**A Novel and Efficient Synthesis of Bicyclo[2.2.2]octenones and
Sigmatropic shifts in Ground and Excited states: Stereoselective
Route to *cis*-Decalins and Diquinane Frameworks**

Vishwakarma Singh,^{*a} Sridhar R. Iyer^a and Shaikh M. Mobin^b

^aDepartment of Chemistry, ^bNational Single Crystal X-ray Diffraction Facility, Indian
Institute of Technology, Bombay, Mumbai 400 076 (India)

e-mail: vks@chem.iitb.ac.in

Contents:

General procedure for the preparation of AgNO ₃ impregnated silica gel	S2
¹³ C NMR spectra of compounds 12a-c, 15, 17, 19, 20, 22, 24, 25-28, 30, 13a-c, 16, 31-40 and ¹ H NMR spectra of 18, 21 and 23	S3-S33

General procedure for the preparation of silver nitrate impregnated silica gel

Silver nitrate ($1/9^{\text{th}}$ g of the required amount of silica gel) was dissolved in minimum amount of distilled water and methanol (150 mL per gram of silver nitrate) was added, followed by the addition of the required amount of silica gel. The methanol was then removed on the rotary evaporator and the silica gel was activated in the oven at 120 °C for 6 hours.

S4

CDCl₃

CDCl₃

52.983
49.833
44.948
40.630
26.055
20.931

77.419
77.000
76.581
73.315

96.213

118.807
114.678

140.373
145.842

208.688

exp3 c2pu1

SAMPLE
 date Jan 14 2004
 solvent CDCl3
 file CDC13
 ACQUISITION
 sw 28125.6
 at 1.199
 rb 60276
 fs 134698
 di 15
 nt 2.000
 ct 3200
 SPECIAL
 temp not used
 gain not used
 spin not used
 hsc 8.000
 p420 14.000
 a17a 28.000
 FLAGS
 1) n
 15 n
 16 n
 17 y
 18 n
 19 n
 20 n
 21 n
 22 n
 23 n
 24 n
 25 n
 26 n
 27 n
 28 n
 29 n
 30 n
 31 n
 32 n
 33 n
 34 n
 35 n
 36 n
 37 n
 38 n
 39 n
 40 n
 41 n
 42 n
 43 n
 44 n
 45 n
 46 n
 47 n
 48 n
 49 n
 50 n
 51 n
 52 n
 53 n
 54 n
 55 n
 56 n
 57 n
 58 n
 59 n
 60 n
 61 n
 62 n
 63 n
 64 n
 65 n
 66 n
 67 n
 68 n
 69 n
 70 n
 71 n
 72 n
 73 n
 74 n
 75 n
 76 n
 77 n
 78 n
 79 n
 80 n
 81 n
 82 n
 83 n
 84 n
 85 n
 86 n
 87 n
 88 n
 89 n
 90 n
 91 n
 92 n
 93 n
 94 n
 95 n
 96 n
 97 n
 98 n
 99 n
 100 n
 101 n
 102 n
 103 n
 104 n
 105 n
 106 n
 107 n
 108 n
 109 n
 110 n
 111 n
 112 n
 113 n
 114 n
 115 n
 116 n
 117 n
 118 n
 119 n
 120 n
 121 n
 122 n
 123 n
 124 n
 125 n
 126 n
 127 n
 128 n
 129 n
 130 n
 131 n
 132 n
 133 n
 134 n
 135 n
 136 n
 137 n
 138 n
 139 n
 140 n
 141 n
 142 n
 143 n
 144 n
 145 n
 146 n
 147 n
 148 n
 149 n
 150 n
 151 n
 152 n
 153 n
 154 n
 155 n
 156 n
 157 n
 158 n
 159 n
 160 n
 161 n
 162 n
 163 n
 164 n
 165 n
 166 n
 167 n
 168 n
 169 n
 170 n
 171 n
 172 n
 173 n
 174 n
 175 n
 176 n
 177 n
 178 n
 179 n
 180 n
 181 n
 182 n
 183 n
 184 n
 185 n
 186 n
 187 n
 188 n
 189 n
 190 n
 191 n
 192 n
 193 n
 194 n
 195 n
 196 n
 197 n
 198 n
 199 n
 200 n
 201 n
 202 n
 203 n
 204 n
 205 n
 206 n
 207 n
 208 n
 209 n
 210 n
