Supporting Information for:

Ionic Liquid-Promoted, Highly Regioselective Heck

Arylation of Electron-Rich Olefins by Aryl Halides

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CONTENTS

- (A) **Materials**
- (B) **General procedure for the Heck arylation of vinyl ethers in ionic liquid**
- (C) **General procedure for the Heck arylation of enamides in ionic liquid-DMSO**
- (D) **General procedure for the Heck arylation of allyltrimethylsilane in ionic liquid**
- (E) **Compounds characterized**
- (F) **Sample ^1H NMR spectra**
- (G) **Tables**
- (H) **References**

A. Materials

All reactions were carried out under a nitrogen atmosphere. Chromatographic purifications were performed on silica gel (mesh 230-400) by the flash technique. 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) was prepared according to the literature method.¹ Following vacuum-drying at 80 °C for 8 h, the ionic liquid was

stored under nitrogen at ambient temperature and prior to use, it was vacuum-dried again at 80 °C for 1 h. However, our more recent experiments have shown that water (up to 10 wt%) does not have an adverse effect on the arylation of this study. AgNO₃ titration showed the chloride content of the ionic liquid to be below detection limit (<0.2%). Vinyl ether **1a-d**, enamides **1e-g**, allyltrimethylsilane **1h**, aryl halides **2a-x**, Pd(OAc)₂, 1,2-bis(diphenylphosphino)methane (DPPM), 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), 1,4-bis(diphenylphosphino)butane (DPPB), 1,1-bis(diphenylphosphino)ferrocene (DPPF), *R*-2,2'-bis(diphenylphosphino)-1,1'-binaphthyl (*R*-BINAP), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (XANTPHOS), and triethylamine were purchased from Lancaster and Aldrich and were used as received. ¹H and ¹³C NMR spectra were recorded on a Gemini 400 spectrometer at 400 (¹H) and 100 MHz (¹³C) in ppm with reference to TMS internal standard in CDCl₃. Mass spectra were obtained by electron impact (EI) or chemical ionization (CI). All the products were satisfactorily characterized by ¹H and ¹³C NMR, MS, HRMS and/or elemental analysis and when possible, comparison of their NMR spectra has been made with available literature data and/or those of authentic samples. The following compounds (*E/Z*)-4-(2-butoxyethenyl)benzaldehyde **4a**,² (*E/Z*)-4-(2-butoxyethenyl)benzonitrile **4b** [127087-66-5],³ (*E/Z*)-1-butoxy-2-(4-acetylphenyl)ethylene **4c**,⁴ (*E/Z*)-1-(2-butoxyethenyl)naphthalene **4q** [127087-65-4],³ ketones **5a** [3457-45-2],⁵ **5b** [1443-80-7],⁶ **5c** [1009-61-6],⁶ **5d** [3609-53-8],⁶ **5e** [403-42-9],⁶ **5f** [98-86-2],⁶ **5g** [122-00-9],⁶ **5h** [100-06-1],⁶ **5i** [6136-68-1],⁶ **5j** [586-37-8],⁶ **5k** [41908-11-6],⁷ **5l** [455-36-7],⁶ **5m** [585-74-0],⁶ **5n** [586-37-8],⁶ **5o** [445-27-2],⁶ **5p** [4079-52-1],⁶ **5q** [941-98-0],⁶ 4-(1-trimethylsilanylmethyl-vinyl)benzaldehyde (**3ha**) [137190-

14-8],⁸ 4-(1-trimethylsilanylmethyl-vinyl)benzonitrile (**3hb**),⁹ 1-[4-(1-trimethylsilanylmethyl-vinyl)-phenyl]ethanone (**3hc**),⁹ [2-(4-fluorophenyl)-allyl]trimethylsilane (**3he**) [139214-37-2],¹⁰ (2-phenylallyl)trimethylsilane (**3hf**) [77130-15-5],¹¹ and trimethyl-(2-*p*-tolyl-allyl)silane (**3hg**) [139214-35-0]¹¹ have all been reported previously.

B. General procedure for the Heck arylation of vinyl ethers in ionic liquid

An oven-dried, two-necked round-bottom flask containing a stir bar was charged with an aryl halide **2** (1.0 mmol), Pd(OAc)₂ (0.025 mmol), DPPP (0.05 mmol), and [bmim][BF₄] (2 mL) under nitrogen at room temperature. Following degassing three times, vinyl ether **1** (5.0 mmol) and NEt₃ (1.2 mmol) were injected sequentially. The flask was placed in an oil bath, and the mixture was stirred and heated at the desired temperature. After an appropriate reaction time, the flask was removed from the oil bath and cooled to room temperature. A small sample was then taken for NMR analysis. To the rest of the mixture, aqueous HCl (5%, 5 mL) was added and following stirring for 0.5 h, CH₂Cl₂ (20 mL) was added. After separation of the CH₂Cl₂ phase, the aqueous layer was extracted with CH₂Cl₂ (2 × 20 mL), and the combined organic layer was washed with water until neutrality, dried (Na₂SO₄), filtered, and concentrated *in vacuo*. The aryl methyl ketone **5** was isolated out of the crude product by flash chromatography on silica gel using a mixture of ethyl acetate and hexane (1/99 to 10/90) as eluant. The identity and purity of the product was confirmed by ¹H and ¹³C NMR, MS, HRMS, and elemental analysis, and by comparison of their NMR spectra with available literature data. The isolated yields of the product are given in Tables 4-6. Similar procedures were adopted for the arylation in molecular solvents.

