BEILSTEIN JOURNAL OF ORGANIC CHEMISTRY

Supporting Information

for

Unexpected one-pot formation of the 1*H*-6a,8a-epiminotricyclopenta[*a*,*c*,*e*][8]annulene system from cyclopentanone, ammonia and dimethyl fumarate. Synthesis of highly strained polycyclic nitroxide and EPR study

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Beilstein J. Org. Chem. **2019,** *15,* 2664–2670. doi:10.3762/bjoc.15.259

Copies of the IR and ^{1}H, ^{13}C, HMBC, HSQC NMR spectra and X-ray analysis data

Table of contents

X-ray analysis data

X-ray diffraction experiments for the compounds **1** and **6** were performed on a Bruker KAPPA APEX II diffractometer (MoKα radiation, CCD detector, ω-φ scanning, 296 K). The absorption corrections were introduced with the SADABS program [1]. The structures were solved by direct methods and refined anisotropically (except H atoms) using the SHELX2014 programs [2]. The hydrogen atom positions were calculated geometrically and refined in riding model. H atoms at N1 (**1**) and O6 (**6**) were located from difference maps and refined isotropically.

1. Sheldrick G. M., SADABS V. 2.01, Bruker AXS Inc. *Madison, Wisconsin, USA*. **2004**.

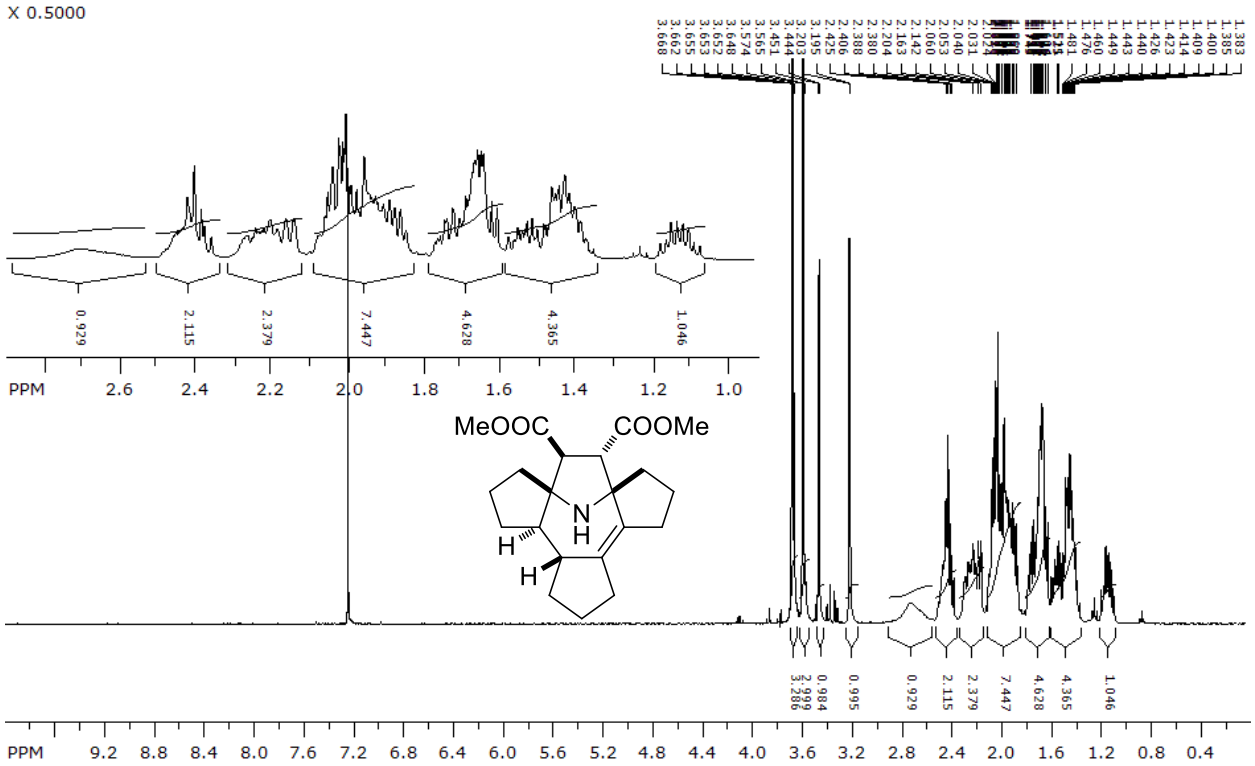
2. Sheldrick G. M. SHELXT–Integrated space-group and crystal-structure determination. *Acta Crystallogr., Sect. A: Found. Adv.* **2015**, 71, 3-8.

