.5 μL), 1a (1.50 mmol, 333.3 mg) and pivalonitrile (1.50 mmol, 166.3 μL) were loaded in a crimp-cap microwave vial with a stirrer bar. The vial was sealed and the mixture was stirred at 115 °C for 16 h. On completion, a given amount of 1,3-dinitrobenzene was added as internal standard in CDCl3. The crude was then filtered through a cotton plug directly into an NMR tube for analysis (see Table S6).

Procedure 9: C–H arylation of 1a with catalyst C5 (under air)
C5 (0.02 mmol, 15.5 mg), (NMe4)4-fluorobenzoate (0.175 mmol, 37.3 mg), (NMe4)OPiv (0.2 mmol, 35.1 mg), (NMe4)OC(CF3)3 (1.25 mmol, 386.5 mg), bromobenzene (0.5 mmol, 53.5 μL), 1a (333.3 mg, 1.50 mmol) and pivalonitrile (166.3 μL, 1.50 mmol) were loaded in a crimp-cap microwave vial with a stirrer bar. The vial was capped and the mixture was stirred at 115 °C for 16 h. On completion, a given amount of 1,3-dinitrobenzene was added as internal standard in CDCl3. The crude mixture was then filtered through a cotton plug directly into an NMR tube for analysis (See Table S6).
\[
\begin{align*}
\text{1a} + \text{2a-2b} \rightarrow [\text{Ru(BuCN)}_2\text{(BF}_3)_2 \text{(C5)}] & \quad \text{base, additive(s)} \\
\text{solvent, T, 16 h, N}_2 & \rightarrow \text{3aa-3ab}
\end{align*}
\]

\[R = \text{OMe (2a), H (2b)}\]

| entry | C5 (mol%) | base (equiv) | additive(s) (equiv) | 1a (equiv) | 2a, 2b (1 equiv) | T (°C) | BuCN (equiv) | 3aa, 3ab (%) |
|-------|-----------|--------------|---------------------|------------|-----------------|--------|-------------|---------------|
| 1     | 10        | (NMe_2)(C\_F_3)_2 (2) | (NMe_2)4-fluorobenzoate (0.2) | 5          | 2b              | 120     | 8           | 59            |
| 2     | 10        | (NMe_2)(C\_F_3)_2 (2) | (NMe_2)4-fluorobenzoate (0.2) | 5          | 2a              | 120     | 8           | 61            |
| 3     | 10        | (NMe_2)(C\_F_3)_2 (2) | (NMe_2)4-fluorobenzoate (0.2) | 5          | 2b              | 120     | 8           | 72            |
| 4     | 10        | (NMe_2)(C\_F_3)_2 (2) | (NMe_2)4-fluorobenzoate (0.2) | 5          | 2a              | 120     | 8           | 71            |
| 5a    | 10        | (NMe_2)(C\_F_3)_2 (2) | (NMe_2)4-fluorobenzoate (0.2) | 5          | 2b              | 120     | 8           | 71            |
| 6b    | 2.5       | (NMe_2)(C\_F_3)_2 (2.2)| (NMe_2)4-fluorobenzoate (0.6) | 3          | 2b              | 120     | 8           | 68            |
| 7c    | 2.5       | (NMe_2)(C\_F_3)_2 (2.2)| (NMe_2)4-fluorobenzoate (0.6) | 3          | 2b              | 120     | 3           | 72            |
| 8d    | 4         | (NMe_2)(C\_F_3)_2 (2.2)| (NMe_2)4-fluorobenzoate (0.6) | 3          | 2b              | 120     | 3           | 80            |
| 9e    | 4         | (NMe_2)(C\_F_3)_2 (2.5)| (NMe_2)3-fluorobenzoate (0.35) | 3          | 2b              | 115     | 3           | 82 (76)       |
| 10f   | 4         | KO\_Me (2.5) | (NMe_2)3-fluorobenzoate (0.35) | 3          | 2b              | 115     | 3           | 0             |
| 11g   | 4         | KO\_Bu (2.5) | (NMe_2)3-fluorobenzoate (0.35) | 3          | 2b              | 115     | 3           | 13            |
| 12h   | 4         | (NMe_2)(C\_F_3)_2 (2.5)| (NMe_2)3-fluorobenzoate (0.35) | 3          | 2b              | 115     | 3           | 81            |
| 13i   | 4         | (NMe_2)(C\_F_3)_2 (2.5)| (NMe_2)OPiv (0.4) | 3          | 2b              | 115     | 3           | 0             |
| 14j   | 4         | (NMe_2)(C\_F_3)_2 (2.5)| (NMe_2)3-fluorobenzoate (0.35) | 3          | 2b              | 115     | 3           | 0             |
| 15k   | 4         | (NMe_2)(C\_F_3)_2 (2.5)| (NMe_2)3-fluorobenzoate (0.35) | 3          | 2b              | 115     | 3           | <1            |
| 16l   | 4         | (NMe_2)(C\_F_3)_2 (2.5)| (NMe_2)3-fluorobenzoate (0.35) | 3          | 2a              | 115     | 3           | 83 (82)       |

\(^a\) Reaction conditions: 2a or 2b (0.10 mmol, 1.0 equiv), 1a (see above), C5 (see above), base and additive(s) were stirred under N\(_2\) in a closed vessel in \(^1\)BuCN at the specified temperature for 16 h (see above); yield is estimated by \(^1\)H-NMR using 1,3-dinitrobenzene as internal standard. \(^b\) 2a or 2b (0.50 mmol, 1.0 equiv), 1a (see above). \(^c\) Reaction carried out in glove box. \(^d\) Reaction under air. \(^e\) TEMPO (1.0 equiv). Yield in parenthesis refers to isolated material.

**Table S6.** Optimization of the Ru-catalyzed C–H arylation of 1a with catalyst C5.
General Procedure 10: time-dependent C–H arylation of 1a with catalyst C2

C2 (0.01 mmol, 4.4 mg), 3-acetylbenzoic acid (0.03 mmol, 4.9 mg), (NMe₄)OC(CF₃)₃ (0.23 mmol, 71.1 mg) were weighed in the open air and placed in a crimp-cap Schlenk microwave vial (10 mL) with a magnetic stirrer bar. The reaction vessel was capped, evacuated and backfilled with N₂ three times, then left under vacuum for 30 min. The vial was backfilled with N₂ then 1a (111.1 mg, 0.5 mmol), 2a (12.5 μL, 0.1 mmol) and pivalonitrile (88.4 μL, 0.8 mmol) were added via syringe. The vial was resealed with a new cap under a stream of N₂ and the reaction was heated at 120 °C for the appropriate time. Upon completion, the vial was quickly cooled in a dry ice/acetone bath and a given amount of 1,3,5-trimethoxybenzene was added as internal standard in CDCl₃. The crude was then filtered through a cotton plug directly to an NMR tube for analysis (see Table S7).

![Reaction Scheme]

| entry | time (min) | free p-cymene (%) | 3aa (%) |
|-------|------------|-------------------|--------|
| 1     | 2          | 0.8               | 0.2    |
| 2     | 5          | 3.8               | 1.5    |
| 3     | 8          | 6.0               | 3.9    |
| 4     | 10         | 7.0               | 6.8    |
| 5     | 15         | 8.4               | 16.7   |
| 6     | 30         | 9.9               | 34.3   |
| 7     | 16 h       | 9.9               | 66.2   |

* Reaction conditions: 2a (1.0 equiv, 0.1 mmol), 1a (5.0 equiv), C2 (10 mol %), 3-acetylbenzoic acid (0.3 equiv), (NMe₄)OC(CF₃)₃ (2.3 equiv), tBuCN (8.0 equiv) were stirred under N₂ in a closed vessel at 120 °C for the appropriate time; yield is evaluated by ¹H-NMR using 1,3,5-trimethoxybenzene as internal standard; % of free (η⁶-arene) is based on the loading of C2.

Table S7. Kinetic profile for the arylation of 1a with 2a employing catalyst C2.
General Procedure 11: time-dependent C–H arylation of 1a with catalyst C5

C5 (0.01 mmol, 7.7 mg), 3-acetylbenzoic acid (0.03 mmol, 4.9 mg), (NMe₄)OPiv (0.02 mmol, 3.5 mg), (NMe₄)OC(CF₃)₃ (0.23 mmol, 71.1 mg) were weighed in the open air and placed in a crimp-cap Schlenk microwave vial (10 mL) with a magnetic stirrer bar. The reaction vessel was capped, evacuated and backfilled with N₂ three times, then left under vacuum for 30 min. The vial was backfilled with N₂ then 1a (111.1 mg, 0.5 mmol), 2a (12.5 μL, 0.1 mmol) and pivalonitrile (88.4 μL, 0.8 mmol) were added via syringe. The vial was resealed with a new cap under a stream of N₂ and the reaction was heated at 120 °C for the appropriate time. Upon completion, the vial was quickly cooled in a dry ice/acetone bath and a given amount of 1,3,5-trimethoxybenzene (and C₆F₆, if needed, 0.5 equiv, 0.05 mmol, 5.8 μL) was added as internal standard in CDCl₃. The crude was then filtered through a cotton plug directly to an NMR tube for analysis (see Table S8).

| entry | time (min) | 3aa (%) | Ru2a (%) |
|-------|------------|---------|----------|
| 1     | 2          | 0.8     | NA       |
| 2     | 5          | 8.4     | NA       |
| 3     | 8          | 13.4    | NA       |
| 4     | 10         | 16.7    | NA       |
| 5     | 15         | 23.9    | NA       |
| 6     | 30         | 38.1 (38.5) | (5.0) |
| 7     | 16 h       | 72.4    | NA       |

* Reaction conditions: 2a (1.0 equiv, 0.1 mmol), 1a (5.0 equiv), C5 (10 mol %), 3-acetylbenzoic acid (0.3 equiv), (NMe₄)OPiv (0.2 equiv), (NMe₄)OC(CF₃)₃ (2.3 equiv), tBuCN (8.0 equiv) were stirred under N₂ in a closed vessel at 120 °C for the appropriate time; yield is evaluated by ¹H-NMR using 1,3,5-trimethoxybenzene as internal standard and also by quantitative ¹⁹F-NMR using hexafluorobenzene as internal standard for entry 6 (numbers in parenthesis are ¹⁹F-NMR yields).

Table S8. Kinetic profile for the arylation of 1a with 2a employing catalyst C5.
Figure S3.

$^{19}$F-NMR expansion of the reactions illustrated in Table S8 entry 6 displaying 1a, 3aa and Ru2a with relative integrations with respect to the internal standard C$_6$F$_6$. 
General Procedure 12: arylation of Ru2c with bromoarene 2c

All solid reagents, except Ru2c, were dried at 70 °C in a vacuum oven over night. All liquid reagents were dried over 4 Å molecular sieves and degassed with 3 freeze-pump-thaw cycles. In a glove box, Ru2c (0.03 mmol, 22.6 mg), additive (if any, see Table S9), 2c (12.2 μL, 0.09 mmol) and pivalonitrile (100 μL, 0.3 M) were loaded in a crimp-cap microwave vial with a stirrer bar. The vial was sealed and the mixture was stirred at 115 °C for 16 h. On completion, the mixture was filtered through a plug of silica with Et2O, the solvent was evaporated and octafluorotoluene (8.5 μL, 0.06 mmol, 2.0 equiv) was added as internal standard in CDCl3 for quantitative 19F-NMR analysis.

Table S9. Arylation of Ru2c with bromoarene 2c.

| entry | additive (2.5 equiv) | 3cc (%) | 3cc’ (%) |
|-------|----------------------|---------|----------|
| 1     | none                 | -       | -        |
| 2     | (NMe₄)O(CCF₃)₃      | -       | -        |
| 3     | (NMe₄)OPiv           | -       | -        |
| 4     | (NMe₄)4-fluorobenzoate | 35.0   | 13.5     |

Figure S4.

19F-NMR expansion of the reaction described in entry 4 of Table S9, displaying 3cc and 3cc’ with relative integration with respect to the internal standard octafluorotoluene.
General Procedure 13: arylation of fluoroarene 1d with catalyst Ru2c or Ru1c with bromoarene 2c

All solid reagents, except for Ru2c and Ru1c, were dried at 70 °C in a vacuum oven over night. All liquid reagents were dried over 4Å molecular sieves and degassed with 3 freeze-pump-thaw cycles. In glove box, Ru2c or Ru1c (0.05 mmol, 10 mol %), (NMe4)4-fluorobenzoate (0.175 mmol, 37.3 mg), (NMe4)OPiv (0.4 or 0.3 equiv: 0.20 mmol, 35.1 mg or 0.15 mmol 26.3 mg), (NMe4)OC(CF3)3 (1.25 mmol, 386.5 mg), 2c (0.50 mmol, 67.9 μL), 1d (182.7 μL, 1.50 mmol) and pivalonitrile (166.3 μL, 1.50 mmol) were loaded in a crimp-cap microwave vial with a stirrer bar. The vial was sealed, taken outside the box and the mixture was stirred at 115 °C for 16 h. On completion, the mixture was filtered through a plug of silica with Et2O, the solvent evaporated and hexafluorobenzene (28.9 μL, 0.25 mmol, 0.5 equiv) was added as internal standard in CDCl3 for quantitative 19F-NMR analysis (see Table S10).

Table S10. Arylation of fluoroarene 1d with catalyst Ru2c or Ru1c with bromoarene 2c.

| entry | [Ru]  | 3dc (%) | 3cc (%) | 3cc' (%) |
|-------|-------|---------|---------|---------|
| 1     | Ru2c  | 78.0    | 4.0     | 4.0     |
| 2b    | Ru1c  | 70.5    | 2.5     | 1.5     |

* Reaction conditions: Ru2c or Ru1c (10 mol %), 1d (3.0 equiv, 1.50 mmol), 2c (1.0 equiv, 0.50 mmol), (NMe4)OPiv (0.4 equiv), (NMe4)4-fluorobenzoate (0.35 equiv), (NMe4)OC(CF3)3 (2.5 equiv) and pivalonitrile (3.0 equiv) were stirred under N2 in a closed vessel at 120 °C for 16 h; yield is evaluated by quantitative 19F-NMR using C6F6 (0.5 equiv, 0.25 mmol) as internal standard. b (NMe4)OPiv (26.3 mg, 0.15 mol, 0.3 equiv).
**Procedure 14: D/H – H/D scrambling experiment with fluoroarenes d1-1a and 1b under arylation conditions with bromobenzene 2b**

All solid reagents, except C5, were dried at 70 °C in a vacuum oven over night. All liquid reagents were dried over 4Å molecular sieves and degassed with 3 freeze-pump-thaw cycles. In a glove box, C5 (7.8 mg, 0.025 mmol), (NMe₄)₄-fluorobenzoate (0.0875 mmol, 18.7 mg), (NMe₄)OPiv (17.6 mg, 0.100 mmol), (NMe₄)OC(CF₃)₃ (193.3 mg, 0.625 mmol), 2b (26.3 μL, 0.250 mmol), d1-1a (83.7 mg, 0.375 mmol), 1b (41.6 μL, 0.375 mmol) and pivalonitrile (58.2 μL, 0.750 mmol) were loaded in a crimp-cap microwave vial with a stirrer bar. The vial was sealed, taken outside the box and the mixture was stirred at 115 °C for 10 min. On completion, the vial was quickly cooled in a dry ice/acetone bath and octafluorotoluene (17.7 μL, 0.125 mmol, 0.5 equiv) was added as internal standard in CDCl₃. The crude mixture was then filtered through a cotton plug directly into an NMR tube for quantitative ¹⁹F-NMR analysis.
Scheme S1. D/H – H/D scrambling experiment with fluoroarenes d$_1$-1a and 1b under arylation conditions with bromobenzene 2b.

Figure S6. $^{19}$F-NMR expansion of the reaction illustrated in Scheme S1, displaying 1a, d$_1$-1a, 1b, d$_1$-1b, 3aa, 3ba with relative integrations with respect to the internal standard octafluorotoluene.

Procedure 15: KIE experiment of fluoroarenes d$_1$-1a and 1y with bromobenzene 2b

All solid reagents, except C5, were dried at 70 °C in a vacuum oven over night. All liquid reagents were dried over 4Å molecular sieves and degassed with 3 freeze-pump-thaw cycles. In a glove box, C5 (7.8 mg, 0.0250 mmol), (NMe$_4$)$_4$-fluorobenzoate (0.0875 mmol, 18.7 mg), (NMe$_4$)OPiv (17.6 mg, 0.100 mmol), (NMe$_4$)OC(CF$_3$)$_3$ (193.3 mg, 0.625 mmol), 2b (26.3 μL, 0.250 mmol), d$_1$-1a (83.7 mg, 0.375 mmol), 1y (52.2 μL, 0.375 mol) and pivalonitrile (58.2 μL, 0.75 mmol) were loaded in a crimp-cap microwave vial with a stirrer bar. The vial was sealed, taken outside the box and the mixture was stirred at 115 °C for 8 min. Upon completion, the vial was quickly cooled in a dry ice/acetone bath and hexafluorobenzene (14.4 μL, 0.125 mmol, 0.5 equiv.) was added as internal standard in CDCl$_3$. The crude was then filtered through a cotton plug directly into an NMR tube for quantitative $^{19}$F-NMR analysis.

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Scheme S2. KIE experiment with fluoroarenes d$_{1}$-1a and 1y with bromobenzene 2b.

Figure S7.

$^{19}$F-NMR expansion of the reaction illustrated in Scheme S2, displaying 1a, d$_{1}$-1a, 1y, d$_{1}$-1y, 3aa, 3ya with relative integrations with respect to the internal standard C$_6$F$_6$. 

\[ \text{KIE} = \frac{0.065}{0.03} = 2.2 \]
General Procedure 16: KIE experiment of fluoroarenes d₁-1a and 1a with bromobenzene 2b in Separate Flasks

All solid reagents, except C₅, were dried at 70 °C in a vacuum oven over night. All liquid reagents were dried over 4Å molecular sieves and degassed with 3 freeze-pump-thaw cycles. In a glove box, C₅ (7.8 mg, 0.025 mmol), (NMe₄)₄-fluorobenzoate (0.0875 mmol, 18.7 mg), (NMe₄)OPiv (17.6 mg, 0.100 mmol), (NMe₄)OC(CF₃)₃ (193.3 mg, 0.625 mmol), 2a (26.3 μL, 0.250 mmol), 1a or d₁-1a (166.6 mg or 167.4 mg, 0.750 mmol) and pivalonitrile (58.2 μL, 0.750 mmol) were loaded in a crimp-cap microwave vial with a stirrer bar. The vial was sealed, taken outside the box and the mixture was stirred at 115 °C for the appropriate time. Upon completion, the vial was quickly cooled in a dry ice/acetone bath and a given amount of hexafluorobenzene was added as internal standard in CDCl₃. The crude mixture was then filtered through a cotton plug directly into an NMR tube for quantitative ¹⁹F-NMR analysis.

![Chemical reaction diagram]

Table S11. KIE experiment for fluoroarenes d₁-1a and 1a with bromobenzene 2b in separate flasks.
Graph S2.  
Rate of formation of \(3ab\) for C–H arylation of \(1a\) and \(d_{1}\)-\(1a\) with \(2b\) (%/min).

\[
\text{KIE} = \frac{kH}{kD} = \frac{1.405}{0.590} = 2.4
\]

General Procedure 17: preparation of \(\text{Ru(OCOR)}_{2}(\eta^{6}-\text{arene})\) C2, C3 and C4

\([\text{RuCl}_{2}(\eta^{6}-\text{arene})]_2\) (1.0 equiv, 0.5 mmol) and \(\text{KOCOR}\) (20.0 equiv, 10 mmol) were weighed in a Schlenk flask with a magnetic stirrer bar. The reaction vessel was evacuated and backfilled with \(N_2\) three times, then left under vacuum for 30 min. The vial was backfilled with \(N_2\) then dry toluene (20.0 mL, 0.025 M), which was degassed with 3 freeze-pump-thaw cycles, was added \textit{via} syringe. The reaction was then heated at 70 °C for 12 h. Note: if the reaction is left longer than 12 h, partial decomposition and lower yields were observed. Upon completion, the reaction mixture was cooled to room temperature, and evaporated to dryness under reduced pressure. 50 mL of \(\text{CH}_2\text{Cl}_2\) were added to the crude, then the resulting mixture was filtered through a plug of Celite® and the remaining yellow/orange solution evaporated under reduced pressure affording the final complex as a yellow/orange solid. If needed, crystallization from \(\text{CH}_2\text{Cl}_2/\text{hexane}\) or cold Et\(_2\)O was effectuated.
Characterization data of C2-C4

The General Procedure 17 was applied with [RuCl₂(p-cymene)]₂ (306.2 mg, 0.5 mmol) and KOPiv (1.40 g, 10.0 mmol). Crystallization from CH₂Cl₂/hexane afforded Ru(OPiv)₂(p-cymene) (C2) as a yellow solid (371.9 mg, 85%). Spectroscopic data matched those previously reported.⁹

¹H NMR (500 MHz; CDCl₃): δ 5.71 (d, J = 5.5 Hz, 2H), 5.49 (d, J = 5.5 Hz, 2H), 2.88 (septet, J = 6.9 Hz, 1H), 2.24 (s, 3H), 1.32 (d, J = 6.9 Hz, 6H), 1.06 (s, 18H); ¹³C NMR: (126 MHz; CDCl₃): δ 192.0, 98.7, 94.3, 78.3, 76.9, 40.0, 31.6, 27.7, 22.6, 18.6.

The General Procedure 17 was applied with [RuCl₂(p-cymene)]₂ (306.2 mg, 0.5 mmol) and KOBz (1.60 g, 10.0 mmol). Crystallization from cold Et₂O afforded Ru(OBz)₂(p-cymene) (C3) as an orange solid (277.0 mg, 58%).

¹H NMR (400 MHz, CDCl₃): δ 7.86 - 7.83 (m, 4H), 7.37 (tt, J = 7.4, 1.5 Hz, 2H), 7.28 - 7.24 (m, 4H), 5.99 (d, J = 6.1 Hz, 2H), 5.78 (d, J = 6.1 Hz, 2H), 2.97 (septet, J = 6.9 Hz, 1H), 2.36 (s, 3H), 1.41 (d, J = 6.9 Hz, 6H); ¹³C NMR (126 MHz, CDCl₃): δ 178.9, 134.3, 131.7, 129.2, 128.2, 98.5, 93.5, 79.5, 78.1, 32.0, 22.7, 18.9. IR (ATR) 3082, 2964, 1633, 829; m.p. 105-110 °C. Anal. Calcd for C₂₄H₂₄O₄Ru: C, 60.37; H, 5.07. Found: C, 60.41; H, 5.11. MS (ES⁺, MeCN) m/z 477.1 (10%) [M – (H)]⁺, MS (ES⁺, MeCN) m/z 398.1 (100%) [M – (C₇H₅O₂+MeCN)]⁺.

The General Procedure 17 was applied with [RuCl₂(C₆Me₆)]₂ (334.2 mg, 0.5 mmol) and KOPiv (1.40 g, 10.0 mmol) affording Ru(OPiv)₂(C₆Me₆) (C4) as a dark orange solid (419.0 mg, 90%).

¹H NMR (500 MHz, CDCl₃): δ 2.08 (s, 18H), 1.07 (s, 18H); ¹³C NMR (126 MHz, CDCl₃): δ 190.0, 88.4, 40.0, 28.1, 15.4. IR (ATR) 2953, 2923, 1557, 866; m.p. 95-100 °C. Anal. Calcd for C₂₂H₃₆O₄Ru: C, 56.75; H, 7.79. Found: C, 56.80; H, 7.84. MS (ES⁺, MeCN) m/z 365.2 (100%) [M – (C₃H₅O₂)]⁺, m/z 447.2 (50%) [M – (C₅H₉O₂ + 2MeCN)]⁺.
Procedure 18: Synthesis of hexakis(pivalonitrile-$\kappa$N)ruthenium(II) bis(tetrafluoroborate) C5

Neither Schlenk nor anhydrous conditions are needed for the synthesis of C5. 1.0 g RuCl$_3$•xH$_2$O (Reagent Grade purity ≥ 95%, 4.6 mmol based on anhydrous molecular weight), 1.0 g of Zn dust (<10 μm, 15.3 mmol) and 70.0 mL of pivalonitrile were loaded in a 100 mL Ace pressure tube and heated for 1 h at 115 °C. Note: 1) a change in colour from dark green to blue and finally to deep yellow/brown is observed; 2) if the mixture is left longer than 1 h, lower yields were observed. Then, the reaction mixture was cooled to room temperature, filtered through a plug of Celite® and the resulting solution was loaded again into an Ace pressure tube with 1.5 g of NaBF$_4$ (13.7 mmol). After heating the mixture for 16 h at 115 °C, the reaction was cooled to room temperature, filtered through a plug of Celite® and evaporated to dryness. Note: the solvent pivalonitrile can be easily distilled, recovered and reused at this stage. The crude was dissolved in CH$_2$Cl$_2$, filtered through a plug of Celite® and the pale green solution was reduced in vacuo. Crystallization of the crude with CH$_2$Cl$_2$ /Et$_2$O gave a white/grey solid, which was filtered and washed with Et$_2$O. Repetition of the crystallization procedure a further 3 times provided 1.6 g of a white solid. This compound is a mixture of the desired complex C5 and of C5’ [hexakis(pivalonitrile-$\kappa$N)ruthenium(II)]di-$\mu$-chlorobis[chlororuthenium(II)]. The molecular structure of C5’ ([Ru(tBuCN)$_6$][Ru$_2$Cl$_6$]) was determined by X-ray (see crystallographic section, suitable crystals were grown by slow crystallization from CH$_2$Cl$_2$ /Et$_2$O). Subsequently, the mixture of C5 and C5’ (1.6 g) was mixed with AgBF$_4$ (9.5 mmol, 1.85 g), and pivalonitrile (50 mL) in an Ace pressure tube and heated for 4 h at 100 °C. After this time, the reaction was cooled to room temperature, filtered through a plug of Celite® and evaporated to dryness. Note: the solvent pivalonitrile can be distilled and recovered again at this stage. The crude was dissolved in CH$_2$Cl$_2$, filtered through a plug of Celite® and the pale yellow solution was reduced in vacuo. Crystallization of the crude with CH$_2$Cl$_2$ /Et$_2$O gave an off-white solid, which was filtered and washed with Et$_2$O. Repetition of the crystallization procedure an additional 2 times provided title complex C5 as a bench stable white solid (1.55 g, 2.0 mmol, 43.5%). Suitable crystals of C5 for X-ray crystallography were grown by slow crystallization from CH$_2$Cl$_2$ /Et$_2$O (see crystallographic section).

$^1$H NMR (400 MHz, (CD$_3$)$_2$CO): $\delta$ 1.56 (s, 54H); $^{13}$C NMR (126 MHz, (CD$_3$)$_2$CO): $\delta$ 134.7, 31.3, 28.1; $^{19}$F NMR (376 MHz, (CD$_3$)$_2$CO) $\delta$ –151.2 (s), –151.2 (s); IR (ATR) 1097, 1055; m.p. > 230 °C decomposition. Anal. Calcd for C$_{30}$H$_{54}$B$_2$F$_8$N$_6$Ru: C, 46.59; H, 7.04; N, 10.87. Found: C, 46.50; H, 7.14; N, 10.81. MS (ES$^+$, CH$_2$Cl$_2$) m/z 687.5 (100%) [M – (BF$_4$)]$^+$. 
General Procedure 19 for the preparation of Ru2a and Ru2c

Ru1a or Ru1c (1.0 equiv, 0.25 mmol) and NaBF4 (82.4 mg, 0.75 mmol) were weighed in a crimp-cap Schlenk microwave vial (20 mL) with a magnetic stirrer bar. Note: the use of an oversized stirrer bar is advised. The reaction vessel was capped, evacuated and backfilled with N2 three times, then left under vacuum for 30 min. The vial was backfilled with N2 then pivalonitrile (5.0 mL, 0.05 M), which was dried over 4Å molecular sieves and degassed with 3 freeze-pump-thaw cycles, was added via syringe. The vial was resealed with a new cap under a stream of N2 and the reaction was heated at 120 °C for 75 min with vigorous stirring. Upon completion, the reaction mixture was cooled to room temperature, diluted with 3 mL of pivalonitrile, filtered through a plug of Celite® and the remaining pale yellow/greenish solution evaporated under reduced pressure. The crude was then purified by crystallization from 'BuCN/Et2O affording the final products as white solids, which were washed with Et2O. The final complexes are stable under air for a few hours, but decompose if exposed to oxygen for longer. Storage of Ru2a and Ru2c in a desiccator under vacuum or in glove box is needed. Suitable crystals of Ru2c for X-ray crystallography were grown by slow crystallization from CH2Cl2/Et2O (see crystallographic section).

Characterization data of Ru2a and Ru2c

The General Procedure 19 was applied with Ru1a (139.4 mg, 0.25 mmol) affording Ru2a (105.1 mg, 51%).

1H NMR (400 MHz, CDCl3): δ 4.14 (t, J = 6.5 Hz, 2H), 1.78 (app quintet, J = 7.0 Hz, 2H), 1.57 (s, 9H), 1.52 (app t, J = 7.5 Hz, 2H), 1.42 (s, 36H), 0.98 (t, J = 7.4 Hz, 3H); 13C NMR (126 MHz, CDCl3): δ 153.4 (dm, J = 226.2 Hz), 140.2 (dm, J = 246.3 Hz), 131.8 - 131.8 (m), 131.3, 129.2, 124.3 - 123.5 (m), 74.9, 32.2, 30.3, 29.8, 28.6, 28.5, 19.1, 14.0; 19F NMR (471 MHz, CDCl3) δ −121.8 (dd, J = 26.9, 9.5 Hz, 2F), −154.0 (s), −154.1 (s), −160.9 (dd, J = 26.6, 9.3 Hz, 2F); IR (ATR) 2954, 2252, 1424, 999; m.p. 160 °C decomposition; Anal. Calcd for C35H54BF8N5ORu: C, 50.97; H, 6.60; N, 8.49. Found: C, 51.04; H, 6.67; N, 8.43. MS (ES+, CH2Cl2) m/z 655.4 (35%) [M − (BF4 + 'BuCN)]+. The General Procedure 19 was applied with Ru1c (121.4 mg, 0.25 mmol) affording Ru2c (127.9 mg, 68%).

1H NMR (400 MHz, CD2Cl2): δ 6.67 - 6.58 (m, 1H), 1.53 (s, 9H), 1.39 (s, 36H); 13C NMR (101 MHz, CD2Cl2): δ 153.7 (dddd, J = 226.3, 19.3, 9.8, 2.5 Hz), 144.8 (dddd, J = 246.0,
22.7, 9.4, 2.2 Hz), 136.0 (tt, J = 44.1, 3.7 Hz), 131.5, 129.1, 99.7 (t, J = 23.6 Hz), 30.4, 29.9, 28.6, 28.4; \(^{19}\)F NMR (376 MHz, CD\(_2\)Cl\(_2\)) \(\delta -121.4 - 121.6\) (m), \(-144.9 - 145.0\) (m), \(-153.7\) (s), \(-153.2\) (s); IR (ATR) 2929, 2272, 1436, 1052; m.p. 170 °C decomposition; Anal. Calcd for C\(_{31}\)H\(_{46}\)BF\(_{8}\)N\(_{5}\)Ru: C, 49.47; H, 6.16; N, 9.31. Found: C, 49.52; H, 6.20; N, 9.25. MS (ES\(^+\), CH\(_2\)Cl\(_2\)) \(m/z\) 583.4 (50%) [M − (BF\(_4\) + \(^1\)BuCN)]\(^+\).

**General procedure 20 for the preparation of tetramethylammonium salts**

A round bottom flask equipped with a magnetic stirrer bar was loaded with 50.0 mL (50.0 mmol) of (NMe\(_4\))OH • 5H\(_2\)O solution (1.0 M in EtOH) and placed in an ice bath. Subsequently, a solution of the acid, or (CF\(_3\))\(_3\)COH in EtOH (50 mL, 50 mmol, 1.0 M) was added at 0 °C. Then the ice bath was removed and the solution allowed to stir at room temperature of 1 h. The solvent was removed under reduced pressure affording the salts as white solid in quantitative yield.

**Characterization data of tetramethylammonium salts**

The General Procedure 20 was applied with perfluoro-tert-butyl alcohol affording tetramethylammonium perfluoro-tert-butyl alkoxide (15.44 g, 100%).

\(^1\)H NMR (400 MHz, D\(_2\)O): \(\delta 3.14\) (s, 12H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta 122.6\) (q, \(J = 294.3\) Hz), 82.1 - 81.0 (m), 55.1 - 55.1 (m); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -75.4\) (s); IR (ATR) 1249, 1194, 949, 721; m.p. 170 – 175 °C.

The General Procedure 20 was applied with pivalic acid affording tetramethylammonium pivalate (8.75 g, 100%).

\(^1\)H NMR (400 MHz, D\(_2\)O): \(\delta 3.14\) (s, 12H), 1.06 (s, 9H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta 188.7, 55.2 - 55.1\) (m), 39.7, 27.4; IR (ATR) 1609, 1356, 920, 780; m.p. 235 – 240 °C.

The General Procedure 20 was applied with 4-fluorobenzoic acid affording tetramethylammonium 4-fluorobenzoate (10.6 g, 100%).

\(^1\)H NMR (400 MHz, D\(_2\)O): \(\delta 7.84\) (dd, \(J = 8.9, 5.6\) Hz, 2H), 7.12 (app t, \(J = 8.9\) Hz, 2H), 3.14 (s, 12H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta 174.5, 164.3\) (d, \(J = 248.0\) Hz), 132.4 (d, \(J = 2.7\) Hz), 131.2 (d, \(J = 9.1\) Hz), 114.9 (d, \(J = 21.8\) Hz), 55.1 - 55.1 (m); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -110.4 - 110.4\) (m, 1F); IR (ATR) 2944, 1565, 1348, 951; m.p. 225 – 230 °C.
General procedure 21 for the preparation of 1a, 1o, and 1h

1-bromobutane (23.5 mmol) was added to a stirred suspension of perfluoro(thio)phenol (25.0 mmol) and K$_2$CO$_3$ (30.0 mmol) in MeCN (40.0 mL) under reflux conditions and stirred for a further 5 h. Upon completion, the reaction mixture was allowed to cool to ambient temperature; then H$_2$O (100 mL) and pentane (200 mL) were added. After phase separation, the organic layer was washed with 1 M NaOH (100 mL), H$_2$O (2 × 100 mL) and brine (100 mL), dried over MgSO$_4$ and evaporated to dryness affording a pale yellow oil. Purification via a silica plug eluted with pentane gave the title product as a colorless oil. For the synthesis of 1a and 1o the reaction can be carried out under air. Schlenk conditions and lower temperatures are required for the synthesis of 1h (50 °C for 3 h after addition of the electrophile).

