

**SUPPORTING INFORMATION**

**Title:** Intermolecular and Intramolecular Pauson–Khand Reactions of Functionalized Allenes

**Author(s):** Álvaro González-Gómez, Loreto Añorbe, Amalia Poblador, Gema Domínguez, Javier Pérez-Castells\*

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The allenes used in this work were obtained as follow except (propa-1,2-diene-1-sulfinyl)-benzene **3k** and (propa-1,2-diene-1-sulfonyl)-benzene **3l** which were obtained following literature procedures (see refs. 13 and 14 in the text).

#### **Procedure for the acetylation of amines.**

To a solution of the amine (1 mmol) in diethyl ether (3 mL), triethylamine (2 mmol) was added and the mixture was cooled to 0 °C. Then, acetyl chloride (2 mmol) was added dropwise. The solution was stirred at 0 °C for 5 min and left at room temperature until completion the reaction (TLC). The reaction was quenched with ice-water and extracted with AcOEt. The organic layer was washed with NaHCO<sub>3</sub> (sat.) and brine, dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure.

#### **Typical procedure for the tosylation of amines.**

To a solution of the amine (1.0 mmol) in pyridine (5 mL), *p*-toluenesulfonyl chloride (1.35 mmol) was added and the mixture was heated at reflux for 16 h. The solvent was removed under reduced pressure and the crude residue was extracted with AcOEt and washed with HCl (1N), water and brine. The organic layer was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The crude residue was purified by flash chromatography on silica gel.

#### **Typical procedure for the synthesis of *N*-propargyl-amides.**

To a suspension of KOH (2.0 mmol) and Bu<sub>4</sub>NI (1.0 mmol) in THF (5 mL) a solution of amide (1.0 mmol) in THF (5 mL) was added. The mixture was stirred in an ultrasound bath until completion the reaction (TLC). The solution was filtered through Celite, the solvent was removed under reduced pressure and the residue was purified on silica gel.

#### **Typical procedure for the synthesis of allenes from alkynes.**

To a solution of the starting alkyne (1.0 mmol) in THF (5 mL) under Ar, <sup>t</sup>BuOK (0.5 mmol) was added at 0 °C. The mixture is stirred at room temperature until completion the reaction (TLC). The solution was filtered through Celite, the solvent was removed under reduce pressure and the residue was purified on silica gel.

#### **Typical procedure for Sonogashira reactions.**

To a solution of iodo-arene (1.0 mmol) in dry Et<sub>3</sub>N (5 mL) ethynyl-trimethyl-silane (2.0 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.02 mmol) and CuI (0.005 mmol) was added. The mixture was heated at reflux for 4h. The solvent was removed under reduced pressure and the residue was filtered through Celite using toluene as solvent. The solvent was removed and the crude residue was purified by flash chromatography on silica gel.

#### **Typical procedure for Mitsunobu reactions.**

To a solution of the phenol (1.0 mmol) in THF (4 mL), 2-propyn-1-ol (2.5 mmol), PPh<sub>3</sub> (1.0 mmol) and diethyl azodicarboxylate (1.0 mmol) in THF (5 mL) was added. The mixture was heated at

reflux until completion of the reaction (TLC). The solvent was removed and the crude residue was purified by flash chromatography on silica gel.

