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Push–pull alkenes from cyclic ketene-*N*,*N*′-acetals: a wide span of double bond lengths and twist angles

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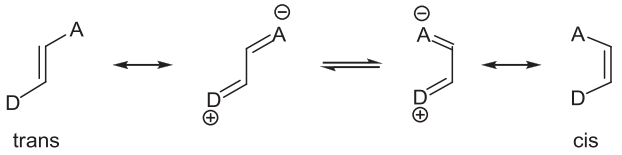
ABSTRACT

Push–pull alkenes can be quickly accessed by cyclic ketene-*N*,*N*′-acetal chemistry. A number of push–pull structures with a wide span of double bond lengths and twist angles were synthesized from the reactions of (1) *N*,*N*′-dimethyl cyclic ketene-*N*,*N*′-acetals with isocyanates, (2) the products from (**1**) with isocyanates, (3) 2-methylimidazoline and 2-methyl-1,4,5,6-tetrahydropyrimidine with diacid chlorides, (4) 2-methylimidazoline, and 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine with benzoyl chlorides, and (5) 1,2-dimethylimidazoline and 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine with aryl isocyanates. These reactions proceed under very mild conditions and give moderate to excellent yields. X-ray crystallographic analysis of eight pxush–pull alkenes indicates that the central double bond lengths and twists are sensitive to the ring sizes (5 or 6), ring structures (fused or non-fused), electron donating and withdrawing strengths of pushing and pulling portions, respectively, number of electron pushing or pulling groups and substituent steric effects.

1. Introduction

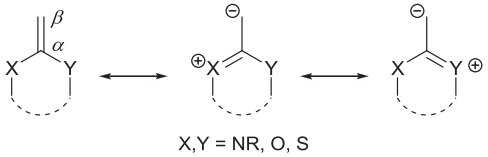
Push–pull alkenes are substituted alkenes with electron-donating groups (push) and electron-withdrawing groups (pull) at both ends of the alkene double bond (D–π-A). Intramolecular charge transfer in the D–π-A framework occurs with profound consequences on the molecular structure and properties. These include central double bond elongation,[1] facile out-of-plane rotation,[2] strong charge-transfer absorption bands,[3] large dipole moments,[4] huge ^{13}C chemical shift differences[5] between the alkene carbons and high hyperpolarizabilities, which are prerequisite for organic nonlinear optical materials.[6] For an example, the lowered barrier to rotation about the central double bond (Scheme 1) results from the push–pull effect, which reduces the double bond order by intramolecular charge transfer.



Scheme 1. Lowering of the barrier to rotation about C=C bond due to the push–pull effect.

These unusual effects stimulated extensive research on push–pull alkenes including their synthesis, characterization, and applications[7–19] along with theoretical investigations to understand, quantify, and predict these effects.[20–27]

Ketene acetals (Scheme 2) are an important class of neutral carbon nucleophiles. They combine two electron-donating groups (N, O, or S) at one end of a double bond. The lone-pair electrons on both heteroatoms delocalize to the C=C bond. As result, the double bond is polarized and exhibits significant nucleophilicity at the β-carbon. Ketene acetal chemistry has been increasingly studied and applied in organic synthesis[28,29] and polymer synthesis[30] since the pioneering work by McElvain and co-workers in 1930–1940s.[31]



Scheme 2. Basic structure of ketene acetals and origin of their nucleophilicity.

Ketene acetal reactivities vary with many structural factors. The selection of heteroatoms is central to the ketene acetal's nucleophilicity.[32] Cyclic ketene-*N*,*N*′-acetals are more reactive than their

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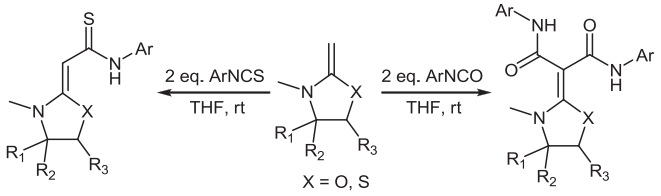
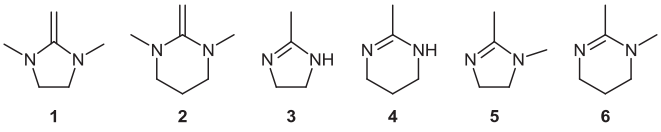
acyclic analogs.[33] The reactivity of cyclic ketene-*O*,*O*-acetals in cationic 1,2-vinyl addition polymerizations is modulated by substituent effects.[30a–c] Finally, the combination of substituent and ring-size effects allow diverse reaction paths to exist from in situ generated ketene-*N*,*N*′-acetals.[34]

Ketene acetals are ideal building blocks for push–pull alkenes because pushing function (D) and nucleophilic double bond (π) are already present in their structures. Moreover, ketene acetals' tunable nucleophilicity also makes them appealing for synthesizing push–pull alkenes. Ideally, a large pool of push–pull alkenes with various magnitudes of push–pull activity can be accessed by altering the heteroatoms (six combinations available from N, O, and S), varying substituents, selecting cyclic/acyclic structures, and changing ring-size of ketene acetals. However, studies of such cyclic ketene acetal (CKA) conversions are sparse due to their handling difficulties.[35]

Pittman et al. reported the reactions of cyclic ketene-*N*,*X*-acetals (X=O,S) with aryl isocyanates and isothiocyanates.[36] Push–pull alkenes were synthesized in excellent yields at very mild conditions (Scheme 3). In this report, the conversion of *N*,*N*′-dimethyl cyclic ketene-*N*,*N*′-acetals **1** and **2** (Scheme 4) to push–pull alkenes via reactions with isocyanates will be demonstrated. The push–pull alkene structures from cyclic ketene-*N*,*N*′-acetals generated in situ from cyclic amidines **3**–**6** will also be discussed. The detailed syntheses of starting materials **1**–**6** can be found in our previous reports.[34b,35]



Scheme 3. push–pull alkenes from cyclic ketene-*N*,*X*-acetals (X=O, S).



Scheme 4. Substrates for push–pull alkene synthesis.

2. Results and discussion

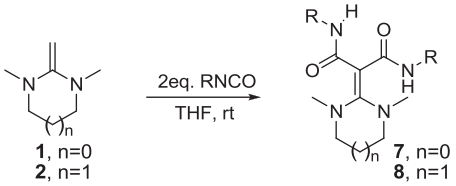
Cyclic ketene-*N*,*N*-acetals **1** and **2** readily react with two equivalents of isocyanates in THF at rt (Table 1). After stirring for 3 h, tetrasubstituted push–pull alkenes **7a**–**d** and **8a**–**d** were isolated simply by pouring the reaction mixture into hexane. Excellent yields were achieved for most of the examples (Table 1). The electron-pushing five or six-membered cyclic ketene-*N*,*N*′-acetal moieties interact directly with the two amide groups in these products.

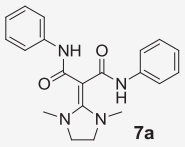
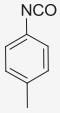
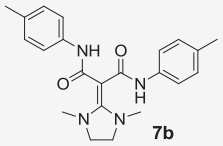
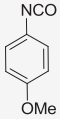
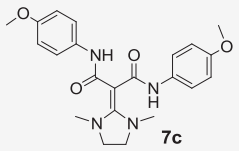
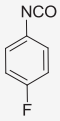
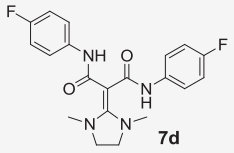
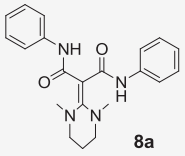
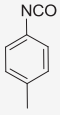
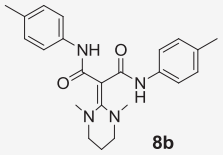
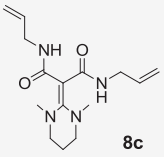
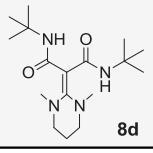
A mechanism in accord with the formation of **7a** is shown in Scheme 5. Nucleophilic attack of the β-carbon in **1** on the first equivalent of phenyl isocyanate gives zwitterion **9**, which rapidly transfers the acidic hydrogen from the β-carbon to produce monoadduct **10** with regeneration of ketene acetal double bond. Compound **10** then reacts with the second equivalent of phenyl isocyanate to generate zwitterion **11**. Proton transfer in **11** finally gives structure **7a**.

The isolated products **7a**–**d** and **8a**–**d** were further treated with excess isocyanate to probe the reactivities of these tetrasubstituted polarized alkenes (Table 2). Trisisocyanate adducts **12a** and **12b** were obtained from the six-membered systems **8a** and **8b**, respectively. However, **7a**–**d** and **8c**–**d** did not form analogous trisadducts using the isocyanates examined herein.

