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Stereoselective Crossed Aldol Reaction via Boron Enolates Generated from α-Iodo Ketones and 9-Borabicyclo[3.3.1]nonane

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Boron enolates were in situ-generated reductively by treating various α-iodo ketones such as 2-iodo-1-phenylpropan-1-one, 2-iodo-1-(4-methoxyphenyl)propan-1-one, 2-iodopentan-3-one, 2-iodo-2-methyl-1-phenylpropan-1-one, 3,4-dihydro-2-iodo-1(2*H*)-naphthalenone, 2-iodo-1-phenylethan-1-one and 1-iodo-4-phenylbutan-2-one with 9-borabicyclo[3.3.1]nonane (9-BBN). Aldols were produced in good yields with good to high diastereoselectivities by subsequent reaction of boron enolates thus formed with various aldehydes. Several boron enolates derived from α-iodo ketones and pinacolatoborane were successfully isolated by distillation, though the yields were rather moderate.

Aldol reaction is one of the most fundamental and frequently employed tools for C–C bond formation. There have been many useful methods developed for the synthesis of various aldols using metal enolates as aldol donors. Since reactions of metal enolates depend on the nature of the metal atoms, various metal enolates such as Na, Li, Mg, Zn, Si, B, Sn(II) and Sn(IV) enolates[1] were investigated in detail to examine their behavior as aldol donors. Of these metal enolates, boron atom was noted to have strong affinity toward carbonyl oxygen atom. The length of the B–O bond (1.36–1.47 Å) was shorter than other metal–O bonds such as Ti–O (1.62–1.73 Å), Al–O (1.92 Å), Mg–O (2.01–2.13 Å) and Sn–O (2.70 Å).[2] Thus, the aldol reaction of boron enolates with aldehydes proceeded via rigid chair-like six-membered transition state to afford the corresponding aldols stereoselectively. Accordingly, the aldol reactions using boron enolates are employed frequently as useful tools in many strategies for natural products' synthesis.[3]

Concerning generation of boron enolates, there are several methods reported: for example, Hooz et al. reported that the boron enolates were generated by treating tributylborane with diazoketones.[4] Köster showed that the enolates were generated also by treating ketones with Et_3B at 130–150 °C.[5] Further, the boron enolates were generated from methyl vinyl ketone and tri-*n*-butylborane,[6a] and subsequent reaction of boron enolates thus formed with aldehydes,[6b,6c] effectively affording aldols, which was the first example of using boron enolate as a useful aldol-donor. Our laboratory reported that the regioselective generation of boron enolates was directly carried out from unsymmetrical ketones by treating them with dialkylborane triflate using tertiary amines under neutralization conditions (1976).[7] This simple method for the generation of boron enolates has contributed considerably to the development of aldol chemistry. Also, stereoselective boron aldol reactions for the synthesis of optically active compounds were established by using chiral auxiliary groups. For example, Evans et al. reported *syn*-selective asymmetric aldol reactions[8] and Abiko and co-workers recently reported[9] *anti*-selective ones.

Boron enolates were generated by treating unsymmetrical ketones with the dialkylborane triflates in the presence of tertiary amines under neutralization conditions, because the triflates behave as a counter anion of a strong acid. Therefore, a new method for the generation of boron enolates under milder conditions was still needed. Despite the employment of Et_3B as a reductant for the aldol reaction between α-iodo ketones with several aldehydes was reported,[10] no satisfactory results were shown concerning the diastereoselectivities. The regioselective generation of boron enolates might successfully be performed by simple and straightforward hydride reduction of α-halo ketones with dialkyl- or dialkoxylboranes. Further, the aldol reaction using boron enolate generated by hydride reduction might be superior to that using boron triflate, in terms of their applicability to the total synthesis of complicated natural compounds, since boron hydrides behave as a milder Lewis acid compared with boron trifrates. Actually, boron hydride reduced α-iodo ketone smoothly to afford boron enolate, and the treatment with aldehydes that followed afforded various aldols.

Preliminary results on the aldol reaction of boron enolates generated from α-iodo ketones and 9-BBN with several aldehydes were reported in the previous communication.[11] After screening the reaction conditions of the above reaction, it was found that the α-iodo ketones were smoothly reduced to generate boron enolates when catecholatoborane, pinacolatoborane or 9-BBN was used in the presence of tertiary amines. The boron enolates, 9-BBN enolates in particular, afforded aldols in a diastereoselective manner by successive treatment with aldehydes. Here, we would like to describe in detail the diastereoselective aldol reaction of α-iodo carbonyl compounds with various aldehydes.

Results and Discussion

Isolation of Boron Enolates and Their Aldol Reactions. Isolation of boron enolates by reductive treatment of α-iodo ketones with pinacolatoborane was first tried; several boron

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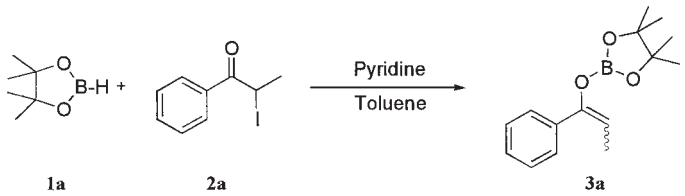
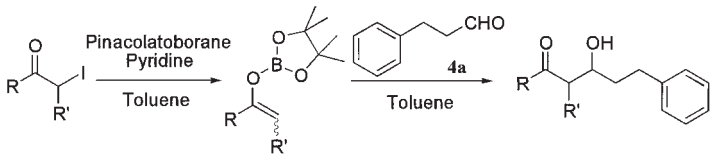
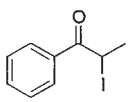
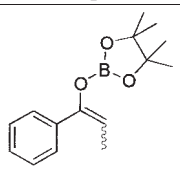
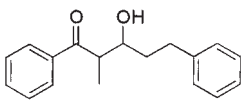
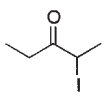
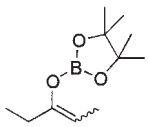
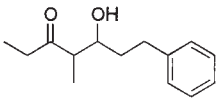
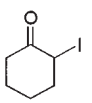
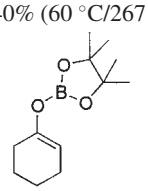
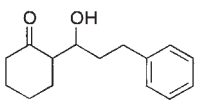
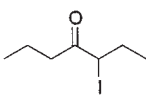
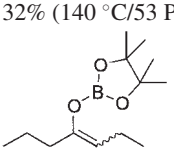
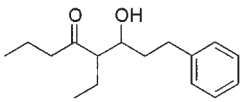


Scheme 1.

Table 1. Isolations of Boron Enolates following Aldol Reactions with Aldehyde (**4a**)



Iodo ketone	Isolated yield (bp)	Aldol adduct/yield/%
		
2a	**3a** 43% (106 °C/33 Pa)	**5** 72%
		
2b	**3b** 40% (60 °C/267 Pa)	**6** 58%
		
2c	**3c** 32% (140 °C/53 Pa)	**7** 61%
		
2d	**3d** 40% (130 °C/93 Pa)	**8** 38%

enolates were obtained in 32–43% yields by distillation (Scheme 1).[12] Next, these isolated boron enolates were allowed to react with 3-phenylpropionaldehyde, and the desired aldols were obtained in 38–72% yields (Table 1). The low-yields of the above boron enolates and aldol adducts were ascribed to the decomposition of labile boron enolates during isolating procedure or to reaction with aldehydes.

Aldol Reaction of Aldehydes with Boron Enolates In Situ Formed from Several α-Iodo Ketones and Catecholatoborane. Boron enolates were generated in situ by treating α-iodo ketones with catecholatoborane. The corresponding aldols were obtained by successive addition of aldehydes in one pot manner: that is, the generation of enol borate derived from 2-iodo-1-phenylethan-1-one was tried in the coexistence of K_2CO_3 using catecholatoborane as a reducing reagent at −78 °C in CH_2Cl_2. The subsequent treatment with benzaldehyde afforded the corresponding aldol in 95% yield, as shown in Table 2, entry 1. When 2-iodo-1-phenylpropan-1-one was used as an enolate precursor, the desired aldol adduct was obtained in 92% yield with relatively low diastereoselectivities (entry 2). In cases of using 2-iodopentan-3-one and 2-iodo-1,2-diphenylethan-1-one in the present reaction, the corresponding aldols were obtained in 95% and 81% yields, respectively although the diastereoselectivities of the produced aldols were not yet improved (entries 3 and 4).

