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Supplemental Information

for

Synthesis of Vinyl Substituted β -Diketones for Polymerizable Metal Complexes

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General procedure for chalcone synthesis: Sodium hydroxide (45 mmol) and halogenated acetophenone (36 mmol) were dissolved in water (18 mL) and ethanol (50 mL). A benzaldehyde (36 mmol) in ethanol (20 mL) was added dropwise to the acetophenone solution. A slurry quickly formed, which was allowed to stir overnight. The slurry was filtered, washed with water until the filtrate was neutral to pH paper, and dried at 100°C for 12 hours. The chalcones were used without any further purification.

General procedure for dibrominated chalcone synthesis: A chalcone (35 mmol) was dissolved in refluxing chloroform (300 mL) and bromine (35 mmol) was added dropwise. A precipitate immediately formed. The solution was cooled to room temperature, the precipitate was isolated by filtration, and was washed with cool chloroform (100 mL). The light pink precipitate was air dried and used without any further purification.

General procedure for compounds 2-5: Sodium metal (85.5 mmol) was reacted with excess methanol (100 mL). A dibrominated chalcone (34.2 mmol) was suspended in methanol (50 mL) and the methanolic sodium methoxide solution was added dropwise. The mixture soon cleared and the reaction solution was heated to reflux for 1 hour. Concentrated hydrochloric acid (5 mL) was added, the solution was allowed to reflux for an additional 5 minutes before water (50 mL), and the solution was allowed to cool to room temperature. Filtration of the resulting precipitate gave pale yellow crystals, which were allowed to air dry, and were recrystallized from hexanes before further use.

Synthesis of 4-bromo-1-naphthoyltrifluoroacetone (6): Ethyltrifluoroacetate (6.91 g, 49 mmol) was added dropwise to an ether (10 mL) solution containing sodium t-

butoxide (6.7 g, 52 mmol), which formed a slurry. The 4-bromo-1-acetylnaphthalene (12.2 g, 49 mmol) was added to the slurry in several large additions and the solution was allowed to stir for 18 hours. The solution was diluted with additional ether (50 mL) and was washed with 1 M hydrochloric acid (2 x 50 mL). The ethereal solution was dried over magnesium sulfate, filtered and the solvent removed. The 4-bromonaphthoyltrifluoroacetone could be separated from the unreacted 4-bromo-1-acetylnaphthalene by forming the copper bis(diketonate) from a methanolic solution of the raw β -diketone and cupric chloride. The first band collected resulted in a yellow powder (9.8 g, 58 % yield) upon solvent removal. $^1\text{H-NMR}$ (90 MHz, 25°C, CDCl_3): δ 14.15 (s, 1 H), 8.40 (m, 2 H), 7.67 (m, 4 H), 6.47 (s, 1 H). Anal.: (found/calc for $\text{C}_{14}\text{H}_8\text{BrF}_3\text{O}_2$) 48.93 (48.72), H 2.38 (2.34).

Synthesis of 5-bromothienoyltrifluoroacetone (7): Ethyltrifluoroacetate (6.91 g, 49 mmol) was added dropwise to an ether (10 mL) solution containing sodium methoxide (2.8 g, 52 mmol) which formed a slurry. The 5-bromo-2-acetylthiophene (10 g, 49 mmol) was added to the slurry in several large additions and the solution was allowed to stir for 18 hours. The solution was diluted with additional ether (50 mL) and was washed with 1 M hydrochloric acid (2 x 50 mL). The ethereal solution was dried over magnesium sulfate, filtered and the solvent removed. The 5-bromothienoyltrifluoroacetone could be separated from the unreacted 2-bromothiophene by vacuum distillation (150°C, 2 torr) or be isolated by forming the copper bis(diketonate) from a methanolic solution of the raw β -diketone and cupric chloride. The first band collected resulted in a yellow powder (7.4 g, 50 % yield) upon solvent

removal. ^1H -NMR (90 MHz, 25°C, CDCl_3): δ 14.25 (bs, 1 H), 7.63 (d, 2 H), 7.12 (s, 1 H). Anal.: (found/calc for $\text{C}_8\text{H}_4\text{BrF}_3\text{O}_2\text{S}$) 31.82 (31.92), H 1.35 (1.33).