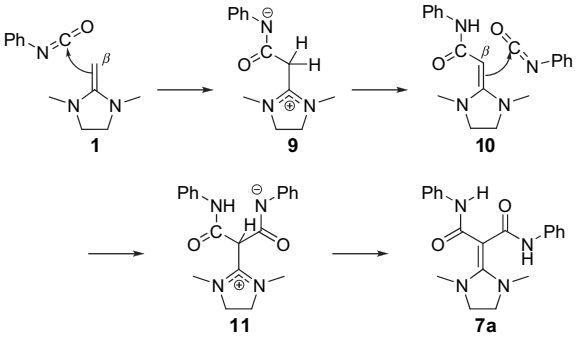
The single crystal structure of **7d** was determined and shown in Figure 1. A remarkable feature of this structure is the elongated central carbon–carbon double bond (C14–C16: 1.45 Å), which is substantially longer than the normal carbon–carbon double bond

Table 1
Reactions of *N*,*N*′-dimethyl cyclic ketene-*N*,*N*′-acetals with isocyanates



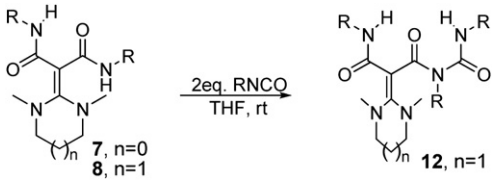
Substrate	Isocyanate	Product	Yield (%)[a]
		 **7a**	90
		 **7b**	93
		 **7c**	94
		 **7d**	95
		 **8a**	84
		 **8b**	81
		 **8c**	89
		 **8d**	93

[a] Yields are based on substrate **1** or **2**.



Scheme 5. A mechanism consistent with the formation of push–pull alkene **7a**.

Table 2
Reactions of push–pull alkenes with isocyanates



Substrate	R[a]	Product	Yield(%)
7a	Ph	No reaction	—
7b	*p*-$CH_3C_6H_4$	No reaction	—
7c	*p*-$MeOC_6H_4$	No reaction	—
7d	*p*-FC_6H_4	No reaction	—
8a	Ph	**12a**	32
8b	*p*-$CH_3C_6H_4$	**12b**	37
8c	CH_2=CH–CH_2–	No reaction	—
8d	*t*-Bu	No reaction	—

[a] The R group in push–pull reagent alkenes and R group in isocyanates were the same for each reaction reported here.

of ethylene (1.34 Å).[37] In addition to the longer central carbon–carbon double bond, a concomitant twisting of this double bond occurs (twist angle[38] 56.72°). This is the synergistic outcome of (1) steric repulsion between the *N*-substituents and the β-carbon-substituents, and (2) the push–pull effect, which reduces the C14–C16 bond order, making it easier to twist out-of-plane. The extent of twisting reflects a compromise between the relaxation of the steric hindrance (energy drop) and the deviation of the alkene substituents from the ideal co-planar geometry (energy rise).

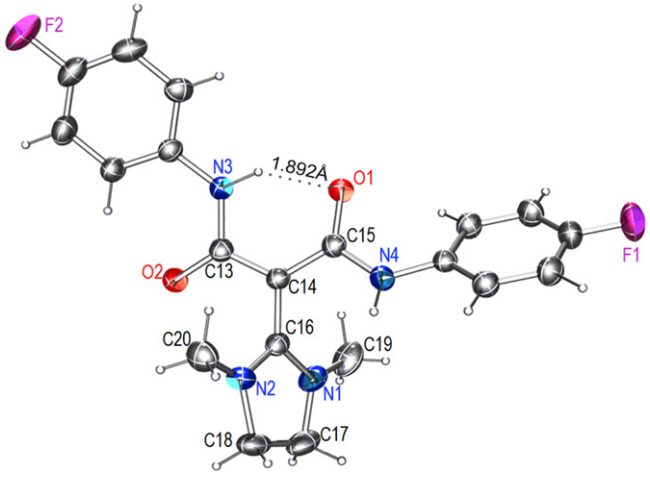


Figure 1. Crystal structure of **7d**. A water molecule is not shown for clarity. The thermal ellipsoids are drawn with 50% probability. CCDC: 689417.

The short enamine carbon–nitrogen bonds (N1–C16: 1.33 Å; N2–C16: 1.32 Å) and the near planar configurations (vs pyramidal) of N1 and N2 suggest N1–C16 and N2–C16 bonds have considerable double bond character. N1 and N2 are sp^2-hybridized. An intramolecular hydrogen-bond exists in the crystal (O1···H–N3), which further stabilizes the observed molecular geometry in the crystal.

The crystal structure of **8a** was also obtained (Fig. 2). Its central carbon–carbon double bond (C8–C16: 1.47 Å) is slightly longer (~0.02 Å) than that in **7d**. The length of the central double bond was demonstrated to be a reliable parameter for quantifying push–pull effect in push–pull alkenes based on NBO analysis (the longer the double bond, the stronger the push–pull effect).[25] The longer C=C bond length of **8a** versus **7d** helps to explain why the push–pull alkenes containing six-membered cyclic ketene-*N*,*N*′-acetal donors (**8a** and **8b**) each underwent a further reaction with isocyanates (phenyl and *p*-tolyl, respectively), while those having five-membered cyclic ketene-*N*,*N*′-acetal donors (**7a** and **7b**) did not.

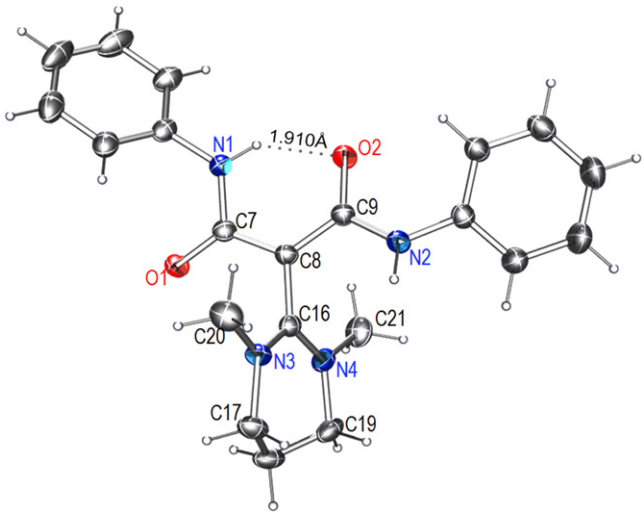
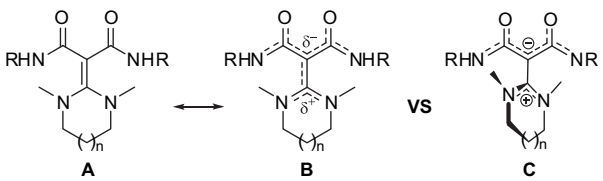


Figure 2. Crystal structure of **8a**. Disordered $CHCl_3$ molecules are present and not shown for clarity. CCDC: 719324

The central carbon–carbon double bond in **8a** has a larger twist angle (67.44°) than that in **7d** (56.72°). This enhanced twist is due to stronger steric repulsions between donor and accepter portions in **8a** versus that in **7d**. This larger twist angle is closer to the totally zwitterionic geometry (90° twist, Scheme 6). Thus, the minimum energy geometry, **8a**, has more zwitterionic character than the five-membered analog. In other words, the acceptor portion of a six-membered push–pull alkene is more negatively charged and is more nucleophilic than the acceptor portions of the five-membered analog. This explains the higher reactivities of **8a** and **8b** toward adding a third equivalent of isocyanate versus **7a** and **7b**.



Scheme 6. The dependence of the charge separation on the geometry of a push–pull alkene. **A**: resonance structure showing no charge separation; **B**: resonance structure showing partial charge separation and a partial central double bond (central double bond may be twisted depending on steric factors); **C**: structure showing full charge separation in the 90° twisted geometry where the central bond is actually a single bond because no conjugation (π-bonding) is possible between donor and acceptor portions.

The crystal structure of the trisadduct **12a** was determined (Fig. 3). Its central carbon–carbon double bond length (C8–C9: 1.47 Å) is comparable with that in **8a**, but this double bond is further twisted (twist angle: 75.52°) compared to **8a** due to **12a**'s larger acceptor groups. Two intramolecular hydrogen-bonds exist in the **12a** crystal structure (O3···H-N4 and O3···H-N1).

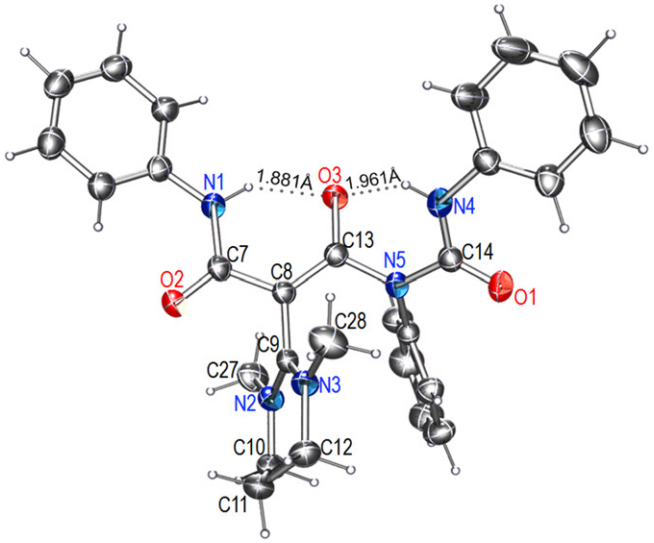


Figure 3. Crystal structure of **12a**. The thermal ellipsoids are drawn with 50% probability. CCDC: 689418.

