Table S1 (**Supplementary Information)** Optimized geometries [B3LYP/6-311++G(d,p)] for the conformers of methyl 3-methyl-2*H*-azirine-2-carboxylate.

	Ct	***Cc***
ΔE_{corr} / kJ mol^{-1}	0.0	2.3
Dipolar moment / debye	3.1	3.7
Bond length/Å		
C_1-C_2	1.463	1.463
C_1=N_3	1.246	1.247
C_1-C_5	1.475	1.475
C_2-N_3	1.552	1.555
C_2-C_4	1.488	1.488
C_2-H_{15}	1.085	1.085
C_4=O_9	1.209	1.209
C_4-O_{10}	1.350	1.350
C_5-H_6	1.091	1.091
C_5-H_7	1.093	1.093
C_5-H_8	1.093	1.093
O_{10}-C_{11}	1.440	1.439
C_{11}-H_{12}	1.088	1.088
C_{11}-H_{13}	1.091	1.091
C_{11}-H_{14}	1.091	1.091
Bond angle/°		
C_2-C_1-C_5	147.8	147.9
N_3=C_1-C_5	142.8	142.6
C_1-C_2-C_4	119.2	122.6
C_1-C_2-H_{15}	121.5	121.2
N_3-C_2-C_4	116.2	119.0
N_3-C_2-H_{15}	116.3	116.3
C_4-C_2-H_{15}	116.6	113.3
C_2-C_4=O_9	125.2	123.6
C_2-C_4-O_{10}	110.8	112.5
O_9=C_4-O_{10}	124.0	123.9
C_1-C_5-H_6	110.4	110.5
C_1-C_5-H_7	110.1	110.0
C_1-C_5-H_8	109.4	109.6
H_6-C_5-H_7	109.7	109.6
H_6-C_5-H_8	109.5	109.5
H_7-C_5-H_8	107.7	107.6
C_4-O_{10}-C_{11}	115.9	115.9
O_{10}-C_{11}-H_{12}	105.5	105.5
O_{10}-C_{11}-H_{13}	110.4	110.5
O_{10}-C_{11}-H_{14}	110.5	110.4
H_{12}-C_{11}-H_{13}	110.7	110.7
H_{12}-C_{11}-H_{14}	110.7	110.6
H_{13}-C_{11}-H_{14}	109.2	109.2
Dihedral angle/°		
C_5-C_1-C_2-C_4	-77.8	-77.8
C_5-C_1-C_2-H_{15}	82.8	81.3
C_2-C_1-C_5-H_6	-180.0	-179.3
C_2-C_1-C_5-H_7	-58.7	-58.1
C_2-C_1-C_5-H_8	59.5	60.0
N_3-C_1-C_5-H_6	2.6	1.3
N_3=C_1-C_5-H_7	123.9	122.5

N_3=C_1-C_5-H_8	-118.0	-119.4
C_1-C_2-C_4=O_9	-18.0	158.2
C_1-C_2-C_4-O_{10}	161.4	-21.0
N_3-C_2-C_4=O_9	37.4	-144.6
N_3-C_2-C_4-O_{10}	-143.2	36.2
H_{15}-C_2-C_4=O_9	-179.6	-2.4
H_{15}-C_2-C_4-O_{10}	-0.2	178.5
C_2-C_4-O_{10}-C_{11}	-179.3	-178.3
O_9=C_4-O_{10}-C_{11}	0.0	2.6
C_4-O_{10}-C_{11}-H_{12}	179.6	179.3
C_4-O_{10}-C_{11}-H_{13}	-60.8	-61.0
C_4-O_{10}-C_{11}-H_{14}	60.0	59.9

[a] See Figure 1 for atom numbering scheme.

Table S2 (Supplementary Information) Definition of internal coordinates used in the normal coordinate analysis of methyl 3-methyl-2*H*-azirine-2-carboxylate.

