Palladium-Catalyzed Allylic Alkylations via Titanated Nucleophiles: A New Early−Late Heterobimetallic System

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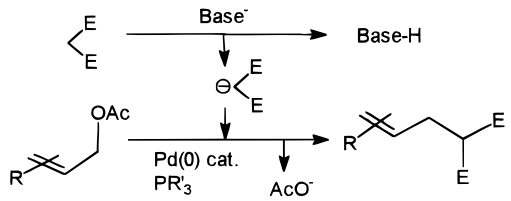
The palladium(0)-catalyzed allylic alkylation of soft carbon nucleophiles is a very useful organometallic transformation[1] that allows the clean allylation of a great variety of active methylene compounds with high and predictable regio-, diastereo-, and enantioselection. In the presence of suitable ligands, the allylic system is known to interact with the palladium(0) complex to generate a cationic π-allyl palladium species, which is in turn intercepted by the anion of the carbon nucleophile (Scheme 1).

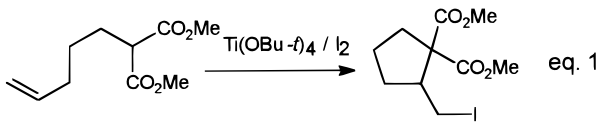
The way the nucleophile is deprotonated is dependent on a few parameters. In particular, when the pK_a value of the conjugated acid of the displaced group is higher than that of the active methylene, deprotonation may take place in situ by the displaced anion itself. Such an *endogenous* deprotonation mode can be at work on a wide variety of carbon acids when allylic carbonates,[2] phenoxides,[3] and oxiranes are used.[4] In the case of the more common allylic acetates, the carbanionic species is generally, either preformed or generated in situ by the explicit addition of a stoichiometric amount of base. We recently found that *endogenous* deprotonation is viable with allylic acetates too, though on a more restricted pK_a window.[5] As an extension of this investigation, we next decided to look for alternative enolizing conditions, so as to enable reaction of a broader range of carbanionic nucleophiles.

Taguchi and co-workers reported that the iodocarbocyclization of 4-pentenyl malonates could be achieved in the presence of I_2 and Ti(OBu-*t*)$_4$.[6] According to the authors, the mechanism of this cyclization involves the titanium alkoxide-mediated generation of a titanium

Scheme 1



enolate,[7] which cyclizes onto the concomitantly generated iodonium ion (eq 1).



Since the chemistry of the palladium-catalyzed allylic alkylations has been mainly focused on alkali metal enolates of active methylenes, we decided to investigate such postulated titanium enolates in the contest of allylic alkylations.[8] Our results are reported in Table 1.

In a preliminary experiment, we heated diethyl malonate (**1a**) with cinnamyl acetate (**2a**) in CH_2Cl_2 for 9 h in the presence of Ti(OPr-*i*)$_4$ (1.2 equiv), $Pd_2(dba)_3$ (0.05 equiv), and PPh_3 (0.5 equiv) (entry 1A). Much to our satisfaction, we isolated the expected allylated product **3aa** in a very encouraging 86% yield. Two comments are worthy of note: (a) No apparent Lewis acid−base conflict between Ti(OPr-*i*)$_4$ and PPh_3 ensued. (b) The same allylic alkylation under neutral conditions failed, since the pK_a value of diethyl malonate is not in the suitable *base-free window*.[5] When, for comparison, the same reaction was run in the presence of BSA/AcOK[9] as the enolizing system, **3aa** was obtained in a slightly decreased 83% yield (entry 1B). In order to evaluate the scope of this new method, we extended such a comparative study (method A, Ti(OPr-*i*)$_4$; method B, BSA/AcOK cat.) to other palladium-catalyzed allylic alkylations. Methyl nitroacetate (**1b**) reacted with cinnamyl acetate (**2a**) only under method A, with method B affording just recovered starting material (entries 2A and 2B). Method A was also successful in the reaction between diphenyl disulfone (**1c**) and either geranyl acetate (**2b**) (entry 3) or cinnamyl acetate (**2a**) (entry 4A). The reactions between (*Z*)-1,4-diacetoxy-but-2-ene (**2c**) and diethyl malonate (**1a**) (en-

