Face selectivity in the reactions of Grignard reagents with 5-substituted-2-dicyanomethyleneadamantanes

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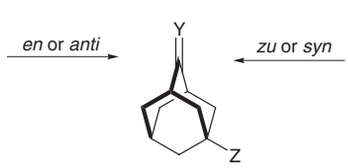
Reactions of 5-substituted-2-dicyanomethyleneadamantanes (**4-Z**) with benzylmagnesium bromide ($C_6H_5CH_2MgBr$) or alkylmagnesium halides (RMgX) generated the 1,4-addition (**5-Z (R)**) and/or the hydrogenation (**5-Z (H)**) products. A variety of substituents X were used: hydro, fluoro, chloro, bromo and phenyl groups. The generation of the different isomeric products from the *zu*-face or *en*-face by the transfer of the benzyl or alkyl groups, or the hydride from the Grignard reagents is discussed in terms of the electrostatic field influence and the steric hindrance between the Grignard reagents and the substrate **4-Z**. Reactions of **4-Br** or **4-Ph** with phenylmagnesium bromide generated 1,2-addition products **6-Br**, **7-Br** or **8-Ph** when the intermediate **A** was added to dry methanol or to dilute ice-cold hydrochloric acid solution.

Introduction

Grignard reagents are the most important of the group IIA organometallics and are widely used as nucleophiles in conjugate additions due to the high electron density on the reactive carbon atom. α,β-Unsaturated ketone, aldehyde, ester, nitrile, nitro or sulfonyl compounds are the substrates most often used in the Michael reaction. Ylidenemalononitriles (alkylidenemalononitriles and arylidenemalononitriles) are useful intermediates in organic synthesis.[1] Reactions of organomagnesium halides with ylidenemalononitriles proceeding through an ionic reaction mechanism to generate 1,4-addition and/or hydrogenation products have been well studied by Latif *et al.*[2] It was concluded that the nature of the products is dependent on the nature of the Grignard reagents as well as the substrate ylidenemalononitriles, in particular their stereochemical requirements.[2a]

5-Substituted adamantan-2-ones **1-Z** and their derivatives **2-Z** and **3-Z** each have a trigonal center at the C-2 site, which have proved to be useful probes in studies into the electronic factors that influence face selection.[3] These model substrates are appropriate and attractive for this study for essentially two reasons. Firstly, the rigid molecular framework ensures that ambiguities associated with conformational uncertainty are precluded. Secondly, the trigonal C-2 center can be electronically perturbed through distal modification without introducing steric bias into the system.



1-Z, Y = O, Z = F, Cl, Br and Ph

2-Z, Y = S, Z = F, Cl and Br

3-Z, Y = CH_2, Z = F, Cl, Br and Ph

4-Z, Y = $C(CN)_2$, Z = H, F, Cl, Br, and Ph

Studies of a variety of reactions by le Noble and his coworkers found that the reagent prefers to attack the face which is antiperiplanar to the more electron rich vicinal bonds. If the 5-substituent is electron withdrawing, it will direct reagents to the *zu* face.[3] All these observations are explained by Cieplak and co-workers' transition-state hyperconjugation model.[4] Cieplak's model stresses that, regardless of the types of reactions (nucleophilic, electrophilic, radical addition *etc.*), the newly developing σ* orbital should attract electron density with the same directional preference provided the transition states are electron deficient (Fig. 1).

Z = electron-donating Z = electron-withdrawing

Fig. 1 Cieplak preference for nucleophilic (or electrophilic) addition *anti* to electron-donating (left) and *syn* to electron-withdrawing substituents (right).

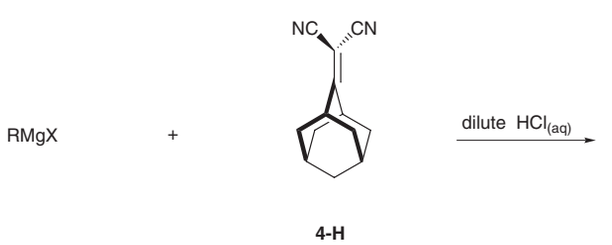
The ^{13}C-NMR chemical shifts of a series of 5-aryladamantan-2-ones **1-Ph** were reported by Adcock and co-workers.[5a] The carbonyl and ethyleneic ^{13}C substituted chemical shifts are shown to be proportional to substituent field effects. Polar field parameters (σ_F values) have been calculated for a series of *p*-XC_6H_4 substituents by the use of the polar field susceptibility parameter (ρ_F) for the carbonyl shifts. π-Facial diastereoselectivities for the reduction ($NaBH_4$) and methylation (MeLi) of *para*-substituted phenyl derivatives of 5-aryladamantan-2-ones **1-Ph** and also for the hydrochlorination of similarly substituted alkenes **3**, have been determined and corrected successfully against polar field parameters ($\Delta\sigma_F$ values). Based on these observations, Adcock concludes: "The results ... strongly suggest that it is unnecessary to invoke transition-state hyperconjugation in terms of Cieplak's model to explain π-facial selectivity for the reduction and methylation of 5-disubstituted (X) adamantan-2-ones. For the most part, the results appear to be accommodated by an electrostatic field model". It was in 1997 that Adcock *et al.* observed that the reduction of the 5-substituted (X) 2,2-dimethoxyadamantanes under ionic conditions with triethylsilane or phenylsilane provides π-facial diastereoselectivities for hydride trapping of 5-substituted (X) 2-methoxy-2-adamantyl cations. They concluded that the stereoselectivity is a function of electron

demand after comparing the experimental data with known diastereoselectivities for nucleophilic capture of tertiary and secondary 5-substituted (X) 2-adamantyl cations.[6] In the same paper, Adcock also reported the diastereoselectivities for the hydrochlorination of 2-methylene-5-*tert*-butyladamantane (**3-*tert*-Bu**) and 2-methylene-5-trimethylsilyladamantane (**3-Me_3Si**) in methylene chloride and nitromethane as solvent. It was found that rather than a long-range steric factor, low electron demand coupled with the stereoelectronic requirement of double hyperconjugation is the most reasonable explanation for the total lack of stereoselectivity in the Cl^- capture of the 2-methyl-5-(trimethylsilyl)-2-adamantyl cation in nitromethane.[5,6]

Based on the above literature study,[1–6] we wish to report the results of the reactions of 5-substituted-2-dicyanomethyleneadamantanes (**4-Z**) with various Grignard reagents and to discuss how the experimental data are consistent with the Cieplak or electrostatic field model.

Results and discussion

At room temperature, 2-dicyanomethyleneadamantane **4-H** reacted with various Grignard reagents RMgX in diethyl ether solution to generate high yields (89–100%) of the addition products **5-H (R)** and/or the hydrogenation products **5-H (H)** after quenching the mixture with ice-cold dilute hydrochloric acid solution. All the individual yields are shown in Scheme 1.



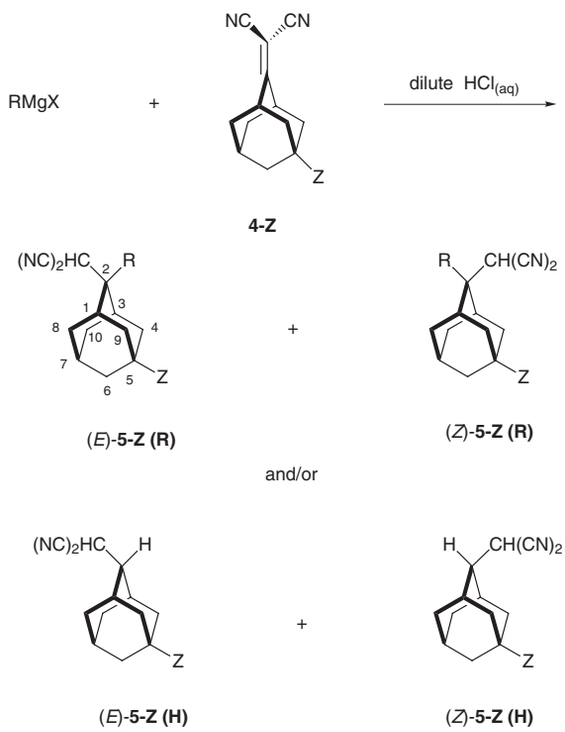
$PhCH_2MgBr$	96%	—
CH_3MgI	100%	—
CH_3CH_2MgBr	35%	57%
$(CH_3)_2CHMgBr$	10%	90%
$(CH_3)_3CMgCl$	—	89%

Scheme 1

The generation of the addition product **5-H (R)** can be explained by the addition of the R group from the Grignard reagents RMgX to **4-H** to generate an intermediate which was then hydrolyzed to yield the final product(s). The formation of the product **5-H (H)** indicates that some of the Grignard reagents RMgX not only transfer the R group but also transfer the hydride simultaneously whereas some of the Grignard reagents only transfer the hydride to the substrate **4-H** to yield exclusively the reduction product.[1,2,7] When bulky Grignard reagents such as CH_3CH_2MgBr, $(CH_3)_2CHMgBr$ and $(CH_3)_3$-CMgCl were used, the yields of the reduction product **5-H (H)** always increased and the yields of the addition product **5-H (R)** decreased dramatically compared with use of CH_3MgI or $PhCH_2MgBr$.

