Synthesis of carotol using a formal (4 + 1)-cycloaddition of chiral dialkoxycarbenes.

*Machhindra Gund, Martin Déry, and Claude Spino**

Université de Sherbrooke, Département de chimie, 2500 Boul. Université, Sherbrooke, QC, J1K 2R1,
Canada

Claude.Spino@USherbrooke.ca

Supporting Information

¹HNMR AND ¹³CNMR SPECTRAL TRACES FOR THE COMPOUNDS:

Contents

¹ HNMR for Compound 32: (E)-4-Iodo-3-methylbut-3-en-1-ol	10
¹³ CNMR for Compound 32:	11
¹ HNMR for Compound 33: (3E,5E)-8-Hydroxy-6-methylocta-3,5-dien-2-one	12
¹³ CNMR for Compound 33:	13
¹ HNMR for Carbene precursor 29: (3E,5E)-8-(2-methoxy-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl- oxy)-6-methylocta-3,5-dien-2-one	14
¹³ CNMR for Carbene precursor 29:	15
DEPT135-Carbon for Carbene precursor 29:	16
DEPT90-Carbon for Carbene precursor 29:	17
¹ HNMR for Compound 36a: 3,3-dimethylbutan-2-yl phenyl carbonate	18
¹ HNMR for Compound 36b: Phenyl-1,1,1-trifluoro-3-methylbutan-2-yl carbonate	19
¹ HNMR for Compound 36c: (1S,2S)-2-(benzyloxy)cyclopentyl phenyl carbonate	20
¹³ CNMR for Compound 36c:	21
DEPT135-Carbon for Compound 36c:	22
¹ HNMR for Compound 36d: (1S,2S)-2-(benzyloxy)cyclohexyl phenyl carbonate	23
¹³ CNMR for compound 36d:	24
DEPT135-Carbon for Compound 36d:	25
¹ HNMR for Compound 36e: Phenyl (1S,2R)-2-phenylcyclohexyl carbonate	26
¹ HNMR for Compound 36f: Phenyl (1S,2R)-2-(2-phenylpropan-2-yl)cyclohexyl carbonate	27
¹³ CNMR for Compound 36f:	28

¹ HNMR for Compound 36h: (1S,2R,4S)-4-isopropyl-2-(2-phenylpropan-2-yl)cyclohexyl phenyl carbonate	29
¹³ CNMR for Compound 36h:	30
DEPT135-Carbon for Compound 36h:.....	31
¹ HNMR for Compound 36i: (2S,6S)-2,6-dimethylcyclohexyl phenyl carbonate	32
¹³ CNMR for Compound 36i:	33
¹ HNMR for Compound 37a: 3,3-dimethylbutan-2-yl hydrazinecarboxylate	34
¹ HNMR for Compound 37b: 1,1,1-trifluoro-3-methylbutan-2-yl hydrazinecarboxylate	35
¹³ CNMR for Compound 37b:	36
DEPT135-Carbon for Compound 37b:.....	37
¹ HNMR for Compound 37c: (1S,2S)-2-(benzyloxy)cyclopentyl hydrazinecarboxylate	38
¹³ CNMR for Compound 37c:.....	39
DEPT135-Carbon for Compound 37c:	40
¹ HNMR for Compound 37d: (1S,2S)-2-(benzyloxy)cyclohexyl hydrazinecarboxylate.....	41
¹³ CNMR for Compound 37d:	42
DEPT135-Carbon for Compound 37d:.....	43
¹ HNMR for Compound 37e: (1S,2R)-2-phenylcyclohexyl hydrazinecarboxylate	44
¹³ CNMR for Compound 37e:	45
¹ HNMR for Compound 37f: (1S,2R)-2-(2-Phenylpropan-2-yl)cyclohexyl hydrazinecarboxylate	46
¹³ CNMR for Compound 37f:	47
DEPT135-Carbon for Compound 37f:	48
¹ HNMR for Compound 37h: (1S,2R,4S)-4-isopropyl-2-(2-phenylpropan-2-yl)cyclohexyl hydrazinecarboxylate	49
¹³ CNMR for Compound 37h:	50
DEPT135-Carbon for Compound 37h:.....	51
¹ HNMR for Compound 37i: (2S,6S)-2,6-dimethylcyclohexyl hydrazinecarboxylate	52
¹³ CNMR for Compound 37i:	53
DEPT135-Carbon for Compound 37i:.....	54
¹ HNMR for Compound 38a: 3,3-dimethylbutan-2-yl 2-(propan-2-ylidene)hydrazinecarboxylate	55
¹³ CNMR for Compound 38a:	56
DEPT-135-Carbon for Compound 38a:.....	57
¹ HNMR for Compound 38b: 1,1,1-trifluoro-3-methylbutan-2-yl 2-(propan-2-ylidene)hydrazinecarboxylate	58
¹³ CNMR for Compound 38b:	59

