The Suzuki–Miyaura Coupling of Aryl Sulfones

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We describe conditions under which aryl sulfones act as electrophilic coupling partners in the palladium-catalyzed Suzuki–Miyaura cross-coupling (SMC) reaction. Sequential cross-coupling of arenes bearing sulfone, halide and nitro leaving groups permits rapid access to non-symmetric terphenyls and quaterphenyls starting from common functional groups. Mechanistic experiments and DFT calculations are consistent with oxidative addition into the sulfone C–S bond as the turnover-limiting step.

File list (3)

ESI-5a-Cross-Coupling.pdf (4.80 MiB)	view on ChemRxiv • download file
Sulfone V16.pdf (557.17 KiB)	view on ChemRxiv • download file
jmpc181205.cif (1.40 MiB)	view on ChemRxiv • download file

Supporting Information

The Suzuki–Miyaura Coupling of Aryl Sulfones

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1. General Information.

All cross-coupling reactions were performed in 10 mL sealed tubes under a nitrogen atmosphere. Purification of reaction products was carried out by flash column chromatography using Biotage® KP-Sil (40-63 μ m). Analytical thin layer chromatography (TLC) was performed on aluminum sheets pre-coated with silica gel 60 F254 (E. Merck), cut to size. Visualization was accomplished with UV light.

¹H NMR spectra were recorded on a Bruker Avance500 (500 MHz) spectrometer at ambient temperature unless otherwise noted and are reported in ppm using solvent as the internal standard (CDCl₃ at 7.26 ppm). Data are reported as: multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration and coupling constant(s) in Hz. **¹³C NMR** spectra were recorded on a Bruker Avance500 (125 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane, with the residual solvent resonance employed as the internal standard (CDCl₃ at 77.0 ppm). **¹⁹F NMR** spectra were recorded on a Bruker Avance400 (376 MHz) spectrometer.

High resolution mass spectrometry (HRMS) analysis was performed on instruments GCT 1er Waters (EI and CI) and MicroTOF-Q Bruker (ESI).

2. Materials:

Unless otherwise noted, all commercially available starting materials were purchased from *Sigma-Aldrich*, *TCI* or *fluorochem* and used without further purification.

3. Optimization table (Table S1)

Entry	Catalyst (Loading mol%)	Ligand	Base	additive	Solvent	Yield ^[a] (%)
1	Pd(acac) ₂ 5	RuPhos 20	K ₃ PO ₄	DMSO 10 μL	Dioxane	95
2	Pd(acac) ₂ 5	RuPhos 20	K ₂ PO ₄	H ₂ O 2 μL	Dioxane	38
3	Pd(acac) ₂ 5	XPhos 20	K ₂ PO ₄	-	Dioxane	55
4	Pd(acac) ₂ 5	RuPhos 20	K ₃ PO ₄	-	Dioxane	68
5	Pd(acac) ₂ 5	Dppp 10	K ₃ PO ₄	-	Dioxane	0
6	Pd(acac) ₂ 5	RuPhos 20	K ₃ PO ₄	-	EtOH	60
7	Pd(acac) ₂ 5	SIPr 20	K ₃ PO ₄	-	EtOH	51
8	Pd(acac) ₂ 5	SPhos 20	K ₃ PO ₄	-	EtOH	50
9	Pd(acac) ₂ 5	P(Cy) ₃ 40	K ₃ PO ₄	-	EtOH	0
10	Pd(acac) ₂ 5	RuPhos 20	K ₃ PO ₄	HMPA 10 μL	Dioxane	73
11	Pd(acac) ₂ 5	RuPhos 20	NaOEt	DMSO 10 μL	Dioxane	0
12	Pd(acac) ₂ 5	RuPhos 20	CSF	DMSO 10 μL	Dioxane	57
13	Pd(acac) ₂ 5	RuPhos 20	K ₂ CO ₃	DMSO 10 μL	Dioxane	79
14	Pd(acac) ₂ 5	RuPhos 20	K ₃ PO ₄	-	DMSO	0
16	Pd(acac) ₂ 5	RuPhos 20	K ₃ PO ₄	DMSO 10 μL	THF	52
18	Pd(acac) ₂ 5	RuPhos 20	K ₃ PO ₄	DMSO 10 μL	PhMe	83
19	Pd(acac) ₂ 5	RuPhos 20	K ₃ PO ₄	DMSO 10 μL	PhCF ₃	65
20	Pd(OAc) ₂ 5	RuPhos 20	K ₃ PO ₄	DMSO 10 μL	Dioxane	65
21	Pd ₂ (dba) ₃ 5	RuPhos 20	K ₃ PO ₄	DMSO 10 μL	Dioxane	0
22	Pd ₂ (dba) ₃ 5	^t BuDavePhos 20	K ₃ PO ₄	DMSO 10 μL	Dioxane	70
23	Pd(acac) ₂ 5	DavePhos 20	K ₃ PO ₄	DMSO 10 μL	Dioxane	81
24	Pd(acac) ₂ 5	BrettPhoss 20	K ₃ PO ₄	DMSO 10 μL	Dioxane	19
25	Pd(acac) ₂ 5	RuPhos 20	K ₃ PO ₄	DPESO 10 mg	Dioxane	5

4. Representative experimental procedure for cross-coupling reactions.

Boronic acid (0.30 mmol), Pd(acac)₂ (5 mol%), RuPhos (20 mol%) and K₃PO₄ (0.60 mmol) were weighed into a microwave vial, sealed, evacuated and backfilled with nitrogen 3 times. Then, 1.0 ml anhydrous dioxane, sulfone (0.20 mmol) and 10 μ L DMSO were added (solid sulfones were added prior to putting the tube under vacuum). The solutions were stirred and heated at 80°C for 16h. The reaction was determined to be complete by TLC. After the reaction was cooled to room temperature, the crude mixture was filtered through a bed of Celite and washed with dichloromethane. Then, the solution was concentrated *in vacuo* and purified by column chromatography.

5. Substrate Scope.

4-Methoxy-1,1'-biphenyl (1). Following the general procedure, 4-methoxyphenylboronic acid (46 mg, 0.30 mmol) and phenyl trifluoromethyl sulfone (30 μ L, 0.20 mmol) afforded **1** as a white solid (35 mg, 95%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.55 (t, *J* = 8.4 Hz, 4H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.86 (d, *J* = 0.9 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 159.1, 140.8, 133.8, 128.7, 128.2, 126.75, 126.66, 114.2, 55.4. Spectral data are in agreement with the literature.¹

4-Trifluoromethane-1,1'-biphenyl (2). Following the general procedure, 4-(trifluoromethyl)phenylboronic acid (42 mg, 0.30 mmol) and phenyl trifluoromethyl sulfone (30 μ L, 0.20 mmol) afforded **2** as a white solid (33 mg, 75%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (s, 4H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 (t, *J*

= 7.3 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.7, 139.8, 129.4 (q, 37.4 Hz) 129.0, 128.2, 127.6, 127.4, 127.3, 125.7 (q, 3.7 Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -62.4. Spectral data are in agreement with the literature.²

3-Nitro-1,1'-biphenyl (3). Following the general procedure, 3-nitrobenzeneboronic acid (50 mg, 0.30 mmol) and phenyl trifluoromethyl sulfone (30 μL , 0.20 mmol) afforded **3** as a white solid (27 mg, 68%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). ^1H NMR (400 MHz, CDCl_3) δ 8.37 (s, 1H), 8.12 (d, J = 9.2 Hz, 1H), 7.83 (d, J = 7.7 Hz, 1H), 7.54 (dd, J = 7.7, 2.6 Hz, 3H), 7.42 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.2 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 141.8, 137.6, 132.0, 128.6, 128.1, 127.5, 126.1, 121.0, 120.9. Spectral data are in agreement with the literature.³

1-Phenylnaphthalene (4). Following the general procedure, 2-naphthylboronic acid (52 mg, 0.30 mmol) and phenyl trifluoromethyl sulfone (30 μL , 0.20 mmol) afforded **4** as a white solid (40 mg, 98%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). ^1H NMR (400 MHz, CDCl_3) δ 7.99 – 7.86 (m, 3H), 7.62 – 7.39 (m, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 140.3, 133.9, 131.7, 130.1, 128.3(2C), 127.7, 127.3, 127.0, 126.1 (2C), 125.8, 125.4. Spectral data are in agreement with the literature.⁴

***N,N*-Dimethyl-[1,1'-biphenyl]-3-amine (5).** Following the general procedure, 3-(*N,N*-dimethylamino)phenylboronic acid (50 mg, 0.30 mmol) and phenyl trifluoromethyl sulfone (30 μL , 0.20 mmol) afforded **5** as a white solid (26 mg, 68%) after purification by automated

flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). **¹H NMR** (500 MHz, CDCl₃) δ 7.63 (d, *J* = 7.1 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.35 (dt, *J* = 10.6, 7.6 Hz, 2H), 7.00 – 6.93 (m, 2H), 6.78 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.03 (s, 6H). **¹³C NMR** (126 MHz, CDCl₃) δ 151.0, 142.3, 142.3, 129.5, 128.6, 127.4, 127.1, 115.9, 111.7, 111.6, 40.8. Spectral data are in agreement with the literature.⁵

2-Phenylthiophene (6). Following the general procedure, 3-thienylboronic acid (38 mg, 0.30 mmol) and phenyl trifluoromethyl sulfone (30 μL, 0.20 mmol) afforded **6** as a white solid (24 mg, 97%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). **¹H NMR** (400 MHz, CDCl₃) δ 7.51 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.35 (m, 1H), 7.33 – 7.28 (m, 4H), 7.20 (t, *J* = 7.4 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 142.4, 135.9, 128.8, 126.5, 126.4, 126.2, 126.1, 119.8. Spectral data are in agreement with the literature.⁶

[1,1'-Biphenyl]-4-carbaldehyde (7). Following the general procedure, 4-formylphenylboronic acid (45 mg, 0.30 mmol) and phenyl trifluoromethyl sulfone (30 μL, 0.20 mmol) afforded **7** as a white solid (10 mg, 28%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). **¹H NMR** (400 MHz, CDCl₃) δ 9.99 (s, 1H), 7.88 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 7.3 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 192.0, 147.2, 139.7, 135.2, 130.3, 129.0, 128.5, 127.7, 127.4. Spectral data are in agreement with the literature.⁷

***N,N*-Diphenyl-[1,1'-biphenyl]-4-amine (8).** Following the general procedure, 4-(diphenylamino)phenylboronic acid (87 mg, 0.30 mmol) and phenyl trifluoromethyl sulfone (30 μ L, 0.20 mmol) afforded **8** as a white solid (63 mg, 98%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). **¹H NMR** (400 MHz, CDCl₃) δ 7.47 (d, J = 7.7 Hz, 2H), 7.38 (d, J = 8.5 Hz, 2H), 7.31 (t, J = 7.7 Hz, 2H), 7.16 (q, J = 8.3 Hz, 5H), 7.04 (d, J = 7.8 Hz, 6H), 6.93 (t, J = 7.3 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 147.8, 147.2, 140.7, 135.2, 129.3, 128.8, 127.8, 126.9, 126.7, 124.5, 124.0, 123.0. Spectral data are in agreement with the literature.⁸

2-Phenylanthracene (9). Following the general procedure, 2-anthraceneboronic acid (67 mg, 0.30 mmol) and phenyl trifluoromethyl sulfone (30 μ L, 0.20 mmol) afforded **9** as a white solid (45 mg, 89%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). **¹H NMR** (400 MHz, CDCl₃) δ 8.47 (d, J = 14.2 Hz, 2H), 8.21 (s, 1H), 8.09 (d, J = 8.8 Hz, 1H), 8.02 (dd, J = 6.7, 2.9 Hz, 2H), 7.78 (t, J = 7.7 Hz, 3H), 7.56 – 7.44 (m, 4H), 7.42 (s, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 141.0, 137.8, 132.1, 131.9, 131.8, 130.9, 128.9, 128.8, 128.2, 128.2, 127.4, 127.4, 126.6, 126.0, 125.7, 125.5, 125.5, 125.4. Spectral data are in agreement with the literature.⁹

9-([1,1'-Biphenyl]-3-yl)-9H-carbazole (10). Following the general procedure, 3-(9H-carbazol-9-yl)phenylboronic acid (86 mg, 0.30 mmol) and phenyl trifluoromethyl sulfone (30

μL , 0.20 mmol) afforded **10** as a white solid (60 mg, 93%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). ^1H NMR (400 MHz, CDCl_3) δ 8.24 (d, $J = 7.7$ Hz, 2H), 7.88 (s, 1H), 7.73 (dd, $J = 12.9$, 5.1 Hz, 4H), 7.62 (t, $J = 6.8$ Hz, 1H), 7.58 – 7.42 (m, 7H), 7.38 (t, $J = 7.4$ Hz, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 143.2, 140.9, 140.2, 138.3, 130.3, 129.0, 127.9, 127.2, 126.2, 126.1, 125.9, 125.8, 123.5, 120.4, 120.0, 109.9. Spectral data are in agreement with the literature.¹⁰