It has been reported by le Noble *et al.* that room temperature addition of the *para*-substituted phenyl Grignard reagents to 5-fluoroadamantan-2-one **1-F** generates the 1,2-addition product (*E*)- and (*Z*)-cumyl alcohols in yields from 66 to 96%.[8] The generation of the *E* isomer as the major product can be explained by the addition of the nucleophiles from the direction antiperiplanar to the most electron rich bond which is consistent with the Cieplak's model prediction.

After observing the above report,[8] and in view of our interesting results as shown in Scheme 1, we tried to focus our study on the reactions of 5-substituted-2-dicyanomethyleneadamantanes **4-Z**, again with the same Grignard reagents RMgX. As expected, medium to excellent yields of the 1,4-addition compounds (*E*)-**5-Z (R)** and (*Z*)-**5-Z (R)**, and/or the hydrogenation compounds, (*E*)-**5-Z (H)** and (*Z*)-**5-Z (H)**, were isolated after flash column chromatography (Scheme 2).



Scheme 2

Reaction of **4-F** with benzylmagnesium bromide gave a 62 : 38 mixture of the 1,4-addition products (*E*)-**5-F (Bz)** and (*Z*)-**5-F (Bz)** in 96% yield by NMR analysis (Table 1). Both adducts were stable to the reaction conditions and they were characterized as 2-benzyl-5-fluoro-2-dicyanomethyladamantane on the basis of their mass spectral, IR, ^{1}H-, and ^{13}C-NMR data. 98% of the 1,4-addition products (*E*)-**5-F (Me)** and (*Z*)-**5-F (Me)** were generated and the ratio of the two isomers was 74 : 26 when **4-F** reacted with methylmagnesium chloride under similar conditions. The stereochemistries of the *E* and *Z* isomers can be determined by X-ray crystallography, and ^{1}H- and ^{13}C-NMR spectroscopy. Structures of ((*Z*)-**5-F (Bz)**) and ((*Z*)-**5-F (Me)**) are shown in Figs. 2 and 3 and the crystal data are listed in Table 2.[9] The ^{1}H-NMR analysis indicates that the methine proton of the dicyanomethyl group in the *Z* isomer is always located downfield compared to the *E* isomer due to the deshielding effect of the fluorine atom. In contrast the ^{13}C-NMR analysis indicates that the C-5 of the *Z* isomer is located upfield compared to the *E* isomer due to the shielding effect of the two nitrile groups.

Under similar procedures and conditions, reactions of **4-Cl**

Table 1 Reactions of 5-substituted-2-dicyanomethyleneadamantanes **4-Z** with various Grignard reagents RMgX under a nitrogen atmosphere

			Product ratio and yield[a] (%)			
Entry	4-Z	RMgX	(*E*)-**5-Z (R)**:(*Z*)-**5-Z (R)**	(%)	(*E*)-**5-Z (H)**:(*Z*)-**5-Z (H)**	(%)
1	4-F	$PhCH_2MgBr$	62:38	(96)	—	
2	4-F	CH_3MgCl	74:26	(98)	—	
3	4-Cl	$PhCH_2MgBr$	63:37	(95)	—	
4	4-Cl	CH_3MgI	73:27	(97)	—	
5	4-Br	$PhCH_2MgBr$	64:36	(62)	—	
6	4-Br	CH_3MgI	73:27	(98)	—	
7	4-Br	CH_3CH_2MgBr	48:52	(24)	59:41	(68)
8	4-Br	$(CH_3)_2CHMgBr$	43:57	(10)	60:40	(89)
9	4-Br	$(CH_3)_3CMgCl$	—		61:39	(71)
10	4-Ph	$PhCH_2MgBr$	59:41	(95)	—	
11	4-Ph	CH_3MgI	74:26	(64)	—	
12	4-Ph	CH_3CH_2MgBr	54:46	(24)	59:41	(75)
13	4-Ph	$(CH_3)_2CHMgBr$	52:48	(8)[b]	59:41	(71)
14	4-Ph	$(CH_3)_3CMgCl$	—		56:44	(70)

[a] Product ratios and yields were measured by ^1H NMR from integrations with a known amount of toluene, diiodomethane, dibromomethane or *N*,*N*-dimethylformamide as an internal standard. [b] These two isomers could not be isolated in pure form.

