SUPPORTING INFORMATION

Hydrogenative Metathesis of Enynes via Pianostool Ruthenium Carbene Complexes Formed by Alkyne *gem*-Hydrogenation

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SUPPORTING CRYSTALLOGRAPHIC DATA

Single Crystal Structure Analysis of 14a

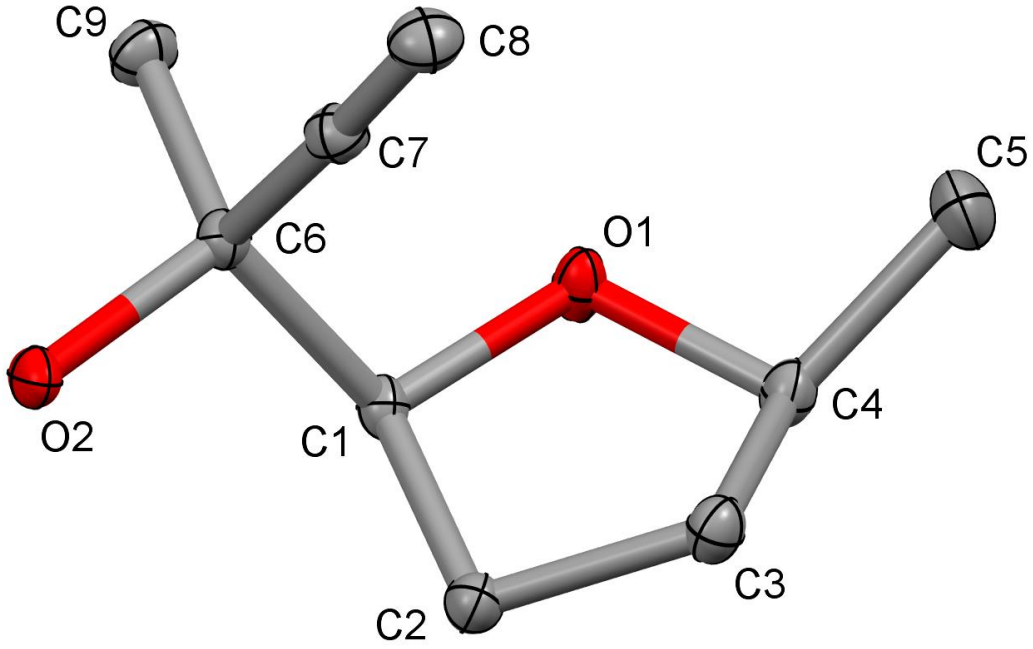


Figure S1. Molecular structure of **14a**. Atomic displacement ellipsoids shown at the 50 % probability level. H atoms are omitted for clarity.

X-ray Crystal Structure Analysis of 14a: $C_9\,H_{14}\,O_2$, M_r = 154.20 g · mol^{-1}, colourless prism, crystal size 0.050 x 0.093 x 0.221 mm^3, orthorhombic, space group $P2_12_12_1$ [19], a = 8.0553(5) Å, b = 10.2611(6) Å, c = 10.6161(7) Å, V = 877.49(9) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.167 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.081 mm^{-1}, face-indexed absorption correction (*SADABS*, T_{min} = 0.99006, T_{max} = 0.99763), Bruker-AXS Mach3 diffractometer with Kappa-CCD detector and FR591 molybdenum rotating anode X-ray source equipped with Incoatec Helios X-ray optics, 2.761 < θ < 35.146 °, 34599 measured reflections, 3874 independent reflections, 3342 reflections with $I > 2\sigma(I)$, R_{int} = 0.0445, 99.4 % coverage with an average redundancy of 15.46 to 0.62 Å resolution.

INTENSITY STATISTICS FOR DATASET (mmm averaging)

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.91	34	34	100.0	21.91	99.11	142.76	0.0193	0.0060
2.91 - 1.84	78	78	100.0	27.32	34.64	142.82	0.0213	0.0057
1.84 - 1.41	113	113	100.0	29.27	19.23	111.54	0.0271	0.0071
1.41 - 1.21	113	113	100.0	30.65	12.56	91.86	0.0348	0.0084
1.21 - 1.09	115	115	100.0	28.23	12.96	85.44	0.0385	0.0093
1.09 - 1.00	122	122	100.0	20.99	8.77	55.46	0.0528	0.0145
1.00 - 0.94	106	106	100.0	17.32	5.24	36.57	0.0746	0.0227
0.94 - 0.89	113	113	100.0	15.16	4.31	29.31	0.0880	0.0287
0.89 - 0.85	116	116	100.0	13.49	3.85	23.36	0.1033	0.0351
0.85 - 0.82	94	94	100.0	13.51	3.85	21.50	0.1089	0.0363
0.82 - 0.79	112	112	100.0	12.40	3.51	19.06	0.1032	0.0416
0.79 - 0.76	128	128	100.0	12.21	3.34	17.46	0.1302	0.0462
0.76 - 0.74	93	93	100.0	12.19	2.80	15.67	0.1506	0.0550
0.74 - 0.72	117	117	100.0	10.94	3.16	16.05	0.1359	0.0562
0.72 - 0.70	118	118	100.0	10.87	3.05	15.85	0.1518	0.0588
0.70 - 0.68	137	137	100.0	10.86	2.79	13.70	0.1643	0.0648
0.68 - 0.66	153	153	100.0	10.31	2.09	10.07	0.2144	0.0891
0.66 - 0.65	84	84	100.0	9.50	1.83	7.73	0.2650	0.1074
0.65 - 0.64	84	84	100.0	9.69	1.48	7.34	0.2818	0.1275
0.64 - 0.63	94	94	100.0	9.71	1.73	8.06	0.2615	0.1116
0.63 - 0.62	111	124	89.5	5.43	1.22	4.48	0.3384	0.2198
Inf - 0.62	2235	2248	99.4	15.46	7.68	37.14	0.0446	0.0218

The structure was solved by *SHELXT* and refined as a perfect inversion twin by full-matrix least-squares (*SHELXL*) against F^2. The postion and atomic displacement parameter of the hydroxyl hydrogen atom were refined. Otherwise, hydrogen atoms were refined using a riding model. Refinement of the structure resulted in $R1$ = 0.0384 for 3342 [$I > 2\sigma(I)$] and 0.0521 for all 3874 data, 106 parameters refined, $wR2$ = 0.0988, *GooF* = S = 1.037, residual electron density +0.37 (0.76 Å from C3) / -0.23 (0.61 Å from C3) e · Å^{-3}. **CCDC-2016740**.

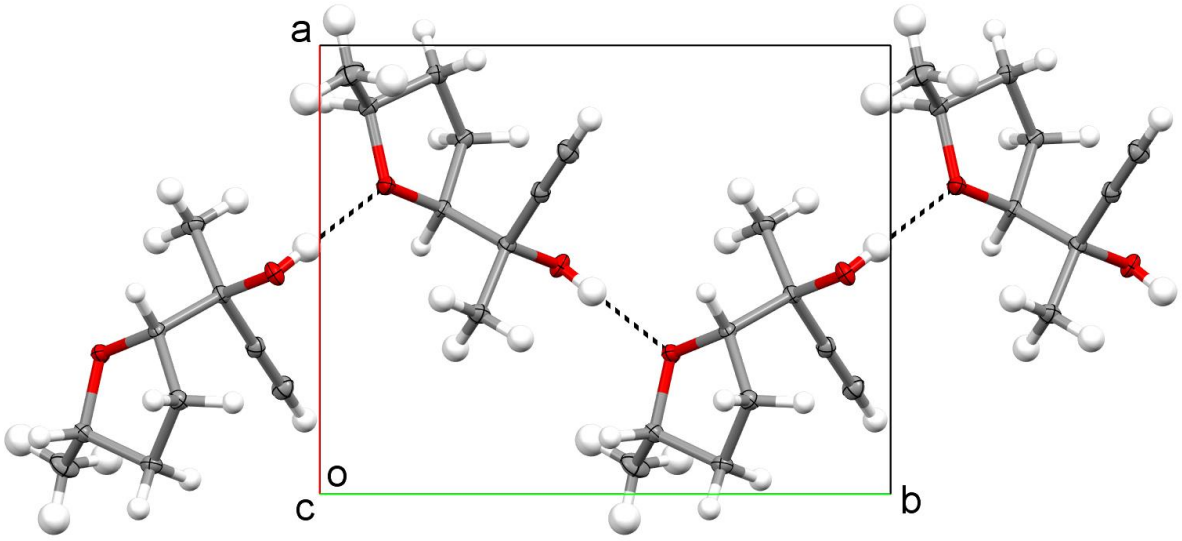


Figure S2. O-H···O hydrogen bonding interactions in solid **14a**.

Single Crystal Structure Analysis of 14a'

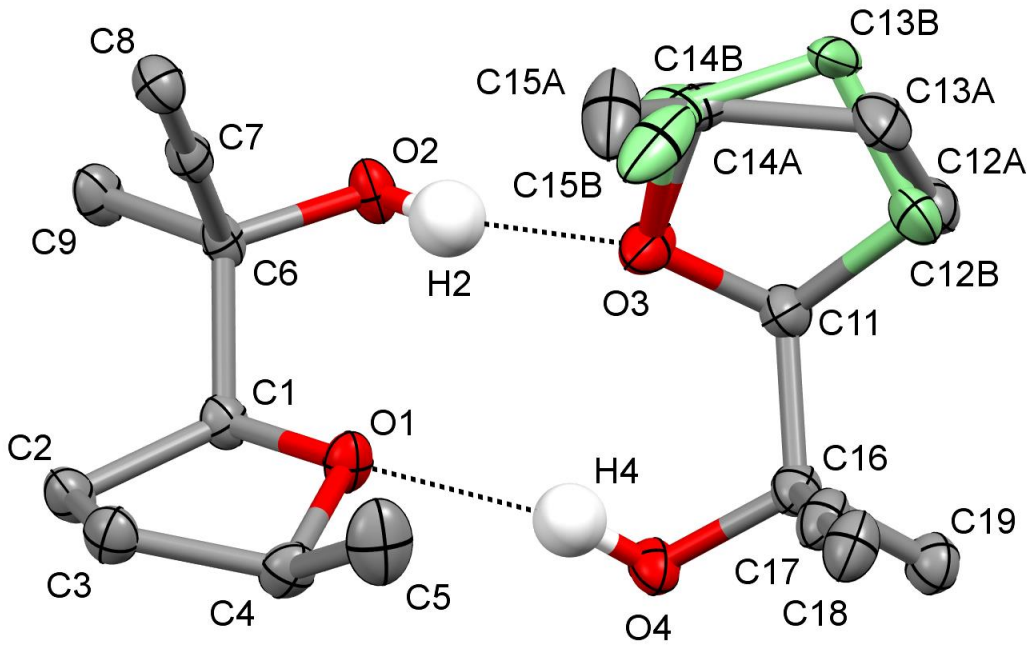


Figure S3. Molecular structure of the two independent molecules of **14a'** in the unit cell, showing the O-H···O hydrogen bonding interactions. The minor component of the disordered molecule (40%) is coloured light green. Atomic displacement ellipsoids shown at the 50 % probability level. H atoms, except for OH, are omitted for clarity.

X-ray Crystal Structure Analysis of 14a': $C_9\,H_{14}\,O_2$, M_r = 154.20 g · mol^{-1}, colourless prism, crystal size 0.051 x 0.111 x 0.132 mm^3, monoclinic, space group $P2_1/n$ [14], a = 8.9181(4) Å, b = 21.7716(9) Å, c = 9.1550(4) Å, β = 94.822(2)°, V = 1771.3(1) Å^3, T = 100(2) K, Z = 8, D_{calc} = 1.157 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.080 mm^{-1}, face-indexed absorption correction (*SADABS*, T_{min} = 0.99275, T_{max} = 0.99680), Bruker-AXS Mach3 diffractometer with Kappa-CCD detector and FR591 molybdenum rotating anode X-ray source equipped with Incoatec Helios X-ray optics, 1.871 < θ < 35.262 °, 71080 measured reflections, 7848 independent reflections, 5775 reflections with $I > 2\sigma(I)$, R_{int} = 0.0374, 98.8 % coverage with an average redundancy of 8.88 to 0.62 Å resolution.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.60	121	121	100.0	16.54	61.87	144.33	0.0176	0.0051
2.60 - 1.70	290	290	100.0	18.22	18.48	115.29	0.0174	0.0058
1.70 - 1.34	401	401	100.0	18.30	8.21	81.19	0.0261	0.0080
1.34 - 1.17	399	399	100.0	17.98	6.13	64.45	0.0339	0.0100
1.17 - 1.06	424	424	100.0	15.43	5.78	55.02	0.0356	0.0120
1.06 - 0.98	412	412	100.0	11.37	3.26	31.64	0.0567	0.0217
0.98 - 0.92	424	424	100.0	9.58	2.17	22.49	0.0747	0.0321
0.92 - 0.88	340	340	100.0	8.23	1.51	15.70	0.0945	0.0464
0.88 - 0.84	417	417	100.0	7.82	1.54	14.47	0.0998	0.0491
0.84 - 0.80	514	514	100.0	7.34	1.23	11.12	0.1246	0.0631
0.80 - 0.78	284	284	100.0	7.11	1.25	10.82	0.1193	0.0654
0.78 - 0.75	495	495	100.0	6.77	1.16	9.70	0.1370	0.0751
0.75 - 0.73	383	383	100.0	6.63	1.22	9.65	0.1460	0.0766
0.73 - 0.71	412	412	100.0	6.32	0.96	7.98	0.1772	0.0973
0.71 - 0.69	470	470	100.0	6.08	1.00	7.63	0.1721	0.0992
0.69 - 0.68	264	264	100.0	5.84	0.70	5.71	0.2146	0.1379
0.68 - 0.66	564	564	100.0	5.73	0.69	5.37	0.2372	0.1458
0.66 - 0.65	316	316	100.0	5.47	0.61	4.60	0.2722	0.1747
0.65 - 0.64	306	306	100.0	5.51	0.50	3.96	0.3175	0.2096
0.64 - 0.62	798	897	89.0	4.20	0.40	2.89	0.3561	0.3115
0.72 - 0.62	2920	3019	96.7	5.33	0.65	5.03	0.2390	0.1653
Inf - 0.62	8034	8133	98.8	8.88	3.56	24.91	0.0365	0.0258

The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2. One of the two independent molecules in the asymmetric unit is partially disordered (0.6:0.4). The postions and atomic displacement parameters of the hydroxyl hydrogen atoms and neighbouring C-H hydrogen atoms were refined. Otherwise, hydrogen atoms were refined using a riding model. Refinement of the structure resulted in $R1 = 0.043$ for 5775 [$I > 2\sigma(I)$] and 0.0657 for all 7848 data, 260 parameters refined, $wR2 = 0.1237$, $GooF = S = 1.034$, residual electron density +0.35 (0.74 Å from C16) / -0.26 (0.59 Å from C6) e · Å^{-3}. **CCDC-2016741**.

Single Crystal Structure Analysis of 24b

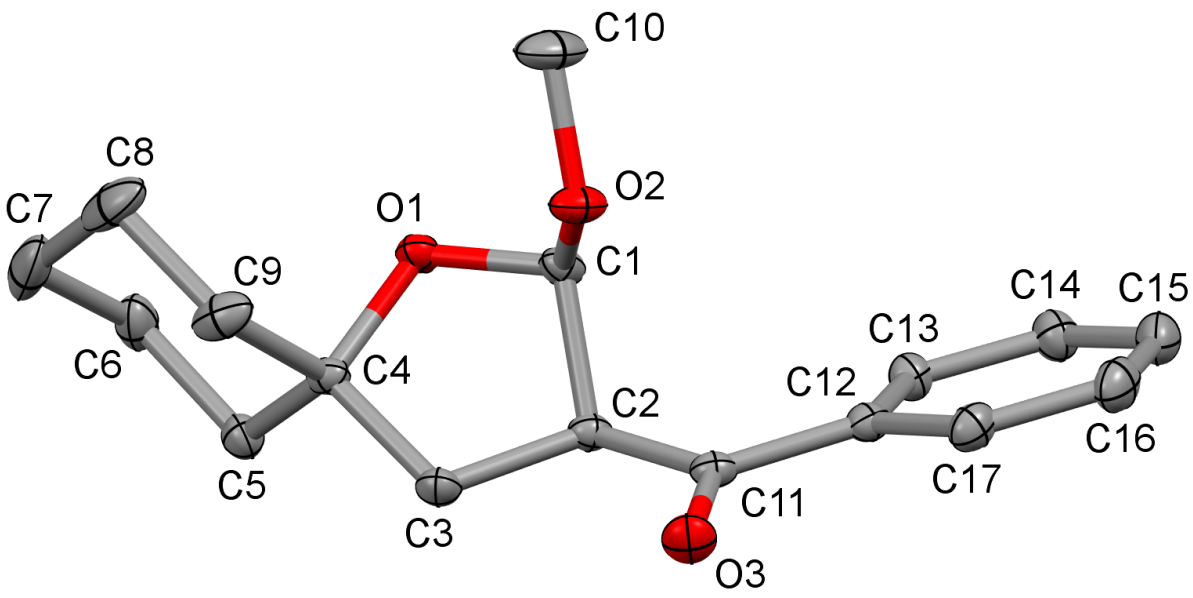


Figure S4. Molecular structure of **24b**. Atomic displacement ellipsoids shown at the 50 % probability level. H atoms are omitted for clarity.

X-ray Crystal Structure Analysis of 24b: $C_{17}H_{22}O_3$, M_r = 274.34 g · mol^{-1}, colourless prism, crystal size 0.11 x 0.12 x 0.32 mm^3, monoclinic, space group $P2_1/n$ [14], a = 12.5303(15) Å, b = 5.8923(5) Å, c = 20.003(3) Å, β = 91.647(10)°, V = 1476.3(3) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.234 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.083 mm^{-1}, face-indexed absorption correction (*SADABS*, T_{min} = 0.98109, T_{max} = 0.99299), Bruker-AXS Mach3 diffractometer with Kappa-CCD detector and FR591 molybdenum rotating anode X-ray source equipped with Incoatec Helios X-ray optics, 3.253 < θ < 33.152°, 31477 measured reflections, 5619 independent reflections, 4315 reflections with $I > 2\sigma(I)$, R_{int} = 0. 0407, 99.8 % coverage with an average redundancy of 5.42 to 0.65 Å resolution.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.76	93	101	92.1	8.96	138.82	74.36	0.0271	0.0116
2.76 - 1.82	217	217	100.0	8.15	63.12	63.03	0.0251	0.0116
1.82 - 1.43	304	305	99.7	7.44	28.12	50.39	0.0254	0.0138
1.43 - 1.25	299	299	100.0	7.31	20.36	43.97	0.0297	0.0155
1.25 - 1.13	308	308	100.0	6.70	19.13	35.60	0.0299	0.0179
1.13 - 1.04	330	330	100.0	6.58	17.42	34.76	0.0299	0.0190
1.04 - 0.98	283	283	100.0	6.26	8.68	23.84	0.0456	0.0291
0.98 - 0.93	315	316	99.7	5.72	8.02	20.91	0.0498	0.0325
0.93 - 0.89	292	292	100.0	5.76	5.55	16.85	0.0696	0.0430
0.89 - 0.85	341	341	100.0	5.56	5.10	14.28	0.0741	0.0479
0.85 - 0.82	313	313	100.0	5.04	4.41	12.26	0.0816	0.0607
0.82 - 0.79	358	358	100.0	4.91	4.20	11.62	0.0897	0.0653
0.79 - 0.77	253	253	100.0	4.77	4.27	10.98	0.0944	0.0679
0.77 - 0.75	294	294	100.0	4.70	4.23	10.33	0.1068	0.0731
0.75 - 0.73	324	324	100.0	4.46	4.27	10.09	0.1091	0.0797
0.73 - 0.71	394	394	100.0	4.26	3.76	8.92	0.1171	0.0987
0.71 - 0.70	190	190	100.0	4.04	2.93	6.72	0.1516	0.1391
0.70 - 0.68	447	447	100.0	4.09	3.07	6.52	0.1589	0.1457
0.68 - 0.67	219	219	100.0	4.08	2.66	4.92	0.1729	0.1892
0.67 - 0.66	232	232	100.0	3.88	2.41	4.27	0.2051	0.2365
0.66 - 0.65	279	282	98.9	3.85	2.41	4.01	0.2166	0.2542
0.75 - 0.65	2085	2088	99.9	4.12	3.17	6.79	0.1476	0.1434
Inf - 0.65	6085	6098	99.8	5.42	12.00	20.15	0.0401	0.0320

The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2 using aspherical atomic scattering factors [J. Lübben *et al*., *Acta Cryst.* **2019**, *A75*, 50-62]. The hydrogen atoms were refined using a riding model. Refinement of the structure resulted in $R1$ = 0.0383 for 4315 [$I > 2\sigma(I)$] and 0.0583 for all 5619 data, 185 parameters refined, $wR2$ = 0.0965, *GooF* = *S* = 1.039, residual electron density +0.21 (0.71 Å from C1) / -0.21 (0.80 Å from C14) e · Å^{-3}. **CCDC-2016742**.

Single Crystal Structure Analysis of 38

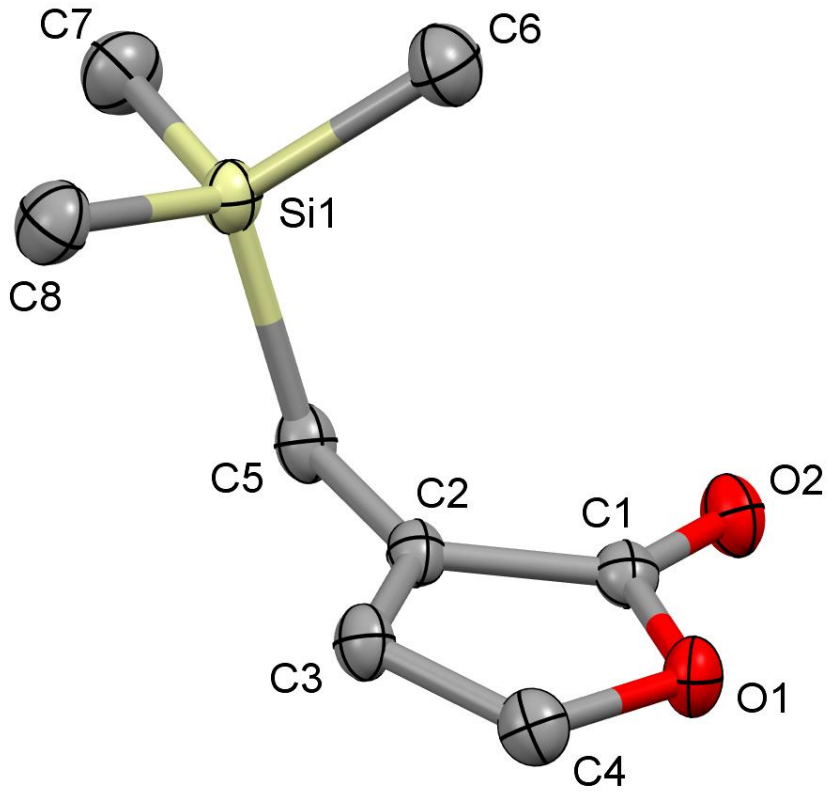


Figure S5. Molecular structure of **38**. Atomic displacement ellipsoids shown at the 50 % probability level. H atoms are omitted for clarity.

X-ray Crystal Structure Analysis of 38: $C_8 H_{14} O_2 Si$, M_r = 170.28 g · mol^{-1}, colourless plate, crystal size 0.010 x 0.145 x 0.330 mm^3, monoclinic, space group $P2_1/c$ [14], a = 13.8465(6) Å, b = 6.4641(3) Å, c = 11.3247(5) Å, β = 107.264(2)°, V = 967.95(8) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.168 g · cm^3, λ = 1.54178 Å, μ(*Cu-K*$_\alpha$) = 1.78 mm^{-1}, face-indexed absorption correction (*SADABS*, T_{min} = 0. 72475, T_{max} = 0. 98217), Bruker-AXS Mach3 diffractometer with Apex II detector and FR591 copper rotating anode X-ray source equipped with Montel X-ray optics, 3.342 < θ < 63.198°, 17601 measured reflections, 1560 independent reflections, 1407 reflections with $I > 2\sigma(I)$, R_{int} = 0. 0552, 98.9 % coverage with an average redundancy of 10.66 to 0.86 Å resolution.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 3.73	26	27	96.3	8.07	149.36	31.43	0.0303	0.0224
3.73 - 2.49	60	60	100.0	9.88	90.47	35.82	0.0327	0.0230
2.49 - 1.94	86	86	100.0	8.06	44.85	29.65	0.0380	0.0251
1.94 - 1.67	87	87	100.0	9.78	41.43	31.51	0.0580	0.0230
1.67 - 1.51	91	91	100.0	9.42	39.00	32.06	0.0476	0.0227
1.51 - 1.40	82	82	100.0	8.61	24.42	26.37	0.0483	0.0270
1.40 - 1.31	88	88	100.0	7.56	20.95	23.06	0.0605	0.0293
1.31 - 1.24	91	91	100.0	8.10	22.18	25.33	0.0598	0.0331
1.24 - 1.19	72	72	100.0	16.74	18.31	32.04	0.0644	0.0211
1.19 - 1.14	94	94	100.0	16.46	15.89	33.72	0.0674	0.0218
1.14 - 1.10	82	82	100.0	15.38	15.63	30.53	0.0627	0.0237
1.10 - 1.06	100	100	100.0	15.21	12.00	27.81	0.0712	0.0255
1.06 - 1.03	82	82	100.0	14.84	10.51	24.34	0.0714	0.0274
1.03 - 1.00	95	95	100.0	12.82	12.20	25.29	0.0686	0.0289
1.00 - 0.98	72	72	100.0	10.14	7.44	19.19	0.0906	0.0399
0.98 - 0.95	103	103	100.0	10.20	9.73	21.18	0.0726	0.0336
0.95 - 0.93	76	81	93.8	8.96	8.58	19.15	0.0889	0.0377
0.93 - 0.91	93	94	98.9	8.73	7.51	18.29	0.0928	0.0407
0.91 - 0.90	55	56	98.2	9.04	6.27	17.86	0.1038	0.0425
0.90 - 0.88	100	101	99.0	8.56	7.07	18.09	0.0941	0.0401
0.88 - 0.86	80	90	88.9	5.51	6.96	15.38	0.1092	0.0537
0.96 - 0.86	441	459	96.1	8.27	7.70	18.27	0.0903	0.0410
Inf - 0.86	1715	1734	98.9	10.66	22.16	25.41	0.0549	0.0265

The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2. The hydrogen atoms were refined using a riding model. Refinement of the structure resulted in $R1$ = 0.0322 for 1407 [$I > 2\sigma(I)$] and 0.0368 for all 1560 data, 103 parameters refined, $wR2$ = 0.0863, *GooF* = *S* = 1.046, residual electron density +0.27 (0.93 Å from C5) / -0.28 (0.92 Å from Si1) e · Å^{-3}. **CCDC-2016743**.

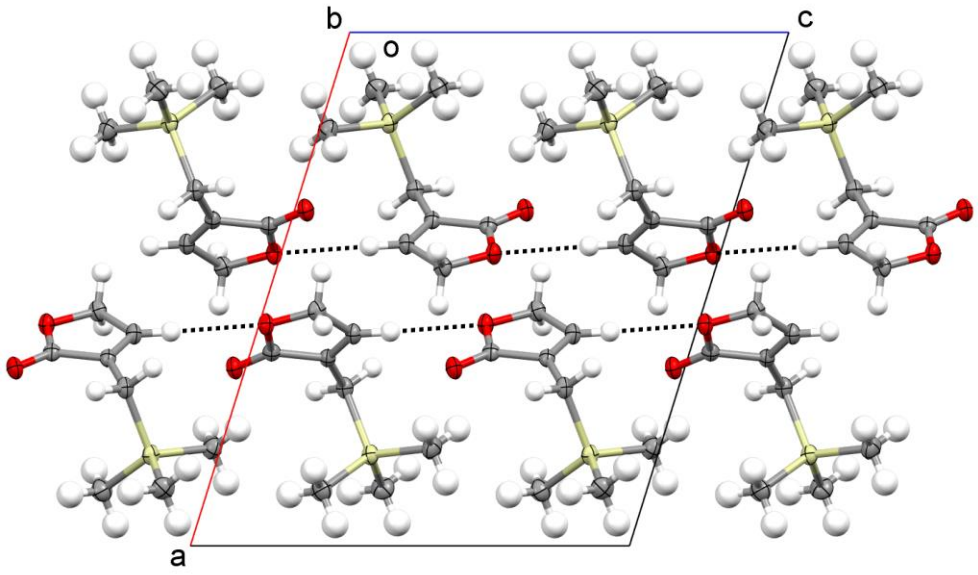


Figure S6. Molecular packing of **38**, showing the shortest C-H···O intermolecular distances.

Single Crystal Structure Analysis of 39

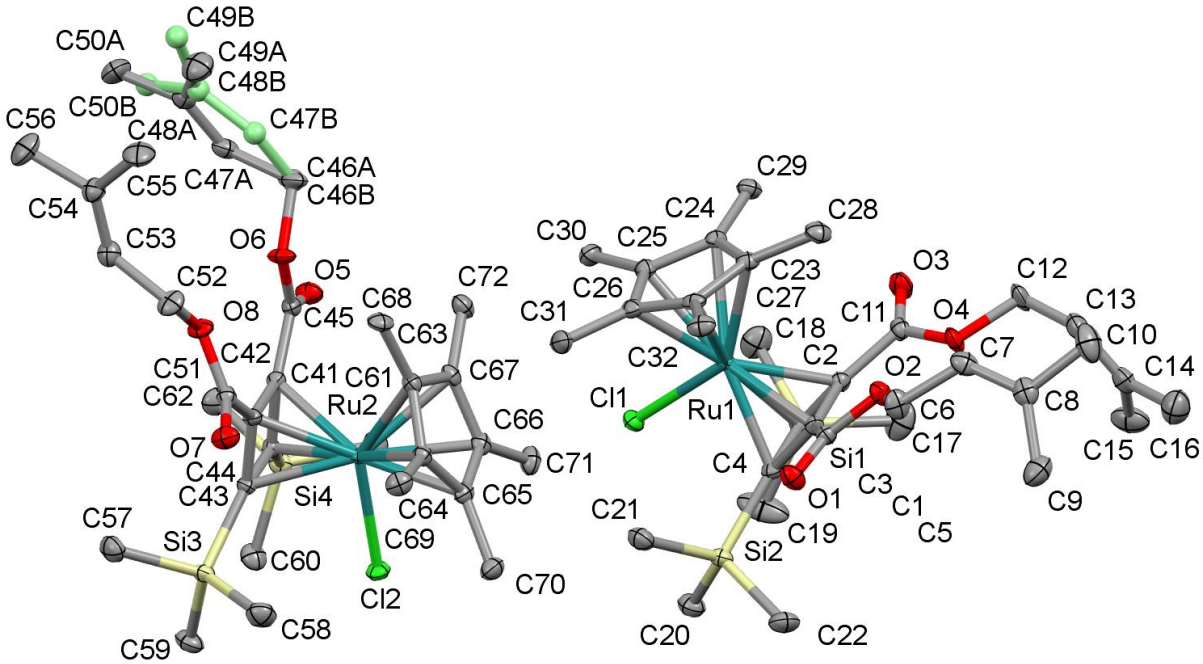


Figure S7. Molecular structure of the two independent molecules of **39**. Atomic displacement ellipsoids shown at the 50 % probability level. The partially disordered dimethyl propenyl group (ca. 12%) is shown in light green. H atoms are omitted for clarity.

X-ray Crystal Structure Analysis of 39: $C_{32}H_{51}ClO_4RuSi_2$, M_r = 692.42 g · mol^{-1}, orange-red prism, crystal size 0.031 x 0.037 x 0.060 mm^3, triclinic, space group *P*-1[2], a = 10.5379(6) Å, b = 15.7120(10) Å, c = 20.9915(14) Å, α = 89.810(3)°, β = 89.849(3)°, γ = 84.937(3)°, V = 3462.0(4) Å^3, T = 100(2) K, Z = 4, D_{calc} = 1.328 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*α) = 0.632 mm^{-1}, face-indexed absorption correction (*SADABS*, T_{min} = 0.96950, T_{max} = 0.98790), Bruker-AXS Mach3 diffractometer with Kappa-CCD detector and FR591 molybdenum rotating anode X-ray source equipped with Incoatec Helios X-ray optics, 0.970 < θ < 30.998 °, 115799 measured reflections, 22052 independent reflections, 15513 reflections with $I > 2\sigma(I)$, R_{int} = 0.0765, 98.8 % coverage with an average redundancy of 5.02 to 0.67 Å resolution.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.73	354	354	100.0	9.34	74.37	47.89	0.0307	0.0139
2.73 - 1.83	828	828	100.0	9.44	45.27	40.62	0.0367	0.0172
1.83 - 1.45	1199	1199	100.0	9.34	37.10	34.90	0.0405	0.0200
1.45 - 1.27	1177	1177	100.0	9.25	20.81	25.31	0.0589	0.0282
1.27 - 1.15	1200	1200	100.0	8.86	19.22	21.34	0.0682	0.0321
1.15 - 1.07	1160	1160	100.0	7.79	17.79	18.46	0.0849	0.0395
1.07 - 1.00	1344	1344	100.0	5.95	16.33	14.43	0.0884	0.0509
1.00 - 0.95	1194	1194	100.0	5.02	14.05	11.81	0.1003	0.0646
0.95 - 0.91	1164	1164	100.0	4.51	11.65	9.42	0.1122	0.0794
0.91 - 0.88	1009	1009	100.0	4.16	9.74	7.91	0.1279	0.0980
0.88 - 0.85	1191	1191	100.0	3.93	9.66	7.47	0.1306	0.1030
0.85 - 0.82	1317	1317	100.0	3.80	8.45	6.50	0.1507	0.1222
0.82 - 0.80	1026	1026	100.0	3.66	7.64	5.70	0.1674	0.1393
0.80 - 0.77	1745	1745	100.0	3.55	6.73	4.98	0.1920	0.1625
0.77 - 0.76	591	591	100.0	3.41	6.71	4.77	0.2091	0.1753
0.76 - 0.74	1409	1409	100.0	3.37	6.38	4.50	0.2120	0.1863
0.74 - 0.72	1531	1538	99.5	3.25	5.26	3.76	0.2485	0.2305
0.72 - 0.71	800	802	99.8	3.16	4.93	3.39	0.2755	0.2586
0.71 - 0.69	1813	1825	99.3	3.05	4.75	3.18	0.2898	0.2745
0.69 - 0.68	985	990	99.5	2.84	3.87	2.51	0.3355	0.3661
0.68 - 0.67	491	744	66.0	1.27	3.68	1.81	0.3626	0.5065
0.77 - 0.67	7620	7899	96.5	2.99	5.14	3.51	0.2573	0.2532
Inf - 0.67	23528	23807	98.8	5.02	13.60	11.92	0.0758	0.0745

The structure was solved by *SHELXT* and refined by full-matrix least-squares (*SHELXL*) against F^2. One of the dimethylpropenyl groups is slightly disordered [0.879(6):0.121(6)]. The positions of C46A and C46B were contrained to be equal in order to avoid high correlations in the refinement. The isotropic atomic displacement parameters of the C atoms of the minor component were constrained to be equal. The hydrogen atoms were refined using a riding model. Refinement of the structure resulted in $R1$ = 0.046 for 15513 [$I > 2\sigma(I)$] and 0.0792 for all 22052 data, 767

parameters refined, *wR*2 = 0.1147, *GooF* = *S* = 1.013, residual electron density +1.16 (1.1 Å from Ru2) / -1.41 (0.68 Å from Ru1) e · Å^{-3}. **CCDC-2016744**.

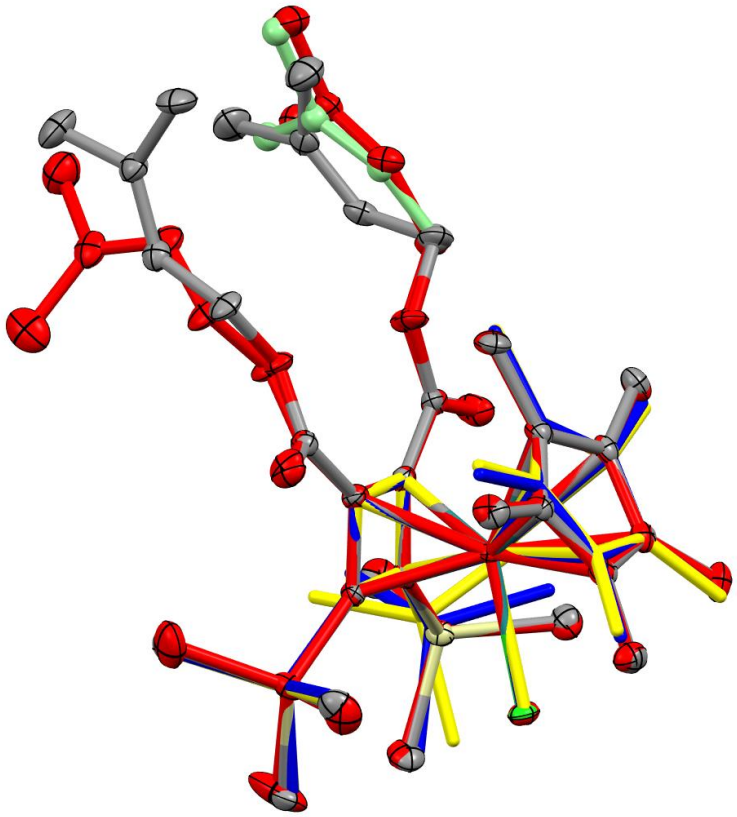


Figure S8. Superposition of the C_4RuCl units of the two independent molecules of **39** (atom colouring and red) and the two independent molecules of chloro-(η^5-pentamethyl-cyclopentadienyl)-(η^4-1,2-bis(trimethylsilyl)cyclobuta-2,4-diene)-ruthenium(II) with the CSD refcode VEBQOI (blue and yellow). The partially disordered dimethyl propenyl group is shown in light green. H atoms are omitted for clarity.

Single Crystal Structure Analysis of 41

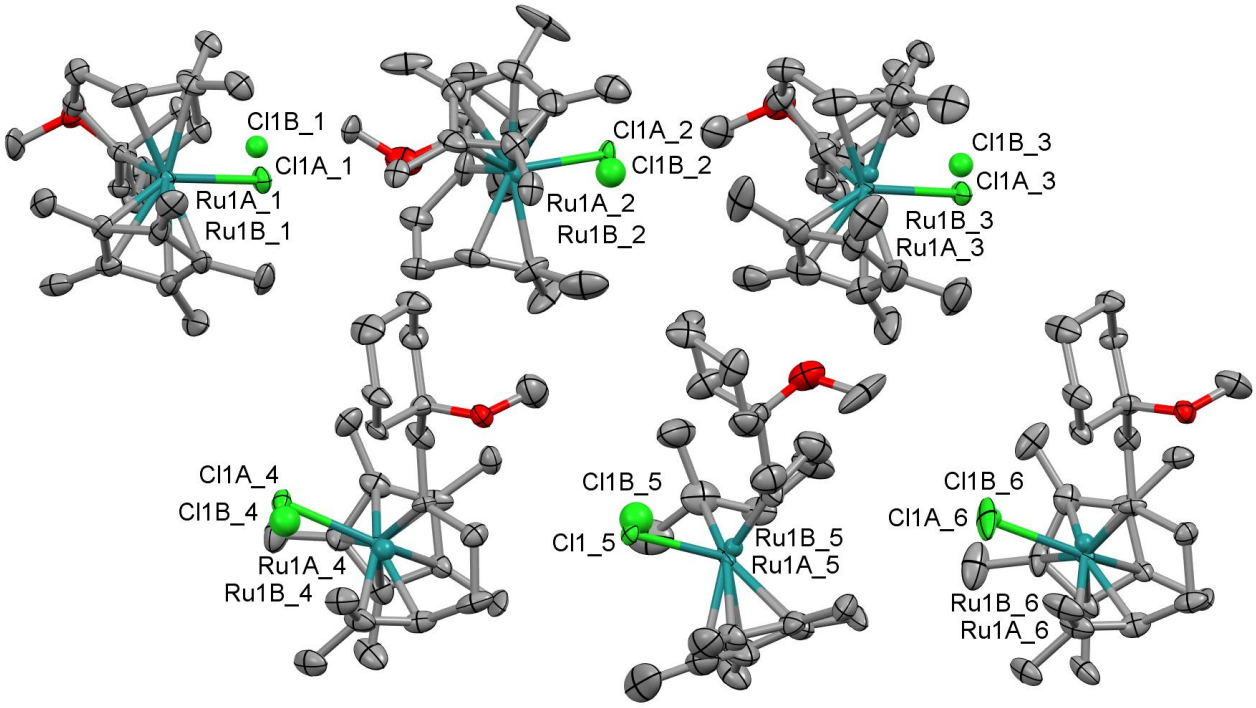


Figure S9. Molecular structure of the six independent molecules of **41**. Atomic displacement ellipsoids shown at the 50 % probability level. Partially disordered Ru and Cl atoms shown with the suffix A and B. H atoms are omitted for clarity.

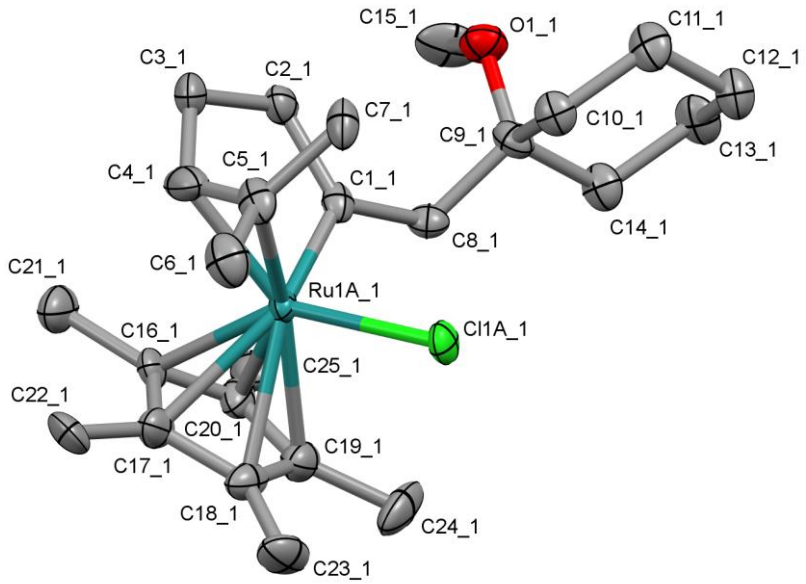


Figure S10. Molecular structure of the one of the independent molecules of **41**. Atomic displacement ellipsoids shown at the 50 % probability level. H atoms are omitted for clarity.

Selected average distances (Å) and angles (°) over all major components: Ru1A-Cl1A 2.44(2), Ru1A-C1 1.90(4), Ru1A-C4 2.17(4), Ru1A-C5 2.22(5), C1-C2 1.53(3), C2-C3 1.55(5), C3-C4 1.52(4), C4-C5 1.39(4), C5-C6 1.56(5), C5-C7 1.54(1), C1-C8 1.47(3), C8-C9 1.55(2), C8-C1-C2 117(2), C1-C2-C3 113(1), C2-C3-C4 109(1), C3-C4-C5 125(1), C1-Ru1A-Cl1A 95(1), C1-Ru1A-C4/5 86(2), C1-Ru1A-Cp 122(3), C4/5-Ru1A-Cp 129(1), Cl1A-Ru1A-Cp 114(1). Cp is the midpoint of C16 - C20; C4/5 is the midpoint between C4 and C5.

X-ray Crystal Structure Analysis of 41: $C_{25}H_{41}ClORu$, M_r = 494.10 g · mol^{-1}, red prism, crystal size 0.10 x 0.14 x 0.16 mm^3, monoclinic, space group *P*n [7], a = 19.802(3) Å, b = 16.260(2) Å, c = 23.261(2) Å, β = 107.910(8)°, V = 7126.5(16) Å^3, T = 100(2) K, Z = 12, D_{calc} = 1.382 g · cm^3, λ = 0.71073 Å, μ(*Mo-K*$_\alpha$) = 0.785 mm^{-1}, face-indexed absorption correction (*SADABS*, T_{min} = 0.83421, T_{max} = 0.90734), Bruker-AXS Mach3 diffractometer with Kappa-CCD detector and FR591 molybdenum rotating anode X-ray source equipped with Incoatec Helios X-ray optics, 3.721 < θ < 32.030 °, 222409 measured reflections, 48407 independent reflections, 34434 reflections with $I > 2\sigma(I)$, R_{int} = 0.0647, 99.7 % coverage with an average redundancy of 8.55 to 0.65 Å resolution.

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	Rmerge	Rsigma
Inf - 2.66	421	450	93.6	10.77	53.24	41.24	0.0410	0.0143
2.66 - 1.78	979	981	99.8	12.53	42.85	40.89	0.0375	0.0133
1.78 - 1.41	1410	1410	100.0	12.88	24.38	38.75	0.0409	0.0149
1.41 - 1.23	1396	1396	100.0	12.33	14.28	31.27	0.0470	0.0190
1.23 - 1.11	1505	1505	100.0	11.45	11.54	26.46	0.0559	0.0235
1.11 - 1.03	1418	1418	100.0	10.74	10.74	23.70	0.0615	0.0268
1.03 - 0.97	1394	1394	100.0	10.09	7.99	20.18	0.0725	0.0339
0.97 - 0.92	1450	1450	100.0	9.46	6.33	16.46	0.0881	0.0426
0.92 - 0.88	1409	1409	100.0	9.04	4.99	14.08	0.1041	0.0540
0.88 - 0.85	1214	1215	99.9	8.60	4.05	11.74	0.1285	0.0674
0.85 - 0.82	1424	1425	99.9	8.12	3.97	10.69	0.1387	0.0751
0.82 - 0.79	1656	1657	99.9	7.81	3.55	9.23	0.1548	0.0877
0.79 - 0.77	1224	1224	100.0	7.49	3.18	8.00	0.1757	0.1017
0.77 - 0.75	1376	1377	99.9	7.08	2.99	7.18	0.1937	0.1140
0.75 - 0.73	1517	1521	99.7	6.76	2.45	6.07	0.2314	0.1444
0.73 - 0.71	1686	1688	99.9	6.64	2.27	5.55	0.2483	0.1619
0.71 - 0.70	955	955	100.0	6.39	1.96	4.57	0.2766	0.1940
0.70 - 0.68	2006	2009	99.9	6.21	1.80	4.13	0.3128	0.2183
0.68 - 0.67	1113	1113	100.0	6.03	1.54	3.49	0.3584	0.2641
0.67 - 0.66	1154	1156	99.8	5.88	1.36	3.07	0.3852	0.3041
0.66 - 0.65	1291	1339	96.4	5.50	1.09	2.42	0.4667	0.3950
0.75 - 0.65	9722	9781	99.4	6.23	1.82	4.30	0.2978	0.2142
Inf - 0.65	27998	28092	99.7	8.55	7.89	14.54	0.0697	0.0438

The crystal structure appears to be best described as *P*n. There appears to be an additional slight modulation of the structure along the *c* unit cell axis whereby the molecules are partially replaced by their enantiomers. This results in higher than expected residual electron density close to all the ruthenium and chlorine atoms and significantly less residual density elsewhere corresponding to the lighter atoms. Two crystals from the same batch were investigated and both showed a similar effect. The data set for which the shadowing was less pronounced was selected for analysis. Nevertheless, some residual electron density remains, expecially close to the ruthenium atoms. The structure was solved by *SHELXT* and refined as a partial inversion twin [BASF 0.27(5)] by full-matrix least-squares (*SHELXL*) against F^2. The hydrogen atoms on the five methyl groups on the pentamethylcyclopentadienyl ligands were refined using a riding model that maximizes the sum of the difference densities at the three hydrogen positions on each methyl group followed by refinement of the torsion angle (AFIX 137), and resulted in a short intramolecular H···H distance of ca. 1.7 A. The positions of the hydrogen atoms on the methyl groups cannot be completely relied upon owing to residual electron density resulting from the disordered components. A number of diffraction intensites were shadowed by the beamstop (> 5.5 Å) and removed from the dataset before the final refinement cycles. Refinement of the structure with partially disordered ruthenium and chlorine atoms (ca. 8 - 34 %) resulted in $R1$ = 0.0809 for 34434 [$I > 2\sigma(I)$] and 0.1196 for all 48407 data, 1616 parameters refined, using 1010 restraints (ISOR 0.01), $wR2$ = 0.2286, $GooF = S$ = 1.061, residual electron density +3.38 (0.19 Å from Ru1B_5) / -1.45 (0.90 Å from Ru1A_4) e · Å^{-3}. **CCDC-1994299**.

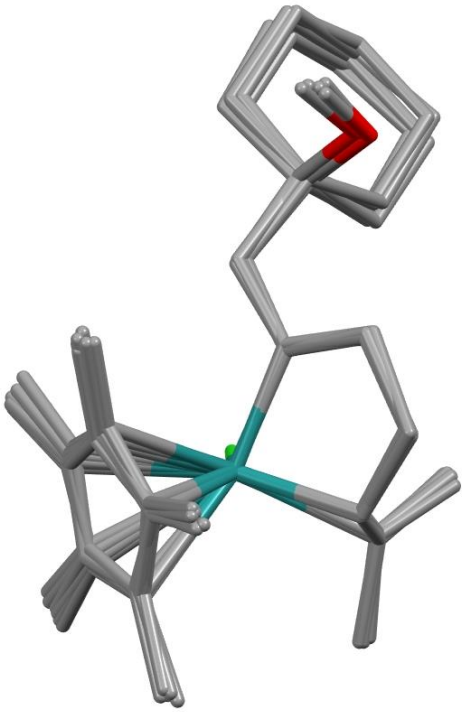


Figure S11. Superposition of Ru1A, Cl1A, C1 and C4 of the six independent molecules or their enantiomers in the asymmetric unit of **41**, showing the similarity between the different conformations in the crystal.

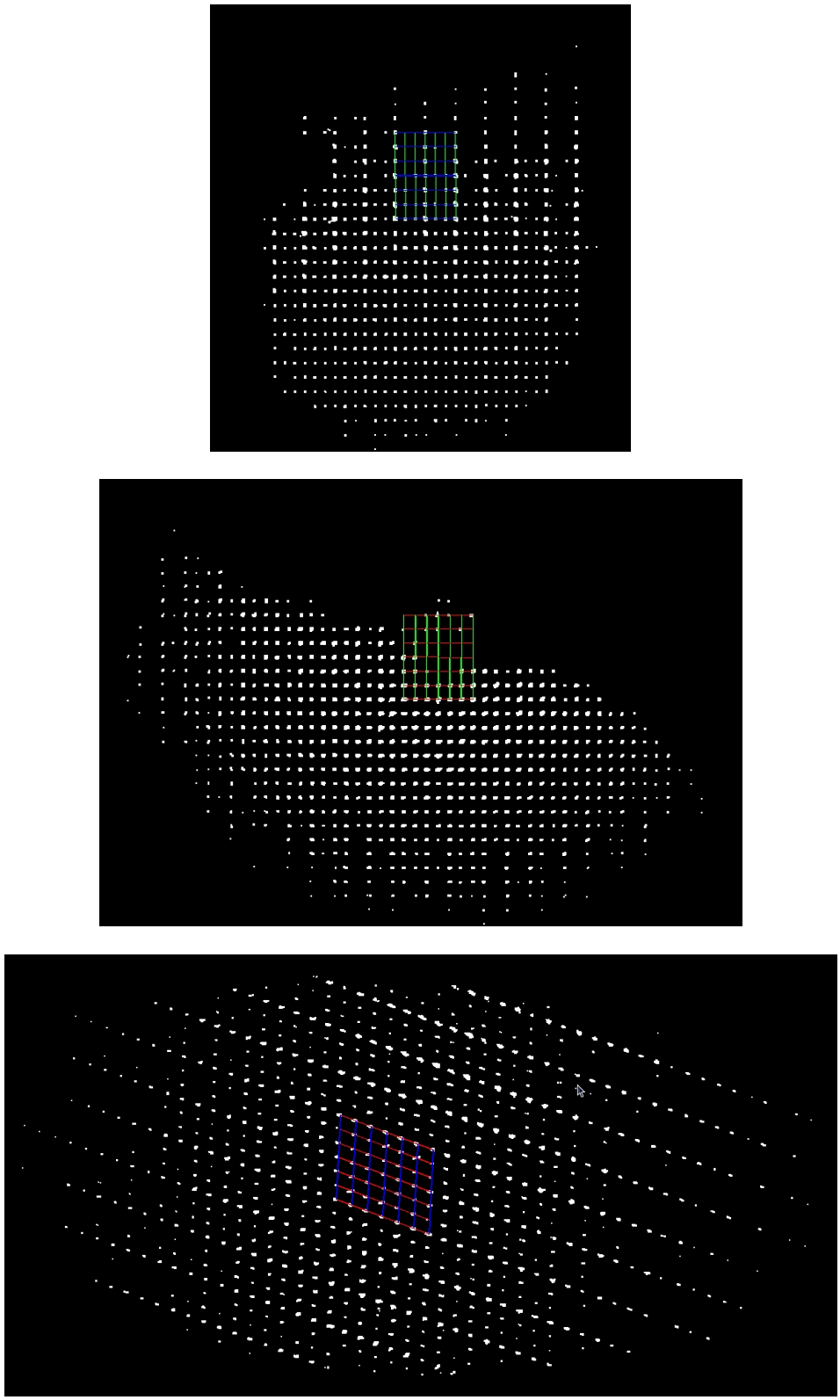


Figure S12. Reciprocal lattice representations along the a*, c* and b/b* directions of **41**, highlighting the systematically weaker reflections along the c* axis (blue), consistent with replacement of molecules by their enantiomers as illustrated in Figure S9.

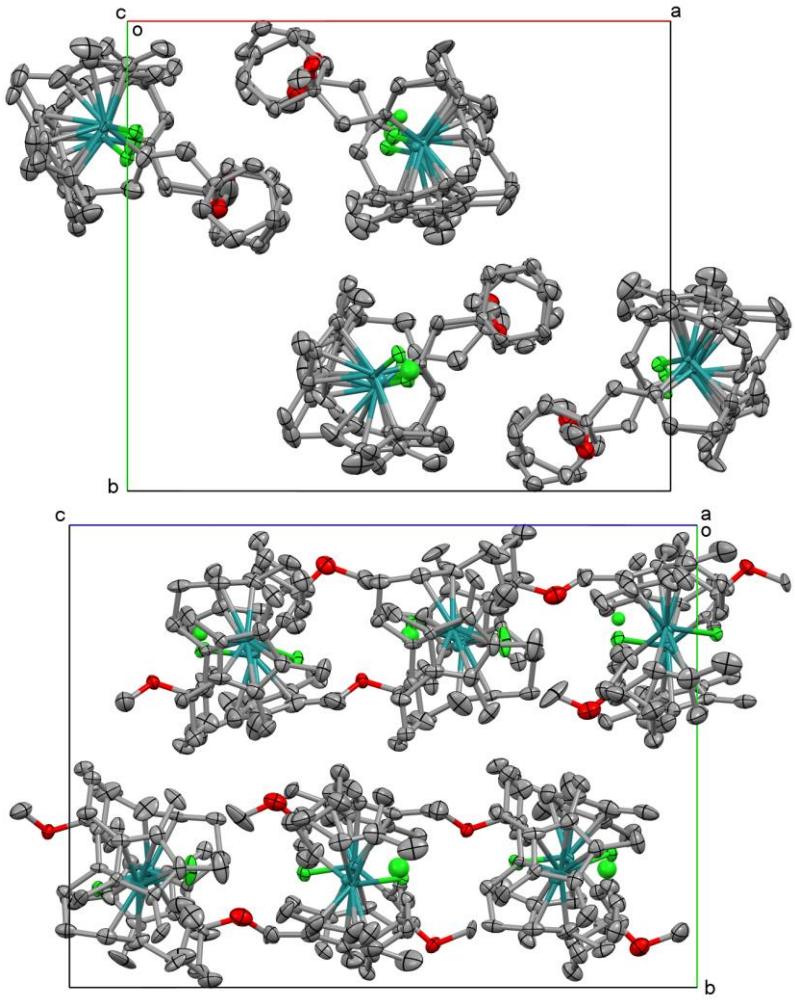
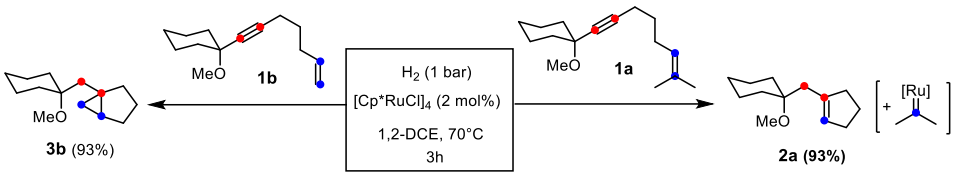
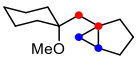
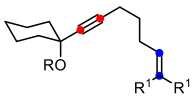
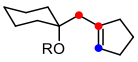
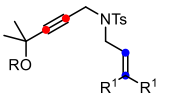
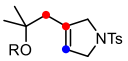
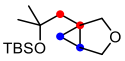
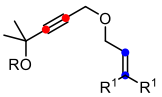
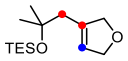
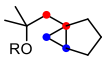
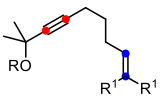
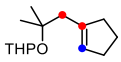
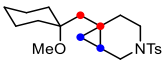
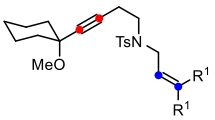
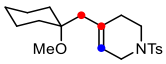


Figure S13. Packing of the molecules in the unit cell of **41**. There is a local inversion center at x = 0.248, y = 0.243, z = 0.381. Atomic displacement ellipsoids shown at the 50 % probability level. H atoms are omitted for clarity.

HYDROGENATIVE CYCLOPROPANATION AND HYDROGENATIVE METATHESIS: SCOPE AND LIMITATIONS

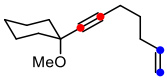
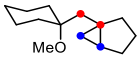
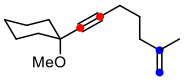
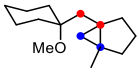
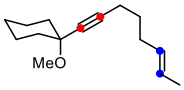
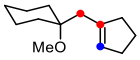
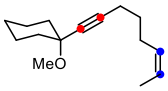
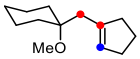
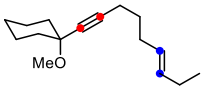
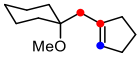
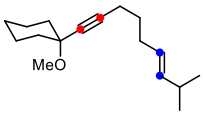
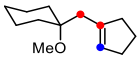
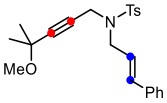
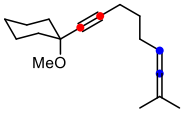
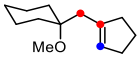
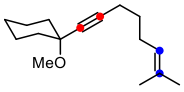
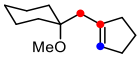
Table S1. The substituents on the alkene determine the reaction outcome.[a]



Yield[b]	R^1 = H	Substrate	R^1 = Me	Yield[b]
93%				R = Me, 93% R = MOM, 80% R = TBS, 69%
78%[c]				R = TBS, 76% R = Me, 78%
56%[c]				95%
R = TBS, 91%[d] R = MOM, 79%[d] R = SEM, quant.[d]				85%
77%				59%[e]

[a] Unless stated otherwise, all reactions were performed using $[Cp^*RuCl]_4$ (2 mol%) in 1,2-dichloroethane at 70°C under a hydrogen atmosphere (1 atm); [b] yield of analytically pure product; [c] at 90°C; [d] at RT; [e] using $[Cp^ERu(MeCN)_3]PF_6$ (**19**, 10 mol%) in combination with nBu$_4$NCl (11 mol%) as the catalyst and a reaction time of 8 h; Cp^E = 2,4-dimethylcyclopentadienylcarboxylic acid ethyl ester

Table S2. Further study on the correlation between alkene substitution and the reaction outcome (all reactions were performed using $[Cp^*RuCl]_4$ (2 mol%) in 1,2-dichloroethane at 70°C for 3 h under a hydrogen atmosphere (1 atm)).

Entry	Substrate	Product	Yield (%)[a]
1			93
2			91
3			49[b]
4			40
5			60
6			93[c]
7		---	n. r.
8			33[d]
9			93[c]

[a] NMR yield, unless stated otherwise; [b] competing enyne cycloisomerization via oxidative metallacycle formation was observed, see Table S3, entry 5; [c] yield of isolated pure material; [d] complex mixture; n. r. = no reaction

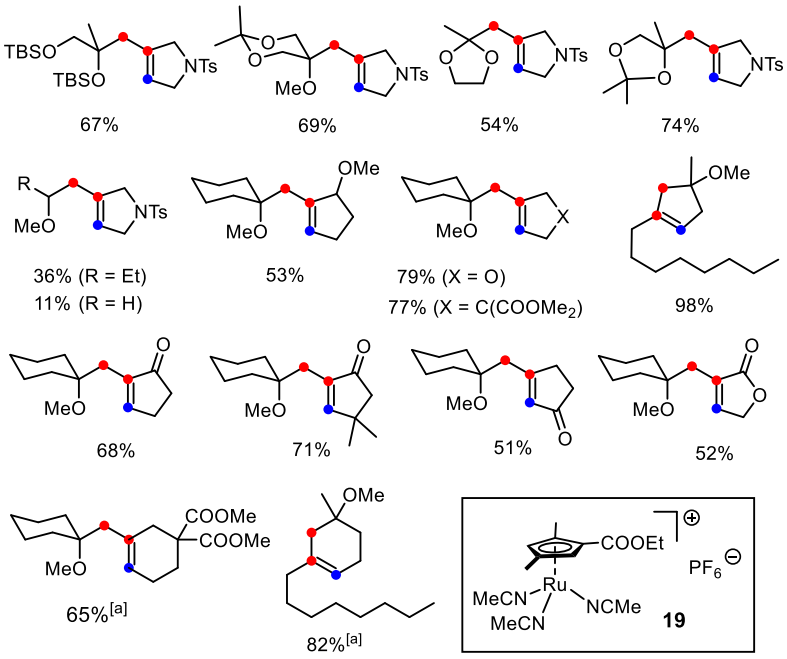
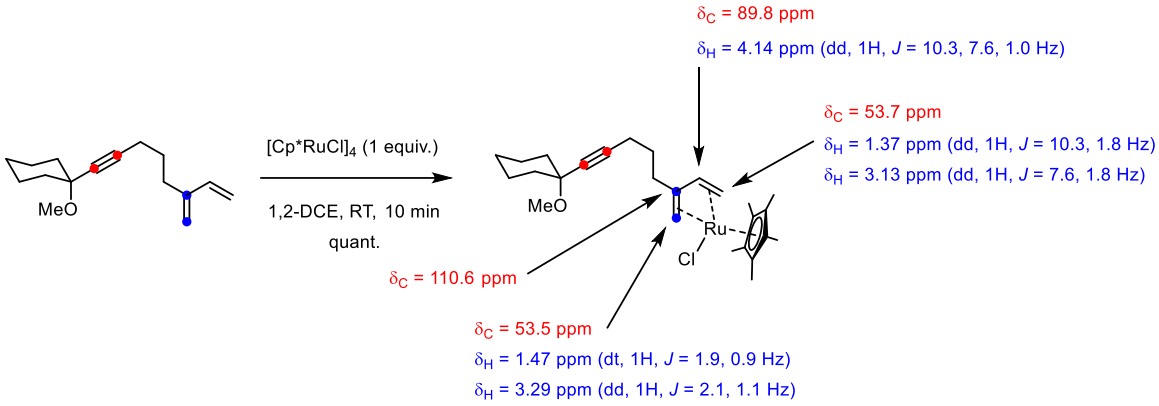
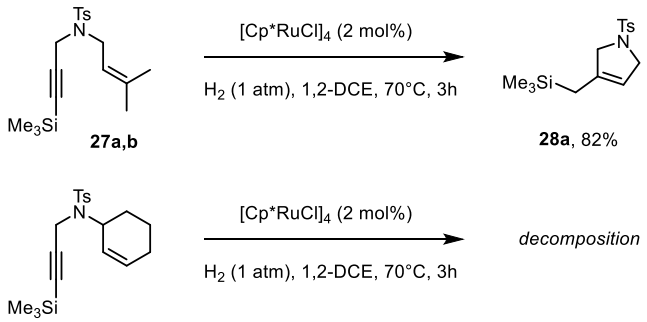


Chart S1. Products formed by "hydrogenative metathesis" of enyne derivatives comprising a 1,1-dimethylated olefin; the color code is analogous to that used in Table S1; unless stated otherwise, the reactions were performed with $[Cp^*RuCl]_4$ (2 mol%) under H_2 atmosphere (1 atm) in 1,2-dichloroethane at 70°C for 3 h; [a] the reaction was performed with complex **19** (10 mol%) in combination with nBu$_4$NCl (11 mol%) and a reaction time of 8 h

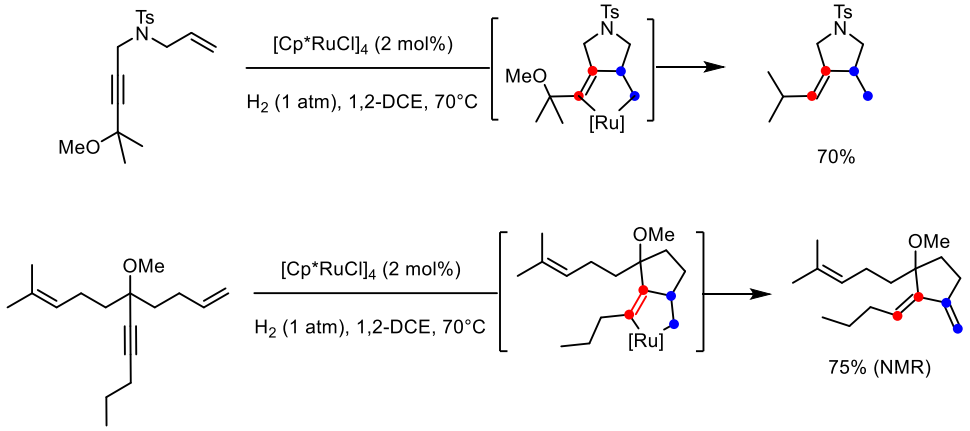
Limitations



Scheme S1. Representative example for the competitive formation of a stable π-complex

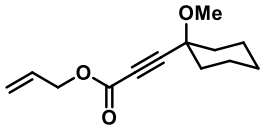
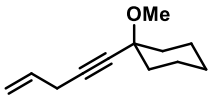
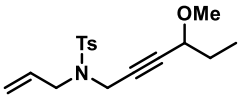
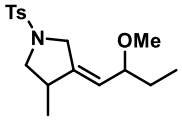
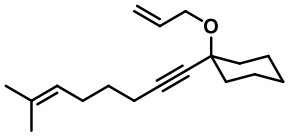
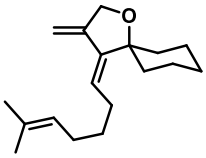
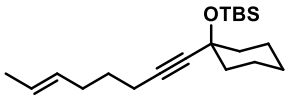
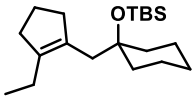
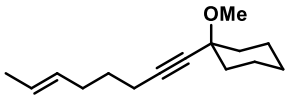
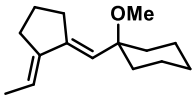
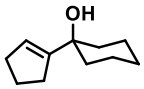
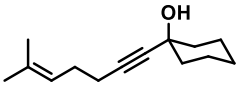
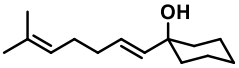
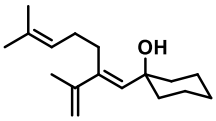


Scheme S2. Substrates comprising a cycloalkene unit tend to give complex mixtures: note that the secondary carbene formed upon metathesis is tethered to the product.



Scheme S3. Competing enyne cycloisomerization with (top) or without (bottom) subsequent hydrogenative cleavage of the transient metallacycle formed by oxidative cyclization; bottom: the competition experiment shows that the terminal alkene reacts preferentially, as expected.

Table S3. Side reactions under standard conditions ($(Cp^*RuCl)_4$ cat., H_2, 1,2-DCE, 70 °C, 3 h).

entry	substrate	identified side products	comment
1			allylic substitution/ decarboxylation
2			oxidative cyclization/ hydrogenation
3			oxidative cyclization
4			oxidative cyclization/ hydrogenation
5			oxidative cyclization
			hydrogenative metathesis
6			*trans*-hydrogenation
			enyne addition/ isomerization

GENERAL INFORMATION

Unless stated otherwise, all reactions were carried out under argon atmosphere in flame dried Schlenk glassware. The solvents were purified by distillation over the indicated drying agents under argon: THF, Et_2O (Mg/anthacene), hexanes (Na/K), EtOH, MeOH (Mg), 1,2-dichloroethane, CD_2Cl_2, EtOAc, THP (CaH_2), 2-butanone (B_2O_3). DMF, MeCN and Et_3N were dried by an absorption solvent purification system based on molecular sieves. 1,2-Dichloroethane, CD_2Cl_2, THP and 2-butanone were degassed via freeze-pump-thaw procedure (3 x) and stored over molecular sieves (except 2-butanone). Flash chromatography: Merck Geduran silica gel 60 (40 – 63 µm). TLCs were stained with $KMnO_4$, anisaldehyde, or molybdatophosphoric acid (5% in EtOH).

NMR spectra were recorded on Bruker DPX 300, AMX 300, AV 400 or AV III 600 spectrometers in the solvents indicated; chemical shifts (δ) are given in ppm relative to TMS, coupling constants (J) in Hz. The solvent signals were used as references and the chemical shifts converted to the TMS scale ($CDCl_3$: δ_C = 77.16 ppm; residual $CHCl_3$: δ_H = 7.26 ppm; CD_2Cl_2: δ_C = 54.00 ppm; residual $CHDCl_2$: δ_H = 5.32 ppm; C_6D_6: δ_C = 128.06 ppm; residual C_6HD_5: δ_H = 7.16 ppm; [D_3]-acetonitrile: δ_C = 118.26 ppm ; residual [D_2]-acetonitrile: δ_H = 1.94 ppm; [D_6]-acetone: δ_C = 29.8 ppm; residual [D_5]-acetone: δ_H = 2.05 ppm). Proton and carbon assignments were established using HSQC, HMBC and NOESY experiments.

IR: Alpha Platinum ATR (Bruker), wavenumbers ($\tilde{\nu}$) in cm^{-1}.

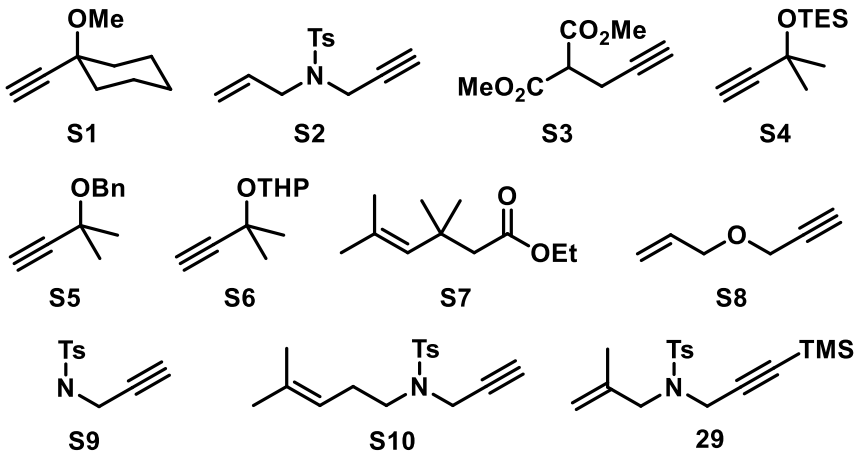
MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: ESQ 3000 (Bruker) or Thermo Scientific LTQ-FT or Thermo Scientific Exactive. HRMS: Bruker APEX III FT-MS (7 T magnet) or MAT 95 (Finnigan) or Thermo Scientific LTQ-FT or Thermo Scientific Exactive. GC-MS was measured on a Shimadzu GCMS-QP2010 Ultra instrument.

Headspace GC-FID samples were measured on an Agilent Technology 6890 or 7890 chromatograph with a 30 m HP-plot Al_2O_3 column (0.25 mm Ø, 5 µm film) using H_2 as the carrier gas. Headspace GC/MS samples were measured on an Agilent Technology 7890A instrument with AT 5975C MSD detection.

