Electronic Supplementary Information for:

One-pot Suzuki-Heck relay to prepare industrially valuable intermediates using the Pd-Cy*Phine catalyst system

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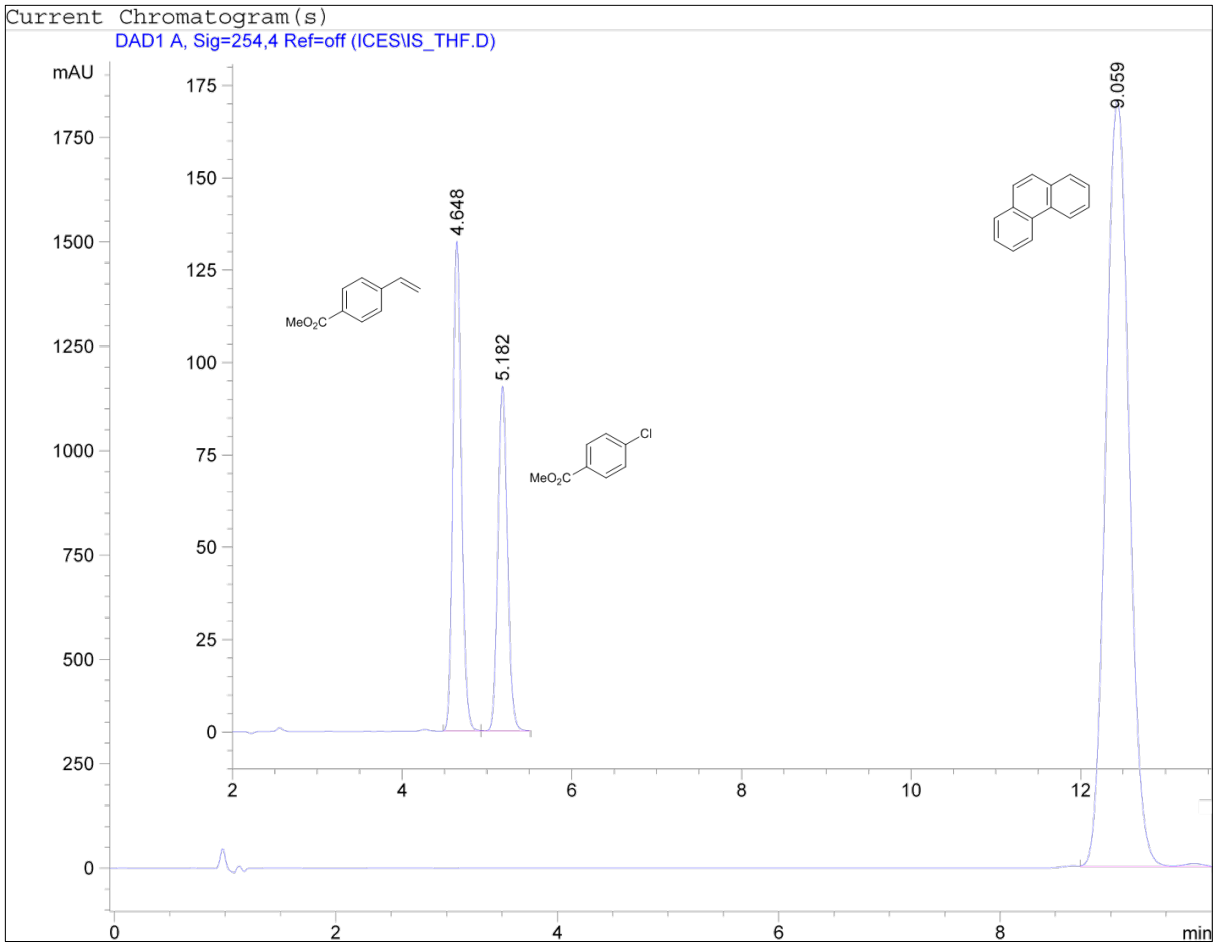
Table of Contents

Experimental:

General methods and materials. All reactions were performed under nitrogen atmosphere in a glovebox. Commercial reagents were purchased from Aldrich and used without further purification; solvents were obtained from a solvent purification system (< 2.0 ppm of H_2O) and acetonitrile was dried by refluxing over CaH_2, distilled and further dried over activated Al_2O_3. Solid bases and boron reagents were dispensed by Unchained Labs' Freeslate system using the SV-vial technology, with the exception of the vinylboronic anhydride complex, which was weighted out manually; liquid reagents and solutions were dispensed by pipette. Reactions were conducted in 1.2 mL glass shell vials equipped with parylene-coated stir bars in 96-well aluminum plates, which were sealed with a PFA sheet, rubber gasket, and top stainless steel plate. HPLC analysis was performed on an Agilent 1100 system equipped with a DAD detector, GC-FID analysis on an Agilent 6850 instrument, and GC/MS analysis on an Agilent 6890/5975 instrument. ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on a 400 MHz Bruker Avance instrument at room temperature (21−25°C). NMR spectra were referenced to the residual proton peaks associated with the deuterated solvents (for ^{1}H NMR, $CDCl_3$: 7.26 ppm and for ^{13}C NMR, $CDCl_3$: 77.16 ppm). ^{19}F NMR spectra were referenced to internal 1,3-bis(trifluoromethyl)benzene (BTB) (Aldrich, 99%, deoxygenated by purging with nitrogen, stored over activated 4 Å molecular sieves), set to −63.5 ppm. For electron impact high-resolution mass spectra (HRMS-EI), solid samples were prepared by drying products under vacuum, and a Kratos Concept S1 (Hres 7000−10000) mass spectrometer was used.

General procedure for Suzuki coupling: Substrate concentration was 0.25 M, with 1.2 equivalents of boron coupling reagent (0.4 equivalents for the vinylboronic anhydride complex) and 2.0 equivalents of base. Phenanthrene was used as internal standard, and the catalyst solution was prepared in toluene at room temperature. The plate was sealed and heated/stirred at 90 °C for 12 hours. After cool-down, aliquots of 10 uL were flushed through silica on a multi-well filtration plate with a 50:50 MeCN:MeOH solution to a total volume of about 800 uL.

For Suzuki coupling with methyl-4-chlorobenzoate, samples were analyzed by HPLC [Zorbax Extend C8 column (4.6 x 150 mm), THF:H_2O 40:60 at 1.5 mL/min, detection at 254 nm, column temperature of 30 °C];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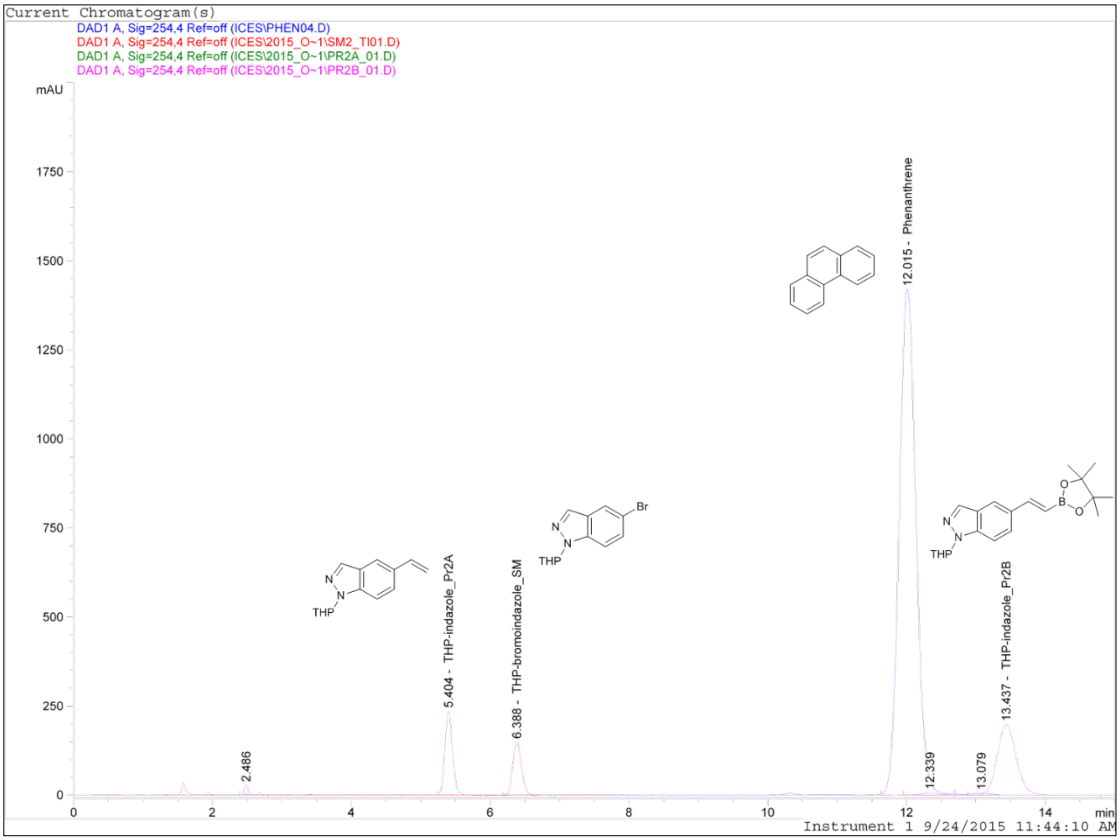
MeO2C
Cl
min