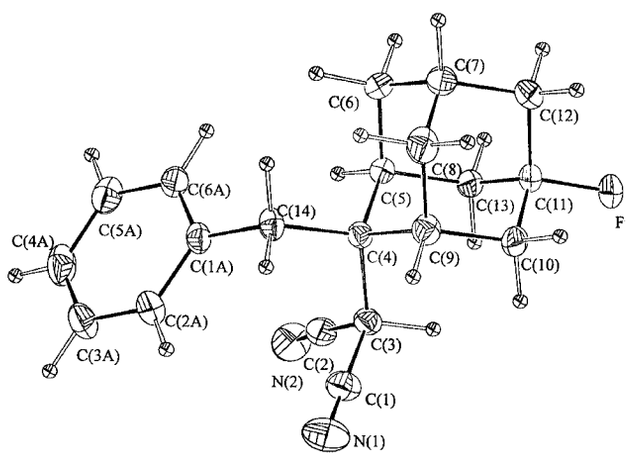


Fig. 2

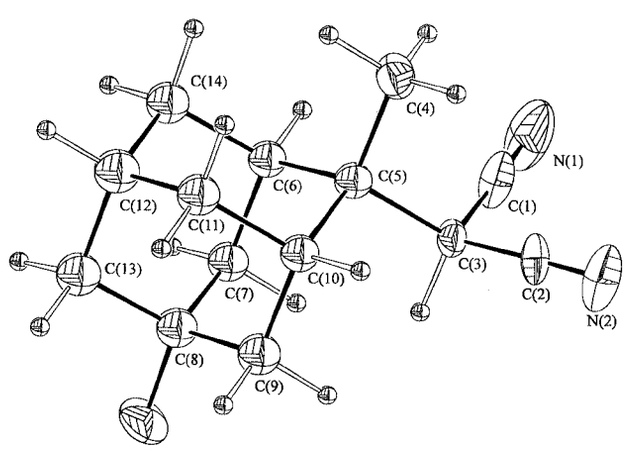


Fig. 3

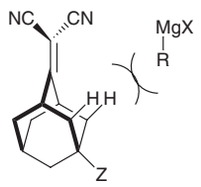
with benzylmagnesium bromide and methylmagnesium iodide, respectively, gave a 63:37 mixture of the (*E*)-**5-Cl (Bz)** and (*Z*)-**5-Cl (Bz)** in 95% yield and a 73:27 mixture of (*E*)-**5-Cl (Me)** and (*Z*)-**5-Cl (Me)** in 97% yield. A 64:36 mixture of (*E*)-**5-Br (Bz)** and (*Z*)-**5-Br (Bz)** in 62% yield or a 73:27 mixture of the (*E*)-**5-Br (Me)** and (*Z*)-**5-Br (Me)** in 98% yield was also observed when **4-Br** was used to react with the same Grignard reagents. In addition to methylmagnesium halides, we also tried to react other alkyl Grignard reagents such as CH_3CH_2MgBr, $(CH_3)_2CHMgBr$, and $(CH_3)_3CMgCl$ with **4-Br**. Surprisingly, not only the 1,4-addition products (*E*)-**5-Br (R)** and (*Z*)-**5-Br (R)** but also the hydrogenation products (*E*)-**5-Br (H)** and (*Z*)-**5-Br (H)** were generated when ethylmagnesium bromide or isopropylmagnesium bromide was used. With ethylmagnesium bromide, the yield of the adducts (*E*)-**5-Br (Et)** and (*Z*)-**5-Br (Et)** decreased to 24% and the ratio of the two isomers was 48:52 while the yield of the hydrogenation products (*E*)-**5-Br (H)** and (*Z*)-**5-Br (H)** increased to 68% and the ratio of the two isomers was 59:41. Only 10% of the 1,4-addition products (*E*)-**5-Br (*i*-Pr)** and (*Z*)-**5-Br (*i*-Pr)** (the ratio was 43:57) and 89% of the reductive products (*E*)-**5-Br (H)** and (*Z*)-**5-Br (H)** (the ratio was 60:40) were generated when isopropylmagnesium bromide was used. Reaction of *tert*-butylmagnesium chloride with **4-Br** generated only 71% of the reduction products (*E*)-**5-Br (H)** and (*Z*)-**5-Br (H)** and the ratio was 61:39. None of the addition products could be detected by GC-MS, nor could they be isolated after column chromatography. Similar results were also observed when substrates **4-Ph** reacted with the same Grignard reagents RMgX, as described above.

All experimental data indicate that F, Cl, Br, and Ph are electron-withdrawing substituents and the transfer of the benzyl or methyl groups, or hydride from the Grignard reagents to the substrate **4-Z** prefer to attack the *zu*-face but the transfer of the ethyl or isopropyl groups to the *zu*-face is partially retarded due to the strong steric hindrance between the substrate **4-Z** and the bulky Grignard reagents. We are

Table 2 Crystallographic and refinement data for compounds (*Z*)-**5-F (Bz)** and (*Z*)-**5-F (Me)**

Compound	(*Z*)-**5-F (Bz)**	(*Z*)-**5-F (Me)**
Chemical formula	$C_{20}H_{21}FN_2$	$C_{14}H_{17}FN_2$
Formula weight	308.39	232.30
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$
μ/mm^{-1}	0.08	0.04
R^a	0.052	0.067
Rw^a	0.056	0.066
Unit cell dimensions		
a/Å	7.5393(9)	8.767(4)
b/Å	9.1199(10)	24.309(6)
c/Å	23.597(5)	12.476(4)
β/°	95.474(13)	110.44(3)
V/Å^3	1615.0(4)	2491.4(16)
Temperature of data collection	298 K	298 K
Z	4	8
Measured/independent reflections	4802/4702	5956/5704
No. obsd $I_o > 2.5\sigma(I_o)$	3145	1233

[a] $R = \Sigma|F_o - F_c|/\Sigma F_o$, $Rw = [\Sigma w(F_o - F_c)^2/\Sigma w(F_o)^2]^{1/2}$, GOF = $[\Sigma w(F_o - F_c)^2/(N_{obsd} - N_{param})]^{1/2}$.



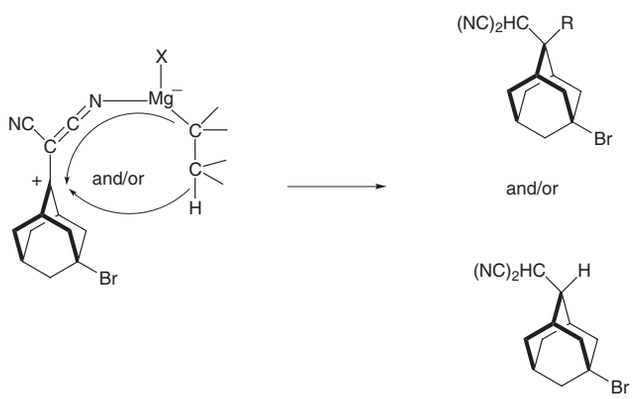
4-Z

Fig. 4 Steric hindrance between **4-Z** and RMgX.

surprised to find that the observed face selectivity is invariable for the halogens F, Cl, Br (entries 1,3,5 and 2,4,6 in Table 1) and this result indicates that the face selectivity is governed by an electrostatic field influence rather than the hyperconjugative effect. Direct evidence is that various empirical scales (σ_I or σ_F) have been reported by Adcock *et al.* and the polar field effects of halogens are found to be similar, *i.e.* F ~ Cl ~ Br ~ I in these systems.[5,6]

The generation of the 1,4-addition **5-Z (R)** and/or the reduction products **5-Z (H)** evidently supports the conclusion that the products obtained by the reaction of ylidenemalononitriles with Grignard reagents depends on both the nature of the substrates and the organometallic reagents.[2] The basic skeleton of the substrate **4-Z** is rigid and therefore the nature of reaction products is, in the main, dependent on the organomagnesium halides employed.[2a] Only high yields of the addition products were generated when MeMgX or $PhCH_2MgBr$ was used. The ratios of the (*E*)-**5-Z (Me)** isomer to the (*Z*)-**5-Z (Me)** isomer are always larger than the ratios of the (*E*)-**5-Z (Bz)** isomer to the (*Z*)-**5-Z (Bz)** isomer indicating that the steric hindrance between **4-Z** and $PhCH_2MgBr$ is larger than the same effect between **4-Z** and MeMgX (Fig. 4). The decrease of the 1,4-addition and the increase of the hydrogenation product yields and the different ratios of the (*E*)-**5-Br (R)** to (*Z*)-**5-Br (R)** or (*E*)-**5-Br (H)** to (*Z*)-**5-Br (H)** indicate that the steric effect is an important factor in the competition between alkylation and hydrogenation products. With ethylmagnesium bromide or isopropylmagnesium bromide, the yields of the 1,4-addition products decreased while the reductive products increased dramatically. Only the reduction product was generated when *tert*-butylmagnesium chloride was used.

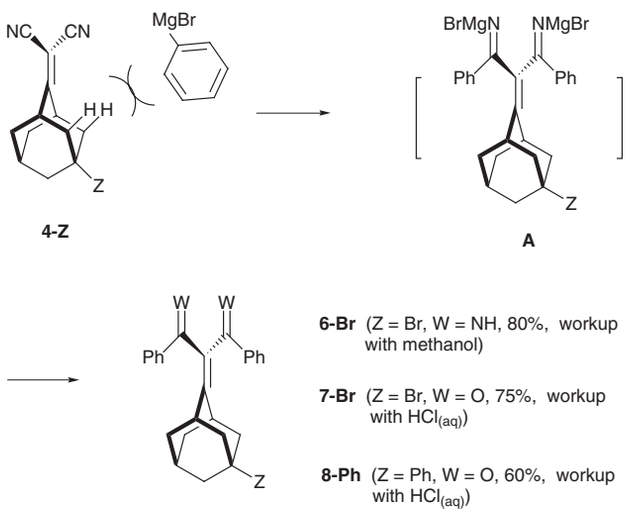
The mechanism of the conjugated addition of Grignard reagents to **4-Z** is proposed to proceed through the formation of a cyclic transition state which is similar to that reported in the literature.[10] For benzyl and methyl groups, the requirement of reaction space is small so that the 1,4-addition occurs easily. When other Grignard reagents are used, the 1,4-addition becomes difficult due to the steric hindrance and the hydrogenation reaction takes place predominantly. The generation of **6-Z (H)** is also proposed to proceed through a β-hydride transfer of the Grignard reagents to the substrate and the mechanism is shown in Scheme 3.[10,11]



Scheme 3

Not only the benzylmagnesium bromide $C_6H_5CH_2MgBr$ or alkylmagnesium halides RMgX but also phenylmagnesium bromide was used to react with **4-Z** under similar conditions. Surprisingly, neither the 1,4-addition products **5-Z (Ph)** nor the hydrogenation products **5-Z (H)** were obtained and only compound **6-Z** or **7-Z** was isolated after the intermediate **A** was quenched. When intermediate **A**, generated from substrate **4-Br** and phenylmagnesium bromide, was quenched with dry methanol,[12] 80% of the diimine **6-Br** was isolated after column chromatography. On the other hand, hydrolyzed product dione **7-Br** (75%) was the only product to be separated when the same intermediate **A** was added to dilute ice-cold hydrochloric acid.[13]

The generation of the different products indicates that the 1,4-addition reaction is blocked by the steric hindrance between substrate **4-Br** and phenylmagnesium bromide. 1,2-Addition reaction occurs exclusively by the addition of the phenyl group to the cyano groups to form intermediate **A**.[14] Similarly, only 60% of the 2-dibenzoylmethylene-5-phenyladamantane **8-Ph** was isolated when **4-Ph** reacted with phenylmagnesium bromide and workup with dilute ice cold hydrochloric acid solution. The mechanism of formation of the products **6-Br**, **7-Br**, and **8-Ph** is proposed as is shown in Scheme 4.