Aldol Reaction of Aldehydes with Boron Enolates In Situ Formed from α-Iodo Ketones and 9-BBN. Our laboratory reported that a certain kind of vinyloxy borane was formed by 1,4-addition of *n*-dibutyltiophenyllborane to vinyl methyl ketone; the corresponding aldol was obtained by the subsequent reaction with benzaldehyde in a highly diastereoselective manner.[6b] Further, a highly diasteleoselective aldol reaction was achieved by treating several aldehydes with *Z*-boron enolates which were derived from α,β-unsaturated ketones and catecholatoborane.[13] These meant that the present procedure has not generated the boron enolates stereoselectively (Fig. 1). Then, it was assumed that the aldol reaction would diastereoselectively proceed when Lewis

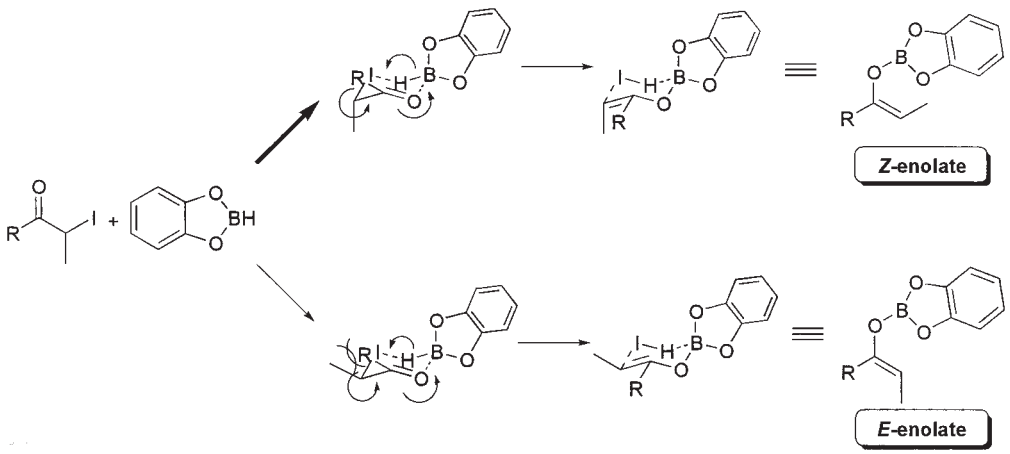
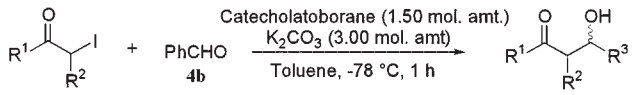
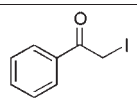
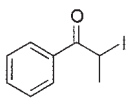
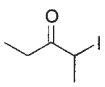
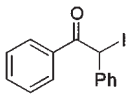


Fig. 1.

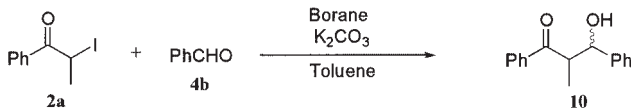
Table 2. Aldol Reaction Using Catecholatoborane

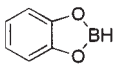
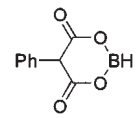
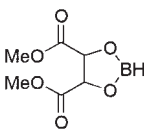


Entry	α-Iodo ketone	Aldol adduct/yield/%	*syn*/*anti*[a)]
1	 **2e**	**9** 95	—
2	 **2a**	**10** 92	55/45
3	 **2b**	**11** 95	50/50
4	 **2f**	**12** 81	72/28

a) Determined by ^{1}H NMR.

Table 3. Aldol Reactions Using Several Boranes



Entry	Borane (mol. amt.)	Temp./°C	Yield/%	*syn*/*anti*[b)]
1	 (1.5)	−78	92	53/47
2	 (1.5)	−78	N.D.	—
3	 (1.5)	−78–−23	21	50/50
4	 (1.5)	−78–−23	41	46/54
5	Et_2BH (2.1)	−78	77	>99/<1
6	$EtBH_2$ (2.1)	−78	79	95/5
7	9-BBN[a)] (3.0)	0	48	95/5

a) 9-Borabicyclo[3.3.1]nonane. b) Determined by ^{1}H NMR.

acidity and/or bulkiness of the substituents of boron increased.

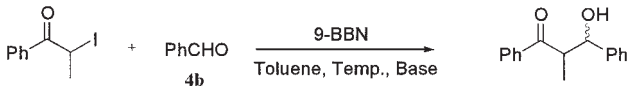
Several boron hydrides were examined by taking generation and aldol reaction of boron enolate from 2-iodo-1-phenylpropan-1-one as models (Table 3). When pinacolatoborane was used, the desired aldol adduct was not obtained at all because the reduction of coexisting carbonyl acceptor, benzaldehyde, took place in preference to that of 2-iodo-1-phenylpropan-1-one (entry 2). In the cases when boron hydride derived from 2-phenylmalonic acid was used, the desired aldol was obtained only in 21% yield with no diastereoselection (entry 3). On the other hand, the diastereoselectivity was greatly improved by using alkylboranes such as monoethylborane or diethylborane as a reducing reagent (entries 5 and 6).

These alkylboranes are known to exist in equilibrium with each other and it is difficult to show which one is the key reductant for the generation of enol borate. The desired aldol, on the other hand, was obtained in a moderate yield with high diastereoselectivity when the above reaction was carried out by using 9-BBN as a single-structured reducing reagent (entry 7). These results indicated that the most suitable reagent for reducing α-iodo ketone was a bulky alkyl group-substituted boron hydride such as 9-BBN.

In order to find appropriate reaction conditions, bases, solvents and reaction temperature were carefully investigated. Concerning bases, the aldol reaction of 2-iodo-1-phenylpropan-1-one with benzaldehyde using 9-BBN in toluene proceeded smoothly in the presence of several bases (Table 4). In cases of using solid bases such as K_2CO_3 and KF, the yields of the reactions were moderate and a considerable amount of propiophenone was formed as a by-product (entries 1 and 2). It was considered that propiophenone was given either by direct reduction of α-iodo ketone with boron hydride or by decomposition of initially formed boron enolate with HI formed at the same time.

When organic bases such as triethylamine or ethyldiisopropylamine were used (entries 3 and 4), yields of the desired aldols

Table 4. Aldol Reaction Using Various Bases under Several Temperature

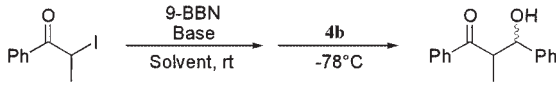


2a 10

Entry	Base (mol. amt.)	Temp./°C	Time/h	Yield/%	*syn*/*anti*[a)]
1	K_2CO_3 (3.0) + MS4A	rt[b)]	20	62	93/7
2	KF (3.0) + MS4A	rt	20	43	69/31
3	Et_3N (1.1)	rt	20	37	95/5
4	$^iPr_2NEt$ (1.1)	rt	20	38	95/5
5	DBU (1.1)	rt	3	59	85/15
6	2,6-Lutidine (1.1)	rt	20	85	90/10
7	Pyridine (1.1)	rt	3	98	90/10
8	None	rt	1	11	46/54
9	Pyridine (1.1)	−10	30	92	99/1
10	Pyridine (1.1)	−23	60	39	92/8

a) Determined by ^1H NMR and HPLC. b) Room Temperature.

Table 5. Aldol Reactions Using Several Bases or Several Solvents



2a 10

Entry	Base (mol. amt.)	Solvent	Yield/%	*syn*/*anti*[a)]
1	Pyridine (1.5)	Toluene	18 (68)[b)]	99/1
2	Pyridine (3.0)	Toluene	10 (78)[b)]	99/1
3	2,6-Lutidine (1.5)	Toluene	52	99/1
4	2,6-Lutidine (1.5)	CH_2Cl_2	trace	99/1
5	2,6-Lutidine (1.5)	Et_2O	trace	—
6	2,6-Lutidine (1.5)	EtCN	NR[c)]	—
7	2,6-Lutidine (1.5)	THF	91	99/1

a) Determined by HPLC. b) Numbers in parentheses are yields of propiophenone. c) No Reaction.

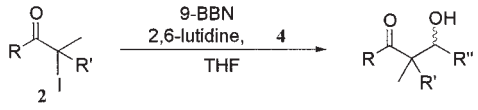
extremely decreased even after prolonged reaction times. The reaction smoothly proceeded, however, to afford β-hydroxy ketones in higher yields with good *syn*-selectivities (entries 6 and 7) when aromatic amines such as pyridine or 2,6-lutidine were used. The yield of the reaction was relatively low in the absence of base and little diastereoselectivity was observed (entry 8).

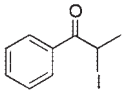
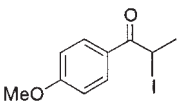
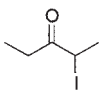
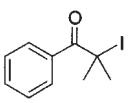
The reaction proceeded slowly as the temperature lowered, and the yield of the product markedly decreased at −23 °C (Table 4, entry 10). The reaction rate of α-iodo ketone reduction with 9-BBN somewhat decreased at temperatures below −10 °C, while the aldol products were obtained with high diastereoselectivity at the same temperature. Based on these results, the following procedure was employed thereafter: generation of boron enolate was carried out at room temperature, and aldehyde was subsequently added at −78 °C. Investigations on the effect of bases under the above conditions where enolates were generated in advance showed that the aldol reaction took place and gave the adduct in 18% yield in the presence of 1.5 molar amounts of pyridine. This accompanied the formation of propiophenone in 68% yield after purification procedure (Table 5, entry 1). Also, the yield of the desired aldol decreased down to 10% in the presence of 3.0 molar amounts of pyridine (entry 2) and propiophenone was obtained in 78% yield. Such low-yielding of the aldol adducts may be attributed to the coordination of pyridine to Lewis acidic boron enolate which prevented the formation of the key six-membered cyclic intermediates formed from boron enolate and aldehyde. The desired aldol reaction should proceed smoothly if amines having bulky substituents were used, as they could not coordinate to the boron enolate. Actually, the aldol was obtained in moderate yield (entry 3) when 2,6-lutidine was used.

