JOC The Journal of Organic Chemistry

J. Org. Chem., 1998, 63(4), 1185-1189, DOI:10.1021/jo970282u

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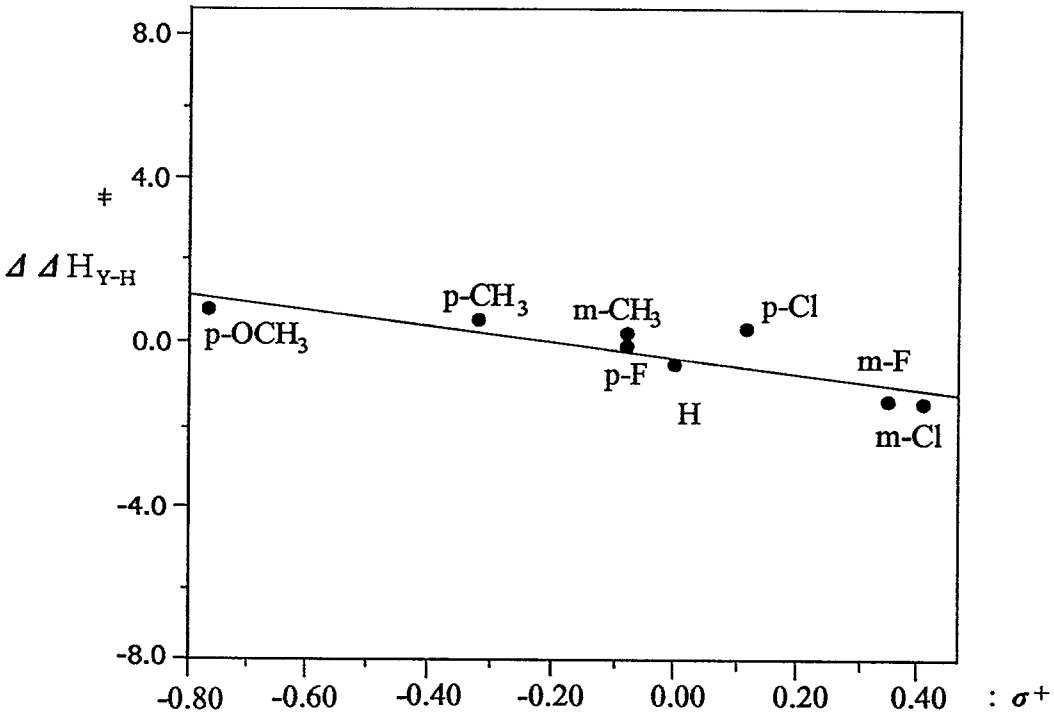
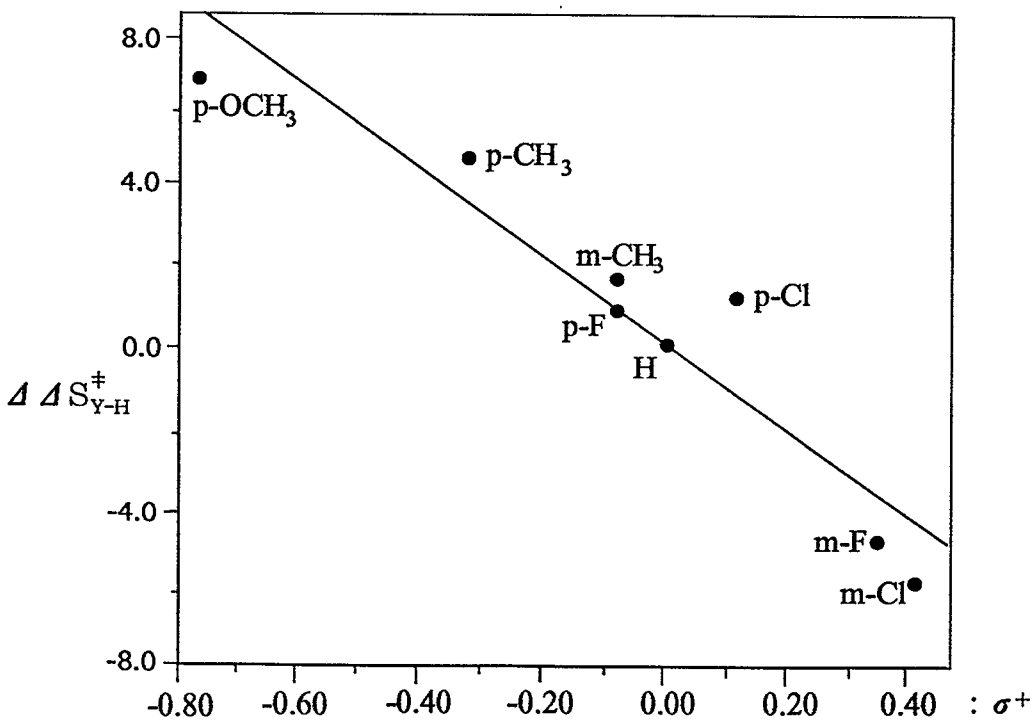
JACS **1985**, *107*,4234 : $YC_6H_4CH_2\text{-}H + Br\bullet \longrightarrow YC_6H_4CH_2\bullet + H\text{-}Br$

