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Reaction of 1-Chlorovinyl *p*-Tolyl Sulfoxides with Carbanion of Acetonitrile: A Novel Synthesis of Cyclopentanone Derivatives with Three Consecutive Carbon–Carbon Bond-Formations via the Enaminonitriles

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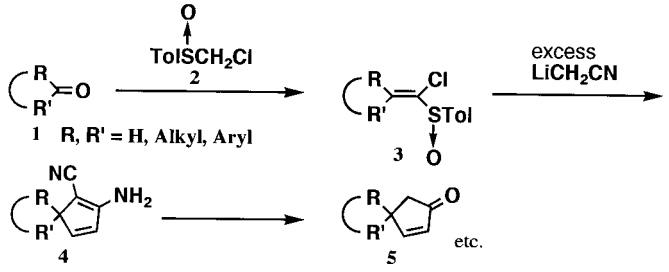
Abstract—Treatment of 1-chlorovinyl *p*-tolyl sulfoxides derived from ketones with cyanomethyllithium gave cyclopentadienyl enaminonitriles in high yields with three consecutive carbon–carbon bond-formations. However, the 1-chlorovinyl *p*-tolyl sulfoxides derived from aldehydes did not give good results. The mechanism of this reaction and the reaction of the enaminonitriles to convert cyclopentanone derivatives were investigated. Several α-carbanion of nitriles other than acetonitrile added to the 1-chlorovinyl *p*-tolyl sulfoxides at low temperature in good yield; however, they did not cyclize upon warming to room temperature.

Cyclopentanones are obviously one of the most widely distributed carbon skeletal structures in natural and unnatural organic compounds. Because cyclization leading to the five-membered ring is much easier than that of other ring sizes, numerous methods for the synthesis of cyclopentane derivatives have been published.[1] However, in view of the importance of cyclopentanone derivatives, new methods for their synthesis are still eagerly sought. On the other hand, the formation of several carbon–carbon bonds in a one-flask multistep reaction, sometimes called a tandem or cascade reaction, is of high value in the construction of complex organic molecules and the methodology has received much attention these days.[2]

Recently, we have been investigating the use of 1-chlorovinyl *p*-tolyl sulfoxides **3**, derived from carbonyl compounds **1** and chloromethyl *p*-tolyl sulfoxide **2**, in organic synthesis.[3] In continuation of our studies on developing new synthetic methods by using 1-chloroalkyl *p*-tolyl sulfoxides, herein we report in detail the reaction of 1-chlorovinyl *p*-tolyl sulfoxides **3** with the α-carbanion of acetonitrile and related compounds. Especially, the reaction of **3** with the cyanomethyllithium gave the enaminonitrile **4** in high yields. We also report in detail the transformation of **4** to various kinds of cyclopentanone derivatives such as **5**[4] (Scheme 1).

Results and Discussion

1-Chlorovinyl *p*-tolyl sulfoxide **6**, which was synthesized from benzophenone and chloromethyl *p*-tolyl sulfoxide in



Scheme 1.

Keywords: 1-chlorovinyl *p*-tolyl sulfoxides; acetonitrile; enaminonitriles.

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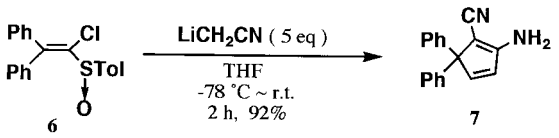


Scheme 2.

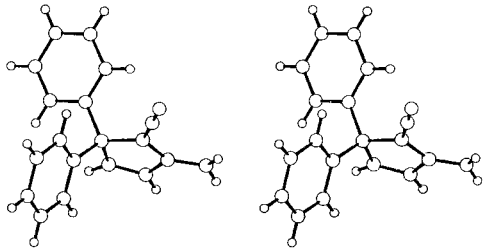
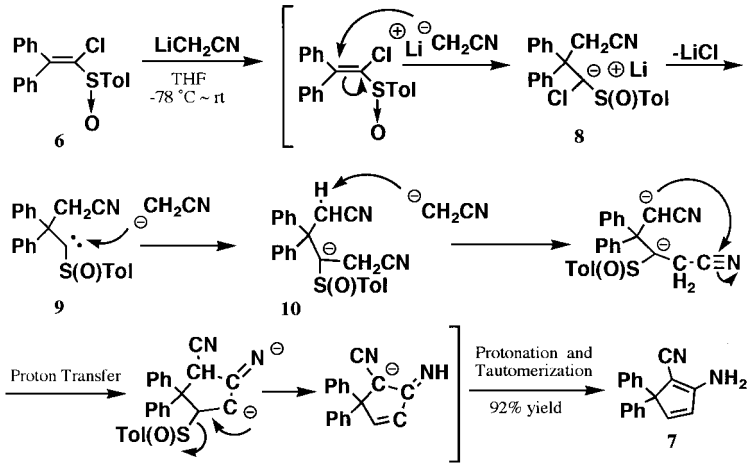


Figure 1. Stereoview of the enaminonitrile **7**.

The proposed mechanism was supported by the experiments shown in Scheme 4. The reaction of **6** with the cyanomethyllithium at −78°C for 2 min was quenched with water to afford the adduct **11** in 90% yield with a trace of the enaminonitrile **7**. When the quench was carried out with deuterio methanol, deuterated adduct **12** with 96% deuterium content was obtained. These results show that one of the intermediates of the reaction should be the α-sulfinyl carbanion **8** (Scheme 3). Furthermore, the adduct **11** was treated with 3-equivalents of LDA at −78°C for 10 min, then the cyanomethyllithium was added and the reaction temperature was allowed to warm to room temperature to give the enaminonitrile **7** in good yield. These results support the validity of the proposed mechanism shown in Scheme 3.

The results for the reaction of several α-chlorovinyl *p*-tolyl sulfoxides with the cyanomethyllithium are summarized in



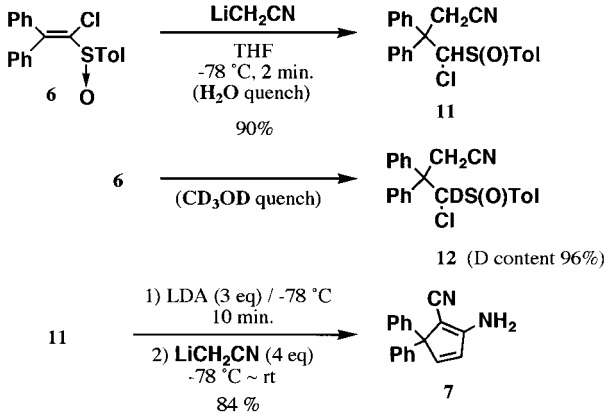
Scheme 3. The proposed mechanism for the generation of the enaminonitrile **7** from 1-chlorovinyl *p*-tolyl sulfoxide **6** and cyanomethyllithium.

good yield,[3c] was treated with 5-equivalents of the cyanomethyllithium (prepared from acetonitrile and *n*-BuLi in THF at −78°C) at −78°C to room temperature for 2 h. The reaction gave a clean reaction mixture, from which a crystalline product **7** was obtained in 92% yield (Scheme 2).