Characterization data of 1a, 1o and 1h

The General Procedure 21 was applied with 2,3,5,6-tetrafluorophenol (4.15 g 25.0 mmol) affording 3-butoxy-1,2,4,5-tetrafluorobenzene (1a) (4.39 g, 84%). Spectroscopic data matched those previously reported. 10

$^1$H NMR (500 MHz, CDCl$_3$): δ 6.74 (tt, $J = 10.0, 7.0$ 1H), 4.22 (t, $J = 6.7$ Hz, 2H), 1.76 (app quintet, $J = 7.0$ Hz, 2H), 1.51 (app sextet, $J = 7.5$ Hz, 2H), 0.97 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 146.5 (dtd, $J = 246.5, 12.6, 4.0$ Hz), 141.4 (ddt, $J = 246.7, 14.6, 3.9$ Hz), 138.5 (tt, $J = 12.1, 3.6$ Hz), 99.3 (t, $J = 23.1$ Hz), 75.2 (t, $J = 3.2$ Hz), 32.1, 18.9, 13.7; $^{19}$F NMR (471 MHz, CDCl$_3$) δ –140.5 –140.6 (m, 2F), –157.4 –157.4 (m, 2F); IR (ATR) 2964, 1488, 1171, 1087, 713; HRMS (APCI) $m/z$ calcd. C$_{10}$H$_{10}$F$_4$O: 222.0668; found [M+H]$^+$ 223.0737.

The General Procedure 21 was applied with 2,4,5-trifluorophenol (3.70 g 25.0 mmol) affording 1-butoxy-2,4,5-trifluorobenzene (1o) (3.89 g, 81%).

$^1$H NMR (500 MHz, CDCl$_3$): δ 6.97 - 6.91 (m, 1H), 6.79 (app dt, $J = 11.5, 7.7$ Hz, 1H), 3.96 (t, $J = 6.5$ Hz, 2H), 1.78 (app quintet, $J = 7.1$ Hz, 2H), 1.49 (app sextet, $J = 7.5$ Hz, 2H), 0.97 (t, $J = 7.4$ Hz, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 147.9 (ddd, $J = 245.1, 9.0, 3.3$ Hz), 146.2 (ddd, $J = 243.8, 13.2, 3.8$ Hz), 143.6 - 143.5 (m), 143.3 (ddd, $J = 242.9, 14.1, 10.5$ Hz), 105.9 (app t, $J = 23.0$ Hz), 104.1 (d, $J = 22.1$ Hz), 70.1, 31.2, 19.2, 13.8; $^{19}$F NMR (471 MHz, CDCl$_3$) δ –136.3 –136.4 (m, 1F), –141.3 –141.5 (m, 1F), –145.4 (app dt $J = 21.3, 8.9$ Hz, 1F); IR (ATR) 2962, 1485, 1173, 912, 712. HRMS (APCI) $m/z$ calcd. C$_{10}$H$_{10}$F$_4$O: 204.0757; found [M]$^+$ 204.0749.
The General Procedure 21 was applied with 2,3,5,6-tetrafluorobenzenethiol (4.55 g, 25.0 mmol) affording butyl(2,3,5,6-tetrafluorophenyl)sulfane (1h) (4.37 g, 78%).

\[ \text{1H NMR (500 MHz, CDCl}_3\text{): } \delta 7.05 - 6.98 (m, 1H), 2.93 (t, J = 7.4 Hz, 2H), 1.54 (app quintet, J = 7.4 Hz, 2H), 1.42 (app sextet, J = 7.4 Hz, 2H), 0.89 (t, J = 7.4 Hz, 3H); \]

\[ \text{13C NMR (126 MHz, CDCl}_3\text{): } \delta 147.0 (app ddt, J = 244.8, 13.6, 3.3 Hz), 146.0 (dm, J = 249.6 Hz), 115.8 (t, J = 20.2 Hz), 105.7 (t, J = 22.9 Hz), 34.4, 32.0, 21.6, 13.6; \]

\[ \text{19F NMR (471 MHz, CDCl}_3\text{)} \delta -134.0 - -134.1 (m, 2F), -138.4 - -138.6 (m, 2F); \]

\[ \text{IR (ATR) 2962, 1524, 1217, 1167, 855. HRMS (EI) m/z calcd. C}_{10}\text{H}_{10}\text{F}_4\text{S: [M] }^+ 238.0434; \text{ found: [M] }^+ 238.0438. \]

**Procedure 22: preparation of 3-butoxy-1,2,4,5-tetrafluorobenzene-6-d (d\textsubscript{1}-1a)**

Compound 1a (5.00 g, 22.5 mmol) was dissolved in anhydrous THF (70 mL, 0.33 M) in a flame-dried Schlenk flask under a N\textsubscript{2} atmosphere. The stirred solution was left to cool to −78 °C then a solution of \textsuperscript{\textit{t}}BuLi in pentane (15.5 mL, 24.8 mmol, 1.6 M) was added dropwise. The mixture was allowed to stir at −78 °C for an additional 15 min before being quenched with D\textsubscript{2}O [10 M in anhydrous THF] (22.5 mL, 225 mmol). The reaction mixture was then allowed to warm to ambient temperature and stirred for a further 30 min. After this time, the solution was diluted with TBME (150 mL), pentane (50 mL) and H\textsubscript{2}O (150 mL). The organic phase was separated, washed with H\textsubscript{2}O (3×100 mL) and brine (100 mL), dried over MgSO\textsubscript{4} and evaporated under reduced pressure affording a pale yellow oil. Purification \textit{via} a silica plug eluted with pentane gave the title product as a colourless oil (4.25 g, 84%, > 99 atom % D).

\[ \text{1H NMR (500 MHz, CDCl}_3\text{): } \delta 4.22 (t, J = 6.5 Hz, 2H), 1.76 (app quintet, J = 7.0 Hz, 2H), 1.50 (app sextet, J = 7.5 Hz, 2H), 1.97 (t, J = 7.4 Hz, 3H); \]

\[ \text{13C NMR (126 MHz, CDCl}_3\text{): } \delta 146.5 (dtd, J = 246.7, 12.6, 3.9 Hz), 141.4 (app ddt, J = 246.3, 14.5, 3.7 Hz), 138.5 (tt, J = 12.1, 3.6 Hz), 99.5 - 99.7 (m), 71.16 (t, J = 3.1 Hz), 32.0, 18.9, 13.8; \]

\[ \text{19F NMR (471 MHz, CDCl}_3\text{)} \delta -140.7 (dd, J = 21.3, 9.1 Hz, 2F), -157.3 (dd, J = 21.0, 9.1 Hz, 2H); \]

\[ \text{IR (ATR) 2966, 1491, 1167, 1094, 708;HRMS (APCI) m/z calcd. C}_{10}\text{H}_{9}\text{DF}_4\text{O: 223.0731; found [M+H]}^+ 224.0801. \]

**Procedure 23: preparation of N-(2,3,5,6-tetrafluorophenyl)pivalamide 1f**

NE\textsubscript{3} (1.4 mL, 10.0 mmol) and trimethylacetyl chloride (553.6 µL, 4.5 mmol) were added \textit{via} syringe to a solution containing 2,3,5,6-tetrafluoroaniline (825.5 mg, 5.0 mmol) in toluene (15.0 mL, 0.33 M), and the mixture was heated to reflux for 16 h. After this time, the reaction mixture
was allowed to cool to ambient temperature and concentrated under reduced pressure to dryness. CH$_2$Cl$_2$ (100 mL) and H$_2$O (100 mL) were added to the crude, the organic phase phase was separated, washed with 1 M NaOH (100 mL), H$_2$O (100 mL) and brine (100 mL), dried over MgSO$_4$ and evaporated under reduced pressure. Purification by flash chromatography with a 0-30% CH$_2$Cl$_2$-hexane gradient afforded the product as a white solid (997.0 mg, 89%).

**Procedure 24: preparation of tert-butyl 2,3,5,6-tetrafluorobenzoate 1i**

Tosyl chloride (1.91 g, 10.0 mmol) was added to an ice-cold solution of 2,3,5,6-tetrafluorobenzoic acid (970.0 mg, 5.0 mmol) in pyridine (10.0 mL, 0.5 M). After 10 min, tert-butanol (741.2 mg, 10.0 mmol) was added and the solution was stirred for a further 1 h at 0 °C. Then, the reaction mixture was allowed to warm to room temperature and stirred for an additional 16 h. The solvent was evaporated to dryness and the residue was partitioned between EtOAc (100 mL) and saturated NaHCO$_3$ (100 mL). The organic layer was separated, washed with saturated NaHCO$_3$ (2×100 mL) and brine (100 mL) and dried over MgSO$_4$ giving a pale yellow oil. Purification via silica plug with 5% of CH$_2$Cl$_2$ in hexane afforded the title compound as colourless oil (1.20 g, 96%).
Characterization data of biaryl compounds

4-butoxy-2,3,5,6-tetrafluoro-4'-methoxy-1,1'-biphenyl (3aa).

The General Procedure 1 was applied with 4-bromoanisole (62.6 μL, 0.50 mmol) and 3-butoxy-1,2,4,5-tetrafluorobenzene (333.3 mg, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (134.6 mg, 82%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.38 (d, \(J = 8.9\) Hz, 2H), 7.00 (d, \(J = 8.9\) Hz, 2H), 4.25 (t, \(J = 6.5\) Hz, 2H), 3.86 (s, 3H), 1.79 (app quintet, \(J = 7.0\) Hz, 2H), 1.52 (app sextet, \(J = 7.5\) Hz, 2H), 1.99 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ 160.0, 144.4 (dm, \(J = 245.1\) Hz), 141.7 (app ddt, \(J = 246.5, 15.7, 4.3\) Hz), 136.6 - 136.4 (m), 131.6, 119.6, 114.2 - 114.0 (m, 2C), 75.2 (t, \(J = 3.0\) Hz), 55.5, 32.1, 19.0, 13.9; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) δ –145.7 (dd, \(J = 22.4, 8.8\) Hz, 2F), 157.7 (dd, \(J = 22.4, 8.8\) Hz, 2F); IR (ATR) 2934, 1476, 1080, 974, 826. m.p. 49 - 51 °C; HRMS (EI) \(m/z\) calcd. C\(_{17}\)H\(_{16}\)F\(_4\)O\(_2\) [M]+ 328.1081 found: [M]+ 328.1077.

4-butoxy-2,3,5,6-tetrafluoro-1,1'-biphenyl (3ab).

The General Procedure 1 was applied with bromobenzene (52.7 μL, 0.50 mmol) and 3-butoxy-1,2,4,5-tetrafluorobenzene (333.3 mg, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (113.4 mg, 76%).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): δ 7.51 - 7.40 (m, 5H), 4.29 (t, \(J = 6.5\) Hz, 2H), 1.85 - 1.79 (m, 2H), 1.59 - 1.52 (m, 2H), 1.02 (t, \(J = 7.4\) Hz, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ 144.4 (dm, \(J = 245.7\) Hz), 141.6 (ddt, \(J = 246.6, 15.6, 4.4\) Hz), 137.0 (tt, \(J = 12.3, 3.5\) Hz), 130.3, 128.9, 128.7, 127.5, 114.3 (t, \(J = 17.2\) Hz), 75.2, 32.1, 19.0, 13.8; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) δ –145.7 (dd, \(J = 21.9, 8.9\) Hz, 2F), –157.6 (dd, \(J = 22.2, 8.7\) Hz, 2F); IR (ATR) 2934, 1476, 1080, 974, 826. m.p. 35 - 29 °C; HRMS (EI) \(m/z\) calcd. C\(_{16}\)H\(_{14}\)F\(_4\)O: [M]+ 298.0975 found: [M]+ 298.0986.

2,3,4,5,6-pentafluorobiphenyl (3bb)

The General Procedure 1 was applied with bromobenzene (52.7 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (116.0 mg, 95%).

Spectroscopic data matched those previously reported.\(^{11}\)

\(^1\)H NMR (400 MHz, CDCl\(_3\)): δ 7.52 - 7.45 (m, 3 H), 7.45 - 7.41 (m, 2 H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): δ 144.3 (dm, \(J = 247.5\) Hz), 140.5 (dm, \(J = 252.7\) Hz), 138.0 (dm, \(J = 250.6\) Hz), 130.3,
129.4, 128.9, 126.5, 116.1 (app td, $J = 17.4$, 4.0 Hz), $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ –143.2 (dd, $J = 22.9$, 8.2 Hz, 2F), –155.6 (t, $J = 21.1$ Hz, 1F), –162.2 – –162.3 (m, 2F).

3',5'-dimethyl-2,3,4,5,6-pentafluorobiphenyl (3bc)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (126.6 mg, 93%).

Spectroscopic data matched those previously reported.$^{12}$

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.10 (s, 1H), 7.02 (s, 2H), 2.38 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 144.3 (dm, $J = 247.1$ Hz), 140.4 (dm, $J = 253.3$ Hz), 138.5, 137.9 (dm, $J = 250.3$ Hz), 131.1, 127.9, 126.3, 116.4, (app td, $J = 17.6$, 3.9 Hz), 21.4; $^{19}$F NMR (376 MHz, CDCl$_3$) δ –143.0 (dd, $J = 23.2$, 8.2 Hz, 2F), –156.1 (t, $J = 21.0$ Hz, 1F), –162.5 (app td, $J = 22.1$, 7.6 Hz, 2F).

2,3,4,5,6-pentafluoro-4'-methylbiphenyl (3bd)

The General Procedure 1 was applied with 4-bromotoluene (61.5 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (108.4 mg, 84%).

Spectroscopic data matched those previously reported.$^{12}$

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.31 (app s, 4H), 2.42 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 144.3 (dm, $J = 247.5$ Hz), 140.4 (dm, $J = 253.0$ Hz), 139.6, 138.0 (dm, $J = 251.6$ Hz), 130.1, 129.6, 123.5, 116.1 (app td, $J = 17.3$, 3.7 Hz), 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$) δ –143.4 (dd, $J = 23.1$, 8.2 Hz, 2F), –156.1 (t, $J = 21.0$ Hz, 1F), –162.4 (app td, $J = 22.1$, 8.0 Hz, 2F).

2,3,4,5,6-pentafluoro-2'-methylbiphenyl (3be)

The General Procedure 1 was applied with 2-bromotoluene (60.1 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colorless oil (56.8 mg, 44%).

Spectroscopic data matched those previously reported.$^{11}$
$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41 - 7.34 (m, 2H), 7.30 (app td, $J = 7.3$, 1.4 Hz, 1H), 7.19 (d, $J = 7.5$ Hz, 1H), 2.19 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 144.2 (dm, $J = 246.4$ Hz), 140.7 (dm, $J = 253.9$ Hz), 137.8 (dm, $J = 250.8$ Hz), 137.5, 130.7, 130.6, 129.8, 126.1, 126.0, 115.6 (app td, $J = 19.9$, 4.2 Hz), 19.8; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -140.5 (dd, $J = 23.3$, 8.3 Hz, 2F), -155.3 (t, $J = 20.9$ Hz, 1F), -162.2 (app td, $J = 22.1$, 7.7 Hz, 2F).

2,3,4,5,6-pentafluoro-4'-methoxybiphenyl (3ba)

The General Procedure 1 was applied with 4-bromoanisole (62.6 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (117.9 mg, 86%).

Spectroscopic data matched those previously reported.$^{11}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.36 (d, $J = 8.9$ Hz, 2 H), 7.02 (d, $J = 8.9$ Hz, 2 H), 3.87 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 160.4, 144.3 (dm, $J = 246.7$ Hz), 140.2 (dm, $J = 252.5$ Hz), 138.0 (dm, $J = 250.6$ Hz), 131.6, 118.5, 115.8 (app td, $J = 17.1$, 3.9 Hz), 114.3, 55.4; $^{19}$F NMR (376 MHz, CDCl$_3$): $\delta$ -143.6 (dd, $J = 23.2$, 8.2 Hz, 2F), -156.5 (t, $J = 21.0$ Hz, 1F), -162.5 (app dt, $J = 22.3$, 7.6 Hz, 2F).

3'-methoxy-2,3,4,5,6-pentafluorobiphenyl (3bf)

The General Procedure 1 was applied with 3-bromoanisole (63.3 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (109.7 mg, 80%).

Spectroscopic data matched those previously reported.$^{11}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.41 (app t, $J = 8.0$ Hz, 1H), 7.02 - 6.98 (m, 2H), 6.95 - 6.94 (m, 1H), 3.85 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 159.8, 144.3 (dm, $J = 247.7$ Hz), 140.6 (dm, $J = 253.6$ Hz), 138.0 (dm, $J = 249.5$ Hz), 129.9, 127.6, 122.6, 116.2 - 115.8 (m, 2C), 115.0, 55.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -142.8 (dd, $J = 23.0$, 8.1 Hz, 2F), -155.5 (t, $J = 20.9$ Hz, 1F), -162.2 (app td, $J = 22.1$, 7.4 Hz, 2F).
The General Procedure 1 was applied with 2-bromoanisole (62.3 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colourless oil (91.8 mg, 67%).

Spectroscopic data matched those previously reported.$^{13}$

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.46 (ddd, $J = 8.3$, 7.5, 1.7 Hz, 1 H), 7.23 (dd, $J = 7.5$, 1.4 Hz, 1 H), 7.08 - 7.02 (m, 2H), 3.81 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 157.3, 144.6 (dm, $J = 247.1$ Hz), 140.7 (dm, $J = 252.5$ Hz), 137.7 (dm, $J = 249.8$ Hz), 131.9, 131.3, 120.7, 115.4, 112.9 (app td, $J = 19.2$, 4.0 Hz), 111.4, 55.7; $^{19}$F NMR (376 MHz, CDCl$_3$) δ –140.2 (dd, $J = 23.0$, 7.9 Hz, 2F), –156.2 (t, $J = 20.9$ Hz, 1F), –163.1 - –163.3 (m, 2F).

The General Procedure 1 was applied with 1-bromo-4-fluorobenzene (54.9 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (106.2 mg, 81%).

Spectroscopic data matched those previously reported.$^{11}$

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.44 - 7.40 (m, 2H), 7.19 (app t, $J = 8.7$ Hz, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 163.3 (d, $J = 250.0$ Hz), 144.3 (dm, $J = 247.6$ Hz), 140.6 (dm, $J = 254.2$ Hz), 138.0 (dm, $J = 251.1$ Hz), 132.2 (d, $J = 8.4$ Hz), 122.4, 116.1 (d, $J = 21.9$ Hz), 115.1, (app td, $J = 17.1$, 3.9 Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) δ –111.2 - –111.3 (m, 1F), –143.3 (dd, $J = 22.9$, 8.2 Hz, 2F), –155.1 (t, $J = 21.0$ Hz, 1F), –161.9 (app td, $J = 21.9$, 7.7 Hz, 2F).

The General Procedure 1 was applied with 1-bromo-2-fluorobenzene (54.7 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (82.6 mg, 63%).

Spectroscopic data matched those previously reported.$^{14}$

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.51 - 7.47 (m, 1H), 7.35 (app t, $J = 7.1$ Hz, 1H), 7.28 (app t, $J = 8.2$ Hz, 1H), 7.23 (app t, $J = 9.1$ Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 160.0 (d, $J = 250.7$ Hz),
144.5 (dm, $J = 249.2$ Hz), 141.2 (dm, $J = 254.4$ Hz), 137.9 (dm, $J = 251.1$ Hz), 132.1, 131.9 (d, $J = 8.3$ Hz), 124.5 (d, $J = 3.6$ Hz), 116.3 (d, $J = 21.6$ Hz), 114.3 (d, $J = 15.9$ Hz), 110.3 (app td, $J = 18.6, 3.9$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-112.71$ - $-112.82$ (m, 1F), $-140.3$ (app dt, $J = 23.0, 9.1$ Hz, 2F), $-154.0$ (t, $J = 21.0$ Hz, 1F), $-162.0$ (app td, $J = 21.7, 7.4$ Hz, 2F).

2,3,4,5,6-pentafluoro-3'-trifluoromethyl)biphenyl (3bj)

The General Procedure 1 was applied with 3-bromobenzotrifluoride (69.7 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colourless oil (98.3 mg, 63%).

Spectroscopic data matched those previously reported.$^{13}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.75 - 7.71 (m, 2H), 7.66 - 7.62 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 144.3 (dm, $J = 248.7$ Hz), 141.1 (dm, $J = 253.4$ Hz), 138.1 (dm, $J = 251.3$ Hz), 133.6, 131.5 (q, $J = 32.9$ Hz), 129.5, 127.4, 127.2, 126.3 (q, $J = 3.6$ Hz), 123.8 (q, $J = 272.5$ Hz), 114.6 (td, $J = 16.7, 4.4$ Hz); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-62.8$ (s, 3F), $-143.0$ (dd, $J = 22.7, 8.2$ Hz, 2F), $-153.8$ (t, $J = 21.0$ Hz, 1F), $-161.4$ (app td, $J = 21.9, 7.9$ Hz, 2F).

2,3,4,5,6-pentafluoro-4'-trifluoromethylbiphenyl (3bk)

The General Procedure 1 was applied with 4-bromobenzotrifluoride (70.0 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (96.8 mg, 62%).

Spectroscopic data matched those previously reported.$^{11}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.77 (d, $J = 8.1, 2$H), 7.57 (d, $J = 8.1, 2$H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 144.3 (dm, $J = 249.1$ Hz), 141.1 (dm, $J = 255.2$ Hz), 138.1 (dm, $J = 251.9$ Hz), 131.6 (q, $J = 32.9$ Hz), 130.8, 130.3, 125.9 (q, $J = 3.6$ Hz), 123.9 (q, $J = 272.4$ Hz), 114.7 (app td, $J = 16.8, 4.1$ Hz), $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-62.9$ (s, 3F), $-142.9$ (dd, $J = 22.7, 8.2$ Hz, 2F), $-153.7$ (t, $J = 21.0$ Hz, 1F), $-161.3$ (app td, $J = 21.7, 7.6$ Hz, 2F).
methyl(2',3',4',5',6'-pentafluoro-[biphenyl]-4-yl)sulfane (3bl)

The General Procedure 1 was applied with 4-bromothioanisole (101.6 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane/EtOAc 99:1) afforded the title product as a white solid (104.4 mg, 72%).

Spectroscopic data matched those previously reported.\textsuperscript{15}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.34 (app s, 4H), 2.53 (s, 3H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): δ 144.3 (dm, J = 247.9 Hz), 140.8, 140.4 (dm, J = 253.5 Hz), 138.0 (dm, J = 250.4 Hz), 130.5, 126.1, 122.7, 115.6 (app td, J = 17.0, 3.8 Hz), 15.3; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) δ –143.3 (dd, J = 23.0, 8.1 Hz, 2F), –155.7 (t, J = 21.0 Hz, 1F), –162.1 (app td, J = 22.1, 7.6 Hz, 2F).

4'-dimethylamino-2,3,4,5,6-pentafluorobiphenyl (3bm)

The General Procedure 1 was applied with 4-bromo-N,N-dimethylaniline (100.0 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane/EtOAc 98:2) afforded the title product as a white solid (114.9 mg, 80%).

Spectroscopic data matched those previously reported.\textsuperscript{12}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.31 (d, J = 8.9 Hz, 2H), 6.79 (d, J = 8.9 Hz, 2H), 3.02 (s, 6H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): δ 150.9, 144.3 (dm, J = 245.9 Hz), 139.6 (dm, J = 252.2 Hz), 138.0 (dm, J = 249.8 Hz), 131.1, 116.5 (app td, J = 17.0, 3.8 Hz), 113.4, 112.0, 40.3; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) δ –144.1 (dd, J = 23.5, 8.1 Hz, 2F), –157.9 (t, J = 21.1 Hz, 1F), –163.0 (app td, J = 22.3, 7.6 Hz, 2F).

1-(2',3',4',5',6'-pentafluoro-biphenyl-4-yl)ethanone (3bn)

The General Procedure 1 applied with 4-bromoacetophenone (99.5 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane/EtOAc 98:2) afforded the title product as a white solid (83.0 mg, 58%).

Spectroscopic data matched those previously reported.\textsuperscript{13}

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 8.08 (d, J = 8.5 Hz, 2 H), 7.55 (d, J = 8.5 Hz, 2 H), 2.66 (s, 3H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}): δ 197.4, 144.2 (dm, J = 248.9 Hz), 141.0 (dm, J = 255.1 Hz), 138.3 (dm, J = 251.4 Hz), 137.6, 131.2, 130.6, 128.7, 115.0 (app td, J = 16.9, 3.9 Hz), 26.8; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) δ –144.1 (dd, J = 23.5, 8.1 Hz, 2F), –157.9 (t, J = 21.1 Hz, 1F), –163.0 (app td, J = 22.3, 7.6 Hz, 2F).
MHz, CDCl$_3$) $\delta$ –142.8 (dd, $J = 22.6$, 8.1 Hz, 2F), –153.9 (t, $J = 21.0$ Hz, 1F), –162.5 (app dt, $J = 21.9$, 7.8 Hz, 2F).

methyl 2',3',4',5',6'-pentafluorobiphenyl-4-carboxylate (3bo)

The General Procedure 1 was applied with methyl-4-bromobenzoate (107.5 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane/EtOAc 98:2) afforded the title product as a white solid (89.1 mg, 59%).

Spectroscopic data matched those previously reported.$^{13}$

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.16 (d, $J = 8.4$ Hz, 2H), 7.51 (d, $J = 8.4$ Hz, 2H), 3.95, (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ (1 carbon missing)$^{13}$ 166.5, 144.2 (dm, $J = 248.7$ Hz), 140.9 (dm, $J = 255.1$ Hz), 138.0 (dm, $J = 251.0$ Hz), 131.0, 130.4, 130.0, 115.1 (app td, $J = 17.0$, 3.9 Hz), 52.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –142.8 (dd, $J = 22.7$, 8.0 Hz, 2F), –153.9 (t, $J = 21.0$ Hz, 1F), –162.5 (app td, $J = 21.9$, 7.8 Hz, 2F).

2-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl)-1,3-dioxolane (3bp)

The General Procedure 1 was applied with 1-bromo-4-(1,3-dioxolan-2-yl)benzene (114.5 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane/EtOAc 97:3) afforded the title product as a white solid (112.3 mg, 71%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.62 (d, $J = 8.2$ Hz, 2H), 7.45 (d, $J = 8.2$, 2H), 5.88 (s, 1H), 4.20 - 4.04 (m, 4H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 144.3 (dm, $J = 248.0$ Hz), 140.6 (dm, $J = 254.2$ Hz), 139.3, 138.0 (dm, $J = 250.8$ Hz), 130.4, 127.3, 126.9, 115.7 (app td, $J = 17.2$, 4.0 Hz), 103.3, 65.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –143.0 (dd, $J = 22.9$, 8.1 Hz, 2F), –155.2 (t, $J = 21.0$ Hz, 1F), –162.1 (app td, $J = 22.0$, 7.7 Hz, 2F); IR (ATR) 2886, 1491, 1093, 982, 834; m.p. 125-127 °C; HRMS (EI) m/z calcd. C$_{15}$H$_9$F$_5$O$_2$: [M+H]$^+$ 317.0601; found: [M+H]$^+$ 317.0608.

2,3,4,5,6-pentafluoro-4'-iodo-3',5'-dimethyl-1,1'-biphenyl (3bq)

The General Procedure 1 was applied with 5-bromo-2-iodo-$m$-xylene (155.5 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane/EtOAc 95:5) afforded the title product as a white solid (165.2 mg, 83%).
$^1$H NMR (400 MHz, CDCl$_3$): δ 7.09 (s, 2H), 2.53 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 144.1 (dm, $J = 247.6$ Hz), 143.0, 140.5 (dm, $J = 254.5$ Hz), 138.0 (dm, $J = 249.9$ Hz), 128.3, 125.8, 115.3 (app td, $J = 17.5$, 3.7 Hz), 110.0, 29.9; $^{19}$F NMR (376 MHz, CDCl$_3$) δ −142.8 (dd, $J = 22.9, 8.1$ Hz, 2F), −115.2 (t, $J = 21.0$ Hz, 1F), −162.0 (app dt, $J = 22.1$, 7.7 Hz, 2F); IR (ATR) 2953, 1521, 1496, 1026, 991; m.p. 68 - 70 °C; HRMS (EI) m/z calcd. C$_{14}$H$_8$F$_5$I: [M]$^+$ 397.9585; found: [M]$^+$ 397.9592.

2,3,4,5,6-pentafluoro-4'-vinylbiphenyl (3br)

The General Procedure 1 was applied with 4-bromostyrene (65.4 μL, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (54.0 mg, 40%). Spectroscopic data matched those previously reported.$^{16}$

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.53 (d, $J = 8.2$ Hz, 2H), 7.40 (d, $J = 8.2$ Hz, 2H), 6.77 (dd, $J = 17.6$, 10.9 Hz, 1H), 5.85 (dd, $J = 17.6$, 0.6 Hz, 1H), 5.36 (dd, $J = 10.9$, 0.6 Hz, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 144.3 (dm, $J = 247.6$ Hz), 140.5 (dm, $J = 259.0$ Hz), 138.7, 138.0 (dm, $J = 250.4$ Hz), 136.1, 130.5, 126.6, 125.7, 115.8 (app td, $J = 17.2$, 3.7 Hz), 115.6; $^{19}$F NMR (376 MHz, CDCl$_3$) δ −143.2 (dd, $J = 23.0$, 8.1 Hz, 2F), −155.5 (t, $J = 21.0$ Hz, 1F), −162.2 (app td, $J = 22.1$, 7.7 Hz, 2F).

(E)-2,3,4,5,6-pentafluoro-4'-styryl-1,1'-biphenyl (3bs)

The General Procedure 1 was applied with 4-bromostilbene (129.6 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane/EtOAc 95:5) afforded the title product as a white solid (117.7 mg, 68%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.64 (d, $J = 8.3$ Hz, 2H), 7.55 (d, $J = 7.3$ Hz, 2H), 7.43 (d, $J = 8.3$ Hz, 2H), 7.39 (app t, $J = 7.4$ Hz, 2H), 7.30 (tt, $J = 7.4$, 1.5 Hz, 1H), 7.21 (d, $J = 16.3$ Hz, 1H), 7.14 (d, $J = 16.3$ Hz, 1H); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$CO): δ 144.1 (dm, $J = 247.0$ Hz), 140.1 (dm, $J = 250.6$ Hz), 138.6, 137.7 (dm, $J = 243.6$ Hz), 137.1, 130.4, 130.1, 128.6, 127.8, 127.4, 126.7, 126.6, 125.1, 115.9 - 115.6, (m); $^{19}$F NMR (376 MHz, CDCl$_3$) δ −143.2 (dd, $J = 23.1$, 8.1 Hz, 2F), −155.5 (t, $J = 21.0$ Hz, 1F), −162.1 (app td, $J = 22.0$, 7.7 Hz, 2F); IR (ATR) 2924, 1528, 1489, 982; m.p. 175 - 178 °C; HRMS (EI) m/z calcd. C$_{20}$H$_{11}$F$_5$: [M]$^+$ 346.0775; found: [M]$^+$ 346.0775.
2-(perfluorophenyl)naphthalene (3bt)

The General Procedure 1 was applied with 2-bromonapthalene (103.5 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (61.8 mg, 42%).

Spectroscopic data matched those previously reported.\textsuperscript{11}

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.97 - 7.89\) (m, 4H), \(7.60 - 7.49\) (m, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta 144.5\) (dm, \(J = 248.3\) Hz), \(140.6\) (dm, \(J = 252.3\) Hz), \(138.1\) (dm, \(J = 250.6\) Hz), 133.4, 133.2, 130.3, 128.6, 128.5, 127.9, 127.3, 127.2, 126.9, 123.9, 116.3 - 116.0 (m); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -143.0\) (dd, \(J = 23.0, 8.2\) Hz, 2F), –155.4 (t, \(J = 21.0\) Hz, 1F), –162.1 (app td, \(J = 22.0, 7.6\) Hz, 2F).

1-methyl-5-(perfluorophenyl)-1\textit{H}-indole (3bu)

The General Procedure 1 was applied with 5-bromo-1-methylindole (105.0 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol). Column chromatography (hexane/EtOAc 98:2) afforded the title product as a white solid (87.7 mg, 59%).

Spectroscopic data matched those previously reported.\textsuperscript{13}

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.70\) (s, 1H), \(7.44\) (d, \(J = 8.6\) Hz, 1H), \(7.27 - 7.24\) (m, 1H), \(7.14\) (d, \(J = 3.1\) Hz, 1H), \(6.57\) (d, \(J = 3.1\) Hz, 1H), \(3.84\) (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta 144.5\) (dm, \(J = 246.4\) Hz), \(140.0\) (dm, \(J = 254.9\) Hz), \(138.0\) (dm, \(J = 250.1\) Hz), \(136.9, 130.0, 128.7, 123.4, 123.2, 117.4\) (app td, \(J = 17.7, 3.7\) Hz), \(117.1, 109.6, 101.7, 33.0\); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta -143.4\) (dd, \(J = 23.5, 8.1\) Hz, 2F), –157.2 (t, \(J = 21.1\) Hz, 1F), –162.9 (app td, \(J = 22.2, 7.3\) Hz, 2F).

2',3',4',5',6'-pentafluoro-biphenyl-4-carbonitrile (3bv).

The General Procedure 1 was applied with [Ru(\(t\)BuCN)_6](BF\(_4\))\(_2\) (31.0 mg, 0.040 mmol), 4-bromobenzonitrile (91.0 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol) for 1 h. Column chromatography (hexane/CH\(_2\)Cl\(_2\) 95:5) afforded the title product as a white solid (33.6 mg, 25%).

Spectroscopic data matched those previously reported.\textsuperscript{16}

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta 7.80\) (d, \(J = 8.2\) Hz, 2H), \(7.57\) (d, \(J = 8.2\) Hz, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta 144.2\) (dm, \(J = 249.4\) Hz), \(141.3\) (dm, \(J = 257.9\) Hz), \(138.1\) (dm, \(J = 251.9\) Hz),
132.6, 131.3, 131.1, 118.3, 114.2 (app td, $J = 16.6, 4.0$ Hz), 113.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 142.7 - -142.8 (m, 2F), –152.8 (t, $J = 21.0$ Hz, 1F), –160.8 - -161.0 (m, 2F).

Analysis of the crude $^1$H NMR showed 13% recovery of 4-bromobenzonitrile. Decomposition and/or polymerization likely account for the remaining mass recovery of 4-bromobenzonitrile.

Following the General Procedure 1 in the absence of [Ru(tBuCN)$_6$](BF$_4$)$_2$ (C5), arene, (NMe$_4$)$_4$-fluorobenzoate and (NMe$_4$)OPiv- i.e. only 4-bromobenzonitrile (91.0 mg, 0.50 mmol), (NMe$_4$)OC(CF$_3$)$_3$ (386.5 mg, 1.250 mmol) and pivalonitrile (166.3 μL, 1.50 mmol) were added-gave quantitative recovery of 4-bromobenzonitrile by $^1$H NMR.

2,3,4,5,6-pentafluoro-4'-nitrobiphenyl (3bw)

The General Procedure 1 was applied with 1-bromo-4-nitrobenzene (101.0 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol) for 16 h. Analysis of the crude by $^1$H NMR showed <5% yield of the desired product 3bw$^{15}$ and 75% recovery of 1-bromo-4-nitrobenzene. Decomposition and/or polymerization likely account for the remaining mass recovery of 1-bromo-4-nitrobenzene.

Following the General Procedure 1 in the absence of [Ru(tBuCN)$_6$](BF$_4$)$_2$, (C5), arene, (NMe$_4$)$_4$-fluorobenzoate and (NMe$_4$)OPiv- i.e. only 1-bromo-4-nitrobenzene (101.0 mg, 0.50 mmol), (NMe$_4$)OC(CF$_3$)$_3$ (386.5 mg, 1.250 mmol) and pivalonitrile (166.3 μL, 1.50 mmol) were added-gave quantitative recovery of 1-bromo-4-nitrobenzene by $^1$H NMR.