Hydrogen gas (N50, ≥99.999 Vol.%) was purchased from AirLiquide and was used without further purification. Deuterium gas (99.8 atom% D, 99.995% purity) was purchased from SigmaAldrich. Both hydrogen and deuterium were handled with standard balloon techniques.

Unless stated otherwise, all commercially available compounds (abcr, Acros, TCI, Aldrich, Alfa Aesar) were used as received. The ruthenium complexes $[Cp^*RuCl]_4$[1] and $[Cp(Me_2CO_2Et)Ru(NCMe)_3][PF_6]$ (**27**, abbreviated $[Cp^ERu(NCMe)_3][PF_6]$)[2] were prepared according to literature procedures.

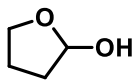
HYDROGENATIVE CYCLOPROPANATION AND METATHESIS



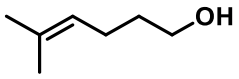
The compounds **S1**[3], **S2**[4], **S3**[5], **S4**[6], **S5**[7], **S6**[8], **S7**[9], **S8**[10], **S9**[11], **S10**[12], **29** [13] were prepared according to literature procedures

BUILDING BLOCKS

Tetrahydrofuran-2-ol (S11). DIBAL-H (1 M in CH_2Cl_2, 34.8 mL, 34.8 mmol) was slowly added to a solution of γ-butyrolactone (2.5 g, 29.0 mmol) in CH_2Cl_2 (12 mL) at −78 °C and stirring was continued for 1.5 h at that temperature. MeOH (3 mL) and sat. Rochelle salt solution (3 mL) were introduced, the mixture was warmed to room temperature and vigorously stirred for 2 h until clean separation of the layers was reached. The aqueous phase was extracted with CH_2Cl_2 (3 x 25 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was used without further purification (colorless oil, 1.06 g, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.53 (dd, *J* = 4.4, 1.6 Hz, 1H), 4.04 (td, *J* = 7.7, 7.2, 4.9 Hz, 1H), 3.89 – 3.80 (m, 1H), 2.12 – 1.99 (m, 1H), 1.99 – 1.80 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 98.5, 67.5, 33.3, 23.6. The spectral data is consistent with previously reported values.[14]



5-Methylhex-4-en-1-ol (S12). A solution of KO^{t}Bu (1.16 g, 10.4 mmol) in THF (7.7 mL) was added to a suspension of isopropyltriphenylphosphonium iodide (4.1 g, 9.5 mmol) in THF (10.0 mL) at −78 °C. The mixture was warmed to 0 °C and stirred for 30 min at that temperature before a solution of lactol **S11** (0.76 g, 8.63 mmol) in THF (4.2 mL) was introduced. The mixture was stirred at room temperature for 18 h before water (10 mL) and Et_2O (50 mL) were added. The layers were separated, the aqueous phase was extracted with Et_2O (2 x 50 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, pentane/Et_2O, 7:3) to furnish the product as a colorless liquid (444 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 3.64 (t, *J* = 6.5 Hz, 2H), 2.11 – 2.02 (m, 2H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.65 – 1.57 (m, 5H), 1.40 (br, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 124.0, 62.9, 32.9, 25.9, 24.5, 17.8. The spectral data is consistent with previously reported values.[15]



6-Bromo-2-methylhex-2-ene (S13). Br_2 (0.38 mL, 7.2 mmol) was added dropwise to a solution of PPh_3 (2.0 g, 7.7 mmol) and imidazole (870 mg, 12.7 mmol) in CH_2Cl_2 (13.6 mL) at 0 °C. The mixture was stirred for 15 min before alcohol **S12** (440 mg, 3.9 mmol) was added at 0 °C. Stirring was continued for 45 min at 0 °C and for another 1 h at room temperature. The suspension was successively washed with H_2O_2 solution (3 % H_2O_2 in water, 2 x 3 mL) and aq. $Na_2S_2O_3$ solution (1 M, 2 x 10 mL). The combined thiosulfate layers were extracted with CH_2Cl_2 (2 x 40 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure. The solid residue was suspended in hexanes (20 mL) by means of short ultrasonication and the resulting suspension filtered through a short plug of silica, thoroughly rinsing with hexanes (200 mL). The combined filtrates were concentrated under reduced pressure to give the product as a colorless liquid (622 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.07 (tdq, *J* = 7.3, 2.9, 1.3 Hz, 1H), 3.40 (t, *J* = 6.7 Hz, 2H), 2.13 (q, *J* = 7.1 Hz, 2H), 1.89 (p, *J* = 6.9 Hz, 2H), 1.70 (q, *J* = 1.3 Hz, 3H), 1.63 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.3, 122.6, 33.8, 33.0, 26.6, 25.9, 17.9. The spectral data is consistent with previously reported values.[16]

4-Methyl-N-(3-methylbut-2-en-1-yl)-N-(prop-2-yn-1-yl)benzenesulfonamide (S14). 1-Bromo-3-methyl-2-butene (0.66 mL, 5.7 mmol) was added to a solution of N-tosylpropargylamine **S9** (1.00 g, 4.8 mmol and K_2CO_3 (1.32 g, 9.6 mmol) in MeCN (8 mL). The mixture was stirred at 60 °C for 6 h before it was cooled to room temperature and diluted with MeCN (10 mL). The suspension was filtered through a pad of Celite and the filter cake was washed with EtOAc (40 mL). The combined filtrates were evaporated and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 6:1 – 4:1) to give the title compound as a colorless oil (923 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.31 – 7.27 (m, 2H), 5.10 (tdq, *J* = 7.2, 2.8, 1.4 Hz, 1H), 4.07 (d, *J* = 2.5 Hz, 2H), 3.81 (d, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 1.98 (t, *J* = 2.5 Hz, 1H), 1.72 (q, *J* = 1.1 Hz, 3H), 1.67 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.2, 136.3, 129.5, 128.0, 118.1, 77.2, 73.5, 44.1, 35.5, 26.0, 21.7, 18.0. The spectral data is consistent with previously reported values.[17]

5-Methylhex-4-enal (S15). 2-Methyl-3-buten-2-ol (8.0 g, 93 mmol), ethyl vinyl ether (17.8 mL, 186 mmol) and H_3PO_4 (85%, 0.1 mL, 1.4 mmol) were stirred in a sealed thick-walled pressure Schlenk flask for 2.5 h at 150 °C. The mixture was cooled to room temperature before Et_3N (0.6 mL, 4.2 mmol) was added. The crude product was purified by distillation under reduced pressure (60 mbar, 120 °C bath temperature). The product was obtained as a colorless oil by collecting the fraction boiling at ≈72 °C (2.38 g, 23%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.8 Hz, 1H), 5.09 (tdq, *J* = 7.1, 2.9, 1.5 Hz, 1H), 2.48 – 2.43 (m, 2H), 2.37 – 2.26 (m, 2H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.63 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 202.8, 133.4, 122.3, 44.1, 25.8, 21.1, 17.9. The spectral data is consistent with previously reported values.[18]

3-Methylbut-2-en-1-yl propiolate (S16). Propiolic acid (500 mg, 7.1 mmol) and 1-bromo-3-methyl-2-butene (1.65 mL, 14.3 mmol) were added to a stirred suspension of $NaHCO_3$ (1.2 g, 14.3 mmol) in DMF (8.8 mL) at room temperature. The mixture was stirred for 18 h before it was diluted with water (60 mL) and Et_2O (30 mL). The aqueous phase was extracted with Et_2O (2 x 30 mL) and the combined organic layers were washed with water (60 mL) and

dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, pentane/Et_2O 10:1) to give the title compound as a colorless oil (993 mg, quant.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (tdq, *J* = 7.2, 2.9, 1.5 Hz, 1H), 4.69 (dt, *J* = 7.4, 0.8 Hz, 2H), 2.85 (s, 1H), 1.80 – 1.74 (m, 3H), 1.75 – 1.70 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.91, 140.95, 117.46, 74.90, 74.57, 63.22, 25.93, 18.21. IR (film) ν 3271, 2975, 2937, 2119, 1707 cm^{-1}. HRMS (ESI$^+$) for $C_8H_{10}O_2$ $[M+H]^+$: calcd: 139.0734, found: 139.0754.

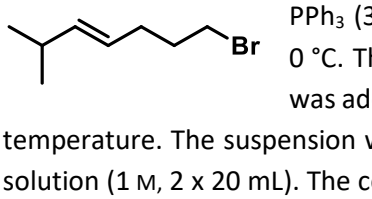
4-Methylpent-1-en-3-ol (S17). Freshly distilled isobutyraldehyd (3.02 g, 41.7 mmol) in Et_2O (44 mL) was added over 30 min to a stirred solution of vinylmagnesium bromide (1 M in THF, 50 mL, 50 mmol) at −78 °C. The mixture was stirred for 1 h at −78 °C before being allowed to reach room temperature. The mixture was acidified with aqueous HCl (1 M, 55 mL) and the layers were separated. The aqueous phase was extracted with Et_2O (3 x 100 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting crude product used without further purification (light yellow liquid, 3.75 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.86 (ddd, *J* = 17.1, 10.4, 6.4 Hz, 1H), 5.22 (dt, *J* = 17.2, 1.5 Hz, 1H), 5.15 (ddd, *J* = 10.4, 1.7, 1.1 Hz, 1H), 3.88 – 3.83 (m, 1H), 1.80 – 1.67 (m, 1H), 0.93 (d, *J* = 6.8 Hz, 3H), 0.90 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 115.7, 78.4, 33.7, 18.3, 17.9. The spectral data is consistent with previously reported values.[19]

Methyl (*E*)-6-methylhept-4-enoate (S18). Alcohol **S17** (3.75 g, 37.4 mmol) was added to trimethylorthoacetate (14.3 mL, 112 mmol) and propionic acid (138 mg, 1.9 mmol) in a thick-walled pressure Schlenk flask. The sealed flask was immersed in a heating bath at 120 °C and the mixture stirred for 14 h. The mixture was allowed to cool to room temperature and then stirred again at 120 °C open to air. After reaching ambient temperature, the solution was diluted with CH_2Cl_2 (50 mL) and aqueous HCl (1 M, 10 mL). The mixture was stirred for 1 h at room temperature before the layers were separated and the aqueous phase extracted with CH_2Cl_2 (2 x 100 mL). The combined organic layers were washed with sat. aq. $NaHCO_3$ and dried over $MgSO_4$. The solvent was removed under reduced pressure and the resulting crude product was used without further purification in the next step (colorless oil, 5.45 g, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 (ddt, *J* = 15.4, 6.2, 1.0 Hz, 1H), 5.34 (dtd, *J* = 15.3, 6.0, 1.0 Hz, 1H), 3.66 (s, 3H), 2.40 – 2.33 (m, 2H), 2.33 – 2.26 (m, 2H), 2.26 – 2.17 (m, 1H), 0.95 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.9, 139.1, 125.0, 51.6, 34.4, 31.1, 28.0, 22.7.

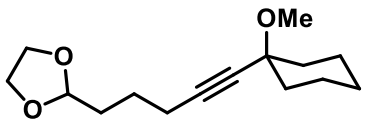
(*E*)-6-Methylhept-4-en-1-ol (S19). $LiAlH_4$ (1.7 g, 45 mmol) was added in portions to a solution of ester **S18** (2.0 g, 12.8 mmol) in Et_2O (40 mL) at 0 °C. The mixture was warmed to room temperature and stirring was continued for 4 h before water (2 mL) and NaOH (2 mL, 15% in water) were carefully added. The mixture was stirred for 15 min at room temperature before more water (6 mL) was added. After stirring for additional 15 min, the suspension was filtrated through a glass frit, the residue was washed with Et_2O (20 mL) and the combined filtrates were dried over Na_2SO_4. The solvent was removed under reduced pressure and the resulting crude material used in the next step without further purification (colorless liquid, 1.65 g, quant.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.47 – 5.32 (m, 2H), 3.65 (t, *J* = 6.5 Hz, 2H), 2.30 – 2.17 (m, 1H), 2.11 – 2.03 (m, 2H),

1.69 – 1.57 (m, 2H), 0.96 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.5, 126.5, 62.8, 32.6, 31.1, 29.0, 22.8. The spectral data is consistent with previously reported values.[20]

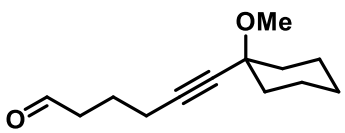
(*E*)-7-Bromo-2-methylhept-3-ene (S20). Br_2 (0.67 mL, 13.0 mmol) was added dropwise to a solution of PPh_3 (3.60 g, 13.7 mmol) and imidazole (1.54 g, 22.6 mmol) in CH_2Cl_2 (24 mL) at 0 °C. The mixture was stirred for 15 min before alcohol **S19** (880 mg, 6.9 mmol) was added at 0 °C. Stirring was continued for 30 min at 0 °C and for 1 h at ambient temperature. The suspension was washed with H_2O_2 solution (3 % H_2O_2 in water, 2 x 6 mL) and $Na_2S_2O_3$ solution (1 M, 2 x 20 mL). The combined thiosulfate layers were extracted with CH_2Cl_2 (2 x 80 mL) and the combined organic phases were dried over $MgSO_4$. The solvent was removed under reduced pressure. The solid white residue was suspended in hexanes (30 mL) by means of short ultrasonication and the suspension filtered through a plug of silica. The filter cake and silica were thoroughly rinsed with hexanes (300 mL) and the combined filtrates were evaporated to give the product as a colorless liquid (1.08 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.45 (ddt, *J* = 15.3, 6.5, 1.3 Hz, 1H), 5.30 (dtd, *J* = 15.3, 6.7, 1.2 Hz, 1H), 3.40 (t, *J* = 6.8 Hz, 2H), 2.31 – 2.17 (m, 1H), 2.18 – 2.07 (m, 2H), 1.91 (p, *J* = 7.0 Hz, 2H), 0.96 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 124.9, 33.5, 32.7, 31.2, 31.0, 22.7.



2-(5-(1-Methoxycyclohexyl)pent-4-yn-1-yl)-1,3-dioxolane (S21). *n*-BuLi (1.6 M in hexanes, 1.63 mL, 2.60 mmol) was added slowly to a solution of alkyne **S1** (300 mg, 2.17 mmol) in THF (7.6 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of 2-(3-bromopropyl)-1,3-dioxolane (508 mg, 2.60 mmol) in THF (4.9 mL) and DMPU (1.3 mL) was added. The mixture was stirred at room temperature for 18 h. sat. NH_4Cl solution (3 mL), *tert*-butyl methyl ether (20 mL) and water (3 mL) were added and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 40 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 80:1 – 40:1) to give the product as a colorless oil (301 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 (t, *J* = 4.7 Hz, 1H), 4.01 – 3.92 (m, 2H), 3.90 – 3.81 (m, 2H), 3.34 (s, 3H), 2.30 (t, *J* = 7.0 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.82 – 1.74 (m, 2H), 1.65 (m, 5H), 1.57 – 1.45 (m, 4H), 1.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 104.36, 85.93, 81.62, 74.16, 65.03, 50.63, 37.16, 33.15, 25.70, 23.61, 23.06, 18.82. IR (film) $\tilde{\nu}$ 2935, 2859, 1449, 1142, 1091 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{24}O_3$ $[M+Na]^+$: calcd: 275.1618, found: 275.1618.

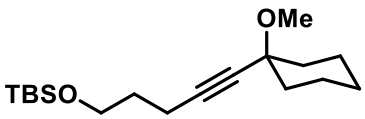


6-(1-Methoxycyclohexyl)hex-5-ynal (S22). A solution of dioxolane **S21** (150 mg, 0.59 mmol) in acetone (2.7 mL) was added to a solution of *p*-TsOH·H_2O (6 mg, 0.03 mmol) in water (2.7 mL). The mixture was stirred at 70 °C for 3 h before sat. $NaHCO_3$ solution (2 mL) was introduced. The mixture was diluted with *tert*-butyl methyl ether (10 mL) and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to give the title compound as a colorless oil (110 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (t, *J* = 1.4 Hz, 1H), 3.33 (s, 3H), 2.59 (td, *J* = 7.2, 1.4 Hz, 2H), 2.33 (t, *J* = 6.9 Hz, 2H), 1.90 – 1.80 (m, 4H), 1.69 – 1.59 (m, 2H), 1.59 – 1.44 (m, 5H), 1.33 – 1.23

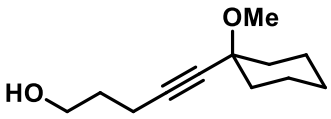


(m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 202.0, 84.9, 82.5, 74.1, 50.6, 43.0, 37.1, 25.6, 23.0, 21.5, 18.3. IR (film) $\tilde{\nu}$ 2935, 2857, 1725, 1448, 1091 cm^{-1}. HRMS (ESI$^+$) for $C_{13}H_{20}O_2$ [M+Na]$^+$: calcd: 231.1355, found: 231.1357.

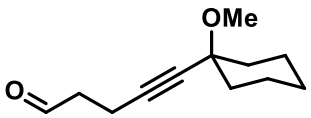
***tert*-Butyl((5-(1-methoxycyclohexyl)pent-4-yn-1-yl)oxy)dimethylsilane (S23).** *n*-BuLi (1.6 M in hexanes, 1.63 mL, 2.60 mmol) was slowly added to a solution of alkyne **S1** (300 mg, 2.17 mmol) in THF (7.5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of (3-bromopropoxy)(*tert*-butyl)dimethylsilane (659 mg, 2.60 mmol) in THF (5 mL) and DMPU (1.3 mL) was added. The mixture was allowed to reach room temperature and stirring was continued for 22 h. sat. NH_4Cl solution (4 mL), *tert*-butyl methyl ether (20 mL) and water (4 mL) were added and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 40 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 50:1 – 40:1) to give the title compound as a colorless oil (396 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (t, *J* = 6.1 Hz, 2H), 3.34 (s, 3H), 2.32 (t, *J* = 7.0 Hz, 2H), 1.90 – 1.78 (m, 2H), 1.72 (p, *J* = 7.0 Hz, 2H), 1.68 – 1.58 (m, 2H), 1.58 – 1.45 (m, 5H), 1.32 – 1.23 (m, 1H), 0.90 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.1, 81.3, 74.2, 61.8, 50.6, 37.2, 32.1, 26.1, 25.7, 23.1, 18.5, 15.2, -5.2. IR (neat) ν̃ 2933, 2857, 1255, 1096, 836 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{34}O_2Si$ [M+Na]$^+$: calcd 333.2220, found 333.2222.



5-(1-Methoxycyclohexyl)pent-4-yn-1-ol (S24). TBAF (1 M in THF, 1.88 mL, 1.88 mmol) was added to a solution of silyl ether **S23** (390 mg, 1.26 mmol) in THF (8 mL) at 0 °C. The mixture was allowed to reach room temperature and was stirred for 30 min before sat. NH_4Cl solution (2 mL) and water (2 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 5:1 – 2:1) to obtain the title compound as a colorless oil (186 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 (t, *J* = 6.2 Hz, 2H), 3.34 (s, 3H), 2.37 (t, *J* = 6.9 Hz, 2H), 1.89 – 1.82 (m, 2H), 1.79 (m, 2H), 1.69 – 1.59 (m, 2H), 1.58 – 1.44 (m, 6H), 1.32 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 85.5, 81.9, 74.1, 62.0, 50.6, 37.1, 31.7, 25.7, 23.0, 15.5. IR (neat) ν̃ 3364 (br), 2932, 2856, 2231, 1446, 1078 cm^{-1}. HRMS (EI) for $C_{12}H_{20}O_2$ [M+Na]$^+$: calcd 196.1458, found 196.1457.

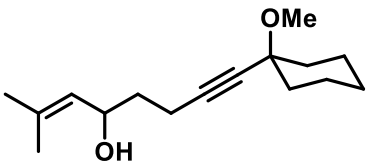


5-(1-Methoxycyclohexyl)pent-4-ynal (S25). $NaHCO_3$ (336 mg, 4.0 mmol) and Dess-Martin periodinane (508 mg, 1.2 mmol) were added to a solution of alcohol **S24** (157 mg, 0.8 mmol) in wet CH_2Cl_2 (7.4 mL) at 0 °C. The mixture was stirred at room temperature for 30 min before aq. sat. $Na_2S_2O_3$ (3 mL) and water (3 mL) were added. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/ methyl *tert*-butyl ether 1:0 – 10:1 – 5:1) to give the product as a colorless oil (109 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.81 (t, *J* = 1.4 Hz, 1H), 3.32 (s, 3H), 2.67 (tt, *J* = 6.9, 1.3 Hz, 2H), 2.57 (td, *J* = 7.0, 1.2 Hz, 2H), 1.87 – 1.77 (m, 2H), 1.62 (m, 2H), 1.56 – 1.40 (m, 5H), 1.32 – 1.18 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.7, 84.1, 82.5, 74.1, 50.7, 43.0, 37.0,

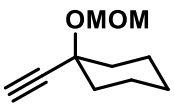


25.6, 23.0, 12.3. IR (neat) ṽ 2933, 2856, 1725, 1446, 1089 cm^{-1}. HRMS (ESI^+) for $C_{12}H_{18}O_2$ $[M+Na]^+$: calcd 217.1199, found 217.1201.

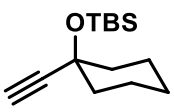
8-(1-Methoxycyclohexyl)-2-methyloct-2-en-7-yn-4-ol (S26). A solution of aldehyde **S25** (100 mg, 0.51 mmol) in Et_2O (2 mL) was slowly added to a solution of (2-methylprop-1-en-1-yl)magnesium bromide (0.5 M in THF, 1.54 mL, 0.77 mmol) in Et_2O (5.4 mL) at – 78 °C and the mixture was stirred for 1 h at that temperature. The mixture was allowed to reach room temperature before sat. NH_4Cl solution (1 mL) was added and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 4:1) to yield the title compound as a colorless oil (74 mg, 57%). ^1H NMR (400 MHz $CDCl_3$) δ 5.17 (ddq, *J* = 8.6, 2.8, 1.4 Hz, 1H), 4.52 (ddd, *J* = 8.8, 7.4, 5.8 Hz, 1H), 3.34 (s, 3H), 2.36 (dt, *J* = 16.9, 7.2 Hz, 1H), 2.28 (dt, *J* = 16.8, 7.0 Hz, 1H), 1.85 (m, 2H), 1.79 (dd, *J* = 13.4, 7.2 Hz, 1H), 1.73 (d, *J* = 1.4 Hz, 3H), 1.70 (d, *J* = 1.4 Hz, 3H), 1.68 – 1.59 (m, 3H), 1.58 – 1.46 (m, 6H), 1.28 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 127.5, 85.9, 81.6, 74.2, 67.9, 50.6, 37.2, 37.1, 36.7, 26.0, 25.7, 23.1 (2C), 18.4, 15.3. IR (neat) ṽ 3371 (br), 2932, 2231, 1445, 1079 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{26}O_2$ $[M+Na]^+$: calcd 273.1825, found 273.1825.



1-Ethynyl-1-(methoxymethoxy)cyclohexane (S27). A solution of 1-ethynyl-1-cyclohexanol (4.0 g, 32.2 mmol) in THF (15 mL) was slowly added to a stirred suspension of NaH (1.55 g, 64.4 mmol) in THF (65 mL) at 0 °C. The mixture was stirred for 30 min at room temperature before MOMCl (0.61 mL, 8.1 mmol) was added at 0 °C. Stirring was continued for 2 h at room temperature before aq. sat. NH_4Cl (6 mL), water (4 mL) and *tert*-butyl methyl ether (80 mL) were introduced. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 100 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaported and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to give the title compound as a colorless oil (5.06 g, 93%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.94 (s, 2H), 3.40 (s, 3H), 2.52 (s, 1H), 2.01 – 1.91 (m, 2H), 1.73 – 1.48 (m, 7H), 1.33 – 1.18 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 92.9, 84.9, 74.8, 74.7, 56.0, 38.6, 25.4, 23.0. IR (film) *ṽ* 3305, 3264, 2934, 1149, 1023 cm^{-1}. HRMS (ESI^+) for $C_{10}H_{16}O_2$ $[M+Na]^+$: calcd: 191.1042, found: 191.1042.

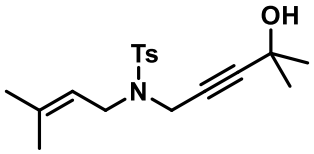


***tert*-Butyl((1-ethynylcyclohexyl)oxy)dimethylsilane (S28)**. TBSOTf (0.83 mL, 3.6 mmol) was added to a solution of 1-ethynyl-1-cyclohexanol (500 mg, 4.0 mmol) and 2,6-lutidine (0.94 mL, 8.1 mmol) in CH_2Cl_2 (10.8 mL) at 0 °C. The mixture was stirred for 2 h before water (2 mL) was added. After reaching room temperature, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes) to yield the title compound as a colorless oil (610 mg, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (s, 1H), 1.84 – 1.74 (m, 2H), 1.71 – 1.57 (m, 4H), 1.57 – 1.47 (m, 2H), 1.47 – 1.38 (m, 1H), 1.37 – 1.25 (m, 1H), 0.88 (s, 9H), 0.17 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 88.7, 72.8,



69.2, 41.2, 26.0, 25.4, 22.8, 18.3, -2.7. IR (film) $\tilde{\nu}$ 3310, 2932, 2856, 1252, 1101, 835, 774 cm^{-1}. HRMS (ESI^+) for $C_{14}H_{26}OSi$ $[M+H]^+$: calcd: 239.1826, found: 239.1825.

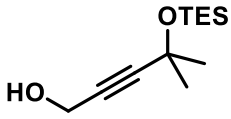
N-(4-Hydroxy-4-methylpent-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S29).



n-BuLi (1.6 M in hexanes, 1.35 mL, 2.16 mmol) was slowly added to a solution of alkyne **S14** (460 mg, 1.66 mmol) in THF (17.5 mL) at 0 °C. The solution was stirred for 30 min at 0 °C before acetone (1.22 mL, 16.6 mmol) was introduced. After stirring at room temperature for 30 min, sat. NH_4Cl solution (3 mL) and EtOAc (30 mL) were added, the layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 4:1 – 2:1) to yield the title compound as a pale yellow amorphous solid (297 mg, 53%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.34 – 7.29 (m, 2H), 5.11 (ddq, *J* = 8.8, 5.8, 1.4 Hz, 1H), 4.07 (s, 2H), 3.81 (d, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 1.73 (s, 3H), 1.68 (s, 3H), 1.47 (br, 1H), 1.25 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.1, 136.6, 129.6, 128.1, 118.1, 90.1, 75.3, 64.9, 44.1, 35.7, 31.1, 26.0, 21.6, 18.0. IR (film) $\tilde{\nu}$ 3522, 2979, 2921, 1596, 1327, 1152 cm^{-1}. HRMS (ESI^+) for $C_{18}H_{25}O_3S$ $[M+Na]^+$: calcd: 358.1447, found: 358.1444.

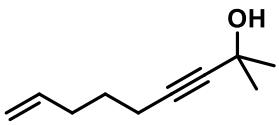
N-Allyl-N-(4-hydroxy-4-methylpent-2-yn-1-yl)-4-methylbenzenesulfonamide (S30). *n*-BuLi (1.6 M in hexanes, 0.59 mL, 0.94 mmol) was added slowly to a solution of alkyne **S2** (181 mg, 0.73 mmol) in THF (7.6 mL) at 0 °C. The solution was stirred for 30 min at 0 °C before acetone (0.75 mL, 10.1 mmol) was introduced. The mixture was warmed to room temperature and stirring continued for 30 min. sat. NH_4Cl solution (3 mL) and EtOAc (30 mL) were added, the layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 2:1 – 1:1) to yield the title compound as a pale yellow amorphous solid (72 mg, 32%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 5.75 (ddt, *J* = 17.1, 10.0, 6.5 Hz, 1H), 5.32 – 5.22 (m, 2H), 4.10 (s, 2H), 3.82 (dt, *J* = 6.4, 1.2 Hz, 2H), 2.43 (s, 3H), 1.45 (br, 1H), 1.27 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 136.4, 132.1, 129.7, 128.1, 120.0, 90.6, 74.8, 64.9, 49.2, 36.1, 31.2, 21.6. IR (neat) $\tilde{\nu}$ 3510, 2981, 2929, 1598, 1160 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{22}NO_3S$ $[M+Na]^+$: calcd: 308.1315, found: 308.1316.

4-Methyl-4-((triethylsilyl)oxy)pent-2-yn-1-ol (S31). *n*-BuLi (1.6 M in hexanes, 1.57 mL, 2.5 mmol) was added at 0 °C to a solution of alkyne **S4** (500 mg, 2.5 mmol) in THF (10 mL). The mixture was stirred for 1 h at this temperature before powdered paraformaldehyde (90 mg, 3.0 mmol) was slowly introduced and stirring was continued overnight at ambient temperature. The reaction was quenched with sat. NH_4Cl solution (10 mL). The aqueous phase was extracted with Et_2O (3 x 40 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under vacuum. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 9:1) to give the title compound as a colorless oil (529 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.28 (d, *J* = 6.2 Hz, 2H), 1.42 (t, *J* = 6.2 Hz, 1H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.74 –

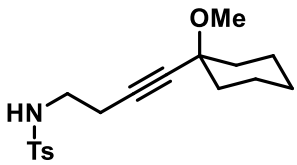


0.62 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 91.4, 80.4, 66.3, 51.4, 33.1, 7.1, 6.2. IR (film) $\tilde{\nu}$ 3340, 2955, 2876, 1377, 1239, 1160, 1035, 1002, 724 cm^{-1}. HRMS (ESI$^+$) for $C_{12}H_{24}O_2Si$ [M+Na]$^+$: calcd: 251.1438, found: 251.1436.

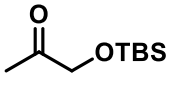
2-Methylnon-8-en-3-yn-2-ol (S32). *n*-BuLi (1.6 M in hexanes, 19.3 mL, 30.1 mmol) was added at 0 °C to a solution of 2-methyl-3-butin-2-ol (1.50 mL, 15.5 mmol) in THF (45 mL) and HMPA (18 mL). After 1 h at 0 °C, the reaction mixture was cooled to −78 °C and 5-bromo-1-pentene (1.53 mL, 12.9 mmol) was slowly introduced. The mixture was warmed to room temperature during 1 h and then stirred at 70 °C for another 18 h. The mixture was cooled to room temperature and the reaction quenched with sat. NH_4Cl solution (50 mL). The aqueous phase was extracted with Et_2O (3 x 40 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, hexanes/EtOAc 5:1) to give the title compound as a colorless oil (1.54 g, 78%) ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.08 – 4.95 (m, 2H), 2.19 (t, *J* = 7.1 Hz, 2H), 2.17 – 2.10 (m, 2H), 1.86 (s, 1H), 1.63 – 1.55 (m, 1H), 1.50 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 137.9, 115.1, 85.4, 82.2, 65.3, 32.8, 31.7, 27.8, 18.0. IR (film) $\tilde{\nu}$ 3331, 2980, 2933, 1641, 1439, 1364, 1240, 1163, 1133, 1083, 950, 912, 838 cm^{-1}. HRMS (ESI$^+$) for $C_{10}H_{16}O$ [M+Na]$^+$: calcd: 175.1093, found: 175.1094.



N-(4-(1-Methoxycyclohexyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (S33). *n*-BuLi (1.6 M in hexanes, 2.0 mL, 3.2 mmol) was slowly added to a solution of alkyne **S1** (400 mg, 2.9 mmol) in THF (5.0 mL) at 0 °C. A solution of *N*-tosylaziridine (428 mg, 2.2 mmol) in THF (3.3 mL) and DMPU (0.9 mL) was slowly added and the mixture was stirred at room temperature for 3 h. sat. NH_4Cl solution (2 mL), water (2 mL) and EtOAc (20 mL) were introduced before the layers were separated. The aqueous phase was extracted with EtOAc (2 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 5:1 – 4:1 – 3:1) to give the title compound as a colorless oil (405 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.73 (m, 2H), 7.34 – 7.29 (m, 2H), 4.71 (t, *J* = 6.3 Hz, 1H), 3.28 (s, 3H), 3.10 (q, *J* = 6.5 Hz, 2H), 2.45 – 2.39 (m, 5H), 1.84 – 1.74 (m, 2H), 1.68 – 1.57 (m, 2H), 1.57 – 1.36 (m, 5H), 1.34 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.7, 137.1, 129.9, 127.2, 84.0, 81.9, 74.0, 50.7, 42.2, 36.9, 25.5, 22.9, 21.7, 20.1. IR (film) $\tilde{\nu}$ 3283 (br), 2933, 2857, 1446, 1090 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{25}NO_3S$ [M+Na]$^+$: calcd: 358.1447, found: 358.1444.



1-((*tert*-Butyldimethylsilyl)oxy)propan-2-one (S34). Imidazole (1.0 g, 14.8 mmol) was added in portions to a stirred solution of hydroxyacetone (90%, 555 mg, 6.7 mmol) and TBSCl (1.53 g, 10.1 mmol) in CH_2Cl_2 (26 mL) at 0 °C. The mixture was stirred at room temperature for 1 h before brine (10 mL) was added. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2 x 50 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was evaporated and the crude product purified by flash chromatography (silica, pentane/Et_2O 20:1 – 10:1) to give the title compound as a colorless oil (1.1 g, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (s, 2H), 2.17 (s,



3H), 0.92 (s, 9H), 0.09 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.4, 69.7, 26.1, 25.9, 18.4, -5.4. The spectral data is consistent with previously reported values.[21]

N-(5-((*tert*-Butyldimethylsilyl)oxy)-4-hydroxy-4-methylpent-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S35). *n*-BuLi (1.6 M in hexanes, 1.46 mL, 2.34 mmol) was slowly added to a solution of alkyne **S14** (500 mg, 1.80 mmol) in THF (19.0 mL) at 0 °C. The solution was stirred for 20 min at 0 °C before ketone **S34** (509 mg, 2.7 mmol) was introduced. The mixture was warmed to room temperature and stirred for 5 min before sat. NH_4Cl solution (10 mL) and EtOAc (50 mL) were introduced. The aqueous phase was extracted with EtOAc (2 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 6:1 – 4:1) to yield the title compound as a colorless oil (503 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.70 (m, 2H), 7.32 – 7.27 (m, 2H), 5.11 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.09 (s, 2H), 3.81 (d, *J* = 7.3 Hz, 2H), 3.40 (d, *J* = 9.5 Hz, 1H), 3.29 (d, *J* = 9.4 Hz, 1H), 2.51 (br, 1H), 2.42 (s, 3H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.15 (s, 3H), 0.89 (s, 9H), 0.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 139.0, 136.6, 129.6, 128.0, 118.2, 87.7, 76.5, 70.8, 67.8, 44.0, 35.8, 26.0, 26.0, 25.2, 21.7, 18.5, 18.1, -5.2, -5.3. IR (film) $\tilde{\nu}$ 3513 (br), 2929, 2858, 1347, 1160, 1093 cm^{-1}. HRMS (ESI$^+$) for $C_{24}H_{39}NO_4SSi$ [M+Na]$^+$: calcd: 488.2261, found: 488.2264.

4-Methyl-N-(3-methylbut-2-en-1-yl)-N-(4-oxopent-2-yn-1-yl)benzenesulfonamide (S36). *n*-BuLi (1.6 M in hexanes, 1.46 mL, 2.34 mmol) was slowly added to a solution of alkyne **S14** (500 mg, 1.80 mmol) in THF (19.0 mL) at 0 °C. The solution was stirred for 20 min at 0 °C before *N*-methoxy-*N*-methylacetamide (0.29 mL, 2.7 mmol) was introduced. After reaching room temperature, the mixture was stirred for 5 min before sat. NH_4Cl solution (10 mL) and EtOAc (50 mL) were added. The layers were separated, the aqueous phase was extracted with EtOAc (2 x 50 mL), and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 6:1 – 4:1) to yield the title compound as a yellow oil (248 mg, 43%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.36 – 7.29 (m, 2H), 5.10 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.21 (s, 2H), 3.82 (d, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 2.08 (s, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.66 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 183.3, 144.0, 139.9, 135.8, 129.8, 127.9, 117.6, 84.9, 84.6, 44.6, 35.7, 32.4, 26.0, 21.7, 18.0. IR (film) $\tilde{\nu}$ 2974, 2921, 2209, 1679, 1348, 1162 cm^{-1}. HRMS (ESI$^+$) for $C_{17}H_{21}NO_3S$ [M+Na]$^+$: calcd: 342.1134, found: 342.1135.

N-(4-Hydroxyhex-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S37). *n*-BuLi (1.6 M in hexanes, 1.35 mL, 2.16 mmol) was added slowly to a solution of alkyne **S14** (460 mg, 1.66 mmol) in THF (17.5 mL) at 0 °C. The solution was stirred for 30 min at 0 °C before freshly distilled propionaldehyde (1.20 mL, 16.6 mmol) was introduced. Stirring was continued at room temperature for 30 min before sat. NH_4Cl solution (3 mL) and EtOAc (30 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, the solvent was removed under reduced pressure and the crude product

was purified by flash chromatography (silica, hexanes/EtOAc 8:1 – 4:1 – 3:1) to yield the title compound as a light yellow oil which was directly used in the subsequent step.

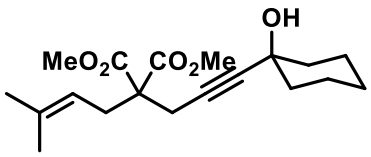
N-(4-Hydroxybut-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S38). *n*-BuLi (1.6 M in hexanes, 0.59 mL, 0.94 mmol) was slowly added to a solution of alkyne **S14** (200 mg, 0.72 mmol) in THF (7.6 mL) at −78 °C. The solution was stirred for 3 h at −78 °C before powdered paraformaldehyde (28 mg, 0.94 mmol) was introduced. After stirring at room temperature for 1h, sat. NH_4Cl solution (3 mL) and EtOAc (30 mL) were added, the layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 4:1 – 2:1) to yield the title compound as a light yellow oil (159 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.72 (m, 2H), 7.34 – 7.28 (m, 2H), 5.10 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.07 (t, *J* = 2.0 Hz, 2H), 3.97 (dt, *J* = 6.1, 2.0 Hz, 2H), 3.80 (d, *J* = 7.3 Hz, 2H), 2.43 (s, 3H), 1.72 (d, *J* = 1.2 Hz, 3H), 1.67 (d, *J* = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 139.2, 136.4, 129.4, 128.1, 118.0, 83.5, 79.2, 50.9, 44.2, 35.8, 26.0, 21.7, 18.0. The spectral data is consistent with previously reported values.[22]

1-(1-Methoxycyclohexyl)-7-methyloct-6-en-1-yn-3-ol (S39). *n*-BuLi (1.6 M in hexanes, 3.6 mL, 5.8 mmol) was slowly added to a solution of alkyne **S1** (800 mg, 5.8 mmol) in THF (47 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of the freshly distilled aldehyde **S15** (500 mg, 4.5 mmol) in THF (3 mL) was introduced. After warming to room temperature, the mixture was stirred for 10 min before water (5 mL) and EtOAc (50 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 7:1 - 5:1) to yield the title compound as a colorless oil (647 mg, 58%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.14 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.44 (t, *J* = 6.5 Hz, 1H), 3.35 (s, 3H), 2.27 – 2.08 (m, 2H), 1.93 – 1.83 (m, 2H), 1.81 – 1.67 (m, 2H), 1.70 (q, *J* = 4.0 Hz, 3H), 1.70 – 1.62 (m, 2H), 1.63 (s, 3H), 1.61 – 1.46 (m, 5H), 1.35 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.8, 123.4, 87.2, 86.1, 74.0, 62.4, 50.8, 38.2, 36.9, 36.8, 25.9, 25.6, 24.0, 23.0, 17.8. IR (film) $\tilde{\nu}$ 3416 (br), 2933, 2857, 1446, 1079 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{26}O_2$ [M+Na]$^+$: calcd: 273.1825, found: 273.1823.

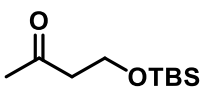
Dimethyl 2-(3-methylbut-2-en-1-yl)-2-(prop-2-yn-1-yl)malonate (S40). Cs_2CO_3 (1.45 g, 4.5 mmol) and 1-bromo-3-methyl-2-butene (0.67 mL, 5.8 mmol) were added to a solution of malonate **S3** (330 mg, 1.9 mmol) in acetone (12.8 mL). The mixture was stirred at reflux temperature for 18 h before it was allowed to cool to room temperature. After dilution with *tert*-butyl methyl ether (40 mL), the mixture was filtered through a pad of Celite and the filter cake was washed with *tert*-butyl methyl ether (100 mL). The combined filtrates were evaporated and the crude product was purified by flash chromatography (silica, hexanes/*tert*-butyl methyl ether 1:0 – 20:1 – 10:1 – 6:1) to give the title compound as a colorless oil (412 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$)

δ 4.89 (tdq, *J* = 7.3, 2.9, 1.4 Hz, 1H), 3.73 (s, 6H), 2.80 – 2.76 (m, 4H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.70 (q, *J* = 1.2 Hz, 3H), 1.66 – 1.64 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.6, 137.1, 117.1, 79.4, 71.3, 57.3, 52.9, 30.9, 26.2, 22.7, 18.1. The spectral data is consistent with previously reported values.[23]

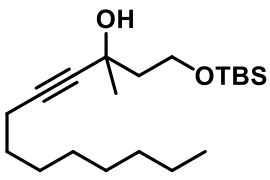
Dimethyl 2-(3-(1-hydroxycyclohexyl)prop-2-yn-1-yl)-2-(3-methylbut-2-en-1-yl)malonate (S41). LiHMDS (1 M in THF, 1.0 mL, 1.0 mmol) was slowly added to a solution of alkyne **S40** (200 mg, 0.84 mmol) in THF (8.2 mL) at −78 °C and the resulting mixture was stirred for 30 min at that temperature. Cyclohexanone (0.13 mL, 1.26 mmol) was slowly added at −78 °C and the resulting mixture warmed to room temperature. After 5 min, sat. NH_4Cl solution (1 mL) and EtOAc (20 mL) were added and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to give the title compound as a colorless oil (189 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (tp, *J* = 7.7, 1.5 Hz, 1H), 3.72 (s, 6H), 2.79 (s, 2H), 2.76 (d, *J* = 7.7 Hz, 2H), 1.87 – 1.72 (m, 5H), 1.70 (d, *J* = 1.4 Hz, 3H), 1.65 (d, *J* = 1.4 Hz, 3H), 1.58 – 1.44 (m, 5H), 1.23 – 1.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 136.9, 117.2, 87.1, 79.6, 68.9, 57.6, 52.8, 40.2, 31.0, 26.2, 25.3, 23.5, 22.9, 18.1. IR (film) $\tilde{\nu}$ 3468 (br), 2933, 2858, 1732, 1437 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{28}O_5$ [M+Na]$^+$: calcd: 359.1829, found: 359.1829.



4-((*tert*-Butyldimethylsilyl)oxy)butan-2-one (S42). Imidazole (3.2 g, 47.1 mmol) was added in portions to a stirred solution of 4-hydroxy-2-butanone (90%, 2.1 g, 21.5 mmol) and TBSCl (4.85 g, 32.2 mmol) in CH_2Cl_2 (83 mL) at 0 °C. The mixture was stirred at room temperature for 1 h before brine (20 mL) was added and the layers were separated. The aqueous phase was extracted with CH_2Cl_2 (2 x 100 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, pentane/Et_2O 20:1 – 10:1) to give the title compound as a colorless oil (4.05 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (t, *J* = 6.3 Hz, 1H), 2.61 (t, *J* = 6.3 Hz, 1H), 2.18 (s, 1H), 0.87 (s, 4H), 0.05 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.2, 59.0, 46.7, 31.0, 26.0, 18.4, -5.3. The spectral data is consistent with previously reported values.[24]

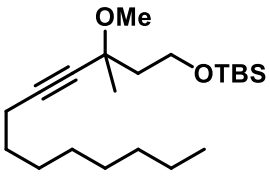


1-((*tert*-Butyldimethylsilyl)oxy)-3-methyltridec-4-yn-3-ol (S43). *n*-BuLi (1.6 M in hexanes, 7.04 mL, 11.3 mmol) was slowly added to a solution of 1-decyne (2.03 mL, 11.3 mmol) in THF (100 mL) at 0 °C. The solution was stirred for 20 min at 0 °C before ketone **S42** (1.9 g, 9.4 mmol) was introduced. After stirring at room temperature for 20 min, aq. sat. NH_4Cl (10 mL) and *tert*-butyl methyl ether (100 mL) were added. The layers were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 100 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to yield the title compound as a colorless oil (2.65 g, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.53 (br, 1H), 4.23 (ddd, *J* = 10.8, 10.0, 3.1 Hz, 1H), 3.87 (ddd, *J* = 10.1, 4.5, 3.4 Hz, 1H), 2.20 (t, *J* = 7.1 Hz, 2H), 1.95 (ddd, *J* = 14.1, 10.8, 4.5 Hz, 1H), 1.69 (dt, *J* = 14.1, 3.2 Hz, 1H), 1.56 – 1.45 (m, 2H), 1.46 (s, 3H), 1.42 – 1.33 (m, 2H), 1.33 – 1.22 (m, 8H), 0.91 (s, 9H), 0.88 (t, *J* = 7.1 Hz, 3H), 0.11 (s, 3H), 0.09 (s,

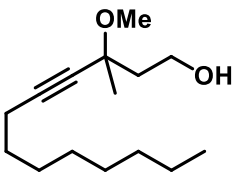


3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 84.1, 83.5, 68.8, 62.1, 43.6, 32.0, 30.9, 29.4, 29.3, 29.1, 29.0, 26.0, 22.8, 18.9, 18.3, 14.3, -5.4, -5.5. IR (film) $\tilde{\nu}$ 3503 (br), 2954, 2928, 2856, 1255, 1093 cm^{-1}. HRMS (ESI$^+$) for $C_{20}H_{40}O_2Si$ [M+Na]$^+$: calcd: 363.2690, found: 363.2691.

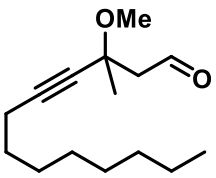
***tert*-Butyl((3-methoxy-3-methyltridec-4-yn-1-yl)oxy)dimethylsilane (S44)**. A solution of alcohol **S43** (1.8 g, 5.3 mmol) in THF (5 mL) was added to a stirred suspension of NaH (317 mg, 13.2 mmol) in THF (23 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (1.66 mL, 26.4 mmol) was added. After stirring for 1 h at room temperature, sat. NH_4Cl solution (10 mL), water (10 mL) and *tert*-butyl methyl ether (60 mL) were added to the mixture and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 100 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the title compound as a colorless oil (1.77 g, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.80 (ddd, *J* = 7.9, 6.6, 1.1 Hz, 2H), 3.31 (s, 3H), 2.20 (t, *J* = 7.0 Hz, 2H), 1.99 – 1.84 (m, 2H), 1.54 – 1.46 (m, 2H), 1.42 – 1.34 (m, 2H), 1.39 (s, 3H), 1.34 – 1.21 (m, 8H), 0.89 (s, 9H), 0.88 (t, *J* = 7.0 Hz, 3H), 0.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.2, 80.8, 72.5, 60.0, 51.2, 44.2, 32.0, 29.4, 29.2, 29.0, 28.9, 26.6, 26.1, 22.8, 18.8, 18.5, 14.3, -5.1, -5.1. IR (film) $\tilde{\nu}$ 2955, 2928, 2856, 1463, 1254, 1079 cm^{-1}. HRMS (ESI$^+$) for $C_{21}H_{42}O_2Si$ [M+Na]$^+$: calcd: 377.2846, found: 377.2846.



3-Methoxy-3-methyltridec-4-yn-1-ol (S45). TBAF (1 M in THF) was added to a solution of silyl ether **S44** (1.77 g, 4.98 mmol) in THF (32 mL) at room temperature. The mixture was stirred for 1 h before sat. NH_4Cl solution (5 mL), water (5 mL) and EtOAc (30 mL) were introduced. The aqueous phase was extracted with EtOAc (2 x 80 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 4:1) to give the title compound as a colorless oil (1.03 g, 86%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.98 (ddd, *J* = 11.6, 8.3, 3.5 Hz, 1H), 3.76 (ddd, *J* = 11.3, 6.0, 3.8 Hz, 1H), 3.34 (s, 3H), 2.74 (br, 1H), 2.21 (t, *J* = 7.1 Hz, 2H), 1.97 (ddd, *J* = 14.4, 8.3, 3.9 Hz, 1H), 1.86 (ddd, *J* = 14.4, 6.0, 3.5 Hz, 1H), 1.56 – 1.46 (m, 2H), 1.42 (s, 3H), 1.38 (m, 2H), 1.33 – 1.22 (m, 8H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 87.3, 80.2, 75.0, 60.4, 51.3, 44.1, 32.0, 29.3, 29.2, 29.0, 28.9, 26.1, 22.8, 18.7, 14.3. IR (film) $\tilde{\nu}$ 3424 (br), 2927, 2856, 1464, 1078 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{28}O_2$ [M+Na]$^+$: calcd: 263.1981, found: 263.1981.

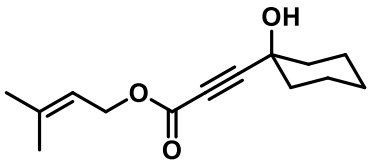


3-Methoxy-3-methyltridec-4-ynal (S46). $NaHCO_3$ (874 mg, 10.4 mmol) and Dess-Martin periodinane (1.06 g, 2.5 mmol) were added to a solution of alcohol **S45** (500 mg, 2.08 mmol) in wet CH_2Cl_2 (19 mL) at 0 °C. The mixture was stirred at room temperature for 30 min before sat. $Na_2S_2O_3$ solution (7 mL) and water (4 mL) were introduced. The layers were separated, the aqueous phase was extracted with CH_2Cl_2 (2 x 60 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1). The product was obtained as a colorless oil (421 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.85 (t, *J* = 2.9 Hz, 1H), 3.37 (s, 3H), 2.64 (dd, *J* = 15.3, 3.0 Hz, 1H), 2.58 (dd, *J* = 15.3, 2.8 Hz, 1H), 2.22 (t, *J* = 7.1 Hz, 2H), 1.51 (m, 2H), 1.47 (s, 3H), 1.42 – 1.33 (m, 2H), 1.27 (m, 8H), 0.88 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$)

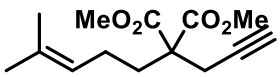


δ 201.9, 88.4, 79.5, 70.9, 54.5, 51.6, 32.0, 29.3, 29.2, 29.0, 28.7, 26.5, 22.8, 18.7, 14.3. IR (film) $\tilde{\nu}$ 2928, 2856, 1726, 1463, 1075 cm^{-1}. HRMS (ESI^+) for $C_{15}H_{26}O_2$ $[M+Na]^+$: calcd: 261.1825, found: 261.1827.

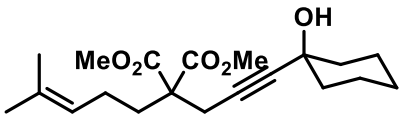
3-Methylbut-2-en-1-yl 3-(1-hydroxycyclohexyl)propiolate (S47). LiHMDS (1 M in THF, 1.7 mL, 1.7 mmol) was slowly added to a solution of alkyne **S16** (200 mg, 1.45 mmol) in THF (14.1 mL) at −78 °C and the resulting mixture was stirred for 30 min at that temperature. Cyclohexanone (0.23 mL, 2.17 mmol) was slowly added at −78 °C to the mixture allowed to reach room temperature. After 5 min sat., NH_4Cl solution (1 mL) and EtOAc (20 mL) were introduced, the layers were separated, the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, the solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 7:1 – 5:1) to give the title compound as a colorless oil (312 mg, 91%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.30 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.60 (d, *J* = 7.4 Hz, 2H), 1.92 – 1.84 (m, 2H), 1.70 (d, *J* = 1.3 Hz, 3H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.65 – 1.41 (m, 7H), 1.28 – 1.15 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.7, 140.4, 117.6, 90.3, 76.0, 68.5, 62.9, 39.1, 25.8, 24.9, 22.8, 18.1. IR (film) $\tilde{\nu}$ 3401 (br), 2935, 2860, 2227, 1709, 1228 cm^{-1}. HRMS (ESI^+) for $C_{14}H_{20}O_3$ $[M+Na]^+$: calcd: 259.1346, found: 259.1304.



Dimethyl 2-(4-methylpent-3-en-1-yl)-2-(prop-2-yn-1-yl)malonate (S48). Cs_2CO_3 (3.4 g, 10.5 mmol) and 5-bromo-2-methyl-2-pentene (1.40 mL, 10.5 mmol) were added to a solution of malonate **S3** (594 mg, 3.5 mmol) in acetone (23.1 mL). The mixture was stirred at reflux temperature for 18 h before it was cooled to room temperature and diluted with *tert*-butyl methyl ether (40 mL). The mixture was filtered through a pad of Celite and the filter cake was washed with *tert*-butyl methyl ether (100 mL). The combined filtrates were evaporated and the residue was purified by flash chromatography (silica, hexanes/*tert*-butyl methyl ether 40:1 – 20:1 – 15:1 – 10:1) to give the title compound as a colorless oil (740 mg, 84%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.09 (tdq, *J* = 6.9, 2.6, 1.3 Hz, 1H), 3.73 (s, 6H), 2.85 (d, *J* = 2.7 Hz, 2H), 2.12 – 2.06 (m, 2H), 2.00 (t, *J* = 2.7 Hz, 1H), 1.93 – 1.85 (m, 2H), 1.67 (q, *J* = 1.3 Hz, 3H), 1.58 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.8, 133.0, 122.9, 79.0, 71.4, 56.8, 52.9, 32.2, 25.8, 23.0, 22.9, 17.7. The spectral data is consistent with previously reported values.[25]

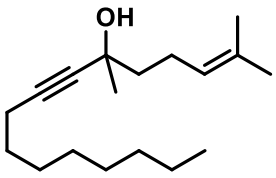


Dimethyl 2-(3-(1-hydroxycyclohexyl)prop-2-yn-1-yl)-2-(4-methylpent-3-en-1-yl)malonate (S49). LiHMDS (1 M in THF, 1.9 mL, 1.9 mmol) was slowly added to a solution of alkyne **S48** (400 mg, 1.59 mmol) in THF (15.4 mL) at −78 °C and the resulting mixture was stirred for 30 min at this temperature. Cyclohexanone (0.25 mL, 2.38 mmol) was slowly added at −78 °C and the resulting mixture was warmed to room temperature. After 5 min, sat. NH_4Cl solution (1 mL) and EtOAc (20 mL) were introduced and the layers were separated, the aqueous phase was extracted with EtOAc (3 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1). The product was obtained as a colorless oil (351 mg, 63%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.08 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 3.72 (s, 6H), 2.87 (s, 2H), 2.11 – 2.03 (m, 2H), 1.93 – 1.77 (m, 5H), 1.70 – 1.63 (m, 5H), 1.58

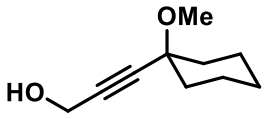


(d, *J* = 1.4 Hz, 3H), 1.50 (qd, *J* = 10.6, 9.6, 3.2 Hz, 5H), 1.25 – 1.13 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 132.9, 123.0, 87.1, 79.2, 68.9, 57.2, 52.8, 40.3, 32.3, 25.8, 25.3, 23.5, 23.2, 22.9, 17.7. IR (film) $\tilde{\nu}$ 3498 (br), 2933, 2857, 1733, 1438, 1171 cm^{-1}. HRMS (ESI$^+$) for $C_{20}H_{30}O_5$ [M+Na]$^+$: calcd: 373.1985, found: 373.1983.

2,6-Dimethylhexadec-2-en-7-yn-6-ol (S50). *n*-BuLi (1.6 M in hexanes, 1.78 mL, 2.85 mmol) was slowly added to a solution of 1-decyne (0.51 mL, 2.85 mmol) in THF (25 mL) at 0 °C. The solution was stirred for 20 min at 0 °C before 6-methyl-5-hepten-2-one (300 mg, 2.38 mmol) was introduced. After stirring at room temperature for 20 min, sat. NH_4Cl solution (2 mL) and *tert*-butyl methyl ether (25 mL) were added, the layers were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 25 mL). The combined organic layers were washed with brine and dried over $MgSO_4$, the solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless oil (546 mg, 87%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.20 – 5.14 (m, 1H), 2.32 – 2.22 (m, 1H), 2.19 (t, *J* = 7.1 Hz, 2H), 1.85 (br, 1H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.68 – 1.66 (m, 2H), 1.65 (d, *J* = 1.2 Hz, 3H), 1.54 – 1.46 (m, 2H), 1.45 (s, 3H), 1.42 – 1.33 (m, 2H), 1.32 – 1.22 (m, 9H), 0.91 – 0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 124.2, 84.2, 84.0, 68.7, 43.8, 32.0, 30.4, 29.3, 29.2, 29.0, 28.9, 25.9, 24.0, 22.8, 18.8, 17.8, 14.3. IR (film) $\tilde{\nu}$ 3384 (br), 2925, 2856, 1455, 1375 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{32}O$ [M+Na]$^+$: calcd: 287.2345, found: 287.2345.

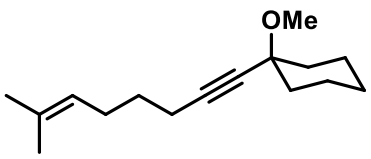


3-(1-Methoxycyclohexyl)prop-2-yn-1-ol (S51). *n*-BuLi (1.6 M in hexanes, 2.94 mL, 4.7 mmol) was slowly added to a solution of alkyne **S1** (500 mg, 3.6 mmol) in THF (38 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before powdered paraformaldehyde (141 mg, 4.7 mmol) was introduced. After stirring at room temperature for 18 h the reaction was quenched with water (10 mL) and EtOAc (50 mL). The layers were separated and the aqueous phase was extracted with EtOAc (2 x 50 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 4:1) to yield the title compound as a colorless oil (371 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.33 (s, 2H), 3.35 (s, 3H), 1.92 – 1.83 (m, 2H), 1.70 – 1.44 (m, 8H), 1.37 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 87.0, 84.1, 73.9, 51.3, 50.8, 36.7, 25.5, 22.8. IR (film) $\tilde{\nu}$ 3423 (br), 2935, 2858, 1448, 1077 cm^{-1}. HRMS (ESI$^+$) for $C_{10}H_{16}O_2$ [M+Na]$^+$: calcd: 191.1042, found: 191.1042.



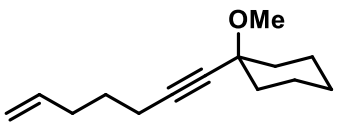
SUBSTRATES

1-Methoxy-1-(7-methyloct-6-en-1-yn-1-yl)cyclohexane (1a). *n*-BuLi (1.6 M in hexanes, 1.08 mL, 1.74 mmol) was slowly added to a solution of alkyne **S1** (200 mg, 1.45 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S13** (307 mg, 1.74 mmol) in THF (3.3 mL) and DMPU (0.9 mL) was added. The mixture was warmed to room temperature and stirring was continued for 18 h. Sat. NH_4Cl solution (2 mL), *tert*-butyl methyl ether (10 mL) and water (2 mL) were added and the layers were

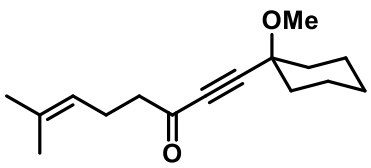


separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 80:1 – 40:1) to give the product as a colorless oil (183 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (tdq, *J* = 7.2, 2.9, 1.5 Hz, 1H), 3.35 (s, 3H), 2.24 (d, *J* = 7.0 Hz, 2H), 2.09 (q, *J* = 7.3 Hz, 2H), 1.90 – 1.81 (m, 2H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.65 – 1.60 (m, 2H), 1.62 (s, 3H), 1.59 – 1.47 (m, 7H), 1.26 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 123.8, 86.6, 81.2, 74.2, 50.6, 37.2, 29.3, 27.3, 25.9, 25.7, 23.1, 18.4, 17.8. IR (film) $\tilde{\nu}$ 2932, 2857, 1446, 1092 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{26}O$ [M+Na]$^+$: calcd: 257.1876, found: 257.1877.

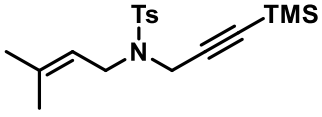
1-(Hept-6-en-1-yn-1-yl)-1-methoxycyclohexane (1b). *n*-BuLi (2.26 mL, 3.6 mmol, 1.6 M in hexane) was added at 0 °C to a solution of alkyne **S1** (500 mg, 3.6 mmol) in THF (16 mL) and HMPA (7 mL). After stirring for 1 h at 0 °C, the mixture was cooled to −78 °C and 5-bromo-1-pentene (0.24 mL, 1.8 mmol) was slowly introduced. The mixture was allowed to reach ambient temperature overnight. The reaction was quenched with NH_4Cl (sat. aq. 20 mL), the aqueous phase was extracted with Et_2O (3 x 10 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2, 2% EtOAc in hexane) to give the title compound as a colorless oil (370 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.10 – 4.92 (m, 2H), 3.34 (s, 3H), 2.25 (t, *J* = 7.1 Hz, 2H), 2.23 – 2.11 (m, 2H), 1.91 – 1.80 (m, 2H), 1.70 – 1.41 (m, 9H), 1.34 – 1.21 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.1, 115.3, 86.1, 81.5, 74.2, 50.6, 37.2, 32.9, 28.3, 25.7, 23.1, 18.2. IR (film) $\tilde{\nu}$ 2935, 2857, 1446, 1292, 1092, 1080, 921, 910 cm^{-1}. ESI-MS calcd for $C_{14}H_{22}O$ [M+Na]$^+$: calcd: 229.1563, found: 229.1565.



1-(1-Methoxycyclohexyl)-7-methyloct-6-en-1-yn-3-one (4). $NaHCO_3$ (336 mg, 4.0 mmol) and Dess-Martin periodinane (508 mg, 1.2 mmol) were added to a solution of alcohol **S39** (200 mg, 0.8 mmol) in wet CH_2Cl_2 (7.4 mL) at 0 °C. The mixture was stirred at room temperature for 30 min before aq. sat. $Na_2S_2O_3$ (3 mL) and water (3 mL) were introduced. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 30:1 – 20:1) to give the product as a colorless oil (193 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (tdq, *J* = 7.2, 2.9, 1.5 Hz, 1H), 3.38 (s, 3H), 2.60 (t, *J* = 7.2 Hz, 2H), 2.36 (q, *J* = 7.5 Hz, 2H), 1.99 – 1.88 (m, 2H), 1.70 – 1.61 (m, 3H), 1.68 (q, *J* = 1.4 Hz, 3H), 1.62 (s, 3H), 1.59 – 1.45 (m, 4H), 1.38 – 1.28 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.7, 133.5, 122.1, 93.2, 85.1, 74.0, 51.4, 46.0, 36.2, 25.8, 25.4, 23.0, 22.6, 17.8. IR (film) $\tilde{\nu}$ 2934, 2859, 2204, 1676, 1120 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{24}O_2$ [M+Na]$^+$: calcd: 271.1668, found: 271.1668.

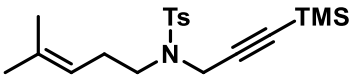


4-Methyl-N-(3-methylbut-2-en-1-yl)-N-(3-(trimethylsilyl)prop-2-yn-1-yl)benzenesulfonamide (27a). *n*-BuLi (1.6 M in hexanes, 1.00 mL, 1.60 mmol) was added to a stirred solution of alkyne **S14** (348 mg, 1.25 mmol) in THF (13.2 mL) at 0 °C and the mixture was stirred for 20 min at that temperature before TMSCl (0.48 mL, 3.76 mmol) was introduced. The mixture was allowed to reach room temperature and stirring was



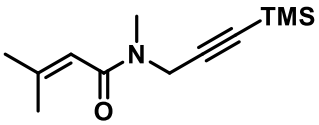
continued for 30 min before sat. NH_4Cl solution and EtOAc (20 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 10:1). The title compound was obtained as a colorless solid (225 mg, 51%). ^{1}H NMR (400 MHz, , $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.30 – 7.27 (m, 2H), 5.11 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.08 (s, 2H), 3.81 (d, *J* = 7.2 Hz, 1H), 2.42 (s, 3H), 1.73 (q, *J* = 1.1 Hz, 3H), 1.68 – 1.66 (m, 3H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 139.0, 136.3, 129.6, 128.0, 118.2, 98.6, 90.6, 44.1, 36.5, 26.0, 21.7, 18.0, -0.3. IR (film) ṽ 2961, 2926, 2175, 1342, 1161 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{27}NO_2SSi$ [M+Na]$^+$: calcd 372.1424, found 372.1431.

4-Mmethyl-N-(4-methylpent-3-en-1-yl)-N-(3-(trimethylsilyl)prop-2-yn-1-yl)benzenesulfonamide (27b).



n-BuLi (1.6 M in hexanes, 1.00 mL, 1.65 mmol) was added to a stirred solution of alkyne **S10** (400 mg, 1.37 mmol) in THF (14.4 mL) at 0 °C. the mixture was stirred for 30 min at that temperature before TMSCl (0.52 mL, 4.12 mmol) was introduced. The mixture was allowed to reach room temperature and stirred for 30 min before sat. NH_4Cl solution and EtOAc (20 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1). The title compound was obtained as a colorless solid (325 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.30 – 7.25 (m, 2H), 5.09 (tdq, *J* = 7.3, 3.0, 1.5 Hz, 1H), 4.15 (s, 2H), 3.19 – 3.12 (m, 2H), 2.41 (s, 3H), 2.26 (q, *J* = 7.3 Hz, 2H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.62 (s, 3H), -0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 136.2, 134.7, 129.6, 127.9, 120.1, 98.2, 90.9, 46.1, 37.4, 26.8, 25.8, 21.7, 18.0, -0.3. IR (film) ṽ 2962, 2922, 2176, 1324, 1161 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{29}NO_2SSi$ [M+Na]$^+$: calcd 386.1580, found 386.1582.

***N*,3-Dimethyl-N-(3-(trimethylsilyl)prop-2-yn-1-yl)but-2-enamide (31).**

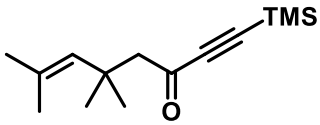


3,3-Dimethylacryloyl chloride (0.81 mL, 7.24 mmol) was added to a stirred solution of *N*-methylpropargylamine (500 mg, 7.24 mmol), Et_3N (2.0 mL, 14.5 mmol) and DMAP (44 mg, 0.36 mmol) in CH_2Cl_2 (30 mL) at 0 °C. The mixture was allowed to reach room temperature and stirred for 2 h before water (10 mL) and CH_2Cl_2 (20 mL) were added. The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue purified by flash chromatography (silica, hexanes/EtOAc 4:1 – 2:1) to yield the corresponding amide as a pale yellow oil (931 mg, 85%) which was directly used in the next step.

LiHMDS (1 M in THF, 3.73 mL, 3.73 mmol) was added to a solution of this amide (460 mg, 3.04 mmol) in THF (30 mL) at – 78 °C and the mixture was stirred for 30 min at the same temperature before TMSCl (1.16 mL, 9.13 mmol) was added. The mixture was allowed to reach room temperature and stirring was continued for 30 min before sat. NH_4Cl solution (20 mL) and EtOAc (10 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 4:1) to give the title compound as a colorless oil (554 mg, 82%). ^{1}H NMR (500 MHz, CD_3CN, 70 °C) δ 5.86 (hept, *J* = 1.4 Hz, 1H), 4.16 (s (br), 3H), 2.99 (s (br), 3H), 1.89

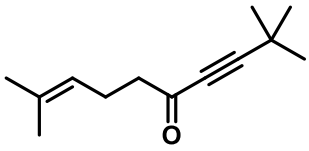
(d, *J* = 1.3 Hz, 3H), 1.86 (d, *J* = 1.5 Hz, 3H), 0.17 (s, 9H). ^{13}C NMR (500 MHz, CD_3CN, 70 °C) δ 169.0, 147.8, 119.1, 103.0, 89.4, 37.7, 35.1, 26.4, 20.5, 0.3. IR (film) ṽ 2960, 2176, 1627, 1395, 1249 cm^{-1}. HRMS (EI$^+$) for $C_{12}H_{21}NOSi$ [M+Na]$^+$: calcd 223.1387, found 223.1339.

5,5,7-Trimethyl-1-(trimethylsilyl)oct-6-en-1-yn-3-one (33). *n*-BuLi (1.6 M, 1.13 mL, 1.81 mmol) was added



to a solution of trimethylsilylacetylene (207 mg, 2.11 mmol) in THF (6.1 mL) at 0 °C and the resulting mixture was stirred for 30 min at that temperature. A solution of Weinreb amide **18** (300 mg, 1.51 mmol) in THF (1 mL) was added and the mixture was stirred for 1 h at room temperature before sat. NH_4Cl solution was introduced. The mixture was extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 100:1 - 50:1) to yield the title compound as a colorless oil (109 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (hept, *J* = 1.4 Hz, 1H), 2.67 (s, 2H), 1.73 (d, *J* = 1.4 Hz, 3H), 1.68 (d, *J* = 1.5 Hz, 3H), 1.23 (s, 6H), 0.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.3, 132.3, 132.1, 103.7, 97.2, 57.6, 35.6, 29.5, 28.2, 19.3, -0.6. IR (film) ṽ 2963, 2927, 1664, 1252, 1078 cm^{-1}. HRMS (ESI$^+$) for $C_{14}H_{24}OSi$ [M+Na]$^+$: calcd 237.1669, found 237.1670.

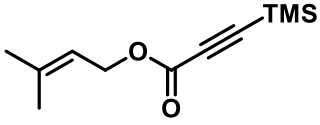
2,2,9-Trimethyldec-8-en-3-yn-5-one (35). *n*-BuLi (1.6 M in hexanes, 1.23 mL, 2.03 mmol) was slowly added



to a solution of 3,3-dimethyl-1-butyne (195 mg, 2.37 mmol) in THF (13.7 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of aldehyde **S15** (250 mg, 1.69 mmol) in THF (1 mL) was introduced. The mixture was stirred for 5 min before sat. NH_4Cl solution (4 mL) and EtOAc (20 mL) were added. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 30 mL). The combined organic layers were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1) to yield the corresponding secondary alcohol (216 mg, 66%) which was immediately used in the next step.

$NaHCO_3$ (443 mg, 5.28 mmol) and Dess-Martin periodinane (671 mg, 1.58 mmol) were added to a solution this alcohol (205 mg, 1.06 mmol) in wet CH_2Cl_2 (10.0 mL) at 0 °C. The mixture was stirred at room temperature for 30 min before aq. sat. $Na_2S_2O_3$ (3 mL) and water (3 mL) were added. The layers were separated and the aqueous phase was extracted with methyl *tert*-butyl ether (2 x 25 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 50:1) to give the title compound as a colorless oil (169 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (tdq, *J* = 7.2, 2.9, 1.5 Hz, 1H), 2.57 – 2.51 (m, 2H), 2.38 – 2.30 (m, 2H), 1.68 (q, *J* = 1.3 Hz, 3H), 1.63 (s, 3H), 1.28 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 133.2, 122.4, 101.8, 79.4, 45.9, 30.3, 27.9, 25.8, 23.1, 17.8. IR (film) ṽ 2971, 2929, 2205, 1673, 1266, 1124 cm^{-1}. HRMS (CI$^+$) for $C_{13}H_{20}O$ [M+H]$^+$: calcd 193.1587, found 193.1588.

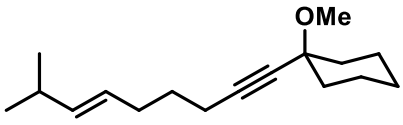
3-Methylbut-2-en-1-yl 3-(trimethylsilyl)propiolate (37). LiHMDS (1 M in THF, 12.9 mL, 12.9 mL) was added



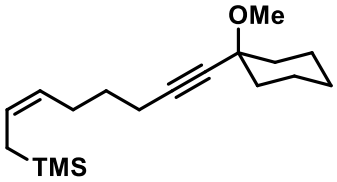
to a solution of alkyne **S16** (1.49 g, 10.8 mmol) in THF (100 ml) at – 78 °C and the mixture was stirred for 30 min at that temperature before TMSCl (4.10 mL, 32.3 mmol) was added. The mixture was allowed to reach room temperature and stirring was continued for 30 min before sat. NH_4Cl solution

(20 mL) and EtOAc (50 mL) were introduced. The layers were separated and the aqueous phase was extracted with EtOAc (2 x 100 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1).The title compound was obtained as a colorless oil (2.02 g, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.66 (dt, *J* = 7.4, 0.8 Hz, 2H), 1.76 (m, 3H), 1.72 – 1.70 (m, 3H), 0.23 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.3, 140.6, 117.7, 94.8, 93.9, 62.9, 25.9, 18.2, -0.7. IR (film) ṽ 2965, 2176, 1708, 1213 cm^{-1}. HRMS (ESI$^+$) for $C_{11}H_{18}O_2Si$ [M+Na]$^+$: calcd 233.0968, found 233.0969.