The five-membered ring *N*,*O*-analog, **13** (Fig. 4), was also synthesized according to a literature method.[36] The crystal structure of **13** was determined in order to compare with those of **7d**, **8a**, and **12a**. The central double bond length in **13** (C6–C7: 1.39 Å) is considerably shorter than those in **7d** (1.45 Å), **8a** (1.47 Å), and **12a** (1.47 Å). This was attributed to the weaker electron-donating ability of the ketene-*N*,*O*-acetal versus the stronger donation by ketene-*N*,*N*′-acetals. This agrees with a recent computational analysis of ketene-*N*,*N*′- versus -*N*,*O*- versus -*N*,*S*- versus -*O*,*O*- versus -*S*,*S*- versus -*O*,*S*-acetals.[32] The central carbon–carbon double bond of **13** is also less twisted (twist angle: 25.34°) versus those of **7d** (56.72°), **8a** (67.44°), and **12a** (75.52°) because one *N*-methyl group is replaced by oxygen atom. This dramatically reduced the magnitude of steric repulsions.

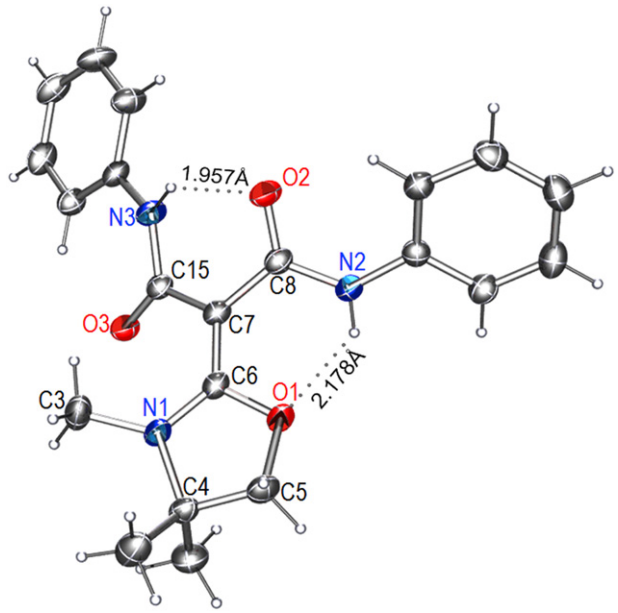
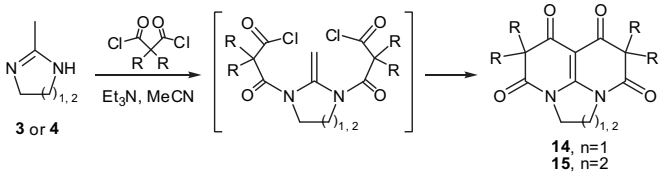
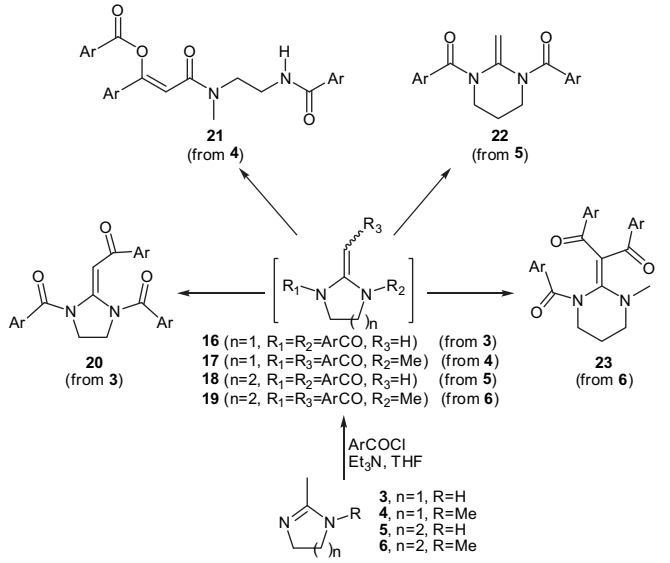


Figure 4. Crystal structure of **13**. The thermal ellipsoids are drawn with 50% probability. CCDC: 719325

We explored the possibility of forming push–pull structures from in situ generated *N*-acyl cyclic ketene-*N*,*N*′-acetals. 1,8-Naphthyridinetetraones were synthesized from 2-methylimidazoline **3** and 2-methyl-1,4,5,6-tetrahydropyrimidine **4** via cyclic ketene-*N*,*N*′-acetal intermediates (Scheme 7) and reported previously.[39] The diverse reactivities of in situ generated ketene acetals were further demonstrated by reactions of **3**–**6** with aroyl chlorides (Scheme 8).[34] Structures **14**, **15**, **20**, and **23** should also exhibit push–pull character based on their ketene acetal precursors' nucleophilicity. The carbonyl groups present on the ring nitrogens in **14**, **15**, **20**, and **23** weaken the electron-donating capability in these compounds versus those in **7**, **8**, and **12**. Since one crystal structure is available for each type of these products, a direct comparison of these weaker push–pull alkenes with the preceding stronger ones can be made at this point.



Scheme 7. Synthesis of 1,8-naphthyridinetetraones.



Scheme 8. Diverse reactivities of cyclic ketene-*N*,*N*′-acetals generated in situ by reactions of cyclic amidines with aroyl chlorides.

The structure of ketene acetal **22a** (not a push–pull species) (Fig. 5) serves as good reference for the push–pull structures of **20a** (Ar=Ph) (Fig. 6), **23a** (Ar=Ph) (Fig. 7), and **14a** (R=Pr) (Fig. 8). The C6–C21 double bond in **22a** (Ar=*m*-MeOPh) (Fig. 5) is 1.33 Å, which is a normal C=C double bond length.

The two *N*-benzoyl groups in **20a** (Fig. 6) diminished the pushing ability of two nitrogen atoms. Furthermore, only one pulling function (phenyl keto group on C7) is present in **20a**. Thus, a weak push–pull activity is expected. The C6–C7 (1.35 Å) length in **20a** is only slightly longer than the corresponding double bond in **22a**. The twist angle is smaller (14.63°) compared to preceding stronger push–pull alkenes.

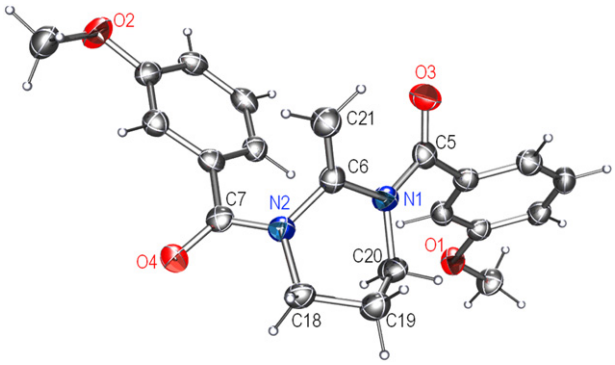


Figure 5. Crystal structure of **22a**. CCDC: 753288.

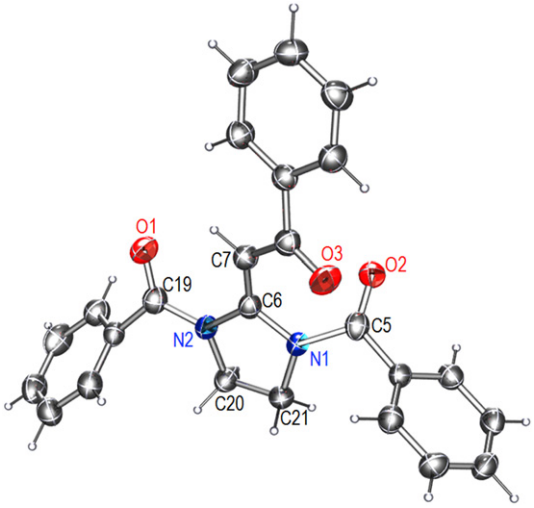


Figure 6. Crystal structure of **20a**. CCDC: 753287.

In contrast, push–pull alkene **23a** (Fig. 7) has a much longer and more twisted C=C bond (C8–C16: 1.42 Å; twist angle: 39.54°) than that in **20a**. The replacement of *N*-benzoyl group with *N*-methyl group (which is a stronger pushing function) and an additional pulling function (phenyl keto group on the β-carbon) enhanced **23a**'s push–pull activity compared to **20a**. Both the phenyl groups attached to C7 and C9 are pointing away from the hexahydropyrimidine ring to avoid steric hindrance with hexahydropyrimidine ring's *N*-substituents.

