Supporting Information for:

Developing Five-membered Heterocycle Substituted Phosphinous Acids as Ligands for Palladium-Catalyzed Suzuki-Miyaura and Catellani Reactions

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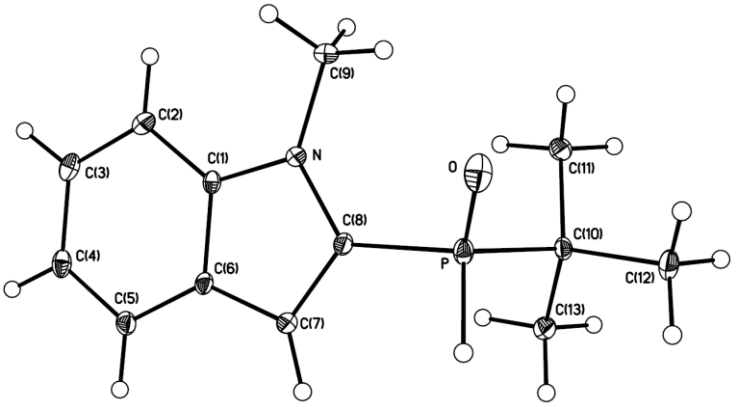
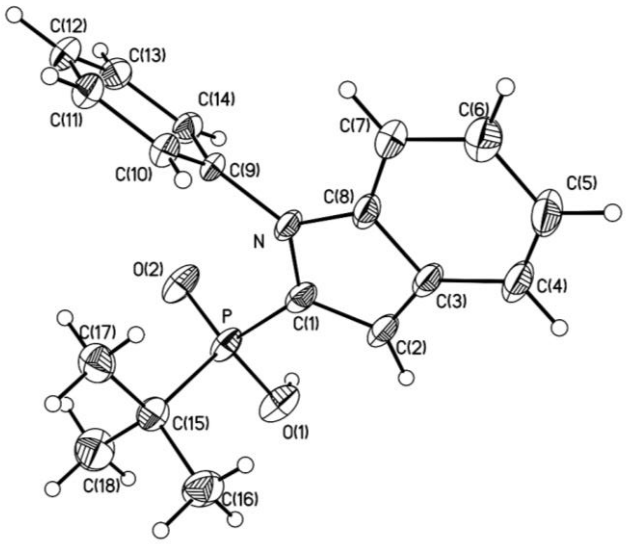
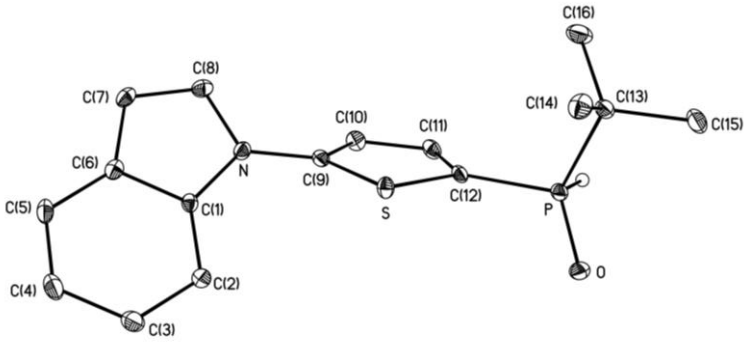
Contents

S1. ORTEP drawings of ***5a***, ***5d_O***, ***5f***, ***6c*** *and* ***9k***.







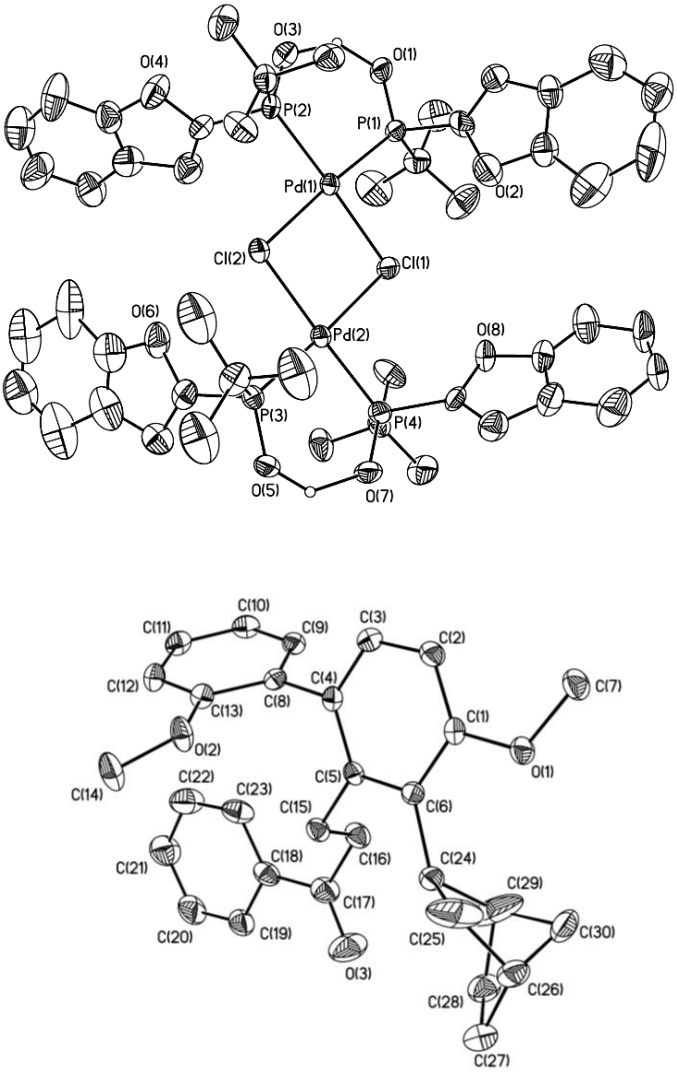


Figure S1. ORTEP drawings of **5a**, **5d_O**, **5f**, **6c** and **9k**. The structural data of **9k** exhibits distortion during the Chechcif process.

S2. Optimized condition for Suzuki-Miyaura reactions

Several factors that potentially affect the efficiency of the reaction, including temperature, time, concentration, base, transition metal/ligand ratio and solvent etc., had been screened to access its optimized reaction condition.

Table S1. Suzuki-Miyaura coupling reactions of 4-bromoanisole and phenylbronic acid employed various ligands[a].

