Supplemental Materials

Solvent-free Diels-Alder Reactions of *in situ* Generated Cyclopentadiene

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Table of Contents

(1) Additional Experimental Information

Dicyclopentadiene. Dicyclopentadiene (*endo* isomer) was purchased from Acros Organic and used without further purification. GC-MS analysis showed a presence of ~4% *exo* isomer and less than 1% of heavier oligomers.

Separation of the products. Separations were done either by column chromatography or by preparative radial thin layer chromatography (Harrison Chromatotron). Separations on a small scale (up to ~1g) were done using Harrison Chromatotron on a 4 mm plate. Separations on a larger scale were done by gravity column chromatography. *Exo* isomer was eluted first closely followed by the *endo* isomer. *Exo* isomer exhibited tailing and sometimes continued to elute even after elution of the *endo* isomer was completed. Thus, the *endo* isomer was usually contaminated by the *exo* isomer. Usually, a repeated chromatography was needed to obtain a pure *endo* isomer.

Scaled up experimental procedure. Maleic anhydride (33.81 g, 0.345 mol) was placed in a 200 mL round bottom flask equipped with a condenser. It was heated with stirring until it began to boil. Dicyclopentadiene (24.9 mL, 0.150 mol) was added in a single portion and the reaction was continued until the reflux stopped and the reaction mixture turned yellow (~25 min). Column chromatography on silica gel (10 cm x 40 cm) eluting with ethyl acetate: acetone: hexanes (1:2:6 by volume) gave a pure *exo* isomer (15.7 g, 32%) and a mixture of *exo* and *endo* isomers. The mixture was chromatographed again using the same column. Additional 4.4 g (9%, or 41% combined yield) of *exo* isomer were obtained as well as 21.3 g (43%) of 93:7 mixture (GLC analysis) of *endo* and *exo* isomers.

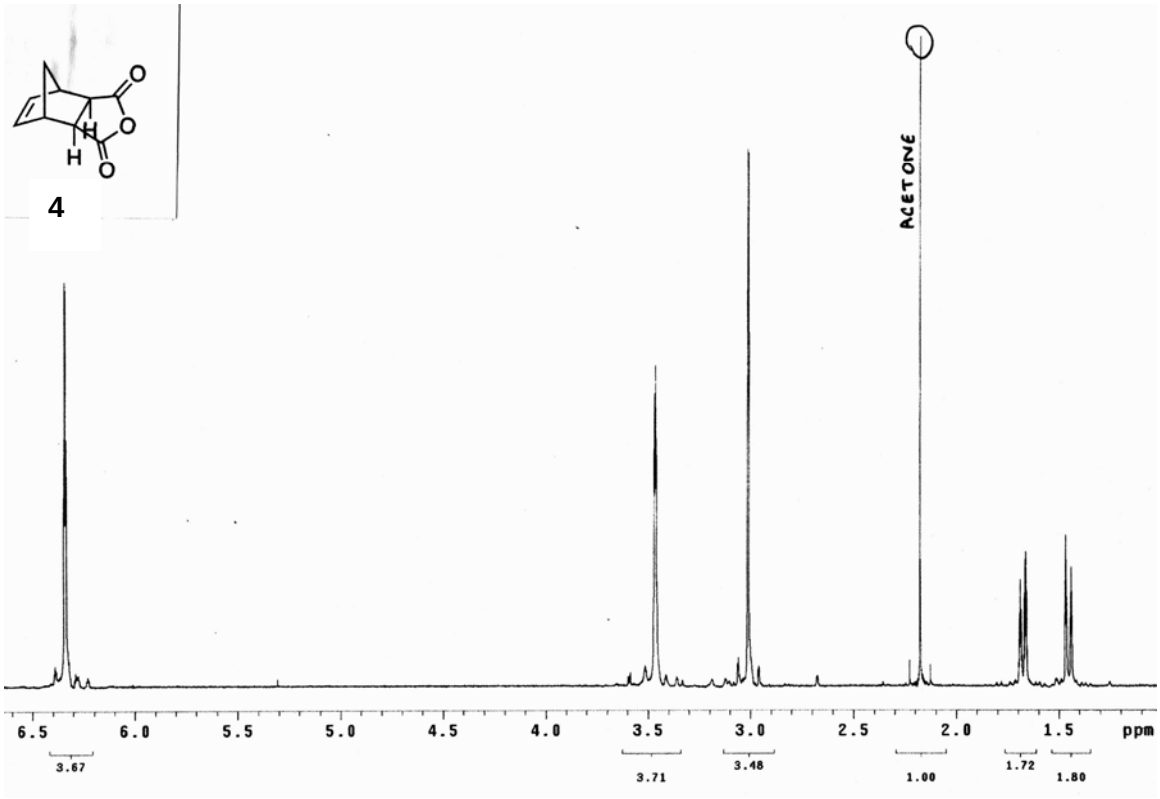
Reaction was also done on twice the scale (67.6 g maleic anhydride and 49.8 mL dicyclopentadiene in 300 mL flask refluxed for 30 min), but separation of the isomers was not attempted. GC-MS analysis showed that, in the crude product mixture, *exo* and *endo* isomers were present in the amounts of 47% and 42%, respectively.

