Stereocontrolled Synthesis and Cycloaddition of 1,2,4-Trioxygenated-1,3-dienes

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General experimental section: NMR analyses were conducted at room temperature at 500, 300 or 200 MHz for ¹H NMR spectra and 125, 75 or 50 MHz for ¹³C NMR spectra. Chemical shifts (δ) are given in ppm and the coupling constant (*J*) in hertz. The solvent was deuteriochloroform, with a calibration at 7.26 for ¹H spectra and 77.36 for ¹³C spectra. IR spectra were realized by transmission on a IRTF spectrometer. The mass spectra were obtained under electron impact conditions (EI) at 70 eV ionizing potential; ammonia (NH₃) was used for chemical ionization (CI). The silica gel used for flash chromatography was 0.040-0.063 mm. All reagents were of reagent grade and were used as such or distilled prior to use.

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S7 : 1,1-Bis-(1-ethylpropyloxy)-propan-2-one **14b** (75 MHz, CDCl₃)

S8 : Cyclohexyl-(2,2-dimethoxy-1-methylethylidene)-amine **15a** (200 MHz, CDCl₃)

S9 : Cyclohexyl-(2,2-dimethoxy-1-methylethylidene)-amine **15a** (75 MHz, CDCl₃)

S10 : 2,2-Bis-(1-ethylpropyloxy)-1-methylethylidenecyclohexylamine **15b** (200 MHz, CDCl₃)

S11 : 2,2-Bis-(1-ethylpropyloxy)-1-methylethylidenecyclohexylamine **15b** (50 MHz, CDCl₃)

S12 : 1,1,4-Trimethoxybutan-2-one **18** (300 MHz, CDCl₃)

S13 : 1,1,4-Trimethoxybutan-2-one **18** (75 MHz, CDCl₃)

S14 : 4-Ethoxy-1,1-dimethoxybutan-2-one **19** (300 MHz, CDCl₃)

S15 : 4-Ethoxy-1,1-dimethoxybutan-2-one **19** (75 MHz, CDCl₃)

S16 : 4-Ethoxy-1,1-bis-(1-ethylpropyloxy)-butan-2-one **20** (300 MHz, CDCl₃)

S17 : 4-Ethoxy-1,1-bis-(1-ethylpropyloxy)-butan-2-one **20** (75 MHz, CDCl₃)

S18 : 1,1,4-Trimethoxy-2-triethylsilyloxybut-2-ene **12a** (300 MHz, CDCl₃)

- S19 : 1,1,4-Trimethoxy-2-triethylsilyloxybut-2-ene **12a** (75 MHz, CDCl₃)
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- S30 : 2-(*tert*-Butyldiphenylsilyloxy)-4-ethoxy-1,1-dimethoxybut-2-ene **12g** (300 MHz, CDCl₃)
- S31 : 2-(*tert*-Butyldiphenylsilyloxy)-4-ethoxy-1,1-dimethoxybut-2-ene **12g** (75 MHz, CDCl₃)
- S32 : 4-Ethoxy-1-[bis-(1-ethylpropyloxy)]-2-triethylsilyloxybut-2-ene **12h** (200 MHz, CDCl₃)
- S33 : 4-Ethoxy-1-[bis-(1-ethylpropyloxy)]-2-triethylsilyloxybut-2-ene **12h** (50 MHz, CDCl₃)
- S34 : 1,4-Dimethoxy-2-triethylsilyloxy-1,3-butadiene **13a** (300 MHz, CDCl₃)
- S35 : 1,4-Dimethoxy-2-triethylsilyloxy-1,3-butadiene **13a** (75 MHz, CDCl₃)

