Supporting Information

A pseudopericyclic [3,5]-sigmatropic rearrangement of a coumarin trichloroacetimidate derivative

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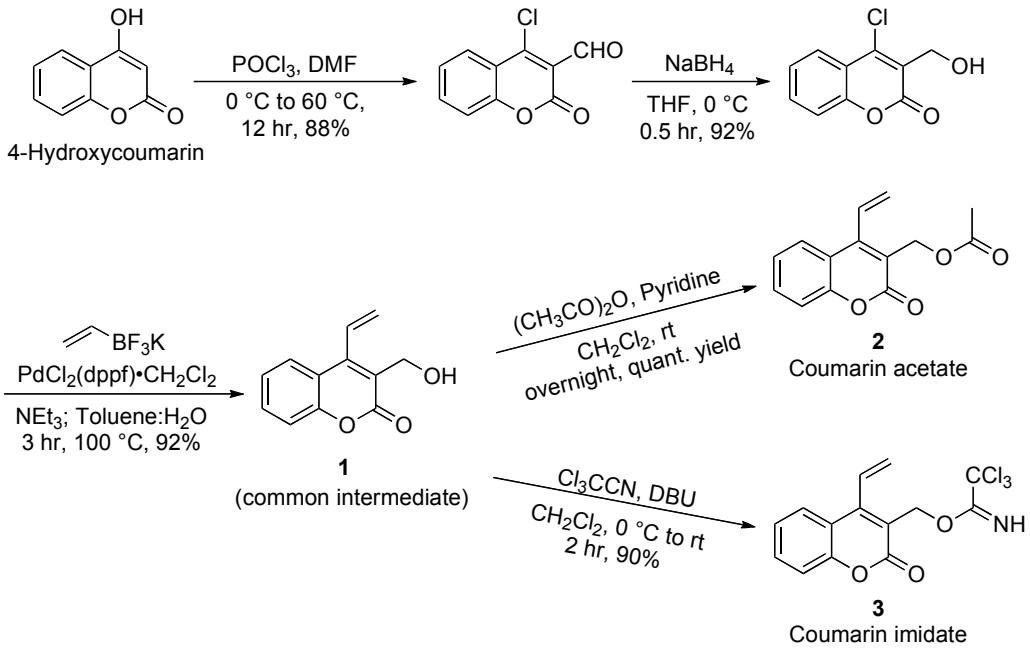
Experimental Section

General Information

All the synthesis reactions were performed under nitrogen atmosphere in oven-dried glassware with magnetic stirring unless otherwise specified. Pyrolysis studies were carried out in J Young NMR tubes and thick-walled glass tubes with Teflon seal. Solvents, reagents and starting material were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was distilled from sodium metal and benzophenone. The progress of reactions was monitored by thin layer chromatography (TLC) with 0.175-0.225 mm pre-coated silica gel plates (60 F_{254}) or by ^{1}H-NMR spectroscopy. TLC plates were visualized under UV light, or by immersion in ethanolic solutions of phosphomolybdic acid or $KMnO_4$ followed by heating. Flash chromatography was carried out on either silica gel (230-400 mesh) or neutral alumina (activated) using either mixtures of hexane and ethyl acetate or dichloromethane as the eluents. NMR spectra were recorded on a JEOL spectrometer. ^{1}H-NMR spectra were recorded at 400 MHz and were referenced to the residual solvents ($CDCl_3$ at 7.26 ppm, C_6D_6 at 7.16 ppm and toluene-d_8 at 2.08 ppm) and reported in part per million (ppm) relative to TMS (0 ppm). ^{13}C-NMR spectra were recorded at 100 MHz and were referenced to the residual solvents ($CDCl_3$ at 77.16 ppm). Coupling constants (*J*) are reported in Hertz (Hz) and ^{1}H-NMR multiplicity data are denoted by s (singlet), bs (broad singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets) and m (multiplet). High-resolution mass spectra (HRMS) were recorded with an ORBITRAP mass analyzer (Exactive).

Synthesis scheme for **2** and **3**

Compounds **2** and **3** were prepared in four steps from commercially available 4-hydroxy-coumarin following the literature procedure.[1]



Thermolysis of coumarin acetate 2 and imidate 3

Thermolysis of coumarin acetate **2**

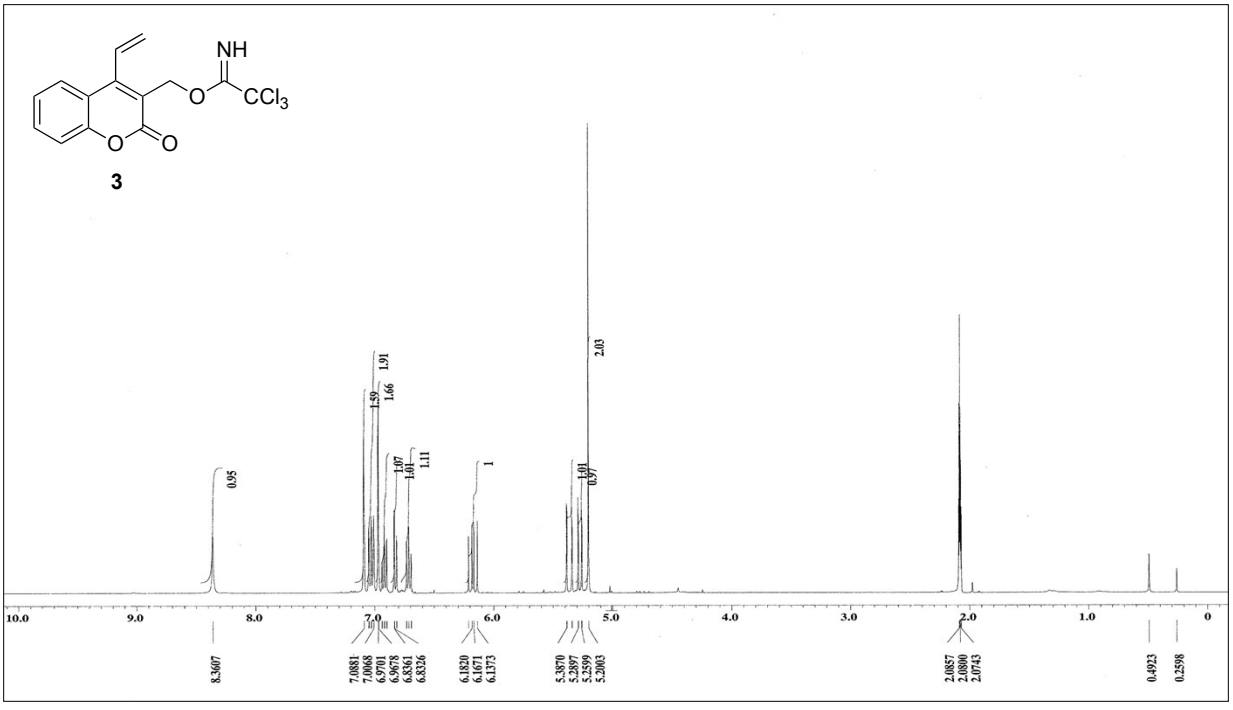
A solution of **2** (10 mg) in 2 mL C_6D_6 was transferred to a thick-walled glass reaction tube. The solution was purged with argon (UHP: ultra high purity) and sealed with a Teflon cap. The solution was then heated at 250 °C for nearly 10 hours. Upon cooling an aliquot was withdrawn. ^{1}H-NMR analysis showed signals corresponding to the starting acetate and no new signals were observed.

Thermolysis of coumarin imidate **3**

A solution of (2-oxo-4-vinyl-2H-chromen-3-yl)methyl-2,2,2-trichloroacetimidate (**3**, 100 mg, 0.29 mmol) in dry toluene (10 mL) was refluxed in an oil bath held at 130 °C in a 25 mL round bottom flask equipped with water condenser under nitrogen atmosphere. The reaction progress was monitored by thin layer chromatography and ^{1}H-NMR. After refluxing for 16 h TLC and ^{1}H-NMR confirmed complete conversion. TLC analysis (eluent: 20% ethyl acetate in hexane) showed the absence of imidate and the formation of a more polar spot. The reaction