Preparation of 5-norbornene-2-carboxylic acid. Dicyclopentadiene (3.31 g, 0.025 mol) and hydroquinone (0.0100g) were placed in a 50 mL round bottom flask and stirred for 10 minutes. Mixture was heated to 160ºC and acrylic acid (3.61 g, 0.050 mol) was added over a period of one hour. Heating was continued for another 6 hours. Column chromatography on silica gel (4 cm x 20 cm) eluting with ethyl acetate: hexanes (1:2 by volume) give a mixture of *exo*- and *endo*- methyl 5-norbornene-2-carboxylate (2.76 g, 40% yield).

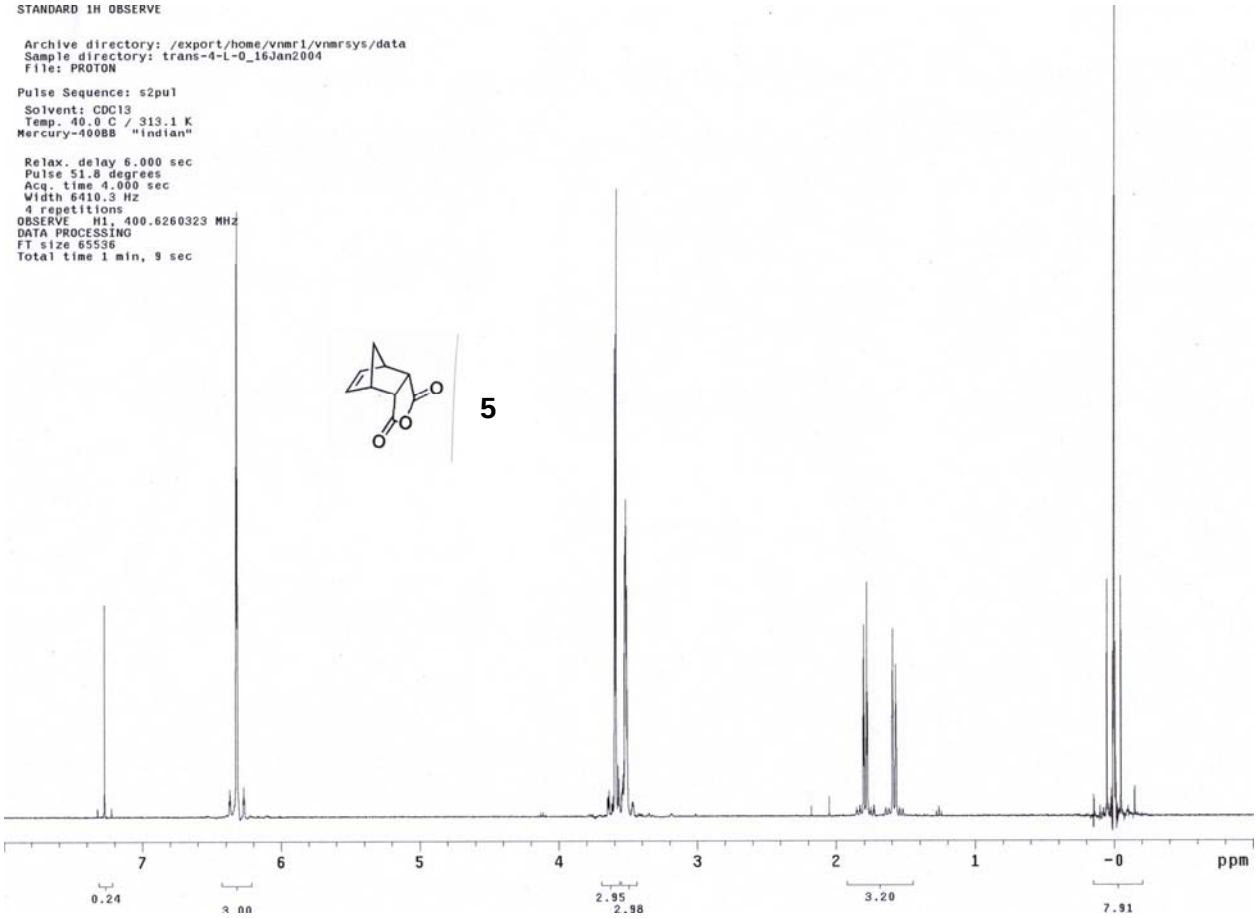
Preparation of methyl 5-norbornene-2-carboxylate by inverse addition. Acrylic acid (3.61 g, 0.050 mol) and hydroquinone (0.0100g) were placed in a 50 mL round bottom flask. Mixture was heated to 160ºC and dicyclopentadiene (3.31 g, 0.025 mol) was added over a period of three hours. Heating was continued for another 30 minutes. Methanol (20 mL) and sulfuric acid (0.5 mL) were added to the resulting mixture and the reflux was continued for 1 h. The resulting solution was partitioned between water and ethyl acetate. Ethyl acetate extract was rinsed with water, aqueous $NaHCO_3$, aqueous NaCl, dried (anh. $MgSO_4$) and chromatographed on silica gel (4 cm x 30 cm) eluting with ethyl acetate-hexanes 1:4 to give methyl 5-norbornene-*exo*-2-carboxylate (2.28 g, 30% overall yield) and methyl 5-norbornene-*endo*-2-carboxylate (2.43 g, 32% overall yield).