Next, the effect of solvents was examined in order to find a suitable solvent for the formation of enol borate by reduction of α-iodo ketone. Of the solvents tested, THF was found to be most effective for the generation of the corresponding boron enolates using 9-BBN as a reductant, and the subsequent reaction with aldehyde afforded the desired aldol in 91% yield with high diastereoselectivity (entry 7).

The yields and ratios of two aldol isomers produced by using secondary α-iodo ketones and several aldehydes are summarized in Table 6. By adding aldehydes at −78 °C after the formation of boron enolates (method A), both aromatic and aliphatic α-iodo ketones reacted smoothly to give the corresponding aldol products in good yields with good *syn*-diastereoselectivities. Further, when aldehydes were added at −10 °C before the addition of 9-BBN (method B), aromatic α-iodo ketones reacted with aldehydes to give aldols also in good yields with good diastereoselectivity (entries 2, 4, 6, 8 and 10), while diastereoselectivity of the aldol products of aliphatic α-iodo ketones decreased (entries 17, 19, 21 and 23). This was probably because the reaction temperatures

Table 6. Aldol Reaction Using Several α-Iodo Ketones with Several Aldehydes



Entry	α-Iodo ketone	Aldehyde		Reaction type[a]	Aldol adduct	Yield/%	*syn*/*anti*[b]
1		PhCHO	**4b**	A	**10**	95	99/1[c]
2				B		99	97/3
3		Ph–CHO	**4a**	A	**5**	97	98/2[c]
4				B		98	98/2
5		^{i}PrCHO	**4c**	A	**13**	94	98/2[c]
6				B		96	98/2
7			**4d**	A	**14**	95	97/3[c]
8				B		81	92/8
9		Ph–CH=CH–CHO	**4e**	A	**15**	96	99/1[c]
10				B		89	97/3
11			**4b**	A	**16**	93	>99/<1
12			**4a**	A	**17**	98	>99/<1
13			**4c**	A	**18**	90	>99/<1
14			**4d**	A	**19**	99	>99/<1
15			**4e**	A	**20**	94	>99/<1
16			**4b**	A	**11**	82	95/5[c]
17				B		88	93/7
18			**4a**	A	**6**	81	99/1[c]
19				B		85	83/17
20			**4d**	A	**21**	90	88/12
21				B		71	85/15
22			**4e**	A	**22**	94	94/6[c]
23				B		48[d]	72/28
24			**4b**	B[e]	**23**	96	—
25			**4a**	B[e]	**24**	99	—
26			**4c**	B[e]	**25**	96	—
27			**4d**	B[e]	**26**	82	—
28			**4e**	B[e]	**27**	77	—

a) Type A: Boron enolate were previously generated at room temperature, then aldehydes were added at -78 °C. Type B: Boron hydride was added to the mixture of α-iodo ketone, amine and aldehyde at -10 °C. b) Determined by ^{1}H NMR. c) Determined by HPLC. d) 49% of cinnamyl alcohol was obtained. e) Reactions were performed at room temperature.

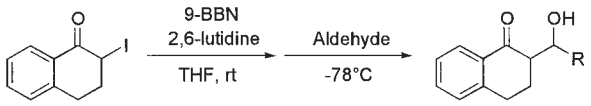
were too high to control diastereoselectivity of the aldol reaction of enol borate derived from aliphatic α-iodo ketones. Further, the desired products were obtained in good yields (entries 24–28) by treating 2-iodo-2-methyl-1-phenylpropan-1-one with several aldehydes at room temperature according to method B. On the other hand, the desired aldol adduct was obtained in 48% yield and cinnamyl alcohol was obtained in 49% yield as a by-product when cinnamaldehyde was used as a carbonyl acceptor under the above conditions (entry 23).

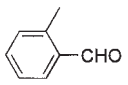
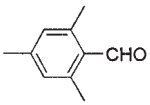
The boron enolate generated from 3,4-dihydro-2-iodo-1(2*H*)-naphthalenone and 9-BBN in THF at room temperature reacted with several aldehydes at -78 °C to give *anti*-aldol adducts (Table 7) as major products because *E*-enolates were formed from cyclic ketones.[14] On the other hand, it was found that *anti*-diastereoselectivity of the products decreased when bulky aldehyde was used (entry 1 vs 8) since the bulky substituent of aldehydes prevented the formation of the characteristic rigid six-membered transition state with the enol borate.

In the cases of using primary α-iodo ketones, the generated boron enolates were very labile to be converted to the ketones, reduced forms, probably because the enolates were decomposed by HI that formed synchronously. Then, 9-BBN was added to a mixture of primary α-iodo ketone, 2,6-lutidine, and aldehyde on the assumption that the formed boron enolates would react immediately with the coexisting aldehyde. As shown in Table 8, aldol reaction of primary α-iodo ketones with aldehydes gave the corresponding aldol adducts in good yields, however, the dehydration of the formed aldols sometimes took place to afford α,β-unsaturated ketones as by-products (entries 5, 6 and 10).

A proposed reaction pathway is shown in Fig. 2: α-Iodo ketone was reduced with 9-BBN in the coexistence of 2,6-lutidine and thus formed boron enolates reacted with aldehydes via the six-membered cyclic transition state to form the desired aldols stereoselectively.

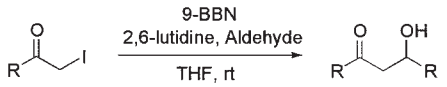
Table 7. Aldol Reaction of 3,4-Dihydro-2-iodo-1(2*H*)-naphthalenone with Various Aldehydes

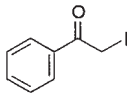
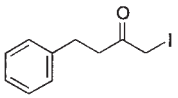


Entry	Aldehyde	Aldol adduct	yield/%	*syn*/*anti*[a)]
1	**4b**	**28**	99	16/84
2[b)]	**4b**		87	34/66
3	**4a**	**29**	98	23/77
4	**4c**	**30**	82	10/90
5	**4d**	**31**	98	20/80
6	**4e**	**32**	82	19/81
7		**33**	76	26/74
8		**34**	84	36/64

a) Determined by ^{1}H NMR. b) Aldehyde was added at room temperature.

Table 8. Aldol Reactions of Primary α-Iodo Ketones with Several Aldehydes



Entry	α-Iodo ketone	Aldehyde	Aldol adduct	Yield/%[a)]
1		**4b**	**9**	91
2		**4a**	**35**	91
3		**4c**	**36**	90
4		**4d**	**37**	82
5		**4e**	**38**	50 (21)
6		**4b**	**39**	71 (12)
7		**4a**	**40**	84
8		**4c**	**41**	88
9		**4d**	**42**	86
10		**4e**	**43**	61 (13)

a) Numbers in parentheses are yields of α,β-unsaturated ketones formed by dehydration of aldol adducts.

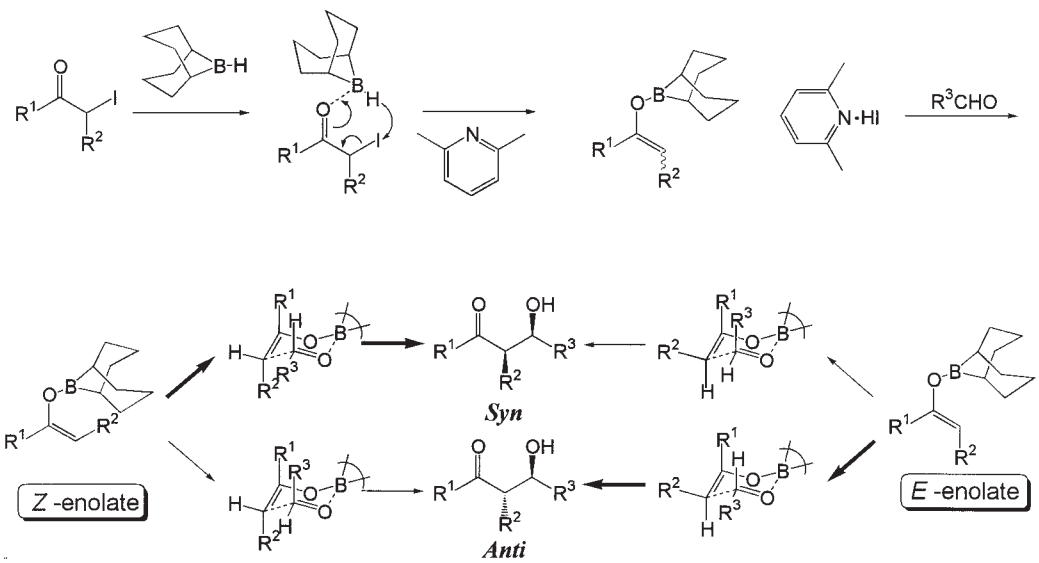


Fig. 2.

Conclusion

In summary, a new method for the generation of boron enolates was established by simple and straightforward 9-BBN reduction of α-iodo ketones in the coexistence of 2,6-lutidine. Thus generated boron enolates reacted smoothly with various aldehydes to afford β-hydroxy ketones in good to high yields with good to high diastereoselectivities.