For Suzuki coupling with 5-bromo-1-(tetrahydro-pyran-2-yl)-1*H*-indazole), substrate **4a** was prepared according to a previously reported procedure[1]; samples were analyzed by HPLC [Zorbax Extend C8 column (4.6 x 150 mm), MeCN:H_2O 50:50 at 1.5 mL/min, detection at 254 nm, column temperature of 30 °C];



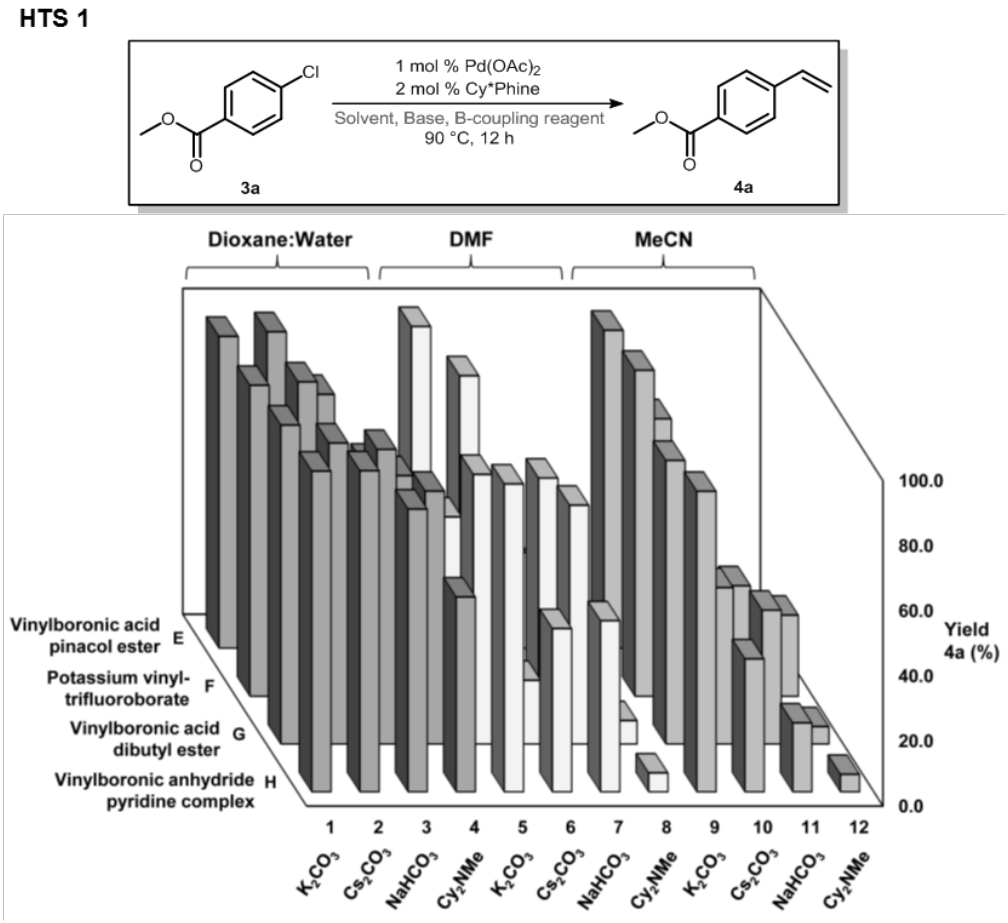
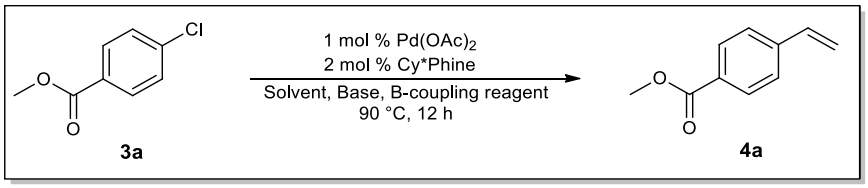


Figure S1. Solvent, base and vinylic boron reagent optimization for **HTS 1**. Reaction conditions: **3a** (0.125 mmol), boron reagent (0.150 mmol), base (0.250 mmol), solvent (475 μL). Pd-Cy*Phine catalyst (25 μL). Yields were calculated by HPLC using phenanthrene as the internal standard.

Table S1: Product yields for Suzuki coupling of methyl-4-chlorobenzoate (**3a**)



Entry	Reaction Vials	Solvent	Coupling reagent	Base	Yield 4a (%)	Starting Material 3a (%)
1	*E1*	Dioxane:H_2O	Vinylboronic acid pinacol ester	K_2CO_3	95.7	
2	*E2*			Cs_2CO_3	97.1	
3	*E3*			$NaHCO_3$	77.9	14.2
4	*E4*			Cy_2NMe	56.8	29.7
5	*F1*		Potassium vinyltrifluoroborate	K_2CO_3	95.4	
6	*F2*			Cs_2CO_3	96.4	
7	*F3*			$NaHCO_3$	54.5	36.5
8	*F4*			Cy_2NMe	67.7	29.2
9	*G1*		Vinylboronic acid dibutyl ester	K_2CO_3	97.9	
10	*G2*			Cs_2CO_3	92.4	
11	*G3*			$NaHCO_3$	90.5	
12	*G4*			Cy_2NMe	77.6	
13	*H1*		Vinylboronic anhydride pyridine complex	K_2CO_3	98.6	
14	*H2*			Cs_2CO_3	98.7	
15	*H3*			$NaHCO_3$	86.9	6.1
16	*H4*			Cy_2NMe	59.9	30.7
17	*E5*	DMF	Vinylboronic acid pinacol ester	K_2CO_3	98.7	
18	*E6*			Cs_2CO_3	83.6	
19	*E7*			$NaHCO_3$	29.4	54.3
20	*E8*			Cy_2NMe	3.6	86.7
21	*F5*		Potassium vinyltrifluoroborate	K_2CO_3	55.0	29.2
22	*F6*			Cs_2CO_3	8.0	55.2
23	*F7*			$NaHCO_3$	66.9	26.4
24	*F8*			Cy_2NMe	21.7	59.9
25	*G5*		Vinylboronic acid dibutyl ester	K_2CO_3	82.8	
26	*G6*			Cs_2CO_3	19.6 (55.0)[1]	
27	*G7*			$NaHCO_3$	73.3	
28	*G8*			Cy_2NMe	7.2	76.9
29	*H5*		Vinylboronic anhydride pyridine complex	K_2CO_3	94.6	
30	*H6*			Cs_2CO_3	50.2	13.8
31	*H7*			$NaHCO_3$	52.6	36.3
32	*H8*			Cy_2NMe	5.8	88.1
33	*E9*	MeCN	Vinylboronic acid pinacol ester	K_2CO_3	97.6	
34	*E10*			Cs_2CO_3	70.4	
35	*E11*			$NaHCO_3$	4.5	97.5
36	*E12*			Cy_2NMe	3.6	90.4
37	*F9*		Potassium vinyltrifluoroborate	K_2CO_3	100.4	
38	*F10*			Cs_2CO_3	7.3	35.0
39	*F11*			$NaHCO_3$	33.9	34.0
40	*F12*			Cy_2NMe	24.9	74.9
41	*G9*		Vinylboronic acid dibutyl ester	K_2CO_3	87.1	
42	*G10*			Cs_2CO_3	48.0 (30.4)[2]	
43	*G11*			$NaHCO_3$	41.1	40.5

44	*G12*			Cy_2NMe	5.4	83.6
45	*H9*		Vinylboronic anhydride pyridine complex	K_2CO_3	92.4	
46	*H10*			Cs_2CO_3	40.9	
47	*H11*			$NaHCO_3$	21.3	70.6
48	*H12*			Cy_2NMe	5.4	88.6

[1] *Estimated yield for 4-vinyl-benzoic acid butyl ester*

4-vinyl benzoic acid butyl ester was observed in two of the reactions (*Table S1,* entries *26* and *42*), both involving the vinylboronic acid dibutyl ester and Cs_2CO_3 in MeCN and DMF – identification established by GC/MS analysis.

