Supporting Information

'Solvent Free Enantioselective C–C Bond Forming Reactions with Very High Catalyst Turnover Numbers'

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Table of Contents

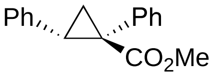
1. Experimental Section

1.1 General Considerations

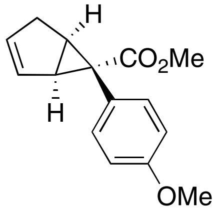
All reactions were conducted in flame-dried glassware. Reagents were used as received from commercial suppliers unless otherwise noted. Methyl phenyldiazoacetate, methyl *p*-methoxyphenyldiazoacetate, methyl phenylvinyldiazoacetate and methyl diazomalonate were prepared by standard methods. Dichloromethane was purified by passage through a bed of activated alumina (Grubbs-type solvent purifier). Styrene was filtered through a plug of silica before use. Cyclopentadiene was obtained from thermal cracking of dicyclopentadiene. NMR spectra were recorded on Varian 500, 400 and 300 MHz NMR spectrometers, calibrated using residual solvent peak. Melting points were obtained with an Electrothermal melting point apparatus and are uncorrected. Elemental analyses were provided by Atlantic Microlabs, Inc.

Safety Note: *Since the solvent-free reaction conditions are relatively exothermic, care is required for conducting reactions beyond the 50 mmol scale reported herein. The reactions are best started with a minute amount of catalyst, followed by addition of more catalyst as needed. Due to the potential instability of diazo compounds, excessive heating should be avoided and the work should be conducted behind a blast shield.*

1.2 Representative Procedures and Characterization Data

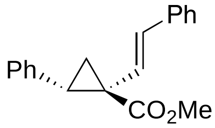


(1R,2S)-methyl 1,2-diphenylcyclopropanecarboxylate (4a). Methyl phenyldiazoacetate (8.81 g, 50.0 mmol) was dissolved in styrene (9.0 mL, 78.5 mmol). The solution was cooled to –30 °C. Rh_2(*S*-DOSP)$_4$ (3.0 mg, 0.00158 mmol) in styrene (1.0 mL) was added. The solution was allowed to stir at –30 °C for 3 h and warmed to ambient temperature. A sample was acquired and analyzed (d.r. = 40:1 by crude ^{1}H NMR, ee = 75% by HPLC: 1.5% *i*-PrOH/hexanes, 0.9 mL/min, R,R-Whelk). The crude material was then recrystallized from EtOH to give **4a** as a white powder (8.00 g, 63%, >99% ee). Data for **4a**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.11-7.09 (m, 3H), 7.03-7.00 (m, 5H), 6.76-6.74 (m, 2H), 3.63 (s, 3H), 3.11 (dd, 1H, *J*=7.0, 9.5 Hz), 2.13 (dd, 1H, *J*=5.0, 9.5 Hz), 1.86 (dd, 1H, *J*=5.0, 7.0 Hz). The data corresponds to reported literature values.[1]

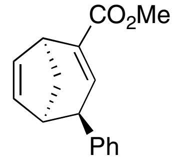


(*R,S,S*)-Methyl 6-(4-methoxyphenyl)bicyclo[3.1.0]hex-2-ene-6-carboxylate (*ent*-5). Methyl 4-methoxyphenyldiazoacetate **1b** (10.30 g, 50 mmol) was dissolved in cyclopentadiene (12.5 mL, 153 mmol). Rh_2(*S*-PTAD)$_4$ (0.05 mg, 0.000032 mmol) was added and the reaction was allowed to stir at ambient temperature for 72 h. Excess cyclopentadiene was removed by Kügelrohr distillation to afford ***ent*-5** (10.1 g, 41.3 mmol, 83%, 76% ee). Data for ***ent*-5**: Mp = 128-130 °C. $[\alpha]_D^{20}$ (c 1.05): -153.0. HPLC (Chiracel OJ, 3% *i*-PrOH/hexanes, 1.5 mL/min): t_R = 11.0, 15.9 min. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.03 (d, 2H, *J* = 8.2 Hz), 6.82 (d, 2H, *J* = 8.5 Hz), 5.75-5.74 (m, 1H), 5.24-5.23 (m, 1H), 3.79 (s, 3H), 3.60 (s, 3H), 2.92-2.91 (m, 1H), 2.67-2.60 (m, 2H), 2.07 (dd, 1H, *J* = 18.1, 2.1 Hz). ^{13}C NMR (500 MHz, $CDCl_3$): δ 174.6, 158.1, 133.7, 132.8, 129.5, 124.9, 113.0, 54.9, 52.2, 40.8, 36.9, 33.9, 32.3. FTIR (neat film): ν/cm^{-1} 3015, 2950, 2901, 2840, 1704, 1524, 1246, 1217. HRMS (CI): Calcd. for $[C_{15}H_{16}O_3+H]$