- S36 : 1,4-Dimethoxy-2-*triisobutylsilyloxy*-1,3-butadiene **13b** (200 MHz, CDCl₃)
- S37 : 1,4-Dimethoxy-2-*triisobutylsilyloxy*-1,3-butadiene **13b** (50 MHz, CDCl₃)
- S38 : 4-Ethoxy-1-methoxy-2-*triethylsilyloxy*-1,3-butadiene **13d** (200 MHz, CDCl₃)
- S39 : 4-Ethoxy-1-methoxy-2-*triethylsilyloxy*-1,3-butadiene **13d** (75 MHz, CDCl₃)
- S40 : 2-*tert*Butyldimethylsilyloxy-4-ethoxy-1-methoxy-1,3-butadiene **13e** (300 MHz, CDCl₃)
- S41 : 2-*tert*Butyldimethylsilyloxy-4-ethoxy-1-methoxy-1,3-butadiene **13e** (75 MHz, CDCl₃)
- S42 : 4-Ethoxy-1-methoxy-2-*triisopropylsilyloxy*-1,3-butadiene **13f** (200 MHz, CDCl₃)
- S43 : 4-Ethoxy-1-methoxy-2-*triisopropylsilyloxy*-1,3-butadiene **13f** (50 MHz, CDCl₃)
- S44 : 2-*tert*Butyldiphenylsilyloxy-4-ethoxy-1-methoxy-1,3-butadiene **13g** (300 MHz, CDCl₃)
- S45 : 2-*tert*Butyldiphenylsilyloxy-4-ethoxy-1-methoxy-1,3-butadiene **13g** (75 MHz, CDCl₃)
- S46 : 4-Ethoxy-1-(1-ethylpropyloxy)-2-*triethylsilyloxy*-1,3-butadiene **13h** (300 MHz, CDCl₃)
- S47 : 4-Ethoxy-1-(1-ethylpropyloxy)-2-*triethylsilyloxy*-1,3-butadiene **13h** (75 MHz, CDCl₃)
- S48: 7-Ethoxy-4-methoxy-2-methyl-5-*triethylsilyloxy*-3a,4,7,7a-tetrahydro*iso*indole-1,3-dione **28 trans** (300 MHz, CDCl₃)
- S49 : 7-Ethoxy-4-methoxy-2-methyl-5-*triethylsilyloxy*-3a,4,7,7a-tetrahydro*iso*indole-1,3-dione **28 trans** (75 MHz, CDCl₃)
- S50 : 7-Ethoxy-4-methoxy-2-methyl-5-*triethylsilyloxy*-3a,4,7,7a-tetrahydro*iso*indole-1,3-dione **28 cis** (300 MHz, CDCl₃)
- S51 : 7-Ethoxy-4-methoxy-2-methyl-5-*triethylsilyloxy*-3a,4,7,7a-tetrahydro*iso*indole-1,3-dione **28 cis** (75 MHz, CDCl₃)

- S52 : 2-Ethoxy-5-methoxy-4-triethylsilyloxycyclohex-3-enecarboxylic acid phenyl ester **29 trans** (300 MHz, CDCl₃)
- S53 : 2-Ethoxy-5-methoxy-4-triethylsilyloxycyclohex-3-enecarboxylic acid phenyl ester **29 trans** (75 MHz, CDCl₃)
- S54 : 2-Ethoxy-5-methoxy-4-triethylsilyloxycyclohex-3-enecarboxylic acid phenyl ester **29 cis** (300 MHz, CDCl₃)
- S55 : 2-Ethoxy-5-methoxy-4-triethylsilyloxycyclohex-3-enecarboxylic acid phenyl ester **29 cis** (75 MHz, CDCl₃)
- S56 : 5-*tert*Butyldiphenylsilyloxy-7-ethoxy-4-methoxy-2-methyl-3a,4,7,7a-tetrahydro*iso*indole-1,3-dione **30 trans** (300 MHz, CDCl₃)
- S57 : 5-*tert*Butyldiphenylsilyloxy-7-ethoxy-4-methoxy-2-methyl-3a,4,7,7a-tetrahydro*iso*indole-1,3-dione **30 trans** (75 MHz, CDCl₃)
- S58 : 5-*tert*Butyldiphenylsilyloxy-7-ethoxy-4-methoxy-2-methyl-3a,4,7,7a-tetrahydro*iso*indole-1,3-dione **30 cis** (300 MHz, CDCl₃)
- S59 : 5-*tert*Butyldiphenylsilyloxy-7-ethoxy-4-methoxy-2-methyl-3a,4,7,7a-tetrahydro*iso*indole-1,3-dione **30 cis** (75 MHz, CDCl₃)
- S60 : 4-*tert*-Butyldiphenylsilyloxy-2,5-dimethoxycyclohex-3-enecarboxylic acid phenyl ester **31 trans** (300 MHz, CDCl₃)
- S61 : 4-*tert*-Butyldiphenylsilyloxy-2,5-dimethoxycyclohex-3-enecarboxylic acid phenyl ester **31 trans** (75 MHz, CDCl₃)

S6

1,1-Bis-(1-ethylpropyloxy)-propan-2-one **14b**

(300 MHz, CDCl₃)

S7

1,1-Bis-(1-ethylpropyloxy)-propan-2-one **14b**

(75 MHz, CDCl₃)

S8

Cyclohexyl-(2,2-dimethoxy-1-methylethylidene)-amine **15a**

(200 MHz, CDCl₃)

S9

Cyclohexyl-(2,2-dimethoxy-1-methylethylidene)-amine **15a**

(75 MHz, CDCl₃)

S10

2,2-Bis-(1-ethylpropyloxy)-1-methylethylenecyclohexylamine **15b**

(200 MHz, CDCl₃)