The IR spectra of the product **7** showed NH absorption at 3468 and 3324 cm^{-1}. The absorption at 2188 cm^{-1} was considered to be a nitrile; however, the value was abnormally low compared to that of the usual nitriles (2285–2200 cm^{-1}).[5] From other spectral data and X-ray crystallographic analysis (see Fig. 1),[6] the structure of the product was established as an enaminonitrile **7**.

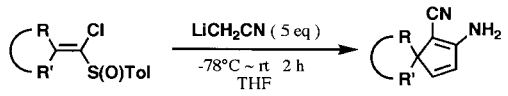
The mechanism of this interesting reaction was considered to be as follows (Scheme 3). Michael-type addition of the cyanomethyllithium to the double bond of **6** gave the α-sulfinyl carbanion having a chlorine atom **8**. Elimination of lithium chloride from **8** afforded an α-sulfinyl carbene (or carbenoid),[7] which was attacked by a second cyanomethyllithium to give an α-sulfinyl carbanion of dinitrile compound **10**. The Thorpe–Ziegler reaction[8] of the dinitrile **10** with the elimination of the sulfinyl group took place to give the enaminonitrile **7** in high yield.

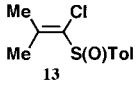
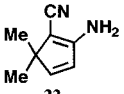
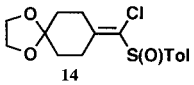
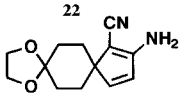
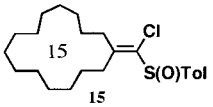
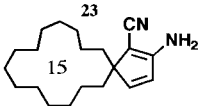
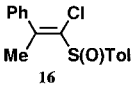
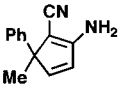
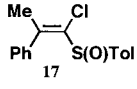
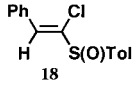
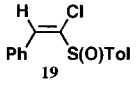
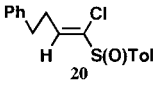
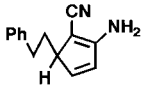
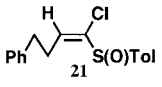
Table 1. Entries 1–5 show that, when both R and R′ in the 1-chlorovinyl *p*-tolyl sulfoxides are an alkyl or an aryl group, the reaction gives high yields of the products. Entries 2 and 3 show that spiro-type enaminonitriles are obtained without any problem. We propose that this reaction offers a good method for the synthesis of spiro-cyclic compounds[9] having a cyclopentane moiety. Entries 4 and 5 indicate that



Scheme 4. Supporting experiments for the mechanism shown in Scheme 3.

Table 1. Reaction of 1-chlorovinyl *p*-tolyl sulfoxides with $LiCH_2CN$



Entry	Starting Material	Product	Yield / %[a)]
1	 13	 22	87
2	 14	 23	97
3	 15	 24	77
4	 16	 25	96
5	 17		93
6	 18	Complex mixture	
7	 19		
8	 20	 26	28
9	 21		23

a) Isolated yield after silica gel column chromatography.

both geometrical isomers react similarly with the cyanomethyllithium.

In contrast to the good results described above, the α-chlorovinyl sulfoxides having a hydrogen on their β-position showed very different results. Entries 6 and 7 show that the α-chlorovinyl sulfoxides derived from benzaldehyde gave only a tarry complex mixture. The 1-chlorovinyl sulfoxides derived from 3-phenylpropanal gave the desired product; however, the reaction mixture was rather complex and the yield of the enaminonitrile was low (entries 8 and 9).

To elucidate the reason why the reaction with the 1-chlorovinyl sulfoxides derived from aldehydes gave a complex mixture, we investigated an experiment shown in Scheme 5.

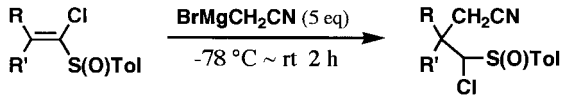
Thus, 1-chlorovinyl *p*-tolyl sulfoxide **18** was treated with the cyanomethyllithium at −78°C for 10 min, then quenched with water to afford the adduct **27** together with the rearranged products **28** and **29**. The rearranged products **28** and **29** were thought to be produced from the adduct **30** through the rearrangement of the hydrogen in the carbenoid **31**. These products would produce several compounds under the basic conditions to give a complex mixture at elevated temperature.

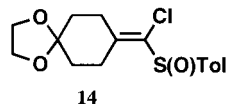
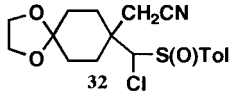
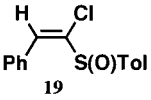
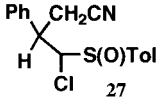
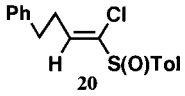
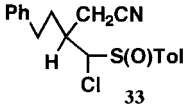
Reaction of the 1-chlorovinyl *p*-tolyl sulfoxides with other carbanions of alkylcyanides

We also investigated the reaction of the 1-chlorovinyl *p*-tolyl sulfoxides with the cyanomethylmagnesium bromide, which was generated from the cyanomethyllithium with magnesium bromide etherate, and the results are summarized in Table 2.

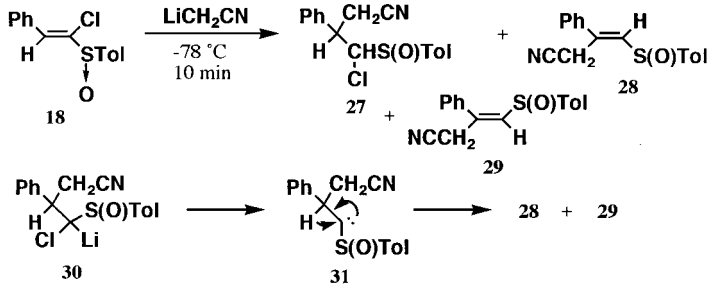
Similarly to the cyanomethyllithium, the cyanomethylmagnesium bromide added to the 1-chlorovinyl *p*-tolyl sulfoxides in moderate to good yields. However, in contrast to the cyanomethyllithium the reaction did not give the enaminonitrile upon warming to room temperature. This implies that the intermediate magnesium carbenoide is stable and also has low reactivity toward the cyanomethylmagnesium bromide. As shown in entries 2 and 3, even the 1-chlorovinyl *p*-tolyl sulfoxides derived from aldehydes

Table 2. Reaction of 1-chlorovinyl *p*-tolyl sulfoxides with $BrMgCH_2CN$



Entry	Starting Material	Product	Yield/%[a)]
1	 **14**	 **32**	83
2	 **19**	 **27**	45
3	 **20**	 **33**	66

a) Isolated yield after silica gel column chromatography.



Scheme 5.