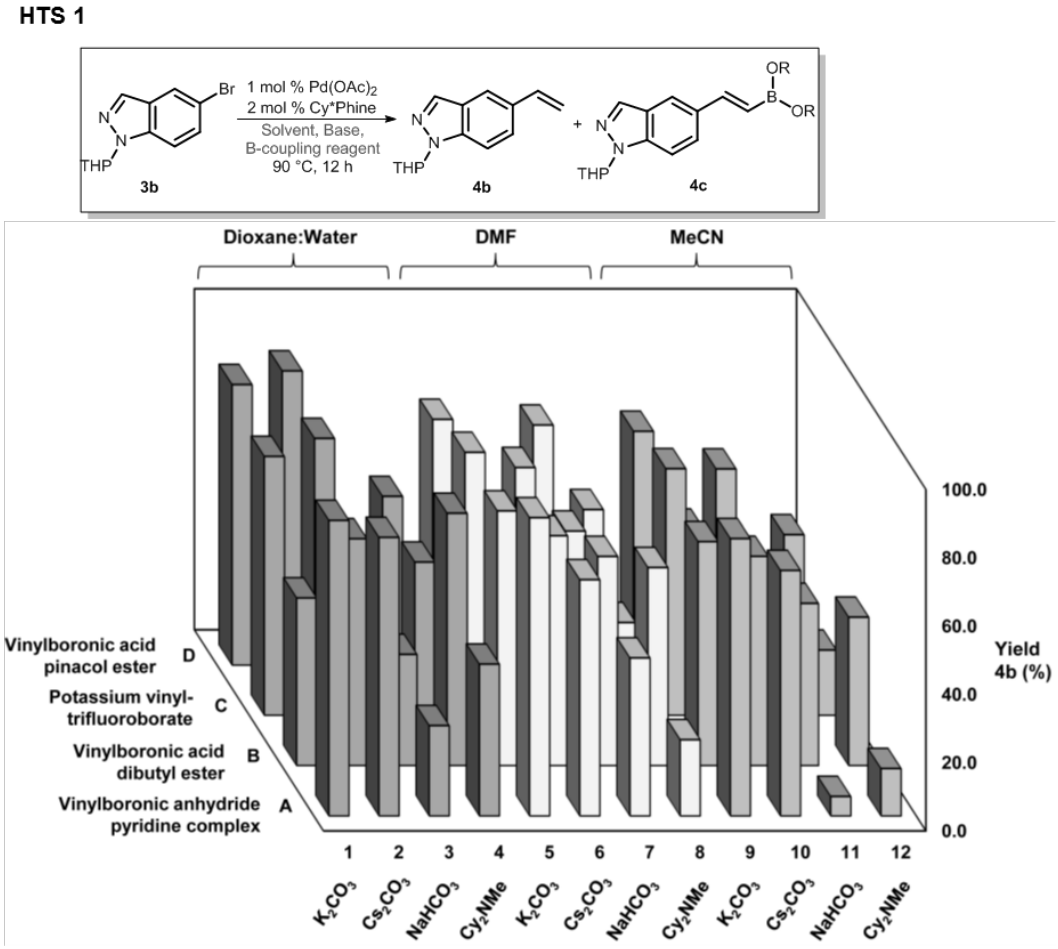
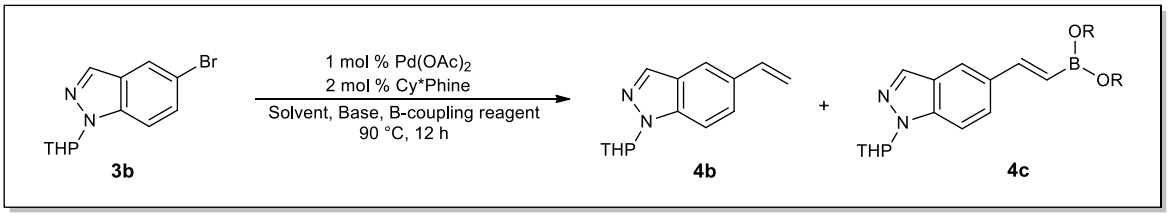


Figure S2. Solvent, base and vinylic boron reagent optimization for **HTS 1**. Reaction conditions: **3b** (0.125 mmol), boron reagent (0.150 mmol), base (0.250 mmol), solvent (475 μL). Pd-Cy*Phine catalyst (25 μL). Yields were calculated by HPLC using phenanthrene as the internal standard and quantified through the calibration curves.

Table S2: Product yields for Suzuki coupling of 5-bromo-1-(tetrahydro-pyran-2-yl)-1H-indazole (**3b**)



Entry	Reaction Vials	Solvent	Coupling reagent	Base	Yield 4b (%)[1]	Starting material 3b (%)
1	*A1*	Dioxane:H_2O	Vinylboronic acid pinacol ester	K_2CO_3	86.5	
2	*A2*			Cs_2CO_3	81.5	
3	*A3*			$NaHCO_3$	26.4	28.1
4	*A4*			Cy_2NMe	44.4	
5	*B1*		Potassium vinyltrifluoroborate	K_2CO_3	49.1	
6	*B2*			Cs_2CO_3	66.4	
7	*B3*			$NaHCO_3$	32.5	31.6
8	*B4*			Cy_2NMe	73.9	
9	*C1*		Vinylboronic acid dibutyl ester	K_2CO_3	75.9	
10	*C2*			Cs_2CO_3	81.2	
11	*C3*			$NaHCO_3$	34.3	16.1
12	*C4*			Cy_2NMe	44.9	
13	*D1*		Vinylboronic anhydride pyridine complex	K_2CO_3	82.2	
14	*D2*			Cs_2CO_3	86.2	
15	*D3*			$NaHCO_3$	33.6	
16	*D4*			Cy_2NMe	49.4	
17	*A5*	DMF	Vinylboronic acid pinacol ester	K_2CO_3	87.3	
18	*A6*			Cs_2CO_3	69.1	
19	*A7*			$NaHCO_3$	46.2	
20	*A8*			Cy_2NMe	22.2	
21	*B5*		Potassium vinyltrifluoroborate	K_2CO_3	74.6	
22	*B6*			Cs_2CO_3	67.3	
23	*B7*			$NaHCO_3$	61.3	
24	*B8*			Cy_2NMe	58.0	
25	*C5*		Vinylboronic acid dibutyl ester	K_2CO_3	77.1	
26	*C6*			Cs_2CO_3	72.6	
27	*C7*			$NaHCO_3$	54.0	
28	*C8*			Cy_2NMe	27.2	
29	*D5*		Vinylboronic anhydride pyridine complex	K_2CO_3	72.0	
30	*D6*			Cs_2CO_3	31.1	
31	*D7*			$NaHCO_3$	70.4	
32	*D8*			Cy_2NMe	45.6	
33	*A9*	MeCN	Vinylboronic acid pinacol ester	K_2CO_3	81.2	
34	*A10*			Cs_2CO_3	71.8	
35	*A11*			$NaHCO_3$	5.6	61.3
36	*A12*			Cy_2NMe	13.8	14.3
37	*B9*		Potassium vinyltrifluoroborate	K_2CO_3	65.6	20.0
38	*B10*			Cs_2CO_3	61.3	
39	*B11*			$NaHCO_3$	47.5	28.7
40	*B12*			Cy_2NMe	43.5	50.8
41	*C9*		Vinylboronic acid	K_2CO_3	72.3	

42	*C10*		dibutyl ester	Cs_2CO_3	72.2	
43	*C11*			$NaHCO_3$	17.2	31.7
44	*C12*			Cy_2NMe	19.1	
45	*D9*		Vinylboronic anhydride pyridine complex	K_2CO_3	68.5	
46	*D10*			Cs_2CO_3	39.9	
47	*D11*			$NaHCO_3$	19.1	64.9
48	*D12*			Cy_2NMe	38.2	

[1]*Does not include values for* ***4c*** *for entries 1-4, 17-18, 33-36*

General procedure for Suzuki-Heck Relay (SHR) reaction: Substrate concentration was 0.25 M, with 1.01 equivalent of boron coupling reagent (0.33 equivalents for the vinylboronic anhydride complex). For combinations involving a single base, 5.0 equivalents were added at the beginning; for dual base combinations, 2.0 equivalents of each base were added at each step. Phenanthrene was used as internal standard, and the catalyst solution was prepared in toluene at room temperature. The plate was sealed and heated/stirred at 90 °C overnight. 1.1 equivalent of 3-chloropyridine and Cy_2NMe were added as required. The plate was re-sealed and heated/stirred at 120 °C overnight. After cool-down, aliquots of 10 uL were flushed through silica on a multi-well filtration plate with a 50:50 MeCN:MeOH solution to a total volume of about 500 uL. An additional equivalent of the catalyst solution was added to the reactions and the plate was run once again overnight at 120 °C, after which a second set of aliquots was filtered/diluted. Reactions were analyses by GC-FID [inlet = 250 °C; split ratio = 50:1; inlet pressure = 13.0 psi; oven initial temperature = 65 °C, program holds initial temperature for 0.5 minute, then ramp (40 °C/min) to 150 °C, held for 0.5 minute, ramp (45 °C/min) to 250 °C, held for 2.5 minutes, ramp (45 °C/min) to 275 °C, held for 1.5 minutes (total runtime of 9.91 minutes); detector temperature = 275 °C];