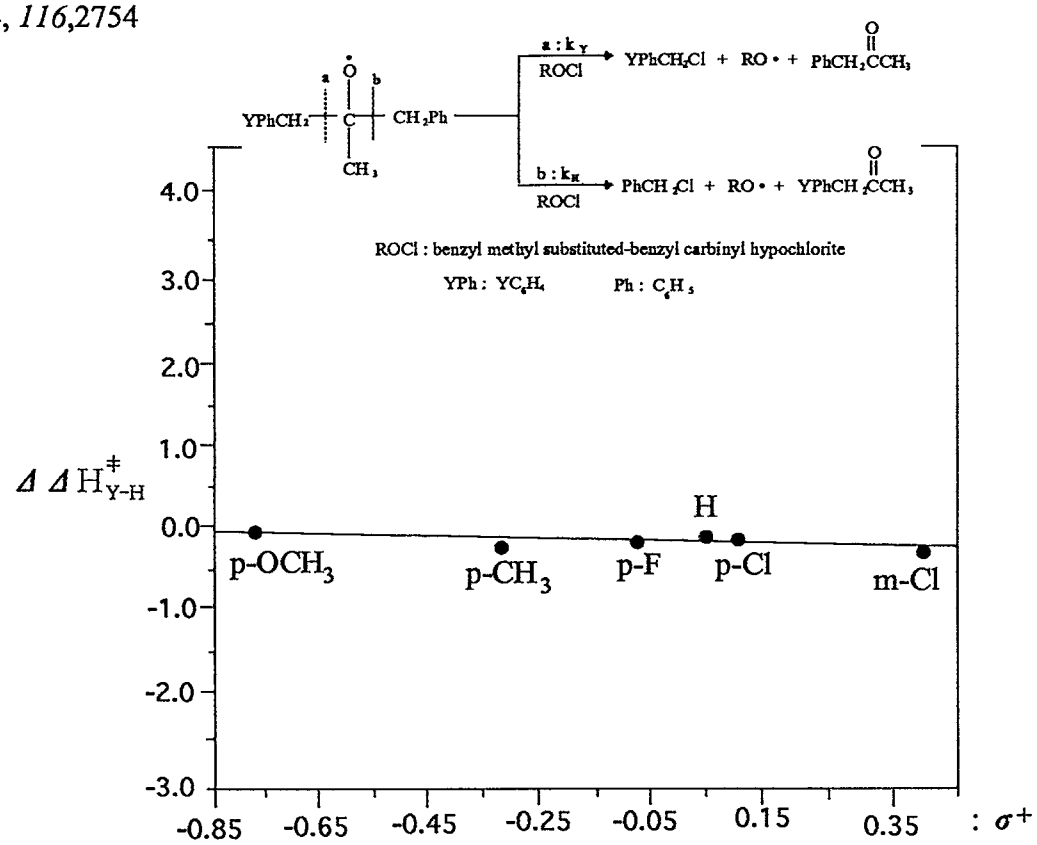


Plot of $\Delta\Delta H^{\ddagger}_{Y\text{-}H}$ *vs* σ^{+}



Plot of $\Delta\Delta S^{\ddagger}_{Y\text{-}H}$ *vs* σ^{+}

JACS **1994**, *116*,2754



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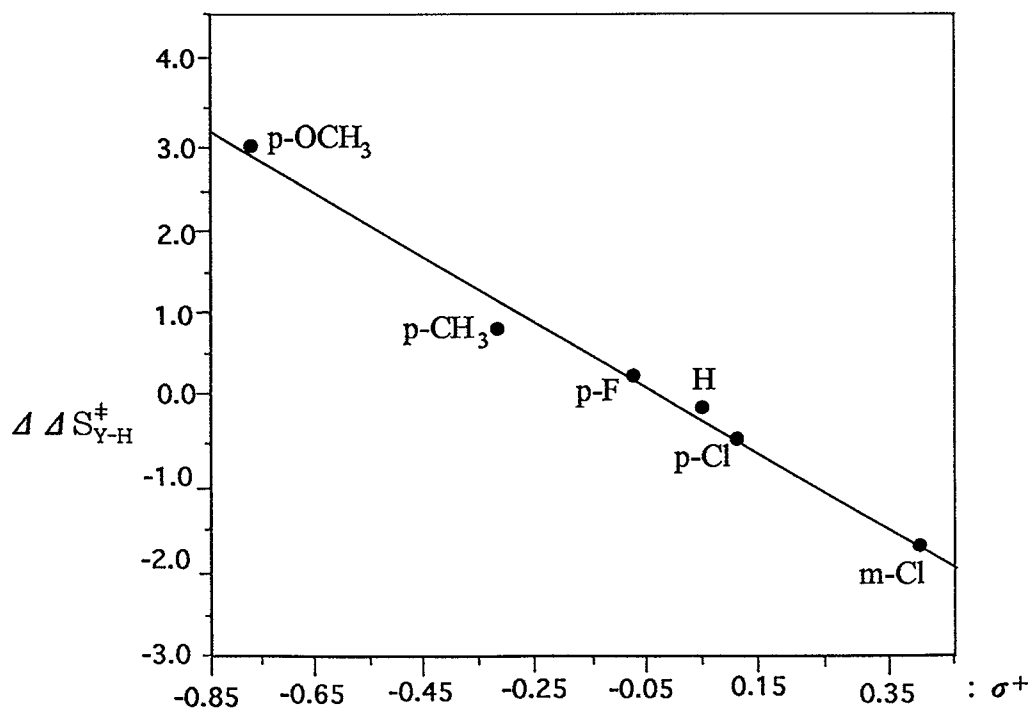

