Intramolecular 1,3-Dipolar Cycloadditions of Norbornadiene-Tethered Nitrile Oxides

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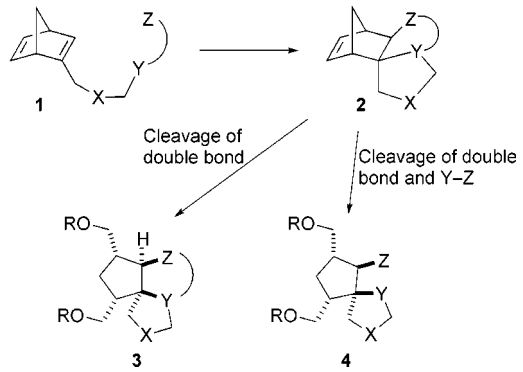
Efficient routes to the synthesis of norbornadiene-tethered nitrile oxides have been developed, and their intramolecular 1,3-dipolar cycloadditions were studied. The cycloadditions occurred in good yields for a variety of substrates and were found to be highly regio- and stereoselective, giving single regio- and stereoisomers in most cases.

Introduction

Cycloaddition reactions are among the most powerful methods for the construction of rings.[1] In particular, intramolecular cycloadditions with high regio- and stereocontrol are important tools for the efficient assembly of complex molecular structures. We have recently initiated a program on the study of various types of intramolecular cycloadditions of substituted norbornadienes. Our long-term goal is to develop an efficient route for the construction of angular fused tricyclic frameworks and spirocyclic frameworks with high regio- and stereocontrol (Scheme 1).

1,3-Dipolar cycloadditions offer a convenient one-step route for the construction of a variety of complex five-membered heterocycles.[2] 1,3-Dipolar cycloadditions of nitrile oxides are well-documented and provide efficient entries to the synthesis of 2-isoxazolines.[3] Reductive cleavage of the N−O bond of 2-isoxazolines has proven to be a useful routes to amino ketones, oxo alcohols, and a number of natural products.[2,3] Here we report our results on the intramolecular 1,3-dipolar cycloadditions of norbornadiene-tethered nitrile oxides.[4a]

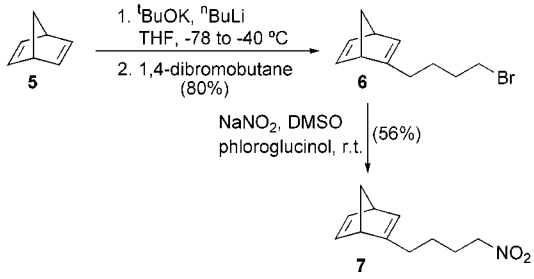
Scheme 1. General Outline for Construction of Tricyclic and Spirocyclic Frameworks via Intramolecular Cycloadditions of Norbornadienes and Subsequent Cleavage of the Cycloadducts



Results and Discussion

One of the most common methods to prepare nitrile oxides is dehydration of the corresponding nitroalkanes. An efficient route to the synthesis of norbornadiene-tethered nitro compound **7** was developed, and **7** served as a precursor of the required nitrile oxide for the cycloaddition (Scheme 2). Deprotonation of norbornadiene **5** with Schlosser's base (^{t}BuOK/^{n}BuLi) in THF at −78 °C,[5] followed by addition of the resulting norbornadienyl anion to an excess of 1,4-dibromobutane, provided the norbornadiene-tethered bromide **6**. Displacement of the bromide with $NaNO_2$ in the presence of phloroglucinol[6] in DMSO afforded the required nitro compound **7**. As NO_2^- is an ambident anion, both nitrogen atom and oxygen atom could act as the nucleophile, leading to the

Scheme 2. Synthesis of Norbornadiene-Tethered Nitro Compound 7



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(1) (a) *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon: Oxford, 1991; Vol. 5, Chapters 1−9. (b) *Advances in Cycloaddition*; JAI Press: Greenwich, 1988−1999; Vols. 1−6. (c) Lautens, M.; Klute, W.; Tam, W. *Chem. Rev.* **1996**, *96*, 49.

(2) (a) *1,3-Dipolar Cycloaddition Chemistry*; Padwa, A., Ed.; John Wiley & Sons: New York, 1984; Vols. 1 and 2. (b) Gothelf, K. V.; Jø rgensen, K. A. *Chem. Rev.* **1998**, *98*, 863.

(3) (a) Kozikowski, A. P. *Acc. Chem. Res.* **1984**, *17*, 410. (b) Curran, D. P. In *Advances in Cycloaddition*; Curran, D. P., Ed.; JAI Press: Greenwich, 1988; Vol. 1, pp 129−189. (c) *Nitrile Oxides, Nitrones, and Nitronates in Organic Synthesis*; Torssell, K. B. G., Ed.; VCH: New York, 1988. (d) Kanemasa, S.; Tsuge, O. *Heterocycles* **1990**, *30*, 719.

(4) (a) Preliminary results of this work have been published as a communication: Yip, C.; Handerson, S.; Jordon, R.; Tam, W. *Org. Lett.* **1999**, *1*, 791. (b) For a similar study on nitrone cycloaddition, see: Tranmer, G. K.; Keech, P.; Tam, W. *Chem. Commun.* **2000**, 863.

(5) (a) Stäble, M.; Lehmann, R.; Kramar, J.; Schlosser, M. *Chimia* **1985**, *39*, 229. (b) Brandsma, L.; Verkuruijsse, H. D. *Recl. Trav. Chim. Pays-Bas* **1986**, *105*, 66.

(6) *Organic Functional Group Preparation*; Sandler S. R., Karo, W., Eds.; Academic Press: New York, 1968; Vol. 1, pp 425−429.

10.1021/jo005611o CCC: $20.00
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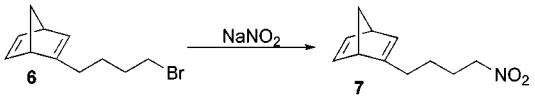
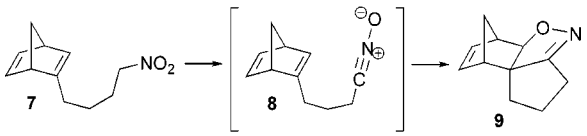
Table 1. Conversion of Bromide 6 to Nitro Compound 7



entry	solvent[a]	temp[b] (°C)	additive	yield[c] (%)
1	DMF	25	none	30[d]
2	DMF	25	phloroglucinol	44[e]
3	DMF	60	phloroglucinol	48[e]
4	DMSO	25	none	37[d]
5	DMSO	25	phloroglucinol	56[e]
6	DMSO	60	phloroglucinol	55[e]

[a] Much lower yields were obtained with other solvents such as THF, CH_2Cl_2, and toluene. [b] All reactions were stirred for 48 h. [c] Isolated yields after column chromatography. [d] 20−30% of the corresponding nitrite was obtained. [e] <10% of the corresponding nitrite was obtained.

Table 2. Three Different Methods to Generate Nitrilie Oxide 8 and Cycloadduct 9



entry	method	solvent	temp[a] (°C)	yield[b] (%)
1	PhNCO, Et_3N	toluene	90	54
2		$CHCl_3$	60	76
3	EtOCOCl, Et_3N, DMAP	toluene	90	25
4		$CHCl_3$	60	72
5	$(BOC)_2O$, DMAP	toluene	90	**86**
6		$CHCl_3$	60	61

[a] All reactions were stirred for 48 h. [b] Isolated yields after column chromatography.

desired nitro compound (RNO_2) and the undesired nitrite (RONO). In the absence of phloroglucinol, a significant amount of the corresponding nitrite was obtained and the yield of nitro compound **7** was much lower (Table 1).

The most commonly used method for converting nitroalkanes to the corresponding nitrile oxides is the Mukaiyama aromatic isocyanate method.[7] Thus, treatment of norbornadiene-tethered nitro compound **7** with phenyl isocyanate and Et_3N in toluene or $CHCl_3$ provided the cycloadduct **9** in 54% and 76% yields (Table 2, entries 1 and 2). Two other methods were employed to generate the corresponding nitrile oxide in situ from **7**, the Shimizu ethyl chloroformate method (Table 2, entries 3 and 4)[8] and the Hassner $(BOC)_2O$/DMAP method (Table 2, entries 5 and 6).[9] The use of $(BOC)_2O$ and DMAP in toluene at 90 °C was found to be the best method in our system, giving the highest yield in the cycloaddition.

Four different cycloadducts are theoretically possible in the cycloaddition (Scheme 3). Cycloaddition of the tethered nitrile oxide on the C_2-C_3 double bond from the *exo* and *endo* faces would provide the *exo* and *endo* cycloadducts **9** and **10**. Formation of the cycloadducts **11** (with the distal C_5-C_6 double bond) and **12** (with both of the double bonds in the norbornadiene) are not very likely as a result of the high strain in these resulting molecules. The intramolecular cycloaddition of the norbornadiene-tethered nitrile oxide **8** was found to be highly

Scheme 3. Possible Cycloadducts

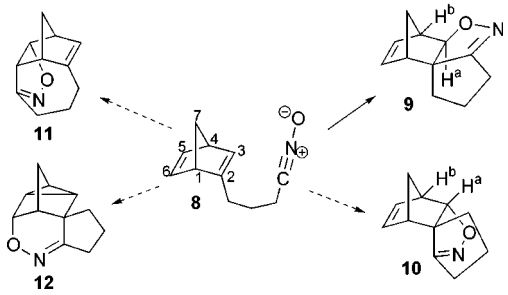
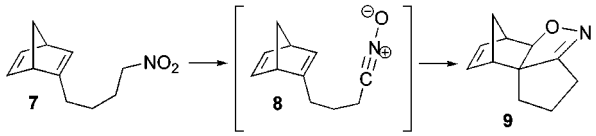


Table 3. Effect of Solvent



entry	solvent	temp[a] (°C)	yield[b] (%)
1	hexanes	60	50
2	THF	60	76
3	Et_2O	35	39
4	DME	90	72
5	1,2-dichloroethane	80	67
6	$CHCl_3$	60	61
7	toluene	90	**86**

[a] All reactions were carried out using the $(BOC)_2O$/DMAP method and were stirred for 48 h. [b] Isolated yields after column chromatography.

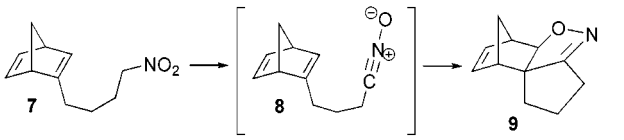
regio- and stereoselective, giving the *exo* cycloadduct **9** as a single regio- and stereosomer. It is noteworthy to mention here that the intermolecular 1,3-dipolar cycloaddition of norbornadiene with benzonitrile oxide is known to produce a 4:1 *exo*/*endo* cycloadducts.[10]

The regio- and stereochemistry of the cycloadduct **9** was proven by NMR techniques. The presence of two olefinic protons in the ^1H NMR spectrum eliminated the possibilities of cycloadducts **11** and **12** (Scheme 3). The *exo* and *endo* stereochemistry of the cycloadduct can easily be distinguished by the coupling constant of H^a and H^b in the ^1H NMR.[11] As the dihedral angle between H^a and H^b in the *exo* cycloadduct **9** is close to 90°, the coupling constant between H^a and H^b would be very small ($J \approx 0-2$ Hz). In the *endo* cycloadduct **10**, the dihedral angle between H^a and H^b is approximately 42° and would give a doublet with $J \approx 5$ Hz.[12] NOESY NMR experiment also provided an additional confirmation of the *exo* stereochemistry of the cycloadduct.

To optimize the yield of the cycloaddition, the effect of different solvents and different reaction temperatures on the cycloaddition of norbornadiene-tethered nitro compound **7**, using the $(BOC)_2O$ and DMAP method, were studied (Tables 3 and 4). Among various solvents tested, toluene was found to be the best choice, giving the highest yield in the cycloaddition (Table 3, entry 7). An increase

(7) Mukaiyama, T.; Hoshino, T. *J. Am. Chem. Soc.* **1960**, *82*, 5339.
(8) Shimizu, T.; Hayashi, T.; Shibafuchi, H.; Teramura, K. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2827.
(9) Basel, Y.; Hassner, A. *Synthesis* **1997**, 309.
(10) De Micheli, C.; Gandolfi, R.; Oberti, R. *J. Org. Chem.* **1980**, *45*, 1209.
(11) (a) Flautt, T. J.; Erman, W. F. *J. Am. Chem. Soc.* **1963**, *85*, 3212. (b) Mazzocchi, P. H.; Stahly, B.; Dodd, J.; Rondan, N. G.; Domelsmith, L. N.; Rozeboom, M. D.; Caramella, P.; Houk, K. N. *J. Am. Chem. Soc.* **1980**, *102*, 6482.
(12) The *exo* and *endo* cycloadducts **9** and **10** were modeled for energy minimization at the PM3 level (CS Chem 3D Pro Version 3.5.1) using MOPAC for the assessment of the dihedral angles between H^a and H^b. These dihedral angles were then compared to the Karplus curve for the determination of the theoretical coupling constants.