Entry	Ligand	Yield (%)	
1	**5g**	64	75[b]
2	**5h**	95	> 99[b]
3	**5i**	74	85[b]
4	**5j**	31	42[b]

[a] Conditions: 1.0 mmol 4-bromoanisole, 1.5 mmol phenylboronic acid, 3.0 mmol NaO^tBu, 1.0 mL of THF, 1.0 mol% $Pd(OAc)_2$, 2.0 mol% Ligand, 60 ^oC, 1 h. The yield was determined by ^1H NMR, average of two runs; [b] 2 h.

The efficiency of **5h** is too high for this reaction. It is no good for the next optimization processes which is to distinguish the catalytic efficiencies among other reaction conditions. As shown in Table S2, the employment of **5g** and **5i** as ligands in the presence of NaO^tBu exhibited better performances than others, therefore, ligands **5g** and **5i** were chosen for the next optimization processes.

Table S2. Suzuki-Miyaura coupling reactions of 4-bromoanisole and phenylbronic acid employed various bases[a].

Entry	Base	Yield (%)				
		5a	**5b**	**5c**	**5g**	**5i**
1	NaO^{t}Bu	19	37	50	64, 75[b]	74, 85[b]
2	KOH	77	18	21	4	40
3	K_2CO_3	27	20	31	7	22
4	CsF	41	64	67	11	35
5	Cs_2CO_3	24	28	33	5	11
6	-	0	0	0	0	0

[a] Conditions: 1.0 mmol 4-bromoanisole, 1.5 mmol phenylboronic acid, 3.0 mmol base, 1.0 mL of THF, 1.0 mol% $Pd(OAc)_2$, 2.0 mol% Ligand, 60 ^{o}C, 1 h. The yield was determined by ^{1}H NMR, average of two runs; [b] 2 h.

Table S3. Suzuki-Miyaura coupling reactions of 4-bromoanisole and phenylbronic acid employed various solvents[a].

Entry	Solvent	Yield (%)	
1	THF	74	85[b]
2	1,4-dioxane	33	60[b]
3	1,2-dichloroethane	-	4[b]
4	Toluene	52	57[b]
5	EtOH	-	16[b]
6	DMSO	9	16[b]
7	H_2O	19	32[b]

[a] Conditions: 1.0 mmol 4-bromoanisole, 1.5 mmol phenylboronic acid, 3.0 mmol NaO^{t}Bu, 1.0 mL of solvent, 1.0 mol% $Pd(OAc)_2$, 2.0 mol% **5i**, 60 ^{o}C, 1 h. The yield was determined by ^{1}H NMR, average of two runs; [b] 2 h.

Table S4. Suzuki-Miyaura coupling reactions of 4-bromoanisole and phenylbronic acid employed various palladium sources[a].

Entry	Palladium source	Yield (%)	
1	$Pd(OAc)_2$	74	85[b]
2	$Pd(cod)Cl_2$	39	50[b]
3	$Pd(NO_3)_2$	21	35[b]
4	$PdBr_2$	-	29[b]
5	$PdCl_2$	-	28[b]
6	$PdCl_2(CH_3CN)_2$	44	79[b]
7	$Pd(dba)_2$	-	19[b]

[a] Conditions: 1.0 mmol 4-bromoanisole, 1.5 mmol phenylboronic acid, 3.0 mmol NaO^tBu, 1.0 mL of THF, 1.0 mol% palladium sources, 2.0 mol% **5i**, 60 °C, 1 h. The yield was determined by ^1H NMR, average of two runs; [b] 2 h.

Table S5. Suzuki-Miyaura coupling reactions of 4-bromoanisole and phenylbronic acid employed various [Pd]/Ligand ratio[a].

Entry	[Pd]/Ligand ratio	Yield (%)			
		5g		**5i**	
1	1/1	30	47[b]	16	28[b]
2	1/2	64	75[b]	74	85[b]
3	1/3	65	> 99[b]	58	76[b]

[a] Conditions: 1.0 mmol 4-bromoanisole, 1.5 mmol phenylboronic acid, 3.0 mmol NaO^tBu, 1.0 mL of THF, 1.0 mol% $Pd(OAc)_2$, 60 °C, reacted 1 h. The yield was determined by ^1H NMR, average of two runs; [b] 2 h.

Table S6. Suzuki-Miyaura coupling reactions of 4-bromoanisole and phenylbronic acid employed different loading of $Pd(OAc)_2$[a].

Entry	mol%	Yield (%)			
		5g		**5i**	
1	1.0	64	75[b]	74	85[b]
2	2.0	90	> 99[b]	79	85[b]

[a] Conditions: 1.0 mmol 4-bromoanisole, 1.5 mmol phenylboronic acid, 3.0 mmol NaO^tBu, [Pd]/Ligand = 1/2, 60 °C, 1 h. The yield was determined by ^1H NMR, average of two runs; [b] 2 h.

Table S7. Suzuki-Miyaura coupling reactions of 4-bromoacetophenone and phenylbronic acid under different temperatures and times.[a]

Entry	Time (min.)	Temp. (°C)	Yield (%)
1	5	60	82
2	15	60	>99
3	120	25	68

[a] Conditions: 1.0 mmol 4-bromoacetophenone, 1.5 mmol phenylboronic acid, 3.0 mmol NaO^tBu, 1.0 mL of THF, 1.0 mol% $Pd(OAc)_2$, 2.0 mol% Ligand. Average of two runs, yield was determined by ^1H NMR.

It was found that the optimal reaction condition for this reaction is as the follows: ligand/$Pd(OAc)_2$ in the ratio of 2:1 as the catalyst precursor with the combination of KOH/THF and reacting under 60 °C for less than 1 h.

*S3. Optimized conditions for the formations of **8**, **9** and **10** in Heck-type Catellani reactions*

Several factors that potentially affect the efficiency of the reaction, including temperature, time, solvent, base, transition metal/ligand ratio etc., had been screened to access its optimized reaction condition.

