SUPPORTING INFORMATION

Cationic Intermediates in Friedel-Crafts Acylation: Structural Information from Theory and Experiment

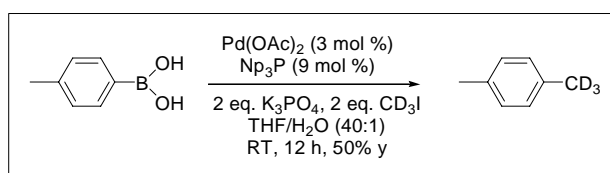*Hui Zhu and Matthew P. Meyer**

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Table of Contents

Synthesis of *d₃*-Xylene

To a 250 mL RBF with a stir bar, 0.22 g (1.0 mmol) of palladium acetate, 0.96 g (2.3 mmol) of tri(1-naphthyl)phosphine, 4.5 g (33 mmol) of p-tolylboronic acid, 15.3g (66 mmol) of K$_3$PO$_4$·H$_2$O, 120 mL of THF and 3 mL of water were added. While stirring, 4 mL (9.6 g, 66 mmol) of d_3-iodomethane was added. The reaction was allowed to stir overnight – at which time the reaction mixture was poured into 500 mL of water. It was then extracted with 3×200 mL pentane, and dried with anhydrous magnesium sulfate. The solution was then vacuum filtered and distilled. The distillate with a boiling range of 130-145°C was collected, weighed 1.8 g (50% yield), and identified as pure product by ^{1}H NMR.

^{1}H NMR (400MHz, CDCl$_3$) δ: 7.075 (s,4H), 2.320 (s, 3H).
^{13}C NMR (100MHz, CDCl$_3$) δ: 134.886 (s,1C [C4]), 134.768 (s,1C [C1]), 129.107 (s,4C [C2,C3,C5,C6]), 21.195 (s,1C [CH$_3$]), 20.205 (sept,1C [CD$_3$])
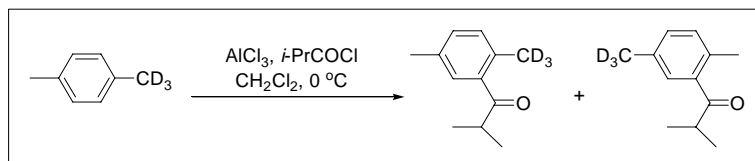
Procedure for Measuring Intramolecular ^{2}H KIEs

Intramolecular Competition Reaction. A 100 mL 3-neck RBF was mounted with a 25 mL pressure-equalizing dropping funnel and a stir bar. The apparatus was dried by heating intensively with heat gun while purging with dry nitrogen gas. After the apparatus cooled to room temperature, 232 μL (200 mg, 1.83 mmol, 1.0 eq) of d_3-p-xylene was added to the RBF while purging with a stream of dry nitrogen. To the RBF, 20 mL of dry dichloromethane (Sigma-Aldrich, Sure/Seal™ bottle, used as-is) was transferred into the 3-neck RBF via cannula. The 3-neck RBF was then placed into an ice-water bath. The mixture was stirred for at least 15 minutes to ensure equilibration to 0 °C. Another 100 mL RBF with a stir bar was dried by heating intensively with heat gun while purging with dry nitrogen gas. After the apparatus cooled to room temperature, 1.13 g (1.72 mmol, 0.9 eq) of anhydrous aluminum chloride was added quickly, followed by the cannula transfer of 20 mL of dry dichloromethane (Sigma-Aldrich, Sure/Seal™ bottle, used as-is). With stirring, 0.17 mL (0.17g, 1.6 mmol, 0.85 eq) of redistilled isobutyryl chloride was injected into the slurry. The mixture was stirred under room temperature for 10 minutes. During this time, the isobutyryl chloride/AlCl$_3$ solution became translucent. The isobutyryl chloride/AlCl$_3$ solution was then transferred to the pressure-equalizing dropping funnel fitted to the 3-neck RBF containing the d_3-p-xylene. The electrophile solution was added at a rate of one drop per second over a period of approximately 10 minutes. The reaction mixture was stirred at 0 °C for 2 hours. The reaction was then poured into a 125 mL separatory funnel charged with 50 mL of crushed ice. The separatory funnel was capped and shaken vigorously, and put aside until the aqueous and organic layers separated. The organic layer was recovered and collected, and the aqueous layer was extracted with 2 × 50 mL of dichloromethane. The combined organic layers were dried with anhydrous magnesium sulfate. The dried solution was filtered, and the solvent was removed by rotary evaporation *in vacuo*.