DEPT135-Carbon for Compound 38b:.....	60
¹ HNMR for Compound 38c: (1S,2S)-2-(benzyloxy)cyclopentyl 2-(propan-2-ylidene)hydrazinecarboxylate	61
¹³ CNMR for Compound 38c:.....	62
DEPT135-Carbon for Compound 38c:	63
¹ HNMR for Compound 38d: (1S,2S)-2-(benzyloxy)cyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate	64
¹³ CNMR for Compound 38d:	65
DEPT135-Carbon for Compound 38d:.....	66
¹ HNMR for Compound 38e: (1S,2R)-2-phenylcyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate ..	67
¹³ CNMR for Compound 38e:	68
DEPT135-Carbon for Compound 38e:.....	69
¹ HNMR for Compound 38f: (1S,2R)-2-(2-Phenylpropan-2-yl)cyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate	70
¹³ CNMR for Compound 38f:	71
DEPT135-Carbon for Compound 38f:.....	72
¹ HNMR for Compound 38g: (1S,2R,4R)-4-methyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate	73
¹³ CNMR for Compound 38g:	74
¹ HNMR for Compound 38h: (1S,2R,4S)-4-isopropyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate	75
¹³ CNMR for Compound 38h:	76
DEPT135-Carbon for Compound 38h:.....	77
¹ HNMR for Compound 38i: (2S,6S)-2,6-dimethylcyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate	78
¹³ CNMR for Compound 38i:	79
DEPT135-Carbon for Compound 38i:.....	80
¹ HNMR for Oxadiazoline 39a: 2-(3,3-dimethylbutan-2-yloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate	81
¹³ CNMR for Oxadiazoline 39a:	82
DEPT-135-Carbon for Oxadiazoline 39a:.....	83
¹ HNMR for Oxadiazoline 39b: 5,5-dimethyl-2-(1,1,1-trifluoro-3-methylbutan-2-yloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate.....	84
¹³ CNMR for Oxadiazoline 39b:	85
DEPT135-Carbon for Oxadiazoline 39b:.....	86

¹ HNMR for Oxadiazoline 39c: 2-((1R,2R)-2-(benzyloxy)cyclopentyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate	87
¹³ CNMR for Oxadiazoline 39c:.....	88
DEPT135-Carbon for Oxadiazoline 39c:	89
¹ HNMR for Oxadiazoline 39d: 2-((1S,2S)-2-(benzyloxy)cyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate	90
¹³ CNMR for Oxadiazoline 39d:	91
DEPT135-Carbon for Oxadiazoline 39d:.....	92
¹ HNMR for Oxadiazoline 39e: 5,5-dimethyl-2-((1S,2R)-2-phenylcyclohexyloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate	93
¹³ CNMR for Oxadiazoline 39e:	94
DEPT135-Carbon for Oxadiazoline 39e:.....	95
¹ HNMR for Oxadiazoline 39f: 5,5-Dimethyl-2-((1R,2S)-2-(2-phenylpropan-2-yl)cyclohexyloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate	96
¹³ CNMR for Oxadiazoline 39f:	97
DEPT135-Carbon for Oxadiazoline 39f:.....	98
¹ HNMR for Oxadiazoline 39h: 2-((1S,2R,4S)-4-isopropyl-2-(2-phenylpropan-2-yl)cyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate	99
¹³ CNMR for Oxadiazoline 39h:	100
DEPT135-Carbon for Oxadiazoline 39h:.....	101
¹ HNMR for Oxadiazoline 39i: 2-((2S,6S)-2,6-dimethylcyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate	102
¹³ CNMR for Oxadiazoline 39i:	103
DEPT135-Carbon for Oxadiazoline 39i:.....	104
¹ HNMR for Carbene precursor 30a: (3E,5E)-8-(2-(3,3-dimethylbutan-2-yloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one	105
¹³ CNMR for Carbene precursor 30a:	106
DEPT-135-Carbon for Carbene precursor 30a:	107
¹ HNMR for Carbene precursor 30b: (3E,5E)-8-(5,5-dimethyl-2-(1,1,1-trifluoro-3-methylbutan-2-yloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one	108
¹³ CNMR for Carbene precursor 30b:.....	109
DEPT135-Carbon for Carbene precursor 30b:	110
¹ HNMR for Carbene precursor 30c: (3E,5E)-8-(2-((1R,2R)-2-(benzyloxy)cyclopentyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one	111
¹³ CNMR for Carbene precursor 30c:	112

DEPT135-Carbon for Carbene precursor 30c:	113
¹ HNMR for Carbene precursor 30d: (3E,5E)-8-(2-((1S,2S)-2-(benzyloxy)cyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one	114
¹³ CNMR for Carbene precursor 30d:	115
DEPT135-Carbon for Carbene precursor 30d:	116
¹ HNMR for Carbene precursor 30e: (3E,5E)-8-(5,5-dimethyl-2-((1S,2R)-2-phenylcyclohexyloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one	117
¹³ CNMR for Carbene precursor 30e:	118
DEPT135-Carbon for Carbene precursor 30e:	119
¹ HNMR for Carbene precursor 30f: (3E,5E)-8-(5,5-Dimethyl-2-((1R,2S)-2-(2-phenylpropan-2-yl)cyclohexyloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one	120
¹³ CNMR for Carbene precursor 30f:	121
DEPT135-Carbon for Carbene precursor 30f:	122
¹ HNMR for Carbene precursor 30g: (3E,5E)-8-(5,5-dimethyl-2-((1S,2R,4R)-4-methyl-2-(2-phenylpropan-2-yl)cyclohexyloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one	123
¹³ CNMR for Carbene precursor 30g:	124
¹ HNMR for Carbene precursor 30h: (3E,5E)-8-(2-((1S,2R,4S)-4-isopropyl-2-(2-phenylpropan-2-yl)cyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one	125
¹³ CNMR for Carbene precursor 30h:	126
DEPT135-Carbon for Carbene precursor 30h:	127
¹ HNMR for Carbene precursor 30i: (3E,5E)-8-(2-((2S,6S)-2,6-dimethylcyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one	128
¹³ CNMR for Carbene precursor 30i:	129
DEPT135-Carbon for Carbene precursor 30i:	130
¹ HNMR for Cycloadduct 25: rac-1-((3aS,6R,6aR)-6a-Methoxy-3a-methyl-3,3a,6,6a-tetrahydro-2H-cyclopenta[b]furan-6-yl)ethanone	131
¹³ CNMR for Cycloadduct 25:	132
DEPT135-Carbon for Cycloadduct 25:	133
DEPT90-Carbon for Cycloadduct 25:	134
¹ HNMR for Cycloadducts 26a + 41a:	135
¹³ CNMR for Cycloadducts 26a + 41a:	136
DEPT-135-Carbon for Cycloadducts 26a + 41a:	137
¹ HNMR for Cycloadducts 26b + 41b:	138
¹³ CNMR for Cycloadducts 26b + 41b:	139