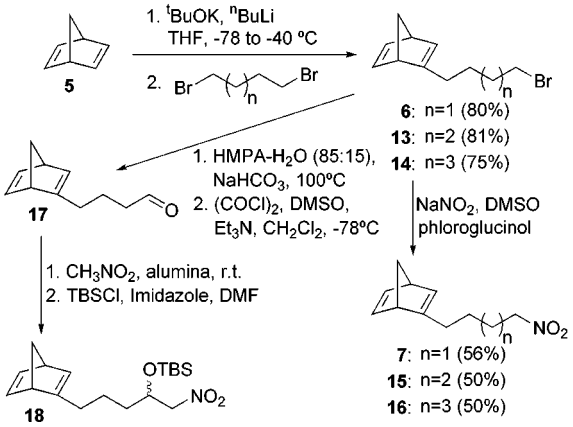
Table 4. Effect of Temperature



entry	solvent	temp[a] (°C)	yield[b] (%)
1	toluene	25	46
2	toluene	60	66
3	toluene	90	**86**
4	toluene	110	70

[a] All reactions were carried out using the $(BOC)_2O$/DMAP method and were stirred for 48 h. [b] Isolated yields after column chromatography.

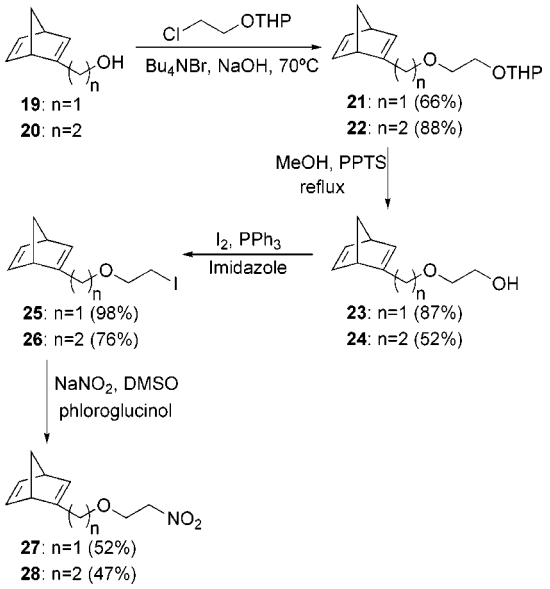
Scheme 4. Synthesis of All-Carbon Tethered Nitro Compounds 7, 15, 16, and 18



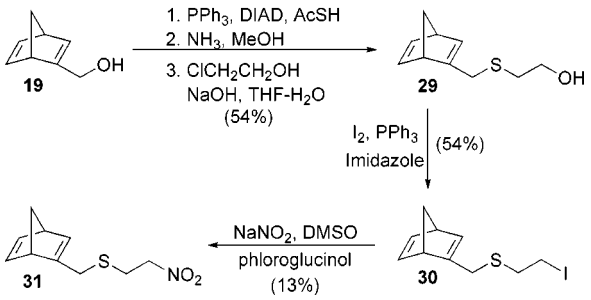
in temperature from 25 to 90 °C led to an increase in yield (Table 4, entries 1−3), but further increase in temperature to 110 °C led to a lower yield, probably as a result of decomposition of the cycloadduct **9**. In two control experiments, when pure cycloadduct **9** was resubmitted to the cycloaddition conditions at 90 and 110 °C for 48 h, 96% of the cycloadduct was recovered for the reaction at 90 °C but only 72% of the cycloadduct was recovered for the reaction at 110 °C. This proved that cycloadduct **9** tends to decompose slowly at temperature above 90 °C. Thus, under the optimized conditions, by using the $(BOC)_2O$ and DMAP method in toluene at 90 °C for 48 h, norbornadiene-tethered nitro compound **7** was converted to the cycloadduct **9** as a single regio- and stereoisomer in 86% yield.

To study the generality of the cycloaddition, a variety of norbornadiene-tethered nitro compounds were synthesized (Schemes 4−6) and subjected to the optimized cycloaddition conditions (Table 5). Nitro compounds **15** and **16** were synthesized using the same protocol as nitro compound **7** (Scheme 4). Nitro compound **18** with an α-silyl ether substituent was synthesized through the following sequence: hydration and Swern oxidation to the corresponding aldehyde **17**;[13] addition of nitromethane in the presence of alumina,[14] followed by TBS-protection (Scheme 4). Nitro compounds with an oxygen atom within the tether were prepared as shown in Scheme 5. Norbornadiene-tethered allylic and homoallylic alcohols **19** and **20** were prepared according to literature procedures.[5b]

Scheme 5. Synthesis of Nitro Compounds (27 and 28) with an Oxygen Atom within the Tether



Scheme 6. Synthesis of Nitro Compound (31) with a Sulfur Atom within the Tether

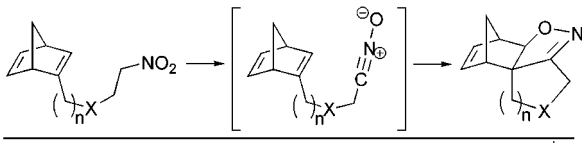


Two-carbon homologation of **19** and **20** to the alcohols **23** and **24** was achieved by a two-step sequence.[15] Conversion of the alcohols **23** and **24** to the corresponding iodides **25** and **26** using I_2, PPh_3, and imidazole[16] followed by displacement with $NaNO_2$ afforded the nitro compounds **27** and **28**. Nitro compound **31**, with a sulfur atom within the tether, was prepared as in Scheme 6. Conversion of the alcohol **19** to the corresponding thiol was achieved using the Mitsunobu conditions followed by hydrolysis of the thioacetate.[17] Two-carbon homologation of the thiol with 2-chloroethanol and NaOH produced alcohol **29**. Conversion of the alcohol **29** to the corresponding iodide **30** using I_2, PPh_3, and imidazole followed by displacement with $NaNO_2$ afforded the nitro compound **31**.

The results of the intramolecular 1,3-dipolar cycloadditions of norbornadiene-tethered nitrile oxides generated from the nitro compounds **7**, **15**, **16**, **18**, **27**, **28**, and **31** are shown in Table 5. Similar to the 3-carbon tethered nitrile oxide **8** (generated in situ from nitro compound **7**), which provided cycloadduct **9** as the single cycloadduct (Table 5, entry 1), cycloaddition of the 4-carbon tethered nitrile oxide (generated in situ from nitro compound **15**) was also highly regio- and stereoselective, giving the *exo*

(13) Lautens M.; Edwards, L. G.; Tam, W.; Lough, A. J. *J. Am. Chem. Soc.* **1995**, *117*, 10276.
(14) Rosini, G.; Ballini, R.; Sorrenti, P. *Synthesis* **1983**, 1014.
(15) Heinze, I.; Knoll, K.; Mòller, R.; Eberbach, W. *Chem. Ber.* **1989**, *122*, 2147.
(16) Lange, G. L.; Gottardo, C. *Synth. Commun.* **1990**, *20*, 1473.
(17) McClure, K. F.; Renold, P.; Kemp, D. S. *J. Org. Chem.* **1995**, *60*, 454.

Table 5. Intramolecular 1,3-Dipolar Cycloaddition of Norbornadiene-tetherd Nitrile Oxides



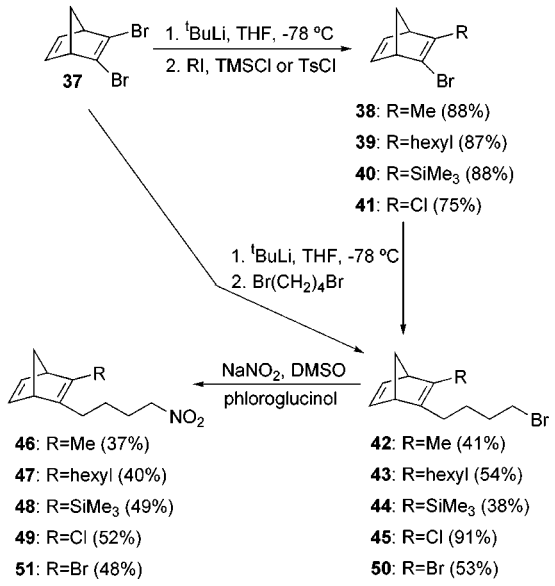
Entry	Nitro compound	Cycloadduct[a]		Yield[b]
1	**7**: n=1	**9**: n=1	n=1	86%
2	**15**: n=2	**32**: n=2	n=2	75%
3	**16**: n=3		n=3	0%[c]
4	**18**	**33**		78%
5	**27**: n=1	**34**: n=1	n=1	69%
6	**28**: n=2	**35**: n=2	n=2	52%[d]
7	**31**	**36**		61%

[a] Typical cycloaddition conditions: $(BOC)_2O$ (2−3 equiv) in toluene was added to the nitroalkane, DMAP (10 mol %) in toluene ,and the reaction mixture was stirred at 90 °C for 24−96 h. [b] Isolated yields after column chromatograph. [c] No cycloadduct was obtained. [d] Accompanied with an unidentified product (∼20%).

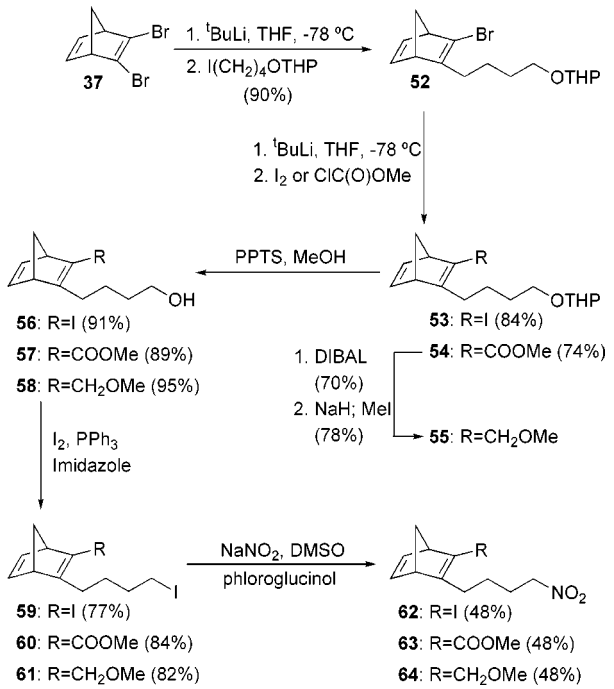
cycloadduct **32** as the only cycloadduct in good yield (Table 5, entry 2). However, no cycloadduct was formed with the corresponding 5-carbon tethered nitrile oxide (Table 5, entry 3). In this case, only polymeric material was obtained. As the length of the tether increases, the rate of intramolecular cycloaddition decreases and side reactions such as rearragement and dimerization of the nitrile oxide, and polymerization could occur. Nitrile oxide generated from nitro compound **18** with an α-silyl ether substituent also provided the corresponding *exo* cycloadduct **33** in good yield (Table 5, entry 4). Formation of the five- and six-membered ring cycloadducts, **34** and **35**, with an oxygen atom within the tether were also found to be successful, giving moderate yields of the cycloadducts (Table 5, entries 5 and 6). In case of the cycloaddition with the nitrile oxide generated from nitro compound **28**, other than the *exo* cycloadduct **35**, an unidentified product (∼20%) was also detected.[18] This is the only case where we observed a product other than the *exo* cycloadducts in the cycloadditions. Cycloaddition of the nitrile oxide generated from nitro compound **31**, with a sulfur atom within the tether, was also found to be successful, giving cycloadduct **36** in moderate yield (Table 5, entry 7). Thus, except with nitro compound **28**, in all other cases, the cycloadditions were found to be highly regio- and stereoselective, giving single regio- and stereoisomers in moderate to good yields.

(18) Based on ^{1}H NMR, the minor product is likely to be the *endo* cycloadduct.

Scheme 7. Synthe sis of Nitro Compounds 46−49 and 51



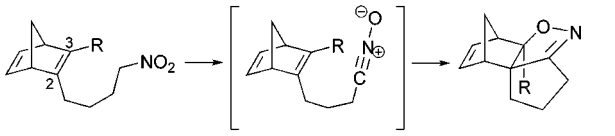
Scheme 8. Synthesis of Nitro Compounds 62−64



The regio- and stereochemistry of the cycloadducts were confirmed by using NMR techniques as described earlier with cycloadduct **9**. The small coupling constant between H^a and H^b (Scheme 3) of cycloadducts **9** and **32**−**36** in ^{1}H NMR (normally a singlet or a doublet with J < 1.5 Hz) indicated the *exo* stereochemistry of the cycloadducts. NOESY NMR experiments also provided an additional confirmation of the *exo* stereochemistry of the cycloadducts.

