SUPPORTING INFORMATION

Gas-phase Fragmentation of Deprotonated *p*-Hydroxyphenacyl Derivatives

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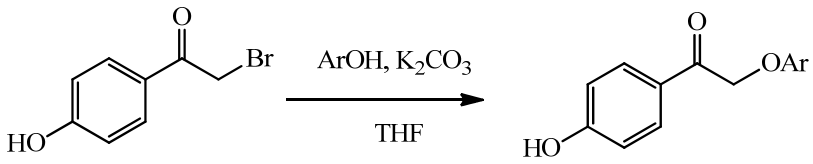
Contents

Synthesis and spectral properties of new pHP esters

I. Phenolates (X = C_6H_5O, *p*-$CF_3C_6H_4O$, and *p*-$CH_3OC_6H_4O$)

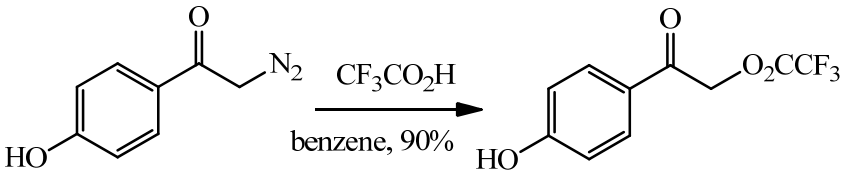


2'-Phenoxy-4-hydroxyacetophenone (pHP OC_6H_5). To a solution of 0.7g (7.4 mmol) of phenol and 1.0 g (7.4 mmol) potassium carbonate in 20 mL of THF in ice bath, was added dropwise to a solution of 1.3g (8.7 mmol) of α-bromo pHP in 20 mL THF by an additional funnel. After 2 h, the white solid was filtered and the remaining solution of filtrate was stirred with a magnetic stir bar at room temperature for an additional 24 h. The mixture was filtered, the filtrate was concentrated using a rotary evaporator. Flash chromotography 3/1 hexane/EtOAc was used to separate the mixture and to obtain the product 0.5 g, (Procedure **A**). Needle crystals with mp 167-169 °C. Spectral data: UV ε_{271}=18000, ε_{218}=19000. (KBr), 3211(OH), 1664 (C=O). ^{1}H NMR ($CDCl_3$) δ 5.25 (s, 2H), 6.8-7.9 (m, 9H); ^{13}C NMR ($CDCl_3$) δ (ppm) 70.2, 114.8, 115.5, 121.3, 129.5, 130.8, 158.7, 163.6, 194.4. HRMS, $[M+Na]^+$, calc. 251.0684, found, 251.0678.

2'-(4'-Trifluoromethylphenoxy)-4-hydroxyacetophenone (pHP *p*-$CF_3C_6H_4O$). This was synthesized by procedure **A** above. White solid with mp174-175 ^{o}C. Spectral data: UV ε_{271}=238000, ε_{223}=251000. IR (KBr), 3151(OH), 1668 (C=O). ^{1}H NMR ($CDCl_3$) δ (ppm) 5.47 (s, 2H), 6.98 (d, *J* = 8.8 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.62 (d, *J* = 8.8 Hz, 2H), 7.95 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ (ppm) 71.1, 116.1, 116.5, 118.4, 127.1, 136.8, 123.4 (q, J= 32.4 Hz, 1C), 131.8, 125.7 (q, *J* = 268.5 Hz, 1C), 162.2, 163.2, 193.1. HRMS, $[M+H]^+$, calc. 297.0739, found, 297.0739.

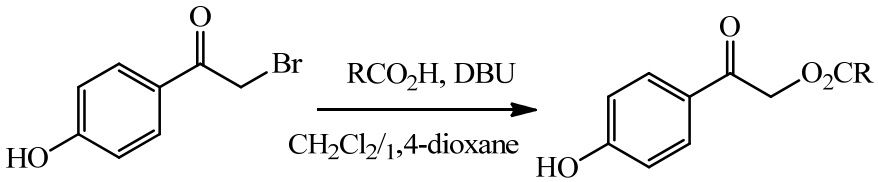
2'-(4'-Methoxyphenoxy)-4-hydroxyacetophenone (pHP *p*-$CH_3OC_6H_4O$)**.** This was synthesized by procedure **A** above. Solid with mp 133-134 ^{o}C. Spectral data: UV ε_{273}=181000, ε_{220}=185000. IR (KBr), 3323(OH), 1666 (C=O). ^{1}H NMR ($CDCl_3$) δ (ppm) 3.75 (s, 3H), 5.29 (s, 2H), 6.87 (m, 4H), 6.92 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ (ppm) 55.6, 71.0, 114.9, 115.7, 115.9, 127.6, 131.1, 152.7, 154.6, 162.3, 193.6. HRMS, $[M+H]^+$, calc. 259.0970, found, 259.0967.

II. pHP trifluoroacetate (pHP CF_3COO).



***p*-Hydroxyphenacyl trifluoroacetate (pHP CF_3COO).** To a cooled (0 °C), stirred solution of α-diazo-*p*-hydroxyacetophenone (10 mg, 0.062 mmol) in benzene (6 mL), trifluoroacetic acid (14 mg, 0.12 mmol) was added dropwise at 0 °C. The resulting mixture was stirred at 0 °C to rt and the progress of the reaction was monitored by TLC. After 1 h the benzene layer was washed sequentially with saturated $NaHCO_3$ (20 mL) and water (20 mL) and dried over anhydrous $MgSO_4$. The solvent was evaporated to give crude trifluoroacetate ester as a yellowish brown solid that was chromatographed on silica gel (EtOAc/hexane 1:1) to give pure pHP CF_3COO as a white solid (14 mg, 0.056 mmol, 94% yield)with mp = 128-131 °C. Spectral data: ^{1}H NMR (CD_3COCD_3) δ (ppm) 9.43 (1H, s), 7.95-7.93 (2H, dd, *J* = 6.8 Hz, 2 Hz), 7.00-6.98 (2H, dd, *J* = 6.8 Hz, 2 Hz), 5.81 (2H, s), ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -75.7 (3F, s); ^{13}C NMR (125 MHz, CD_3COCD_3) δ (ppm) 188.6, 163.9, 157.5, 131.5, 126.8, 116.9, 114.7, 69.9; IR (KBr, cm^{-1}) 3240, 1782, 1674, 1605, 1574, 960, 845, 725; ESI-HRMS, $[M-H]^+$, calc. 247.0218, found: 247.0218.

III. pHP formate and *p*-methoxybenzoate (pHP HCOO and pHP *p*-$MeOC_6H_4COO$).



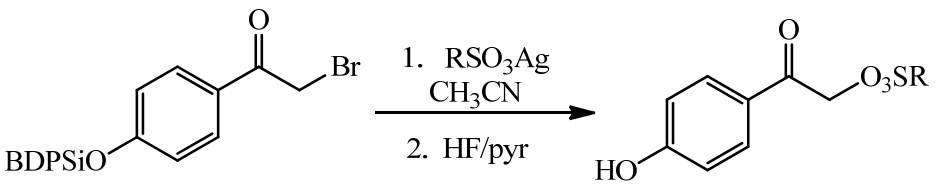
***p*-Hydroxyphenacyl Formate (pHP HCOO).** Method **A**. Carboxylate esters were synthesized according to a method based upon a method used by Buu-Hoi and Lavit.[S1] α-Bromo-*p*-hydroxyacetophenone (1.2 g, 5.4 mmol) and DBU (1.7 mL, 11 mmol), were combined.and placed in a 250 mL round bottom flask and dissolved in 100 mL of 1:1 CH_2Cl_2/1,4-dioxane and cooled to 0° C. Once the acid and base solutions were cool, the formic acid (0.50 mL, 8.1 mmol) was slowly added to the base making sure to keep the flask cold. When the acid had dissolved, the solution was stirred and was monitored by TLC (1:1 hexanes/EtOAc). When the reaction was judged to be complete, equal volumes of CH_2Cl_2 and H_2O were added to the reaction mixture. The organic layer was washed 3 times with 50 mL of H_2O, 50 mL saturated $NaHCO_3$ solution, and dilute HCl and then washed once with

brine, dried over $MgSO_4$, and gravity filtered. The solvent was removed using rotoevaporation. Purification was performed using column chromatography (6:4 hexanes/EtOAc) or by recrystallization in EtOAc to yield a white crystalline solid (0.34 g, 1.9 mmol, 35%; mp: 146 – 147 °C). Spectral data: ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 10.58 (s, 1H), 8.46 (s, 1H), 7.91 (d, 2H), 6.94 (d, 2H), 5.54 (s, 2H). ^{13}C NMR (500 MHz, DMSO-d_6): δ (ppm) 190.1, 162.7, 161.6, 130.4, 125.2, 115.4, 65.5. IR (KBr, cm^{-1}): 3350, 2925, 1730, 1683, 1602, 1586, 1500, 822 cm^{-1}. UV-VIS (9:1 CH_3CH/H_2O) λ 220 (ε = 5,200) and 280 (ε = 10,000). HRMS, $[M+H]^+$, calc. 181.052, found 181.0501 (M +H).