C. General procedure for the Heck arylation of enamides in ionic liquid-DMSO

An oven-dried, two-necked round-bottom flask containing a stir bar was charged with an aryl bromide **2** (1.0 mmol), enamide **1** (1.0 mmol), Pd(OAc)₂ (0.04 mmol), DPPP (0.08 mmol), DMSO (1 mL), and [bmim][BF₄] (1 mL) under nitrogen at room temperature. Following degassing three times NEt₃ (1.2 mmol) was injected. The flask was placed in an oil bath, and the mixture was stirred and heated at 115 °C. After a reaction time of 36 h, the flask was removed from the oil bath and cooled to room temperature. A small sample was then taken for NMR analysis. For all the reactions, the β arylated product was not detected. The rest of the mixture was extracted with CH₂Cl₂ (3 × 20 mL), and the combined organic layer was washed with water until neutrality, dried (Na₂SO₄), filtered, and concentrated *in vacuo*. The α arylated product was isolated out of the crude product by flash chromatography on silica gel using a mixture of ethyl acetate and hexane (30/70 to 70/30) as eluant. The identity and purity of the product was confirmed by ¹H and ¹³C NMR, MS, HRMS, and by comparison of their NMR spectra with available literature data. The isolated yields of the product are given in Table 7.

D. General procedure for the Heck arylation of allyltrimethylsilane in ionic liquid

An oven-dried, two-necked round-bottom flask containing a stir bar was charged with an aryl bromide **2** (1.0 mmol), Pd(OAc)₂ (0.04 mmol), DPPP (0.08 mmol), and [bmim][BF₄] (2 mL) under nitrogen at room temperature. Following degassing three times, allyltrimethylsilane **1h** (4.0 mmol) and NEt₃ (1.2 mmol) were injected sequentially. The flask was placed in an oil bath, and the mixture was stirred and heated at 115 °C. After a reaction time of 36 h, the flask was removed from the oil bath and cooled to room temperature. A small sample was then taken for NMR analysis. For all

the reactions in [bmim][BF₄], the γ arylated product was not detected. The rest of the mixture was extracted with CH₂Cl₂ (3 $\times$ 20 mL), and the combined organic layer was washed with water until neutrality, dried (Na₂SO₄), filtered, and concentrated *in vacuo*. The β arylated product was isolated out of the crude product by flash chromatography on silica gel using a mixture of ethyl acetate and hexane (5/95 to 20/80) as eluant. The identity and purity of the product was confirmed by ¹H and ¹³C NMR, MS, HRMS, and elemental analysis, and by comparison of their NMR spectra with available literature data. The isolated yields of the products are given in Table 8.

E. Compounds characterized

4-Acetylbenzaldehyde (5a). ¹H NMR (400 MHz, CDCl₃) δ 10.03 (s, 1H), 8.03 (d, *J* = 6.7 Hz, 2H), 7.91 (d, *J* = 6.7 Hz, 2H), 2.59 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.3, 190.5, 140.3, 138.1, 128.8, 127.8, 25.9; CI-MS *m/z* 149 [(M + H)⁺, 100], 133 (33); HRMS Calcd for C₉H₉O₂ (M + H)⁺: 149.0603. Found: 149.0599; Anal. Calcd for C₉H₈O₂: C, 72.96; H, 5.44. Found: C, 72.87; H, 5.51.

4-Acetylbenzonitrile (5b). ¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 6.8 Hz, 2H), 7.78 (d, *J* = 6.8 Hz, 2H), 2.64 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 196.6, 140.0, 132.5, 128.7, 117.9, 116.5, 26.7; CI-MS *m/z* 145 (M⁺, 45), 130 (100), 102 (90), 75 (30), 43 (30); HRMS Calcd for C₉H₇NO: 145.0528. Found: 145.0529; Anal. Calcd for C₉H₇NO: C, 74.47; H, 4.86; N, 9.65. Found: C, 74.57; H, 4.82; N, 9.70.

1,4-Diacetylbenzene (5c). ¹H NMR (400 MHz, CDCl₃) δ 8.03 (s, 4H), 2.65 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 140.6, 128.8, 27.5; CI-MS *m/z* 162 (M⁺, 38), 147 (100), 119 (38), 91 (45), 43 (53); HRMS Calcd for C₁₀H₁₀O₂: 162.0681. Found: 162.0678; Anal. Calcd for C₁₀H₁₀O₂: C, 74.06; H, 6.21. Found: C, 73.83; H, 6.14.