To investigate the effect of a C_3 subtitutent on the norbornadiene in the cycloaddition, nitro compounds **46**−**49**, **51**, and **62**−**64** were prepared (Schemes 7 and 8). Monolithium-halide exchange of 2,3-dibromonorbornadiene **37** with ^{t}BuLi, followed by trapping the resulting organolithiums with methyl iodide, hexyl iodide, TMSCl, and TsCl, provided bromides **38**−**41** in good yields (Scheme 7).[19] A second lithium-halide exchange of these

Table 6. Intramolecular 1,3-Dipolar Cycloaddition of C_3-Substituted Norbornadiene-Tethered Nitrile Oxides



entry	R	nitro compound	cycloadduct[a]	yield[b] (%)
1	H	**7**	**9**	86
2	Me	**46**	**65**	82
3	hexyl	**47**	**66**	83
4	$SiMe_3$	**48**	**67**	0[c]
5	Cl	**49**	**68**	89
6	Br	**51**	**69**	69
7	I	**62**	**70**	5[d]
8	COOMe	**63**	**71**	71
9	CH_2OMe	**64**	**72**	66

[a] Typical cycloaddition conditions: $(BOC)_2O$ (2−3 equiv) in toluene was added to the nitroalkane, DMAP (10 mol %) in toluene, and the reaction mixture was stirred at 90 °C for 24−96 h. [b] Isolated yields after column chromatograph. [c] No cycloadduct was obtained. [d] Cycloadduct **70** decomposed gradually on standing at rt.

bromides followed by trapping with 1,4-dibromobutane afforded norbornadiene-tethered bromides **42**−**45**. Displacement of these bromides with $NaNO_2$ provided C_3-substituted norbornadiene-tethered nitro compounds **46**−**49**. Nitro compound **51** was synthesized by monolithium-halide exchange of 2,3-dibromonorbornadiene **37** with ^{t}BuLi followed by trapping with 1,4-dibromobutane and displacement of the resulting norbornadiene-tethered bromide **50** with $NaNO_2$. Syntheses of nitro compounds with an I, COOMe, and CH_2OMe group attached to C_3 of the norbornadiene are shown in Scheme 8. Monolithium-halide exchange of 2,3-dibromonorbornadiene **37** with ^{t}BuLi followed by trapping with THP-protected 4-iodobutanol produced **52**. A second lithium-halide exchange of **52** followed by trapping with iodine or methyl chloroformate afforded **53** and **54**. DIBAL reduction of ester **54** followed by methylation of the resulting alcohol provided **55**. Removal of the THP group in compounds **53**−**55** with PPTS in MeOH, conversion of the resulting alcohols **56**−**58** to the corresponding iodides **59**−**61** using I_2, PPh_3, and imidazole,[16] followed by displacement with $NaNO_2$, afforded C_3-substituted norbornadiene-tethered nitro compounds **62**−**64**.

We anticipated that a C_3 substitutent may retard the cycloaddition because of steric hindrance, but in fact cycloadditions of most of the nitrile oxides, generated from the C_3-substituted norbornadiene-tethered nitro compounds, occurred smoothly, giving the corresponding *exo* cycloadducts as the only regio- and stereoisomers in moderate to good yields (Table 6). With R = H, Me, and hexyl, cycloadducts **9**, **65**, and **66** were produced in the cycloadditions with yields of 82−86% (Table 6, entries 1−3). However, with a very bulky group at C_3 of norbornadiene (**48**, R = $SiMe_3$), no cycloadduct was formed. With halides at C_3 of norbornadiene, R = Cl gave a yield of 89%, R = Br gave 69% yield, and the R = I gave only 5% yield of the cycloadducts (Table 6, entries 5−7). Cycloadduct **70** (with R = I) was rather unstable and decomposed gradually upon standing even at room temperature. With an ester or an ether functionality attached to C_3 of norbornadiene, cycloadditions occurred smoothly and provided cycloadducts **71** and **72** in moderate yields (Table 6, entries 8 and 9). The regio- and stereochemistry of these cycloadducts were confirmed by using NMR techniques (HCOSY, HSQC and NOESY experiments). Furthermore, these assignments were also supported by X-ray crystallography.[20]

Conclusion

We have demonstrated the first examples of the intramolecular 1,3-dipolar cycloadditions of norbornadiene-tethered nitrile oxides. Although four possible cycloadducts could be formed in the cycloadditions, single regio- and stereoisomers were formed. Thus, these cycloadditions were found to be highly regio- and stereoselective, giving the *exo* cycloadducts in good yields. Further investigations on subsequent cleavage reactions of the cycloadducts (Scheme 1) for the construction of angular-fused tricyclic and spirocyclic frameworks are ongoing in our laboratory.

Experimental Section

General. 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.[21] Analytical thin-layer chromatography (TLC) was conducted on Merck pre-coated silica gel 60 F_{254} plates. All glassware was flame-dried under an inert atmosphere of dry nitrogen. Chemical shifts for ^{1}H NMR spectra are reported in parts per million (ppm) from tetramethylsilane with the solvent resonance as the internal standard (deuteriochloroform, 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 (deuteriochloroform, δ 77.0).

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, acetonitrile, nitromethane); from sodium (toluene); from potassium/benzophenone (THF); and from sodium/benzophenone (Et_2O). Norbornadiene (**5**), 1,5-dibromopentane, 1,6-dibromohexane, and 2-chloroethanol were purified by distillation from 4 Å molecular sieves under dry nitrogen. Substituted norbornadienes **38**−**43**, **50**, **52**, and **54** were prepared according to literature procedures.[19] Norbornadienes **6**, **17**, **19**, and **20** are known compounds, and detailed procedures for their preparation can be found in the Supporting Information.

Preparation of 2-(5-Bromopentyl)norbornadiene (13). Norbornadiene **5** (24.0 mL, 222 mmol) was added to a flame-dried three-neck flask containing potassium *tert*-butoxide (18.7 g, 167 mmol) and THF (220 mL) which was cooled at −78 °C (cryobath). *n*-Butyllithium (66.8 mL, 2.5M, 167 mmol) was added dropwise through a dropping funnel to the solution over 1 h, and the temperature was maintained below −65 °C. The reaction mixture was stirred at −65 °C for 30 min and at −40 °C for 30 min. After cooling of the mixture to −78 °C, this light brown solution was added via cannula over 30 min to a cooled flask containing 1,5-dibromopentane (100 mL, 734 mmol) in THF (80 mL) at −65 °C. The reaction mixture was stirred at −40 °C for 2 h and at 0 °C for 2 h. After the reaction mixture was quenched with saturated ammonium chloride (200 mL) and water (200 mL), the aqueous layer was extracted with diethyl ether (3 × 300 mL), and the combined organic layers

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were washed sequentially with water (400 mL) and brine (400 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by vacuum distillation to give three fractions. The first fraction (3−5 Torr at 65 °C−80 °C) contained mainly the excess 1,5-dibromopentane. The second fraction (1−3 Torr at 60 °C−70 °C) contained 1,5-dibromopentane and product in a ratio of 3:1 as determined by ^{1}H NMR. The third fraction (0.2−0.8 Torr at 70−85 °C) contained pure bromide **13** (32.5 g, 135 mmol, 81%) as a colorless oil: R_f 0.65 (hexanes); IR (neat, NaCl) 3117 (w), 3064 (w), 2966 (s), 2933 (s), 2863 (m), 1622 (w), 1555 (w), 1460 (w), 1430 (w), 1301 (m), 1262 (w), 1246 (w), 1184 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.75 (m, 2H), 6.13 (m, 1H), 3.49 (m, 1H), 3.40 (t, 2H, J = 6.8 Hz), 3.27 (m, 1H), 2.20 (m, 2H), 1.98 (dt, 1H, J = 5.7, 1.5 Hz), 1.94 (dm, 1H, J = 5.7 Hz), 1.85 (m, 2H), 1.48−1.36 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.5, 143.8, 142.3, 133.6, 73.5, 53.4, 50.0, 33.9, 32.7, 31.2, 27.8, 26.3; HRMS calcd for $C_{12}H_{17}Br$ m/z 240.0514, found m/z 240.0516.

Preparation of 2-(6-Bromohexyl)norbornadiene (14). Norbornadiene **5** (4.50 mL, 41.7 mmol) was added to a flame-dried three-neck flask containing potassium *tert*-butoxide (3.42 g, 30.5 mmol) and THF (40 mL) which was cooled at −78 °C (cryobath). *n*-Butyllithium (12.2 mL, 2.5M, 30.5 mmol) was added dropwise through a dropping funnel to the solution over 1 h, and the temperature was maintained below −65 °C. The reaction mixture was stirred at −65 °C for 30 min and at −40 °C for 30 min. After cooling of the mixture to −78 °C, this light brown solution was added via cannula over 30 min to a cooled flask containing 1,6-dibromohexane (15.0 mL, 97.6 mmol) in THF (30 mL) at −65 °C. The reaction mixture was stirred at −40 °C for 2 h and at 0 °C for 2 h. After the reaction mixture was quenched with saturated ammonium chloride (40 mL) and water (40 mL), the aqueous layer was extracted with diethyl ether (3 × 100 mL), and the combined organic layers were washed sequentially with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by vacuum distillation to give three fractions. The first fraction (4−6 Torr at 90−100 °C) contained mainly the excess 1,6-dibromohexane. The second fraction (1−2 Torr at 90−100 °C) contained 1,6-dibromohexane and product in a ratio of 5:1 as determined by ^{1}H NMR. The third fraction (0.2 Torr at 80 °C−100 °C) contained pure bromide **14** (5.83 g, 22.9 mmol, 75%) as a colorless oil: R_f 0.35 (hexanes); IR (neat, NaCl) 3116 (w), 3064 (m), 2966 (s), 2931 (s), 2857 (s), 1622 (s), 1555 (m), 1463 (m), 1430 (m), 1302 (m), 1256 (m), 1184 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.75 (m, 2H), 6.12 (m, 1H), 3.49 (br. s, 1H), 3.40 (t, 2H, J = 6.9 Hz), 3.27 (br. s, 1H), 2.19 (m, 2H), 1.96 (qt, 2H, J = 5.7, 1.6 Hz), 1.85 (p, 2H, J = 6.9 Hz), 1.47−1.36 (m, 4H), 1.28 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.7, 143.8, 142.3, 133.3, 73.4, 53.4, 50.0, 33.9, 32.7, 31.3, 28.4, 27.9, 26.9; HRMS calcd for $C_{13}H_{19}Br$ m/z 254.0671, found m/z 254.0675.

Preparation of THP-Protected Alcohol 21. To a flame-dried flask containing alcohol **19** (1.03 g, 8.46 mmol), THP-protected 2-chloroethanol[22] (2.79 g, 17.0 mmol), and tetrabutylammonium bromide (565 mg, 1.70 mmol) was added 50% NaOH (2.6 g in 2.6 mL water, 65.0 mmol) at 0 °C.[15] The reaction mixture was stirred at 70 °C for 42 h. After quenching of the reaction with saturated sodium chloride (25 mL) and water (50 mL), the aqueous layer was extracted with diethyl ether (3 × 100 mL), and the combined organic layers were washed sequentially with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:4) to give **21** (1.41 g, 5.63 mmol, 66%) as a colorless oil: R_f 0.47 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3065 (w), 2939 (s), 2868 (s), 1556 (w), 1352 (m), 1260 (w), 1202 (m), 1185 (m), 1127 (s), 1077 (s), 1036 (s), 1021 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.76 (m, 1H), 6.69 (dd, 1H, J = 5.0, 3.0 Hz), 6.43 (m, 1H), 4.61 (t, 1H, J = 3.6 Hz), 4.16 (ddd, 1H, J = 13.1, 3.0, 1.4 Hz), 4.10 (dt, 1H, J = 13.4, 1.7 Hz), 3.86−3.78 (m, 2H), 3.58−3.43 (m, 6H), 2.00 (m, 1H), 1.95 (dt, 1H, J = 5.9, 1.4 Hz), 1.80 (m, 1H), 1.69 (m, 1H), 1.62−1.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.91, 154.87, 143.2, 142.50, 142.46, 138.43, 138.39, 98.71, 98.66, 73.54, 73.50, 69.44, 69.43, 68.7, 66.48, 66.46, 62.0, 51.2, 51.1, 50.1, 30.4, 25.3, 19.3. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found C, 71.92; H, 8.89.

