Diels-Alder Reaction of β-Fluoro-β-nitrostyrenes with Cyclic Dienes

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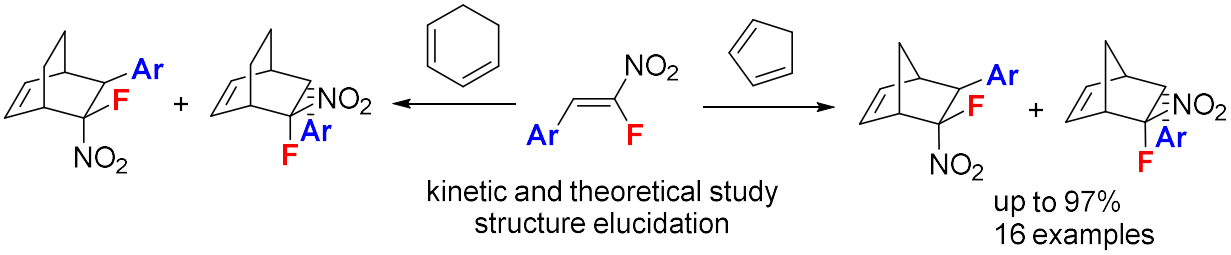
Abstract: The Diels-Alder reaction of β-fluoro-β-nitrostyrenes with cyclic 1,3-dienes was investigated. A series of novel monofluorinated norbornenes was prepared in up to 97% yield. The reaction with 1,3-cyclohexadiene permits the preparation of monofluorinated bicyclo[2.2.2]oct-2-enes. The kinetic data of the reaction with cyclopentadiene and cyclohexadiene-1,3 were used to calculate activation parameters. Furthermore, the synthetic utility of the cycloadducts obtained was demonstrated.

Graphical abstract:



Introduction

Organofluorine compounds play an exceptionally important role in various fields of science and technology. Incorporation of a fluorine into molecules can significantly influence their pharmacokinetic and physicochemical properties and enhance their metabolic and chemical stability.[1] For instance, nearly a quarter of the currently manufactured agrochemical and

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pharmaceutical products contains at least one fluorine atom.[2] Fluorinated functional materials have also found wide application as durable ion exchange membranes e.g. in fuel cells [3], as thermoplastic polymers[4], in electronic and optoelectronic technologies[5] and in liquid crystal display applications[6], etc[7]. The use of fluorinated building blocks is a very convenient approach and in many cases represents an indispensable alternative to late-stage fluorinations in the preparation of such unique materials.[8]

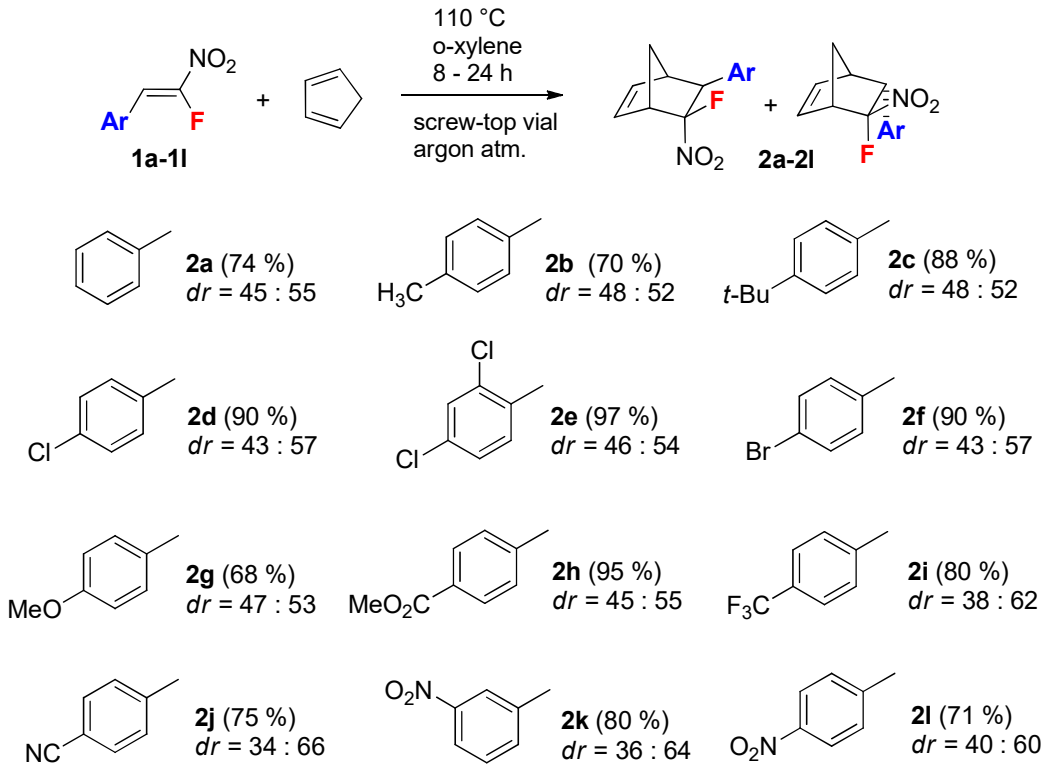
The Diels–Alder reaction is considered a versatile and powerful tool for assembling variety of fluorinated carbo- and heterocycles using either the diene[9,10,11] or the dienophile component[12, 13,14] as fluorine-containing building blocks. The application of [4+2]-cycloadditions for the preparation of fluorinated bicyclic compounds has attracted much attention.[15] In this regard, the development of new protocols to relevant monofluorinated bicyclic molecules involving novel versatile fluorine-containing building blocks is of key importance. Fluoroalkenes are recognized to be one of the most widely used fluorine-containing building blocks [16] Recently, we have developed an efficient stereoselective synthesis of β-fluoro-β-nitrostyrenes **1** based on the radical nitration of 2-bromo-2-fluorostyrenes.[17] This process takes place with simultaneous elimination of bromine, and gives the target structures solely in Z-isomer form in high yields (up to 92 %). These fluorine-containing olefins activated by the nitro group proved to be the appealing building blocks for the construction of numerous monofluorinated compounds.[18] This paper is devoted to a new synthetic approach to novel monofluorinated bicyclic compounds, namely norbornenes and bicyclo[2.2.2]oct-2-enes and their subsequent functionalization. The present study is our follow-up work on the Diels-Alder reaction involving β-fluoro-β-nitrostyrenes.[19]

A recent review reported that by 2018, the total number of publications and patents related to the production and use of norbornene and norbornadiene derivatives had exceeded 30,000.[20] Indeed, norbornene and its derivatives have found application in medicine, agriculture, microelectronics and rocket technology as well as in production of polymeric materials, efficient gas separation membranes and solar energy converters.[20] Considering the high interest in such structures and the unique role of fluorine, we believe that novel norbornene derivatives obtained in framework of this study can become relevant compounds in practical use.

Results and discussion

Initially, we studied the Diels-Alder reaction of β-fluoro-β-nitrostyrenes **1** with 1,3-cyclopentadiene (CPD) to prepare a series of novel monofluorinated norbornenes. The starting nitrostyrenes were used in form of their *Z*-isomers. The transformations were conducted in screw-top vials in *o*-xylene at 110 °C using a fivefold excess of the diene (Scheme 1). The reaction proceeded smoothly under these conditions to give target cycloadducts **2** as a mixture of *exo*- and *endo*-isomers in high isolated yield

(up to 97 %). It should be noted that in the present work we indicate an isomer as e*xo*- or *endo*- according to the stereo-position of the fluorine atom. Thus ***exo*-2** and ***endo*-2** means 5-*exo*-fluoro-5-*endo*-nitro-6-*exo*-aryl-norbornene and 5-*endo*-fluoro-5-*exo*-nitro-6-*endo*-aryl-norbornene respectively (Fig. 1). Both diastereomers are formed in a nearly 1:1-ratio for the majority of substituents on the aryl group of the nitrostyrenes **1**. However, a higher diastereoselectivity towards *endo*-isomer was observed when strong electron withdrawing groups (EWGs) were present in the dienophile. For example, in the case of the 4-CN- and the 3-NO_2-substituted derivative, the ratio of *endo*/*exo* was 2:1.



Scheme 1. Scope of nitrostyrenes **1** in the Diels-Alder reaction with CPD (*dr* = *exo* : *endo*)

The stereochemistry of **2a-l** can be unambiguously assigned using ^{1}H NMR. According to the literature data[21] the dienophile-derived proton at C6 resonates at lower field in the *exo*-form than that the corresponding proton of the *endo*-isomer. For example, in the case of **2l**, the ^{1}H NMR spectrum shows a doublet of doublet signal for H6 at 3.89 ppm for the minor isomer and at 4.27 ppm for the major isomer (Fig 1a). A significant chemical shift difference is observed for the aryl proton signals of *exo*- and *endo*-isomeric norbornenes **2**. Most probably, such significant difference in the chemical shifts can be explained by the double bond anisotropy of the norbornene molecule.[22] The stereochemical assignments are in full accordance with the values of vicinal ($^3J_{H6\text{-}F}$ and $^3J_{H1\text{-}H6}$) and long-range coupling constants ($^4J_{H6\text{-}H7a}$). According to literature data, the value of $^3J_{H1\text{-}H6}$ is larger than that of $^4J_{H6\text{-}H7a}$.[23] For example, the ^{1}H NMR spectrum of the minor isomer of **2l** showed the constants $^3J_{H6\text{-}F}$ = 10.7 Hz; $^4J_{H6\text{-}H7a}$ = 2.9 Hz consistent with an *exo*-geometry. In contrast, the major isomer having constants $^3J_{H6\text{-}F}$ = 9.1 Hz; $^3J_{H1\text{-}H6}$ = 3.1 Hz was ascribed to the *endo*-form (Fig 1). It

should be noted that this observation applies for all cases investigated. The value of coupling constant $^{3}J_{H6\text{-}F}$ between *exo*-F and *endo*-H6 was always larger than the corresponding value between *endo*-F and *exo*-H6. The stereochemical assignments were additionally confirmed by nuclear Overhauser effect spectroscopy (NOE). The peak of H6 was selected to be selectively excited for each isomer. As expected, in case of ***endo*-2l** the NOE peaks resulted from the interaction of *exo*-H6 with H1 and H7a were observed. Whereas for ***exo*-2l** due to opposite side position of *endo*-H6 there was no interactions observed. Thus, using these spectral data all the pairs of *exo*- and *endo*-isomers **2** obtained can be assigned unambiguously.

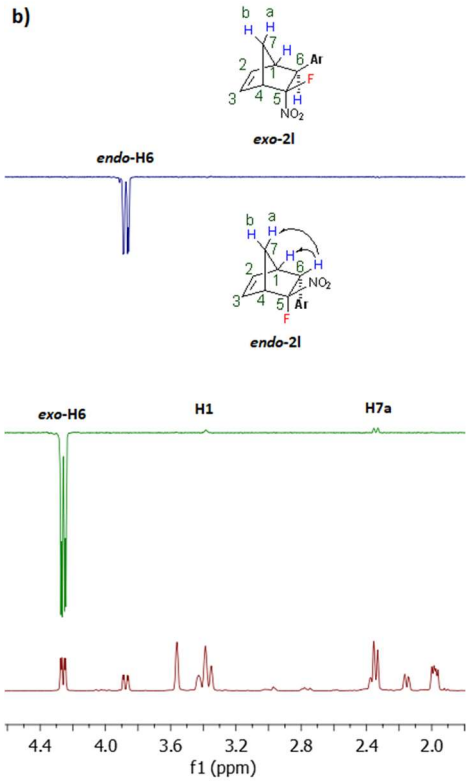


Fig. 1 The structure assignment of norbornenes **2** by ^{1}H (a) and NOE (b) NMR spectroscopy

Moreover, the ^{13}C NMR spectra of *exo*- and *endo*-isomers exhibit a significant difference (approximately 3 ppm) in chemical shifts for some carbon atoms (Fig 2). The considerable difference in chemical shifts was observed for C-7 of methylene bridge (46.1 for *exo*- *vs* 48.9 ppm for *endo*-isomer), C-6 (51.3 for *exo vs* 53.4 for *endo*-isomer), C-4 (52.4 for *exo*- *vs* 55.3 ppm for *endo*-isomer) and C-2 (139.7 for *endo*- *vs* 143.0 ppm for *exo*-isomer). The same pattern in chemical shifts and coupling constants was observed for all structures **2** synthesized.

