Update of Tables in the Review "Chiral Methyl-branched Pheromones"

Original Tables: *Natural Product Reports*, 2015, **32**: 1007-1041

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Lists of non-terpene semiochemicals with a methyl-branched structure identified from Arthropod and their syntheses

[a] Refer to the following database for the chemical structure and IUPAC name of each compound;

https://lepipheromone.sakura.ne.jp/pdb_top.html

[b] Some achiral compounds are included.

Table 1. Hydrocarbons: Pheromones and related compounds identified from insects. [a]

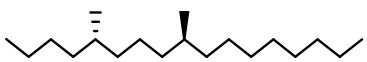
Pheromone				Insect		Reference [e]	
	Structure	Configuration [b]		Group [c]	Species [d]	Identification	Stereoselective synthesis
C_5	Δ1,Me2,Me3-5:H	?	B24	[Heteroptera]	*Tessaratoma papillosa*	554 [09]	
C_8	E2,Me3,E4,Me5,E6-8:H	achiral	B17	[Coleoptera]	*Colopterus truncatuss*	521 (00)	
C_9	E2,E4,Me4,E6,Me6-9:H	achiral	B17	[Coleoptera]	*Colopterus truncatuss*	521 (00)	
	E2,Me3,E4,Et5,E6-9:H	achiral	B17	[Coleoptera]	(1) *Carpophilus freeman,* (2) *Carpophilus davidsoni*	(1) 515 (90), (2) 519 (94)	
C_{10}	E2,Me3,E4,Me5,E6,Me7,E8-10:H	achiral	B17	[Coleoptera]	(1) *Carpophilus hemipterus,* (2) *Carpophilus brachypterus*, (3) *Colopterus truncatus*	(1) 514 (90), 516 (92), (2) 624 (95), (3) 521 (00)	
	E3,Me4,E5,Et6,E7-10:H	achiral	B17	[Coleoptera]	(1) *Carpophilus mutilates,* (2) *Carpophilus davidsoni*	(1) 517 (93), (2) 519 (94)	
	E2,Me3,E4,Me5,E6,Et7,E8-10:H	achiral	B17	[Coleoptera]	(1) *Carpophilus hemipterus,* (2) *Carpophilus brachypterus*	(1) 516 (92), (2) 624 (95)	
C_{11}	Me2-11:H	achiral	B16	[Isoptera]	*Amitermes dentatus*	500 (15)	
	Me3-11:H	?	B31	[Hymenoptera]	*Camponotus intrepidus*	730 [73]	
	E2,Me3,E4,Me5,E6,Me7,E8-11:H	achiral	B17	[Coleoptera]	(1) *Carpophilus hemipterus,* (2) *Carpophilus davidsoni,* (3) *Carpophilus obsoletus,* (4) *Carpophilus brachypterus*	(1) 514 (90), 516 (92), (2) 519 (94), (3) 623 (94), (4) 624 (95)	
	E3,E5,Et5,E7,Me7-11:H	achiral	B17	[Coleoptera]	*Carpophilus mutilatus*	517 (93)	
	E2,Me3,E4,Me5,E6,Et7,E8-11:H	achiral	B17	[Coleoptera]	(1) *Carpophilus freemani,* (2) *Carpophilus hemipterus,* (3) *Carpophilus davidsoni,* (4) *Carpophilus lugubris*	(1) 515 (90), (2) 516 (92), (3) 519 (94) (4) 624 (95)	
C_{12}	Me6-12:H	?	B31	[Hymenoptera]	*Pogonomyrmex barbatus,* *Pogonomyrmex rugosus*	731 [73]	

	Me3,Me5-12:H	?	B31	[Hymenoptera]	*Pogonomyrmex barbatus, Pogonomyrmex rugosus*	731 [73]	
	E3,Me4,E5,Et6,E7,Et8,E9-12:H	achiral	B17	[Coleoptera]	(1) *Carpophilus antiquus,* (2) *Carpophilus dimidiatus*	(1) 518 (93), (2) 520 (95)	
C_{13}	Me3-13:H	?	B31	[Hymenoptera]	*Camponotus intrepidus*	730 [73]	
	Me5-13:H	?	B31	[Hymenoptera]	*Pogonomyrmex barbatus*	731 [73]	
	E3,E5,Et5,E7,Et7,E9,Me9-13:H	achiral	B17	[Coleoptera]	*Carpophilus dimidiatus*	520 (95)	
	Δ2,Δ4,Me4, Me6,Me8,Me10-13:H (**1**) + primary alcohol (**35**)	2*E*,4*E*,*syn*,*syn*	B1	[Hymenoptera]	*Trichogramma turkestanica*	15 [05], 16 (14)	16 (14)
	E2,E4,Me4, Me6,E8,Me8, Me10-13:H	2*E*,4*E*,8*E*,6*S*, 10*S*	B12	[Hymenoptera]	*Tetrastichus planipennisi*	442 (20)	442 (20)
C_{14}	Me3,Me7-14:H	?	A	Lyonetiidae	*Leucoptera sinuella*	522 [20]	
C_{15}	Me7-15:H	?	A	Lyonetiidae	*Leucoptera sinuella*	522 [20]	
	Me3,Me7-15:H	?	A	Lyonetiidae	*Leucoptera sinuella*	522 [20]	
	Me5,Me9-15:H (**2**)	5*S*,9*R*	A	Lyonetiidae	*Perileucoptera coffeella*	17 [88], 18 (09)	19 (03), 20 (08)
C_{16}	Me3-16:H	?	B31	[Hymenoptera]	*Camponotus intrepidus*	730 [73]	
C_{17}	Me2-17:H	achiral	A	Erebidae	*Holomelina aurantiaca, Holomelina immaculate*	524 (71)	
					Isia isabella	525 (88)	
			B18	[Coleoptera]	*Phyllophaga opaca*	526 (19)	
	Me2,Me5-17:H (**3**)	*S*	A	Geometridae	*Lambdina fiscellaria*	21 (91)	22 (93)
	Me3,Me13-17:H (**4**)	3*S*,13*R*	A	Geometridae	*Nepytia freemani*	23 [93], 24 (95)	24 (95)
	Me5,Me9-17:H (**5**)	5*S*,9*S*	A	Lyonetiidae	*Leucoptera scitella* #1	25 [87], 26 (89)	27 (91), 28 (99), 29 (00), 30 (05), 31 (09), 32 (12), 655 (13), 683 (23)
	Me5,Me11-17:H (**6**)	5*R*,11*S*	A	Geometridae	*Lambdina fiscellaria*	33 [93], 34 (93)	35 (96), 695 (23)
	Me7-17:H (**7**)	*S*	A	Erebidae	*Anomis texana*	36 (93)	22 (93), 37 (00)

		S	A	Geometridae	*Lambdina fiscellaria* *Lambdina athasaria* #2	33 [93] 39 [94], 40 (01)	38 (99), 40 (01), 695 (23)
	Me7,Me11-17:H (**8**)	7*S*,11*R*	A	Geometridae	*Lambdina pellucidaria* #3	41 [98], 40 (01)	38 (99), 42 (02), 43 (04), 44 (07)
C_{18}	Δ1,Me14-18:H (**9**) (= Me5,Δ17-18:H)	*S*	A	Lyonetiidae	*Lyonetia clerkella*	45 [84], 46 (85)	47 (85), 638 (85), 48 (95), 49 (13), 663 (13), 664 (20), 602 (21), 628 (22)
	Δ1,Me10,Me14-18:H (**10**) (= Me5,Me9,Δ17-18:H)	10*S*,14*S*	A	Lyonetiidae	*Lyonetia prunifoliella*	50 [97], 51 (02)	28 (99), 52 (00), 31 (09), 53 (14), 54 (14), 683 (23)
C_{19}	Me9-19:H (**11**)	*S*	A	Erebidae	*Alabama argillacea*	36 (93)	55 (03), 56 (13)
	Me3,Me7-19:H		B15	[Diptera]	*Agromyza frontella*	501 [88]	
C_{21}	Δ6,Me13-21:H (**12**)	6*Z*,13*S*	A	Erebidae	*Scoliopteryx libatrix*	57 [00], 58 (03)	58 (03)
	Me5,Me9,Me17-21:H (**13**)	?	B2	[Heteroptera]	*Phthia picta*	59 [12]	
C_{22}	Me2-22:H	achiral	B19	[Diptera]	*Culicoides melleus*	537 (78)	
			B20	[Coleoptera]	*Chrysochus cobaltinus*	538 (07)	
			B13	[Coleoptera]	*Anoplophora glabripennis*	539 (14)	
C_{22}	Me4,Me6,Me8,Me10,Me16,Me18-22:H (**14**) + Me4,Me6,Me8,Me10,Me16-22:H (**15**)	4*S*,6*R*,8*R*,10*S*, 16*R*,18*S* $[\alpha]_D$ (+10.7),	B3	[Coleoptera]	*Antitrogus parvulus*	60 [03], 61 [05], 62 (07)	62 (07), 63 (07), 64 (08) 65 (12), 658 (14)
C_{23}	Me3-23:H	?	B22	[Coleoptera]	*Agrilus planipennis*	555 [09]	
	Me7-23:H (**16**)	?	B4	[Thysanoptera]	*Frankliniella occidentalis*	66 [13]	740 (24)
	Me11-23:H (**17**)	*SR*	B5	Gelechiidae	*Anarsia lineatella*	67 (05)	67 (05)
C_{25}	Me3-25:H (**18**) + Me3-27:H + Me3-29:H	?	B6	[Hymenoptera]	*Camponotus floridanus*	68 [04], 69 [14]	
	Me3-25:H (**18**)	?	B13	[Coleoptera]	*Xylotrechus colonus*	447 [03]	
	Me3-25:H (**18**) + Me3,Me13-25:H	?	B13	[Coleoptera]	*Semanotus japonicus*	627 [93]	
	Me5,Me11-25:H (**19**)	?	B7	Pyralidae	*Galleria mellonella*	70 [14]	656 (15)

	Me7-25:H	*R*	B8	[Coleoptera]	*Neoclytus acuminatus*	71 [08], 348 (15)	
	Me9-25:H	?	B13	[Coleoptera]	*Xylotrechus colonus*	447 [03]	
		?	B22		*Agrilus planipennis*	708 [09]	709 (23)
C_{26}	Me2-26:H	achiral	B13	[Coleoptera]	*Mallodon dasystomus*	546 (10)	
C_{27}	Me7-27:H (**20**)	*R*	B8	[Coleoptera]	*Neoclytus acuminatus* #4	71 [08], 348 (15)	72 (13)
	Me5-27:H + Me5,M17-27:H	*S*, 5*R*,17*S*	B11	[Hymenoptera]	*Ooencyrtus kuvanae*	347 (12)	348 (12)
	Me9-27:H	?	B13	[Coleoptera]	*Anoplophora malasiaca*	690 [00], 691 [23]	
		R	B8		*Neoclytus acuminatus*	71 [08], 348 (15)	
		?	B27		*Gastrophysa atrocyanea*	579 [06]	
	Me11-27:H	?	B27	[Coleoptera]	*Gastrophysa atrocyanea*	579 [06]	
		S	B13		*Tetropium fuscum, Tetropium cinnamopterum*	547 (11)	547 (11), 643 (22)
	Me13-27:H	?	B23	[Homoptera]	*Cacopsylla pyricola*	556 [09]	557 (01), 558 (11), 559 (21)
C_{28}	Me2-28:H	achiral	B14	[Diptera]	*Drosophila arizonae, Drosophila mojavensis, Drosophila navojoa*	448 (01)	
			B13	[Coleoptera]	*Mallodon dasystomus*	546 (10)	
C_{29}	Me3-29:H	?	B21	[Hymenoptera]	*Dibrachys cavus*	543 [11]	
	Me9-29:H	?	B13	[Coleoptera]	*Anoplophora malasiaca*	690 [00], 691 [23]	
		?	B27		*Gastrophysa atrocyanea*	579 [06]	
	Me11-29:H	?	B27	[Coleoptera]	*Gastrophysa atrocyanea*	579 [06]	
	Z7,Me15-29:H + Me3,Me7,Me11-29:H *etc.*	?	B10	[Hymenoptera]	*Eurytoma maslovskii*		349 [16]
	Me5,Me17-29:H	?	B13	[Coleoptera]	*Callidiellum rufipenne*	560 [09]	
C_{31}	Me3-31:H	?	B21	[Hymenoptera]	*Dibrachys cavus*	543 [11]	
	Δ1,Me13-31:H	?	B30	[Diptera]	*Stomoxys calcitrans*	713 [79]	
	Me3,Me7,Me11-31:H	?	B32	[Hymenoptera]	*Atta colombica*	367 [70]	
	Me3,Me7,Me11,Me15-31:H	?	B25	[Diptera]	*Glossina brevipalpis*	573 [88]	
C_{32}	Me4,Me8,Me12-32:H	?	B32	[Hymenoptera]	*Atta colombica*	367 [70]	

C_{33}	Me15-33:H (**21**)	?	B9	[Diptera]	*Stomoxys calcitrans* #4	73 [75], 74 [77]	75 (84), 76 (87)
	Δ1,Me13-33:H	?	B30	[Diptera]	*Stomoxys calcitrans*	713 [79]	
	Me15,Me19-33:H	?	B9	[Diptera]	*Stomoxys calcitrans* *Glossina austeni*	73 [75], 74 [77] 707 [80]	75 (84)
	Δ1,Me13,Me17-33:H	13*S*,17*R*	B26	[Diptera]	*Glossina austeni*	576 [00], 578 (05)	577 (01)
	Δ1,Me19,Me23-33:H	?	B28	[Diptera]	*Glossina morsitans*	629 [91]	
	Me3,Me7,Me11-33:H	?	B32	[Hymenoptera]	*Atta colombica*	367 [70]	
C_{34}	Me4,Me8,Me12-34:H	?	B32	[Hymenoptera]	*Atta colombica*	367 [70]	
C_{35}	Z8,Me21-35:H	*R*	B13	[Coleoptera]	*Psacothea hilari*	548 [96], 549 (97)	550 (98), 551 (99), 552 (21)
	Me13,Me17-35:H	?	B29	[Phasmatodea]	*Diapheromera femorata*	710 [81]	
	Me13,Me23-35:H	13*R*,23*S*	B26	[Diptera]	*Glossina pallidipes*	570 [84], 571 (85), 572 [86]	569 (83)
	Δ1,Me13,Me17-35:H	13*S*,17*R*	B26	[Diptera]	*Glossina austeni*	576 [00], 578 (05)	577 (01)
	Me11,Me15,Me19,Me23-35:H	?	B25	[Diptera]	*Glossina palpalis*	573 [88]	
C_{37}	Me11,Me23-37:H	?	B26	[Diptera]	*Glossina tachinoides*	573 [88], 575 [98]	574 [94]
	Me13,Me25-37:H	?	B26	[Diptera]	*Glossina tachinoides*	573 [88], 575 [98]	574 [94]
	Me17,Me21-37:H	?	B25	[Diptera]	*Glossina morsitans*	567 [78], 572 [86]	567 [78], 587 [80]
	Me15,Me19,Me23-37:H	?	B26	[Diptera]	*Glossina morsitans*	567 [78], 572 [86]	567 [78], 568 [80]



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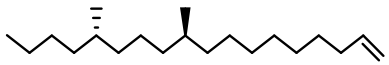

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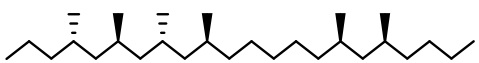

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[a] Compounds are arranged in order of length of the main chains. A, sex pheromones of female moths; B1, sex pheromone from females of a parasitoid wasp; B2, sex pheromone from males of a true bug; B3, cuticular hydrocarbon from females of a scarab beetle; B4, sex pheromone from males of a thrip; B5, scent in body scales of female moths; B6, queen pheromone from several social insects; B7, sex pheromone from males of a moth; B8, cuticular hydrocarbon from females of a longhorn beetle; B9, sex pheromone from females of a fly; B10, cuticular hydrocarbons from females of a wasp; B11, sex pheromone from males of a parasitoid wasp; B12, sex pheromone from females of a wasp; B13, sex pheromone from females of a longhorn beetle; B14, sex pheromone from females of a fruit fly; B15, sex

pheromone from females of a leaf-minor fly; B16, trail pheromone from a termite; B17, aggregation pheromone from males of a sap beetle; B18, sex pheromone (?) from a scarab beetle; B19, sex pheromone from females of a biting midge; B20, sex pheromone (?) from a leaf midge; B21, sex pheromone from females of a parasitoid wasp; B22, sex pheromone from females of a jewel beetle; B23, sex pheromone from females of a psylla; B24, alarm pheromone of a true bug; B25, cuticular hydrocarbon from females of a tsetse fly; B26, sex pheromone from females of a tsetse fly; B27, sex pheromone from females of a leaf beetle; B28, anti-aphrodisiac pheromone from males of a tsetse fly; B29, cuticular hydrocarbon from females of a stick insect; B30, sex pheromone from females of a stable fly; B31, gland secretion of ant; B32, cuticular hydrocarbon from an ant.

[b] Configurations of moth pheromones were mainly assigned by biological activity (field evaluation of synthetic isomers).

[c] Family in Lepidoptera or [order of other insects].

[d] Also identified from *Lyonetia prunifoliella* (#1); *Lambdina pellucidaria.* (#2); *Lambdina athasaria* (#3); and several species in Coleoptera and Hymenoptera (#4).

[e] (Year of publication, 19XX or 20XX). [ ] indicates year when the publication was reported before determination of the absolute configuration.

Table 2. Primary alcohols and their derivatives (aldehydes and esters): Pheromones and related compounds identified from insects, mites, and spiders. [a]

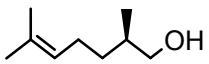
Pheromone					Insecta and [Arachnida]		Reference [e]	
	Structure [Trivial name]	Configuration and analytical method [b]		Function (Producer)	Order [c]	Species [d]	Identification	Stereoselective synthesis
C_3	Me1-3:OAc	?		aggregation (M)	Coleo.	*Strategus aloeus* (scarab beetle)	449 [00]	
C_4	Me2-4:OH (**22**)	*R*	GC* #A	aggregation (M)	Coleo.	(1) *Phymatodes lecontei,* (2) *Phymatodes amoenus, Phymatodes varius, Phymatodes lengi,* (3) *Phymatodes pusillus,* (4) *Pyrrhidium sanguineum, Phymatodes alni* (longhorn beetle)	(1) 77 (07) (2) 531 (15) (3) 532 [18] (4) 533 (19)	77 (07)
	Me2-4:OH (**22**)	*S*		aggregation (M)	Coleo.	*Megacyllene acuta* (longhorn beetle)	523 (18)	
	Me2-4:OH (**22**)	?		primer (queen)	Iso.	*Reticulitermes speratus* (termit)	441 [10]	
	Me2-4:OH (**22**) + Me4-7:OH (**23**)	*S* *R*	GC* #B	sex (F)	Hetero.	*Triatoma brasiliensis* (assassin bug)	78 (09)	78 (09)
	Me2-4:OCOPr	*S*		(1) gland secretion, (2) aggregation (F)	Hetero.	(1) *Megalotomus quinquespinosus* (2) *Alydus eurinus* (broad-headed bug)	(1) 605 [75] (2) 606 (00)	
	E2,Me2-4:OCOPr	?		aggregation (F)	Hetero.	*Alydus eurinus* (broad-headed bug)	606 [00]	
C_5	Me2-5:OH	*R*		aggregation (M)	Coleo.	*Sphaerion inerme* (longhorn beetle)	734 (24)	
	Me2-5:OCOR (stearate etc.) (**24**)	*S*	HPLC* #C		[Astigmata]	*Sancassania shanghaiensis*	79 (01)	79 (01)

	+ Me2,Me4-6:OCOR (stearate etc.) (**25**)	2*S*,4*S*				(acarid mite)		
C_6	Me2-6:OH (**26**)	*S*	GC* #D	(mandibular gland)	Hymeno.	*Cataglyphis bicolor* (ant) #1	80 [92], 81 (96)	81 (96)
	E2,Me2,E4,Me4-6:OH	achiral		allomone ?	[Opiliones]	*Leiobunum leiopenis, Leiobunum calcar* (spider: harvestman)	686 (77)	
C_7	Me2,Δ5,Me6-7:OH (**27**) + Ald derivative	*R*	GC* #E	sex (F)	[Astigmata]	*Tyreophagus* sp (acarid mite)	82 (09)	82 (09)
	E2,Me2,E4,Me4-7:OH	achiral		allomone ?	[Opiliones]	*Leiobunum leiopenis,* (spider: harvestman)	686 (77)	
C_8	Me7-8:OCOR (COR = Me7-8)	achiral		sex (F)	Coleo.	*Elater ferrugineus* *Agriotes ferrugineipennis* (click beetle)	460 (07) 631 (22)	
	Me7-8:OCOR (COR = Z4-10)	achiral		sex (F)	Coleo.	*Elater ferrugineus* (click beetle)	460 (07)	
C_9	Me4-9:OH (**28**)	*R*	HPLC #F	sex (F)	Coleo.	*Tenebrio molitor* (mealworm)	83 [86], 84 (89),	84 (89), 85 (03), 86 (10), 659 (15), 660 (16), 661 [17], 662 [18], 513 (20)
C_{10}	E2,Me2-10:Ald	achiral		gland secretion	Hymeno.	*Apterostigma dentigerum* (ant)	451 (17)	E2,Me2-10:Ald
	Me2,Me8-10:OCOEt	2*S*,10*S*		sex (F)	Hymeno.	*Eurytoma maslovskii* (wasp)	431 (20)	
	Me4,Me5-10:Ald	?		aggregation (M)	Coleo.	*Tribolium castaneum* (darkling beetle)	635 [91]	
	Me4,Me8-10:Ald (**29**) [tribolure]	4*R*,8*R*		aggregation	Coleo.	(1)(2) *Tribolium castaneum* (1)(4) *Tribolium confusum,* (3)(4) *Tribolium freemani,* (4) *Tribolium madens* (flour beetle) #2	(1) 87 [81], (2) 88 (83), 428 (83), 711 (84), 89 (11), (3)	90 (83), 91 (85), 92 (88), 93 (02), 94 (06), 95 (06), 96 (11), 670(15), 671 (19), 672 (20),
		mixture	HPLC #J					

							647 (87), (4) 474 [02]	746 (25)
C_{11}	Me4,Me6-11:OH	?		trail	Isoptera	*Hodotermopsis sjoestedti* (termite)	502 [11]	
	Me4,Me6-11:Ald	?		sex (M)	Isoptera	*Hodotermopsis sjoestedti* (termite)	502 [11]	
	Me2,Me4,Me6,Me8-11:OH [prieskanol]	2*R*,4*R*,6*R*,8*R*	NMR	sex (F)	Homo.	*Margarodes prieskaensis* (scale)	350 (17)	350 (17)
C_{12}	Me10-12:OH	?		sex (M)	Cole.	*Compsibidion graphicum, C. sommeri* (longhorn beetle)	667 [20]	667 [20]
	Me10-12:OAc (**30**)	*R*		sex (F)	Lepido.	*Adoxophyes honmai* (leafroller moth)	97 [79], 98 (83)	99 (79), 100 (85), 48 (95), 101 (98), 102 (01), 103 (14)
	Me10-12:Ald	?		sex (M)	Cole.	*Eburodacrys vittata* *E. assimilis, E. lenkoi, etc.* (longhorn beetle)	351 [16] 667 [20]	667 [20]
	Me3,Δ6,Et7,Δ10,Me11-12:Ald (**31**) + C11 analogue (**32**)	3*S*,6*E*	GC* #G	sex (F)	Coleo.	*Callosobruchus rhodesianus* (seed beetle)	104 (10), 105 (10)	104 (10)
	Me3,Δ6,Me7,Δ10,Me11-12:OH (**33**) [2,3-dihydrofarnesol] + Ald derivative	3*S*,6*E*	GC* #H	marking (M)	Hymeno.	*Bombus terrestris* (bumblebee) #3	432 (70), 106 (04)	106 (04)
	Me3,Me5,Me9-12:Ald (**34**) [stylopsal]	3*R*,5*R*,9*R*		sex (F)	Strepsi.	*Stylops melittae* *S. muelleri* (twisted-wing parasite)	107 (12) 108 [12], 109 (13)	107 (12) 109 (13)
	Me4,Me6-12:Ald	?		sex (M), trail	Iso.	*Zootermopsis nevadensis, Z. angusticollis* (termite)	352 [10]	353 [11]
	Me2,Me10-12:OCOEt	2*S*,10*R*		sex (F)	Hymeno.	*Eurytoma maslovskii* (wasp)	431 (20)	

C_{13}	Me11-13:Ald	?		sex (F)	Coleo.	*Eburodacrys dubitata, E. assimilis, E. flexuosa, etc.* (longhorn beetle)	667 [20]	667 [20]
	Δ2,Δ4,Me4,Me6,Me8,Me10-13:OH (**35**)	2*E*,4*E*,*syn*, *syn*		sex (F)	Hymeno.	*Trichogramma turkestanica* (parasitoid wasp)	15 [05], 16 (14)	110 (14)
	Me3,Me4,Δ6,Me7,Δ10,Me11-13:Ald (**36**) [faranal]	3*S*,4*R*, 6*E*,10*Z*	NMR #I	trail	Hymeno.	*Monomorium pharaonis* (ant)	111 (77), 429 (80)	111 (77), 429 (80), 112 (95), 113 (10), 354 (88), 355 (19)
	Me3,Me5,Δ7,Me9, Δ11,Me11-13:Ald [peckidienal]	3*R*,5*S*,9*R* 7*E*,11*E*	GC* #J	sex (F)	Strepsi.	*Xenos peckii* (twisted-wing parasite)	356 [15], 357 (16)	357 (16)
C_{14}	Me6,Me10,Me13-14:OH (**37**)	?		aggregation (M)	Hetero.	*Stiretrus anchorago* (stink bug)	114 [86], 115 [89]	
	Me6,Me10,Me13-14:$OCOC_4H_9$	?		gland secretion (M)	Hetero.	(1) *Perillus bioculatus, Oplomus severus* (2) *Eocanthecona furcellata* (stink bug)	(1) 114 [86] (2) 589 [03], 590 [05]	
	Me2,Me4,Me8,Me13-14:OH	2*R*,4*R*,8*R*		sex (M)	Hetero.	*Pellaea stictica* (stink bug)	536 [15], 630 (22)	630 (22)
C_{15}	Me10,Me14-15:OCOiPr (**38**)	*R*		sex (F)	Lepido.	*Arna pseudoconspersa, Artaxa subflava* (tussock moth)	116 [94], 117 (96), 118 (07)	119 (95), 358 (88), 359 (17), 360 (18), 739, (24)
C_{16}	Z8,Me14-16:OH (**39**)	*R*	$[\alpha]_D$ (-)	sex (F)	Coleo.	*Trogoderma inclusum* (hide beetle)	120 [69], 122 (74)	122 (74)
	E8,Me14-16:OH	?		sex (F)	Coleo.	*Trogoderma glabrum* (hide beetle)	511 [75]	
	Z8,Me14-16:Ald (**40**) [trogodermal]	*R* *S*		sex (F)	Coleo.	*Trogoderma granarium* (hide beetle) #4	123 [76], 121 (80), 726 (80) 714 (78), 715 (79)	125 (78), 126 (82), 103 (14) 124 (77)
	E8,Me14-16:Ald	*R*		sex (F)	Coleo.	*Trogoderma granarium*	123 [76],	126 (82)

	[trogodermal]	*S*			(hide beetle) #5	121 (80), 726 (80) 714 (78), 715 (79)	124 (77)
C_{29}	Me12,Me20-29:OMe	?	species recognition	[Araneae]	*Tetragnatha extensa* (long jawed spider)	540 [21]	
	Me8,Me14,Me20-29:OMe	?	species recognition	[Araneae]	*Tetragnatha extensa* (long jawed spider)	540 [21]	



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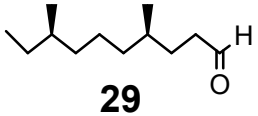

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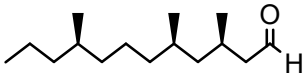

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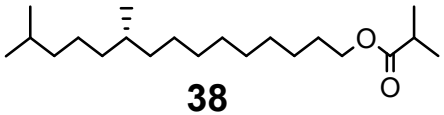

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[a] Compounds are arranged in order of length of the main chains.

[b] GC* and HPLC* indicate analyses with the following enantioselective columns; #A, Cyclodex-B; #B, CycloSil-B (30% heptakis (2,3-di-*O*-methyl-6-*O*-*t*-butyl dimethylsilyl)-ß-cyclodextrin in DB-1701); #C, Shiseido Ceramospher chiral RU-1 S-5; #D, octakis(6-*O*-methyl-2,3-di-*O*-phenyl)-γ-cyclodextrin; #E, CP-cyclodextrin-β-2,3,6-M-19; #G, β–DEX 225; #H, heptakis(2,3-di-*O*-acetyl-6-*O*-TBDMS)-β–cyclodextrin. #F: Analysis after oxidation and derivatizaiton with (*R*)-1-phenylethylamine. #I: The coupling constant ($J_{3,4}$ = 4 Hz) indicates *syn* configuration. #J: Chirasil-DEX CB

[c] Coleo. = Coleoptera, Hetero. = Heteroptera, Hymeno. = Hymenoptera, Lepido. = Lepidoptera, Strepsi. = Strepsiptera.

[d] Also identified from *Cataglyphis diehlii, C. savignyi,* and *C. viaticus* (#1); *Tribolium audax, T. brevicornis, and T. destructor* (#2); *Bombus impatiens and B. jonellus* (#3); *Trogoderma glabrum, T. inclusum* and *T. variabile* (#4). and *Trogoderma glabrum* (#5)

[e] (Year of publication, 19XX or 20XX). [ ] indicates year when the publication was reported before determination of the absolute configuration.

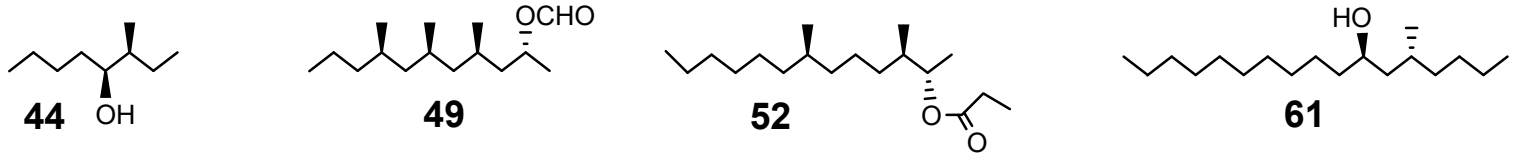
Table 3. Secondary alcohols and their esters: Pheromones and related compounds identified from insects and mites. [a]

Pheromone				Insecta and [Arachnida]		Reference [e]	
	Structure [Trivial name]	Configuration and analytical method [b]	Function (Producer)	Order [c]	Species [d]	Identification	Stereoselective synthesis
C_3	(NMe$_2$)1,Me2-3:2-OH	achiral	aggregation	Dictyo..	*Blattella germanica* (cockroach)	634 (90)	
C_5	Me3-5:2-OH	?	gland secretion	Hymeno.	*Crematogaster nigriceps* (ant)	603 [02]	
C_6	Me3-6:2-OH	?	gland secretion	Hymeno.	*Pseudomyrmex nigrocincta* (ant)	588 [05]	
	Me3,Me5-6:2-OH (**41**)	?	sex	Hetero.	*Triatoma dimidiata* (assassin bug)	127 [13]	
	Me4-6:3-OH (**42**) + Me4-6:3-one (**64**)	3*R*,4*S* GC #A		Hymeno.	*Tetramorium impurum* (ant)	128 (81)	129 (00)
C_7	Me2-7:4-OH	?	aggregation (M)	Coleo.	*Metamasius hemipterus* *Rhabdoscelus obscurus* (weevil) *Scyphophorus acupunctatus* (bark beetle)	433 [97] 465 [00] 561 [03], 562 [08]	
	Me4-7:3-OH (**43**) (= Me4-7:5-OH)	3*S*,4*S* GC* #C	aggregation	Coleo.	(1) *Scolytus multistriatus, S. amygdali,* (2) *S. scolytus*	(1) 131 [75], 132 (77). 133 (04) (2) 362 [77], 697 [83]	133 (04), 361 (17)
		3*R*,4*S*			(3) *Scolytus laevis* (bark beetle)	(3) 669 (10)	
		3*R*,4*S* GC* #B	trail	Hymeno.	*Leptogenys diminuta*	130 (88), 444 [00]	361 (17)
		?	gland secretion		*Paraponera clavata*	618 [84]	

		?		alarm		*Ooceraea biroi* (ant)	689 [23]	
		?		allomone ?	[Opiliones]	*Leiobunum townsendi* (spider: harvestman)	687 [85]	
	E4,Me4-7:3-OH	?		allomone ?	[Opiliones]	*Leiobunum townsendi* (spider: harvestman)	687 [85]	
	Me4-7:3-OR (= Me4-7:5-OR)	?		gland secretion	Hymeno.	*Leptogenys diminuta* (ant)	444 [00]	
	Me6-7:2-OH	?		alarm ?	Hetero.	*Triatoma phyllosoma, T. longipennis, T. pallidipennis*	733 [18]	
	E2,Me6-7:4-OH [rhynchophorol]	*S*		aggregation (M)	Coleo.	*Rhynchophorus palmarum,* *Rhabdoscelus obscurus* (weevil)	467 (92) 465 [00]	467 (92), 580 (92)
C_8	Me7-8:2-OH	achiral		allomone ?	[Opiliones]	*Gonyleptes horridus* (spider: harvestman)	716 (23)	
	Me2-8:4-OH	*S*		aggregation (M)	Coleo.	*Metamasius hemipterus* *Rhabdoscelus obscurus* *Sphenophorus levis* (weevil) *Scyphophorus acupunctatus* (bark beetle)	433 [97] 465 [00] 466 (03) 561 [03], 562 [08]	
	Me3-8:4-OH (**44**) (= Me6-8:5-OH) [phoenicol]	3*S*,4*S*	GC* #D	aggregation (M)	Coleo.	*Rhynchophorus phoenicis* (weevil) #1	134 [93], 135 (94)	136 (93), 135 (94), 137 (99), 138 (11)
	Me5-8:4-OH (**45**) (= Me4-8:5-OH) [cruentol]	4*S*,5*S*	GC* #D	aggregation (M)	Coleo.	*Rhynchophorus cruentatus* (weevil)	139 [94], 135 (94)	135 (94), 137 (99), 636 (14)
C_9	Me4-9:5-OH (**46**) [ferrugineol]	4*S*,5*S*	GC* #D	aggregation (M)	Coleo.	(1) *Rhynchophorus ferrugineus,* (2) *Metamasius hemipterus* (weevil) #2	(1) 140 [93], 141 (95), (2) 433 (97)	142 (93), 137 (99), 138 (11), 636 (14), 665 [17], 666 [21]
	E6,Me7-9:3-OAc [quadrilure]	3*R*		aggregation (M)	Coleo.	*Cathartus quadricollis* (flat bark beetle)	646 (88)	
C_{10}	Me8-10:2-OCOEt (**47**)	2*R*,8*R*		sex (F)	Coleo.	*Diabrotica virgifera*	143 [82],	145 (84), 146 (85),

		2*S*,8*R*			(leaf beetle) *Diabrotica longicornis* (leaf beetle)	144 (84) 649 (86)	147 (86), 225 (02), 363 (90), 364 (18), 657 [15]
C_{11}	Me4,Me6,Δ7,Me8,Δ9-11:5-OH (**48**)	4*R**,5*R**,6*S**, 7*E*,9*E* #a	gland secretion	Dictyo.	*Cryptocercus punctulatus* (cockroach) #3	148 [91]	149 (90)
	Me4,Me6,Me8-11:2-OFo (**49**) [lardolure]	2*R*,4*R*,6*R*,8*R*	aggregation	[Astigmata]	*Lardoglyphus konoi* (acarid mite)	150 [82], 151 (86), 152 (94)	153 (86), 154 (90), 155 (95), 156 (96), 157 (05), 158 (12)
	Me3,Me9-11:2-OCOEt (**50**)	2*S*,3*R*,9*S*	sex (F)	Hymeno.	*Diprion nipponica* (sawfly)	159 (98), 160 (02)	
C_{12}	Me3,Me9-12:6-OH	?	trail	Hymeno.	*Leptogenys peuqueti* (ant)	443 [97]	
C_{13}	Me4,Me10-13:7-OH	4*R*,10*R*	trail	Hymeno.	*Leptogenys peuqueti* (ant)	443 (97)	
	Me3,Me7-13:2-OAc (**51**) + Me3,Me7-13:2-OCOEt (**52**) < Me3,Me7-13:2-OH>[f]	2*S*,3*R*,7*R* 2*S*,3*R*,7*R* GC #A	sex (F)	Hymeno.	*Diprion pini* (sawfly) #4	161 (95), 162 (11)	163 (04), 164 (06)
	Me3,Me7,Me9-13:2-OAc (**53**) <Me3,Me7,Me9-13:2-OH>[f]	2*S*,3*R*,7*R*,9*S* GC* #E	sex (F)	Hymeno.	*Macrodiprion nemoralis* (sawfly)	165 (00)	166 (11)
	Me3,Me7,Me11-13:2-OCOEt (**54**) <Me3,Me7,Me11-13:2-OH>[f]	2*S*,3*S*,7*S*,11*R*	sex (F)	Hymeno.	*Microdiprion pallipes* (sawfly)	167 [98], 168 (03)	169 (99), 170 (04)
C_{14}	Me3,Me7-14:2-OCOEt (**55**)	2*S*,3*R*,7*R*	sex (F)	Hymeno.	*Gilpinia pallida* (sawfly)	171 (06)	171 (06), 365 (13), 366 (14)
	Me4-14:7-OAc + Me4-14:7-OH	? ?	trail	Hymeno.	*Leptogenys peuqueti* (ant)	443 [97]	
C_{15}	Me3,Me7-15:2-OAc (**56**) [diprionyl acetate] <Me3,Me7-15:2-OH>[f] (**58**)	2*S*,3*S*,7*S* GC #A	sex (F)	Hymeno.	(1)(2) *Neodiprion lecontei*, (1)(3)(5)(6) *N. sertifer*, (3) *N. nannulus, N. sertifer*, (4) *N. pinetum* (sawfly) #5	(1) 172 [76], (2) 614 [79] (3) 475 (87). (4) 476 (88), (5) 173 (00),	174 (81), 175 (01), 176 (04), 367 (07), 177 (12), 178 (12), 645 (22)

							(6) 162 (11)	
	Me3,Me7-15:2-OCOEt (**57**) <Me3,Me7-15:2-OH>[f] (**58**)	2*R*,3*R*,7*R* 2*S*,3*R*,7*R* 2*S*,3*S*,7*S*	GC #A	sex (F)	Hymeno.	*Diprion similis* *Neodiprion sertifer* (sawfly)	172 [76], 701 (80), 702 (82), 476 (88) 173 (00), 162 (11)	174 (81), 175 (01), 176 (04), 177 (12), 178 (12), 367 (07), 503 [82]
	<Me3-15:2-OH>[f] (**59**) <Me3,Me7-15:2-OH>[f] (**58**)	2*S*,3*R* 2*S*,3*R*,7*R*	GC* #E	sex (F)	Hymeno.	*Gilpinia frutetorum* (sawfly) #6	179 (09)	179 (09)
	Me6,Me10,Me14-15:2-OH (**60**)	2*R*,6*R*,10*R*		sex (F)	Lepido.	(1) *Corcyra cephalonica,* (2) *Aphomia sociella* (pyralid moth)	(1) 180 [87], 181 (91), (2) 368 (12)	182 (00), 183 (11)
C_{17}	Me5-17:7-OH (**61**)	5*R*,7*R*		sex (F)	Lepido.	*Miltochrista calamine* (lichen moth)	184 (11)	185 (14), 615 (22)
C_{29}	Me19-29:6-OAc (**62**) + Me15-29:7-OAc (**63**)	6*R*,19*R* 7*R*,15*SR*	HPLC #F	sex (F)	Diptera	*Cochliomyia hominivorax* (blowfly)	186 [93], 187 [07], 188 (09)	189 (04), 190 (04)



[a] Compounds are arranged in order of length of the main chains.

[b] #A, Analyzed after derivatization with (*S*)-2-acetoxypropionyl chloride. GC* indicates analyses with the following enantioselective columns; #B, Mn(II)-bis[3-heptafluorobutyryl-(1*R*)-camphorate] in methylsilicone OV-101; #C, Lipodex G, octakis-(2,3-di-*O*-pentyl-6-*O*-methyl)-γ-cyclodextrin; #D, Cyclodex-B; #E, XE-60-(*S*)-valine-(*S*)-2-phenylethylamide. #G, Synthetic alcohol intermediates were analyzed after derivatizaiton with (1*R*,2*R*)-2-(2,3-anthracenedicarboximido)cyclohexanecarboxylic acid.

[c] Coleo. = Coleoptera, Dictyo. = Dictyoptera, Hymeno. = Hymenoptera, Lepido. = Lepidoptera.

[d] Also identified from *Rhynchophorus cruentatus* (#1); *Rhynchophorus bilineatus, R. vulneratus, Dynamis borassi*, and *Metamasius hemipterus* (#2); *Cryptocercus kyebangensis* (#3); *Diprion jingyuanensis* (#4); *Neodiprion pratti and N. taedae* (#5); and *Gilpinia socia* (#6).

[e] (Year of publication, 19XX or 20XX). [ ] indicates year when the publication was reported before determination of the absolute configuration.

[f] Identification of alcohols as biosynthetic precursors.

Table 4. Ketones: Pheromones and related compounds identified from insects, spiders, and mites. [a]

Pheromone				Insecta and [Arachnida]		Reference [e]	
	Structure [Trivial name]	Configuration and analytical method [b]	Function (Producer)	Order [c]	Species [d]	Identifi-cation	Stereoselective synthesis
C_5	Me4-5:4-OH, 2-one	achiral	alarm	Hymeno.	*Tapinoma simrothi* (ant)	564 (83)	
			sex (M) ?	Hetero.	*Halobates hawaiiensis* (water strider)	566 (01)	
C_6	Me3-6:2-one	?	alarm	Hetero.	*Dipetalogaster maximus* *Triatoma phyllosoma, T. longipennis, T. pallidipenni* (assassin bug)	696 [83] 733 [18]	
		?	gland secretion	Hymeno.	*Pseudomyrmex spinicola, P. nigrocincta* (ant)	588 [05]	
	Me4-6:2-one	?	alarm	Hymeno.	*Polyrhachis vicina* (ant)	427 [19]	
	Me4-6:3-one (**64**)	*S*	alarm	Hymeno.	*Manica mutica* (ant) #1	191 [72], 192 (92)	129 (00)
		?	allomone	Coleoptera	*Staphylinus olens.* (rove beetle)	712 [75]	
		?	allomone	[Opiliones]	*Leiobunum nigripalpi* (spider: harvestman)	686 [77]	
	E4,Me4-6:3-one	achiral	allomone	[Opiliones]	*Leiobunum nigripalpi* (spider: harvestman)	686 (77)	
	Δ1,Me4-6:3-one	?	allomone ?	Coleo.	*Amarygmus tristis*	703 [82]	
		?			*Byrsax macleayi*	704 [92]	
		?		[Opiliones].	*Gonyleptes curvicornis, Parampheres* sp.	544 [05]	

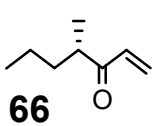
		R				*Gonyleptes saprophilus, Acanthogonyleptes pulche* (spider: harvestman)	545 (13)	
	Δ1,Me5-6:3-one	achiral		allomone ?	[Opiliones]	*Neosadocus maximus, Zortalia inscripta*	544 (05)	
						Sodreana lprevosti, S. barbiellini (spider: harvestman)	545 (13)	
	Me3,Me4-6:2-one	?		alarm ?	Hymeno.	*Apterostigma pilosum* (ant)	499 [17]	
C_7	Me2-7:4-one	achiral		alarm	Hymeno.	*Tapinoma simrothi* (ant)	564 (83)	
				aggregation (M)	Coleo.	*Halobates hawaiiensis*	565 (07)	
						Scyphophorus acupunctatus (bark beetle)	561 (08)	
	Me4-7:3-one (**65**)	*S*	$[\alpha]_D$ (+)	alarm	Hymeno.	*Atta texana*	193 (74),	198 (74)
		?				*A. colombica, A. cephalotes*	499 [17]	
		?				*Ooceraea biroi* (ant) #2	689 [23]	
		S	GC* #A	trail		*Aphaenogaster cockerelli, A. albisetosus* (ant)	194 (95)	
		S		allomone		*Dasymutilla occidentalis* (wasp, velvet ant) #4	196 (80)	
		?		gland secretion		*Paraponera clavata* (ant)	618 [84]	
		S		aggregation ?	Coleo..	*Scolytus scolytus, S. multistriatus* (bark beetle)	697 (83)	
		?		allomone ?		*Ocypus similis, O. olens* (rove beetle)	698 [90]	
		S	GC* #B	sex (F)	Tricho.	*Potamophylax latipennis* (caddis fly) #3	195 (01)	

	S		allomone	[Opiliones]	*Leiobunum vittatum* *Leiobunum formosum, Leiobunum speciosum,* *Leiobunum ventricosum Hadrobunus maculosus* *Leiobunum townsendi* (spider: harvestman)	197 (71) 687 [71] 685 [76] 688 [85]	
Δ1,Me4-7:3-one (**66**) [chichimol ketone]	*S*	$[\alpha]_D$ (+)	allomone	Phasmatodea	*Agathemera elegans* (walking stick)	199 (06)	200 (09)
	?		allomone ?	[Opiliones]	*Gonyleptes horridus, Gonyleptes curvicornis* (harvestman)	716 [23]	
Δ4,Me4-7:3-one	achiral		gland secretion	Hymeno.	*Leptanilla* sp, *Atta laevigata* (ant)	612 (98) 613 (99)	
Δ2,Me6-7:4-one	achiral		aggregation (M)	Coleo.	*Metamasius spinolae* (bark beetle)	565 (07)	
Me2-7:2-OH, 4-one	achiral		aggregation (M)	Coleo.	*Metamasius spinolae* (bark beetle)	565 (07)	
Me4-7:5-OH, 3-one (**67**) [sitophinone, sitophilure]	4*S*,5*R*		aggregation	Coleo.	*Sitophilus oryzae* (weevil) #5 *Rhinostomus barbirostris* (weevil)	201 [84], 507 [85], 202 (87) 369 (18)	203 (86), 204 (88), 205 (06)
	4*S*,5*S*		aggregation	Coleo.	*Sitona discoideus* (weevil)	509 (13)	
Me4-7:3-one, 5-one	achiral		aggregation	Coleo.	*Sitona lineatus* *Sitona discoideus* (weevil)	508 (84) 509 (13)	
Me3,Me6-7:2-one, 4-one	?		sex (F)	Diptera	*Megaselia halterata* (humpbacked fly)	510 [82]	

C_8	Me2-8:4-one	achiral		aggregation (M)	Coleo.	*Scyphophorus acupunctatus* (bark beetle)	561 (08)	
	Me3,Me5-8:2-one	?		alarm?	Hymeno.	*Apterostigma pilosum*	499 [17]	
	E4,Me4,Me6-8:3-one (**68**) [manicone]	*S*	GC* #C	alarm	Hymeno.	*Manica mutica, M. bradleyi* *M. rubida* (ant) #1	191 [72] 206 (88)	206 (88)
	Me4,E6,Me6-8:3-one	?		allomone	[Opiliones]	*Leiobunum calcar* (spider: harvestman)	685 [76], 686 [77]	
	Me6-8:3-one (**69**)	?		alarm gland secretion	Hymeno.	*Crematogaster ashmeadi* *Myrmica scabrinodis* (ant) #6	207 [72] 717 [78], 718 [78]	208 (88), 209 (10), 210 (13), 477 [15]
	Me7-8:4-one	achiral		gland secretion	Hymeno.	*Andrena clarkella, A. fucata* (mining bee)	727, (76)	
	E6,Me6-8:3-one, 8-OH	achiral		aggregation (M)	Coleo.	*Oulema melanopus* (leaf beetle)	446 (02), 596 (03)	446 (02)
	Me3,Δ6,Me7-8:1-OH,3-OH,2-one[f] (**70**)	*S*	GC* #D	aggregation (M)	Coleo.	*Leptinotarsa decemlineata* (leaf beetle)	211 (02), 430 (02)	212 (05), 213 (09), 214 (13), 215 (14)
C_9	Me3-9:2-one	?		gland secretion	Hymeno.	*Apterostigma dentigerum* (ant)	451 [17]	
	Me8-9:2-one	achiral		sex (F)	[Araneae]	*Agelenopsis aperta* (spider)	468 (01)	
	Me6-9:3-one	?		sex (F)	Tricho.	*Hesperophylax occidentalis* (caddis fly)	604 [96]	675 [18]
	Me4-9:5-one [ferruginone]	?		aggregation (M)	Coleo.	*Rhynchophorus ferrugineus, R. vulneratus* (weevil)	607 [93]	665 [17], 676 [18], 666 [21]
	Me4,Δ7,Me8-9:2-one	?		alarm	Hymeno.	*Vespa velutina* (wasp)	743 [17], 744 [23]	
	Me4,Me6-9:3-one (**71**) + C8 derivatives	4S,6S	GC* #B	sex (F)	Tricho.	*Potamophylax latipennis* (caddis fly) #3	195 (01)	195 (01)

	Me4,E6,Me6-9:3-one	?	allomone	[Opiliones]	*Leiobunum longipes* (spider: harvestman)	685 [76]	
	Me4,Me6-9:7-OH,3-one (**72**) [serricornin]	4*S*,6*S*,7*S*	sex (F)	Coleo.	*Lasioderma serricorne* (deathwatch beetle)	216 [79], 639 (82), 217 (84), 218 (01)	639 (82), 640 (85), 219 (85), 220 (11), 678 (20)
C_{10}	Me2-10:5-one	achiral	gland secretion	Hymeno.	*Andrena clarkella, A. fucata* (mining bee)	727, (76)	
	E2,Me5,E6,Me7,E8-10:4-one	*R*	sex (F)	Homo.	*Matsucoccus josephi* (scale)	491 [93], 492 (95)	493 [93], 494 (94), 486 [95], 487 [95], 489 [97], 490 (00)
	E2,Me5,Z6,Me7,E8-10:4-one	*R*	sex (F)	Homo.	*Matsucoccus josephi* (scale)	491 [93], 492 (95)	
	Me4,Me6,Me8-10:2-one (**73**) [chortolure]	4*R*,6*R*,8*R* GC* #E	aggregation (F &M)	[Astigmata]	*Chortoglyphus arcuatus* (storage mite)	221 (04)	221 (04)
C_{11}	Me4,Me6,E7,Me8,E9-11:3-one [graphisurone]	4*R*,6*S*	aggregation (M)	Coleo.	*Graphisurus fasciatus, Eutrypanus dorsalis* (longhorn beetle)	737 (24)	737 (24)
C_{12}	Me3,Me7,E8,Me9,E10-12:6-one	3*S*,7*R*	sex (F)	Homo.	*Matsucoccus feytaudi* (scale)	497 [90], 498 (94)	495 (91), 496 (93), 494 (94), 486 [95], 487 [95], 489 [97], 490 (00)
	Me3,Me7,Z8,Me9,E10-12:6-one	?	sex (F)	Homo.	*Matsucoccus feytaudi* (scale)	497 [90], 498 (94)	487 [95]
C_{13}	Me10-13:2-one (**74**)	*R*	sex (F)	Coleo.	*Diabrotica undecimpunctata* (leaf beetle)	222 (83)	223 (83), 224 (85), 225 (02), 226 (03), 55 (03), 227 (09), 228 (12), 657 [15], 673 (16)
	E2,E4,Me4,Me6,Me10,Me12-13:7-one [matsuone]	6*R*,10*R*	sex (F)	Homo.	(1)(2) *Matsucoccus matsumurae* (1)(2)(3) *M. thunbergianae*	(1) 478 [89], (2) 479 [91],	482 (91), 483 (93), 484 (93), 485 (95),

						(1)(2)(4) *M. resinosae* (scale)	(3) 480 (94), (4) 481 (95)	481 (95), 486 [95], 487 [95], 488 (96), 489 [97], 490 (00), 677 [19]
C_{14}	Me6,Me10,Me13-14:2-one (**75**) [pallantione]	6*R*,10*S*	GC* #F	sex (M)	Hetero.	*Pallantia macunaima* (stink bug)	229 (13)	230 (13) , 370 (18)
	dimer of Δ1,Me5-6:3-one	?		allomone ?	[Opiliones].	*Sodreana lprevosti, Sodreana barbiellini*	545 [13]	
						Gonyleptes horridus, Gonyleptes curvicornis (spider: harvestman)	716 [23]	
	dimer of Δ1,Me4-6:3-one	?		allomone ?	[Opiliones].	*Gonyleptes saprophilus*	545 [13]	
						Gonyleptes horridus, Gonyleptes curvicornis (spider: harvestman)	716 [23]	
C_{15}	Me6,Me12-15:2-one (**76**)	6*R*,12*R*		sex (F)	Coleo.	*Diabrotica balteata* (leaf beetle)	231 [87], 232 (91)	233 (88), 234 (95), 225 (02), 674 (15), 729 (24)
	Me6,Me10, Me14-15:2-one (+ Me6,Me10, Me14-15:2-OH)	6*R*,10*R*	GC* #I	sex (M)	Lepido.	*Bicyclus anynana* (butterfly) #7	371 [08], 372 (15)	372 (15)
				sex (F)	Lepido.	*Aphomia sociella* (pyralid moth)	368 (12)	
C_{18}	Me6-18:2-one (**77**)	*S*	HPLC*	sex (F)	Lepido.	*Lyclene dharma* (lichen moth)	235 [07], 236 (10)	237 (09), 238 (12), 738 (24)
	+ Me14-18:2-one (**78**)	*S*	#G					
	+ Me6,Me14-18:2-one (**79**)							
C_{27}	Me3,Me11-27:2-one (**81**)	3*S*,11*S*		sex (F)	Dictyo.	*Blattella germanica* (cockroach)	243 (04)	242 (08)
	+ Me3,Me11-27:2-one, 27-OH						725 [08]	
C_{29}	Me3,Me11-29:2-one (**80**)	3*S*,11*S*	ORD #H	sex (F)	Dictyo.	*Blattella germanica* (cockroach)	239 [74], 240 (79)	241 (81), 242 (08)
	+ Me3,Me11-29:2-one, 29-OH						723 [76], 725 [08]	724 [77]



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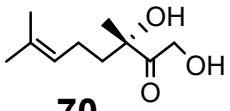

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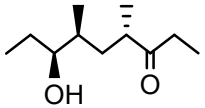

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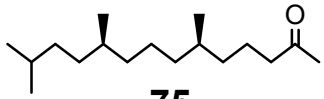

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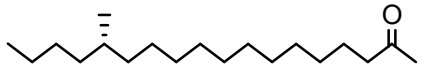

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[a] Compounds are arranged in order of length of the main chains.

[b] GC* and HPLC* indicate analyses with the following enantioselective columns; .#A, 6-*O*-methyl-2,3-di-*O*-pentyl-γ-cyclodextrin; #B, 60% octakis-(6-*O*-methyl-2,3-di-*O*-pentyl)-γ-cyclodextrin in OV1701, #C, FSCC coated with OV-1 containing 1% nickel(II) bis[3-(heptafluorobutyryl)-(1*R*)-camphorate]; #D, Chiraldex™ B-DM; #E, heptakis(2,6-di-*O*-dimethyl-3-*O*-pentyl)-β-cyclodextrin; #F, β-DEX 325 (2,3-di-*O*-methyl-6-*O*-TBDMS-β-cyclodextrin, after $LiAlH_4$ reduction); #G, Chiralpak AD-H. #H: ORD measurement and NMR analysis with a chiral shift reagent; #I: Analyzed as (*S*)-2-acetoxypropionyl ester after reduction to alcohol.

[c] Coleo. = Coleoptera, Dictyo. = Dictyoptera, Hymeno. = Hymenoptera, Lepido. = Lepidoptera, Tricho. = Trichoptera.

[d] Also identified from mandibular glands of *Manica bradleyi* and a head of *Tetramorium impurum* (#1, see Table 3); several species in *Atta*, *Aphaenogaster*, *Pseudomyrmex, Pogonomyrmex*, and *Sericomyrmex* (**#2**); *Potamophylax cingulatus* and *Glyphotaelius pellucidus* (#3); several species in Hymenoptera and Coleoptera (#4); *Sitophilus zeamai*s (#5); several species in Hymenoptera and Trichoptera (#6); and several species in *Bicyclus* (#7).

[e] (Year of publication, 19XX or 20XX). [ ] indicates year when the publication was reported before determination of the absolute configuration.

[f] 1,3-Dihydroxy-3,7-dimethyl-6-octen-2-one

Table 5. Carboxylic acids and their derivatives: Pheromones and allomones identified from insects and spiders. [a]

Pheromone			Insecta			Reference [e]	
	Structure [trivial name]	Configuration and analytical method [b]	Function (Producer)	Order [c]	Species [d]	Identification	Stereoselective synthesis
C_3	Me2-3:acid	achiral	allomone ?	Lepido.	*Graphium doson, G. sarpedon* (butterfly)	610 (80)	
			aggregation	Hetero.	*Rhodnius prolixus*	445 (02)	
			alarm ?		*Triatoma phyllosoma, T. longipennis, T. pallidipennis* (assassin bug)	733 (18)	
			aggregation	[Ixodida]	*Amblyomma hebraeum* (tick)	611 (02)	
	Me2-3:Me ester	achiral	allomone ?	Lepido.	*Graphium doson, G. sarpedon*	610 (80)	
					Parnassius glacialis	616 (95)	
					Chilasa epycides, Papilio demoleus, P. macilentus, P. troilus (butterfly)	617 (06)	
C_4	Me2-4:acid	?	allomone	Lepido.	*Papilio machaon, P. protenor* (butterfly)	461 [65] 462 [80]	
				Coleo.	*Oodes vicarious* (ground beetle)	463 [82]	
				Thysano.	*Varshneyia pasaniae* (thrips)	464 [88]	
	Me2-4:Z3-6-OH ester	?	allomone	Coleo.	*Chrysomela lapponica*	608 [97]	
					C. mainensis, C. walshi (leaf beetle)	609 [99]	
	Z2,Me2-4:acid [angelic acid]	achiral	allomone ?	Coleo.	*Pterostichus subsulcatus*	637 (89)	

				Carabus violaceus (ground beetle)	706 (20)	
Me2,E2-4:acid [tiglic acid]	achiral	allomone ?	Coleo.	*Carabus yaconinus* *C. montivagus, C. caelatus* *Pterostichus subsulcatus* *P. californicus* (ground beetle) *Trachypachus slevini* (false ground beetle)	599 (85) 706 (20) 637 (89) 601 (07) 600 (04)	
E2,Me2-4:Et ester [ethyl tiglate]	achiral	aggregation (M)	Diptera	*Drosophila virilis* *D. americana, D. lummei, D. novamexicana* *D. hydei* *D. borealis, D. littoralis* (fruit fly)	597 (85) 684 (86) 648 (87) 598 (88)	
E2,Me2-4:iPr ester [isopropyl tiglate]	achiral	aggregation (M)	Diptera	*Drosophila hydei* (fruit fly)	648 (87)	
E2,Me2-4:E2-6-OH ester	achiral	gland secretion	Hetero.	*Pachylis laticornis* (true bug)	705 (82)	
Et2-4:2-OH, β-lactone	2*S*,3*S*	sex (M)	Lepido.	*Idea leuconoe* (butterfly)	469 [96], 470 (02)	
iPro2-4:2-OH, β-lactone [viridifloric β-lactone]	2*S*,3*S*	sex (M)	Lepido.	*Idea leuconoe* (butterfly)	469 [96], 470 (02)	
$NH_2$2,Me3-4:Me ester [L-valine methyl ester]	*S*	sex (F)	Coleo.	*Phyllophaga anxia*, *P. georgiana* (scarab beetle)	458 (97), 471 (09)	
Me2-4:Me2-4-OH ester	?	aggregation (M)	Hetero.	*Clavigralla elongate* (true bug)	742 [24]	
Me2-4:Me2-4-NH_2 amide	*2S,2'S*	sex (F)	Coleo.	*Migdolus fryanus* (longhorn beetle)	472 (94)	641 (01), 642 (22)
($CHOHCH_3$)2,Me3-4:γ-lactone	2*S*,3*R*,1'*S*	sex (M) ?	Lepido.	*Hymenitis dercetis*	529 [76]	

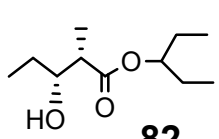
	[ithomiolide A]					*Ceratinia tutia* *Ithomia salapia* (butterfly)	530 (04) 668 [20]		
	Ac2,Me3-4:γ-lactone [ithomiolide B]	2*S*,3*R*		sex (M) ?	Lepido.	*Prittwitzia hymaenea* *Episcada clausina* (butterfly)	722 (92) 530 (04)		
C_5	Me2-5:acid	?		allomone ?	(Geophilomorpha)	*Clinopodes flavidus* (centipede)	735 [24]		
	Me2-5:3-OH, Et-Pr ester [f] (**82**) [sitophilate]	2*S*,3*R*	NMR #A	aggregation (M)	Coleo.	*Sitophilus granaries* (weevil)	244 (87), 245 (89)	246 (89), 247 (89), 248 (96), 249 (01), 250 (07), 251 (12), 252 (13)	
	E2,(C_2H_4OH)3,Me4-5:Me ester	achiral		sex (M)	Coleo.	*Diaprepes abbreviates* (weevil)	542 (12)		
	$NH_2$2,Me3-5:Me ester [L-isoleucine methyl ester]	2*S*,3*S*		sex (F)	Coleo.	*Holotrichia parallela* *Phyllophaga anxia* *Phyllophaga elenans* (scarab beetle)	457 (92) 458 (97) 459 (03)		
	HCONH2,Me3-5:Me ester [N-formyl L-isoleucine methyl ester]	2*S*,3*S*		sex (F)	Coleo.	*Phyllophaga elenans* (scarab beetle)	459 (03)		
	MeCONH2,Me3-5:Me ester [N-acetyl L-isoleucine methyl ester]	2*S*,3*S*		sex (F)	Coleo.	*Phyllophaga elenans* (scarab beetle)	459 (03)		
	$NH_2$2,Me4-5:Me ester [L-leucine methyl ester]	*S*		sex (F)	Coleo.	*Phyllophaga lanceolata* (scarab beetle)	473 (03)		
	E2,Me2-5:iPr ester [trunc-call 1]	achiral		aggregation (M)	Coleo.	*Prostephanus truncates* (auger beetle)	581 (91), 582 (91), 583 (04)		
	E2,Me2-5:Me1-4-OH ester [dominicalure 1]	*S*		aggregation (M)	Coleo.	*Rhyzopertha dominica* (auger beetle)	584 [81], 585 (81), 586 [83], 692 [03], 693 [22]		644 (22)
	E2,Me2,Me4-5:iPr ester [trunc-cal 2]	achiral		aggregation (M)	Coleo.	*Prostephanus truncates* (auger beetle)	582, (91), 583, (04)		

	E2,Me2,Me4-5:Me1-4-OH ester [dominicalure 2]	*S*		aggregation (M)	Coleo.	*Rhyzopertha dominica* (auger beetle)	584 [81], 585 (81), 586 [83], 692 [03], 693 [22]	644 (22)
C_6	Me2-6:acid	?		alarm ?	Hetero.	*Triatoma phyllosoma, T. longipennis, T. pallidipennis* (assassin bug)	733 [18]	
	Me4-6:*n*-Bu ester (**83**)	*S*		aggregation	Hetero.	*Neomegalotomus parvus* (broad-headed bug)	253 (12)	
	Z3,Me4,Δ5-6:acid	achiral		marking (M) ?	Diptera	*Urophora cardui, U. stylata* (fruit fly)	633 (90)	
	Δ2,Me2,Me4-6:acid	?		allomone?	Hymeno.	*Myrmecocystus christineae, M. colei, M. depilis. M. romaine, M. semirufus, M. wheeleri* (ant)	450 [89]	
	Me4,Δ5-6:γ-lactone [lavender lactone]	*S*		sex (M) ?	Lepido.	*Celastrina argiolus* (butterfly)	541 (13)	
	Me2-6:δ-lactone	2*R**,5*S**		gland secretion (M)	Hymeno.	*Bombus griseocollis* (carpenter bee)	591 [76]	592 (78)
	Me2,Me4-6:δ-lactone [g] (**84**)	2*S*,4*R*,5*S*		trail	Hymeno.	(1)(2) *Camponotus herculeanus,* (2)(4) *C. socius,* (2) *C. ligniperdus, C. vagus, C. pennsylvanicus,* (3) *C. modoc,* (5) *C.kaura* (ant)	(1) 254 [95], (2) 255 (99), (3) 434 (19), (4) 435 (01), (5) 436 [01]	255 (99)
C_7	Me2,Me4,Me6-7:δ-lactone [h] (**85**)	2*S*,4*R*,5*S*		sex (F)	Hymeno.	*Macrocentrus grandii* (parasitoid wasp)	256 [93], 257 (94)	258 (93), 745 [94],259 (96), 260 (11), 373 (19)
	Me3-7:acid (**86**)	*R*	GC* #B	sex (M)	Coleo.	*Kheper nigroaeneus* (scarab)	261 (02)	261 (02), 680 (15), 675 [18]
	Me4-7:Et ester (**88**)	?		aggregation	Coleo.	*Oryctes rhinoceros*	263 [95]	

			(M)		(scarab) *Nicrophorus vespilloides* (burying beetle) #1	437 [08], 374 [17]	
	3-hydroxy-3-methoxycarbonyl-2-methylpentanedioic acid dimethyl ester [trimethyl methylcitrate]	2*R*,3*S*	sex (F)	[Araneae]	*Argiope bruennichi* (spider)	527 (10)	
C_8	Me4-8:acid		aggregation (M)	Coleo.	*Oryctes monoceros* *Oryctes rhinoceros*	264 [94] 263 [95],	679 [13]
		R				625 (22)	660 (16), 682 (21), 625 (22)
					Oryctes elegans	534 [04]	
					Oryctes agamemnon (scarab)	535 [15]	
	Me4-8:Et ester (**89**) [oryctelure]	*S*	aggregation (M)	Coleo.	*Oryctes monoceros* *Oryctes rhinoceros*	264 [94] 263 (95)	263 (95), 665 [17], 681 (18)
		R				625 (22)	665 [17], 625 (22)
					Oryctes elegans	534 [04]	
					Oryctes Agamemnon (scarab)	535 [15]	
	E4,Me7-8:iPr ester	achiral	sex (F)	Homo.	*Crisicoccus azalea* (mealybug)	632 (22)	
	Me2-8:acid, 8-acid [2-methylsuberic acid]	?	secretion (F)	Coleo.	*Callosobruchus rhodesianus* (seed beetle)	728 [17]	
	Me3-8:acid, 8-acid [3-methylsuberic acid]	?	secretion (F)	Coleo.	*Callosobruchus rhodesianus* (seed beetle)	728 [17]	
	Me2,Me4,Me6-8:δ-lactone	?	trail	Hymeno.	*Camponotus atriceps* *Camponotus castaneus* (ant)	452 [96] 453 [03]	
C_9	E4,Me7-9:Et ester	*S*	sex (F)	Homo.	*Crisicoccus azalea* (mealybug)	632 [22], 741 (24)	741 (24)
	E4,Me7-9:iPr ester	*S*	sex (F)	Homo.	*Crisicoccus azalea* (mealybug)	632 [22], 741 (24)	741 (24)

	Me2,Me4,Me6-9:δ-lactone [i] (**90**) [invictolide]	2*R*,4*R*,5*S*, 6*R*		queen recognition	Hymeno.	*Solenopsis invicta* (ant)	265 [83], 266 (86)	266 (86), 267 (86), 268 (87), 269 (96), 270 (12)
	Z2,Me2,Z4,Me4,Me6-9:δ-lactone			aggregation (M)	Coleo.	*Rosalia alpina* (longhorn beetle)	528 [17]	
C_{10}	Me9-10:Me7-8-OH ester	achiral		sex (F)	Coleo.	*Ectinus aterrimus* (click beetle)	563 (08)	563 (08)
C_{11}	Me2,Me4,Me6,Me8,Me10-11:β-lactone [j] (**91**) [vittatalactone]	2*R*,3*R*,4*S*, 6*S*,8*S*	NMR #A	aggregation (M)	Coleo.	*Acalymma vittatum* (leaf beetle)	271 [05]	272 (09), 273 (10), 274 (11), 275 (11), 276 (12)
	Me2,Me8-11:Me2-11-OH ester + Me2,Me8-11:Me2,Me8-11-OH ester + others	? ?		cuticular lipid (F)	[Araneae]	*Argyrodes elevatus* (spider)	375 [16]	375 [16]
C_{12}	Me3,Me5-12:acid (**92**)	3*R*,5*S*		sex (F)	Coleo.	*Prionus californicus* (longhorn beetle)	277 [09], 278 (11), 279 (11)	278 (11)
	Me3,Δ6,Me7,Δ10,Me11-12:Me ester (**93**) [methyl 2,3-dihydrofarnesoate]	3*R*,6*E*	GC #C	sex (M)	Hetero.	*Chlorochroa ligata* (stink bug) #2	280 [01], 281 (01)	281 (01)
C_{13}	Me2-13:11-OH ester	?		cuticular lipid (M)	[Araneae]	*Argyrodes elevatus* (spider)	375 [16]	375 [16]
C_{15}	Me4,Me8,Me12-15:Me ester (**96**)	?		sex (M)	Hetero.	*Edessa meditabunda* (stink bug)	285 [12]	504 (20)
	Me3,Me13-15:Et-Me-Pr ester [k] (**97**)	3*R*,13*R*,3'*S*		sex (F)	Lepido.	*Clania variegata* (bagworm moth)	286 [06], 287 (10)	288 (09), 287 (10), 289 (13), 376 (17), 732 (24)
	Me2,Me14-15:Glu amide	2*R* [(*S*)-L-Glu]		marking	Diptera	*Ceratitis rosa* (fruit fly)	699 (03), 700 (10)	700 (10), 721 (23)
C_{7+5}	Me2,Me4-7:α-pyrone [l] (**98**) [supellapyrone]	2*R*,4*R*	GC* #D	sex (F)	Dictyo.	*Supella longipalpa* (cockroach)	290 [93], 291 (95)	292 (95), 293 (01)
C_{16}	Z8,Me14-16:Me ester	?		sex (F)	Coleo.	*Trogoderma inclusum* (hide beetle)	120 [69], 512 [77]	122 (74)
	E8,Me14-16:Me ester	?		sex (F)	Coleo.	*Trogoderma glabrum (hide beetle)*	511 [75]	
C_{17}	Me2,Me4-17:13-OH ester	2*R*,4*R*		cuticular	[Aranea	*Argiope bruennichi*	626 (22)	

			lipid (M)	e]	(spider)		
C_{19}	Me2,Me4-19:13-OH ester	?	cuticular lipid (M,F)	[Aranea e]	*Argiope bruennichi* (spider)	626 [22]	



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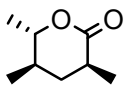

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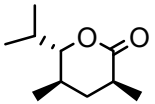

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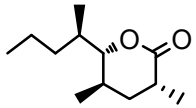

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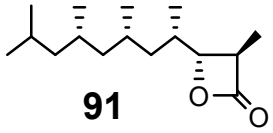

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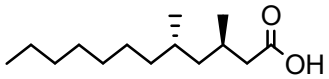

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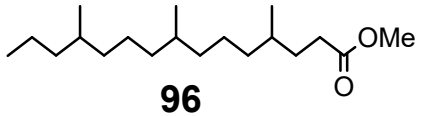

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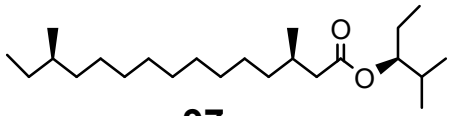

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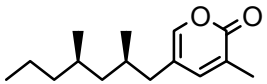

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[a] Compounds are arranged in order of length of the main chains.

[b] #A, determination by Mosher's method. GC* indicates analyses with the following enantioselective columns;#B, 10% heptakis(2,3,6-tri-*O*-methyl)-β-cyclodextrin in OV-1701-OH; #C, analysis after hydrolysis and derivatization with (*S*)-methylbenzylamine; #D, trifluoroacetylated γ-cyclodextrin phase, Chiraldex GTA.

[c] Coleo. = Coleoptera, Hetero. = Heteroptera, Hymeno. = Hymenoptera, Lepido. = Lepidoptera, Dictyo. = Dictyoptera.

[d] Also identified from *Nicrophorus interruptus*, *N. tomentosus* and *N. pustulatus* (#1); and *Chlorochroa sayi* and *C. uhleri* (#2).

[e] (Year of publication, 19XX or 20XX). [ ] indicates year when the publication was reported before determination of the absolute configuration.

[f] 1-Ethylpropyl 2-methyl-3-hydroxypentanoate.

[g] 2,4-Dimethyl-5-hexanolide.

[h] Tetrahydro-3,5-dimethyl-6-isopropyl-2*H*-pyran-2-one.

[i] Tetrahydro-3,5-dimethyl-6-(1-methylbutyl)-2*H*-pyran-2-one.

[j] 3-Methyl-4-(1,3,5,7-tetramethyloctyl)oxetan-2-one.

[k] 1-Ethyl-2-methylpropyl 3,13-dimethylpentadecanoate.

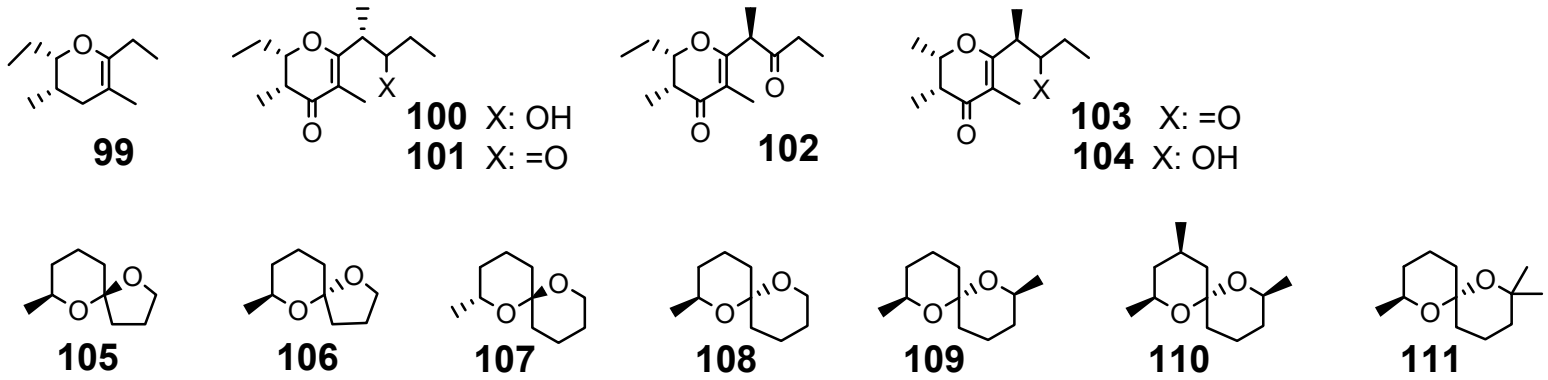
[l] 5-(2',4'-Dimethylheptanyl)-3-methyl-2*H*-pyran-2-one.

Table 6. Dihydropyrans and spiroacetals: Pheromones and allomones identified from insects.

Pheromone			Insecta		Reference [d]	
	Configuration and analytical method [a]	Function (Producer)	Order [b]	Species [c]	Identifi-cation	Stereoselective synthesis
dihydropyran (DP)						
Et2,Me3,Me5,Et6-DP [anhydroserricornin] (**99**) [e]	2*S*,3*S*	sex (F)	Coleo.	*Lasioderma serricorne* (deathwatch beetle)	294 [81], 295 (86)	296 (84), 297 (85)
Et2,Me3,Me5,($C_5H_{10}OH$)6-DP-4-one [serricorole] (**100**) [f]	2*S*,3*R*,1'*S*,2'*S*	sex (F)	Coleo.	*L. serricorne*	298 [83], 299 [85], 300 (87)	300 (87)
Et2,Me3,Me5,(C_5H_9O)6-DP-4-one [α-serricorone] (**101**) [g]	2*S*,3*R*,1'*S* CD	sex (F) + marking	Coleo.	*L. serricorne*	298 [83], 301 (90)	300 (87)
+Et2,Me3,Me5,(C_5H_9O)6-DP-4-one [β-serricorone] (**102**)	2*S*,3*R*,1'*R*					
Me2,Me3,Me5,(C_5H_9O)6-DP-4-one [stegobinone] (**103**) [h]	2*S*,3*R*,1'*R*	sex (F)	Coleo.	*Stegobium paniceum* (deathwatch beetle)	302 [78], 303 (81)	304 (79), 305 (81), 306 (12)
				Anobium punctatum (deathwatch beetle)	377 (87)	
Me2,Me3,Me5,($C_5H_{10}OH$)6-DP-4-one [stegobiol] (**104**) [i]	2*S*,3*R*,1'*S*	sex (F)	Coleo.	*Stegobium paniceum* (deathwatch beetle)	307 (87)	308 (86), 306 (12)
Spiroacetal (SA)						
1,6-dioxaspiro[4.5]decane ([4.5]SA)						
Me7-[4.5]SA [conophthorin] [j] (**105**)	5*R*,7*S*	sex (M)	Diptera	*Bactrocera xanthodes* (fruit fly)	309 (92)	309 (92)
(**106**)	5*S*,7*S*	sex (M)	Coleo.	*Conophthorus coniperda* (bark beetle) #1	310 (98)	311 (81)
	5*S*,7*S*	allomone ?	Hymeno.	*Vespula vulgaris* (= *Paravespula vulgaris*) (wasp)	719 [78], 438 [79], 720 [97]	
Me2,Et7-[4.5]SA	?	gland	Hymeno.	*Paravespula vulgaris, P.*	438 [79]	

			secretion		*germanica, Dolichovespula saxonica*		
					Parischnogaster jacobsoni (wasp)	595 [98]	
					Andrena haemorrhoa (mining bee)	593 [81]	
					Coelioxys quadridentata, C. mandibularis (leafcutter bee)	594 [82]	
Me2,Bu7-[4.5]SA			gland secretion	Hymeno.	*Andrena haemorrhoa* (mining bee)	593 [81]	
1,7-dioxaspiro[5.5]undecane ([5.5]SA)							
Me2-[5.5]SA (**107**)	2*R*,6*S*	GC* #A	(mandibular gland)	Hymeno.	*Goniozus nephantidis* (wasp) #2	312 (08)	312 (08)
Me2-[5.5]SA (**108**)	2*S*,6*R*	GC* #B	allomone	Phasmatodea	*Asceles glaber* (walking stick) #3	313 (12)	313 (12)
Me2,Me8-[5.5]SA (**109**)	2*S*,6*R*,8*S*	GC* #C	sex (F)	Hymeno.	*Andrena wilkella* (wild bee)	314 [80], 315 (90)	316 (81), 317 (87)
			alarm	Hymeno.	*Polybia occidentalis* (social wasp) #4	378 (00)	
			sex (F)	Diptera	*Bactrocera dorsalis, B. cucurbitae*	454 [85],	318 (89)
			sex (M)		*B. cucumis, B. halfordiae,*	439 (86), 318 (89)	
			sex (M)		*B. nigrotibialis.*	440 (90)	
			sex (M)		*B. kirki, B. kraussi* (fruit fly)	309 (92)	
			allomone	Coleo.	*Ontholestes murinus, O. tesselatus* (rove beetle)	323 (99)	323 (99)
Me2,Et8-[5.5]SA	2*S*,6*R*,8*S*		sex (F) sex (M)	Diptera	*Bactrocera dorsalis* *B. halfordiae*	454 [85], 318 [89]	

				sex (M) sex (F) sex (M)		*B. kirki, B. kraussi* *B. latifrons* *B. frauenfeldi* (fruit fly)	309 [92], 553 (97), 455 [20]	
Me2,Me4,Me8-[5.5]SA	(**110**)	2*S*,4*R*,6*R*,8*S*		aggregation	Hetero.	*Cantao parentum* (shield bug)	319 (94)	320 (95), 321 (01), 322 (14)
Me2,Me2,Me8-[5.5]SA	(**111**)	6*R*,8*S*	GC* #D	allomone	Coleo.	*Ontholestes murinus* (rove beetle)	323 (99)	323 (99)



[a] GC* indicates analyses with the following enantioselective columns: #A, 1:1 mixture of OV1701 and hexakis(6-*tert*-butyl-2,3-dimethyl)-β-cyclodextrin; #B, Beta DEX 120 column; #C, per-*n*-hexyl-α-cyclodextrin; #D, Cyclodex-B.

[b] Coleo. = Coleoptera, Hetero. = Heteroptera, Hymeno. = Hymenoptera.

[c] Also identified from *Conophthorus ponderosae, Pityophthorus carmeli*, and *Pityophthorus nitidulus* (#1); *Goniozus legneri* (#2); *Goniozus legneri* and *G. nephantidis* as a minor component (#3); several species in Hymenoptera (#4)

[d] (Year of publication, 19XX or 20XX). [ ] indicates year when the publication was reported before determination of the absolute configuration.

[e] 2,6-Diethyl-3,5-dimethyl-3,4-dihydro-2*H*-pyran

[f] 2,3-Dihydro-3,5-dimethyl-2-ethyl-6-(1-methyl-2-hydroxybutyl)-4*H*-pyran-4-one

[g] 2,3-Dihydro-3,5-dimethyl-2-ethyl-6-(1-methyl-2-oxobutyl)-4*H*-pyran-4-one

[h] 2,3-Dihydro-2,3,5-trimethyl-6-(1-methyl-2-oxobutyl)-4*H*-pyran-4-one

[i] 2,3-Dihydro-2,3,5-trimethyl-6-(1-methyl-2-hydroxybutyl)-4*H*-pyran-4-one

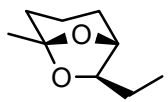
[j] 7-Methyl-1,6-dioxaspiro[4.5]decane

Table 7. Dioxabicyclo and dioxatricyclo compounds (cyclic acetals): Pheromones and allomones identified from insects.

Pheromone			Insecta		Reference [d]	
	Configuration and analytical method [a]	Function	Order [b] Family	Species [c]	Identification	Stereoselective synthesis
exo-7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane [(+)-exo-brevicomin] (**112**)	1*R*,5*S*,7*R* NMR (#A)	aggregation	Coleo. Scolytidae	*Dendroctonus brevicomis*	381 [68], 382 (76), 383 (77)	384 (74), 385 (83), 386 (96), 387 (96),
				D. ponderosae	389 (83)	388 (09), 650 (13)
				Dryocoetes confuses	619 (93)	
				Dryo. affaber	619 (93), 620 (94)	
				Hylesinus pruinosus (bark beetle)	621 (10)	
	?			*D. adjunctus* #1		
endo-7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane [(+)-endo-brevicomin] (**113**)	1*R*,5*S*,7*S* GC (#F)	aggregation	Coleo. Scolytidae	*Dendroctonus ponderosae*	389 (83), 390 (96)	391 (95), 390 (96),
				Dryocoetes confuses	619 (93)	388 (09), 651 (14),
				Dryo. affaber	619 (93), 620 (94)	652 (19)
				Hylesinus pruinosus	621 (10)	
				D. Mesoamericanus (bark beetle)	622 (15)	
	?			*D. brevicomis* #2		
exo- and *endo*-7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octan-2-ol [breviomin-2-ol] (**114**)	1*R*,2*R*,5*S*,7*R* + 1*R*,2*R*,5*S*,7*S*	aggregation	Coleo. Scolytidae	*Dendroctonus ponderosae* (bark beetle)	390 (96)	390 (96)
exo-7-(1'-hydroxyethyl)-5-methyl-6,8-dioxabicyclo[3.2.1]octane [1-hydroxy-exo-brevicomin]	1*R*,l'*R*,5*R*,7*R*	aggregation	Coleo. Scolytidae	*Dendroctonus ponderosae* (bark beetle)	390 (96)	390 (96), 650 (13)
exo-5-ethyl-7-methyl-6,8-dioxabicyclo[3.2.1]octane [isobrevicomin] (**115**)	1*S*,5*R*,7*S*	aggregation	Coleo. Scolytidae	*Dendroctonus ponderosae* (bark beetle)	390 (96)	390 (96)
1,5-dimethyl-	1*S*,5*R* $[\alpha]_D$ (-)	aggregation	Coleo.	*Dendroctonus frontalis*	392 [69], 383 (77)	(-)-isomer: 394 (75),

6,8-dioxabicyclo[3.2.1]octane [frontalin] (**116**)	NMR (#A) + 1*R*,5*S* (2:1) GC (#G)		Scolytidae	(bark beetle) #3 *D. jeffreyi*	393 (99)	395 (76), 396 (83), 397 (86), 398 (87), 399 (99), 400 (02), 401 (03), 653 (13)
	?			*D. adjunctus* #4		(+)-isomer: 394 (75), 402 (78), 397 (86) 403 (98), 404 (00)
5-ethyl-2,4-dimethyl-6,8-dioxabicyclo[3.2.1]octane [α-multistriatin] (**117**)	1*S*,2*R*,4*S*,5*R* $[\alpha]_D$ (-)	aggregation	Coleo. Scolytidae	*Scolytus multistriatus, S. pygmaeus* (bark beetle) #5	131 [75], 505 [75], 324 (76), 132 (77), 694 (79)	324 (76), 326 (76), 325 (77), 327 (79), 694 (79), 328 (82),
	?		Dryophthoridae	*Diocalandra frumenti* (weevil)	506 [17]	329 (87)
2-ethyl-1,5-dimethyl-6,8-dioxabicyclo[3.2.1]octane [bicolorin] (**118**)	1*S*,2*R*,5*R* GC (#B)	aggregation	Coleo. Scolytidae	*Taphrorychus bicolor* (bark beetle)	405 [95], 406 (96)	406 (96), 407 (97), 654 [13]
1-ethyl-3,5,7-trimethyl-2,8-dioxabicyclo[3.2.1]octane [sordidin] (**119**)	1*S*,3*R*,5*R*,7*S* $[\alpha]_D$ (+),GC (#G) + 1*S*,3*R*,5*R*,7*R*	aggregation	Coleo. Curculionidae	*Cosmopolites sordidus* (weevil)	408 [95], 409 (96) 410 (97)	409 (96), 412 (05), 413 (08)
	1*R*,3*S*,5*S*,7*S* GC (#C)	?	Trico. Limnephilidae	*Potamophylax latipennis* (caddis fly) #6	411 (04)	
1,3-diethyl-4,6-dimethyl-2,7-dioxabicyclo[2.2.1]heptane (**120**)	1*S*,3*S*,4*R*,6*S* or 1*R*,3*R*,4*S*,6*S*	aggregation	Trico. Limnephilidae	*Glyphotaelius pellucidus* (caddis fly)	411 (04)	
1,3,3-trimethyl-2,7-dioxabicyclo[2.2.1]heptane (**121**)	?	gland secretion (defense substance ?)	Hymeno. Formicidae	*Iridomyrmex purpureus* *Eciton burchelli,* *Aenictus rotundatus* (ant)	414 [84] 456 [93] 415 [94]	
3-isopentenyl-1,3-dimethyl-2,7-dioxabicyclo[2.2.1]heptane (**122**)	?	gland secretion	Hymeno. Apidae	*Nannotrigona testaceicornis* (bee)	416 [01]	

3-ethyl-1,8-dimethyl-2,9-dioxabicyclo[3.3.1]non-7-ene (**123**)	1*R*,3*S*,5*S* GC (#D)	?	Lepido. Hepialidae	*Hepialus hecta* (swift moth)	417 [85], 418 (90)	419（86）
+ 6-keto derivative (**124**)	1*R*,3*S*,5*R*	?			418 (90)	
1,3,8-trimethyl derivative (**125**)	1*R*,3*S*,5*S*	?		*Endoclita excrescens*	420(02)	420 (02)
3,3,7-trimethyl-2,9-dioxatricyclo[3.3.1.0^{4,7}]nonane [lineatin] (**126**)	1*R*,4*S*,5*R*,7*R* $[\alpha]_D$ (+) X-ray (#E)	aggregation	Coleo. Scolytidae	*Trypodendron lineatum* (bark beetle)	421 [77], 422 (80) 424 (82)	422(80), 423 (80), 424 (82), 425 (85), 426 (08)



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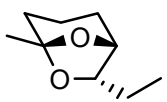

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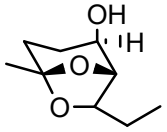

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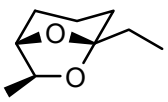

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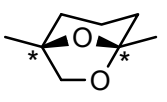

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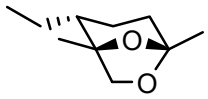

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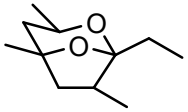

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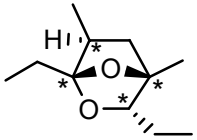

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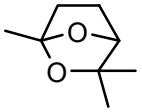

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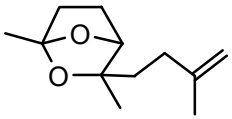

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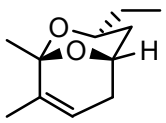
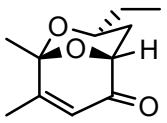
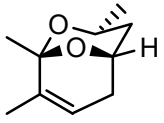


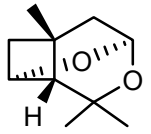
123



124



125



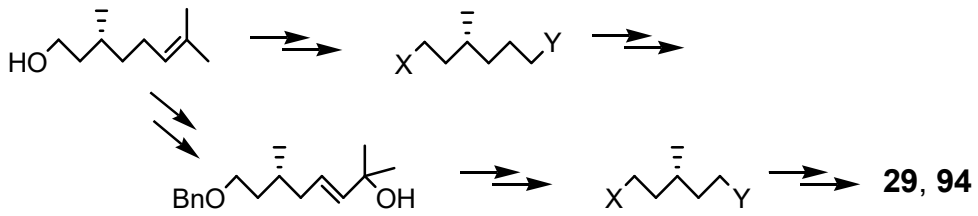
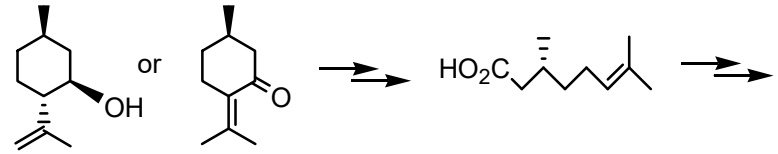
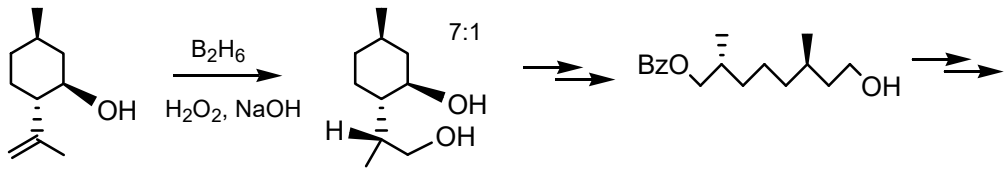
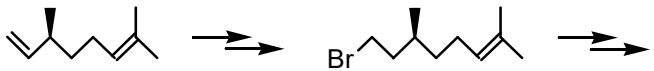
126

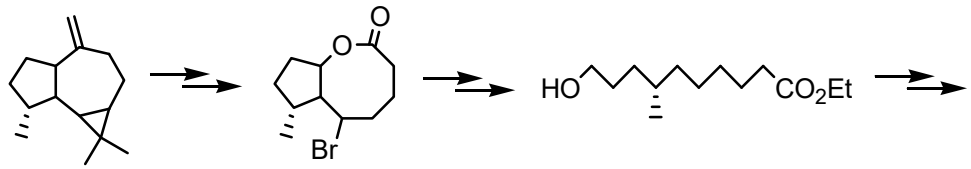
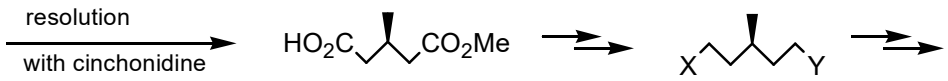
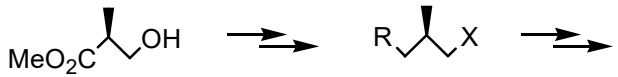
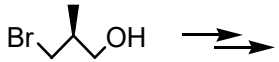
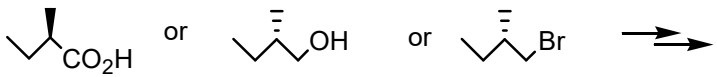
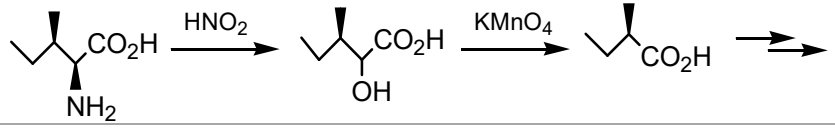
[a] #A: Analysis using a chiral sift reagent [Eu(hfbc)$_3$], #B: analysis with an enantioselective column coated with a 1:1 mixture of heptakis(2,6-di-*O*-methyl-3-*O*-pentyl)-β-cyclodextrin and OV1701, #C: analysis with an enantioselective column coated with a 1:1 mixture of heptakis-(2,3-di-O-methyl-6-O-tert-butyldimethylsilyl)- β-cyclodextrin and OV1701, #D: analysis with an enantioselective column coated with Ni(II)-bis(heptafluorobutanoyl-(l*R*,5*S*)-pinan-4-onate) in OV-1, #E: crystallographic analysis of a synthetic intermediate, #F: analysis with an enantioselective column coated with manganese(II)-bis(1*R*-3-heptafluorobutyrylcamphorate) in OV-101, #G: Cyclodex B column.

[b] Coleo. = Coleoptera, Hetero. = Heteroptera, Hymeno. = Hymenoptera, Lepido. = Lepidoptera, Strepsi. = Strepsiptera.

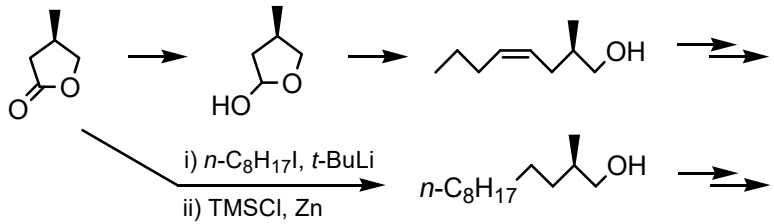
[c] Also identified from *D. armandi, D. frontalis, D. jeffreyi, D. terebrans, Leperisinus varius,* and *Dryo. autographus* (#1); *D. frontalis, Dryo. autographus* (2), *D. brevicomis* and *D. simplex* (#3); *D. armandi, D. ponderosa, D. pseudotsugae, D. rufipennis, and D. terebrans* (#4); *S. scolytus.* (#5); *P. cinqulatus* (#6)

Table 8. Chiral synthons (S1 – S14) for enantioserective syntheses of methyl-branched pheromones.

Synthon	Chemical structure and the synthetic route	Targeted pheromone
1a. Citronellol (**S1a**) or citronellal (**S1b**)	 **29**, **94**	Me10-12:OAc (**30**)[99] Me6,Me12-15:2-one (**76**)[233] and **2**[20], **5**[27], **10**[28], **28**[84], **29**[90,95,96], **38**[119], **62**[189], **63**[190], **74**[223], **77**–**79**[237,238] ,**80**[242] ,**86**[261], **94**[284], **97**[287,288], **112**[326]
1b. Citronellic acid (**S1c**) derived from isopulegol or pulegone		Δ 8,Me14-16:Ald (**40**)[125,126] Me8-10:2-OPr (**47**)[145] Me3,Me11-29: 2-one (**80**)[241] and **21**,[76] **69**,[208] **110**[320]
2. Isopulegol (**S2**) or neoisopulegol		Me5,Me9-15:H (**2**)[19]
3. Dihydromyrcene (**S3**)		Me4-9:OH (**28**)[85]

4. Aromadendrene (**S4**) 	Me9-19:H (**11**)[55] Me10-13:2-one (**74**)[55]
5. 3-Methylglutaric acid monomethyl ester (**S5**) 	Me8-10:2-OPr (**47**)[147] Me10-13:2-one (**74**)[224]
6. 3-Hydroxy-2-methylpropionate (Roche ester, **S6**) 	Me11-23:H (**17**)[67] vittatalactone (**91**)[272,273] and **5**[27-29], **6**[35], **9**[47], **10**[52], **29**[95], **74**[228], **78**[237], **79**[237], **94**[284]
7. 3-Bromo-2-methylpropanol (**S7**) 	Me3,Me5,Me9-12:Ald (**34**)[107] supellapyrone (**98**)[292]
8a. 2-Methylbutanoic acid (**S8a**), 2-methylbutan-1-ol (**S8b**), or 1-bromo-2-methylbutane (**S8c**) 	Me3,Me13-15: ester (**97**)[287,288] and **29**[96], **39**[122], **40**[124], **68**[206]
8b. (*R*)-2-Methylbutanoic acid [(*R*)-**S8a**] from L-isoleucine 	Me8-10: 2-OPr (**47**)[146]

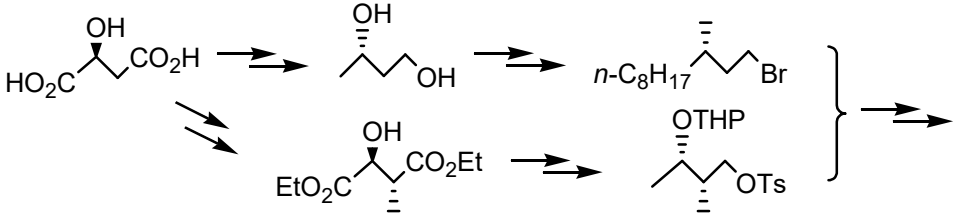
9. 3-Methyl-4-butanolide (**S9**)



Me5,Me9-15:H (**2**)[20]
invictolide (**90**)[267]

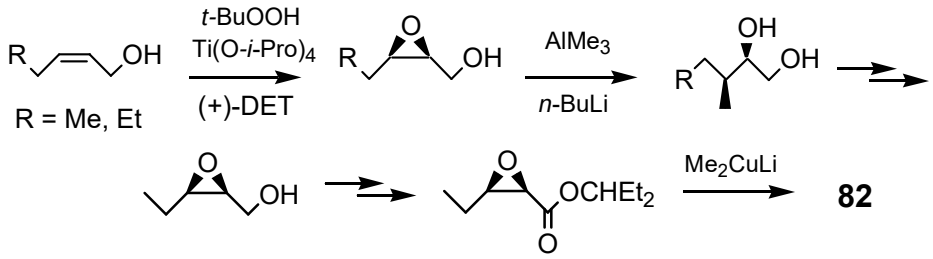
Me9-19:H (**11**)[56]

10. Malic acid (**S10**)



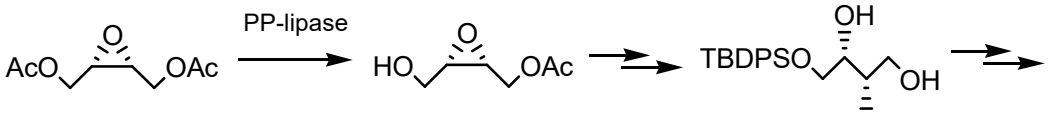
Me3,Me7-15:2-OAc (**56**)[176,178]

11. Chiral epoxide: 2,3-Epoxyalkan-1-ol (**S11**) produce by Sharpless asymmetric epoxidation



Me3-8:4-OH (**44**)[135]
Me5-8:4-OH (**45**)[135]
sitophilate (**82**)[246]
invictolide (**90**)[266]

12. Chiral epoxide: (3-Hydroxymethyloxiranyl)methyl acetate (**S12**)



Me3-8:4-OH (**44**)[136]
Me4-9:5-OH (**46**)[142]

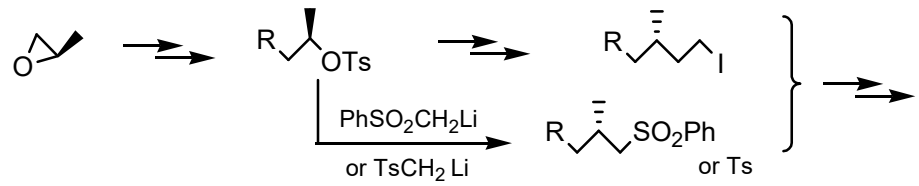
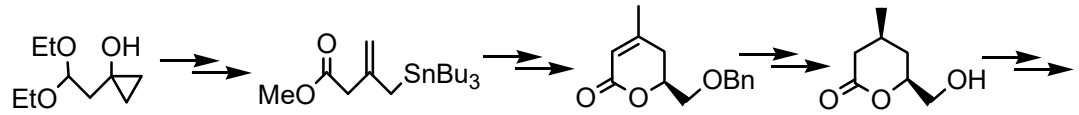
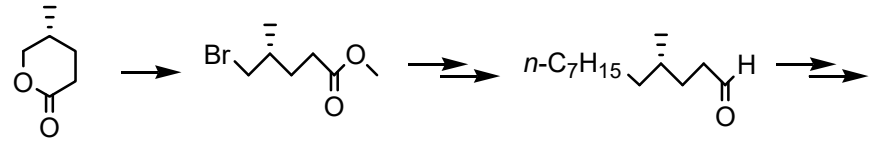
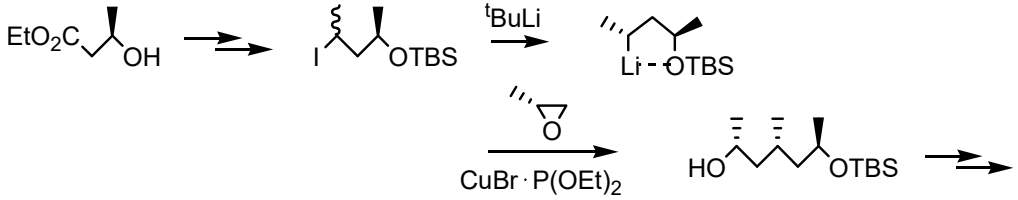
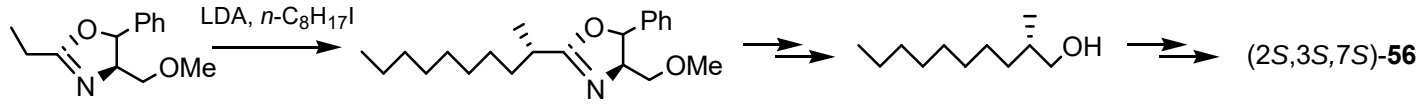
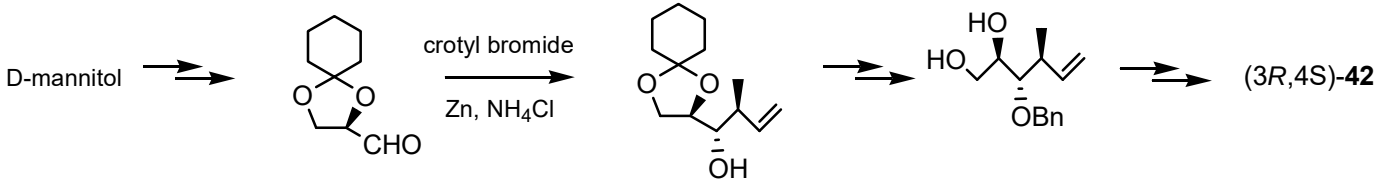
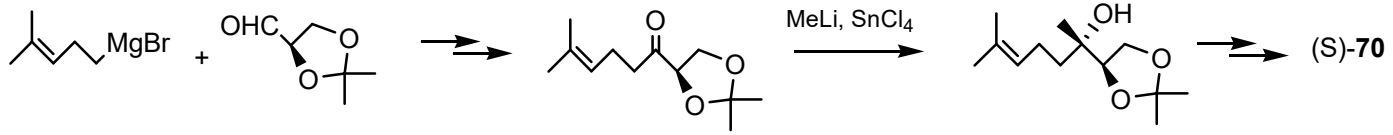
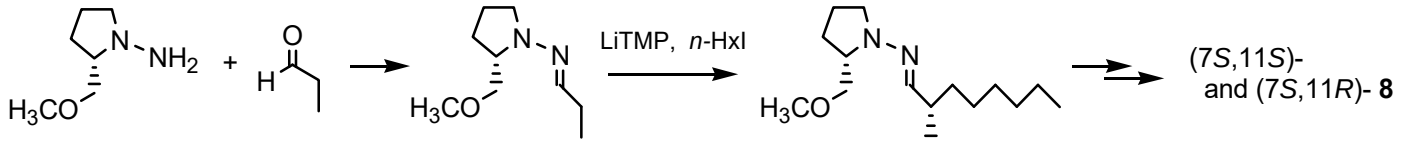
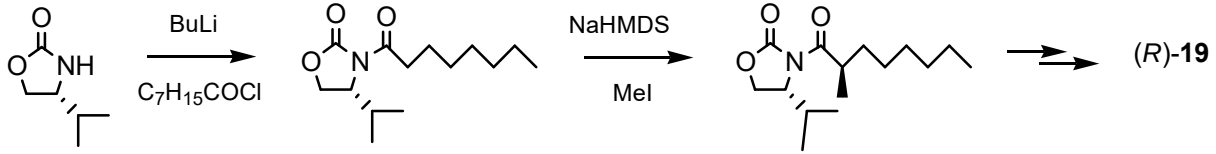
13. Chiral epoxide: Propylene oxide (**S13**) 	Me5,Me9-17:H (**5**)[32] Δ1,Me10,Me14-18:H (**10**)[53] Me5-17:7-OH (**61**)[185] and **75**[230], **97**[289]
14. Chiral lactone (**S14**) 	Δ1,Me10,Me14-18:H (**10**)[54] Me10-12:OAc (**30**)[103] faranal (**36**)[113] and **40**[103], **110**[322]
15. 4-Methyl-δ-valerolactone (**S15**) 	Me3,Me7-15:2-OAc (**56**)[367]
16. Ethyl (*R*)-3-hydroxybutyrate (**S16**) 	lardolure (**49**)[379]

Table 9. Syntheses of methyl-branched pheromones applying an enantioselective organic or biochemical reaction (R-1 – R-5).

Reaction type
Synthetic route for a targeted chiral pheromone
1. C-C coupling with a chiral intermediate
R-1-1. 2-Oxazoline derivative
Me3,Me7-15:2-OAc (**56**)[174]

R-1-2. [1,3]Dioxolane-4-carbaldehyde and a keto derivative
a. Me4-6:3-OH (**42**)[129]

b. Me3,Δ6,Me7-8:1-OH,3-OH,2-one (**70**)[213]

R-1-3. Enders SAMP/RAMP hydrazone-alkylation reaction
Me7,Me11-17:H (**8**)[42]


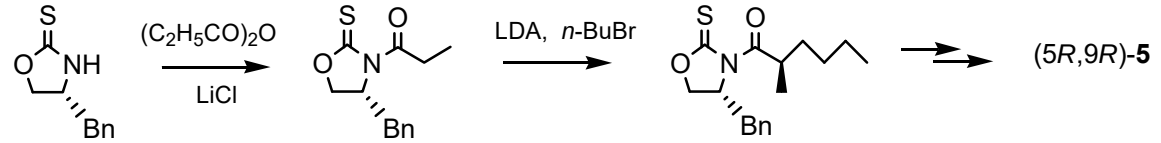
R-1-4. Evans' chiral auxiliaries

a. Me7-27:H (**20**)[72]

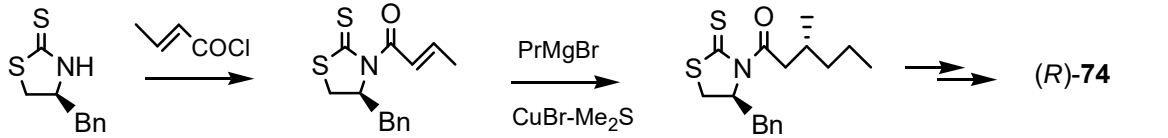


b. Δ1, Me14-18:H (**9**)[49]

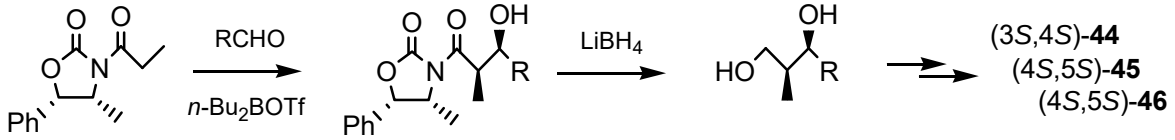
c. Me5,Me9-17:H (**5**)[31]



d. Me10-13:2-one (**74**)[227]



e. Me3-8:4-OH (**44**)[137] etc.

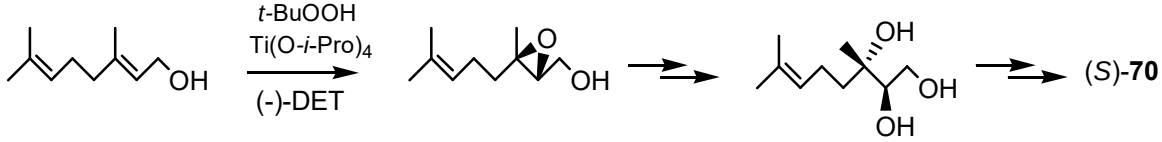


2. Reaction *via* an epoxy compound

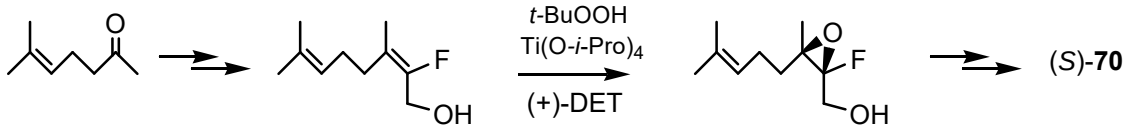
R-2-1. Sharpless asymmetric epoxydation

Me3,Δ6,Me7-8:1-OH,3-OH,2-one (**70**)[214, 215]

a

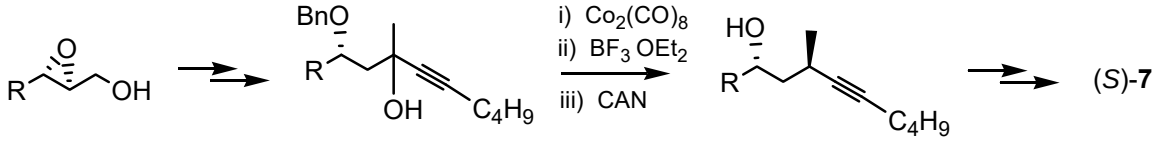


b



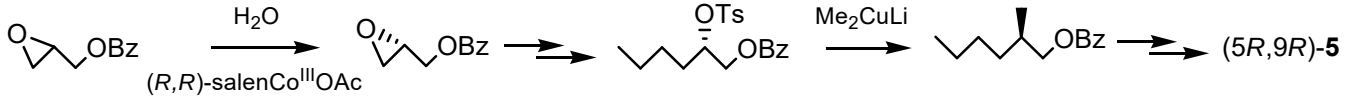
R-2-2. Intermolecular hydride transfer

Me7-17:H (**7**)[37]

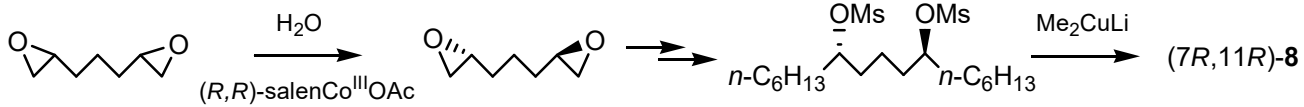


R-2-3. Hydrolytic kinetic resolution (HKR)

a. Me5,Me9-17:H (**5**)[31]

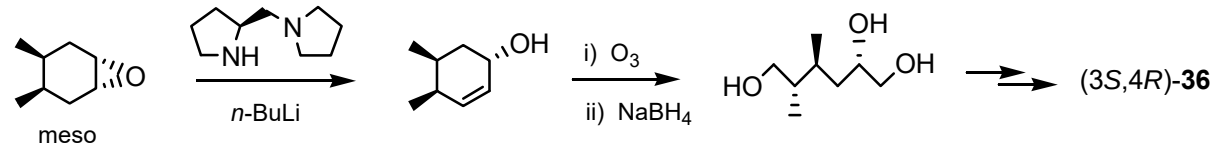


b. Me7,Me11-17:H (**8**)[43]



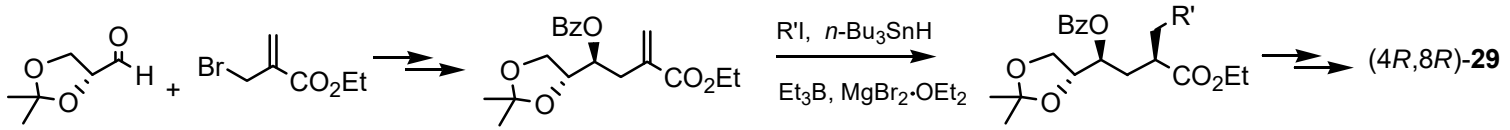
R-2-4. Asymmetric cleavage of an epoxy ring

faranal (**36**)[112]



3. Chelation-controlled radical reaction

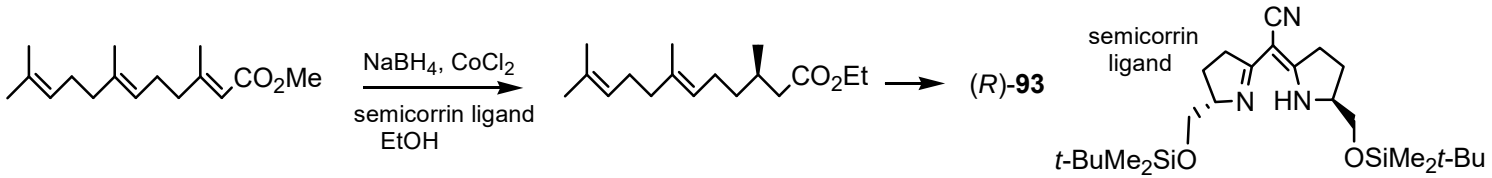
R-3 Me4,Me8-10:Ald (**29**)[94]



4. Reaction with a chiral catalyst

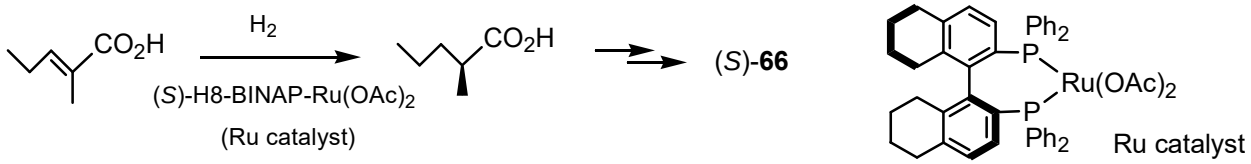
R-4-1. $NaBH_4$ reduction with a chiral cobalt semicorrin complex

dihydrofarnesoate (**93**)[281]

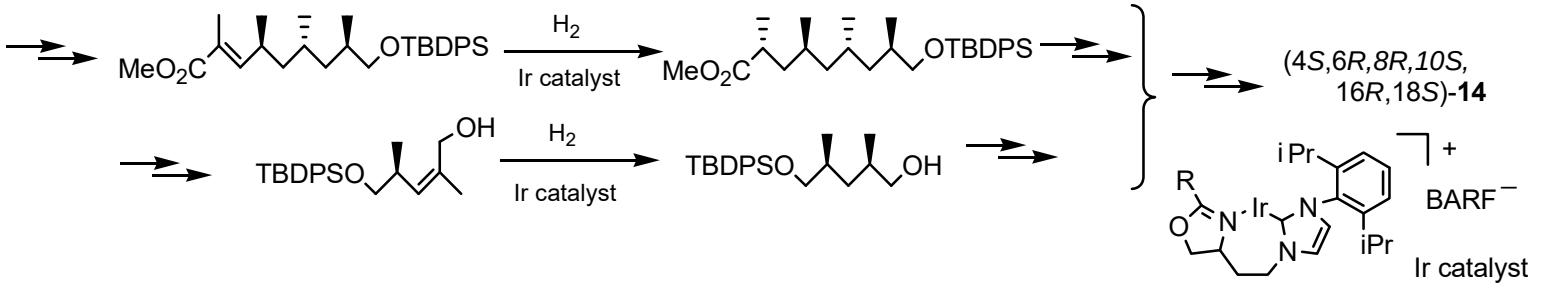


R-4-2. Hydrogenation over a chiral catalyst

a. Δ1,Me4-7:3-one (**66**)[200]

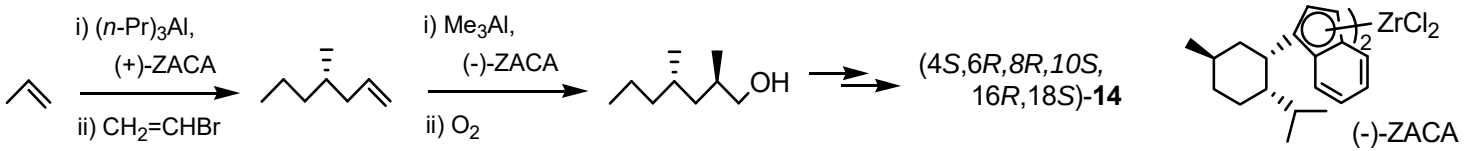


b. Me4,Me6,Me8,Me10,Me16,Me18-22:H (**14**)[63]



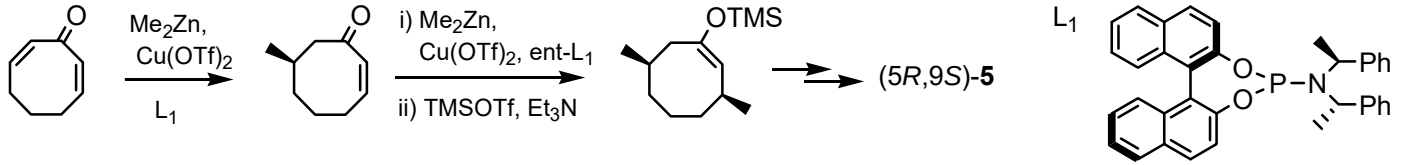
R-4-3. Zr-catalyzed asymmetric carboalumination of alkenes (ZACA reaction)

Me4,Me6,Me8,Me10,Me16,Me18-22:H (**14**)[64]

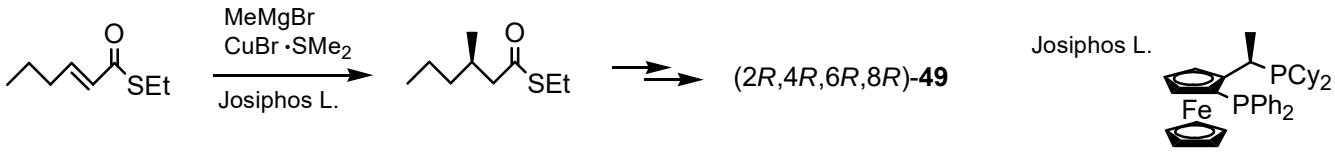


R-4-4. Cu-catalyzed asymmetric Michael addition of organometallic reagents

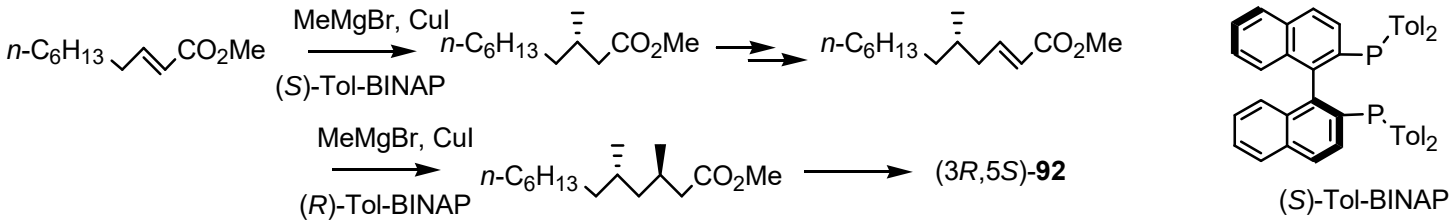
a. Me5,Me9-17:H (**5**)[30]



b. lardolure (**49**)[157]

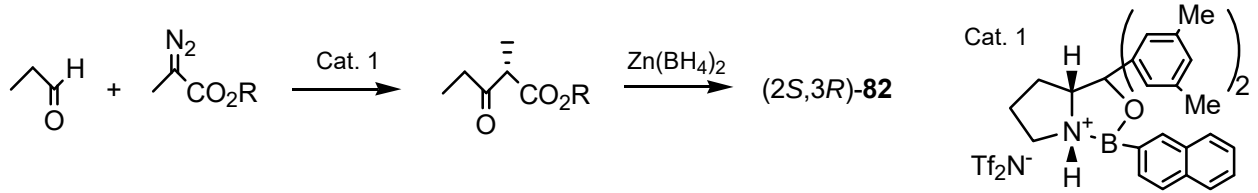


c. Me3,Me5-12:acid (**92**)[278]



R-4-5. Asymmetric Roskamp reaction catalyzed by an oxazaborolidium ion

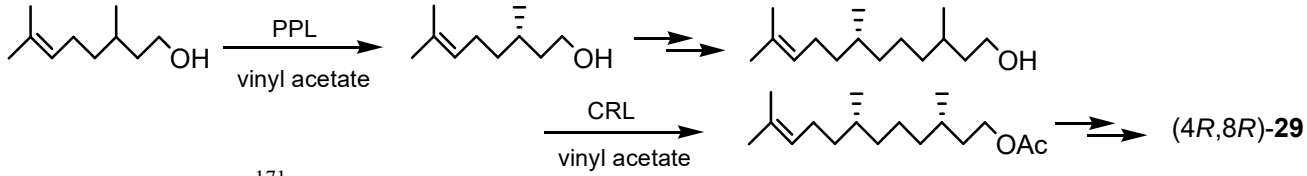
sitophilate (**82**)[251]



5. Chemoenzymatic reaction

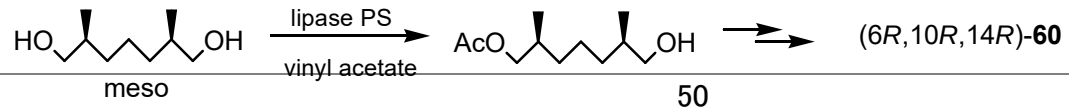
R-5-1. Lipase-catalyzed kinetic resolution

a. Me4,Me8-10:Ald (**29**)[93]



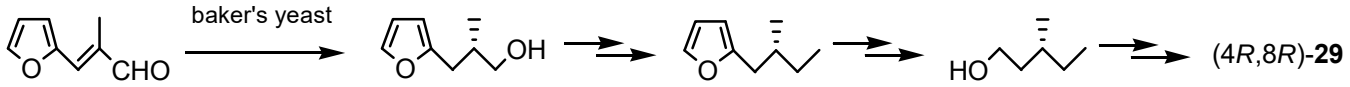
b. Me3,Me7-14:2-OPr (**55**)[171]

c. Me6,Me10,Me14-15:2-OH (**60**)[182]

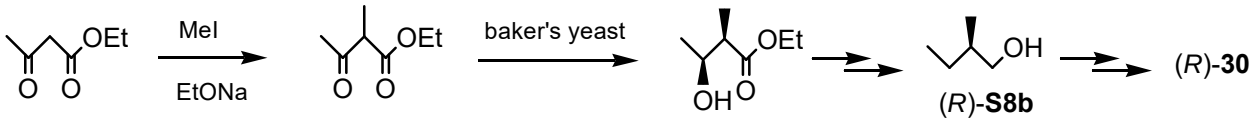


R-5-2. Reduction by baker's yeast

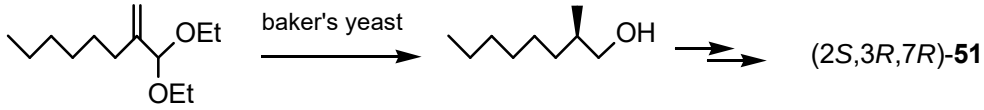
a. Me4,Me8-10:Ald (**29**)[92]



b. Me10-12:OAc (**30**)[101]

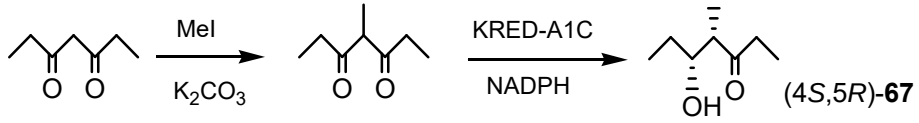


c. Me3,Me7-13:2-OAc (**51**)[164]



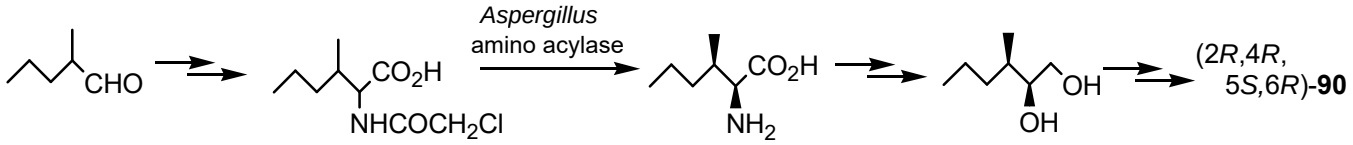
R-5-3. Reduction by isolated ketoreductase

sitophinone (**67**)[205, 380]



R-5-4. *Aspergillus* amino acylase

invictolide (**90**)[268]



R-5-5. Ene-reductase-mediated hydrogenation

Me4-7:3-OH (**43**)[361]

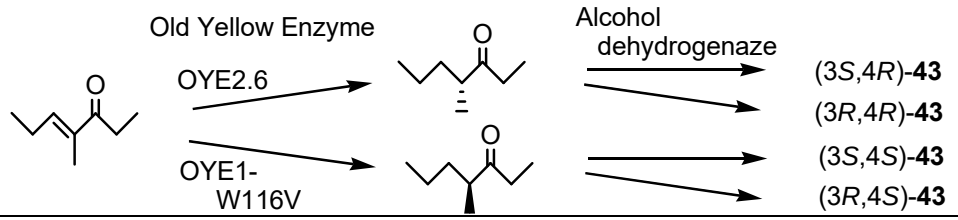
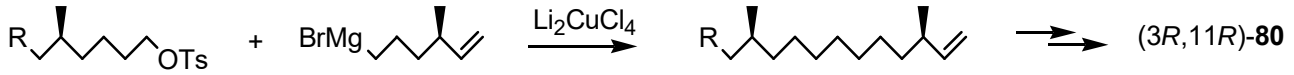
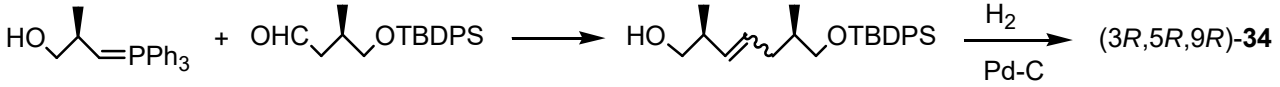
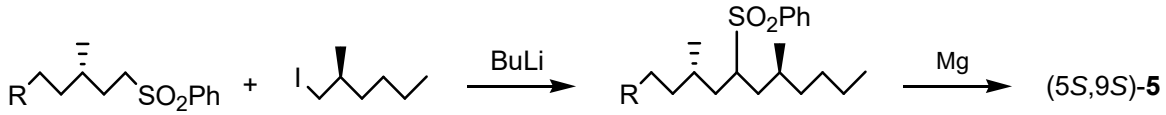
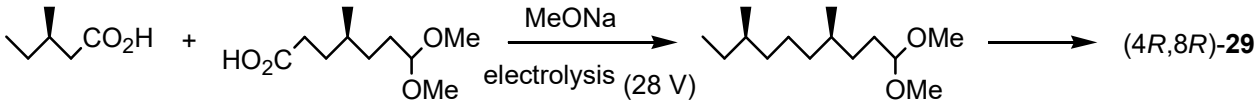
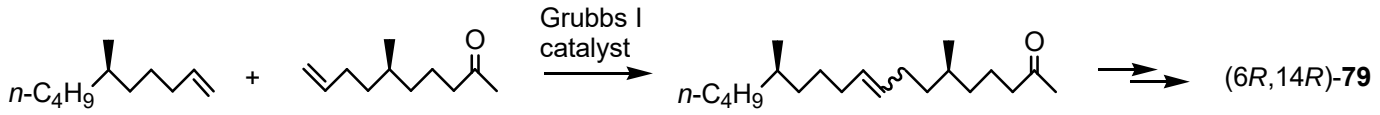


Table 10. Coupling reactions of two chiral blocks (R-6 – R-11) for the syntheses of dimethyl pheromones.

Reaction type
Synthetic route for a targeted chiral pheromone
R-6. Reaction of a Grignard reagent a. Δ1,Me10,Me14-18:H (**10**)[28]    b. Me3,Me11-29:2-one (**80**)[241] 
R-7. Wittig reaction Me3,Me5.Me9-12:Ald (**34**)[107] 
R-8. Coupling of RSO_2Ph with R'I Me5,Me9-17:H (**5**)[27] 
R-9. Kolbe electrolysis Me4,Me8-10:Ald (**29**)[91] 

R-10. Olefin cross metathesis

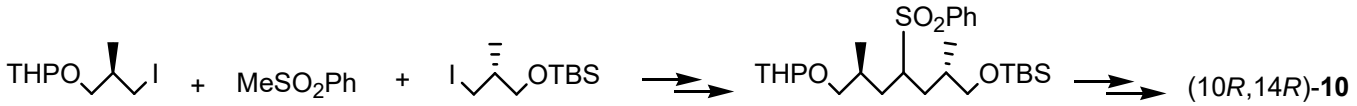
Me6,Me14-18:2-one (**79**)[237]



R-11. Coupling with a linchpin

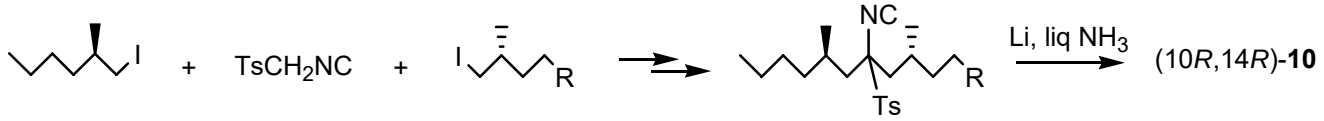
11-1. Methyl phenyl sulfone ($MeSO_2Ph$)

Δ1,Me10,Me14-18:H (**10**)[52]



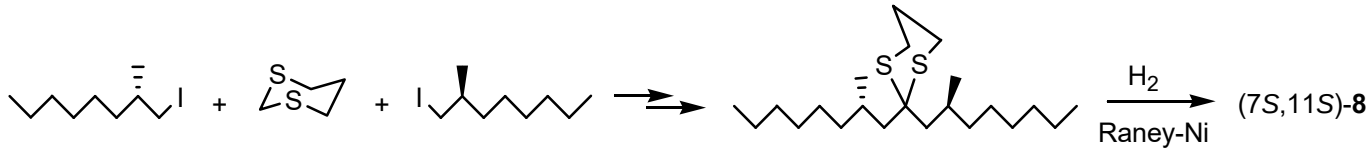
11-2. *p*-Toluenesulfonylmethyl isocyanide [$CH_2(NC)SO_2Ts$, TosMIC]

Δ1,Me10,Me14-18:H (**10**)[31]

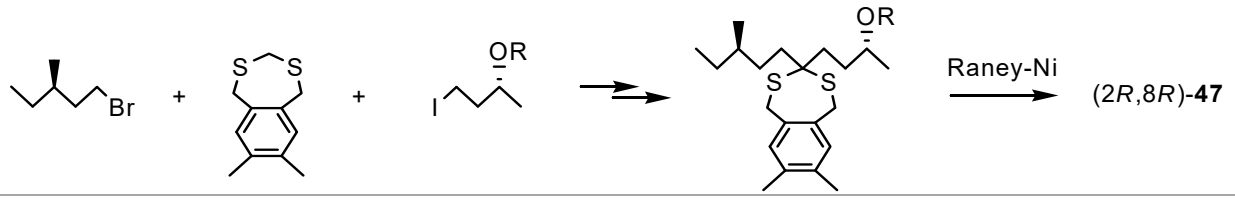


11-3. 1,3-Dithiane

a. Me7,Me11-17:H (**8**)[42]

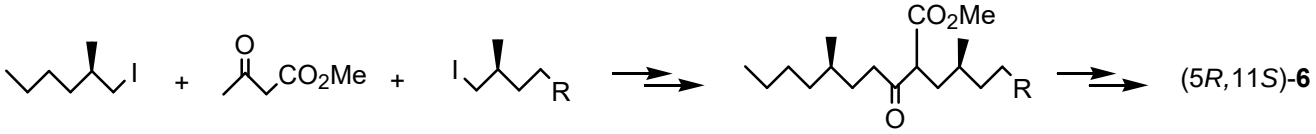


b. Me8-10:2-OPr (**47**)[145]



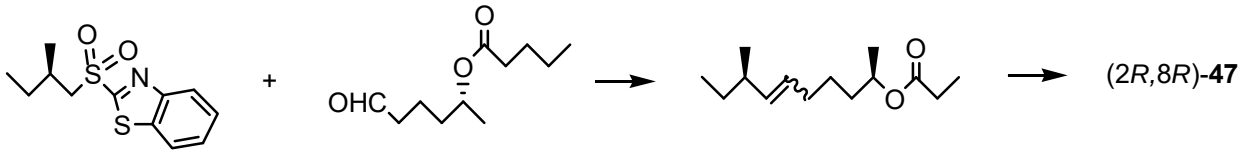
11-4. Methyl acetoacetate

Me5,Me11-17:H (**6**)[35]



R-12. Julia-Kocienski olefination

Me8 -10:2-OPro (**47**)[364]



Other target

Me10,Me14-15: OisoBu (**38**)[360]

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