(*E*)-1-Methoxy-1-(8-methylnon-6-en-1-yn-1-yl)cyclohexane (1c). *n*-BuLi (1.6 M in hexanes, 1.08 mL, 1.74 mmol) was slowly added to a solution of alkyne **S1** (200 mg, 1.45 mmol) in THF (5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S20** (332 mg, 1.74 mmol) in THF (3.3 mL) and DMPU (0.9 mL) was introduced. The mixture was stirred at room temperature for 18 h before sat. NH_4Cl solution (2 mL), *tert*-butyl methyl ether (10 mL) and water (2 mL) were added. The layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 80:1 – 40:1) to give the product as a colorless oil (216 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (ddt, *J* = 15.3, 6.1, 1.0 Hz, 1H), 5.32 (dtd, *J* = 15.3, 6.4, 0.9 Hz, 1H), 3.35 (s, 3H), 2.23 (t, *J* = 7.1 Hz, 2H), 2.24 (m, 1H), 2.09 (m, 2H), 1.90 – 1.82 (m, 2H), 1.70 – 1.46 (m, 9H), 1.28 (m, 1H), 0.96 (d, *J* = 6.7 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.8, 126.1, 86.4, 81.3, 74.2, 50.6, 37.2, 31.8, 31.2, 29.0, 25.7, 23.1, 22.8, 18.2. IR (film) ṽ 2932, 2858, 2822, 1448, 1093 cm^{-1}. HRMS (ESI$^+$) for $C_{17}H_{28}O$ [M+Na]$^+$: calcd: 271.2032, found: 271.2032.



(*Z*)-(8-(1-Methoxycyclohexyl)oct-2-en-7-yn-1-yl)trimethylsilane (1d) (*E*/*Z* = 1:6). PhLi (1.8 M in dibutyl ether, 0.76 mL, 1.37 mmol) was slowly added to a solution of (2-trimethylsilylethyl)triphenylphosphonium iodide (671 mg, 1.37 mmol) in THF (5.8 mL) at room temperature. The resulting mixture was stirred for 1 h before aldehyde **S22** (150 mg, 0.72 mmol) in THF (1 mL) was introduced. Stirring was continued for 18 h at ambient temperature before sat. NH_4Cl solution (3 mL) and methyl *tert*-butyl ether (10 mL) were added. The layers were separated and the aqueous phase was extracted with methyl *tert*-butyl ether (2 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 100:1 – 50:1) to obtain the title compound as a colorless oil (dr = 6:1, 158 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) major: δ 5.48 – 5.36 (m, 1H), 5.29 – 5.18 (m, 1H), 3.35 (s, 3H), 2.25 (t, *J* = 7.0 Hz, 2H), 2.11 (qd, *J* = 7.3, 1.7 Hz, 2H), 1.90 – 1.80 (m, 2H), 1.69 – 1.45 (m, 11H), 1.33 – 1.23 (m, 1H), -0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) major: δ 126.6, 126.5, 86.5, 81.3, 74.2, 50.6, 37.2, 29.2, 26.3, 25.7, 23.1, 18.6, 18.5, −1.7. IR (film) ṽ 2933, 2857, 1447, 1247, 1093 cm^{-1}. HRMS (CI) for $C_{18}H_{32}OSi$ [M+H]$^+$: calcd 293.2295, found 293.2292.



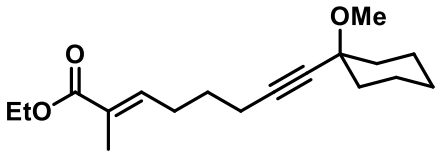
1-Methoxy-1-(7-methoxyhept-6-en-1-yn-1-yl)cyclohexane (1e). PhLi (1.8 M in *n*-Bu_2O, 0.41 mL, 0.73 mmol) was slowly added to a solution of (methoxymethyl)triphenylphosphonium chloride (263 mg, 0.77 mmol) in Et_2O (3.2 mL) at 0 °C. The mixture was stirred for 10 min at 0 °C before a solution of aldehyde **S22** (80 mg, 0.38 mmol) in Et_2O (1 mL) was introduced. The mixture was stirred at room temperature for 10 min before sat. NH_4Cl solution (1 mL) and *tert*-butyl methyl ether (5 mL) were added. The layers were separated and the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the title compound as a pale yellow oil (44 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ (mixture of *E*/*Z* isomers: 54/46) 6.30 (dt, *J* = 12.7, 1.2 Hz, 0.54H), 5.90 (dt, *J* = 6.2, 1.4 Hz, 0.46H), 4.70 (dt, *J* = 12.6, 7.4 Hz, 0.54H), 4.33 (td, *J* = 7.4, 6.2 Hz, 0.46H), 3.57 (s, 1.08H), 3.51 (s, 1.62H), 3.35 (s, s, 3H), 2.24 (t, *J* = 7.1 Hz, 2H), 2.17 (qd, *J* = 7.4, 1.5 Hz, 0.92H), 2.05 (qd, *J* = 7.4, 1.2 Hz, 1.08H), 1.90 – 1.80 (m, 2H), 1.68 – 1.45 (m, 9H), 1.33 – 1.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.8, 105.9, 102.0, 86.6, 86.2, 81.4, 81.2, 74.2, 74.2, 59.6, 56.1, 50.6, 37.2, 37.2, 30.0, 29.3, 26.9, 25.8, 25.7, 23.3, 23.1, 18.4, 18.0. IR (film) $\tilde{\nu}$ 2932, 2856, 1656, 1448, 1210, 1110, 1090 cm^{-1}. HRMS (EI) for $C_{15}H_{24}O_2$ $[M]^+$: calcd: 236.1771, found: 236.1773.

1-(7,7-Difluorohept-6-en-1-yn-1-yl)-1-methoxycyclohexane (1f). A solution of aldehyde **S22** (110 mg, 0.53 mmol) in DMF (2.3 mL) was added to solid PPh_3 (277 mg, 1.06 mmol) and sodium chlorodifluoroacetate (161 mg, 1.06 mmol). The mixture was stirred at 100 °C for 10 min before it was allowed to reach room temperature. Water (3 mL) and *tert*-butyl methyl ether (10 mL) were added and the layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 10 mL) and the combined organic layers were washed with brine (2 mL), H_2O_2 solution (6% in water, 4 mL) and again brine. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 50:1) to give the title compound as a colorless oil (62 mg, 48%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (dtd, *J* = 25.3, 7.9, 2.5 Hz, 1H), 3.34 (s, 3H), 2.27 (t, *J* = 7.0 Hz, 2H), 2.11 (qt, *J* = 7.6, 1.8 Hz, 2H), 1.89 – 1.78 (m, 2H), 1.71 – 1.43 (m, 9H), 1.34 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.5 (dd, *J* = 287.5, 285.1 Hz), 85.3, 81.7, 77.3 (d, *J* = 21.6 Hz), 74.0, 50.4, 37.0, 28.6 (t, *J* = 2.5 Hz), 25.5, 22.9, 21.3 (d, *J* = 4.5 Hz), 19.0. ^{19}F NMR (282 MHz, $CDCl_3$) δ -88.8 (d, *J* = 47.3 Hz), -91.3 (d, *J* = 47.4 Hz). IR (film) $\tilde{\nu}$ 2935, 2859, 1746, 1448, 1229, 1092 cm^{-1}. HRMS (EI) for $C_{14}H_{20}F_2O$ $[M\text{-}H]^+$: calcd: 241.1398, found: 241.1398.

1-(7-Chlorohept-6-en-1-yn-1-yl)-1-methoxycyclohexane (1g). *n*-BuLi (1.6 M in hexanes, 1.08 mL, 1.73 mmol) was slowly added to a solution of (chloromethyl)triphenylphosphonium chloride (666 mg, 1.92 mmol) in THF (9.3 mL) at 0 °C. The mixture was stirred for 30 min at room temperature before a solution of aldehyde **S22** (200 mg, 0.96 mmol) in THF (1 mL) was introduced. The mixture was stirred at room temperature for 1 h before sat. NH_4Cl solution (1 mL) and *tert*-butyl methyl ether (10 mL) were added. The layers were separated and the aqueous phase

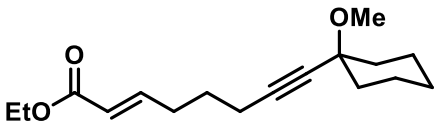
was extracted with *tert*-butyl methyl ether (3 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 40:1) to give the title compound as a pale colorless oil (183 mg, 79%, *E*/*Z* = 1 : 0.66). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.05 (dt, *J* = 7.1, 1.5 Hz, 0.66H), 5.98 (dt, *J* = 13.3, 1.1 Hz, 1H), 5.89 (dt, *J* = 13.2, 7.1 Hz, 1H), 5.77 (q, *J* = 7.2 Hz, 0.66H), 3.35 (s, 2H), 3.34 (s, 3H), 2.36 (qd, *J* = 7.4, 1.5 Hz, 1.5H), 2.27 (dt, *J* = 8.0, 7.0 Hz, 4H), 2.19 (qd, *J* = 7.4, 1.1 Hz, 2.5H), 1.85 (m, 4H), 1.71 – 1.43 (m, 18H), 1.35 – 1.17 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.0, 130.9, 118.9, 117.7, 85.8, 85.5, 82.0, 81.8, 74.2, 74.2, 50.6, 50.6, 37.2, 37.2, 30.0, 28.1, 27.8, 26.4, 25.7, 25.7, 23.1, 18.5, 18.1. IR (film) ṽ 2933, 2857, 1630, 1447, 1090 cm^{-1}. HRMS (CI$^+$) for $C_{14}H_{21}ClO$ $[M+H]^+$: calcd 241.1353, found 241.1351.

Ethyl (*E*)-8-(1-methoxycyclohexyl)-2-methyloct-2-en-7-ynoate (1h). In a two-neck round-bottom flask



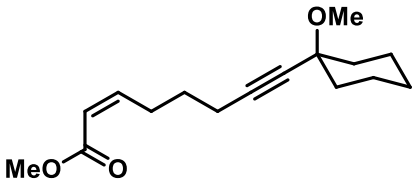
equipped with a reflux condenser was added (1-ethoxycarbonylethylidene)-triphenylphosphorane (502 mg, 1.39 mmol) to a solution of aldehyde **S22** (170 mg, 0.82 mmol) in THF (4.6 mL) at room temperature. The resulting mixture was stirred for 3 h at 60 °C. Sat. NH_4Cl solution (1 ml) and EtOAc (5 mL) were added and the layers separated. The aqueous phase was extracted with EtOAc (2 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 40:1 – 20:1) to yield the title compound as a colorless oil (156 mg, 65%, *E*/*Z* = 20:1). Diethyl 2,3-dimethylfumarate impurities were removed by bulb-to-bulb distillation (70 – 90 °C, 1 x 10^{-2} mbar). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.74 (tq, *J* = 7.5, 1.5 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.34 (s, 3H), 2.35 – 2.24 (m, 4H), 1.91 – 1.79 (m, 5H), 1.72 – 1.43 (m, 9H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 141.1, 128.8, 85.6, 81.9, 74.2, 60.6, 50.6, 37.1, 28.0, 27.8, 25.7, 23.1, 18.5, 14.5, 12.5. IR (film) ṽ 2933, 2858, 1709, 1447, 1255, 1081 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{28}O_3$ $[M+Na]^+$: calcd 315.1931, found 315.1931.

Ethyl (*E*)-8-(1-methoxycyclohexyl)oct-2-en-7-ynoate (1i). (Carbethoxymethylene)triphenylphosphorane



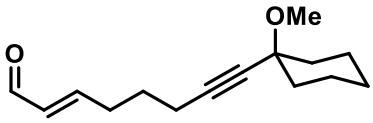
(376 mg, 1.08 mmol) was added to a solution of aldehyde **S22** (150 mg, 0.72 mmol) in $CHCl_3$ (4.0 mL) at room temperature and the resulting mixture was stirred for 18 h. Sat. NH_4Cl solution (1 mLl) and EtOAc (4 mL) were added and the layers were separated. The aqueous phase was extracted with EtOAc (2 x 10 mL) and the combined organic layers wre washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 15:1 – 10:1) to yield the title compound as a colorless oil (144 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (dt, *J* = 15.7, 7.0 Hz, 1H), 5.84 (dt, *J* = 15.7, 1.6 Hz, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.34 (s, 3H), 2.33 (qd, *J* = 7.2, 1.7 Hz, 2H), 2.28 (t, *J* = 6.9 Hz, 2H), 1.89 – 1.78 (m, 2H), 1.73 – 1.43 (m, 10H), 1.28 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.7, 148.2, 122.1, 85.4, 82.1, 74.1, 60.4, 50.6, 37.1, 31.3, 27.4, 25.7, 23.1, 18.3, 14.4. IR (film) ṽ 2933, 2857, 1719, 1655, 1446, 1091 cm^{-1}. HRMS (CI) for $C_{17}H_{26}O_3$ $[M]^+$: calcd 278.1876, found 278.1876.

Methyl (*Z*)-8-(1-methoxycyclohexyl)oct-2-en-7-ynoate (1j). 18-Crown-6 (545 mg, 2.06 mmol) was added



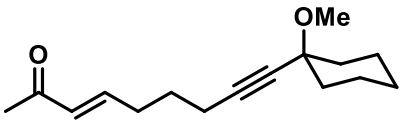
to a solution of KHMDS (239 mg, 1.20 mmol) in THF (4.2 mL) at room temperature. The solution was cooled to –78 °C before bis(2,2,2-trifluoroethyl) (methoxycarbonylmethyl)phosphonate (0.25 mL, 1.20 mmol) was added dropwise and stirring was continued for 20 min at that temperature. A solution of aldehyde **S22** (179 mg, 0.86 mmol) in THF (1 mL) was slowly introduced and the mixture stirred for 3 h at –78 °C before sat. NH_4Cl solution and EtOAc (3 mL) were added. The layers were separated and the aqueous phase extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 15:1 – 10:1) to yield the title compound as a colorless oil (129 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.24 (dt, *J* = 11.5, 7.5 Hz, 1H), 5.80 (dt, *J* = 11.5, 1.7 Hz, 1H), 3.70 (s, 3H), 3.34 (s, 3H), 2.76 (qd, *J* = 7.5, 1.7 Hz, 2H), 2.29 (t, *J* = 7.2 Hz, 2H), 1.89 – 1.79 (m, 2H), 1.73 – 1.58 (m, 4H), 1.51 (h, *J* = 9.7 Hz, 5H), 1.32 – 1.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.8, 149.6, 120.1, 85.8, 81.7, 74.1, 51.2, 50.6, 37.1, 28.5, 28.4, 25.7, 23.0, 18.6. IR (film) ṽ 2933, 2857, 1722, 1646, 1438, 1176 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{24}O_3$ [M+Na]$^+$: calcd 287.1618, found 287.1622.

(*E*)-8-(1-Methoxycyclohexyl)oct-2-en-7-ynal (1k). (Formylmethylene)triphenylphosphorane (315 mg,



1.04 mmol) was added to a solution of aldehyde **S22** (180 mg, 0.86 mmol) in CH_2Cl_2 (4.4 mL) at room temperature and the resulting mixture was stirred for 4 d. Sat. NH_4Cl solution (1 ml) and EtOAc (5 mL) were added and the layers separated. The aqueous phase was extracted with EtOAc (2 x 15 mL) and the combined organic layers washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1–10:1) to yield the title compound as a colorless oil (28 mg, 14%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.52 (d, *J* = 7.9 Hz, 1H), 6.85 (dt, *J* = 15.6, 6.8 Hz, 1H), 6.15 (ddt, *J* = 15.6, 7.8, 1.5 Hz, 1H), 3.34 (s, 3H), 2.48 (dtd, *J* = 8.2, 6.9, 1.5 Hz, 2H), 2.32 (t, *J* = 6.9 Hz, 2H), 1.85 (m, 2H), 1.75 (dq, *J* = 8.0, 6.9 Hz, 2H), 1.69 – 1.42 (m, 7H), 1.33 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.0, 157.6, 133.6, 85.0, 82.4, 74.1, 50.6, 37.1, 37.1, 31.8, 27.2, 25.6, 23.0, 23.0, 18.4. IR (film) ṽ 2933, 2856, 2235, 1688, 1447, 1088 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{22}O_2$ [M+Na]$^+$: calcd 257.1512, found 257.1513.

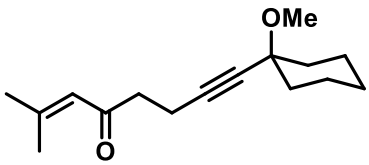
(*E*)-9-(1-Methoxycyclohexyl)non-3-en-8-yn-2-one (1l). In a two-necked round-bottom flask equipped with



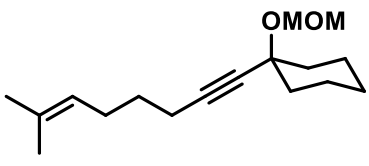
a reflux condenser was added (acetylmethylene)- triphenyl-phosphorane (344 mg, 1.08 mmol) to a solution of aldehyde **S22** (150 mg, 0.72 mmol) in THF (4.0 mL) at room temperature and the resulting mixture was stirred for 18 h at 60 °C. Sat. NH_4Cl solution (1 mL) and EtOAc (4 mL) were added and the layers separated. The aqueous phase was extracted with EtOAc (2 x 20 mL) and the combined organic layers washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 4:1) to yield the title compound as a colorless oil (133 mg, 74%). ^{1}H NMR (400 MHz, , $CDCl_3$) δ 6.79 (dt, *J* = 16.0, 6.9 Hz, 1H), 6.10 (dt, *J* = 16.0, 1.5 Hz, 1H), 3.34 (s, 3H), 2.36 (qd, *J* = 7.0, 1.6 Hz, 2H), 2.29 (t, *J* = 7.0 Hz, 2H), 2.24 (s, 3H), 1.89 – 1.77 (m, 2H), 1.75 – 1.42 (m, 9H), 1.28 (td, *J* = 10.4, 6.2 Hz, 1H). ^{13}C NMR (101 MHz,

$CDCl_3$) δ 198.6, 147.2, 131.9, 85.2, 82.2, 74.1, 50.6, 37.1, 31.5, 27.4, 27.1, 25.7, 23.0, 18.4. IR (film) ṽ 2933, 2857, 2233, 1675, 1628, 1360, 1252, 1089 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{24}O_2$ $[M+Na]^+$: calcd 271.1668, found 271.1667.

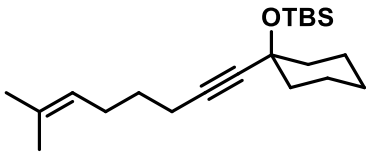
8-(1-Methoxycyclohexyl)-2-methyloct-2-en-7-yn-4-one (1m). $NaHCO_3$ (109 mg, 1.3 mmol) and Dess-Martin periodinane (165 mg, 0.39 mmol) were added to a solution of alcohol **S26** (65 mg, 0.26 mmol) in wet CH_2Cl_2 (2.4 mL) at 0 °C. The mixture was stirred at room temperature for 30 min before aq. sat. $Na_2S_2O_3$ (1 mL) and water (1 mL) were added. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 40:1 – 20:1) to give the product as a colorless oil (44 mg, 68%, accompanied by small amounts (12 mol%) of an impurity). ^1H NMR (400 MHz, , $CDCl_3$) δ 6.08 (hept, *J* = 1.3 Hz, 1H), 3.32 (s, 3H), 2.68 – 2.61 (m, 2H), 2.54 – 2.48 (m, 2H), 2.14 (d, *J* = 1.2 Hz, 3H), 1.89 (d, *J* = 1.3 Hz, 3H), 1.86 – 1.80 (m, 2H), 1.65 – 1.57 (m, 2H), 1.55 – 1.43 (m, 5H), 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 156.0, 123.5, 85.4, 81.5, 74.1, 50.6, 43.4, 37.1, 27.8, 25.7, 23.0, 21.0, 13.8. IR (neat) ṽ 2933, 2856, 2237, 1689, 1620, 1446, 1091 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{24}O_2$ $[M+Na]^+$: calcd 271.1688, found 271.1688.



1-(Methoxymethoxy)-1-(7-methyloct-6-en-1-yn-1-yl)cyclohexane (S52). *n*-BuLi (1.6 M in hexanes, 12.2 mL, 19.5 mmol) was slowly added to a solution of alkyne **S27** (2.73 g, 16.2 mmol) in THF (57 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S13** (3.73 g, 21.1 mmol) in THF (37 mL) and DMPU (9.8 mL) was added. The resulting mixture was stirred at room temperature for 18 h. sat. NH_4Cl solution (10 mL), *tert*-butyl methyl ether (50 mL) and water (10 mL) were added, the aqueous phase was extracted with *tert*-butyl methyl ether (3 x 100 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the title compound as a colorless oil (4.12 g, 96%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.10 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.94 (s, 2H), 3.39 (s, 3H), 2.23 (t, *J* = 7.1 Hz, 2H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.96 – 1.86 (m, 2H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.68 – 1.62 (m, 3H), 1.61 (s, 3H), 1.59 – 1.48 (m, 6H), 1.30 – 1.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 123.8, 92.9, 87.5, 80.9, 75.5, 55.8, 39.1, 29.2, 27.3, 25.9, 25.6, 23.4, 18.4, 17.8. IR (film) *ṽ* 2931, 2857, 1447, 1149, 1026 cm^{-1}. HRMS (ESI^+) for $C_{17}H_{28}O_2$ $[M+Na]^+$: calcd: 287.1981, found: 287.1980.

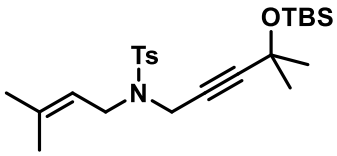


***tert*-Butyldimethyl((1-(7-methyloct-6-en-1-yn-1-yl)cyclohexyl)oxy)silane (S53)**. *n*-BuLi (1.6 M in hexanes, 1.3 mL, 2.1 mmol) was slowly added to a solution of alkyne **S28** (412 mg, 1.7 mmol) in THF (6.0 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of alkyl bromide **S13** (398 mg, 2.2 mmol) in THF (3.9 mL) and DMPU (1.0 mL) was added. The mixture was stirred at room temperature for 18 h. sat. NH_4Cl solution (3 mL), *tert*-butyl methyl ether (20 mL) and water (2 mL) were introduced, the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined

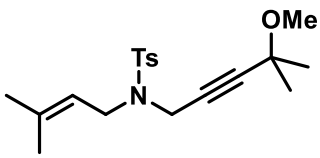


organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes) to give the title compound as a colorless oil (523 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (m, 1H), 2.20 (t, *J* = 7.1 Hz, 2H), 2.08 (q, *J* = 7.4 Hz, 2H), 1.77 – 1.69 (m, 2H), 1.70 (q, *J* = 1.3 Hz, 3H), 1.67 – 1.59 (m, 2H), 1.62 (s, 3H), 1.59 – 1.45 (m, 6H), 1.46 – 1.34 (m, 1H), 1.35 – 1.24 (m, 1H), 0.88 (s, 9H), 0.15 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 123.9, 85.0, 84.9, 69.4, 41.6, 29.1, 27.4, 26.1, 25.9, 25.6, 23.0, 18.5, 18.3, 17.9, -2.7. IR (film) $\tilde{\nu}$ 2930, 2855, 1446, 1250, 1095, 1052 cm^{-1}. HRMS (ESI$^+$) for $C_{21}H_{38}OSi$ [M+Na]$^+$: calcd: 357.2584, found: 257.2585.

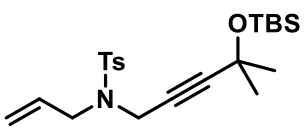
N-(4-((*tert*-butyldimethylsilyl)oxy)-4-methylpent-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)-benzenesulfonamide (S54). TBSOTf (82 µL, 0.36 mmol) was added to a solution of alcohol **S29** (100 mg, 0.30 mmol) and 2,6-lutidine (69 µL, 0.60 mmol) in CH_2Cl_2 (0.8 mL) at −15 °C (ice/acetone bath). Stirring was continued for 2 h before water (0.5 mL) was added. After reaching room temperature, the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless amorphous solid (126 mg, quant.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.71 (m, 2H), 7.30 – 7.27 (m, 2H), 5.12 (dddd, *J* = 8.6, 5.7, 2.8, 1.4 Hz, 1H), 4.09 (s, 2H), 3.81 (d, *J* = 7.2 Hz, 2H), 2.41 (s, 3H), 1.72 (s, 3H), 1.67 (s, 3H), 1.21 (s, 6H), 0.82 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.1, 138.6, 136.6, 130.0, 127.7, 118.2, 90.5, 75.4, 66.1, 44.0, 35.7, 32.6, 25.8, 25.6, 21.5, 17.9, 17.9, -3.0. IR (film) $\tilde{\nu}$ 2929, 2855, 1451, 1343, 1160 cm^{-1}. HRMS (ESI$^+$) for $C_{24}H_{39}NO_3SSi$ [M+Na]$^+$: calcd: 472.2312, found: 472.2313.



N-(4-Methoxy-4-methylpent-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S55). NaH (38 mg, 1.58 mmol) was added to a solution of alcohol **S29** (106 mg, 0.32 mmol) in THF (1.4 mL) at room temperature. The suspension was stirred for 10 min before MeI (0.2 mL, 3.16 mmol) was slowly added. After stirring for another 1 h at room temperature, water (1 mL) and *tert*-butyl methyl ether (5 mL) were introduced, the layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to yield the title compound as a colorless oil (106 mg, 96%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.70 (m, 2H), 7.32 – 7.27 (m, 2H), 5.13 (tdq, *J* = 7.3, 2.9, 1.3 Hz, 1H), 4.12 (s, 2H), 3.82 (d, *J* = 7.3 Hz, 2H), 3.11 (s, 3H), 2.41 (s, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 138.8, 136.5, 129.5, 127.7, 118.1, 87.0, 77.2, 70.2, 51.5, 43.9, 35.6, 28.0, 25.9, 21.5, 17.9. IR (film) $\tilde{\nu}$ 2982, 2932, 1738, 1346, 1159 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{27}NO_3S$ [M+Na]$^+$: calcd: 372.1604, found: 372.1603.

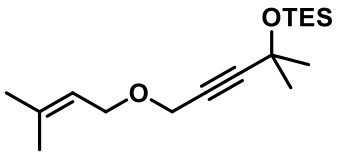


N-Allyl-N-(4-((*tert*-butyldimethylsilyl)oxy)-4-methylpent-2-yn-1-yl)-4-methylbenzenesulfonamide (S56). TBSOTf (54 µL, 0.23 mmol) was added to a solution of alcohol **S30** (60 mg, 0.20 mmol) and 2,6-lutidine (46 µL, 0.39 mmol) in CH_2Cl_2 (0.6 mL) at −15 °C (ice/acetone bath). The mixture was stirred for 2 h before water (0.5 mL) was

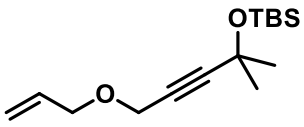


added. After reaching room temperature the layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless amorphous solid (67 mg, 81%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 1H), 5.74 (ddt, *J* = 17.1, 10.0, 6.4 Hz, 1H), 5.28 (dq, *J* = 17.2, 1.4 Hz, 1H), 5.23 (dq, *J* = 10.1, 1.2 Hz, 1H), 4.12 (s, 2H), 3.83 (d, *J* = 6.4 Hz, 2H), 2.41 (s, 3H), 1.21 (s, 6H), 0.82 (s, 9H), 0.05 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 136.6, 132.2, 129.7, 127.8, 119.9, 91.1, 75.1, 66.2, 49.1, 36.1, 32.8, 25.8, 21.6, 18.0, -2.8. IR (film) $\tilde{\nu}$ 2929, 2856, 1352, 1162, 1042 cm^{-1}. HRMS (ESI$^+$) for $C_{22}H_{35}NO_3SSi$ [M+Na]$^+$: calcd: 444.1999, found: 444.2001.

Triethyl((2-methyl-5-((3-methylbut-2-en-1-yl)oxy)pent-3-yn-2-yl)oxy)silane (S57). Alcohol **S31** (150 mg, 0.66 mmol) was added at 0 °C to a suspension of NaH (15.7 mg, 0.66 mmol) in THF (5 mL). The mixture was stirred for 1 h at 0 °C before 1-bromo-3-methyl-2-butene (0.15 mL, 1.3 mmol) was slowly introduced. The mixture was allowed to reach ambient temperature overnight. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 3 mL) and the combined organic layers were washed with sat. aq. NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 50:1) to give the title compound as a colorless oil (126 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.26 (m, 1H), 4.14 (s, 2H), 4.03 (d, *J* = 6.7 Hz, 2H), 1.81 – 1.67 (m, 6H), 1.48 (s, 6H), 0.96 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.2, 120.6, 91.6, 78.7, 66.3, 66.0, 57.4, 33.2, 26.0, 18.1, 7.1, 6.2. IR (film) $\tilde{\nu}$ 2956, 1716, 1362, 1237, 1163, 1037, 1004, 726 cm^{-1}. HRMS (ESI$^+$) for $C_{17}H_{32}O_2Si$ [M+Na]$^+$: calcd: 319.2064, found: 319.2063.



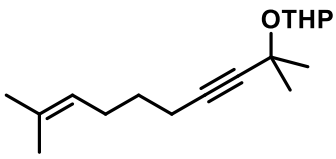
((5-(Allyloxy)-2-methylpent-3-yn-2-yl)oxy)(*tert*-butyl)dimethylsilane (S58). To a solution of allyl propargyl ether **S8** (150 mg, 1.5 mmol) in THF (6 mL) was added *n*-BuLi (1.6 M in hexanes, 0.97 mL, 1.56 mmol) at −78 °C. The mixture was stirred for 1 h at this temperature before acetone (0.17 mL, 2.3 mmol) was slowly introduced. The mixture was allowed to reach ambient temperature overnight. The reaction was quenched with sat. NH_4Cl solution (10 mL). The aqueous phase was extracted with Et_2O (3 x 10 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was used directly in the next step.



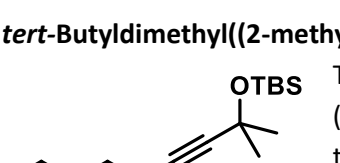
2,6-Lutidine (0.2 mL, 1.74 mmol) and TBSOTf (0.24 mL, 1 mmol) were added at −15 °C to a solution of the crude alcohol (134 mg, 0.89 mmol) in CH_2Cl_2 (2.5 mL). The mixture was warmed to ambient temperature over 2 h and stirring was continued for another 14 h. The reaction was quenched with sat. aq. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 3 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, hexanes/EtOAc 99:1) to give the title compound as a colorless oil (220 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (ddt, *J* = 17.2, 10.4, 5.8 Hz, 1H), 5.31 (ddd, *J* = 17.2, 1.6, 1.6 Hz, 1H), 5.22 (ddd, *J* = 10.4, 1.4, 1.3 Hz, 1H), 4.17 (s, 2H), 4.05 (dt, *J* = 5.8, 1.4 Hz, 2H), 1.46 (s, 6H), 0.86 (s, 9H), 0.16 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 117.9, 91.9, 78.4, 70.6, 66.4, 57.6, 33.0, 25.8, 18.1,

-2.8. IR (film) $\tilde{\nu}$ 2930, 1721, 1360, 1248, 1162, 1035, 828, 775, 678 cm^{-1}. HRMS (ESI^+) for $C_{15}H_{28}O_2Si$ $[M+H]^+$: calcd: 269.1931, found: 269.1933.

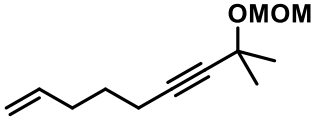
2-((2,9-Dimethyldec-8-en-3-yn-2-yl)oxy)tetrahydro-2*H*-pyran (S59). *n*-BuLi (1.6 M in hexanes, 0.54 mL, 0.86 mmol) was slowly added to a solution of alkyne **S6** (120 mg, 0.71 mmol) in THF (2.5 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before alkyl bromide **S13** (164 mg, 0.93 mmol) dissolved in THF (1.6 mL) and DMPU (0.43 mL) was added. The mixture was allowed to warm to room temperature and stirring was continued for 22 h. Sat. NH_4Cl solution (2 mL), methyl *tert*-butyl ether (20 mL) and water (1 mL) were added and the layers were separated. The aqueous layer was extracted with methyl *tert*-butyl ether (2 x 30 mL) and the combined organic layers were washed with sat. NaCl solution and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (silica, hexanes/EtOAc 1:0 – 20:1). The product was obtained as a colorless oil (147 mg, 78%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.10 (m, 1H), 5.07 – 5.03 (m, 1H), 3.98 – 3.90 (m, 1H), 3.53 – 3.45 (m, 1H), 2.19 (t, *J* = 7.1 Hz, 2H), 2.07 (q, *J* = 7.1 Hz, 2H), 1.90 – 1.78 (m, 1H), 1.73 – 1.66 (m, 1H), 1.69 (q, *J* = 1.3 Hz, 3H), 1.62 (s, 3H), 1.59 – 1.51 (m, 6H), 1.50 (s, 3H), 1.46 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 123.8, 96.3, 84.6, 82.8, 71.5, 63.6, 32.2, 31.3, 30.3, 29.1, 27.2, 25.9, 25.6, 20.9, 18.3, 17.9. IR (film) ṽ 2937, 2860, 1440, 1378, 1022, 987 cm^{-1}. HRMS (ESI^+) for $C_{17}H_{28}O_2$ $[M+Na]^+$: calcd: 287.1981, found: 287.1983.



***tert*-Butyldimethyl((2-methylnon-8-en-3-yn-2-yl)oxy)silane (S60)**. 2,6-Lutidine (0.4 mL, 3.4 mmol) and TBSOTf (0.47 mL, 2.0 mmol) were added at −15 °C to a solution of alcohol **S32** (260 mg, 1.7 mmol) in CH_2Cl_2 (8 mL).The mixture was warmed to ambient temperature over the course of 2 h and stirring was continued for 14 h. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, hexanes/EtOAc 100:1) to give the title compound as a colorless oil (349 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$): δ 5.65 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 4.88 (ddd, *J* = 17.1, 1.7, 1.7 Hz, 1H), 4.85 – 4.80 (m, 1H), 2.08 – 1.93 (m, 5H), 1.50 – 1.37 (m, 2H), 1.27 (s, 6H), 0.71 (s, 9H), 0.00 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$): δ 138.1, 115.2, 86.1, 82.5, 66.5, 33.4, 33.0, 28.0, 25.9, 25.9, 18.2, 18.1, -2.8. IR (film) $\tilde{\nu}$ 2930, 1247, 1159, 1035, 834, 774 cm^{-1}. HRMS (CI) for $C_{16}H_{30}OSi$ $[M+H]^+$: calcd: 267.2137, found: 267.2139.

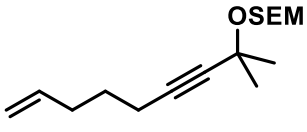


8-(Methoxymethoxy)-8-methylnon-1-en-6-yne (S61). Hünig's base (1.17 mL, 6.7 mmol) and MOMCl (0.26 mL, 3.37 mmol) were added at 0 °C to a solution of alcohol **S32** (171 mg, 1.12 mmol) in CH_2Cl_2 (5 mL). The mixture was warmed to ambient temperature over 2 h and stirring was continued for another 14 h. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 97:3) to give the title compound as a colorless oil (156 mg, 71%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.06 – 4.95 (m, 2H), 4.89 (s, 2H), 3.37 (s,

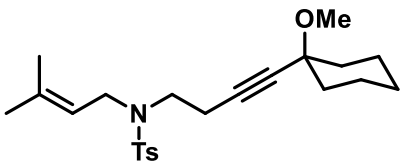


3H), 2.21 (t, *J* = 7.1 Hz, 2H), 2.18 – 2.11 (m, 2H), 1.64 – 1.56 (m, 2H), 1.48 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 115.3, 93.2, 85.1, 82.3, 71.4, 55.5, 32.9, 30.7, 28.0, 18.1. IR (film) $\tilde{\nu}$ 2934, 1256, 1144, 1031, 1001, 917, 810 cm^{-1}. HRMS (ESI$^+$) for $C_{12}H_{20}O_2$ [M+Na]$^+$: calcd: 219.1356, found: 219.1356.

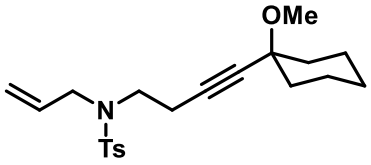
Trimethyl(2-(((2-methylnon-8-en-3-yn-2-yl)oxy)methoxy)ethyl)silane (S62). Hünig's base (1.21 mL, 6.9 mmol) and SEMCl (0.62 mL, 3.48 mmol) were added at 0 °C to a solution of alcohol **S32** (176.9 mg, 1.16 mmol) in CH_2Cl_2(5 mL). The mixture was warmed to ambient temperature over 2 h and stirring was continued for another 14 h. The reaction was quenched with sat. NH_4Cl solution (5 mL), the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL) and the combined organic layers were washed with sat. NaCl solution, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash chromatography (silica, hexanes/EtOAc 100:1) to give the title compound as a colorless oil (311 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.79 (ddt, *J* = 16.9, 10.1, 6.7 Hz, 1H), 5.06 – 4.95 (m, 2H), 4.94 (s, 2H), 3.71 – 3.59 (m, 2H), 2.21 (t, *J* = 7.1 Hz, 2H), 2.18 – 2.09 (m, 2H), 1.67 – 1.55 (m, 2H), 1.48 (s, 6H), 0.99 – 0.89 (m, 2H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.2, 116.6, 92.7, 86.2, 83.7, 72.5, 66.6, 34.2, 31.9, 29.3, 19.6, 19.4, 0.0. IR (film) $\tilde{\nu}$ 2953, 1248, 1095, 1027, 919, 857, 834 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{30}O_2Si$ [M+Na]$^+$: calcd: 305.1907, found: 305.1908.



N-(4-(1-Methoxycyclohexyl)but-3-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S63). 1-Bromo-3-methyl-2-butene (0.28 mL, 2.4 mmol) was added to a stirred suspension of K_2CO_3 (494 mg, 3.6 mmol) and sulfonamide **S33** (400 mg, 1.2 mmol) in MeCN (3.8 mL). The mixture was stirred at 60 °C for 2 h before additional K_2CO_3 (494 mg, 3.6 mmol) and 1-bromo-3-methyl-2-butene (0.28 mL, 2.4 mmol) were added. After stirring for another 18 h at 60 °C, the mixture was cooled to room temperature and diluted with MeCN (10 mL). The suspension was filtered through a plug of cotton wool and the filtrate was evaporated. The residue was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 6:1) to yield the title compound as pale yellow oil (306 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.66 (m, 2H), 7.32 – 7.27 (m, 2H), 5.01 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 3.82 (d, *J* = 7.1 Hz, 2H), 3.31 (s, 3H), 3.28 – 3.22 (m, 2H), 2.53 – 2.47 (m, 2H), 2.42 (s, 3H), 1.85 – 1.77 (m, 2H), 1.66 (q, *J* = 1.2 Hz, 3H), 1.65 – 1.57 (m, 5H), 1.57 – 1.41 (m, 5H), 1.32 – 1.22 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 137.4, 137.3, 129.7, 127.3, 119.1, 83.0, 82.8, 74.0, 50.6, 46.5, 46.2, 36.9, 25.9, 25.6, 22.9, 21.6, 19.8, 17.9. IR (film) $\tilde{\nu}$ 2933, 2857, 1448, 1341, 1157 cm^{-1}. HRMS (ESI$^+$) for $C_{23}H_{33}NO_3S$ [M+Na]$^+$: calcd: 426.1073, found: 426.2072.

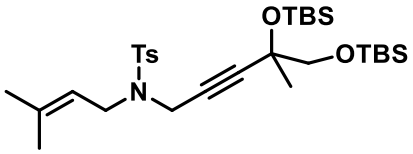


N-Allyl-N-(4-(1-methoxycyclohexyl)but-3-yn-1-yl)-4-methylbenzenesulfonamide (S64). Allyl bromide (0.08 mL, 0.95 mmol) was added to a stirred suspension of K_2CO_3 (131 mg, 0.95 mmol) and sulfonamide **S33** (160 mg, 0.48 mmol) in MeCN (0.8 mL). After stirring for 18 h at 60 °C the mixture was allowed to cool to ambient temperature and diluted with MeCN (10 mL). The suspension was filtered through a plug of cotton wool and the filtrate was concentrated under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 6:1) to yield the title compound as a colorless oil (105 mg, 59%). ^{1}H NMR

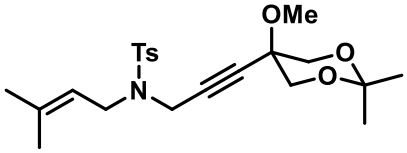


(400 MHz, $CDCl_3$) δ 7.75 – 7.68 (m, 2H), 7.33 – 7.28 (m, 2H), 5.66 (ddt, *J* = 17.1, 10.1, 6.3 Hz, 1H), 5.23 – 5.14 (m, 2H), 3.85 (dt, *J* = 6.3, 1.4 Hz, 2H), 3.32 – 3.26 (m, 5H), 2.55 – 2.48 (m, 2H), 2.43 (s, 3H), 1.86 – 1.76 (m, 2H), 1.67 – 1.42 (m, 7H), 1.35 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 137.2, 133.2, 129.9, 127.3, 119.2, 83.1, 82.6, 74.0, 51.4, 50.7, 46.5, 36.9, 25.6, 22.9, 21.7, 19.7. IR (film) $\tilde{\nu}$ 2935, 2857, 1449, 1345, 1158, 1092 cm^{-1}. HRMS (ESI^+) for $C_{21}H_{29}NO_3S$ $[M+Na]^+$: calcd: 398.1760, found: 398.1762.

N-(4,5-bis((*tert*-Butyldimethylsilyl)oxy)-4-methylpent-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S65). TBSOTf (0.15 mL, 0.64 mmol) was added to a solution of alcohol **S35** (250 mg, 0.0.54 mmol) and 2,6-lutidine (0.13 mL, 1.07 mmol) in CH_2Cl_2 (2.1 mL) at −78 °C. The mixture was allowed to reach room temperature and stirring was continued for 2 h before sat. NH_4Cl solution (0.5 mL) was added. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (3 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to yield the title compound as a light yellow oil (281 mg, 90%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.30 – 7.26 (m, 2H), 5.12 (tdq, *J* = 7.2, 2.9, 1.3 Hz, 1H), 4.10 (s, 2H), 3.82 (d, *J* = 7.2 Hz, 2H), 3.29 (s, 2H), 2.41 (s, 3H), 1.71 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.18 (s, 3H), 0.87 (s, 9H), 0.82 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H), 0.02 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.2, 138.7, 136.9, 129.6, 127.8, 118.3, 88.5, 77.4, 71.6, 70.0, 44.0, 35.9, 27.2, 26.0, 26.0, 25.8, 21.7, 18.5, 18.1, -2.7, -2.9, -5.2. IR (film) $\tilde{\nu}$ 2929, 2857, 1351, 1162, 1112 cm^{-1}. HRMS (ESI^+) for $C_{30}H_{53}NO_4SSi_2$ $[M+Na]^+$: calcd: 602.3126, found: 602.3128.



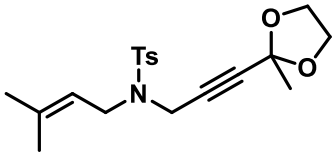
N-(3-(5-Methoxy-2,2-dimethyl-1,3-dioxan-5-yl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S66). *n*-BuLi (1.6 M in hexanes, 1.00 mL, 1.60 mmol) was slowly added to a solution of alkyne **S14** (400 mg, 1.44 mmol) in THF (12 mL) at 0 °C and the resulting mixture was stirred for 30 min at that temperature before 2,2-dimethyl-1,3-dioxan-5-one (282 mg, 2.17 mmol) in THF (1 mL) was introduced. The mixture was allowed to reach room temperature and stirring continued for 30 min before sat. NH_4Cl solution (5 mL) was added. The layers were separated and the aqueous phase was extracted with EtOAc (3 x 30 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 4:1 – 2:1) to yield the tertiary alcohol (241 mg, 41 %) which was immediately used in the next step.



NaH (43 mg, 1.77 mmol) was added to a solution of this alcohol (241 mg, 0.59 mmol) in THF (2.5 mL) at room temperature. The suspension was stirred for 10 min before MeI (0.22 mL, 3.53 mmol) was slowly added. Stirring was continued for 1 h before water (2 mL) and EtOAc (30 mL) were introduced. The aqueous phase was extracted with EtOAc (2 x 30 mL) and the combined organic phases were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (silica, hexanes/EtOAc 45:1) to yield the title compound as a pale yellow oil (151 mg, 61%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.33 – 7.29 (m, 2H), 5.12 (m, 1H), 4.14 (s, 2H), 3.82 (d, *J* = 7.3 Hz, 2H), 3.67 (dt, *J* = 12.7, 0.9 Hz, 2H), 3.60 (dt, *J* = 12.2, 1.0 Hz, 2H), 3.17 (s, 3H), 2.42 (s, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.3 Hz, 3H), 1.39 (s, 3H), 1.39 (s, 3H). ^{13}C NMR (101 MHz,

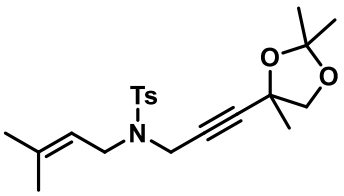
$CDCl_3$) δ 143.6, 139.2, 136.5, 129.7, 127.9, 118.0, 98.4, 81.6, 81.4, 67.0, 65.4, 51.8, 44.2, 35.7, 26.6, 26.0, 21.7, 20.3, 18.0. IR (neat) ṽ 2990, 2930, 1450, 1346, 1159, 1090 cm^{-1}. HRMS (ESI^+) for $C_{22}H_{31}NO_5S$ $[M+Na]^+$: calcd 444.1815, found 444.1817.

4-Methyl-N-(3-(2-methyl-1,3-dioxolan-2-yl)prop-2-yn-1-yl)-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S67). *p*-TsOH · H_2O (7.4 mg, 0.04 mmol) was added to a vigorously stirred suspension of ynone **S36**



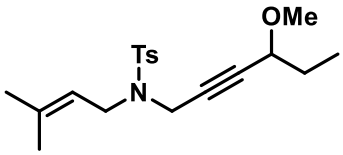
(125 mg, 0.39 mmol) and triethylorthoformate (70 mg, 0.47 mmol) in ethylene glycol (1.9 mL). The mixture was stirred at room temperature for 24 h before solid $NaHCO_3$ (30 mg) and sat. aq. $NaHCO_3$ solution (1 mL) were added. The mixture was diluted with EtOAc (20 mL) and water (5 mL), the layers were separated, the aqueous phase was extracted with EtOAc (2 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 6:1 – 4:1) to give the title compound as a colorless amorphous solid (116 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.34 – 7.29 (m, 2H), 5.10 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 4.11 (s, 2H), 3.91 – 3.83 (m, 2H), 3.82 – 3.77 (m, 4H), 2.42 (s, 3H), 1.72 (d, *J* = 1.2 Hz, 3H), 1.67 (d, *J* = 1.3 Hz, 3H), 1.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 139.1, 136.3, 129.7, 127.8, 118.1, 100.5, 83.9, 76.3, 64.6, 44.2, 35.6, 26.2, 26.0, 21.7, 18.0. IR (film) ṽ 2973, 2895, 1347, 1185, 1161 cm^{-1}. HRMS (ESI^+) for $C_{19}H_{25}NO_4S$ $[M+Na]^+$: calcd: 386.1397, found: 386.1399.

4-Methyl-N-(3-methylbut-2-en-1-yl)-N-(3-(2,2,4-trimethyl-1,3-dioxolan-4-yl)prop-2-yn-1-yl)benzenesulfonamide (S68). TBAF (1 M in THF, 0.82 mL, 0.82 mmol) was added to a solution of silyl ether **S65**

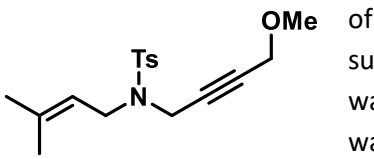


(190 mg, 0.41 mmol) in THF (4 M) at 0 °C. The mixture was allowed to reach room temperature and stirring was continued for 30 min before sat. NH_4Cl solution (1 mL) and water (1 mL) were introduced. The layers were separated and the aqueous phase was extracted with EtOAc (3 x 10 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product was filtered through a short plug of silica, eluting with hexanes/EtOAc (1:2). The crude product was used in the next step without further purification. *p*-TsOH (6.8 mg, 0.04 mmol) was added to a solution of the crude diol and 2,2-dimethoxypropane (0.09 mL, 0.72 mmol) in acetone (1.0 mL) at room temperature. The mixture was stirred for 18 h at room temperature before sat. aq. $NaHCO_3$ solution (0.5 mL) was added. The mixture was extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 4:1) to obtain the title compound as a colorless oil (121 mg, 76%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.32 – 7.27 (m, 2H), 5.11 (tdq, *J* = 7.2, 2.9, 1.5 Hz, 1H), 4.10 (s, 2H), 3.80 (d, *J* = 7.2 Hz, 2H), 3.76 (d, *J* = 8.1 Hz, 1H), 3.57 (d, *J* = 8.1 Hz, 1H), 2.42 (s, 3H), 1.72 (d, *J* = 1.4 Hz, 3H), 1.67 (d, *J* = 1.3 Hz, 3H), 1.34 (s, 6H), 1.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 139.0, 136.6, 129.7, 127.9, 118.1, 110.8, 87.4, 75.5, 73.5, 44.1, 35.8, 27.1, 26.8, 26.2, 26.0, 21.7, 18.1. IR (film) ṽ 2985, 1452, 1346, 1203, 1093, 1062 cm^{-1}. HRMS (ESI^+) for $C_{21}H_{29}NO_4S$ $[M+Na]^+$: calcd 414.1710, found 414.1715.

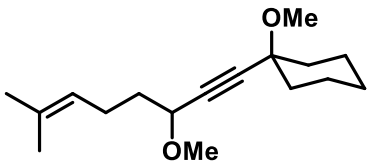
N-(4-Methoxyhex-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S69). A solution of alcohol **S37** in THF (3 mL) was slowly added to a suspension of NaH (214 mg, 8.9 mmol) in THF (7.7 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (1.12 mL, 17.9 mmol) was carefully added at 0 °C. After stirring for another 1 h at room temperature, water (1 mL) and *tert*-butyl methyl ether (10 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 50 mL), the combined organic layers were washed with brine and dried over $MgSO_4$, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to yield the title compound as a colorless oil (235 mg, 40% over two steps). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.30 – 7.26 (m, 2H), 5.12 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.14 (d, *J* = 1.8 Hz, 2H), 3.81 (d, *J* = 7.3 Hz, 2H), 3.61 (tt, *J* = 6.3, 1.8 Hz, 1H), 3.18 (s, 2H), 2.41 (s, 3H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.67 (d, *J* = 1.3 Hz, 3H), 1.57 – 1.36 (m, 2H), 0.81 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 139.0, 136.5, 129.6, 127.9, 118.2, 84.1, 79.1, 72.4, 56.4, 44.1, 35.8, 28.6, 26.0, 21.6, 18.0, 9.7. IR (film) $\tilde{\nu}$ 2971, 2932, 1449, 1343, 1159 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{27}NO_3S$ [M+Na]$^+$: calcd: 372.1604, found: 372.1604.



N-(4-Methoxybut-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide (S70). A solution of alcohol **S38** (150 mg, 0.49 mmol) in THF (2 mL) was slowly added to a suspension of NaH (59 mg, 2.4 mmol) in THF (2.1 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.31 mL, 4.9 mmol) was carefully added at 0 °C. Stirring was continued for 1 h at room temperature before water (0.5 mL) and *tert*-butyl methyl ether (10 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the crude product purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to yield the title compound as a colorless oil (126 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.32 – 7.27 (m, 2H), 5.11 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.10 (t, *J* = 1.9 Hz, 2H), 3.82 (t, *J* = 1.9 Hz, 2H), 3.80 (d, *J* = 7.3 Hz, 3H), 3.18 (s, 3H), 2.42 (s, 3H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.66 (d, *J* = 1.3 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 139.1, 136.3, 129.5, 128.0, 118.1, 81.2, 79.8, 59.7, 57.5, 44.2, 35.9, 26.0, 21.7, 18.0. IR (film) $\tilde{\nu}$ 2975, 2926, 1598, 1343, 1090 cm^{-1}. HRMS (ESI$^+$) for $C_{17}H_{23}NO_3S$ [M+Na]$^+$: calcd: 344.1291, found: 344.1294.

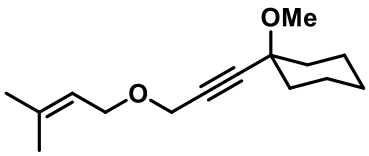


1-Methoxy-1-(3-methoxy-7-methyloct-6-en-1-yn-1-yl)cyclohexane (S71). A solution of alcohol **S39** (200 mg, 0.8 mmol) in THF (1 mL) was added to a stirred suspension of NaH (96 mg, 4.0 mmol) in THF (3.2 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.50 mL, 8.0 mmol) was introduced. After stirring for 1 h at room temperature, sat. aq. NH_4Cl solution (2 mL), water (4 mL) and *tert*-butyl methyl ether (30 mL) were introduced and the layers separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the title compound as a colorless oil (184 mg, 87%). ^{1}H NMR (400 MHz,



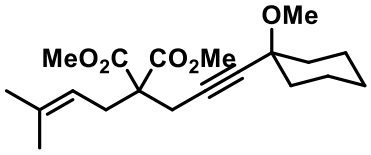
$CDCl_3$) δ 5.11 (tdq, *J* = 7.3, 2.9, 1.4 Hz, 1H), 4.00 (t, *J* = 6.6 Hz, 1H), 3.40 (s, 3H), 3.37 (s, 3H), 2.19 – 2.10 (m, 2H), 1.95 – 1.86 (m, 2H), 1.82 – 1.71 (m, 2H), 1.69 (d, *J* = 1.0 Hz, 3H), 1.70 – 1.60 (m, 2H), 1.62 (s, 3H), 1.60 – 1.47 (m, 5H), 1.35 – 1.19 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.6, 123.5, 87.0, 85.1, 74.2, 70.9, 56.5, 50.8, 37.0, 36.0, 25.9, 25.6, 24.1, 23.1, 17.8. IR (film) $\tilde{\nu}$ 2934, 2857, 1447, 1290, 1094 cm^{-1}. HRMS (EI) for $C_{17}H_{28}O_2$ [M]$^+$: calcd: 264.1084, found: 264.2085.

1-Methoxy-1-(3-((3-methylbut-2-en-1-yl)oxy)prop-1-yn-1-yl)cyclohexane (S72). A solution of alcohol **S51**



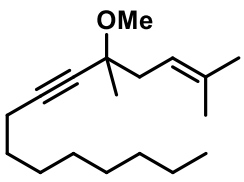
(360 mg, 2.1 mmol) in THF (1 mL) was added to a stirred suspension of NaH (87 mg, 3.6 mmol) in THF (13.9 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before 1-bromo-3-methyl-2-butene (0.30 mL, 2.6 mmol) was added. After stirring for 1 h at room temperature, the reaction was quenched with sat. aq. NH_4Cl solution (2 mL), water (4 mL) and *tert*-butyl methyl ether (30 mL). The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 40:1 – 20:1) to give the title compound as a colorless oil (266 mg, 53%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.35 (tdq, *J* = 7.1, 2.8, 1.4 Hz, 1H), 4.20 (s, 2H), 4.06 (d, *J* = 7.1 Hz, 2H), 3.36 (s, 3H), 1.94 – 1.82 (m, 2H), 1.76 (s, 3H), 1.70 (s, 3H), 1.69 – 1.45 (m, 7H), 1.37 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.4, 120.5, 87.3, 82.2, 74.1, 65.9, 57.28, 50.9, 36.8, 26.0, 25.6, 22.9, 18.2. IR (film) $\tilde{\nu}$ 2933, 2856, 1674, 1446, 1073 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{24}O_2$ [M+Na]$^+$: calcd: 259.1668, found: 259.1669.

Dimethyl 2-(3-(1-methoxycyclohexyl)prop-2-yn-1-yl)-2-(3-methylbut-2-en-1-yl)malonate (S73). A



solution of alcohol **S41** (180 mg, 0.54 mmol) in THF (1 mL) was slowly added to a suspension of NaH (64 mg, 2.7 mmol) in THF (2.2 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.34 mL, 5.4 mmol) was carefully added at 0 °C. After stirring for 1 h at room temperature, water (0.5 mL) and *tert*-butyl methyl ether (10 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 40:1 – 20:1 – 15:1) to yield the title compound as a colorless oil (84 mg, 45%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (dddd, *J* = 9.2, 5.9, 2.9, 1.5 Hz, 1H), 3.72 (s, 6H), 3.31 (s, 3H), 2.83 (s, 2H), 2.77 (d, *J* = 7.8 Hz, 2H), 1.88 – 1.77 (m, 2H), 1.70 (d, *J* = 1.3 Hz, 3H), 1.65 (d, *J* = 1.3 Hz, 3H), 1.64 – 1.41 (m, 8H), 1.31 – 1.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.7, 136.9, 117.3, 84.2, 81.2, 74.1, 57.6, 52.8, 50.7, 37.0, 31.0, 26.2, 25.6, 23.0, 22.9, 18.1. IR (film) $\tilde{\nu}$ 2935, 2857, 1738, 1437, 1224 cm^{-1}. HRMS (ESI$^+$) for $C_{20}H_{30}O_5$ [M+Na]$^+$: calcd: 373.1985, found: 373.1983.

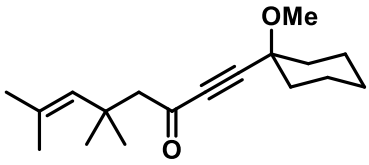
5-Methoxy-2,5-dimethylpentadec-2-en-6-yne (S74). *n*-BuLi (1.6 M in hexanes, 0.60 mL, 0.96 mmol) was



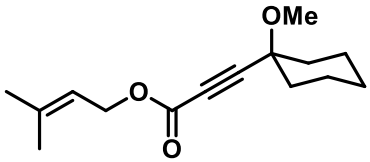
slowly added to a stirred suspension of isopropyltriphenylphosphonium iodide (492 mg, 1.14 mmol) in THF (5.7 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of aldehyde **S46** (208 mg, 0.88 mmol) in THF (1.4 mL) was added. After stirring at 0 °C for 1 h, sat. NH_4Cl solution (2 mL) and *tert*-butyl methyl

ether (10 mL) were introduced and the layers separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined organic layers were dried over $MgSO_4$. The solvent was evaported and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 75:1 – 50:1) to yield the title compound as a colorless oil (55 mg, 24%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.24 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 3.35 (s, 3H), 2.43 – 2.30 (m, 2H), 2.21 (t, *J* = 7.0 Hz, 2H), 1.74 (q, *J* = 1.3 Hz, 3H), 1.63 (s, 3H), 1.55 – 1.46 (m, 2H), 1.43 – 1.36 (m, 2H), 1.34 (s, 3H), 1.32 – 1.23 (m, 8H), 0.91 – 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.2, 119.5, 85.9, 81.4, 74.0, 51.4, 39.8, 32.0, 29.4, 29.2, 29.0, 26.2, 25.9, 22.8, 18.8, 18.3, 14.3. IR (film) $\tilde{\nu}$ 2928, 2857, 1458, 1367, 1089 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{32}O$ [M+H]$^+$: calcd: 265.2526, found: 265.2526.

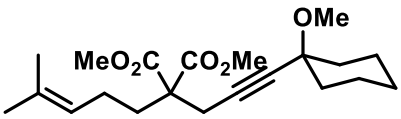
1-(1-Methoxycyclohexyl)-5,5,7-trimethyloct-6-en-1-yn-3-one (S75). *n*-BuLi (1.6 M in hexanes, 0.64 mL, 1.02 mmol) was added dropwise to a stirred solution of alkyne **S1** (153 mg, 1.11 mmol) in THF (3.5 ml) at 0 °C and the resulting mixture was stirred for 20 min at that temperature. The mixture was cooled to – 78 °C and a solution of amide **37** (170 mg, 0.85 mmol) in THF (0.6 mL) was added. The mixture was allowed to reach – 10 °C and stirring was continued for 1 h at that temperature. Sat. NH_4Cl solution (1 mL) and EtOAc (3 mL) were introduced and the layers separated. The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and excess alkyne removed under high vacuum (10^{-3} mbar, rt). The residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 40:1) to give the title compound as a colorless oil (201 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (hept, *J* = 1.4 Hz, 1H), 3.37 (s, 3H), 2.68 (s, 2H), 1.92 (m, 2H), 1.73 (d, *J* = 1.4 Hz, 3H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.67 – 1.44 (m, 7H), 1.39 – 1.29 (m, 1H), 1.24 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.1, 132.3, 132.0, 92.6, 86.7, 73.9, 58.0, 51.4, 36.2, 35.7, 29.5, 28.2, 25.4, 22.6, 19.2. IR (film) $\tilde{\nu}$ 2935, 2860, 2204, 1667, 1447, 1094, 1079 cm^{-1}. HRMS (CI$^+$) for $C_{18}H_{28}O_2$ [M+H]$^+$: calcd 277.2162, found 277.2159.



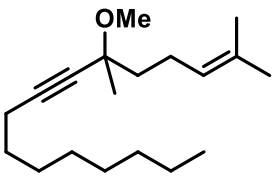
3-Methylbut-2-en-1-yl 3-(1-methoxycyclohexyl)propiolate (S76). A solution of alcohol **S47** (300 mg, 1.27 mmol) in THF (1 mL) was slowly added to a suspension of NaH (152 mg, 6.3 mmol) in THF (5.5 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.80 mL, 12.7 mmol) was carefully added at 0 °C. Stirring was continued for 1 h at room temperature before water (2 mL) and *tert*-butyl methyl ether (30 mL) were introduced. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless oil (129 mg, 41%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (ddp, *J* = 8.8, 5.7, 1.4 Hz, 1H), 4.67 (dt, *J* = 7.3, 0.9 Hz, 2H), 3.37 (s, 3H), 1.98 – 1.85 (m, 2H), 1.77 (d, *J* = 1.2 Hz, 3H), 1.73 (d, *J* = 1.3 Hz, 3H), 1.73 – 1.58 (m, 4H), 1.59 – 1.44 (m, 4H), 1.38 – 1.25 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.8, 140.4, 117.8, 88.5, 77.9, 73.9, 63.0, 51.4, 36.1, 26.0, 25.3, 22.5, 18.2. IR (film) $\tilde{\nu}$ 2937, 2860, 2238, 1711, 1230 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{23}O_3$ [M+Na]$^+$: calcd: 273.1461, found: 273.1459.



Dimethyl 2-(3-(1-methoxycyclohexyl)prop-2-yn-1-yl)-2-(4-methylpent-3-en-1-yl)malonate (S77). A solution of alcohol **S49** (340 mg, 0.97 mmol) in THF (1 mL) was slowly added to a suspension of NaH (70 mg, 2.9 mmol) in THF (3.9 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.31 mL, 4.9 mmol) was carefully added at 0 °C. Stirring was continued for 1 h at room temperature before water (1 mL) and *tert*-butyl methyl ether (20 mL) were introduced and the layers were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (2 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1 – 5:1) to yield the title compound as a colorless oil (263 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.08 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 3.72 (s, 6H), 3.31 (s, 3H), 2.90 (s, 2H), 2.12 – 2.00 (m, 2H), 1.93 – 1.78 (m, 4H), 1.70 – 1.56 (m, 3H), 1.67 (q, *J* = 1.9 Hz, 3H), 1.58 (s, 3H), 1.55 – 1.40 (m, 6H), 1.30 – 1.18 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.0, 132.8, 123.0, 84.3, 80.9, 74.2, 57.2, 52.8, 50.7, 37.0, 32.3, 25.8, 25.6, 23.2, 23.0, 22.9, 17.7. IR (film) $\tilde{\nu}$ 2934, 2857, 1735, 1436, 1167 cm^{-1}. HRMS (ESI$^+$) for $C_{21}H_{32}O_5$ [M+Na]$^+$: calcd: 387.2142, found: 387.2142.



6-Methoxy-2,6-dimethylhexadec-2-en-7-yne (S78). A solution of alcohol **S50** (300 mg, 1.13 mmol) in THF (1 mL) was added to a stirred suspension of NaH (68 mg, 2.84 mmol) in THF (4.9 mL) at 0 °C. The mixture was stirred for 10 min at room temperature before MeI (0.36 mL, 5.67 mmol) was added. Stirring was continued for 1 h at room temperature before sat. aq. NH_4Cl solution (2 mL), water (2 mL) and *tert*-butyl methyl ether (20 mL) were introduced. The layers were separated, the aqueous phase was extracted with *tert*-butyl methyl ether (2 x 30 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the product as a colorless oil (284 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.13 (tdq, *J* = 7.2, 2.9, 1.4 Hz, 1H), 3.33 (s, 3H), 2.21 (t, *J* = 7.0 Hz, 2H), 2.17 – 2.06 (m, 3H), 1.68 (q, *J* = 1.2 Hz, 3H), 1.67 – 1.58 (m, 2H), 1.62 (d, *J* = 1.2 Hz, 3H), 1.54 – 1.46 (m, 2H), 1.42 – 1.35 (m, 2H), 1.37 (s, 3H), 1.33 – 1.23 (m, 8H), 0.91 – 0.86 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 131.8, 124.3, 86.0, 81.2, 73.7, 51.3, 41.6, 32.0, 29.4, 29.2, 29.0, 29.0, 26.1, 25.9, 23.4, 22.8, 18.8, 17.8, 14.3. IR (film) $\tilde{\nu}$ 2926, 2856, 1459, 1173, 1088, 1073 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{34}O$ [M+H]$^+$: calcd: 279.2682, found: 279.2680.



CYCLOPROPANATION AND METATHESIS REACTIONS

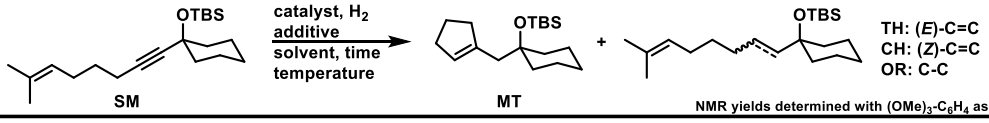
Representative Procedure A. Preparation of Cycloalkene 2a. $[Cp^*RuCl]_4$ (2.3 mg, 2 mol%) was added to a stirred solution of enyne **1a** (24.8 mg, 0.11 mmol) in 1,2-dichloroethane (1 mL, 0.1 M) in a flame dried Schlenk tube under argon. H_2 was bubbled through the mixture for 2 min before the flask was immersed into a pre-heated oil bath at 70 °C keeping a static H_2 atmosphere (ambient pressure, H_2 filled balloon). After stirring for 3 h at 70 °C, the mixture was allowed to cool to room temperature, the solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, pentane/Et_2O 100:1) to yield the title product as colorless oil (20.4 mg, 93%).

Representative Procedure B. Preparation of Cycloalkene S104. TBACl (0.021 M in 1,2-dichloroethane, 0.42 mL, 11 mol%) was added to solid $[Cp(Me_2CO_2Et)Ru(NCMe)_3][PF_6]$ (**19**, 4.3 mg, 10 mol%) in a flame dried Schlenk tube under argon. The mixture was stirred for 5 min at room temperature before a solution of enyne **S77** (29.3 mg, 0.08 mmol) in 1,2-dichloroethane (0.5 mL, 0.1 M) was added. H_2 was bubbled through the mixture for 2 min before the flask was immersed into a pre-heated oil bath at 70 °C keeping a static H_2 atmosphere (ambient pressure, H_2 filled balloon). After stirring for 3 h at 70 °C, the mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 40:1 – 20:1 – 10:1) to yield the title product as pale grey oil (16.9 mg, 65%).

Representative Procedure C. Preparation of Cyclopropane S89. $[Cp^*RuCl]_4$ (2.6 mg, 2 mol%) was added to a stirred solution of enyne **S60** (31.6 mg, 0.12 mmol) in CH_2Cl_2 (1.2 mL, 0.1 M) in a flame dried Schlenk tube under argon. H_2 was bubbled through the mixture for 2 min and stirring was continued for 18h under H_2 atmosphere (ambient pressure, H_2 filled balloon). The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 100:1) to yield the title product as colorless oil (29.1 mg, 91%).

Representative Procedure D. Preparation of Cyclopropane 85. $[Cp^*RuCl]_4$ (1.0 mg, 2 mol%) was added to a stirred solution of enyne **S56** (20.0 mg, 0.05 mmol) in 1,2-dichloroethane (1 mL, 0.5 M) in a flame dried thick-walled Schlenk tube under argon. H_2 was bubbled through the mixture for 2 min before the tube was sealed and immersed into a pre-heated oil bath at 90 °C keeping a static H_2 atmosphere. The mixture was stirred for 18 h at 90 °C before it was cooled to room temperature. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography (silica, hexanes/EtOAc 97:3) to yield the title product as colorless solid (15.6 mg, 78%).

Selected experimental data on the influence of various reaction parameters is summarized below.

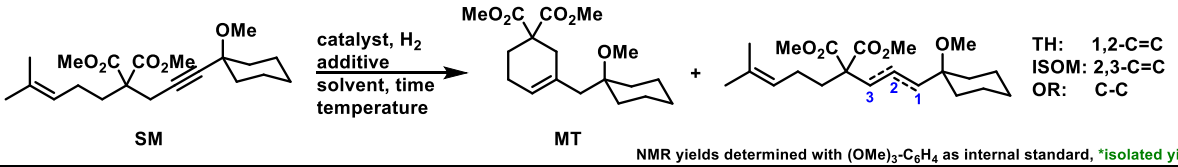


NMR yields determined with $(OMe)_3$-C_6H_4 as internal standard

	catalyst (8% [Ru])	additive	solvent	temp.	time	SM	MT	TH	CH	OR
temp. time	$[Cp^*RuCl]_4$		DCE	rt	10 h	89	5	0	0	1
	$[Cp^*RuCl]_4$		DCE	70 °C	5 min	93	6	0	0	0
	$[Cp^*RuCl]_4$		DCE	70 °C	30 min	66	31	2	0	1
	$[Cp^*RuCl]_4$	--- condition A ---	DCE	70 °C	3 h	4	85	5	0	3
Cp^X	$[Cp^*Ru(cod)Cl]$		DCE	70 °C	3 h	5	85	5	0	0
	$[Cp^*Ru(MeCN)_3][PF_6]$		DCE	70 °C	3 h	0	30	13	0	15
	$[Cp^*Ru(MeCN)_3][PF_6]$	TBACl	DCE	70 °C	3 h	6	75	12	0	3
	$[CpRu(cod)Cl]$		DCE	70 °C	3 h	93	5	0	0	0
	$[CpRu(MeCN)_3][PF_6]$		DCE	70 °C	3 h	34	17	0	0	0
	$[CpRu(MeCN)_3][PF_6]$	TBACl	DCE	70 °C	3 h	5	77	5	0	0
	$[Cp^ERu(MeCN)_3][PF_6]$		DCE	70 °C	3 h	20	66	0	0	0
	$[Cp^ERu(MeCN)_3][PF_6]$	TBACl	DCE	70 °C	3 h	28	62	1	0	0
Cp*RuX	$[Cp^*RuI]_4$		DCE	70 °C	3 h	37	33	7	0	22
	$[Cp^*Ru(OMe)]_2$		DCE	70 °C	3 h	21	71	3	5	0
	$[Cp^*Ru(CO)(MeCN)_2][PF_6]$		DCE	70 °C	3 h	60	9	29	0	0
	$[Cp^*Ru(CN)(cod)]$		DCE	70 °C	3 h	100	0	0	0	0
[M]	$[Cp^*IrCl_2]_2$		DCE	70 °C	3 h	88	0	0	0	0
	$[Cp^*RhCl_2]_2$		DCE	70 °C	3 h	98	0	0	0	0
	$[Cp^*Rh(MeCN)_3][SbF_6]_2$		DCE	70 °C	3 h	0	0	0	0	0
	$[Cp^*Rh(MeCN)_3][SbF_6]_2$	TBACl	DCE	70 °C	3 h	0	0	0	0	0
solv.	$[Cp^*RuCl]_4$		butanone	70 °C	3 h	31	57	3	9	0
	$[Cp^*RuCl]_4$		EtOAc	70 °C	3 h	63	30	1	6	0
	$[Cp^*RuCl]_4$		THP	70 °C	3 h	64	35	1	0	0
	$[Cp^*RuCl]_4$		MeCN	70 °C	3 h	100	0	0	0	0
	$[Cp^*RuCl]_4$		DCE/THP 1:1	70 °C	3 h	28	68	3	0	0

[in case of the dicationic [Cp*Rh] catalysts, a complex mixture of unidentified products was formed]

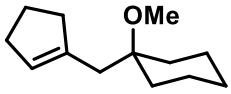
Selected experimental data on the optimization of six membered ring formation is summarized below.