NMR Measurement and Calculation. Approximately 100 mg of sample was dissolved in 0.75 mL of benzene-d_6 and filled to the 5.0 cm mark in a standard 5 mm NMR tube. ^{2}H NMR spectra were recorded at 61.364 MHz on a Varian Unity 400 MHz NMR using a sweep width (200.0 Hz - 10 times the difference between the 2'-CD$_3$ and 5'-CD$_3$ resonances). The sweep width was then centered about the two peaks of interest. A calibrated 90° pulse width and an acquisition time of 8.00 s were used to collect a total of 3200 points. A delay of 12.0 s (approximately 10 times the duration of the T$_1$ value for the longest relaxing methyl group) was used to ensure quantitative relative ^{2}H measurement. The peaks at δ 2.32 ppm (2'-CD$_3$) and δ 1.99 ppm (5'-CD$_3$) were integrated separately using an integration cut that was five times of their line widths (FWHM). The ratio of the integration of these peaks represents the intramolecular ^{2}H KIE. A weighted average was then applied to the individual KIE measurements according to a method reported by Mandel to yield a value of 1.043 ± 0.002.[1]

1. Mandel, J *The Statistical Analysis of Experimental Data, pp 132-135*; Dover: Mineola, NY, 1984.

Raw Data from Intramolecular ^{2}H KIE Experiments

Table S1. Average ^{2}H integrations with errors for isolated product.

Experiment 1								
Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
2'-CD$_3$ integration	960.37	958.84	960.82	962.98	960.86	960.56	962.49	960.17
5'-CD$_3$ integration	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
Spectrum	**9**	**10**	**11**	**12**	**13**	**14**		
2'-CD$_3$ integration	947.56	952.76	956.36	954.47	972.31	959.86		
5'-CD$_3$ integration	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00		
[5'-CD$_3$]/[2'-CD$_3$] =1.042 ± 0.006								

Experiment 2								
Spectrum	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
2'-CD$_3$ integration	955.92	966.12	965.80	954.87	986.90	987.36	988.52	985.70
5'-CD$_3$ integration	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
Spectrum	**9**	**10**						
2'-CD$_3$ integration	985.47	988.66						
5'-CD$_3$ integration	1000.00	1000.00						
[5'-CD$_3$]/[2'-CD$_3$] =1.023 ± 0.015								

Experiment 3								
Spectrum	**1**	**2**	**3**	**4**	**5**	**6**		
2'-CD$_3$ integration	967.15	951.46	962.71	959.33	964.10	959.68		
5'-CD$_3$ integration	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00		
[5'-CD$_3$]/[2'-CD$_3$] =1.041 ± 0.006								

Experiment 4								
Spectrum	**1**	**2**	**3**	**4**	**5**	**6**		
2'-CD$_3$ integration	956.37	958.34	955.78	960.85	961.80	956.48		
5'-CD$_3$ integration	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00		
[5'-CD$_3$]/[2'-CD$_3$] =1.044 ± 0.003								
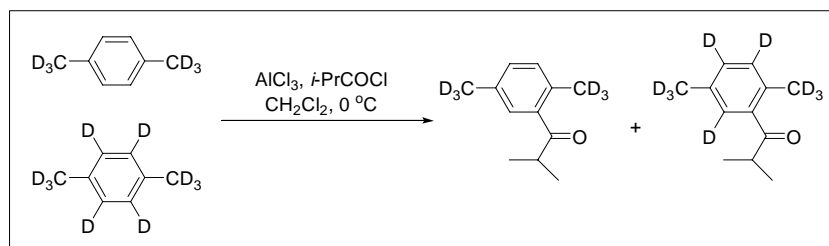
Procedure for Measuring Intermolecular ^{2}H KIEs (d_6- vs d_{10}-xylene)

Competition Reaction Experiment. The acylation for the intermolecular KIE measurement of the deprotonation step was performed identicalyl with that for intramolecular KIE measurement, except an approximately 1:1 mixture of d_{10}-p-xylene- and d_6-p-xylene served as the aromatic substrate. After drying the extracted mixture of unreacted starting material and converted product, the removal of solvent dichloromethane was accomplished using gentle distillation. In this distillation process, a water bath at 70 ^{o}C was utilized to limit the distillation rate in order to preserve the unreacted d_{10}-p-xylene- and d_6-p-xylene (bp ~133 ^{o}C) in the reaction mixture.

NMR Measurement and Calculation.
The sample was dissolved in 0.75 mL of CD_2Cl_2 and filled to the 5.0 cm mark in a standard 5 mm NMR tube.