Table S8. Heck-type Catellani employed various bases[a]

Entry	Base	Yield(%)[b]
1	Na_2CO_3	26
2	K_2CO_3	68
3	CS_2CO_3	34
4	NaOH	11
5	KOH	9
6	NaF	9
7	KF	28
8	CsF	66
9	KO^tBu	9
10	NaO^tBu	9
11	NEt_3	trace

[a] Conditions: 2.0 mmol 2-iodotoluene, 1.1 mmol allylic alcohol, 0.5 mmol norbornene, 2.0 mmol base, 2 mol% $Pd(OAc)_2$, 4 mol% **5f**, 5 mL DMF, 105 ^oC, 8h; [b] Determined by GC-MS using calibration curve.

Table S9. Heck-type Catellani employed various Palladium sources[a]

Entry	Palladium source	Yield(%)[b]
1	$Pd(OAc)_2$	68
2	$Pd(NO_3)_2•2H_2O$	54
3	$Pd[COD]Cl_2$	34
4	$PdCl_2$	46
5	$PdCl_2(CH_3CN_2)_2$	54
6	$Pd(PPh_3)_4$	15

[a] Conditions: 2.0 mmol 2-iodotoluene, 1.1 mmol allylic alcohol, 0.5 mmol norbornene, 2.0 mmol K_2CO_3, 2 mol% Palladium sources, 4 mol% **5f**, 5 mL DMF, 105 ^oC, 8h; [b] Determined by GC-MS using calibration curve.

Table S10. Heck-type Catellani employed various [Pd]/Ligand ratios[a]

Entry	[Pd]/Ligand ratio	Yield(%)[b]
1	1/1	58
2	1/1.5	50
3	1/2	68
4	1/2.5	70

[a] Conditions: 2.0 mmol 2-iodotoluene, 1.1 mmol allylic alcohol, 0.5 mmol norbornene, 2.0 mmol K_2CO_3, 2 mol% $Pd(OAc)_2$, **5f**, 5 mL DMF, 105 °C, 8h; [b] Determined by GC-MS using calibration curve.

Table S11. Heck-type Catellani employed various solvents[a]

Entry	Solvent	Yield(%)[b]
1	DMF	68
2	DMSO	37
3	DMA	55
4	DMF/H_2O[c]	54
5	DMF/H_2O[d]	65
6	DMF/MeOH[e]	40
7	Toluene/CH_3CN[f]	11

[a] Conditions: 2.0 mmol 2-iodotoluene, 1.1 mmol allylic alcohol, 0.5 mmol norbornene, 2.0 mmol K_2CO_3, 2 mol% $Pd(OAc)_2$, 4 mol% **5f**, 5 mL of solvent, 105 °C, 8h; [b] Determined by GC-MS using calibration curve; [c] DMF/H_2O = 9:1; [d] DMF/H_2O = 19:1; [e] DMF/MeOH = 9:1; [f] Toluene/CH_3CN = 9:1.

It was found that the optimal reaction condition for this reaction is as the follows: ligand/$Pd(OAc)_2$ in the ratio of 2:1 as the catalyst precursor with the combination of DMF/THF and reacting under 105 °C for 8 h.

*S4. The formation of **8** in Heck-type Catellani reactions under three different conditions*

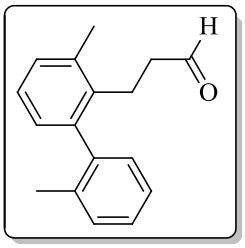
Table S12. Heck-type Catellani reactions in various conditions[a]

Entry	Time (hr)	Yield (%)[b]		
		Condition[c]	Condition[d]	Condition[e]
1	0.5	27	55	52
2	1	87	56	59
3	2	87	76	76
4	4	76	77	72
5	6	75	74	67
6	8	68	69	48
7	10	65	63	44

[a] Conditions: 2.0 mmol 2-iodotoluene, 1.1 mmol allylic alcohol, 0.5 mmol norbornene, 2.0 mmol K_2CO_3, 5 mL of DMF, 105 ^oC; [b] Determined by GC-MS using calibration curve; [c] 2.0 mol% $Pd(OAc)_2$ + 4.0 mol% **5f**; [d] 2.0 mol% $Pd(OAc)_2$; [e] 5.0 mol% $Pd(OAc)_2$.

*S5. Characterizations of selected **8**, **9** and **10**:*

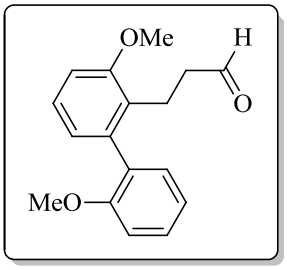
*‡ Spectroscopic data for **8a**:*



^{1}H NMR ($CDCl_3$, δ/ppm): 2.04(s, 3H, CH_3); 2.37(s, 3H, CH_3), 2.38~2.43(m, 2H), 2.54~2.59(m, 1H); 2.82~2.87(m, 1H); 6.94~6.96(m, 1H); 7.09~7.11(m. 1H); 7.16~7.25(m, 5H); 9.55(t, 1H, *J* = 1.2 Hz, HCO); ^{13}C NMR ($CDCl_3$, δ/ppm): 19.82(s, CH_3), 20.04(s, CH_3), 22.2(s, CH_2), 43.45(s, CH_2CO), 125.42(s, Ar), 126.01(s, Ar), 127.32(s, Ar), 127.58(s, Ar), 127.58(s, Ar), 129.25(s, Ar), 129.95(s, Ar), 135.58(s, Ar),

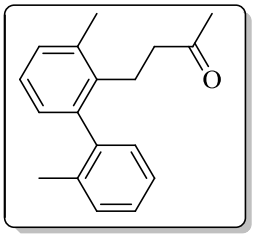
136.19(s, Ar), 136.32(s, Ar), 141.19(s, Ar), 141.62(s ,Ar), 201.43(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{17}H_{18}O$: 238.1358. Found: 238.1352; EA (%): Anal. calcd. for $C_{17}H_{18}O$: C, 85.67%; H, 7.61%. Found: C, 84.93%; H, 6.9%.