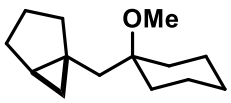
NMR yields determined with $(OMe)_3$-C_6H_4 as internal standard, *isolated yield

catalyst (8% [Ru])	additive	solvent	temp.	time	SM	MT	TH	ISOM	OR
$[Cp^*RuCl]_4$		DCE	70 °C	3 h	17 selectivity:	21 0.26	41 0.49	7 0.09	14 0.17
$[Cp^*RuCl]_4$		DCE/THP 1:1	70 °C	3 h	47	21 0.40	10 0.18	6 0.11	16 0.31
$[Cp^*Ru(OMe)]_2$		DCE	70 °C	3 h	29	27 0.42	10 0.16	6 0.10	20 0.32
$[CpRu(MeCN)_3][BF_4]$	TBACl	DCE	70 °C	3 h	9	60 0.77	19 0.23	0 0.00	0 0.00
$[Cp^ERu(MeCN)_3][PF_6]$	TBACl	DCE	70 °C	3 h	34	42 0.82	9 0.18	0 0.00	0 0.00
the catalyst loading was increased to 10 mol% [Ru] and the reaction time to 8 h to arrive at --- condition B ---									

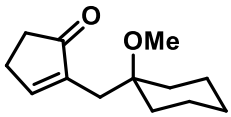
1-(Cyclopent-1-en-1-ylmethyl)-1-methoxycyclohexane (2a). According to the Representative Procedure A from enyne **1a** (24.8 mg, 0.11 mmol), colorless oil (20.4 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.36 (m, 1H), 3.18 (s, 3H), 2.36 – 2.26 (m, 4H), 2.27 – 2.21 (m, 2H), 1.90 – 1.77 (m, 2H), 1.73 – 1.64 (m, 2H), 1.59 – 1.37 (m, 5H), 1.32 – 1.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.7, 127.6, 75.6, 48.3, 37. 5, 36.9, 34.5, 32.6, 26.0, 23.9, 22.1. IR (film) $\tilde{\nu}$ 3038, 2929, 2848, 1455, 1444, 1081 cm^{-1}. HRMS (ESI$^+$) for $C_{13}H_{22}O$ [M+H]$^+$: calcd: 195.1734, found: 195.1741.



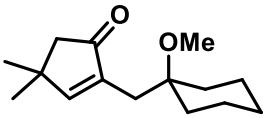
(1S*,5R*)-1-((1-Methoxycyclohexyl)methyl)bicyclo[3.1.0]hexane (3b). According to the Representative Procedure A from enyne **1b** (31.2 mg, 0.15 mmol); colorless oil (29.3 mg, 93%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.15 (s, 3H), 1.92 – 1.72 (m, 4H), 1.71 – 1.47 (m, 7H), 1.47 – 1.35 (m, 2H), 1.36 – 1.24 (m, 3H), 1.24 – 1.06 (m, 2H), 0.86 (dt, *J* = 8.1, 4.1 Hz, 1H), 0.40 (t, *J* = 4.2 Hz, 1H), 0.31 (dd, *J* = 8.0, 5.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 77.4, 48.2, 42.6, 35.1, 34.5, 32.5, 27,1, 26.1, 25.0, 23.9, 22.1, 22.1, 13.5. IR (film) $\tilde{\nu}$ 2930, 2853, 1456, 1288, 1080 1026, 806 cm^{-1}. HRMS (ESI$^+$) calcd for $C_{14}H_{24}O$ [M+H]$^+$: calcd: 209.1810; found: 209.1901.



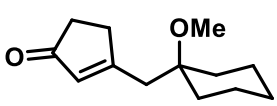
2-((1-Methoxycyclohexyl)methyl)cyclopent-2-en-1-one (5). According to the Representative Procedure A from enyne **4** (25.4 mg, 0.10 mmol); yellow oil (14.5 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 1H), 3.22 (s, 3H), 2.64 – 2.55 (m, 2H), 2.40 – 2.36 (m, 2H), 2.34 (q, *J* = 1.3 Hz, 2H), 1.71 – 1.60 (m, 2H), 1.58 – 1.49 (m, 1H), 1.49 – 1.41 (m, 4H), 1.32 – 1.16 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 160.8, 141.9, 75.4, 48.5, 34.2, 34.0, 30.1, 26.9, 25.9, 21.9. IR (film) $\tilde{\nu}$ 2931, 2856, 1700, 1444, 1074 cm^{-1}. HRMS (ESI$^+$) for $C_{13}H_{20}O_2$ [M+Na]$^+$: calcd: 231.1355, found: 231.1357.



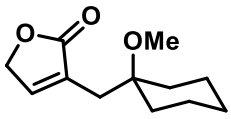
2-((1-Mmethoxycyclohexyl)methyl)-4,4-dimethylcyclopent-2-en-1-one (6). According to General Procedure A from enyne **S75** (23.1 mg, 0.08 mmol); colorless oil (14.1 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (t, *J* = 1.1 Hz, 1H), 3.19 (s, 3H), 2.28 (d, *J* = 1.1 Hz, 2H), 2.25 (s, 2H), 1.70 – 1.61 (m, 2H), 1.57 – 1.39 (m, 5H), 1.27 – 1.15 (m, 3H), 1.20 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.9, 170.2, 138.5, 75.3, 49.9, 48.4, 39.1, 34.1, 29.7, 28.5, 25.9, 21.9. IR (film) ν̃ 2930, 2861, 1703, 1073 cm^{-1}. HRMS (CI$^+$) for $C_{15}H_{24}O_2$ [M+Na]$^+$: calcd 237.1849, found 237.1849.



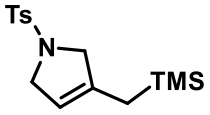
3-((1-Mmethoxycyclohexyl)methyl)cyclopent-2-en-1-one (7). According to General Procedure A from enyne **1m** (27.5 mg, 0.11 mmol); colorless oil (11.8 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.01 (tt, *J* = 1.9, 1.0 Hz, 1H), 3.21 (s, 3H), 2.71 – 2.65 (m, 2H), 2.56 (s, 2H), 2.40 – 2.36 (m, 2H), 1.79 – 1.68 (m, 2H), 1.61 – 1.49 (m, 3H), 1.49 – 1.39 (m, 2H), 1.34 – 1.22 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.3, 179.1, 132.9, 75.7, 48.5, 39.5, 35.6, 34.7, 33.3, 25.7, 22.0. IR (neat) ν̃ 2930, 2856, 1702, 1674, 1610, 1072 cm^{-1}. HRMS (ESI$^+$) for $C_{13}H_{20}O_2$ [M+Na]$^+$: calcd 231.1355, found 231.1357.



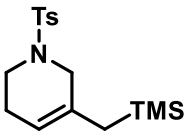
3-((1-Methoxycyclohexyl)methyl)furan-2(5*H*)-one (8). According to the Representative Procedure A from enyne **S76** (27.1 mg, 0.11 mmol); light yellow oil (11.9 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (p, *J* = 1.6 Hz, 1H), 4.80 (q, *J* = 1.7 Hz, 2H), 3.22 (s, 3H), 2.46 (q, *J* = 1.6 Hz, 2H), 1.75 – 1.67 (m, 2H), 1.59 – 1.42 (m, 5H), 1.36 – 1.20 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 147.4, 129.6, 75.3, 70.5, 48.6, 34.1, 30.8, 25.8, 21.8. IR (film) $\tilde{\nu}$ 2931, 2856, 1730, 1455, 1346, 1071 cm^{-1}. HRMS (ESI$^+$) for $C_{12}H_{18}O_3$ [M+H]$^+$: calcd: 211.1329, found: 211.1329.



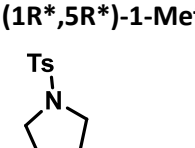
1-Tosyl-3-((trimethylsilyl)methyl)-2,5-dihydro-1*H*-pyrrole (28a). According to General Procedure A from enyne **27a** (36.1 mg, 0.10 mmol); colorless oil (26.3 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.66 (m, 2H), 7.35 – 7.28 (m, 2H), 5.03 (m, 1H), 4.08 (m, 2H), 3.93 (m, 2H), 2.42 (s, 3H), 1.43 (dd, *J* = 2.2, 0.9 Hz, 2H), -0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 136.9, 134.3, 129.8, 127.6, 115.9, 58.2, 55.5, 21.6, 19.1, -1.4. IR (film) $\tilde{\nu}$ 2950, 2846, 1330, 1248, 1157, 1103 cm^{-1}. HRMS (EI$^+$) for $C_{15}H_{23}NO_2SSi$ [M]$^+$: calcd 309.1219, found 309.1218.



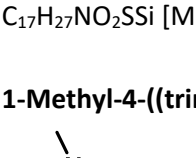
1-Tosyl-5-((trimethylsilyl)methyl)-1,2,3,6-tetrahydropyridine (28b). According to General Procedure B (with 20 mol% $[Cp(Me_2CO_2Et)Ru(NCMe)_3][PF_6]$ and 25 mol% TBACl (0.04 M), for 16 h) from enyne **27b** (37.4 mg, 0.10 mmol); colorless oil (19.6 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.33 – 7.29 (m, 2H), 5.24 (m, 1H), 3.38 (q, *J* = 2.4 Hz, 2H), 3.08 (t, *J* = 5.8 Hz, 2H), 2.43 (s, 3H), 2.17 (m, 2H), 1.36 (s, 2H), -0.03 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.6, 131.8, 129.7, 127.8, 116.9, 48.9, 42.8, 25.4, 24.9, 21.7, -1.2. IR (film) $\tilde{\nu}$ 2953, 2845, 1341, 1247, 1162 cm^{-1}. HRMS (EI$^+$) for $C_{16}H_{25}NO_2SSi$ [M]$^+$: calcd 323.1370, found 323.1366.



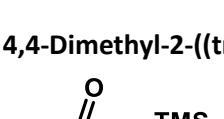
(1R*,5R*)-1-Methyl-3-tosyl-5-((trimethylsilyl)methyl)-3-azabicyclo[3.1.0]hexane (30). According to General Procedure A from known enyne **29** (18.0 mg, 0.54 mmol); colorless oil (13.0 mg, 72%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.35 – 7.30 (m, 2H), 3.54 (d, *J* = 8.9 Hz, 1H), 3.49 (d, *J* = 8.9 Hz, 1H), 2.78 – 2.71 (m, 2H), 2.44 (s, 3H), 1.01 (s, 3H), 0.70 (d, *J* = 4.9 Hz, 1H), 0.67 (dd, *J* = 14.8, 1.0 Hz, 1H), 0.38 (d, *J* = 14.9 Hz, 1H), 0.09 (dt, *J* = 5.0, 1.0 Hz, 1H), 0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.7, 129.7, 127.7, 55.3, 55.2, 28.1, 25.9, 21.7, 20.1, 17.3, 14.8, -0.5. IR (film) $\tilde{\nu}$ 2953, 2854, 1339, 1246, 1159 cm^{-1}. HRMS (CI$^+$) for $C_{17}H_{27}NO_2SSi$ [M+H]$^+$: calcd 338.1605, found 338.1604.



1-Methyl-4-((trimethylsilyl)methyl)-1,5-dihydro-2H-pyrrol-2-one (32). According to General Procedure A from enyne **31** (24.8 mg, 0.11 mmol); light yellow oil (14.5 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (m, 1H), 3.78 (s, 2H), 2.97 (s, 3H), 1.86 (m, 2H), 0.06 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 157.9, 119.9, 58.1, 29.0, 21.6, -1.5. IR (film) $\tilde{\nu}$ 2953, 2845, 1341, 1247, 1162 cm^{-1}. HRMS (EI$^+$) for $C_9H_{17}NOSi$ [M]$^+$: calcd 183.1074, found 183.1071.



4,4-Dimethyl-2-((trimethylsilyl)methyl)cyclopent-2-en-1-one (34). According to General Procedure A from enyne **33** (25.0 mg, 0.11 mmol); colorless oil (13.0 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.85 (t, *J* = 1.1 Hz, 1H), 2.24 (s, 2H), 1.59 (d, *J* = 1.1 Hz, 2H), 1.19 (s, 6H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.6, 164.4, 140.8, 50.1, 38.6, 28.8, 14.0, -1.6. IR



(film) ṽ 2955, 1703, 1247, 1160, 1039 cm^{-1}. HRMS (CI^+) for $C_{11}H_{20}OSi$ $[M]^+$: calcd 196.1278, found 196.1277.

2-Neopentylcyclopent-2-en-1-one (36). According to General Procedure A from enyne **35** (25.3 mg, 0.13 mmol); light yellow oil (12.8 mg, 64%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.34 (tt, *J* = 2.8, 0.9 Hz, 1H), 2.61 – 2.56 (m, 2H), 2.40 – 2.36 (m, 2H), 2.10 (q, *J* = 1.2 Hz, 2H), 0.87 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.2, 160.1, 144.2, 37.7, 34.3, 31.5, 29.4, 26.5. IR (film) ṽ 2952, 2856, 1698, 1365 cm^{-1}. HRMS (CI^+) for $C_{10}H_{16}O$ $[M+H]^+$: calcd 153.1274, found 153.1273.

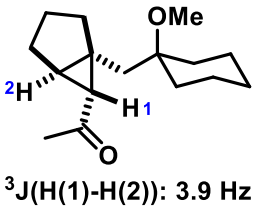
3-((Trimethylsilyl)methyl)furan-2(5*H*)-one (38). According to General Procedure A from enyne **37** (27.8 mg, 0.13 mmol); light brown oil (12.7 mg, 56%). On larger scale a slightly modified protocol was followed (see preparation of **39**). ^1H NMR (400 MHz, $CDCl_3$) δ 6.88 (td, *J* = 1.9, 1.0 Hz, 1H), 4.74 (q, *J* = 1.7 Hz, 2H), 1.78 (q, *J* = 1.5 Hz, 2H), 0.05 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 140.5, 132.2, 70.1, 15.6, -1.7. IR (film) ṽ 2955, 1745, 1249, 1159, 1064, 1037 cm^{-1}. HRMS (CI^+) for $C_8H_{14}O_2Si$ $[M+H]^+$: calcd 171.0836, found 171.0836.

Ethyl (1S*,5R*,6R*)-1-((1-methoxycyclohexyl)methyl)bicyclo[3.1.0]hexane-6-carboxylate (3i). According to General Procedure A from enyne **1i** (34.0 mg, 0.12 mmol); colorless oil (22.8 mg, 67%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.10 (q, *J* = 7.1 Hz, 2H), 3.14 (s, 3H), 2.00 (ddd, *J* = 13.4, 8.4, 1.1 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.89 (d, *J* = 7.0 Hz, 2H), 1.83 – 1.67 (m, 5H), 1.65 – 1.33 (m, 7H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.22 – 1.05 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.4, 76.3, 60.3, 48.1, 36.9, 34.9, 33.8, 33.7, 33.5, 33.1, 27.2, 26.3, 26.0, 21.9, 21.8, 21.1, 14.5. IR (film) ṽ 2931, 2859, 1718, 1176, 1154, 1079 cm^{-1}. HRMS (ESI^+) for $C_{17}H_{28}O_3$ $[M+H]^+$: calcd 281.2111, found 281.2110.

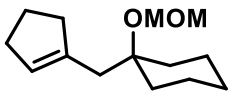
Methyl (1S*,5R*,6S*)-1-((1-methoxycyclohexyl)methyl)bicyclo[3.1.0]hexane-6-carboxylate (3j). According to General Procedure A from enyne **1j** (32.1 mg, 0.12 mmol); colorless oil (29.6 mg, 92%). ^1H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 3.14 (s, 3H), 2.10 (ddd, *J* = 13.1, 8.8, 1.9 Hz, 1H), 1.95 – 1.79 (m, 5H), 1.78 – 1.64 (m, 2H), 1.63 – 1.29 (m, 10H), 1.27 – 1.12 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 76.4, 51.7, 48.1, 43.3, 34.7, 34.3, 33.7, 31.5, 31.3, 30.3, 26.0, 25.7, 24.6, 22.0, 22.0. IR (film) ṽ 2931, 2859, 1728, 1436, 1152, 1078 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{26}O_3$ $[M+Na]^+$: calcd 289.1774, found 289.1779.

(1S*,5R*,6R*)-1-((1-Methoxycyclohexyl)methyl)bicyclo[3.1.0]hexane-6-carbaldehyde (3k). According to General Procedure A from enyne **1k** (20.1 mg, 0.09 mmol); colorless oil (12.5 mg, 62%). ^1H NMR (400 MHz, $CDCl_3$) δ 9.49 (d, *J* = 4.8 Hz, 1H), 3.13 (s, 3H), 2.06 (dd, *J* = 13.4, 8.3 Hz, 1H), 1.99 (t, *J* = 3.6 Hz, 1H), 1.97 – 1.70 (m, 8H), 1.69 – 1.37 (m, 6H), 1.27 – 1.06 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.5, 76.1, 48.1, 40.3, 36., 35.11, 35.0, 35.0, 34.0, 33.6, 27.2, 25.9, 21.9, 21.8, 21.0. IR (film) *ṽ* 2932, 2858, 1695, 1075 cm^{-1}. HRMS (ESI^+) for $C_{15}H_{24}O_2$ $[M+Na]^+$: calcd 259.1668, found 259.1669.

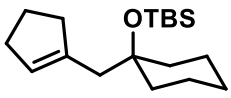
1-((1S*,5R*,6R*)-1-((1-Methoxycyclohexyl)methyl)bicyclo[3.1.0]hexan-6-yl)ethan-1-one (3l). According to General Procedure A from enyne **1l** (27.3 mg, 0.11 mmol); colorless oil (22.7 mg, 82%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.12 (s, 3H), 2.22 (s, 3H), 2.02 (ddd, *J* = 13.5, 8.5, 1.1 Hz, 1H), 1.99 – 1.34 (m, 15H), 1.23 – 1.10 (m, 3H), 1.05 (ddd, *J* = 13.3, 11.7, 4.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 76.2, 48.1, 41.2, 36.1, 35.0, 33.8, 33.3, 32.9, 32.3, 27.4, 25.9, 21.8, 21.1. IR (film) $\tilde{\nu}$ 2931, 2858, 1688, 1361, 1185, 1077 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{26}O_2$ [M+Na]$^+$: calcd 273.1825, found 273.1821.



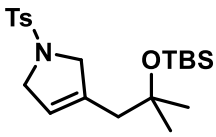
1-(Cyclopent-1-en-1-ylmethyl)-1-(methoxymethoxy)cyclohexane (S81). According to the Representative Procedure A from enyne **S52** (26.6 mg, 0.10 mmol), colorless oil (18.0 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.43 – 5.38 (m, 1H), 4.73 (s, 2H), 3.41 (s, 3H), 2.34 – 2.26 (m, 6H), 1.83 (m, 2H), 1.76 – 1.20 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 128.1, 90.8, 77.8, 55.9, 39.5, 37.1, 35.5, 32.6, 25.9, 24.0, 22.5. IR (film) $\tilde{\nu}$ 2927, 2849, 1448, 1140, 1028 cm^{-1}. HRMS (ESI$^+$) for $C_{14}H_{24}O_2$ [M+Na]$^+$: calcd: 247.1668, found: 247.1671.



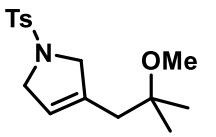
***tert*-Butyl((1-(cyclopent-1-en-1-ylmethyl)cyclohexyl)oxy)dimethylsilane (S82)**. According to the Representative Procedure A from enyne **S53** (31.4 mg, 0.09 mmol), colorless oil (19.0 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.40 (m, 1H), 2.34 – 2.25 (m, 6H), 1.83 (m, 2H), 1.70 – 1.57 (m, 2H), 1.53 – 1.24 (m, 8H), 0.88 (s, 9H), 0.08 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.4, 127.9, 75.9, 43.8, 38.2, 37.4, 32.6, 26.3, 25.9, 24.2, 23.0, 18.6, -1.4. IR (film) $\tilde{\nu}$ 2927, 2853, 1471, 1251, 1056, 769 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{34}OSi$ [M+Na]$^+$: calcd: 317.2271, found: 317.2271.



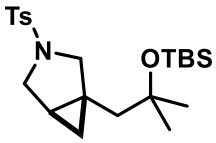
3-(2-((*tert*-Butyldimethylsilyl)oxy)-2-methylpropyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (S83). According to the Representative Procedure A from enyne **S54** (44.8 mg, 0.10 mmol); colorless solid (31.0 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.68 (m, 2H), 7.33 – 7.28 (m, 2H), 5.34 – 5.27 (m, 1H), 4.14 – 4.03 (m, 4H), 2.42 (s, 3H), 2.15 (s, 2H), 1.13 (s, 6H), 0.83 (s, 9H), 0.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 137.1, 134.6, 129.8, 127.6, 121.7, 73.5, 57.7, 54.8, 45.0, 30.0, 26.0, 21.7, 18.1, -1.9. IR (film) $\tilde{\nu}$ 3039, 2928, 2856, 1337, 1161, 1102 cm^{-1}. HRMS (ESI$^+$) for $C_{21}H_{35}NO_3SSi$ [M+Na]$^+$: calcd: 432.1999, found: 432.2000.



3-(2-Methoxy-2-methylpropyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (S84). According to the Representative Procedure A from enyne **S55** (34.8 mg, 0.1 mmol), colorless solid (24.0 mg, 78%). Single crystals suitable for X-ray analysis were grown by vapor diffusion of pentane into a saturated solution of product in CH_2Cl_2 at room temperature. mp.: 76-77 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.33 – 7.28 (m, 2H), 5.33 – 5.29 (m, 1H), 4.14 – 4.05 (m, 4H), 3.14 (s, 3H), 2.42 (s, 3H), 2.17 (s, 2H), 1.04 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 136.7, 134.5, 129.8, 127.6, 121.7, 74.5, 57.6, 54.9, 49.4, 40.2, 24.8, 21.7. IR (film) $\tilde{\nu}$ 2962, 2860, 2829, 1336, 1155, 1055 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{23}NO_3S$ [M+Na]$^+$: calcd: 332.1291, found: 332.1288.

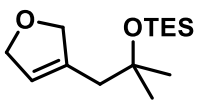


(1R*,5R*)-1-(2-((*tert*-Butyldimethylsilyl)oxy)-2-methylpropyl)-3-tosyl-3-azabicyclo[3.1.0]hexane (S85).

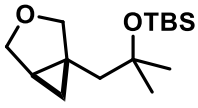


According to the Representative Procedure D from enyne **S56** (20.0 mg, 0.05 mmol); colorless solid (15.6 mg, 78%). Single crystals suitable for X-ray analysis were grown by slowly cooling a saturated solution of product in Et_2O to −20 °C. m.p.: 104-105 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.27 (m, 2H), 3.64 (d, *J* = 9.6 Hz, 1H), 3.47 (d, *J* = 9.0 Hz, 1H), 2.98 (dd, *J* = 9.0, 3.9 Hz, 1H), 2.91 (d, *J* = 9.9 Hz, 1H), 2.43 (s, 3H), 1.96 (d, *J* = 14.2 Hz, 1H), 1.26 (s, 3H), 1.18 (s, 3H), 1.09 – 0.97 (m, 2H), 0.89 (s, 9H), 0.74 (t, *J* = 4.9 Hz, 1H), 0.59 (dd, *J* = 7.9, 5.1 Hz, 1H), 0.10 (s, 3H), 0.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 133.6, 129.6, 127.8, 74.9, 54.3, 49.6, 49.2, 31.4, 28.8, 26.2, 25.0, 21.7, 21.2, 18.2, 15.2, -1.7, -1.7. IR (film) $\tilde{\nu}$ 2928, 2855, 1462, 1347, 1163, 1132, 1027, 832, 771, 664, 567, 548 cm^{-1}. HRMS (ESI$^+$) for $C_{22}H_{37}NO_3SSi$ [M+Na]$^+$: calcd: 446.2156, found: 446.2155.

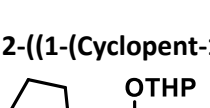
((1-(2,5-Dihydrofuran-3-yl)-2-methylpropan-2-yl)oxy)triethylsilane (S86). According to the Representative Procedure A from enyne **S57** (27.0 mg, 0.09 mmol), colorless oil (22.2 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.54 – 5.50 (m, 1H), 4.67 – 4.57 (m, 4H), 2.29 (s, 2H), 1.23 (s, 6H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.63 – 0.54 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 138.0, 122.6, 78.1, 75.5, 73.3, 43.7, 30.1, 7.2, 6.9. IR (film) $\tilde{\nu}$ 3412, 2973, 1735, 1370, 1234, 1072, 1010, 901, 736 cm^{-1}. HRMS (ESI$^+$) for $C_{14}H_{28}O_2Si$ [M+Na]$^+$: calcd: 279.1751; found: 279.1753.



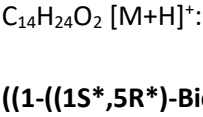
((1-((1R*,5R*)-3-Oxabicyclo[3.1.0]hexan-1-yl)-2-methylpropan-2-yl)oxy)(tert-butyl)dimethylsilane (S87). According to the Representative Procedure D from enyne **S58** (22.3 mg, 0.08 mmol), colorless oil (12.7 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.90 (d, *J* = 8.5 Hz, 1H), 3.76 – 3.64 (m, 2H), 3.62 (d, *J* = 8.5 Hz, 1H), 2.13 (d, *J* = 14.2 Hz, 1H), 1.32 (d, *J* = 14.3 Hz, 1H), 1.28 (s, 3H), 1.24 (s, 3H), 1.20 (d, *J* = 12.1 Hz, 1H), 1.13 (td, *J* = 6.0, 2.8 Hz, 1H), 0.86 (s, 9H), 0.63 (d, *J* = 6.4 Hz, 2H), 0.10 (s, 3H), 0.08 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 75.0, 74.1, 69.0, 48.8, 31.2, 29.2, 26.1, 25.9, 22.9, 18.2, 14.7, -1.7. IR (film) $\tilde{\nu}$ 2956, 2856, 1780, 1364, 1252, 1131, 1024, 830, 770, 690 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{30}O_2Si$ [M+H]$^+$: calcd: 271.2088, found: 271.2087.



2-((1-(Cyclopent-1-en-1-yl)-2-methylpropan-2-yl)oxy)tetrahydro-2H-pyran (S88). According to General Procedure A from enyne **S59** (29.0 mg, 0.11 mmol); colorless oil (21.0 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.41 (m, 1H), 4.80 – 4.75 (m, 1H), 3.99 – 3.90 (m, 1H), 3.49 – 3.40 (m, 1H), 2.37 – 2.24 (m, 6H), 1.89 – 1.78 (m, 2H), 1.70 – 1.56 (m, 2H), 1.56 – 1.44 (m, 4H), 1.23 (s, 3H), 1.19 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.6, 127.9, 94.1, 76.7, 63.3, 44.0, 37.0, 32.6, 32.6, 27.5, 26.1, 25.7, 24.2, 20.9. IR (film) ν̃ 2939, 2847, 1382, 1129, 1023, 991 cm^{-1}. HRMS (APCI) for $C_{14}H_{24}O_2$ [M+H]$^+$: calcd: 225.1849, found: 225.1848.

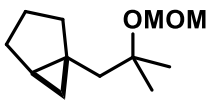


((1-((1S*,5R*)-Bicyclo[3.1.0]hexan-1-yl)-2-methylpropan-2-yl)oxy)(tert-butyl)dimethylsilane (S89). According to the Representative Procedure C from enyne **S60** (31.6 mg, 0.12 mmol); colorless oil (29.1 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.92 (dd, *J* = 14.1, 1.4 Hz, 1H), 1.81 (dd, *J* = 12.0, 7.8 Hz, 1H), 1.74 – 1.51 (m, 4H), 1.29 (d, *J* = 14.4 Hz, 1H), 1.27 (s, 3H), 1.24 (s, 3H), 1.18 (d, *J* = 8.3 Hz, 1H), 0.87 – 0.86 (m, 1H), 0.86 (s, 9H), 0.44 – 0.31 (m, 2H), 0.08 (s, 3H), 0.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 75.6, 52.2, 33.1, 30.9, 30.3, 27.0, 26.1, 26.0, 24.0, 22.3, 18.2, 13.6, -



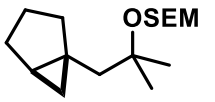
1.7. IR (film) $\tilde{\nu}$ 2954, 2929, 2857, 1462, 1251, 1144, 1031, 832, 769, 689 cm^{-1}. HRMS (CI) for $C_{16}H_{32}OSi$ $[M+H]^+$: calcd: 269.2295, found: 269.2295.

(1S*,5R*)-1-(2-(Methoxymethoxy)-2-methylpropyl)bicyclo[3.1.0]hexane (S90). According to the



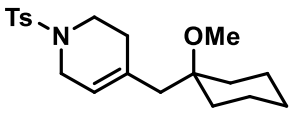
Representative Procedure C from enyne **S61** (34.3 mg, 0.17 mmol); colorless oil (27.4 mg, 79%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (q, *J* = 7.2 Hz, 2H), 3.36 (s, 3H), 2.00 (dd, *J* = 14.4, 1.5 Hz, 1H), 1.86 – 1.78 (m, 1H), 1.73 – 1.48 (m, 5H), 1.35 (d, *J* = 14.4 Hz, 1H), 1.29 (s, 3H), 1.26 (s, 3H), 1.22 – 1.08 (m, 1H), 0.87 (dt, *J* = 8.2, 4.1 Hz, 1H), 0.45 – 0.40 (m, 1H), 0.39 – 0.32 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 91.1, 78.1, 55.2, 48.6, 33.0, 27.3, 27.0, 26.9, 25.6, 24.1, 22.3, 13.6. IR (film) $\tilde{\nu}$ 2928, 1715, 1449, 1259, 1087, 1030, 919, 806 cm^{-1}. HRMS (ESI^+) for $C_{12}H_{22}O_2$ $[M+Na]^+$: calcd: 221.1511, found: 221.1514.

(2-(((1-((1S*,5R*)-Bicyclo[3.1.0]hexan-1-yl)-2-methylpropan-2-yl)oxy)methoxy)ethyl)trimethylsilane



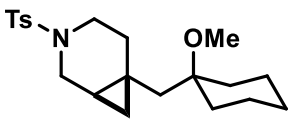
(S91). According to the Representative Procedure C from enyne **S62** (27.6 mg, 0.10 mmol); colorless oil (28.0 mg, quant.). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.77 – 4.71 (m, 2H), 3.67 – 3.55 (m, 2H), 1.97 (d, *J* = 14.4 Hz, 1H), 1.85 – 1.76 (m, 1H), 1.70 – 1.48 (m, 4H), 1.34 (d, *J* = 14.5 Hz, 1H), 1.28 (s, 3H), 1.24 (s, 3H), 1.18 – 1.07 (m, 1H), 0.97 – 0.82 (m, 3H), 0.43 – 0.38 (m, 1H), 0.34 (dd, *J* = 7.9, 4.8 Hz, 1H), -0.00 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 89.3, 77.9, 64.9, 48.6, 33.0, 27.3, 27.0, 25.7, 24.1, 22.3, 18.4, 13.6, -1.2. IR (film) $\tilde{\nu}$ 2955, 1259, 1091, 1023, 858, 833, 797, 692 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{32}O_2Si$ $[M+Na]^+$: calcd: 307.2064, found: 307.2066.

4-((1-Methoxycyclohexyl)methyl)-1-tosyl-1,2,3,6-tetrahydropyridine (S92). According to the



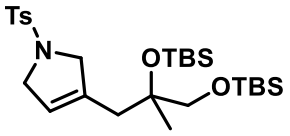
Representative Procedure B from enyne **S63** (33.7 mg, 0.08 mmol), colorless oil (17.9 mg, 59%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.64 (m, 2H), 7.33 – 7.28 (m, 2H), 5.36 – 5.28 (m, 1H), 3.60 – 3.52 (m, 2H), 3.14 (t, *J* = 5.7 Hz, 2H), 3.13 (s, 3H), 2.42 (s, 3H), 2.28 – 2.22 (m, 2H), 2.07 (s, 2H), 1.68 – 1.31 (m, 6H), 1.31 – 1.11 (m, 3H), 0.96 – 0.81 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 133.6, 133.5, 129.7, 127.9, 120.0, 75.7, 48.2, 45.0, 43.2, 42.7, 34.4, 29.9, 25.9, 22.0, 21.7. IR (film) $\tilde{\nu}$ 2929, 2854, 1458, 1341, 1161 cm^{-1}. HRMS (ESI^+) for $C_{20}H_{29}NO_3S$ $[M+Na]^+$: calcd: 386.1760, found: 386.1758.

(1R*,6R*)-6-((1-Methoxycyclohexyl)methyl)-3-tosyl-3-azabicyclo[4.1.0]heptane (S93). According to the

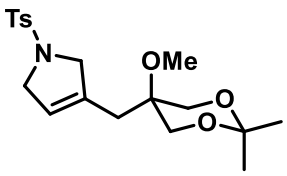


Representative Procedure A from enyne **S64** (35.0 mg, 0.09 mmol); colorless oil (27.2 mg, 77%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.59 (m, 2H), 7.31 – 7.28 (m, 2H), 3.31 (dt, *J* = 11.4, 1.4 Hz, 1H), 3.22 (dd, *J* = 11.6, 5.4 Hz, 1H), 3.08 (s, 3H), 2.91 – 2.84 (m, 1H), 2.71 (ddd, *J* = 12.0, 8.2, 5.3 Hz, 1H), 2.42 (s, 3H), 2.12 (dt, *J* = 13.7, 5.8 Hz, 1H), 1.92 (ddd, *J* = 13.8, 8.2, 5.3 Hz, 1H), 1.81 – 1.67 (m, 2H), 1.60 – 1.33 (m, 6H), 1.28 – 1.08 (m, 4H), 0.82 (dtd, *J* = 8.8, 5.4, 1.9 Hz, 1H), 0.51 (dd, *J* = 8.7, 4.9 Hz, 1H), 0.42 (t, *J* = 5.2 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 133.9, 129.7, 127.7, 76.7, 47.9, 45.0, 44.9, 42.9, 35.1, 34.9, 28.0, 26.0, 21.9, 21.8, 21.7, 17.8, 17.2, 15.1. IR (film) $\tilde{\nu}$ 2929, 2854, 1455, 1339, 1160, 1075 cm^{-1}. HRMS (ESI^+) for $C_{21}H_{31}NO_3S$ $[M+Na]^+$: calcd: 400.1917, found: 400.1917.

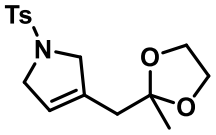
3-(2,3-Bis((*tert*-Butyldimethylsilyl)oxy)-2-methylpropyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (S94). According to the Representative Procedure A from enyne **S65** (55.0 mg, 0.09 mmol), colorless oil (34.2 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.33 – 7.28 (m, 2H), 5.32 (m, 1H), 4.11 – 4.01 (m, 4H), 3.26 – 3.20 (m, 2H), 2.42 (s, 3H), 2.27 – 2.21 (m, 1H), 2.20 – 2.11 (m, 1H), 1.10 (s, 3H), 0.86 (s, 9H), 0.83 (s, 9H), 0.03 (s, 3H), 0.03 (s, 3H), 0.00 (s, 3H), -0.02 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 136.6, 134.5, 129.8, 127.7, 121.8, 76.2, 69.8, 57.9, 54.8, 39.6, 26.1, 26.0, 25.4, 21.7, 18.4, 18.3, -1.7, -1.8, -5.4, –5.4. IR (film) $\tilde{\nu}$ 2954, 2929, 2856, 1163, 1096 cm^{-1}. HRMS (ESI$^+$) for $C_{27}H_{49}NO_4SSi_2$ [M+Na]$^+$: calcd: 562.2813, found: 562.2814.



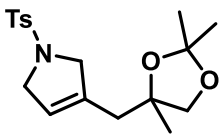
3-((5-Methoxy-2,2-dimethyl-1,3-dioxan-5-yl)methyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (S95). According to General Procedure A from enyne **S66** (39.4 mg, 0.09 mmol); colorless oil (24.6 mg, 69%).^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.67 (m, 2H), 7.34 – 7.29 (m, 2H), 5.45 – 5.40 (m, 1H), 4.08 (s, 4H), 3.65 (d, *J* = 11.9 Hz, 2H), 3.49 (d, *J* = 12.0 Hz, 2H), 3.25 (s, 3H), 2.42 (s, 3H), 2.34 (s, 2H), 1.39 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 134.5, 134.3, 129.9, 127.6, 122.6, 98.8, 71.7, 65.2, 57.4, 54.9, 50.1, 30.8, 24.4, 23.0, 21.7. IR (neat) $\tilde{\nu}$ 2990, 2941, 2249, 1340, 1160, 1092 cm^{-1}. HRMS (ESI$^+$) for $C_{19}H_{27}NO_5S$ [M+Na]$^+$: calcd 404.1502, found 404.1504.



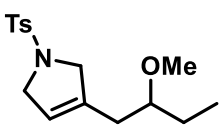
3-((2-Methyl-1,3-dioxolan-2-yl)methyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (S96). According to the Representative Procedure A from enyne **S67** (36.0 mg, 0.10 mmol); colorless oil (17.3 mg, 54%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.69 (m, 2H), 7.34 – 7.28 (m, 2H), 5.39 (m, 1H), 4.09 (s, 4H), 3.91 – 3.84 (m, 2H), 3.84 – 3.77 (m, 2H), 2.41 (s, 3H), 2.35 (s, 2H), 1.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.4, 135.2, 134.4, 129.8, 127.6, 122.4, 109.0, 64.8, 57.3, 55.1, 38.9, 23.9, 21.6. IR (film) $\tilde{\nu}$ 2983, 2875, 1341, 1161, 1046 cm^{-1}. HRMS (ESI$^+$) for $C_{16}H_{21}NO_4S$ [M+Na]$^+$: calcd: 346.1084, found: 346.1083.



1-Ttosyl-3-((2,2,4-trimethyl-1,3-dioxolan-4-yl)methyl)-2,5-dihydro-1*H*-pyrrole (S97). According to General Procedure A from enyne **S68** (43.8 mg, 0.11 mmol); colorless oil (29.0 mg, 74%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.69 (m, 2H), 7.34 – 7.28 (m, 2H), 5.35 (m, 1H), 4.26 – 4.18 (m, 1H), 4.10 (m, 2H), 4.04 – 3.95 (m, 1H), 3.71 (d, *J* = 8.4 Hz, 1H), 3.68 (d, *J* = 8.4 Hz, 1H), 2.42 (s, 3H), 2.33 – 2.17 (m, 2H), 1.35 (d, *J* = 0.8 Hz, 3H), 1.30 (d, *J* = 0.8 Hz, 3H), 1.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 136.1, 134.4, 129.8, 127.6, 122.4, 109.8, 80.2, 74.4, 57.6, 55.0, 39.6, 27.3, 27.2, 24.6, 21.7. IR (film) ν̃ 2983, 2868, 1341, 1160, 1100, 1055 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{25}NO_4S$ [M+H]$^+$: calcd 352.1577, found 352.1581.

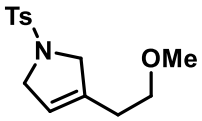


3-(2-Methoxybutyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (S98). According to the Representative Procedure A from enyne **S69** (41.8 mg, 0.12 mmol), pale brown oil (13.3 mg, 36%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 5.32 (s, 1H), 4.13 – 3.99 (m, 4H), 3.25 (s, 3H), 3.16 – 3.09 (m, 1H), 2.42 (s, 3H), 2.17 (d, *J* = 5.9 Hz, 2H), 1.48 – 1.31 (m, 2H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 137.0,

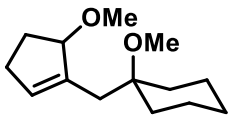


134.4, 129.8, 127.6, 120.3, 80.5, 57.1, 56.6, 55.1, 32.8, 25.8, 21.7, 9.3. IR (film) $\tilde{\nu}$ 2967, 2930, 1598, 1341, 1160 cm^{-1}. HRMS (ESI^+) for $C_{16}H_{23}NO_3S$ $[M+Na]^+$: calcd: 332.1291, found: 332.1291.

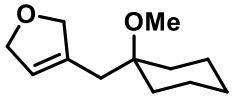
3-(2-Methoxyethyl)-1-tosyl-2,5-dihydro-1*H*-pyrrole (S99). According to the Representative Procedure A from enyne **S70** (34.8 mg, 0.11 mmol), colorless oil (3.5 mg, 11%). ^1H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.34 – 7.29 (m, 2H), 5.34 (hept, *J* = 1.6 Hz, 1H), 4.13 – 4.05 (m, 2H), 4.06 – 4.01 (m, 2H), 3.42 (t, *J* = 6.3 Hz, 2H), 3.30 (s, 3H), 2.43 (s, 3H), 2.31 – 2.23 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5, 137.0, 134.5, 129.9, 127.6, 119.6, 70.5, 58.8, 56.8, 55.1, 29.3, 21.7. IR (film) $\tilde{\nu}$ 2921, 2863, 1341, 1160, 1100 cm^{-1}. HRMS (ESI^+) for $C_{14}H_{19}NO_3S$ $[M+H]^+$: calcd: 282.1158, found: 282.1158.



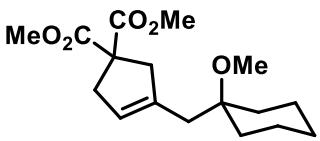
1-Methoxy-1-((5-methoxycyclopent-1-en-1-yl)methyl)cyclohexane (S100). According to the Representative Procedure A from enyne **S71** (30.5 mg, 0.12 mmol); colorless oil (13.7 mg, 53%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.67 (m, 1H), 4.42 – 4.36 (m, 1H), 3.28 (s, 3H), 3.21 (s, 3H), 2.45 – 2.35 (m, 2H), 2.29 – 2.18 (m, 1H), 2.17 – 2.04 (m, 2H), 1.82 – 1.70 (m, 2H), 1.69 – 1.60 (m, 2H), 1.59 – 1.37 (m, 3H), 1.34 – 1.18 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0, 132.0, 87.9, 75.7, 55.6, 48.3, 35.0, 34.2, 33.5, 30.3, 28.9, 26.1, 22.1, 22.0. IR (film) $\tilde{\nu}$ 2931, 2853, 1456, 1260, 1083 cm^{-1}. HRMS (ESI^+) for $C_{14}H_{24}O_2$ $[M+Na]^+$: calcd: 247.1668, found: 247.1668.



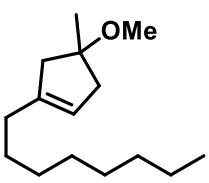
3-((1-Methoxycyclohexyl)methyl)-2,5-dihydrofuran (S101). According to the Representative Procedure A from enyne **S72** (25.9 mg, 0.11 mmol); pale yellow oil (16.9 mg, 79%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.60 – 5.52 (m, 1H), 4.67 – 4.61 (m, 2H), 4.61 – 4.55 (m, 2H), 3.16 (s, 3H), 2.31 – 2.28 (m, 2H), 1.76 – 1.65 (m, 2H), 1.65 – 1.48 (m, 3H), 1.48 – 1.37 (m, 2H), 1.34 – 1.21 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.4, 122.6, 77.9, 75.7, 75.2, 48.3, 34.3, 34.1, 25.9, 22.1. IR (film) $\tilde{\nu}$ 2932, 2855, 1750, 1145, 1073 cm^{-1}. HRMS (ESI^+) for $C_{12}H_{20}O_2$ $[M+Na]^+$: calcd: 219.1357, found: 219.1355.



Dimethyl 3-((1-methoxycyclohexyl)methyl)cyclopent-3-ene-1,1-dicarboxylate (S102). According to the Representative Procedure A from enyne **S73** (24.6 mg, 0.07 mmol); colorless oil (16.8 mg, 77%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.27 (m, 1H), 3.72 (s, 6H), 3.17 (s, 3H), 3.03 – 2.96 (m, 4H), 2.22 (q, *J* = 1.2 Hz, 2H), 1.70 – 1.60 (m, 2H), 1.57 – 1.45 (m, 3H), 1.46 – 1.35 (m, 2H), 1.31 – 1.17 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.9, 138.1, 124.2, 75.5, 59.6, 52.9, 48.3, 44.4, 40.6, 36.9, 3.3, 25.9, 22.1. IR (film) $\tilde{\nu}$ 2931, 2855, 1734, 1434, 1250 cm^{-1}. HRMS (ESI^+) for $C_{17}H_{26}O_5$ $[M+Na]^+$: calcd: 333.1672, found: 333.1673.

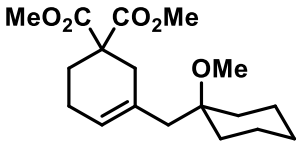


4-Methoxy-4-methyl-1-octylcyclopent-1-ene (S103). According to the Representative Procedure A from enyne **S74** (30.3 mg, 0.11 mmol), colorless oil (25.2 mg, 98%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.23 (hept, *J* = 2.2 Hz, 1H), 3.20 (s, 3H), 2.58 – 2.45 (m, 2H), 2.28 – 2.12 (m, 2H), 2.05 – 1.97 (m, 2H), 1.46 – 1.35 (m, 2H), 1.33 (s, 3H), 1.30 – 1.23 (m, 10H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.9, 121.0, 83.9, 50.7, 47.0, 44.5, 32.0,

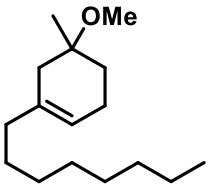


31.5, 29.6, 29.6, 29.4, 27.7, 25.6, 22.8, 14.3. IR (film) $\tilde{\nu}$ 2959, 2924, 2854, 1461, 1077 cm^{-1}. HRMS (ESI^+) for $C_{15}H_{28}O$ [M+Na]+: calcd: 247.2032, found: 247.2032.

Dimethyl 3-((1-methoxycyclohexyl)methyl)cyclohex-3-ene-1,1-dicarboxylate (S104). According to the Representative Procedure B from enyne **S77** (29.3 mg, 0.08 mmol), colorless oil (16.9 mg, 65%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.37 (m, 1H), 3.71 (s, 6H), 3.18 (s, 3H), 2.58 (s, 2H), 2.13 (s, 2H), 2.09 (s, 4H), 1.68 (dt, *J* = 13.4, 4.0 Hz, 2H), 1.60 – 1.36 (m, 5H), 1.29 – 1.14 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.3, 131.9, 123.8, 75.8, 53.9, 52.7, 48.3, 44.0, 35.4, 34.3, 27.3, 26.0, 22.8, 22.1. IR (film) $\tilde{\nu}$ 2931, 2852, 1733, 1435, 1253 cm^{-1}. HRMS (ESI^+) for $C_{18}H_{28}O_5$ [M+Na]$^+$: calcd: 347.1829, found: 347.1830.

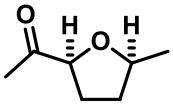


5-Methoxy-5-methyl-1-octylcyclohex-1-ene (S105). According to the Representative Procedure B from enyne **S78** (31.0 mg, 0.11 mmol), colorless oil (22.7 mg, 82%). ^1H NMR (400 MHz, $CDCl_3$) δ 5.40 – 5.32 (m, 1H), 3.24 (s, 3H), 2.20 – 2.05 (m, 2H), 2.04 – 1.88 (m, 4H), 1.73 – 1.65 (m, 1H), 1.57 – 1.48 (m, 1H), 1.38 (m, 2H), 1.26 (m, 10H), 1.16 (s, 3H), 0.91 – 0.85 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 135.9, 119.4, 73.5, 49.0, 39.9, 37.9, 32.1, 31.9, 29.7, 29.5, 29.5, 27.8, 23.5, 22.8, 22.7, 14.3. IR (film) $\tilde{\nu}$ 2923, 2853, 1462, 1369, 1095 cm^{-1}. HRMS (CI) for $C_{16}H_{30}O$ [M+NH_4]$^+$: calcd: 256.2635, found: 256.2632.

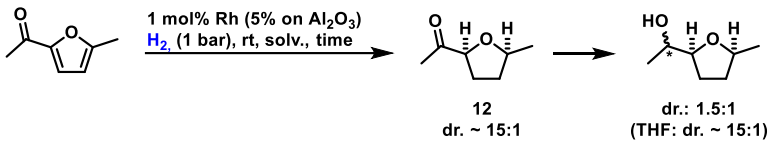


TOTAL SYNTHESES OF SINULARONE E AND F

1-((2S*,5S*)-5-Methyltetrahydrofuran-2-yl)ethan-1-one (12). A flame dried two-necked round-bottom flask was charged with Rh/Al_2O_3 (5% Rh *w/w*, 300 mg, 0.15 mmol). The flask was evacuated and refilled with H_2 (by means of attaching a balloon filled with hydrogen via needle and septum). A solution of 2-acetyl-5-methylfuran **11** (2.00 g, 16.1 mmol) in Et_2O (50 mL) was introduced and the mixture stirred at ambient temperature to the point of complete consumption of the starting material (typically 3 h, see below). The mixture was filtered through a pad of Celite and the solvent was evaporated. The residue was purified by flash chromatography (silica, pentane/Et_2O 4:1 – 2:1) to yield the title compound as a colorless liquid (1.23 g, 59%). ^1H NMR (400 MHz, $CDCl_3$) δ 4.19 (dd, *J* = 8.6, 5.9 Hz, 1H), 4.06 (dp, *J* = 8.1, 6.0 Hz, 1H), 2.14 (s, 3H), 2.13 – 2.07 (m, 1H), 2.00 – 1.87 (m, 2H), 1.43 – 1.33 (m, 1H), 1.25 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.9, 84.1, 77.3, 32.8, 29.4, 26.2, 21.1. IR (film) ν̃ 2972, 1715, 1354, 1086 cm^{-1}. HRMS (CI^+) for $C_7H_{12}O_2$ [M+H]$^+$: calcd 129.0910, found 129.0909.



Care must be taken to thoroughly monitor the reaction progress. Otherwise the yield of the desired ketone is reduced by subsequent reduction to the alcohol. As soon as all UV active material (TLC) is consumed, the reaction mixture should be purged by an inert gas. Premature quenching leads to purification issues due to the copolarity of starting material and desired product. Selected experimental data is summarized below.

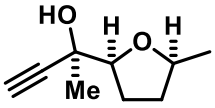


SM [%]	solvent	time	H_4 [%]	H_6 [%]	comment
25	MeOH	30 min	30	45	protic solvent favors over-reduction
0		3 h	30	70	
0		4.5 h	25	75	
0		68 h	0	100	
70	EtOAc	30 min	25	5	aprotic solvents retard over-reduction
0		3 h	75	25	
0		4.5 h	60	40	
70	Et_2O	30 min	25	5	Et_2O facilitates isolation (product volatility)
0		3 h	75	25	59 % ketone isolated
0		4.5 h	70	30	
50	EtOAc	30 min	35	10	sacrificial ketone does not improve selectivity
0	acetone	3 h	75	25	hydrogenation generates protic conditions *in-situ*
0	(4:1)	4.5 h	65	35	

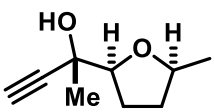
* GCMS TIC ratios

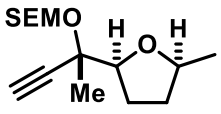
(S*)-2-((2S*,5S*)-5-Methyltetrahydrofuran-2-yl)but-3-yn-2-ol (14a) and (R*)-2-((2S*,5S*)-5-Methyltetrahydrofuran-2-yl)but-3-yn-2-ol (14a'). $LaCl_3 \cdot 2\ LiCl$ (0.6 M in THF, 13.6 mL, 9.53 mmol) was added to a solution of ketone **12** (1.11 g, 8.66 mmol) in THF (14 mL) at room temperature. After stirring for 1 h, the mixture was cooled to 0 °C and ethynylmagnesium bromide (0.5 M in THF, 26.0 mL, 13.0 mmol) was slowly added. Stirring was continued for 1 h at the same temperature before sat. aq. NH_4Cl solution (10 mL) was introduced. The layers were separated, the aqueous phase was extracted with EtOAc (3 x 60 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 4:1 – 3:1) to yield the two title compounds.

The minor diastereomer (**14a'**) was obtained as a colorless oil (176 mg, 12%). Single crystals suitable for X-ray analysis were obtained by sublimation (10^{-3} mbar, 40 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 – 4.02 (m, 1H), 3.85 – 3.80 (m, 1H), 2.38 (s, 1H), 2.03 – 1.93 (m, 3H), 1.66 – 1.56 (m, 1H), 1.44 (s, 3H), 1.27 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 85.7, 85.4, 76.6, 72.1, 70.4, 33.3, 27.7, 26.4, 21.1. IR (film) ṽ 3429 (br), 3290 (br), 2973, 2873, 2109, 1376, 1088 cm^{-1}. HRMS (ESI$^+$) for $C_9H_{14}O_2$ $[M+Na]^+$: calcd 177.0886, found 177.0888.

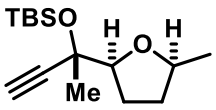


The major diastereomer (**14a**) was obtained as a colorles oil (695 mg, 54%). Single crystals suitable for X-ray analysis were obtained by slow cooling of the neat material to –20 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.14 (dq, *J* = 12.4, 6.2 Hz, 1H), 3.94 (t, *J* = 7.3 Hz, 1H), 2.55 (br, 1H), 2.44 (s, 1H), 2.07 – 1.95 (m, 1H), 1.95 – 1.83 (m, 2H), 1.55 – 1.47 (m, 1H), 1.44 (s, 3H), 1.26 (d, *J* = 6.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 87.1, 85.3, 76.4, 71.3, 68.4, 33.0, 25.8, 25.1, 21.4. IR (film) ṽ 3407 (br), 3295 (br), 2973, 2872, 2109, 1446, 1379, 1087 cm^{-1}. HRMS (CI$^+$) for $C_9H_{14}O_2$ $[M+H]^+$: calcd 155.1067, found 155.1066.

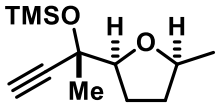


Trimethyl(2-((((S*)-2-((2S*,5S*)-5-methyltetrahydrofuran-2-yl)but-3-yn-2-yl)oxy)methoxy)ethyl)silane (14b). 

SEMCl (0.41 mL, 2.33 mmol) was added to a solution of alcohol **14a** (120 mg, 0.78 mmol) and *i*Pr_2NEt (0.68 mL, 3.89 mmol) in CH_2Cl_2 (3.0 mL) at 0 °C. The mixture was allowed to reach room temperature and stirring was continued for 16 h before sat. NH_4Cl solution was introduced. The layers were separated and the aqueous layer extracted with methyl *tert*-butyl ether (3 x 20 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to yield the title compound as a colorless oil (207 mg, 94%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.10 (d, *J* = 7.0 Hz, 1H), 4.87 (d, *J* = 7.1 Hz, 1H), 4.08 – 3.98 (m, 1H), 3.92 (dd, *J* = 7.3, 6.4 Hz, 1H), 3.72 (td, *J* = 9.7, 7.0 Hz, 1H), 3.60 (td, *J* = 9.7, 7.0 Hz, 1H), 2.48 (s, 1H), 2.07 – 1.87 (m, 3H), 1.56 – 1.47 (m, 1H), 1.52 (s, 3H), 1.26 (d, *J* = 6.0 Hz, 3H), 0.97 – 0.90 (m, 2H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 91.5, 84.6, 83.5, 76.6, 76.0, 74.8, 65.5, 33.0, 27.8, 24.5, 21.0, 18.3, -1.3. IR (film) ṽ 3310, 2954, 2879, 1248, 1096, 1020 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{28}O_3Si$ [M+Na]$^+$: calcd 307.1700, found 307.1701.

***tert*-Butyldimethyl(((S*)-2-((2S*,5S*)-5-methyltetrahydrofuran-2-yl)but-3-yn-2-yl)oxy)silane (14c).** 

2,6-lutidine (0.19 mL, 1.62 mmol) was added to a solution of alcohol **14a** (125 mg, 0.81 mmol) in CH_2Cl_2 (3.1 mL). The mixture was cooled to 0 °C before TBSOTf (0.22 mL, 0.97 mmol) was slowly added. After stirring for 2 h at room temperature, sat. aq. NH_4Cl solution (1 mL) and water (1 mL) were added and the layers separated. The aqueous phase was extracted with methyl *tert*-butyl ether (3 x 10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the title compound as a colorless oil (211 mg, 97%).^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 – 3.97 (m, 1H), 3.70 (dd, *J* = 7.4, 6.2 Hz, 1H), 2.39 (s, 1H), 2.11 – 2.00 (m, 1H), 1.97 – 1.85 (m, 2H), 1.60 – 1.52 (m, 1H), 1.48 (s, 3H), 1.25 (d, *J* = 6.0 Hz, 3H), 0.86 (s, 9H), 0.19 (s, 3H), 0.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.7, 86.3, 76.6, 73.0, 71.5, 33.0, 28.9, 27.4, 25.9, 21.3, 18.2, -2.6, -3.0. IR (film) ṽ 3311, 2930, 2857, 1251, 1121, 1094 cm^{-1}. HRMS (CI$^+$) for $C_{15}H_{28}O_2Si$ [M+H]$^+$: calcd 269.1931, found 269.1929.

Trimethyl(((S*)-2-((2S*,5S*)-5-methyltetrahydrofuran-2-yl)but-3-yn-2-yl)oxy)silane (14d). 

2,6-Lutidine (1.00 mL, 8.82 mmol) was added to a solution of alcohol **14a** (680 mg, 4.41 mmol) in CH_2Cl_2 (17.0 mL). The mixture was cooled to 0 °C before TMSOTf (0.96 mL, 5.29 mmol) was slowly added. After 5 min, sat. aq. NH_4Cl solution (2 mL) and water (2 mL) were added and the layers separated. The aqueous phase was extracted with methyl *tert*-butyl ether (3 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/methyl *tert*-butyl ether 1:0 – 10:1) to give the title compound as a pale yellow oil (923 mg, 92%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.05 (m, 1H), 3.75 (dd, *J* = 7.3, 6.2 Hz, 1H), 2.42 (s, 1H), 2.09 – 1.97 (m, 1H), 1.97 – 1.85 (m, 2H), 1.62 – 1.53 (m, 1H), 1.48 (s, 3H), 1.24 (d, *J* = 6.1 Hz, 3H), 0.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 86.7, 86.2, 76.6, 73.3, 71.7, 33.1, 28.5, 27.5, 21.3, 2.1. IR (film) ṽ 3310, 2970, 2871, 1249, 1094 cm^{-1}. HRMS (CI$^+$) for $C_{12}H_{22}O_2Si$ [M]$^+$: calcd 226.1384, found 226.1381.

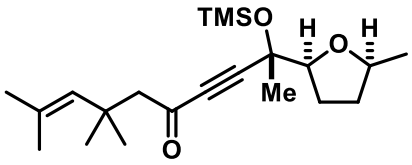
***N*-Methoxy-N,3,3,5-tetramethylhex-4-enamide (18)**. A solution of *i*-PrMgBr (2 M in THF, 5.56 mL, 11.1 mmol) was added to a stirred solution of ester **S7** (410 mg, 2.22 mmol) and *N*,*O*-dimethylhydroxylamine hydrochloride (650 mg, 6.67 mmol) in THF (7.2 mL) at –20 °C. After 30 min, sat. aq. NH_4Cl solution (2 mL) was added and the mixture allowed to reach room temperature. After extraction with EtOAc (3 x 30 mL), the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1 – 4:1) to give the title compound as a colorless oil (420 mg, 95%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 (hept, *J* = 1.4 Hz, 1H), 3.66 (s, 3H), 3.16 (s, 3H), 2.51 (s, 2H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.24 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.5 (br), 133.6, 130.9, 61.1, 43.6 (br), 35.3, 32.0 (br), 29.3, 28.3, 19.1. IR (film) ṽ 2962, 2931, 1660, 1444, 1372, 1005 cm^{-1}. HRMS (ESI$^+$) for $C_{11}H_{21}NO_2$ [M+Na]$^+$: calcd 222.1464, found 222.1463.

(S*)-7,7,9-Trimethyl-2-((2S*,5S*)-5-methyltetrahydrofuran-2-yl)-2-((2-(trimethylsilyl)ethoxy)methoxy)-dec-8-en-3-yn-5-one (15b). *n*-BuLi (1.65 M in hexanes, 0.36 mL, 0.60 mmol) was added dropwise to a stirred solution of alkyne **14b** (154 mg, 0.54 mmol) in THF (2.2 ml) at –50 °C and the resulting mixture was stirred for 30 min at that temperature. A solution of amide **18** (130 mg, 0.65 mmol) in THF (0.4 mL) was added and the mixture was allowed to reach room temperature. After stirring for 2 h., sat. aq. NH_4Cl solution (1 mL) and EtOAc (5 mL) were added and the layers separated. The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to give the title compound as a colorless oil (120 mg, 52%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (hept, *J* = 1.4 Hz, 1H), 5.04 (d, *J* = 7.2 Hz, 1H), 4.84 (d, *J* = 7.2 Hz, 1H), 4.09 – 3.96 (m, 1H), 3.92 (dd, *J* = 7.5, 6.1 Hz, 1H), 3.71 (td, *J* = 9.7, 6.8 Hz, 1H), 3.59 (td, *J* = 9.7, 6.8 Hz, 1H), 2.69 (d, *J* = 14.1 Hz, 1H), 2.65 (d, *J* = 14.1 Hz, 1H), 2.06 – 1.89 (m, 3H), 1.72 (d, *J* = 1.4 Hz, 3H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.56 (s, 3H), 1.54 – 1.46 (m, 1H), 1.26 (d, *J* = 6.0 Hz, 3H), 1.23 (s, 6H), 0.93 (ddd, *J* = 10.7, 6.5, 3.5 Hz, 2H), 0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.6, 132.3, 132.0, 91.7, 90.9, 86.8, 84.2, 76.7, 76.2, 65.7, 57.8, 35.6, 33.0, 29.4, 29.4, 28.2, 28.0, 23.9, 21.0, 19.2, 18.3, –1.3. IR (film) ṽ 2956, 2879, 2213, 1668, 1248, 1095, 1014 cm^{-1}. HRMS (ESI$^+$) for $C_{24}H_{42}O_4Si$ [M+Na]$^+$: calcd 445.2745, found 445.2745.

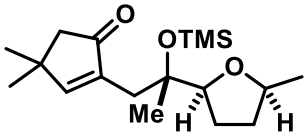
(S*)-2-((*tert*-Butyldimethylsilyl)oxy)-7,7,9-trimethyl-2-((2S*,5S*)-5-methyltetrahydrofuran-2-yl)dec-8-en-3-yn-5-one (15c). *n*-BuLi (1.6 M in hexanes, 0.24 mL, 0.32 mmol) was added dropwise to a stirred solution of alkyne **14c** (85 mg, 0.32 mmol) in THF (1.3 ml) at 0 °C and the resulting mixture was stirred for 15 min at that temperature. The mixture was then cooled to –78 °C before a solution of amide **18** (75 mg, 0.38 mmol) in THF (0.3 mL) was added. The mixture was allowed to reach 0 °C and stirring was continued for 2 h at that temperature. Sat. NH_4Cl solution (1 mL) and EtOAc (3 mL) were added and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 40:1) to give the title compound as a colorless oil (78 mg, 61%). ^{1}H NMR

(400 MHz, $CDCl_3$) δ 5.22 (hept, *J* = 1.4 Hz, 1H), 4.02 (m, 1H), 3.73 (dd, *J* = 7.3, 6.0 Hz, 1H), 2.69 (d, *J* = 14.3 Hz, 1H), 2.64 (d, *J* = 14.3 Hz, 1H), 2.10 – 1.87 (m, 3H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.53 (s, 3H), 1.25 (d, *J* = 5.9 Hz, 3H), 1.24 (s, 6H), 0.86 (s, 9H), 0.21 (s, 3H), 0.18 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.6, 132.5, 131.8, 93.7, 86.1, 85.5, 76.7, 72.2, 57.5, 35.6, 33.0, 29.4, 29.4, 28.3, 28.2, 27.8, 25.8, 21.2, 19.2, 18.2, -2.6, -2.9. IR (film) ṽ 2957, 2930, 2858, 2210, 1667, 1250, 1094 cm^{-1}. HRMS (ESI^+) for $C_{24}H_{42}O_3Si$ $[M+Na]^+$: calcd 429.2795, found 429.2796.

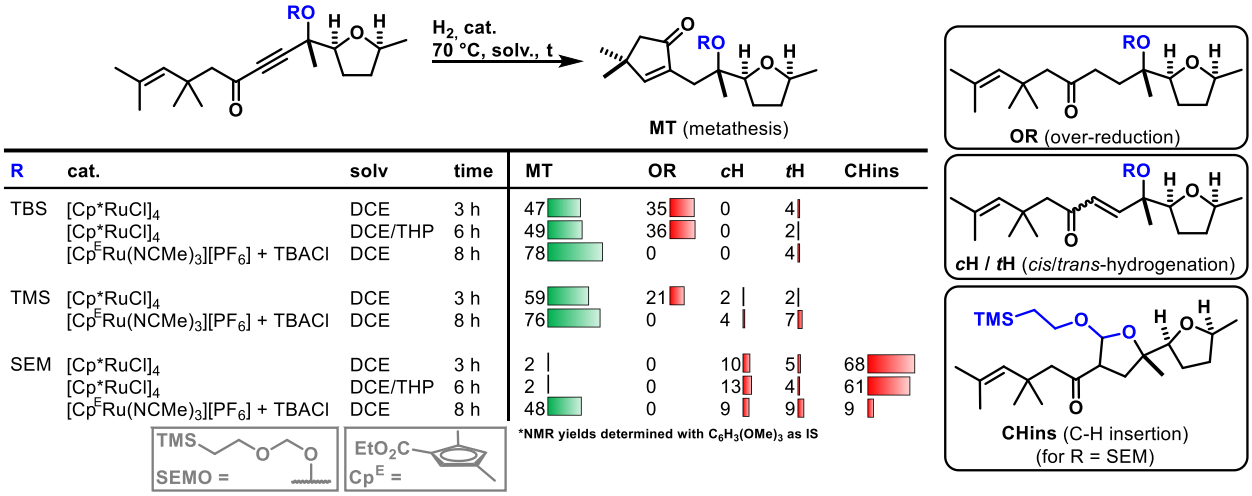
(S*)-7,7,9-Trimethyl-2-((2S*,5S*)-5-methyltetrahydrofuran-2-yl)-2-((trimethylsilyl)oxy)dec-8-en-3-yn-5-one (15d). *n*-BuLi (1.6 M in hexanes, 0.47 mL, 0.75 mmol) was added dropwise to a stirred solution of alkyne **14d** (185 mg, 0.82 mmol) in THF (2.5 ml) at 0 °C and the resulting mixture was stirred for 20 min at that temperature. The mixture was then cooled to –78 °C before a solution of amide **18** (125 mg, 0.63 mmol) in THF (0.6 mL) was added. The mixture was allowed to reach 0 °C and stirring was continued for 2 h at that temperature. Sat. NH_4Cl solution (1 mL) and EtOAc (3 mL) were added and the layers separated. The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and excess alkyne removed by bulb-to-bulb destillation (10^{-3} mbar, 50 °C, 1 h). The residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 40:1 – 20:1) to give the title compound as a colorless oil (149 mg, 65%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (hept, *J* = 1.4 Hz, 1H), 4.09 – 3.99 (m, 1H), 3.77 (dd, *J* = 7.2, 6.1 Hz, 1H), 2.69 (d, *J* = 14.3 Hz, 1H), 2.64 (d, *J* = 14.3 Hz, 1H), 2.08 – 1.85 (m, 3H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.54 (m, 1H), 1.52 (s, 3H), 1.25 (d, *J* = 6.7 Hz, 3H) 1.24 (s, 6H), 0.20 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.6, 132.4, 131.8, 93.6, 85.9, 85.6, 76.8, 72.2, 57.5, 35.6, 33.0, 29.5, 29.4, 28.2, 27.9, 27.8, 21.2, 19.2, 2.0. IR (film) ṽ 2967, 2871, 2210, 1666, 1250, 1093 cm^{-1}. HRMS (ESI^+) for $C_{21}H_{36}O_3Si$ $[M+Na]^+$: calcd 387.2326, found 387.2330.



4,4-Dimethyl-2-((S*)-2-((2S*,5S*)-5-methyltetrahydrofuran-2-yl)-2-((trimethylsilyl)oxy)propyl)cyclopent-2-en-1-one (S79). TBACl (0.04 M in 1,2-dichloroethane, 0.20 mL, 8 µmol) was added to a solution of $[Cp(Me_2CO_2Et)Ru(NCMe)_3][PF_6]$ (**19**, 3.90 mg, 7 µmol) in 1,2-dichloroethane (0.16 mL, *aliquot from 0.04* M *stock solution*) at room temperature and the mixture was stirred for 5 min. Enyne **15d** (24.0 mg, 0.07 mmol) in 1,2-dichloroethane (0.36 mL) was added and H_2 was bubbled through the mixture for 2 min before the flask was immersed into a pre-heated oil bath at 70 °C keeping a static H_2 atmosphere (ambient pressure, H_2 filled balloon). After stirring for 8 h at 70 °C, the mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to yield the title product as colorless oil (16.2 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 1.1 Hz, 1H), 3.93 (dp, *J* = 8.2, 6.0 Hz, 1H), 3.64 (t, *J* = 7.2 Hz, 1H), 2.36 (dd, *J* = 13.5, 1.1 Hz, 1H), 2.25 (s, 2H), 2.22 (d, *J* = 13.1 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.85 – 1.76 (m, 2H), 1.43 – 1.32 (m, 1H), 1.22 (d, *J* = 6.1 Hz, 3H), 1.20 (s, 3H), 1.20 (s, 3H), 1.07 (s, 3H), 0.09 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.8, 171.2, 139.1, 85.0, 77.3, 75.7, 50.1, 38.9, 33.3, 32.7, 28.5, 28.5, 27.0, 23.2, 21.1, 2.7. IR (film) ṽ 2957, 2867, 1705, 1247, 1092 cm^{-1}. HRMS (ESI^+) for $C_{18}H_{32}O_3Si$ $[M+Na]^+$: calcd 347.2013, found 347.2012.



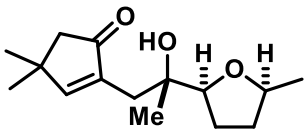
Care must be taken to completely quench the highly Lewis-acidic precatalyst **19** with sufficient amounts of TBACl before addition of the enyne. Otherwise substantial amounts of silyl ether may get cleaved under the reaction conditions leading to irreproducible yields. Selected experimental data is summarized below.