^{1}H NMR spectra were recorded at 399.754 MHz using a Varian Unity 400 MHz instrument. A sweep width of 408.2 Hz was utilized with the spectral features of interest centered. An acquisition time of 16.00 s was used to collect a total of 13062 points. A delay of 60.0 s (>5 × T_1 based on an inversion recovery experiment) was used to ensure quantitative ^{1}H integrations. After acquisition, the spectrum was phased properly and a zero order correction was applied to the baseline. The singlet at δ 7.34 ppm (6'-H from product) and the singlet at δ 7.09 ppm (Ar-H, 4H, from reactant) were integrated separately using an integral cut of five times of their line widths (FWHM). The percent conversion (F_H) of p-xylene-*dimethyl-d_6* was calculated and recorded.

^{2}H NMR spectra were recorded at 92.278 MHz using a Brucker Avance 600 MHz instrument. A sweep width of 992.7 Hz was utilized with the spectral features of interest centered. An acquisition time of 6.00 s was used to collect a total of 11072 points. A delay of 3.0 s (>5 × T_1 based on an inversion recovery experiment) was used to ensure quantitative ^{2}H integrations. After acquisition, the spectrum was phased properly and a zero-order correction was applied to the baseline. The integrations of the singlet at δ 7.63 ppm (6'-D from product) and the singlet at δ 7.38 ppm (Ar-D, 4D, from reactant) were obtained using deconvolution with a mixed Gaussian-Lorentzian peak shape. The percent conversion (F_D) of p-xylene-d_{10} was calculated and recorded. The ^{2}H KIE was computed using eq. S1. A weighted average was then applied to the individual KIE measurements according to a method reported by Mandel to yield a value of 1.010 ± 0.007.[1]

$$KIE = \frac{k_H}{k_D} = \frac{\ln(1-F_H)}{\ln(1-F_D)} \tag{S1}$$

Raw Data from Intermolecular d_6- vs d_{10}-xylene Competition

Table S2. Integrations (^{1}H and ^{2}H) from which F_H and F_D are computed.

Experiment 1								
^{1}H Spectrum	1	2	3	4	5	6		
aryl (4H) p-xylene	709.12	706.205	708.986	714.356	721.611	727.455		
6'-H product	56.128	56.069	55.962	55.881	55.794	56.151		
F_H=0.239 ±0.002	0.240472	0.241032	0.239966	0.238329	0.236218	0.235914		
^{2}H Spectrum	1	2	3	4	5	6	7	8
aryl (4D) p-xylene	6.822	5.239	4.525	5.513	4.813	4.903	4.672	4.548
6'-D product	0.522	0.402	0.347	0.423	0.369	0.376	0.358	0.35
F_D=0.2348 ±0.0003	0.234343	0.234847	0.234737	0.234837	0.234696	0.234743	0.2346	0.235373
KIE=1.019±0.011								
Experiment 2								
^{1}H Spectrum	1	2	3	4				
aryl (4H) p-xylene	28.63	28.48	28.14	28.14				
6'-H product	400.00	400.00	400.00	400.00				
F_H=0.221 ±0.002	0.222576	0.221669	0.219604	0.219604				
^{2}H Spectrum	1	2	3	4	5	6	7	8
aryl (4D) p-xylene	19.55	8.969	10.259	10.529	12.113	14.62	11.283	13.821
6'-D product	1.415	0.652	0.74	0.751	0.84	1.044	0.795	0.951
F_D=0.221 ±0.003	0.224514	0.225274	0.22392	0.221976	0.217152	0.222175	0.219871	0.21583
KIE=0.998±0.010								
Experiment 3								
^{1}H Spectrum	1	2	3	4	5	6	7	8
aryl (4H) p-xylene	400.00	400.00	400.00	400.0	400.00	400.00	400.00	400.00
6'-H product	26.65	27.05	26.87	27.22	27.1	26.84	26.49	26.42
F_H=0.212 ±0.002	0.210422	0.212908	0.211792	0.21396	0.213218	0.211605	0.209424	0.208986
^{2}H Spectrum	1	2	3	4	5	6	7	8
aryl (4D) p-xylene	28.495	29.909	30.929	34.191	30.457	35.477	32.218	30.746
6'-D product	1.909	1.99	2.052	2.284	2.024	2.356	2.144	2.046
F_D=0.2103 ±0.0005	0.211342	0.210198	0.209725	0.210862	0.209997	0.209884	0.210227	0.210223
KIE=1.007±0.010								
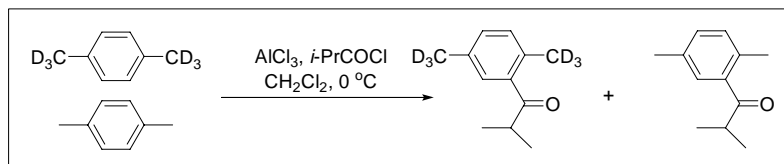
Procedure for Measuring Intermolecular ^{2}H KIEs (d_6-xylene vs xylene)