Symbol	Definition[a]
S_1	ν (C_1-C_2)
S_2	ν (C_1=N_3)
S_3	ν (C_1-C_5)
S_4	ν (C_2-N_3)
S_5	ν (C_2-C_4)
S_6	ν (C_2-H_{15})
S_7	ν (C_4=O_9)
S_8	ν (C_4-O_{10})
S_9	ν (C_5-H_6)
S_{10}	ν (C_5-H_7)
S_{11}	ν (C_5-H_8)
S_{12}	ν (C_{11}-O_{10})
S_{13}	ν (C_{11}-H_{12})
S_{14}	ν (C_{11}-H_{13})
S_{15}	ν (C_{11}-H_{14})
S_{16}	δ (C_2-C_1-C_5) - δ (N_3=C_1-C_5)
S_{17}	γ (C_2-C_1(=N_3)-C_5)
S_{18}	δ (C_1-C_2-C_4) - δ (N_3=C_2-C_4)
S_{19}	γ (C_1-C_2(-N_3)-C_4)
S_{20}	δ (C_1-C_2-H_{15}) - δ (N_3-C_2-H_{15})
S_{21}	γ (C_1-C_2(-H_{15})-N_3)
S_{22}	δ (H_6-C_5-H_7) + δ (H_6-C_5-H_8) + δ (H_7-C_5-H_8) - δ (C_1-C_5-H_6) - δ (C_1-C_5-H_7) - δ (C_1-C_5-H_8)
S_{23}	2 δ (H_6-C_5-H_7) - δ (H_6-C_5-H_8) - δ (H_7-C_5-H_8)
S_{24}	δ (H_6-C_5-H_8) - δ (H_7-C_5-H_8)
S_{25}	2 δ (C_1-C_5-H_6) - δ (C_1-C_5-H_7) - δ (C_1-C_5-H_8)
S_{26}	δ (C_1-C_5-H_7) - δ (C_1-C_5-H_8)
S_{27}	δ (H_{12}-C_{11}-H_{13}) + δ (H_{12}-C_{11}-H_{14}) + δ (H_{13}-C_{11}-H_{14}) - δ (O_{10}-C_{11}-H_{12}) - δ (O_{10}-C_{11}-H_{13}) - δ (O_{10}-C_{11}-H_{14})
S_{28}	2 δ (H_{12}-C_{11}-H_{13}) - δ (H_{12}-C_{11}-H_{14}) - δ (H_{13}-C_{11}-H_{14})
S_{29}	δ (H_{12}-C_{11}-H_{14}) - δ (H_{13}-C_{11}-H_{14})
S_{30}	2 δ (O_{10}-C_{11}-H_{12}) - δ (O_{10}-C_{11}-H_{13}) - δ (O_{10}-C_{11}-H_{14})
S_{31}	δ (O_{10}-C_{11}-H_{13}) - δ (O_{10}-C_{11}-H_{14})
S_{32}	2 δ (C_2-C_4=O_9) - δ (O_9=C_4-O_{10}) - δ (C_2-C_4-O_{10})
S_{33}	δ (O_9=C_4-O_{10}) - δ (C_2-C_4-O_{10})
S_{34}	γ (C_2-C_4(=O_9)-O_{10})
S_{35}	δ (C_4-O_{10}-C_{11})
S_{36}	τ (C_2-C_1-C_5-H_6) + τ (N_3=C_1-C_5-H_6) + τ (C_2-C_1-C_5-H_7) + τ (N_3=C_1-C_5-H_7) + τ (C_2-C_1-C_5-H_8) + τ (N_3=C_1-C_5-H_8)
S_{37}	τ (C_1-C_2-C_4=O_9) + τ (N_3=C_2-C_4=O_9) + τ (H_{15}-C_2-C_4=O_9) + τ (C_1-C_2-C_4-O_{10}) + τ (N_3=C_2-C_4-O_{10}) + τ (H_{15}-C_2-C_4-O_{10})
S_{38}	τ (C_2-C_4-C_{10}-O_{11}) + τ (O_9=C_4-C_{10}-O_{11})
S_{39}	τ (C_4-O_{10}-C_{11}-H_{12}) + τ (C_4-O_{10}-C_{11}-H_{13}) + τ (C_4-O_{10}-C_{11}-H_{14})

[a] See Figure 1 for atom numbering, ν – bond stretching, δ – bending, γ – out-of-plane bending, w – wagging, τ – torsion.