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(1) (a) Hegedus L. S. In *Organometallics in Synthesis*; Schlosser, M., Ed.; John Wiley: Chichester, 1994; Chapter 5, pp 385−459. (b) Tsuji, J. *Palladium Reagents and Catalysts*; John Wiley: New York, 1995. (c) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: Orlando, 1985. (d) Frost, C. G.; Howarth, J.; Williams, J. M. J. *Tetrahedron: Asymmetry* **1992**, *3*, 1089. (e) Harrington P. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 12, Chapter 8.2, pp 798−903. (f) Heumann, A.; Réglier, M. *Tetrahedron* **1995**, *51*, 975.

(2) (a) Tsuji, J.; Minami, I. *Acc. Chem. Res.* **1987**, *20*, 140. (b) Tsuji, J. *Tetrahedron* **1986**, *42*, 4361. (c) Safi, M.; Sinou, D. *Tetrahedron Lett.* **1991**, *32*, 2025.

(3) Tsuji, J.; Okumoto, H.; Kobayashi, Y.; Takahashi, T. *Tetrahedron Lett.* **1981**, *22*, 1357.

(4) Tsuji, J.; Kataoka, H.; Kobayashi, Y. *Tetrahedron Lett.* **1981**, *22*, 2575.

(5) Poli, G.; Giambastiani, G. *J. Org. Chem.* **1998**, *63*, 9608.

(6) (a) Kitagawa, O.; Inoue, T.; Hirano, K.; Taguchi, T. *J. Org. Chem.* **1993**, *58*, 3106. (b) Inoue, T.; Kitagawa, O.; Oda, Y.; Taguchi, T. *J. Org. Chem.* **1996**, *61*, 8256.

(7) For other recent reports on titanium enolates, see: (a) Evans, D. A.; Urpi, F.; Somers, T. C.; Clark, J. S.; Bilodeau, M. T. *J. Am. Chem. Soc.* **1990**, *112*, 8215. (b) Williams, R. M.; Esslinger, C. S. *Tetrahedron Lett.* **1991**, *32*, 3635. (c) Mahrwald, R. *Chem. Ber.* **1995**, *128*, 919. (d) Bernardi, A.; Cavicchioli, M.; Potenza, D.; Scolastico, C. *J. Org. Chem.* **1994**, *59*, 3690. (e) Mahrwald, R. *Tetrahedron* **1995**, *51*, 9015. (f) Mahrwald, R.; Costisella, B. *Synthesis* **1996**, 1087. (g) Matsumura, Y.; Nishimura, M.; Hiu, H.; Watanabe, M.; Kise, N. *J. Org. Chem.* **1996**, *61*, 2809.

(8) To the best of our knowledge, the only precedents combining palladium catalysis and Ti(OPr-*i*)$_4$, deal with the addition of CO, Zn(acac)$_2$, and phenols to allylic alcohols: (a) Itoh, K.; Hamaguchi, N.; Miura, M.; Nomura, M. *J. Mol. Catal.* **1992**, *75*, 117. (b) Itoh, K.; Hamaguchi, N.; Miura, M.; Nomura, M. *J. Chem. Soc., Perkin Trans. 1* **1992**, 2833. (c) Satoh, T.; Ikeda, M.; Miura, M.; Nomura, M. *J. Org. Chem.* **1997**, *62*, 4877. For the structure of a Ti(IV)/Pd(II)-based complex, see: (d) Kless, A.; Lefeber, C.; Spannenberg, A.; Kempe, R.; Baumann, W.; Holz, J.; Börner, A. *Tetrahedron* **1996**, *52*, 14599.

(9) BSA/AcOK cat. is a standard enolizing system in palladium-catalyzed allylic alkylations. Trost, B. M.; Murphy, D. J. *Organometallics* **1985**, *4*, 1143.

