Selective Ruthenium Catalyzed Transformations of Enynes with Diazoalkanes into Alkenyl Bicyclo[3.1.0]hexanes.

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Supplementary material :

Complete reference 32

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford CT, 2004.

Supplementary material : DFT calculations

Cartesian Coordinates of the optimized structures.

Structure B

E=-943.8805057

1	Ru	0.128043	-0.198915	-0.101094
2	Cl	-1.176205	-1.634904	1.435544
3	C	-1.346362	0.934907	-1.462997
4	H	-2.145627	1.549132	-1.077313
5	C	-0.003963	1.357315	-1.759025
6	H	0.397170	2.353146	-1.650119
7	C	0.710758	0.221710	-2.266908
8	H	1.734416	0.223344	-2.611714
9	C	-0.215303	-0.887349	-2.354214
10	H	0.009464	-1.878484	-2.717119
11	C	-1.463258	-0.449033	-1.844102
12	H	-2.342775	-1.060333	-1.708727
13	C	1.587687	-1.890862	0.049967
14	C	2.087170	-0.837353	0.826659
15	C	0.201348	1.031335	1.365919
16	H	1.069498	-2.722829	0.511774
17	H	1.993584	-2.073597	-0.941338
18	H	1.969229	-0.866291	1.905311
19	H	2.887482	-0.200238	0.462244
20	H	0.393522	0.633310	2.371005
21	C	-0.060957	2.460136	1.393914
22	C	-0.039706	3.172258	2.545734
23	H	-0.284574	2.974107	0.463473
24	H	0.177025	2.696887	3.499095
25	H	-0.241299	4.239099	2.567635

Structure C

E= -943.8740607

1	Ru	-0.326841	0.185834	0.040139
2	Cl	-1.472193	2.225692	-0.289771
3	C	-1.397996	-1.751617	-1.138072
4	H	-1.648130	-1.812515	-2.187235
5	C	-0.099226	-2.024746	-0.565326
6	H	0.755752	-2.387838	-1.113121
7	C	-0.167836	-1.841496	0.857224
8	H	0.591836	-2.090234	1.581557
9	C	-1.474749	-1.287923	1.137476
10	H	-1.873422	-1.059197	2.114173
11	C	-2.232025	-1.284039	-0.111364
12	H	-3.243253	-0.920904	-0.222848
13	C	0.580699	1.070275	1.746853
14	C	2.034576	0.821752	1.335901
15	C	1.788006	0.465020	-0.130321
16	H	0.296247	2.122977	1.788256
17	H	0.253002	0.549003	2.651782
18	H	2.718884	1.670806	1.481076
19	H	2.468734	-0.037707	1.864649
20	H	1.616791	1.359454	-0.758830
21	C	2.652785	-0.520434	-0.797156
22	C	3.000416	-0.501162	-2.099079
23	H	3.057482	-1.307208	-0.156690
24	H	2.640201	0.271194	-2.774456
25	H	3.666245	-1.245071	-2.525128

Structure C'

E=-1060.5856786

1	Ru	-0.524420	-0.132270	0.016877
2	Cl	-1.994920	1.806566	0.339285

3	C	-1. 712613	-1. 766994	-1. 389634
4	H	-1. 943113	-1. 658891	-2. 439290
5	C	-0. 474077	-2. 252892	-0. 843009
6	H	0. 363409	-2. 625519	-1. 411789
7	C	-0. 567929	-2. 239016	0. 597870
8	H	0. 150866	-2. 647807	1. 291219
9	C	-1. 829501	-1. 624941	0. 934933
10	H	-2. 233879	-1. 481814	1. 924777
11	C	-2. 528316	-1. 360357	-0. 312836
12	H	-3. 485510	-0. 867602	-0. 390626
13	C	0. 423334	0. 530346	1. 812279
14	C	1. 842695	0. 692903	1. 256272
15	C	1. 615152	0. 078247	-0. 146830
16	H	-0. 055568	1. 446802	2. 159891
17	H	0. 335657	-0. 259855	2. 563724
18	C	2. 260751	2. 150808	0. 961207
19	H	2. 604784	0. 163327	1. 841314
20	C	1. 188762	1. 207159	-1. 052841
21	C	2. 472852	-1. 030250	-0. 599108
22	C	2. 924605	-1. 276362	-1. 843243
23	H	2. 785173	-1. 703872	0. 200325
24	H	2. 676942	-0. 649008	-2. 694830
25	H	3. 578993	-2. 118025	-2. 046342
26	C	1. 481647	2. 548260	-0. 323925
27	H	3. 342327	2. 190427	0. 773587
28	H	2. 044429	2. 819548	1. 801672
29	H	0. 045778	1. 155408	-1. 282836
30	H	1. 587350	1. 129557	-2. 068145
31	H	2. 062439	3. 220510	-0. 964177
32	H	0. 543876	3. 053610	-0. 075730

Structure F

E=-943.8698523

1	Ru	0. 094898	-0. 476547	-0. 188776
2	Cl	-1. 428819	-1. 417596	1. 495029
3	C	-1. 790608	0. 519611	-1. 307365
4	H	-2. 783159	0. 458986	-0. 886849
5	C	-0. 852361	1. 548681	-1. 075132
6	H	-1. 003161	2. 431486	-0. 474250
7	C	0. 388718	1. 175178	-1. 727794
8	H	1. 278340	1. 782484	-1. 791558
9	C	0. 159365	-0. 063153	-2. 421248
10	H	0. 871590	-0. 574570	-3. 050939
11	C	-1. 174540	-0. 497323	-2. 126286
12	H	-1. 656284	-1. 391727	-2. 490262
13	C	1. 010503	-2. 094982	-0. 439548
14	C	1. 612031	-0. 351556	1. 471517
15	C	0. 819550	0. 794482	1. 628981
16	H	1. 503265	-2. 699191	0. 329701
17	H	1. 050327	-2. 567664	-1. 429815
18	H	1. 406945	-1. 227827	2. 076127
19	H	2. 624207	-0. 261686	1. 086811
20	H	-0. 039231	0. 740916	2. 292823
21	C	1. 316286	2. 139674	1. 309448
22	C	0. 770897	3. 275393	1. 780234
23	H	2. 215035	2. 188423	0. 694381
24	H	-0. 116508	3. 263961	2. 408235
25	H	1. 204013	4. 247581	1. 569401

Structure E

E=-943.9019197

1	Ru	0. 083876	0. 020042	0. 066348
2	Cl	-0. 675183	2. 231061	-0. 753517
3	C	1. 815030	-1. 188409	0. 890413
4	H	1. 758198	-1. 752955	1. 809282

5	C	1.488710	-1.673822	-0.416385
6	H	1.160138	-2.672304	-0.660530
7	C	1.734718	-0.596471	-1.355762
8	H	1.599065	-0.633361	-2.425144
9	C	2.239376	0.523800	-0.617035
10	H	2.466160	1.495314	-1.027998
11	C	2.290523	0.171658	0.761612
12	H	2.612672	0.813176	1.567018
13	C	-1.277895	-0.896630	-1.456267
14	C	-2.396218	-1.426270	-0.549770
15	C	-2.127022	-0.363863	0.483779
16	H	-1.591716	-0.076898	-2.100737
17	H	-0.705148	-1.652742	-1.991804
18	H	-3.403560	-1.406092	-0.977311
19	H	-2.186827	-2.435134	-0.177211
20	H	-2.557269	0.614361	0.282300
21	C	-1.336757	-0.516628	1.645722
22	C	-0.633781	0.660970	2.064762
23	H	-1.142965	-1.493373	2.080245
24	H	-1.076056	1.641797	1.922004
25	H	0.074794	0.582327	2.883966

Structure D

E=-943.8970293

1	Ru	-0.281214	-0.111349	-0.429113
2	Cl	-0.869680	2.129995	-0.974082
3	C	-0.828783	-1.769312	-1.709888
4	H	-0.564652	-1.825751	-2.754719
5	C	-0.053348	-2.285160	-0.604423
6	H	0.905332	-2.776450	-0.676611
7	C	-0.788157	-2.020316	0.602309
8	H	-0.484491	-2.282603	1.603894
9	C	-2.058473	-1.426121	0.233774
10	H	-2.823134	-1.100634	0.923813
11	C	-2.089258	-1.271719	-1.172869
12	H	-2.880478	-0.812686	-1.745910
13	C	1.091421	0.906210	2.969164
14	C	2.550634	1.231664	2.768905
15	C	1.597154	1.223700	1.562218
16	H	0.450291	1.638531	3.448019
17	H	0.822305	-0.123546	3.184848
18	H	2.926195	2.194210	3.099994
19	H	3.273435	0.425170	2.843630
20	H	1.323456	2.194804	1.162458
21	C	1.733583	0.152967	0.540602
22	C	1.848447	0.406516	-0.835091
23	H	2.053358	-0.815774	0.925777
24	H	1.862981	1.426612	-1.206918
25	H	2.274058	-0.342996	-1.496121

Structure TS_{BC}

E=-943.8648986

1	Ru	0.192071	0.060390	0.230867
2	Cl	-0.215857	-0.445188	2.519076
3	C	2.237997	-0.686491	-0.133471
4	H	2.568143	-1.551614	0.424402
5	C	1.460512	-0.718797	-1.371119
6	H	1.136212	-1.598001	-1.906619
7	C	1.225992	0.637319	-1.733849
8	H	0.694592	0.983144	-2.606985
9	C	1.961444	1.481660	-0.797919
10	H	1.953035	2.562513	-0.808123
11	C	2.618890	0.677422	0.141208
12	H	3.193630	1.012716	0.990628
13	C	-0.883923	1.844705	0.131387

14	C	-2.144571	0.962134	0.179895
15	C	-1.737642	-0.530585	-0.196083
16	H	-0.672298	2.438892	1.021900
17	H	-0.768104	2.418014	-0.786095
18	H	-2.573637	0.961947	1.183603
19	H	-2.888368	1.317464	-0.546244
20	H	-2.106235	-1.234720	0.553448
21	C	-2.022946	-0.951961	-1.583636
22	C	-2.423676	-2.181856	-1.956719
23	H	-1.881003	-0.191712	-2.355582
24	H	-2.587285	-2.972484	-1.228226
25	H	-2.602698	-2.436434	-2.996714