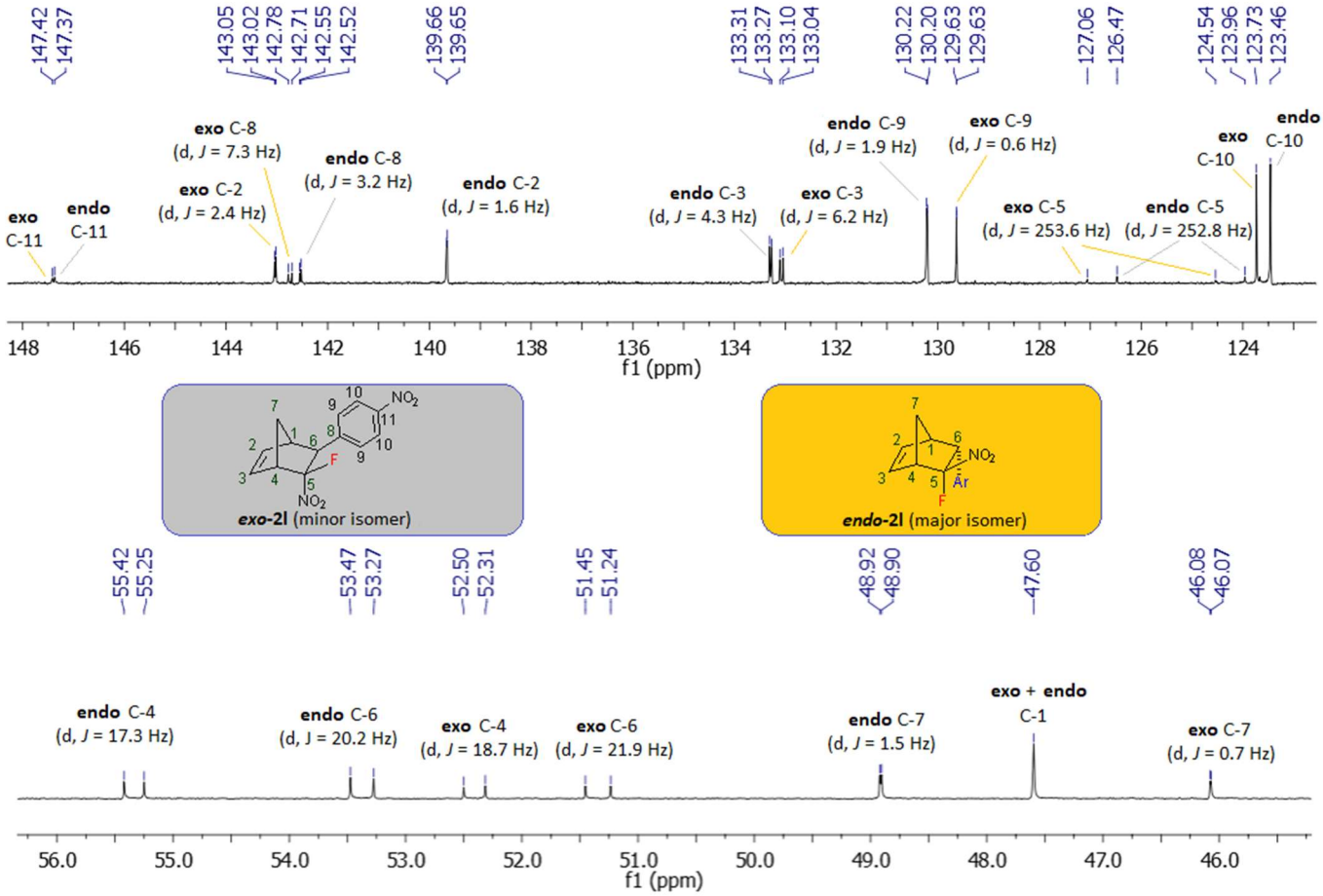


Fig. 2 ^{13}C-NMR spectrum of mixture of *exo*- and *endo*- isomers of norbornene **2l**.

For further insights into the mechanistic background of the *endo-exo* selectivity, the Diels–Alder reaction of CPD with the model nitrostyrene **1h** was simulated *in silico* to predict the reaction pathway, the reaction rate constants and the activation enthalpies. Density functional theory calculations were conducted for the reactants, products and transition states using the B3LYP[24]and M062X[25]level of theory in combination with a Pople basis set and the IEFPCM[26] solvation model for *o*-xylene. Both functionals are already known to the literature for the investigation of cycloadditions.[27] For the computational details the reader is referred to the Supporting Information. The predicted reaction pathways for the formation of *exo*- and *endo*-isomeric norbornene **2h** using M062X are displayed in Fig. 3. For each isomer one transition state ***exo*-TS** and ***endo*-TS** was identified. The former transition state is higher in energy and leads to the less exergonic product ***exo*-2h**. The *exo*- and *endo*-isomer were predicted to have free energies of activation ($\Delta G^{\ddagger}_{383.15}$) of 120.62 and 119.64 kJ mol^{-1}, respectively. The corresponding predicted reaction free energies ($\Delta G_{383.15}$) are -39.66 and -42.07 kJ mol^{-1}. With the former values of $\Delta G^{\ddagger}$, the reaction rate coefficient k can be calculated using the Eyring equation:[28]

$$k(T) = \frac{k_B T}{hc^0} e^{-\Delta G^{\ddagger}_{383.15\mathrm{K}}/RT} \qquad \text{(eq. 1)}$$

For T=110 °C, the predicted ratio of k_{endo}/k_{exo}=1.36 (1.68 for B3LYP) is in good accordance with the experimentally observed diastereomeric ratio of 1.22. The larger discrepancy in case of the B3LYP functional may be due to the fact that dispersion effects are not included, whereas M062X includes nonlocal effects of electronic dispersion.[30b,29]

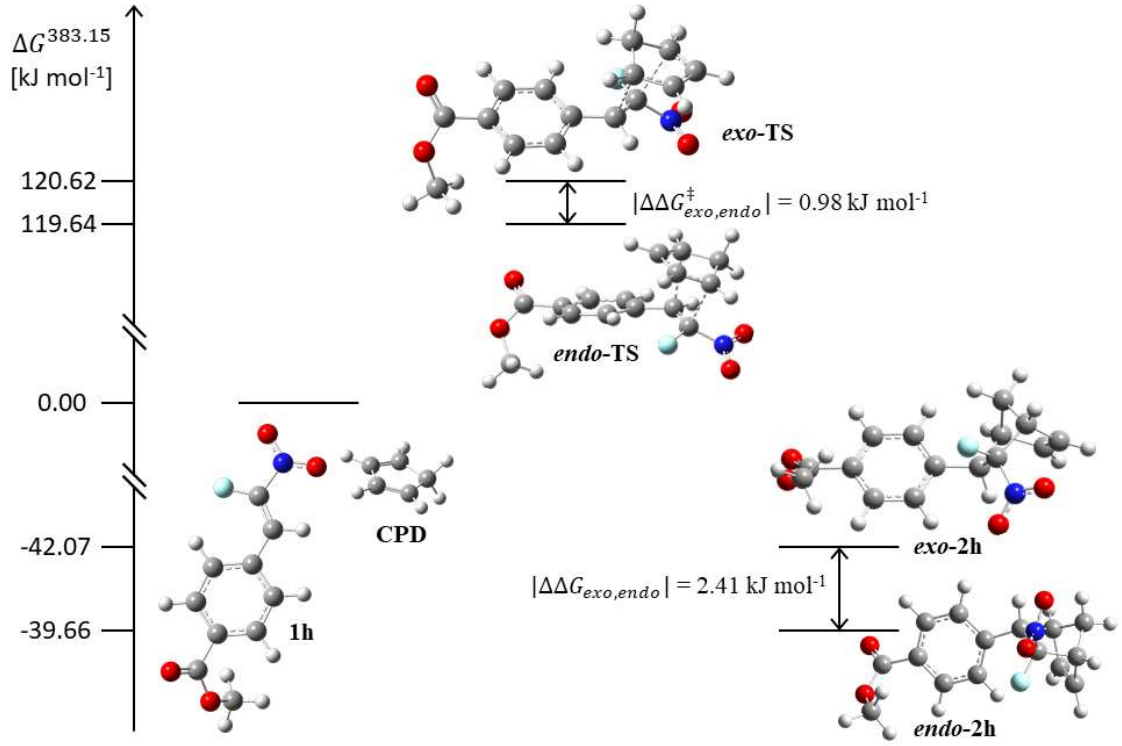
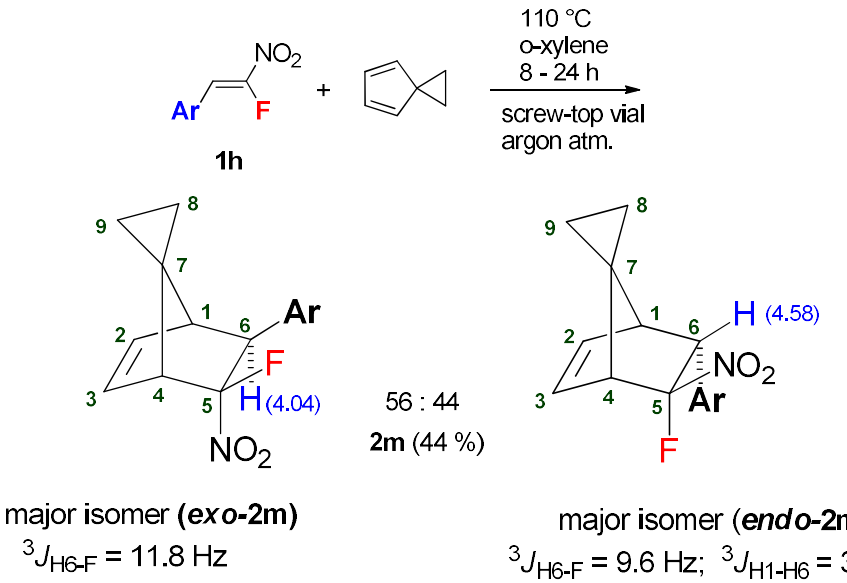


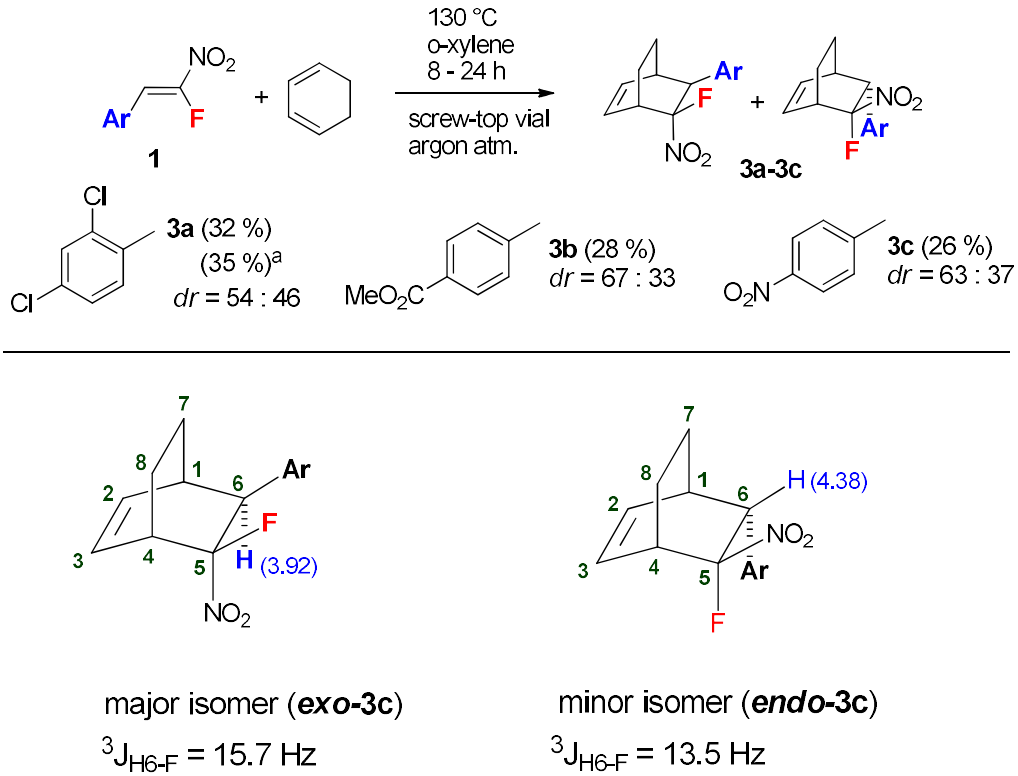
Fig. 3 The predicted reaction pathway for the Diels–Alder reaction of nitrostyrene **1h** with CPD is displayed. The path leading to the ***endo*-2h** isomer has a lower lying transition state and is more exergonic than the path resulting in the ***exo*-2h** isomer. Energies are given in [kJ mol^{-1}] and were calculated with M062X/6-311+G(d,p) at 383.15 K in *o*-xylene (the corresponding B3LYP reaction pathway is not shown).

We also demonstrate the preparation of norbornene structures substituted at the methylene bridge. The reaction of model nitrostyrene **1g** with spiro[2.4]hepta-4,6-diene was carried out (Scheme 2). As a result, the corresponding norbornene **2m** having a cyclopropane ring was obtained in moderate yield (44%). The cycloaddition proceeds much more slowly as a result of the high steric demand of fluorinated nitrostyrenes. We believe that this is the reason of lower yields in comparison to CPD. The stereochemical assignment was performed using ^{1}H-NMR spectroscopy (Scheme 2) to show similar peculiarities of the spectra. In contrast to the reaction with CPD, slight prevalence in formation of *exo*-isomer (*exo*:*endo* = 56:44) was observed for **2m.**



Scheme 2 The Diels-Alder reaction of nitrostyrene **1h** with spiro[2.4]hepta-4,6-diene.

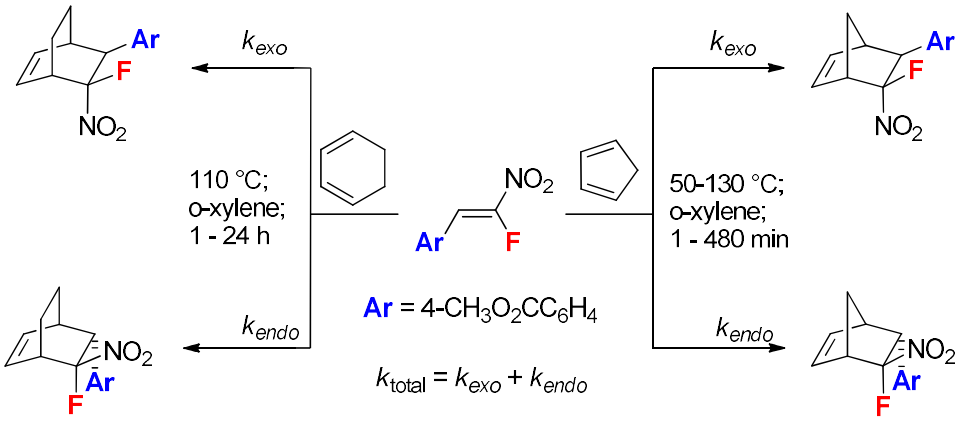
Next, the reaction with 1,3-cyclohexadiene (CHD) was investigated. It was found that the reaction is very sensitive to the structure of starting diene and in the case of CHD proceeds much more slowly. Both thermal and microwave (MW) activation (Scheme 3) was investigated to accelerate the reaction with CHD. However, in all cases, the yields of the target cycloadducts **3** were below 35% despite the full conversion of nitrostyrenes **1** which is common for this type of dienophiles (Scheme 3). The stereochemical assignment was made similarly to the norbornene structures using ^{1}H-NMR (Scheme 3). Larger values of $^{3}J_{H6\text{-}F}$ were observed for the *exo*-F isomers. The presence of a strong EWG on the aryl substituent led to higher stereoselectivity. For example, approximately a 2:1 ratio was observed for nitro- and carboxymethyl-substituted products (**3b**, **3c**), whereas in absence of a strong EWG, the ratio was about 1:1 (**3a**). However, in contrast to CPD derivatives, the major products formed in the reaction with CHD have *exo*-configuration.