^{1}H NMR Spectra. All of the isolated compounds are known and their ^{1}H NMR spectra have been reported (**4**,[1] **5**,[2] **7**,[3] **8**,[3] **9**,[4] **12**,[5] 5-norbornene-2-carboxylic acid[6] and methyl 5-norbornene-2-carboxylate[7]).

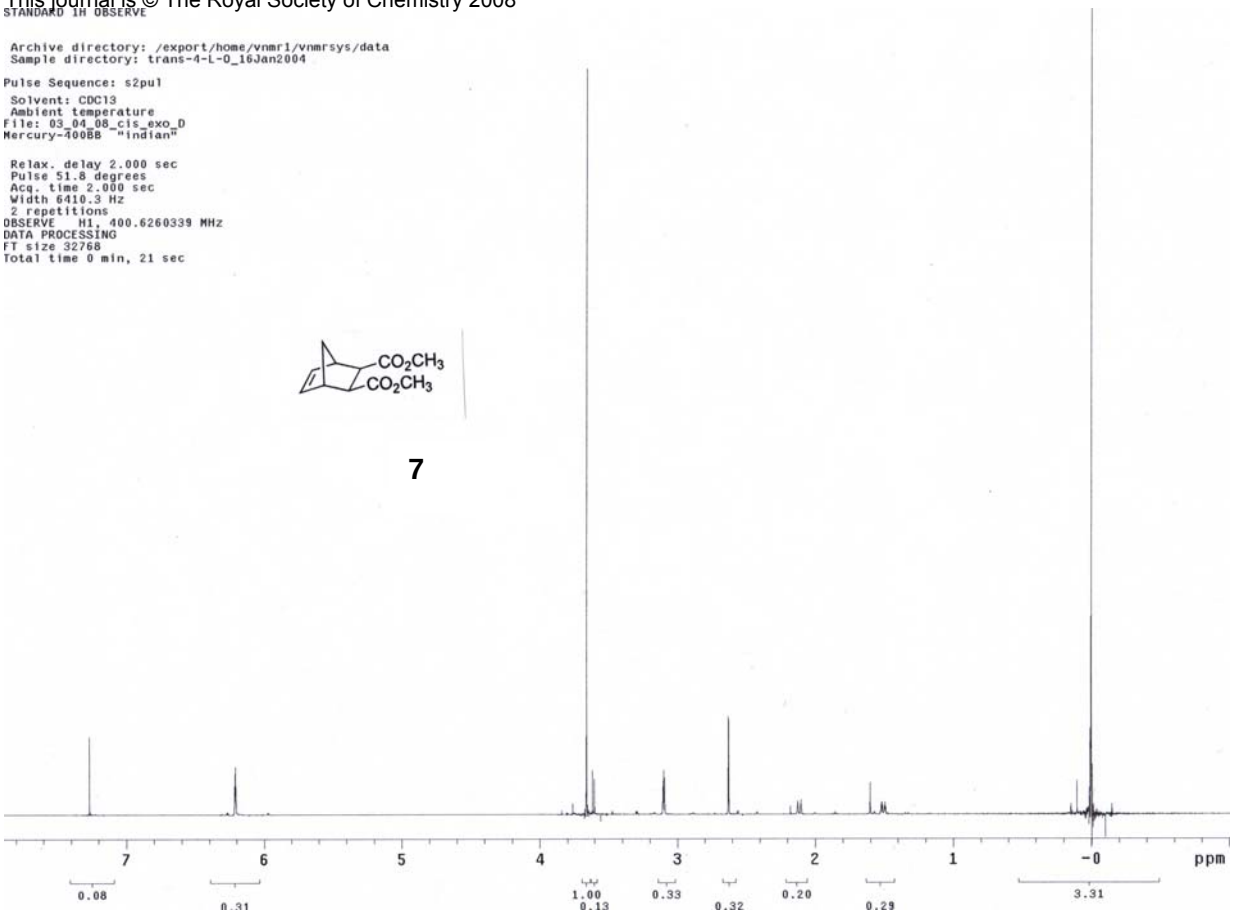
(2) ^{1}H NMR Spectra



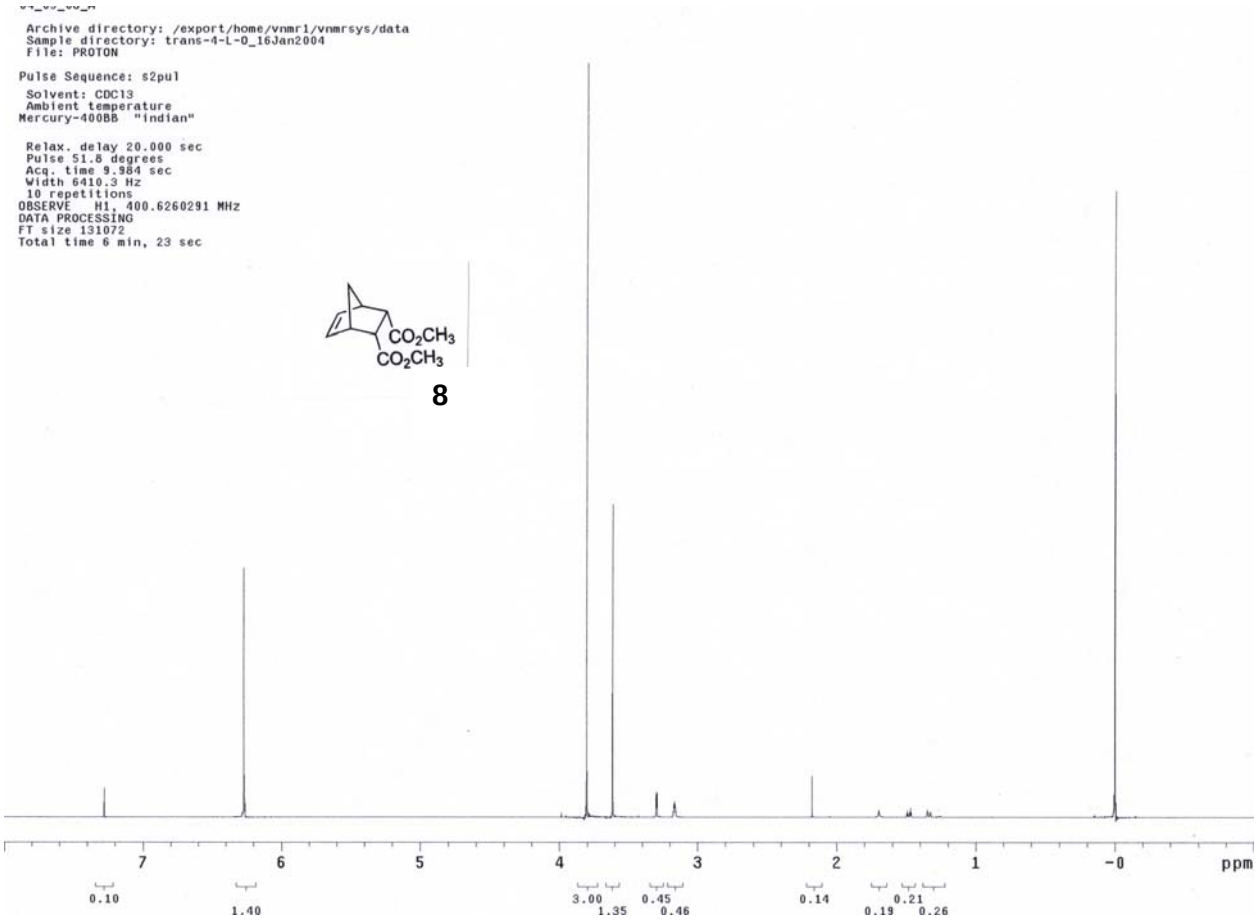
cis-5-norbornene-*exo*-2,3-dicarboxylic anhydride (**4**)



