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Efficient generation of an oxidopyrylium ylide using a Pd catalyst and its [5+2] cycloadditions with several dipolarophiles

Hiroyuki Suga, Taichi Iwai, Masahiro Shimizu, Kie Takahashi, and Yasunori Toda*

Department of Materials Chemistry, Faculty of Engineering, Shinshu University

Wakasato, Nagano 380-8553, Japan

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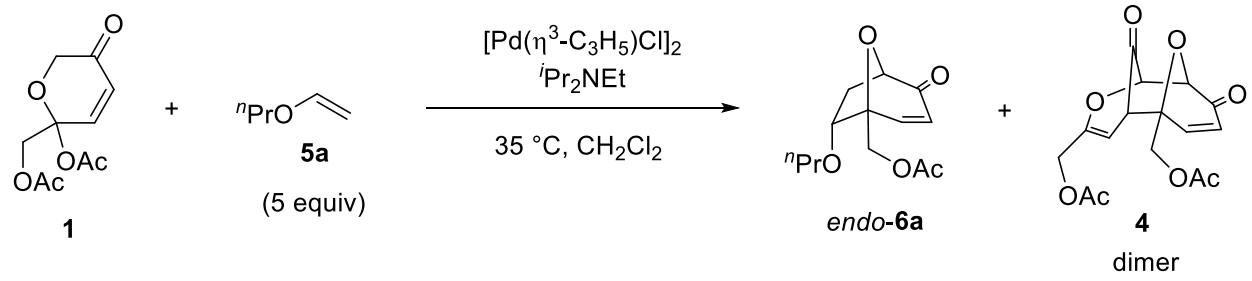
Optimization of reaction conditions for the cycloaddition with *n*-propyl vinyl ether

Table S1. Reactions of 2*H*-pyran-3(6*H*)-one **1** with *n*-propyl vinyl ether (**5a**) in the presence of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ [a]

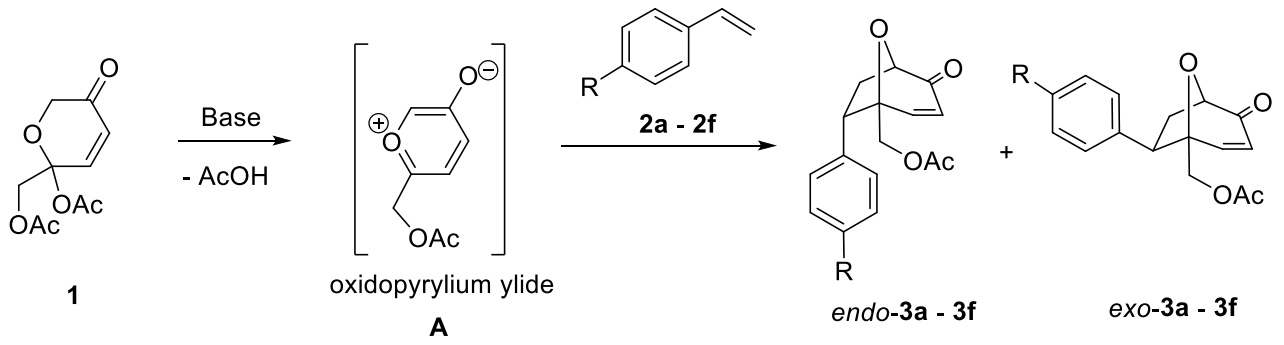


entry	$[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (mol%)	$^{i}Pr_2NEt$ (equiv)	conc. (M)	time (h)	yield of *endo*-**6a** (%)	yield of **4** (%)
1	none	1	0.063	20	10 [b,c]	trace
2	10	1	0.063	25	55	15
3	10	1	0.13	12	61	14
4	10	0.5	0.13	16	66	10
5	10	0.2	0.13	40	71	4

[a] The reaction of 2*H*-pyran-3(6*H*)-one **1** with *n*-propyl vinyl ether (**5a**) (5.0 equiv) was carried out at 35 ºC in the presence $^{i}Pr_2NEt$ and $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ in CH_2Cl_2. [b] Determined by ^1H NMR analysis using 1,1,2,2-tetrachloroethane as an internal standard. [c] 86% of 2*H*-pyran-3(6*H*)-one **1** was recovered.

HOMO and LUMO energies by DFT calculations

All calculations were performed using B3LYP/6-311G*//B3LYP/6-31G* level of theory with Spartan '08. To evaluate the reactivity of styrene derivatives toward oxidopyrylium ylide **A** generated from 2*H*-pyran-3(6*H*)-one **1**, HOMO and LUMO energies of the oxidopyrylium ylide and *p*-substituted styrene derivatives were calculated (Table S2).



Scheme S1. [5 + 2] cycloadditions between oxidopyrylium ylide **A** and styrenes

Table S2. HOMO and LUMO energies of oxidopyrylium ylide **A** and *p*-substituted styrene derivatives **2a** – **2f** [a]

Reactant (R)	HOMO	LUMO	$LUMO_{A} - HOMO_{2\ or\ A}$	$LUMO_{2\ or\ A} - HOMO_{A}$
ylide **A**	-137.36	-67.37	**69.99**	**69.99**
2a (H)	-144.64	-26.31	**77.27**	111.05
2b (Cl)	-147.47	-33.20	**80.10**	104.16
2c (CO_2Me)	-151.15	-43.32	**83.78**	94.04
2d (CN)	-157.56	-49.57	90.19	**87.79**
2e (Me)	-140.21	-24.03	**72.84**	113.33
2f (OMe)	-132.39	-19.46	**65.02**	117.90

[a] All energies in kcal mol^{-1}.

The HOMO–LUMO gaps between the oxidopyrylium ylide **A** and non- or *p*-substituted styrene derivatives **2** are smaller for $LUMO_A$–$HOMO_2$ than for $LUMO_2$–$HOMO_A$ except in the case of **2c**, and suggest that the [5+2] cycloadditions proceed in an inverse electron-demand fashion. Importantly, the reactivity of styrenes evaluated from the HOMO–LUMO gaps was parallel with the yields obtained experimentally in the Pd-catalyzed cycloadditions (see Scheme 2a in the text).

Hammett plots for styrene cycloadducts

To further analyze the reactivity of styrenes **2** toward oxidopyrylium ylide **A**, we constructed Hammett plots using σ_p^+ values[1] to assess the chemical yield of cycloadducts **3** for the *p*-substituent (R) of the styrenes **2a** – **2c**, **2e**, and **2f** (Figure S1). The negative slope was observed, implying that electron-rich styrenes are more favored reaction partners with **A** than electron-deficient styrenes on the basis of their electronic properties. The plot of styrene **2d** was deviated from the linear approximation (σ_p^+: 0.66, yield: 53%, log (yield): 1.72).

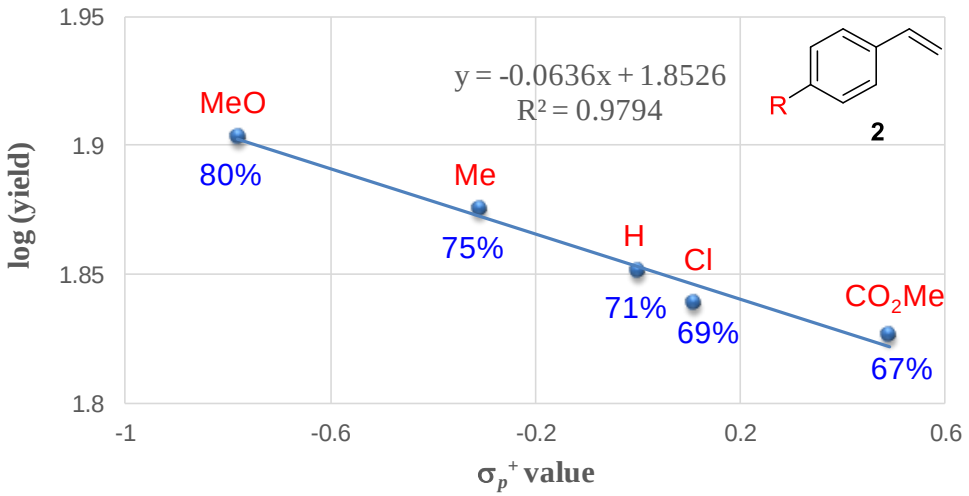


Figure S1. The logarithm of the chemical yield of **2** is plotted against σ_p^+ values.

The reaction of 2*H*-pyran-3(6*H*)-one 1 with $Pd_2(dba)_3$ in methanol-*d*$_4$

According to the literature reported by Feringa et al.,[2] the reaction of 2*H*-pyran-3(6*H*)-one **1** with methanol-*d*$_4$ in the presence of $Pd_2(dba)_3$ (10 mol%) was carried out and monitored by ^{1}H NMR. Although the Pd-allyl intermediate could not be observed, the reaction proceeded cleanly to afford the corresponding methanol adduct **S1** (Figure S2).

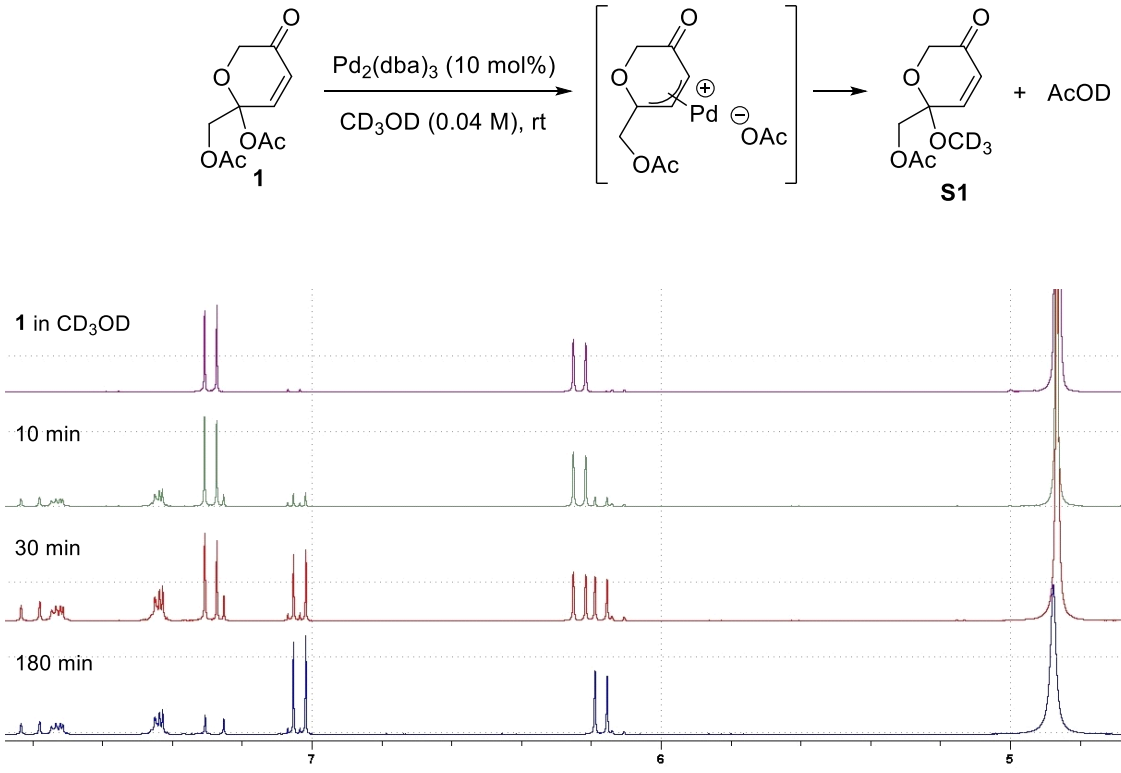


Figure S2. The reaction of 2*H*-pyran-3(6*H*)-one **1** with $Pd_2(dba)_3$ in methanol-*d*$_4$

S1: ^{1}H NMR (300 MHz, CD_3OD) δ 2.08 (3H, s), 4.13 (1H, d, *J* = 12.0 Hz), 4.18 (1H, d, *J* = 17.1 Hz), 4.39 (1H, d, *J* = 17.1 Hz), 4.44 (1H, d, *J* = 12.0 Hz), 6.17 (1H, d, *J* = 10.5 Hz), 7.04 (1H, d, *J* = 10.5 Hz).

AcOD: ^{1}H NMR (300 MHz, CD_3OD) δ 1.99 (3H, s).

Experimental section

General.

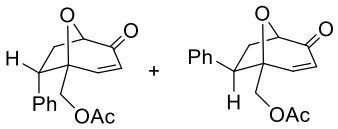
Melting points were determined on a Yanaco MP-13 melting point apparatus and are uncorrected. IR spectra were taken with a JASCO FT/IR-5300S spectrophotometer. ^{1}H NMR spectra were recorded on BRUKER AVANCE III Fourier 300 (300 MHz) and Ascend 500 (500 MHz) spectrometers. Chemical shifts are expressed in parts per million downfield from tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded on BRUKER AVANCE III Fourier 300 (75 MHz) and Ascend 500 (125 MHz) spectrometers using broadband proton decoupling. Chemical shifts are expressed in parts per million using the middle resonance of $CDCl_3$ (77.0 ppm) and C_6D_6 (128.06 ppm) as an internal standard. Hydrogen multiplicity (C, CH, CH_2, CH_3) information was obtained from carbon DEPT spectrum. High-resolution mass spectra were obtained on a BRUKER micrOTOF II ESI-TOF spectrometer. For preparative column chromatography, Wakogel C-300HG or Fuji Silysia PSQ60B was employed. All reactions were carried out under an argon atmosphere in dried glassware.

Materials.

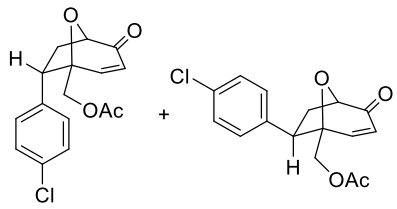
6-Acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (**1**) was prepared according to the procedure reported in the literature.[3,4] Styrene derivatives **2a**, **2b**, **2e**, **2f**, vinyl ethers **5a** – **5d**, *t*-butyl acrylate (**7a**), *N*-phenylmaleimide (**7c**), and α-methylene-γ-butyrolactone (**9c**) are commercially available, and were purified by distillation or recrystallization before used. Other styrene derivatives **2c**,[5] **2d**,[6] **2g**,[7] **2h**,[8] and **2i**[3] were prepared by the procedure reported in the literature. 2-Acryloyl-1-benzyl-5,5-dimethyl-3-pyrazolidinone (**7b**) was prepared by the procedure reported previously.[9] 1-Methylene-1,2,3,4-tetrahydronaphthalene (**9a**),[10] 1-methylene-2,3-dihydro-1*H*-indene (**9b**),[11] α-methylene-δ-valerolactone (**9d**),[12] and 3,4-dihydro-2-methylene-1(2*H*)-naphthalenone (**9e**)[13] were prepared according to the procedure reported in the literature. $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$, $PdCl_2$, $Pd(PPh_3)_4$, and $Pd_2(dba)_3$ are commercially available, and were used without further purification.

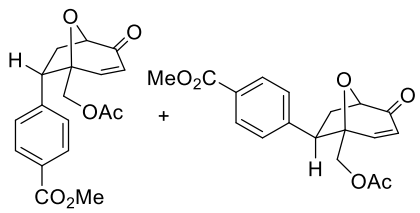
General procedure for the Pd-catalyzed cycloaddition was exemplified by the reaction of 6-acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (1) with styrene (2a). $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (9.2 mg, 0.025 mmol, 10 mol%), styrene (143 μL, 1.25 mmol, 5.0 equiv), and *N*,*N*-diisopropylethylamine (43.5

μL, 0.25 mmol, 1.0 equiv) were successively added into a Schlenk tube. A solution of 6-acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (**1**) (57.1 mg, 0.25 mmol) in CH_2Cl_2 (1.0 mL) was added to the mixture by cannula transfer, and then a vessel was washed with CH_2Cl_2 (1.0 mL x 3). The mixture was stirred at 35 ºC for 20 h, and then filtered through a plug of Celite with EtOAc (30 mL). The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (20 g) with CH_2Cl_2/EtOAc (97 : 3, v/v) to give cycloadducts **3a** (48.2 mg, 71%, *endo* : *exo* = 81 : 19) as colorless oil. Dimer **4** (5.5 mg, 13%) was obtained by the same column chromatography with CH_2Cl_2/EtOAc (80 : 20, v/v) as an eluent.

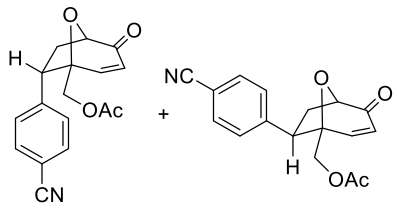
***endo*- and *exo*-5-Acetoxymethyl-6-phenyl-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-3a and *exo*-3a).**[3]  R_f = 0.29 (Hexane/EtOAc, 67 : 33, v/v); IR (KBr) 1747, 1704, 1228, 1050, 772, 713 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.02 (3H x 19/100, s), 2.08 (1H x 81/100, *J* = 1.5, 6.9, 13.8 Hz), 2.10 (3H x 81/100, s), 2.45 (1H x 19/100, ddd, *J* = 1.8 , 9.0, 14.1 Hz), 2.59 (1H x 19/100, ddd, *J* = 3.3, 8.7, 14.1 Hz), 2.99 (1H x 81/100, ddd, *J* = 8.7, 10.2, 13.8 Hz), 3.42 (1H x 19/100, dd, *J* = 3.3, 9.0 Hz), 3.55 (1H x 81/100, dd, *J* = 6.9, 10.2 Hz), 3.65 (1H x 19/100, d, *J* = 12.0 Hz), 4.07 (1H x 19/100, d, *J* = 12.0 Hz), 4.25 (1H x 81/100, d, *J* = 12.0 Hz), 4.52 (1H x 81/100, d, *J* = 12.0 Hz), 4.70 (1H x 81/100, ddd, *J* = 1.5, 1.5, 8.7 Hz), 4.83 (1H x 19/100, ddd, *J* = 1.2, 1.8, 8.7 Hz), 6.11 (1H x 19/100, dd, *J* = 1.2, 9.9 Hz), 6.29 (1H x 81/100, dd, *J* = 1.5, 9.9 Hz), 6.65 (1H x 81/100, d, *J* = 9.9 Hz), 7.13-7.16 (2H x 81/100, m), 7.21-7.34 (3H x 81/100 + 6H x 19/100, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5 (CH_3, *exo*), 20.6 (CH_3, *endo*), 33.7 (CH_2, *endo*), 36.3 (CH_2, *exo*), 49.1 (CH, *exo*), 49.7 (CH, *endo*), 64.9 (CH_2, *endo*), 65.2 (CH_2, *exo*), 80.8 (CH, *endo*), 81.4 (CH, *exo*), 83.6 (C, *endo*), 84.2 (C, *exo*), 126.1 (CH, *exo*), 127.5 (CH, *exo*), 127.7 (CH, *endo*), 128.2 (CH, *exo*), 128.60 (CH x 2, *endo*), 128.65 (CH, *exo*), 128.67 (CH, *endo*), 136.0 (C, *endo*), 139.4 (C, *exo*), 150.9 (CH, *endo*), 152.9 (CH, *exo*), 170.2 (C, *exo*), 170.5 (C, *endo*), 196.0 (C, *endo*), 196.1 (C, *exo*); HRMS (ESI) Exact mass calcd for $C_{16}H_{16}O_4Na$ $[M+Na]^+$ 295.0941, Found: 295.0944.

The stereochemistry of cycloadducts **3a** – **3i** was determined by comparison with ^1H NMR data reported for **3a** and **3i** in the literature.[3]

***endo*- and *exo*-5-Acetoxymethyl-6-(4-chlorophenyl)-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-3b and *exo*-3b).**  Isolated as yellow oil (53.2 mg, 69%, *endo* : *exo* = 86 : 14) after silica gel column chromatography (12 g, eluent: Hexane/EtOAc (80 : 20, v/v)) following the general procedure (24 h) using *p*-chlorostyrene (**2b**) (150 μL, 1.25 mmol, 5.0 equiv). R_f = 0.31 (*endo*), 0.22 (*exo*) (Hexane/EtOAc, 67 : 33, v/v); IR (neat) 3022, 1745, 1706, 1495, 1230, 1049, 824, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.01 (1H x 86/100, ddd, *J* = 1.8, 6.9, 13.8 Hz), 2.03 (3H x 14/100, s), 2.10 (3H x 86/100, s), 2.42-2.57 (2H x 14/100, m,), 3.00 (1H x 86/100, ddd, *J* = 8.7, 10.2, 13.8 Hz), 3.40 (1H x 14/100, dd, *J* = 3.9, 8.1 Hz), 3.54 (1H x 86/100, dd, *J* = 6.9, 10.2 Hz), 3.68 (1H x 14/100, d, *J* = 12.0 Hz), 4.02 (1H x 14/100, d, *J* = 12.0 Hz), 4.23 (1H x 86/100, d, *J* = 12.0 Hz), 4.49 (1H x 86/100, d, *J* = 12.0 Hz), 4.69 (1H x 86/100, ddd, *J* = 1.5, 1.8, 8.7 Hz), 4.82 (1H x 14/100, ddd, *J* = 1.2, 2.7, 7.8 Hz), 6.11 (1H x 14/100, dd, *J* = 1.2, 9.9 Hz), 6.29 (1H x 86/100, dd, *J* = 1.5, 9.9 Hz), 6.64 (1H x 86/100, d, *J* = 9.9 Hz), 7.07-7.32 (4H x 86/100 + 5H x 14/100, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5 (CH_3, *exo*), 20.6 (CH_3, *endo*), 33.7 (CH_2, *endo*), 36.4 (CH_2, *exo*), 48.5 (CH, *exo*), 49.1 (CH, *endo*), 64.6 (CH_2, *endo*), 65.0 (CH_2, *exo*), 80.8 (CH, *endo*), 81.3 (CH, *exo*), 83.4 (C, *endo*), 84.0 (C, *exo*), 126.2 (CH, *exo*), 128.75 (CH, *endo*), 128.81 (CH, *exo*), 128.9 (CH, *endo*), 129.5 (CH, *exo*), 129.9 (CH, *endo*), 133.4 (C, *exo*), 133.6 (C, *endo*), 134.6 (C, *endo*), 138.0 (C, *exo*), 150.4 (CH, *endo*), 152.5 (CH, *exo*), 170.1 (C, *exo*), 170.4 (C, *endo*), 195.75 (C, *endo*), 195.79 (C, *exo*); HRMS (ESI) Exact mass calcd for $C_{16}H_{15}ClNaO_4$ $[M+Na]^+$ 329.0551, found 329.0554.

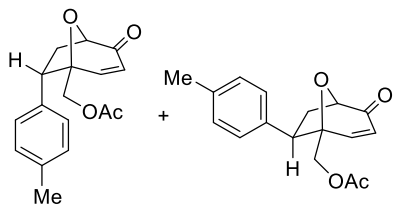
***endo*- and *exo*-5-Acetoxymethyl-6-[4-(methoxycarbonyl)phenyl]-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-3c and *exo*-3c).**  Isolated as yellow oil (55.7 mg, 67%, *endo* : *exo* = 78 : 22) after silica gel column chromatography (15 g, eluent: Hexane/EtOAc (60 : 40, v/v)) following the general procedure (20 h) using *p*-(methoxycarbonyl)styrene (**2c**) (230 mg, 1.25 mmol, 5.0 equiv). Before addition of *N*,*N*-diisopropylethylamine, a solution of styrene **2c** in CH_2Cl_2 (1.0 mL) was added into a Schlenk tube. A vessel used for cannula transfer of **1** was washed with CH_2Cl_2 (0.67 mL x 3). R_f = 0.19 (*endo*), 0.13 (*exo*) (Hexane/EtOAc, 67 : 33, v/v); IR (KBr) 1720, 1283, 1229, 1112,

1050, 849, 777, 718 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.02 (3H x 22/100, s), 2.09 (1H x 78/100, m), 2.10 (3H x 78/100, s), 2.47 (1H x 22/100, ddd, *J* = 2.1, 9.0, 14.1 Hz), 2.59 (1H x 22/100, ddd, *J* = 3.3, 8.4, 14.1 Hz), 3.02 (1H x 78/100, ddd, *J* = 8.7, 10.2, 13.8 Hz), 3.48 (1H x 22/100, dd, *J* = 3.3, 9.0 Hz), 3.63 (1H x 78/100, dd, *J* = 6.9, 10.2 Hz), 3.68 (1H x 22/100, d, *J* = 12.0 Hz), 3.92 (3H x 78/100, s), 3.92 (3H x 22/100, s), 4.00 (1H x 22/100, d, *J* = 12.0 Hz), 4.25 (1H x 78/100, d, *J* = 12.0 Hz), 4.50 (1H x 78/100, d, *J* = 12.0 Hz), 4.72 (1H x 78/100, ddd, *J* = 1.2, 1.5, 8.7 Hz), 4.86 (1H x 22/100, ddd, *J* = 1.2, 2.1, 8.4 Hz), 6.13 (1H x 22/100, dd, *J* = 1.2, 9.9 Hz), 6.31 (1H x 78/100, dd, *J* = 1.2, 9.9 Hz), 6.62 (1H x 78/100, d, *J* = 9.9 Hz), 7.22-7.32 (2H x 78/100 + 3H x 22/100, m), 7.95-8.02 (2H x 78/100 + 2H x 22/100, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5 (CH_3, *exo*), 20.6 (CH_3, *endo*), 33.6 (CH_2, *endo*), 36.3 (CH_2, *exo*), 49.0 (CH, *exo*), 49.7 (CH, *endo*), 52.08 (CH_3, *exo*), 52.12 (CH_3, *endo*), 64.6 (CH_2, *endo*), 64.7 (CH_2, *exo*), 80.8 (CH, *endo*), 81.3(CH, *exo*), 83.5(C, *endo*), 84.0 (C, *exo*), 126.3 (CH, *exo*), 128.3 (CH, *exo*), 128.7 (CH, *endo*), 128.9 (CH, *endo*), 129.4 (C, *exo*), 129.6 (C, *endo*), 129.7 (CH, *endo*), 129.9 (CH, *exo*), 141.4 (C, *endo*), 144.8 (C, *exo*), 150.3 (CH, *endo*), 152.4 (CH, *exo*), 166.4 (C, *endo*), 166.5 (C, *exo*), 170.0 (C, *exo*), 170.4 (C, *endo*), 195.70 (C, *endo*), 195.73 (C, *exo*); HRMS (ESI) Exact mass calcd for $C_{18}H_{18}NaO_6$ $[M+Na]^+$ 353.0996, found 353.1004.

***endo*- and *exo*-5-Acetoxymethyl-6-(4-cyanophenyl)-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-3d and *exo*-3d).** 

Isolated as yellow oil (39.5 mg, 53%, *endo* : *exo* = 84 : 16) after silica gel column chromatography (20 g, eluent: CH_2Cl_2/EtOAc (90 : 10, v/v) and then CH_2Cl_2/EtOAc (97 : 3, v/v)) following the general procedure (20 h) using *p*-cyanostyrene (**2d**) (161 mg, 1.25 mmol, 5.0 equiv). Before addition of *N*,*N*-diisopropylethylamine, a solution of styrene **2d** in CH_2Cl_2 (1.0 mL) was added into a Schlenk tube. A vessel used for cannula transfer of **1** was washed with CH_2Cl_2 (0.67 mL x 3). R_f = 0.28 (CH_2Cl_2/EtOAc, 95 : 5, v/v); IR (KBr) 2228, 1743, 1706, 1230, 1050, 834 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.02 (3H x 16/100, s), 2.05 (1H x 84/100, ddd, *J* = 1.8, 6.9, 13.8 Hz), 2.10 (3H x 84/100, s), 2.49-2.54 (2H x 16/100, m), 3.04 (1H x 84/100, ddd, *J* = 8.7, 10.2, 13.8 Hz), 3.48 (1H x 16/100, dd, *J* = 4.5, 7.8 Hz), 3.63 (1H x 84/100, dd, *J* = 6.9, 10.2 Hz), 3.70 (1H x 16/100, d, *J* = 12.0 Hz), 3.97(1H x 16/100, d, *J* = 12.0 Hz), 4.24 (1H x 84/100, d, *J* = 12.0 Hz), 4.49 (1H

x 84/100, d, *J* = 12.0 Hz), 4.72 (1H x 84/100, ddd, *J* = 1.5, 1.8, 8.7 Hz), 4.85 (1H x 16/100, m), 6.14 (1H x 16/100, dd, *J* = 1.2, 9.9 Hz), 6.32 (1H x 84/100, dd, *J* = 1.5, 9.9 Hz), 6.62 (1H x 84/100, d, *J* = 9.9 Hz), 7.25 (1H x 16/100, d, *J* = 9.9 Hz), 7.27-7.38 (2H x 84/100 + 2H x 16/100, m), 7.59-7.65 (2H x 84/100 + 2H x 16/100, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.4 (CH_3, *exo*), 20.6 (CH_3, *endo*), 33.7 (CH_2, *endo*), 36.4 (CH_2, *exo*), 49.1 (CH, *exo*), 49.8 (CH, *endo*), 64.3 (CH_2, *endo*), 64.5 (CH_2, *exo*), 80.8 (CH, *endo*), 81.2 (CH, *exo*), 83.5 (C, *endo*), 84.0 (C, *exo*), 111.5 (C, *exo*), 111.8 (C, *endo*), 118.2 (C, *endo*), 118.3 (C, *exo*), 126.4 (CH, *exo*), 129.1 (CH, *exo*), 129.2 (CH, *endo*), 129.5 (CH, *endo*), 132.3 (CH, *endo*), 132.4 (CH, *exo*), 141.8 (C, *endo*), 145.2 (C, *exo*), 149.7 (CH, *endo*), 151.9 (CH, *exo*), 169.9 (C, *exo*), 170.3 (C, *endo*), 195.4 (C, *endo*, *exo*); HRMS (ESI) Exact mass calcd for $C_{17}H_{15}NNaO_4$ $[M+Na]^+$ 320.0893, found 320.0895.

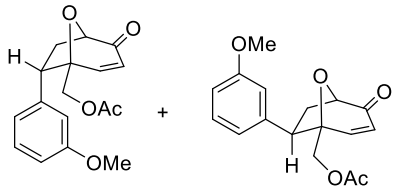
***endo*- and *exo*-5-Acetoxymethyl-6-(4-methylphenyl)-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-3e and *exo*-3e).** 

Isolated as colorless needles (53.6 mg, 75%, *endo* : *exo* = 82 : 18) after silica gel column chromatography (10 g, eluent: CH_2Cl_2/EtOAc (95 : 5, v/v) and then CH_2Cl_2/EtOAc (97 : 3, v/v)) following the general procedure (24 h) using *p*-methylstyrene (**2e**) (165 μL, 1.25 mmol, 5.0 equiv). R_f = 0.34 (*endo*), 0.31 (*exo*) (CH_2Cl_2/EtOAc, 95 : 5, v/v); IR (KBr) 2979, 1744, 1704, 1230, 1030, 816 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.02 (3H x 18/100, s), 2.05 (1H x 82/100, ddd, *J* = 1.8, 6.9, 13.8 Hz), 2.10 (3H x 82/100, s), 2.32 (3H x 82/100, s), 2.33 (3H x 18/100, s), 2.43 (1H x 18/100, ddd, *J* = 2.1, 9.0, 14.1 Hz), 2.56 (1H x 18/100, ddd, *J* = 3.3, 8.7, 14.1 Hz), 2.97 (1H x 82/100, ddd, *J* = 8.7, 10.2, 13.8 Hz), 3.38 (1H x 18/100, dd, *J* = 3.3, 9.0 Hz), 3.51 (1H x 82/100, dd, *J* = 6.9, 10.2 Hz), 3.64 (1H x 18/100, d, *J* = 12.0 Hz), 4.06 (1H x 18/100, d, *J* = 12.0 Hz), 4.24 (1H x 82/100, d, *J* = 12.0 Hz), 4.51 (1H x 82/100, d, *J* = 12.0 Hz), 4.68 (1H x 82/100, ddd, *J* = 1.5, 1.8, 8.7 Hz), 4.82 (1H x 18/100, ddd, *J* = 1.5, 2.1, 8.7 Hz), 6.09 (1H x 18/100, dd, *J* = 1.5, 9.9 Hz), 6.28 (1H x 82/100, dd, *J* = 1.5, 9.9 Hz), 6.65 (1H x 82/100, d, *J* = 9.9 Hz), 7.01-7.12 (4H x 82/100 + 4H x 18/100, m), 7.25 (1H x 18/100, d, *J* = 9.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6 (CH_3, *exo*), 20.7 (CH_3, *endo*), 20.9 (CH_3, *endo*), 21.0 (CH_3, *exo*), 33.7 (CH_2, *endo*), 36.3 (CH_2, *exo*), 48.7 (CH, *exo*), 49.3 (CH, *endo*), 65.0 (CH_2, *endo*), 65.4 (CH_2, *exo*), 80.9 (CH, *endo*), 81.4 (CH, *exo*), 83.5 (C, *endo*), 84.2 (C, *exo*), 126.1

(CH, *exo*), 128.1 (CH, *exo*), 128.5 (CH, *endo*), 128.6 (CH, *endo*), 129.26 (CH, *endo*), 129.33 (CH, *exo*), 132.9 (C, *endo*), 136.3 (C, *exo*), 137.2 (C, *exo*), 137.5 (C, *endo*), 151.1 (CH, *endo*), 153.0 (CH, *exo*), 170.3 (C, *exo*), 170.6 (C, *endo*), 196.1 (C, *endo*), 196.2 (C, *exo*); HRMS (ESI) Exact mass calcd for $C_{17}H_{18}NaO_4$ $[M+Na]^+$ 309.1097, found 309.1106.

