

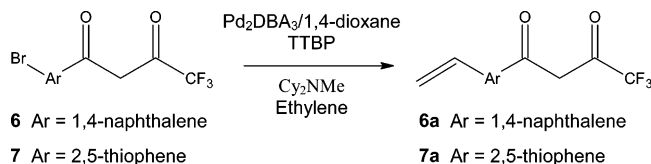
## Synthesis of Vinyl-Substituted $\beta$ -Diketones for Polymerizable Metal Complexes

Glen E. Southard\* and George M. Murray

Applied Physics Laboratory, Johns Hopkins University,  
11100 Johns Hopkins Road, Laurel, Maryland 20723-6099

jslfick3o@yahoo.com; george.murray@jhuapl.edu

Received May 25, 2005



Polymerizable  $\beta$ -diketones for application to metal ion coordination have been prepared and characterized. Bromine-substituted  $\beta$ -diketones were synthesized under Claisen–Schmidt-type condensation conditions. Vinyl groups were substituted for the halide by one of two types of Heck coupling with high-pressure ethylene. The type of Heck coupling employed was dictated by the thermal sensitivity of the substrate. Seven vinyl-substituted  $\beta$ -diketones were synthesized, including several new ones, by this method. The  $\beta$ -diketones were characterized by GC-MS, FT-NMR, FT-IR, and microanalysis.

Since its discovery some thirty years ago, the Heck cross-coupling procedure has been utilized in a wide variety of reactions in a number of fields including natural synthesis, materials, and surface chemistry.<sup>1</sup> The palladium-catalyzed reaction (Figure 1) is remarkably tolerant toward functional groups, does not require rigorously oxygen or water free systems to proceed, and has the additional advantage of utilizing cheap and readily available olefins and aryl halide substrates instead of expensive, sometimes dangerous, and procedurally difficult to use metalated or main group substituted organic compounds, such as Suzuki,<sup>2</sup> Negishi,<sup>3</sup> or Stille<sup>4</sup> coupling techniques.

The synthesis of polymerizable ligands for complexing metals has always suffered from the lack of utilization of state of the art techniques. Subsequently, investigators have either been forced to purchase readily available, but

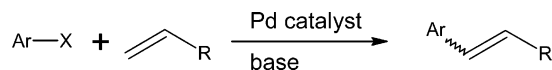


FIGURE 1. Palladium-catalyzed cross-coupling.

not always the most desirable ligands, or have relied upon noncatalytic and conventional carbon–carbon bond reactions, such as Wittig or Friedel–Crafts techniques. We hope to demonstrate that modern cross-coupling reactions have a role for readily synthesizing specialized ligands for polymerizable metal complexes that have been difficult, if not impossible, to generate by more traditional chemical reactions.

**Vinyl-Substituted Monomers.** We originally attempted to synthesize a number of vinyl-substituted  $\beta$ -diketones by a modified reaction used by Shea et al.,<sup>5</sup> where 4-methyl methylbenzoate is reacted with NBS to give 4-bromomethyl methylbenzoate, from which the phosphonium salt was generated by addition of triphenyl phosphine. The salt was converted to vinyl methylbenzoate by Wittig coupling with formaldehyde. **1a** was realized by the base-catalyzed condensation of acetone and vinyl methylbenzoate. The method proved adequate for synthesizing **1a**, but resulted in poor yields for compounds **2a–5a** because of the slower reactivity of the acetophenone derivative vs acetone. Hence, the precursor and/or the products would often autopolymerize before meaningful amounts of **2a–5a** would form. Because of the autopolymerization problem and also because the former procedure was fairly tedious, we decided to look into other types of coupling reactions.

It was found that Pd-catalyzed Heck coupling of a halogenated substrate with high-pressure ethylene gas would be the most efficient and least costly of the possible carbon–carbon bond-forming reactions. Heck chemistry is well established with a very good tolerance toward functional groups and does not require exotic transfer groups (Figure 2). Until recently the reaction conditions for Heck couplings have been somewhat harsh, often reactions were carried out in excess of 100 °C. However, recent advances (vide infra) have successfully reduced reaction temperatures to room temperature for many substrates.

