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1,3-Dipolar cycloaddition of nitrile oxides with unsymmetrically substituted norbornenes

Peter Mayo, Tiffany Hecnar and William Tam*

Department of Chemistry and Biochemistry, Guelph-Waterloo Center for Graduate Work in Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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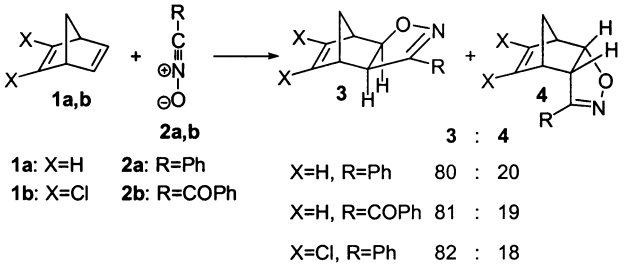
Abstract—1,3-Dipolar cycloadditions of nitrile oxides with unsymmetrically substituted norbornenes were investigated. The cycloadditions were found to be completely stereoselective, giving only the *exo* cycloadducts in moderate to good yields. Regioselectivities in the cycloadditions ranging from 50:50 to 100:0 were observed with various unsymmetrically substituted norbornenes.

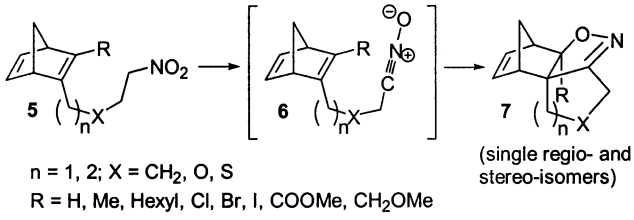
1. Introduction

1,3-Dipolar cycloadditions offer a convenient one-step route for the construction of a variety of complex five-membered heterocycles.[1] 1,3-Dipolar cycloadditions of nitrile oxides are well-documented and provide efficient entries to the synthesis of 2-isoxazolines.[2] Reductive cleavage of the N–O bond of 2-isoxazolines has proven to be a useful route to amino ketones, oxo alcohols, and a number of natural products.[1,2] 1,3-Dipolar cycloadditions of nitrile oxides with bicyclic alkenes have also been studied.[3,4] For example, norbornadiene **1a** (X=H) or **1b** (X=Cl) reacted with benzonitrile oxide **2a** or phenylglyoxynitrile oxide **2b** to provide a mixture of *exo* and *endo* cycloadducts **3** and **4** in a ratio of about 80:20 (Scheme 1). These nitrile oxides were generated from the corresponding hydroimoyl chlorides by dehydrohalogenation with the removal of HCl using Et_3N.[5] During our studies on the intramolecular cycloadditions of norbornadiene-tethered nitrile oxides,[6,7] we noticed that using different methods and different conditions to generate the nitrile oxides could affect the stereoselectivity of the cycloaddition. Other than generation from the corresponding hydroimoyl chlorides, another widely used method to generate nitrile oxides is the dehydration of the corresponding nitroalkanes. The two most commonly used methods for converting nitroalkanes to the corresponding nitrile oxides are the Mukaiyama aromatic isocyanate method and the Shimizu ethyl chloroformate method.[8,9] All the above mentioned methods suffer from a limitation: a high reaction temperature (above 80°C) is usually required, sometimes leading to lower yields and lower stereoselectivities. More recently Hassner and co-workers have reported an improved procedure to generate nitrile oxides from the corresponding nitroalkanes at *room temperature* using di-*tert*-butyl dicarbonate, $(BOC)_2O$, in the presence of a catalytic amount of 4-dimethylaminopyridine (DMAP).[10] Under these reaction conditions, we obtained excellent yields of single regio- and stereoisomers in our intramolecular 1,3-dipolar cycloadditions of norbornadiene-tethered nitrile oxides (Scheme 2).



Scheme 1.

To our knowledge, all the bicyclic alkenes that have been studied in the intermolecular nitrile oxide cycloadditions are



Scheme 2. Intramolecular 1,3-dipolar cycloadditions of norbornadiene-tethered nitrile oxides.

Keywords: 1,3-dipolar cycloadditions; nitrile oxides; bicyclic alkenes; norbornenes; regioselectivity; stereoselectivity; remote substituent effects.
* Corresponding author. Tel.: +519-824-4120, ext. 2268; fax: +519-766-1499; e-mail: tam@chembio.uoguelph.ca

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symmetrical and thus no regiochemistry questions could be addressed. In this paper we report our studies on the 1,3-dipolar cycloadditions of nitrile oxides with unsymmetrically substituted norbornenes **8**–**11** (Fig. 1). We would like to address both the questions of regiochemistry and stereochemistry.

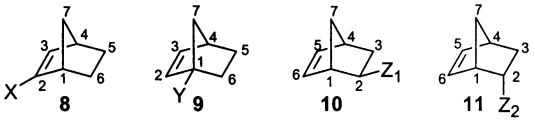
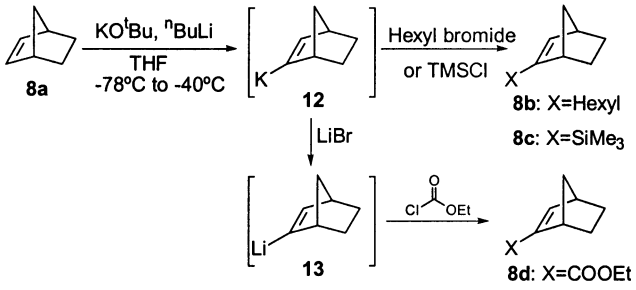


Figure 1. Unsymmetrically substituted norbornenes.

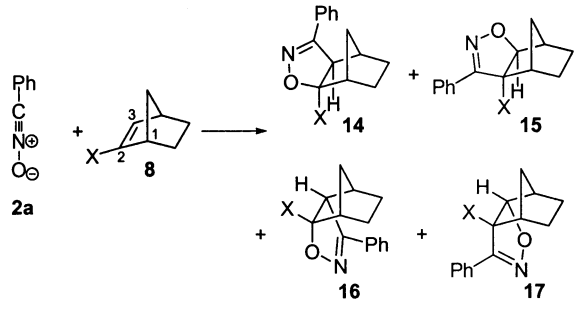
2. Results and discussion

2.1. Nitrile oxide cycloadditions of norbornene (8a) and 2-substituted-2-nornornenes (8b–8d)

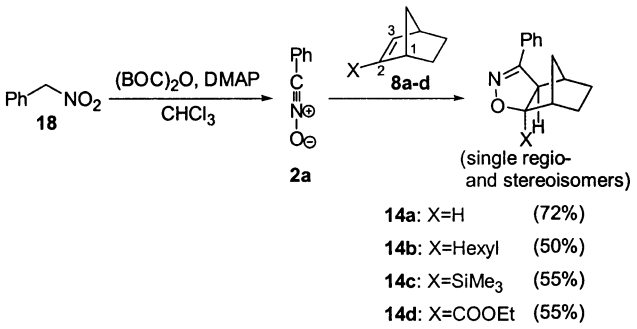
Several 2-substituted-2-norbornenes **8b**–**8d** were prepared as shown in Scheme 3. Deprotonation of norbornene (**8a**) with Schlosser's base (^{t}BuOK/^{n}BuLi) in THF at −78°C,[11] followed by trapping with hexyl bromide, TMSCl or ethyl chloroformate provided the 2-substituted-2-norbornenes **8b**–**8d**. Four different cycloadducts (**14**–**17**) could be formed from a 2-substituted-2-norbornene **8** reacting with benzonitrile oxide **2a** (Scheme 4). Cycloaddition could occur with the oxygen of the nitrile oxide attached to C_2 of the norbornene **8** to produce *exo*-cycloadduct **14** or *endo*-cycloadduct **16**, or the oxygen of the nitrile oxide attached to C_3 to give *exo*-cycloadduct **15** or *endo*-cycloadduct **17**. The benzonitrile oxide **2a** was generated from nitromethylbenzene (**18**)[12] using Hassner's method ($(BOC)_2O$ and DMAP) and its cycloadditions with norbornene (**8a**) and 2-substituted-2-norbornenes **8b**–**8d** were studied (Scheme 5).



Scheme 3. Synthesis of 2-substituted-2-norbornenes **8b**–**8d**.



Scheme 4. Possible cycloadducts.



Scheme 5. Nitrile oxide cycloadditions of 2-substituted-2-norbornenes.

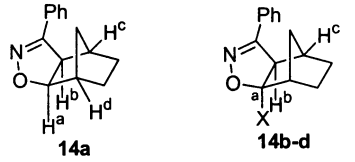


Figure 2. Assignment of regiochemistry of cycloadducts **14a**–**d**.

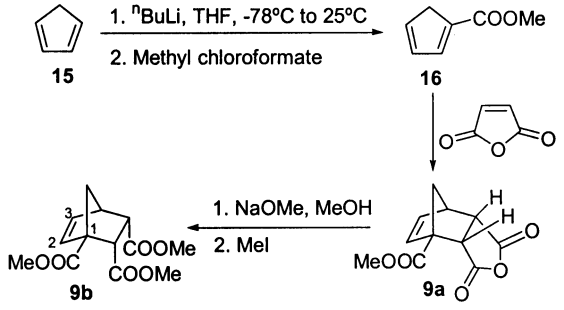
These cycloadditions were found to be completely regio- and stereoselective, giving single regio- and stereoisomers **14a**–**14d** in moderate to good yields. Only the *exo*-cycloadducts were formed, and regardless of the electronic nature of the substituent at C_2 of the 2-norbornene **8**, only the regioisomers with the oxygen of the nitrile oxide attached to C_2 of the norbornene **8** were produced. The complete control of the regiochemistry by the substitutent at C_2 of the 2-norbornene **8** was expected as similar regiochemical control was observed previously in acyclic systems.[13a,b] Usually the oxygen of the nitrile oxide becomes bonded to the most substituted carbon of the olefin regardless of the electronic nature of the substituent. The lower yields of the cycloadditions of substituted norbornenes **8b**–**8d** (50–55%) can be explained by the fact that these substituted norbornenes are less reactive than the unsubstituted norbornene (**8a**), and the nitrile oxide (**2a**) is prone to undergo dimerization, rearrangement and polymerization when reacted with less reactive dipolarophiles.[1a,2b] In fact, for the cycloadditions of substituted norbornenes **8b**–**8d**, we obtained a significant amount of polymeric material at the end of the reactions.