 211 n
 212 n
 213 n
 214 n
 215 n
 216 n
 217 n
 218 n
 219 n
 220 n
 221 n
 222 n
 223 n
 224 n
 225 n
 226 n
 227 n
 228 n
 229 n
 230 n
 231 n
 232 n
 233 n
 234 n
 235 n
 236 n
 237 n
 238 n
 239 n
 240 n
 241 n
 242 n
 243 n
 244 n
 245 n
 246 n
 247 n
 248 n
 249 n
 250 n
 251 n
 252 n
 253 n
 254 n
 255 n
 256 n
 257 n
 258 n
 259 n
 260 n
 261 n
 262 n
 263 n
 264 n
 265 n
 266 n
 267 n
 268 n
 269 n
 270 n
 271 n
 272 n
 273 n
 274 n
 275 n
 276 n
 277 n
 278 n
 279 n
 280 n
 281 n
 282 n
 283 n
 284 n
 285 n
 286 n
 287 n
 288 n
 289 n
 290 n
 291 n
 292 n
 293 n
 294 n
 295 n
 296 n
 297 n
 298 n
 299 n
 300 n
 301 n
 302 n
 303 n
 304 n
 305 n
 306 n
 307 n
 308 n
 309 n
 310 n
 311 n
 312 n
 313 n
 314 n
 315 n
 316 n
 317 n
 318 n
 319 n
 320 n
 321 n
 322 n
 323 n
 324 n
 325 n
 326 n
 327 n
 328 n
 329 n
 330 n
 331 n
 332 n
 333 n
 334 n
 335 n
 336 n
 337 n
 338 n
 339 n
 340 n
 341 n
 342 n
 343 n
 344 n
 345 n
 346 n
 347 n
 348 n
 349 n
 350 n
 351 n
 352 n
 353 n
 354 n
 355 n
 356 n
 357 n
 358 n
 359 n
 360 n
 361 n
 362 n
 363 n
 364 n
 365 n
 366 n
 367 n
 368 n
 369 n
 370 n
 371 n
 372 n
 373 n
 374 n
 375 n
 376 n
 377 n
 378 n
 379 n
 380 n
 381 n
 382 n
 383 n
 384 n
 385 n
 386 n
 387 n
 388 n
 389 n
 390 n
 391 n
 392 n
 393 n
 394 n
 395 n
 396 n
 397 n
 398 n
 399 n
 400 n
 401 n
 402 n
 403 n
 404 n
 405 n
 406 n
 407 n
 408 n
 409 n
 410 n
 411 n
 412 n
 413 n
 414 n
 415 n
 416 n
 417 n
 418 n
 419 n
 420 n
 421 n
 422 n
 423 n
 424 n
 425 n
 426 n
 427 n
 428 n
 429 n
 430 n
 431 n
 432 n
 433 n
 434 n
 435 n
 436 n
 437 n
 438 n
 439 n
 440 n
 441 n
 442 n
 443 n
 444 n
 445 n
 446 n
 447 n
 448 n
 449 n
 450 n
 451 n
 452 n
 453 n
 454 n
 455 n
 456 n
 457 n
 458 n
 459 n
 460 n
 461 n
 462 n
 463 n
 464 n
 465 n
 466 n
 467 n
 468 n
 469 n
 470 n
 471 n
 472 n
 473 n
 474 n
 475 n
 476 n
 477 n
 478 n
 479 n
 480 n
 481 n
 482 n
 483 n
 484 n
 485 n
 486 n
 487 n
 488 n
 489 n
 490 n
 491 n
 492 n
 493 n
 494 n
 495 n
 496 n
 497 n
 498 n
 499 n
 500 n
 501 n
 502 n
 503 n
 504 n
 505 n
 506 n
 507 n
 508 n
 509 n
 510 n
 511 n
 512 n
 513 n
 514 n
 515 n
 516 n
 517 n
 518 n
 519 n
 520 n
 521 n
 522 n
 523 n
 524 n
 525 n
 526 n
 527 n
 528 n
 529 n
 530 n
 531 n
 532 n
 533 n
 534 n
 535 n
 536 n
 537 n
 538 n
 539 n
 540 n
 541 n
 542 n
 543 n
 544 n
 545 n
 546 n
 547 n
 548 n
 549 n
 550 n
 551 n
 552 n
 553 n
 554 n
 555 n
 556 n
 557 n
 558 n
 559 n
 560 n
 561 n
 562 n
 563 n
 564 n
 565 n
 566 n
 567 n
 568 n
 569 n
 570 n
 571 n
 572 n
 573 n
 574 n
 575 n
 576 n
 577 n
 578 n
 579 n
 580 n
 581 n
 582 n
 583 n
 584 n
 585 n
 586 n
 587 n
 588 n
 589 n
 590 n
 591 n
 592 n
 593 n
 594 n
 595 n
 596 n
 597 n
 598 n
 599 n
 600 n
 601 n
 602 n
 603 n
 604 n
 605 n