Experimental

General. All melting points were determined on a Yanagimoto micro melting point apparatus (Yanaco MP-S3) and are uncorrected. Infrared (IR) spectra were recorded on a Horiba FT300 FT-IR spectrometer. ^{1}H NMR spectra were recorded on a JEOL 270 (270 MHz) or a JEOL JNM-LA300 (300 MHz) spectrometer; chemical shifts (δ) are reported in parts per million relative to tetramethylsilane. Splitting patterns are designed as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. ^{13}C NMR spectra were recorded on a JEOL EX270 (68 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in parts per million relative to tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$; δ 77.0 ppm). High resolution mass spectra (HRMS) were recorded on a JEOL JMS-700T mass spectrometer. Analytical TLC was performed on Merk precoated TLC plates (silica gel 60 GF254, 0.25 mm). Silica gel column chromatography was carried out on Merck silica gel 60 (0.063–0.200 mm). Preparative thin-layer chromatography (PTLC) was carried out on silica gel Wacogel B-5F.

Solvents were freshly distilled when dry solvents were needed. Aldehydes and 2-iodo-1-phenylethan-1-one were purchased from Tokyo Kasei Kogyo, Kanto Chemical, Aldrich Chemical, or Merck, and were used after purification by distillation or recrystallization.

Other α-iodo ketones were prepared according to the literature procedures.[10,15–18]

General Procedure for Isolation of Boron Enolates (Table 1). To a solution of α-iodo ketone (14.1 mmol) and pyridine (21.2 mmol) in toluene (100 mL) was added pinacolatoborane (21.2 mmol) under argon atmosphere at room temperature, and the reaction mixture was stirred for 1 h. The precipitate was removed by filtration under argon atmosphere and the filtrate was concentrated in vacuo. The crude product was purified by distillation under reduced pressure to afford the corresponding pinacol boron enolate.

4,4,5,5-Tetramethyl-2-(1-phenylprop-1-enyloxy)[1,3,2]dioxaborolane (3a): Isolated as a colorless oil: bp 106 °C/33 Pa; ^{1}H NMR (270 MHz, C_6D_6) δ 0.91 (s, 12H), 1.71 (d, J = 6.9 Hz, 3H), 5.40 (q, J = 6.9 Hz, 1H), 7.10 (m, 3H), 7.50 (d, J = 8.1 Hz, 1H); ^{13}C NMR (68 MHz, C_6D_6) δ 11.4, 24.5, 83.1, 106.5, 124.7, 127.7, 128.5, 137.5, 149.1.

2-(1-Ethylprop-1-enyloxy)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (3b): Isolated as a colorless oil: bp 60 °C/267 Pa; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.93–1.06 (m, 5H), 1.21 (s, 12H), 1.45 (d, J = 6.7 Hz, 3H), 4.64 (q, J = 6.7 Hz, 1H); ^{13}C NMR (68 MHz, C_6D_6) δ 10.7, 11.7, 24.74 (×4), 28.6, 82.7, 82.8, 103.1, 152.2.

2-(Cyclohex-1-enyloxy)-4,4,5,5-tetramethyl[1,3,2]dioxaborolane (3c): Isolated as a colorless oil: bp 140 °C/53 Pa; ^{1}H NMR (270 MHz, C_6D_6) δ 1.05 (s, 12H), 1.34–1.56 (m, 6H), 2.21–2.26 (m, 2H), 5.46–5.49 (m, 1H); ^{13}C NMR (68 MHz, C_6D_6) δ 22.5, 23.3, 24.0, 24.76, 24.79, 26.0, 27.1, 28.8, 41.9, 82.7, 83.0, 107.0, 149.6.

4,4,5,5-Tetramethyl-2-(1-propylbut-1-enyloxy)[1,3,2]dioxaborolane (3d): Isolated as a colorless oil: bp 130 °C/93 Pa; ^{1}H NMR (270 MHz, C_6D_6) δ 0.81 (t, J = 7.4 Hz, 3H), 0.93 (t, J = 7.4 Hz, 3H), 1.09 (s, 12H), 1.46–1.64 (m, 2H), 1.86–1.99 (m, 2H), 2.23 (t, J = 7.4 Hz, 2H), 4.67 (t, J = 7.1 Hz, 1H); ^{13}C NMR (68 MHz, C_6D_6) δ 14.2, 14.6, 17.6, 18.0, 24.70, 24.72, 24.8 (×2), 44.6, 82.8, 83.0, 112.3, 149.2.

Aldol Reaction between Isolated Pinacolatoboron Enolates and Aldehydes. The isolated pinacolatoboron enolate (0.25 mmol) was dissolved in toluene (3 mL), and this solution was added to a solution of an aldehyde (0.28 mmol) in toluene (3 mL). After the reaction mixture was stirred for 3 h at room temperature, the reaction was quenched by adding phosphate buffer (pH 7). The mixture was extracted with ether (3 mL × 3), and the combined organic layer was concentrated in vacuo. The residue was dissolved in methanol (3 mL), and the solution was treated with 30% hydrogen peroxide (2 mL) at 0 °C. The mixture was extracted with ether (3 mL × 3), and the combined organic layer was washed with saturated sodium hydrogencarbonate (3 mL) and brine, dried over Na_2SO_4, and concentrated in vacuo. The crude product was purified by preparative TLC to afford the corresponding β-hydroxy ketone.

3-Hydroxy-2-methyl-1,5-diphenylpentan-1-one (5):[11] Isolated as a mixture of diastereomers (*syn*/*anti* = 98/2): IR (neat, cm^{-1}) 3448, 1666; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.27 (d, J = 7.3 Hz, 3H), 1.64–1.76 (m, 1H), 1.89–2.03 (m, 1H), 2.65–2.76 (m, 1H), 2.85–2.95 (m, 1H), 3.26 (s, 0.98H), 3.44 (dq, J = 7.3, 2.6 Hz, 0.98H), 3.52–3.57 (m, 0.02H), 3.82–3.92 (m, 0.02H), 4.06–4.10 (m, 0.98H), 7.15–7.31 (m, 5H), 7.44–7.49 (m, 2H), 7.55–7.61 (m, 1H), 7.89–7.95 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.2, 32.4, 36.1, 44.6, 70.5, 125.8, 128.25 (×2), 128.29 (×2), 128.34 (×2), 128.4, 128.7, 133.4, 135.5, 141.8, 205.7.

5-Hydroxy-4-methyl-7-phenylheptan-3-one (6):[20] Isolated as a mixture of diastereomers (*syn*/*anti* = 83/17): IR (neat, cm^{-1}) 3440, 3340, 1705; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.04 (t, J = 7.3 Hz, 3H), 1.13 (d, J = 7.0 Hz, 0.51H), 1.15 (d, J = 7.3 Hz, 2.49H), 1.52–1.65 (m, 1H), 1.77–1.89 (m, 1H), 2.39–2.75 (m, 4H), 2.77–2.85 (m, 1H), 2.88 (d, J = 2.7 Hz, 1H), 3.95 (m, 1H), 7.19–7.29 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 7.67, 10.2, 32.4, 35.1, 35.8, 49.8, 70.2, 125.8, 128.3 (×2), 128.4 (×2), 141.7, 216.5.

2-(1-Hydroxy-3-phenylpropyl)cyclohexanone (7):[19] *Syn*-isomer: IR (neat, cm^{-1}) 3574, 1698; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.76–1.54 (m, 4H), 1.81–2.09 (m, 4H), 2.27–2.41 (m, 3H), 2.60–2.70 (m, 1H), 2.76 (d, J = 3.3 Hz, 1H), 2.84–2.90 (m, 1H), 4.09–4.13 (m, 1H), 7.16–7.25 (m, 3H), 7.27–7.29 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 24.9, 26.5, 27.6, 32.3, 34.8, 42.6, 55.1, 68.4, 125.7, 128.3 (×2), 128.4 (×2), 142.1, 214.9.

5-Ethyl-6-hydroxy-8-phenyloctan-4-one (8): *Syn*-isomer: IR (neat, cm^{-1}) 3687, 3602, 1697; ^{1}H NMR (270 MHz, $CDCl_3$) δ 0.85–0.92 (m, 6H), 1.50–1.85 (m, 6H), 2.37–2.68 (m, 5H), 2.78–2.89 (m, 1H), 3.77 (t, J = 3.7 Hz, 1H), 7.17–7.29 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 12.5, 13.7, 16.6, 19.8, 32.4, 36.3, 46.5, 58.2, 60.4, 70.8, 125.8, 128.3 (×2), 128.3 (×2), 141.6, 215.5; HRMS (FAB) Calcd for $C_{16}H_{25}O_2$: (M^+ + H) 249.1855. Found: m/z 249.1851.