3'-Nitro-[1,1'-biphenyl]-4-carbonitrile (11). Following the general procedure, 3-nitrobenzeneboronic acid (50 mg, 0.30 mmol) and 4-(trifluoromethyl)sulphonylbenzonitrile (47 mg, 0.20 mmol) afforded **11** as a white solid (41 mg, 91%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). ^1H NMR (400 MHz, CDCl_3) δ 8.45 (t, $J = 1.8$ Hz, 1H), 8.31 – 8.26 (m, 1H), 7.93 (d, $J = 7.7$ Hz, 1H), 7.84 – 7.77 (m, 2H), 7.77 – 7.72 (m, 2H), 7.68 (t, $J = 8.0$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 148.8, 143.0, 140.8, 133.1, 133.0, 130.2, 127.9, 123.3, 122.1, 118.4, 112.4. Spectral data are in agreement with the literature.¹¹

2'-Formyl-[1,1'-biphenyl]-4-carbonitrile (12). Following the general procedure, 2-formylphenylboronic acid (45 mg, 0.30 mmol) and 4-(trifluoromethyl)sulphonylbenzonitrile (47 mg, 0.20 mmol) afforded **12** as a white solid (10 mg, 26 %) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). ^1H NMR (400 MHz, CDCl_3) δ 9.94 (s, 1H), 8.05 (d, $J = 7.7$ Hz, 1H), 7.78 (d, $J = 8.2$ Hz, 2H), 7.69 (t, $J = 7.5$ Hz, 1H), 7.58 (t, $J = 7.6$ Hz, 1H), 7.51 (d, $J = 8.2$ Hz, 2H), 7.41 (d, $J = 7.6$ Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 191.2, 143.5, 142.8, 133.9, 133.6, 132.2, 130.7, 130.6, 128.9, 128.7, 118.4, 112.2. Spectral data are in agreement with the literature.¹²

4-(Thiophen-2-yl)benzonitrile (13). Following the general procedure, 3-thienylboronic acid (38 mg, 0.30 mmol) and 4-(trifluoromethyl)sulphonylbenzonitrile (47 mg, 0.20 mmol) afforded **13** as a white solid (24 mg, 65 %) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). **¹H NMR** (400 MHz, CDCl₃) δ 7.68 (s, 4H), 7.59 – 7.56 (m, 1H), 7.44 (dd, *J* = 4.9, 3.0 Hz, 1H), 7.40 (d, *J* = 5.0 Hz, 1H). **¹³C NMR** (101 MHz, CDCl₃) δ 140.4, 140.0, 132.7, 127.2, 126.9, 125.9, 122.6, 119.0, 110.5. Spectral data are in agreement with the literature.¹³

4'-Fluoro-[1,1'-biphenyl]-4-carbonitrile (14). Following the general procedure, 4-fluorophenylboronic acid (42 mg, 0.30 mmol) and 4-(trifluoromethyl)sulphonylbenzonitrile (47 mg, 0.20 mmol) afforded **14** as a yellow solid (32 mg, 82 %) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). **¹H NMR** (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.3 Hz, 2H), 7.64 (d, *J* = 8.3 Hz, 2H), 7.59 – 7.51 (m, 2H), 7.17 (t, *J* = 8.6 Hz, 2H). **¹³C NMR** (101 MHz, CDCl₃) δ 164.4, 162.0, 144.6, 135.3, 132.7, 129.0, 128.9, 127.6, 118.9, 116.3 (d, *J* = 21.7 Hz), 111.0. Spectral data are in agreement with the literature.¹⁴

4'-Methoxy-[1,1'-biphenyl]-4-carbonitrile (15). Following the general procedure, 4-methoxyphenylboronic acid (46 mg, 0.30 mmol) and 4-(trifluoromethyl)sulphonylbenzonitrile (47 mg, 0.20 mmol) afforded **15** as a yellow solid (35 mg, 84 %) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). **¹H NMR** (400 MHz, CDCl₃) δ 7.73 – 7.60 (m, 4H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.01 (d,

$J = 8.7$ Hz, 2H), 3.86 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.2, 145.2, 132.6, 131.5, 128.4, 127.1, 119.1, 114.6, 110.1, 55.4. Spectral data are in agreement with the literature.¹⁵

4'-(Trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile (16). Following the general procedure, 4-(trifluoromethyl) phenylboronic acid (42 mg, 0.3 mmol) and 4-(trifluoromethyl)sulphonylbenzonitrile (47 mg, 0.2 mmol) afforded **16** as a white solid (30 mg, 68 %) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). ^1H NMR (500 MHz, CDCl_3) δ 7.80 – 7.63 (m, 8H). ^{13}C NMR (126 MHz, CDCl_3) δ 144.1, 142.7, 132.8, 130.7 (q, $J = 32.7$ Hz), 127.9, 127.65, 126.10 (q, $J = 3.7$ Hz), 124.0 (d, $J = 272.2$ Hz), 118.6, 112.0. Spectral data are in agreement with the literature.¹⁶

3'-(Dimethylamino)-[1,1'-biphenyl]-4-carbonitrile (17). Following the general procedure, 3-(*N,N*-dimethylamino)phenylboronic acid (50 mg, 0.30 mmol) and 4-(trifluoromethyl)sulphonylbenzonitrile (47 mg, 0.20 mmol) afforded **17** as a yellow solid (43 mg, 90%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). ^1H NMR (400 MHz, CDCl_3) δ 8.09 (d, $J = 8.3$ Hz, 2H), 7.88 (d, $J = 8.3$ Hz, 2H), 7.22 (t, $J = 8.1$ Hz, 1H), 6.87 (d, $J = 6.9$ Hz, 2H), 6.67 (d, $J = 9.3$ Hz, 1H), 2.92 (s, 6H). Spectral data are in agreement with the literature.¹⁷

4'-Carbonitrile-*N,N*-diphenyl-[1,1'-biphenyl]-4-amine (18). Following the general procedure, 4-(diphenylamino)phenylboronic acid (87 mg, 0.30 mmol) and 4-(trifluoromethyl)sulphonylbenzonitrile (47 mg, 0.20 mmol) afforded **18** as a yellow solid (52 mg, 75%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.70 (q, J = 8.4 Hz, 4H), 7.50 (d, J = 8.6 Hz, 2H), 7.33 (t, J = 7.8 Hz, 4H), 7.18 (dd, J = 8.4, 2.2 Hz, 6H), 7.11 (t, J = 7.3 Hz, 2H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 148.6, 147.3, 145.1, 132.6, 132.1, 129.5, 127.9, 127.0, 125.0, 123.6, 123.0, 119.2, 110.1. Spectral data are in agreement with the literature.¹⁸

4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (19). Following the general procedure, 4-(trifluoromethyl) phenylboronic acid (42 mg, 0.30 mmol) and 1-methoxy-4-trifluoromethanesulfonyl-benzene (48 mg, 0.20 mmol) afforded **19** as a yellow solid (28 mg, 56%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.66 (s, 4H), 7.55 (d, J = 8.7 Hz, 2H), 7.01 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 159.8, 144.3, 132.2, 128.8, 128.4, 126.9, 125.8 (q, J = 3.5 Hz), 123.0, 114.4, 55.4. $^{19}\text{F NMR}$ (377 MHz, CDCl_3) δ -62.3. Spectral data are in agreement with the literature.¹⁹

1-(4-Methoxyphenyl)naphthalene (20). Following the general procedure, 2-naphthylboronic acid (52 mg, 0.30 mmol) and 1-methoxy-4-trifluoromethanesulfonyl-benzene (48 mg, 0.20 mmol) afforded **20** as a yellow solid (27 mg, 56%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.96 – 7.89 (m, 2H), 7.85 (d, J = 8.2 Hz, 1H), 7.51 (q, J = 8.9, 8.1 Hz, 2H), 7.46 – 7.40 (m, 4H), 7.05 (d, J = 8.6 Hz, 2H), 3.91 (s, 3H). $^{13}\text{C NMR}$ (101 MHz, CDCl_3)

δ 159.1, 140.0, 134.0, 133.3, 132.0, 131.3, 128.4, 127.5, 127.0, 126.2, 126.1, 125.8, 125.5, 113.9, 55.5. Spectral data are in agreement with the literature.²⁰

4'-Methoxy-*N,N*-diphenyl-[1,1'-biphenyl]-4-amine (22). Following the general procedure, 4-(diphenylamino)phenylboronic acid (87 mg 0.30 mmol) and 1-methoxy-4-trifluoromethanesulfonyl-benzene (48 mg, 0.20 mmol) afforded **22** as a yellow solid (46 mg, 73%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). Spectral data are in agreement with the literature. **¹H NMR** (400 MHz, CDCl₃) δ 7.42 (d, J = 8.7 Hz, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.21 – 7.14 (m, 4H), 7.05 (d, J = 7.6 Hz, 6H), 6.94 (t, J = 7.3 Hz, 2H), 6.88 (d, J = 8.7 Hz, 2H), 3.76 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 158.9, 147.9, 146.7, 135.1, 133.4, 129.4, 129.4, 127.8, 127.5, 124.4, 122.9, 114.3, 55.5. Spectral data are in agreement with the literature.⁸

2-Fluoro-4'-methoxy-1,1'-biphenyl (21). Following the general procedure, 4-methoxyphenylboronic acid (46 mg, 0.30 mmol) and 1-fluoro-2-[(trifluoromethyl)sulfonyl]benzene (33 μ L, 0.20 mmol) afforded **21** as a white solid (34 mg, 84%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). **¹H NMR** (400 MHz, CDCl₃) δ 7.57 – 7.50 (m, 2H), 7.45 (td, J = 7.8, 1.8 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.25 – 7.13 (m, 2H), 7.05 – 6.98 (m, 2H), 3.89 (s, 3H). **¹³C NMR** (101 MHz, CDCl₃) δ 161.0, 159.3, 158.6, 130.6 (d, J = 3.6 Hz), 130.2 (d, J = 3.3 Hz), 129.0 – 128.01 (m, 2C), 124.3 (d, J = 3.7 Hz), 116.2 (d, J = 22.8), 114.0, 55.3. **¹⁹F NMR** (376 MHz, CDCl₃) δ -118.23. Spectral data are in agreement with the literature.²¹

2'-Fluoro-[1,1'-biphenyl]-2-carbaldehyde (23). Following the general procedure, 2-formylphenylboronic acid (45 mg, 0.30 mmol) and 1-fluoro-2-[(trifluoromethyl)sulfonyl]benzene (33 μ L, 0.20 mmol) afforded **23** as a white solid (24 mg, 60%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.75 (d, J = 3.0 Hz, 1H), 7.90 – 7.84 (m, 1H), 7.51 (td, J = 7.6, 1.3 Hz, 1H), 7.38 (t, J = 7.6 Hz, 1H), 7.30 – 7.23 (m, 2H), 7.17 (td, J = 7.5, 1.8 Hz, 1H), 7.12 – 7.08 (m, 1H), 7.02 (t, J = 9.0 Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 191.7 (d, J = 2.3 Hz), 159.6 (d, J = 246.7 Hz), 138.9, 133.9, 133.8, 132.0 (d, J = 2.9 Hz), 131.4 (d, J = 0.9 Hz), 130.4 (d, J = 8.1 Hz), 128.5, 127.7, 125.5 (d, J = 15.7 Hz), 124.44 (d, J = 3.8 Hz), 115.8 (d, J = 22.2 Hz). $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -115.6. Spectral data are in agreement with the literature.²²

2-Fluoro-3'-nitro-1,1'-biphenyl (24). Following the general procedure, 3-nitrobenzeneboronic acid (50 mg, 0.30 mmol) and 1-fluoro-2-[(trifluoromethyl)sulfonyl]benzene (33 μ L, 0.20 mmol) afforded **24** as a yellow solid (34 mg, 78%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (500 MHz, $\text{Chloroform-}d$) δ 8.39 (s, 1H), 8.24 – 8.15 (m, 1H), 7.90 – 7.83 (m, 1H), 7.59 (t, J = 8.0 Hz, 1H), 7.44 (td, J = 7.7, 1.7 Hz, 1H), 7.38 (tdd, J = 8.1, 5.1, 1.7 Hz, 1H), 7.28 – 7.21 (m, 1H), 7.21 – 7.15 (m, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.7, 158.7, 148.4, 137.4, 135.1 (d, J = 3.5 Hz), 130.5 (d, J = 2.8 Hz), 130.4 (d, J = 8.3 Hz), 129.4, 126.6 (d, J = 13.0 Hz), 124.4 (dd, J = 3.8 Hz), 122.6, 116.4 (d, J = 22.4 Hz). $^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -117.9. Spectral data are in agreement with the literature.²³

3',5'-Dimethyl-2-nitro-1,1'-biphenyl (25). Following the general procedure, 3,5-dimethylphenylboronic acid (45 mg, 0.30 mmol) and 3-nitro-phenyl trifluoromethyl sulfone (51 mg, 0.20 mmol) afforded **25** as a white solid (31 mg, 68%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.44 (t, $J = 1.9$ Hz, 1H), 8.18 (ddd, $J = 8.2, 2.2, 0.9$ Hz, 1H), 7.93 - 7.84 (m, 1H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.24 (s, 2H), 7.08 (s, 1H), 2.41 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 148.6, 143.1, 138.8, 138.62, 133.1, 130.2, 129.6, 125.0, 121.95, 121.86, 21.4. Spectral data are in agreement with the literature.²⁴