Preparation of THP-Protected Alcohol 22. To a flame-dried flask containing alcohol **20** (2.87 g, 21.0 mmol), THP-protected 2-chloroethanol[22] (6.97 g, 42.3 mmol), and tetrabutylammonium bromide (1.42 g, 4.28 mmol) was added 50% NaOH (6.50 g in 6.5 mL water, 163 mmol) at 0 °C.[15] The reddish-brown reaction mixture was stirred at 70 °C for 48 h. After quenching of the reaction with saturated sodium chloride (20 mL) and water (30 mL), the aqueous layer was extracted with diethyl ether (3 × 50 mL), and the combined organic layers were washed sequentially with water (50 mL) and brine (50 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:4) to give **22** (4.88 g, 18.5 mmol, 88%) as a colorless oil: R_f 0.54 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3065 (w), 2938(s), 2867 (s), 1556 (w), 1352 (w), 1307 (m), 1202 (m), 1184 (m), 1126 (s), 1077 (s), 1037 (s), 1021 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.69 (m, 2H), 6.17 (m, 1H), 4.60 (m, 1H), 3.82 (m, 2H), 3.58−3.47 (m, 6H), 3.44 (m, 1H), 3.30 (m, 1H), 2.46 (m, 2H), 1.94 (dm, 1H, J = 5.6 Hz), 1.89 (dm, 1H, J = 5.6 Hz), 1.80 (m, 1H), 1.68 (m, 1H), 1.58−1.46 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.2, 143.6, 142.3, 134.9, 98.7, 73.5, 69.9, 69.5, 66.4, 61.9, 53.5, 50.0, 31.6, 30.4, 25.3, 19.3. Anal. Calcd for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found C, 72.78; H, 9.11.

Preparation of Alcohol 23. To a flame-dried flask containing **21** (1.31 g, 5.22 mmol) in MeOH (43 mL) was added pyridium *p*-toluenesulfonate (PPTS, 143 mg, 0.569 mmol) at room temperature. The reaction mixture was stirred at 55 °C for 45 min. After quenching of the reaction with water (30 mL), the aqueous layer was extracted with diethyl ether (3 × 50 mL), and the combined organic layers were washed sequentially with water (50 mL) and brine (50 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:4) to give **23** (754 mg, 4.54 mmol, 87%) as a colorless oil: R_f 0.10 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3412 (s), 3065 (w), 2968 (s), 2934 (s), 2866 (s), 1556 (w), 1449 (w), 1351 (m), 1187 (w), 1129 (s), 1110 (s), 1064 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.77 (dd, 1H, J = 5.2, 3.1 Hz), 6.71 (dd, 1H, J = 5.1, 3.0 Hz), 6.44 (m, 1H), 4.15 (dd, 1H, J = 13.0, 1.3 Hz), 4.09 (dd, 1H, J = 13.0, 1.5 Hz), 3.67 (t, 2H, J = 4.5 Hz), 3.53 (m, 1H), 3.47−3.37 (m, 3H), 2.63 (br. s, 1H), 2.00 (dt, 1H, J = 5.9, 1.6 Hz), 1.96 (dm, 1H, J = 5.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.6, 143.2, 142.4, 138.7, 73.6, 70.9, 69.5, 61.6, 51.2, 50.1. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.49. Found C, 72.46; H, 8.43.

Preparation of Alcohol 24. To a flame-dried flask containing **22** (4.58 g, 17.3 mmol) in MeOH (140 mL) was added pyridium *p*-toluenesulfonate (PPTS, 529 mg, 2.11 mmol) at room temperature. The reaction mixture was stirred at 55 °C for 45 min. Approximately 100 mL of MeOH was removed by rotary evaporation. After quenching of the reaction with water (100 mL), the aqueous layer was extracted with diethyl ether (4 × 100 mL), and the combined organic layers were washed sequentially with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:4) to give **24** (1.61 g, 8.93 mmol, 52%) as a colorless oil: R_f 0.16 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3421 (s), 3064 (w), 2964 (s), 2933 (s), 2866 (s), 1686 (w), 1556 (w), 1457 (w), 1357 (w), 1306 (m), 1226 (w), 1122 (s), 1057 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.73 (m, 2H), 6.20 (m, 1H), 3.67 (m, 2H), 3.53 (t, 2H, J = 6.9 Hz), 3.50 (m, 2H), 3.48 (m, 1H), 3.30 (m, 1H), 2.53−2.41 (m, 3H), 1.96 (dm, 1H, J = 5.8 Hz), 1.92 (dm, 1H, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.1, 143.7, 142.3, 135.2, 73.6, 71.6, 69.2,

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61.6, 53.5, 50.0, 31.6. Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found C, 73.12; H, 8.99.

Preparation of Iodide 25. To a flame-dried flask containing PPh_3 (296 mg, 1.13 mmol), imidazole (170 mg, 2.49 mmol), acetonitrile (1.5 mL), and THF (0.5 mL) was added I_2 (318 mg, 2.51 mmol) at 0 °C. The reddish-brown reaction mixture was stirred for 15 min at 0 °C. Alcohol **23** (93.1 mg, 0.560 mmol) in acetonitrile (1 mL) was added via a cannula at 0 °C. The reaction mixture was stirred at room temperature for 5.5 h. The reaction mixture was diluted with CH_2Cl_2 (15 mL) and quenched with water (15 mL). The aqueous layer was extracted with diethyl ether (3 × 20 mL), and the combined organic layers were washed sequentially with water (20 mL) and brine (20 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:19) to give iodide **25** (151 mg, 0.55 mmol, 98%) as a colorless oil: R_f 0.40 (EtOAc/hexanes 1:19); IR (neat, NaCl) 3064 (w), 2934 (m), 2866 (m), 1556 (w), 1350 (w), 1261 (w), 1187 (m), 1126 (m), 1085 (s), 1059 (m), 1019 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.78 (dd, 1H, J = 5.1, 3.2 Hz), 6.71 (dd, 1H, J = 5.0, 3.0 Hz), 6.46 (m, 1H), 4.16 (dd, 1H, J = 12.9, 1.2 Hz), 4.10 (dd, 1H, J = 12.9, 1.5 Hz), 3.59−3.53 (m, 3H), 3.46 (m, 1H), 3.20 (t, 2H, J = 6.8 Hz), 2.01 (dt, 1H, J = 5.9, 1.5 Hz), 1.97 (dm, 1H, J = 5.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.3, 143.1, 142.3, 138.9, 73.5, 70.0, 69.0, 51.1, 50.0, 3.17; HRMS calcd for $C_{10}H_{13}IO$ m/z 276.0013, found m/z 276.0009.

Preparation of Iodide 26. To a flame-dried flask containing PPh_3 (4.38 g, 16.7 mmol), imidazole (2.51 g, 36.9 mmol), acetonitrile (15 mL), and THF (7.5 mL) was added I_2 (4.76 g, 37.5 mmol) at 0 °C. The reddish-brown reaction mixture was stirred for 15 min at 0 °C. Alcohol **24** (1.50 g, 8.33 mmol) in acetonitrile (23 mL) was added via a cannula at 0 °C. The reaction mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with CH_2Cl_2 (25 mL) and quenched with water (25 mL). The aqueous layer was extracted with diethyl ether (3 × 50 mL), and the combined organic layers were washed sequentially with water (50 mL) and brine (50 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:19) to give iodide **26** (1.85 g, 6.38 mmol, 76%) as a colorless oil: R_f 0.39 (EtOAc/hexanes 1:19); IR (neat, NaCl) 3064 (w), 2968 (m), 2932 (m), 2865 (m), 1555 (w), 1357 (w), 1306 (m), 1262 (w), 1168 (w), 1118 (s), 1098 (s), 1040 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.74 (m, 2H), 6.22 (m, 1H), 3.68 (t, 2H, J = 7.0 Hz), 3.55 (t, 2H, J = 7.0 Hz), 3.49 (m, 1H), 3.33 (m, 1H), 3.22 (t, 2H, J = 7.0 Hz), 2.48 (m, 2H), 1.99 (dt, 1H, J = 5.7, 1.6 Hz), 1.93 (dt, 1H, J = 5.7, 1.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.9, 143.7, 142.2, 135.3, 73.6, 71.3, 69.1, 53.5, 50.0, 31.6, 3.0; HRMS calcd for $C_{11}H_{15}IO$ m/z 290.0169, found m/z 290.0164.

Preparation of Alcohol 29. To a flame-dried flask containing PPh_3 (2.65 g, 10.1 mmol) in THF (25 mL) was added diisopropyl azodicarboxylate (DIAD, 1.80 mL, 9.14 mmol) dropwise at 0 °C. The pasty white reaction mixture was stirred for 30 min at 0 °C. A solution of alcohol **19** (1.03 g, 8.40 mmol) and thiolacetic acid (0.70 mL, 9.8 mmol) in THF (20 mL) was added via a cannula at 0 °C. The reaction mixture was stirred at 0 °C for 2 h and at room temperature for 1 h. The solvent was removed by rotary evaporation and the crude reaction mixture was purified by column chromatography (EtOAc/hexanes 1:19). To the crude product was added MeOH (20 mL), followed by a saturated solution of ammonia in MeOH (20 mL). The reaction mixture was stirred at room temperature for 18 h. The solvent was removed by rotary evaporation and the cloudy brown oil, 2-norbornadienylmethanethiol, was used in the next step of the procedure without further purification. To a flask containing the crude thiol was added sodium hydroxide (0.362 g, 9.18 mmol), which was dissolved in a deoxygenated mixture of H_2O (10 mL) and THF (14 mL), via a cannula at 0 °C. After 20 min, 2-chloroethanol (0.75 mL, 11.2 mmol) was added dropwise to the solution. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for 9 h. After adjusting the reaction mixture to a pH of 6 using diluted HCl, the aqueous layer was extracted with diethyl ether (3 × 25 mL). The combined organic layers were washed sequentially with water (25 mL) and brine (25 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:4) to give alcohol **29** (826 mg, 4.53 mmol, 54%) as a clear yellow oil: R_f 0.27 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3372 (br. s), 3116 (w), 3064 (m), 2978 (s), 2934 (s), 2866 (s), 1555 (m), 1417 (m), 1305 (s), 1047 (s), 1016 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.80 (m, 1H), 6.65 (dd, 1H, J = 4.2, 2.8 Hz), 6.28 (s, 1H), 3.59 (m, 2H), 3.52 (br. s, 1H), 3.37 (br. s, 1H), 3.31 (m, 2H), 2.44 (m, 2H), 2.31 (br. s, 1H), 1.98 (m, 1H), 1.95 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.5, 142.5, 142.2, 137.9, 73.0, 59.8, 52.7, 50.2, 33.4, 31.8. Anal. Calcd for $C_{10}H_{14}SO$: C, 65.89; H, 7.74. Found C, 65.91; H, 7.73.

Preparation of Iodide 30. To a flame-dried flask containing PPh_3 (2.35 g, 8.97 mmol), imidazole (1.37 g, 20.1 mmol), acetonitrile (20 mL), and THF (9 mL) was added I_2 (2.63 g, 20.7 mmol) at 0 °C. The reaction mixture was stirred for 15 m at 0 °C. Alcohol **29** (801 mg, 4.39 mmol) in acetonitrile (5 mL) was added via a cannula at 0 °C. The reaction mixture was stirred at room temperature for 3 h. After the reaction mixture was quenched with saturated sodium thiosulfate (25 mL), the aqueous layer was extracted with diethyl ether (3 × 25 mL), and the combined organic layers were washed sequentially with water (25 mL) and brine (25 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:19) to give iodide **30** (689 mg, 2.36 mmol, 54%) as a colorless oil: R_f 0.85 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3115 (w), 3063 (m), 2979 (s), 2933 (s), 2865 (m), 1554 (m), 1424 (m), 1304 (s), 1156 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.82 (m, 1H), 6.69 (m, 1H), 6.33 (m, 1H), 3.57 (br. s, 1H), 3.38 (br. s, 1H), 3.40 (d_{AB}, 1H, J = 14.0 Hz), 3.33 (d_{AB}, 1H, J = 14.0 Hz), 3.18 (m, 2H), 2.69 (m, 2H), 2.02 (m, 1H), 1.98 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.4, 142.7, 142.3, 138.3, 73.1, 52.8, 50.4, 33.1, 32.4, 3.1.