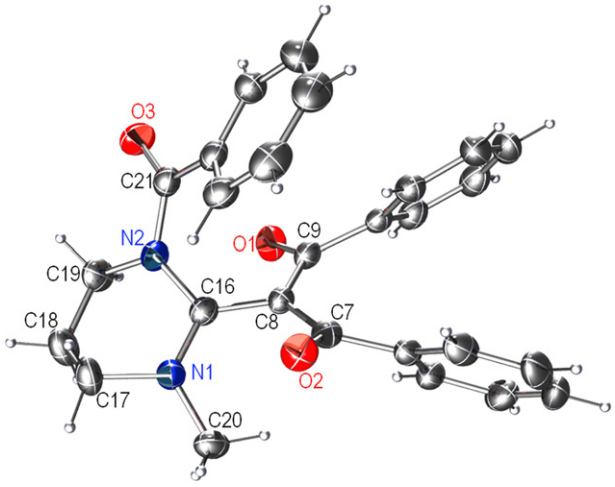


Figure 7. Crystal structure of **23a**. CCDC: 682487.

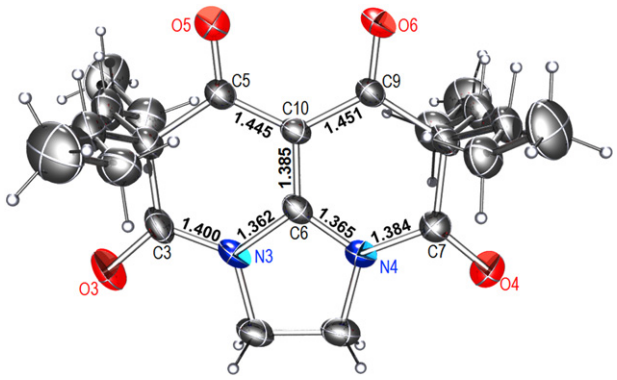
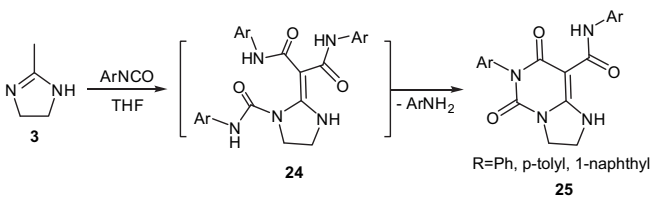


Figure 8. Crystal structure of **14a**. CCDC: 684834.

A single crystal of **14a** (R=Pr) was obtained by slow evaporation of pentane into a THF solution of **14a**. Two independent molecules of **14a** with associated THF molecules were found in the crystal structure (See Supplementary data: 14a.cif), one of which is numbered and shown in Figure 8. Some important bond lengths are also shown for convenient comparison. The amide carbon–nitrogen bonds (C3–N3: 1.40 Å, C7–N4: 1.38 Å) are longer than a normal value of 1.32 Å.[40] The central C=C bonds (C6–C10:1.38 Å) is longer than 1.33 Å in **22a**. The enamine carbon–nitrogen single bonds (C6–N3:1.36 Å, C6–N4:1.36 Å) have considerable double bond character. The β-keto carbon–carbon single bonds (C5–C10: 1.44 Å, C9–C10: 1.45 Å) also have significant double bond character, and they are even shorter than corresponding C1–C2 single bond in acrolein (1.47 Å).[20,41] The near-perfect coplanarity of the three fused rings indicates a well conjugated π-bond system exists among the amide and methylenedione functions. The C6–C10 bond twist is very small (0.90°). The elongation of amide carbon–nitrogen bonds and the shortening of β-keto carbon–carbon single bonds, indicate a considerable amount of nitrogen lone-pair electron density is withdrawn from the amide moiety into the methylenedione moiety. In other words, **14a** exhibits significant push–pull electronic character.

Finally, we investigated the reactions of amidines **3**–**6** with isocyanates hoping to produce another type of push–pull systems. A literature search showed that 2-methylimidazoline **3** reacts with aryl isocyanates to give pyrimidinedione[42] structure **25** (Scheme 9) presumably through push–pull intermediate **24**. However, no crystal data was ever obtained for **24** or **25**. We herein extend this chemistry to 1,2-dimethylimidazoline **5** and their six-membered analogs **4** and **6** in order to (1) explore the scope of this pyrimidinedione formation reaction and (2) investigate push–pull character in the pyrimidinedione products.



Scheme 9. Reactions of 2-methylimidazoline **3** with aryl isocyanates.

Compound **5** and **6** each reacted with an excess of several different aryl isocyanates in refluxing acetonitrile for 12 h. Pyrimidinedione derivatives **26a**–**h** were isolated in moderate yields (Table 3). These reactions are similar to those of **3** as shown in Scheme 9. Unexpectedly, no reaction took place (monitored by TLC) when 2-methyl-1,4,5,6-tetrahydropyrimidine **4** was treated with phenyl isocyanate, 4-methoxyphenyl isocyanate or

Table 3
Reactions of **4**–**6** with isocyanates

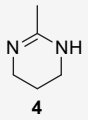
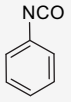
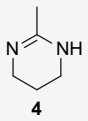
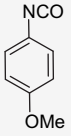
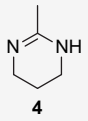
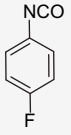
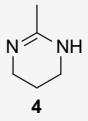
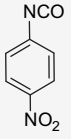
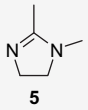
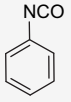
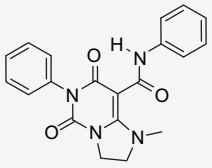
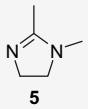
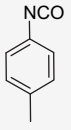
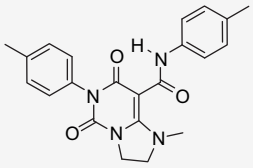
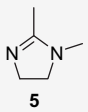
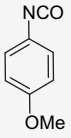
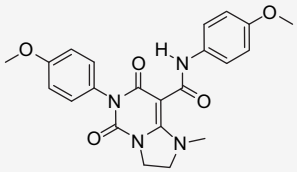
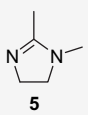
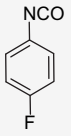
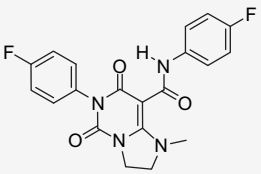
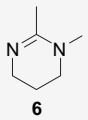
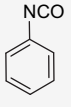
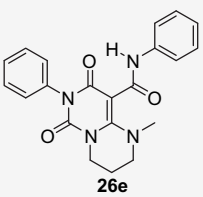
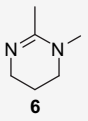
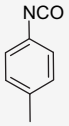
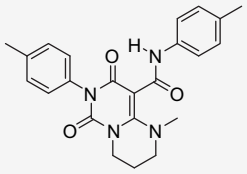
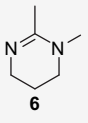
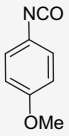
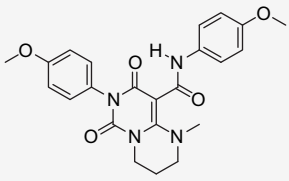
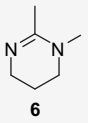
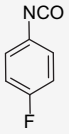
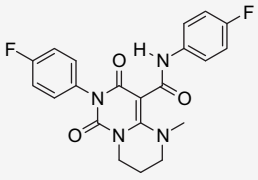
Entry	Substrate	Isocyanate	Product	Yield (%)
1	 **4**		No reaction	—
2	 **4**		No reaction	—
3	 **4**		No reaction	—
4	 **4**		Complex mixture	—
5	 **5**		 **26a**	65
6	 **5**		 **26b**	70
7	 **5**		 **26c**	62
8	 **5**		 **26d**	73
9	 **6**		 **26e**	71

Table 3 (*continued*)

Entry	Substrate	Isocyanate	Product	Yield (%)
10	 **6**		 **26f**	74
11	 **6**		 **26g**	63
12	 **6**		 **26h**	76

4-fluorophenyl isocyanate under the same conditions (Table 3, entries 1–3). The reaction of **4** with the more electrophilic isocyanate, 4-nitrophenyl isocyanate, gave a very complex mixture with many spots on the TLC plate (entry 4). No major product is formed and thus no further isolation was performed. Since **22** was formed from two ArCOCl equivalents and **4** when aroyl chlorides were used as the electrophile, the lack of reactivity of **4** with aryl isocyanates is puzzling.