Scheme 4

Conclusion

In summary, we have found that 5-substituted-2-dicyanomethyleneadamantanes (**4-Z**) reacted with various Grignard reagents to undergo Michael type and/or β-hydride transfer reactions to generate 1,4-addition and/or hydrogenation products. The generation of (*E*)-**5-Z (R)** and (*E*)-**5-Z (H)** as the major products by transfer of the alkyl and benzyl groups or the hydride to the *zu*-face is governed by an electrostatic field influence. The formation of the (*Z*)-**5-Br (CH_3CH_2)** and (*Z*)-**5-Br ($(CH_3)_2CH$)** as the major products by the addition of an ethyl or isopropyl group to the *en*-face and the generation of 1,2-addition products **6-Br**, **7-Br**, and **8-Ph** is mainly attributed to the steric hindrance between the Grignard reagents RMgX and substrates **4-Z**.

Experimental

All reactions were performed in flame or oven-dried glassware under a positive pressure of nitrogen. Air and moisture sensitive compounds were introduced by the use of a syringe or cannula through a rubber septum. Diethyl ether and THF were distilled from sodium–benzophenone ketyl. Analytical thin layer chromatography was performed with E. Merck silica gel 60F glass plates and flash chromatography by the use of E.

Merck silica gel 60 (230–400 mesh). GC-MS were recorded on a HP 5890 GC/HP 5970B MSD spectrometer, MS or HRMS were measured on a JEOL JMS-D300 or JEOL JMS-HX110 spectrometer where tr represents trace. ^{1}H and ^{13}C NMR spectra were recorded on either a JEOL EX-400 or a Varian Gemini-200 spectrometer. All NMR data were obtained in $CDCl_3$ solution; chemical shifts (δ) are given in ppm relative to TMS and J values are given in Hz. IR spectra were recorded on a JASCO FT/IR-5300 spectrometer. Elemental analysis was performed by a Perkin-Elmer 2400 instrument. All melting points were determined on a MEL-TEMP II melting point apparatus and were uncorrected. Compounds 5-substituted-2-dicyanomethyleneadamantanes **4-H**, **4-F**, **4-Cl**, **4-Br**, and **4-Ph** were prepared by reacting malonitrile with adamantan-2-one (Aldrich), 5-fluoroadamantan-2-one,[15] 5-chloroadamantan-2-one,[16] 5-bromoadamantan-2-one,[16] and 5-phenyladamantan-2-one,[16] respectively, by modifying the literature reports[17,18] as described in the following procedures.

Typical experimental procedure for the synthesis of starting material 5-substituted-2-dicyanomethyleneadamantanes 4-Z

Adamantan-2-one (10 mmol) and $CH_2(CN)_2$ (11 mmol) were dissolved in 250 ml ethanol with a catalytic amount of ammonium acetate (1 mmol). After stirring for 30 minutes at room temperature, the solution turned cloudy and a white precipitate was formed. The solution was poured onto brine and extracted with dichloromethane, dried over $MgSO_4$, filtered and the solvent was evaporated to obtain 98% yield of **4-H**. The crude product was recrystallized with *n*-hexane–ethyl acetate to obtain pure 2-dicyanomethyleneadamantane.[18,19]

2-Dicyanomethyleneadamantane (4-H). This compound is colorless and the melting point is 183–184 °C (lit.[18,19] 183–185 °C); ^{1}H NMR ($CDCl_3$) δ 3.28 (s, 2H) and 2.23–1.86 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 193.66, 111.62, 77.52, 39.72, 38.81, 35.78 and 27.02; MS (EI) *m*/*z* (rel int) 198 (M^+, 100%), 170 (16), 156 (27), 142 (55), 115 (14) and 93 (14). Calc. for $C_{13}H_{14}N_2$: C, 78.75; H, 7.12; N, 14.13. Found: C, 78.43; H, 6.95; N, 14.70%.

5-Fluoro-2-dicyanomethyleneadamantane (4-F). This compound is colorless and the melting point is 154–155 °C; ^{1}H NMR ($CDCl_3$) δ 3.47 (d, J 0.6, 2H) and 2.45–1.80 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 188.13 (d, J 2.3), 111.03, 89.24 (d, J 185.9), 79.71 (d, J 1.6), 42.39 (d, J 20.5), 41.06 (d, J 17.5), 40.11 (d, J 9.9), 38.56 (d, J 2.3) and 30.34 (d, J 9.9); MS (EI) *m*/*z* (rel int) 216 (M^+, 100%), 196 (25), 174 (21), 160 (62), 142 (21), 133 (32), 111 (30) and 91 (56) (HRMS (EI) Calc. for $C_{13}H_{13}N_2F$: M, 216.1063. Found 216.1062).

5-Chloro-2-dicyanomethyleneadamantane (4-Cl). This compound is colorless and the melting point is 213–215 °C; ^{1}H NMR ($CDCl_3$) δ 3.40 (s, 2H) and 2.44–1.83 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 188.15, 111.00, 79.58, 62.98, 47.41, 45.76, 40.47, 38.10 and 30.21; MS (EI) *m*/*z* (rel int) 234 [$(M + 2)^+$, 28%], 232 (M^+, 94), 196 (80), 183 (47), 154 (67), 142 (100), 115 (53) and 91 (64). Calc. for $C_{13}H_{13}N_2Cl$: C, 67.09; H, 5.63; N, 12.04. Found: C, 67.04; H, 5.71; N, 12.18%.

5-Bromo-2-dicyanomethyleneadamantane (4-Br). This compound is colorless and the melting point is 235–239 °C; ^{1}H NMR ($CDCl_3$) δ 3.36 (s, 2H) and 2.62–1.87 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 187.97, 110.96, 79.72, 57.72, 48.98, 47.16, 41.21, 37.98 and 30.83; MS (EI) *m*/*z* (rel int) 278 [$(M + 2)^+$, 14%], 276 (M^+, 14), 197 (100), 155 (28), 144 (20) and 91 (15). Calc. for $C_{13}H_{13}N_2Br$: C, 56.34; H, 4.73; N, 10.11. Found: C, 56.35; H, 4.71; N, 9.76%.

2-Dicyanomethylene-5-phenyladamantane (4-Ph). This compound is colorless and the melting point is 153–155 °C; ^{1}H NMR ($CDCl_3$) δ 7.39–7.20 (m, 5H), 3.41 (s, 2H) and 2.29–1.91 (m, 11H); ^{13}C NMR ($CDCl_3$) δ 192.39, 146.93, 128.55, 126.57, 124.64, 111.49, 78.05, 44.50, 41.52, 39.06, 39.04, 35.76 and 27.81; MS (EI) *m*/*z* (rel int) 274 (M^+, 55), 129 (39), 131 (20), 115 (17), 91 (100) and 77 (10) (HRMS (EI) Calc. for $C_{19}H_{18}N_2$: M, 274.1470. Found: 274.1461). Calc.: C, 83.17; H, 6.61; N, 10.21. Found: C, 83.17; H, 6.65; N, 9.83%.

Typical experimental procedures for the reaction of 2-dicyanomethyleneadamantane 4-H with Grignard reagents (see Scheme 1)

A solution of 2.0 mmol of 2-dicyanomethyleneadamantane **4-H** in 30 ml diethyl ether was added to 6 mmol of freshly prepared benzylmagnesium bromide slowly at −5 °C and then the temperature was raised to room temperature after addition. After the starting material disappeared as shown by TLC, the solution was poured into an ice-cold dilute hydrochloric solution. The solution was extracted with dichloromethane, dried over $MgSO_4$, filtered and the solvent was evaporated to obtain the oily mixture. The NMR analysis indicated that the mixture contained **5-H (Bz)** in 96% yield using dibromomethane or dimethylformamide as an internal standard. Flash column chromatography using *n*-hexane–ethyl acetate as the eluent was used to purify the mixture to obtain the pure products. Similar procedures were repeated when *tert*-butylmagnesium chloride reagent was used and only product **6-H** was obtained (89% of NMR yield).