 606 n
 607 n
 608 n
 609 n
 610 n
 611 n
 612 n
 613 n
 614 n
 615 n
 616 n
 617 n
 618 n
 619 n
 620 n
 621 n
 622 n
 623 n
 624 n
 625 n
 626 n
 627 n
 628 n
 629 n
 630 n
 631 n
 632 n
 633 n
 634 n
 635 n
 636 n
 637 n
 638 n
 639 n
 640 n
 641 n
 642 n
 643 n
 644 n
 645 n
 646 n
 647 n
 648 n
 649 n
 650 n
 651 n
 652 n
 653 n
 654 n
 655 n
 656 n
 657 n
 658 n
 659 n
 660 n
 661 n
 662 n
 663 n
 664 n
 665 n
 666 n
 667 n
 668 n
 669 n
 670 n
 671 n
 672 n
 673 n
 674 n
 675 n
 676 n
 677 n
 678 n
 679 n
 680 n
 681 n
 682 n
 683 n
 684 n
 685 n
 686 n
 687 n
 688 n
 689 n
 690 n
 691 n
 692 n
 693 n
 694 n
 695 n
 696 n
 697 n
 698 n
 699 n
 700 n
 701 n
 702 n
 703 n
 704 n
 705 n
 706 n
 707 n
 708 n
 709 n
 710 n
 711 n
 712 n
 713 n
 714 n
 715 n
 716 n
 717 n
 718 n
 719 n
 720 n
 721 n
 722 n
 723 n
 724 n
 725 n
 726 n
 727 n
 728 n
 729 n
 730 n
 731 n
 732 n
 733 n
 734 n
 735 n
 736 n
 737 n
 738 n
 739 n
 740 n
 741 n
 742 n
 743 n
 744 n
 745 n
 746 n
 747 n
 748 n
 749 n
 750 n
 751 n
 752 n
 753 n
 754 n
 755 n
 756 n
 757 n
 758 n
 759 n
 760 n
 761 n
 762 n
 763 n
 764 n
 765 n
 766 n
 767 n
 768 n
 769 n
 770 n
 771 n
 772 n
 773 n
 774 n
 775 n
 776 n
 777 n
 778 n
 779 n
 780 n
 781 n
 782 n
 783 n
 784 n
 785 n
 786 n
 787 n
 788 n
 789 n
 790 n
 791 n
 792 n
 793 n
 794 n
 795 n
 796 n
 797 n
 798 n
 799 n
 800 n
 801 n
 802 n
 803 n
 804 n
 805 n
 806 n
 807 n
 808 n
 809 n
 810 n
 811 n
 812 n
 813 n
 814 n
 815 n
 816 n
 817 n
 818 n
 819 n
 820 n
 821 n
 822 n
 823 n
 824 n
 825 n
 826 n
 827 n
 828 n
 829 n
 830 n
 831 n
 832 n
 833 n
 834 n
 835 n
 836 n
 837 n
 838 n
 839 n
 840 n
 841 n
 842 n
 843 n
 844 n
 845 n
 846 n
 847 n
 848 n
 849 n
 850 n
 851 n
 852 n
 853 n
 854 n
 855 n
 856 n
 857 n
 858 n
 859 n
 860 n
 861 n
 862 n
 863 n
 864 n
 865 n
 866 n
 867 n
 868 n
 869 n
 870 n
 871 n
 872 n
 873 n
 874 n
 875 n
 876 n
 877 n
 878 n
 879 n
 880 n
 881 n
 882 n
 883 n
 884 n
 885 n
 886 n
 887 n
 888 n
 889 n
 890 n
 891 n
 892 n
 893 n
 894 n
 895 n
 896 n
 897 n
 898 n
 899 n
 900 n
 901 n
 902 n
 903 n
 904 n
 905 n
 906 n
 907 n
 908 n
 909 n
 910 n
 911 n
 912 n
 913 n
 914 n
 915 n
 916 n
 917 n
 918 n
 919 n
 920 n
 921 n
 922 n
 923 n
 924 n
 925 n
 926 n
 927 n
 928 n
 929 n
 930 n
 931 n
 932 n
 933 n
 934 n
 935 n
 936 n
 937 n
 938 n
 939 n
 940 n
 941 n
 942 n
 943 n
 944 n
 945 n
 946 n
 947 n
 948 n
 949 n
 950 n
 951 n
 952 n
 953 n
 954 n
 955 n
 956 n
 957 n
 958 n
 959 n
 960 n
 961 n
 962 n
 963 n
 964 n
 965 n
 966 n
 967 n
 968 n
 969 n
 970 n
 971 n
 972 n
 973 n
 974 n
 975 n
 976 n
 977 n
 978 n
 979 n
 980 n
 981 n
 982 n
 983 n
 984 n
 985 n
 986 n
 987 n
 988 n
 989 n
 990 n
 991 n
 992 n
 993 n
 994 n
 995 n
 996 n
 997 n
 998 n
 999 n
 1000 n