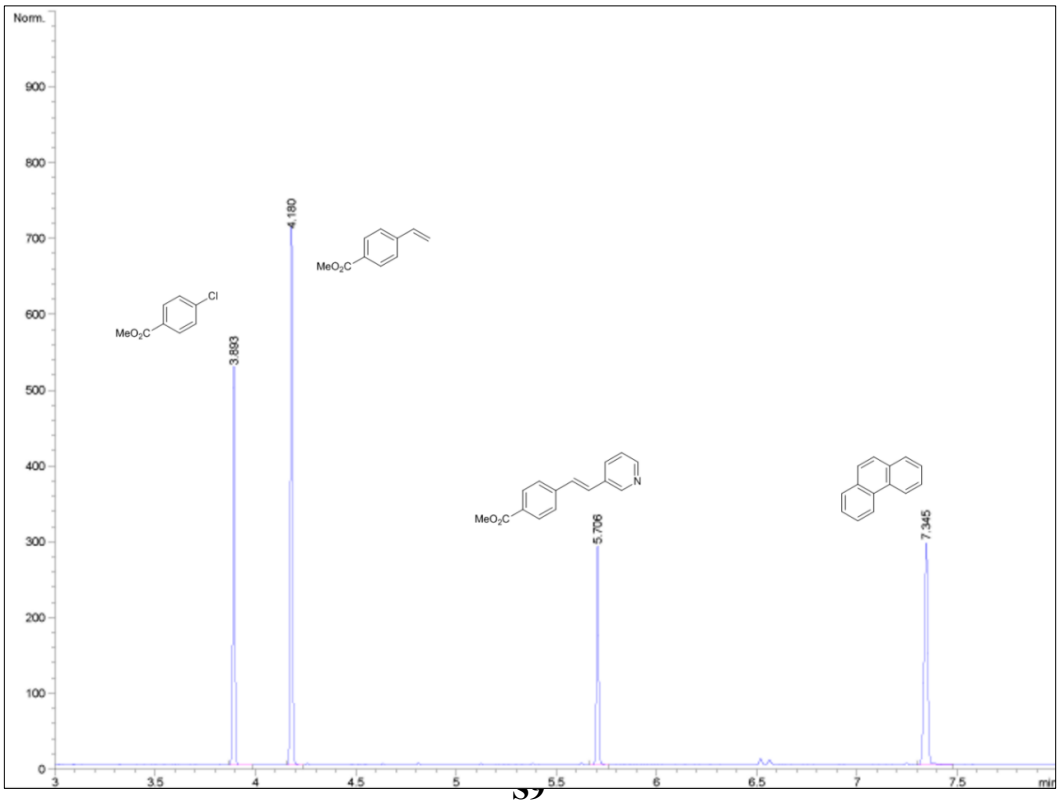
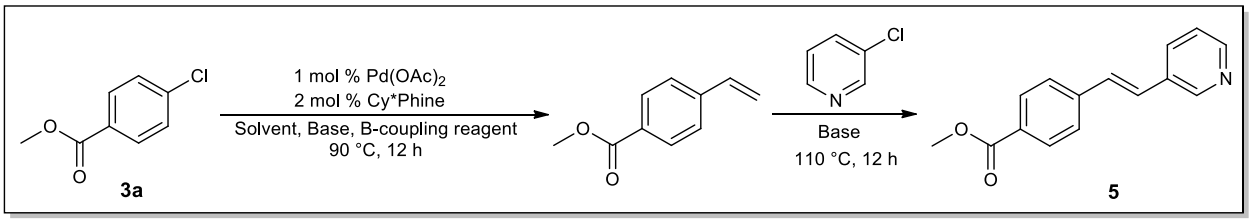


Table S3: Product yields for the Suzuki-Heck relay reaction of methyl-4-chlorobenzoate with 3-chloropyridine

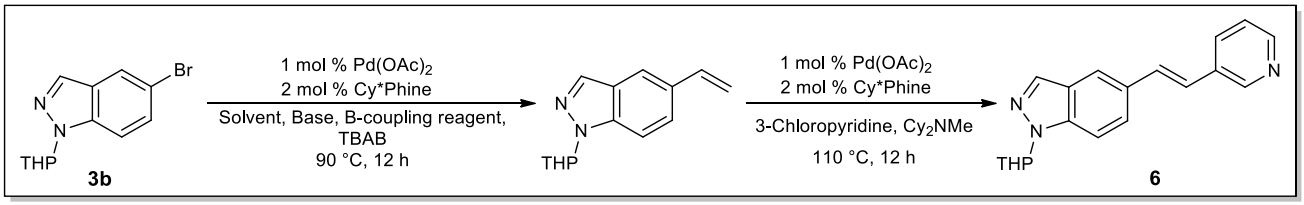


Entry	Reaction vial	Solvent	Coupling reagent	Base	Yield 5 (%)	Yield 5′ (%)
1	*A1*	**Dioxane**	Vinylboronic acid pinacol ester	K_2CO_3	-	11.0
2	*B1*			K_2CO_3, Cy_2NMe	10.8	25.3
3	*C1*			$NaHCO_3$	16.4	26.7
4	*D1*			$NaHCO_3$, Cy_2NMe	11.9	62.8
5	*E1*			Cs_2CO_3, Cy_2NMe	20.7	29.9
6	*F1*			Cy_2NMe	3.0	-
7	*A2*		Potassium vinyltrifluoroborate	K_2CO_3	-	18.2
8	*B2*			K_2CO_3, Cy_2NMe	8.2	-
9	*C2*			$NaHCO_3$	17.5	13.4
10	*D2*			$NaHCO_3$, Cy_2NMe	9.9	68.1
11	*E2*			Cs_2CO_3, Cy_2NMe	-	24.8
12	*F2*			Cy_2NMe	14.1	-
13	*A3*		Vinylboronic acid dibutyl ester	K_2CO_3	-	30.0
14	*B3*			K_2CO_3, Cy_2NMe	-	30.0
15	*C3*			$NaHCO_3$	10.5	53.9
16	*D3*			$NaHCO_3$, Cy_2NMe	19.0	42.1
17	*F3*			Cy_2NMe	-	15.1
18	*A4*		Vinylboronic anhydride pyridine complex	K_2CO_3	10.9	43.8
19	*B4*			K_2CO_3, Cy_2NMe	71.7	92.5
20	*C4*			$NaHCO_3$	-	22.5
21	*D4*			$NaHCO_3$, Cy_2NMe	9.5	34.4
22	*E4*			Cs_2CO_3, Cy_2NMe	-	12.9
23	*F4*			Cy_2NMe	7.8	19.6
24	*A5*	**DMF**	Vinylboronic acid pinacol ester	K_2CO_3	5.2	8.4
25	*B5*			K_2CO_3, Cy_2NMe	25.9	70.3
26	*C5*			$NaHCO_3$	64.4	70.4
27	*D5*			$NaHCO_3$, Cy_2NMe	69.5	75.8
28	*E5*			Cs_2CO_3, Cy_2NMe	14.8	25.1
29	*A6*		Potassium vinyltrifluoroborate	K_2CO_3	11.8	20.2
30	*B6*			K_2CO_3, Cy_2NMe	16.3	40.5
31	*C6*			$NaHCO_3$	11.8	32.7
32	*D6*			$NaHCO_3$, Cy_2NMe	19.0	36.5
33	*F6*			Cy_2NMe	5.9	12.1
34	*A7*		Vinylboronic acid dibutyl ester	K_2CO_3	-	-
35	*B7*			K_2CO_3, Cy_2NMe	6.8	27.6
36	*C7*			$NaHCO_3$	50.8	79.5
37	*D7*			$NaHCO_3$, Cy_2NMe	38.0	72.0
38	*A8*		Vinylboronic anhydride pyridine complex	K_2CO_3	6.9	43.4
39	*B8*			K_2CO_3, Cy_2NMe	61.1	87.5
40	*C8*			$NaHCO_3$	31.1	75.1

41	*D8*			$NaHCO_3$, Cy_2NMe	23.3	56.2
42	*E8*			Cs_2CO_3, Cy_2NMe	28.6	37.5
43	*A9*	**Acetonitrile**	Vinylboronic acid pinacol ester	K_2CO_3	-	-
44	*B9*			K_2CO_3, Cy_2NMe	-	12.2
45	*E9*			Cs_2CO_3, Cy_2NMe	-	10.3
46	*A10*		Potassium vinyltrifluoroborate	K_2CO_3	-	5.7
47	*B10*			K_2CO_3, Cy_2NMe	3.5	16.5
48	*C10*			$NaHCO_3$	47.0	69.7
49	*D10*			$NaHCO_3$, Cy_2NMe	18.3	34.4
50	*F10*			Cy_2NMe	-	11.3
51	*A11*		Vinylboronic acid dibutyl ester	K_2CO_3	-	-
52	*B11*			K_2CO_3, Cy_2NMe	-	13.2
53	*C11*			$NaHCO_3$	61.1	70.3
54	*D11*			$NaHCO_3$, Cy_2NMe	44.1	55.6
55	*A12*		Vinylboronic anhydride pyridine complex	K_2CO_3	-	4.8
56	*B12*			K_2CO_3, Cy_2NMe	33.4	62.0
57	*C12*			$NaHCO_3$	35.6	57.9
58	*D12*			$NaHCO_3$, Cy_2NMe	22.7	42.7
59	*E12*			Cs_2CO_3, Cy_2NMe	4.5	9.6

4-vinyl benzoic acid butyl ester was observed in three of the reactions (*Table S3,* entries *3, 7,* and *11)*; the corresponding Suzuki-Heck product was only observed in the case of entry 3 (confirmed by GC/MS). Yield **5'** (%) = increased yield (%) of compound **5** after addition of more catalyst**.**

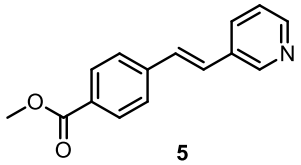
Table S4: Conversion values for the Suzuki-Heck relay reaction of 5-bromo-1-(tetrahydropyran-2-yl)-1H-indazole with 3-chloropyridine



Entry	Bases	Solvent	Coupling reagent	GC/MS conversion (%)
1	K_2CO_3/Cy_2NMe	DMF	Vinylboronic anhydride pyridine complex	91
2		Dioxane	Vinylboronic anhydride pyridine complex	89
3		DMF	Vinylboronic acid pinacol ester	92

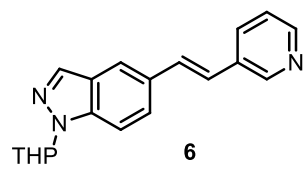
Representative procedure for scale-up Suzuki-Heck Relay (SHR) reaction: An 8 ml vial fitted with a Teflon-lined septum and a magnetic stir bar was charged with aryl halide (0.5 mmol, 1 equiv.), vinylboronic anhydride pyridine complex (0.165 mmol, 0.33 equiv.), K_2CO_3 (1 mmol, 2 equiv.), TBAB (0.1 mmol, 0.2 equiv.), DMF (1.9 mL), Pd-Cy*Phine catalyst (100 μL, 1 mol% $Pd(OAc)_2$ + 2 mol% Cy*Phine) [the catalyst solution was prepared *in situ* by dissolving $Pd(OAc)_2$ (12 mg, 0.05 mmol) and Cy*Phine (52 mg, 0.1 mmol) in toluene (1000 μL)]. The vial was sealed and then heated at 90 °C for 12 h. An aliquot of the reaction mixture was sampled for GC-MS analysis to determine the Suzuki completion. To the same vial, aryl halide (0.55 mmol, 1.1 equiv.) and Cy_2NMe (1 mmol, 2 equiv.) and Pd-Cy*Phine catalyst (100 μL) were added. The vial was sealed and allowed to heat at 110 °C for another 12 h. The completion of the Heck reaction was confirmed by GC/MS analysis. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and the solution was transferred to a separatory funnel (150 mL). The dilute solution was then washed with water (3 × 15 mL) and dried over anhydrous $MgSO_4$. CH_2Cl_2 was removed *in vacuo* to afford the crude mixture which was finally purified by flash chromatography to obtain the desired product.