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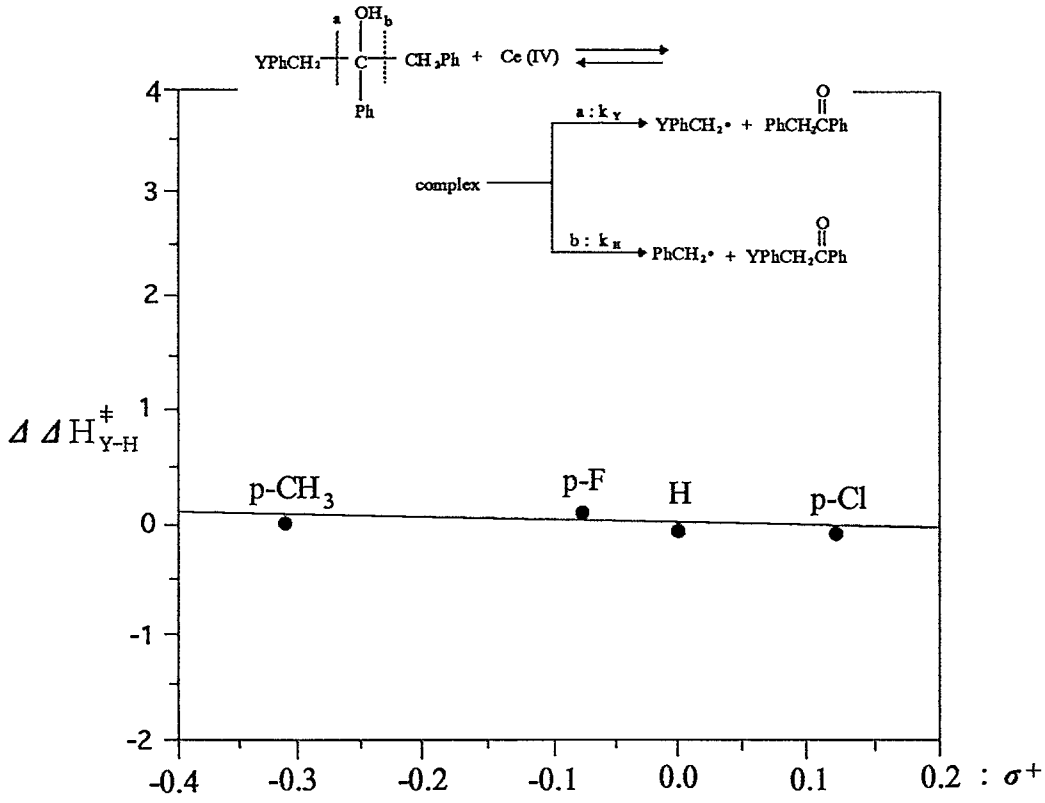
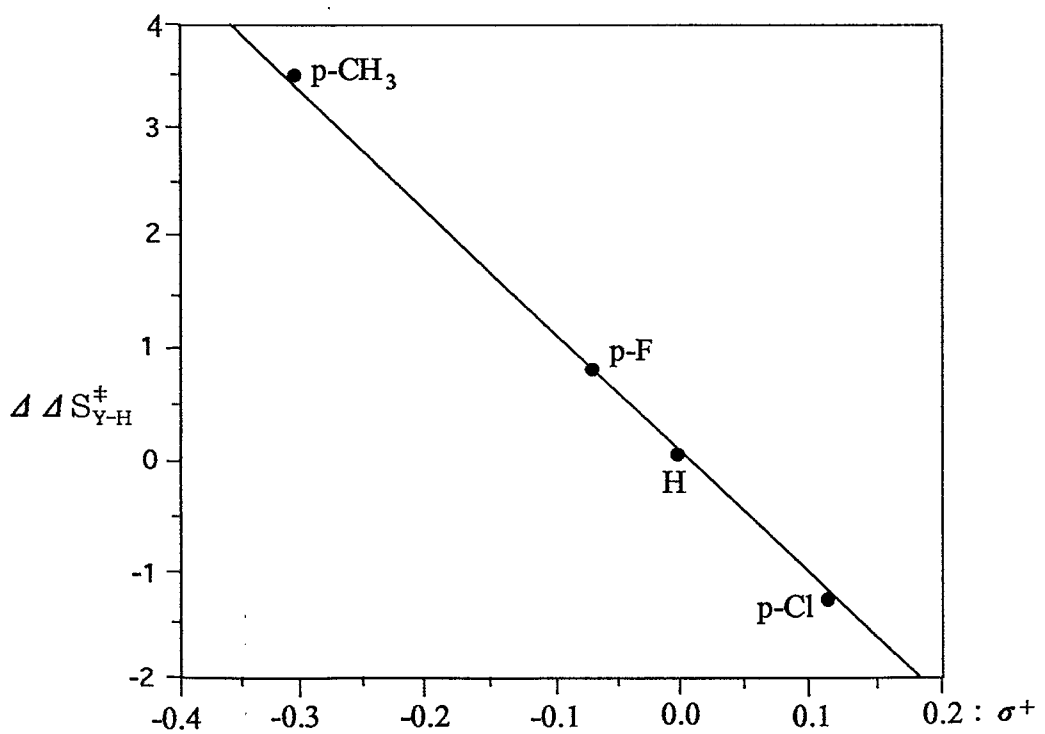
