Synthesis of Vinylcyclopropanes, Cyclopropyl Vinyl Ketones, and 3-Pyrazolyl Vinyl Ketones from 1-Diazo-3-trimethylsilylpropanone

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Reaction of 1-diazo-3-trimethylsilylpropanone with olefins in the presence of cupric acetylacetonate ($Cu(acac)_2$) affords cyclopropyl trimethylsilylmethyl ketones. One-flask procedure for the formation of these silylated ketones and subsequent treatment with organometallics or with lithium diisopropylamide (LDA) and then carbonyl compounds gives a variety of vinylcyclopropanes or cyclopropyl vinyl ketones in good yields, respectively. Cycloaddition of 1-diazo-3-trimethylsilylpropanone with acetylenes and similar carbon–carbon bond formation at the side chain of the cycloadducts lead to 3-pyrazolyl vinyl ketones.

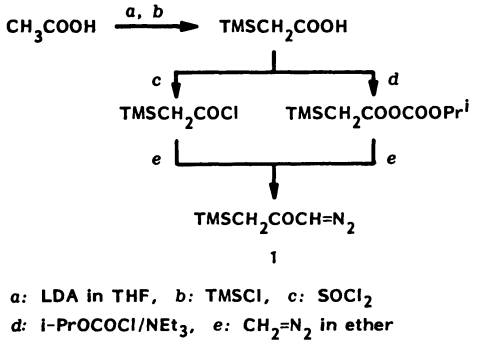
Rapidly growing importance of organosilanes in recent organic synthesis owes to their wide utility in carbanion chemistry. Silicon–carbon bond can be smoothly desilylated by action with a silylophile leading to the regioselective formation of carbanion, and deprotonation can be performed by action with a base at the carbon substituted by the silyl moiety generating silyl-stabilized carbanion.[1] The resulting carbanionic species can be utilized for carbon–carbon bond-forming reactions. Accordingly, addition of a silyl moiety to functionalized molecule produces a new reagent of multi-functionalized type.[2]

Silicon–carbon bond is relatively inert under normal conditions so that the compounds bearing this bond may be often isolated and the silyl moiety may survive on a chemoselective reaction at the preexisting functionality. Use of the both functionalities in separate steps, one by one in two different orders, adds new synthetic potentials to the parent molecule providing a new reagent.

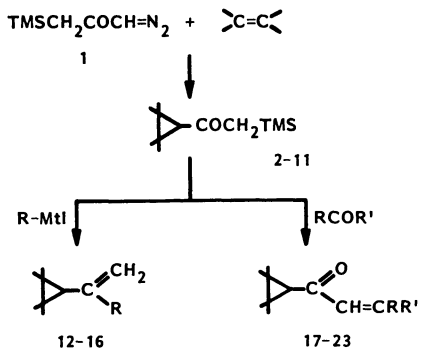
The present report describes the synthetic utility of 1-diazo-3-trimethylsilylpropanone (**1**) which bears a diazo ketone and a silyl functionalities. Though this diazo compound **1** has been known for these seven years, there is no report available on its utilization to organic synthesis.[3] Here, the diazo ketone functionality is to be first used for the cyclopropanation of olefins or the cycloaddition reaction with acetylenes, and the silyl functionality on the resulting cyclopropanes or cycloadducts is to be utilized for the subsequent carbon–carbon bond formation.

Results and Discussion

1-Diazo-3-trimethylsilylpropanone (**1**) was previously synthesized by the reaction of diazomethane with trimethylsilylacetyl chloride,[3] which is available from commercially available chloromethyltrimethylsilane via trimethylsilylacetic acid.[4] We first investigated to open a more convenient route to **1** starting from readily available materials. For this purpose, acetic acid was converted into its dianion by treatment with LDA and the anion was silylated with two equivalent amounts of chlorotrimethylsilane to give 70% of trimethylsilylacetic acid after hydrolysis (Scheme 1). The carboxylic acid was then transformed into trimethylsilylacetyl chloride or isopropyl trimethylsilylacetyl carbonate in 83 or 89% yield, respectively. The diazo compound **1** was obtained by the subsequent treatment of the silylacetyl chloride or the silylacetyl carbonate with diazomethane in ether. This method makes possible to prepare large quantities of **1** from less expensive acetic acid and chlorotrimethylsilane.

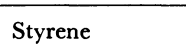
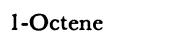
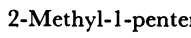
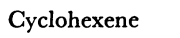
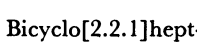
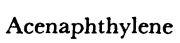
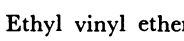
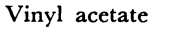


Scheme 1.



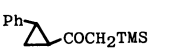
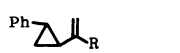
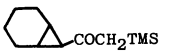
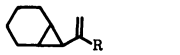
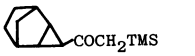
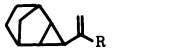
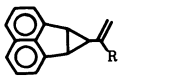
Scheme 2.

Table 1. Cyclopropanation of Olefins with 1-Diazo-3-trimethylsilylpropanone (**1**)[a]

Olefin	Solvent[b]	Product		Yield/%[c]
Styrene	A		**2**	55
1-Octene	A		**3**	49 (72[d])
2-Methyl-1-pentene	A		**4**	57 (68[d])
Cyclohexene	A		m=$(CH_2)_4$ **5**	65
Cycloheptene	A		m=$(CH_2)_5$ **6**	53 (62[d])
Cyclooctene	A		m=$(CH_2)_6$ **7**	50
Bicyclo[2.2.1]hept-2-ene	B		**8**	60
Acenaphthylene	B		**9**	61[d]
Ethyl vinyl ether	A		**10**	45
Vinyl acetate	A		**11**	51

a) All reactions were carried out at 60 °C in the presence of 5 mol% of $Cu(acac)_2$. b) A: Olefin (0.5 ml for 1 mmol of **1**) was used as solvent. B: Benzene. c) Isolated yield by vacuum distillation. d) Determined by GLC.

Table 2. One-Pot Synthesis of Vinylcyclopropanes **12**—**16** from **1**[a]

Cyclopropyl silylmethyl ketone	Organometallics[b]	Conditions[c]	Product	R		Yield/%[d]
	*n*-BuLi	A		**12a**	*n*-Bu	50
	n-HepMgBr	B		**12b**	*n*-Hep	56
2	CH_2=CHLi	B	**12**	**12c**	CH_2=CH[e]	50[f]
	PhLi	A		**13a**	Ph	60
	PhMgBr	B		**13a**	Ph	50
	n-BuLi	A		**13b**	*n*-Bu	55
5	*n*-HepMgBr	B	**13**	**13c**	*n*-Hep	57
	CH_2=CHLi	B		**13d**	CH_2=CH[e]	51[f]
	PhLi	A		**14a**	Ph	53
	PhMgBr	B		**14a**	Ph	41
	n-BuLi	A		**14b**	*n*-Bu	42
7	CH_2=CHLi	B	**14**	**14c**	CH_2=CH[e]	53[f]
	PhLi	A		**15a**	Ph	53
	PhMgBr	B		**15a**	Ph	40
	n-BuLi	A		**15b**	*n*-Bu	57
8	CH_2=CHLi	B	**15**	**15c**	CH_2=CH[g]	49[h]
	PhLi	A		**16a**	Ph	51
	PhMgBr	B		**16a**	Ph	40
	n-BuLi	A		**16b**	*n*-Bu	45
9	CH_2=CHLi	B	**16**	**16c**	CH_2=CH[e]	44[f]

a) Cyclopropyl silylmethyl ketones are first prepared from **1** and olefins according to the procedure shown in Table 1. Dry THF and then organometallics are added by syringe. All reactions are carried out under dry nitrogen. b) PhLi: In cyclohexane-diethyl ether (7 : 3); PhMgBr: In THF; *n*-BuLi: In hexane; *n*-HepMgBr: In THF; CH_2=CHLi: Prepared in situ from tetravinyltin and butyllithium in THF. These organometallics are used in a slight excess (1.2—1.3 equivalent to **1**). c) A: 1 h at 0 °C; B: 1 h at −78 °C and then 30 min at room temperature. After the reaction is completed, the mixture is treated with aqueous acetic acid. d) Isolated yield based on **1**. e) Isolated as a cycloadduct with dimethyl fumarate. f) Yield of the fumarate cycloadduct. g) Isolated as a cycloadduct with *N*-methylmaleimide. h) Yield of the maleimide cycloadduct.

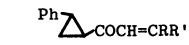
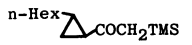
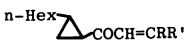
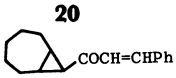
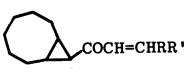
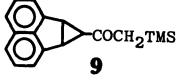
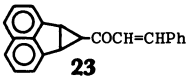
Reactions of **1** with a variety of olefins proceeded rapidly and cleanly at 60 °C in the presence of a catalytic amount of $Cu(acac)_2$ to give cyclopropyl trimethylsilylmethyl ketones **2**—**11** (Scheme 2 and Table 1). As the carbene generated from **1** by the elimination of nitrogen tends to undergo ready coupling dimerization reaction giving 3-hexene-2,5-dione after spontaneous desilylation, this reactive species has to be captured as soon as it is generated.[5] Therefore, olefins were used as solvents if they are liquid, and were used in large excess in dry benzene if solid. When the diazo compound **1** was slowly added by syringe to the mixture of olefin and catalyst preheated at 60 °C, formation of the coupling product became negligible. This addition took at least 30 min when 1 mmol of **1** was employed. Copper powder could be used instead of $Cu(acac)_2$, but yields of the cyclopropanes were found less satisfactory.