3-Nitro-3-(dimethylamino)-biphenyl (26). Following the general procedure, 3-(*N,N*-dimethylamino)phenylboronic acid (50 mg, 0.30 mmol) and 3-nitro-phenyl trifluoromethyl sulfone (51 mg, 0.20 mmol) afforded **26** as a white solid (26 mg, 54%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.46 – 8.43 (m, 1H), 8.20 – 8.16 (m, 1H), 7.93 (s, 1H), 7.59 (t, $J = 8.0$ Hz, 1H), 7.38 – 7.33 (m, 1H), 6.95 (d, $J = 7.5$ Hz, 1H), 6.91 – 6.88 (m, 1H), 6.80 (dd, $J = 8.2, 2.3$ Hz, 1H), 3.04 (s, 6H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 151.1, 148.6, 143.9, 139.7, 133.3, 129.8, 129.5, 122.1, 121.9, 115.5, 112.6, 111.0, 40.7. Spectral data are in agreement with the literature.²⁵

2-(4-Methoxyphenyl)pyridine (27). Following the general procedure, 4-methoxyphenylboronic acid (46 mg, 0.30 mmol) and 2-((trifluoromethyl)sulfonyl)pyridine (42 mg, 0.20 mmol) afforded **27** as a white solid (30 mg, 81%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.65 (s, 1H), 7.98 - 7.91 (m, 2H), 7.67 (s, 2H), 7.17 (ddd, $J = 7.2, 4.8, 1.3$ Hz, 1H), 7.02 - 6.97 (m, 2H), 3.86 (s, 3H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 160.4, 157.1, 149.5, 136.7, 132.0, 128.2, 121.4, 119.8, 114.1, 55.4. Spectral data are in agreement with the literature.²⁶

4-(Pyridin-2-yl)benzonitrile (28). Following the general procedure, 4-cyanobenzeneboronic acid (44 mg, 0.30 mmol) and 2-((trifluoromethyl)sulfonyl)pyridine (42 mg, 0.20 mmol) afforded **28** as a white solid (27 mg, 75%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.77 - 8.69 (m, 1H), 8.15 - 8.07 (m, 2H), 7.82 (td, $J = 7.8, 1.8$ Hz, 1H), 7.75 (s, 3H), 7.32 (ddd, $J = 7.3, 4.8, 1.1$ Hz, 1H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 155.2, 150.0, 143.5, 137.2, 132.6, 127.5, 123.4, 121.0, 118.8, 112.4. Spectral data are in agreement with the literature.²⁷

2-(4-Fluorophenyl)pyridine (29). Following the general procedure, 4-fluorophenylboronic acid (42 mg, 0.30 mmol) and 2-((trifluoromethyl)sulfonyl)pyridine (42 mg, 0.20 mmol) afforded **28** as a white solid (25 mg, 72%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.67 (m, 1H), 8.00 - 7.96 (m, 2H), 7.75 (td, $J = 7.9, 1.8$ Hz, 1H), 7.68 (d, $J = 8.0$ Hz, 1H), 7.23 (ddd, $J = 7.3, 4.8, 1.0$ Hz, 1H), 7.19 - 7.13 (m, 2H). $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 163.5 (d, $J = 248.4$ Hz), 156.4, 149.7, 136.8, 135.5 (d, $J = 3.1$ Hz), 122.0, 128.7, 120.2, 115.7 ($J = 21.6$ Hz). Spectral data are in agreement with the literature.²⁸

9-(3-(Pyridin-2-yl)phenyl)-9H-carbazole (30). Following the general procedure, 3-(9H-carbazol-9-yl)phenylboronic acid (86 mg, 0.30 mmol) and 2-((trifluoromethyl)sulfonyl)pyridine (42 mg, 0.20 mmol) afforded **30** as a white solid (45 mg, 70%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). $^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.67 (dt, $J = 4.9, 1.4$ Hz, 1H), 8.17 (t, $J = 1.9$ Hz, 1H), 8.12 (d, $J = 7.7$ Hz, 2H), 8.08 (dt, $J = 7.8, 1.3$ Hz, 1H), 7.74-7.70 (m, 2H),

7.67 (t, $J = 7.8$ Hz, 1H), 7.58 (ddd, $J = 7.8, 1.9, 1.0$ Hz, 1H), 7.43 (d, $J = 8.2$ Hz, 2H), 7.40 – 7.36 (m, 2H), 7.28–7.24 (m, 2H), 7.22 (ddd, $J = 6.6, 5.2, 2.5$ Hz, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 156.4, 149.9, 141.4, 140.9, 138.3, 137.0, 130.3, 127.6, 126.01, 125.98, 125.7, 123.4, 122.7, 120.7, 120.3, 120.0, 109.9. Spectral data are in agreement with the literature.²⁹

6. Sequential Cross-Coupling.

3'-Nitro-3-((trifluoromethyl)sulfonyl)-1,1'-biphenyl (1a). 3-Nitrophenylboronic acid (91 mg, 0.60 mmol), $\text{Pd}(\text{OAc})_2$ (1 mg, 1 mol%), XPhos (6 mg, 3 mol%) and K_3PO_4 (254 mg, 1.20 mmol) were weighed into a microwave vial, sealed and placed under vacuum for 15 min. Then the vial was filled with N_2 followed by the addition of 2.0 ml anhydrous THF and 3-chlorophenyl trifluoromethyl sulfone (116 mg, 0.40 mmol). The solutions were stirred at ambient temperature (roughly 22 °C) for 16 h. The reaction was determined to be complete by TLC. The reaction crude mixture was filtered through a bed of Celite and washed with dichloromethane. Then, the solution was concentrated *in vacuo* and purified by column chromatography over silica (using petroleum ether and dichloromethane as eluents) to afford **1a** as a colorless oil (87 mg, 62%). ^1H NMR (500 MHz, CDCl_3) δ 8.48 (t, $J = 1.9$ Hz, 1H), 8.34 – 8.30 (m, 1H), 8.28 – 8.24 (m, 1H), 8.15 – 8.07 (m, 2H), 7.97 – 7.94 (m, 1H), 7.86 (s, 1H), 7.71 (s, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 148.9, 141.0, 139.9, 135.1, 134.1, 133.1, 130.9, 130.5 (m), 129.1, 128.2, 127.0, 123.6, 122.2. ^{19}F NMR (471 MHz, CDCl_3) δ -78.0. ESI-MS for $\text{C}_{30}\text{H}_{20}\text{N}_2\text{O}_2^+$ (M) $^+$ calculated: 331.0126; found: 331.0121.

9-(3''-Nitro-[1,1':3',1''-terphenyl]-4-yl)-9*H*-carbazole (1b). After the standard procedure of our coupling reaction, 3-(9*H*-carbazol-9-yl)phenylboronic acid (86 mg, 0.30 mmol) and sulfone **28** (42 mg, 0.20 mmol) afforded **1b** as a colorless oil (30 mg, 81%) after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents). ¹H NMR (500 MHz, CDCl₃) δ 8.54 - 8.50 (m, 1H), 8.25 - 8.17 (m, 3H), 7.96 (d, *J* = 7.7 Hz, 1H), 7.90 - 7.85 (m, 2H), 7.76 (s, 3H), 7.64 (s, 4H), 7.50 (s, 2H), 7.45 (d, *J* = 7.1 Hz, 2H), 7.32 (d, *J* = 7.0 Hz, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 148.7, 142.6, 141.2, 140.9, 139.5, 138.4, 133.2, 130.5, 129.9, 127.4, 126.7, 126.3, 126.3, 126.1, 126.1, 125.9, 123.5, 122.3, 122.1, 120.4, 120.1, 109.8. ESI-HRMS for C₃₀H₂₀N₂O₂⁺ (M)⁺ calculated: 440.1525; found: 440.1519.

4'''-(9*H*-Carbazol-9-yl)-*N,N*-dimethyl-[1,1':3',1'':3'',1'''-quaterphenyl]-4-amine (1c). Following the reported reaction procedure³⁰ compound **1b** (50 mg, 0.11 mmol) reacted with 3-(*N,N*-dimethylamino)phenylboronic acid (28 mg, 0.17 mmol) and was purified by column chromatography over silica (with a mixture of petroleum ether and ethyl acetate) to afford **1c** as a yellow oil (20 mg, 34%). ¹H NMR (500 MHz, CDCl₃) δ 8.17 (d, *J* = 7.7 Hz, 2H), 7.93 - 7.83 (m, 3H), 7.79 - 7.75 (m, 1H), 7.72 - 7.64 (m, 3H), 7.63 - 7.55 (m, 4H), 7.51 (dd, *J* = 15.1, 7.8 Hz, 3H), 7.45 - 7.40 (m, 2H), 7.35 - 7.28 (m, 3H), 7.05 - 6.92 (m, 2H), 6.77 (d, *J* = 7.3 Hz, 1H), 3.01 (s, 6H). ¹³C NMR (126 MHz, CDCl₃) δ 151.0, 143.1, 142.2, 142.2, 141.3, 140.9, 140.7, 138.3, 130.3, 129.5, 129.4, 129.1, 126.8, 126.6, 126.4, 126.3, 126.2, 126.1, 126.0, 125.8, 123.4, 120.3, 120.0, 115.9, 111.8, 111.6, 109.8, 40.8. ESI-HRMS for C₃₈H₃₀N₂H⁺ (M+H)⁺ calculated: 515.2487; found: 515.2481.

4'-Methoxy-2-nitro-4-((trifluoromethyl)sulfonyl)-1,1'-biphenyl (2a).

4-Methoxyphenylboronic acid (91 mg, 0.60 mmol), Pd(OAc)₂ (1 mg, 1 mol%), XPhos (6 mg, 3 mol%) and K₃PO₄ (254 mg, 1.20 mmol) were weighed into a microwave vial, sealed and placed under vacuum for 15 min. Then the vial was filled with N₂ followed by the addition of 2.0 ml anhydrous THF and 1-chloro-2-nitro-4-((trifluoromethyl)sulfonyl)benzene (116 mg, 0.40 mmol). The solutions were stirred at ambient temperature for 16 h. The reaction was determined to be complete by TLC. After the reaction, the crude mixture was filtered through a bed of Celite and washed with dichloromethane. Then, the solution was concentrated *in vacuo* and purified by column chromatography over silica (using petroleum ether and dichloromethane as eluents) to afford **2a** as a colorless oil (87 mg, 62%). ¹H NMR (400 MHz, CDCl₃) δ 8.42 (d, *J* = 1.9 Hz, 1H), 8.21 (dd, *J* = 8.2, 1.9 Hz, 1H), 7.78 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.27 (m, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 161.1, 149.5, 143.83, 133.7, 133.4, 130.6 (q, *J* = 1.6 Hz), 129.3, 126.7, 126.6, 119.6 (q, 327 Hz), 114.9, 55.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -77.6. ESI-HRMS for C₁₄H₁₀F₃NO₅S⁺ (M)⁺ calculated:361.0232; found: 361.0226.

4''-Methoxy-3'-nitro-*N,N*-diphenyl-[1,1':4',1''-terphenyl]-4-amine (2b). Following the general procedure, 4-(diphenylamino)phenylboronic acid (44 mg, 0.15 mmol) and sulfone **2a** (35 mg, 0.1 mmol) afforded, after purification by automated flash column chromatography over silica (using petroleum ether and dichloromethane as eluents), **2b** as a yellow oil (35 mg, 75%). ¹H NMR (500 MHz, CDCl₃) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.77 (dd, *J* = 8.0, 1.9 Hz, 1H), 7.48 (dd, *J* = 14.8, 8.4 Hz, 3H), 7.33 – 7.26 (m, 6H), 7.20 – 7.11 (m, 6H), 7.08 (t, *J* = 7.4 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 159.7, 149.7, 148.3, 147.3, 140.6, 133.7, 132.3, 131.6, 129.8, 129.4, 129.3, 129.1, 127.7, 124.8, 123.5, 123.3, 121.8, 114.3, 55.3. ESI-HRMS for C₃₁H₂₄N₂O₃⁺ (M)⁺ calculated:472.1787; found:472.1762.