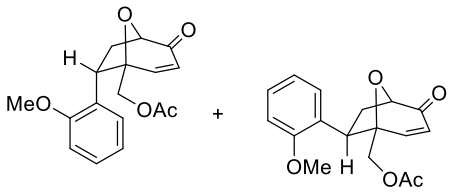
***endo*- and *exo*-5-Acetoxymethyl-6-(4-methoxylphenyl)-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-3f and *exo*-3f).** Isolated as yellow oil (60.7 mg, 80%, *endo* : *exo* = 88 : 12) after silica gel column chromatography (20 g, eluent: Hexane/EtOAc (80 : 20, v/v)) following the general procedure (20 h) using *p*-methoxystyrene (**2f**) (166 μL, 1.25 mmol, 5.0 equiv). R_f = 0.27 (*endo*), 0.21 (*exo*) (Hexane/EtOAc, 67 : 33, v/v); IR (KBr) 1744, 1703, 1515, 1253, 1031, 832 cm^{-1}, ^1H NMR (300 MHz, $CDCl_3$) δ 2.02 (1H x 88/100, ddd, *J* = 1.8, 6.9, 13.8 Hz), 2.03 (3H x 12/100, s), 2.10 (3H x 88/100, s), 2.43 (1H x 12/100, ddd, *J* = 2.1, 8.7, 14.1 Hz), 2.54 (1H x 12/100, ddd, *J* = 3.6, 8.4, 14.1 Hz), 2.97 (1H x 88/100, ddd, *J* = 8.7, 10.2, 13.8 Hz), 3.38 (1H x 12/100, dd, *J* = 3.6, 8.7 Hz), 3.50 (1H x 88/100, dd, *J* = 6.9, 10.2 Hz), 3.64 (1H x 12/100, d, *J* = 12.0 Hz), 3.79 (3H x 88/100, s), 3.80 (3H x 12/100, s), 4.06 (1H x 12/100, d, *J* = 12.0 Hz), 4.23 (1H x 88/100, d, *J* = 12.0 Hz), 4.50 (1H x 88/100, d, *J* = 12.0 Hz), 4.67 (1H x 88/100, ddd, *J* = 1.2, 1,8, 8.7 Hz), 4.81 (1H x 12/100, ddd, *J* = 1.2, 2.1, 8.4 Hz), 6.09 (1H x 12/100, dd, *J* = 1.2, 9.9 Hz), 6.28 (1H x 88/100, dd, *J* = 1.2, 9.9 Hz), 6.66 (1H x 88/100, d, *J* = 9.9 Hz), 6.80-6.87 (2H x 88/100 + 2H x 12/100, m), 7.04-7.08 (2H x 88/100, m), 7.12-7.15 (2H x 12/100, m), 7.25 (1H x 12/100, d, *J* = 9.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5 (CH_3, *exo*), 20.6 (CH_3, *endo*), 33.8 (CH_2, *endo*), 36.3 (CH_2, *exo*), 48.3 (CH, *exo*), 48.9 (CH, *endo*), 55.2 (CH_3, *endo*, *exo*), 64.9 (CH_2, *endo*), 65.4 (CH_2, *exo*), 80.8 (CH, *endo*), 81.4 (CH, *exo*), 83.5 (C, *endo*), 84.2 (C, *exo*), 113.9 (CH, *endo*), 114.0 (CH, *exo*), 126.0 (CH, *exo*), 127.8 (C, *endo*), 128.6 (CH, *endo*), 129.2 (CH, *exo*), 129.6 (CH, *endo*), 131.3 (C, *exo*), 151.1 (CH, *endo*), 153.0 (CH, *exo*), 158.9 (C, *exo*), 159.0 (C, *endo*), 170.2 (C, *exo*), 170.5 (C, *endo*), 196.0 (C, *endo*), 196.1 (C, *exo*); HRMS (ESI) Exact mass calcd for $C_{17}H_{18}NaO_5$ $[M+Na]^+$ 325.1046, found 325.1050.

***endo*- and *exo*-5-Acetoxymethyl-6-(3-methoxylphenyl)-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-3g and *exo*-3g).** Isolated as yellow oil (57.0 mg, 75%, *endo* : *exo* = 81 : 19) after silica gel column



chromatography (15 g, eluent: Hexane/EtOAc (80 : 20, v/v)) following the general procedure (24 h) using *m*-methoxystyrene (**2g**) (173 μL, 1.25 mmol, 5.0 equiv). R_f = 0.25 (*endo*), 0.19 (*exo*) (Hexane/EtOAc, 67 : 33, v/v); IR (neat) 1743, 1231, 1046, 906, 786, 754, 698 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.03 (3H x 19/100, s), 2.06 (1H x 81/100, ddd, *J* = 1.8, 6.9, 13.8 Hz), 2.10 (1H x 81/100, s), 2.43 (1H x 19/100, ddd, *J* = 1.8, 9.0, 14.1 Hz), 2.59 (1H x 19/100, ddd, *J* = 3.3, 8.7, 14.1 Hz), 2.98 (1H x 81/100, ddd, *J* = 8.7, 10.2, 13.8 Hz), 3.38 (1H x 19/100, dd, *J* = 3.3, 9.0 Hz), 3.52 (1H x 81/100, dd, *J* = 6.9, 10.2 Hz), 3.69 (1H x 19/100, d, *J* = 12.0 Hz), 3.78 (3H x 81/100, s), 3.81 (3H x 19/100, s), 4.12 (1H x 19/100, d, *J* = 12.0 Hz), 4.25 (1H x 81/100, d, *J* = 12.0 Hz), 4.52 (1H x 81/100, d, *J* = 12.0 Hz), 4.68 (1H x 81/100, ddd, *J* = 1.5, 1.8, 8.7 Hz), 4.82 (1H x 19/100, ddd, *J* = 1.2, 1.8, 8.7 Hz), 6.10 (1H x 19/100, dd, *J* = 1.2, 9.9 Hz), 6.28 (1H x 81/100, dd, *J* = 1.5, 9.9 Hz), 6.68 (1H x 81/100, d, *J* = 9.9 Hz), 6.66-6.83 (3H x 81/100 + 4H x 19/100, m), 7.19-7.27 (1H x 81/100 + 1H x 19/100, m); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.5 (CH_3, *exo*), 20.6 (CH_3, *endo*), 33.6 (CH_2, *endo*), 36.1 (CH_2, *exo*), 49.1 (CH, *exo*), 49.6 (CH, *endo*), 55.1 (CH_3, *endo*, *exo*), 64.8 (CH_2, *endo*), 65.2 (CH_2, *exo*), 80.8 (CH, *endo*), 81.4 (CH, *exo*), 83.5 (C, *endo*), 84.1 (C, *exo*), 112.3 (CH, *exo*), 112.4 (CH, *endo*), 114.4 (CH, *exo*), 114.9 (CH, *endo*), 120.6 (CH, *exo*), 120.9 (CH, *endo*), 126.1 (CH, *exo*), 128.5 (CH, *endo*), 129.59 (CH, *endo*), 129.63 (CH, *exo*), 137.7 (C, *endo*), 141.0 (C, *exo*), 150.9 (CH, *endo*), 152.9 (CH, *exo*), 159.57 (C, *endo*), 159.62 (C, *exo*), 170.2 (C, *exo*), 170.5 (C, *endo*), 196.0 (C, *endo*), 196.1 (C, *exo*); HRMS (ESI) Exact mass calcd for $C_{17}H_{18}NaO_5$ $[M+Na]^+$ 325.1046, found 325.1048.

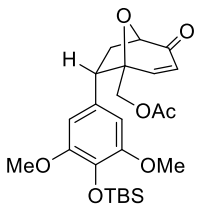
***endo*- and *exo*-5-Acetoxymethyl-6-(2-methoxylphenyl)-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-3h and *exo*-3h).** Isolated as colorless prisms (60.9 mg, 80%, *endo* : *exo* = 85 : 15) after silica gel column chromatography (10 g, eluent: Hexane/EtOAc (80 : 20, v/v) and then CH_2Cl_2/EtOAc (92 : 8, v/v)) following the general procedure (22 h) using *o*-methoxystyrene (**2h**) (166 μL, 1.25 mmol, 5.0 equiv). R_f = 0.28 (CH_2Cl_2/EtOAc, 67 : 33, v/v); IR (KBr) 2976, 1735, 1701, 1493, 1251, 1037, 888, 755, 448 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 2.01 (3H x 15/100, s), 2.03 (1H x 85/100, ddd, *J* = 1.5, 7.0, 13.5 Hz), 2.09 (3H x 85/100, s), 2.36 (1H x 15/100, ddd,



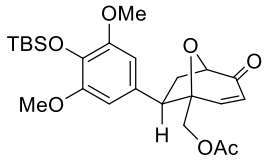
J = 1.5, 9.5, 14.0 Hz), 2.57 (1H x 15/100, ddd, *J* = 3.5, 9.0, 14.0 Hz), 2.91 (1H x 85/100, ddd, *J* = 9.0, 10,5, 13.5 Hz), 3.58 (1H x 15/100, d, *J* = 12.0 Hz), 3.84 (3H x 15/100, s,), 3.85 (3H x 85/100, s), 4.11 (1H x 15/100, m), 4.19 (1H x 85/100, dd, *J* = 7.0, 10.5 Hz), 4.20 (1H x 15/100, d, *J* = 12.0 Hz), 4.30 (1H x 85/100, d, *J* = 12.5 Hz), 4.46 (1H x 85/100, d, *J* = 12.5 Hz), 4.71 (1H x 85/100, ddd, *J* = 1.5, 1.5, 9.0 Hz), 4.83 (1H x 15/100, ddd, *J* = 1.0, 1.5, 9.0 Hz), 6.09 (1H x 15/100, dd, *J* = 1.0, 10.0 Hz), 6.26 (1H x 85/100, dd, *J* = 1.5, 10.0 Hz), 6.66 (1H x 85/100, d, *J* = 10.0 Hz), 6.86-6.90 (1H x 15/100 + 2H x 85/100, m), 6.97 (1H x 15/100, m), 7.01 (1H x 85/100, m), 7.21-7.26 (2H x 15/100 + 1H x 85/100, m), 7.28 (1H x 15/100, d, *J* = 10.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.6 (CH_3, *exo*), 20.7 (CH_3, *endo*), 33.4 (CH_2, *endo*), 35.3 (CH_2, *exo*), 39.5 (CH, *exo*), 40.8 (CH, *endo*), 55.4 (CH_3, *endo*), 55.5 (CH_3, *exo*), 65.2 (CH_2, *exo*), 65.9 (CH_2, *endo*), 81.3 (CH, *endo*), 81.6 (CH, *exo*), 84.1 (C, *endo*), 84.4 (C, *exo*), 110.4 (CH, *exo*), 110.5 (CH, *endo*), 120.4 (CH, *endo*), 121.0 (CH, *exo*), 124.1 (C, *endo*), 126.0 (CH, *endo*), 127.3 (C, *exo*), 128.4 (CH x 3, *exo*), 128.5 (CH x 2, *endo*), 152.0 (CH, *endo*), 153.6 (CH, *exo*), 156.7 (C, *exo*), 157.6 (C, *endo*), 170.4 (C, *exo*), 170.7 (C, *endo*), 196.4 (C, *endo*), 196.5 (C, *exo*); HRMS (ESI) Exact mass calcd for $C_{17}H_{18}NaO_5$ $[M+Na]^+$ 325.1046, found 325.1040.

***endo*- and *exo*-5-Acetoxymethyl-6-[(6-*t*-butyldimethylsilyloxy-3,5-dimethoxy)phenyl]-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-3i and *exo*-3i).**[3] Isolated as colorless prisms (91.6 mg, 79%, *endo* : *exo* = 92 : 8) after silica gel column chromatography (15 g, eluent: Hexane/EtOAc (80 : 20, v/v) and then CH_2Cl_2/EtOAc (95 : 5, v/v)) following the general procedure (20 h) using (6-*t*-butyldimethylsilyloxy-3,5-dimethoxy)styrene (**2i**) (368 mg, 1.25 mmol, 5.0 equiv). Cycloadducts ***endo*-3i** and ***exo*-3i** could be separated by careful silica gel column chromatography (eluent: Hexane/EtOAc (90 : 10 – 80 : 20, v/v)).

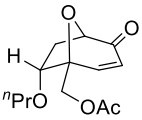
***endo*-5-Acetoxymethyl-6-[(6-*t*-butyldimethylsilyloxy-3,5-dimethoxy)phenyl]-8-oxabicyclo[3.2.1]-oct-3-en-2-one (*endo*-3i).** R_f = 0.32 (Hexane/EtOAc, 67 : 33, v/v); Colorless plates; mp 111 – 113 ºC; IR ($CHCl_3$) 1736, 1701, 1514, 1463, 1247, 1211, 1132, 776, 767, 751, 738, 669, 505 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.11 (6H, s), 0.99 (9H, s), 2.01 (1H, ddd, *J* = 1.7, 7.1, 13.8 Hz), 2.10 (3H, s), 2.96 (1H, ddd, *J* = 8.8, 10.2, 13.8 Hz), 3.43 (1H, dd, *J* = 7.1, 10.2 Hz), 3.74 (6H, s), 4.30 (1H, d, *J* = 12.0 Hz), 4.48 (1H, d, *J* = 12.0 Hz), 4.67



(1H, ddd, *J* = 1.1, 1.7, 8.8 Hz), 6.26 (1H, dd, *J* = 1.1, 9.9 Hz), 6.29 (2H, s), 6.69 (1H, d, *J* = 9.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ -4.6 (CH_3), 18.7 (C), 20.8 (CH_3), 25.7 (CH_3), 33.9 (CH_2), 49.9 (CH), 55.9 (CH_3), 65.0 (CH_2), 80.9 (CH), 83.6 (C), 105.8 (CH), 128.26 (C), 128.28 (CH), 134.1 (C), 151.48 (C), 151.55 (CH), 170.6 (C), 196.3 (C); HRMS (ESI) Exact mass calcd for $C_{24}H_{34}O_7SiNa$ $[M+Na]^+$ 485.1966, found 485.1965.

***exo*-5-Acetoxymethyl-6-[(6-*t*-butyldimethylsilyloxy-3,5-dimethoxy)phenyl]-8-oxabicyclo[3.2.1]-oct-3-en-2-one (*exo*-3i).** 

R_f = 0.23 (Hexane/EtOAc, 67 : 33, v/v); Colorless prisms; mp 122 – 123 ºC; IR (KBr) 2955, 2930, 1747, 1706, 1588, 1514, 1465, 1249, 1223, 1129, 839, 783 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.12 (6H, s), 1.00 (9H, s), 2.03 (3H, s), 2.40 (1H, ddd, *J* = 1.7, 9.1, 14.0 Hz), 2.57 (1H, ddd, *J* = 3.3, 8.7, 14.0 Hz), 3.32 (1H, dd, *J* = 3.3, 9.1 Hz), 3.69 (1H, d, *J* = 12.3 Hz), 3.78 (6H, s), 4.17 (1H, d, *J* = 12.3 Hz), 4.81 (1H, ddd, *J* = 1.2, 1.7, 8.7 Hz), 6.08 (1H, dd, *J* = 1.2, 9.9 Hz), 6.38 (2H, s), 7.24 (1H, d, *J* = 9.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ -4.7 (CH_3), 18.7 (C), 20.7 (CH_3), 25.8 (CH_3), 36.3 (CH_2), 49.6 (CH), 55.9 (CH_3), 65.4 (CH_2), 81.5 (CH), 84.4 (C), 105.4 (CH), 126.2 (CH), 131.8 (C), 133.9 (C), 151.6 (C), 153.2 (CH), 170.3 (C), 196.2 (C); HRMS (ESI) Exact mass calcd for $C_{24}H_{34}O_7SiNa$ $[M+Na]^+$ 485.1966, found 485.1970.

***endo*-5-Acetoxymethyl-6-(1-propoxy)-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-6a).** Isolated as yellow oil (44.9 mg, 71%) after silica gel column chromatography (15 g, eluent: Hexane/EtOAc (80 : 20, v/v) and then 20 g, eluent: Hexane/EtOAc (80 : 20, v/v)) following the general procedure (40 h) using *n*-propyl vinyl ether (**5a**) (140 μL, 1.25 mmol, 5.0 equiv) and *N*,*N*-diisopropylethylamine (8.71 μL, 0.050 mmol, 0.2 equiv). A solution of 6-acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (**1**) (57.1 mg, 0.25 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture by cannula transfer, and then a vessel was washed with CH_2Cl_2 (0.5 mL x 3). 

R_f = 0.33 (Hexane/EtOAc, 67 : 33, v/v); IR (neat) 2965, 2877, 1745, 1703, 1230, 1083, 1049, 859 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.87 (3H, t, *J* = 7.5 Hz), 1.53 (2H, tq, *J* = 6.7, 7.5 Hz), 1.67 (1H, ddd, *J* = 1.8, 4.2, 13.5 Hz), 2.13 (3H, s), 2.73 (1H, ddd, *J* = 8.7, 8.7, 13.5 Hz), 3.31-3.43 (2H, m), 4.08 (1H, dd, *J* = 4.2, 8.7 Hz), 4.25 (1H, d, *J* = 12.0 Hz), 4.49 (1H, ddd, *J* = 1.2, 1.8, 8.7 Hz), 4.62 (1H, d, *J* = 12.0 Hz), 6.21

(1H, dd, *J* = 1.2, 9.9 Hz), 7.08 (1H, d, *J* = 9.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 10.4 (CH_3), 20.7 (CH_3), 22.8 (CH_2), 33.0 (CH_2), 65.0 (CH_2), 72.8 (CH_2), 80.7 (CH), 81.2 (C), 82.1 (CH), 128.0 (CH), 150.6 (CH), 170.6 (C), 196.2 (C); HRMS (ESI) Exact mass calcd for $C_{13}H_{18}NaO_5$ $[M+Na]^+$ 277.1046, found 277.1066.

The stereochemistry of cycloadducts **6a** – **6d** was determined by comparison with ^{1}H NMR data reported for *endo*-5-(*t*-butyldimethylsilyloxy)methyl-6-ethoxy-8-oxabicyclo[3.2.1]oct-3-en-2-one in the literature.[14]

***endo*-5-Acetoxymethyl-6-ethoxy-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-6b).** Isolated as yellow oil (39.0 mg, 65%) after silica gel column chromatography (15 g, eluent: Hexane/EtOAc (80 : 20, v/v)) following the general procedure (48 h) using ethyl vinyl ether (**5b**) (120 μL, 1.25 mmol, 5.0 equiv) and *N*,*N*-diisopropylethylamine (8.71 μL, 0.050 mmol, 0.2 equiv). A solution of 6-acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (**1**) (57.1 mg, 0.25 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture by cannula transfer, and then a vessel was washed with CH_2Cl_2 (0.5 mL x 3). R_f = 0.31 (Hexane/EtOAc, 67 : 33, v/v); IR (neat) 2979, 2879, 1745, 1703, 1446, 1385, 1231, 1124, 1084, 1049, 903, 857 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.15 (3H, t, *J* = 6.9 Hz), 1.68 (1H, ddd, *J* = 1.5, 3.9, 13.5 Hz), 2.13 (3H, s), 2.74 (1H, ddd, *J* = 8.7, 8.7, 13.5 Hz), 3.40-3.56 (2H, m), 4.08 (1H, dd, *J* = 3.9, 8.7 Hz), 4.25 (1H, d, *J* = 12.0 Hz), 4.49 (1H, ddd, *J* = 1.5, 1.5, 8.7 Hz), 4.63 (1H, d, *J* = 12.0 Hz), 6.22 (1H, dd, *J* = 1.5, 9.9 Hz), 7.08 (1H, d, *J* = 9.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 15.2 (CH_3), 20.6 (CH_3), 33.1 (CH_2), 64.9 (CH_2), 66.6 (CH_2), 80.7 (CH), 81.1 (C), 82.0 (CH), 128.1 (CH), 150.5 (CH), 170.6 (C), 196.1 (C); HRMS (ESI) Exact mass calcd for $C_{12}H_{16}NaO_5$ $[M+Na]^+$ 263.0890, found 263.0900.

***endo*-5-Acetoxymethyl-6-(cyclohexyloxy)-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-6c).** Isolated as yellow oil (56.2 mg, 76%) after silica gel column chromatography (15 g, eluent: Hexane/EtOAc (80 : 20, v/v)) following the general procedure (40 h) using cyclohexyl vinyl ether (**5c**) (177 μL, 1.25 mmol, 5.0 equiv) and *N*,*N*-diisopropylethylamine (8.71 μL, 0.050 mmol, 0.2 equiv). A solution of 6-acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (**1**) (57.1 mg, 0.25 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture by cannula transfer, and

then a vessel was washed with CH_2Cl_2 (0.5 mL x 3). R_f = 0.39 (Hexane/EtOAc, 67 : 33, v/v); IR (neat) 2933, 2857, 1746, 1704, 1450, 1365, 1229, 1081, 1048, 956, 861, 756 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19-1.28 (5H, m), 1.50 (1H, m), 1.65 (1H, ddd, *J* = 1.8, 4.2, 13.5 Hz), 1.65-1.86 (4H, m), 2.13 (3H, s), 2.73 (1H, ddd, *J* = 8.7, 8.7, 13.5 Hz), 3.26 (1H, m), 4.17 (1H, dd, *J* = 4.2, 8.7 Hz), 4.24 (1H, d, *J* = 12.0 Hz), 4.47 (1H, ddd, *J* = 1.2, 1.8, 8.7 Hz), 4.57 (1H, d, *J* = 12.0 Hz), 6.20 (1H, dd, *J* = 1.2, 9.9 Hz), 7.07 (1H, d, *J* = 9.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6 (CH_3), 23.7 (CH_2), 23.8 (CH_2), 25.4 (CH_2), 31.9 (CH_2), 32.8 (CH_2), 34.0 (CH_2), 64.9 (CH_2), 78.3 (CH), 79.7 (CH), 80.8 (CH), 81.1 (C), 127.9 (CH), 150.9 (CH), 170.6 (C), 196.2 (C); HRMS (ESI) Exact mass calcd for $C_{16}H_{22}NaO_5$ $[M+Na]^+$ 317.1359, found 317.1353.

***endo*-5-Acetoxymethyl-6-*t*-butoxy-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-6d).** Isolated as yellow oil (40.5 mg, 60%) after silica gel column chromatography (12 g, eluent: Hexane/EtOAc (85 : 15, v/v)) following the general procedure (40 h) using *t*-butyl vinyl ether (**5d**) (164 μL, 1.25 mmol, 5.0 equiv) and *N*,*N*-diisopropylethylamine (8.71 μL, 0.050 mmol, 0.2 equiv). A solution of 6-acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (**1**) (57.1 mg, 0.25 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture by cannula transfer, and then a vessel was washed with CH_2Cl_2 (0.5 mL x 3). R_f = 0.37 (Hexane/EtOAc, 67 : 33, v/v); IR (KBr) 1743, 1704, 1369, 1239, 1080, 1026, 936, 688, 444 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.15 (9H, s), 1.61 (1H, ddd, *J* = 1.8, 4.2, 13.5 Hz), 2.13 (3H, s), 2.71 (1H, ddd, *J* = 8.7, 8.7, 13.5 Hz), 4.22 (1H, d, *J* = 12.0 Hz), 4.23 (1H, dd, *J* = 4.2, 8.7 Hz), 4.46 (1H, ddd, *J* = 1.2, 1.8, 8.7 Hz), 4.54 (1H, d, *J* = 12.0 Hz), 6.19 (1H, dd, *J* = 1.2, 9.9 Hz), 7.02 (1H, d, *J* = 9.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.7 (CH_3), 28.1 (CH_3), 35.8 (CH_2), 64.4 (CH_2), 74.4 (CH), 74.5 (C), 80.8 (CH), 81.0 (C), 127.8 (CH), 151.0 (CH), 170.6 (C), 196.4 (C); HRMS (ESI) Exact mass calcd for $C_{14}H_{20}NaO_5$ $[M+Na]^+$ 291.1203, found 291.1206.

***endo*- and *exo*-5-Acetoxymethyl-6-(*t*-butoxycarbonyl)-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-8a and *exo*-8a).** Isolated as yellow oil (42.4 mg, 62% including 3% of regioisomer, *endo* : *exo* = 66 : 34) after silica gel column chromatography (15 g, eluent: Hexane/EtOAc (80 : 20, v/v) and then 25 g, eluent: Toluene/EtOAc (90 : 10, v/v)) following the general procedure (24 h) using [Pd(η^3-

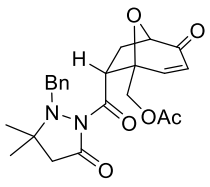
$C_3H_5)Cl]_2$ (4.6 mg, 0.0125 mmol, 5.0 mol%), *t*-butyl acrylate (**7a**) (181 μL, 1.25 mmol, 5.0 equiv), *N*,*N*-diisopropylethylamine (8.7 μL, 0.05 mmol, 0.2 equiv), and 6-acetoxymethyl-6-(*t*-butoxycarbonyloxy)-2*H*-pyran-3(6*H*)-one (71.6 mg, 0.25 mmol). A solution of 6-acetoxymethyl-6-(*t*-butoxycarbonyloxy)-2*H*-pyran-3(6*H*)-one in CH_2Cl_2 (0.5 mL) was added to the mixture by cannula transfer, and then a vessel was washed with CH_2Cl_2 (0.5 mL x 3). R_f = 0.26 (Hexane/EtOAc, 67 : 33, v/v); IR (neat) 2979, 1734, 1229, 1151, 1032, 757 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.45 (9H x 66/100, s), 1.49 (9H x 34/100, s), 1.99 (1H x 34/100, ddd, *J* = 1.5, 8.7, 13.5 Hz), 2.12 (3H x 34/100, s), 2.14 (3H x 66/100, s), 2.19 (1H x 66/100, ddd, *J* = 1.5, 5.7, 13.5 Hz), 2.66 (1H x 66/100, ddd, *J* = 8.7, 10.8, 13.5 Hz), 2.83 (1H x 34/100, ddd, *J* = 3.6, 8.7, 13.5 Hz), 3.00 (1H x 34/100, dd, *J* = 3.6, 8.7 Hz), 3.20 (1H x 66/100, dd, *J* = 5.7, 10.8 Hz), 4.17 (1H x 34/100, d, *J* = 12.0 Hz), 4.35 (1H x 66/100, d, *J* = 12.0 Hz), 4.58 (1H x 66/100, ddd, *J* = 1.2, 1.5, 8.7 Hz), 4.67 (1H x 34/100, d, *J* = 12.0 Hz), 4.73 (1H x 34/100, ddd, *J* = 1.2, 1.5, 8.7 Hz), 4.84 (1H x 66/100, d, *J* = 12.0 Hz), 6.07 (1H x 34/100, dd, *J* = 1.2, 9.9 Hz), 6.14 (1H x 66/100, dd, *J* = 1.2, 9.9 Hz), 7.07 (1H x 66/100, d, *J* = 9.9 Hz), 7.21 (1H x 34/100, d, *J* = 9.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.65 (CH_3, *exo*), 20.70 (CH_3, *endo*), 27.88 (CH_3, *endo*), 27.92 (CH_3, *exo*), 29.2 (CH_2, *endo*), 30.2 (CH_2, *exo*), 49.1 (CH, *exo*), 49.9 (CH, *endo*), 64.6 (CH_2, *exo*), 65.2 (CH_2, *endo*), 81.0 (CH, *endo*), 81.6 (CH, *exo*), 81.8 (C, *endo*), 82.4 (C, *endo*), 82.5 (C, *exo*), 83.0 (C, *exo*), 126.8 (CH, *exo*), 128.4 (CH, *endo*), 149.3 (CH, *endo*), 151.7 (CH, *exo*), 168.7 (C, *endo*), 169.8 (C, *exo*), 170.4 (C, *exo*), 170.5 (C, *endo*), 195.55 (C, *endo*), 195.63 (C, *exo*); HRMS (ESI) Exact mass calcd for $C_{15}H_{20}NaO_6$ $[M+Na]^+$ 319.1152, found 319.1152.

The stereochemistry of cycloadducts **8a** was determined by comparison with ^1H NMR data of the cycloadducts of ethyl acrylate for the synthesis of englerin A in the literature.[15]

***endo*- and *exo*-5-Acetoxymethyl-6-[(1-benzyl-5,5-dimethyl-3-pyrazolidinonyl)carbonyl]-8-oxabicyclo[3.2.1]oct-3-en-2-one (*endo*-8b and *exo*-8b).** The ^1H NMR yield (62%, *endo* : *exo* = 63 : 37) of **8b** was determined using $Cl_2CHCHCl_2$ as an internal standard. The reaction was carried out following the general procedure (20 h) using 2-acryloyl-1-benzyl-5,5-dimethyl-3-pyrazolidinone (**7b**) (216 mg, 1.25 mmol, 5.0 equiv). A solution of 6-

acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (**1**) (57.1 mg, 0.25 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture by cannula transfer, and then a vessel was washed with CH_2Cl_2 (0.5 mL x 3). The sample (41.3 mg, *endo* : *exo* = 71 : 29) for ^1H and ^{13}C NMR spectra were obtained by purification with silica gel column chromatography (CH_2Cl_2/EtOAc (90 : 10, v/v)) followed by GPC ($CHCl_3$). R_f = 0.30 (CH_2Cl_2/EtOAc, 90 : 10, v/v); ^1H NMR (300 MHz, C_6D_6) δ 0.68 (3H x 71/100, s), 0.73 (3H x 29/100, s), 0.82 (3H x 71/100, s), 0.83 (3H x 29/100, s), 1.55-1.62 (1H x 71/100 + 1H x 29/100, m), 1.63 (3H x 29/100, s), 1.68 (3H x 71/100, s), 2.00 (1H x 71/100, d, *J* = 17.1 Hz), 2.07 (1H x 71/100, d, *J* = 17.1 Hz), 2.02 (1H x 29/100, d, *J* = 17.1 Hz), 2.08 (1H x 29/100, d, *J* = 17.1 Hz), 2.74 (1H x 29/100, ddd, *J* = 4.2, 8.7, 12.9 Hz), 2.82 (1H x 71/100, ddd, *J* = 8.4, 10.5, 12.9 Hz), 3.48 (1H x 71/100, d, *J* = 13.8 Hz), 3.61 (1H x 29/100, d, *J* = 14.1 Hz), 3.69 (1H x 71/100, d, *J* = 13.8 Hz), 3.79 (1H x 29/100, d, *J* = 14.1 Hz), 4.21 (1H x 29/100, d, *J* = 11.4 Hz), 4.21 (1H x 29/100, dd, *J* = 4.2, 8.4 Hz), 4.27 (1H x 71/100, d, *J* = 12.0 Hz), 4.28 (1H x 71/100, dd, *J* = 7.2, 10.5 Hz), 4.38 (1H x 71/100, d, *J* = 12.0 Hz), 4.47 (1H x 71/100, ddd, *J* = 1.5, 1.8, 8.4 Hz), 4.68 (1H x 29/100, ddd, *J* = 1.2, 1.2, 8.7 Hz), 4.79 (1H x 29/100, d, *J* = 11.4 Hz), 5.84 (1H x 29/100, dd, *J* = 1.2, 9.9 Hz), 5.89 (1H x 71/100, dd, *J* = 1.5, 9.9 Hz), 6.95 (1H x 29/100, d, *J* = 9.9 Hz), 6.97 (1H x 71/100, d, *J* = 9.9 Hz), 7.05-7.20 (3H x 71/100 + 3H x 29/100, m), 7.41-7.44 (2H x 71/100, m), 7.49-7.54 (2H x 29/100, m); ^{13}C NMR (75 MHz, C_6D_6) δ 20.2 (CH_3, *exo*), 20.3 (CH_3, *endo*), 25.4 (CH_3, *endo*), 25.7 (CH_3, *exo*), 26.0 (CH_3, *endo*), 26.2 (CH_3, *exo*), 30.9 (CH_2, *exo*), 31.5 (CH_2, *endo*), 43.0 (CH_2, *endo*), 43.4 (CH_2, *exo*), 48.9 (CH, *exo*), 51.6 (CH, *endo*), 56.7 (CH_2, *exo*), 57.1 (CH_2, *endo*), 60.2 (C, *exo*), 60.5 (C, *endo*), 64.3 (CH_2, *endo*), 65.7 (CH_2, *exo*), 80.7 (CH, *endo*), 82.2 (CH, *exo*), 82.3 (C, *endo*), 84.2 (C, *exo*), 125.5 (CH, *endo*), 126.9 (CH, *exo*), 127.6 (CH, *exo*), 127.8 (CH, *endo*), 128.4 (CH, *exo*), 128.5 (CH, *endo*), 129.0 (CH, *exo*), 129.3 (CH, *endo*), 138.3 (C, *endo*), 138.9 (C, *exo*), 151.1 (CH, *endo*), 152.1 (CH, *exo*), 167.1 (C, *exo*), 167.3 (C, *endo*), 169.9 (C, *exo*), 170.4 (C, *endo*), 174.1 (C, *endo*), 174.9 (C, *exo*), 195.1 (C, *exo*), 195.9 (C, *endo*).