2',3',4',5',6'-pentafluoro-[biphenyl]-4-carbaldehyde (3bx).

The General Procedure 1 was applied with 4-bromobenzaldehyde (92.5 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol) for 16 h. Analysis of the crude by $^1$H NMR showed 0% yield of the desired product and 25% recovery of 4-bromobenzaldehyde. Decomposition and/or polymerization likely account for the remaining mass recovery of 4-bromobenzaldehyde.

Following the General Procedure 1 in the absence of [Ru(tBuCN)$_6$](BF$_4$)$_2$, (C5), arene, (NMe$_4$)$_4$-fluorobenzoate and (NMe$_4$)OPiv- i.e. only 4-bromobenzaldehyde (92.5 mg, 0.50 mmol), (NMe$_4$)OC(CF$_3$)$_3$ (386.5 mg, 1.250 mmol) and pivalonitrile (166.3 μL, 1.50 mmol) were added-gave 75% recovery of 4-bromobenzaldehyde. No other products were observed by $^1$H NMR, thus decomposition and/or polymerisation likely account for the remaining mass recovery of 4-bromobenzaldehyde by $^1$H NMR.
2',3',4',5',6'-pentafluoro-[biphenyl]-4-ol (3by).

The General Procedure 1 was applied with 4-bromophenol (86.5 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol) for 16 h.
Analysis of the crude by $^1$H NMR showed 0% yield of the desired product 3by and 0% recovery of 4-bromophenol. Products 3by', 3by'', 3by''' are proposed to form in approximately 10%, 9% and 8% yield respectively from analysis of the crude $^1$H NMR and GC-MS. Decomposition and/or polymerization likely account for the remaining mass recovery of 4-bromophenol.

Following the General Procedure 1 in the absence of $[\text{Ru('BuCN)}_6](\text{BF})_2$, (C5), arene, (NMe$_4$)4-fluorobenzoate and (NMe$_4$)OPiv- i.e. only 4-bromophenol (86.5 mg, 0.50 mmol), (NMe$_4$)OC(CF$_3$)$_3$ (386.5 mg, 1.250 mmol) and pivalonitrile (166.3 μL, 1.50 mmol) were added- gave quantitative recovery of 4-bromophenol by $^1$H NMR.

4'-ethynyl-2,3,4,5,6-pentafluorobiphenyl (3bz)

The General Procedure 1 was applied with 1-bromo-4-ethynylbenzene (90.5 mg, 0.50 mmol) and pentafluorobenzene (166.5 μL, 1.50 mmol) for 16 h. Analysis of the crude by $^1$H NMR showed 0% yield of the desired product 3bz and 0% recovery of 1-bromo-4-ethynylbenzene. Decomposition and/or polymerization likely account for the remaining mass recovery of 1-bromo-4-ethynylbenzene.

Following the General Procedure 1 in the absence of $[\text{Ru('BuCN)}_6](\text{BF})_2$, (C5), arene, (NMe$_4$)4-fluorobenzoate and (NMe$_4$)OPiv- i.e. only 1-bromo-4-ethynylbenzene (90.5 mg, 0.50 mmol), (NMe$_4$)OC(CF$_3$)$_3$ (386.5 mg, 1.250 mmol) and pivalonitrile (166.3 μL, 1.50 mmol) were added- gave quantitative recovery of 1-bromo-4-ethynylbenzene by $^1$H NMR.
2,3,4,5,6-pentafluoro-2'-phenoxy-1,1'-biphenyl (3ba')

The General Procedure 1 was applied with 1-bromo-2-phenoxybenzene (2a')\(^2\) (124.6 mg, 0.50 mmol) and pentafluorobenzene (166.5 \(\mu\)L, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colorless oil (132.8 mg, 79%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.43 - 7.40 (m, 1H), 7.37 - 7.32 (m, 3H), 7.21 (t, \(J = 7.6\) Hz, 1H), 7.13 (t, \(J = 7.5\) Hz, 1H) 7.01 - 6.97 (m, 3H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 156.4, 155.8, 144.6 (dm, \(J = 247.5\) Hz), 140.8 (dm, \(J = 253.6\) Hz), 137.7 (dm, \(J = 250.3\) Hz), 132.3, 131.3, 130.0, 124.1, 123.2, 119.5, 118.2, 117.6, 112.4 (app td, \(J = 19.0, 3.8\) Hz); \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –140.1 (dd, \(J = 23.4, 8.1\) Hz, 2F), –155.3 (t, \(J = 21.0\) Hz, 1F), –162.6 - –162.7 (m, 2F); IR (ATR) 2924, 1488, 1237, 1061, 987, 749; HRMS (EI) \(m/z\) calcd. C\(_{18}\)H\(_9\)F\(_5\)O: [M]\(^+\) 336.0568 found: [M]\(^+\) 336.0566.

2'-benzyl-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3bb')

The General Procedure 1 was applied with 1-benzyl-2-bromobenzene (2b') (123.6 mg, 0.50 mmol) and pentafluorobenzene (166.5 \(\mu\)L, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colourless oil (70.2 mg, 42%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.43 (t, \(J = 7.4\) Hz, 1H), 7.36 - 7.31 (m, 2H), 7.20 - 7.13 (m, 4H), 6.91 (d, \(J = 7.2\) Hz, 2H), 3.85 (s, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 144.1 (dm, \(J = 247.3\) Hz), 140.8 (dm, \(J = 254.2\) Hz), 140.7, 139.8, 137.6 (dm, \(J = 251.9\) Hz), 131.1, 130.8, 130.0, 128.7, 128.4, 126.9, 126.4, 126.2, 115.6 - 115.3 (m), 39.9; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) –140.1 (dd, \(J = 23.4, 8.1\) Hz, 2F), –155.3 (t, \(J = 21.0\) Hz, 1F), –162.6 - –162.5 (m, 2F); IR (ATR) 2924, 1488, 1237, 1061, 987, 749; HRMS (EI) \(m/z\) calcd. C\(_{19}\)H\(_{11}\)F\(_5\): [M]\(^+\) 334.0775 found: [M]\(^+\) 334.0760.

2'-(benzyloxy)-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3bc')

The General Procedure 1 was applied with 1-(benzyloxy)-2-bromobenzene (3c')\(^3\) (131.6 mg, 0.50 mmol) and pentafluorobenzene (166.5 \(\mu\)L, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colorless oil (117.3 mg, 67%).

\(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.46 (td, \(J = 7.9, 1.6\) Hz, 1H), 7.41 - 7.31 (m, 6H), 7.12 (t, \(J = 7.7\) Hz, 2H), 5.14 (s, 2H); \(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 156.4, 144.6 (dm, \(J = 247.1\) Hz), 140.6 (dm,
$J = 253.0$ Hz), 137.7 (dm, $J = 249.9$ Hz), 136.7. 132.0, 128.7, 128.1, 127.1, 121.1, 115.9, 113.2 - 112.8 (m, 2C), 70.6; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –139.9 (dd, $J = 23.1, 7.9$ Hz, 2F), –156.0 (t, $J = 21.0$ Hz, 1F), –163.1 - –163.3 (m, 2F); IR (ATR) 2924, 1490, 1449, 1061, 986, 865, 751; HRMS (EI) $m/z$ calcd. C$_{19}$H$_{11}$F$_5$O [M]$^+$ 350.0725 found: [M]$^+$ 350.0738.

2,3,5,6-tetrafluoro-3',5'-dimethylbiphenyl (3cc) and 2',3',5',6'-tetrafluoro-3,3'',5,5''-tetramethyl-1,1':4',1''-terphenyl (3cc')

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 1,2,4,5-tetrafluorobenzene (167.5 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded both 2,3,5,6-tetrafluoro-3',5'-dimethylbiphenyl (94.1 mg, 74%) and 2',3',5',6'-tetrafluoro-3,3'',5,5''-tetramethyl-1,1':4',1''-terphenyl (17.8 mg, 10%) as white solids.

2,3,5,6-tetrafluoro-3',5'-dimethylbiphenyl (3cc)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.11 (s, 1H), 7.09 - 7.01 (m, 3H), 2.39 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 146.3 (dm, $J = 247.7$ Hz), 143.9 (dm, $J = 246.2$ Hz), 138.3, 131.0, 127.9 (t, $J = 1.7$ Hz), 127.4 (t, $J = 2.3$ Hz), 122.0 (t, $J = 16.9$ Hz), 104.7 (t, $J = 22.7$ Hz), 21.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –139.4 (ddd, $J = 22.5, 12.8, 9.7$ Hz, 2F), –143.6 (ddd, $J = 21.9, 13.4, 7.9$ Hz, 2F); IR (ATR) 2292, 1494, 1172, 929, 848, 705; m.p. 42-44 °C; HRMS (EI) $m/z$ calcd. C$_{14}$H$_{10}$F$_4$: [M]$^+$ 254.0707; found: 254.0713.

2',3',5',6'-tetrafluoro-3,3'',5,5''-tetramethyl-1,1':4',1''-terphenyl (3cc')

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.12 - 7.11 (m, 6H), 2.40 (s, 12H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 144.2 (dm, $J = 250.3$ Hz), 138.3, 130.9, 128.0, 127.5, 119.9 – 119.7 (m); $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ – 144.3 (s, 4F). IR (ATR) 2922, 1420, 984, 846; m.p. 214-215 °C; HRMS (EI) $m/z$ calcd. C$_{22}$H$_{18}$F$_4$: [M]$^+$ 358.1339; found: [M]$^+$ 358.1335.
The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 2,3,5,6-tetrafluorotoluene (182.7 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colourless oil (106.0 mg, 79%).

Spectroscopic data matched those previously reported.\textsuperscript{12}

\[ ^1H \text{NMR} \ (400 \text{ MHz, } \text{CDCl}_3): \delta \ 7.07 - 7.05 \text{ (m, 3H), 2.37 - 2.31 \text{ (m, 9H)}; }{ ^13}C \text{NMR} \ (126 \text{ MHz, } \text{CDCl}_3): \delta \ 145.4 \text{ (dm, } J = 243.7 \text{ Hz), 143.8 \text{ (dm, } J = 245.2 \text{ Hz), 138.2, 130.7, 128.0, 127.6, 118.4 \text{ (t, } J = 17.0 \text{ Hz), 114.9 \text{ (t, } J = 19.2 \text{ Hz), 21.4, 7.60; } { ^19}F \text{NMR} \ (376 \text{ MHz, } \text{CDCl}_3) \delta -144.4 \text{ (dd, } J = 22.6, 12.6 \text{ Hz, 2F), } -145.4 \text{ (dd, } J = 22.3, 12.8 \text{ Hz, 2F). IR (ATR) 2923, 1482, 922, 851; HRMS (EI) } m/z \text{ calcd. C}_{15}H_{12}F_4: [M]^{+} 268.0870; \text{ found: [M]}^{+} 268.0867. \]

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 2,3,5,6-tetrafluorotoluene (204.3 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (106.3 mg, 66%).

\[ ^1H \text{NMR} \ (400 \text{ MHz, } \text{CDCl}_3): \delta \ 7.14 \text{ (s, 1H), 7.06 \text{ (s, 2H), 2.39 \text{ (s, 6H); } }{ ^13}C \text{NMR} \ (126 \text{ MHz, } \text{CDCl}_3): \delta \ 145.6 - 143.2 \text{ (m, } 2C), 138.7, 131.8, 127.7, 126.0, 125.5 \text{ (t, } J = 16.8 \text{ Hz), 121.1 (q, } J = 274.3 \text{ Hz), 108.8 -107.9 \text{ (m), 21.4; } { ^19}F \text{NMR} \ (376 \text{ MHz, } \text{CDCl}_3) \delta -144.4 \text{ (dd, } J = 22.6, 12.6 \text{ Hz, 2F), } -145.4 \text{ (dd, } J = 22.3, 12.8 \text{ Hz, 2F). IR (ATR) 2923, 1495, 1484, 1139, 990; m.p. 68-71 \degree C; HRMS (EI) } m/z \text{ calcd. C}_{15}H_{9}F_7: [M]^{+} 322.0587; \text{ found: [M]}^{+} 322.0582. \]

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and \( N \)-(2,3,5,6-tetrafluoro-3',5'-dimethyl-biphenyl-4-yl)pivalamide (3fc)

\[ ^1H \text{NMR} \ (400 \text{ MHz, } \text{CDCl}_3): \delta \ 7.26 \text{ (s, 1H) 7.08 \text{ (s, 1H), 7.03 \text{ (s, 2H), 2.37 \text{ (s, 6H), 1.36 \text{ (s, 9H); } }{ ^13}C \text{NMR} \ (126 \text{ MHz, } \text{CDCl}_3): \delta \ 177.2, 144.0 \text{ (dm, } J = 245.4 \text{ Hz), 142.7 \text{ (app dt, } J = 249.0 15.8, 3.9 \text{ Hz), 138.3, 131.0, 127.9, 126.9, 119.1 \text{ (t, } J = 17.3 \text{ Hz), 115.3 (tt, } J = 14.7, 2.4 \text{ Hz), 39.7, 27.6, 21.4; } { ^19}F \text{NMR} \ (376 \text{ MHz, } \text{CDCl}_3) \delta -144.1 \text{ (dd, } J = 22.3, 9.8 \text{ Hz, 2F), } -146.6 - -146.7 \text{ (m, 2F); IR S50} \]
(ATR) 3294, 2972, 1674, 1479, 1190, 988; m.p. 184 - 188 °C; HRMS (EI) m/z calcd. C\textsubscript{16}H\textsubscript{15}NF\textsubscript{4}: [M]\textsuperscript{+} 353.1403; found: [M+K]\textsuperscript{+} 392.1034.

2,3,5,6-tetrafluoro-N,N,3',5'-tetramethyl-biphenyl-4-amine (3gc)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 2,3,5,6-tetrafluoro-N,N-dimethylaniline (1g)\textsuperscript{1} (289.7 mg, 1.50 mmol). Column chromatography with a 0-20% CH\textsubscript{2}Cl\textsubscript{2}-hexane gradient afforded the title product as a white solid (98.1 mg, 66%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.06 (app s, 3H), 3.00 (s, 6H), 2.38 (s, 6H); 13\textsuperscript{C} NMR (126 MHz, CDCl\textsubscript{3}): δ 144.6 (dm, J = 244.5 Hz), 142.6 (dm, J = 244.5 Hz), 138.2, 130.4 - 130.1 (m, 2C), 128.0, 127.7, 113.2 (t, J = 17.7 Hz), 43.5 (t, J = 3.8 Hz), 21.4; 19\textsuperscript{F} NMR (376 MHz, CDCl\textsubscript{3}) δ -146.0 (dd, J = 21.2, 9.0 Hz, 2F), -151.9 - -152.0 (m, 2F); IR (ATR) 2923, 1650, 1488, 1450, 1437, 1077, 982; m.p. 83 - 84 °C; HRMS (EI) m/z calcd. C\textsubscript{16}H\textsubscript{15}NF\textsubscript{4}: [M]\textsuperscript{+} 297.1135; found: [M]\textsuperscript{+} 297.1126.

butyl(2,3,5,6-tetrafluoro-3',5'-dimethyl-[1,1'-biphenyl]-4-yl)sulfane (3hc)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and butyl(2,3,5,6-tetrafluorobenzoate (357.4 mg, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colorless oil (111.3 mg, 65%).

\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}): δ 7.11 (s, 1H), 7.09 (s, 2H), 2.98 (t, J = 7.4 Hz, 2H), 2.40 (s, 6H), 1.61 (app quintet, J = 7.4 Hz, 2H), 1.48 (app sextet, J = 7.4 Hz, 2H), 0.95 (t, J = 7.3 Hz, 3H); 13\textsuperscript{C} NMR (126 MHz, CDCl\textsubscript{3}): δ 147.4 (app ddt, J = 244.6, 14.8, 4.0 Hz), 142.4 (app ddt, J = 247.9, 15.5, 5.0 Hz), 138.3, 131.0, 127.9, 127.1, 120.9 (t, J = 17.2 Hz), 113.2 (t, J = 20.6 Hz), 34.6 (t, J = 2.5 Hz), 32.0, 21.7, 21.4, 13.7; 19\textsuperscript{F} NMR (376 MHz, CDCl\textsubscript{3}) δ -134.7 (dd, J = 24.3, 11.9 Hz, 2F), -143.3 (dd, J = 24.0, 11.6 Hz, 2F); IR (ATR) 2960, 2929, 1650, 1488, 1450, 1437, 1077, 982; m.p. 83-84 °C; HRMS (EI) m/z calcd. C\textsubscript{18}H\textsubscript{18}F\textsubscript{4}S\textsubscript{1}: [M]\textsuperscript{+} 342.1060 found: [M]\textsuperscript{+} 342.1075.

tert-butyl 2,3,5,6-tetrafluoro-3',5'-dimethyl-biphenyl-4-carboxylate (3ic)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and tert-butyl 2,3,5,6-tetrafluorobenzoate (375.3 mg, 1.50 mmol) for 2 h. Column chromatography (hexane 100%) afforded the title product as a colorless oil (136.4 mg, 77%).
$^1$H NMR (400 MHz, CDCl$_3$): δ 7.11 (s, 1H), 7.05 (s, 2H), 2.38 (s, 6H), 1.62 (s, 9H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 158.9, 144.6 (app ddt, $J$ = 254.0, 15.9, 4.9 Hz), 143.9 (app ddt, 247.9, 14.0, 4.6 Hz), 138.5, 131.4, 127.8, 126.7, 123.3 (t, $J$ = 16.9 Hz), 113.3 (t, $J$ = 16.9 Hz), 84.7, 28.3, 21.4; $^{19}$F NMR (376 MHz, CDCl$_3$) δ −141.4 - −141.5 (m, 2F), −142.6 - −142.8 (m, 2F); IR (ATR) 2982, 1732, 1478, 1328, 1288, 1142, 989; HRMS (EI) m/z calcd. C$_{19}$H$_{18}$O$_2$F$_4$: [M$^+$] 354.1237; found: [M$^+$] 354.1231.

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 1,2,3,5-tetrafluorobenzene (161.6 μL, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colorless oil (94.0 mg, 74%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.07 (s, 1H), 7.02 (s, 2H), 6.88 - 6.81 (m, 1H), 2.37 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 154.4 (dm, $J$ = 246.3 Hz), 149.8 (dm, $J$ = 250.6 Hz), 149.1 (dm, $J$ = 249.8 Hz), 138.3, 137.6 (dm, $J$ = 248.0 Hz), 130.7, 128.0, 127.4, 116.7 - 116.4 (m), 100.9 (ddd, $J$ = 29.2, 21.3, 3.9 Hz), 21.4; $^{19}$F NMR (376 MHz, CDCl$_3$) δ −117.9 (app t, $J$ = 10.0 Hz, 1F), −133.9 (ddd, $J$ = 21.6, 9.8, 5.0, 1F), −135.2 (d, $J$ = 20.0, 1F), −165.0 (app tdd, $J$ = 21.6, 11.0, 6.1 Hz, 1F); IR (ATR) 2921, 1515, 1049, 787; HRMS (EI) m/z calcd. C$_{14}$H$_{10}$F$_4$: [M$^+$] 254.0713; found: [M$^+$] 254.0720.

2,3,4,6-tetrafluoro-3',5'-dimethylbiphenyl (3jc)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 1,2,3,4-tetrafluorobenzene (160.8 μL, 5.00 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (90.3 mg, 71%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.08 - 7.00 (m, 4H), 2.38 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 147.1 (dm, $J$ = 246.6 Hz), 145.0 (dm, $J$ = 248.5 Hz), 141.3 (dm, $J$ = 252.6 Hz), 139.7 (dm, $J$ = 253.1 Hz), 138.6, 133.1, 130.5, 126.7 (d, $J$ = 2.7 Hz), 126.0 - 125.8 (m), 111.5 (app dt, $J$ = 19.6, 3.1 Hz), 21.4; $^{19}$F NMR (376 MHz, CDCl$_3$) δ −139.8 - −140.0 (m, 1F), −143.5 - −143.6 (m, 1F), −155.4 (app t, $J$ = 20.3 Hz, 1F), −157.5 - −157.6 (m, 1F); IR (ATR) 2926, 1526, 1487, 845; m.p. 86 - 87 °C; HRMS (EI) m/z calcd. C$_{14}$H$_{10}$F$_4$: [M$^+$] 254.0713; found: [M$^+$] 254.0708.

2,3,4,5-tetrafluoro-3',5'-dimethylbiphenyl (3kc)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 1,2,3,4-tetrafluorobenzene (160.8 μL, 5.00 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (90.3 mg, 71%).
2,4,6-trifluoro-3',5'-dimethylbiphenyl (3lc)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 1,3,5-trifluorobenzene (517.1 μL, 5.00 mmol). Column chromatography (hexane 100%) afforded the title product as a colourless oil (56.7 mg, 48%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.05 (s, 1H), 7.03 (s, 2H), 6.74 (dd, $J = 8.6$, 8.0 Hz, 2H), 2.37 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 161.7 (dt, $J = 248.7$, 15.7 Hz), 160.4 (ddd, $J = 249.1$, 14.7, 9.9 Hz), 138.0, 130.2, 128.2, 128.1, 115.4 (td, $J = 19.7$, 4.8 Hz), 100.7 - 100.2 (m), 21.4; $^{19}$F NMR (376 MHz, CDCl$_3$) δ –109.6 (tt, $J = 8.7$, 5.9 Hz, 1F), –111.1 (app t, $J = 6.6$ Hz, 2F); IR (ATR) 2920, 1636, 1597, 1120, 1030, 839; HRMS (EI) $m/z$ calcd. C$_{14}$H$_{11}$F$_3$: [M]$^+$ 236.0807; found: [M]$^+$ 226.0808.

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 1,2,4-trifluorobenzene (522.5 μL, 5.00 mmol). Column chromatography (hexane, 100%) afforded a 1.00 : 0.95 : 0.13 mixture of 2,3,6-trifluoro-3',5'-dimethylbiphenyl, 2,3,5-trifluoro-3',5'-dimethylbiphenyl and 2,4,5-trifluoro-3',5'-dimethylbiphenyl respectively as a colorless oil (83.9 mg, 71%) and 2',3',5'-trifluoro-3,3'',5,5''-tetramethylterphenyl as a white solid (6.1 mg, 5%). Milligrams (5 - 10 mg) of 2,3,6-trifluoro-3',5'-dimethylbiphenyl and 2,4,5-trifluoro-3',5'-dimethylbiphenyl were isolated as colorless oils by column chromatography (hexane, 100%) for analysis.

2,3,6-trifluoro-3',5'-dimethylbiphenyl (3mc), 2,3,5-trifluoro-3',5'-dimethylbiphenyl (3mc'), 2,4,5-trifluoro-3',5'-dimethylbiphenyl (3mc''), and 2',3',5'-trifluoro-3,3'',5,5''-tetramethylterphenyl (3mc''')

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 1,2,4-trifluorobenzene (522.5 μL, 5.00 mmol). Column chromatography (hexane, 100%) afforded a 1.00 : 0.95 : 0.13 mixture of 2,3,6-trifluoro-3',5'-dimethylbiphenyl, 2,3,5-trifluoro-3',5'-dimethylbiphenyl and 2,4,5-trifluoro-3',5'-dimethylbiphenyl respectively as a colorless oil (83.9 mg, 71%) and 2',3',5'-trifluoro-3,3'',5,5''-tetramethylterphenyl as a white solid (6.1 mg, 5%). Milligrams (5 - 10 mg) of 2,3,6-trifluoro-3',5'-dimethylbiphenyl and 2,4,5-trifluoro-3',5'-dimethylbiphenyl were isolated as colorless oils by column chromatography (hexane, 100%) for analysis.

2,3,6-trifluoro-3',5'-dimethylbiphenyl (3mc)

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.18 - 7.10 (m, 2H), 7.06 (s, 2H), 6.94 (app tdd, $J = 9.1$, 3.9, 2.2 Hz, 1H), 2.37 (d, $J = 0.8$ Hz, 6H); $^1$H {$^{19}$F} (500 MHz, CD$_2$Cl$_2$): δ 7.14 (d, $J = 9.2$ Hz, 1H), 7.10 (s, 1H), 7.06 (s, 2H), 6.94 (d, $J = 9.1$ Hz, 1H), 2.38 (s, 6H); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): δ 155.8 (ddd, $J = 243.8$, 5.0, 2.7 Hz), 148.2 (ddd, $J = 248.4$, 14.2, 7.5 Hz), 147.8 (ddd, $J = 243.7$, 13.8, 3.6 Hz), 138.5, 130.8, 128.4 (d, $J = 2.1$ Hz).
Hz), 128.1 (t, J = 1.8 Hz), 120.9 (dd, J = 21.3, 15.7 Hz), 115.9 (ddd, J = 19.5, 9.9, 1.5 Hz), 111.2 (ddd, J = 25.7, 6.9, 4.1 Hz), 214; $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ -120.1 - -120.2 (m, 1F), -138.6 (dd, J = 21.7, 8.6 Hz, 1F), -143.1 - -143.2 (m, 1F); $^{19}$F $^1$H NMR (376 MHz, CD$_2$Cl$_2$) δ -120.2 (dd, J = 15.1, 3.6 Hz, 1F) -138.6 (dd, J = 21.7, 3.7 Hz, 1F), -143.2 (dd, J = 21.4, 15.1 Hz, 1F); IR (ATR) 2924, 1491, 1243, 786; HRMS (EI) m/z calcd. C$_{14}$H$_{11}$F$_3$: [M]$^+$ 236.0807; found: [M]$^+$ 236.0800.

2,3,5-trifluoro-3',5'-dimethylbiphenyl (3mc') and 2,4,5-trifluoro-3',5'-dimethylbiphenyl (3mc'')

$^1$H NMR (400 MHz, CD$_2$Cl$_2$): δ 7.26 (minor, ddd, J = 11.0, 8.9, 7.1 Hz, 1H) 7.14 (major, s, 2H), 7.10 (minor, s, 2H), 7.09 (major, s, 1H), 7.07 - 7.00 (minor, m, 1H) 7.05 (minor, s, 1H), 6.98 - 6.89 (major, m, 2H), 2.38 (major, d, J = 0.7 Hz, 6H), 2.37 (minor, d J = 0.7 Hz, 6H); $^1$H $^{19}$F (500 MHz, CD$_2$Cl$_2$): δ 7.26 (minor, s, 1H), 7.14 (major, s, 2H), 7.10 (minor, s, 2H), 7.09 (major, s, 1H), 7.06 (minor, s, 1H), 7.03 (minor, s, 1H), 6.96 (major, d, J = 3.3 Hz, 1H), 6.93 (major, d, J = 3.3 Hz, 1H), 2.38 (major, s, 6H), 2.37 (minor, s, 6H); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): δ 158.0 (major, ddd, J = 244.2, 11.3, 3.3 Hz), 155.1 (minor, ddd, J = 246.1, 9.2, 2.4 Hz), 151.2 (major, ddd, J = 249.3, 15.5, 13.4 Hz), 149.6 (minor, ddd, J = 250.4, 14.5, 12.3 Hz), 147.2 (minor, ddd, J = 243.5, 12.4, 3.7 Hz), 145.0 (major, ddd, J = 244.3, 13.1, 4.1 Hz), 138.8 (major), 138.7 (minor), 134.2 (minor), 134.0 - 133.9 (major + minor, m), 132.6 (major, dd, J = 12.3, 9.5 Hz),
130.7 (major), 130.2 (minor), 127.0 - 126.9 (major + minor, m), 118.6 (minor, dd, J = 19.7, 5.3 Hz), 112.1 (major, dm, J = 23.9 Hz), 106.3 (minor, dd, J = 29.2, 20.8 Hz), 104.3 (major, dd, J = 27.5, 21.4 Hz), 21.4 (major + minor); $^{19}$F NMR (376 MHz, CD$_2$Cl$_2$) δ −116.4 - −116.5 (major, m), 118.6 (minor, m, 1F), −134.3 (major, ddd, J = 20.0, 10.4, 2.9 Hz, 1F), −136.4 - −136.5 (minor, m, 1F), −143.8 - −144.0 (minor, m, 1F), −148.9 - −149.1 (major, m, 1F); $^{19}$F $^1$H NMR (376 MHz, CD$_2$Cl$_2$) δ −116.4 (major, dd, J = 14.9, 3.3 Hz, 1F), −119.7 (minor, dd, J = 15.1, 3.8 Hz, 1F), −134.3 (major, dd, J = 20.7, 3.3 Hz, 1F), −136.5 (minor, dd, J = 21.7, 3.8 Hz, 1F), −143.9 (minor, dd, J = 21.7 15.1 Hz, 1F), −149.0 (major, dd, J = 20.7, 14.6, Hz, 1F); IR (ATR) 2924, 1600, 1496, 1113, 850, 786; HRMS (EI) m/z calcd. C$_{14}$H$_{11}$F$_3$: [M]$^+$ 236.0807; found: [M]$^+$ 236.0799.

$^{13}$C NMR (101 MHz, CD$_2$Cl$_2$): δ 155.3 (ddd, J = 244.1, 6.9, 3.6 Hz), 148.8 (ddd, J = 248.5, 16.2, 9.1 Hz), 145.4 (ddd, J = 246.4, 15.2, 3.7 Hz), 138.8, 138.5, 133.9,
130.7, 130.6, 130.3 (dd, J = 12.0, 2.2 Hz), 128.4, 128.1, 126.9 (d, J = 2.9 Hz), 119.2 (dd, J = 21.3, 16.1 Hz), 111.7 (dt, J = 25.8, 3.4), 21.4, 21.4; 19F NMR (376 MHz, CD2Cl2) δ −120.9 - −120.9 (m, 1F), 138.6 (d, J = 20.8 Hz, 1F), −148.1 (ddd, J =20.5, 14.5, 5.6 Hz, 1F); 19F {1H} NMR (471 MHz, CD2Cl2) δ −120.9 (dd, J = 14.8, 3.5 Hz), −138.6, (dd, J = 21.0, 4.0 Hz), −148.1 (dd, J = 21.2, 14.7 Hz); IR (ATR) 2972, 1501, 1218, 1133, 835; m.p. 200 - 203 °C; HRMS (EI) m/z calcd. C22H19F3: [M]+ 340.1439; found: [M]+ 340.1445.

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 1,2,3-trifluorobenzene (515.9 μL, 5.00 mmol). Column chromatography (hexane, 100%) afforded a 1.0:0.3 mixture of 2,3,4-trifluoro-3',5'-dimethylbiphenyl (3nc) and 3,4,5-trifluoro-3',5'-dimethylbiphenyl (3nc').

Milligrams (5 - 10 mg) of each regioisomer were isolated by column chromatography (hexane, 100%): 30nc as a colorless oil and 3nc' as a white solid.
2,3,4-trifluoro-3',5'-dimethylbiphenyl (3nc)

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.15 - 7.10 (m, 3H), 7.05 (s, 1H), 7.00 (app dtd, $J = 9.2$, 7.1, 2.0 Hz, 1H), 2.38 (s, 6H); $^1$H $\{^{19}$F$\}$ NMR (500 MHz, CDCl$_3$): $\delta$ 7.12 (d, $J = 8.8$ Hz, 1H), 7.10 (s, 2H), 7.05 (s, 1H), 7.01 (d, $J = 8.8$ Hz, 1H), 2.38 (s, 6H) $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 150.9 (ddd, $J = 157.8$, 10.1, 3.1 Hz), 148.4 (ddd $J = 159.2$, 10.3, 3.2 Hz), 140.4, (dt, $J = 250.7$, 15.6 Hz), 138.4, 134.1, 130.0, 127.1 (dd, $J = 11.0$, 3.9 Hz), 126.8 (d, $J = 2.9$ Hz), 124.0 (dt, $J = 7.8$, 4.0 Hz), 112.1 (dd, $J = 17.1$, 4.0 Hz), 21.5; $^{19}$F NMR (471 MHz, CDCl$_3$) $\delta$ -135.7 - -136.4 (m, 1F), -138.6 (app dt, $J = 20.2$, 6.9 Hz, 1F), -160.3 (app td, $J = 20.7$, 7.5 Hz, 1F); $^{19}$F $\{^1$H$\}$ NMR (471 MHz, CDCl$_3$) $\delta$ -136.2 (dd, $J = 20.2$, 6.8 Hz, 1F), -138.6 (dd, $J = 20.7$, 6.9 Hz, 1F), -160.3, (app t, $J = 20.6$ Hz, 1F); IR (ATR) 2924, 1511, 1039, 807, 706; HRMS (EI) m/z calcd: C$_{14}$H$_{11}$F$_3$: [M]+ 236.0807 found: [M]+ 236.0801.

3,4,5-trifluoro-3',5'-dimethylbiphenyl (3nc')

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.22 (app dd, $J = 9.3$, 6.5 Hz, 2H), 7.13 (s, 2H), 7.05 (s, 1H), 2.37 (s, 6H); $^1$H $\{^{19}$F$\}$ NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.22 (s, 2H), 7.13 (s, 2H), 7.04 (s, 1H), 2.36 (s, 6H) $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): $\delta$ 151.7 (ddd, $J = 248.1$, 10.0, 4.3 Hz), 139.4 (dt, $J = 249.8$, 15.4 Hz), 139.2, 138.3 - 138.3 (m), 138.1 (td, $J = 7.7$ Hz), 130.4, 125.0, 111.3 (dd, $J = 16.6$, 4.9 Hz), 21.4; $^{19}$F NMR
(471 MHz, CD₂Cl₂) δ −135.5 - −135.6 (m, 2F), −164.3 (tt, J = 20.6, 6.2 Hz, 1F); ¹⁹F {¹H} NMR (471 MHz, CD₂Cl₂) δ −135.5 (d, J = 19.9 Hz, 2F), −164.3 (t, J = 19.9 Hz, 1F); m.p. 35 - 37 °C; IR (ATR) 2930, 1487, 1039, 826, 751, 706; HRMS (EI) m/z calcd. C₁₄H₁₁F₃: [M]+ 236.0807 found: [M]+ 236.0799.

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 1-butoxy-2,4,5-trifluorobenzene (510.5 mg, 2.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colorless oil (63.2 mg, 41%).

¹H NMR (500 MHz, CDCl₃): δ 7.08 (app s, 3H), 6.81 (app dt, J = 11.5, 7.7 Hz, 1H), 4.02 (t, J = 6.5 Hz, 2H), 2.39 (s, 6H), 1.82 (app quintet, J = 7.0 Hz, 2H), 1.52 (app sextet, J = 7.5, 2H), 1.00 (t, J = 7.4, 3H); ¹H {¹⁹F} NMR (500 MHz, CDCl₃): δ 7.08 (app s, 3H), 6.80 (s, 1H), 4.01 (t, J = 6.5 Hz, 2H), 2.38 (s, 6H), 1.81 (app quintet, J = 7.0 Hz, 2H), 1.52 (app sextet, J = 7.5, 2H), 1.00 (t, J = 7.4, 3H); ¹³C NMR (126 MHz, CDCl₃): δ 146.5 (ddd, J = 243.6, 14.4, 4.0 Hz), 145.5 (app dt, J = 244.3, 3.8 Hz), 143.6 - 143.4 (m), 141.4 (ddd, J = 241.7, 14.1, 5.4 Hz), 138.0, 130.5, 128.4 (d, J = 1.8 Hz), 128.0, 120.9 (app t, J = 17.3 Hz), 102.4 (dd, J = 22.2, 2.1 Hz), 70.1, 31.3, 21.4, 19.2, 13.9; ¹⁹F NMR (376 MHz, CDCl₃) δ −140.7, (dd J = 12.8, 7.7 Hz, 1F), −141.5 - −141.6 (m, 1F), −149.6 (dd,
$J = 23.0, 7.6 \text{ Hz, } 1F); \ ^{19}F \ {^1H} \text{ NMR (471 MHz, CDCl}_3 \delta -140.6, (d, J = 13.0 \text{ Hz, } 1F), -141.5 \text{ (dd, } J = 22.9, 13.0 \text{ Hz, } 1F), -149.6 \text{ (d, } J = 22.9 \text{ Hz, } 1F); \text{ IR (ATR) 2961, 1494, 1238, 1150, 929, 850; HRMS (EI) } m/z \text{ calcd. } C_{18}H_{19}F_3O: [M]^+ 308.1381 \text{ found: } [M]^+ 308.1380.