Methyl 4-acetylbenzoate (5d). ^1H NMR (400 MHz, CDCl_3) δ 8.09-8.07 (m, 2H), 7.99-7.96 (m, 2H), 3.88 (s, 3H), 2.57 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 166.2, 141.1, 136.6, 129.8, 127.9, 51.5, 25.9; CI-MS m/z 178 (M^+ , 100), 145 (33); HRMS Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_3$: 178.0630. Found: 178.0628; Anal. Calcd for $\text{C}_{10}\text{H}_{10}\text{O}_3$: C, 67.41; H, 5.66. Found: C, 67.63; H, 5.72.

4'-Fluoroacetophenone (5e). ^1H NMR (400 MHz, CDCl_3) δ 8.00-7.96 (m, 2H), 7.15-7.11 (m, 2H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.8, 166.2 (d, $J_{\text{CF}} = 223$ Hz), 133.3, 131.3 (d, $J_{\text{CF}} = 10$ Hz), 115.9 (d, $J_{\text{CF}} = 23$ Hz), 26.8; CI-MS m/z 138 (M^+ , 23), 123 (100), 109 (34), 95 (67), 73 (51); HRMS Calcd for $\text{C}_8\text{H}_7\text{OF}$: 138.0481. Found: 138.0484; Anal. Calcd for $\text{C}_8\text{H}_7\text{OF}$: C, 69.56; H, 5.11. Found: C, 69.61; H, 5.15.

Acetophenone (5f). ^1H NMR (400 MHz, CDCl_3) δ 7.88-7.84 (m, 2H), 7.47-7.44 (m, 1 H), 7.39-7.35 (m, 2H), 2.56 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.8, 136.8, 132.3, 127.5, 126.7, 25.5; CI-MS m/z 138 (M^+ , 23), 123 (100), 109 (34), 95 (67), 73 (51); HRMS Calcd for $\text{C}_8\text{H}_8\text{O}$: 120.0575. Found: 120.0576; Anal. Calcd for $\text{C}_8\text{H}_8\text{O}$: C, 79.97; H, 6.71. Found: C, 79.94; H, 6.77.

4'-Methylacetophenone (5g). ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.84 (m, 2H), 7.26-7.22 (m, 2H), 2.56 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 198.1, 144.2, 135.2, 129.9, 128.8, 26.9, 21.9; CI-MS m/z 135 (M^+ , 100), 119 (21); HRMS Calcd for $\text{C}_9\text{H}_{10}\text{O}$: 134.0732. Found: 134.0736; Anal. Calcd for $\text{C}_9\text{H}_{10}\text{O}$: C, 80.56; H, 7.51. Found: C, 80.63; H, 7.62.

4'-Methoxyacetophenone (5h). ^1H NMR (400 MHz, CDCl_3) δ 7.87-7.84 (m, 2H), 6.88-6.84 (m, 2H), 3.78 (s, 3H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 195.7, 129.4, 129.3, 126.7, 112.9, 54.4, 25.2; CI-MS m/z 151 [$(\text{M} + \text{H})^+$, 100], 135 (20); HRMS

Calcd for $C_9H_{11}O_2$ ($M + H$)⁺: 151.0759. Found: 151.0761; Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.82; H, 6.75.

3-Acetylbenzonitrile (5i). ¹H NMR (400 MHz, $CDCl_3$) δ 8.25-8.24 (m, 1 H), 8.20-8.18 (m, 1H), 7.87-7.85 (m, 1H), 7.65-7.61 (m, 1H), 2.65 (s, 3H); ¹³C NMR (100 MHz, $CDCl_3$) δ 196.3, 138.1, 136.4, 132.6, 132.4, 130.1, 118.3, 113.6, 27.0; CI-MS m/z 163 [$(M + NH_4)^+$, 100], 130 (72); HRMS Calcd for $C_9H_{11}ON_2$ ($M + NH_4$)⁺: 163.0871. Found: 163.0875; Anal. Calcd for C_9H_7NO : C, 74.47; H, 4.86; N, 9.65. Found: C, 74.61; H, 4.84; N, 9.47.

1,3-Diacetylbenzene (5j). ¹H NMR (400 MHz, $CDCl_3$) δ 8.50-8.49 (m, 1H), 8.15-8.13 (m, 2H), 7.60-7.57 (m, 1H), 2.66 (s, 6H); ¹³C NMR (100 MHz, $CDCl_3$) δ 197.6, 137.8, 132.8, 129.4, 128.6, 26.7; CI-MS m/z 180 [$(M + NH_4)^+$, 100], 147 (29); HRMS Calcd for $C_{10}H_{14}O_2N$ ($M + NH_4$)⁺: 180.1024. Found: 180.1022; Anal. Calcd for $C_{10}H_{10}O_2$: C, 74.06; H, 6.21. Found: C, 73.89; H, 6.25.