The regio- and stereochemistry of the cycloadducts **14a**–**14d** were easily assigned by ^{1}H and ^{13}C NMR. For cycloadduct **14a** (X=H), the *exo* stereochemistry was proven by the coupling pattern of H^a and H^b in the ^{1}H NMR spectra (Fig. 2). As the dihedral angles between H^a and H^d, and H^b and H^c in the *exo* cycloadducts are close to 90°, their coupling constants would be very small (J=∼0–2 Hz). The corresponding dihedral angles of the *endo* cycloadducts would be approximately 42° and would give coupling constants of ∼5 Hz. In **14a**, both H^a and H^b are doublets (coupled only with each other but not with H^c or H^d), therefore this cycloadduct must possess *exo* stereochemistry.[14] Similarly for cycloadducts **14b**–**14d** (X≠H), the singlet of H^b in the ^{1}H NMR (does not couple with H^c) indicated the *exo* stereochemistry of the cycloadducts. The regiochemistry of cycloadducts **14b**–**14d** were proven by the fact that in the APT-^{13}C NMR,[15] the carbons attached to the oxygen in the isoxazoline rings (C_a) are quaternary carbons.

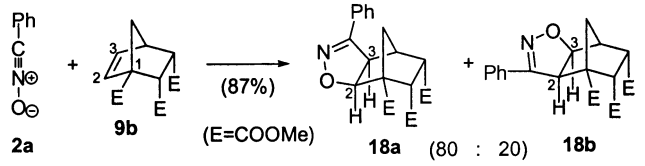
2.2. Nitrile oxide cycloadditions of 1-substituted-2-norbornene (9b)

1-Substituted-2-norbornene **9b** was prepared as shown in Scheme 6. Deprotonation of freshly cracked cyclopentadiene **15** with ^{n}BuLi followed by trapping of the resulting anion with methyl chloroformate afforded 1-methoxycarbonylcyclopentadiene (**16**).[16,17] Diels–Alder reaction of **16** with freshly recrystallized maleic anhydride provided 1-substituted-2-norbornene **9a**.[17] As **9a** is not quite soluble in most organic solvents such as THF, Et_2O, toluene and $CHCl_3$ (the solvent that we used to carried out the 1,3-dipolar cycloadditions), we decided to convert **9a** to **9b** before studying the nitrile oxide cycloaddition. Thus, treatment of **9a** with sodium methoxide in methanol at 0°C, followed by trapping with methyl iodide provided **9b**. Benzonitrile oxide (**2a**) was generated from nitromethylbenzene (**18**) using $(BOC)_2O$ and DMAP and its cycloaddition with 1-substituted-2-norbornene **9b** was studied (Scheme 7). Similar to the nitrile oxide cycloadditions with 2-substituted-2-norbornenes **8b**–**8d**, cycloaddition of nitrile oxide **2a** with 1-substituted-2-norbornene **9b** was also completely stereoselective, only the *exo* cycloadducts were obtained. Two regioisomers **18a** and **18b** were obtained in a ratio of 80:20 with an overall isolated yield of 87%. The major regioisomer was found to be the one with the oxygen of the nitrile oxide attached to C_2 of the norbornene **9b**.

The stereochemistry of the cycloadducts **18a** and **18b** were proven by the coupling pattern of H^a and H^b in the ^{1}H NMR spectra, similar to **14a** as described earlier. The regiochemistry of the cycloadducts were determined by GOESY experiments (gradient NOE experiments), Fig. 3.[18] In the



Scheme 6. Synthesis of 1-substituted-2-norbornene **9b**.



Scheme 7. Nitrile oxide cycloadditions of 1-substituted-2-norbornene **9b**.

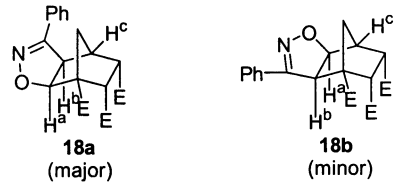


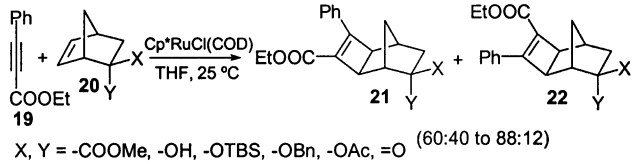
Figure 3. Assignment of regiochemistry of cycloadducts **18a/18b**.

major cycloadduct, H^b (4.62 ppm, the proton next to the carbon adjacent to the C=N in the isoxazoline ring) showed positive NOE effect with H^a (5.10 ppm), H^c (2.80 ppm) and the phenyl ring. H^a (the proton attached to the carbon next to the oxygen in the isoxazoline ring) in the major cycloadduct showed positive NOE only with H^b. In the minor cycloadduct, H^a showed positive NOE effect with H^b and H^c; and H^b showed positive NOE effect with H^a and the phenyl ring.

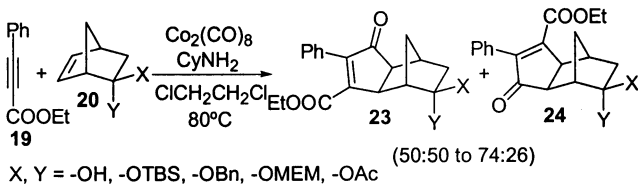
2.3. Nitrile oxide cycloadditions of 2-substituted-5-norbornenes (10 and 11)

Although the substituents (Z_1 and Z_2) in 2-substituted-5-norbornenes **10** and **11** (Fig. 1) are far away from the reaction center (the double bond), previous examples in the literature have shown that these remote substituents could have a significant effect on the regiochemical control in cycloaddition reactions.[19–22] We have recently reported the remote substituent effects on the regioselectivity of the ruthenium-catalyzed [2+2] cycloadditions and Pauson–Khand [2+2+1] cycloadditions of 2-substituted-5-norbornenes.[19,20] Regioselectivities of up to 88:12 were observed in the ruthenium-catalyzed [2+2] cycloadditions (Scheme 8), and regioselectivities of up to 74:26 were observed in the Pauson–Khand reactions (Scheme 9).

exo-2-Substituted-5-norbornenes **10a**–**10g** and *endo*-2-substituted-5-norbornenes **11a**–**11f** were prepared according to our previously reported procedures.[20,21] Benzonitrile oxide (**2a**) was generated from nitromethylbenzene (**18**) using $(BOC)_2O$ and DMAP and its cycloaddition with *exo*- and *endo*-2-substituted-5-norbornenes are shown in Table 1. Similar to norbornenes **8** and **9**, the cycloadditions of **10** and **11** were completely stereoselective, giving only the *exo* cycloadducts. Generally the yields of the cycloadditions were good but the regioselectivities were very low. Unlike the ruthenium-catalyzed [2+2] cycloadditions and Pauson–Khand [2+2+1] cycloadditions in which the remote substituents showed a significant effect on the regioselectivity of the cycloadditions, very little remote substituent effects were observed in the 1,3-dipolar nitrile oxide cycloadditions. The highest regioselectivity observed

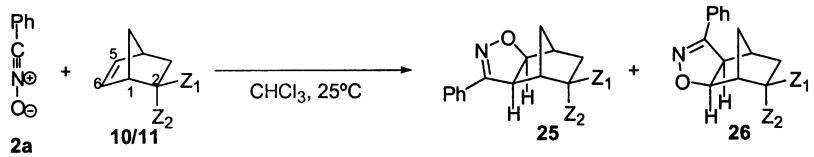


Scheme 8. Ruthenium-catalyzed [2+2] cycloadditions of 2-substituted-5-norbornenes.



Scheme 9. Cobalt-catalyzed Pauson-Khand reactions of 2-substituted-5-norbornenes.