Although they are able to be isolated, the cyclopropyl trimethylsilylmethyl ketones **2**—**11** thus obtained are quite sensitive to moisture in the air suffering from ready protodesilylation. As the separation or purification procedure through column chromatography on silica gel met with awful loss of the silylated products, the crude reaction mixture was directly subjected to vacuum distillation to give pure **2**—**11** in fairly good yields (Table 1). The yields of some high-boiling products were determined on the basis of GLC analysis.

Nucleophilic addition of organometallics onto the carbonyl group of trimethylsilylacetyl substituent of **2**, **5**, and **7**—**9** gave vinylcyclopropanes **12**—**16** after elimination of trimethylsilanol (Scheme 2). One-flask procedure was most conveniently applied to the sequence of cyclopropanation and nucleophilic addition. Thus, the reaction of **1** with an olefin was first carried out under the conditions shown in Table 1. The reaction mixture was diluted with dry tetrahydrofuran (THF) and an organometallic reagent previously prepared was added. After the completion of nucleophilic addition, the mixture was treated with acetic acid to give vinylcyclopropanes **12**—**16** (Table 2).

Use of Grignard reagents as organometallics at the

Table 3. One-Pot Synthesis of Cyclopropyl Vinyl Ketones **17**—**23** from **1**[a]

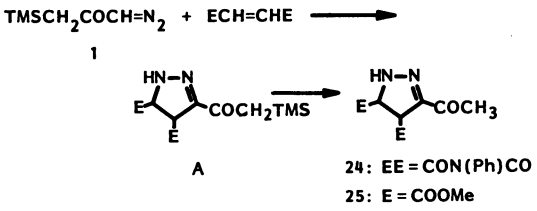
Cyclopropyl silylmethyl ketone	Carbonyl compounds	Product		R	R′	Yield/%[b]
 **2**	PhCHO	 **17**	**17a**	H	Ph	60
	PhCH=CHCHO (t)		**17b**	H	PhCH=CH (t)	55
	EtCHO		**17c**	H	Et	50
	i-PrCHO		**17d**	H	*i*-Pr	52
	MeCOMe		**17e**	Me	Me	49
 **3**	PhCHO	 **18**	**18a**	H	Ph	58
	2-furyl-CHO		**18b**	H	2-furyl	50
	EtCHO		**18c**	H	Et	55
	i-PrCHO		**18d**	H	*i*-Pr	56
 **4**	PhCHO	 **19**	**19a**	H	Ph	59
	EtCHO		**19b**	H	Et	59
	i-PrCHO		**19c**	H	*i*-Pr	58
 **5**	PhCHO	 **20**	**20a**	H	Ph	69
	EtCHO		**20b**	H	Et	58
	i-PrCHO		**20c**	H	*i*-Pr	54
	MeCOMe		**20d**	Me	Me	52
 **6**	PhCHO	 **21**				49
 **7**	PhCHO	 **22**	**22a**	H	Ph	59
	2-furyl-CHO		**22b**	H	2-furyl	55
	EtCHO		**22c**	H	Et	53
	i-PrCHO		**22d**	H	*i*-Pr	50
 **9**	PhCHO	 **23**				50

a) Cyclopropyl silylmethyl ketones are first prepared from **1** and olefins according to the procedure shown in Table 1 under argon. The resulting mixture is added slowly by syringe to a solution of LDA, previously prepared from butyllithium and diisopropylamine in THF, at −78 °C. After 45 min, carbonyl compounds are added and the mixture is allowed to stir at −78 °C for 1 h and then at room temperature for 1 h (under nitrogen). b) Isolated yield based on **1**.

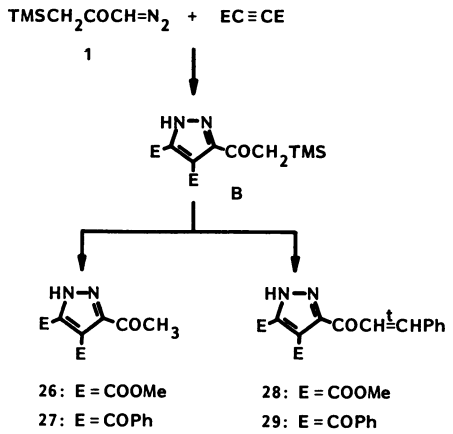
second step in the above one-flask procedure resulted in extremely decreased yields of vinylcyclopropanes. Coupling reaction products of the Grignard reagents were far major products in these cases. When the Grignard reagents were slowly added at −78 °C, this undesired coupling reaction could be significantly suppressed. However, yields of the vinylcyclopropanes were not satisfactory yet. Employment of organolithiums instead of Grignard reagents afforded better yields of the vinylcyclopropanes **13**—**16** (Table 2).

The silyl-stabilized carbanions generated by the deprotonation of cyclopropyl silylmethyl ketones **2**—**7** and **9** with LDA smoothly reacted with a variety of carbonyl compounds to afford cyclopropyl vinyl ketones **17**—**23** (Scheme 2). One-flask procedure for the sequence of cyclopropanation, anion generation, carbonyl addition, and silanol elimination was again employed without any serious troubles (Table 3).

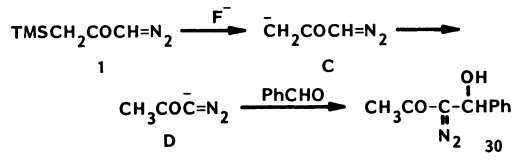
Thus, 1-diazo-3-trimethylsilylpropanone (**1**) was successfully utilized to the synthesis of a variety of vinylcyclopropanes **12**—**16** and cyclopropyl vinyl ketones **17**—**23** through a simple one-flask procedure.



Scheme 3.



Scheme 4.



Scheme 5.

We further continued to use **1** in the synthesis of heterocyclic compounds. Cycloaddition reaction of **1** with *N*-phenylmaleimide or dimethyl fumarate produced the corresponding cycloadducts **A**. However, these cycloadducts were found to undergo ready protodesilylation during their separation procedure through column chromatography over silica gel to give 3-acetyl-2-pyrazolines **24** and **25** (Scheme 3).

Similar reaction of **1** with an acetylenic dipolarophile such as dimethyl acetylenedicarboxylate or dibenzoylacetylene produced the corresponding cycloadduct **B**, which again suffered from ready desilylation to give 3-acetylpyrazole **26** or **27** in excellent yield. Treatment of the crude reaction mixture, which nearly consisted of silylated cycloadduct **B**, with more than two equivalents of LDA and the subsequent reaction with benzaldehyde gave 3-pyrazolyl vinyl ketone **28** or **29** (Scheme 4).

Although all the above one-flask reactions are successful examples of consecutive use of the diazo ketone functionality and then the silyl moiety of 1-diazo-3-trimethylsilylpropanone (**1**), use of these functional groups in the different order was found not fruitful. For example, **1** was treated with benzaldehyde in the presence of tetrabutylammonium fluoride (TBAF) to give 60% yield of 3-diazo-4-hydroxy-4-phenyl-2-butanone (**30**). This product was presumably formed by the initial generation of carbanion **C** through desilylation of **1**, a 1,3-proton migration leading to another carbanion **D**, and its addition with benzaldehyde (Scheme 5).

Experimental

General. Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-702 spectrometer. ^{1}H NMR spectra were recorded on a Hitachi R-40 (90 MHz) or a JEOL FX-100 instrument (100 MHz) and ^{13}C NMR spectra on a JEOL FX-100 spectrometer at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as internal standard. Mass spectra were measured with a JEOL JMS-01SG-2 spectrometer at 70 eV of ionization energy. Elemental analyses were performed on a Hitachi 026 CHN micro analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2 mm precoated plates of silica gel 60 F-254 (Merck) or of aluminum oxide 60 F-254 type-E (Merck). Visualization was made with ultraviolet light (254 and 365 nm), iodine, molybdophosphoric acid (5% in ethanol), or *p*-anisaldehyde (5% in ethanol containing 5% of sulfuric acid). For preparative column chromatography, Wakogel C-200, C-300 (Wako), or Kieselgel 60 (Merck, 230—400 mesh) was used. Flash chromatography was carried out on an EYELA EF-10 apparatus using a column (20×180 mm) packed with Silicagel 60 (Merck, size: 0.04—0.063 mm). Gas liquid chromatography (GLC) was accomplished on a Yanaco G-2800 gas chromatography (Yanagimoto) with a flame ionization detector using a glass column (SE-30, 3×

2000 mm). Micro vacuum distillation was carried out with a Sibata GTO-250R Kugelrohr distilling apparatus. Solvents were evaporated with a Tokyo Rikakikai rotary evaporator type-V at about 50 °C unless otherwise stated.

Trimethylsilylacetic Acid. To a solution of diisopropylamine (3.0 g, 29.7 mmol) in dry THF (20 ml) was added dropwise butyllithium (18.7 ml, 29.7 mmol) at 0 °C under nitrogen. After 10 min, acetic acid (0.84 g, 14 mmol) in THF (1 ml) was added dropwise. After 1.5 h at 0 °C chlorotrimethylsilane (3.64 ml, 28 mmol) was added, the mixture was stirred for 2 h, poured into saturated sodium chloride solution, acidified to pH 3 with 1 M-HCl (1 M=1 mol dm^{-3}), and extracted with ether (20 ml). The ether was evaporated and the residue was treated with aqueous methanol overnight. This mixture was poured into ice water and extracted with ether (20 ml). The ether was dried and evaporated to give colorless solid of the acid (1.3 g, 70%): Mp 40 °C; ^{1}H NMR ($CDCl_3$) δ=0.23 (9H, s, TMS), 1.98 (2H, s, CH_2), and 10.20 (1H, br, OH).