Crystals of **26e** were obtained by slow evaporation of pentane into a chloroform solution of **26e**. The crystal structure was then obtained and it is shown in Figure 9 with selected bond lengths. **26e** shares several characteristics with the crystal structure of **14a** (Fig. 8): (1) The amide carbon–nitrogen bonds (N3–C21: 1.40 Å, N3–

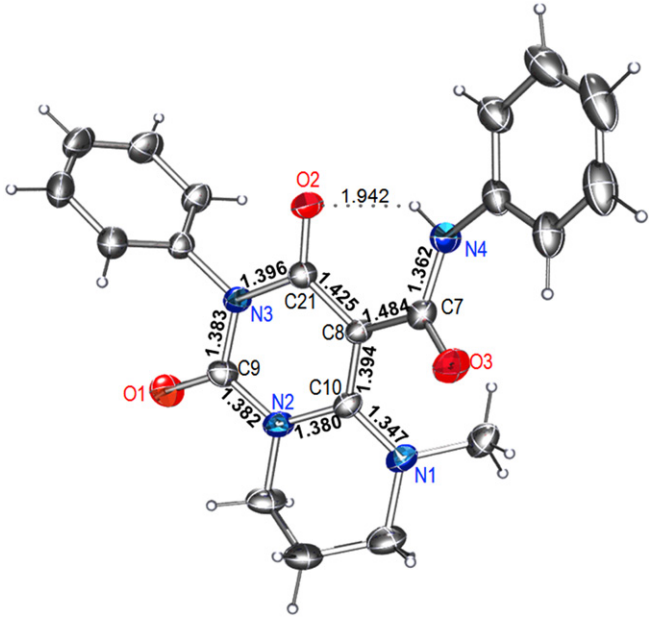


Figure 9. Crystal structure of **26e**. CCDC: 755872.

C9: 1.38 Å, N2–C9: 1.38 Å, N4–C7: 1.36 Å) are longer than a normal amide carbon–nitrogen value of 1.32 Å;[40] (2) the carbon–carbon double bond (C8–C10: 1.39 Å) is longer than 1.34 Å in ethylene;[37] (3) C10–N2 (1.38 Å) and C10–N1 (1.35 Å) have considerable double bond character. These bond length changes, especially the elongation of the central carbon–carbon double bond (C8–C10), indicate that **26e** has significant push–pull electronic character. The reduced C8–C10 double bond character facilitates the observed twisting of the C8–C10 central double bond (twist angle: 19.11°) by the repulsion between O3 and the N1-methyl group.

The pyrimidinedione ring (N2–C9–N3–C21–C8–C10) takes on a roughly planar geometry, indicating good conjugation exists in the ring system. The repulsion between O3 and N1-methyl group turns the exocyclic β-keto group (C7–O3) out of the optimal planar geometry for conjugation with pyrimidinedione plane (O3–C7–C8–C10: 21.95°). Therefore, the exocyclic carbon–carbon single bond (C7–C8: 1.48 Å) is longer than the endocyclic carbon–carbon (C21–C8: 1.43 Å). The N4-phenyl group points away from the fused bicycle's structure to (1) avoid the steric hindrance with N1-methyl group and C21–O2 carbonyl group and to (2) allow intramolecular hydrogen-bonding between O2 and N4-hydrogen (O2–H6: 1.94 Å).

3. Conclusions

A variety of push–pull alkene structures were obtained from cyclic ketene-*N*,*N*′-acetals or their in situ generated analogs. A wide range of push–pull double bond lengths and twist angles is accessible by varying ring sizes (5 or 6), ring structures (fused or non-fused), electron donating or withdrawing strength of substituents, number of electron pushing or pulling units and substituent steric effects. The push–pull activity can be controlled by a number of tunable factors synthetically accessible through cyclic ketene-*N*,*N*′-acetal chemistry.

4. Experimental

4.1. General methods

Melting points were recorded with a Mel-Temp apparatus and were uncorrected. The FTIR spectra were recorded on a Thermo Nicolet spectrometer as films on KBr plates. The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker model AMX-300 300 MHz spectrometer operating at 300 MHz for proton and 75 MHz for carbon. Chemical shifts were reported in parts per million downfield from Me_4Si, which was used as the internal standard for all NMR spectra. Splitting patterns are designed as 's, d, t, q, and m'; these symbols indicate 'singlet, doublet, triplet, quartet, and multiplet', respectively. All reactions were carried out under nitrogen. Tetrahydrofuran (THF) was distilled from Na/benzophenone under nitrogen. Acetonitrile and triethylamine were distilled from calcium hydride under nitrogen. All other commercially obtained reagents were used as received. The silica gel used for the column chromatography was purchased from Aldrich Company (70–230 mesh, 60 Å).

4.2. General procedure for synthesis of push–pull structures 7a–d and 8a–d

Phenyl isocyanate (0.24 g, 2 mmol) was added dropwise into a stirred solution of 1,3-dimethyl-2-methyleneimidazolidine **1** (0.112 g, 1 mmol) in 10 mL of THF under nitrogen at rt. The reaction mixture was stirred at rt under nitrogen for 3 h and then poured into *n*-hexane (80 mL) to precipitate the product. The precipitates were filtered, washed with dry ethyl acetate and dried at 80 °C/2 mmHg. The product was identified as 2-(1,3-dimethylimidazolidin-2-ylidene)-N^1,N^3-diphenylmalonamide **7a** (315 mg, 90%). Compound **7a** can be further purified by flash chromatography (silica gel, hexane–acetone, 1:1 → pure acetone). Compounds **7b–d**, **8a–d** were similarly prepared.

*4.2.1. 2-(1,3-Dimethylimidazolidin-2-ylidene)-N^1,N^3-diphenylmalonamide (**7a**).* Yield 90%; R_f=0.29 (acetone); white solid; mp 206–208 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.63 (br, 1H), 7.50–6.93 (m, 10H), 3.29 (s, 4H), 2.88 (s, 6H). Only one N*H* peak can be located; ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.9, 166.4, 140.2, 128.5, 121.8, 119.5, 71.1, 48.3, 35.6; IR (KBr, cm^{-1}): 3306, 3025, 2921, 1633, 1494, 1428; HRMS (ESI, $[M+Na]^+$): calcd for $C_{20}H_{22}N_4NaO_2$, 373.1640; found, 373.1626.

*4.2.2. 2-(1,3-Dimethylimidazolidin-2-ylidene)-N^1,N^3-di-p-tolylmalonamide (**7b**).* Yield 93%; R_f=0.30 (acetone); white solid; mp 203–205 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.35 (br, 1H), 7.34–7.04 (m, 8H), 3.44 (s, 4H), 2.95 (s, 6H), 2.28 (s, 6H). Only one N*H* peak can be located; ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.5, 166.3, 137.6, 129.1, 119.9, 71.0, 48.6, 36.1, 20.6; IR (KBr, cm^{-1}): 3270, 2919, 1638, 1614, 1587, 1563, 1513, 1486; HRMS (ESI, $[M+Na]^+$): calcd for $C_{22}H_{26}N_4NaO_2$, 401.1953; found, 401.1942.

*4.2.3. 2-(1,3-Dimethylimidazolidin-2-ylidene)-N^1,N^3-bis(4-methoxyphenyl)malonamide (**7c**).* Yield 94%; R_f=0.17 (acetone); white solid; mp 194–196 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.53 (br, 1H), 7.38–6.80 (m, 8H), 3.75 (s, 6H), 3.43 (s, 4H), 2.95 (s, 6H). Only one N*H* peak can be located; ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.4, 166.4, 154.9, 133.4, 121.5, 113.8, 70.5, 55.4, 48.5, 36.0; IR (KBr, cm^{-1}): 3285, 2951, 1634, 1588, 1557, 1509, 1471; HRMS (ESI, $[M+H]^+$): calcd for $C_{22}H_{26}N_4O_4$, 411.2032; found, 411.2031.

*4.2.4. 2-(1,3-Dimethylimidazolidin-2-ylidene)-N^1,N^3-bis(4-fluorophenyl)malonamide (**7d**).* Yield 95%; R_f=0.28 (acetone); white solid; mp 170–172 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.80 (br, 1H), 7.43–6.93 (m, 8H), 3.60 (s, 4H), 3.02 (s, 6H). Only one N*H* peak exists; ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 169.6, 166.2, 158.3 (d, $^{1}J_{CF}$=239.1 Hz), 136.0, 115.2 (d, $^{2}J_{CF}$=22.1 Hz), 121.4, 70.5, 48.7, 36.3; IR (KBr, cm^{-1}): 3366, 3278, 2933, 1615, 1593, 1615, 1593, 1573, 1503; HRMS (ESI, $[M+H]^+$): calcd for $C_{20}H_{21}F_2N_4O_2$, 387.1633; found, 387.1633.

*4.2.5. 2-(1,3-Dimethyltetrahydropyrimidin-2(1H)-ylidene)-N^1,N^3-diphenylmalonamide (**8a**).* Yield 84%; R_f=0.20 (acetone); white solid; mp 193–195 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.55 (br, 1H), 7.61–6.97 (m, 10H), 6.07 (br, 1H), 3.38 (br, 4H), 3.28 (s, 6H), 2.02 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 166.1, 165.8, 140.5, 128.6, 119.6, 112.1, 75.9, 47.9, 41.9, 20.7; IR (KBr, cm^{-1}): 3289, 3053, 2926, 1609, 1591, 1573, 1486, 1428; HRMS (ESI, $[M+Na]^+$): calcd for $C_{21}H_{24}N_4NaO_2$, 387.1797; found, 387.1790.