Table 1. Nitrile oxide cycloadditions of 2-substituted-5-norbornenes



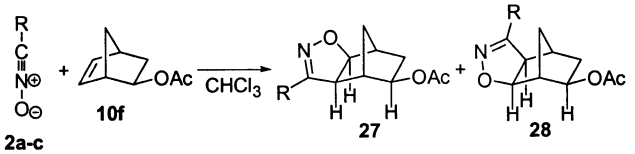
Exo-substituents (Z_2=H)						*Endo*-substituents (Z_1=H)					
Entry	Norbornene	Z_1	Yield (%)[a]	Cycloadducts	**25**:**26**	Entry	Norbornene	Z_2	Yield (%)[a]	Cycloadducts	**25**:**2**[b]
1	**10a**	COOMe	79	**25a/26a**	54:46	8	**11a**	COOMe	46	**25h/26h**	50:50
2	**10b**	OH	82	**25b/26b**	50:50	9	**11b**	OH	72	**25i/26i**	58:42
3	**10c**	OTBS	82	**25c/26c**	50:50	10	**11c**	PTBS	90	**25j/26j**	50:50
4	**10d**	OMEM	94	**25d/26d**	50:50	11	**11d**	OMEM	86	**25k/26k**	55:45
5	**10e**	OBn	95	**25e/26e**	53:47	12	**11e**	OBn	76	**25l/26l**	51:49
6	**10f**	OAc	95	**25f/26f**	62:38	13	**11f**	OAc	95	**25m/26m**	55:45
7	**10g**	X=Y=O (ketone)	89	**25g/26g**	57:43						

[a] Isolated yields of pure products after column chromatography.
[b] Measured by integration on 400 MHz ^{1}H NMR spectra.

was 62:38 with the *exo*-OAc norbornene **10f**. We have also studied the effect of different solvents on the regioselectivity of the cycloadditions between *exo*-OAc norbornene **10f** with benzonitrile oxide (**2a**). Very little changes on the regioselectivity were observed using different solvents, but different solvents have significant effect on the chemical yields. The highest yields were observed using $CHCl_3$ as solvent (95%). In toluene, the yield was 65%, in THF 46%, in Et_2O 47%, in DME 49%, in hexanes 53%, and in DMF 16%. We have also studied the effect of different nitrile oxides on the regioselectivity of the cycloadditions. The nitrile oxide cycloadditions of *exo*-OAc norbornene **10f** with three different nitrile oxides (generated from the corresponding nitroalkanes using the $(BOC)_2O$/DMAP method)) are shown in Table 2. Both phenylglyoxynitrile oxide (**2b**) and methyl nitrile oxide (**2c**) are less reactive than benzonitrile oxide (**2a**), giving lower chemical yields in the cycloadditions. In case of methyl nitrile oxide (**2c**), very little reaction was observed when the reaction was carried out at room temperature. Both the cycloadditions of **10f** with nitrile oxide **2a** and **2c** gave regioselectivities of 62:38 while the cycloadditions of **10f** with nitrile oxide **2b** was non-selective, giving a 50:50 ratio of the regioisomers.

In order to explain the regiochemistry of the cycloadditions and the observed trend of regioselectivity, we have performed theoretical calculations of some of the norbornenes using the GAUSSIAN 98 suite of programs (Scheme 10).[23,24] Natural population analysis shows that the charges on the C_5 and C_6 atoms of the 2-substituted norbornenes **10** are slightly negative and slightly different. With Z_1=OAc, OCH_3 (used to model the experimentally used OCH_2Ph) or OH, C_6 is always more 'negative' than C_5. This explains the regiochemistry of the cycloadditions that we observed: the major isomers formed (cycloadduct **25**) are the isomers with the oxygen of the nitrile oxide (the 'negative' end of the 1,3-dipole) attached to C_5 (the less negatively charged carbon of the double bond) and the carbon of the nitrile oxide (the 'positive' end of the 1,3-dipole) attached to C_6 (the more negatively charged carbon of the double bond). For the regioselectivity in the cycloadditions, one would expect the greater the difference of the charges between C_5 and C_6 in **10**, the higher the regioselectivity. This is exactly what we observed. When Z_1=OAc, the difference in the charges between C_5 and C_6 (qC_5-C_6) is 0.015 and the regioselectivity is 62:38. Changing Z_1 from OAc to OCH_3 (Z_1=OCH_3 was used to model the experimentally used OCH_2Ph), the difference in the charges between C_5 and C_6 is smaller (0.007) and the regioselectivity decreased to 53:47. For Z_1=OH, the difference in the charges between C_5 and C_6 is very small (0.003) and the cycloaddition is non-selective (50:50).

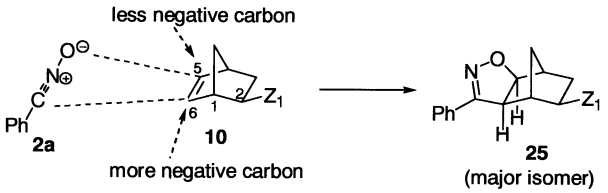
Table 2. Cycloadditions of 2-substituted-5-norbornene **10f** with different nitrile oxides



Entry	Nitrile oxide	R	Temperature (°C)	Yield (%)[a]	**27**:**28**[b]
1	**2a**	Ph	25	95	62:38
2	**2b**	COPh	25	30	50:50
3	**2c**	CH_3	60	54	62:38

[a] Isolated yields of prue products after column chromatography.
[b] Measured by integration on 400 MHz ^{1}H NMR spectra of the crude reaction mixtures.

We observed stronger remote substituent effects on the regioselectivity in the ruthenium-catalyzed [2+2] cycloadditions[19] and Pauson–Khand [2+2+1] cycloadditions[20] than the 1,3-dipolar nitrile oxide cycloadditions. The 1,3-dipolar cycloadditions of nitrile oxides with alkenes are usually concerted processes and their regioselectivities are determined by the ground state of the reaction partners. As indicated in the theoretical calculations shown in Scheme 10, although there is a slight difference in the charge distribution between C_5 and C_6 in **10**, the difference is in fact very small and this account for the low levels of the regioselectivity in the 1,3-dipolar cycloadditions. Unlike 1,3-dipolar cycloadditions of nitrile oxides, metal-catalyzed cycloaddition reactions are normally stepwise processes and the regioselectivity is not only governed by the ground state of the reaction partners but also controlled by the relative stability of the metallacycles involved in the stepwise process.[20]



Z_1	Charge on C_6 (qC_6)	Charge on C_5 (qC_5)	$q(C_5-C_6)$	Observed Regioselectivity
OAc	-0.244	-0.229	0.015	62:38
OCH_3[a]	-0.243	-0.236	0.007	53:47
OH	-0.240	-0.237	0.003	50:50

[a] Z_1=OCH_3 was used to in the calculation to model the experimentally used OCH_2Ph

Scheme 10. Explanation of the regiochemistry and regioselectivity of the cycloadditions.

The stereochemistry of the cycloadducts **25** and **26** were proven by the coupling pattern of H^a and H^b in the ^1H NMR spectra, similar to **14a**, **18a** and **18b** as described earlier. The regiochemistry of the cycloadducts were determined by ^1H NMR and GOESY experiments (Fig. 4). From ^1H NMR, H^d in all the minor cycloadducts is more downfield than H^d and H^c in the major cycloadducts as it is next to two adjacent C–O bonds instead of one. Also, H^c in the major cycloadducts (next to an adjacent C–O bond) is always more downfield than H^c in the minor cycloadducts (next to an adjacent C–C=N group). From GOESY experiments, in the major cycloadducts H^a (the proton attached to the carbon next to the oxygen in the isoxazoline ring) showed positive NOE effect with H^b and H^c but not with H^d while in the minor cycloadducts, H^a showed positive NOE effect with H^b and H^d but not with H^c.

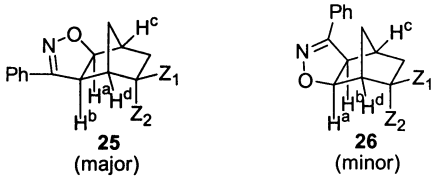


Figure 4. Assignment of regiochemistry of cycloadducts **25**/**26**.

3. Conclusions

We have studied the 1,3-dipolar cyloadditions of nitrile oxides with various unsymmetrical bicyclic norbornenes. Cycloadditions of all the substituted norbornenes were found to be highly stereoselective, giving only *exo* cycloadducts in moderate to excellent yields. Cycloadditions of 2-substituted-2-norbornenes **8b**–**8d** with benzonitrile oxide (**2a**) were completely regioselective, and regardless of the electronic nature of the substitutent at C_2 on 2-norbornenes **8**, only the regioisomers with the oxygen of the nitrile oxide attached to C_2 of the norbornenes **8** were produced. For 1-substituted-2-norbornene **9b**, the cycloaddition was also regioselective, giving two regioisomers in a ratio of 80:20. 2-Substituted-5-norbornenes **10** and **11** showed very little remote substituent effect on the regioselectivity of the nitrile oxide cycloaddition, and low levels of regioselectivity (50:50 to 62:38) were observed.

4. Experimental

4.1. General information

All reactions were carried out in an atmosphere of dry nitrogen at ambient temperature unless otherwise stated. Standard column chromatography was performed on 230–400 mesh silica gel (obtained from Silicycle) by use of flash column chromatography techniques.[25] Analytical thin-layer chromatography (TLC) was conducted on Merck precoated silica gel 60 F_{254} plates. All glassware was flame dried under an inert atmosphere of dry nitrogen. Infrared spectra were taken on a Bomem MB-100 FTIR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a Bruker-400 spectrometer. Chemical shifts for ^1H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (chloroform: δ 7.26). Chemical shifts for ^{13}C NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent as the internal standard (deuterochloroform: δ 77.0). High resolution mass spectra were done by McMaster Regional Centre for Mass Spectrometry at McMaster University, Hamilton, Ontario. Elemental analyses were performed by Canadian Microanalytical Service Ltd., British Columbia or by Quantitative Technologies Inc., New Jersey.

4.2. Materials

Unless stated otherwise, commercial reagents were used without purification. Solvents were purified by distillation under dry nitrogen: from CaH_2 (CH_2Cl_2, 1,2-dichloroethane, chloroform, DMF, Et_3N, pyridine); from 4 Å molecular sieves (DMSO); from sodium (toluene); from potassium/benzophenone (THF); and from sodium/benzophenone (Et_2O). Nitromethylbenzene (**18**),[12] 2-substituted-2-norbornane **8d**,[11b] 1-substituted-2-norbornene **9a**,[17] and *exo*-2-substituted-5-nornornenes **10a**–**10g**[20,21] and *endo*-2-substituted-5-nornornenes **11a**–**11f**[20,21] were prepared according to literature procedures.