Preparation of 2-(4-Bromobutyl)-3-chloronorbornadiene (45). *tert*-Butyllithium (12.5 mL, 1.7 M, 21.3 mmol) was added to a flame-dried flask containing 2-bromo-3-chloronorbornadiene **41**[19] (2.07 g, 10.1 mmol) in THF (50 mL) at −78 °C. After the reaction mixture stirred for 1 h, the resulting yellow mixture was added to a flame-dried flask containing 1,4-dibromobutane (3.5 mL, 29.3 mmol) in THF (52 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and at room temperature for 19 h. After quenching of the reaction mixture with water (150 mL), the aqueous layer was extracted with diethyl ether (4 × 150 mL), and the combined organic layers were washed sequentially with water (150 mL) and brine (150 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by vacuum distillation to give two fractions. The first fraction (2−5.5 Torr at 70−80 °C) contained mainly the excess 1,4-dibromobutane. The second fraction (0.5 Torr at 70−80 °C) contained pure **45** (2.40 g, 9.17 mmol, 91%) as a colorless oil: R_f 0.63 (hexanes); IR (neat, NaCl) 2974 (s), 2938 (s), 2867 (m), 1639 (w), 1558 (w), 1452 (m), 1297 (s), 1267 (m), 1249 (m), 1225 (m), 1093 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.86 (dd, 1H, J = 5.0, 3.0 Hz), 6.78 (dd, 1H, J = 5.0, 3.0 Hz), 3.45 (br. s, 1H), 3.40 (t, 2H, J = 6.7 Hz), 3.38 (br. s, 1H), 2.28−2.14 (m, 3H), 2.03 (dm, 1H, J = 6.0 Hz), 1.76 (m, 2H), 1.56 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 146.4, 142.2, 141.8, 140.8, 71.2, 56.3, 52.9, 33.7, 31.9, 26.6, 25.0.

Preparation of 2-Iodo-3-(4-tetrahydropyranyloxybutyl)norbornadiene (53). *tert*-Butyllithium (8.4 mL, 1.7 M, 14.3 mmol) was added to a flame-dried flask containing bromide **52**[19] (2.12 g, 6.48 mmol) in THF (15 mL) at −78 °C. After the reaction mixture stirred for 30 min, the resulting yellow mixture was added via a cannula to a flame-dried flask containing I_2 (1.73 g, 13.6 mmol) in THF (18 mL) at −78 °C. The reaction mixture was stirred at −78 °C for 3 h and at room temperature for 30 min. After quenching of the reaction mixture with water (50 mL), the aqueous layer was extracted with diethyl ether (4 × 50 mL), and the combined organic

layers were washed sequentially with water (50 mL) and brine (50 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:19) to give **53** (2.03 g, 5.42 mmol, 84%) as a colorless oil: R_f 0.70 (EtOAc/hexanes 1:4); IR (neat, NaCl) 2938 (s), 2866 (m), 1557 (w), 1453 (w), 1440 (w), 1352 (w), 1323 (w), 1297 (m), 1259 (w), 1200 (m), 1137 (m), 1120 (m), 1077 (m), 1034 (s), 1023 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.83 (dd, 1H, J = 5.0, 2.9 Hz), 6.70 (dd, 1H, J = 5.0, 2.9 Hz), 4.56 (m, 1H), 3.85 (m, 1H), 3.72 (m, 1H), 3.57 (br. s, 1H), 3.49 (m, 1H), 3.42 (br. s, 1H), 3.38 (m, 1H), 2.25 (m, 1H), 2.17−2.10 (m, 2H), 1.99 (dm, 1H, J = 6.0 Hz), 1.82 (m, 1H), 1.70 (m, 1H), 1.60−1.44 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.5, 142.0, 141.4, 101.0, 98.8, 98.7, 72.1, 67.3, 67.2, 62.2, 60.95, 60.88, 53.4, 31.8, 30.7, 29.1, 25.4, 23.2, 19.6.

Preparation of 2-Methoxymethyl-3-(4-tetrahydropyranyloxybutyl)norbornadiene (55). To a flame-dried flask containing 2-methoxycarbonyl-3-(4-tetrahydropyranyloxybutyl) norbornadiene **54**[19] (1.84 g, 6.00 mmol) in CH_2Cl_2 (10 mL) was added DIBAL (16.0 mL, 1.0 M, 16.0 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 50 min. After quenching of the reaction mixture with water (10 mL), the aqueous layer was extracted with CH_2Cl_2 (4 × 25 mL), and the combined organic layers were washed sequentially with water (30 mL) and brine (30 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:4) to give the corresponding alcohol (1.17 g, 4.20 mmol, 70%) as a colorless oil: R_f 0.16 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3423 (m), 3062 (w), 2939 (s), 2865 (s), 1658 (w), 1556 (w), 1453 (m), 1441 (m), 1353 (m), 1323 (w), 1201 (m), 1137 (m), 1120 (m), 1076 (m), 1023 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.78 (dd, 1H, J = 5.0, 2.9 Hz), 6.71 (dd, 1H, J = 5.0, 2.9 Hz), 4.54 (m, 1H), 4.23 (d_{AB}, 1H, J = 12.2 Hz), 4.11 (d_{AB}d, 1H, J = 12.2, 2.0 Hz), 3.85 (m, 1H), 3.71 (m, 1H), 3.53 (br. s, 1H), 3.49 (m, 1H), 3.39−3.33 (m, 2H), 2.25 (m, 1H), 2.15 (m, 1H), 1.93 (dm, 1H, J = 5.8 Hz), 1.88 (dm, 1H, J = 5.8 Hz), 1.80 (m, 1H), 1.67 (m, 1H), 1.56−1.38 (m, 9H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.1, 145.7, 143.0, 142.13, 142.11, 98.79, 98.76, 71.4, 67.3, 62.34, 62.31, 58.8, 53.5, 51.87, 51.85, 30.7, 28.94, 28.92, 27.8, 25.4, 23.9, 19.62, 19.60. This alcohol (1.01 g, 3.63 mmol) in THF (1.3 mL) was added via a cannula to a flame-dried flask containing NaH (212 mg, 8.83 mmol) in THF (4 mL). The reaction mixture was stirred at room temperature for 30 min and at 30 °C for 1.5 h. Iodomethane (1.20 mL, 19.3 mmol) was then added, and the reaction mixture was allowed to stir at room temperature for 3 h. After quenching of the reaction mixture with water (20 mL), the aqueous layer was extracted with diethyl ether (4 × 20 mL), and the combined organic layers were washed sequentially with water (20 mL) and brine (20 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:9) to give **55** (831 mg, 2.84 mmol, 78%) as a colorless oil: R_f 0.55 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3064 (w), 2936 (s), 2865 (s), 2815 (m), 1658 (w), 1557 (w), 1453 (m), 1441 (m), 1376 (m), 1353 (m), 1323 (w), 1305 (w), 1260 (w), 1229 (w), 1200 (m), 1191 (m), 1160 (m), 1139 (s), 1120 (s), 1077 (s), 1035 (s), 1023 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.73 (dd, 1H, J = 5.0, 3.0 Hz), 6.65 (dd, 1H, J = 5.0, 3.1 Hz), 4.50 (m, 1H), 3.99 (d_{AB}, 1H, J = 11.8 Hz), 3.83 (d_{AB}, 1H, J = 11.8 Hz), 3.79 (m, 1H), 3.67 (m, 1H), 3.47−3.41 (m, 2H), 3.32−3.30 (m, 2H), 3.16 (s, 3H), 2.21 (m, 1H), 2.11 (m, 1H), 1.89 (dm, 1H, J = 5.8 Hz), 1.83 (dm, 1H, J = 5.8 Hz), 1.77 (m, 1H), 1.66 (m, 1H), 1.55−1.35 (m, 8H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.1, 143.4, 142.8, 141.8, 98.62, 98.60, 71.1, 67.9, 67.1, 62.1, 57.3, 53.5, 51.9, 30.6, 29.1, 27.9, 25.3, 23.9, 19.5. Anal. Calcd for $C_{18}H_{28}O_3$: C, 73.93; H, 9.65. Found C, 73.96; H, 9.64.

Preparation of Alcohol 56. To a flame-dried flask containing **53** (1.93 g, 5.15 mmol) in MeOH (43 mL) was added pyridium *p*-toluenesulfonate (PPTS, 332 mg, 1.28 mmol) at room temperature. The reaction mixture was stirred at 55 °C for 1 h. After quenching of the reaction mixture with water (50 mL), the aqueous layer was extracted with diethyl ether (4 × 50 mL), and the combined organic layers were washed sequentially with water (50 mL) and brine (50 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:4) to give **56** (1.36 g, 4.69 mmol, 91%) as a colorless oil: R_f 0.25 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3334 (s), 3066 (w), 2971 (s), 2935 (s), 2865 (s), 1653 (w), 1617 (w), 1557 (m), 1456 (m), 1296 (s), 1259 (w), 1224 (m), 1160 (w), 1052 (s), 1023 (m), 1000 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.82 (dd, 1H, J = 5.0, 2.9 Hz), 6.70 (dd, 1H, J = 5.0, 2.9 Hz), 3.63−3.57 (m, 3H), 3.41 (br. s, 1H), 2.25 (m, 1H), 2.16−2.08 (m, 2H), 2.00 (m, 1H), 1.53−1.40 (m, 5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.4, 142.0, 141.4, 101.2, 72.1, 62.5, 60.9, 53.4, 32.0, 31.8, 22.6. Anal. Calcd for $C_{11}H_{15}IO$: C, 45.54; H, 5.21. Found C, 45.84; H, 5.05.

Preparation of Alcohol 57. To a flame-dried flask containing **54** (412 mg, 1.34 mmol) in MeOH (11.2 mL) was added pyridium *p*-toluenesulfonate (PPTS, 69.3 mg, 0.276 mmol) at room temperature. The reaction mixture was stirred at 55 °C for 1 h. After quenching of the reaction mixture with water (10 mL), the aqueous layer was extracted with diethyl ether (4 × 25 mL), and the combined organic layers were washed sequentially with water (25 mL) and brine (25 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 2:3) to give **57** (265 mg, 1.19 mmol, 89%) as a colorless oil: R_f 0.35 (EtOAc/hexanes 2:3); IR (neat, NaCl) 3393 (m), 2938 (s), 2867 (m), 1700 (s), 1695 (s), 1683 (s), 1653 (m), 1628 (m), 1558 (w), 1436 (m), 1345 (m), 1295 (s), 1239 (s), 1193 (m), 1160 (m), 1103 (m), 1070 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.85 (dd, 1H, J = 5.0, 3.0 Hz), 6.68 (dd, 1H, J = 5.0, 3.2 Hz), 3.86 (br. s, 1H), 3.69 (s, 3H), 3.63 (t, 2H, J = 5.9 Hz), 3.50 (br. s, 1H), 2.77−2.63 (m, 2H), 2.01 (dm, 1H, J = 6.4 Hz), 1.95 (dm, 1H, J = 6.4 Hz), 1.79 (br. s, 1H), 1.61−1.24 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 173.6, 166.3, 143.8, 140.7, 138.6, 71.2, 62.4, 56.0, 51.0, 50.9, 32.0, 29.7, 23.0. Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found C, 70.39; H, 8.13.

Preparation of Alcohol 58. To a flame-dried flask containing **55** (690 mg, 2.36 mmol) in MeOH (20 mL) was added pyridium *p*-toluenesulfonate (PPTS, 149 mg, 0.593 mmol) at room temperature. The reaction mixture was stirred at 55 °C for 1 h. After quenching of the reaction mixture with water (20 mL), the aqueous layer was extracted with diethyl ether (4 × 40 mL), and the combined organic layers were washed sequentially with water (40 mL) and brine (40 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:4) to give **58** (466 mg, 2.24 mmol, 95%) as a colorless oil: R_f 0.30 (EtOAc/hexanes 2:3); IR (neat, NaCl) 3394 (m), 3064 (w), 2975 (s), 2934 (s), 2864 (s), 2819 (m), 1556 (w), 1451 (m), 1376 (m), 1355 (m), 1307 (m), 1190 (m), 1141 (m), 1073 (s), 1025 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.75 (dd, 1H, J = 4.8, 3.0 Hz), 6.67 (dd, 1H, J = 4.8, 3.0 Hz), 4.01 (d_{AB}, 1H, J = 11.8 Hz), 3.85 (d_{AB}, 1H, J = 11.8 Hz), 3.56 (t, 2H, J = 6.2 Hz), 3.46 (br. s, 1H), 3.34 (br. s, 1H), 3.18 (s, 3H), 2.28 (br. s, 1H), 2.19−2.26 (m, 2H), 1.91 (dm, 1H, J = 5.8 Hz), 1.85 (dm, 1H, J = 5.8 Hz), 1.34−01.55 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.3, 143.3, 142.9, 141.8, 71.2, 68.0, 62.4, 57.3, 53.5, 51.9, 32.1, 27.9, 23.5. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.68. Found C, 74.77; H, 9.79.