S11

2,2-Bis-(1-ethylpropyloxy)-1-methylethylenecyclohexylamine **15b**

(50 MHz, CDCl₃)

S12

1,1,4-Trimethoxybutan-2-one **18**

(300 MHz, CDCl₃)

S13

1,1,4-Trimethoxybutan-2-one **18**

(75 MHz, CDCl₃)

S14

4-Ethoxy-1,1-dimethoxybutan-2-one **19**

(300 MHz, CDCl₃)

S15

4-Ethoxy-1,1-dimethoxybutan-2-one **19**

(75 MHz, CDCl₃)

S16

4-Ethoxy-1,1-bis-(1-ethylpropyloxy)-butan-2-one **20**

(300 MHz, CDCl₃)

S17

4-Ethoxy-1,1-bis-(1-ethylpropyloxy)-butan-2-one **20**

(75 MHz, CDCl₃)

S18

1,1,4-Trimethoxy-2-triethylsilyloxybut-2-ene **12a**

(300 MHz, CDCl₃)

S19

1,1,4-Trimethoxy-2-triethylsilyloxybut-2-ene **12a**

(75 MHz, CDCl₃)

S20

1,1,4-Trimethoxy-2-triisobutylsilyloxybut-2-ene **12b**

(300 MHz, CDCl₃)

S21

1,1,4-Trimethoxy-2-triisobutylsilyloxybut-2-ene **12b**

(75 MHz, CDCl₃)

S22

2-(*tert*-Butyldiphenylsilyloxy)-1,1,4-trimethoxybut-2-ene **12c**

(300 MHz, CDCl₃)

S23

2-(*tert*-Butyldiphenylsilyloxy)-1,1,4-trimethoxybut-2-ene **12c**

(75 MHz, CDCl₃)

S24

4-Ethoxy-1,1-dimethoxy-2-triethylsilyloxybut-2-ene **12d**

(300 MHz, CDCl₃)

S25

4-Ethoxy-1,1-dimethoxy-2-triethylsilyloxybut-2-ene **12d**

(75 MHz, CDCl₃)

S26

2-(*tert*-Butyldimethylsilyloxy)-4-ethoxy-1,1-dimethoxybut-2-ene **12e**

(300 MHz, CDCl₃)

S27

2-(*tert*-Butyldimethylsilyloxy)-4-ethoxy-1,1-dimethoxybut-2-ene **12e**

(75 MHz, CDCl₃)

S28

4-Ethoxy-1,1-dimethoxy-2-triisopropylsilyloxybut-2-ene **12f**

(300 MHz, CDCl₃)

S29

4-Ethoxy-1,1-dimethoxy-2-triisopropylsilyloxybut-2-ene **12f**(75 MHz, CDCl₃)

S30

2-(*tert*-Butyldiphenylsilyloxy)-4-ethoxy-1,1-dimethoxybut-2-ene **12g**

(300 MHz, CDCl₃)

S31

2-(*tert*-Butyldiphenylsilyloxy)-4-ethoxy-1,1-dimethoxybut-2-ene **12g**

(75 MHz, CDCl₃)

S32

4-Ethoxy-1-[bis-(1-ethylpropyloxy)]-2-triethylsilyloxybut-2-ene **12h**

(200 MHz, CDCl₃)

Chemical structure of compound 10: CCOC/C=C/C(OC(C)CC)OC(C)CC

¹³C NMR spectrum (ppm):

- 145.9850
- 107.7143
- 100.6174
- 78.8679
- 77.9828
- 77.3600
- 76.7208
- 65.5428
- 64.9855
- 26.4198
- 26.0593
- 15.5860
- 9.8987
- 9.5873
- 7.1124
- 6.7191
- 6.1126
- 5.8176

Chemical structure of compound 10: CCOC/C=C/C(OC(C)CC)OC(C)CC

¹³C NMR spectrum (CDCl₃):

Peak list (ppm): 145.9850, 107.7143, 100.6174, 78.8679, 77.9828, 77.3600, 76.7208, 65.5428, 64.9855, 26.4198, 26.0593, 15.5860, 9.8987, 9.5873, 7.1124, 6.7191, 6.1126, 5.8176.

Chemical structure of compound 10: CCOC/C=C/C(OC(C)CC)OC(C)CC

¹³C NMR spectrum (CDCl₃):

Peak list (ppm): 145.9850, 107.7143, 100.6174, 78.8679, 77.9828, 77.3600, 76.7208, 65.5428, 64.9855, 26.4198, 26.0593, 15.5860, 9.8987, 9.5873, 7.1124, 6.7191, 6.1126, 5.8176.