3-Acetylbenzaldehyde (5k). ¹H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.45-8.41 (m, 1H), 8.19-8.15 (m, 1H), 8.05-8.01 (m, 1H), 7.60-7.56 (m, 1H), 2.66 (s, 3H); ¹³C NMR (100 MHz, $CDCl_3$) δ 197.5, 191.8, 137.0, 134.8, 134.0, 130.5, 129.8, 128.2 27.0; CI-MS m/z 148 [$(M + H)^+$, 100], 119 (43); HRMS Calcd for $C_9H_9O_2$ ($M + H$)⁺: 148.0524. Found: 148.0527; Anal. Calcd for $C_9H_8O_2$: C, 72.96; H, 5.44. Found: C, 73.02; H, 5.53.

3'-Fluoroacetophenone (5l). ¹H NMR (400 MHz, $CDCl_3$) δ 7.75-7.73 (m, 1H), 7.64-7.62 (m, 1H), 7.46-7.42 (m, 1H), 7.27-7.26 (m, 1 H), 2.60 (s, 3H); ¹³C NMR (100 MHz, $CDCl_3$) δ 197.0, 163.2 (d, J_{CF} = 247 Hz), 139.6 (d, J_{CF} = 8 Hz), 130.6 (d, J_{CF} = 8 Hz), 124.4 (d, J_{CF} = 3 Hz), 120.4 (d, J_{CF} = 21 Hz), 115.3 (d, J_{CF} = 22 Hz), 27.0; CI-MS

m/z 138 (M^+ , 26), 123 (100), 95 (57), 73 (31); HRMS Calcd for C_8H_7OF : 138.0481. Found: 138.0482; Anal. Calcd for C_8H_7OF : C, 69.56; H, 5.11. Found: C, 69.51; H, 5.12.

3'-Methylacetophenone (5m). 1H NMR (400 MHz, $CDCl_3$) δ 7.54-7.50 (m, 2H), 7.36-7.32 (m, 3H), 2.59 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 138.7, 137.6, 134.2, 129.4, 128.5, 125.9, 26.9, 21.7; CI-MS m/z 135 (M^+ , 100), 119 (26); HRMS Calcd for $C_9H_{10}O$: 134.0732. Found: 134.0731; Anal. Calcd for $C_9H_{10}O$: C, 80.56; H, 7.51. Found: C, 80.74; H, 7.57.

3'-Methoxyacetophenone (5n). 1H NMR (400 MHz, $CDCl_3$) δ 7.53-7.52 (m, 1H), 7.49-7.48 (m, 1H), 7.38-7.34 (m, 1H), 7.12-7.11 (m, 1H), 3.84 (s, 3H), 2.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 140.2, 138.9, 129.9, 121.4, 119.9, 112.8, 55.8, 27.0; CI-MS m/z 150 (M^+ , 100), 135 (48); HRMS Calcd for $C_9H_{10}O_2$: 150.0681. Found: 150.0682; Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.00; H, 6.74.

2'-Fluoroacetophenone (5o). 1H NMR (400 MHz, $CDCl_3$) δ 7.88-7.87 (m, 1H), 7.54-7.52 (m, 1H), 7.25-7.21 (m, 1H), 7.17-7.12 (m, 1H), 2.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.9, 162.3 (d, J_{CF} = 253 Hz), 134.6 (d, J_{CF} = 9 Hz), 130.6 (d, J_{CF} = 3 Hz), 125.8 (d, J_{CF} = 23 Hz), 124.4 (d, J_{CF} = 3 Hz), 116.7 (d, J_{CF} = 24 Hz), 31.5; CI-MS m/z 138 (M^+ , 33), 123 (100), 95 (77), 73 (53); HRMS Calcd for C_8H_7OF : 138.0481. Found: 138.0483; Anal. Calcd for C_8H_7OF : C, 69.56; H, 5.11. Found: C, 69.80; H, 5.15.

2'-Methoxyacetophenone (5p). 1H NMR (400 MHz, $CDCl_3$) δ 7.72-7.70 (m, 1H), 7.43-7.41 (m, 1H), 6.98-6.93 (m, 2H), 3.87 (s, 3H), and 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.0, 159.3, 134.0, 130.6, 128.6, 120.9, 112.0, 55.8, 32.1; CI-MS m/z 150 (M^+ , 25), 135 (90), 92 (85), 76 (35), 43 (95); HRMS Calcd for $C_9H_{10}O_2$: 150.0681. Found: 150.0684; Anal. Calcd for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 71.85; H, 6.80.