The precursors to the halogenated  $\beta$ -diketones employed for this work were readily synthesized by condensation reaction, while  $\beta$ -diketones **2–5** required a couple of additional but undemanding steps (Figure 3). Compound **1** was synthesized by the condensation of 4-bromomethylbenzoate with acetone under basic conditions. The precursors of compounds **2–5** were synthesized by

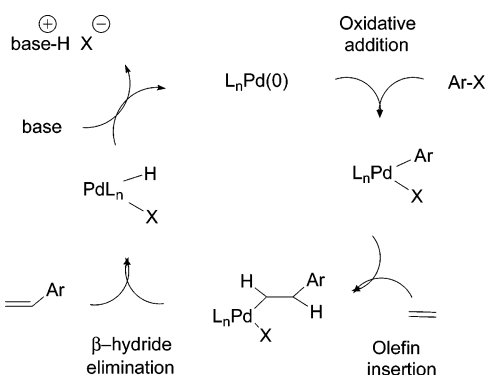
(1) (a) Deluge, M.; Cai, C. *Langmuir* **2005**, *21* (5), 1917–1922. (b) Calo, V.; Nacci, A.; Monopoli, A.; Ieva, E.; Cioffi, N. *Org. Lett.* **2005**, *7* (4), 617–620. (c) Arvela, R. K.; Leadbeater, N. E. *J. Org. Chem.* **2005**, *70* (11), 2101–2104. (d) Mo, J.; Xu, L.; Xiao, J. *J. Am. Chem. Soc.* **2005**, *127* (2), 751–760. (e) Frstrup, P.; Le Quement, S.; Tanner, D.; Norrby, P.-O. *Organometallics* **2004**, *23* (26), 6160–6165. (f) Calo, V.; Nacci, A.; Monopoli, A.; Fornaro, A.; Sabbatini, L.; Cioffi, N.; Ditaranto, N. *Organometallics* **2004**, *23* (22), 5154–5158. (g) Yao, Q.; Kinney, E. P.; Zheng, C. *Org. Lett.* **2004**, *6* (17), 2997–2999. (h) Eberhard, M. R. *Org. Lett.* **2004**, *6* (13), 2125–2128. (i) Lin, B.-L.; Liu, L.; Fu, Y.; Luo, S.-W.; Chen, Q.; Guo, Q.-X. *Organometallics* **2004**, *23* (9), 2114–2123. (j) Moore, L. R.; Shaughnessy, K. H. *Org. Lett.* **2004**, *6* (2), 225–228. (k) Na, Y.; Park, S.; Han, S. B.; Han, H.; Ko, S.; Chang, S. *J. Am. Chem. Soc.* **2004**, *126* (1), 250–258. (l) Jung, I. G.; Son, S. U.; Park, K. H.; Chung, K.-C.; Lee, J. W.; Chung, Y. K. *Organometallics* **2003**, *22* (23), 4715–4720.

(2) (a) Chen, C.-L.; Liu, Y.-H.; Peng, S.-M.; Liu, S.-T. *Organometallics* **2005**, *24* (6), 1075–1081. (b) Brenstrum, T.; Gerristma, D. A.; Adjabeng, G. M.; Frampton, C. S.; Britten, J.; Robertson, A. J.; McNulty, J.; Capretta, A. *J. Org. Chem.* **2004**, *69* (22), 7635–7639.

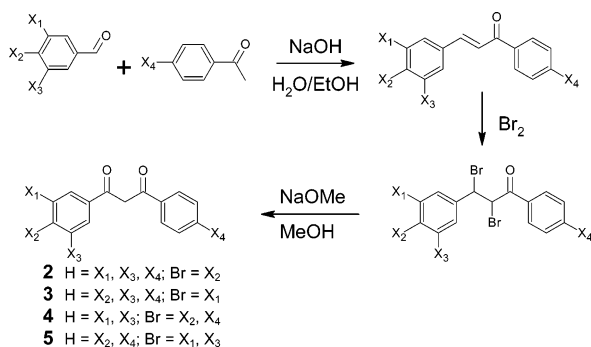
(3) (a) Knochel, P.; Singer, R. D. *Chem. Rev.* **1993**, *93*, 2117–2188. (b) Knochel, P.; Langer, F.; Longeau, A.; Rottländer, M.; Stüdemann, T. *Chem. Ber.* **1997**, *130*, 1021–1027.