4.2.1. 2-Hexylbicyclo[2.2.1]hept-2-ene (8b). A solution of norbornene (2.57 g, 27.3 mmol) in THF (6 mL) was added via a cannula to a flame-dried flask containing KO^{t}Bu (1.01 g, 9.00 mmol) in THF (5 mL) at −78°C. The temperature was kept below −60°C during this addition. ^{n}BuLi

(5.60 mL, 8.96 mmol, 1.6 M in hexanes) was added to the reaction mixture over 15 min, with the temperature kept below −70°C. The reaction mixture was warmed to −40°C and stirred for 1 h, then cooled to −78°C. Hexyl bromide (1.50 mL, 10.7 mmol) was added to the reaction mixture, and the reaction mixture was warmed to room temperature and stirred for 17 h. After quenching with water (20 mL), the layers were separated and the aqueous layer was extracted with Et_2O (2×30 mL). The combined organic layers were washed with brine (30 mL), dried ($MgSO_4$), and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography (hexanes) to give **8b** (1.1983 g, 6.72 mmol, 75%) as a clear, transparent liquid. R_f 0.93 (hexanes); IR (neat, NaCl) 3048 (w), 2958 (s), 2926 (s), 2869 (s), 2858 (s), 1621 (w), 1467 (m), 1378 (w), 1274 (w), 1120 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 5.50 (d, 1H, J=0.5 Hz), 2.76 (m, 1H), 2.65 (br. s, 1H), 2.06 (m, 2H), 1.60 (m, 2H), 1.43–1.27 (m, 10H), 1.00 (m, 2H), 0.89 (t, 3H, J=6.6 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 150.1, 126.8, 48.3, 45.0, 42.0, 31.7, 29.8, 29.1, 27.5, 26.6, 24.5, 22.6, 14.0. HRMS calcd for $C_{13}H_{22}$: m/z 178.1722, found m/z 178.1718.

4.2.2. 2-(Trimethylsilyl)bicyclo[2.2.1]hept-2-ene (8c). A solution of norbornene (2.50 g, 26.6 mmol) in THF (6 mL) was added via a cannula to a flame-dried flask containing KO^{t}Bu (1.51 g, 13.5 mmol) in THF (20 mL) at −78°C. The temperature was kept below −60°C during this addition. ^{n}BuLi (8.40 mL, 13.4 mmol, 1.6 M in hexanes) was added to the reaction mixture over 15 min, with the temperature kept below −70°C. The reaction mixture was warmed to −40°C and stirred for 1 h, then cooled to −78°C. TMSCl (1.10 mL, 8.70 mmol) was added to the reaction mixture, and the reaction mixture was warmed to room temperature and stirred for 18 h. After quenching with water (20 mL), the layers were separated and the aqueous layer was extracted with Et_2O (3×30 mL). The combined organic layers were washed with brine (30 mL) and dried ($MgSO_4$). The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (hexanes) to give **8c** (1.27 g, 7.63 mmol, 88%) as a clear, transparent liquid. R_f 0.98 (hexanes); IR (neat, NaCl) 3033 (m), 2959 (s), 2918 (s), 2900 (m), 2870 (s), 1557 (s), 1448 (m), 1403 (w), 1299 (m), 1248 (s), 1215 (w), 1170 (w), 1122 (m), 1040 (s), 1019 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.29 (d, 1H, J=2.8 Hz), 2.96 (s, 1H), 2.86 (s, 1H), 1.59 (m, 2H), 1.27 (m, 1H), 1.11 (dm, 1H, J=1.8 Hz), 0.95 (td, 1H, J=9.4, 2.1 Hz), 0.83 (td, 1H, J=9.4, 2.2 Hz), 0.07 (s, 9H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 148.8, 145.0, 48.8, 44.5, 43.2, 24.7, 24.6, −1.6.

4.2.3. 1,5,6-Tris(methoxycarbonyl)bicyclo[2.2.1]hept-2-ene (9b). NaOMe (24.3 mg, 0.450 mmol) was added to a solution of norbornene **9a** (114 mg, 0.513 mmol) in MeOH (1 mL) cooled to 0°C, and the reaction mixture was stirred for 15 min. Methyl iodide (0.150 mL, 2.41 mmol) was added to the reaction mixture at 0°C, and the reaction mixture was warmed to room temperature and stirred for 24 h. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes=2:3) to give **9b** (81.4 mg, 0.303 mmol, 67%) as a white solid. R_f 0.20 (EtOAc/hexanes=2:3); IR (CH_2Cl_2) 3063 (m), 2998 (s), 2954 (s), 2880 (w), 2847 (w), 1724 (s), 1437 (m), 1368 (s), 1202 (s), 1121 (s), 1074 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.47 (d, 1H, J=5.6 Hz), 6.23 (dd, 1H, J=5.6, 3.0 Hz), 3.75 (s, 3H), 3.70 (d, 1H, J=10.4 Hz), 3.60 (s, 6H), 3.52 (dd, 1H, J=10.4, 3.5 Hz), 3.25 (m, 1H), 1.75 (d_{AB}d 1H, J=8.5, 1.7 Hz), 1.68 (br. d, 1H, J=8.5 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 172.6, 171.9, 171.5, 134.74, 134.71, 61.2, 53.1, 52.2, 51.7, 51.0, 49.3, 47.1. HRMS calcd for $C_{13}H_{16}O_6$: m/z 268.0947, found m/z 268.0950.

4.2.4. Cycloaddition of norbornene 8a with benzonitrile oxide (2a). A solution of **18** (49.2 mg, 0.359 mmol) in toluene (1 mL) was added to a flame-dried flask containing norbornene **8a** (187 mg, 1.99 mmol), $(BOC)_2O$ (124 mg, 0.569 mmol), DMAP (5.2 mg, 0.043 mmol), and toluene (2 mL) via a cannula. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give **14a** (55.2 mg, 0.259 mmol, 72%) as a light yellow solid. R_f 0.24 (EtOAc/hexanes=1:19); IR (CH_2Cl_2) 3066 (w), 3044 (w), 2969 (s), 2878 (m), 1594 (w), 1500 (w), 1446 (m), 1354 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.71 (m, 2H), 7.39 (m, 3H), 4.64 (d, 1H, J=8.4 Hz), 3.50 (d, 1H, J=8.4 Hz), 2.63 (m, 1H) 2.53 (m, 1H), 1.51–1.61 (m, 3H), 1.36 (m, 1H), 1.20 (m, 2H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 156.8, 129.6, 129.3, 128.6, 126.8, 87.8, 57.0, 43.0, 39.2, 32.3, 27.4, 22.7. Anal. Calcd for $C_{14}H_{15}NO$: C, 78.84; H, 7.09. Found C, 78.80; H, 7.23.

4.2.5. Cycloaddition of 2-substituted-2-norbornene 8b with benzonitrile oxide (2a). A solution of **18** (17.9 mg, 0.131 mmol) in $CHCl_3$ (0.2 mL) was added to a flame-dried vial containing norbornene **8b** (20.3 mg, 0.114 mmol), $(BOC)_2O$ (83.8 mg, 0.384 mmol), DMAP (5.5 mg, 0.045 mmol), and $CHCl_3$ (1.6 mL) via a cannula and rinsed with $CHCl_3$ (0.2 mL). The reaction mixture was stirred at 60°C for 6 days. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (Et_2O/hexanes=1:49) to give **14b** (16.9 mg, 0.0568 mmol, 50%) as a clear, transparent liquid. R_f 0.16 (EtOAc/hexanes=1:49); IR (neat) 3060 (w), 2961 (s), 2930 (s), 2872 (s), 2858 (s), 1705 (w), 1592 (m), 1563 (m), 1464 (s), 1445 (s), 13257 9s), 1326 (m), 1310 (m), 1266 (m), 1235 (w), 1073 (w), 1025 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.69 (m, 2H), 7.37 (m, 3H), 2.90 (d, 1H, J=1.6 Hz), 2.55 (d, 1H, J=4.0 Hz), 2.49 (d, 1H, J=4.3 Hz), 1.24–1.74 (m, 15H), 1.19 (dd, 1H, J=10.4, 1.5 Hz), 0.87 (t, 3H, J=6.9 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 157.0, 129.8, 129.4, 128.6, 126.6, 96.7, 61.1, 45.6, 40.8, 35.0, 34.5, 31.7, 29.7, 27.4, 24.1, 23.1, 22.6, 14.1. Anal. Calcd for $C_{20}H_{27}NO$: C, 80.76; H, 9.15. Found C, 80.88; H, 9.01.

4.2.6. Cycloaddition of 2-substituted-2-norbornene 8c with benzonitrile oxide (2a). A solution of **18** (18.9 mg, 0.138 mmol) in $CHCl_3$ (0.2 mL) was added to a flame-dried vial containing norbornene **8c** (8.9 mg, 0.0535 mmol), $(BOC)_2O$ (41.6 mg, 0.191 mmol), DMAP (4.9 mg, 0.040 mmol), and $CHCl_3$ (1.6 mL) via a cannula and rinsed with $CHCl_3$ (0.2 mL). The reaction mixture was stirred at room temperature for 48 h. The solvent was removed by rotary evaporation, and the crude product was purified by

column chromatography (Et_2O/hexanes=1:49) to give **14c** (8.4 mg, 0.0294 mmol, 55%) as white crystals. R_f 0.15 (Et_2O/hexanes=1:49); IR (CH_2Cl_2) 1965 (s), 2878 (w), 1594 (w), 1445 (w), 1351 (m), 1260 (s), 1005 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.72 (m, 2H), 7.38 (m, 3H), 3.29 (s, 1H), 2.68 (d, 1H, J=4.4 Hz), 2.52 (d, 1H, J=4.3 Hz), 1.62 (m, 2H), 1.48 (tt, 1H, J=12.8, 4.7 Hz), 1.37 (m, 1H), 1.26 (m, 1H), 1.19 (ddd, 1H, J=10.4, 2.7, 1.3 Hz), 0.13 (s, 9H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 156.6, 129.8, 129.4, 128.0, 126.8, 91.3, 59.3, 46.3, 40.8, 34.4, 26.9, 22.6, −2.8. Anal. Calcd for $C_{17}H_{23}SiNO$: C, 71.53; H, 8.12. Found C, 71.94; H, 7.84.