***endo*-5-Acetoxymethyl-6-[(1-benzyl-5,5-dimethyl-3-pyrazolidinonyl)carbonyl]-8-oxabicyclo-**



[3.2.1]oct-3-en-2-one (*endo*-8b). Isolated as colorless prisms (23.9 mg, *endo* only) after silica gel column chromatography (12 g, eluent: Hexane/EtOAc (60 : 40, v/v), 15 g, eluent: Toluene/EtOAc (80 : 20, v/v), and then 12 g, eluent: CH_2Cl_2/EtOAc (90 : 10,

v/v)) followed by washing with Et_2O (1 mL). R_f = 0.29 (CH_2Cl_2/EtOAc, 90 : 10, v/v); mp 156 – 159 ºC; IR (KBr) 2993, 1747, 1693, 1362, 1237, 1035, 864, 824, 771, 720, 695, 645, 630, 451 cm^{-1}; ^1H NMR (300 MHz, C_6D_6) δ 0.67 (3H, s), 0.82 (3H, s), 1.58 (1H, ddd, *J* = 1.8, 7.5, 12.9 Hz), 1.68 (3H, s), 2.00 (1H, d, *J* = 17.2 Hz), 2.05 (1H, d, *J* = 17.2 Hz), 2.82 (1H, ddd, *J* = 8.4, 10.5, 12.9 Hz), 3.46 (1H, d, *J* = 13.8 Hz), 3.68 (1H, d, *J* = 13.8 Hz), 4.26 (1H, d, *J* = 12.0 Hz), 4.28 (1H, dd, *J* = 7.5, 10.5 Hz), 4.38 (1H, d, *J* = 12.0 Hz), 4.47 (1H, ddd, *J* = 1.5, 1.8, 8.4 Hz), 5.88 (1H, dd, *J* = 1.5, 9.9 Hz), 6.96 (1H, d, *J* = 9.9 Hz), 7.05-7.19 (3H, m), 7.41-7.44 (2H, m); ^{13}C NMR (75 MHz, C_6D_6) δ 20.3 (CH_3), 25.4 (CH_3), 26.0 (CH_3), 31.5 (CH_2), 43.0 (CH_2), 51.6 (CH), 57.1 (CH_2), 60.5 (C), 64.3 (CH_2), 80.7 (CH), 82.3 (C), 125.5 (CH), 127.8 (CH), 128.5 (CH), 129.3 (CH), 138.3 (C), 151.0 (CH), 167.3 (C), 170.4 (C), 174.1 (C), 195.9 (C); HRMS (ESI) Exact mass calcd for $C_{23}H_{26}N_2NaO_6$ $[M+Na]^+$ 449.1683, found 449.1676.

The stereochemistry of cycloadducts **8b** was determined by comparison with ^1H NMR data of the cycloadducts of ethyl acrylate for the synthesis of englerin A in the literature.[15]

***exo*- and *endo*-8-(Acetoxy)methyl-3a,4,8,8a-tetrahydro-2-phenyl-4,8-epoxycyclohepta[*c*]pyrrole-1,3,5(2*H*)-trione (*endo*-8c and *exo*-8c).** Isolated as colorless prisms (55.4 mg, 65%, *exo* : *endo* = 57 : 43) after silica gel column chromatography (20 g, eluent: CH_2Cl_2/EtOAc (90 : 10, v/v)) following the general procedure (64 h) using *N*-phenylmaleimide (**7c**) (216 mg, 1.25 mmol, 5.0 equiv). A solution of 6-acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (**1**) (57.1 mg, 0.25 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture by cannula transfer, and then a vessel was washed with CH_2Cl_2 (0.5 mL x 3). R_f = 0.30 (CH_2Cl_2/EtOAc, 90 : 10, v/v); IR (KBr) 1716, 1496, 1387, 1224, 1197, 1037, 756, 692 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.06 (3H x 57/100, s), 2.16 (3H x 43/100, s), 3.47 (1H x 57/100, dd, *J* = 0.9, 7.5 Hz), 3.54 (1H x 57/100, d, *J* = 7.5 Hz), 3.86 (1H x 43/100, d, *J* = 9.3 Hz), 4.18 (1H x 43/100, dd, *J* = 9.0, 9.3 Hz), 4.34 (1H x 57/100, d, *J* = 12.6 Hz), 4.40 (1H x 43/100, d, *J* = 12.3 Hz), 4.77 (1H x 43/100, d, *J* = 12.3 Hz), 4.80 (1H x 57/100, d, *J* = 12.6 Hz), 5.00 (1H x 43/100, dd, *J* = 1.2, 9.0 Hz), 5.02 (1H x 57/100, dd, *J* = 0.9, 1.2 Hz), 6.16 (1H x 57/100, dd, *J* = 1.2, 9.9 Hz), 6.28 (1H x 43/100, dd, *J* = 1.2, 9.9 Hz), 7.05-7.09 (1H x 43/100 + 1H x 57/100, m), 7.21-7.32 (2H x 43/100 + 2H x 57/100, m), 7.38-7.51 (3H x 43/100 + 3H x 57/100, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5 (CH_3, *exo*), 20.7 (CH_3, *endo*), 47.6

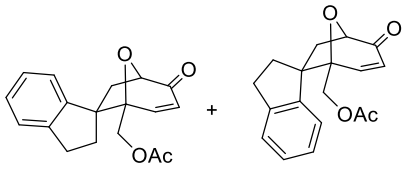
(CH, *endo*), 47.9 (CH, *exo*), 51.1 (CH, *exo*), 51.7 (CH, *endo*), 63.6 (CH_2, *exo*), 64.2 (CH_2, *endo*), 82.2 (C, *endo*), 82.3 (CH, *endo*), 82.9 (C, *exo*), 84.0 (CH, *exo*), 126.1 (CH, *endo*), 126.2 (CH, *exo*), 127.2 (CH, *exo*), 129.1 (CH, *endo*), 129.19 (CH, *exo*), 129.22 (CH, *exo*), 129.4 (CH x 2, *endo*), 130.8 (C, *endo*), 131.2 (C, *exo*), 148.9 (CH, *endo*), 151.1 (CH, *exo*), 170.0 (C, *exo*), 170.3 (C, *endo*), 171.4 (C, *endo*), 171.7 (C, *exo*), 172.1 (C, *endo*), 173.6 (C, *exo*), 190.7 (C, *endo*), 191.8 (C, *exo*); HRMS (ESI) Exact mass calcd for $C_{18}H_{15}NNaO_6$ $[M+Na]^+$ 364.0792, found 364.0789.

The stereochemistry of cycloadducts **8c** was determined by coupling constants between H_{3a} and H_4 of ^{1}H NMR.

***exo*- and *endo*-5-[(Acetyloxy)methyl]-3',4'-dihydro-2'*H*-spiro[8-oxabicyclo[3.2.1]-oct-3-en-2-one-6,1'-naphthalene] (*exo*-10a and *endo*-10a).** Isolated as yellow viscous oil (68.3 mg, 88%, *exo* : *endo* = 76 : 24) after silica gel column chromatography (15 g, eluent: Toluene/EtOAc (93 : 7, v/v)) following the general procedure (12 h) using α-methylenetetralin (**9a**) (180 mg, 1.25 mmol, 5.0 equiv). A solution of 6-acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (**1**) (57.1 mg, 0.25 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture by cannula transfer, and then a vessel was washed with CH_2Cl_2 (0.5 mL x 3). R_f = 0.28 (Toluene/EtOAc, 93 : 7, v/v); IR (neat) 3020, 2944, 1742, 1707, 1489, 1448, 1382, 1217, 1040, 754, 667 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.67-1.97 (4H x 76/100 + 4H x 24/100, m), 1.93 (3H x 24/100, s), 2.03 (1H x 76/100, dd, *J* = 1.8, 13.8 Hz), 2.03 (3H x 76/100, s), 2.33 (1H x 24/100, dd, *J* = 2.7, 13.8 Hz), 2.40 (1H x 24/100, m), 2.66 (1H x 24/100, dd, *J* = 9.0, 13.8 Hz), 2.81-2.85 (2H x 76/100 + 1H x 24/100, m), 2.90 (1H x 76/100, dd, *J* = 9.0, 13.8 Hz), 3.57 (1H x 76/100, d, *J* = 12.3 Hz), 4.34 (1H x 76/100, d, *J* = 12.3 Hz), 4.36 (1H x 24/100, d, *J* = 11.7 Hz), 4.42 (1H x 24/100, d, *J* = 11.7 Hz), 4.62 (1H x 24/100, ddd, *J* = 1.5, 2.7, 9.0 Hz), 4.73 (1H x 76/100, ddd, *J* = 1.2, 1.8, 9.0 Hz), 6.21 (1H x 76/100, dd, *J* = 1.2, 9.9 Hz), 6.30 (1H x 24/100, dd, *J* = 1.5, 9.9 Hz), 7.05 (1H x 24/100, d, *J* = 9.9 Hz), 7.06-7.21 (3H x 76/100 + 3H x 24/100, m), 7.22 (1H x 76/100, d, *J* = 9.9 Hz), 7.37 (1H x 24/100, m), 7.47 (1H x 76/100, m); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.4 (CH_3, *endo*), 20.6 (CH_3, *exo*), 20.7 (CH_2, *endo*), 20.8 (CH_2, *exo*), 29.9 (CH_2, *exo*), 30.5 (CH_2, *endo*), 35.5 (CH_2, *endo*), 35.6 (CH_2, *exo*), 46.0 (CH_2, *exo*), 46.6 (CH_2, *endo*), 50.9 (C, *endo*), 51.7 (C, *exo*), 65.1 (CH_2, *endo*), 66.1 (CH_2, *exo*), 79.3 (CH,

endo), 80.3 (CH, *exo*), 86.4 (C, *endo*), 87.2 (C, *exo*), 125.6 (CH, *endo*), 126.3 (CH, *exo*), 126.7 (CH, *endo*), 126.79 (CH, *exo*), 126.83 (CH, *endo*), 127.5 (CH, *exo*), 128.6 (CH, *endo*), 128.8 (CH, *exo*), 129.3 (CH, *exo*), 129.8 (CH, *endo*), 135.0 (C, *endo*), 136.9 (C, *exo*), 138.6 (C, *exo*), 139.3 (C, *endo*), 152.9 (CH, *exo*), 154.1 (CH, *endo*), 170.4 (C, *endo*), 170.5 (C, *exo*), 196.0 (C, *endo*), 196.1 (C, *exo*); HRMS (ESI): Exact mass calcd for $C_{19}H_{20}NaO_4$ $[M+Na]^+$ 335.1254, found 335.1242.

The stereochemistry of *exo*-**10a** was determined by a 2D NOESY experiment, which showed NOEs between the methylene hydrogen of 1,2,3,4-tetrahydronaphthalene at δ 1.67-1.97 and H_4 at δ 7.22.

***exo*- and *endo*-5-[(Acetyloxy)methyl]-2',3'-dihydro-spiro[8-oxabicyclo[3.2.1]-oct-3-en-2-one-6,1'-[1*H*]-indene] (*exo*-10b and *endo*-10b).** 

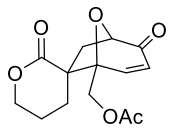
Isolated as yellow viscous oil (63.0 mg, 84%, *exo* : *endo* = 72 : 28) after silica gel column chromatography (15 g, eluent: Toluene/EtOAc (93 : 7, v/v)) following the general procedure (24 h) using 1-methyleneindan (**9b**) (163 mg, 1.25 mmol, 5.0 equiv). A solution of 6-acetoxy-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one (**1**) (57.1 mg, 0.25 mmol) in CH_2Cl_2 (0.5 mL) was added to the mixture by cannula transfer, and then a vessel was washed with CH_2Cl_2 (0.5 mL x 3). R_f = 0.28 (Toluene/EtOAc, 93 : 7, v/v); IR (KBr) 1731, 1694, 1268, 1247, 1027, 882, 765, 448 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.98 (3H x 28/100, s), 2.04 (3H x 72/100, s), 2.09-2.29 (3H x 72/100 + 1H x 28/100, m), 2.48 (1H x 28/100, dd, *J* = 2.4, 13.8 Hz), 2.63 (1H x 28/100, dd, *J* = 8.7, 13.8 Hz), 2.71 (1H x 28/100, m), 2.81 (1H x 72/100, dd, *J* = 9.0, 13.8 Hz), 2.87-3.06 (2H x 28/100 + 2H x 72/100, m), 3.75 (1H x 72/100, d, *J* = 12.3 Hz), 4.13 (1H x 72/100, d, *J* = 12.3 Hz), 4.22 (1H x 28/100, d, *J* = 11.7 Hz), 4.39 (1H x 28/100, d, *J* = 11.7 Hz), 4.67 (1H x 28/100, ddd, *J* = 1.5, 2.4, 8.7 Hz), 4.72 (1H x 72/100, ddd, *J* = 1.2, 1.8, 9.0 Hz), 6.19 (1H x 72/100, dd, *J* = 1.2, 9.9 Hz), 6.25 (1H x 28/100, dd, *J* = 1.5, 9.9 Hz), 6.78 (1H x 28/100, d, *J* = 9.9 Hz), 7.06 (1H x 28/100, m), 7.16 (1H x 28/100, m), 7.21-7.32 (2H x 28/100 + 4H x 72/100, m), 7.23 (1H x 72/100, d, *J* = 9.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5 (CH_3, *endo*), 20.6 (CH_3, *exo*), 30.8 (CH_2, *exo*), 30.9 (CH_2, *endo*), 34.9 (CH_2, *exo*), 39.1 (CH_2, *endo*), 44.28 (CH_2, *exo*), 44.32 (CH_2, *endo*), 59.3 (C, *endo*), 59.9 (C, *exo*), 64.0 (CH_2, *endo*), 65.0 (CH_2, *exo*), 80.0 (CH, *endo*), 80.2 (CH, *exo*), 85.3 (C, *exo*), 86.0 (C, *endo*) 124.4 (CH, *endo*, *exo*), 124.6 (CH, *exo*), 125.1 (CH, *endo*), 126.4 (CH, *endo*), 126.6 (CH, *endo*), 126.9 (CH, *exo*), 127.1 (CH, *exo*), 127.7 (CH, *exo*),

127.9 (CH, *endo*), 141.3 (C, *endo*), 142.8 (C, *exo*), 144.3 (C, *endo*), 145.3 (C, *exo*), 152.3 (CH, *exo*), 152.4 (CH, *endo*), 170.3 (C, *exo*), 170.5 (C, *endo*), 196.0 (C, *endo*), 196.3 (C, *exo*); HRMS (ESI): Exact mass calcd for $C_{18}H_{18}NaO_4$ $[M+Na]^+$ 321.1097, found 321.1088.

The stereochemistry of *exo*-**10b** was determined by a 2D NOESY experiment, which showed NOEs between the methylene hydrogen of indane at δ 2.09-2.29 and H_4 at δ 7.23.

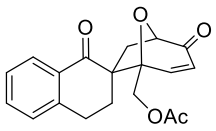
***exo*-(2,2'-Dioxo-4',5'-dihydro-2'*H*-8-oxaspiro[bicyclo[3.2.1]oct[3]ene-6,3'-furan]-5-yl)methyl acetate (*exo*-10c).**[4] Isolated as yellow plates (47.0 mg, 71%, *exo* : *endo* = 97 : 3) after silica gel column chromatography (7 g, eluent: Hexane/EtOAc (50 : 50, v/v)) following the general procedure (50 ºC, 16 h) using $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ (4.6 mg, 0.0125 mmol, 5.0 mol%), α-methylene-γ-butyrolactone (**9c**) (109 μL, 1.25 mmol, 5.0 equiv), and *N*,*N*-diisopropylethylamine (8.7 μL, 0.05 mmol, 0.2 equiv), and 6-acetoxymethyl-6-(*t*-butoxycarbonyloxy)-2*H*-pyran-3(6*H*)-one (71.6 mg, 0.25 mmol). A solution of 6-acetoxymethyl-6-(*t*-butoxycarbonyloxy)-2*H*-pyran-3(6*H*)-one in $ClCH_2CH_2Cl$ (1.0 mL) was added to the mixture by cannula transfer, and then a vessel was washed with $ClCH_2CH_2Cl$ (0.5 mL x 2). R_f = 0.16 (Hexane/EtOAc, 67 : 33, v/v); IR (KBr) 3046, 1755, 1701, 1441, 1378, 1251, 1176, 1065, 874 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.96 (1H, dd, *J* = 1.5, 13.5 Hz), 2.13 (3H, s), 2.24 (1H, ddd, *J* = 4.7, 7.5, 13.2 Hz), 2.48 (1H, ddd, *J* = 7.9, 8.1, 13.2, Hz), 2.98 (1H, dd, *J* = 8.7, 13.5 Hz), 4.27 (1H, ddd, *J* = 7.5, 7.9, 9.3 Hz), 4.40 (1H, ddd, *J* = 4.7, 8.1, 9.3 Hz), 4.47 (1H, d, *J* = 11.7 Hz), 4.55 (1H, d, *J* = 11.7 Hz), 4.74 (1H, ddd, *J* = 1.3, 1.5, 8.7 Hz), 6.23 (1H, dd, *J* = 1.3, 10.0 Hz), 7.23 (1H, d, *J* = 10.0 Hz); The olefinic protons of *endo*-**10c** could be observed: 6.16 (1H, dd, *J* = 1.2, 9.9 Hz), 7.33 (1H, d, *J* = 9.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5 (CH_3), 32.9 (CH_2), 40.0 (CH_2), 52.9 (C), 63.5 (CH_2), 65.2 (CH_2), 80.8 (CH), 82.7 (C), 128.2 (CH), 150.1 (CH), 169.9 (C), 176.7 (C), 194.9 (C); HRMS (ESI) Exact mass calcd for $C_{13}H_{14}NaO_6$ $[M+Na]^+$ 289.0683, found 289.0689.

The stereochemistry of *exo*-**10c** was determined by a 2D NOESY experiment, which showed NOEs between the methylene hydrogen of γ-butyrolactone at δ 2.48 and H_4 at δ 7.23, according to the literature.[4]

***exo*-(2,2'-Dioxo-2',4',5',6'-tetrahydro-8-oxaspiro[bicyclo[3.2.1]oct[3]ene-6,3'-pyran]-5-yl)methyl acetate (*exo*-10d).**  Isolated as colorless plates (42.6 mg, 61%, *exo* : *endo* = > 99 : 1) after silica gel column chromatography (10 g, eluent: Hexane/EtOAc (50 : 50, v/v)) following the general procedure (40 h) using α-methylene-δ-valerolactone (**9d**) (135 μL, 1.25 mmol, 5.0 equiv). R_f = 0.12 (Hexane/EtOAc, 67 : 33, v/v); IR (KBr) 2970, 1738, 1692, 1399, 1253, 1155, 1099, 1038, 1011, 886 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.76 (1H, dd, *J* = 1.7, 13.4 Hz), 1.83-2.07 (4H, m), 2.14 (3H, s), 3.09 (1H, dd, *J* = 8.8, 13.4, Hz), 4.34-4.52 (2H, m), 4.41 (1H, d, *J* = 11.8 Hz), 4.46 (1H, d, *J* = 11.8 Hz), 4.72 (1H, ddd, *J* = 1.4, 1.7, 8.8 Hz), 6.24 (1H, dd, *J* = 1.4, 9.9 Hz), 7.16 (1H, d, *J* = 9.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5 (CH_3), 21.7 (CH_2), 32.0 (CH_2), 42.2 (CH_2), 54.5 (C), 64.5 (CH_2), 70.5 (CH_2), 80. 6 (CH), 84.9 (C), 128.3 (CH), 150.4 (CH), 169.9 (C), 171.3 (C), 195.2 (C); HRMS (ESI) Exact mass calcd for $C_{14}H_{16}NaO_6$ $[M+Na]^+$ 303.0839, found 303.0864.

The stereochemistry of *exo*-**10d** was determined by a 2D NOESY experiment, which showed NOEs between the methylene hydrogen of δ-valerolactone at δ 1.83-2.07 and H_4 at δ 7.16.

***exo*- and *endo*-(1',2-Dioxo-3',4'-dihydro-1'*H*-8-oxaspiro[bicyclo[3.2.1]oct[3]ene-6,2'-naphthalene]-5-yl)methyl acetate (*exo*-10e and *endo*-10e).** Isolated *exo*-**10e** as colorless plates (51.1 mg, 63%) and *endo*-**10e** as colorless plates (5.2 mg, 6%) after silica gel column chromatography (18 g, eluent: Toluene/EtOAc (91 : 9, v/v) and then 13 g, Hexane/EtOAc (67 : 33, v/v)) following the general procedure (20 h) using 3,4-dihydro-2-methylene-1(2*H*)-naphthalenone (**9e**) (198 mg, 1.25 mmol, 5.0 equiv).

***exo*-(1',2-Dioxo-3',4'-dihydro-1'*H*-8-oxaspiro[bicyclo[3.2.1]oct[3]ene-6,2'-naphthalene]-5-yl)-methyl acetate (*exo*-10e).**  R_f = 0.40 (Toluene/EtOAc, 83 : 17, v/v); IR (KBr) 2945, 1744, 1682, 1604, 1450, 1365, 1232, 1031, 910, 760 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.57 (1H, dd, *J* = 1.7, 13.3 Hz), 1.93 (3H, s), 2.22 (1H, ddd, *J* = 4.8, 9.6, 14.3 Hz), 2.35 (1H, ddd, *J* = 4.9, 10.8, 14.3, Hz), 2.96 (1H, ddd, *J* = 4.9, 9.6, 17.5 Hz), 3.10 (1H, ddd, *J* = 4.8 10.8, 17.5 Hz), 3.32 (1H, dd, *J* = 9.0, 13.3 Hz), 3.92 (1H, d, *J* = 12.1 Hz), 4.40 (1H, d, *J* = 12.1 Hz), 4.71 (1H, ddd, *J* = 1.2, 1.7, 9.0 Hz), 6.28 (1H, dd, *J* = 1.2, 10.0 Hz), 7.27 (1H, d, *J* = 10.0 Hz), 7.26-7.39 (2H, m), 7.53 (1H, dt, *J* = 1.4, 7.5 Hz), 8.09 (1H, dd, *J* = 1.2, 7.8 Hz); ^{13}C NMR (75 MHz,

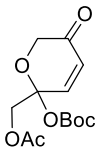
$CDCl_3$) δ 20.3 (CH_3), 26.5 (CH_2), 32.7 (CH_2), 38.0 (CH_2), 58.3 (C), 64.5 (CH_2), 80.4 (CH), 85.5 (C), 127.3 (CH), 128.0 (CH), 128.6 (CH), 128.7 (CH), 132.2 (C), 133.9 (CH), 142.3 (C), 150.3 (CH), 170.0 (C), 195.6 (C), 196.4 (C); HRMS (ESI): Exact mass calcd for $C_{19}H_{18}NaO_5$ $[M+Na]^+$ 349.1046, found 349.1053.

The stereochemistry of *exo*-**10e** was determined by a 2D NOESY experiment, which showed NOEs between the methylene hydrogen of cyclohexanone at δ 2.22, 2.35 and H_4 at δ 7.27.

***endo*-(1',2-Dioxo-3',4'-dihydro-1'*H*-8-oxaspiro[bicyclo[3.2.1]oct[3]ene-6,2'-naphthalene]-5-yl)-methyl acetate (*endo*-10e).** R_f = 0.28 (Toluene/EtOAc, 83 : 17, v/v); IR (KBr) 2941, 1747, 1692, 1601, 1455, 1313, 1231, 1031, 848, 742 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.85 (1H, dd, *J* = 2.3, 13.4 Hz), 2.00 (3H, s), 2.25 (1H, ddd, *J* = 3.1, 5.2, 13.3 Hz), 2.36 (1H, ddd, *J* = 5.1, 11.4, 13.3 Hz), 2.78 (1H, dd, *J* = 8.6, 13.4 Hz), 3.07 (1H, ddd, *J* = 3.1, 5.1, 17.7 Hz), 3.22 (1H, ddd, *J* = 5.2, 11.4, 17.7 Hz), 4.35 (1H, d, *J* = 11.8 Hz), 4.39 (1H, d, *J* = 11.8 Hz), 4.60 (1H, ddd, *J* = 1.4, 2.3, 8.6 Hz), 6.04 (1H, dd, *J* = 1.4, 10.0 Hz), 7.26-7.35 (2H, m), 7.51 (1H, dt, *J* = 1.4, 7.5 Hz), 7.64 (1H, d, *J* = 10.0 Hz), 7.91 (1H, d, *J* = 1.1, 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.5 (CH_3), 25.9 (CH_2), 29.8 (CH_2), 34.6 (CH_2), 60.4 (C), 63.7 (CH_2), 80.0 (CH), 84.1 (C), 122.7 (CH), 127.0 (CH), 127.9 (CH), 128.7 (CH), 132.3 (C), 133.9 (CH), 142.6 (C), 154.0 (CH), 170.4 (C), 196.5 (C), 197.0 (C); HRMS (ESI): Exact mass calcd for $C_{19}H_{19}O_5$ $[M+H]^+$ 327.1227, found 327.1233.

(1*R,4*S**,8*S**,12*R**)-5,10,13-Trioxatetracyclo[6.5.1.$0^{4,12}$.$0^{8,12}$]tetradecane-2,9-dione (11).**[4] A solution of **10c** (26.5 mg, 0.10 mmol) and Cs_2CO_3 (163 mg, 0.50 mmol) in THF (0.5 mL) and H_2O (0.5 mL) was stirred at 35 ºC for 14 h. The mixture was cooled to 25 ºC and acidified with 10% hydrochloric acid (0.4 mL) to pH 1. The resulting solution was stirred at 25 ºC for 3 h and THF was removed under reduced pressure. The residue was diluted with brine (3.75 mL) and extracted with EtOAc (7.5 mL x 3). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (7.0 g) with Hexane/EtOAc (50 : 50, v/v) to give 17.0 mg (76%) of **11** as colorless prisms. R_f = 0.34 (Hexane/EtOAc, 50 : 50, v/v); ^1H NMR (300 MHz, $CDCl_3$) δ 1.85 (1H, ddd, *J* = 4.8, 12.6, 14.4 Hz), 1.93 (1H, dd, *J* = 1.5,14.1 Hz), 2.06 (1H, ddd, *J* = 1.5, 2.1, 14.4 Hz), 2.52 (1H, d, *J* = 18.0 Hz), 2.92 (1H,

dd, *J* = 9.0, 14.1 Hz), 3.11 (1H, dd, *J* = 10.2, 18.0 Hz), 3.20 (1H, ddd, *J* = 2.1, 12.6, 12.9 Hz), 3.70 (1H, ddd, *J* = 1.5, 4.8, 12.9 Hz), 4.46 (1H, d, *J* = 10.8 Hz), 4.49 (1H, d, *J* = 10.2 Hz), 4.51 (1H, dd, *J* = 1.5, 9.0 Hz), 4.54 (1H, dd, *J* = 10.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 28.4 (CH_2), 38.0 (CH_2), 42.1 (CH_2), 48.8 (C), 55.2 (CH_2), 67.4 (CH), 69.4 (CH_2), 82.1 (C), 82.2 (CH), 178.9 (C), 210.2 (C).



6-[(*tert*-Butoxycarbonyl)oxy]-6-acetoxymethyl-2*H*-pyran-3(6*H*)-one. To a cold (0 ºC) solution of 6-acetoxymethyl-6-hydroxy-2*H*-pyran-3(6*H*)-one[3,4] (1.53 g, 8.20 mmol) in CH_2Cl_2 (16.4 mL) were added di-*tert*-butyl dicarbonate (2.68 g, 12.3 mmol) and *N*,*N*-dimethyl-4-aminopyridine (0.10 g, 0.82 mmol), successively. The mixture was stirred for 2 h at 0 ºC. The resulting solution was directly purified by silica gel column chromatography (40 g) with CH_2Cl_2 as eluent to give 1.24 g (53%) of the title compound as colorless needles. R_f = 0.60 (Hexane/EtOAc, 50 : 50, v/v); IR (KBr) 2983, 2903, 1745, 1702, 1286, 1251, 971 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.48 (9H, s), 2.11 (3H, s), 4.31 (1H, d, *J* = 17.3 Hz), 4.44 (1H, d, *J* = 11.6 Hz), 4.61 (1H, d, *J* = 11.6 Hz), 4.66 (1H, d, *J* = 17.3 Hz), 6.27 (1H, d, *J* = 10.5 Hz), 7.16 (1H, d, *J* = 10.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.6 (CH_3), 27.6 (CH_3), 65.2 (CH_2), 68.1 (CH_2), 83.6 (C), 97.2 (C), 128.5 (CH), 142.9 (CH), 150.7 (C), 170.0 (C), 193.0 (C). The corresponding molecular ion peak was not observed by HRMS (ESI) probably due to instability.