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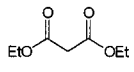
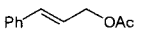
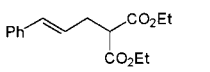
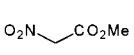
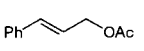
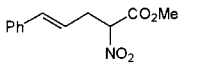
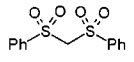
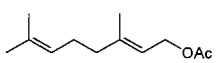
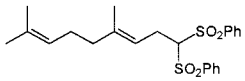
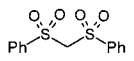
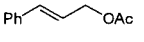
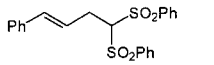
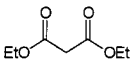
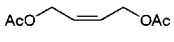
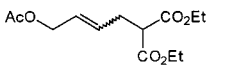
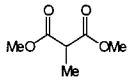
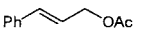
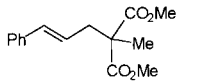
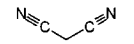
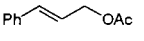
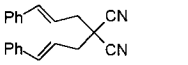
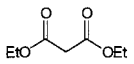
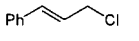
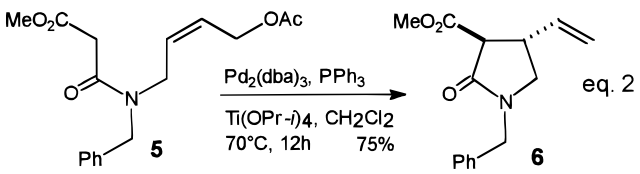
Table 1. Palladium-Catalyzed Allylic Alkylations: A Comparison between Ti(OPr-*i*)$_4$ and BSA/AcOK as Promoters[a]

Entry	Nucleophile		Acetate		Method[b]	Solvent	T (°C)	time (h)	Product		Yield[c] (%)
1A		**1a**		**2a**	A	CH_2Cl_2	40	9		**3aa**	86
1B					B	THF	70	4.5			83
2A		**1b**		**2a**	A	CH_2Cl_2	40	0.25		**3ba**	89
2B					B	THF	70	20			-
3		**1c**		**2b**	A	$C_2H_4Cl_2$	85	12		**3cb**	88
4A		**1c**		**2a**	A	$C_2H_4Cl_2$	85	12		**3ca**	80
4B					B	THF	70	12			73
5A		**1a**		**2c**	A	CH_2Cl_2	40	9		**3ac**	61
5B					B	THF	70	4.5			66
6A		**1d**		**2a**	A	CH_2Cl_2	40	6		**3da**	64
6B					B	THF	70	6			76
7A		**1e**		**2a**	A	$C_2H_4Cl_2$	85	12		**4ea**	39[d]
7B					B	THF	70	12			38[d]
8		**1a**		**2d**	A	CH_2Cl_2	40	20	-	-	-

[a] All the reactions were run at reflux of the solvent. [b] Method A: $Pd_2(dba)_3$ 0.05 equiv, PPh_3 0.5 equiv, Ti(OPr-*i*)$_4$ 1.2-1.5 equiv. Method B: $Pd_2(dba)_3$ 0.05 equiv, PPh_3 0.5 equiv, BSA (1.2−1.5 equiv)/AcOK (0.1 equiv). [c] Yields of isolated product. [d] Since the calculation is based on the reacted acetate, a theoretical yield of 50% has to be considered.

tries 5A and 5B) and those between cinnamyl acetate (**2a**) and dimethyl methylmalonate (**1d**) (entries 6A and 6B) all worked straightforwardly. The reaction between cinnamyl acetate (**2a**) and malononitrile (**1e**) gave the diallylated product **4ea** exclusively, with both methods (entries 7A and 7B). As a further experiment, we tested the intramolecular allylic alkylation of the amide **5**, a precursor of the 3,4-disubstituted pyrrolidin-2-one **6**, recently studied by us.[10] Here again, method A proved to be superior with respect to the reference method B (eq 2).



eq. 2

Worthy of note, although Ti(OPr-*i*)$_4$ is a known transesterification promoter,[11] no trace, or only tiny amounts, of isopropyl esters have been detected in the experiments involving esters as nucleophiles. Some preliminary NMR experiments helped to clarify the mechanism of this new process (Figure 1).