*4.2.6. 2-(1,3-Dimethyltetrahydropyrimidin-2(1H)-ylidene)-N^1,N^3-di-p-tolylmalonamide (**8b**).* Yield 81%; R_f=0.22 (acetone); white solid; mp 183–185 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.51 (br, 1H), 7.49–7.03 (m, 8H), 6.25 (br, 1H), 3.30 (br, 4H), 3.18 (s, 6H), 2.27 (s, 6H), 1.87 (br, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 165.8, 165.8, 137.5, 128.9, 119.5, 75.6, 47.6, 41.6, 20.5; IR (KBr, cm^{-1}): 3284, 3206, 2922, 1621, 1590, 1573, 1504; HRMS (ESI, $[M+Na]^+$): calcd for $C_{23}H_{28}N_4NaO_2$, 415.2110; found, 415.1945.

*4.2.7. N^1,N^3-Diallyl-2-(1,3-dimethyltetrahydropyrimidin-2(1H)-ylidene)malonamide (**8c**).* Yield 89%; R_f=0.25 (AcOEt–MeOH, 2:1); colorless viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 9.26 (br, 1H), 5.90 (m, 2H), 5.19–5.02 (m, 4H), 3.89 (br, 4H), 3.45 (t, *J*=5.3 Hz, 4H), 3.20 (s, 6H), 2.12 (br, 2H). Only one N*H* peak can be located; ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.1, 166.3, 136.3, 113.8,

73.6, 47.4, 41.2, 40.8, 20.72; IR (KBr, cm^{-1}): 3358, 2926, 1587, 1504; HRMS (ESI, $[M+Na]^+$): calcd for $C_{15}H_{24}N_4NaO_2$, 315.1797; found, 315.1779.

*4.2.8. N^1,N^3-Di-tert-butyl-2-(1,3-dimethyltetrahydropyrimidin-2(1H)-ylidene)malonamide (**8d**).* Yield 93%; R_f=0.40 (CH_2Cl_2–AcOEt, 1:1); colorless liquid; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 3.40 (t, J=5.7 Hz, 4H), 3.18 (s, 6H), 2.10 (quintet, J=5.7 Hz, 2H), 1.36 (s, 18H). No N*H* peak was located due to the fast exchange of the amide-*H* between amide nitrogen and solvent molecules or other hydrogen-bond acceptors. ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 168.0, 167.7, 75.7, 49.5, 47.8, 41.7, 29.9, 21.6; IR (KBr, cm^{-1}): 3310, 3070, 2965, 2927, 1631, 1530, 1484; HRMS (ESI, $[M+Na]^+$): calcd for $C_{17}H_{32}N_4NaO_2$, 347.2423; found, 347.2396.

4.3. General procedure for synthesis of push–pull alkenes 12a,b

2-(1,3-Dimethyltetrahydropyrimidin-2(1*H*)-ylidene)-N^1,N^3-diphenylmalonamide **8a** (0.36 g, 1 mmol) was added to a stirred solution of phenyl isocyanate (0.24 g, 2 mmol) in 20 mL of THF. The reaction mixture was then stirred for 8 h under nitrogen at rt. The solvent was then removed by rotary evaporation. The residue was purified by flash column chromatography (silica gel, hexane–acetone, 4:1 → 1:2) to give **12a** (154 mg, 32%). Compound **12b** was similarly prepared.

*4.3.1. 2-(1,3-Dimethyltetrahydropyrimidin-2(1H)-ylidene)-N^1,N^3-diphenyl-N^1-(phenylcarbamoyl)malonamide (**12a**).* Yield 32%; R_f=0.62 (acetone); white solid; mp 173–175 °C; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.53 (s, 1H), 10.12 (s, 1H), 7.68–6.97 (m, 15H), 3.22 (m, 2H), 3.03 (m, 2H), 2.90 (s, 6H), 1.86 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.7, 165.6, 163.1, 152.9, 139.7, 139.5, 138.6, 128.7, 128.6, 128.3, 127.8, 126.4, 123.0, 122.2, 119.9, 119.5, 84.5, 46.9, 41.7, 18.9; IR (KBr, cm^{-1}): 3193, 3023, 2939, 1693, 1633, 1605, 1563, 1519; HRMS (ESI, $[M+Na]^+$): calcd for $C_{28}H_{29}N_5NaO_3$, 506.2168; found, 506.2150.

*4.3.2. 2-(1,3-Dimethyltetrahydropyrimidin-2(1H)-ylidene)-N^1,N^3-di-p-tolyl-N^1-(p-tolylcarbamoyl)malonamide (**12b**).* Yield 37%; R_f=0.80 (acetone); white solid; mp 168–170 °C; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 11.45 (s, 1H), 10.01 (s, 1H), 7.55–7.08 (m, 12H), 3.20 (m, 2H), 3.02 (m, 2H), 2.88 (s, 6H), 2.33 (s, 3H), 2.29 (s, 3H), 2.28 (s, 3H), 1.91 (m, 1H), 1.78 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 167.7, 165.5, 163.4, 153.1, 137.2, 137.0, 136.1, 136.1, 132.3, 131.4, 129.1, 129.0, 128.7, 127.7, 119.8, 119.5, 84.1, 46.9, 41.6, 20.8, 20.6, 20.6, 18.9; IR (KBr, cm^{-1}): 3193, 3022, 2917, 1688, 1682, 1626, 1598, 1563, 1504; HRMS (ESI, $[M+H]^+$): calcd for $C_{31}H_{36}N_5O_3$, 526.2818; found, 526.2821.

4.4. General procedure for synthesis of push–pull alkenes 26a–h

1,2-Dimethylimidazoline **5** (0.098 g, 1 mmol) was dissolved in 10 mL of MeCN and then added dropwise into a stirred solution of phenyl isocyanate (0.48 g, 4 mmol) in 10 mL of MeCN under nitrogen at rt. The above solution was then refluxed for 12 h and the solvent was removed by rotary evaporation. The residue was purified by flash column chromatography (silica gel, hexane–ethyl acetate, 1:1) to give **26a** (235 mg, 65%). Compounds **26b**–**h** were similarly prepared.

*4.4.1. 1-Methyl-5,7-dioxo-N,6-diphenyl-1,2,3,5,6,7-hexahydroimidazo[1,2-c]pyrimidine-8-carboxamide (**26a**).* Yield 65%; R_f=0.18 (CH_2Cl_2–AcOEt, 1:1); white solid; mp 291–293 °C; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 10.67 (s, 1H), 7.60–7.01 (m, 10H), 4.12 (t, J=8.5 Hz, 2H), 3.90 (t, J=8.5 Hz, 2H), 3.26 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 164.6, 161.6, 156.8, 147.8, 138.6, 134.6, 129.4, 128.8, 128.7, 128.5, 123.4, 120.1, 83.8, 51.8, 41.8, 39.3; IR (KBr, cm^{-1}): 3240, 3051, 2970, 1709, 1665, 1624, 1580, 1545, 1496; HRMS (ESI, $[M+Na]^+$): calcd for $C_{20}H_{18}N_4NaO_3$, 385.1277; found, 385.1256.

*4.4.2. 1-Methyl-5,7-dioxo-N,6-di-p-tolyl-1,2,3,5,6,7-hexahydroimidazo[1,2-c]pyrimidine-8-carboxamide (**26b**).* Yield 70%; R_f=0.29 (1:1 hexane–acetone); white solid; mp 266–268 °C; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 10.62 (s, 1H), 7.47–7.07 (m, 8H), 4.09 (t, J=8.5 Hz, 2H), 3.87 (t, J=8.5 Hz, 2H), 3.24 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 164.7, 161.5, 156.7, 147.9, 138.7, 136.1, 132.8, 132.0, 130.0, 129.2, 128.2, 120.1, 83.9, 51.8, 41.8, 39.3, 21.2, 20.7; IR (KBr, cm^{-1}): 3221, 3113, 3015, 2938, 1706, 1676, 1581, 1524, 1498; HRMS (ESI, $[M+H]^+$): calcd for $C_{22}H_{23}N_4O_3$, 391.1770; found, 391.1775.

*4.4.3. N,6-Bis(4-methoxyphenyl)-1-methyl-5,7-dioxo-1,2,3,5,6,7-hexahydroimidazo[1,2-c]pyrimidine-8-carboxamide (**26c**).* Yield 62%; R_f=0.48 (hexane–acetone, 1:2); white solid; mp=216–218 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.56 (s, 1H), 7.50–6.82 (m, 8H), 4.11 (t, J=8.5 Hz, 2H), 3.89 (t, J=8.5 Hz, 2H), 3.83 (s, 3H), 3.77 (s, 3H), 3.26 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 164.8, 161.5, 159.5, 156.6, 155.7, 148.1, 131.9, 129.5, 127.1, 121.7, 114.7, 113.9, 83.8, 55.4, 55.4, 51.8, 41.9, 39.3; IR (KBr, cm^{-1}): 3228, 3057, 2935, 1706, 1667, 1576, 1539, 1510, 1497; HRMS (ESI, $[M+H]^+$): calcd for $C_{22}H_{23}N_4O_5$, 423.1668; found, 423.1661.