4.2.7. Cycloaddition of 2-substituted-2-norbornene 8d with benzonitrile oxide (2a). A solution of **18** (37.1 mg, 0.271 mmol) in $CHCl_3$ (1.2 mL) was added to a flame-dried vial containing norbornene **8d** (19.3 mg, 0.116 mmol), $(BOC)_2O$ (124.5 mg, 0.570 mmol), DMAP (10.8 mg, 0.088 mmol), and $CHCl_3$ (1.6 mL) via a cannula and rinsed with $CHCl_3$ (0.2 mL). The reaction mixture was stirred at 60°C for 10 days. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:19) to give **14d** (18.1 mg, 0.0634 mmol, 55%) as white crystals. R_f 0.22 (EtOAc/hexanes=1:19); IR (CH_2Cl_2) 3065 (w), 2976 (s), 2883 (m), 1733 (s), 1446 (m), 1358 (m), 1324 (w), 1290 (s), 1210 (s), 1180 (m), 1156 (m), 1050 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.72 (m, 2H), 7.40 (m, 3H), 4.26 (m, 2H), 3.90 (d, 1H, J=1.7 Hz), 2.83 (d, 1H, J=3.6 Hz), 2.60 (d, 1H, J=4.0 Hz), 1.47–1.75 (m, 4H), 1.33 (t, 3H, J=7.1 Hz), 1.32 (m, 1H), 1.29 (m, 1H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 169.6, 157.5, 130.0, 128.7, 127.0, 96.5, 61.7, 58.7, 45.5, 40.7, 34.6, 26.7, 22.2, 14.1. Anal. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71. Found C, 71.24; H, 6.85.

4.2.8. Cycloaddition of 1-substituted-2-norbornene 9b with benzonitrile oxide (2a). A solution of **18** (51.6 mg, 0.376 mmol) in $CHCl_3$ (1.2 mL) was added to a flame-dried vial containing norbornene **9b** (32.7 mg, 0.122 mmol), $(BOC)_2O$ (182.8 mg, 0.838 mmol), DMAP (10.0 mg, 0.082 mmol), and $CHCl_3$ (1.6 mL) via a cannula and rinsed with $CHCl_3$ (0.2 mL). The reaction mixture was stirred at 60°C for 7 days. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=2:3) to give an inseparable mixture of **18a** and **18b** (41.3 mg, 0.107 mmol, 87%, **18a**:**18b**=80:20 measured by 400 MHz ^1H NMR) as a light yellow solid. R_f 0.43 (EtOAc/hexanes=2:3); IR (CH_2Cl_2) 3065 (m), 2998 (m), 2954 (m), 2848 (m), 1740 (s), 1499 (m), 1437 (s), 1366 (s), 1213 (s), 1175 (m), 1125 (m), 1069 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.90 (m, 1.6H), 7.69 (m, 0.4H), 7.40 (m, 3H), 5.23 (dd, 0.2H, J=8.3, 1.4 Hz), 5.10 (dd, 0.8H, J=8.1, 1.3 Hz), 4.96 (d, 0.2H, J=8.2 Hz), 4.62 (dd, 0.8H, J=8.1, 1.3 Hz), 3.80 (s, 2.4H), 3.76 (s, 0.6H), 3.72 (s, 2.4H), 3.71 (s, 2.4H), 3.70 (s, 0.6H), 3.49 (d, 0.8H, J=11.9 Hz), 3.41 (dd, 0.2H, J=12.2, 4.8 Hz), 3.18 (d, 0.2H, J=12.3 Hz), 3.14 (dd, 0.8H, J=11.9, 3.6 Hz), 3.06 (dd, 0.2H, J=2.9, 1.0 Hz), 2.88 (s, 0.6H), 2.81 (m, 0.8H), 2.21 (dd, 0.2H, J=11.1, 1.5 Hz), 2.02 (dd, 0.8H, J=11.2, 1.6 Hz), 1.71 (dd, 0.8H, J=11.2, 1.4 Hz), 1.61 (dd, 0.2H, J=11.1, 1.4 Hz),; ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ major isomer **18a**: 171.3, 170.7, 170.6, 157.5, 130.1, 128.8, 128.4, 127.1, 84.2, 61.4, 52.4, 52.34, 51.9, 51.8, 47.9, 46.4, 42.3, 35.7; visible peaks of minor isomer **18b**: 128.7, 126.5, 85.0, 52.29, 52.2, 51.1, 46.0, 45.4, 44.8, 37.8. HRMS calcd for $C_{20}H_{21}NO_7$: m/z 387.1318, found m/z 387.1290.

4.2.9. Cycloaddition of *exo*-2-substituted-5-norbornene 10a with benzonitrile oxide (2a). A solution of **18** (50.6 mg, 0.369 mmol) in $CHCl_3$ (1 mL) was added to a flame-dried vial containing norbornene **10a** (39.3 mg, 0.258 mmol) and DMAP (5.3 mg, 0.043 mmol) via a cannula and rinsed with $CHCl_3$ (1 mL). $(BOC)_2O$ (85.2 mg, 0.390 mmol) was then added to the reaction mixture. The reaction mixture was stirred at room temperature for 72 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **25a** and **26a** (55.3 mg, 0.204 mmol, 79%, **25a**:**26a**=54:46 measured by 400 MHz ^1H NMR) as a light yellow solid. R_f 0.22 (EtOAc/hexanes=1:19); IR (neat) 3000 (m), 2966 (s), 2952 (s), 2887 (w), 1733 (s), 1593 (w), 1565 (w), 1497 (w), 1355 (s), 1290 (w), 1213 (s), 1159 (m), 1058 (m), 1040 (m), 1025 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.71 (m, 2H), 7.40 (m, 3H), 4.72 (d, 0.46H, J=8.9 Hz), 4.69 (d, 0.54H, J=8.6 Hz), 3.71 (s, 1.38H), 3.69 (s, 1.62H), 3.60 (d, 0.54H, J=8.2 Hz), 3.56 (d, 0.46H, J=8.2 Hz), 2.90 (s, 0.46H), 2.80 (s, 0.54H), 2.71 (d, 0.54H, J=4.7 Hz), 2.61 (d, 0.46H, J=3.6 Hz), 2.51 (ddd, 0.54H, J=8.8, 4.8, 1.4 Hz), 2.34 (dd, 0.46H, J=8.8, 5.7 Hz), 2.00 (m, 1H), 1.67 (ddd, 0.54H, J=11.4, 8.9, 2.4 Hz), 1.54–1.43 (m, 2.46 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ major isomer **25a**: 175.0, 156.0, 129.86, 128.9, 128.74, 126.8, 87.3, 57.0, 51.99, 43.0, 42.8, 39.1, 30.49, 27.4; minor isomer **26a**: 174.9, 156.6, 129.87, 128.9, 128.71, 126.8, 87.1, 56.9, 52.05, 47.1, 44.5, 40.3, 32.0, 30.53. Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found C, 70.54; H, 6.46.

4.2.10. Cycloaddition of *exo*-2-substituted-5-norbornene 10b with benzonitrile oxide (2a). A solution of **18** (50.6 mg, 0.369 mmol) in $CHCl_3$ (1 mL) was added to a flame-dried vial containing norbornene **10b** (30.3 mg, 0.275 mmol) via a cannula and rinsed with $CHCl_3$ (2×0.5 mL). Et_3N (0.020 mL, 0.143 mmol) and phenylisocyanate (0.090 mL, 0.828 mmol) were added. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=2:3) to give an inseparable mixture of **25b** and **26b** (52.0 mg, 0.227 mmol, 82%, **25b**:**26b**=50:50 measured by 400 MHz ^1H NMR) as white crystals. R_f 0.14 (EtOAc/hexanes=2:3); IR (CH_2Cl_2) 3412 (br. s), 3060 (m), 2971 (s), 2939 (s), 1648 (m), 1593 (m), 1498 (w), 1445 (s), 1356 (s), 1316 (m), 1265 (m), 1071 (s), 1027 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 7.70 (m, 2H), 7.38 (m, 3H), 4.63 (d, 0.5H, J=8.4 Hz), 4.60 (d, 0.5H, J=8.3 Hz), 3.99 (d, 0.5H, J=6.3 Hz), 3.89 (d, 0.5H, J=6.1 Hz), 3.47 (d, 0.5H, J=8.3 Hz), 3.43 (d, 0.5H, J=8.2 Hz), 2.65 (d, 0.5H, J=4.6 Hz), 2.63 (s, 0.5H), 2.58 (d, 0.5H, J=3.8 Hz), 2.47 (s, 0.5H), 1.91 (ddd, 0.5H, J=13.3, 6.9, 2.4 Hz), 1.80–1.61 (m, 2.5H), 1.53–1.48 (m, 1H), 1.44 (ddd, 0.5H, J=13.4, 4.3, 2.8 Hz), 1.37 (ddd, 0.5H, J=13.9, 5.0, 1.5 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 156.6, 155.9, 129.8, 128.8, 128.7, 126.7, 87.3, 84.6, 72.6, 69.3, 56.8, 53.2, 51.8, 47.1,

42.0, 40.3, 38.6, 35.7, 28.8, 28.5. HRMS calcd for $C_{14}H_{15}NO_2$: *m/z* 229.1103, found *m/z* 229.1100.