This silylacetic acid was also obtained in 81% yield from chloromethyltrimethylsilane via its Grignard reagent according to the known method.[4]

Isopropyl Trimethylsilylacetyl Carbonate. To a mixture of trimethylsilylacetic acid (2.32 g, 17.6 mmol) and isopropyl chloroformate (2 ml, 17.6 mmol) in dry ether (20 ml) was added slowly triethylamine (2.44 ml, 17.6 mmol) at room temperature. The mixture was stirred for 12 h and colorless precipitate separated was removed by filteration. The filtrate was distilled under vacuum to give colorless liquid of the carbonate (3.4 g, 89%): Bp 101—103 °C/8398 Pa; IR (neat) 1790, 1250, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.18 (9H, s, TMS), 1.32 (6H, d, *i*-Pr), 2.00 (2H, s, CH_2), and 4.91 (1H, m, *i*-Pr); MS *m/z* (rel intensity, %) 117 (41), 75 (93), and 43 (base peak). Found: C, 49.65; H, 8.26%. Calcd for $C_9H_{18}O_4Si$: C, 49.52; H, 8.32%.

1-Diazo-3-trimethylsilylpropanone (1). To a solution of trimethylsilylacetic acid (5.2 g, 39 mmol) in dry petr. ether (10 ml) was added dropwise thionyl chloride (5.01 g, 42 mmol). The mixture was heated at 45—50 °C for 1 h and distilled under vacuum to give trimethylsilylacetyl chloride (bp 60—61 °C/4000 Pa, 4.88 g, 83%): IR (neat) 1805, 1715, 1250, 1095, and 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.22 (9H, s, TMS) and 2.51 (2H, s, CH_2).

The chloride (3 g, 19.9 mmol) was slowly added to the ether solution of diazomethane at 0 °C, which was previously prepared from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (21.5 g, 100 mmol) and distilled with ether. The mixture was stirred at 0 °C for 30 min and then at room temperature for 12 h. The ether and unreacted diazomethane were removed under vacuum below room temperature. The residue was distilled under vacuum to give **1** (bp 46 °C/107 Pa, 2.24 g, 72%): IR (neat) 2110, 1620, 1330, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.14 (9H, s, TMS), 2.03 (2H, s, CH_2), and 5.04 (1H, s, CH=N_2); MS *m/z* (rel intensity, %) 156 (M^+, 10), 116 (22), 84 (65), 75 (31), and 73 (base peak).

When isopropyl trimethylsilylacetyl carbonate was employed instead of trimethylsilylacetyl chloride in the above procedure, 62% yield of **1** was obtained.

General Procedure for the Cyclopropanation of Olefins with 1. A mixture of olefins (0.5 ml) and $Cu(acac)_2$ (13 mg, 0.05 mmol) was heated at 60 °C under nitrogen. When olefins are solid, they were dissolved in dry benzene (4 mmol in 1 ml). To this mixture, **1** (1 mmol) was slowly added by syringe in a period of 30 min. After the addition was completed, the mixture was subjected to vacuum distillation on a Kugelrohr micro distilling apparatus to give pure cyclopropyl trimethylsilylacetyl ketones **2—11**, except for **9** which could not be distilled. Results are summarized in Table 1.

2: Colorless liquid; bp 135 °C/53 Pa; IR (neat) 1675, 1250, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.08 (9H, s, TMS), 1.1—2.2 (4H, m, *c*-Pr), 2.32 (2H, s, CH_2), and 6.9—7.4 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=−1.06 (q, TMS), 18.71 (t, CH_2 of *c*-Pr), 28.65, 33.47 (each d, CH of *c*-Pr), 39.83 (t, CH_2), 126.07, 126.48, 128.60 (each d), 140.72 (s), and 206.90 (s, CO); MS *m/z* (rel intensity, %) 232 (M^+, 24), 142 (23), 141 (35), 115 (35), 75 (24), and 73 (base peak). HRMS Found: *m/z* 232.1287. Calcd for $C_{14}H_{20}OSi$: M, 232.1284.

3: Colorless liquid; bp 145 °C/67 Pa; IR (neat) 1675, 1410, 1255, and 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.03 (9H, s, TMS), 0.6—2.0 (17H, m, *n*-Hex and *c*-Pr), and 2.30 (2H, s, CH_2); MS *m/z* (rel intensity, %) 240 (M^+, 6), 115 (38), 75 (46), and 73 (base peak). HRMS Found: *m/z* 240.1898. Calcd for $C_{14}H_{28}OSi$: M, 240.1908.

4 (Mixture of two stereoisomers): Colorless liquid; bp 80 °C/67 Pa; IR (neat) 1670, 1255, and 855 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.12 (9H, s, TMS), 0.7—1.8 (10H, m, *n*-Pr and *c*-Pr), 1.10, 1.13 (3H, each s, Me), 2.30, and 2.35 (2H, each s, CH_2, 3:1); ^{13}C NMR ($CDCl_3$) δ=−0.94 (q, TMS), 14.24, 15.41, 20.06, 20.59 (each q, Me), 22.59, 23.30, 24.65 (each t), 30.24, 30.71 (each s, q-C), 33.36 (t), 35.65, 36.24 (each d), 40.71, 40.94, 43.71 (each t), and 207.31 (s, CO); MS *m/z* (rel intensity, %) 212 (M^+, 11), 115 (37), 93 (27), 75 (44), and 73 (base peak). HRMS Found: *m/z* 212.1515. Calcd for $C_{12}H_{24}OSi$: M, 212.1595.

5: Colorless liquid; bp 100 °C/27 Pa; IR (neat) 1680, 1660, 1405, 1245, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.12 (9H, s, TMS), 1.1—1.9 (11H, m, CH_2 and CH), and 2.29 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ=−1.00 (q, TMS), 21.12, 23.12 (each t), 25.06, 35.65 (each d), 39.71 (t), and 208.60 (s, CO); MS *m/z* (rel intensity, %) 210 (M^+, 35), 75 (55), and 73 (base peak). HRMS Found: *m/z* 210.1436. Calcd for $C_{12}H_{22}OSi$: M, 210.1439.

6: Colorless liquid; bp 110 °C/20 Pa; IR (neat) 1660, 1420, 1240, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.11 (9H, s, TMS), 0.8—2.4 (13H, m, CH_2 and CH), and 2.28 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ=−1.06 (q, TMS), 28.77, 29.71 (each t), 30.53 (d), 32.47 (t), 37.59 (d), 39.65 (t), and 208.02 (s, CO); MS *m/z* (rel intensity, %) 224 (M^+, 4), 75 (32), and 73 (base peak). HRMS Found: *m/z* 224.1573. Calcd for $C_{13}H_{24}OSi$: M, 224.1594.

7: Colorless liquid; bp 140 °C/53 Pa; IR (neat) 1670, 1430, 1250, and 850 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.12 (9H, s, TMS), 1.1—2.2 (15H, m, CH_2 and CH), and 2.29 (2H, s, CH_2); MS *m/z* (rel intensity, %) 238 (M^+, 9), 115 (25), 75 (36), and 73 (base peak). HRMS Found: *m/z* 238.1774. Calcd for $C_{14}H_{26}OSi$: M, 238.1752.

8: Colorless liquid; bp 150 °C/200 Pa; IR (neat) 1670, 1245, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.12 (9H, s, TMS), 0.6—1.9 (11H, m, CH_2 and CH), and 2.24 (2H, s, CH_2); ^{13}C NMR ($CDCl_3$) δ=1.17 (q, TMS), 25.41 (d), 28.47 (t), 28.71 (d), 28.94 (t), 36.00 (d), 40.12 (t), and 208.54 (s, CO); MS *m/z* (rel intensity, %) 222 (M^+, 34), 75 (25), and 73 (base peak). HRMS Found: *m/z* 222.1438. Calcd for $C_{13}H_{22}OSi$: M,

222.1439.

9: Colorless liquid; ^{1}H NMR ($CDCl_3$) δ=0.12 (9H, s, TMS), 1.91 (1H, t, J=2.5 Hz, CH), 2.33 (2H, s, CH_2), 3.49 (2H, t, J=2.5 Hz, CH), and 7.3—7.6 (6H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=0.99 (q, TMS), 30.65 (d), 39.98 (t), 49.50 (d), 120.41, 123.64, 127.46 (each d), 131.39, 142.90, 143.25 (each s), and 204.66 (s, CO). As pure **9** could not be obtained, its protodesilylated derivative was submitted for elemental analysis: Colorless prisms (hexane); mp 98—99 °C; IR (KBr) 1660 cm^{-1}; MS m/z (rel intensity, %) 208 (M^+, 10) and 165 (base peak). HRMS Found: m/z 208.0894. Calcd for $C_{15}H_{12}O$: M, 208.0888.

10: Colorless liquid; bp 90 °C/40 Pa; IR (neat) 1670, 1425, 1240, and 840 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.15 (9H, s, TMS), 1.0—1.3 (5H, m, Et and CH_2), 2.22 (2H, s, CH_2TMS), 2.2—2.4 (1H, m, CH), and 3.2—3.6 (3H, m, Et and CH); ^{13}C NMR ($CDCl_3$) δ=−1.06 (q, TMS), 15.00 (q), 17.71 (t), 30.18 (d), 39.53 (t), 62.77 (d), 66.65 (t), and 206.90 (s, CO); MS m/z (rel intensity, %) 200 (M^+, 3), 81 (42), 75 (28), and 73 (base peak). HRMS Found: m/z 200.1251. Calcd for $C_{10}H_{20}O_2Si$: M, 200.1231.

