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Supporting Information For:

NHC Ligand-Powered Palladium-Catalyzed Carbonylative C-S Bond Cleavage of Vinyl Sulfides: Efficient Access to *tert*-Butyl Arylacrylates

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General Information

Unless otherwise noted, materials were purchased from commercial suppliers (Sigma-Aldrich, TCI, ABCR and Acros) and used without further purification. Flash column chromatography was performed using 200-300 mesh silica gel. ¹H NMR spectra were recorded on Bruker Avance III HD 300 NMR (300 MHz) or ARX 400 NMR(400 MHz) spectrometers spectrophotometers at ambient temperature. Chemical shifts are reported in ppm relative to tetra methylsilane (TMS) with the solvent resonance employed as the internal standard (CDCl₃: $\delta = 7.26$ ppm). ¹³C NMR was recorded at 75 MHz or 100 MHz: chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard (CDCl₃: $\delta = 77.0$ ppm). Data for ¹H are reported as follows: chemical shift(δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, m = multiplet, br = broad), coupling constant (Hz), and integration. Coupling constants are reported to 0.5 or 1 Hz accuracy. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). High resolution mass spectra (HR-MS) were recorded on Agilent 6210. The data were given as mass units per charge (m/z)Gas chromatography analysis was performed on an Agilent HP-5890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5 % phenyl groups, 30 m, 0.32 mm i.d., 0.25 µm film thickness) using argon as carrier gas. The preparation of Bis(arylvinyl)sulfides was carried out easily according to reported methods¹.

Table S1. Identification of the Optimal Reaction Conditions





 $\begin{array}{c} R^{1} & R^{3} & R^{3} & R^{1} \\ & & & \\ &$

Entry	[Pd]	Ligand	Base	Additive	Solvent	Т	CO	Yield(%)
						(°C)	(bar)	
1	Pd(OAc) ₂	PPh ₃	NaO ^t Bu	-	Toluene	120	1	-
2	Pd(OAc) ₂	PCy ₃	NaO ^t Bu	-	Toluene	120	1	-
3	Pd(OAc) ₂	$BuPAd_2$	NaO ^t Bu	-	Toluene	120	1	-
4	Pd(OAc) ₂	dppp	NaO ^t Bu	-	Toluene	120	1	trace
5	Pd(OAc) ₂	XantPhos	NaO ^t Bu	-	Toluene	120	1	-
6	Pd(OAc) ₂	DPEPhos	NaO ^t Bu	-	Toluene	120	1	trace
7	Pd(OAc) ₂	RuPhos	NaO ^t Bu	-	Toluene	120	1	-
8	Pd(OAc) ₂	XPhos	NaO ^t Bu	-	Toluene	120	1	-
9	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	-	Toluene	120	1	40
10	Pd(OAc) ₂	IMes·HCl	NaO ^t Bu	-	Toluene	120	1	38
11	Pd(OAc) ₂	Me IPr·HCl	NaO ^t Bu	-	Toluene	120	1	27
12	Pd(OAc) ₂	MeIMes·HCl	NaO ^t Bu	-	Toluene	120	1	31
13	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	-	Toluene	120	6	37
14	Pd(OAc) ₂	IPr·HCl	KO ^t Bu	-	Toluene	120	1	8
15	$Pd(OAc)_2$	IPr·HCl	LiO ^t Bu	-	Toluene	120	1	-
16	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	-	1,4-dioxane	120	1	trace
17	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	-	THF	120	1	trace
18	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	-	CH ₃ CN	120	1	-
19	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	-	DMF	120	1	-
20	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	-	DMAc	120	1	-
21	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	-	o-Xylene	120	1	41
22	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	FeCl ₃ 1 equiv	Toluene	120	1	trace
23	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	CuI 1 equiv	Toluene	120	1	-
24	Pd(OAc) ₂	IPr·HCl	NaO ^t Bu	LiOH 0.5 equiv	Toluene	120	1	34
25	Pd(dba) ₂	IPr·HCl	NaO ^t Bu	-	Toluene	120	1	32
26	PdCl ₂	IPr·HCl	NaO ^t Bu	-	Toluene	120	1	30
27	[Pd(allyl)Cl] ₂	IPr·HCl	NaO ^t Bu	-	Toluene	120	1	8
28	Pd-PEPPSI-	-	NaO'Bu	-	Toluene	120	1	45
	IPr							
29	Pd-PEPPSI-	-	NaO'Bu	-	Toluene	140	1	30
	IPr							
30	Pd-PEPPSI-	dppp	NaO ^t Bu	-	Toluene	120	1	72
	IPr							