Preparation of Iodide 59. To a flame-dried flask containing PPh_3 (4.20 g, 16.0 mmol), imidazole (2.52 g, 37.0 mmol), acetonitrile (12 mL), and THF (8.1 mL) was added I_2 (4.30 g, 33.9 mmol) at 0 °C. The reddish-brown reaction mixture was stirred for 15 m at 0 °C. Alcohol **56** (1.06 g, 3.65 mmol) in acetonitrile (6 mL) was added via a cannula at 0 °C. The reaction mixture was stirred at room temperature for 4 h. After the reaction mixture was quenched with water (20 mL), the aqueous layer was extracted with diethyl ether (4 × 20 mL), and the combined organic layers were washed sequentially with water (20 mL), saturated sodium thiosulfate (20 mL) and brine (20 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was

purified by column chromatography (hexanes) to give iodide **59** (1.13 g, 2.82 mmol, 77%) as a colorless oil: R_f 0.80 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3065 (w), 2971 (s), 2934 (s), 2864 (m), 1616 (w), 1557 (m), 1449 (m), 1426 (m), 1295 (s), 1260 (m), 1216 (s), 1181 (m), 1163 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.85 (dd, 1H, J = 5.1, 2.9 Hz), 6.73 (dd, 1H, J = 5.1, 2.9 Hz), 3.60 (br. s, 1H), 3.43 (br. s, 1H), 3.20 (t, 2H, J = 6.8 Hz), 2.27 (m, 1H), 2.17 (dm, 1H, J = 6.0 Hz), 2.15 (m, 1H), 2.02 (dm, 1H, J = 6.0 Hz), 1.73 (m, 2H), 1.53 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.0, 142.0, 141.4, 101.6, 72.2, 61.0, 53.4, 32.5, 30.9, 27.2, 7.1.

Preparation of Iodide 60. To a flame-dried flask containing PPh_3 (1.10 g, 4.19 mmol), imidazole (651 mg, 9.56 mmol), acetonitrile (2.9 mL), and THF (2 mL) was added I_2 (1.18 g, 9.30 mmol) at 0 °C. The reddish-brown reaction mixture was stirred for 15 min at 0 °C. Alcohol **57** (216 mg, 0.970 mmol) in acetonitrile (2 mL) was added via a cannula at 0 °C. The reaction mixture was stirred at room temperature for 21 h. The reaction mixture was diluted with CH_2Cl_2 (20 mL) and quenched with water (20 mL). The aqueous layer was extracted with diethyl ether (3 × 40 mL), and the combined organic layers were washed sequentially with water (40 mL), saturated sodium thiosulfate (40 mL), and brine (40 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:9) to give iodide **60** (272 mg, 0.82 mmol, 84%) as a colorless oil: R_f 0.68 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3067 (w), 2970 (s), 2937 (s), 2867 (m), 1694 (s), 1682 (m), 1626 (s), 1558 (m), 1433 (s), 1340 (s), 1294 (s), 1249 (s), 1239 (s), 1191 (s), 1155 (s), 1102 (s), 1068 (m), 1038 (w), 1019 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.87 (dd, 1H, J = 5.0, 3.0 Hz), 6.71 (dd, 1H, J = 5.0, 3.2 Hz), 3.88 (br. s, 1H), 3.71 (s, 3H), 3.51 (br. s, 1H), 3.19 (t, 2H, J = 6.8 Hz), 2.71 (m, 2H), 2.03 (dm, 1H, J = 6.4 Hz), 1.97 (dm, 1H, J = 6.4 Hz), 1.75 (p, 2H, J = 7.1 Hz), 1.67−1.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 172.6, 166.1, 143.8, 140.7, 139.0, 71.2, 55.9, 51.1, 51.0, 32.6, 28.9, 27.5, 6.8. Anal. Calcd for $C_{13}H_{17}IO_2$: C, 47.01; H, 5.16. Found C, 46.87; H, 5.18.

Preparation of Iodide 61. To a flame-dried flask containing PPh_3 (2.56 g, 9.86 mmol), imidazole (1.54 g, 22.6 mmol), acetonitrile (8 mL), and THF (5 mL) was added I_2 (2.76 g, 21.7 mmol) at 0 °C. The reddish-brown reaction mixture was stirred for 15 m at 0 °C. Alcohol **58** (466 mg, 2.24 mmol) in acetonitrile (3 mL) was added via a cannula at 0 °C. The reaction mixture was stirred at room temperature for 3 h. After the reaction mixture was quenched with water (20 mL), the aqueous layer was extracted with diethyl ether (4 × 20 mL), and the combined organic layers were washed sequentially with water (40 mL), saturated sodium thiosulfate (40 mL), and brine (40 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:9) to give iodide **61** (584 mg, 1.84 mmol, 82%) as a colorless oil: R_f 0.44 (EtOAc/hexanes 1:9); IR (neat, NaCl) 3062 (w), 2968 (s), 2931 (s), 2863 (s), 2814 (m), 1556 (w), 1449 (m), 1376 (w), 1354 (w), 1307 (m), 1288 (m), 1216 (m), 1189 (m), 1170 (m), 1141 (m), 1098 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.79 (dd, 1H, J = 5.0, 3.0 H), 6.73 (dd, 1H, J = 5.0, 3.0 Hz), 4.02 (d_{AB}, 1H, J = 11.8 Hz), 3.88 (d_{AB}, 1H, J = 11.8 Hz), 3.50 (br. s, 1H), 3.38 (br. s, 1H), 3.23 (s, 3H), 3.17 (t, 2H, J = 6.8 Hz), 2.26 (m, 1H), 2.15 (m, 1H), 1.95 (dm, 1H, J = 5.8 Hz), 1.89 (dm, 1H, J = 5.8 Hz), 1.72 (m, 2H), 1.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.6, 144.0, 143.0, 141.9, 71.4, 68.1, 57.6, 53.6, 52.1, 32.8, 28.1, 27.1, 6.9. Anal. Calcd for $C_{13}H_{17}IO$: C, 49.07; H, 6.02. Found C, 48.91; H, 6.23.

General Procedure for the Conversion of Norbornadiene-Tethered Bromides or Iodides to Norbornadiene-Tethered Nitro Compounds (7, 15, 16, 27, 28, 31, 46, 47, 49, 51, and 62−64). Norbornadiene-tethered bromide or iodide (1 equiv) in DMSO was added via cannula to a flask containing $NaNO_2$ (2.5−3.5 equiv) and phloroglucinol (1.2−1.5 equiv) in DMSO. The light brown reaction mixture was stirred at room temperature for 8−69 h. After quenching of the reaction with water, the aqueous layer was extracted with diethyl ether and the combined organic layers were washed with water and brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography.

Nitro Compound 7. Bromide **6** (4.00 g, 17.6 mmol) in DMSO (10 mL) was added via cannula to a flask containing $NaNO_2$ (3.01 g, 43.6 mmol) and phloroglucinol (3.55 g, 21.9 mmol) in DMSO (8 mL). The light brown reaction mixture was stirred at room temperature for 48 h. After quenching of the reaction with water (100 mL), the aqueous layer was extracted with diethyl ether (4 × 40 mL) and the combined organic layers were washed with water (100 mL) and brine (100 mL) and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:9) to give **7** (1.91 g, 9.88 mmol, 56%) as a colorless viscous oil: R_f 0.40 (EtOAc/hexanes 1:9); IR (neat, NaCl) 3065 (w), 2969 (s), 2933 (s), 2866 (m), 1553 (s), 1434 (m), 1382 (m), 1301 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.73 (m, 2H), 6.15 (m, 1H), 4.35 (t, 2H, J = 7.0 Hz), 3.49 (m, 1H), 3.25 (m, 1H), 2.24 (m, 2H), 1.97−1.90 (m, 4H), 1.51 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.2, 143.7, 142.1, 134.4, 75.4, 73.4, 53.2, 50.0, 30.4, 26.7, 23.6; HRMS calcd for $C_{11}H_{15}NO_2$ m/z 193.1103, found m/z 193.1105. Anal. Calcd for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found C, 68.59; H, 7.79; N, 7.20.

Nitro Compound 15. R_f 0.43 (EtOAc/hexanes 1:19); IR (neat, NaCl) 3065 (w), 2969 (m), 2932 (m), 2864 (m), 1553 (s), 1461 (w), 1435 (m), 1383 (m), 1301 (m), 1185 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.73 (m, 2H), 6.12 (m, 1H), 4.35 (t, 2H, J = 7.0 Hz), 3.48 (m, 1H), 3.25 (m, 1H), 2.20 (m, 2H), 2.02−1.92 (m, 4H), 1.46 (m, 2H), 1.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.9, 143.7, 142.1, 133.8, 75.5, 73.4, 53.3, 49.9, 30.9, 27.1, 26.2, 25.7; HRMS calcd for $C_{12}H_{17}NO_2$ m/z 207.1259, found m/z 207.1258. Anal. Calcd for $C_{12}H_{17}NO_2$: C, 69.54; H, 8.27; N, 6.76. Found C, 69.39; H, 8.29; N, 6.79.

Nitro Compound 16. R_f 0.57 (EtOAc/hexanes 1:9); IR (neat, NaCl) 3117 (w), 3064 (m), 2968 (s), 2931 (s), 2862 (s), 1653 (w), 1622 (w), 1561 (s), 1556 (s), 1231 (w), 1184 (w), 1150 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.75 (m, 2H), 6.11 (m, 1H), 4.36 (t, 2H, J = 7.1 Hz), 3.49 (m, 1H), 3.26 (m, 1H), 2.18 (m, 2H), 2.03−1.93 (m, 4H), 1.47−1.26 (m, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 158.4, 143.8, 142.3, 133.5, 75.6, 73.5, 53.4, 50.0, 31.2, 28.4, 27.3, 26.7, 26.0. Anal. Calcd for $C_{13}H_{19}NO_2$: C, 70.56; H, 8.65; N, 6.33. Found C, 70.71; H, 8.64; N, 6.35.

Nitro Compound 18. R_f 0.43 (EtOAc/hexanes 1:19); IR (neat, NaCl) 3066 (w), 2958 (s), 2932 (s), 2859 (m), 1557 (s), 1472 (w), 1463 (w), 1386 (w), 1362 (w), 1301 (w), 1258 (m), 1112 (m), 1021 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.74 (m, 2H), 6.14 (m, 1H), 4.39−4.30 (m, 3H), 3.50 (m, 1H), 3.26 (m, 1H), 2.20 (m, 2H), 1.96 (m, 2H), 1.55−1.41 (m, 4H), 0.85 (s, 9H), 0.06 (s, 3H), 0.01 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.7, 153.6, 143.84, 143.80, 142.15, 142.09, 134.2, 134.1, 81.01, 80.99, 73.5, 70.0, 69.9, 53.3, 50.0, 34.7, 34.6, 31.2, 31.1, 25.6, 22.4, 22.1, 17.8, −4.7, −5.2, −5.3; HRMS calcd for $C_{18}H_{31}SiNO_3$ m/z 337.2073, found m/z 337.2078.

Nitro Compound 27. R_f 0.44 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3066 (w), 2980 (m), 2936 (m), 2868 (m), 1557 (s), 1466 (w), 1421 (m), 1372 (m), 1309 (w), 1300 (w), 1283 (w), 1218 (m), 1187 (w), 1129 (m), 1091 (m), 1032 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.77 (dd, 1H, J = 5.2, 3.1 Hz), 6.72 (dd, 1H, J = 5.1, 3.0 Hz), 6.49 (m, 1H), 4.49 (t, 2H, J = 4.9 Hz), 4.17 (dd, 1H, J = 12.9, 1.3 Hz), 4.10 (dd, 1H, J = 12.9, 1.5 Hz), 3.82 (m, 2H), 3.55 (m, 1H), 3.40 (m, 1H), 2.01 (m, 1H), 1.97 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 153.8, 143.2, 142.4, 139.7, 75.1, 73.7, 69.5, 64.8, 51.1, 50.1. Anal. Calcd for $C_{10}H_{13}NO_3$: C, 61.53; H, 6.71; N, 7.17. Found C, 61.44; H, 6.70; N, 7.31.

Nitro Compound 28. R_f 0.45 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3065 (w), 2969 (m), 2933 (m), 2867 (m), 1559 (s), 1421 (w), 1380 (m), 1364 (m), 1307 (w), 1219 (w), 1125 (m), 1042 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.70 (m, 2H), 6.17 (m, 1H), 4.48 (t, 2H, J = 5.0 Hz), 3.91 (t, 2H, J = 5.1 Hz), 3.52 (t, 2H, J = 6.9 Hz), 3.45 (m, 1H), 3.27 (m, 1H), 2.44 (m, 2H), 1.94 (dt, 1H, J = 5.7, 1.6 Hz), 1.90 (dm, 1H, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 154.7, 143.6, 142.1, 135.3, 75.0, 73.5,

69.5, 65.9, 53.4, 50.0, 31.3; HRMS calcd for $C_{11}H_{15}NO_3$ *m/z* 209.1052, found *m/z* 209.1051.