CDCl₃

45.696
40.967
35.251
33.589

77.419
77.000
76.581
71.456

98.287

107.654
113.239

130.355
134.229

143.515

152.291

SAMPLE		DEC. & VT	
data	Mar 24 2003	dfreq	288.949
solvent	CDC13	dn	not used
file /output/name/	nmr1/epoc/2dmr/~	df	1800.0
nmr1/epoc/2dmr/~	ACQUSY-13C.fid	dm	xy
ACQUSY-13C.fid	ACQUISITION	dm	xy
dfreq	75.432	dmr	3900
in	75.432	dmr	3900
at	1.048	dfreq	1.1
np	49320	dmr	1.1
sw	2324.5	nmr	3.00
fb	12800	nmr	3.00
bw	6	lb	wtfile
pw	8.7	proc	ft
d1	2.000	fn	not used
tor	3101.4	math	
nt	6400	werr	
ct	130	wsp	
alock	20	wsp	
gain	20	wnt	
flags			
display			
sp	-84.8		
bp	18763.1		
vp	36		
ec	0		
cc	250		
zmm	67.05		
is	98408.36		
rs	1138.4		
rfs	0		
rfs	0		
zth	100.000		
ims			
no			
ph			

→ CDCl₃

ppm

S14

→ CCl₄

20.26

31.83

38.03

38.84

39.45

54.43

76.59

77.00

77.43

98.23

114.23

118.26

140.97

146.73

211.02

ppm

50

100

150

200

[illegible]

exp4 std13c

data Sep 2001 DEC. & VT
 solvent CDC13 dn 289.848
 file not used
 ACQUISITION exp
 srrq 75.432
 tn 1.000
 at 1.000
 np 40720
 tw 23564.3
 fb 12860
 bs 4
 pw 8.7
 di 3.000
 nt 3101.4
 ct 3206
 ct 276
 clock n
 gain 20
 flags n
 il n
 in n
 op y
 ns mn
 sp -88.7
 wp 17339.1
 vt 57
 sc 0
 uc 230
 h2mm 89.60
 lc 131315.15
 rf1 1140.1
 rf2 0
 rf3 7
 rms 100.000
 run no ph

exp2 32pu1

SAMPLE		SPECIAL	
date	Oct 27 2003	temp	not used
solvent	CDCl3	gain	not used
file	exp	spin	not used
ACQUISITION		bits	16.000
sw	25125.6	freq	20.000
at	1.190	flao	
no	66278		
bs	13000		
di	2.000		
ni	2.000		
ct	540		
TRANSMITTER		td	PROCESSING
tn	100.000	tn	not used
sfq	1550.7	sp	DISPLAY
tpw	50	wp	-1000.0
pw	7.000	fp	25125.6
DECOUPLER		fp	9200.0
dn	H1	fp	7700.0
dot	0	fp	100.4
dm	VVY	fp	-513.1
dpm	V	plot	
dpr	41		
day	11890		
no	ph		