(*E*)-Methyl 4-(2-(pyridin-3-yl)vinyl)benzoate (5): off-white solid, yield (78%). The spectroscopic data (^{1}H and ^{13}C NMR) of **5** are identical to those reported in literature.[2] HRMS (EI) calcd for $C_{15}H_{13}NO_2^+$ $[M]^+$: 239.0946, found: 239.0939.



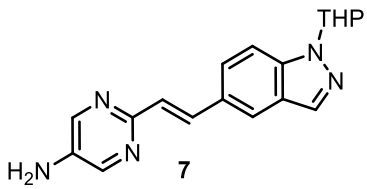
5

(*E*)-1-(tetrahydropyran-2-yl)-(2-(pyridine-3-yl)vinyl)-1H-indazole (6): brown solid, yield (40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 8.46 (d, J = 4.5 Hz, 1H), 8.02 (s, 1H), 7.81 (dt, J = 8.0 Hz, 1H), 7.78 (s, 1H), 7.63 (d, J = 8.5 Hz, 1H), 7.58 (d, J = 8.5 Hz, 1H), 7.27 (d, J = 12.8 Hz, 1H), 7.24 (d, J = 16.5 Hz, 1H), 7.03 (d, J = 16.5 Hz, 1H), 5.71 (dd, J = 9.5, 2.7 Hz, 1H), 4.05–4.01 (m, 1H), 3.78–3.71 (m, 1H), 2.61–2.51 (m, 1H), 2.18–2.03 (m, 2H), 1.82–1.61 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.41, 148.31, 139.39, 134.30, 133.20, 132.46, 131.02, 130.35, 125.21, 124.94, 123.63, 123.55, 119.87, 110.61, 85.47, 77.29, 67.49, 29.44, 25.12, 22.56. HRMS (EI) calcd for $C_{19}H_{19}N_3O^+$ $[M]^+$: 305.1528, found: 305.1498.



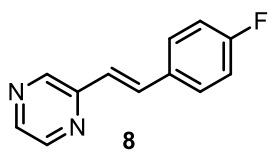
6

(*E*)-2-amino-(2-(1-tetrahydropyran-2-yl-1H-indazole)vinyl) pyrimidine (7): yellow solid, yield (50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 2H), 8.01 (s, 1H), 7.75 (s, 1H), 7.61–7.56 (m, 2H), 7.09 (d, J = 16.5 Hz, 1H), 6.87 (d, J = 16.5 Hz, 1H), 5.71 (dd, J = 9.4, 2.7 Hz, 1H), 5.13 (s br, 2H), 4.06–4.02 (m, 1H), 3.79–3.73 (m, 1H), 2.63–2.52 (m, 1H), 2.19–2.06 (m, 2H), 1.84–1.63 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.87, 156.01, 139.22, 134.24, 130.59, 127.87, 125.24, 124.77, 122.06, 120.75, 119.31, 110.56, 85.48, 77.22, 67.51, 29.45, 25.14, 22.58. HRMS (EI) calcd for $C_{18}H_{19}N_5O^+$ $[M]^+$: 321.1590, found: 321.1596.



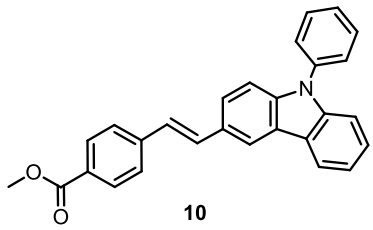
7

(*E*)-2-(4-fluorobenzene)vinyl pyrazine (8): white solid, yield (40%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, J = 1.5 Hz, 1H), 8.54 (dd, J = 2.5, 1.5 Hz, 1H), 8.41 (d, J = 2.5 Hz, 1H), 7.72 (d, J = 16.0 Hz, 1H), 7.70 (s, 1H), 7.58 (d, J = 5.4 Hz, 1H), 7.56 (d, J = 5.4 Hz, 1H), 7.09 (t, J = 8.7 Hz, 2H), 7.07 (d, J = 16.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.52, 162.04, 151.26, 144.50, 143.89, 142.97, 134.08, 132.44 (d, J_{C-F} = 3.5 Hz), 129.13 (d, J_{C-F} = 8.1 Hz), 123.91 (d, J_{C-F} = 2.3 Hz), 116.06 (d, J_{C-F} = 21.8 Hz), 77.36. ^{19}F NMR (376 MHz, $CDCl_3$) δ -111.83. HRMS (EI) calcd for $C_{12}H_8N_2F^+$ $[M-H]^+$: 199.0672, found: 199.0652.



8

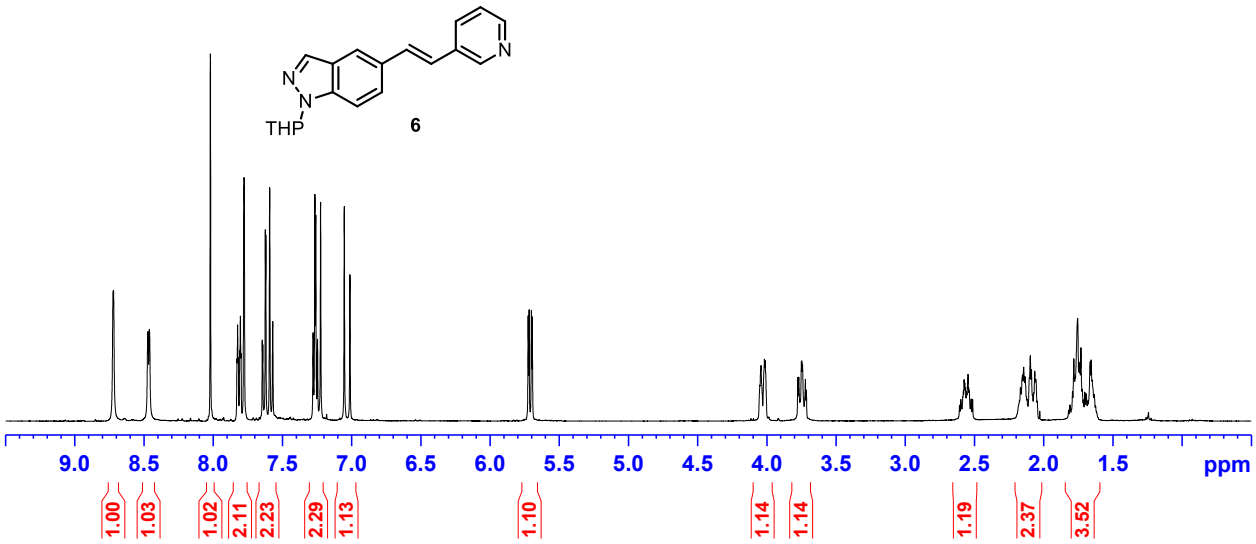
(*E*)-Methyl 4-(9-phenyl carbazole)vinyl benzoate (10): lime green solid, yield (81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.16 (d, J = 7.5 Hz, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.62–7.55 (m, 7H), 7.49–7.44 (m, 2H), 7.41–7.37 (m, 3H), 7.32–7.28 (m, 1H), 7.16 (d, J = 16.5 Hz, 1H), 3.91 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.16, 142.61, 141.55, 141.11, 137.60, 132.23, 130.21, 130.10, 129.71, 129.21, 129.03, 128.52, 127.81, 127.21, 126.43, 126.17, 125.43, 125.07, 123.97, 123.44, 120.53, 120.44, 119.17, 110.27, 110.18, 77.36, 52.19, 14.37. HRMS (EI) calcd for $C_{28}H_{21}NO_2$ $[M]^+$: 403.1572, found: 403.1546.