2-Benzyl-2-dicyanomethyladamantane (5-H (Bz)). This compound is colorless and the melting point is 122–124 °C; ^{1}H NMR ($CDCl_3$) δ 7.40–7.31 (m, 5H), 4.52 (s, 1H), 3.25 (s, 2H) and 2.43–1.76 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 135.34, 130.66, 128.76, 127.91, 110.92, 46.72, 39.22, 39.05, 32.91, 32.65, 32.34, 28.32, 27.15 and 26.76; MS (EI) *m*/*z* (rel int) 290 (M^+, 52%), 199 (23), 133 (15), 91 (100) and 65 (10). Calc. for $C_{20}H_{22}N_2$: C, 82.70; H, 7.63; N, 9.65. Found: C, 82.68; H, 7.63; N, 9.88%.

2-Methyl-2-dicyanomethyladamantane (5-H (Me)). This compound is colorless and the melting point is 70–71 °C; ^{1}H NMR ($CDCl_3$) δ 4.48 (s, 1H), 2.09–1.70 (m, 14H) and 1.40 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 111.89, 43.30, 38.54, 33.55, 32.65, 32.41, 31.94, 26.89, 26.58 and 21.04; MS (EI) *m*/*z* (rel int) 214 (M^+, tr), 149 (100), 107 (5), 93 (8) and 79 (6) (HRMS (EI) Calc. for $C_{14}H_{18}N_2$: M, 214.1470. Found 214.1474).

2-Ethyl-2-dicyanomethyladamantane (5-H (Et)). This compound is colorless and the melting point is 79–80 °C; ^{1}H NMR ($CDCl_3$) δ 4.54 (s, 1H), 2.12–1.94 (m, 8H), 1.80–1.67 (m, 8H) and 1.12 (t, J 7.6, 3H); ^{13}C NMR ($CDCl_3$) δ 112.27, 45.16, 38.87, 32.87, 32.33, 32.01, 28.37, 27.28, 26.96, 26.69 and 7.62; MS (EI) *m*/*z* (rel int) 228 (M^+, 2%), 199 (7), 163 (100), 121 (12), 91 (13), 81 (26) and 77 (12). Calc. for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.94; H, 8.73; N, 12.59%.

2-Dicyanomethyl-2-isopropyladamantane (5-H (*i*-Pr)). This compound is colorless and the melting point is 103–104 °C; ^{1}H NMR ($CDCl_3$) δ 4.60 (s, 1H), 2.67 (septet, J 7.2, 1H), 2.16–1.67 (m, 14H) and 1.23 (d, J 7.2, 6H); ^{13}C NMR ($CDCl_3$) δ 112.79, 46.83, 39.22, 33.26, 32.10, 31.21, 30.33, 26.59, 26.53, 24.31 and 16.92; MS (EI) *m*/*z* (rel int) 242 (M^+, 3%), 227 (28), 200 (27), 177 (43), 173 (100), 117 (13), 91 (18) and 55 (5). Calc. for $C_{16}H_{22}N_2$: C, 79.30; H, 9.15; N, 11.56. Found: C, 79.42; H, 9.03; N, 11.47%.

2-Dicyanomethyladamantane (5-H (H)). This compound is colorless and the melting point is 150–151 °C; ^{1}H NMR ($CDCl_3$) δ 3.96 (d, J 11.8, 1H) and 2.40–1.63 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 112.35, 45.93, 37.80, 37.31, 30.75, 29.45, 26.96 and 25.52; MS (EI) *m*/*z* (rel int) 200 (M^+, 27%), 135 (100), 107 (10), 93 (16), 79 (16) and 67 (13). Calc. for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.87; H, 8.01; N, 14.05%.

Typical experimental procedures for the reaction of 5-substituted-2-dicyanomethyleneadamantanes 4-Z with Grignard reagents (see Scheme 2 and Table 1)

A solution of 2.0 mmol of 5-fluoro-2-dicyanomethyleneadamantane **4-F** in 30 ml diethyl ether was added to 6 mmol of freshly prepared benzylmagnesium bromide slowly at −5 °C and then the temperature was kept at room temperature after addition. After the starting material disappeared as shown by TLC, the solution was poured into ice-cold dilute hydrochloric acid solution. The solution was extracted with dichloromethane, dried over $MgSO_4$, filtered and the solvent was evaporated to obtain the oily mixture. The NMR analysis indicated that the mixture contained 96% yield of (*E*)-**5-F (Bz)** and (*Z*)-**5-F (Bz)** and the ratio was 62 : 38 by using dibromomethane or DMF as an internal standard. Flash column chromatography using *n*-hexane–ethyl acetate as the eluent was used to obtain pure products. Similar procedures were repeated when other substrates **4-Z** reacted with the same Grignard reagents and all the experimental results are shown in Table 1. The X-ray crystal data of (*E*)-**5-F (Bz)** and (*E*)-**5-F (Me)** are listed in Table 2, and the X-ray molecular structures are presented in Figs. 2 and 3.

(*E*)-2-Benzyl-5-fluoro-2-dicyanomethyladamantane ((*E*)-5-F (Bz)). This compound is colorless and the melting point is 171–172 °C; ^{1}H NMR ($CDCl_3$) δ 7.36 (s, 5H), 4.33 (s, 1H), 3.23 (s, 2H) and 2.62–1.71 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 134.55, 130.59, 128.97, 128.25, 110.61, 90.88 (d, *J* 185.1), 45.58, 43.92 (d, *J* 17.5), 39.22, 37.47 (d, *J* 19.0), 35.54 (d, *J* 9.9), 31.25 (d, *J* 2.3), 29.49 (d, *J* 9.9) and 27.84 (d, *J* 3.1); MS (EI) *m*/*z* (rel int) 308 (M^+, 5%), 128 (1), 117 (1), 91 (100) and 65 (8); FTIR 2247 cm^{-1} (HRMS (EI) Calc. for $C_{20}H_{21}N_2F$: *M*, 308.1689. Found: 308.1678). Calc.: C, 77.89; H, 6.90; N, 9.10. Found: C, 77.81; H, 6.89; N, 9.05%.

(*Z*)-2-Benzyl-5-fluoro-2-dicyanomethyladamantane ((*Z*)-5-F (Bz)). This compound is colorless and the melting point is 228–230 °C; ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 5H), 4.42 (s, 1H), 3.18 (s, 2H) and 2.40–1.71 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 134.87, 130.57, 128.98, 128.27, 110.38, 90.28 (d, *J* 186.7), 45.58 (d, *J* 1.6), 43.91 (d, *J* 16.7), 38.40 (d, *J* 1.5), 37.79 (d, *J* 19.0), 35.56 (d, *J* 9.9), 31.06 (d, *J* 1.5), 29.83 (d, *J* 9.1) and 28.36; MS (EI) *m*/*z* (rel int) 308 (M^+, 5%), 128 (1), 117 (2), 91 (100) and 65 (7); FTIR 2251 cm^{-1} (HRMS (EI) Calc. for $C_{20}H_{21}N_2F$: *M*, 308.1689. Found 308.1694). Calc.: C, 77.89; H, 6.90; N, 9.10. Found: C, 77.81; H, 6.86 ; N, 9.00%.

(*E*)-5-Fluoro-2-methyl-2-dicyanomethyladamantane ((*E*)-5-F (Me)). This compound is colorless and the melting point is 83–85 °C; ^{1}H NMR ($CDCl_3$) δ 4.30 (s, 1H), 2.32–1.69 (m, 13H) and 1.49 (d, *J* 1.0, 3H); ^{13}C NMR ($CDCl_3$) δ 111.58, 90.75 (d, *J* 185.1), 43.55 (d, *J* 17.5), 42.30 (d, *J* 1.6), 37.57 (d, *J* 19.8), 36.76 (d, *J* 10.7), 31.39 (d, *J* 3.1), 30.89 (d, *J* 1.5), 29.39 (d, *J* 10.6) and 21.17; MS (EI) *m*/*z* (rel int) 232 (M^+, 14%), 217 (17), 167 (100), 147 (31), 105 (10), 97 (14) and 91 (11); FTIR 2253 cm^{-1} (HRMS (EI) Calc. for $C_{14}H_{17}N_2F$: *M*, 232.1375. Found 232.1365). Calc.: C, 72.39; H, 7.40; N, 12.06. Found: C, 72.15; H, 7.44 ; N, 12.08%.