2,3,6-trifluoro-3',5'-dimethyl-4-(trifluoromethyl)-biphenyl (3pc)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 $\mu$L, 0.50 mmol) and 2,3,5-trifluorobenzotrifluoride (300.0 mg, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colorless oil (141.5 mg, 93%).

$^1H \text{ NMR (400 MHz, CDCl}_3 \delta 7.23 \text{ (ddd, } J = 8.7, 5.4, 2.3 \text{ Hz, } 1H), 7.14 \text{ (s, } 1H), 7.10 \text{ (s, } 2H), 2.42 \text{ (s, } 6H); \ ^{1}H \ {^{19}F} \text{ NMR (400 MHz, CDCl}_3 \delta 7.24 \text{ (s, } 1H), 7.15 \text{ (s, } 1H), 7.10 \text{ (s, } 2H), 2.42 \text{ (s, } 6H); \ ^{13}C \text{ NMR (100 MHz, CDCl}_3 \delta 154.7 \text{ (dd, } J = 247.4, 5.2, 3.3 \text{ Hz), 148.7 \text{ (dd, } J = 252.1, 13.2, 7.3 \text{ Hz), 145.4 \text{ (dm, } J = 256.4 \text{ Hz), 138.5, 131.3, 127.8, 126.9, 124.8 \text{ (dd, } J = 20.5, 15.6 \text{ Hz), 121.7 \text{ (app \text{ qt, } J = 272.6, 2.8 \text{ Hz), 119.2 - 117.9 \text{ (m), 108.9 \text{ (app \text{ dquintet = 28.7, 4.4 \text{ Hz), 21.4; } ^{19}F \text{ NMR (376 MHz, CDCl}_3 \delta -61.3 \text{ (d, } J = 12.7 \text{ Hz, } 3F), -116.7 - -116.8 \text{ (m, } 1F), -134.3 \text{ (dd, } J = 20.9, 2.3 \text{ Hz, } 1F), -143.0 - -143.2 \text{ (m, } 1F); \ ^{1}H \ {^{19}F} \text{ NMR (471 MHz, CDCl}_3 \delta -61.3 \text{ (d, } J = 13.1 \text{ Hz, } 3F), -116.7 \text{ (dd, } J = 15.4, 4.9 \text{ Hz, } 1F), -134.3 \text{ (dd, } J = 20.9, 4.5 \text{ Hz, } 1F), -143.1 - -143.2 \text{ (m, } 1F) \text{ IR
The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 2,3,4-trifluorobenzotrifluoride (500.0 mg, 2.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (88.2 mg, 58%).

$^1$H NMR (400 MHz, CDCl$_3$): δ 7.44 (app t, $J = 7.3$ Hz, 1H), 7.09 (app s, 3H), 2.39 (s, 6H); $^1$H {${}^{19}$F} NMR (500 MHz, CDCl$_3$): δ 7.44 (s, 1H), 7.09 (app s, 3H), 2.39 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 151.0 (dm, $J = 256.1$ Hz), 148.2 (dm, $J = 260.4$ Hz), 140.8 (ddd, $J = 253.9, 16.1, 14.4$ Hz), 138.7, 132.7, 130.8, 127.3 (dd, $J = 11.8, 4.2$ Hz), 126.7 (d, $J = 2.4$), 122.0 (q, $J = 272.9$ Hz), 121.8 - 121.7 (m), 115.7 (ddd, $J = 34.3, 9.3, 4.3$ Hz), 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$) δ −60.7 (d, $J = 12.6$ Hz, 3F), −130.9 - −131.0 (m, 1F), −136.4 - −136.6 (m, 1F), −156.5 (app t, $J = 20.3$ Hz, 1F); $^{19}$F {$^1$H} NMR (471 MHz, CDCl$_3$) δ −60.7 (d, $J = 12.6$ Hz, 3F), −131.0 (dd, $J = 20.6$, 11.0 Hz, 1F) −136.4 - −136.6 (m, 1F), −156.6 (app t, $J = 20.5$ Hz, 1F); IR (ATR) 2924, 1488, 1371, 1211, 1136, 851, 646; m.p. 35 - 38 °C; HRMS (EI) m/z calcd. C$_{15}$H$_{10}$F$_6$ [M]+ 304.0687; found: [M]+ 304.0700.
The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 3,4-difluorobenzotrifluoride (455.2 mg, 2.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colorless oil (78.7 mg, 55%).

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.50 (app d, $J = 5.6$ Hz, 1H), 7.44 - 7.40 (m, 1H), 7.16 (s, 2H), 7.10 (s, 1H), 2.41 (s, 6H); $^1$H {${}^{19}$F} (500 MHz, CDCl$_3$): δ 7.48 (d, $J = 2.4$ Hz, 1H), 7.48 (d, $J = 2.4$ Hz, 1H), 7.14 (s, 2H), 7.09 (s, 1H), 2.39 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 151.0 (dd, $J = 251.0$, 14.3 Hz) 150.0 (dd, $J = 255.7$, 12.9 Hz), 138.6, 133.3, 132.7 (d, $J = 11.6$ Hz), 130.7, 127.3 - 126.4 (m, 2C), 123.2 (qd $J = 272.2$, 2.4 Hz), 123.0 - 122.9 (m), 113.5 (dq, $J = 20.2$, 3.3 Hz), 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$) δ −62.2 (s, 3F), −134.7 (dd, $J = 20.7$, 9.6 Hz, 1F), −136.9 - −137.0 (dm, $J = 20.7$ Hz, 1F); $^{19}$F {$^1$H} NMR (471 MHz, CDCl$_3$) δ −62.3 (s, 3F), −134.7 (d, $J = 20.7$ Hz, 1F), −137.0 (d, $J = 20.7$ Hz, 1F); IR (ATR) 2923, 1371, 1294, 1129, 652; HRMS (El) m/z calcd. $^{13}$C$_{15}$H$_{11}$F$_5$: [M]$^+$ 286.0775; found: [M]$^+$ 286.0774.

2,3-difluoro-3',5'-dimethyl-6-(trifluoromethyl)-biphenyl (3rc)
The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 2,3-difluorobenzotrifluoride (455.2 mg, 2.50 mmol). Column chromatography (hexane 100%) afforded a 1.00 : 0.03 mixture of 2,3-difluoro-3',5'-dimethyl-4-(trifluoromethyl)-biphenyl and 3,4-difluoro-3',5'-dimethyl-5-(trifluoromethyl)-biphenyl (3sc') as a colorless oil (82.1 mg, 54%).

1H NMR (400 MHz, CDCl3): δ (minor isomer not observed) 7.44 - 7.39 (m, 1H), 7.32 - 7.27 (m, 1H), 7.17 (s, 2H), 7.12 (s, 1H), 2.41 (s, 6H); 1H {19F} NMR (500 MHz, CDCl3): δ (minor isomer not observed) 7.40 (d, J = 8.3 Hz, 1H), 7.28 (d, 8.3 Hz, 1H), 7.15 (s, 2H), 7.09 (s, 1H), 2.39 (s, 6H); 13C NMR (100 MHz, CDCl3): δ (minor isomer not observed) 148.9 (dm, J = 258.7 Hz), 148.4 (dd, J = 251.5, 12.0 Hz), 138.6, 135.7 (d, J = 10.7 Hz), 133.4, 130.8, 126.8 (d, J = 2.8 Hz), 125.1 (dd, J = 3.8, 2.6 Hz), 122.3 (qd, J = 272.3, 3.2 Hz), 121.2 (app quintet J = 4.5 Hz), 118.7 (qd, J = 33.6, 9.7 Hz), 21.4; 19F NMR (376 MHz, CDCl3) δ −61.0 (major, d, J = 12.5 Hz, 3F), −61.0 (minor, d, J = 12.7 Hz, 3F), −135.3 (minor, dd, J = 20.8, 10.7, 1F), −138.8 - −139.0 (major, m, 1F), −140.8 (major,
dd, $J = 20.1, 6.2$ Hz, 1F) $-142.0 - -142.2$ (minor, m, 1F); $^{19}$F \{\text{H}\} NMR (376 MHz, CDCl$_3$) $\delta$ $-61.0$ (major d, $J = 12.7$ Hz, 3F), $-61.0$ (minor, d, $J = 12.7$ Hz, 3F), $-135.3$ (minor, d, $J = 20.7$ Hz, 1F), $-138.8$ (major, dq, $J = 20.0, 12.3$ Hz, 1F), $-140.8$ (major, d, $J = 20.5, 1F)$, $-142.1$ (minor, dq, $J = 20.7, 12.8$ Hz, 1F); IR (ATR) 2923, 1477, 1328, 1137, 1118, 823; HRMS (EI) m/z calcd. C$_{13}$H$_{11}$F$_5$ [M]$^+$ 286.0775 found: [M]$^+$ 286.0774.

![NMR Spectra](image)

2,6-difluoro-3',5'-dimethyl-4-(trifluoromethyl)-biphenyl (3tc)

The general procedure was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 3,5-difluorobenzotrifluoride (455.2 mg, 2.50 mmol). Column chromatography (hexane 100%) afforded the title product as a colorless oil (78.7 mg, 55%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.28 (d, $J = 6.7$ Hz, 2H), 7.11 (s, 1H), 7.09 (s, 2H), 2.40 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 160.1 (dd, $J = 250.9, 7.5$ Hz), 138.2, 131.2 (qt, $J = 34.5 10.1$ Hz), 130.9, 127.9, 127.6, 123.0 (qt, $J = 272.3, 3.2$ Hz), 122.7 (t, $J = 18.9$ Hz), 109.6 – 109.2 (m), 21.4; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ $-63.0$ (s, 3F), $-110.5$ (d, $J = 6.4$ Hz, 2F); IR (ATR) 2921, 1477, 1069, 918, 660; HRMS (EI) m/z calcd. C$_{13}$H$_{11}$F$_5$ [M]$^+$ 286.0775 found: [M]$^+$ 286.0764.
2,5-difluoro-3',5'-dimethyl-biphenyl (3uc)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 µL, 0.50 mmol) and 1,4-difluorobenzene (513.9 µL, 5.00 mmol). Column chromatography (hexane 100%) afforded the title product as a colorless oil (19.6 mg, 18%).

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.15 - 7.05 (m, 5H) 7.00 - 6.95 (m, 1H), 2.39 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 158.8 (dd, $J = 242.0, 2.2$ Hz) 155.9 (dd, $J = 243.3, 2.4$ Hz) 138.3, 134.8, 130.8 (dd, $J = 16.0, 7.8$ Hz), 130.0, 126.8, (d, $J = 2.9$ Hz), 117.3 - 117.0 (m, 2C), 115.0 (dd, $J = 24.0, 8.6$ Hz), 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –119.3 - –119.4 (m, 1F), –123.8 - –123.9 (m, 1F); IR (ATR) 2922, 1499. 1172, 851, 756; HRMS (EI) $m/z$ calcd. C$_{14}$H$_{12}$F$_2$: [M]$^+$ 218.0902; found: [M]$^+$ 218.0900.

2,6-difluoro-3',5'-dimethyl-1,1'-biphenyl (3vc), 3,5-difluoro-3',5'-dimethylbiphenyl (3vc$^a$) and 2,4-difluoro-3',5'-dimethyl-1,1'-biphenyl (3vc$^{\text{**}}$)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 µL, 0.50 mmol) and 1,3-difluorobenzene (490.5 µL, 5.0 mmol). Column chromatography (hexane, 100%) afforded a 1.00 : 0.63 : 0.06 mixture of 2,6-difluoro-3',5'-dimethyl-1,1'-biphenyl, 3,5-difluoro-3',5'-dimethylbiphenyl and 2,4-difluoro-3',5'-dimethyl-1,1'-biphenyl respectively as a colourless oil (13.1 mg, 12%). Milligrams (<3 mg) of 2,6-difluoro-3',5'-dimethyl-1,1'-biphenyl, 3,5-difluoro-3',5'-dimethylbiphenyl and 2,4-difluoro-3',5'-dimethyl-1,1'-biphenyl were isolated for analysis by column chromatography (hexane 100%).

$^1$H NMR (500 MHz, (CD$_2$Cl)$_2$): $\delta$ 7.30 (tt, $J = 8.4, 6.3$ Hz, 1H), 7.07 (s, 1H), 7.06 (s, 2H), 7.02 - 6.96 (m, 2H), 2.37 (s, 6H); $^1$H $^{19}$F NMR (500 MHz, (CD$_2$Cl)$_2$): $\delta$ 7.30 (t, $J = 8.4, 6.3$ Hz, 1H), 7.07 (s, 1H), 7.06 (s, 2H), 6.99 (d, $J = 8.4, 2H$), 2.37 (s, 6H); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): $\delta$ 160.5 (dd, $J = 247.1, 7.3$ Hz), 138.3, 130.3, 129.2 (d, $J = 10.0$ Hz), 129.1, 128.3, 119.1 (t, $J = 19.3$ Hz), 112.9 - 110.9 (m), 21.4; $^{19}$F NMR (471 MHz, CD$_2$Cl$_2$) $\delta$ –115.0 (t, $J = 6.8$ Hz, 2F); $^{19}$F $^1$H NMR (471 MHz, CD$_2$Cl$_2$) $\delta$ –115.0 (s, 2F); IR (ATR) 2921, 1468, 1230, 1013, 784; HRMS (EI) $m/z$ calcd. C$_{14}$H$_{12}$F$_2$: [M]$^+$ 218.0902 found: [M]$^+$ 218.0907.
3,5-difluoro-3',5'-dimethylbiphenyl (3vc')

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.18 (s, 2H), 7.15 - 7.11 (m, 2H), 7.05 (s, 1H), 6.70 (tt, $J = 9.0$, 2.3 Hz, 1H), 2.37 (s, 6H); $^1$H $\{^{19}$F$\}$ NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.18 (s, 2H), 7.13 (d, $J = 2.3$ Hz, 2H), 7.05 (s, 1H), 6.79 (t, $J = 2.3$ Hz, 1H), 2.37 (s, 6H); $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): $\delta$ 163.6 (dd, $J = 247.0$, 13.2 Hz), 145.3 (t, $J = 9.5$ Hz), 139.1, 139.0 (t, $J = 2.5$ Hz), 130.5, 125.1, 110.6 - 109.7 (m), 102.5 (t, $J = 25.6$ Hz), 21.5; $^{19}$F NMR (471 MHz, CD$_2$Cl$_2$) $\delta$ –110.8 (app t, $J = 8.6$ Hz, 2F). $^{19}$F $\{^1$H$\}$ NMR (471 MHz, CD$_2$Cl$_2$) $\delta$ –110.8 (s, 2F). IR (ATR) 3025, 1599, 1589, 1117, 987, 843; HRMS (EI) $m/z$ calcd. C$_{14}$H$_{12}$F$_2$: [M]$^+$ 218.0902 found: [M]$^+$ 218.0901.
2,4-difluoro-3',5'-dimethyl-1,1'-biphenyl (3vc"")

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.40 (td, $J = 8.7$, 6.5 Hz, 1H), 7.10 (s, 2H), 7.03 (s, 1H), 6.98 - 6.89 (m, 2H), 2.36 (s, 6H); $^1$H \{19F\} NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.40 (d, $J = 8.5$ Hz, 1H), 7.10 (s, 2H), 7.03 (s, 1H), 6.96 (dd, $J = 8.5$, 2.9 Hz, 1H), 6.92 (d, $J = 2.9$ Hz, 1H), 2.36 (s, 6H) $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$): $\delta$ 162.5 (dd, $J = 247.8$, 11.9 Hz), 160.1 (dd, $J = 249.4$, 11.9 Hz), 138.5, 135.1, 132.0 (dd, $J = 9.5$, 5.1 Hz), 129.7, 127.0 (d, $J = 2.6$ Hz), 126.0 (dd, $J = 13.9$, 3.9 Hz), 111.8 (dd, $J = 21.0$, 3.9 Hz), 104.5 (dd, $J = 27.0$, 25.3, Hz), 21.4; $^{19}$F NMR (471 MHz, CD$_2$Cl$_2$) $\delta$ -112.7 - -112.8 (m, 1F), -114.0 - -114.1 (m, 1F); $^{19}$F \{1H\} NMR (471 MHz, CD$_2$Cl$_2$) $\delta$ -112.8 (d, $J = 7.4$ Hz, 1F), -114.1 (d, $J = 7.4$ Hz, 1F). IR (ATR) 2960, 1613, 1149, 990, 813; HRMS (EI) m/z calcd. C$_{14}$H$_{12}$F$_2$: [M]$^+$ 218.0902 found: [M]$^+$ 218.0908.
2-phenylbenzo[b]thiophene (4b)

The General Procedure 1 was applied with bromobenzene (52.7 μL, 0.50 mmol) and benzo[b]thiophene (201.3 mg, 1.50 mmol). Column chromatography (hexane 100%) afforded the title product as a white solid (29.4 mg, 28%).

Spectroscopic data matched those previously reported.\textsuperscript{18}

\[
\begin{align*}
\text{1H NMR} & (400 \text{ MHz, CDCl}_3): \delta 7.84 (d, J = 7.8 \text{ Hz, 1H}), 7.78 (d, J = 7.6 \text{ Hz, 1H}), 7.73 (d, J = 7.8 \text{ Hz, 2H}), 7.55 (s, 1H), 7.43 (t, J = 7.6 \text{ Hz, 2H}), 7.37 - 7.30 (m, 3H); \\
\text{13C NMR} & (126 \text{ MHz, CDCl}_3): \delta 144.4, 140.8, 139.6, 134.4, 129.1, 128.4, 126.6, 124.6, 124.5, 123.7, 122.4, 119.6.
\end{align*}
\]

8-(3,5-dimethylphenyl)-1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione (5c)

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol), caffeine (291.3 mg, 1.50 mmol) and pivalonitrile (554.3 μL, 5.00 mmol). Column chromatography (hexane/CH\textsubscript{2}Cl\textsubscript{2} 100:0 – 40:60) afforded the title product as a white solid (88.6 mg, 59%).

Spectroscopic data matched those previously reported.\textsuperscript{19}
1H NMR (400 MHz, CDCl₃): δ 7.27 (s, 2H), 7.15 (s, 1H), 4.03 (s, 3H), 3.63 (s, 3H), 3.43 (s, 3H), 2.40 (s, 6H); 13C NMR (126 MHz, CDCl₃): δ 155.7, 152.7, 151.9, 148.4, 138.8, 132.2, 128.3, 127.0, 108.6, 34.0, 29.9, 28.1, 21.5.

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and benzo[h]quinoline (89.6 mg, 0.50 mmol). Column chromatography (Et₂O 100%) afforded the title product as a viscous yellow oil (137.4 mg, 97%).

Spectroscopic data matched those previously reported.²⁰

1H NMR (400 MHz, CDCl₃): δ 8.47 (dd, J = 4.2, 1.9 Hz, 1H), 8.09 (dd, J = 8.0, 1.8 Hz, 1H), 7.90 (dd, J = 7.9, 2.7 Hz, 1H), 7.85 (d, J = 8.8 Hz, 1H), 7.70 - 7.65 (m, 2H), 7.56 (dd, J = 7.3, 1.4 Hz, 1H), 7.33 (dd, J = 8.0, 4.3 Hz, 1H), 7.00 (app s, 3H), 2.36 (s, 6H); 13C NMR (126 MHz, CDCl₃): δ 147.0, 147.0, 146.3, 142.1, 136.7, 135.3, 135.2, 131.7, 129.2, 128.5, 127.9, 127.5, 127.3, 127.1, 126.7, 126.0, 121.2, 21.6.

2-(3',5'-dimethyl-[biphenyl]-2-yl)pyridine (7c) and 2-(3,3",5,5"-tetramethyl-[1,1':3',1"-terphenyl]-2'-yl)pyridine (7c')

The General Procedure 1 was applied with 1-bromo-3,5-dimethylbenzene (67.9 μL, 0.50 mmol) and 2-phenylpyridine (71.5 μL, 0.5 mmol). Column chromatography (hexane/CH₂Cl₂/AcOH 80:17:3) afforded 2-(3',5'-dimethyl-[biphenyl]-2-yl)pyridine as a clear oil (41.4 mg, 32%) and 2-(3,3",5,5"-tetramethyl-[1,1':3',1"-terphenyl]-2'-yl)pyridine as a white solid (54.5 mg, 30%).

2-(3',5'-dimethyl-[biphenyl]-2-yl)pyridine (7c)

1H NMR (400 MHz, CDCl₃): δ 8.64 (ddd, J = 4.9, 1.7, 0.9 Hz, 1H), 7.71 - 7.67 (m, 1H), 7.46 - 7.37 (m, 4H), 7.10 (ddd, J = 7.5, 4.9, 1.1 Hz, 1H), 6.91 (dt, J = 7.9, 1.0 Hz, 1H), 6.86 (s, 1H), 6.77 (s, 2H), 2.20 (s, 6H); 13C NMR (126 MHz, CDCl₃): δ 159.5, 149.4, 141.3, 140.9, 139.5, 137.5, 135.2, 130.5, 130.5, 128.5, 128.4, 127.7, 127.5, 125.5, 121.3, 21.3; IR (ATR) 2918, 1584, 1461, 746; HRMS (EI) m/z calcd. C₁₉H₁₇N: [M]+ 259.1356; found: [M]+ 259.1350.
2-(3,3″,5,5″-tetramethyl-[1,1′:3′,1″-terphenyl]-2′-yl) pyridine (7c′)

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 8.34 (ddd, $J = 4.9, 1.7, 1.0$ Hz, 1H), 7.50 - 7.41 (m, 3H), 7.33 (td, $J = 7.7, 1.8$ Hz, 1H), 6.93 - 6.88 (m, 2H), 6.77 (s, 2H), 6.72 (s, 4H), 2.15 (s, 12H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 159.5, 148.3, 142.0, 141.6, 138.6, 137.0, 134.8, 129.3, 128.1, 127.9, 127.7, 126.9, 120.8, 21.3; IR (ATR) 2916, 1587, 1454, 808, 707; m.p. 130 - 132 °C; HRMS (EI) $m/z$ calcd. C$_{27}$H$_{25}$N: [M]$^+$ 363.1982; found: [M]$^+$ 363.1964.

2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1H-indole (8a)

The General Procedure 1 was applied with 4-bromoanisole (62.6 µL, 0.50 mmol) and 1-(pyrimidin-2-yl)-1H-indole (8) $^6$ (97.6 mg, 0.5 mmol). Column chromatography (hexane/AcOH 90:10 – 30:70) afforded 2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1H-indole (48.2 mg, 32%) as a colourless solid. Spectroscopic data matched those previously reported. $^6$

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 8.66 (d, $J = 4.8$ Hz, 2H), 8.08 (d, $J = 8.0$ Hz, 1H), 7.61 (d, $J = 7.5$ Hz, 1H), 7.26 - 7.19 (m, 4H), 7.08 (t, $J = 4.8$ Hz, 1H), 6.82 (d, $J = 8.4$ Hz, 2H), 6.72 (s, 1H), 3.79 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): $\delta$ 159.0, 158.4, 158.3, 140.4, 138.1, 129.5, 129.5, 126.6, 123.3, 122.2, 120.6, 117.7, 113.8, 112.8, 107.4, 55.4.

1-(4′-methoxy-[biphenyl]-2-yl)-1H-pyrazole (9a) and 1-(4,4″-dimethoxy-[terphenyl]-2′-yl)-1H-pyrazole (9a′)

The General Procedure 1 was applied with 4-bromoanisole (62.6 µL, 0.50 mmol) and 1-phenylpyrazole (66.1 µL, 0.5 mmol). Column chromatography (hexane/AcOH 90:10 – 40:60) afforded 1-(4′-methoxy-[biphenyl]-2-yl)-1H-pyrazole as a clear oil (38.8 mg, 31%) and 2-(4,4″-dimethoxy-[terphenyl]-2′-yl)-1H-pyrazole as a white solid (60.6 mg, 34%).

1-(4′-methoxy-[biphenyl]-2-yl)-1H-pyrazole (9a)

Spectroscopic data matched those previously reported. $^{21}$

$^1$H NMR (500 MHz, CDCl$_3$): $\delta$ 7.54 (s, 1H), 7.49 - 7.48 (m, 1H), 7.35 - 7.33
(m, 3H), 7.00 (s, 1H), 6.92 (d, J = 7.9 Hz, 2H), 6.71 (d, J = 7.9 Hz, 2H), 6.10 (s, 1H), 3.68 (s, 3H); $^1$C NMR (126 MHz, CDCl$_3$): δ 159.1, 140.2, 138.6, 136.5, 131.4, 131.0, 130.9, 129.7, 128.3, 128.0, 126.7, 114.0, 106.4, 55.2.

1-(4,4''-dimethoxy-[terphenyl]-2'-yl)-1H-pyrazole (9a')

Spectroscopic data matched those previously reported.$^{22}$

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.47 (t, J = 7.6 Hz, 1H), 7.40 (s, 1H), 7.38 (d, J = 4.4 Hz, 2H), 7.05 (s, 1H), 6.98 (d, J = 7.5 Hz, 4H), 6.72 (d, J = 7.5 Hz, 4H), 6.04 (app d, J = 1.5 Hz, 1H), 3.73 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 158.9, 140.2, 139.5, 136.4, 132.5, 131.3, 129.8, 129.5, 129.2, 113.0, 106.2, 55.2.

The General Procedure 1 was applied with 4-bromoanisole (62.6 μL, 0.50 mmol) and 2-phenoxypyridine (10) (85.6 mg, 0.5 mmol). Column chromatography (hexane/AcOH 90:10 – 40:60) afforded 2-((4'-methoxy-[biphenyl]-2'-yl)oxy)pyridine (59.6 mg, 43%) and 2-((4,4''-dimethoxy-[terphenyl]-2'-yl)oxy)pyridine (40.3 mg, 21%) both as white solids.

Spectroscopic data matched those previously reported.$^{23}$

2-((4'-methoxy-[biphenyl]-2'-yl)oxy)pyridine (10a)

$^1$H NMR (500 MHz, CDCl$_3$): δ 8.14 (d, J = 4.6 Hz, 1H), 7.56 (t, J = 7.7 Hz, 1H), 7.45 (t, J = 9.1 Hz, 3H), 7.36, (t, J = 7.5 Hz, 1H), 7.29, (t, J = 7.4 Hz, 1H), 7.17 (d, J = 8.0 Hz, 1H), 6.90 - 6.85 (m, 3H), 6.76 (d, J = 8.2 Hz, 1H), 3.78 (s, 3H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 163.9, 158.9, 151.0, 134.5, 131.2, 130.3 (2C), 128.3, 125.5, 122.8, 118.1, 113.6, 111.3, 111.3, 55.3.

2-((4,4''-dimethoxy-[terphenyl]-2'-yl)oxy)pyridine (10a')

$^1$H NMR (500 MHz, CDCl$_3$): δ 7.92 (d, J = 3.9 Hz, 1H), 7.42 - 7.32 (m, 8H), 6.81 (d, J = 8.0 Hz, 4H), 6.66 (t, J = 5.8 Hz, 1H), 6.49 (d, J = 8.0 Hz, 1H), 3.76 (s, 6H); $^{13}$C NMR (126 MHz, CDCl$_3$): δ 163.4, 158.8, 147.9, 147.3, 138.7, 135.9, 130.8, 130.4, 130.1, 125.9, 117.3, 113.5, 110.8.
2-([1,1'-biphenyl]-2-yl)-4,5-dihydrooxazole (11b) and 2-([1,1':3',1"-terphenyl]-2'-yl)-4,5-dihydrooxazole (11b')

The General Procedure 1 was applied with bromobenzene (52.5 μL, 0.50 mmol) and 2-phenyl-2-oxazoline (65.8 μL, 0.5 mmol). 10% yield of 2-([1,1'-biphenyl]-2-yl)-4,5-dihydrooxazole evaluated by 1H-NMR. Column chromatography (hexane/AcOH 90:20 – 35:65) afforded 2-([1,1':3',1"-terphenyl]-2'-yl)-4,5-dihydrooxazole as a white solid (54.9 mg, 36%).

Spectroscopic data matched those previously reported.24

2-([1,1':3',1"-terphenyl]-2'-yl)-4,5-dihydrooxazole (11b')

1H NMR (500 MHz, CDCl₃): δ 7.53 (t, J = 7.6 Hz, 1H), 7.48 (d, J = 7.7 Hz, 4H), 7.40 (app t, J = 7.8 Hz, 6H), 7.35 (app t, J = 7.2 Hz, 2H), 3.90 (t, J = 9.4 Hz, 2H), 3.60 (t, J = 9.4 Hz, 2H); 13C NMR (126 MHz, CDCl₃): δ 164.1, 142.4, 141.0, 129.7, 128.9, 128.7, 127.6, 127.3, 67.4, 55.2.

5-([biphenyl]-2-yl)-IH-tetrazol-1-yl)(phenyl)methanone (12b) and 5-([terphenyl]-2'-yl)-IH-tetrazol-1-yl)(phenyl)methanone (12b')

The General Procedure 1 was applied with bromobenzene (52.5 μL, 0.50 mmol) and 1-benzyl-5-phenyl-IH-tetrazole (12)5 (118.1 mg, 0.5 mmol). Column chromatography (hexane/AcOH 90:20 – 40:60) afforded 5-([biphenyl]-2-yl)-1H-tetrazol-1-yl)(phenyl)methanone (96.8 mg, 62%) and 5-([terphenyl]-2'-yl)-1H-tetrazol-1-yl)(phenyl)methanone (5.8 mg, 3%) both as white solids.

Spectroscopic data matched those previously reported.25

5-([biphenyl]-2-yl)-IH-tetrazol-1-yl)(phenyl)methanone (12b)

1H NMR (500 MHz, CDCl₃): δ 7.62 (t, J = 7.5 Hz, 1H), 7.56 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.5 Hz, 1H), 7.33 (d, J = 7.7 Hz, 1H), 7.29 - 7.26 (m, 3H), 7.19 - 7.11 (m, 5H), 6.74 (d, J = 7.6 Hz, 2H), 4.76 (s, 2H); 13C NMR (126 MHz, CDCl₃): δ 154.7, 141.6, 138.8, 133.1, 131.6, 131.2, 130.3, 129.0, 128.7, 128.6, 128.6, 128.1, 128.1, 127.8 122.7, 50.8.
(5-[terphenyl]-2'-yl)-1H-tetrazol-1-yl)(phenyl)methanone (12b')

\[ \text{H NMR (500 MHz, CDCl}_3\text{): } \delta 7.70 (t, J = 7.7 Hz, 1H), 7.50 (d, J = 7.7 Hz, 2H), 7.24 - 7.13 (m, 9H), 6.97 (d, J = 7.5 Hz, 4H), 6.69 (d, J = 7.5 Hz, 2H), 4.70 (s, 2H); \]
\[ \text{C NMR (126 MHz, CDCl}_3\text{): } \delta 153.1, 143.7, 139.1, 132.8, 131.3, 129.7, 129.1, 128.9, 128.4, 127.9, 121.5, 50.8. \]

Experimental results for direct arylation of 1r with Ru, Pd and Cu catalysts

| entry | [metal] | 3rc (%) | 3rc' (%) | 3rc'' (%) | ratio (3rc : 3rc' : 3rc'') |
|-------|---------|---------|----------|-----------|--------------------------|
| 1\(^a\) | [Ru]   | 55      | -        | -         | 1 : 0 : 0                 |
| 2\(^b\) | [Pd]  | 39      | 13       | 17        | 1 : 0.33 : 0.44           |
| 3\(^c\) | [Cu] | 10      | 5        | 1         | 1 : 0.5 : 0.1             |
| 4\(^d\) | [Cu] | <1      | 2        | -         | <0.5 : 1 : 0              |

\(^a\) Reaction conditions: C5 (15.5 mg, 0.020 mmol, 4 mol %), 1r (325.2 μL, 2.50 mmol), 2c (67.9 μL, 0.50 mmol), (NMe\(_4\))OPiv (35.1 mg, 0.20 mmol), (NMe\(_4\))4-fluorobenzoate (37.3 mg, 0.175 mmol), (NMe\(_4\))OC(CF\(_3\))\(_3\) (386.5 mg, 1.250 mmol) and pivalonitrile (166.3 μL, 1.50 mmol) were stirred under N\(_2\) in a closed vessel at 115 °C for 16 h; yield refers to isolated material (see General Procedure 1).

\(^b\) Reaction conditions: Pd(OAc)\(_2\) (2.2 mg, 0.01 mmol, 5 mol %), P\(_t\)BuMe•HBF\(_4\) (5.0 mg, 0.02 mmol), 1r (78.0 μL, 0.60 mmol), 2c (27.2 μL, 0.20 mmol), K\(_2\)CO\(_3\) (30.4 mg, 0.22 mmol) and DMA (78.0 μL) were stirred under N\(_2\) in a closed vessel at 120 °C for 12 h; yield are evaluated by quantitative \(^{19}\)F-NMR using C\(_6\)F\(_6\) (11.5 μL, 0.10 mmol, 0.5 equiv) as internal standard (see ref 8).

\(^c\) Reaction conditions: CuI (3.8 mg, 0.02 mmol, 10 mol %), 1,10-phenanthroline (3.6 mg, 0.02 mmol), 1r (78.0 μL, 0.60 mmol), 5-iodo-m-xylene (28.9 μL, 0.20 mmol), LiO'Bu (32.0 mg, 0.40 mmol) and DMF (200.0 μL) were stirred under N\(_2\) in a closed vessel at 130 °C for 24 h; yield are evaluated by quantitative \(^{19}\)F-NMR using C\(_6\)F\(_6\) (11.5 μL, 0.10 mmol, 0.5 equiv) as internal standard (see ref 26).

\(^d\) Reaction conditions: CuI (3.8 mg, 0.02 mmol, 10 mol %), 1,10-phenanthroline (3.6 mg, 0.02 mmol), 1r (78.0 μL, 0.60 mmol), 5-iodo-m-xylene (28.9 μL, 0.20 mmol), K\(_3\)PO\(_4\) (106.1 mg, 0.50 mmol) and DMF (120.0 μL) were stirred under N\(_2\) in a closed vessel at 130 °C for 24 h; yield are evaluated by quantitative \(^{19}\)F-NMR using C\(_6\)F\(_6\) (11.5 μL, 0.10 mmol, 0.5 equiv) as internal standard (see ref 26).

**Table S12.** Arylation of 1r with Ru, Pd or Cu displaying different regioselectivity.
19F-NMR expansion of the reaction illustrated in Table S12 in: 1) entry 2 [Pd]19; 1#) entry 2 [Pd]19, 19F {1H} NMR; 2) entry 3 [Cu]3; 3) entry 4 [Cu]3 displaying 3rc, 3rc', 3rc'' with relative integrations with respect to the internal standard C6F6.