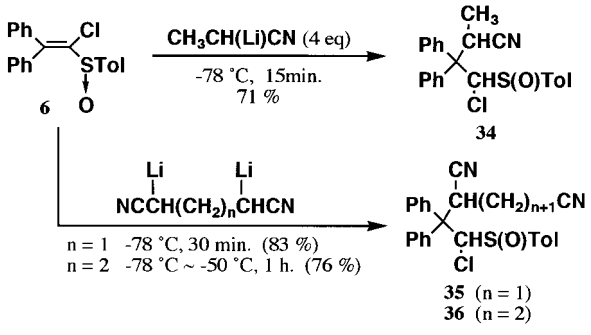
gave the adduct without rearrangement products (compare to the results in Scheme 5).

Finally, we investigated the reaction of the 1-chlorovinyl *p*-tolyl sulfoxide **6** with the 1-cyanoalkyllithium other than cyanomethyllithium (Scheme 6). The reaction of **6** with the 1-cyanoethyllithium at −78°C gave the adduct **34** in good yield. However, upon warming the reaction temperature, the reaction gave a complex mixture and the expected cyclized product was not obtained. The dianion of glutaronitrile and adiponitrile also added to **6** to give the adduct **35** and **36**, respectively, in good yields. Again, elevation of the reaction temperature gave a complex mixture and the expected cyclized product could not be obtained.

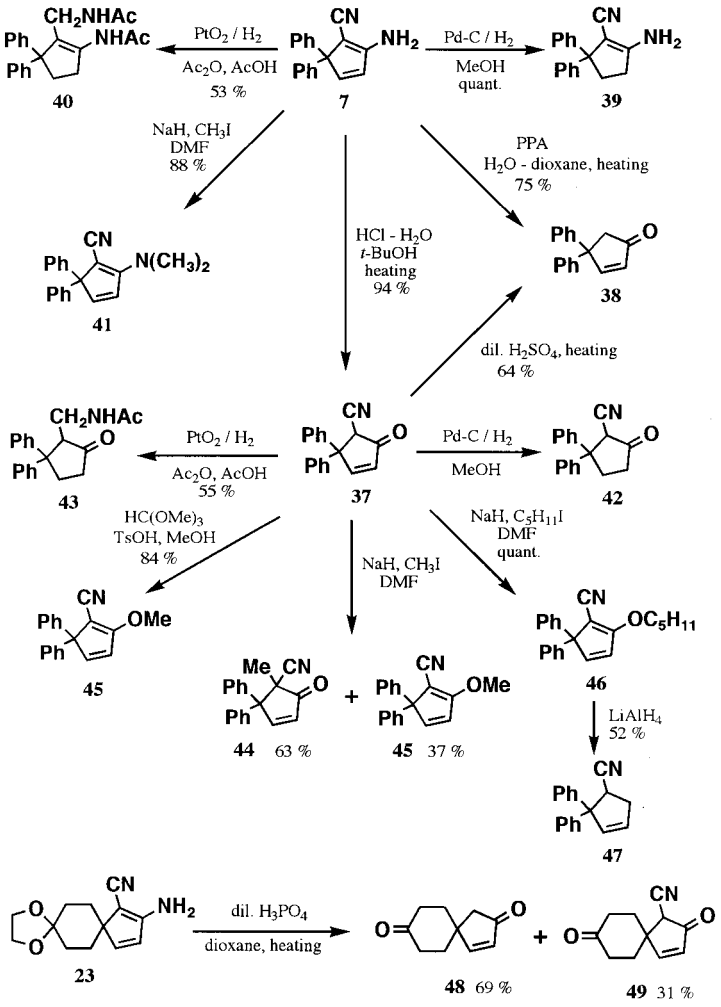
Conversion of the enaminonitriles to several cyclopentanone derivatives

In order to convert the enaminonitriles to compounds useful in organic synthesis, we tried some reactions to **7** and **23** (Scheme 7). Acidic hydrolysis of the enaminonitrile **7** with diluted hydrochloric acid in refluxing *tert*-BuOH[10] gave the enone **37** in high yield. The acidic hydrolysis under more vigorous conditions gave decyanated enone **38** in 75% yield.

Catalytic hydrogenation of **7** with Pd–C in methanol gave enaminonitrile **39** in quantitative yield. The tetra-substituted double bond could not be reduced under these conditions. Catalytic hydrogenation of **7** with PtO_2 in acetic anhydride gave an acetamide **40** in moderate yield. *N*-Methylation of **7**



Scheme 6.



Scheme 7.

was successful with iodomethane and sodium hydride to give *N*,*N*-dimethyl product **41** in good yield. The cyano group of **7** is so stable that it was not reacted with DIBAL, $LiAlH_4$, and EtMgBr.

Catalytic hydrogenation of the enone **37** gave ketone **42** in quantitative yield. Again, we could not reduce the cyano group of **42**. Alkylation of **37** with iodomethane in the presence of sodium hydride gave a mixture of *C*-methylated product **44** and *O*-methylated product **45**. The reaction of **37** with iodopentane gave only *O*-pentyl product **46** in quantitative yield. Attempts to protect the carbonyl group of **37** with dimethyl acetal with methyl orthoformate gave only an enolether **45**. Treatment of **46** with $LiAlH_4$ gave cyanoolefine **47** in moderate yield and no reduction of the cyano group was effected.

Spiro-type enaminonitrile **23** was heated in aqueous phosphoric acid to give quite interesting spiro enediones **48** and **49** in quantitative yield in total.

We are continuing work on the reaction of the 1-chlorovinyl *p*-tolyl sulfoxides with several carbanions, and the extension of the presented reaction to asymmetric synthesis. The results will be reported in due course.

Experimental

Mps were measured with a Yanagimoto micro melting point apparatus and are uncorrected. ^1H NMR spectra were measured in a $CDCl_3$ solution with JEOL JNM-LA 400 and 500 spectrometers. Electron-impact mass spectra (MS) were obtained at 70 eV by direct insertion. Silica gel 60 (Merck) containing 0.5% fluorescence reagent 254 and a quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring a dry solvent, THF was distilled from sodium diphenylketyl; DMSO, DMF, and acetonitrile were distilled from CaH_2.

2-Amino-1-cyano-5,5-diphenyl-1,3-cyclopentadiene (7). Acetonitrile (0.094 ml; 1.8 mmol) was added to a solution of *n*-BuLi (1.5 mmol) in 3 ml of dry THF at −78°C with stirring. The solution was stirred for 10 min, then a solution of **6**[3c] (111.3 mg; 0.3 mmol) in THF (1 ml) was added. The temperature of the reaction mixture was gradually allowed to warm to room temperature for 2 h. The reaction was quenched by sat. aq. NH_4Cl. The whole was extracted with AcOEt. The organic layer was washed once with sat. aq. NH_4Cl. The product was isolated by silica gel column chromatography to give 71 mg (92%) of **7** as colorless

crystals. Mp 170–172°C (AcOEt–hexane); IR (KBr) 3468 (NH), 3324 (NH), 2188 (CN), 1655, 762, 700 cm^{-1}; ^1H NMR δ 4.75 (2H, br s), 6.17, 6.95 (each 1H, d, J=5.6 Hz), 7.2–7.4 (10H, m). ^{13}C NMR δ 67.8, 86.7, 118.4, 125.6, 127.2, 127.4, 128.6, 141.4, 152.0, 159.7. MS m/z (%) 258 (M^+, 100), 181 (27), 28 (36). Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46; N, 10.84. Found: C, 83.75; H, 5.31; N, 10.72.