11: Colorless liquid; bp 95 °C/53 Pa; IR (neat) 1750, 1670, 1240, 1225, and 845 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.15 (9H, s, TMS), 1.1—1.5 (2H, m, c-Pr), 2.00 (3H, s, MeCO), 2.37 (2H, s, CH_2), and 4.25 (1H, m, c-Pr); ^{13}C NMR ($CDCl_3$) δ=−1.06 (q, TMS), 15.68 (t, CH_2), 20.72 (q, MeCO), 28.88 (d), 39.98 (t, CH_2TMS), 56.36 (d), 170.74 (s, COO), and 205.72 (s, CO); MS m/z (rel intensity, %) 154 (M^+−70, 16), 75 (40), 73 (93), 45 (23), and 43 (base peak). This compound showed no parent ion peak, the elemental analysis through HRMS being impossible.

General Procedure for the One-Pot Synthesis of Vinylcyclopropanes 12—16 from 1. Cyclopropyl silylmethyl ketones **2**, **5**, and **7**—**9** were prepared according to the method mentioned above. To the crude product was added dry THF (2 ml for 1 mmol of **1**), and then a solution of organometal previously prepared was added dropwise by syringe. When the reaction was over (the reaction conditions are shown in Table 2), aqueous acetic acid was added and the mixture was stirred at room temperature for 1 h. This acidic solution was neutralized with aqueous sodium hydrogencarbonate and extracted with diethyl ether (10 ml×2). The combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate (15:1) to give vinylcyclopropanes **12**—**16**. The results are listed in Table 2.

12a: Colorless liquid; IR (neat) 1640 and 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.87 (3H, t, Me of n-Bu), 0.7—2.2 (10H, m, CH_2 and CH), 4.60 (2H, s, =CH_2), and 6.9—7.3 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=13.94 (q, Me), 15.50, 22.42 (each t, CH_2), 25.49, 28.56 (each d, CH), 30.26, 36.11 (each t, CH_2), 106.28 (t, =CH_2), 125.43, 125.63, 128.20 (each d), 142.88 (s), and 149.90 (s); MS m/z (rel intensity, %) 200 (M^+, 7), 143 (base peak), 141 (33), 129 (69), 128 (65), 116 (22), 115 (81), 104 (23), 103 (21), 91 (95), 80 (44), 79 (23), 78 (27), and 77 (46). HRMS Found: m/z 200.1552. Calcd for $C_{15}H_{20}$: M, 200.1564.

12b: Colorless liquid; IR (neat) 1640 and 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.91 (3H, m, Me of n-Hep), 1.0—2.2 (16H, m, CH_2 and CH), 4.65 (2H, s, =CH_2), and 6.9—7.3 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=14.08 (q, Me), 15.50, 22.66 (each t, CH_2), 25.53 (d, CH), 28.12 (t, CH_2), 28.60 (d, CH), 29.19, 29.34, 31.87, 36.45 (each t, CH_2), 106.28 (t, =CH_2), 125.43, 125.67, 128.20 (each d), 142.92 (s), and 149.99 (s); MS m/z (rel intensity, %) 242 (M^+, 8), 143 (base peak), 129 (35), 128 (26), 115 (25), 91 (48), and 80 (31). HRMS Found: m/z 242.2037. Calcd for $C_{18}H_{26}$: M, 242.2033.

Diels-Alder Cycloadduct of 12c with Dimethyl Fumarate (Mixture of two stereoisomers): Colorless liquid; IR (neat) 1740 and 1610 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.9—2.9 (10H, m, CH_2 and CH), 3.60 (6H, s, COOMe), 5.37 (1H, m, 2-H), and 6.8—7.3 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=14.00, 14.65 (each t, CH_2), 23.12, 23.71 (each d, CH), 28.00 (t, CH_2), 29.12 (d, CH), 29.88, 30.06 (each t, CH_2), 41.35, 41.65 (each d, CH), 51.89 (q, COOMe), 118.13 (d, 2-C), 125.77, 125.89, 128.48 (each d), 135.83 (s), 142.83 (s, 1-C), and 175.36 (s, COOMe); MS m/z (rel intensity, %) 314 (M^+, 15), 255 (22), 254 (base peak), 195 (52), 194 (33), 117 (64), 115 (27), and 91 (87). Found: C, 72.62; H, 7.09%. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.06%.

13a: Colorless liquid; IR (neat) 1625 and 1450 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.1—2.2 (11H, m, CH_2 and CH), 4.73, 5.08 (each 1H, d, J=1.5 Hz, =CH_2), and 7.1—7.5 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=20.37 (d, CH), 22.13, 24.19 (each t, CH_2), 29.06 (d, CH), 108.20 (t, =CH_2), 126.70, 127.87, 128.75, 129.34 (each d), 142.72 (s), and 150.71 (s); MS m/z (rel intensity, %) 198 (M^+, 14), 155 (30), 142 (31), 141 (67), 129 (33), 128 (64), 115 (84), 103 (24), 102 (32), 91 (52), 89 (21), 79 (20), 78 (27), 77 (79), and 38 (base peak). HRMS Found: m/z 198.1390. Calcd for $C_{15}H_{18}$: M, 198.1408.

13b: Colorless liquid; IR (neat) 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.8—2.1 (20H, m, Me, CH_2, and CH), 4.43, and 4.48 (each 1H, br s, =CH_2); ^{13}C NMR ($CDCl_3$) δ=14.03 (q, Me), 19.54 (d, CH), 21.49, 22.52, 23.59 (each t, CH_2), 29.04 (d, CH), 30.46, 36.60 (each t, CH_2), 103.84 (t, =CH_2), and 152.09 (s); MS m/z (rel intensity, %) 178 (M^+, 18), 136 (58), 135 (26), 121 (84), 107 (32), 95 (23), 94 (34), 93 (73), 81 (62), 80 (25), 79 (84), 77 (42), and 42 (base peak). HRMS Found: m/z 178.1697. Calcd for $C_{13}H_{22}$: M, 178.1698.

13c: Colorless liquid; IR (neat) 1640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.87 (3H, m, Me of n-Hep), 1.1—2.1 (23H, m, CH_2 and CH), 4.39, and 4.43 (each 1H, br s, =CH_2); ^{13}C NMR ($CDCl_3$) δ=14.08 (q, Me), 19.49 (d, CH), 21.49, 22.71, 23.63 (each t, CH_2), 28.26 (d, CH), 29.04, 29.38, 29.73, 31.92, 36.94 (each t, CH_2), 103.89 (t, =CH_2), and 151.98 (s); MS m/z (rel intensity, %) 220 (M^+, 7), 136 (20), 121 (22), 93 (26), 91 (24), 81 (27), 79 (39), 77 (22), and 40 (base peak). HRMS Found: m/z 220.2203. Calcd for $C_{16}H_{28}$: M, 220.2190.

Diels-Alder Cycloadduct of 13d with Dimethyl Fumarate (Mixtures of two stereoisomers): Colorless liquid; IR (neat) 1730 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.7—2.9 (17H, m, CH_2 and CH), 3.65 (6H, s, COOMe), and 5.28 (1H, m, 2-H); ^{13}C NMR ($CDCl_3$) δ=16.94, 17.59 (each d, CH), 21.47, 23.53, 28.18 (each t, CH_2), 29.77 (d, CH), 30.18 (t, CH_2), 41.59, 41.89 (each d, CH), 51.83 (q, COOMe), 115.95 (d, 2-C), 137.43 (s, 1-C), 175.48, and 175.60 (each s, COOMe); MS m/z (rel intensity, %) 292 (M^+, 13), 232 (base peak), 173 (49), 172 (20), 105 (25), and 91 (66). Found: C, 69.88; H, 7.99%. Calcd for $C_{17}H_{24}O_4$: C, 69.84; H, 8.27%.

14a: Colorless liquid; IR (neat) 1620, 1485, 1460, and 1440 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.7—2.3 (15H, m, CH_2 and CH), 4.80, 5.10 (each 1H, d, J=1.5 Hz, =CH_2), and 7.0—7.6 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=25.47 (d, CH_2), 26.71, 26.88 (each t, CH_2), 28.77 (d, CH), 29.71 (t, CH_2), 108.13 (t,

=CH_2), 126.24, 127.42, 128.31 (each d), 142.25, and 149.89 (s); MS *m/z* (rel intensity, %) 226 (M^+, base peak), 169 (27), 156 (38), 155 (67), 143 (48), 142 (24), 141 (40), 130 (30), 129 (45), 128 (32), 115 (29), and 91 (36). HRMS Found: *m/z* 226.1717. Calcd for $C_{17}H_{22}$: M, 226.1720.

14b: Colorless liquid; IR (neat) 1630, 1460, and 1440 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.8—2.1 (24H, m, Me, CH_2, and CH), 4.39, and 4.44 (each 1H, br s, =CH_2); ^{13}C NMR ($CDCl_3$) δ=14.06 (q, Me), 22.53 (t, CH_2), 25.18 (d, CH), 26.71, 26.94 (each t, CH_2), 29.36 (d, CH), 29.71, 30.48, 36.71 (each t, CH_2), 104.54 (t, =CH_2), and 151.89 (s); MS *m/z* (rel intensity, %) 206 (M^+, 8), 149 (25), 107 (22), 95 (24), 93 (39), 91 (35), 81 (47), 79 (59), 77 (36), and 42 (base peak). HRMS Found: *m/z* 206.2039. Calcd for $C_{15}H_{26}$: M, 206.2033.

Diels-Alder Cycloadduct of 14c with Dimethyl Fumarate (Mixture of two stereoisomers): Colorless liquid; IR (neat) 1730, 1460, and 1430 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.6—2.9 (21H, m, CH_2 and CH), 3.60 (6H, s, COOMe), and 5.25 (1H, m, 2-H); ^{13}C NMR ($CDCl_3$) δ=22.77, 23.41, 26.64, 26.88, 28.18, 29.71, 30.06, 30.24, 41.59 (d), 41.89 (d), 51.89 (q, COOMe), 116.30 (d, 2-C), 137.13 (s, 1-C) and 175.66 (s, COOMe); MS *m/z* (rel intensity, %) 320 (M^+, 3), 91 (23), and 59 (base peak). Found: C, 70.75; H, 9.01%. Calcd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81%.