1-Acetonaphthone (5q). ^1H NMR (400 MHz, CDCl_3) δ 8.78 (m, 1H), 7.99 (m, 1H), 7.94 (m, 1H), 7.83 (m, 1H), 7.62 (m, 1H), 7.55-7.48 (m, 2H), 2.75 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 202, 135, 134, 133, 130, 129, 129, 128, 127, 126, 124, 30; CI-MS m/z 170 (M^+ , 70), 155 (100), 127 (100); HRMS Calcd for $\text{C}_{12}\text{H}_{10}\text{O}$: 170.0732. Found: 170.0729; Anal. Calcd for $\text{C}_{12}\text{H}_{10}\text{O}$: C, 84.68; H, 5.92. Found: C, 84.37; H, 5.93.

***N*-[1-(4-Acetylphenyl)vinyl]-*N*-methylacetamide (3ec).** ^1H NMR (400 MHz, CDCl_3) δ 7.99-7.98 (m, 2H), 7.52-7.51 (m, 2H), 5.82 (s, 1H), 5.37 (s, 1H), 3.11 (s, 3H), 2.62 (s, 3H), 2.02 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.5, 171.2, 148.7, 140.4, 137.5, 126.4, 126.2, 114.9, 36.0, 27.0, 22.2; CI-MS m/z 218 ($\text{M} + \text{H}^+$); HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{NO}_2$ ($\text{M} + \text{H}^+$): 218.1181. Found: 218.1183.

***N*-[1-(4-Fluorophenyl)vinyl]-*N*-methylacetamide (3ee).** ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.38 (m, 2H), 7.10-7.06 (m, 2H), 5.62 (s, 1H), 5.21 (s, 1H), 3.08 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.2, 163.5 (d, $J_{\text{CF}} = 239$ Hz), 148.6, 132.5, 127.9 (d, $J_{\text{CF}} = 8$ Hz), 127.8, 116.4 ($J_{\text{CF}} = 18$ Hz), 112.4, 35.8, 22.1; CI-MS m/z 194 ($\text{M} + \text{H}^+$); HRMS Calcd for $\text{C}_{11}\text{H}_{13}\text{FNO}$ ($\text{M} + \text{H}^+$): 194.0981. Found: 194.0978.

***N*-Methyl-*N*-(1-phenylvinyl)acetamide (3ef).** ^1H NMR (400 MHz, CDCl_3) δ 7.40-7.37 (m, 3H), 7.26-7.25 (m, 2H), 5.69 (s, 1H), 5.23 (s, 1H), 3.10 (s, 3H), 2.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 149.5, 136.0, 129.5, 129.3, 126.0, 112.6, 35.9, 22.2; CI-MS m/z 176 ($\text{M} + \text{H}^+$); HRMS Calcd for $\text{C}_{11}\text{H}_{14}\text{NO}$ ($\text{M} + \text{H}^+$): 176.1075. Found: 176.1074.

***N*-[1-(2-Fluorophenyl)vinyl]-*N*-methylacetamide (3eo)** ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.31 (m, 1H), 7.28-7.24 (m, 1H), 7.18-7.10 (m, 2H), 5.78 (s, 1H), 5.45 (s, 1H), 3.03 (s, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 171.3, 161.5 (d, $J_{\text{CF}} = 251$

Hz), 144.2, 130.9 (d, $J_{\text{CF}} = 9$ Hz), 129.2, 126.0, 124.8 (d, $J_{\text{CF}} = 4$ Hz), 117.6, 117.0 (d, $J_{\text{CF}} = 22$ Hz), 35.5, 22.1; CI-MS m/z 216 ($\text{M} + \text{H}$)⁺; HRMS Calcd for $\text{C}_{11}\text{H}_{13}\text{FNO}$ ($\text{M} + \text{H}$)⁺: 194.0981. Found: 194.0978.

***N*-Methyl-*N*-[1-(naphthalen-2-yl)vinyl]acetamide (3er).** ¹H NMR (400 MHz, CDCl_3) δ 7.87-7.82 (m, 3H), 7.78-7.77 (m, 1H), 7.60-7.57 (m, 1H), 7.54-7.49 (m, 2H), 5.84 (s, 1H), 5.34 (s, 1H), 3.18 (s, 3H), 2.09 (s, 3H); ¹³C NMR (100 MHz, CDCl_3) δ 171.5, 149.6, 134.0, 133.7, 133.2, 129.3, 128.9, 128.0, 127.3, 127.2, 125.3, 123.6, 113.2, 36.1, 22.2; CI-MS m/z 226 ($\text{M} + \text{H}$)⁺; HRMS Calcd for $\text{C}_{15}\text{H}_{16}\text{NO}$ ($\text{M} + \text{H}$)⁺: 226.1232. Found: 226.1227.