Method **B**. Potassium formate (2.7 g, 32 mmol) and a large stir bar were placed in a 500 mL Erlenmeyer flask. Absolute EtOH (150 mL) was added and the mixture was allowed to stir and heat at 55 – 60 °C for 15 minutes. α-Bromo-*p*-hydroxyacetophenone (2.0 g, 44 mmol) was added to the flask and the reaction was heated to between 55 and 60 °C 24 h. The solution was hot filtered and the ethanol was removed. The resulting solid was dissolved in EtOAc and washed twice with water and once with saturated $NaHCO_3$ and then brine. The organic layer was separated, dried, and the solvent was removed with rotoevaporation to afford a yellow solid. This solid was dissolved in acetone and purified by flash chromatography (1:1 hexane/EtOAc) to afford a white solid (0.33 g, 18 mmol, 41%; mp = 145 – 147 °C). The solid was recrystallized using 1:1 hexanes/Et_2O affording colorless crystals. This ester was also synthesized by the method employed for pHP trifluoroacetate.

***p*-Hydroxyphenacyl *p*-methoxybenzoate (pHP *p*-$MeOC_6H_4COO$)** α-Bromo-*p*-hydroxyacetophenone (5.0 g, 23 mmol), DBU (5.2 mL, 35 mmol), and *p*-methoxybenzoic acid (4.6 g, 30 mmol) were combined in the procedure outline above. The reaction was judged to be complete after 6 hours. The crude solid was purified by flash chromatography (7:3 hexanes/EtOAc) and then by recrystallization in 8:2 hexanes/EtOAc resulting in colorless crystals (4.9 g, 17 mmol, 75%; mp: 184 – 185 °C) Spectral data: ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 10.52 (s, 1h), 7.98 (d, 2H), 7.88 (d, 2H), 7.09 (m, 4H), 6.89 (d, 2H), 5.59 (s, 2H), 3.85 (s, 3H). ^{13}C NMR (500 MHz, DMSO-d_6): δ (ppm) 191.2, 165.3, 163.7, 163.1, 131.9, 130.7, 125.9, 121.8, 115.9, 114.5, 66.8, 56.0. IR (KBr, cm^{-1}): 3357, 16805 1680, 1604, 1583, 1500. UV-VIS (7:3 CH_3CN/H_2O) λ 273 (ε = 23000)

IV. pHP mesylate and pHP tosylate (pHP MsO and pHP TsO).



R = CH_3, *p*-$CH_3C_6H_4$,

***p*-Hydroxyphenacyl Mesylate pHP MsO.** *tert*-Butyldiphenylsilyl protected *p*-hydroxyphenacyl mesylate was prepared according to a general method for carboxylate esters as described by Phillips and coworkers.[S2] 2-(4-(*tert*-Butyldiphenylsilyloxy)phenyl)-2-oxoethyl methanesulfonate was prepared according to a method based on one described by Emmons and Ferris.[S4] Silver oxide (5.0 g, 40 mmol) was placed in a 250 mL round bottom flask with a stir bar. Acetonitrile (50 mL) was added to the flask and stirred vigorously to form a suspension. Methanesulfonic acid (1.8 mL, 2.6 g, 27 mmol) was added to the silver oxide suspension. The solution was allowed to stir at room temperature for 45 minutes. In a 500 mL Erlenmeyer flask, 2-(4-(*tert*-Butyldiphenylsilyloxy)phenyl)-2-oxoethyl bromide (9.4 g, 21 mmol) was dissolved in 100 mL CH_3CN. After the time, the silver oxide solution was filtered and the filtrate was added to the bromide solution. This reaction mixture was stirred at 70 °C for 3 days. The mixture was filtered and the solvent removed. The yellow solid was dissolved in acetone and filtered again. Flash chromatography (7:3 hexane/Et_2O) was used to purify the crude material resulting in a white solid (6.8 g, 14 mmol, 69 %) with mp: 108 – 110 °C. Spectral data: ^{1}H NMR (500 MHz, DMSO): δ (ppm) 7.69 (d, 2H), 7.58 (m, 4H), 7.37 (m, 6H), 6.88 (d, 2H), 5.47 (s, 2H), 2.04 (s, 3H), 0.98 (s, 9H). ^{13}C NMR (500 MHz, DMSO): δ (ppm) 192.5, 159.9, 134.9, 131.1, 130.5, 129.2, 127.2, 119.9, 71.0, 37.4, 29.0, 18.9. IR (KBr, cm^{-1}): 1704, 1598, 1508, 1370, 1159, 821. HRMS, $[M+H]^+$, calc. 469.1505, found 469.1505 ($^+$).

Deprotection (Method **A**) involved placing the 4-*tert*-butyldiphenylsilyloxyphenacyl mesylate (1.5 g, 3.2 mmol) in a 100 mL round bottom flask equipped with stirring and cooling to 0 °C. The solid dissolved in 10 mL THF and allowed to cool for 5 minutes. TBAF (1M in THF, 3.60 mL, 3.24 mmol) was added to the solution. After 15 minutes the reaction was quenched with cold DI water and extracted with EtOAc. The organic layer was washed with $NaHCO_3$, dilute HCL, and brine. The organic layer was dried over $MgSO_4$, filtered, and the solvent removed. The crude solid was purified using flash chromatography (6:4 hexanes/EtOAc) resulting in an off white solid (0.41 g, 55%) with mp = 154 – 156 °C). Spectral data: ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 10.56 (s, 1H), 7.85 (d, 2H), 6.90 (d, 2H), 5.61 (s, 2H), 3.36 (s, 3H). ^{13}C NMR (500 MHz, DMSO-d_6): δ (ppm) 189.5, 162.8, 130.5,

125.1, 115.4, 70.9, 37.6. IR (KBr, cm^{-1}): 3418, 1684, 1603, 1580, 1526, 1443, 1427, 1367, 1211, 1168, 1053, 839. UV-VIS (1:1 CH_3CN/H_2O): λ 273 (ε = 16,000), 219 (ε = 11,000). HRMS, $[M+H]^+$, calc. 231.033, found 231.0327. Method B *p*-Hydroxyphenacyl mesylate was prepared according to a method based on one described by McDevitt and coworkers.[S3] Protected mesylate (1.0 g, 2.1 mmol) was dissolved in 15 mL dry THF in a 100 mL round bottom flask. The flask was equipped with stirring and placed in an ice bath. Hydrogen fluoride in pyridine (0.20 mL, 2.4 mmol) was slowly added to the round bottom flask. The mixture was allowed to stir for 1 h and then quenched with water. The mixture was extracted twice with 20 mL EtOAc. The organic layer was then washed with saturated $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and the solvent was removed using rotary evaporation. The crude solid was purified using flash chromatography (1:1 hexanes/EtOAc) resulting in a white solid (0.48 g, 2.1 mmol, 100%) with mp = 155 – 157 °C. This solid was recrystallized in 9:1 hexanes/EtOAc resulting in colorless crystals. This ester was also synthesized by the method employed for pHP trifluoroacetate.

***p*-Hydroxyphenacyl Tosylate (pHP TsO).** *p*-Hydroxyphenacyl tosylate was prepared according to a method based on one described by McDevitt and coworkers.[3] 2-(4-(*tert*-Butyldiphenylsilyloxy)phenyl)-2-oxoethyl 4-methylbenzene-sulfonate was prepared according to a method based on one described by Emmons and Ferris.[S4] Silver oxide (5.0 g, 40 mmol) was placed in a 250 mL round bottom flask with a stir bar. Acetonitrile (50 mL) was added to the flask and stirred vigorously to form a suspension. *p*-Toluenesulfonic acid (5.1 g, 27 mmol) was added to the silver oxide suspension. The solution was allowed to stir at rt for 45 min. In a 500 mL Erlenmeyer flask, BDPSi protected *p*-hydroxyphenacyl bromide (9.4 g, 21 mmol) was dissolved in 100 mL CH_3CN. After the time, the silver oxide solution was filtered and the filtrate was added to the bromide solution. This reaction mixture was stirred at 70 °C for 3 d. The mixture was filtered and the solvent removed. The orange solid was dissolved in acetone and filtered again. Flash chromatography (9:1 hexanes/Et_2O) was used to purify the crude material resulting in an off-white solid (8.0 g, 15 mmol, 70 %) with mp = 120 – 122 °C. Spectral data: ^{1}H NMR (500 MHz, DMSO): δ (ppm) 7.90 (d, 2H), 7.80 (d, 2H), 7.70 (M, 4H), 7.54, (m, 6H), 6.82 (d, 2H), 5.41 (s, 2H), 3.42 (s, 3H), 1.08 (s, 9H). ^{13}C NMR (500 MHz, DMSO): δ (ppm) 192.5, 160.5, 145.8, 145.0, 134.9, 131.2, 130.5, 130.0, 128.4, 127.7, 126.2, 119.9, 71.0, 26.1, 21., 18.9. IR (KBr, cm^{-1}): 1697, 1596, 1573, 1508, 1467, 1460, 1371, 1367, 1166, 827. HRMS, $[M+H]^+$, calc. 545.182, found 545.1818.

