Effect of Catalysts on the 1,3-dipolar cycloaddition reaction

S. No	Catalyst	Combined Yield	Ratio of 8 : 9
1	$Rh_2(OCHO)_4$	79%	58:42
2	$Pd[P\text{-}(o\text{-tol})_3]_3Cl_2$	42%	57:43
3	$Rh_2(tpa)_4$	65%	55:45
4	$Rh_2(tfb)_4$	63%	52:48
5	$Rh_2(OAc)_4$	73%	52:48
6	$Rh_2(OCOPhMe)_4$	89%	52:48
7	$Rh_2(Oct)_4$	66%	52:48
8	$Rh_2(OCOPh)_4$	90%	50:50
9	$Rh_2(OCOPhNMe_2)_4$	76%	50:50
10	$Rh_2(adc)_4$	88%	50:50
11	$Rh_2(tfa)_4$	87%	50:50
12	$Rh_2(OCOCH_2Cl)_4$	89%	47:53
13	$Rh_2(OCOPhF)_4$	80%	46:54
14	$Rh_2(OPiv)_4$	87%	46:54
15	$Pd(PPh_3)_3Cl_2$	57%	46:54
16	$Rh_2(OCOPhCOOMe)_4$	93%	45:55
17	$Rh_2(OCOPhCl)_4$	89%	45:55
18	$Rh_2(OCOPhCF_3)_4$	94%	45:55
19	$Rh_2(cap)_4$	65%	45:55
20	$Rh_2(OCOPhOMe)_4$	66%	43:57
21	Rh_2(*m*-chlorobenzoate)$_4$	99%	40:60
22	$Rh_2(OCOPhNO_2)_4$	81%	38:62
23	$Cu(acac)_2$	62%	35:65
24	$Ni(acac)_2$	No reaction	
25	$Ru(PPh_3)_3Cl_2$	No reaction	

General experimental procedure:

To a benzene solution (3 mL) of the diazoketone **7** (0.046 g, 0.3 mmole) at rt was added benzoquinone (0.049 g, 0.45 mmole)[Since yields are also determined using the internal standard, 1.5 eq of benzoquinone was used to make sure that all the ylide formed are used up in the dipolar cycloaddition reaction] and stirred for 5 min, before adding 1-2 mg of the catalyst. The resulting solution was stirred for 6-8h and filtered over a small pad of Celite and washed with more solvent. To the filtrate was added the internal standard 1,3,5-trimethoxybenzene (0.051 g, 0.3 mmole) and the solvent was evaporated to afford a brown residue. In some cases, 3,4,5-trimethoxybenzaldehyde was used as an internal standard. The ratio of **8** and **9** and their combined yield were determined by the crude ^{1}H NMR spectrum.

Effect of Solvents on the 1,3-dipolar cycloaddition reaction

S.No	Solvent	Combined Yield	Ratio of 8 : 9
1	Nitromethane	69%	77:23
2	Pentane	79%	71:29
3	Hexane	78%	70:30
4	Cyclohexane	74%	68:32
5	Hexafluorobenzene	82%	66:34
6	CCl_2FCF_2Cl	91%	65:35
7	^{t}BuOMe	71%	63:37
8	Tetrachloroethylene	85%	61:39
9	CS_2	71%	61:39
10	Ether	71%	61:39
11	CCl_4	81%	61:39
12	DMF	47%	60:40
13	Chlorobenzene	97%	57:43
14	$CHCl_3$	75%	56:44
15	Trichloroethylene	75%	56:44
16	*p*-Xylene	78%	55:45
17	CH_2Cl_2	83%	54:46
18	DME	76%	54:46
19	Ethylacetate	65%	54:46
20	THF	62%	53:47
21	*m*-Xylene	76%	53:47
22	CH_2ClCH_2Cl	84%	52:48
23	Benzene	66%	52:48
24	MEK	72%	50:50
25	Flurobenzene	88%	49:51
26	*o*-Xylene	92%	48:52
27	1,4-Dioxane	85%	46:54
28	Toluene	62%	45:55
29	CH_3CN	65%	41:59

General experimental procedure:

To a solution (3 mL of the respective solvent) of the diazoketone **7** (0.046 g, 0.3 mmole) at rt was added benzoquinone (0.049 g, 0.45 mmole) and stirred for 5 min, before adding 1-2 mg of $Rh_2(Oct)_4$. The resulting solution was stirred for 6-8h and filtered over a small pad of Celite and washed with more solvent. To the filtrate was added the internal standard 1,3,5-trimethoxybenzene (0.051 g, 0.3 mmole) and the solvent was evaporated. In some cases, 3,4,5-trimethoxybenzaldehyde was used as an internal standard. The ratio of **8** and **9** and their combined yield were determined by the crude ^{1}H NMR spectrum.