Competition Reaction Experiment. The acylation for the intermolecular KIE measurement resulting in fractionation of d_6-p-xylene and p-xylene was performed identically with that used for the intramolecular KIE measurement, except an approximately 1:1 mixture of d_6-p-xylene- and p-xylene served as the aromatic substrate. After drying the extracted mixture of unreacted starting material and converted product, the removal of solvent dichloromethane was accomplished using gentle distillation. In this distillation process, a water bath at 70 ^{o}C was utilized to limit the distillation rate in order to preserve the unreacted d_6-p-xylene- and p-xylene (bp ~133 ^{o}C) in the reaction mixture.

NMR Measurement and Calculation.
The sample was dissolved in 0.75 mL of CD_2Cl_2 and filled to the 5.0 cm mark in a standard 5 mm NMR tube.

^{1}H NMR spectra were recorded at 399.753 MHz using a Varian Unity 400 MHz instrument. A sweep width of 6387.7 Hz was utilized with the spectral features of interest centered. An acquisition time of 16.00 s was used to collect a total of 204408 points. A delay of 84.0 s (>5 × T_1 based on an inversion recovery experiment) was used to ensure quantitative ^{1}H integrations. After acquisition, the spectrum was phased properly, and a zero order correction was applied to the baseline. The doublet centered at δ 2.34 ppm (2'- and 5'-CH_3 from product) and the singlet at δ 2.29 ppm (methyl groups from reactant) were integrated separately using an integral cut of five times of their line widths (FWHM). These integrations were used to compute the fractional conversion (F_H) of p-xylene.

^{2}H NMR spectra were recorded at 61.364 MHz using a Varian Unity 400 MHz instrument. A sweep width of 200.0 Hz was utilized with the spectral features of interest centered. An acquisition time of 6.00 s was used to collect a total of 11072 points. A delay of 20.0 s was used to ensure quantitative ^{2}H integrations. After acquisition, the spectrum was phased properly and zeroth order correction was applied to the baseline. The two resonances centered at δ 2.32 ppm (2'- and 5'-CD_3 from product) and the singlet at δ 2.27 ppm (deuterated methyl groups from reactant) were integrated separately using an integral cut of three times their line widths (FWHM). In Table S3, the integrations for the 2'- and 5'-methyl groups are combined. These integrations were used to compute the fractional conversion (F_D) of d_6-p-xylene. The ^{2}H KIE was computed using eq. S1. A weighted average was then applied to the individual KIE measurements according to a method reported by Mandel to yield a value of 0.949 ± 0.004.[1]

Raw Data from Intermolecular d_6-p-xylene vs p-xylene Competition

Table S3. Integrations (^{1}H and ^{2}H) from which F_H and F_D are computed.

Experiment 1						
^{1}H Spectrum	1	2	3	4	5	6
1,4-(CH$_3$)$_2$	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
2'-,5'-CH$_3$	244.43	241.61	247.4	245.63	245.56	245.06
F_H=0.197 ±0.001	0.19641	0.19459	0.19833	0.19719	0.19714	0.19682
^{2}H Spectrum	1	2	3	4	5	6
1,4-(CD$_3$)$_2$	264.83	266.23	267.81	263.34	260.22	259.64
2'-,5'-CD$_3$	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
F_D=0.209 ±0.002	0.20938	0.21025	0.21124	0.20845	0.20649	0.20612
KIE = 0.936 ± 0.012						

Experiment 2						
^{1}H Spectrum	1	2	3	4	5	6
1,4-(CH$_3$)$_2$	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
2'-,5'-CH$_3$	286.40	286.13	286.06	286.57	286.73	285.37
F_H=0.2225 ±0.0003	0.22264	0.22247	0.22243	0.22274	0.22284	0.22201
^{2}H Spectrum	1	2	3	4	5	6
1,4-(CH$_3$)$_2$	306.13	305.56	300.13	300.3	303.26	298.44
2'-,5'-CH$_3$	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
F_D=0.232 ±0.002	0.23438	0.23405	0.23085	0.23095	0.23269	0.22985
KIE = 0.953 ± 0.009						