Nitro Compound 31. R_f 0.67 (EtOAc/hexanes 1:4); IR (neat, NaCl) 2977 (m), 2935 (m), 2867 (w), 1554 (s), 1430 (m), 1376 (m), 1306 (m), 1184 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.83 (dd, 1H, J = 5.0, 3.1 Hz), 6.69 (dd, 1H, J = 5.0, 3.0 Hz), 6.37 (dm, 1H, J = 1.6 Hz), 4.43 (td, 2H, J = 7.2, 1.1 Hz), 3.58 (dm, 1H, J = 1.2 Hz), 3.40 (d_{AB}, 1H, J = 14.0 Hz), 3.38 (br. s, 1H), 3.35 (d_{AB}d, 1H, J = 14.0, 1.1 Hz), 2.80 (td, 2H, J = 7.2, 4.8 Hz), 2.02 (d_{AB}t, 1H, J = 6.0, 1.5 Hz), 1.99 (d_{AB}m, 1H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 152.0, 142.7, 142.3, 138.9, 74.2, 73.1, 52.8, 50.5, 32.7, 26.6. Anal. Calcd for $C_{10}H_{13}SNO_2$: C, 56.85; H, 6.20. Found C, 56.87; H, 6.19.

Nitro Compound 46. R_f 0.40 (EtOAc/hexanes 1:9); IR (neat, NaCl) 3063 (w), 2964 (s), 2932 (s), 2863 (m), 1556 (s), 1436 (m), 1382 (m), 1302 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.73 (m, 1H), 6.70 (m, 1H), 4.33 (t, 2H, J = 7.0 Hz), 3.26 (br. s, 1H), 3.21 (br. s, 1H), 2.18 (m, 1H), 2.10 (m, 1H), 1.90−1.81 (m, 4H), 1.68 (s, 3H), 1.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 144.6, 144.2, 142.5, 142.1, 75.5, 70.9, 55.2, 52.9, 27.0, 26.7, 23.9, 14.1; HRMS calcd for $C_{12}H_{17}NO_2$ *m/z* 207.1259, found *m/z* 207.1255.

Nitro Compound 47. R_f 0.76 (EtOAc/hexanes 1:9); IR (neat, NaCl) 3063 (w), 2960 (s), 2929 (s), 2859 (s), 1555 (s), 1465 (m), 1457 (m), 1435 (m), 1381 (m), 1303 (m), 1229 (w), 1200 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.70 (m, 2H), 4.35 (t, 2H, J = 7.0 Hz), 3.32 (m, 1H), 3.27 (m, 1H), 2.23−1.97 (m, 4H), 1.92−1.83 (m, 4H), 1.50−1.33 (m, 4H), 1.30−1.17 (m, 6H), 0.87 (t, 3H, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 148.3, 145.0, 142.6, 142.2, 75.6, 71.1, 53.2, 52.9, 31.7, 29.0, 28.2, 27.5, 27.2, 26.8, 24.1, 22.6, 14.1; HRMS calcd for $C_{17}H_{27}NO_2$ *m/z* 277.2042, found *m/z* 277.2047.

Nitro Compound 49. R_f 0.63 (EtOAc/hexanes 1:4); IR (neat, NaCl) 2976 (m), 2939 (m), 2869 (m), 1639 (w), 1553 (s), 1453 (m), 1434 (m), 1382 (m), 1297 (m), 1226 (w), 1097 (w), 1045 (m), 1015 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.86 (dd, 1H, J = 5.0, 2.7 Hz), 6.76 (dd, 1H, J = 5.0, 2.9 Hz), 4.36 (t, 2H, J = 6.9 Hz), 3.39 (br.s, 2H), 2.25 (m, 2H), 2.17 (dm, 1H, J = 6.0 Hz), 2.03 (dm, 1H, J = 6.0 Hz), 1.89 (p, 2H, J = 7.3 Hz), 1.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 145.8, 142.1, 141.9, 141.4, 75.3, 71.3, 56.4, 52.9, 26.7, 26.5, 23.2. Anal. Calcd for $C_{11}H_{14}ClNO_2$: C, 58.03; H, 6.20. Found C, 58.01; H, 6.21.

Nitro Compound 51. R_f 0.68 (EtOAc/hexanes 1:9); IR (neat, NaCl) 3067 (w), 2975 (m), 2938 (m), 2867 (m), 1633 (w), 1553 (s), 1455 (w), 1434 (m), 1383 (m), 1297 (m), 1261 (w), 1225 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.84 (dd, 1H, J = 5.1, 3.3 Hz), 6.73 (dd, 1H, J = 5.1, 2.9 Hz), 4.35 (t, 2H, J = 2.0 Hz), 3.46 (m, 1H), 3.40 (br. s, 1H), 2.29−2.14 (m, 3H), 2.02 (dt, 1H, J = 6.0, 1.6 Hz), 1.89 (m, 2H), 1.49 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 149.7, 141.9, 141.6, 130.4, 75.2, 71.6, 57.9, 53.2, 28.1, 26.4, 22.9; HRMS calcd for $C_{11}H_{14}BrNO_2$ *m/z* 271.0208, found *m/z* 271.0207.

Nitro Compound 62. R_f 0.61 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3066 (w), 2973 (m), 2936 (m), 2866 (m), 1560 (s), 1556 (s), 1549 (s), 1453 (m), 1434 (m), 1382 (m), 1296 (m), 1258 (w), 1225 (w), 1190 (w), 1163 (w), 1131 (w), 1022 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.85 (dd, 1H, J = 5.0, 2.9 Hz), 6.71 (dd, 1H, J = 5.0, 2.9 Hz), 4.38 (t, 2H, J = 6.8 Hz), 3.60 (br. s, 1H), 3.41 (br. s, 1H), 2.31 (m, 1H), 2.18 (m, 1H), 2.16 (dm, 1H, J = 6.1 Hz), 2.03 (dm, 1H, J = 6.1 Hz), 1.90 (m, 2H), 1.52 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.4, 142.2, 141.2, 102.3, 75.4, 72.3, 61.0, 53.4, 31.1, 26.5, 23.1. Anal. Calcd for $C_{11}H_{14}INO_2$: C, 41.40; H, 4.42. Found C, 41.75; H, 4.32.

Nitro Compound 63. R_f 0.75 (EtOAc/hexanes 2:3); IR (neat, NaCl) 3068 (w), 2972 (s), 2949 (s), 2869 (m), 1704 (s), 1699 (s), 1683 (s), 1626 (s), 1563 (s), 1557 (s), 1549 (s), 1455 (m), 1435 (s), 1384 (s), 1295 (s), 1239 (s), 1193 (m), 1162 (s), 1135 (w), 1103 (s), 1072 (s), 1019 (w), 1004 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.87 (dd, 1H, J = 4.9, 3.1 Hz), 6.69 (dd, 1H, J = 4.9, 3.3 Hz), 4.39 (t, 2H, J = 6.9 Hz), 3.89 (br. s, 1H), 3.71 (s, 3H), 3.48 (br. s, 1H), 2.75 (m, 2H), 2.03 (dm, 1H, J = 6.5 Hz), 1.98 (dm, 1H, J = 6.5 Hz), 1.93 (p, 2H, J = 7.2 Hz), 1.65−1.50 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.9, 166.0, 143.9, 140.6, 139.7, 75.2, 71.4, 55.8, 51.1, 51.0, 28.9, 26.5, 23.3. Anal. Calcd for $C_{13}H_{17}NO_4$: C, 62.14; H, 6.82. Found C, 63.56; H, 6.74.

Nitro Compound 64. R_f 0.73 (EtOAc/hexanes 2:3); IR (neat, NaCl) 3064 (w), 2969 (s), 2932 (s), 2865 (s), 2818 (m), 1660 (w), 1552 (s), 1452 (m), 1435 (m), 1382 (s), 1355 (m) 1306 (m), 1288 (w), 1247 (w), 1230 (w), 1190 (m), 1141 (m), 1095 (s) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.79 (dd, 1H, J = 5.1, 3.0 Hz), 6.70 (dd, 1H, J = 5.1, 3.0 Hz), 4.35 (t, 2H, J = 6.9 Hz), 4.02 (d_{AB}, 1H, J = 11.8 Hz), 3.88 (d_{AB}, 1H, J = 11.8 Hz), 3.50 (br. s, 1H), 3.34 (br. s, 1H), 3.23 (s, 3H), 2.29 (m, 1H), 2.19 (m, 1H), 1.94 (dm, 1H, J = 5.9 Hz), 1.89 (dm, 1H, J = 5.9 Hz), 1.87 (m, 2H), 1.45 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 151.8, 144.7, 143.1, 141.8, 75.4, 71.5, 68.1, 57.7, 53.5, 52.2, 27.3, 26.7, 23.9; HRMS calcd for $C_{13}H_{19}NO_3$ *m/z* 237.1365, found *m/z* 237.1367.

General Procedure for in Situ Formation of Nitrile Oxides from the Corresponding Nitro Compounds and Subsequent Intramolecular 1,3-Dipolar Cycloadditions (9, 32−36, 65, 66, 68−72). Di-*tert*-butyl dicarbonate, $(BOC)_2O$ (2−3 equiv) in toluene was added via a cannula to a flame-dried flask containing the nitro compound (1 equiv) and 4-(dimethylamino)pyridine (DMAP, 10−20 mol %) in toluene. The reaction mixture was stirred at 90 °C for 18−96 h. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography to provide the pure cycloadducts.

Cycloadduct 9. Di-*tert*-butyl dicarbonate, $(BOC)_2O$ (274 mg, 1.25 mmol) in toluene (2.5 mL) was added via a cannula to a flame-dried flask containing the nitro compound **7** (100 mg, 0.518 mmol) and 4-(dimethylamino)pyridine (DMAP, 12.4 mg, 0.101 mmol) in toluene (2.5 mL). The reaction mixture was stirred at 90 °C for 96 h. The solvent was removed by rotary evaporation and the crude product was purified by column chromatography (EtOAc/hexanes 1:9) to give cycloadduct **9** (77.6 mg, 0.443 mmol, 86%) as white crystals. Recrystallization with 10% EtOAc/hexanes provided colorless needle-like crystals: R_f 0.25 (EtOAc/hexanes 1:9); mp 67.5 °C; IR (CH_2Cl_2) 3073 (w), 2979 (s), 2949 (s), 1647 (w), 1446 (w), 1430 (w), 1320 (m), 1256 (m), 1246 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.27 (dd, 1H, J = 5.7, 3.0 Hz), 6.00 (dd, 1H, J = 5.7, 3.2 Hz), 4.33 (s, 1H), 3.18 (m, 1H), 2.75 (br. s, 1H), 2.34 (t, 2H, J = 7.8 Hz), 2.16−1.96 (m, 2H), 1.77 (m, 1H), 172 (d, 1H, J = 9.3 Hz), 1.57 (dd, 1H, J = 9.1 Hz, J = 1.1 Hz), 1.31 (ddd, 1H, J = 12.8, 7.9, 2.3 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 167.5, 138.0, 135.3, 92.6, 76.2, 50.5, 46.7, 44.4, 32.0, 24.0, 20.2; HRMS calcd for $C_{11}H_{13}NO$ *m/z* 175.0997, found *m/z* 175.0999. Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48; N, 7.99. Found C, 75.60; H, 7.55; N, 7.88.

Cycloadduct 32. R_f 0.23 (EtOAc/hexanes 1:9); IR (neat, NaCl) 3062 (w), 2975 (s), 2936 (s), 2859 (m), 1626 (w), 1448 (m), 1354 (w), 1326 (m), 1255 (w), 1232 (w), 1148 (w), 1049 (w) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.29 (dd, 1H, J = 5.8, 3.0 Hz), 5.97 (dd, 1H, J = 5.7, 3.2 Hz), 4.02 (t, 1H, J = 1.3 Hz), 3.16 (m, 1H), 2.90 (m, 1H), 2.59 (dm, 1H, J = 13.6 Hz), 2.08 (td, 1H, J = 13.3, 5.3 Hz), 1.98 (m, 1H), 1.72−1.65 (m, 2H), 1.61−1.52 (m, 3H), 1.49−1.40 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.8, 137.9, 133.9, 90.9, 67.8, 50.7, 44.7, 44.3, 36.7, 27.4, 23.8, 22.6; HRMS calcd for $C_{12}H_{15}NO$ *m/z* 189.1154, found *m/z* 189.1159.