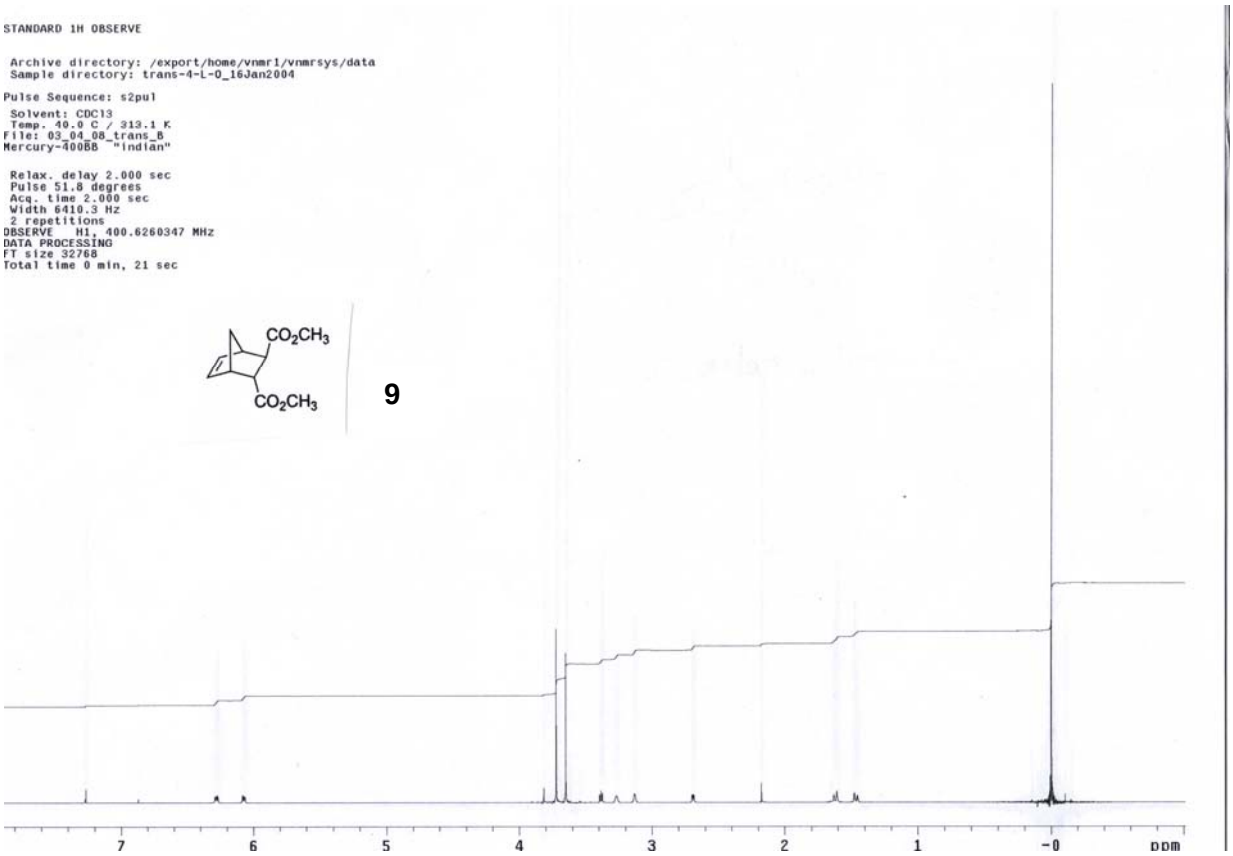
cis-5-norbornene-*endo*-2,3-dicarboxylic anhydride (**5**)