exp3 81d13c

S18

DATE Mar 20 2001 dfrq 288.848
SOLVENT CDCl3 dn H1
FILE /exp01/name/~ not used
VNAME1/spec/shaft/5- 100.0
I-PROB13C.fid de 13C
ACQUISITION 75.432 dm 8880
IN C13 8880
AT 1.888 dres 1.8
NP 48828 homo n
SV 23884.5 12800 1b PROCESSING 5.00
BS 4 12800 1b
PC 8.7 vtrf1a
d1 2.000 7n
toF 3181.4 math not used
nt 6400
ct 518
clock 518
gain 20
FLAOS n
11 n
in n
dp y
ne mn
SP DISPLAY 5.2
WD 17532.5
VE 72
SC 8
WC 258
B2mm 78.13
1c 106214.78
FT1 8884.4
FTP 5815.8
th 7
ins no ph 100.000

exp4 s2pu1

SAMPLE		SPECIAL	
date	Aug 11 2003	temp	not used
solvent	CDCl3	gain	not used
file	exp4	spin	not used
ACQUISITION		hst	0.000
sw	1000.13	pw	8.500
st	1.015	at	20.000
ns	10000	fl	0
ds	10000	h	0
bs	4	in	0
dl	3.000	dp	0
hl	3200	hs	0
cl	600	ps	0
TRANSMITTER		PROCESSING	
ch	C13	lb	4.00
off	75.430	fn	not used
cof	746.8	sp	0
lph	58	wp	10000.0
pw	4.750	rf	0.000
DECOUPLER		ctf	0.000
ch	H1	tp	120.1
dot	0	lp	-251.7
dm	yyy	PLOT	
dmu	yy	vc	250
dmu	yy	vc	0
dmu	yy	vc	150
dmu	yy	vc	4
dmu	yy	vc	150
dmu	yy	vc	4

Current Data Parameters

NAME	PCAC
EXPNO	2
PROCNO	1

F2 - Acquisition Parameters

Date_	Time
20010602	17.17
INSTRUM	spect
PROBHD	5mm BBO BB-1
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	387
DS	4
SWH	25125.628 Hz
FIDRES	0.383387 Hz
AQ	1.3042184 sec
RG	16384
DW	18.500 usec
DE	6.00 usec
TE	300.0 K
D1	2.00000000 sec
D11	0.03000000 sec
Q12	0.00002000 sec

===== CHANNEL f1 =====

NUC1	IC
P1	13C
PL1	15.25 usec
SFO1	100.623759 MHz

===== CHANNEL f2 =====

CPDPRG2	NUC2	IC2
NOE1115	1H	1H
PCPD2	107.50 usec	
PL2	0.00 dB	
PL12	24.00 dB	
PL13	24.00 dB	
SFO2	400.1318005 MHz	

F2 - Processing parameters

SI	SF
51	32768
SF	100.6127731 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

1D NMR plot parameters

CX	20.00 cm
F1P	220.000 ppm
F1	22134.81 Hz
F2P	-10.000 ppm
F2	-1006.13 Hz
PPMCH	11.50000 ppm/cm
HZCH	1157.04608 Hz/cm

exp4 std13c

SAMPLE DEC. 4 VI
date May 21 2001 dfrq 298.848
solvent CDCl3 dn M1
f116 ACQUISITION exp dprf not used
75.432 1000.0
ln C13 dm yyy
at 1.000 dmf 8800
no 48920 dmf 8800
sv 23864.5 dfrs 1.0
tb 12800 homo n
bs 12800 PROCESSING
pu 3.7 1b
al 3.000 wtf116
tot 5181.4 proc f1
nt 6400 in not used
ct 1280 math
clock gain 20 n
gain 20 n
11 11 n
in 11 n
dp 11 n
hs 11 n
DISPLAY nm
sr -1138.5
wp 23864.5
vs 51.0
ec 840
wc 1.52
hz 508.00
f1 8824.4
f1 8815.0
f1 100.008
nm no ph