General Procedure for Reductive Borylation of CO

A 4 mL screw-cap vial was charged with Pd-PEPPSI-IPr (5 mol%), dppp (5 mol%), bis(arylvinyl)sulfide (0.2 mmol), sodium *tert*-butoxide (0.4 mmol) and an oven-dried stirring bar. The vial was closed by Teflon septum and phenolic cap and connected with atmosphere with a needle. After flashed the vials with argon and vacuum three times, dry toluene (2 mL) was injected by syringe. The vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL) under argon atmosphere. At room temperature, the autoclave is flushed with carbon monoxide for three times and 1 bar of carbon monoxide was charged. The autoclave was reacted at 120°C for 16 hours. After the reaction had finished, the autoclave was cooled down to room temperature and flushed with nitrogen for three times. The reaction mixture was diluted with DCM and passed through a short pad of Celite. After evaporation of the solvent, the residue was adsorbed on silica gel and the crude product was purified by column chromatography using *n*-pentane/diethyl ether.

tert-(E)-Butyl cinnamate (2a)²

Yellow oil (26.5 mg, 65% yield). ¹**H NMR** (300 MHz, CDCl₃)δ 7.59 (d, *J* = 16.0 Hz, 1H), 7.53 – 7.48 (m, 2H), 7.39 – 7.33 (m, 3H), 6.37 (d, *J* = 16.0 Hz, 1H), 1.54 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃)δ 166.3, 143.5, 134.7, 130.0, 128.8, 128.0, 120.2, 80.5, 28.2. **GC-MS** (EI, 70 eV): m/z (%) = 204 (10), 147 (100), 131 (70), 103 (40), 77 (35).

tert-Butyl (E)-3-(p-tolyl) acrylate (2b)²

Yellow oil (19.6 mg, 45% yield). ¹**H NMR** (300 MHz, CDCl₃)δ 7.56 (d, *J* = 16.0 Hz, 1H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.32 (d, *J* = 16.0 Hz, 1H), 2.36 (s, 3H). ¹³**C NMR** (75 MHz, CDCl₃)δ 166.6, 143.6, 140.3, 131.9, 129.6, 128.0, 119.1, 80.4, 28.2, 21.4. **GC-MS** (EI, 70 eV): m/z (%)=218 (15), 162 (100), 145 (60), 115 (55), 91 (25), 57 (25).

tert-Butyl (E)-3-(3,5-dimethylphenyl) acrylate (2c)³

O^tBu

Yellow oil (20.9 mg, 45% yield). ¹**H NMR** (400 MHz, CDCl₃)δ7.53 (d, *J* = 16.0 Hz, 1H), 7.12 (s, 2H), 7.00 (s, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 2.32 (s, 6H), 1.53 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃)δ166.5, 143.8, 138.3, 134.6, 131.7, 125.8, 119.8, 80.3, 28.2, 21.2. **GC-MS** (EI, 70 eV): m/z (%) = 232 (20), 176 (70), 161 (100), 115 (35).