Typical Procedure of Aldol Reaction between α-Iodo Ketones and Aldehydes Using 9-BBN (Method A). To a solution of 2-iodo-1-phenylpropan-1-one (0.25 mmol) and 2,6-lutidine (0.38 mmol) in THF (3 mL) was added 9-BBN (0.5 M in THF, 0.38 mmol) under argon atmosphere at room temperature. After the mixture was stirred for 2 h, the reaction mixture was cooled down to −78 °C, and benzaldehyde (0.28 mmol) was added dropwise. The same work up as described above gave 3-hydroxy-2-methyl-1,3-diphenylpropan-1-one (**10**)[20] (95%, *syn*/*anti* = 97/3) as a colorless oil: IR (neat, cm^{-1}) 3467, 1678; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.20 (d, J = 7.3 Hz, 3H), 3.69 (s, 1H), 3.70 (dq, J = 7.3, 3.1 Hz, 1H), 4.98 (m, 0.03H), 5.24 (d, J = 2.3 Hz, 0.97H), 7.61–7.22 (m, 8H), 7.93 (d, J = 8.6 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.2, 47.0, 73.0, 125.9 (×2), 127.2, 128.1 (×2), 128.3 (×2), 128.7 (×2), 133.5, 135.4, 141.6, 205.5.

Typical Procedure of Aldol Reaction between α-Iodo Ketones and Aldehydes Using 9-BBN (Method B). To a solution of 2-iodo-1-phenylpropan-1-one (0.25 mmol), 2,6-lutidine (0.38 mmol) and benzaldehyde (0.28 mmol) in THF (3 mL) was added 9-BBN (0.5 M in THF, 0.38 mmol) under argon atmosphere at −10 °C. After the mixture was stirred for 2 h, the same work up as described above gave 3-hydroxy-2-methyl-1,3-diphenylpropan-1-one (**10**) (95%).

3-Hydroxy-1,3-diphenylpropan-1-one (9):[20] IR (neat, cm^{-1}) 3509, 1681; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.33 (d, J = 4.5 Hz, 1H), 3.34 (d, J = 7.9 Hz, 1H), 3.70 (d, J = 3.0 Hz, 1H), 5.34–5.29 (m, 1H), 7.58–7.22 (m, 8H), 7.91 (d, J = 7.0 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 47.3, 69.9, 125.6 (×2), 128.5, 128.0 (×2), 128.4 (×2), 128.5 (×2), 133.4, 136.3, 142.8, 199.8.

1-Hydroxy-2-methyl-1-phenylpentan-3-one (11):[20] Isolated as a mixture of diasteromers (*syn*/*anti* = 93/7): IR (neat, cm^{-1}) 3462, 1707; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.00 (t, J = 7.3 Hz, 3H), 1.08 (d, J = 7.3 Hz, 3H), 2.29 (q, J = 7.3 Hz, 0.07H), 2.37 (q, J = 7.3 Hz, 0.93H), 2.55 (q, J = 7.3 Hz, 0.07H), 2.84 (dq, J = 7.3, 4.1 Hz, 1H), 3.17 (d, J = 2.5 Hz, 1H), 4.75 (dd, J = 8.2, 4.3 Hz, 0.07H), 5.05 (dd, J = 3.8, 2.1 Hz, 0.93H), 7.22–7.36 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 7.6, 10.7, 35.5, 52.2, 73.3, 125.8 (×2), 127.2, 128.1, 128.4, 141.6, 216.1.

3-Hydroxy-1,2,3-triphenylpropan-1-one (12):[21] Isolated as a mixture of diasteromers (*syn*/*anti* = 72/28): IR (neat, cm^{-1}) 3448, 3301, 1673; ^{1}H NMR (270 MHz, $CDCl_3$) δ 3.31 (d, J = 3.7 Hz, 0.28H), 3.38 (d, J = 2.1 Hz, 0.72H), 4.57 (d, J = 6.1 Hz, 0.28H), 4.81 (d, J = 5.5 Hz, 0.72H), 5.54 (dd, J = 5.5, 2.1 Hz, 0.72H), 5.96 (d, J = 6.1 Hz, 0.28H), 7.13–7.49 (m, 13H), 7.82–8.01 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 60.8, 74.6, 126.2, 126.5, 127.36, 127.43, 127. 5, 127.8, 127.9, 128.0, 128.4, 128.5, 128.6, 129.6, 130.5, 133.2, 134.0, 136.0, 141.1, 142.5, 200.3.

3-Hydroxy-2,4-dimethyl-1-phenylpentan-1-one (13):[20] *Syn*-isomer: IR (neat, cm^{-1}) 3448, 3340, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 0.96 (t, $J = 6.6$ Hz, 3H), 1.03 (d, $J = 6.6$ Hz, 3H), 1.25 (d, $J = 6.8$ Hz, 3H), 1.72–1.82 (m, 1H), 3.96–4.04 (m, 1H), 7.26–7.62 (m, 3H), 7.95–7.99 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.3, 18.0, 18.6, 33.1, 42.0, 72.4, 128.0 (×2), 128.5 (×2), 133.4, 136.7, 201.1.

3-Cyclohexyl-3-hydroxy-2-methyl-1-phenylpropan-1-one (14):[20] Isolated as a mixture of diastereomers (*syn*/*anti* = 97/3): IR (neat, cm^{-1}) 3442, 1704; ^1H NMR (270 MHz, $CDCl_3$) δ 1.23 (d, $J = 7.1$ Hz, 3H), 0.90–1.37 (m, 5H), 1.42–1.54 (m, 1H), 1.66–1.80 (m, 4H), 2.05 (d, $J = 13.0$ Hz, 1H), 3.03 (s, 0.03H), 3.13 (d, $J = 2.3$ Hz, 0.97H), 3.55–3.58 (m, 0.06H), 3.64–3.72 (m, 1.94H), 7.26–7.62 (m, 3H), 7.92–7.93 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.6, 25.9, 26.2, 26.4, 29.2, 29.5, 40.2, 41.3, 75.4, 128.2, 128.3, 128.6 (×2), 133.3, 135.7, 205.7.

3-Hydroxy-2-methyl-1,5-diphenylpent-4-en-1-one (15):[20] Isolated as a mixture of diastereomers (*syn*/*anti* = 97/3): IR (neat, cm^{-1}) 3509, 1667; ^1H NMR (270 MHz, $CDCl_3$) δ 1.31 (d, $J = 2.0$ Hz, 3H), 3.48 (q, $J = 8.4$ Hz, 0.03H), 3.64 (dq, $J = 7.1$, 3.3 Hz, 0.97H), 4.78–4.81 (m, 0.97H), 4.57–4.61 (m, 0.03H), 6.24 (dd, $J = 16.0$, 5.6 Hz, 1H), 6.71 (dd, $J = 16.0$, 1.2 Hz, 0.97H), 6.82 (d, $J = 15.8$ Hz, 0.03H), 7.20–7.62 (m, 8H), 7.95–7.98 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.9, 45.4, 72.2, 126.34 (×2), 127.5, 128.39 (×2), 128.42 (×2), 128.7 (×2), 130.0, 130.9, 133.5, 135.6, 136.5, 205.1.

3-Hydroxy-1-(4-methoxyphenyl)-2-methyl-3-phenylpropan-1-one (16): *Syn*-isomer: IR (neat, cm^{-1}) 3656, 3463, 1658, 1596; ^1H NMR (270 MHz, $CDCl_3$) δ 1.07 (d, $J = 7.3$ Hz, 3H), 2.44 (s, 1H), 3.54 (td, $J = 7.3$, 3.1 Hz, 1H), 3.77 (s, 3H), 5.11 (d, $J = 3.3$ Hz, 1H), 6.83 (d, $J = 8.9$ Hz, 2H), 7.12–7.14 (m, 5H), 7.81 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.3, 46.5, 55.5, 73.1, 113.8 (×2), 113.9, 125.9 (×2), 127.1, 128.0 (×2), 130.7 (×2), 141.7, 163.7, 204.1; HRMS (FAB) Calcd for $C_{17}H_{19}O_3$: (M^+) 271.1334. Found: m/z 271.1324.

3-Hydroxy-1-(4-methoxyphenyl)-2-methyl-5-phenylpentan-1-one (17): *Syn*-isomer: IR (neat, cm^{-1}) 3471, 3401, 1658, 1596; ^1H NMR (270 MHz, $CDCl_3$) δ 1.27 (d, $J = 7.1$ Hz, 3H), 1.66–1.99 (m, 2H), 2.59–2.76 (m, 1H), 2.86–2.94 (qd, $J = 7.1$, 2.7 Hz, 1H), 3.50 (br, 1H), 3.88 (s, 3H), 4.06 (dt, $J = 8.7$, 3.3 Hz, 1H), 6.94 (d, $J = 8.9$ Hz, 2H), 7.16–7.32 (m, 5H), 7.90 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.4, 32.4, 36.1, 44.1, 55.5, 70.6, 113.8 (×2), 125.7, 128.2 (×2), 128.3 (×2), 128.4, 130.7 (×2), 141.8, 163.6, 204.3; HRMS (FAB) Calcd for $C_{19}H_{23}O_3$: (M^+) 299.1647. Found: m/z 299.1631.

3-Hydroxy-1-(4-methoxyphenyl)-2,4-dimethylpentan-1-one (18):[22] *Syn*-isomer: IR (neat, cm^{-1}) 3563, 3424, 1658, 1596; ^1H NMR (270 MHz, $CDCl_3$) δ 0.91 (d, $J = 6.7$ Hz, 3H), 0.99 (d, $J = 6.7$ Hz, 3H), 1.20 (d, $J = 6.9$ Hz, 3H), 1.65–1.81 (m, 1H), 3.35 (s, 1H), 3.56–3.64 (m, 2H), 3.85 (s, 3H), 6.92 (d, $J = 8.9$ Hz, 2H), 7.90 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 11.0, 19.1, 19.2, 30.7, 41.2, 55.5, 76.7, 113.8 (×2), 128.6, 130.6 (×2), 163.6, 204.3.