Scheme 3 The Diels-Alder reaction of nitrostyrenes **1** with CHD (*dr* = *exo* : *endo*).

(a) – the reaction under microwave activation

To gain deeper insight to the reaction, we carried out some kinetic studies to evaluate and compare the reactivities of CHD and CPD in reactions with model nitrostyrene **1h** (Scheme 4). All the kinetic runs were performed using a *ca* 43-49 molar excess of the diene in o-xylene (1:1) to provide pseudo-first order conditions. Conversions (*F*) of **1** were measured by ^{1}H NMR spectroscopy. The reactions were found to proceed under the kinetic control since the isomer ratio remained constant throughout the reactions course regardless of the temperature (Table 1).



Scheme 4 Kinetic study of reactions of **1g** with CPD and CHD

The total effective pseudo-first order rate constants *k** were obtained by plotting the experimental values of ln (C_0/C) *versus* time with good correlations (Table 1). The overall second-order rate total

constants k_{total} were calculated from effective k^* and initial concentration of diene (Table 1). The individual constant for *endo*- and *exo*-isomers (k_{endo} and k_{exo}) were evaluated by multiplication of k_{total} with the molar fractions of isomers (Table 1). The data obtained demonstrated that the overall reaction rate for CHD is 267 times lower than that for CPD at 110 °C (Fig. 4, Table 1). Such a large difference in reactivity CHD and CPD was described in literature. For example, in model reactions with tetracyanoethene, the difference was 2600-fold at 20 °C. [30] The activation parameters were estimated for reaction of **1g** with CPD by plotting ln(k/T) versus 1/T according to the Eyring equation (eq. 1-3).[31]

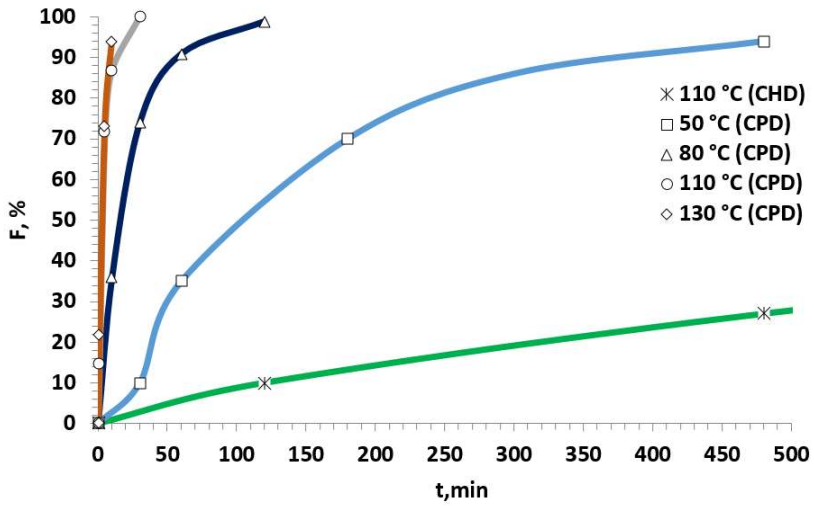


Fig. 4 Kinetic curve for reactions of nitrostyrene **1g** with CPD and CHD at 110 °C

Table 1. Kinetic parameters for the reactions of **1h** with CPD and CHD

Entry	Diene	T, °C	**Molar ratio *exo*/*endo***	$k^*\cdot10^4$ s^{-1}	$k_{total}\cdot10^5$ l/mol·s	$k_{exo}\cdot10^5$, l/mol·s	$k_{endo}\cdot10^5$, l/mol·s	R_{corr}
1	**CPD**	50	46:54	1.00	1.67	0.090	0.077	0.997
2	**CPD**	80	46:54	5.78	9.72	5.26	4.46	0.998
3	**CPD**	110	46:54	35.62	59.91	32.39	27.53	0.990
4	**CPD**	130	46:54	46.20	77.71	41.99	35.72	0.999
5	**CHD**	110	61:39	0.12	0.224	0.137	0.087	0.999

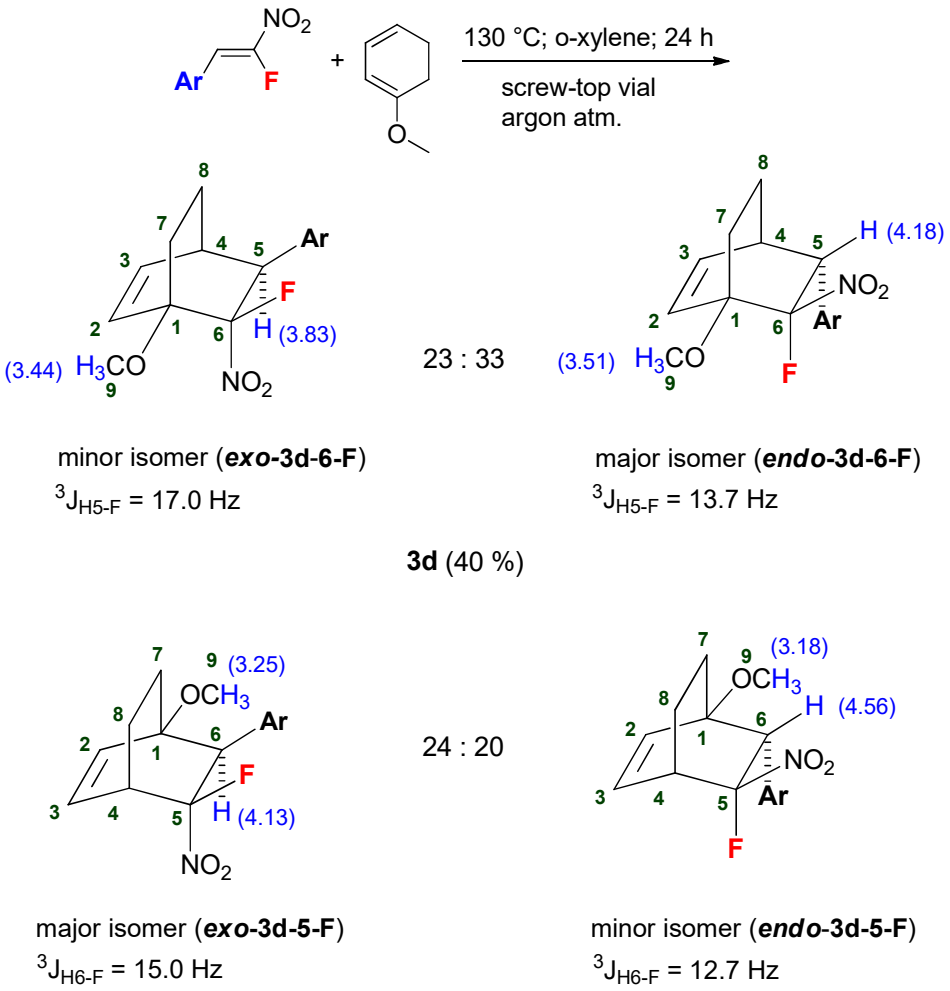
The activation enthalpies ($\Delta H^{\neq}$) for the *exo*- and *endo*-**1g** were found to be identical for both reaction pathways (51.6 kJ mol^{-1}). Whereas the entropies of activation ($\Delta S^{\neq}$) were -181.8 and -183.1 J mol^{-1} K^{-1} for the formation of *endo*- and *exo*-isomers, respectively. The values obtained are typical for concerted [4+2]-cycloaddition reactions. [25] Free energies of activation ($\Delta G^{\ddagger}_{383.15}$) were calculated 121.26 kJ mol^{-1} for ***endo*-1g** and 121.75 kJ mol^{-1} for ***exo*-1g** and were consistent with the predicted ones.

$$\ln(k/T) = \ln(k_b/\hbar) + \Delta S^{\neq}/R - \Delta H^{\neq}/RT \qquad \text{(eq. 1)}$$

$$\ln(k_{endo}/T) = 1.89 - 6208/T \quad (R_{corr} = 0.989) \qquad \text{(eq. 2)}$$

$$\ln(k_{exo}/T) = 1.72 - 6207/T \qquad (R_{corr} = 0.989) \qquad \text{(eq. 3)}$$

Next, the reaction with some other cyclic dienes was investigated. The reaction with the unsymmetrical 1-methoxy-1,3-cyclohexadiene (Scheme 5) led to the formation of the mixture of four products (regioisomers and stereoisomers, respectively) **3d** in 40 % overall yield. Two pairs of regioisomes were partially separated by column chromatography with sufficiently slow elution and analyzed by ^{1}H-NMR. The structure assignment was made as depicted in Scheme 5. The structures of two pairs of regioisomers were assigned by chemical shifts of the singlet of the methoxy-group. The products having MeO- and NO_2-group in the adjacent position have the signal of methoxy protons shifted to lower field. The assignment of the exo/endo-isomers was carried out by the position of the benzylic proton (H5 or H6) and its coupling constant to fluorine ($^{3}J_{H5\text{-}F}$ or $^{3}J_{H6\text{-}F}$).

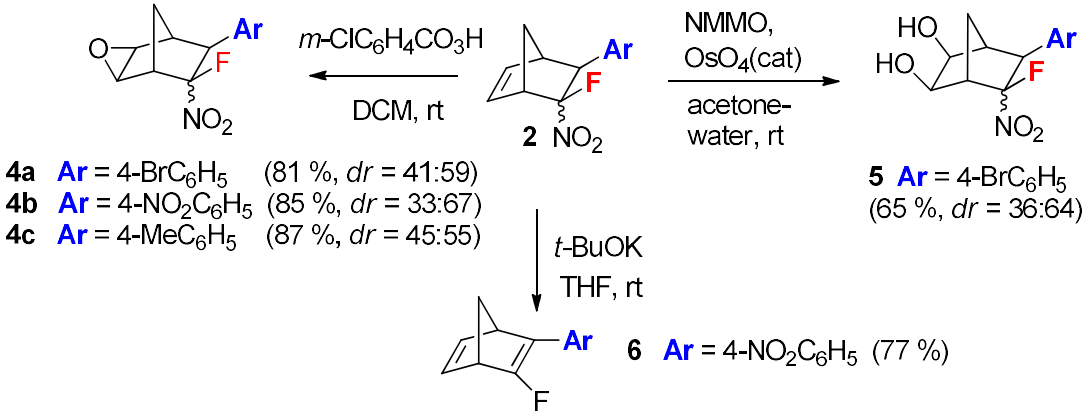


Scheme 5 The Diels-Alder reaction of nitrostyrene **1h** with 1-methoxy-1,3-cyclohexadiene

The reaction with 7- and 8-membered cyclic dienes (1,3-cycloheptadiene and 1,3-cyclooctadiene) did not result in the formation of the corresponding cycloadducts confirming that the reaction is very sensitive to the structure of dienes. Moreover, it was found that furan did not react with nitrostyrenes **1**.

Furthermore, we performed some subsequent transformations of fluorinated norbornenes prepared to investigate their chemical properties and to demonstrate their utility (Scheme 6). These reactions were

carried out to involve either the double bond or the nitro-group of the norbornene products. The treatment of cycloadducts **2** with *m*-chloroperbenzoic acid afforded a series of novel fluorinated epoxynorbornane derivatives **4** in high yields (up to 87%). In all cases, the formation of mixtures of only two products was observed in ratios similar to those of starting mixture **2.** We believe that this is a result of *exo*-epoxidation which is preferred in norbornene systems.[32] Such a functionalization is very attractive to produce new reactive building blocks bearing the norbornane scaffold. This approach can pave a straightforward way to numerous fluorine-containing bicyclic compounds not previously available. *Syn*-dihydroxylation of **2f** with the *N*-methylmorpholine-*N*-oxide (NMMO) – OsO_4 system resulted in a mixture of the corresponding diols **7** in a 36:64 ratio in 65 % yield. Again, *exo*-dihydroxylation is to be expected.[33] The treatment of norbornene **2l** with *t*-BuOK resulted in the selective elimination of nitrous acid to form the desired monofluorinated norbornadiene **8** in 77% yield. No competitive elimination of HF was observed.



Scheme 6. Selected chemical transformations of norbornenes **2** (dr = *exo*:*endo*)

In summary, the Diels-Alder reaction of β-fluoro-β-nitrostyrenes with cyclic 1,3-dienes was investigated. A series of novel monofluorinated norbornenes was prepared in high yield up to 97%. A number of novel monofluorinated bicyclo[2.2.2]oct-2-enes was obtained in up to 40% yield. The reactivity of CPD and its homologues was evaluated and compared. The reaction rate for CHD proved to be 267 times lower than that for CPD in a model reaction, whereas 1,3-cycloheptadiene and 1,3-cyclooctadiene were found to be unable to react. The activation parameters of the reaction of nitrostyrene **1g** with CPD were estimated. In addition, the synthetic utility of norbornenes obtained was demonstrated. All the structures obtained in this work were elucidated by NMR spectroscopy and elemental analysis or HRMS.