In particular, the ^{1}H NMR spectrum of an equimolar mixture of diethyl malonate and Ti(OPr-*i*)$_4$ (spectrum c) in $CDCl_3$ showed no significant deviation with respect to the simple superimposition of the spectra of the two single components (spectra a and b). On the other hand, the IR spectrum of the same mixture in CH_2Cl_2 showed the presence of two bands at 1729 and 1625 cm^{-1}, which can be assigned to the free and Ti-coordinated carbonyl stretching, respectively.[12,13] Since no apparent enolization was detectable in the presence of only Ti(OPr-*i*)$_4$,[14,15] it was concluded that either the enolization equilibrium is dramatically shifted to the left side or another anionic species, present in the medium, had to be responsible for the deprotonation step. Indeed, when a catalytic amount of *n*-Bu$_4$N$^+$AcO$^-$ was added to the solution of spectrum c, as a soluble acetate source, the immediate and total disappearance of the methylene singlet of the malonate indicated that a rapidly equilibrating enolate species was generated (spectrum d). This fact suggested that the acetate counterion of the transiently formed π-allyl complex is the previously postulated external deprotonating agent.[16] The results obtained are consistent with the following sequence of events: (a) coordination of the titanium complex on the basic site(s) of the nucleophile and concomitant oxidative addition of the Pd(0) catalyst to form a cationic π-allyl-complex, (b) acetate anion-mediated deprotonation of the Ti-coordinated nucleophile

(10) Giambastiani, G.; Pacini, B.; Porcelloni, M.; Poli, G. *J. Org. Chem.* **1998**, *63*, 804.

(11) Seebach, D.; Weidmann, B.; Widler, L. In *Modern Synthetic Methods*; Scheffold, R., Ed. Salle + Sauerlander: Aarau, 1983; pp 217−351. As expected, copious or total transesterification products can be detected with highly prolonged reaction times.

(12) Finn, M. G. Sharpless, K. B. In *Asymmetric Synthesis*; Morrison, J. D., Ed.; Academic Press: New York, 1985; Vol. 5, Chapter. 8.

(13) The Lewis base/acid interaction between carbonyl esters and Ti(OPr-*i*)$_4$ is a rapid process on the NMR time scale at room temperature, involving the fluxional exchange between bound and unbound carbonyl esters. See ref 12.

(14) A slow Ti(OPr-*i*)$_4$-mediated monotransesterification was the only detectable reaction.

(15) For a hint on the weak basic character of Ti(OR)$_4$, see: Sasai, H.; Suzuki, T.; Arai, S.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1992**, *114*, 4418.

(16) This result suggests that the mechanism leading to the titanium enolates postulated by Taguchi in the iodocarbocyclization process might need a slight revision, i.e., the requirement of an external deprotonating agent, such as the iodide anion released in the iodionium ion formation, or an added base.