7. Isolation of palladium complex X1.

Pd-complex X1: A 25 mL flask was charged with (cod)Pd(CH₂SiMe₃)₂ (90 mg, 0.23 mmol), RuPhos (97 mg, 0.21 mmol), phenyl trifluoromethyl sulfone (34 μ L, 0.23 mmol) in dioxane (4 mL). The reaction mixture was stirred at 40 °C for 48 h inside the glovebox. The solvent was removed under reduced pressure and the residual brown solid was washed three times with 2.0 mL of hexane to remove unreacted ligand and phenyl trifluoromethyl sulfone. The residue was then dissolved in 4 mL CHCl₃ and was filtered through a bed of Celite. Removal of the CHCl₃ under reduced pressure gave the compound **X1** as a light brown solid. Recrystallization by slow diffusion of pentane into CHCl₃ in a 3:1 volume ratio at room temperature gave **X1** as light brown crystals (61 mg, 37%). ESI-HRMS for C₃₆H₄₈F₃O₂PPd⁺ (M)⁺ calculated: 649.2427; found: 649.2426. ¹H NMR (500 MHz, CDCl₃) δ 7.67 -7.54 (m, 2H), 7.47 -7.34 (m, 2H), 7.16 (d, *J* = 6.6 Hz, 2H), 7.00 - 6.79 (m, 4H), 6.66 (d, *J* = 8.6 Hz, 2H), 4.62 (hept, *J* = 6.0 Hz, 2H), 2.13 (q, *J* = 13.0, 11.4 Hz, 2H), 1.84 -1.54 (m, 12H), 1.41 (d, *J* = 6.0 Hz, 5H), 1.30 -1.06 (m, 7H), 1.04 (s, 6H), 0.84 - 0.70 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ 136.8, 136.5, 136.5, 130.5, 127.9, 127.2, 126.5, 126.4, 125.0, 107.3, 70.8, 34.2, 34.0, 28.1, 27.9, 27.1, 27.0, 26.8, 26.7, 26.0, 22.2, 21.9, 21.8, 21.5.

8. DFT Calculations

Calculated Gibbs energies for the oxidative addition of the sulfone to Pd(0)-RuPhos (kcal/mol).

	R=Ph	R=CF ₃
π -complex	-15.6	-18.4
TS	9.4	3.6
intermediate	-22.0	-16.9

DFT calculations were performed using ORCA 4.0.1.2.^a Gibbs energy corrections were determined using frequency analysis at the PBE/def2-SVP level. Structures were optimized using B3LYP/def2-TZVP^b with the D3 correction for dispersion with Becke-Johnson damping.^{c,d} The solvation energy was calculated using the SMD model for dioxane.^e

The optimized structure of the transition state corresponding to the oxidative addition of Ph-SO₂CF₃ to Pd(0)-RuPhos. Hydrogen atoms are removed for clarity.

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10. NMR Spectra.

¹H NMR of Compound 1 (CDCl₃, 400 MHz)

¹³C NMR of Compound 1 (CDCl₃, 101 MHz)

^1H NMR of Compound **2** (CDCl_3 , 400 MHz)

^{13}C NMR of Compound **2** (CDCl_3 , 101 MHz)

^{19}F NMR of compound **2** (376 MHz, CDCl_3)

¹H NMR of Compound **3** (CDCl₃, 400 MHz)

¹³C NMR of Compound **3** (CDCl₃, 101 MHz)

AS-CC-8.4.11.fid

¹H NMR of Compound 4 (CDCl₃, 400 MHz)

AS-CC-8.4.10.fid

¹³C NMR of Compound 4 (CDCl₃, 101 MHz)

¹H NMR of Compound **5** (CDCl₃, 500 MHz)

¹³C NMR of Compound **5** (CDCl₃, 101 MHz)

¹H NMR of Compound **6** (CDCl₃, 400 MHz)

¹³C NMR of Compound **6** (CDCl₃, 101 MHz)

^1H NMR of Compound **7** (CDCl_3 , 400 MHz)

^{13}C NMR of Compound **7** (CDCl_3 , 101 MHz)

¹H NMR of Compound **8** (CDCl₃, 400 MHz)

¹³C NMR of Compound **8** (CDCl₃, 101 MHz)

^1H NMR of Compound **9** (CDCl_3 , 400 MHz)

^{13}C NMR of Compound **9** (CDCl_3 , 101 MHz)

¹H NMR of Compound **10** (CDCl₃, 400 MHz)

¹³C NMR of Compound **10** (CDCl₃, 101 MHz)

^1H NMR of Compound **11** (CDCl_3 , 400 MHz)

^{13}C NMR of Compound **11** (CDCl_3 , 101 MHz)

¹H NMR of Compound **12** (CDCl₃, 400 MHz)

¹³C NMR of Compound **12** (CDCl₃, 101 MHz)

¹H NMR of Compound **13** (CDCl₃, 400 MHz)

¹³C NMR of Compound **13** (CDCl₃, 101 MHz)

¹H NMR of Compound **14** (CDCl₃, 400 MHz)

¹³C NMR of Compound **14** (CDCl₃, 101 MHz)

¹H NMR of Compound **15** (CDCl₃, 400 MHz)

¹³C NMR of Compound **15** (CDCl₃, 101 MHz)

^1H NMR of Compound **16** (CDCl_3 , 500 MHz)

^{13}C NMR of Compound **16** (CDCl_3 , 126 MHz)

^{19}F NMR of Compound **16** (CDCl_3 , 282 MHz)

PC-Scope5.2-F2.10.fid

¹H NMR of Compound **17** (CDCl₃, 400 MHz)

^1H NMR of Compound **18** (CDCl_3 , 400 MHz)

^{13}C NMR of Compound **19** (CDCl_3 , 100 MHz)

¹H NMR of Compound **19** (CDCl₃, 400 MHz)

¹³C NMR of Compound **19** (CDCl₃, 100 MHz)

¹⁹F NMR of Compound **19** (CDCl₃, 376 MHz)

¹H NMR of Compound **20** (CDCl₃, 400 MHz)

¹³C NMR of Compound **20** (CDCl₃, 100 MHz)

AS-15.2.10.fid

¹H NMR of Compound **22** (CDCl₃, 400 MHz)

AS-15.2.11.fid

¹³C NMR of Compound **22** (CDCl₃, 100 MHz)

^1H NMR of Compound **21** (CDCl_3 , 400 MHz)

^{13}C NMR of Compound **21** (CDCl_3 , 100 MHz)

^{19}F NMR of Compound **21** (CDCl_3 , 376 MHz)

¹H NMR of Compound **23** (CDCl₃, 400 MHz)

¹³C NMR of Compound **23** (CDCl₃, 100 MHz)

¹⁹F NMR of Compound **23** (CDCl₃, 282MHz)

^1H NMR of Compound **24** (CDCl_3 , 400 MHz)

^{13}C NMR of Compound **24** (CDCl_3 , 100 MHz)

^{19}F NMR of Compound **24** (CDCl_3 , 282 MHz)

^1H NMR of Compound **25** (CDCl_3 , 400 MHz)

^{13}C NMR of Compound **25** (CDCl_3 , 101 MHz)

¹H NMR of Compound **26** (CDCl₃, 500 MHz)

¹³C NMR of Compound **26** (CDCl₃, 126 MHz)

^1H NMR of Compound **27** (CDCl_3 , 500 MHz)

^{13}C NMR of Compound **27** (CDCl_3 , 126 MHz)

¹H NMR of Compound **28** (CDCl₃, 500 MHz)

¹³C NMR of Compound **28** (CDCl₃, 126 MHz)

^1H NMR of Compound **29** (CDCl_3 , 500 MHz)

^{13}C NMR of Compound **29** (CDCl_3 , 126 MHz)

¹H NMR of Compound **30** (CDCl₃, 500 MHz)

¹³C NMR of Compound **30** (CDCl₃, 126 MHz)

^1H NMR of Compound **2a** (CDCl_3 , 400 MHz)

^{13}C NMR of Compound **2a** (CDCl_3 , 126 MHz)

^{19}F NMR of Compound **2a** (376 MHz, CDCl_3).

¹H NMR of Compound **2b** (CDCl₃, 500 MHz)

¹³C NMR of Compound **2b** (CDCl₃, 126 MHz)

¹H NMR of Compound **Pd-Complex** (CDCl₃, 500 MHz)

11. Optimized Cartesian Coordinates

X=CF₃

Substrate

18

Coordinates from ORCA-job substrate

C	2.56194313637816	0.66398896705431	-3.59400527819646
C	2.97566568532260	-0.00885103476837	-2.45306601010302
C	3.03406109000061	0.68719109517507	-1.24867294583453
C	2.68954786131861	2.03306282990333	-1.16158360183024
C	2.27436324897919	2.69176101722564	-2.31050550086245
C	2.21290203881503	2.00908241281391	-3.52139257529632
H	2.50555367880561	0.13765939485170	-4.53762229287094
H	3.23717902217903	-1.05695693560948	-2.48315259106288
H	2.73354509340828	2.53899820529416	-0.20752258375687
H	1.99330198031827	3.73508380745477	-2.25978688795745
O	3.11274850733374	0.56191446733888	1.37529933274586
O	3.29428597849275	-1.57565358999274	0.05572830661517
S	3.53610045495567	-0.16880966676804	0.21340352988322
H	1.88526844297227	2.52699705292468	-4.41364823877632
C	5.40450740872699	0.02169199382197	0.17280460889191
F	5.91013832237660	-0.53471192501350	-0.93117702656717
F	5.91864945883878	-0.58244388529205	1.23991776486675
F	5.73843465077778	1.31451768358575	0.19404838011168

Reactant Complex

95

Coordinates from ORCA-job react

C	-0.95694493241063	2.23206546129179	0.59683930971078
C	0.05421924428123	2.45877024090901	1.60294719918005
C	0.88776860838515	3.60845113552673	1.53156759775327
C	0.69839251705789	4.53784469979328	0.50655051794035
C	-0.27344629065467	4.35045882743080	-0.48822659492519
C	-1.09765588206983	3.20802511635831	-0.45133291177288
C	-2.13072395112779	1.34108561025873	0.91102860379148
C	-3.24397330092743	1.94393692153748	1.53645367169667
C	-4.36237863332194	1.18898307969291	1.90831759200174
C	-4.38602498218261	-0.19418416063962	1.66309663481619
C	-3.29349366474579	-0.80379590853254	1.03433338412383
C	-2.16801526094702	-0.04801196143468	0.64325482267997
H	1.66546351980740	3.78384943815024	2.28410479254376
H	-0.39235587833899	5.10596338287257	-1.27164794412048
H	-5.21807903567033	1.67471916078424	2.40231578486357
H	-5.25781435611187	-0.79460608695871	1.96510133029180
P	-0.69578732534653	-0.76858154646083	-0.19258809795020
C	-1.25354717178575	-1.22723799520588	-1.92099180962529

C	-2.48108241994307	-2.14350279056551	-2.02454561882516
C	-1.43051398923333	0.03655634678638	-2.77710840825853
C	-2.77908311323766	-2.50296143549763	-3.48884399662366
H	-2.33952263664688	-3.06469609888255	-1.42134703637933
C	-1.73029499273814	-0.32287885570386	-4.23701071632044
H	-2.26064884680506	0.64317716742473	-2.35446778034994
C	-2.95068141630443	-1.24557098567992	-4.35067726486010
H	-1.93931749884405	-3.11203355102103	-3.89387648699125
H	-0.84153765904134	-0.83445532417615	-4.67122373636553
H	-3.13542377706976	-1.52258064431359	-5.40987186986245
C	-0.41881123573758	-2.39946440973443	0.67707165815176
C	0.48965144914733	-3.33429803520499	-0.14031857755351
C	0.19178879691767	-2.08208723175418	2.05675033697827
C	0.85935282080777	-4.59386174401226	0.65807119715184
H	-0.00173092689881	-3.62887786762225	-1.09127433906470
C	0.56594670356982	-3.34975543310662	2.83168266827478
H	1.10343963812235	-1.46769870670948	1.89410663645941
C	1.50195773343455	-4.23997125806505	2.00460385341308
H	-0.05877698280900	-5.20016936124486	0.83704328410906
H	-0.35793177120018	-3.91667337726431	3.09022186513572
H	1.76486874379293	-5.16234823876580	2.56376195511881
H	-1.40384021424414	-2.89907398079633	0.83041192890706
H	1.42044146094643	-2.78905013542425	-0.40589678029592
H	1.54240812288794	-5.22788873304919	0.05428016117988
H	2.45046614097403	-3.69079519917693	1.81632222533555
H	1.03849196717928	-3.06921419526719	3.79660442658071
H	-0.50876115151384	-1.44938451896695	2.63847340450127
H	-3.36035902562372	-1.61427223912553	-1.59596749982856
H	-3.68609757441120	-3.14115608625463	-3.54795965399114
H	-3.85537153625353	-0.69326623071874	-4.00853879337901
H	-1.88213769825649	0.59943861223481	-4.83749731741472
H	-0.51384481921226	0.66085377243072	-2.69696111186404
H	-0.36432805252884	-1.77475096543060	-2.31233445293953
Pd	0.84645593383333	0.95349089276763	-0.26153224047799
C	2.42653947034907	0.67262955722353	-3.57089583705817
C	2.73418403016737	-0.09342414917943	-2.46116398287332
C	2.74978029302562	0.53166511892401	-1.16285429276810
C	2.60028734387964	1.97165723707915	-1.02369799823590
C	2.28174666632910	2.70411692777437	-2.21322868115648
C	2.17221837899347	2.07151682843760	-3.44559858965499
H	2.38190123713427	0.19723170816596	-4.56284540023929
H	2.94396458443787	-1.17006111151631	-2.53411104010161
H	2.99081125230215	2.50132324077614	-0.14227222903585
H	2.14890603098507	3.79333165688978	-2.13334504146680
O	3.37385335786436	0.33527036116817	1.46078552391520
O	3.43406020130614	-1.80389920469623	-0.00205971695538
H	1.92038696093126	2.65864385416825	-4.34112779953453
S	3.58825007735976	-0.33656035332466	0.15424532522253
C	5.42960945339289	-0.01906273072525	-0.21605458768024
F	6.16987548615803	-0.65517614221657	0.69936021934364
F	5.74783620983350	-0.47427219693421	-1.43754929059632
F	5.68593536804876	1.29753316732602	-0.16028891496320