EXPERIMENTAL SECTION

All reagents were purchased from commercial sources and used without any further purification. CPD was prepared by monomerization of dicyclopentadiene (DCPD). *o*-Xylene was dried before use by passing through a column charged with activated neutral alumina[34]. Melting points (M.p.) were

measured with a Büchi B-545 melting point apparatus. NMR (^{1}H, ^{13}C and ^{19}F) spectra were obtained with Bruker AV-400 and Agilent 400-MR spectrometers using deuterated chloroform ($CDCl_3$). Chemical shifts for ^{1}H NMR spectroscopic data were referenced to internal tetramethylsilane (δ = 0.0 ppm) and the residual solvent resonance (δ = 7.26 ppm); chemical shifts for ^{13}C NMR spectroscopic data were referenced to residual solvent resonance (δ = 77.16 ppm); chemical shifts for ^{19}F NMR spectroscopic data were referenced to $PhCF_3$ (δ = –63.72 ppm). Data are reported as follows: chemical shift, integration multiplicity (s = singlet, d = doublet, t = triplet, q = quadruplet, qui = quintet, sext = sextet, sept = septet, br = board, m = multiplet, dd = *doublet of doublets*, ddd = *doublet of doublet of doublets*) and coupling constants (Hz). Starting β-fluoro-β-nitrostyrenes were prepared according to the described procedure and all are known compounds. [20, 21]

General procedure for the Diels-Alder reaction of β-fluoro-β-nitrostyrenes and 1,3-dienes

In a typical experiment, β-fluoro-β-nitrostyrene **1** (0.5 mmol), *o*-xylene (0.2 ml) and diene (2.5 mmol) were successively loaded into a screw-top vial filled with argon. After the cap was screwed tightly, the reaction mixture was heated at 110-130 °C with vigorous stirring for appropriate time (8-24 h). After completion of the reaction (^{1}H NMR analysis monitoring), the excess of the diene and *o*-xylene were evaporated under vacuum. The pure product was isolated by column chromatography using mixture of Hex/DCM as eluent.

(1R*,4S*,5R*,6R*)-5-Fluoro-5-nitro-6-phenylbicyclo[2.2.1]hept-2-ene (major isomer) and (1R*,4S*,5S*,6S*)-5-fluoro-5-nitro-6-phenylbicyclo[2.2.1]hept-2-ene (minor isomer) (**2a**). Eluent: Hex/DCM 4:1, Hex/DCM 1:1; 0.097 g (74 %); *dr* = 45:55; yellowish oil. Anal. calcd for $C_{13}H_{12}FNO_2$ (%): C, 66.94; H, 5.19; N, 6.01; Found: C, 66.88; H, 5.31; N, 6.21. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.88 – 2.00 (m, 1H), 2.38 (dd, *J* = 9.6, 0.7 Hz, 1H), 3.37 (s, 1H), 3.52 (s, 1H), 4.21 (dd, *J* = 9.4, 3.0 Hz, 1H), 6.30 (dd, *J* = 5.3, 3.5 Hz, 1H), 6.68 – 6.80 (m, 2H), 7.18 (d, *J* = 7.51H), 7.26 – 7.45 (m, 4H) ppm; (minor isomer) δ = 2.12 (dd, *J* = 9.6, 1.3 Hz, 1H), 2.45 (d, *J* = 9.5 Hz, 1H), 3.34 (s, 1H), 3.38 – 3.42 (m, 1H), 3.84 (dd, *J* = 10.9, 2.8 Hz, 1H), 6.17 – 6.22 (m, 1H), 6.68 – 6.80 (m, 1H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.45 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 47.6, 48.9 (d, $^3J_{CF}$ = 1.1 Hz), 53.6 (d, $^2J_{CF}$ = 20.5 Hz), 55.9 (d, $^2J_{CF}$ = 17.8 Hz), 125.6 (d, $^1J_{CF}$ = 252.3 Hz), 127.7, 128.4, 128.7, 132.5 (d, $^3J_{CF}$ = 4.4 Hz), 135.1 (d, $^3J_{CF}$ = 3.4 Hz), 140.3 (d, $^4J_{CF}$ = 1.2 Hz) ppm; (minor isomer) δ = 46.4, 48.0, 51.6 (d, $^2J_{CF}$ = 22.5 Hz), 52.8 (d, $^2J_{CF}$ = 19.2 Hz), 125.8 (d, $^1J_{CF}$ = 253.2 Hz), 127.7, 128.6, 129.2 (d, $^4J_{CF}$ = 1.1 Hz), 132.7 (d, $^3J_{CF}$ = 6.3 Hz), 135.2 (d, $^3J_{CF}$ = 7.1 Hz), 143.4 (d, $^4J_{CF}$ = 2.2 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -127.56 (s) ppm; (minor isomer) δ = -122.81 (s) ppm.

(1R*,4S*,5R*,6R*)-5-fluoro-5-nitro-6-(p-tolyl)bicyclo[2.2.1]hept-2-ene (major isomer) and (1R*,4S*,5S*,6S*)-5-fluoro-5-nitro-6-(p-tolyl)bicyclo[2.2.1]hept-2-ene (minor isomer) (**2b**). Eluent: Hex/DCM 3:1; Hex/DCM, 2:1; Hex/DCM, 1:1. 0.238 g (70 %); *dr* (48:52); yellowish oil.

Anal. calcd for $C_{14}H_{14}FNO_2$ (%):C, 68.00; H, 5.71; N, 5.66; Found: C, 68.19; H, 5.67; N, 5.58. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.93 – 2.00 (m, 1H), 2.41 (s, 3H), 2.55 – 2.51 (m, 1H), 3.37 (s, 1H), 3.54 (s, 1H), 4.20 (dd, *J* = 9.4, 3.0 Hz, 1H), 6.31 (dd, *J* = 5.4, 3.4 Hz, 1H), 6.78 (dd, *J* = 5.6, 2.9 Hz, 1H), 7.17 (d, *J* = 8.1 Hz, 2H), 7.23 (s, 2H) ppm; (minor isomer) δ = 2.14 (dd, *J* = 9.6, 1.3 Hz, 1H), 2.38 (s, 3H), 2.39 – 2.44 (m, 1H), 3.33 (s, 1H), 3.39 – 3.44 (m, 1H), 3.83 (dd, *J* = 10.8, 2.8 Hz, 1H), 6.18 – 6.25 (m, 1H), 6.72 – 6.76 (m, 1H), 7.11 (d, *J* = 7.6 Hz, 2H), 7.23 (s, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 21.0, 47.5, 48.9 (d, $^3J_{CF}$ = 1.0 Hz), 53.5 (d, $^2J_{CF}$ = 20.5 Hz), 55.65 (d, $^2J_{CF}$ = 17.8 Hz), 125.5 (d, $^1J_{CF}$ = 252.0 Hz), 129.1, 129.3, 132.0 (d, $^3J_{CF}$ = 3.5 Hz), 132.3 (d, $^3J_{CF}$ = 4.4 Hz), 137.4, 140.3 (d, $^4J_{CF}$ = 1.1 Hz) ppm; (minor isomer) δ = 21.1, 46.4, 47.0, 51.5 (d, $^2J_{CF}$ = 22.5 Hz), 52.5 (d, $^2J_{CF}$ = 19.2 Hz), 125.7 (d, $^1J_{CF}$ = 252.7 Hz), 128.4, 129.1, 132.1 (d, $^3J_{CF}$ = 7.3 Hz), 132.5 (d, $^3J_{CF}$ = 6.2 Hz), 137.3, 143.3 (d, $^4J_{CF}$ = 2.3 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.64 (s) ppm; (minor isomer) δ = -123.79 – -123.79 (m) ppm.

(1R*,4S*,5R*,6R*)-6-(4-(tert-butyl)phenyl)-5-fluoro-5-nitrobicyclo[2.2.1]hept-2-ene (major isomer) and (1R*,4S*,5S*,6S*)-6-(4-(tert-butyl)phenyl)-5-fluoro-5-nitrobicyclo[2.2.1]hept-2-ene (minor isomer) (**2c**). Eluent: Hex/DCM 4:1, Hex/DCM 2:1; 0.114 g, 88 % yield; *dr* = 48:52; yellowish oil. Anal. calcd for $C_{17}H_{20}FNO_2$ (%): C, 70.57; H, 6.97; N, 4.84, Found: C, 70.37; H, 7.17; N, 4.85. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.32 (s, 9H), 1.89 – 1.97 (m, 1H), 2.38 (dd, *J* = 9.6, 0.9 Hz, 1H), 3.35 (s, 1H), 3.50 – 3.54 (m, 1H), 4.18 (dd, *J* = 9.5, 3.0 Hz, 1H), 6.30 (dd, *J* = 5.5, 3.4 Hz, 1H), 6.76 (dd, *J* = 5.6, 2.9 Hz, 1H), 7.07 – 7.14 (m, 2H), 7.31 – 7.37 (m, 2H) ppm; (minor isomer) δ = 1.34 (s, 9H), 2.11 (dd, *J* = 9.6, 1.4 Hz, 1H), 2.42 – 2.49 (m, 1H), 3.31 (s, 1H), 3.37 – 3.42 (m, 1H),), 3.79 (dd, *J* = 11.0, 2.8 Hz, 1H), 6.16 – 6.22 (m, 1H), 6.68 – 6.74 (m, 1H), 7.23 (d, *J* = 8.3 Hz, 2H), 7.37 – 7.43 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 31.4, 34.5, 47.7, 49.0 (d, $^3J_{CF}$ = 1.0 Hz), 53.7 (d, $^2J_{CF}$ = 20.5 Hz), 55.7 (d, $^2J_{CF}$ = 18.0 Hz), 125.3, 125.6 (d, $^1J_{CF}$ = 252.0 Hz), 128.3, 132.1 (d, $^3J_{CF}$ = 3.4 Hz), 132.4 (d, $^3J_{CF}$ = 4.4 Hz), 140.4 (d, $^4J_{CF}$ = 1.1 Hz), 150.6 ppm; (minor isomer) δ = 31.4, 34.6, 46.6, 48.0, 51.6 (d, $^2J_{CF}$ = 22.4 Hz), 52.6 (d, $^2J_{CF}$ = 19.4 Hz), 125.6, 125.8 (d, $^1J_{CF}$ = 253.0 Hz), 129.0 (d, $^4J_{CF}$ = 1.0 Hz), 132.1 (d, $^3J_{CF}$ = 7.3 Hz), 132.6 (d, $^3J_{CF}$ = 6.1 Hz), 143.4 (d, $^4J_{CF}$ = 2.3 Hz), 150.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.55 (s) ppm; (minor isomer) δ = -123.90 – - 123.81 (m) ppm.

(1R*,4S*,5R*,6R*)-6-(4-Chlorophenyl)-5-fluoro-5-nitrobicyclo[2.2.1]hept-2-ene (major isomer) and (1R*,4S*,5S*,6S*)-6-(4-chlorophenyl)-5-fluoro-5-nitrobicyclo[2.2.1]hept-2-ene (minor isomer) (**2d**)**.** Eluent: Hex/DCM 4:1, Hex/DCM 2:1; 0.123 g (90 %); 1.057 g (83 %), *dr* (41:59); colorless oil. Anal. calcd for $C_{13}H_{11}ClFNO_2$ (%): C, 58.33; H, 4.14; N, 5.23, Found: C, 58.61; H, 4.09; N, 5.31. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.89 – 1.99 (m, 1H), 2.35 (dd, *J* = 9.8, 0.9 Hz, 1H), 3.32 (s, 1H), 3.53 (s, 1H), 4.14 (dd, *J* = 9.3, 3.1 Hz, 1H), 6.30 (dd, *J* = 5.5, 3.4 Hz, 1H), 6.66 – 6.73 (m, 1H), 7.09 (d, *J* = 7.2 Hz, 2H), 7.24 – 7.30 (m, 2H) ppm; (minor isomer) δ = 2.11

(dd, J = 9.7, 1.4 Hz, 1H), 2.34- 2.40 (m, 1H), 3.28 (s, 1H), 3.36 – 3.43 (m, 1H), 3.76 (dd, J = 10.7, 2.8 Hz, 1H), 6.15 – 6.22 (m, 1H), 6.66 – 6.74 (m, 1H), 7.22 (d, J = 8.5 Hz, 2H), 7.30 – 7.36 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 47.6, 48.9 (d, $^3J_{CF}$ = 1.2 Hz), 53.5 (d, $^2J_{CF}$ = 20.4 Hz), 55.3 (d, $^2J_{CF}$ = 17.7 Hz), 125.3 (d, $^1J_{CF}$ = 252.2 Hz), 128.5, 130.6 (d, $^4J_{CF}$ = 1.3 Hz), 132.8 (d, $^3J_{CF}$ = 4.5 Hz), 133.6 (d, $^3J_{CF}$ = 3.1 Hz), 133.7, 140.0 (d, $^4J_{CF}$ = 1.1 Hz); (minor isomer) δ = 46.3, 47.7, 51.4 (d, $^2J_{CF}$ = 22.3 Hz), 52.2 (d, $^2J_{CF}$ = 19.0 Hz), 125.6 (d, $^1J_{CF}$ = 252.8 Hz), 128.79, 130.0, 132.8 (d, $^3J_{CF}$ = 6.0 Hz), 133.6, 133.7 (d, $^3J_{CF}$ = 7.3 Hz), 143.2 (d, $^4J_{CF}$ = 2.2 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.63 (s) ppm; (minor isomer) δ = -123.69 – -123.53 (s) ppm.