(4) (a) Gallagher, W. P.; Maleczka, R. E., Jr. *J. Org. Chem.* **2005**, *70* (3), 841–846. (b) Amatore, C.; Bahsoun, A. A.; Jutand, A.; Meyer, G.; Ndedi Ntepe, A. N.; Ricard, L. *J. Am. Chem. Soc.* **2003**, *125* (14), 4212–4222.

(5) Shea, K. I.; Stoddard, G. J. *Macromolecules* **1991**, *24* (5), 1207–1209.



**FIGURE 2.** Synopsis of the catalytic cycle for Heck coupling.

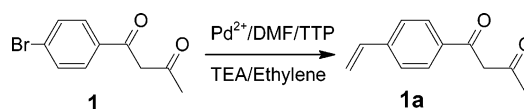


**FIGURE 3.** Preparation of dibenzoylmethane derivatives.

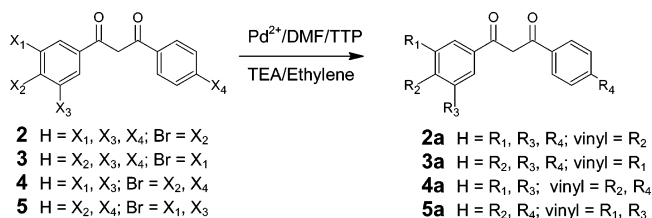
a Claisen–Schmidt base-catalyzed condensation of the appropriate acetophenones with the appropriate benzaldehydes giving the desired chalcones,<sup>6</sup> which were subsequently reacted with elemental bromine followed by bromide elimination with sodium methoxide. Hydrolysis of the methoxide intermediate gave the halogenated  $\beta$ -diketone in good yield.<sup>7</sup>

$\beta$ -Diketones **6** and **7** were synthesized by the Claisen condensation of acetyl bromoarene with ethyltrifluoroacetate under basic conditions in ether.<sup>8</sup> It was found that potassium *tert*-butoxide gave better results for **6**, while sodium methoxide was an excellent base for generating **7**. Small amounts of unreacted precursor were removed by dissolving **6** or **7** in methanol and adding the solution to methanolic copper(II) heptahydrate. The bis( $\beta$ -diketonate)copper(II) complex readily precipitates from solution. The complex was dissolved in an ether/THF solution and was washed with 1 M hydrochloric acid to remove the copper.

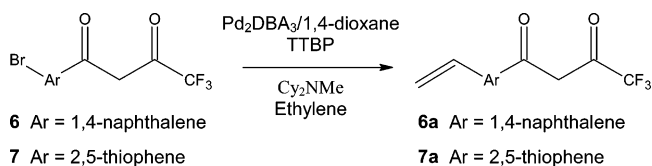
The vinyl-substituted  $\beta$ -diketones were found to be readily synthesized by utilizing Heck coupling techniques.<sup>9</sup> Compounds **1–5** were reacted with 300 psi ethylene at 100 °C in DMF. Palladium acetate and tri-*o*-tolyl phosphine (TPP) formed the catalyst, while triethylamine (TEA) acted as a base. The vinyl-substituted monomers **1a–5a** were formed in moderate to good



**FIGURE 4.** Heck coupling of ethylene with **1**.



**FIGURE 5.** Heck coupling of halogenated dibenzoylmethanes with ethylene.



**FIGURE 6.** Synthesis of vinyl-substituted aryl-4,4,4-trifluorobutane-1,3-diones.

yields; however, care must be taken to avoid extended reaction times (greater than 12 h) as hydrogenation of the vinyl moiety predominates. Two equivalents of triethylamine was needed to neutralize the hydrogen bromide generated during the reaction and labile proton of the enolate tautomer of the  $\beta$ -diketones. Compounds **1a–5a** were seen to be stable at –20 °C for several weeks without stabilizer, but were found to autopolymerize after several months of storage. Some monomer could be recovered by column chromatography on silica gel with hexanes as eluent.