H	1.33462343774959	5.43522529941472	0.47253580697096
H	-3.20773288938502	3.02578310638448	1.73862988031097
H	-3.30754752486959	-1.88810219429694	0.84421852939773
O	0.04137005521247	1.59258644976292	2.64824569253177
O	-2.11670492505631	2.93546383799618	-1.30436195910414
C	0.96350391331805	1.77333296919214	3.74838771929611
H	1.92771778529159	2.14948663909561	3.34550489232086
C	1.21610168762084	0.40027406506699	4.35317501459318
H	1.73258281374850	-0.25435697743649	3.62670807344031
H	1.85783770900750	0.50316152593364	5.25042412409845
H	0.26016264405321	-0.07058098937637	4.65900326278639
C	0.37419315264961	2.76718209315524	4.74737337175431
H	0.15422595602875	3.74571835655158	4.27743188859912
H	-0.57149791428116	2.36777270582410	5.16649274958568
H	1.08493391337703	2.93798553120583	5.58101669668099
C	-2.45890711023649	3.70407770640286	-2.47383653690807
H	-3.26980100015782	3.07771373441496	-2.90471939196664
C	-1.34194717866424	3.75950083455182	-3.51708618011735
H	-0.46046103188961	4.33321398654289	-3.17770163660674
H	-0.99879129329374	2.74187752418882	-3.77912128072359
H	-1.73278980730194	4.24254465232323	-4.43515134856925
C	-3.07278467826268	5.06182478356828	-2.12045790912583
H	-3.57039656176525	5.49162605035485	-3.01260614796179
H	-3.83520848087572	4.93506063196864	-1.32631456029951
H	-2.32177946146650	5.79280233438642	-1.76419527979615

Oxidative Addition TS

Coordinates from ORCA-job ts

C	1.96773098639084	-0.97647021030408	3.22070768233474
C	3.20083294179723	-0.30608468408418	3.09891684905028
C	3.24390939387143	1.09180817749476	3.10457729457719
C	2.06416104732531	1.80452336429408	3.22883937749129
C	0.84083210486072	1.17015827995177	3.37153310537429
C	0.79286915916630	-0.22215268421538	3.38213048264131
C	1.91687055277027	-2.46005832825806	3.36703212964695
C	1.91321543134246	-2.96235536791435	4.67066673055216
C	1.85285462280839	-4.32285796456382	4.92349909683988
C	1.79153144347153	-5.21464095919682	3.85978647262169
C	1.79712814212192	-4.73006812390405	2.56171309175343
C	1.85866115205895	-3.35781982843647	2.28831377105909
H	4.17200449659972	1.61961060299507	2.97065171758792
H	-0.05550343408481	1.75838589105237	3.45304945249972
H	1.85628702174705	-4.68588019915985	5.94353496522033
H	1.74355193958821	-6.28166665566339	4.03846567632666
P	1.92710586308750	-2.74466489997917	0.55761442282326
C	0.22222813331306	-2.95826751397983	-0.14191956748353
C	-0.39258624513819	-4.35156886485767	0.01087358361955
C	-0.72464414680026	-1.87944913566999	0.39423080248850
C	-1.76611556657262	-4.42852339953868	-0.66200245124768
H	0.26686493652126	-5.11466270504676	-0.40914739899228
C	-2.09418152464519	-1.95916006064807	-0.28132427434294

H	-0.83869467686479	-2.00611160447966	1.47207376475158
C	-2.71036087564559	-3.35048929918133	-0.12887577727791
H	-1.64376122470535	-4.29829646701621	-1.74285742083540
H	-1.98718345791109	-1.72626168249499	-1.34704051697746
H	-3.67276928423517	-3.40083433986436	-0.64379508974624
C	2.93238387461435	-4.04134667660485	-0.30341379960047
C	2.83111314579775	-3.90428474144210	-1.82753657442098
C	4.38702052878694	-3.91935832611756	0.16596312796527
C	3.76947356989611	-4.87575228226506	-2.54650601527724
H	1.80650530896362	-4.08433204952882	-2.15729777788255
C	5.30536625063041	-4.90691427377375	-0.55019788139787
H	4.72268233757183	-2.89879479890693	-0.03881274805795
C	5.21373508706829	-4.74064080473027	-2.06604315426184
H	3.42924170767382	-5.90367427051979	-2.37169604696002
H	5.02655968091301	-5.93138683496099	-0.27752417323672
H	5.85060030940359	-5.47079624090311	-2.57138020112107
H	2.55548558808510	-5.03031761299869	-0.02965014620043
H	3.07661851208910	-2.88323780271492	-2.11676625482413
H	3.71010550738656	-4.70589113689801	-3.62479845201849
H	5.59171341722561	-3.74947417503980	-2.33952151069058
H	6.33514292735062	-4.76353074625165	-0.21202007161052
H	4.44673578422587	-4.05165704039717	1.24807121698587
H	-0.50230530879438	-4.57640014174989	1.07559605030216
H	-2.19815681997193	-5.42215514611670	-0.51246454142508
H	-2.91001862457498	-3.54119646975130	0.93197846697274
H	-2.76152405037084	-1.20039328348881	0.13589445578832
H	-0.27762619769625	-0.89298667293200	0.24632887483902
H	0.37703808292896	-2.75766447422855	-1.20857591530338
Pd	2.72269382911826	-0.55808249035102	0.32199131947602
C	4.55169841884546	-1.05526728363315	-3.38905851535547
C	4.45855870764260	-0.52721342320864	-2.11029663827655
C	3.22625386125643	-0.04187868919162	-1.64877963349438
C	2.11677310747231	-0.01430556572200	-2.50752694272341
C	2.22389511979248	-0.55583718892731	-3.77854494933507
C	3.43758172836235	-1.07706086583707	-4.22313643078175
H	5.49788959161739	-1.44916117684140	-3.73733048914784
H	5.32634837920899	-0.47954450201865	-1.46691983095059
H	1.18972465677931	0.42623342636407	-2.16852070582166
H	1.36045242001976	-0.55874295085416	-4.43201548873984
O	2.21841561437110	2.26450148820279	-0.02737856964248
O	4.68522562199695	1.63374733146586	0.32115421306387
H	3.51731405697195	-1.48293011935812	-5.22283537598078
S	3.44328959832805	1.59534558021783	-0.44788158039592
C	3.94728619735440	2.74945643135770	-1.89055699362620
F	4.13685565434088	3.96603471702853	-1.36880190006417
F	5.08556680908546	2.36200810668908	-2.47606856410455
F	2.99541804858436	2.83707440098156	-2.82662411632498
H	2.09814361810006	2.88505977839402	3.19120077481554
H	1.96189606994980	-2.26026317981644	5.49318746493900
H	1.75600119866718	-5.43932301095125	1.74814441880421
O	4.29644120319264	-1.10570952064330	3.01948868449390
O	-0.33855403174020	-0.96747015609909	3.51449975649336

C	5.61067567073990	-0.51441551359066	2.91331705312393
H	5.54900170931137	0.35054551121120	2.25204094138650
C	6.48784301166854	-1.56396694693937	2.25942138608046
H	6.13850730762855	-1.77806538053808	1.25079206541424
H	7.51667151202693	-1.20531679181799	2.20133431264608
H	6.47212284367871	-2.48999889937121	2.83652511362196
C	6.10633056310381	-0.11005334896887	4.29367387284145
H	5.42094536363342	0.58987088050642	4.77214533997125
H	6.20049134341659	-0.99174364452019	4.93067369453524
H	7.08391929545574	0.36970173101449	4.21722065193419
C	-1.57679157068993	-0.47512132228717	4.06382596968674
H	-2.14344448200495	-1.40424425909097	4.15406185211268
C	-2.34604782183768	0.43165452692703	3.10699910047898
H	-1.97249640355107	1.45357535593175	3.09149993250607
H	-2.30413897397025	0.03555988686380	2.09313384276631
H	-3.39266764439171	0.46690140642334	3.41645765787572
C	-1.40142744837718	0.10147711661064	5.46204340759067
H	-2.38322317792701	0.28240731966904	5.90307729104620
H	-0.86496485936450	-0.60535511464066	6.09620385854119
H	-0.85368200930947	1.04244727434914	5.45572766759945

Intermediate

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Coordinates from ORCA-job inter

C	-0.96406943992846	2.28437525867880	0.65054333062040
C	0.04094478109041	2.48325290287055	1.62561521814195
C	0.90485183230294	3.57846793343527	1.53804263507344
C	0.77104526564732	4.46504831185517	0.48143638320042
C	-0.18869045451860	4.28739714019927	-0.50377860096523
C	-1.06053265224719	3.19837753860119	-0.42172027523617
C	-2.09484967753742	1.34408068602259	0.94682010731326
C	-3.15162886120820	1.88304946408096	1.68752519829466
C	-4.23250410084286	1.10803340356551	2.07614695684881
C	-4.26904682643244	-0.23946475871178	1.73725061904532
C	-3.23048063697364	-0.78465221895216	0.99952105742397
C	-2.14422593105950	-0.00888025458319	0.57922906204601
H	1.67358259254330	3.73983588309900	2.27607645115055
H	-0.26132458307063	4.99861818073825	-1.30732289259600
H	-5.03593005871194	1.55000770313074	2.65218217648728
H	-5.09807555003874	-0.86196429836367	2.04949960363691
P	-0.77615626607259	-0.73246298011560	-0.40459840418669
C	-1.53905805138274	-1.24020489502838	-2.02359964480153
C	-2.68953910538474	-2.24756464295883	-1.98209073535521
C	-1.93606933329932	0.00688440038119	-2.81897939965343
C	-3.15447062478031	-2.61145099858777	-3.39532773690917
H	-2.39212545234877	-3.15119257433915	-1.44594765844343
C	-2.42469060476587	-0.34408685341051	-4.22440034022741
H	-2.72107839366415	0.54190404766294	-2.27691414820102
C	-3.55960258260846	-1.36841388940026	-4.18757340493105
H	-2.34187138858568	-3.12674043400569	-3.92006166484097
H	-1.58956070509422	-0.75233575166346	-4.80454210041196

H	-3.85634197183565	-1.64507175437777	-5.20252259836868
C	-0.41690971833904	-2.32045547231659	0.46784912208222
C	0.55522898299263	-3.18171387869928	-0.34940554140810
C	0.15434576091240	-2.00696258192431	1.85667158478844
C	0.94547293283404	-4.45162594883125	0.41182635885641
H	0.10855194890515	-3.45060338159925	-1.30968979232451
C	0.54465392582015	-3.27915305164337	2.60725144364793
H	1.03373908695613	-1.37179007371526	1.73250314079001
C	1.52084903902006	-4.12782854388808	1.79148293111950
H	0.06039265563491	-5.08849947480956	0.52915910502755
H	-0.35693730391110	-3.86439735713157	2.82464222579722
H	1.75992664038435	-5.05154087384335	2.32507329816424
H	-1.35175143743847	-2.87718261874141	0.59435884670923
H	1.45272305999512	-2.59626445573802	-0.56343360095206
H	1.66880735473536	-5.02318899264517	-0.17595210870977
H	2.45644847695880	-3.57542472643533	1.66643583738658
H	0.98472111225124	-3.01420323498394	3.57204897942193
H	-0.56754457110291	-1.42703441312727	2.43328670123399
H	-3.53165079989222	-1.81333574322036	-1.43720935215589
H	-3.98898746539118	-3.31586428058794	-3.34023094439268
H	-4.43909888231160	-0.91423929342098	-3.71703816261744
H	-2.74943731770419	0.56380539356528	-4.74081627307886
H	-1.08075761822094	0.68369561543391	-2.86868817496093
H	-0.69367071102861	-1.70767937187195	-2.54189075543476
Pd	0.89933170606088	0.81794764965870	-0.64161908885426
C	3.12725569589334	0.57136430180114	-3.48071441732289
C	3.34869142083416	-0.07452361597886	-2.29325273129613
C	3.07117349109135	0.60099612510495	-1.07229624775140
C	2.66669568827925	1.97224381204759	-1.06682136491067
C	2.42072346541715	2.58039099790878	-2.32307503747996
C	2.62926068875751	1.89279633303632	-3.49649069995683
H	3.31972328845201	0.05887975844761	-4.41379001948926
H	3.71231038125920	-1.09133066062793	-2.26105313691311
H	2.75835825657823	2.57316199204725	-0.17282179960015
H	2.08309936734793	3.60711608665626	-2.33863265838818
O	3.27173079511696	0.66441368579094	1.56489080020810
O	3.59155542732488	-1.53324759808332	0.38787366843316
H	2.43443307780576	2.37703922296279	-4.44459145065164
S	3.69002713948274	-0.09752326156683	0.41621953999426
C	5.53697715766407	0.24580634934905	0.31591769830618
F	6.11317310871772	-0.16884312989171	1.44518758445785
F	6.09408041409974	-0.39882455560769	-0.71420779454697
F	5.76496479441232	1.55588968012388	0.17122689158338
H	1.43745181900281	5.31631145122797	0.41897320106201
H	-3.10800557977861	2.92764038380092	1.96846921714877
H	-3.25781641948396	-1.83696287073679	0.75592207533308
O	0.06380957499141	1.57092656405483	2.62165730817728
O	-2.06948990681793	2.92915867169574	-1.28472428664663
C	0.96958992052645	1.73300482386943	3.73396884355123
H	1.93349451440874	2.06834863963140	3.34909240342237
C	1.15390518811158	0.35726346802221	4.34165744033244
H	1.63380995530982	-0.30963286489514	3.62903688897790