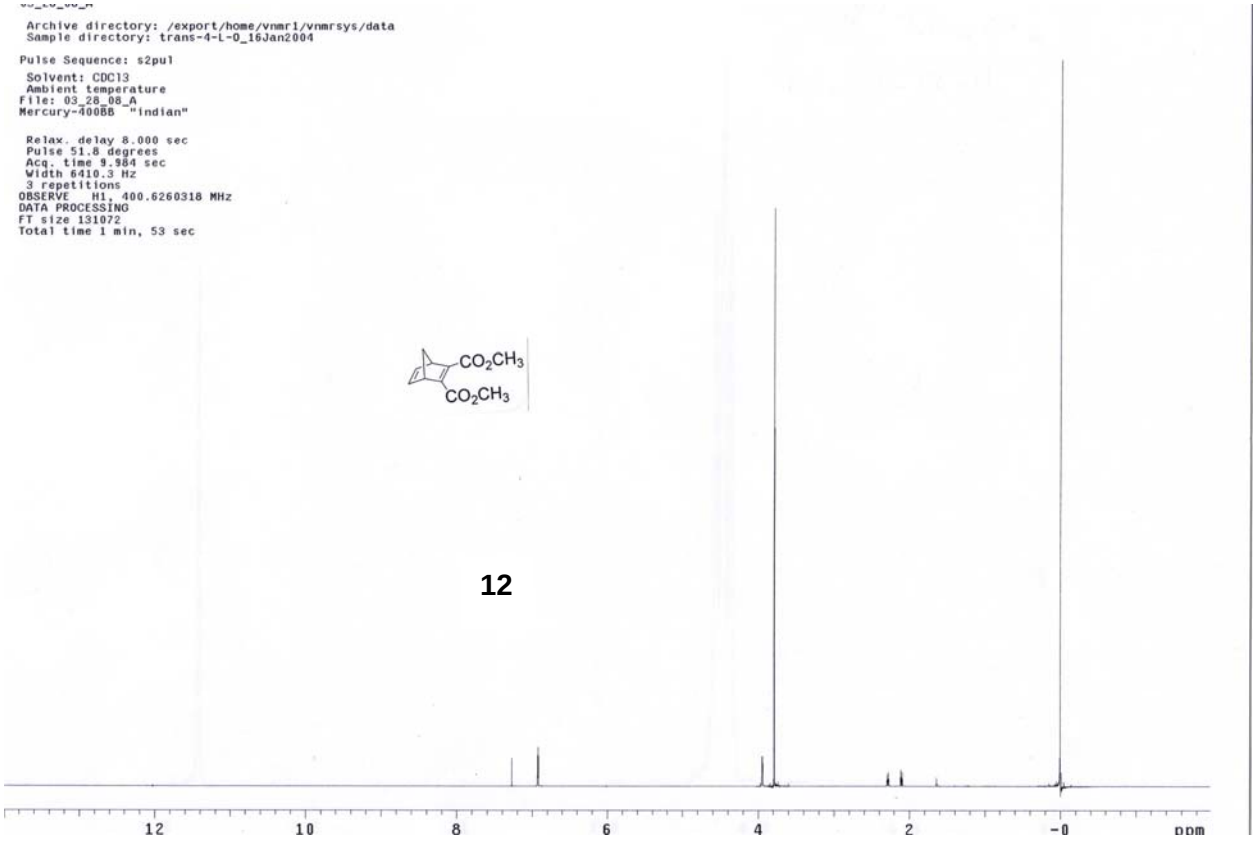
dimethyl *cis*-5-norbornene-*exo*-2,3-dicarboxylate (**7**)