S34

1,4-Dimethoxy-2-triethylsilyloxy-1,3-butadiene **13a**

(300 MHz, CDCl₃)

S35

1,4-Dimethoxy-2-triethylsilyloxy-1,3-butadiene **13a**

(75 MHz, CDCl₃)

S36

1,4-Dimethoxy-2-triisobutylsilyloxy-1,3-butadiene **13b**

(200 MHz, CDCl₃)

S37

1,4-Dimethoxy-2-triisobutylsilyloxy-1,3-butadiene **13b**

(50 MHz, CDCl₃)

S38

4-Ethoxy-1-methoxy-2-triethylsilyloxy-1,3-butadiene **13d**

(200 MHz, CDCl₃)

S39

4-Ethoxy-1-methoxy-2-triethylsilyloxy-1,3-butadiene **13d**

(75 MHz, CDCl₃)

S40

2-*tert*Butyldimethylsilyloxy-4-ethoxy-1-methoxy-1,3-butadiene **13e**

(300 MHz, CDCl₃)

S41

2-*tert*Butyldimethylsilyloxy-4-ethoxy-1-methoxy-1,3-butadiene **13e**

(75 MHz, CDCl₃)

S42

4-Ethoxy-1-methoxy-2-triisopropylsilyloxy-1,3-butadiene **13f**

(200 MHz, CDCl₃)

S43

4-Ethoxy-1-methoxy-2-triisopropylsilyloxy-1,3-butadiene **13f**

(50 MHz, CDCl₃)

S44

2-*tert*Butyldiphenylsilyloxy-4-ethoxy-1-methoxy-1,3-butadiene **13g**

(300 MHz, CDCl₃)

S45

2-*tert*Butyldiphenylsilyloxy-4-ethoxy-1-methoxy-1,3-butadiene **13g**

(75 MHz, CDCl₃)

S46

4-Ethoxy-1-(1-ethylpropyloxy)-2-triethylsilyloxy-1,3-butadiene **13h**

(300 MHz, CDCl₃)

S47

4-Ethoxy-1-(1-ethylpropyloxy)-2-triethylsilyloxy-1,3-butadiene **13h**

(75 MHz, CDCl₃)

7-Ethoxy-4-methoxy-2-methyl-5-triethylsilyloxy-3a,4,7,7a-tetrahydroisoindole-1,3-dione **28 trans**(300 MHz, CDCl₃)

S49

7-Ethoxy-4-methoxy-2-methyl-5-triethylsilyloxy-3a,4,7,7a-tetrahydroisindole-1,3-dione **28 trans**

(75 MHz, CDCl₃)

S50

7-Ethoxy-4-methoxy-2-methyl-5-triethylsilyloxy-3a,4,7,7a-tetrahydroisoindole-1,3-dione **28 cis**

(300 MHz, CDCl₃)

S51

7-Ethoxy-4-methoxy-2-methyl-5-triethylsilyloxy-3a,4,7,7a-tetrahydro*iso*indole-1,3-dione **28 cis**

(75 MHz, CDCl₃)

S52

2-Ethoxy-5-methoxy-4-triethylsilyloxycyclohex-3-enecarboxylic acid phenyl ester **29 trans**

(300 MHz, CDCl₃)

S53

2-Ethoxy-5-methoxy-4-triethylsilyloxycyclohex-3-enecarboxylic acid phenyl ester **29 trans**

(75 MHz, CDCl₃)

2-Ethoxy-5-methoxy-4-triethylsilyloxycyclohex-3-enecarboxylic acid phenyl ester **29 cis**(300 MHz, CDCl₃)

S55

2-Ethoxy-5-methoxy-4-triethylsilyloxycyclohex-3-enecarboxylic acid phenyl ester **29 cis**

(75 MHz, CDCl₃)

S56

5-*tert*Butyldiphenylsilyloxy-7-ethoxy-4-methoxy-2-methyl-3a,4,7,7a-tetrahydroisindole-1,3-dione **30 trans**

(300 MHz, CDCl₃)

S58

5-*tert*Butyldiphenylsilyloxy-7-ethoxy-4-methoxy-2-methyl-3a,4,7,7a-tetrahydroisoindole-1,3-dione **30 cis**

(300 MHz, CDCl₃)

S59

5-*tert*Butyldiphenylsilyloxy-7-ethoxy-4-methoxy-2-methyl-3a,4,7,7a-tetrahydroisoindole-1,3-dione **30 cis**

(75 MHz, CDCl₃)

S60

4-*tert*-Butyldiphenylsilyloxy-2,5-dimethoxycyclohex-3-enecarboxylic acid phenyl ester **31 trans**

(300 MHz, CDCl₃)

S61

4-*tert*-Butyldiphenylsilyloxy-2,5-dimethoxycyclohex-3-enecarboxylic acid phenyl ester **31 trans**

(75 MHz, CDCl₃)