JACS **1994**, *116*,2754



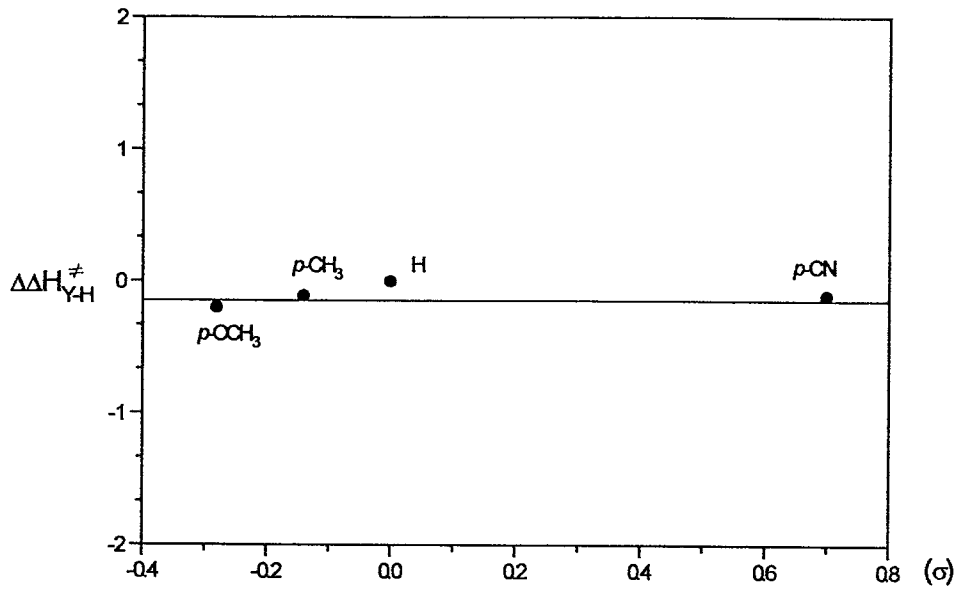
Plot of $\Delta\Delta H^{\ddagger}_{Y\text{-}H}$ *vs* σ^{+}