exp2 s2pu1

SAMPLE		SPECIAL	
date	Oct 17 2003	teap	not used
solvent	CDCl3	spin	not used
file	exp	nsin	not used
ACQUISITION		nsin	not used
sw	25125.6	psa	14.000
at	11.155	afra	20.000
td	0.0270	flags	
fb	13800	11	n
ds	4	1n	n
dl	2.000	dp	y
nt	2400	hs	nn
ct	1432	PROCESSING	3.50
TRANSMITTER		1b	not used
tn	C13	fn	DISP
trf9	180.867	9d	not used
tof	1556.7	9d	-1500.0
tpw	56	wd	25125.6
pw	7.000	r71	9266.0
DECOUPLER		r7d	7756.0
dn	H1	td	50.0
dof	0	td	-271.4
dm	yyv	plot	
dmm	v	vc	250
dpr	41	sc	0
dpr	11800	th	440
dpr		nm	7
no	ph		

expd st13c

date	SEP 18 2001	DEC. & VI	239.949
solvent	CDC13	not used	H1
file	exp	not used	1000.0
ACQUISITION	75.432	dm	YYY
sfreq	1.000	dmf	8800
at	48728	freq	1.0
mp	23364.5	freq	1.0
sw	12800	homo	1.00
fb	8.7	lb	3.000
bs	3181.4	ut/ile	PROC
pv	1400	fn	not used
dl	1400	smth	not used
lof	1400	smth	not used
nt	1400	smth	not used
ct	1400	smth	not used
alock	1400	smth	not used
gain	20	verr	verr
11	1400	verr	verr
12	1400	verr	verr
13	1400	verr	verr
14	1400	verr	verr
15	1400	verr	verr
16	1400	verr	verr
17	1400	verr	verr
18	1400	verr	verr
19	1400	verr	verr
20	1400	verr	verr
21	1400	verr	verr
22	1400	verr	verr
23	1400	verr	verr
24	1400	verr	verr
25	1400	verr	verr
26	1400	verr	verr
27	1400	verr	verr
28	1400	verr	verr
29	1400	verr	verr
30	1400	verr	verr
31	1400	verr	verr
32	1400	verr	verr
33	1400	verr	verr
34	1400	verr	verr
35	1400	verr	verr
36	1400	verr	verr
37	1400	verr	verr
38	1400	verr	verr
39	1400	verr	verr
40	1400	verr	verr
41	1400	verr	verr
42	1400	verr	verr
43	1400	verr	verr
44	1400	verr	verr
45	1400	verr	verr
46	1400	verr	verr
47	1400	verr	verr
48	1400	verr	verr
49	1400	verr	verr
50	1400	verr	verr
51	1400	verr	verr
52	1400	verr	verr
53	1400	verr	verr
54	1400	verr	verr
55	1400	verr	verr
56	1400	verr	verr
57	1400	verr	verr
58	1400	verr	verr
59	1400	verr	verr
60	1400	verr	verr
61	1400	verr	verr
62	1400	verr	verr
63	1400	verr	verr
64	1400	verr	verr
65	1400	verr	verr
66	1400	verr	verr
67	1400	verr	verr
68	1400	verr	verr
69	1400	verr	verr
70	1400	verr	verr
71	1400	verr	verr
72	1400	verr	verr
73	1400	verr	verr
74	1400	verr	verr
75	1400	verr	verr
76	1400	verr	verr
77	1400	verr	verr
78	1400	verr	verr
79	1400	verr	verr
80	1400	verr	verr
81	1400	verr	verr
82	1400	verr	verr
83	1400	verr	verr
84	1400	verr	verr
85	1400	verr	verr
86	1400	verr	verr
87	1400	verr	verr
88	1400	verr	verr
89	1400	verr	verr
90	1400	verr	verr
91	1400	verr	verr
92	1400	verr	verr
93	1400	verr	verr
94	1400	verr	verr
95	1400	verr	verr
96	1400	verr	verr
97	1400	verr	verr
98	1400	verr	verr
99	1400	verr	verr
100	1400	verr	verr

PHOTO
Pulse Sequence: preset