1-[1-(4-Acetylphenyl)vinyl]-2-pyrrolidinone (3fc). ¹H NMR (400 MHz, CDCl_3) δ 7.93-7.92 (m, 2H), 7.44-7.41 (m, 2H), 5.40 (s, 1H), 5.30 (s, 1H), 3.60 (t, $J = 7.0$ Hz, 2H), 2.60 (s, 3H), 2.59 (t, $J = 7.5$ Hz, 2H), 2.15-2.17 (m, 2H); ¹³C NMR (100 MHz, CDCl_3) δ 198.8, 174.8, 143.6, 140.6, 137.3, 128.9, 126.9, 110.4, 49.9, 32.5, 27.0, 19.0; CI-MS m/z 230 ($\text{M} + \text{H}$)⁺; HRMS Calcd for $\text{C}_{14}\text{H}_{16}\text{NO}_2$ ($\text{M} + \text{H}$)⁺: 230.1181. Found: 230.1183.

1-[1-(4-Fluorophenyl)vinyl]-2-pyrrolidinone (3fe). ¹H NMR (400 MHz, CDCl_3) δ 7.33-7.28 (m, 2H), 7.06-7.00 (m, 2H), 5.30 (s, 1H), 5.23 (s, 1H), 3.55 (t, $J = 7.0$ Hz, 2H), 2.56 (t, $J = 8.0$ Hz, 2H), 2.12-2.14 (m, 2H); ¹³C NMR (100 MHz, CDCl_3) δ 174.8, 163.3 (d, $J_{\text{CF}} = 247$ Hz), 143.3, 132.1, 128.6 (d, $J_{\text{CF}} = 9$ Hz), 115.7 (d, $J_{\text{CF}} = 22$ Hz), 109.1, 49.9, 32.3, 19.0; CI-MS m/z 230 ($\text{M} + \text{H}$)⁺; HRMS Calcd for $\text{C}_{12}\text{H}_{13}\text{FNO}$ ($\text{M} + \text{H}$)⁺: 206.0981. Found: 206.0985.

1-[1-(4-Tolyl)vinyl]-2-pyrrolidinone (3fg). ¹H NMR (400 MHz, CDCl_3) δ 7.27-7.23 (m, 2H), 7.15-7.13 (m, 2H), 5.35 (s, 1H), 5.24 (s, 1H), 3.55-3.52 (m, 2H), 2.60-2.55

(m, 2H), 2.41 (s, 3H), 2.16-2.11 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.9, 144.0, 138.8, 133.8, 129.5, 126.7, 109.0, 50.0, 32.3, 22.0, 19.0; CI-MS m/z 202 ($\text{M} + \text{H}$) $^+$; HRMS Calcd for $\text{C}_{13}\text{H}_{16}\text{NO}$ ($\text{M} + \text{H}$) $^+$: 202.1232. Found: 202.1226.

1-[1-(Naphthalen-2-yl)vinyl]-2-pyrrolidinone (3fr). ^1H NMR (400 MHz, CDCl_3) δ 7.85-7.78 (m, 3H), 7.54-7.44 (m, 3H), 7.34-7.32 (m, 1H), 5.51 (s, 1H), 5.39 (s, 1H), 3.59 (t, $J = 7.0$ Hz, 2H), 2.61 (t, $J = 8.0$ Hz, 2H), 2.29 (tt, $J = 7.0, 8.0$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 175.0, 144.1, 134.2, 133.7, 133.6, 128.9, 128.6, 128.4, 128.0, 126.7, 125.9, 124.7, 110.1, 50.0, 32.3, 19.0; CI-MS m/z 238 ($\text{M} + \text{H}$) $^+$; HRMS Calcd for $\text{C}_{16}\text{H}_{16}\text{NO}$ ($\text{M} + \text{H}$) $^+$: 238.1232. Found: 238.1230.

1-(1-Phenylvinyl)-2-azepanone (3gf). ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.38 (m, 2H), 7.35-7.26 (m, 3H), 5.60 (s, 1H), 5.19 (s, 1H), 3.52 (t, $J = 5.5$ Hz, 2H), 2.69 (t, $J = 4.5$ Hz, 2H), 1.86-1.71 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.2, 149.6, 136.9, 128.9, 128.8, 126.3, 116.6, 52.3, 38.1, 30.5, 29.2, 24.0; CI-MS m/z 216 ($\text{M} + \text{H}$) $^+$; HRMS Calcd for $\text{C}_{14}\text{H}_{18}\text{NO}$ ($\text{M} + \text{H}$) $^+$: 216.1388. Found: 216.1388.

1-[1-(Naphthalen-2-yl)vinyl]-2-azepanone (3gr). ^1H NMR (400 MHz, CDCl_3) δ 7.83-7.79 (m, 4H), 7.57-7.54 (m, 1H), 7.49-7.45 (m, 2H), 5.74 (s, 1H), 5.29 (s, 1H), 3.56 (t, $J = 5.2$ Hz, 2H), 2.73 (t, $J = 5.5$ Hz, 2H), 1.90-1.78 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 176.3, 149.5, 134.3, 133.8, 133.7, 128.7, 128.6, 128.0, 126.7, 126.3, 125.5, 124.3, 112.3, 52.3, 38.1, 30.5, 29.2, 24.0; CI-MS m/z 266 ($\text{M} + \text{H}$) $^+$; HRMS Calcd for $\text{C}_{18}\text{H}_{20}\text{NO}$ ($\text{M} + \text{H}$) $^+$: 266.1545. Found: 266.1542.