Table S1: Crystallographic data and structure refinement parameters of dimethyl 2,3,3a,3b,4,5,6,7,8,9,10,11-dodecahydro-1*H*-6a,8a-epiminotricyclopenta[*a*,*c*,*e*][8]annulene-7,8-dicarboxylate (**1**) and 3a-hydroxy-7,8-bis(methoxycarbonyl)-2,3,3a,3b,4,5,6,7,8,9,10,11-dodecahydro-1*H*-6a,8a-epiminotricyclopenta[*a*,*c*,*e*][8]annulene *N*-oxyl (**6**).

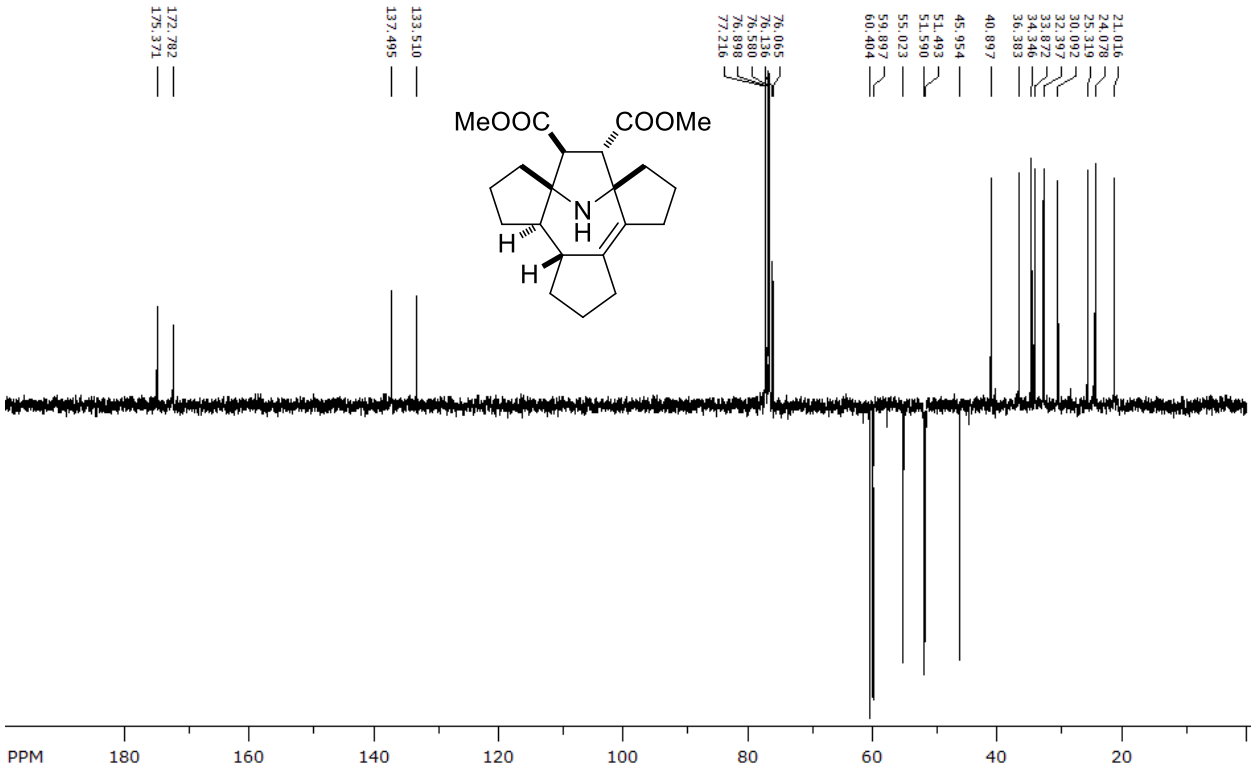
Parameter	**1**	**6**
Chemical formula	$C_{21}H_{29}NO_4$	$C_{21}H_{28}NO_6$
Formula weight	359.45	390.44
Temperature (K)	296	296
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
a (Å)	6.2467(4)	8.2240(5)
b (Å)	9.2039(8)	10.9423(6)
c (Å)	16.7575(15)	11.4515(8)
α (deg)	98.858(4)	83.440(3)
β (deg)	94.176(3)	75.611(3)
γ (deg)	95.362(3)	83.119(2)
Cell volume (Å^3)	944.07(13)	987.17(11)
Z	2	2
d_{calc} (g cm^{-3})	1.264	1.314
μ (mm^{-1})	0.087	0.096
Crystal dimensions (mm)	0.14×0.27×0.57	0.31×0.47×0.59
θ max (deg)	27.27	27.29
Reflections collected/ unique	20324/4168	25779
R (int)	0.0429	0.0375
Reflections with $I > 2\sigma(I)$	3234	3451
Parameters	241	258
Final R_1 ($I > 2\sigma(I)$)	0.0602	0.0439
Final wR_2 ($I > 2\sigma(I)$)	0.1696	0.1215
Final R_1 (all data)	0.0784	0.0585
Final wR_2 (all data)	0.2013	0.1390
Goodness-of-fit on F^2	1.030	1.011
CCDC number	1947797	1947798