‡ *Spectroscopic data for* ***8b****:*



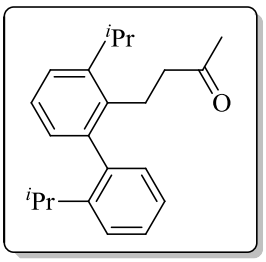
^{1}H NMR ($CDCl_3$, δ/ppm): 2.50~2.54(m, 2H), 2.66~2.73(m, 1H), 2.78~2.85(m, 1H), 3.74(s, 3H, CH_3O), 3.85(s, 3H, CH_3O), 6.79(d, 1H, *J* = 8.4 Hz), 6.88(d, 1H, *J* = 8.8 Hz), 6.93~7.01(m, 2H), 7.10(dd, 1H, *J* = 7.2, 1.6 Hz), 7.23(d, 1H, *J* = 8 Hz), 7.34(t, 1H, *J* = 6.4 Hz), 9.62(t, 1H, *J* = 1.6 Hz, HCO); ^{13}C NMR ($CDCl_3$, δ/ppm): 20.51(s, CH_2), 43.31(s, CH_2CO), 55.13(s, CH_3O), 55.18(s, CH_3O), 109.21(s, Ar), 110.50(s, Ar), 120.33(s, Ar), 122.59(s, Ar), 126.73(s, Ar), 127.45(s, Ar), 128.74(s, Ar), 129.91(s, Ar), 130.86(s, Ar), 139.66(s, Ar), 156.26(s, Ar), 157.16(s, Ar), 203.06(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{17}H_{18}O_3$: 270.1256. Found: 270.1253; EA (%): Anal. calcd. for $C_{17}H_{18}O_3$: C, 75.53%; H, 6.71%. Found: C, 75.26%; H, 6.75%.

‡ *Spectroscopic data for* ***8d****:*



^{1}H NMR ($CDCl_3$, δ/ppm): 1.92(s, 3H, CH_3CO), 2.04(s, 3H, CH_3), 2.34~2.38(m, 5H, CH_2CO, CH_3 centred at 2.36), 2.45~2.52(m, 1H, CH), 2.76~2.84(m, 1H, CH), 6.93~6.95(m, 1H), 7.10~7.13(m, 1H), 7.15~7.17(m, 2H), 7.18~7.25(m, 3H); ^{13}C NMR ($CDCl_3$, δ/ppm): 19.73(s, CH_3), 20.02(s, CH_3), 24.10(s, CH_2), 29.29(s, CH_3CO), 43.15(s, CH_2CO), 125.31(s, Ar), 125.82(s, Ar), 127.24(s, Ar), 127.44(s, Ar), 129.23(s, Ar), 129.45(s, Ar), 129.88(s, Ar), 135.60(s, Ar), 136.18(s, Ar), 136.80(s, Ar), 141.28(s, Ar), 141.57(s, Ar), 207.93(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{18}H_{20}O$: 252.1514. Found: 252.1513; EA (%): Anal. calcd. for $C_{18}H_{20}O$: C, 85.67%; H, 7.99%. Found: C, 85.20%; H, 8.04%.

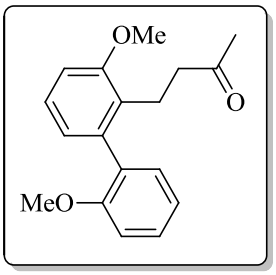
‡ *Spectroscopic data for* ***8e***



^{1}H NMR ($CDCl_3$, δ/ppm): 1.06(d, 3H, *J* = 6.8 Hz, CH_3CH), 1.18(d, 3H, *J* = 7.2 Hz, CH_3CH), 1.27(d, 3H, *J* = 6.8 Hz, CH_3CH), 1.29(d, 3H, *J* = 6.8 Hz, CH_3CH), 1.90(s, 3H, CH_3CO), 2.30~2.56(m, 3H, CH_2CO、CH), 2.63(m, 1H, *J* = 6.8 Hz, $(CH_3)_2CH$), 2.80~2.88(m, 1H, CH), 3.11(m, 1H, *J* = 6.8 Hz, $(CH_3)_2CH$), 6.94(dd, 1H, *J* = 1.2, 7.6 Hz), 7.08(dd, 1H, *J* = 1.6, 7.6 Hz), 7.16~7.24(m, 2H), 7.28~7.40(m, 3H); ^{13}C NMR ($CDCl_3$, δ/ppm): 22.86(s, CH_3CH), 23.56(s, CH_2), 24.01(s, CH_3CH), 24.70(s,

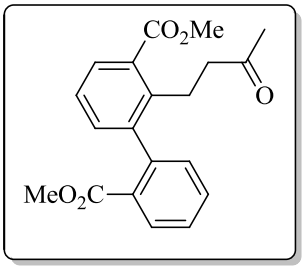
CH_3CH), 25.08(s, CH_3CH), 28.92(s, $CH(CH_3)_2$), 29.30(s, CH_3CO), 29.85(s, $CH(CH_3)_2$), 44.70(s, CH_2CO), 124.52(s, Ar), 125.04(s, Ar), 125.42(s, Ar), 125.84(s, Ar), 127.49(s, Ar), 127.68(s, Ar), 129.46(s, Ar), 135.50(s, Ar), 140.40(s, Ar), 141.49(s, Ar), 146.35(s, Ar), 146.92(s, Ar), 207.91(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{22}H_{28}O$: 308.2140. Found: 308.2143; EA (%): Anal. calcd. for $C_{22}H_{28}O$: C, 85.66%; H, 9.15%; O, 5.19%. Found: C, 85.36%; H, 8.63%; O, 4.76%.

‡ *Spectroscopic data for* ***8f****:*



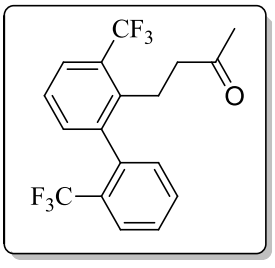
^1H NMR ($CDCl_3$, δ/ppm): 2.0(s, 3H, CH_3CO), 2.53~2.56(m, 2H, CH_2CO), 2.58~2.61(m, 1H, CH), 2.73~2.74(m, 1H, CH), 3.74(s, 1H, CH_3O), 3.85(s, 1H, CH_3O), 6.78(d, 1H, *J* = 7.2 Hz), 6.87(d, 1H, *J* = 8.4 Hz), 6.93~7.0(m, 2H), 7.10(d, 1H, *J* = 7.6 Hz), 7.21(d, 1H, *J* = 8.4 Hz), 7.33(t, 1H, *J* = 7.2 Hz); ^{13}C NMR ($CDCl_3$, δ/ppm): 22.10(s, CH_2), 29.31(s, CH_3CO), 43.18(s, CH_2CO), 55.18(s, $2CH_3O$, coincidentally overlaped), 109.17(s, Ar), 110.48(s, Ar), 120.25(s, Ar), 122.53(s, Ar), 126.47(s, Ar), 128.02(s, Ar), 128.65(s, Ar), 129.98(s, Ar), 130.84(s, Ar), 139.62(s, Ar), 156.28(s, Ar), 157.24(s, Ar), 209.01(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{18}H_{20}O_3$: 284.1412. Found: 284.1404; EA (%): Anal. calcd. for $C_{18}H_{20}O_3$: C, 76.03%; H, 7.09%. Found: C, 75.24%; H, 7.29%.