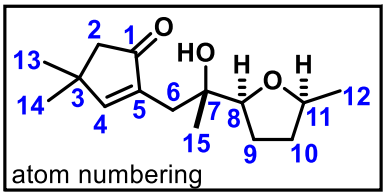


R	cat.	solv	time	MT	OR	*c*H	*t*H	CHins
TBS	$[Cp^*RuCl]_4$	DCE	3 h	47	35	0	4	
	$[Cp^*RuCl]_4$	DCE/THP	6 h	49	36	0	2	
	$[Cp^ERu(NCMe)_3][PF_6]$ + TBACl	DCE	8 h	78	0	0	4	
TMS	$[Cp^*RuCl]_4$	DCE	3 h	59	21	2	2	
	$[Cp^ERu(NCMe)_3][PF_6]$ + TBACl	DCE	8 h	76	0	4	7	
SEM	$[Cp^*RuCl]_4$	DCE	3 h	2	0	10	5	68
	$[Cp^*RuCl]_4$	DCE/THP	6 h	2	0	13	4	61
	$[Cp^ERu(NCMe)_3][PF_6]$ + TBACl	DCE	8 h	48	0	9	9	9

*NMR yields determined with $C_6H_3(OMe)_3$ as IS

(±)-Sinularone F (10). TBAF (1 M in THF, 0.13 mL, 0.13 mmol) was added to a solution of silyl ether **S79** (21.0 mg, 65 µmol) in THF (1.0 mL) at 0 °C. After stirring for 1 h, sat. aq. NH_4Cl solution was added and the mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 4:1 – 2:1) to give the title compound as a colorless oil (14.4 mg, 88%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 1.0 Hz, 1H), 4.03 – 3.94 (m, 1H), 3.69 (t, *J* = 7.5 Hz, 1H), 2.81 (s, 1H), 2.52 (dd, *J* = 14.0, 1.0 Hz, 1H), 2.28 (dd, *J* = 14.1, 0.9 Hz, 1H), 2.28 (s, 2H), 1.99 – 1.89 (m, 1H), 1.89 – 1.73 (m, 2H), 1.46 – 1.34 (m, 1H), 1.23 – 1.17 (m, 9H), 1.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 210.7, 170.6, 139.5, 85.1, 75.7, 72.4, 50.1, 39.2, 34.7, 33.1, 28.4 (2C), 26.1, 22.5, 21.4. ^{1}H NMR (400 MHz, d_6-DMSO) δ 7.36 (t, *J* = 0.7 Hz, 1H), 4.00 (s, 1H), 3.86 (dp, *J* = 8.0, 6.0 Hz, 1H), 3.56 (t, *J* = 7.3 Hz, 1H), 2.21 (s, 2H), 2.19 (s, 2H), 1.87 (m, 1H), 1.83 – 1.74 (m, 1H), 1.74 – 1.65 (m, 1H), 1.36 – 1.25 (m, 1H), 1.15 (d, *J* = 6.0 Hz, 3H), 1.15 (s, 6H), 0.84 (s, 3H). ^{13}C NMR (101 MHz, d_6-DMSO) δ 208.9, 170.2, 138.4, 84.7, 74.7, 71.8, 49.3, 38.5, 32.7, 31.7, 28.1, 28.0, 25.6, 22.9, 20.9. IR (film) ṽ 3442 (br), 2961, 2867, 1702, 1092 cm^{-1}. HRMS (EI$^+$) for $C_{15}H_{25}O_3$ $[M+H]^+$: calcd 253.1798, found 253.1802. The spectral data is consistent with previously reported values.[26]





Sinularone F

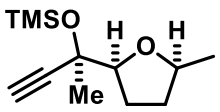
^{13}C [#]	natural[A] δ^{13}C [ppm]	synthetic[B] δ^{13}C [ppm]	difference $\Delta\delta^{13}$C [ppm]	drift corrected[C] difference $\Delta\delta^{13}$C [ppm]
1	209,4	208,9	0,5	0
2	49,8	49,3	0,5	0
3	38,9	38,5	0,4	-0,1
4	170,7	170,2	0,5	0
5	138,9	138,4	0,5	0
6	32,2	31,7	0,5	0
7	72,3	71,8	0,5	0
8	85,2	84,7	0,5	0
9	26,1	25,6	0,5	0
10	33,2	32,7	0,5	0
11	75,2	74,7	0,5	0
12	21,4	20,9	0,5	0
13	28,5	28,1	0,4	-0,1
14	28,5	28,0	0,5	0
15	23,4	22,9	0,5	0

[A] 125 MHz, d_6-DMSO

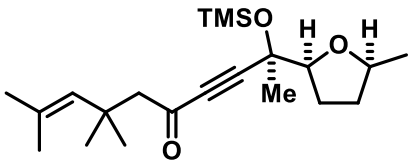
[B] 101 MHz, d_6-DMSO

[C] 0.5 ppm systematic drift

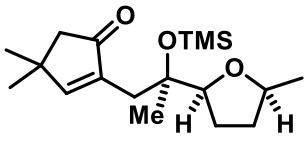
Trimethyl(((R*)-2-((2S*,5S*)-5-methyltetrahydrofuran-2-yl)but-3-yn-2-yl)oxy)silane (14d'). 2,6-Lutidine



(0.24 mL, 2.08 mmol) was added to a solution of alcohol **14a'** (160 mg, 1.04 mmol) in CH_2Cl_2 (4.00 mL). The mixture was cooled to 0 °C before TMSOTf (0.23 mL, 1.25 mmol) was slowly added. After 5 min, sat. aq. NH_4Cl solution (1 mL) and water (1 mL) were introduced and the layers were separated. The aqueous phase was extracted with methyl *tert*-butyl ether (3 x 20 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/methyl *tert*-butyl ether 1:0 – 10:1) to give the title compound as a light yellow oil (208 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.12 – 4.02 (m, 1H), 3.87 (dd, *J* = 7.5, 5.4 Hz, 1H), 2.43 (s, 1H), 2.07 – 1.96 (m, 1H), 1.96 – 1.83 (m, 2H), 1.53 – 1.46 (m, 1H), 1.44 (s, 3H), 1.23 (d, *J* = 6.0 Hz, 3H), 0.19 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 87.3, 85.9, 76.8, 73.1, 71.3, 33.3, 27.6, 27.0, 21.2, 2.0. IR (film) $\tilde{\nu}$ 3310, 2969, 2870, 1249, 1081 cm^{-1}. HRMS (ESI$^+$) for $C_{12}H_{22}O_2Si$ [M+Na]$^+$: calcd 249.1281, found 249.1282.

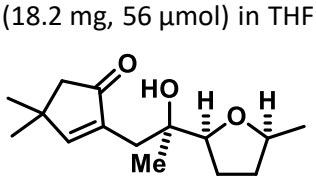
(R*)-7,7,9-Trimethyl-2-((2S*,5S*)-5-methyltetrahydrofuran-2-yl)-2-((trimethylsilyl)oxy)dec-8-en-3-yn-5-one (17). 

n-BuLi (1.6 M in hexanes, 0.51 mL, 0.82 mmol) was added dropwise to a stirred solution of alkyne **14d'** (200 mg, 0.88 mmol) in THF (2.8 ml) at 0 °C and the resulting mixture was stirred for 20 min at that temperature. The mixture was then cooled to – 78 °C before a solution of amide **18** (135 mg, 0.68 mmol) in THF (0.6 mL) was added. The mixture was allowed to reach 0 °C and stirring was continued for 2 h at that temperature. Sat. aq. NH_4Cl solution (1 mL) and EtOAc (3 mL) were added and the layers were separated. The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and excess alkyne removed by bulb-to-bulb destillation (10^{-3} mbar, 50 °C). The residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 40:1 – 20:1) to give the title compound as a colorless oil (193 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.21 (hept, *J* = 1.4 Hz, 1H), 4.11 – 4.02 (m, 1H), 3.88 – 3.82 (m, 1H), 2.66 (s, 2H), 2.05 – 1.86 (m, 3H), 1.72 (d, *J* = 1.4 Hz, 3H), 1.68 (d, *J* = 1.4 Hz, 3H), 1.56 – 1.49 (m, 1H), 1.48 (s, 3H), 1.23 (s, 6H), 1.22 (*J* = 6.2 Hz, 3H), 0.21 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.7, 132.4, 131.9, 93.8, 85.6, 85.5, 76.8, 71.8, 57.5, 35.6, 33.2, 29.5 (2C), 28.2, 28.0, 26.8, 21.2, 19.2, 2.0. IR (film) ṽ 2967, 2872, 2212, 1667, 1249, 1092 cm^{-1}. HRMS (ESI$^+$) for $C_{21}H_{36}O_3Si$ [M+Na]$^+$: calcd 387.2326, found 387.2331.

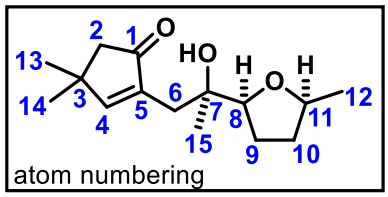
4,4-Dimethyl-2-((R*)-2-((2S*,5S*)-5-methyltetrahydrofuran-2-yl)-2-((trimethylsilyl)oxy)propyl)cyclopent-2-en-1-one (S80). 

TBACl (0.02 M in 1,2-dichloroethane, 0.56 mL, 12 µmol) was added to solid $[Cp(Me_2CO_2Et)Ru(NCMe)_3][PF_6]$ (5.3 mg, 10 µmol) in a flame dried Schlenk tube under argon. The mixture was stirred for 5 min at room temperature before a solution of enyne **17** (36.0 mg, 0.10 mmol) in 1,2-dichloroethane (0.5 mL) was added. H_2 was bubbled through the mixture for 2 min before the flask was immersed into a pre-heated oil bath at 70 °C keeping a static H_2 atmosphere (ambient pressure, H_2 filled balloon). After stirring for 3 h at 70 °C, the mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 20:1) to yield the title product as a pale yellow oil (22.0 mg, 67%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* = 0.9 Hz, 1H), 3.90 (dp, *J* = 8.4, 6.0 Hz, 1H), 3.65 (t, *J* = 7.3 Hz, 1H), 2.30 (m, 2H), 2.25 (s, 2H), 1.95 – 1.70 (m, 3H), 1.44 – 1.30 (m, 1H), 1.21 (d, *J* = 10.1 Hz, 3H), 1.21 (s, 6H), 1.15 (s, 3H), 0.11 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.8, 170.5, 139.2, 85.2, 76.9, 75.7, 50.1, 39.0, 33.5, 33.2, 28.6, 28.4, 26.5, 23.7, 21.0, 2.9. IR (film) ṽ 2957, 2867, 1708, 1248, 1091 cm^{-1}. HRMS (ESI$^+$) for $C_{18}H_{32}O_3Si$ [M+Na]$^+$: calcd 347.2013, found 347.2011.

(±)-Sinularone E (9). TBAF (1 M in THF, 0.11 mL, 0.11 mmol) was added to a solution of silyl ether **S80** (18.2 mg, 56 µmol) in THF (0.9 mL) at 0 °C. After 1 h, sat. aq. NH_4Cl solution was added and the mixture was extracted with EtOAc (3 x 5 mL). The combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 4:1 – 2:1) to give the title compound as a colorless oil (13.7 mg, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 1.0 Hz, 1H), 3.98 (dp, *J* = 7.9, 6.1 Hz, 1H), 3.70 (t, *J* = 7.3 Hz, 1H), 2.79 (br, 1H), 2.45 – 2.31 (m, 2H), 2.31 (s, 2H), 2.00 – 1.92 (m, 1H), 1.91 – 1.83 (m, 2H), 1.45 – 1.35 (m, 1H), 1.22 (s, 6H), 1.22



(d, *J* = 5.9 Hz, 3H), 1.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.4, 172.0, 139.3, 85.4, 75.8, 73.0, 50.2, 39.4, 33.4 (2C), 28.4, 28.4, 26.2, 22.7, 21.2. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.35 (t, *J* = 1.0 Hz, 1H), 4.13 (br, 1H), 3.83 (m, 1H), 3.57 (dd, *J* = 7.6, 6.6 Hz, 1H), 2.27 (dd, *J* = 13.8, 0.9 Hz, 1H), 2.19 (s, 2H), 2.08 (dd, *J* = 13.8, 1.2 Hz, 1H), 1.92 – 1.70 (m, 3H), 1.33 – 1.23 (m, 1H), 1.15 (s, 6H), 1.13 (d, *J* = 6.1 Hz, 3H), 0.87 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 208.9, 170.3, 138.3, 84.7, 74.8, 72.0, 49.3, 38.5, 33.0, 32.8, 28.1, 28.0, 25.8, 21.4, 20.9. IR (film) ṽ 3446, 2962, 2867, 1689, 1091 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{24}O_3$ [M+Na]$^+$: calcd 275.1618, found 275.1619. The spectral data is consistent with previously reported values.[26]



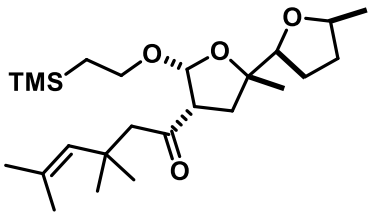
Sinularone E

^{13}C [#]	natural[A] δ^{13}C [ppm]	synthetic[B] δ^{13}C [ppm]	difference $\Delta\delta^{13}$C [ppm]	drift corrected[C] difference $\Delta\delta^{13}$C [ppm]
1	209,4	208,9	0,5	0
2	49,8	49,3	0,5	0
3	38,9	38,5	0,4	-0,1
4	170,8	170,3	0,5	0
5	138,8	138,3	0,5	0
6	33,5	33,0	0,5	0
7	72,5	72,0	0,5	0
8	85,2	84,7	0,5	0
9	26,2	25,8	0,4	-0,1
10	33,3	32,8	0,5	0
11	75,3	74,8	0,5	0
12	21,3	20,9	0,4	-0,1
13	28,6	28,1	0,5	0
14	28,4	28,0	0,4	-0,1
15	21,9	21,4	0,5	0

[A] 125 MHz, d_6-DMSO

[B] 101 MHz, d_6-DMSO

[C] 0.5 ppm systematic drift

1-((2S*,2'S*,4S*,5R*,5'S*)-2,5'-Dimethyl-5-(2-(trimethylsilyl)ethoxy)octahydro-[2,2'-bifuran]-4-yl)-3,3,5-trimethylhex-4-en-1-one (16). 

According to Representative Procedure A from enyne **15b** (24.0 mg, 57 µmol); 68% (NMR), dr.= 6:1. *Major diastereomer*: colorless oil (8.8 mg, 36%): ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.26 (d, *J* = 5.1 Hz, 1H), 5.20 (hept, *J* = 1.4 Hz, 1H), 3.98 (m, 1H), 3.90 (t, *J* = 7.4 Hz, 1H), 3.80 (ddd, *J* = 10.9, 9.7, 6.1 Hz, 1H), 3.40 (ddd, *J* = 11.0, 9.7, 5.9 Hz, 1H), 3.23 (ddd, *J* = 11.9, 7.9, 5.1 Hz, 1H), 2.63 (d, *J* = 15.6 Hz, 1H), 2.44 (d, *J* = 15.6 Hz, 1H), 2.28 (t, *J* = 12.3 Hz, 1H), 1.98 – 1.86 (m, 2H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.5 Hz, 3H), 1.66 – 1.58 (m, 2H), 1.41 – 1.35 (m, 1H), 1.24 (d, *J* = 6.0 Hz, 3H), 1.20 (s, 4H), 1.19 (s, 4H), 1.18 (s, 3H), 0.84 (qdd, *J* = 13.8, 10.8, 5.9 Hz, 2H), -0.02 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$)

δ 204.5, 133.3, 131.1, 102.5, 86.5, 85.9, 76.1, 64.6, 57.7, 54.7, 34.9, 33.3, 32.5, 29.6, 29.2, 28.2, 27.5, 22.0, 21.0, 19.2, 18.1, −1.3. IR (film) ṽ 2965, 1719, 1363, 1248, 1098, 1017 cm^{-1}. HRMS (ESI^+) for $C_{24}H_{44}O_4Si$ $[M+Na]^+$: calcd 447.2901, found 447.2908.

Minor diastereomer: colorless oil (2.5 mg, 10%): ^1H NMR (600 MHz, $CDCl_3$) δ 5.24 (d, *J* = 5.2 Hz, 1H), 5.20 (hept, *J* = 1.4 Hz, 1H), 3.99 (m, 1H), 3.79 (td, *J* = 9.8, 6.7 Hz, 1H), 3.72 (t, *J* = 7.4 Hz, 1H), 3.41 (ddd, *J* = 10.3, 9.6, 6.2 Hz, 1H), 3.33 (ddd, *J* = 11.3, 8.6, 5.2 Hz, 1H), 2.61 (d, *J* = 15.5 Hz, 1H), 2.42 (d, *J* = 15.6 Hz, 1H), 2.26 (dd, *J* = 12.7, 11.3 Hz, 1H), 1.93 (dd, *J* = 12.7, 8.6 Hz, 1H), 1.92 (m, 1H), 1.80 (m, 2H), 1.72 (d, *J* = 1.3 Hz, 3H), 1.68 (d, *J* = 1.5 Hz, 3H), 1.44 (m, 1H), 1.29 (s, 3H), 1.21 (d, *J* = 6.1 Hz, 3H), 1.19 (s, 3H), 1.19 (s, 3H), 0.86 (m, 2H), -0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.7, 133.3, 130.8, 102.8, 85.4, 85.4, 75.7, 64.4, 58.9, 54.4, 34.6, 33.8, 33.0, 29.4, 29.1, 28.0, 26.7, 25.1, 21.2, 19.0, 18.1, −1.4.

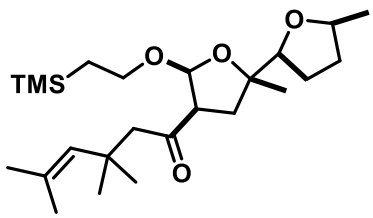
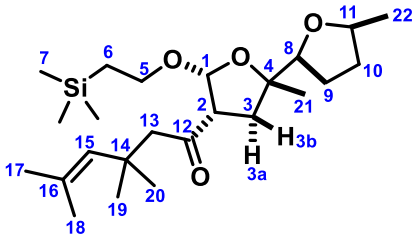


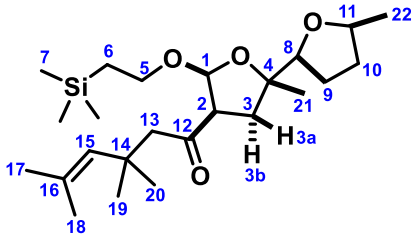
Table S4: Detailed NMR analysis of the major diastereomer ($CDCl_3$, 600 MHz)



Atom [#]		δ [ppm]	J [Hz]	COSY	HMBC	NOESY
C	H					
1		102.33			3b	
	1	5.26	5.1	2	3, 4, 5	2, 5a, 5b, 6a, 6b, 13a, 13b, 18, 21
2		57.49			3a, 3b	
	2	3.23	5.1, 7.9, 11.9	1, 3a, 3b		1, 3b, 13a, 13b, 15, 21
3		32.34			1, 21	
	3a	2.28	11.9, 12.3	2, 3b	2, 4, 8, 12, 21	3b, 8, 9a, 9b, 10b
	3b	1.61	7.9, 12.3	2, 3a	1, 2, 21	2, 3a, 21
4		86.30			1, 3a, 8, 21	
5		64.45			1, 6a, 6b	
	5a	3.80	6.1, 9.7, 10.8	5b, 6a, 6b		1, 7, 8
	5b	3.40	9.7, 11.0, 5.8	5a, 6a, 6b		1, 7
6		17.98			7	
	6a	0.86	10.8, 5.8, 14.0	5a, 5b	5	1, 7
	6b	0.81	6.1, 11.0, 14.0	5a, 5b	5	1, 7
7		-1.45			7	
	7	-0.02			6, 7	5a, 5b, 6a, 6b, 8, 19, 20
8		85.77			3a	
	8	3.90	7.4, 7.4	9a, 9b	4, 21	3a, 5a, 7, 9a, 10a, 11, 21
9		27.33				

	9a	1.90	7.4	8, 9b	10	3a, 8, 9b, 11
	9b	1.63	7.4	8, 9a, 10b		3a, 9a, 10a, 21, 22
10		33.15			9a, 22	
	10a	1.93		10b, 11		8, 9b, 10b, 11, 22
	10b	1.38		9b, 10a, 11		3a, 10a, 11, 21, 22
11		75.90			22	
	11	3.98	6.1, 8.1, 6.0	10a, 10b, 22		8, 9a, 10a, 10b, 22
12		204.38			3a, 13a, 13b	
13		54.53			15, 19, 20	
	13a	2.63	15.6	13b	12, 14, 15, 19, 20	1, 2, 15, 18, 19, 20
	13b	2.44	15.6	13a	12, 14, 15, 19, 20	1, 2, 15, 18, 19, 20
14		34.72			13a, 13b, 15, 19, 20	
15		133.18			13a, 13b, 17, 18, 19, 20	
	15	5.20	1.5, 1.4	17, 18	13, 14, 17, 18	2, 13a, 13b, 17, 18, 19, 20
16		130.92			17, 18	
17		28.01			15, 18	
	17	1.68	1.5	15	15, 16, 18	15
18		19.04			15, 17	
	18	1.72	1.4	15	15, 16, 17	1, 13a, 13b, 15, 19, 20
19		29.02, 29.46			13a, 13b, 20	
	19	1.19, 1.20			13, 14, 15, 20	7, 13a, 13b, 15, 18
20		29.02, 29.46			13a, 13b, 19	
	20	1.19, 1.20			13, 14, 15, 19	7, 13a, 13b, 15, 18
21		21.85			3a, 3b, 8	
	21	1.18			3, 4	1, 2, 3b, 8, 9b, 10b
22		20.85				
	22	1.24	6.1	11	10, 11	9b, 10a, 10b, 11

Table S5: Detailed NMR analysis of the minor diastereomer ($CDCl_3$, 600 MHz)

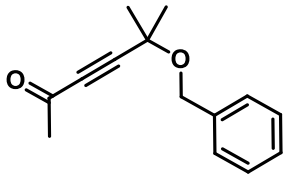


Atom [#]		δ [ppm]	J [Hz]	COSY	HMBC	NOESY
C	**H**					
1		102.81			3b	
	1	5.24	5.2	2	2, 3, 4, 5	2, 5a, 5b, 13a, 13b
2		58.86			1, 3a, 3b	
	2	3.33	8.6, 11.3, 5.2	1, 3a, 3b		1, 8, 13a, 19, 20, 22
3		33.75			1, 21	
	3a	2.26	11.3, 12.8	2, 3b	2, 4, 12, 21	21
	3b	1.93	8.6, 12.8	2, 3a	1, 2, 4	8

4		85.40			1, 3a, 3b, 9, 21	
5		64.36			1, 6	
	5a	3.79	9.6, 10.0, 6.7	5b, 6		1, 7, 21
	5b	3.41	9.6, 6.2, 10.3	5a, 6		1, 7
6		18.06			7	
	6a	0.86		5a, 5b	5	7
	6b	-1.40			7	
7		-0.01			6, 7	5a, 5b, 6, 21
	7	85.37	7.4, 7.4			
8		3.72		9		2, 3b, 9, 11, 21
	8	26.71				
9		1.80		8, 10a, 10b	4, 10, 11	8, 21
	9a	33.04			9, 22	
	9b	1.92		9, 10b, 11		10b, 11
10		1.44		9, 10a, 11		10a, 22
	10a	75.67			9, 22	
	10b	3.99	6.1	10a, 10b, 22		8, 10a, 22
11		204.66			3a, 13a, 13b	
	11	54.41			15, 19, 20	
12		2.61	15.6	13b	12, 14, 15, 19, 20	1, 2, 15, 18, 19, 20
13		2.42	15.6	13a	12, 14, 15, 19, 20	1, 18, 19, 20
	13a	34.63			13a, 13b, 15, 19, 20	
	13b	133.31			13a, 13b, 17, 18, 19, 20	
14		5.20	1.3, 1.5	17	13, 14, 17, 18, 19, 20	13a, 17, 19, 20
15		130.84			17, 18	
	15	28.03			15, 18	
16		1.68	1.5	15	15, 16, 18	15
17		19.04			15, 17	
	17	1.72	1.4		15, 16, 17	13a, 13b, 19, 20
18		29.09, 29.39			13a, 13b, 15, 20	
	18	1.19, 1.19			13, 14, 15, 20	2, 13a, 13b, 15, 18
19		29.09, 29.39			13a, 13b, 15, 19	
	19	1.19, 1.19			13, 14, 15, 19	2, 13a, 13b, 15, 18
20		25.07			3a	
	20	1.29			3, 4	3a, 5a, 7, 8, 9
21		21.18				
	21	1.21	6.1	11	10, 11	2, 10b, 11
22		20.85				
	22	1.24				

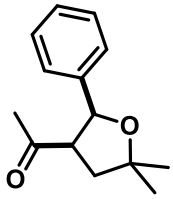
C-H INSERTIONS

5-(Benzyloxy)-5-methylhex-3-yn-2-one (20a). *n*-BuLi (1.6 M, 1.23 mL, 1.96 mmol) was added to a solution

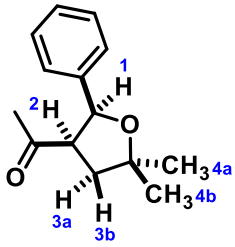


of the alkyne **S5** (300 mg, 1.72 mmol) in THF (18.8 mL) at 0 °C and the resulting mixture was stirred for 30 min at that temperature. A solution of *N*-methoxy-*N*-methylacetamide (0.28 mL, 2.68 mmol) in THF (1 mL) was added and stirring continued for 30 min at room temperature before sat. NH_4Cl solution was introduced. The mixture was extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless oil (213 mg, 57%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.18 (m, 5H), 4.54 (s, 2H), 2.26 (s, 3H), 1.51 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.4, 138.5, 128.5, 127.8, 127.7, 93.4, 84.0, 70.7, 67.1, 32.9, 28.4. IR (film) ṽ 2987, 2213, 1680, 1359, 1244, 1158, 1051 cm^{-1}. HRMS (CI$^+$) for $C_{14}H_{16}O_2$ [M+H]$^+$: calcd 217.1223, found 216.1224.

1-((2S*,3R*)-5,5-Dimethyl-2-phenyltetrahydrofuran-3-yl)ethan-1-one (21). According to Representative

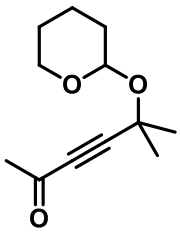


Procedure A from alkyne **20a** (25.5 mg, 0.12 mmol); colorless oil (12.8 mg, 50%, dr = 17:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.21 (m, 5H), 5.32 (d, *J* = 8.5 Hz, 1H), 3.65 (td, *J* = 8.4, 7.1 Hz, 1H), 2.36 (dd, *J* = 12.8, 7.1 Hz, 1H), 1.91 (dd, *J* = 12.8, 8.3 Hz, 1H), 1.55 (s, 3H), 1.53 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 207.6, 138.9, 128.5, 128.2, 127.0, 81.3, 80.8, 58.5, 40.5, 30.8, 28.4, 27.3. IR (film) ṽ 2970, 2871, 1709, 1455, 1367, 1294, 1165 cm^{-1}. HRMS (CI$^+$) for $C_{14}H_{28}O_2$ [M]$^+$: calcd 218.1301, found 218.1300.



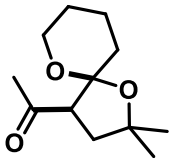
diagnostic NOEs:
H(1) - CH_3(4a)
H(2) - CH_3(4a)
H(3a) - CH_3(4a)
H(3b) - CH_3(4b)
H(1) - H(2)

5-Methyl-5-((tetrahydro-2H-pyran-2-yl)oxy)hex-3-yn-2-one (20b). *n*-BuLi (1.6 M, 1.23 mL, 1.96 mmol)

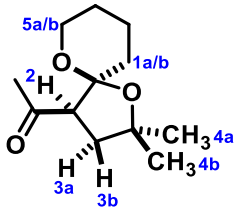


was added to a solution of alkyne **S6** (300 mg, 1.78 mmol) in THF (18.8 mL) at 0 °C and the resulting mixture was stirred for 30 min at that temperature. A solution of *N*-methoxy-*N*-methylacetamide (0.28 mL, 2.68 mmol) in THF (1 mL) was added and stirring continued for 30 min at room temperature before sat. NH_4Cl solution was added. The mixture was extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless oil (236 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.02 – 4.98 (m, 1H), 4.00 – 3.90 (m, 1H), 3.55 – 3.47 (m, 1H), 2.34 (s, 3H), 1.91 – 1.76 (m, 1H), 1.78 – 1.65 (m, 1H), 1.61 – 1.42 (m, 4H), 1.58 (s, 3H), 1.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.5, 96.3, 94.0, 83.4, 70.6, 63.4, 32.9, 31.9, 29.7, 29.4, 25.4, 20.3. IR (film) ṽ 2942, 2214, 1681, 1358, 1245, 1022 cm^{-1}. HRMS (CI$^+$) for $C_{12}H_{18}O_3$ [M+H]$^+$: calcd 211.1329, found 211.1326.

1-((4S*,5S*)-2,2-Dimethyl-1,6-dioxaspiro[4.5]decan-4-yl)ethan-1-one (22). According to Representative Procedure A from alkyne **20b** (24.7 mg, 0.12 mmol); colorless oil (11.3 mg, 45%, dr = 7:1).

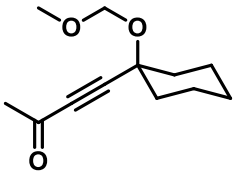


^{1}H NMR (600 MHz, $CDCl_3$, major isomer): δ 3.86 (td, *J* = 12.2, 11.8, 3.2 Hz, 1H), 3.61 – 3.55 (m, 1H), 2.89 (dd, *J* = 11.6, 8.2 Hz, 1H), 2.49 (t, *J* = 11.9 Hz, 1H), 2.23 (s, 3H), 1.98 (dd, *J* = 13.5, 8.2 Hz, 1H), 1.89 (dd, *J* = 12.2, 8.2 Hz, 1H), 1.86 – 1.80 (m, 1H), 1.66 (m, 2H), 1.51 (m, 2H), 1.40 (s, 3H), 1.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$, major isomer): δ 206.0, 105.2, 80.8, 61.9, 61.2, 39.3, 34.0, 30.2 (2C), 29.5, 25.1, 20.1. IR (film) ṽ 2941, 2874, 1712, 1595, 1364 cm^{-1}. HRMS (CI$^+$) for $C_{12}H_{20}O_3$ $[M+H]^+$: calcd 213.1485, found 213.1486.



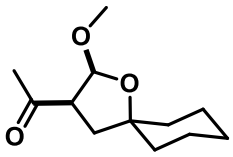
diagnostic NOEs:
H(2) - CH_3(4a)
H(2) - H(1a/b)
H(3a) - H(2)
H(3a) - H(4a)
H(5a/b) - CH_3(4b)

4-(1-(Methoxymethoxy)cyclohexyl)but-3-yn-2-one (23a). *n*-BuLi (1.6 M, 1.23 mL, 1.96 mmol) was added to a solution of alkyne **S27** (300 mg, 1.78 mmol) in THF (18.8 mL) at 0 °C and the resulting mixture was stirred for 30 min at that temperature. A solution of *N*-methoxy-*N*-methylacetamide (0.28 mL, 2.68 mmol) in THF (1 mL) was added and stirring was continued for 30 min at room temperature before sat. NH_4Cl solution was introduced. The mixture was extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless oil (293 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 (s, 2H), 3.42 (s, 3H), 2.36 (s, 3H), 1.99 (m, 2H), 1.76 – 1.65 (m, 4H), 1.61 – 1.49 (m, 3H), 1.37 – 1.25 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3, 93.1, 92.7, 85.9, 74.4, 56.1, 37.9, 33.0, 25.2, 22.9. IR (film) ṽ 2935, 2860, 2216, 1681, 1358, 1211 cm^{-1}. HRMS (ESI$^+$) for $C_{12}H_{13}O_3$ $[M+Na]^+$: calcd 233.1148, found 233.1151.

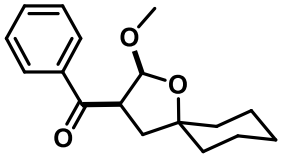


3-(1-(Methoxymethoxy)cyclohexyl)-1-phenylprop-2-yn-1-one (23b). *n*-BuLi (1.6 M, 1.23 mL, 1.96 mmol) was added to a solution of alkyne **S27** (300 mg, 1.78 mmol) in THF (18.8 mL) at 0 °C and the resulting mixture was stirred for 30 min at that temperature. A soluiton of *N*-methoxy-*N*-methylbenzamide (441 mg, 2.68 mmol) in THF (1 mL) was added and stirring was continued for 30 min at room temperature before sat. NH_4Cl solution was introduced. The mixture was extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 20:1 – 10:1) to yield the title compound as a colorless oil (410 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.11 (m, 2H), 7.61 (tt, *J* = 7.9, 1.3 Hz, 1H), 7.52 – 7.45 (m, 2H), 4.99 (s, 2H), 3.45 (s, 3H), 2.16 – 2.07 (m, 2H), 1.78 (m, 4H), 1.70 – 1.52 (m, 3H), 1.35 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 136.9, 134.3, 129.7, 128.8, 95.2, 93.2, 84.2, 74.6, 56.1, 38.0, 25.2, 23.0. IR (film) ṽ 2935, 2206, 1644, 1449, 1247, 1017 cm^{-1}. HRMS (ESI$^+$) for $C_{17}H_{20}O_3$ $[M+Na]^+$: calcd 295.1308, found 295.1305.

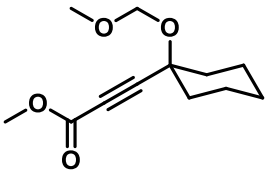
1-((2S*,3R*)-2-Methoxy-1-oxaspiro[4.5]decan-3-yl)ethan-1-one (24a). According to Representative Procedure A from alkyne **23a** (22.3 mg, 0.11 mmol); colorless oil (14.7 mg, 65%, dr = 6:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.16 (d, *J* = 4.9 Hz, 1H), 3.31 (s, 3H), 3.21 (ddd, *J* = 11.3, 8.6, 4.9 Hz, 1H), 2.24 – 2.18 (m, 1H), 2.17 (s, 3H), 1.84 (dd, *J* = 12.6, 8.6 Hz, 1H), 1.73 – 1.60 (m, 4H), 1.52 (m, 1H), 1.47 – 1.29 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.2, 103.2, 85.2, 57.8, 54.4, 40.3, 38.2, 29.7, 25.4, 23.9. IR (film) ṽ 2929, 1716, 1448, 1362, 1110, 1041 cm^{-1}. HRMS (ESI$^+$) for $C_{12}H_{20}O_3$ [M+Na]$^+$: calcd 235.1305, found 235.1306.



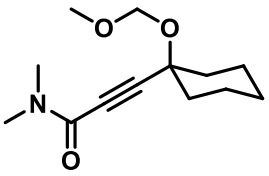
((2S*,3R*)-2-Methoxy-1-oxaspiro[4.5]decan-3-yl)(phenyl)methanone (24b). According to Representative Procedure A from alkyne **23b** (30.6 mg, 0.11 mmol) with 5 mol% $[Cp^*RuCl]_4$ over 16 h; colorless oil (15.6 mg, 51%, dr = 8:1). Single crystals suitable for X-ray analysis were obtained by storage of the neat material at −20 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 – 7.92 (m, 2H), 7.60 – 7.52 (m, 1H), 7.47 (m, 2H), 5.24 (d, *J* = 5.0 Hz, 1H), 4.06 (ddd, *J* = 11.0, 8.5, 5.0 Hz, 1H), 3.14 (s, 3H), 2.58 (dd, *J* = 12.7, 11.0 Hz, 1H), 1.94 (dd, *J* = 12.7, 8.5 Hz, 1H), 1.79 – 1.33 (m, 10H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 137.6, 133.0, 128.8, 128.1, 103.9, 84.8, 54.6, 53.0, 40.3, 38.5, 34.7, 25.5, 24.1, 24.0. IR (film) ṽ 2930, 2856, 1686, 1448, 1218, 1109, 1039 cm^{-1}. HRMS (EI$^+$) for $C_{17}H_{22}O_3$ [M]$^+$: calcd 274.1569 , found 274.1572.



Methyl 3-(1-(methoxymethoxy)cyclohexyl)propiolate (25). *n*-BuLi (1.6 M, 1.23 mL, 1.96 mmol) was added to a solution of alkyne **S27** (300 mg, 1.78 mmol) in THF (18.8 mL) at 0 °C and the resulting mixture was stirred for 30 min at that temperature. A solution of methyl chloroformate (337 mg, 3.57 mmol) in THF (1 mL) was added at –78 °C, the mixture was allowed to warm to room temperature and stirring was continued for 30 min before sat. aq. $NaHCO_3$ solution (10 mL) was added. The mixture was extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography (silica, hexanes/EtOAc 10:1) to yield the title compound as a colorless oil (385 mg, 89%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.89 (s, 2H), 3.77 (s, 3H), 3.41 (s, 3H), 2.05 – 1.94 (m, 2H), 1.76 – 1.48 (m, 7H), 1.37 – 1.17 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.0, 93.1, 88.7, 78.0, 74.3, 56.1, 52.9, 37.8, 25.2, 22.8. IR (film) ṽ 2937, 2229, 1715, 1435, 1238, 1017 cm^{-1}. HRMS (ESI$^+$) for $C_{12}H_{18}O_4$ [M+Na]$^+$: calcd 249.1098, found 249.1010.



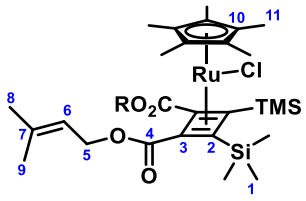
3-(1-(Methoxymethoxy)cyclohexyl)-N,N-dimethylpropiolamide (26). *n*-BuLi (1.6 M, 0.49 mL, 0.79 mmol) was added to a solution of alkyne **S27** (111 mg, 0.67 mmol) in THF (10.0 mL) at 0 °C and the resulting mixture was stirred for 30 min at that temperature. A solution of dimethylcarbamoyl chloride (142 mg, 1.32 mmol) in THF (1 mL) was added at – 78 °C, the mixture was allowed to warm to room temperature and stirring was continued for 30 min before sat. aq. $NaHCO_3$ solution (10 mL) was introduced. The mixture was extracted with EtOAc (3 x 50 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was evaporated and the residue purified by flash chromatography to yield the title compound as a colorless oil (134 mg, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.91 (s, 2H), 3.40 (s, 3H), 3.20 (s, 3H), 2.97 (s, 3H), 2.06 – 1.95 (m, 2H), 1.71 (m, 4H), 1.61 – 1.48 (m, 3H), 1.30 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.2, 93.1, 92.1, 79.3, 74.6, 56.0, 38.4, 38.0, 34.2, 25.2, 22.9.



IR (film) ṽ 2933, 2859, 2229, 1633, 1392, 1146, 1020 cm^{-1}. HRMS (CI^+) for $C_{13}H_{21}NO_3$ $[M+H]^+$: calcd 240.1594, found 240.1592.

RUTHENIUM COMPLEXES

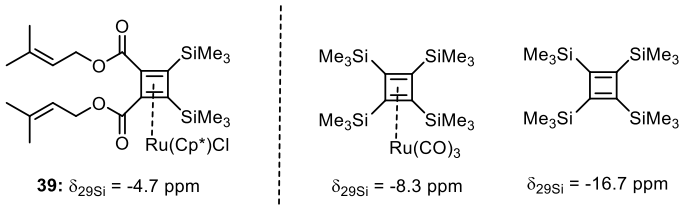
Ruthenium Cyclobutadiene Complex 39. To a flame dried two-necked round-bottom flask was charged with $[Cp^*RuCl]_4$ (103 mg, 95 µmol). The flask was evacuated and refilled with H_2 (by means of attaching a balloon filled with hydrogen via needle and septum). A solution of enyne **37** (1.00 g, 4.75 mmol) in 1,2-dichloroethane (50 mL) was introduced before the flask was immersed into a pre-heated oil bath at 70 °C keeping a static H_2 atmosphere (ambient pressure, H_2 filled balloon). After stirring for 3 h at 70 °C, the mixture was allowed to cool to room temperature and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (silica, hexanes/EtOAc 10:0 – 4:1) to yield butenolide **56** (480 mg, 59%) as an off-white solid. Single crystals suitable for X-ray analysis were obtained by slowly cooling a concentrated solution in Et_2O to – 80 °C over the course of 24 h.



A second fraction (less polar than the butenolide) contained the title complex which was obtained as a brown solid (95.5 mg, 48% with regard to [Ru]). Single crystals suitable for X-ray analysis were obtained by slow evaporation of a concentrated solution in CH_2Cl_2. ^1H NMR (400 MHz, $CDCl_3$) δ 5.40 (tdq, *J* = 7.4, 2.9, 1.4 Hz, 2H), 4.65 (dt, *J* = 7.4, 0.8 Hz, 4H), 1.76 (m, 6H), 1.71 (m, 6H), 1.61 (s, 15H), 0.11 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 139.5, 118.3, 101.9, 86.0, 81.3, 61.8, 25.9, 18.2, 9.3, 2.2. ^{29}Si NMR (119 MHz, $CDCl_3$) δ -4.7. IR (film) ṽ 2899, 1701, 1471, 1377, 1170, 1084 cm^{-1}. HRMS (ESI^+) for $C_{32}H_{51}ClO_4RuSi_2$ $[M+Na]^+$: calcd 715.1950, found 715.1958.

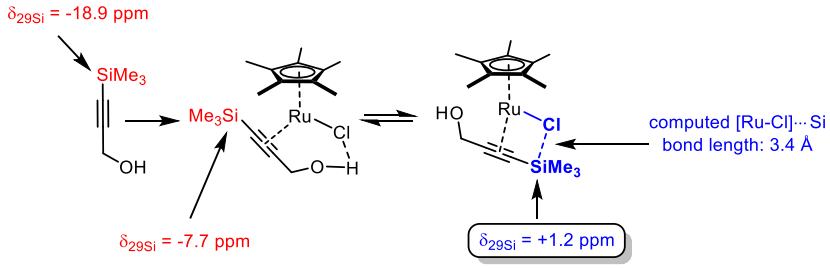
Table S6: NMR analysis of Cyclobutadiene Complex **39** ($CDCl_3$, 400 MHz)

Atom [#] C	H	δ [ppm]		J [Hz]	COSY	HMBC
1		2.2				
	1		0.11			2
2		86.0				1
3		81.3				
4		165.2				5
5		61.8				
	5		4.65	7.4	5	4, 6, 7
6		118.3				5, 8, 9
	6		5.40	7.4, 1.4	6	8, 9
7		139.5				5, 8, 9
8		25.9				6, 9
	8		1.76	1.4		6, 7, 9
9		18.2				6, 8
	9		1.71	1.4		6, 7, 8
10		101.9				11
11		9.3				
	11		1.61			10



39: δ_{29Si} = -4.7 ppm δ_{29Si} = -8.3 ppm δ_{29Si} = -16.7 ppm

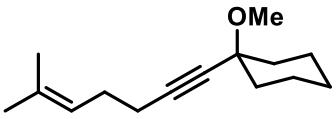
Scheme S4. Comparison of the ^{29}Si NMR shift of the new complex **39** which features notably short [Ru–Cl]···Si contacts in the solid state (see Figure 1 in the main text of the publication) with that of a related ruthenium complex reported in the literature devoid of such an interaction and the respective ligand.[27,28]



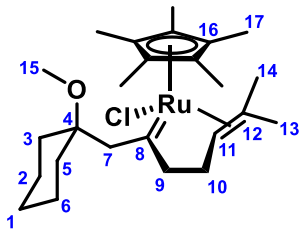
Scheme S5. Literature precedent for an ^{29}Si NMR shift responsive to attractive [Ru–Cl]···Si contacts.[29]

RUTHENIUM CARBENE/OLEFIN COMPLEX

1-Methoxy-1-(6-methylhept-5-en-1-yn-1-yl)cyclohexane (40). *n*-BuLi (1.6 M in hexanes, 3.54 mL, 5.66 mmol) was slowly added to a solution of alkyne **S1** (652 mg, 4.72 mmol) in THF (16 mL) at 0 °C. The mixture was stirred for 30 min at 0 °C before a solution of 5-bromo-2-methyl-2-pentene (1.00 g, 6.13 mmol) in THF (10.7 mL) and DMPU (2.9 mL) was added. The mixture was warmed to room temperature and stirring was continued for 18 h. sat. aq. NH_4Cl solution (5 mL), methyl *tert*-butyl ether (20 mL) and water (5 mL) were introduced and the layers were separated. The aqueous phase was extracted with methyl *tert*-butyl ether (3 x 100 mL) and the combined organic layers were washed with brine and dried over $MgSO_4$. The solvent was removed and the residue was purified by flash chromatography (silica, hexanes/EtOAc 1:0 – 40:1) to give the title compound as a colorless oil (401 mg, 39%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.17 (m, 1H), 3.34 (s, 3H), 2.29 – 2.16 (m, 4H), 1.90 – 1.81 (m, 2H), 1.70 (q, *J* = 1.3 Hz, 3H), 1.68 – 1.59 (m, 2H), 1.63 (d, *J* = 1.3 Hz, 4H), 1.57 – 1.45 (m, 4H), 1.31 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.9, 123.2, 86.5, 81.2, 74.2, 50.6, 37.2, 27.9, 25.9, 25.7, 23.0, 19.4, 18.0. IR (film) ṽ 2932, 2856, 1447, 1093 cm^{-1}. HRMS (ESI$^+$) for $C_{15}H_{24}O$ $[M+Na]^+$: calcd 243.1719, found 243.1721.



Ruthenium Carbene Complex 41. $[Cp^*RuCl]_4$ (123 mg, 0.11 mmol) was added to a stirred solution of enyne **40** (100 mg, 0.45mmol) in CH_2Cl_2 (10.0 mL) in a flame dried Schlenk tube at room temperature under argon.



H_2 was bubbled through the mixture for 2 min before the mixture was stirred for 1.5 h at room temperature under an hydrogen atmosphere (balloon). The solvent was removed by purging the mixture with argon and subsequent evacuation of the tube. The residue was washed with pentane (3.5 mL) by means of cannula filtration. Crystals suitable for X-ray analysis were obtained by extracting the residue with Et_2O (2 mL) followed by slow cooling of the filtrate to – 50 °C over the course of 48 h. ^{1}H NMR: see Table S7; ^{13}C NMR: see Table S7; IR (film) ṽ 2927, 2851, 1442, 1375, 1164, 1069 cm^{-1}. HRMS (ESI$^+$) for $C_{25}H_{41}ClORu$ [M]$^+$: calcd 494.1884, found 494.1893.

Table S7: NMR analysis of Carbene Complex **41** (CD_2Cl_2, –20 °C, 400/101 MHz)

Atom [#]		δ [ppm]	J [Hz]	COSY	HMBC	NOESY
C	**H**					
1		25.7				
	1	1.40 - 1.21				
2		21.8, 21.6				
	2	1.40 - 1.21				
3		35.6			7b	
	3	1.30				
4		76.6			7b, 15	
5		34.4			7a	
	5	1.81, 1.19				
6		21.8, 21.6				
	6	1.40 - 1.21				
7		65.9				
	7a	4.29	17.1	7b	5, 9	7b, 15, 17
	7b	2.13	17.1	7a	3, 4	7a
8		368.4			7a, 7b, 9a, 9b	
9		67.3			7a, 10a, 11	
	9a	3.08	23.9, 9.1, 5.6	9b, 10a, 10b		9b, 13
	9b	2.20		9a, 10a, 10b		9a
10		25.9				
	10a	2.45		9a, 9b, 10b, 11	9, 11	10b, 11, 17
	10b	2.17		9a, 9b, 10a, 11	11	10a
11		79.7			10a, 10b, 13, 14	
	11	4.42	8.0, 1.9	10a, 10b, 13, 14	9, 12	10a, 14, 17
12		79.4			11	
13		25.0			14	
	13	1.29			11, 14	9a
14		27.8			13	
	14	1.22			11, 13	11, 17
15		48.5				
	15	3.00			4	7a
16		99.7			17	
17		10.1				
	17	1.55			16	7a, 10a, 11, 14

Decomposition of Carbene Complex 41

Complex **41** slowly decomposes into isomeric alkene **B** when left in CD_2Cl_2 solution under Ar at room temperature (approx. 70 % (GC) after 7 days). The structure of the product was established by deconvolution of the diagnostic olefin signals (8 and 9) in C_6D_6 showing characteristic ^3J(H-H)-couplings (^3J(H9-H10) = 6.2 Hz, ^3J(H8-H7) = 6.8 Hz) to the neighboring methylene groups.

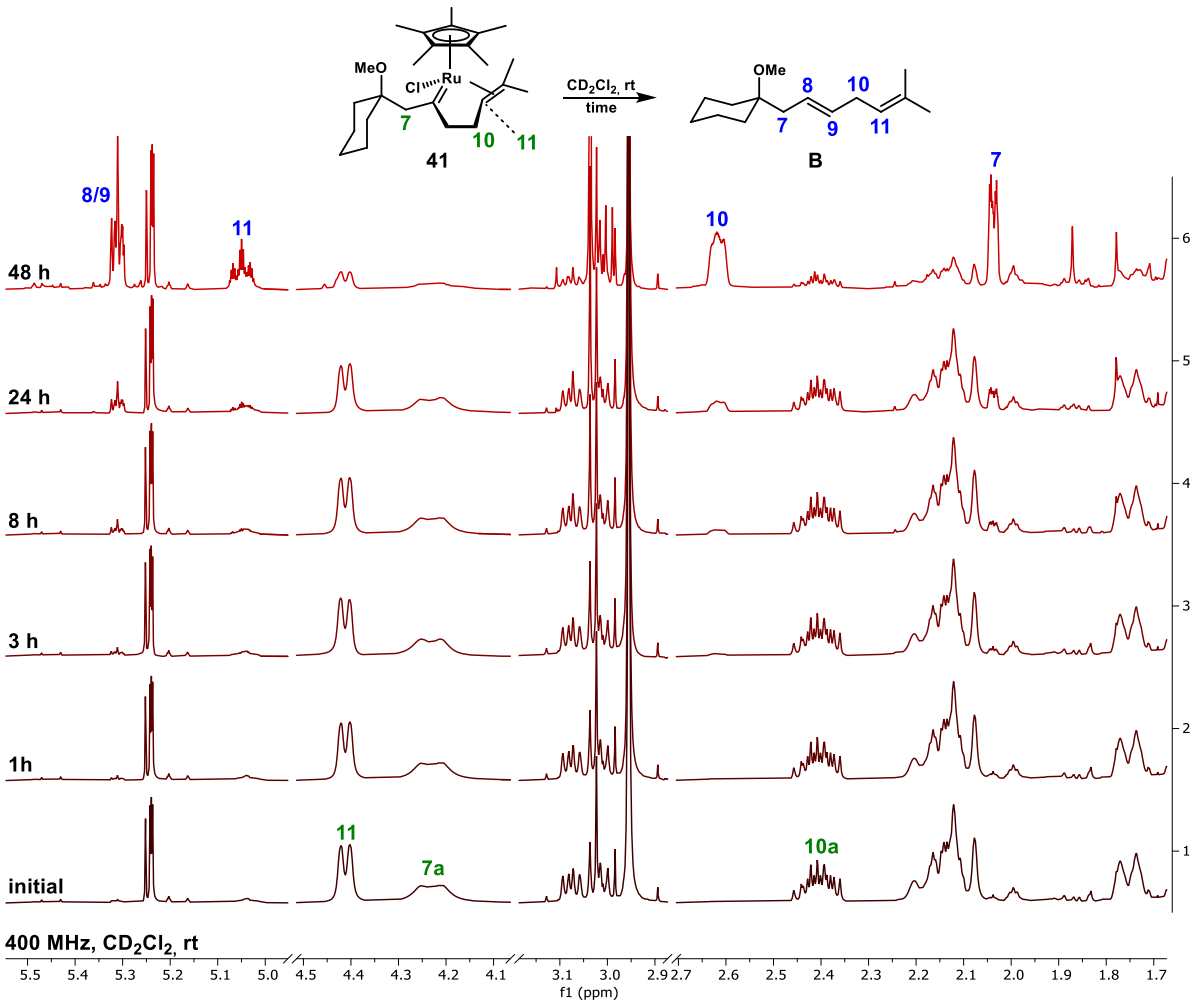
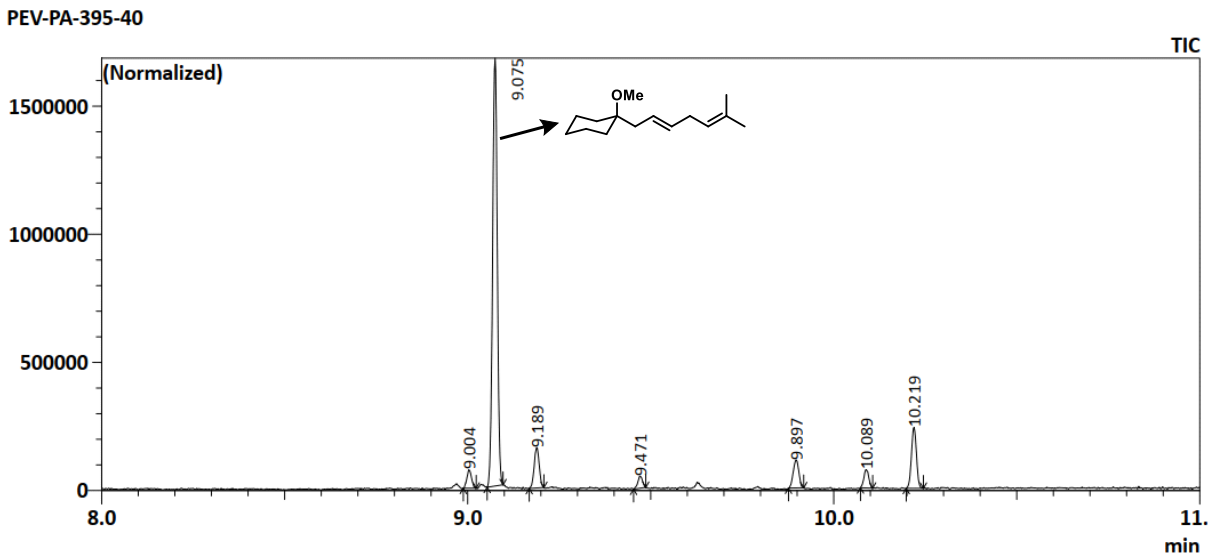


Figure S14. Evolution of Complex **41** in CD_2Cl_2 solution at room temperature over time (selected regions of the stacked spectra).



Sample Information
Fri 12.07.2019 - 08:57:10

PEV-PA-395-40

C:\GCMSsolution\Data\Methode\50_20.qgm
C:\GCMSsolution\Data\User\Peil\PEV-PA-395-40.qgd

Peak Report

Peak	Time	%
1	9.00	2.9
2	9.07	69.0
3	9.19	7.1
4	9.47	2.0
5	9.90	5.4
6	10.09	3.1
7	10.22	10.5
		100.0

Figure S15. GCMS analysis of the reaction mixture after 7 days at room temperature showing the quite selective formation of **B** (approx. 70% TIC ratio of volatile material).

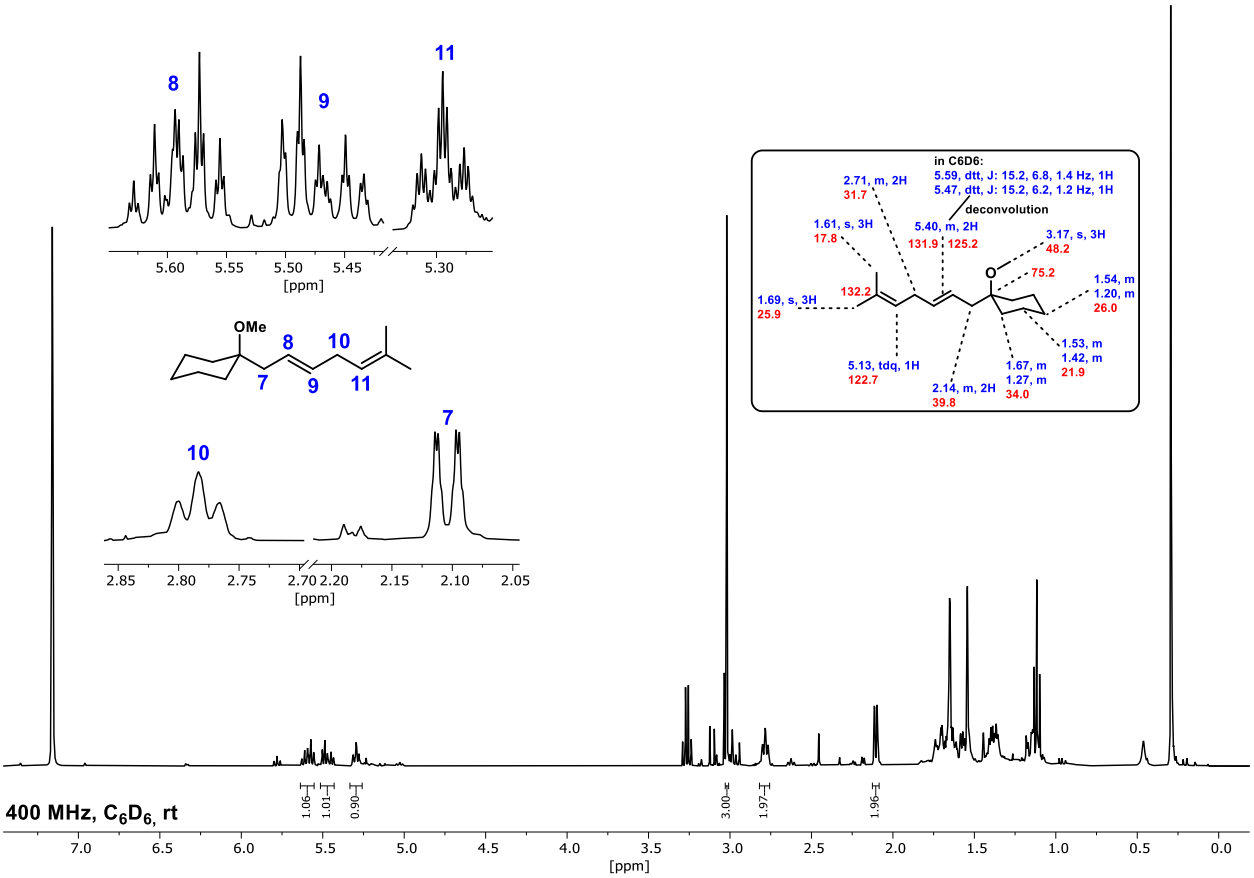


Figure S16. Diagnostic ^{1}H-spectrum (C_6D_6) of the decomposition mixture and chemical shift assignments based on 2D spectra (insert).

BRIDGED CARBENOID COMPLEX 43

A. Variable-temperature NMR Control of the Stoichiometric Reaction of Enyne 1a with [Cp*RuCl]$_4$ under H_2. [Cp*RuCl]$_4$ (16.1 mg, 0.015 mmol) was added to a stirred solution of enyne **1a** (13.9 mg, 0.059 mmol) in CD_2Cl_2 (0.7 mL) under argon in a flame-dried Schlenk tube. The mixture was transferred into a flame-dried J-Young-NMR tube under argon before it was cooled to −78 °C (dry ice/acetone bath). The atmosphere was exchanged for H_2 by purging the system with a H_2 for 2 min and the NMR tube was quickly closed under a H_2 current. The NMR tube was shaken before being introduced into the NMR spectrometer, the internal temperature of which had been set to −50°C. ^{1}H NMR spectra were recorded at temperatures from −50 °C to room temperature in 10 °C intervals (series of ^{1}H excerpts see Figure S17).

Figures S17 and S18*: The formation of the metathesis product **2a** starts at −30 °C (signals **C** + **D**) with steady increase upon raising the temperature in increments of 10°C. An additional signal (**E**) appears in parallel, which was attributed to the bridged carbenoid **43**. Conversion was incomplete even at room temperature, likely because of insufficient H_2 in solution and slow transfer from the gas phase.*

B. Room Temperature NMR Spectra of a Stoichiometric Reaction of Enyne 1a with [Cp*RuCl]$_4$ under H_2. [Cp*RuCl]$_4$ (15.3 mg, 0.014 mmol) was added to a stirred solution of enyne **1a** (14.5 mg, 0.062 mmol) in CD_2Cl_2 (0.7 mL) under argon in a flame dried Schlenk tube at room temperature. H_2 was bubbled gently through the mixture for 2 min and stirring was continued for 30 min under a H_2 atmosphere. The mixture was transferred into a flame dried J-Young-NMR tube under argon for analysis.

Figures S19-S22: *The spectra show complete conversion of enyne* **1a** *(signals **A** + **B** missing) to product **2a** (signals **C** + **D**). Significant quantities of the bridged carbenoid **43** are detected (approx. 15% by comparison of signals **D** and **E**). ^{13}C NMR, HSQC and HMBC spectra were recorded to characterize the carbenoid species; the data is summarized in* **Tab. S8**.

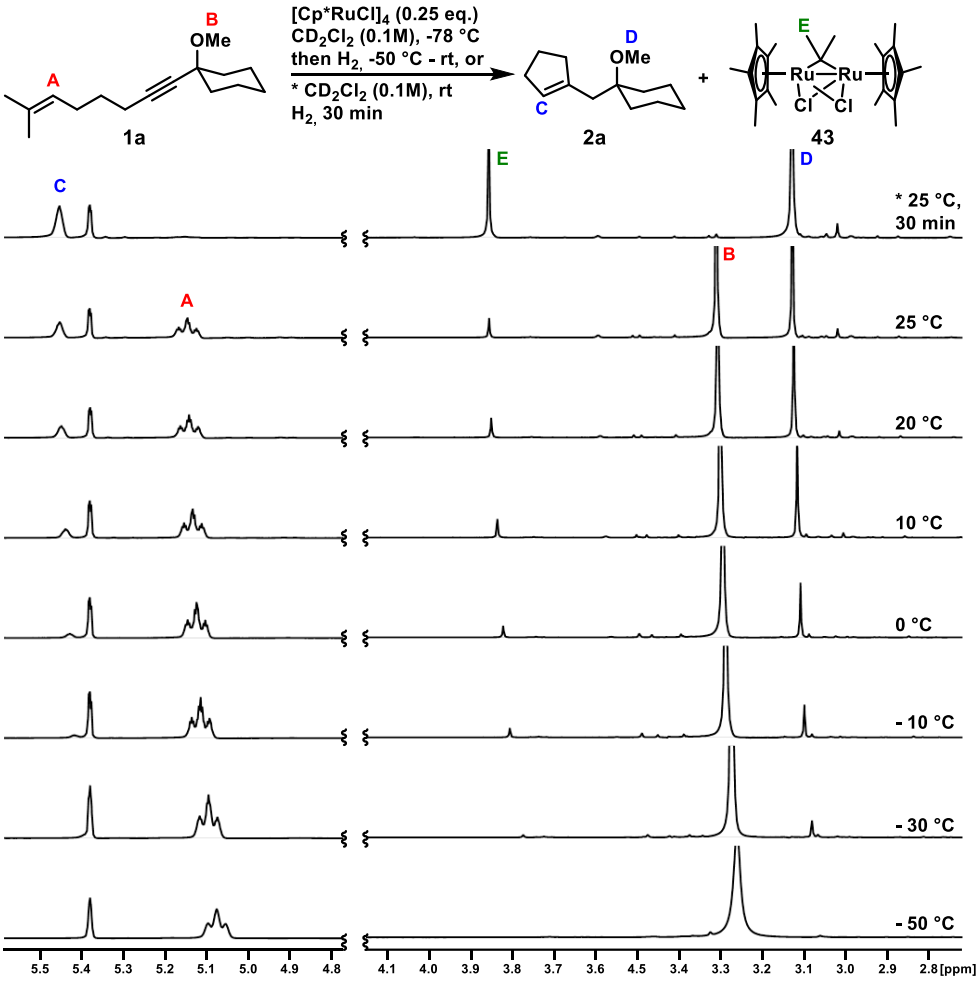


Figure S17. Low and room temperature stoichiometric NMR experiments. Shown is the relevant region in the ^1H spectra recorded at the specified temperatures (complete spectra see Figure S18). Excerpt 1 (top) refers to experiment **B**, excerpts 2 – 8 refer to experiment **A**.

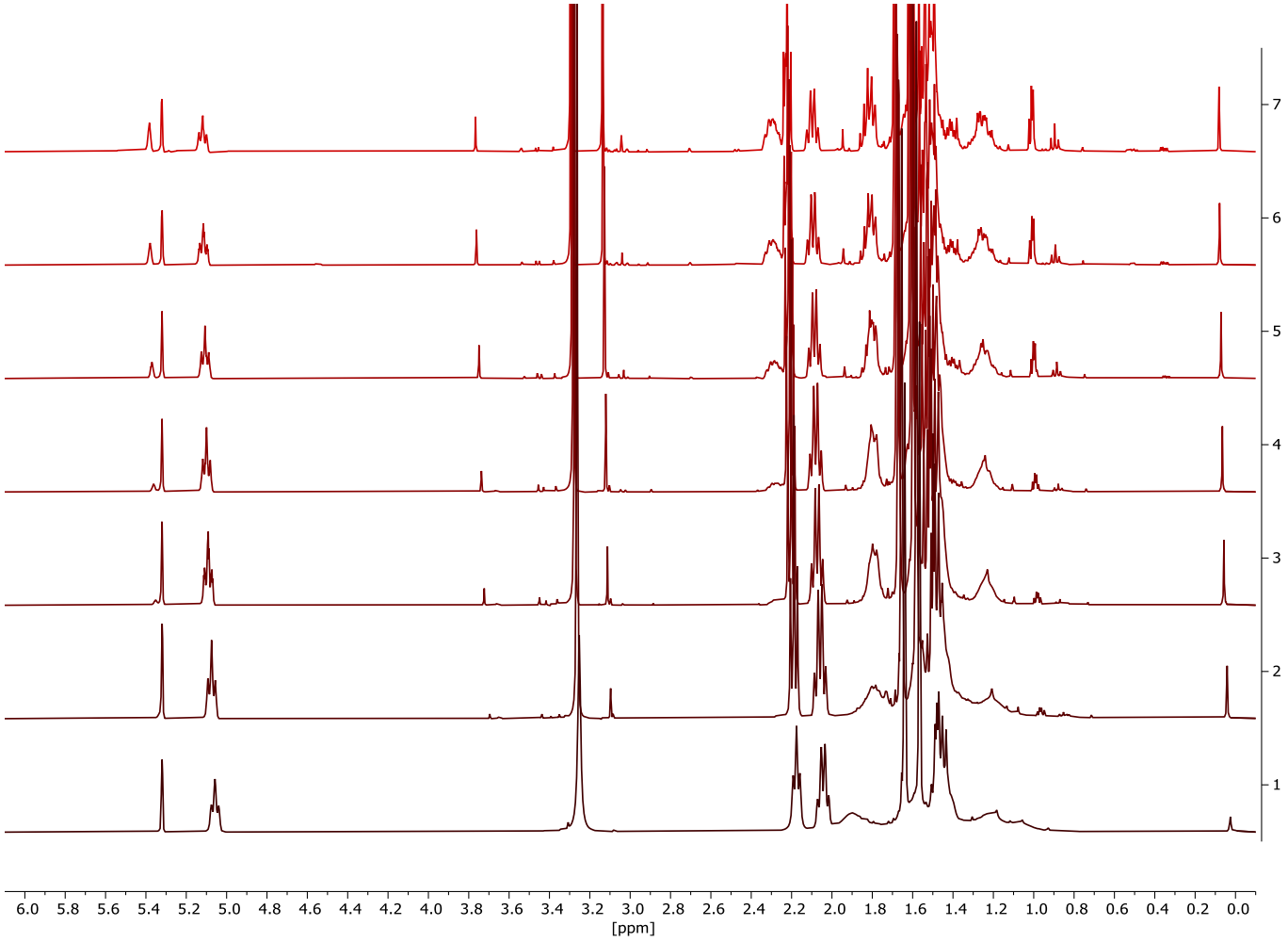


Figure S18. ^{1}H NMR spectra of low temperature stoichiometric NMR experiment **A**. Spectra are stacked according to Figure S17 (lane 1 @ −50 °C to lane 7 @ 25 °C)

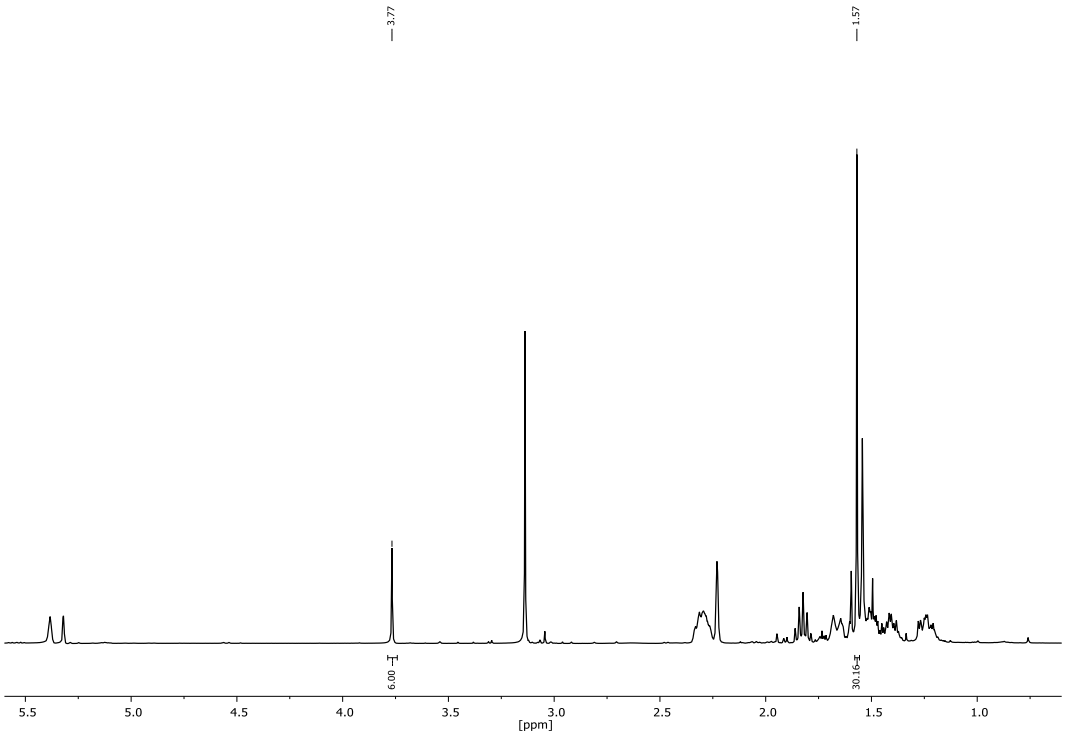


Figure S19. ^{1}H NMR spectrum stoichiometric experiment **B** performed at room temperature; peak-picking and integrals shown for signals attributed to carbenoid **43**.

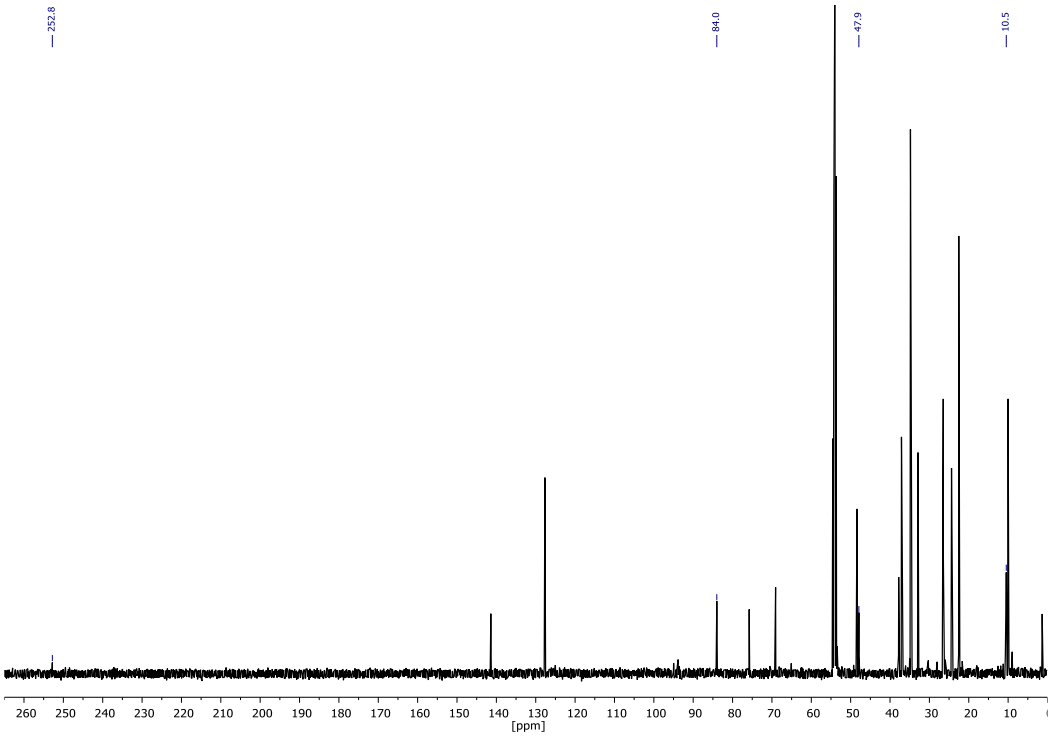


Figure S20. ^{13}C NMR spectrum of the stoichiometric NMR experiment **B** performed at room temperature; peak-picking shown for signals attributed to carbenoid **43**.