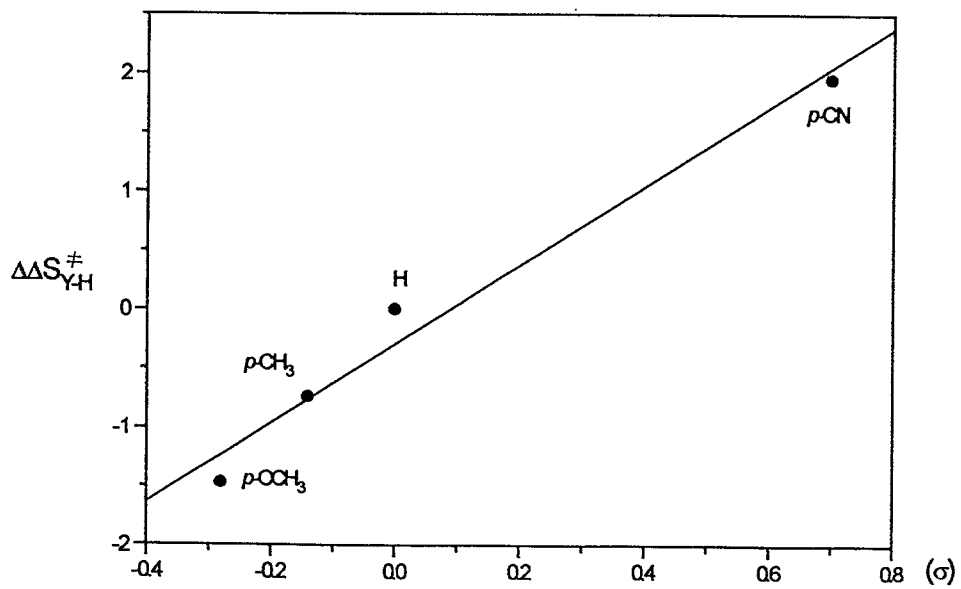
Plot of $\Delta\Delta S^{\ddagger}_{Y\text{-}H}$ *vs* σ^{+}

Tetrahedron Lett. **1997**, *38*, 5303

$$YC_6H_4CH_2NC + (n\text{-}Bu)_3Sn^{\bullet} \rightarrow YC_6H_4CH_2^{\bullet} + (n\text{-}Bu)_3Sn\text{-}CN$$

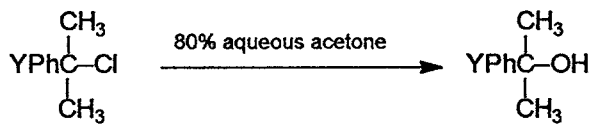


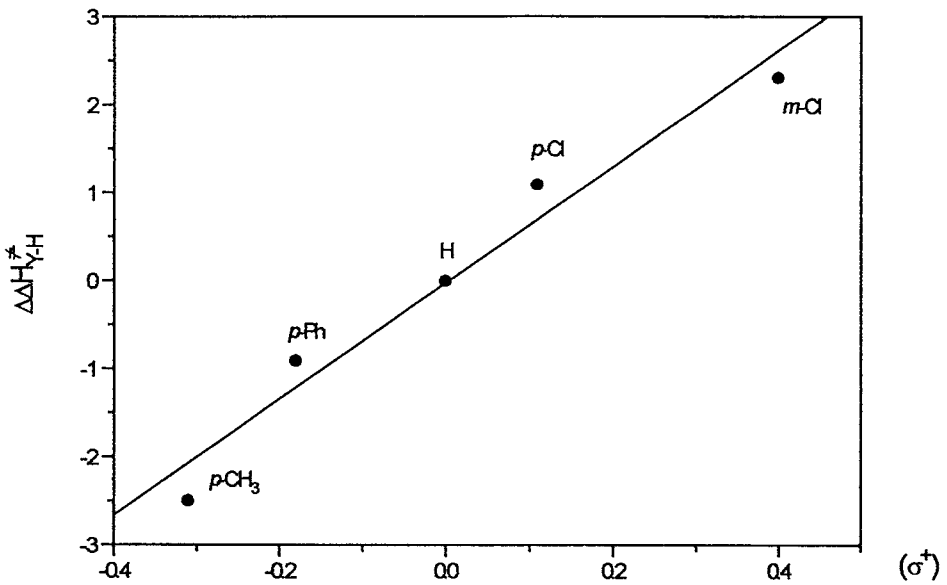
Plot of $\Delta\Delta H^{\neq}_{Y\text{-}H}$ *vs* σ