Cycloadducts 33. Two separable diasteromers **33a** and **33b**. Cycloadduct **33a**: R_f 0.31 (EtOAc/hexanes 1:19); IR (neat, NaCl) 3064 (w), 2934 (s), 2857 (m), 1555 (w), 1361 (w), 1257 (m), 1115 (m), 1063 (m), 1027 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.34 (dd, 1H, J = 5.7, 3.0 Hz), 6.00 (dd, 1H, J = 5.7, 3.2 Hz), 4.68 (t, 1H, J = 2.4 Hz), 4.07 (s, 1H), 3.36 (br. s, 1H), 3.20 (t, 1H, J = 1.4 Hz), 2.07−1.94 (m, 2H), 1.73−1.46 (m, 4H), 0.89 (br. s, 9H), 0.10 (br. s, 3H), 0.06 (br. s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.4, 138.8, 134.0, 92.2, 67.1, 64.7, 50.7, 46.6, 44.6, 37.1, 36.2, 25.7, 17.7, −5.0, −5.2. Cycloadduct **33b.** R_f 0.23 (EtOAc/hexanes 1:19); IR (neat, NaCl) 3064 (w), 2934 (s), 2857 (m), 1555 (w), 1361 (w), 1257 (m), 1115 (m), 1063 (m), 1027 (m) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 6.29 (dd, 1H, J = 5.7, 3.0 Hz), 6.01 (dd, 1H, J = 5.7, 3.2 Hz), 4.43−4.39 (m, 1H), 4.14−4.13 (m, 1H), 3.22 (t, 1H, J = 1.4 Hz), 2.85 (m,

1H), 2.17 (m, 1H), 1.80−1.59 (m, 4H), 1.42 (m, 1H), 0.94 (br. s, 1H), 0.91 (m, 8H), 0.14 (br. s, 3H), 0.09 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.1, 137.8, 134.2, 91.8, 69.4, 68.4, 50.9, 45.3, 44.4, 38.1, 36.2, 25.8, 22.1, −4.9, −5.4.

Cycloadduct 34. R_f 0.28 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3055 (m), 2986 (m), 2878 (w), 1422 (w), 1348 (w), 1325 (w), 1266 (s), 1012 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.39 (dd, 1H, J = 5.8, 3.0 Hz), 6.15 (dd, 1H, J = 5.7, 3.3 Hz), 4.68 (t, 1H, J = 1.5 Hz), 4.40 (m, 2H), 3.88 (d, 1H, J = 8.6 Hz), 3.51 (d, 1H, J = 8.5 Hz), 3.36 (m, 1H), 3.08 (m, 1H), 1.91 (dm, 1H, J = 9.4 Hz), 1.77 (dm, 1H, J = 9.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.6, 138.2, 136.7, 92.9, 76.7, 73.2, 61.0, 50.6, 47.1, 44.7. Anal. Calcd for $C_{10}H_{11}NO_2$: C, 67.78; H, 6.26; N, 7.90. Found C, 68.02; H, 6.23; N, 7.86.

Cycloadduct 35. R_f 0.23 (EtOAc/hexanes 1:4); IR (neat, NaCl) 2976 (m), 2853 (w), 1460 (w), 1326 (w), 1094 (s), 1081 (s), 1054 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.34 (dd, 1H, J = 5.8, 3.0 Hz), 6.06 (dd, 1H, J = 5.7, 3.3 Hz), 4.50 (d, 1H, J = 12.6 Hz), 4.19 (s, 1H), 4.10 (d, 1H, J = 12.6 Hz), 3.92 (ddd, 1H, J = 12.0, 4.6, 1.5 Hz), 3.70 (td, 1H, J = 12.3, 2.0 Hz), 3.26 (m, 1H), 3.09 (m, 1H), 2.18 (td, 1H, J = 13.3, 4.6 Hz), 1.64−1.63 (m, 2H), 1.45 (dm, 1H, J = 13.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 156.2, 137.8, 134.5, 91.4, 69.7, 64.8, 62.3, 50.1, 44.7, 44.4, 38.3; HRMS calcd for $C_{11}H_{13}NO_2$: (CI, $[M + H]^+$) m/z 192.1025, found m/z 192.1032.

Cycloadduct 36. R_f 0.50 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3065 (m), 2979 (s), 2946 (s), 2881 (m), 1758 (w), 1694 (s), 1633 (w), 1459 (m), 1326 (s), 1298 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.40 (dd, 1H, J = 5.7, 3.0 Hz), 6.14 (dd, 1H, J = 5.7, 3.0 Hz), 4.48 (s, 1H), 3.57 (d_{AB}, 1H, J = 13.2 Hz), 3.48 (d_{AB}, 1H, J = 13.2 Hz), 3.37 (tm, 1H, J = 1.6 Hz), 3.08 (d, 1H, J = 10.8 Hz), 3.06 (br. s, 1H), 2.35 (d, 1H, J = 10.8 Hz), 1.80 (d_{AB}, 1H, J = 9.6 Hz), 1.72 (d_{AB}d, 1H, J = 9.6, 1.2 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 162.9, 138.1, 135.9, 93.3, 77.1, 51.4, 46.5, 44.7, 34.9, 23.4. Anal. Calcd for $C_{10}H_{11}SNO$: C, 62.15; H, 5.74. Found C, 62.17; H, 5.73.

Cycloadduct 65. R_f 0.49 (EtOAc/hexanes 1:9); mp 83 °C; IR (CH_2Cl_2) 3055 (w), 2975 (m), 2881 (w), 2307 (w), 1638 (w), 1448 (w), 1374 (w), 1326 (w), 1266 (s), 1139 (w), 1101 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.17 (m, 2H), 3.01 (br. s, 1H), 2.92 (br. s, 1H), 2.43 (t, 2H, J = 8.5 Hz), 2.26−2.06 (m, 2H), 1.73 (d, 1H, J = 9.0 Hz), 1.58 (m, 1H), 1.49 (d, 1H, J = 9.1 Hz), 1.09 (s, 3H), 1.05 (ddd, 1H, J = 13.0, 7.8, 2.4 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.1, 136.5, 135.1, 97.9, 74.6, 54.9, 48.9, 44.4, 29.3, 25.6, 21.3, 21.0. Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N 7.40; Found C, 76.29; H, 7.93; N, 7.55.

Cycloadduct 66. R_f 0.33 (EtOAc/hexanes 1:9); IR (CH_2Cl_2) 3135 (w), 3062 (m), 2956 (s), 2857 (s), 1638 (m), 1569 (w), 1455 (s), 1436 (m), 1378 (w), 1326 (s), 1264 (m), 1212 (w), 1145 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.15 (dd, 1H, J = 5.7, 2.9 Hz), 6.11 (dd, 1H, J = 5.5, 3.1 Hz), 3.16 (br. s, 1H), 2.91 (br. s,1H), 2.41 (t, 2H, J = 6.9 Hz), 2.19 (m, 1H), 2.09 (m, 1H), 1.70−1.31 (m, 6H), 6.12−6.10 (m, 6H), 1.01 (ddd, 1H, J = 12.8, 7.7, 2.4 Hz), 0.90 (dd, 1H, J = 12.9, 4.0 Hz), 0.84 (t, 3H, J = 6.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.3, 136.0, 135.2, 100.2, 75.1, 51.9, 48.9, 44.1, 35.3, 31.6, 29.7, 29.0, 25.6, 24.4, 22.5, 21.2, 14.0; HRMS calcd for $C_{17}H_{25}NO$ m/z 259.1936, found m/z 259.1932.

Cycloadduct 68. R_f 0.47 (EtOAc/hexanes 1:4); IR (CH_2Cl_2) 3073 (w), 2979 (s), 2883 (m), 1454 (m), 1429 (m), 1326 (s), 1251 (m), 1062 (m), 1013 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.35 (dd, 1H, J = 5.7, 3.0 Hz), 6.25 (dd, 1H, J = 5.7, 3.1 Hz), 3.54 (dm, 1H, J = 1.4 Hz), 3.08 (br. s, 1H), 2.61−2.48 (m, 2H), 2.33−2.17 (m, 2H), 2.10−2.02 (m, 1H), 1.81 (dm, 1H, J = 9.6 Hz), 1.73 (dm, 1H, J = 9.6 Hz), 1.39 (ddd, 1H, J = 13.1, 7.0, 3.0 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.0, 136.6, 135.9, 118.3, 78.9, 57.0, 47.9, 44.3, 31.3, 26.0, 21.6. Anal. Calcd for $C_{11}H_{12}ClNO$: C, 63.01; H, 5.77; Found C, 63.00; H, 5.74.

Cycloadduct 69. R_f 0.28 (EtOAc/hexanes 1:9); IR (CH_2Cl_2) 3074 (w), 3025 (m), 3011 (s), 2980 (s), 2879 (m), 1648 (w), 1463 (m), 1456 (m), 1452 (m), 1434 (m), 1252 (m), 1218 (w), 1180 (m), 1130 (m), 1103 (w), 1059 (m) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.36 (dd, 1H, J = 5.7, 3.0 Hz), 6.21 (dd, 1H, J = 5.6, 3.1 Hz), 3.68 (m, 1H), 3.03 (m, 1H), 2.58−2.53 (m, 2H), 2.28−2.12 (m, 3H), 1.83 (dm, 1H, J = 9.5 Hz), 1.75 (dm, 1H, J = 9.6 Hz), 1.37 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 171.0, 137.4, 136.0, 114.1, 79.1, 58.5, 47.1, 44.0, 34.1, 25.9, 21.6. Anal. Calcd for $C_{11}H_{12}BrNO$: C, 51.99; H, 4.76; N, 5.51; Found C, 51.79; H, 4.79; N, 5.54.

Cycloadduct 70. Unstable, gradually decomposed upon standing at room temperature (>80% pure by NMR): R_f 0.69 (EtOAc/hexanes 2:3); IR (CH_2Cl_2) 2967 (m), 2884 (w), 1748 (s), 1721 (s), 1716 (s), 1453 (w), 1405 (w), 1371 (w), 1320 (w), 1274 (m), 1148 (m) cm^{-1};^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.63 (dd, 1H, J = 5.5, 2.8 Hz), 6.24 (dd, 1H, J = 5.4, 3.4 Hz), 3.11 (dd, 1H, J = 3.1, 1.5 Hz), 3.03 (m, 1H), 2.93 (dm, 1H, J = 9.7 Hz), 2.45−2.30 (m, 2H), 2.17−2.04 (m, 3H), 1.87 (m, 1H), 1.73−1.66 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 215.3, 211.8, 142.1, 134.0, 60.7, 56.0, 47.8, 46.1, 39.3, 36.7, 19.6.

Cycloadduct 71. R_f 0.25 (EtOAc/hexanes 1:4); IR (neat, NaCl) 3070 (w), 2979 (s), 2956 (s), 2882 (m), 2847 (w), 1732 (s), 1571 (w), 1456 (m), 1435 (s), 1325 (s), 1286 (s), 1256 (s), 1193 (m), 1168 (w), 1129 (m), 1104 (m), 1081 (s), 1054 (w), 1008 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.32 (dd, 1H, J = 5.6, 3.2 Hz), 6.25 (dd, 1H, J = 5.6, 3.1 Hz), 3.72 (s, 3H), 3.37 (m, 1H), 2.98 (br. s, 1H), 2.54−2.41 (m, 2H), 2.29−2.10 (m, 2H), 1.83 (dm, 1H, J = 9.4 Hz), 1.81 (m, 1H), 1.61 (dm, 1H, J = 9.4 Hz), 1.22 (ddd, 1H, J = 12.9, 7.5, 2.6 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.2, 168.9, 137.4, 134.5, 99.4, 81.4, 52.7, 52.2, 48.9, 44.5, 30.4, 25.8, 20.7. Anal. Calcd for $C_{13}H_{15}NO_3$: C, 66.94; H, 6.84. Found C, 66.71; H, 6.49.

Cycloadduct 72. R_f 0.50 (EtOAc/hexanes 2:3); IR (neat, NaCl) 3072 (w), 2998 (m), 2973 (s), 2950 (s), 2876 (m), 2816 (w), 2752 (w), 1637 (w), 1475 (w), 1450 (m), 1391 (w), 1329 (m), 1299 (w), 1271 (w), 1254 (w), 1247 (m), 1202 (m), 1148 (w), 1129 (m), 1111 (s), 1098 (s) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.21 (dd, 1H, J = 5.7, 3.0 Hz), 6.17 (dd, 1H, J = 5.6, 3.1 Hz), 3.36 (s, 3H), 3.27 (d, 1H, J = 10.5 Hz), 3.21 (br. s, 1H), 3.16 (d, 1H, J = 10.5 Hz), 2.94 (br. s, 1H), 2.46−2.42 (m, 2H), 2.22 (m, 1H), 2.11 (m, 1H), 1.76 (dm, 1H, J = 9.2 Hz), 1.71 (m, 1H), 1.54 (dm, 1H, J = 9.2 Hz), 0.96 (ddd, 1H, J = 12.7, 7.7, 2.5 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 169.5, 136.3, 135.3, 99.5, 75.5, 74.9, 59.6, 51.6, 49.1, 44.4, 28.5, 25.7, 21.1. Anal. Calcd for $C_{13}H_{17}NO_2$: C, 71.21; H, 7.81. Found C, 70.87; H, 7.84.

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Supporting Information Available: Experimental procedures for preparation of all cycloadducts and their precursors that are not included in the Experimental Section; ^{1}H and ^{13}C NMR spectra for compounds **13, 14, 25, 26, 30, 45, 53, 59**; nitro compounds **18, 28, 46, 47, 51, 64**; and all cycloadducts **9, 32−36, 65, 66, 68−72**. This material is available free of charge via the Internet at http://pubs.acs.org.

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