3-Cyclohexyl-3-hydroxy-1-(4-methoxyphenyl)-2-methylpropan-1-one (19): *Syn*-isomer: IR (neat, cm^{-1}) 3833, 3401, 1658, 1596; ^1H NMR (270 MHz, $CDCl_3$) δ 0.87–1.13 (m, 2H), 1.03–1.25 (m, 4H), 1.19 (d, $J = 7.0$ Hz, 3H), 1.62–1.75 (m, 4H), 3.32 (s, 1H), 3.57–3.64 (m, 2H), 3.85 (s, 1H), 6.92 (d, $J = 8.9$ Hz, 2H), 7.89 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 10.8, 25.9, 26.1, 26.4, 29.1, 29.5, 40.1, 40.6, 55.5, 75.5, 113.8, 128.6, 130.6, 163.6, 204.4; HRMS (FAB) Calcd for $C_{19}H_{25}O_3$: (M^+) 277.1804. Found: m/z 277.1807.

3-Hydroxy-1-(4-methoxyphenyl)-2-methyl-5-phenylpent-4-en-1-one (20): *Syn*-isomer: IR (neat, cm^{-1}) 3864, 3440, 1666, 1604; ^1H NMR (270 MHz, $CDCl_3$) δ 1.23 (d, $J = 7.2$ Hz, 3H), 2.44 (s, 1H), 3.52 (td, $J = 7.2$, 3.3 Hz, 1H), 3.81 (s, 3H), 4.71 (ddd, $J = 5.3$, 3.5, 1.7 Hz, 1H), 6.18 (dd, $J = 16.0$, 5.6 Hz, 1H), 6.65 (dd, $J = 16.0$, 1.3 Hz, 1H), 6.89 (d, $J = 8.9$ Hz, 2H), 7.12–7.33 (m, 5H), 7.89 (d, $J = 8.9$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 12.0, 44.9, 55.5, 72.2, 113.8 (×2), 120.2, 126.3 (×2), 127.4, 128.3 (×2), 128.5, 129.2, 130.6, 130.7 (×2), 136.6, 203.6; HRMS (FAB) Calcd for $C_{19}H_{21}O_3$: (M^+) 297.1491. Found: m/z 297.1493.

1-Cyclohexyl-1-hydroxy-2-methylpentan-3-one (21):[20] Isolated as a mixture of diastereomers (*syn*/*anti* = 85/15): IR (neat, cm^{-1}) 3409, 3255, 1704; ^1H NMR (270 MHz, $CDCl_3$) δ 0.99 (t, $J = 7.3$ Hz, 3H), 1.15 (d, $J = 7.1$ Hz, 3H), 0.79–1.22 (m, 5H), 1.23–1.98 (m, 5H), 2.00 (br, $J = 13.2$ Hz, 1H), 2.46 (m, 2H), 2.67 (dq, $J = 7.1$, 3.0 Hz, 1H), 2.74 (d, $J = 3.0$ Hz, 1H), 3.35 (m, 0.15H), 3.52 (dt, $J = 8.6$, 3.0 Hz, 0.85H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 7.58, 9.46, 26.1, 26.4, 29.0, 29.5, 34.8, 40.0, 46.6 (×2), 75.0, 216.7.

5-Hydroxy-4-methyl-7-phenylhept-6-en-3-one (22):[20] Isolated as a mixture of diastereomers (*syn*/*anti* = 72/28): IR (neat, cm^{-1}) 3440, 3370, 1697; ^1H NMR (270 MHz, $CDCl_3$) δ 1.06 (t, $J = 7.3$ Hz, 2.16H), 1.62 (d, $J = 7.3$ Hz, 0.84H), 1.18 (d, $J = 8.6$ Hz, 2.16H), 1.26 (t, $J = 7.1$ Hz, 0.84H), 2.43–2.64 (m, 2H), 2.73–2.82 (m, 1H), 2.96 (s, 0.72H), 4.37 (br, 0.28H), 4.61 (br, 0.72H), 6.16 (dd, $J = 5.9$, 16.0 Hz, 0.72H), 6.17 (dd, $J = 16.0$, 7.3 Hz, 0.28H), 6.61 (dd, $J = 16.0$ Hz, 0.28H), 6.63 (dd, $J = 16.0$, 1.2 Hz, 0.72H), 7.21–7.39 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 7.6, 11.0, 35.5, 50.5, 72.4, 126.3, 126.4, 127.6, 128.4, 128.5, 128.9, 131.0, 136.5, 215.6.

3-Hydroxy-2,2-dimethyl-1,3-diphenylpropan-1-one (23):[15] IR (neat, cm^{-1}) 3540, 3494, 3424, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 1.10 (s, 3H), 1.16 (s, 3H), 2.93 (d, $J = 3.4$ Hz, 1H), 5.03 (d, $J = 3.4$ Hz, 1H), 7.19–7.47 (m, 10H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.6, 24.2, 52.5, 78.8, 127.1 (×2), 127.68, 127.74, 127.93 (×2), 127.97, 130.5, 139.7, 140.2, 211.9.

3-Hydroxy-2,2-dimethyl-1,5-diphenylpentan-1-one (24):[21] IR (neat, cm^{-1}) 3579, 3401, 3355, 1666; ^1H NMR (270 MHz, $CDCl_3$) δ 1.30 (s, 6H), 1.71–1.75 (m, 1H), 2.37–2.41 (m, 1H), 2.58–2.85 (m, 1H), 2.96 (ddd, $J = 14.4$, 9.3, 5.8 Hz, 1H), 3.89 (t, $J = 6.5$ Hz, 1H), 7.14–7.49 (m, 8H), 7.58 (dd, $J = 8.3$, 1.3 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.2, 25.7, 33.0, 33.6, 41.9, 52.0, 125.7, 127.3, 128.0, 128.25, 128.35, 130.8, 138.8, 141.9, 210.8.

3-Hydroxy-2,2,4-trimethyl-1-phenylpentan-1-one (25):[10] IR (neat, cm^{-1}) 3471, 3363, 1666; ^1H NMR (270 MHz, $CDCl_3$) δ 0.89 (d, $J = 6.8$ Hz, 3H), 0.94 (d, $J = 6.8$ Hz), 1.32 (s, 3H), 1.39 (s, 3H), 1.62–1.93 (m, 1H), 2.91 (d, $J = 5.7$ Hz, 1H), 3.66–3.67 (m, 1H), 7.29–7.47 (m, 3H), 7.59 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 17.8, 22.4, 23.3, 24.3, 30.2, 51.5, 82.2, 127.5 (×2), 128.0 (×2), 130.7, 139.3, 211.8.

3-Cyclohexyl-3-hydroxy-2,2-dimethyl-1-phenylpropan-1-one (26): IR (neat, cm^{-1}) 3610, 3432, 3370, 1666; ^1H NMR (270 MHz, $CDCl_3$) δ 1.09–1.28 (m, 4H), 1.31 (s, 3H), 1.38 (s, 3H), 1.36–1.70 (m, 6H), 1.80–1.90 (m, 1H), 2.36–2.40 (m, 1H), 3.63 (d, $J = 3.8$ Hz, 1H), 7.37–7.45 (m, 3H), 7.59 (dd, $J = 8.3$, 1.7 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 23.4, 24.1, 24.7, 26.2, 26.7, 27.2, 28.4, 32.3, 40.5, 41.9, 82.2, 127.5 (×2), 127.9 (×2), 130.7, 139.3, 211.7; HRMS (FAB) Calcd for $C_{17}H_{25}O_2$: ($M^+ + H$) 261.1855. Found: m/z 261.1858.

3-Hydroxy-2,2-dimethyl-1,5-diphenylpent-4-en-1-one (27):[21] IR (neat, cm^{-1}) 3710, 3540, 3363, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 1.30 (s, 3H), 1.31 (s, 3H), 2.79 (br, 1H), 4.51 (d, $J = 7.0$ Hz, 1H), 6.20 (dd, $J = 15.8$, 7.0 Hz, 1H), 6.57 (d, $J = 15.8$ Hz, 1H), 7.16–7.40 (m, 9H), 7.56–7.60 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 20.7, 23.9, 52.0, 78.3, 126.4, 127.39, 127.44, 127.7, 128.0, 128.5, 129.0, 130.8,

132.9, 136.4, 210.6.

2-[Hydroxy(phenyl)methyl]-3,4-dihydronaphthalen-1(2*H*)-one (28):[15] Isolated as a mixture of diastereomers (*syn*/*anti* = 16/84): IR (neat, cm^{-1}) 3571, 3455, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 1.62–1.72 (m, 2H), 2.70–2.96 (m, 3H), 4.95 (d, J = 8.8 Hz, 0.84H), 5.68 (d, J = 2.8 Hz, 0.16H), 7.19–7.52 (m, 9H), 8.03–8.08 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.3, 28.9, 53.8, 76.5, 126.7, 127.1 (×2), 127.4, 127.9, 128.1 (×2), 128.6, 132.1, 133.9, 140.9, 144.3, 202.2.