Experiment 3						
^{1}H Spectrum	1	2	3	4	5	6
1,4-(CH$_3$)$_2$	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
2'-,5'-CH$_3$	1840.73	1838.42	1841.14	1855.75	1854.1	1849.04
F_H=0.6487 ±0.0009	0.647978	0.647691	0.648029	0.649829	0.649627	0.649005
^{2}H Spectrum	1	2	3	4	5	6
1,4-(CH$_3$)$_2$	1984.59	2010.34	2011.4	2013.2	2012.8	1991.25
2'-,5'-CH$_3$	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
F_D=0.667 ±0.001	0.664946	0.667812	0.667929	0.668127	0.668083	0.6656916
KIE = 0.951 ± 0.004						

Experiment 4						
^{1}H Spectrum	1	2	3	4	5	6
1,4-(CH$_3$)$_2$	1000.00	1000.00	1000.00	1000.00	1000.00	1000.00
2'-,5'-CH$_3$	381.57	382.37	380.76	381.77	385.44	384.51
F_H=0.277 ±0.001	0.27619	0.27660	0.27576	0.27629	0.27821	0.27772
^{2}H Spectrum	1	2	3	4	5	
1,4-(CH$_3$)$_2$	405.29	413.42	407.57	407.25	417.39	
2'-,5'-CH$_3$	1000.00	1000.00	1000.00	1000.00	1000.00	
F_D=0.291 ±0.002	0.2884031	0.2924962	0.2895558	0.2893942	0.2944779	
KIE = 0.943 ± 0.010						

Computed Structures

All quantum mechanical calculations were performed with Gaussian09.[1] All structures were fully optimized using the M06-2X hybrid functional together with the 6-31+G(d,p) basis set.

Solvent effects (dichloromethane) in the computed geometries and frequencies were taken into account by means of the IEFPCM solvation model as implemented in Gaussian09. All IEFPCM calculations were carried out at the M06-2X/6-31+G(d,p) level of theory. The solute cavities were generated using the United Atom Topological Model UA0 set of radii.

1.   Gaussian 09, Revision A.1, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.

η^6-π-complex (gas phase)

E(RM062X) = -542.238874007

```
Zero-point correction=                                  0.261239
(Hartree/Particle)
 Thermal correction to Energy=                          0.276626
 Thermal correction to Enthalpy=                        0.277570
 Thermal correction to Gibbs Free Energy=               0.217536
 Sum of electronic and zero-point Energies=            -541.977635
 Sum of electronic and thermal Energies=               -541.962248
 Sum of electronic and thermal Enthalpies=             -541.961304
 Sum of electronic and thermal Free Energies=          -542.021338
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	E (Thermal)	CV	S
	KCal/Mol	Cal/Mol-Kelvin	Cal/Mol-Kelvin
Total	173.585	55.210	126.352

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C        0      2.619048   -0.677784    1.355691
H        0      2.200802    0.318261    1.495297
H        0      2.236827   -1.347795    2.127449
H        0      3.706152   -0.626896    1.443773
C        0      2.314111   -1.192417   -0.062603
H        0      2.733700   -2.204714   -0.189149
C        0      2.811073   -0.277236   -1.198340
H        0      2.578072   -0.682476   -2.184382
H        0      2.383363    0.719437   -1.097066
H        0      3.896249   -0.212787   -1.095417
C        0      0.889680   -1.473404   -0.224819
C        0     -1.849359    0.394961   -1.132655
C        0     -2.349320   -0.142693    0.061370
C        0     -0.710657    1.196339   -1.142128
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C        0     -0.516925    0.936524    1.241352
H        0     -2.033139   -0.254670    2.188440
O        0     -0.127925   -1.915501   -0.394051
H        0     -0.037051    1.188718    2.185277
C        0     -3.578868   -1.011558    0.062606
H        0     -3.323314   -2.047619   -0.187323
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H        0     -4.305513   -0.665686   -0.676030
C        0      1.041231    2.562372    0.074724
H        0      1.851732    2.333451    0.773886
H        0      1.470193    2.734191   -0.916087
H        0      0.604997    3.511666    0.402392
H        0     -2.372795    0.198432   -2.065029
```

η¹-π-complex (gas phase)

η¹-π-complex (gas phase)

SCF Done: E(RM062X) = -542.236964346

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Zero-point correction=                               0.260940
(Hartree/Particle)
 Thermal correction to Energy=                       0.275592
 Thermal correction to Enthalpy=                     0.276536
 Thermal correction to Gibbs Free Energy=            0.219259
 Sum of electronic and zero-point Energies=         -541.976024
 Sum of electronic and thermal Energies=            -541.961372
 Sum of electronic and thermal Enthalpies=          -541.960428
 Sum of electronic and thermal Free Energies=       -542.017705
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	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	172.937	53.263	120.550