(1R*,4S*,5R*,6R*)-6-(2,4-Dichlorophenyl)-5-fluoro-5-nitrobicyclo[2.2.1]hept-2-ene (major isomer) and (1R*,4S*,5S*,6S*)-6-(2,4-dichlorophenyl)-5-fluoro-5-nitrobicyclo[2.2.1]hept-2-ene (minor isomer) (**2e**). Eluent: Hex/DCM 4:1, Hex/DCM 1:1; 0.125 g (97 %), *dr* (46:54); yellowish solid; M.p. 93-94 °C. Anal. calcd for $C_{13}H_{10}Cl_2FNO_2$ (%): C, 51.68; H, 3.34; N, 4.64; found: C, 51.97; H, 3.59; N, 4.71. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.93 (dd, J = 9.4, 5.1 Hz, 1H), 2.44 (d, J = 9.6 Hz, 1H), 3.31 (s, 1H), 3.45 (s, 1H), 4.78 (dd, J = 10.0, 2.8 Hz, 1H), 6.32 (dd, J = 8.7, 3.5 Hz, 1H), 6.74 (dd, J = 5.4, 2.8 Hz, 1H), 7.09 – 7.22 (m, 1H), 7.28 (s, 1H), 7.32 – 7.42 (m, 1H) ppm; (minor isomer) δ = 2.10 (d, J = 9.4 Hz, 1H), 2.34 (d, J = 9.3 Hz, 1H), 3.25 (s, 1H), 3.36 (s, 1H), 4.10 (dd, J = 10.3, 2.5 Hz, 1H), 6.16 (s, 1H), 6.70 (s, 1H), 7.09 – 7.22 (m, 1H), 7.28 (s, 1H), 7.32 – 7.42 (m, 1H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 47.5, 49.2 (d, $^3J_{CF}$ = 1.1 Hz), 51.5 (d, $^2J_{CF}$ = 17.4 Hz), 54.4 (d, $^2J_{CF}$ = 20.2 Hz), 125.0 (d, $^1J_{CF}$ = 254.1 Hz), 127.0, 129.4, 130.6 (d, $^3J_{CF}$ = 3.8 Hz), 131.95 (d, $^3J_{CF}$ = 2.6 Hz), 132.9, 132.9, 136.2, 140.1 ppm; (minor isomer) δ = 46.8, 48.4, 50.4 (d, $^2J_{CF}$ = 18.6 Hz), 53.0 (d, $^2J_{CF}$ = 22.2 Hz), 123.3 (d, $^1J_{CF}$ = 256.7 Hz), 127.4, 129.0, 129.5, 132.9, 132.9 (d, $^3J_{CF}$ = 5.3 Hz), 134.2, 136.4, 141.7 (d, $^4J_{CF}$ = 2.5 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.84 (s) ppm; (minor isomer) δ = -126.50 (s) ppm.

(1R*,4S*,5R*,6R*)-6-(4-Bromophenyl)-5-fluoro-5-nitrobicyclo[2.2.1]hept-2-ene (major isomer) and (1R*,4S*,5S*,6S*)-6-(4-bromophenyl)-5-fluoro-5-nitrobicyclo[2.2.1]hept-2-ene (minor isomer) (**2f**). Eluent: Hex/DCM 4:1, Hex/DCM 2:1; 0.115 g, 90 % yield; 0.926 g, 73 % yield; *dr* = 43:57; yellowish oil. Anal. calcd for $C_{13}H_{11}BrFNO_2$ (%): C, 50.02; H, 3.55; N, 4.49; found: C, 50.02; H, 3.67; N, 4.40. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.88 – 1.98 (m, 1H), 2.34 (d, J = 9.8 Hz, 1H), 3.32 (s, 1H), 3.52 (s, 1H), 4.12 (dd, J = 9.3, 3.0 Hz, 1H), 6.30 (dd, J = 5.4, 3.5 Hz, 1H), 6.64 – 6.74 (m, 1H), 7.03 (d, J = 7.6 Hz, 2H), 7.39 – 7.45 (m, 2H) ppm; (minor isomer) δ = 2.10 (dd, J = 9.7, 1.3 Hz, 1H), 2.36 (d, J = 9.8 Hz, 1H), 3.27 (s, 1H), 3.39 (s, 1H), 3.75 (dd, J = 10.7, 2.7 Hz, 1H), 6.15 – 6.21 (m, 1H), 6.64 – 6.74 (m, 1H), 7.16 (d, J = 8.4 Hz, 2H), 7.44 – 7.52 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 47.6, 48.9 (d, $^3J_{CF}$ = 1.0 Hz), 53.5 (d, $^2J_{CF}$ =

20.4 Hz), 55.3 (d, $^{2}J_{CF}$ = 17.7 Hz), 121.9, 125.3 (d, $^{1}J_{CF}$ = 252.2 Hz), 131.0 (d, $^{4}J_{CF}$ = 1.2 Hz), 131.6, 132.86 (d, $^{3}J_{CF}$ = 4.2 Hz), 134.1 (d, $^{3}J_{CF}$ = 3.4 Hz), 140.0 ppm; (minor isomer) δ = 46.3, 47.8, 51.5 (d, $^{2}J_{CF}$ = 22.2 Hz), 52.3 (d, $^{2}J_{CF}$ = 19.1 Hz), 121.8, 125.6 (d, $^{1}J_{CF}$ = 253.2 Hz), 130.4, 131.8, 132.9 (d, $^{3}J_{CF}$ = 6.3 Hz), 134.3 (d, $^{3}J_{CF}$ = 7.2 Hz), 143.2 (d, $^{4}J_{CF}$ = 2.3 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.60 (s) ppm; (minor isomer) -123.57 (s) ppm.

(1R*,4S*,5R*,6R*)-5-Fluoro-6-(4-methoxyphenyl)-5-nitrobicyclo[2.2.1]hept-2-ene (major isomer) and (1R*,4S*,5S*,6S*)-5-Fluoro-6-(4-methoxyphenyl)-5-nitrobicyclo[2.2.1]hept-2-ene (minor isomer) (**2g**). Eluent: Hex/DCM 10:1, Hex/DCM 5:1; 0.095 g (68 %); *dr* (45:55); pale brown oil. Anal. calcd for $C_{14}H_{14}FNO_3$ (%): C, 63.87; H, 5.36; N, 5.32; Found: C, 63.92; H, 5.40; N, 5.27. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.88 –1.96 (m, 1H), 2.36 (dd, *J* = 9.6, 0.9 Hz, 1H), 3.30 (s, 1H), 3.51 (s, 1H), 3.78 (s, 3H), 4.12 (dd, *J* = 9.5, 3.0 Hz, 1H), 6.29 (dd, *J* = 5.4, 3.4 Hz, 1H), 6.67 – 6.75 (m, 1H), 6.81 – 6.87 (m, 2H), 7.09 (dd, *J* = 8.8, 0.7 Hz, 2H) ppm; (minor isomer) δ = 2.09 (dd, *J* = 9.6, 1.3 Hz, 1H), 2.42 (d, *J* = 9.5 Hz, 1H), 3.26 (s, 1H), 3.43 – 3.41 (m, 1H), 3.74 (dd, *J* = 10.5, 2.3 Hz, 1H), 3.81 (s, 3H), 6.14 – 6.22 (m, 1H), 6.67 – 6.75 (m, 1H), 6.81 – 6.87 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 47.8, 49.0 (d, $^{3}J_{CF}$ = 1.2 Hz), 53.6 (d, $^{2}J_{CF}$ = 20.5 Hz), 55.3, 55.4 (d, $^{2}J_{CF}$ = 18.1 Hz), 113.8, 125.5 (d, $^{1}J_{CF}$ = 251.6 Hz), 127.1 (d, $^{3}J_{CF}$ = 4.0 Hz), 129.7, 132.5 (d, $^{3}J_{CF}$ = 4.4 Hz), 140.32 (d, $^{4}J_{CF}$ = 1.2 Hz), 159.1 ppm; (minor isomer) δ = 46.7, 47.9, 51.5 (d, $^{2}J_{CF}$ = 22.5 Hz), 52.4 (d, $^{2}J_{CF}$ = 19.3 Hz), , 55.3, 114.1, 125.6 (d, $^{1}J_{CF}$ = 252.6 Hz), 127.1 (d, $^{3}J_{CF}$ = 7.0 Hz), , 130.4 (d, $^{4}J_{CF}$ = 1.0 Hz), 132.6 (d, $^{3}J_{CF}$ = 6.2 Hz), 143.4 (d, $^{4}J_{CF}$ = 2.3 Hz), 159.2 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.61 (s) ppm, (minor isomer) δ = -123.8 (s) ppm.

Methyl 4-((1R*,2R*,3R*,4S*)-3-fluoro-3-nitrobicyclo[2.2.1]hept-5-en-2-yl)benzoate (major isomer) and methyl 4-((1R*,2S*,3S*,4S*)-3-fluoro-3-nitrobicyclo[2.2.1]hept-5-en-2-yl)benzoate (minor isomer) (**2h**). Eluent: Hex/DCM 2:1, Hex/DCM 1:1, Hex/DCM 1:2; 0.127 g (95 %), *dr* (45:55); pale yellow solid; M.p. 72-75 °C. Anal. calcd for $C_{15}H_{14}FNO_4$ (%): C, 61.85; H, 4.84; N, 4.81, Found: C, 62.11; H, 4.90; N, 4.94. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.88 – 1.97 (m, 1H), 2.33 (dd, *J* = 9.7, 1.0 Hz, 1H), 3.35 (br s, 1H), 3.48 – 3.53 (m, 1H), 3.87 (s, 3H), 4.21 (dd, *J* = 9.2, 3.1 Hz, 1H), 6.27 (dd, *J* = 5.6, 3.4 Hz, 1H), 6.69 (dd, *J* = 5.5, 2.9 Hz, 1H), 7.14 – 7.24 (m, 2H), 7.90 – 7.97 (m, 2H) ppm; (minor isomer) δ = 2.07 – 2.14 (m, 1H), 2.35 – 2.41 (m, 1H), 3.32 (br s, 1H), 3.35 – 3.40 (m, 1H), 3.83 (dd, *J* = 10.5, 3.2 Hz, 1H), 3.89 (s, 3H), 6.11 – 6.20 (m, 1H), 6.69 (dd, *J* = 5.5, 2.9 Hz, 1H), 7.31 – 7.36 (m, 2H), 7.97 –8.01 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 47.4, 48.8 (d, $^{3}J_{CF}$ = 1.5 Hz), 52.2, 53.5 (d, $^{2}J_{CF}$ = 20.4 Hz), 55.6 (d, $^{2}J_{CF}$ = 17.6 Hz), 125.4 (d, $^{1}J_{CF}$ = 252.7 Hz), 129.2 (d, $^{4}J_{CF}$ = 1.8 Hz), 129.4, 129.5, 132.8 (d, $^{3}J_{CF}$ = 4.5 Hz), 140.0

(d, $^4J_{CF}$ = 1.5 Hz), 140.2 (d, $^3J_{CF}$ = 3.4 Hz), 166.7 ppm; (minor isomer) δ = 46.1 (d, $^3J_{CF}$ = 0.9 Hz), 47.8 (d, $^3J_{CF}$ = 1.1 Hz), 51.5 (d, $^2J_{CF}$ = 22.2 Hz), 52.2, 52.6 (d, $^2J_{CF}$ = 19.0 Hz), 125.8 (d, $^1J_{CF}$ = 253.4 Hz), 128.6 (d, $^4J_{CF}$ = 0.7 Hz), 129.5, 129.8, 132.8 (d, $^3J_{CF}$ = 6.3 Hz), 140.4 (d, $^3J_{CF}$ = 7.2 Hz), 143.1 (d, $^4J_{CF}$ = 2.4 Hz), 166.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.55 (s) ppm; (minor isomer) -123.67 (s) ppm.

(1R*,4S*,5R*,6R*)-5-Fluoro-5-nitro-6-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]hept-2-ene (major isomer) and (1R*,4S*,5S*,6S*)-5-Fluoro-5-nitro-6-(4-(trifluoromethyl)phenyl)bicyclo[2.2.1]hept-2-ene (minor isomer) (**2i**). Eluent: Hex/DCM, 5:1, Hex/DCM, 2:1; 0.130 g; 80 % yield; *dr* = 38:62; colorless oil. Anal. calcd for $C_{14}H_{11}F_4NO_2$: C, 55.82; H, 3.68; N, 4.65; found: C, 56.06; H, 3.50; N, 4.49. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.92 – 2.03 (m, 1H), 2.31 – 2.46 (m, 1H), 3.38 (s, 1H), 3.56 (s, 1H), 4.24 (dd, *J* = 9.0, 2.1 Hz, 1H), 6.29 – 6.37 (m, 1H), 6.65 – 6.77 (m, 1H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H) ppm; (minor isomer) δ = 2.15 (d, *J* = 9.5 Hz, 1H), 2.31 – 2.46 (m, 1H), 3.34 (s, 1H), 3.42 (s, 1H), 3.86 (dd, *J* = 10.6, 1.6 Hz,1H), 6.17– 6.24 (m, 1H), 6.65 – 6.77 (m, 1H), 7.42 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 47.6, 48.9 (d, $^3J_{CF}$ = 1.0 Hz), 53.5 (d, $^2J_{CF}$ = 20.3 Hz), 55.5 (d, $^2J_{CF}$ = 17.5 Hz), 124.1 (q, $^1J_{CF}$ = 272.1 Hz), 125.3 (q, $^3J_{CF}$ = 3.6 Hz), 125.4 (d, $^1J_{CF}$ = 252.6 Hz), 129.7 (d, $^4J_{CF}$ = 1.2 Hz), 130.0 (q, $^2J_{CF}$ = 32.0 Hz), 133.0 (d, $^3J_{CF}$ = 4.0 Hz), 139.2, 139.9 (d, $^4J_{CF}$ = 0.9 Hz) ppm; (minor isomer) δ = 46.2, 47.8, 51.5 (d, $^2J_{CF}$ = 22.2 Hz), 52.5 (d, $^2J_{CF}$ = 19.0 Hz), 124.1 (q, $^1J_{CF}$ = 272.1 Hz), 125.6 (q, $^3J_{CF}$ = 3.6 Hz), 125.8 (d, $^1J_{CF}$ = 253.4 Hz), 129.1, 130.0 (q, $^2J_{CF}$ = 32.0 Hz), 133.0 (d, $^3J_{CF}$ = 5.2 Hz), 139.4 (d, $^3J_{CF}$ = 7.9 Hz), 143.2 (d, $^4J_{CF}$ = 2.2 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.41 (s, 1F), -63.70 (s, 3F) ppm; (minor isomer) δ = 123.38 (s, 1F), -63.65 (s, 3F) ppm.

4-((1R*,2R*,3R*,4S*)-3-Fluoro-3-nitrobicyclo[2.2.1]hept-5-en-2-yl)benzonitrile (major isomer) and 4-((1R*,2S*,3S*,4S*)-3-fluoro-3-nitrobicyclo[2.2.1]hept-5-en-2-yl)benzonitrile (minor isomer) (**2j**). Eluent: Hex/DCM, 1:1; Hex/DCM, 1:2; 0.101 g (75 %); *dr* = 34:66; colorless oil. Anal. calcd for $C_{14}H_{11}FN_2O_2$ (%): C, 65.11; H, 4.29; N, 10.85; Found: C, 65.38; H, 4.32; N, 10.51. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.91 – 2.01 (m, 1H), 2.32 (s, 1H), 3.37 (s, 1H), 3.55 (s, 1H), 4.21 (dd, *J* = 9.1, 3.0 Hz, 1H), 6.31 (dd, *J* = 5.4, 3.4 Hz, 1H), 6.66 – 6.73 (m, 1H), 7.25 – 7.30 (m, 2H), 7.61 – 7.66 (m, 2H) ppm; (minor isomer) δ = 2.13 (dd, *J* = 9.8, 1.4 Hz, 1H), 2.35 (s, 1H), 3.33 (s, 1H), 3.39 – 3.43 (m, 1H), 3.83 (dd, *J* = 10.7, 2.8 Hz, 1H), 6.16 – 6.21 (m, 1H), 6.66 – 6.73 (m, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.60 – 7.67 (m, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 47.4, 48.8 (d, $^3J_{CF}$ = 1.1 Hz), 53.3 (d, $^2J_{CF}$ = 20.3 Hz), 55.5 (d, $^2J_{CF}$ = 17.4 Hz), 111.6, 118.6, 125.2 (d, $^1J_{CF}$ = 252.7 Hz), 130.0 (d, $^4J_{CF}$ = 1.5 Hz), 132.1, 133.1 (d, $^3J_{CF}$ = 4.4 Hz), 139.7 (d, $^4J_{CF}$ = 1.0 Hz), 140.5 (d, $^3J_{CF}$ = 3.1 Hz) ppm; (minor isomer) δ = 45.9, 47.6, 51.28 (d, $^2J_{CF}$

= 22.1 Hz), 52.53 (d, $^{2}J_{CF}$ = 18.9 Hz), 111.6, 118.6, 125.74 (d, $^{1}J_{CF}$ = 253.2 Hz), 129.45, 132.32, 133.0 (d, $^{3}J_{CF}$ = 6.2 Hz), 140.67 (d, $^{3}J_{CF}$ = 7.4 Hz), 143.01 (d, $^{4}J_{CF}$ = 2.2 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.48 (s) ppm ; (minor isomer) δ = -123.31 (s) ppm.

(1R*,4S*,5R*,6R*)-5-Fluoro-5-nitro-6-(3-nitrophenyl)bicyclo[2.2.1]hept-2-ene (major isomer) and (1R*,4S*,5S*,6S*)-5-Fluoro-5-nitro-6-(3-nitrophenyl)bicyclo[2.2.1]hept-2-ene (minor isomer) (**2k**). Eluent: Hex/DCM, 3:1, Hex/DCM, 2:1; 0.112 g; 80% yield; *dr* = 31:69; greenish oil; anal. calcd for $C_{13}H_{11}FN_2O_4$ (%): C, 56.12; H, 3.98; N, 10.07; Found: C, 56.33; H, 3.99; N, 9.95; ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.93 – 2.06 (m, 1H), 2.36 (dd, *J* = 9.8, 1.0 Hz, 1H), 3.41 (s, 1H), 3.58 (s, 1H), 4.27 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.37 (dd, *J* = 5.5, 3.4 Hz, 1H), 6.69 – 6.78 (m, 1H), 7.44 – 7.52 (m, 2H), 8.04 (s, 1H), 8.09 – 8.19 (m, 1H) ppm; (minor isomer) δ = 2.18 (dd, *J* = 9.9, 1.3 Hz, 1H), 2.40 (dd, *J* = 9.9, 1.2 Hz, 1H), 3.38 (s, 1H), 3.45 (dd, *J* = 8.5, 6.7 Hz, 1H), 3.89 (dd, *J* = 10.6, 2.7 Hz, 1H), 6.15 – 6.27 (m, 1H), 6.69 – 6.78 (m, 1H), 7.44 – 7.57 (m, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 8.09 – 8.19 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 47.6, 48.9 (d, $^{3}J_{CF}$ = 1.5 Hz), 53.4 (d, $^{2}J_{CF}$ = 20.3 Hz), 55.2 (d, $^{2}J_{CF}$ = 17.4 Hz), 122.8, 124.0 (d, $^{4}J_{CF}$ = 1.8 Hz), 125.1 (d, $^{1}J_{CF}$ = 252.5 Hz), 129.4, 133.4 (d, $^{3}J_{CF}$ = 4.3 Hz), 135.8 (d, $^{3}J_{CF}$ = 1.8 Hz), 137.2 (d, $^{3}J_{CF}$ = 3.4 Hz), 139.6 (d, $^{4}J_{CF}$ = 1.5 Hz), 148.3 ppm; (minor isomer) δ = 46.1 (d, $^{3}J_{CF}$ = 0.6 Hz), 47.6, 51.3 (d, $^{2}J_{CF}$ = 22.1 Hz), 52.2 (d, $^{2}J_{CF}$ = 18.8 Hz), 122.9, 123.0 (d, $^{4}J_{CF}$ = 0.6 Hz), 125.7 (d, $^{1}J_{CF}$ = 253.1 Hz), 129.6, 133.1 (d, $^{3}J_{CF}$ = 6.2 Hz), 135.5 (d, $^{3}J_{CF}$ = 0.5 Hz), 137.4 (d, $^{3}J_{CF}$ = 7.5 Hz), 143.0 (d, $^{4}J_{CF}$ = 2.3 Hz), 148.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.40 (s) ppm; (minor isomer) δ = -123.02 (s) ppm.

(1R*,4S*,5R*,6R*)-5-Fluoro-5-nitro-6-(4-nitrophenyl)bicyclo[2.2.1]hept-2-ene (major isomer) and (1R*,4S*,5S*,6S*)-5-fluoro-5-nitro-6-(4-nitrophenyl)bicyclo[2.2.1]hept-2-ene (minor isomer) (**2l**). Eluent: Hex/DCM, 3:1; Hex/DCM, 2:1; 0.705 g (71 %); 0.089 g (67 %), *dr* (40:60); brown oil. Anal. calcd for $C_{13}H_{11}FN_2O_4$ (%): C, 56.12; H, 3.98; N, 10.07, Found: C, 56.36; H, 4.18; N, 9.95. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.96 – 2.03 (m, 1H), 2.32 – 2.41 (m, 1H), 3.38 – 3.42 (m, 1H), 3.56 – 3.59 (m, 1H), 4.27 (dd, *J* = 9.1, 3.1 Hz, 1H), 6.34 (dd, *J* = 5.6, 3.4 Hz, 1H), 6.70 (dd, *J* = 5.7, 2.8 Hz, 1H), 7.32 – 7.37 (m, 2H), 8.10 – 8.16 (m, 2H) ppm; (minor isomer) δ = 2.17 (dtd, *J* = 9.8, 2.8, 1.5 Hz, 1H), 2.32 – 2.41 (m, 2H), 3.34 – 3.39 (m, 1H), 3.41 – 3.46 (m, 1H), 3.89 (dd, *J* = 10.7, 2.9 Hz, 1H), 6.18 – 6.23 (m, 1H), 6.71 – 6.75 (m, 1H), 7.44 – 7.51 (m, 2H), 8.16 – 8.22 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 47.6, 48.9 (d, $^{3}J_{CF}$ = 1.5 Hz), 53.4 (d, $^{2}J_{CF}$ = 20.2 Hz), 55.3 (d, $^{2}J_{CF}$ = 17.3 Hz), 123.5, 125.2 (d, $^{1}J_{CF}$ = 252.8 Hz), 130.2 (d, $^{4}J_{CF}$ = 1.9 Hz), 133.3 (d, $^{3}J_{CF}$ = 4.3 Hz), 139.7 (d, $^{4}J_{CF}$ = 1.6 Hz), 142.5 (d, $^{3}J_{CF}$ = 3.2 Hz), 147.3 ppm; (minor isomer) δ = 46.1 (d, $^{3}J_{CF}$ = 0.6 Hz), 47.6, 51.3 (d, $^{2}J_{CF}$ = 21.9 Hz), 52.4 (d, $^{2}J_{CF}$ = 18.7 Hz), 123.7, 125.8 (d, $^{1}J_{CF}$ = 253.6 Hz), 129.6 (d, $^{4}J_{CF}$ = 0.6 Hz), 133.1 (d, $^{3}J_{CF}$ = 6.2 Hz), 142.7 (d, $^{3}J_{CF}$ = 7.3

Hz), 143.0 (d, $^{4}J_{CF}$ = 2.4 Hz), 147.4 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.39 (s) ppm; (minor isomer) δ = -123.23 (s) ppm.

Methyl 4-((1R*,4S*,5S*,6S*)-5-fluoro-5-nitrospiro[bicyclo[2.2.1]heptane-7,1'-cyclopropan]-2-en-6-yl)benzoate (major isomer) and methyl 4-((1R*,4S*,5R*,6R*)-5-fluoro-5-nitrospiro[bicyclo[2.2.1]heptane-7,1'-cyclopropan]-2-en-6-yl)benzoate (minor isomer) (**2m**). Eluent: Hex/DCM, 2:1; Hex/DCM, 1:1; Hex/DCM, 1:3; 0.070 g, 44 % yield; *dr* = 44:56; yellowish oil; Anal. calcd for $C_{17}H_{16}FNO_4$ (%): C, 64.35; H, 5.08; N, 4.41; found: C, 64.18; H, 5.18; N, 4.24. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 0.53 – 0.68 (m, 2H), 0.71 – 0.81 (m, 1H), 0.96 (dd, *J* = 14.8, 7.6 Hz, 1H), 2.84 – 2.89 (m, 1H), 3.00 (br s, 1H), 3.90 (s, 3H), 4.04 (d, *J* = 11.8 Hz, 1H), 6.21 – 6.27 (m, 1H), 6.81 (dd, *J* = 5.8, 3.2 Hz, 1H), 7.37 (d, *J* = 8.3 Hz, 2H), δ 7.99 (d, *J* = 8.4 Hz, 2H) ppm; (minor isomer) δ = 0.53 – 0.68 (m, 2H), 0.71 – 0.81 (m, 1H), 1.01 – 1.11 (m, 1H), 2.68 – 2.74 (m, 1H), 3.18 (br s, 1H), 3.89 (s, 3H), 4.58 (dd, *J* = 9.6, 3.2 Hz, 1H), 6.40 (dd, *J* = 5.5, 3.5 Hz, 1H), 6.77 (dd, *J* = 5.7, 2.8 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 10.2, 11.3 (d, $^{4}J_{CF}$ = 2.9 Hz), 44.8, 50.6, 52.2, 54.7 (d, $^{2}J_{CF}$ = 18.3 Hz), 57.3 (d, $^{2}J_{CF}$ = 21.0 Hz), 125.5 (d, $^{1}J_{CF}$ = 256.3 Hz), 129.3, 129.5 (d, $^{4}J_{CF}$ = 1.1 Hz), 129.6, 132.0 (d, $^{3}J_{CF}$ = 5.8 Hz), 140.1, 140.1 (d, $^{3}J_{CF}$ = 6.4 Hz), 166.8 ppm; (minor isomer) δ = 3.8, 5.4, 44.4 (d, $^{3}J_{CF}$ = 3.5 Hz), 52.2, 53.6, 55.0 (d, $^{2}J_{CF}$ = 17.7 Hz), 56.0 (d, $^{2}J_{CF}$ = 20.4 Hz), 126.4 (d, $^{1}J_{CF}$ = 252.0 Hz), 129.3, 129.4, 129.6, 132.2 (d, $^{3}J_{CF}$ = 3.1 Hz), 140.3 (d, $^{3}J_{CF}$ = 3.5 Hz), 143.5 (d, $^{4}J_{CF}$ = 1.5 Hz), 166.9 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -127.47 (dd, *J* = 10.8, 5.7 Hz) ppm; (minor isomer) δ = -124.77 (d, *J* = 9.3 Hz) ppm;

(1R*,4S*,5S*,6S*)-6-(2,4-Dichlorophenyl)-5-fluoro-5-nitrobicyclo[2.2.2]oct-2-ene (major isomer) and (1R*,4S*,5R*,6R*)-6-(2,4-dichlorophenyl)-5-fluoro-5-nitrobicyclo[2.2.2]oct-2-ene (minor isomer) (**3a**). Eluent: Hex/DCM, 3:1; 0.051 g, 32 % yield; 0.119 g, 35 % yield; *dr* = 41:59; viscous pale yellow oil; Anal. calcd for $C_{14}H_{12}Cl_2FNO_2$: C, 53.19; H, 3.83; N, 4.43; found: C, 53.45; H, 3.87: N, 4.25; ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.32 – 1.62 (m, 2H), 1.88 –2.06 (m, 2H), 2.71 – 2.80 (m, 1H), 3.27 – 3.38 (m, 1H), 4.43 (dt, *J* = 14.4, 1.8 Hz, 1H), 6.22 – 6.29 (m, 1H), 6.67 (t, *J* = 7.4 Hz, 1H), 7.22 – 7.51 (m, 3H) ppm; (minor isomer) δ = 1.20 – 1.33 (m, 2H), 2.11 – 2.24 (m, 2H), 2.93 – 3.01 (m, 1H), 3.14 – 3.21 (m, 1H), 4.68 (dd, *J* = 12.4, 1.3 Hz, 1H), 6.29 – 6.35 (m, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 7.15 – 7.21 (m, 1H), 7.22 – 7.51 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 17.2, 19.8 (d, $^{3}J_{CF}$ = 3.9 Hz), 36.3, 39.4 (d, $^{2}J_{CF}$ = 21.9 Hz), 44.2 (d, $^{2}J_{CF}$ = 16.5 Hz), 124.0 (d, $^{1}J_{CF}$ = 247.6 Hz), 127.1, 128.99, 129.92, 130.62 (d, $^{4}J_{CF}$ = 2.2 Hz), 131.41, 134.09 (d, $^{3}J_{CF}$ = 11.6 Hz), 136.13, 137.89 ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (minor isomer) δ = 19.99 (d, $^{3}J_{CF}$ = 4.3 Hz), 24.40, 36.58, 40.41 (d, $^{2}J_{CF}$ = 21.4 Hz), 48.85 (d, $^{2}J_{CF}$ = 17.6 Hz), 122.32 (d, $^{1}J_{CF}$ = 247.8 Hz), 126.88, 128.94 (d, $^{3}J_{CF}$ = 4.1 Hz), 129.35, 131.36 (d, $^{4}J_{CF}$ = 3.2 Hz), 131.51, 132.93