(*Z*)-5-Fluoro-2-methyl-2-dicyanomethyladamantane ((*Z*)-5-F (Me)). This compound is colorless and the melting point is 90–91 °C; ^{1}H NMR ($CDCl_3$) δ 4.39 (s, 1H), 2.30–1.59 (m, 13H) and 1.44 (d, *J* 1.0, 3H); ^{13}C NMR ($CDCl_3$) δ 111.38, 90.22 (d, *J* 185.9), 43.61 (d, *J* 16.7), 42.37 (d, *J* 2.3), 37.56 (d, *J* 19.0), 36.71 (d, *J* 9.9), 31.95, 31.18 (d, *J* 1.5), 29.73 (d, *J* 9.9) and 20.10 (d, *J* 2.3); MS (EI) *m*/*z* (rel int) 232 (M^+, 16%), 217 (17), 167 (100), 147 (33), 105 (14), 91 (14) and 77 (10); FTIR 2251 cm^{-1} (HRMS (EI) Calc. for $C_{14}H_{17}N_2F$: *M*, 232.1375. Found: 232.1375). Calc.: C, 72.39; H, 7.40; N, 12.06. Found: C, 72.33; H, 7.47; N, 12.07%.

(*E*)-2-Benzyl-5-chloro-2-dicyanomethyladamantane ((*E*)-5-Cl (Bz)). This compound is colorless and the melting point is 142 °C; ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 5H), 4.36 (s, 1H), 3.25 (s, 2H) and 2.83–1.78 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 134.52, 130.63, 129.01, 128.31, 110.52, 65.20, 48.81, 45.44, 42.36, 39.21, 35.61, 31.07, 29.69 and 27.90; MS (EI) *m*/*z* (rel int) 326 [(M + 2)$^+$, 2%], 324 (M^+, 6), 289 (34), 207 (9), 117 (2), 91 (100) and 65 (8); FTIR 2251 cm^{-1}. Calc. for $C_{20}H_{21}N_2Cl$: C, 73.95; H, 6.52; N, 8.62. Found: C, 73.84; H, 6.67; N, 8.22%.

(*Z*)-2-Benzyl-5-chloro-2-dicyanomethyladamantane ((*Z*)-5-Cl (Bz)). This compound is colorless and the melting point is 154–155 °C; ^{1}H NMR ($CDCl_3$) δ 7.36 (s, 5H), 4.45 (s, 1H), 3.17 (s, 2H) and 2.41–1.77 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 134.75, 130.57, 129.00, 128.28, 110.33, 64.56, 48.81, 45.38, 42.65, 38.49, 35.61, 30.82, 30.04 and 28.39; MS (EI) *m*/*z* (rel int) 326 [(M + 2)$^+$, 1%], 324 (M^+, 3), 198 (1), 117 (2), 91 (100) and 65 (8); FTIR 2251 cm^{-1}. Calc. for $C_{20}H_{21}N_2Cl$: C, 73.95; H, 6.52; N, 8.62. Found: C, 73.83; H, 6.74; N, 8.57%.

(*E*)-5-Chloro-2-methyl-2-dicyanomethyladamantane ((*E*)-5-Cl (Me)). This compound is colorless and the melting point is 110 °C; ^{1}H NMR ($CDCl_3$) δ 4.32 (s, 1H), 2.51–2.06 (m, 9H), 1.74 (s, 4H) and 1.49 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 114.47, 65.12, 48.39, 42.42, 42.13, 36.84, 31.45, 30.66, 29.57 and 21.11; MS (EI) *m*/*z* (rel int) 250 [(M + 2)$^+$, 1%], 248 (M^+, 3), 185 (33), 183 (100), 147 (47), 105 (14), 91 (19) and 77 (14). Calc. for $C_{14}H_{17}N_2Cl$: C, 67.60; H, 6.89; N, 11.26. Found: C, 67.44; H, 7.01; N, 11.27%.

(*Z*)-5-Chloro-2-methyl-2-dicyanomethyladamantane ((*Z*)-5-Cl (Me)). This compound is colorless and the melting point is 179 °C; ^{1}H NMR ($CDCl_3$) δ 4.42 (s, 1H), 2.20–1.66 (m, 13H) and 1.43 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 111.34, 64.65, 48.49, 42.41, 42.17, 36.78, 31.95, 30.94, 29.95 and 20.24; MS (EI) *m*/*z* (rel int) 250 [(M + 2)$^+$, 1%], 248 (M^+, 3), 185 (32), 183 (100), 147 (45), 105 (14), 91 (20) and 77 (14). Calc. for $C_{14}H_{17}N_2Cl$: C, 67.60; H, 6.89; N, 11.26. Found: C, 67.18; H, 7.00; N, 11.33%.

(*E*)-2-Benzyl-5-bromo-2-dicyanomethyladamantane ((*E*)-5-Br (Bz)). This compound is colorless and the melting point is 159–161 °C; ^{1}H NMR ($CDCl_3$) δ 7.37 (s, 5H), 4.35 (s, 1H), 3.26 (s, 2H) and 3.04–1.83 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 134.41, 130.58, 128.98, 128.29, 110.44, 60.96, 50.32, 45.47, 43.80, 39.29, 36.35, 31.11, 30.49 and 28.10; MS (EI) *m*/*z* (rel int) 370 [(M + 2)$^+$, 15%], 368 (M^+, 15), 289 (34), 198 (8), 156 (7) and 91 (100). Calc. for $C_{20}H_{21}N_2Br$: C, 65.05; H, 5.73; N, 7.59. Found: C, 65.01; H, 5.58; N, 7.52%.

(*Z*)-2-Benzyl-5-bromo-2-dicyanomethyladamantane ((*Z*)-5-Br (Bz)). This compound is colorless and the melting point is 153–155 °C; ^{1}H NMR ($CDCl_3$) δ 7.36 (s, 5H), 4.48 (s, 1H), 3.17 (s, 2H) and 2.47–1.83 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 134.67, 130.60, 129.05, 128.35, 110.32, 60.07, 50.32, 45.42, 44.12, 38.64, 36.36, 30.84, 29.64 and 28.44; MS (EI) *m*/*z* (rel int) 370 [(M + 2)$^+$, 35], 368 (M^+, 35), 289 (34), 198 (8), 156 (7) and 91 (100). Calc. for $C_{20}H_{21}N_2Br$: C, 65.05; H, 5.73; N, 7.59. Found: C, 65.01; H, 5.82; N, 7.56%.

(*E*)-5-Bromo-2-methyl-2-dicyanomethyladamantane ((*E*)-5-Br (Me)). This compound is colorless and the melting point is 143–144 °C; ^{1}H NMR ($CDCl_3$) δ 4.30 (s, 1H), 2.72–2.06 (m, 9H), 1.79 (s, 4H) and 1.51 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 111.40, 60.99, 49.87, 43.85, 42.14, 37.55, 31.58, 30.67, 30.33 and 21.15; MS (EI) *m*/*z* (rel int) 294 [(M + 2)$^+$, 10%], 292 (M^+, 10), 213 (100), 147 (26), 105 (13), 91 (18) and 77 (10). Calc. for $C_{14}H_{17}N_2Br$: C, 57.35; H, 5.84; N, 9.55. Found: C, 57.38; H, 5.68; N, 9.44%.

(*Z*)-5-Bromo-2-methyl-2-dicyanomethyladamantane ((*Z*)-5-Br (Me)). This compound is colorless and the melting point is

207 °C; ^{1}H NMR ($CDCl_3$) δ 4.44 (s, 1H), 2.34–1.71 (m, 13H) and 1.42 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 111.30, 60.35, 49.96, 43.82, 42.19, 37.49, 31.99, 30.90, 30.72 and 20.38; MS *m*/*z* (relative intensity) 294 [(M + 2)$^+$, 5%], 292 (M$^+$, 5), 213 (100), 147 (26), 105 (13), 91 (18) and 77 (10). Calc. for $C_{14}H_{17}N_2Br$: C, 57.35; H, 5.84; N, 9.55. Found: C, 57.42; H, 5.84; N, 9.55%.