**Synthesis of *N*-(4-methoxyphenyl)-*N*-propa-1,2-dienylacetamide, **3a**.** Following the typical procedure for acetylation of amines, the reaction of 4-methoxy-phenylamine (1.00 g, 8.13 mmol) afforded *N*-(4-methoxy-phenyl)-acetamide (1.17 g, 88%) as yellow solid. This compound (1.15 g, 7.00 mmol) was treated following the typical procedure for the synthesis of *N*-propargyl-amides, giving after flash chromatography (Hex:AcOEt 2:1) the *N*-(4-methoxy-phenyl)-*N*-prop-2-ynyl-acetamide (1.30 g, 91%) as yellow solid. From this alkyne (3.20 g, 15.79 mmol) the desired allene was obtained following the general procedure. After purification by flash chromatography (Hex:AcOEt 2:1), pure **3a** (2.24 g, 70%) as a yellow solid (m.p. 72-74 °C). <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>): δ= 1.85 (s, 3H), 3.80 (s, 3H), 4.96 (d, 2H, J= 6.0 Hz), 6.89 (d, 2H, J= 6.6 Hz), 7.06 (d, 2H, J= 6.6 Hz), 7.64 (t, 1H, J= 6.1 Hz). <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>): δ= 22.8, 55.3, 86.3, 101.0, 114.4, 129.3, 132.8, 159.2, 168.9, 202.6. IR (KBr) 3040, 1960, 1910, 1670. C<sub>12</sub>H<sub>13</sub>NO<sub>2</sub> (203.24): calcd. C 70.92, H 6.45, N 6.89; found C 70.65, H 6.63, N 6.78.

**Synthesis of *N*-(4-fluorophenyl)-*N*-propa-1,2-dienylacetamide, **3b**.** Following the typical procedure of acetylation of amines, the reaction of 4-fluoro-phenylamine (2.00 g, 18.02 mmol) afforded after flash chromatography the *N*-(4-fluoro-phenyl)-acetamide (2.53 g, 92%) as brown solid. This compound (2.00 g, 13.07 mmol) was treated following the typical procedure for the synthesis of *N*-propargyl-amides, giving after flash chromatography the *N*-(4-fluoro-phenyl)-*N*-prop-2-ynyl-acetamide (2.03 g, 81%) as an orange solid. From this alkyne (2.03 g, 10.60 mmol), the desired allene was obtained following the general procedure. After purification by flash chromatography (Hex:AcOEt 20:1), pure **3b** (1.40 g, 69%) as yellow solid (m.p. 75-77 °C). <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>): δ= 1.90 (s, 3H), 5.02 (d, 2H, J= 6.1 Hz), 7.09-7.19 (m, 4H), 7.68 (t, 1H, J= 6.3 Hz). <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>): δ= 22.7, 86.5, 100.8, 116.3 (d, J= 22.5 Hz), 130.1 (d, J= 8.9 Hz), 135.9 (d, J= 3.1 Hz), 163.5 (d, J= 247.2 Hz), 168.2, 202.2. IR (KBr) 3040, 1960, 1910, 1670. C<sub>11</sub>H<sub>10</sub>FNO (191.20): calcd. C 69.10, H 5.27, N 7.33; found C 69.30, H 5.47, N 7.11.

**Synthesis of *N*-propa-1,2-dienyl-*N*-(2-vinylphenyl)acetamide, **3c**.** A solution of *N*-(2-yodo-phenyl)-acetamide (1.40 g, 5.50 mmol) in THF (20 mL), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.19 g, 0.30 mmol) and tributyl(vinyl)tin (1.92 g, 6.1 mmol) was refluxed for 18h under Ar. The mixture was cooled and filtered through Celite. The organic layer was extracted with Et<sub>2</sub>O/water and dried over MgSO<sub>4</sub>. The solvent was removed and the residue was purified by flash chromatography (Hex:AcOEt 2:1). *N*-(2-Vinyl-phenyl)-acetamide (0.61 g, 71%) was afforded as colorless oil. This compound (0.42 g, 2.60 mmol) was treated following the typical procedure for the synthesis of *N*-propargylamides, giving after flash chromatography (Hex:AcOEt 4:1) the *N*-prop-2-ynyl-*N*-(2-vinyl-phenyl)-acetamide (0.51 g, 89%) as colourless oil. From this alkyne (2.60 g, 13.09 mmol) the desired allene was obtained following the general procedure. After purification by flash chromatography (hexane), pure **3c** (2.16 g, 82%) as yellow solid (m.p. 62-64 °C). <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>): δ= 1.82 (s, 3H), 4.99 (d, 2H, J= 6.6 Hz), 5.37 (d, 1H, J= 11.0 Hz), 5.80 (d, 1H, J= 17.0 Hz), 6.68 (dd, 1H, J<sub>1</sub>= 17.0 Hz, J<sub>2</sub>= 11.0 Hz), 7.13 (dd, 1H, J<sub>1</sub>= 7.7 Hz, J<sub>2</sub>= 1.6 Hz), 7.32-7.41 (m, 2H), 7.65-7.73 (m, 2H). <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>): δ= 22.2, 85.9, 99.8, 116.7, 125.6, 128.4, 128.6, 128.6, 130.9, 135.3, 137.0, 168.0, 202.1. IR (KBr) 2000, 1650. C<sub>13</sub>H<sub>13</sub>NO (199.25): calcd. C 78.36, H 6.58, N 7.03; found C 78.69, H 6.35, N 7.13.