Removal of the protecting group from 4-*tert*-butyldiphenylsilyloxyphenacyl tosylate (1.0 g, 1.8 mmol) was accomplished by dissolving it in 15 mL dry THF in a 100 mL round bottom flask. The flask was equipped with stirring and placed in an ice bath. Hydrogen fluoride in pyridine (0.18 mL, 2.0 mmol) was slowly added to the round bottom flask. The mixture was allowed to stir for 1 h and then quenched with water. The mixture was extracted twice with 20 mL EtOAc. The organic layer was then washed with saturated $NaHCO_3$ and brine. The organic layer was dried over $MgSO_4$ and the solvent was removed using rotary evaporation. The crude solid was purified using flash chromatography (1:1 hexanes/EtOAc) resulting in a white solid (0.55 g, 1.8 mmol, 100%) with mp = 133 - 135° C. This solid was recrystallized in 9:1 hexanes/EtOAc resulting in colorless crystals. Spectral data: ^{1}H NMR (500 MHz, DMSO-d_6): δ (ppm) 10.54 (s, 1H), 7.86 (d, 2H), 7.78 (d, 2H), 7.49 (d, 2H), 6.85 (d, 2H), 5.46 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (500 MHz, DMSO-d_6): δ (ppm) 188.8, 162.8, 145.0, 132.7, 130.6, 130.1, 127.7, 125.0, 115.4, 70.9, 21.1. IR (KBr, cm^{-1}): 3420, 1689, 1599, 1576, 1510, 1463, 1458, 1369, 1361, 1167, 831. UV-VIS (1:1 CH_3CN/H_2O): λ 283 (ε = 16,000) and 225 (ε = 20,000). HRMS, $[M–H]^+$, calc. $C_{15}H_{14}O_5S$ 305.048, found 305.0484. This ester was also synthesized by the method employed for pHP trifluoroacetate.

References

S1 Buu-Hoi, N. P.; Lavit, D. J. *J. Chem. Soc.* **1955**, 18.

S2 Ma, C.; Kwok, W. M.; Chan, W. S.; Zuo, P.; Kan, J. T. W.; Toy, P. H.; Phillips, D. L. *J. Am. Chem. Soc.* **2005**, *127*, 1463.

S3 McDevitt, J. P.; Lansbury, J. P. T. *J. Am. Chem. Soc.* **1996**, *118*, 3818.

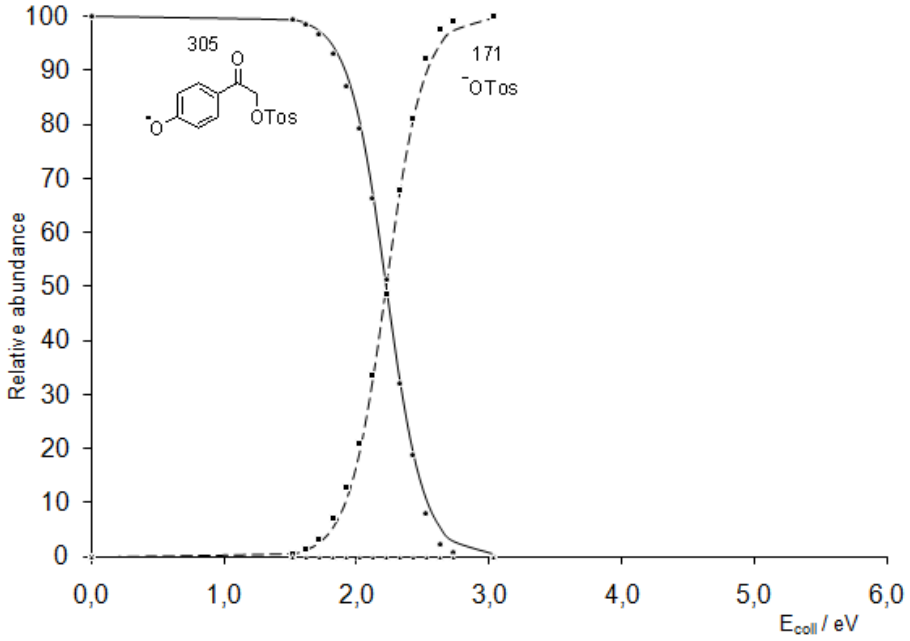
S4 Emmons, W. D.; Ferris, A. F. *J. Am. Chem. Soc.* **1953**, *75*, 2257.

Table S1: Products of CID of the mass-selected ions.

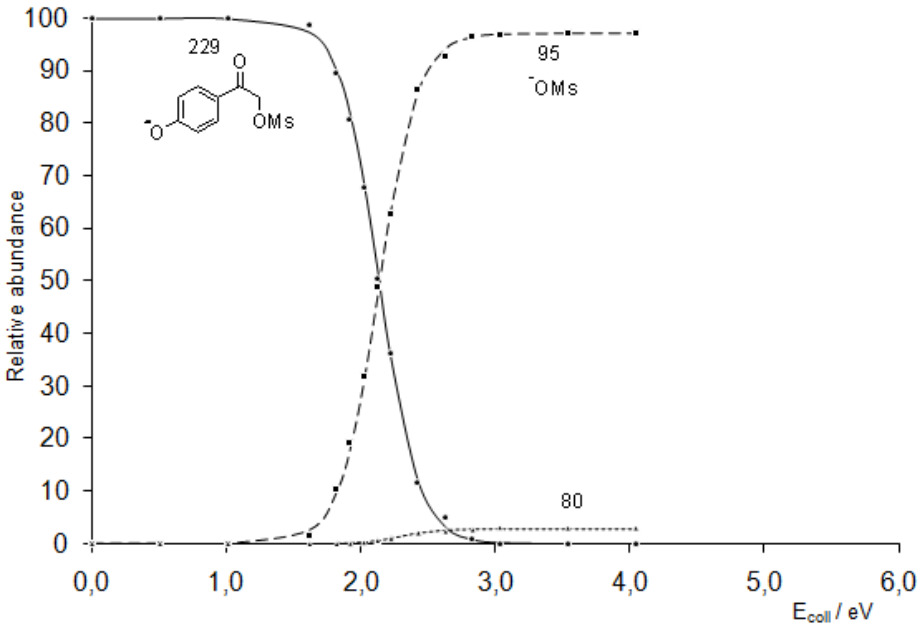
X =	ΔH_{acid}(HX)	*AE*(others)	BR(others)	others (*m/z*)
TosO	*1298*			
MsO	1343			
CF_3COO	1355	2.24	1	133 $C_8H_5O_2^-$
$OP(O)(OEt)_2$	*1387*	2.46	2	133 $C_8H_5O_2^-$
p-$CF_3C_6H_4O$	1410	2.81	26	133 $C_8H_5O_2^-$ 123 $C_7H_7O_2^-$ 105 $C_7H_5O^-$ 93 $C_6H_5O^-$ 161 $C_7H_4F_3O^-$ 201 $C_9H_4F_3O_2^-$ 275 237
p-$MeOC_6H_4COO$	1426	2.90	10	133 $C_8H_5O_2^-$
CH_3COO	1436	2.52	100	- CH_2CO
HCOO	1449	2.18	100	- CO
$H_2N(CH_2)_3COO$	*1451*	2.65	98	- C_4H_7NO
$H_2N(CH_2)_3COO$	*1451*	2.42	2	133 $C_8H_5O_2^-$
C_6H_5O	1463	2.99	36	133 $C_8H_5O_2^-$
p-$MeOC_6H_4O$	1466	3.03	97	134 $C_8H_6O_2^{\bullet-}$ 123 $C_7H_7O_2^-$ 93 $C_6H_5O^-$ 163 $C_9H_7O_3^-$ 242 $C_{14}H_{10}O_4^{\bullet-}$ 148 $C_9H_8O_2^{\bullet-}$ 108 $C_6H_4O_2^{\bullet-}$

Breakdown diagrams for the CID of the mass-selected ions.