4.2.11. Cycloaddition of *exo*-2-substituted-5-norbornene 10c with benzonitrile oxide (2a). A solution of **18** (25.1 mg, 0.183 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **10c** (31.6 mg, 0.141 mmol), $(BOC)_2O$ (47.5 mg, 0.218 mmol), DMAP (5.1 mg, 0.042 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give an inseparable mixture of **25c** and **26c** (40.0 mg, 0.116 mmol, 82%, **25c**:**26c**=50:50 measured by 400 MHz ^{1}H NMR) as a white solid. R_f 0.31 (EtOAc/hexanes=1:19); IR (CH_2Cl_2) 2956 (s), 1931 (s), 2887 (m), 2852 (m), 1472 (m), 1446 (m), 1357 (m), 1330 (w), 1274 (s), 1173 (w), 1094 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (m, 2H), 7.40 (m, 3H), 4.59 (d, 0.5H, *J*=8.2 Hz), 4.57 (d, 0.5H, *J*=8.2 Hz), 3.87 (d, 0.5H, *J*=6.3 Hz), 3.77 (d, 0.5H, *J*=6.2 Hz), 3.43 (d, 0.5H, *J*=8.2 Hz), 3.37 (d, 0.5H, *J*=8.2 Hz), 2.61 (d, 0.5H, *J*=4.8 Hz), 2.54 (s, 0.5H), 2.53 (d, 0.5H, *J*=4.7 Hz), 2.36 (s, 0.5H), 1.83 (ddd, 0.5H, *J*=13.0, 6.7, 2.3 Hz), 1.31–1.69 (m, 3.5H), 0.88 (s, 4.5H), 0.87 (s, 4.5H), 0.08 (s, 3H), 0.07 (s, 1.5H), 0.06 (s, 1.5H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 156.6, 155.9, 129.8, 129.2, 129.1, 128.73, 128.69, 126.8, 126.7, 87.7, 84.8, 73.0, 69.7, 57.0, 53.1, 52.0, 47.4, 42.0, 41.5, 38.5, 36.5, 29.0, 28.6, 25.80, 25.76, 18.02, 17.98, −4.66, −4.73, −4.8. Anal. Calcd for $C_{20}H_{29}SiNO_2$: C, 69.92; H, 8.51. Found C, 69.54; H, 8.40.

4.2.12. Cycloaddition of *exo*-2-substituted-5-norbornene 10d with benzonitrile oxide (2a). A solution of **18** (29.8 mg, 0.217 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **10d** (31.1 mg, 0.157 mmol), $(BOC)_2O$ (53.9 mg, 0.247 mmol), DMAP (5.2 mg, 0.043 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=2:3) to give an inseparable mixture of **25d** and **26d** (46.8 mg, 0.147 mmol, 94%, **25d**:**26d**=50:50 measured by 400 MHz ^{1}H NMR) as a clear, transparent liquid. R_f 0.41 (EtOAc/hexanes=2:3); IR (neat) 3060 (w), 2972 (s), 2920 (s), 2886 (s), 2818 (m), 1592 (m), 1565 (m), 1497 (m), 1446 (s), 1357 (s), 1241 (w), 1190 (w), 1047 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.68 (m, 2H), 7.38 (m, 3H), 7.47 (2ABq, 2H), 4.62 (d, 0.5H, *J*=8.3 Hz), 4.59 (d, 0.5H, *J*=8.3 Hz), 3.85 (d, 0.5H, *J*=6.8 Hz), 3.76 (dd, 0.5H, *J*=7.0, 2.1 Hz), 3.65–3.74 (m, 2H), 3.52–3.59 (m, 2H), 3.46 (d, 0.5H, *J*=8.3 Hz), 3.41 (d, 0.5H, *J*=8.3 Hz), 3.40 (s, 1.5H), 3.36 (s, 1.5H), 2.77 (s, 0.5H), 2.62 (d, 0.5H, *J*=5.1 Hz), 2.61 (s, 0.5H), 2.56 (d, 0.5H, *J*=3.9 Hz), 1.86 (ddd, 0.5H, *J*=13.3, 7.0, 2.2 Hz), 1.67 (ddd, 0.5H, *J*=13.9, 6.9, 2.1 Hz), 1.43–1.58 (m, 3H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 156.5, 155.8, 129.8, 129.0, 128.9, 128.70, 128.66, 126.74, 126.72, 94.2, 94.0, 87.6, 84.8, 77.4, 73.9, 71.7, 67.0, 66.9, 59.0, 58.95, 57.0, 53.2, 48.9, 44.2, 41.8, 38.4, 38.1, 33.4, 29.4, 28.9. HRMS calcd for $C_{18}H_{23}NO_4$: *m/z* 317.1627, found *m/z* 317.1630.

4.2.13. Cycloaddition of *exo*-2-substituted-5-norbornene 10e with benzonitrile oxide (2a). A solution of **18** (29.7 mg, 0.217 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **10e** (33.5 mg, 0.167 mmol), $(BOC)_2O$ (54.2 mg, 0.248 mmol), DMAP (4.9 mg, 0.040 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **25e** and **26e** (50.8 mg, 0.159 mmol, 95%, **25e**:**26e**=53:47 measured by 400 MHz ^{1}H NMR) as a clear, transparent liquid. R_f 0.22 (EtOAc/hexanes=1:9); IR (neat) 3062 (w), 3030 (s), 2938 (s), 2881 (m), 1592 (w), 1564 (w), 1497 (m), 1446 (s), 1356 (s), 1318 (w), 1266 (w), 1208 (w), 1173 (w), 1093 (s), 1028 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (m, 2H), 7.41 (m, 3H), 7.35 (m, 5H), 4.61 (d, 0.53H, *J*=8.2 Hz), 4.60 (d, 0.47H, *J*=8.2 Hz), 4.52 (AB, 2H), 3.66 (d, 0.53H, *J*=6.5 Hz), 3.57 (dd, 0.47H, *J*=6.8, 1.5 Hz), 3.48 (d, 0.47H, *J*=8.2 Hz), 3.37 (d, 0.53H, *J*=8.2 Hz), 2.88 (s, 0.47H), 2.66 (d, 0.53H, *J*=4.4 Hz), 2.65 (s, 0.53H), 2.59 (d, 0.47H, *J*=4.0 Hz), 1.86 (ddd, 0.53H, *J*=13.2, 6.9, 2.4 Hz), 1.50–1.69 (m, 3.47H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 156.6, 155.8, 138.2, 129.8, 129.0, 128.9, 128.71, 128.68, 128.4, 127.63, 127.61, 127.58, 126.8, 126.7, 87.7, 84.9, 79.7, 76.3, 70.73, 70.70, 57.1, 53.3, 48.0, 43.6, 41.9, 38.4, 38.1, 33.3, 29.3, 29.0. HRMS calcd for $C_{21}H_{21}NO_2$: *m/z* 319.1572, found *m/z* 319.1570.

4.2.14. Cycloaddition of *exo*-2-substituted-5-norbornene 10f with benzonitrile oxide (2a). A solution of **18** (37.0 mg, 0.270 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **10f** (28.6 mg, 0.188 mmol), $(BOC)_2O$ (67.0 mg, 0.307 mmol), DMAP (5.5 mg, 0.045 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **25f** and **26f** (48.3 mg, 0.178 mmol, 95%, **25f**:**26f**=62:38 measured by 400 MHz ^{1}H NMR) as a clear, transparent liquid. R_f 0.35 (EtOAc/hexanes=1:4); IR (neat) 3060 (w), 2978 (s), 2944 (s), 2888 (m), 1750 (s), 1593 (w), 1565 (w), 1498 (w), 1446 (m), 1376 (m), 1359 (s), 1320 (w), 1247 (s), 1207 (m), 1062 (s), 1017 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.66 (m, 2H), 7.35 (m, 3H), 4.74 (dm, 0.62H, *J*=5.3 Hz), 4.62–4.67 (m, 0.76H), 4.58 (d, 0.62H, *J*=8.2 Hz), 3.50 (d, 1H, *J*=8.2 Hz), 2.71 (s, 0.38H), 2.63 (d, 0.62H, *J*=4.8 Hz), 2.57 (s, 0.62H), 2.56 (d, 0.38H, *J*=4.2 Hz), 2.00 (s, 1.14H), 1.98 (s, 1.86H), 1.73 (ddd, 0.62H, *J*=14.2, 6.9, 1.2 Hz), 1.44–1.55 (m, 3.38H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer **25f**: δ 170.4, 155.4, 129.7, 128.6, 128.2, 126.55, 87.0, 74.6, 52.8, 44.2, 41.9, 32.8, 29.1, 21.0; minor isomer **26f**: δ 170.3, 156.3, 129.7, 128.5, 127.1, 126.58, 84.1, 71.7, 56.6, 48.7, 38.4, 37.9, 29.5, 21.0. Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found C, 70.67; H, 6.38.

4.2.15. Cycloaddition of 2-substituted-5-norbornene 10g with benzonitrile oxide (2a). A solution of **18** (48.1 mg, 0.351 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **10g** (30.1 mg, 0.278 mmol), $(BOC)_2O$ (89.7 mg, 0.411 mmol), DMAP (5.0 mg, 0.041 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction

mixture was stirred at room temperature for 1 days. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **25g** and **26g** (56.0 mg, 0.246 mmol, 89%, **25g**:**26g**=57:43 measured by 400 MHz ^{1}H NMR) as a white solid. R_f 0.22 (EtOAc/hexanes=1:4); IR (CH_2Cl_2) 3063 (w), 2950 (w), 1752 (s), 1447 (m), 1409 (w), 1355 (m), 1263 (m), 1156 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (m, 2H), 7.41 (m, 3H), 4.90 (d, 1H, J=8.2 Hz), 3.90 (d, 0.57H, J=8.2 Hz), 3.86 (d, 0.43H, J=8.2 Hz), 3.06 (s, 0.43H), 3.05 (d, 0.57H, J=2.5 Hz), 3.01 (d, 0.43H, J=2.4 Hz), 2.81 (s, 0.57H), 2.09–2.26 (m, 1H), 1.87–2.03 (m, 2H), 1.74 (m, 1H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer **25g**: δ 213.5, 154.5, 130.2, 128.9, 128.0, 126.7, 86.5, 58.1, 52.2, 42.6, 39.9, 31.4; minor isomer **26g**: δ 212.8, 156.6, 130.2, 128.9, 128.2, 126.8, 82.8, 56.8, 51.8, 44.4, 39.6, 32.0. Anal. Calcd for $C_{14}H_{13}NO_2$: C, 73.99; H, 5.77. Found C, 73.65; H, 5.86.