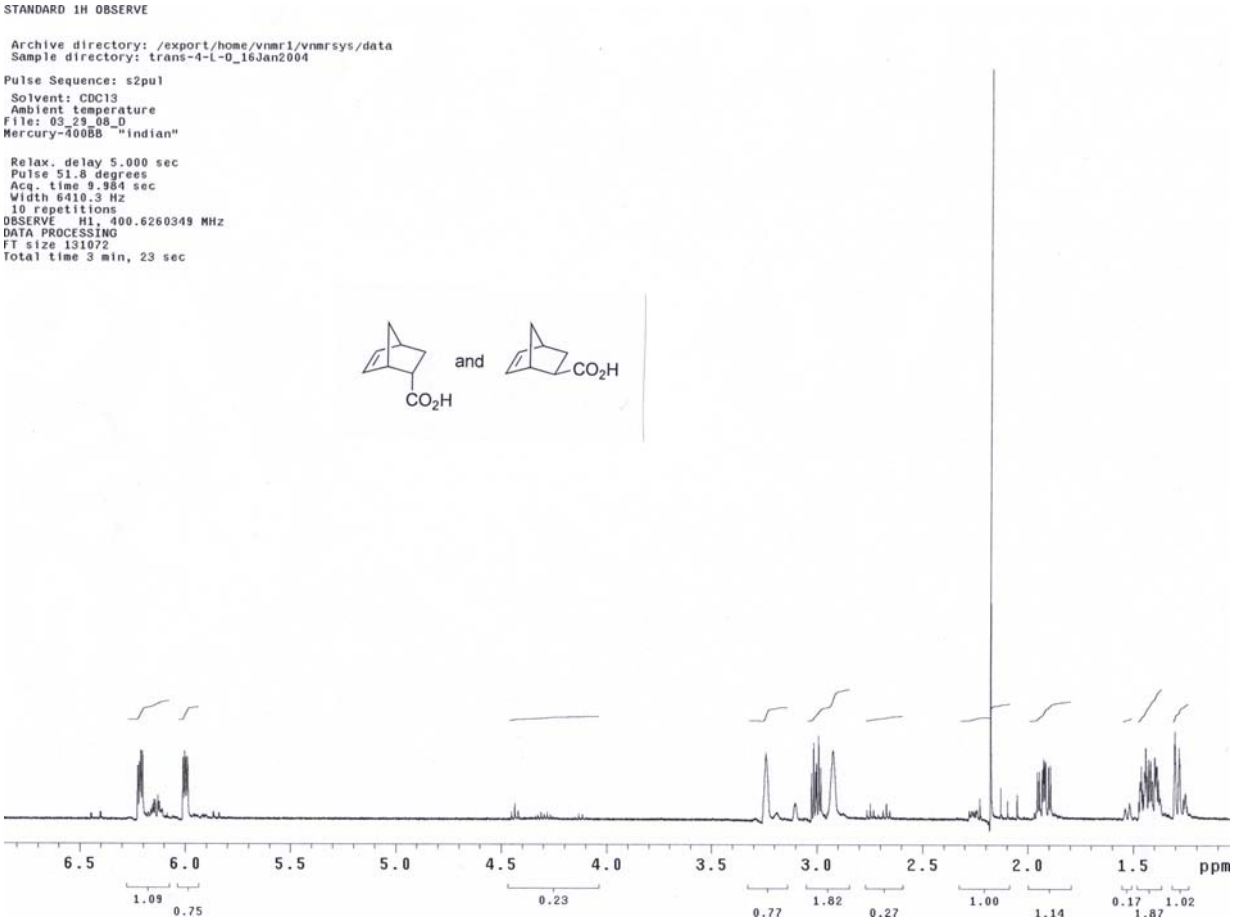
dimethyl *cis*-5-norbornene-*endo*-2,3-dicarboxylate (**8**)