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C       0      -0.961967     -1.106813      1.662493
H       0       0.012617     -0.893361      1.222011
H       0      -1.255827     -0.289619      2.323278
H       0      -0.904657     -2.027665      2.246463
C       0      -1.997650     -1.361758      0.550867
H       0      -2.977455     -1.623500      0.987447
C       0      -1.570770     -2.440747     -0.468824
H       0      -2.311889     -2.588087     -1.255843
H       0      -0.603405     -2.181635     -0.900652
H       0      -1.471927     -3.370756      0.094721
C       0      -2.343528     -0.129257     -0.140882
C       0       0.289400      0.787180     -1.145944
C       0       0.301792      1.687751     -0.073426
C       0       1.219575     -0.258018     -1.225474
C       0       1.267262      1.494332      0.927411
C       0       2.183308     -0.441936     -0.233922
H       0       1.219614     -0.907197     -2.098458
C       0       2.187896      0.456857      0.845525
H       0       1.314480      2.189207      1.762506
O       0      -2.802718      0.764181     -0.641589
H       0       2.940154      0.347197      1.622914
C       0      -0.620260      2.881317     -0.025902
H       0      -1.254739      2.874321      0.867858
H       0      -0.039429      3.807335      0.007669
H       0      -1.260903      2.933426     -0.909710
C       0       3.206617     -1.544530     -0.315407
H       0       3.082983     -2.259602      0.504284
H       0       3.131047     -2.090071     -1.258149
H       0       4.218772     -1.137594     -0.240637
H       0      -0.387749      0.957884     -1.982093
```

σ-complex (gas phase)

```
SCF Done:  E(RM062X) =  -542.233849762

Zero-point correction=                             0.261940
(Hartree/Particle)
 Thermal correction to Energy=                     0.276452
 Thermal correction to Enthalpy=                   0.277397
 Thermal correction to Gibbs Free Energy=          0.220895
 Sum of electronic and zero-point Energies=            -541.971909
 Sum of electronic and thermal Energies=               -541.957397
 Sum of electronic and thermal Enthalpies=             -541.956453
 Sum of electronic and thermal Free Energies=          -542.012955
```

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	173.477	53.951	118.918

```
C        0        -0.807295   -1.083429    1.817963
H        0         0.253216   -0.869428    1.669036
H        0        -1.291929   -0.210714    2.264688
H        0        -0.882598   -1.907298    2.532364
C        0        -1.475641   -1.513594    0.510248
H        0        -2.520188   -1.780978    0.704548
C        0        -0.778500   -2.713883   -0.138379
H        0        -1.160416   -2.924102   -1.140951
H        0         0.305766   -2.583916   -0.180927
H        0        -0.974064   -3.592605    0.481386
C        0        -1.637101   -0.330730   -0.427453
C        0        -0.225461    0.542309   -0.953777
C        0        -0.178279    1.691078   -0.052832
C        0         0.961424   -0.288538   -1.070984
C        0         0.945034    1.847777    0.749494
C        0         2.067914   -0.106684   -0.279517
H        0         0.961427   -1.061964   -1.835704
C        0         2.030104    0.981510    0.630182
H        0         1.000300    2.683385    1.440263
O        0        -2.649374    0.117170   -0.834273
H        0         2.906368    1.162017    1.250968
C        0        -1.314302    2.660321    0.005412
H        0        -2.101690    2.281484    0.669881
H        0        -0.978020    3.618104    0.405835
H        0        -1.770625    2.813075   -0.973859
C        0         3.290572   -0.977144   -0.373785
H        0         3.466643   -1.496595    0.573147
H        0         3.181299   -1.726800   -1.159393
H        0         4.178870   -0.378799   -0.593531
H        0        -0.650176    0.783825   -1.932997
```

xylene (gas phase)

```
SCF Done:  E(RM062X) =  -310.749750401

Zero-point correction=                            0.156243
(Hartree/Particle)
 Thermal correction to Energy=                    0.164272
 Thermal correction to Enthalpy=                  0.165216
 Thermal correction to Gibbs Free Energy=         0.122879
 Sum of electronic and zero-point Energies=          -310.593507
 Sum of electronic and thermal Energies=             -310.585479
 Sum of electronic and thermal Enthalpies=           -310.584535
 Sum of electronic and thermal Free Energies=        -310.626871

                      E (Thermal)             CV              S
                       KCal/Mol        Cal/Mol-Kelvin  Cal/Mol-Kelvin
    Total               103.082            29.212           89.105