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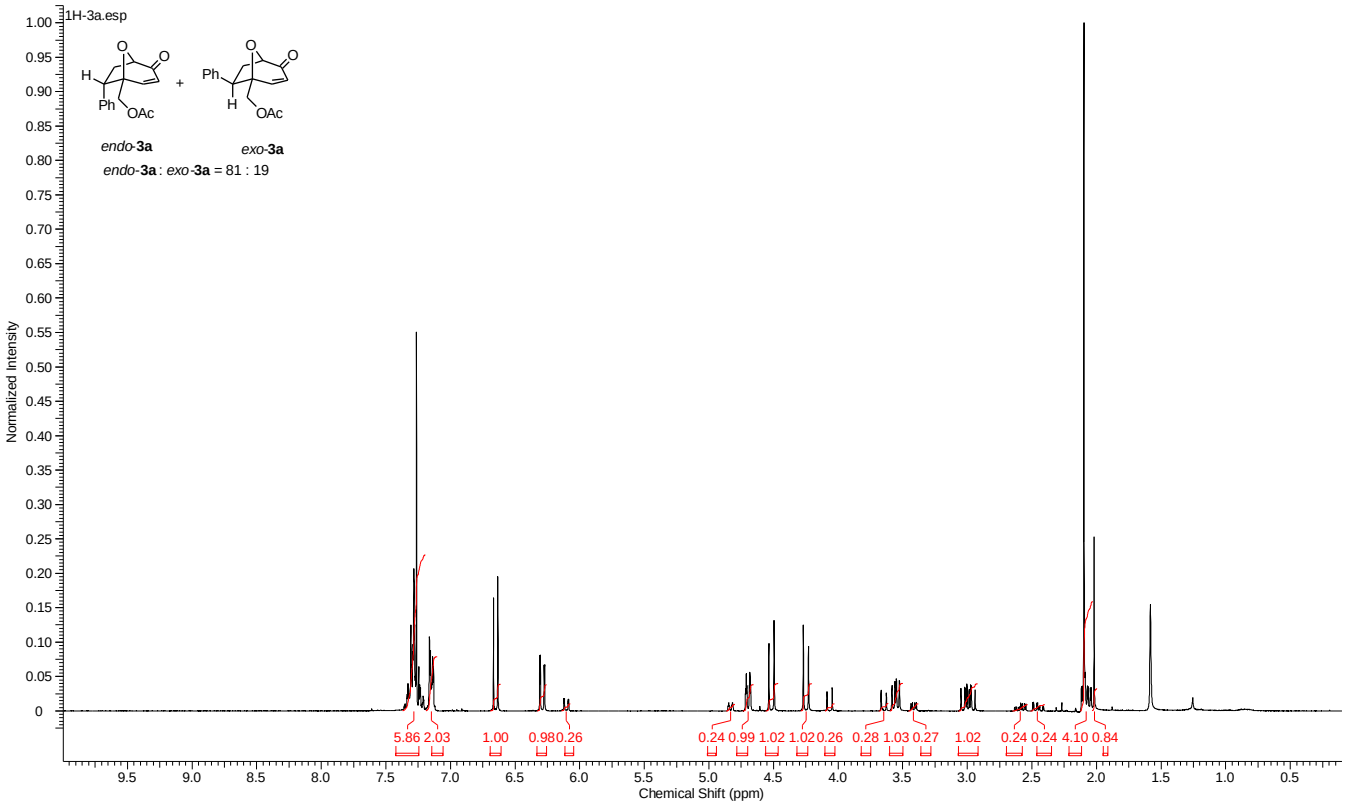
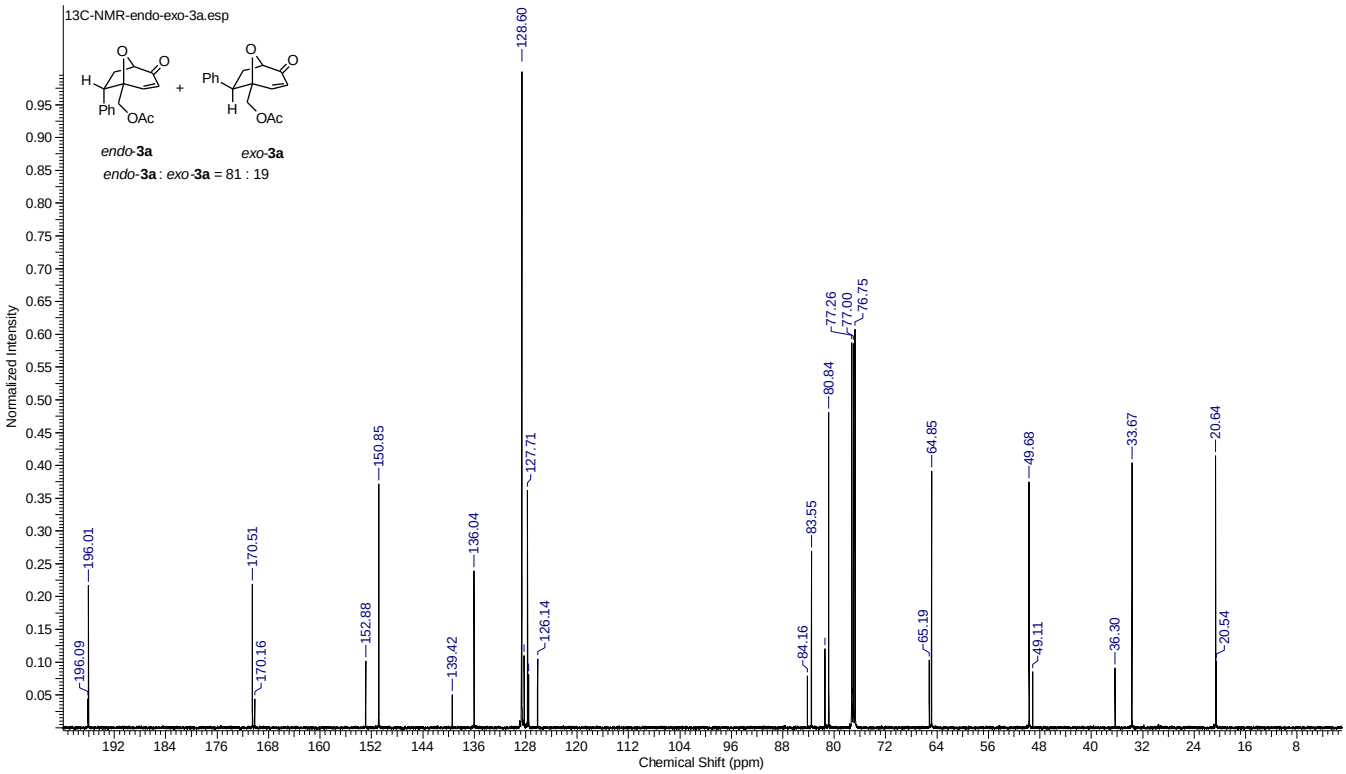
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (125 MHz, $CDCl_3$)



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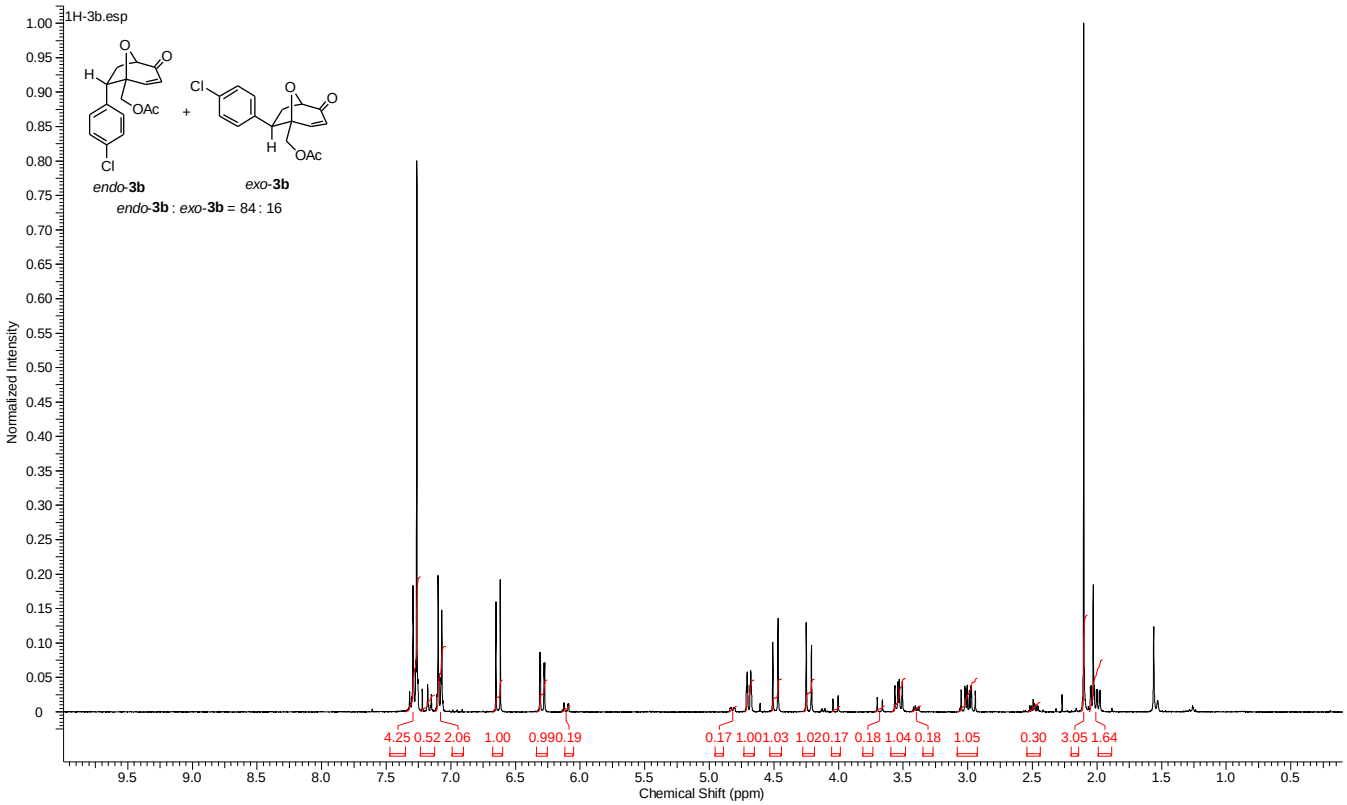

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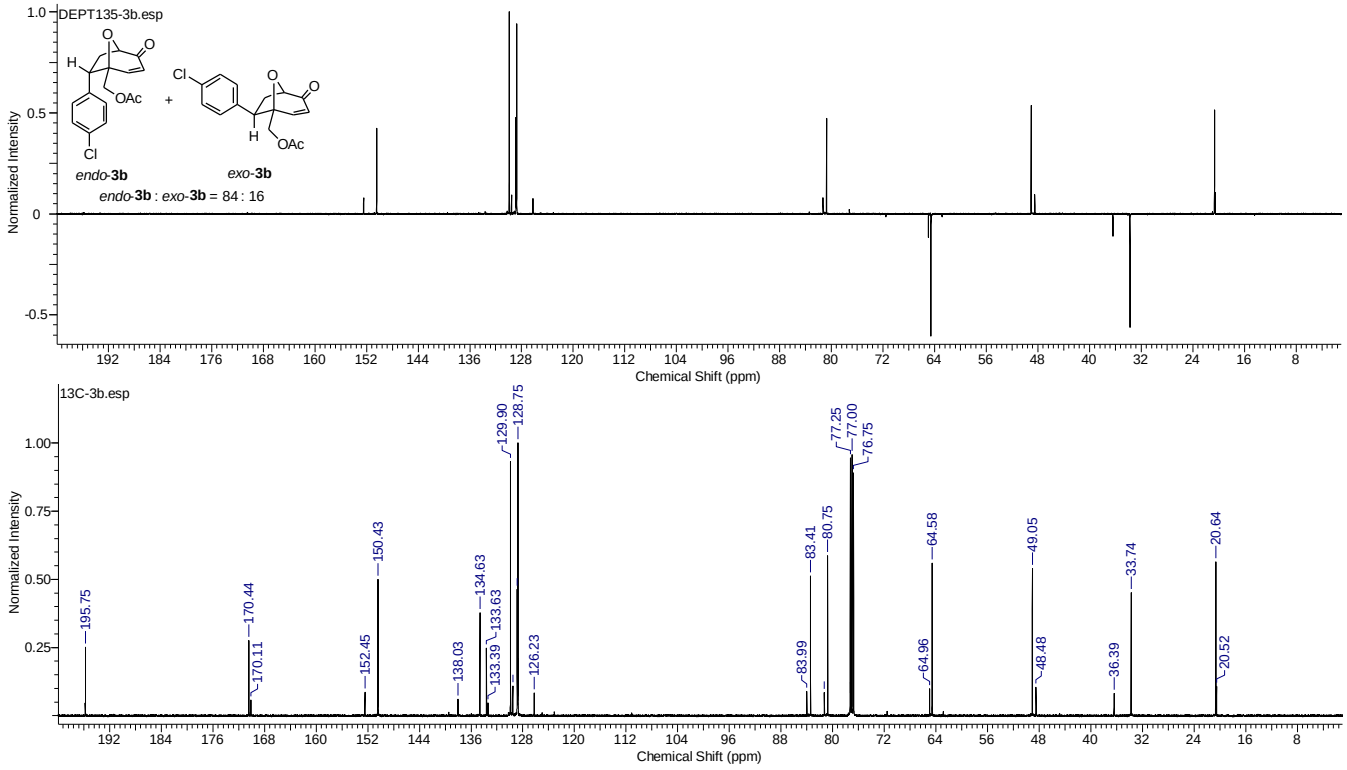

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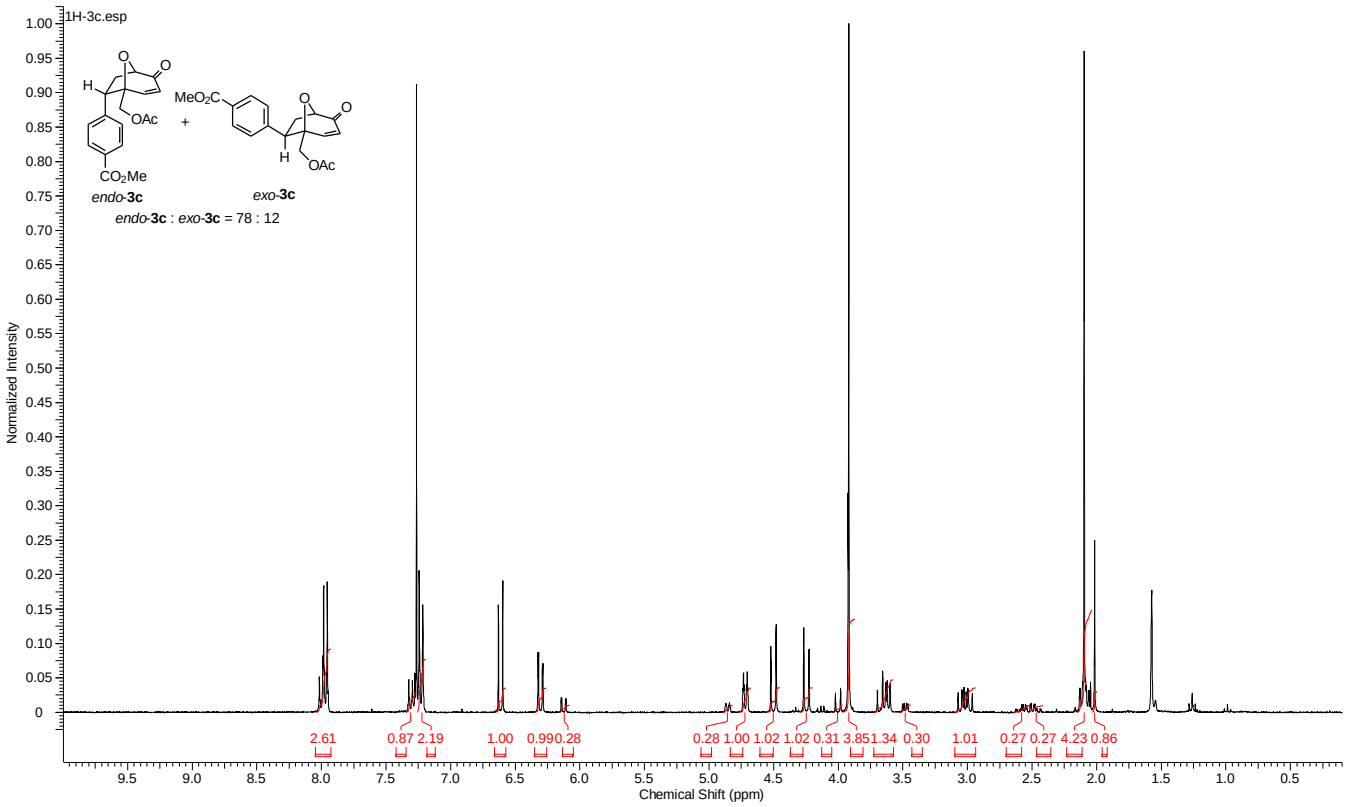

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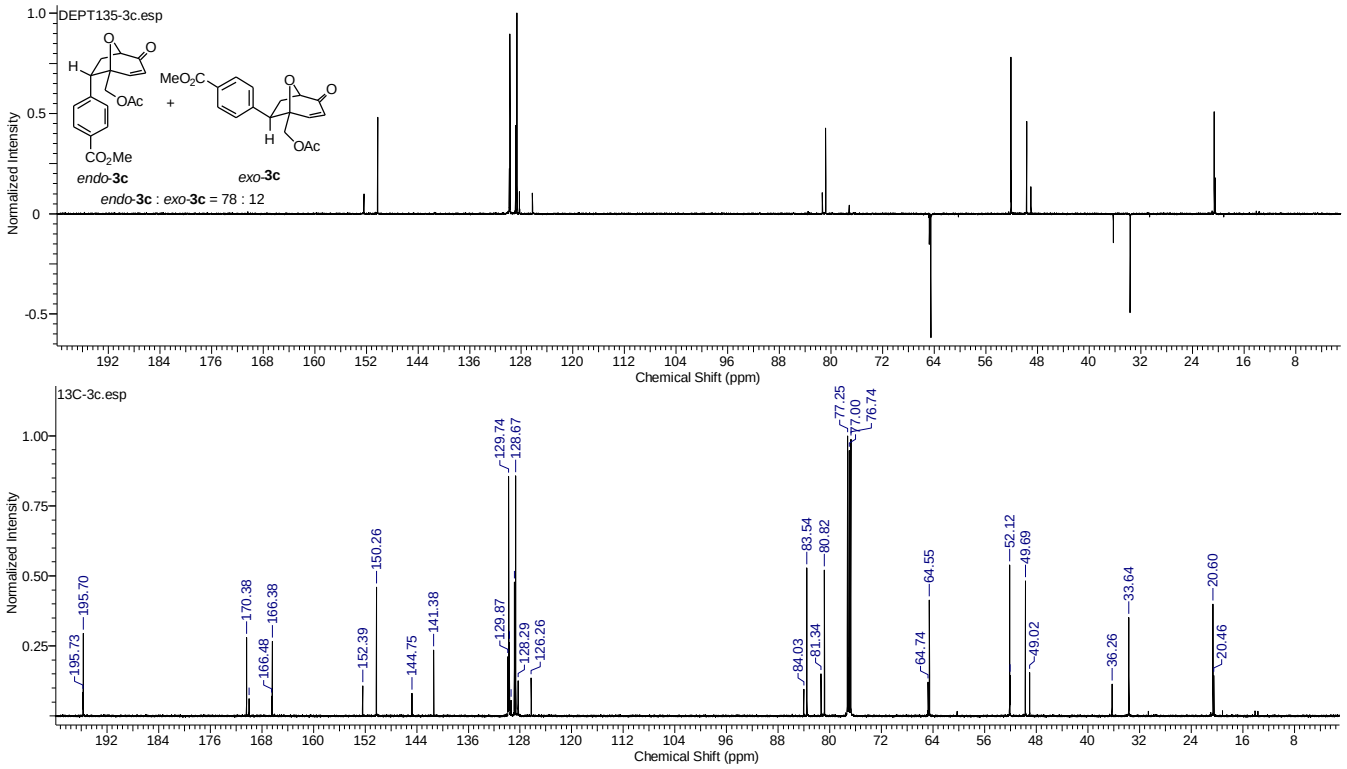

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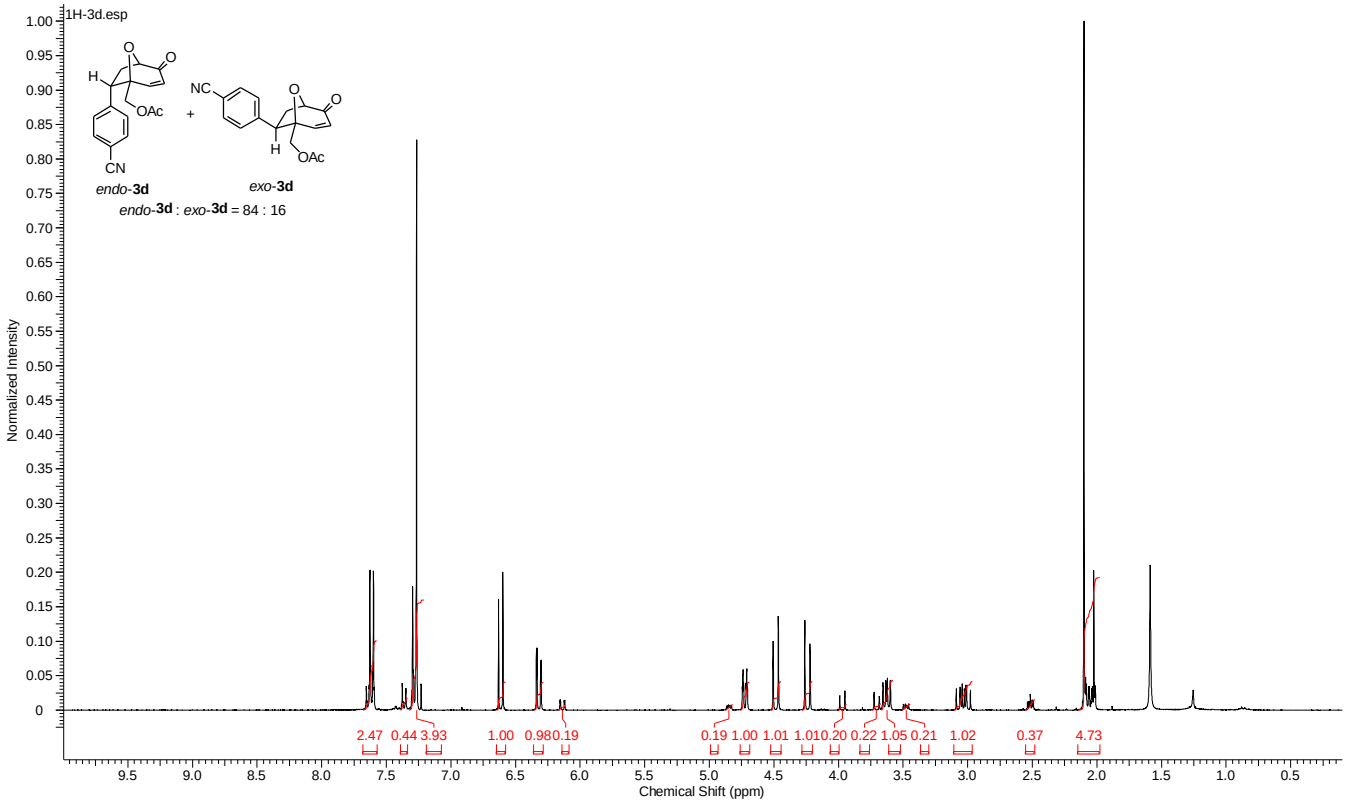

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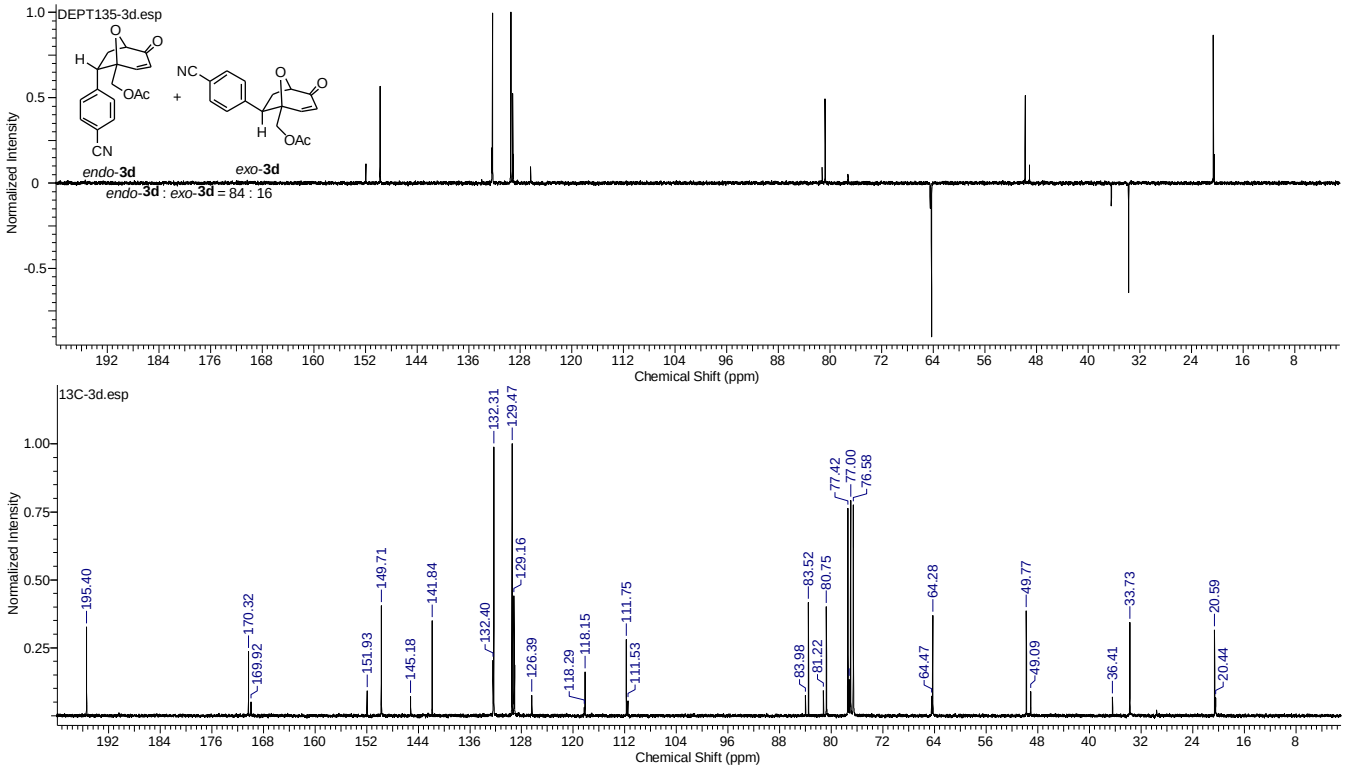

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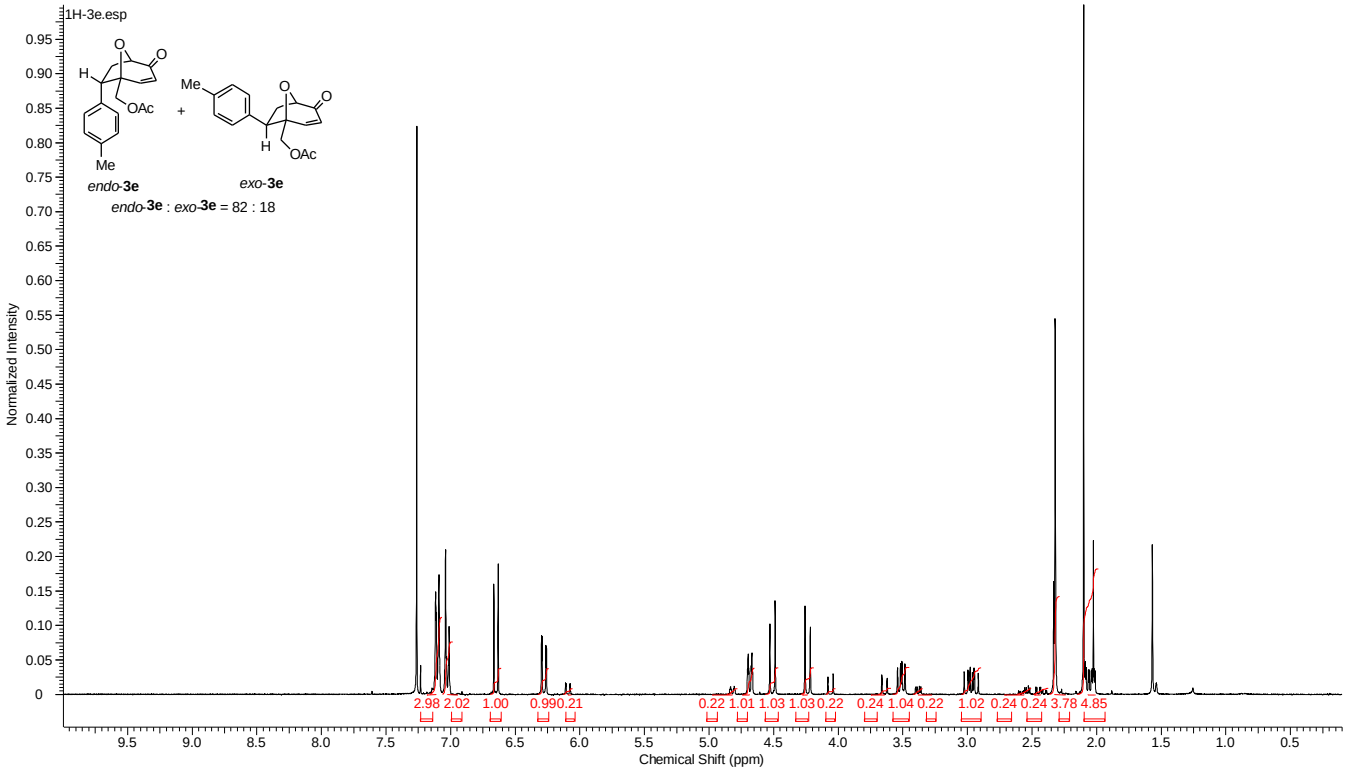

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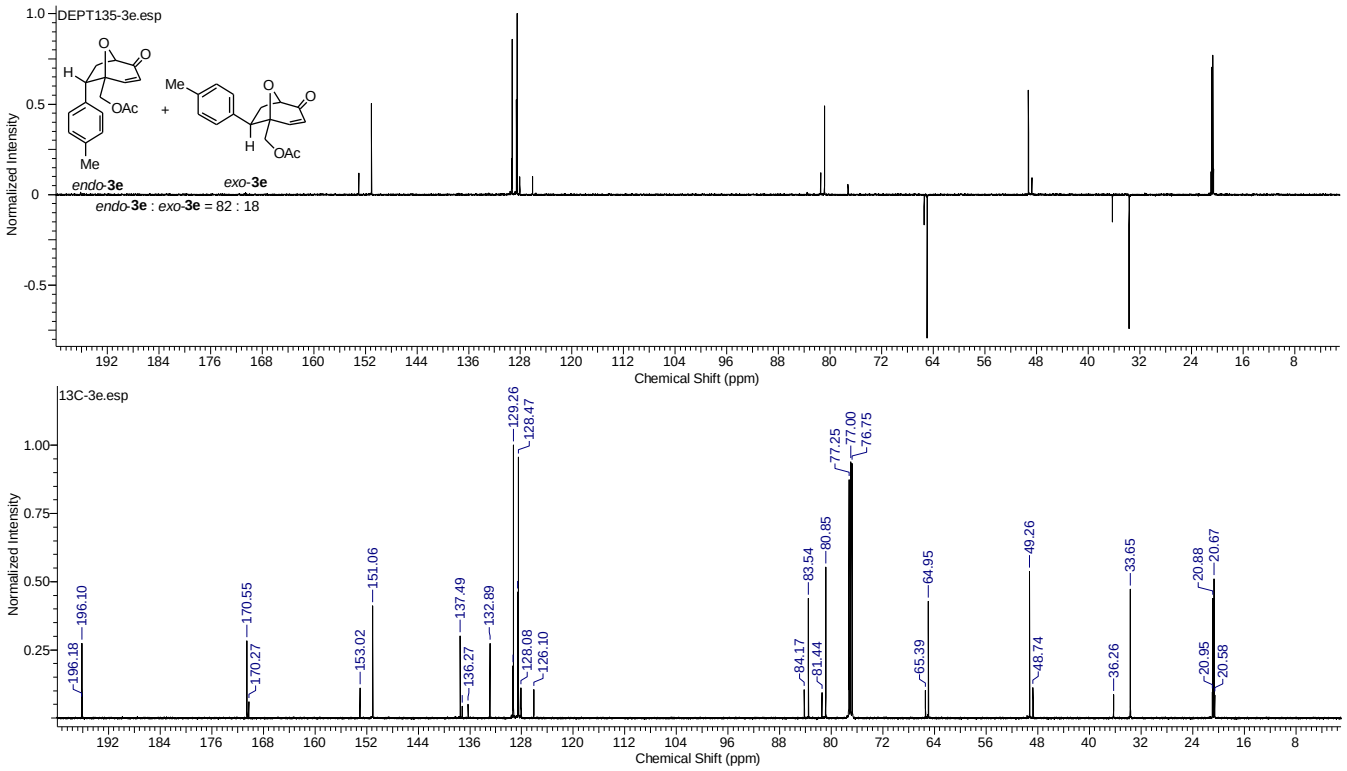