Structure TS_{CF}

E=-943.8635644

1	Ru	0.036348	-0.419499	-0.200451
2	Cl	-1.438500	-1.497866	1.451313
3	C	-1.712044	0.671637	-1.354837
4	H	-2.699987	0.746044	-0.926525
5	C	-0.678656	1.625044	-1.243977
6	H	-0.734424	2.563242	-0.713946
7	C	0.507632	1.092348	-1.884496
8	H	1.447215	1.610072	-2.005931
9	C	0.170152	-0.184276	-2.436407
10	H	0.816092	-0.813605	-3.030564
11	C	-1.196411	-0.476639	-2.071064
12	H	-1.762714	-1.353064	-2.344961
13	C	1.091366	-1.993131	-0.110036
14	C	1.691022	-0.400557	1.412417
15	C	0.790299	0.695304	1.585228
16	H	0.954488	-2.766713	0.652523
17	H	1.869440	-2.237501	-0.846869
18	H	1.599026	-1.233842	2.100878
19	H	2.689651	-0.213577	1.026798
20	H	0.006304	0.576471	2.328498
21	C	1.236951	2.077336	1.331330
22	C	0.704391	3.160950	1.922379
23	H	2.079435	2.196834	0.649179
24	H	-0.127839	3.080955	2.616880
25	H	1.090262	4.158250	1.738357

Structure TS_{CE}

E=-943.8699883

1	Ru	0.200839	0.094593	0.141349
2	Cl	0.534633	-0.918569	2.269700
3	C	2.160661	0.092589	-1.184154
4	H	2.811681	-0.765947	-1.268785
5	C	0.946657	0.308678	-1.966249
6	H	0.612311	-0.312904	-2.782135
7	C	0.361595	1.537936	-1.543779
8	H	-0.495624	2.028106	-1.977619
9	C	1.147516	2.012648	-0.417150
10	H	0.981056	2.925344	0.133380
11	C	2.297114	1.146662	-0.263261
12	H	3.059115	1.240518	0.495403
13	C	-1.456778	1.346147	0.793416
14	C	-2.559153	0.582305	0.061436
15	C	-1.809406	-0.739343	0.092959
16	H	-1.492220	1.223333	1.877703
17	H	-1.294370	2.387191	0.512550
18	H	-3.546137	0.575981	0.545410
19	H	-2.687877	0.944982	-0.966260
20	H	-1.895473	-1.250086	1.054656
21	C	-1.618684	-1.625688	-1.046949
22	C	-1.167947	-2.905014	-0.954373
23	H	-1.817358	-1.203771	-2.033264

24	H	-0.953542	-3.359852	0.008307
25	H	-1.016673	-3.520829	-1.834960

S6

Structure TS_{ED}

E=-943.8926333

1	Ru	0.165729	-0.116121	-0.011908
2	Cl	-0.113981	0.135205	2.430912
3	C	1.647073	-0.891184	-1.435182
4	H	1.498602	-1.816553	-1.971921
5	C	1.286301	0.422951	-1.898739
6	H	0.839063	0.661000	-2.852516
7	C	1.743675	1.374419	-0.908249
8	H	1.618298	2.446763	-0.951986
9	C	2.343209	0.657789	0.156942
10	H	2.717150	1.084664	1.075018
11	C	2.281407	-0.754021	-0.142751
12	H	2.690968	-1.547811	0.461542
13	C	-1.593685	1.620779	-0.284139
14	C	-2.943825	1.093759	-0.737182
15	C	-2.257322	-0.024794	-0.039783
16	H	-1.556205	2.181467	0.641737
17	H	-0.948944	1.966923	-1.080947
18	H	-3.824756	1.499862	-0.248067
19	H	-3.071782	0.997389	-1.813896
20	H	-2.458619	-0.106385	1.024068
21	C	-1.593126	-1.163692	-0.650486
22	C	-0.861554	-2.034518	0.207336
23	H	-1.683944	-1.340244	-1.719590
24	H	-1.120597	-2.127727	1.257044
25	H	-0.366531	-2.897449	-0.228629

Characterization Data

^1H and ^{13}C NMR spectra were recorded on Bruker AM 3000 WB and DPX 200 spectrometers in deuterated chloroform solutions at 298 K. ΔCH_n refers to cyclopropane nuclei. IR spectra were recorded on Bruker IFS28. Mass spectra were obtained on VARIAN MATT 311 high resolution spectrometer in Centre Regional de Mesures de l'Ouest (CRMPO) of the university of Rennes1.

3a: Z stereoisomer : ^1H NMR (300.130 MHz, CDCl_3) δ ppm : 0.09 (s, 9H, SiMe_3) ; 0.85-0.94 (m, 2H, ΔCH_2) ; 1.32-1.37 (m, 1H, ΔCH) ; 2.46 (s, 3H, CH_3) ; 2.99 (d, 1H, $J = 9.2$ Hz, NCH_2) ; 3.13 (dd, 1H, $J = 9.3$ Hz, $J = 3.9$ Hz, NCH_2) ; 3.52 (d, 1H, $J = 9.4$ Hz, NCH_2) ; 3.57 (d, 1H, $J = 9.2$ Hz, NCH_2) ; 5.61 (d, 1H, $J = 14.7$ Hz, $=\text{CH}$) ; 6.28 (d, 1H, $J = 14.6$ Hz, $=\text{CH}$) ; 7.35 (d, 2H, $J = 8.1$ Hz, Ph) ; 7.70 (d, 2H, $J = 8.1$ Hz, Ph). ^{13}C NMR (75.467 MHz, CDCl_3) δ ppm : 145.4, 144.0, 134.5, 133.5, 130.1, 128.0, 53.4, 50.4, 30.8, 24.0, 22.0, 16.3, 0.8. E stereoisomer : ^1H NMR (300.130 MHz, CDCl_3) δ ppm : 0.03 (s, 9H, SiMe_3) ; 0.85-0.94 (m, 2H, ΔCH_2) ; 1.49-1.45 (m, 1H, ΔCH) ; 2.46 (s, 3H, CH_3) ; 3.10 (m, 1H, NCH_2) ; 3.20 (d, 1H, $J = 8.9$ Hz, NCH_2) ; 3.53 (d, 1H, $J = 9.3$ Hz, NCH_2) ; 3.54 (d, 1H, $J = 9.2$ Hz, NCH_2) ; 5.53 (d, 1H, $J = 18.9$ Hz, $=\text{CH}$) ; 5.71 (d, 1H, $J = 18.9$ Hz, $=\text{CH}$) ; 7.28 (d, 2H, $J = 8.1$ Hz, Ph) ; 7.71 (d, 1H, $J = 8.1$ Hz, Ph). HRMS calcd for $\text{C}_{17}\text{H}_{25}\text{O}_2\text{NsiS}$ 335.1370, found 335.1375; FT-IR (KBr), ν (cm^{-1}): 3050, 1599, 840.

3b : Z stereoisomer : ^1H NMR (300.130 MHz, CDCl_3) δ ppm : 0.17 (s, 9H, SiMe_3); 0.66 (t, 1H, $J = 4.6$ Hz, ΔCH_2) ; 1.07 (m, 1H, ΔCH_2) ; 1.46 (m, 1H, ΔCH) ; 3.43 (d, 1H, $J = 10.8$ Hz, CH_2) ; 3.65 (m, 2H, CH_2) ; 3.77 (d, 1H, $J = 10.8$ Hz, CH_2) ; 5.13 (s, 2H, OCH_2) ; 5.66 (dd, 1H, $J = 14.6$ Hz, $J = 9.2$ Hz, $=\text{CHSiMe}_3$) ; 6.45 (dd, 1H, $J = 14.6$ Hz, $J = 9.2$ Hz, $=\text{CH}$) ; 7.37 (m, 5H, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm : 155.3, 145.8, 136.9, 133.6, 128.5, 127.9, 66.7, 52.3, 48.9, 30.9, 24.1, 17.6, 0.5. HRMS calcd for $\text{C}_{18}\text{H}_{25}\text{NO}_2\text{Si}$ 315.1655, found 315.1673.

3c: Z stereoisomer: ^1H NMR (500.130 MHz, CDCl_3) δ ppm : 0.06 (s, 9H, SiMe_3); 0.62 (d, 1H, $J=5.0$ Hz, ΔCH_2); 0.91 (d, 1H, $J=5.0$ Hz, ΔCH_2); 0.99 (s, 3H, Me); 2.40 (s, 3H, Me); 2.80 (d, 1H, $J=9.1$ Hz, NCH_2); 2.94 (d, 1H, $J=9.3$ Hz, NCH_2); 3.50 (d, 1H, $J=9.3$ Hz, NCH_2); 3.51 (d, 1H, $J=9.3$ Hz, NCH_2); 5.69 (d, 1H, $J=14.6$ Hz, $=\text{CH}$); 6.14 (d, 1H, $J=14.6$ Hz, $=\text{CH}$); 7.29 (d, 2H, $J=8.1$ Hz, Ph); 7.64 (d, 2H, $J=8.1$ Hz, Ph). ^{13}C (50.329 MHz, CDCl_3) δ ppm : 143.9, 143.1, 136.9, 133.8, 130.1, 128.0, 55.2, 54.2, 33.8, 28.1, 22.0, 21.4, 15.4, 0.8. HRMS calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2\text{SiS}$ 349.1532, found 349.1509; FT-IR (KBr), ν (cm^{-1}): 3060, 1599, 1494, 840. % found (calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2\text{SiS}$), C: 62.67 (61.85); H: 8.02 (7.79).

3d: Z stereoisomer : ^1H NMR (200.131 MHz, CDCl_3) δ ppm : Major diastereoisomer: 0.05 (s, 9H, SiMe_3); 0.99 (d, 3H, $J=6.2$ Hz, CH_3); 1.06 (m, 1H, ΔCH); 1.15 (m, 1H, ΔCH); 2.45 (s, 3H, Me); 3.00 (d, 1H, $J=9$ Hz, NCH_2); 3.17 (dd, 1H, $J=9.1$ Hz, $J=3.9$ Hz, NCH_2); 3.57 (d, 1H, $J=9.1$ Hz, NCH_2); 3.64 (d, 1H, $J=9$ Hz, NCH_2); 5.76 (d, 1H, $J=15$ Hz, $=\text{CH}$); 6.25 (d, 1H, $J=15$ Hz, $=\text{CH}$); 7.34 (d, 2H, $J=8$ Hz, Ph); 7.69 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (50.329 MHz, CDCl_3) δ ppm: 143.9, 143.4, 136.5, 133.6, 130.0, 128.0, 54.8, 50.6, 34.2, 31.6, 21.9, 21.3, 13.9, 0.4. Minor diastereoisomer: 0.10 (s, 9H, SiMe_3); 0.99 (d, 3H, $J=6.2$ Hz, CH_3); 1.06 (m, 1H, ΔCH); 1.15 (m, 1H, ΔCH); 2.45 (s, 3H, Me); 3.26 (d, 1H, $J=9.6$ Hz, NCH_2); 3.37 (m, 1H, NCH_2); 3.44 (d, 1H, $J=9.3$ Hz, NCH_2); 3.53 (d, 1H, $J=9.6$ Hz, NCH_2); 5.42 (d, 1H, $J=15.1$ Hz, $=\text{CH}$); 6.25 (d, 1H, 15.1 Hz, $=\text{CH}$); 7.34 (d, 2H, $J=8$ Hz, Ph); 7.69 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (50.329 MHz, CDCl_3) δ ppm: 148.1, 143.9, 133.9, 132.6, 130.1, 127.9, 50.9, 47.4, 34.5, 28.2, 22.5, 21.9, 6.6, 0.7. HRMS calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2\text{SiS}$ 349.1532, found 349.1509.