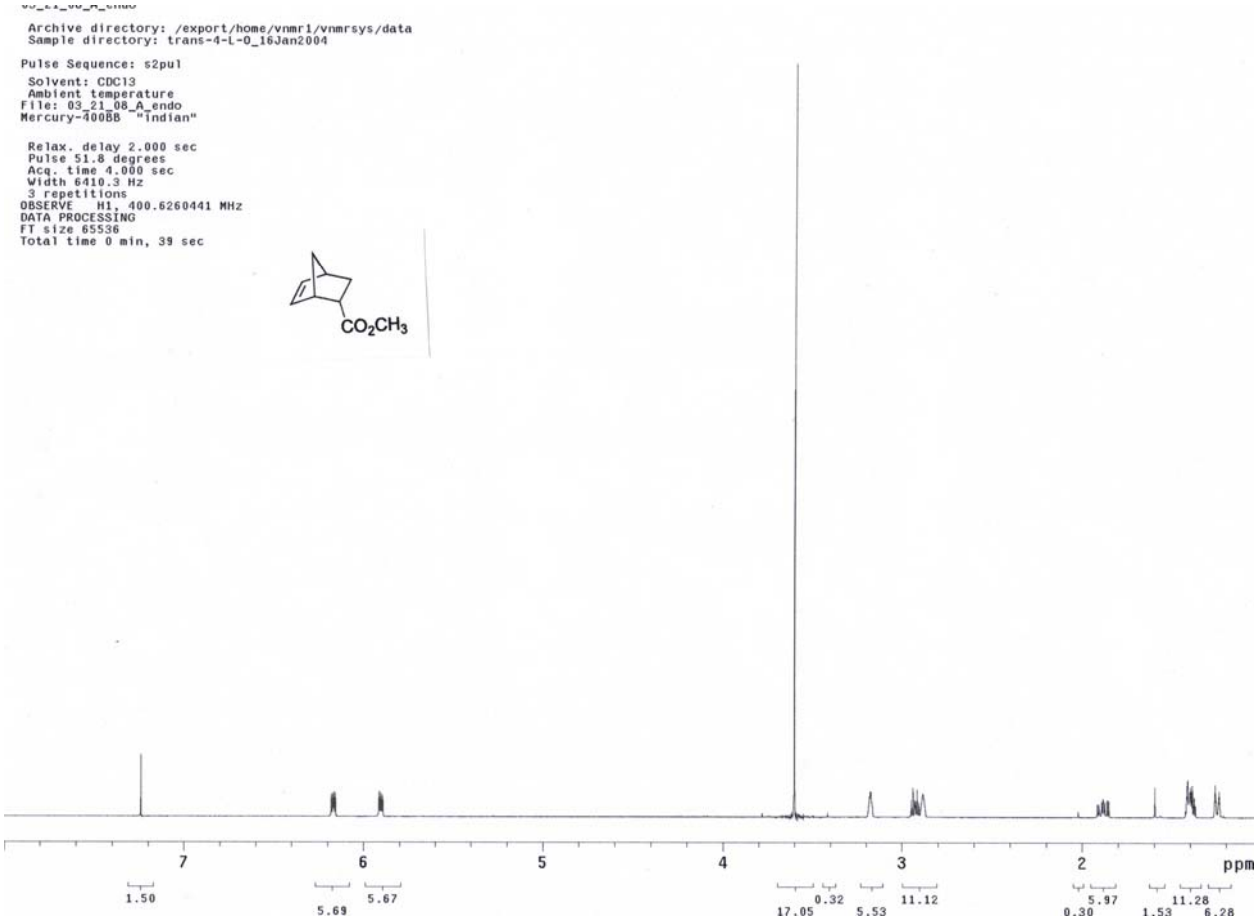
dimethyl 5-norbornene-2-*endo*,3-*exo*-dicarboxylate (**9**)



dimethyl bicyclo[2,2,1]hept-2,5-diene-2,3-dicarboxylate (**12**)



5-norbornene-2-carboxylic acid.



methyl 5-norbornene-*endo*-2-carboxylate.

References

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