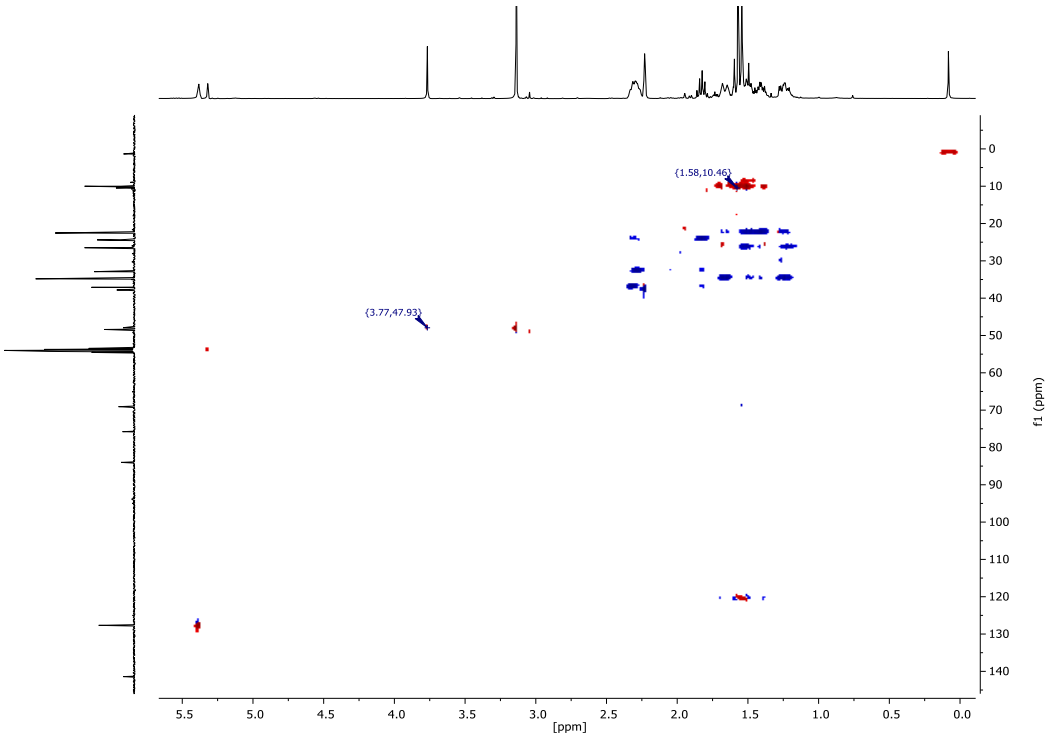


Figure S21. HSQC spectrum of experiment **B**, cross-peaks for carbenoid **43** are indicated

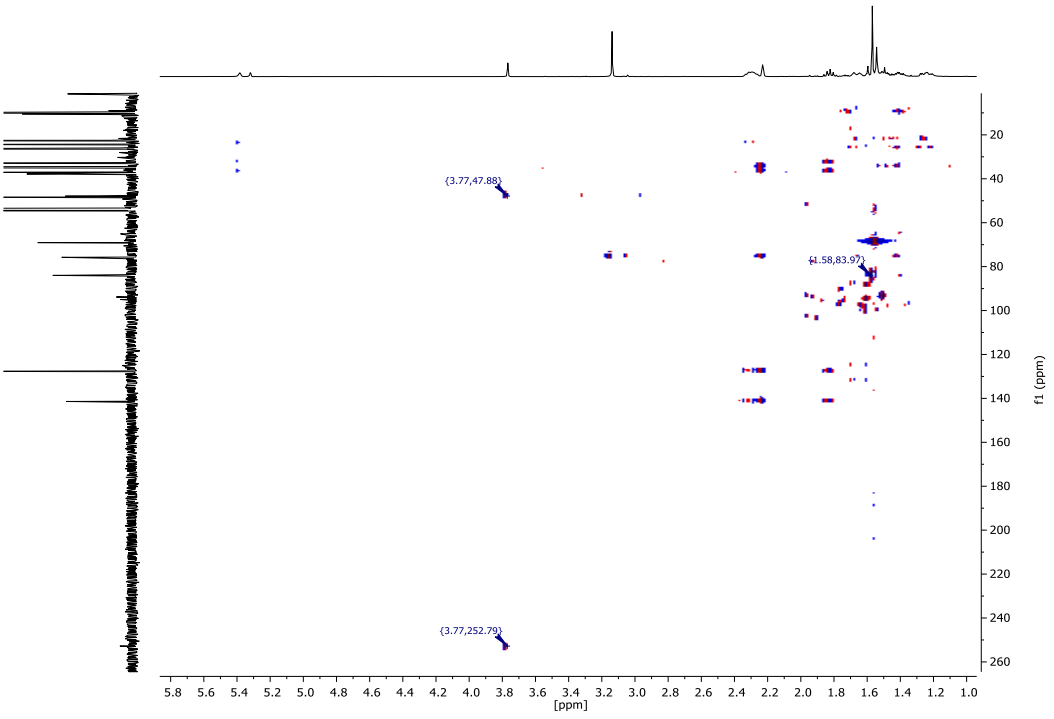


Figure S22. HMBC spectrum of experiment **B**, cross-peaks for carbenoid **43** are indicated

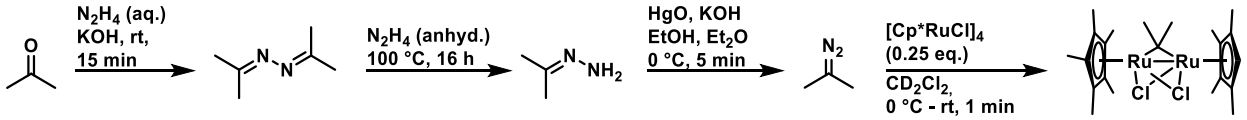


Figure S23. Synthesis of bridged carbenoid **43** from 2-diazopropane.

Independent Synthesis. 2-Diazopropane (0.2 M in Et_2O, 92 µL, 0.02 mmol)[30][31] was added dropwise to a stirred solution of $[Cp^*RuCl]_4$ (10 mg, 0.01 mmol) in CH_2Cl_2 (0.4 mL) at 0 °C in a flame-dried Schlenk tube under argon. The mixture was stirred for 1 min before it was allowed to warm to room temperature. The solvent was removed by purging with argon and subsequent evacuation of the tube, and the green residue was dissolved in CD_2Cl_2 for immediate NMR analysis.

Figures S24-S26*: Identical sets of ^1H and ^{13}C resonances were found as for the in-situ generated carbenoid* **43** *from NMR experiment* **B** (Figures S19 – S22)*, thus strongly supporting the structural assignment. nOe data confirm the shown structure, which is also consistent with a previously reported dimeric carbenoid.*[32]

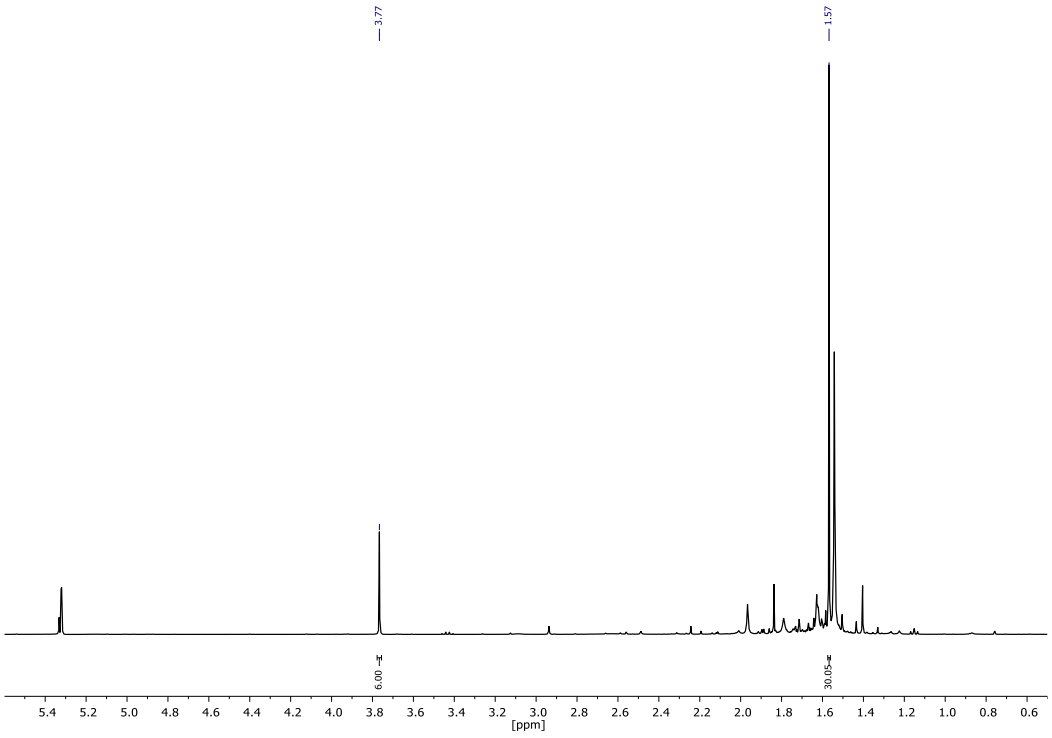


Figure S24. ^1H NMR spectrum of the crude reaction mixture comprising carbenoid **43** prepared by decomposition of 2-diazopropane

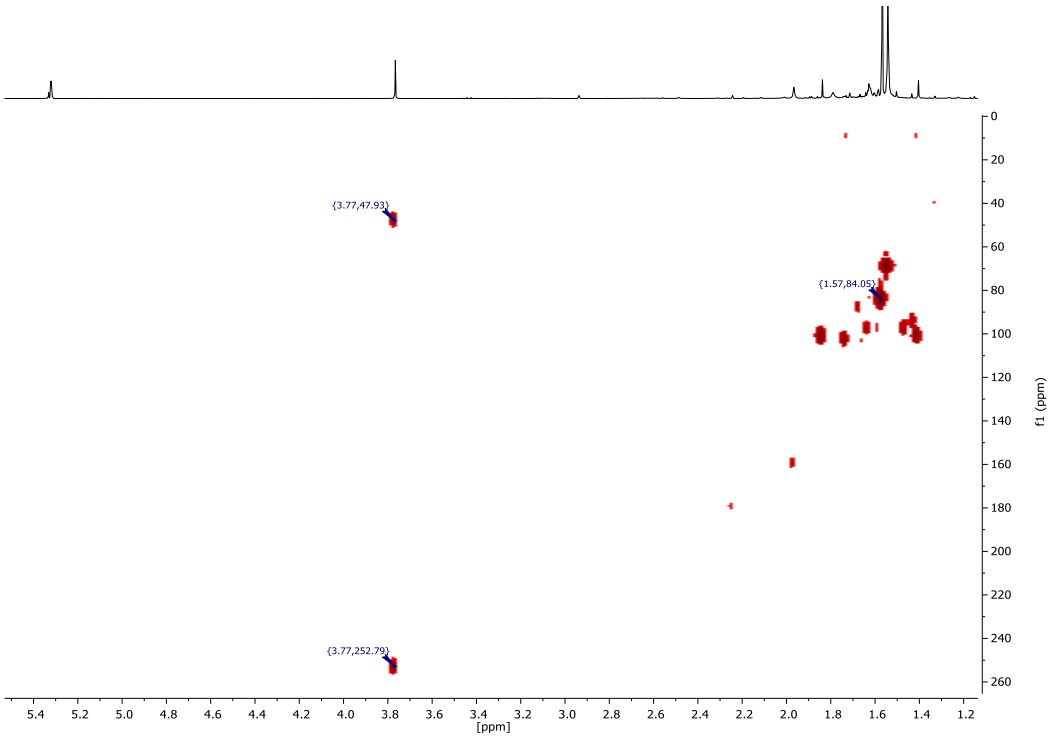


Figure S25. HMBC spectrum of carbenoid **43** generated from diazopropane

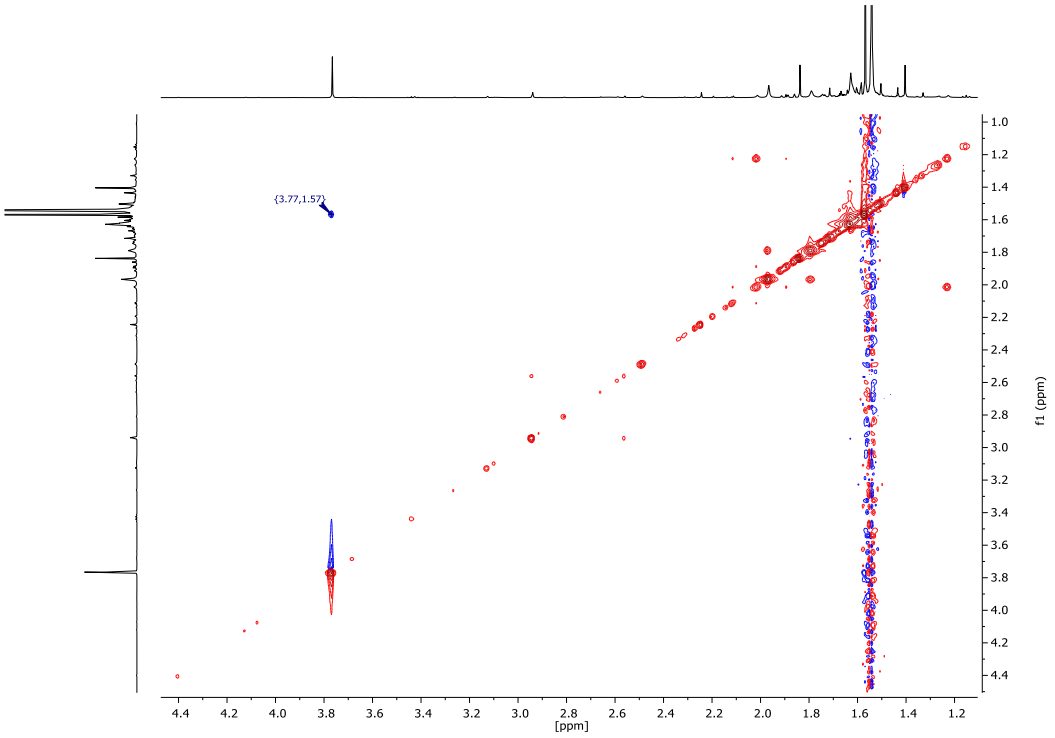
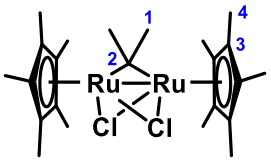


Figure S26. NOESY spectrum of of carbenoid **43** generated from diazopropane

Table S8: Detailed NMR analysis of bridged carbenoid **43**



Atom [#] C	H	δ [ppm]	HMBC	NOESY
1		47.9		
	1	3.77	2	4
2		252.8	1	
3		84.0	4	
4		10.5		
	4	1.57	3	1

HEADSPACE GC ANALYSIS

The reactions were setup as described in the Experimental Section (see above). After completion of the reaction, the mixture was allowed to cool to room temperature and a needle connected to a gas tight analysis bag was pierced through the septum used to seal the Schlenk tube. The headspace gases were transferred by purging the gas contained in the Schlenk tube into the gas bag by a stream of argon (approx. 50 mL). An aliquot of the gas mixture was analyzed by GC-FID and GC-MS. Retention times and fragmentation patterns of the analytes were compared with reference samples ("Phillips 40"), which unambiguously confirmed the formation of propane/propene from enyne **1a** and of isobutane/isobutene from enyne **1c** as the starting material (Figure S27).

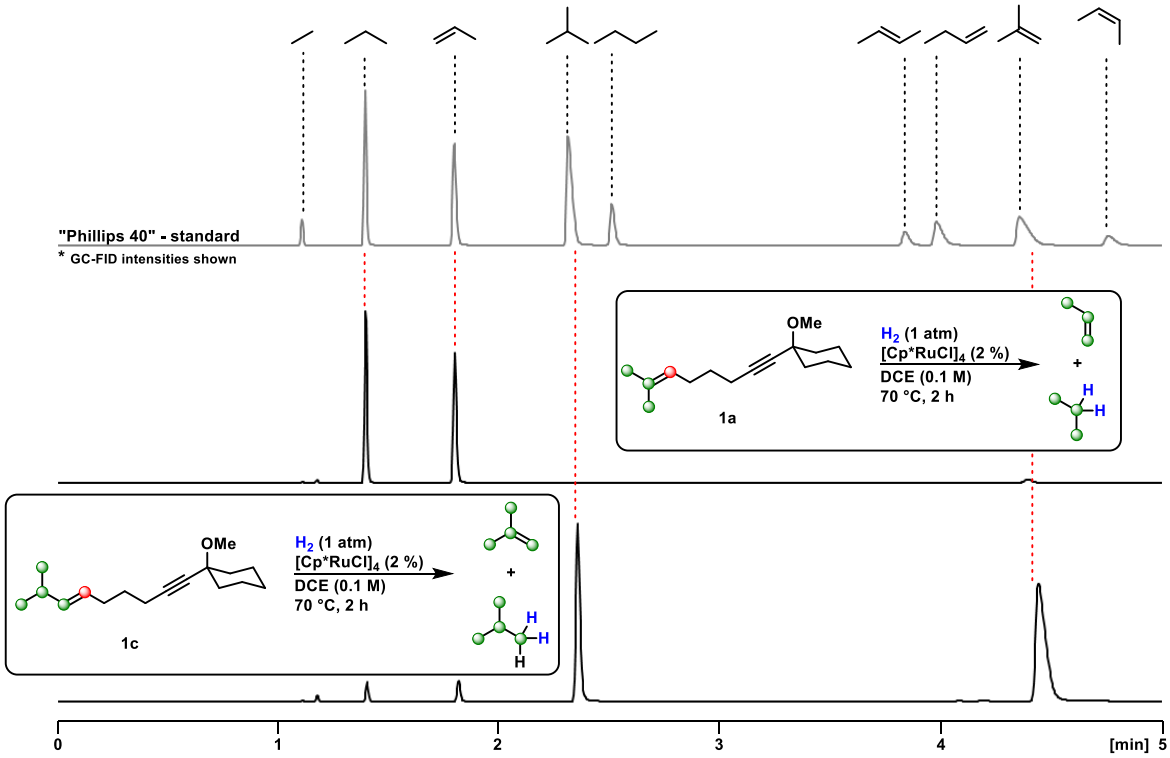


Figure S27. Excerpt of GC-FID traces of the headspace analytes formed in the shown reactions.

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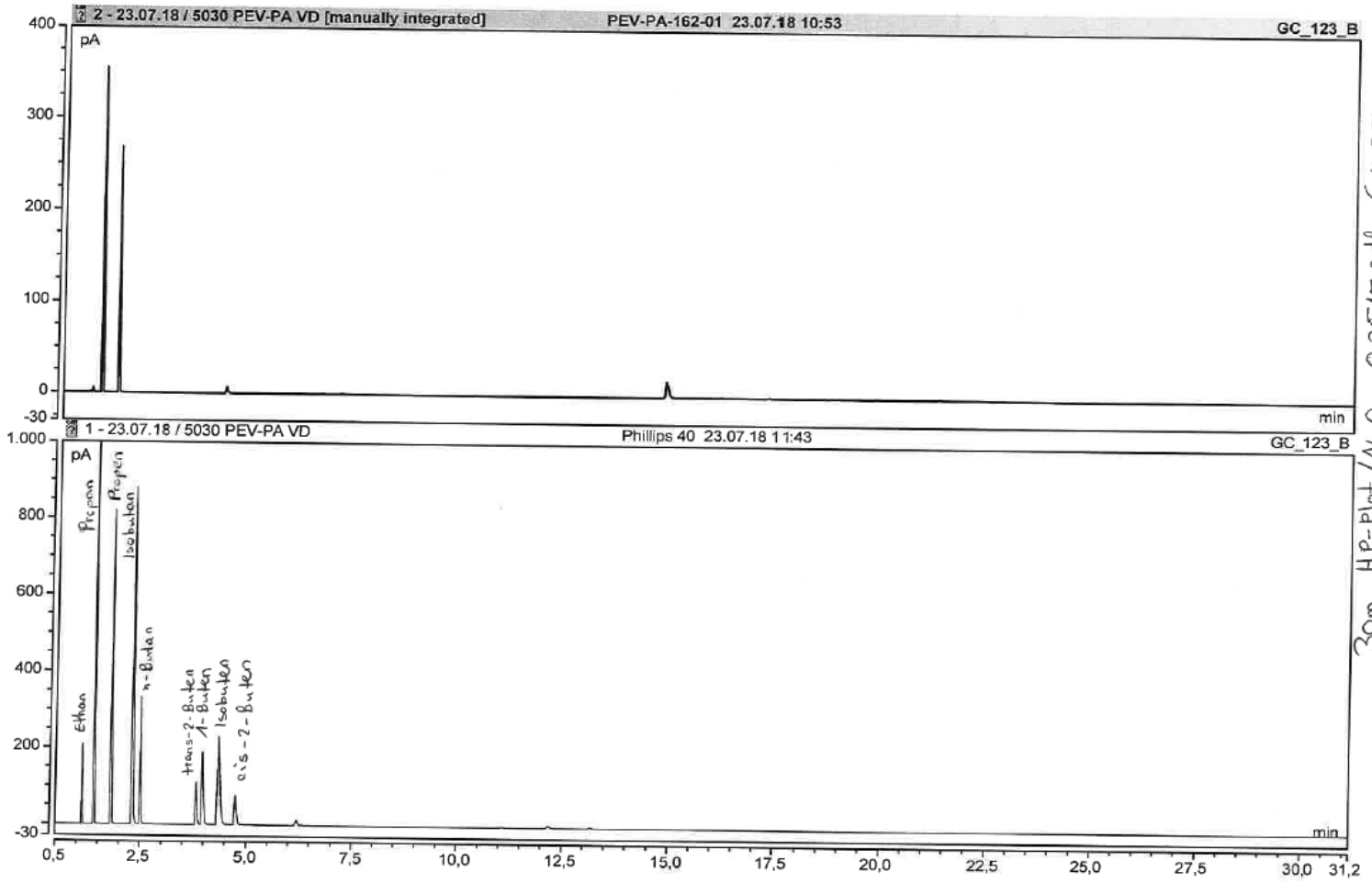
Injection #2: PEV-PA-162-01

Chromatogram



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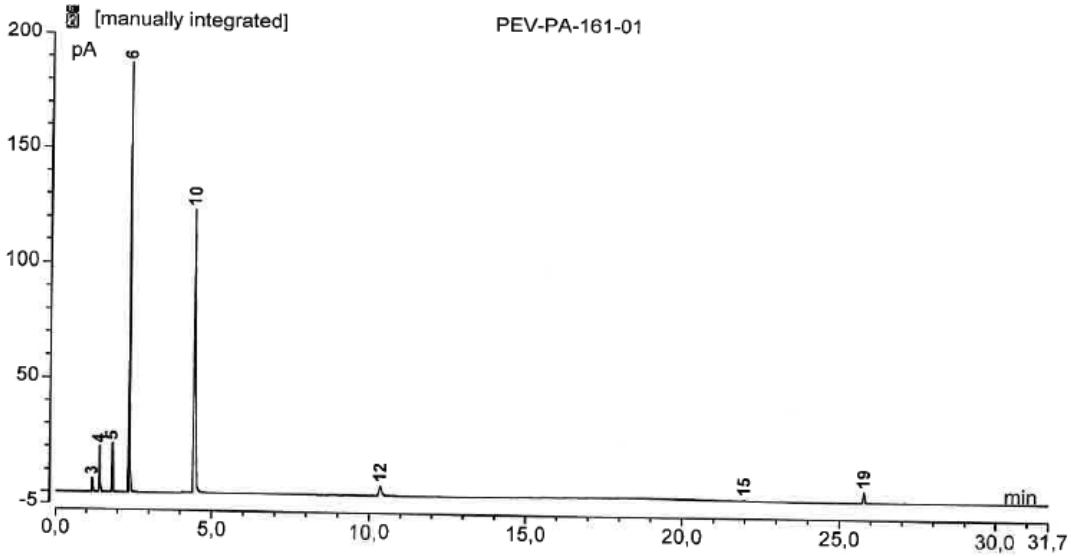


Sample: **PEV-PA-161-01**
Sequenz: **5031 PEV-PA VD**
Sequenz date: **23.07.18**

Instrument: **GC_123**
Measured: **23.07.18 13:55**
Processing M.: **Übersicht PEV-PA**
Report-File: **Übersicht 161-01**

Zuordnung mit Vergleichssubstanzen (Gasmischung Phillips 40)

No.	Ret.Time min	area-% %	Peak Name
1	1,04	0,07	
2	1,12	0,06	
3	1,19	0,63	
4	1,41	2,19	Propan
5	1,82	2,93	Propen
6	2,36	33,46	Isobutan
7	2,55	0,01	
8	4,07	0,17	
9	4,18	0,59	
10	4,43	53,96	Isobuten
11	7,30	0,03	
12	10,35	3,25	
13	15,14	0,06	
14	17,55	0,05	
15	21,97	0,23	
16	22,09	0,04	
17	22,37	0,02	
18	23,30	0,04	
19	25,77	2,18	
20	27,08	0,04	

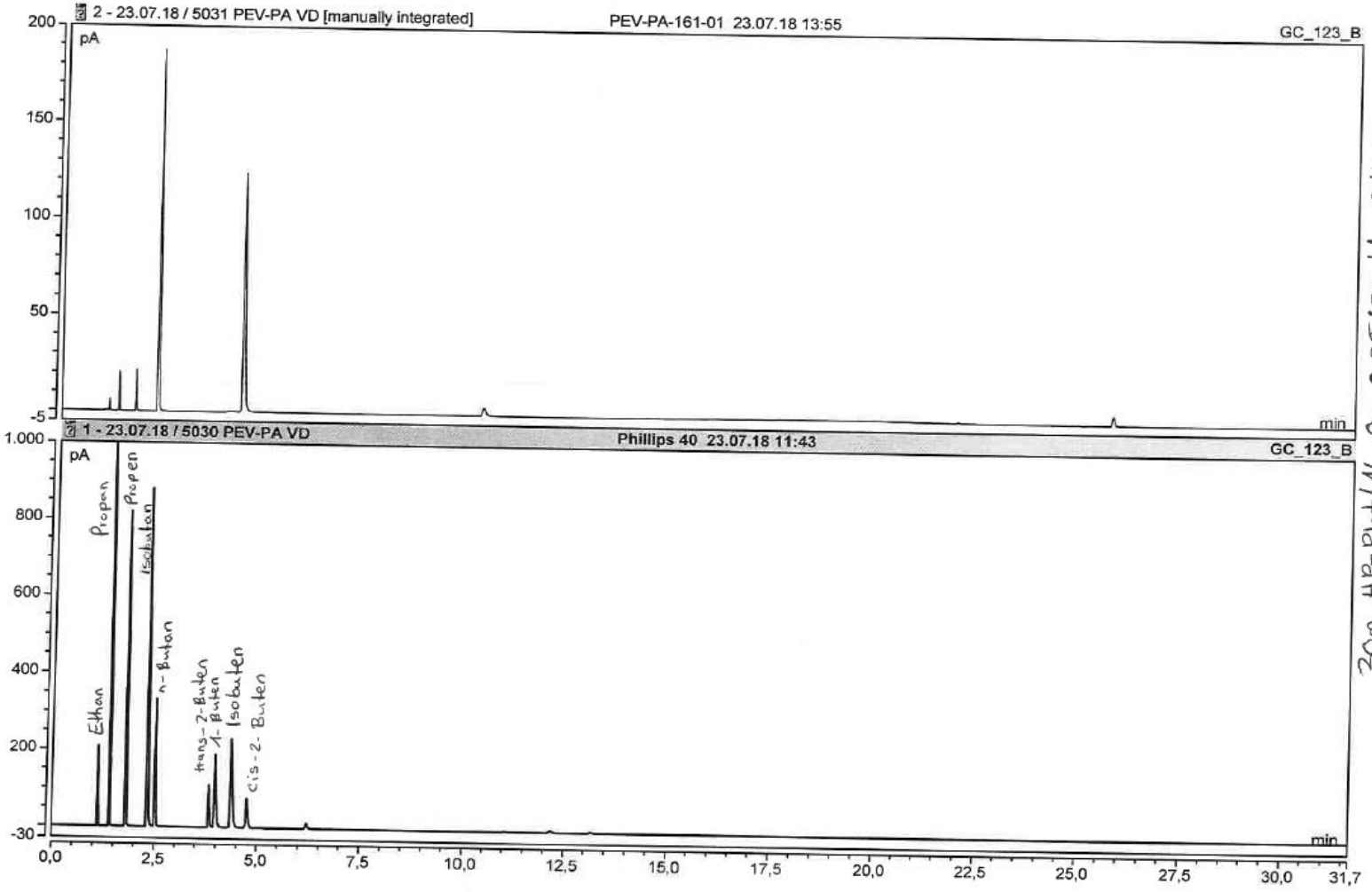
Instrument parameters:

Column:	30,0 m	HP-Plot/Al203 0,25/5,0df G/425
Temperature:	220/ 80, 10 min iso 6/min 180, 5 min iso/ 350	
Gas:	0,80 bar	H2
Sample size:	250,0 µL	

V. Diehl

Sequence: 5030 PEV-PA VD
Injection #3: Phillips 40

Chromatogram



30m HP-Plot/Al$_2$O$_3$ 0,25 15,0d4 G/425
220/80, 10min iso 6/min 180, 5min iso /350
0,8 bar H$_2$

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Version 7.2.5.9717, Thermo Fisher Scientific

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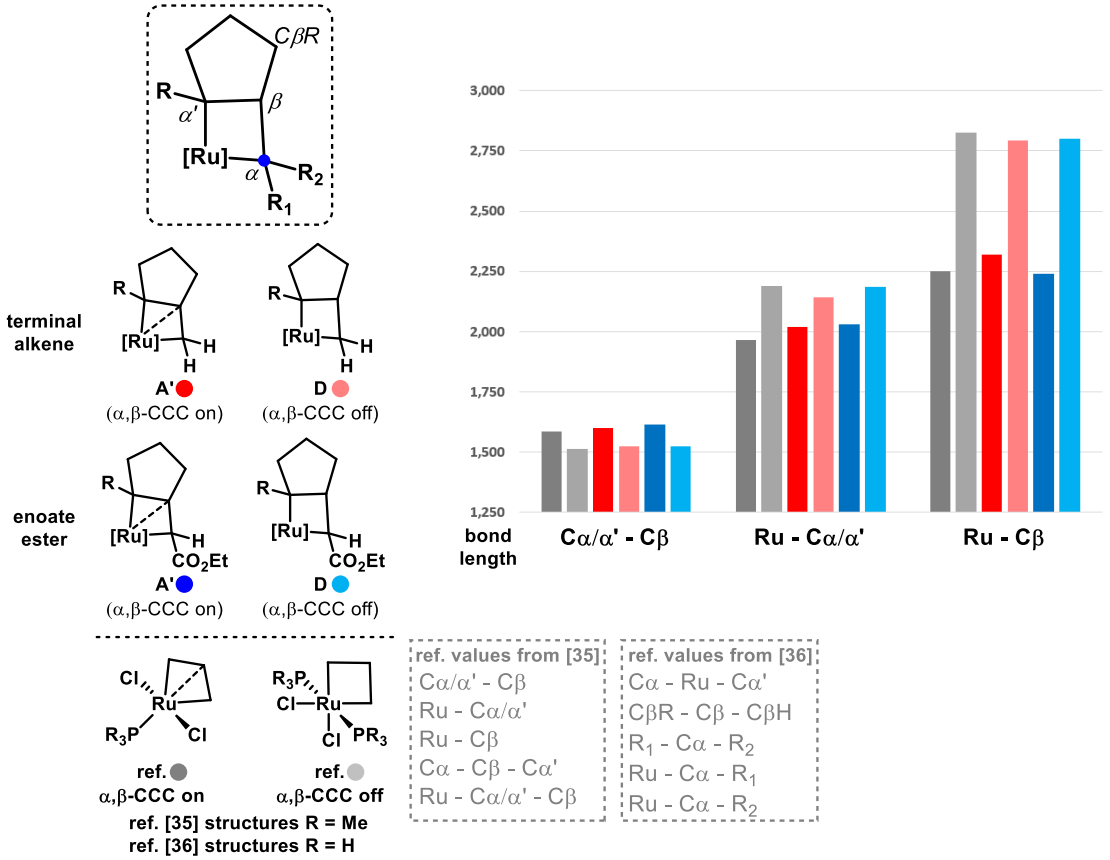
ANALYSIS OF RUTHENACYCLOBUTANES A' AND D



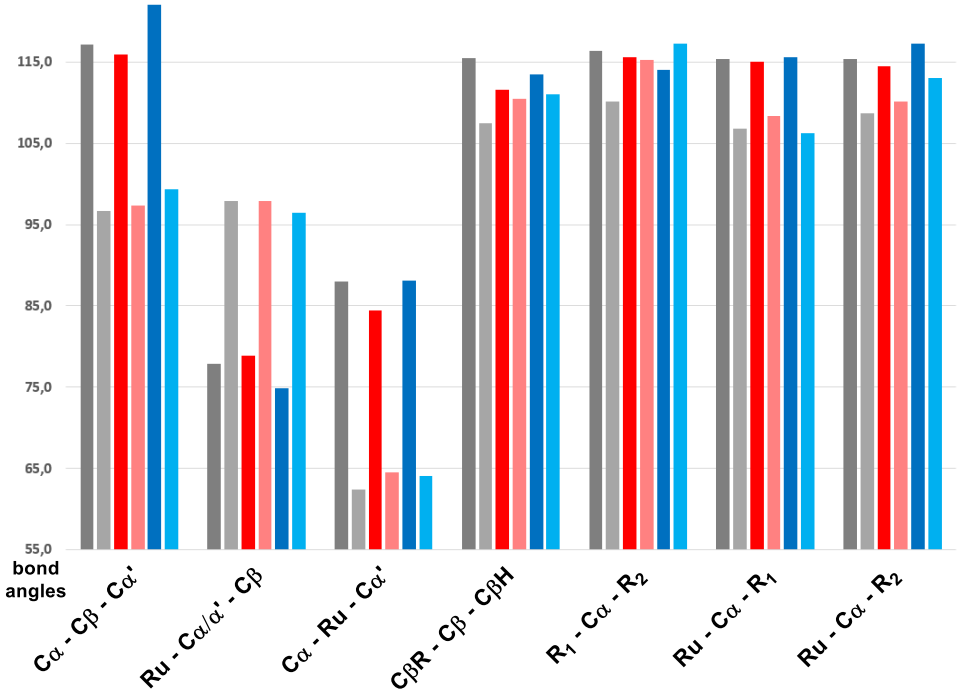


Figure S28. Comparison of the structural fingerprint of **A'** and **D** with reference compounds

To test the importance of the structurally different ruthenacyclobutanes (RCBs) the metric data of RCBs **A'** and **D** were compared to previously described complexes in which the agostic interaction was present or absent.[33][34] The reference structures correspond to active ("α,β-CCC on") and dormant ("α,β-CCC off") metathesis intermediates with the ligand set derived from 1st generation Grubbs catalysts (Figure S28). **A'** and **D** for the terminal alkene and enoate ester cases were evaluated to ensure uniform behavior. Figure S28 shows the comparison of a range of geometric descriptors (lengths and angles) extracted from these six structures. Despite being embedded in very different ligand environments (Grubbs vs. pianostool) the agreement is very good and hence a convincing assignment based on this fingerprint can be made.

Most notably, RCBs **A'** which are direct precursors for cycloreversion show the crucial agostic interaction manifested in short Ru-C_β contacts and wide C_α-C_β-$C_{\alpha'}$ angles. The $C_{\alpha/\alpha'}$-C_β bonds are weakend (lengthened) whereas the Ru-$C_{\alpha/\alpha'}$ bonds are short. The residual alkylidene character at C_α (represented by the α_{ene} angle, Figure S29), which becomes the secondary carbene after cycloreversion, is considerably higher in **A'** then in **D** (which is close to sp^3-hybridized).

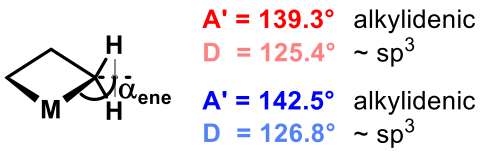


Figure S29. α_{ene} angles of RCBs **A'** and **D**

This analysis shows that the two distinct ruthenacycles **A'** and **D** fulfill the two very different requirements for cycloreversion and reductive elimination, respectively. In the case of **A'** the agostic interaction helps to weaken the C-C bond which is about to be broken in the cycloreversion, whereas reductive elimination is precluded by the strong Ru-C_β interaction. On the other hand, reductive elimination from **D** is facilitated by weaker Ru-$C_{\alpha/\alpha'}$ bonds and a narrow C_α-C_β-$C_{\alpha'}$ angle holding the two alkyl fragments closely together.

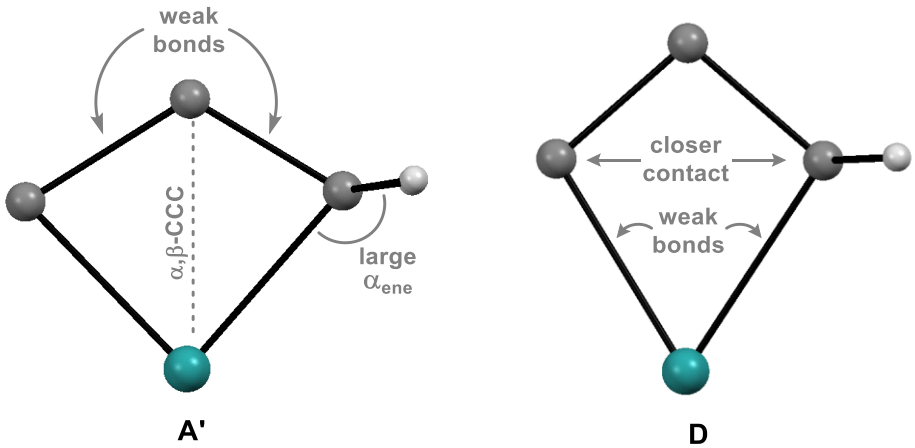


Figure S30. Summary and visual comparison of **A'** and **D** (excised from CCSD(T) structures)

The barrier height for cycloreversion (TS_{AB}) correlates to the stability of the secondary carbene complex (energies relative to initial carbene complex **A**) in that a more exergonic cycloreversion process exhibits a lower activation barrier (Bell-Evans-Polanyi principle, Figure S31).

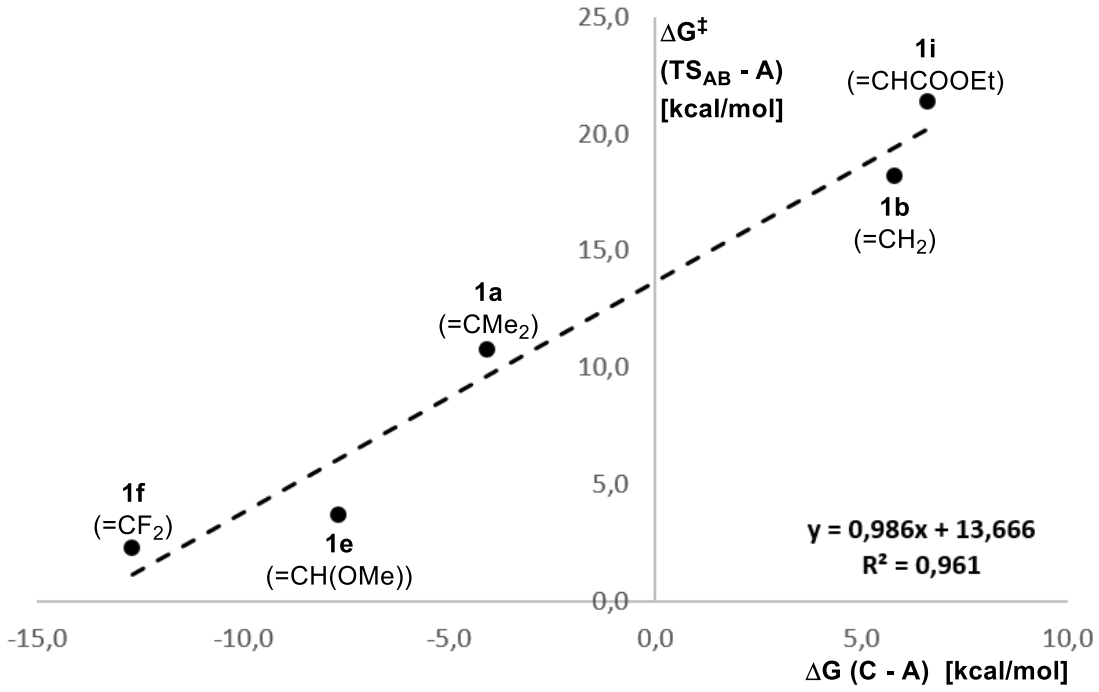


Figure S31. Correlation between thermodynamics and kinetics on the metathesis pathway

COMPUTATIONAL DETAILS

Unless otherwise specified, all calculations were carried out using a development version of the ORCA suite of programs based on version 4.2.[35] Analytical frequency calculations were done to characterize local minima (no imaginary frequencies) and transition states (TS's, one imaginary frequency) and to compute free energy corrections.

For all intermediates and transition states, a preliminary exploration of the conformational space was carried out using the semiempirical tight-binding based quantum chemistry method GFN2-xTB. For these calculations, the XTB code (version 6.1) was used (*Xtb, Version 6.1; University Bonn: 2019; please contact xtb@thch.uni-bonn.de for access to the program*). The low-energy conformers were further optimized at the B3LYP-D3 level [36,37] with the def2-TZVP(-f) basis sets.[38] For complex **41**, the structure obtained was found to be fully consistent with that experimentally found in the solid state by means of X-Ray spectroscopy (see Figure S37). For transition states, the conformers were generated using a series of constrained/unconstrained geometry optimizations at the B3LYP-D3/def2-TZVP(f) level, as detailed in Ref.[39]

Electronic energies were further refined by means of single point energy calculations at the DLPNO-CCSD(T)/TightPNO level.[40] For these calculations, the def2-TZVPP basis set was used in conjunction with its matching auxiliary /C counterpart. A solvation correction was computed in dichloromethane using the continuum solvation model C-PCM[41] at the same level of theory used for the geometry optimizations and added to the DLPNO-CCSD(T) electronic energy.

The data compiled in Table S9 confirm that SMD and C-PCM solvation schemes provide essentially the same results for all relevant stationary points found along the potential energy surface.

Table S9. The effect of different solvation schemes (C-PCM vs SMD) on the key free energy barriers determining the evolution of **A**.

	$\Delta G^{\neq}(TS_{AB})$		$\Delta G^{\neq}(TS_{AD})$	
	C-PCM	SMD	C-PCM	SMD
1b	17.8	18.1	15.9	15.3
1i	21.4	21.2	11.2	10.8
1a	10.8	10.8	21.6	21.3
1f	2.3	2.1	10.6	9.8
1e	3.7	3.9	15.5	15.3

In all cases, the RIJCOSX approximation was used to approximate the two-electron integrals in DFT calculations as well as for the reference part in DLPNO-CCSD(T) calculations. In all cases, the def2/J auxiliary basis set was used in conjunction with the large grid "GridX7".

INFLECTION POINTS

As discussed in the main manuscript, depending on the substitution pattern of the substrate and on the transition state conformer considered, the metallacycle **A'** is either a minimum or an "inflection point" on the B3LYP potential energy surface. In order to clarify this aspect, the minimum energy path (MEP) connecting **A** and **D** for substrate **1b** was computed (Figure S32). It was calculated using the Climbing Image Nudged Elastic Band (CI-NEB) method [42] at the B3LYP-D3 level of theory. In this case, a small def2-svp basis set was used in order to speed up the calculation.

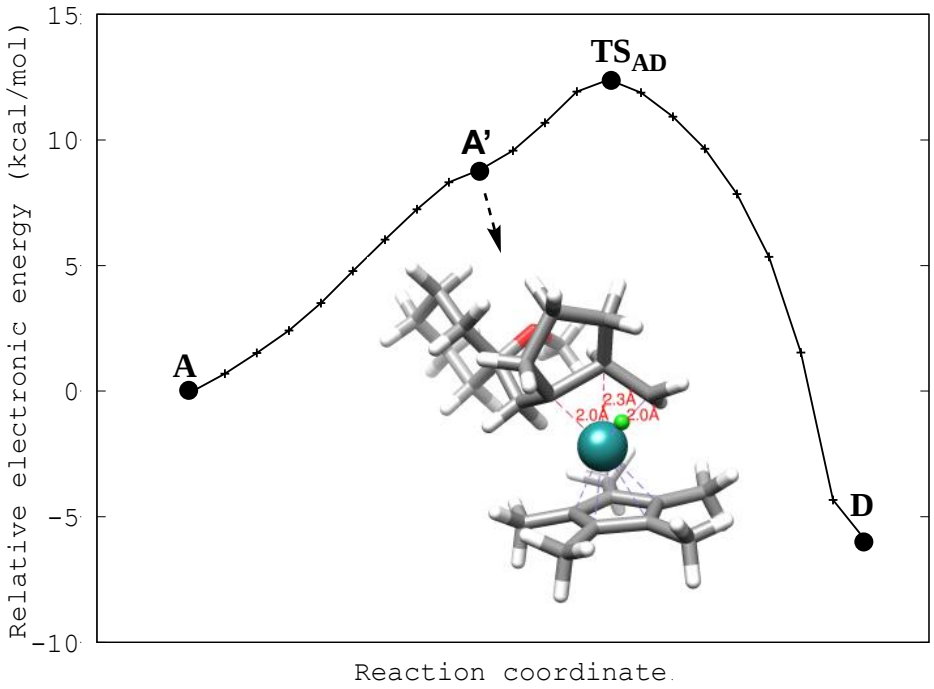


Figure S32. Minimum energy path for the first step of the cyclopropanation pathway for substrate **1b.**

From visual inspection of Figure S32, **A'** appears as an inflection point along the MEP. Its energy is ~3.5 kcal/mol below that of **TS$_{AD}$**. The full theoretical characterization of **A'** in these situations is beyond the scope of the present work. However, as **A'** is the bifurcation point between the metathesis and the cyclopropanation pathway, its structure is shown in all energy profiles, irrespective of whether it corresponds to a minimum or to an inflection point. In the latter case, the associated Chemdraw structure is shown in gray. For substrates **1a** and **1e**, the relative energy between **A'** and **TS$_{AD}$** was estimated from relaxed scans at the B3LYP-D3/def2-svp level of theory.

ENERGY PROFILES FOR ADDITIONAL SUBSTRATES

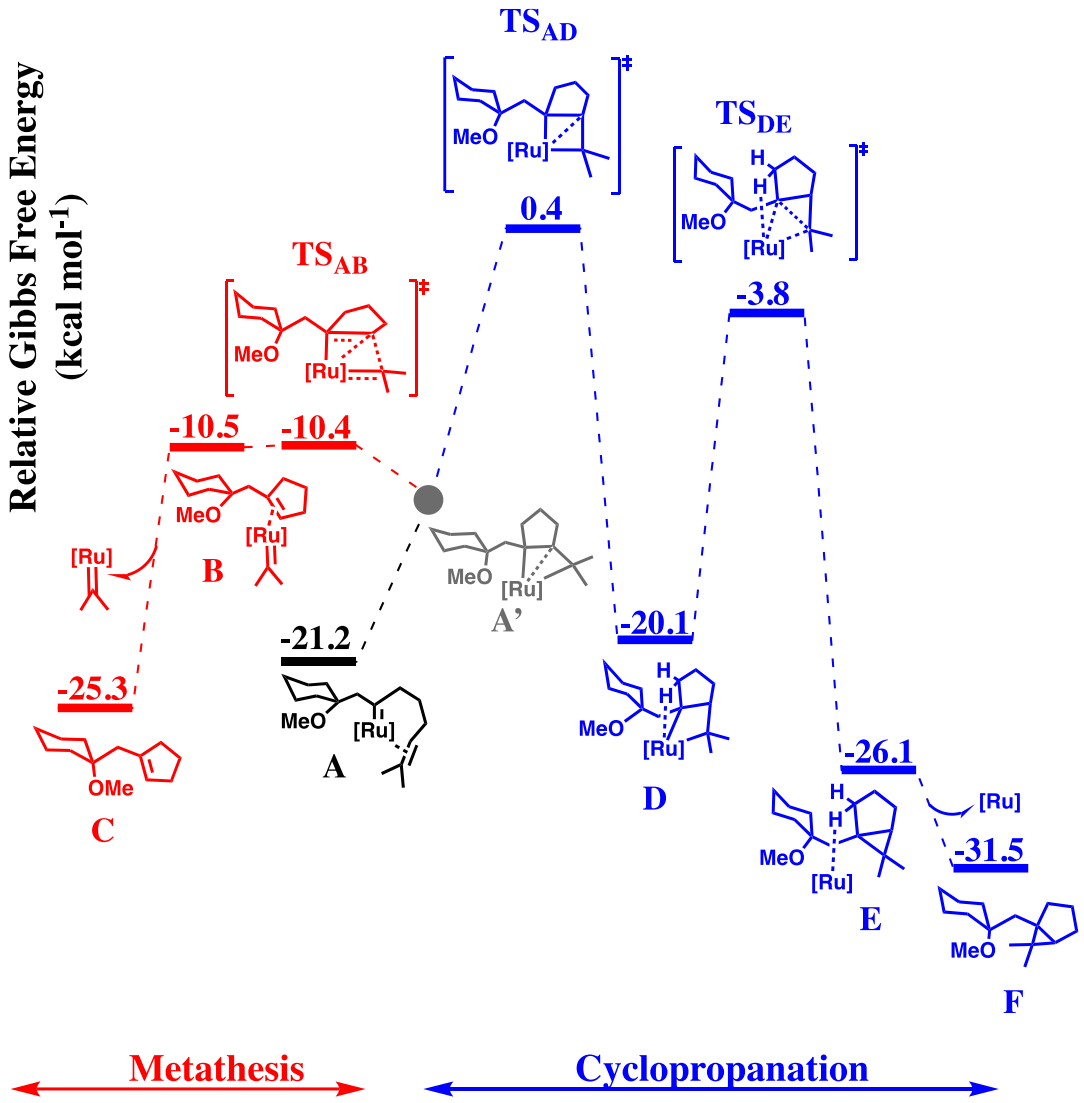


Figure S33. Metathesis versus cyclopropanation pathways for a carbene complex derived from enyne **1a**.

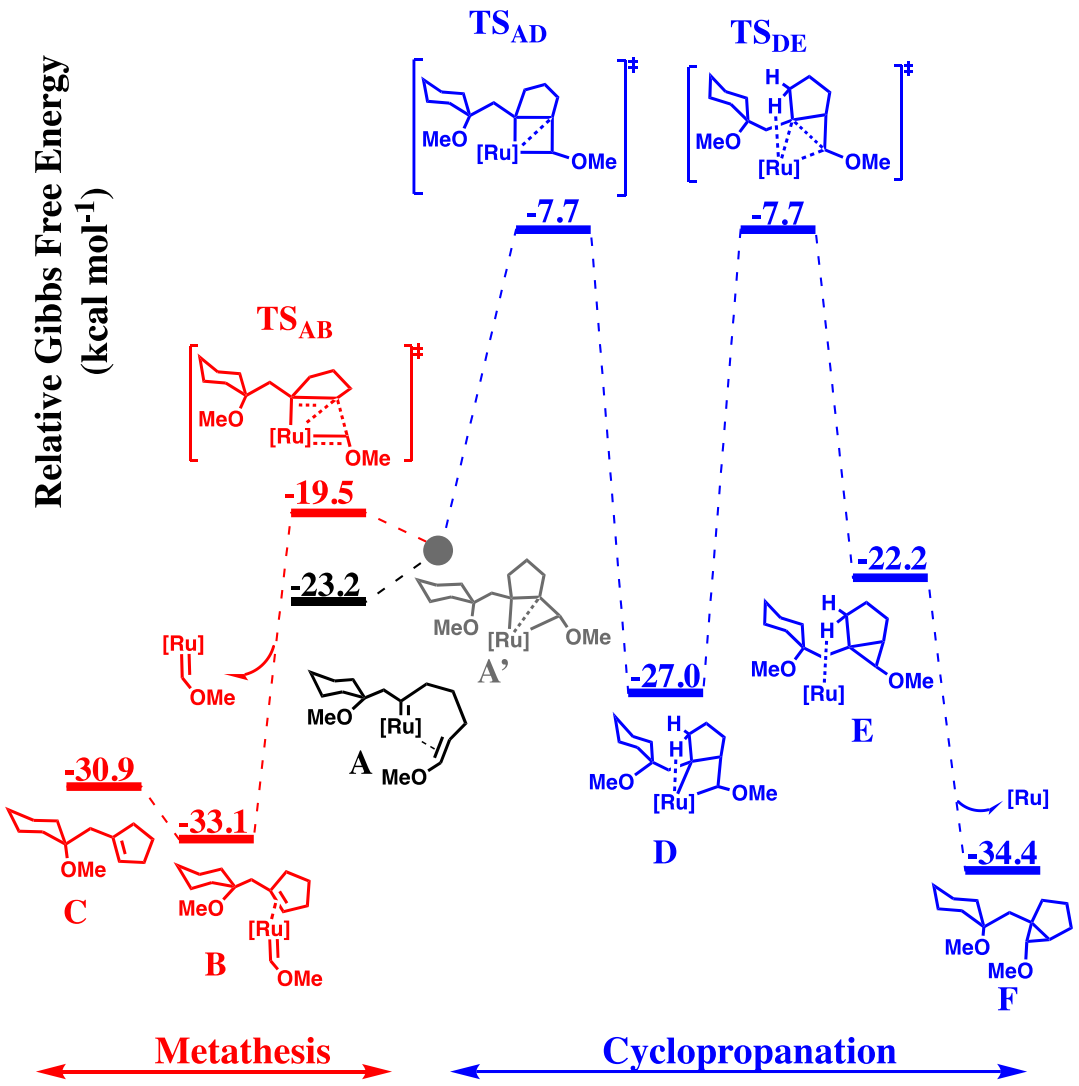


Figure S34. Metathesis versus cyclopropanation pathways for a carbene complex derived from enyne **1e**.

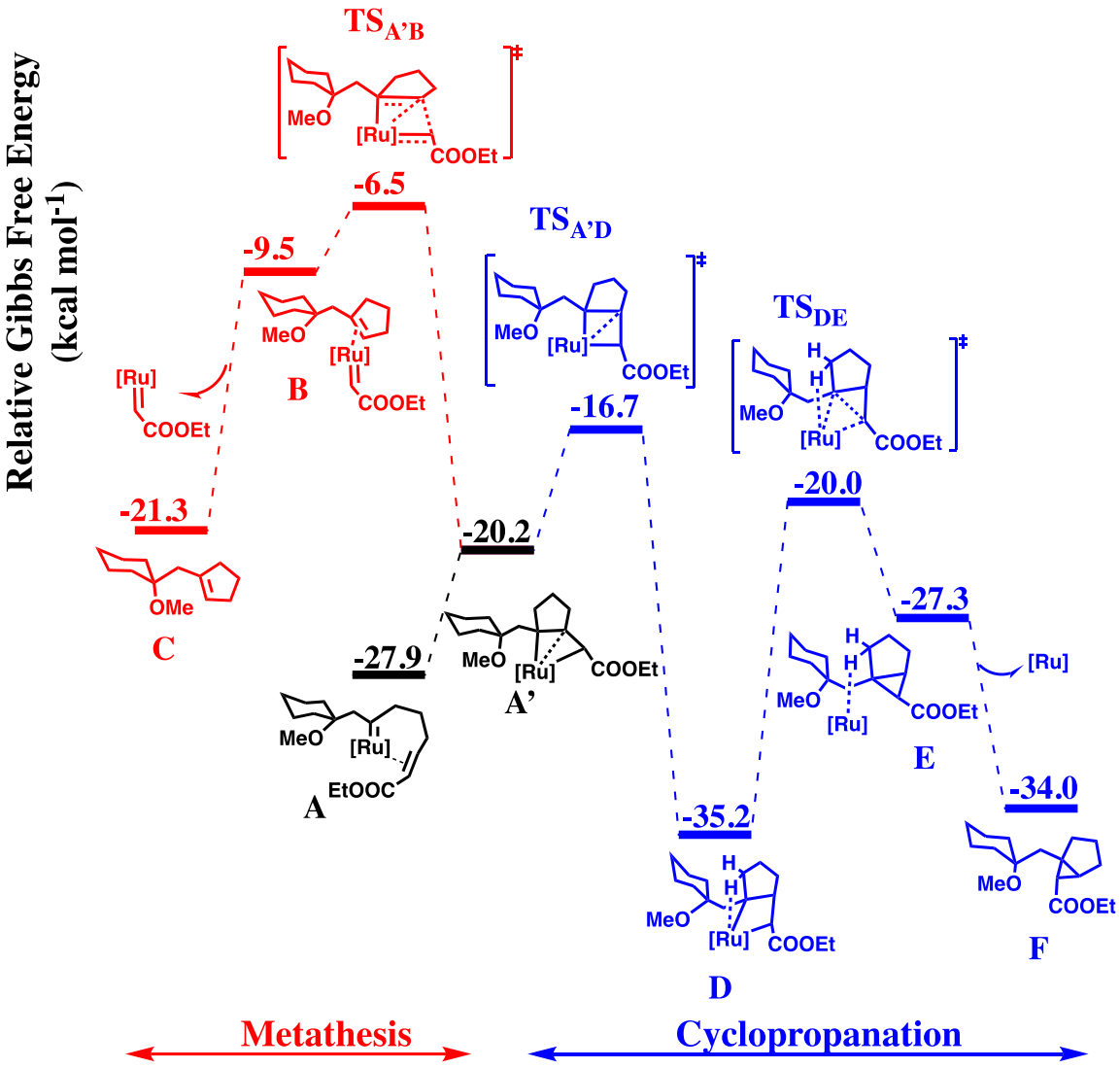


Figure S35. Metathesis versus cyclopropanation pathways for a carbene complex derived from enyne **1i**.

OUTER-SPHERE VERSUS INNER-SPHERE MECHANISM

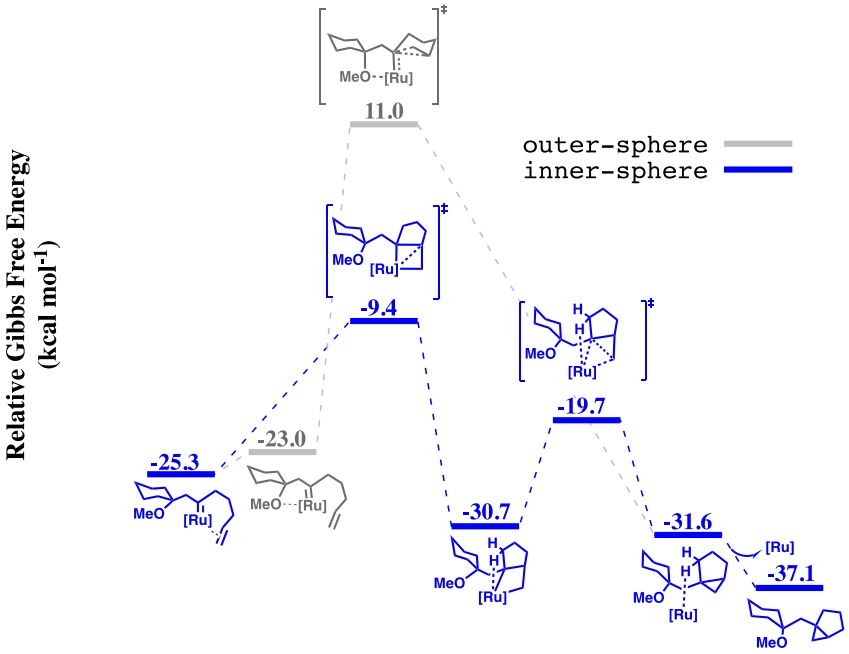


Figure S36. Outer-sphere vs inner-sphere cyclopropanation pathways for a carbene complex derived from enyne **1b**.

HYDROGENATIVE C–H FUNCTIONALIZATION OF COMPOUND 20a

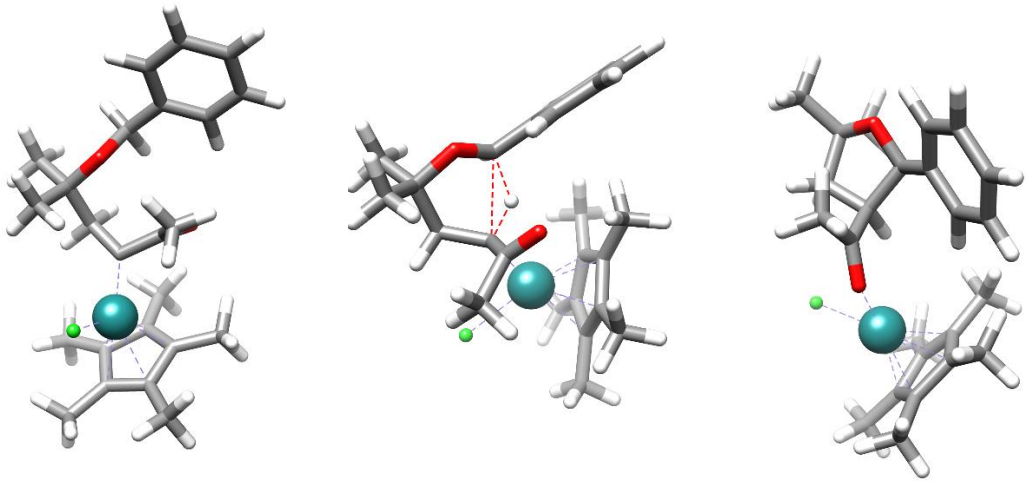


Figure S37. Left: Optimized structure for the carbene complex **G** proposed in Scheme 6 of the main manuscript. Centre: Optimized Transition state structure (**H**) for the corresponding C-H functinalization step. The associated free energy barrier was found to be 25.1 kcal/mol. Right: the resulting product in which compound **21** is coordinated to the Ru catalyst; its energy is with respect to the carbene complex **G** is –30.7 kcal/mol.

STRUCTURE OF COMPLEX 41

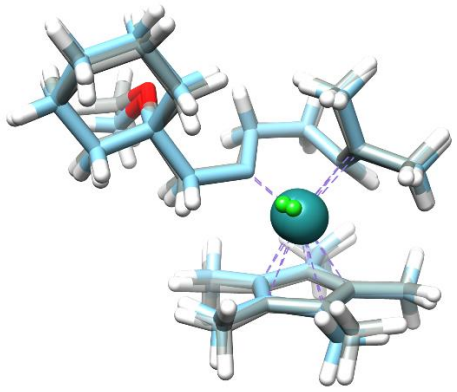


Figure S38. Superimposition of computed and experimental structures for complex **41**. The associated root mean square deviation (RMSD) is 0.33 Å

OPTIMIZED STRUCTURES OF INTERMEDIATES AND TRANSITION STATES IN XYZ FORMAT

Structures along the reaction profile for Substrate 1a

A

C	5.56911358233041	10.95202469369266	5.79762654199605
C	5.16745964886155	12.27179301896823	5.42179680042936
C	5.12780416668584	12.32205490368231	3.96935675904403
C	5.65365245378540	11.12516580506712	3.48501532234186
C	5.96247640420105	10.27180263121796	4.62907639276271
C	4.51965810013892	13.26697605609110	6.32827823943529
Ru	7.34282460808572	12.13135226277509	4.81789128941340
Cl	9.00333179913475	10.90797885943375	3.47827560827265
C	4.50131703937755	13.42368154974762	3.18165963062124
C	5.83760214389492	10.70946150133144	2.06493181227998
C	6.43069911196528	8.86058135844324	4.51247213186228
C	5.49663647619375	10.39761739054902	7.18165496072732
C	8.30894782501254	11.90491482502500	6.42545809551013

C	8.86719896244525	10.54189583907395	6.73318236887195
C	10.35768881911556	10.43833261708734	7.17052967353959
C	11.24574581547264	11.40121139734556	6.38207619875730
C	12.73671551881095	11.19663059682982	6.65348012940358
C	13.16331008305585	9.74901065569419	6.41186031242641
C	12.30337736783473	8.78677409180787	7.23226280693806
C	10.82127690557693	8.99271734020979	6.92388663016682
O	10.54126666864367	10.82742931012847	8.55122925673343
C	10.00995080444582	9.98488031517076	9.55034335702029
C	8.32850862975184	12.85044543376784	7.59221927295030
C	8.71392920054274	14.29577584166333	7.28145385161785
C	7.45771419199670	14.30987812395338	4.98924076395079
C	8.36462911511447	13.91839394808474	3.98420031050695
C	9.86042759838248	14.00817290245861	4.14837950480509
C	7.96137424891714	14.06244937765440	2.53041513547441
H	8.98479946459906	12.46690072946097	8.37467368529581
H	7.31120301731918	12.84168469280269	8.00792628004788
H	9.74113070012747	14.32238529006714	6.92109512874496
H	8.71329658555515	14.85927446497653	8.21853457603688
H	8.37121245675822	13.24723523728170	1.93325111798206
H	8.36549285513521	15.00165865063748	2.13260713322450
H	6.88298251305482	14.08567936334011	2.39764684403879
H	10.35757621928168	13.34369615603411	3.44357071988064
H	10.20173459362063	13.74529922116249	5.14076967753687
H	10.18448816543621	15.03431920199937	3.93434762477967
H	8.74503482971747	9.89835594197726	5.86892077364422
H	8.26368124517650	10.11701770621434	7.54372657390674
H	10.96492103894471	12.42101229505051	6.64533689014674
H	11.02305891241991	11.26804649860574	5.32204865816841
H	13.31371234868748	11.87230939394697	6.01695107251476
H	12.95462085771275	11.46934991001332	7.68923828865188
H	13.05306327033219	9.50983774302501	5.34831223305243
H	14.22024322367698	9.61828936989940	6.65803202633009
H	12.49027314684565	8.95399386184215	8.29703887795218
H	12.57989477995528	7.75067416325429	7.02052425839629
H	10.19894902140996	8.29503315994193	7.49037950407832
H	10.64103297454411	8.77683197112421	5.86805534384823
H	8.93595796969163	9.80485205093878	9.42380194502415
H	10.16095387552008	10.50061084689402	10.49820841713839
H	10.51921646540477	9.01747778757544	9.59460829516863

H	4.64241570509992	14.28517574015524	5.96166500725450
H	4.93507770109682	13.22373346431589	7.33438034777498
H	3.44417681387880	13.07513798805875	6.40716682639638
H	5.67598289009281	11.54065400080427	1.38025013991140
H	5.13506066559592	9.91325299663940	1.80114157350132
H	6.84998688082488	10.33523375928221	1.90622487203374
H	5.64186971507676	8.22893393210760	4.09283077811366
H	6.70850959352395	8.44748201307605	5.48099363740944
H	7.30008173760240	8.79910834139543	3.85718298423773
H	4.45971530599834	10.14712616119952	7.42469572103987
H	5.83917264801504	11.11174037772336	7.93026983244174
H	6.08636777939526	9.48945365740435	7.28495784692402
C	7.77152984404811	14.98727012801695	6.30381436981336
H	4.73105801693579	13.34226287542706	2.12100557917014
H	4.81646736472272	14.41206030879387	3.51816384350673
H	3.41280844406875	13.38463218681979	3.28833563775573
H	6.82079452871228	15.15058991544450	6.81956402922133
H	8.16582566438894	15.98842492053570	6.08567227984723
H	6.50165088022025	14.65116887777835	4.60962559019740

TS_{AB}

C	-0.44762419890621	-2.70535634034037	1.23908455439385
C	-1.10803405818582	-3.14287069553608	-0.08416424822908
C	-0.81921993654800	-2.01417160850887	-1.09058203644919
C	-0.61438824992369	-0.76327318439114	-0.23112213672284
C	-0.34347308646896	-1.18157181916830	1.15895408405554
Ru	1.39903640571622	-0.15134290537771	0.14603198351660
C	1.27785874144873	-0.55761297248986	2.05821596723767
C	-1.57316253409076	0.40080369021009	-0.40825324367202
C	-3.10132495203970	0.18117875481221	-0.23931938123735
C	-3.77969048831425	1.56298756701015	-0.33055142122209
C	-5.29397322849532	1.49439736621138	-0.13879089878826
C	-5.64547850540269	0.83648379914747	1.19570742241771
C	-4.99057834171176	-0.53914722310216	1.31312428912260
C	-3.47776521374775	-0.46687531713214	1.09627499291828
O	-3.63648639839594	-0.72081667894458	-1.22925114651904
C	-3.60533494098252	-0.30889259917421	-2.58000969416418
C	1.35351926538818	2.13689660871636	-0.32585354005291
C	2.56158856326464	1.77988114552602	0.34384378432016
C	3.26593713031195	0.83732233612318	-0.46516553004446

C	2.51359886712924	0.67500254591814	-1.69158632145283
C	1.36563766976210	1.47727458441038	-1.60878233289852
C	0.42864128261231	3.23455083346730	0.09185500662493
C	3.09245551195533	2.41865892314119	1.58506279915203
C	4.62421834546112	0.27104553689068	-0.21155969062723
C	2.94881282114056	-0.13320306661250	-2.86726866821392
C	0.41672812204939	1.71098491355270	-2.74112979548673
Cl	2.34895460747600	-2.36336210715671	-0.36943474538516
H	0.07876295752923	-2.23859251243719	-1.66046597835633
H	-1.64623216433698	-1.88350161553126	-1.78162578508175
H	-0.72295846459158	-4.10474470020883	-0.42387582593334
H	-2.18752729477740	-3.24483075381400	0.04613950019161
H	-1.43529634299618	0.83714317502499	-1.39311002646135
H	-1.30202179397530	1.17588315010473	0.30707708181675
H	-3.52888890387170	2.04016114053684	-1.28104748620756
H	-3.34646906760634	2.19600514139542	0.44949100581586
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H	-5.74167350814404	0.91762030438640	-0.95249820650661
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H	-6.72969129373920	0.75169458622605	1.30357369929986
H	-5.42146249383924	-1.21240645774351	0.56891043364614
H	-5.19542407637582	-0.97452970497811	2.29456084802759
H	-3.05095718798955	-1.46732866964428	1.14251393075416
H	-3.02252153813194	0.11918286451930	1.90066749720542
H	-2.59471684298439	-0.06572813861971	-2.92339584626076
H	-4.25446677953298	0.55169124353729	-2.76935992618136
H	-3.97119440003833	-1.15280689074803	-3.16368881493805
H	3.74643467942727	3.25404215486653	1.31603352022859
H	3.68227835736083	1.72226289388730	2.17974272035614
H	2.29821257876568	2.81658269970885	2.21337796967712
H	2.11733194618552	-0.32829635025253	-3.54376251498658
H	3.35001400518318	-1.09414329783580	-2.54974316334765
H	3.72317357940981	0.39853124040830	-3.42975455735746
H	0.05355309722866	0.77767692657316	-3.17238687520330
H	0.92521622232377	2.26032211995713	-3.53861417075274
H	-0.44287613761028	2.30530828381688	-2.43944177376267
H	-0.54479863731645	3.14950447878745	-0.38746301102569
H	0.83988392672467	4.21366777499442	-0.17584246241483
H	0.26630545767305	3.23715116749739	1.17032042449979
H	-1.03955721412840	-2.98804136440777	2.11206513179100

H	0.52593331729486	-3.17062856583267	1.33374648213531
H	4.87312162012551	0.29906428910507	0.84898943177438
H	5.38910981356462	0.83950788438603	-0.75102862227423
H	4.67395922319502	-0.76786748492834	-0.53349553087642
C	1.93848974726293	-1.69244034945332	2.78810117828710
H	-0.92663309461946	-0.63051153488160	1.88353446995935
C	0.83970270441442	0.51317406562233	3.03447913702776
H	2.82352593800727	-1.26944759622219	3.27662102144306
H	1.30359815010183	-2.09519768830608	3.58469018274701
H	2.27335357948470	-2.48603592924073	2.13078630214339
H	0.23956627186888	0.09034530084270	3.84732604665082
H	1.72400595880978	0.95206533545012	3.50055369792907
H	0.27036720243731	1.30895699531314	2.55730183288098

B

C	-0.34713512058428	-2.87329252936159	-0.44324034371648
C	-0.36612274264116	-2.24068491816468	-1.84054147396450
C	-1.14358730758794	-0.93147463167864	-1.63668136540122
C	-0.89680637361003	-0.55104259004650	-0.18206501347398
C	-0.40564908551604	-1.68123097490567	0.47787977745978
Ru	1.33978665658549	-0.25841059695401	0.35601264510516
C	0.91999755284050	0.30613531435996	2.10097301964815
C	-1.74441139695917	0.51211967584646	0.47108345958504
C	-3.27910794679359	0.31518656641745	0.42979353869816
C	-3.92856002841738	1.39371379153139	1.31670794806182
C	-5.44638095531142	1.24290616502942	1.40338565952883
C	-5.82761705848189	-0.14706200367868	1.91562373735674
C	-5.19502282351212	-1.24220686207335	1.05636920358479
C	-3.67913180210934	-1.07067083762797	0.94553493645426
O	-3.81600814209113	0.36623456815983	-0.90857888476162
C	-3.65722828037646	1.56539771813585	-1.63496410485245
C	1.59248343478637	1.54434093745911	-1.12513209673621
C	2.60591026914713	1.59290381416259	-0.13177429135029
C	3.38834193347246	0.41135055829604	-0.26349096377989
C	2.98042568897064	-0.26058055444732	-1.49157183456764
C	1.91770471234193	0.44793823048863	-2.03092426932418
C	0.61799339382820	2.63419317261564	-1.43470354012333
C	2.97680076598924	2.76248863993502	0.72017661905859
C	4.64231202285559	0.10391232734657	0.48597413675452
C	3.65588182687257	-1.46357668353824	-2.05551340701403

