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Supporting Information

A Materials Approach to Site-Isolation of the Grubbs' Catalysts from Incompatible Solvents and Reagent

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General procedure for olefin metathesis reactions. Cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester. In a glove box, Grubbs' second generation catalyst (43 mg, 0.05 mmole) was placed in a PDMS thimble contained in a Schlenk flask. The flask was sealed, removed from the glove box, and placed under N_2. Solvent mixtures (1 mL of 1/1 CH_2Cl_2/BMIM and 4 mL of 1/1 MeOH/H_2O) were added to the interior and exterior of the thimble. Next, diethyl diallylmalonate (300 μL, 1.25 mmoles) was added to the exterior of the thimble and the flask was placed in an oil bath maintained at 45 °C for 2.5 h. The reaction was cooled to room temperature and product extracted with 3 x 10 mL hexanes. The hexane extracts were dried over anhydrous $MgSO_4$, solvent was removed *in vacuo*, and the product was purified by passing through a silica gel column eluting with 5% EtOAc in hexanes to give the title compound as a light yellow liquid (0.25 mg, 1.16 mmoles, 93% yield). The ^{1}H and ^{13}C NMR data matched literature values.[1-3] ^{1}H NMR ($CDCl_3$): δ 1.26 (t, 6H, *J* = 7.2 Hz), 3.02 (br s, 4H), 4.21 (q, 4H, *J* = 7.2 Hz), 5.61 (br s, 2H). ^{13}C NMR ($CDCl_3$): δ 13.59, 40.38, 58.33, 61.04, 127.36, 171.68.

***N*-Tosyl-2,5-dihydropyrolle.** Reaction of *N*,*N*-diallyl tosylamine with Grubbs' second generation catalyst for 2 h gave the title compound in 83% yield. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[1,3] ^{1}H NMR ($CDCl_3$): δ 2.44 (s, 3H), 4.13 (s, 4H), 5.66 (s, 2H), 7.33 (d, 2H, *J* = 7.8 Hz), 7.71 (d, 2H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$): δ 21.52, 54.83, 125.43, 127.40, 129.75, 134.21, 143.42.

(*E*)-Stilbene. Reaction of styrene with Grubbs' second generation catalyst for 19 h gave the title compound in 94% yield. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[4,5] ^{1}H NMR ($CDCl_3$): δ 7.11 (s, 2H), 7.25 (tt, 2H, *J* = 7.2, 1.2 Hz), 7.34 (m, 4H), 7.50 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 126.51, 127.62, 128.65, 128.68, 137.28.

(*E*)-4,4'-Acetoxystilbene. Reaction of 4-acetoxystyrene with Grubbs' second generation catalyst for 5 h gave the title compound in 80% yield. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[6-8] ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 6H), 7.04 (s, 2H), 7.08 (d, 4H, *J* = 8.4 Hz), 7.51 (d, 4H, *J* = 8.4

Hz). ^{13}C NMR ($CDCl_3$): δ 21.15, 121.81, 127.40, 127.87, 134.96, 150.07, 169.46. HRMS: calculated for $C_{16}H_{16}O_4$ 296.1049, Found: 296.1052.

(*E)*-4,4'-Dimethylstilbene. Reaction of 4-methylstyrene with Grubbs' second generation catalyst for 8.5 h gave the title compound in 76% yield. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[4,6,9-11] ^{1}H NMR ($CDCl_3$): δ 2.34 (s, 6H), 7.03(s, 2H), 7.14 (d, 4H, *J* = 7.8 Hz), 7.39 (d, 4H, *J* = 7.8 Hz). ^{13}C NMR ($CDCl_3$): δ 21.22, 126.29, 127.62, 129.34, 134.72, 137.23.

Procedure for metathesis-epoxidation cascade reactions. Diethyl 6-oxa-bicyclo[3.1.0]hexane-3,3-dicarboxylate. In a glove box, Grubbs' second generation catalyst (43 mg, 0.05 mmole) was placed in a PDMS thimble contained in a Schlenk flask. The flask was sealed, removed from the glove box, and placed under N_2. Solvent (1 mL of 1/1 CH_2Cl_2/BMIM) was added to the interior of the thimble followed by diethyl diallylmalonate (300 μL, 1.25 mmoles). The reaction mixture was allowed to stir at ambient conditions for 3 h after which the flask was slowly charged with MCPBA (1 g, 3.7 mmole in 8 mL of 1/1 MeOH/water) on the exterior of the thimble and allowed to continue stirring for a further 12 h. Solvent on the exterior of the thimble was removed, washed repeatedly with saturated $NaHCO_3$, and extracted using 3 x 10 mL CH_2Cl_2. Thimble contents were extracted with 10 mL of hexanes. The hexane and CH_2Cl_2 extracts were pooled, washed with brine, and dried over anhydrous $MgSO_4$. Solvent was then removed *in vacuo* and the product was purified using a silica gel column eluting with 10% EtOAc in hexanes to give the target epoxide in 71 % yield (0.203 g, 0.89 mmoles). ^{1}H NMR ($CDCl_3$): δ 1.21-1.30 (overlapping triplets, 6H), 2.20 (d, 2H, *J* = 14.7 Hz), 3.03 (d, 2H, *J* = 14.7 Hz), 3.53 (s, 2H), 4.15-4.22 (2 overlapping quartets, 4H). ^{13}C NMR ($CDCl_3$): δ 13.80, 13.82, 31.43, 35.70, 55.36, 55.61, 61.48, 61.82, 170.76, 171.06. HRMS (m/z): Calcd for $C_{11}H_{16}O_5$: 228.0998; found, 228.0998.

***trans*-Stilbene oxide.** Reaction of styrene with Grubbs' second generation catalyst for 6 h, followed by reaction of the subsequent product with 5 equivalents of site-isolated MCPBA for 14 h gave *trans*-stilbene oxide in 83% yield. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[12-14] ^{1}H NMR ($CDCl_3$): δ 7.33-7.38 (m, 10H), 3.87 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 62.81, 125.47, 128.29, 128.53, 137.07.

***trans*-2,3-Bis(4-acetoxyphenyl)oxirane.** Reaction of 4-acetoxystyrene with Grubbs' second generation catalyst for 6 h, followed by reaction of the subsequent product with 5 equivalents of site-isolated MCPBA for 9 h gave the target epoxide, in 67% yield. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[8] ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 3H) 3.82 (s, 1H), 7.19-7.24 (overlapping doublets, 4H). ^{13}C NMR ($CDCl_3$): δ 21.20, 62.77, 125.41, 129.21, 134.21, 138.06.

***trans*-2,3-Bis(4-(chloromethyl)phenyl)oxirane.** Reaction of 4-vinylbenzyl chloride with Grubbs' second generation catalyst for 5 h, followed by reaction of the subsequent product with 5 equivalents of site-isolated MCPBA for 11 h gave target epoxide in 68% isolated yield. ^{1}H NMR ($CDCl_3$): δ 3.87 (s, 3H), 4.39 (s 1H), 6.95-7.22 (m, 8H). ^{13}C NMR ($CDCl_3$): δ 62.81, 125.47, 128.29, 128.53, 137.07, 77.03, 51.44.

***trans*-2,3-Bis(4-methylphenyl)oxirane.** Reaction of 4-methylstyrene with Grubbs' second generation catalyst for 5 h, followed by reaction of the subsequent product with 5 equivalents of site-isolated MCPBA for 15 h gave target epoxide in 69% isolated yield. The ^{1}H and ^{13}C NMR spectra agreed with those reported in the literature.[5,12-14] ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 3H) 3.82 (s, 1H), 7.19-7.24 (overlapping doublets, 4H) ^{13}C NMR ($CDCl_3$): δ 21.20, 62.77, 125.41, 129.21, 134.21, 138.06.