Table S3 (Supplementary Information) B3LYP/6-311++G(d,p) calculated frequencies and intensities, and normal coordinate analysis for conformer *Ct* of methyl 3-methyl-2*H*-azirine-2-carboxylate [a].

Calculated frequency	Intensity	PED[b]	Approximate Description
3087	15.4	$S_{13}(80) + S_{14}(11) + S_{15}(9)$	ν (OCH_3') as
3086	9.6	$S_6(99)$	ν C-H
3054	18.7	$S_{14}(47) + S_{15}(45) + S_9(5)$	ν (OCH_3'') as
3054	7.6	$S_9(67) + S_{11}(14) + S_{10}(11)$	ν (CCH_3') as
3032	2.7	$S_{11}(50) + S_{10}(49)$	ν (OCH_3'') as
2983	32.7	$S_{15}(42) + S_{14}(38) + S_{13}(19)$	ν (OCH_3) s
2970	7.0	$S_{10}(38) + S_{11}(34) + S_9(27)$	ν (CCH_3) s
1841	24.3	$S_2(74) + S_3(14) + S_1(7)$	ν C=N
1742	214.4	$S_7(79) + S_{33}(6) + S_5(5)$	ν C=O
1465	9.9	$S_{29}(55) + S_{28}(24) + S_{30}(11) + S_{27}(9)$	δ (OCH_3'') as
1450	9.4	$S_{28}(65) + S_{29}(27) + S_{31}(8)$	δ (OCH_3') as
1442	13.7	$S_{24}(82) + S_{25}(9) + S_{23}(6)$	δ (CCH_3'') as
1439	6.4	$S_{23}(52) + S_{27}(32)$	δ (CCH_3') as
1437	24.0	$S_{27}(54) + S_{23}(29)$	δ (OCH_3) s
1372	7.8	$S_{22}(88) + S_3(9)$	δ (CCH_3) s
1338	136.5	$S_{21}(63) + S_5(14) + S_8(6)$	γ C-H
1246	9.6	$S_1(48) + S_2(10) + S_{25}(9) + S_3(8) + S_{16}(5)$	ν C-Cα
1188	336.7	$S_8(32) + S_{30}(32) + S_{21}(9)$	ν C-O, γ (OCH_3)
1175	179.0	$S_{30}(32) + S_{21}(13) + S_8(13) + S_5(10) + S_{33}(7) + S_{32}(7)$	γ (OCH_3)
1145	0.8	$S_{31}(92)$	γ (OCH_3')
1038	9.9	$S_{26}(27) + S_{20}(25) + S_{25}(19) + S_{12}(8) + S_5(5)$	γ (CCH_3'), δ C-H
1031	16.7	$S_{26}(35) + S_{12}(20) + S_{25}(14) + S_{23}(6)$	γ (CCH_3')
993	14.7	$S_{12}(34) + S_{20}(24) + S_{25}(12) + S_5(10) + S_{26}(6)$	ν O-CH_3, δ C-H
961	12.8	$S_{20}(43) + S_{25}(21) + S_3(10) + S_2(6) + S_{12}(6) + S_{26}(5)$	δ C-H
907	7.1	$S_{12}(21) + S_8(20) + S_5(15) + S_3(7) + S_{19}(7) + S_4(5)$	ν O-CH_3, ν C-O
883	5.3	$S_4(29) + S_3(24) + S_{19}(11) + S_1(6) + S_{33}(6)$	ν C-N, ν C-CH_3
787	8.8	$S_{34}(72) + S_{18}(15)$	γ C=O
707	13.9	$S_{32}(20) + S_{19}(17) + S_{33}(16) + S_{35}(15) + S_8(12) + S_5(7)$	δ O=C-O, γ C-N, w C=O, δ COC
639	7.9	$S_4(51) + S_3(18) + S_1(14)$	ν C-N
442	4.9	$S_{16}(17) + S_{18}(16) + S_{17}(14) + S_{33}(7) + S_4(7) + S_5(7) + S_{19}(5)$	δ C_1-C_5, δ C_2-C_4, γ C=N
389	5.3	$S_{17}(27) + S_{32}(21) + S_{18}(15) + S_{35}(10) + S_{33}(6) + S_{26}(6)$	γ C=N, δ O=C-O
335	8.9	$S_{16}(44) + S_{17}(18) + S_{25}(7)$	δ C_1-C_5
309	14.3	$S_{35}(38) + S_{19}(19) + S_{33}(11) + S_{32}(9) + S_{18}(6)$	δ COC
223	2.7	$S_{33}(19) + S_{35}(16) + S_{16}(13) + S_{32}(11) + S_{18}(10) + S_{38}(10) + S_{19}(7)$	w C=O, δ COC, δ C_1-C_5
174	2.7	$S_{38}(42) + S_{19}(12) + S_{36}(8) + S_{39}(7) + S_{32}(5)$	τ C_4-C_{10}
137	0.0	$S_{36}(80) + S_{19}(7)$	τ C_1-C_5
121	0.6	$S_{39}(72) + S_{19}(6)$	τ C_{11}-O_{10}
101	3.5	$S_{18}(25) + S_{38}(18) + S_{17}(14) + S_{19}(12) + S_{39}(7) + S_{34}(7)$	δ C_2-C_4, τ C_4-C_{10}, γ C=N
55	3.9	$S_{37}(78)$	τ C_2-C_4