4-Chloro-3,3-diphenyl-4-(*p*-tolylsulfinyl)butyronitrile (11). Acetonitrile (0.047 ml; 0.9 mmol) was added to a solution of *n*-BuLi (0.75 mmol) in 2 ml of dry THF at −78°C with stirring. The solution was stirred for 10 min, then a solution of **6** (53.0 mg; 0.15 mmol) in THF (1 ml) was added. The solution was stirred for 2 min, then the reaction was quenched by adding sat. aq. NH_4Cl. The whole was extracted with AcOEt. The product was purified by silica gel column chromatography to afford **11** (53.2 mg; 90%) as colorless crystals; mp 189–192°C (AcOEt–hexane); IR (KBr) 2245 (CN), 1050 (SO), 705 cm^{-1}; ^1H NMR δ 2.44 (3H, s), 3.54, 4.35 (each 1H, d, J=16.3 Hz), 5.31 (1H, s), 7.2–7.8 (14H, m). MS m/z (%) 393 (M^+, trace), 254 (61), 178 (58), 140 (100). Anal. Calcd for $C_{23}H_{20}ClNOS$: C, 70.13; H, 5.12; N, 3.56; Cl, 9.00; S, 8.14. Found: C, 70.03; H, 5.10; N, 3.41; Cl, 9.15; S, 8.20.

4-Chloro-4-deuterio-3,3-diphenyl-4-(*p*-tolylsulfinyl)-butyronitrile (12). Colorless crystals; IR (KBr) 2241 (CN), 1053 (SO), 699 cm^{-1}; ^1H NMR: the signal of the hydrogen on the carbon bearing the chlorine atom (δ 5.31) almost disappeared.

1-Chloro-2-methyl-1-(*p*-tolylsulfinyl)-1-propene (13). A solution of **2** (755 mg; 4 mmol) in dry THF (4 ml) was added dropwise to a solution of LDA (5 mmol) in 15 ml of THF at −78°C. The solution was stirred at −78°C for 10 min, then acetone (0.23 ml; 5 mmol) was added. The reaction mixture was stirred for 10 min and the reaction was quenched by sat. aq. NH_4Cl. The whole was extracted with AcOEt. The organic layer was washed once with sat. aq. NH_4Cl and dried over $MgSO_4$. The solvent was evaporated to leave colorless crystals. The crystals were washed with a mixture of hexane–AcOEt (10:1) to give pure chloro alcohol. Recrystallization of the crystals from AcOEt–hexane gave colorless crystals (699 mg; 71%); mp 136–138°C (AcOEt–hexane); IR (KBr) 3389 (OH), 1044 (SO) cm^{-1}; ^1H NMR δ 1.60 (6H, s), 2.43 (3H, s), 2.71 (1H, br s), 4.27 (1H, s), 7.35, 7.49 (each 2H, d, J=8.3 Hz). MS m/z (%) 246 (M^+, 4), 140 (100), 92 (56). Calcd for $C_{11}H_{15}ClO_2S$: M, 246.0481. Found: m/z 246.0491.

4-Dimethylaminopyridine (65.4 mg; 0.54 mmol) was added to a suspension of the chloro alcohol (661 mg; 2.68 mmol) in a mixture of acetic anhydride (5 ml) and pyridine (5 ml). The suspension was stirred at room temperature for 13 h. The acetic anhydride and pyridine were evaporated under vacuum and the residue was purified by silica gel column chromatography to give acetate (774 mg; quantitive yield) as colorless crystals; mp 68–70°C (AcOEt–hexane). IR (KBr) 1727 (CO), 1241 cm^{-1}; ^1H NMR δ 1.67, 1.78 (each 3H, s), 2.12 (3H, s), 2.42 (3H, s), 5.30 (1H, s), 7.33, 7.47 (each 2H, d, J=8 Hz). MS m/z (%) 289 ($[M+H]^+$, trace), 149 (36), 43 (100). Anal. Calcd for $C_{13}H_{17}ClO_3S$: C, 54.07; H, 5.93; Cl, 12.28; S, 11.10. Found: C, 53.97; H, 5.81; Cl, 12.19; S, 11.18.

The acetate (152 mg; 0.53 mmol) was dissolved in 2 ml of DMSO. To this was added NaH (42 mg; 1.05 mmol) and the suspension was stirred for 3 h. The solution was diluted with ether (10 ml) and cooled in an ice bath. The reaction was quenched by adding a solution of acetic acid (1 ml) in 10 ml of ether. The whole was extracted with ether–benzene, washed once with half-saturated aq. NH_4Cl. The product was isolated by flash chromatography using silica gel to give 64 mg (53%) of **13** and starting acetate (47%). **13**: colorless crystals; mp 103–104°C (AcOEt–hexane). IR (KBr) 1084, 1058 cm^{-1}; ^1H NMR δ 2.01 (3H, s), 2.33 (3H, s), 2.41 (3H, s), 7.31, 7.48 (each 2H, d, J=8 Hz). MS m/z (%) 228 (M^+, 78), 211 (87), 53 (100). Anal. Calcd for $C_{11}H_{13}ClOS$: C, 57.76; H, 5.73; Cl, 15.50; S, 14.02. Found: C, 57.71; H, 5.65; Cl, 15.36; S, 14.14.

The 1-chlorovinyl *p*-tolyl sulfoxides **14**–**17** are known compounds.[3c]

(*Z*)-1-Chloro-2-phenyl-1-(*p*-tolylsulfinyl)ethene (18) and (*E*)-isomer (19). These compounds were synthesized from chloromethyl *p*-tolyl sulfoxide **2** and benzaldehyde in a similar way as described for **13**. Chloro alcohol: yellow viscous oil. IR (KBr) 3356 (OH), 1043 (SO) cm^{-1}. To a solution of the chloro alcohol (1.13 g; 3.83 mmol) in dry CH_2Cl_2 was added triethylamine (0.7 ml) followed by methanesulfonyl chloride (0.39 ml; 5 mmol) with stirring at 0°C. The reaction mixture was stirred at 0°C for 30 min, then at room temperature for 4 h. The reaction was quenched with water, and the whole was extracted with CH_2Cl_2. The organic layer was washed successively with 10% HCl, sat. $NaHCO_3$, then sat. brine. The usual workup followed by silica gel column chromatography gave **18** (0.44 g; 42%) and **19** (0.53 g; 50%). **18**: Colorless crystals; mp 136–138°C (AcOEt–hexane); IR (KBr) 1084, 1052 cm^{-1}; ^1H NMR δ 2.42 (3H, s), 7.31–7.54 (10H, m). MS m/z (%) 276 (M^+, 7), 228 (100), 140 (61). Anal. Calcd for $C_{15}H_{13}ClOS$: C, 65.09; H, 4.73; Cl, 12.81; S, 11.59. Found: C, 64.98; H, 4.62; Cl, 12.92; S, 11.78. **19**: Colorless crystals; mp 59–61°C (AcOEt–hexane); IR (KBr) 1082, 1065 cm^{-1}; ^1H NMR δ 2.42 (3H, s), 7.31–7.77 (10H, m). MS m/z (%) 276 (M^+, 10), 228 (100). Anal. Calcd for $C_{15}H_{13}ClOS$: C, 65.09; H, 4.73; Cl, 12.81; S, 11.59. Found: C, 64.77; H, 4.61; Cl, 12.82; S, 11.70.