‡ Spectroscopic data for ***8g****:*



^{1}H NMR ($CDCl_3$, δ/ppm): 1.98(s, 3H, CH_3CO), 2.50~2.59(m, 2H, CH_2CO), 2.85~2.88(m, 1H, CH), 2.99~3.03(m, 1H, CH), 3.63(s, 3H, CH_3CO_2), 3.89(s, 3H, CH_3CO_2), 7.19(dd, 1H, *J* = 1.2, 7.6 Hz), 7.22(d, 1H, *J* = 7.6 Hz), 7.28(d, 1H, *J* = 7.6 Hz), 7.46(td, 1H, *J* = 1.2, 7.6 Hz), 7.55(td, 1H, *J* = 1.6, 7.2 Hz), 7.88(dd, 1H, *J* = 1.6, 7.6 Hz) , 8.02(dd, 1H, *J* = 0.8, 7.6 Hz); ^{13}C NMR ($CDCl_3$, δ/ppm): 25.19(s, CH_2), 29.29(s, CH_3CO), 44.01(s, CH_2CO), 51.74(s, CH_3O_2C), 51.93(s, CH_3O_2C), 125.22(s, Ar), 127.62(s, Ar), 129.76(s, Ar), 129.79(s, Ar), 129.95(s, Ar), 130.35(s, Ar), 130.91(s, Ar), 134.55(s, Ar), 132.45(s, Ar), 139.71(s, Ar), 141.68(s, Ar), 143.00(s, Ar), 166.94(s, CO_2Me), 168.00(s, CO_2Me), 207.68(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{20}H_{20}O_5$: 340.1311 Found: 340.1318; EA (%): Anal. calcd. for $C_{20}H_{20}O_5$: C, 70.57%; H, 5.92%. Found: C, 69.73%; H, 5.84%.

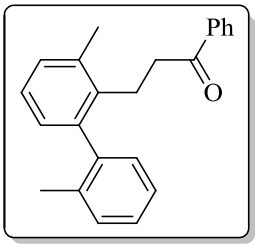
‡ Spectroscopic data for ***8h****:*



^{1}H NMR ($CDCl_3$, δ/ppm): 1.95(s, 3H, CH_3CO), 2.35~2.50(m, 2H, CH_2CO), 2.64~2.72(m, 1H, CH), 2.93~3.01(m, 1H, CH), 7.18~7.35(m, 2H), 7.42~7.59(m, 3H), 7.68~7.78(m, 2H); ^{13}C NMR ($CDCl_3$, δ/ppm): 23.87(s, CH_2), 29.35(s, CH_3CO), 43.88(s, CH_2CO), 125.51(s, Ar), 126.36(q, $J_{C\text{-}F}$ = 6 Hz, CF_3), 126.62(q, $J_{C\text{-}F}$ = 5.3 Hz,

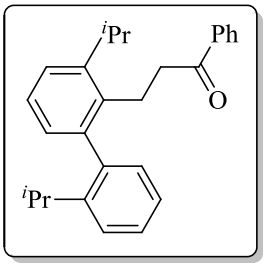
CF_3), 128.30(s, Ar), 128.96(s, Ar), 131.37(s, Ar), 131.58(s, Ar), 132.10(s, Ar), 133.70(s, Ar), 133.82(s, Ar),135.21(s, Ar), 138.33(s ,Ar), 139.82(s, Ar), 141.05(s, Ar), 206.65(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{18}H_{14}F_6O$: 360.0949. Found: 360.0948; EA (%): Anal. calcd. for $C_{18}H_{14}F_6O$: C, 60.00%; H, 3.92%. Found: C, 61.04%; H, 4.34%.

‡ *Spectroscopic data for* ***8i****:*



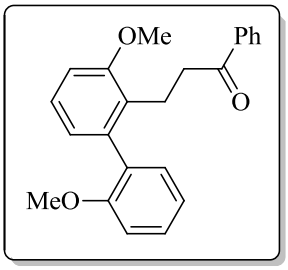
^{1}H NMR ($CDCl_3$, δ/ppm): 2.07(s, 3H, CH_3), 2.43(s, 3H, CH_3), 2.52~3.0(m, 4H, CH_2CH_2), 6.97~7.0(m, 1H), 7.16~7.35(m, 8H), 7.47~7.52(m, 1H), 7.55~7.57(m, 2H); ^{13}C NMR ($CDCl_3$, δ/ppm): 19.75(s, CH_3), 20.03(s, CH_3), 25.59(s, CH_2), 38.61(s, CH_2CO), 125.51(s, Ar), 125.93(s, Ar), 127.24(s, Ar), 127.45(s, Ar), 127.95(s, Ar), 128.39(s, Ar), 129.35(s, Ar), 129.55(s, Ar), 130.01(s, Ar), 132.76(s, Ar), 135.71(s, Ar), 136.06(s, Ar), 136.33(s, Ar), 136.84(s, Ar), 141.40(s, Ar), 141.56(s, Ar), 199.28(s, CO), two *ipso*-carbons are absented. HRMS (EI, M^+, *m/z*): Calcd. for $C_{23}H_{22}O$: 314.1671. Found: 314.1676; EA (%): Anal. calcd. for $C_{23}H_{22}O$: C, 87.86%; H, 7.05%. Found: C, 85.42; H, 7.62%.