**Synthesis of *N*-(4-methoxyphenyl)-4-methyl-*N*-propa-1,2-dienylbenzenesulfonamide, **3d**.** Following the typical procedure for tosylation of amines, the reaction of 4-methoxy-phenylamine (3.00 g, 24.30 mmol) afforded after flash chromatography (Hex:AcOEt 4:1) the *N*-(4-methoxy-phenyl)-4-methylbenzenesulfonamide (6.60 g, 97%) as yellow solid. This compound (0.89 g, 15.88 mmol) was treated following the typical procedure for the synthesis of *N*-propargylamides, giving after flash chromatography (Hex:AcOEt 5:1) the *N*-(4-methoxy-phenyl)-4-methyl-*N*-prop-2-ynylbenzenesulfonamide (1.53 g, 67%) as yellow solid. From this alkyne (2.40 g, 7.55 mmol) the desired allene was obtained following the general procedure. After purification by flash chromatography (Hex:AcOEt 9:1), pure **3d** (1.80 g, 74%) as yellow solid (m.p. 103-105 °C). <sup>1</sup>H RMN (300 MHz,

CDCl<sub>3</sub>):  $\delta$ = 2.45 (s, 3H), 3.80 (s, 3H), 5.04 (d, 2H, J= 6.0 Hz), 6.76-6.81 (m, 2H), 6.88-6.93 (m, 2H), 7.13 (t, 1H, J= 6.0 Hz), 7.28 (d, 2H, J= 7.7 Hz), 7.56 (d, 2H, J= 6.6 Hz). <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>):  $\delta$ = 21.6, 55.3, 87.5, 102.7, 113.8, 127.7, 129.5, 129.5, 130.7, 135.1, 143.8, 159.5, 200.9. IR (KBr) 1960, 1890, 1500, 1100. C<sub>17</sub>H<sub>17</sub>NSO<sub>3</sub> (315.39): calcd. C 64.74, H 5.43, N 4.44, S 10.17; found C 64.85, H 5.60, N 4.20, S 10.03.