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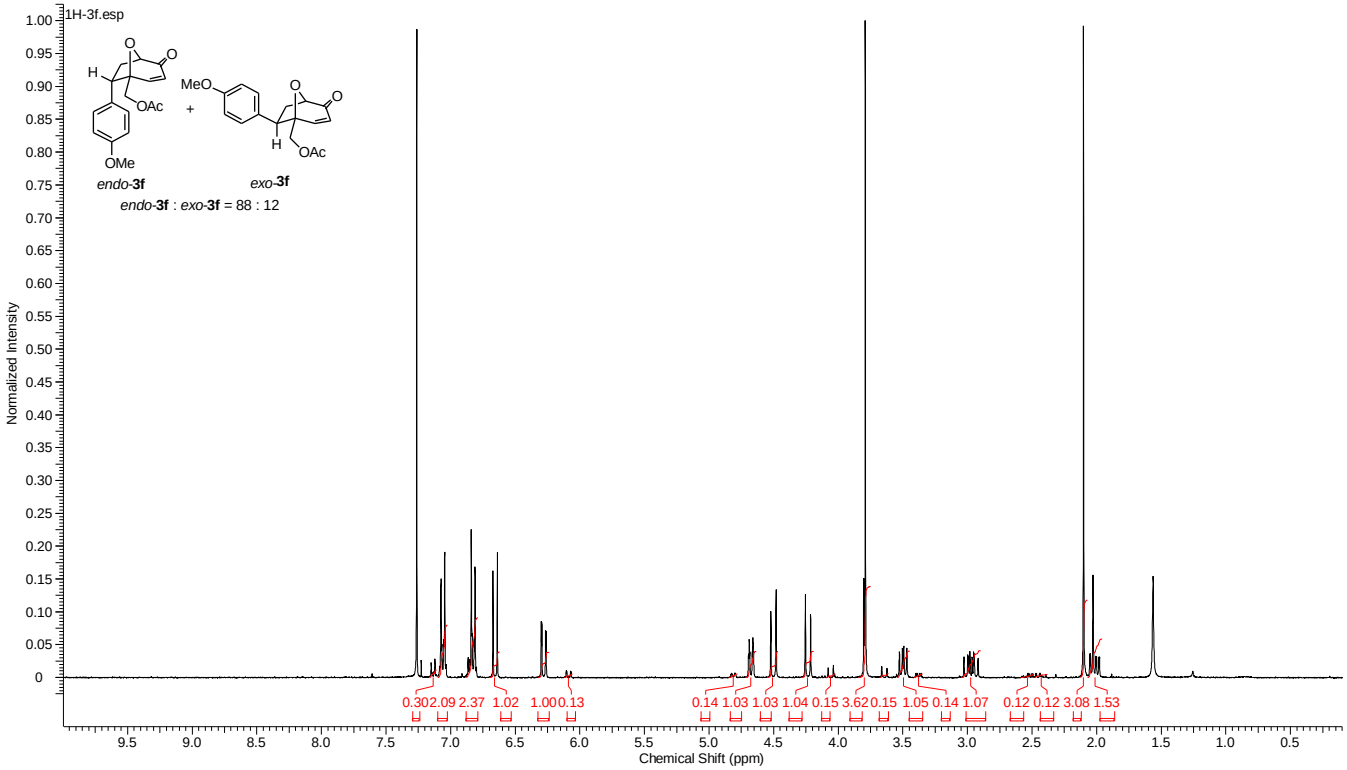

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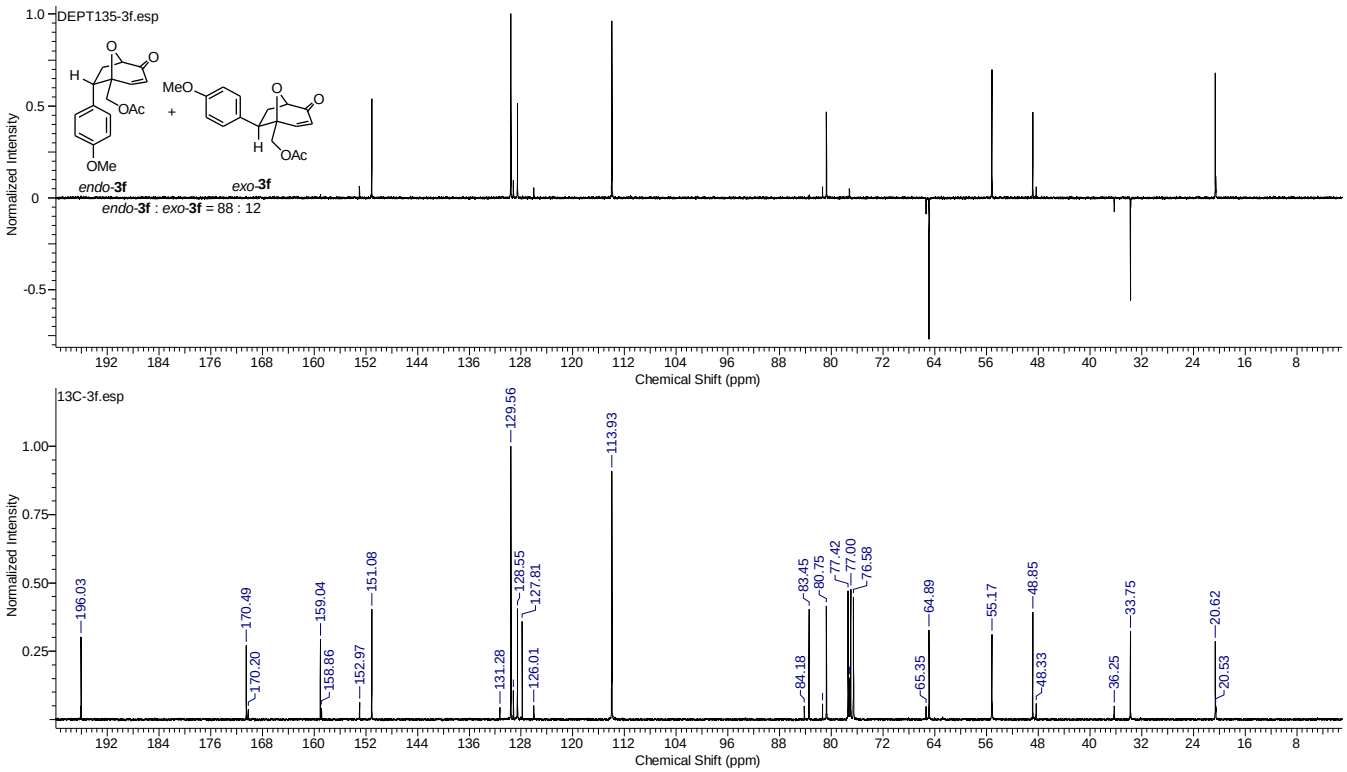

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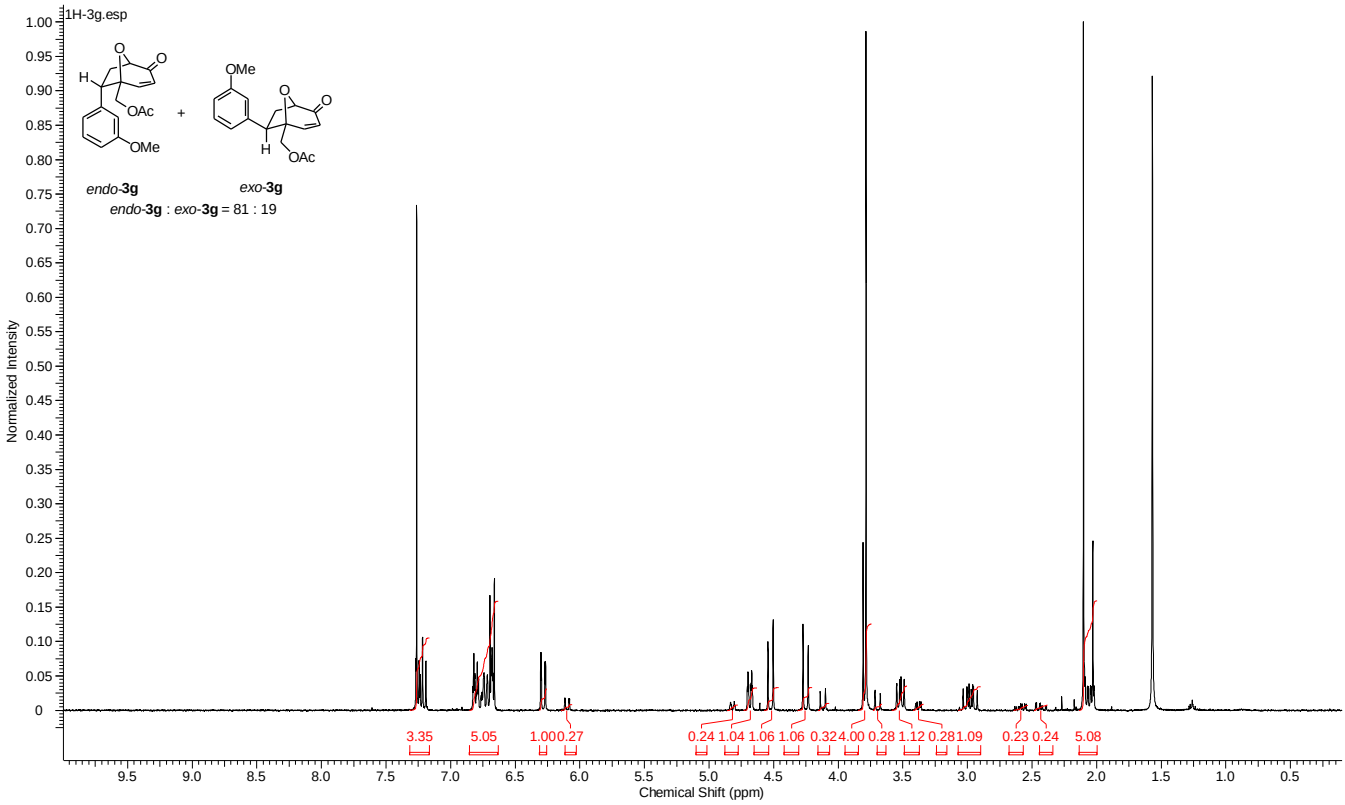

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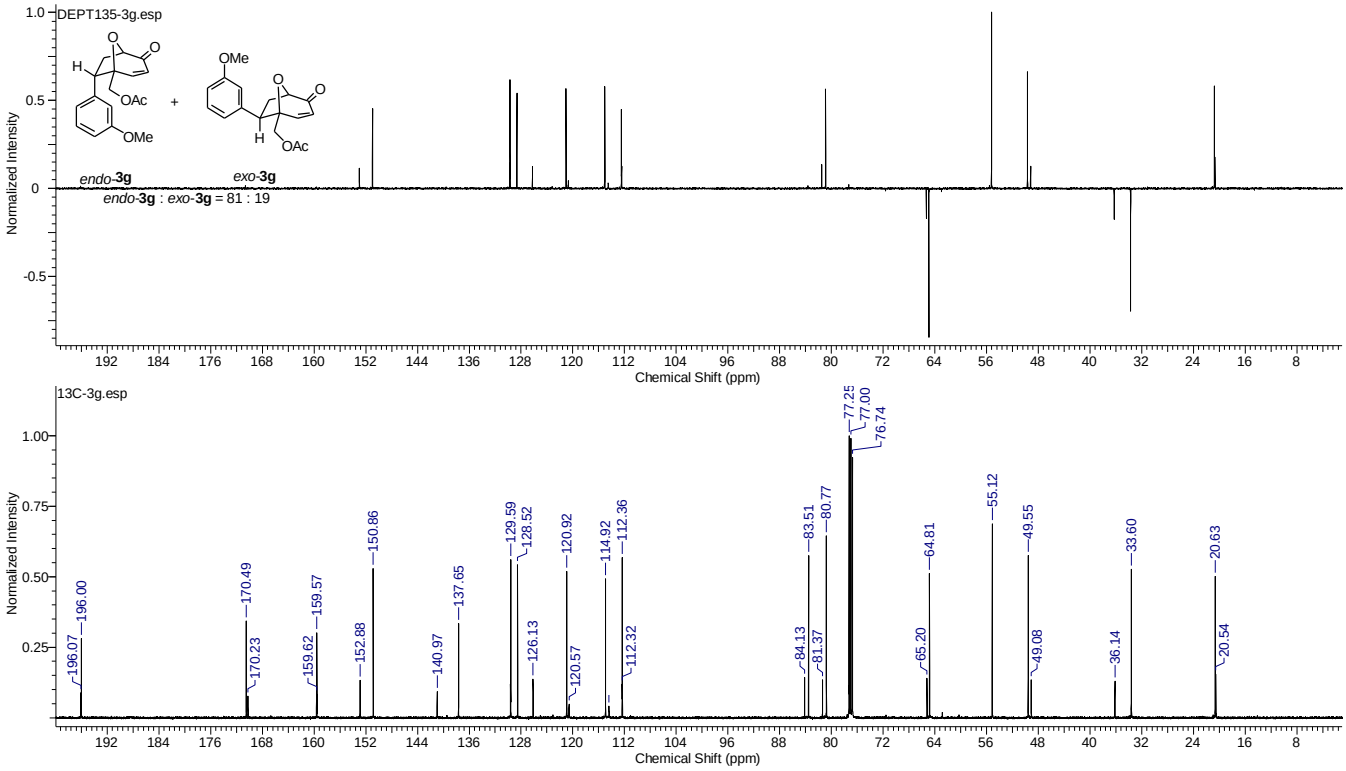

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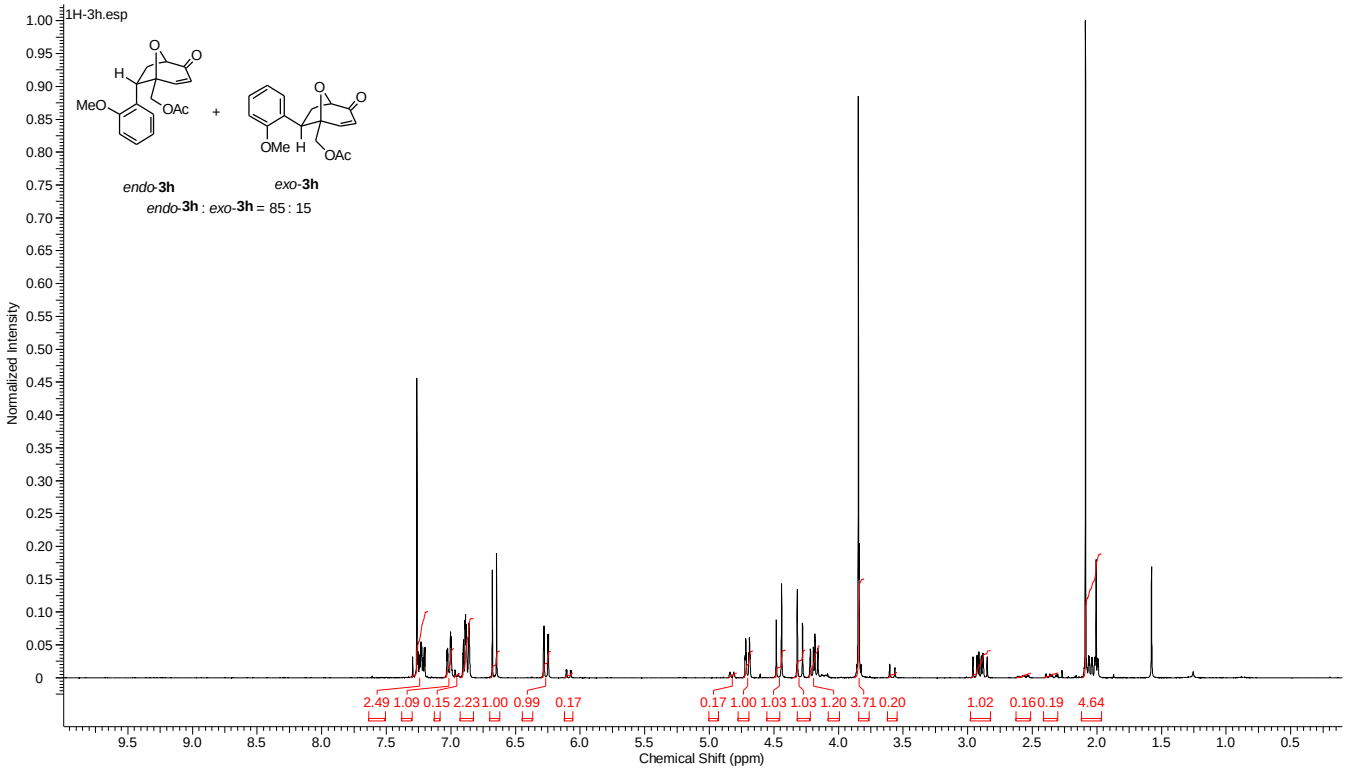

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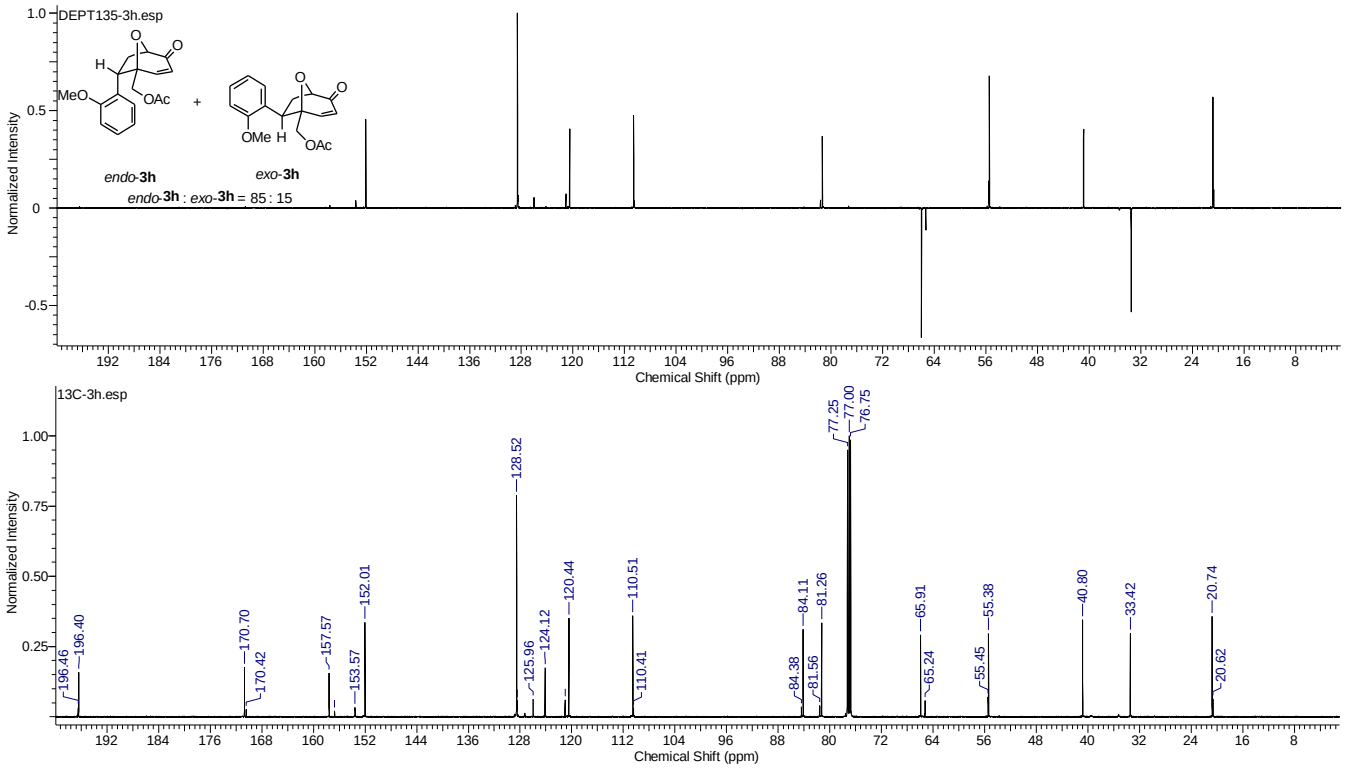

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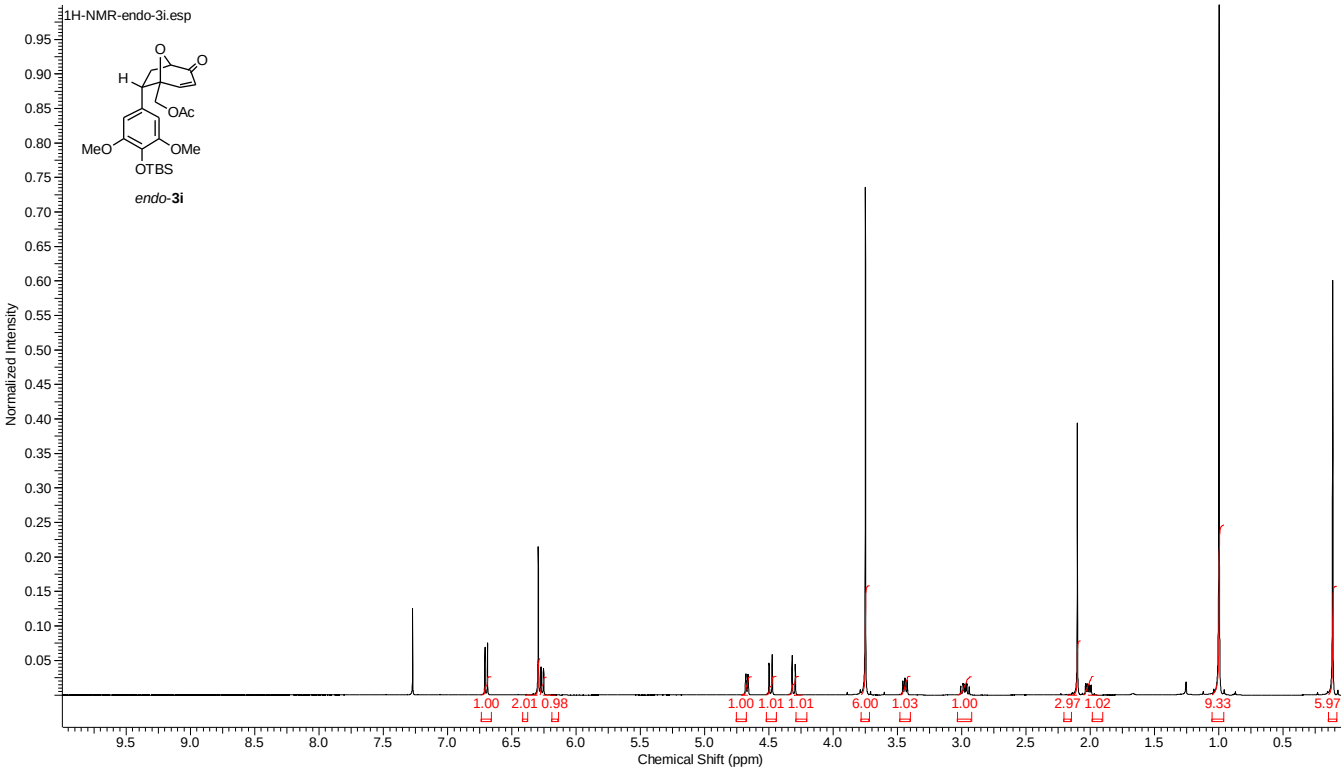

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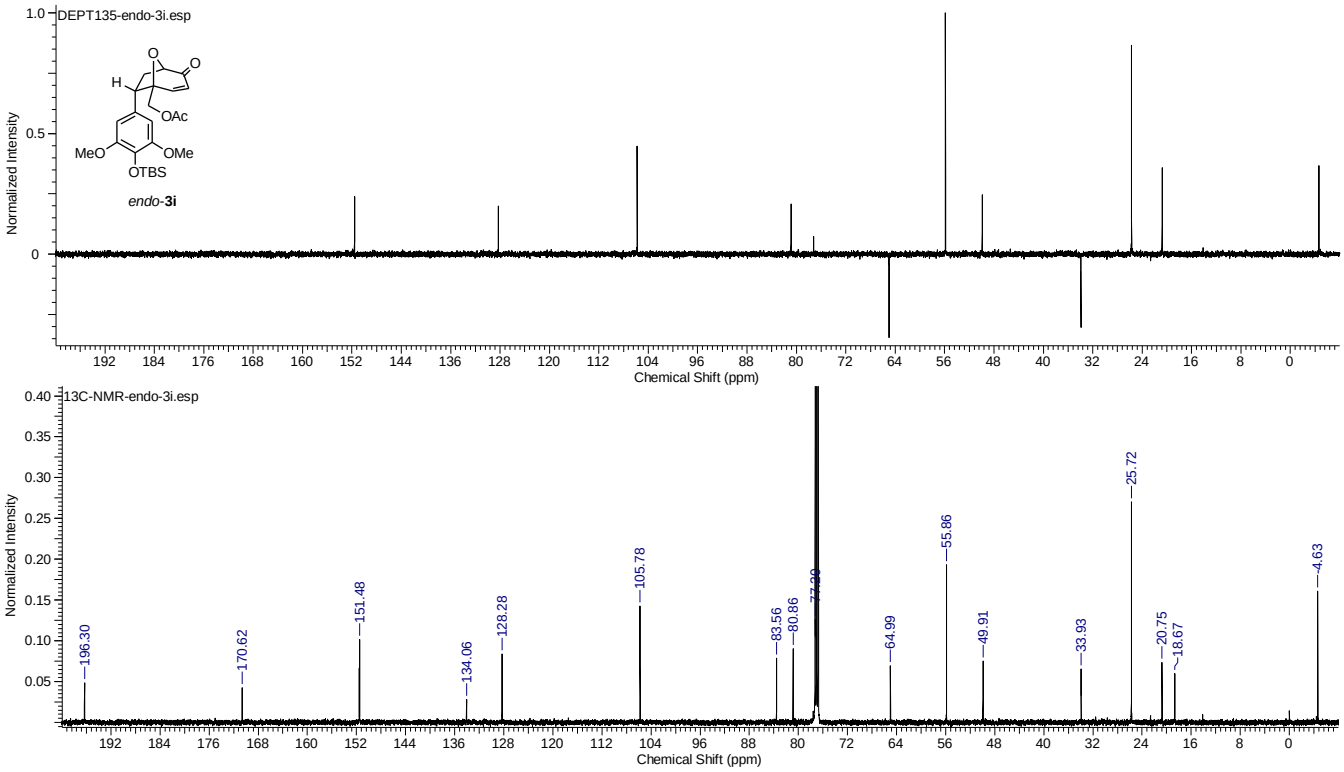

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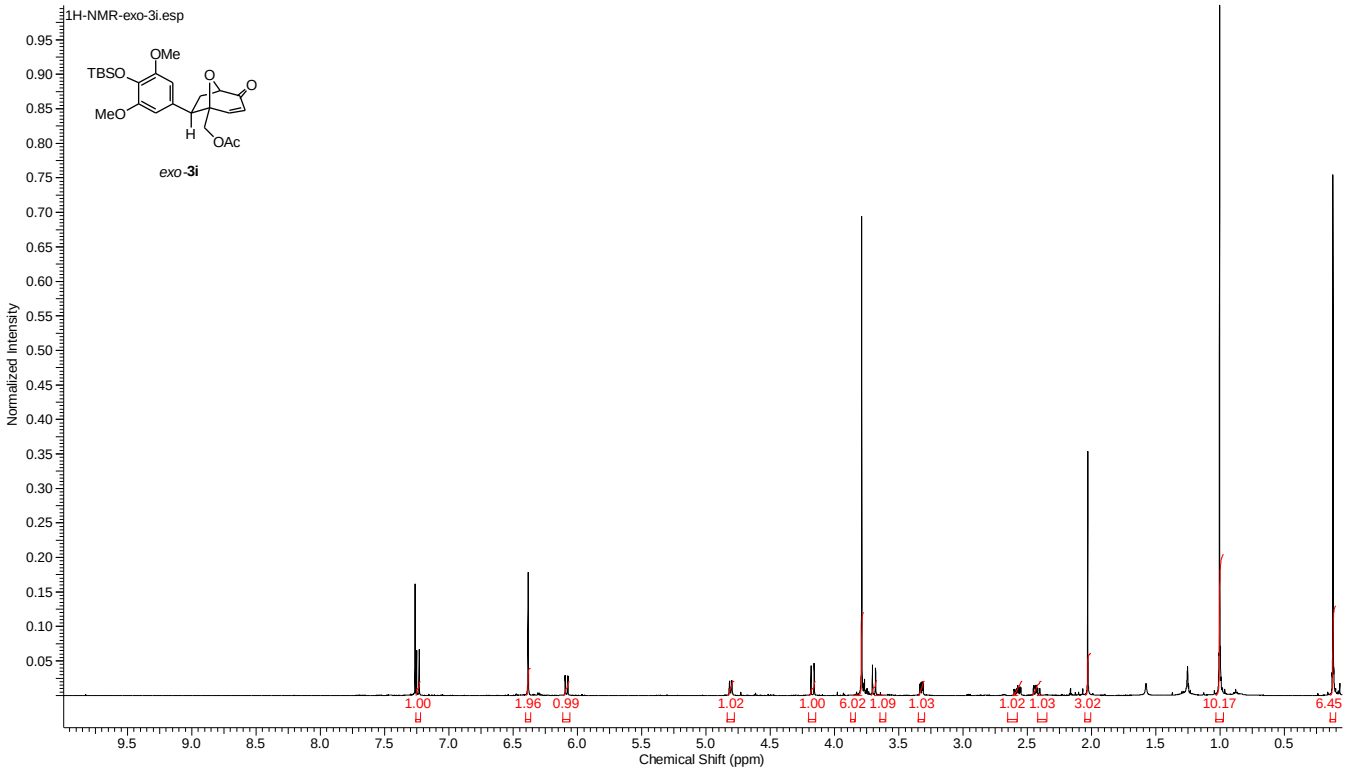

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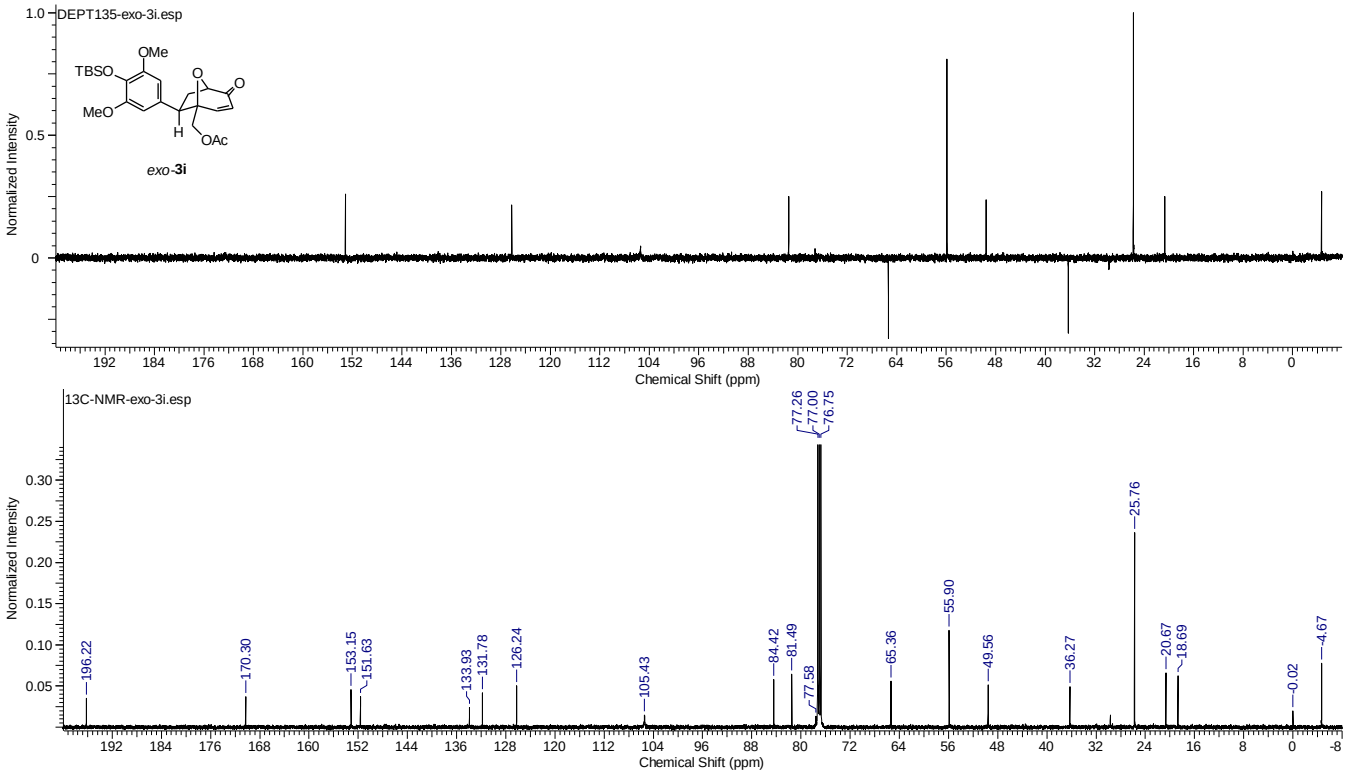