tert-Butyl (E)-3-(2-fluorophenyl) acrylate (2d)⁴

Yellow oil (20.7 mg, 47% yield). ¹**H NMR** (400 MHz, CDCl₃) δ 7.72 (d, J = 16.0 Hz, 1H), 7.52 (td, J = 7.5, 1.5 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.14 (td, J = 7.5, 1.5 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.46 (d, J = 16.0 Hz, 1H), 1.54 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃) δ 166.1, 161.3 (d, J = 253.5 Hz), 136.1 (d, J = 3.0 Hz), 131.3 (d, J = 9.0 Hz), 129.0 (d, J = 3.0 Hz), 124.4 (d, J = 4.0 Hz), 122.8 (d, J = 6.5 Hz), 122.7 (d, J = 12.5 Hz), 116.1 (d, J = 22.0 Hz), 80.7, 28.2. **GC-MS** (EI, 70 eV): m/z (%) = 222 (10), 166 (60), 149 (100), 118 (70), 101 (70), 75 (35), 57 (75).

tert-Butyl (E)-3-(3-fluorophenyl) acrylate (2e)⁴



Yellow oil (23.5 mg, 53% yield). ¹**H NMR** (300 MHz, CDCl₃) δ 7.53 (d, J = 16.0 Hz, 1H), 7.34 (td, J = 8.0, 5.5 Hz, 1H), 7.29 – 7.24 (m, 1H), 7.23 – 7.17 (m, 1H), 7.09 – 7.01 (m, 1H), 6.36 (d, J = 16.0 Hz, 1H), 1.53 (s, 9H). ¹³C NMR (75 MHz, CDCl₃) δ 165.9, 163.0 (d, J = 246.4 Hz), 142.1 (d, J = 2.7 Hz), 136.9 (d, J = 7.9 Hz), 130.4 (d, J = 8.2 Hz), 123.9 (d, J = 2.8 Hz), 121.6, 116.8 (d, J = 21.5 Hz), 114.2 (d, J = 21.7 Hz), 80.8, 28.2. **GC-MS** (EI, 70 eV): m/z (%) = 222 (10), 166 (75), 149 (100), 121 (40), 101 (55), 75 (25), 57 (75).

tert-Butyl (E)-3-(2-chlorophenyl) acrylate (2f)⁵



Yellow oil (30.4 mg, 64% yield). ¹**H NMR** (400 MHz, CDCl₃)δ 8.00 (d, *J* = 16.0 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.45 – 7.38 (m, 1H), 7.31 – 7.23 (m, 2H), 6.36 (d, *J* = 16.0 Hz, 1H), 1.54 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃)δ 165.8, 139.3, 134.8, 132.9, 130.7, 130.1, 127.6, 127.0, 122.8, 80.8, 28.2. **GC-MS** (EI, 70 eV): m/z (%) = 238 (5), 182 (10), 165 (35), 147 (100), 101 (30), 57 (40).

tert-Butyl (E)-3-(4-chlorophenyl) acrylate $(2g)^2$

White solid (30.2 mg, 63% yield). ¹**H NMR** (300 MHz, CDCl₃) δ 7.53 (d, J = 16.0 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.37 – 7.30 (m, 2H), 6.34 (d, J = 16.0 Hz, 1H), 1.53 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃) δ 166.1, 142.1, 135.8, 133.2, 129.1, 120.8, 80.7, 28.2. **GC-MS** (EI, 70 eV): m/z(%) = 238 (10), 182 (100), 165 (60), 137 (20), 102 (35), 57 (45).

tert-Butyl (E)-3-(3,4-dichlorophenyl) acrylate (2h)⁶

White solid (35.4 mg, 65% yield). ¹**H NMR** (300 MHz, CDCl₃)δ 7.58 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 16.0 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.32 (dd, *J* = 8.5, 2.0 Hz, 1H), 6.35 (d, *J* = 16.0 Hz, 1H), 1.53 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃)δ 165.6, 140.8, 134.7, 133.8, 133.2, 130.8, 129.5, 126.9, 122.1, 81.0, 28.2. **GC-MS** (EI, 70 eV): m/z (%) = 272 (10), 216 (100), 199 (55), 136 (45), 57 (55).