**Synthesis of ethyl *N*-(methoxyphenyl)propa-1,2-dienylcarbamate, 3e.** A solution of 4-methoxyphenylamine (1.00 g, 8.06 mmol) and K<sub>2</sub>CO<sub>3</sub> (1.10 g, 8.06 mmol) in DMF (13 mL) was stirred for 16h under Ar. A solution of 3-bromo-propyne (1.2 mL, 0.86 mmol) in DMF (1.7 mL) was added and the mixture was heated to 80 °C for 48h. The solvent was removed and the residue was extracted with Et<sub>2</sub>O/H<sub>2</sub>O (2x 20/20 mL). The organic layer was dried over MgSO<sub>4</sub> and the solvent was removed under reduced pressure. The crude residue was purified by flash chromatography on silica gel (Hex:AcOEt 9:1). They were afforded: (4-methoxy-phenyl)-di-prop-2-ynyl-amine (0.49 g, 30%) as yellow solid and (4-methoxy-phenyl)-prop-2-ynyl-amine (0.87 g, 67%) as brown oil. A solution of (4-methoxy-phenyl)-prop-2-ynyl-amine (0.85 g, 5.25 mmol) in DCM (52 mL) under Ar, was added NaHCO<sub>3</sub> (0.88 g, 10.49 mmol) and ethyl chloroformate (0.75 mL, 7.87 mmol). The mixture was stirred for 4h and was filtered through Celite and was washed with DCM (2x 20 mL), the solvent was removed and the residue was purified on silica gel (Hex:AcOEt 4:1). It was afforded ethyl (4-methoxy-phenyl)-prop-2-ynyl-carbamate (1.00 g, 86%) as yellow oil. From this alkyne (0.83 g, 3.76 mmol) the desired allene was obtained following the general procedure. After purification by flash chromatography (Hex:AcOEt 9:1), pure **3e** (0.37 g, 45%) as yellow oil. <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>):  $\delta$ = 1.23 (bs, 3H), 3.82 (s, 3H), 4.20 (q, 2H, J= 6.6 Hz), 5.04 (d, 2H, J= 6.0 Hz), 6.89 (d, 2H, J= 6.6 Hz), 7.10 (d, 2H, J= 8.8 Hz), 7.32 (bs, 1H). <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>):  $\delta$ = 13.8, 54.6, 61.6, 86.1, 102.0, 113.3, 128.5, 130.9, 153.0, 158.0, 200.9. IR (film) 2980, 2000, 1710. C<sub>13</sub>H<sub>15</sub>NO<sub>3</sub> (233.26): calcd. C 66.94, H 6.48, N 6.00; found C 67.03, H 6.38, N 6.09.

**Synthesis of *N*-(2-ethynylphenyl)-*N*-propa-1,2-dienylacetamide, 3f.** Following the typical procedure for Sonogashira reactions, the reaction of 2-iodo-phenylamine (2.00 g, 9.13 mmol) afforded after flash chromatography (Hex:AcOEt 20:1) 2-trimethylsilanylethynyl-phenylamine (1.70 g, 100%) as orange oil. This compound (1.00 g, 5.29 mmol) was treated following the typical procedure for acetylation of amines, giving after flash chromatography the *N*-(2-trimethylsilanylethynyl-phenyl)-acetamide (1.20 g, 98%) as yellow oil. This compound (5.84 g, 25.28 mmol) was treated following the typical procedure for the synthesis of *N*-propargylamides, giving after flash chromatography (Hex:AcOEt 2:1) *N*-(2-ethynyl-phenyl)-*N*-prop-2-ynyl-acetamide (4.98 g, 100%) as brown solid. From this alkyne (1.70 g, 8.63 mmol) the desired allene was obtained following the general procedure. After purification by flash chromatography (Hex:AcOEt 4:1), pure **3f** (1.33 g, 78%) as yellow solid (m.p. 79-81 °C). <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>):  $\delta$ = 1.91 (s, 3H), 3.23 (s, 1H), 4.97-5.07 (m, 2H), 7.22 (dd, 1H, J<sub>1</sub>= 7.9 Hz, J<sub>2</sub>= 1.2 Hz), 7.37 (td, 1H, J<sub>1</sub>= 7.9 Hz, J<sub>2</sub>= 1.2 Hz), 7.44 (td, 1H, J<sub>1</sub>= 7.3 Hz, 1.8 Hz), 7.60 (dd, 1H, J<sub>1</sub>= 7.3 Hz, J<sub>2</sub>= 1.8 Hz), 7.68 (t, 1H, J= 6.1 Hz). <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>):  $\delta$ = 22.5, 78.9, 82.2, 86.5, 100.3, 122.2, 128.6, 129.1, 129.8, 133.7, 141.9, 168.3, 202.3. IR (KBr) 3280, 3220, 3040, 2100, 1960, 1660, 1590. C<sub>13</sub>H<sub>11</sub>NO (197.23): calcd. C 79.16, H 5.62, N 7.10; found C 79.59, H 5.10, N 6.83.