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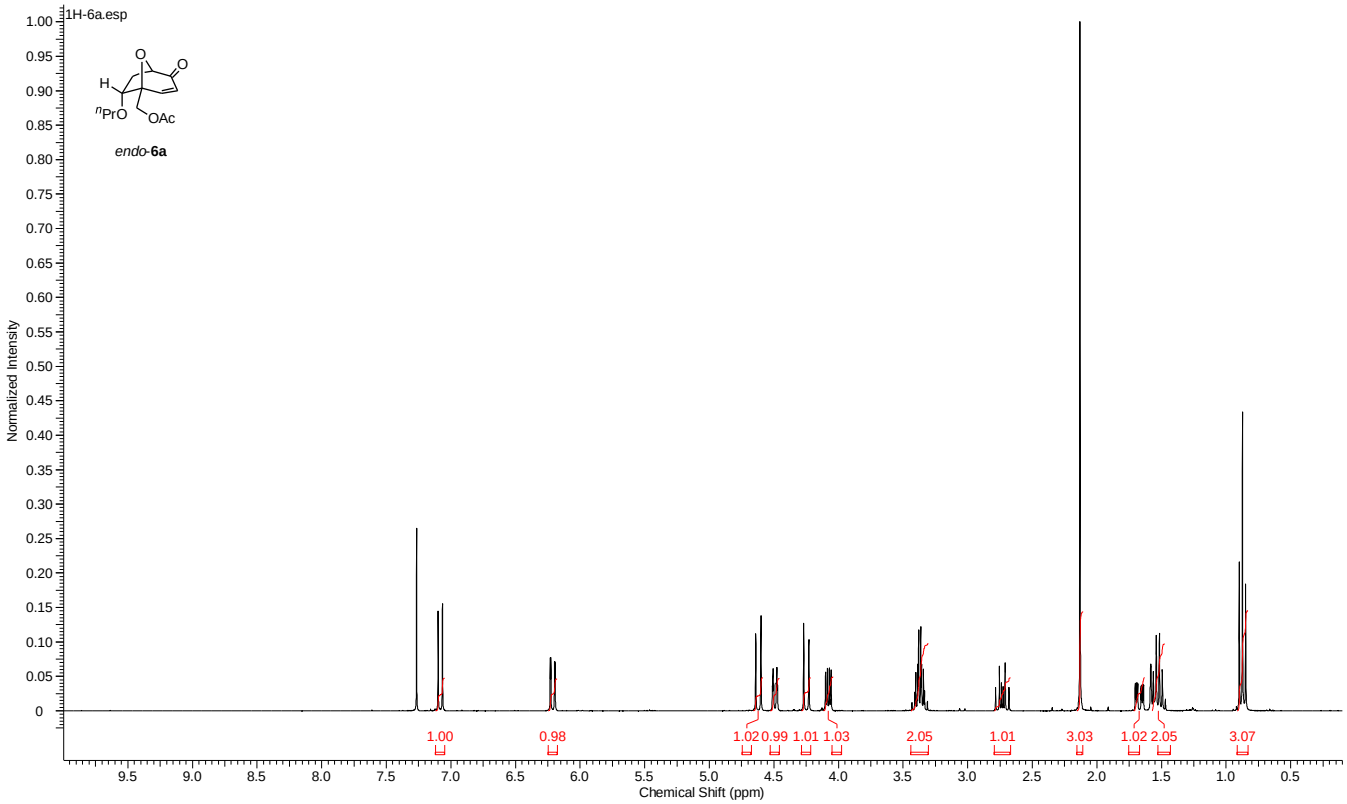

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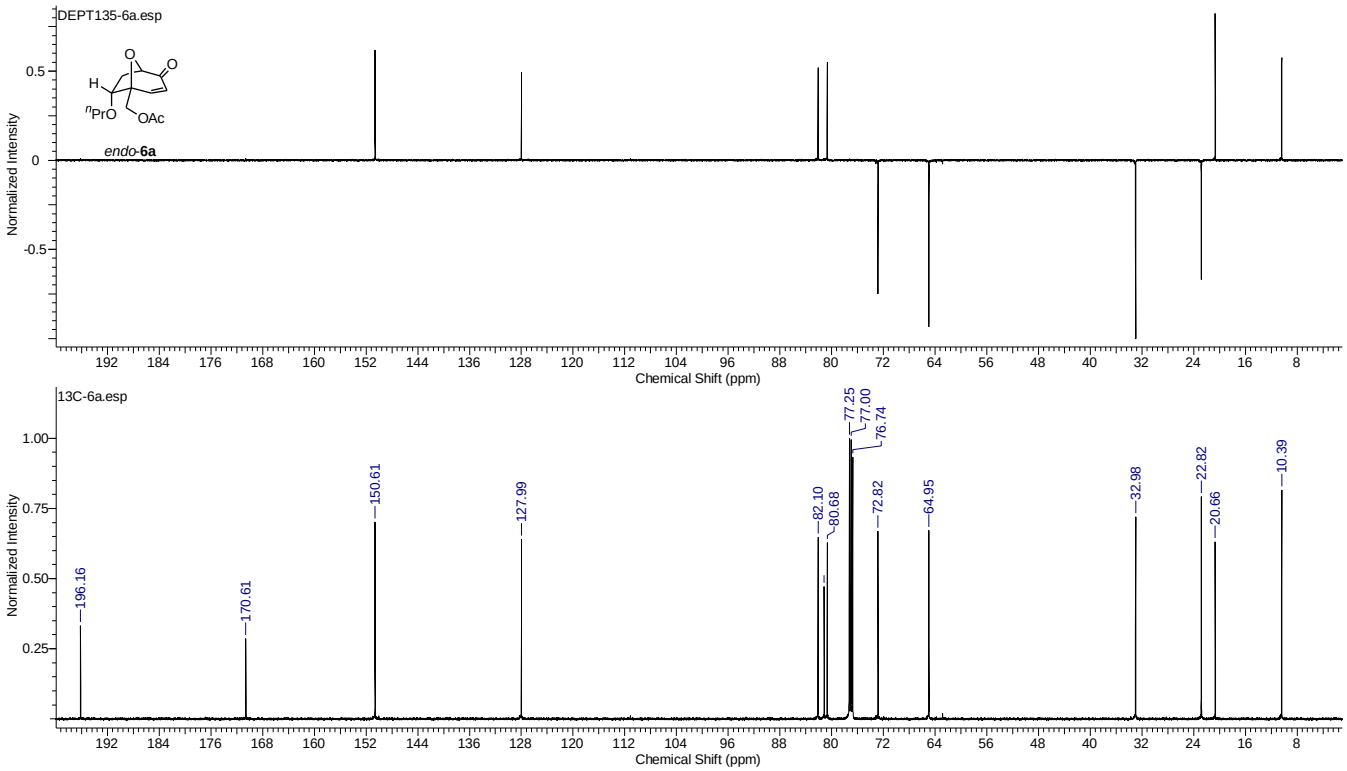

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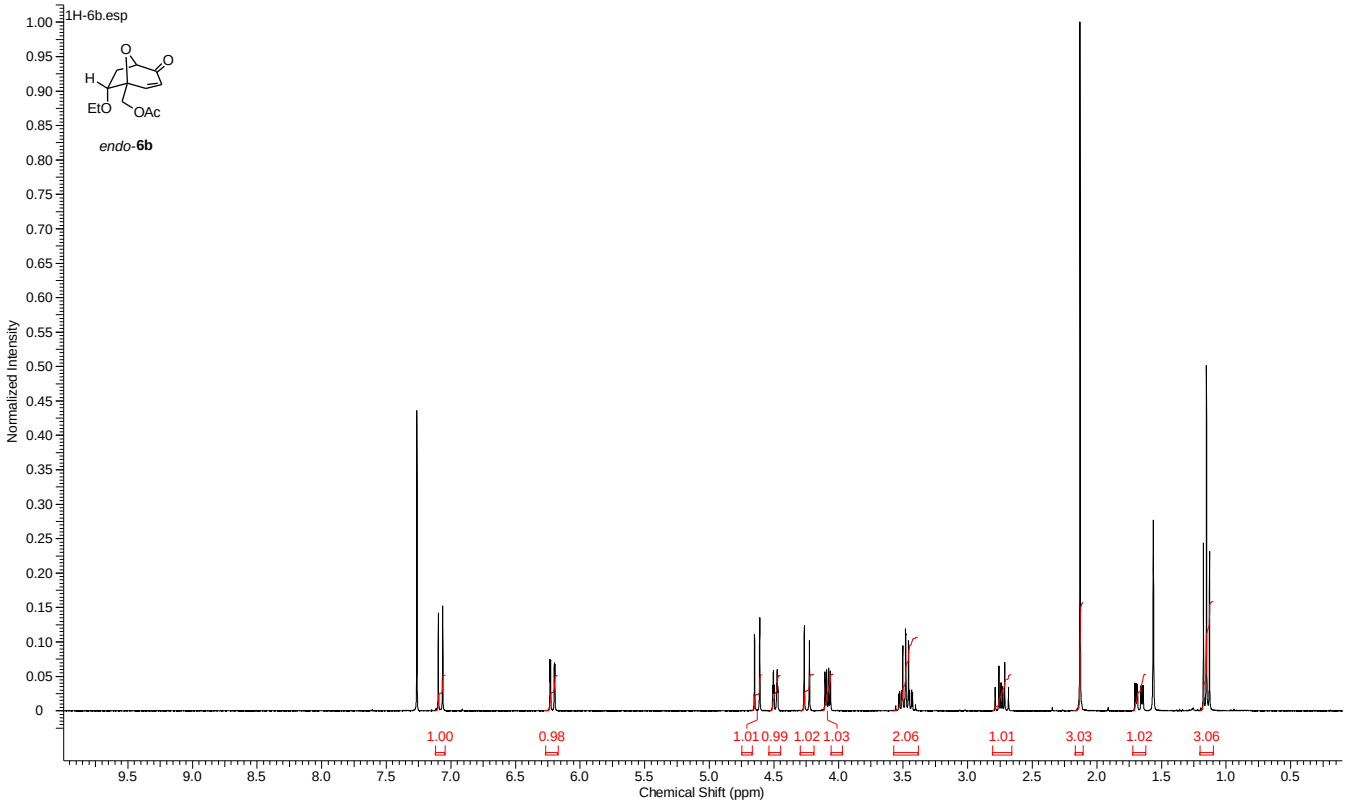

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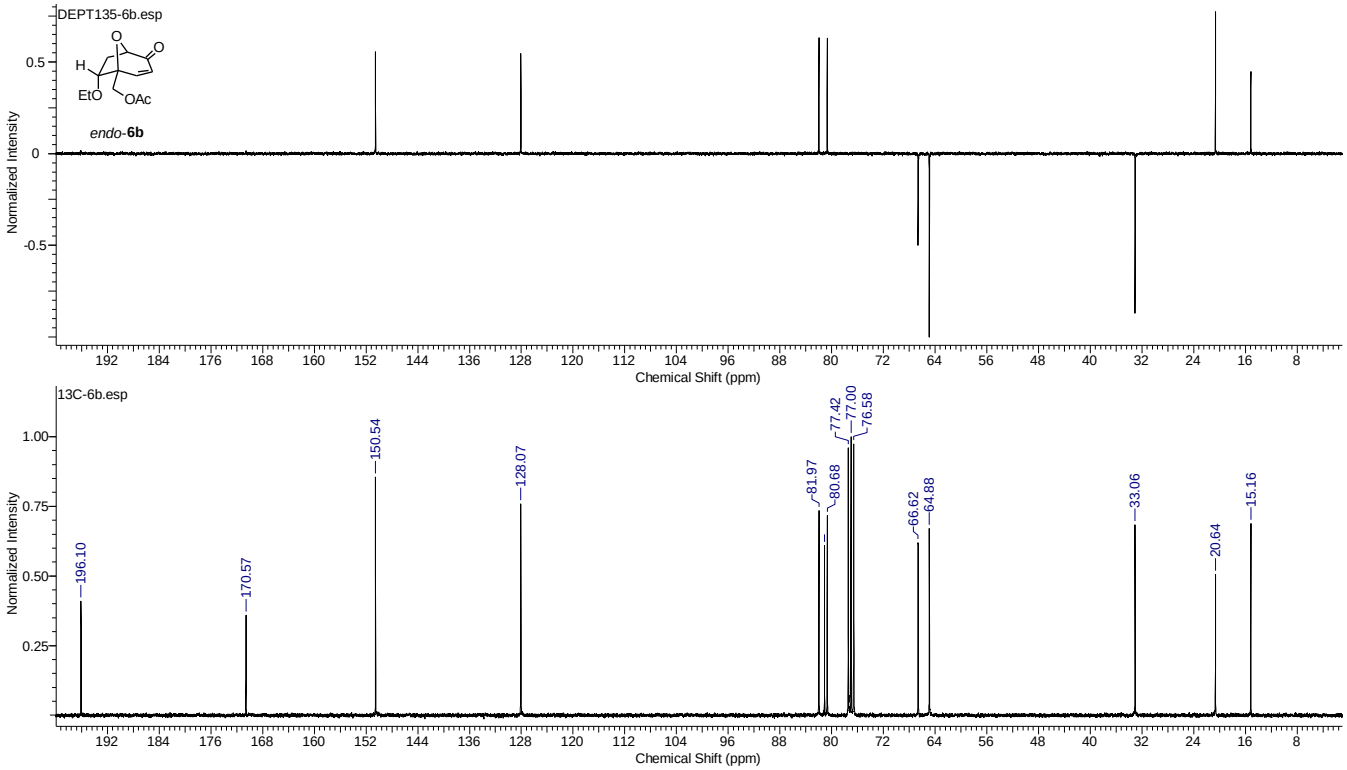

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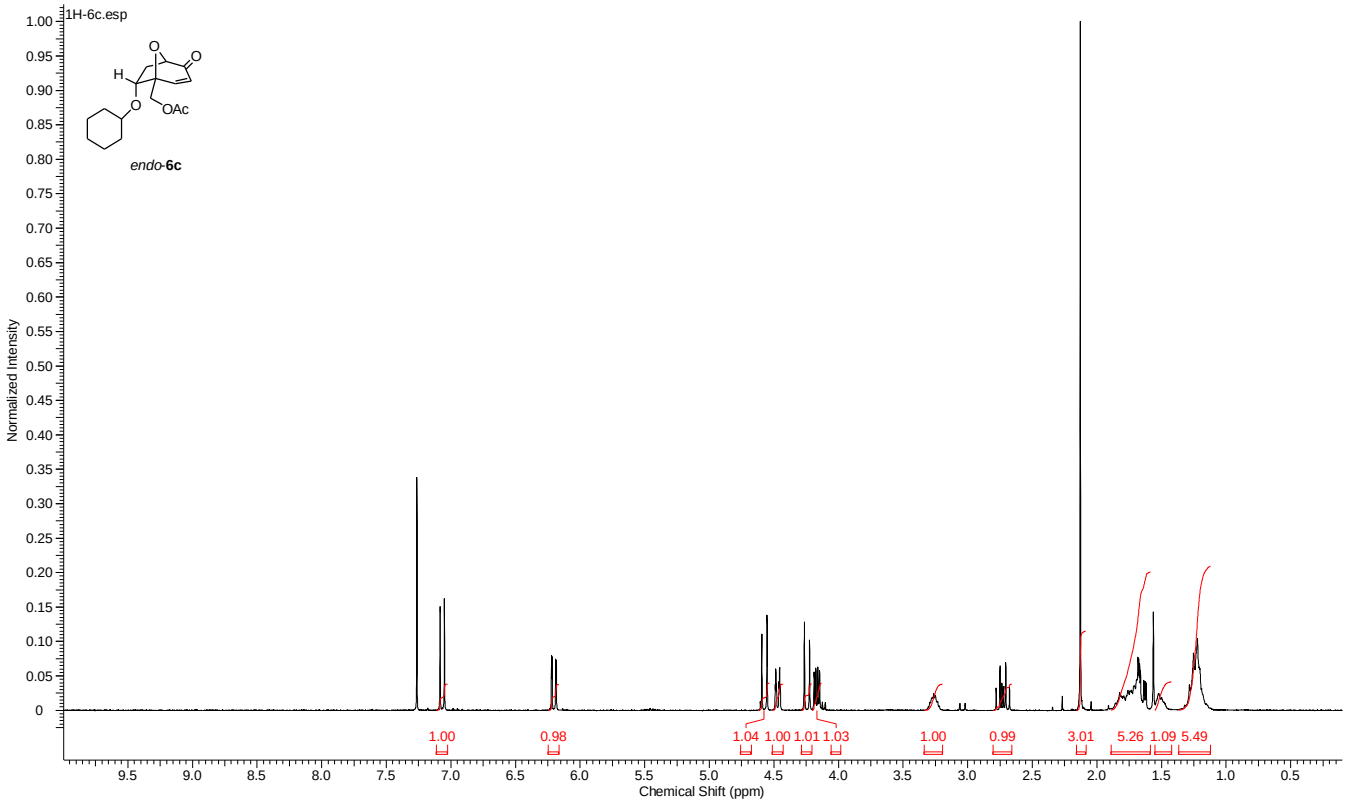

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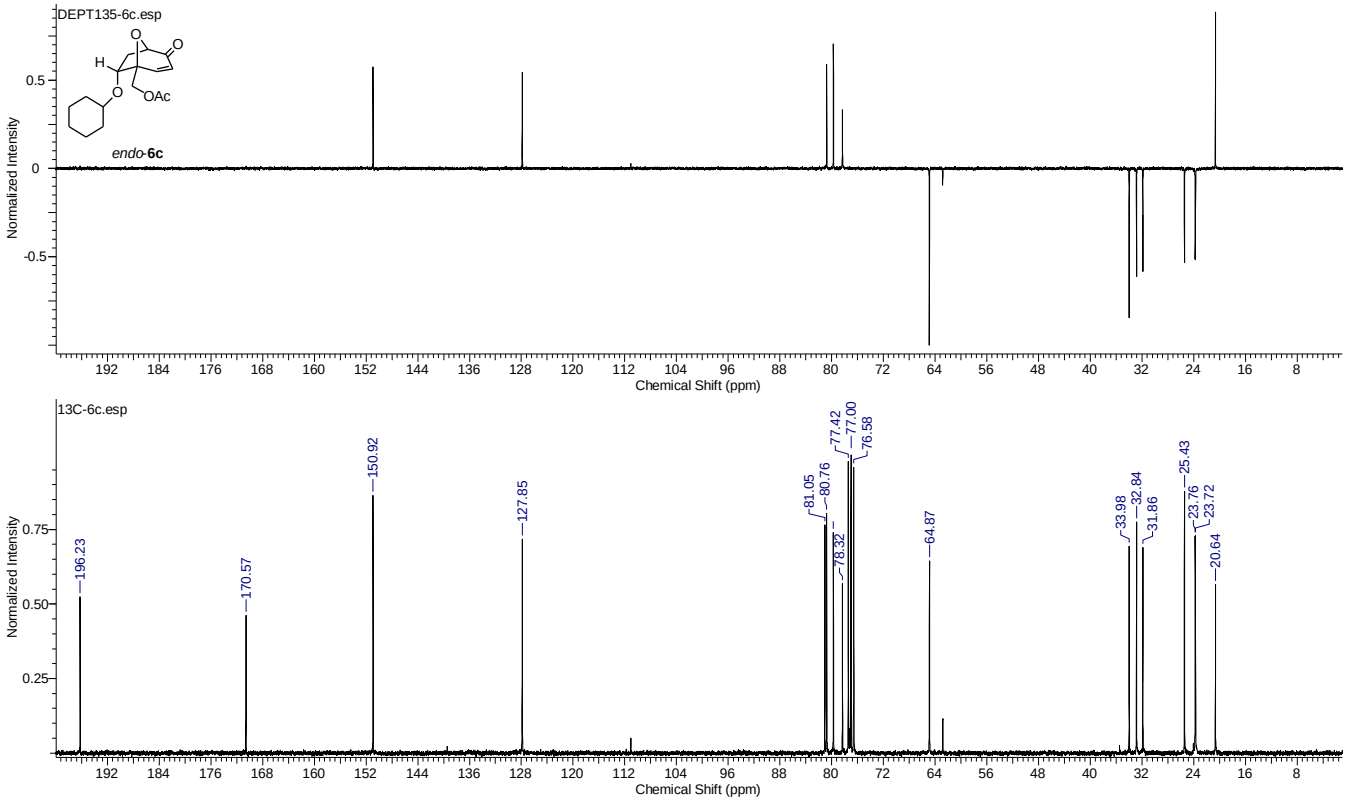

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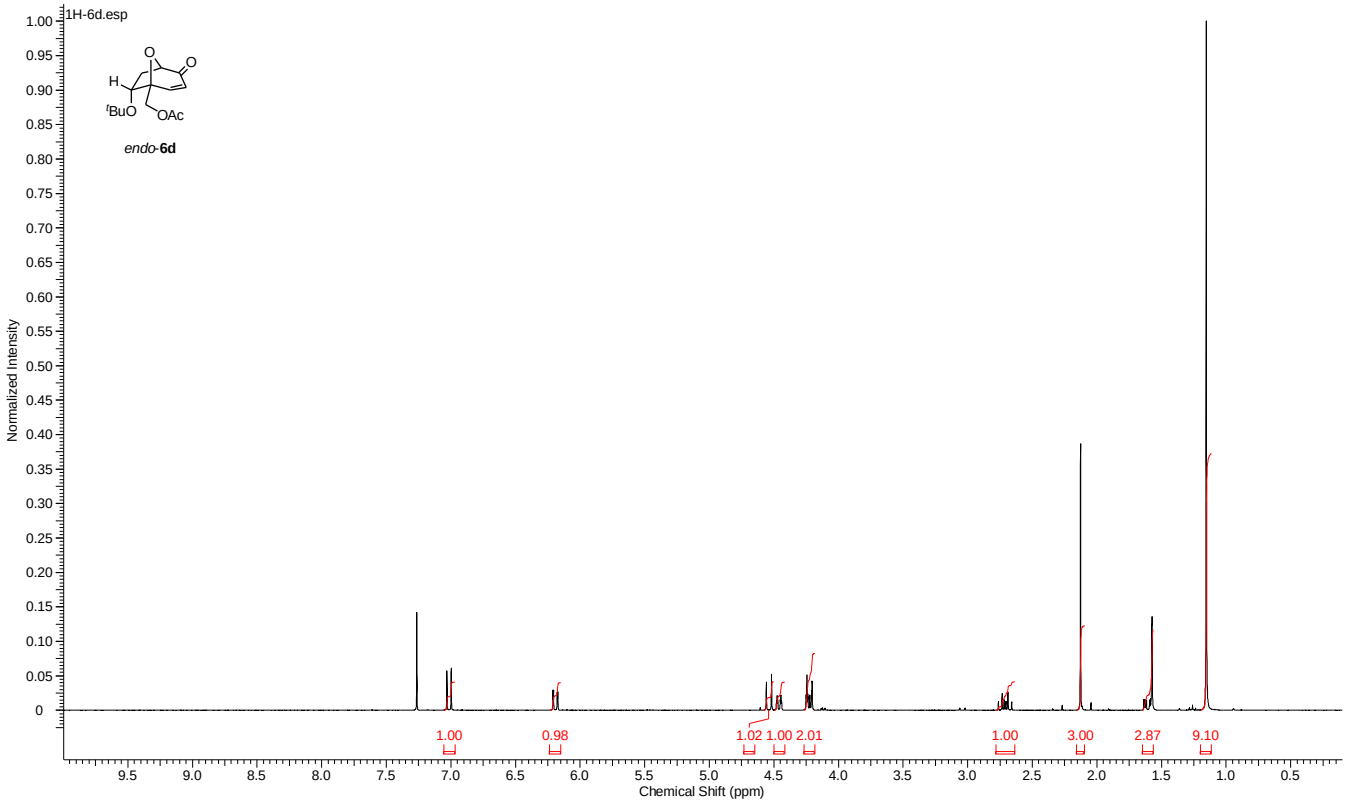

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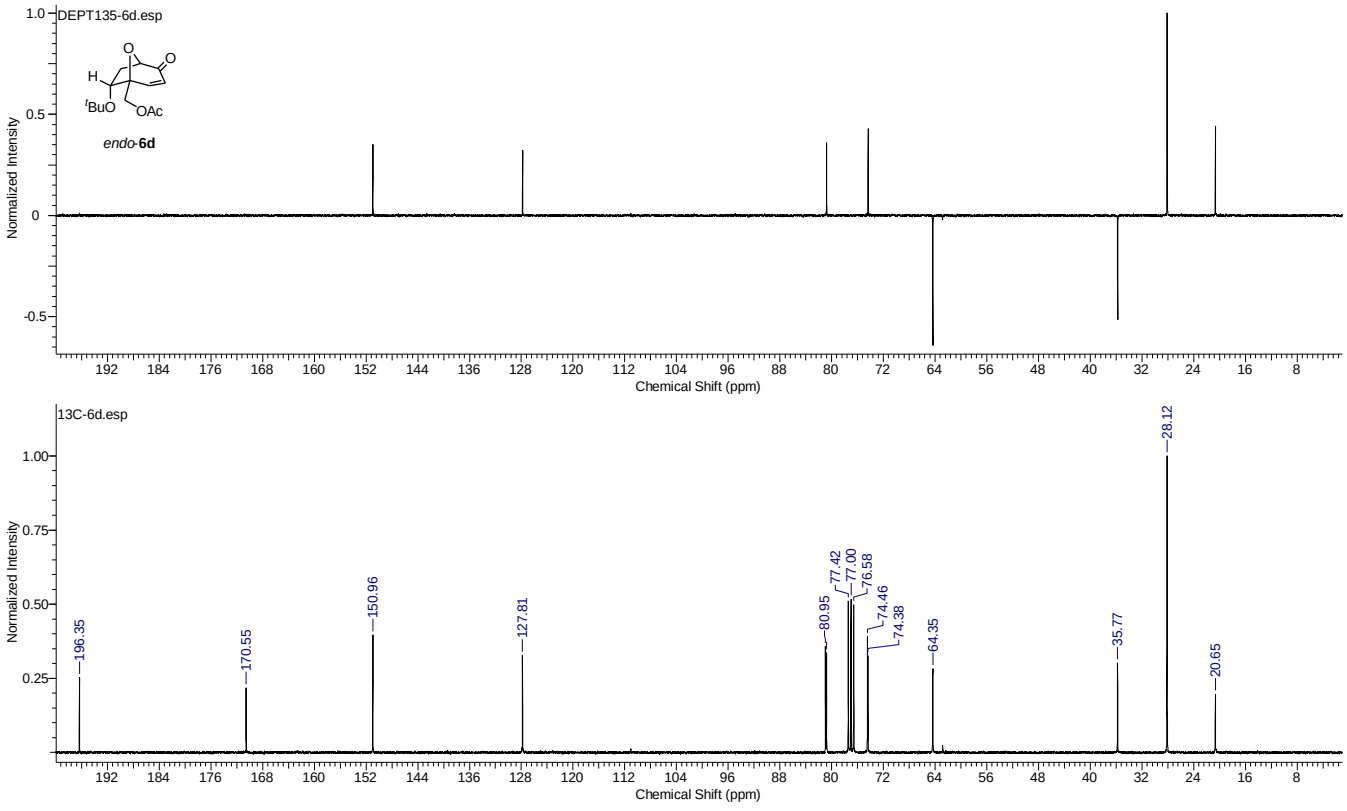

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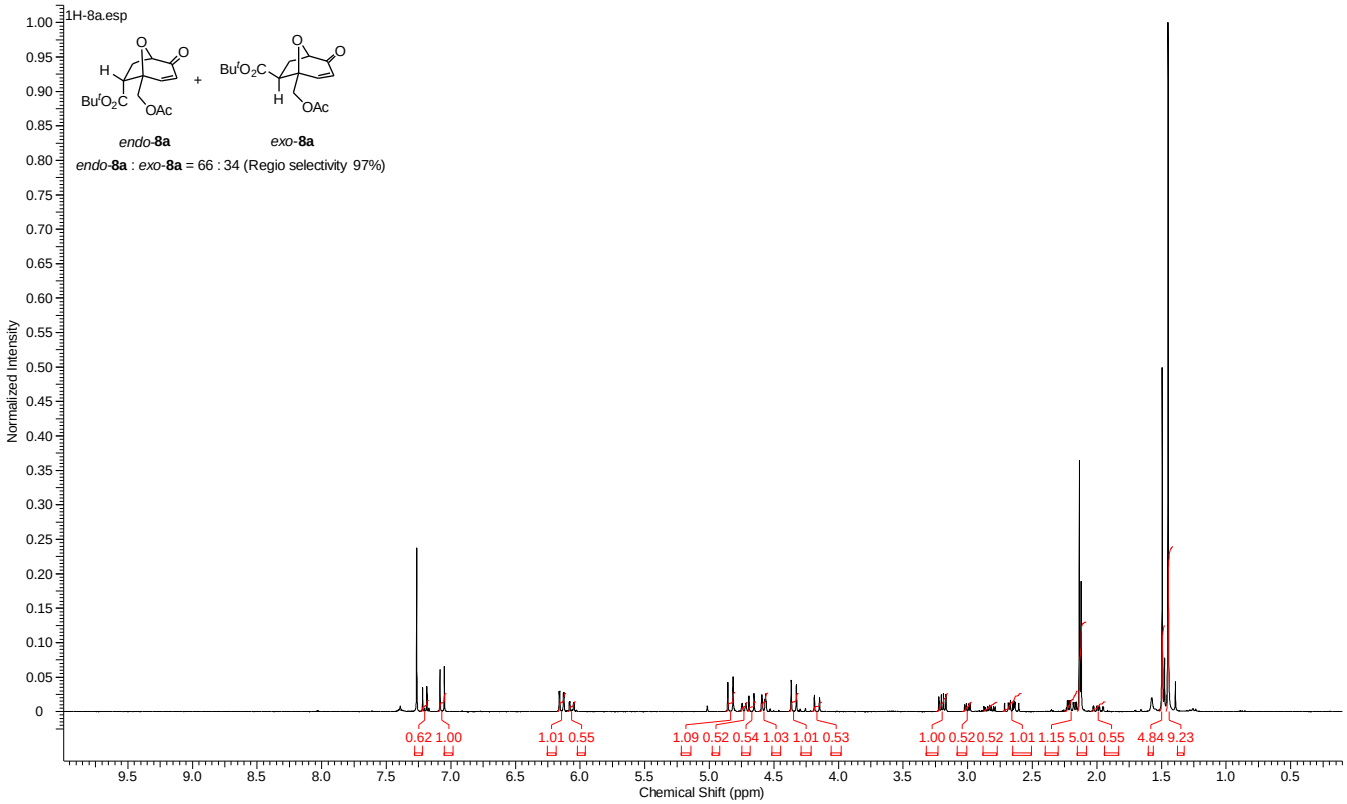

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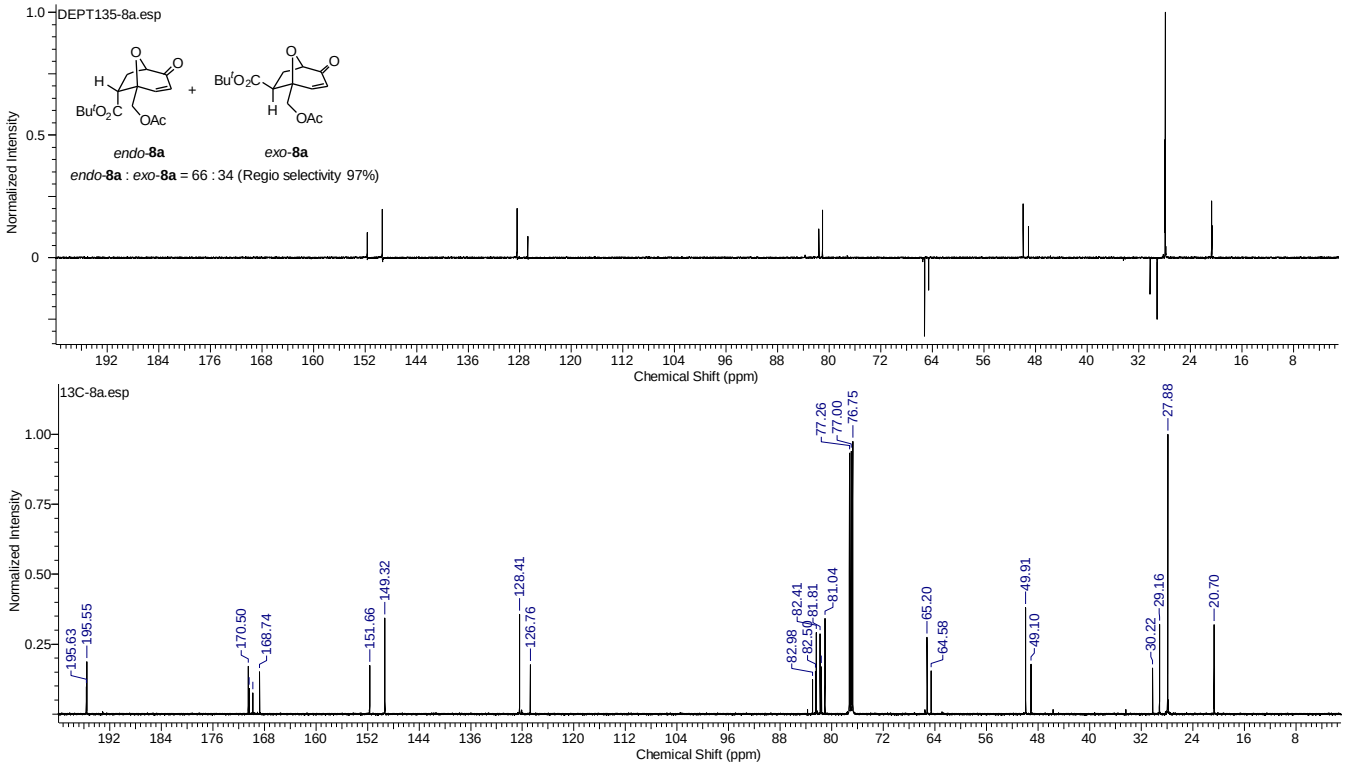