TosO-pHP

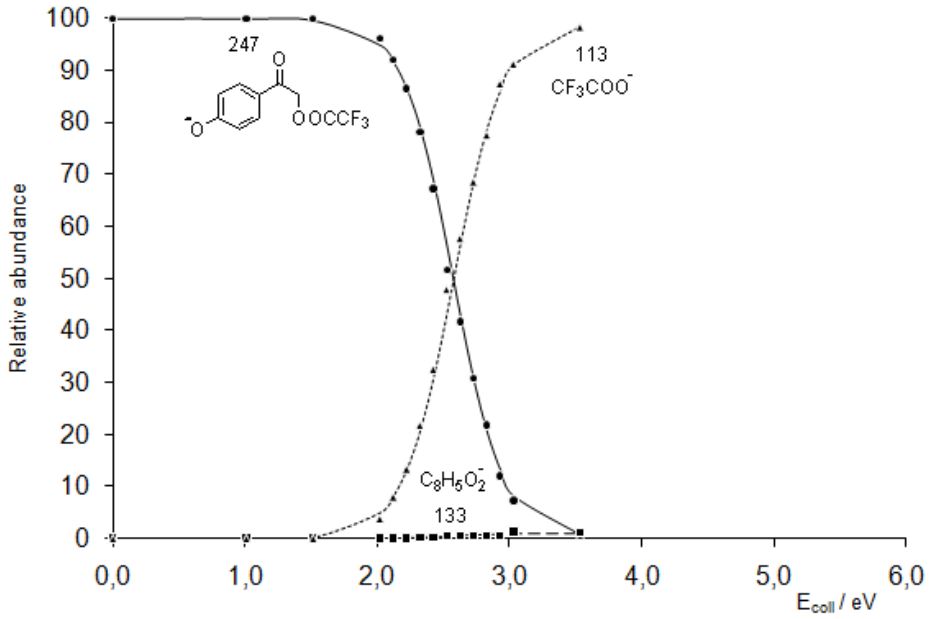


MsO-pHP

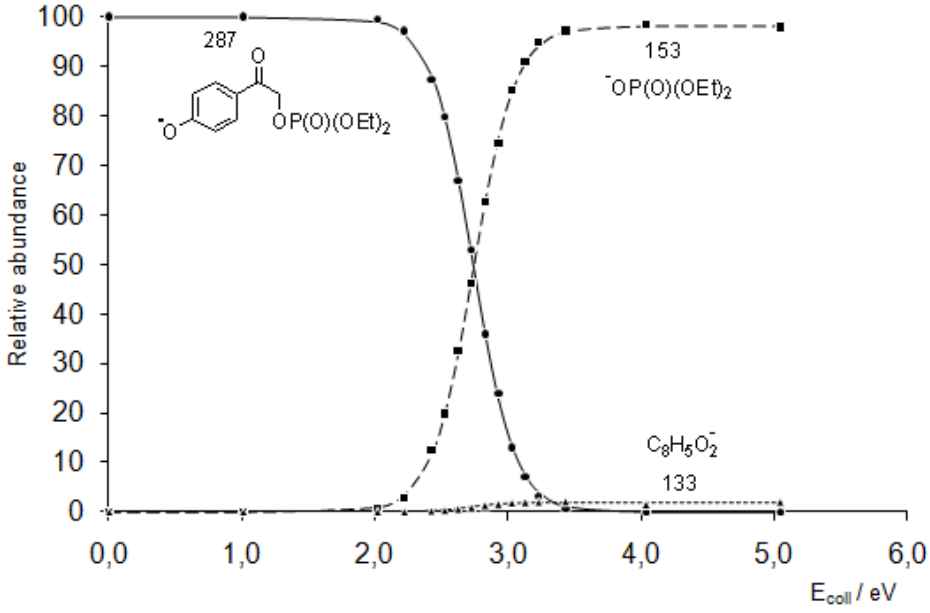


Branching ratio given in Table 1 corresponds to sum of m/z 95 and 80, where m/z 80 accords to SO_3^- which results from dissociation of $^-$OMs.