1. NMR spectra

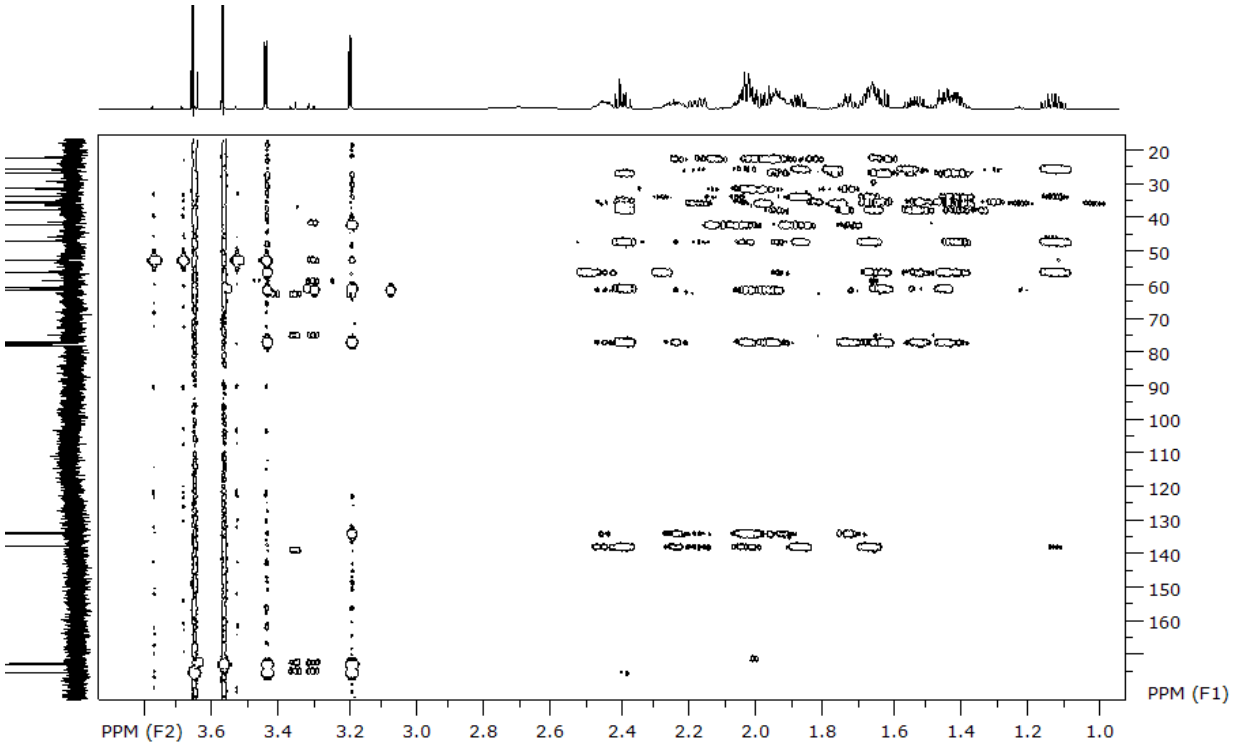
^{1}H NMR (400 MHz, $CDCl_3$) of dimethyl 2,3,3a,3b,4,5,6,7,8,9,10,11-dodecahydro-1*H*-6a,8a-epiminotricyclopenta[*a*,*c*,*e*][8]annulene-7,8-dicarboxylate (**1**)