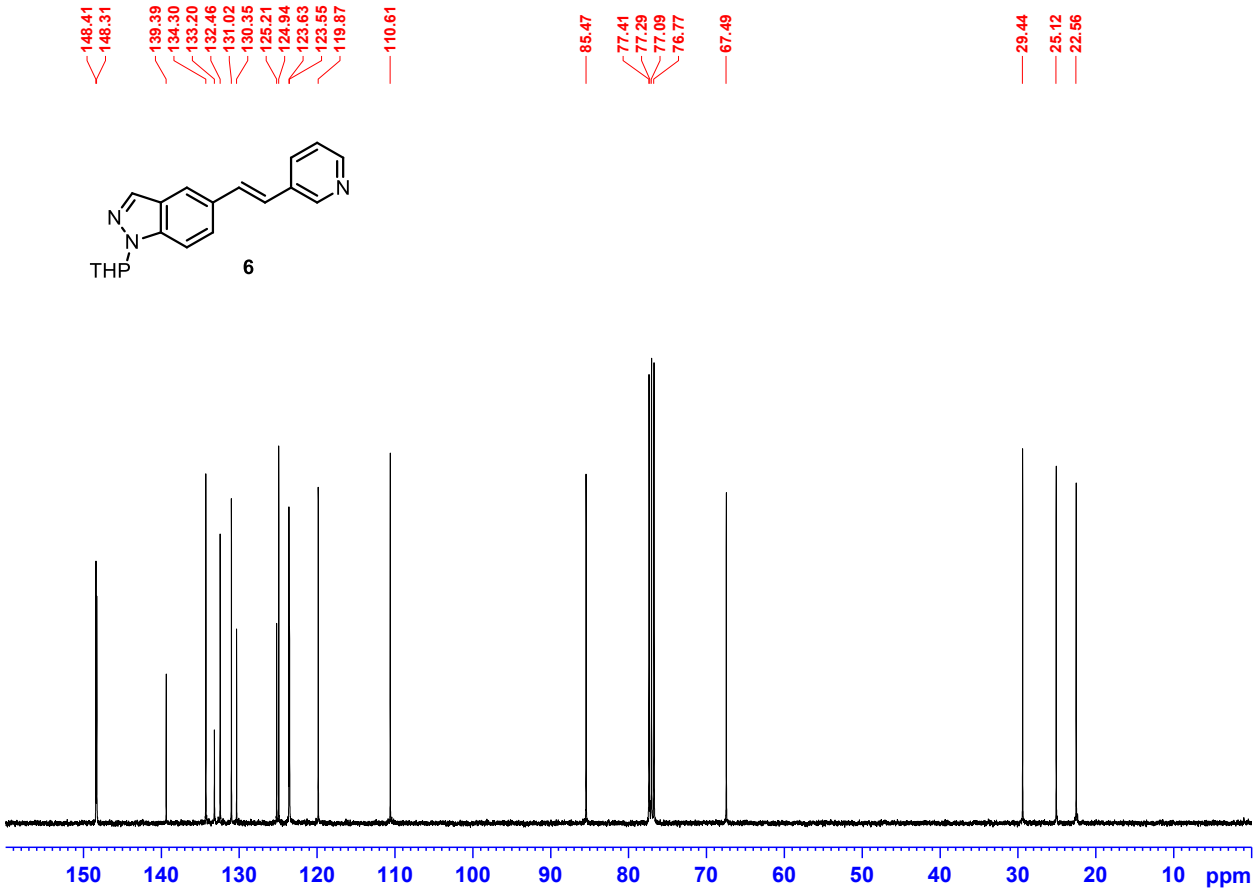
10

NMR spectra of one-pot Suzuki-Heck Relay products:

(*E*)-1-(tetrahydropyran-2-yl)-(2-(pyridine-3-yl)vinyl)-1H-indazole (6)

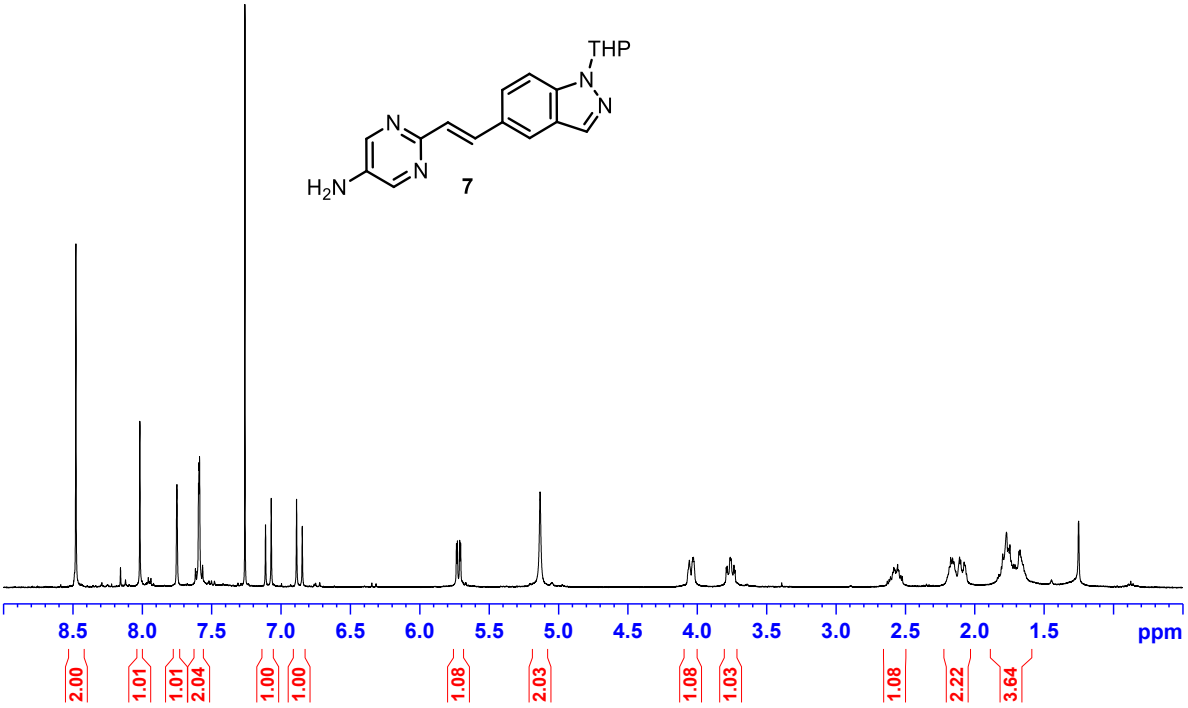


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **6**

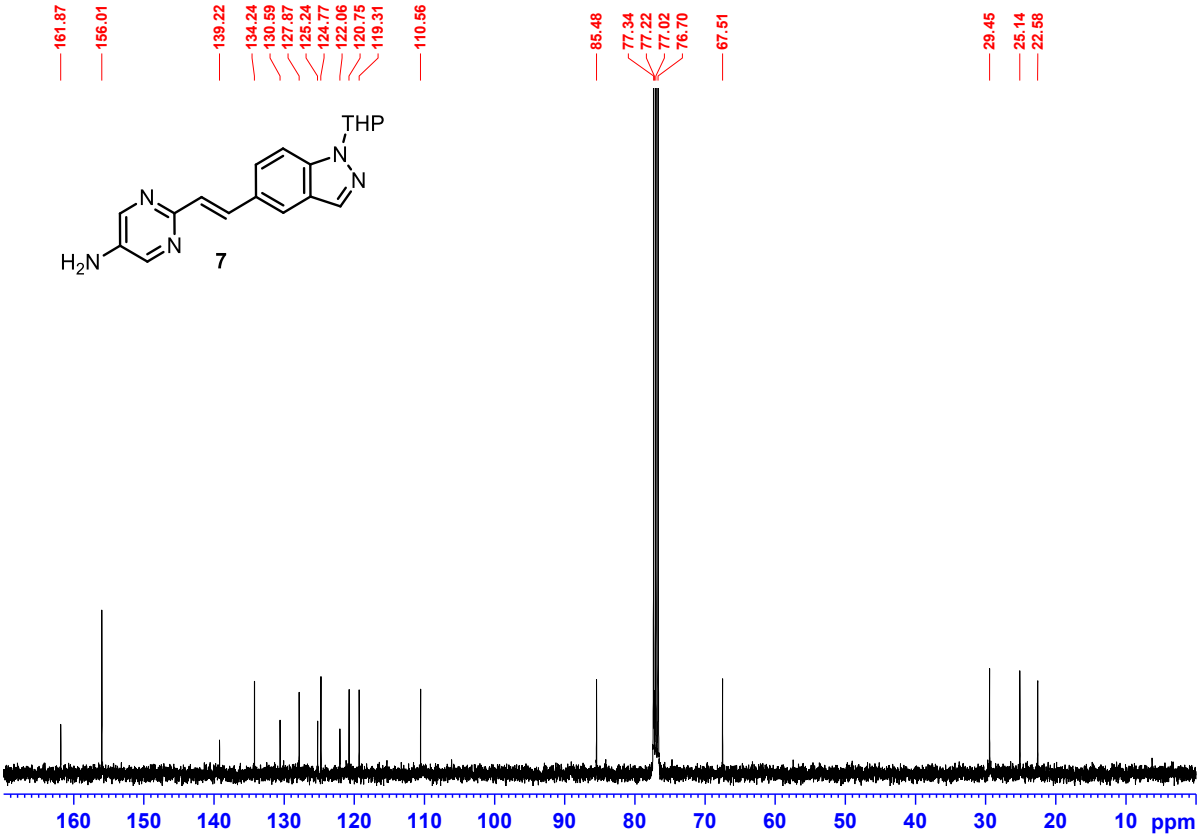


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **6**

(*E*)-2-amino-(2-(1-tetrahydropyran-2-yl-1H-indazole)vinyl) pyrimidine (7)