The yields in the two types of reactions to create the vinyl  $\beta$ -diketones are telling. The yield from the condensation reaction to create **1a** was 43%, while the yield from Heck coupling was 55% (Figure 4). The differences between the two reactions become greater with increasing complexity of the product (Figure 5). The condensation yields for **2a** and **4a** were 6.5% and 0%, respectively, whereas the Heck coupling yields were 45% and 62%. The remaining monomers, **3a** and **5a**, were not prepared by condensation techniques. It is interesting to note that the divinyl monomers, **4a** and **5a**, enjoyed slightly greater yields than the monovinyl monomers.

Unfortunately, the electron-rich compounds **6** and **7** failed to give vinyl-substituted products under the relatively harsh reaction conditions. Fortunately, recent work by Fu described an improved, low-temperature Heck chemistry that dramatically reduced the thermal demands required for olefin substitution.<sup>10</sup> Compounds **6** and **7** were reacted with 300 psi of ethylene at 24 °C in 1,4-dioxane. Dipalladium tris(dibenzylideneacetone) and tri-*tert*-butyl phosphine (TTBP) in hexanes formed the catalyst, while dicyclohexylmethylamine (Cy<sub>2</sub>NMe) acted as a base (Figure 6). Accordingly, compounds **6a** and **7a** were synthesized in moderate to very good, 97% and 32%

(6) (a) Dhar, D. N.; Lal, J. B. *J. Org. Chem.* **1958**, *23* (8), 1159–1161. (b) Bradsher, C.; Brown, F.; Blue, W. *J. Am. Chem. Soc.* **1949**, *71* (10), S3570–3570.

(7) Hammond, G. S.; Borduin, W. G.; Guter, G. A. *J. Am. Chem. Soc.* **1959**, *81* (17), 4682–4686.

(8) (a) Levine, R.; Sneed, J. K. *J. Am. Chem. Soc.* **1951**, *73* (9), 4478–4478. (b) Barkley, L. B.; Levine, R. *J. Am. Chem. Soc.* **1951**, *73* (10), 4625–4627.

(9) Detert, H.; Sugiono, E. *J. Prakt. Chem.* **1999**, *341* (4), 358–362.

(10) Littke, A. F.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123* (29), 6989–7000.

**TABLE 1. Preparation of Vinyl-Substituted  $\beta$ -Diketones**

compd	Heck yield and prep <sup>a</sup>	vinyl <sup>1</sup> H NMR ( $\delta$ )		
<b>1a</b>	55% (a, d)	6.70 (dd, 1 H),	5.82 (d, 1 H),	5.35 (d, 1 H)
<b>2a</b>	45% (b, d)	6.86 (dd, 1 H),	5.90 (d, 1 H),	5.40 (d, 1 H)
<b>3a</b>	50% (b, d)	6.79 (dd, 1 H),	5.91 (d, 1 H),	5.36 (d, 1 H)
<b>4a</b>	62% (b, d)	6.80 (dd, 2 H),	5.90 (d, 2 H),	5.40 (d, 2 H)
<b>5a</b>	56% (b, d)	6.77 (dd, 2 H),	5.92 (d, 2 H),	5.40 (d, 2 H)
<b>6a</b>	97% (c, e)	7.20 (dd, 1 H),	5.91 (d, 1 H),	5.62 (d, 1 H)
<b>7a</b>	32% (c, e)	6.74 (dd, 1 H),	5.86 (d, 1 H),	5.43 (d, 1 H)

<sup>a</sup> Key: (a) bromomethyl methylbenzoate, NaH, acetone; (b) benzaldehyde, acetophenone, NaOH, Br<sub>2</sub>, NaOMe; (c) sodium alkoxide, aromatic acetyl, ethyl trifluoroacetate; (d)  $\beta$ -diketone, Pd(OAc)<sub>2</sub>, TPP, TEA, ethylene, DMF; (e)  $\beta$ -diketone, Pd<sub>2</sub>DBA<sub>3</sub>, TBPP, 1,4-dioxane, ethylene, Cy<sub>2</sub>NMe.