Determination of amount of ruthenium that leached from the interior of the thimble under the conditions used in Figure 2 and reported in Table 2 in the text. In a glovebox, Grubbs' second generation catalyst (43 mg, 0.05 mmole) was placed in a PDMS thimble contained in a Schlenk flask. The flask was sealed, removed from the glove box, and placed under N_2. To interior of the thimble was added 1 mL of CH_2Cl_2/BMIM followed by diethyl diallylmalonate (300 μL, 1.25 mmoles). To the exterior of the thimble was added 4 of mL 1/1 MeOH/H_2O. After 4, 8, 12, and 16 h, an aliquot (0.5 mL) of solvent on the exterior of the thimble was removed and these samples were analyzed using ICP-MS for ruthenium concentration.

Determination of amount of ruthenium that leached during the recycling reactions as shown in Figure 5 in the text. In a glovebox, Grubbs' second generation catalyst (43 mg, 0.05 mmole) was placed in a PDMS thimble contained in a Schlenk flask. The flask was sealed, removed from the glove box, and placed under N_2. To the thimble was added 1 mL of CH_2Cl_2 followed by diethyl diallylmalonate (300 μL, 1.25 mmoles), and the reaction was left stirring for 1 h. To the exterior of the thimble, 20 mL of MeOH was added and allowed to stir for 1 h. All solvent on the exterior of the thimble was then removed and the concentration of ruthenium in the solvent was analyzed using ICP-MS. For cycles 2 through 4 we added an additional 20 mL of MeOH to the exterior of the thimble and allowed it to stir for 1 h. The solvent on the exterior was removed after each cycle and analyzed for ruthenium using ICP-MS. Our results are summarized below (Table 1).

Table 1. Summary of ICP-MS data showing that the Grubbs' catalyst remained >97% encapsulated for each recycling cycle.

Cycle	[a][Ru] (mg/mL)	[a][G2]$_{exterior}$ (mg/mL)	$\frac{[G2]_{interior}}{{}^{a}[G2]_{exterior}}$	[b]Total Ru in exterior (%)
1	0.007	0.060	720	2.8
2	0.007	0.056	760	2.6
3	0.006	0.054	770	2.6
4	0.004	0.034	1170	1.7

[a] These calculations assume that the Ru on the exterior was the Grubbs' catalyst. This assumption is unlikely, but it is used to illustrate the upper limit for how much of the Grubbs' catalyst (as opposed to Ru) leached from the interior of the thimbles. [b] Amount of Ru that leached from the interior to the exterior of the thimble

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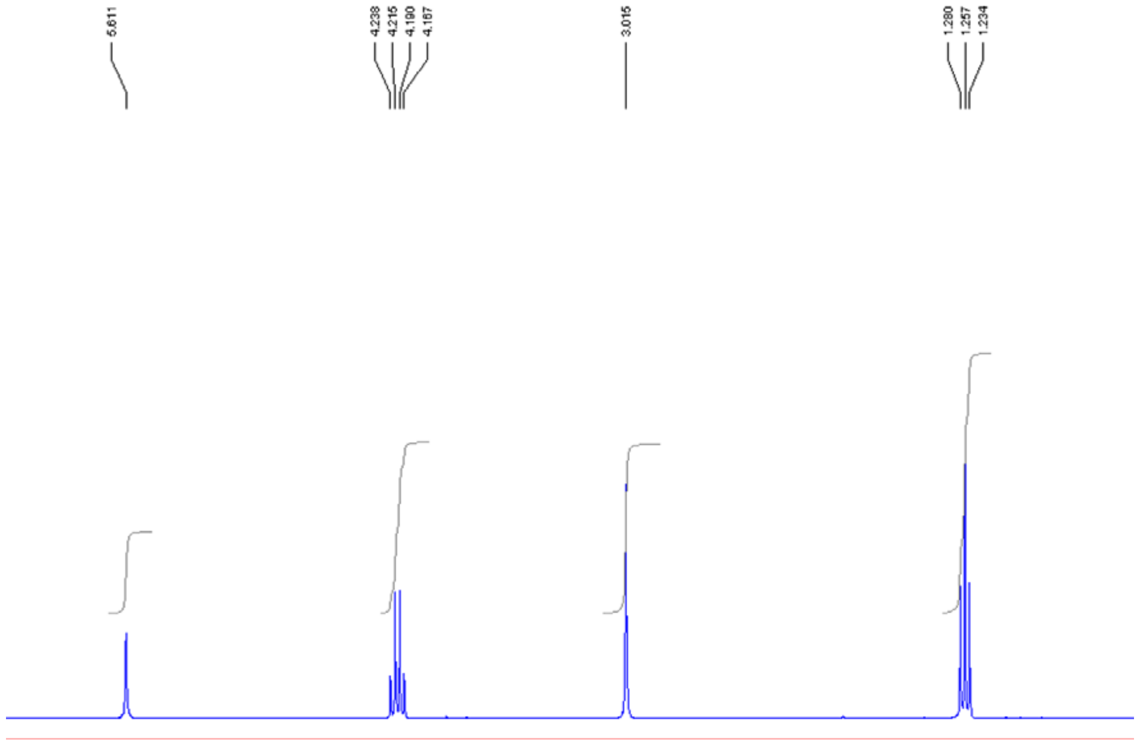
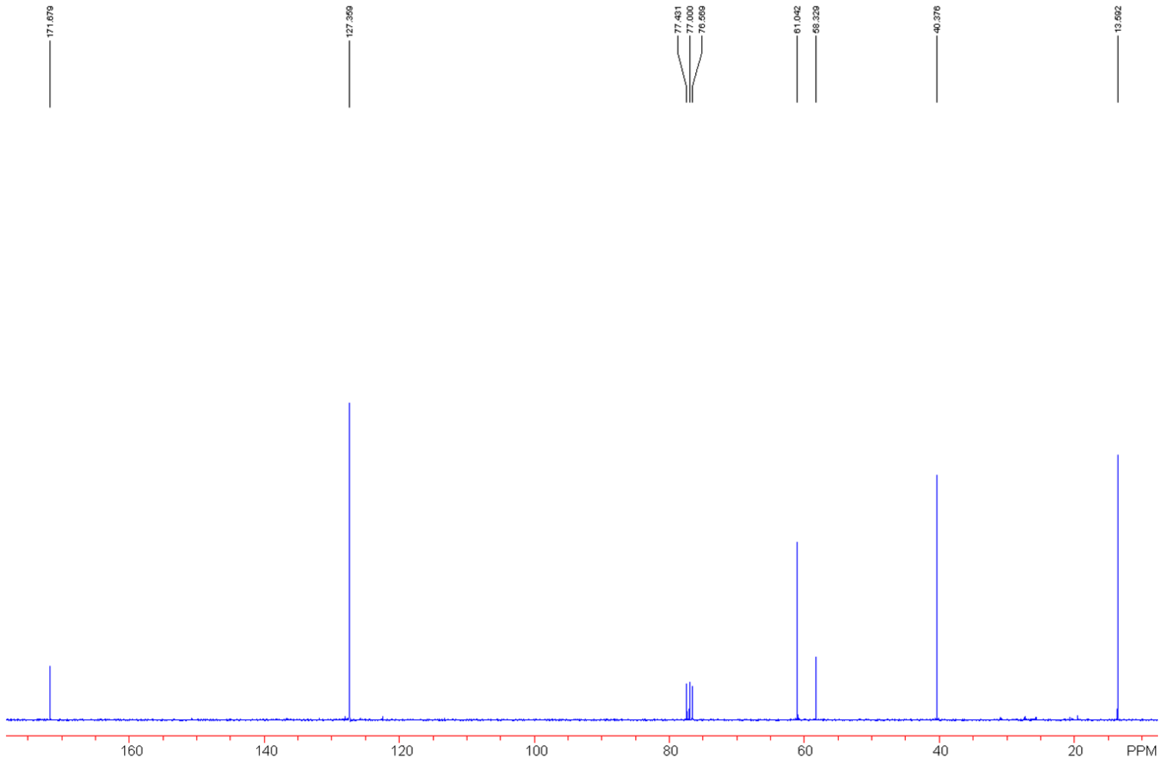
NMR spectra for all synthesized compounds.