tert-Butyl (E)-3-(4-(trifluoromethyl)phenyl) acrylate (2i)²

Colorless oil (30.2 mg, 55% yield). ¹**H NMR** (300 MHz, CDCl₃) δ 7.66 – 7.55 (m, 5H), 6.44 (d, *J* = 16.0 Hz, 1H), 1.54 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃) δ 165.7, 141.6, 138.1, 131.5 (d, *J* = 32.5 Hz), 128.0, 125.8 (q, *J* = 3.8 Hz), 123.9 (d, *J* = 272.0 Hz), 122.8, 81.0, 28.2. **GC-MS** (EI, 70 eV): m/z (%) = 272 (5), 217 (45), 199 (100), 171 (30), 151 (70), 57 (85), 41 (40).

tert-Butyl (E)-3-(naphthalen-1-yl) acrylate (2j)⁴



Colorless oil (34.1 mg, 67% yield). ¹**H NMR** (300 MHz, CDCl₃) δ 8.44 (d, *J* = 16.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.84 (m, 2H), 7.74 (d, *J* = 7.0 Hz, 1H), 7.60 – 7.42 (m, 3H), 6.47 (d, *J* = 16.0 Hz, 1H), 1.59 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃) δ 166.2, 140.6, 133.7, 132.1, 131.4, 130.2, 128.7, 126.7, 126.2, 125.5, 124.9, 123.5, 122.9, 80.6, 28.3. **GC-MS** (EI, 70 eV): m/z (%) = 254 (15), 198 (25), 181 (20), 153 (100).

tert-Butyl (E)-3-(naphthalen-2-yl) acrylate (2k)⁶



Colorless oil (27.2 mg, 53% yield).¹**H NMR** (300 MHz, CDCl₃) δ 7.91 (s, 1H), 7.87 – 7.80 (m, 3H), 7.76 (d, *J* = 16.0 Hz, 1H), 7.66 (dd, *J* = 8.5, 1.5 Hz, 1H), 7.56 – 7.46 (m, 2H), 6.50 (d, *J* = 16.0 Hz, 1H), 1.57 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃) δ 166.3, 143.5, 134.1, 133.3, 132.1, 129.6, 129.5, 128.6, 128.5, 127.7, 127.0, 126.6, 123.6, 120.4, 80.5, 28.2. **GC-MS** (EI, 70 eV): m/z (%) = 254 (20), 198 (100), 181 (35), 152 (60).

tert-Butyl (E)-3-(thiophen-3-yl) acrylate $(2l)^8$



Yellow oil (29.9 mg, 71% yield). ¹**H NMR** (300 MHz, CDCl₃) δ 7.57 (d, J = 15.9 Hz, 1H), 7.51 – 7.41 (m, 1H), 7.35 – 7.30 (m, 1H), 7.29 – 7.24 (m, 1H), 6.19 (d, J = 15.9 Hz, 1H), 1.52 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃) δ

166.6, 137.1, 129.5, 127.4, 126.8, 125.2, 119.9, 80.4, 28.2.**GC-MS** (EI, 70 eV): m/z (%) = 210 (20), 154 (100), 137 (70), 112 (40), 57 (35).

tert-Butyl (E)-3-(pyridin-3-yl) acrylate (2m)⁸

Colorless oil (27.6 mg, 67% yield) ¹**H NMR** (300 MHz, CDCl₃) δ 8.71 (d, J = 2.5 Hz, 1H), 8.57 (dd, J = 5.0, 1.5 Hz, 1H), 7.80 (dt, J = 8.0, 2.0 Hz, 1H), 7.55 (d, J = 16.0 Hz, 1H), 7.30 (dd, J = 8.0, 5.0 Hz, 1H), 6.42 (d, J = 16.0 Hz, 1H), 1.53 (s, 9H). ¹³**C NMR** (75 MHz, CDCl₃) δ 165.5, 150.7, 149.6, 139.7, 134.1, 130.4, 123.6, 122.4, 80.9, 28.1. **GC-MS** (EI, 70 eV): m/z (%) = 212 (100), 178 (40), 167 (25), 134 (30), 121 (30), 91 (30), 77 (50).

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NMR Spectra of products: ¹H, ¹³C NMR

















S15





S17