4-{1-[(Trimethylsilyl)methyl]ethenyl}benzaldehyde (3ha). ^1H NMR (400 MHz, CDCl_3) δ 10.09 (s, 1H), 7.92-7.90 (m, 2H), 7.66-7.64 (m, 2H), 5.34 (s, 1H), 5.10 (s, 1H), 2.24 (s, 2H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 191.7, 148.9, 145.6, 135.0,

129.6, 126.7, 112.6, 26.1, -1.4; CI-MS m/z 218 (M^+ , 31), 92 (100); HRMS Calcd for $C_{13}H_{18}OSi$: 218.1127. Found: 218.1131; Anal. Calcd for $C_{13}H_{18}OSi$: C, 71.50; H, 8.31. Found: C, 71.62; H, 8.35.

4-(1-Trimethylsilanylmethyl-vinyl)benzonitrile (3hb). 1H NMR (400 MHz, $CDCl_3$) δ 7.70-7.67 (m, 2H), 7.59-7.57 (m, 2H), 5.31 (s, 1H), 5.10 (s, 1H), 2.11 (s, 2H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.3, 145.0, 131.6, 126.5, 118.7, 115.3, 112.7, 25.6, -1.4; CI-MS m/z 216 [$(M + H)^+$, 41], 90 (100); HRMS Calcd for $C_{13}H_{18}NSi$ ($M + H$) $^+$: 216.1209. Found: 216.1211; Anal. Calcd for $C_{13}H_{17}OSi$: C, 72.50; H, 7.96. Found: C, 72.61; H, 8.01.

1-[4-(1-Trimethylsilanylmethyl-vinyl)-phenyl]ethanone (3hc). 1H NMR (400 MHz, $CDCl_3$) δ 7.99-7.97 (m, 2H), 7.59-7.57 (m, 2H), 5.32 (s, 1H), 5.07 (s, 1H), 2.67 (s, 3H), 2.13 (s, 2H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 149.0, 147.2, 137.4, 129.8, 117.9, 113.6, 28.0, 27.1, -1.4; CI-MS m/z 232 (M^+ , 53), 73 (100); HRMS Calcd for $C_{14}H_{20}OSi$: 232.1283. Found: 232.1286; Anal. Calcd for $C_{14}H_{20}OSi$: C, 72.36; H, 8.67; Found: C, 72.51; H, 8.71.

Methyl 4-{1-[(trimethylsilyl)methyl]vinyl}benzoate (3hd). 1H NMR (400 MHz, $CDCl_3$) δ 8.07 (m, 2H), 7.56 (m, 2H), 5.31 (s, 1H), 5.06 (br, 1H), 4.01 (s, 3H), 2.14 (d, J = 1.0 Hz, 2H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.4, 148.9, 147.4, 131.0, 130.3, 127.7, 113.4, 54.8, 27.5, -0.4; CI-MS m/z 249 ($M + H$) $^+$ (20), 227 (31), 197 (36), 126 (63), 90 (30), 74 (100); HRMS Calcd for $C_{14}H_{21}O_2Si$ ($M + H$) $^+$: 249.1310. Found: 249.1310; Anal. Calcd for $C_{14}H_{20}O_2Si$: C, 67.70; H, 8.12. Found: C, 67.71; H, 8.15.

[2-(4-Fluorophenyl)allyl]trimethylsilane (3he). 1H NMR (400 MHz, $CDCl_3$) δ 7.24-7.20 (m, 2H), 6.94-6.91 (m, 2H), 5.22 (s, 1H), 5.01 (s, 1H), 2.03 (s, 2H), -0.01 (s,

9H); ^{13}C NMR (100 MHz, CDCl_3) δ 162.1 (d, $J_{\text{CF}} = 238$ Hz), 145.7, 128.4 (d, $J_{\text{CF}} = 8$ Hz), 115.8 (d, $J_{\text{CF}} = 23$ Hz), 114.9, 110.6, 26.1, -1.5; CI-MS m/z 208 (M^+ , 63), 73 (100); HRMS Calcd for $\text{C}_{12}\text{H}_{17}\text{FSi}$: 208.1084. Found: 208.1086; Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{FSi}$: C, 69.18; H, 8.22; Found: C, 69.29; H, 8.17.

(2-Phenylallyl)trimethylsilane (3hf). ^1H NMR (400 MHz, CDCl_3) δ 7.50-7.48 (m, 2H), 7.40-7.34 (m, 3H), 5.22 (s, 1H), 4.97 (s, 1H), 2.12 (s, 2H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 151.5, 128.0, 127.4, 126.4, 125.6, 110.0, 21.6, -1.4; CI-MS m/z 190 (M^+ , 53), 73 (100); HRMS Calcd for $\text{C}_{12}\text{H}_{18}\text{Si}$: 190.1178. Found: 190.1181; Anal. Calcd for $\text{C}_{12}\text{H}_{18}\text{Si}$: C, 75.37; H, 9.49; Found: C, 75.31; H, 9.54.