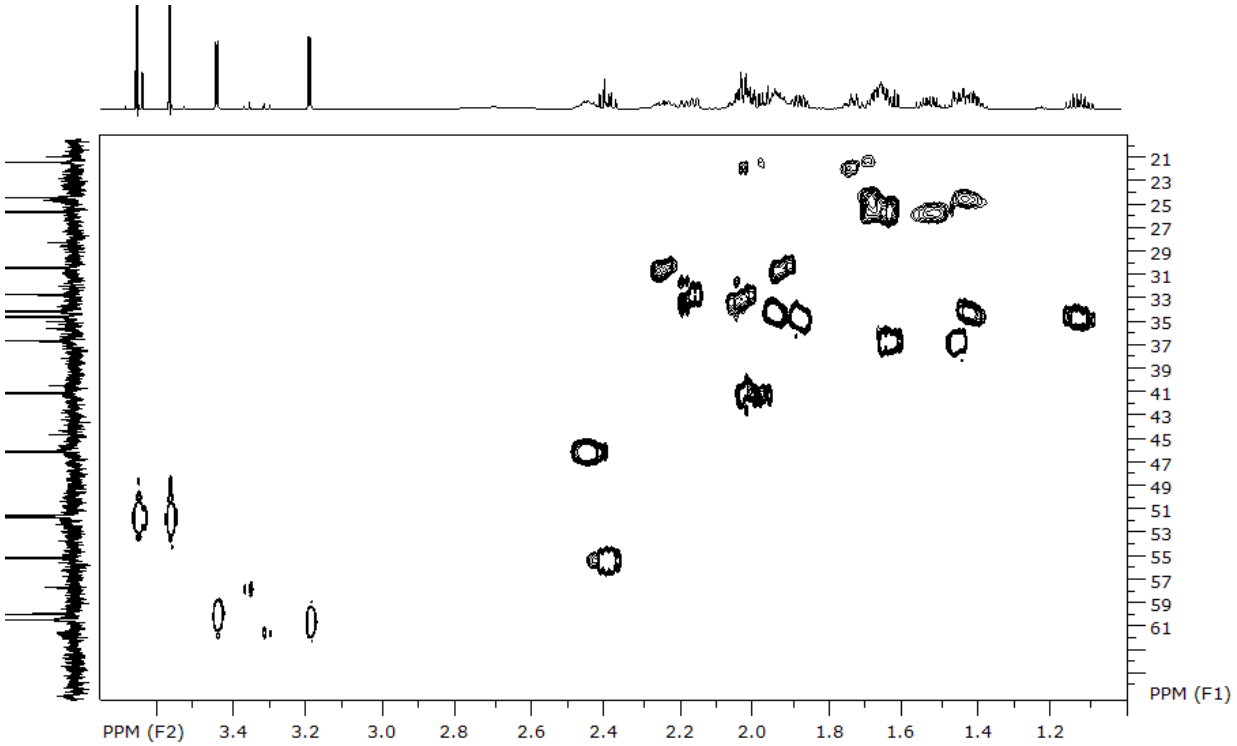
^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) of dimethyl 2,3,3a,3b,4,5,6,7,8,9,10,11-dodecahydro-1*H*-6a,8a-epiminotricyclopenta[*a*,*c*,*e*][8]annulene-7,8-dicarboxylate (**1**)