3e: Z stereoisomer: ^1H NMR (300.080 MHz, CDCl_3) δ ppm : -0.06 (s, 9H, SiMe_3); 1.95 (m, 1H, ΔCH); 2.20 (d, 1H, ΔCH); 2.47 (s, 3H, Me); 3.19 (d, 1H, $J=9.5$ Hz, NCH_2); 3.39 (dd, 1H, $J=9.4$ Hz, $J=3.9$ Hz, NCH_2); 3.76 (d, 1H, $J=9.4$ Hz, NCH_2); 3.84 (d, 1H, $J=9.5$ Hz, NCH_2); 5.68 (d, 1H, $J=15.1$ Hz, $=\text{CH}$); 6.04 (d, 1H, $J=15.1$ Hz, $=\text{CH}$); 7.27-6.96 (m, 5H, Ph); 7.39 (d, 2H, $J=8.1$ Hz, Ph); 7.77 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm: 143.8, 141.7, 137.0, 136.7, 133.3, 129.8, 128.2, 128.1, 128.0, 127.7, 126.1, 55.2, 50.7, 37.3, 31.3, 30.8, 21.6, -0.1. HRMS calcd for $\text{C}_{23}\text{H}_{29}\text{NO}_2\text{SiS}$ 411.1688, found 411.1669.

3f: Z stereoisomer: ^1H NMR (300.080 MHz, CDCl_3) δ ppm : 0.11 (s, 9H, SiMe_3); 1.25-1.18 (m, 1H, ΔCH); 1.61-1.34 (m, 4H, $\Delta\text{CH} + \text{CH}_2$); 2.06-1.77 (m, 3H, CH_2); 2.46 (s, 3H, Me); 3.59 (m, 2H, NCH_2); 4.23 (m, 1H, NCH); 5.48 (d, 1H, $J=14.5$ Hz, $=\text{CH}$); 6.07 (d, 1H, $J=14.5$ Hz, $=\text{CH}$); 7.33 (d, 2H, $J=8$ Hz, Ph); 7.75 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm: 148.1, 143.1, 135.7, 132.2, 129.6, 127.4, 56.5, 53.0, 28.7, 27.1, 22.7, 21.5, 16.9, 16.2, 0.2. HRMS calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_2\text{SiS}$ 375.1688, found 375.1684.

3g: Z stereoisomer : ^1H NMR (300.131 MHz, CDCl_3) δ ppm : 0.03 (s, 9H, SiMe_3); 1.43-1.26 (m, 1H, ΔCH); 1.49 (t, 1H, $J=3.1$ Hz, ΔCH); 1.89 (s, 1H, OH); 2.43 (s, 3H, CH_3); 2.95 (d, 1H, $J=9.0$ Hz, NCH_2); 3.17 (dd, 1H, $J=9.3$ Hz, $J=6.0$ Hz, NCH_2); 3.58 (d, 1H, $J=9.3$ Hz, NCH_2); 3.69 (d, 1H, $J=9.0$ Hz, NCH_2); 3.83 (m, 2H, CH_2); 5.77 (d, 1H, $J=15.1$ Hz, $=\text{CHSiMe}_3$); 6.32 (d, 1H, $J=15.1$ Hz, $=\text{CH}$); 7.33 (d, 2H, $J=8.1$ Hz, Ph); 7.68 (d, 2H, $J=8.3$ Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm: 142.1, 141.1, 136.9, 133.7, 129.7, 127.6, 61.8, 54.3, 50.0, 33.7, 30.3, 28.5, 21.5, -0.0. HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}$ 365.1481, found 365.1482.

3h: Z stereoisomer: ^1H NMR (300.131 MHz, CDCl_3) δ ppm : 0.04 (s, 9H, SiMe_3); 1.12 (d, 1H, $J=4.6$ Hz, ΔCH); 1.22 (s, 3H, CH_3); 1.26 (s, 3H, CH_3); 1.34 (s, 1H, OH); 1.81 (t, 1H, $J=4.2$ Hz, ΔCH); 2.42 (s, 3H, CH_3); 2.88 (d, 1H, $J=9.0$ Hz, NCH_2); 3.15 (dd, 1H, $J=9.2$ Hz, $J=3.8$ Hz, NCH_2); 3.55 (d, 1H, $J=9.2$ Hz, NCH_2); 3.71 (d, 1H, $J=9.0$ Hz, NCH_2); 5.71 (d, 1H, $J=15.3$ Hz, $=\text{CHSiMe}_3$); 6.53 (d, 1H, $J=15.3$ Hz, $=\text{CH}$); 7.33 (d, 2H, $J=8.0$ Hz, Ph); 7.67 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm: 144.4, 143.6, 134.5, 132.9, 129.6, 127.6, 69.3, 55.3, 50.2, 37.0, 34.3, 30.8, 30.1, 26.4, 21.5, 0.2. HRMS calcd for $[\text{M}-\text{C}_4\text{H}_7\text{O}] + \text{C}_{16}\text{H}_{24}\text{NO}_2\text{SiS}$ 322.12970, found 322.1309.

3i: Z stereoisomer: ^1H NMR (200.131 MHz, CDCl_3) δ ppm : 0.04 (s, 9H, SiMe_3); 2.06 (d, 1H, $J=3.8$ Hz, ΔCH); 2.19 (m, 1H, ΔCH); 2.45 (s, 3H, Me); 3.03 (d, 1H, $J=9.6$ Hz, NCH_2); 3.21 (dd, 1H, $J=9.5$ Hz, $J=3.5$ Hz, NCH_2); 3.62 (d, 1H, $J=9.5$ Hz, NCH_2); 3.65 (s, 3H, OMe); 3.77 (d, 1H, $J=9.6$ Hz, NCH_2); 5.80 (d, 1H, $J=15.2$ Hz, $=\text{CH}$); 6.29 (d, 1H, $J=15.1$ Hz, $=\text{CH}$); 7.35 (d, 2H, $J=8.1$ Hz, Ph); 7.69 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm: 170.5, 143.9, 140.2, 137.3, 132.8, 129.8, 127.6, 54.3, 51.8, 49.7, 37.7, 31.3, 29.4, 21.5, -0.1. HRMS calcd for $\text{C}_{19}\text{H}_{27}\text{NO}_4\text{SiS}$ 393.1430, found 393.1444.

3j: E stereoisomer : ^1H NMR (300.131 MHz, CDCl_3) δ ppm : 0.02 (s, 9H, SiMe_3); 1.05 (s, 6H, CH_3); 1.40-1.24 (m, 1H, ΔCH); 2.42 (s, 3H, CH_3); 3.57-3.09 (m, 4H, NCH_2); 5.55 (d, 1H, $J=19.0$ Hz, $=\text{CH}$); 5.89 (d, 1H, $J=19$ Hz, $=\text{CH}$); 7.31 (d, 2H, $J=8.0$ Hz, Ph); 7.70 (d, 2H, $J=8.1$ Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm: 144.4, 143.3, 134.5, 133.9, 129.6, 127.4, 49.9, 47.7, 39.8, 34.8, 26.8, 23.2, 21.5, 14.5, -1.2. Z stereoisomer : ^1H NMR (300.131 MHz, CDCl_3) δ ppm : 0.02 (s, 9H, SiMe_3); 0.97 (s, 3H, CH_3); 1.08 (s, 3H, CH_3); 1.40-1.24 (m, 1H, ΔCH); 2.42 (s, 3H, CH_3); 3.57-3.09 (m, 4H, NCH_2); 5.66 (d, 1H, $J=15.1$ Hz, $=\text{CH}$); 6.26 (d, 1H,

J=15.1 Hz, =CH); 7.31 (d, 2H, J=8.0 Hz, Ph); 7.70 (d, 2H, J=8.1 Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm: 145.8, 143.4, 134.3, 133.9, 129.6, 127.4, 52.8, 47.8, 37.8, 35.0, 25.4, 24.1, 21.5, 14.1, -0.1. HRMS calcd for $\text{C}_{19}\text{H}_{29}\text{NO}_2\text{SiS}$ 363.1688, found 363.1698

4 : Z stereoisomer : ^1H NMR (300.131 MHz, CDCl_3) δ ppm : 0.06 (s, 9H, SiMe_3); 2.43 (s, 3H, CH_3); 4.17 (m, 4H, NCH_2); 5.52 (s, 1H, =CH); 5.73 (d, 1H, J=15.5 Hz, = CHSiMe_3); 6.59 (d, 1H, J=15.5 Hz, =CH); 7.33 (d, 2H, J=8.1 Hz, Ph); 7.73 (d, 2H, J=8.2 Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm: 143.4, 137.9, 137.8, 135.0, 133.8, 129.8, 127.5, 123.6, 56.0, 54.5, 21.5, 0.3. HRMS calcd for $\text{C}_{16}\text{H}_{23}\text{NO}_2\text{SiS}$ 321.1219, found 321.1208.

5 : ^1H NMR (300.131 MHz, CDCl_3) δ ppm : 1.75 (s, 3H, CH_3); 1.78 (s, 3H, CH_3); 2.43 (s, 3H, CH_3); 4.37 (m, 4H, NCH_2); 5.39 (s, 1H, =CH); 5.62 (s, 1H, =CH); 7.33 (d, 2H, J=8.1 Hz, Ph); 7.74 (d, 2H, J=8.2 Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm: 143.4, 138.9, 136.3, 133.8, 129.8, 127.5, 120.9, 118.0, 56.3, 55.0, 27.2, 21.5, 19.9. HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}$ 277.1137, found 277.1139.