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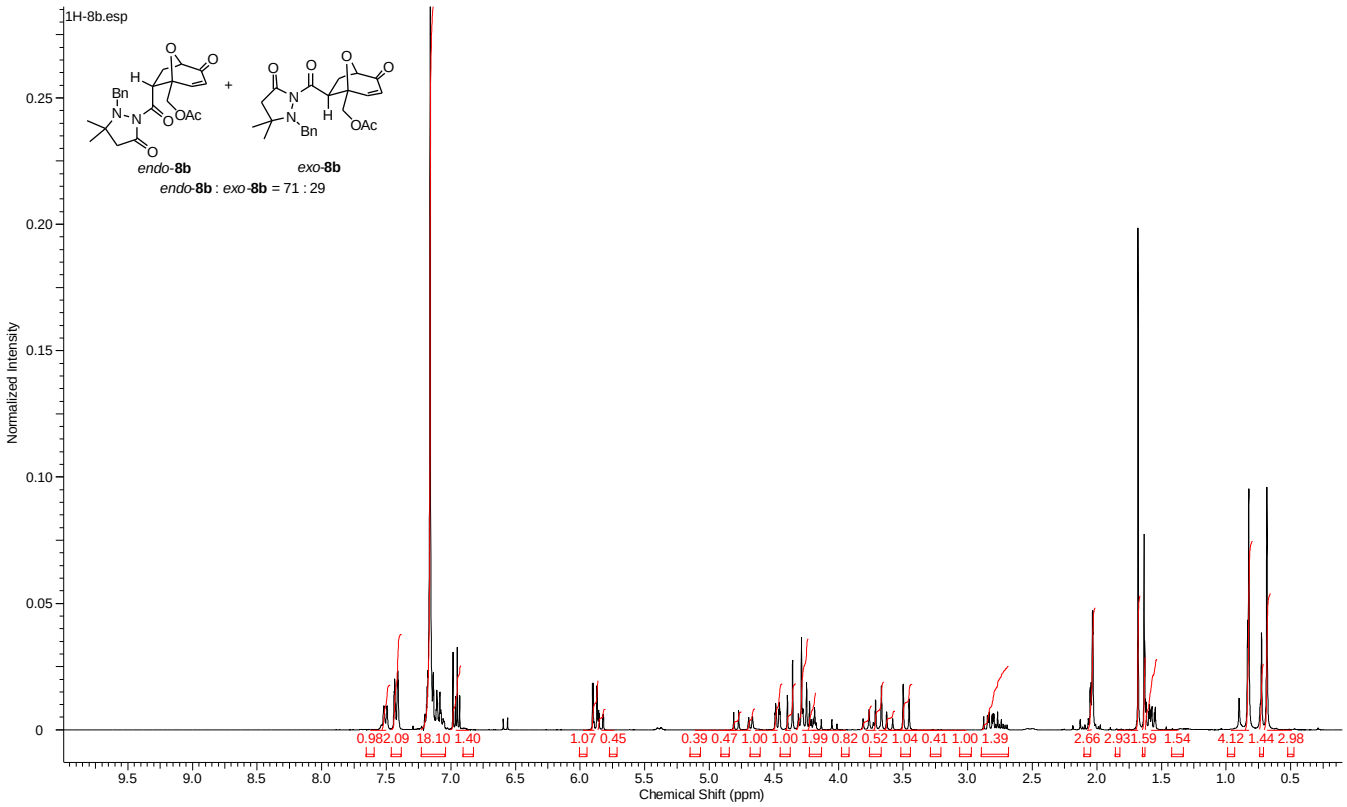

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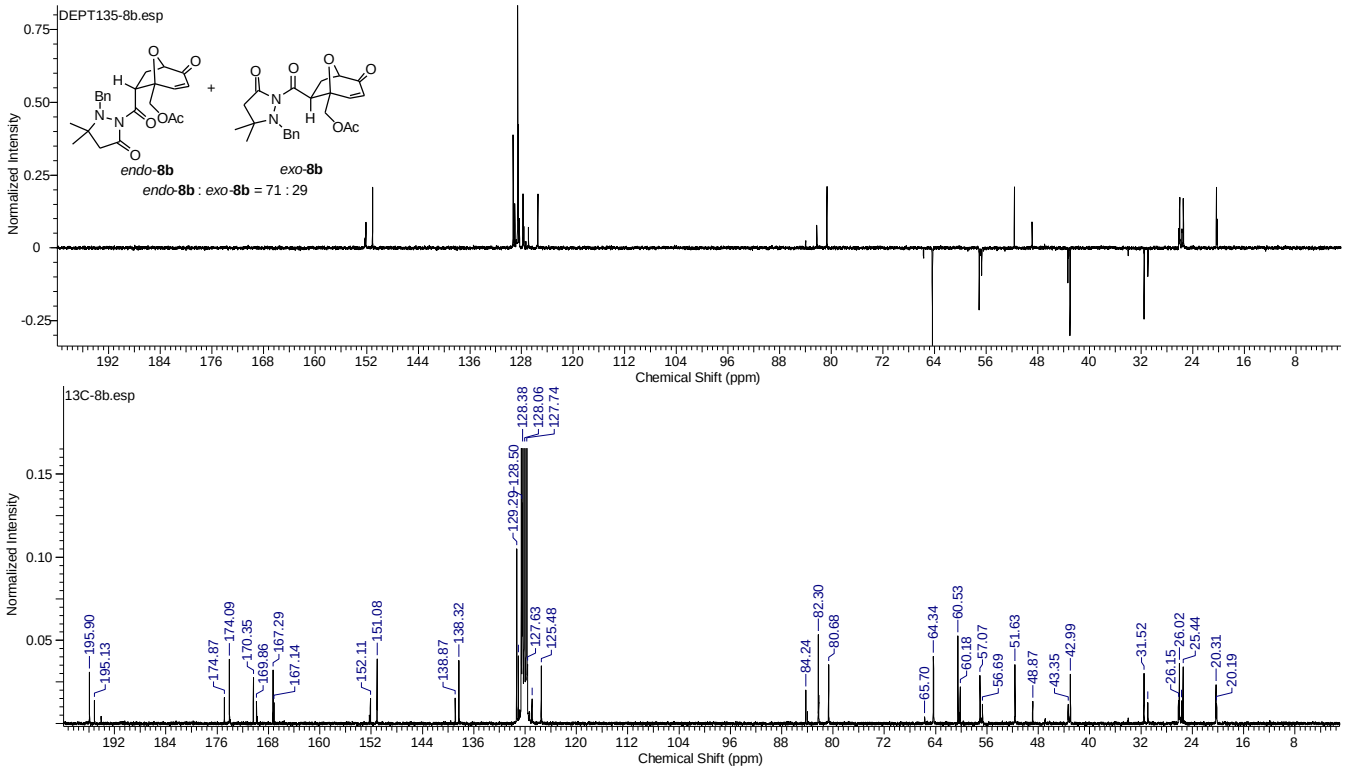

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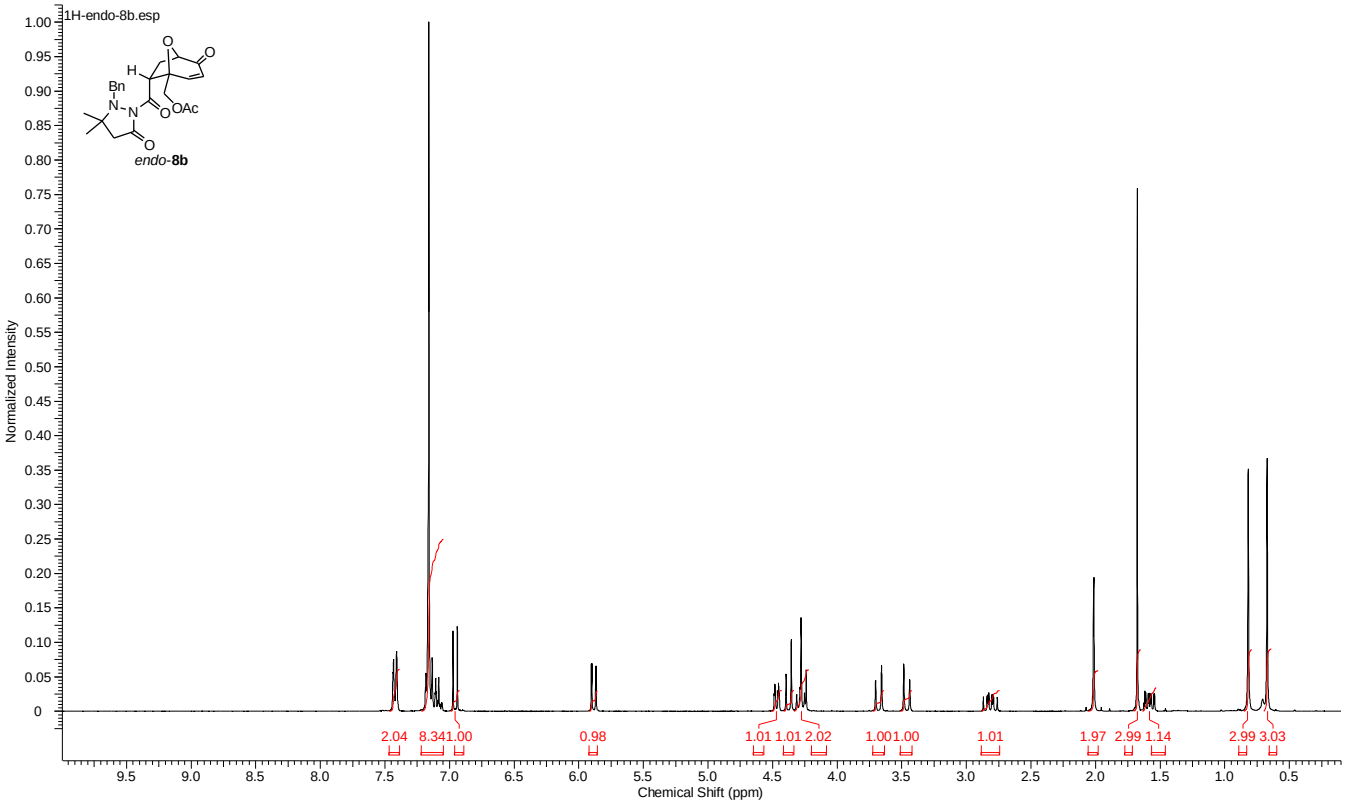

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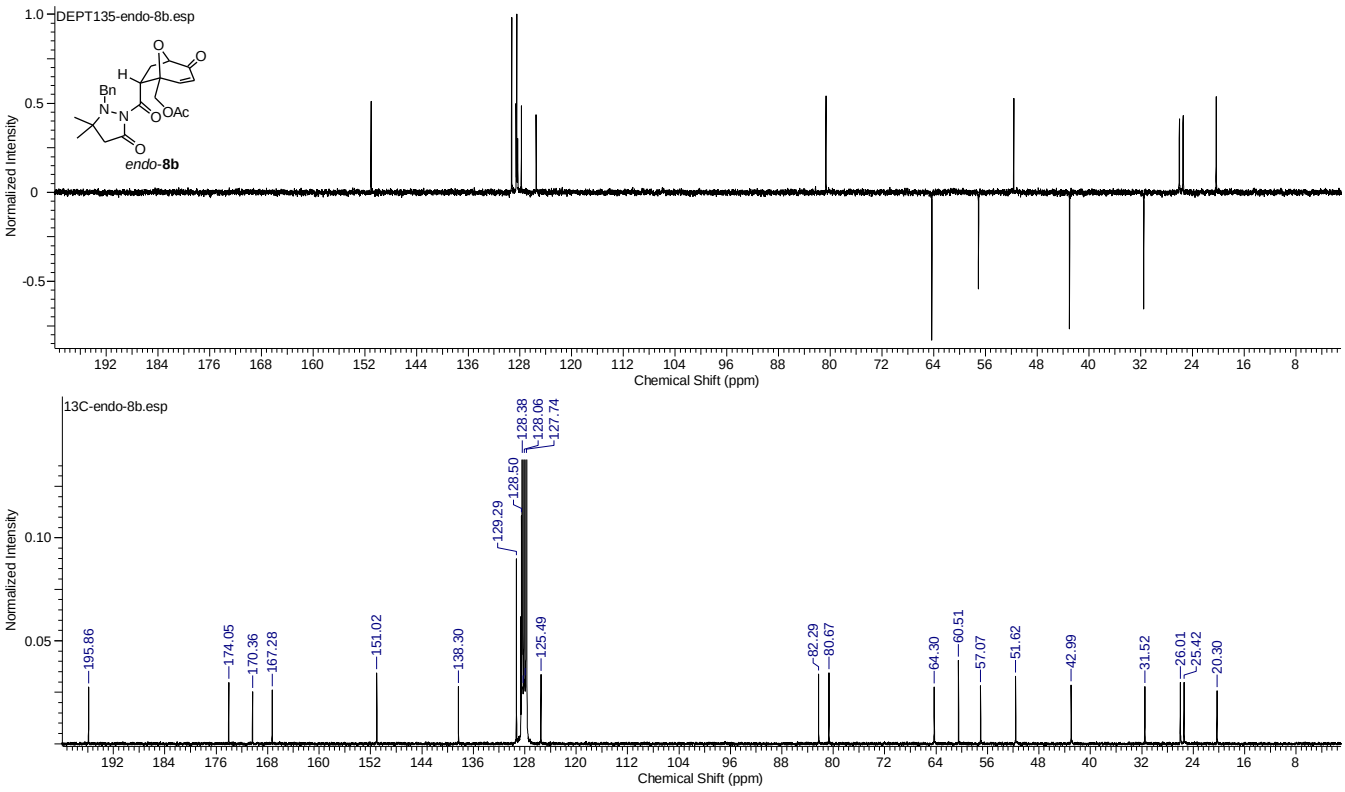

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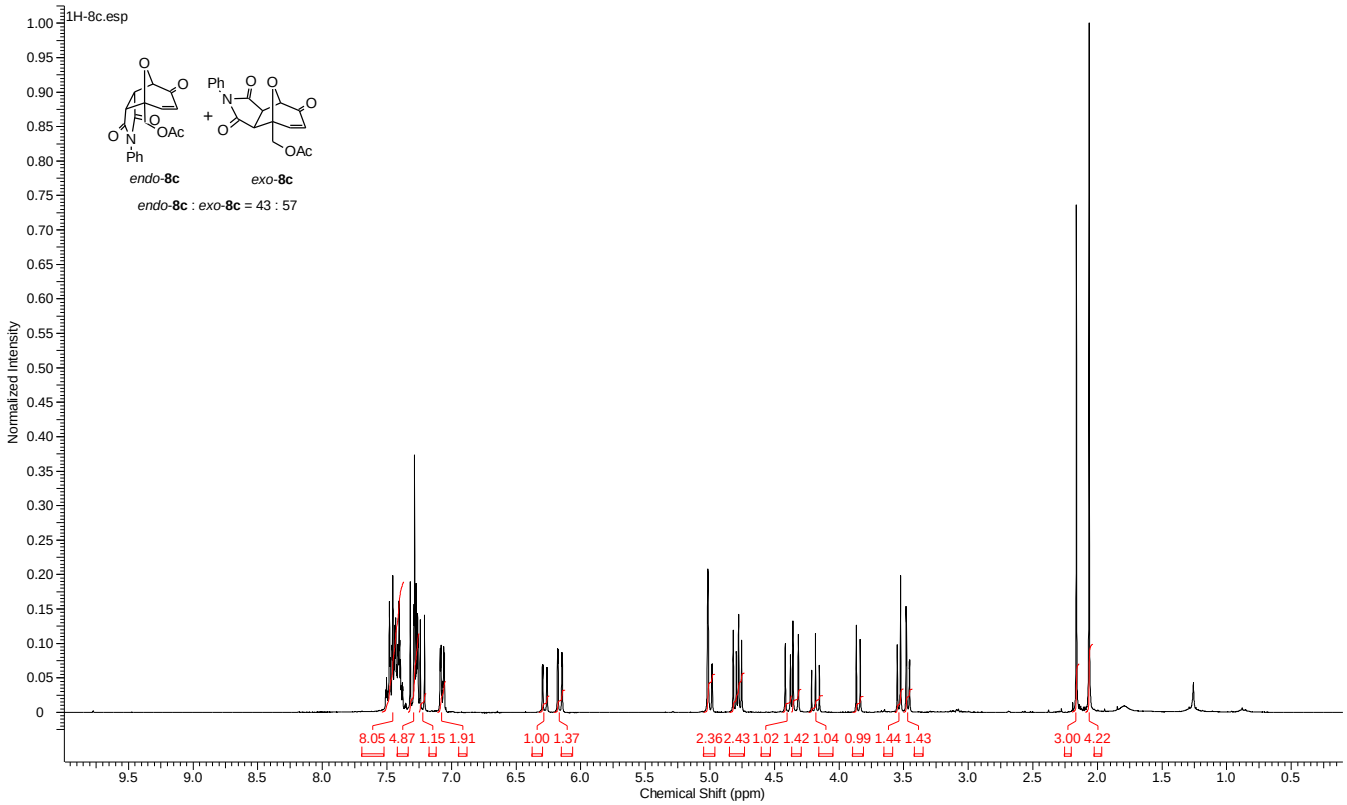

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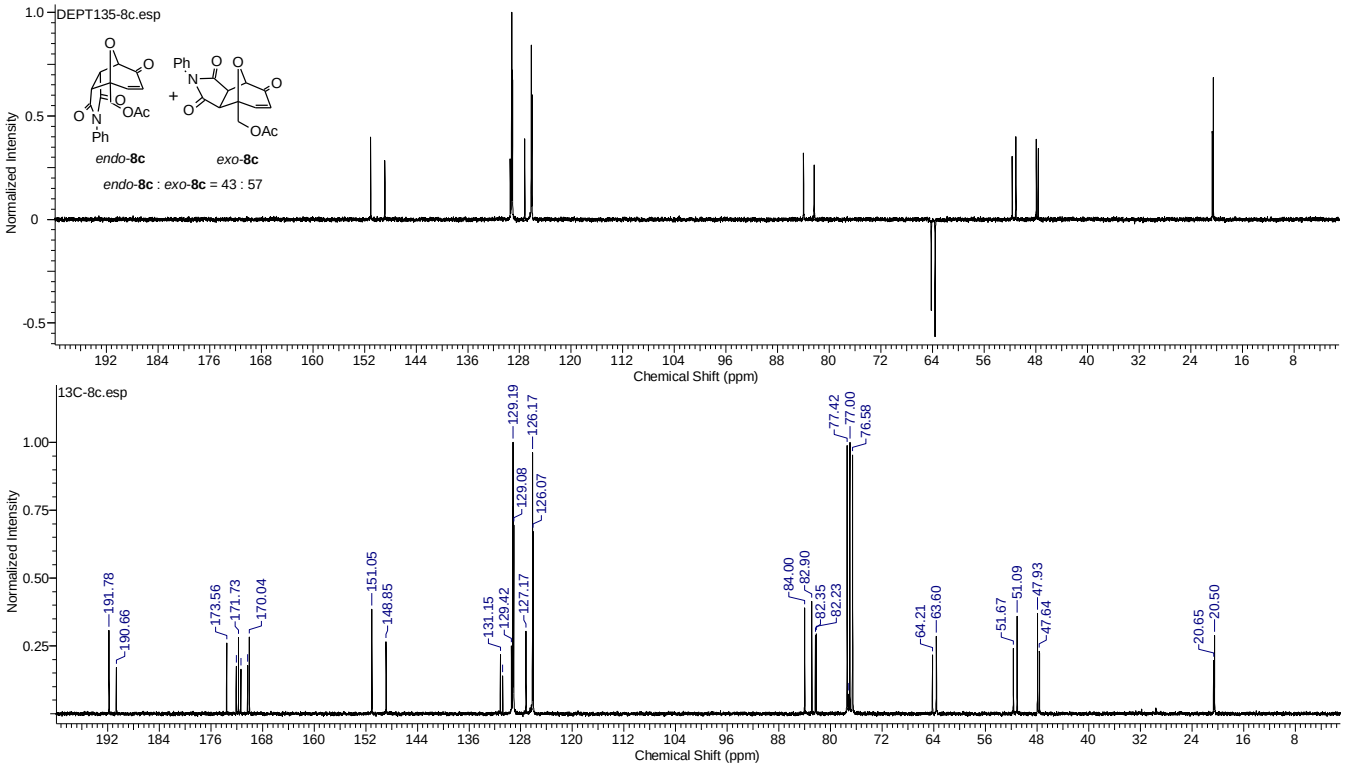

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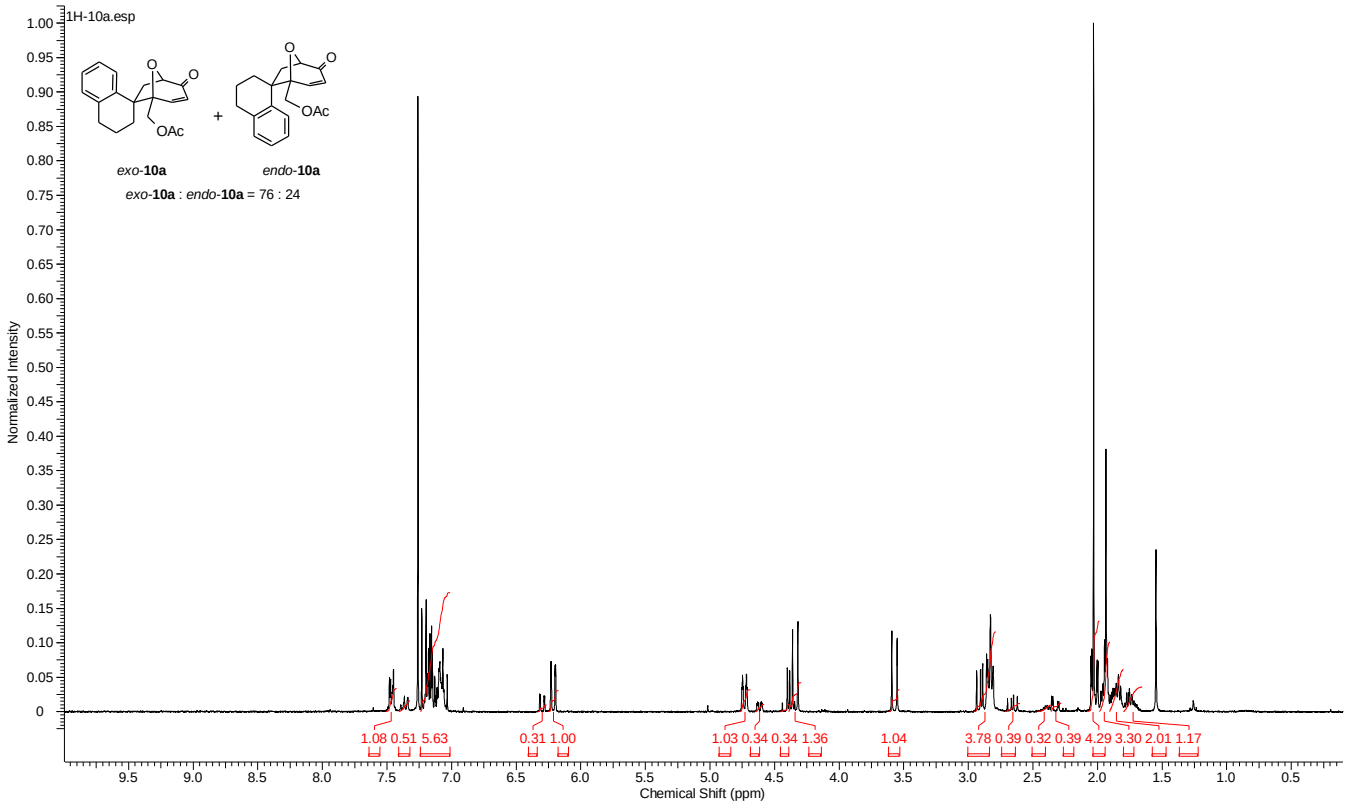

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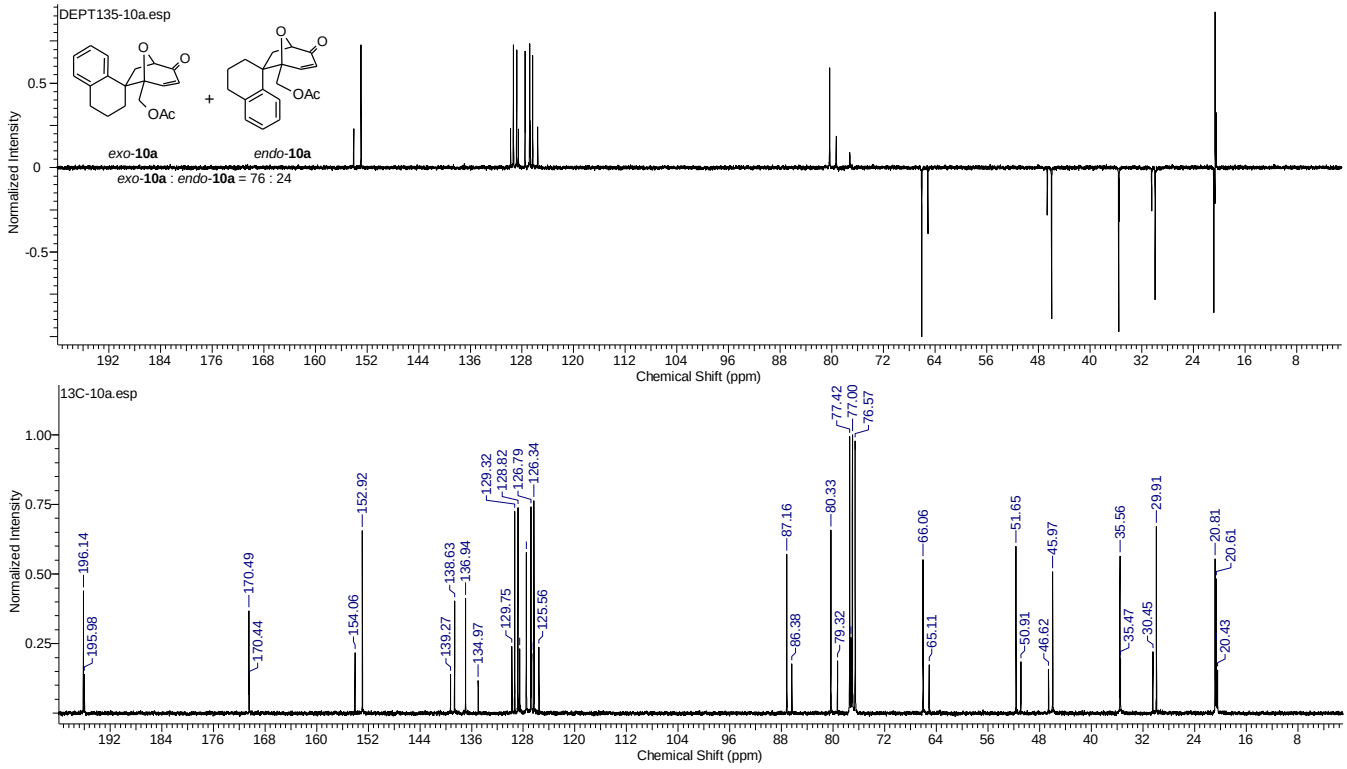

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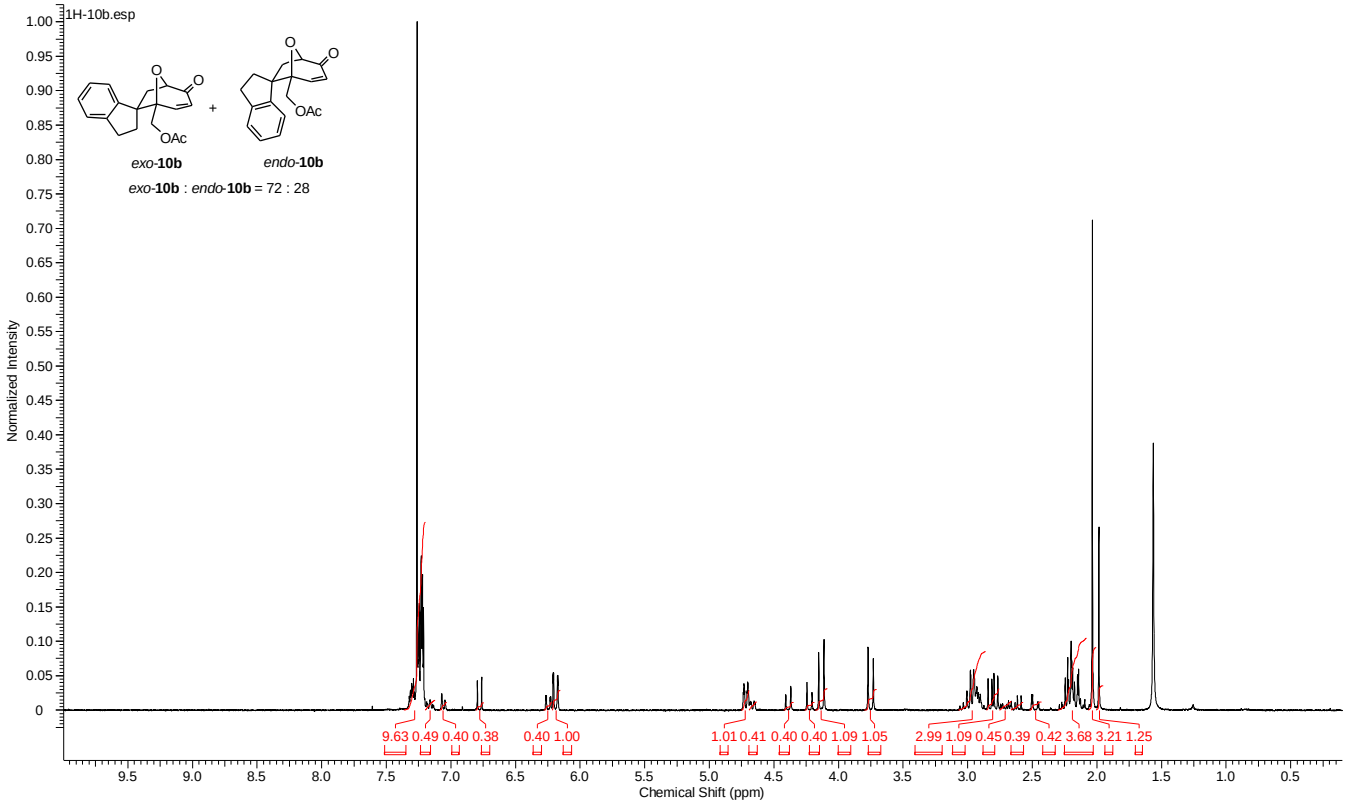