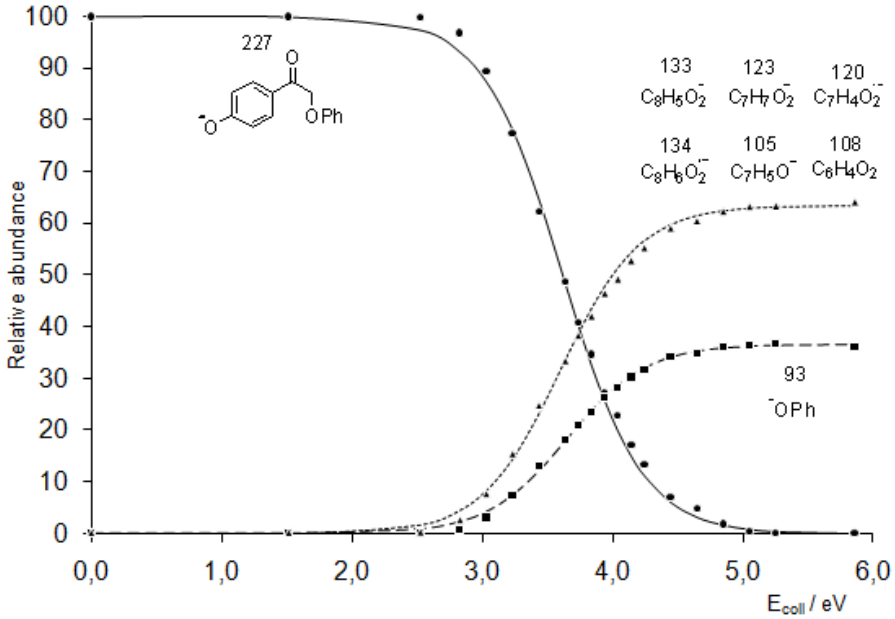
CF_3COO-pHP



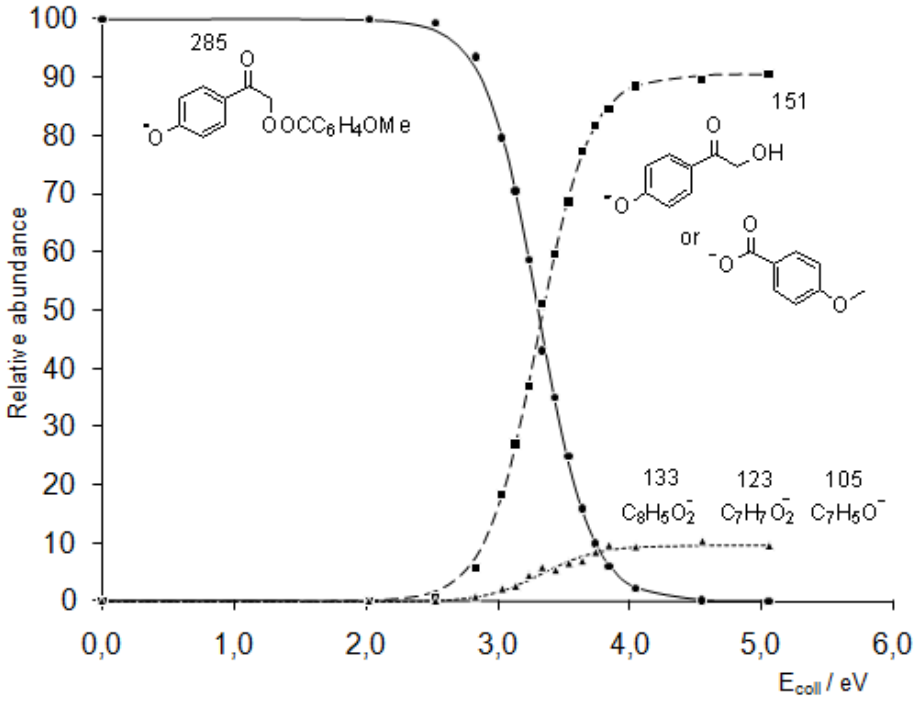
$(EtO)_2P(O)O$-pHP



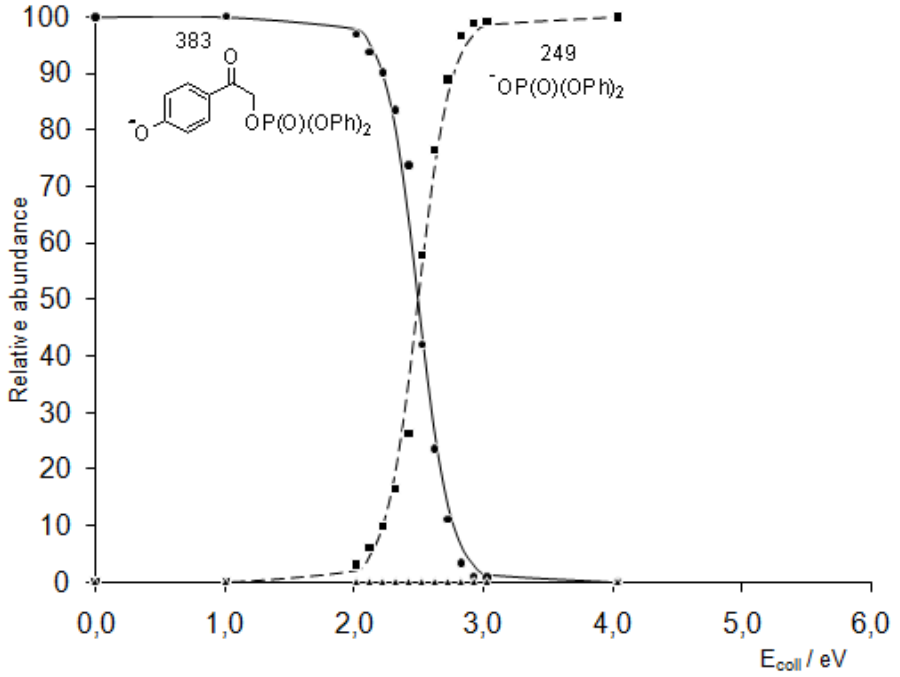
PhO-pHP



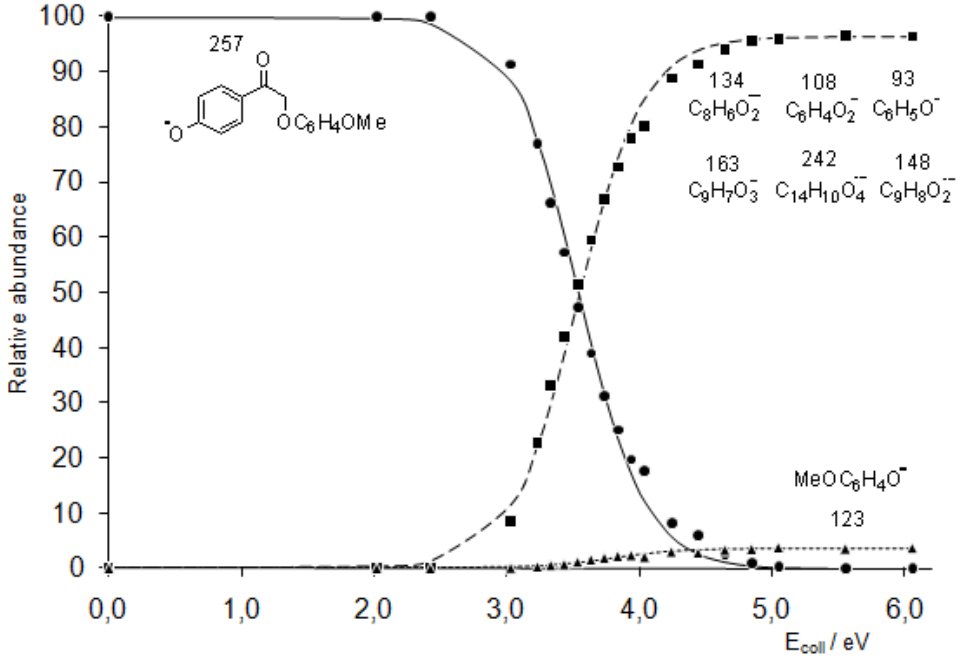
p-MeO-C_6H_4COO-pHP



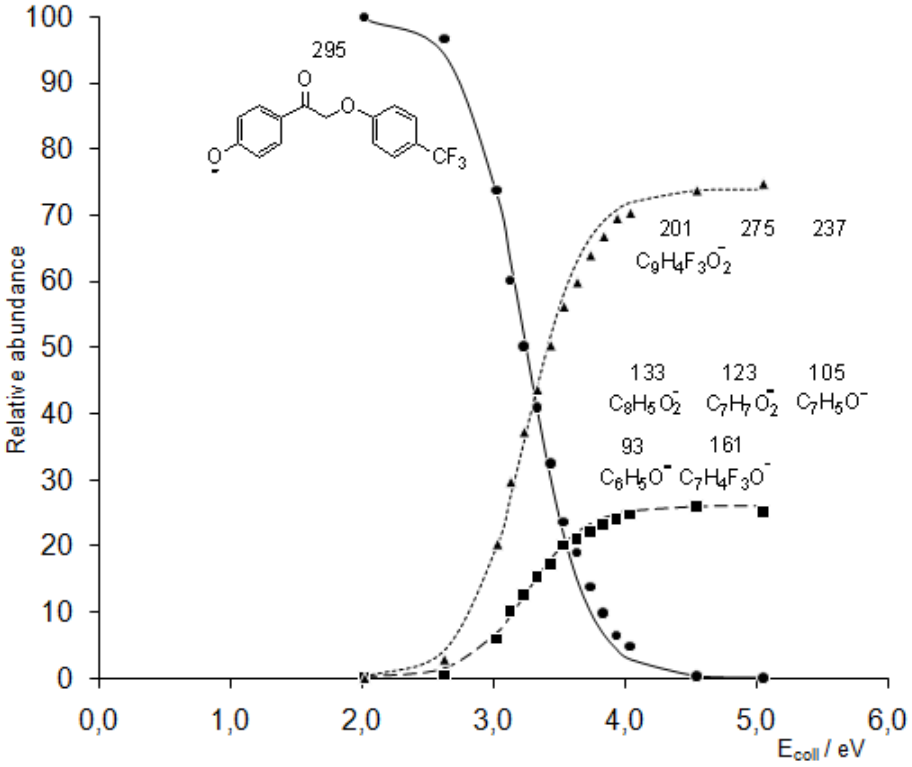
$(PhO)_2P(O)O$-pHP



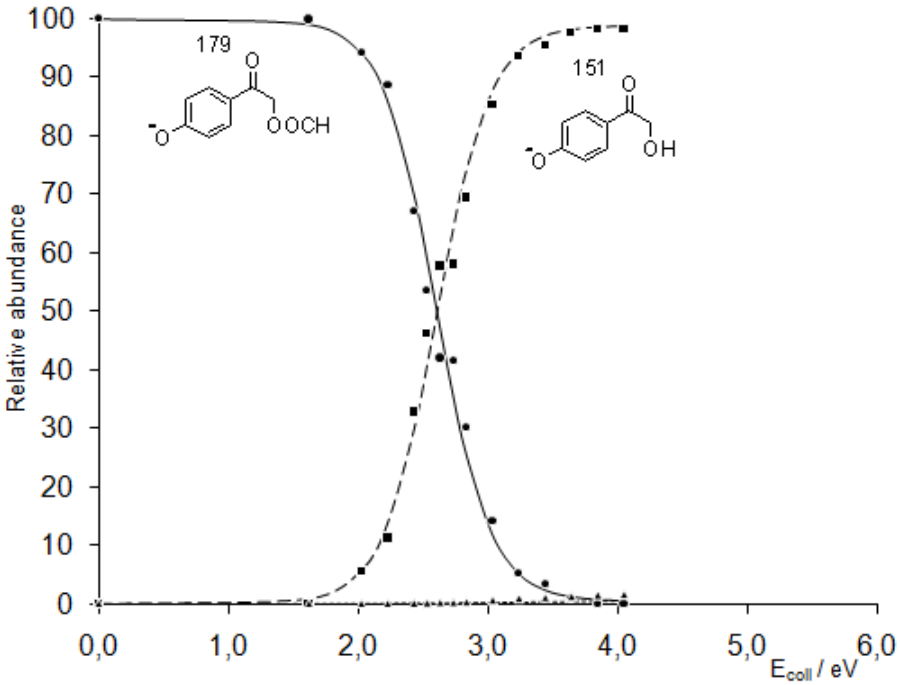
p-MeO-C_6H_4O-pHP



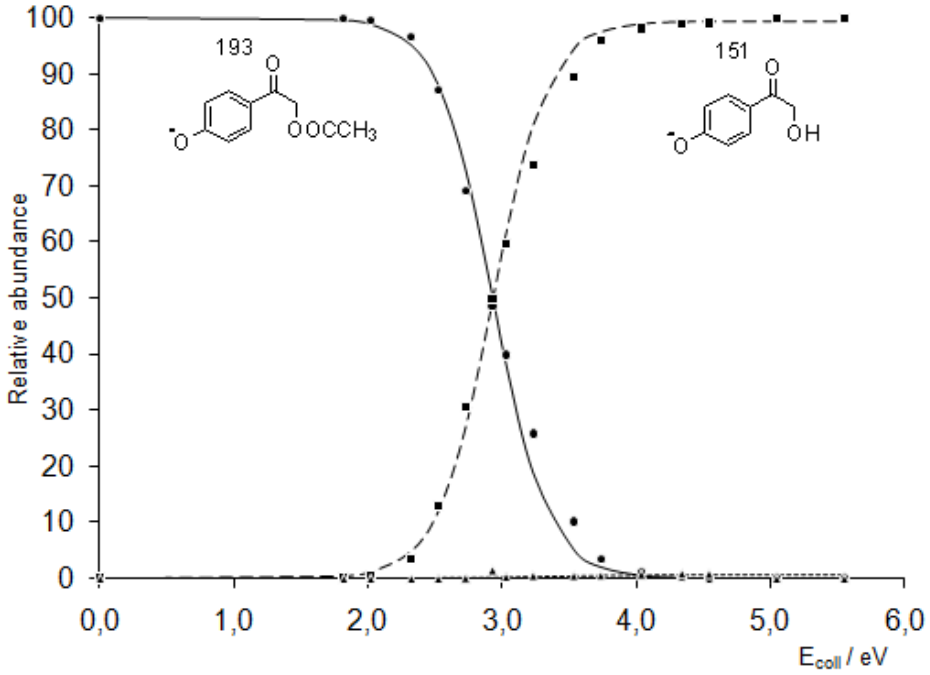
p-CF_3-C_6H_4O-pHP



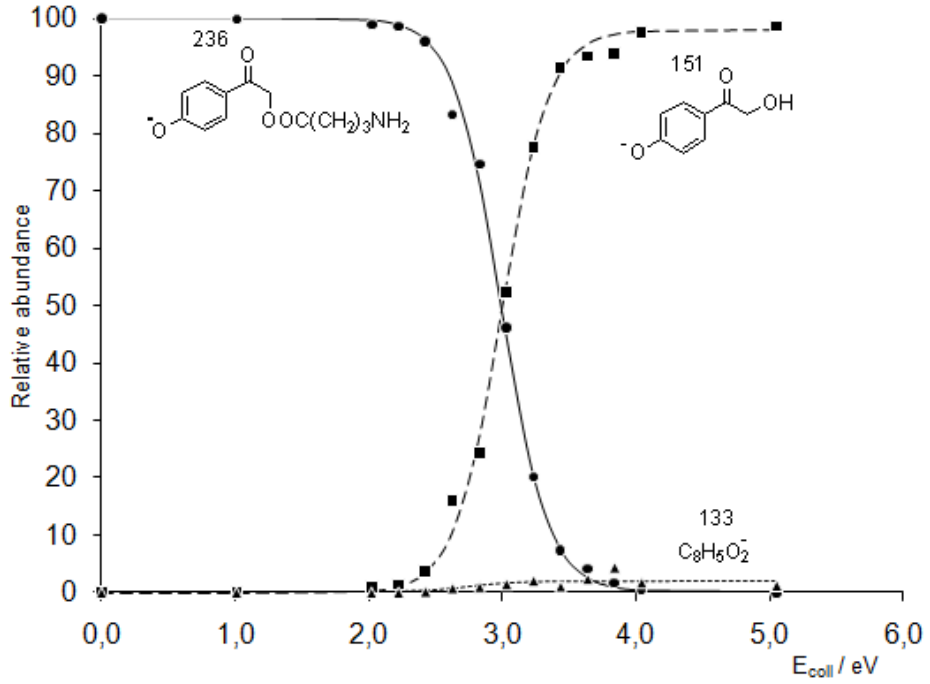
HCOO-pHP



CH_3COO-pHP

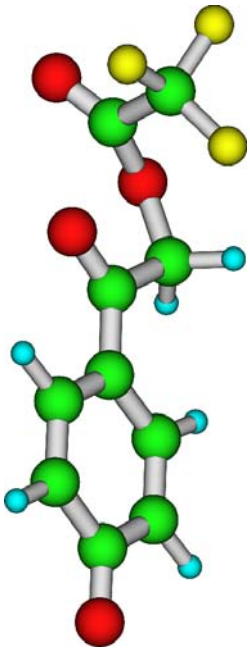


$NH_2(CH_2)_3COO$-pHP



Energies and Cartesian coordinates of the calculated structures

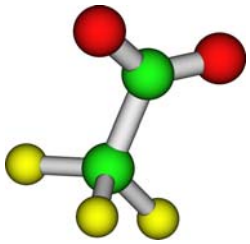
Table S2: Geometries and energetics for structures optimized at the **B3LYP/cc-pVTZ** level of theory. Oxygen is in red, carbon in green, fluor in yellow and hydrogen atoms are in blue.



[**1**-H$^-$]

Zero-point correction= 0.148472 (Hartree/Particle)
Thermal correction to Energy= 0.162943
Thermal correction to Enthalpy= 0.163887
Thermal correction to Gibbs Free Energy= 0.105262
Sum of electronic and zero-point Energies= -985.384563
Sum of electronic and thermal Energies= -985.370092
Sum of electronic and thermal Enthalpies= -985.369148
Sum of electronic and thermal Free Energies= -985.427773

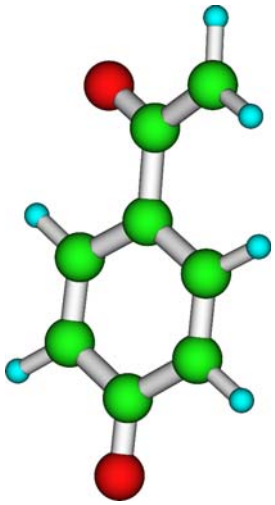
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.256138	-0.494344	0.130429
2	6	0	-0.716655	-0.277380	1.232429
3	6	0	0.708296	-0.022544	1.374355
4	6	0	1.289638	0.217316	2.584588
5	6	0	0.539821	0.230502	3.794469
6	6	0	-0.858624	-0.019279	3.684142
7	6	0	-1.457863	-0.256597	2.484990
8	1	0	1.296206	-0.027374	0.464382
9	1	0	2.358264	0.399739	2.614805