**Synthesis of *N*-(2-ethynylphenyl)-4-methyl-*N*-propa-1,2-dienylbenzenesulfonamide, 3g.** Following the typical procedure for tosylation of amines, the reaction of 2-trimethylsilanylethynyl-phenylamine (3.35 g, 17.70 mmol) afforded after flash chromatography (Hex:AcOEt 20:1) the 4-methyl-*N*-(2-trimethylsilanylethynyl-phenyl)-benzenesulfonamide (5.92 g, 97%) as yellow oil. This compound (6.85 g, 19.97 mmol) was treated following the typical procedure for *N*-propargylation of amides, giving after flash chromatography (Hex:AcOEt 9:1) the *N*-(2-ethynyl-phenyl)-4-methyl-*N*-prop-2-ynyl-benzenesulfonamide (4.54 g, 74%) as yellow oil. From this alkyne (0.97 g, 3.30 mmol) the desired allene was obtained following the general procedure. After purification by flash chromatography (Hex:AcOEt 4:1), pure **3g** (0.83 g, 86%) as yellow oil. <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>):  $\delta$ = 2.44 (s, 3H), 3.02 (s, 1H), 5.03 (d, 2H, J= 6.3 Hz), 6.94-6.97 (m, 1H), 7.12 (t, 1H, J= 6.3 Hz), 7.24-7.33 (m, 4H), 7.49-7.52 (m, 1H), 7.65 (d, 2H, J= 8.2 Hz). <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>):  $\delta$ = 21.5, 79.5, 81.7, 87.6, 102.0, 123.8, 127.7,

128.7, 129.1, 129.5, 130.3, 133.9, 135.9, 138.7, 143.9, 201.1. IR (film) 3300, 2100, 1960, 1165, 1360. C<sub>18</sub>H<sub>15</sub>NO<sub>2</sub>S (309.38): calcd. C 69.88, H 4.89, N 4.53; found C 69.71, H 4.56, N 4.70.

**Synthesis of 1-chloro-4-propa-1,2-dienylsulfanylbenzene, 3h.** A solution of 4-chloro-benzenethiol (1.50 g, 10.41 mmol) in THF (20 mL) was cooled to 0 °C. <sup>t</sup>BuOK (0.4 mL, 1M in THF) was added and the mixture was stirred for 1h at RT. The solvent was removed and the residue was dissolved in toluene anh. (200 mL), 3-bromo-propyne was added and the mixture was refluxed for 16h. The solvent was removed and the residue was purified by flash chromatography (hexane). 1-Chloro-4-prop-2-ynylsulfanyl-benzene (1.32 g, 70%) was afforded as colorless oil and 1-chloro-4-propa-1,2-dienylsulfanyl-benzene (0.20 g, 11%) was afforded as yellow oil. To a solution of 1-chloro-4-prop-2-ynylsulfanyl-benzene (0.10 g, 0.55 mmol) in THF (1.7 mL) at 0 °C was added NaH (44 mg, 1.10 mmol) and the mixture was stirred for 24h at RT. The reaction was quenched with ice-water and extracted with AcOEt (2x 10 mL). The organic layer was washed with water (10 mL) and brine (10 mL), dried over MgSO<sub>4</sub> and the solvent was removed and the residue was purified by flash chromatography (hexane). **3h** (60 mg, 60%) was afforded as yellow oil. <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>): δ= 5.01 (d, 2H, J= 6.6 Hz), 5.92 (t, 1H, J= 6.0 Hz), 7.32-7.46 (m, 2H). <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>): δ= 79.1, 85.5, 129.1, 130.0, 132.3, 132.9, 209.4. IR (film) 1900. C<sub>9</sub>H<sub>7</sub>ClS (182.67): calcd. C 59.18, H 3.86, S 17.55; found C 59.43, H 3.63, S 17.18.