4.2.16. Cycloaddition of *endo*-2-substituted-5-norbornene 11a with benzonitrile oxide (2a). A solution of **18** (49.4 mg, 0.360 mmol) in $CHCl_3$ (1 mL) was added to a flame-dried vial containing norbornene **11a** (42.8 mg, 0.281 mmol) and $(BOC)_2O$ (87.5 mg, 0.401 mmol) via a cannula and rinsed with $CHCl_3$ (2×0.5 mL). DMAP (5.4 mg, 0.044 mmol) was added to the reaction mixture. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **25h** and **26h** (34.8 mg, 0.128 mmol, 46%, **25h**:**26h**=50:50 measured by 400 MHz ^{1}H NMR) as a clear, transparent oil. R_f 0.42 (EtOAc/hexanes=1:4); IR (neat) 3056 (m), 2973 (s), 2953 (s), 2886 (m), 2843 (w), 1734 (s), 1593 (w), 1564 (w), 1499 (m), 1446 (m), 1436 (m), 1356 (s), 1309 (m), 1267 (m), 1197 (m), 1116 (m), 1041 (m), 1023 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (m, 2H), 7.39 (m, 3H), 4.67 (d, 0.5H, J=8.3 Hz), 4.66 (d, 0.5H, J=8.3 Hz), 3.81 (s, 1.5H), 3.72 (s, 1.5H), 3.70 (dd, 0.5H, J=8.3, 1.4 Hz), 3.66 (dd, 0.5H, J=8.4, 0.9 Hz), 2.95 (d, 0.5H, J=4.8 Hz), 2.88–2.81 (m, 1.5H), 2.68 (d, 0.5H, J=5.2 Hz), 2.567 (d, 0.5H, J=3.7 Hz), 1.91–1.78 (m, 1.5H), 1.67–1.62 (m, 1H), 1.56 (ddd, 0.5H, J=13.4, 4.8, 2.4 Hz), 1.35 (dd, 0.5H, J=2.9, 1.4 Hz), 1.33 (dd, 0.5H, J=2.9, 1.4 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 174.3, 174.1, 156.9, 156.5, 129.9, 129.8, 129.0, 128.75, 128.73, 126.8, 126.7, 87.1, 84.3, 56.7, 52.3, 51.9, 46.2, 43.8, 43.6, 42.3, 41.3, 40.1, 34.0, 33.4, 30.3, 26.0. Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found C, 70.43; H, 6.37.

4.2.17. Cycloaddition of *endo*-2-substituted-5-norbornene 11b with benzonitrile oxide (2a). A solution of **18** (55.6 mg, 0.405 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **11b** (35.6 mg, 0.323 mmol), $(BOC)_2O$ (106.5 mg, 0.488 mmol), DMAP (5.1 mg, 0.042 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=3:2) to give an inseparable mixture of **25i** and **26i** (53.6 mg, 0.234 mmol, 72%, **25i**:**26i**=58:42 measured by 400 MHz ^{1}H NMR) as a white solid. R_f 0.33 (EtOAc/hexanes=2:3); IR (CH_2Cl_2) 3608 (s), 3061 (m), 2971 (s), 2890 (w), 2868 (m), 1594 (w), 1471 (w), 1446 (m), 1357 (w), 1244 (w), 1152 (m), 1121 (w), 1072 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (m, 2H), 7.38 (m, 3H), 5.27 (d, 0.42H, J=8.4 Hz), 4.74 (d, 0.58H, J=8.3 Hz), 4.33 (m, 1H), 4.30 (d, 0.58H, J=8.3 Hz), 3.74 (d, 0.42H, J=8.4 Hz), 2.77 (d, 0.42H, J=4.5 Hz), 2.56 (d, 0.58H, J=5.4 Hz), 2.54 (d, 0.58H, J=4.2 Hz), 2.49 (dd, 0.42H, J=4.5 Hz), 2.41 (br. s, 0.58H), 2.25 (br. s, 0.42H), 2.04 (m, 1H), 1.54 (m, 0.84H), 1.28 (m, 1.16H), 1.18 (dt, 0.42H, J=13.2, 3.4 Hz), 0.88 (dt, 0.58H, J=13.2, 3.4 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer **25i**: δ 157.5, 129.8, 129.07, 128.66, 126.9, 87.4, 70.5, 48.4, 45.4, 43.8, 33.5, 31.2; minor isomer **26i**: δ 157.0, 129.8, 129.06, 128.70, 126.8, 82.7, 69.7, 57.1, 49.2, 40.2, 37.7, 31.9. Anal. Calcd for $C_{14}H_{15}NO_2$: C, 73.34; H, 6.59. Found C, 73.65; H, 6.48.

4.2.18. Cycloaddition of *endo*-2-substituted-5-norbornene 11c with benzonitrile oxide (2a). A solution of **18** (25.5 mg, 0.186 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **11c** (30.5 mg, 0.136 mmol), $(BOC)_2O$ (45.1 mg, 0.207 mmol), DMAP (5.3 mg, 0.043 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give an inseparable mixture of **25j** and **26j** (42.0 mg, 0.122 mmol, 90%, **25j**:**26j**=50:50 measured by 400 MHz ^{1}H NMR) as a white solid. R_f 0.35 (EtOAc/hexanes=1:19); IR (CH_2Cl_2) 2957 (s), 2885 (s), 2857 (s), 1593 (w), 1565 (m), 1472 (s), 1446 (m), 1359 (s), 1275 (s), 1154 (s), 1122 (s), 1093 (s), 1071 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70 (m, 2H), 7.38 (m, 3H), 5.24 (d, 0.5H, J=8.4 Hz), 4.71 (d, 0.5H, J=8.3 Hz), 4.27 (d, 0.5H, J=8.3 Hz), 4.20 (m, 1H), 3.71 (d, 0.5H, J=8.4 Hz), 2.69 (d, 0.5H, J=4.5 Hz), 2.55 (d, 0.5H, J=5.1 Hz), 2.46 (d, 0.5H, J=4.4 Hz), 2.43 (d, 0.5H, J=3.9 Hz), 1.93 (m, 1H), 1.50 (m, 1H), 1.23 (m, 1H), 1.12 (dt, 0.5H, J=12.9, 3.2 Hz), 0.95 (s, 4.5H), 0.90 (s, 4.5H), 0.83 (dt, 0.5H, J=13.3, 3.3 Hz), 0.12 (s, 1.5H), 0.081 (s, 1.5H), 0.079 (s, 1.5H), 0.06 (s, 1.5H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 157.5, 156.9, 129.6, 129.4, 129.3, 128.6, 126.77, 126.76, 87.5, 83.1, 70.9, 70.0, 57.0, 49.5, 48.6, 45.9, 43.7, 40.1, 38.8, 34.2, 31.5, 30.7, 25.8, 18.02, 17.99, −4.7, −4.89, −4.94. HRMS calcd for $C_{20}H_{29}SiNO_2$: m/z 343.1968, found m/z 343.1965.

4.2.19. Cycloaddition of *endo*-2-substituted-5-norbornene 11d with benzonitrile oxide (2a). A solution of **18** (28.1 mg, 0.205 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **11d** (32.6 mg, 0.164 mmol), $(BOC)_2O$ (59.0 mg, 0.270 mmol), DMAP (5.2 mg, 0.043 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=2:3) to give an inseparable mixture of **25k** and **26k** (44.6 mg, 0.141 mmol, 86%, **25k**:**26k**=55:45 measured by 400 MHz ^{1}H NMR) as a clear, transparent liquid. R_f 0.40 (EtOAc/hexanes=2:3); IR (neat) 3060 (w), 2969 (s), 2940 (s), 2887 (s), 2818 (m), 1592 (w), 1564 (w), 1498 (w), 1446 (s), 1355 (w), 1307 (w), 1244 (w), 1177 (s), 1085 (s), 1048 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70

(m, 2H), 7.37 (m, 3H), 5.13 (d, 0.45H, J=8.4 Hz), 4.80 (AB, 1.1H), 4.73 (AB, 0.9H), 4.70 (d, 0.55H, J=8.0 Hz), 4.10–4.19 (m, 1.55H), 3.67–3.77 (m, 2.45H), 3.56–3.59 (m, 2H), 3.40 (s, 1.35H), 3.38 (s, 1.65H), 2.87 (d, 0.45H, J=4.4 Hz), 2.64 (d, 0.55H, J=3.8 Hz), 2.57 (d, 0.55H, J=5.2 Hz), 2.49 (d, 0.45H, J=4.5 Hz), 2.05 (ddd, 0.45H, J=13.2, 10.2, 4.8 Hz), 1.99 (ddd, 0.55H, J=13.6, 10.4, 5.4 Hz), 1.55 (d, 0.45H, J=16 Hz), 1.52 (d, 0.55H, J=1.6 Hz), 1.24 (m, 1.45H), 0.97 (dt, 0.55H, J=13.6, 3.5 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 157.1, 156.8, 129.7, 129.2, 129.1, 128.65, 128.62, 126.8, 126.7, 94.9, 94.8, 87.4, 82.8, 75.8, 74.3, 71.7, 67.4, 67.2, 59.0, 57.1, 49.1, 47.2, 43.30, 43.25, 39.6, 35.6, 31.4, 31.1, 30.8. HRMS calcd for $C_{18}H_{23}NO_4$: m/z 317.1627, found m/z 317.1620.