DEPT135-Carbon for Cycloadducts 26b + 41b:	140
¹ HNMR for Cycloadducts 26c + 41c: (90:10 mixture)	141
¹ HNMR for Cycloadducts 26c + 41c: (58:42 mixture)	142
¹³ CNMR for Cycloadducts 26c + 41c:	143
DEPT135-Carbon for Cycloadducts 26c + 41c:	144
¹ HNMR for Cycloadducts 26d + 41d:.....	145
¹³ CNMR for Cycloadducts 26d + 41d:.....	146
DEPT135-Carbon for Cycloadducts 26d + 41d:	147
¹ HNMR for Cycloadducts 26e + 41e:	148
¹³ CNMR for Cycloadducts 26e + 41e:	149
DEPT135-Carbon for Cycloadducts 26e + 41e:	150
¹ HNMR for Cycloadduct 26f:	151
¹³ CNMR for Cycloadduct 26f:	152
DEPT135-Carbon for Cycloadduct 26f:	153
¹ HNMR for Cycloadduct 41f:	154
¹³ CNMR for Cycloadduct 41f:	155
DEPT135-Carbon for Cycloadduct 41f:	156
¹ HNMR for Cycloadducts 26g+ 41g:.....	157
¹³ CNMR for Cycloadducts 26g+ 41g:	158
¹ HNMR for Cycloadducts 26h+ 41h:.....	159
¹³ CNMR for Cycloadducts 26h+ 41h:.....	160
DEPT135-Carbon for Cycloadducts 26h+ 41h:	161
¹ HNMR for Cycloadducts 26i+ 41i:	162
¹³ CNMR for Cycloadducts 26i+ 41i:	163
DEPT135-Carbon for Cycloadducts 26i+ 41i:	164
¹ HNMR for Ketone (±)-42: rac-(2R,5R)-2-(2-Hydroxyethyl)-5-isopropyl-2-methylcyclopentanone	165
¹³ CNMR for Ketone (±)-42:	166
DEPT135 for Ketone (±)-42:	167
¹ HNMR for Ketone (-)-42: (2R,5R)-2-(2-Hydroxyethyl)-5-isopropyl-2-methylcyclopentanone	168
¹³ CNMR for Ketone (-)-42:.....	169
DEPT135 for Ketone (-)-42:	170
DEPT90 for Ketone (-)-42:	171

¹ HNMR for compound 45: (±)-(1S,2R,5R)-1-(3-(benzyloxy)but-1-ynyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol	172
¹³ CNMR for compound 45:.....	173
¹ HNMR for compound 46: (±)-(1S,2R,5R)-1-butyl-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol	174
¹³ CNMR for compound 46:.....	175
¹ HNMR for compound 47a: (±)-(1S,2R,5R)-1-((S,Z)-3-hydroxybut-1-enyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol	176
¹ HNMR for Compound 47b: (±)-(1S,2R,5R)-1-((R,Z)-3-hydroxybut-1-enyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol	177
X-Ray analysis for compound 47b: (±)-(1S,2R,5R)-1-((R,Z)-3-hydroxybut-1-enyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol	178
¹ HNMR for compound 48: (±)-(1S,2R,5R)-1-(3-hydroxybutyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol	181
¹³ CNMR for Compound 48:	182
¹ HNMR for compound 49: (±)-(But-3-yn-2-yloxy)(tert-butyl)dimethylsilane	183
¹³ CNMR for compound 49:.....	184
¹ HNMR for compound 50: (±)-(1S,2R,5R)-1-(3-(tert-butyldimethylsilyloxy)but-1-ynyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol	185
¹³ CNMR for compound 50:.....	186
DEPT135 for compound 50:	187
¹ HNMR for compound 51: (±)-(1S,2R,5R)-1-(3-hydroxybut-1-ynyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol	188
¹³ CNMR for compound 51:.....	189
¹ HNMR for Compound 54a (Acetylation of 50): (±)-2-((1R,2S,3R)-2-(3-(tert-butyldimethylsilyloxy)but-1-ynyl)-2-hydroxy-3-isopropyl-1-methylcyclopentyl)ethyl acetate	190
¹³ CNMR for compound 54a (Acetylation of compound 50):.....	191
DEPT135 for compound 54a (Acetylation of compound 50):.....	192
¹ HNMR for compound 54: (±)-2-((1R,2S,3R)-2-hydroxy-2-(3-hydroxybut-1-ynyl)-3-isopropyl-1-methylcyclopentyl)ethyl acetate	193
¹³ CNMR for compound 54:.....	194
DEPT135 for compound 54:	195
¹ HNMR for compound 55: (±)-2-((1R,2S,3R)-2-hydroxy-3-isopropyl-1-methyl-2-(3-oxobut-1-ynyl)cyclopentyl)ethyl acetate	196
¹³ CNMR for compound 55:.....	197
DEPT135 for Compound 55:.....	198