**Synthesis of 1-bromo-4-propa-1,2-dienyloxybenzene, 3i.** Following the typical procedure for Mitsunobu reactions, the reaction of 4-bromo-phenol (3.00 g, 17.34 mmol) afforded after flash chromatography (Hex:AcOEt 9:1) the 1-bromo-4-prop-2-ynyloxy-benzene (3.27 g, 89%) as colourless oil. From this alkyne (2.85 g, 13.51 mmol) the desired allene was obtained following the general procedure. After purification by flash chromatography (hexane), pure **3i** (2.05 g, 72%) as colourless oil. <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>): δ= 5.48 (d, 2H, J= 6.1 Hz), 6.81 (t, 1H, J= 6.1 Hz), 6.96 (d, 2H, J= 8.8 Hz), 7.43 (d, 2H, J= 8.8 Hz). <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>): δ= 89.9, 115.1, 117.5, 118.5, 132.3, 156.0, 202.4. IR (film) 2000. C<sub>9</sub>H<sub>7</sub>BrO (211.06): calcd. C 51.22, H 3.34; found C 51.46, H 3.67.

**Synthesis of 1-ethynyl-2-(propa-1,2-dien-1-yloxy)benzene, 3j.** Following the procedure for Sonogashira reactions, the reaction of 2-iodo-phenol (2.00 g, 9.09 mmol) and 2-trimethylsilyl ethynyl-phenol (1.40 g, 81%) was afforded after flash chromatography (Hex:AcOEt 9:1) as colourless oil. This compound (4.20 g, 22.10 mmol) was treated following the procedure for Mitsunobu reactions, giving after flash chromatography (Hex:AcOEt 5%) trimethyl-(2-prop-2-ynyloxy-phenylethynyl)-silane (4.90 g, 98%) as colourless oil. A solution of this compound (3.70 g, 16.22 mmol) in THF (100 mL) was treated with KOH (9.10 g, 162.2 mmol) and the mixture was stirred for 16h at RT. The reaction was filtered through Celite and it was extracted with AcOEt (3x 40mL). The organic layer was washed with water (40 mL) and brine (40 mL), dried over MgSO<sub>4</sub>, the solvent was removed and the residue was purified by silica gel chromatography (Hex:AcOEt 1% to 2%) affording 1-ethynyl-2-prop-2-ynyloxy-benzene (2.36 g, 93%) as colorless oil. From this alkyne (2.59 g, 16.60 mmol), the desired allene was obtained following the general procedure. After purification by flash chromatography (hexane), pure **3j** (1.93 g, 74%) was obtained as a yellow oil. <sup>1</sup>H RMN (300 MHz, CDCl<sub>3</sub>): δ= 3.33 (s, 1H), 5.47 (d, 2H, J= 6.0 Hz), 6.87 (t, 1H, J= 6.0 Hz), 7.03 (td, 1H, J<sub>1</sub>= 1.1 Hz, J<sub>2</sub>= 7.7 Hz), 7.12 (dd, 1H, J<sub>1</sub>= 1.1 Hz, J<sub>2</sub>= 8.2 Hz), 7.32 (td, 1H, J<sub>1</sub>= 1.6 Hz, J<sub>2</sub>= 7.7 Hz), 7.50 (dd, 1H, J<sub>1</sub>= 1.6 Hz, J<sub>2</sub>= 7.7 Hz). <sup>13</sup>C RMN (75 MHz, CDCl<sub>3</sub>): δ= 79.2, 81.7, 90.0, 112.8, 115.8, 117.9, 122.6, 129.9, 134.1, 158.0, 202.6. IR (film) 3280, 3060, 2100, 1940, 1600, 1570. C<sub>11</sub>H<sub>8</sub>O (156.18): calcd. C 84.59, H 5.16; found C 84.28, H 5.31.