245.11722, found [M+H] 245.11737. Elemental analysis: calcd. C: 73.75%, H: 6.60%, found: C: 73.64%, H: 6.54%.

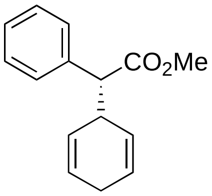


(1*S*,2*S*,*E*)-Methyl 2-phenyl-1-styrylcyclopropanecarboxylate (8). Methyl styryldiazoacetate **7** (10.1 g, 50.0 mmol) was dissolved in styrene (7.60 mL, 66.3 mmol). Rh_2(*S*-DOSP)$_4$ (3.0 mg, 0.00158 mmol) in styrene (1.0 mL, 8.7 mmol) was added. The solution was allowed to stir at ambient temperature for 6 h. A sample of the crude material was acquired (d.r. = 16:1 by crude NMR, ee = 81% by HPLC: S,S-Whelk, 1% *i*-PrOH/hexanes, 1mL/min). The crude material was recrystallized from EtOH to afford **8** as a white powder (10.0 g, 72%, >99% e.e). Data for **8**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.21-7.13 (m, 10H), 6.34 (d, 1H, *J*=16 Hz), 6.13 (d, 1H, *J*=16 Hz), 3.74 (s, 3H), 3.00 (dd, 1H, *J*=7.0, 9.0 Hz), 2.02 (dd, 1H, *J*=9.0, 5.0 Hz), 1.82 (dd, 1H, *J*=5.0, 7.0 Hz). The data corresponds to reported literature values.[2]



(1*S*,4*S*,5*R*)-methyl 4-phenylbicyclo[3.2.1]octa-2,6-diene-2-carboxylate (9). Methyl styryldiazoacetate **7** (10.1 g, 50.0 mmol) was dissolved in cyclopentadiene (5.0 g, 75.0 mmol) and the solution cooled to 10 °C. Rh_2(*S*-DOSP)$_4$ (3.0 mg, 0.00158 mmol) in cyclopentadiene (0.500 mL, 6.1 mmol) was added in one portion. The reaction was allowed to slowly warm to ambient temperature over 10 h. The product was then purified by Kügelrohr distillation to afford **9** as a yellow oil (10.1 g, 84%, 81% ee). Data for **9**: ^{1}H

NMR ($CDCl_3$, 300 MHz): δ 7.32-7.16 (m, 3H), 7.06 (d, 2H, *J* = 6.6 Hz), 6.63 (s, 1H), 6.35 (dd, 1H, *J* = 5.4, 2.7 Hz), 5.27 (dd, 1H, *J* = 5.4, 2.7 Hz), 3.78 (dd, 1H, *J* = 4.2, 3.3 Hz), 3.76 (s, 3H), 3.32 (t, 1H, *J* = 3.8 Hz), 3.02 (ddd, 1H, *J* = 4.7, 4.6, 2.4 Hz), 2.24 (ddd, 1H, *J* = 9.9, 4.8, 4.8 Hz), 1.98 (d, 1H, *J* = 9.9 Hz). The data corresponds to reported literature values.[3]