[a] Frequencies (scaled by 0.978) in cm^{-1}, calculated intensities in km mol^{-1}, ν – bond stretching, δ – bending, γ – out-of-plane bending, w – wagging, τ – torsion. See Table S2 for definition of symmetry coordinates. [b] Only PED values ≥ than 5 % are given.

Table S4 (Supplementary Information) B3LYP/6-311++G(d,p) calculated frequencies and intensities, and normal coordinate analysis for conformer *Cc* of methyl 3-methyl-2*H*-azirine-2-carboxylate [a].

Calculated frequency	Intensity	PED[b]	Approximate Description
3087	19.0	$S_6(75) + S_{13}(19)$	ν C-H
3087	2.8	$S_{13}(61) + S_6(24) + S_{15}(8) + S_{14}(7)$	ν (OCH_3') as
3054	18.4	$S_{15}(51) + S_{14}(49)$	ν (OCH_3'') as
3054	7.6	$S_9(72) + S_{11}(15) + S_{10}(13)$	ν (CCH_3') as
3031	3.0	$S_{11}(50) + S_{10}(49)$	ν (CCH_3'') as
2983	32.9	$S_{14}(42) + S_{15}(38) + S_{13}(19)$	ν (OCH_3) s
2970	6.8	$S_{10}(38) + S_{11}(34) + S_9(27)$	ν (CCH_3) s
1839	26.8	$S_2(73) + S_3(13) + S_1(7)$	ν C=N
1736	347.3	$S_7(79) + S_{33}(6)$	ν C=O
1466	9.0	$S_{29}(60) + S_{28}(19) + S_{30}(11) + S_{27}(9)$	δ (OCH_3'') as
1450	8.6	$S_{28}(68) + S_{29}(23) + S_{31}(8)$	δ (OCH_3') as
1442	13.8	$S_{24}(77) + S_{23}(11) + S_{25}(9)$	δ (CCH_3'') as
1439	3.2	$S_{27}(50) + S_{23}(31) + S_{24}(5)$	δ (OCH_3) s
1437	22.2	$S_{23}(45) + S_{27}(37) + S_{24}(6)$	δ (CCH_3') as
1372	10.6	$S_{22}(89) + S_3(9)$	δ (CCH_3) s
1314	3.6	$S_{21}(83) + S_1(5)$	γ C-H
1247	368.7	$S_8(32) + S_5(30) + S_{32}(10) + S_{33}(6) + S_{27}(6)$	ν C-O, ν C-C
1243	52.8	$S_1(42) + S_{25}(10) + S_3(9) + S_2(8) + S_{21}(5)$	ν C-Cα
1180	11.7	$S_{30}(77) + S_{29}(7) + S_{35}(5)$	γ (OCH_3)
1146	1.0	$S_{31}(92)$	γ (OCH_3')
1040	35.9	$S_{26}(29) + S_{12}(28) + S_{20}(18)$	γ (CCH_3'), ν O-CH_3