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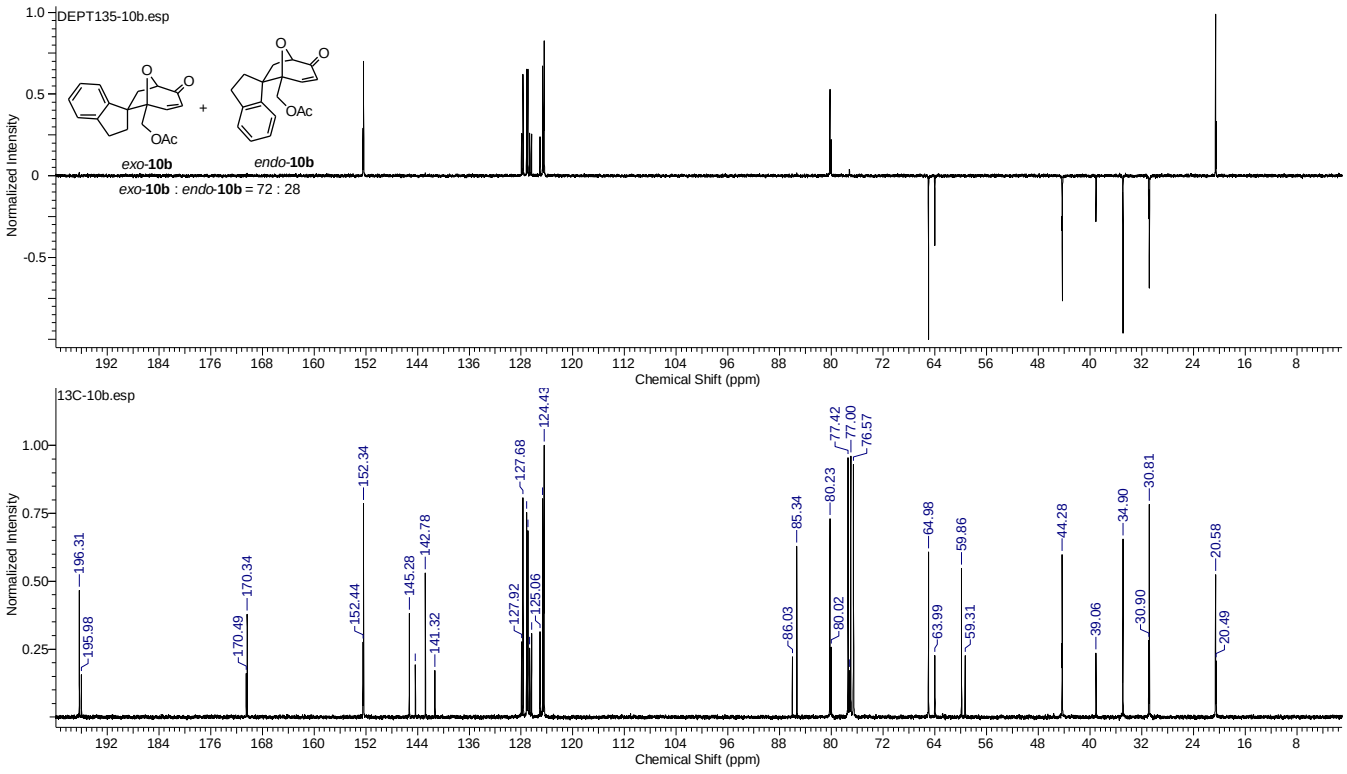

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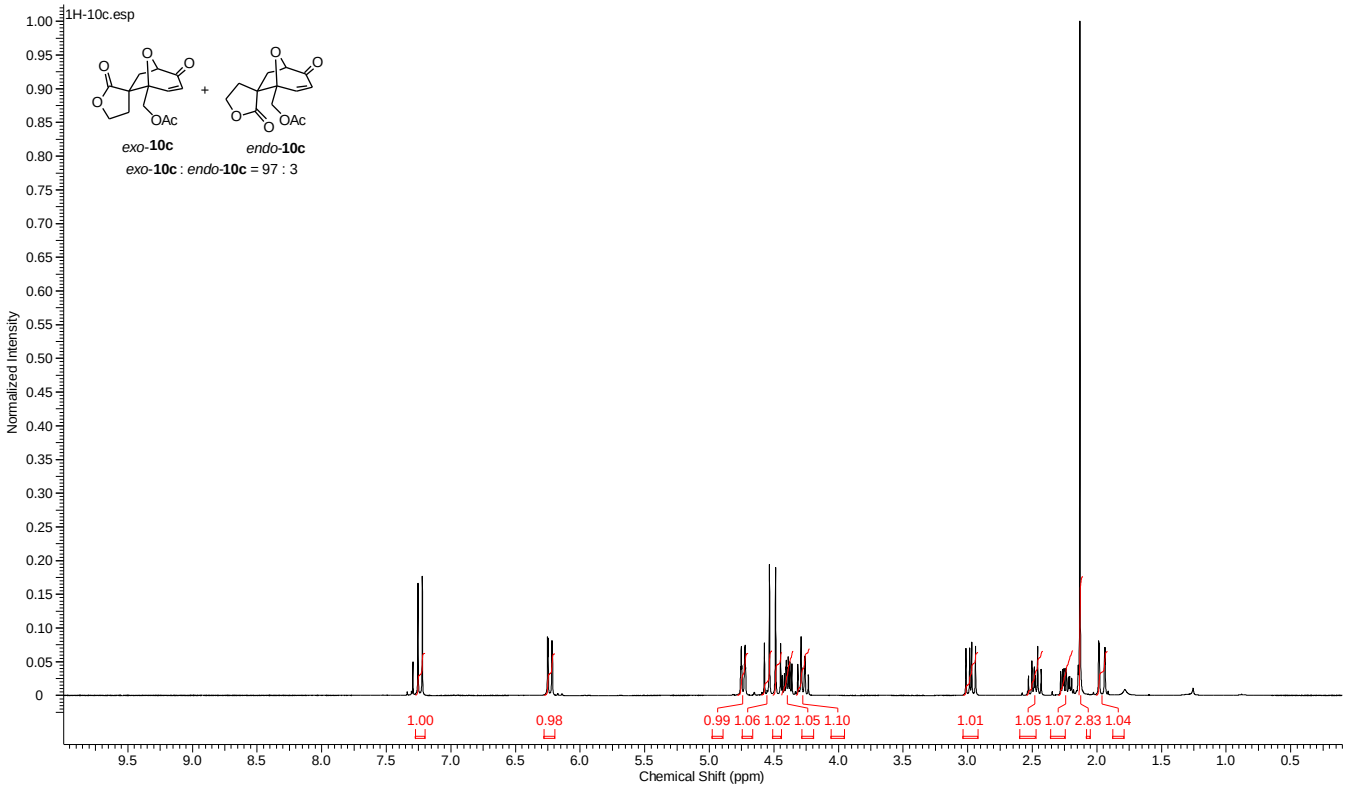

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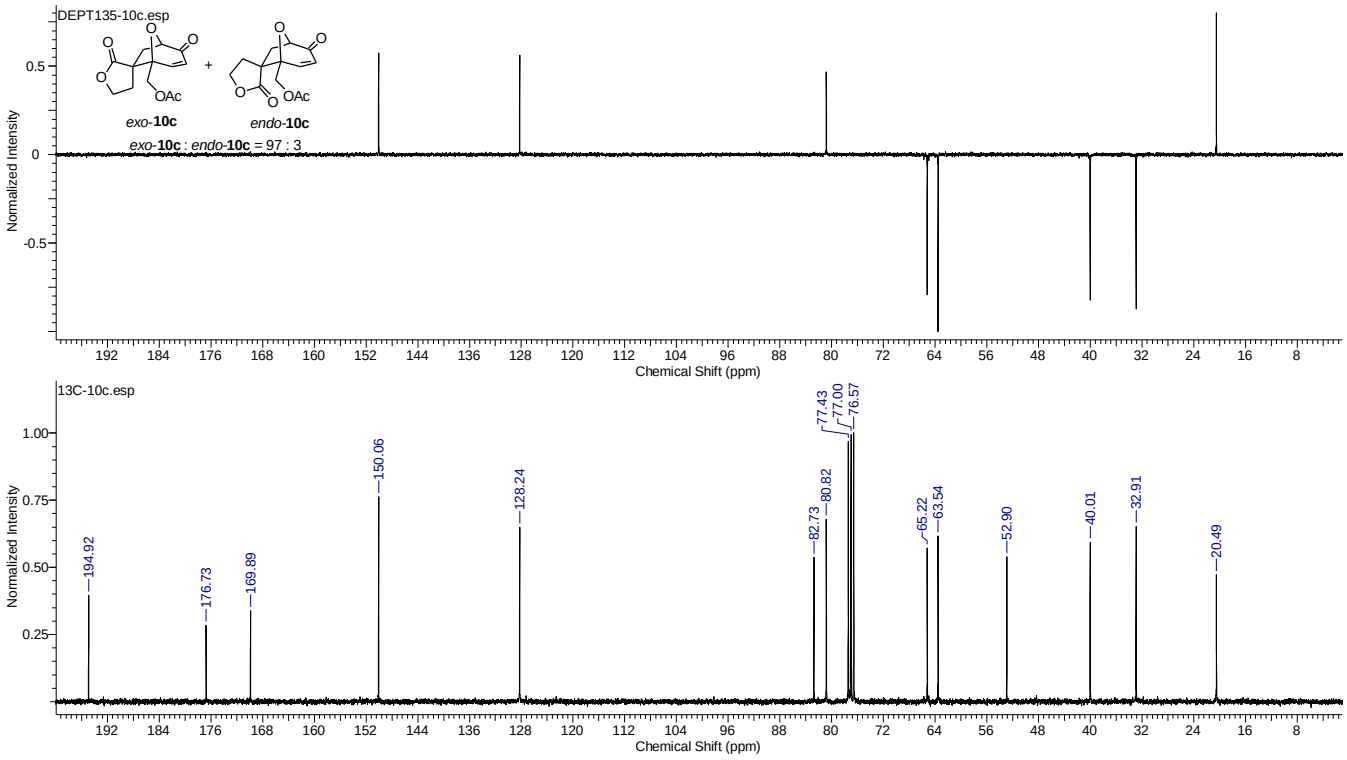

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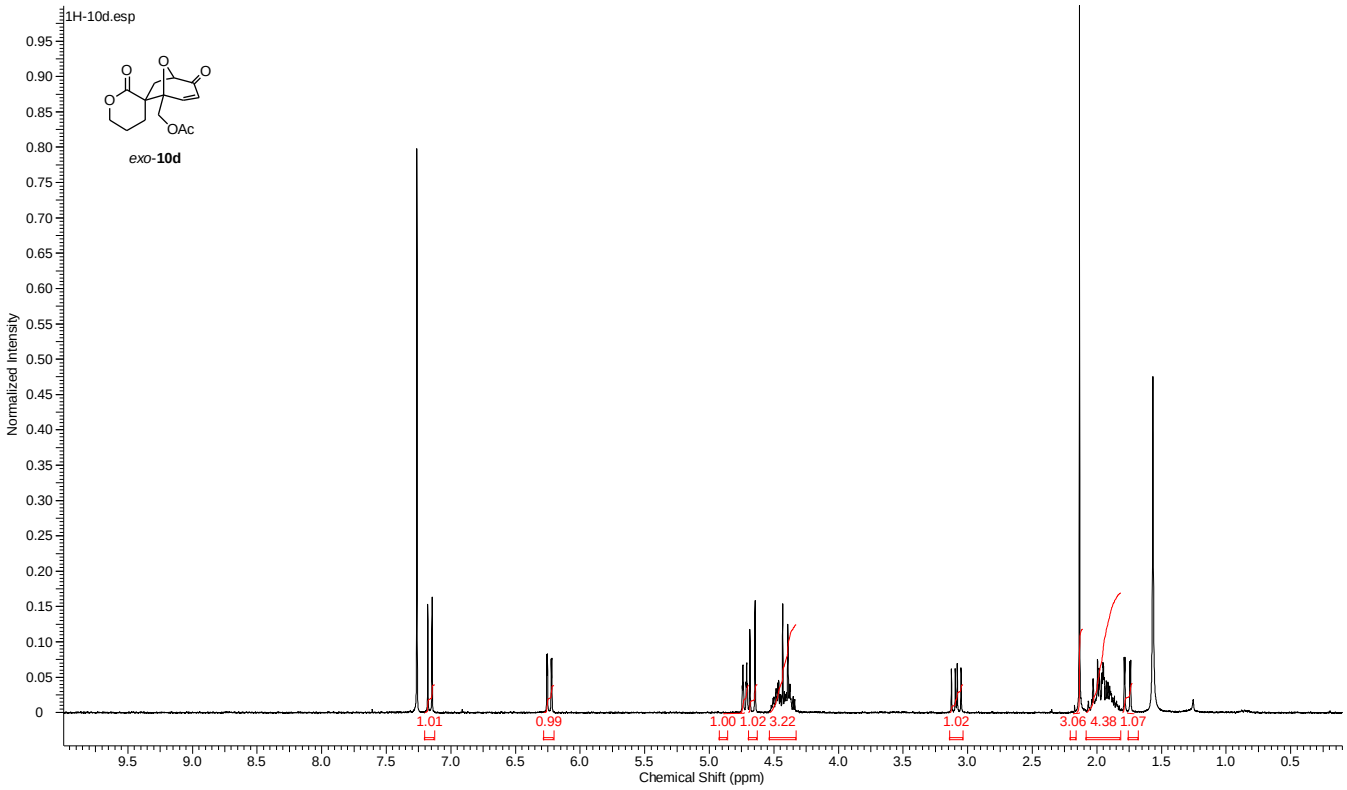

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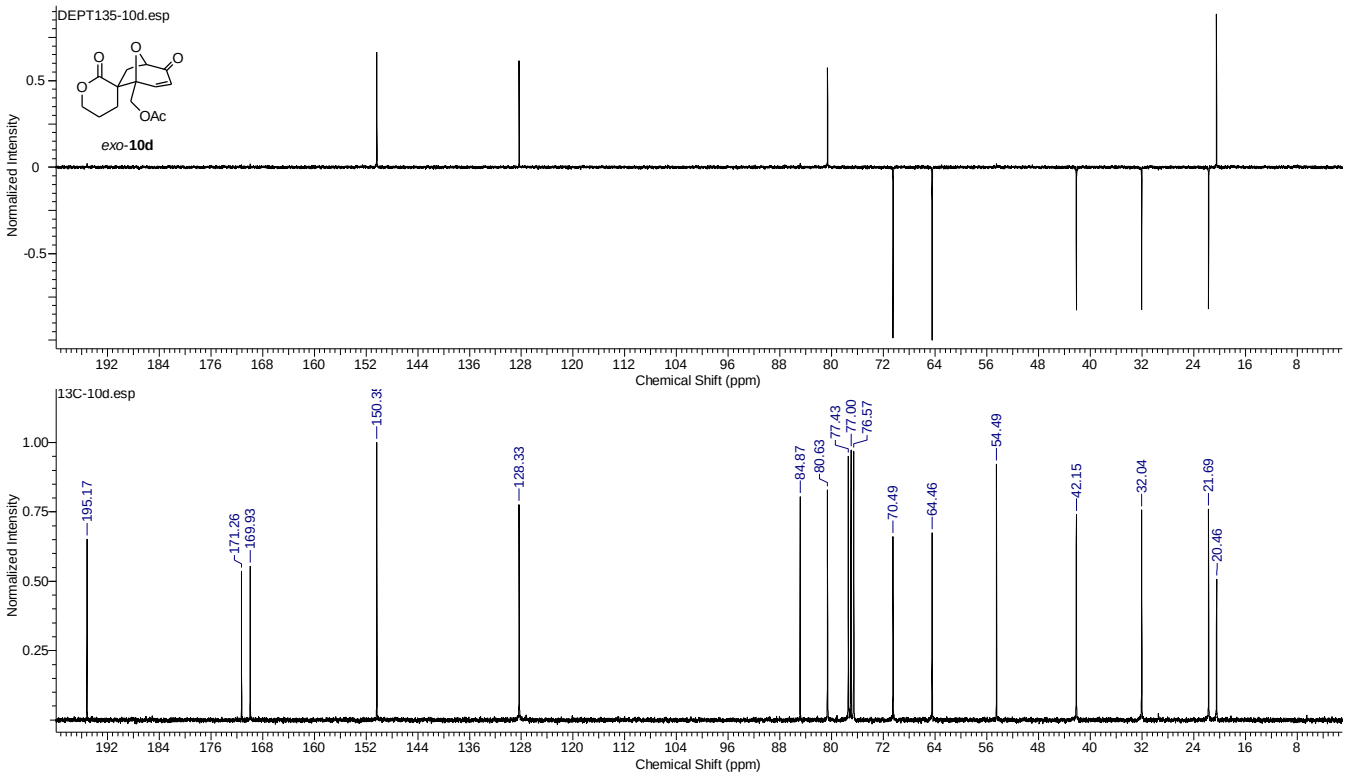
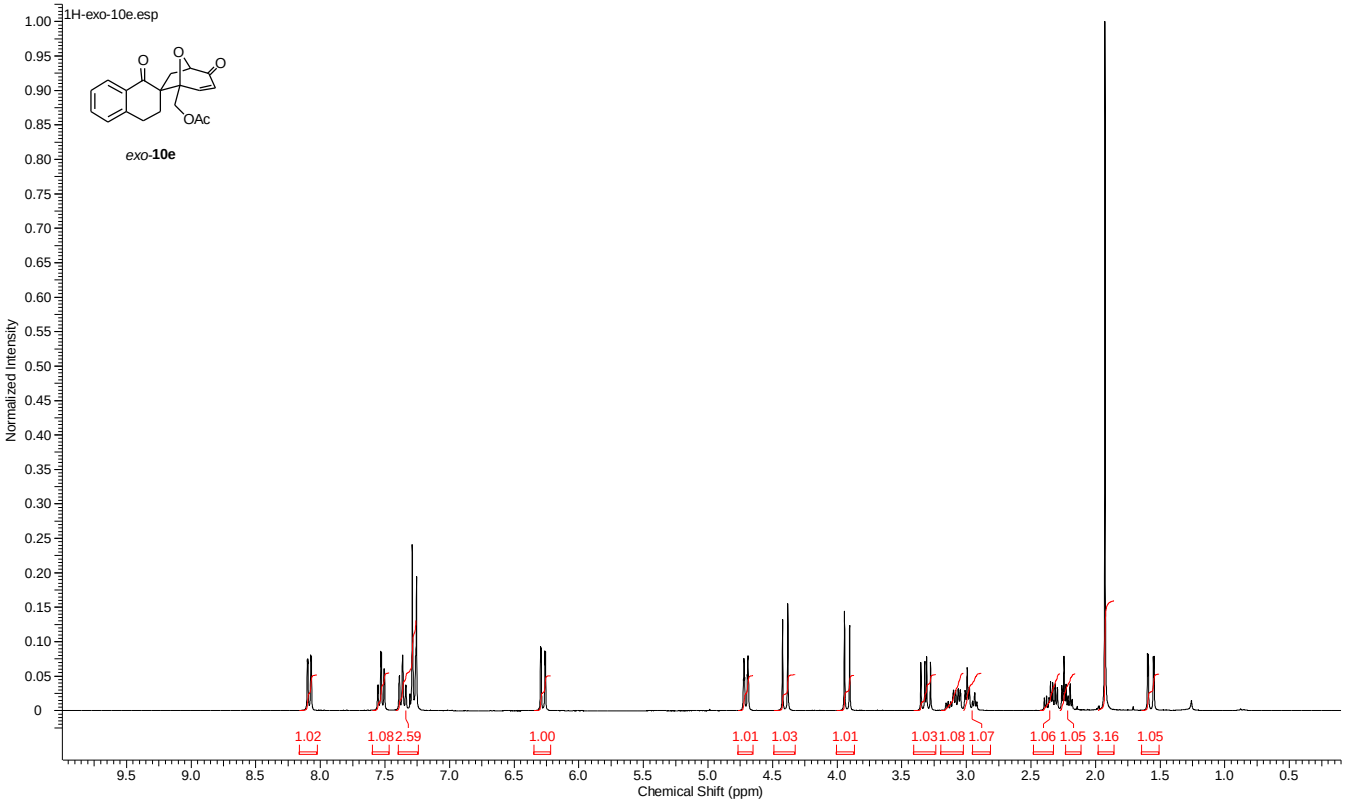
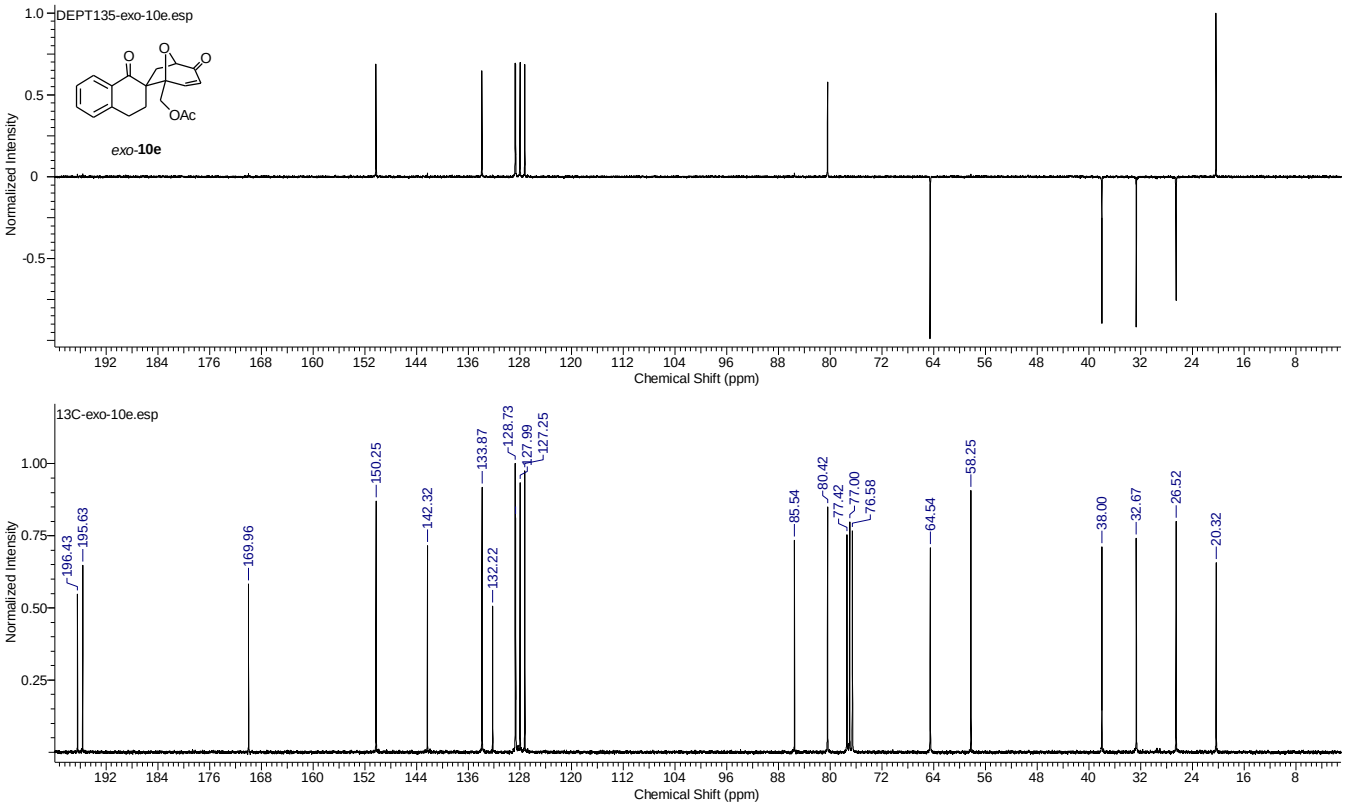


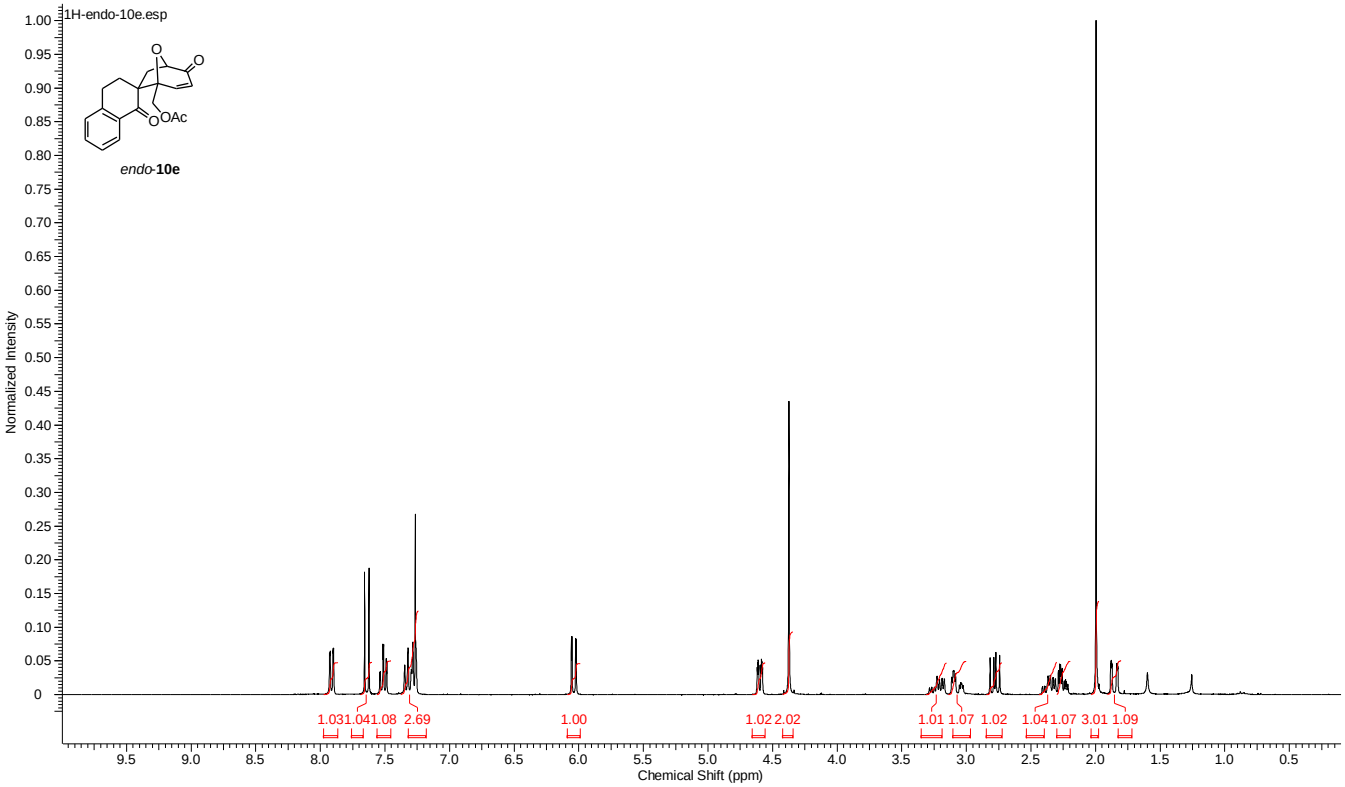
^{1}H NMR (300 MHz, $CDCl_3$)



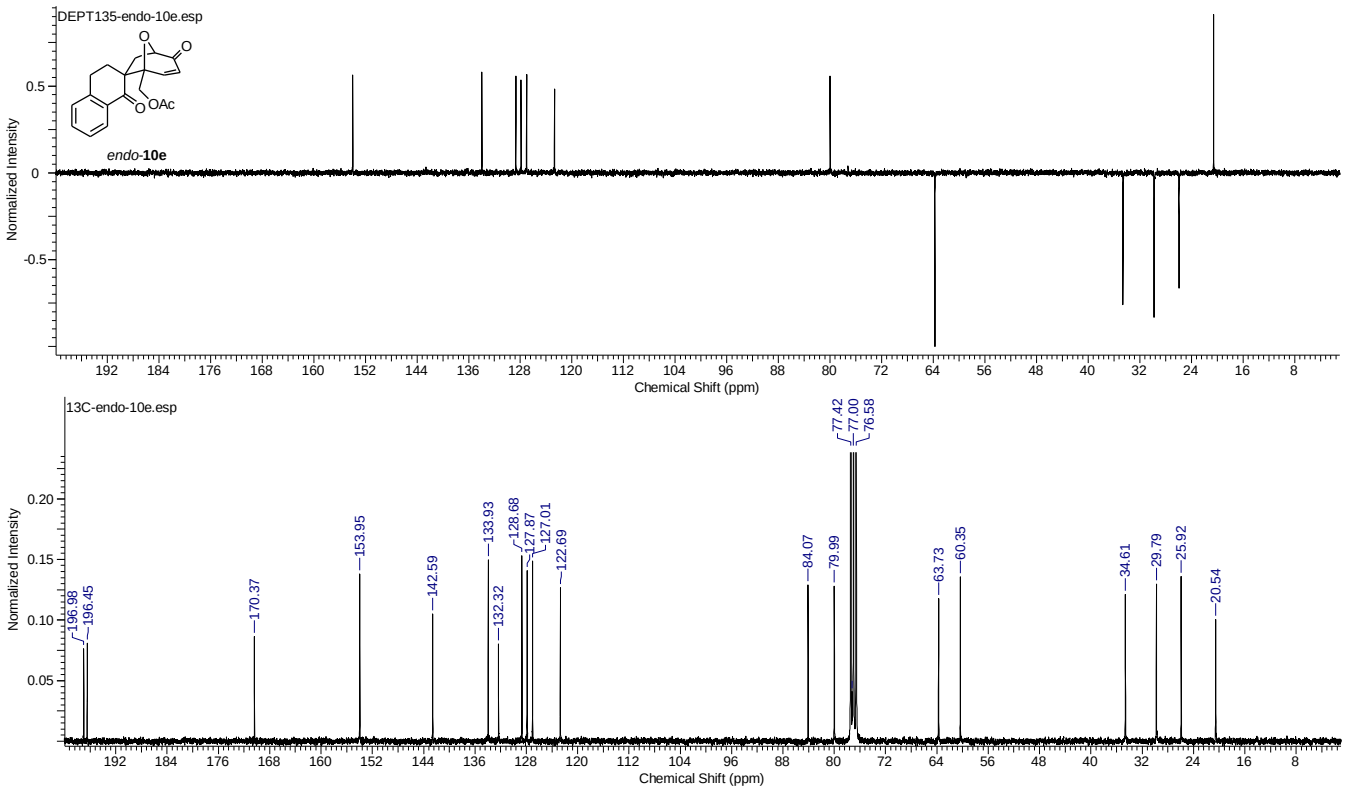
^{13}C NMR (75 MHz, $CDCl_3$)



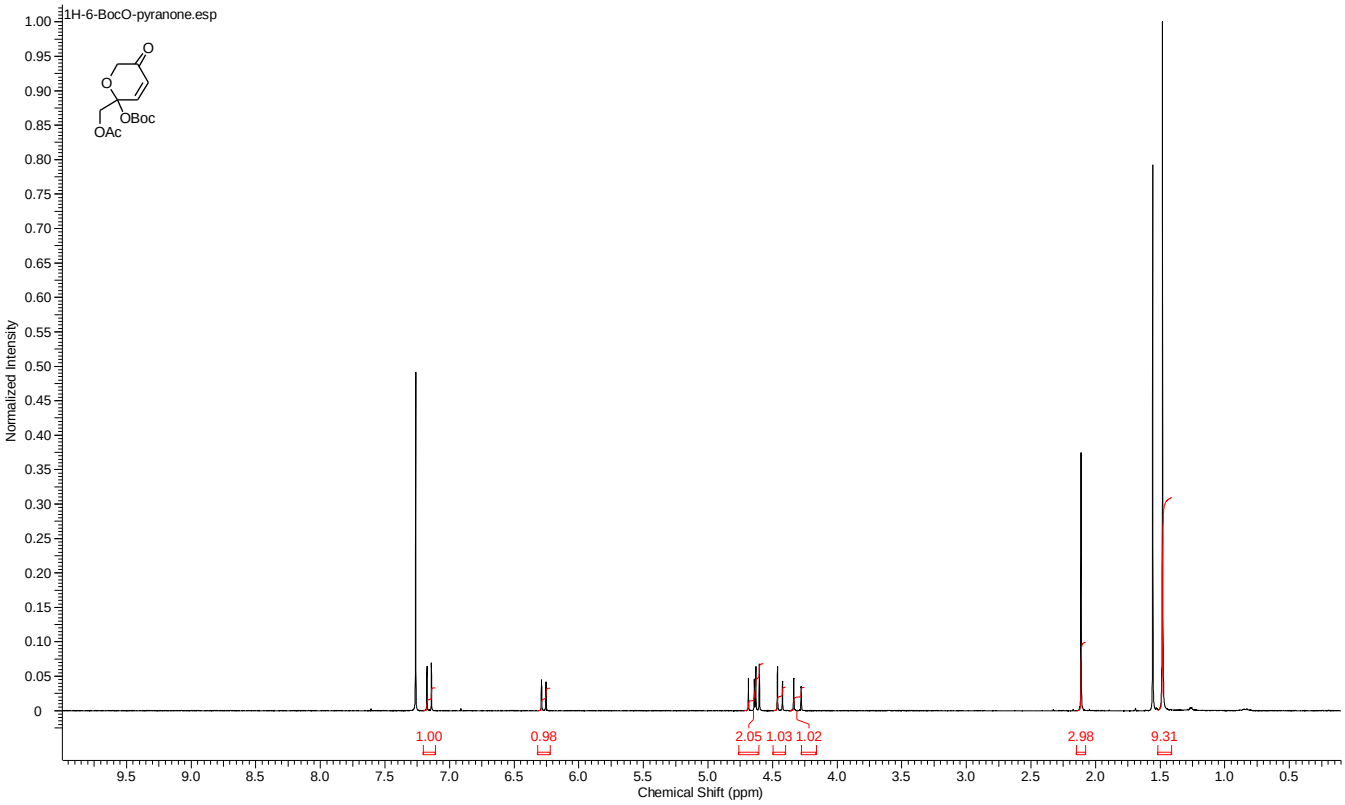
^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)



^{1}H NMR (300 MHz, $CDCl_3$)



^{13}C NMR (75 MHz, $CDCl_3$)