C	1.35335074736730	0.28100483894796	-3.40512301128885
Cl	2.45522226776732	-2.28688461321968	1.15215909997632
H	-0.90195314743143	-0.15139025144962	-2.35236189455178
H	-2.21635520680334	-1.11264694184819	-1.73796544472131
H	0.65875284828863	-2.04015074533550	-2.14666541732657
H	-0.82003716486587	-2.88217908112023	-2.59615829457418
H	-1.51087441238371	1.49809661922480	0.06600467678732
H	-1.48589138425526	0.55977391011681	1.52559618218702
H	-3.65376673764578	2.38910629152293	0.95927177851444
H	-3.49867128553199	1.30304037390781	2.31861960159136
H	-5.85702134400647	2.01652255615747	2.05729354445987
H	-5.88574567372559	1.39633470299430	0.41397440190261
H	-5.48446002831248	-0.25372149792636	2.95159969740372
H	-6.91455975631145	-0.25968741002521	1.93283596237230
H	-5.62834098031946	-1.21224345295760	0.05409562650825
H	-5.42037004605828	-2.22740012977495	1.47239168128697
H	-3.26100546632181	-1.83222420827145	0.28699301875598
H	-3.21659889318234	-1.21270125533985	1.92682797918381
H	-2.60579953749795	1.83907495087149	-1.76618457092818
H	-4.18102776057797	2.40839967019774	-1.17276951881528
H	-4.09113561414661	1.38656066235395	-2.61809387558092
H	3.78875022375843	3.30926689101420	0.23032332548848
H	3.33675545006850	2.46095162323821	1.70197795849841
H	2.15436636832326	3.46045869299343	0.85641069087249
H	3.11058968462078	-1.86557020709976	-2.90895275229059
H	3.73274013499167	-2.24497118489725	-1.29732537264631
H	4.66913861452451	-1.22038782313227	-2.39004651153747
H	1.18646020314284	-0.75978974512983	-3.67635520229455
H	2.06097575640069	0.69498304376597	-4.13038020568778
H	0.41770215168060	0.81976095442842	-3.53489408637479
H	-0.29090119326582	2.24025218614387	-1.88852511065459
H	1.04429395055209	3.35973017998076	-2.13574473317329
H	0.32729192081341	3.17959861683759	-0.53720119867549
H	-1.25226785733003	-3.47273292905849	-0.27904768849827
H	0.51278221659215	-3.51427703274476	-0.26258256634164
H	4.64097064980661	0.57244570779203	1.46935230005531
H	5.51383730144183	0.47410316934388	-0.06446367947523
H	4.75332147608267	-0.96819820807075	0.63376870735278
C	0.77217853962133	-0.58597326828794	3.30029122738882
H	-0.55175999188658	-1.84694512598175	1.53398188976039

C	0.64521601945992	1.73483140450743	2.48651997465343
H	1.27680428245038	-0.14463832590804	4.16782174426994
H	-0.29218141434333	-0.63501727853693	3.56829978317196
H	1.14412887579125	-1.59099004072239	3.13718224496538
H	-0.23351722213759	1.77721392294447	3.13914025127161
H	1.47542357834035	2.13043186899482	3.08069228846220
H	0.47385666275662	2.39206362125112	1.64110040606586

C (secondary carbene)

C	5.84056000000000	10.79262200000000	5.27629100000000
C	5.16364200000000	11.94161400000000	4.67590600000000
C	5.45125800000000	11.92958500000000	3.27480900000000
C	6.42032300000000	10.89193600000000	3.05300000000000
C	6.56348900000000	10.13381700000000	4.28173200000000
C	4.16395600000000	12.80293500000000	5.37300600000000
Ru	7.25163600000000	12.36550800000000	4.39444000000000
Cl	9.40530800000000	11.92146700000000	5.19674000000000
C	4.81318200000000	12.77613000000000	2.22492600000000
C	7.00643500000000	10.49793200000000	1.74017600000000
C	7.48164000000000	8.96773200000000	4.43971600000000
C	5.76672700000000	10.44556000000000	6.72486100000000
C	7.38842100000000	14.17424000000000	3.92088600000000
C	7.61036300000000	14.72862800000000	2.55299400000000
C	7.23200500000000	15.22198600000000	4.98456800000000
H	6.47684600000000	15.96625900000000	4.70138300000000
H	8.18364600000000	15.75787800000000	5.09100900000000
H	6.97805400000000	14.80976600000000	5.96009300000000
H	7.62413100000000	13.96235900000000	1.78128400000000
H	8.58591500000000	15.23060200000000	2.53983200000000
H	6.86480400000000	15.49292100000000	2.29753400000000
H	4.04049900000000	13.75664600000000	4.86104800000000
H	4.47042900000000	13.01292200000000	6.39779400000000
H	3.18454600000000	12.31462200000000	5.41364300000000
H	7.06967600000000	11.34743400000000	1.06159500000000
H	6.39035300000000	9.72990400000000	1.25977600000000
H	8.00923100000000	10.09242300000000	1.86734500000000
H	7.19115900000000	8.15404100000000	3.77024400000000
H	7.46684100000000	8.58576400000000	5.45849900000000
H	8.51158900000000	9.24816900000000	4.21083700000000
H	4.82001100000000	9.94789300000000	6.95652900000000

H	5.82793200000000	11.34181600000000	7.34286300000000
H	6.58018200000000	9.78591900000000	7.01931700000000
H	5.48592000000000	12.95427400000000	1.38732400000000
H	4.51059600000000	13.74488600000000	2.62091000000000
H	3.91984500000000	12.28208700000000	1.83067300000000

TS_{AD}

C	3.91999957714485	0.75581646554822	-0.62674279944961
C	3.20517669490933	0.67027996715275	-1.82354179535478
C	1.88982939013445	1.26687402666238	-1.61825977785307
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H	9.26931930679646	9.68831550615221	4.33940904896551
H	10.23563805095881	10.94944984358666	3.62949378966297
H	8.26675461359277	9.52240995944271	6.81242004145246

H	9.31543828121766	8.59134338431886	7.89438368815849
H	9.37067417418147	8.30796573017368	6.14344421058588
H	5.00146605943213	12.65039627783689	1.55426220597041
H	4.65696733698199	13.86723755702540	2.76973202444211
H	3.39334869873236	12.72721846891890	2.29086396149432
H	6.77831150457732	8.23247445388166	4.16752521807075
H	5.19255047810548	7.89615768880609	4.86073557029560
H	6.50900049705680	8.44741492826134	5.89401513054288
H	4.43552882669111	10.52986534354631	7.54756607187572
H	5.73630224824639	11.71746972697545	7.62471021402478
H	6.11433528201650	10.01325378322958	7.41708523543097
H	3.38647311660520	13.40949000829546	5.78266029714699
H	4.69727795453210	14.28852003115927	4.99253528680048
H	4.95068274298774	13.57241641719920	6.58135920210725
C	7.40220263685610	14.17175101741783	8.36786471798702
H	6.31398666458788	9.10869121209490	2.09093219370170
H	5.71463472116496	10.53534636174386	1.25311913168911
H	4.58037027518024	9.30069028859620	1.81598523864939
H	6.34457625043256	13.96776171977361	8.18725787621024
H	7.45074520521413	15.16785021021558	8.81483516166505
H	7.62790921530692	14.35570022209389	6.15234206138626

F (cyclopropanation product)

C	9.06801089929163	12.89569950349947	7.06200496325230
C	9.07822690464171	11.94748547106910	5.87968403898728
C	10.24617547252105	10.94402963992814	5.78678089080748
C	11.60496646166433	11.63677712451168	5.92832521645196
C	12.77999257246899	10.67745504276137	5.73586679772031
C	12.69685092677459	9.95334012839137	4.39197344320849
C	11.35183753046525	9.24220733535271	4.23553618464377
C	10.18931016807197	10.21512571036104	4.43310443265414
O	10.21875902051791	10.00430612017139	6.88602188015888
C	9.18343366941225	9.04618387204165	6.90878173025994
C	8.96238548237216	12.25327633459813	8.44886685890750
C	8.12870214353017	13.19140961362001	9.35293862500813
C	8.17918822135221	14.12563195585089	7.09012339045782
C	9.67951064544571	14.29289741973073	6.99004299265147
C	10.52199520214037	14.84862238071159	8.11985558475334
C	10.16415480245585	14.83188503894220	5.65595792604983
H	9.93716968646694	12.02252627162895	8.88064736892037

H	8.45209250008167	11.29755211732532	8.33666490790133
H	8.75547707847032	13.68504970082784	10.09433188600943
H	7.38171856404189	12.62924376806633	9.91529825044485
H	11.20501238973796	14.55994824270632	5.46813806815628
H	10.10766491491102	15.92418234973242	5.66511576476254
H	9.56679052693725	14.48531717070410	4.81423467165447
H	11.57835978182774	14.63754420136378	7.93113823837470
H	10.27994887893724	14.43871123242318	9.09497112043940
H	10.41360015328364	15.93540582370653	8.17864939041708
H	9.06890755117139	12.51458072689108	4.94930876223549
H	8.14015654262990	11.38276941552388	5.88168709160825
H	11.65845787340511	12.11381758614203	6.90737344655910
H	11.65756127064409	12.43089446109688	5.18003818827493
H	13.71910656719402	11.23226853130213	5.80929950580412
H	12.77750852359586	9.94438372602875	6.54559893422076
H	12.81507434397094	10.68046422631250	3.57962907272911
H	13.51724325468340	9.23775517647753	4.29380162185472
H	11.28599413927821	8.43597164369921	4.97110756073809
H	11.27840065417367	8.77689227193781	3.24910196541894
H	9.22955406386532	9.70454150191676	4.32126334024999
H	10.21994239126462	10.97636859593364	3.64781322245807
H	8.18688419047378	9.49526455994942	6.84221362708275
H	9.26361819252948	8.53253036733246	7.86654059092679
H	9.28137795301564	8.30514755503063	6.10861683384653
C	7.46266077551893	14.22933432989630	8.42041170658316
H	6.40641533342698	13.99167666103380	8.27144890674913
H	7.50020333555419	15.23698512610352	8.84263579485737
H	7.61753844578246	14.39802996736518	6.20329520474948

Structures along the reaction profile for Substrate 1b

A

C	5.51063356233800	10.97201775108864	5.79656156999132
C	5.14637112394931	12.28366896198720	5.35354290602085
C	5.21190973073257	12.29292758492632	3.89896730958321
C	5.73220860142848	11.06726187482305	3.48916401135855
C	5.95860590408816	10.24631407025859	4.67521070546861
C	4.45190941914580	13.30738241090007	6.19055107810845
Ru	7.34529587101204	12.08565729484037	4.91220799765479
Cl	9.03973904335932	10.89276563411425	3.59267889944834

C	4.73777460422535	13.40338703326398	3.02044126460325
C	5.98512816402160	10.59909548168446	2.09715107790149
C	6.41460612873246	8.82695965877849	4.62934826358808
C	5.37461832089939	10.47125762970272	7.19642810923597
C	8.28929700402647	11.86270525883844	6.53414541974886
C	8.82485141250684	10.49862449705983	6.86348115234904
C	10.34446179410290	10.40573517466880	7.21212308485581
C	11.18423370948964	11.39188507514088	6.39504885900665
C	12.68771565021152	11.20054569633320	6.60106458090188
C	13.11865072387193	9.76287739783018	6.31215893198540
C	12.30686683446436	8.77456267770443	7.15032157367192
C	10.80978662151010	8.97053043731572	6.91612410111810
O	10.59425887415759	10.77465071957893	8.58796484206141
C	10.12966165544757	9.90841150617161	9.59991637480768
C	8.40791339996585	12.84191454049443	7.66555722795027
C	8.75882605947358	14.27487700769675	7.26943767612362
C	7.43725446014968	14.28392442829455	5.08114093727321
C	8.42591523014863	13.82511187036844	4.20259302910273
H	9.12992952427564	12.47647133400698	8.39770515522570
H	7.43360903546869	12.84290395290547	8.17662228831847
H	9.71665604925190	14.28063057569128	6.74432477693066
H	8.90690892573975	14.86196391925440	8.17916196789572
H	8.64111405627796	9.82247075913202	6.03594299983618
H	8.26948592053408	10.11684835031387	7.72872925752834
H	10.90412083985737	12.40817795189080	6.67351961596807
H	10.92088421180802	11.26187268645996	5.34466762426733
H	13.22934594966367	11.89404081321905	5.95269889248471
H	12.94809552467386	11.45655888308842	7.63132218030165
H	12.96331669132812	9.54381531485862	5.25001711967265
H	14.18685254485048	9.63920771196462	6.50857315284591
H	12.54194837744569	8.92081890870580	8.20864310728985
H	12.58291484403033	7.74607876500545	6.90349982996644
H	10.22195167486239	8.25530844455933	7.49759767874553
H	10.58128483761666	8.77505823895838	5.86572993029939
H	9.05251776588295	9.71628149229698	9.53001661187915
H	10.32682808057188	10.40996233955938	10.54688059907370
H	10.65211016179401	8.94715121368913	9.59842010374084
H	4.59290140670522	14.31436322508234	5.80087831389169
H	4.81203723468849	13.29488399009358	7.21864413431815
H	3.37417492993035	13.11478973216849	6.21573012441763

H	5.86419746904694	11.40445848104787	1.37441681246199
H	5.28555906457338	9.80078255657660	1.83143956882373
H	6.99935869262453	10.20911026506152	2.00305657534049
H	5.65254228351680	8.19314469749741	4.16604833444468
H	6.61119905842082	8.43517353413260	5.62621316918283
H	7.32983066117477	8.73832418829794	4.04215960069047
H	4.33584268357684	10.19086776565326	7.39455000591588
H	5.65161310739301	11.22981696239636	7.92832188536676
H	5.99200568551942	9.59264485222727	7.37118796140332
C	7.68665387514864	14.93058266125828	6.41709539448139
H	6.75026352460200	14.95358613773374	6.98273908116780
H	7.95529337350689	15.97962531687191	6.23887194381649
H	5.22052492352253	13.37615871650180	2.04452930213664
H	4.92718318026043	14.38380747024582	3.45692002520991
H	3.65771114883077	13.33119284080788	2.85913155441912
H	9.46549561874403	13.77964811282410	4.49447956252692
H	6.52728057954659	14.64269498437077	4.61761863270131
H	8.26328257927374	13.87214017972463	3.13306414109225

TS_{AB}

C	1.59683971374018	-1.42587516128003	1.42829522843098
C	1.48857640064423	-2.02847278599615	0.11712057228874
C	2.62637006251172	-1.62114371779822	-0.63780120113315
C	3.38429869144173	-0.70059304243596	0.16082509429742
C	2.73735809927640	-0.61593320126698	1.45528412738828
C	0.57913919636013	-3.15471340416298	-0.26123133254419
Ru	1.48403094638144	0.24624155522106	-0.32155290249093
Cl	2.38527968299577	2.46854780008284	0.10583625577635
C	3.01740955270027	-2.16009061670020	-1.97411397876924
C	4.71406092818374	-0.10390019181343	-0.16401889911149
C	3.25007137640232	0.18215314050382	2.60634513126109
C	0.71887141166886	-1.71748452464543	2.60289908902798
C	-0.62638007968587	0.85900598106231	0.22847265290863
C	-1.49513035202733	-0.32455319746746	0.60139771449538
C	-2.96827600376629	-0.29818039702588	0.12167401993244
C	-3.70642287686066	0.99337281712002	0.48277762944644
C	-5.18741301515645	0.94934828327307	0.10054149026804
C	-5.89459139761685	-0.25710764086831	0.71826892665715
C	-5.17509491983154	-1.55840054000575	0.36019455665748
C	-3.70130157627130	-1.49366935065725	0.75795020067794

O	-3.05281839394093	-0.35075231789591	-1.31931910379702
C	-2.52487152951283	-1.48546074329377	-1.97426257781414
C	-0.67100058688370	2.09231599906900	1.13199312834395
C	-0.73292807122879	3.31158698393129	0.18508526397609
C	-0.50221385749587	1.26147089751877	-1.12140914440785
C	1.41689527407257	0.66727760473036	-2.15398847809067
H	0.20470457670724	2.14299704473222	1.77595801285722
H	-1.54714779206248	2.04261158293909	1.77950593986497
H	0.03248905652554	4.03996588058776	0.43922974768499
H	-1.70484206045546	3.80283567432387	0.26187273817673
H	-1.51276452170717	-0.41985265678897	1.68607047089739
H	-1.06595269429684	-1.24385448074892	0.22060453722786
H	-3.21860651825841	1.83284052900170	-0.01233773137180
H	-3.61165804081489	1.15197532915434	1.56056788304058
H	-5.67158078604434	1.87581648373762	0.41941790212037
H	-5.27145733425593	0.90293416246446	-0.98735716464991
H	-5.91481588326175	-0.14749138595217	1.80909544140077
H	-6.93566508123464	-0.29646947498671	0.38821973517592
H	-5.25550238180505	-1.73116620363151	-0.71647718303524
H	-5.65320756709537	-2.40763402950225	0.85500295532159
H	-3.18928225174857	-2.42632071687232	0.50862624018166
H	-3.62326571763232	-1.38723335981162	1.84392466007628
H	-1.44046338927295	-1.57138875811285	-1.85102936212514
H	-2.74268281149808	-1.35318056340019	-3.03366152040630
H	-2.98782354924725	-2.41886606314516	-1.64054618623543
H	-0.36438879267033	-3.12690657326671	0.28127816424647
H	1.04988210068910	-4.11701082502467	-0.03331373768794
H	0.35187052567672	-3.14880813192980	-1.32689724056829
H	5.51907670098706	-0.67144061384887	0.31394282311220
H	4.76612492599361	0.92819503313725	0.17901208492973
H	4.89502504357850	-0.10206954045254	-1.23819385989430
H	2.51651519530579	0.23867625146229	3.40962712699227
H	3.48646196710300	1.19916328540844	2.29205220312672
H	4.15951078575321	-0.27052261676195	3.01309424775823
H	1.22120127968956	-2.41785832070255	3.27690384137689
H	-0.22244235018099	-2.17342109641109	2.30633279127466
H	0.49295003454504	-0.81844052991718	3.17618803917556
C	-0.51761881901586	2.77159305492591	-1.24895018047575
H	-1.34363377368244	3.04124204465736	-1.91249549437324
H	0.39387117846298	3.17325240586902	-1.68465848849134

H	3.58703459077096	-3.08710514074563	-1.86020719371630
H	3.63886950621049	-1.45359541991369	-2.52296739625787
H	2.14554620801619	-2.38547204187877	-2.58896088060901
H	1.48878846565436	1.66975721372765	-2.57672783789198
H	-0.96907288288270	0.67586993865681	-1.89614970160679
H	1.37683304915351	-0.10599151697849	-2.92941348049816

B

C	1.59948505368500	-1.42653704747629	1.37303363450968
C	1.52505179541602	-1.96924406981409	0.02422964089581
C	2.74664011548032	-1.62564433177177	-0.64596950710290
C	3.45784347232467	-0.71638491550409	0.19941588420085
C	2.75407387213503	-0.66346369430950	1.47626671971719
C	0.59278318373438	-3.05341026907165	-0.41906814941862
Ru	1.62335408263966	0.21486745042010	-0.51061601782619
Cl	2.42475633186094	2.35698150469964	0.20848419035508
C	3.26239210696586	-2.25354595729148	-1.89653932930860
C	4.82312492170592	-0.15817032020820	-0.02960725530185
C	3.23053283139215	0.09895924365520	2.66366130355608
C	0.64561976941324	-1.71918005532257	2.48638450523026
C	-0.89114654971180	1.05723190000033	0.14573615913204
C	-1.60388457800681	-0.18534846113166	0.58796845167644
C	-3.09374017178533	-0.26173675219224	0.16661465191534
C	-3.88883474082745	0.97271516939976	0.60155179690867
C	-5.38199556816212	0.84555301900678	0.29491698536574
C	-5.97872043167428	-0.41991568589170	0.91131743842034
C	-5.20169785940442	-1.66284087895313	0.47446569811147
C	-3.71519664470198	-1.51972861720306	0.79828712459082
O	-3.22589729134547	-0.27514489715936	-1.26586245061087
C	-2.67127428109742	-1.36607653454008	-1.97216622301191
C	-0.77948913024124	2.26632687969369	1.05224705530861
C	-0.65522196252033	3.47079753330920	0.08838916330365
C	-0.62820678062480	1.39475026339635	-1.14183995796689
C	1.73691599977573	0.44446725155509	-2.34656339104636
H	0.09176293351689	2.18310874860210	1.70366826297225
H	-1.65901545493132	2.33916728985769	1.69500148923987
H	0.15586977363937	4.13123940639992	0.38300441361242
H	-1.58146334695357	4.04820592785518	0.09355009715740
H	-1.56605102439825	-0.26541027363997	1.67344763787069
H	-1.11140164139024	-1.06635345339445	0.19145027536314

H	-3.47652800610490	1.84994458514204	0.10148557859114
H	-3.74436028612761	1.11110012671988	1.67718595986418
H	-5.90593342625611	1.73042619312104	0.66493341936413
H	-5.51961112162834	0.82239803364111	-0.78833471562017
H	-5.94610678989767	-0.34253794359206	2.00463201954794
H	-7.03183698355396	-0.51565621293633	0.63551984038796
H	-5.32792356256829	-1.80729917818043	-0.60198626050585
H	-5.60132370895673	-2.55459094010853	0.96399914669998
H	-3.16191132235312	-2.40943563770925	0.48761877147684
H	-3.58536898624734	-1.44469470123777	1.88205322826634
H	-1.58893835793610	-1.44926121868104	-1.83385849372256
H	-2.86914371573488	-1.17567061466892	-3.02640739290946
H	-3.13343471411949	-2.32036679218158	-1.70043800015478
H	-0.40259474004663	-2.94541989995298	0.00931135529583
H	0.96941847700123	-4.03433898493652	-0.10908999349944
H	0.48745628522841	-3.06669063948967	-1.50289156301622
H	5.57853865771764	-0.76370941557643	0.48196158690832
H	4.88700797942480	0.86219912436820	0.34521597822507
H	5.06833636281467	-0.13650841681450	-1.09026471787903
H	2.52511854858366	0.03456743680254	3.49097645372405
H	3.36799822640883	1.15185124345439	2.40891745668454
H	4.19259630631862	-0.29087419443117	3.00834496637894
H	1.08912277700689	-2.44260924995804	3.17699934712617
H	-0.28358502109997	-2.14980480239695	2.12220624235126
H	0.40173280576970	-0.82613016967600	3.06221652270113
C	-0.40982516425582	2.87341863117390	-1.32267760911621
H	-1.12358987031502	3.25782227012445	-2.05689886230584
H	0.59024199779628	3.10331715997109	-1.69209800459267
H	3.76468111039336	-3.19551588075758	-1.65757261086167
H	3.98710874624693	-1.61519862765344	-2.40003381522263
H	2.46066652947643	-2.47242176909191	-2.60166116210036
H	1.21544338020420	1.20866204837157	-2.92956631286238
H	-0.84344246850954	0.74682444923227	-1.97468268649682
H	2.39896226941155	-0.15564038506709	-2.97477797054738

C (secondary carbene)

C	5.81715427290330	10.63589447170751	5.38659121838532
C	5.26807890654660	11.82929575189100	4.92047669121193
C	5.53213268611139	11.94067729971136	3.48883774929500
C	6.23249828764787	10.75917500631773	3.08371261274110

C	6.52039781738501	10.01285383396162	4.28342194235631
Ru	7.51532524517857	11.92229723896645	4.34222230608742
C	8.56794623562642	12.55325742229618	2.96096648859865
H	8.69012460303232	13.63497840142994	2.81646630228630
C	4.54045798627684	12.86110700484955	5.71319191298518
C	4.95062855441360	12.98526962366244	2.59503171480679
C	6.54092418521844	10.32809805238843	1.68989367155230
C	7.22338931689238	8.70076743563932	4.35949954806383
C	5.85412748667319	10.13520027367212	6.79115327692781
Cl	8.81489977647764	11.97766990019434	6.27315929742603
H	9.00489857842326	11.97215621373025	2.14670383422927
H	5.51350102145173	13.06421173261406	1.66584685986539
H	4.96048619283149	13.96473913269258	3.07275854550279
H	3.91186894889374	12.74892505996729	2.34211333664120
H	7.93356765480408	8.58423732058098	3.54284523041362
H	6.50139338298885	7.87906006751945	4.30124257060204
H	7.76822212145545	8.60568329629188	5.29745651861604
H	5.45939662054383	9.11777637550295	6.84575777939996
H	5.25945195321583	10.76194569300580	7.45284834063216
H	6.87704403031755	10.12623855068971	7.17322081142691
H	3.46328759801062	12.79481419440729	5.53209451003870
H	4.85885457081813	13.86490641313457	5.43068246951923
H	4.71506723986209	12.74387095411387	6.78049134395937
H	7.47083760183703	9.76192333244739	1.64591275258262
H	6.64066301053338	11.18413895588573	1.02323420885667
H	5.74261111362900	9.68902399072763	1.30107815498984

TS_{AD}

C	4.04825173727285	0.74493892977234	-0.34241425341548
C	3.24609079641937	0.83167153725514	-1.50959021687710
C	2.00326378074791	1.52811857981124	-1.19371141313576
C	2.01619619646792	1.76823299498409	0.19963862822237
C	3.26817038383364	1.24187250930639	0.71929769291646
Ru	1.96587694611011	-0.44347186258115	-0.26714336578343
Cl	2.92302591684791	-2.53288005399914	-0.73923272516905
C	3.63375690200734	0.36722553342544	-2.87417449688323
C	1.04663038052801	2.06595469160006	-2.20440384259982
C	1.07711725612928	2.62644616935113	0.97756640657311
C	3.71060474363756	1.34607743037735	2.13930711947047
C	5.39073856785688	0.09947251935822	-0.26042847013753

C	-0.32087899986681	-2.48016093689868	-0.91127214834518
C	-0.54767847896638	-3.54393714618573	0.17794242062910
C	0.29482843305771	-3.07391549988085	1.36875455595942
C	0.18795913045980	-1.54539142457195	1.33913549398659
C	-0.02349498025692	-1.15359681931869	-0.16615351967990
C	-1.02560825130043	-0.02350933732597	-0.42172894574276
C	-2.52469233130274	-0.07937526429236	-0.00972232265603
C	-3.30848225582514	-1.24607926303446	-0.61821625686402
C	-4.80962089934787	-1.17487311153952	-0.32735579036898
C	-5.41695209722880	0.15080751666859	-0.78162004411890
C	-4.66471746106714	1.32839885208746	-0.16242299678811
C	-3.17114084083516	1.24378879195626	-0.47203526091686
C	1.43139611596621	-0.78109334053792	1.74072199956147
H	1.23312482647174	0.11919945086127	2.31028088594489
O	-2.69482663684603	-0.25925075041523	1.41694965027487
C	-2.26280898213398	0.77940344591446	2.26743316194632
H	2.24042791577221	-1.36078544845055	2.18210415273518
H	0.50944547372252	-2.78230547609734	-1.54331586476807
H	-1.18640390748622	-2.37437688695135	-1.56393497290086
H	-0.27133903786682	-4.54574927456478	-0.15568164480743
H	-1.60152733500091	-3.57627459822062	0.46657364817193
H	-1.02920273426357	0.17938084599737	-1.49606217944148
H	-0.63799090109445	0.88394706132455	0.03707339019161
H	-2.90982027384670	-2.18142146597932	-0.23352948883791
H	-3.14398706134515	-1.24134971747215	-1.69956780729844
H	-5.31199094650176	-2.01126942728762	-0.82040832842507
H	-4.96723321184010	-1.29693711011880	0.74672325861264
H	-5.36064979135515	0.22282757277422	-1.87443404477084
H	-6.47693428733022	0.19542662821587	-0.51831786991634
H	-4.81740274636265	1.32158632815985	0.92036357248024
H	-5.06429779054838	2.27639101614384	-0.53272265123339
H	-2.63750218896065	2.09187605925868	-0.03530087399218
H	-3.02413744068670	1.31967160731250	-1.55343736084776
H	-2.84630011178935	1.69695572181969	2.14006508316939
H	-1.20462434884184	1.02015169070964	2.13192711246906
H	-2.40488875673754	0.41998479590101	3.28645065366899
H	0.08394461300415	2.30642370212662	-1.75978962905786
H	0.87155918454828	1.35177101919331	-3.00921552984742
H	1.44831476700465	2.97897702769052	-2.65589300692936
H	2.86873602906052	1.42430908648470	2.82324446175666

H	4.32194690764327	2.24423632364181	2.26855203422052
H	4.31174090340270	0.48855397490084	2.43817505925634
H	6.13471276843383	0.66994483008500	-0.82263179756146
H	5.35725180044382	-0.91273741787299	-0.66874767217573
H	5.73446032645880	0.03062433137111	0.77026248587128
H	2.77539066618115	-0.02508622215344	-3.42048297756365
H	4.38561545627322	-0.41712173206045	-2.82579259835930
H	4.03738843608527	1.20322192266208	-3.45472970351292
H	-0.05247954646955	-3.48174638581844	2.32010409257493
H	1.33126641305484	-3.38164735919119	1.23033985052053
H	1.54100277826153	3.59154797898949	1.20312697957143
H	0.80141946354527	2.17260667952642	1.93041052694010
H	0.16081259861792	2.82327034695910	0.42500806401708
H	-0.67285298202308	-1.22895017115694	1.92808863001659

D

C	3.96217071673959	0.42394004728533	-0.76949204589818
C	2.98234809246162	0.75073474923770	-1.71971412849284
C	1.94096686196876	1.48126334857822	-1.05564678325686
C	2.30188203823177	1.63155566275723	0.32486573375976
C	3.53396776643228	0.91903007901496	0.52351645655794
Ru	1.97766418225372	-0.50435044766616	0.05173378021147
Cl	3.34142381144055	-2.46576941658097	0.44897252942869
C	3.01518859852450	0.44217128462329	-3.18078274680559
C	0.88479107468934	2.25111665539159	-1.78097452161162
C	1.64143156234417	2.53376775062446	1.31403474773289
C	4.35461304746450	0.87269534221007	1.76995344041099
C	5.25494790770118	-0.26802494471775	-1.03021226544237
C	0.15179677689577	-1.87262332048931	-0.53020502250912
C	0.01697997763575	-3.16309787231779	0.29684855403051
C	-0.41581110435711	-2.69647270426987	1.70598037732106
C	-0.10000745517068	-1.19643423433078	1.78503642989656
C	-0.14389417648316	-0.70534841726737	0.33664480645156
C	-1.12438830370084	0.34086240829976	-0.11747707270063
C	-2.63609653786861	0.03396048521090	0.03719420429989
C	-3.03938872344078	-1.27212788191780	-0.65458748642914
C	-4.55030847195643	-1.51015579932921	-0.63266015016823
C	-5.31775188690225	-0.33368775203893	-1.23447534558773
C	-4.93958403617205	0.97592985795780	-0.54174475905698
C	-3.42855031543434	1.19928083369808	-0.58459019342994

C	1.35002022684346	-0.85246925664346	2.06235036969862
H	1.45670805692533	0.07440527518308	2.62121028410254
O	-3.00532473975579	-0.17023750054124	1.41504082761778
C	-2.90569309370273	0.93181143263874	2.29201011449246
H	1.94978308462980	-1.63996909722145	2.50948961960348
H	1.25312992069039	-1.82892700564760	-0.96210071419209
H	-0.37904491984838	-1.85931051541232	-1.48097183646811
H	0.96327966407060	-3.69815968447396	0.32551339462724
H	-0.72508732284952	-3.82284808240762	-0.15517908218738
H	-0.96435369688635	0.54892858497988	-1.17422052651936
H	-0.93083650748177	1.27687070803900	0.40815280508336
H	-2.52858388966714	-2.10352312086546	-0.17147468873029
H	-2.68921103420927	-1.23268068894878	-1.69076375677001
H	-4.78026127694205	-2.43084626288127	-1.17491535129709
H	-4.86804255117756	-1.66089403227550	0.40139920965580
H	-5.08475742961885	-0.25499451415780	-2.30314999053870
H	-6.39450984709027	-0.50507543110738	-1.16036562819695
H	-5.27610807502313	0.94278028926741	0.49799007192053
H	-5.44981279335620	1.81953424343743	-1.01365444411173
H	-3.15941577044638	2.13840326833887	-0.09498087231990
H	-3.10823926329736	1.29872328304245	-1.62604845871940
H	-3.61487690381972	1.72810076956061	2.04477623454891
H	-1.89742644693856	1.35772603232080	2.32034189574582
H	-3.14414448558895	0.55316793846963	3.28518978315833
H	0.11239970698345	2.62201767970758	-1.11357537716059
H	0.40522195723764	1.65975557870338	-2.56107270983797
H	1.34264813943516	3.11791528306221	-2.26833397304558
H	3.74214545064455	1.04738051534801	2.65271576662946
H	5.14061161842474	1.63405978663718	1.74935374909858
H	4.82581154513261	-0.10295994817930	1.88350770368880
H	6.05025516053695	0.47495836865975	-1.14943318372688
H	5.21433865997453	-0.86948525399497	-1.93652046485696
H	5.51901144877731	-0.92986522278292	-0.20905349720604
H	2.01534439783106	0.24204800719177	-3.56665555421628
H	3.63559176977206	-0.42783700230220	-3.38977322410114
H	3.42125084496358	1.28505662226279	-3.74940839237906
H	-1.49097267977471	-2.83802692286903	1.83369925301181
H	0.08722943486841	-3.25621731578646	2.49577486685816
H	2.04221914160969	3.54848240450281	1.22798873442954
H	1.81110446217011	2.20005172860441	2.33589919193747

H	0.56528090038847	2.59005366395284	1.15693589064217
H	-0.80143026773250	-0.69269031937538	2.44583842131856

TS_{DE}

C	3.42357070017775	0.66290377624142	-0.89240410651079
C	2.42135297926154	0.91441505709733	-1.86428776296693
C	1.41741621173325	1.77185566461772	-1.28718706452556
C	1.79420596062369	2.02036350553891	0.06876369251474
C	3.01859939696761	1.31331915911804	0.33514744575386
Ru	1.52039090042022	-0.12129209624570	-0.13654528103290
Cl	2.71050843246926	-2.11497359321287	0.71949300683618
C	2.42477467971554	0.43994847850541	-3.28038222169994
C	0.34643198045124	2.46965282384337	-2.06019950666573
C	1.11076827712286	2.94710288763764	1.01828386509896
C	3.81139708288636	1.34399740934349	1.59932793594274
C	4.69147641309551	-0.09574985343120	-1.09000968060207
C	-0.26475350486896	-1.63992071635971	-0.75218485701793
C	-0.40962428921058	-3.03437092409838	-0.11811318438826
C	-0.60625298190796	-2.81276289049199	1.40244635045125
C	-0.90108103998888	-1.32292748781923	1.59433615681565
C	-0.69375175215310	-0.63150307004107	0.28379155251198
C	-1.58138133288850	0.52733172429792	-0.10980794797246
C	-3.10994486385279	0.32393718015667	-0.01000202094765
C	-3.55923581640461	-1.00494691087368	-0.62466970400653
C	-5.08100148380409	-1.15824678707692	-0.64805498244062
C	-5.75534141179269	0.01492472828847	-1.35956745875736
C	-5.32690154433126	1.34917508617772	-0.74643358494903
C	-3.80490729479201	1.48436948714879	-0.74530939778362
C	0.27604494815830	-0.42823241544433	1.83173038268187
H	0.03959017288234	0.54017182312622	2.25160034605733
O	-3.55461695060582	0.24521525675653	1.36193731666164
C	-3.39100599980176	1.38541676292864	2.17910955862916
H	1.17016403568522	-0.89945716160284	2.21480290441319
H	0.80416684524905	-1.53398074617052	-1.15819085711579
H	-0.84827973087120	-1.50291928427693	-1.66168220824016
H	0.46005534183745	-3.65551907589978	-0.31820686217403
H	-1.28308871865400	-3.52435326571671	-0.55286686125397
H	-1.35776727670474	0.78754497285024	-1.14086848925441
H	-1.32195474608555	1.40686647416522	0.47664672789920
H	-3.10936817250876	-1.82545683641027	-0.06557027762998

H	-3.17023839110982	-1.05663636660478	-1.64618059964933
H	-5.34406844067662	-2.09978414729787	-1.13655459326709
H	-5.44573068055544	-1.21869227479583	0.37954616438032
H	-5.48064646976237	0.00341082916792	-2.42107731336673
H	-6.84216692278545	-0.09022587983483	-1.31651670289114
H	-5.70132160407632	1.41147092474648	0.27885306381064
H	-5.77006833158933	2.18235595633039	-1.29762800514010
H	-3.49730569062978	2.44040720709960	-0.31422298482923
H	-3.44191595124152	1.48752931896315	-1.77725999350377
H	-3.97856267473415	2.23982036704333	1.82879412140590
H	-2.34439857258651	1.69449163743199	2.26779736453082
H	-3.74853831665629	1.10329171320574	3.16856516756878
H	-0.43452240364880	2.86366250866856	-1.41299122204678
H	-0.12411658681405	1.81104794355427	-2.79145944832372
H	0.77098485331851	3.31435759111883	-2.61278713843732
H	3.17947692718895	1.57706968780021	2.45594629451666
H	4.60107811379554	2.10080263432092	1.55034804901497
H	4.27508625207524	0.37601182463033	1.78466479505698
H	5.51964258470710	0.59617155585375	-1.27391159865199
H	4.62171821159263	-0.77340192973051	-1.93947088626087
H	4.92604345892149	-0.69794601826041	-0.21483241959864
H	1.41140483585337	0.25953233985968	-3.64015298233978
H	2.98861498419886	-0.48529759682996	-3.38705512542926
H	2.87939220781979	1.18803061905250	-3.93762012689946
H	-1.43260802019051	-3.41381476068246	1.78319177656668
H	0.29395901008557	-3.10280543326937	1.94200636709543
H	1.56098422226275	3.94312500897146	0.96676545559815
H	1.19955235009080	2.60174588637240	2.04771038218480
H	0.05145802163008	3.05499495249673	0.78846104450549
H	-1.81040842399361	-1.08447324204982	2.12790317006758

E

C	1.76742685591091	1.52590755267973	14.28160782930861
C	2.76460917312780	2.23110572806247	13.38285505625989
H	3.36812499433499	2.89593976718855	14.00394122491218
H	2.18890981616921	2.88802882565796	12.72146366630564
C	3.69735077489380	1.46134526717959	12.44155913789019
C	4.54451747582798	0.38435376566858	13.12723458256702
H	5.12200709608727	-0.14693202992893	12.36743133720092
H	3.91450717428539	-0.35422418496597	13.61657288884124

C	5.54209728590896	1.00114194438751	14.11334958986970
C	6.47951808780706	1.97869770450927	13.40243447577337
H	7.16136266173521	2.44226895179214	14.11934115761431
H	7.10147636037830	1.42075585750763	12.69349654840217
C	5.69702317786649	3.05343326461064	12.64608831164087
H	6.37802186015743	3.66969165554215	12.05376972663360
H	5.22023670167100	3.72886803176793	13.36131872093658
C	4.63838924434885	2.44008932372791	11.72411774860814
H	4.03784864154140	3.21574276143499	11.25567400832049
H	5.14608542129836	1.90060702200276	10.92014787762687
C	3.30285203085455	-0.12822960992526	10.56869711914283
H	2.47664539369051	-0.41141707284660	9.92449297230816
H	3.62478039769195	-1.00892333955850	11.12353555457831
H	4.13009713858960	0.25569091815496	9.96648138703675
C	1.30300835204160	4.12836843210767	10.27381013963722
C	-0.06935453964079	3.83135475917520	10.59527277149937
C	-0.61438539312811	2.98417812877266	9.57164757100271
C	0.45126669833395	2.69495262127784	8.65048962012025
C	1.63326554483059	3.40665958153220	9.08805343976388
C	2.14655132330715	5.13990310080548	10.97966304689839
H	2.05641778781334	5.06660750852868	12.06375581523904
H	1.83998716254896	6.15162614504973	10.69490961819555
H	3.20049595142062	5.03936903829036	10.72630386441069
C	-0.82575289565856	4.40144011241846	11.74773655346501
H	-1.60069618873481	3.71686226851693	12.09009737297576
H	-1.31160875042056	5.34008912589379	11.46040609080686
H	-0.16822070984427	4.61291929094697	12.59003353260193
C	2.93679635605379	3.43366166282540	8.36070771725932
H	3.76328612409435	3.67631553978011	9.02678924534300
H	2.92206096647853	4.18088969952661	7.56050624303943
H	3.15284471526402	2.46757777094450	7.90401879117844
Cl	-0.10580753059952	-0.09692632623297	10.90534110811723
O	2.78861996899084	0.87443389650574	11.44843353795468
Ru	0.96908651948945	1.97893483609123	10.54768895876565
C	-2.02350219000963	2.50573902299860	9.47218726592001
H	-2.06977029540519	1.51351146440772	9.02683342765569
H	-2.62428288466411	3.18841927060678	8.86271688081790
H	-2.48384340469878	2.43490982207372	10.45672760456576
C	0.33871186461703	1.86047636184748	7.41930342755707
H	1.28907837104866	1.38655393357739	7.17384269882294

H	0.03992364005796	2.47420528778680	6.56269592221786
H	-0.40198490193222	1.07313086166598	7.54778508287439
C	0.72896811053000	2.47129928982263	14.88002877418246
C	0.14046970844508	1.74345073562197	16.10052167748638
H	-0.03626519318284	2.74849341247390	14.15213568012275
H	1.23211028209807	3.39330014627263	15.19295505904538
C	1.26991256443005	0.81819427237959	16.59363928841395
H	-0.72519292741062	1.15125858136730	15.80234436968289
H	-0.19973433080702	2.43423640047123	16.87259433525311
C	2.06526270813430	0.48702241374715	15.34572350703286
H	0.88299861342597	-0.06791858310621	17.10315700673194
H	1.91366334585887	1.34612012352290	17.30417429204649
C	1.29528358722952	0.11084761876285	14.10469711320295
H	3.06106225093504	0.08604291300813	15.47368663234608
H	0.23585312643162	-0.09556892574236	14.17031339723748
H	1.78973661371204	-0.48465911482857	13.35505180527361
H	6.11901447880237	0.20238242900891	14.58521504568412
H	5.00820663553620	1.51416296484733	14.91704674577333

F (cyclopropanation product)

C	9.28396508627056	13.43542430886715	6.11370463450151
C	9.27271790087579	11.93511622634349	5.94170571115377
C	10.29732866152581	11.12714274544055	6.75973114245339
C	11.72619257617962	11.63331328977269	6.53261020605630
C	12.77648819489322	10.77435664904081	7.23795380122389
C	12.66431539004286	9.30345395574345	6.83765966433309
C	11.24905248270378	8.77842469923844	7.08234624930333
C	10.21187119471596	9.64272933245184	6.36573280480406
O	10.08499309168899	11.30613241106234	8.17865527714033
C	8.91985565229578	10.74597853826815	8.74544327857603
C	8.92233860687383	14.04234835638162	7.46431603420635
C	8.50376618371762	15.49447526230886	7.16749326905151
C	8.67580630347154	14.33245070017928	5.05495525199251
C	10.17054136852895	14.27846045047489	5.22988907794280
H	9.73165779750627	13.97567124051224	8.19132034585159
H	8.07719190384947	13.48471825227657	7.87829056150715
H	9.37311668258981	16.15278525745195	7.20799495849229
H	7.78701723146079	15.87683799256290	7.89491497890872
H	9.44239624412835	11.70210867052127	4.88691622718194
H	8.26949063882483	11.55767250292920	6.16784725876699

H	11.79063238556575	12.66662126126688	6.87302685114863
H	11.91808786458624	11.63931951285069	5.45530064787464
H	13.77444194445824	11.15550391816797	7.00599445054145
H	12.64233501977952	10.86731147135018	8.31813682402283
H	12.90877184924049	9.19575816975700	5.77408136266117
H	13.39208742790566	8.70254748121836	7.38900834317497
H	11.04790924937832	8.77880084357795	8.15718656970284
H	11.16177364600095	7.74251115580306	6.74447032794307
H	9.20152786319020	9.26590082241031	6.54299342356673
H	10.37361994550387	9.57826089505297	5.28550956002426
H	8.00672296025692	11.05028197485061	8.22464484190450
H	8.86932949281159	11.11671315754407	9.76885890694780
H	8.95516713411770	9.65173287537340	8.77367308680560
C	7.93004268035763	15.46218691106908	5.73697985404661
H	6.86215337022145	15.22541083863920	5.75901537577669
H	8.03952019750209	16.42202642341242	5.22601550353483
H	10.68586148466370	15.13313479050890	5.65044511619758
H	8.25491137559491	13.89991879518808	4.15551150419712
H	10.73570091672076	13.75897786013104	4.46771671648104

Structures along the reaction profile for Substrate 1f

A

C	10.82323668992533	9.07665202699176	6.88778408035944
C	10.33761538961795	10.49161243627684	7.24282962844737
C	11.19264284980249	11.52369418112835	6.50156440443287
C	12.69120802923316	11.33159514071261	6.74125125767460
C	13.14184187964863	9.91384402809734	6.39091649723219
C	12.31468394815987	8.87842989336561	7.15373917348760
C	8.82516429234171	10.58778412529259	6.86093006997228
C	8.28174036443541	11.95796072578059	6.56776817588434
C	8.38443943755125	12.89371158318133	7.73446434763999
C	8.70925010583332	14.34149836608146	7.37802705181867
C	7.60490622225591	14.99433890119468	6.56826357039403
C	7.31802067746677	14.36557540704287	5.23004010129885
C	8.27802195086555	14.04609530115161	4.25831056799654
Ru	7.33895211181827	12.20748717086462	4.93661689420300
Cl	9.12009496095271	11.08239514986183	3.65388104239957
O	10.54792222336706	10.79235613526350	8.64199815047491
C	10.06426711423083	9.87292819521077	9.59651824772289

C	5.54891100669975	10.88785765257977	5.71963622037899
C	5.14834045238588	12.23229366741768	5.41602906283300
C	5.21339320014801	12.39663907961237	3.97233019521684
C	5.79111696394996	11.24308386893186	3.44280988207592
C	6.01786491217937	10.30008946992466	4.53477790880517
C	5.43488354039229	10.24813045802320	7.06368294573984
C	4.43329418946485	13.13741397677896	6.36560203962144
C	4.71853775277012	13.57288947859590	3.19282348472578
C	6.07465963010207	10.95705590037891	2.00719361743811
C	6.52974967523669	8.91293241078307	4.34556944974449
H	9.11013308931707	12.51434445509777	8.45556106015395
H	7.40925830887088	12.86260717680230	8.24340273448386
H	9.65442502438028	14.37516546464397	6.83004892320000
H	8.86819236100126	14.90649236103647	8.29983018820105
H	8.66177815084062	9.93522144876570	6.01066576221728
H	8.25524975048944	10.17667739170526	7.70232124396200
H	10.89770244395847	12.52289599123874	6.82250578201849
H	10.96138671334151	11.44427601529141	5.43879157737768
H	13.24581379143452	12.06165397474163	6.14599642066131
H	12.91967054591231	11.53539641960053	7.79051228423374
H	13.01776239380709	9.74892773367369	5.31491274171426
H	14.20512401675652	9.78723330964140	6.61075794539096
H	12.51931414803548	8.97139289637397	8.22434064676002
H	12.60549778287388	7.86583914591178	6.86221066821740
H	10.22516135730758	8.32923276504892	7.41585819220965
H	10.62476100510826	8.93380803667464	5.82296009740819
H	8.99157174042423	9.67472595318395	9.48665524127782
H	10.22966318901685	10.32863892180298	10.57224685714023
H	10.59640613556722	8.91758599583975	9.56212516955344
H	4.52731672031169	14.18305764808139	6.07825633425932
H	4.82154268583778	13.03712926184294	7.37873681880696
H	3.36504371385014	12.89877398317952	6.39585793911978
H	6.01818401761932	11.86443875802344	1.40712840843969
H	5.35017705417145	10.24156448333612	1.60553952879472
H	7.07198057421207	10.53268111817983	1.88806241835885
H	5.80885644322725	8.31252481764835	3.78276988514245
H	6.70617528227169	8.41514915147983	5.29809429282723
H	7.46766221022566	8.92378248499554	3.78820732686146
H	4.40077075940486	9.94214362116283	7.24842111278188
H	5.71757636438074	10.93289438495161	7.86356439001276

H	6.06008432262545	9.36114181267481	7.14331839155860
H	6.68577587143424	14.98611919621632	7.16246464693826
H	7.84700612063704	16.05143814981838	6.40135084935431
H	3.83773296101614	13.29642792742257	2.60701685558741
H	5.47961983354393	13.95090473956108	2.51075081858426
H	4.42463240923586	14.39184353019897	3.84744232143492
H	9.34188839606814	14.02051236132134	4.47326453247809
H	6.39571105498699	14.73420314682029	4.79822546974838
O	7.96808348446024	14.39927050905312	2.95448439093241
C	8.88851385716916	13.97195162319989	1.95430346587525
H	8.62627148243236	14.51592632001570	1.04787481901009
H	9.91513560316481	14.21994187929756	2.24181748795820
H	8.82277425843245	12.89746990391622	1.79158689093326

TS_{AB}

C	-0.53693110930941	-2.78454006635064	1.03289017350369
C	-0.44920933286650	-3.22226525632099	-0.42607413841548
C	-0.99456073951457	-2.01927181858937	-1.20187598587917
C	-0.67455285118009	-0.78177952547918	-0.36123521109093
C	-0.17072735809801	-1.28571139469212	1.03984962842952
Ru	1.24780842362665	-0.03652859593339	-0.13173095695299
C	1.50690042637395	-1.22609667774939	1.38755073059631
C	-1.71359053624023	0.33053664634719	-0.36525779165380
C	-3.22804093549085	0.08714696891224	-0.13610794911271
C	-3.90801393299491	1.47104251675800	-0.06674323964297
C	-5.40839621318142	1.37758005320485	0.20196532000753
C	-5.68052433149207	0.61121001283063	1.49699540694236
C	-5.02023015866600	-0.76679281032748	1.46484508129716
C	-3.52381219170913	-0.67605878059994	1.15635852949128
O	-3.83893692035683	-0.71691028730759	-1.16543425939347
C	-3.74477776379448	-0.26428149858909	-2.50083914483279
C	2.17954340816711	1.61656559815658	-1.35231590057503
C	1.04501392811726	2.22925127153780	-0.76139909730248
C	1.19189284477325	2.15430420030904	0.65514228305930
C	2.47881795092239	1.58081817259105	0.93253390735075
C	3.09493018902848	1.23724653510214	-0.29511892813771
C	2.48570853750892	1.53323136528456	-2.81005731921310
C	-0.04114696815585	2.93084079067880	-1.50739213767610
C	0.28425804339779	2.74861137882884	1.68339557097952
C	3.08064731565295	1.46890042653882	2.29405069469632

C	4.46148256395401	0.67831361300925	-0.51077172370014
Cl	2.15541049690458	-1.64647434578940	-1.71127296987608
H	-0.55347710255210	-1.94300086289735	-2.19542941872715
H	-2.07528460663771	-2.10631828514316	-1.31061408349924
H	0.58823978823602	-3.40343094253403	-0.69568643674709
H	-1.02082223863246	-4.13325963561089	-0.61182244959788
H	-1.63285987334372	0.83921550875980	-1.32654844882669
H	-1.42470104743616	1.06735241614166	0.38098414910045
H	-3.71064733263792	2.03161909418541	-0.98348130221223
H	-3.43309935758295	2.03530051022621	0.74173682194977
H	-5.83730380635777	2.38162160898806	0.25490436898412
H	-5.89689984456734	0.86579651514914	-0.63139545059893
H	-5.28493398414889	1.18567336276543	2.34339609607706
H	-6.75641147293347	0.51183951580391	1.66156143204221
H	-5.49947387445958	-1.38025448183779	0.69880649011853
H	-5.16391136108846	-1.27877321229272	2.41997000845737
H	-3.10649300113708	-1.67743616908990	1.07545891362872
H	-3.00639174203458	-0.17135130719389	1.97824422364701
H	-4.31052927563831	-0.97491118261600	-3.10205899370688
H	-2.71269756615956	-0.25064854969341	-2.86373471108809
H	-4.18110292682722	0.73012583077408	-2.63789480576536
H	0.29277305459652	3.93319798506772	-1.79304602611577
H	-0.94370174999089	3.04501624022778	-0.91092037985788
H	-0.30753470998975	2.40479093590795	-2.42378662211678
H	3.86912833469903	0.71826731766192	2.32429605080348
H	2.33734947060501	1.20647731932751	3.04880465917827
H	3.51947740813391	2.42415352034336	2.59643217878623
H	4.88661925082506	0.30045729796945	0.41886258310416
H	5.14008656851620	1.44205857867488	-0.90308121608126
H	4.42558370022686	-0.14926969784771	-1.21970400553357
H	3.18257819634264	2.32662711645560	-3.09861878352111
H	1.58474205108750	1.64110529630939	-3.41277254168112
H	2.93247461470104	0.57058457322223	-3.05311227829546
H	-1.56459396038949	-2.85408801795788	1.39290491849125
H	0.09225636714929	-3.37326217194773	1.69618636560357
H	-0.71827609770122	2.91222930379026	1.29103548708965
H	0.66213804111160	3.71718113464381	2.02594095630196
H	0.19706538450809	2.10774454016616	2.56254824805495
O	2.12674364908837	-2.43321538041448	1.36990820514194
H	-0.62560326598260	-0.72551838145061	1.85130701140022

H	1.61289757435925	-0.75454659742106	2.36918992205267
C	3.01260714473089	-2.68911883069331	2.45279746686522
H	3.32286114846523	-3.72752752284259	2.36264875044169
H	3.89272192749738	-2.04352545066642	2.39100124443694
H	2.51453828587249	-2.53590171487208	3.41545855471617

B

C	-0.59731997668462	-1.41625978024169	2.53666025196891
C	-0.67549287235695	-2.71208293555342	1.69442257536316
C	-1.06006940014551	-2.27370875399581	0.26117892519893
C	-0.93076186095063	-0.75996539578159	0.24222242812494
C	-0.59160465747252	-0.30153889354179	1.51699694643985
Ru	1.21771126213131	0.01212737530154	0.25887299514305
C	2.15598735875378	-1.52401430148922	0.78079518632012
C	-1.68567474730725	0.06765095953841	-0.76855343840960
C	-3.22477784112018	-0.06522476627263	-0.76829004731960
C	-3.80913277507834	1.02963008558192	-1.68108729310148
C	-5.33643720951242	1.01580670176083	-1.70415596718185
C	-5.90467294778252	1.16365621679101	-0.29161182958314
C	-5.34128996952215	0.09218625552096	0.64275091789864
C	-3.81174118224207	0.08565918958556	0.63853880345480
O	-3.66884157607998	-1.36822803526267	-1.19922347011494
C	-3.24723111749233	-1.81299012881533	-2.47564319632374
C	1.58082991334532	2.18998865066495	-0.66266954670077
C	0.87904569289112	2.39676931796266	0.52371570529320
C	1.63919259739253	1.79873656007581	1.61009829225603
C	2.86977623321843	1.32911394930084	1.07427623272973
C	2.80828053317417	1.47713228097908	-0.34111976851656
C	1.19795740820696	2.60304702875247	-2.04277751162573
C	-0.38857277673954	3.16499678443795	0.70265243971187
C	1.32166326401384	1.95143180991342	3.06196666569247
C	4.03657080763005	0.83978529429631	1.86344097014534
C	3.88990208487706	1.18298578585820	-1.32727527778691
Cl	1.18893844964198	-0.88266672137039	-2.01252491562635
H	-0.44010924919599	-2.74305342147125	-0.50201200400685
H	-2.09690715310996	-2.52890108459988	0.04053054771811
H	0.27864151640900	-3.23019201866812	1.69589306841640
H	-1.41102009218888	-3.40297284375615	2.10764039826007
H	-1.30998677543425	-0.14540573626153	-1.76816035930598
H	-1.46979465763914	1.11961796352066	-0.58998095706466

H	-3.40099591109972	0.93123235467860	-2.68941511961852
H	-3.46129429418453	1.99705200005899	-1.30590983893912
H	-5.70434954436691	1.81843835031611	-2.34876956867258
H	-5.68418433984183	0.07417629879915	-2.13723876411758
H	-5.64603376331852	2.15646472580276	0.09640831680852
H	-6.99633472215879	1.11087340688195	-0.31336510680180
H	-5.69802179996142	-0.88989722027846	0.32446145892191
H	-5.70437591575420	0.24959524566242	1.66201089773614
H	-3.43671957468804	-0.72196752362212	1.26845042878369
H	-3.43625709918182	1.02228787599030	1.06289532257317
H	-3.70381883714846	-2.79172602475720	-2.61956193993595
H	-2.16133204520338	-1.91921846775509	-2.54271153478814
H	-3.58647871704017	-1.15159792496899	-3.27936008897272
H	-0.18788970248457	4.11494457848358	1.20718515726642
H	-1.11838423369634	2.63089101964928	1.31334777392936
H	-0.85923213920599	3.39111269456051	-0.25238195247240
H	4.65423937488374	0.15350036383082	1.28423771485707
H	3.72267037377312	0.32471475815708	2.77232902064846
H	4.67141294794866	1.67726520582151	2.16569691410183
H	4.62993002321433	0.49909257766467	-0.91292736559511
H	4.40772567374110	2.10180875867956	-1.62020713396999
H	3.47547337980679	0.71940428705543	-2.22195881122917
H	1.89410838430997	3.35380110244042	-2.42758456392609
H	0.19549062682316	3.02700823937037	-2.07329896273507
H	1.22272385601779	1.74166987879685	-2.71284998164023
H	-1.49242381670403	-1.30362699756711	3.15997132833119
H	0.25796465724248	-1.39627519853223	3.21419472619390
H	0.25005891117482	1.89762467667667	3.25080485553054
H	1.66888651699343	2.92109533165515	3.43355755834814
H	1.80099081969994	1.17612418104333	3.65862404028978
O	2.09777250939674	-2.74477992711972	0.27961735953975
H	-0.87396926826606	0.68681277337769	1.84812192249445
H	2.95832014373983	-1.45478674079719	1.53352196277625
C	3.10353379420261	-3.70325844133462	0.63252377636555
H	2.60481495592482	-4.65948227636979	0.77880098960872
H	3.81503948991617	-3.78039813672929	-0.18977711158854
H	3.61850200186505	-3.40365219838255	1.54776655243070

C (secondary carbene)

C	6.54538194717361	10.05004977731411	4.27144969329349

C	5.82090112967224	10.63544989344868	5.39003154862430
C	5.18973815317936	11.79148368559783	4.93327477522879
C	5.46445823142651	11.93642153362853	3.50613292345711
C	6.21591001110915	10.79318296721300	3.08834821142086
Ru	7.42337505976596	12.00196536762308	4.41353542048603
Cl	8.66480131861550	12.53547243828909	6.30717481780414
C	5.89190251430046	10.12329745333407	6.78988967874298
C	4.40175310907489	12.77392952373515	5.73194837160225
C	4.84737424317975	12.97077509625801	2.62359906214645
C	6.56088033736460	10.40993442088795	1.68874170045742
C	7.29061558112853	8.75908558099770	4.32696995352395
C	8.62081426315364	12.51096508904922	3.03880205288960
O	9.07419868726021	13.74495255070830	2.84188071681424
H	8.92618429605261	11.83997576498484	2.21989135208906
H	5.40884790995393	13.08395264958851	1.69687421801233
H	4.82104844022667	13.94316561393990	3.11512937134247
H	3.81845029297883	12.70150114602501	2.36208981470167
H	8.00966444382374	8.68071530377909	3.51289308604978
H	6.59928729529448	7.91266698026255	4.24947897467021
H	7.83483617965840	8.66186625388469	5.26542986064193
H	5.40442139932106	9.14759783535182	6.86963452147045
H	5.40611563247774	10.80128274144005	7.48851906467583
H	6.92851343772492	10.01144787676452	7.11114955923592
H	3.33272696242835	12.67563842070293	5.51993813184843
H	4.69292312614960	13.79623368474448	5.48744567654297
H	4.55083497132928	12.63363799780054	6.80043252063319
H	7.51972034065932	9.89277295187119	1.64057807382335
H	6.62030554487221	11.28347490009153	1.03912513984509
H	5.80413394471585	9.73760221323248	1.27413208266260
C	9.72184427904171	14.04523344150629	1.59401849439592
H	10.31254639507725	14.94365983237021	1.75508385620143
H	10.37046537337647	13.21971624893808	1.29553324140541
H	8.97105214843292	14.22893276463612	0.82338403326014

TS_{AD}

C	3.85938827515857	0.81286920350524	-0.51820789951663
C	3.06587239286633	0.94143332102062	-1.66751241346984
C	1.79223496188233	1.55836671079568	-1.29742575786220
C	1.82127005418228	1.78672664763437	0.10507531760835
C	3.07021951997563	1.25887519062146	0.58713630850573

Ru	1.82423389487594	-0.40196438610654	-0.36249903104880
Cl	2.73539119826695	-2.44023017107061	-1.10836962880209
C	3.44207008674694	0.54544489974234	-3.05530139678020
C	0.82031001803022	2.10170132150814	-2.29233953131517
C	0.89664369159929	2.63267648913798	0.91600278101215
C	3.57930789282844	1.45507719545872	1.97492946235351
C	5.21954781381419	0.20409139125361	-0.45561995165737
C	-0.47822588761308	-2.41206895425106	-0.72493498766505
C	-0.32971494651271	-3.41019978927088	0.43291286655888
C	-0.70124356291199	-2.60792439588100	1.68605911396743
C	-0.17161407408413	-1.19718031763294	1.40804663385464
C	-0.23352640272559	-1.00199117954138	-0.12732690986287
C	-1.21579994232665	0.06037704645591	-0.62747989337686
C	-2.73546324804014	0.05865634207618	-0.26571532574919
C	-3.50651298973395	-1.19911674515746	-0.68354266063201
C	-5.01889860639946	-1.07247376418768	-0.48254148056257
C	-5.59258058181932	0.14569411364058	-1.20152289205400
C	-4.86484931406040	1.41485147672588	-0.76190990909240
C	-3.35797998720414	1.28045190768216	-0.97492172359811
C	1.29782975598640	-0.96575567334255	1.67734389397269
H	1.52685728256077	-0.12592104115426	2.33118597986362
O	-2.95629332603309	0.12003602545483	1.16347161973865
C	-2.62892959761206	1.31326534606047	1.83816502498262
O	1.95447385793728	-2.11081534496442	2.06728831254317
H	0.19333620185419	-2.65269629609399	-1.54494009491802
H	-1.48549172034618	-2.46005427703163	-1.13225288710735
H	0.70380374919290	-3.74586363987319	0.50098909315886
H	-0.96104105152060	-4.29127948211542	0.29882111082764
H	-1.17498724478824	0.07571393497369	-1.71992424861919
H	-0.85779814303650	1.03749443912766	-0.31270330355775
H	-3.14079813651659	-2.04621364762928	-0.10702637636290
H	-3.29224356389873	-1.40303795985105	-1.73649789933480
H	-5.50438849724410	-1.98625986482674	-0.83497931089457
H	-5.22734106401707	-0.99308645277235	0.58692383693140
H	-5.47713196746883	0.02000922014268	-2.28471685441604
H	-6.66469754429215	0.23449000790455	-1.00779532834971
H	-5.07516577407404	1.59827071901873	0.29535347704880
H	-5.23675605038407	2.28271006978433	-1.31332013627136
H	-2.84214011713475	2.19223888863554	-0.66290199214033
H	-3.15710525276639	1.17254773443587	-2.04471934568719

H	-3.27554558924167	2.14938777093649	1.55269970518603
H	-1.58917253911349	1.61178155318146	1.68385119638730
H	-2.77448687219373	1.11400463595157	2.89994397950904
H	-0.10846114971115	2.41759766013598	-1.82560672582724
H	0.57444600494124	1.36580564403097	-3.05817834726785
H	1.25594660843873	2.96922398727481	-2.79822484204335
H	2.78739434714491	1.40412795888532	2.71963323015887
H	4.02572438426466	2.45172316322041	2.04967690904434
H	4.34523106793967	0.73047014050545	2.23993658630537
H	5.97839818983929	0.89851388306787	-0.82700376968096
H	5.26446620750510	-0.70422663913324	-1.05753663080101
H	5.48895241871996	-0.06251626365892	0.56524605694263
H	2.58646323228954	0.14129477460434	-3.59652460645622
H	4.22141758319135	-0.21335926816387	-3.05302730659193
H	3.80539321227790	1.41462561459883	-3.61310439317446
H	-1.78678041874637	-2.53738994692243	1.78873580258876
H	-0.30280642861676	-3.04164901295498	2.60325173309915
H	1.35607997824948	3.60341573976452	1.12857748472052
H	0.65663925502714	2.17035411777560	1.87367816420016
H	-0.03824610047247	2.82314194706869	0.39400470416472
H	-0.74994437234905	-0.44800364362742	1.94165724655767
C	3.32751787802462	-2.01245708977559	2.39069955651535
H	3.61031487210812	-2.96788868632365	2.82813049281797
H	3.92186122461746	-1.84287048308003	1.49004365504513
H	3.50512495267179	-1.21503881740499	3.11868645637643

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C	3.45303218007251	0.76604596192430	-0.95908500781897
C	2.47229134299392	0.97489814191089	-1.94112192622708
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C	1.72131359039286	1.95204515847421	0.03438287817957
C	2.98591567835322	1.32555807417441	0.28832240224141
Ru	1.47589224040823	-0.21371943716240	-0.12129355732179
Cl	2.88679551781727	-2.16578990015710	0.09656103633047
C	2.54529594230075	0.55946261712479	-3.37389286272023
C	0.32212993257359	2.37719094358641	-2.13858069836313
C	1.02409731506674	2.88779691170176	0.96618031941623
C	3.81762306094272	1.51146002280800	1.51380348952035
C	4.77726166199328	0.11718562254253	-1.16498464425367
C	-0.35884282437975	-1.58475950049382	-0.64102401699795

C	-0.48738765173886	-2.84644690235574	0.23102261051804
C	-0.98056899977084	-2.33355934677760	1.59909892257614
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C	-0.63763590056058	-0.38536585694942	0.19341367086881
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C	-5.45500339922652	1.25248823283066	-0.69712371096542
C	-3.94458254016482	1.47860957998182	-0.74607896961556
C	0.84782372359675	-0.55427023901309	1.93590735159608
H	0.97484988967414	0.42837270397490	2.40216203520088
O	-3.50720989684632	0.12800494531782	1.26346447412721
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O	1.40581535879311	-1.53593243419616	2.75404436218888
H	0.72941416789243	-1.55753968613061	-1.09252793498308
H	-0.90642070020034	-1.59735192905852	-1.58251419871781
H	0.47605461067116	-3.34337895966816	0.32087930545647
H	-1.18764961308294	-3.55246524112294	-0.21799441813197
H	-1.48806418132505	0.80647670679089	-1.34962472616204
H	-1.45082480588676	1.58843537265047	0.20670996321889
H	-3.03580761333032	-1.81969628514540	-0.31466176639655
H	-3.20674085046612	-0.95760836233826	-1.83728439251700
H	-5.29117175315339	-2.15909490374327	-1.29969105889121
H	-5.37351469866340	-1.37436605739610	0.26954073637098
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H	-5.78877880545110	1.22781241330490	0.34374324584840
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H	-3.67671092040741	2.42186577915067	-0.26374691779083
H	-3.62763209155286	1.57160086585929	-1.78919898641380
H	-4.15601752310193	2.01537721784001	1.88532082330327
H	-2.42252876788315	1.69867176809126	2.12322090477416
H	-3.62137359648459	0.87020003100240	3.12829330298230
H	-0.45901566380523	2.79901653619642	-1.51348123889167
H	-0.14404305567913	1.70710809258604	-2.86120327646722
H	0.77103017302608	3.19918588034888	-2.70503091338039
H	3.20230665482100	1.59064683399596	2.40778165741369
H	4.40845353389646	2.43007354558122	1.43476616447234

H	4.50724865787851	0.68233607622400	1.65667692088633
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H	4.73622109155368	-0.64024154806272	-1.94502249944993
H	5.12630588224119	-0.36946182239898	-0.25812984933935
H	1.55663964457418	0.33056938751840	-3.77211848399790
H	3.16802960214035	-0.32561658936806	-3.49686445212638
H	2.97140660998956	1.35504929935110	-3.99381996402673
H	-2.06721065766285	-2.41022065513427	1.66576356393229
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H	1.50124077626859	3.87247095665663	0.94487784192478
H	1.05913209048228	2.53090007745394	1.99508722929840
H	-0.02155635737803	3.02382001574498	0.69689846993213
H	-1.28213462865693	-0.30792384482057	2.31415763241486
C	2.67548335677913	-1.23604520780130	3.28801592688659
H	2.92992726359550	-2.04259406048561	3.97463394160189
H	3.42729665458893	-1.18593237376647	2.49990474052105
H	2.65345843766477	-0.28731635421055	3.84127332917354

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C	1.58782661184945	1.45005943321447	-1.89063885199947
C	1.42831114361773	2.07900379130756	-0.62055751029153
C	2.57296261537297	1.73191425390864	0.18128873674934
Ru	1.60747144046818	-0.11335061191864	-0.42060543815445
Cl	2.74967582162016	-2.25530728093671	-0.18106355220413
C	3.46782865714951	0.03050966626374	-3.05719662496646
C	0.65386307088202	1.56394305427242	-3.04999042340672
C	0.41447773268535	3.10971489949186	-0.24785143164483
C	2.84241404944442	2.27306980135417	1.54619827101559
C	4.81320044356934	0.45305981673897	-0.21680289791063
C	-0.35933804377374	-1.52726267956430	-0.96523917845568
C	-0.50140898106118	-3.03583505367643	-0.69268899681797
C	-0.62026281175550	-3.20466046727207	0.83862208181772
C	-0.96932525312355	-1.82740114324709	1.40468000830383
C	-0.60949468006605	-0.79000965696376	0.34406829456635
C	-1.43647129457744	0.48377376900002	0.28358149768081
C	-2.97335288538407	0.38601265599943	0.41121336334990
C	-3.56787686770081	-0.71570237931944	-0.47221933913882
C	-5.09682942930254	-0.73504091326943	-0.44379946059331

C	-5.68264731836472	0.62307391907159	-0.82963332254776
C	-5.11175302667513	1.73584755901213	0.05045288332141
C	-3.58416207275657	1.73972195359346	0.00521523469799
C	0.15341287205126	-1.04004427323876	1.91652359998899
H	-0.08059507701274	-0.11817002499781	2.44454503512321
O	-3.37303588967947	0.02316698740602	1.75404099145914
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O	1.20988711951604	-1.71756483720484	2.43061918655638
H	0.62174648241197	-1.35192326466627	-1.49896120159829
H	-1.08092249829184	-1.16633213117091	-1.69775724033227
H	0.34955475598539	-3.58931449334347	-1.08298495128356
H	-1.40075504772027	-3.39972399953210	-1.19397971913301
H	-1.22771077158813	0.96333087629149	-0.66940585054406
H	-1.08751349477100	1.18919801593504	1.03643740170546
H	-3.17473778374035	-1.68208352061231	-0.15804746815332
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H	-5.46291891519568	-1.51175887451129	-1.11987721180552
H	-5.42950077699496	-1.00336197707423	0.56125294758846
H	-5.44446037399528	0.83682513267444	-1.87841450568368
H	-6.77258050671847	0.60183238104812	-0.75403488168753
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H	-5.49124986087743	2.70929536350179	-0.27025686174463
H	-3.17556115416566	2.53813789761809	0.62950758431065
H	-3.25610032523682	1.95645369816997	-1.01573710070677
H	-3.79359745878376	1.83967676119746	2.69958473711415
H	-2.10900972613852	1.29482865332224	2.83847881293250
H	-3.38890022328771	0.44702522619292	3.71929740073092
H	-0.37079161611519	1.74154607905381	-2.72307885229201
H	0.65893573309009	0.65636445058606	-3.65349720767484
H	0.94259567845545	2.39495014914999	-3.70118029212549
H	1.94106823307881	2.27799966479908	2.15998636830888
H	3.20252210031735	3.30515519106596	1.48107462365849
H	3.59944123104135	1.69265523234471	2.06929507223682
H	5.59111581763552	1.12916555069739	-0.58503588134088
H	4.99506899638096	-0.54261372567797	-0.61588933949808
H	4.90840582531751	0.39084771057233	0.86634930799345
H	2.70528775108873	-0.32488245597545	-3.75011913057589
H	4.03072499226292	-0.83664093275430	-2.71566440756341
H	4.14576062367565	0.68613157796153	-3.61353886858568
H	-1.38955965457390	-3.92880270280241	1.10597710602443