(*Z*)-1-Chloro-4-phenyl-1-(*p*-tolylsulfinyl)-1-butene (20) and (*E*)-isomer (21). These compounds were synthesized from chloromethyl *p*-tolyl sulfoxide **2** and 3-phenylpropanal in a similar way as described for **13**. Chloro alcohol: colorless crystals. IR (KBr) 3364 (OH), 1032 (SO) cm^{-1}; ^1H NMR δ 1.89–2.12 (2H, m), 2.44 (3H, s), 2.68–2.92 (2H, m), 3.9–4.5 (3H, m), 7.1–7.5 (9H, m).

To a solution of the chloro alcohol (1.71 g; 5.3 mmol) in dry CH_2Cl_2 was added triethylamine (1.5 ml) followed by methanesulfonyl chloride (0.82 ml; 10.6 mmol) with stirring at 0°C. The reaction mixture was stirred at 0°C for 30 min, then 1,8-diazabicyclo[5.4.0]undec-7-ene (3.0 ml; 20 mmol) was added to the reaction mixture at room temperature. The reaction mixture was stirred for 10 min

at room temperature. The reaction was quenched with water, and the whole was extracted with CH_2Cl_2. The organic layer was washed successively with 10% HCl, sat. $NaHCO_3$, then sat. brine. The usual workup followed by silica gel column chromatography gave **20** (0.63 g; 39%) and **21** (0.85 g; 53%). **20**: Colorless crystals; mp 87–89°C (AcOEt–hexane); IR (KBr) 1083, 1057 cm^{-1}; ^1H NMR δ 2.41 (3H, s), 2.57–2.84 (4H, m), 6.76 (1H, t, J=7.2 Hz), 7.2–7.5 (9H, m). MS m/z (%) 304 (M^+, 1), 287 (100), 91 (90). Anal. Calcd for $C_{17}H_{17}ClOS$: C, 66.98; H, 5.62; Cl, 11.63; S, 10.52. Found: C, 66.92; H, 5.56; Cl, 11.71; S, 10.68. **21**: Colorless crystals; mp 56–58°C (AcOEt–hexane); IR (KBr) 1086, 1058 cm^{-1}; ^1H NMR δ 2.40 (3H, s), 2.77–3.08 (4H, m), 6.32 (1H, t, J=7.8 Hz), 7.2–7.5 (9H, m). MS m/z (%) 304 (M^+, 20), 197 (59), 91 (100). Anal. Calcd for $C_{17}H_{17}ClOS$: C, 66.98; H, 5.62; Cl, 11.63; S, 10.52. Found: C, 66.78; H, 5.54; Cl, 11.88; S, 10.71.

2-Amino-1-cyano-5,5-dimethyl-1,3-cyclopentadiene (22). Colorless crystals; mp 93–94°C (AcOEt–hexane); IR (KBr) 3432 (NH), 3341 (NH), 2166 (CN), 1649 cm^{-1}; ^1H NMR δ 1.27 (6H, s), 4.46 (2H, br s), 5.97, 6.46 (each 1H, d, J=5.5 Hz). MS m/z (%) 134 (M^+, 45), 119 (100), 92 (21). Anal. Calcd for $C_8H_{10}N_2$: C, 71.61; H, 7.51; N, 20.88. Found: C, 71.29; H, 7.47; N, 20.64.

2-Amino-1-cyano-8,8-ethylenedioxyspiro[4.5]daca-1,3-diene (23). Colorless crystals; mp 249–251°C (AcOEt–hexane); IR (KBr) 3418 (NH), 3347 (NH), 2162 (CN), 1660, 1613 cm^{-1}; ^1H NMR δ 1.49–1.53, 1.71–1.78, 1.92–1.96, 2.03–2.10 (each 2H, m), 3.96–4.00 (4H, m), 4.53 (2H, br s), 6.08, 6.83 (each 1H, d, J=5.6 Hz). ^{13}C NMR δ 30.8, 33.4, 55.6, 64.4, 87.1, 108.0, 118.1, 126.1, 149.8, 158.2. MS m/z (%) 232 (M^+, 43), 204 (57), 118 (100). Anal. Calcd for $C_{13}H_{16}N_2O_2$: C, 67.22; H, 6.94; N, 12.06. Found: C, 66.87; H, 6.84; N, 11.87.

2-Amino-1-cyanospiro[4.14]nonadeca-1,3-diene (24). Colorless crystals; mp 152–154°C (AcOEt–hexane); IR (KBr) 3450 (NH), 3348 (NH), 2169 (CN), 1642 cm^{-1}; ^1H NMR δ 1.3–1.7 (28H, m), 4.48 (2H, br s), 5.99, 6.55 (each 1H, d, J=5.6 Hz). MS m/z (%) 300 (M^+, 100), 119 (85), 118 (67). Anal. Calcd for $C_{20}H_{32}N_2$: C, 79.94; H, 10.73; N, 9.32. Found: C, 79.53; H, 10.68; N, 9.20.

2-Amino-1-cyano-5-methyl-5-phenyl-1,3-cyclopentadiene (25). Colorless crystals; mp 161–164°C (AcOEt–hexane); IR (KBr) 3433 (NH), 3346 (NH), 2167 (CN), 1649 cm^{-1}; ^1H NMR δ 1.68 (3H, s), 4.69 (2H, br s), 6.07, 6.67 (each 1H, d, J=5.5 Hz), 7.2–7.3 (5H, m). ^{13}C NMR δ 22.2, 59.0, 88.0, 118.1, 125.1, 125.8, 126.9, 128.6, 140.4, 153.6, 158.9. MS m/z (%) 196 (M^+, 100), 181 (89), 154 (12). Calcd for $C_{13}H_{12}N_2$: M, 196.1000. Found: m/z 196.1004.

2-Amino-1-cyano-5-(2-phenylethyl)-1,3-cyclopentadiene (26). Colorless crystals; mp 95–98°C (AcOEt–hexane); IR (KBr) 3411 (NH), 3344 (NH), 2172 (CN), 1647 cm^{-1}; ^1H NMR δ 1.82–1.89 (1H, m), 2.04–2.11 (1H, m), 2.66–2.78 (2H, m), 3.43 (1H, dd, J=7.3, 6.1 Hz), 4.59 (2H, br s), 6.16, 6.56 (each 1H, d, J=5.5 Hz), 7.1–7.4 (5H, m). MS m/z (%) 210 (M^+, 54), 119 (82), 91 (100). Calcd for $C_{14}H_{14}N_2$: M, 210.1155. Found: m/z 210.1153.