Cyclopent-3-ene-1,1-dicarboxylic acid diethyl ester





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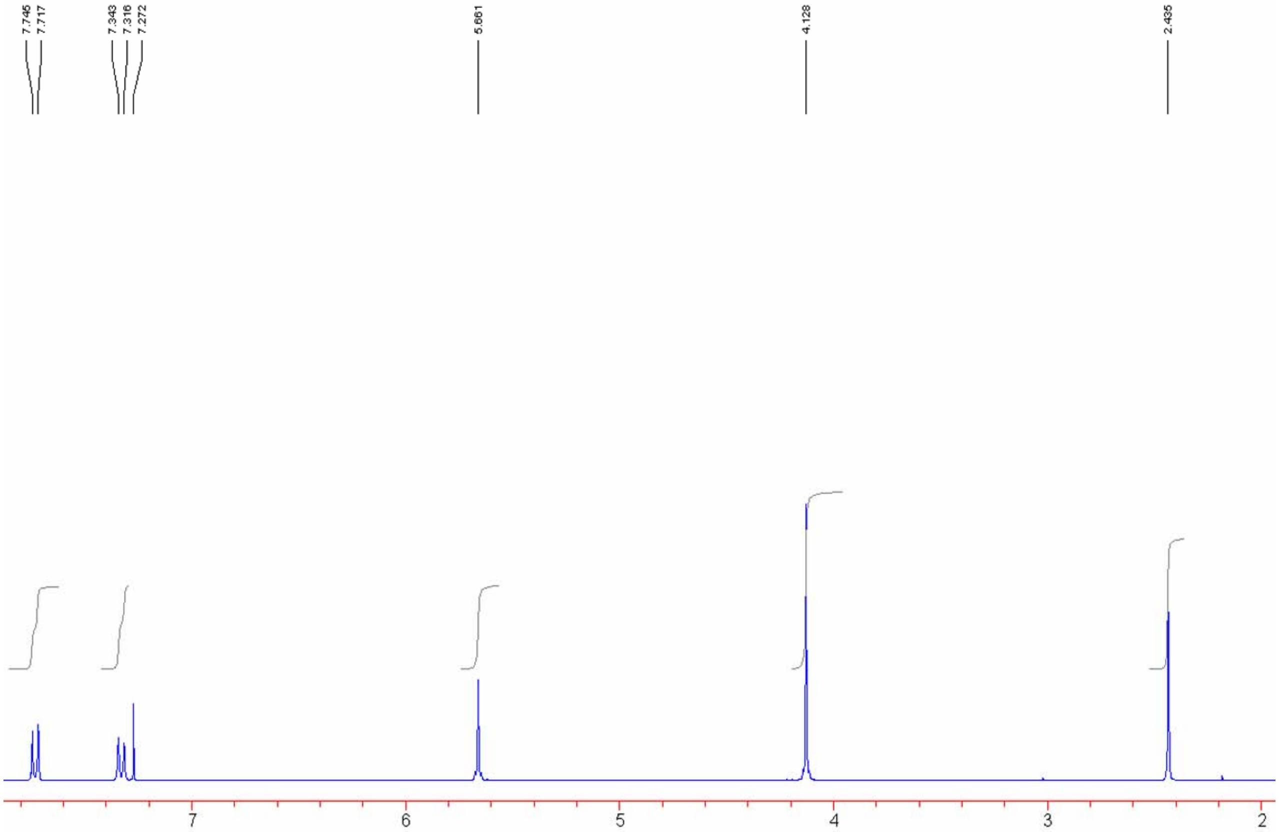