respectively, yield without hydrogenation of the vinyl group or autopolymerization. The coupling reaction required 48 h for complete consumption of the halogenated precursor. Two equivalents of Cy<sub>2</sub>NMe was needed to neutralize the hydrogen bromide generated during the reaction and labile proton of the enolate tautomer of the  $\beta$ -diketones. Compounds **6a** and **7a** were both susceptible to autopolymerization within days despite addition of stabilizer and storage at  $-20$  °C. To stabilize the compounds for both characterization and storage both **6a** and **7a** were converted to copper(II) bis  $\beta$ -diketonate salts by addition of a methanolic solution of copper(II) chloride hexahydrate to a methanol solution of the  $\beta$ -diketone. The copper(II) complex of **7a** was found to be stable indefinitely at room temperature; however, the copper(II) complex of **6a** would still autopolymerize at  $-20$  °C after several weeks. Normally, copper(II) complexes are known for quenching or retarding free-radical polymerizations. It is quite interesting to see that **6a** could stabilize the redox couple of copper(II) to the point where free-radical polymerization would propagate at  $-20$  °C. Thus **6a** should be used immediately upon isolation for subsequent chemical reactions.

Compound **3a** was prepared by the low-temperature Heck method for comparison. The yield was the same as the high-temperature Heck method, but there was no evidence of hydrogenation to the vinyl moiety.

In conclusion, a number of new vinyl-substituted aryl  $\beta$ -diketones were prepared by Heck coupling in fair to good yield. The aryl groups varied from benzene derivatives to polyaromatic hydrocarbons to heterocycles. High-temperature Heck coupling was found to work adequately for preparing vinyl-substituted aryl  $\beta$ -diketones from benzene derivatives; however, the products did suffer from partial hydrogenation of the vinyl group. The high-temperature Heck coupling also failed to give any product with the electron-rich polyaromatic and heterocyclic substrates. A low-temperature Heck coupling devised by Fu succeeded in preparing vinyl-substituted aryl  $\beta$ -diketones from those electron-rich substrates without hydrogenation of the vinyl group.<sup>10</sup> The low-temperature method was also shown to work well with the benzene derivatives without the hydrogenation suffered by the high-temperature method.

## Experimental Section

**General.** 1,4-Dioxane (anhydrous; Sure-Seal; Aldrich), Pd<sub>2</sub>(dba)<sub>3</sub> (Aldrich), and TTBP (10 wt % solution in hexane; Sure-Seal; Strem), and Cy<sub>2</sub>NMe (Aldrich) were used as received.

4-Bromobenzoylacetone was synthesized by a modified Shea method.<sup>5</sup> The bromine-substituted  $\beta$ -diketones were synthesized by modified literature procedures.<sup>6,7</sup> The 1-acetyl-4-bromonaphthalene was synthesized by standard Friedel–Crafts acylation of 1-bromonaphthalene with acetyl chloride and aluminum chloride. The Heck couplings were performed with either a Parr Instruments HC 677 100 mL reactor (compounds **1a–5a**) or a PPI LC series 300 mL reactor (compounds **3a**, **6a**, and **7a**).

**Procedure A.** Dimethyl formamide, palladium acetate, tri-*o*-tolyl phosphine, triethylamine, and brominated  $\beta$ -diketone were added to a 100 mL Parr high-pressure reactor with an inner glass liner. The solution was degassed with nitrogen for 10 min before the reactor was cooled to  $-196$  °C and ethylene was condensed for 20 min. The reactor was allowed to warm to room temperature before heating to 100 °C in an oil bath. The pressure was bled off until 300 psi was achieved and the reaction was allowed to proceed for 12 h. The reaction vessel was cooled to room temperature, the extra pressure bled, and the contents dissolved in water (50 mL) and ether (50 mL). The aqueous phase was made acidic by addition of concentrated hydrochloric acid followed by extraction with ether (2  $\times$  50 mL). The combined organic phase was rinsed with saturated sodium chloride solution, and the organic phase was dried over magnesium sulfate overnight. The solution was filtered, the solvent was removed by vacuum, and the residue was dissolved in chloroform (3 mL). The product was isolated by column chromatography from silica gel (Selecto, mesh size 63–200) with chloroform as eluent.