 C        0      -1.417429    0.002110    0.013038
 C        0      -0.695872   -1.195707    0.007408
 C        0       0.695873   -1.195708   -0.007418
 C        0       1.417429    0.002109   -0.013028
 C        0       0.697016    1.197979   -0.007471
 C        0      -0.697015    1.197979    0.007461
 H        0      -1.232881   -2.141561    0.013090
 H        0       1.232880   -2.141563   -0.013119
 H        0       1.233231    2.144065   -0.013317
 H        0      -1.233230    2.144066    0.013288
 C        0       2.925488   -0.002412    0.005088
 H        0       3.304038   -0.127428    1.025335
 H        0       3.325753   -0.822387   -0.597648
 H        0       3.328316    0.935502   -0.385685
 C        0      -2.925489   -0.002413   -0.005077
 H        0      -3.328316    0.935483    0.385742
 H        0      -3.304054   -0.127384   -1.025323
 H        0      -3.325743   -0.822413    0.597630
```

η^6-π-complex (PCM)

```
SCF Done:  E(RM062X) =  -542.305880156

Zero-point correction=                           0.261071
(Hartree/Particle)
 Thermal correction to Energy=                   0.276541
 Thermal correction to Enthalpy=                 0.277485
 Thermal correction to Gibbs Free Energy=        0.216688
 Sum of electronic and zero-point Energies=          -542.044809
 Sum of electronic and thermal Energies=             -542.029339
 Sum of electronic and thermal Enthalpies=           -542.028395
 Sum of electronic and thermal Free Energies=        -542.089192
```

	E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total	173.532	55.207	127.957

C	0	2.619643	-0.593587	1.359200
H	0	2.128127	0.374780	1.445120
H	0	2.286461	-1.250446	2.162866
H	0	3.699345	-0.457030	1.436779
C	0	2.360999	-1.204809	-0.031756
H	0	2.855411	-2.186105	-0.112118
C	0	2.781193	-0.302255	-1.209066
H	0	2.572225	-0.766236	-2.173213
H	0	2.283861	0.665198	-1.143380
H	0	3.858305	-0.157732	-1.111721
C	0	0.965892	-1.581861	-0.165929
C	0	-1.827027	0.334387	-1.155778
C	0	-2.330714	-0.176903	0.045461
C	0	-0.731758	1.196270	-1.168701
C	0	-1.695317	0.197281	1.235073
C	0	-0.108960	1.590562	0.022695
H	0	-0.374074	1.595830	-2.114715
C	0	-0.601071	1.060108	1.225177
H	0	-2.066272	-0.186100	2.182354
O	0	-0.072596	-1.985153	-0.284592
H	0	-0.145011	1.358585	2.166954
C	0	-3.491599	-1.137009	0.051782
H	0	-3.140036	-2.166984	-0.077770
H	0	-4.038413	-1.089875	0.996263
H	0	-4.186281	-0.921306	-0.763495
C	0	0.965431	2.649632	0.024054
H	0	1.755548	2.441523	0.751780
H	0	1.421159	2.762567	-0.963107
H	0	0.530708	3.617457	0.295006
H	0	-2.300559	0.056197	-2.094123

η^1-π-complex (PCM)

```
SCF Done:  E(RM062X) =  -542.305651141

Zero-point correction=                            0.261544
(Hartree/Particle)
 Thermal correction to Energy=                    0.276905
 Thermal correction to Enthalpy=                  0.277849
 Thermal correction to Gibbs Free Energy=         0.218216
 Sum of electronic and zero-point Energies=          -542.044108
 Sum of electronic and thermal Energies=             -542.028746
 Sum of electronic and thermal Enthalpies=           -542.027802
 Sum of electronic and thermal Free Energies=        -542.087436

                      E (Thermal)             CV                   S
                       KCal/Mol        Cal/Mol-Kelvin      Cal/Mol-Kelvin
       Total            173.760            54.929              125.509


   C        0        -1.060177    -1.005754     1.633253
   H        0        -0.099484    -0.821328     1.150857
   H        0        -1.317687    -0.171903     2.286982
   H        0        -0.997487    -1.918115     2.228440
   C        0        -2.147495    -1.266316     0.570036
   H        0        -3.111399    -1.497939     1.050464
   C        0        -1.772461    -2.367926    -0.445736
   H        0        -2.547917    -2.514147    -1.197343
   H        0        -0.820178    -2.130397    -0.922143
   H        0        -1.662487    -3.286055     0.133540
   C        0        -2.458240    -0.042014    -0.137138
   C        0         0.402398     0.806905    -1.161386
   C        0         0.469376     1.700141    -0.086285
   C        0         1.251478    -0.301402    -1.233137
   C        0         1.419156     1.447871     0.912494
   C        0         2.191766    -0.555928    -0.231856
   H        0         1.192859    -0.964751    -2.093195
   C        0         2.264591     0.344613     0.839677
   H        0         1.503351     2.133637     1.752156
   O        0        -2.767991     0.891449    -0.674243
   H        0         2.998038     0.179718     1.625021
   C        0        -0.423719     2.913275    -0.003659
   H        0        -1.152527     2.815710     0.809120
   H        0         0.163245     3.812850     0.200858
   H        0        -0.970230     3.072079    -0.936379
   C        0         3.083755    -1.769437    -0.290945
   H        0         2.617805    -2.616105     0.225261
   H        0         3.269803    -2.072634    -1.324136
   H        0         4.044892    -1.577107     0.191629
   H        0        -0.289243     1.000728    -1.979095
```

σ-complex (PCM)