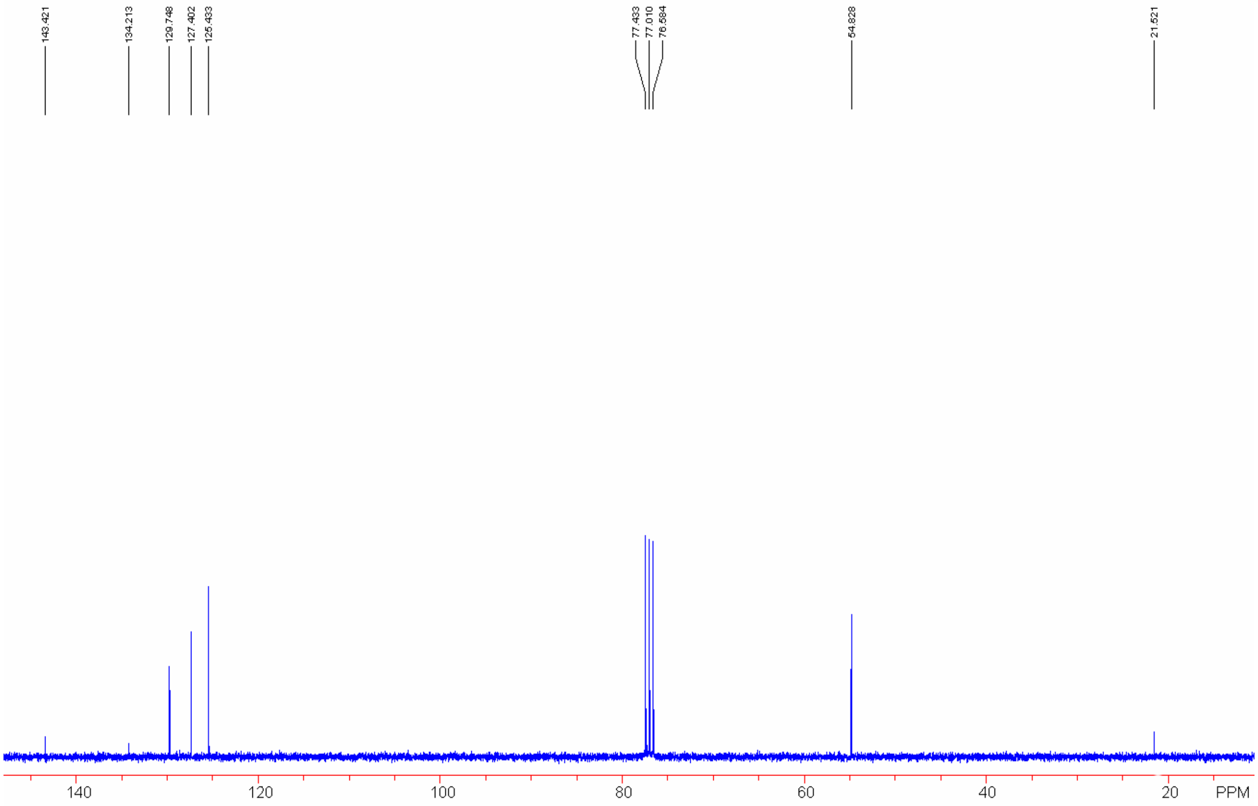

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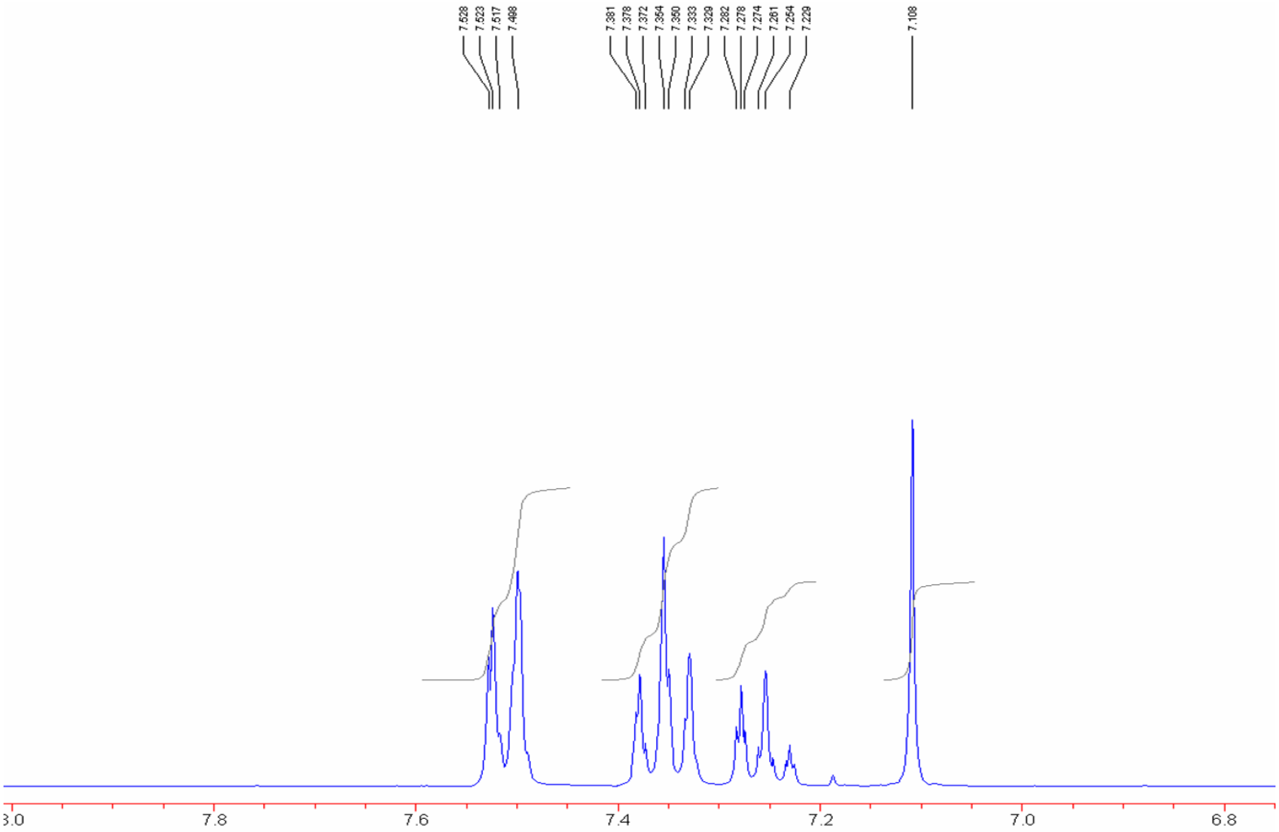
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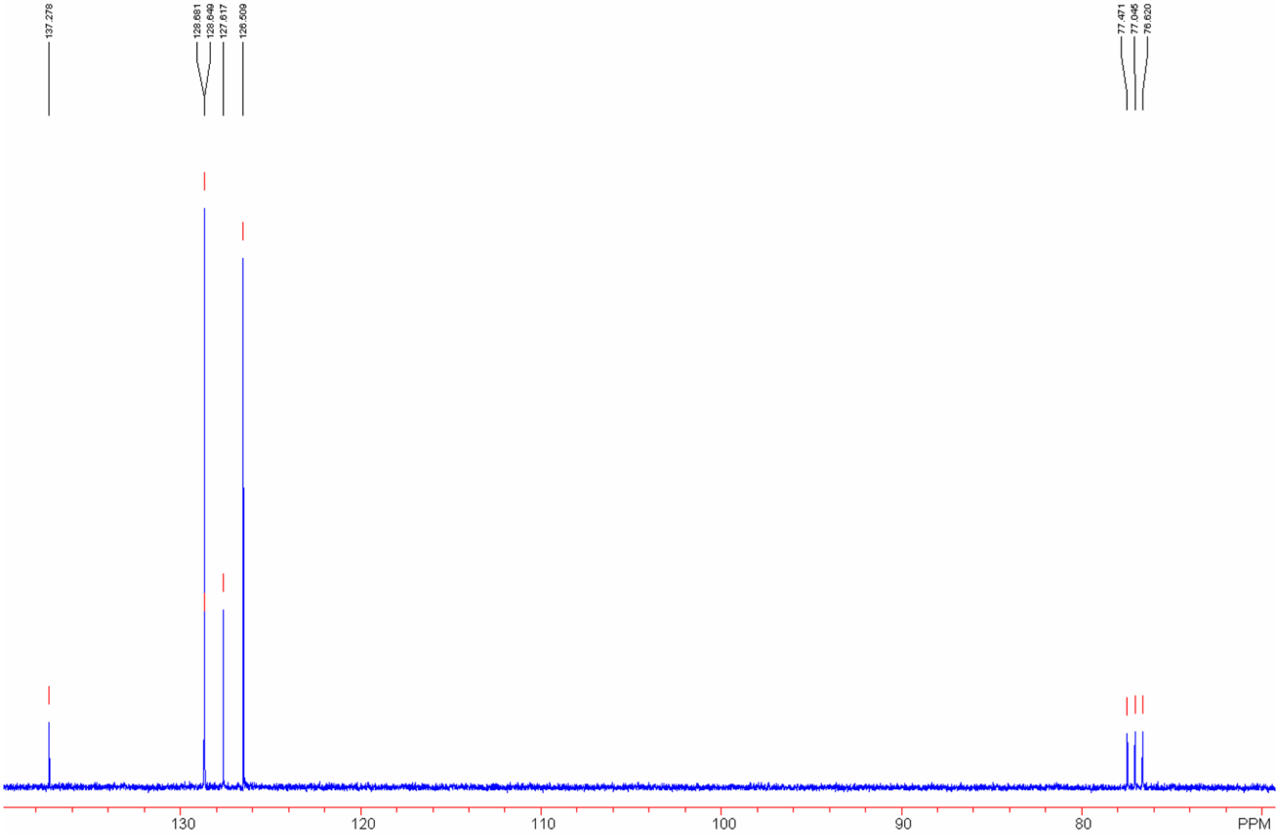
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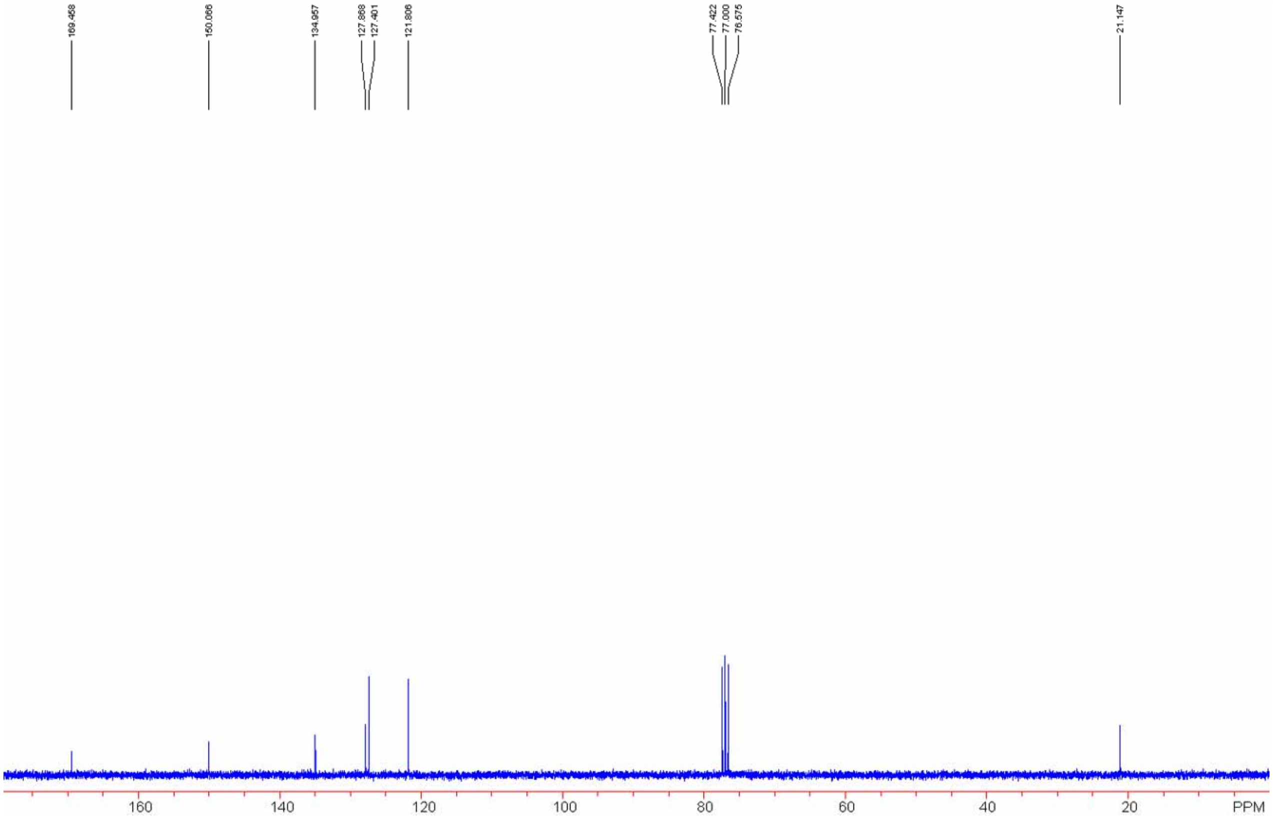

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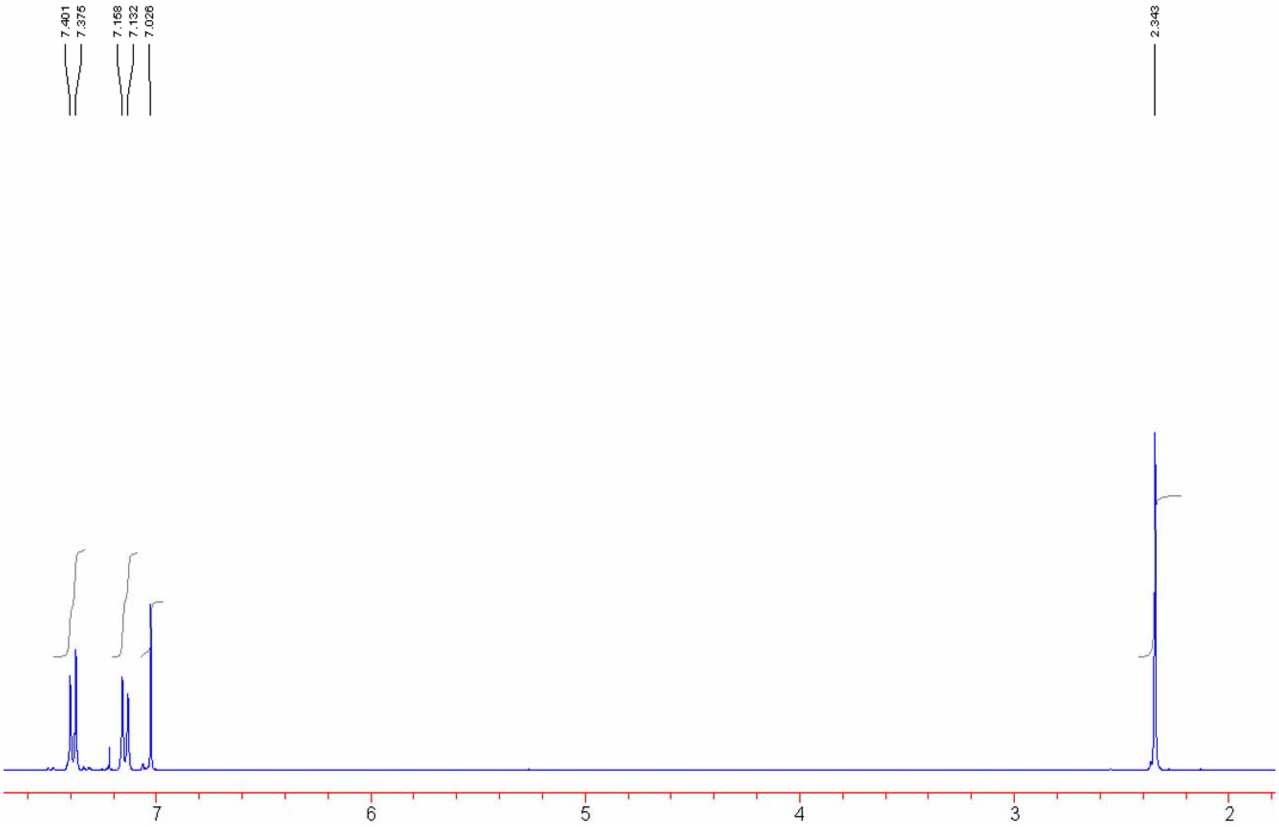
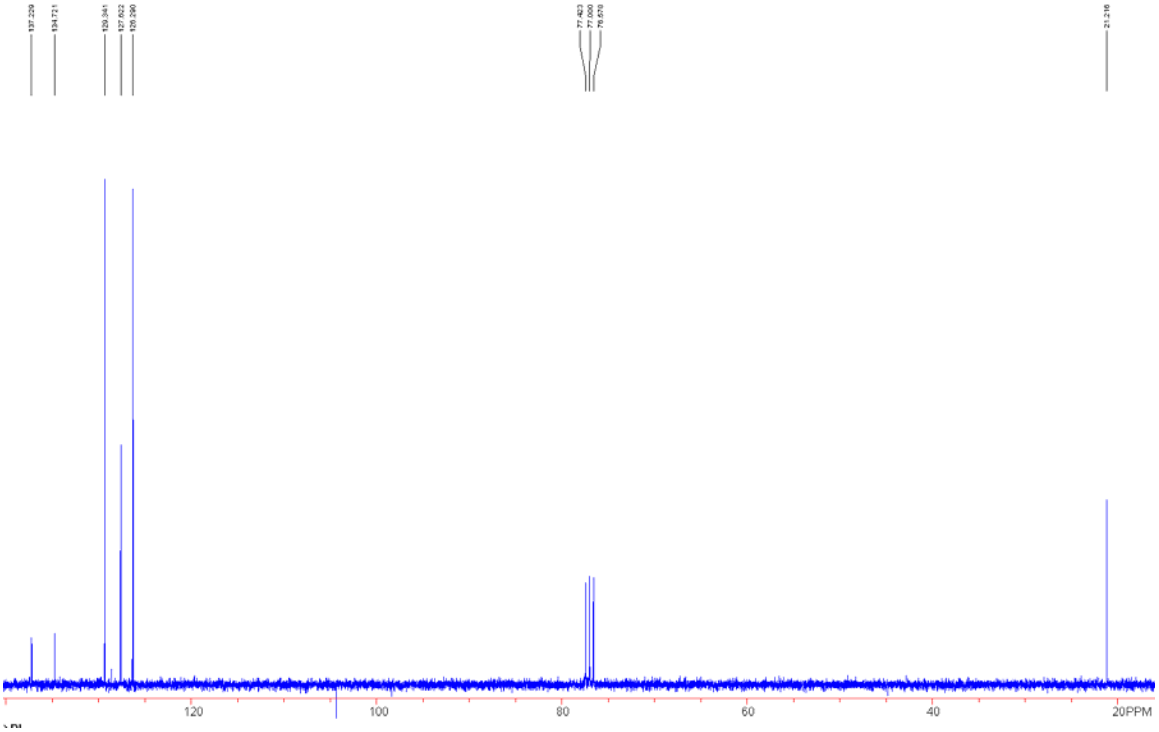
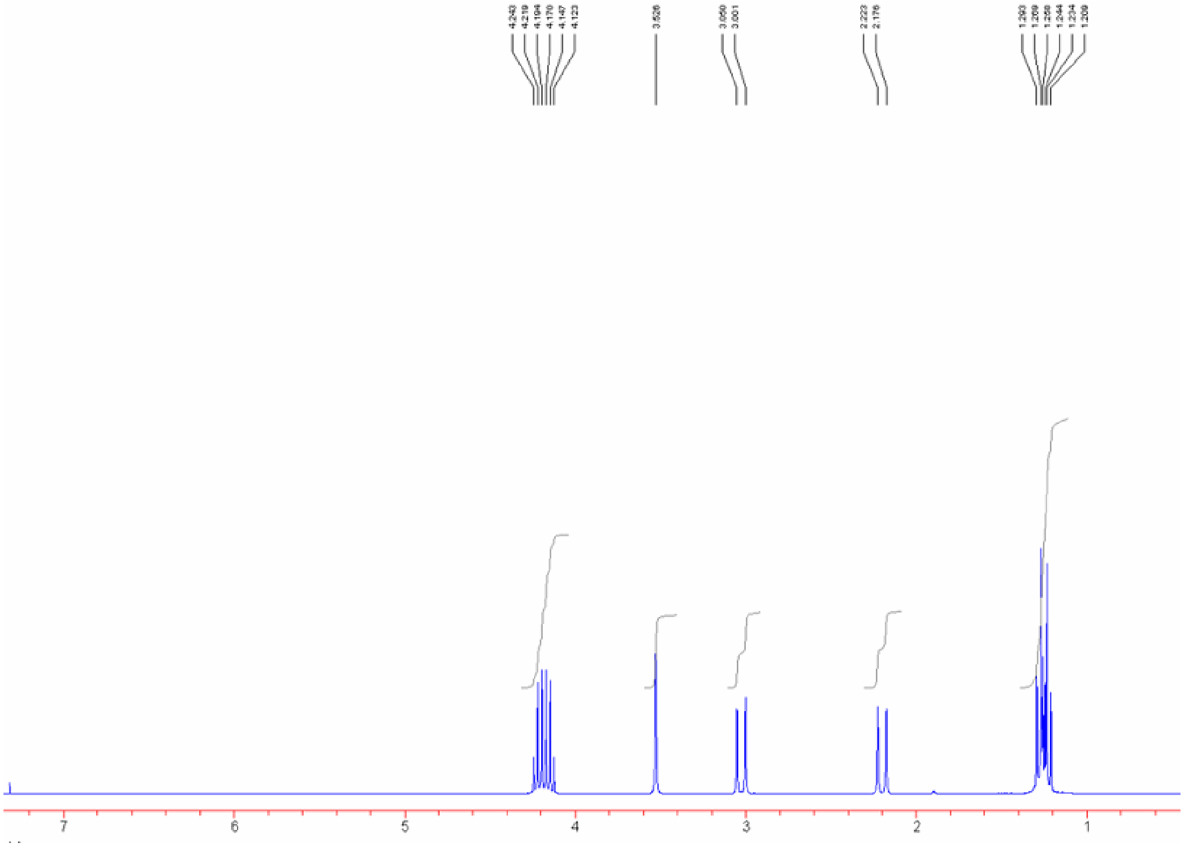
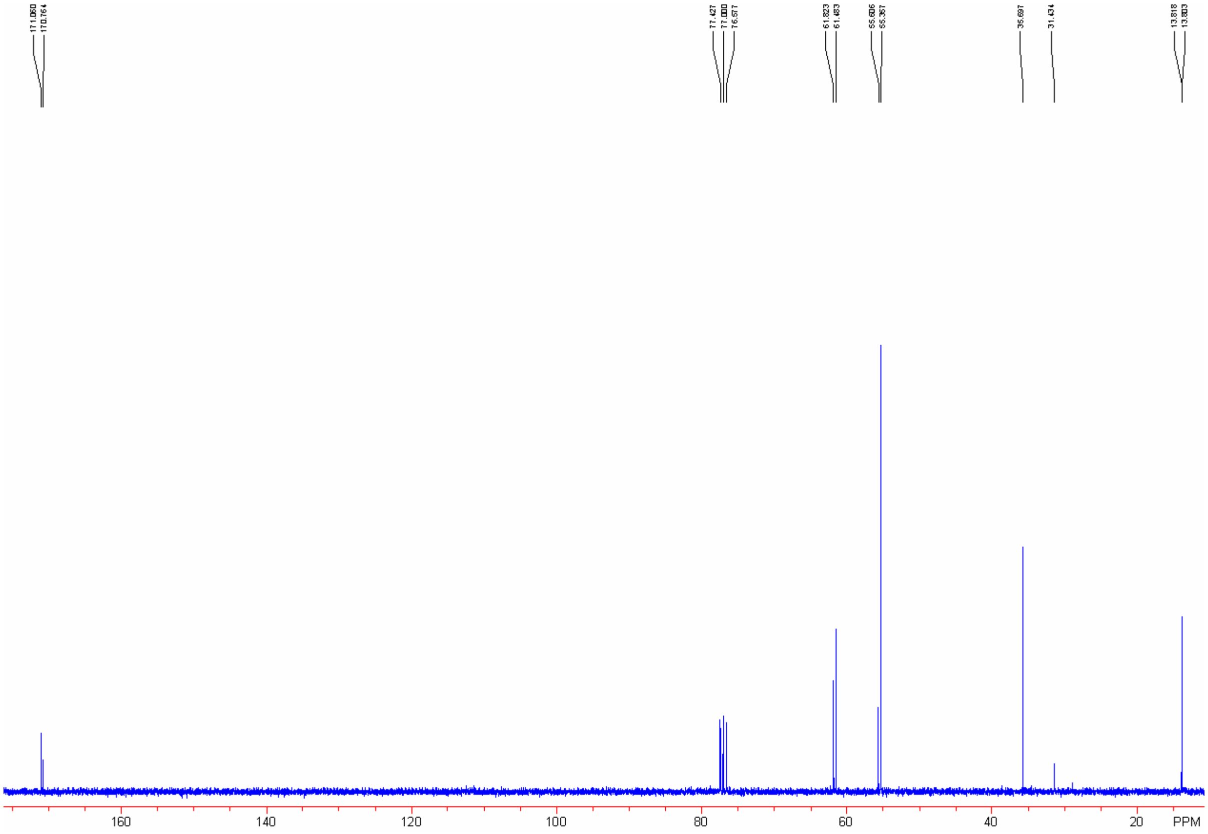


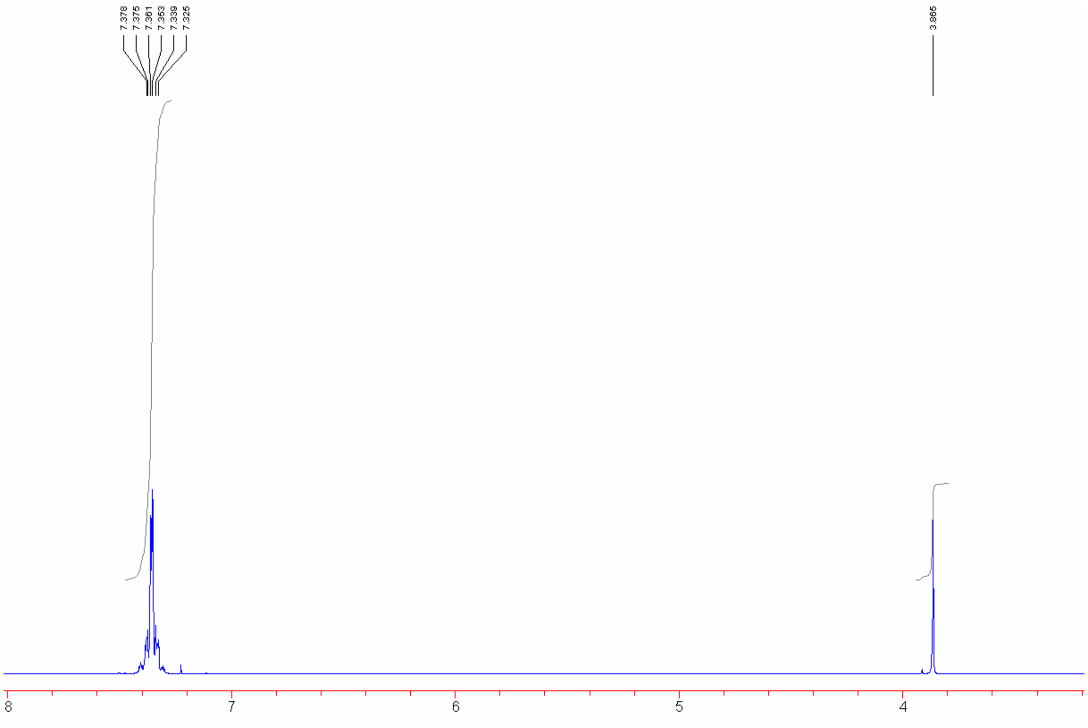


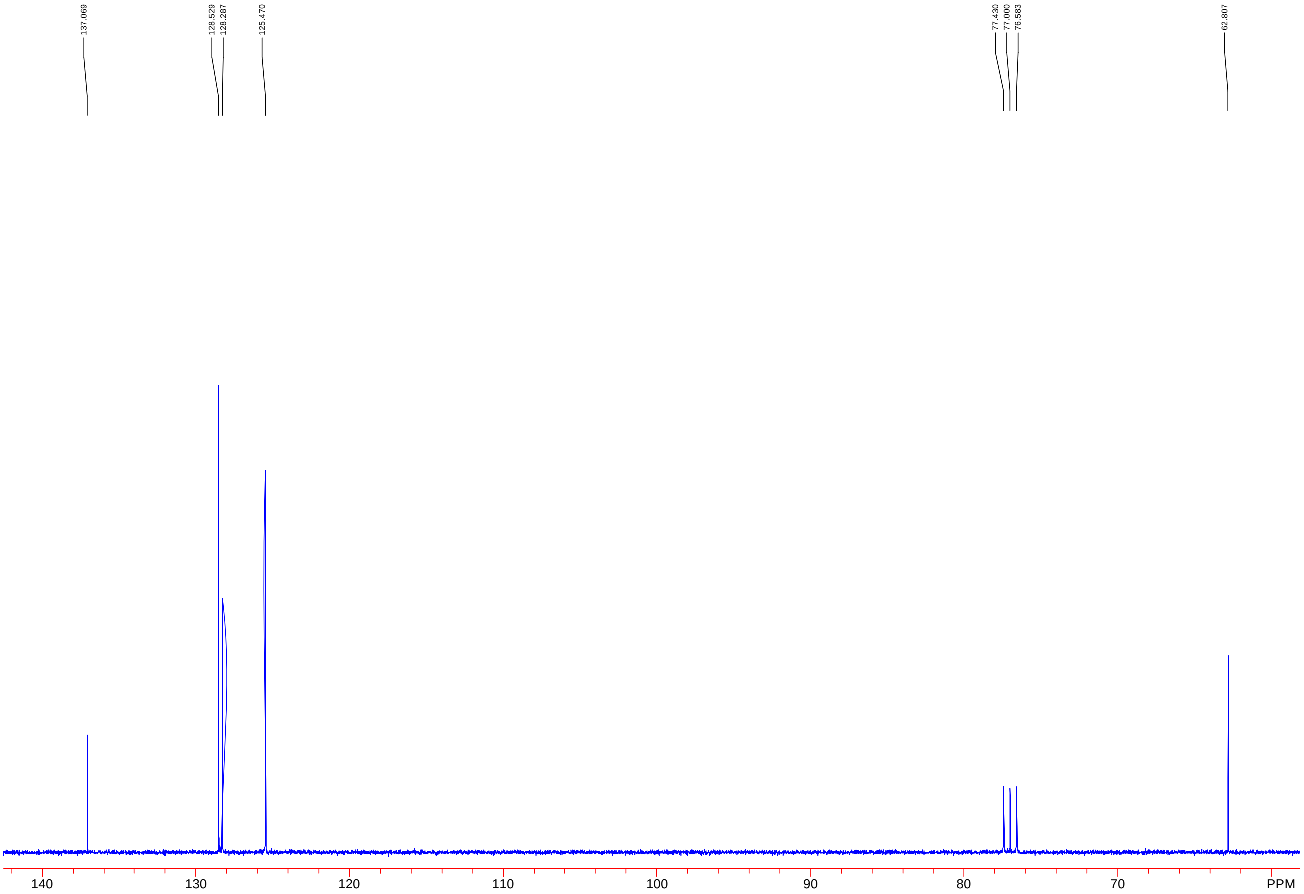
Diethyl 6-oxa-bicyclo[3.1.0]hexane-3,3-dicarboxylate





trans-stilbene oxide

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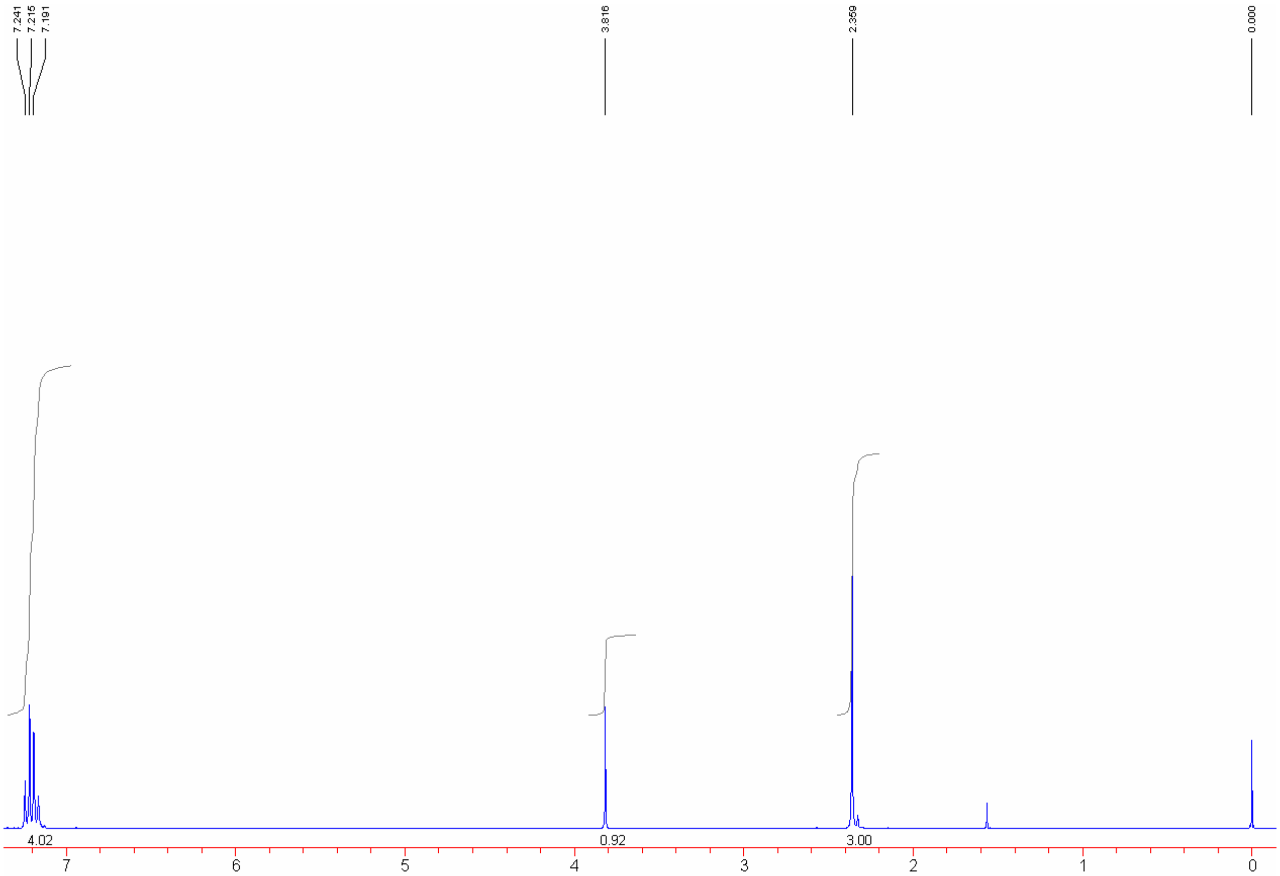
2,3-bis(4-methylphenyl)oxirane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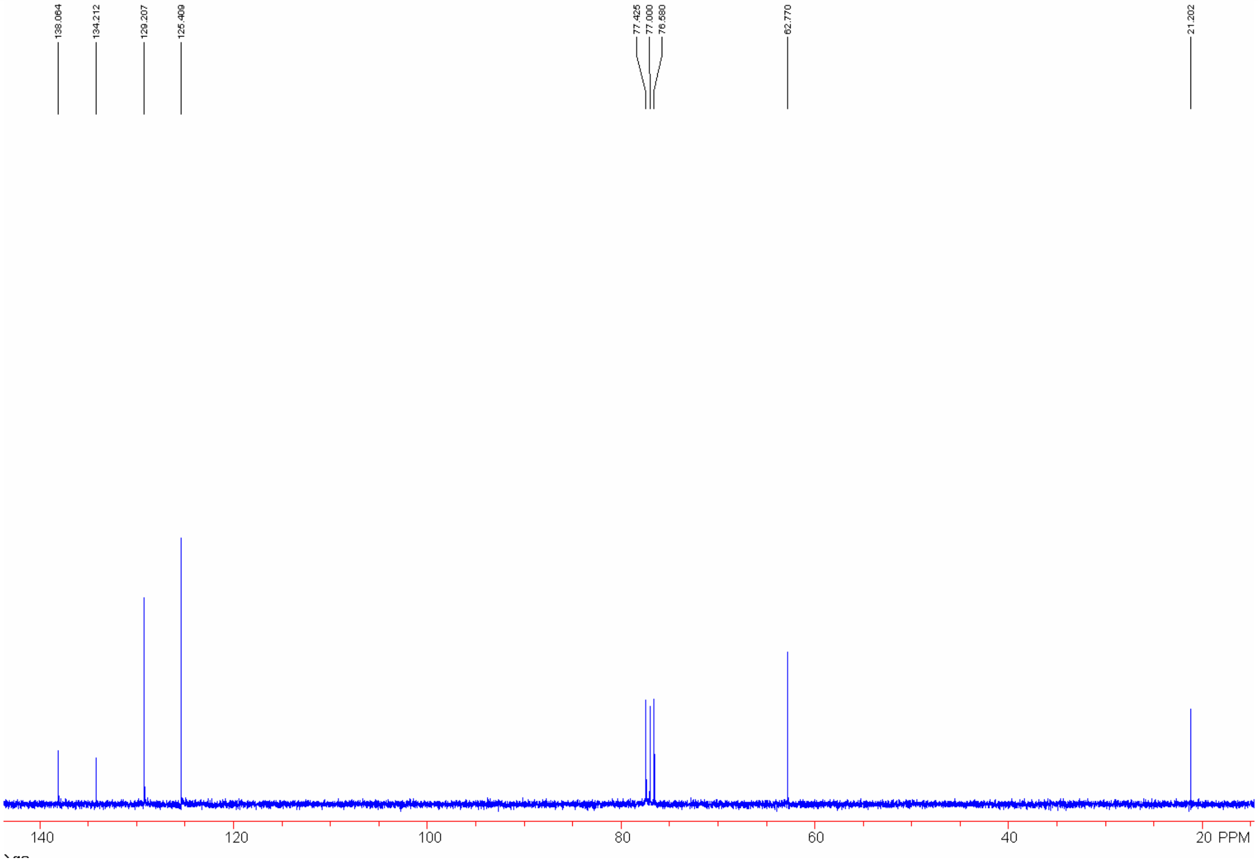
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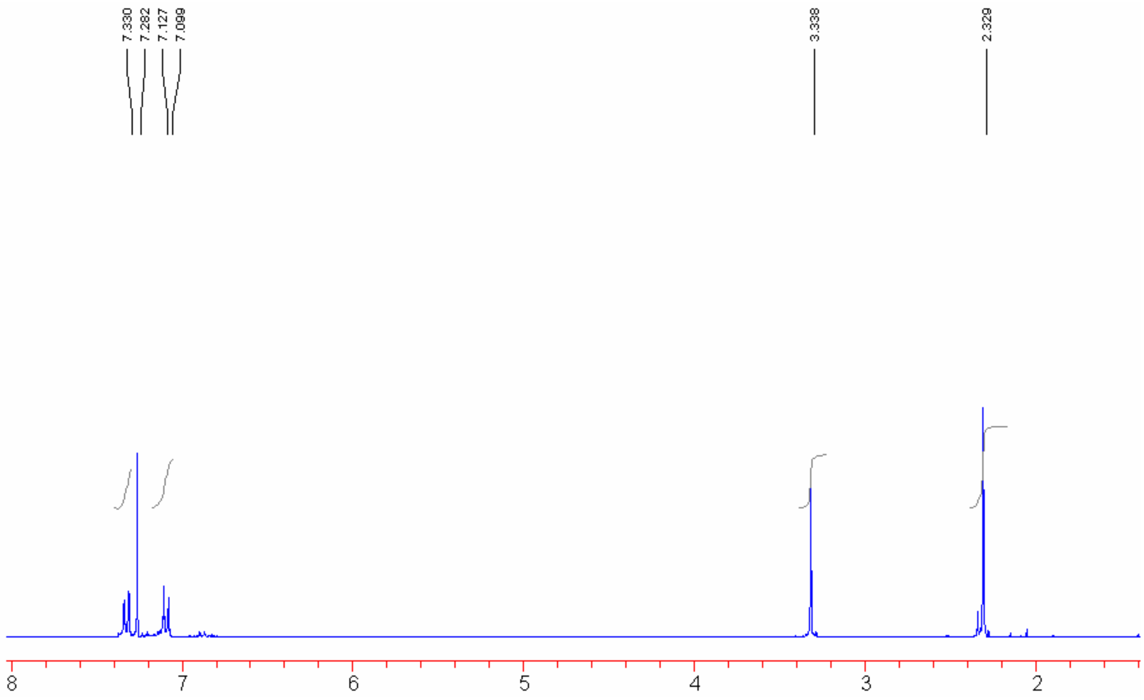
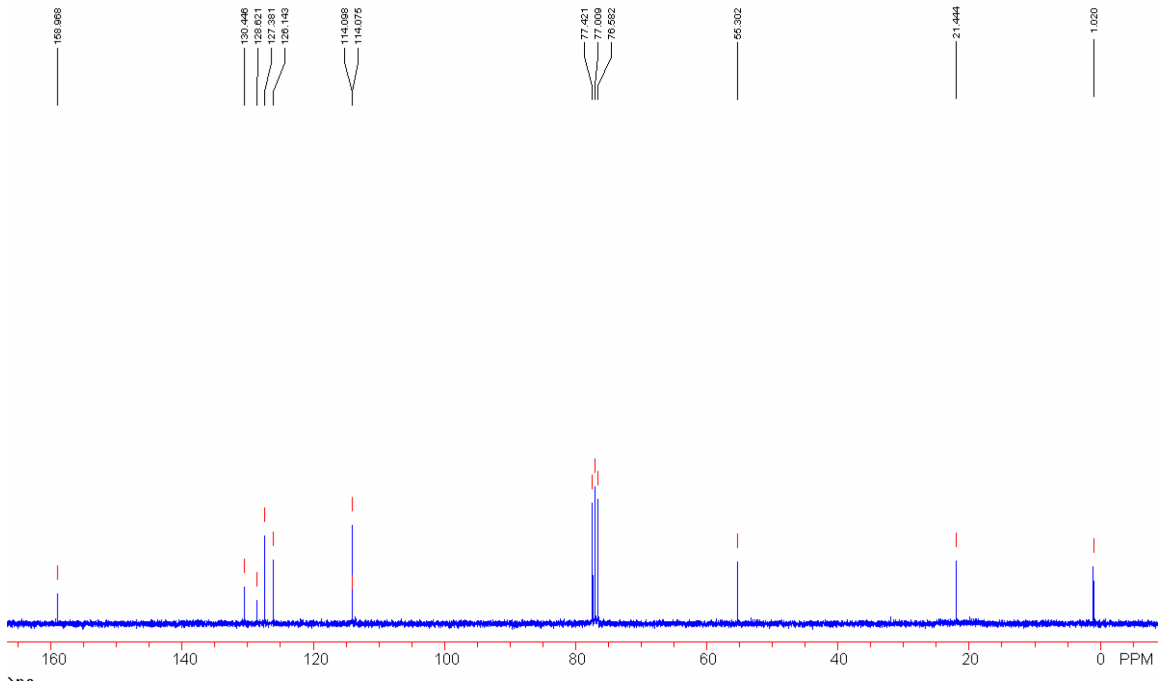
***trans*-2,3-bis(4-acetoxyphenyl)oxirane.**





***trans*-2,3-bis(4-(chloromethyl)phenyl)oxirane.**