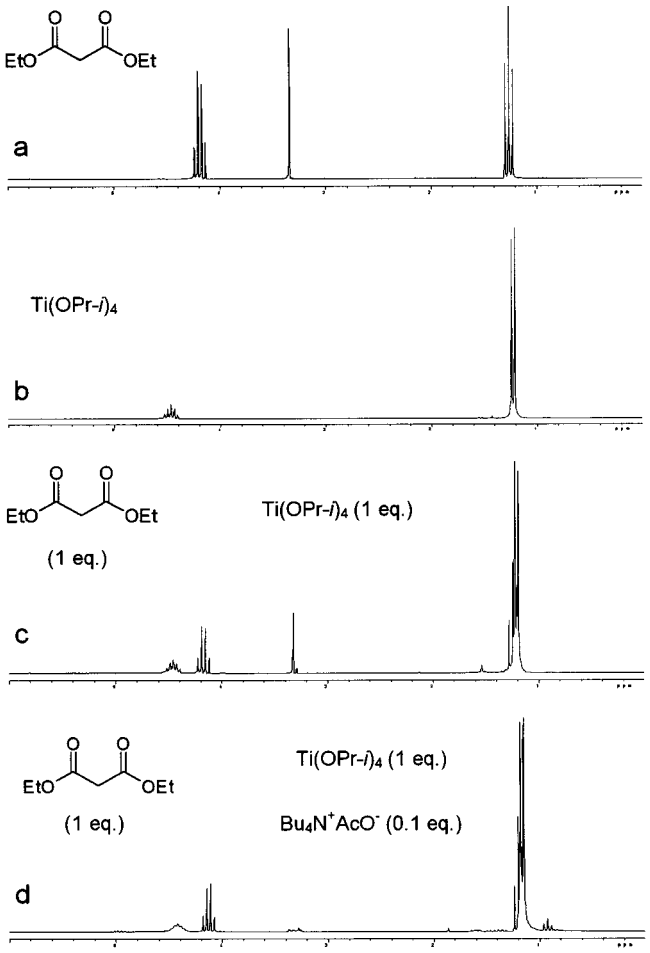


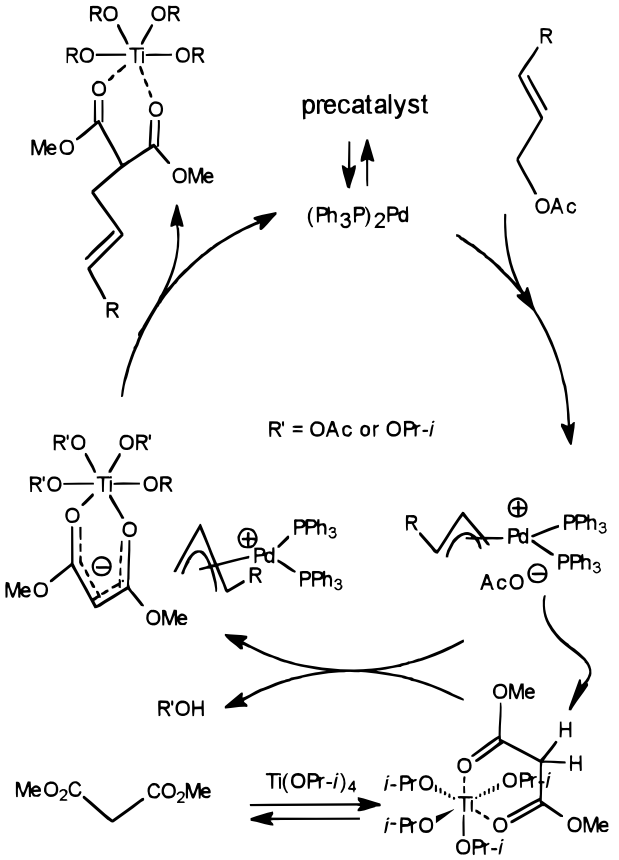
Figure 1. Generation of the titanium enolate of diethyl malonate. ^{1}H NMR 200 MHz spectra in $CDCl_3$ at rt: (a) diethyl malonate; (b) Ti(OPr-*i*)$_4$; (c) diethyl malonate/Ti(OPr-*i*)$_4$ 1.0:1.0 equiv; (d) diethyl malonate/Ti(OPr-*i*)$_4$/*n*-$Bu_4N^+AcO^-$ 1.0:1.0:0.1 equiv.

to generate a titanium enolate, or titanated species,[17] and (c) reductive coupling between the two organometallic species to give the allylated product (Scheme 2).

It should be noted that the acetate anion-promoted deprotonation is a mechanistic feature in common with the previously reported *acetate/base-free* mechanism. However, in the present case the greater Lewis acidity of Ti(IV) with respect to that of Pd(II) lowers the pK_a value of the coordinated active methylene[18] to the point that deprotonation of a wider range of nucleophilic species becomes now possible.

In summary, we have shown that Ti(OPr-*i*)$_4$ promotes the palladium-catalyzed addition of a wide range of carbon acids on allylic acetates. This new protocol is operationally very simple, it spans a wide nucleophile pK_a window, and it often compares favorably with the most popular enolizing system based on BSA/AcOK.[9] Extension of the present method to asymmetric variants by the use of chiral titanium alkoxides, possibly in substoichiometric amounts, is currently under investigation.