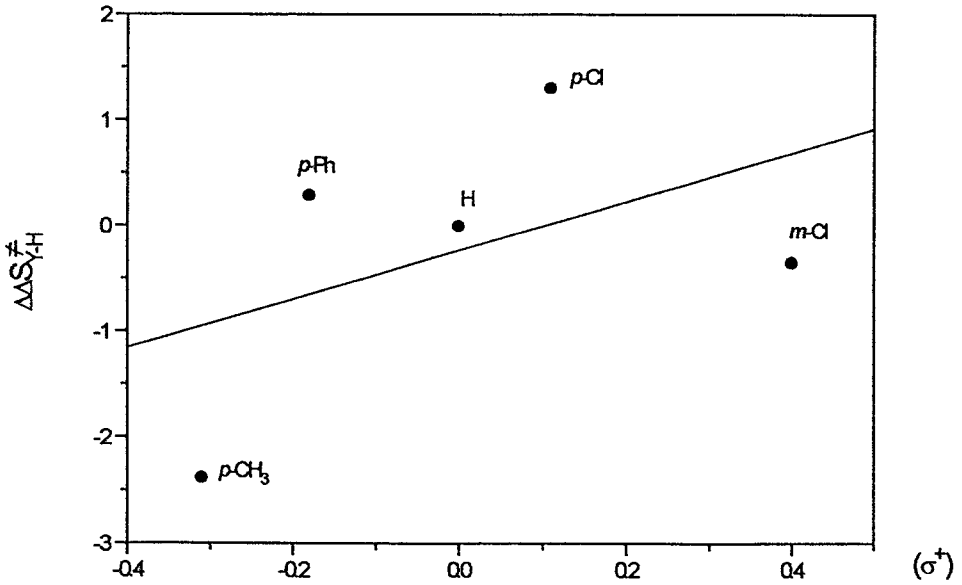
Plot of $\Delta\Delta S^{\neq}_{Y\text{-}H}$ *vs* σ

Unpublished Results (Enthalpy Control of Reactivities)



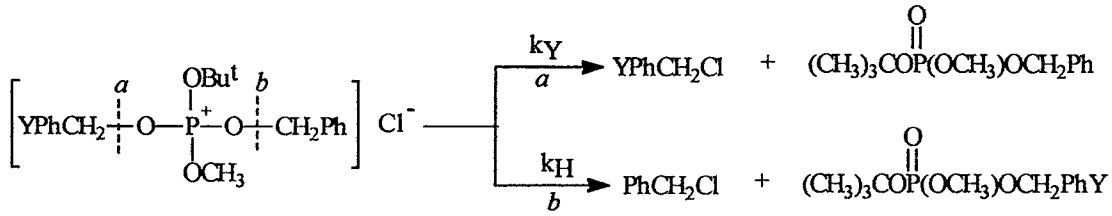


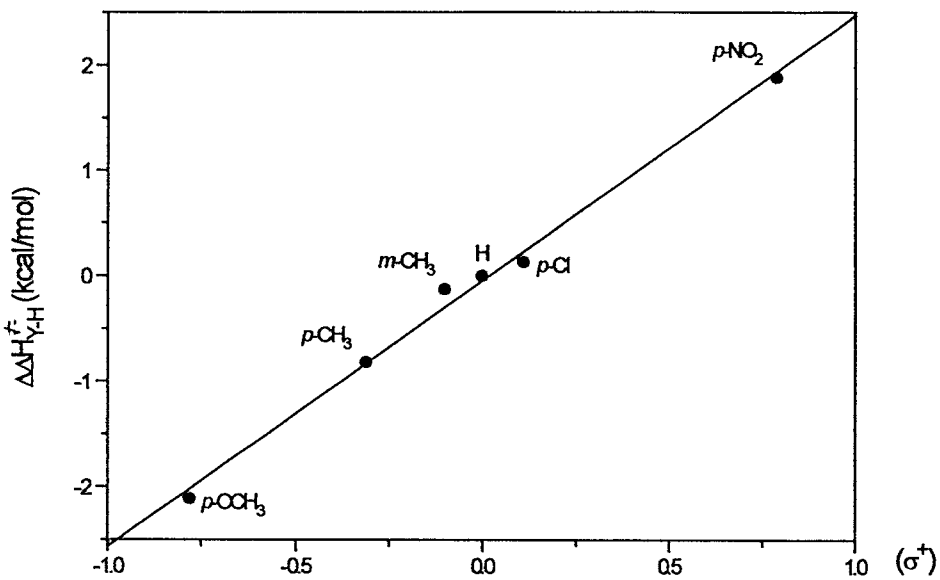
Plot of $\Delta\Delta H^{\neq}_{Y\text{-}H}$ *vs* σ^{+}