15a (Mixture of two stereoisomers): Colorless liquid; IR (neat) 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.7—1.6 (10H, m, CH_2 and CH), 2.47 (1H, br s, CH), 4.78, 5.12 (each 1H br s, =CH_2), and 7.1—7.5 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=14.16, 18.36 (each d, CH), 22.75 (t, CH_2), 25.49 (d, CH), 28.95, 29.54, 31.69 (each t, CH_2), 36.23 (d, CH), 109.13 (t, =CH_2), 126.27, 127.54, 128.32 (each d), 142.48 (s), and 148.63 (s); MS *m/z* (rel intensity, %) 210 (M^+, 97), 195 (22), 182 (30), 181 (21), 168 (25), 167 (58), 165 (31), 156 (67), 155 (48), 154 (22), 153 (27), 152 (24), 143 (30), 142 (50), 141 (69), 130 (30), 129 (51), 128 (66), 115 (83), 103 (42), 91 (94), and 77 (base peak). HRMS Found: *m/z* 210.1411. Calcd for $C_{16}H_{18}$: M, 210.1408.

15b (Mixture of two stereoisomers): Colorless liquid; IR (neat) 1640 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.5—2.1 (19H, m, Me, CH_2, and CH), 2.23 (1H, br s, CH), 4.40, and 4.45 (each 1H, br s, =CH_2); ^{13}C NMR ($CDCl_3$) δ=14.11 (q, Me), 18.69 (d, CH), 22.66 (t, CH_2), 24.95, 28.90, 29.64 (each t, CH_2), 30.37, 30.66 (t, CH_2), 35.28, 36.72 (d, CH), 36.91, 37.21 (t, CH_2), 105.61 (t, =CH_2), and 150.59 (s); MS *m/z* (rel intensity, %) 190 (M^+, 24), 148 (36), 133 (41), 120 (25), 105 (24), 94 (37), 92 (21), 91 (57), 82 (24), 81 (88), 80 (base peak), 79 (26), and 78 (62). HRMS Found: *m/z* 190.1677. Calcd for $C_{14}H_{22}$: M, 190.1720.

Diels-Alder Cycloadduct of 15c with *N*-Methylmaleimide (Mixture of stereoisomers): Colorless liquid; IR (neat) 1775, 1710, and 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.5—2.7 (16H, m, CH_2 and CH), 2.90 (3H, s, NMe), 3.00 (1H, m, CH), and 5.42 (1H, m, 6-H); ^{13}C NMR ($CDCl_3$) δ=19.30, 22.47, 22.83 (each d, CH), 24.24 (t, CH_2), 24.94 (d, CH), 25.83, 28.53, 29.47 (each t, CH_2), 35.88, 39.53, 39.77 (each d, CH), 118.42 (d, 6-C), 140.54 (s), 180.25, and 180.54 (each s, CON); MS *m/z* (rel intensity, %) 271 (M^+, 23), 216 (24), 192 (35), 129 (24), 128 (22), 117 (32), 116 (37), 93 (21), 92 (25), 91 (base peak), 80 (52), 79 (50), 78 (40), and 77 (57). Found: C, 75.01; H, 7.99; N, 5.11%. Calcd for $C_{17}H_{21}NO_2$: C, 75.25 H, 7.80; N, 5.16.

16a: Pale yellow liquid; IR (neat) 1610, 1605, and 1490 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.82 (1H, t, *J*=3.0 Hz, CH), 3.16 (2H, d, *J*=3.0 Hz, CH_2), 5.00, 5.27 (each 1H, s, =CH_2), and 7.1—7.5 (11H, m, Ar); ^{13}C NMR ($CDCl_3$) δ=33.24, 44.12 (each d, CH), 109.66 (t, =CH_2), 119.66, 123.19, 126.13, 127.66, 127.89, 128.13, 128.48, 128.90 (each d), 132.13, 137.60, 140.96, 145.42, and 147.42 (each s); MS *m/z* (rel intensity, %) 268 (M^+, 44) and 165 (base peak). HRMS Found: *m/z* 268.1248. Calcd for $C_{21}H_{16}$: M, 268.1251.

16b: Pale yellow liquid; IR (neat) 1625, 1605, and 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.8—2.2 (9H, m, Me, CH_2, and CH), 2.90, 3.04, 3.32 (each 1H, m, CH), 4.65, 4.72 (each 1H, br s, =CH_2), and 6.8—7.7 (6H, m, Ar); MS *m/z* (rel intensity, %) 248 (M^+, 8), 166 (58), 165 (base peak), 153 (39), and 152 (29). HRMS Found: *m/z* 248.1563. Calcd for $C_{19}H_{20}$: M, 258.1564.

Diels-Alder Cycloadduct of 16c with Dimethyl Fumarate (Mixture of stereoisomers): Pale yellow liquid; IR (neat) 1738 and 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.41 (1H, t, *J*=3.0 Hz, CH), 2.25 (4H, m, CH_2), 2.82 (2H, m, CH), 3.01 (2H, d, *J*=3.0 Hz, CH), 5.34 (1H, m, 2-H), and 7.1—7.5 (6H, (m, Ar); ^{13}C NMR ($CDCl_3$) δ=27.88, 29.41 (each t, CH_2), 30.36, 30.94, 41.24, 41.53, 45.65 (each d, CH), 51.95 (q, NMe), 118.95, 119.48, 122.95, 127.54, 128.48 (each d), 132.01, 135.01, 137.36, 145.48 (each s), 175.19, and 175.36 (each s, COOMe); MS *m/z* (rel intensity, %) 362 (M^+, 5), 165 (62), 152 (23), 91 (29), and 59 (base peak). HRMS Found: *m/z* 362.1627. Calcd for $C_{23}H_{22}O_4$: M, 362.1517.

General Procedure for the One-Pot Synthesis of Cyclopropyl Vinyl Ketones 17—23 from 1. Cyclopropyl silylmethyl ketones **2—7** and **9** were prepared under argon according to the procedure described above. The resulting mixture was slowly added at −78 °C by syringe to a solution of lithium diisopropylamide (1.1 equivalent) which had been previously prepared from butyllithium (in hexane) and diisopropylamine in THF at −78 °C. After 45 min, a carbonyl compound (1 equivalent) in dry THF (1 ml/1 mmol) was added, the mixture was stirred at −78 °C for 1 h, and then at room temperature for 1 h. All these procedures were carried out under nitrogen. The resulting mixture was poured into aqueous ammonium chloride, extracted with diethyl ether (20 ml×2), the combined extracts were dried over magnesium sulfate, and finally evaporated in vacuo. The residue was chromatographed over silica gel with hexane-ethyl acetate (20—50:1) to give cyclopropyl vinyl ketones **17—23**. The results are listed in Table 3.

17a: Colorless prisms (ethyl acetate-hexane); mp 80—81 °C; IR (KBr) 1655 and 1595 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.2—1.4, 1.6—1.8 (each 1H, m, CH_2 of *c*-Pr), 2.2—2.6 (2H, m, CH of *c*-Pr), 6.63, 7.38 (each 1H, d, *J*=16.5 Hz, -CH=CHPh), and 6.8—7.4 (10H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=19.26 (t, CH_2 of *c*-Pr), 29.65, 31.70 (each d, CH of *c*-Pr), 126.05, 126.46, 128.28, 128.46, 128.87, 130.34 (each d), 134.50, 140.49 (each s), 142.31 (d, =CHPh), and 197.74 (s, CO); MS *m/z* (rel intensity, %) 248 (M^+, 24), 131 (59), 117 (21), 116 (48), 115 (94), 104 (30), 103 (83), 102 (33), 91 (54), 89 (22), 78 (26), and 77 (base peak). HRMS Found: *m/z* 248.1175. Calcd for $C_{18}H_{16}O$: M, 248.1200.

17b: Colorless prisms (ethyl acetate-hexane); mp 128.5—129.5 °C; IR (KBr) 1650 and 1575 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.2—1.5, 1.6—1.9 (each 1H, m, CH_2 of *c*-Pr), 2.2—2.7 (2H, m, CH of *c*-Pr), 6.23 (1H, d, *J*=15.0 Hz, -COCH=), and 6.6—7.4 (13H, m, Ph and =CHPh); ^{13}C NMR ($CDCl_3$) δ=19.18 (t, CH_2 of *c*-Pr), 29.47, 31.59 (each d, CH of *c*-Pr), 126.24, 126.60, 126.83, 127.36, 128.65, 128.95, 130.01 (each d), 136.18, 140.83 (each s), 141.66, 142.60 (each d, COCH=CHCH=

CHPh), and 198.01 (s, CO); MS *m/z* (rel intensity, %) 274 (M^+, base peak), 183 (39), 170 (28), 157 (67), 129 (37), 128 (71), 127 (30), 117 (31), 115 (38), 104 (21), and 91 (38). Found: C, 87.56; H, 6.61%. Calcd for $C_{20}H_{17}O$: C, 87.88; H, 6.66%.