10	6	0	1.123423	0.459111	5.069681
11	1	0	-1.438174	-0.014405	4.598919
12	1	0	-2.523343	-0.443143	2.420489
13	8	0	0.516345	0.479897	6.156570
14	6	0	2.641925	0.667659	5.185182
15	1	0	3.030679	1.341484	4.426906
16	8	0	2.947574	1.302178	6.430206
17	1	0	3.156637	-0.290586	5.099435
18	6	0	2.270795	1.005957	7.565094
19	8	0	1.993665	1.849097	8.371155
20	6	0	2.291518	-0.467753	8.051442
21	9	0	2.462377	-1.399310	7.095472
22	9	0	3.348780	-0.603625	8.897709
23	9	0	1.193507	-0.775851	8.739110



CF_3COO^-

Zero-point correction= 0.025565 (Hartree/Particle)
Thermal correction to Energy= 0.031643
Thermal correction to Enthalpy= 0.032587
Thermal correction to Gibbs Free Energy= -0.005936
Sum of electronic and zero-point Energies= -526.443846
Sum of electronic and thermal Energies= -526.437768
Sum of electronic and thermal Enthalpies= -526.436824
Sum of electronic and thermal Free Energies= -526.475347

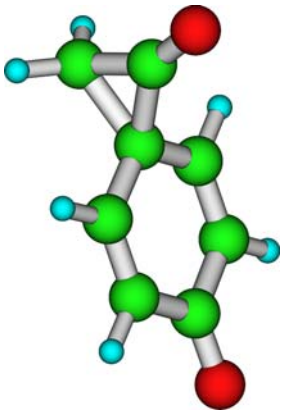
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.029981	0.000000	0.029104
2	6	0	0.148907	0.000000	1.262689
3	8	0	1.132631	0.000000	2.019017
4	6	0	-1.218743	0.000000	2.063456
5	9	0	-2.333599	0.000000	1.290220
6	9	0	-1.340639	-1.086990	2.878114
7	9	0	-1.340639	1.086990	2.878114



^{3}**3**

Zero-point correction= 0.115231 (Hartree/Particle)
Thermal correction to Energy= 0.123764
Thermal correction to Enthalpy= 0.124708
Thermal correction to Gibbs Free Energy= 0.080075
Sum of electronic and zero-point Energies= -458.863584
Sum of electronic and thermal Energies= -458.855051
Sum of electronic and thermal Enthalpies= -458.854107
Sum of electronic and thermal Free Energies= -458.898740