2-(1-Hydroxy-3-phenylpropyl)-3,4-dihydronaphthalen-1-(2*H*)-one (29):[23] Isolated as a mixture of diastereomers (*syn*/*anti* = 23/77): IR (neat, cm^{-1}) 3448, 3355, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 1.75–2.17 (m, 4H), 2.48–2.56 (m, 1H), 2.66–2.77 (m, 1H), 2.80–3.00 (m, 2H), 3.96 (td, J = 8.2, 3.3 Hz, 0.77H), 4.25 (td, J = 6.3, 3.1 Hz, 0.23H), 7.16–7.31 (m, 7H), 7.46 (td, J = 7.4, 1.5 Hz, 1H), 7.98 (dd, J = 7.8, 1.0 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.7, 29.0, 31.5, 35.8, 52.8, 71.2, 125.6, 126.6, 127.2, 128.2 (×2), 128.4 (×2), 128.5, 132.2, 133.7, 142.1, 144.0, 202.1.

2-(1-Hydroxy-2-methylpropyl)-3,4-dihydronaphthalen-1-(2*H*)-one (30):[15] *Syn*-isomer: IR (neat, cm^{-1}) 3448, 3332, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 0.90 (d, J = 6.7 Hz, 3H), 1.09 (d, J = 6.7 Hz, 3H), 1.62–1.97 (m, 1H), 2.12–2.21 (m, 2H), 2.69 (td, J = 8.7, 1.6 Hz, 1H), 3.05 (t, J = 6.9 Hz, 2H), 4.07 (dd, J = 9.3, 2.3 Hz), 7.23–7.34 (m, 2H), 7.47 (td, J = 7.6, 1.6 Hz, 1H), 8.02 (dd, J = 7.9, 1.6 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.1, 19.8, 22.0, 29.1, 30.0, 50.7, 74.9, 126.5, 127.1, 128.5, 128.7, 132.8, 133.4, 133.7, 200.8. *Anti*-isomer: IR (neat, cm^{-1}) 3586, 3478, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 0.97 (d, J = 6.7 Hz, 3H), 1.07 (d, J = 6.7 Hz, 3H), 1.67–1.97 (m, 2H), 2.14–2.22 (m, 1H), 2.54–2.64 (m, 1H), 3.00–3.06 (m, 2H), 3.77 (dd, J = 7.9, 3.5 Hz, 1H), 7.23–7.34 (m, 2H), 7.49 (td, J = 7.4, 1.4 Hz, 1H), 8.02 (dd, J = 7.4, 1.4 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 14.9, 20.2, 25.8, 28.9, 29.6, 50.7 (×2), 126.4, 126.6, 127.3, 128.5, 128.6, 133.7, 202.8.

2-(Cyclohexylhydroxymethyl)-3,4-dihydronaphthalen-1-(2*H*)-one (31): *Syn*-isomer: IR (neat, cm^{-1}) 3486, 3455, 1666; ^1H NMR (270 MHz, $CDCl_3$) δ 0.92–1.75 (m, 10H), 2.09–2.18 (m, 3H), 2.62–2.70 (m, 1H), 3.02 (t, J = 5.9 Hz, 2H), 4.13 (dd, J = 9.2, 2.5 Hz, 1H), 7.21–7.31 (m, 2H), 7.45 (td, J = 7.4, 1.4 Hz, 1H), 7.99–8.02 (m, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 22.1, 25.9, 26.2, 26.5, 29.0, 30.1, 39.3, 50.3, 73.7, 126.5, 127.1, 128.7, 133.4 (×2), 144.0, 200.9; HRMS (FAB) Calcd for $C_{17}H_{23}O_2$: (M^+) 259.1698. Found: m/z 259.1690. *Anti*-isomer: IR (neat, cm^{-1}) 3579, 3486, 1658; ^1H NMR (270 MHz, $CDCl_3$) δ 1.20–1.94 (m, 12H), 2.12–2.18 (m, 1H), 2.60 (ddd, J = 12.2, 7.6, 4.6 Hz), 3.00 (dd, J = 9.9, 5.1 Hz, 2H), 3.72 (dd, J = 7.6, 3.3 Hz, 1H), 7.21–7.32 (m, 2H), 7.47 (td, J = 7.6, 1.4 Hz, 1H), 7.99 (dd, J = 7.6, 1.4 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 25.6, 25.9, 26.4, 26.5, 26.8, 29.0, 30.4, 39.8, 50.2, 75.8, 126.6, 127.3, 128.5 (×2), 133.7, 144.0, 200.9; HRMS (FAB) Calcd for $C_{17}H_{23}O_2$: (M^+) 259.1698. Found: m/z 259.1690.

2-(1-Hydroxycinnamyl)-3,4-dihydronaphthalen-1(2*H*)-one (32): *Syn*-isomer: IR (neat, cm^{-1}) 3818, 3509, 3332, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 2.04–2.20 (m, 2H), 2.82 (ddd, J = 13.1, 5.0, 3.3 Hz, 1H), 4.88–4.89 (m, 1H), 6.30 (dd, J = 15.8, 6.2 Hz, 1H), 6.67 (dd, J = 15.8, 1.2 Hz, 1H), 7.21–7.50 (m, 8H), 8.03 (dd, J = 7.8, 1.3 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 24.3, 29.2, 52.8, 72.5, 126.4, 126.6, 127.2, 127.5, 128.4, 128.7, 128.8, 131.5, 132.6, 133.7, 136.5, 144.2, 200.3; HRMS (FAB) Calcd for $C_{19}H_{18}O_2$: (M^+) 278.1307. Found: m/z 278.1311. *Anti*-isomer: IR (neat, cm^{-1}) 3571, 3471, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 1.77–1.93 (m, 1H), 2.17–2.27 (m, 1H), 2.66 (ddd, J = 13.2, 7.8, 4.5 Hz, 1H), 2.97–3.03 (m, 2H), 4.66 (td, J = 5.8, 3.0 Hz, 1H), 6.26 (dd, J = 16.0, 7.4 Hz, 1H), 6.66 (d, J = 16.0 Hz, 1H), 7.20–7.42 (m, 7H), 7.49 (td, J = 7.6, 1.5 Hz), 8.03 (dd, J = 7.9, 1.3 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.0, 28.9, 52.8, 73.8, 126.5, 126.7, 127.4, 127.7, 128.4, 128.6, 128.7, 132.2, 132.5, 133.9, 136.4, 144.2, 201.6; HRMS (FAB) Calcd for $C_{19}H_{18}O_2$: (M^+) 278.1307. Found: m/z 278.1311.

2-(Hydroxy-*o*-tolylmethyl)-3,4-dihydronaphthalen-1(2*H*)-one (33): *Syn*-isomer: IR (neat, cm^{-1}) 3602, 3548, 3478, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 1.59–1.91 (m, 2H), 2.30 (s, 3H), 2.65–2.98 (m, 3H), 5.98 (s, 1H), 7.04–7.35 (m, 5H), 7.44–7.57 (m, 2H), 8.07 (d, J = 7.7 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.1, 21.8, 29.1, 52.3, 67.8, 125.7, 126.4, 126.5, 126.7, 126.8, 126.9, 127.3, 132.7, 133.6, 134.0, 139.8, 144.3, 199.6; HRMS (FAB) Calcd for $C_{18}H_{19}O_2$: (M^+ + H) 267.1385. Found: m/z 267.1396. *Anti*-isomer: IR (neat, cm^{-1}) 3579, 3548, 3517, 1666; ^1H NMR (270 MHz, $CDCl_3$) δ 1.53–1.88 (m, 2H), 2.36 (s, 3H), 2.78–2.92 (m, 3H), 5.27 (d, J = 9.1 Hz, 1H), 7.13–7.36 (m, 5H), 7.47–7.54 (m, 2H), 8.07 (d, J = 7.8 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 19.9, 26.0, 29.2, 54.2, 71.2, 126.5, 126.7, 126.8, 127.4, 127.5, 128.6, 130.2, 132.2, 134.0, 144.3, 150.4, 165.6, 202.8; HRMS (FAB) Calcd for $C_{18}H_{19}O_2$: (M^+ + H) 267.1385. Found: m/z 267.1396.

2-[Hydroxy(mesityl)methyl]-3,4-dihydronaphthalen-1(2*H*)-one (34): *Syn*-isomer: IR (neat, cm^{-1}) 3440, 3363, 1673; ^1H NMR (270 MHz, $CDCl_3$) δ 2.14–2.19 (m, 2H), 2.24 (s, 3H), 2.37 (s, 6H), 2.81–3.08 (m, 3H), 5.98 (d, J = 3.1 Hz, 1H), 6.82 (s, 2H), 7.21–7.32 (m, 2H), 7.46 (td, J = 7.6, 1.5 Hz, 1H), 8.00 (dd, J = 7.6, 1.2 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 21.3 (×2), 23.8, 28.8, 53.6, 69.6, 126.5, 127.3 (×2), 128.7 (×2), 130.2 (×2), 133.4 (×2), 136.2, 136.3, 144.1, 199.2; HRMS (FAB) Calcd for $C_{20}H_{23}O_2$: (M^+ + H) 295.1698. Found: m/z 295.1692. *Anti*-isomer: IR (neat, cm^{-1}) 3586, 3455, 1666; ^1H NMR (270 MHz, $CDCl_3$) δ 1.59–1.72 (m, 2H), 2.24 (s, 3H), 2.42 (s, 6H), 2.85–2.94 (m, 2H), 3.17–3.28 (m, 1H), 4.64 (br, 1H), 5.50 (d, J = 9.4 Hz, 1H), 6.82 (s, 2H), 7.19 (t, J = 7.6 Hz, 1H), 7.33 (t, J = 7.6 Hz, 1H), 7.48 (td, J = 7.4, 1.5 Hz, 1H), 8.07 (dd, J = 8.0, 1.5 Hz, 1H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 20.8, 21.2, 26.0, 29.4, 51.6, 71.1, 126.7 (×2), 127.3 (×2), 128.6 (×2), 132.2, 132.8, 133.8 (×2), 136.8, 144.3, 203.2; HRMS (FAB) Calcd for $C_{20}H_{23}O_2$: (M^+ + H) 295.1698. Found: m/z 295.1702.