17c: Colorless liquid; IR (neat) 1670, 1650, and 1615 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.05 (3H, t, Me of Et), 0.8—1.8 (3H, m, CH_2 and CH of *c*-Pr), 2.23 (2H, m, CH_2 of Et), 2.2—2.7 (1H, m, CH of *c*-Pr), 6.12 (1H, br d, *J*=15.5 Hz, -COCH=), 6.84 (1H, dt, *J*=15.5, 6.6, and 6.6 Hz, EtCH=), and 6.9—7.3 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=12.24 (q, Me of Et), 18.88 (t, CH_2 of *c*-Pr), 25.53 (t), 29.12, 30.59 (each d), 126.18, 126.54, 128.60, 129.83 (each d), 140.83 (s), 148.83 (d, =CHEt), and 198.25 (s, CO); MS *m/z* (rel intensity, %) 200 (M^+, 4), 117 (28), 116 (35), 115 (base peak), 91 (70), 89 (24), 83 (57), 78 (22), and 77 (25). HRMS Found: *m/z* 200.1198. Calcd for $C_{14}H_{16}O$: M, 200.1196.

17d: Colorless liquid; IR (neat) 1675, 1650, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.02, 1.09 (each 3H, d, *J*=7.3 Hz, Me of *i*-Pr), 1.2—1.8 (3H, m, CH_2 and CH of *c*-Pr), 2.2—2.7 (2H, m, CH of *c*-Pr and CH of *i*-Pr), 6.04 (1H, br d, *J*=15.9 Hz, -COCH=), 6.78 (1H, dd, *J*=15.9 and 6.9 Hz, *i*-PrCH=), and 6.2—7.3 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=19.14 (t, CH_2 of *c*-Pr), 21.31 (q, Me of *i*-Pr), 29.24, 30.76, 31.18 (each d), 126.05, 126.35, 127.75, 128.40 (each d), 140.61 (s), 153.41 (d, *i*-PrCH=), and 198.32 (s, CO); MS *m/z* (rel intensity, %) 214 (M^+, 23), 171 (21), 117 (29), 116 (30), 115 (70), 97 (55), 91 (56), and 41 (base peak). HRMS Found: *m/z* 214.1355. Calcd for $C_{15}H_{18}O$: M, 214.1355.

17e: Colorless liquid; IR (neat) 1670 and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.2—1.8 (3H, CH_2 and CH of *c*-Pr), 1.85, 2.13 (each 3H, s, Me), 2.3—2.6 (1H, m, CH of *c*-Pr), 6.12 (1H, br s, -COCH=), and 6.9—7.3 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=18.88 (t, CH_2 of *c*-Pr), 20.82, 27.65 (each q, Me), 29.06, 34.24 (each d, CH of *c*-Pr), 124.72, 126.24, 126.48, 128.60 (each d), 141.13 (s), 155.13 (s, $=C(Me)_2$), and 198.60 (s, CO); MS *m/z* (rel intensity, %) 200 (M^+, 44), 115 (37), 91 (26), 83 (base peak), and 55 (53). HRMS Found: *m/z* 200.2794. Calcd for $C_{14}H_{16}O$: M, 200.2794.

18a: Colorless liquid; IR (neat) 1675, 1645, and 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.86 (3H, m, Me of *n*-Hex), 1.1—2.1 (14H, CH_2 and CH), 6.72 (1H, d, *J*=16.5 Hz, -COCH=), 7.2—7.5 (5H, m, Ph), and 7.47 (1H, d, *J*=16.5 Hz, PhCH=); ^{13}C NMR ($CDCl_3$) δ=14.12 (q, Me of *n*-Hex), 18.71 (t, CH_2 of *c*-Pr), 22.71, 26.88, 27.94, 29.06, 29.24, 31.88, 33.53 (CH_2 and CH), 126.77, 128.88, 129.13, 130.42 (each d), 135.01 (s), 141.89 (d, =CHPh), and 199.78 (s, CO); MS *m/z* (rel intensity, %) 256 (M^+, 8), 147 (27), 131 (base peak), 103 (79), 91 (26), and 77 (50). HRMS Found: *m/z* 256.1826. Calcd for $C_{18}H_{24}O$: M, 256.1826.

18b: Pale yellow liquid; IR (neat) 1670, 1635, and 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.87 (3H, t, Me of *n*-Hex), 1.1—1.5 (11H, m, CH_2 and CH), 1.90 (1H, m, CH of *c*-Pr), 6.46 (1H, dd, *J*=3.5 and 2.0 Hz, 4-H of furyl), 6.63 (1H, d, *J*=3.5 Hz, 3-H of furyl), 6.75 (1H, d, *J*=15.8 Hz, -COCH=), 7.34 (1H, d, *J*=15.8 Hz, furylCH=), and 7.46 (1H, d, *J*=2.0 Hz, 5-H of furyl); ^{13}C NMR ($CDCl_3$) δ=14.12 (q, Me of *n*-Hex), 18.59 (t, CH_2 of *c*-Pr), 22.71 (t), 26.83, 28.47 (each d, CH of *c*-Pr), 29.06, 29.30, 31.88, 33.54 (each t, CH_2), 112.65, 115.59 (each d, 3- and 4-C of furyl), 123.89 (d, -COCH=), 128.07 (d, furylCH=), 144.89 (d, 5-C of furyl), 151.66 (s, 2-C of furyl), and 199.31 (s, CO); MS *m/z* (rel intensity, %) 246 (M^+, 11), 121 (65), 65 (82), and 41 (base peak). HRMS Found: *m/z* 246.1628. Calcd for $C_{16}H_{22}O_2$: M, 246.1619.

18c (Mixture of two stereoisomers): Colorless liquid; IR (neat) 1680, 1660, and 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.85, 1.06 (each 3H, t, Me of *n*-Hex and Et), 1.2—2.4 (16H, m, CH_2 and CH), 6.59 (1H, br d, *J*=16.0 Hz, -COCH=), and 6.81 (1H, dt, *J*=16.0, 5.7, and 5.7 Hz, *n*-HexCH=); ^{13}C NMR ($CDCl_3$) δ=12.41, 13.82, 14.11 (each q, Me of *n*-Hex and Et), 18.24 (CH_2 of *c*-Pr), 22.71, 24.47, 25.59, 26.35, 26.53, 26.93, 29.06, 29.30, 29.83, 31.88, 33.53 (CH_2 and CH), 129.95, 131.19 (each d, -COCH=), 147.54, 148.01 (each d, EtCH=), 198.72, and 200.07 (each s, CO); MS *m/z* (rel intensity, %) 208 (M^+, 9), 98 (28), 95 (21), 83 (base peak), and 55 (69). HRMS Found: *m/z* 208.1829. Calcd for $C_{14}H_{24}O$: M, 208.1821.

18d (Mixture of two stereoisomers): Colorless liquid; IR (neat) 1675, 1650, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.89 (3H, m, Me of *n*-Hex), 1.09 (6H, d, Me of *i*-Pr), 1.2—2.7 (15H, CH_2 and CH), 6.12 (1H, br d, *J*=16.2 Hz, -COCH=), and 6.79 (1H, dd, *J*=16.2, 6.3, and 6.3 Hz, *i*-PrCH=); ^{13}C NMR ($CDCl_3$) δ=14.06 (q, Me of *n*-Hex), 18.24 (t, CH_2 of *c*-Pr), 21.43, 22.65, 24.47, 25.65, 26.35, 26.47, 26.94, 29.00, 29.24, 29.77, 31.18, 31.88, 33.43 (CH_2 and CH), 128.01, 129.24 (each d, -COCH=), 152.30, 152.72 (each d, *i*-PrCH=), 198.96, and 200.25 (each s, CO); MS *m/z* (rel intensity, %) 222 (M^+, 6), 97 (49), 69 (25), and 40 (base peak). HRMS Found: *m/z* 222.1978. Calcd for $C_{15}H_{26}O$: M, 222.1982.

19a (Mixture of two stereoisomers): Colorless liquid; IR (neat) 1675, 1650, and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.9—1.6 (9H, m, Me, CH_2, and CH), 1.20 (3H, s, Me), 2.24 (1H, m, CH of *c*-Pr), 6.97 (1H, br d, *J*=16.0 Hz, -COCH=), 7.4—7.7 (5H, m, Ph), and 7.68 (1H, d, *J*=16.0 Hz, PhCH=); ^{13}C NMR ($CDCl_3$) δ=14.24, 15.53 (each q, Me of *n*-Pr and Me), 20.12, 20.47, 22.18, 22.94, 24.41, 31.18, 31.77, 33.77, 34.12, 34.65, 43.47 (CH_2 and CH), 128.18, 128.36, 129.07, 130.30 (each d), 135.01 (s), 141.42 (d, PhCH=), and 198.01 (s, CO); MS *m/z* (rel intensity, %) 228 (M^+, 49), 146 (28), 131 (base peak), 129 (20), 128 (21), 115 (26), 103 (74), 102 (27), 91 (34), and 77 (68). HRMS Found: *m/z* 228.1504. Calcd for $C_{16}H_{20}O$: M, 228.1513.

19b (Mixture of two stereoisomers): Colorless liquid; IR (neat) 1680, 1655, and 1620 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.6—2.3 (18H, m, Me, CH_2, and CH), 6.00 (1H, br d, *J*=15.5 Hz, -COCH=), and 6.66 (1H, dt, *J*=15.5, 6.0, and 6.0 Hz, EtCH=); ^{13}C NMR ($CDCl_3$) δ=12.41, 14.24, 15.47 (each q, Me of *n*-Pr, Me of Et, and Me), 20.06, 20.41, 21,65, 22.34, 24.35, 25.47, 30.30, 30.88, 33.06, 33.59, 33.77, 43.53 (CH_2 and CH), 131.30 (d, -COCH=), 147.31, 147.42 (each d, EtCH=), and 198.13 (s, CO); MS *m/z* (rel intensity %) 180 (M^+, 16), 83 (76), 81 (21), 67 (22), and 55 (base peak). HRMS Found: *m/z* 180.1619. Calcd for $C_{12}H_{20}O$: M, 180.1513.