7a : Z isomer : ^1H NMR (300.080 MHz, CDCl_3) δ ppm : 0.16 (s, 9H, SiMe_3); 0.84-0.81 (m, 1H, ΔCH_2); 1.00-0.95 (m, 1H, ΔCH_2); 1.50-1.43 (m, 1H, ΔCH); 3.67 (d, 1H, J=8.2 Hz, OCH_2); 3.83-3.80 (m, 3H, OCH_2); 5.68 (d, 1H, J=14.6 Hz, = CHSiMe_3); 6.53 (d, 1H, J=14.6 Hz, =CH). ^{13}C (75.468 MHz, CDCl_3) δ ppm : 145.0, 133.8, 72.4, 69.9, 32.0, 25.1, 15.3, 0.5. E isomer : ^1H NMR (300.080 MHz, CDCl_3) δ ppm : 0.08 (s, 9H, SiMe_3); 0.95-0.84 (m, 2H, ΔCH_2); 1.62-1.53 (m, 1H, ΔCH); 3.92-3.80 (m, 4H, OCH_2); 5.61 (d, 1H, J=19.0 Hz, = CHSiMe_3); 5.96 (d, 1H, J=19.0 Hz, =CH). ^{13}C (75.468 MHz, CDCl_3) δ ppm : 145.7, 127.2, 70.7, 69.5, 33.3, 26.8, 15.0, -1.2. HRMS calcd for $\text{C}_{10}\text{H}_{18}\text{OSi}$ 182.1127, found 182.1128.

7b : Z stereoisomer: ^1H NMR (200.080 MHz, CDCl_3) δ ppm : 0.07 (s, 9H, SiMe_3); 2.08-2.07 (m, 1H, ΔCH); 2.24 (d, 1H, J=4.4 Hz, ΔCH); 3.86 (d, 1H, J=8.3 Hz, OCH_2); 4.06 (m, 2H, OCH_2); 4.11 (d, 1H, J=8.3 Hz, OCH_2); 5.78 (d, 1H, J=15.1 Hz, = CHSiMe_3); 6.31 (d, 1H, J=15.1 Hz, =CH); 7.33-7.09 (m, 5H, Ph). ^{13}C (75.468 MHz, CDCl_3) δ ppm : 141.4, 138.0, 136.7, 128.2, 127.9, 125.8, 74.3, 70.4, 39.0, 32.6, 31.2, -0.0. HRMS calcd for $\text{C}_{16}\text{H}_{22}\text{OSi}$ 258.1440, found 258.1444.

7c: E stereoisomer, 2 diastereoisomers: ^1H NMR (200.131 MHz, CDCl_3) δ ppm : -0.15 (s, 9H, SiMe_3 major); 0.09 (s, 9H, SiMe_3 minor); 1.10-1.90 (m, 10H, Cy); 2.00 (d, 1H, J=4.2 Hz, ΔCH minor); 2.17 (d, 1H, J=4.2 Hz, ΔCH major); 2.25 (d, 1H, J=4.2 Hz, ΔCH -Ph minor); 2.37 (d, 1H, J=4.2 Hz, ΔCH -Ph major); 3.88 (m, 2H, CH_2O); 5.40 (d, 1H, J=18.7 Hz, =CH major); 5.70 (d, 1H, J=18.7 Hz, =CH major); 5.74 (d, 1H, J=18.4 Hz, =CH minor); 6.43 (d, 1H, J=18.4 Hz, =CH minor); 6.95-7.25 (m, 5H, Ph). ^{13}C (50.329 MHz, CDCl_3) Major diastereoisomer, δ ppm : 138.5, 138.1, 135.0, 129.5, 128.0, 125.9, 83.2, 67.1, 49.5, 32.9, 32.7, 30.3, 27.2, 26.3, 23.5, 22.3, -1.0. HRMS calcd for $\text{C}_{21}\text{H}_{30}\text{OSi}$ 326.2066, found 326.2068.

7d : Z isomer : ^1H NMR (500.130 MHz, CDCl_3) δ ppm : 0.11 (s, 9H, SiMe_3); 0.75 (m, 2H, ΔCH_2); 1.10-1.90 (m, 11H, Cy + ΔCH); 3.67 (d, 1H, J=8.5 Hz, OCH_2); 3.78 (dd, 1H, J=8.5 Hz, J=2.5 Hz, OCH_2); 5.52 (d, 1H, J=14.6 Hz, = CHSiMe_3); 6.55 (d, 1H, J=14.6 Hz, =CH). ^{13}C (50.329 MHz, CDCl_3) δ ppm : 145.2, 132.4, 83.4, 66.9, 39.3, 33.2, 31.7, 26.4, 24.1, 23.6, 22.2, 14.3, 1.1. E isomer : ^1H NMR (500.130 MHz, CDCl_3) δ ppm : 0.03 (s, 9H, SiMe_3); 0.75 (m, 2H, ΔCH_2); 1.10-1.90 (m, 11H, Cy + ΔCH); 3.60-3.70 (m, 2H, OCH_2); 5.55 (d, 1H, J=18.6 Hz, = CHSiMe_3); 6.26 (d, 1H, J=18.6 Hz, =CH). HRMS calcd for $\text{C}_{15}\text{H}_{26}\text{OSi}$ 250.1753, found 250.1772. FT-IR (KBr), $\nu(\text{cm}^{-1})$: 3050, 2932, 1605, 839.

8b : ^1H NMR (300.080 MHz, CDCl_3) δ ppm : 0.18 (s, 9H, SiMe_3); 0.21 (s, 9H, SiMe_3); 4.16 (s, 2H, OCH_2); 4.20-4.17 (m, 2H, OCH_2); 5.68 (d, 1H, $J=14.7$ Hz, $=\text{CHSiMe}_3$); 5.83 (s, 1H, $=\text{CHSiMe}_3$); 6.34 (dt, 1H, $J=16.0$ Hz, $J=6.0$ Hz, $\text{CH}=\text{CHPh}$); 6.66 (d, 1H, $J=16.0$ Hz, $=\text{CHPh}$); 6.97 (d, 1H, $J=14.7$ Hz, $\text{CH}=\text{CHSiMe}_3$); 7.44-7.26 (m, 5H, Ph). ^{13}C (75.468 MHz, CDCl_3) δ ppm : 153.8, 149.0, 136.8, 132.4, 132.0, 131.4, 128.6, 127.6, 126.5, 126.2, 71.6, 70.8, 0.5, 0.3. HRMS calcd for 271.1518, found 271.1531.

9d : ^1H NMR (200.130 MHz, CDCl_3) δ ppm : -0.02 (s, 9H, SiMe_3); 0.87-1.65 (m, 11H, Cy + ΔCH_2); 2.00 (m, 1H, ΔCH_2); 2.41 (m, 1H, ΔCH); 3.21 (dd, 1H, $J=10$ Hz, $J=7.7$ Hz, OCH_2); 3.54 (m, 1H, ΔCH); 4.02 (t, 1H, $J=7.5$ Hz, OCH_2); 5.31 (m, 1H, $=\text{CH}$). ^{13}C (50.329 MHz, CDCl_3) δ ppm : 157.4, 119.4, 78.5, 71.4, 53.9, 41.1, 37.3, 36.9, 30.3, 23.6, 23.5, -2.8. HRMS calcd for $\text{C}_{15}\text{H}_{26}\text{OSi}$ 250.17529, found 250.17476.

9e : ^1H NMR (300.130 MHz, CDCl_3) δ ppm : -0.04 (s, 9H, SiMe_3); 1.20-1.35 (m, 4H, Cy + ΔCH_2); 1.59-1.72 (m, 8H, Cy + ΔCH); 2.01-2.12 (m, 1H, ΔCH_2); 2.32-2.28 (m, 1H, ΔCH); 2.41 (s, 3H, CH_3); 2.74-2.71 (m, 1H, NCH_2); 3.74-3.69 (m, 1H, NCH_2); 5.51 (s, 1H, $=\text{CH}$); 7.26 (d, 2H, $J=8.1$ Hz, Ph); 7.73 (d, 2H, $J=8.3$ Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm : 152.5, 142.4, 139.2, 129.4, 127.0, 122.2, 68.5, 53.8, 48.9, 39.4, 35.7, 35.2, 29.6, 24.8, 24.1, 23.9, 21.5, -3.3. HRMS calcd for $\text{C}_{22}\text{H}_{33}\text{NO}_2\text{SiS}$ 403.20013, found 403.2004.

11a : Z stereoisomer : ^1H NMR (300.130 MHz, CDCl_3) δ ppm : 0.12 (s, 9H, SiMe_3); 0.91 (m, 1H, ΔCH_2); 1.06 (m, 1H, ΔCH_2); 1.35 (m, 1H, ΔCH); 2.64 (d, 1H, $J=16.2$ Hz, CH_2); 2.83 (d, 2H, $J=5.8$ Hz, CH_2); 3.05 (dd, 1H, $J=16.2$ Hz, $J=6.4$ Hz, CH_2); 5.50 (d, 1H, $J=14.4$ Hz, $=\text{CHSiMe}_3$); 6.09 (d, 1H, $J=14.4$ Hz, $=\text{CH}$); 7.68 (m, 4H, Ph); 7.73 (m, 2H, Ph); 8.06 (m, 4H, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm : 148.1, 137.1, 136.1, 134.7, 134.6, 133.1, 131.7, 131.2, 128.9, 128.8, 98.3, 40.7, 36.1, 34.6, 27.8, 24.6, 0.3. HRMS calcd for $\text{C}_{17}\text{H}_{22}\text{O}_2\text{SiS}$ 318.1110, found 318.1086.

11b : Z stereoisomer: ^1H NMR (200.130 MHz, CDCl_3) δ ppm : 0.16 (s, 9H, SiMe_3); 0.52 (m, 1H, ΔCH_2); 0.82 (m, 1H, ΔCH_2); 1.25 (q, 6H, CH_3); 1.31 (m, 1H, ΔCH); 2.48 (m, 3H, CH_2); 2.71 (d, 1H, $J=13.7$ Hz, CH_2); 4.18 (m, 4H, CH_2CH_3); 5.54 (d, 1H, $J=14.5$ Hz, $=\text{CHSiMe}_3$); 6.46 (d, 1H, $J=14.6$ Hz, $=\text{CH}$). ^{13}C (75.328 MHz, CDCl_3) δ ppm: 173.1, 172.2, 149.9, 131.7, 62.1, 62.0, 60.4, 40.7, 36.4, 32.4, 25.5, 17.9, 14.4, 0.9. HRMS calcd for $\text{C}_{17}\text{H}_{28}\text{O}_4\text{Si}$ 324.1757, found 324.1748.

14a : Z stereoisomer : ^1H NMR (500.131 MHz, CDCl_3) δ ppm : 0.11 (s, 9H, SiMe_3); 0.79-0.77 (m, 1H, ΔCH_2); 0.89-0.86 (m, 1H, ΔCH_2); 1.02-0.97 (m, 1H, ΔCH); 1.90-1.82 (m, 1H, CH_2); 2.05-1.99 (m, 1H, CH_2); 2.40-2.33 (m, 1H, NCH_2); 2.40 (s, 3H, Me); 2.70 (d, 1H, $J=11.4$ Hz, NCH_2); 3.38-3.34 (m, 1H, NCH_2); 3.68 (d, 1H, $J=11.4$ Hz, NCH_2); 5.53 (d, 1H, $J=14.5$ Hz, $=\text{CHSiMe}_3$); 6.31 (d, 1H, $J=14.5$ Hz, $=\text{CH}$); 7.31 (d, 2H, $J=8.0$ Hz, Ph); 7.62 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm: 149.5, 143.4, 133.8, 132.4, 129.6, 127.5, 48.4, 42.9, 23.5, 23.3, 21.5, 18.3, 15.9, 0.4. HRMS calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2\text{SiS}$ 349.1532, found 349.1541.

14b : Z stereoisomer : ^1H NMR (300.131 MHz, CDCl_3) δ ppm : 0.13 (s, 9H, SiMe_3); 0.68 (m, 1H, ΔCH_2); 0.90 (m, 1H, ΔCH); 1.07 (m, 1H, ΔCH_2); 1.99 (t, 2H, $J=6$ Hz, CH_2); 2.45 (s, 3H, CH_3); 2.86 (m, 2H, NCH_2); 3.28 (m, 2H, NCH_2); 5.44 (d, 1H, $J=14.4$ Hz, $=\text{CHSiMe}_3$); 6.33 (d, 1H, $J=14.4$ Hz, $=\text{CH}$); 7.33 (d, 2H, $J=8.0$ Hz, Ph); 7.65 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (75.467

MHz, CDCl₃) δ ppm: 152.2, 143.5, 134.1, 130.1, 129.6, 127.6, 44.7, 42.5, 29.9, 29.0, 21.5, 18.2, 17.9, 0.5. HRMS calcd for C₁₈H₂₇NO₅SiS 349.1532, found 349.1541.

16b : ¹H NMR (300.130 MHz, CDCl₃) δ ppm : 0.04 (s, 9H, SiMe₃); 0.85 (m, 3H, Δ CH, Δ CH₂); 1.75 (s, 3H, CH₃); 2.45 (s, 3H, CH₃); 3.07 (m, 2H, NCH₂); 3.56 (m, 2H, NCH₂); 5.41 (s, 1H, =CH); 7.34 (d, 2H, J=8.0 Hz, Ph); 7.69 (d, 2H, J=8.3 Hz, Ph).

16c : ¹H NMR (300.130 MHz, CDCl₃) δ ppm : 0.1 (s, 9H, SiMe₃); 0.82-1.43 (m, 3H, Δ CH + Δ CH₂); 2.46 (s, 3H, CH₃); 2.74-3.02 (m, 2H, CH₂); 3.08-3.21 (m, 2H, NCH₂); 3.52-3.59 (m, 2H, NCH₂); 5.19, 5.46 (s, 1H, =CHSiMe₃); 5.62 (d, 1H, J=14.6 Hz, =CH₂); 5.69-5.96 (m, 1H, =CH); 6.29 (d, 1H, J=14.6 Hz, =CH₂); 7.35 (d, 2H, J=7.9 Hz, Ph); 7.70 (d, 2H, J=8.2 Hz, Ph). ¹³C NMR (75.467 MHz, CDCl₃) δ ppm: 152.6, 144.9, 143.5, 136.4, 134.1, 129.8, 127.6, 116.6, 53.0, 49.9, 44.2, 30.4, 23.6, 21.5, 15.9, 0.4.

16d : ¹H NMR (200.130 MHz, CDCl₃) δ ppm : Z stereoisomer: 0.11 (s, 9H, SiMe₃); 0.55 (m, 1H, Δ CH₂); 1.03-0.49 (m, 6H, CH₃); 0.99 (m, 1H, Δ CH₂); 1.49 (m, 1H, Δ CH); 1.67-1.60 (m, 1H, CH₂); 2.13-1.92 (m, 2H, CH₂); 2.39-2.29 (m, 1H, CH₂); 2.43 (s, 3H, CH₃); 3.42-3.37 (m, 1H, NCH₂); 3.78-3.64 (m, 1H, NCH₂); 5.42 (d, 1H, J=15.0 Hz, =CHSiMe₃); 6.65 (d, 1H, J=15.0 Hz, =CH); 7.27 (d, 2H, J=7.9 Hz, Ph); 7.70 (d, 2H, J=8.3 Hz, Ph). ¹³C(75.467 MHz, CDCl₃) δ ppm : 146.3, 143.1, 138.6, 130.0, 129.8, 127.2, 75.4, 52.9, 37.8, 31.2, 29.8, 24.1, 21.9, 15.4, 9.3, 1.2. E stereoisomer: 0.11 (s, 9H, SiMe₃); 0.55 (m, 1H, Δ CH₂); 1.03-0.49 (m, 6H, CH₃); 0.99 (m, 1H, Δ CH₂); 1.49 (m, 1H, Δ CH); 1.67-1.60 (m, 1H, CH₂); 2.13-1.92 (m, 2H, CH₂); 2.39-2.29 (m, 1H, CH₂); 2.43 (s, 3H, CH₃); 3.42-3.37 (m, 1H, NCH₂); 3.78-3.64 (m, 1H, NCH₂); 5.46 (d, 1H, =CHSiMe₃); 6.37 (d, 1H, J=18.6 Hz, =CH); 7.27 (d, 2H, J=7.9 Hz, Ph); 7.70 (d, 2H, J=8.3 Hz, Ph). HRMS calcd for [M-CH₃] + C₂₀H₃₀NO₂SiS 376.1767, found 376.1760.

16e : Z stereoisomer : ¹H NMR (300.130 MHz, CDCl₃) δ ppm : 0.11 (s, 9H, SiMe₃) ; 0.49 (m, 1H, Δ CH₂); 0.86 (m, 1H, Δ CH₂); 1.23 (m, 1H, Δ CH) ; 1.20-1.43 (m, 10H, Cy); 2.41 (s, 3H, PhCH₃) ; 3.40 (d, 1H, J = 9.8 Hz, CH₂) ; 3.73 (d, 1H, J = 9.8 Hz, CH₂) ; 5.43 (d, 1H, J = 14.5 Hz, =CHSiMe₃) ; 6.77 (d, 1H, J = 14.5 Hz, =CH) ; 7.26 (d, 2H, J = 8.1 Hz, Ph) ; 7.68 (d, 2H, J = 8.2 Hz, Ph). ¹³C(75.467 MHz, CDCl₃) δ ppm : 147.5, 142.6, 139.8, 130.0, 129.3, 126.7, 71.6, 48.9, 40.4, 34.6, 32.9, 25.3, 24.2, 23.7, 22.3, 21.5, 15.1, 0.3. HRMS calcd for C₂₂H₃₃NO₂SiS 403.2001, found 403.2004.

17a : Major diastereoisomer : ¹H NMR (300.080 MHz, CDCl₃) δ ppm : -0.04 (s, 9H, SiMe₃); -0.02 (s, 9H, SiMe₃); 0.38 (m, 1H, Δ CH₂) ; 0.44 (m, 1H, Δ CH); 0.87 (m, 1H, Δ CH₂) ; 1.19 (m, 1H, Δ CH) ; 2.41 (s, 3H, PhCH₃) ; 2.59 (dd, 1H, J = 12.9 Hz, J = 10.2 Hz, NCH₂) ; 3.75 (dd, 1H, J = 12.9 Hz, J = 4.0 Hz, NCH₂) ; 4.28 (m, 2H, NCH₂) ; 7.27 (d, 2H, J = 7.8 Hz, Ph) ; 7.69 (d, 2H, J = 8.3 Hz, Ph). ¹³C(75.468 MHz, CDCl₃) δ ppm : 143.2, 135.9, 129.4, 127.8, 98.1, 90.8, 48.5, 36.8, 21.5, 14.6, 9.1, 1.3, -0.2, -0.5. Minor diastereoisomer : ¹H NMR (300.080 MHz, CDCl₃) δ ppm : -0.06 (s, 9H, SiMe₃); 0.04 (s, 9H, SiMe₃); 0.44 (m, 1H, Δ CH); 0.45 (m, 1H, Δ CH₂) ; 0.80 (m, 1H, Δ CH₂) ; 1.25 (m, 1H, Δ CH) ; 2.41 (s, 3H, PhCH₃) ; 3.12 (d, 1H, J = 6.6 Hz, NCH₂) ; 3.82 (m, 1H, NCH₂) ; 4.1 (m, 1H, NCH₂) ; 7.27 (d, 2H, J = 7.8 Hz, Ph) ; 7.71 (d, 2H, J = 8.3 Hz, Ph). ¹³C(75.468 MHz, CDCl₃) δ ppm : 143.2, 135.9, 129.4, 127.7, 98.1, 91.0, 51.6, 36.9, 21.5, 13.1, 7.6, 3.1, -0.4, -2.5. HRMS calcd for C₂₀H₃₃NO₂Si₂S 407.1771, found 407.1782.

17e : Major diastereoisomer : ^1H NMR (200.131 MHz, CDCl_3) δ ppm : -0.22 (m, 1H, ΔCH); 0.07 (s, 9H, SiMe_3); 0.27 (m, 1H, ΔCH_2); 0.87 (m, 1H, ΔCH_2); 1.36 (m, 1H, ΔCH); 1.57 (s, 6H, Me); 3.55 (m, 2H, OCH_2); 7.25-7.32 (m, 3H, Ph); 7.36-7.45 (m, 2H, Ph). ^{13}C (50.329 MHz, CDCl_3) δ ppm: 132.1, 128.7, 128.6, 123.4, 92.2, 84.5, 70.6, 67.5, 29.4, 29.4, 17.2, 8.1, 2.9, 0.3. Minor diastereoisomer: ^1H NMR (200.131 MHz, CDCl_3) δ ppm : -0.46 (m, 1H, ΔCH); -0.04 (s, 9H, SiMe_3); 0.52 (m, 2H, ΔCH_2); 1.00 (m, 1H, ΔCH); 1.55 (s, 6H, Me); 3.22 (dd, 1H, $J=9.6$ Hz, $J=7.9$ Hz, OCH_2); 3.74 (m, 1H, OCH_2); 7.25-7.32 (m, 3H, Ph); 7.36-7.45 (m, 2H, Ph). ^{13}C (50.329 MHz, CDCl_3) δ ppm: 132.1, 128.7, 128.6, 123.4, 92.3, 84.3, 70.7, 70.5, 29.6, 29.5, 16.1, 8.5, 2.5, -1.9. HRMS calcd for $[\text{M}-\text{CH}_3]$ $\text{C}_{17}\text{H}_{23}\text{OSi}$ 271.1518, found 271.1505. FT-IR (KBr), ν (cm^{-1}): 3054, 2986, 2140, 1598.