H	0.32511367447882	-3.55409592703664	1.24763794578249
H	0.83094117842619	4.11092473698793	-0.40090295245415
H	0.12440030923295	3.03765315980372	0.80034424019905
H	-0.48981028356377	3.03831396045962	-0.84903562464744
H	-1.92736564241784	-1.72205954781939	1.89484772953945
C	2.31617386704257	-0.94238856915983	2.86442308873400
H	2.95959136838486	-1.61531872753148	3.42598188041979
H	2.85720428737798	-0.54954210906889	2.00480593244038
H	1.98184957437879	-0.12176276718897	3.50913817235734

E

C	4.20488046962089	1.20823719725429	-1.14037573599365
C	3.20745546463984	0.88076135402955	-2.12403357707271
C	1.95081397895888	1.43870520758570	-1.67271716835278
C	2.17347195761974	2.11726887859145	-0.43405983219171
C	3.55495324602360	1.95423999401391	-0.08688284289040
Ru	2.71248957848145	0.01100005355786	-0.27688136277451
Cl	3.49593576376829	-2.18607238357991	-0.24813833406193
C	3.43798735586959	0.15797428955943	-3.40782520187536
C	0.66522554993708	1.37375914293228	-2.42659107033933
C	1.15883242979151	2.87810752710388	0.35468432882563
C	4.22692778502350	2.51534686897566	1.12140771196289
C	5.65495444871521	0.87010544424108	-1.21275703480350
C	-0.46488505243701	-1.50398890124765	-0.26875773200882
C	-0.24557237607134	-2.99853095783289	0.02056419783203
C	-1.26340043264213	-3.36546028036681	1.12054763467518
C	-1.62704659741872	-2.06671737882791	1.81593104668692
C	-1.16306608364443	-0.89733781271379	0.94349149728312
C	-1.93712622797643	0.39347469603976	0.74678040074391
C	-3.45331575805883	0.29720582478145	0.49320628889092
C	-3.78599698342215	-0.68994987724740	-0.63034355866177
C	-5.27806885663033	-0.71842276847146	-0.96548721701042
C	-5.80566436305645	0.67533338298232	-1.30720610341013
C	-5.49191114157142	1.67131626912000	-0.18943259108375
C	-3.99620590277322	1.68860658268226	0.12302138268068
C	-0.52939767574652	-1.18110370749187	2.28703425060607
H	-0.78340604925260	-0.47378734721932	3.07703761411693
O	-4.14418016034737	-0.23843538520758	1.64421239595765
C	-4.13261962167493	0.51916678131329	2.83493688170957
O	0.76404904699586	-1.69702587260097	2.41471686224504

H	0.48102451529299	-0.99380515569849	-0.50278140188189
H	-1.10089817299604	-1.36014606735594	-1.14403622231046
H	0.77020569670731	-3.16077437489713	0.37009479271615
H	-0.38177502192583	-3.60389537001424	-0.87622816254553
H	-1.50696464704145	0.91788088728205	-0.10955093990351
H	-1.77765892384340	1.05911360870984	1.59872424066753
H	-3.44463676772443	-1.68316351215386	-0.33880208630546
H	-3.21649965908299	-0.39897564249359	-1.51824302629480
H	-5.45077525697880	-1.40363345727806	-1.79933677460580
H	-5.82609130227788	-1.11458903482180	-0.10787412620283
H	-5.34007983208860	1.02229488709049	-2.23751021120878
H	-6.88242319654945	0.63891159855335	-1.49072622240285
H	-6.04955335385686	1.39202049408500	0.70862178164623
H	-5.82231308764966	2.67504318458482	-0.46878549671455
H	-3.77120187576024	2.40435769125841	0.91768900169601
H	-3.44693377178567	2.03306810289282	-0.75856061671076
H	-4.63917156703458	1.48340769906515	2.72457994626632
H	-3.12000775713997	0.69985908989698	3.21061092632818
H	-4.67229351973066	-0.07005107799477	3.57559793353627
H	-0.19143635816257	1.49913301246159	-1.76724861688013
H	0.55381614659603	0.41891010163189	-2.93925723233621
H	0.62519871678345	2.16539127213807	-3.18154001865162
H	3.53345335271335	2.60191851136143	1.95754217316283
H	4.62406919550844	3.51450152905182	0.91444652119923
H	5.05787849685553	1.88660015178738	1.43917033321115
H	6.20775095937594	1.66217719976798	-1.72828899681683
H	5.81306165829326	-0.06281023734988	-1.75049455791190
H	6.08310310901158	0.75315763278500	-0.21813109280042
H	2.54635109344443	-0.38478082781622	-3.71952862979519
H	4.24519756294910	-0.56575546625521	-3.30986023040731
H	3.70166902881748	0.85987983219767	-4.20573356508888
H	-2.17432422287425	-3.78690175964210	0.68700513477863
H	-0.86073715085578	-4.10806358407867	1.81189857716271
H	1.15979497345171	3.93576589732081	0.07284160561576
H	1.36339185123303	2.82315676973308	1.42397861537264
H	0.15431103569167	2.49198556718649	0.19222428493279
H	-2.57051939422933	-2.01445919776629	2.33809329632425
C	1.75162759935879	-0.70135397752481	2.37861579400527
H	2.72154468916033	-1.18813276257868	2.40019303136104
H	1.64357918403484	-0.05722238133768	1.46510064273201

H	1.66015818158771	-0.00020165574134	3.21926146337498

Structures along the reaction profile for Substrate 1g

A

C	10.76351156999318	8.97790887531543	6.95888184718096
C	10.33024771539206	10.42664713279892	7.23564251955217
C	11.18735847063094	11.38521731100543	6.40471753334380
C	12.68672284950087	11.16400808160520	6.61040777841007
C	13.08659586668250	9.71413966254854	6.33877119862207
C	12.25691849848861	8.75402120621720	7.19200947247111
C	8.80777086479200	10.54228011244721	6.88956859183807
C	8.31175932866473	11.90959588641803	6.52804970747590
C	8.44361335067249	12.90334720408701	7.64009088441278
C	8.80750191346991	14.32814352242789	7.23307039956304
C	7.75016278139367	14.98198391095668	6.35833989478121
C	7.40095549108722	14.25650047549533	5.08675868231751
C	8.33273934891005	13.77423731354484	4.14384113094024
Ru	7.35695901294906	12.09578420594380	4.89068657916975
Cl	9.02245671064215	10.85589366558371	3.62417261008289
O	10.58236179554013	10.81021041894906	8.60566119902519
C	10.11228394196841	9.95993923139907	9.62892792388834
C	5.52578388235290	10.89464116248447	5.78419240391469
C	5.16362024725590	12.22342530933470	5.38277429252103
C	5.21552820042683	12.27906763485324	3.92989487769073
C	5.74479326216402	11.07010662649886	3.48117468891545
C	5.96144084342233	10.20727401368853	4.64149209536749
C	5.40774315219248	10.36052923983840	7.17343864099484
C	4.49202306824289	13.22165105857717	6.26858944319748
C	4.73656516495646	13.40909382367231	3.07790902871767
C	5.99093660632559	10.65542645025689	2.07147867003904
C	6.42792323949957	8.79503209549416	4.54902165707328
H	9.15847893269871	12.53799263996205	8.37924052819424
H	7.46529143115345	12.91181254583955	8.14522036400560
H	9.76827022557645	14.31940197978281	6.71932959062303
H	8.93922030625818	14.92577785452958	8.13828620142981
H	8.60271293232107	9.84598728718895	6.08423580429518
H	8.25146020418394	10.20311023488459	7.77106727021990
H	10.93039311629814	12.41119915856854	6.66718288703048

H	10.92114036242963	11.25085809614789	5.35605410411591
H	13.23956615879686	11.83807766952024	5.95169287608217
H	12.95556639964377	11.42755846270570	7.63666746813070
H	12.92347301420741	9.48473745655542	5.28003352505158
H	14.15241977965821	9.57019960356341	6.53387729364608
H	12.49806416560559	8.90899164543754	8.24773198073938
H	12.50983909848118	7.71657500860669	6.95832956719592
H	10.16213935915014	8.28322848556032	7.55144037756918
H	10.52870550886626	8.77366278346994	5.91158068625488
H	9.03518941759455	9.76703991619107	9.55661057245675
H	10.30493251800613	10.47611411923268	10.56883277171598
H	10.63404954443966	8.99864955770193	9.64431771975219
H	4.59689383120849	14.23709183465844	5.89101911674331
H	4.90092028824281	13.19844850159111	7.27814095792719
H	3.42071007508102	13.00804560400582	6.34085493728827
H	5.90917958334136	11.50011153372349	1.38960308890450
H	5.26264850021722	9.89877166886608	1.76375730214243
H	6.98985716910159	10.23156891356572	1.96489224188898
H	5.68310396377844	8.18155843091120	4.03393587118667
H	6.59608422873627	8.35998062001727	5.53303582349373
H	7.35988913542954	8.73811691331342	3.98434188317637
H	4.36704522892018	10.10117693373144	7.38911707730033
H	5.71938760101611	11.09291317017099	7.91836642740526
H	6.00660108659627	9.46293648287056	7.31230803393625
H	6.83246513522955	15.10062993853910	6.94242402556670
H	8.07611611534439	15.99547777124077	6.09358339243163
H	5.37931855560351	13.55954752126375	2.21174624347364
H	4.69826138057327	14.34720337645763	3.62968351598644
H	3.72306734270522	13.21022353415204	2.71751634084903
F	9.66237351820415	13.93305332700814	4.33882671011382
H	6.49216428202444	14.61956472727200	4.62777462799834
F	8.08951132565930	13.98531605974922	2.81524104217092

A’

C	-0.26238926898089	-2.78581541261584	1.08336187833032
C	-1.06959517223596	-3.25675641674461	-0.12945460030921
C	-0.81911727073762	-2.21005104723389	-1.22629810923606
C	-0.54028231087749	-0.87871870818720	-0.52636402550790
C	-0.22706072063927	-1.25380860732245	1.01359524479554
Ru	1.35606812935661	-0.16400981963676	-0.15646638670845

C	1.06967930798860	-0.65337992509900	1.70402016086541
C	-1.55602096745767	0.23283579985530	-0.75551205007528
C	-3.02404685434630	0.16908897704614	-0.24308970790690
C	-3.82988484318161	-1.00898920883104	-0.79672271854322
C	-5.31059261652857	-0.95085595228964	-0.41548499348161
C	-5.95654804656689	0.36314928104355	-0.84881791078284
C	-5.18398905053710	1.55366733223878	-0.28241303269783
C	-3.70713093331608	1.48388503416750	-0.66924223708467
O	-3.06847928771156	-0.00641682860491	1.19056312252178
C	-2.66844454113492	1.08428322597898	2.00268178038198
C	2.58030620356524	0.95253632830338	-1.59917294074127
C	1.45780724124523	1.79549044388474	-1.32611673397961
C	1.50755797117552	2.14827676083147	0.05244085184289
C	2.73340636053313	1.61475518649586	0.60055080665682
C	3.39134140014831	0.88199124912890	-0.39794335335566
C	2.97990535826922	0.40304913555185	-2.92891209263116
C	0.49854266147516	2.31461854501359	-2.34549894216320
C	0.60081693563403	3.10301983475387	0.75707454295431
C	3.24286768609707	1.87291371059150	1.98025125112857
C	4.71001389487079	0.19367365752224	-0.29764599402613
Cl	2.36725903546715	-2.27968902765985	-0.77852245858338
H	0.05162193758927	-2.50109688711167	-1.80999538728526
H	-1.66457912806237	-2.12204454299325	-1.90706272096152
H	-0.76948953515392	-4.25654025920164	-0.44532695247836
H	-2.13013131451250	-3.30083527742968	0.12416513819160
H	-1.61943595464925	0.38116526765608	-1.83605792583439
H	-1.14838759566061	1.15721734099301	-0.35212501225656
H	-3.39922080380402	-1.93846156893845	-0.43465929094210
H	-3.73138931232293	-1.00721078267068	-1.88613125159100
H	-5.83193965783456	-1.79857966121474	-0.86706231760502
H	-5.40132296765220	-1.06118430216296	0.66770797453475
H	-5.96201911545683	0.42404788463011	-1.94353215690450
H	-7.00021239652407	0.40015385201578	-0.52702085625218
H	-5.28151030883438	1.55716664091636	0.80660415422445
H	-5.61075970622388	2.49415487538854	-0.64027273827629
H	-3.16045880839707	2.33754239052046	-0.26183161178657
H	-3.61789864007902	1.55935951569458	-1.75694474507560
H	-3.37508568242972	1.91708515029000	1.95375713570323
H	-1.67119086515407	1.45303188151848	1.75079933397480
H	-2.64473865338718	0.70867809588150	3.02481829075145

H	-0.44748158803212	2.61899439588624	-1.90294845288071
H	0.28760244739858	1.57325061220027	-3.11507868645171
H	0.92605878031733	3.19129594321215	-2.84182086259875
H	2.43292018406739	2.03141072293484	2.68754779882261
H	3.86836401955667	2.77077010339006	1.98016531912451
H	3.84961977316627	1.04589421787936	2.34523168009571
H	5.48137289261082	0.76834509097689	-0.81946585718217
H	4.66050490523288	-0.80029349900050	-0.74068352695263
H	5.01944658425415	0.07930068058867	0.73996138975592
H	2.12214310647220	0.30345548550609	-3.59307418491255
H	3.43043647315770	-0.58152055644395	-2.81988999909846
H	3.70518693939738	1.06570370523910	-3.41217898169387
H	-0.70630026949042	-3.09421441302177	2.03116072837023
H	0.74766470414877	-3.17833362939350	1.03816120305986
H	1.02638223627722	4.11158063069189	0.75556629363416
H	0.44693570879309	2.81210820310691	1.79503302931335
H	-0.37393304869956	3.16265377848144	0.27450295857701
F	1.80213798861108	-1.53543481266867	2.40903192433442
H	-1.03944202560996	-0.77493636860863	1.55018324248801
F	0.73646539534570	0.31919754707883	2.61730957240091

$TS_{A'B}$

C	-0.33058936168007	-2.79988378277527	0.96857582303268
C	-0.98691789497187	-3.26278342410221	-0.34090068523530
C	-0.78852884903920	-2.12325196984522	-1.35386086197864
C	-0.55252439719938	-0.84273422960218	-0.55190765717800
C	-0.28069849269652	-1.26320145629122	0.93620197757408
Ru	1.36412981430513	-0.15804770147910	-0.10666606009072
C	1.07962775450082	-0.72087167508025	1.71536257784650
C	-1.55128698578040	0.28295400089330	-0.77268087678485
C	-3.00832034317056	0.21000583489556	-0.23167778978093
C	-3.78973755071847	-1.01740299056961	-0.70506614297567
C	-5.26182089576398	-0.98157012201497	-0.28894333173632
C	-5.95481785248969	0.29345483852143	-0.76561680262969
C	-5.20199669029582	1.53170045145779	-0.27938261608030
C	-3.73555076038298	1.48290296701721	-0.70647994543143
O	-3.02656561950831	0.10347246297215	1.20923093627695
C	-2.59880661543646	1.22315520865468	1.96443507456817
C	2.56723891166727	0.94496358849489	-1.61663569744110
C	1.44874272391986	1.78775685415634	-1.36866125727667

C	1.47940345453365	2.17026811846291	0.00686627668330
C	2.68126242591399	1.63118802249807	0.58337237736308
C	3.35141305342498	0.87063872879107	-0.39812652961165
C	2.97614505298458	0.36435718394847	-2.92958950316559
C	0.49808405981555	2.28838935927379	-2.40526950736650
C	0.57614679025608	3.15222038241673	0.67770358852956
C	3.17053635849539	1.90787841436517	1.96697375385407
C	4.67402229394377	0.19332090140876	-0.27057327702729
Cl	2.35117908353431	-2.28140200257918	-0.75952154243338
H	0.08006269018734	-2.32995129720596	-1.97530402623960
H	-1.64937490722326	-2.01393133388490	-2.01231046587040
H	-0.54128425691929	-4.19339093261321	-0.69248531834476
H	-2.04998097312058	-3.45267903201152	-0.18432005113345
H	-1.63215388890797	0.43545480219669	-1.85049964797264
H	-1.13833987117039	1.20387706668911	-0.36834065536754
H	-3.31968402306486	-1.91272756837432	-0.30543680338510
H	-3.71826710123063	-1.07029348039822	-1.79500363329823
H	-5.77040830077476	-1.86262791911436	-0.68823545644168
H	-5.32355541953182	-1.04382192254905	0.79992978877171
H	-5.99155475524908	0.30134718513660	-1.86140938558609
H	-6.99013815268803	0.31760835440607	-0.41680943659780
H	-5.26771528039472	1.58589995575429	0.81070421866313
H	-5.66638051599400	2.44091252912600	-0.66964924273665
H	-3.20108145063312	2.37090454350477	-0.36065026599833
H	-3.67917085088992	1.50243036269773	-1.79873843554734
H	-3.26829618521503	2.08016653743345	1.85116406656840
H	-1.58187472667452	1.53332525013462	1.71392872510582
H	-2.61204500654313	0.90760551336280	3.00675487856011
H	-0.45057867379771	2.60379633948245	-1.97659866190591
H	0.29223962888784	1.53358954797089	-3.16293355670712
H	0.93163052965876	3.15507126011231	-2.91361597408649
H	2.34890546127549	2.04471399543292	2.66607262592170
H	3.77093139066968	2.82266864921739	1.97103234125672
H	3.79589799693052	1.09860857052587	2.33984599041669
H	5.45761489239628	0.79478134720189	-0.74193097427955
H	4.65433275993711	-0.78561375442703	-0.74674767101745
H	4.94474046655106	0.04643489176645	0.77387439450993
H	2.13089088032438	0.29091320279545	-3.61288788099453
H	3.38424764288050	-0.63614816641759	-2.79799610284218
H	3.73880528647664	0.99105361115139	-3.40286938159169

H	-0.89133751960236	-3.11487902281176	1.84995700900866
H	0.67156197934875	-3.20443327016195	1.04694143538132
H	1.00811425394126	4.15763870915912	0.64547926779966
H	0.41947296185223	2.89655908803519	1.72491796480349
H	-0.39788913718005	3.20402126321603	0.19301534106466
F	1.71434581553641	-1.68097259553399	2.40391601775335
H	-1.05127836985632	-0.77951001604263	1.52638294138067
F	0.73648378374566	0.20444615754791	2.66984802697421

B

C	-0.43017850187981	-2.98785560769875	-0.22293889848120
C	-0.12091143437511	-2.68659440623811	-1.69671375511544
C	-0.86221125533411	-1.36796355207041	-1.96157841759782
C	-0.94395220111132	-0.69579271422609	-0.59773128611449
C	-0.66346759992187	-1.62465916092483	0.36765269839563
Ru	1.38638377580919	-0.10092907276237	0.33737963096257
C	0.96741723356763	0.01191400340416	2.15343760756063
C	-1.76633426395992	0.55424675154562	-0.41233963344955
C	-3.19425483653930	0.33737932374193	0.14870061535102
C	-3.97842266965914	-0.72063017633170	-0.63277163684325
C	-5.42682703572336	-0.84764516982679	-0.15817202134979
C	-6.15405475092262	0.49616137109599	-0.20198267664694
C	-5.39053352473524	1.55752293275900	0.59118512572771
C	-3.94858359735605	1.67707684244489	0.09906321575530
O	-3.13403060459438	-0.18557161974488	1.48801129648990
C	-2.61700910748231	0.65530390403406	2.50131327138004
C	2.80135438045090	0.35350267414355	-1.48841128074347
C	1.68333187983552	1.16711785616504	-1.71672844192709
C	1.46829908788653	2.00193842344230	-0.56070868473794
C	2.55617516362987	1.77649766033904	0.33761297410186
C	3.34887639433621	0.71292183020914	-0.19017715185479
C	3.39574234361779	-0.66744410416452	-2.39923333098526
C	0.92411611797801	1.29980639641504	-2.99239036169940
C	0.51365910326087	3.15005405130505	-0.48341427348161
C	2.93494786271574	2.64914840429125	1.48857915732145
C	4.65967299879302	0.24243253467169	0.34319075463194
Cl	2.49084319272195	-2.23761950336102	0.63515226052976
H	-0.40480066347104	-0.75796149177816	-2.73357954169441
H	-1.89093368278742	-1.55897441419393	-2.28907230187518
H	0.95406395691655	-2.54124782161601	-1.80452168925462

H	-0.42706882139359	-3.48558081483799	-2.37156562615071
H	-1.86256173597768	1.06382016298077	-1.37278230803980
H	-1.26199992523529	1.25147178711789	0.24883679540900
H	-3.46798345812909	-1.67953127406671	-0.53492393937166
H	-3.96087698992172	-0.44671398432041	-1.69216832397556
H	-5.94919139066001	-1.58221792485684	-0.77617224101460
H	-5.43042500677901	-1.23015245017687	0.86482504645604
H	-6.24942104067902	0.82540979499436	-1.24358252377817
H	-7.16961628916787	0.39039918030952	0.18730088339331
H	-5.39490739029272	1.28670259045228	1.65040332779088
H	-5.88807397250611	2.52720151434937	0.50984454560079
H	-3.40321144573692	2.43432028562484	0.66742883367902
H	-3.94948092988863	2.01842726126224	-0.94056048514571
H	-3.29237220479526	1.48397261976558	2.73587194205007
H	-1.63529690870651	1.06572807562925	2.24797437998321
H	-2.50668707460293	0.03261971133888	3.38769572604163
H	-0.14264831778891	1.44197744402309	-2.82825201843985
H	1.06327931515987	0.44180843333499	-3.64641826350066
H	1.28752462974187	2.18209088298663	-3.52890522870668
H	2.07078956317648	3.13819790932070	1.93081276744101
H	3.61847592572374	3.42698207898185	1.13391313734058
H	3.44312569868079	2.09168066614349	2.27208773106154
H	5.47740618535869	0.78549441708880	-0.14193296596534
H	4.79227948037509	-0.82236363114163	0.16655787632472
H	4.73248497272212	0.40893015468455	1.41661389738506
H	2.73352171596694	-0.89626655802187	-3.23335122222755
H	3.58735774188380	-1.59330668516337	-1.85451675543285
H	4.34580262559313	-0.31589276524197	-2.81235815745155
H	-1.37167735662788	-3.54530133319357	-0.12341829622940
H	0.35135100534687	-3.55455178576684	0.27559979247112
H	0.98184676159976	4.06603482332143	-0.85927767136223
H	0.20130741172219	3.34068925870676	0.54321184695790
H	-0.38159284323271	2.97495646721371	-1.07620615635153
F	0.56019697498589	-0.94621139723547	2.98607413785117
H	-0.94603444597565	-1.50960585372411	1.39834206627309
F	1.10103177839370	1.08172779304641	2.95574422527823

C (secondary carbene)

C	6.53496038427883	10.03341218496046	4.21325836925002
C	5.88145431248520	10.63797193376879	5.36682403885446

C	5.23209311372532	11.80656474994531	4.93841350145830
C	5.47147042089409	11.95882478547087	3.51034535305889
C	6.18957533896025	10.80668182662210	3.06125830518526
Ru	7.40998531439757	11.98919992007644	4.45973953858448
Cl	8.15085006813714	13.18415030948829	6.30273424897043
C	5.96064038463012	10.11064053136538	6.75932370249519
C	4.48178072098552	12.78108804508976	5.78186616595497
C	4.89957511093847	13.03407387546377	2.65090048292376
C	6.50738932519434	10.46751107563261	1.64192994754959
C	7.26017264191505	8.73076261610125	4.21861803115473
C	8.74741077340160	12.17203284044716	3.13382312926098
F	8.71057002154725	12.98867171706813	2.07924332274323
F	9.70283086487906	11.28685964412937	2.84366448640426
H	5.49652524179623	13.18149740579697	1.75251936926014
H	4.85816480657641	13.98221429033630	3.18503128931248
H	3.88039846169693	12.77846585097973	2.34265833308045
H	7.96037797319711	8.66383922734525	3.38766011853039
H	6.55439979579247	7.89780446530411	4.13435563432472
H	7.82350127403066	8.59806430911244	5.14114638086165
H	5.19720516098602	9.34423991562527	6.92302001846353
H	5.81368621212731	10.90183344964768	7.49148320046220
H	6.93372158603555	9.66046390929261	6.95225433698007
H	3.40460958831035	12.60780125195657	5.70193087949216
H	4.68149262956995	13.80519847313439	5.46829456204071
H	4.76494673257811	12.69834285185267	6.82890347919134
H	7.41987055194173	9.87826196075993	1.56386512299317
H	6.63210382992957	11.36186504610160	1.03340488451853
H	5.69334335906146	9.87975953712407	1.20844376663968

$TS_{A'D}$

C	0.31366243852167	-3.14316887067340	1.15238336559721
C	-0.51127142178452	-3.57074456392018	-0.06928881148915
C	-0.38958883233159	-2.41799791427238	-1.08549579200046
C	-0.07460027452454	-1.14062398873687	-0.27109800540229
C	0.15755704610844	-1.62119555477847	1.19888621625325
Ru	1.93598811350299	-0.44543867038160	-0.28812428948795
C	1.36412471040909	-0.81997327554179	1.65192984026523
C	-1.07151436089124	0.00540762358731	-0.45965944849395
C	-2.54449237462840	-0.05661209147828	0.03807246087505
C	-3.33838670146273	-1.26129088183008	-0.47519085356859

C	-4.81906462200022	-1.20745998632651	-0.09280603244634
C	-5.48021109523886	0.08447944132025	-0.56827196471789
C	-4.72098321333225	1.30215729131738	-0.04243193494747
C	-3.24380030941267	1.23600928531107	-0.42897199882793
O	-2.61032684884726	-0.19100156766755	1.47829257343502
C	-2.22126729329841	0.91777899865297	2.26523718331252
C	3.33330240896027	0.76988564188059	-1.46586614406175
C	2.08961772800296	1.50568693956075	-1.23582415012756
C	2.03512307959316	1.80034095592202	0.14506229527330
C	3.23932028945983	1.25960809229366	0.75076012978572
C	4.05409590652667	0.68815791764932	-0.24760726943821
C	3.80710081242392	0.29966930374191	-2.80027268259107
C	1.18672901014009	2.01971817672084	-2.30582102389508
C	1.09290539576238	2.75421451484257	0.80172229578550
C	3.64327794694123	1.42394432879766	2.17826653042161
C	5.37120392152282	0.01354093013359	-0.05926644546288
Cl	2.80386192477530	-2.49838154098626	-1.00573154099733
H	0.39819245131903	-2.64022831763242	-1.79935230724857
H	-1.30585474972849	-2.29665640974294	-1.66072015225444
H	-0.16193430532661	-4.51934809503007	-0.47930674775214
H	-1.55492251043712	-3.70974940822330	0.22285416201728
H	-1.12307628528359	0.21726917362165	-1.53138974691221
H	-0.65566129970696	0.90527378785509	-0.01006657479664
H	-2.89439180065747	-2.17273973063697	-0.08135064653942
H	-3.24456178336687	-1.29636921740384	-1.56411218279176
H	-5.33226025588621	-2.07504785888398	-0.51570065240424
H	-4.90713353929031	-1.28249215244416	0.99344395513040
H	-5.48687315015804	0.10907498964872	-1.66457436596988
H	-6.52437901762731	0.12014364269887	-0.24710984248021
H	-4.81714096953865	1.33965489798081	1.04597723827201
H	-5.16030151110399	2.22518439043393	-0.43018570355331
H	-2.70554136543013	2.10805623184499	-0.04895482100054
H	-3.15750593913808	1.27802693601110	-1.51875958096996
H	-2.93751681220865	1.74273536562143	2.19952292424725
H	-1.22846280515914	1.28863428383129	2.00633169561762
H	-2.19281229799431	0.56528465322811	3.29572108461253
H	0.19250961828349	2.23400016053623	-1.92021749080029
H	1.08344039278403	1.30228008308747	-3.11963060141861
H	1.59125430196282	2.94443174429075	-2.73054702376331
H	2.81446328469832	1.74329190831365	2.80154989116469

H	4.43061520020884	2.18095064355117	2.23988052844214
H	4.03870247920692	0.49799683240983	2.59253819162113
H	6.18133541570869	0.60486703583947	-0.49535610731914
H	5.37325964050349	-0.96783690832873	-0.53601387130850
H	5.59211135876059	-0.12950387453328	0.99694772397453
H	2.98429212715556	-0.07190273504697	-3.41033570200742
H	4.53680701875466	-0.50014493070134	-2.70272549553089
H	4.26987310535531	1.13280494347377	-3.33950829711211
H	-0.03072387751879	-3.60560732787382	2.07801767179249
H	1.35651460059464	-3.41728309461721	1.01182623509158
H	1.53795476888304	3.75412337356333	0.82770890683173
H	0.86566769058851	2.46426947911074	1.82360724681295
H	0.15537801480844	2.83161984199672	0.25431237406616
F	2.31721027758331	-1.49606806238917	2.35694747930779
H	-0.68508436465755	-1.33134226414917	1.83049413596776
F	0.98419450816046	0.21563745354974	2.46934896591504

D

C	-0.59420447260974	-2.68672600338069	1.20271170080391
C	-0.56907385426307	-2.91316514695610	-0.32560641695113
C	-0.37825227732744	-1.52626322859400	-0.94406962703082
C	-0.70975900052772	-0.49368801686364	0.05805848763867
C	-0.65546702192566	-1.16304148112813	1.44494181112316
Ru	1.42044411563257	-0.22265899144685	-0.12110900032583
C	0.65657957600723	-0.53790092032586	1.81901611160666
C	-1.67605255157076	0.61687939089727	-0.24269100232511
C	-3.18204848564663	0.34280900696662	-0.01104958220572
C	-3.64141134692152	-0.95507057803201	-0.68075940970997
C	-5.15331234005821	-1.16701740066568	-0.58167995248854
C	-5.93167570737928	0.02837867835313	-1.13121455728574
C	-5.49232500355482	1.32749224485108	-0.45408958110066
C	-3.98345003421781	1.52510312172056	-0.58711982486511
O	-3.48699034246196	0.14332888762869	1.38168273769066
C	-3.22788707914542	1.20942275415750	2.27714619947865
C	2.61491405101169	0.85581613796799	-1.84094199378941
C	1.49348302600020	1.63543249702585	-1.38519883280266
C	1.70272650033790	1.95934099865150	-0.00560223371301
C	2.90422094612494	1.28846103011038	0.41464428988491
C	3.48894986308507	0.67506276185847	-0.75451038643992
C	2.82531502936473	0.37018813602746	-3.23780122928958

C	0.47573479212210	2.24393983441777	-2.29511816821609
C	0.96706482274434	2.99860975332267	0.77229847464867
C	3.56173308452128	1.39671994966266	1.75112582854188
C	4.80481438745415	-0.01882085956064	-0.79254135853153
Cl	2.70128462516517	-2.23240727453995	0.24307860144262
H	0.76344139131451	-1.46324148094512	-1.26209178171503
H	-0.83275892996864	-1.36729562617919	-1.92153366468973
H	0.22048027572633	-3.60180381438036	-0.61951766744797
H	-1.51729925813754	-3.32085051098096	-0.67987971198969
H	-1.56792169108368	0.90410079676333	-1.28755804832031
H	-1.41321811427255	1.49478711251533	0.34631435068458
H	-3.12036707337647	-1.79238380378490	-0.21755989550462
H	-3.33981450868733	-0.92526441770833	-1.73271732978935
H	-5.42900963136144	-2.07847816897456	-1.11819226549742
H	-5.41771786081349	-1.32107115309450	0.46666930190690
H	-5.75903772508422	0.11073052937965	-2.21107422454363
H	-7.00515754874745	-0.12561498690374	-0.99672751697330
H	-5.76368846294206	1.29355333417976	0.60433400453121
H	-6.01633882932303	2.18170982751033	-0.89023086041776
H	-3.66805126027253	2.45814219708943	-0.11410712768184
H	-3.72354946295867	1.61860808591306	-1.64598913716882
H	-3.79186347912153	2.11226248536626	2.02374760358124
H	-2.16392371204716	1.45498666048312	2.33682234424589
H	-3.55393599268135	0.86385988773274	3.25721256147458
H	-0.34011399601649	2.70025054470212	-1.74115084815617
H	0.05216556125375	1.51230384751446	-2.98416397933333
H	0.94264716037231	3.02680374867489	-2.90054057894406
H	2.82891686411072	1.59822688317499	2.52918156947822
H	4.30240687719285	2.20245502265907	1.75667222003570
H	4.06665179305432	0.46724786388028	2.01020423361269
H	5.58618635740475	0.70520570891090	-1.04683828730465
H	4.81952247356810	-0.81424894995578	-1.53465897660486
H	5.04682910052901	-0.46227808554453	0.16952937898739
H	1.87673897635860	0.18976883614440	-3.74342309778947
H	3.39592223863249	-0.55753471942584	-3.25219171663060
H	3.37571024534589	1.10878211595526	-3.82917497598231
H	-1.46264309511493	-3.16708042396834	1.65199776756507
H	0.29300525178222	-3.10666253713187	1.66932050101819
H	1.41338408256089	3.97920229762296	0.57826383586658
H	1.01580015636388	2.80575846827178	1.83920015605101

H	-0.08232026651190	3.05617504254985	0.48963104991935
F	1.39905914445847	-1.22248820665068	2.73900552457272
H	-1.46244808980499	-0.88861342556497	2.12045383355344
F	0.37688073633707	0.68138373207366	2.46656636961118

TS_{DE}

C	-0.56285381462822	-3.06083153953292	1.01047263441274
C	-0.55214932485141	-3.03428737452206	-0.53356185462179
C	-0.40469931603195	-1.56147060667888	-0.95345688159437
C	-0.65488660918489	-0.69997384451767	0.27998849693064
C	-0.90959530265441	-1.64428543727767	1.47293480234017
Ru	1.58118177543643	-0.14203350828747	-0.40705186374989
C	0.21840069625243	-0.76673590399073	1.74779929121584
C	-1.52824556139036	0.53000167156624	0.09408513628669
C	-3.05724593169739	0.35962300342551	0.25555173219194
C	-3.60659352962660	-0.85402045380788	-0.50156608943949
C	-5.13230445750595	-0.94395033015116	-0.44401172942729
C	-5.78969921402602	0.33682504138485	-0.95694499540624
C	-5.26511203599405	1.55957391978635	-0.20346877647436
C	-3.74011775001841	1.63419104801234	-0.27350520541149
O	-3.41243059627891	0.10995946069094	1.63233255671996
C	-3.24372756543774	1.16448551639442	2.56259839564991
C	2.76635804870222	0.80002638154674	-1.91087433691506
C	1.56114921447004	1.58147212271441	-1.70640644146280
C	1.55730864828766	2.04742232641091	-0.35964236377509
C	2.73314564091095	1.51860149660470	0.29169810159025
C	3.50179934556049	0.80651174830635	-0.68527119110483
C	3.20951092450760	0.18290126650074	-3.19557481635346
C	0.57852516354657	1.93053414983763	-2.77513606428271
C	0.63327883104136	3.04836483826891	0.25018622781206
C	3.13451376571752	1.78553325157956	1.70392891978031
C	4.83193927130940	0.17547572705988	-0.45749979278834
Cl	2.67038423710259	-2.32285987115539	-0.18999340133271
H	0.57309114808608	-1.42096118170558	-1.49331901382662
H	-1.13192725186114	-1.26495319067381	-1.70743811099831
H	0.25902135817420	-3.64085677738089	-0.92803812278395
H	-1.49329319139361	-3.41909334808055	-0.93094014864493
H	-1.34324221233770	0.90888633728946	-0.90902870065553
H	-1.21414316031540	1.31709560011094	0.76902686932521
H	-3.16545846566311	-1.76349010525475	-0.09410809915026

H	-3.28691525907547	-0.77890822130744	-1.54515604809910
H	-5.46748517744485	-1.80361188427950	-1.02958931634096
H	-5.43761437187227	-1.12176184220450	0.58933355095463
H	-5.57515347362758	0.45317692160633	-2.02591143042855
H	-6.87610495268695	0.27024192157975	-0.86100170206571
H	-5.58341595176871	1.50114334236494	0.84061943152881
H	-5.69590928129842	2.47590571072915	-0.61457160277541
H	-3.36652841220712	2.50911456701470	0.26384531559648
H	-3.43444321607655	1.76406882753643	-1.31593591949304
H	-3.95621927472303	1.97786915564749	2.39620550172504
H	-2.23002790457135	1.57126917253605	2.55761436665530
H	-3.43284824068713	0.73364037374035	3.54481011486462
H	-0.36737435852861	2.27157406003313	-2.35645352427629
H	0.37212823087304	1.07647585007465	-3.42107192716278
H	0.96700194364568	2.73415202584738	-3.40855350035372
H	2.26245114924642	1.87325525741018	2.35058911936306
H	3.70458595247766	2.71784085902413	1.77615370237554
H	3.75467627634750	0.98027066695451	2.09382891766123
H	5.62477519112066	0.90026385199740	-0.66883046555407
H	4.97263670858229	-0.69341290288986	-1.09556539814455
H	4.93863792423091	-0.16039660169721	0.57190591734296
H	2.35767587112816	-0.06591240990251	-3.82849630225278
H	3.76584730868764	-0.73494217518152	-3.01279212370616
H	3.85305222243026	0.86779288479132	-3.75729937296184
H	-1.29424623492595	-3.76776408004883	1.40014064618604
H	0.41783880788963	-3.35372069472963	1.38046750889172
H	1.11257996189161	4.03238696307123	0.26579351992540
H	0.38512359135315	2.79171638227687	1.28002462130280
H	-0.29437537489288	3.14548504826018	-0.31007915061308
F	1.36455760774115	-1.27484115412241	2.25073113065785
H	-1.81165701276619	-1.48616226167729	2.04861798111381
F	-0.06520702870096	0.34773095107105	2.48627227402652

E

C	-1.17620703653748	-3.08935683965288	1.05702800605771
C	-0.47776213187112	-2.98944815742721	-0.31444609413182
C	-0.81899211553679	-1.59480545620703	-0.87393917561545
C	-1.22288127702915	-0.70859092081157	0.30385505249101
C	-1.37965039625273	-1.66612681457653	1.53439961753073
Ru	2.61129328278189	-0.17931509594847	-0.32065291459966

C	-0.27682646342852	-0.70441468188653	1.43863902788704
C	-2.09125792892529	0.50613776078440	0.03603333662727
C	-3.60873118934929	0.35041688136620	0.25607143227396
C	-4.17250148504040	-0.87900567321063	-0.46415040316909
C	-5.69370059307949	-0.98401701794040	-0.34454136961579
C	-6.38581017810304	0.28582242959992	-0.83980902495000
C	-5.84316697142511	1.52194349622402	-0.12113058622486
C	-4.32353568541583	1.61184324161575	-0.25733646900433
O	-3.90293443786444	0.11083841203830	1.64877310459783
C	-3.65760975418233	1.15984385938779	2.56701633118028
C	3.40421926086197	0.87489376118495	-1.94719941360448
C	2.12590615543871	1.45523754011563	-1.59512362613847
C	2.21106203491790	1.96495122968387	-0.26021931170379
C	3.51564922517226	1.66155919606025	0.24215954129413
C	4.26719646033757	1.00484750355807	-0.80638744570502
C	3.77094327992564	0.29528064433065	-3.27148409662100
C	0.95267915998096	1.57636052931011	-2.50867051213607
C	1.14544405071436	2.71174077410010	0.47064136499897
C	4.03598060905039	2.01680849536417	1.59446372785794
C	5.69231119571286	0.57348851074319	-0.72592759211970
Cl	3.20028173544717	-2.42564811868909	-0.54551645400392
H	0.02402878908241	-1.16824324220834	-1.42424655717324
H	-1.66304826822883	-1.63880508265023	-1.56276614548844
H	0.59912086822563	-3.08882256545747	-0.20035582098584
H	-0.80434145938981	-3.78033768559152	-0.98935713696224
H	-1.93870508512304	0.79979557122107	-1.00477990687271
H	-1.74645867902682	1.34941438268335	0.63436818320717
H	-3.70131115389030	-1.77476625580771	-0.05922360515094
H	-3.89151244877728	-0.81380100426921	-1.51962951111218
H	-6.04375703309821	-1.85169209116397	-0.90932428688423
H	-5.95530566910764	-1.15661807653611	0.70170238387851
H	-6.21840441388269	0.39456486462873	-1.91795625072927
H	-7.46645079272465	0.20880050321351	-0.69695728513938
H	-6.11412586470793	1.47056616294912	0.93682161164800
H	-6.30223410939348	2.42903278423776	-0.52201755811228
H	-3.93718342965982	2.49689161707057	0.25382469917850
H	-4.06224420856816	1.73308339643552	-1.31289684169446
H	-4.31503872880135	2.01861773012945	2.40114900266224
H	-2.61847630033475	1.49958097804052	2.54958126001259
H	-3.86746382364155	0.75134097484150	3.55479352054391

H	0.01941518807374	1.63394508786294	-1.95070148632384
H	0.88693097068085	0.72506235444128	-3.18573002794458
H	1.03159691975641	2.48168847477374	-3.11954724181545
H	3.23470013460724	2.03872805102985	2.33252365884472
H	4.50666705791643	3.00558590276360	1.58098255039121
H	4.78206325577599	1.29830370816716	1.93223333223847
H	6.35856764307962	1.38500691463517	-1.03642481160408
H	5.87844379906993	-0.28581573542287	-1.36763024256562
H	5.96053873364454	0.28867889143353	0.29079435671400
H	2.90449189872037	-0.15021181342009	-3.75923205121795
H	4.52213526420675	-0.48498977809729	-3.16290669282019
H	4.17214266093011	1.06815582045499	-3.93528194408667
H	-2.16066600283602	-3.55480123539446	0.96802013336139
H	-0.59852791772392	-3.68681320545989	1.76435031189949
H	1.28891396679500	3.79175641633612	0.36246746890344
H	1.14909159760369	2.47834673418737	1.53413603273598
H	0.15635268225493	2.47119170528037	0.08507391571270
F	1.03404810594961	-1.11672680999744	1.28893090697879
H	-2.13421580667866	-1.45098311648952	2.27658750359149
F	-0.26764414707885	0.35642118203182	2.28827351872761

F (cyclopropanation product)

C	7.92432827998223	15.48541355375569	5.77420810497634
C	8.51007611072068	15.48509035398042	7.20031779344095
C	8.98439887676562	14.04255234696128	7.45799183975719
C	9.29344401333167	13.42007628701306	6.09906793793697
C	8.63657028635046	14.36701510902512	5.04137313207911
C	10.10101943399163	14.24105252859513	5.16605750038052
C	9.25724030445791	11.91818566653094	5.93700912230000
C	10.28117730417043	11.12048419659452	6.76796391615704
C	11.70483068685927	11.64616282063905	6.55638059737773
C	12.75838627363543	10.79739768438839	7.26901177310259
C	12.66714663260856	9.32715338047766	6.86111916312193
C	11.25640742406883	8.78383022771188	7.09137236399046
C	10.21578340839005	9.63760085593630	6.36707136252201
O	10.04493987252489	11.29675278473733	8.18295880153017
C	8.88682825774898	10.70959653672965	8.73664087093514
H	9.83165480271439	13.99413464761954	8.13992283711270
H	8.18349314705151	13.45320943071404	7.90950772749946
H	9.35231889716401	16.17205072531842	7.25582226660182

H	7.77748625766705	15.80802484327877	7.94026744382906
H	9.42082763042496	11.66889167468404	4.88799396758478
H	8.24958430091201	11.56722149517682	6.17837297662369
H	11.75708907943410	12.67805041041876	6.90615601933739
H	11.90560157825477	11.66462114179951	5.48247235802466
H	13.75272452488918	11.19198391330424	7.04572688384097
H	12.61528303494511	10.88394517476480	8.34864059022662
H	12.92186235519674	9.22740510473099	5.79941620631603
H	13.39696924761710	8.73255301050991	7.41638776661047
H	11.04535278712304	8.77765922398126	8.16433262471967
H	11.18428023042970	7.74841541983555	6.74878044902897
H	9.20808181645611	9.24768453844290	6.53123899128216
H	10.39116232456340	9.58045619297089	5.28880414045037
H	7.97123687757914	10.99661626063771	8.20893021118817
H	8.81938834226660	11.07443153138206	9.76115592481076
H	8.94403013178656	9.61655488296667	8.76013912406436
H	6.85593924803172	15.25601442395035	5.79345581619700
H	8.03979886859044	16.45292251524117	5.28227130719535
F	10.88977621529908	15.26355497891515	5.59540582165650
H	8.19856809570320	13.94853231446197	4.14335284845863
F	10.75560604029321	13.60922081181777	4.15095241773212

Structures along the reaction profile for Substrate 1j

A

C	5.86129459575891	10.25795450816250	4.60456277899770
C	5.47288500804508	10.86210710591403	5.81621717409795
C	5.03779749366903	12.19243568942261	5.51793454124698
C	4.99379067825580	12.32924305514698	4.06943428782784
C	5.53569553979385	11.17356265208737	3.51410533639731
Ru	7.21127071826977	12.10926648193710	4.92403789839728
Cl	8.87458955390385	10.90756674188277	3.56763600526499
C	5.43777171075083	10.22692856382241	7.16665634580755
C	4.36654159713241	13.10837464763203	6.48725259048832
C	4.38745850787339	13.47503498004069	3.33181820301983
C	5.72854213693863	10.87002823685272	2.06781900666735
C	6.33948969550593	8.85980984746082	4.41123798357319
C	8.19459013671027	11.88393064876563	6.52769843885702
C	8.25716299289124	12.83504711791766	7.68684559735155
C	8.51042014356289	14.30322680128005	7.34600099963768

C	7.42398236834867	14.91499885581129	6.47821054132788
C	7.24141288199967	14.27576526150166	5.12857844467903
C	8.31276513275149	13.88449770399015	4.29910728386036
C	8.23303856104905	14.03990992765549	2.83356792747243
O	7.21745566745696	14.19027483528437	2.18340285173821
C	8.81434863376644	10.54984264863004	6.81925891069627
C	10.35249389626097	10.55653318772654	7.10290531395272
C	10.90183913054103	9.16234416785941	6.76123960886778
C	12.41754285328696	9.06777894022429	6.93087606971021
C	13.12389433307423	10.12456019325186	6.08084104182754
C	12.60773892933029	11.52369084554004	6.41549531410163
C	11.08762300718757	11.61282287739643	6.27225339887592
O	10.62954599876576	10.92118821383606	8.47355042343606
C	10.27852833914820	10.00333166181258	9.48648486848710
O	9.46454929335382	14.01817396663784	2.28850581167512
C	9.53527141836172	14.05306241584609	0.84602844993206
H	9.00455716849090	12.49373766915753	8.40531522352542
H	7.28601720728695	12.75092590397913	8.19663205664094
H	9.48236700805615	14.39630041383426	6.85669677639169
H	8.58684001692647	14.86645448493935	8.27909482643257
H	8.63769280839315	9.87036224583800	5.99270291544271
H	8.32455585629478	10.13122612819928	7.70604209423460
H	10.74969703216554	12.60206572847273	6.58320177342770
H	10.79309721907653	11.48257745231837	5.23028482058940
H	13.07293941602553	12.26434755516789	5.76018772138935
H	12.89126717489303	11.77940263187599	7.43966461595432
H	12.93984981374361	9.91385018316898	5.02165280173796
H	14.20522549766662	10.07198411938715	6.23173391049119
H	12.68604547551984	9.21146482506610	7.98154657307889
H	12.75308275006111	8.06547565417997	6.65236166563661
H	10.38961376639423	8.39927872802827	7.35324998044660
H	10.64316717423503	8.96844411482085	5.71765183474794
H	9.22097223665264	9.71683130168821	9.44892256256125
H	10.46300746900761	10.50783782172904	10.43435632263361
H	10.88390130180375	9.09287050128675	9.45122542063253
H	4.42913314068475	14.14796778935261	6.17130319141071
H	4.80458775837823	13.03343383964985	7.48192304685666
H	3.30438432735329	12.85696581699636	6.57517455514171
H	5.66940371279392	11.77671156867495	1.46834917389402
H	4.96370400100241	10.17236396505739	1.71251425945048

H	6.70601108936245	10.41707226601654	1.90019991238946
H	5.53679176699488	8.24290369943079	3.99597246436409
H	6.65562928180335	8.40878617159926	5.35074940027804
H	7.18367579670928	8.83296759299056	3.72290065070856
H	4.42492642983981	9.87666978229499	7.38691173148635
H	5.71670668104058	10.92717161982254	7.95367504558989
H	6.10308265618678	9.36838548471176	7.22665703595688
H	6.47513066845651	14.88589674662687	7.02003432347462
H	7.64453879257333	15.97796928750365	6.31815622087519
H	4.92189633942373	13.68455036160579	2.40940782947270
H	4.38995126191519	14.38712072742870	3.92718149897718
H	3.34298689500400	13.24878029568469	3.09500335589397
H	9.32262752622620	13.85057957960318	4.67867871244297
H	6.37440598511437	14.64192700935906	4.59360516374342
H	10.53417869446771	14.43408208594722	0.63739033685820
C	9.33308143031497	12.67307079844323	0.25183520104946
H	8.79417674045143	14.75931765634585	0.47313675013462
H	9.47211037256128	12.71766876585774	-0.83128716619760
H	10.04617851222761	11.96461300880929	0.67219588610618
H	8.32843479267502	12.30864683571862	0.45908507537361

A’

C	1.22681535858602	-0.34993117441757	-2.19377219233018
C	2.48713488197212	-0.08629282076139	-1.57251741797525
C	2.94193721510694	-1.27936437775768	-0.94479153993387
C	1.95843718257831	-2.30955685015466	-1.20655661872614
C	0.93104998252099	-1.73746419615828	-1.99466947638566
Ru	1.08679193047449	-0.72291138637662	0.11449336682463
Cl	1.78611987677028	-1.91371024271608	2.12956987668277
C	3.24785737774042	1.19242295721805	-1.68723498791739
C	4.25169326325307	-1.49002973621508	-0.26080451954504
C	2.09253271476059	-3.74262503612921	-0.81346815528265
C	-0.19186937240454	-2.50063227488420	-2.61763121798284
C	0.49747780463596	0.61282018008947	-3.07241035101976
C	-0.87235758250326	-0.93488026581517	0.56411952794347
C	-1.33889672136554	-1.96266050486652	1.58691752478755
C	-1.33931419812436	-1.31533673669775	2.98194314354441
C	-0.67608003089159	0.07104757664747	2.86892703262712
C	-0.34430395645510	0.42009964552687	1.40097641279198

C	-1.87120072432699	-0.62975307000624	-0.53782106630005
C	-3.19000738226873	0.16475064924163	-0.27165045471569
C	-3.99408826317490	-0.32202080747862	0.93644373860574
C	-5.34719453096257	0.37955927189707	1.06759635788605
C	-6.18499596080186	0.22722613197001	-0.20011344468919
C	-5.41296600479357	0.73212809143989	-1.41842308083568
C	-4.05780403265750	0.03484170428007	-1.53919287275535
O	-2.90259822809685	1.54214406655204	0.03466027743381
C	-2.46979142660162	2.38749671951058	-1.02139860289907
C	1.10121453709283	0.95316098066953	1.26960384923066
C	1.27770524105394	2.24479094748760	0.58478001341045
O	2.40345594202239	2.86458952700042	1.01060670904517
C	2.68657338296313	4.14993599433546	0.41957693301098
O	0.55152278988756	2.72188926751684	-0.26487659198116
H	-0.64826569638497	-2.80303915402029	1.57173076141450
H	-2.32438041505044	-2.34327190135566	1.32420635414700
H	-0.78241488880757	-1.93489642360685	3.68175772970035
H	-2.35743245052104	-1.22685894276202	3.36277498110696
H	-2.17637824355717	-1.59383247809427	-0.94712727736342
H	-1.36719621435021	-0.09199929888682	-1.33577881804168
H	-3.41096404166157	-0.16008443811889	1.84020144202981
H	-4.15361532747217	-1.39872561727699	0.83874724649510
H	-5.88192103751790	-0.02909584043648	1.92872611310230
H	-5.17923984877304	1.43994500991866	1.26868679757244
H	-6.43878823660465	-0.82960485066355	-0.34485660227726
H	-7.13028604966879	0.76633696347386	-0.10030107462311
H	-5.26825898062482	1.81144649173367	-1.32644206393051
H	-5.98878200832390	0.56811376988346	-2.33294295002979
H	-3.50729191329715	0.40470032982372	-2.40722395620740
H	-4.22169633612377	-1.03247257622572	-1.71380901308023
H	-2.14033364829130	3.31146366207841	-0.55288931100928
H	-3.28017650167618	2.60611980616496	-1.72219454420823
H	-1.61905486465424	1.97573601408216	-1.56313353538765
H	4.67311466663970	-0.54614239213532	0.08307657254914
H	4.97130175150486	-1.95271528359927	-0.94407976502915
H	4.13587043862530	-2.13403735292285	0.60901747872635
H	0.16977408451982	-3.02203203243249	-3.50896848192865
H	-1.00724413035379	-1.85178491929535	-2.92833807406100
H	-0.59465457132741	-3.25309020933813	-1.94058778867512
H	-0.51636245324606	0.27777221119027	-3.28626900380321

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H	0.44011173367465	1.59827227263148	-2.61090505758165
H	3.85908194958382	1.37947876099001	-0.80633405373191
H	2.57822750359260	2.03867340731265	-1.82579232243477
H	3.91364277423822	1.14985567973694	-2.55477317086769
H	-1.33701361481593	0.85831686337208	3.23756392594815
H	0.22864247396218	0.09717362794779	3.46756863648080
H	2.47599593633131	-3.82855932518070	0.20188253800245
H	2.77816763653146	-4.26380546881317	-1.48919910394567
H	1.13220578555923	-4.25589114808716	-0.84980838516283
H	1.66020140923691	0.88008274520408	2.19362465624516
H	-1.00124924028266	1.17359615734228	0.97479765528022
C	4.00628225097961	4.62802626314966	0.97983636991023
H	2.71971304596232	4.04576728042633	-0.66520221009984
H	1.86895850740801	4.83141124609769	0.66066313392707
H	4.25157590931093	5.60638041058759	0.56221682757193
H	3.95912594150974	4.71861070984367	2.06570746578961
H	4.81016294651713	3.93503437902983	0.72746676589053

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C	1.09506569965775	-0.38567930449885	-2.08305567099831
C	2.38397274933212	-0.06645431919827	-1.57177428607140
C	2.88304324679532	-1.22094717886497	-0.87411328480336
C	1.93707733166129	-2.29912217053489	-1.08747107633096
C	0.86128160680851	-1.79269562404057	-1.81976122601684
Ru	1.17137698883118	-0.48945105773799	0.22484786019874
Cl	1.88976198436888	-1.67982367247632	2.21264425998781
C	3.17271812954074	1.15815256295929	-1.89723546067185
C	4.24518795576408	-1.38500774610257	-0.28552409856356
C	2.12433709436007	-3.70006451762304	-0.61221231030660
C	-0.26520245987789	-2.61784888976143	-2.35457247441845
C	0.32080204786887	0.49144003336452	-3.01596989607421
C	-1.19140278762150	-0.78717728151595	0.70701961178635
C	-1.37328806632162	-2.08272479849727	1.49309487342093
C	-1.24954500180285	-1.67843861891217	2.98293225549397
C	-0.80012030616307	-0.19527074259207	3.00079337996810
C	-0.83363333063553	0.23572040630553	1.56232525722222
C	-1.99898148621408	-0.52512555161905	-0.53988879029635
C	-3.37051075531669	0.16261288755419	-0.31403134612327
C	-4.23678495996388	-0.55736925482306	0.72389855534578

C	-5.63216163250667	0.05715036875806	0.84931235492956
C	-6.34942047243497	0.10805291111777	-0.49975167225684
C	-5.50058004044011	0.83211949883135	-1.54589008899824
C	-4.11605231851632	0.19618577491919	-1.66098981588996
O	-3.20831144852577	1.48543465026269	0.22484754637596
C	-2.52964184433691	2.44755636432906	-0.56647563460855
C	1.47338353000364	1.15556134162494	1.07827897832793
C	1.70741833733897	2.46831421918047	0.44039665696256
O	2.85419874696976	3.03501029694323	0.86792868856027
C	3.18312772729032	4.32493140722946	0.29830116283314
O	0.96195503530564	2.99528177773270	-0.35952523669744
H	-0.62267354573702	-2.82393574918203	1.22155895357785
H	-2.34941474295251	-2.51564465395151	1.26954037401773
H	-0.52902563869837	-2.30600762096060	3.49930155731162
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H	-2.18995656089761	-1.46272158396514	-1.05554877042774
H	-1.44245579589271	0.10464589431393	-1.22435492918159
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H	-4.32340122688847	-1.60771414771787	0.43037142205663
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H	-7.32045818263448	0.59830753347574	-0.39435968971827
H	-5.39612013382819	1.88267036053019	-1.26174306043565
H	-5.99677370216872	0.81363268510687	-2.51959561983601
H	-3.51207296915076	0.71105561671558	-2.41174052095961
H	-4.21934083101489	-0.83620595489644	-2.00866279060846
H	-2.52655064213184	3.36699428132103	0.01719762612284
H	-3.04185772060138	2.64123068395829	-1.51344716722552
H	-1.49135552846668	2.17518168422593	-0.76976186235549
H	4.66240443062628	-0.42450975850660	0.01358558155520
H	4.92531149708522	-1.84054754469181	-1.01276572332843
H	4.20856072501871	-2.01699481820854	0.59976235287775
H	0.11232535703838	-3.29393778918610	-3.12675231556655
H	-1.03861787053355	-2.00492790000229	-2.80964720331468
H	-0.72719297062441	-3.23410956792801	-1.58276850190478
H	-0.70220105288644	0.14495791573255	-3.15039323394629
H	0.78779990542754	0.50488272875394	-4.00638486745658
H	0.28436705541071	1.51716055032060	-2.64986799335537
H	3.86594063425843	1.41687039014298	-1.09838182243835

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H	3.76219271365777	0.97875514000137	-2.80170749246030
H	-1.49872803522256	0.43736657289202	3.55650243149738
H	0.18129146724073	-0.07702258724109	3.45854177909821
H	2.38866438124466	-3.71291552553003	0.44611064412824
H	2.92768894827258	-4.19134502416273	-1.16973579867716
H	1.21777743115501	-4.28998365402102	-0.74293672163000
H	1.51289899557569	1.22936359012035	2.16892018960126
H	-0.98206003432780	1.26880269754548	1.30066474789749
C	4.51110830637011	4.75208328266258	0.87789010758256
H	3.22153650616444	4.22853552484488	-0.78754300594288
H	2.38306238907162	5.02508724739456	0.54238684870129
H	4.79193713225754	5.72651873332888	0.47375835611260
H	4.45426116202946	4.83267104451182	1.96414534469111
H	5.29481717301038	4.03626512429395	0.62650824307271

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C	1.21656433781261	-0.74882450324065	-1.91002498058393
C	2.44799656897430	-0.25570542643461	-1.39522660062148
C	2.95615251898012	-1.22979849215780	-0.48451031932029
C	2.10174685865252	-2.40457245714786	-0.55837361197128
C	1.06703392528757	-2.11282821816634	-1.45054628194862
Ru	1.07921171013257	-0.43572895716355	0.38365576963648
Cl	2.08002364442979	-0.95417848620187	2.52367345847038
C	3.20955785684245	0.92389291284651	-1.90143641698264
C	4.29835825961293	-1.18998255667745	0.16552977916797
C	2.35999429132614	-3.67877200548208	0.17333578380268
C	0.07408018374054	-3.06760020922121	-2.02002199850146
C	0.43089593768511	-0.10882886614353	-3.00938406359250
C	-1.26978865068951	-0.90489999464266	0.56149437000198
C	-1.55326397053166	-2.38749977243766	0.79678427721867
C	-0.93619956848545	-2.69451153294530	2.16822457549530
C	-0.97248160246760	-1.34251714824403	2.89038518227924
C	-0.89353314135589	-0.34630436905911	1.76738998512230
C	-1.97102891754483	-0.16963943576446	-0.55627154530389
C	-3.32107422471358	0.50275795250690	-0.18814954409794
C	-4.31141170814665	-0.46235412377310	0.47052118126996
C	-5.68644398985596	0.16775194236029	0.69921806166817
C	-6.27315715010502	0.72892513411488	-0.59531912804298

C	-5.30450623937485	1.71572552715415	-1.24740441814470
C	-3.93805153818408	1.07150176915168	-1.47847494040626
O	-3.12430093335246	1.52757284081612	0.80078786750404
C	-2.42342652529162	2.69409908083461	0.40509746594726
C	1.02398546314031	1.39535901287281	0.73012145076165
C	1.35692631953953	2.52401178073687	-0.16267732713491
O	2.41784277175988	3.22470847207723	0.28074035008186
C	2.79392960370959	4.38699835122793	-0.49714054840696
O	0.73021280590895	2.82523088577172	-1.15902011159440
H	-1.19902316228862	-3.04164776870439	0.00932612939274
H	-2.64014234917202	-2.50826084696146	0.83134688026744
H	0.10181530724329	-3.00607104229042	2.05678364240377
H	-1.47154395395085	-3.47961666842310	2.70219685212553
H	-2.16618850914715	-0.86638720952601	-1.37340595184686
H	-1.32970923295568	0.60506595685060	-0.96656109252935
H	-3.89597178818677	-0.79530941234248	1.42215640413111
H	-4.41271016039773	-1.34372623893273	-0.17015515352109
H	-6.36008035046752	-0.57715098821383	1.13066176399378
H	-5.58773466208874	0.97195256319342	1.43176069731729
H	-6.47297429381250	-0.09379443059333	-1.29232279078775
H	-7.23301876605336	1.21297902558203	-0.39839021431473
H	-5.19378218842929	2.58998162815983	-0.60025020671517
H	-5.70606738792853	2.07498237865258	-2.19837257377840
H	-3.24543512603927	1.77891642317982	-1.93977221557303
H	-4.04590443336370	0.24413955331335	-2.18656216000602
H	-2.18972720115962	3.23376137605275	1.32274700013294
H	-3.03401232684274	3.34282063077860	-0.23108280353856
H	-1.49153771991444	2.47366045692791	-0.11835912754083
H	4.59631503248824	-0.16855714248984	0.39593164947359
H	5.04762397272515	-1.62282242434296	-0.50586582267644
H	4.30046774733778	-1.74840000637059	1.09792606739302
H	0.39569379070197	-3.34819369660540	-3.02812775402271
H	-0.91922709046861	-2.63126881450181	-2.11313431399675
H	-0.00228653809441	-3.98254539640910	-1.43632181521475
H	-0.57611697497967	-0.51527527446992	-3.07474376935685
H	0.91674614457391	-0.28093140166238	-3.97580491213815
H	0.35010828926260	0.96678060837046	-2.85844013351338
H	3.78470120571272	1.40600596495110	-1.11291619334003
H	2.55547551658033	1.66273236710181	-2.35767797614136
H	3.91561174129978	0.58722781094063	-2.66687328067615

H	-1.94349470870471	-1.18627920119544	3.38010483393280
H	-0.19495069292693	-1.22889865938189	3.64066794079841
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H	3.23285873383439	-4.19725000627581	-0.23472041627755
H	1.51006360340052	-4.35729596352983	0.11098706021376
H	0.76356018281420	1.77509498283676	1.72374956282256
H	-0.99757286075739	0.70526222458863	1.97162012227887
C	4.01484960082884	4.99193766923588	0.15520219827132
H	2.99022586137295	4.07368719905829	-1.52305430512895
H	1.95084517537985	5.07890292336207	-0.51532790974516
H	4.32814038467777	5.87785102915828	-0.40042576595709
H	3.80121389709645	5.28694753936516	1.18316028544422
H	4.84270329810415	4.28177164841661	0.16645166746156

C (Secondary carbene)

C	5.77167002398753	10.69262276932413	3.04092400527137
C	6.41957118323680	10.02468214335501	4.12525746121247
C	6.07189065000389	10.71799713828374	5.35149362260131
C	5.32485660923967	11.85918826360026	5.01063896368416
C	5.17331988182448	11.88202048690922	3.56044082835970
Ru	7.28527977949614	12.02636771663222	3.96770870612983
C	8.06017882156162	12.30517276673496	2.28389264234206
C	8.97578983692528	11.39694351276707	1.58206517143198
O	8.96299498133316	10.18137697544800	1.61211122927596
C	7.17827934036993	8.74715462810893	4.02999839845238
C	6.52085357467356	10.31264731776751	6.71468088129291
C	4.79531618104078	12.90030755526633	5.93729150284013
C	4.36421859715961	12.87096898066930	2.79316384036042
C	5.70433130753254	10.20722507967856	1.63203219343598
Cl	8.53093681460889	13.08359871875886	5.59982574117762
O	9.89067228864162	12.10394255682467	0.87807904510987
C	10.93790767138185	11.33402425384634	0.24420508144472
H	7.73609201149965	13.14774270706114	1.66606634801844
H	4.69521861109215	12.93342143919818	1.75747189385650
H	4.43855498946760	13.86520048926395	3.23165687786895
H	3.30743797008339	12.58488491325550	2.79056826852918
H	7.76847826849688	8.71966632849887	3.11631246546633
H	6.48742596065008	7.89747745622582	4.03123102124441
H	7.85399734967768	8.62917394631136	4.87550528365609
H	5.86776887103217	9.53304497400505	7.11767244330120

H	6.51174688286313	11.15629849980270	7.40141198665858
H	7.53740524524385	9.92193138516690	6.69247852017583
H	3.74853848422292	12.69892392725746	6.18425489524924
H	4.84789102196199	13.89037873286348	5.48562702784698
H	5.36583507007742	12.93159048436305	6.86312308252687
H	6.59551254377770	9.64363226601342	1.36744121698076
H	5.60252746272260	11.03217186590776	0.92806305121850
H	4.83271947391349	9.55658696861664	1.51167574699023
C	11.88813683340800	12.31110903171026	-0.40814783200014
H	11.43213499993650	10.72601164069818	1.00318255696385
H	10.48311630998279	10.65784971264923	-0.48123129304848
H	12.69530477479027	11.76601075474254	-0.90141481587793
H	11.37338527463350	12.91482710082977	-1.15690945438716
H	12.32675204744857	12.98038851158300	0.33289539433873

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C	3.23192359023361	-1.62396870096812	-0.70915562157742
C	2.22560255158562	-2.64743171601531	-0.87369943398431
C	1.15176957285708	-2.07733612644404	-1.55526040348389
Ru	1.66784910944868	-0.77924456889155	0.48362886438003
Cl	2.52954173102549	-1.80721380839613	2.48899687305936
C	3.57093566449886	0.80209873293094	-1.63322575121891
C	4.60720284176125	-1.84072724369430	-0.16834874724820
C	2.34088924641332	-4.04664468137198	-0.37069007118397
C	-0.06178362607358	-2.83872109367876	-1.98715743053188
C	0.69813839367257	0.24311943927052	-2.73735454793497
C	-0.37588798912284	-0.77525452181763	0.84805946320377
C	-0.82486643834438	-1.93008620248533	1.73495452038189
C	-1.16876071667669	-1.26525195842493	3.08484901816718
C	-0.17365482231952	-0.10227535512061	3.23020413002185
C	0.10637199530325	0.38876910491931	1.80582995845929
C	-1.29063710981391	-0.28159729337033	-0.25142609364739
C	-2.77306065300481	0.13548772443709	0.02245464773585
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H	4.54853005066087	-3.34866655483521	-0.03961119473151
H	-0.27941818646676	-2.91677067201821	-3.16874820933329
H	-0.95242871059267	-1.51647238574429	-2.34138616447958
H	-0.70285006228474	-3.02044275403585	-1.46095570324146
H	-0.09562503935809	0.49482492870977	-2.54653049142386
H	1.26022117038279	0.71921672915344	-3.65180166322338
H	1.27457746143140	1.47866627020207	-2.06052639309598
H	4.78969063656994	0.35711691681085	-0.94516224959072
H	3.50628757776728	1.40490977080954	-1.53995036485921
H	4.49455217117819	0.49192565410167	-2.68354904627917
H	-2.24614766284909	0.37152700049352	3.83967951025172
H	-0.66144899929003	0.94961847439495	4.34952056806273
H	2.64074744064166	-4.55379004993042	-0.23282882803959
H	2.19677985143339	-4.84168492725665	-1.91769636285325
H	0.95031019887583	-4.47635635489591	-0.72290338814281
H	0.96331278799783	0.88484755720370	1.92318041365682
H	-1.80912135608224	2.23263468110675	2.20987590609363
C	3.76048912195622	4.00586128885109	0.23229279270372
H	2.10215605785710	3.73299588900829	-1.14326327407842
H	1.71856853709720	4.74375159506971	0.24590075217762

H	4.17079213935393	4.86540520928600	-0.30124785907105
H	3.91887874716528	4.15417109375128	1.30098844832848
H	4.31007496734592	3.11513571505812	-0.07229724309032

F (cyclopropanation product)

C	7.47734880767229	15.43263100525389	5.86775297549103
C	7.82834412193821	15.33709406393736	7.37138678962693
C	8.66142602840531	14.04655245780933	7.55642110444824
C	9.01482965883821	13.52046798771298	6.16869598937613
C	8.31911662791226	14.38807782840044	5.16185081155769
C	9.83230798550785	14.42104685938628	5.23326905248310
C	9.15825746360893	12.02922548800891	5.96445999611836
C	10.29276893091302	11.32226088820747	6.73314055187808
C	11.64151329857520	12.01964120476568	6.52525969633003
C	12.80270968241781	11.26546478412768	7.17358012343862
C	12.87408636028830	9.81583359699195	6.69483684628141
C	11.54138435775655	9.10154110110208	6.92282705723119
C	10.39262006498995	9.86177657568559	6.26056009568526
O	10.07688425080605	11.40188115480025	8.15948440149007
C	9.01158918698284	10.65598859353205	8.70846210962390
H	9.54306360262763	14.21095833962106	8.17551819294010
H	8.07497831978844	13.27676978509732	8.05900568282331
H	8.40366461307386	16.20507678916735	7.67436430044070
H	6.92488706652685	15.30590850832940	7.98219544327159
H	9.30990160778606	11.83246905292344	4.90018349151674
H	8.20869554673415	11.54878161423647	6.22172425959694
H	11.58300764294477	13.02973882332425	6.92737180414780
H	11.81923533988848	12.11724726856000	5.45067246020538
H	13.73924715744517	11.78453803749153	6.95334425934812
H	12.67504345417825	11.28360591443330	8.25836638347088
H	13.11377126383404	9.79671691811940	5.62497637722375
H	13.68089500325384	9.28513123917022	7.20667998033142
H	11.35784073432915	9.02007341052212	7.99768985528026
H	11.58152313973617	8.08212397860504	6.53049231780680
H	9.44113721456315	9.34892216049074	6.42182165152334
H	10.54906963557029	9.87606774339887	5.17777993675730
H	8.05422997334767	10.85743440468434	8.21688292786814
H	8.93101018342528	10.96142266307889	9.75121088370523

H	9.19732745114493	9.57745714086656	8.67520704123487
H	6.42630148054082	15.18958792937983	5.69376829166738
H	7.64517945572698	16.43812835458937	5.48038614302908
C	10.67031465478443	15.54482922146261	5.70022705049623
H	7.92517038265733	13.95348150887596	4.25065781178234
H	10.32364031100144	13.86576846033842	4.44686260339943
O	11.93941602089114	15.37417850021746	5.24646103052690
O	10.34078760829924	16.48188671345669	6.38862740370858
C	12.91859726419178	16.33729179695321	5.69565285262498
H	13.69067676259945	16.31539024096080	4.92771619964485
H	12.45965004605641	17.32453604848780	5.72069843520511
C	13.47537201368869	15.95392014359807	7.05287107650332
H	14.26563999926946	16.65111746146384	7.33982944502884
H	12.69498428260878	15.99005934951791	7.81262967797538
H	13.89671894087153	14.94776988885401	7.02729712785396

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