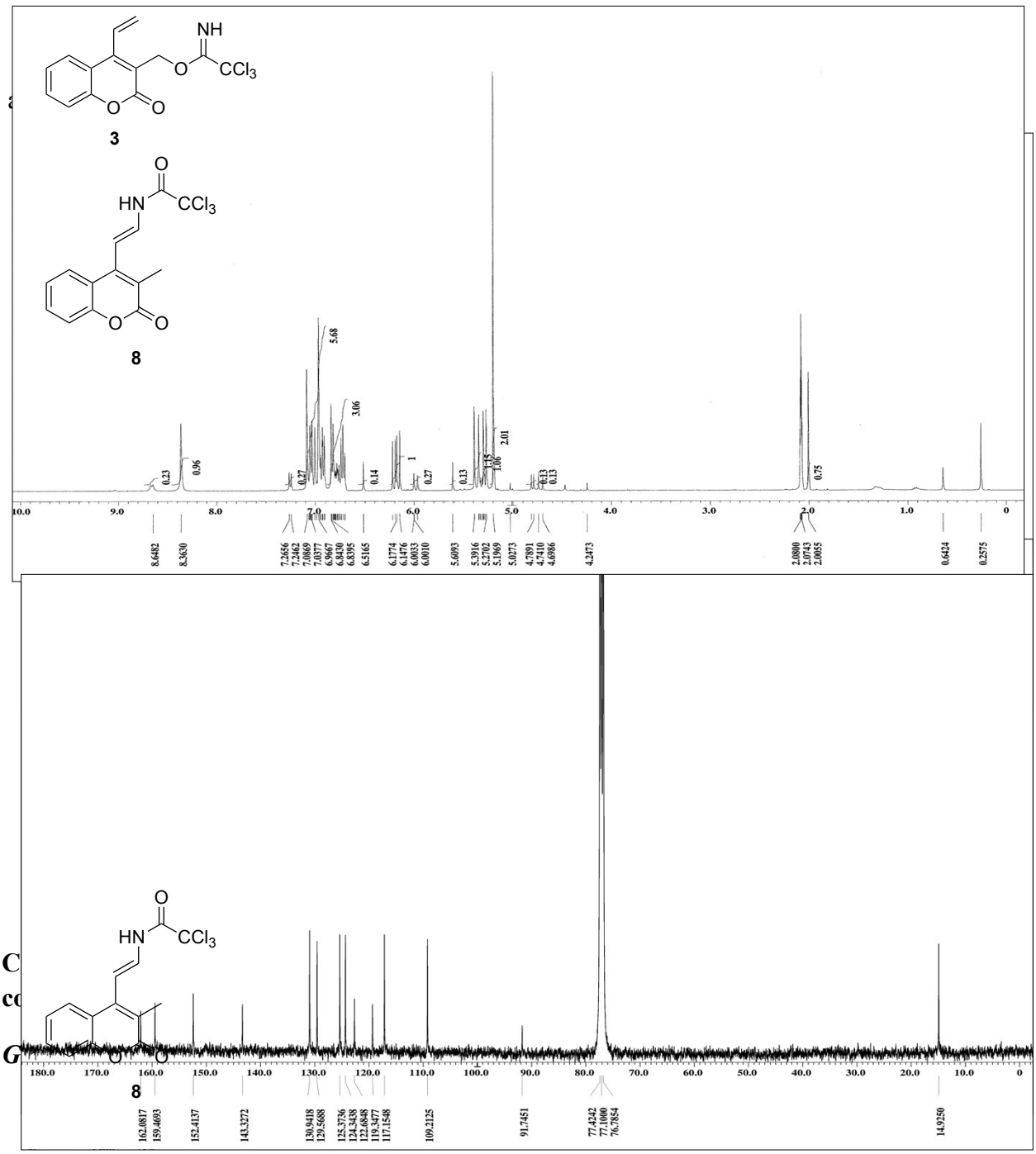
mixture was concentrated by rotary evaporation. Purification by silica gel column chromatography (eluent: 20-30% ethyl acetate in hexane) yielded **8** as white solid (76 mg, 76% yield).

(*E*)-2,2,2-Trichloro-*N*-(2-(3-methyl-2-oxo-2H-chromen-4-yl)vinyl)acetamide (**8**) mp 178-180 °C; ^{1}H-NMR (400 MHz, $CDCl_3$): δ_H 8.59 (bs, 1H, NH), 7.65 (dd, J = 1.4 Hz, 7.8 Hz, 1H), 7.50 (dt, J = 1.4 Hz, 8.0 Hz, 1H), 7.34 (dd, J = 1.0 Hz, 8.2 Hz, 1H), 7.30-7.26 (m, 1H), 7.15 (dd, J = 10.1 Hz, 14.6 Hz, 1H), 6.50 (d, J = 14.6 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 162.1, 159.5, 152.4, 143.3, 130.9, 129.6, 125.4, 124.3, 122.7, 119.3, 117.2, 109.2, 91.7, 14.9. EI-MS (EI) m/z: 345 (M+), 228, 200, 184, 156, 145, 128, 115. HRMS (ESI) calculated for $C_{14}H_{10}NCl_3NaO_3[M + Na]^+$ 367.9624, found 367.9617. Single crystals of **8**, suitable for X-ray crystallography, were obtained by recrystallization from dichloromethane. Structural data has been deposited with CCDC (1568018). Crystallography details can be found below.



^{1}H-NMR of **3** in toluene-d_8

^{1}H-NMR of **3** in toluene-d_8 after heating at 110 °C for 8h



Bruker PLATFORM

three circle diffractometer equipped with an APEX II CCD detector and operated at 1500 W (50kV, 30 mA) to generate (graphite monochromated) Mo Kα radiation (λ = 0.71073 Å). Crystals were transferred from the vial and placed on a glass slide in polyisobutylene. A Zeiss Stemi 305 microscope was used to identify a suitable specimen for X-ray diffraction from a representative sample of the material. The crystal and a small amount of the oil were collected on a MiTiGen cryoloop and transferred to the instrument where it was placed under a cold nitrogen stream (Oxford) maintained at 100K throughout the duration of the experiment. The sample was optically centered with the aid of a video camera to insure that no translations were observed as the crystal was rotated through all positions.

A unit cell collection was then carried out. After it was determined that the unit cell was not present in the CCDC database a sphere of data was collected. Omega scans were carried out with a 40 sec/frame exposure time and a rotation of 0.50° per frame. After data collection, the crystal was measured for size, morphology, and color. These values are reported in Table 1.

Refinement Details

After data collection, the unit cell was re-determined using a subset of the full data collection. Intensity data were corrected for Lorentz, polarization, and background effects using the Bruker program APEX 3. A semi-empirical correction for adsorption was applied using the program *SADABS*. The *SHELXL-2014*, series of programs was used for the solution and refinement of the crystal structure. Hydrogen atoms bound to carbon and nitrogen atoms were located in the difference Fourier map and were geometrically constrained using the appropriate AFIX commands. The molecule was crystallized from a solvent mixture containing deuterated chloroform and dichloromethane with both molecules located at the same interstitial site with

partial occupancies of 0.876:0.124, respectively. To help model the small amount of dichloromethane, SADI and EADP restraints were used.

Table S1. Crystal data and structure refinement for **8**

Identification code	bir16_01
Crystal Color	colorless
Crystal Habit	chip
Empirical formula	C15 H10.25 Cl5.88 D0.88 N O3
Formula weight	462.52
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.5591(9) Å alpha = 90 °.
	b = 13.2129(11) Å beta = 90.8840(10) °.
	c = 12.0726(10) Å gamma = 90 °.
Volume	1843.6(3) $Å^3$
Z	4
Calculated density	1.666 Mg/m^3
Absorption coefficient	0.929 mm^{-1}
F(000)	928
Crystal size	0.320 x 0.150 x 0.060 mm
Theta range for data collection	1.762 to 27.942 °.
Limiting indices	-15<=h<=15, -17<=k<=17, -15<=l<=15
Reflections collected / unique	22244 / 4409 [R(int) = 0.0245]
Completeness to theta = 25.242°	100.0 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4409 / 3 / 240
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0279, wR2 = 0.0699

R indices (all data)	R1 = 0.0334, wR2 = 0.0731
Largest diff. peak and hole	0.471 and -0.383 e.A^{-3}

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for bir16_01. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Cl(1)	8318(1)	-436(1)	5488(1)	22(1)
Cl(2)	6156(1)	-801(1)	4312(1)	27(1)
Cl(3)	8253(1)	-479(1)	3109(1)	32(1)
O(1)	5118(1)	5960(1)	6492(1)	15(1)
O(2)	3768(1)	5528(1)	7660(1)	19(1)
O(3)	7350(1)	1501(1)	3418(1)	20(1)
N(1)	6759(1)	1397(1)	5201(1)	13(1)
C(1)	4552(1)	5234(1)	7084(1)	14(1)
C(2)	4912(1)	4186(1)	6963(1)	15(1)
C(3)	5827(1)	3935(1)	6312(1)	13(1)
C(4)	6478(1)	4739(1)	5774(1)	14(1)
C(5)	7514(1)	4605(1)	5196(1)	18(1)
C(6)	8090(1)	5417(1)	4744(1)	23(1)
C(7)	7648(2)	6394(1)	4844(1)	23(1)
C(8)	6644(1)	6555(1)	5422(1)	19(1)
C(9)	6087(1)	5733(1)	5887(1)	14(1)
C(10)	6158(1)	2864(1)	6211(1)	14(1)
C(11)	6468(1)	2426(1)	5266(1)	14(1)
C(12)	7203(1)	1020(1)	4257(1)	13(1)
C(13)	7490(1)	-131(1)	4294(1)	16(1)
C(14)	4220(2)	3428(1)	7593(1)	22(1)
Cl(4)	9537(1)	2370(1)	5602(1)	22(1)
Cl(5)	10508(1)	3048(1)	7701(1)	37(1)
Cl(6)	8833(1)	1432(1)	7655(1)	29(1)
C(15)	9279(2)	2537(3)	7026(2)	21(1)
D(15)	8638	3040	7093	25
C(16)	9080(19)	2690(30)	6954(12)	21(1)
Cl(7)	10286(9)	2703(10)	7850(9)	87(4)

Table S3. Bond lengths [Å] and angles [°] for bir16_01.

Cl(1)-C(13)	1.7640(15)
Cl(2)-C(13)	1.7778(16)
Cl(3)-C(13)	1.7541(15)
O(1)-C(1)	1.3685(17)
O(1)-C(9)	1.3801(17)
O(2)-C(1)	1.2141(18)
O(3)-C(12)	1.2105(17)
N(1)-C(12)	1.3517(18)
N(1)-C(11)	1.4035(17)
N(1)-H(1)	0.8800
C(1)-C(2)	1.454(2)

C(2)-C(3)	1.367(2)
C(2)-C(14)	1.498(2)
C(3)-C(4)	1.4600(19)
C(3)-C(10)	1.4721(19)
C(4)-C(9)	1.3959(19)
C(4)-C(5)	1.406(2)
C(5)-C(6)	1.379(2)
C(5)-H(5)	0.9500
C(6)-C(7)	1.395(2)
C(6)-H(6)	0.9500
C(7)-C(8)	1.381(2)
C(7)-H(7)	0.9500
C(8)-C(9)	1.386(2)
C(8)-H(8)	0.9500
C(10)-C(11)	1.333(2)
C(10)-H(10)	0.9500
C(11)-H(11)	0.9500
C(12)-C(13)	1.557(2)
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800
Cl(4)-C(15)	1.763(2)
Cl(4)-C(16)	1.776(15)
Cl(5)-C(15)	1.763(3)
Cl(6)-C(15)	1.727(4)
C(15)-D(15)	1.0000
C(16)-Cl(7)	1.751(16)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900

C(1)-O(1)-C(9)	121.44(11)
C(12)-N(1)-C(11)	119.95(12)
C(12)-N(1)-H(1)	120.0
C(11)-N(1)-H(1)	120.0
O(2)-C(1)-O(1)	116.22(13)
O(2)-C(1)-C(2)	125.37(13)
O(1)-C(1)-C(2)	118.40(12)
C(3)-C(2)-C(1)	120.89(13)
C(3)-C(2)-C(14)	123.65(13)
C(1)-C(2)-C(14)	115.46(12)
C(2)-C(3)-C(4)	119.21(13)
C(2)-C(3)-C(10)	119.01(13)
C(4)-C(3)-C(10)	121.73(13)
C(9)-C(4)-C(5)	116.52(13)
C(9)-C(4)-C(3)	118.06(13)
C(5)-C(4)-C(3)	125.33(13)
C(6)-C(5)-C(4)	121.23(14)
C(6)-C(5)-H(5)	119.4
C(4)-C(5)-H(5)	119.4
C(5)-C(6)-C(7)	120.43(15)
C(5)-C(6)-H(6)	119.8
C(7)-C(6)-H(6)	119.8
C(8)-C(7)-C(6)	119.83(14)
C(8)-C(7)-H(7)	120.1

C(6)-C(7)-H(7)	120.1
C(7)-C(8)-C(9)	118.96(14)
C(7)-C(8)-H(8)	120.5
C(9)-C(8)-H(8)	120.5
O(1)-C(9)-C(8)	115.42(12)
O(1)-C(9)-C(4)	121.59(13)
C(8)-C(9)-C(4)	122.98(14)
C(11)-C(10)-C(3)	124.18(13)
C(11)-C(10)-H(10)	117.9
C(3)-C(10)-H(10)	117.9
C(10)-C(11)-N(1)	122.43(13)
C(10)-C(11)-H(11)	118.8
N(1)-C(11)-H(11)	118.8
O(3)-C(12)-N(1)	124.89(13)
O(3)-C(12)-C(13)	120.28(13)
N(1)-C(12)-C(13)	114.80(12)
C(12)-C(13)-Cl(3)	110.02(10)
C(12)-C(13)-Cl(1)	111.02(10)
Cl(3)-C(13)-Cl(1)	109.47(8)
C(12)-C(13)-Cl(2)	107.60(10)
Cl(3)-C(13)-Cl(2)	109.05(8)
Cl(1)-C(13)-Cl(2)	109.63(8)
C(2)-C(14)-H(14A)	109.5
C(2)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(2)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5
Cl(6)-C(15)-Cl(5)	111.35(13)
Cl(6)-C(15)-Cl(4)	112.27(18)
Cl(5)-C(15)-Cl(4)	110.58(18)
Cl(6)-C(15)-D(15)	107.5
Cl(5)-C(15)-D(15)	107.5
Cl(4)-C(15)-D(15)	107.5
Cl(7)-C(16)-Cl(4)	109.0(12)
Cl(7)-C(16)-H(16A)	109.9
Cl(4)-C(16)-H(16A)	109.9
Cl(7)-C(16)-H(16B)	109.9
Cl(4)-C(16)-H(16B)	109.9
H(16A)-C(16)-H(16B)	108.3

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters ($Å^2$ x 10^3) for bir16_01. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Cl(1)	26(1)	22(1)	17(1)	-1(1)	-4(1)	10(1)
Cl(2)	28(1)	13(1)	39(1)	2(1)	-8(1)	-4(1)
Cl(3)	49(1)	31(1)	17(1)	-2(1)	10(1)	21(1)
O(1)	19(1)	11(1)	17(1)	-1(1)	4(1)	1(1)
O(2)	21(1)	17(1)	18(1)	-3(1)	6(1)	2(1)
O(3)	28(1)	17(1)	14(1)	2(1)	6(1)	1(1)
N(1)	17(1)	9(1)	12(1)	1(1)	3(1)	0(1)
C(1)	18(1)	13(1)	12(1)	-1(1)	0(1)	0(1)
C(2)	19(1)	13(1)	13(1)	0(1)	2(1)	0(1)
C(3)	17(1)	11(1)	11(1)	-1(1)	-1(1)	0(1)
C(4)	17(1)	12(1)	12(1)	-1(1)	0(1)	0(1)
C(5)	19(1)	14(1)	21(1)	-4(1)	3(1)	1(1)
C(6)	21(1)	20(1)	28(1)	-3(1)	10(1)	-3(1)
C(7)	27(1)	16(1)	27(1)	0(1)	8(1)	-7(1)
C(8)	26(1)	11(1)	21(1)	-1(1)	3(1)	-1(1)
C(9)	16(1)	14(1)	12(1)	-2(1)	0(1)	1(1)
C(10)	17(1)	10(1)	16(1)	1(1)	2(1)	0(1)
C(11)	15(1)	9(1)	16(1)	1(1)	1(1)	1(1)
C(12)	12(1)	12(1)	15(1)	-1(1)	0(1)	1(1)
C(13)	19(1)	15(1)	14(1)	-1(1)	0(1)	5(1)
C(14)	29(1)	16(1)	22(1)	2(1)	12(1)	0(1)
Cl(4)	19(1)	30(1)	19(1)	-3(1)	3(1)	1(1)
Cl(5)	35(1)	48(1)	29(1)	-16(1)	2(1)	-19(1)
Cl(6)	36(1)	26(1)	24(1)	-1(1)	10(1)	-9(1)
C(15)	17(1)	27(2)	20(1)	-3(1)	4(1)	3(1)
C(16)	17(1)	27(2)	20(1)	-3(1)	4(1)	3(1)
Cl(7)	59(6)	141(10)	58(5)	-62(6)	-32(4)	62(6)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x 10^3) for bir16_01.

	x	y	z	U(eq)
H(1)	6653	998	5773	15
H(5)	7823	3943	5116	21
H(6)	8791	5309	4361	27
H(7)	8038	6949	4515	28
H(8)	6339	7218	5500	23
H(10)	6150	2458	6861	17
H(11)	6494	2826	4613	16
H(14A)	4148	2803	7160	34
H(14B)	3447	3703	7731	34
H(14C)	4609	3281	8302	34
H(16A)	8709	3367	6944	25

H(16B)	8507	2192	7213	25

Table S6. Hydrogen bonds for bir16_01 [Å and °].

D-H	d(D-H)	d(H..A)	<DHA	d(D..A)	A
N1-H1	0.880	2.057	160.36	2.900	O2 [-x+1,y-1/2,-z+3/2]
C10-H10	0.950	2.617	137.02	3.375	O2 [-x+1,y-1/2,-z+3/2]
C15_a-D15_a	1.000	2.283	136.52	3.087	O3 [x,-y+1/2,z+1/2]
C16_b-H16A_b	0.990	2.398	110.20	2.893	O3 [x,-y+1/2,z+1/2]

Computational data

All calculations were performed with Gaussian09.[2]

Table S7. Energies and low or imaginary frequencies of the stationary points for the reactions of acetate **2** at B3LYP/6-31G(d,p) level of theory

Structure	Frequency	B3LYP energy[a]	ZPVE[b]	B3LYP energy[b,c]	Gibbs Free Energy	Relative Gibbs Free Energy[b,e]
str-**2**	26.3	-841.6290	145.3	0.0	-841.44282	0.0
str-**4**	23.4	-841.5977	144.1	18.4	-841.41226	19.2
str-**5**	24.3	-841.6168	145	7.4	-841.43120	7.3
str-**9**	27.2	-841.6378	144.8	-6.0	-841.45250	-6.1
[3,3]-**TS1**	428.8i	-841.5622	143.4	40.0	-841.37715	41.2
[3,5]-**TS2**	508.0i	-841.5686	144.8	37.4	-841.38145	38.5
[3,3]-**TS3**	302.0i	-841.5500	142.9	47.2	-841.36608	48.2
[1,5]-**TS4**	1427.2i	-841.5787	142.3	21.2[d]	-841.39581	22.2[d]

[a] Energies in atomic units (au); [b] Energies in kcal/mol; [c]Relative (B3LYP + ZPVE) energy;
[d] Relative to str-**5**; [e] Relative Gibbs Free Energies (B3LYP)

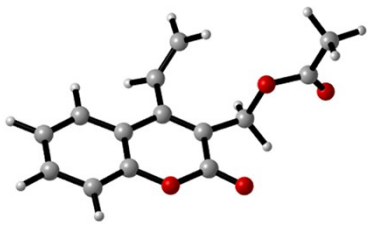
Table S8. Energies and low or imaginary frequencies of the stationary points for the reactions of coumarin trichloroacetimidate **3** at B3LYP/6-31G(d,p) level of theory

Structure	Frequency	B3LYP energy[a]	ZPVE[b]	Relative energy[b,c]	Gibbs Free Energy	Relative Gibbs Free Energy[b,e]
str-**3**	15.8	-2200.4885	135.2	0.0	-2200.32364	0.0
str-**6**	14.7	-2200.4825	134.2	2.8	-2200.31883	3.0
str-**7**	10.9	-2200.5045	135.2	-10.1	-2200.34130	-11.1
str-**8**	8.8	-2200.5288	135.1	-25.4	-2200.36539	-26.2
str-**10**	9.8	-2200.5220	135.7	-20.6	-2200.35653	-20.6
[3,3]-**TS5**	450.3i	-2200.4345	133.4	32.0	-2200.27141	32.8
[3,5]-**TS6**	416.4i	-2200.4413	135.2	29.6	-2200.27432	31.0
[1,3]-**TS7**	328.1i	-2200.4191	132.6	40.9	-2200.25840	40.9
[1,5]-**TS8**	1404.6i	-2200.4678	132.5	20.3[d]	-2200.30670	21.7[d]

[a] Energies in atomic units (au); [b] Energies in kcal/mol; [c]Relative (B3LYP + ZPVE) energy; [d] Relative to str-**7**; [e] Relative Gibbs Free Energies (B3LYP)

Table S9. Optimized Cartesian coordinates in .mol2 format of all the B3LYP/6-31G(d,p) optimized structures.

str-**2** optimized structure: minimum



2

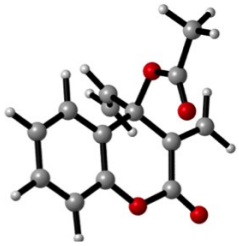
```
@<TRIPOS>MOLECULE
Molecule Name
30 31
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     -0.1898      2.2109     -0.5554 C
2 H2     -0.8730      2.7903     -1.1740 H
3 O3      4.4643     -0.1386     -0.8388 O
4 C4      3.9144     -0.0436      0.2352 C
5 C5      4.6028     -0.0236      1.5791 C
```

```
6 H6     4.3610    -0.9403     2.1259 H
7 H7     5.6804     0.0405     1.4322 H
8 H8     4.2514     0.8187     2.1808 H
9 O9     2.5681     0.0483     0.3827 O
10 C10    -0.5492     0.7894    -0.3690 C
11 C11     0.3559    -0.2321    -0.4905 C
12 C12    -1.9450     0.4709    -0.0783 C
13 C13    -0.0475    -1.6333    -0.2994 C
14 C14    -2.9562     1.4381     0.0951 C
15 C15    -2.3070    -0.8807     0.0637 C
16 C16    -4.2647     1.0655     0.3676 C
17 H17    -5.0277     1.8262     0.4959 H
18 C18    -3.6205    -1.2673     0.3381 C
19 C19    -4.5977    -0.2912     0.4843 C
20 H20    -5.6210    -0.5843     0.6975 H
21 H21    -2.7022     2.4899     0.0289 H
22 H22    -3.8430    -2.3242     0.4339 H
23 O23    -1.3882    -1.8812    -0.0503 O
24 O24     0.6940    -2.5871    -0.3629 O
25 C25     0.8604     2.8263    -0.0020 C
26 H26     1.5496     2.3038     0.6531 H
27 H27     1.0459     3.8803    -0.1842 H
28 C28     1.8022    -0.0555    -0.8500 C
29 H29     1.9632     0.8466    -1.4424 H
30 H30     2.1623    -0.9220    -1.4044 H
@<TRIPOS>BOND
1 1 2 1
2 1 10 1
3 1 25 2
4 3 4 2
5 4 5 1
6 4 9 1
7 5 6 1
8 5 7 1
9 5 8 1
10 9 28 1
11 10 11 2
12 10 12 1
13 11 13 1
14 11 28 1
15 12 14 Ar
16 12 15 Ar
17 13 23 1
18 13 24 2
19 14 16 Ar
20 14 21 1
21 15 18 Ar
22 15 23 1
23 16 17 1
24 16 19 Ar
25 18 19 Ar
26 18 22 1
27 19 20 1
28 25 26 1
```

```
29 25 27 1
30 28 29 1
31 28 30 1
```

str-**4** optimized structure: minimum



4

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@<TRIPOS>MOLECULE
Molecule Name
30 31
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1      0.7512     0.0761    -2.2189 C
2 H2      0.3851     0.9664    -2.7249 H
3 O3      1.2435     1.4229    -0.3676 O
4 C4      1.2438     1.8017     0.9410 C
5 C5      1.9136     3.1456     1.0987 C
6 H6      1.9367     3.4141     2.1542 H
7 H7      2.9305     3.1094     0.6978 H
8 H8      1.3660     3.9053     0.5331 H
9 O9      0.7730     1.1410     1.8373 O
10 C10     0.5978     0.1436    -0.7052 C
11 C11     1.2977    -1.0021     0.0114 C
12 C12    -0.8848     0.2145    -0.3754 C
13 C13     0.5280    -2.0388     0.7619 C
14 C14    -1.6732     1.2874    -0.8118 C
15 C15    -1.5073    -0.8074     0.3410 C
16 C16    -3.0393     1.3323    -0.5499 C
17 H17    -3.6294     2.1757    -0.8939 H
18 C18    -2.8775    -0.7826     0.6043 C
19 C19    -3.6433     0.2883     0.1561 C
20 H20    -4.7085     0.3111     0.3639 H
21 H21    -1.1997     2.1036    -1.3487 H
22 H22    -3.3114    -1.6016     1.1673 H
23 O23    -0.8309    -1.9037     0.8372 O
24 O24     1.0302    -3.0021     1.2885 O
25 C25     1.2184    -0.9440    -2.9350 C
26 H26     1.5851    -1.8585    -2.4821 H
27 H27     1.2405    -0.8889    -4.0188 H
28 C28     2.6287    -1.1345    -0.0150 C
29 H29     3.2560    -0.4212    -0.5381 H
30 H30     3.1004    -1.9585     0.5078 H
@<TRIPOS>BOND
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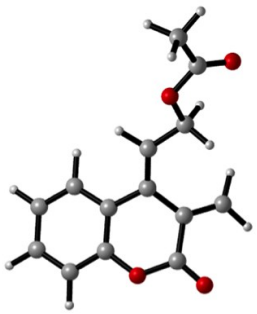
2 1 10 1
3 1 25 2
4 3 4 1
5 3 10 1
6 4 5 1
7 4 9 2
8 5 6 1
9 5 7 1
10 5 8 1
```

```
11 10 11 1
12 10 12 1
13 11 13 1
14 11 28 2
15 12 14 Ar
16 12 15 Ar
17 13 23 1
18 13 24 2
19 14 16 Ar
20 14 21 1
21 15 18 Ar
22 15 23 1
23 16 17 1
24 16 19 Ar
25 18 19 Ar
26 18 22 1
27 19 20 1
28 25 26 1
29 25 27 1
30 28 29 1
31 28 30 1
```

str-**5** optimized structure: minimum



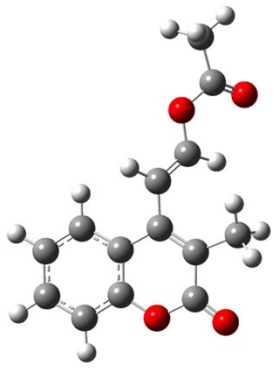
5

```
@<TRIPOS>MOLECULE
Molecule Name
30 31
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     -0.8802     0.5370     0.3732 C
2 H2     -0.9157     1.6190     0.2763 H
3 O3     -3.1191     0.6884    -0.3587 O
4 C4     -4.4396     0.4168    -0.2080 C
5 C5     -5.2732     1.2974    -1.1065 C
6 H6     -5.0316     1.0934    -2.1540 H
7 H7     -6.3294     1.1010    -0.9264 H
8 H8     -5.0481     2.3509    -0.9191 H
9 O9     -4.8649    -0.4271     0.5492 O
10 C10     0.3283    -0.0679     0.3742 C
11 C11     0.5235    -1.5319     0.4350 C
12 C12     1.5828     0.7005     0.2340 C
13 C13     1.6535    -2.1185    -0.3592 C
14 C14     1.7363     2.0418     0.6208 C
15 C15     2.6974     0.0569    -0.3222 C
16 C16     2.9392     2.7144     0.4315 C
17 H17     3.0332     3.7498     0.7431 H
18 C18     3.9084     0.7168    -0.5209 C
19 C19     4.0268     2.0517    -0.1454 C
20 H20     4.9690     2.5701    -0.2930 H
21 H21     0.9043     2.5519     1.0957 H
22 H22     4.7330     0.1703    -0.9651 H
```

```
23 O23     2.6544    -1.2624    -0.7413 O
24 O24     1.7422    -3.2797    -0.6718 O
25 C25    -2.2225    -0.1107     0.4468 C
26 H26    -2.2120    -1.1400     0.0713 H
27 H27    -2.6197    -0.1480     1.4692 H
28 C28    -0.2118    -2.3957     1.1559 C
29 H29     0.0003    -3.4577     1.1031 H
30 H30    -0.9979    -2.0670     1.8252 H
@<TRIPOS>BOND
1 1 2 1
2 1 10 2
3 1 25 1
4 3 4 1
5 3 25 1
6 4 5 1
7 4 9 2
8 5 6 1
9 5 7 1
10 5 8 1
11 10 11 1
12 10 12 1
13 11 13 1
14 11 28 2
15 12 14 Ar
16 12 15 Ar
17 13 23 1
18 13 24 2
19 14 16 Ar
20 14 21 1
21 15 18 Ar
22 15 23 1
23 16 17 1
24 16 19 Ar
25 18 19 Ar
26 18 22 1
27 19 20 1
28 25 26 1
29 25 27 1
30 28 29 1
31 28 30 1
```

str-**9** optimized structure: minimum



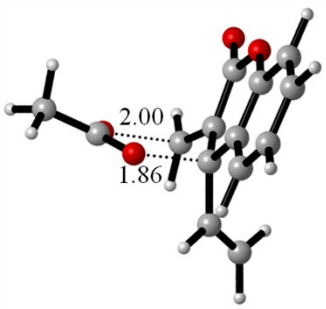
```
@<TRIPOS>MOLECULE
Molecule Name
30 31
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1      0.9468    -0.4164    -0.5705 C
2 H2      0.9716    -1.2519    -1.2656 H
```

```
3 C3     4.4255    -0.3219     0.2857 C
4 O4     4.4782     0.5694     1.0955 O
5 C5    -0.3650     0.1929    -0.2915 C
6 C6    -0.5739     1.5469    -0.2316 C
7 C7    -1.4994    -0.7152    -0.1130 C
8 C8    -1.9168     2.0858     0.0382 C
9 C9    -1.3973    -2.1211    -0.1233 C
10 C10    -2.7738    -0.1626     0.1011 C
11 C11    -2.5173    -2.9246     0.0415 C
12 H12    -2.4130    -4.0048     0.0283 H
13 C13    -3.9079    -0.9598     0.2684 C
14 C14    -3.7772    -2.3422     0.2327 C
15 H15    -4.6543    -2.9686     0.3621 H
16 H16    -0.4242    -2.5826    -0.2469 H
17 H17    -4.8651    -0.4755     0.4269 H
18 O18    -2.9616     1.1863     0.1679 O
19 O19    -2.1816     3.2636     0.1371 O
20 C20     2.0978    -0.0517     0.0032 C
21 H21     1.3124     2.2322    -1.0308 H
22 H22     2.2176     0.7252     0.7477 H
23 C23     0.4678     2.6103    -0.4528 C
24 H24     0.8541     2.9963     0.4985 H
25 H25     0.0173     3.4612    -0.9678 H
26 O26     3.2571    -0.7160    -0.3330 O
27 C27     5.5738    -1.1606    -0.2046 C
28 H28     5.3831    -2.2166     0.0080 H
29 H29     5.6747    -1.0593    -1.2891 H
30 H30     6.4907    -0.8400     0.2878 H
@<TRIPOS>BOND
1 1 2 1
2 1 5 1
3 1 20 2
4 3 4 2
5 3 26 1
6 3 27 1
7 5 6 2
8 5 7 1
9 6 8 1
10 6 23 1
11 7 9 Ar
12 7 10 Ar
13 8 18 1
14 8 19 2
15 9 11 Ar
16 9 16 1
17 10 13 Ar
18 10 18 1
19 11 12 1
20 11 14 Ar
21 13 14 Ar
22 13 17 1
23 14 15 1
24 20 22 1
25 20 26 1
```

```
26 21 23 1
27 23 24 1
28 23 25 1
29 27 28 1
30 27 29 1
31 27 30 1
```

str-[3,3]-**TS1** optimized structure: transition state



[3,3]-**TS1**

```
@<TRIPOS>MOLECULE
Molecule Name
30 30
SMALL
NO_CHARGES

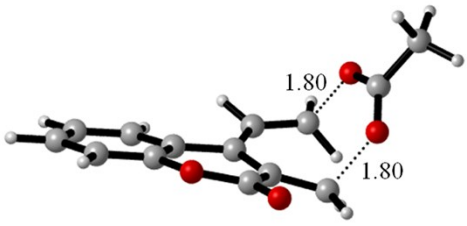

@<TRIPOS>ATOM
1 C1      0.5153    -1.5024     1.7163 C
2 H2      0.4512    -2.5234     1.3531 H
3 O3      1.0032    -1.2764    -0.7454 O
4 C4      2.1192    -0.8481    -1.2313 C
5 C5      2.3912    -1.2507    -2.6668 C
6 H6      3.4625    -1.2139    -2.8700 H
7 H7      1.9928    -2.2479    -2.8644 H
8 H8      1.8828    -0.5442    -3.3322 H
9 O9      2.9696    -0.1305    -0.6431 O
10 C10     0.2160    -0.4378     0.7111 C
11 C11     0.9026     0.8331     0.7964 C
12 C12    -1.1760    -0.3799     0.2194 C
13 C13     0.3551     2.0530     0.2134 C
14 C14    -2.0188    -1.5053     0.1753 C
15 C15    -1.6909     0.8495    -0.2239 C
16 C16    -3.3233    -1.4094    -0.2874 C
17 H17    -3.9558    -2.2905    -0.3159 H
18 C18    -3.0075     0.9570    -0.6828 C
19 C19    -3.8172    -0.1705    -0.7161 C
20 H20    -4.8381    -0.0861    -1.0760 H
21 H21    -1.6378    -2.4644     0.5067 H
22 H22    -3.3633     1.9288    -1.0066 H
23 O23    -0.9655     2.0068    -0.2282 O
24 O24     0.9273     3.1151     0.1142 O
25 C25     0.7864    -1.2593     2.9993 C
26 H26     0.8387    -0.2483     3.3915 H
27 H27     0.9490    -2.0727     3.6990 H
28 C28     2.2755     0.7923     0.9933 C
29 H29     2.7312     0.0098     1.5813 H
30 H30     2.8452     1.7035     0.8547 H
@<TRIPOS>BOND
1 1 2 1
2 1 10 1
3 1 25 2
4 3 4 Ar
```

```
5 4 5 1
6 4 9 2
7 5 6 1
8 5 7 1
9 5 8 1
10 10 11 Ar
11 10 12 1
12 11 13 1
13 11 28 Ar
14 12 14 Ar
15 12 15 Ar
16 13 23 1
17 13 24 2
18 14 16 Ar
19 14 21 1
20 15 18 Ar
21 15 23 1
22 16 17 1
23 16 19 Ar
24 18 19 Ar
25 18 22 1
26 19 20 1
27 25 26 1
28 25 27 1
29 28 29 1
30 28 30 1
```

str-[3,5]-**TS2** optimized structure: transition state

```
@<TRIPOS>MOLECULE
Molecule Name
30 30
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     -0.4188    -1.7906    -0.5610 C
2 H2      0.1112    -2.6412    -0.1502 H
3 O3     -2.8833    -1.4923     0.4620 C
4 C4     -3.3227    -0.3018     0.5279 C
5 C5     -4.3668    -0.0471     1.5974 C
6 H6     -4.8636    -0.9750     1.8798 H
7 H7     -3.8597     0.3655     2.4757 H
8 H8     -5.0884     0.6929     1.2485 H
9 O9     -2.9975     0.7155    -0.1595 O
10 C10     0.2494    -0.5637    -0.5161 C
11 C11    -0.3421     0.7209    -0.7243 C
12 C12     1.6743    -0.5533    -0.1329 C
13 C13     0.2980     1.9467    -0.2463 C
14 C14     2.4964    -1.6984    -0.1379 C
15 C15     2.2734     0.6618     0.2411 C
16 C16     3.8301    -1.6388     0.2409 C
17 H17     4.4384    -2.5373     0.2195 H
```



[3,5]-**TS2**

```
18 C18      3.6120     0.7327     0.6380 C
19 C19      4.3881    -0.4180     0.6412 C
20 H20      5.4298    -0.3645     0.9425 H
21 H21      2.0857    -2.6440    -0.4723 H
22 H22      4.0132     1.6978     0.9271 H
23 O23      1.5907     1.8439     0.2508 O
24 O24     -0.1930     3.0563    -0.2481 O
25 C25     -1.7821    -2.0329    -0.8552 C
26 H26     -2.3000    -1.5049    -1.6428 H
27 H27     -2.0882    -3.0726    -0.7997 H
28 C28     -1.6189     0.9388    -1.3008 C
29 H29     -1.9779     0.2758    -2.0743 H
30 H30     -1.8562     1.9823    -1.4676 H
@<TRIPOS>BOND
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2 1 10 Ar
3 1 25 Ar
4 3 4 2
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6 4 9 2
7 5 6 1
8 5 7 1
9 5 8 1
10 10 11 Ar
11 10 12 1
12 11 13 1
13 11 28 Ar
14 12 14 Ar
15 12 15 Ar
16 13 23 1
17 13 24 2
18 14 16 Ar
19 14 21 1
20 15 18 Ar
21 15 23 1
22 16 17 1
23 16 19 Ar
24 18 19 Ar
25 18 22 1
26 19 20 1
27 25 26 1
28 25 27 1
29 28 29 1
30 28 30 1
```

str-[3,3]-**TS3** optimized structure: transition state

```
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Molecule Name
30 30
SMALL
NO_CHARGES
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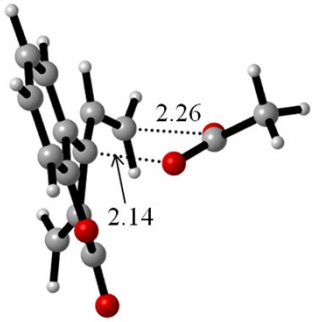

[3,3]-**TS3**

```
@<TRIPOS>ATOM
1 C1      1.1229    -0.6159     1.8049 C
2 H2      0.7445    -1.5514     2.2009 H
3 O3      3.0584    -1.1555    -0.2508 O
4 C4      2.0761    -1.1988    -1.0319 C
5 C5      2.0643    -2.2519    -2.1329 C
6 H6      1.6173    -1.8457    -3.0438 H
7 H7      3.0785    -2.6049    -2.3305 H
8 H8      1.4516    -3.1024    -1.8122 H
9 O9      1.0400    -0.4401    -0.9822 O
10 C10     0.2811     0.1311     0.9363 C
11 C11     0.5306     1.5496     0.6174 C
12 C12    -1.0815    -0.2984     0.6148 C
13 C13    -0.0744     2.0849    -0.6411 C
14 C14    -1.7424    -1.3750     1.2343 C
15 C15    -1.7685     0.3992    -0.3987 C
16 C16    -3.0293    -1.7385     0.8609 C
17 H17    -3.5245    -2.5647     1.3600 H
18 C18    -3.0523     0.0286    -0.7938 C
19 C19    -3.6811    -1.0387    -0.1612 C
20 H20    -4.6843    -1.3237    -0.4625 H
21 H21    -1.2482    -1.9213     2.0293 H
22 H22    -3.5335     0.5888    -1.5874 H
23 O23    -1.2201     1.4593    -1.0758 O
24 O24     0.3200     3.0486    -1.2419 O
25 C25     2.4738    -0.4183     1.8028 C
26 H26     2.9311     0.4715     1.4009 H
27 H27     3.1323    -1.1014     2.3270 H
28 C28     1.1553     2.4211     1.4237 C
29 H29     1.5424     2.1267     2.3916 H
30 H30     1.2591     3.4562     1.1180 H
@<TRIPOS>BOND
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2 1 10 Ar
3 1 25 2
4 3 4 2
5 4 5 1
6 4 9 2
7 5 6 1
8 5 7 1
9 5 8 1
10 10 11 1
11 10 12 1
12 11 13 1
13 11 28 2
14 12 14 Ar
15 12 15 Ar
16 13 23 1
17 13 24 2
18 14 16 Ar
19 14 21 1
20 15 18 Ar
21 15 23 1
22 16 17 1
```
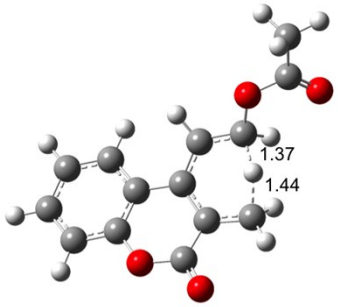

```
23 16 19 Ar
24 18 19 Ar
25 18 22 1
26 19 20 1
27 25 26 1
28 25 27 1
29 28 29 1
30 28 30 1
```

str-[1,5]-H-shift-**TS4** optimized structure: transition state

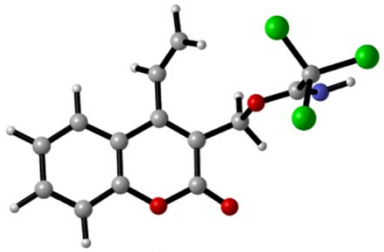


[1,5]-H-shift-**TS4**

```
@<TRIPOS>MOLECULE
Molecule Name
30 30
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     -0.8348    -0.6943    -0.2472 C
2 H2     -0.8173    -1.6868     0.1948 H
3 C3     -4.3983    -0.4790     0.0953 C
4 O4     -4.7381     0.1877    -0.8530 O
5 C5      0.3750    -0.0101    -0.3645 C
6 C6      0.3682     1.4105    -0.3710 C
7 C7      1.6646    -0.6887    -0.2003 C
8 C8      1.5096     2.1429     0.2139 C
9 C9      1.8630    -2.0625    -0.4176 C
10 C10      2.7744     0.0816     0.1780 C
11 C11      3.1143    -2.6427    -0.2442 C
12 H12      3.2473    -3.7050    -0.4214 H
13 C13      4.0362    -0.4875     0.3538 C
14 C14      4.2023    -1.8523     0.1445 C
15 H15      5.1824    -2.2999     0.2768 H
16 H16      1.0266    -2.6692    -0.7506 H
17 H17      4.8595     0.1518     0.6531 H
18 O18      2.6754     1.4307     0.4184 O
19 O19      1.5090     3.3172     0.5037 O
20 C20     -2.1082    -0.0635    -0.3551 C
21 H21     -1.7610     1.2229    -0.0562 H
22 H22     -2.5209     0.2374    -1.3170 H
23 C23     -0.8129     2.1371    -0.6359 C
24 H24     -1.3091     1.9967    -1.5942 H
25 H25     -0.8375     3.1634    -0.2759 H
26 C26     -5.3123    -1.1754     1.0683 C
27 H27     -5.0704    -2.2408     1.1166 H
28 H28     -5.1685    -0.7626     2.0713 H
```

```
29 H29    -6.3464    -1.0378     0.7554 H
30 O30    -3.0877    -0.6940     0.4358 O
@<TRIPOS>BOND
1 1 2 1
2 1 5 Ar
3 1 20 Ar
4 3 4 2
5 3 26 1
6 3 30 1
7 5 6 Ar
8 5 7 1
9 6 8 1
10 6 23 Ar
11 7 9 Ar
12 7 10 Ar
13 8 18 1
14 8 19 2
15 9 11 Ar
16 9 16 1
17 10 13 Ar
18 10 18 1
19 11 12 1
20 11 14 Ar
21 13 14 Ar
22 13 17 1
23 14 15 1
24 20 22 1
25 20 30 1
26 23 24 1
27 23 25 1
28 26 27 1
29 26 28 1
30 26 29 1
```

str-**3** optimized structure: minimum

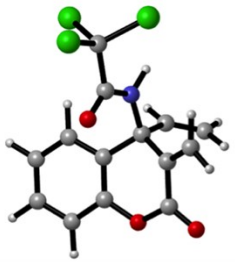


3

```
@<TRIPOS>MOLECULE
Molecule Name
31 32
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1    -1.6684     2.1847    -0.8836 C
2 H2    -2.4507     2.7624    -1.3730 H
3 C3     2.4663    -0.0534    -0.8592 C
4 C4     3.3691    -0.0117     0.4032 C
5 O5     1.1855     0.0087    -0.4715 O
6 C6    -2.0023     0.7713    -0.6101 C
7 C7    -1.1542    -0.2664    -0.8966 C
8 C8    -3.3175     0.4764    -0.0477 C
9 C9    -1.5356    -1.6612    -0.6290 C
10 C10    -4.2588     1.4616     0.3148 C
```

```
11 C11    -3.6637    -0.8685     0.1748 C
12 C12    -5.4918     1.1121     0.8461 C
13 H13    -6.2025     1.8859     1.1175 H
14 C14    -4.9016    -1.2316     0.7095 C
15 C15    -5.8146    -0.2384     1.0393 C
16 H16    -6.7788    -0.5133     1.4554 H
17 H17    -4.0066     2.5085     0.1899 H
18 H18    -5.1168    -2.2840     0.8574 H
19 O19    -2.8026    -1.8850    -0.1142 O
20 O20    -0.8413    -2.6278    -0.8452 O
21 C21    -0.5271     2.7952    -0.5477 C
22 H22     0.2685     2.2799    -0.0200 H
23 H23    -0.3717     3.8441    -0.7811 H
24 C24     0.1945    -0.1128    -1.5339 C
25 H25     0.2527     0.7764    -2.1634 H
26 H26     0.4411    -0.9957    -2.1235 H
27 N27     2.8261    -0.1322    -2.0685 N
28 H28     3.8381    -0.1804    -2.1667 H
29 Cl29     5.1087    -0.0924    -0.0491 Cl
30 Cl30     2.9779    -1.4010     1.4695 Cl
31 Cl31     3.0807     1.5364     1.2888 Cl
@<TRIPOS>BOND
1 1 2 1
2 1 6 1
3 1 21 2
4 3 4 1
5 3 5 Ar
6 3 27 2
7 4 29 1
8 4 30 1
9 4 31 1
10 5 24 1
11 6 7 2
12 6 8 1
13 7 9 1
14 7 24 1
15 8 10 Ar
16 8 11 Ar
17 9 19 1
18 9 20 2
19 10 12 Ar
20 10 17 1
21 11 14 Ar
22 11 19 1
23 12 13 1
24 12 15 Ar
25 14 15 Ar
26 14 18 1
27 15 16 1
28 21 22 1
29 21 23 1
30 24 25 1
31 24 26 1
32 27 28 1
```

str-**6** optimized structure: minimum

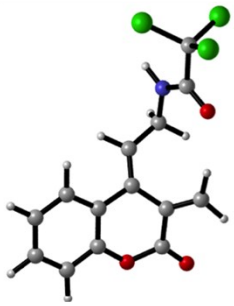


6

```
@<TRIPOS>MOLECULE
Molecule Name
31 32
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     -1.3315    -0.8814    -2.0660 C
2 H2     -1.1618    -0.0663    -2.7678 H
3 C3      1.2513     0.0301     0.4359 C
4 C4      2.8074     0.1039     0.1624 C
5 O5      0.7971     0.3669     1.5060 O
6 C6     -0.9373    -0.5358    -0.6247 C
7 C7     -1.3985    -1.6182     0.3483 C
8 C8     -1.6222     0.7903    -0.2863 C
9 C9     -2.8181    -1.5938     0.8209 C
10 C10    -1.1013     2.0289    -0.6745 C
11 C11    -2.8661     0.7699     0.3467 C
12 C12    -1.7958     3.2103    -0.4253 C
13 H13    -1.3684     4.1612    -0.7265 H
14 C14    -3.5754     1.9423     0.6023 C
15 C15    -3.0369     3.1654     0.2140 C
16 H16    -3.5843     4.0811     0.4140 H
17 H17    -0.1352     2.0639    -1.1680 H
18 H18    -4.5351     1.8706     1.1021 H
19 O19    -3.4887    -0.4039     0.7380 O
20 O20    -3.4016    -2.5495     1.2707 O
21 C21    -1.8607    -2.0284    -2.4881 C
22 H22    -2.0620    -2.8594    -1.8203 H
23 H23    -2.1193    -2.1630    -3.5336 H
24 C24    -0.6352    -2.6332     0.7621 C
25 Cl25     3.1131     1.4016    -1.0626 Cl
26 Cl26     3.6744     0.4739     1.6612 Cl
27 Cl27     3.3980    -1.4790    -0.5037 Cl
28 N28      0.5304    -0.3972    -0.6337 N
29 H29     -1.0507    -3.3852     1.4229 H
30 H30      0.4028    -2.7283     0.4646 H
31 H31      1.0160    -0.7431    -1.4488 H
@<TRIPOS>BOND
1 1 2 1
2 1 6 1
3 1 21 2
4 3 4 1
5 3 5 2
6 3 28 Ar
7 4 25 1
8 4 26 1
9 4 27 1
10 6 7 1
```

```
11 6 8 1
12 6 28 1
13 7 9 1
14 7 24 2
15 8 10 Ar
16 8 11 Ar
17 9 19 1
18 9 20 2
19 10 12 Ar
20 10 17 1
21 11 14 Ar
22 11 19 1
23 12 13 1
24 12 15 Ar
25 14 15 Ar
26 14 18 1
27 15 16 1
28 21 22 1
29 21 23 1
30 24 29 1
31 24 30 1
32 28 31 1
```

str-**7** optimized structure: minimum



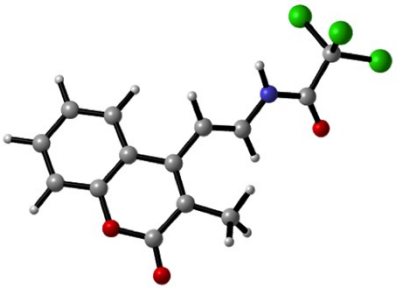
7

```
@<TRIPOS>MOLECULE
Molecule Name
31 32
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1    -0.7100    -0.0403    -0.7422 C
2 H2    -0.4056     1.0039    -0.7408 H
3 C3     2.7890    -0.3326    -0.7388 C
4 C4     3.9065     0.2038     0.2370 C
5 O5     3.0212    -0.4681    -1.9232 O
6 C6    -2.0193    -0.3193    -0.5523 C
7 C7    -2.5801    -1.6852    -0.4733 C
8 C8    -3.0185     0.7452    -0.3228 C
9 C9    -3.6690    -1.9289     0.5301 C
10 C10    -2.9055     2.0564    -0.8124 C
11 C11    -4.1556     0.4320     0.4356 C
12 C12    -3.8725     3.0162    -0.5305 C
13 H13    -3.7654     4.0216    -0.9246 H
14 C14    -5.1308     1.3822     0.7298 C
15 C15    -4.9850     2.6795     0.2466 C
16 H16    -5.7439     3.4234     0.4676 H
17 H17    -2.0585     2.3137    -1.4405 H
18 H18    -5.9839     1.0862     1.3302 H
19 O19    -4.3597    -0.8297     0.9713 O
20 O20    -3.9759    -3.0128     0.9599 O
21 C21     0.4253    -1.0118    -0.8913 C
```

```
22 H22     0.1361    -2.0154    -0.5596 H
23 H23     0.7555    -1.0944    -1.9326 H
24 C24    -2.2259    -2.7281    -1.2428 C
25 H25    -1.5118    -2.6290    -2.0519 H
26 H26    -2.6881    -3.6963    -1.0855 H
27 N27     1.5976    -0.5658    -0.1396 N
28 Cl28     5.4877     0.1699    -0.5635 Cl
29 Cl29     3.4794     1.9050     0.6857 Cl
30 Cl30     3.9739    -0.8004     1.7455 Cl
31 H31     1.5110    -0.4513     0.8601 H
@<TRIPOS>BOND
1 1 2 1
2 1 6 2
3 1 21 1
4 3 4 1
5 3 5 2
6 3 27 Ar
7 4 28 1
8 4 29 1
9 4 30 1
10 6 7 1
11 6 8 1
12 7 9 1
13 7 24 2
14 8 10 Ar
15 8 11 Ar
16 9 19 1
17 9 20 2
18 10 12 Ar
19 10 17 1
20 11 14 Ar
21 11 19 1
22 12 13 1
23 12 15 Ar
24 14 15 Ar
25 14 18 1
26 15 16 1
27 21 22 1
28 21 23 1
29 21 27 1
30 24 25 1
31 24 26 1
32 27 31 1
```

str-**8** optimized structure: minimum

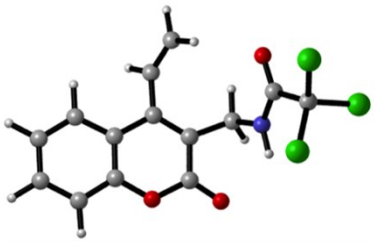
```
@<TRIPOS>MOLECULE
Molecule Name
31 32
SMALL
NO_CHARGES
```



```
@<TRIPOS>ATOM
1 C1    -0.7470     0.1293     0.4809 C
2 H2    -0.6182     0.9674     1.1642 H
3 C3     2.7352    -0.4847    -0.4608 C
4 C4     4.0942     0.1755    -0.0274 C
5 O5     2.6964    -1.3744    -1.2809 O
6 C6    -2.1331    -0.2997     0.2357 C
7 C7    -2.5203    -1.6148     0.1842 C
8 C8    -3.1431     0.7504     0.0861 C
9 C9    -3.9302    -1.9714    -0.0450 C
10 C10    -2.8575     2.1308     0.0816 C
11 C11    -4.4855     0.3702    -0.0836 C
12 C12    -3.8668     3.0746    -0.0514 C
13 H13    -3.6207     4.1315    -0.0509 H
14 C14    -5.5101     1.3094    -0.2177 C
15 C15    -5.1982     2.6626    -0.1953 C
16 H16    -5.9892     3.3986    -0.2996 H
17 H17    -1.8288     2.4624     0.1657 H
18 H18    -6.5272     0.9546    -0.3418 H
19 O19    -4.8512    -0.9419    -0.1389 O
20 O20    -4.3504    -3.1036    -0.1358 O
21 C21     0.3442    -0.3988    -0.0978 C
22 H22    -0.7321    -2.5514     0.9565 H
23 H23     0.3095    -1.1955    -0.8299 H
24 C24    -1.6229    -2.8070     0.3803 C
25 H25    -1.2964    -3.2263    -0.5794 H
26 H26    -2.1764    -3.5996     0.8874 H
27 N27     1.6391     0.0470     0.1646 N
28 Cl28     5.4474    -0.6179    -0.8453 Cl
29 Cl29     4.0511     1.9324    -0.4661 Cl
30 Cl30     4.2853     0.0234     1.7679 Cl
31 H31     1.7699     0.7849     0.8438 H
@<TRIPOS>BOND
1 1 2 1
2 1 6 1
3 1 21 2
4 3 4 1
5 3 5 2
6 3 27 Ar
7 4 28 1
8 4 29 1
9 4 30 1
10 6 7 2
11 6 8 1
12 7 9 1
13 7 24 1
14 8 10 Ar
15 8 11 Ar
16 9 19 1
17 9 20 2
18 10 12 Ar
19 10 17 1
20 11 14 Ar
21 11 19 1
```

```
22 12 13 1
23 12 15 Ar
24 14 15 Ar
25 14 18 1
26 15 16 1
27 21 23 1
28 21 27 1
29 22 24 1
30 24 25 1
31 24 26 1
32 27 31 1
```

str-**10** optimized structure: minimum

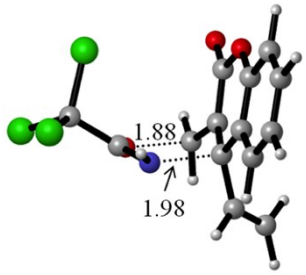


10

```
@<TRIPOS>MOLECULE
Molecule Name
31 32
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1    -2.0028     2.4020    -0.6912 C
2 H2    -2.8798     2.8701    -1.1365 H
3 C3     2.1335     0.6416    -0.2314 C
4 C4     3.3675    -0.1191     0.3909 C
5 C5    -2.0986     0.9304    -0.5484 C
6 C6    -1.1428     0.0515    -0.9827 C
7 C7    -3.3276     0.3942     0.0357 C
8 C8    -1.3448    -1.3974    -0.8829 C
9 C9    -4.3606     1.1965     0.5626 C
10 C10    -3.4944    -1.0002     0.0998 C
11 C11    -5.5060     0.6268     1.0997 C
12 H12    -6.2883     1.2628     1.5006 H
13 C13    -4.6424    -1.5858     0.6350 C
14 C14    -5.6492    -0.7674     1.1308 C
15 H15    -6.5453    -1.2137     1.5504 H
16 H16    -4.2457     2.2744     0.5608 H
17 H17    -4.7166    -2.6674     0.6545 H
18 O18    -2.5292    -1.8543    -0.3544 O
19 O19    -0.5352    -2.2279    -1.2530 O
20 C20    -0.9932     3.1788    -0.2868 C
21 H21    -0.0957     2.7880     0.1821 H
22 H22    -1.0432     4.2543    -0.4292 H
23 C23     0.1556     0.4133    -1.6781 C
24 H24     0.2767     1.4898    -1.7605 H
25 H25     0.1469    -0.0194    -2.6843 H
26 Cl26     4.0229     0.8100     1.7596 Cl
27 Cl27     4.6178    -0.2639    -0.9063 Cl
28 Cl28     2.9162    -1.7757     0.9629 Cl
29 N29     1.3270    -0.1258    -0.9880 N
30 O30     2.0224     1.8436    -0.0596 O
31 H31     1.4022    -1.1354    -0.9802 H
@<TRIPOS>BOND
1 1 2 1
```

```
2 1 5 1
3 1 20 2
4 3 4 1
5 3 29 Ar
6 3 30 2
7 4 26 1
8 4 27 1
9 4 28 1
10 5 6 2
11 5 7 1
12 6 8 1
13 6 23 1
14 7 9 Ar
15 7 10 Ar
16 8 18 1
17 8 19 2
18 9 11 Ar
19 9 16 1
20 10 13 Ar
21 10 18 1
22 11 12 1
23 11 14 Ar
24 13 14 Ar
25 13 17 1
26 14 15 1
27 20 21 1
28 20 22 1
29 23 24 1
30 23 25 1
31 23 29 1
32 29 31 1
```

str-[3,3]-**TS5** optimized structure: transition state

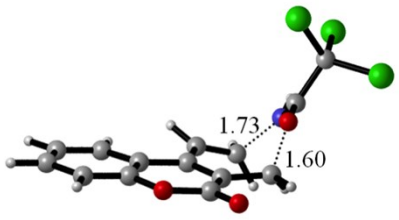


[3,3]-**TS5**

```
@<TRIPOS>MOLECULE
Molecule Name
31 31
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1    -1.5928     1.6779     1.9664 C
2 H2    -1.3521     1.1404     2.8778 H
3 C3     1.4351     0.4580     0.6115 C
4 C4     2.5271    -0.5739     0.1516 C
5 O5     1.6651     1.6505     0.2441 O
6 C6    -1.3344     0.9503     0.6839 C
7 C7    -0.8750     1.6775    -0.4650 C
8 C8    -2.1987    -0.2184     0.4114 C
9 C9    -1.0475     1.1708    -1.8235 C
10 C10    -2.8240    -0.9657     1.4273 C
```

```
11 C11    -2.4159    -0.6041    -0.9228 C
12 C12    -3.6275    -2.0566     1.1259 C
13 H13    -4.0989    -2.6206     1.9239 H
14 C14    -3.2316    -1.6965    -1.2345 C
15 C15    -3.8303    -2.4204    -0.2119 C
16 H16    -4.4607    -3.2701    -0.4555 H
17 H17    -2.6786    -0.6774     2.4626 H
18 H18    -3.3751    -1.9519    -2.2785 H
19 O19    -1.8708     0.0563    -1.9841 O
20 O20    -0.5814     1.6545    -2.8296 O
21 C21    -2.1399     2.8925     2.0289 C
22 H22    -2.4027     3.4502     1.1354 H
23 H23    -2.3525     3.3590     2.9855 H
24 C24     0.1422     2.6258    -0.2733 C
25 H25     0.1686     3.2158     0.6315 H
26 H26     0.5824     3.0727    -1.1567 H
27 Cl27     2.1804    -0.9677    -1.5737 Cl
28 Cl28     4.1565     0.1420     0.3031 Cl
29 Cl29     2.4640    -2.0928     1.1319 Cl
30 N30     0.3519     0.0638     1.2286 N
31 H31     0.2658    -0.9444     1.3330 H
@<TRIPOS>BOND
1 1 2 1
2 1 6 1
3 1 21 2
4 3 4 1
5 3 5 2
6 3 30 2
7 4 27 1
8 4 28 1
9 4 29 1
10 6 7 Ar
11 6 8 1
12 7 9 1
13 7 24 Ar
14 8 10 Ar
15 8 11 Ar
16 9 19 1
17 9 20 2
18 10 12 Ar
19 10 17 1
20 11 14 Ar
21 11 19 1
22 12 13 1
23 12 15 Ar
24 14 15 Ar
25 14 18 1
26 15 16 1
27 21 22 1
28 21 23 1
29 24 25 1
30 24 26 1
31 30 31 1
```

str-[3,5]-**TS6** optimized structure: transition state

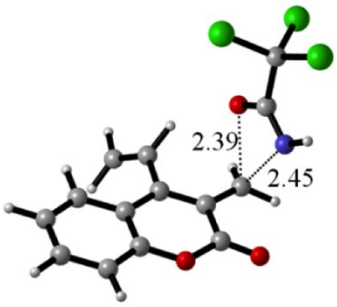


[3,5]-**TS6**

```
@<TRIPOS>MOLECULE
Molecule Name
31 31
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1      0.9070    -1.5406    -1.1087 C
2 H2      1.1590    -2.4908    -0.6558 H
3 C3     -1.9598    -0.1370    -0.4553 C
4 C4     -3.2323    -0.1171     0.4304 C
5 O5     -1.2203     0.8898    -0.2399 O
6 C6      1.6571    -0.4158    -0.7394 C
7 C7      1.2373     0.9342    -0.8711 C
8 C8      2.9746    -0.6236    -0.1021 C
9 C9      2.0132     2.0500    -0.3623 C
10 C10      3.5829    -1.8858     0.0519 C
11 C11      3.6998     0.4906     0.3542 C
12 C12      4.8200    -2.0316     0.6637 C
13 H13      5.2586    -3.0192     0.7665 H
14 C14      4.9473     0.3575     0.9735 C
15 C15      5.5037    -0.9033     1.1339 C
16 H16      6.4727    -1.0088     1.6124 H
17 H17      3.0847    -2.7656    -0.3372 H
18 H18      5.4522     1.2565     1.3096 H
19 O19      3.2466     1.7682     0.2155 O
20 O20      1.6930     3.2249    -0.3897 O
21 C21     -0.2140    -1.5595    -1.9965 C
22 H22     -0.1923    -0.8907    -2.8517 H
23 H23     -0.5013    -2.5609    -2.3138 H
24 C24     -0.0999     1.3337    -1.2986 C
25 H25     -0.5032     0.9301    -2.2208 H
26 H26     -0.2056     2.4143    -1.2601 H
27 N27     -1.7306    -1.0957    -1.2989 N
28 Cl28     -4.2403    -1.6067     0.2180 Cl
29 Cl29     -2.7430    -0.0077     2.1516 Cl
30 Cl30     -4.2080     1.3118    -0.0382 Cl
31 H31     -2.4363    -1.8242    -1.3179 H
@<TRIPOS>BOND
1 1 2 1
2 1 6 Ar
3 1 21 Ar
4 3 4 1
5 3 5 2
6 3 27 2
7 4 28 1
8 4 29 1
9 4 30 1
10 6 7 Ar
11 6 8 1
```

```
12 7 9 1
13 7 24 1
14 8 10 Ar
15 8 11 Ar
16 9 19 1
17 9 20 2
18 10 12 Ar
19 10 17 1
20 11 14 Ar
21 11 19 1
22 12 13 1
23 12 15 Ar
24 14 15 Ar
25 14 18 1
26 15 16 1
27 21 22 1
28 21 23 1
29 24 25 1
30 24 26 1
31 27 31 1
```

str-[1,3]-**TS7** optimized structure: transition state



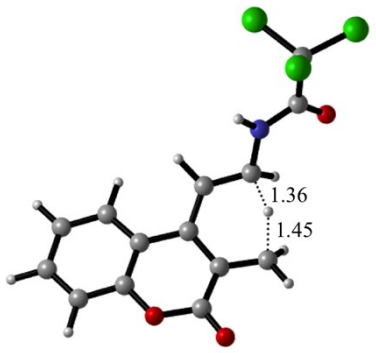
[1,3]-**TS7**

```
@<TRIPOS>MOLECULE
Molecule Name
31 31
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     -1.7679    -2.2019     1.0876 C
2 H2     -2.6455    -2.7931     1.3419 H
3 C3      2.0811     0.1393     0.4432 C
4 C4      3.3724     0.0250    -0.4536 C
5 O5      1.8445    -0.8976     1.1165 O
6 C6     -2.0541    -0.7899     0.7846 C
7 C7     -1.2881     0.2834     1.2559 C
8 C8     -3.2294    -0.4994    -0.0099 C
9 C9     -1.6951     1.6852     0.9908 C
10 C10    -4.0576    -1.4980    -0.5795 C
11 C11    -3.5522     0.8470    -0.2893 C
12 C12    -5.1518    -1.1640    -1.3566 C
13 H13    -5.7711    -1.9452    -1.7842 H
14 C14    -4.6551     1.1915    -1.0740 C
15 C15    -5.4531     0.1863    -1.6009 C
16 H16    -6.3106     0.4489    -2.2124 H
17 H17    -3.8154    -2.5416    -0.4199 H
18 H18    -4.8569     2.2414    -1.2536 H
19 O19    -2.8095     1.8787     0.1875 O
20 O20    -1.1555     2.6651     1.4346 O
21 C21    -0.5789    -2.8154     1.0135 C
22 C22    -0.1414     0.1511     2.0702 C
```

```
23 H23     0.2624     1.0428     2.5226 H
24 H24     0.1186    -0.8057     2.4885 H
25 N25     1.3472     1.2043     0.4545 N
26 Cl26     3.7515     1.5363    -1.3793 Cl
27 Cl27     4.7836    -0.3614     0.5920 Cl
28 Cl28     3.1183    -1.3103    -1.6436 Cl
29 H29     1.6454     1.9960    -0.1071 H
30 H30     0.3386    -2.3039     0.7352 H
31 H31    -0.5131    -3.8776     1.2313 H
@<TRIPOS>BOND
1 1 2 1
2 1 6 1
3 1 21 2
4 3 4 1
5 3 5 2
6 3 25 2
7 4 26 1
8 4 27 1
9 4 28 1
10 6 7 Ar
11 6 8 1
12 7 9 1
13 7 22 Ar
14 8 10 Ar
15 8 11 Ar
16 9 19 1
17 9 20 2
18 10 12 2
19 10 17 1
20 11 14 Ar
21 11 19 1
22 12 13 1
23 12 15 Ar
24 14 15 Ar
25 14 18 1
26 15 16 1
27 21 30 1
28 21 31 1
29 22 23 1
30 22 24 1
31 25 29 1
```

str-[1,5]-H-shift-**TS8** optimized structure: transition state

```
@<TRIPOS>MOLECULE
Molecule Name
31 31
SMALL
NO_CHARGES


@<TRIPOS>ATOM
1 C1     0.7990    -0.3467    -0.5967 C
```



[1,5]-H-shift-**TS8**

```
2 H2     0.6351    -1.3639    -0.2480 H
3 C3    -2.7892     0.3238    -0.6574 C
4 C4    -3.9820    -0.2387     0.2005 C
5 O5    -2.9884     0.9533    -1.6743 O
6 C6     2.0993     0.1489    -0.5300 C
7 C7     2.3041     1.5534    -0.4392 C
8 C8     3.2474    -0.7265    -0.2708 C
9 C9     3.4528     2.0685     0.3332 C
10 C10     3.2725    -2.0992    -0.5694 C
11 C11     4.3990    -0.1570     0.2931 C
12 C12     4.3949    -2.8721    -0.2953 C
13 H13     4.3960    -3.9297    -0.5382 H
14 C14     5.5328    -0.9209     0.5718 C
15 C15     5.5262    -2.2805     0.2789 C
16 H16     6.4068    -2.8789     0.4906 H
17 H17     2.4085    -2.5509    -1.0470 H
18 H18     6.3944    -0.4332     1.0141 H
19 O19     4.4651     1.1751     0.6242 O
20 O20     3.5834     3.2110     0.7075 O
21 C21    -0.3605     0.4776    -0.7864 C
22 H22     0.1477     1.6755    -0.3903 H
23 H23    -0.6019     0.8715    -1.7725 H
24 C24     1.2895     2.4645    -0.7969 C
25 H25     0.8993     2.4432    -1.8122 H
26 H26     1.3669     3.4645    -0.3754 H
27 N27    -1.5557     0.0137    -0.1659 N
28 Cl28    -5.5257     0.3519    -0.4346 Cl
29 Cl29    -3.9338    -2.0466     0.1231 Cl
30 Cl30    -3.7920     0.2815     1.9258 Cl
31 H31    -1.4820    -0.4546     0.7271 H
@<TRIPOS>BOND
1 1 2 1
2 1 6 Ar
3 1 21 Ar
4 3 4 1
5 3 5 2
6 3 27 Ar
7 4 28 1
8 4 29 1
9 4 30 1
10 6 7 Ar
11 6 8 1
12 7 9 1
13 7 24 Ar
14 8 10 Ar
15 8 11 Ar
16 9 19 1
17 9 20 2
18 10 12 Ar
19 10 17 1
20 11 14 Ar
21 11 19 1
22 12 13 1
23 12 15 Ar
```

```
24 14 15 Ar
25 14 18 1
26 15 16 1
27 21 23 1
28 21 27 1
29 24 25 1
30 24 26 1
31 27 31 1
```

References:

1) Rajale, T.; Sharma, S.; Stroud, D.A.; Unruh, D.K.; Miaou, E.; Lai, K.; Birney, D.M. *Tetrahedron Lett*. **2014**, *55*, 6627-6630.

2) Full Gaussian 09 Reference (reference 27 in main text) Revision D.01, 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, T. Keith, 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, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.