(*E*)-5-Bromo-2-ethyl-2-dicyanomethyladamantane ((*E*)-5-Br (Et)). This compound is colorless and the melting point is 145–146 °C; ^{1}H NMR ($CDCl_3$) δ 4.36 (s, 1H), 2.72–2.13 (m, 11H), 2.08 (q, *J* 7.8, 2H), 1.82 (s, 2H) and 1.16 (t, *J* 7.8, 3H); ^{13}C NMR ($CDCl_3$) δ 111.68, 60.93, 50.16, 43.91, 43.53, 36.02, 31.01, 30.66, 28.12, 27.42 and 7.54; MS (EI) *m*/*z* (rel int) 308 [(M + 2)$^+$, tr], 306 (M$^+$, tr), 279 (tr), 277 (tr), 227 (2), 197 (100), 155 (15) and 141 (10). Calc. for $C_{15}H_{19}N_2Br$: C, 58.64; H, 6.23; N, 9.12. Found: C, 58.71; H, 6.36; N, 8.86%.

(*Z*)-5-Bromo-2-ethyl-2-dicyanomethyladamantane ((*Z*)-5-Br (Et)). This compound is colorless and the melting point is 163–164 °C; ^{1}H NMR ($CDCl_3$) δ 4.49 (s, 1H), 2.38–2.08 (m, 11H), 1.95 (q, *J* 7.8, 2H), 1.74–1.68 (m, 2H) and 1.14 (t, *J* 7.8, 3H); ^{13}C NMR ($CDCl_3$) δ 111.53, 60.65, 50.23, 44.17, 43.92, 36.13, 30.60, 30.53, 28.56, 26.91 and 7.80; MS (EI) *m*/*z* (rel int) 308 [(M + 2)$^+$, tr], 306 (M$^+$, tr), 227 (100), 161 (21) and 105 (5). Calc. for $C_{15}H_{19}N_2Br$: C, 58.64; H, 6.23; N, 9.12. Found: C, 58.70; H, 6.18; N, 9.07%.

(*E*)-5-Bromo-2-dicyanomethyl-2-isopropyladamantane ((*E*)-5-Br (*i*-Pr)). This compound is colorless and the melting point is 134 °C; ^{1}H NMR ($CDCl_3$) δ 4.41 (s, 1H), 2.72–1.85 (m, 14H) and 1.25 (d, *J* 7.2, 6H); ^{13}C NMR ($CDCl_3$) δ 112.26, 60.90, 50.45, 45.55, 43.30, 35.26, 31.36, 30.59, 30.24, 24.10 and 16.77; GC-MS (EI) *m*/*z* (rel int) 322 [(M + 2)$^+$, 46], 320 (M$^+$, 52), 241 (100), 207 (17), 169 (8), 149 (24), 131 (19) and 91 (27) (HRMS (EI) Calc. for $C_{15}H_{18}N_2Br$: M − 15, 305.0653. Found 305.0653).

(*Z*)-5-Bromo-2-dicyanomethyl-2-isopropyladamantane ((*Z*)-5-Br (*i*-Pr)). ^{1}H NMR ($CDCl_3$) δ 4.60 (s, 1H), 2.67 (septet, *J* 7.2, 1H), 2.16–1.66 (m, 13H) and 1.23 (d, *J* 7.2, 6H); ^{13}C NMR ($CDCl_3$) δ 112.84, 46.97, 39.37, 33.43, 32.26, 31.36, 30.50, 29.85, 26.75, 24.48 and 17.11; MS (EI) *m*/*z* (rel int) 322 [(M + 2)$^+$, tr], 320 (M$^+$, tr), 241 (6), 199 (100), 172 (6), 133 (20) and 91 (17) (HRMS (EI) Calc. for $C_{16}H_{22}N_2Br$: M + 1, 321.0789. Found 321.0815. Calc.: M − 1, 319.0851. Found 319.0790).

(*E*)-2-Benzyl-2-dicyanomethyl-5-phenyladamantane ((*E*)-5-Ph (Bz)). This compound is colorless and the melting point is 178–180 °C; ^{1}H NMR ($CDCl_3$) δ 7.42–7.20 (m, 10H), 4.54 (s, 1H), 3.26 (s, 2H) and 2.62–1.85 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 148.81, 135.10, 130.72, 128.89, 128.55, 128.11, 126.38, 124.71, 110.92, 46.12, 44.96, 39.25, 37.99, 35.84, 33.08, 32.11, 28.10 and 27.36; MS (EI) *m*/*z* (rel int) 366 (M$^+$, 37%), 275 (7), 249 (24), 129 (6), 115 (8) and 91 (100). Calc. for $C_{26}H_{26}N_2$: C, 85.20; H, 7.15; N, 7.64. Found: C, 85.22; H, 7.15; N, 7.68%.

(*Z*)-2-Benzyl-2-dicyanomethyl-5-phenyladamantane ((*Z*)-5-Ph (Bz)). This compound is colorless and the melting point is 200–201 °C; ^{1}H NMR ($CDCl_3$) δ 7.44–7.22 (m, 10H), 4.49 (s, 1H), 3.29 (s, 2H) and 2.51–1.86 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 148.43, 135.30, 130.71, 128.92, 128.56, 128.11, 126.44, 124.54, 110.78, 46.07, 45.38, 38.84, 38.08, 35.54, 33.09, 31.84, 28.35 and 27.73; MS (EI) *m*/*z* (rel int) 366 (M$^+$, 37%), 275 (7), 249 (24), 129 (6), 115 (8) and 91 (100). Calc. for $C_{26}H_{26}N_2$: C, 85.20; H, 7.15; N, 7.64. Found: C, 84.62; H, 7.38; N, 7.64%.

(*E*)-2-Methyl-2-dicyanomethyl-5-phenyladamantane ((*E*)-5-Ph (Me)). This compound is colorless and the melting point is 148–149 °C; ^{1}H NMR ($CDCl_3$) δ 7.34–7.20 (m, 5H), 4.48 (s, 1H), 2.29–1.77 (m, 13H) and 1.40 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 148.84, 128.41, 126.20, 124.64, 111.86, 44.50, 42.88, 38.16, 35.67, 34.43, 31.79, 31.59, 27.29 and 21.20; MS *m*/*z* (relative intensity) 290 (M$^+$, 100%), 225 (65), 169 (21), 155 (56), 115 (18), 91 (45) and 77 (12). Calc. for $C_{20}H_{22}N_2$: C, 82.71; H, 7.63; N, 9.64. Found: C, 82.38; H, 7.82; N, 9.71%.

(*Z*)-2-Methyl-2-dicyanomethyl-5-phenyladamantane ((*Z*)-5-Ph (Me)). This compound is colorless and the melting point is 138–140 °C; ^{1}H NMR ($CDCl_3$) δ 7.36–7.19 (m, 5H), 4.42 (s, 1H), 2.16–1.74 (m, 13H) and 1.50 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 148.56, 128.46, 126.30, 124.47, 111.71, 45.00, 42.77, 37.72, 35.43, 34.35, 32.01, 31.96, 27.60 and 20.67; MS (EI) *m*/*z* (rel int) 290 (M$^+$, 100%), 225 (65), 169 (21), 155 (56), 115 (18), 91 (45) and 77 (12). Calc. for $C_{20}H_{22}N_2$: C, 82.71; H, 7.63; N, 9.64. Found: C, 82.62; H, 7.45; N, 9.74%.

(*E*)-2-Ethyl-2-dicyanomethyl-5-phenyladamantane ((*E*)-5-Ph (Et)). This compound is colorless and the melting point is 139–140 °C; ^{1}H NMR ($CDCl_3$) δ 7.36–7.17 (m, 5H), 4.56 (s, 1H), 2.32–1.85 (m, 13H), 2.04 (q, *J* 7.8, 2H) and 1.16 (t, *J* 7.8, 3H); ^{13}C NMR ($CDCl_3$) δ 148.98, 128.48, 126.26, 124.70, 112.18, 44.76, 44.58, 37.74, 35.40, 32.79, 32.11, 28.19, 27.58, 27.37 and 7.63; MS (EI) *m*/*z* (rel int) 304 (M$^+$, 89%), 276 (46), 239 (63), 155 (100), 91 (41) and 77 (10) (HRMS (EI) Calc. for $C_{21}H_{24}N_2$: *M*, 304.1940. Found: 304.1944. Calc.: C, 82.85; H, 7.95; N, 9.20. Found: C, 82.93; H, 7.48; N, 9.41%).