4-Chloro-3-phenyl-4-(p-tolylsulfinyl)butyronitrile (27). Colorless crystals; mp 184–186°C (AcOEt–hexane). IR (KBr) 2250 (CN), 1087, 1050, 698, 514 cm^{-1}; ^1H NMR δ 2.43 (3H, s), 2.95 (1H, dd, J=3.7, 17.1 Hz), 3.05 (1H, dd, J=8.3, 17.1 Hz), 3.73–3.79 (1H, m), 4.69 (1H, d, J=9.8 Hz), 7.2–7.5 (9H, m). MS m/z (%) 317 (M^+, 14), 178 (70), 140 (100). Anal. Calcd for $C_{17}H_{16}ClNOS$: C, 64.24; H, 5.07; N, 4.41; Cl, 11.15; S, 10.09. Found: C, 63.87; H, 4.93; N, 4.33; Cl, 11.20; S, 10.17.

(E)-3-Cyano-2-phenyl-1-(p-tolylsulfinyl)-1-propene (28) and (Z)-isomer (29). 28: This compound was decided by ^1H NMR spectra; δ 4.22, 4.37 (each 1H, d, J=13 Hz), 5.73 (1H, s, vinyl-H). **29**: Colorless oil; IR (neat) 2216 (CN), 1086, 1048 cm^{-1}; ^1H NMR δ 2.40 (3H, s), 3.88, 3.99 (each 1H, d, J=13 Hz), 5.39 (1H, s), 7.26–7.43 (9H, m). MS m/z (%) 281 (M^+, 6), 139 (100). Calcd for $C_{17}H_{15}NOS$: M, 281.0873. Found: m/z 281.0877.

1-[Chloro-(p-tolylsulfinyl)methyl]-1-cyanomethyl-4,4-ethylenedioxycyclohexane (32). Acetonitrile (0.063 ml; 1.2 mmol) was added to a solution of n-BuLi (1.0 mmol) in 2 ml of dry THF at −78°C with stirring. The solution was stirred for 10 min, then a solution of magnesiumbromide etherate (310 mg; 1.2 mmol) in THF (10 ml) was added. The reaction mixture was stirred for 10 min at −78°C, then a solution of **14** (65.4 mg; 0.2 mmol) in THF (1 ml) was added. The temperature of reaction mixture was gradually allowed to warm to room temperature for 2 h. The reaction was quenched by sat. aq. NH_4Cl. The whole was extracted with AcOEt. The organic layer was washed once with sat. aq. NH_4Cl. The product was isolated by silica gel column chromatography to give 59 mg of **32** as colorless crystals. Less polar **32**: colorless crystals; mp 112–114°C (AcOEt–hexane); IR (KBr) 2241 (CN), 1104, 1080, 1052 cm^{-1}; ^1H NMR δ 1.6–1.8 (4H, m), 1.8–1.9 (1H, m), 2.0–2.1 (1H, m), 2.2–2.3 (1H, m), 2.4 (1H, m), 2.44 (3H, s), 2.90, 3.45 (each 1H, d, J=17.1 Hz), 3.96 (4H, s), 4.69 (1H, s), 7.34, 7.76 (each 2H, d, J=8.3 Hz). MS m/z (%) 367 (M^+, 2), 228 (100). Anal. Calcd for $C_{18}H_{22}ClNO_3S$: C, 58.77; H, 6.03; N, 3.81; Cl, 9.62; S, 8.72. Found: C, 58.52; H, 5.81; N, 3.72; Cl, 9.60; S, 8.71. More polar **32**: colorless crystals; mp 167–169°C (AcOEt–hexane); IR (KBr) 2240 (CN), 1110, 1084, 1051 cm^{-1}; ^1H NMR δ 1.67–1.76 (4H, m), 1.97–2.05 (1H, m), 2.08–2.20 (2H, m), 2.28–2.40 (1H, m), 2.44 (3H, s), 2.90, 2.99 (each 1H, d, J=17.3 Hz), 3.97 (4H, s), 4.48 (1H, s), 7.36, 7.48 (each 2H, d, J=8.0 Hz). MS m/z (%) 367 (M^+, 13), 228 (100), 192 (85). Calcd for $C_{18}H_{22}ClNO_3S$: M, 367.1009. Found: m/z 367.1013.

3-[Chloro-(p-tolylsulfinyl)methyl]-5-phenylvaleronitrile (33). Less polar **33**: colorless oil; IR (neat) 2240 (CN), 1084, 1050, 700 cm^{-1}; ^1H NMR δ 2.0–2.2 (3H, m), 2.45 (3H, s), 2.6–2.7 (2H, m), 2.8–3.0 (2H, m), 4.43 (1H, d, J=1.9 Hz), 7.1–7.7 (9H, m). MS m/z (%) 345 (M^+, trace), 292 (25), 140 (81), 91 (100). Calcd for $C_{19}H_{20}ClNOS$: M, 345.0955. Found m/z 345.0955. More polar **33**: colorless oil; IR (neat) 2242 (CN), 1495, 1455, 1089, 1058, 701 cm^{-1}; ^1H NMR δ 1.9–2.0 (1H, m), 2.3–2.4 (1H, m), 2.42 (3H, s), 2.43–2.54 (1H, m), 2.5–2.8 (4H, m), 4.54 (1H, d, J=4.6 Hz), 7.1–7.5 (9H, m). MS m/z (%) 345 (M^+, 1), 140 (83), 91 (100). Calcd for $C_{19}H_{20}ClNOS$: M, 345.0954. Found m/z 345.0948.

4-Chloro-2-methyl-3,3-diphenyl-4-(*p*-tolylsulfinyl)butyronitrile (34). Propionitrile (0.05 ml; 0.7 mmol) was added to a solution of *n*-BuLi (0.6 mmol) in 2 ml of dry THF at −78°C with stirring. The solution was stirred for 10 min, then a solution of **6** (52.9 mg; 0.15 mmol) in THF (1 ml) was added. The reaction mixture was stirred for 15 min at −78°C. The reaction was quenched by sat. aq. NH_4Cl. The whole was extracted with AcOEt. The organic layer was washed once with sat. aq. NH_4Cl. The product was isolated by silica gel column chromatography to give 43 mg (71%) of **34** as colorless crystals; mp 215–217°C (AcOEt–hexane). IR (KBr) 2237 (CN), 1083, 1063 (SO) cm^{-1}; ^1H NMR δ 1.13 (3H, d, J=7.0 Hz), 2.43 (3H, s), 5.35 (1H, br s), 5.69 (1H, s), 7.25–7.75 (14H, m). MS *m/z* (%) 408 ($[M+H]^+$, trace), 268 (56), 214 (100), 179 (63). Anal. Calcd for $C_{24}H_{22}ClNOS$: C, 70.66; H, 5.44; N, 3.43; Cl. 8.69; S, 7.86. Found: C, 70.50; H, 5.51; N, 3.37; Cl, 8.65; S, 7.86.