18b : Z stereoisomer : ^1H NMR (300.130 MHz, CDCl_3) δ ppm : 0.05 (s, 9H, SiMe_3) ; 1.50 (d, 3H, $J = 14.9$ Hz, CH_3) ; 2.42 (s, 3H, PhCH_3) ; 2.70 (t, 1H, $J = 9.7$ Hz, NCH_2) ; 3.32 (m, 1H, CH) ; 3.63 (m, 2H, NCH_2) ; 4.00 (d, 1H, $J = 14.3$ Hz, NCH_2) ; 5.15 (m, 1H, $=\text{CH}$) ; 5.63 (d, 1H, $J = 13.8$ Hz, $=\text{CHSiMe}_3$) ; 5.80 (dd, 1H, $J = 13.8$ Hz, $J = 9.3$ Hz, $\underline{\text{CH}}=\text{CHSiMe}_3$) ; 7.33 (d, 2H, $J = 8.1$ Hz, Ph) ; 7.71 (d, 2H, $J = 8.1$ Hz, Ph). ^{13}C NMR (75.467 MHz, CDCl_3) δ ppm : 145.0, 143.7, 143.6, 138.0, 133.0, 129.7, 127.8, 118.8, 53.4, 49.8, 46.8, 21.5, 14.6, 0.2. HRMS calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_2\text{SiS}$ 349.1532, found 349.1519.

18c : Z stereoisomer : ^1H NMR (300.130 MHz, CDCl_3) δ ppm : 0.06 (s, 9H, SiMe_3); 2.41 (s, 3H, PhCH_3); 2.64 (m, 2H, CH_2); 2.72 (m, 1H, NCH_2); 3.33 (m, 1H, CH); 3.64 (m, 2H, NCH_2) ; 4.02 (dd, 1H, $J = 14.5$ Hz, $J = 1.1$ Hz, NCH_2) ; 4.96 (m, 2H, $=\text{CH}_2$) ; 5.13 (m, 1H, $=\text{CH}$) ; 5.65 (d, 1H, $J = 13.9$ Hz, $=\text{CHSiMe}_3$) ; 5.68 (m, 1H, $\underline{\text{CH}}=\text{CH}_2$) ; 5.82 (dd, 1H, $J = 13.9$ Hz, $J = 9.3$ Hz, $\underline{\text{CH}}=\text{CHSiMe}_3$) ; 7.32 (d, 2H, $J = 8.3$ Hz, Ph) ; 7.70 (d, 2H, $J = 8.3$ Hz, Ph). ^{13}C NMR (75.467 MHz, CDCl_3) δ ppm : 144.8 143.8, 138.5, 135.3, 133.2, 132.7, 129.8, 127.8, 121.5, 115.2, 53.3, 49.7, 46.9, 33.4, 21.5, 0.2. HRMS calcd for $\text{C}_{20}\text{H}_{29}\text{NO}_2\text{SiS}$ 375.1688, found 375.1669.

18d : Z stereoisomer : ^1H NMR (200.130 MHz, CDCl_3) δ ppm : 0.08 (s, 9H, SiMe_3); 1.03-0.75 (m, 6H, CH_3); 1.72-1.45 (m, 2H, CH_2); 2.39-2.29 (m, 2H, CH_2); 2.43 (s, 3H, CH_3); 2.99-2.75 (m, 1H, NCH_2); 3.42-3.37 (m, 1H, CH); 3.78-3.64 (m, 1H, NCH_2) ; 4.88 (dd, 2H, $J=21.5$ Hz, $J=2.7$ Hz, $=\text{CH}_2$) ; 5.76 (d, 1H, $J=13.7$ Hz, $=\text{CH}$) ; 5.93 (dd, 1H, $J=13.7$ Hz, $J=8.8$ Hz, $=\text{CH}$) ; 7.27 (d, 2H, $J=7.9$ Hz, Ph) ; 7.77 (d, 2H, $J=8.3$ Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm : 154.5, 144.9, 143.0, 138.6, 134.3, 129.8, 129.8, 107.6, 77.1, 53.6, 47.0, 33.6, 32.2, 21.9, 10.9, 0.6. HRMS calcd for $[\text{M}-\text{C}_2\text{H}_5]$ + $\text{C}_{19}\text{H}_{28}\text{NO}_2\text{SiS}$ 362.1610, found 362.1617.

18e: Z stereoisomer: ^1H NMR (500.130 MHz, CDCl_3) δ ppm : 0.09 (s, 9H, SiMe_3); 1.19-1.56 (m, 3H, Cy); 1.68-1.76 (m, 7H, Cy); 2.43 (s, 3H, CH_3); 2.92-3.05 (m, 1H, NCH_2); 3.40-3.56 (m, 1H, CH); 3.68-3.75 (m, 1H, NCH_2); 4.85 (s, 1H, $=\text{CH}_2$); 5.32 (s, 1H, $=\text{CH}_2$); 5.79 (d, 1H, $J=15.0$ Hz, $=\text{CH}$); 5.93 (dd, 1H, $J=15.0$ Hz, $J=5.0$ Hz, $=\text{CH}$); 7.29 (d, 2H, $J=7.9$ Hz, Ph); 7.75 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (75.467 MHz, CDCl_3) δ ppm : 155.8, 144.5, 142.7, 139.0, 134.3, 129.4, 127.0, 108.8, 70.4, 51.8, 45.8, 36.4, 34.1, 24.6, 23.3, 22.8, 21.5, 0.1.

19a: ^1H NMR (300.130 MHz, CDCl_3) δ ppm : 0.86 (m, 2H, ΔCH_2); 1.44 (m, 1H, ΔCH); 2.45 (s, 3H, PhCH_3); 3.12 (m, 2H, CH_2); 3.54 (m, 2H, CH_2); 4.94 (m, 2H, $=\text{CH}_2$); 5.59 (dd, 1H, $J = 10.8$ Hz, $J = 6.5$ Hz, $=\text{CH}$); 7.35 (d, 2H, $J = 8.1$ Hz, Ph); 7.70 (d, 2H, $J = 8.1$ Hz, Ph). ^{13}C NMR (75.467 MHz, CDCl_3) δ ppm : 143.6, 138.1, 133.4, 129.7, 127.6, 112.7, 50.9, 49.7, 30.0, 24.4, 21.5, 15.1. HRMS calcd for $\text{C}_{14}\text{H}_{17}\text{NO}_2\text{S}$ 263.0980, found 263.0970.

19c: ^1H NMR (200.131 MHz, CDCl_3) δ ppm : 0.67 (d, 1H, $J=4.7$ Hz, ΔCH_2); 1.00 (d, 1H, $J=5.5$ Hz, ΔCH_2); 1.08 (s, 3H, CH_3); 2.46 (s, 3H, CH_3); 2.85 (d, 1H, $J=9.3$ Hz, NCH_2); 3.15 (d, 1H, $J=8.8$ Hz, NCH_2); 3.60 (d, 2H, $J=9.1$ Hz, NCH_2); 4.96 (d, 1H, $J=17.4$ Hz, $=\text{CH}_2$); 5.08 (d, 1H, $J=10.7$ Hz, $=\text{CH}_2$); 5.60 (dd, 1H, $J=17.4$ Hz, $J=11.0$ Hz, $=\text{CH}$); 7.36 (d, 2H, $J=8.0$ Hz, Ph); 7.71 (d, 2H, $J=8.0$ Hz, Ph). ^{13}C (50.329 MHz, CDCl_3) δ ppm: 143.9, 135.8, 133.7, 130.1, 127.9, 114.9, 55.3, 52.6, 33.6, 30.1, 21.9, 20.2, 15.2. HRMS calcd for $\text{C}_{15}\text{H}_{19}\text{NO}_2\text{S}$ 277.11365, found 277.1139.

19d: ^1H NMR (200.131 MHz, CDCl_3) δ ppm : Major diastereoisomer : 1.04 (d, 3H, $J=5.3$ Hz, CH_3); 1.08 (m, 1H, ΔCH); 1.20 (m, 1H, ΔCH); 2.44 (s, 3H, CH_3); 3.04 (dd, 1H, $J=8.9$ Hz, $J=2.9$ Hz, NCH_2); 3.15 (d, 1H, $J=8.6$ Hz, NCH_2); 3.56 (d, 1H, $J=9.1$ Hz, NCH_2); 3.57 (d, 1H, $J=8.9$ Hz, NCH_2); 4.96 (d, 1H, $J=17.3$ Hz, $=\text{CH}_2$); 5.08 (d, 1H, $J=11.0$ Hz, $=\text{CH}_2$); 5.70 (dd, 1H, $J=17.2$ Hz, $J=10.8$ Hz, $=\text{CH}$); 7.32 (d, 2H, $J=8.1$ Hz, Ph); 7.70 (d, 2H, $J=8.0$ Hz, Ph). ^{13}C (50.329 MHz, CDCl_3) δ ppm : 143.5, 135.0, 133.3, 129.6, 127.5, 114.7, 51.5, 49.9, 33.8, 30.5, 21.5, 21.5, 12.5. Minor diastereoisomer : 1.04 (d, 3H, $J=5.3$ Hz, CH_3); 1.08 (m, 1H, ΔCH); 1.20 (m, 1H, ΔCH); 2.44 (s, 3H, CH_3); 3.04 (dd, 1H, $J=8.9$ Hz, $J=2.9$ Hz, NCH_2); 3.15 (d, 1H, $J=8.6$ Hz, NCH_2); 3.40 (d, 1H, $J=9.1$ Hz, NCH_2); 3.41 (d, 1H, $J=8.9$ Hz, NCH_2); 4.84 (d, 1H, $J=17.3$ Hz, $=\text{CH}_2$); 4.92 (d, 1H, $J=11.0$ Hz, $=\text{CH}_2$); 5.52 (dd, 1H, $J=17.2$ Hz, $J=10.8$ Hz, $=\text{CH}$); 7.32 (d, 2H, $J=8.1$ Hz, Ph); 7.70 (d, 2H, $J=8.0$ Hz, Ph).