(*Z*)-2-Ethyl-2-dicyanomethyl-5-phenyladamantane ((*Z*)-5-Ph (Et)). This compound is colorless and the melting point is 110 °C; ^{1}H NMR ($CDCl_3$) δ 7.39–7.17 (m, 5H), 4.47 (s, 1H), 2.16–1.69 (m, 13H), 2.05 (q, *J* 7.8, 2H) and 1.17 (t, *J* 7.8, 3H); ^{13}C NMR ($CDCl_3$) δ 148.67, 128.51, 126.36, 124.55, 112.06, 45.29, 44.47, 37.99, 35.69, 32.77, 31.53, 28.43, 27.33, 26.93 and 7.74; MS (EI) *m*/*z* (rel int) 304 (M$^+$, 100%), 276 (12), 239 (70), 155 (75), 91 (31) and 77 (6) (HRMS (EI) Calc. for C $_{21}H_{24}N_2$: *M*, 304.1940. Found: 304.1934. Calc.: C, 82.85; H, 7.95; N, 9.20. Found: C, 82.53; H, 7.29; N, 9.24%).

(*E*)-5-Bromo-2-dicyanomethyladamantane ((*E*)-5-Br (H)). This compound is colorless and the melting point is 187–189 °C; ^{1}H NMR ($CDCl_3$) δ 3.90 (d, *J* 12.0, 1H) and 2.57–1.65 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 111.83, 60.68, 48.67, 48.63, 44.23, 33.13, 30.87, 28.92 and 25.10; MS (EI) *m*/*z* (rel int) 280 [(M + 2)$^+$, 35%], 278 (M$^+$, 35), 199 (60), 108 (45) and 91 (100). Calc. for $C_{13}H_{15}N_2Br$: C, 55.93; H, 5.41; N, 10.03. Found: C, 56.00; H, 5.44; N, 9.90%.

(*Z*)-5-Bromo-2-dicyanomethyladamantane ((*Z*)-5-Br (H)). This compound is colorless and the melting point is 137–138 °C; ^{1}H NMR ($CDCl_3$) δ 3.96 (d, *J* 12.2, 1H) and 2.35–1.78 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 111.74, 60.74, 48.76, 44.21, 42.29, 35.83, 33.49, 30.99 and 25.34; MS (EI) *m*/*z* (rel int) 280 [(M + 2)$^+$, 15%], 278 (M$^+$, 15), 199 (60), 108 (45) and 91 (100). Calc. for $C_{13}H_{15}N_2Br$: C, 55.93; H, 5.41; N, 10.03. Found: C, 56.31; H, 5.32; N, 10.05%.

(*E*)-2-Dicyanomethyl-5-phenyladamantane ((*E*)-5-Ph (H)). This compound is colorless and the melting point is 167 °C; ^{1}H NMR ($CDCl_3$) δ 7.35–7.22 (m, 5H), 4.02 (d, *J* 12.0, 1H), 2.46 (d, *J* 12.0, 1H) and 2.36–1.73 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 148.84, 128.37, 126.16, 124.69, 112.31, 45.31, 43.15, 42.91, 35.44, 30.06, 29.89, 27.62 and 25.25; MS (EI) *m*/*z* (rel int) 276 (M$^+$, 88%), 169 (11), 155 (100), 115 (14), 91 (30) and 77 (8). Calc. for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.28; H, 7.57; N, 10.23%.

(*Z*)-2-Dicyanomethyl-5-phenyladamantane ((*Z*)-5-Ph (H)). This compound is colorless and the melting point is 145 °C; ^{1}H NMR ($CDCl_3$) δ 7.34–7.20 (m, 5H), 3.95 (d, *J* 12.0, 1H) and 2.46–1.77 (m, 14H); ^{13}C NMR ($CDCl_3$) δ 148.96, 128.48,

126.31, 124.49, 112.22, 45.06, 43.50, 36.93, 35.98, 35.52, 30.27, 27.68 and 25.42; MS (EI) *m/z* (rel int) 276 (M^+, 88%), 169 (11), 155 (100), 115 (14), 91 (30) and 77 (8). Calc. for $C_{19}H_{20}N_2$: C, 82.57; H, 7.29; N, 10.14. Found: C, 82.49; H, 7.28; N, 10.22%.

Typical experimental procedures for the reaction of 5-bromo-2-dicyanomethyleneadamantane 4-Br with phenylmagnesium bromide (see Scheme 4)

A solution of 5-bromo-2-dicyanomethyleneadamantane (2 mmol in dry ether 20 mL) was added dropwise at −5 °C to a diethyl ether solution of phenylmagnesium bromide (20 mmol in dry ether 100 mL) and a vigorous reaction occurred upon each addition. After addition, the temperature was kept at room temperature and the mixture was stirred for 30 min to obtain intermediate **A** and then 20 mmol dry methanol was added rapidly to the solution. The insoluble material was filtered and the solvent was removed under reduced pressure to obtain the oily mixture. The crude product was purified by flash column chromatography to isolate **6-Br** in 80% yield. The intermediate **A** was poured into ice cold dilute acid aqueous solution, extracted with dichloromethane and then the solvent was evaporated to obtain the crude product. The mixture was purified by flash column chromatography to obtain 75% of the hydrolyzed product **7-Br**.

5-Bromo-2-{bis[imino(phenyl)methyl]methylene}adamantane (6-Br). This compound is colorless and the melting point is 171–173 °C; ^{1}H NMR ($CDCl_3$) δ 9.54 (s br, 2H), 7.79–7.26 (m, 10H) and 2.81–1.85 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 175.33, 149.13, 138.07, 130.92, 128.67, 127.52, 62.83, 49.56, 48.01, 38.28, 37.15 and 31.68; MS (EI) *m/z* (rel int) 434 [$(M + 2)^+$, 15%], 432 (M^+, 15), 353 (86), 329 (61), 250 (42), 208 (18), 194 (100), 156 (24), 104 (60) and 77 (62). Calc. for $C_{25}H_{25}N_2Br$: C, 69.28; H, 5.81; N, 6.46. Found: C, 69.12; H, 5.80; N, 6.30%.

5-Bromo-2-dibenzoylmethyleneadamantane (7-Br). This compound is colorless and the melting point is 135–138 °C; ^{1}H NMR ($CDCl_3$) δ 8.07–8.03 (m, 4H), 7.62–7.40 (m, 6H) and 2.79–1.80 (m, 13H). ^{13}C NMR ($CDCl_3$) δ 194.71, 153.87, 137.31, 133.88, 133.54, 130.00, 128.73, 62.24, 49.49, 48.00, 38.34, 37.20 and 31.66; MS (EI) *m/z* (rel int) 436 [$(M + 2)^+$, 91%], 434 (M^+, 91), 355 (100), 337 (17), 299 (24), 261 (13), 221 (14), 195 (9), 178 (14), 165 (22) and 149 (29). Calc. for $C_{25}H_{23}O_2Br$: C, 68.97; H, 5.33. Found: C, 68.86; H, 5.46%.

2-Dibenzoylmethylene-5-phenyladamantane (8-Ph). This compound is colorless and the melting point is 130 °C; ^{1}H NMR ($CDCl_3$) δ 8.12–8.06 (m, 4H), 7.59–7.17 (m, 11H), 2.83 (s, 2H) and 2.21–1.82 (m, 13H); ^{13}C NMR ($CDCl_3$) δ 195.31, 157.61, 149.13, 137.75, 133.59, 131.95, 130.01, 128.62, 128.33, 126.04, 124.81, 44.11, 42.35, 38.33, 35.96, 35.57 and 28.36; MS (EI) *m/z* (rel int), 432 (M^+, 37%), 414 (4), 327 (10), 299 (7), 280 (3), 221 (2), 195 (7), 155 (6), 115 (7), 105 (100) and 77 (37) (HRMS (EI) Calc. for $C_{31}H_{28}O_2$: *M*, 432.2089. Found: 432.2065). Calc.: C, 86.08; H, 6.52. Found: C, 85.60; H, 6.22%.

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