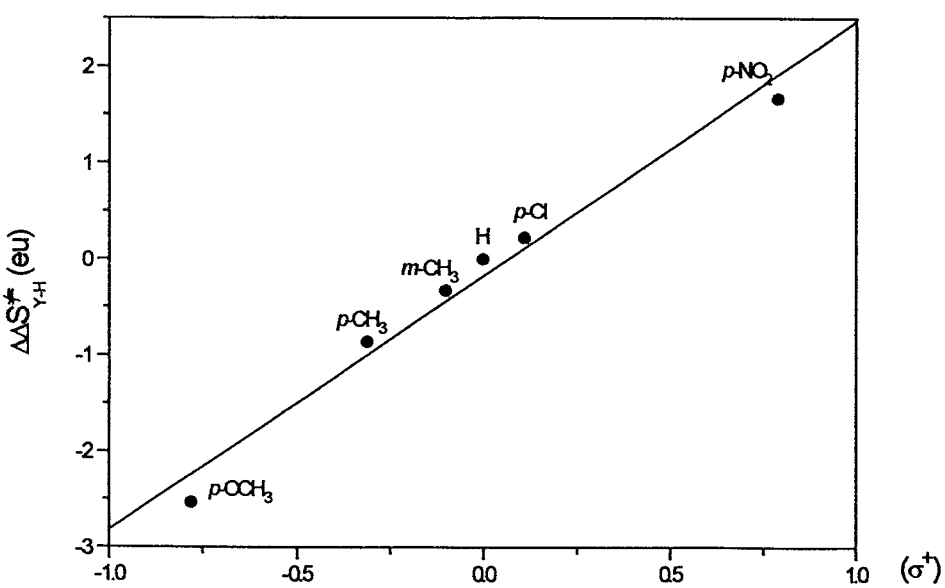
Plot of $\Delta\Delta S^{\neq}_{Y\text{-}H}$ *vs* σ^{+}

Unpublished Results (Enthalpy Control of Reactivities)