H	1.78628480758075	0.42898378268249	5.22808486654226
H	0.19114954370366	-0.06408468693663	4.63556869194092
C	0.39153510156091	2.73843693548324	4.71927288961912
H	0.20382979619418	3.70244773056049	4.24593073649694
H	-0.55230028885097	2.36417333275857	5.12008226054245
H	1.08307655184927	2.89351458225960	5.54936906578021
C	-2.34609712872573	3.66794709153093	-2.48988371877079
H	-3.13558002280954	3.05328362954888	-2.92693895740220
C	-1.18773889882944	3.68349100378354	-3.48228611702585
H	-0.42087903582738	4.41432429797062	-3.23484230673848
H	-0.71907534084051	2.70247037631808	-3.53631020700411
H	-1.57691114588306	3.93263376961028	-4.47142181844662
C	-2.94028283191688	5.04012387178191	-2.19615922218836
H	-3.32720806614149	5.47267413448340	-3.12087452128928
H	-3.76609746846344	4.94596242865794	-1.49002729648352
H	-2.20981136471776	5.73259949000903	-1.78014229589786

XRD Structure

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Coordinates from ORCA-job react-restart

C	2.73288467255555	10.99292616902170	7.90548030971179
H	2.06971171512430	11.78194726177213	7.53773577983096
C	2.06554637711861	9.64024011196222	7.62613975672461
H	1.89736944678369	9.52293221585502	6.55364878928968
H	2.76139327239254	8.85146995429671	7.91829902018923
C	0.75827059903184	9.48768937974035	8.40302923654989
H	0.02666378504652	10.21257458042314	8.02835413791686
H	0.33446141079294	8.49598639874286	8.22165399501704
C	0.97325591528500	9.71095044321326	9.90045763072898
H	1.62487185781502	8.92254964372759	10.29240569307247
H	0.02487768550127	9.63228013054167	10.43715672195077
C	1.62140959806108	11.07010921251097	10.16866841823326
H	1.80249771773914	11.20185727511054	11.23836563502009
H	0.93052214823462	11.86610074660234	9.86630595528696
C	2.94179464632910	11.22503249662955	9.40813865482105
H	3.35193119731476	12.22092458335839	9.58473850500211
H	3.66654918719204	10.50998538826728	9.79497924216878
C	5.11003043371074	12.67123583623833	7.42289728215547
H	5.34453400594035	12.47142475233481	8.47349990286383
C	4.27457788996119	13.95299909303180	7.34690988853437
H	4.01364818035068	14.15005853035023	6.30394080617046
H	3.33747907196956	13.84351491484234	7.89716429514109
C	5.06709763486910	15.14499073363143	7.89243475903782
H	5.26378898347648	14.99208806439581	8.95944374344289
H	4.46691750116645	16.05521392214604	7.81151862927015
C	6.39310986881130	15.31471120232070	7.14916377606890
H	6.95976062031015	16.14957392736083	7.56895231312536
H	6.18509938781373	15.56841724424947	6.10308619821764
C	7.22226657136375	14.03064097632152	7.19436726158362
H	8.14318775182814	14.14812298713941	6.61880372466713
H	7.52886139517438	13.82912971594935	8.22688073376059

C	6.43346827811950	12.83394384019632	6.66439351026527
H	7.02463475082340	11.92008438223953	6.74439498556617
H	6.21830637403712	12.96725450343762	5.60087153512161
C	3.64662828764205	11.40374517764805	5.20223447763459
C	2.61872995705092	12.31781765814474	4.94378693128770
H	2.15681592824684	12.85897616353921	5.75637394668850
C	2.17641273352887	12.54689134399831	3.65159486197245
H	1.38079281300645	13.25701446495762	3.46905670567255
C	2.76103833470326	11.86138623900129	2.59254736558844
H	2.42520687507533	12.03411039475080	1.57820389359863
C	3.76801001350110	10.94408550765370	2.84075183325135
H	4.21783399262924	10.39633591170963	2.02302363239215
C	4.21819761013901	10.69597218054185	4.14024030115155
C	5.27282916121038	9.64567581003035	4.29907022656918
C	6.60586901001713	9.93933842450523	3.90565916979176
C	7.51994530876713	8.91507463534532	3.68769201780833
H	8.55169745324772	9.12700226089488	3.46426033098300
C	7.10204954751152	7.60051760714945	3.82077119230104
H	7.82451110655634	6.80940822672778	3.68097495792826
C	5.80136999428458	7.26623063465608	4.15806711373630
H	5.53008599612627	6.22965397350636	4.27176528808906
C	4.87959472049235	8.28398191379224	4.39298790220511
C	8.17293430447113	11.68060159552616	3.27333745357198
H	8.51151856443938	10.96984169826403	2.51467849126909
C	7.93553443574767	13.02879623414941	2.61617555680479
H	7.22398083142897	12.93742180241142	1.79429989287042
H	8.87178171309023	13.42705723833104	2.22284729863455
H	7.53684322556210	13.73928125142458	3.34260316630373
C	9.16782456835279	11.73380279833750	4.42160095378558
H	8.91318291552447	12.54401093987032	5.10434351871962
H	10.16906645950345	11.92259689548938	4.02853299526983
H	9.19292242042655	10.81202926035209	5.00196447993159
C	3.08083575876391	6.74689190952371	4.91767578850252
H	3.48458434264834	6.08281899692552	4.14811010681634
C	3.51255261714479	6.26699648841486	6.29696732261743
H	4.59005453342341	6.34893422304137	6.43752162546537
H	3.22935961075993	5.22110817515943	6.42964602615701
H	3.02067657097553	6.85563725344177	7.06996190789464
C	1.57412668246946	6.82375253479907	4.75618941764379
H	1.14142969240937	7.49457625475249	5.50009962455548
H	1.13038329138587	5.83499750892602	4.88238128854919
H	1.31405804037088	7.19419078061847	3.76405978932542
C	5.82299334569562	9.43352036799225	8.80413850354259
C	5.16332386294074	8.40859272243536	9.47975201590395
H	4.57243902393416	7.68552321495622	8.93467967054892
C	5.26035283504427	8.29869708667456	10.86383630559891
H	4.74272080495703	7.49601128403605	11.37687615058271
C	6.01768432297942	9.21417817720832	11.58684301826849
H	6.09772585644735	9.12651678506169	12.66341384296542
C	6.68734255949419	10.22953741067521	10.91445092057053
H	7.29398452308872	10.93805305362288	11.46703830602818
C	6.59444963687619	10.33722941616426	9.52827695493132

H	7.15783021572790	11.10786914919817	9.02169840208379
C	9.73526323771662	7.23317343221649	6.42818597658576
O	6.86936830455958	11.24977611345302	3.73285055151239
O	3.56649282574143	8.08158921697391	4.65956030789230
O	7.26243177905114	7.97487748172036	6.74345173673514
O	9.03510464730498	9.67812310047781	7.15140461603383
F	9.97999769053974	7.76407520202969	5.21757874256876
F	9.25310856693922	5.99094423805585	6.24401889709755
F	10.91243792154908	7.12505049836639	7.07179063029967
P	4.26934888815931	11.11996981240167	6.89353627763539
S	8.56368378215345	8.31929348193217	7.49607040564908
Pd	5.74300579001913	9.44348772271658	6.81101847449200

R=Ph

Substrate

Coordinates from ORCA-job substrate

C	2.39901467324529	0.63657590854812	-3.60883514194498
C	2.87495913493430	-0.01352765847804	-2.47789097524764
C	3.01126612938927	0.70124154078561	-1.29298044649790
C	2.67534228977202	2.04840222607048	-1.21931365631831
C	2.20002519483573	2.68938763254414	-2.35598823827154
C	2.06545144168873	1.98579933291587	-3.54852983412876
H	2.28208147292732	0.08885396398284	-4.53496458298536
H	3.12155877304488	-1.06572717449479	-2.50010628676748
H	2.76898343643914	2.57271513616454	-0.27844053801538
H	1.92833277978015	3.73572857273222	-2.30916741284578
O	3.17231864484592	0.59614503860301	1.31513329741055
O	3.37925110659872	-1.53820744897316	-0.00383785053783
S	3.63725336743678	-0.12675363672174	0.15514525494508
H	1.69226486194605	2.48828875359335	-4.43175351911575
C	5.39606729773470	0.12358169078219	0.03909509919491
C	6.17246827725555	-0.78586209502187	-0.67009980679783
C	5.96364573178783	1.23355675961476	0.65449617963779
C	7.54065261941501	-0.57112749817809	-0.77116875002697
H	5.70765463651763	-1.65459379212588	-1.11478951638407
C	7.33276113805253	1.43873004423824	0.54838823321917
H	5.33778561235590	1.90971797146176	1.21972842140095
C	8.11855429170380	0.54123679385021	-0.16734125090640
H	8.15665618033715	-1.27571055008751	-1.31475189379967
H	7.78667969642635	2.29604727975004	1.02801872679218
H	9.18571595152926	0.70493899844371	-0.24765567200899

Oxidative Addition TS

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Coordinates from ORCA-job ts-opt

C	2.49972521542662	-1.02680290049650	3.28701026854296
C	3.87659542779060	-0.75837630370190	3.39065373637952
C	4.34164727703031	0.55452601197135	3.44868952796890
C	3.42500995696970	1.59239921786037	3.41420210455337

C	2.06288730364241	1.36119138632904	3.31912000202167
C	1.59154148946824	0.04877389905490	3.25714200650870
C	2.01957891683438	-2.43565493531613	3.41767881371720
C	1.80466723149331	-2.90896546752766	4.71460434219351
C	1.44635315249123	-4.22594429720396	4.95361047994427
C	1.31100964362195	-5.10628452132011	3.88656952681790
C	1.51089186318609	-4.64700812715629	2.59424511890817
C	1.84464707004726	-3.31248644524830	2.33583830006248
H	5.39608195918799	0.77342078780500	3.48967483360556
H	1.39429610882891	2.19695477933961	3.24371444717358
H	1.28866507394609	-4.56800247373258	5.96876228841868
H	1.04756503597640	-6.14234414419202	4.05926571949858
P	2.04456670121682	-2.69864353554347	0.62072559798088
C	0.41637788334203	-2.98597490210468	-0.21721167069462
C	-0.11807865764970	-4.41857672140583	-0.28174406092526
C	-0.64353117381724	-2.03853171817258	0.35683864205864
C	-1.40392307082780	-4.47696459231122	-1.11372109604659
H	0.62822056773938	-5.09603805258847	-0.70224141358721
C	-1.94320020847701	-2.10251657796881	-0.44647148358586
H	-0.83535583091719	-2.30428849305269	1.39988723146978
C	-2.47087545029796	-3.53418348521116	-0.55530965727507
H	-1.17503737164271	-4.19409852867464	-2.14739641715486
H	-1.76249664645528	-1.70826971547414	-1.45322290429314
H	-3.36762705281163	-3.56414920136396	-1.17951279231955
C	3.19766752907980	-3.91903516383758	-0.15474029196182
C	3.23644777760900	-3.73149564271216	-1.67684702138285
C	4.59008677455915	-3.73378739931758	0.46154632252468
C	4.29262252583893	-4.62214280924202	-2.33178958650176
H	2.25818461930127	-3.94174583453381	-2.11251591702389
C	5.63151598884147	-4.63437296351704	-0.19948486911499
H	4.88281064591856	-2.68557654647118	0.33894961190469
C	5.67300293795778	-4.41062263693197	-1.71064690563706
H	4.00488901352688	-5.67490816436114	-2.21925066700302
H	5.39136549346566	-5.68431094363865	0.00460761232976
H	6.40541527727011	-5.07497452928458	-2.17623326154574
H	2.84960827944857	-4.93330155966144	0.06739678293764
H	3.45942866953032	-2.68766651396825	-1.90088129994001
H	4.32279766375289	-4.41843545081819	-3.40529716044788
H	6.00215761809917	-3.38486103408861	-1.91226026220475
H	6.61482222721776	-4.44873909721564	0.24207021823665
H	4.54738231997459	-3.91572216232850	1.53627897578159
H	-0.33730756873645	-4.77042551351061	0.73005626664373
H	-1.78188602050472	-5.50255222519301	-1.14494369215902
H	-2.76907928274231	-3.88267294867616	0.43997840221189
H	-2.69504270187246	-1.45397024590579	0.01146678152368
H	-0.25010497720633	-1.02073376091296	0.37135324968833
H	0.63076043692563	-2.65529503400149	-1.24047705929345
Pd	2.56818737754979	-0.46435287998297	0.49855202235982
C	3.97125766281931	-0.47841392504446	-3.40438250668168
C	3.87542645078130	0.00162492405501	-2.10764198571874
C	2.61617244153717	0.12273379033045	-1.49123810449827
C	1.46009905203755	-0.14524233513982	-2.24684527210365