(d, $^{3}J_{CF}$ = 7.6 Hz), 134.75, 135.69 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -128.89 (dd, *J* = 14.4, 2.1 Hz) ppm; (minor isomer) δ = -117.92 – -117.79 (m) ppm

Methyl 4-((1R*,2S*,3S*,4S*)-3-fluoro-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate (major isomer) and methyl 4-((1R*,2R*,3R*,4S*)-3-fluoro-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate (minor isomer) (**3b**). Eluent: Hex/DCM, 1:1; Hex/DCM, 2:3; Hex/DCM, 1:3; Hex/DCM, 1:5; Hex/DCM, 1:10; DCM; 0.042 g, 28 % yield; *dr* = 33:67; yellowish oil. Anal. calcd for $C_{16}H_{16}FNO_4$ (%):C, 62.95; H, 5.28; N, 4.59; Found: C, 63.14; H, 5.27; N, 4.59. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.40 – 1.55 (m, 2H), 1.98 – 2.25 (m, 2H), 3.03 – 3.10 (m, 1H), 3.25 – 3.34 (m, 1H), 3.88 (d, $^{3}J_{HF}$ = 15.8 Hz, 1H), 3.92 (s, 3H), 6.25 – 6.33 (m, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.38 (m, 2H), 7.97 – 8.07 (m, 2H) ppm; (minor isomer) δ = 1.30 – 1.41 (m, 2H), 1.77 – 1.97 (m, 2H), 3.02 (dd, *J* = 2.9, 1.6 Hz, 1H), 3.31 – 3.36 (m, 1H), 3.90 (s, 3H), 4.33 (d, $^{3}J_{HF}$ = 13.6 Hz, 1H), 6.29 – 6.36 (m, 1H), 6.75 (t, *J* = 7.2 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.91 – 7.98 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 17.2, 20.5 (d, $^{3}J_{CF}$ = 5.2 Hz), 35.7, 39.7 (d, $^{2}J_{CF}$ = 22.2 Hz), 49.6 (d, $^{2}J_{CF}$ = 18.7 Hz), 52.3, 121.6 (d, $^{1}J_{CF}$ = 250.9 Hz), 129.0, 129.4 (d, $^{3}J_{CF}$ = 3.0 Hz), 129.5, 129.8, 137.4, 140.0 (d, $^{3}J_{CF}$ = 5.4 Hz), 166.8 ppm; (minor isomer) δ = 19.0 (d, $^{3}J_{CF}$ = 4.2 Hz), 25.1, 36.5, 40.0 (d, $^{2}J_{CF}$ = 21.5 Hz), 51.9 (d, $^{2}J_{CF}$ = 17.8 Hz), 52.2, 123.8 (d, $^{1}J_{CF}$ = 245.6 Hz), 128.5 (d, $^{3}J_{CF}$ = 2.6 Hz), 129.0, 129.5, 129.7, 135.3, 141.0 (d, $^{3}J_{CF}$ = 8.2 Hz), 166.8 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -127.25 (d, $^{3}J_{HF}$ = 15.8 Hz) ppm; (minor isomer) δ = -116.42 (d, $^{3}J_{HF}$ = 13.6 Hz) ppm

(1R*,4S*,5S*,6S*)-5-Fluoro-5-nitro-6-(4-nitrophenyl)bicyclo[2.2.2]oct-2-ene (major isomer) and (1R*,4S*,5R*,6R*)-5-fluoro-5-nitro-6-(4-nitrophenyl)bicyclo[2.2.2]oct-2-ene (minor isomer) (**3c**). Eluent: Hex/DCM, 2:1; Hex/DCM, 1:1; 0.038 g, 26 % yield; *dr* = 37:63; viscous pale brown oil. Anal. calcd for $C_{14}H_{13}FN_2O_4$ (%):C, 57.53; H, 4.48; N, 9.59; Found : C, 57.81; H, 4.49; N, 9.42. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.44 – 1.56 (m, 2H), 1.98 – 2.10 (m, 1H), 2.11 – 2.22 (m, 1H), 3.04 – 3.10 (m, 1H), 3.30 – 3.41 (m, 1H), 3.92 (d, $^{3}J_{HF}$ = 15.7 Hz, 1H), 6.28 – 6.34 (m, 1H), 6.67 (t, *J* = 7.3 Hz, 1H), 7.38 – 7.50 (m, 2H), 8.16 – 8.27 (m, 2H) ppm; (minor isomer) δ = 1.33 – 1.44 (m, 2H), 1.76 – 1.86 (m, 1H), 1.94 (td, *J* = 9.4, 2.8 Hz, 1H), 2.99 – 3.05 (m, 1H), 3.30 – 3.41 (m, 1H), 4.38 (d, *J* = 13.5 Hz, 1H), 6.34 – 6.40 (m, 1H), 6.75 (t, *J* = 7.2 Hz, 1H), 7.35 (d, *J* = 8.8 Hz, 2H), 8.10 – 8.17 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 17.2, 20.3 (d, $^{3}J_{CF}$ = 5.1 Hz), 35.7, 39.5 (d, $^{2}J_{CF}$ = 22.1 Hz), 49.5 (d, $^{2}J_{CF}$ = 18.6 Hz), 121.3 (d, $^{1}J_{CF}$ = 250.6 Hz), 123.7, 129.6 (d, $^{3}J_{CF}$ = 7.1 Hz), 130.5 (d, $^{4}J_{CF}$ = 3.0 Hz), 137.2, 142.2 (d, $^{3}J_{CF}$ = 5.4 Hz), 147.3 ppm; (minor isomer) δ = 18.9 (d, $^{3}J_{CF}$ = 4.2 Hz), 25.04, 36.6, 39.8 (d, $^{2}J_{CF}$ = 21.3 Hz), 51.6 (d, $^{2}J_{CF}$ = 17.6 Hz), 123.6 (d, $^{1}J_{CF}$ = 245.8 Hz), 123.6, 129.0 (d, $^{3}J_{CF}$ = 2.4 Hz), 130.0, 134.9, 143.3 (d, $^{3}J_{CF}$ = 8.2 Hz), 147.5 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -127.03 (d, $^{3}J_{HF}$ = 15.7 Hz) ppm; (minor isomer) δ = -116.12 (d, $^{3}J_{HF}$ = 13.5 Hz) ppm.

Methyl 4-(3-fluoro-4-methoxy-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate and methyl 4-(3-fluoro-1-methoxy-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate (**3d**). Eluent: Hex/DCM, 1:1; Hex/DCM, 2:3; Hex/DCM, 1:3; Hex/DCM, 1:5; Hex/DCM, 1:10; DCM. 0.067 g, 40 % yield; isomers ratio = (24:20) : (23:33); yellowish oil; $C_{17}H_{18}FNO_5$: C, 60.89; H, 5.41; N, 4.18; found: C, 60.85; H, 5.66; N, 4.08. ^{1}H NMR (400 MHz, $CDCl_3$): (**methyl 4-((1R*,2R*,3S*,4R*)-3-fluoro-4-methoxy-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate** (24 %)) δ = 1.57 – 1.68 (m, 2H), 2.22 – 2.32 (m, 2H), 2.94 – 3.01 (m, 1H), 3.51 (d, J = 1.3 Hz, 3H), 3.90 (s, 3H), 4.18 (d, $^3J_{HF}$ = 13.7 Hz, 1H), 6.50 (d, J = 8.6 Hz, 1H), 6.74 (dd, J = 8.6, 6.4 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.92 – 7.97 (m, 2H) ppm; (**methyl 4-((1R*,2S*,3R*,4R*)-3-fluoro-4-methoxy-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate** (20 %)) δ = 1.57 – 1.68 (m, 2H), 2.22 – 2.32 (m, 2H), 3.11 – 3.21 (m, 1H), 3.44 (s, 3H), 3.83 (d, $^3J_{HF}$ = 17.0 Hz, 1H), 3.91 (s, 3H), 6.37 – 6.44 (m, 1H), 6.61 (dd, J = 8.6, 6.7 Hz, 1H), 7.22 (d, J = 8.2 Hz, 2H), 7.98 – 8.02 (m, 2H) ppm; **(methyl 4-((1S*,2R*,3S*,4S*)-3-fluoro-1-methoxy-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate** (33 %)) δ = 1.51 – 1.74 (m, 2H), 2.07 – 2.34 (m, 2H), 3.25 (s, 3H), 3.26 – 3.34 (m, 1H), 3.91 (s, 3H), 4.13 (d, $^3J_{HF}$ = 15.0 Hz, 1H), 6.19 – 6.32 (m, 1H), 6.75 (d, J = 8.8 Hz, 1H), 7.37 (dd, J = 8.2, 1.4 Hz, 2H), 8.02 (d, J = 8.3 Hz, 2H) ppm; **methyl 4-((1S*,2S*,3R*,4S*)-3-fluoro-1-methoxy-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate** (23 %)) δ = 1.51 – 1.74 (m, 2H), 2.07 – 2.34 (m, 2H), 3.18 (s, 3H), 3.26 – 3.34 (m, 1H), 3.89 (s, 3H), 4.56 (d, $^3J_{HF}$ = 12.7 Hz, 1H), 6.19 – 6.32 (m, 1H), 6.68 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 5.2 Hz, 2H), 7.95 (d, J = 8.3 Hz, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 18.7, 18.8, 20.5 (d, $^3J_{CF}$ = 3.4 Hz), 23.2, 23.8, 26.0, 27.4, 29.8, 34.1, 36.1, 39.0 (d, $^2J_{CF}$ = 22.2 Hz), 39.6 (d, $^2J_{CF}$ = 21.7 Hz), 41.2, 50.8, 51.8, 52.2, 52.3, 52.3, 53.1 (d, $^2J_{CF}$ = 18.5 Hz), 53.2 (d, $^2J_{CF}$ = 19.7 Hz), 53.6 (d, $^3J_{CF}$ = 2.1 Hz), 55.0 (d, $^2J_{CF}$ = 18.7 Hz), 55.4 (d, $^2J_{CF}$ = 17.7 Hz), 77.4, 79.0, 80.1, 81.3 (d, $^3J_{CF}$ = 4.3 Hz), 81.5, 120.8 (d, $^1J_{CF}$ = 250.1 Hz), 122.0 (d, $^1J_{CF}$ = 249.9 Hz), 123.1 (d, $^1J_{CF}$ = 246.4 Hz), 123.5 (d, $^1J_{CF}$ = 250.5 Hz), 126.5 (d, $^4J_{CF}$ = 1.2 Hz), 127.3 (d, $^3J_{CF}$ = 7.8 Hz), 128.1, 128.8 (d, $^4J_{CF}$ = 1.7 Hz), 128.8, 129.2 (d, $^4J_{CF}$ = 2.8 Hz), 129.4, 129.5, 129.7 (d, $^3J_{CF}$ = 10.9 Hz), 129.8, 129.9, 129.9, 130.0, 130.4, 130.5, 131.3 (d, J = 2.7 Hz), 133.2 (d, $^3J_{CF}$ = 4.6 Hz), 134.1 (d, $^3J_{CF}$ = 5.3 Hz), 137.0 (d, $^3J_{CF}$ = 5.6 Hz), 137.5 (d, $^3J_{CF}$ = 8.4 Hz), 137.9, 138.9, 139.4 (d, $^3J_{CF}$ = 5.8 Hz), 140.2 (d, $^3J_{CF}$ = 8.6 Hz), 166.7, 166.8, 166.9, 166.9 ppm. ^{19}F NMR (376 MHz, $CDCl_3$): (**methyl 4-((1R*,2R*,3S*,4R*)-3-fluoro-4-methoxy-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate**) δ = -127.17 (dd, J = 13.7, 6.2 Hz) ppm; (**methyl 4-((1R*,2S*,3R*,4R*)-3-fluoro-4-methoxy-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate**) δ = -136.93 (d, J = 17.0 Hz) ppm; (**methyl 4-((1S*,2R*,3S*,4S*)-3-fluoro-1-methoxy-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate**) δ = -123.81 (d, J = 15.0 Hz) ppm; (**methyl 4-((1S*,2S*,3R*,4S*)-3-fluoro-1-methoxy-3-nitrobicyclo[2.2.2]oct-5-en-2-yl)benzoate**)
δ = -114.71 – -114.50 (m) ppm.

General procedure for epoxidation of cycloadducts 2. In a typical experiment, m-chloroperbenzoic acid (0.6 mmol) was added to solution of norbornene **2** (0.2 mmol) in DCM (1 mL). The reaction mixture was stirred overnight at room temperature. The reaction was monitored by TLC. After completion of the reaction the reaction mixture was poured into saturated solution of $Na_2S_2O_3$ (10 mL) The resulting mixture was then extracted with DCM (3 × 15 mL). The combined organic layer was washed with saturated solution of $NaHCO_3$ (3 × 50 mL), dried over Na_2SO_4, filtered and concentrated under vacuum. The pure product was isolated by column chromatography on neutral alumina using mixture of Hex/DCM in appropriate ratio as eluent.