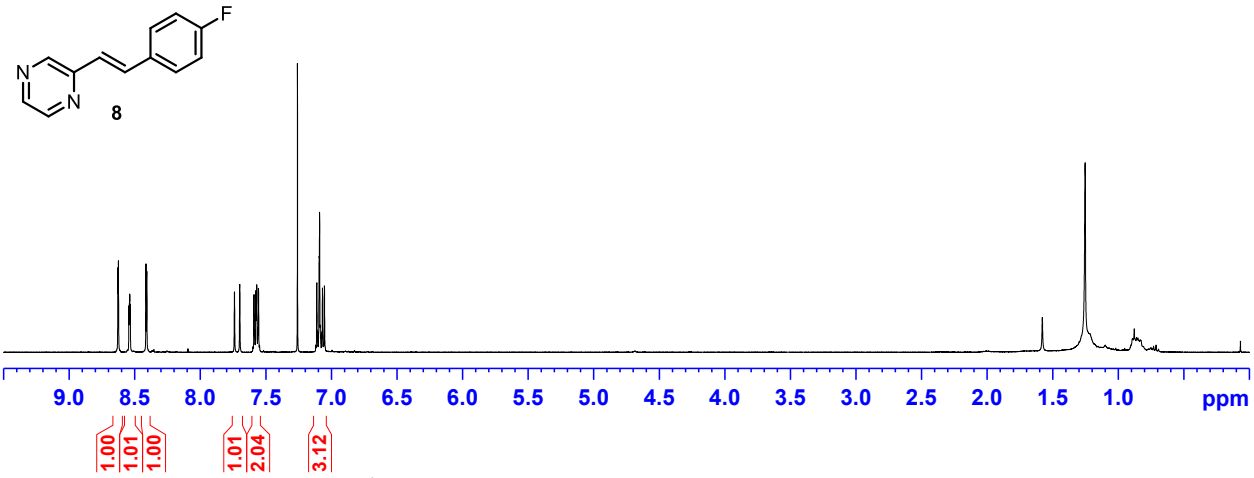


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **7**

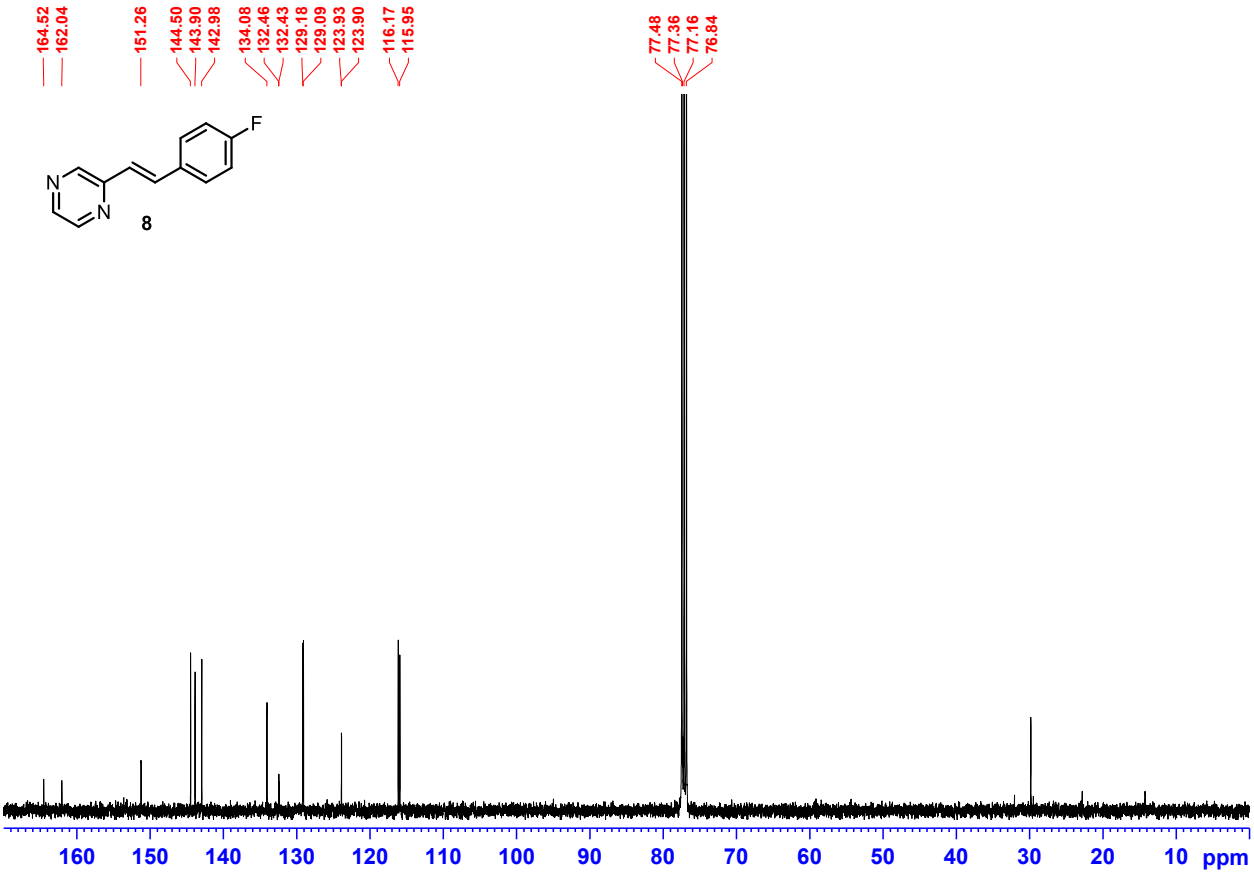


^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **7**

(*E*)-2-(4-fluorobenzene)vinyl pyrazine (8)

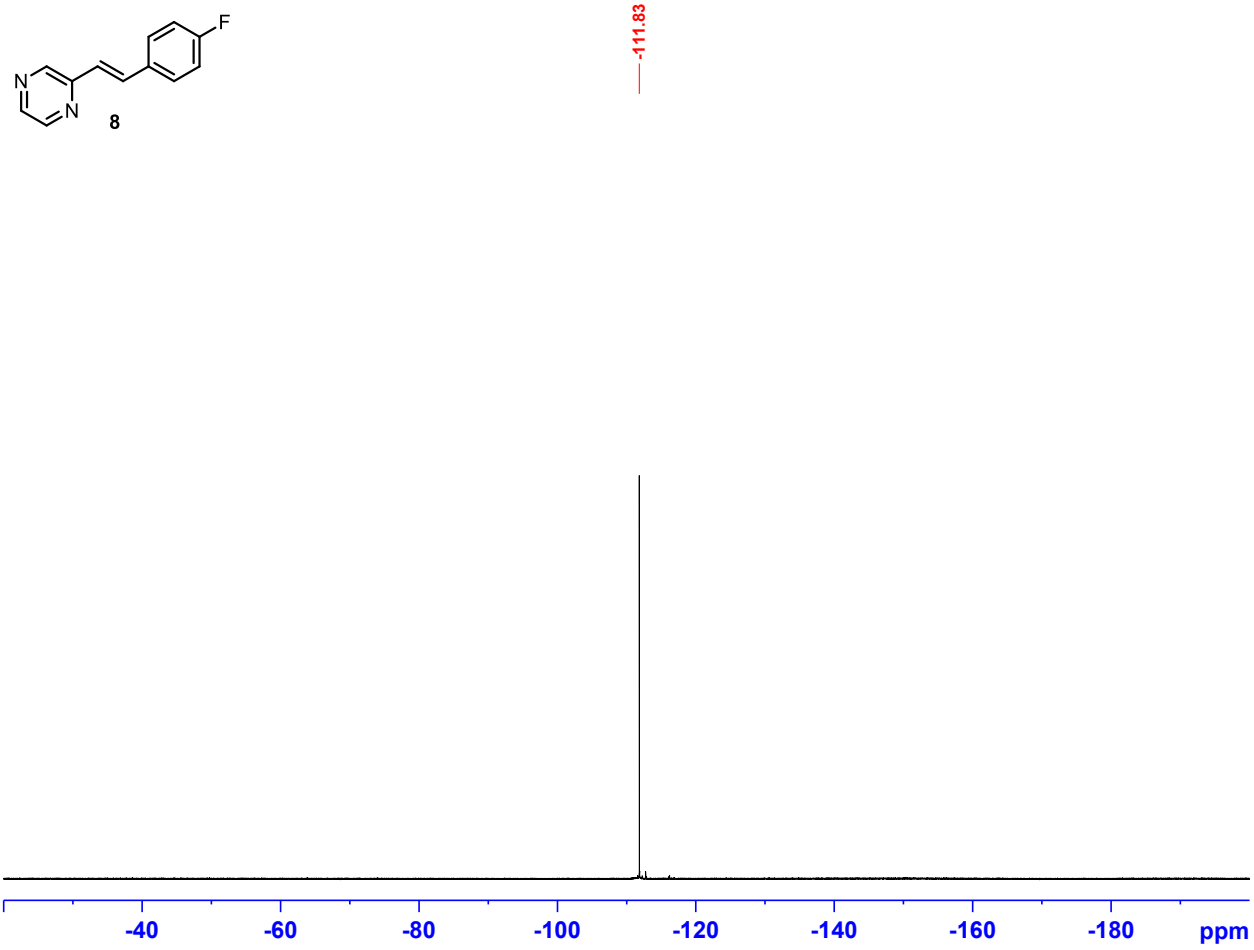


^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **8**



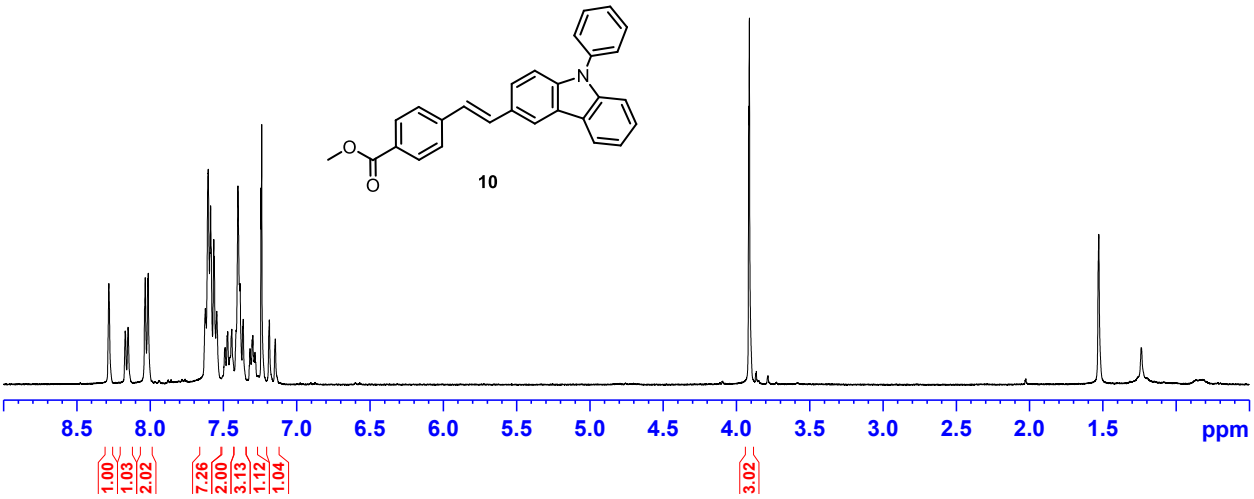
^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **8**