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.043170	0.082877	0.081615
2	8	0	-0.079120	0.172351	1.323903
3	6	0	1.215691	-0.037694	-0.631706
4	6	0	1.248005	-0.128918	-1.995614
5	6	0	0.054126	-0.111686	-2.752091
6	6	0	-1.188933	-0.010338	-2.083616
7	6	0	-1.249629	0.089056	-0.723666
8	1	0	2.118332	-0.054302	-0.036709
9	1	0	2.201254	-0.229288	-2.495120
10	6	0	0.042471	-0.217762	-4.238751
11	1	0	-2.085507	-0.012291	-2.686499
12	1	0	-2.191124	0.175129	-0.198916
13	8	0	-1.041876	-0.389901	-4.827890
14	6	0	1.239285	-0.109756	-5.010743
15	1	0	2.203985	0.127505	-4.590102
16	1	0	1.152284	-0.234148	-6.079512



^{1}**4**

Zero-point correction= 0.117223 (Hartree/Particle)
Thermal correction to Energy= 0.125472
Thermal correction to Enthalpy= 0.126416
Thermal correction to Gibbs Free Energy= 0.083803
Sum of electronic and zero-point Energies= -458.867723
Sum of electronic and thermal Energies= -458.859474
Sum of electronic and thermal Enthalpies= -458.858530
Sum of electronic and thermal Free Energies= -458.901144

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.052369	-0.293015	-0.196754
2	6	0	-0.000007	-0.152112	1.016788
3	6	0	1.209492	0.043639	1.834693
4	6	0	1.152833	0.186011	3.165492
5	6	0	-0.119790	0.129236	3.889269
6	6	0	-1.333666	-0.013798	3.081375
7	6	0	-1.277401	-0.156202	1.750563
8	1	0	2.150251	0.072448	1.301779
9	1	0	2.057676	0.329344	3.744866
10	6	0	-0.114165	-0.521555	5.268470
11	1	0	-2.286623	-0.019753	3.597901
12	1	0	-2.172775	-0.274941	1.155534
13	6	0	-0.229792	0.914260	5.276274
14	1	0	-1.191107	1.362657	5.495561
15	1	0	0.630792	1.509031	5.557196
16	8	0	-0.050433	-1.557455	5.844378

^{1}**5**

Zero-point correction= 0.108886 (Hartree/Particle)
Thermal correction to Energy= 0.115278
Thermal correction to Enthalpy= 0.116222
Thermal correction to Gibbs Free Energy= 0.079072
Sum of electronic and zero-point Energies= -345.557439
Sum of electronic and thermal Energies= -345.551048
Sum of electronic and thermal Enthalpies= -345.550104
Sum of electronic and thermal Free Energies= -345.587254
Charge = 0 Multiplicity = 1
O,0,0.,0.,0.1333536931
C,0,0.,0.,1.3572690381
C,0,1.2507609724,0.,2.1363923493
C,0,1.2434836285,0.,3.4777848401
C,0,0.,0.,4.2367300397

C,0,-1.2434836285,0.,3.4777848401
C,0,-1.2507609724,0.,2.1363923493
H,0,2.1701657037,0.,1.5664070008
H,0,2.1714855868,0.,4.037183667
C,0,0.,0.,5.5827020067
H,0,-2.1714855868,0.,4.037183667
H,0,-2.1701657037,0.,1.5664070008
H,0,-0.9230103721,0.,6.1467047541
H,0,0.9230103721,0.,6.1467047541

^{3}**5**

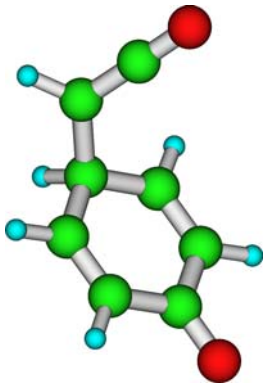
Zero-point correction= 0.104549 (Hartree/Particle)
Thermal correction to Energy= 0.111463
Thermal correction to Enthalpy= 0.112408
Thermal correction to Gibbs Free Energy= 0.073432
Sum of electronic and zero-point Energies= -345.493301
Sum of electronic and thermal Energies= -345.486387
Sum of electronic and thermal Enthalpies= -345.485443
Sum of electronic and thermal Free Energies= -345.524418

Charge = 0 Multiplicity = 3
O,0,0.,0.,0.0822704281
C,0,0.,0.,1.3603805464
C,0,1.2216026824,0.,2.1034121097
C,0,1.2119216718,0.,3.4845009357
C,0,0.,0.,4.2022936698
C,0,-1.2119216718,0.,3.4845009357
C,0,-1.2216026824,0.,2.1034121097
H,0,2.1470357836,0.,1.5442160467
H,0,2.1461362735,0.,4.0310740258
C,0,0.,0.,5.6551160466
H,0,-2.1461362735,0.,4.0310740258
H,0,-2.1470357836,0.,1.5442160467
H,0,-0.9278967421,0.,6.2062665369
H,0,0.9278967421,0.,6.2062665369

^{1}**7**

Zero-point correction= 0.118903 (Hartree/Particle)
Thermal correction to Energy= 0.126965
Thermal correction to Enthalpy= 0.127909
Thermal correction to Gibbs Free Energy= 0.085724
Sum of electronic and zero-point Energies= -458.866414
Sum of electronic and thermal Energies= -458.858352
Sum of electronic and thermal Enthalpies= -458.857408
Sum of electronic and thermal Free Energies= -458.899594

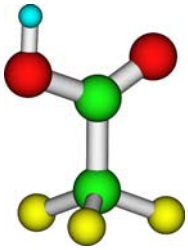
Charge = 0 Multiplicity = 1
O,0,-0.0533173384,-0.0262859195,0.1102853264
C,0,-0.0218090043,-0.0033832986,1.3361946269
C,0,1.2398478672,0.1102056767,2.0826374931
C,0,1.268463486,0.1348400004,3.4270199962
C,0,0.0479928914,0.0498029284,4.1999286026
C,0,-1.2106634179,-0.0628862877,3.4928816825
C,0,-1.2454986649,-0.0880135182,2.1488786796
H,0,2.1442622192,0.1729385812,1.4928542582
H,0,2.207532555,0.2190207988,3.9606745559
C,0,0.0921405267,0.0756408614,5.5418153663
H,0,-2.1205489856,-0.1261604051,4.0763325107
H,0,-2.1774241934,-0.1717689785,1.6061833284
O,0,-0.7529854433,0.0250041803,6.5733830238
C,0,0.7159240345,0.1470357087,6.8278523871
H,0,1.1556143931,-0.7368984227,7.2729136577
H,0,1.0079833515,1.103936648,7.2423264345



^{1}**8**

Zero-point correction= 0.117632 (Hartree/Particle)
Thermal correction to Energy= 0.126251
Thermal correction to Enthalpy= 0.127195
Thermal correction to Gibbs Free Energy= 0.082794
Sum of electronic and zero-point Energies= -458.889785
Sum of electronic and thermal Energies= -458.881166
Sum of electronic and thermal Enthalpies= -458.880222
Sum of electronic and thermal Free Energies= -458.924622

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.107386	-0.550993	-0.038320
2	6	0	0.064036	-0.256967	1.145105
3	6	0	1.290462	-0.054866	1.943222
4	6	0	1.249146	0.276850	3.234391
5	6	0	-0.029532	0.479783	3.989865
6	6	0	-1.256544	0.252754	3.153154
7	6	0	-1.212852	-0.080926	1.862286
8	1	0	2.227013	-0.187786	1.417877
9	1	0	2.164778	0.422758	3.795979
10	6	0	-0.082008	-0.331444	5.283350
11	1	0	-2.208123	0.369814	3.658763
12	1	0	-2.111753	-0.242648	1.282061
13	1	0	-0.736586	-0.020625	6.085650
14	6	0	0.580851	-1.446725	5.472478
15	8	0	1.183119	-2.422427	5.652136
16	1	0	-0.043602	1.532490	4.308393



CF_3COOH

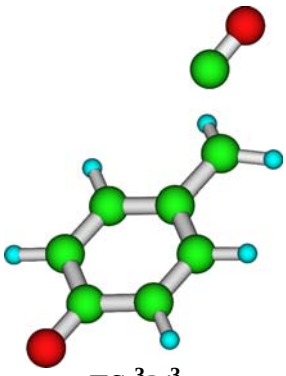
Zero-point correction= 0.038824 (Hartree/Particle)
Thermal correction to Energy= 0.045057
Thermal correction to Enthalpy= 0.046001
Thermal correction to Gibbs Free Energy= 0.007481
Sum of electronic and zero-point Energies= -526.965937
Sum of electronic and thermal Energies= -526.959704
Sum of electronic and thermal Enthalpies= -526.958759
Sum of electronic and thermal Free Energies= -526.997279

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.023036	-0.015000	0.052847
2	9	0	-0.389638	0.159232	1.331214
3	9	0	1.298712	-0.140632	0.003020
4	6	0	-0.707153	-1.272758	-0.538511
5	8	0	-2.035709	-1.136052	-0.483057
6	9	0	-0.376551	1.078337	-0.638985
7	8	0	-0.108350	-2.210199	-0.972350
8	1	0	-2.433054	-1.936419	-0.859194