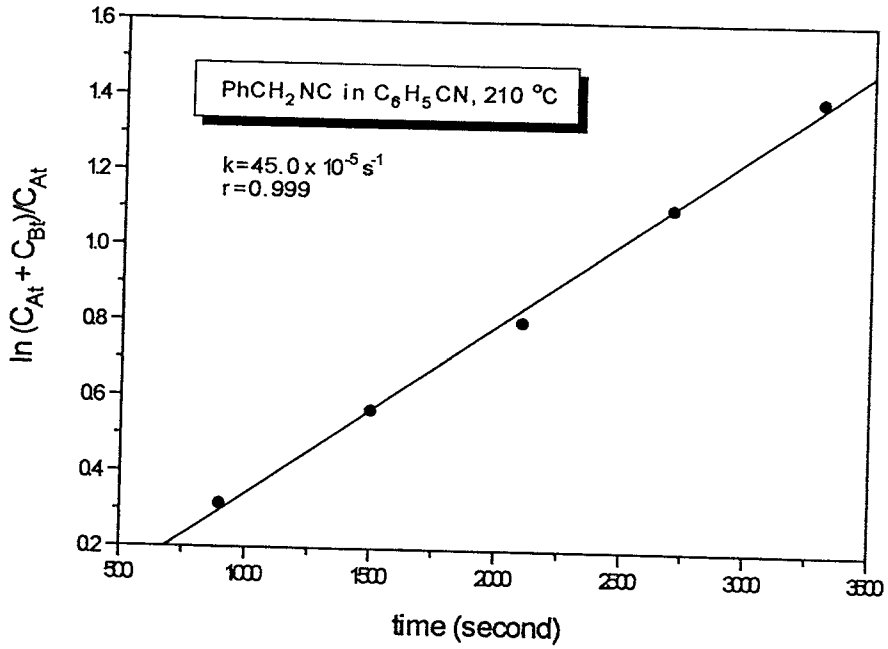




Plot of $\Delta\Delta H^{\ddagger}_{Y\text{-}H}$ *vs* σ^{+}



Plot of $\Delta\Delta S^{\ddagger}_{Y\text{-}H}$ *vs* σ^{+}


PhCH2NC in C6H5CN, 210 °C
k=45.0 x 10-5 s-1
r=0.999
ln (CAt + CBt)/CAt
time (second)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
500
1000
1500
2000
2500
3000
3500

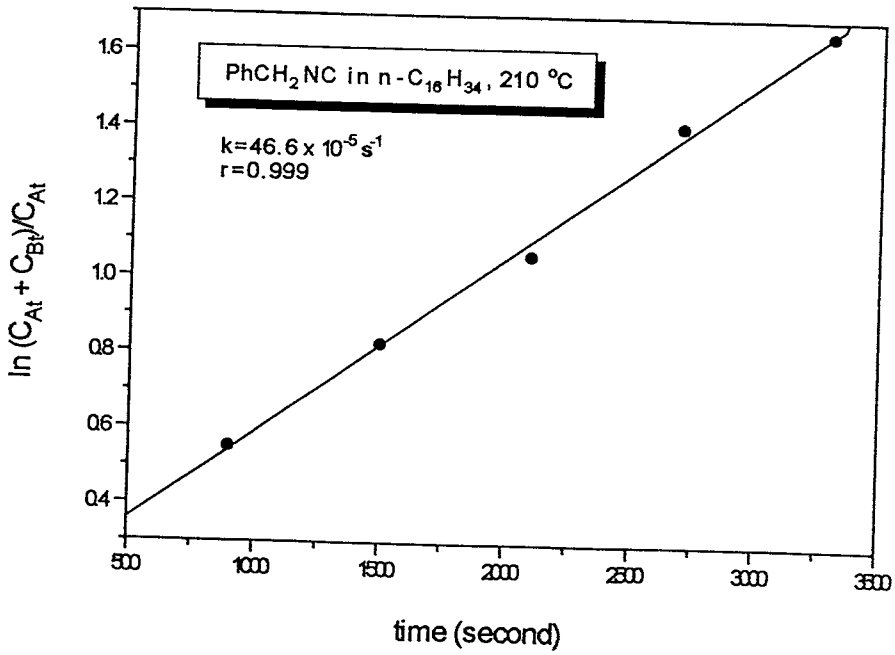

PhCH2NC in n-C16H34, 210 °C
k=46.6 x 10-5 s-1
r=0.999
ln (CAt + CBt)/CAt
time (second)
1.6
1.4
1.2
1.0
0.8
0.6
0.4
500
1000
1500
2000
2500
3000
3500

Table 1. Material Balance of Thermal Rearrangement of *p*-$CH_3OC_6H_4NC$ at 230 °C in C_6H_6.

		t (min.)				
entry	$k_{p\text{-}OCH3} \times 10^{-5}\ s^{-1}$	2	3	4	5	6
1	388	100%	98.6%	101.0%	101.0%	99.8%
2	390	100%	97.6%	104.7%	101.8%	100.1%

Table 2. Material Balance of Thermal Rearrangement of C_6H_5NC at 230 °C in C_6H_6.

		t (min)				
entry	$k_H \times 10^{-5}\ s^{-1}$	3	5	7	9	11
1	233	100%	----	98.5%	97.9%	----
2	222	100%	99.0%	101.2%	100.5%	102.2%

Table 3. Material Balance of Thermal Rearrangement of *p*-ClC_6H_4NC at 230 °C in C_6H_6.

		t (min)					
entry	$k_{p\text{-}Cl} \times 10^{-5}\ s^{-1}$	3	5	7	8.5	9	11
1	218	105.5%	100.0%	95.3%	---	95.6%	94.6%
2	225	100%	101.3%	103.8%	----	106.4%	104.0%

Table 4. Material Balance of Thermal Rearrangement of C_6H_5NC at 210 °C in C_6H_5CN.

		t (min)				
entry	$k_H \times 10^{-5}\ s^{-1}$	20	30	40	50	60
1	45.3	100%	102.3%	----	96.5%	100.5%
2	45.0	100%	95.8%	99.1%	97.7%	101.6%