(*E*)-2-(4-fluorobenzene)vinyl pyrazine (8)

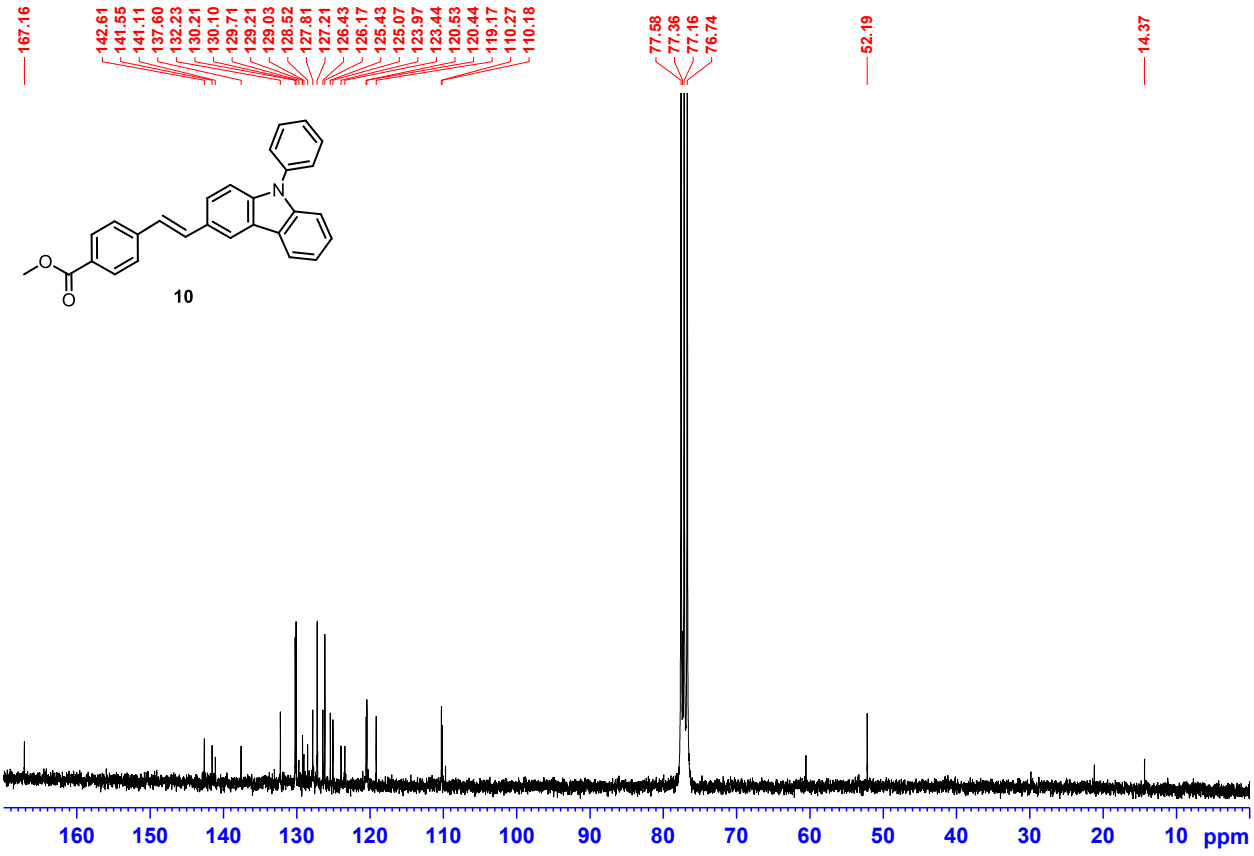


^{19}F NMR (376 MHz, $CDCl_3$) spectrum of **8**

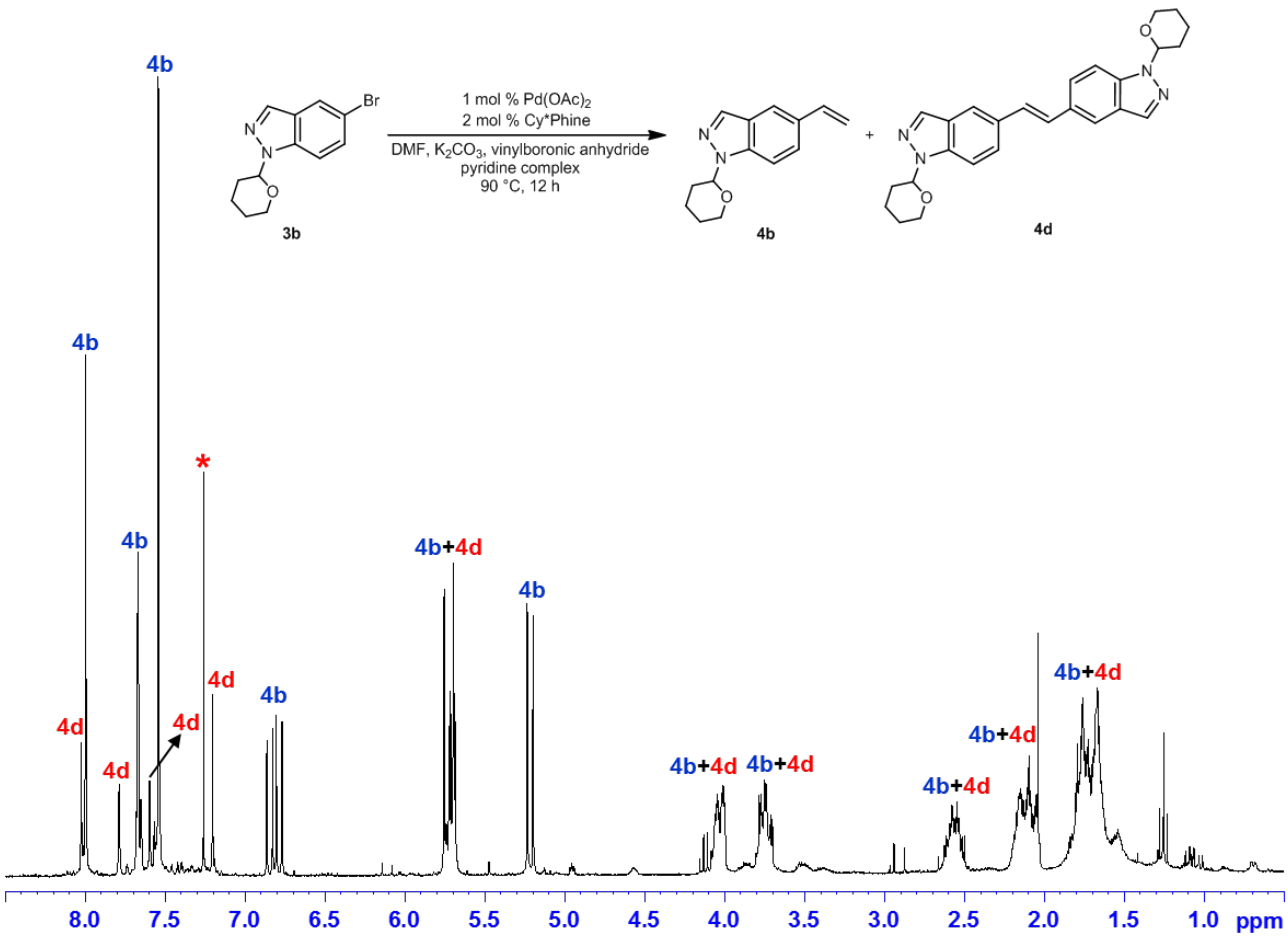
(*E*)-Methyl 4-(9-phenyl carbazole)vinyl benzoate (10)



^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **10**



^{13}C NMR (100 MHz, $CDCl_3$) spectrum of **10**



^{1}H NMR (300 MHz, $CDCl_3$) spectrum of mixture of Suzuki product and homocoupling byproduct

References:

1. D. J. Slade, N. F. Pelz, W. Bodnar, J. W. Lampe and P. S. Watson, *J. Org. Chem.* 2009, **74**, 6331-6334.
2. C. I. Traficante, C. Fagundez, G. L. Serra, E. G. Mata and C. M. L. Delpiccolo, *ACS Comb. Sci.* 2016, **18**, 225−229.