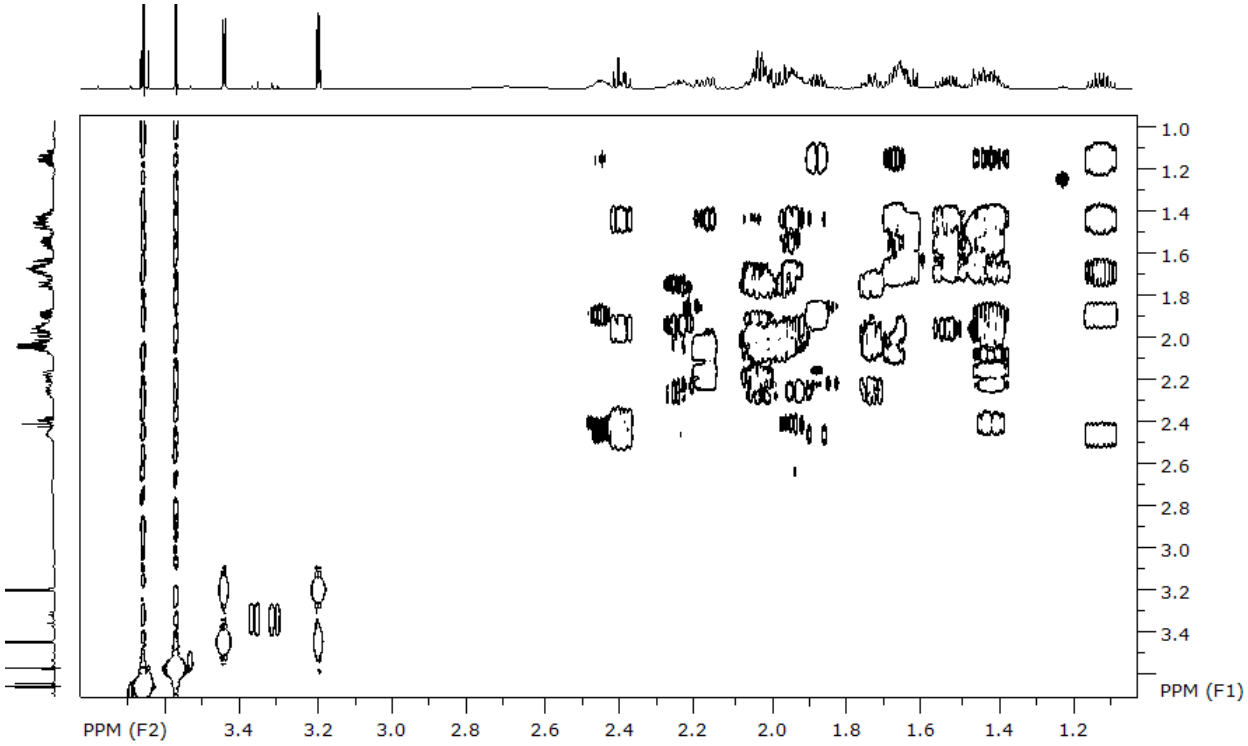
HMBC (600 MHz, $CDCl_3$) of dimethyl 2,3,3a,3b,4,5,6,7,8,9,10,11-dodecahydro-1*H*-6a,8a-epiminotricyclopenta[*a*,*c*,*e*][8]annulene-7,8-dicarboxylate (**1**)



HSQC (600 MHz, $CDCl_3$) of dimethyl 2,3,3a,3b,4,5,6,7,8,9,10,11-dodecahydro-1*H*-6a,8a-epiminotricyclopenta[*a*,*c*,*e*][8]annulene-7,8-dicarboxylate (**1**)

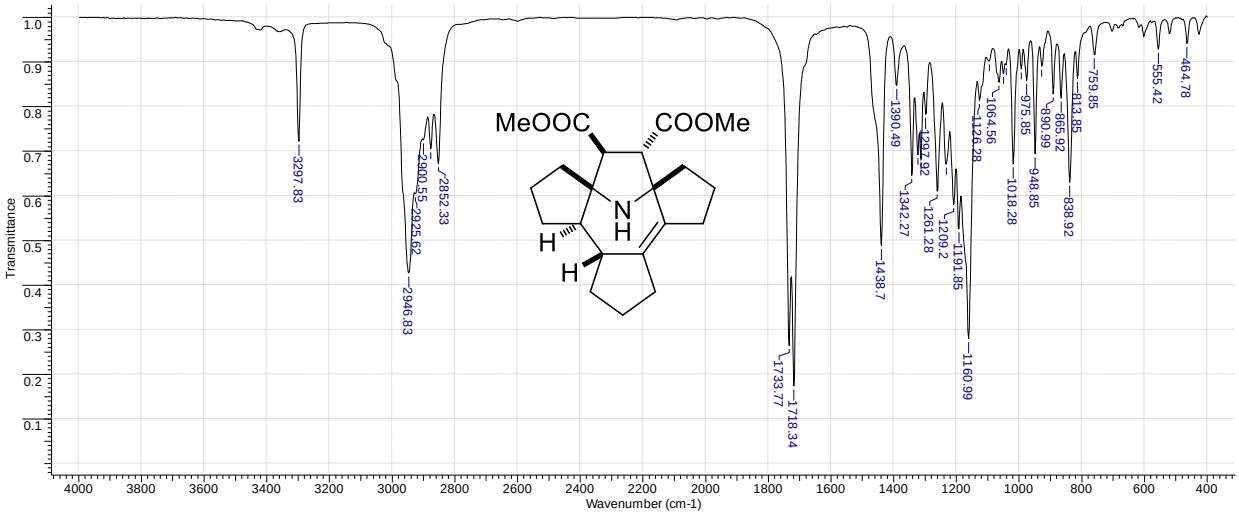


COSY (600 MHz, $CDCl_3$) of dimethyl 2,3,3a,3b,4,5,6,7,8,9,10,11-dodecahydro-1*H*-6a,8a-epiminotricyclopenta[*a*,*c*,*e*][8]annulene-7,8-dicarboxylate (**1**)