‡ *Spectroscopic data for* ***8j****:*



^{1}H NMR ($CDCl_3$, δ/ppm): 1.07(d, 3H, *J* = 6.8 Hz, CH_3CH), 1.14(d, 3H, *J* = 6.8 Hz, CH_3CH), 1.29(d, 3H, *J* = 6.8 Hz, CH_3CH), 1.32(d, 3H, *J* = 6.8 Hz, CH_3CH), 2.64~2.83(m, 3H, CH_2CO、CH), 2.95~3.04(m, 2H, $(CH_3)_2CH$、CH), 3.22(quint, 1H, *J* = 6.8 Hz, $(CH_3)_2CH$), 6.98(dd, 1H, *J* = 1.6, 7.4 Hz), 7.16~7.25(m, 3H), 7.27~7.42(m, 5H), 7.47~7.55(m, 3H); ^{13}C NMR ($CDCl_3$, δ/ppm): 22.78(s, CH_3CH), 24.03(s, CH_3CH), 24.76(s, CH_3CH), 25.02(s, CH_2), 25.22(s, CH_3CH), 28.94(s, $CH(CH_3)_2$), 29.91(s, $CH(CH_3)_2$), 40.25(s, CH_2CO), 124.65(s, Ar), 125.30(s, Ar), 125.61(s, Ar), 125.99(s, Ar), 127.59(s, Ar), 127.73(s, Ar), 128.04(s, Ar), 128.48(s, Ar), 129.65(s, Ar), 132.86(s, Ar), 135.60(s, Ar), 136.15(s, Ar), 140.54(s, Ar), 141.55(s, Ar), 146.55(s, Ar), 147.08(s, Ar), 199.49(s, CO), two *ipso*-carbons are absented. HRMS (EI, M^+, *m/z*): Calcd. for $C_{27}H_{30}O$: 370.2297. Found: 370.2292; EA (%): Anal. calcd. for $C_{27}H_{30}O$: C, 87.52%; H, 8.16%; O, 4.32%. Found: C, 87.09%; H, 8.54%; O, 4.06%.

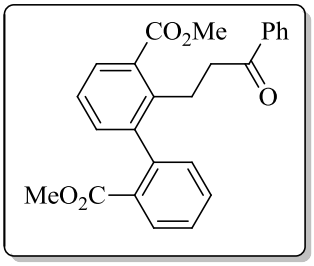
‡ *Spectroscopic data for* ***8k****:*



^{1}H NMR ($CDCl_3$, δ/ppm): 2.74~2.81(m, 1H, CH), 2.97(m, 1H, CH), 3.03~3.11(m, 2H, CH_2CO), 3.71(s, 3H, CH_3O), 3.85(s, 3H, CH_3O), 6.82(dd, 1H, *J* = 1.2, 7.6 Hz), 6.89~6.95(m, 2H), 7.00(td, 1H, *J* = 1.2, 7.2 Hz), 7.15(dd, 1H, *J* = 2, 7.2 Hz),

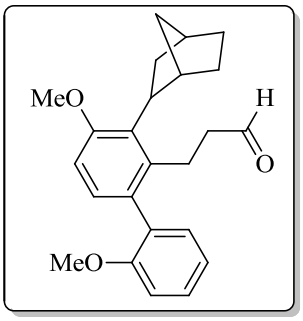
7.23~7.40(m, 4H), 7.50(tt, 1H, *J* = 1.2, 7.6 Hz), 7.80(dt, 2H, *J* = 2.4, 8 Hz); ^{13}C NMR ($CDCl_3$, δ/ppm): 23.07(s, CH_2), 38.44(s, CH_2CO), 55.17(s, $2CH_3O$, coincidentally overlaped), 109.21(s, Ar), 110.55(s, Ar), 120.34(s, Ar), 122.55(s, Ar), 126.18(s, Ar), 126.56(s, Ar), 127.94(s, Ar), 128.19(s, Ar), 129.29(s, Ar), 128.34(s, Ar), 128.67(s, Ar), 130.02(s, Ar), 130.87(s, Ar), 132.57(s, Ar), 136.57(s, Ar), 139.72(s, Ar), 156.31(s, Ar), 157.31(s, Ar), 200.27(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{23}H_{22}O_3$: 346.1569. Found: 346.1560; EA (%): Anal. calcd. for $C_{23}H_{22}O_3$: C, 79.74%; H, 6.40%. Found: C, 78.24%; H, 5.94%.

‡ *Spectroscopic data for* ***8l****:*



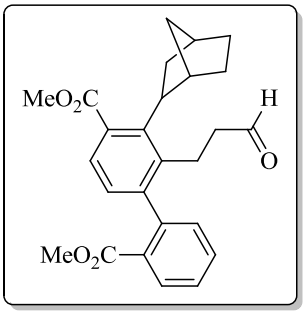
^{1}H NMR ($CDCl_3$, δ/ppm): 3.00~3.09(m, 2H), 3.11~3.21(m, 2H), 3.62(s, 3H, CH_3CO_2), 3.88(s, 3H, CH_3CO_2), 7.22(dd, 1H, *J* = 1.6, 7.2 Hz), 7.28~7.38(m, 3H), 7.41~7.56(m, 4H), 7.75~7.77(m, 2H), 7.90(dd, 1H, *J* = 1.2, 8 Hz), 8.01(dd, 1H, *J* = 1.2, 8 Hz); ^{13}C NMR ($CDCl_3$, δ/ppm): 25.85(s, CH_2), 39.24(s, CH_2CO), 51.74(s, CH_3O_2C), 51.96(s, CH_3O_2C), 125.30(s, Ar), 127.60(s, Ar), 127.80(s, Ar), 128.24(s, Ar), 129.80(s, Ar), 130.29(s, Ar), 130.40(s, Ar), 130.97(s, Ar), 131.63(s, Ar), 132.45(s, Ar), 132.59(s, Ar), 136.48(s, Ar), 139.74(s, Ar), 141.75(s, Ar), 143.08(s, Ar), 166.97(s, CO_2Me), 168.12(s, CO_2Me), 198.97(s, CO), three *ipso*-carbons are absented. HRMS (EI, M^+, *m/z*): Calcd. for $C_{25}H_{22}O_5$: 402.1467. Found: 402.1463; EA (%): Anal. calcd. for $C_{25}H_{22}O_5$: C, 74.61%; H, 5.51%. Found: C, 74.53%; H, 5.45%.