Trimethyl-(2-*p*-tolyl-allyl)silane (3hg). ^1H NMR (400 MHz, CDCl_3) δ 7.29-7.27 (m, 2H), 7.11-7.08 (m, 2H), 5.09 (s, 1H), 4.81 (s, 1H), 2.31 (s, 3H), 2.01 (s, 2H), -0.01 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.6, 137.5, 136.4, 129.1, 126.2, 113.3, 24.6, 20.9, -1.4; CI-MS m/z 204 (M^+ , 53), 73 (100); HRMS Calcd for $\text{C}_{13}\text{H}_{20}\text{Si}$: 204.1334. Found: 204.1335; Anal. Calcd for $\text{C}_{13}\text{H}_{20}\text{Si}$: C, 76.40; H, 9.86; Found: C, 76.51; H, 9.94.

F. Sample ^1H NMR spectra

3-Acetylbenzonitrile (**5i**).

before chromatographic purification

3-Acetylbenzonitrile (**5i**).

After chromatographic purification

2'-Methoxyacetophenone (**5p**).

3'-Methylacetophenone (**5m**)

3'-Methoxyacetophenone (**5n**)

4-Acetylbenzonitrile (**5b**)

Acetophenone (**5f**)

1-[4-(Trimethylsilylmethyl)vinyl]-phenyl]ethanone (**3hc**).

N-[1-(4-Acetylphenyl)vinyl]-*N*-methylacetamide (**3ec**)

N-[1-(4-Fluorophenyl)vinyl]-*N*-methylacetamide (**3ee**)

N-Methyl-*N*-[1-(naphthalen-2-yl)vinyl]acetamide (**3er**)

1-(1-Phenylvinyl)-2-azepanone (**3gf**)

G. Tables

Table 4. Heck arylation of butyl vinyl ether **1a** by aryl bromides **2a-q** in [bmim][BF₄]^a

Substrate	Product ^b	Yield ^c (%)	Substrate	Product ^b	Yield ^c (%)
		93			87
		94			83
		92			81
		90			80
		96			86
		97			81
		88			86
		81			95
		95			

^a Reaction time: 24 h for **2a**, **c-g**, and **q**; 36 h for others. ^b All reactions gave 100% conversion and >99/1 α/β selectivity as determined by ¹H NMR before acidification. ^c Isolated yield of **5**. ^d 4.0 mol% Pd(OAc)₂ and 8.0 mol% DPPP were used.

Table 5. Heck arylation of butyl vinyl ether **1a** by aryl iodides **2s-x** in [bmim][BF₄]

Substrate	Product ^a	Yield (%) ^b
2s	5c	96
2t	5a	96
2u	5f	91
2v	5g	98
2w	5h	98
2x	5q	94

^a All reactions gave 100% conversion and >99/1 α/β selectivity as determined by ¹H NMR before acidification. ^b Isolated yield of **5**.

Table 6. Heck arylation of vinyl ethers **1b-d** with aryl halides **2** in [bmim][BF₄]

Substrate	Product ^a	1b	1c	1d
		Yield (%) ^b		
2f	5f	93	90	86
2e	5e	96	92	87
2b	5b	95	91	85
2c	5c	94	90	88
2a	5a	96	90	84
2h^c	5h	89	87	83
2x^d	5q	95	92	89

^a All reactions gave 100% conversion and >99/1 α/β selectivity as determined by ¹H NMR before acidification. ^b Isolated yield of **5**. ^c Reaction time: 36 h. ^d Reaction temperature: 80 °C.

Table 7. Heck arylation of enamides **1e-g** by aryl bromides **2**

$\text{Ar-Br} \quad \text{2} + \quad \text{Enamides} \quad \text{1e-g}$		$\xrightarrow[\text{NEt}_3, 115^\circ\text{C}, 36\text{ h}]{\begin{matrix} 4.0\text{ mol\% Pd(OAc)}_2 \\ 8.0\text{ mol\% DPPP} \\ [\text{bmim}][\text{BF}_4]\text{-DMSO} \end{matrix}}$		$\text{Ar} \quad \text{3e-g}$
Aryl bromides	Enamides	Products ^a		Yield (%) ^b
2c	1e		3ec	85
2e	1e		3ee	80
2f	1e		3ef	82
2o	1e		3eo	74
2r	1e		3er	86
2c	1f		3fc	83
2e	1f		3fe	85
2g	1f		3fg	73
2r	1f		3fr	78
2f	1g		3gf	76
2r	1g		3gr	71

^a Full conversions and >99/1 α/β selectivity for all as determined by ¹H NMR. ^b Isolated yield.

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