C	1.57315857580844	-0.62611729572418	-3.54069981299207
C	2.82568189410893	-0.80301988400268	-4.12755885136231
H	4.94831107317478	-0.59624679804818	-3.85711108454489
H	4.76407249240261	0.28144612765901	-1.55788247823916
H	0.48571192780645	0.01524381682323	-1.80495225969746
H	0.67597775520137	-0.85919682219920	-4.10168583844417
O	1.21242936917583	2.11123785883906	0.24986390009754
O	3.75974513107449	2.25982365605363	0.23753681022757
H	2.90565123154876	-1.16850311778150	-5.14243245940978
S	2.49988280304164	1.90252352067564	-0.41378876972626
H	3.78513785762845	2.61193560674741	3.41499122229040
H	1.94010024576132	-2.22559197491393	5.54335505193320
H	1.40134534968941	-5.34077052603071	1.77253548072823
O	4.67559507271841	-1.86029508474594	3.41998256985157
O	0.29445790618297	-0.33147592302061	3.13988575788445
C	6.04132890481818	-1.76163876439030	3.85527077423790
H	6.53273302343471	-0.95289292667751	3.30711899054145
C	6.68914705268985	-3.07803725807171	3.46812439265113
H	6.65077419624497	-3.22452668024733	2.38900072344711
H	7.73296669428284	-3.09014336851612	3.78528251470317
H	6.17011750156210	-3.90934807691614	3.94845683979957
C	6.10349675734931	-1.49986049340406	5.35338470085881
H	5.60128945001532	-0.56936079543498	5.61753970062682
H	5.62005382009280	-2.31765577220511	5.89163362878999
H	7.14193765398038	-1.43303647646689	5.68267527493141
C	-0.83533545143611	0.56452065998330	3.15954588840333
H	-1.65942896092887	-0.15089176095654	3.11362945042741
C	-0.93100016495699	1.44107337081739	1.91564500902446
H	-0.18817315605001	2.23269768550723	1.88055298354910
H	-0.80581914400950	0.83841633266088	1.01733027743589
H	-1.92129008021947	1.90094246348247	1.88589065218321
C	-0.95885474554765	1.31662966057807	4.47956975689275
H	-1.94710010529114	1.77703988406852	4.53785194454665
H	-0.85507441810308	0.62464373584368	5.31622603672170
H	-0.21439305365630	2.10367279558324	4.58972163923271
C	2.42355643658070	2.95989355333387	-1.86999017106680
C	3.60158669628060	3.41869681432545	-2.44375999456727
C	1.18510193502182	3.31351980250869	-2.38860807045114
C	3.53571437350388	4.25198280144164	-3.55292407878089
H	4.55068111457989	3.13688212388455	-2.01078198956910
C	1.12715215558427	4.14711759580425	-3.49796578449410
H	0.28549336307684	2.95083822804481	-1.91213816703804
C	2.30069421046001	4.61363669789676	-4.08104792487066
H	4.44787184570644	4.62106762076206	-4.00373927201374
H	0.16660155701620	4.43482934785229	-3.90565955324090
H	2.25266274527043	5.26222539189361	-4.94672586637509

Intermediate

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Coordinates from ORCA-job inter

C	2.14515033295684	-1.36823319908913	2.80127871466623

C	3.48002433267405	-0.89227023659442	2.91226075497212
C	3.73183393515129	0.41855654168053	3.31596169795235
C	2.66880487611199	1.23496487210908	3.65331200656247
C	1.35422055587287	0.80521942831768	3.57482767040197
C	1.08221269096623	-0.47646322049134	3.12239501730809
C	1.89098121965888	-2.84330400280908	2.91761497371917
C	1.82218777928681	-3.34919076771680	4.22007193669566
C	1.62848891425622	-4.69938246291444	4.45912406527413
C	1.50516031360476	-5.57907570949025	3.38885939052101
C	1.56599713968251	-5.09078714248588	2.09446164913829
C	1.74587898448489	-3.72512532545713	1.84353647358571
H	4.73324730514008	0.81207113962764	3.35370525626628
H	0.56415725486681	1.49269211089677	3.81462207426129
H	1.58178216168126	-5.06683741647635	5.47640749565759
H	1.36245317437993	-6.63820263729682	3.56246778159950
P	1.82359079880572	-3.04764996364406	0.15424978135476
C	0.16575610229580	-3.31024991191501	-0.62118159014806
C	-0.38094137632360	-4.74036258352755	-0.59918659328687
C	-0.85671860389119	-2.32895301357324	-0.04154654838244
C	-1.70793598853097	-4.82267858735874	-1.36003820661216
H	0.33828106506154	-5.44056808266833	-1.02862205496126
C	-2.19446838281291	-2.41759374112971	-0.77596802551800
H	-0.99636996151712	-2.54396970285666	1.02096106913714
C	-2.73737656390732	-3.84705168681803	-0.78820139024359
H	-1.53198407789260	-4.58831277850799	-2.41553023665514
H	-2.06005277295719	-2.07335139765235	-1.80763513443617
H	-3.66610027639091	-3.89662597091201	-1.36148084342750
C	2.94804211211839	-4.23163282888280	-0.71614308332483
C	2.84414574624390	-4.20854370937532	-2.24675484412273
C	4.38409186420162	-3.98930116401344	-0.24087024047405
C	3.83100094288948	-5.19801542446661	-2.87046099554661
H	1.82943925178854	-4.45358264720868	-2.56433614005344
C	5.36626883033523	-4.96410326596488	-0.88731031893685
H	4.66730724318904	-2.96570958911434	-0.49314428295787
C	5.26377711710832	-4.92770693277571	-2.41123159020458
H	3.54978886139489	-6.22124169841202	-2.59286149256601
H	5.15604758218373	-5.98020962684674	-0.53321459632140
H	5.94923036426541	-5.65275411641096	-2.85668218885022
H	2.64963411620406	-5.22964725438425	-0.37909376439144
H	3.05673469332997	-3.20931779537789	-2.62036495142201
H	3.76361718608519	-5.13792911237114	-3.95943315491165
H	5.57093282345103	-3.93904135908530	-2.76959303997568
H	6.38385734540507	-4.72638057709745	-0.56601848494777
H	4.43161815179409	-4.06299000537345	0.84637155589913
H	-0.54820147312125	-5.04723019606796	0.43664561834411
H	-2.09257464366470	-5.84549519658413	-1.32510116913450
H	-2.98361656717637	-4.14787827996669	0.23652880723847
H	-2.91583529945354	-1.73839428729625	-0.31395765994935
H	-0.45681958197616	-1.31571625526339	-0.10016489278148
H	0.34568118941462	-3.02776901799950	-1.66383150797682
Pd	2.32003364306335	-0.78033289446494	0.28974888734552
C	4.26840441828188	-0.85441125645877	-3.48601349458397

C	3.97633833017745	-0.81410405104207	-2.12623889040270
C	2.65357757403056	-0.80516415226965	-1.68830848646141
C	1.62965625863595	-0.80995989883173	-2.63057620548976
C	1.92198509556218	-0.84446830953032	-3.99040225294902
C	3.24246359935960	-0.87801293468024	-4.42356248830419
H	5.30197417196819	-0.85885801318695	-3.81155936531232
H	4.78548500504218	-0.76211151172060	-1.41010632987454
H	0.59540477236312	-0.76111825477484	-2.31595900691029
H	1.11341455871756	-0.83378740286258	-4.71103651579994
O	1.89079446664718	2.31661677753567	1.12224309418307
O	4.16164044097081	1.82128084314162	0.16749937375091
H	3.46957516800475	-0.90463880525190	-5.48184470778426
S	2.71264899633695	1.56319987516126	0.15976094264178
H	2.86691905512685	2.25552319850252	3.94821777711523
H	1.92915478025183	-2.66274957818530	5.05036587505059
H	1.47386331759997	-5.78402661020034	1.27098706434878
O	4.44478297686836	-1.80623874806534	2.65351126237722
O	-0.15299707206195	-1.01915104239644	3.01072668057372
C	5.83541089417053	-1.44666432637275	2.81458499929162
H	5.97822564205516	-0.43935051450305	2.41861393121944
C	6.63176511823743	-2.41826918345747	1.96729264038897
H	6.37819488200362	-2.31319498164864	0.91370667606392
H	7.69852930143856	-2.22067924382623	2.08671435859308
H	6.43407942947131	-3.44706431962348	2.27488200008126
C	6.21904907443820	-1.50860438342221	4.28512216055165
H	5.58909205501376	-0.85699089045534	4.88911755378298
H	6.11519300543602	-2.53080431762222	4.65416898894592
H	7.25728377511395	-1.19794599002669	4.41663942839156
C	-1.36071501051863	-0.22641660490168	2.89880670341992
H	-2.06335937966157	-0.97611745688853	2.52925299629066
C	-1.26462925418742	0.87603811988891	1.85161605669055
H	-0.68938139272321	1.73760896100603	2.17832669314561
H	-0.79448950308254	0.49993187107604	0.94531944006106
H	-2.27387237380532	1.20984262890662	1.60347716578936
C	-1.86019387049233	0.23867476889916	4.26100507048537
H	-2.87560938403153	0.62720657064053	4.15959714082840
H	-1.88263496907368	-0.59978934327729	4.95842056801731
H	-1.24229578855447	1.02645880925812	4.68821604512777
C	2.11386050584534	2.16872063675256	-1.43430478508727
C	2.99599079738690	2.37505033844516	-2.48343109914636
C	0.74890430229482	2.36756982689456	-1.59985816607748
C	2.50209048039606	2.77130318200937	-3.72079470224287
H	4.05229922925793	2.21548291750786	-2.32159198795060
C	0.26006209422905	2.76496267993957	-2.83731658228131
H	0.08504910152722	2.21915672453211	-0.75900611995685
C	1.13665539348559	2.96086675488073	-3.90055169267334
H	3.18396376164054	2.92418906311932	-4.54773824099895
H	-0.80251068995882	2.92648565503529	-2.97235080881009
H	0.75498124697561	3.26590832590718	-4.86686645349062

XRD Structure

Coordinates from ORCA-job xrd-restart

C	3.09280712556500	10.61031990564026	7.87572845956625
H	2.46682856483670	11.50658329391357	7.81448811907916
C	2.25401254091277	9.41043662796995	7.42095987076363
H	1.90208189498932	9.57106239242948	6.40027535724320
H	2.90229349532088	8.53240507995869	7.39193566040229
C	1.08078343848170	9.14474079744728	8.36194011639456
H	0.37213234472837	9.97918141829235	8.30561466272888
H	0.54128751068310	8.25292483056103	8.03133132517319
C	1.55429334862449	8.97985384961462	9.80572421694677
H	2.18386249547825	8.08585658445380	9.88058486044124
H	0.70074488865108	8.82217539216182	10.46982551100722
C	2.36067108061257	10.19746568525099	10.25646214646848
H	2.72260808599237	10.05556946057886	11.27742888121742
H	1.70579698096965	11.07712631911375	10.27278269566091
C	3.55154282459436	10.46103911970961	9.33231424990111
H	4.07657390355281	11.35898266508083	9.66041836454749
H	4.25537618630376	9.63528011076739	9.41315628323354
C	5.51923621765968	12.20211743651709	7.37803342502591
H	5.86055979978375	11.75877677025729	8.31917452851139
C	4.80456672364946	13.51786824632537	7.69650990873288
H	4.43790921523430	13.96339293384633	6.76825209039920
H	3.93275804119550	13.34593873730691	8.33181011853862
C	5.76173970097819	14.50149729053977	8.37549415525923
H	6.06592276187670	14.09616473872241	9.34668063828342
H	5.24282811599022	15.44226062203959	8.57656852573154
C	7.00216851536120	14.74813632637553	7.51705284726985
H	7.68832655489533	15.42742849760469	8.02984046081375
H	6.69840854022400	15.24526179731694	6.58866459667850
C	7.70504436869804	13.43529136259986	7.17204589898130
H	8.56223615029141	13.62073685571168	6.52168498980870
H	8.10562910509307	12.98516706153504	8.08758385250816
C	6.75482725927340	12.44265272087575	6.50230550201977
H	7.27181282467247	11.50204863538108	6.30429766681280
H	6.43649412870815	12.82926865999136	5.53124887986815
C	3.61198200565923	11.55442838868868	5.20646291821648
C	2.63292683356968	12.54804470014251	5.32634244145279
H	2.35995468692713	12.92293526844174	6.30206157924177
C	1.99825922378629	13.06856328660450	4.21049533130710
H	1.24552585333095	13.83794178151039	4.32720250901245
C	2.33444410763698	12.59654366440750	2.94645980585731
H	1.84822463164227	12.99667053371602	2.06605528779779
C	3.29152031175391	11.60405241915002	2.81829212370899
H	3.55047080618895	11.22260703870592	1.83893247095810
C	3.93668945349995	11.06795834735059	3.93608699773419
C	4.93183863596225	9.98199207999643	3.67133136143455
C	6.20306454405090	10.33267133501903	3.14934077518208
C	7.01295412468100	9.36894506518844	2.55346025696088
H	8.00881343890451	9.60689446895045	2.21895575982651
C	6.53716958208146	8.07254316307579	2.43222609122020
H	7.17879292879337	7.32055289726425	1.99337782386226