Characterization of biaryls 3rc' and 3rc''

2,3-difluoro-3',5'-dimethyl-6-(trifluoromethyl)-1,1'-biphenyl (3rc')

Milligrams were isolated for characterization by column chromatography (hexane 100%).

1H NMR (500 MHz, CD2Cl2): δ 7.54 (ddd, J = 9.2, 4.8, 1.9, 1H), 7.30 (app. q, J = 8.4 Hz, 1H) 7.11 (s, 1H), 6.91 (s, 2H), 2.36 (s, 6H); 1H {19F} NMR (500 MHz, CD2Cl2): 7.54 (d, J = 8.9 Hz, 1H), 7.30 (d, J = 8.9 Hz, 1H), 7.11 (s, 1H), 6.91 (s, 2H), 2.36 (s, 6H); 13C NMR (126 MHz, CDCl3): δ 152.6 (dd, J = 255.8, 13.7 Hz), 148.6 (dd, J = 247.0, 12.7 Hz), 137.6, 132.3 (d, J = 16.8 Hz), 130.6, 130.6, 127.4, 126.5 - 125.8 (m), 124.3 (only 1 peak of quartet observed for -CF3), 122.3 - 122.1 (m), 116.0 (d, J = 17.8 Hz), 21.4; 19F NMR (471 MHz, CDCl3) δ −57.0 (s, 3F), −131.2 (dm, J = 24.7 Hz, 1F); −135.6 (dd, J = 22.5, 7.3 Hz, 1F); 19F NMR (471 MHz, CD2Cl2) δ −57.3 (s, 3F), −132.1 (dm, J = 22.0 Hz, 1F), 136.7 (dd, J = 22.3, 7.3 Hz, 1F); 19F {1H} NMR (471 MHz, CD2Cl2) δ −57.3 (s, 3F), −132.1 (d, J = 22.0 Hz, 1F), 136.7 (dd, J = 22.0 Hz, 1F); IR (ATR) 2920, 1322, 1166, 1135; HRMS (EI) m/z calcd. C15H11F5: [M]+ 286.0775; found: [M]+ 286.0782.
2',3'-difluoro-3",5","5"-tetramethyl-5'-((trifluoromethyl)-1,1':4',1"-terphenyl (3rc"'))

Milligrams were isolated for characterization by column chromatography (hexane 100%).

\(^1\)H NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.61 (d, \(J = 6.3\) Hz, 1H), 7.20 (s, 2H), 7.10 (app s, 2H), 6.95 (s, 2H), 2.42 (s, 6H), 2.38 (s, 6H); \(^1\)H \{\(^{19}\)F\}

NMR (500 MHz, CDCl\(_3\)): \(\delta\) 7.60 (s, 1H), 7.20 (s, 2H), 7.12 - 7.07 (m, 2H), 6.95 (s, 2H), 2.41 (s, 6H), 2.38 (s, 6H)

\(^{13}\)C NMR (126 MHz, CDCl\(_3\)): \(\delta\) 149.8 (dd, \(J = 256.2, 14.5\) Hz), 144.0 (dd, \(J = 246.8, 13.5\) Hz), 138.6, 137.6, 133.5, 130.8, 130.6 (d, \(J = 11.3\) Hz), 130.3, 130.2 (d, \(J = 11.5\) Hz), 127.5, 126.8, 126.8, 125.9 - 125.1 (m), 123.3 (qd, \(J = 274.0, 3.2\) Hz), 122.9 - 122.8 (m), 21.5, 21.5; \(^{19}\)F NMR (471 MHz, CDCl\(_3\)) \(\delta\) −56.9 (s, 3F), −135.1 (d, \(J = 22.0\) Hz, 1F), −136.1 (dd, \(J = 22.0, 6.0\) Hz, 1F); \(^{19}\)F \{\(^1\)H\} NMR (471 MHz, CDCl\(_3\)) \(\delta\) −56.9 (s, 3F), −135.2 (d, \(J = 22.0\) Hz, 1F), −136.3 (d, \(J = 22.0\) Hz, 1F); IR(ATR) 2920, 1364, 1294, 1132, 848; m.p. 185 - 187 °C; HRMS (EI) m/z calcd. C\(_{23}\)H\(_{19}\)F\(_5\): [M]\(^+\) 390.1393 found: [M]\(^+\) 390.1394.
Evidence for the formation of a pivalate-containing Ru(II) species

Figure S9.

1) $^1$H-NMR of (NMe)$_4$OPiv in acetonene-d$_6$; 2) $^1$H-NMR of $t$BuCN in acetonene-d$_6$; 3) $^1$H-NMR of Ru($t$BuCN)$_6$][BF$_4$)$_2$ C5 in acetonene-d$_6$; 4) $^1$H-NMR of 10.0 mg of Ru($t$BuCN)$_6$][BF$_4$)$_2$ C5 in 0.5 mL of acetonene-d$_6$ after 30 min at 50 °C; 5) $^1$H-NMR of 10.0 mg of Ru($t$BuCN)$_6$][BF$_4$)$_2$ C5 (0.013 mmol, 1.0 equiv) and 11.3 mg of (NMe)$_4$OPiv (0.052 mmol, 4.0 equiv) in 0.5 mL of acetonene-d$_6$ after 30 min at 50 °C. All the samples were prepared in glove box using Young’s type NMR tubes.
Figure S10.

1) $^1$H-NMR of (NMe)$_4$OPiv in CD$_2$Cl$_2$; 2) $^1$H-NMR of $^t$BuCN in CD$_2$Cl$_2$; 3) $^1$H-NMR of Ru($^t$BuCN)$_6$][BF$_4$)$_2$ C5 in CD$_2$Cl$_2$; 4) $^1$H-NMR of 10.0 mg of Ru($^t$BuCN)$_6$][BF$_4$)$_2$ C5 in 0.5 mL of CD$_2$Cl$_2$ after 30 min at 50 °C; 5) $^1$H-NMR of 10.0 mg of Ru($^t$BuCN)$_6$][BF$_4$)$_2$ C5 (0.013 mmol, 1.0 equiv) and 11.3 mg of (NMe)$_4$OPiv (0.052 mmol, 4.0 equiv) in 0.5 mL of CD$_2$Cl$_2$ after 30 min at 50 °C. All the samples were prepared in glove box using Young’s type NMR tubes.
Computational methods

All the calculations were performed at the DFT level with Gaussian 09, revision B.01\textsuperscript{27} using the Becke three-parameter hybrid functional\textsuperscript{28} with Lee, Yang and Parr correlation term.\textsuperscript{29} Stuttgart/Dresden base and ECPs for transition metals\textsuperscript{30} (Pd or Ru) and 6-31G basis set with polarization functions for all other atoms\textsuperscript{31} (C, H, O, N, F and P). Stationary points were characterized as minima or saddle points by frequencies analysis, representative transition states were confirmed to correspond to the desired C–H activation step by optimization through the internal reaction coordinate to starting materials and products.\textsuperscript{32} Dispersion corrections where calculated from single point calculations at the optimized geometries. Distortion-interaction analysis was performed by single point calculations on fragments of the corresponding optimized transition states. Distortion of the starting complex ($\Delta E_{\text{dist(M)}}$) corresponds to the difference between the energy of the fragment containing the original metal complex in the TS geometry and that of its optimized (minimum) geometry. Distortion of the fluoroarene ($\Delta E_{\text{dist(ArH)}}$) is the difference between the energy of the arene fragment in the TS geometry and that of the optimized arene. $\Delta E_{\text{dist(ArH)}}$ could be further deconvoluted in C–H elongation energy ($\Delta E_{\text{elon(ArH)}}$) and bending energy ($\Delta E_{\text{bend(ArH)}}$), which correspond, respectively, to the energy cost of elongating the C–H bond to the distance it displays in the TS and the remaining cost of distortion, of which the main contribution is bending the C–H bond out of plane. Finally, interaction energy is the difference between the TS energy and the metal and arene individual fragments in the TS geometry.

**Barriers for C–H activation of pentafluorobenzene with Ru complexes**

![General scheme of the Ru-mediated CMD C–H activation](image)

Figure S11.

General scheme of the Ru-mediated CMD C–H activation. M: starting material, TS: transition state, P: product.
Figure S12.
Optimized geometries of calculated CMD-type transition states.
| M                           | TS geometry | TS       | P       |
|-----------------------------|-------------|----------|---------|
| Ru(η⁶-C₆H₆)(OAc)₂ (M1)      | CMD         | 18.2     | 29.5    | 7.2     | 7.2   |
|                             | external base | 32.7     | 44.6    |         |       |
| [Ru(κ²-OAc)(MeCN)₄]⁺ (M2)   | CMD         | 15.8     | 28.8    | -1.8    | 12.1  |
|                             | external base* | 38.3     | -       |         |       |
| Ru(κ²-OAc)₂(MeCN)₂ (M4)     | cis-mer     | 9.8      | 21.1    | -3.7    | 8.6   |
|                             | trans-mer   | 11.2     | 23.0    |         |       |
|                             | cis-fac     | 12.2     | 23.9    | -1.0    | 10.9  |
| Ru(κ²-OAc)(κ¹-OAc)(MeCN)₃ (M5) | fac-cis     | 13.8     | 24.4    | 1.3     | 13.4  |
|                             | mer-cis     | 13.2     | 23.4    |         |       |
|                             | mer-trans   | 11.9     | 22.2    | -0.5    | 10.0  |
| Ru(κ²-OAc)(OC(CF₃))₃(MeCN)₃ (M6) | fac-cis     | 14.4     | 25.0    | 2.0     | 12.8  |
|                             | mer-cis     | 13.8     | 24.0    |         |       |
|                             | mer-trans   | 12.6     | 23.2    | -3.4    | 7.2   |

Table S13. Energies in kcal/mol (relative to starting materials) of TS and products for the different Ru model complexes. * Not fully optimized structure.
Barriers for C–H activation of 3,4-difluorobenzotrifluoride with Ru and Pd complexes

Figure S13.
Optimized geometries of calculated structures.

| \( M \) | Regioisomer | \( \Delta E^\dagger \) | \( \Delta G^\dagger \) | \( \Delta G^\dagger \) (disp) | \( \Delta G^\dagger \) (disp+solv) |
|---|---|---|---|---|---|
| \([\text{Ru}(\kappa_2^2\text{-OAc})(\text{MeCN})_4]^+\) (M2-Ru) | \( a \) | 26.9 | 41.9 | 22.0 |
| | \( b \) | 29.9 | 44.8 | 25.5 |
| | \( c \) | 25.0 | 38.7 | 21.2 |
| \([\text{Pd}(\kappa_2^2\text{-CO}_3\text{H})(\text{Ph})(\text{PMe}_3)]\) (M2-Pd) | \( a \) | 19.7 | 31.4 | 12.7 |
| | \( b \) | 24.6 | 35.7 | 16.8 |
| | \( c \) | 23.4 | 33.8 | 18.5 |
| \([\text{Ru}(\kappa_2^2\text{-OPiv})(\text{tBuCN})_4]^+\) (M3-Ru) | \( a \) | 24.8 | 41.5 | 16.5 | 19.2 |
| | \( b \) | 28.2 | 44.2 | 20.4 | 21.9 |
| | \( c \) | 22.3 | 38.0 | - | 18.3 |
| \([\text{Pd}(\kappa_2^2\text{-CO}_3\text{H})(\text{Ph})(\text{PMeBu}_2)]\) (M3-Pd) | \( a \) | 21.0 | 32.8 | 12.0 | 16.0 |
| | \( b \) | 26.3 | 37.9 | 17.6 | 22.2 |
| | \( c \) | 24.7 | 34.9 | 17.2 | 21.4 |

Table S14. Energies in kcal/mol (relative to starting materials) of TS for the different catalyst models. \( \Delta G^\dagger \) (disp): Activation Gibbs free energy with dispersion corrections. \( \Delta G^\dagger \) (disp+solv): Activation Gibbs free energy with dispersion and solvation corrections.
$^1$H NMR, $^{19}$F NMR and $^{13}$C NMR spectra

**Ru1a**

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
Ru1b

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
\(^{19}\text{F NMR (CDCl}_3\)}\)
Ru1c

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
Ru(OPiv)$_2$(p-cymene) (C2)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
Ru(OBz)$_2$(p-cymene) (C3)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
Ru(0Piv)$_2$(C$_6$Me$_6$) (C4)  

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
[Ru(\textsuperscript{15}BuCN)\textsubscript{6}]BF\textsubscript{4})_2 (C5)

\textsuperscript{1}H NMR ((CD\textsubscript{3})\textsubscript{2}CO)

\textsuperscript{13}C NMR ((CD\textsubscript{3})\textsubscript{2}CO)
$^{19}$F NMR ((CD$_3$)$_2$CO)
Ru2a

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
Ru2c

$^1$H NMR (CD$_2$Cl$_2$)

$^{13}$C NMR (CD$_2$Cl$_2$)
$^{19}$F NMR (CD$_2$Cl$_2$)
tetramethylammonium perfluoro-tert-butyl alkoxide

$^{1}$H NMR (D$_{2}$O)

$^{13}$C NMR (D$_{2}$O)
$^{19}$F NMR (D$_2$O)
tetramethylammonium pivalate

$^1$H NMR (D$_2$O)

$^{13}$C NMR (D$_2$O)
tetramethylammonium 4-fluorobenzoate

$^{1}H$ NMR (D$_2$O)

$^{13}C$ NMR (D$_2$O)
$^{19}$F NMR (D$_2$O)
3-butoxy-1,2,4,5-tetrafluorobenzene (1a)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
**1-butoxy-2,4,5-trifluorobenzene (1o)**

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR ($\text{CDCl}_3$)
butyl(2,3,5,6-tetrafluorophenyl)sulfane (1h)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
$3$-butoxy-$1,2,4,5$-tetrafluorobenzene-$6$-d ($d_1$-$1a$)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}\text{F NMR (CDCl}_3\text{)}$
N-(2,3,5,6-tetrafluorophenyl)pivalamide (1f)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}\text{F NMR (CDCl}_3\text{)}$
tert-butyl 2,3,5,6-tetrafluorobenzoate (1i)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
4-butoxy-2,3,5,6-tetrafluoro-4'-methoxy-1,1'-biphenyl (3aa).

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
4-butoxy-2,3,5,6-tetrafluoro-1,1'-biphenyl (3ab)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,4,5,6-pentafluorobiphenyl (3bb)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
3',5’-dimethyl-2,3,4,5,6-pentafluorobiphenyl (3bc)

**$^{1}H$ NMR (CDCl$_3$)**

![NMR spectrum for 3bc](image)

**$^{13}C$ NMR (CDCl$_3$)**

![NMR spectrum for 3bc](image)

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$^{19}$F NMR (CDCl$_3$)
2,3,4,5,6-Pentafluoro-4'-methylbiphenyl (3bd)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}\text{F NMR (CDCl}_3\text{)}$
2,3,4,5,6-pentafluoro-2'-methylbiphenyl (3be)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
2,3,4,5,6-pentafluoro-4’-methoxybiphenyl (3ba)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
3'-Methoxy-2,3,4,5,6-pentafluorobiphenyl (3bf)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}\text{F NMR (CDCl}_3\text{)}$
2,3,4,5,6-Pentafluoro-2'-methoxybiphenyl (3bg)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,4,4',5,6-Hexafluorobiphenyl (3bh)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,2',3,4,5,6-hexafluorobiphenyl (3bi)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,4,5,6-Pentafluoro-3'-(trifluoromethyl)biphenyl (3bj)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,4,5,6-Pentafluoro-4'-trifluoromethylbiphenyl (3bk)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
Methyl(2',3',4',5',6'-pentafluoro-[biphenyl]-4-yl)sulfane (3bl)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
4'-dimethylamino-2,3,4,5,6-pentafluorobiphenyl (3bm)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}\text{F NMR (CDCl}_3\text{)}$
$1-(2',3',4',5',6'$-pentafluoro-biphenyl-4-yl)ethanone (3bn)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
Methyl 2',3',4',5',6'-pentafluorobiphenyl-4-carboxylate (3bo)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2-(2',3',4',5',6'-pentafluoro-[1,1'-biphenyl]-4-yl)-1,3-dioxolane (3bp)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,4,5,6-pentafluoro-4'-iodo-3',5'-dimethyl-1,1'-biphenyl (3bq)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,4,5,6-pentafluoro-4'-vinylbiphenyl (3br)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,4,5,6-pentafluoro-4'-styrylbiphenyl (3bs)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR ((CD$_3$)$_2$CO)
$^{19}F$ NMR (CDCl$_3$)
2-Pentafluorophenylnaphthalene (3bt)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
**1-Methyl-5-(perfluorophenyl)-1H-indole (3bu)**

$^1$H NMR (CDCl$_3$)

![1H NMR spectrum](image)

$^{13}$C NMR (CDCl$_3$)

![$^{13}$C NMR spectrum](image)
$^{19}$F NMR (CDCl$_3$)
2',3',4',5',6'-pentafluoro-biphenyl-4-carbonitrile (3bv)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,4,5,6-pentafluoro-2'-phenoxy-1,1'-biphenyl (3ba')

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2'-benzyl-2,3,4,5,6-pentafluoro-1,1'-biphenyl (3bb')

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}\text{F NMR (CDCl}_3\text{)}$
2'- (benzyloxy) - 2, 3, 4, 5, 6-pentafluoro-1, 1'- biphenyl (3bc')

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,5,6-tetrafluoro-3',5'-dimethylbiphenyl (3cc)

\(^1\)H NMR (CDCl\(_3\))

\(^{13}\)C NMR (CDCl\(_3\))
$^{19}$F NMR (CDCl$_3$)
$2',3',5',6'$-tetrafluoro-$3'',5,5''$-tetramethyl-$1',4',1''$-terphenyl ($3cc'$)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}\text{F NMR (CDCl}_3\text{)}$
2,3,5,6-tetrafluoro-3',4,5'-trimethylbiphenyl (3dc)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,5,6-tetrafluoro-3',5'-dimethyl-4-(trifluoromethyl)biphenyl (3ec)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
$N$-(2,3,5,6-tetrafluoro-3',5'-dimethyl-biphenyl-4-yl)pivalamide (3fc)

$^1$H NMR (CDCl$_3$)

$^1$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
$2,3,5,6$-tetrafluoro-$N,N,3',5'$-tetramethyl--biphenyl-4-amine ($3\text{gc}$)

$^1\text{H NMR (CDCl}_3)$

$^1\text{C NMR (CDCl}_3)$
$^{19}$F NMR (CDCl$_3$)
**butyl(2,3,5,6-tetrafluoro-3',5'-dimethyl-[1,1'-biphenyl]-4-yl)sulfane (3hc)**

$^1$H NMR (CDCl$_3$)

![NMR spectrum of 3hc](image)

$^{13}$C NMR (CDCl$_3$)

![NMR spectrum of 3hc](image)
$^{19}\text{F NMR (CDCl}_3\text{)}$
tert-butyl 2,3,5,6-tetrafluoro-3',5'-dimethyl-biphenyl-4-carboxylate (3ic)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,3,4,6-tetrafluoro-3',5'-dimethylbiphenyl (3jc)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
2,3,4,5-tetrafluoro-3',5'-dimethylbiphenyl (3kc)

\(^1\)H NMR (CDCl\(_3\))

\(^{13}\)C NMR (CDCl\(_3\))
$^{19}$F NMR (CDCl$_3$)
2,4,6-trifluoro-3',5'-dimethylbiphenyl (3ic)

\(^1\)H NMR (CDCl\(_3\))

\(^{13}\)C NMR (CDCl\(_3\))
$^{19}$F NMR (CDCl$_3$)
2,3,6-trifluoro-3',5'-dimethylbiphenyl (3mc)

$^1$H NMR (CD$_2$Cl$_2$)

$^1$H {^{19}F} NMR (CD$_2$Cl$_2$)
$^{13}$C NMR (CD$_2$Cl$_2$)

$^{19}$F NMR (CD$_2$Cl$_2$)
$^{19}\text{F} \{^1\text{H}\} \text{ NMR (CD}_2\text{Cl}_2\}$
$2,3,5$-trifluoro-$3',5'$-dimethylbiphenyl \((3mc')\) and $2',3',5'$-trifluoro-$3''',5'''$-tetramethylterphenyl \((3mc'')\)

$^1\text{H}$ NMR (CD$_2$Cl$_2$)

$^1\text{H} \{^{19}\text{F}\}$ NMR (CD$_2$Cl$_2$)
$^{13}$C NMR (CD$_2$Cl$_2$)

$^{19}$F NMR (CD$_2$Cl$_2$)
$^{19}\text{F} \{^1\text{H}\} \text{ NMR (CD}_2\text{Cl}_2\)$
2',3',5'-trifluoro-3'',5,5''-tetramethylterphenyl (3mc''')

$^1$H NMR (CD$_2$Cl$_2$)

$^1$H $^{19}$F NMR (CD$_2$Cl$_2$)
$^{13}$C NMR (CD$_2$Cl$_2$)

$^{19}$F NMR (CD$_2$Cl$_2$)
\(^{19}\text{F} \{^{1}\text{H}\} \text{ NMR (CD}_2\text{Cl}_2\)
2,3,4-trifluoro-3',5'-dimethylbiphenyl (3nc)

$^1$H NMR (CDCl$_3$)

$^1$H $\{^{19}F\}$ NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

$^{19}$F NMR (CDCl$_3$)
$^{19}$F NMR $^{1}$H (CDCl$_3$)
3,4,5-trifluoro-3',5'-dimethylbiphenyl (3nc')

$^1$H NMR (CD$_2$Cl$_2$)

$^1$H $^{19}$F NMR (CD$_2$Cl$_2$)
$^{13}\text{C NMR (CD}_2\text{Cl}_2)$

$^{19}\text{F NMR (CD}_2\text{Cl}_2)$
$^{19}\text{F} \{^{1}\text{H}\} \text{ NMR (CD}_2\text{Cl}_2\text{)}$
3-butoxy-2,5,6-trifluoro-3',5'-dimethyl-1,1'-biphenyl (3oc)

$^1\text{H}$ NMR (CDCl$_3$)

$^1\text{H} \{^{19}\text{F}\}$ NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

$^{19}$F NMR (CDCl$_3$)
$^{19}$F $^{1}$H NMR (CDCl$_3$)
2,3,6-trifluoro-3',5'-dimethyl-4-(trifluoromethyl)-biphenyl (3pc)

$^1$H NMR (CDCl$_3$)

$^1$H $^{19}$F NMR (CDCl$_3$)

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\(^{13}\)C NMR (CDCl\(_3\))

\(^{19}\)F NMR (CDCl\(_3\))
$^{19}$F NMR $\{^1H\}$ (CDCl$_3$)
2,3,4-trifluoro-3',5'-dimethyl-5-(trifluoromethyl)-biphenyl (3qc)

$^1$H NMR (CDCl$_3$)

$^1$H {${^{19}}$F} NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

$^{19}$F NMR (CDCl$_3$)
$^{19}$F \{¹H\} NMR (CDCl₃)
2,3-difluoro-3',5'-dimethyl-6-(trifluoromethyl)-biphenyl (3rc)

$^1$H NMR (CDCl$_3$)

$^1$H $^{19}$F NMR (CDCl$_3$)

$^1$H $^{19}$F NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

$^{19}$F NMR (CDCl$_3$)
$^{19}\text{F} \ { }^{1}\text{H} \ \text{NMR (CDCl}_3\text{)}$
2,3-difluoro-3’,5’-dimethyl-4-(trifluoromethyl)-biphenyl (3sc) and 3,4-difluoro-3’,5’-dimethyl-5-(trifluoromethyl)-biphenyl (3sc’)

$^1$H NMR (CDCl$_3$)

$^1$H $^{19}$F NMR (CDCl$_3$)

$^1$H $^{19}$F NMR (CDCl$_3$)
$^{13}$C NMR (CDCl$_3$)

$^{19}$F NMR (CDCl$_3$)
$^{19}$F {${}^1$H} NMR (CDCl$_3$)
2,6-difluoro-3',5'-dimethyl-4-(trifluoromethyl)-1,1'-biphenyl (3tc)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,5-difluoro-3',5'-dimethyl-biphenyl (3uc)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
$^{19}$F NMR (CDCl$_3$)
2,6-difluoro-3',5'-dimethyl-1,1'-biphenyl (3vc)

$^1$H NMR (CD$_2$Cl$_2$)

$^1$H NMR $^1$F (CD$_2$Cl$_2$)
$^{13}$C NMR (CD$_2$Cl$_2$)

$^{19}$F NMR (CD$_2$Cl$_2$)
$^{19}$F $^{1}$H NMR (CD$_2$Cl$_2$)
3,5-difluoro-3',5'-dimethyl-1,1'-biphenyl (3vc')

$^1$H NMR (CD$_2$Cl$_2$)

$^1$H {$^{19}$F} NMR (CD$_2$Cl$_2$)
$^{13}$C NMR (CD$_2$Cl$_2$)

$^{19}$F NMR (CD$_2$Cl$_2$)
$^{19}\text{F} \{^1\text{H}\} \text{ NMR (CD}_2\text{Cl}_2\}$
2,4-difluoro-3',5'-dimethyl-1,1'-biphenyl (3vc'')

$^1$H NMR (CD$_2$Cl$_2$)

$^1$H NMR $^{19}$F (CD$_2$Cl$_2$)
$^{13}$C NMR (CD$_2$Cl$_2$)

$^{19}$F NMR (CD$_2$Cl$_2$)
$^{19}$F NMR $\{^1H\}$ (CD$_2$Cl$_2$)
2-phenylbenzo[b]thiophene (4b)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
8-(3,5-dimethylphenyl)-1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione (5c)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
10-(3,5-Dimethylphenyl)benzo[h]quinolone (6c)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
2-(3',5'-dimethyl-[biphenyl]-2-yl)pyridine (7c)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
2-(3",5",5"-tetramethyl-[1,1':3',1''-terphenyl]-2'-yl)pyridine (7c')

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)

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2-(4-methoxyphenyl)-1-(pyrimidin-2-yl)-1H-indole (8a)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
1-(4′-methoxy-[biphenyl]-2-yl)-1H-pyrazole (9a)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
1-(4,4''-dimethoxy-[terphenyl]-2'-yl)-1H-pyrazole (9a')

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
2-((4'-methoxy-[biphenyl]-2-yl)oxy)pyridine (10a)

$^1$H NMR (CDCl$_3$)
2-((4,4''-dimethoxy-[terphenyl]-2'-yl)oxy)pyridine (10a')

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
2-[[1,1':3',1''-terphenyl]-2'-yl]-4,5-dihydrooxazole (11b')

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
(5-([biphenyl]-2-yl)-1\textit{H}-tetrazol-1-yl)(phenyl)methanone (12b)

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
(5-([(terphenyl]-2'-yl)-1H-tetrazol-1-yl)(phenyl)methanone (12b')

$^1$H NMR (CDCl$_3$)

$^{13}$C NMR (CDCl$_3$)
2,3-difluoro-3',5'-dimethyl-6-(trifluoromethyl)-1,1'-biphenyl (3rc')

$^1$H NMR (CD$_2$Cl$_2$)

$^1$H $^{19}$F NMR (CD$_2$Cl$_2$)

$^1$H $^{19}$F NMR (CD$_2$Cl$_2$)
$^{13}$C NMR (CDCl$_3$)

$^{19}$F NMR (CDCl$_3$)
$^{19}$F NMR (CD$_2$Cl$_2$)

$^{19}$F NMR {$^1$H} (CD$_2$Cl$_2$)
$2',3'-\text{difluoro-3''},5,5''-\text{tetramethyl-5'}-(\text{trifluoromethyl})-1,1'4',1''-\text{terphenyl (3rc''\text{)}}$

$^1\text{H NMR (CDCl}_3\text{)}$

$^1\text{H NMR \{^{19}\text{F}\}} (\text{CDCl}_3)$
$^{13}$C NMR (CDCl$_3$)

$^{19}$F NMR (CDCl$_3$)
$^{19}\text{F} \{^1\text{H}\} \text{ NMR (CDCl}_3\text{)}$
Crystallographic section

Crystallographic data of C5

The crystal structure was deposited at the Cambridge Crystallographic Data Centre.

CCDC: 1420657

![Crystal structure diagram]

Table 1 Crystal data and structure refinement for C5

| Property                  | Value                  |
|---------------------------|------------------------|
| Empirical formula         | C_{30}H_{54}B_{2}F_{8}N_{6}Ru |
| Formula weight            | 773.48                 |
| Temperature/K             | 150.03(10)             |
| Crystal system            | orthorhombic           |
| Space group               | Pban                   |
| a/Å                       | 10.8977(3)             |
| b/Å                       | 34.0657(11)            |
| c/Å                       | 11.0451(4)             |
| α/°                       | 90                     |
| β/°                       | 90                     |
| γ/°                       | 90                     |
| Volume/Å³                 | 4100.4(2)              |
| Z                         | 4                      |
| ρ_{calc}/g/cm³            | 1.253                  |
| μ/mm⁻¹                    | 0.445                  |
| F(000)                    | 1608.0                 |
| Crystal size/mm³          | 0.27 × 0.25 × 0.15     |
| Radiation                 | MoKα (λ = 0.71073)     |
2θ range for data collection/° 7.054 to 58.492

Index ranges -12 ≤ h ≤ 13, -26 ≤ k ≤ 45, -8 ≤ l ≤ 14

Reflections collected 16335

Independent reflections 4871 [Rint = 0.0735, Rsigma = 0.0954]

Data/restraints/parameters 4871/73/253

Goodness-of-fit on F² 1.043

Final R indexes [I>2σ (I)]
R1 = 0.0573, wR2 = 0.1217

Final R indexes [all data]
R1 = 0.1126, wR2 = 0.1505

Largest diff. peak/hole / e Å⁻³ 1.32/-1.07

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for C5. Ueq is defined as 1/3 of the trace of the orthogonalised Uij tensor.

| Atom | x   | y   | z   | U(eq) |
|------|-----|-----|-----|-------|
| Ru1  | 2500| 3958.5(2) | 5000 | 17.77(14) |
| C2   | 169(4) | 4797.7(12) | 2636(4) | 24(1) |
| N3   | 1525(3) | 3555.1(10) | 4081(3) | 22.9(8) |
| N4   | 1530(3) | 4363.2(10) | 4058(3) | 22.0(8) |
| C5   | 91(4) | 3110.6(14) | 2766(4) | 31.5(11) |
| N6   | 1229(3) | 3912.9(10) | 6318(3) | 24.0(8) |
| C7   | 562(4) | 3787.2(12) | 7008(4) | 23.3(9) |
| C8   | -618(4) | 3390.2(13) | 1931(4) | 33.1(11) |
| C9   | -619(4) | 4519.0(14) | 1873(4) | 35.7(12) |
| C10  | -639(4) | 5069.9(13) | 3415(4) | 35.4(12) |
| C11  | 942(4) | 4556.7(12) | 3457(4) | 21.9(9) |
| C12  | 910(4) | 3357.1(13) | 3526(4) | 27.8(10) |
| C13  | -236(4) | 3562.5(13) | 7867(4) | 29.2(10) |
| C15  | -798(5) | 2889.8(15) | 3596(5) | 48.1(15) |
| C16  | 1018(4) | 5040.2(14) | 1824(4) | 35.6(12) |
| C17  | -1048(5) | 3847.3(15) | 8579(5) | 43.3(13) |
| C18  | 613(4) | 3330.2(15) | 8700(5) | 43.5(13) |
| C19  | -1016(4) | 3287.5(14) | 7096(5) | 38.5(12) |
| C21  | 886(5) | 2828.8(16) | 2009(6) | 58.7(18) |
| F20  | 1897(5) | 3947.1(16) | 10830(5) | 50.1(16) |
| F24  | 1660(5) | 4408.4(17) | 9423(5) | 52.5(16) |
| B25  | 2500 | 4175(2) | 10000 | 35(3) |
| B4   | -2500 | 2500 | 0 | 52(3) |
| F5   | -2620(20) | 2897.4(11) | -160(19) | 78(5) |
| F2   | -2707(17) | 2449(5) | 1212(3) | 61(4) |
| F7   | -1281(4) | 2430(6) | -204(17) | 75(5) |
| B2   | -2500 | 4097.1(12) | 5000 | 34.9(17) |
| F1   | -1638(3) | 3868.4(11) | 4440(3) | 78.4(12) |

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Table 3 Anisotropic Displacement Parameters (Å² × 10³) for C5

The Anisotropic displacement factor exponent takes the form: -2π²[h⁵a*²U₁₁+2hka*b*U₁₂+…]

| Atom | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|------|------|------|------|------|------|------|
| Ru1  | 20.7(2) | 14.5(2) | 18.1(2) | 0     | -1.6(2) | 0     |
| C2   | 26(2)   | 22(2)   | 25(2)   | -2(2) | -4.2(19) | 3.3(17) |
| N3   | 28.0(19) | 16.8(18) | 23.8(19) | -1.4(16) | -2.8(17) | 2.3(15) |
| N4   | 23.7(18) | 18.5(18) | 23.8(19) | -1.4(16) | -2.4(17) | 0.1(15) |
| C5   | 33(2)   | 24(2)   | 37(3)   | -7(2)  | -12(2)  | -1.4(19) |
| N6   | 27.8(19) | 16.8(18) | 27.5(19) | -2.8(17) | 2.5(17)  | -1.0(15) |
| C7   | 27(2)   | 17(2)   | 26(2)   | -1(2)  | -5(2)   | 2.7(17) |
| C8   | 41(3)   | 27(2)   | 31(3)   | -2(2)  | -6(2)   | -2(2)  |
| C9   | 36(3)   | 34(3)   | 37(3)   | -3(2)  | -9(2)   | 4(2)   |
| C10  | 39(3)   | 29(3)   | 38(3)   | -3(2)  | -8(2)   | 14(2) |
| C11  | 21(2)   | 21(2)   | 24(2)   | -5.9(19) | 0.4(19)  | -2.8(17) |
| C12  | 31(3)   | 21(2)   | 31(3)   | -1(2)  | -1(2)   | 5.6(18) |
| C13  | 33(3)   | 24(2)   | 30(2)   | 1(2)   | 6(2)    | -1.0(19) |
| C15  | 65(4)   | 32(3)   | 47(3)   | 12(3)  | -23(3)  | -20(3) |
| C16  | 43(3)   | 28(3)   | 35(3)   | 14(2)  | -4(2)   | 0(2)   |
| C17  | 47(3)   | 40(3)   | 42(3)   | 2(3)   | 15(3)   | 4(2)   |
| C18  | 49(3)   | 43(3)   | 39(3)   | 12(3)  | 1(3)    | 1(2)   |
| C19  | 45(3)   | 34(3)   | 36(3)   | 4(2)   | 4(3)    | -14(2) |
| C21  | 54(3)   | 41(3)   | 82(5)   | -37(3) | -18(3)  | 17(3) |
| F20  | 43(3)   | 52(4)   | 55(4)   | 12(3)  | 13(3)   | -4(3) |
| F24  | 49(4)   | 56(4)   | 53(4)   | 0(4)   | -13(3)  | 8(3)   |
| B25  | 23(7)   | 41(9)   | 40(9)   | 0      | 2(9)    | 0      |
| B4   | 51(5)   | 68(6)   | 37(5)   | 0      | 0       | 0      |
| F5   | 91(11)  | 86(6)   | 58(11)  | 16(5)  | -44(8)  | 11(6) |
| F2   | 86(12)  | 46(10)  | 50(5)   | -5(5)  | 5(5)    | -39(7) |
| F7   | 62(5)   | 83(13)  | 80(13)  | -27(8) | 7(5)    | 0(5)   |
| B2   | 45(4)   | 26(4)   | 34(4)   | 0      | 6(5)    | 0      |
| F1   | 81(3)   | 78(3)   | 76(3)   | -25(2) | 15(2)   | 22(2) |
| F3   | 82(2)   | 85(3)   | 68(3)   | -39(2) | -16(2)  | -7(2) |
| F4   | 77(9)   | 109(11) | 71(9)   | -32(8) | -27(7)  | -7(7) |

Table 4 Bond Lengths for C5

| Atom | Atom | Length/Å |
|------|------|----------|
| Ru1  | N3   | 2.012(3) |
| C7   | C13  | 1.498(6) |

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| Atom | Atom | Atom | Angle/°   | Atom | Atom | Atom | Angle/°   |
|------|------|------|----------|------|------|------|----------|
| N3   | Ru1  | N3   | 93.84(19)| C7   | N6   | Ru1  | 162.3(3) |
| N3   | Ru1  | N4   | 179.36(14)| N6   | C7   | C13  | 171.3(4) |
| N3   | Ru1  | N4   | 179.36(14)| N4   | C11  | C2   | 177.9(5) |
| N3   | Ru1  | N4   | 86.00(13) | N3   | C12  | C5   | 177.7(5) |
| N3   | Ru1  | N6   | 87.06(14) | C7   | C13  | C17  | 109.7(4) |
| N3   | Ru1  | N6   | 87.06(14) | C7   | C13  | C19  | 106.5(4) |
| N3   | Ru1  | N6   | 86.90(14) | C18  | C13  | C17  | 111.7(4) |
| N3   | Ru1  | N6   | 86.90(14) | C19  | C13  | C17  | 110.8(4) |
| N4   | Ru1  | N4   | 94.17(19) | C19  | C13  | C18  | 110.9(4) |
| N6   | Ru1  | N4   | 92.31(13) | F20  | B25  | F20  | 110.8(7) |
| N6   | Ru1  | N4   | 93.71(14) | F24  | B25  | F20  | 108.6(4) |
| N6   | Ru1  | N4   | 92.31(13) | F24  | B25  | F20  | 108.6(4) |
| N6   | Ru1  | N4   | 93.71(14) | F24  | B25  | F20  | 109.8(4) |
| N6   | Ru1  | N6   | 171.16(19)| F24  | B25  | F20  | 109.8(4) |
| C9   | C2   | C10  | 111.1(3) | F24  | B25  | F24  | 109.1(7) |
| C11  | C2   | C9   | 108.1(4) | F2   | B4   | F5   | 103.6(8) |
| C11  | C2   | C10  | 108.5(4) | F7   | B4   | F5   | 104.2(8) |
| C11  | C2   | C16  | 108.2(3) | F7   | B4   | F2   | 107.4(8) |
| C16  | C2   | C9   | 110.5(4) | F4   | B4   | F5   | 110.6(8) |
| C16  | C2   | C10  | 110.3(4) | F4   | B4   | F2   | 114.9(7) |

1/2-X, +Y, 1-Z; 2/2-X, +Y, 2-Z; 1/2-X, +Y, 1-Z

Table 5 Bond Angles for C5
Table 6 H-Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for C5

| Atom | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H8A  | -1160 | 3241  | 1423  | 50    |
| H8B  | -1088 | 3570  | 2412  | 50    |
| H8C  | -50   | 3534  | 1436  | 50    |
| H9A  | -1128 | 4669  | 1335  | 54    |
| H9B  | -96   | 4350  | 1409  | 54    |
| H9C  | -1128 | 4364  | 2397  | 54    |
| H10A | -1145 | 5228  | 2897  | 53    |
| H10B | -1149 | 4914  | 3936  | 53    |
| H10C | -125  | 5237  | 3896  | 53    |
| H15A | -1333 | 2729  | 3115  | 72    |
| H15B | -341  | 2727  | 4143  | 72    |
| H15C | -1276 | 3075  | 4049  | 72    |
| H16A | 534   | 5198  | 1286  | 53    |
| H16B | 1523  | 5207  | 2317  | 53    |
| H16C | 1531  | 4867  | 1360  | 53    |
| H17A | -1559 | 3702  | 9128  | 65    |
| H17B | -540  | 4026  | 9028  | 65    |
| H17C | -1555 | 3993  | 8027  | 65    |
| H18A | 131   | 3182  | 9266  | 65    |
| H18B | 1106  | 3155  | 8226  | 65    |
| H18C | 1136  | 3508  | 9133  | 65    |
| H19A | -1546 | 3136  | 7610  | 58    |
| H19B | -1502 | 3439  | 6542  | 58    |
| H19C | -490  | 3114  | 6649  | 58    |
| H21A | 366   | 2668  | 1514  | 88    |
| H21B | 1429  | 2978  | 1502  | 88    |
| H21C | 1359  | 2665  | 2540  | 88    |

^1/2-X,+Y,1-Z; ^21/2-X,+Y,2-Z; ^31/2-X,+Y,1-Z
Crystallographic data of C5’

The crystal structure was deposit at the Cambridge Crystallographic Data Centre.