1025	46.4	$S_{12}(44) + S_{26}(22) + S_{20}(9) + S_5(9)$	ν O-CH_3
1019	7.2	$S_{25}(39) + S_{20}(17) + S_{26}(10) + S_{12}(7) + S_1(6)$	γ (CCH_3)
964	12.7	$S_{20}(46) + S_{25}(17) + S_{26}(11) + S_3(6)$	δ C-H
911	1.8	$S_3(33) + S_4(27) + S_8(6)$	ν C-CH_3
822	18.8	$S_8(34) + S_{35}(12) + S_{12}(9) + S_{33}(9) + S_4(8) + S_5(6) + S_{30}(5)$	ν C-O
784	7.3	$S_{34}(71) + S_{18}(15)$	γ C=O
675	9.9	$S_{33}(32) + S_{19}(28) + S_{12}(10) + S_5(8) + S_{35}(7)$	w C=O, γ C-N
636	9.0	$S_4(51) + S_3(18) + S_1(14)$	ν C-N
475	6.7	$S_{32}(29) + S_5(15) + S_4(10) + S_{16}(9) + S_{19}(9) + S_{21}(6) + S_{18}(5)$	δ O=C-O, ν C-C
405	2.0	$S_{17}(29) + S_{18}(27) + S_{32}(14) + S_{16}(7) + S_{34}(7) + S_{26}(7)$	γ C=N, δ C_2-C_4
337	9.6	$S_{16}(47) + S_{17}(22) + S_{25}(8)$	δ C_1-C_5
310	18.6	$S_{35}(54) + S_{19}(15) + S_{32}(7) + S_{33}(6)$	δ COC
219	2.8	$S_{33}(17) + S_{38}(16) + S_{18}(13) + S_{16}(12) + S_{35}(10) + S_{32}(8) + S_{19}(5)$	w C=O, τ C_4-C_{10}, δ C_2-C_4, δ C_1-C_5
159	3.6	$S_{38}(40) + S_{36}(12) + S_{19}(12) + S_{39}(8) + S_{33}(8) + S_{32}(5)$	τ C_4-C_{10}
127	0.4	$S_{36}(64) + S_{39}(16) + S_{19}(6)$	τ C_1-C_5
124	0.2	$S_{39}(60) + S_{39}(10) + S_{19}(8)$	τ C_{11}-O_{10}
98	1.8	$S_{18}(29) + S_{38}(22) + S_{17}(11) + S_{19}(9) + S_{34}(8)$	δ C_2-C_4, τ C_4-C_{10}
62	2.9	$S_{37}(77)$	τ C_2-C_4

[a] Frequencies (scaled by 0.978) in cm^{-1}, calculated intensities in km mol^{-1}, ν – bond stretching, δ – bending, γ – out-of-plane bending, w – wagging, τ – torsion. See Table S2 for definition of symmetry coordinates. [b] Only PED values ≥ than 5 % are given.

TABLE S5 (Supplementary Information) – DFT(B3LYP)/6-311++G(d,p) calculated frequencies and intensities for nitrile ylide, P1.