19c (Mixture of two stereoisomers): Colorless liquid; IR (neat) 1675, 1650, and 1610 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.7—2.6 (14H, Me, CH_2, and CH), 1.06 (6H, d, Me of *i*-Pr), 6.11 (1H, br d, *J*=16.5 Hz, *i*-PrCH=), and 6.73 (1H, dd, *J*=16.5 and 6.3 Hz, -COCH=); ^{13}C NMR ($CDCl_3$) δ=14.30, 15.47 (each q, Me of *n*-Pr and Me), 19.30, 20.06, 20.41, 21.53, 21.77, 22.47, 24.41, 30.36, 30.93, 31.12, 33.18, 33.77, 43.59 (Me, CH_2, and CH), 129.42 (d, -COCH=), 152.19, 152.30 (each d, *i*-PrCH=), and 198.48 (s, CO); MS *m/z* (rel intensity, %) 194 (M^+, 7), 97 (34), 69 (24), and 40 (base peak). HRMS Found: *m/z* 194.1670. Calcd for $C_{13}H_{22}O$: M, 194.1670.

20a: Colorless liquid; IR (neat) 1670, 1645, and 1605 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.7—2.0 (11H, m, CH_2 and CH), 6.64

(1H, d, J=16.2 Hz, -COCH=), 7.1—7.4 (5H, m, Ph), and 7.35 (1H, d, J=16.2 Hz, PhCH=); ^{13}C NMR ($CDCl_3$) δ=21.14 23.45 (each t, CH_2), 26.36, 34.30 (each d, CH), 126.70, 128.16, 128.81, 130.10 (each d), 134.86 (s), 141.08 (d, PhCH=), and 199.32 (s, CO); MS m/z (rel intensity, %) 226 (M^+, 82), 225 (23), 183 (base peak), 145 (37), 134 (21), 131 (28), 129 (35), 105 (22), 103 (56), 102 (34), 91 (49), and 75 (35). HRMS Found: m/z 226.1349. Calcd for $C_{16}H_{18}O$: M, 226.1357.

20b: Colorless liquid; IR (neat) 1680, 1655, and 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.09 (3H, t, Et), 1.2—2.0 (11H, m, CH_2 and CH), 2.25 (2H, q, Et), 6.15 (1H, d, J=16.2 Hz, -COCH=), and 6.87 (1H, dt, J=16.2, 6.3, and 6.3 Hz, EtCH=); ^{13}C NMR ($CDCl_3$) δ=12.29 (q, Me of Et), 21.12, 23.18, 25.47 (each t, CH_2), 25.71, 33.12 (each d, CH), 129.95 (d, -COCH=), 147.36 (d, EtCH=), and 199.95 (s, CO); MS m/z (rel intensity, %) 178 (M^+, 12), 107 (28), 91 (21), 83 (37), 79 (32), 77 (30), 67 (31), and 40 (base peak). HRMS Found: m/z 178.1357. Calcd for $C_{12}H_{18}O$: M, 178.1357.

20c: Colorless liquid; IR (neat) 1675, 1655, and 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.06 (6H, d, Me of i-Pr), 1.1—2.0 (10H, CH_2 and CH), 2.44 (1H, m, CH of i-Pr), 6.05 (1H, br d, J=16.0 Hz, -COCH=), and 6.70 (1H, dd, J=16.0 and 6.3 Hz, i-PrCH=); ^{13}C NMR ($CDCl_3$) δ=21.14, 21.43, 23.25, 25.95, 31.12, 33.35 (Me, CH_2, and CH), 127.87 (d, -COCH=), 152.00 (d, i-PrCH=), and 200.09 (s, CO); MS m/z (rel intensity, %) 192 (M^+, 14), 149 (39), 107 (43), 97 (25), 91 (26), 81 (24), 79 (35), 77 (33), 69 (23), and 41 (base peak). HRMS Found: m/z 192.1511. Calcd for $C_{13}H_{20}O$: M, 192.1513.

20d: Colorless liquid; IR (neat) 1660 and 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.1—1.8 (11H, m, CH_2 and CH), 1,83, 2.10 (each 3H, br s, Me), and 6.16 (1H, br s, -COCH=); ^{13}C NMR ($CDCl_3$) δ=20.24 (q, Me), 20.65, 21.18 (each t, CH_2), 23.30 (d, CH), 25.53 (q, Me), 36.59 (d, CH), 125.07 (d, -COCH=), 153.13 (s, $(Me)_2C$=), and 200.72 (s, CO); MS m/z (rel intensity, %) 178 (M^+, 46), 163 (22), 135 (base peak), 122 (22), 121 (38), 109 (70), 96 (26), 83 (97), 79 (23), 67 (21), and 55 (75). HRMS Found: m/z 178.1331. Calcd for $C_{12}H_{18}O$: M, 178.1357.

21: Colorless needles (ethyl acetate–hexane); mp 85—86 °C; IR (KBr) 1655, 1640, and 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.8—2.1 (13H, m, CH_2 and CH), 6.66 (1H, d, J=16.5 Hz, -COCH=), 7.1—7.5 (5H, m, Ph), and 7.41 (1H, d, J=16.5 Hz, PhCH=) ^{13}C NMR ($CDCl_3$) δ=28.71, 29.83 (each t, CH_2), 31.65 (d, CH), 32.41 (t, CH_2), 38.36 (d, CH), 126.78, 128.36, 129.01, 130.30, each d), 135.01 (s), 141.48 (d, PhCH=), and 198.90 (s, CO); MS m/z (rel intensity, %) 240 (M^+, base peak), 183 (91), 131 (46), 103 (40), 91 (25), and 77 (40). Found: C, 84.77; H, 8.37%. Calcd for $C_{17}H_{20}O$: C, 84.96; H, 8.39%.

22a: Colorless needles (ethyl acetate–hexane); mp 94—95 °C; IR (KBr) 1650, 1625, and 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=0.8—2.2 (15H, m, CH_2 and CH), 6.70 (1H, d, J=16.5 Hz, -COCH=), 7.1—7.6 (5H, m, Ph), and 7.42 (1H, d, J=16.5 Hz, PhCH=); ^{13}C NMR ($CDCl_3$) δ=26.35, 29.24 (CH_2), 31.41, 34.41 (each d, CH), 127.07, 128.42, 129.07, 130.36 (each d), 135.13 (s), 141.54 (d, PhCH=), and 199.60 (s, CO); MS m/z (rel intensity, %) 254 (M^+, 15), 183 (53), 146 (45), 131 (97), 128 (20), 103 (base peak), 102 (23), 91 (33), and 77 (93). Found: C, 85.12; H, 8.85%. Calcd for $C_{22}H_{16}O$: C, 84.99; H, 8.72%.

22b: Colorless prisms (ethyl acetate–hexane); mp 74—75 °C; IR (KBr) 1650 and 1595 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ= 1.1—2.2 Z(15H, m, CH_2 and CH), 6.36 (1H, dd, J=3.3 and 2.0 Hz, 4-H of furyl), 6.52 (1H, d, J=3.3 Hz, 3-H of furyl), 6.59 (1H, d, J=16.2 Hz, -COCH=), 7.20 (1H, d, J=16.2 Hz, furylCH=), and 7.37 (1H, d, J=2.0 Hz, 5-H of furyl); ^{13}C NMR ($CDCl_3$) δ=26.35, 26.47, 29.24 (each t, CH_2), 31.36, 34.93 (each d, CH), 112.60, 115.36, 124.18, 127.77 (each d), 144.77 (d, 5-C of furyl), 151.66 (s, 2-C of furyl), and 199.24 (s, CO); MS m/z (rel intensity, %) 244 (M^+, 12), 173 (20), 121 (80), 94 (22), 91 (23), 81 (28), 79 (24), 77 (22), and 65 (base peak). Found: C, 78.65; H, 8.25%. Calcd for $C_{16}H_{20}O_2$: C, 78.87; H, 8.33%.

22c: Colorless needles (ethyl acetate–hexane); mp 28—29 °C; IR (KBr) 1670, 1650, and 1620 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.06 (3H, t, Et), 1.2—2.1 (15H, m, CH_2 and CH), 2.19 (2H, m, Et), 6.12 (br d, J=15.9 Hz, -COCH=), and 6.83 (1H, dt, J=15.9, 6.0, and 6.0 Hz, EtCH=); ^{13}C NMR ($CDCl_3$) δ=12.35 (q, Me of Et), 25.51, 26.30, 26.47, 29.23 (each t, CH_2), 30.77, 33.30 (each d, CH), 130.07 (d, -COCH=), 147.60 (d, EtCH=), and 199.84 (s, CO); MS m/z (rel intensity, %) 206 (M^+, 1), 83 (49), 81 (21), 79 (30), 77 (23), 67 (27), and 56 (base peak). HRMS Found: m/z 206.1682. Calcd for $C_{14}H_{22}O$: M, 206.1670.

22d: Colorless plates (ethyl acetate–hexane); mp 52.5—54 °C; IR (KBr) 1650 and 1600 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.07 (6H, d, Me of i-Pr), 0.8—2.1 (15H, m, CH_2 and CH), 2.45 (1H, m, CH of i-Pr), 6.07 (1H, br d, J=15.6 Hz, -COCH=), and 6.73 (1H, dd, J=15.6 and 6.0 Hz, i-PrCH=); ^{13}C NMR ($CDCl_3$) δ=21.41 (q, Me), 26.30, 26.47, 29.18 (each t, CH_2), 30.94, 31.12, 33.47 (each d, CH), 128.13 (d, -COCH=), 152.42 (d, i-PrCH=), and 200.25 (s, CO); MS m/z (rel intensity, %) 220 (M^+, 4), 177 (20), 149 (23), 107 (28), 97 (base peak), 95 (26), 93 (28), 91 (38), 81 (55), 79 (58), 77 (31), and 69 (39). HRMS Found: m/z 220.1835. Calcd for $C_{15}H_{24}O$: M, 220.1826.