Scheme 2



Experimental Section

General Procedure for the Palladium-Catalyzed Allylic Alkylation via Titanated Species (Table 1, Entries 1A, 2A, 3, 4A, 5A, 6A, 7A, and 8). To a solution of the allylic acetate (0.5 mmol) and the carbon nucleophile (0.6 mmol) in the appropriate solvent (10 mL) at room temperature and under nitrogen atmosphere was added Ti(OPr-*i*)$_4$ (0.7 equiv) dropwise and the resulting solution stirred for 10 min. $Pd_2(dba)_3$ (0.025 mmol) and PPh_3 (0.25 mmol) were then premixed in a separated vessel and added. After the appropriate reflux time (see Table 1), the reaction was then treated with H_2O (10 mL), and the resulting white precipitate (TiO_2) was filtered off on a Celite pad, washing with CH_2Cl_2. The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (3 × 5 mL). The collected organic layers were dried, and the solvent was removed in vacuo to afford the crude product.

General Procedure for the Palladium-Catalyzed Allylic Alkylation via BSA/AcOK (Table 1, Entries 1B, 2B, 4B, 5B, 6B, and 7B). To a solution of the allylic acetate (0.5 mmol) and the carbon nucleophile (0.6 mmol) in THF (10 mL) were added bis(trimethylsilyl)acetamide (0.6 mmol) and AcOK (0.05 mmol) in this order with stirring under nitrogen atmosphere. $Pd_2(dba)_3$ (0.025 mmol) and PPh_3 (0.25 mmol), were then premixed in a separated vessel and added. After the appropriate reflux time (see table) a saturated aqueous solution of NH_4Cl (10 mL) was added and the organic phase was extracted with Et_2O (5 × 3 mL). The collected organic layers were dried and the solvent was removed in vacuo to afford the crude product.

(*E*)-5-Phenyl-2-nitropent-4-enoic Acid Methyl Ester (3ba). Flash chromatography (hexanes/AcOEt 80:20) gave pure **3ba** as an oil. ^{1}H NMR ($CDCl_3$): δ 7.34−7.24 (5H), 6.56 (d, 1H, J =

(17) At present we do not have structural information on these transiently generated titanated species. In particular, study of the titanated derivative of the disulfone (**1c**), for which a true *enolate* form is forbidden, might prove of structural interest. For studies on the structure of α-lithiated sulfones, see: (a) Gais, H.-J.; Hellmann, G.; Günther, H.; Lopez, F.; Lindner, H. J.; Braun, S. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1025. (b) Hollstein, W.; Harms, K.; Marsch, M.; Boche, G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 846. (c) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277.

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16.1 Hz), 6.09 (dt, 1H, J = 16.1, 7.3 Hz), 5.24 (dd, 1H, J = 8.8, 5.9 Hz), 3.84 (s, 3H), 3.17−3.06 (2H). ^{13}C NMR ($CDCl_3$): δ 33.74, 53.66, 87.49, 121.06, 126.43, 128.05, 128.65, 135.48, 136.22, 164.52. IR ($CDCl_3$): 3033, 2960, 1754 cm^{-1}. MS m/z: 235 (M^+, 3); 188 (14); 129 (100); 117 (13); 91 (58). Anal. Calcd for $C_{12}H_{13}NO_4$: C, 61.27; H, 5.57; N, 5.95. Found: C, 61.32; H, 5.70; N, 6.03.

(*E*)-4,4-Bis(phenylsulfonyl)-1-phenylbutene (3ca). Flash chromatography (hexanes/AcOEt 80:20) gave the pure **3ca** as white crystals. Mp 151−152 °C. ^{1}H NMR ($CDCl_3$): δ 8.00−7.95 (4H), 7.73−7.51 (6H), 7.34−7.19 (5H), 6.31 (d, 1H, J = 15.8 Hz), 6.06 (dt, 1H, J = 15.8, 6.6 Hz), 4.56 (t, 1H, J = 6.2 Hz), 3.13−3.06 (2H). ^{13}C NMR ($CDCl_3$): δ 29.39, 82.72, 123.43, 126.36, 127.89, 128.58, 129.18, 129.71, 134.15, 134.70, 136.34, 138.01. IR ($CDCl_3$): 3067, 3030, 2929, 1329, 1147 cm^{-1}. MS m/z: 413 ($M + 1^+$, 2); 271 (14); 129 (57); 128 (100); 91 (27); 77 (78). Anal. Calcd for $C_{22}H_{20}O_4S_2$: C, 64.06; H, 4.89. Found: C, 64.31; H, 5.07.