CCDC: 1420658

Table 7 Atomic Occupancy for C5

| Atom | Occupancy | Atom | Occupancy | Atom | Occupancy |
|------|-----------|------|-----------|------|-----------|
| F20  | 0.5       | F24  | 0.5       | B25  | 0.5       |
| F5   | 0.25      | F2   | 0.25      | F7   | 0.25      |
| F4   | 0.25      |      |           |      |           |

Table 1 Crystal data and structure refinement for C5’

| Empirical formula | C_{32}H_{58}Cl_{10}N_{6}Ru_{3} |
|-------------------|-------------------------------|
| Formula weight    | 1184.55                       |
| Temperature/K     | 100.(2)                       |
| Crystal system    | monoclinic                    |
| Space group       | C2/m                          |
| a/Å               | 21.221(7)                     |
| b/Å               | 13.810(4)                     |
| c/Å               | 9.163(3)                      |
| α/°               | 90                            |
| β/°               | 103.056(7)                    |

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$\gamma^0$ 90
Volume/Å$^3$ 2615.9(14)
Z 2
$\rho_{\text{calc}}$/g/cm$^3$ 1.504
$\mu$/mm$^{-1}$ 1.393
F(000) 1188.0
Crystal size/mm$^3$ 0.200 $\times$ 0.130 $\times$ 0.100
Radiation MoK$\alpha$ ($\lambda = 0.71073$)
$2\theta$ range for data collection/° 3.54 to 57.52
Index ranges $-28 \leq h \leq 27$, $-18 \leq k \leq 17$, $-12 \leq l \leq 12$
Reflections collected 13063
Independent reflections 3453 [R$_{\text{int}} = 0.0554$, R$_{\text{sigma}} = 0.0542$]
Data/restraints/parameters 3453/0/139
Goodness-of-fit on F$^2$ 1.092
Final R indexes [$I > 2\sigma(I)$] $R_1 = 0.0656$, wR$2 = 0.2019$
Final R indexes [all data] $R_1 = 0.0867$, wR$2 = 0.2187$
Largest diff. peak/hole / e Å$^{-3}$ 3.59/3.02

Table 2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters (Å$^2 \times 10^3$) for C5$'$

| Atom | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| C1   | 5805 | 5000 | 7496 | 9.3   |
| C2   | 6261 | 5000 | 6486 | 9.4   |
| C3   | 6677 | 5910 | 6828 | 17.5  |
| C4   | 5873 | 5000 | 4859 | 27    |
| C5   | 4092 | 3272 | 8635 | 10.8  |
| C6   | 3685 | 2394 | 8227 | 12    |
| C7   | 3106 | 2498 | 8987 | 20.3  |
| C8   | 4093 | 1504 | 8823 | 16.2  |
| C9   | 3451 | 2358 | 6517 | 20.1  |
| C10  | 3186 | 0    | 2554 | 21    |
| C11  | 2815 | 0    | 604  | 26.3  |
| C12  | 2586 | 0    | 3623 | 34.8  |
| C13  | 4343 | 0    | 5770 | 14.6  |
| C14  | 5562 | 2030 | 6905 | 25.0  |
| N1   | 5484 | 5000 | 8333 | 7.8   |
| N2   | 4396 | 3930 | 9004 | 8.3   |
| Element | Zeta | Theta | Eta | Delta |
|---------|------|-------|-----|-------|
| Ru1     | 5000 | 5000  | 10000 | 4.0(2) |
| Ru2     | 5000 | 1178.8(7) | 5000 | 31.3(3) |

### Table 3 Anisotropic Displacement Parameters (Å²×10³) for C5'

| Atom | U₁₁  | U₂₂  | U₃₃  | U₁₂  | U₁₃  | U₂₃  |
|------|------|------|------|------|------|------|
| C1   | 5(3) | 13(4) | 10(3) | 0    | 1(3) | 0    |
| C2   | 4(3) | 17(4) | 8(3)  | 0    | 3(3) | 0    |
| C3   | 18(3) | 15(3) | 25(3) | -2(2) | 14(2) | 3(2) |
| C4   | 12(5) | 60(8) | 10(4) | 0    | 3(3) | 0    |
| C5   | 13(3) | 10(3) | 11(2) | 2(2) | 8(2) | -1(2) |
| C6   | 11(3) | 10(3) | 16(3) | -6(2) | 5(2) | -4(2) |
| C7   | 15(3) | 17(3) | 33(4) | -7(2) | 14(3) | -7(3) |
| C8   | 19(3) | 10(3) | 19(3) | -2(2) | 5(2) | -3(2) |
| C9   | 22(3) | 21(3) | 16(3) | -6(3) | 1(2) | -5(2) |
| C10  | 21(5) | 24(5) | 19(4) | 0    | 5(4) | 0    |
| Cl1  | 34.4(14) | 24.4(12) | 19.2(11) | 0    | 4.2(10) | 0    |
| Cl2  | 30.6(14) | 47.1(17) | 32.9(14) | 0    | 19.9(11) | 0    |
| Cl3  | 15.9(10) | 13.6(9) | 17.3(9) | 0    | 9.8(8) | 0    |
| Cl4  | 34.2(9) | 23.6(8) | 19.3(7) | -14.1(7) | 10.5(7) | -8.2(6) |
| N1   | 10(3) | 7(3)  | 7(3)  | 0    | 4(2) | 0    |
| N2   | 9(2)  | 7(2)  | 11(2) | 0.2(17) | 7.0(17) | 0.4(17) |
| Ru1  | 4.4(4) | 1.9(4) | 7.5(4) | 0    | 4.8(3) | 0    |
| Ru2  | 35.8(6) | 28.9(5) | 30.9(5) | 0    | 11.2(4) | 0    |

### Table 4 Bond Lengths for C5'

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| C1   | N1   | 1.135(11) | Cl3  | Ru2  | 2.3528(17) |
| C1   | C2   | 1.481(11) | Cl3  | Ru2² | 2.3528(17) |
| C2   | C3   | 1.527(8)  | Cl4  | Ru2  | 2.2167(17) |
| C2   | C3¹  | 1.527(8)  | N1   | Ru1  | 2.025(7)   |
| C2   | C4   | 1.531(12) | N2   | Ru1  | 2.032(5)   |
| C5   | N2   | 1.122(8)  | Ru1  | N1³  | 2.025(7)   |
| C5   | C6   | 1.487(8)  | Ru1  | N2³  | 2.032(5)   |
| C6   | C8   | 1.531(9)  | Ru1  | N2¹  | 2.032(5)   |
| C6   | C9   | 1.533(9)  | Ru1  | N2⁴  | 2.032(5)   |
| C6   | C7   | 1.551(8)  | Ru2  | Cl4  | 2.2167(17) |
| C10  | Cl2  | 1.773(10) | Ru2  | Cl3² | 2.3528(17) |
| C10  | Cl1  | 1.782(10) |      |      |           |
Table 5 Bond Angles for C5'

| Atom | Atom | Atom | Angle/°   | Atom | Atom | Atom | Angle/°   |
|------|------|------|-----------|------|------|------|-----------|
| N1   | C1   | C2   | 176.3(8)  | N1   | Ru1  | N2   | 92.14(18) |
| C1   | C2   | C3   | 107.5(4)  | N1   | Ru1  | N2   | 92.14(18) |
| C1   | C2   | C31  | 107.5(4)  | N1   | Ru1  | N2   | 87.86(18) |
| C3   | C2   | C31  | 110.8(7)  | N2   | Ru1  | N2   | 180.0     |
| C1   | C2   | C4   | 109.0(7)  | N1   | Ru1  | N2   | 87.86(18) |
| C3   | C2   | C4   | 111.0(5)  | N1   | Ru1  | N2   | 92.14(18) |
| C31  | C2   | C4   | 111.0(5)  | N2   | Ru1  | N2   | 93.3(3)   |
| N2   | C5   | C6   | 177.0(6)  | N2   | Ru1  | N2   | 86.7(3)   |
| C5   | C6   | C8   | 108.4(5)  | N1   | Ru1  | N2   | 87.86(18) |
| C5   | C6   | C9   | 108.6(5)  | N1   | Ru1  | N2   | 86.7(3)   |
| C8   | C6   | C9   | 111.4(5)  | N2   | Ru1  | N2   | 93.3(3)   |
| C5   | C6   | C7   | 106.6(5)  | N2   | Ru1  | N2   | 180.0     |
| C8   | C6   | C7   | 110.8(5)  | N2   | Ru1  | N2   | 180.0     |
| C9   | C6   | C7   | 110.7(5)  | Cl4  | Ru2  | Cl4  | 115.89(11)|
| Cl2  | C10  | Cl1  | 110.1(5)  | Cl4  | Ru2  | Cl3  | 110.70(7) |
| Ru2  | Cl3  | Ru21  | 87.56(8)  | Cl4  | Ru2  | Cl3  | 112.39(7) |
| C1   | N1   | Ru1  | 173.9(7)  | Cl4  | Ru2  | Cl3  | 110.70(7) |
| C5   | N2   | Ru1  | 170.4(5)  | Cl41  | Ru2 | Cl3  | 92.44(8)  |
| N11  | Ru1  | N1   | 180.0     | Cl32  | Ru2 | Cl3  | 92.44(8)  |
| N11  | Ru1  | N2   | 87.86(18) |

Table 6 H-Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for C5'

| Atom | x     | y     | z     | U(eq) |
|------|-------|-------|-------|-------|
| H3A  | 6405  | 6484  | 6546  | 26    |
| H3B  | 7015  | 5896  | 6255  | 26    |
| H3C  | 6877  | 5934  | 7901  | 26    |
| H4A  | 5680(50)| 4480(70)| 4760(110)| 41    |
| H4B  | 6190(80)| 5000  | 4480(170)| 41    |
| H4C  | 5680(50)| 5520(70)| 4760(110)| 41    |
| H7A  | 3263  | 2478  | 10077 | 30    |
| H7B  | 2801  | 1965  | 8668  | 30    |
| H7C  | 2887  | 3116  | 8695  | 30    |
| H8A  | 4474  | 1479  | 8386  | 24    |
| H8B  | 3834  | 916   | 8549  | 24    |
| H8C  | 4233  | 1546  | 9916  | 24    |
| H9A  | 3165  | 2910  | 6179  | 30    |
Crystallographic data of Ru1c

The crystal structure was deposited at the Cambridge Crystallographic Data Centre.

**CCDC**: 1420695

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### Table 1 Crystal data and structure refinement for Ru1c

| Empirical formula | C₂₂H₂₅Cl₃F₄O₂Ru |
|-------------------|-----------------|
| Formula weight    | 604.84          |
| Temperature/K     | 100.2           |
| Crystal system    | triclinic       |
| Space group       | P-1             |

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### Table 7 Atomic Occupancy for C5’

| Atom | Occupancy | Atom | Occupancy | Atom | Occupancy |
|------|-----------|------|-----------|------|-----------|
| H4A  | 0.5       | H4C  | 0.5       | H10A | 0.5       |
| H10B | 0.5       |      |           |      |           |
Table 2 Fract. Atom. Coord. (×10^4) and Equiv. Isotropic Displacement Parameters (Å^2×10^3) for Ru1c

| Atom | x      | y       | z        | U(eq)  |
|------|--------|---------|----------|--------|
| C1   | 2471.2(13) | 3133.3(13) | 2885.9(11) | 12.4(2) |
| C2   | 940.1(14) | 3210.2(15) | 2736.2(11) | 15.5(3) |
| C3   | 240.1(16) | 1709.3(17) | 2122.8(16) | 29.5(4) |
| C4   | 502.2(17) | 3744(2)  | 3816.1(14) | 34.8(4) |
| C5   | 569.9(16) | 4143.3(19) | 2059.4(15) | 27.4(3) |
| C6   | 3740.6(13) | 518.6(13)  | 2435.2(11) | 11.9(2) |
| C7   | 3330.9(14) | -136.0(14) | 3133.7(11) | 14.8(3) |
| C8   | 2513.7(15) | -1419.1(15) | 2789.7(12) | 17.4(3) |
| C9   | 2063.6(15) | -2141.7(15) | 1713.4(12) | 18.5(3) |
| C10  | 2471.8(14) | -1520.6(15) | 1001.1(11) | 16.5(3) |
| C11  | 3278.7(14) | -235.2(14)  | 1355.6(11) | 13.6(2) |
Table 3 Anisotropic Displacement Parameters (Å²×10³) for Ru1c

The Anisotropic displacement factor exponent takes the form: -2π²[h²a*²U₁₁+2hka*b*U₁₂+...].

| Atom | U₁₁   | U₂₂   | U₃₃   | U₁₂   | U₁₃   | U₂₃   |
|------|-------|-------|-------|-------|-------|-------|
| C1   | 11.5(6)| 9.2(6)| 14.5(6)| 0.9(5)| 2.8(5)| 1.0(5)|
| C2   | 9.1(6)| 17.3(6)| 17.4(6)| 2.1(5)| 2.9(5)| 1.6(5)|
| C3   | 13.2(7)| 20.3(8)| 48.6(11)| -1.5(6)| 2.3(7)| 4.5(7)|
| C4   | 15.2(7)| 64.0(13)| 20.8(8)| 12.2(8)| 7.5(6)| 3.4(8)|
| C5   | 16.3(7)| 31.9(9)| 39.5(9)| 10.0(6)| 4.7(6)| 18.0(7)|
| C6   | 9.6(6)| 11.2(6)| 15.1(6)| 2.3(5)| 2.1(5)| 4.2(5)|
| C7   | 15.1(6)| 14.7(6)| 14.0(6)| 1.4(5)| 1.5(5)| 4.5(5)|
| C8   | 17.3(7)| 15.9(7)| 22.5(7)| 1.6(5)| 5.0(5)| 10.7(6)|
| C9   | 16.2(7)| 11.8(6)| 24.9(7)| -0.6(5)| 1.5(5)| 4.0(5)|
| C10  | 16.0(6)| 14.4(6)| 14.7(6)| 2.8(5)| -0.3(5)| -0.3(5)|
| C11  | 13.6(6)| 14.0(6)| 14.1(6)| 3.7(5)| 4.0(5)| 4.6(5)|
| C12  | 8.2(5)| 11.4(6)| 14.6(6)| -0.1(4)| 2.4(4)| 4.0(5)|
| C13  | 9.8(6)| 11.6(6)| 13.2(6)| 0.7(5)| 1.5(5)| 1.8(5)|
| C14  | 9.4(6)| 14.8(6)| 12.3(6)| 0.7(5)| 0.7(5)| 4.3(5)|
Table 4 Bond Lengths for Ru1c

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| C1   | O1   | 1.2699(17)| C12  | C19  | 1.5126(18) |
| C1   | O2   | 1.2744(16)| C12  | Ru1  | 2.2576(13) |
| C1   | C2   | 1.5181(18)| C13  | C14  | 1.4330(18) |
| C1   | Ru1  | 2.5125(13)| C13  | Ru1  | 2.2291(13) |
| C2   | C4   | 1.523(2)  | C14  | C15  | 1.4127(18) |
| C2   | C5   | 1.527(2)  | C14  | Ru1  | 2.1701(13) |
| C2   | C3   | 1.537(2)  | C15  | C16  | 1.4284(19) |
| C6   | C7   | 1.3887(18)| C15  | C18  | 1.5037(19) |
| C6   | C11  | 1.3894(18)| C15  | Ru1  | 2.1907(13) |
| C6   | Ru1  | 2.0846(13)| C16  | C17  | 1.4107(19) |
| C7   | F1   | 1.3572(16)| C16  | Ru1  | 2.1549(13) |
| C7   | C8   | 1.3826(19)| C17  | Ru1  | 2.1484(12) |
| C8   | F2   | 1.3576(16)| C19  | C21  | 1.527(2)   |
| C8   | C9   | 1.378(2)  | C19  | C20  | 1.534(2)   |
| C9   | C10  | 1.382(2)  | C22  | C11  | 1.7557(16) |
| C10  | F3   | 1.3563(16)| C22  | C12  | 1.7635(16) |
| C10  | C11  | 1.3792(19)| C22  | C13  | 1.7651(16) |
Table 5 Bond Angles for Ru1c

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| O1   | C1   | O2   | 116.92(12) | C12  | C19  | C20  | 108.68(11) |
| O1   | C1   | C2   | 122.38(12)  | C21  | C19  | C20  | 110.78(12) |
| O2   | C1   | C2   | 120.48(12)  | C11  | C22  | C12  | 110.39(9)  |
| O1   | C1   | Ru1  | 59.10(7)    | C11  | C22  | C13  | 110.53(8)  |
| O2   | C1   | Ru1  | 58.25(7)    | C12  | C22  | C13  | 110.45(8)  |
| C2   | C1   | Ru1  | 168.97(9)   | C1   | O1   | Ru1  | 90.54(8)   |
| C1   | C2   | C4   | 110.90(12)  | C1   | O2   | Ru1  | 91.28(8)   |
| C1   | C2   | C5   | 110.10(12)  | C6   | Ru1  | O2   | 83.64(4)   |
| C4   | C2   | C5   | 110.49(14)  | C6   | Ru1  | C17  | 122.54(5)  |
| C1   | C2   | C3   | 105.32(11)  | O2   | Ru1  | C17  | 99.98(4)   |
| C4   | C2   | C3   | 110.56(14)  | C6   | Ru1  | C16  | 94.19(5)   |
| C5   | C2   | C3   | 109.34(13)  | O2   | Ru1  | C16  | 125.51(4)  |
| C7   | C6   | C11  | 114.34(12)  | C17  | Ru1  | C16  | 38.27(5)   |
| C7   | C6   | Ru1  | 122.56(10)  | C6   | Ru1  | O1   | 83.59(4)   |
| C11  | C6   | Ru1  | 123.02(10)  | O2   | Ru1  | O1   | 60.67(4)   |
| F1   | C7   | C8   | 117.11(12)  | C17  | Ru1  | O1   | 147.31(4)  |
| F1   | C7   | C6   | 119.77(12)  | C16  | Ru1  | O1   | 173.26(4)  |
| C8   | C7   | C6   | 123.11(13)  | C6   | Ru1  | C14  | 115.97(5)  |
| F2   | C8   | C9   | 119.23(13)  | O2   | Ru1  | C14  | 156.57(5)  |
| F2   | C8   | C7   | 119.41(13)  | C17  | Ru1  | C14  | 80.72(5)   |
| C9   | C8   | C7   | 121.35(13)  | C16  | Ru1  | C14  | 68.53(5)   |
| C8   | C9   | C10  | 116.67(13)  | O1   | Ru1  | C14  | 106.69(4)  |
| F3   | C10  | C11  | 119.51(13)  | C6   | Ru1  | C15  | 91.35(5)   |
| F3   | C10  | C9   | 119.13(13)  | O2   | Ru1  | C15  | 162.91(4)  |
| C11  | C10  | C9   | 121.36(13)  | C17  | Ru1  | C15  | 69.02(5)   |
| F4   | C11  | C10  | 117.13(12)  | C16  | Ru1  | C15  | 38.37(5)   |
| F4   | C11  | C6   | 119.72(12)  | O1   | Ru1  | C15  | 135.13(4)  |
| C10  | C11  | C6   | 123.15(13)  | C14  | Ru1  | C15  | 37.80(5)   |
| C13  | C12  | C17  | 117.36(12)  | C6   | Ru1  | C13  | 153.49(5)  |
| C13  | C12  | C19  | 122.31(12)  | O2   | Ru1  | C13  | 120.60(4)  |
| C17  | C12  | C19  | 120.29(11)  | C17  | Ru1  | C13  | 67.28(5)   |
| C13  | C12  | Ru1  | 70.66(7)    | C16  | Ru1  | C13  | 80.54(5)   |
C17  C12  Ru1  66.91(7)  O1  Ru1  C13  98.61(4)
C19  C12  Ru1  132.02(9)  C14  Ru1  C13  37.99(5)
C12  C13  C14  120.73(12)  C15  Ru1  C13  68.37(5)
C12  C13  Ru1  72.87(7)  C6  Ru1  C12  160.47(5)
C14  C13  Ru1  68.77(7)  O2  Ru1  C12  98.40(4)
C15  C14  C13  121.54(12)  C17  Ru1  C12  37.93(5)
C15  C14  Ru1  71.89(8)  C16  Ru1  C12  68.72(5)
C13  C14  Ru1  72.87(7)  O2  Ru1  C12  114.45(4)
C14  C15  C16  117.99(12)  C14  Ru1  C12  36.47(5)
C14  C15  C18  129.60(9)  C17  Ru1  C12  30.47(4)
C16  C15  C18  121.05(12)  C14  Ru1  C12  127.35(5)
C16  C15  Ru1  70.31(7)  C6  Ru1  C1  80.31(5)
C16  C15  Ru1  69.46(7)  O2  Ru1  C1  30.47(4)
C18  C15  Ru1  129.60(9)  C17  Ru1  C1  127.35(5)
C17  C16  C15  119.99(12)  C16  Ru1  C1  155.47(5)
C17  C16  Ru1  70.62(7)  O1  Ru1  C1  30.36(4)
C15  C16  Ru1  72.17(7)  O1  Ru1  C1  135.30(5)
C16  C17  C12  122.18(12)  C15  Ru1  C1  163.59(5)
C16  C17  Ru1  71.11(7)  C13  Ru1  C1  114.52(4)
C12  C17  Ru1  75.16(7)  C12  Ru1  C1  111.14(4)
C12  C19  C21  113.56(11)

Table 6 Hydrogen Bonds for Ru1c

| D   | H   | A       | d(D-H)/Å | d(H-A)/Å | d(D-A)/Å | D-H-A/° |
|-----|-----|---------|----------|----------|----------|---------|
| C22 | H22 | O2⁻     | 1.00     | 2.07     | 3.0583(18)| 170.7   |

Table 7 Torsion Angles for Ru1c

| A   | B   | C   | D   | Angle/°  | A   | B   | C   | D   | Angle/° |
|-----|-----|-----|-----|----------|-----|-----|-----|-----|----------|
| O1  | C1  | C2  | C4  | 21.11(19)| C19 | C12 | C13 | Ru1 | 128.13(12)|
| O2  | C1  | C2  | C4  | -164.48(14) | C12 | C13 | C14 | C15 | 2.30(19)  |
| Ru1 | C1  | C2  | C4  | 115.4(5)   | Ru1 | C13 | C14 | C15 | 55.54(11) |
| O1  | C1  | C2  | C5  | 143.71(14) | C12 | C13 | C14 | Ru1 | -53.24(11)|
| O2  | C1  | C2  | C5  | -41.88(18) | C13 | C14 | C15 | C16 | -3.92(19) |
| Ru1 | C1  | C2  | C5  | -122.0(5)  | Ru1 | C14 | C15 | C16 | 52.24(11) |
| O1  | C1  | C2  | C3  | -98.52(15) | C13 | C14 | C15 | C18 | 178.76(12)|
| O2  | C1  | C2  | C3  | 75.89(16)  | Ru1 | C14 | C15 | C18 | -125.08(12)|
| Ru1 | C1  | C2  | C3  | -4.2(6)    | C13 | C14 | C15 | Ru1 | -56.16(11)|
Table 8 H-Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Ru1c

| Atom | x    | y    | z    | U(eq) |
|------|------|------|------|-------|
| H3A  | 540  | 1379 | 1434 | 44    |
| H3B  | -759 | 1687 | 1994 | 44    |
| H3C  | 494  | 1105 | 2549 | 44    |
| H4A  | 730  | 3125 | 4234 | 52    |
| H4B  | -491 | 3765 | 3700 | 52    |
| H4C  | 986  | 4687 | 4208 | 52    |
| H5A  | 1042 | 5094 | 2438 | 41    |
| H5B  | -426 | 4150 | 1938 | 41    |
| H5C  | 856  | 3785 | 1368 | 41    |
| H9   | 1501 | -3023| 1473 | 22    |
| H13  | 6455 | 4976 | 4676 | 15    |
| H14  | 6690 | 2796 | 4923 | 15    |
Crystallographic data of Ru2c

The crystal structure was deposit at the Cambridge Crystallographic Data Centre.

CCDC: 1420659
Table 1 Crystal data and structure refinement for Ru2c

| Parameter                  | Value                          |
|----------------------------|--------------------------------|
| Empirical formula          | C31H46BF8N5Ru                  |
| Formula weight             | 752.61                         |
| Temperature/K              | 100.2                          |
| Crystal system             | triclinic                      |
| Space group                | P1                             |
| a/Å                        | 9.1210(14)                     |
| b/Å                        | 10.6390(16)                    |
| c/Å                        | 11.3056(18)                    |
| α/°                        | 67.036(4)                      |
| β/°                        | 73.952(4)                      |
| γ/°                        | 85.831(4)                      |
| Volume/Å³                  | 970.0(3)                       |
| Z                          | 1                              |
| \( \rho_{\text{calc}} \)/cm³ | 1.288                          |
| μ/mm⁻¹                     | 0.468                          |
| F(000)                     | 388.0                          |
| Crystal size/mm³           | 0.200 × 0.100 × 0.050          |
| Radiation                  | MoKα (λ = 0.71073)             |
| 2Θ range for data collection/° | 4.06 to 56.7                |
| Index ranges               | -12 ≤ h ≤ 12, -14 ≤ k ≤ 14, -15 ≤ l ≤ 15 |
| Reflections collected      | 17723                          |
| Independent reflections    | 8574 [R(int) = 0.0265, R(sigma) = 0.0396] |
| Data/restraints/parameters | 8574/3/431                     |
| Goodness-of-fit on F²      | 1.020                          |
| Final R indexes [I>=2σ(I)] | R₁ = 0.0293, wR₂ = 0.0679       |
| Final R indexes [all data] | R₁ = 0.0302, wR₂ = 0.0684       |
| Largest diff. peak/hole / e Å³ | 0.98/-0.45                |
| Flack parameter            | 0.16(3)                        |

Table 2 Fractional Atomic Coordinates (×10⁴) and Equivalent Isotropic Displacement Parameters (Å²×10³) for Ru2c. \( U_{eq} \) is defined as 1/3 of of the trace of the orthogonalised \( U_{ij} \) tensor.

| Atom | x    | y    | z    | \( U(eq) \) |
|------|------|------|------|--------------|
| B1   | 4619(6) | 3390(5) | 7079(5) | 29.6(10)     |
| C1   | 6094(7) | 9510(7) | 7642(6) | 17.7(13)     |
|   |   |   |   |
|---|---|---|---|
| C2 | 5118(7) | 9385(7) | 6836(7) | 21.4(15) |
| C3 | 5181(8) | 7915(8) | 6928(7) | 31.3(17) |
| C4 | 3471(7) | 9723(8) | 7405(7) | 31.1(16) |
| C5 | 5754(8) | 10383(8) | 5400(7) | 32.7(16) |
| C6 | 10124(7) | 11960(6) | 6283(6) | 14.4(12) |
| C7 | 5181(8) | 7915(8) | 6928(7) | 31.3(17) |
| C8 | 3471(7) | 9723(8) | 7405(7) | 31.1(16) |
| C9 | 5754(8) | 10383(8) | 5400(7) | 32.7(16) |
| C10 | 10124(7) | 11960(6) | 6283(6) | 14.4(12) |
| C11 | 5181(8) | 7915(8) | 6928(7) | 31.3(17) |
| C12 | 3471(7) | 9723(8) | 7405(7) | 31.1(16) |
| C13 | 5754(8) | 10383(8) | 5400(7) | 32.7(16) |
| C14 | 10124(7) | 11960(6) | 6283(6) | 14.4(12) |
| C15 | 5181(8) | 7915(8) | 6928(7) | 31.3(17) |
| C16 | 3471(7) | 9723(8) | 7405(7) | 31.1(16) |
| C17 | 5754(8) | 10383(8) | 5400(7) | 32.7(16) |
| C18 | 10124(7) | 11960(6) | 6283(6) | 14.4(12) |
| C19 | 5181(8) | 7915(8) | 6928(7) | 31.3(17) |
| C20 | 3471(7) | 9723(8) | 7405(7) | 31.1(16) |
| C21 | 5754(8) | 10383(8) | 5400(7) | 32.7(16) |
| C22 | 10124(7) | 11960(6) | 6283(6) | 14.4(12) |
| C23 | 5181(8) | 7915(8) | 6928(7) | 31.3(17) |
| C24 | 3471(7) | 9723(8) | 7405(7) | 31.1(16) |
| C25 | 5754(8) | 10383(8) | 5400(7) | 32.7(16) |
| C26 | 10124(7) | 11960(6) | 6283(6) | 14.4(12) |
| C27 | 5181(8) | 7915(8) | 6928(7) | 31.3(17) |
| C28 | 3471(7) | 9723(8) | 7405(7) | 31.1(16) |
| C29 | 5754(8) | 10383(8) | 5400(7) | 32.7(16) |
| C30 | 10124(7) | 11960(6) | 6283(6) | 14.4(12) |
| C31 | 5181(8) | 7915(8) | 6928(7) | 31.3(17) |
| F1 | 9506(2) | 8967(2) | 6442(2) | 23.3(5) |
| F2 | 3671(5) | 3334(4) | 6363(4) | 84.0(14) |
| F3 | 6087(5) | 3123(4) | 6438(4) | 71.9(12) |
| F4 | 11152(3) | 7026(3) | 5922(3) | 36.2(6) |
| F5 | 11152(3) | 7026(3) | 5922(3) | 36.2(6) |
| F6 | 11152(3) | 7026(3) | 5922(3) | 36.2(6) |
| F7 | 11152(3) | 7026(3) | 5922(3) | 36.2(6) |
| F8 | 11152(3) | 7026(3) | 5922(3) | 36.2(6) |
| N1 | 6905(6) | 9557(5) | 8223(5) | 16.0(11) |
| N2 | 9634(5) | 11128(6) | 7320(5) | 16.6(12) |
Table 3 Anisotropic Displacement Parameters (Å²×10³) for Ru2c. The Anisotropic displacement factor exponent takes the form: \(-2\pi^2[U_{11}a^2+2hka*b*U_{12}+\ldots]\).