23: Colorless needles (ethyl acetate–hexane); mp 154.5—155.5 °C; IR (KBr) 1660 and 1605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.30 (1H, t, J=2.8 Hz, CH of c-Pr), 3.59 (1H, d, J=2.8 Hz, CH of c-Pr), 6.64 (1H, d, J=15.5 Hz, -COCH=), 7.1—7.5 (11H, m, Ar), and 7.38 (1H, d, J=15.5 Hz, PhCH=); ^{13}C NMR ($CDCl_3$) δ=35.30, 46.53 (each d, CH), 120.95, 124.01, 126.36, 127.71, 128.48, 129.07, 130.65, 131.67, 134.66, 143.01 (d), 143.54 (s), and 195.89 (s, CO); MS m/z (rel intensity, %) 296 (M^+, 13), 165 (base peak), 164 (28), 163 (32), 131 (65), 103 (32), and 77 (27). Found: C, 89.24; H, 5.60%. Calcd for $C_{22}H_{16}O$: C, 89.16; H, 5.44%.

Reaction of 1 with *N*-Phenylmaleimide Leading to 24. A mixture of **1** (312 mg, 2 mmol) and *N*-phenylmaleimide (346 mg, 2 mmol) in dry benzene (5 ml) was stirred under nitrogen at room temperature for 10 h. The solvent was evaporated in vacuo and the residue was chromatographed over silica gel with hexane–ethyl acetate (1:1) to tive **24** (262 mg, 51%): Pale yellow prisms (ethyl acetate–hexane); mp 160.5—161.5 °C; IR (KBr) 3400, 1720, and 1670 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=2.41 (3H, s, COMe), 4.72, 5.06 (each 1H, d, J=10.5 Hz, 3a- and 6a-H), and 7.1—7.6 (6H, m, Ph and NH); ^{13}C NMR ($CDCl_3$) δ=25.92 (q, COMe), 50.34 (d, 3a-C), 64.42 (d, 6a-C), 126.21, 128.94, 129.13 (each d), 131.12 (s), 143.70 (s, 3-C), 170.85, 173.18 (each s, CON), and 192.09 (s, CO); MS m/z (rel intensity %) 257 (M^+, 75), 228 (46), 119 (base peak), 95 (78), 93 (29), 91 (20), and 55 (54). HRMS Found: m/z 257.0800. Calcd for $C_{13}H_{11}N_3O_3$: M, 257.0800.

Reaction of 1 with Dimethyl Fumarate Leading to 25. The reaction of **1** (156 mg, 1 mmol) with dimethyl fumarate (144 mg, 1 mmol) under the same conditions gave

25 (139 mg, 62%): Pale yellow liquid; IR (neat) 3350, 1740, and 1660 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.26 (3H, s, COMe), 3.60, 3.64 (each 3H, s, COOMe), 4.21, 4.60 (each 1H, d, J=5.4 Hz, 4- and 5-H), and 7.07 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ=25.58 (q, COMe), 50.92 (d, 4-C), 53.02, 53.16 (each q, COOMe), 66.42 (d, 5-C), 146.87 (s, 3-C), 169.87, 170.21 (each s, COOMe), and 192.87 (s, CO); MS m/z (rel intensity, %) 228 (M^+, 9), 195 (24), 169 (83), 137 (48), 125 (33), 95 (33), 93 (base peak), 83 (29), and 59 (32). HRMS Found: m/z 228.0745. Calcd for $C_9H_{12}N_2O_5$: M, 228.0756.

Reaction of 1 with Dimethyl Acetylenedicarboxylate Leading to 26. A mixture of **1** (312 mg, 2 mmol) and dimethyl acetylenedicarboxylate (284 mg, 2 mmol) in dry benzene (4 ml) was heated under reflux for 3.5 h under nitrogen. The solvent was evaporated in vacuo. ^1H NMR of the residue showed a quantitative formation of the cycloadduct **B** (E=COOMe). The residue was chromatographed over silica gel with hexane–ethyl acetate (3:1) to give **26** (431 mg, 95%): pale yellow plates (ethyl ether); mp 55—56 °C; IR (KBr) 3200, 1730, and 1680 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.58 (3H, s, COMe), 3.87, 3.95 (each 3H, s, COOMe), and 7.29 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ=26.77 (q, COMe), 52.90, 53.13 (each q, COOMe), 117.54, 135.03, 146.89 (each s), 158.99, 164.45 (each s, COOMe), and 191.98 (s, CO); MS m/z (rel intensity, %) 226 (M^+, 4), 195 (13), 93 (33), 79 (14), 67 (17), 66 (13), 65 (19), and 43 (base peak). HRMS Found: m/z 226.0591. Calcd for $C_9H_{10}N_2O_5$: M, 226.0589.

Reaction of 1 with Dibenzoylacetylene Leading to 27. The reaction of **1** (134 mg, 0.86 mmol) with dibenzoylacetylene (218 mg, 0.86 mmol) under reflux in dry THF (2 ml) for 3 h and the followed chromatographic separation gave **27** (198 mg, 73%): Colorless prisms; mp 154—155 °C; IR (KBr) 3220, 1660, and 1630 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.36 (3H, s, COMe), 7.1—8.0 (10H, m, Ph), and 11.70 (1H, br, NH); ^{13}C NMR ($CDCl_3$) δ=27.94 (q, COMe), 116.89, 125.42 (each s), 128.54, 128.89, 129.36, 130.30 (each d), 133.66, 134.07, 136.13, 137.42 (each s), 186.13, 190.01, and 191.84 (each s, CO); MS m/z (rel intensity, %) 318 (M^+, 44), 241 (45), 223 (22), 105 (66), and 77 (base peak). Found: C, 71.43; H, 4.39; N, 9.01%. Calcd for $C_{19}H_{14}N_2O_3$: C, 71.64; H, 4.43; N, 8.80%.

General Procedure for the One-Pot Synthesis of 3-Pyrazolyl Vinyl Ketones 28 and 20. 3-Silylacetylpyrazoles **B** (E=COOMe or COPh) were prepared in dry THF (1 mmol in 2 ml) according to the method shown above. This mixture was added to LDA (2 mmol in THF) at −78 °C. After 30 min at −78 °C, benzaldehyde (1 mmol) in THF (1 ml) was added dropwise, the mixture was stirred at 0 °C for 2 h, poured into aqueous ammonium chloride, and extracted with diethyl ether (20 ml). The ether was dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with chloroform-ethyl acetate (12:1) to give **28** or **29**.

28: Yield 53%; Colorless plates (ethyl ether); mp 145—146 °C; IR (KBr) 3200, 1720, 1650, and 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.86, 3.92 (each 3H, s, COOMe), 7.2—7.5 (6H, m, Ph and NH), 7.51, and 7.81 (each 1H, d, J=15.6 Hz, CH=CH); ^{13}C NMR ($CDCl_3$) δ=53.12, 53.32 (each q, COOMe), 118.41 (s), 121.39, 129.05, 131.20 (each d), 134.62, 135.16 (each s), 146.04 (d), 148.09 (s), 159.37, 164.50 (each s, COOMe), and 182.56 (s, CO); MS m/z (rel intensity, %) 314 (M^+, 28), 283 (27), 282 (80), 224 (20), 131 (26), 103 (base peak), 102 (38), 93 (24), and 77 (65); Found: C, 61.34; H, 4.63; N, 8.96%. Calcd for $C_{16}H_{14}N_2O_5$: C, 61.14; H, 4.49; N, 8.91%.

29: Yield 41%; Pale yellow prisms (ethyl ether); mp 180—181 °C; IR (KBr) 3170, 1640, and 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.9—7.6 (12H, m, Ar), 7.44, 7.77 (each 1H, d, J=15.8 Hz, CH=CH), and 7.7—8.0 (4H, m, Ar); MS m/z (rel intensity, %) 406 (M^+, 12), 105 (56), 103 (30), and 77 (base peak). Found: C, 76.71; H, 4.40; N, 6.95%. Calcd for $C_{26}H_{18}N_2O_3$: C, 76.83; H, 4.46; N, 6.89%.

Reaction of 1 with Benzaldehyde in the presence of TBAF Leading to 30. To a mixture of **1** (232 mg, 1.5 mmol) and benzaldehyde (160 mg 1.5 mmol) in dry THF (2 ml) was added TBAF (2.25 ml, 2.25 mmol) at room temperature. The mixture was stirred under nitrogen at room temperature for 30 min and poured into water (30 ml). Organic layer was extracted with dichloromethane (20 ml×2), the combined extracts were dried over magnesium sulfate and evaporated in vacuo. The residue was chromatographed over silica gel with hexane–ethyl acetate (1:1) to give **30** (170 mg, 60%): Colorless liquid; IR (neat) 3400, 2050, and 1625 cm^{-1}; ^1H NMR ($CDCl_3$) δ=2.22 (3H, s, COMe), 3.40 (1H, br s, OH), 5.94 (1H, s, CH), and 7.2—7.5 (5H, m, Ph); ^{13}C NMR ($CDCl_3$) δ=25.54 (q, COMe), 67.11 (d, CH), 125.41, 127.93, 128.52 (each d), 139.32 (s), and 190.80 (s, CO); MS m/z (rel intensity, %) 190 (M^+, 13), 162 (27), 161 (50), 148 (62), 143 (65), 119 (48), 107 (31), 105 (43), 102 (22), 91 (65), 80 (39), 78 (77), and 43 (base peak). Found: C, 61.30; H, 4.57; N, 8.65%. Calcd for $C_{16}H_{14}O_5$: C, 61.14; H, 4.49; N, 8.91%.

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