19e: ^1H NMR (200.131 MHz, CDCl_3) δ ppm : 2.05 (m, 1H, ΔCH); 2.50 (d, 1H, $J=4.4$ Hz, ΔCH); 2.50 (s, 3H, CH_3); 3.25 (dd, 1H, $J=9.3$ Hz, $J=4.2$ Hz, NCH_2); 3.30 (d, 1H, $J=9.2$ Hz, NCH_2); 3.74 (d, 1H, $J=9.2$ Hz, NCH_2); 3.75 (d, 1H, $J=9.2$ Hz, NCH_2); 4.95 (d, 1H, $J=17.6$ Hz, $=\text{CH}_2$); 4.96 (d, 1H, $J=10.5$ Hz, $=\text{CH}_2$); 5.32 (dd, 1H, $J=17.9$ Hz, $J=10.3$ Hz, $=\text{CH}$); 7.08-7.36 (m, 5H, Ph); 7.40 (d, 2H, $J=7.7$ Hz, Ph); 7.76 (d, 2H, $J=8.4$ Hz, Ph). ^{13}C (50.329 MHz, CDCl_3) δ ppm : 144.1, 136.7, 135.1, 133.6, 130.2, 129.2, 128.7, 128.0, 126.9, 114.9, 51.9, 50.5, 31.8, 28.7, 22.0. HRMS calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_2\text{S}$ 339.12930, found 339.1301.

19f: ^1H NMR (200.130 MHz, CDCl_3) δ ppm : 0.56 (m, 1H, ΔCH_2); 0.72 (m, 1H, ΔCH_2); 1.25 (m, 6H, CH_3); 1.39 (m, 1H, ΔCH); 2.53 (m, 4H, CH_2); 4.18 (m, 4H, CH_2CH_3); 4.97 (m, 2H, $=\text{CH}_2$); 5.64 (dd, 1H, $J=10.5$ Hz, $J=6.8$ Hz, $=\text{CH}$). ^{13}C (75.467 MHz, CDCl_3) δ ppm : 172.7, 171.8, 141.9, 110.9, 61.7, 61.6, 59.5, 37.1, 35.6, 31.4, 26.2, 17.0, 14.0. HRMS calcd for $\text{C}_{14}\text{H}_{20}\text{O}_4$ 252.1362, found 252.1365.

20a: E stereoisomer : ^1H NMR (500.130 MHz, CDCl_3) δ ppm : 1.00 (m, 1H, ΔCH); 1.14 (m, 1H, ΔCH_2); 1.20 (t, 3H, $J=7.0$ Hz, CH_3); 1.64 (m, 1H, ΔCH_2); 2.38 (s, 3H, CH_3); 3.01 (d, 1H, $J=9.6$ Hz, $J=3.6$ Hz, NCH_2); 3.07 (d, 1H, $J=9.0$ Hz, NCH_2); 3.53 (d, 1H, $J=9.6$ Hz, NCH_2); 3.54 (d, 1H, $J=9.0$ Hz, NCH_2); 4.10 (q, 2H, $J=7.0$ Hz, OCH_2); 5.63 (d, 1H, $J=15.8$ Hz, $=\text{CHCO}_2\text{Et}$); 6.58 (d, 1H, $J=15.8$ Hz, $=\text{CH}$); 7.29 (d, 2H, $J=8.0$ Hz, Ph); 7.63 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (50.329 MHz, CDCl_3) δ ppm : 166.5, 149.2, 144.3, 133.2, 130.2, 128.0, 118.8, 60.8, 50.4, 49.8, 30.2, 26.9, 21.9, 17.6, 14.7. HRMS calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$ 335.1191, found 335.1206. % found (calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_4\text{S}$), C:61.09 (60.87); H: 6.31 (6.64).

20c: E stereoisomer : ^1H NMR (200.130 MHz, CDCl_3) δ ppm : 0.89 (d, 1H, $J=5.3$ Hz, ΔCH_2); 1.16 (s, 3H, CH_3); 1.26 (t, 3H, $J=7.1$ Hz, CH_3); 1.29 (d, 1H, $J=5.3$ Hz, ΔCH_2); 2.44 (s, 3H, CH_3); 2.80 (d, 1H, $J=9.1$ Hz, NCH_2); 3.10 (d, 1H, $J=9.0$ Hz, NCH_2); 3.60 (d, 2H, $J=9.1$ Hz, NCH_2); 4.16 (q, 2H, $J=7.1$ Hz, OCH_2); 5.68 (d, 1H, $J=15.8$ Hz, $=\text{CHCO}_2\text{Et}$); 6.66 (d, 1H, $J=15.8$ Hz, $=\text{CH}$); 7.34 (d, 2H, $J=8.0$ Hz, Ph); 7.68 (d, 2H, $J=8.0$ Hz, Ph). ^{13}C (50.329 MHz, CDCl_3) δ ppm : 166.5, 147.3, 144.2, 133.3, 130.2, 128.1, 120.1, 60.8, 55.1, 51.7, 33.4,

33.3, 23.2, 22.0, 15.8, 14.7. HRMS calcd for $C_{18}H_{23}NO_4S$ 349.1347, found 349.1348. FT-IR (KBr), ν (cm^{-1}): 2928, 1707, 1637, 1598. Anal. Calcd for $C_{18}H_{23}NO_4S$: C, 61.87; H, 6.63. found C, 61.87; H, 6.71. % found (calcd for $C_{18}H_{23}NO_4S$), C:61.87 (61.87); H: 6.63 (6.71).

20e : E stereoisomer : 1H NMR (300.130 MHz, $CDCl_3$) δ ppm : 1.20 (t, 3H, $J = 7.1$ Hz, CH_3); 2.32 (m, 1H, ΔCH); 2.47 (s, 3H, CH_3); 2.80 (d, 1H, $J = 5.0$ Hz, ΔCH); 3.21 (dd, 1H, $J = 9.3$ Hz, $J = 3.9$ Hz, NCH_2); 3.26 (d, 1H, $J = 3.9$ Hz, NCH_2); 3.80 (d, 1H, $J = 9.2$ Hz, NCH_2); 3.81 (d, 1H, $J = 9.3$ Hz, NCH_2); 4.09 (q, 2H, $J = 7.1$ Hz, CH_2); 5.70 (d, 1H, $J = 15.9$ Hz, $=CHCO_2Et$); 6.45 (d, 1H, $J = 15.9$ Hz, $CH=$); 7.33-7.12 (m, 5H, Ph); 7.39 (d, 2H, $J = 8.1$ Hz, Ph); 7.75 (d, 2H, $J = 8.1$ Hz, Ph). ^{13}C (75.467 MHz, $CDCl_3$) δ ppm : 165.7, 145.7, 144.0, 135.0, 132.9, 129.9, 128.7, 128.6, 127.6, 127.1, 119.8, 60.3, 50.8, 49.7, 36.4, 33.4, 30.5, 21.6, 14.2. HRMS calcd for $C_{23}H_{25}NO_4S$ 411.1504, found 411.1512.

20g : E stereoisomer : 1H NMR (300.130 MHz, $CDCl_3$) δ ppm : 1.28 (t, 3H, $J=7.1$ Hz, CH_2CH_3); 1.85 (m, 2H, ΔCH); 2.46 (s, 3H, CH_3); 3.06 (dd, 1H, $J=9.2$ Hz, $J=3.6$ Hz, NCH_2); 3.12 (d, 1H, $J=9.1$ Hz, NCH_2); 3.68-3.64 (m, 2H, NCH_2); 3.70-3.66 (m, 1H, CH_2OH); 3.88 (m, 1H, CH_2OH); 4.19 (m, 2H, CH_2CH_3); 5.79 (d, 1H, $J=15.8$ Hz, $=CHCO_2Et$); 6.88 (d, 1H, $J=15.9$ Hz, $=CH$); 7.36 (d, 2H, $J=8.0$ Hz, Ph); 7.70 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (75.467 MHz, $CDCl_3$) δ ppm : 166.1, 145.3, 143.9, 135.8, 129.8, 127.6, 120.7, 60.6, 60.5, 50.7, 49.3, 33.3, 31.1, 30.0, 21.6, 14.3. HRMS calcd for $C_{18}H_{23}NO_5S$ 365.1297, found 365.1294.

20h : E stereoisomer: 1H NMR (300.130 MHz, $CDCl_3$) δ ppm : 1.27 (m, 9H, CH_3); 1.43 (m, 1H, ΔCH); 2.11 (m, 1H, ΔCH); 2.43 (s, 3H, CH_3); 3.01 (m, 2H, NCH_2); 3.61 (m, 2H, NCH_2); 4.13 (q, 2H, $J=7.1$ Hz, CH_2CH_3); 5.66 (d, 1H, $J=16.2$ Hz, $=CHCO_2Et$); 7.33 (d, 2H, $J=8.0$ Hz, Ph); 7.42 (d, 1H, $J=16.2$ Hz, $=CH$); 7.67 (d, 2H, $J=8.2$ Hz, Ph). ^{13}C (75.467 MHz, $CDCl_3$) δ ppm : 166.5, 148.3, 143.8, 132.7, 129.8, 127.6, 118.6, 68.6, 60.3, 51.3, 49.7, 39.5, 33.8, 32.1, 29.8, 28.6, 21.5, 14.2. HRMS calcd for $[M-C_4H_7O] + C_{16}H_{20}NO_4S$ 322.1113, found 322.1115.

21 : E stereoisomer : 1H NMR (300.130 MHz, $CDCl_3$) δ ppm : 0.81 (m, 1H, ΔCH_2); 0.94 (m, 1H, ΔCH_2); 1.25 (m, 9H, CH_3); 1.66 (m, 1H, ΔCH); 2.53 (m, 4H, CH_2); 4.18 (m, 6H, OCH_2); 5.82 (d, 1H, $J = 15.7$ Hz, $=CHCO_2Et$); 6.68 (d, 1H, $J = 15.7$ Hz, $=CH$). ^{13}C (75.467 MHz, $CDCl_3$) δ ppm : 172.4, 171.3, 166.7, 152.9, 117.3, 61.9, 61.8, 60.1, 59.4, 36.4, 35.3, 31.6, 28.5, 19.5, 14.3, 14.0, 13.9. HRMS calcd for $C_{17}H_{24}O_6$ 324.1573, found 324.1558.

22 : E stereoisomer: 1H NMR (500.130 MHz, $CDCl_3$) δ ppm : 0.78 (m, 1H, ΔCH_2); 1.05 (m, 1H, ΔCH_2); 1.30 (t, 3H, $J=7.1$ Hz, CH_3); 1.15-1.70 (m, 10H, Cy); 1.77 (m, 1H, ΔCH); 3.69 (d, 1H, $J=8.6$ Hz, NCH_2); 3.77 (dd, 1H, $J=8.6$ Hz, $J=2.4$ Hz, NCH_2); 4.20 (q, 2H, $J=7.1$ Hz, CH_2); 5.69 (d, 1H, $J=15.6$ Hz, $=CHCO_2Et$); 7.26 (d, 1H, $J=15.6$ Hz, $=CH$). ^{13}C (50.329 MHz, $CDCl_3$) δ ppm : 167.1, 147.7, 120.0, 82.2, 66.5, 60.7, 38.1, 32.9, 31.7, 27.1, 26.1, 23.3, 22.1, 16.3, 14.7. FT-IR (KBr), ν (cm^{-1}): 3054, 2935, 1711, 1647.