*4.4.4. N,6-Bis(4-fluorophenyl)-1-methyl-5,7-dioxo-1,2,3,5,6,7-hexahydroimidazo[1,2-c]pyrimidine-8-carboxamide (**26d**).* Yield 73%; R_f=0.33 (hexane–acetone, 1:1); white solid; mp 295–297 °C; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 10.71 (s, 1H), 7.65–7.04 (m, 8H), 4.24 (t, J=8.5 Hz, 2H), 4.04 (t, J=8.5 Hz, 2H), 3.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 164.6, 162.5 (d, $^1J_{CF}$=248.5 Hz), 161.5, 158.9 (d, $^1J_{CF}$=242.5 Hz), 156.8, 147.8, 134.6 (d, $^4J_{CF}$=1.9 Hz), 130.4 (d, $^3J_{CF}$=8.8 Hz), 121.7 (d, $^3J_{CF}$=7.6 Hz), 116.4 (d, $^2J_{CF}$=22.9 Hz), 115.3 (d, $^2J_{CF}$=22.2 Hz), 83.6, 51.9, 41.9, 39.4; IR (KBr, cm^{-1}): 3245, 3065, 2938, 1707, 1670, 1584, 1550, 1500; HRMS (ESI, $[M+Na]^+$): calcd for $C_{20}H_{16}F_2N_4NaO_3$, 421.1088; found, 421.1070.

*4.4.5. 1-Methyl-6,8-dioxo-N,7-diphenyl-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,6-a]pyrimidine-9-carboxamide (**26e**).* Yield 71%; R_f=0.17 (AcOEt); white solid; mp 263–265 °C; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 10.67 (s, 1H), 7.62–7.00 (m, 10H), 3.99 (br, 2H), 3.48 (t, J=6.0 Hz, 2H), 3.17 (s, 3H), 2.15 (quintet, J=6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 163.3, 161.8, 156.2, 149.2, 138.9, 135.1, 129.3, 128.6, 128.6, 128.3, 123.1, 119.8, 86.1, 50.1, 44.3, 41.4, 20.7; IR (KBr, cm^{-1}): 3234, 3060, 2958, 1713, 1666, 1614, 1590, 1573, 1543, 1504; HRMS (ESI, $[M+Na]^+$): calcd for $C_{21}H_{20}N_4NaO_3$, 399.1433; found, 399.1414.

*4.4.6. 1-Methyl-6,8-dioxo-N,7-di-p-tolyl-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,6-a]pyrimidine-9-carboxamide (**26f**).* Yield 74%; R_f=0.33 (hexane–acetone, 1:1); white solid; mp 270–272 °C; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 10.63 (s, 1H), 7.50–7.06 (m, 8H), 4.03 (br, 2H), 3.52 (t, J=6.0 Hz, 2H), 3.20 (s, 3H), 2.40 (s, 3H), 2.29 (s, 3H), 2.20 (quintet, J=6.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 163.4, 161.8, 156.2, 149.4, 138.6, 136.4, 132.6, 132.5, 130.0, 129.13, 128.0, 119.9, 86.3, 50.1, 44.3, 41.4, 21.1, 20.9, 20.7; IR (KBr, cm^{-1}): 3288, 3024, 2954, 1714, 1665, 1610, 1595, 1562, 1538, 1505; HRMS (ESI, $[M+H]^+$): calcd for $C_{23}H_{25}N_4O_3$, 405.1927; found, 405.1917.

*4.4.7. N,7-Bis(4-methoxyphenyl)-1-methyl-6,8-dioxo-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,6-a]pyrimidine-9-carboxamide (**26g**).* Yield 63%; R_f=0.16 (hexane–acetone, 1:1); white solid; mp 263–265 °C; ^1H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.57 (s, 1H), 7.52–

6.80 (m, 8H), 3.99 (br, 2H), 3.82 (s, 3H), 3.76 (s, 3H), 3.47 (t, J=6.0 Hz, 2H), 3.16 (s, 3H), 2.14 (quintet, J=6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 163.5, 161.7, 159.3, 156.0, 155.5, 149.5, 132.2, 129.2, 127.7, 121.3, 114.6, 113.7, 86.1, 55.3, 50.0, 44.2, 41.4, 20.8; IR (KBr, cm^{-1}): 3328, 2967, 1688, 1650, 1633, 1603, 1580, 1543, 1511, 1502; HRMS (ESI, $[M+Na]^+$): calcd for $C_{23}H_{24}N_4NaO_5$, 459.1644; found, 459.1612.

*4.4.8. N,7-Bis(4-fluorophenyl)-1-methyl-6,8-dioxo-2,3,4,6,7,8-hexahydro-1H-pyrimido[1,6-a]pyrimidine-9-carboxamide (**26h**).* Yield 76%; R_f=0.32 (hexane–acetone, 1:1); white solid; mp 258–260 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ (ppm) 10.64 (s, 1H), 7.57–6.95 (m, 8H), 4.00 (br, 2H), 3.50 (t, J=6.0 Hz, 2H), 3.18 (s, 3H), 2.17 (quintet, J=6.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm) 163.3, 162.3 (d, $^1J_{CF}$=248.3 Hz), 161.7, 158.6 (d, $^1J_{CF}$=242.0 Hz), 156.2, 149.2, 135.0 (d, $^4J_{CF}$=1.9 Hz), 130.9 (d, $^4J_{CF}$=2.5 Hz), 130.1 (d, $^3J_{CF}$=8.6 Hz), 121.3 (d, $^3J_{CF}$=7.6 Hz), 116.2 (d, $^2J_{CF}$=22.8 Hz,), 115.1 (d, $^2J_{CF}$=22.2 Hz), 85.8, 50.1, 44.4, 41.5, 20.7; IR (KBr, cm^{-1}): 3284, 2977, 2881, 1697, 1668, 1623, 1604, 1570, 1542, 1499; HRMS (ESI, $[M+Na]^+$): calcd for $C_{21}H_{18}F_2N_4NaO_3$, 435.1245; found, 435.1212.