```
SCF Done:  E(RM062X) =  -542.297511079

Zero-point correction=                           0.261892
(Hartree/Particle)
 Thermal correction to Energy=                   0.276174
 Thermal correction to Enthalpy=                 0.277118
 Thermal correction to Gibbs Free Energy=        0.221294
 Sum of electronic and zero-point Energies=         -542.035619
 Sum of electronic and thermal Energies=            -542.021337
 Sum of electronic and thermal Enthalpies=          -542.020393
 Sum of electronic and thermal Free Energies=       -542.076217
```

		E (Thermal) KCal/Mol	CV Cal/Mol-Kelvin	S Cal/Mol-Kelvin
Total		173.302	53.417	117.491

```
C        0      -1.059167   -0.667686    1.854361
H        0       0.027795   -0.617616    1.742051
H        0      -1.432896    0.314510    2.156888
H        0      -1.269087   -1.367923    2.666794
C        0      -1.728709   -1.179351    0.579301
H        0      -2.809035   -1.260379    0.735030
C        0      -1.192861   -2.563265    0.180257
H        0      -1.573568   -2.885598   -0.792379
H        0      -0.099038   -2.586158    0.163085
H        0      -1.520571   -3.286396    0.931439
C        0      -1.613199   -0.193047   -0.568602
C        0      -0.174672    0.462418   -0.887961
C        0       0.031122    1.651203   -0.035798
C        0       0.923976   -0.510489   -0.969805
C        0       1.229339    1.783797    0.640500
C        0       2.094377   -0.360818   -0.277988
H        0       0.792041   -1.349337   -1.649702
C        0       2.221819    0.808947    0.517904
H        0       1.411735    2.657056    1.257507
O        0      -2.539545    0.155107   -1.244638
H        0       3.156676    0.959788    1.054611
C        0      -1.045118    2.678516    0.059100
H        0      -1.889687    2.284571    0.638740
H        0      -0.681653    3.579091    0.553217
H        0      -1.435777    2.930549   -0.930477
C        0       3.223497   -1.349314   -0.351902
H        0       3.399279   -1.795800    0.630916
H        0       2.997964   -2.148170   -1.059459
H        0       4.147442   -0.855947   -0.664782
H        0      -0.367692    0.821437   -1.912574
```

xylene (PCM)

```
SCF Done:  E(RM062X) =  -310.752383911

Zero-point correction=                            0.155811
(Hartree/Particle)
 Thermal correction to Energy=                    0.162175
 Thermal correction to Enthalpy=                  0.163119
 Thermal correction to Gibbs Free Energy=         0.125415
 Sum of electronic and zero-point Energies=          -310.596582
 Sum of electronic and thermal Energies=             -310.590217
 Sum of electronic and thermal Enthalpies=           -310.589273
 Sum of electronic and thermal Free Energies=        -310.626977

                      E (Thermal)             CV                S
                       KCal/Mol        Cal/Mol-Kelvin    Cal/Mol-Kelvin
     Total              101.766            25.316            79.354


     C       0      -1.418438    0.002131    0.012453
     C       0      -0.695454   -1.195322    0.007202
     C       0       0.695455   -1.195323   -0.007234
     C       0       1.418439    0.002129   -0.012473
     C       0       0.696641    1.197518   -0.007422
     C       0      -0.696639    1.197519    0.007389
     H       0      -1.234554   -2.142725    0.012735
     H       0       1.234555   -2.142726   -0.012730
     H       0       1.235009    2.145144   -0.013293
     H       0      -1.235003    2.145148    0.013298
     C       0       2.918648   -0.002194    0.004443
     H       0       3.305466   -0.146250    1.021578
     H       0       3.324633   -0.813050   -0.610955
     H       0       3.325747    0.944092   -0.367855
     C       0      -2.918650   -0.002194   -0.004395
     H       0      -3.325727    0.944057    0.368023
     H       0      -3.305542   -0.146151   -1.021515
     H       0      -3.324594   -0.813117    0.610938
```