| Atom  | \(U_{11}\) | \(U_{12}\) | \(U_{13}\) | \(U_{22}\) | \(U_{23}\) | \(U_{33}\) |
|-------|-------------|-------------|-------------|-------------|-------------|-------------|
| B1    | 49(3)       | 20(3)       | 21(2)       | -1(2)       | -12(2)      | -6.4(19)    |
| C1    | 14(3)       | 20(3)       | 19(3)       | -2(2)       | -5(2)       | -7(3)       |
| C2    | 23(3)       | 22(4)       | 20(3)       | -2(3)       | -8(2)       | -6(3)       |
| C3    | 31(4)       | 37(5)       | 37(4)       | -1(3)       | -13(3)      | -22(4)      |
| C4    | 16(2)       | 36(4)       | 44(4)       | 0(2)        | -7(2)       | -19(3)      |
| C5    | 27(3)       | 47(4)       | 25(3)       | 0(2)        | -12(2)      | -11(3)      |
| C6    | 17(2)       | 9(2)        | 18(3)       | -2.3(18)    | -7.3(19)    | -4(2)       |
| C7    | 17(2)       | 16(3)       | 16(2)       | -0.5(18)    | -1.1(17)    | -1(2)       |
| C8    | 23(3)       | 29(3)       | 20(3)       | -1(2)       | -4(2)       | -9(2)       |
| C9    | 25(3)       | 42(4)       | 18(3)       | -4(2)       | -13(2)      | -5(3)       |
| C10   | 37(3)       | 13(3)       | 30(3)       | -2(2)       | -8(2)       | -3(2)       |
| C11   | 13.5(15)    | 23(2)       | 23.2(18)    | -1.3(14)    | -2.6(13)    | -11.2(17)   |
| C12   | 19.0(17)    | 21(2)       | 34(2)       | 0.2(14)     | -5.0(15)    | -16.4(18)   |
| C13   | 24(2)       | 34(3)       | 59(3)       | 5(2)        | -6(2)       | -30(3)      |
| C14   | 30(2)       | 20(2)       | 45(3)       | -2.0(17)    | -11.8(19)   | -8(2)       |
| C15   | 33(2)       | 37(3)       | 42(2)       | -0.1(19)    | -11.8(19)   | -25(2)      |
| C16   | 19(3)       | 13(3)       | 11(3)       | 1(2)        | 0(2)        | -3(2)       |
| C17   | 15(3)       | 33(4)       | 18(3)       | -3(2)       | -8(2)       | -11(3)      |
| C18   | 22(3)       | 30(4)       | 20(2)       | 3(2)        | -14(2)      | -4(2)       |
| C19   | 29(3)       | 46(4)       | 14(3)       | -10(2)      | -4(2)       | -2(3)       |
| C20   | 40(4)       | 27(4)       | 37(4)       | -2(3)       | -16(3)      | -18(3)      |
| C21   | 17(2)       | 24(3)       | 21(3)       | 6(2)        | -4(2)       | -10(3)      |
| C22   | 21(2)       | 19(3)       | 14(2)       | -1.1(19)    | -4.5(18)    | -3(2)       |
| C23   | 26(3)       | 49(4)       | 22(3)       | 10(3)       | 2(2)        | 0(3)        |
| C24   | 25(3)       | 42(5)       | 25(3)       | -2(3)       | -5(2)       | 1(3)        |
| C25   | 70(5)       | 29(4)       | 25(3)       | -7(3)       | -3(3)       | -7(3)       |
| C26   | 9(2)        | 15(3)       | 15(2)       | -1.4(17)    | -2.6(18)    | -5(2)       |
| C27   | 15.5(15)    | 17(2)       | 28.0(19)    | -4.1(13)    | -2.2(14)    | -11.1(16)   |
| C28   | 19.4(16)    | 22(2)       | 31(2)       | -4.6(14)    | 5.0(15)     | -15.6(18)   |
| C29   | 21.0(19)    | 20(2)       | 44(3)       | -0.4(17)    | 1.3(17)     | -14(2)      |
| C30   | 18.3(16)    | 13(2)       | 37(2)       | 2.1(14)     | -4.5(15)    | -3.8(17)    |
| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|------|------|----------|------|------|----------|
| B1   | F5   | 1.356(6) | C17  | C20  | 1.544(10) |
| B1   | F7   | 1.359(6) | C21  | N5   | 1.128(8)  |
| B1   | F8   | 1.383(6) | C21  | C22  | 1.488(9)  |
| B1   | F6   | 1.403(6) | C22  | C23  | 1.511(9)  |
| C1   | N1   | 1.131(8) | C22  | C24  | 1.526(9)  |
| C1   | C2   | 1.483(9) | C22  | C25  | 1.537(10) |
| C2   | C3   | 1.524(10)| C26  | C27  | 1.382(7)  |
| C2   | C5   | 1.525(10)| C26  | C31  | 1.400(7)  |
| C2   | C4   | 1.538(9) | C26  | Ru1  | 2.075(6)  |
| C6   | N2   | 1.147(8) | C27  | F1   | 1.368(4)  |
| C6   | C7   | 1.478(9) | C27  | C28  | 1.391(5)  |
| C7   | C10  | 1.532(9) | C28  | F2   | 1.358(5)  |
| C7   | C9   | 1.539(8) | C28  | C29  | 1.370(6)  |
| C7   | C8   | 1.552(8) | C29  | C30  | 1.382(6)  |
| C11  | N3   | 1.142(7) | C30  | F3   | 1.355(5)  |
| C11  | C12  | 1.482(5) | C30  | C31  | 1.385(5)  |
| C12  | C15  | 1.533(5) | C31  | F4   | 1.361(4)  |
| C12  | C14  | 1.534(6) | N1   | Ru1  | 2.009(5)  |
| C12  | C13  | 1.535(6) | N2   | Ru1  | 2.020(5)  |
| C16  | N4   | 1.142(8) | N3   | Ru1  | 2.105(6)  |

Table 4 Bond Lengths for Ru2c
| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|------|------|------|---------|------|------|------|---------|
| F5   | B1   | F7   | 114.1(4)| C23  | C22  | C25  | 111.7(6) |
| F5   | B1   | F8   | 108.6(4)| C24  | C22  | C25  | 108.6(6) |
| F7   | B1   | F8   | 111.4(4)| C27  | C26  | C31  | 112.4(5) |
| F5   | B1   | F6   | 107.2(4)| C27  | C26  | Ru1  | 124.4(4) |
| F7   | B1   | F6   | 107.7(4)| C31  | C26  | Ru1  | 123.2(4) |
| F8   | B1   | F6   | 107.6(4)| F1   | C27  | C26  | 120.5(4) |
| N1   | C1   | C2   | 175.6(7)| F1   | C27  | C28  | 114.9(3) |
| C1   | C2   | C3   | 107.3(5)| C26  | C27  | C28  | 124.6(4) |
| C1   | C2   | C5   | 108.2(6)| F2   | C28  | C29  | 119.7(4) |
| C3   | C2   | C5   | 111.0(6)| F2   | C28  | C27  | 118.9(4) |
| C1   | C2   | C4   | 109.3(5)| C29  | C28  | C27  | 121.5(4) |
| C3   | C2   | C4   | 110.5(6)| C29  | C28  | C30  | 116.0(4) |
| C5   | C2   | C4   | 110.4(6)| F3   | C30  | C29  | 119.3(4) |
| N2   | C6   | C7   | 175.3(6)| F3   | C30  | C31  | 119.0(4) |
| C6   | C7   | C10  | 108.0(5)| C29  | C30  | C31  | 121.6(4) |
| C6   | C7   | C9   | 107.5(5)| F4   | C31  | C30  | 115.2(3) |
| C10  | C7   | C9   | 111.7(6)| F4   | C31  | C26  | 120.9(4) |
| C6   | C7   | C8   | 108.5(5)| C30  | C31  | C26  | 123.9(4) |
| C10  | C7   | C8   | 110.5(5)| C1   | N1   | Ru1  | 174.9(6) |
| C9   | C7   | C8   | 110.5(5)| C6   | N2   | Ru1  | 171.7(5) |
| N3   | C11  | C12  | 173.4(4)| C11  | N3   | Ru1  | 165.7(5) |
| C11  | C12  | C15  | 106.9(3)| C16  | N4   | Ru1  | 174.7(5) |
| C11  | C12  | C14  | 107.5(3)| C21  | N5   | Ru1  | 174.7(6) |
| C15  | C12  | C14  | 110.2(3)| N1   | Ru1  | N5   | 91.0(2)  |
| C11  | C12  | C13  | 109.8(3)| N1   | Ru1  | N2   | 88.5(2)  |
| C15  | C12  | C13  | 111.8(3)| N5   | Ru1  | N2   | 178.0(3) |
| C14  | C12  | C13  | 110.5(4)| N1   | Ru1  | N4   | 178.9(3) |
| N4   | C16  | C17  | 176.5(7)| N5   | Ru1  | N4   | 88.5(2)  |
| C16  | C17  | C18  | 108.5(5)| N2   | Ru1  | N4   | 92.0(2)  |
| C16  | C17  | C19  | 106.4(5)| N1   | Ru1  | C26  | 90.5(2)  |
| C18  | C17  | C19  | 111.9(6)| N5   | Ru1  | C26  | 90.5(2)  |
| C16  | C17  | C20  | 108.0(5)| N2   | Ru1  | C26  | 91.4(2)  |
Table 6 Hydrogen Bonds for Ru2c

| D  | H   | A     | D-H/Å | D-H-A/° |
|----|-----|-------|-------|---------|
| C29| H29 | F81   | 0.95  | 2.42    | 3.254(5) | 145.8 |

Table 7 Torsion Angles for Ru2c

| A  | B   | C   | D   | Angle/° | A  | B   | C   | D   | Angle/° |
|----|-----|-----|-----|---------|----|-----|-----|-----|---------|
| C31| C26 | C27 | F1  | 180.0(3)| C28| C29 | C30 | F3  | 179.1(4) |
| Ru1| C26 | C27 | F1  | -3.0(6) | C28| C29 | C30 | C31 | -0.1(6)  |
| C31| C26 | C27 | C28 | -1.5(7) | F3 | C30 | C31 | F4  | 1.0(5)   |
| Ru1| C26 | C27 | C28 | 175.5(3)| C29| C30 | C31 | F4  | -179.7(3)|
| F1 | C27 | C28 | F2  | -1.5(5) | F3 | C30 | C31 | C26 | 179.9(4) |
| C26| C27 | C28 | F2  | 180.0(4)| C29| C30 | C31 | C26 | -0.8(6)  |
| F1 | C27 | C28 | C29 | 179.3(3)| C27| C26 | C31 | F4  | -179.6(4)|
| C26| C27 | C28 | C29 | 0.7(6)  | Ru1| C26 | C31 | C30 | 1.5(7)   |
| F2 | C28 | C29 | C30 | -179.1(3)| C27| C26 | C31 | C30 | -175.5(3)|

Table 8 H-Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for Ru2c

| Atom | x   | y   | z   | U(eq) |
|------|-----|-----|-----|-------|
| H3A  | 6244| 7701| 6606| 47    |
| H3B  | 4576| 7805| 6379| 47    |
| H3C  | 4765| 7294| 7859| 47    |
| H4A  | 3094| 9100| 8340| 47    |
| H4B  | 2818| 9617| 6889| 47    |
| H4C  | 3451| 10667| 7348| 47    |
| H5A  | 5659| 11321| 5360| 49    |
| H5B  | 5180| 10258| 4835| 49    |
| H5C  | 6832| 10211| 5080| 49    |
| H8A  | 12987| 12683| 4744| 37    |
| H8B  | 12618| 13270| 3326| 37    |
|   |      |      |      |      |
|---|------|------|------|------|
| H8C | 12237 | 11696 | 4288 | 37   |
| H9A | 9560  | 12055 | 4064 | 43   |
| H9B | 9796  | 13672 | 3251 | 43   |
| H9C | 8488  | 13069 | 4627 | 43   |
| H10A| 9686  | 14607 | 5409 | 43   |
| H10B| 11089 | 15092 | 4093 | 43   |
| H10C| 11400 | 14371 | 5531 | 43   |
| H13A| 4708  | 13973 | 9659 | 54   |
| H13B| 5190  | 14916 | 10310| 54   |
| H13C| 4899  | 13305 | 11142| 54   |
| H14A| 8654  | 14656 | 7901 | 49   |
| H14B| 7644  | 15776 | 8338 | 49   |
| H14C| 6962  | 14902 | 7724 | 49   |
| H15A| 7551  | 13079 | 11494| 50   |
| H15B| 7889  | 14688 | 10685| 50   |
| H15C| 9009  | 13632 | 10231| 50   |
| H18A| 13267 | 8715  | 10997| 36   |
| H18B| 13977 | 9673  | 11510| 36   |
| H18C| 13798 | 10261 | 10023| 36   |
| H19A| 9991  | 9553  | 13200| 49   |
| H19B| 11615 | 9056  | 13456| 49   |
| H19C| 10730 | 8263  | 12897| 49   |
| H20A| 12268 | 12199 | 10391| 47   |
| H20B| 12418 | 11674 | 11884| 47   |
| H20C| 10767 | 11885 | 11616| 47   |
| H23A| 4616  | 7947  | 13941| 59   |
| H23B| 4140  | 6375  | 14853| 59   |
| H23C| 3783  | 7063  | 13431| 59   |
| H24A| 8178  | 6273  | 13632| 53   |
| H24B| 6822  | 5900  | 14977| 53   |
| H24C| 7337  | 7464  | 14061| 53   |
| H25A| 5228  | 5272  | 12676| 66   |
| H25B| 5568  | 4534  | 14100| 66   |
| H25C| 6950  | 5003  | 12769| 66   |
| H29 | 12104 | 5344  | 7885 | 36   |
Coordinates and energies of optimized structures

\[ \text{[Ru(OAc)\(_2\)(\eta^6\text{-benzene})]} \] (M1)

No Imaginary frequencies

\[ E = -784.206282 \text{ Hartree} \]
\[ G = -784.044713 \text{ Hartree} \]

C  
-1.26410200  
-1.81553100  
-0.70714500

C  
-1.26662500  
-1.80508800  
0.72656500

C  
-1.87047600  
-0.73350600  
1.41977600

H  
-0.69032000  
-2.57525100  
-1.21985900

H  
-0.69521100  
-2.55721100  
1.25288900

H  
-1.78707800  
-0.67290700  
2.49937500

C  
-1.86449900  
-0.75486700  
-1.41912300

C  
-2.49624800  
0.32458700  
-0.71410000

C  
-2.50128400  
0.33454600  
0.69720300

H  
-1.77743400  
-0.71060600  
-2.49916700

H  
-2.88473800  
1.17407400  
-1.26435000

H  
-2.89412400  
1.19102300  
1.23323800

Ru  
-0.41071000  
0.10460300  
-0.00169800

O  
0.40380500  
1.76904800  
1.09090000

C  
0.77319600  
2.32193700  
0.00267300

O  
0.39619300  
1.77789300  
-1.08731200

C  
1.64667400  
3.54234300  
0.00471400

H  
1.47185000  
4.13396900  
0.90522700

H  
2.69344900  
3.22043800  
0.00070900

H  
1.46691000  
4.14054600  
-0.89047100

O  
1.57500100  
-0.40278900  
-0.01163300

C  
2.06670900  
-1.61755400  
0.00029500

C  
3.59160500  
-1.62007200  
-0.00808000

H  
3.96059900  
-1.09530400  
-0.89445500

H  
3.96963700  
-1.08362900  
0.86749100

H  
3.96323600  
-2.64530900  
-0.00285800

O  
1.42309500  
-2.66705000  
0.01682700
C₆HF₅

No Imaginary frequencies

E = -728.3743723 Hartree
G = -728.348383 Hartree

[Ru(OAc)₂(η⁶-benzene)] + C₆HF₅

No Imaginary frequencies

E = -1512.591917 Hartree
G = -1512.386142 Hartree
{
[Ru(OAc)$_2$(η$^6$-benzene)]·C$_6$HF$_5$}‡ (TS-M1)

One imaginary frequency: i718.94

E = -1512.551581 Hartree
G = -1512.346057 Hartree

C -0.98795300 0.85139400 -2.43292700
C 0.12509100 -0.01347200 -2.39660900
\{[\text{Ru(OAc)}_2(\eta^6\text{benzene})]\cdot\text{C}_6\text{HF}_5\}^{\ddagger} (\text{TS-M1}_{\text{external}})

One imaginary frequency: \text{i67.48}

E = -1512.578595 Hartree

G = -1512.372052 Hartree

\begin{align*}
\text{C} & \quad -1.76956600 \quad -1.72818000 \quad 1.82189000 \\
\text{C} & \quad -2.41573500 \quad -0.69544900 \quad 1.10546600 \\
\text{C} & \quad -2.71997900 \quad -0.83895000 \quad -0.28485300 \\
\text{H} & \quad -1.46359900 \quad -1.57303400 \quad 2.84990400 \\
\text{H} & \quad -2.56816900 \quad 0.28315100 \quad 1.55053700 \\
\text{H} & \quad -3.08011500 \quad 0.04121200 \quad -0.83659400 \\
\text{C} & \quad -1.40923100 \quad -2.93547400 \quad 1.14041200 \\
\text{C} & \quad -1.72172600 \quad -3.10537800 \quad -0.23353100 \\
\text{C} & \quad -2.36355700 \quad -2.03809200 \quad -0.94343000 \\
\text{H} & \quad -0.82525100 \quad -3.69067300 \quad 1.65603400 \\
\text{H} & \quad -1.38663800 \quad -3.99040100 \quad -0.76251600 \\
\text{H} & \quad -2.48831800 \quad -2.11401000 \quad -2.01867600 \\
\text{Ru} & \quad -0.55069000 \quad -1.26273700 \quad 0.02292400 \\
\text{C} & \quad 0.10913900 \quad 1.02359700 \quad 0.16517700 \\
\text{C} & \quad 0.88342800 \quad 1.26804000 \quad -0.98594500 \\
\text{C} & \quad 0.80581000 \quad 1.05656900 \quad 1.39080900 \\
\text{C} & \quad 2.26012800 \quad 1.43616900 \quad -0.93770500 \\
\text{C} & \quad 2.17669300 \quad 1.24288200 \quad 1.48294900 \\
\text{C} & \quad 2.90062300 \quad 1.42626900 \quad 0.30447400 \\
\text{F} & \quad 0.29276000 \quad 1.31061100 \quad -2.18049400 \\
\text{F} & \quad 2.99369800 \quad 1.57705500 \quad -2.05156400 \\
\text{F} & \quad 0.13006000 \quad 0.89632900 \quad 2.53859400 \\
\text{F} & \quad 2.81351800 \quad 1.22833700 \quad 2.65850100 \\
\text{F} & \quad 4.22213000 \quad 1.57340200 \quad 0.35945100 \\
\text{H} & \quad -1.00985500 \quad 1.44768700 \quad 0.19959900 \\
\text{C} & \quad 1.76314800 \quad -1.80495500 \quad -0.84511200 \\
\text{O} & \quad 1.51410300 \quad -1.77452300 \quad 0.40721500 \\
\text{O} & \quad 0.78079700 \quad -1.58380800 \quad -1.62916900 \\
\text{C} & \quad 3.14253700 \quad -2.05411200 \quad -1.37903100 \\
\text{H} & \quad 3.10056000 \quad -2.80717700 \quad -2.17028900 
\end{align*}
{[Ru(OAc)(η₆-benzene)(C₆F₅)]·(AcOH)}

No Imaginary frequencies

E = -1512.589868 Hartree
G = -1512.382497 Hartree
[Ru(OAc)(C₆F₅)(η⁶-benzene)]

No Imaginary frequencies

E = -1283.481719 Hartree
G = -1283.328834 Hartree

C  -1.58302200  -2.07241800  -0.90492500
C  -1.59358200  -2.19801100   0.52225500
C  -2.52200500  -1.44538100   1.27936000
H  -0.81572300  -2.56510100  -1.48984400
H  -0.83507800  -2.78625300   1.02430300
H  -2.46736100  -1.45880300   2.36206800
C  -2.49996000  -1.19872600  -1.53530500
C  -3.51515900  -0.52707900  -0.76785500
C  -3.52840000  -0.65147200   0.62597000
H  -2.42860500  -1.02398300  -2.60287000
H  -4.20123800   0.15111900  -1.26301100
H  -4.22550100  -0.07199100   1.22096500
AcOH

No Imaginary frequencies

E = -229.0874096 Hartree
G = -229.052774 Hartree
[Ru(OAc)(MeCN)$_4$]$^+$ (M2)

No Imaginary frequencies

\[
E = -854.3873136 \text{ Hartree} \\
G = -854.207582 \text{ Hartree}
\]

\[
\begin{align*}
\text{Ru} & \quad -0.00065500 & \quad 0.07938600 & \quad 0.00001000 \\
\text{N} & \quad -2.02657600 & \quad 0.17044900 & \quad 0.00066200 \\
\text{C} & \quad -3.17632600 & \quad 0.29541600 & \quad 0.00085900 \\
\text{N} & \quad -0.02200000 & \quad -1.33775400 & \quad -1.44707800 \\
\text{C} & \quad -0.03420300 & \quad -2.08531500 & \quad -2.33128700 \\
\text{N} & \quad -0.02081800 & \quad -1.33768100 & \quad 1.44718400 \\
\text{C} & \quad -0.03200000 & \quad -2.08513700 & \quad 2.33149500 \\
\text{N} & \quad 2.02721500 & \quad 0.11191400 & \quad -0.00072600 \\
\text{C} & \quad 3.18051200 & \quad 0.19898800 & \quad -0.00104500 \\
\text{C} & \quad -4.62363600 & \quad 0.46386000 & \quad 0.00110500 \\
\text{H} & \quad -4.93921600 & \quad 0.97269000 & \quad 0.91642700 \\
\text{H} & \quad -4.92851600 & \quad 1.06359200 & \quad -0.86127700 \\
\text{H} & \quad -5.11697500 & \quad -0.51070800 & \quad -0.05183800 \\
\text{C} & \quad -0.04591500 & \quad -3.00766800 & \quad 3.46006800 \\
\text{H} & \quad -0.96460700 & \quad -3.60104200 & \quad 3.45038200 \\
\text{H} & \quad 0.81149400 & \quad -3.68440100 & \quad 3.40471700 \\
\text{H} & \quad 0.00430700 & \quad -2.44856400 & \quad 4.39902900 \\
\text{C} & \quad 4.63268900 & \quad 0.31879300 & \quad -0.00149100 \\
\text{H} & \quad 5.09295200 & \quad -0.67324400 & \quad 0.00154300 \\
\text{H} & \quad 4.96150800 & \quad 0.86006800 & \quad -0.89325200 \\
\text{H} & \quad 4.96158500 & \quad 0.86550500 & \quad 0.88692100 \\
\text{C} & \quad -0.04962300 & \quad -3.00805300 & \quad -3.45967400 \\
\text{H} & \quad -0.87624200 & \quad -3.71674300 & \quad -3.35663100 \\
\text{H} & \quad -0.17365200 & \quad -2.45236600 & \quad -4.39380300 \\
\text{H} & \quad 0.89001400 & \quad -3.56612300 & \quad -3.50248600 \\
\text{O} & \quad 0.02297300 & \quad 1.90228500 & \quad 1.09053400 \\
\text{C} & \quad 0.03502500 & \quad 2.57169900 & \quad -0.00001200 \\
\text{C} & \quad 0.09185800 & \quad 4.06944100 & \quad -0.00003800 \\
\text{H} & \quad -0.38460900 & \quad 4.46602300 & \quad -0.89818900 
\end{align*}
\]
{{[Ru(OAc)(MeCN)₄]^(+)(C₆H₅F₅)}}

No imaginary frequencies

E = -1582.741487 Hartree
G = -1582.509953 Hartree

Ru  -0.82683700  -0.00760400  0.38358700
O  -1.96681500  1.27451100  -0.76891800
C  -2.24485300  1.09322700  -2.03339000
O  -1.79949500  0.18364200  -2.74618700
C  -3.17753200  2.15150900  -2.59955000
H  -2.65295200  3.11170900  -2.63991900
H  -3.49139300  1.87369800  -3.60587500
H  -4.04911600  2.28406500  -1.95318400
C  0.88016400  -0.15070000  -1.57045400
C  1.58601900  -1.30261300  -1.19596200
C  1.51552100  1.08344600  -1.37185100
C  2.82581600  -1.23399400  -0.57298700
C  2.75507100  1.18016900  -0.74735700
C  3.41092900  0.01469000  -0.35250500
F  1.05238000  -2.51107700  -1.39906900
F  3.44260900  -2.34278000  -0.14154200
F  0.91998600  2.21257500  -1.75489600
F  3.30172900  2.37576200  -0.49243200
F  4.58006200  0.09255300  0.27320700
H  -0.04395500  -0.20059400  -2.16992100
N  -1.71625100  -1.62102700  -0.46985100
C  -2.23541700  -2.46106200  -1.06835500
N  -2.28413300  0.11256200  1.71395400
C  -3.17854200  0.23083900  2.43665800
N  0.30390700  -1.21089300  1.60557100
\begin{verbatim}
| C    | 0.96288600  -1.92047500  2.24123000 |
| N    | 0.01880500  1.68246000  1.14563900 |
| C    | 0.47515000  2.69069600  1.48058200 |
| C    | -2.88155500 -3.46961100 -1.89418500 |
| H    | -3.11456800 -3.02670400 -2.86744100 |
| H    | -2.21388000 -4.32340100 -2.03901600 |
| H    | -3.80632800 -3.81439000 -1.42376700 |
| C    | -4.31207900 0.38683700  3.33893700 |
| H    | -5.01749200 1.11235700  2.92362900 |
| H    | -4.82346200 -0.57111900 3.46906200 |
| H    | -3.97055400 0.74189400  4.31534500 |
| C    | 1.83500400  -2.81818400 2.98808500 |
| H    | 2.18935200  -2.33202000 3.90128000 |
| H    | 1.29709000  -3.73159600 3.25691100 |
| H    | 2.69446900  -3.08005400 2.36343900 |
| C    | 1.09014600  3.95837700  1.84902600 |
| H    | 1.30160000  3.98421400  2.92145100 |
| H    | 2.02595100  4.07258400  1.29378300 |
| H    | 0.42036400  4.78466200  1.59481500 |
\end{verbatim}

\begin{equation}
\{[\text{Ru(OAc)}(C_6HF_5)(MeCN)]_4\}^+ (\text{TS-M2})
\end{equation}

One imaginary frequency: \text{i492.18}

\[ E = -1582.736474 \text{ Hartree} \]
\[ G = -1582.510069 \text{ Hartree} \]

\begin{verbatim}
| Ru  | -1.04769800  0.02030400  0.21402400 |
| O   | -1.83252900  1.16042000 -1.35038200 |
| C   | -1.36600300  1.03600800 -2.53814000 |
| O   | -0.38540900  0.29920900 -2.83537700 |
| C   | -2.02566400  1.85538400 -3.62235200 |
| H   | -1.43254500  2.76220600 -3.78259600 |
| H   | -2.03447600  1.29697300 -4.56015200 |
| H   | -3.03682600  2.14532400 -3.33517000 |
\end{verbatim}
C   1.10659900 -0.05199500 -0.69269500
C   1.81655600 -1.24369700 -0.47093700
C   1.87850100  1.12102100 -0.62377400
C   3.16441000 -1.27745900 -0.13633800
C   3.22802900  1.13516700 -0.29614200
C   3.87327800 -0.07783500 -0.04995300
F   1.18791700 -2.43026200 -0.55029100
F   3.78790000 -2.43584600  0.10354900
F   1.30736100  2.30563800 -0.90062600
F   3.91179600  2.28090100 -0.22374100
F   5.16310200 -0.09173700  0.26603600
H   0.28439800  0.00111600 -1.63885700
N  -1.57159000 -1.66844600 -0.78979200
C  -1.85398500 -2.59571100 -1.41874700
N  -2.90026100  0.11340000  1.02732900
C  -3.97812800  0.20512900  1.43613700
N  -0.35088600 -1.06353100  1.79341100
C   0.04909100 -1.69564000  2.67687600
N  -0.58767500  1.76636400  1.14758100
C  -0.35534900  2.80107700  1.60700700
C  -2.17565000 -3.75867100 -2.23409700
H  -2.34277900 -3.44776200 -3.26939900
H  -1.34404400 -4.46874700 -2.20820700
H  -3.07729900 -4.25034500 -1.85879200
C  -5.34087800  0.32681800  1.93871300
H  -5.92891700  0.95753400  1.26583600
H  -5.80890600 -0.65976200  1.99921900
H  -5.33648100  0.77819700  2.93484000
C   0.56635500 -2.49900200  3.77795000
H   0.90416300 -1.85084100  4.59154300
H  -0.21374400 -3.16529100  4.15697900
H   1.41055200 -3.10329900  3.43314500
C  -0.03597800  4.11598200  2.14603200
H   0.27947300  4.03424000  3.18982100
H   0.77507000  4.56021300  1.56140500
H  -0.91233300  4.76760800  2.08811100
H   0.42036400  4.78466200  1.59481500
\[ \{[\text{Ru(OAc)}(\text{C}_6\text{HF}_5)(\text{MeCN})_4]\}^\dagger \] (TS-M2_{\text{external}})

One imaginary frequency: \( i65.92 \)

\( E = -1715.591343 \) Hartree

|      |         |         |         |
|------|---------|---------|---------|
| Ru   | -1.31255000 | -0.90940800 | -0.02837500 |
| N    | -0.32019100 | -1.73597800 | 1.55162700  |
| C    | 0.39097500  | -1.93582500 | 2.44150700  |
| N    | -0.09820100 | -1.87980900 | -1.35447800 |
| C    | 0.70916500  | -2.21828200 | -2.10984300 |
| N    | -2.72865800 | -2.27395500 | -0.09861900 |
| C    | -3.56018600 | -3.07687000 | -0.13951200 |
| N    | -2.01707000 | 0.20809800  | -1.57662800 |
| C    | -2.14474000 | 1.01515200  | -2.39434500 |
| N    | -2.33002000 | 0.25908200  | 1.29008500  |
| C    | -2.74168200 | 1.05031300  | 2.02497700  |
| C    | 1.50445100  | 1.13265000  | -0.09837300 |
| C    | 2.05223100  | 0.87050200  | 1.14485600  |
| C    | 2.25604800  | 0.68583700  | -1.16953900 |
| C    | 3.29882400  | 0.27634600  | 1.33375300  |
| C    | 3.50755700  | 0.08763000  | -1.05384300 |
| C    | 4.03777800  | -0.11881300 | 0.21960400  |
| F    | 1.34805400  | 1.12798000  | 2.28498500  |
| F    | 1.75099200  | 0.75547000  | -2.44072600 |
| F    | 3.76937600  | 0.00399000  | 2.57339200  |
| F    | 5.22473200  | -0.71660800 | 0.37079900  |
| F    | 4.17767200  | -0.36639600 | -2.13799000 |
| C    | 1.76330000  | -2.58752700 | -3.04254300 |
| H    | 2.53301400  | -1.80894800 | -3.02714700 |
| H    | 2.20679600  | -3.54381400 | -2.75200200 |
| H    | 1.35604000  | -2.67334600 | -4.05371300 |
| C    | -2.22280100 | 2.07444100  | -3.38646500 |
| H    | -2.00070200 | 1.68030100  | -4.38173900 |
| H    | -3.21947300 | 2.52389600  | -3.38993100 |
| H    | -1.47598800 | 2.82737000  | -3.11106100 |
No imaginary frequencies

E = -1582.758632 Hartree
G = -1582.526633 Hartree
[Ru(C₆F₅)(MeCN)₅]⁺ (P-M2)

No imaginary frequencies
E = -1486.43275 Hartree
G = -1486.217041 Hartree
C      0.82256200  -3.29499000  -3.26278200
H      1.71656500  -3.92467400  -3.27482000
H     -0.04758300  -3.91620600  -3.03071700
H      0.68723100  -2.85310600  -4.25394500
C      0.82850100  -3.29657000    3.25952700
H      0.69366700  -2.85550600    4.25112100
H     -0.04121300  -3.91855800    3.02791300
H     1.72320500  -3.92528600    3.27022700
C      5.81479200  0.00014800  -0.00327700
H      6.19130400  0.90395200  -0.48392600
H     6.18813300  -0.02897900    1.03080500
H     6.19175500  -0.87431000  -0.53451000

MeCN

No imaginary frequencies
E = -132.7556374 Hartree
G = -132.73318 Hartree
C      0.00000000  0.00000000  -1.18067200
H      0.00000000  1.02604600  -1.55948300
H     -0.88858100  -0.51302300  -1.55948300
H      0.88858100  -0.51302300  -1.55948300
C      0.00000000  0.00000000   0.28008700
N      0.00000000  0.00000000   1.44027900

C_{6}H_{3}F_{2}CF_{3} (1r)

No imaginary frequencies
E = -132.7556374 Hartree
G = -132.73318 Hartree
C      1.31406900  -1.61690500  -0.00716900
C      2.15033600  -0.50941400   0.00489400
C     -0.06812600  -1.43047700  -0.02840600
C      1.61769500   0.78095800  -0.00651200
C     -0.59803500  -0.13881100  -0.03892100
One imaginary frequency: \( \text{i}929.76 \)

\[ E = -1622.093791 \text{ Hartree} \]

\[ G = -1621.837613 \text{ Hartree} \]
{[Ru(OAc)(1r)(MeCN)]+}‡ (TS-M3-Ru(b))

One imaginary frequency: i1003.02

E = -1622.089229 Hartree
G = -1621.833131 Hartree
S295
{[Ru(OAc)(1r)(MeCN)₄]⁺⁺ (TS-M3-Ru(c))

One imaginary frequency: i880.00
E = -1622.0969 Hartree
G = -1621.842883 Hartree
| Element | x     | y     | z     |
|---------|-------|-------|-------|
| C       | -3.93251800 | -1.54989100 | -1.32258500 |
| N       | -0.98726700 | 0.90820700  | -1.81717800  |
| C       | -0.83345700 | 1.58690400  | -2.74193100  |
| N       | -0.18401000 | -1.76034600 | -1.02213700  |
| C       | 0.46213900  | -2.60878700 | -1.46930000  |
| C       | -3.59478600 | 3.09784000  | 2.02832400   |
| H       | -3.73172000 | 2.80108100  | 3.07210200   |
| H       | -3.00077700 | 4.01584300  | 1.99705000   |
| H       | -4.57372700 | 3.29007000  | 1.58071200   |
| C       | -5.15786700 | -2.18614100 | -1.78974800  |
| H       | -5.46245600 | -2.96501900 | -1.08482200  |
| H       | -5.95954400 | -1.44652600 | -1.86894800  |
| H       | -4.99623200 | -2.63988700 | -2.77158900  |
| C       | -0.62837800 | 2.45437700  | -3.89541000  |
| H       | -0.05659000 | 1.92853700  | -4.66527300  |
| H       | -1.59159400 | 2.75779500  | -4.31524500  |
| H       | -0.07601300 | 3.34908800  | -3.59360100  |
| C       | 1.33904500  | -3.64817000 | -1.99198600  |
| H       | 1.27250700  | -3.69048300 | -3.08257800  |
| H       | 2.36877600  | -3.41889400 | -1.70143000  |
| H       | 1.05776000  | -4.62119300 | -1.57964400  |
| H       | 1.70408900  | -1.32806000 | 0.86740300   |
| H       | 4.34836500  | 1.83855500  | -0.35567600  |
| C       | 4.27027300  | -0.85127200 | 0.22323600   |
| F       | 3.83845800  | -2.08811700 | -0.15382800  |
| F       | 4.83757500  | -0.99452000 | 1.43443200   |
| F       | 5.23720400  | -0.48399800 | -0.63919400  |