3-Hydroxy-1,5-diphenylpentan-1-one (35):[24] IR (neat, cm^{-1}) 3602, 3525, 1681; ^1H NMR (270 MHz, $CDCl_3$) δ 1.74–2.01 (m, 2H), 2.69–2.95 (m, 2H), 3.10 (m, 2H), 3.41 (d, J = 3.0 Hz, 1H), 4.24 (ddd, J = 12.0, 8.2, 4.3 Hz, 1H), 7.15–7.60 (m, 8H), 7.93 (d, J = 7.3 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 31.9, 38.1, 45.2, 67.0, 125.7, 127.9, 128.1, 128.27, 128.36, 128.4 (×2), 128.5 (×2), 133.4, 136.5, 141.7, 200.6.

3-Hydroxy-4-methyl-1-phenylpentan-1-one (36):[25] IR (neat, cm^{-1}) 3378, 3347, 1674; ^1H NMR (270 MHz, $CDCl_3$) δ 0.91 (d, J = 5.9 Hz, 3H), 0.94 (d, J = 5.9 Hz, 3H), 1.69–1.77 (m, 1H), 2.95 (dd, J = 17.5, 9.3 Hz, 1H), 3.09 (dd, 17.5, 2.6 Hz, 1H), 3.92 (ddd, J = 9.0, 5.6, 2.6 Hz, 1H), 7.20–7.53 (m, 3H), 7.88 (dd, J = 8.6, 1.5 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 27.9, 28.6, 33.1, 42.0, 72.3, 127.9, 128.0, 128.5 (×2), 133.3, 136.7, 201.0.

3-Cyclohexyl-3-hydroxy-1-phenylpropan-1-one (37):[24] IR (neat, cm^{-1}) 3440, 1681; ^1H NMR (270 MHz, $CDCl_3$) δ 1.06–1.30 (m, 5H), 1.48 (m, 1H), 1.68–1.95 (m, 5H), 3.05 (dd, J = 17.5, 9.2 Hz, 1H), 3.19 (dd, J = 17.5, 2.6 Hz, 1H), 3.99 (m, 1H), 7.44–7.98 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.2, 26.3, 26.5, 28.4, 29.1, 42.1, 43.1, 71.8, 127.9 (×2), 128.5 (×2), 133.3, 136.8, 201.2.

3-Hydroxy-1,5-diphenylpent-4-en-1-one (38):[26] IR (neat, cm^{-1}) 3463, 1681; ^1H NMR (270 MHz, $CDCl_3$) δ 3.20–3.38 (m, 2H), 3.48 (s, 1H), 4.98 (br, 1H), 6.31 (dd, J = 15.8, 5.9 Hz, 1H), 6.71 (d, J = 15.8 Hz, 1H), 7.23–7.61 (m, 8H), 7.96 (d, J = 7.9 Hz, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 45.2, 68.6, 126.4 (×2), 127.6, 128.0 (×2), 128.4 (×2), 128.6 (×2), 130.1, 130.3, 133.5, 136.4 (×2), 199.8.

1-Hydroxy-1,5-diphenylpentan-3-one (39):[27] IR (neat, cm^{-1}) 3440, 1704; ^1H NMR (270 MHz, $CDCl_3$) δ 2.71–2.93 (m, 6H), 3.26 (s, 1H), 5.14 (dd, $J = 8.7, 5.3$ Hz, 1H), 7.14–7.37 (m, 10H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 29.5 (×2), 45.1, 51.3, 69.9, 125.5, 126.1, 127.5, 128.2 (×2), 128.4 (×4), 140.5, 142.6, 210.0.

5-Hydroxy-1,7-diphenylheptan-3-one (40):[28] IR (neat, cm^{-1}) 3355, 1697; ^1H NMR (270 MHz, $CDCl_3$) δ 1.51–1.87 (m, 3H), 2.53 (d, $J = 7.3$ Hz, 1H), 2.53 (d, $J = 3.8$ Hz, 1H), 2.62–2.91 (m, 6H), 4.03 (m, 1H), 7.14–7.30 (m, 10H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 29.5, 31.7, 38.0, 45.0, 49.3, 66.8, 125.7, 126.1, 128.1, 128.26, 128.31, 128.4, 140.5, 141.6, 128.4, 210.8.

5-Hydroxy-6-methyl-1-phenylheptan-3-one (41):[29] IR (neat, cm^{-1}) 3487, 1704; ^1H NMR (270 MHz, $CDCl_3$) δ 0.88 (d, $J = 6.9$ Hz, 3H), 0.91 (d, $J = 6.9$ Hz, 3H), 1.66 (m, 1H), 2.51 (m, 2H), 2.78 (m, 2H), 2.90 (m, 2H), 3.80 (ddd, $J = 9.6, 5.6, 4.0$ Hz, 1H), 7.15–7.31 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 17.8, 18.3, 29.6, 33.1, 45.1, 46.3, 72.2, 126.0, 128.1 (×2), 128.4 (×2), 140.6, 211.2.

1-Cyclohexyl-1-hydroxy-5-phenylpentan-3-one (42):[30] IR (neat, cm^{-1}) 3409, 1704; ^1H NMR (270 MHz, $CDCl_3$) δ 0.94–1.34 (m, 6H), 1.59–1.79 (m, 5H), 2.52 (d, $J = 8.4$ Hz, 1H), 2.53 (m, 2H), 2.74–2.80 (m, 2H), 2.87–2.93 (m, 3H), 3.80 (m, 1H), 7.16–7.31 (m, 5H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 26.1, 26.2, 26.5, 28.3, 28.9, 29.6, 43.0, 45.1, 46.4, 71.7, 126.0, 128.1 (×2), 128.4 (×2), 140.6, 211.3.

5-Hydroxy-1,7-diphenylhept-6-en-3-one (43):[31] IR (neat, cm^{-1}) 3340, 3232, 1704; ^1H NMR (270 MHz, $CDCl_3$) δ 2.68–2.70 (m, 2H), 2.74–2.81 (m, 2H), 2.88–2.94 (m, 2H), 3.15 (d, $J = 3.6$ Hz, 1H), 4.70–4.78 (m, 1H), 6.17 (dd, $J = 15.8$, 6.1 Hz, 1H), 6.60 (d, $J = 15.8$ Hz, 1H), 7.15–7.37 (m, 10H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 29.4, 45.1, 49.2, 68.5, 126.1, 126.3 (×2), 127.6, 128.1 (×2), 128.39 (×2), 128.42 (×2), 129.9, 130.2, 136.3, 140.5, 209.8.

1,5-Diphenylpenta-2,4-dien-1-one:[32] IR (neat, cm^{-1}) 1650, 1573; ^1H NMR (270 MHz, $CDCl_3$) δ 7.02–7.12 (m, 3H), 7.32–7.41 (m, 3H), 7.46–7.52 (m, 4H), 7.55–7.66 (m, 2H), 7.96–8.02 (m, 2H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 125.3, 126.8 (×2), 127.2 (×2), 128.3 (×2), 128.5 (×2), 128.7 (×2), 129.1, 132.5, 136.0, 141.8, 144.7, 190.3.

1,5-Diphenylpent-1-en-3-one:[33] IR (neat, cm^{-1}) 3440, 3347, 1666, 1612; ^1H NMR (270 MHz, $CDCl_3$) δ 7.48–7.57 (m, 3H), 7.37–7.40 (m, 3H), 7.12–7.33 (m, 5H), 6.73 (d, $J = 16.6$ Hz, 1H), 3.00 (s, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 30.2, 42.5, 126.0 (×2), 128.1 (×2), 128.3 (×2), 128.4 (×2), 128.8 (×2), 130.4, 134.3, 141.0,142.5, 199.1.

1,7-Diphenylhepta-4,6-dien-3-one:[34] IR (neat, cm^{-1}) 3787, 1673, 1596; ^1H NMR (270 MHz, $CDCl_3$) δ 7.45 (dd, $J = 1.8, 8.1$ Hz, 2H), 7.16–7.38 (m, 9H), 6.80–6.96 (m, 2H), 6.27 (d, $J = 15.3$ Hz, 1H), 2.89–3.02 (m, 4H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 30.2, 42.3, 126.0, 126.4, 126.5, 127.1, 128.2 (×2), 128.3 (×2), 128.7 (×2), 129.1, 129.3, 135.8, 141.1, 141.2, 142.6, 199.1.

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