C	5.28662874115111	7.69790526762541	2.89261017201064
H	4.97712854791578	6.66978784201827	2.80974858103530
C	4.47881046606826	8.64809231858445	3.51337959619372
C	7.69607189126359	12.16743761567979	2.60584816864203
H	7.85886631812724	11.61098732186145	1.67896752067900
C	7.37071318375605	13.60980265625191	2.26409052192232
H	6.51974805550539	13.66759330956282	1.58382111381972
H	8.23135093930276	14.08349569528206	1.78874533135342
H	7.12676307930515	14.16766497446656	3.16996967564277
C	8.89684192546169	12.02358632405517	3.52628059866901
H	8.80220121217472	12.69835677277245	4.37759363879703
H	9.80834254708361	12.28437872568557	2.98340394386619
H	8.99223264801500	11.01395489604377	3.92378119063003
C	2.71462589221065	7.06696179293527	4.00639908428121
H	2.95569963156037	6.56440780243949	3.06519281359708
C	3.33626588226946	6.31739360800588	5.17527751906784
H	4.42546072521402	6.33491034602134	5.13698645379409
H	3.00564334563794	5.27724580922652	5.16922458678207
H	3.02065441356629	6.77129050570338	6.11453532174115
C	1.20812343652282	7.19509474621621	4.11799914040858
H	0.93977779624111	7.72061579916233	5.03537117144174
H	0.74750602058439	6.20654074747610	4.13723178650545
H	0.80470486618735	7.74934193696835	3.27020240166231
C	6.09482093148546	8.69004596506214	7.89092852015573
C	5.43024069321871	7.58672410866198	8.42200433891572
H	4.70113178194723	7.05136829487808	7.82948853933416
C	5.71460559702097	7.14883030526255	9.71240142761426
H	5.19389822325141	6.28637452032131	10.11056932685804
C	6.66493137458690	7.81025418978080	10.48250730848680
H	6.88678645042282	7.47262231241871	11.48654153578210
C	7.34243995963451	8.89783295387781	9.94461881096002
H	8.10761449469850	9.39918255347922	10.52447280065819
C	7.06304777358278	9.33572194686927	8.65286537394297
H	7.63435350710089	10.14982755980886	8.23029062359105
C	9.43500641665045	7.04706189549509	6.39224688659185
O	6.50337756988853	11.64290813569567	3.23176659939417
O	3.21509714182518	8.41653880069598	3.94384354799546
O	7.06885955192978	7.61708939108131	5.40047350626494
O	8.74831579671568	9.44254541689941	5.54190883296779
P	4.46788555001455	10.86541789962268	6.66694347980659
S	8.54347810594761	8.01721725454880	5.13009974200396
Pd	5.75741117909477	9.16644027134715	5.99544860807403
C	8.84311507809005	6.58317173873513	7.55898908363041
C	10.77220560286754	6.77677466136263	6.12599711045024
C	11.53140794154691	6.05526663186576	7.03938482793494
C	10.94830022783282	5.60583976119303	8.21985497689032
H	11.21552897323681	7.13131765317753	5.20260397737607
H	12.57381303841832	5.84560545230529	6.83438950499863
C	9.60666020261035	5.87225685612887	8.47727109830336
H	9.14968832896430	5.52948875542593	9.39750693202783
H	11.53634503616872	5.04423481522423	8.93548771855175
H	7.79766648376189	6.77632579865675	7.73908188842148

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The Suzuki–Miyaura Coupling of Aryl Sulfones

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Supporting Information Placeholder

ABSTRACT: We describe conditions under which aryl sulfones act as electrophilic coupling partners in the palladium-catalyzed Suzuki–Miyaura cross-coupling (SMC) reaction. Sequential cross-coupling of arenes bearing sulfone, chloride and nitro leaving groups permits rapid access to non-symmetric terphenyls and quaterphenyls starting from common functional groups. Mechanistic experiments and DFT calculations are consistent with oxidative addition into the sulfone C–S bond as the turnover-limiting step.

The Suzuki–Miyaura coupling (SMC) reaction is one of the preferred methods to produce unsymmetrical biaryl compounds that are ubiquitous in bioactive molecules, agrochemicals and organic materials.¹ Boronic acids present many advantages as nucleophiles, due to their stability, ready availability and air- and moisture-tolerance. However, much effort has been made to find alternative to the typical electrophilic partners for the SMC reaction:^{2,3,4,5,6,7,8,9,10} aryl halides (Cl, Br, I) and pseudo-halides (OTs, OTf).¹¹ Due to their many uses in organic synthesis, sulfur-based functional groups are attractive as electrophiles for cross-coupling reactions,^{12,13,14} including the SMC reaction. Aryl sulfonyl chlorides are known electrophiles for the SMC reaction, but their electrophilicity and hydrolytic instability limits their utility and prevents their use with basic heterocycles.¹⁵ Sulfones are relatively common and robust functional groups that act as directing groups for *ortho*-metallation and selective *meta* and *para* functionalization.^{13,16,17,18} They have recently spiked interest in various cross-coupling reactions, but surprisingly, their application to the SMC reaction has so far only been described for the installation of benzylic, α -oxo vinyl, and tetrazolic groups (Scheme 1).^{19,20,21,22} Herein, we report the use of aryl-sulfones in the SMC coupling under relatively mild conditions. We find that aryl sulfones lie between aryl chlorides and nitroarenes on the SMC reactivity scale, making them an attractive option for the synthesis of complex polyaromatic molecules via sequential SMC reactions. This is particularly attractive because of the wide potential therapeutic applications of terphenyls (Figure 1).^{23,24,25}

Our initial experiments focused on identifying aryl-sulfones capable of acting as electrophilic coupling partners (Table 1). When RuPhos was used as ligand in the

presence of K₃PO₄, catalytic Pd(acac)₂, and a small amount of DMSO, diphenyl sulfone underwent coupling with 4-methoxyphenylboronic acid at 130 °C (entry 1). Phenyl methyl sulfone and its mono- and di-fluorinated analogs were not reactive (entry 2-4), but trifluoromethylphenyl sulfone underwent smooth coupling even at 80 °C (entry 5). The presence of DMSO as additive was found to be important for high yields (entry 6). Other additives capable of solubilizing the inorganic base had a similar, though lesser effect (entry 7), whereas water had a detrimental effect (entry 8). Bis-sulfoxides that could potentially act as ligands were not effective (entry 9). DMSO could not be used as the solvent (entry 10), but the reaction could be carried out efficiently in the absence of DMSO by using micellar water (entry 11).^{26,27} Related functional groups, such as trifluoromethyl sulfoxides or trifluoromethyl ketones, did not undergo coupling under these conditions (see Supporting Information).

Scheme 1. Suzuki–Miyaura cross-coupling (SMC) with sulfone electrophiles.

The optimized conditions were then applied to a variety of aryl CF₃ sulfones and aryl boronic acids (Table 2). Electron donating or withdrawing groups were well-tolerated on the boronic acid or on the sulfone. Coupling

was selective for sulfone moieties over nitro groups (**3**, **11**, **24–26**), which opens the possibility for sequential cross-coupling employing the recently disclosed nitro SMC reaction.² Sterically hindered boronic acids underwent cross-coupling in excellent yields (**8–10**, **18** and **22**). Thiophene boronic acids were also well-tolerated (**6** and **13**) although pyridine boronic acids did not react. 2-Fluoroaryl substitution on the sulfone partner did not impair reactivity (**21**, **23**, **24**). 2-Pyridyl sulfones also underwent cross-coupling in good yields (**27–30**). The main limitation of the scope occurs in the case of boronic acids bearing aldehyde groups, where cross-coupling occurred in lower yields in some cases (products **7**, **12** and **23**).

Figure 1. Biologically active teraryls.

Table 1. Evaluation of reaction parameters

entry	R	additive	Yield 1 (%) ^a
1	Ph	DMSO	14 ^b
2	CH ₃	DMSO	<1
3	CH ₂ F	DMSO	<1
4	CHF ₂	DMSO	<1
5	CF ₃	DMSO	95
6	CF ₃	-	55
7	CF ₃	H ₂ O ^c	38
8	CF ₃	HMPA	77
9	CF ₃	(PhSOCH ₂) ₂ ^d	5
10	CF ₃	-	<1 ^e
11	CF ₃	-	90 ^f

^aIsolated yield. ^b130 °C. ^c0.2% (v/v). ^d50 mol%. ^eDMSO as a solvent.

^fTPGS micelles in water as a solvent.

Taking advantage of the very different conditions required for cross-coupling of aryl chlorides (22 °C, using XPhos as ligand), aryl sulfones (80 °C, using RuPhos as ligand) and nitroarenes (130 °C, using BrettPhos as ligand), we developed a sequential SMC protocol for the synthesis of non-symmetric terphenyls and quaterphenyls (Scheme 2). SMC of the chloro group of a 2-chlorophenylsulfone with 3-nitrophenylboronic acid gave biphenyl **1a**, followed by SMC of the sulfone group with 4-*N*-carbazolephenylboronic acid to give terphenyl **1b**,

before a final SMC of the nitro group to afford quaterphenyl **1c**. Interestingly, using XPhos as ligand in place of RuPhos does not enable cross-coupling of sulfones at 80 °C (Table S1). Chloro, sulfone and nitro leaving groups can be differentiated on the same aryl ring, as evidenced by a chloro-selective SMC of 1-chloro-2-nitro-4-((trifluoromethyl)sulfonyl)benzene to give biphenyl **2a**, followed by a sulfone-selective SMC to give **2b**.

Table 2. Substrate scope

Scheme 2. Synthesis of non-symmetric terphenyls and quaterphenyls by taking advantage of the relative SMC reactivity: chloroarenes > sulfonylarene > nitroarenes. a: Pd(OAc)₂ (1 mol %), XPhos (3 mol%), K₃PO₄ (3 equiv), THF, rt, 17 h; b: standard conditions; c: Pd(acac)₂ (5 mol%), BrettPhos (20 mol%), 18-crown-6 (10 mol%), K₃PO₄ (3 equiv), dioxane, 130 °C, 48 h.

To gain insight into the mechanism, a stoichiometric reaction between (1,5-cyclooctadiene)bis(trimethylsilylmethyl)palladium, a Pd(0) precursor, and PhSO₂CF₃ in the presence of RuPhos was undertaken to isolate the reaction intermediate **X1** (eq 1). The X-ray crystal structure of **X1** revealed that after oxidative addition, the palladium is bound to the oxygen of the sulfinate, suggesting that the palladium complex rearranges, after oxidative addition into the C–S bond, to minimize dipole interactions in the apolar solvent used for crystallization. The structure is otherwise similar to what has been observed for oxidative addition to arylhalides²⁸ and nitroarenes², with the palladium in a square planar geometry. Extracting a typical crude reaction mixture (specifically, that described in Table 1, entry 5) in D₂O revealed the presence of trifluoromethanesulfinate as the only compound visible by ¹⁹F NMR. Therefore, although oxidative addition into sulfonyl chlorides is known to release SO₂ and chloride, here the leaving group remains intact as a trifluoromethanesulfinate.¹⁵

DFT calculations were also undertaken to investigate the reaction mechanism and complement our experimental observations. As oxidative addition is typically turnover-limiting in SMC reactions with challenging electrophiles,² the Gibbs energy profiles for the insertion of the catalyst into the C–S bonds of PhSO₂Ph and PhSO₂CF₃ were calculated using B3LYP-D3/def2-TZVP. The first step is the formation of a π -complex and is slightly favored for PhSO₂CF₃ (Figure 2). The Gibbs energy of the transition state corresponding to oxidative addition into the C–S bond has an activation energy for PhSO₂Ph that is 5.8 kcal/mol higher than for PhSO₂CF₃, consistent with the observed experimental trend for the overall catalytic reaction and coinciding with the increased polarization of the C–S bond in the latter case. Oxidative addition into the C–S bond therefore seems likely to be turnover-limiting. The S-bound Pd intermediate is close in energy to the observed O-bound XRD structure **X1**. The full computational details, structures, and a rendering of the transition state structure are included in Supporting Information.

Figure 2. Calculated Gibbs energies for the oxidative addition of sulfones to Pd(0)-RuPhos (kcal/mol).

In summary, we have described the Suzuki–Miyaura cross-coupling of arylsulfones, which involves a relatively rare oxidative addition of palladium into the C–S bond of a sulfone. Trifluoromethylsulfones display an intermediate level of cross-coupling reactivity between that of nitroarenes and aryl halides, enabling the facile synthesis of teraryls and quaterphenyls via sequential cross-coupling of these relatively common functional groups.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Experimental procedures and characterization, spectra (PDF), computational methods and coordinates.

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Notes

The authors declare no competing financial interests.

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