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Supplementary data

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References and notes

1. Adhikesavalu, D.; Venkatesan, K. *Acta Crystallogr.* **1983**, *C39*, 1044 and references therein.
2. (a) Fischer, G.; Rudorf, W.-D.; Kleinpeter, E. *Magn. Reson. Chem.* **1991**, *29*, 212; (b) Fischer, G.; Kleinpeter, E. *Magn. Reson. Chem.* **1991**, *29*, 204.
3. Inoue, S.; Aso, Y.; Otsubo, T. *Chem. Commun.* **1997**, *12*, 1105.
4. Trofimov, B. A.; Modonov, V. B.; Aksamentova, T. N.; Mikhaleva, A. I.; Korostova, S. E.; Sobenina, L. N.; Nesterenko, R. N.; Polovnikova, R. I. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1987**, *6*, 1322.
5. (a) Kleinpeter, E.; Klod, S. *J. Org. Chem.* **2004**, *69*, 4317; (b) Kleinpeter, E.; Thomas, St.; Uhlig, G.; Rudorf, W.-D. *Magn. Reson. Chem.* **1993**, *31*, 714.
6. (a) Prasad, P. N.; Williams, D. J. *Introduction to Nonlinear Optical Effects in Molecules and Polymers*; Wiley: New York, NY, 1991; (b) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195; (c) Dalton, L. R.; Harper, A. W.; Ghosn, R.; Steier, W. H.; Ziari, M.; Fetterman, H.; Shi, Y.; Mustacich, R. V.; Jen, A. K.-Y.; Shea, K. J. *Chem. Mater.* **1995**, *7*, 1060.
7. Markovic, R.; Shirazi, A.; Dzambaski, Z.; Baranac, M.; Minic, D. *J. Serb. Chem. Soc.* **2003**, *68*, 1.
8. Forni, A.; Destro, R. *Chem.—Eur. J.* **2003**, *9*, 5528.
9. Stankovic, E.; Toma, S.; Van Boxel, R.; Asselberghs, I.; Persoons, A. *J. Organomet. Chem.* **2001**, 637.
10. Yavari, I.; Hazeri, N.; Maghsoodlou, M. T.; Moradi, A. *J. Chem. Res., Synop.* **2001**, *7*, 272.
11. Orlewska, C.; Shaker, R. M.; Dees, M.; Otto, H.-H. *Monatsh. Chem.* **2000**, *131*, 889.
12. Wilhelm, P.; Neuenschwander, M. *Helv. Chim. Acta* **1999**, *82*, 338.
13. Zhu, S.; Qin, C.; Xu, G.; Chu, Q. *Tetrahedron Lett.* **1998**, *39*, 5265.
14. Dees, M.; Otto, H.-H. *Monatsh. Chem.* **1998**, *129*, 689.
15. Kleinpeter, E.; Koch, A.; Heydenreich, M.; Chatterjee, S. K.; Rudorf, W.-D. *J. Mol. Struct.* **1995**, *356*, 25.
16. Marder, S. R.; Cheng, L. T.; Tiemann, B. G.; Friedli, A. C.; Blanchard-Desce, M.; Perry, J. W.; Skindhoej, J. *Science* **1994**, *263*, 511.
17. Maas, G.; Feith, B. *Synth. Commun.* **1984**, *14*, 1073.
18. Schubert, H.; Bast, I.; Regitz, M. *Synthesis* **1983**, 661.
19. Lloyd, D.; McNab, H. *Angew. Chem.* **1976**, *88*, 496.
20. Rattananakin, P.; Pittman, C. U., Jr.; Collier, W. E.; Saebo, S. *Struct. Chem.* **2007**, *18*, 399 and references therein.
21. Kleinpeter, E.; Klod, S.; Rudorf, W.-D. *J. Org. Chem.* **2004**, *69*, 4317.
22. Kleinpeter, E. *J. Serb. Chem. Soc.* **2006**, *71*, 1.
23. Benassi, R.; Bertarini, C.; Kleinpeter, E.; Taddei, F. *THEOCHEM* **2000**, *498*, 217.
24. Pappalardo, R. R.; Marcos, E. S.; Ruiz-Lopez, M. F.; Rinaldi, D.; Rivail, J. L. *J. Am. Chem. Soc.* **1993**, *115*, 3722.
25. (a) Kleinpeter, E.; Schulenburg, A. *Tetrahedron Lett.* **2005**, *46*, 5995; (b) Kleinpeter, E.; Klod, S. *J. Org. Chem.* **2004**, *69*, 4317.
26. Matus, M. H.; Contreras, R.; Cedillo, A.; Galvan, M. *J. Chem. Phys.* **2003**, *119*, 4112.
27. Kleinpeter, E.; Stamboliyska, B. A. *Tetrahedron* **2009**, *65*, 9211.
28. For examples of acyclic ketene acetal chemistry, see: (a) Grainger, R. S.; Welsh, E. J. *Angew. Chem., Int. Ed.* **2007**, *46*, 5377; (b) Wang, S.; Liu, X.; Ruiz, M. C.; Gopalsamuthiram, V.; Wulff, W. D. *Eur. J. Org. Chem.* **2006**, *23*, 5219; (c) Martins, M. A. P.; Cunico, W.; Brondani, S.; Peres, R. L.; Zimmermann, N.; Rosa, F. A.; Fiss, G. F.; Zanatta, N.; Bonacorso, H. G. *Synthesis* **2006**, *9*, 1485; (d) Hamasaki, A.; Ducray, R.; Boger, D. L. *J. Org. Chem.* **2006**, *71*, 185; (e) Rustullet, A.; Alibes, R.; De March, P.; Figueredo, M.; Font, J. *Org. Lett.* **2007**, *9*, 2827; (f) Gompper, R.; Elser, W. *Tetrahedron Lett.* **1964**, *29*, 1971; (g) Ziegler, T.; Layh, M.; Effenberger, F. *Chem. Ber.* **1987**, *120*, 1347; (h) Neidlein, R.; Klotz, U. J. *Chem. Ber.* **1985**, *118*, 3217; (i) Gillard, M.; T'Kint, C.; Sonveaux, E.; Ghosez, L. *J. Am. Chem. Soc.* **1979**, *101*, 5837; (j) Sauer, J.; Heldmann, D. K.; Hetzenegger, J.; Krauthan, J.; Sichert, H.; Schuster, J. *Eur. J. Org. Chem.* **1998**, *12*, 2885.
29. For examples of preparation and reactions of cyclic ketene acetals, see: (a) Meyers, A. I.; Nazarendo, N. *J. Am. Chem. Soc.* **1972**, *94*, 3243; (b) Zhou, A.; Pittman, C. U., Jr. *Tetrahedron Lett.* **2004**, *45*, 8899; (c) Quast, H.; Ach, M.; Balthasar, J.; Hergenroether, T.; Regnat, D.; Lehmann, J.; Banert, K. *Helv. Chim. Acta* **2005**, *88*, 1589; (d) Roberts, R. M.; Corse, J.; Boschan, R.; Seymour, D.; Winstein, S. *J. Am. Chem. Soc.* **1958**, *80*, 1247; (e) Chatterjee, S.; Ye, G.; Pittman, C. U., Jr. *Tetrahedron Lett.* **2009**, *51*, 1139; (f) Zhou, A.; Pittman, C. U., Jr. *Tetrahedron Lett.* **2005**, *46*, 3801; (g) Zhu, P. C.; Lin, J.; Pittman, C. U., Jr. *J. Org. Chem.* **1995**, *60*, 5729; (h) Wu, Z.; Stanley, R. R.; Pittman, C. U., Jr. *J. Org. Chem.* **1999**, *64*, 8386; (i) Gruseck, U.; Heuschmann, M. *Chem. Ber.* **1987**, *120*, 2065; (j) Diaz-Ortiz, A. l; Diez-Barra, E.; de la Hoz, A.; Prieto, P.; Moreno, A.; Langa, F.; Prange, T.; Neuman, A. *J. Org. Chem.* **1995**, *60*, 4160; (k) Gruseck, U.; Heuschmann, M. *Chem. Ber.* **1987**, *120*, 2053.
30. For examples, see: (a) Cao, L.; Wu, Z.; Zhu, P. C. *Polym. Prepr.* **1999**, *39*, 406; (b) Wu, Z.; Cao, L.; Pittman, C. U., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1998**, *36*, 861; (c) Wu, Z.; Cao, L.; Zhu, P. C. *Polym. Prep.* **1997**, *38*, 121; (d) Cao, L.; Wu, Z.; Pittman, C. U., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2841; (e) Cao, L.; Pittman, C. U., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 2823; (f) Wu, Z.; Cao, L.; Pittman, C. U., Jr. *Recent Res. Devel. Polym.Sci.* **1998**, *2*, 467; (g) Zhu, P. C.; Pittman, C. U., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 169; (h) Pittman, C. U., Jr.; Wu, Z.; Zhu, P. C. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 485; (i) Zhu, P. C.; Pittman, C. U., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 73; (j) Liu, Y.; Pittman, C. U., Jr. *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 3655.
31. (a) Beyerstedt, F.; McElvain, S. M. *J. Am. Chem. Soc.* **1936**, *68*, 529; (b) Barnes, H. M.; Kundiger, D.; McElvain, S. M. *J. Am. Chem. Soc.* **1940**, *62*, 1281; (c) McElvain, S. M.; Tate, B. E. *J. Am. Chem. Soc.* **1945**, *67*, 202; (d) McElvain, S. M. *Chem. Rev.* **1949**, *45*, 453.
32. Beard, D. J.; Pace, C. R.; Pittman, C. U., Jr.; Saebø, S. *Struct. Chem.* **2009**, *20*, 961.
33. Gruseck, U.; Heuschmann, M. *Tetrahedron Lett.* **1987**, *28*, 6027.
34. (a) Ye, G.; Chen, C.; Chatterjee, S.; Collier, W. E.; Zhou, A.; Song, Y.; Beard, D. J.; Pittman, C. U., Jr. *Synthesis* **2010**, 141; (b) Ye, G. Ph.D. Dissertation, Mississippi State University, 2008.
35. Ye, G.; Henry, W. P.; Chen, C.; Zhou, A.; Pittman, C. U., Jr. *Tetrahedron Lett.* **2009**, *50*, 2135 and reference therein.
36. (a) Zhou, A.; Cao, L.; Li, H.; Liu, Z.; Pittman, C. U., Jr. *Synlett* **2006**, 201; (b) Zhou, A.; Cao, L.; Li, H.; Liu, Z.; Cho, H.; Henry, W. P.; Pittman, C. U., Jr. *Tetrahedron* **2006**, *62*, 4188.
37. Dewar, M. 1. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4907.
38. Twist angle is defined as the angle between the bisectors of the 1, l- and the 2,2-substituent on a Newman diagram projecting down the C=C bond of the alkene. See: (a) Baum, K.; Bigelow, S. S.; Nguyen, N. V.; Archibald, T. G. *J. Org. Chem.* **1992**, *57*, 235; (b) Winkler, F. K.; Dunitz, J. D. *J. Mol. Biol.* **1971**, *59*, 169.
39. Ye, G.; Zhou, A.; Henry, W. P.; Song, Y.; Chatterjee, S.; Beard, D. J.; Pittman, C. U., Jr. *J. Org. Chem.* **2008**, *73*, 5170.
40. Goodman, M.; Ganis, P.; Avitabile, G.; Migdal, S. *J. Am. Chem. Soc.* **1971**, *93*, 3328.
41. Cherniak, E. A.; Costain, C. C. *J. Chem. Phys.* **1966**, *45*, 104.
42. Korshin, E. E.; Sabirova, L. I.; Levin, Y. A.; Arbuzov, A. E. *Izv. Akad. Nauk, Ser. Khim.* **1994**, *8*, 1509.