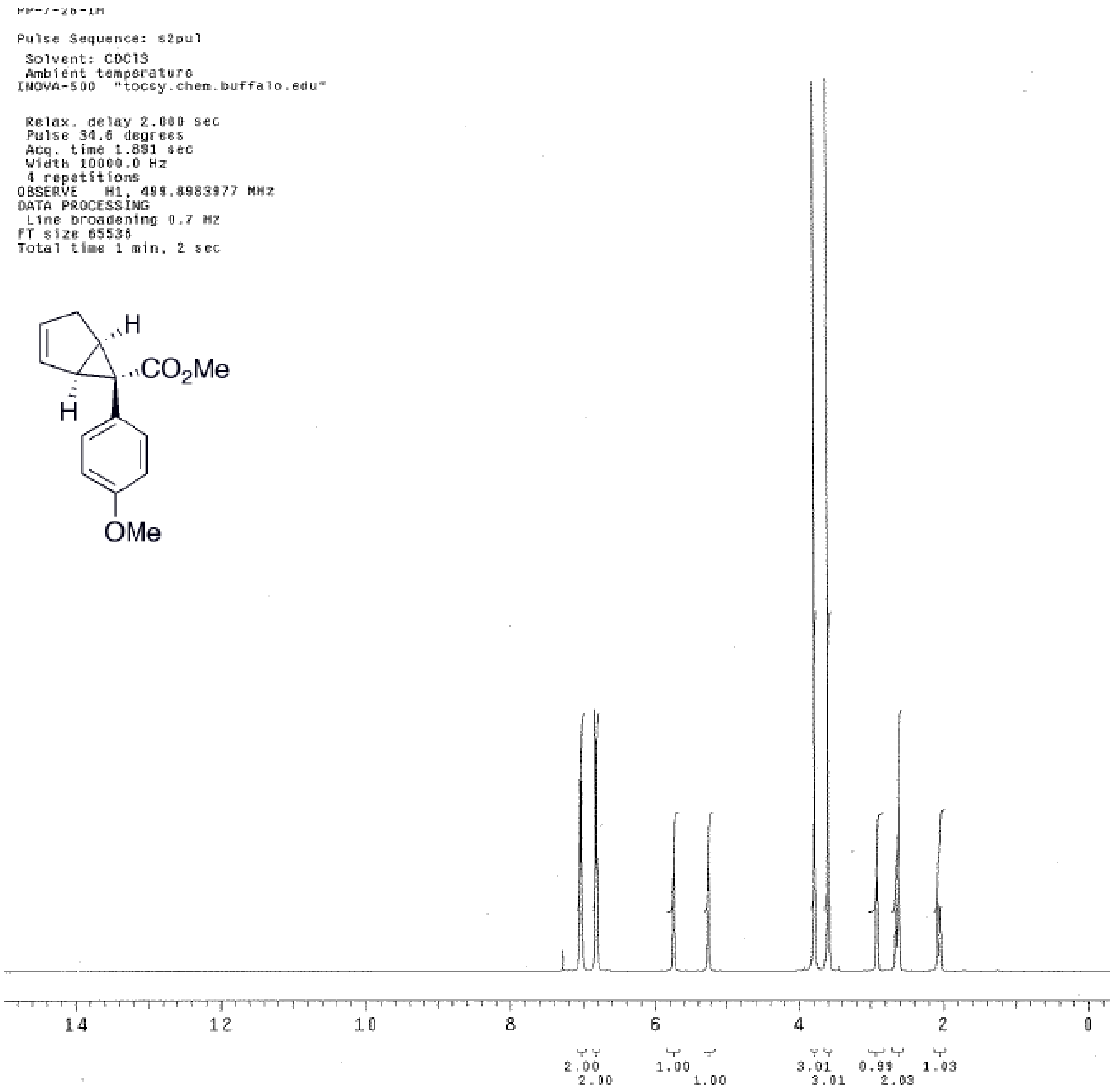


(*R*)-Methyl 2-(cyclohexa-2,5-dienyl)-2-phenylacetate (9). A 50 mL round bottom flask charged with Methyl phenyldiazoacetate **1a** (3.52 g, 20.0 mmol) was added 1,4-cyclohexadiene (4.00 mL, 41.9 mmol). The solution was cooled to 0 °C in an ice/water bath under an inert Ar-atmosphere. A solution of Rh_2(*S*-DOSP)$_4$ (3.8 mg, 0.002 mmol) in 1,4-cyclohexadiene (1.0 mL, 10.5 mmol) was added by syringe in one steady movement. Weak nitrogen evolution was observed shortly after addition. The reaction mixture was allowed to slowly reach ambient temperature over 12 h after which it turned light yellow. Excess 1,4-cyclohexadiene was then removed by Kügelrohr distillation to afford pure **9** as a light yellow oil (4.38 g, 96%). A small amount of the material was subjected to hydrogenation conditions (H_2/Pd in MeOH) to afford Methyl cyclohexylphenylacetate, which was analyzed by HPLC (Chiralcel OJ, 0.7% *i*-PrOH/hexanes, 1.0 mL/min): t_R = 14.5 min (major), 18.6 min (minor), 81% ee. Data for **9**: ^1H NMR (500 MHz, $CDCl_3$): δ 7.33-7.29 (m, 4H), 7.28-7.25 (m, 1H), 5.82-5.79 (m, 1H), 5.73-5.66 (m, 2H), 5.28-5.25 (m, 1H), 3.67 (s, 3H), 3.50-3.46 (m, 1H), 3.42 (d, 1H, *J* = 10.5 Hz), 2.63-2.59 (m, 2H). The data is in good agreement with reported literature values.[4]

1.3 Procedure for ReactIR Studies

General procedure for kinetic measurements: Experiments were carried out with a Mettler Toledo ReactIR™ 45m instrument equipped with a 9.5mm x 12” AgX 1.5m SiComp probe. Stock solutions of methyl phenyldiazoacetate, Ethyl diazoacetate, Methyl diazomalonate and Rh_2(*S*-DOSP)$_4$ in CH_2Cl_2 were prepared. To a dry round bottom flask was added a stir bar, styrene (10 equiv.), CH_2Cl_2 and an aliquot of diazoacetate solution (1.0 equiv., 0.2 M). The ReactIR probe was then inserted and the instrument set up for a continuous scan experiment. The scan was started and, at t_0 = 10 s, an aliquot of the catalyst solution was injected by syringe in one movement with vigorous stirring. All solutions were equilibrated to ambient temperature before use (16 ˚C).

2. Spectral Data for Compound 5



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PP-7-26-1H

Pulse Sequence: s2pul
 Solvent: CDCl3
 Ambient temperature
INOVA-500  "tocsy.chem.buffalo.edu"