[\text{Pd(O}_2\text{COH})(\text{Ph})(\text{PMe}_3)]]

No imaginary frequencies

E = -1085.153536 Hartree

G = -1084.967793 Hartree

| Element | x     | y     | z     |
|---------|-------|-------|-------|
| Pd      | -0.60014800 | -0.19581700 | -0.00123600 |
| C       | 3.35131900  | -1.32807800 | 1.20670200  |
| C       | 2.03135300  | -0.86312100 | 1.20749800  |

S297
[Pd(O₂COH)(Ph)(1r)(PMe₃)]⁺ (TS-M3-Pd(a))

One imaginary frequency: i1051.79
E = -1852.871704 Hartree
G = -1852.614754 Hartree

Pd  0.79580200  -0.03654100  -0.20066200
C  -0.61357000  3.97887600  -0.72638900
C  -0.06605300  2.70704200  -0.92919900
C   0.02553600  1.78829100   0.12863300
C  -0.43844300  2.17564400  1.39503200
C  -0.98267700  3.44984100  1.59516200
C  -1.07005300  4.35674600  0.53772800
H   0.27450400  2.42905500  -1.92324400
H  -1.34117200  3.72915600  2.58322500
H  -1.49264000  5.34511000  0.69558100
H  -0.68300400  4.67222100  -1.56122000
H  -0.39376700  1.47973300  2.22734300
P   2.90536500  0.78126200  0.18837300
C   3.16549600  2.51832800  0.72837400
C   3.99440400  0.59613900  -1.28536600
C   3.74506400  -0.22722400  1.47975000
H   4.23121400  2.72035200  0.87424500
H   2.75860500  3.20045900  -0.02127600
H   2.62657900  2.69232500  1.66229300
H   5.03176800  0.85314400  -1.04707100
H   3.94003200  -0.44115000  -1.62359400
H   3.63802600  1.24495900  -2.08964400
H   4.79607600  0.06064500  1.58618200
H   3.23354800 -0.09312100  2.43636000
H   3.67432600 -1.27893600  1.19352000
O    1.82062000 -1.93619400  -0.62562100
C    1.17353700 -2.84513200  -1.19445500
O   -0.07466600 -2.83123700  -1.47186500
C   -2.04849900 -1.08285800   0.77255400
C   -1.33954700 -0.80564700  -0.42411100
C   -2.05895800 -0.13009700  -1.40534100
C   -3.38001400  0.28331100  -1.23395700
C   -4.04064500  0.01114600  -0.04671200
C   -3.36936400 -0.68232100  0.96502700
F   -1.47071000  0.15635500  -2.58609900
H   -0.56999700 -1.81944100  -0.96282800
F   -4.00363200  0.94190000  -2.22439600
H   -5.06865200  0.33608500  0.07188200
H   -3.88335400 -0.91390400  1.89045100
$\text{[Pd(O}_2\text{COH})(\text{Ph})(\text{1r})(\text{PMe}_3)]^{\ddagger}$ (TS-M3-Pd(b))

One imaginary frequency: i1054.85

E = -1852.863873 Hartree
G = -1852.607803 Hartree
[Pd(O$_2$COH)(Ph)(1r)(PMe$_3$)]$^+$ (TS-M3-Pd(c))

One imaginary frequency: i1011.22

E = -1852.865807 Hartree
G = -1852.610869 Hartree

Pd  -1.18562700 -0.27097000 -0.00398400
C   -0.39464200  3.78481400  1.16838400
C   -0.81871000  2.45107400  1.14753400
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| C    | -0.5925| 1.6455 | 0.02072|
| C    | 0.0637 | 2.2082 | -1.0846|
| C    | 0.4850 | 3.5427 | -1.0618|
| C    | 0.2560 | 4.3364 | 0.0633 |
| H    | -1.3122| 2.0386 | 0.0207 |
| H    | 0.9974 | 3.9574 | 0.0207 |
| H    | 0.5849 | 5.3716 | 0.0207 |
| H    | -0.5719| 4.3895 | 0.0207 |
| P    | -3.2757| 0.3758 | -0.7428|
| C    | -3.7815| -0.5812| 0.0207 |
| C    | -3.6144| 2.1251 | 0.0207 |
| C    | -4.5852| -0.0260| 0.0207 |
| H    | -4.8229| -0.3762| 0.0207 |
| H    | -3.1344| -0.3167| 0.0207 |
| H    | -3.6558| -1.6448| 0.0207 |
| H    | -4.6540| 2.2470 | 0.0207 |
| H    | -3.4129| 2.7690 | 0.0207 |
| H    | -2.9443| 2.4292 | 0.0207 |
| H    | -5.5831| 0.1854 | 0.0207 |
| H    | -4.5108| -1.0856| 0.0207 |
| H    | -4.4273| 0.5628 | 0.0207 |
| O    | -1.9937| -2.3232| 0.0207 |
| C    | -1.3860| -3.2248| 0.5516 |
| O    | -0.2479| -3.1139| 1.1305 |
| C    | 1.8146 | -0.9587| 0.4351 |
| C    | 0.8972 | -0.8241| 0.6301 |
| C    | 1.3750 | -0.1781| 1.7706 |
| C    | 2.6678 | 0.3345 | 1.8627 |
| C    | 3.5435 | 0.2081 | 0.7966 |
| C    | 3.1094 | -0.4456| 0.3635 |
| F    | 0.5670 | -0.0196| 2.8383 |
| H    | 0.1789 | -1.9994| 0.9069 |
| F    | 3.0592 | 0.9583 | 2.9876 |
| H    | 1.5034 | -1.4701| 1.3411 |
| H    | 4.5428 | 0.6201 | 0.8767 |
| C    | 4.0673 | -0.6476| 1.5041 |
cis-Ru(κ²-OAc)₂(MeCN)₂ (cis-M4)

No imaginary frequencies
E = -817.5128659 Hartree
G = -817.364393 Hartree
trans-Ru(κ²-OAc)₂(MeCN)₂ (trans-M4)

No imaginary frequencies

E = -817.5128646 Hartree
G = -817.368594 Hartree
\{[\text{Ru}(\kappa^2-OAc)_2(\text{MeCN})_2]\_C_6\text{HF}_5\}^\dagger \text{ (TS-M4 cis-fac)}

One imaginary frequency: i863.11

E = -1545.867826 Hartree
G = -1545.678837 Hartree

Ru

|        | -1.08042200 | -0.24291400 | -0.04149300 |
|--------|-------------|-------------|-------------|
O       | -1.88899000 | 0.64517900  | 1.68698700  |
C       | -1.36993800 | 1.71453000  | 2.13619500  |
O       | -0.35756600 | 2.28438800  | 1.62341300  |
C       | -1.98128500 | 2.32410100  | 3.37825000  |
H       | -2.03921600 | 3.40998300  | 3.27208800  |
H       | -2.96906800 | 1.90456700  | 3.57146600  |
H       | -1.32922900 | 2.11045000  | 4.23168600  |
C       | 1.04274200  | 0.56574200  | 0.22761700  |
C       | 1.72158400  | 0.94873100  | -0.93615700 |
C       | 1.83050100  | -0.05994800 | 1.20592300  |
C       | 3.06738400  | 0.67691300  | -1.15554300 |
C       | 3.17843900  | -0.35042100 | 1.02919200  |
C       | 3.79657900  | 0.02312100  | -0.16369500 |
F       | 1.07094600  | 1.59591500  | -1.92147800 |
F       | 3.67470800  | 1.03677400  | -2.29684900 |
F       | 1.27906500  | -0.39441900 | 2.38257200  |
F       | 3.89367400  | -0.96527100 | 1.98300000  |
F       | 5.09319800  | -0.23980500 | -0.35358100 |
H       | 0.20341400  | 1.39048000  | 0.78288600  |
N       | -1.68831900 | 1.33031200  | -1.08859900 |
C       | -2.01434700 | 2.24172400  | -1.72691500 |
N       | -2.83088200 | -1.16479500 | -0.28818800 |
C       | -3.83060400 | -1.74120300 | -0.39083100 |
C       | -2.36046100 | 3.39173700  | -2.55163100 |
H       | -2.83113300 | 4.17152400  | -1.94546200 |
H       | -1.45481800 | 3.80226600  | -3.00892500 |
H       | -3.05225500 | 3.09894900  | -3.34711500 |
\[
\text{\{[Ru(κ²-OAc)₃(MeCN)₂]C₆HF₅\}^+ (TS-M4 cis-mer)\}
\]

One imaginary frequency: i789.00

\[E = -1545.871638 \text{ Hartree}\]
\[G = -1545.68335 \text{ Hartree}\]
|       | Ru        | O          | C          | O          | C          | H          | H          | H          |
|-------|-----------|------------|------------|------------|------------|------------|------------|------------|
|       | 1.12045800| 0.28390100 | -0.12532500|            |            |            |            |            |
|       | 1.66551300| 1.05357600 | 1.75128400 |            |            |            |            |            |
|       | 1.12867700| 0.55240300 | 2.79062000 |            |            |            |            |            |
|       | 0.22785300| -0.33939800| 2.75793200 |            |            |            |            |            |
|       | 1.58215500| 1.07307000 | 4.13648000 |            |            |            |            |            |
|       | 0.77129600| 1.65778600 | 4.58278800 |            |            |            |            |            |
|       | 1.78716000| 0.23513800 | 4.80778400 |            |            |            |            |            |
|       | 2.46728300| 1.70111800 | 4.03235700 |            |            |            |            |            |
|       | -0.97680400| -0.35839900| 0.40501700 |            |            |            |            |            |

```
{[Ru(k^2-OAc)_2(MeCN)_2]_C_8HF_5}^{\ddagger} (TS-M4 trans-mer)

One imaginary frequency: i881.87
E = -1545.869318 Hartree
G = -1545.680318 Hartree
```
fac-[Ru(κ²-OAc)(C₆F₅)(MeCN)₃] (fac-P-M4)

No imaginary frequencies

E = -1449.557092 Hartree
G = -1449.380049 Hartree
Ru  1.08747100 -0.00006500 -0.03180900
N  3.18948000 -0.00004500 -0.20161700
C  4.33457400  0.00014800 -0.38162500
N  1.12165400 -1.41429700  1.36223100
C  1.08389400 -2.29463500  2.11625400
N  1.12164400  1.41396700  1.36242100
C  1.08385000  2.29418200  2.11658700
C  0.99539900  0.00003400 -0.01568300
C  1.75617600  1.17151800 -0.04331900
C  1.75622700 -1.17141700 -0.04346200
C  3.14951100  1.19814900 -0.09065200
C  3.14956300 -1.19799600 -0.09080200
C  3.85601800  0.00009300 -0.11255700
F  1.15051400  2.38822000 -0.02999100
F  1.15061100 -2.38814500 -0.03028000
F  3.81953600  2.36651500 -0.11078300
F  5.19988700  0.00013000 -0.15227500
F  3.81963300 -2.36646700 -0.11107900
H  5.77249000  0.00046300 -0.62377500
H  6.05307500  0.87161700 -1.22310600
H  6.31875700  0.03540400  0.32332800
H  6.06377400 -0.90521400 -1.16388500
C  0.97009700 -3.44113800  3.00825100
H  0.10536100 -4.04523100  2.71552900
H  1.86780800 -4.06426800  2.95196600
H  0.83529900 -3.11459600  4.04372100
C  0.97002300  3.44053400  3.00877200
H  1.86710600  4.06447700  2.95149100
H  0.10442200  4.04386500  2.71703800
H  0.83669100  3.11383900  4.04438400
O  1.00945500  1.09437800 -1.88459000
C  0.96055500  0.00003500 -2.53753100
O  1.00943600 -1.09436000 -1.88469100
C  0.80812600  0.00016600 -4.03517900
H  1.25402200 -0.89979200 -4.46323100
mer-[Ru(κ²-OAc)(C₆F₅)(MeCN)]₃ (mer-P-M4)

No imaginary frequencies
E = -1449.561357 Hartree
G = -1449.383707 Hartree

Ru 1.13133900 -0.13395500 0.10910400
N 1.01261900 -1.84379200 -0.93177500
C 0.94487700 -2.80814100 -1.56853300
N 0.86123200 -1.08346100 1.83443800
C 0.73562900 -1.64912600 2.83949000
N 1.30580700 1.61443100 1.07798600
C 1.41427300 2.64672500 1.59057200
C -0.91668000 0.12450600 -0.08352300
C -1.46881600 1.33489900 -0.51884200
C -1.86764000 -0.87490700 0.14418900
C -2.83278300 1.54778200 -0.71478700
C -3.24006000 -0.71201900 -0.03841400
C -3.73159500 0.51428700 -0.47173600
F -0.66953900 2.39823700 -0.78653500
F -1.48302000 -2.11267200 0.56656200
F -3.29200400 2.74236500 -1.13288900
F -5.05112400 0.69761600 -0.65140000
F -4.09448700 -1.72625900 0.20148100
C 0.83414900 -4.01903300 -2.37081600
H -0.05751600 -4.58147300 -2.07816600
H 0.75344100 -3.76069400 -3.43083600
H 1.71450400 -4.65300200 -2.22978600
C 0.55892400 -2.38019400 4.08766300
H -0.33854400 -3.00426700 4.03301600
H 1.42289600 -3.02323400 4.28262000
H 0.44767600 -1.68421900 4.92459100
fac-Ru(κ\textsuperscript{2}-OAc)(κ\textsuperscript{1}-OAc)(MeCN)\textsubscript{3} (fac-M5)

No imaginary frequencies
E = -950.2817677 Hartree
G = -950.095497 Hartree

Ru  -0.35095000  0.04598100  -0.00000100
N   -1.99123200  -1.10870900  0.00000100
C   -2.97199300  -1.72963200  -0.00000400
N   0.57041700  -1.02585900  1.40378200
C   1.21893500  -1.54583800  2.20937100
N   0.57042100  -1.02588000  -1.40376800
C   1.21895100  -1.54587600  -2.20933500
C   -4.21162900  -2.49683000  -0.00000200
H   -4.80581500  -2.25778700  -0.88740300
H   -3.99752300  -3.56988300  -0.00233500
H   -4.80371100  -2.26122400  0.88972200
C   2.12807000  -2.13286500  3.18322800
H   1.91743000  -1.74965300  4.18612700
H   2.03458200  -3.22266800  3.19655900
H   3.15401000  -1.86730200  2.90894400
C   2.12810900  -2.13292200  -3.18316000
H   1.91727600  -1.74999600  -4.18612700
H   3.15402000  -1.86707900  -2.90904400
**mer-Ru(κ²-OAc)(κ¹-OAc)(MeCN)_₃ (mer-M5)**

No imaginary frequencies

E = -950.27944 Hartree

G = -950.094136 Hartree
One imaginary frequency: i939.57

E = -1678.634087 Hartree
G = -1678.405054 Hartree
|   |   |   |   |
|---|---|---|---|
| C | -1.91248400 | -0.01980000 | -1.31390900 |
| C | -3.26799500 | 0.46942200 | 1.04616200 |
| C | -3.20075300 | -0.52041900 | -1.15476100 |
| C | -3.87771500 | -0.27578800 | 0.03834400 |
| F | -1.45156600 | 1.68306300 | 1.84697500 |
| F | -3.93143300 | 0.70844000 | 2.19095100 |
| F | -1.33179200 | -0.21177700 | -2.50389200 |
| F | -3.80752000 | -1.21153300 | -2.13118500 |
| F | -5.11896800 | -0.74162300 | 0.21218300 |
| H | -0.49571700 | 1.62917300 | -0.86922300 |
| N | 1.35162100 | 1.89527600 | 1.04965400 |
| C | 1.54175600 | 2.89748400 | 1.59998600 |
| N | 2.87512000 | -0.48430300 | 0.33613200 |
| C | 3.88840700 | -1.03228600 | 0.42476300 |
| N | 0.42977000 | -0.81636700 | 1.71309500 |
| C | 0.14423900 | -1.52509800 | 2.58117300 |
| C | 1.73737000 | 4.16981600 | 2.28281500 |
| H | 2.54377800 | 4.09214300 | 3.01798900 |
| H | 1.99480300 | 4.95012400 | 1.56031300 |
| H | 0.81750200 | 4.46127100 | 2.79885000 |
| C | 5.09131600 | -1.84708400 | 0.50711100 |
| H | 5.75916400 | -1.63093400 | -0.33177000 |
| H | 5.62629400 | -1.66143700 | 1.44264400 |
| H | 4.78921700 | -2.89854600 | 0.46675600 |
| C | -0.18766400 | -2.50800500 | 3.60230800 |
| H | 0.12384600 | -3.49538900 | 3.24710400 |
| H | 0.33083500 | -2.28458100 | 4.53904500 |
| H | -1.26518200 | -2.51812300 | 3.79024800 |
| O | 0.63168000 | -1.54212200 | -1.05411900 |
| C | 1.00337900 | -2.75405700 | -0.76156500 |
| O | 1.61385500 | -3.13192600 | 0.24601000 |
| C | 0.61011300 | -3.75392400 | -1.85204600 |
| H | 0.81122200 | -4.77459900 | -1.52170000 |
| H | -0.44724300 | -3.64289900 | -2.10893700 |
| H | 1.18360300 | -3.54751500 | -2.76198500 |
\{[\text{Ru}(\kappa^2\text{-OAc})(\kappa^1\text{-OAc})(\text{MeCN})_2]\text{C}_6\text{HF}_5}\}^\dagger \text{(TS-M5 mer-cis)}$

One imaginary frequency: i959.45

$E = -1678.635181$ Hartree

$G = -1678.406554$ Hartree

Ru  
-1.00964100 0.09706300 0.12538400

O  
-1.64078500 1.08672800 1.91069800

C  
-0.98498700 2.09108900 2.31797600

O  
0.08100900 2.52147700 1.76986300

C  
-1.48372900 2.81756400 3.54846200

H  
-0.80363300 2.61279100 4.38174900

H  
-1.47000700 3.89655400 3.37443800

H  
-2.48866000 2.48772900 3.81347600

C  
1.23651400 0.68671400 0.30736100

C  
1.87246400 1.02190800 -0.89513100

C  
2.02474700 -0.04448800 1.20537600

C  
3.15497400 0.59716900 -1.22566500

C  
3.30877500 -0.49217600 0.92027400

C  
3.87419400 -0.16937000 -0.31180500

F  
1.25300900 1.79181700 -1.80667700

F  
3.71328900 0.92178300 -2.40234800

F  
1.54258000 -0.33801300 2.43114700

F  
4.01281000 -1.21264500 1.80971100

F  
5.11121700 -0.58058600 -0.60836700

H  
0.51110600 1.59400600 0.93609100

N  
-1.43462700 1.73775200 -0.95894100

C  
-1.66110000 2.66586900 -1.61108600

N  
-2.87555100 -0.56202500 -0.13380400

C  
-3.91182100 -1.03852100 -0.32137000

N  
-0.64079600 -1.59319900 1.15611700

C  
-0.48190000 -2.61474900 1.67098700

C  
-1.88294700 3.83950300 -2.44431800

H  
-0.93087500 4.16735300 -2.87253900

H  
-2.57246700 3.60345300 -3.25994100

H  
-2.30308600 4.65674500 -1.85087500
$\{[\text{Ru}(\kappa^2-O\text{Ac})(\kappa^1-O\text{Ac})(\text{MeCN})_3] \cdot \text{C}_6\text{HF}_5\}^{\dagger}$ (TS-M5 mer-trans)

One imaginary frequency: i919.56

E = -1678.637241 Hartree
G = -1678.408426 Hartree
| Atom | X  | Y  | Z  |
|------|----|----|----|
| F    | -1.04459400 | -2.26126400 | 1.22232900 |
| F    | -3.51209800 | -2.94327000 | 0.42587300 |
| F    | -1.97372200 | 2.27569000  | 0.15642800 |
| F    | -4.43802900 | 1.56877100  | -0.65733900|
| F    | -5.22662400 | -1.04141600 | -0.51836200|
| H    | -0.61784100 | 0.50503600  | 1.62091900 |
| N    | 1.59577800  | -1.05803600 | 1.25807200 |
| C    | 2.11269800  | -1.82426000 | 1.95029600 |
| N    | 0.54970400  | -1.18661000 | -1.38733800|
| C    | 0.51274600  | -2.06563100 | -2.13828100|
| N    | 0.32917500  | 1.68782100  | -1.39378300|
| C    | 0.12337400  | 2.54286500  | -2.14451800|
| C    | 2.80235500  | -2.80780300 | 2.77140200 |
| H    | 3.19572600  | -2.33929900 | 3.67803200 |
| H    | 2.11741100  | -3.61084400 | 3.05840200 |
| H    | 3.63307600  | -3.23266300 | 2.19983300 |
| C    | 0.58987100  | -3.19032400 | -3.05943700|
| H    | 0.26215300  | -2.89489600 | -4.06023600|
| H    | 1.62967600  | -3.52887500 | -3.10876800|
| H    | -0.03890200 | -4.01558700 | -2.71293500|
| C    | -0.14784300 | 3.63954200  | -3.06390900|
| H    | -0.22365600 | 3.26813800  | -4.08991400|
| H    | -1.08839200 | 4.12927300  | -2.79461000|
| H    | 0.66038600  | 4.37507500  | -3.01535200|
| O    | 2.77233100  | 0.58134100  | -0.82578100|
| C    | 3.62325100  | -0.36414000 | -1.10928400|
| O    | 3.45083700  | -1.58261700 | -1.01637600|
| C    | 4.96009300  | 0.20232000  | -1.59793100|
| H    | 5.63868000  | -0.61046700 | -1.86221400|
| H    | 4.80296200  | 0.85071100  | -2.46550700|
| H    | 5.41117100  | 0.81880800  | -0.81399200|
cis-[Ru(κ^1-OAc)(C_6F_5)(MeCN)₄] (cis-P-M5)

No imaginary frequencies
E = -1582.322308 Hartree
G = -1582.102974 Hartree

Ru                0.82707800  -0.12486900  0.46131400
N                  1.03447700  -1.53822000  -0.95984000
C                 1.24138100   -2.20915900  -1.87678900
N                 2.95050200  -0.22663300   0.75976700
C                 4.06131600   -0.17298900   0.44098000
N                 0.40423100  -1.45748700   1.89524100
C                 0.13714800   -2.25026700   2.69861300
N                 0.67043500   1.40325600   1.76237200
C                 0.56420000   2.33769500   2.43614200
C                 -1.20276300  0.03545100  -0.01400300
C                 -1.87038900   1.25278600  -0.19213200
C                 -2.02255400  -1.08154200  -0.20433700
C                 -3.21687900   1.36194500  -0.54124400
C                 -3.37083200  -1.02434400  -0.55434100
C                 -3.97823100   0.21371100  -0.72812500
F                 -1.23107300   2.43501800  -0.01757500
F                 -1.52509100  -2.34111800  -0.04592900
F                 -3.79266400   2.57038700  -0.69239400
F                 -5.27784000   0.29980500  -1.06222000
F                 -4.09058300  -2.15195400  -0.72133000
C                 1.55315500   -2.95830800  -3.08445500
H                 0.64205400   -3.16361200  -3.65373900
H                 2.23212500  -2.35536900  -3.69562600
H                 2.03713600  -3.90797100  -2.83938900
C                 -0.23661400  -3.26468700   3.67608100
H                 -1.03528400  -3.89410500   3.27117900
H                 0.62052400  -3.89957300   3.92047200
H                 -0.59610100  -2.79500500   4.59664300
C                 0.38080800   3.54682200   3.22719100
H                 1.31522400   4.11285300   3.28294700
trans-[Ru(κ₁-OAc)(C₆F₅)(MeCN)₄] (trans-P-M5)

No imaginary frequencies

E = -1582.325198 Hartree
G = -1582.108401 Hartree

Ru  -0.77158200  -0.00001400  0.24737800
N  -0.62452200  1.42207800  1.66077400
C  -0.58000700  2.25288000  2.46474800
N  -0.62447300  -1.42221300  1.66067500
C  -0.57984500  -2.25311500  2.46453700
N  -1.05840300  -1.39627800  -1.17718500
C  -1.37832600  -2.12036300  -2.01793900
N  -1.05830800  1.39632900  -1.17711400
C  -1.37807800  2.12047900  -2.01787000
C  1.31099000  0.00000100  -0.05409000
C  2.07027000  1.16777800  -0.16792600
C  2.07028500  -1.16775800  -0.16801900
C  3.44896700  1.19686500  -0.37330700
C  3.44898100  -1.19681000  -0.37340000
C  4.14992800  0.00003600  -0.47751600
F  1.47322500  2.38927100  -0.07888500
### Chemical Structure

```
fac-Ru(κ²-OAc)(OC(CF₃)₃)(MeCN), (fac-M6)
```

No imaginary frequencies

E = -1848.002454 Hartree

G = -1847.820988 Hartree

### Molecular Coordinates

| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| Ru   | 1.44143700 | 0.08927300 | -0.11080900 |
| N    | 3.42097500 | -0.09822500 | -0.00686900 |

S320
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| C    | 4.57851600 | -0.14992600 | 0.05498500 |
| N    | 1.22647300 | -1.32063500 | -1.51285000 |
| C    | 0.93168000 | -2.03422800 | -2.37605000 |
| N    | 1.20968200 | -1.22953100 | 1.36476600 |
| C    | 1.04747300 | -1.92551200 | 2.27634800 |
| C    | 6.03364800 | -0.19940300 | -0.12708000 |
| H    | 6.38451700 | 0.27104100  | 1.05071200  |
| H    | 6.38271100 | -1.23624000 | 0.10814800  |
| H    | 6.47160800 | 0.33199700  | -0.72334400 |
| C    | 0.46454200 | -2.89456700 | -3.45427700 |
| H    | -0.62481100| -2.97400000 | -3.38831600 |
| H    | 0.73022600 | -2.46705400 | -4.42557900 |
| H    | 0.90229600 | -3.89365600 | -3.37449300 |
| C    | 0.74393400 | -2.75647200 | 3.43318700  |
| H    | 1.39139000 | -2.49532900 | 4.27544900  |
| H    | -0.29804000| -2.59167800 | 3.72413400  |
| H    | 0.88232000 | -3.81539500 | 3.19639200  |
| O    | 1.56690400 | 1.94179400  | 0.93031800  |
| C    | 1.61113700 | 2.56803100  | -0.18258900 |
| O    | 1.68729700 | 1.88094400  | -1.25447800 |
| C    | 1.53305600 | 4.06779900  | 0.22645200  |
| H    | 2.05905800 | 4.45171200  | -1.10282400 |
| H    | 0.47914500 | 4.35596800  | -0.30347200 |
| H    | 1.94168400 | 4.49865900  | 0.68971700  |
| O    | -0.56871400| 0.56737100  | -0.41479200 |
| C    | -1.79353900| 0.18979900  | -0.02384200 |
| C    | -2.05301500| 0.39167800  | 1.51916600  |
| C    | -2.13910600| -1.29802300 | -0.38681500 |
| C    | -2.79790600| 1.12386300  | -0.79732300 |
| F    | -1.56804900| -0.65006100 | 2.24684800  |
| F    | -1.44373400| 1.49677000  | 1.95801800  |
| F    | -3.36434000| 0.48943500  | 1.82734800  |
| F    | -1.20160500| -2.15446000| 0.07027700  |
| F    | -3.32326500| -1.70715800 | 0.11469500  |
| F    | -2.18979500| -1.46586200 | -1.72958600 |
| F    | -2.48436200| 1.18501400  | -2.09863000 |
| F    | -4.08379300| 0.71492000  | -0.71320700 |
mer-Ru(\kappa^2-OAc)(OC(CF_3)_3)(MeCN)_3 (mer-M6)

No imaginary frequencies
E = -1848.000765 Hartree
G = -1847.82105 Hartree
One imaginary frequency: i993.92

E = -2576.35387 Hartree
G = -2576.129488 Hartree

[[Ru(OAc)(OC(CF_3)_3)(MeCN)_3]·C_6F_5]^+ (TS-M6 fac-cis)
{[Ru(OAc)(OC(CF₃)₃)(MeCN)₃]·C₆F₅}⁺ (TS-M6 mer-cis)

One imaginary frequency: i960.28
E = -2576.354908 Hartree
G = -2576.131142 Hartree

Ru 0.34161100 -1.36264300 -0.05860200
O 1.67244700 -2.96587400 -0.44747600
C 2.81401800 -2.97587600 0.10540000
O 3.26229500 -2.03503500 0.83477000
C 3.70817400 -4.17225700 -0.13193800
H 4.55576900 -3.86485600 -0.75279800
H 4.11330300 -4.52542200 0.81993000
H 3.16273500 -4.97269200 -0.63235000
C 2.01067200 0.20647100 0.36662400
C 1.78495800 1.09814000 1.42512800
C 2.68944100 0.75910600 -0.72830800
C 2.13302600 2.44371000 1.37979500
C 3.04868500 2.09688100 -0.82352000
C 2.76022900 2.94602900 0.24284200
F 1.22230800 0.67574700 2.56922200
F 1.87754000 3.26143200 2.41080400
F 3.05752800 -0.03585400 -1.75757900
F 3.67918900 2.57668900 -1.90860100
F 3.10193400 4.23568700 0.18008400
H 2.48878600 -0.99166300 0.65470800
N 0.24063100 -1.86720000 1.89642000
C 0.13324200 -2.09047900 3.02496400
N -1.14788200 -2.64693200 -0.41725000
C -2.02968700 -3.37312000 -0.59888600
N 0.39566700 -0.87151800 -2.00482700
C 0.41822100 -0.57364600 -3.12094200
C 0.01812200 -2.30077400 4.46101100
H 0.49658900 -1.46890700 4.98651700
H -1.03519900 -2.34110700 4.75256000
H 0.50611300 -3.23452100 4.75430000
\[
\text{\{[Ru(OAc)(OC(F\textsubscript{3})\textsubscript{3})(MeCN)\textsubscript{3}]C\textsubscript{6}F\textsubscript{5}\}^+ (TS-M6 mer-trans)}
\]

One imaginary frequency: \(i740.42\)

\[
\begin{align*}
E &= -2576.356679 \text{ Hartree} \\
G &= -2576.132428 \text{ Hartree}
\end{align*}
\]

\[
\begin{align*}
\text{Ru} & \quad -0.28874700 \quad 0.23218700 \quad 0.16235000 \\
\text{O} & \quad 0.02632800 \quad 1.78657600 \quad 1.53586700 \\
\text{C} & \quad -0.73002400 \quad 1.88065000 \quad 2.55360100 \\
\text{O} & \quad -1.73073800 \quad 1.13041200 \quad 2.76935700 \\
\text{C} & \quad -0.42249500 \quad 2.97654400 \quad 3.55083000 \\
\text{H} & \quad -1.17461700 \quad 3.76639700 \quad 3.45277800 \\
\text{H} & \quad -0.49211700 \quad 2.58341100 \quad 4.56811200
\end{align*}
\]
| Atom | X       | Y       | Z       |
|------|---------|---------|---------|
| H    | 0.56734800 | 3.39639900 | 3.37068100 |
| C    | -2.58418000 | 0.05916000 | 0.52020700 |
| C    | -3.12623900 | -1.23373800 | 0.51158200 |
| C    | -3.41261200 | 1.04944000 | -0.02908700 |
| C    | -4.35028900 | -1.54585200 | -0.06985500 |
| C    | -3.62096300 | 3.58769100 | -3.00454600 |
| F    | -4.80801800 | -2.80747600 | -0.08797700 |
| F    | -3.02883200 | 2.33915100 | 0.01283100 |
| F    | -5.38589300 | 1.76541700 | -1.15262800 |
| F    | -6.29391400 | -0.80827400 | -1.19771100 |
| H    | -1.98551300 | 0.47720000 | 1.57083500 |
| N    | 0.11729400 | -1.07507200 | 1.63241200 |
| C    | 0.37147300 | -1.77210000 | 2.51776200 |
| N    | -0.44591000 | -1.21993900 | -1.21597900 |
| C    | -0.40838700 | -2.04281800 | -2.02902200 |
| N    | -0.58865500 | 1.64530600 | -1.26007500 |
| C    | -0.60887800 | 2.49613900 | -2.04073000 |
| C    | 0.74059200 | -2.63447300 | 3.62991700 |
| H    | 0.26579300 | -2.28463500 | 4.55111300 |
| H    | 0.42178300 | -3.66259300 | 3.43643400 |
| H    | 1.82691800 | -2.61503900 | 3.75809700 |
| C    | -0.26668800 | -3.08341400 | -3.03821700 |
| H    | -0.71814300 | -2.76788800 | -3.98308900 |
| H    | 0.79892200 | -3.27329800 | -3.19833900 |
| H    | -0.75005900 | -4.00697600 | -2.70704000 |
| C    | -0.62096300 | 3.58769100 | -3.00454600 |
| H    | -0.71342400 | 3.19655800 | -4.02163700 |
| H    | -1.46197000 | 4.25751500 | -2.80355500 |
| H    | 0.31173800 | 4.15395400 | -2.92841300 |
| O    | 1.68045600 | 0.54703300 | -0.50015700 |
| C    | 2.90522100 | 0.01623300 | -0.36019700 |
| C    | 3.00216400 | -1.49799900 | -0.76396500 |
| C    | 3.82505400 | 0.83621400 | -1.34321200 |
| C    | 3.50219400 | 0.17787700 | 1.09070400 |
| F    | 3.24458300 | 0.95078200 | -2.54925700 |
cis-Ru(C₆F₅)(OC(CF₃)₃)(MeCN)₄ (cis-P-M6)

No imaginary frequencies

E = -2480.041832 Hartree
G = -2479.829319 Hartree
trans-Ru(C₆F₅)(OC(CF₃)₃)(MeCN)$_4$ (trans-P-M6)

No imaginary frequencies
E = -2480.050539 Hartree
G = -2479.838312 Hartree

Ru  0.43676000  -0.10417600  0.14263800
N  0.36941400  1.34754300  1.53634900
C  0.19658200  2.17821300  2.32127600
N  0.54513600  -1.48537200  1.61355900
C  0.53114400  -2.28371500  2.44883100
N  0.29429100  -1.56323100  -1.24047400
C  0.04327100  -2.38675500  -2.01166800
N  0.29813000  1.27335300  -1.31428400
C  0.21601500  2.07820800  -2.13951500
C  2.51811100  -0.00886800  0.00496900
C  3.24047700  1.18769900  -0.03492600
C  3.32695900  -1.14852800  -0.04828300
C  4.62984400  1.26660700  -0.11959700
C  4.71823300  -1.12501500  -0.13253200
C  5.38109300  0.09727700  -0.16886500
F  2.59537400  2.38629700  0.01057700
F  2.76967800  -2.39018200  -0.01689900
F  5.25263800  2.46026000  -0.15300400
F  6.72152500  0.14799900  -0.25010000
F  5.42685100  -2.26922100  -0.17858300
C  0.50858500  -3.30267800  3.48958100
H  1.21479600  -4.10236900  3.24787500
H  0.78772900  -2.86686300  4.45316400
H  -0.49582600  -3.72775100  3.57323500
C  -0.35055400  -3.40989000  -2.96986700
H  -0.07424600  -4.40198200  -2.60173300
H  -1.43542500  -3.36735300  -3.10528200
H  0.13929900  -3.24293900  -3.93332500
C  0.07081600  3.10560100  -3.16061900
H  -0.95450400  3.48757900  -3.15558100
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