1-Chloro-3,5-dicyano-2,2-diphenyl-1-(*p*-tolylsulfinyl)-pentane (35). Glutaronitrile (0.03 ml; 0.32 mmol) was added to a solution of *n*-BuLi (0.6 mmol) in 2 ml of dry THF at −78°C with stirring. The solution was stirred for 10 min, then a solution of **6** (52.9 mg; 0.15 mmol) in THF (1 ml) was added. The reaction mixture was stirred for 30 min at −78°C. The reaction was quenched by sat. aq. NH_4Cl. The whole was extracted with AcOEt. The organic layer was washed once with sat. aq. NH_4Cl. The product was isolated by silica gel column chromatography to give 71 mg (83%) of **35** as colorless crystals; mp 200–203°C (CH_2Cl_2–hexane); IR (KBr) 2248 (CN), 1042 (SO) cm^{-1}; ^1H NMR δ 1.20–1.29 (2H, m), 2.43 (3H, s), 2.44–2.58 (2H, m), 5.38 (1H, br d, J=10.8 Hz), 5.64 (1H, s), 7.25–7.74 (14H, m). MS *m/z* (%) 447 ($[M+H]^+$, 4), 93 (100). Calcd for $C_{26}H_{24}ClN_2OS$: M, 447.1298. Found: *m/z* 447.1292.

1-Chloro-3,6-dicyano-2,2-diphenyl-1-(*p*-tolylsulfinyl)-hexane (36). Colorless crystals; mp 201–204°C ($CHCl_3$–hexane); IR (KBr) 2241 (CN), 1044 (SO), 708 cm^{-1}; ^1H NMR δ 1.84–1.96 (3H, m), 2.27–2.43 (3H, s), 2.44 (3H, s), 5.25 (1H, br d, J=10.7 Hz), 5.67 (1H, s), 7.32–7.75 (14H, m). MS *m/z* (%) 460 (M, trace), 321 (82), 273 (100), 179 (85). Calcd for $C_{27}H_{25}ClN_2OS$: M, 460.1376. Found: *m/z* 460.1363.

5-Cyano-4,4-diphenyl-2-cyclopentenone (37). 4 ml of 15% HCl was added to a solution of **7** (325 mg; 1.25 mmol) in 10 ml of *t*-BuOH. The reaction mixture was stirred for 2 h at 80°C. The reaction was quenched by sat. aq. $NaHCO_3$. The whole was extracted with ether–benzene, washed once with sat. aq. $NaHCO_3$. The product was isolated by silica gel column chromatography to give **37** (304 mg; 94%) as colorless crystals; mp 121–124°C (AcOEt–hexane). IR (KBr) 2242 (CN), 1742, 1708 (CO) cm^{-1}; ^1H NMR δ 4.12 (1H, s), 6.42, 8.06 (each 1H, d, J=5.8 Hz), 6.9–7.0 (2H, m), 7.2–7.5 (8H, m). MS *m/z* (%) 259 (M^+, 100), 230 (30), 105 (23). Anal. Calcd for $C_{18}H_{13}NO$: C, 83.37; H, 5.05; N, 5.40. Found: C, 83.02; H, 4.94; N, 5.31.

4,4-Diphenyl-2-cyclopentenone (38). To a solution of **7** (65 mg; 0.25 mmol) in a mixture of 1,4-dioxane (2 ml) and water (2 ml) was added 3 ml of PPA (polyphosphoric acid; 75% P_2O_5) and the reaction mixture was stirred for 25 h at 150°C (bath temperature). The reaction was quenched by sat. aq. $NaHCO_3$. The whole was extracted with AcOEt, washed once with sat. aq. $NaHCO_3$. The product was isolated by silica gel column chromatography to give **38** (44 mg; 75%) as colorless oil. IR (neat) 1714 (CO), 1588, 1492, 1446, 758, 699 cm^{-1}; ^1H NMR δ 3.13 (2H, s), 6.25, 7.99 (each 1H, d, J=5.8 Hz), 7.1–7.4 (10H, m). MS *m/z* (%) 234 (M^+, 100), 206 (57), 131 (46). Calcd for $C_{17}H_{14}O$: M, 234.1044. Found: *m/z* 234.1044.

1-Amino-2-cyano-3,3-diphenylcyclopentene (39). To a solution of **7** (52 mg; 0.2 mmol) in 4 ml of MeOH was added 10 mg of Pd–C (10%) and the suspension was stirred under H_2 atmosphere at room temperature for 2 h. The Pd–C was filtered off and the solvent was evaporated to give a residue, which was purified by silica gel column chromatography to give quantitative yield of **39** (52 mg) as colorless crystals; mp 179–181°C (AcOEt–hexane). IR (KBr) 3443 (NH), 3354 (NH), 2177 (CN), 1642, 1599 cm^{-1}; ^1H NMR δ 2.56–2.62 (4H, m), 4.64 (2H, b), 7.2–7.4 (10H, m). MS *m/z* (%) 260 (M^+, 19), 183 (100). Anal. Calcd for $C_{18}H_{16}N_2$: C, 83.04; H, 6.19; N, 10.76. Found: C, 82.98; H, 6.05; N, 10.70.

1-Acetylamino-2-(acetylamino)methyl-3,3-diphenylcyclopentene (40). To a solution of **7** (41 mg; 0.16 mmol) in a mixture of acetic anhydride (5 ml) and acetic acid (2 ml) was added 10 mg of PtO_2 and the suspension was stirred under H_2 atmosphere at room temperature for 65 h. The PtO_2 was filtered off and the solvent was evaporated under vacuum to give a residue, which was purified by silica gel column chromatography to give 53% yield of **40** (29 mg) as colorless crystals; mp 159–162°C (AcOEt–hexane). IR (KBr) 3429 (NH), 1692 (CO), 1664 (CO), 1522, 1376 cm^{-1}; ^1H NMR δ 1.64 (3H, s), 2.12 (3H, s), 2.60, 3.05 (2H, t, J=7.2 Hz), 3.70 (2H, d, J=6.6 Hz), 4.52 (1H, b), 7.1–7.4 (10H, m), 9.77 (1H, b). MS *m/z* (%) 348 (M^+, 25), 289 (100), 230 (72). Calcd for $C_{22}H_{24}N_2O_2$: M, 348.1836. Found: *m/z* 348.1830.