¹ HNMR for compound 56: (±)-(R)-2-(3-isopropyl-1-methyl-2-(3-oxobutyl)cyclopent-2-enyl)ethyl acetate	199
¹³ CNMR for compound 56:.....	200
DEPT135 for compound 56:	201
¹ HNMR for compound 57: (±)-2-((1R,2S,3R)-2-hydroxy-3-isopropyl-1-methyl-2-(3-oxobut-1-ynyl)cyclopentyl)acetaldehyde	202
¹³ CNMR for compound 57:.....	203
¹ HNMR for compound 59: (±)-1-((3R,3aS,7aR)-3a,6-dihydroxy-3-isopropyl-7a-methyloctahydro-1H-inden-5-yl)ethanone	204
¹³ CNMR for compound 59:.....	205
¹ HNMR for compound 59a (Witting reaction of 59): 1-((3R,3aS,7aR)-3a-hydroxy-3-isopropyl-7a-methyl-2,3,3a,4,7,7a-hexahydro-1H-inden-5-yl)ethenone	206
¹ HNMR for compound 60: (±)-(1S,2R,5R)-1-(3-(tert-butyldimethylsilyloxy)butyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol.....	207
¹³ CNMR for compound 60:.....	208
DEPT135 for compound 60:	209
¹ HNMR for compound 61: (±)-(1S,2R,5R)-1-((Z)-3-(tert-butyldimethylsilyloxy)but-1-enyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol	210
¹³ CNMR for compound 61:.....	211
¹ HNMR for aldehyde 62a: (Oxidation of 60) (±)-2-((1R,2S,3R)-2-(3-(tert-butyldimethylsilyloxy)butyl)-2-hydroxy-3-isopropyl-1-methylcyclopentyl)acetaldehyde	212
¹³ CNMR for aldehyde 62a: (Oxidation of 60)	213
DEPT90 for aldehyde 62a: (Oxidation of 60).....	214
DEPT135 for aldehyde 62a: (Oxidation of 60)	215
¹ HNMR for compound 62: (±)-(1S,2R,5R)-2-allyl-1-(3-(tert-butyldimethylsilyloxy)butyl)-5-isopropyl-2-methylcyclopentanol	216
¹³ CNMR for compound 62:.....	217
DEPT135 for Compound 62:.....	218
DEPT90 for Compound 62:.....	219
¹ HNMR for compound 62b: (Olefination of aldehyde 62a using petasis) (±)-(1S,2R,5R)-1-(3-(tert-butyldimethylsilyloxy)butyl)-5-isopropyl-2-methyl-2-((E)-prop-1-enyl)cyclopentanol	220
¹³ CNMR for compound 62b: (Olefination of aldehyde 62a using petasis).....	221
DEPT135 for compound 62b: (Olefination of aldehyde 62a using petasis)	222
¹ HNMR for alcohol 63a: (TBS-deprotection of 62) (±)-(1S,2R,5R)-2-allyl-1-(3-hydroxybutyl)-5-isopropyl-2-methylcyclopentanol	223
¹³ CNMR for alcohol 63a: (TBS-deprotection of 62).....	224

DEPT135 for alcohol 63a: (TBS-deprotection of 62)	225
DEPT90 for alcohol 63a: (TBS-deprotection of 62)	226
¹ HNMR for Ketone 63: (±)-4-((1S,2R,5R)-2-allyl-1-hydroxy-5-isopropyl-2-methylcyclopentyl)butan-2-one	227
¹ HNMR for enol ether 64: (±)- (5S,6R,9R)-6-allyl-9-isopropyl-2,6-dimethyl-1-oxaspiro[4.4]non-2-ene	228
¹³ CNMR for Compound 64:	229
DEPT135 for Compound 64:.....	230
DEPT90 for Compound 64:.....	231
¹ HNMR for Ketone 65: (R)-4-(5-allyl-2-isopropyl-5-methylcyclopent-1-enyl)butan-2-one	232
DEPT90 for Ketone 65:	233
DEPT135 for Ketone 65:	234
¹ HNMR for diene 24: rac-(1S,2R,5R)-2-Allyl-5-isopropyl-2-methyl-1-(3-methylbut-3-enyl)cyclopentanol	235
¹³ CNMR for diene 24:	236
DEPT90 for diene 24:	237
DEPT135 for diene 24:	238
¹ HNMR for rac-Carotol 1: (3R,3aS,8aR)-3-Isopropyl-6,8a-dimethyl-1,2,3,3a,4,5,8,8a-octahydroazulen-3a-ol	239
¹³ CNMR for rac-Carotol 1:	240
DEPT90 for rac-Carotol 1:	241
DEPT135 for rac-Carotol 1:	242
¹ HNMR for Compound 70: (5R,6R,9R)-6-allyl-9-isopropyl-2,2,6-trimethyl-1-oxaspiro[4.4]nonane	243
¹³ CNMR for compound 70:.....	244
DEPT90 for Compound 70:.....	245
DEPT135 for compound 70:	246

¹HNMR for Compound 32: (E)-4-Iodo-3-methylbut-3-en-1-ol **32**

^{13}C NMR for Compound 32:

¹H NMR for Compound 33: (3E,5E)-8-Hydroxy-6-methylocta-3,5-dien-2-one

^{13}C NMR for Compound 33:

¹HNMR for Carbene precursor 29: (3E,5E)-8-(2-methoxy-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one

^{13}C NMR for Carbene precursor 29:

DEPT135-Carbon for Carbene precursor 29:

DEPT90-Carbon for Carbene precursor 29:

¹H NMR for Compound 36a: 3,3-dimethylbutan-2-yl phenyl carbonate

¹H NMR for Compound 36b: Phenyl-1,1,1-trifluoro-3-methylbutan-2-yl carbonate

^1H NMR for Compound 36c: (1S,2S)-2-(benzyloxy)cyclopentyl phenyl carbonate

^{13}C NMR for Compound 36c:

DEPT135-Carbon for Compound 36c:

^1H NMR for Compound 36d: (1S,2S)-2-(benzyloxy)cyclohexyl phenyl carbonate

^{13}C NMR for compound 36d:

DEPT135-Carbon for Compound 36d:

^1H NMR for Compound 36e: Phenyl (1S,2R)-2-phenylcyclohexyl carbonate

¹HNMR for Compound 36f: Phenyl (1S,2R)-2-(2-phenylpropan-2-yl)cyclohexyl carbonate

^{13}C NMR for Compound 36f:

¹HNMR for Compound 36h: (1S,2R,4S)-4-isopropyl-2-(2-phenylpropan-2-yl)cyclohexyl phenyl carbonate

^{13}C NMR for Compound 36h:

DEPT135-Carbon for Compound 36h:

¹HNMR for Compound 36i: (2S,6S)-2,6-dimethylcyclohexyl phenyl carbonate

^{13}C NMR for Compound 36i:

¹H NMR for Compound 37a: 3,3-dimethylbutan-2-yl hydrazinecarboxylate

¹H NMR for Compound 37b: 1,1,1-trifluoro-3-methylbutan-2-yl hydrazinecarboxylate

^{13}C NMR for Compound 37b:

DEPT135-Carbon for Compound 37b:

^1H NMR for Compound 37c: (1S,2S)-2-(benzyloxy)cyclopentyl hydrazinecarboxylate

^{13}C NMR for Compound 37c:

DEPT135-Carbon for Compound 37c:

^1H NMR for Compound 37d: (1S,2S)-2-(benzyloxy)cyclohexyl hydrazinecarboxylate

^{13}C NMR for Compound 37d:

DEPT135-Carbon for Compound 37d:

^1H NMR for Compound 37e: (1S,2R)-2-phenylcyclohexyl hydrazinecarboxylate

^{13}C NMR for Compound 37e:

¹HNMR for Compound 37f: (1S,2R)-2-(2-Phenylpropan-2-yl)cyclohexyl hydrazinecarboxylate

^{13}C NMR for Compound 37f:

DEPT135-Carbon for Compound 37f:

(Traces of diethyl ether)

¹HNMR for Compound 37h: (1S,2R,4S)-4-isopropyl-2-(2-phenylpropan-2-yl)cyclohexyl hydrazinecarboxylate

^{13}C NMR for Compound 37h:

DEPT135-Carbon for Compound 37h:

(traces of diethyl ether δ 15.2, 65.9)

¹HNMR for Compound 37i: (2S,6S)-2,6-dimethylcyclohexyl hydrazinecarboxylate

^{13}C NMR for Compound 37i:

DEPT135-Carbon for Compound 37i:

¹HNMR for Compound 38a: 3,3-dimethylbutan-2-yl 2-(propan-2-ylidene)hydrazinecarboxylate

^{13}C NMR for Compound 38a:

DEPT-135-Carbon for Compound 38a:

¹HNMR for Compound 38b: 1,1,1-trifluoro-3-methylbutan-2-yl 2-(propan-2-ylidene)hydrazinecarboxylate

^{13}C NMR for Compound 38b:

DEPT135-Carbon for Compound 38b:

¹HNMR for Compound 38c: (1S,2S)-2-(benzyloxy)cyclopentyl 2-(propan-2-ylidene)hydrazinecarboxylate

^{13}C NMR for Compound 38c:

DEPT135-Carbon for Compound 38c:

¹HNMR for Compound 38d: (1S,2S)-2-(benzyloxy)cyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate

^{13}C NMR for Compound 38d:

DEPT135-Carbon for Compound 38d:

¹HNMR for Compound 38e: (1S,2R)-2-phenylcyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate

^{13}C NMR for Compound 38e:

DEPT135-Carbon for Compound 38e:

¹HNMR for Compound 38f: (1S,2R)-2-(2-Phenylpropan-2-yl)cyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate

^{13}C NMR for Compound 38f:

DEPT135-Carbon for Compound 38f:

^1H NMR for Compound 38g: (1S,2R,4R)-4-methyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate

^{13}C NMR for Compound 38g:

¹HNMR for Compound 38h: (1S,2R,4S)-4-isopropyl-2-(2-phenylpropan-2-yl)cyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate

^{13}C NMR for Compound 38h:

DEPT135-Carbon for Compound 38h:

¹HNMR for Compound 38i: (2S,6S)-2,6-dimethylcyclohexyl 2-(propan-2-ylidene)hydrazinecarboxylate

^{13}C NMR for Compound 38i:

DEPT135-Carbon for Compound 38i:

¹HNMR for Oxadiazoline 39a: 2-(3,3-dimethylbutan-2-yloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate

^{13}C NMR for Oxadiazoline 39a:

DEPT-135-Carbon for Oxadiazoline 39a:

¹HNMR for Oxadiazoline 39b: 5,5-dimethyl-2-(1,1,1-trifluoro-3-methylbutan-2-yloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate

^{13}C NMR for Oxadiazoline 39b:

DEPT135-Carbon for Oxadiazoline 39b:

^1H NMR for Oxadiazoline 39c: 2-((1R,2R)-2-(benzyloxy)cyclopentyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate

^{13}C NMR for Oxadiazoline 39c:

DEPT135-Carbon for Oxadiazoline 39c:

¹HNMR for Oxadiazoline 39d: 2-((1S,2S)-2-(benzyloxy)cyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate

^{13}C NMR for Oxadiazoline 39d:

DEPT135-Carbon for Oxadiazoline 39d:

¹HNMR for Oxadiazoline 39e: 5,5-dimethyl-2-((1S,2R)-2-phenylcyclohexyloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate

^{13}C NMR for Oxadiazoline 39e:

DEPT135-Carbon for Oxadiazoline 39e:

¹HNMR for Oxadiazoline 39f: 5,5-Dimethyl-2-((1R,2S)-2-(2-phenylpropan-2-yl)cyclohexyloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate

^{13}C NMR for Oxadiazoline 39f:

DEPT135-Carbon for Oxadiazoline 39f:

^1H NMR for Oxadiazoline 39h: 2-((1S,2R,4S)-4-isopropyl-2-(2-phenylpropan-2-yl)cyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate

^{13}C NMR for Oxadiazoline 39h:

DEPT135-Carbon for Oxadiazoline 39h:

¹HNMR for Oxadiazoline 39i: 2-((2S,6S)-2,6-dimethylcyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yl acetate

^{13}C NMR for Oxadiazoline 39i:

DEPT135-Carbon for Oxadiazoline 39i:

^1H NMR for Carbene precursor 30a: (3E,5E)-8-(2-(3,3-dimethylbutan-2-yloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one

^{13}C NMR for Carbene precursor 30a:

DEPT-135-Carbon for Carbene precursor 30a:

¹HNMR for Carbene precursor 30b: (3E,5E)-8-(5,5-dimethyl-2-(1,1,1-trifluoro-3-methylbutan-2-yloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one

^{13}C NMR for Carbene precursor 30b:

DEPT135-Carbon for Carbene precursor 30b:

¹HNMR for Carbene precursor 30c: (3E,5E)-8-(2-((1R,2R)-2-(benzyloxy)cyclopentyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one

^{13}C NMR for Carbene precursor 30c:

DEPT135-Carbon for Carbene precursor 30c:

¹HNMR for Carbene precursor 30d: (3E,5E)-8-(2-((1S,2S)-2-(benzyloxy)cyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one

^{13}C NMR for Carbene precursor 30d:

DEPT135-Carbon for Carbene precursor 30d:

¹HNMR for Carbene precursor 30e: (3E,5E)-8-(5,5-dimethyl-2-((1S,2R)-2-phenylcyclohexyloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one

^{13}C NMR for Carbene precursor 30e:

DEPT135-Carbon for Carbene precursor 30e:

¹HNMR for Carbene precursor 30f: (3E,5E)-8-(5,5-Dimethyl-2-((1R,2S)-2-(2-phenylpropan-2-yl)cyclohexyloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one

^{13}C NMR for Carbene precursor 30f:

DEPT135-Carbon for Carbene precursor 30f:

¹HNMR for Carbene precursor 30g: (3E,5E)-8-(5,5-dimethyl-2-((1S,2R,4R)-4-methyl-2-(2-phenylpropan-2-yl)cyclohexyloxy)-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one

^{13}C NMR for Carbene precursor 30g:

¹HNMR for Carbene precursor 30h: (3E,5E)-8-(2-((1S,2R,4S)-4-isopropyl-2-(2-phenylpropan-2-yl)cyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one

^{13}C NMR for Carbene precursor 30h:

DEPT135-Carbon for Carbene precursor 30h:

¹HNMR for Carbene precursor 30i: (3E,5E)-8-(2-((2S,6S)-2,6-dimethylcyclohexyloxy)-5,5-dimethyl-2,5-dihydro-1,3,4-oxadiazol-2-yloxy)-6-methylocta-3,5-dien-2-one

^{13}C NMR for Carbene precursor 30i:

DEPT135-Carbon for Carbene precursor 30i:

^1H NMR for Cycloadduct 25: rac-1-((3a*S*,6*R*,6a*R*)-6a-Methoxy-3a-methyl-3,3a,6,6a-tetrahydro-2*H*-cyclopenta[*b*]furan-6-yl)ethanone

^{13}C NMR for Cycloadduct 25:

(Carbonyl carbon was observed at δ 207.2)

DEPT135-Carbon for Cycloadduct 25:

DEPT90-Carbon for Cycloadduct 25:

¹HNMR for Cycloadducts 26a + 41a:

^{13}C NMR for Cycloadducts 26a + 41a:

DEPT-135-Carbon for Cycloadducts 26a + 41a:

¹HNMR for Cycloadducts 26b + 41b:

^{13}C NMR for Cycloadducts 26b + 41b:

DEPT135-Carbon for Cycloadducts 26b + 41b:

¹H NMR for Cycloadducts 26c + 41c: (90:10 mixture)

(Traces of diethyl ether)

^1H NMR for Cycloadducts 26c + 41c: (58:42 mixture)

^{13}C NMR for Cycloadducts 26c + 41c:

DEPT135-Carbon for Cycloadducts 26c + 41c:

¹HNMR for Cycloadducts 26d + 41d:

^{13}C NMR for Cycloadducts 26d + 41d:

DEPT135-Carbon for Cycloadducts 26d + 41d:

^1H NMR for Cycloadducts 26e + 41e:

^{13}C NMR for Cycloadducts 26e + 41e:

DEPT135-Carbon for Cycloadducts 26e + 41e:

¹HNMR for Cycloadduct 26f:

^{13}C NMR for Cycloadduct 26f:

DEPT135-Carbon for Cycloadduct 26f:

¹H NMR for Cycloadduct 41f:

^{13}C NMR for Cycloadduct 41f:

DEPT135-Carbon for Cycloadduct 41f:

¹HNMR for Cycloadducts 26g+ 41g:

^{13}C NMR for Cycloadducts 26g+ 41g:

¹H NMR for Cycloadducts 26h+ 41h:

^{13}C NMR for Cycloadducts 26h+ 41h:

DEPT135-Carbon for Cycloadducts 26h+ 41h:

^1H NMR for Cycloadducts 26i+ 41i:

^{13}C NMR for Cycloadducts 26i+ 41i:

DEPT135-Carbon for Cycloadducts 26i+ 41i:

¹HNMR for Ketone (±)-42: rac-(2R,5R)-2-(2-Hydroxyethyl)-5-isopropyl-2-methylcyclopentanone

^{13}C NMR for Ketone ($\pm$)-42:

(Carbonyl carbon was observed at δ 225.1)

DEPT135 for Ketone ($\pm$)-42:

¹HNMR for Ketone (-)-42: (2R,5R)-2-(2-Hydroxyethyl)-5-isopropyl-2-methylcyclopentanone

^{13}C NMR for Ketone (-)-42:

DEPT135 for Ketone (-)-42:

DEPT90 for Ketone (-)-42:

^1H NMR for compound 45: ($\pm$)-(1S,2R,5R)-1-(3-(benzyloxy)but-1-ynyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol

^{13}C NMR for compound 45:

¹HNMR for compound 46: (±)-(1S,2R,5R)-1-butyl-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol

^{13}C NMR for compound 46:

¹HNMR for compound 47a: (±)-(1S,2R,5R)-1-((S,Z)-3-hydroxybut-1-enyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol

^1H NMR for Compound 47b: ($\pm$)-(1*S*,2*R*,5*R*)-1-((*R*,*Z*)-3-hydroxybut-1-enyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol

X-Ray analysis for compound 47b: ($\pm$)-(1*S*,2*R*,5*R*)-1-((*R*,*Z*)-3-hydroxybut-1-enyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol

A Prism-like specimen of $C_{15}H_{28}O_3$, approximate dimensions 0.020 mm x 0.160 mm x 0.660 mm, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured on a Bruker Apex DUO system equipped with a Cu K α ImuS micro—focus source with MX optics ($\lambda = 1.54178$ Å). A total of 1727 frames were collected. The total exposure time was 4.80 hours. The frames were integrated with the Bruker SAINT software package using a wide-frame algorithm. The integration of the data using a triclinic unit cell yielded a total of 8465 reflections to a maximum θ angle of 71.17° (0.81 Å resolution), of which 5724 were independent (average redundancy 1.479, completeness = 94.8%, $R_{\text{int}} = 9.52\%$, $R_{\text{sig}} = 15.53\%$) and 2635 (46.03%) were greater than $2\sigma(F^2)$. The final cell constants of $a = 8.9728(5)$ Å, $b = 11.7223(6)$ Å, $c = 15.3620(7)$ Å, $\alpha = 74.929(4)^\circ$, $\beta = 87.840(4)^\circ$, $\gamma = 88.634(4)^\circ$, volume = $1558.95(14)$ Å³, are based upon the refinement of the XYZ-centroids of 5190 reflections above $20 \sigma(I)$ with $7.810^\circ < 2\theta < 138.8^\circ$. Data were corrected for absorption effects using the multi-scan method (SADABS). The ratio of minimum to maximum apparent transmission was 0.697. The calculated minimum and maximum transmission coefficients (based on crystal size) are 0.6989 and 0.9884. The structure was solved and refined using the Bruker SHELXTL Software Package, using the space group P -1, with $Z = 4$ for the formula unit, $C_{15}H_{28}O_3$. The final anisotropic full-matrix least-squares refinement on F^2 with 339 variables converged at $R1 = 6.95\%$, for the observed data and $wR2 = 21.43\%$ for all data. The goodness-of-fit was 0.929. The

largest peak in the final difference electron density synthesis was $0.266 \text{ e}^-/\text{\AA}^3$ and the largest hole was $-0.279 \text{ e}^-/\text{\AA}^3$ with an RMS deviation of $0.057 \text{ e}^-/\text{\AA}^3$. On the basis of the final model, the calculated density was 1.092 g/cm^3 and $F(000)$, 568 e^- .

Table 1. Crystal data and structure refinement for md_7_55_5.

Identification code	Spino_md_7_55_5	
Empirical formula	$C_{15}H_{28}O_3$	
Formula weight	256.37	
Temperature	173(2) K	
Wavelength	1.54178 Å	
Crystal size	0.020 x 0.160 x 0.660 mm	
Crystal system	triclinic	
Space group	P -1	
Unit cell dimensions	$a = 8.9728(5)$ Å	$\alpha = 74.929(4)^\circ$
	$b = 11.7223(6)$ Å	$\beta = 87.840(4)^\circ$
	$c = 15.3620(7)$ Å	$\gamma = 88.634(4)^\circ$
Volume	$1558.95(14)$ Å ³	
Z	4	
Density (calculated)	1.092 g/cm ³	
Absorption coefficient	0.585 mm ⁻¹	
F(000)	568	
Theta range for data collection	2.98 to 71.17°	
Index ranges	-10 ≤ h ≤ 10, -12 ≤ k ≤ 14, -15 ≤ l ≤ 18	
Reflections collected	8465	
Independent reflections	5724 [R(int) = 0.0952]	
Coverage of independent reflections	94.8%	
Absorption correction	multi-scan	
Max. and min. transmission	0.9884 and 0.6989	
Structure solution technique	direct methods	
Structure solution program	SHELXS-97 (Sheldrick, 2008)	
Refinement method	Full-matrix least-squares on F ²	
Function minimized	$\sum w(F_o^2 - F_c^2)^2$	
Data / restraints / parameters	5724 / 0 / 339	
Goodness-of-fit on F ²	0.929	
$\Delta/\sigma_{\max}$	0.001	
Final R indices	2635 data; I > 2σ(I)	R1 = 0.0695, wR2 = 0.1697
	(all data)	R1 = 0.1572, wR2 = 0.2143
Weighing scheme	$w = 1/[\sigma^2(F_o^2) + (0.0858P)^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$	
Absolute structure parameter	0.0(100)	
Extinction coefficient	0.266 and -0.279 eÅ ⁻³	
Largest diff. peak and hole	0.057 eÅ ⁻³	

¹HNMR for compound 48: (±)-(1S,2R,5R)-1-(3-hydroxybutyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol

^{13}C NMR for Compound 48:

^1H NMR for compound 49: ($\pm$)-(But-3-yn-2-yloxy)(tert-butyl)dimethylsilane

^{13}C NMR for compound 49:

Chemical structure of compound **50**, a bicyclic molecule. It features a five-membered ring fused to a four-membered ring. The five-membered ring has a hydroxyl group (OH) and a TBSO group (tert-butyldimethylsilyloxy) attached. The four-membered ring has an ethyl group attached. The structure is labeled **50**.