**Procedure B.** 1,4-Dioxane, TTBP, and Cy<sub>2</sub>NMe were placed into a 100 mL Schlenk flask and degassed with argon, before transfer by syringe to a PPI LC series 300 mL reactor containing Pd<sub>2</sub>(dba)<sub>3</sub> and the brominated  $\beta$ -diketone under an argon atmosphere. The reactor was charged to 300 psi with ethylene and the reaction was allowed to stir for 48 h at room temperature. Upon completion of the reaction the contents were taken up in water (50 mL) and ether (50 mL) and the aqueous phase was acidified by addition of concentrated hydrochloric acid and extracted with ether (2  $\times$  50 mL). The combined organic phase was rinsed with saturated sodium chloride solution, and the organic phase was dried over magnesium sulfate overnight. The solution was filtered, the solvent was removed by vacuum, and the residue was dissolved in chloroform (3 mL). The product was isolated by column chromatography from silica gel (Selecto, mesh size 63–200) with 10% ether in chloroform as eluent.

**Synthesis of 4-vinylbenzoylacetone (1a):** Procedure A was employed, using dimethyl formamide (30 mL), palladium acetate (0.022 g, 0.1 mmol), tri-*o*-tolyl phosphine (0.060 g, 0.2 mmol), triethylamine (9.1 g, 90 mmol), 4-bromobenzoylacetone (2.41 g, 10 mmol), and ethylene (1.7 g, 61 mmol). The first band collected resulted in a yellow powder (1.03 g, 55% yield) upon solvent removal.

<sup>1</sup>H NMR (200 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  16.12 (s, 1 H), 7.83 (d, 2 H), 7.45 (d, 2 H), 6.70 (dd, 1 H), 6.17 (s, 1 H), 5.82 (d, 1 H), 5.35 (d, 1 H), 2.20 (s, 3 H). Anal. (found/calcd) for C<sub>17</sub>H<sub>14</sub>O<sub>2</sub>: C 76.49/76.57, H 6.33/6.43.

**Synthesis of 4-vinyldibenzoylmethane (2a):** Procedure A was employed, using dimethyl formamide (30 mL), palladium acetate (0.022 g, 0.1 mmol), tri-*o*-tolyl phosphine (0.060 g, 0.2 mmol), triethylamine (9.1 g, 90 mmol), 4-bromodibenzoylmethane (3.03 g, 10 mmol), and ethylene (1.7 g, 61 mmol). The first band collected resulted in a yellow powder (2.2 g, 88% yield) upon solvent removal.

<sup>1</sup>H NMR (200 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  16.91 (s, 1 H), 7.98 (m, 4 H), 7.50 (m, 5 H), 6.96 (s, 1 H), 6.86 (dd, 2 H), 5.90 (d, 2 H), 5.40 (d, 2 H). Anal. (found/calcd) for C<sub>17</sub>H<sub>14</sub>O<sub>2</sub>: C 81.71/81.60, H 5.65/5.64.

**Synthesis of 3-vinyldibenzoylmethane (3a):** Procedure A was employed, using dimethyl formamide (30 mL), palladium acetate (0.022 g, 0.1 mmol), tri-*o*-tolyl phosphine (0.060 g, 0.2 mmol), triethylamine (9.1 g, 90 mmol), 3-bromodibenzoylmethane (3.03 g, 10 mmol), and ethylene. The first band collected resulted in a yellow powder (2.2 g, 88% yield) upon solvent removal.

$^1\text{H}$  NMR (90 MHz, 25 °C,  $\text{CDCl}_3$ ):  $\delta$  16.91 (s, 1 H), 8.00 (m, 4 H), 7.62 (m, 5 H), 6.84 (s, 1 H), 6.81 (dd, 2 H), 5.92 (d, 2 H), 5.40 (d, 2 H). Anal. (found/calcd) for  $\text{C}_{17}\text{H}_{14}\text{O}_2$ : C 81.35/81.60, H 5.06/5.64.

**Synthesis of 4,4'-divinyldibenzoylmethane (4a):** Procedure A was employed, using dimethyl formamide (30 mL), palladium acetate (0.022 g, 0.1 mmol), tri-*o*-tolyl phosphine (0.060 g, 0.2 mmol), triethylamine (9.1 g, 90 mmol), 4,4'-dibromodibenzoylmethane (3.82 g, 10 mmol), and ethylene (1.7 g, 61 mmol). The first band collected resulted in a yellow powder (1.7 g, 62% yield) upon solvent removal.