TS ^{1}**1**/^{1}**9**

Zero-point correction= 0.144915 (Hartree/Particle)
Thermal correction to Energy= 0.160316
Thermal correction to Enthalpy= 0.161261
Thermal correction to Gibbs Free Energy= 0.098128
Sum of electronic and zero-point Energies= -985.348360
Sum of electronic and thermal Energies= -985.332959
Sum of electronic and thermal Enthalpies= -985.332015
Sum of electronic and thermal Free Energies= -985.395147
Charge = -1 Multiplicity = 1
C,0,-0.0382595864,0.062631804,-0.0302603338
C,0,-0.0030222738,-0.1303934796,1.3924587204
C,0,1.1718429069,-0.2273292333,2.0534066173
C,0,2.4612789991,-0.1415723163,1.3623314854
C,0,2.3867780301,0.0515904338,-0.0836948016
C,0,1.2073829606,0.1478336493,-0.7415989663
O,0,3.5353294006,-0.2273905423,1.9712690653
C,0,-1.2272755664,0.1675417383,-0.6919272702
C,0,-1.8870153193,0.3534240095,-1.9419364736
O,0,-2.4820965815,0.146565052,-0.3551493609
O,0,-0.3588273484,0.6118950401,-3.7045170043
C,0,-0.6756382702,-0.2004410497,-4.6085613453

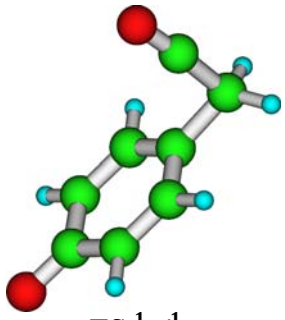
	C,0,0.2697243124,-0.1122176524,-5.8572019615 F,0,0.1532746067,1.0906972117,-6.4749090248 O,0,-1.5950523863,-1.0209532693,-4.6668403931 F,0,1.5724914661,-0.2491067808,-5.518231348 F,0,0.0150458581,-1.0482939931,-6.7913924644 H,0,3.3294724437,0.1151829365,-0.6115895623 H,0,1.1665044125,0.2922745989,-1.814703198 H,0,-0.9461499925,-0.1963346065,1.9220962362 H,0,1.2086458977,-0.3728019248,3.1256982209 H,0,-2.1796063029,-0.4865511482,-2.5520318377 H,0,-2.139332723,1.3497165044,-2.2584865402
TS ^{1}**1**/^{1}**10**	Zero-point correction= 0.143089 (Hartree/Particle) Thermal correction to Energy= 0.158780 Thermal correction to Enthalpy= 0.159724 Thermal correction to Gibbs Free Energy= 0.095513 Sum of electronic and zero-point Energies= -985.333364 Sum of electronic and thermal Energies= -985.317674 Sum of electronic and thermal Enthalpies= -985.316730 Sum of electronic and thermal Free Energies= -985.380941 Charge = -1 Multiplicity = 1 C,0,-2.1981179582,0.4761491861,-0.1806068323 C,0,-2.9355667651,0.649385763,1.0404734652 C,0,-4.1678712252,0.1154593677,1.201372938 C,0,-4.8268701102,-0.6573260739,0.1481388079 C,0,-4.0507553204,-0.8230586461,-1.0783586806 C,0,-2.811618146,-0.2986527886,-1.2229847458 O,0,-5.9574911329,-1.137825764,0.2895009303 C,0,-0.9799584863,1.3044218797,-0.404020129 O,0,-0.7709661056,2.4871717825,-0.3622645342 C,0,-0.2972520841,0.0652568084,-0.2190451666 O,0,2.1955678011,-0.397957095,1.3884631815 C,0,2.6234731708,-0.1875300007,0.2472763128 O,0,2.0248458129,0.084396876,-0.817643705 C,0,4.1792183932,-0.2847140677,0.0578177191 F,0,4.8501157957,-0.5106063207,1.2038301039 F,0,4.5083701091,-1.2953411644,-0.7860327109 F,0,4.6953047928,0.8473799741,-0.4743880554 H,0,-4.514737529,-1.3924250623,-1.8732559034 H,0,-2.2675603748,-0.4377074034,-2.1502740956 H,0,-2.4799854473,1.2334093023,1.8312825167 H,0,-4.7211403791,0.2459854161,2.1226090366 H,0,-0.2826197761,-0.6844335222,-0.9867509415 H,0,0.1897869645,-0.1503824468,0.7278474884
TS ^{1}**4**/^{1}**7**	Zero-point correction= 0.115637 (Hartree/Particle) Thermal correction to Energy= 0.123698 Thermal correction to Enthalpy= 0.124642 Thermal correction to Gibbs Free Energy= 0.082396 Sum of electronic and zero-point Energies= -458.829963 Sum of electronic and thermal Energies= -458.821902 Sum of electronic and thermal Enthalpies= -458.820958 Sum of electronic and thermal Free Energies= -458.863205 Charge = 0 Multiplicity = 1 O,0,-0.0887845795,0.0012257359,0.0619002023 C,0,-0.0318837796,0.001022467,1.2902882898 C,0,1.2494580118,-0.0060026059,2.0076450825 C,0,1.3059939618,-0.0023431448,3.3581901963 C,0,0.1073891214,-0.0079078368,4.1401450442 C,0,-1.1590710584,0.0023970459,3.4743071463 C,0,-1.2377003884,0.0090069842,2.1248934779 C,0,0.1734894836,0.0095258496,5.5352737827 O,0,1.1553526667,0.1828373212,6.3221055578 C,0,-0.8689489858,-0.0766164064,6.5058572981 H,0,-0.7243705008,-0.7767165173,7.3149791332 H,0,-1.6511596117,0.6687694234,6.606629194 H,0,2.1428257924,-0.0262425713,1.3986303102 H,0,2.2538579232,-0.003963557,3.8811618342 H,0,-2.0632293399,-0.0027700508,4.0730382736 H,0,-2.1862931903,0.0277753859,1.6065704684



TS ^{3}**3**/^{3}**5**

NImag=1
Zero-point correction= 0.111765 (Hartree/Particle)
Thermal correction to Energy= 0.121233
Thermal correction to Enthalpy= 0.122177
Thermal correction to Gibbs Free Energy= 0.073417
Sum of electronic and zero-point Energies= -458.837878
Sum of electronic and thermal Energies= -458.828410
Sum of electronic and thermal Enthalpies= -458.827466
Sum of electronic and thermal Free Energies= -458.876226

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.195801	0.512864	0.054858
2	6	0	0.077323	-0.398005	1.121799
3	6	0	1.187827	-0.837705	1.805565
4	6	0	2.503638	-0.379679	1.451961
5	6	0	2.599747	0.549658	0.359583
6	6	0	1.474787	0.975096	-0.309376
7	1	0	-0.905950	-0.753729	1.402152
8	1	0	1.109107	-1.538137	2.625508
9	8	0	3.530987	-0.775508	2.075352
10	1	0	3.587053	0.896741	0.087797
11	1	0	1.566319	1.675437	-1.129807
12	6	0	-0.993699	0.965582	-0.672266
13	1	0	-0.911781	1.820677	-1.328578
14	6	0	-1.268357	-0.498986	-2.351048
15	1	0	-1.969693	0.779062	-0.246493
16	8	0	-2.154435	-0.323168	-3.043898



TS ^{1}**4**/^{1}**5**

Zero-point correction= 0.115947 (Hartree/Particle)
Thermal correction to Energy= 0.124114
Thermal correction to Enthalpy= 0.125059
Thermal correction to Gibbs Free Energy= 0.082281
Sum of electronic and zero-point Energies= -458.853884
Sum of electronic and thermal Energies= -458.845716
Sum of electronic and thermal Enthalpies= -458.844772
Sum of electronic and thermal Free Energies= -458.887550

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.000419	-0.114773	0.002200
2	6	0	-0.002466	-0.047310	1.421776
3	6	0	1.162768	0.007893	2.119704
4	6	0	2.466048	0.025973	1.458067
5	6	0	2.417332	-0.035111	-0.001564
6	6	0	1.243418	-0.090019	-0.684815
7	8	0	3.528179	0.083533	2.085068
8	6	0	-1.297938	-0.098887	-0.765373
9	6	0	-1.285544	1.326412	-0.787622
10	8	0	-1.224074	2.473025	-0.776185
11	1	0	3.366516	-0.047294	-0.519937
12	1	0	1.250666	-0.138714	-1.769512
13	1	0	-0.950091	-0.063291	1.951627
14	1	0	1.165829	0.028133	3.201088
15	1	0	-2.174252	-0.483539	-0.238750
16	1	0	-1.266027	-0.515134	-1.774809