(6,7-*E*)-9,9-Bis(phenylsulfonyl)-2,6-dimethylnona-2,6-diene (3cb). Flash chromatography (hexanes/AcOEt 80:20) gave pure **3cb** as white crystals. Mp: 61−63 °C). ^{1}H NMR ($CDCl_3$): δ 7.95 (4H), 7.72−7.51 (6H), 5.03 (2H), 4.27 (t, 1H, J = 6.3 Hz), 2.90−2.84 (2H), 2.05−1.84 (4H), 1.67 (s, 3H), 1.58 (s, 3H), 1.45 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 16.10, 17.70, 24.60, 25.67, 26.24, 39.42, 84.26, 118.02, 123.81, 129.09, 129.63, 134.55, 138.19, 139.61. IR ($CDCl_3$): 3073, 2970, 2918, 2856, 1329, 1150 cm^{-1}. MS m/z: 432 (M^+, 2); 291 (18).

(*E*)-Bis(3-phenylprop-2-enyl)malononitrile (4ea). Flash chromatography (hexanes/AcOEt 90:10) gave the pure **4ea** as white crystals. Mp 116−118 °C. ^{1}H NMR ($CDCl_3$): δ 7.48−7.25 (10H), 6.71 (d, 2H, J = 15.7 Hz), 6.26 (dt, 2H, J =15.7, 7.7 Hz), 2.90 (dd, 4H, J =7.7, 1.1 Hz). ^{13}C NMR ($CDCl_3$): δ 37.91, 40.37, 115.04, 119.02, 126.74, 128.58, 128.76, 135.70, 138.01. IR ($CHCl_3$): 3686, 3019, 2930, 2230 cm^{-1}. MS m/z: 298 (M^+, 2); 117 (100); 91 (24). Anal. Calcd for $C_{21}H_{18}N_2$: C, 84.53; H, 6.08; N, 9.39. Found: C, 84.29; H, 5.97; N, 9.31.

(*E*)-2-Methyl-2-(3-phenylallyl)malonic Acid Dimethyl Ester (3da). Flash chromatography (hexanes/Et_2O 90:10) gave pure **3da** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ = 7.35-7.20 (5H), 6.45 (d, 1H, J = 15.7 Hz), 6.08 (dt, 1H, J = 15.8, 7.3 Hz), 3.73 (s, 6H), 2.77 (dd, 2H, J = 7.5, 1.4 Hz), 1.45 (s, 3H). ^{13}C NMR ($CDCl_3$): δ 19.76, 39.37, 52.31, 54.01, 124.03, 125.96, 127.20, 128.22, 134.04, 137.29, 172.33. IR ($CDCl_3$): 3032, 3002, 2956, 1728 cm^{-1}. MS m/z: 262 (M^+, 16); 202 (39); 143 (74); 117 (100), 91 (27). Anal. Calcd for $C_{15}H_{18}O_4$: C, 68.69; H, 6.92. Found: C, 68.50; H, 7.01.

2-(4-Acetoxybut-2-enyl)malonic Acid Diethyl Ester (3ac). Flash chromatography (hexanes/AcOEt 75:25) gave pure **3ac** as a colorless oil. ^{1}H NMR ($CDCl_3$): δ 5.67 (2H), 4.49 (d, 2H, J = 4.80 Hz), 4.20 (q, 4H, J = 7.3 Hz), 3.40 (t, 1H, J = 7.7 Hz), 2.65 (2H), 2.04 (s, 3H), 1.26 (t, 6H, J = 7.3 Hz). ^{13}C NMR ($CDCl_3$): δ = 14.04, 20.91, 31.36, 51.55, 61.49, 64.55, 127.12, 130.95, 168.78, 170.75. IR ($CDCl_3$): 2985, 1729 cm^{-1}. MS m/z: 272 (M^+, 22); 212 (20); 199 (29); 113 (100).

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Supporting Information Available: ^{1}H NMR spectra of compounds **3aa**, **3ba**, **3cb**, **3ca**, **3ac**, **3da**, and **4ea**. This material is available free of charge via the Internet at http://pubs.acs.org.

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