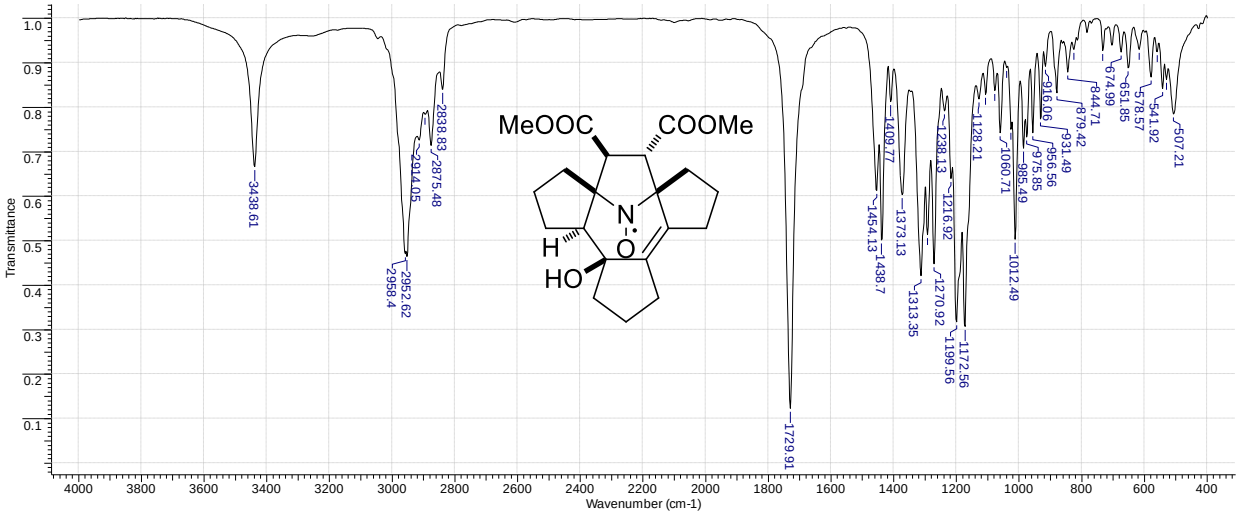
2. IR spectra

IR (KBr) of dimethyl 2,3,3a,3b,4,5,6,7,8,9,10,11-dodecahydro-1*H*-6a,8a-epiminotricyclopenta[*a*,*c*,*e*][8]annulene-7,8-dicarboxylate (**1**)



cm-1	cm-1	cm-1
3297.8	1313.3	1018.3
2946.8	1297.9	993.2
2925.6	1261.3	975.8
2900.5	1232.3	948.8
2877.4	1209.2	927.6
2852.3	1191.8	891.0
1733.8	1161.0	865.9
1718.3	1126.3	838.9
1438.7	1095.4	813.9
1390.5	1064.6	759.9
1342.3	1049.1	555.4
1323.0	1041.4	464.8

IR (KBr) of 3a-hydroxy-7,8-bis(methoxycarbonyl)-2,3,3a,3b,4,5,6,7,8,9,10,11-dodecahydro-1*H*-6a,8a-epiminotricyclopenta[*a*,*c*,*e*][8]annulene *N*-oxyl (**6**)



cm-1	cm-1	cm-1	cm-1
3438.6	1373.1	1060.7	825.4
2958.4	1313.3	1039.5	732.9
2952.6	1292.1	1026.0	675.0
2914.0	1270.9	1012.5	651.9
2894.8	1238.1	985.5	617.1
2875.5	1216.9	975.8	578.6
2838.8	1199.6	956.6	559.3
1729.9	1172.6	931.5	541.9
1454.1	1128.2	916.1	530.4
1438.7	1107.0	879.4	507.2
1409.8	1078.1	844.7	