$^1\text{H}$  NMR (200 MHz, 25 °C,  $\text{CDCl}_3$ ):  $\delta$  16.20 (s, 1 H), 8.00 (d, 4 H), 7.55 (d, 4 H), 6.80 (dd, 2 H), 6.70 (s, 1 H), 5.90 (d, 2 H), 5.40 (d, 2 H). Anal. (found/calcd) for  $\text{C}_{19}\text{H}_{16}\text{O}_2$ : C 82.69/82.58, H 5.97/5.79.

**Synthesis of 3,5-divinyldibenzoylmethane (5a):** Procedure A was employed, using dimethyl formamide (30 mL), palladium acetate (0.022 g, 0.1 mmol), tri-*o*-tolyl phosphine (0.060 g, 0.2 mmol), triethylamine (9.1 g, 90 mmol), 3,5-dibromodibenzoylmethane (3.82 g, 10 mmol), and ethylene (1.7 g, 61 mmol). The first band collected resulted in a yellow powder (1.6 g, 56% yield) upon solvent removal.

$^1\text{H}$  NMR (200 MHz, 25 °C,  $\text{CDCl}_3$ ):  $\delta$  16.88 (s, 1 H), 7.98–7.50 (m, 8 H), 6.82 (s, 1 H), 6.77 (dd, 2 H), 5.92 (d, 2 H), 5.40 (d, 2 H). Anal. (found/calcd) for  $\text{C}_{19}\text{H}_{16}\text{O}_2$ : C 82.62/82.58, H 5.91/5.79.

**Synthesis of 1-vinylnaphthoyltrifluoroacetone (6a):** Procedure B was employed, using 1,4-dioxane (40 mL), TTBP (0.182 g, 0.9 mmol),  $\text{Cy}_2\text{NMe}$  (19.5 g, 100 mmol),  $\text{Pd}_2(\text{dba})_3$  (0.420 g,

0.45 mmol), and 4-bromonaphthoyltrifluoroacetone (10.4 g, 30 mmol). The product was isolated as a light brown oil (9.01 g, 97% yield).

$^1\text{H}$  NMR (90 MHz, 25 °C,  $\text{CDCl}_3$ ):  $\delta$  14.49 (s, 1 H), 8.48 (m, 1 H), 8.06 (m, 1 H), 7.58 (m, 4 H), 7.45 (dd, 1H), 6.45 (s, 1 H), 5.91 (dd, 1 H), 5.62 (dd, 1H). Anal. (found/calcd) for  $\text{C}_{16}\text{H}_{11}\text{F}_3\text{O}_2$ : C 65.75/65.76, H 3.74/3.79.

**Synthesis of 5-vinylthenoyltrifluoroacetone (7a):** Procedure B was employed, using 1,4-dioxane (40 mL), TTBP (0.182 g, 0.9 mmol),  $\text{Cy}_2\text{NMe}$  (19.5 g, 100 mmol),  $\text{Pd}_2(\text{dba})_3$  (0.420 g, 0.45 mmol), and 5-bromothenoyletrifluoroacetone (9 g, 30 mmol). The product was isolated as a light green solid (2.4 g, 32% yield). The solid was reacted with cupric chloride dehydrate in methanol, precipitated by addition of water, and recrystallized from THF/hexanes to give  $(\text{VTTFa})_2\text{Cu}\cdot 1.5\text{THF}$ .

$^1\text{H}$  NMR (free ligand, 90 MHz, 25 °C,  $\text{CDCl}_3$ ):  $\delta$  14.25 (br s, 1 H), 7.63 (d, 2 H), 7.12 (s, 1 H), 6.94 (dd, 1 H), 6.36 (d, 1 H), 5.86 (d, 1 H). Anal. (found/calcd) for  $\text{C}_{26}\text{H}_{24}\text{CuF}_6\text{O}_{5.5}\text{S}_2$ : C 46.75/46.88, H 3.60/3.63.

**Supporting Information Available:** General procedures for the syntheses of chalcone, dibrominated chalcone, and  $\beta$ -diketone precursors and synthetic details for the fluorinated  $\beta$ -diketones with  $^1\text{H}$  NMR and elemental analyses information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO051051N