P1 *Ct*		**P1 *Cc***	
Frequency (cm^{-1})[a]	**Intensity (km mol^{-1})**	**Frequency (cm^{-1})[a]**	**Intensity (km mol^{-1})**
3147	0.6	3146	0.5
3079	19.0	3079	14.5
3045	23.5	3047	22.1
3041	1.9	3039	1.6
3025	10.9	3025	10.7
2978	45.6	2979	41.1
2947	42.0	2946	44.0
2073	430.7	2055	398.4
1696	294.7	1702	687.9
1468	3.1	1468	6.0
1458	78.6	1454	20.9
1449	8.3	1449	8.2
1441	67.9	1439	27.9
1434	17.6	1436	24.8
1414	235.1	1406	80.4
1363	13.1	1363	3.0
1254	97.0	1249	252.1
1182	79.1	1224	217.5
1167	538.8	1179	22.7
1145	0.7	1146	0.8
1027	31.2	1045	93.7
1018	56.3	1024	28.5
1007	206.5	1009	190.3
925	7.5	879	19.1
850	36.5	819	25.9
749	31.4	753	40.2
709	12.1	692	13.5
636	28.0	643	17.1
527	104.3	539	83.1
446	3.9	483	5.3
377	7.9	375	15.8
287	14.5	298	14.0
248	13.6	241	22.1
193	55.7	192	61.2
155	22.6	153	6.9
121	2.4	122	4.0
80	2.2	84	3.0
70	9.3	78	0.9
57	1.8	62	0.9

[a] frequencies scaled by 0.978.

TABLE S6 (Supplementary Information) – DFT(B3LYP)/6-311++G(d,p) calculated frequencies and intensities for ketene imine, P2.

P2 *Ct*		**P2 *Cc***	
Frequency (cm^{-1})[a]	**Intensity (km mol^{-1})**	**Frequency (cm^{-1})[a]**	**Intensity (km mol^{-1})**
3132	4.9	3135	4.9
3082	17.0	3082	14.1
3050	7.3	3050	21.5
3049	21.8	3048	8.1
3043	11.9	3040	12.4
2980	38.5	2980	37.8
2964	50.8	2962	50.9
2116	842.0	2110	789.5
1709	291.4	1722	614.0
1469	8.4	1468	3.4
1466	2.1	1466	29.4
1455	6.9	1455	7.6
1450	8.8	1450	8.6
1443	133.6	1439	36.6
1421	95.6	1417	26.7
1405	14.3	1391	23.8
1198	551.3	1228	455.1
1182	3.2	1181	5.7
1146	0.7	1158	102.4
1136	219.1	1146	0.9
1112	4.6	1111	2.7
1105	53.7	1105	11.7
1009	11.4	1040	68.5
918	9.5	891	15.6
866	14.6	822	19.1
768	42.9	773	47.1
722	7.9	707	5.3
662	16.6	655	12.0
591	49.9	595	39.4
479	0.2	503	0.7
389	11.8	402	5.2
286	12.1	294	18.3
249	10.4	242	12.9
187	18.8	185	20.9
161	7.8	154	4.8
126	1.1	126	1.8
106	0.2	104	0.6
83	3.2	80	0.6
62	5.1	72	1.2

[a] frequencies scaled by 0.978.

TABLE S7 (Supplementary Information) – DFT(B3LYP)/6-311++G(d,p) calculated frequencies and intensities for *N*-prop-1-en-1-ylidenemethanamine (P3) and *N*-(2-methoxyetenylidene)methanamine (P4).

P3		**P4**	
Frequency (cm^{-1})[a]	**Intensity (km mol^{-1})**	**Frequency (cm^{-1})[a]**	**Intensity (km mol^{-1})**
3081	4.0	3068	13.5
3034	17.7	3055	27.1
3032	13.4	3036	11.8
3022	21.2	3025	17.9
2992	23.1	2979	49.6
2949	41.5	2945	56.9
2943	75.6	2925	72.9
2080	453.9	2073	222.1
1479	5.7	1469	5.3
1464	24.0	1464	51.2
1454	6.2	1452	10.0
1451	6.7	1452	4.6
1416	1.1	1447	7.0
1392	13.2	1414	13.7
1380	27.7	1383	108.9
1186	3.3	1217	71.5
1109	3.4	1183	6.9
1104	0.5	1142	4.4
1065	3.8	1122	37.3
1030	0.6	1099	0.8
951	11.2	1081	122.5
816	6.7	953	19.8
686	41.3	873	8.2
593	24.2	707	41.9
573	3.0	617	16.4
285	5.9	559	25.2
222	9.0	411	1.9
153	1.3	256	2.3
140	2.6	241	8.8
127	1.2	192	10.0
		151	1.9
		127	1.0
		60	3.4

[a] frequencies scaled by 0.978.