‡ *Spectroscopic data for* ***9b****:*



^{1}H NMR ($CDCl_3$, δ/ppm): 1.18~1.30(m, 3H), 1.48~1.64(m, 3H), 2.00~2.09(m, 1H), 2.23~2.35(m, 3H), 2.39~2.57(m, 2H), 2.69~2.84(m, 1H), 2.85~2.95(m, 2H), 3.74(d, 3H, *J* = 1.6 Hz, CH_3O), 3.79(s, 3H, CH_3O), 6.80(d, 1H. *J* = 8.4 Hz), 6.92~6.99(m, 3H), 7.08(dt, 1H, *J* = 2, 7.2 Hz), 7.32(td, 1H, *J* = 2, 7.6 Hz), 9.53(dt, 1H, *J* = 1.6, 5.6 Hz, HCO); ^{13}C NMR ($CDCl_3$, δ/ppm): 23.28, 28.20, 33.49, 38.03, 42.73, 42.95, 44.98(norbornene), 37.07, 38.69, 55.27(s, CH_3O), 55.30(s, CH_3O), 109.42(s, Ar), 110.56(s, Ar), 120.38(s, Ar), 128.51(s, Ar), 131.25(s, Ar), 131.42(s, Ar), 131.50(s, Ar), 131.58(s, Ar), 131.72(s, Ar), 139.21(s, Ar), 156.63(s, Ar), 157.72(s, Ar), 201.84(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{24}H_{28}O_3$: 364.2038. Found: 364.2041; EA (%): Anal. calcd. for $C_{24}H_{28}O_3$: C, 79.09%; H, 7.74%. Found: C, 79.34%; H, 7.97%.

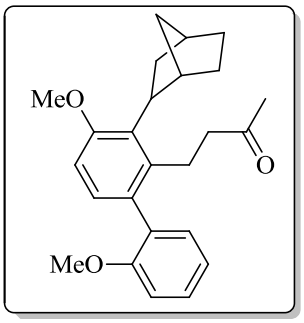
‡ *Spectroscopic data for* ***9c****:*



^{1}H NMR ($CDCl_3$, δ/ppm): 1.33~1.19(m, 1H), 1.24~1.42(m, 2H), 1.45~1.90(m, 3H), 2.29~2.39(m, 2H), 2.41~2.51(m, 3H), 2.79~3.10(m, 2H, CH_2CO), 3.15~3.30(m, 2H,

CH_2), 3.61(q, 3H, *J* = 3.6 Hz, CH_3CO_2), 3.80(s, 3H, CH_3CO_2), 6.77(d, 1H, *J* = 6 Hz,), 7.07~7.14(m, 1H), 7.24~7.30(m, 1H), 7.41(t, 1H, *J* = 7.6 Hz), 7.50(t, 1H, *J* = 8 Hz), 7.93(d, *J* = 7.6 Hz), 9.48(s, HCO); ^{13}C NMR ($CDCl_3$, δ/ppm): 24.67, 32.63, 37.00, 40.20, 42.88, 43.72, 45.09(norbornene), 29.47(s, CH_3CO), 28.12, 36.85, 51.92(s, CH_3O_2C), 52.20(s, CH_3O_2C), 125.57(s, Ar), 126.31(s, Ar), 127.55(s, Ar), 130.13(s, Ar), 130.38(s, Ar), 130.98(s, Ar), 131.48(s, Ar), 132.31(s, Ar), 138.38(s, Ar), 140.95(s, Ar), 142.51(s, Ar), 143.77(s, Ar), 167.44(s, CO_2Me), 172.46(s, CO_2Me), 207.58(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{26}H_{28}O_5$: 420.1937. Found: 420.1931; EA (%): Anal. calcd. for $C_{26}H_{28}O_5$: C, 74.26%; H, 6.71%.

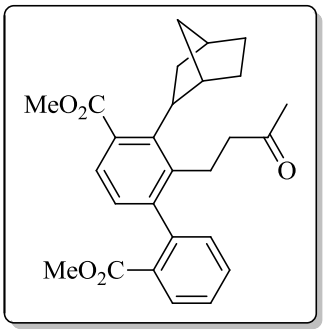
‡ *Spectroscopic data for* ***9f****:*



^{1}H NMR ($CDCl_3$, δ/ppm): 1.17~1.31(m, 3H), 1.47~1.64(m, 3H), 1.91(d, 3H, *J* = 2.8 Hz, CH_3CO), 2.00~2.07(m, 1H), 2.14~2.35(m, 3H), 2.38~2.53(m, 2H, CH_2CO), 2.60~2.73(m, 1H), 2.76~2.90(m, 2H, CH_2), 3.75(d, 3H, *J* = 2.4 Hz, CH_3O), 3.78(s, 3H, CH_3O), 6.78(d, 1H, *J* = 8.4 Hz), 6.93~6.99(m, 3H), 7.09(dt, 1H, *J* = 1.6, 7.6 Hz), 7.31(td, 1H, *J* = 1.6, 7.6 Hz); ^{13}C NMR ($CDCl_3$, δ/ppm): 25.26, 28.24, 29.68, 33.41, 38.07, 42.77, 44.72(norbornene), 28.24(s, CH_3CO), 37.08, 38.76, 55.30(s, CH_3O), 55.32(s, CH_3O), 109.28(s, Ar), 110.59(s, Ar), 120.35(s, Ar), 128.42(s, Ar), 131.36(s, Ar), 131.43(s, Ar),131.54(s, Ar), 131.59(s, Ar), 131.72(s, Ar), 139.72(s, Ar), 156.68(s, Ar), 157.69(s, Ar), 208.24(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{25}H_{30}O_3$: 378.2195. Found: 378.2189; EA (%): Anal. calcd. for $C_{25}H_{30}O_3$: C, 79.33%; H, 7.99%.

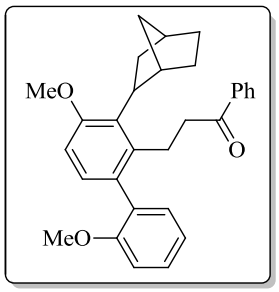
Found: C, 77.86%; H, 7.17%.