(1S*,2S*,4R*,5S*,6S*,7R*)-7-(4-Bromophenyl)-6-fluoro-6-nitro-3-oxatricyclo[3.2.1.02,4]octane (major isomer) **and (1S*,2S*,4R*,5S*,6R*,7S*)-7-(4-bromophenyl)-6-fluoro-6-nitro-3-oxatricyclo[3.2.1.$0^{2,4}$]octane** (minor isomer) (**4a**). Eluent: Hex/DCM, 3:1; Hex/DCM, 2:1; 0.051 g, 81 % yield; *dr* = 41:59; yellowish viscous oil; HRMS (ESI-TOF) m/z: calcd for $C_{13}H_{12}{}^{80}BrFNO_3$ $[M+H]^+$ = 327.9985; found 327.9985. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.73 – 1.78 (m, 2H), 3.08 – 3.19 (m, 1H), 3.29 (s, 1H), 3.47 – 3.52 (m, 1H), 3.58 (dd, *J* = 3.4, 0.8 Hz, 1H), 4.01 (dd, *J* = 11.2, 3.5 Hz, 1H), 7.13 (dd, *J* = 8.4, 1.4 Hz, 2H), 7.44 – 7.52 (m, 2H) ppm; (minor isomer) δ = 1.79 (br s, 1H), 1.85 –1.92 (m, 1H), 3.00 (s, 1H), 3.08 –3.19 (m, 1H), 3.40 (d, *J* = 2.9 Hz, 1H), 3.54 (d, *J* = 2.9 Hz, 1H), 3.81 (dd, *J* = 11.8, 2.7 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.44 –7.52 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 24.6 (d, $^3J_{CF}$ = 4.7 Hz), 41.6, 46.7 (d, $^3J_{CF}$ = 15.3 Hz), 47.9 (d, $^2J_{CF}$ = 16.8 Hz), 48.9, 54.3 (d, $^2J_{CF}$ = 18.5 Hz), 122.2, 123.2 (d, $^1J_{CF}$ = 255.4 Hz), 131.0 (d, $^4J_{CF}$ = 2.7 Hz), 131.4 (d, $^3J_{CF}$ = 2.8 Hz), 131.9 ppm; (minor isomer) δ = 25.2, 41.8, 47.0 (d, $^3J_{CF}$ = 8.6 Hz), 47.4 (d, $^2J_{CF}$ = 22.0 Hz), 50.3, 51.8 (d, $^2J_{CF}$ = 19.0 Hz), 122.3, 124.7 (d, $^1J_{CF}$ = 253.2 Hz), 130.3, 132.0, 132.6 (d, $^3J_{CF}$ = 7.5 Hz) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -134.48 (d, $^3J_{HF}$ = 11.2 Hz) ppm, (minor isomer) δ = -117.21 (dd, *J* = 11.8, 7.3 Hz) ppm.

(1S*,2S*,4R*,5S*,6S*,7R*)-6-Fluoro-6-nitro-7-(4-nitrophenyl)-3-oxatricyclo[3.2.1.$0^{2,4}$]octane (major isomer) **and (1S*,2S*,4R*,5S*,6R*,7S*)-6-fluoro-6-nitro-7-(4-nitrophenyl)-3-oxatricyclo[3.2.1.02,4]octane** (minor isomer) (**4b**). Eluent: Hex/DCM, 2:1; Hex/DCM, 1:1; Hex/DCM, 1:2; 0.048 g, 85 % yield; *dr* = 33:67; pale brown viscous oil; HRMS (ESI-TOF) m/z: calcd for $C_{13}H_{12}FN_2O_5$ $[M+H]^+$ = 295.0730; found 295.0723; ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.71 – 1.87 (m, 2H), 3.25 (br s, 1H), 3.35 (br s, 1H), 3.50 – 3.54 (m, 1H), 3.57 (d, *J* = 3.3 Hz, 1H), 4.16 (dd, *J* = 11.3, 3.5 Hz, 1H), 7.43 – 7.50 (m, 2H), 8.16 – 8.25 (m, 2H) ppm; (minor isomer) δ = 1.71 – 1.87 (m, 1H), 1.90 – 1.98 (m, 1H), 3.09 (d, *J* = 1.0 Hz, 1H), 3.18 (d, *J* = 6.9 Hz, 1H), 3.41 (d, *J* = 3.2 Hz, 1H), 3.57 (d, *J* = 3.2 Hz, 1H), 3.97 (dd, *J* = 11.8, 2.8 Hz, 1H), 7.40 (d, *J* = 8.7 Hz, 2H), 8.25 – 8.16 (m, 2H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 24.6 (d, $^3J_{CF}$ = 4.8 Hz), 41.6, 46.6 (d, $^3J_{CF}$ = 15.4 Hz), 47.7 (d, $^2J_{CF}$ = 16.7 Hz), 54.3 (d, $^2J_{CF}$ = 18.3

Hz), 48.6, 123.0 (d, $^{1}J_{CF}$ = 255.8 Hz), 123.8, 130.3 (d, $^{4}J_{CF}$ = 2.9 Hz), 139.8 (d, $^{3}J_{CF}$ = 2.4 Hz), 147.5 ppm; (minor isomer) δ = 25.1, 41.7, 46.8 (d, $^{3}J_{CF}$ = 8.6 Hz), 47.3 (d, $^{2}J_{CF}$ = 21.9 Hz), 50.1, 51.8 (d, $^{2}J_{CF}$ = 18.7 Hz), 124.0, 124.7 (d, $^{1}J_{CF}$ = 253.5 Hz), 129.7, 140.9 (d, $^{3}J_{CF}$ = 7.6 Hz), 147.7 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -134.34 (d, $^{3}J_{HF}$ = 11.3 Hz) ppm; (minor isomer) δ = -117.10 (dd, *J* = 11.8, 7.3) ppm.

(1S*,2S*,4R*,5S*,6S*,7R*)-6-Fluoro-6-nitro-7-(p-tolyl)-3-oxatricyclo[3.2.1.0^{2,4}]octane (major isomer) **and (1S*,2S*,4R*,5S*,6R*,7S*)-6-fluoro-6-nitro-7-(p-tolyl)-3-oxatricyclo[3.2.1.02,4]octane** (minor isomer) (**4c**). Eluent: Hex/DCM, 3:1; Hex/DCM, 2:1; 0.051 g, 87 % yield; *dr* = 45:55; pale yellow viscous oil; HRMS (ESI-TOF) m/z: calcd for $C_{14}H_{15}FNO_3$ $[M+H]^+$ = 264.1036; found 264.1032. ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 1.77 (s, 1H), 1.79 –1.92 (m, 1H), 2.35 (s, 3H), 3.15 (br s, 1H), 3.27 (s, 1H), 3.51 (dt, *J* = 3.4, 1.6 Hz, 1H), 3.66 (dd, *J* = 3.4, 1.1 Hz, 1H), 4.04 (dd, *J* = 11.7, 3.4 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 7.11 – 7.21 (m, 3H) ppm; (minor isomer) δ = 1.77 (s, 1H), 1.79 –1.92 (m, 1H), 2.35 (s, 3H), 3.02 (s, 1H), 3.10 (d, *J* = 6.6 Hz, 1H), 3.41 (d, *J* = 2.6 Hz, 1H), 3.54 (dd, *J* = 3.3, 1.1 Hz, 1H), 3.83 (dd, *J* = 11.9, 2.4 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 7.11 – 7.21 (m, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 21.1, 24.6 (d, $^{3}J_{CF}$ = 4.6 Hz), 41.7, 46.9 (d, $^{3}J_{CF}$ = 15.5 Hz), 48.0 (d, $^{2}J_{CF}$ = 16.8 Hz), 49.3, 54.7 (d, $^{2}J_{CF}$ = 18.7 Hz), 123.4 (d, $^{1}J_{CF}$ = 255.2 Hz), 129.3 (d, $^{4}J_{CF}$ = 2.4 Hz), 129.4 (d, $^{3}J_{CF}$ = 2.9 Hz), 129.4, 137.8 ppm; (minor isomer) δ = 21.2, 25.3, 41.9, 47.2 (d, $^{3}J_{CF}$ = 8.5 Hz), 47.5 (d, $^{2}J_{CF}$ = 22.2 Hz), 50.5, 52.2 (d, $^{2}J_{CF}$ = 19.2 Hz), 124.9 (d, $^{1}J_{CF}$ = 253.0 Hz), 128.5, 129.6, 130.5 (d, $^{3}J_{CF}$ = 7.4 Hz), 138.0 ppm; ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = -134.50 (d, *J* = 11.7 Hz) ppm; (minor isomer): δ = -117.45 (dd, *J* = 11.9, 7.3 Hz) ppm.

Dihydroxylation of the cycloadduct 2f. N-Methylmorpholine N-oxide (0.031 g, 1.5 mol. equiv.) was added to a solution of **2f** (0.056 g, 1 mol. equiv.) in 1.2 ml of 3:1 acetone-water. Then 100 µl of OsO_4 1 % solution (0.001 g, 2 mol. %) was added. Then reaction mixture was stirred for 5 hours at room temperature. After reaction completion (TLC monitoring), the reaction mixture was concentrated under vacuum, poured in 20 ml of water and then extracted with EtOAc (3 × 20 ml). The combined organic extracts were dried over Na_2SO_4, filtrated and concentrated under vacuum. The pure product was isolated by column chromatography on silica using mixture of Hex/EtOAc as eluent.

(1S*,2S*,3R*,4S*,5S*,6R*)-6-(4-Bromophenyl)-5-fluoro-5-nitrobicyclo[2.2.1]heptane-2,3-diol (major isomer) and (1S*,2S*,3R*,4S*,5R*,6S*)-6-(4-bromophenyl)-5-fluoro-5-nitrobicyclo[2.2.1]heptane-2,3-diol (minor isomer) (**5**) Eluent: Hex/EtOAc 1:1, Hex/EtOAc 1:2; 0.040 g, 65 %, colorless solid. HRMS (ESI) m/z: calcd for $C_{13}H_{13}{}^{107}Ag^{81}BrFNO_4$ $[M+Ag]^+$ = 453.9042; found 453.9042; ^{1}H NMR (400 MHz, $CDCl_3$): (major isomer) δ = 2.15 (d, *J* = 11.7 Hz, 1H), 2.26 (dd, *J* = 11.8, 1.5 Hz, 1H), 2.85 (s, 1H), 2.92 (s, 1H), 3.05 – 3.29 (m, 2H), 3.96 (dd, *J* =

12.7, 4.1 Hz, 1H), 4.22 (s, 1H), 4.26 (s, 1H), 7.07 (d, *J* = 7.7 Hz, 2H), 7.47 (d, *J* = 7.7 Hz, 2H) ppm; (minor isomer) δ = 2.20 (d, *J* = 11.7 Hz, 1H), 2.34 (d, *J* = 11.7 Hz, 1H), 2.67 (s, 1H), 2.74 (d, *J* = 7.4 Hz, 1H), 3.29 – 3.47 (m, 2H), 3.78 (d, *J* = 13.1 Hz, 1H), 4.11 (s, 1H), 4.18 (s, 1H), 7.02 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): (major isomer) δ = 31.7 (d, $^3J_{CF}$ = 3.1 Hz), 47.1, 52.4 (d, $^2J_{CF}$ = 19.6 Hz), 54.7 (d, $^2J_{CF}$ = 17.2 Hz), 67.8 (d, $^3J_{CF}$ = 14.6 Hz), 68.2, 121.7 (d, $^1J_{CF}$ = 255.6 Hz), 121.8, 130.5 (d, $^4J_{CF}$ = 2.3 Hz), 131.2 (d, $^3J_{CF}$ =2.9 Hz), 131.9 ppm; (minor isomer) δ = 32.2, 48.2, 50.7 (d, $^2J_{CF}$ = 19.0 Hz), 53.2 (d, $^2J_{CF}$ = 21.3 Hz), 67.5 (d, $^3J_{CF}$ = 8.3 Hz), 73.0, 122.1, 123.2 (d, $^1J_{CF}$ = 251.2 Hz), 130.0, 132.0, 132.6 (d, $^3J_{CF}$ = 7.8 Hz) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): (major isomer) δ = - 137.76 (s) ppm; (minor isomer) δ =-124.12 (s) ppm.

Base-induced nitrous acid elimination from cycloadduct 3l. Cycloadduct **2l** (0.052 g, 1 mol. equiv.) was dissolved in THF (1 mL) and the solution was loaded into a vial covered with aluminum foil. Then potassium *tert*-butoxide (2 mol. equiv.) was added in darkness in several portion for 20 min to the vigorously stirred reaction mixture. The reaction mixture was stirred overnight at room temperature. The reaction was monitored by TLC. After completion of the reaction the reaction mixture was passed through a column charged with alumina and covered with aluminum foil using DCM as eluent. The solution of the pure product **6** was collected in a flask covered with aluminum foil and then concentrated under vacuum.

2-Fluoro-3-(4-nitrophenyl)bicyclo[2.2.1]hepta-2,5-diene (**6**). 0.034 g, 77 % yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 2.28 (ddd, *J* = 6.5, 4.7, 1.9 Hz, 1H), 2.41 – 2.46 (m, 1H), 3.47 – 3.53 (m, 1H), 3.88 – 3.94 (m, 1H), 6.95 (dd, *J* = 4.5, 3.1 Hz, 1H), 7.05 (dt, *J* = 4.6, 2.2 Hz, 1H), 7.47 – 7.56 (m, 2H), 8.16 – 8.20 (m, 2H) ppm; ^{19}F NMR (376 MHz, $CDCl_3$): δ = -110.34 (s) ppm. The analysis of the sample was consistent with the previously reported data[15a]

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