

## Supporting Information

***S*-[3-Cyano-2-oxo-3-(triphenyl- $\lambda^5$ -phosphanylidene)propyl] *O*-ethyl Carbonodithioate: A Novel Xanthate Reagent for the Synthesis of  $\alpha$ -keto (cyanomethylene)triphenylphosphorane Ylides from Olefins**

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**Table 1.** Concomitant radical addition/partial reduction of xanthate **6** to olefins **7** to provide xanthate adducts **8** & reduced adducts **2''** (where Xa = -S(C=S)OEt).<sup>a</sup>

Run	7	R =	DLP (eq) <sup>b</sup>	time (h)	8/2'' (Yield) <sup>c,d</sup>
1	7a	-(CH <sub>2</sub> ) <sub>4</sub> Me <sup>e</sup>	0.3	3	8a/2''a (72/4)
2	7a	-(CH <sub>2</sub> ) <sub>4</sub> Me <sup>f</sup>	0.3	3	8a/2''a (75/7)
3	7a	-(CH <sub>2</sub> ) <sub>4</sub> Me	0.3	3	8a/2''a (77/7)
4	7b	-Ph	0.3	3	8b/2''b (69/7)
5	7c	2-Cyclohexanoyl-	0.3	3	8c/2''c (78/5)
6	7d	-OAc	0.3	3	8d/2''d (62/9)
7	7e	-CN	0.6 <sup>g</sup>	4.5	8e/2''e (60/9)
8	7f	-OCOCH <sub>2</sub> CN	0.3	3	8f/2''f (60/7)
9	7g	-OCO <sub>2</sub> Ph	0.3	3	8g/2''g (76/5)
10	7h	-OCH <sub>2</sub> Ph	0.6 <sup>g</sup>	4.5	8h/2''h (52/6)

a: Xanthate **6** (0.4 mmol), DCE (2.0 mL), olefin (3.0 eq), reflux, 15 min, cooled to rt, DLP, reflux for designated time, Ar; b: DLP (0.1 eq) was added every hour for designated time; c: Isolated yield by flash column chromatography on SiO<sub>2</sub>; d: Isolated yield was calculated based on the amounts of xanthate **6** used; e: 1-Octene (2.0 eq) was used; f: 1-Octene (2.5 eq) was used; g: DLP (0.2 eq) was added every 1.5 hour for designated time.