4.2.20. Cycloaddition of *endo*-2-substituted-5-norbornene 11e with benzonitrile oxide (2a). A solution of **18** (49.9 mg, 0.364 mmol) in $CHCl_3$ (1 mL) was added to a flame-dried vial containing norbornene **11e** (55.0 mg, 0.275 mmol) and DMAP (5.3 mg, 0.043 mmol) via a cannula and rinsed with $CHCl_3$ (2×0.5 mL). $(BOC)_2O$ (88.9 mg, 0.407 mmol) was added then to the reaction mixture. The reaction mixture was stirred at room temperature for 72 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give an inseparable mixture of **25l** and **26l** (67.1 mg, 0.210 mmol, 76%, **25l**:**26l**=51:49 measured by 400 MHz ^{1}H NMR) as a clear, transparent liquid. R_f 0.25 (EtOAc/hexanes=1:9); IR (neat) 3062 (w), 3031 (w), 2968 (s), 2875 (m), 1592 (w), 1564 (m), 1498 (m), 1475 (m), 1353 (s), 1310 (w), 1267 (m), 1207 (w), 1155 (s), 1121 (w), 1095 (s), 1072 (s), 1027 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.73–7.66 (m, 2H), 7.41–7.30 (m, 8H), 5.20 (d, 0.49H, J=8.4 Hz), 4.75 (d, 0.51H, J=8.4 Hz), 4.61–4.46 (m, 2H), 4.21 (d, 0.49H, J=8.3 Hz), 4.04–3.96 (m, 1H), 3.74 (d, 0.51H, J=8.5 Hz), 2.97 (d, 0.49H, J=4.3 Hz), 2.70 (d, 0.51H, J=3.7 Hz), 2.55 (m, 1H), 2.18–1.95 (m, 1H), 1.60–1.55 (m, 1H), 1.34–1.24 (m, 1.49H), 1.04 (dt, 0.51H, J=13.6, 3.5 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 157.2, 156.9, 138.1, 138.0, 129.7, 129.3, 129.2, 128.69, 128.65, 128.5, 128.4, 127.8, 127.7, 127.6, 127.5, 126.8, 126.7, 87.5, 82.7, 77.9, 76.6, 71.6, 71.5, 57.1, 48.9, 46.4, 43.2, 42.8, 39.6, 35.7, 31.5, 31.2, 30.9. Anal. Calcd for $C_{21}H_{21}NO_2$: C, 78.97; H, 6.63. Found C, 78.62; H, 6.44.

4.2.21. Cycloaddition of *endo*-2-substituted-5-norbornene 11f with benzonitrile oxide (2a). A solution of **18** (35.1 mg, 0.256 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **11f** (32.0 mg, 0.210 mmol), $(BOC)_2O$ (70.4 mg, 0.323 mmol), DMAP (5.1 mg, 0.042 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **25m** and **26m** (54.2 mg, 0.200 mmol, 95%, **25m**:**26m**=55:45 measured by 400 MHz ^{1}H NMR) as a white solid. R_f 0.34 (EtOAc/hexanes=1:4); IR (CH_2Cl_2) 3064 (w), 2980 (m), 2947 (w), 1731 (s), 1446 (m), 1376 (m), 1356 (m), 1247 (s), 1146 (w), 1047 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.71 (m, 2H), 7.39 (m, 3H), 5.10 (d, 0.45H, J=8.4 Hz), 5.05 (dt, 0.45H, J=10.1, 4.0 Hz), 4.98 (dt, 0.55H, J=10.1, 4.0 Hz), 4.73 (d, 0.55H, J=8.3 Hz), 4.04 (d, 0.55H, J=8.3 Hz), 3.72 (d, 0.45H, J=8.4 Hz), 2.93 (d, 0.45H, J=4.5 Hz), 2.79 (d, 0.55H, J=3.8 Hz), 2.62 (d, 0.55H, J=5.2 Hz), 2.54 (d, 0.45H, J=4.2 Hz), 2.17 (m, 1H), 2.14 (s, 1.65H), 2.06 (s, 1.35H), 1.57 (m, 1H), 1.33 (m, 1H), 1.23 (dt, 0.45H, J=13.6, 3.4 Hz), 1.00 (dt, 0.55H, J=14.0, 3.5 Hz); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer **25m**: δ 170.8, 156.5, 129.9, 128.87, 128.73, 126.67, 87.1, 73.3, 49.2, 43.2, 43.0, 31.4, 31.2, 21.1; minor isomer **26m**: δ 170.7, 156.6, 129.8, 128.91, 128.71, 126.74, 82.4, 71.7, 57.0, 46.8, 39.6, 35.6, 30.9, 20.9. Anal. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32. Found C, 70.47; H, 6.41.

4.2.22. Cycloaddition of *exo*-2-substituted-5-norbornene 10f with nitrile oxide 2b. A solution of benzoylnitromethane (35.0 mg, 0.212 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **10f** (24.9 mg, 0.164 mmol), $(BOC)_2O$ (56.2 mg, 0.258 mmol), DMAP (5.4 mg, 0.044 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction mixture was stirred at room temperature for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:9) to give an inseparable mixture of **27b** and **28b** (14.8 mg, 0.0494 mmol, 30%, **27b**:**28b**=50:50 measured by 400 MHz ^{1}H NMR) as a clear, transparent liquid. R_f 0.31 (EtOAc/hexanes=1:4); IR (neat) 3062 (w), 2977 (s), 2890 (w), 1742 (s), 1651 (s), 1582 (m), 1567 (m), 1468 (w), 1448 (m), 1361 (s), 1246 (s), 1211 (m), 1149 (m), 1055 (s), 1017 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.13 (m, 2H), 7.58 (m, 1H), 7.46 (t, 2H, J=7.7 Hz), 4.76 (d, 0.5H, J=8.4 Hz), 4.74 (d, 0.5H, J=8.5 Hz), 4.67 (d, 1H, J=7.7 Hz), 4.19 (dd, 1H, J=8.4, 2.0 Hz), 2.80 (s, 0.5H), 2.72–2.75 (m, 1.5H), 2.04 (s, 1.5H), 2.02 (s, 1.5H), 1.98 (ddd, 0.5H, J=14.0, 7.2, 2.5 Hz), 1.81 (ddd, 0.5H, J=14.4, 6.9, 2.3 Hz), 1.43–1.68 (m, 3H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) δ 186.3, 186.1, 170.5, 170.3, 157.7, 156.8, 136.1, 133.54, 133.52, 130.3, 128.3, 88.7, 86.0, 74.5, 71.7, 56.3, 52.6, 49.0, 44.3, 42.3, 38.7, 37.9, 33.7, 29.7, 29.6, 21.13, 21.11. Anal. Calcd for $C_{17}H_{17}NO_4$: C, 68.22; H, 5.72. Found C, 67.88; H, 5.83.

4.2.23. Cycloaddition of *exo*-2-substituted-5-norbornene 10f with nitrile oxide 2c. A solution of nitroethane (25.1 mg, 0.334 mmol) in $CHCl_3$ (0.8 mL) was added to a flame-dried vial containing norbornene **10f** (39.5 mg, 0.260 mmol), $(BOC)_2O$ (86.6 mg, 0.397 mmol), DMAP (5.0 mg, 0.041 mmol), and $CHCl_3$ (0.7 mL) via a cannula. The reaction mixture was stirred at 60°C for 24 h. The solvent was removed by rotary evaporation, and the crude product was purified by column chromatography (EtOAc/hexanes=1:4) to give an inseparable mixture of **27c** and **28c** (29.2 mg, 0.140 mmol, 54%, **27c**:**28c**=62:38 measured by 400 MHz ^{1}H NMR) as a clear, transparent liquid. R_f 0.42 (EtOAc/hexanes=2:3); IR (neat) 2975 (s), 2888 (w), 1737 (s), 1627 (w), 1467 (m), 1439 (s), 1386 (s), 1360 (s), 1334 (m), 1314 (m), 1248 (s), 1197 (m), 1173 (m), 1059 (s), 1018 (s), 1033 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.63 (dm, 0.62H, J=7.0 Hz), 4.57 (dd, 0.38H, J=7.1, 1.8 Hz), 4.47 (d, 0.38H, J=8.2 Hz), 4.40 (d, 0.62H, J=8.2 Hz), 2.99 (d, 0.62H, J=8.2 Hz), 2.97 (d, 0.38H, J=8.2 Hz), 2.63 (s, 0.38H), 2.56 (d, 0.62H, J=4.9 Hz), 2.43 (s, 0.62H), 2.42 (d, 0.38H, J=5.0 Hz), 2.02 (s, 1.86H), 2.01

(s, 1.14H), 1.895 (s, 1.14H), 1.894 (s, 1.86H), 1.85 (ddd, 0.38H, J=13.8, 7.2, 2.6 Hz), 1.74 (m, 0.38H), 1.67 (ddd, 0.62H, J=14.3, 7.1, 2.3 Hz), 1.41–1.57 (m, 2.62H); ^{13}C NMR (APT, $CDCl_3$, 100 MHz) major isomer **27c**: δ 170.5, 154.0, 85.5, 74.9, 56.5, 43.2, 41.9, 32.9, 29.0, 21.2, 11.9; minor isomer **28c**: δ 170.6, 155.0, 82.6, 71.8, 60.3, 48.7, 38.0, 37.3, 29.4, 21.1, 11.7. HRMS calcd for $C_{11}H_{15}NO_3$: m/z 209.1052, found m/z 209.1050.

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