23 : Z stereoisomer : 1H NMR (300.130 MHz, $CDCl_3$) δ ppm : 0.67 (m, 1H, ΔCH_2); 0.90 (m, 1H, ΔCH_2); 1.38 (m, 1H, ΔCH); 2.48 (s, 3H, $PhCH_3$); 2.95 (d, 1H, $J = 9.4$ Hz, CH_2); 3.11 (dd, 1H, $J = 9.2$ Hz, $J = 3.9$ Hz, CH_2); 3.52 (d, 1H, $J = 9.2$ Hz, CH_2); 3.62 (d, 1H, $J = 9.4$ Hz, CH_2); 5.62 (d, 1H, $J = 11.5$ Hz, $=CHPh$); 6.49 (d, 1H, $J = 11.5$ Hz, $=CH$); 7.19 (m, 5H, Ph); 7.35 (d, 2H, $J = 8.2$ Hz, Ph); 7.65 (d, 2H, $J = 8.2$ Hz, Ph). ^{13}C (50.323 MHz, $CDCl_3$) δ ppm :

143.9, 137.0, 133.5, 130.0, 129.2, 128.4, 128.1, 127.7, 53.2, 50.4, 27.5, 26.6, 22.0, 17.0. E stereoisomer : ^1H NMR (300.130 MHz, CDCl_3) δ ppm : 1.02 (m, 2H, ΔCH_2) ; 1.56 (m, 1H, ΔCH) ; 2.46 (s, 3H, PhCH_3) ; 3.15 (dd, 1H, $J = 9.2$ Hz, $J = 3.8$ Hz, CH_2) ; 3.26 (d, 1H, $J = 9.0$ Hz, CH_2) ; 3.61 (d, 1H, $J = 9.2$ Hz, CH_2) ; 3.69 (d, 1H, $J = 9.0$ Hz, CH_2) ; 6.00 (d, 1H, $J = 16.1$ Hz, $=\text{CHPh}$) ; 6.29 (d, 1H, $J = 16.1$ Hz, $=\text{CH}$) ; 7.31 (m, 5H, Ph) ; 7.37 (d, 2H, $J = 8.2$ Hz, Ph) ; 7.75 (d, 2H, $J = 8.2$ Hz, Ph). ^{13}C (50.323 MHz, CDCl_3) δ ppm : 144.1, 137.3, 133.7, 130.4, 130.2, 129.0, 128.6, 128.1, 127.7, 126.2, 51.8, 50.2, 30.3, 25.4, 22.0, 16.0. HRMS calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_2\text{S}$ 339.1293, found 339.1301.

24 : Z stereoisomer : ^1H NMR (500.130 MHz, CDCl_3) δ ppm : 0.75 (m, 1H, ΔCH_2) ; 1.20-1.80 (m, 12H, Cy + ΔCH + ΔCH_2) ; 3.67 (d, 1H, $J=8.5$ Hz, OCH_2) ; 3.75 (m, 1H, OCH_2) ; 5.90 (d, 1H, $J=11.9$ Hz, $=\text{CHPh}$) ; 6.47 (d, 1H, $J=11.9$ Hz, $=\text{CH}$) ; 7.20-7.45 (m, 5H, Ph). E stereoisomer : ^1H NMR (500.130 MHz, CDCl_3) δ ppm : 0.75 (m, 1H, ΔCH_2) ; 1.20-1.80 (m, 12H, Cy + ΔCH + ΔCH_2) ; 3.73 (d, 1H, $J=8.5$ Hz, OCH_2) ; 3.84 (dd, 1H, $J=8.5$ Hz, $J=2.5$ Hz, OCH_2) ; 6.35 (d, 1H, $J=15.7$ Hz, $=\text{CHPh}$) ; 6.51 (d, 1H, $J=15.7$ Hz, $=\text{CH}$) ; 7.20-7.45 (m, 5H, Ph). ^{13}C (50.323 MHz, CDCl_3) δ ppm : 137.8, 131.0, 129.0, 128.2, 127.7, 126.5, 82.9, 67.0, 38.6, 32.8, 32.0, 26.3, 24.5, 23.5, 22.3, 14.2. HRMS calcd for $\text{C}_{18}\text{H}_{22}\text{O}$ 254.16707, found 254.16703. FT-IR (KBr), ν (cm^{-1}): 3053, 2930, 2850, 1655, 739.

Crystal Structure Analysis

Crystal structure analysis of **3d** : $C_{18}H_{27}NO_2SSi$, Mr = 349.56, monoclinic, $P 2_1/a$, $a = 13.5714(2)$, $b = 7.3787(1)$, $c = 19.5966(4)$ Å, $\beta = 104.157(1)^\circ$, $V = 1902.8(1)$ Å³, $Z = 4$, $D_x = 1.220$ Mg.m⁻³, $\lambda(MoK\alpha) = 0.71073$ Å, $\mu = 2.42$ cm⁻¹, $F(000) = 752$, $T = 120$ K. The sample (0.25*0.12*0.12 mm) is studied on a NONIUS Kappa CCD with graphite monochromatized MoK α radiation. The cell parameters are obtained with Denzo and Scalepack (Otwinowski & Minor, 1997) with 10 frames (psi rotation : 1° per frame). The data collection (Nonius, 1999) ($2\theta_{max} = 54^\circ$, 230 frames via 1.8° omega rotation and 20 s per frame, range HKL : H 0,17 K 0,9 L -25,24) gives 27966 reflections. The data reduction with Denzo and Scalepack (Otwinowski & Minor, 1997) leads to 4323 independent reflections from which 3489 with $I > 2.0\sigma(I)$. The structure was solved with SIR-97 (Altomare & al., 1998) which reveals the non hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. The whole structure was refined with SHELXL97 (Sheldrick, 1997) by the full-matrix least-square techniques (use of F square magnitude ; x, y, z, β_{ij} for Si, S, O, C and N atoms, x, y, z in riding mode for H atoms ; 208 variables and 3489 observations with $I > 2.0\sigma(I)$; calc $w = 1/[\sigma^2(F_o^2) + (0.098P)^2 + 1.48P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R = 0.050$, $R_w = 0.142$ and $S_w = 1.020$, $\Delta\rho < 0.54$ eÅ⁻³. Crystallographic data (excluding structure factors) for **3d** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication N° CCDC 215613. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax : (+44) 1223-336-033 ; e-mail : deposit@ccdc.cam.ac.uk

Crystal structure analysis of **3f** : $C_{20}H_{29}O_2NSSi$, Mr = 375.59, monoclinic, $P 2_1/a$, $a = 12.5560(2)$, $b = 12.5830(2)$, $c = 13.0360(3)$ Å, $\beta = 100.506(1)^\circ$, $V = 2025.1(1)$ Å³, $Z = 4$, $D_x = 1.232$ Mg.m⁻³, $\lambda(MoK\alpha) = 0.71073$ Å, $\mu = 2.32$ cm⁻¹, $F(000) = 808$, $T = 130$ K. The sample (0.32*0.25*0.25 mm) is studied on a NONIUS Kappa CCD with graphite monochromatized MoK α radiation. The cell parameters are obtained with Denzo and Scalepack (Otwinowski & Minor, 1997) with 10 frames (psi rotation : 1° per frame). The data collection (Nonius, 1999) ($2\theta_{max} = 54^\circ$, 210 frames via 2.0° omega rotation and 40 s per frame, range HKL : H 0,16 K 0,16 L -16,16) gives 33636 reflections. The data reduction with Denzo and Scalepack (Otwinowski & Minor, 1997) leads to 4653 independent reflections from which 4250 with $I > 2.0\sigma(I)$. The structure was solved with SIR-97 (Altomare & al., 1998) which reveals the non hydrogen atoms of the molecule. After anisotropic refinement, many hydrogen atoms may be found with a Fourier Difference. The whole structure was refined with SHELXL97 (Sheldrick, 1997) by the full-matrix least-square techniques (use of F square magnitude ; x, y, z, β_{ij} for Si, S, C, N and O atoms, x, y, z in riding mode for H atoms ; 227 variables and 4250 observations with $I > 2.0\sigma(I)$; calc $w = 1/[\sigma^2(F_o^2) + (0.055P)^2 + 1.16P]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R = 0.037$, $R_w = 0.102$ and $S_w = 1.056$, $\Delta\rho < 0.50$ eÅ⁻³. Crystallographic data (excluding structure factors) for **3f** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication N° CCDC 239959. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax : (+44) 1223-336-033 ; e-mail : deposit@ccdc.cam.ac.uk

Crystal structure analysis of **20e** : $C_{23}H_{25}NO_4S$, Mr = 411.50, monoclinic, Cc, $a = 18.624(4)$, $b = 8.143(4)$, $c = 29.188(7)$ Å, $\beta = 104.63(2)^\circ$, $V = 4283(2)$ Å³, $Z = 8$, $D_x = 1.276$ Mg.m⁻³, $\lambda(\text{MoK}\alpha) = 0.71073$ Å, $\mu = 1.80$ cm⁻¹, $F(000) = 1744$, $T = 293$ K. The sample (0.45*0.35*0.33 mm) is studied on an automatic diffractometer CAD4 NONIUS with graphite monochromatized MoK α radiation (Fair, 1990). The cell parameters are obtained by fitting a set of 25 high-theta reflections. The data collection ($2\Theta_{\text{max}} = 54^\circ$, scan $\omega/2\Theta = 1$, $t_{\text{max}} = 60$ s, range HKL : H 0,23 K 0,10 L -37,36) gives 4793 unique reflections from which 2128 with $I > 2.0\sigma(I)$. After Lorenz and polarization corrections (Spek, 1997) the structure was solved with SIR-97 (Altomare & al., 1998) which reveals the non hydrogen atoms of the compound. After anisotropic refinement a Fourier Difference reveals many hydrogen atoms. The whole structure was refined with SHELXL97 (Sheldrick, 1997) by the full-matrix least-square techniques (use of F square magnitude ; x , y , z , β_{ij} for C, O and N atoms, x , y , z in riding mode for H atoms ; 523 variables and 4793 observations ; calc $w = 1/[\sigma^2(F_o^2) + (0.17P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ with the resulting $R = 0.089$, $R_w = 0.206$ and $S_w = 0.966$ (residual $\Delta\rho \leq 0.72$ eÅ⁻³). The whole structure consist of two very similar molecules : the only difference is in the conformation of the ethyl group. Crystallographic data (excluding structure factors) for **20e** have been deposited with the Cambridge Crystallographic Data Center as supplementary publication N° CCDC 634214. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax : (+44) 1223-336-033 ; e-mail : deposit@ccdc.cam.ac.uk