*‡ Spectroscopic data for **9g**:*



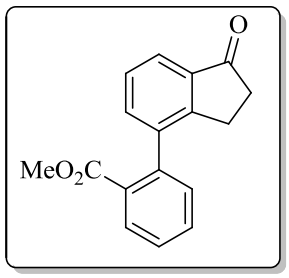
^{1}H NMR ($CDCl_3$, δ/ppm): 1.17~1.36(m, 3H), 1.53~1.85(m, 4H), 1.91(s, 3H, CH_3CO), 2.31~2.36(m, 1H), 2.36~2.52(m, 4H, included CH_2CO), 2.71~2.79(m, 1H), 2.87~2.98(m, 2H, CH_2), 3.62(d, 3H, *J* = 3.2 Hz, CH_3CO_2), 3.88(s, 3H, CH_3CO_2), 6.87(q, 1H, *J* = 4 Hz), 7.05(dd, 1H, *J* = 1.2, 7.6 Hz), 7.19(d, 1H, *J* = 7.6 Hz), 7.43(tt, 1H, *J* = 0.8, 7.6 Hz), 7.53(tt, 1H, *J* = 2, 7.6 Hz), 7.97(qd, 1H, *J* = 1.6, 3.6 Hz); ^{13}C NMR ($CDCl_3$, δ/ppm): 24.67, 32.63, 37.00, 40.20, 42.88, 43.72, 45.09(norbornene), 29.47(s, CH_3CO), 28.12, 36.85, 51.92(s, CH_3O_2C), 52.20(s, CH_3O_2C), 125.57(s, Ar), 126.31(s, Ar), 127.55(s, Ar), 130.13(s, Ar), 130.38(s, Ar), 130.98(s, Ar), 131.48(s, Ar), 132.31(s, Ar), 138.38(s, Ar), 140.95(s, Ar), 142.51(s, Ar), 143.77(s, Ar), 167.44(s, CO_2Me), 172.46(s, CO_2Me), 207.58(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{27}H_{30}O_5$: 434.2093. Found: 434.2088; EA (%): Anal. calcd. for $C_{27}H_{30}O_5$: C, 74.63%; H, 6.96%. Found: C, 73.85%; H, 6.93%.

‡ *Spectroscopic data for* ***9k****:*



^{1}H NMR ($CDCl_3$, δ/ppm): 1.19(d, 1H, *J* = 4.4 Hz), 1.24~1.34(m, 2H), 1.45~1.67(m, 3H), 2.06~2.10(m, 1H), 2.23~2.26(m, 1H), 2.33~2.39(m, 2H), 2.80~3.06(m, 5H), 3.71(d, 3H, *J* = 1.2 Hz, CH_3O), 3.80(s, 3H, CH_3O), 6.82(d, 1H, *J* = 8.4 Hz), 6.93~7.02(m, 3H), 7.16(dq, 1H, *J* = 2, 7.2 Hz), 7.32~7.38(m, 3H), 7.50(td, 1H, *J* = 1.6, 7.2 Hz), 7.64(td, 2H, *J* = 1.2, 8.4 Hz); ^{13}C NMR ($CDCl_3$, δ/ppm): 26.45, 28.23, 33.35, 38.11, 38.72, 40.03, 42.70(norbornene), 37.09, 42.85, 54.51(s, CH_3O), 55.32(s, CH_3O), 109.36(s, Ar), 110.69(s, Ar), 120.48(s, Ar), 127.99(s, Ar), 128.42(s, Ar), 128.47(s, Ar), 128.51(s, Ar), 131.43(s, Ar), 131.52(s, Ar), 131.61(s, Ar), 131.82(s, Ar), 131.87(s, Ar), 132.78(s, Ar), 136.46(s, Ar), 136.50(s, Ar), 139.89(s, Ar), 156.73(s, Ar), 157.76(s, Ar), 199.65(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{30}H_{32}O_3$: 440.5733. Found: 440.2345; EA (%): Anal. calcd. for $C_{30}H_{32}O_3$: C, 81.78%; H, 7.32%. Found: C, 81.90%; H, 7.11%.

‡ *Spectroscopic data for* ***10c***

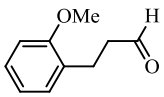
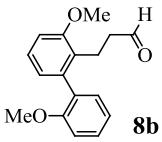
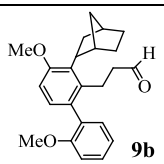


^{1}H NMR ($CDCl_3$, δ/ppm): 2.64~2.67(m, 2H), 2.81~2.84(m, 2H), 3.63(d, 3H, J = 0.8 Hz, CH_3CO_2), 7.29(dt, 1H, *J* = 0.8, 7.6 Hz), 7.39~7.45(m, 2H), 7.50(td, 1H, *J* = 1.6,

7.6 Hz), 7.60(td, 1H, *J* = 1.6, 7.2 Hz), 7.78(dd, 1H, *J* = 1.6, 4.8 Hz), 8.04(dt, 1H, *J* = 0.8, 7.6 Hz); ^{13}C NMR ($CDCl_3$, δ/ppm): 24.93(s, CH_2), 36.2(s, CH_2CO), 52.06(s, CH_3O_2C), 122.66(s, Ar), 127.27(s, Ar), 127.97(s, Ar), 129.89(s, Ar), 130.53(s, Ar), 130.69(s, Ar), 132.01(s, Ar), 133.96(s, Ar), 136.78(s, Ar) 140.13(s, Ar), 140.54(s, Ar), 153.20(s, Ar), 167.44(s, CO_2Me), 207.13(s, CO); HRMS (EI, M^+, *m/z*): Calcd. for $C_{17}H_{14}O_3$: 266.0943. Found: 266.0952; EA (%): Anal. calcd. for $C_{17}H_{14}O_3$: C, 76.68%; H, 5.30%. Found: C, 76.59%; H, 5.57%.

*S6. The formation of **8**, **9b** and **11a** in Heck-type Catellani reactions under conditions with variations in the ratios of norbornene to 2-iodoanisole*

Table S13. Heck-type Catellani reactions with variations in the ratios of norbornene to 2-iodoanisole[a]

Entry	Ratio	 **11a**	 **8b**	 **9b**
1	0.5	65	23	12
2	1.0	31	48	21
3	2.0	3	64	33
4	4.0	2	57	41
5	8.0	-	60	40
6	12.0	-	61	39
7	16.0	-	59	41

[a] Conditions: 2.0 mmol 2-iodoanisole, 1.1 mmol allylic alcohols, norbornene, 2.0 mmol K_2CO_3, 2 mol% $Pd(OAc)_2$, 4 mol% **5f**, 5 mL DMF, 105 °C, 2h; The conversion rate was determined by ^{1}H NMR.