^{13}C NMR for compound 50:

DEPT135 for compound 50:

¹HNMR for compound 51: (±)-(1S,2R,5R)-1-(3-hydroxybut-1-ynyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol

^{13}C NMR for compound 51:

^1H NMR for Compound 54a (Acetylation of 50): ($\pm$)-2-((1R,2S,3R)-2-(3-(tert-butyltrimethylsilyloxy)but-1-ynyl)-2-hydroxy-3-isopropyl-1-methylcyclopentyl)ethyl acetate

^{13}C NMR for compound 54a (Acetylation of compound 50):

DEPT135 for compound 54a (Acetylation of compound 50):

^1H NMR for compound 54: ($\pm$)-2-((1R,2S,3R)-2-hydroxy-2-(3-hydroxybut-1-ynyl)-3-isopropyl-1-methylcyclopentyl)ethyl acetate

^{13}C NMR for compound 54:

DEPT135 for compound 54:

^1H NMR for compound 55: ($\pm$)-2-((1R,2S,3R)-2-hydroxy-3-isopropyl-1-methyl-2-(3-oxobut-1-ynyl)cyclopentyl)ethyl acetate

^{13}C NMR for compound 55:

DEPT135 for Compound 55:

¹HNMR for compound 56: (±)-(R)-2-(3-isopropyl-1-methyl-2-(3-oxobutyl)cyclopent-2-enyl)ethyl acetate

^{13}C NMR for compound 56:

DEPT135 for compound 56:

¹HNMR for compound **57**: (±)-2-((1R,2S,3R)-2-hydroxy-3-isopropyl-1-methyl-2-(3-oxobut-1-ynyl)cyclopentyl)acetaldehyde

^{13}C NMR for compound 57:

^1H NMR for compound 59: ($\pm$)-1-((3R,3aS,7aR)-3a,6-dihydroxy-3-isopropyl-7a-methyloctahydro-1H-inden-5-yl)ethanone

^{13}C NMR for compound 59:

^1H NMR for compound 59a (Witting reaction of 59): 1-((3R,3aS,7aR)-3a-hydroxy-3-isopropyl-7a-methyl-2,3,3a,4,7,7a-hexahydro-1H-inden-5-yl)ethenone

¹HNMR for compound 60: (±)-(1S,2R,5R)-1-(3-(tert-butyldimethylsilyloxy)butyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol

^{13}C NMR for compound 60:

DEPT135 for compound 60:

^1H NMR for compound 61: ($\pm$)-(1S,2R,5R)-1-((Z)-3-(tert-butyldimethylsilyloxy)but-1-enyl)-2-(2-hydroxyethyl)-5-isopropyl-2-methylcyclopentanol

^{13}C NMR for compound 61:

^1H NMR for aldehyde 62a: (Oxidation of 60) ($\pm$)-2-((1R,2S,3R)-2-(3-(tert-butyl)dimethylsilyloxy)butyl)-2-hydroxy-3-isopropyl-1-methylcyclopentyl)acetaldehyde

^{13}C NMR for aldehyde 62a: (Oxidation of 60)

DEPT90 for aldehyde 62a: (Oxidation of 60)

DEPT135 for aldehyde 62a: (Oxidation of 60)

^1H NMR for compound 62: ($\pm$)-(1S,2R,5R)-2-allyl-1-(3-(tert-butyldimethylsilyloxy)butyl)-5-isopropyl-2-methylcyclopentanol

^{13}C NMR for compound 62:

DEPT135 for Compound 62:

DEPT90 for Compound 62:

¹HNMR for compound 62b: (Olefination of aldehyde 62a using petasis) (±)-(1S,2R,5R)-1-(3-(tert-butyldimethylsilyloxy)butyl)-5-isopropyl-2-methyl-2-((E)-prop-1-enyl)cyclopentanol

^{13}C NMR for compound 62b: (Olefination of aldehyde 62a using petasis)

DEPT135 for compound 62b: (Olefination of aldehyde 62a using petasis)

^1H NMR for alcohol 63a: (TBS-deprotection of 62) ($\pm$)-(1S,2R,5R)-2-allyl-1-(3-hydroxybutyl)-5-isopropyl-2-methylcyclopentanol

^{13}C NMR for alcohol 63a: (TBS-deprotection of 62)

DEPT135 for alcohol 63a: (TBS-deprotection of 62)

DEPT90 for alcohol 63a: (TBS-deprotection of 62)

¹HNMR for Ketone 63: (±)-4-((1S,2R,5R)-2-allyl-1-hydroxy-5-isopropyl-2-methylcyclopentyl)butan-2-one

¹HNMR for enol ether 64: (±)- (5S,6R,9R)-6-allyl-9-isopropyl-2,6-dimethyl-1-oxaspiro[4.4]non-2-ene

^{13}C NMR for Compound 64:

DEPT135 for Compound 64:

DEPT90 for Compound 64:

¹H NMR for Ketone 65: (R)-4-(5-allyl-2-isopropyl-5-methylcyclopent-1-enyl)butan-2-one

DEPT90 for Ketone 65:

DEPT135 for Ketone 65:

¹HNMR for diene **24**: rac-(1S,2R,5R)-2-Allyl-5-isopropyl-2-methyl-1-(3-methylbut-3-enyl)cyclopentanol

^{13}C NMR for diene 24:

DEPT90 for diene 24:

DEPT135 for diene 24:

¹HNMR for rac-Carotol 1: (3R,3aS,8aR)-3-Isopropyl-6,8a-dimethyl-1,2,3,3a,4,5,8,8a-octahydroazulen-3a-ol

^{13}C NMR for rac-Carotol 1:

DEPT90 for rac-Carotol 1:

DEPT135 for rac-Carotol 1:

For spectral traces of compound **67-69** refer our preliminary communication (*reference 3*: Gund, M.; Déry, M.; Spino, C. *Org. Lett.* **2016**, *18*, 4280–4283)

¹HNMR for Compound 70: (5R,6R,9R)-6-allyl-9-isopropyl-2,2,6-trimethyl-1-oxaspiro[4.4]nonane

^{13}C NMR for compound 70:

DEPT90 for Compound 70:

DEPT135 for compound 70: