

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

Table 1. Hydrocarbon: Pheromones and related compounds identified from insects.^{a, b}

Table 2. Primary alcohols and their derivatives (aldehydes and esters): Pheromones and related compounds identified from insects, mites, and spiders.^{a, b}

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

Table 4. Ketones: Pheromones and related compounds identified from insects, spiders, and mites.^{a, b}

Table 5. Carboxylic acids and their derivatives: Pheromones and allomones identified from insects and spiders.^{a, b}

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

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

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

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

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

References

^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

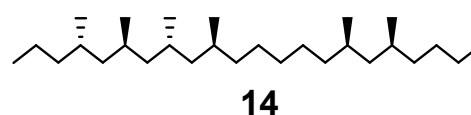
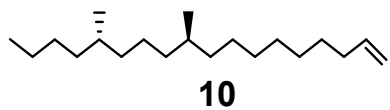
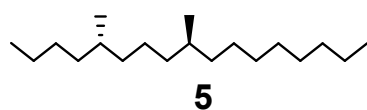
Pheromone		Insect			Reference ^e	
Structure	Configuration ^b	Group ^c	Species ^d	Identification	Stereoselective synthesis	
C ₅	Δ1,Me2,Me3-5:H	?	B24 [Heteroptera]	<i>Tessaratomya papillosa</i>	554 [09]	
C ₈	E2,Me3,E4,Me5,E6-8:H	achiral	B17 [Coleoptera]	<i>Colopterus truncatus</i>	521 (00)	
C ₉	E2,E4,Me4,E6,Me6-9:H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

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

		S	A	Geometridae	<i>Lambdina fiscellaria</i>	33 [93]	38 (99), 40 (01), 695 (23)
					<i>Lambdina athasaria</i> #2	39 [94], 40 (01)	
	Me7,Me11-17:H (8)	7S,11R	A	Geometridae	<i>Lambdina pellucidaria</i> #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	<i>Lyonetia clerkella</i>	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)	10S,14S	A	Lyonetiidae	<i>Lyonetia prunifoliella</i>	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	<i>Alabama argillacea</i>	36 (93)	55 (03), 56 (13)
	Me3,Me7-19:H		B15	[Diptera]	<i>Agromyza frontella</i>	501 [88]	
C ₂₁	Δ6,Me13-21:H (12)	6Z,13S	A	Erebidae	<i>Scoliopteryx libatrix</i>	57 [00], 58 (03)	58 (03)
	Me5,Me9,Me17-21:H (13)	?	B2	[Heteroptera]	<i>Phthia picta</i>	59 [12]	
C ₂₂	Me2-22:H	achiral	B19	[Diptera]	<i>Culicoides melleus</i>	537 (78)	
			B20	[Coleoptera]	<i>Chrysochus cobaltinus</i>	538 (07)	
			B13	[Coleoptera]	<i>Anoplophora glabripennis</i>	539 (14)	
C ₂₂	Me4,Me6,Me8,Me10,Me16,Me18-22:H (14) + Me4,Me6,Me8,Me10,Me16-22:H (15)	4S,6R,8R,10S, 16R,18S [α] _D (+10.7),	B3	[Coleoptera]	<i>Antitrogus parvulus</i>	60 [03], 61 [05], 62 (07)	62 (07), 63 (07), 64 (08) 65 (12), 658 (14)
C ₂₃	Me3-23:H	?	B22	[Coleoptera]	<i>Agrilus planipennis</i>	555 [09]	
	Me7-23:H (16)	?	B4	[Thysanoptera]	<i>Frankliniella occidentalis</i>	66 [13]	
	Me11-23:H (17)	SR	B5	Gelechiidae	<i>Anarsia lineatella</i>	67 (05)	67 (05)
C ₂₅	Me3-25:H (18) + Me3-27:H + Me3-29:H	?	B6	[Hymenoptera]	<i>Camponotus floridanus</i>	68 [04], 69 [14]	
	Me3-25:H (18)	?	B13	[Coleoptera]	<i>Xylotrechus colonus</i>	447 [03]	
	Me3-25:H (18) + Me3,Me13-25:H	?	B13	[Coleoptera]	<i>Semanotus japonicus</i>	627 [93]	
	Me5,Me11-25:H (19)	?	B7	Pyralidae	<i>Galleria mellonella</i>	70 [14]	656 (15)

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

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



^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

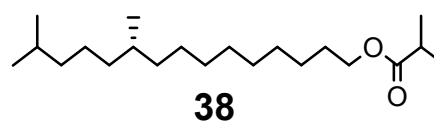
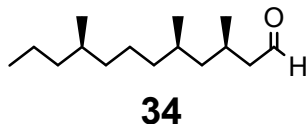
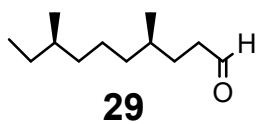
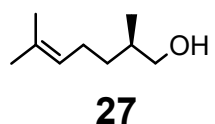
Pheromone			Insecta and [Arachnida]		Reference ^e	
Structure [Trivial name]	Configuration and analytical method ^b	Function (Producer)	Order ^c	Species ^d	Identifi- cation	Stereoselective synthesis
C ₃ Me1-3:OAc	?	aggregation (M)	Coleo.	<i>Strategus aloeus</i> (scarab beetle)	449 [00]	
C ₄ Me2-4:OH (22)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

	+ Me2,Me4-6:OCOR (stearate etc.) (25)					(acarid mite)		
C ₆	Me2-6:OH (26)	S	GC* #D	(mandibular gland)	Hymeno.	<i>Cataglyphis bicolor</i> (ant) #1	80 [92], 81 (96)	81 (96)
	E2,Me2,E4,Me4-6:OH	achiral		allomone ?	[Opiliones]	<i>Leiobunum leiopenis</i> , <i>Leiobunum calcar</i> (spider: harvestman)	686 (77)	
C ₇	Me2,Δ5,Me6-7:OH (27) + Ald derivative	R	GC* #E	sex (F)	[Astigmata]	<i>Tyreophagus</i> sp (acarid mite)	82 (09)	82 (09)
	E2,Me2,E4,Me4-7:OH	achiral		allomone ?	[Opiliones]	<i>Leiobunum leiopenis</i> , (spider: harvestman)	686 (77)	
C ₈	Me7-8:OCOR (COR = Me7-8)	achiral		sex (F)	Coleo.	<i>Elater ferrugineus</i> <i>Agriotes ferrugineipennis</i> (click beetle)	460 (07) 631 (22)	
	Me7-8:OCOR (COR = Z4-10)	achiral		sex (F)	Coleo.	<i>Elater ferrugineus</i> (click beetle)	460 (07)	
C ₉	Me4-9:OH (28)	R	HPLC #F	sex (F)	Coleo.	<i>Tenebrio molitor</i> (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.	<i>Apterostigma dentigerum</i> (ant)	451 (17)	E2,Me2-10:Ald
	Me2,Me8-10:OCOEt	2S,10S		sex (F)	Hymeno.	<i>Eurytoma maslovskii</i> (wasp)	431 (20)	
	Me4,Me5-10:Ald	?		aggregation (M)	Coleo.	<i>Tribolium castaneum</i> (darkling beetle)	635 [91]	
	Me4,Me8-10:Ald (29) [tribolure]	4R,8R		aggregation	Coleo.	(1)(2) <i>Tribolium castaneum</i> (1)(4) <i>Tribolium confusum</i> , (3)(4) <i>Tribolium freemani</i> , (4) <i>Tribolium madens</i> (flour beetle) #2	(1) 87 [81], (2) 88 (83), 428 (83), 711 (84),	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]	
C ₁₁	Me ₄ ,Me ₆ -11:Ald	?		sex (M), trail	Isoptera	<i>Hodotermopsis sjoestedti</i> (termite)		502 [11]	
	Me ₂ ,Me ₄ ,Me ₆ ,Me ₈ -11:OH [prieskanol]	2 <i>R</i> ,4 <i>R</i> ,6 <i>R</i> , ,8 <i>R</i>	NMR	sex (F)	Homo.	<i>Margarodes prieskaensis</i> (scale)		350 (17)	350 (17)
C ₁₂	Me ₁₀ -12:OH	?		sex (M)	Cole.	<i>Compsibidion graphicum</i> , <i>C. sommeri</i> (longhorn beetle)		667 [20]	667 [20]
	Me ₁₀ -12:OAc (30)	<i>R</i>		sex (F)	Lepido.	<i>Adoxophyes honmai</i> (leafroller moth)		97 [79], 98 (83)	99 (79), 100 (85), 48 (95), 101 (98), 102 (01), 103 (14)
	Me ₁₀ -12:Ald	?		sex (M)	Cole.	<i>Eburodacrys vittata</i> <i>E. assimilis</i> , <i>E. lenkoi</i> , etc. (longhorn beetle)		351 [16] 667 [20]	667 [20]
	Me ₃ ,Δ ₆ ,Et ₇ ,Δ ₁₀ ,Me ₁₁ -12:Ald (31) + C ₁₁ analogue (32)	3 <i>S</i> ,6 <i>E</i>	GC* #G	sex (F)	Coleo.	<i>Callosobruchus rhodesianus</i> (seed beetle)		104 (10), 105 (10)	104 (10)
	Me ₃ ,Δ ₆ ,Me ₇ ,Δ ₁₀ ,Me ₁₁ -12:OH (33) [2,3-dihydrofarnesol] + Ald derivative	3 <i>S</i> ,6 <i>E</i>	GC* #H	marking (M)	Hymeno.	<i>Bombus terrestris</i> (bumblebee) #3		432 (70), 106 (04)	106 (04)
	Me ₃ ,Me ₅ ,Me ₉ -12:Ald (34) [stylopsal]	3 <i>R</i> ,5 <i>R</i> ,9 <i>R</i>		sex (F)	Strepsi.	<i>Stylops melittae</i> <i>S. muelleri</i> (twisted-wing parasite)		107 (12) 108 [12], 109 (13)	107 (12) 109 (13)
	Me ₄ ,Me ₆ -12:Ald	?		sex (M), trail	Iso.	<i>Zootermopsis nevadensis</i> , <i>Z. angusticollis</i> (termite)		352 [10]	353 [11]
	Me ₂ ,Me ₁₀ -12:OCOEt	2 <i>S</i> ,10 <i>R</i>		sex (F)	Hymeno.	<i>Eurytoma maslovskii</i> (wasp)		431 (20)	
C ₁₃	Me ₁₁ -13:Ald	?		sex (F)	Coleo.	<i>Eburodacrys dubitata</i> , <i>E. assimilis</i> , <i>E. flexuosa</i> , etc.		667 [20]	667 [20]

						(longhorn beetle)		
	$\Delta 2, \Delta 4, \text{Me}_4, \text{Me}_6, \text{Me}_8, \text{Me}_{10-13}:\text{OH}$ (35)	2 <i>E</i> ,4 <i>E</i> , <i>syn</i> , <i>syn</i>		sex (F)	Hymeno.	<i>Trichogramma turkestanica</i> (parasitoid wasp)	15 [05], 16 (14)	110 (14)
	$\text{Me}_3, \text{Me}_4, \Delta 6, \text{Me}_7, \Delta 10, \text{Me}_{11-13}:\text{Ald}$ (36) [faranal]	3 <i>S</i> ,4 <i>R</i> , 6 <i>E</i> ,10 <i>Z</i>	NMR #I	trail	Hymeno.	<i>Monomorium pharaonis</i> (ant)	111 (77), 429 (80)	111 (77), 429 (80), 112 (95), 113 (10), 354 (88), 355 (19)
	$\text{Me}_3, \text{Me}_5, \Delta 7, \text{Me}_9, \Delta 11, \text{Me}_{11-13}:\text{Ald}$ [peckidienal]	3 <i>R</i> ,5 <i>S</i> ,9 <i>R</i> 7 <i>E</i> ,11 <i>E</i>	GC* #J	sex (F)	Strepsi.	<i>Xenos peckii</i> (twisted-wing parasite)	356 [15], 357 (16)	357 (16)
C ₁₄	$\text{Me}_6, \text{Me}_{10}, \text{Me}_{13-14}:\text{OH}$ (37)	?		aggregation (M)	Hetero.	<i>Stiretrus anchorago</i> (stink bug)	114 [86], 115 [89]	
	$\text{Me}_6, \text{Me}_{10}, \text{Me}_{13-14}:\text{OCOC}_4\text{H}_9$?		gland secretion (M)	Hetero.	(1) <i>Perillus bioculatus</i> , <i>Oplomus severus</i> (2) <i>Eocanthecona furcellata</i> (stink bug)	(1) 114 [86] (2) 589 [03], 590 [05]	
	$\text{Me}_2, \text{Me}_4, \text{Me}_8, \text{Me}_{13-14}:\text{OH}$	2 <i>R</i> ,4 <i>R</i> ,8 <i>R</i>		sex (M)	Hetero.	<i>Pellaea stictica</i> (stink bug)	536 [15], 630 (22)	630 (22)
C ₁₅	$\text{Me}_{10}, \text{Me}_{14-15}:\text{OCOiPr}$ (38)	<i>R</i>		sex (F)	Lepido.	<i>Arna pseudoconspersa</i> , <i>Artaxa subflava</i> (tussock moth)	116 [94], 117 (96), 118 (07)	119 (95), 358 (88), 359 (17), 360 (18)
C ₁₆	$\text{Z}_8, \text{Me}_{14-16}:\text{OH}$ (39)	<i>R</i>	$[\alpha]_D (-)$	sex (F)	Coleo.	<i>Trogoderma inclusum</i> (hide beetle)	120 [69], 122 (74)	122 (74)
	$\text{E}_8, \text{Me}_{14-16}:\text{OH}$?		sex (F)	Coleo.	<i>Trogoderma glabrum</i> (hide beetle)	511 [75]	
	$\text{Z}_8, \text{Me}_{14-16}:\text{Ald}$ (40) [trogodermal]	<i>R</i>		sex (F)	Coleo.	<i>Trogoderma granarium</i> (hide beetle) #4	123 [76], 121 (80), 726 (80)	125 (78), 126 (82), 103 (14)
		<i>S</i>					714 (78), 715 (79)	124 (77)
	$\text{E}_8, \text{Me}_{14-16}:\text{Ald}$ [trogodermal]	<i>R</i>		sex (F)	Coleo.	<i>Trogoderma granarium</i> (hide beetle) #5	123 [76], 121 (80), 726 (80)	126 (82)

		S			714 (78), 715 (79)	124 (77)
C ₂₉	Me12,Me20-29:OMe	?	species recognition	[Araneae] <i>Tetragnatha extensa</i> (long jawed spider)	540 [21]	
	Me8,Me14,Me20-29:OMe	?	species recognition	[Araneae] <i>Tetragnatha extensa</i> (long jawed spider)	540 [21]	



^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)- β -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 derivatization 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.

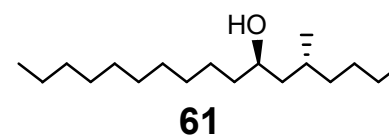
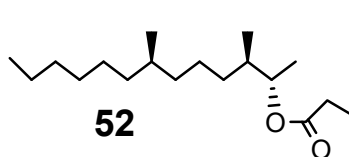
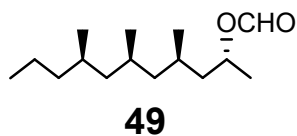
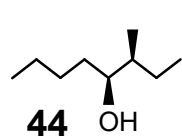
Table 3. Secondary alcohols and their esters: Pheromones and related compounds identified from insects and mites. ^a

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

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

					(leaf beetle)	144 (84)	147 (86), 225 (02), 363 (90), 364 (18), 657 [15]
		2 <i>S</i> ,8 <i>R</i>			<i>Diabrotica longicornis</i> (leaf beetle)	649 (86)	
C ₁₁	Me4,Me6,Δ7,Me8,Δ9-11:5-OH (48)	4 <i>R</i> *,5 <i>R</i> *,6 <i>S</i> *, 7 <i>E</i> ,9 <i>E</i> #a		gland secretion	Dictyo. <i>Cryptocercus punctulatus</i> (cockroach) #3	148 [91]	149 (90)
	Me4,Me6,Me8-11:2-OFo (49) [lardolure]	2 <i>R</i> ,4 <i>R</i> ,6 <i>R</i> ,8 <i>R</i>		aggregation	[Astigmata] <i>Lardoglyphus konoii</i> (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 <i>S</i> ,3 <i>R</i> ,9 <i>S</i>		sex (F)	Hymeno. <i>Diprion nipponica</i> (sawfly)	159 (98), 160 (02)	
C ₁₂	Me3,Me9-12:6-OH	?		trail	Hymeno. <i>Leptogenys peuqueti</i> (ant)	443 [97]	
C ₁₃	Me4,Me10-13:7-OH	4 <i>R</i> ,10 <i>R</i>		trail	Hymeno. <i>Leptogenys peuqueti</i> (ant)	443 (97)	
	Me3,Me7-13:2-OAc (51) + Me3,Me7-13:2-OCOEt (52) <Me3,Me7-13:2-OH> ^f	2 <i>S</i> ,3 <i>R</i> ,7 <i>R</i> 2 <i>S</i> ,3 <i>R</i> ,7 <i>R</i> GC #A		sex (F)	Hymeno. <i>Diprion pini</i> (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 <i>S</i> ,3 <i>R</i> ,7 <i>R</i> ,9 <i>S</i> GC* #E		sex (F)	Hymeno. <i>Macrodiprion nemoralis</i> (sawfly)	165 (00)	166 (11)
	Me3,Me7,Me11-13:2-OCOEt (54) <Me3,Me7,Me11-13:2-OH> ^f	2 <i>S</i> ,3 <i>S</i> ,7 <i>S</i> ,11 <i>R</i>		sex (F)	Hymeno. <i>Microdiprion pallipes</i> (sawfly)	167 [98], 168 (03)	169 (99), 170 (04)
C ₁₄	Me3,Me7-14:2-OCOEt (55)	2 <i>S</i> ,3 <i>R</i> ,7 <i>R</i>		sex (F)	Hymeno. <i>Gilpinia pallida</i> (sawfly)	171 (06)	171 (06), 365 (13), 366 (14)
	Me4-14:7-OAc + Me4-14:7-OH	? ?		trail	Hymeno. <i>Leptogenys peuqueti</i> (ant)	443 [97]	
C ₁₅	Me3,Me7-15:2-OAc (56) [diprionyl acetate] <Me3,Me7-15:2-OH> ^f (58)	2 <i>S</i> ,3 <i>S</i> ,7 <i>S</i> GC #A		sex (F)	Hymeno. (1)(2) <i>Neodiprion lecontei</i> , (1)(3)(5)(6) <i>N. sertifer</i> , (3) <i>N. nannulus</i> , <i>N. sertifer</i> , (4) <i>N. pinetum</i> (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)		sex (F)	Hymeno.	<i>Diprion similis</i>		172 [76], 174 (81), 175 (01),
	<Me3,Me7-15:2-OH> ^f (58)	2R,3R,7R					701 (80) 176 (04), 177 (12),
		2S,3R,7R	GC #A				702 (82), 178 (12), 367 (07),
		2S,3S,7S			<i>Neodiprion sertifer</i>		476 (88) 503 [82]
					(sawfly)		173 (00),
	<Me3-15:2-OH> ^f (59)	2S,3R	GC* #E	sex (F)	Hymeno.	<i>Gilpinia frutetorum</i>	162 (11)
	<Me3,Me7-15:2-OH> ^f (58)	2S,3R,7R				(sawfly) #6	179 (09) 179 (09)
	Me6,Me10,Me14-15:2-OH (60)	2R,6R,10R	sex (F)	Lepido.	(1) <i>Corcyra cephalonica</i> ,		(1) 180 [87], 182 (00), 183 (11)
					(2) <i>Aphomia sociella</i>		181 (91),
					(pyralid moth)		(2) 368 (12)
C ₁₇	Me5-17:7-OH (61)	5R,7R	sex (F)	Lepido.	<i>Miltchrista calamine</i>		184 (11) 185 (14), 615 (22)
					(lichen moth)		
C ₂₉	Me19-29:6-OAc (62)	6R,19R	HPLC #F	sex (F)	Diptera	<i>Cochliomyia hominivorax</i>	186 [93], 189 (04), 190 (04)
	+ Me15-29:7-OAc (63)	7R,15SR				(blowfly)	187 [07],
							188 (09)



^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 derivatization 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.	<i>Tapinoma simrothi</i> (ant)	564 (83)	
		sex (M) ?	Hetero.	<i>Halobates hawaiiensis</i> (water strider)	566 (01)	
C ₆ Me3-6:2-one	?	alarm	Hetero.	<i>Dipetalogaster maximus</i> <i>Triatoma phyllosoma</i> , <i>T.</i> <i>longipennis</i> , <i>T. pallidipenni</i> (assassin bug)	696 [83] 733 [18]	
		gland secretion	Hymeno.	<i>Pseudomyrmex spinicola</i> , <i>P.</i> <i>nigrocincta</i> (ant)	588 [05]	
	Me4-6:2-one	?	alarm	Hymeno.	<i>Polyrhachis vicina</i> (ant)	427 [19]
Me4-6:3-one (64)	S	alarm	Hymeno.	<i>Manica mutica</i> (ant) #1	191 [72], 192 (92)	129 (00)
	?	allomone	Coleoptera	<i>Staphylinus olens</i> . (rove beetle)	712 [75]	
	?	allomone	[Opiliones]	<i>Leiobunum nigripalpi</i> (spider: harvestman)	686 [77]	
E4,Me4-6:3-one	achiral	allomone	[Opiliones]	<i>Leiobunum nigripalpi</i> (spider: harvestman)	686 (77)	
Δ1,Me4-6:3-one	?	allomone ?	Coleo.	<i>Amarygmus tristis</i>	703 [82]	
	?			<i>Byrsax macleayi</i>	704 [92]	
	?		[Opiliones].	<i>Gonyleptes curvicornis</i> , <i>Parampheres</i> sp.	544 [05]	

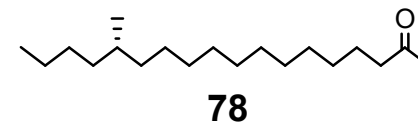
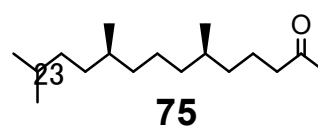
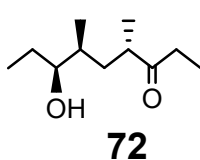
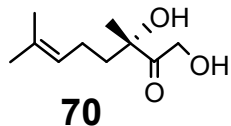
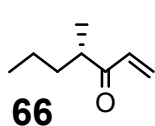
		<i>R</i>				<i>Gonyleptes saprophilus</i> , <i>Acanthogonyleptes pulche</i> (spider: harvestman)	545 (13)	
$\Delta 1, \text{Me}5\text{-}6\text{:}3\text{-one}$	achiral		allomone ?	[Opiliones]		<i>Neosadocus maximus</i> , <i>Zortalia inscripta</i> <i>Sodreana lprevosti</i> , <i>S. barbiellini</i> (spider: harvestman)	544 (05)	545 (13)
$\text{Me}3, \text{Me}4\text{-}6\text{:}2\text{-one}$?		alarm ?	Hymeno.		<i>Apterostigma pilosum</i> (ant)	499 [17]	
C_7 $\text{Me}2\text{-}7\text{:}4\text{-one}$	achiral		alarm	Hymeno.		<i>Tapinoma simrothi</i> (ant)	564 (83)	
			aggregation (M)	Coleo.		<i>Halobates hawaiiensis</i> <i>Scyphophorus acupunctatus</i> (bark beetle)	565 (07)	561 (08)
$\text{Me}4\text{-}7\text{:}3\text{-one}$ (65)	<i>S</i>	$[\alpha]_D (+)$	alarm	Hymeno.		<i>Atta texana</i>	193 (74),	198 (74)
	?					<i>A. colombica</i> , <i>A. cephalotes</i>	499 [17]	
	?					<i>Ooceraea biroi</i> (ant) #2	689 [23]	
	<i>S</i>	GC* #A	trail			<i>Aphaenogaster cockerelli</i> , <i>A. albisetosus</i> (ant)	194 (95)	
	<i>S</i>		allomone			<i>Dasymutilla occidentalis</i> (wasp, velvet ant) #4	196 (80)	
	?		gland secretion			<i>Paraponera clavata</i> (ant)	618 [84]	
	<i>S</i>		aggregation ?	Coleo..		<i>Scolytus scolytus</i> , <i>S. multistriatus</i> (bark beetle)	697 (83)	
	?		allomone ?			<i>Ocypus similis</i> , <i>O. olens</i> (rove beetle)	698 [90]	
	<i>S</i>	GC* #B	sex (F)	Tricho.		<i>Potamophylax latipennis</i> (caddis fly) #3	195 (01)	

	S		allomone	[Opiliones]	<i>Leiobunum vittatum</i> <i>Leiobunum formosum</i> , <i>Leiobunum speciosum</i> , <i>Leiobunum ventricosum</i> <i>Hadrobunus maculosus</i> <i>Leiobunum townsendi</i> (spider: harvestman)	197 (71) 687 [71] 685 [76] 688 [85]	
Δ 1,Me4-7:3-one (66) [chichimol ketone]	S	[α] _D (+)	allomone	Phasmatodea	<i>Agathemera elegans</i> (walking stick)	199 (06)	200 (09)
	?		allomone ?	[Opiliones]	<i>Gonyleptes horridus</i> , <i>Gonyleptes curvicornis</i> (harvestman)	716 [23]	
Δ 4,Me4-7:3-one	achiral		gland secretion	Hymeno.	<i>Leptanilla</i> sp, <i>Atta laevigata</i> (ant)	612 (98)	
						613 (99)	
Δ 2,Me6-7:4-one	achiral		aggregation (M)	Coleo.	<i>Metamasius spinolae</i> (bark beetle)	565 (07)	
Me2-7:2-OH, 4-one	achiral		aggregation (M)	Coleo.	<i>Metamasius spinolae</i> (bark beetle)	565 (07)	
Me4-7:5-OH, 3-one (67) [sitophilone, sitophilure]	4 <i>S</i> ,5 <i>R</i>		aggregation	Coleo.	<i>Sitophilus oryzae</i> (weevil) #5 <i>Rhinostomus barbirostris</i> (weevil)	201 [84], 507 [85], 202 (87)	203 (86), 204 (88), 205 (06)
						369 (18)	
	4 <i>S</i> ,5 <i>S</i>		aggregation	Coleo.	<i>Sitona discoideus</i> (weevil)	509 (13)	
Me4-7:3-one, 5-one	achiral		aggregation	Coleo.	<i>Sitona lineatus</i> <i>Sitona discoideus</i> (weevil)	508 (84)	
						509 (13)	
Me3,Me6-7:2-one, 4-one	?		sex (F)	Diptera	<i>Megaselia halterata</i> (humpbacked fly)	510 [82]	

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

	Me4,Me6-9:7-OH,3-one (72) [serricornin]	4S,6S,7S	sex (F)	Coleo.	<i>Lasioderma serricorne</i> (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.	<i>Andrena clarkella</i> , <i>A. fucata</i> (mining bee)	727, (76)	
	E2,Me5,E6,Me7,E8-10:4-one	R	sex (F)	Homo.	<i>Matsucoccus josephi</i> (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.	<i>Matsucoccus josephi</i> (scale)	491 [93], 492 (95)	
	Me4,Me6,Me8-10:2-one (73) [chortolure]	4R,6R,8R GC* #E	aggregation (F &M)	[Astigmata]	<i>Chortoglyphus arcuatus</i> (storage mite)	221 (04)	221 (04)
C ₁₁	Me4,Me6,E7,Me8,E9-11:3-one [graphisurone]	4R,6S	aggregation (M)	Coleo.	<i>Graphisurus fasciatus</i> , <i>Eutrypanus dorsalis</i> (longhorn beetle)	737 (24)	737 (24)
C ₁₂	Me3,Me7,E8,Me9,E10-12:6-one	3S,7R	sex (F)	Homo.	<i>Matsucoccus feytaudi</i> (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.	<i>Matsucoccus feytaudi</i> (scale)	497 [90], 498 (94)	487 [95]
C ₁₃	Me10-13:2-one (74)	R	sex (F)	Coleo.	<i>Diabrotica undecimpunctata</i> (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]	6R,10R	sex (F)	Homo.	(1)(2) <i>Matsucoccus matsumurae</i> (1)(2)(3) <i>M. thunbergianae</i> (1)(2)(4) <i>M. resinosae</i> (scale)	(1) 478 [89], (2) 479 [91], (3) 480 (94), (4) 481 (95)	482 (91), 483 (93), 484 (93), 485 (95), 481 (95), 486 [95], 487 [95], 488 (96),

									489 [97], 490 (00), 677 [19]
C ₁₄	Me ₆ ,Me ₁₀ ,Me ₁₃₋₁₄ :2-one (75) [pallantione]	6R,10S	GC* #F	sex (M)	Hetero.	<i>Pallantia macunaima</i> (stink bug)	229 (13)	230 (13), 370 (18)	
	dimer of Δ ₁ ,Me ₅₋₆ :3-one	?		allomone ?	[Opiliones].	<i>Sodreana lprevosti</i> , <i>Sodreana barbiellini</i>	545 [13]		
						<i>Gonyleptes horridus</i> , <i>Gonyleptes curvicornis</i> (spider: harvestman)	716 [23]		
	dimer of Δ ₁ ,Me ₄₋₆ :3-one	?		allomone ?	[Opiliones].	<i>Gonyleptes saprophilus</i> <i>Gonyleptes horridus</i> , <i>Gonyleptes curvicornis</i> (spider: harvestman)	545 [13] 716 [23]		
C ₁₅	Me ₆ ,Me ₁₂₋₁₅ :2-one (76)	6R,12R		sex (F)	Coleo.	<i>Diabrotica balteata</i> (leaf beetle)	231 [87], 232 (91)	233 (88), 234 (95), 225 (02), 674 (15), 729 (24)	
	Me ₆ ,Me ₁₀ , Me ₁₄₋₁₅ :2-one (+ Me ₆ ,Me ₁₀ , Me ₁₄₋₁₅ :2-OH)	6R,10R	GC* #I	sex (M)	Lepido.	<i>Bicyclus anynana</i> (butterfly) #7	371 [08], 372 (15)	372 (15)	
				sex (F)	Lepido.	<i>Aphomia sociella</i> (pyralid moth)	368 (12)		
C ₁₈	Me ₆₋₁₈ :2-one (77) + Me ₁₄₋₁₈ :2-one (78) + Me ₆ ,Me ₁₄₋₁₈ :2-one (79)	S S	HPLC* #G	sex (F)	Lepido.	<i>Lyclene dharmia</i> (lichen moth)	235 [07], 236 (10)	237 (09), 238 (12)	
C ₂₇	Me ₃ ,Me ₁₁₋₂₇ :2-one (81) + Me ₃ ,Me ₁₁₋₂₇ :2-one, 27-OH	3S,11S		sex (F)	Dictyo.	<i>Blattella germanica</i> (cockroach)	243 (04) 725 [08]	242 (08)	
C ₂₉	Me ₃ ,Me ₁₁₋₂₉ :2-one (80) + Me ₃ ,Me ₁₁₋₂₉ :2-one, 29-OH	3S,11S	ORD #H	sex (F)	Dictyo.	<i>Blattella germanica</i> (cockroach)	239 [74], 240 (79) 723 [76], 725 [08]	241 (81), 242 (08) 724 [77]	



^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 LiAlH₄ 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 zeamais* (#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	Identifi- cation	Stereoselective synthesis
C ₃ Me2-3:acid	achiral	allomone ? aggregation alarm ? aggregation	Lepido.	<i>Graphium doson</i> , <i>G.</i> <i>sarpedon</i> (butterfly)	610 (80)	
			Hetero.	<i>Rhodnius prolixus</i> <i>Triatoma phyllosoma</i> , <i>T.</i> <i>longipennis</i> , <i>T. pallidipennis</i> (assassin bug)	445 (02) 733 (18)	
			[Ixodida]	<i>Amblyomma hebraeum</i> (tick)	611 (02)	
			Lepido.	<i>Graphium doson</i> , <i>G.</i> <i>sarpedon</i> <i>Parnassius glacialis</i> <i>Chilasa epycides</i> , <i>Papilio</i> <i>demoleus</i> , <i>P. macilentus</i> , <i>P.</i> <i>troilus</i> (butterfly)	610 (80) 616 (95) 617 (06)	
Me2-3:Me ester	achiral	allomone ?	Lepido.	<i>Graphium doson</i> , <i>G.</i> <i>sarpedon</i> <i>Parnassius glacialis</i> <i>Chilasa epycides</i> , <i>Papilio</i> <i>demoleus</i> , <i>P. macilentus</i> , <i>P.</i> <i>troilus</i> (butterfly)	610 (80) 616 (95) 617 (06)	
C ₄ Me2-4:acid	?	allomone	Lepido.	<i>Papilio machaon</i> , <i>P. protenor</i> (butterfly)	461 [65] 462 [80]	
			Coleo.	<i>Oodes vicarious</i> (ground beetle)	463 [82]	
			Thysano.	<i>Varshneyia pasaniae</i> (thrips)	464 [88]	
			Coleo.	<i>Chrysomela lapponica</i> <i>C. mainensis</i> , <i>C. walshi</i> (leaf beetle)	608 [97] 609 [99]	
Z2,Me2-4:acid [angelic acid]	achiral	allomone ?	Coleo.	<i>Pterostichus subsulcatus</i>	637 (89)	

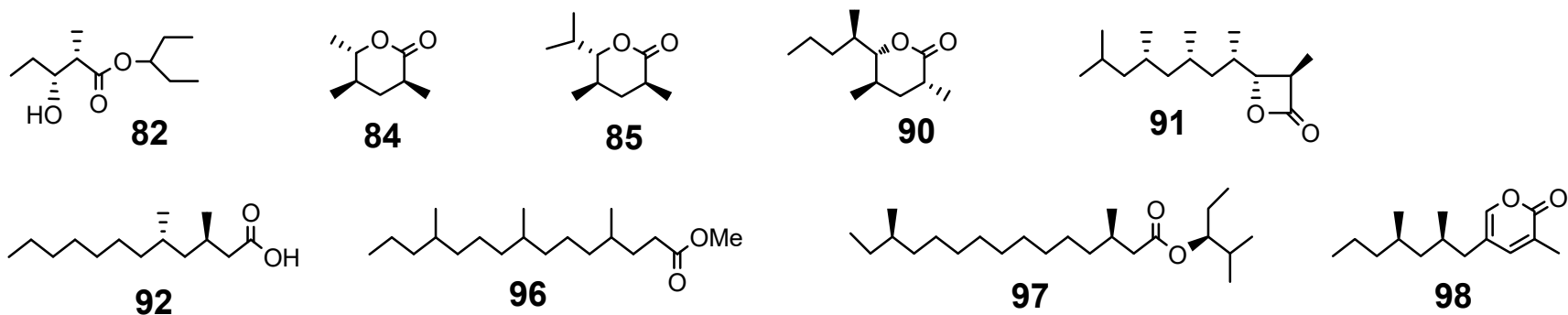
					<i>Carabus violaceus</i> (ground beetle)	706 (20)	
Me ₂ ,E ₂ -4:acid [tiglic acid]	achiral	allomone ?	Coleo.	<i>Carabus yaconinus</i> <i>C. montivagus, C. caelatus</i> <i>Pterostichus subsulcatus</i> <i>P. californicus</i> (ground beetle) <i>Trachypachus slevini</i> (false ground beetle)	599 (85) 706 (20) 637 (89) 601 (07) 600 (04)		
E ₂ ,Me ₂ -4:Et ester [ethyl tiglate]	achiral	aggregation (M)	Diptera	<i>Drosophila virilis</i> <i>D. americana, D. lummei, D. novamexicana</i> <i>D. hydei</i> <i>D. borealis, D. littoralis</i> (fruit fly)	597 (85) 684 (86) 648 (87) 598 (88)		
E ₂ ,Me ₂ -4:iPr ester [isopropyl tiglate]	achiral	aggregation (M)	Diptera	<i>Drosophila hydei</i> (fruit fly)	648 (87)		
E ₂ ,Me ₂ -4:E ₂ -6-OH ester	achiral	gland secretion	Hetero.	<i>Pachylis laticornis</i> (true bug)	705 (82)		
Et ₂ -4:2-OH, β-lactone	2 <i>S</i> ,3 <i>S</i>	sex (M)	Lepido.	<i>Idea leuconoe</i> (butterfly)	469 [96], 470 (02)		
iPro ₂ -4:2-OH, β-lactone [viridifloric β-lactone]	2 <i>S</i> ,3 <i>S</i>	sex (M)	Lepido.	<i>Idea leuconoe</i> (butterfly)	469 [96], 470 (02)		
NH ₂ ,Me ₃ -4:Me ester [L-valine methyl ester]	<i>S</i>	sex (F)	Coleo.	<i>Phyllophaga anxia, P. georgiana</i> (scarab beetle)	458 (97), 471 (09)		
Me ₂ -4:Me ₂ -4-NH ₂ amide	2 <i>S</i> ,2' <i>S</i>	sex (F)	Coleo.	<i>Migdolus fryanus</i> (longhorn beetle)	472 (94)	641 (01), 642 (22)	
(CHOHCH ₃) ₂ ,Me ₃ -4:γ-lactone [ithomiolide A]	2 <i>S</i> ,3 <i>R</i> ,1' <i>S</i>	sex (M) ?	Lepido.	<i>Hymenitis dercetis</i> <i>Ceratinia tutia</i> <i>Ithomia salapia</i>	529 [76] 530 (04) 668 [20]		

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

						693 [22]	
C ₆	Me2-6:acid	?		alarm ?	Hetero.	<i>Triatoma phyllosoma</i> , <i>T. longipennis</i> , <i>T. pallidipennis</i> (assassin bug)	733 [18]
	Me4-6: <i>n</i> -Bu ester (83)	<i>S</i>		aggregation	Hetero.	<i>Neomegalotomus parvus</i> (broad-headed bug)	253 (12)
	Z3,Me4,Δ5-6:acid	achiral		marking (M) ?	Diptera	<i>Urophora cardui</i> , <i>U. stylata</i> (fruit fly)	633 (90)
	Δ2,Me2,Me4-6:acid	?		allomone?	Hymeno.	<i>Myrmecocystus christineae</i> , <i>M. colei</i> , <i>M. depilis</i> , <i>M. romaine</i> , <i>M. semirufus</i> , <i>M. wheeleri</i> (ant)	450 [89]
	Me4,Δ5-6:γ-lactone [lavender lactone]	<i>S</i>		sex (M) ?	Lepido.	<i>Celastrina argiolus</i> (butterfly)	541 (13)
	Me2-6:δ-lactone	2 <i>R</i> *,5 <i>S</i> *		gland secretion (M)	Hymeno.	<i>Bombus griseocollis</i> (carpenter bee)	591 [76] 592 (78)
	Me2,Me4-6:δ-lactone ^s (84)	2 <i>S</i> ,4 <i>R</i> ,5 <i>S</i>		trail	Hymeno.	(1)(2) <i>Camponotus herculeanus</i> , (2)(4) <i>C. socius</i> , (2) <i>C. ligniperdus</i> , <i>C. vagus</i> , <i>C. pennsylvanicus</i> , (3) <i>C. modoc</i> , (5) <i>C. kaura</i> (ant)	(1) 254 [95], 255 (99), (2) 255 (99), (3) 434 (19), (4) 435 (01), (5) 436 [01]
C ₇	Me2,Me4,Me6-7:δ-lactone ^h (85)	2 <i>S</i> ,4 <i>R</i> ,5 <i>S</i>		sex (F)	Hymeno.	<i>Macrocentrus grandii</i> (parasitoid wasp)	256 [93], 257 (94), 258 (93), 259 (96), 260 (11), 373 (19)
	Me3-7:acid (86)	<i>R</i>	GC* #B	sex (M)	Coleo.	<i>Kheper nigroaeneus</i> (scarab)	261 (02), 261 (02), 680 (15), 675 [18]
	Me4-7:Et ester (88)	?		aggregation (M)	Coleo.	<i>Oryctes rhinoceros</i> (scarab) <i>Nicrophorus vespilloides</i>	263 [95] 437 [08],

				(burying beetle) #1	374 [17]	
	3-hydroxy-3-methoxycarbonyl-2-methylpentanedioic acid dimethyl ester [trimethyl methylcitrate]	2 <i>R</i> ,3 <i>S</i>	sex (F)	[Araneae] <i>Argiope bruennichi</i> (spider)	527 (10)	
C ₈	Me4-8:acid	<i>R</i>	aggregation (M)	Coleo. <i>Oryctes monoceros</i> <i>Oryctes rhinoceros</i> <i>Oryctes elegans</i> <i>Oryctes agamemnon</i> (scarab)	264 [94] 263 [95], 625 (22) 534 [04] 535 [15]	679 [13] 660 (16), 682 (21), 625 (22)
	Me4-8:Et ester (89) [oryctelure]	<i>S</i> <i>R</i>	aggregation (M)	Coleo. <i>Oryctes monoceros</i> <i>Oryctes rhinoceros</i> <i>Oryctes elegans</i> <i>Oryctes Agamemnon</i> (scarab)	264 [94] 263 (95) 625 (22) 534 [04] 535 [15]	263 (95), 665 [17], 681 (18) 665 [17], 625 (22)
	E4,Me7-8:iPr ester	achiral	sex (F)	Homo. <i>Crisicoccus azalea</i> (mealybug)	632 (22)	
	Me2-8:acid, 8-acid [2-methylsuberic acid]	?	secretion (F)	Coleo. <i>Callosobruchus rhodesianus</i> (seed beetle)	728 [17]	
	Me3-8:acid, 8-acid [3-methylsuberic acid]	?	secretion (F)	Coleo. <i>Callosobruchus rhodesianus</i> (seed beetle)	728 [17]	
	Me2,Me4,Me6-8:δ-lactone	?	trail	Hymeno. <i>Camponotus atriceps</i> <i>Camponotus castaneus</i> (ant)	452 [96] 453 [03]	
C ₉	E4,Me7-9:Et ester	?	sex (F)	Homo. <i>Crisicoccus azalea</i> (mealybug)	632 [22]	
	E4,Me7-9:iPr ester	?	sex (F)	Homo. <i>Crisicoccus azalea</i> (mealybug)	632, [22]	
	Me2,Me4,Me6-9:δ-lactone ⁱ (90) [invictolide]	2 <i>R</i> ,4 <i>R</i> ,5 <i>S</i> , 6 <i>R</i>	queen recognition	Hymeno. <i>Solenopsis invicta</i> (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.	<i>Rosalia alpina</i> (longhorn beetle)	528 [17]	
C ₁₀	Me9-10:Me7-8-OH ester	achiral		sex (F)	Coleo.	<i>Ectinus aterrimus</i> (click beetle)	563 (08)	563 (08)
C ₁₁	Me2,Me4,Me6,Me8,Me10-11:β-lactone ^j (91) [vittatalactone]	2R,3R,4S, 6S,8S	NMR #A	aggregation (M)	Coleo.	<i>Acalymma vittatum</i> (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)	[Aranea e]	<i>Argyrodes elevatus</i> (spider)	375 [16]	375 [16]
C ₁₂	Me3,Me5-12:acid (92)	3R,5S		sex (F)	Coleo.	<i>Prionus californicus</i> (longhorn beetle)	277 [09], 278 (11), 279 (11)	278 (11)
	Me3,Δ6,Me7,Δ10,Me11-12:Me ester (93) [methyl 2,3-dihydrofarnesoate]	3R,6E	GC #C	sex (M)	Hetero.	<i>Chlorochroa ligata</i> (stink bug) #2	280 [01], 281 (01)	281 (01)
C ₁₃	Me2-13:11-OH ester	?		cuticular lipid (M)	[Aranea e]	<i>Argyrodes elevatus</i> (spider)	375 [16]	375 [16]
C ₁₅	Me4,Me8,Me12-15:Me ester (96)	?		sex (M)	Hetero.	<i>Edessa meditabunda</i> (stink bug)	285 [12]	504 (20)
	Me3,Me13-15:Et-Me-Pr ester ^k (97)	3R,13R,3'S		sex (F)	Lepido.	<i>Clania variegata</i> (bagworm moth)	286 [06], 287 (10)	288 (09), 287 (10), 289 (13), 376 (17), 732 (24)
	Me2,Me14-15:Glu amide	2R [(S)-L-Glu]		marking	Diptera	<i>Ceratitis rosa</i> (fruit fly)	699 (03), 700 (10)	700 (10), 721 (23)
C ₇₊₅	Me2,Me4-7:α-pyrone ^l (98) [supellapyrone]	2R,4R	GC* #D	sex (F)	Dictyo.	<i>Supella longipalpa</i> (cockroach)	290 [93], 291 (95)	292 (95), 293 (01)
C ₁₆	Z8,Me14-16:Me ester	?		sex (F)	Coleo.	<i>Trogoderma inclusum</i> (hide beetle)	120 [69], 512 [77]	122 (74)
	E8,Me14-16:Me ester	?		sex (F)	Coleo.	<i>Trogoderma glabrum</i> (hide beetle)	511 [75]	
C ₁₇	Me2,Me4-17:13-OH ester	2R,4R		cuticular lipid (M)	[Aranea e]	<i>Argiope bruennichi</i> (spider)	626 (22)	
C ₁₉	Me2,Me4-19:13-OH ester	?		cuticular	[Aranea e]	<i>Argiope bruennichi</i>	626 [22]	



^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.

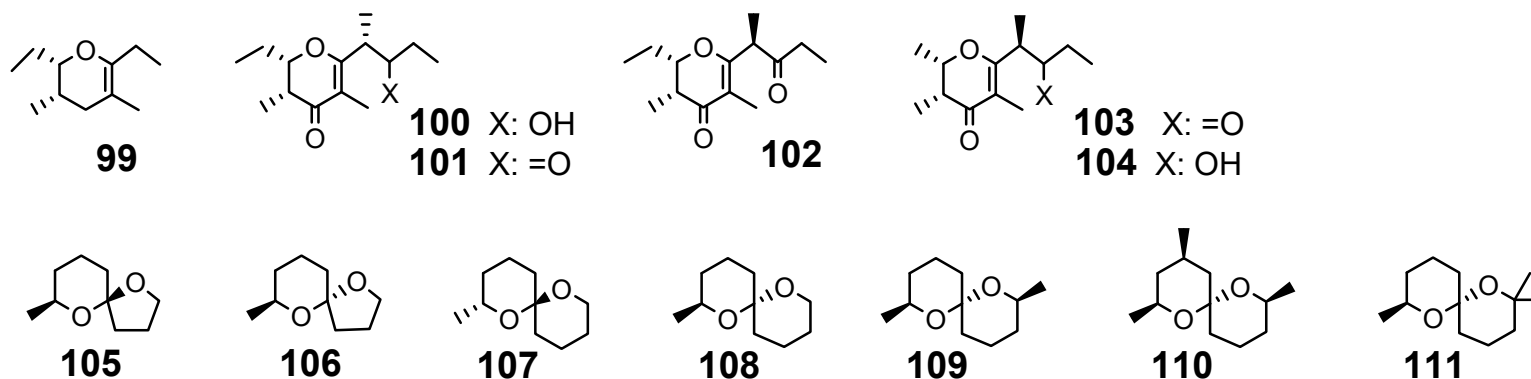
^l 5-(2',4'-Dimethylheptanyl)-3-methyl-2*H*-pyran-2-one.

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

Pheromone	Configuration and analytical method ^a		Function (Producer)	Insecta		Reference ^d	
				Order ^b	Species ^c	Identification	Stereoselective synthesis
dihydropyran (DP)							
Et2,Me3,Me5,Et6-DP [anhydroserricornin] (99) ^e	2 <i>S</i> ,3 <i>S</i>		sex (F)	Coleo.	<i>Lasioderma serricorne</i> (deathwatch beetle)	294 [81], 295 (86)	296 (84), 297 (85)
Et2,Me3,Me5,(C ₅ H ₁₀ OH)6-DP-4-one [serricorole] (100) ^f	2 <i>S</i> ,3 <i>R</i> ,1' <i>S</i> ,2' <i>S</i>		sex (F)	Coleo.	<i>L. serricorne</i>	298 [83], 299 [85], 300 (87)	300 (87)
Et2,Me3,Me5,(C ₅ H ₉ O)6-DP-4-one [α-serricorone] (101) ^g	2 <i>S</i> ,3 <i>R</i> ,1' <i>S</i>	CD	sex (F) + marking	Coleo.	<i>L. serricorne</i>	298 [83], 301 (90)	300 (87)
+Et2,Me3,Me5,(C ₅ H ₉ O)6-DP-4-one [β-serricorone] (102)	2 <i>S</i> ,3 <i>R</i> ,1' <i>R</i>						
Me2,Me3,Me5,(C ₅ H ₉ O)6-DP-4-one [stegobinone] (103) ^h	2 <i>S</i> ,3 <i>R</i> ,1' <i>R</i>		sex (F)	Coleo.	<i>Stegobium paniceum</i> (deathwatch beetle) <i>Anobium punctatum</i> (deathwatch beetle)	302 [78], 303 (81) 377 (87)	304 (79), 305 (81), 306 (12)
Me2,Me3,Me5,(C ₅ H ₁₀ OH)6-DP-4-one [stegobiol] (104) ⁱ	2 <i>S</i> ,3 <i>R</i> ,1' <i>S</i>		sex (F)	Coleo.	<i>Stegobium paniceum</i> (deathwatch beetle)	307 (87)	308 (86), 306 (12)
Spiroacetal (SA)							
1,6-dioxaspiro[4.5]decane ([4.5]SA)							
Me7-[4.5]SA [conophthorin] (105)	5 <i>R</i> ,7 <i>S</i>		sex (M)	Diptera	<i>Bactrocera xanthodes</i> (fruit fly)	309 (92)	309 (92)
(106)	5 <i>S</i> ,7 <i>S</i>		sex (M)	Coleo.	<i>Conophthorus coniperda</i> (bark beetle) #1	310 (98)	311 (81)
	5 <i>S</i> ,7 <i>S</i>		allomone ?	Hymeno.	<i>Vespula vulgaris</i> (= <i>Paravespula vulgaris</i>) (wasp)	719 [78], 438 [79], 720 [97]	
Me2,Et7-[4.5]SA	?		gland	Hymeno.	<i>Paravespula vulgaris</i> , <i>P.</i>	438 [79]	

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

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

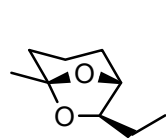
- ^e 2,6-Diethyl-3,5-dimethyl-3,4-dihydro-2*H*-pyran
- ^f 2,3-Dihydro-3,5-dimethyl-2-ethyl-6-(1-methyl-2-hydroxybutyl)-4*H*-pyran-4-one
- ^g 2,3-Dihydro-3,5-dimethyl-2-ethyl-6-(1-methyl-2-oxobutyl)-4*H*-pyran-4-one
- ^h 2,3-Dihydro-2,3,5-trimethyl-6-(1-methyl-2-oxobutyl)-4*H*-pyran-4-one
- ⁱ 2,3-Dihydro-2,3,5-trimethyl-6-(1-methyl-2-hydroxybutyl)-4*H*-pyran-4-one
- ^j 7-Methyl-1,6-dioxaspiro[4.5]decane

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

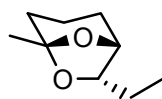
Pheromone			Insecta		Reference ^d	
	Configuration and analytical method ^a	Function	Order ^b Family	Species ^c	Identification	Stereoselective synthesis
<i>exo</i> -7-ethyl-5-methyl-6,8-dioxabicyclo[3.2.1]octane [(+)- <i>exo</i> -brevicomins] (112)	1 <i>R</i> ,5 <i>S</i> ,7 <i>R</i> NMR (#A)	aggregation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

6,8-dioxabicyclo[3.2.1]octane [frontalin] (116)	NMR (#A) + 1 <i>R</i> ,5 <i>S</i> (2:1) GC (#G)		Scolytidae	(bark beetle) #3 <i>D. jeffreyi</i>	393 (99)	395 (76), 396 (83), 397 (86), 398 (87), 399 (99), 400 (02), 401 (03), 653 (13)
	?			<i>D. adjunctus</i> #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 <i>S</i> ,2 <i>R</i> ,4 <i>S</i> ,5 <i>R</i> [α] _D (-)	aggregation	Coleo. Scolytidae	<i>Scolytus multistriatus</i> , <i>S.</i> <i>pygmaeus</i> (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), 329 (87)
	?		Dryophthoridae	<i>Diocalandra frumenti</i> (weevil)	506 [17]	
2-ethyl-1,5-dimethyl- 6,8-dioxabicyclo[3.2.1]octane [bicolorin] (118)	1 <i>S</i> ,2 <i>R</i> ,5 <i>R</i> GC (#B)	aggregation	Coleo. Scolytidae	<i>Taphrorychus bicolor</i> (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 <i>S</i> ,3 <i>R</i> ,5 <i>R</i> ,7 <i>S</i> [α] _D (+),GC (#G) + 1 <i>S</i> ,3 <i>R</i> ,5 <i>R</i> ,7 <i>R</i> 1 <i>R</i> ,3 <i>S</i> ,5 <i>S</i> ,7 <i>S</i> GC (#C)	aggregation	Coleo. Curculionidae	<i>Cosmopolites sordidus</i> (weevil)	408 [95], 409 (96) 410 (97)	409 (96), 412 (05), 413 (08)
		?	Trico. Limnephilidae	<i>Potamophylax latipennis</i> (caddis fly) #6	411 (04)	
1,3-diethyl-4,6-dimethyl- 2,7-dioxabicyclo[2.2.1]heptane (120)	1 <i>S</i> ,3 <i>S</i> ,4 <i>R</i> ,6 <i>S</i> or 1 <i>R</i> ,3 <i>R</i> ,4 <i>S</i> ,6 <i>S</i>	aggregation	Trico. Limnephilidae	<i>Glyphotaelius pellucidus</i> (caddis fly)	411 (04)	
1,3,3-trimethyl- 2,7-dioxabicyclo[2.2.1]heptane (121)	?	gland secretion (defense substance ?)	Hymeno. Formicidae	<i>Iridomyrmex purpureus</i> <i>Eciton burchelli</i> , <i>Aenictus rotundatus</i> (ant)	414 [84] 456 [93] 415 [94]	
3-isopentenyl-1,3-dimethyl- 2,7-dioxabicyclo[2.2.1]heptane (122)	?	gland secretion	Hymeno. Apidae	<i>Nannotrigona testaceicornis</i> (bee)	416 [01]	

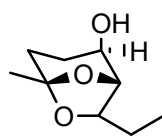
3-ethyl-1,8-dimethyl- 2,9-dioxabicyclo[3.3.1]non-7-ene (123)	1 <i>R</i> ,3 <i>S</i> ,5 <i>S</i> GC (#D)	?	Lepido. Hepialidae	<i>Hepialus hecta</i> (swift moth)	417 [85], 418 (90)	419(86)
+ 6-keto derivative (124)	1 <i>R</i> ,3 <i>S</i> ,5 <i>R</i>	?			418 (90)	
1,3,8-trimethyl derivative (125)	1 <i>R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



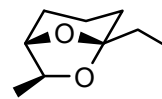
112



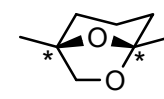
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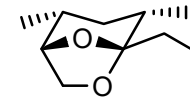
114



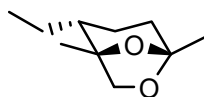
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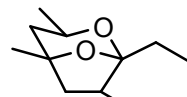
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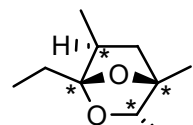
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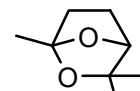
118



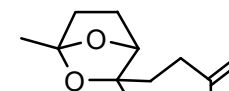
119



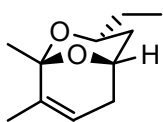
120



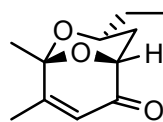
121



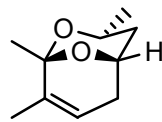
122



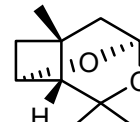
123



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-(1*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.

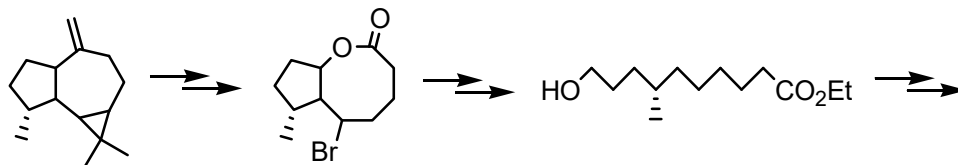
^b Coleo. = Coleoptera, Hetero. = Heteroptera, Hymeno. = Hymenoptera, Lepido. = Lepidoptera, Strepsi. = Strepsiptera.

^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. cinquatus* (#6)

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

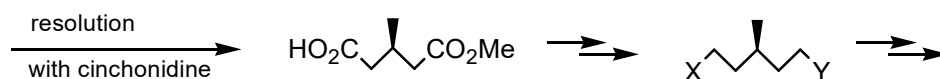
Synthon	Chemical structure and the synthetic route	Targeted pheromone
1a. Citronellol (S1a) or citronellal (S1b)		Me10-12:OAc (30) ⁹⁹ Me6,Me12-15:2-one (76) ²³³ and 2 ²⁰ , 5 ²⁷ , 10 ²⁸ , 28 ⁸⁴ , 29 ^{90,95,96} , 38 ¹¹⁹ , 62 ¹⁸⁹ , 63 ¹⁹⁰ , 74 ²²³ , 77–79 ^{237,238} , 80 ²⁴² , 86 ²⁶¹ , 94 ²⁸⁴ , 97 ^{287,288} , 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)



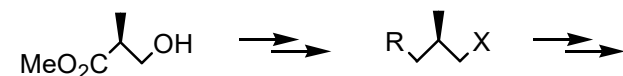
Me9-19:H (11)⁵⁵
Me10-13:2-one (74)⁵⁵

5. 3-Methylglutaric acid monomethyl ester (S5)



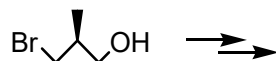
Me8-10:2-OPr (47)¹⁴⁷
Me10-13:2-one (74)²²⁴

6. 3-Hydroxy-2-methylpropionate (Roche ester, S6)



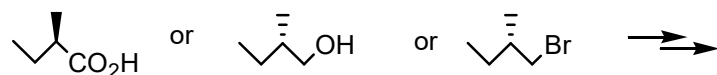
Me11-23:H (17)⁶⁷
vittatalactone (91)^{272,273}
and 5²⁷⁻²⁹, 6³⁵, 9⁴⁷, 10⁵², 29⁹⁵,
74²²⁸, 78²³⁷, 79²³⁷, 94²⁸⁴

7. 3-Bromo-2-methylpropanol (S7)



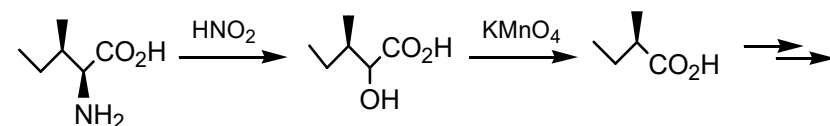
Me3,Me5,Me9-12:Ald (34)¹⁰⁷
supellapyrone (98)²⁹²

8a. 2-Methylbutanoic acid (S8a), 2-methylbutan-1-ol (S8b), or 1-bromo-2-methylbutane (S8c)



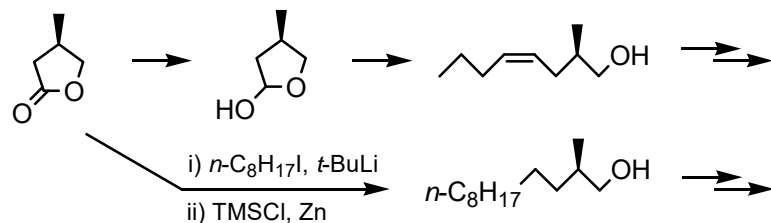
Me3,Me13-15: ester (97)^{287,288}
and 29⁹⁶, 39¹²², 40¹²⁴, 68²⁰⁶

8b. (R)-2-Methylbutanoic acid [(R)-S8a] from L-isoleucine



Me8-10: 2-OPr (47)¹⁴⁶

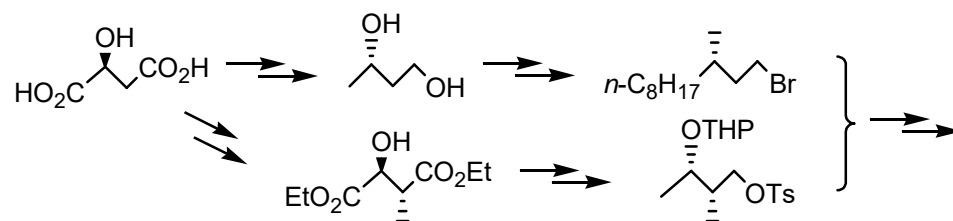
9. 3-Methyl-4-butanolide (**S9**)



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

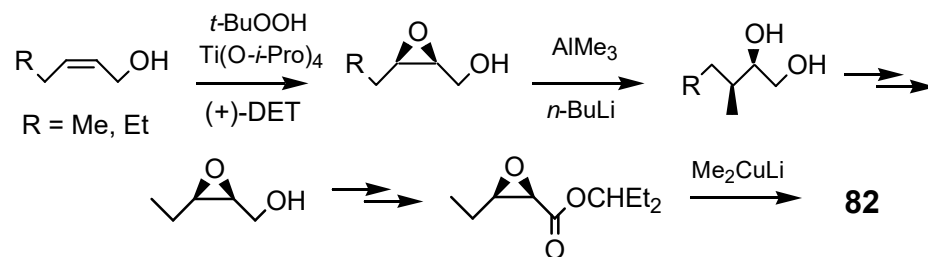
Me₉-19:H (**11**)⁵⁶

10. Malic acid (**S10**)



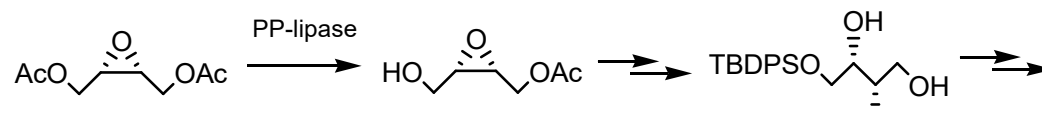
Me₃,Me₇-15:2-OAc (**56**)^{176,178}

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



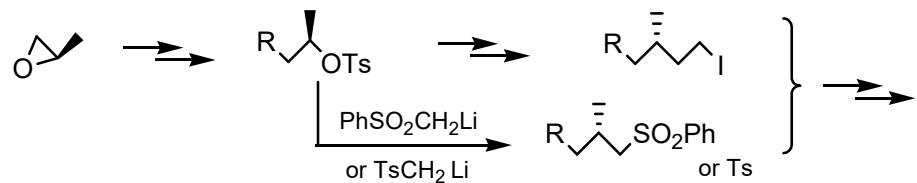
Me₃-8:4-OH (**44**)¹³⁵
 Me₅-8:4-OH (**45**)¹³⁵
 sitophilate (**82**)²⁴⁶
 invictolide (**90**)²⁶⁶

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



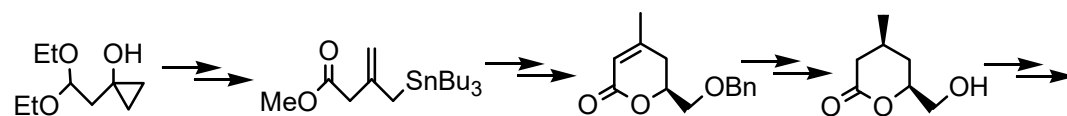
Me₃-8:4-OH (**44**)¹³⁶
 Me₄-9:5-OH (**46**)¹⁴²

13. Chiral epoxide: Propylene oxide (**S13**)



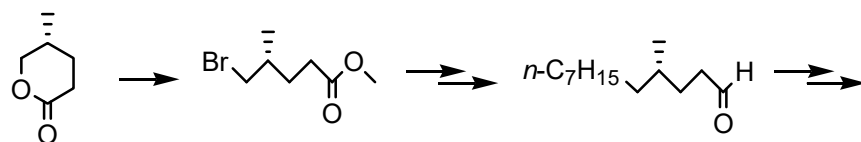
Me5,Me9-17:H (**5**)³²
 Δ 1,Me10,Me14-18:H (**10**)⁵³
 Me5-17:7-OH (**61**)¹⁸⁵
 and **75**²³⁰, **97**²⁸⁹

14. Chiral lactone (**S14**)



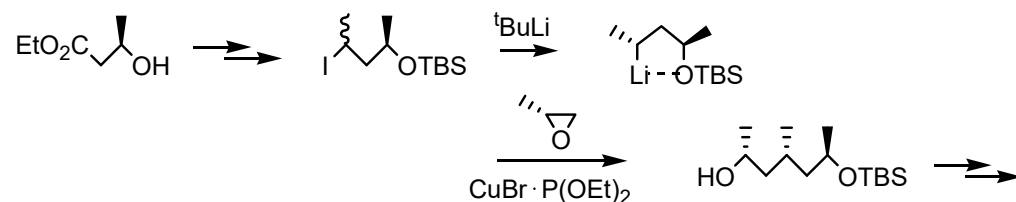
Δ 1,Me10,Me14-18:H (**10**)⁵⁴
 Me10-12:OAc (**30**)¹⁰³
 faranal (**36**)¹¹³
 and **40**¹⁰³, **110**³²²

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).

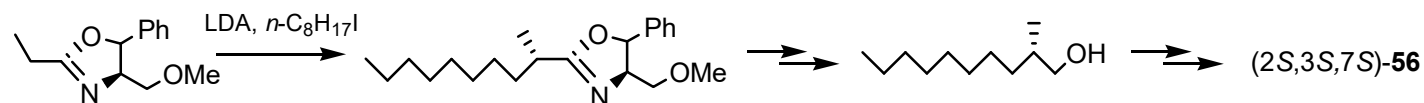
Reaction type

Synthetic route for a targeted chiral pheromone

1. C-C coupling with a chiral intermediate

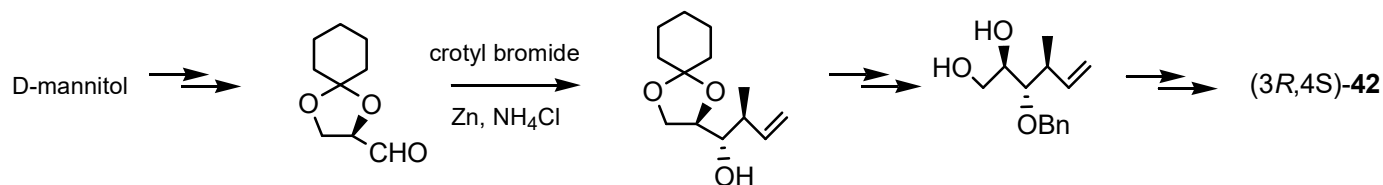
R-1-1. 2-Oxazoline derivative

Me₃,Me₇-15:2-OAc (**56**)¹⁷⁴

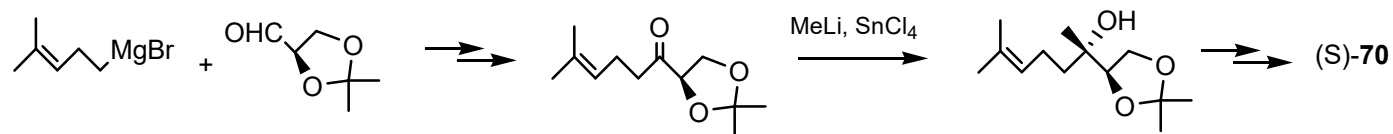


R-1-2. [1,3]Dioxolane-4-carbaldehyde and a keto derivative

a. Me₄-6:3-OH (**42**)¹²⁹

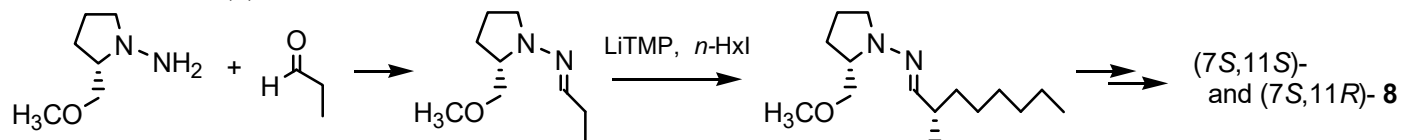


b. Me₃,Δ₆,Me₇-8:1-OH,3-OH,2-one (**70**)²¹³



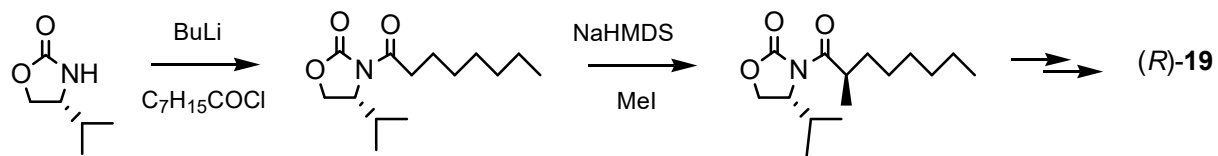
R-1-3. Enders SAMP/RAMP hydrazone-alkylation reaction

Me₇,Me₁₁-17:H (**8**)⁴²

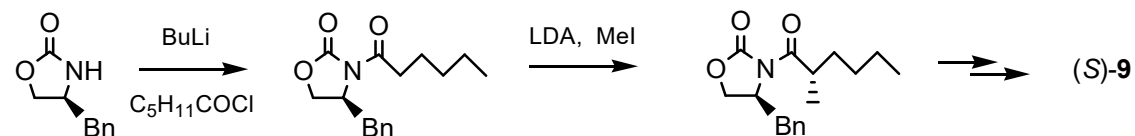


R-1-4. Evans' chiral auxiliaries

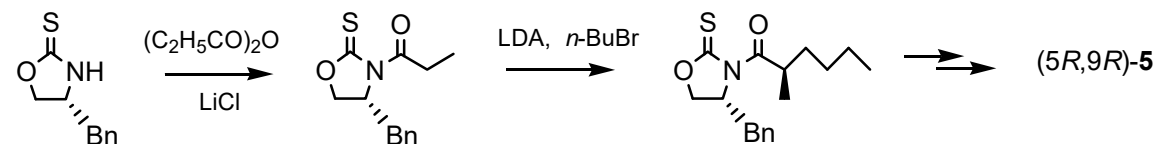
a. Me7-27:H (**20**)⁷²



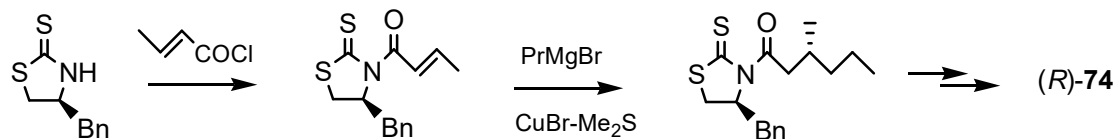
b. Δ1, Me14-18:H (**9**)⁴⁹



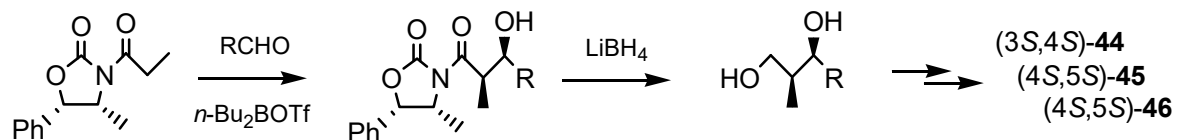
c. Me5,Me9-17:H (**5**)³¹



d. Me10-13:2-one (**74**)²²⁷



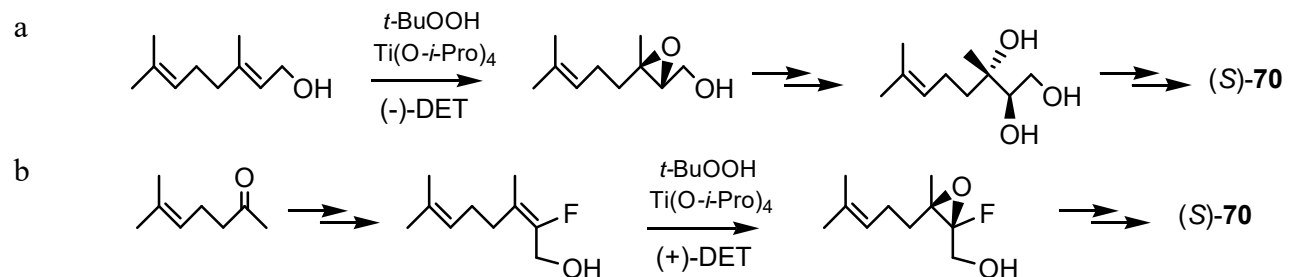
e. Me3-8:4-OH (**44**)¹³⁷ etc.



2. Reaction *via* an epoxy compound

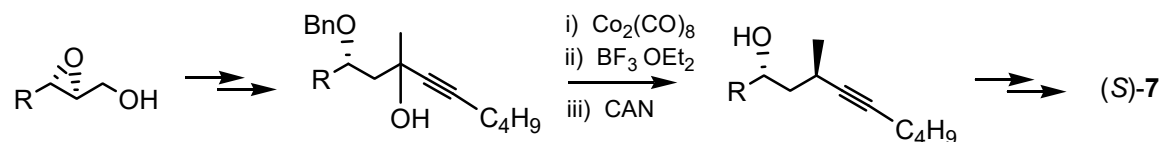
R-2-1. Sharpless asymmetric epoxydation

Me3,Δ6,Me7-8:1-OH,3-OH,2-one (**70**)^{214, 215}



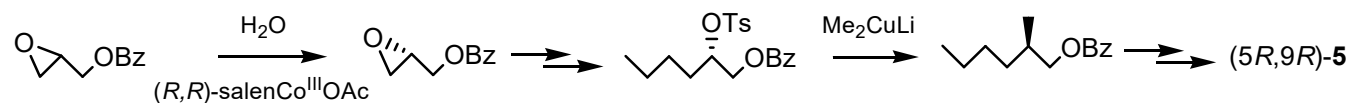
R-2-2. Intermolecular hydride transfer

Me7-17:H (**7**)³⁷

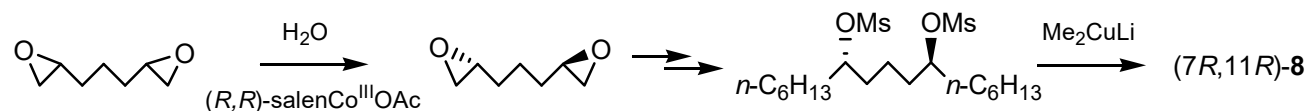


R-2-3. Hydrolytic kinetic resolution (HKR)

a. Me5,Me9-17:H (**5**)³¹

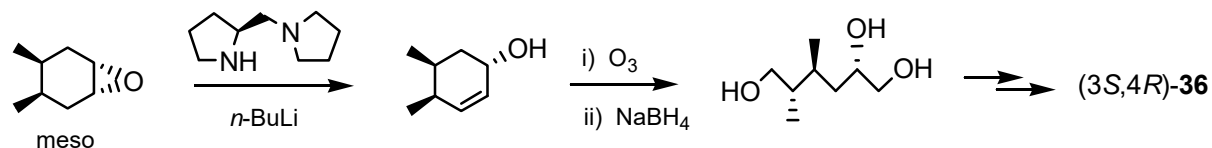


b. Me7,Me11-17:H (**8**)⁴³



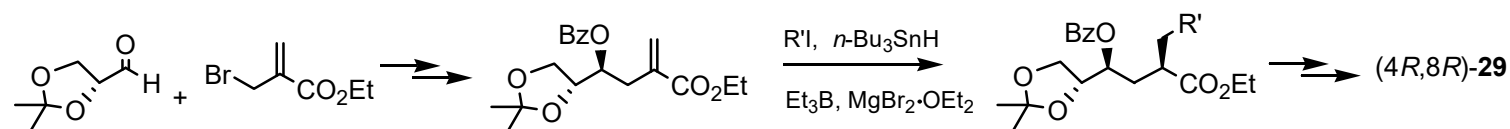
R-2-4. Asymmetric cleavage of an epoxy ring

faranal (**36**)¹¹²



3. Chelation-controlled radical reaction

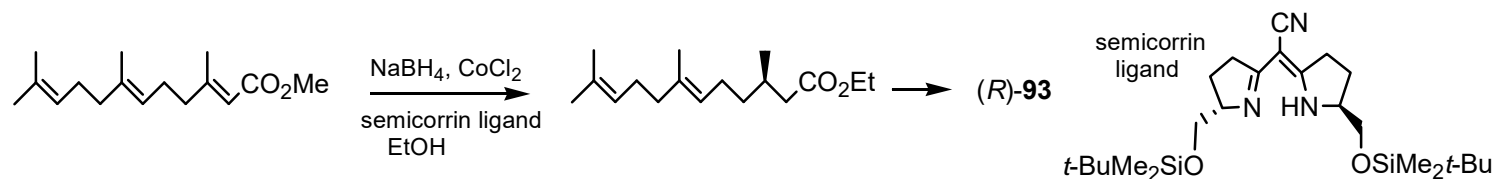
R-3 Me₄,Me₈-10:Ald (**29**)⁹⁴



4. Reaction with a chiral catalyst

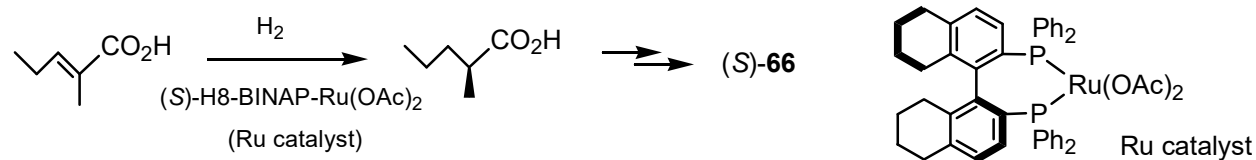
R-4-1. NaBH_4 reduction with a chiral cobalt semicorrin complex

dihydrofarnesoate (**93**)²⁸¹

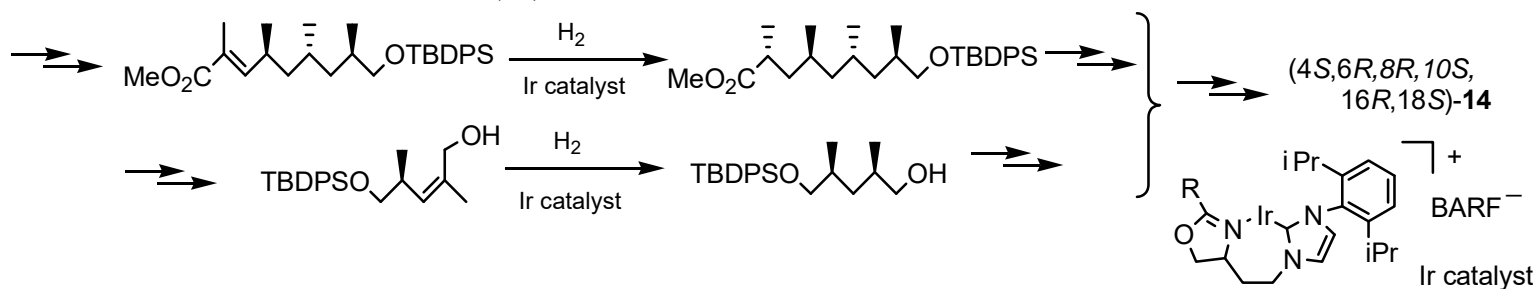


R-4-2. Hydrogenation over a chiral catalyst

a. Δ^1 ,Me₄-7:3-one (**66**)²⁰⁰

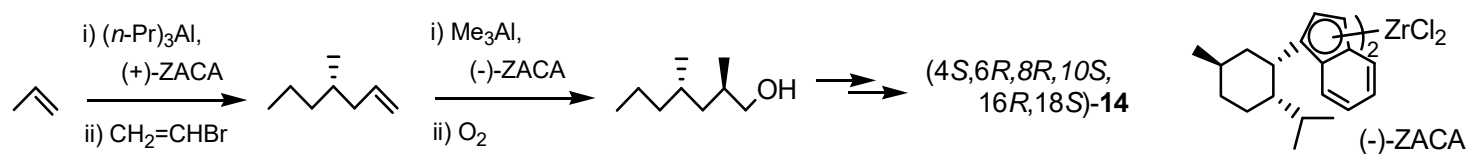


b. Me₄,Me₆,Me₈,Me₁₀,Me₁₆,Me₁₈₋₂₂:H (**14**)⁶³



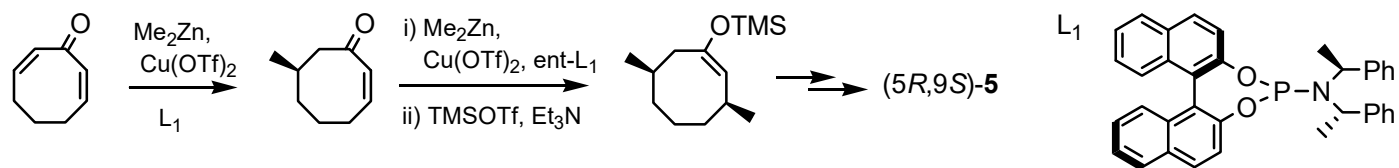
R-4-3. Zr-catalyzed asymmetric carboalumination of alkenes (ZACA reaction)

Me₄,Me₆,Me₈,Me₁₀,Me₁₆,Me₁₈₋₂₂:H (**14**)⁶⁴

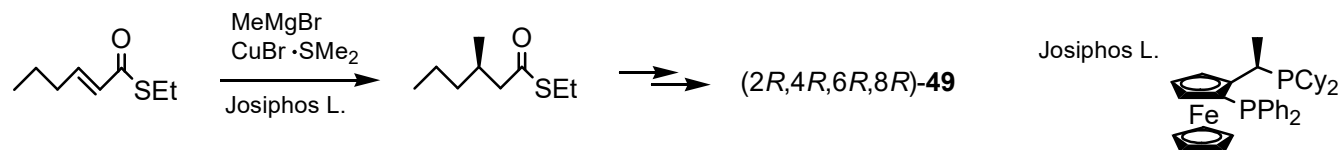


R-4-4. Cu-catalyzed asymmetric Michael addition of organometallic reagents

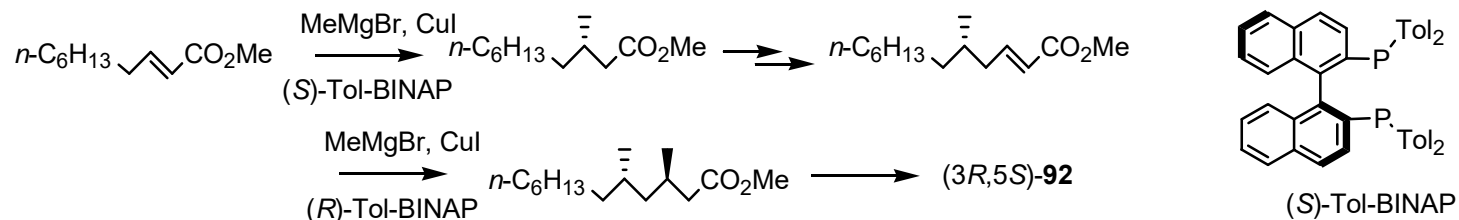
a. Me₅,Me₉₋₁₇:H (**5**)³⁰



b. lardolure (**49**)¹⁵⁷

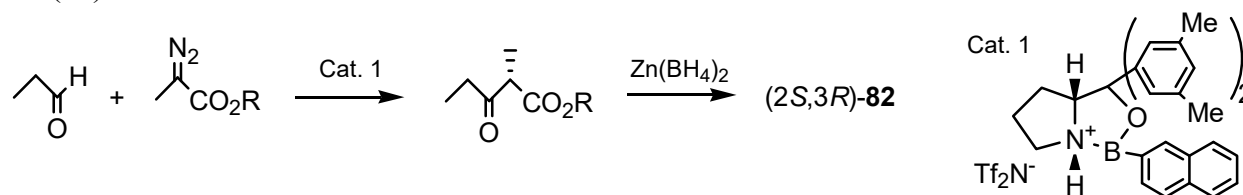


c. Me₃,Me₅-12:acid (**92**)²⁷⁸



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

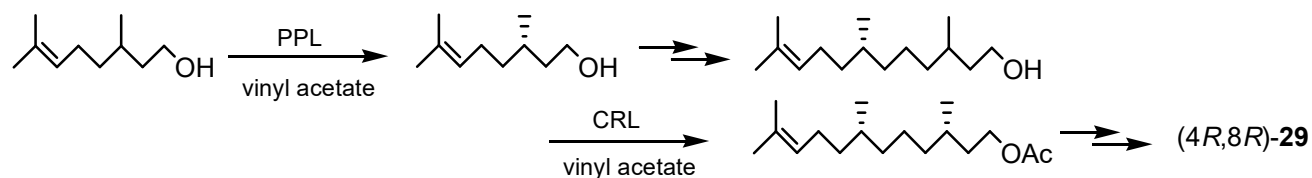
sitophilate (**82**)²⁵¹



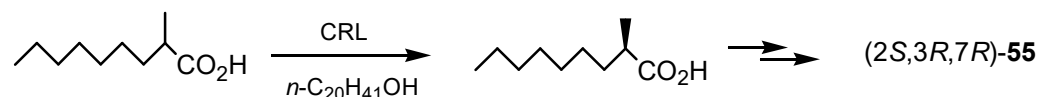
5. Chemoenzymatic reaction

R-5-1. Lipase-catalyzed kinetic resolution

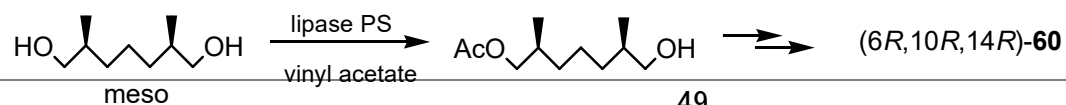
a. Me₄,Me₈-10:Ald (**29**)⁹³



b. Me₃,Me₇-14:2-OPr (**55**)¹⁷¹

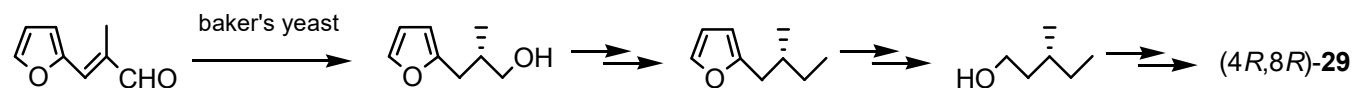


c. Me₆,Me₁₀,Me₁₄-15:2-OH (**60**)¹⁸²

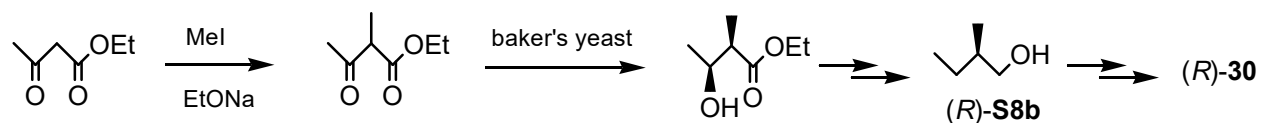


R-5-2. Reduction by baker's yeast

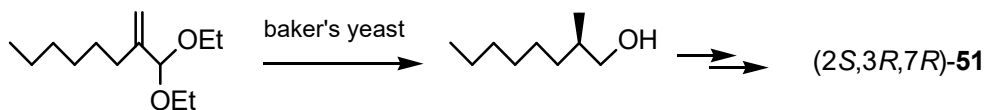
a. Me₄,Me₈-10:Ald (**29**)⁹²



b. Me₁₀-12:OAc (**30**)¹⁰¹

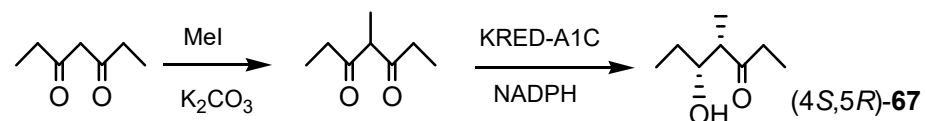


c. Me₃,Me₇-13:2-OAc (**51**)¹⁶⁴



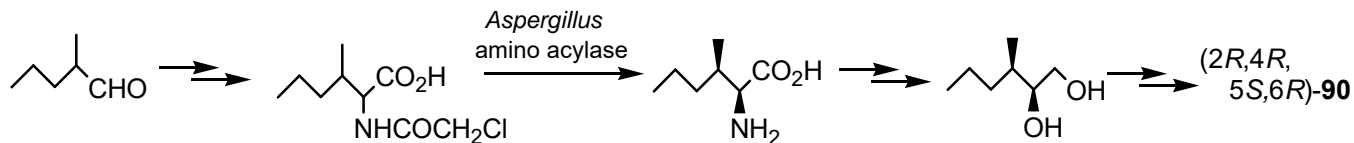
R-5-3. Reduction by isolated ketoreductase

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

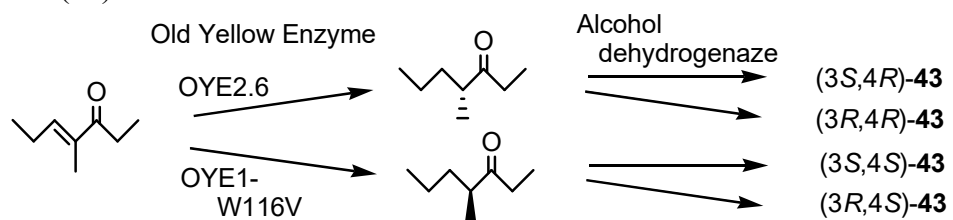
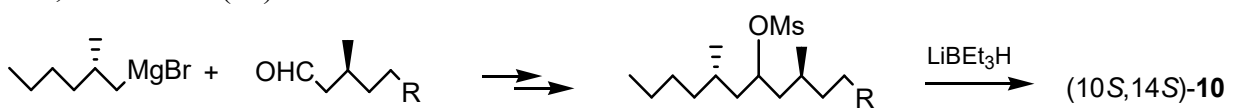
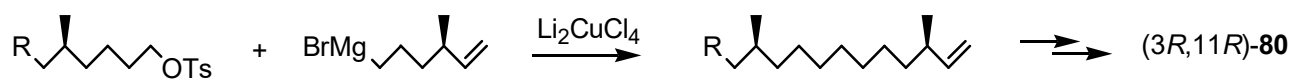
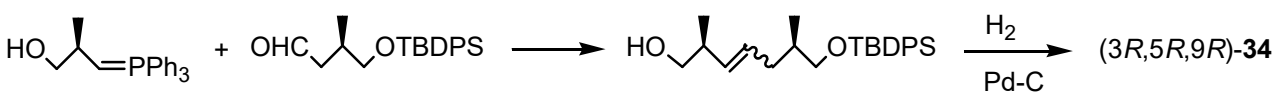
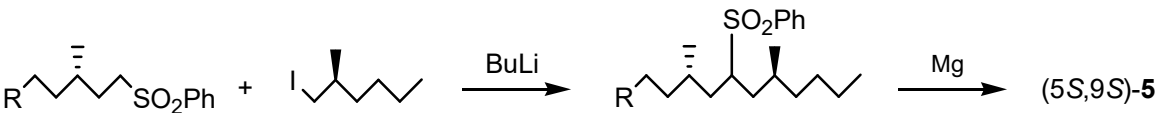
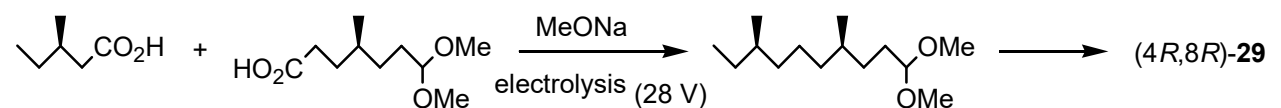
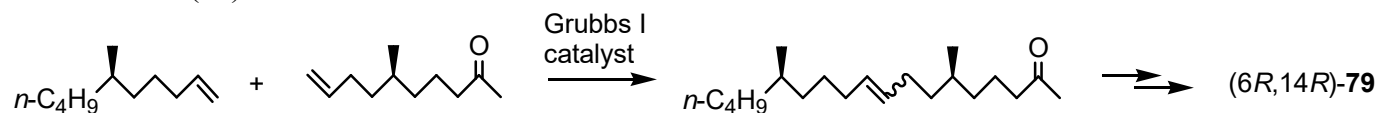


Table 10. Coupling reactions of two chiral blocks (R-6 – R-11) for the syntheses of dimethyl pheromones.

Reaction type
Synthetic route for a targeted chiral pheromone
<p>R-6. Reaction of a Grignard reagent</p> <p>a. $\Delta 1, \text{Me}_{10}, \text{Me}_{14-18}:\text{H}$ (10)²⁸</p>  <p>b. $\text{Me}_3, \text{Me}_{11-29}:\text{2-one}$ (80)²⁴¹</p> 
<p>R-7. Wittig reaction</p> <p>$\text{Me}_3, \text{Me}_5, \text{Me}_9-12:\text{Ald}$ (34)¹⁰⁷</p> 
<p>R-8. Coupling of RSO_2Ph with $\text{R}'\text{I}$</p> <p>$\text{Me}_5, \text{Me}_9-17:\text{H}$ (5)²⁷</p> 
<p>R-9. Kolbe electrolysis</p> <p>$\text{Me}_4, \text{Me}_8-10:\text{Ald}$ (29)⁹¹</p> 

R-10. Olefin cross metathesis

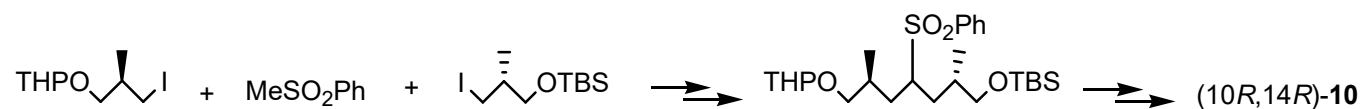
Me6,Me14-18:2-one (**79**)²³⁷



R-11. Coupling with a linchpin

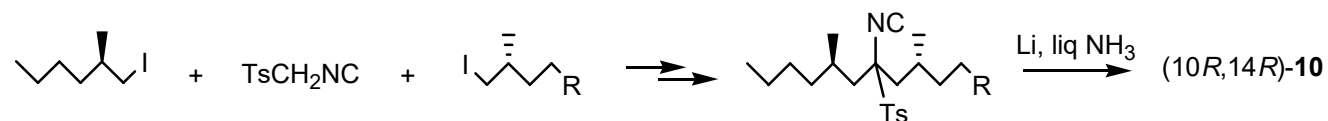
11-1. Methyl phenyl sulfone (MeSO₂Ph)

Δ1,Me10,Me14-18:H (**10**)⁵²



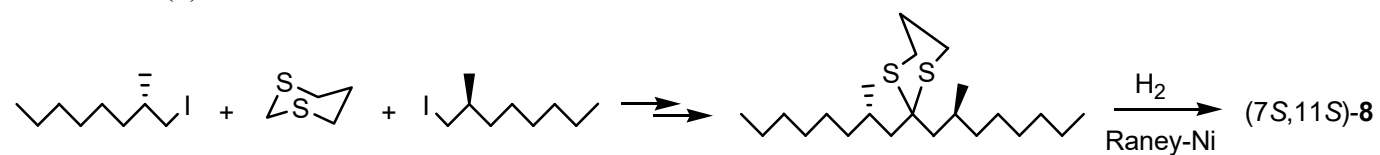
11-2. *p*-Toluenesulfonylmethyl isocyanide [CH₂(NC)SO₂Ts, TosMIC]

Δ1,Me10,Me14-18:H (**10**)³¹

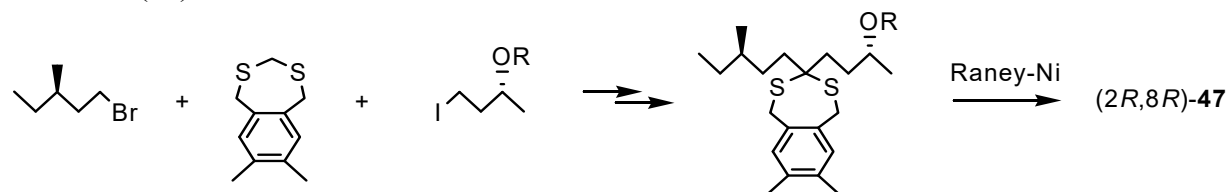


11-3. 1,3-Dithiane

a. Me7,Me11-17:H (**8**)⁴²

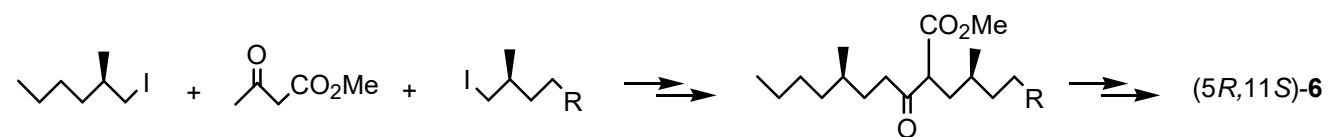


b. Me8-10:2-OPr (**47**)¹⁴⁵



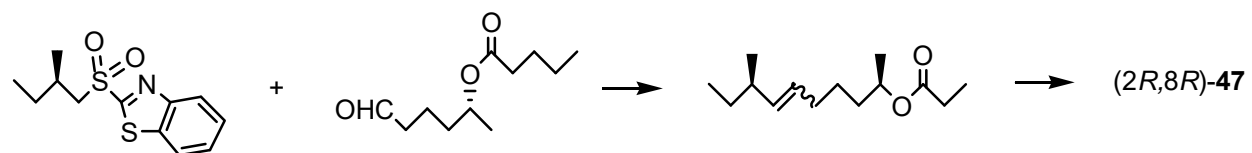
11-4. Methyl acetoacetate

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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