 Relax. delay 2.000 sec
 Pulse 34.6 degrees
 Acq. time 1.891 sec
 Width 10000.0 Hz
 4 repetitions
OBSERVE   H1, 499.8983977 MHz
DATA PROCESSING
 Line broadening 0.7 Hz
FT size 65536
Total time 1 min, 2 sec
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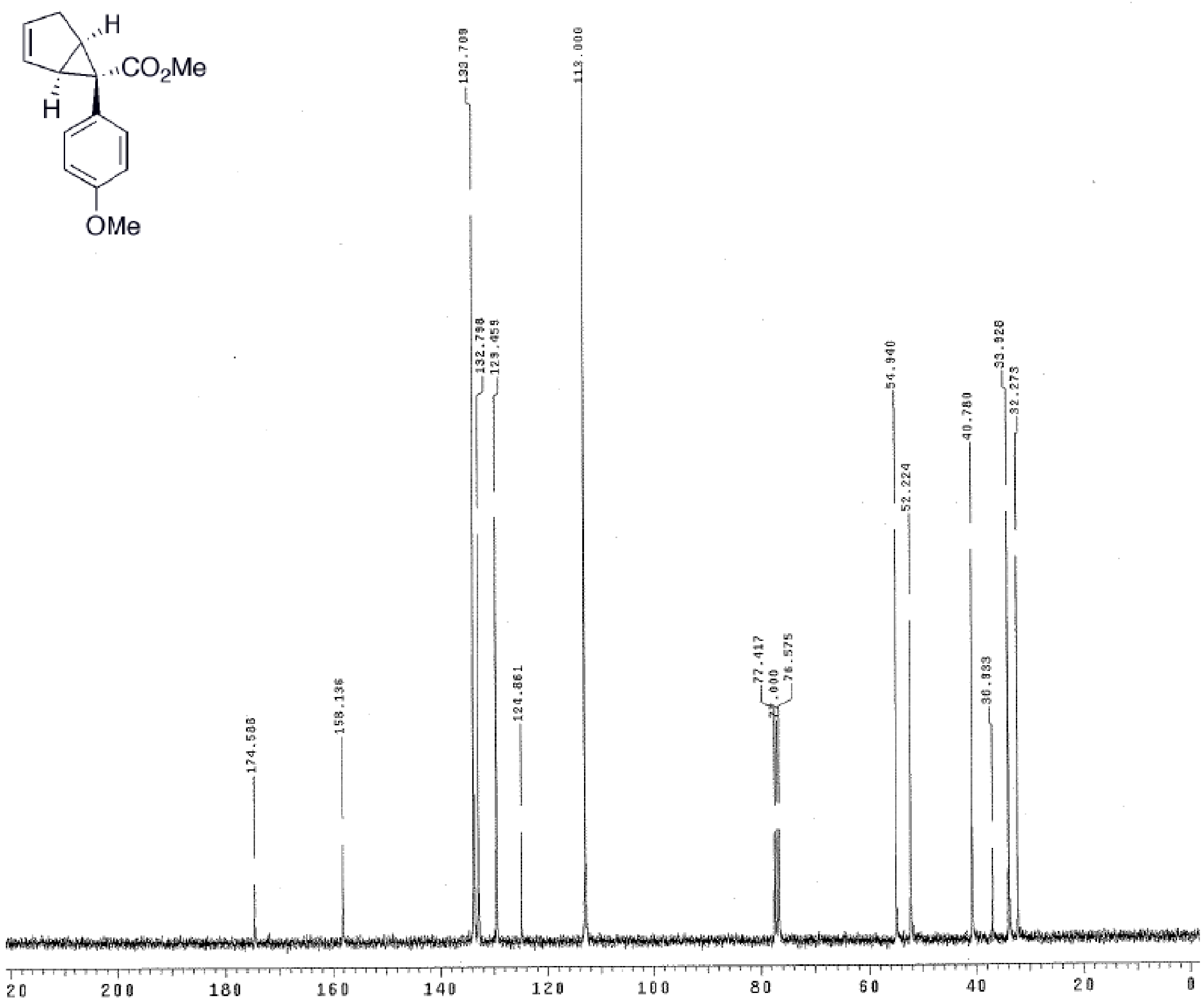
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CO2Me
H
OMe
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113.000
132.798
129.459
54.940
33.928
32.273
40.780
52.224
77.417
.000
76.575
36.833
124.861
158.136
174.588
20
200
180
160
140
120
100
80
60
40
20
0

3. ReactIR Data

The diazoacetate reactions were followed by ReactIR, monitoring the disappearance N=N stretch frequencies of the diazo compounds. Raw data for the four kinetic measurements is given below. The percent conversion, η, was estimated from the following formula:

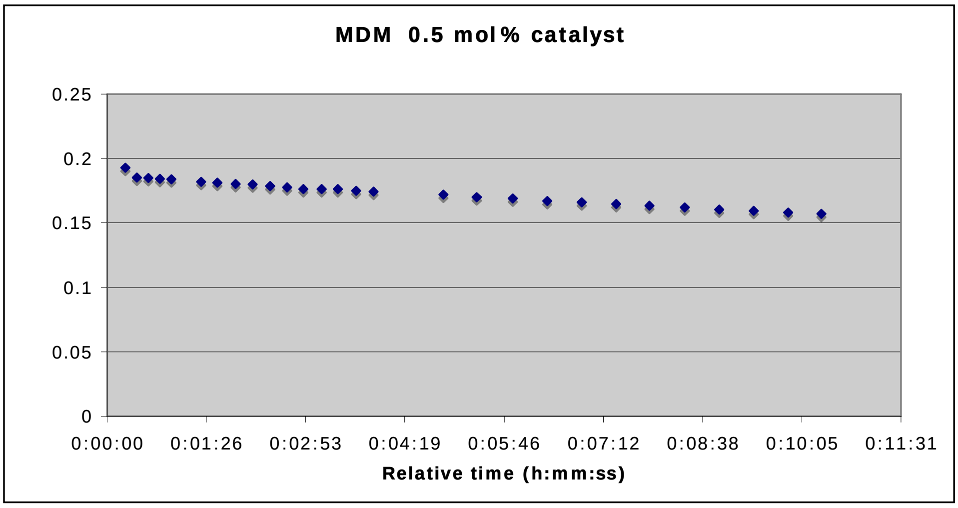
$$\eta = (|A_t - A_\infty| / |A_0 - A_\infty|) * 100\%$$

Where: A_t = Absorbance at time *t*.

A_∞ = Absorbance at full conversion.

A_0 = Initial absorbance before reaction was started.

Methyl diazomalonate : Rh_2(*S*-DOSP)$_4$ = 200 : 1



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0:00:36	0.184569	36
0:00:46	0.184174	46
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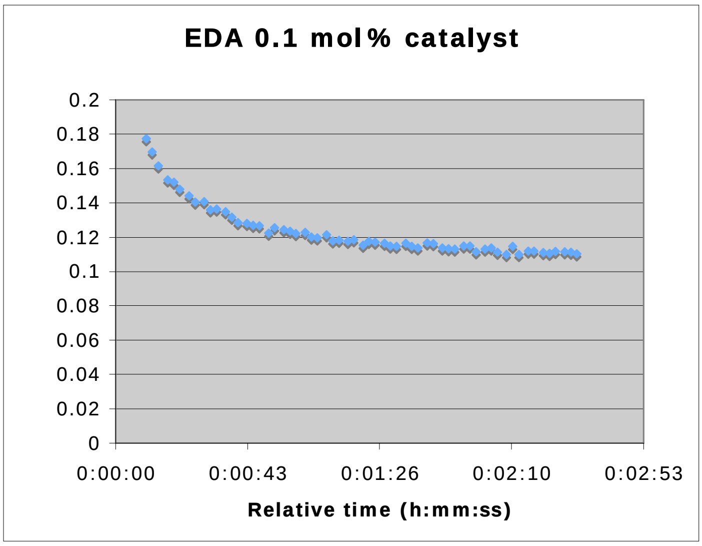
0:01:22	0.181888	82
0:01:36	0.181033	96

0:01:52	0.179983	112
0:02:07	0.179662	127
0:02:22	0.178492	142
0:02:37	0.177501	157
0:02:51	0.176129	171
0:03:07	0.176029	187
0:03:21	0.175973	201
0:03:37	0.174641	217
0:03:52	0.174267	232

Ethyl diazoacetate (EDA) : Rh_2(*S*-DOSP)$_4$ = 1000 : 1



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0:00:19	0.151988	19
0:00:21	0.147899	21
0:00:24	0.144137	24
0:00:26	0.140412	26
0:00:29	0.140729	29
0:00:31	0.135945	31
0:00:33	0.136352	33
0:00:36	0.134875	36
0:00:38	0.131733	38
0:00:40	0.128438	40

0:00:43	0.127998	43
0:00:45	0.126917	45
0:00:47	0.126719	47
0:00:50	0.122426	50
0:00:52	0.125485	52
0:00:55	0.124423	55
0:00:57	0.123477	57
0:00:59	0.122129	59
0:01:02	0.12295	62
0:01:04	0.120203	64
0:01:06	0.119763	66
0:01:09	0.121569	69
0:01:11	0.117884	71
0:01:13	0.11827	73
0:01:16	0.117636	76
0:01:18	0.118593	78
0:01:21	0.115427	81
0:01:23	0.117739	83
0:01:25	0.117191	85
0:01:28	0.116595	88
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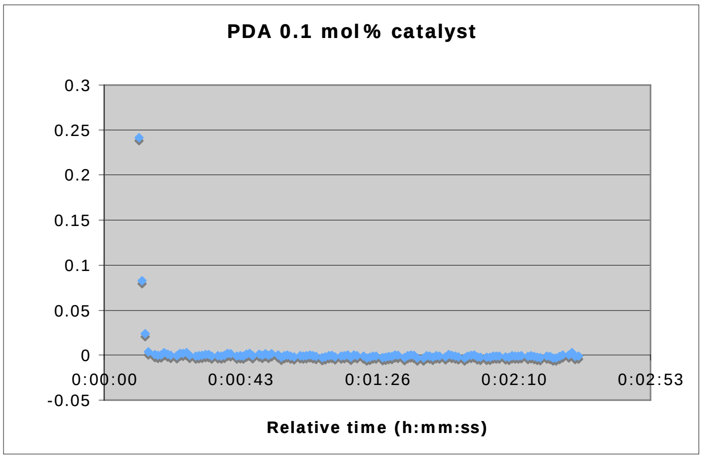
Methyl Phenyldiazoacetate (MPD) : $Rh_2(S\text{-DOSP})_4$ = 1000 : 1



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0:00:33	0.000391774	33
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0:00:36	-0.000903423	36
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0:00:39	0.00181956	39

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0:00:44	-0.00113082	44
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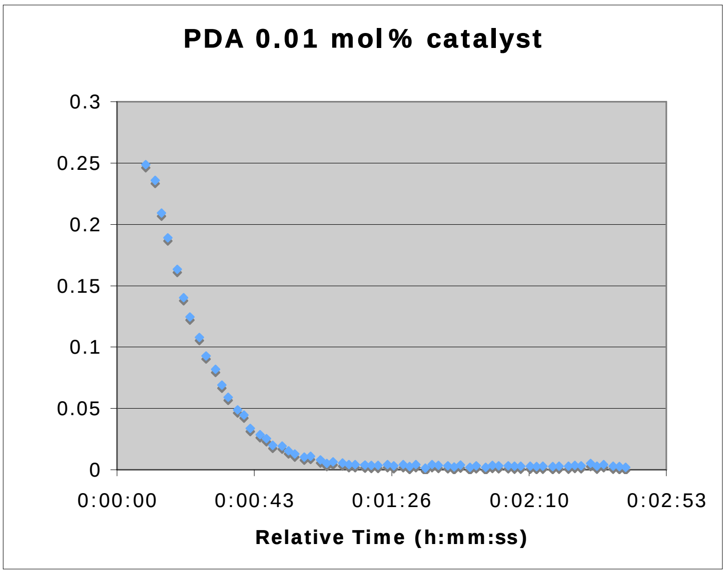
Methyl Phenyldiazoacetate (MPD) : $Rh_2(S\text{-}DOSP)_4$ = 10,000 : 1



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0:01:30	0.00401804	90
0:01:32	0.00252082	92
0:01:34	0.00412696	94
0:01:37	0.00130936	97
0:01:39	0.0042765	99
0:01:41	0.00347596	101
0:01:44	0.00308134	104
0:01:46	0.00228885	106
0:01:48	0.00373604	108
0:01:51	0.00201798	111
0:01:53	0.00306436	113
0:01:56	0.00207249	116
0:01:58	0.00350901	118
0:02:00	0.00326549	120
0:02:03	0.00328234	123
0:02:05	0.00303025	125
0:02:07	0.00272954	127
0:02:10	0.00299942	130
0:02:12	0.00249693	132
0:02:14	0.00293332	134
0:02:17	0.00257351	137
0:02:19	0.00285069	139
0:02:22	0.00292317	142
0:02:24	0.00336909	144
0:02:26	0.00317081	146
0:02:29	0.00511048	149

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