1-Cyano-2-dimethylamino-5,5-diphenyl-1,3-cyclopentadiene (41). A solution of **7** (139 mg; 0.54 mmol) in DMF (3 ml) was added NaH (108 mg; 2.7 mmol) and iodomethane (0.17 ml; 2.7 mmol). The suspension was stirred at room temperature for 2 h and the reaction was quenched by sat. aq. NH_4Cl. The whole was extracted with AcOEt and after the usual workup followed by silica gel column chromatography to give **41** (136 mg; 88%) as colorless crystals; mp 166–169°C (AcOEt–hexane). IR (KBr) 2161 (CN), 1622, 1560, 699 cm^{-1}; ^1H NMR δ 3.20 (6H, s), 6.36 (1H, d, J=5.8 Hz), 6.89 (1H, d, J=5.8 Hz), 7.2–7.3 (10H, m). MS *m/z* (%) 286 (M^+, 100), 209 (34). Anal. Calcd for $C_{20}H_{18}N_2$: C, 83.88; H, 6.34; N, 9.78. Found: C, 83.45; H, 6.24; N, 9.71.

2-Cyano-3,3-diphenylcyclopentanone (42). This compound was synthesized from **37** as described for **39**. Colorless crystals; mp 128–131°C (AcOEt–hexane); IR (KBr) 2214 (CN), 1647, 1399, 703 cm^{-1}; ^1H NMR δ 2.50–2.54 (2H, m), 2.70–2.83 (2H, m), 3.87 (1H, s), 7.1–7.4 (10H, m). MS *m/z* (%) 261 (M^+, 100), 184 (41), 115 (31). Anal. Calcd for $C_{18}H_{15}NO$: C, 82.73; H, 5.79; N, 5.36. Found: C, 82.40; H, 5.77; N, 5.25.

2-(Acetylamino)methyl-3,3-diphenylcyclopentanone (43). This compound was synthesized from **37** as described for **40**. Colorless crystals; mp 148–152°C (AcOEt–hexane); IR (KBr) 3317 (NH), 1736 (CO), 1636 (CO), 701 cm^{-1}; ^1H NMR δ 1.96 (3H, s), 2.35–2.58 (4H, m), 2.94–3.01 (1H, m), 3.28 (1H, dd, J=10.6, 4.0 Hz), 3.71–3.77 (1H, m), 6.22 (1H, b), 7.0–7.4 (10H, m). MS m/z (%) 307 (M^+, 22), 235 (88), 230 (75), 159 (100). Anal. Calcd for $C_{20}H_{21}NO_2$: C, 78.15; H, 6.89; N, 4.56. Found: C, 77.86; H, 6.85; N, 4.39.

5-Cyano-5-methyl-4,4-diphenyl-2-cyclopentenone (44) and 1-Cyano-2-methoxy-5,5-diphenyl-1,3-cyclopentadiene (45). A solution of **37** (54 mg; 0.2 mmol) in DMF (3 ml) was added NaH (12 mg; 0.3 mmol) and iodomethane (0.025 ml; 0.4 mmol). The suspension was stirred at room temperature for 30 min and the reaction was quenched by sat. aq. NH_4Cl. The whole was extracted with AcOEt and after the usual workup followed by silica gel column chromatography to give **44** (35 mg; 63%) and **45** (21 mg; 37%). **44**: Colorless crystals; mp 133–134°C (AcOEt–hexane); IR (KBr) 2242 (CN), 1720 (CO), 706, 699 cm^{-1}; ^1H NMR δ 1.20 (3H, s), 6.23, 7.95 (each 1H, d, J=5.8 Hz), 7.0–7.5 (10H, m). MS m/z (%) 273 (M^+, 100), 258 (38), 230 (26). Calcd for $C_{19}H_{15}NO$: M, 273.1153. Found: m/z 273.1154. **45**: Colorless oil; IR (neat) 2197 (CN), 1614, 1375, 699 cm^{-1}; ^1H NMR δ 4.21 (3H, s), 6.20, 6.96 (each 1H, d, J=5.8 Hz), 7.2–7.4 (10H, m). MS m/z (%) 273 (M^+, 100), 258 (55), 230 (38). Calcd for $C_{19}H_{15}NO$: M, 273.1152. Found: m/z 273.1151.

1-Cyano-2-pentoxy-5,5-diphenyl-1,3-cyclopentadiene (46). This compound was synthesized from **37** and 1-iodopentane as described for **44**. Colorless oil; IR (neat) 2197 (CN), 1611, 1292, 698 cm^{-1}; ^1H NMR δ 0.92 (3H, t, J=7.1 Hz), 1.3–1.4 (4H, m), 1.78 (2H, quint, J=8.1 Hz), 4.48 (2H, t, J=6.6 Hz), 6.21, 6.95 (each 1H, d, J=5.6 Hz), 7.2–7.4 (10H, m). MS m/z (%) 329 (M^+, 23), 259 (100), 231 (45). Calcd for $C_{23}H_{23}NO$: M, 329.1777. Found: m/z 329.1768.

4-Cyano-3,3-diphenylcyclopentene (47). A solution of **46** (47.7 mg; 0.145 mmol) in THF (1 ml) was added to a suspension of $LiAlH_4$ (12.3 mg; 0.3 mmol) at −78°C. The temperature of the reaction mixture was gradually allowed to warm to room temperature for 2 h, then it was stirred for 3 h. The reaction was quenched by adding AcOEt and the whole was extracted with AcOEt and washed with sat. aq. NH_4Cl. The product was isolated by silica gel column chromatography to give **47** (18.5 mg; 52%) as colorless oil. IR (neat) 2240 (CN), 1494, 1446, 700 cm^{-1}; ^1H NMR δ 2.82–2.98 (2H, m), 3.82 (1H, t, J=8.6 Hz), 6.00–6.03 (1H, m), 6.21–6.24 (1H, m), 7.1–7.4 (10H, m). MS m/z (%) 245 (M^+, 57), 205 (42), 192 (100). Calcd for $C_{18}H_{15}N$: M, 245.1204. Found: m/z 245.1206.

Spiro[4.5]dec-1-ene-3,8-dione (48) and 4-cyanospiro[4.5]-dec-1-ene-3,8-dione (49). To a solution of **23** (41 mg; 0.18 mmol) in a mixture of 1,4-dioxane (2 ml) and water (2 ml) was added 2 ml of 85% H_3PO_4. The reaction mixture was stirred for 24 h at 150°C (bath temperature) to give **48** (20 mg; 69 %) and **49** (10 mg; 31%). **48**: Colorless crystals; mp 95–98°C (AcOEt–hexane); IR (KBr) 1706 (CO), 1675, 969, 824 cm^{-1}; ^1H NMR δ 1.85–1.92 (2H, m), 1.98–2.06 (2H, m), 2.47–2.49 (6H, m), 6.18, 7.60 (each 1H, d, J=5.6 Hz). MS m/z (%) 164 (M^+, 100), 94 (38), 55 (82). Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 72.95; H, 7.49. **49**: Colorless oil; IR (neat) 2244 (CN), 1714 (CO), 1591, 1170 cm^{-1}; ^1H NMR δ 2.05–2.14 (3H, m), 2.31–2.38 (1H, m), 2.48–2.82 (3H, m), 2.83–2.86 (1H, m), 3.39 (1H, s), 6.32, 7.79 (each 1H, d, J=5.8 Hz. MS m/z (%) 189 (M^+, 36), 55 (100). Calcd for $C_{11}H_{11}NO_2$: M, 189.0789. Found: m/z 189.0800.

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