N-Heterocyclic Carbene-Catalyzed Conjugate Umpolung for the Synthesis of γ-Butyrolactones

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Dedicated to the memory of Professor Nabi Magomedov and his family.

Abstract: The N-heterocyclic carbene-catalyzed conjugate Umpolung of differently substituted α,β-unsaturated aldehydes, e. g. cinnamaldehydes, α-methylcinnamaldehydes, and crotonaldehydes, is described. Coupling of these compounds with a variety of electrophilic aldehydes and ketones results in the selective formation of highly substituted β- and γ-butyrolactones.

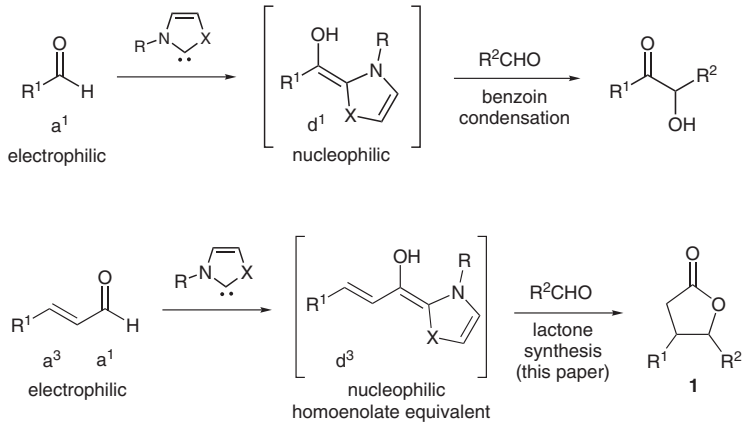
Key words: carbenes, Umpolung, lactones, heterocycles, cyclization

Introduction

The inversion of the commonly accepted reactivity pattern of a functional group, the Umpolung,[1] is a versatile and fertile concept that allows new chemical transformations. Stoichiometric[2] as well as catalytic methods for Umpolung have been known for a long time, and have become standard tools in organic synthesis. The catalytic Umpolung of electrophilic aldehydes upon addition of nucleophilic catalysts like cyanide or thiazolium carbenes is an extraordinarily attractive approach.[3] The resulting nucleophiles can react with aromatic aldehydes (benzoin condensation[4]) or with electron-poor, polarized olefins (Stetter reaction[5]). In contrast to this a^1-to-d^1-Umpolung, the term 'conjugate' Umpolung describes the transformation of α,β-unsaturated aldehydes into d^3-nucleophiles (homoenolate equivalents[6]) upon attack of a suitable nucleophilic catalyst on the aldehyde function (Scheme 1). Here we report an organocatalyzed, chemo- and stereoselective reaction of α,β-unsaturated aldehydes with a variety of different aldehydes and ketones to give substituted β-lactone and γ-butyrolactone products.[7c]

Aromatic Aldehydes as Electrophiles

Our investigation commenced with the reaction of cinnamaldehyde with 4-chlorobenzaldehyde. The Umpolung of these two compounds can lead to a variety of different products: benzoin products, Stetter products and the products arising from conjugate Umpolung (Scheme 2). Many different catalysts were screened and it became obvious that the catalyst has a dramatic influence on the outcome of this transformation. Using a combination of the commercially available thiazolium salt **2** (Figure 1) and an equimolar amount of base resulted in the formation of the corresponding benzoin products only, with no γ-butyrolactone being formed. Interestingly, employing potassium cyanide (30 mol%) in combination with 18-crown-6 (10 mol%) gave lactone **1a**, albeit in low yield (Scheme 3, Table 1, entry 2).



Scheme 1 Umpolung versus conjugate Umpolung

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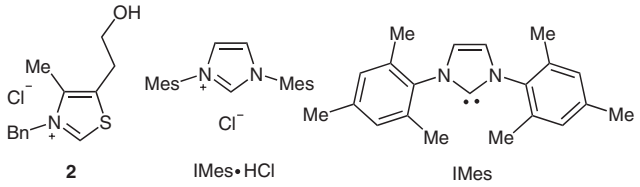


2 IMes•HCl IMes

Figure 1

Recently, imidazolium derived N-heterocyclic carbenes (NHCs) have found numerous applications as ligands in transition metal catalysis and as organocatalysts.[7–15] In parallel, we[7c] and Bode et al.[7d] were the first to find that 1,3-dimesityl-2,3-dihydro-1*H*-imidazol-2-ylidene (IMes) (Figure 1) is a competent catalyst for the conjugate Umpolung of α,β-unsaturated aldehydes resulting in the formation of γ-butyrolactones **1**. Under optimized conditions, a 1:1 mixture of cinnamaldehyde and the benzaldehyde derivative in tetrahydrofuran was treated with IMes (prepared in situ from IMes·HCl and excess KO*t*-Bu) and stirred at ambient temperature for 16 hours (Scheme 3). A variety of differently substituted γ-butyrolactones was formed from aromatic aldehydes in yields

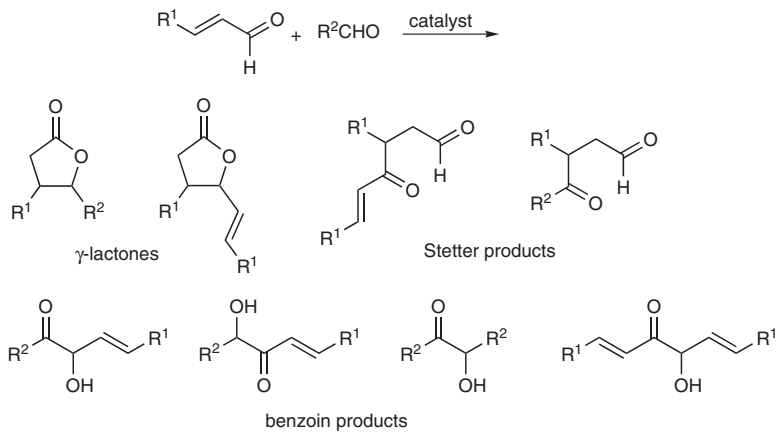
Biographical Sketches

Christian Burstein received his diploma in 2003 from the Universität Duisburg, where he worked in the laboratory of Prof. D. Döpp. His Ph. D. work under the guidance of Prof. F. Glorius commenced at the Max-Planck-Institut für Kohlenforschung in 2003 and was completed at the Universität Marburg in 2006. His main research interests are modern organocatalytic methods, N-heterocyclic carbenes, and organometallic chemistry.

Serena Tschan was born in Hamburg, Germany, in 1981. She obtained her diploma degree in chemistry from Philipps-Universität Marburg in 2006 under the direction of Professor Frank Glorius, where she carried out her graduate work in the area of organocatalyzed reactions for the synthesis of β- and γ-lactones.

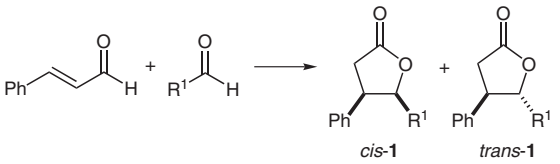
Xiulan Xie was born in Fujian, China, in 1964. She has supervised the NMR centre in the Faculty of Chemistry, Philipps-Universität Marburg since 2002. Her main interest is structure determination by using modern NMR spectroscopic techniques in solution.

Frank Glorius was educated in chemistry at the Universität Hannover, Stanford University (Professor Paul A. Wender), Max-Planck-Institut für Kohlenforschung and Universität Basel (Prof. Andreas Pfaltz), and Harvard University (Professor David A. Evans). In 2001 he began his independent research career at the Max-Planck-Institut für Kohlenforschung in Mülheim, Germany. In 2004 he became Professor of Organic Chemistry at the Philipps-Universität Marburg. The purpose of his research program is to significantly facilitate organic synthesis by developing new concepts for catalysis. At present his group focuses on the design of new N-heterocyclic carbenes, challenging cross-coupling reactions, asymmetric hydrogenations, and organocatalyzed umpolung reactions.



Scheme 2 Possible products of the Umpolung of an α,β-unsaturated aldehyde and another aldehyde

ranging from 30% to 70% with, generally, hardly any benzoin or Stetter product being produced.[16] With the exception of 2-chlorobenzaldehyde (Table 1, entry 10), the *cis*-diastereomer was formed predominantly in all cases (Table 1).[17] The typical *cis*/*trans* ratio was 80:20, and the diastereomers were separated by column chromatography.



Scheme 3

Mechanism

A plausible mechanism for the conjugate Umpolung to give γ-butyrolactones is depicted in Scheme 4. Reaction of the N-heterocyclic carbene with the α,β-unsaturated aldehyde gives rise to a zwitterionic structure **3** that isomerizes by protonation/deprotonation to give the conjugated dienamine **4**. Nucleophilic attack of **4A** or its zwitterionic homoenolate tautomer **4B**[18] onto the electrophilic aldehyde or ketone results in the formation of alkoxide **5**, followed by isomerization to the corresponding tautomer **6**. Related activated carboxylates are thought to be intermediates in N-heterocyclic carbene catalyzed transesterification reactions, leading to ester formation when attacked by alcohol nucleophiles.[8] In analogy, intramolecular attack of the alkoxide of **6** or its protonated form onto the carbonyl group leads to the closing of the lactone ring and the regeneration of the nucleophilic catalyst.

It is tempting to speculate that the steric demand of IMes is key to its success by modulating the reactivity of the nucleophilic species. Namely, the former aldehyde carbons of benzaldehyde and cinnamaldehyde are significantly shielded by the catalyst leading to reduced nucleophilicity of the enamine carbon nearby. In contrast, the conjugate position does not suffer from this shielding and can still react with the electrophile (Figure 2).

Table 1 IMes-Catalyzed Coupling of Cinnamaldehyde with Aromatic Aldehydes[a]

Entry	R^1	**1**	Yield (%)	Ratio[b] *cis*/*trans*
1	4-ClC_6H_4	**a**	0[c]	–
2	4-ClC_6H_4	**a**	33[d,e]	80:20
3	4-ClC_6H_4	**a**	53	81:19
4	4-BrC_6H_4	**b**	49	80:20
5	4-$MeO_2CC_6H_4$	**c**	70	79:21
6	4-$F_3CC_6H_4$	**d**	44	77:23
7	3-FC_6H_4	**e**	52	78:22
8	3-ClC_6H_4	**f**	61	79:21
9	3-BrC_6H_4	**g**	66	79:21
10	2-ClC_6H_4	**h**	32[e]	23:77

[a] General reaction conditions: IMes·HCl (0.05 mmol), KO*t*-Bu (0.1 mmol), THF (3 mL), then cinnamaldehyde (1 mmol), R^1CHO (1.0 mmol), THF, r.t., 16 h. Isolated combined yield of separately isolated diastereomers.
[b] Determined by GC-MS.
[c] Instead of IMes·HCl, thiazolium salt **2** was used as the catalyst.
[d] Instead of IMes·HCl, KCN (0.3 mmol) and 18-crown-6 (0.1 mmol) were employed.
[e] Isolated as mixture of diastereomers.

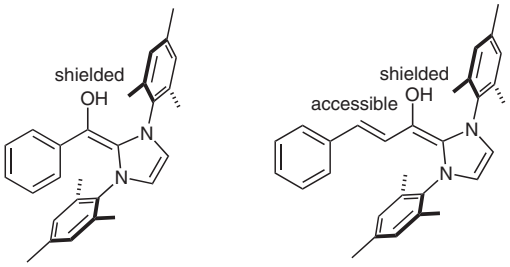
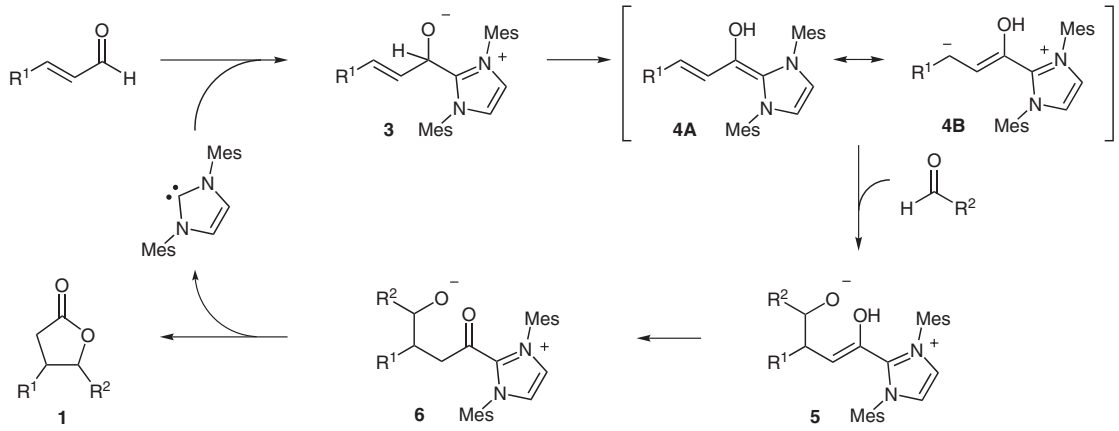


Figure 2 Possible sterical influence of the catalyst on the nucleophilicity



Scheme 4 Suggested mechanism for the formation of γ-butyrolactones

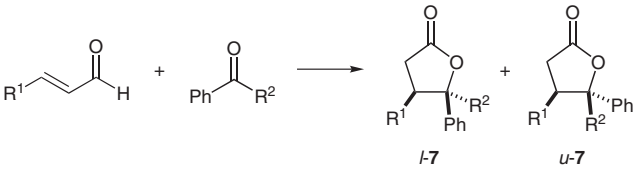
Another Useful Class of Electrophiles: Ketones

For a long time, no efficient benzoin condensation with ketones as electrophiles was known. Only recently, reports appeared describing the use of ketones in intramolecular benzoin condensations.[10a,b,d] We were pleased to find that for the first time ketones could be employed as intermolecular electrophiles in the conjugate Umpolung (Scheme 5).[7c,j] The IMes catalyzed reaction of cinnamaldehyde with one equivalent of α,α,α-trifluoroacetophenone smoothly proceeded to give the corresponding γ-butyrolactone **7a**, which bears a valuable quaternary stereocenter, in 70% yield. Using a twofold excess of the ketone significantly improved the yield to 84% (Table 2, entry 1). The reaction could be scaled up to 30 mmol without a deterioration of the yield (Table 2, entry 2). In addition, the use of 1,8-diazabicyclo[5.4.0]undec-7-ene instead of potassium *tert*-butoxide often resulted in superior results, improving the yield by roughly 10% and in addition simplifying the reaction set up (Table 2, entry 3) Methyl benzoylformate and 1-phenylpropane-1,2-dione were also found to be suitable ketone electrophiles in this reaction resulting in the formation of the corresponding γ-butyrolactones in good yields (Table 2, entries 10–13). The α,β-unsaturated aldehyde component can also be varied in these reactions. Namely, electron-rich methoxy- or dimethylamino-substituted cinnamaldehyde derivatives can successfully be employed (Table 2, entries 8, 9, 12, 13).

In many cases, the *like* and *unlike* diastereomer could be separated by column chromatography. The stereochemistry of *u*-**7b** was unequivocally determined by an X-ray structural analysis.[17]

Asymmetric Conjugate Umpolung

Recently, chiral triazolium salt derived N-heterocyclic carbenes were successfully used in highly enantioselective benzoin condensation[10] and Stetter reactions.[11] Interestingly, triazolium salts **8**[10c] and **9**[11a] and imidazolium salt **10**[19] are unsuitable catalysts for the synthesis of **7a** under standard conditions (Table 2, entries 4–6, 0%, 10%, and 0% yields, respectively). In contrast, the N-heterocyclic carbene derived from imidazolium salt **11**[19] (Table 2, entry 7) is a competent catalyst for this transformation. Using 5 mol% of **11** provides **7a** in 70% yield[10a,d,e] with an improved *l*/*u* ratio of 74:26 and an enantiomeric excess of 12% and 25%, respectively.



Scheme 5

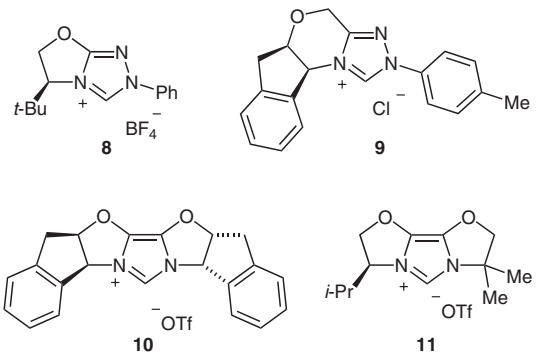


Figure 3 Precursors of chiral N-heterocyclic carbene catalysts

Conjugated Umpolung of Substituted Crotonaldehyde Derivatives: Synthesis of γ-Butyrolactones

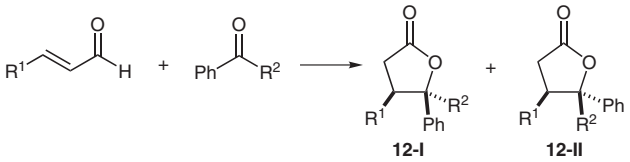
Initially, we reasoned that the aromatic group of cinnamaldehydes would be crucial for success in the conjugate Umpolung.[20] However, we were pleased to find that alkyl-substituted α,β-unsaturated aldehydes can also be successfully used in the conjugate Umpolung (Scheme 6). Using activated ketones as electrophiles, high yields of

Table 2 Reaction of Cinnamaldehydes with Various Ketones[a]

Entry	R^1	R^2	**7**	Yield (%)	Ratio[b] *l*/*u*
1	Ph	CF_3	**a**	84[c]	66:34
2	Ph	CF_3	**a**	84[c,d]	64:36
3	Ph	CF_3	**a**	92[e]	68:32
4	Ph	CF_3	**a**	0[c,f]	–
5	Ph	CF_3	**a**	10[c,g]	nd[h]
6	Ph	CF_3	**a**	0 [c,i]	–
7	Ph	CF_3	**a**	70[c,j]	74:26[k]
8	4-$MeOC_6H_4$	CF_3	**b**	92[c]	66:34
9	4-$Me_2NC_6H_4$	CF_3	**c**	74[c]	70:30
10	Ph	C(O)Me	**d**	55[l]	58:42
11	Ph	CO_2Me	**e**	78	50:50
12	4-$MeOC_6H_4$	CO_2Me	**f**	94	47:53
13	4-$(Me_2N)C_6H_4$	CO_2Me	**g**	98	44:56

[a] General reaction conditions: IMes·HCl (0.05 mmol), DBU (0.05 mmol), cinnamaldehyde derivative (0.5 mmol), ketone (1.0 mmol), THF (2.5 mL), r.t., 16 h. Yields given for the isolated mixture of diastereomers.
[b] Determined by GC-MS.
[c] Reaction conditions: IMes·HCl (0.05 mmol), KO*t*-Bu (0.1 mmol), THF (3 mL), then cinnamaldehyde derivative (1 mmol), ketone (2.0 mmol), r.t., 16 h.
[d] 30 mmol scale.
[e] 10 mmol scale.
[f] Catalyst **8**.
[g] Catalyst **9**.
[h] Not determined.
[i] Catalyst **10**.
[j] Catalyst **11**.
[k] *like*: 12% ee, *unlike*: 25% ee.
[l] Run at 60 °C.

γ-butyrolactones were obtained under our standard conditions. In many cases the diastereomeric ratios were improved compared to the use of cinnamaldehyde (see Table 3), the best was 93:7 favoring the product **12c-I**. In comparison, reduced selectivities were obtained in the cases using methyl benzoylformate.[17]



Scheme 6

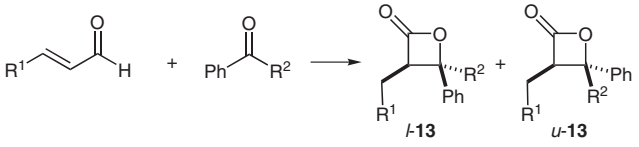
Table 3 Reaction of Alkyl-Substituted α,β-Unsaturated Aldehydes with Ketones[a]

Entry	R^1	R^2	**12**	Yield (%)	Ratio **I/II**[b]
1	Me	CF_3	**a**	82	81:19[c]
2	Pr	CF_3	**b**	90	84:16[c]
3	*i*-Pr	CF_3	**c**	66	93:7[d]
4	Me	CO_2Me	**d**	87	68:32[c]
5[e]	Pr	CO_2Me	**e**	71	67:33[c]
6[f]	*i*-Pr	CO_2Me	**f**	72	65:35[d]

[a] General reaction conditions: IMes·HCl (0.05 mmol), DBU (0.05 mmol), α,β-unsaturated aldehyde (0.5 mmol), ketone (1.0 mmol), THF (2.5 mL), r.t., 16 h. Yield given for the isolated mixture of diastereomers.
[b] Determined by GC-MS.
[c] **I** = *like*, **II** = *unlike*.
[d] **I** = *unlike*, **II** = *like*.
[e] DBU (0.25 mmol), 50 °C.
[f] DBU (0.25 mmol).

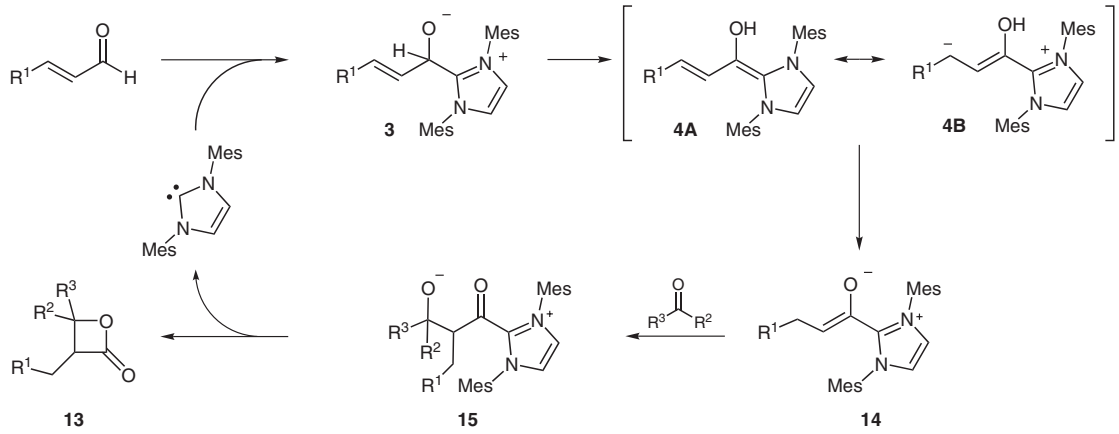
Conjugated Umpolung of Substituted Crotonaldehyde Derivatives: Synthesis of β-Lactones

Under some reaction conditions, an isomeric side product was obtained. Structural investigation revealed the β-lactone structure of this compound. Interestingly, using the same substrates and the same catalyst, but changing the base, the solvent, and the reaction temperature allowed this reaction to be controlled (Scheme 7). Under optimized reaction conditions, β-lactone **13c** formed in 48% yield (Table 4, entry 3). The use of less polar solvents, higher temperatures, and triethylamine as a base were optimal for this reaction. Methyl benzoylformate could also be employed as an electrophile after slightly modifying the reaction conditions.



Scheme 7

Mechanistically, we reason that for the formation of β-lactones a protonation/deprotonation sequence transforms homoenolate **4** into enolate **14** (Scheme 8). Reduced nucleophilicity and a longer lifetime of homoenolate equivalent **15** would favor this process. Finally, attack of the electrophilic carbonyl component, followed by cyclization to the β-lactone liberates the N-heterocyclic carbene catalyst.



Scheme 8 Suggested mechanism for the formation of β-lactones

Table 4 β-Lactone Formation by Conjugate Umpolung[a]

Entry	R^1	R^2	**13**	Yield (%)	Ratio[b] *l*/*u*
1	Me	CF_3	**a**	34	60:40
2	Pr	CF_3	**b**	45	55:45
3	*i*-Pr	CF_3	**c**	48	62:38
4	Ph	CF_3	**d**	30	70:30
5	*i*-Pr	CO_2Me	**e**	22[c]	71:29

[a] General reaction conditions: IMes·HCl (0.05 mmol), Et_3N (2.0 mmol), toluene (2.5 mL), α,β-unsaturated aldehyde (1.0 mmol), ketone (1.0 mmol), 60 °C, 16 h.
[b] Determined by GC-MS.
[c] IMes·HCl (0.1 mmol), DBU (0.1 mmol).

Umpolung of α-Methylcinnamaldehydes

γ-Butyrolactones are ubiquitous motifs in naturally occurring compounds, many of which bear an α-substituent at C3 (Figure 4).[21] Therefore, the reactivity of α-methylcinnamaldehydes was of special interest. Does the conjugate Umpolung tolerate an α-substituent?

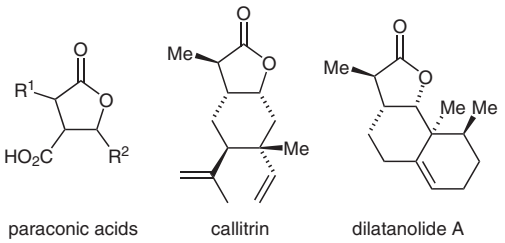


Figure 4 Natural products with α-substituted γ-lactone substructure

Under conditions optimized for the previously mentioned reactions using IMes as the catalyst, the use of α-methylcinnamaldehyde and trifluoroacetophenone did not result in the formation of the desired product. It is reasonable to assume that the α-methyl substituent would exhibit an unfavorable steric interaction with the mesityl rings in conjugated intermediate **16** (Figure 5). Consequently, the use of N-heterocyclic carbenes with smaller groups was investigated. Whereas thiazolium salt **2** failed once again to provide lactone products, the precatalysts 1-mesityl-3-methylimidazolium iodide (**17**) and 1,3-dimethylimidazolium iodide (**18**) resulted in the formation of small amounts of product. Gratefully, 1,3-dimethylbenzimidazolium iodide (**19**), electronically slightly different from **18**, resulted in the formation of the highly substituted γ-butyrolactones **20** (Scheme 9, Table 5). Using *N*,*N*-dimethylformamide as the optimal solvent and α-methylcinnamaldehyde as the substrate, product **20a** was formed in 83% yield (Table 5, entry 8). Of the four possible diastereomers, mainly **20-I** and **20-II** were obtained (Figure 6). In these two major diastereomers the methyl group at C3 is oriented *trans* relative to the R^1 substituent at C4. In agreement with the results obtained for cinnamaldehyde or crotonaldehyde derivatives, **20-I** is formed predominantly in most cases. However, when 2-methyl-5-phenylpenta-2,4-dienal, an α,β-unsaturated aldehyde containing an alkene as R^1 substituent, was used as a substrate, diastereomer **20-II** was obtained in excess (Table 5, entry 11).[17]

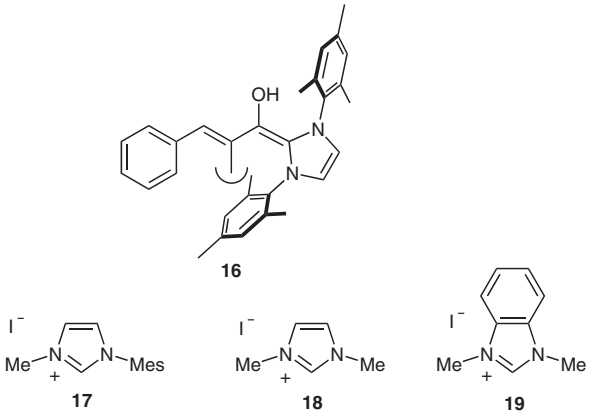
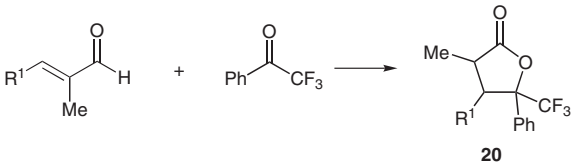


Figure 5 Unfavorable steric interactions in hypothetical intermediate **16** and precatalysts **17**, **18**, and **19**

Table 5 Reaction of α-Methylcinnamaldehydes[a]

Entry	R^1	Catalyst	Solvent	**20**	Yield (%)	dr[b]
1	Ph	**2**	THF	**a**	0	–
2	Ph	IMes	THF	**a**	0	–
3	Ph	IMes	DMF	**a**	0	–
4	Ph	**17**	DMF	**a**	traces	–
5	Ph	**18**	THF	**a**	traces	–
6	Ph	**19**	THF	**a**	37[b]	66:28:5:1
7	Ph	**19**	MeCN	**a**	24[b]	64:27:7:2
8	Ph	**19**	DMF	**a**	83	62:30:6:2
9	Ph	**19**	DMF	**a**	85[c]	63:29:6:2
10	4-ClC_6H_4	**19**	DMF	**b**	71	63:29:6:2
11	CH=CHPh	**19**	DMF	**c**	82	32:66:2:0

[a] General reaction conditions: α,β-unsaturated aldehyde (0.5 mmol), ketone (1.0 mmol), solvent (2.5 mL), catalyst (0.05 mmol), DBU (0.05 mmol), 75 °C.
[b] Determined by GC-MS.
[c] 10 mmol scale.



Scheme 9

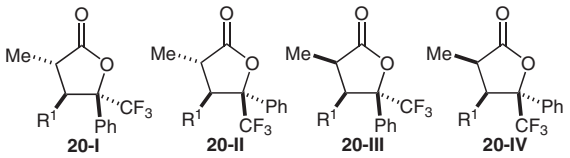


Figure 6 Diastereomers of **20**

Another interesting observation was made when using 4-chlorocinnamaldehyde as the substrate. In this case, only a small amount (20%) of the expected product **20** was obtained. In addition, the isomeric product **21** was formed in 46% yield (Figure 7). This product could result from a protonation/reprotonation sequence analogous to the one shown in Scheme 8.

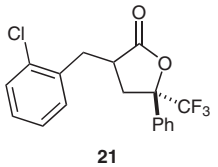


Figure 7

Intramolecular Reaction

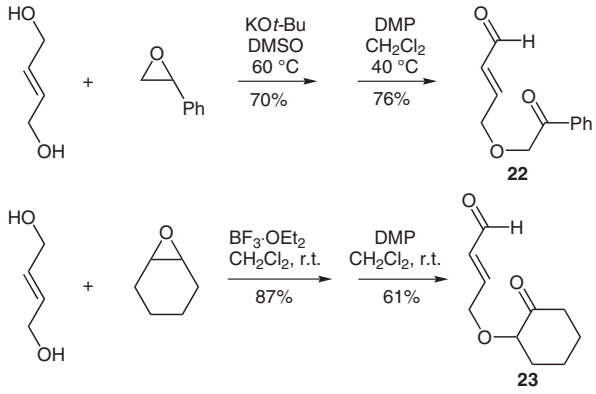
The aforementioned intermolecular reactions generate a γ-butyrolactone with up to three contiguous stereocenters. For a number of reasons an intramolecular variant of this reaction would be attractive. First of all, less reactive electrophiles, namely unactivated ketones, might become suitable reaction partners, thereby significantly expanding the scope of this transformation. Second, in the course of the intramolecular lactone formation an additional ring would be formed, leading to bicyclic products. Finally, an existing stereocenter could influence the reaction leading to the highly selective formation of the lactone products. However, frequently the use of an elaborate, multistep substrate synthesis decreases the attraction of intramolecular approaches.

Consequently, our investigation commenced with the design of readily accessible cyclization precursors. But-2-ene-1,4-diol was identified as an ideally suited building block, allowing the synthesis of the cyclization substrates in only two steps. In this sequence, one hydroxy group of the diol was used for a highly regioselective opening of an epoxide, followed by the parallel oxidation of both hydroxy groups of the resulting diol with Dess–Martin periodinane in good yield (Scheme 10).

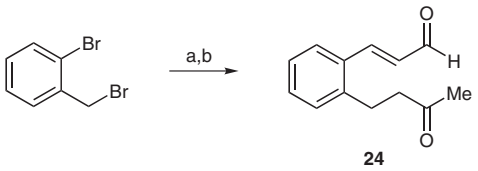
The IMes-catalyzed cyclization of **22** and **23** resulted in the formation of γ-butyrolactones with an annulated tetrahydrofuran ring (Table 6, entries 1 and 2). Interestingly, only a single diastereomer was formed. Moreover, for the first time nonactivated, enolizable ketones proved to be suitable electrophiles in the conjugate Umpolung. Especially, the synthesis of the tricyclic product **28** is rather

complex and demonstrates the potential of this new synthetic method.

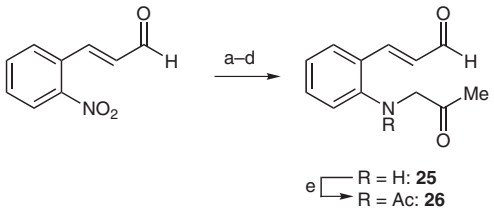
Another class of substrates for an intramolecular homoenolate addition, leading to the formation of six-membered rings, was synthesized. Substrates **24**, **25**, and **26** were easily prepared in two, four, and five steps, respectively (Schemes 11 and 12).[22] Once again, IMes allows the conjugate Umpolung of the unsaturated aldehyde, followed by attack onto the nonactivated ketone and the concluding cyclization. In these cases, besides the formation of the γ-butyrolactone, a tetralin or tetrahydroquinoline ring system formed. Impressively, the cyclization of **24** resulted in the formation of the *trans*-diastereomer **29**, only (Table 6, entry 3). The stereochemical assignment of compounds **27**–**31** was based on elaborate NMR experiments, described in the experimental section.



Scheme 10 Synthesis of substrates suitable for an intramolecular cyclization reaction

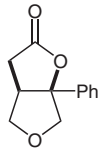
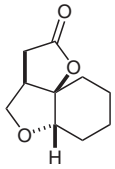
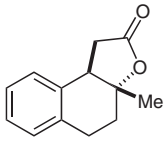
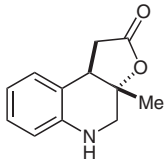
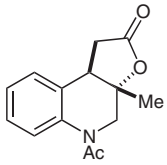


Scheme 11 *Reagents and conditions:* (a) acetylacetone, K_2CO_3, EtOH, 90 °C (75%); (b) $H_2C{=}CHCH(OEt)_2$, $Pd(OAc)_2$, KCl, K_2CO_3, Bu_4NOAc, DMF, 100 °C (49%).



Scheme 12 *Reagents and conditions:* (a) aq $NaBH_4$, EtOH, 0 °C (98%); (b) $FeSO_4{\cdot}7H_2O$, 25% NH_4OH, MeOH, H_2O, 80 °C (79%); (c) $AcCH_2Cl$, $KHCO_3$, KI, acetone, 50 °C (69%); (d) 2-iodylbenzoic acid, EtOAc, 50 °C (78%); (e) AcCl, toluene, 80 °C (30%).

Table 6 Intramolecular Homoenolate Addition[a]

Entry	Substrate	Product	Yield (%)
1[a]	**22**	**27** 	36
2[b]	**23**	**28** 	41
3[c]	**24**	**29** 	55
4[d]	**25**	**30** 	23
5[e]	**26**	**31** 	26

[a] IMes·HCl (0.07 mmol), KO*t*-Bu (0.06 mmol), THF (14 mL), then substrate (0.34 mmol), 60 °C, 16 h.
[b] IMes·HCl (0.11 mmol), KO*t*-Bu (0.1 mmol), THF (20 mL), then substrate (0.55 mmol), 60 °C, 5 h.
[c] IMes·HCl (0.030 mmol), KO*t*-Bu (0.028 mmol), THF (4 mL), then substrate (0.2 mmol), 60 °C, 16 h.
[d] IMes·HCl (0.036 mmol), DBU (0.03 mmol), THF (15 mL), then substrate (0.30 mmol), 60 °C, 16 h.
[e] IMes·HCl (0.036 mmol), DBU (0.03 mmol), THF (6 mL), then substrate (0.285 mmol), 60 °C, 16 h.

Conclusion

The organocatalyzed conjugate Umpolung of α,β-unsaturated aldehydes allows the direct, intermolecular, and cross-linking of an α,β-unsaturated aldehyde with another aldehyde or ketone, resulting in a flexible one-step synthesis of substituted γ-butyrolactones. In intramolecular cases, the use of nonactivated ketones as an electrophilic reaction partner is described, leading to the formation of multicyclic products. In addition, variation of the reaction conditions allows the formation of β-lactones in some cases.

All commercially available compounds were used as received and all reactions were performed under an atmosphere of argon. The solvents used were purified by distillation over the drying agents indicated and were transferred under argon: THF (Na), CH_2Cl_2 (CaH_2), toluene (CaH_2). For flash chromatography, Merck silica gel 60 (230–400 mesh) was used. NMR spectra were recorded on a ARX 300 or DRX 400 spectrometer (Bruker) in the solvents indicated; chemical shifts are relative to TMS. For the stereochemical assignment of lactones 27–31, NMR spectra were recorded on Bruker DRX-500 and AVANCE-600 spectrometers in $CDCl_3$ at concentration of about 0.3 M. Complete signal assignments were carried out on all of the compounds based on ^1H, ^{13}C, HSQC, DQF-COSY, and HMBC spectra. Routine pulse sequences with gradients were used. The pulse sequence DPFGSE-NOE of Shaka[23] was used for the selective transient NOE experiments. Gaussian-shaped pulse was applied for the selective excitation, whose length was optimized for each measurement. Mixing time in the range of 1.0 to 2.0 s was used. 1D-NOE spectra were recorded with 256 scans and a typical experiment time was about 20 min. IR spectra were recorded on a Bruker IFS 88. EI-MS were recorded on a Varian CH7 (70 eV) and HRMS were recorded on a Finnigan LTQ FT or TSQ 700. For MS data of the diastereomeric mixtures a Agilent Technologies System (GC: 6890N, column: HP-5MS (0.25 mm × 30 m × 0.25 μm; Agilent G1701DA GC/MSD ChemStation) with a 5973 Network Mass Selective Detector at 70 eV was used. Method 70_20: 70 °C for 3 min; gradient: 20 °C/min to 280 °C; 280 °C for 3.5 min. Method 50_20: 50 °C for 3 min; gradient: 20 °C/min to 280 °C; 280 °C for 3.5 min.

Conjugate Umpolung; Typical Procedures

Methyl 4-(5-Oxo-3-phenyltetrahydrofuran-2-yl)benzoate (1c); Typical Procedure for Table 1

Generation of the catalyst soln (for multiple reactions): Under an atmosphere of argon, IMes·HCl (85.2 mg, 0.25 mmol) and KO*t*-Bu (56.1 mg, 0.50 mmol) were suspended in THF (5 mL) and stirred for 45 min at r.t. The preformed catalyst soln (1 mL, 0.05 mmol IMes) was added over a period of 1 min to a soln of methyl 4-formylbenzoate (164 mg, 1.0 mmol) and *trans*-cinnamaldehyde (126 μL, 1.0 mmol) in THF (5 mL). The soln was stirred at r.t. for 16 h, after which MeOH (2 mL) was added and the soln was stirred for a further 15 min. The solvent was evaporated in vacuo, and the residue was distilled in a Kugelrohr apparatus (5×10^{-2} mbar, 150–200 °C). Purification of the distillate by column chromatography (silica gel, 2.5 cm × 12 cm, MTBE–hexane 1:3) yielded *cis*-**1c** (164 mg, 56%) and, after crystallization (CH_2Cl_2–hexane), *trans*-**1c** (41 mg, 14%) as colorless solids.

4-Methyl-5-phenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (12a); Typical Procedure for Tables 2 and 3

Under an atmosphere of argon, IMes·HCl (17.0 mg, 0.050 mmol) was dissolved in THF (2.5 mL) in a septum capped vial and crotonaldehyde (35.0 mg, 0.50 mmol) and α,α,α-trifluoroacetophenone (174 mg, 1.0 mmol) were added. DBU (7.60 mg, 0.05 mmol) was added and the soln stirred at r.t. for 16 h. After this time the solvent was evaporated and the residue purified by column chromatography (silica gel, 2.5 cm × 12 cm, hexane–MTBE, 40:1) to give **12a** as a colorless oil; yield: 100 mg (82%).

3-Isobutyl-4-phenyl-4-(trifluoromethyl)oxetan-2-one (13c); Typical Procedure for Table 4

Under an atmosphere of argon, IMes·HCl (17.0 mg, 0.050 mmol) was dissolved in toluene (2.5 mL) and 4-methyl-2-pentenal (116 μL, 1.0 mmol) and α,α,α-trifluoroacetophenone (174 mg, 1.0 mmol) were added. Finally, Et_3N (280 μL, 2.00 mmol) was added and the soln stirred at 60 °C for 16 h. After this time the solvent was evaporated and the residue purified by column chromatography (silica gel, 2.5 cm × 12 cm, pentane–CH_2Cl_2, 15:1) to give **13c** as a colorless oil; yield: 130 mg (48%).

3-Methyl-4,5-diphenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (20a); Typical Procedure for Table 5

Under an atmosphere of argon, **19** (13.7 mg, 0.050 mmol) was dissolved in DMF (2.5 mL) in a septum capped vial and (*E*)-2-methyl-3-phenylprop-2-enal (73.1 mg, 0.50 mmol) and α,α,α-trifluoroacetophenone (174 mg, 1.0 mmol) were added dropwise. Then DBU (7.60 mg, 0.050 mmol) was added and the soln stirred at 75 °C for 16 h. The solvent was then removed by rotary evaporation and the residue was purified by column chromatography (silica gel, 2.5 cm × 12 cm, hexane–MTBE, 40:1) to give **20a** as a mixture of diastereomers; yield: yielding 132 mg (83%).

Stereochemical Assignment

Table 1, Products 1

^1H NMR signals for the ring protons of the lactones **1** are very similar within the *cis* and *trans* series. Thus, based on an X-ray structural analysis of *cis*-**1d**, comparison of the ^1H NMR data allows the assignment of the relative stereochemistry. In addition, some aromatic protons in the *cis*-diastereomer show a significant upfield shift, because they lie in the anisotropic cone of the other aromatic ring. Furthermore the retention times in the GC-MS are consistent, i.e. the *like*-diastereomer has always a shorter retention time than the *unlike*-diastereomer.

Table 2, Lactones 7

As for the lactones **1**, the NMR signals of the ring protons are very similar within the **I** and **II** series. Based on an X-ray structure of *u*-**7b**, the relative configuration could be assigned. For compounds **7a–c** the chemical shift in the ^{19}F NMR of the CF_3 group is also typical. The signal of the CF_3 group in the *like*-diastereomer has a upfield shift compared to the *unlike*-diastereomer. Furthermore the retention times in the GC-MS are consistent, i.e. the *like*-diastereomer has always a shorter retention time than the *unlike*-diastereomer.

Table 3, Products 12

As for the lactones **1**, the NMR signals of the ring protons are very similar within the **I** and **II** series. Based on an X-ray structural analysis of **12c-I**, the relative configuration was assigned. For diastereomer **I** of each compound a significant upfield shift of some aliphatic protons (am Rest R) can be observed, because they lie in the anisotropic cone of the aromatic ring. For compounds **12a–c** the chemical shift in the ^{19}F NMR of the CF_3 group is also typical. The signal of the CF_3 group in diastereomer **I** has a upfield shift compared to the diastereomer **II**. Furthermore the retention times in the GC-MS for diastereomer **I** are always shorter than the retention times for diastereomer **II**.

Table 4, β-Lactones 13

The stereochemical assignment of the β-lactone products is based on the assignment of the γ-lactones as shown above. First of all, in the series assigned to be *like*, the CH group of the substituent on C3 of the β-lactone ring experienced a significant upfield shift (anisotropic cone of the phenyl group). This is supported by NOESY experiments, showing an NOE between this CH group and the phenyl ring. This was not observed for the compounds of the other diastereomeric series. Furthermore, the *like*-isomers exhibit shorter GC retention times and are less polar based on column chromatography.

Table 5, γ-Lactones 20

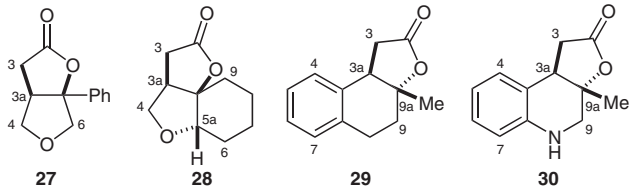
As for the aforementioned lactones, assignment was made based on an X-ray structural analysis of **20c-II** and comparison of the NMR data. Furthermore the coupling constants of the lactone ring protons

are similar to those reported for a comparable structure.[24] Again, the relative GC retention times of the diastereomers and the chemical shift of the CF_3 group allow the stereochemical assignment.

Table 6, Products 27–31

Both ^1H and ^{13}C spectra reveal that the isolated compounds consist of a single diastereomer only. The one-dimensional NOE experiments with pulsed field gradients for the observation of selective transient NOEs delivered high quality spectra. These methods enable the observation of weak NOE enhancements and even can provide quantitative distance information.[23] The configuration of the compounds was thus determined using selective NOE techniques.

Methylene protons in molecules containing chiral centers are diastereotopic and often show resolved NMR signals. In this study we used diastereotopic protons as reference points to deduce the spatial arrangement of the products. Protons attached to the stereocenters were selectively excited resulting in distinct NOE contacts with the diastereotopic methylene protons. The observed NOE contacts allow to predict the configurations for **27**, **29**, and **30** (Table 7).



Scheme 13 Relative configurations given as determined by NMR; numbering used in Table 7

The determination of the conformation of **28** is more complicated. For **28**, which contains three stereocenters, four pairs of enantiomers are possible and two of them might exist in two different favorable conformations. Protons on axial positions of the cyclohexane ring served as reference points. Furthermore, NOE contacts were used in combination with coupling constants. The coupling constant $^3J_{5a–6ax}$ is equal to 9.1 Hz, which reveals the axial orientation of H_{5a}. The NOE contacts detected are given in Table 7. Of the possible configurations, only the one shown for **28** corresponds to the NMR observation and it is thus determined to be the correct configuration of compound **28**.

α,β-Unsaturated Aldehyde Substrates for the Conjugate Umpolung

(*E*)-4-(2-Hydroxy-2-phenylethoxy)but-2-en-1-ol

Styrene oxide (1.14 mL, 10.0 mmol, 1 equiv) was added to a stirred and heated (60 °C) mixture of KO*t*-Bu (3.40 g, 30.3 mmol, 3 equiv) and but-2-ene-1,4-diol (5.30 g, 60.2 mmol, 6 equiv) in DMSO (30 mL). The mixture was stirred for 2 h and then it was poured into a mixture of ice water (100 mL) and toluene (100 mL). The soln was acidified to pH 1 with concd HCl and the layers were separated. The aqueous layer was basified to pH 10–11 using K_2CO_3, then extracted with CH_2Cl_2 (3 × 100 mL). The combined extracts were washed with H_2O (3 × 50 mL) and dried ($MgSO_4$) and the solvent was removed on a rotary evaporator. The residue was purified by column chromatography (CH_2Cl_2–MeOH, 40:1) to afford a colorless oil; yield: 1.45 g (70%).

R_f = 0.22 (CH_2Cl_2–MeOH, 40:1).

IR (film): 3392, 3062, 3030, 2861, 1651, 1494, 1453, 1362, 1199, 1102, 1065, 1005, 904, 833, 760, 701, 633, 419, 408 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.27 (m, 5 H), 5.94–5.77 (m, 2 H), 4.90 (dd, *J* = 3.1, 9.0 Hz, 1 H), 4.15 (d, *J* = 4.4 Hz, 2 H), 4.07 (d, *J* = 5.0 Hz, 2 H), 3.60 (dd, *J* = 3.2, 9.8 Hz, 1 H), 3.47 (t, *J* = 9.4 Hz, 1 H), 2.26 (br s, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.2, 132.6, 128.4, 127.8, 127.3, 126.1, 75.8, 72.8, 71.2, 62.8.

MS (EI): *m*/*z* (%) = 208 [M^+] (1), 107 (100), 105 (34), 104 (10), 91 (12), 79 (49), 77 (31).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{12}H_{16}O_3$: 208.099; found: 208.1102.

(*E*)-4-(2-Oxo-2-phenylethoxy)but-2-enal (22)

A soln of (*E*)-4-(2-hydroxy-2-phenylethoxy)but-2-en-1-ol (0.791 g, 3.80 mmol, 1 equiv) in CH_2Cl_2 (5 mL) was added to a soln of Dess–Martin periodinane (8.20 g, 19.2 mmol, 5 equiv) in CH_2Cl_2 (60 mL) and the mixture was stirred at 40 °C for 3 h. MTBE (70 mL) and sat. $NaHCO_3$ soln (60 mL) containing $Na_2S_2O_3$ (12 g) were added and the mixture was stirred until the white solid had completely dissolved. Further MTBE (50 mL) was added and the organic layer was washed with sat. $NaHCO_3$ soln (50 mL) and then with H_2O (50 mL) and dried ($MgSO_4$). The solvent was removed and the residue purified by column chromatography (hexane–EtOAc, 1.5:1) to afford a white solid; yield: 0.61 g (76%).

R_f = 0.14 (hexane–EtOAc, 1.5:1).

IR (film): 2834, 2740, 1679, 1596, 1579, 1451, 1399, 1301, 1227, 1163, 1133, 1076, 1030, 970, 751, 687, 646, 575, 550 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.60 (d, *J* = 7.9 Hz, 1 H), 7.93–7.90 (m, 2 H), 7.63–7.58 (m, 1 H), 7.51–7.46 (m, 2 H), 6.87 (dt, *J* = 15.8, 4.2 Hz, 1 H), 6.40 (ddt, *J* = 15.8, 7.9, 1.9 Hz, 1 H), 4.85 (s, 2 H, 4.45 (dd, *J* = 4.2, 1.9 Hz, 2 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.6, 193.0, 151.8, 134.6, 133.8, 132.1, 128.8, 127.8, 73.4, 70.0.

MS (ESI, MeOH): *m*/*z* = 227 [M + Na^+].

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{12}H_{12}NaO_3$: 227.0679; found: 227.0677.

Table 7

Lactone	Diastereotopic Protons[a]	NOE[a,b]	Config
27	H_{4A}, H_{4B}; H_{6A}, H_{6B}	H_{3a}–H_{ar} (s), H_{3a}–H_{4A} (s), H_{3a}–H_{6A}; H_{ar}–H_{4A}, H_{ar}–H_{6A} (s)	*unlike*
28	H_{3A}, H_{3B}; H_{4A}, H_{4B}	H_{3a}–H_{4A} (s), H_{3a}–H_{6ax}, H_{3a}–H_{8ax}, H_{3a}–H_{9eq}; H_{5a}–H_{4B}, H_{5a}–H_{3B}, H_{5a}–H_{6eq} (s), H_{5a}–H_{6ax}, H_{5a}–H_{7ax}, H_{5a}–H_{9ax} (s)	as shown in Scheme 13
29	H_{8A}, H_{8B}	H_{3a}–CH_3 (w), H_{3a}–H_{8A}; CH_3–H_{8B}	*like*
30	H_{9A}, H_{9B}	H_{3a}–CH_3 (w), H_{3a}–H_{9A}; CH_3–H_{9B}	*unlike*

[a] The subscripts are positional descriptors.
[b] 's' = strong, 'w' = weak, 'ax' = axial, 'eq' = equatorial.

2-[(*E*)-4-Hydroxybut-2-enyloxy]cyclohexanol

A soln of cyclohexene oxide (1.12 mL, 10.75 mmol, 1 equiv) in CH_2Cl_2 (2 mL) was added dropwise over 5 h to a stirred and cooled (15–20 °C) soln of but-2-ene-1,4-diol (4.74 g, 53.8 mmol, 5 equiv) in CH_2Cl_2 (30 mL) containing $BF_3{\cdot}OEt_2$ (150 μL, 1.19 mmol, 0.11 equiv). The mixture was stirred at r.t. for 30 min and then Et_3N (0.5 mL, 3.6 mmol, 0.34 equiv) was added. The mixture was evaporated to dryness and the residue was purified by column chromatography (CH_2Cl_2–MeOH, 18:1) to afford the product as a colorless oil; yield: 1.74 g (87%) together with but-2-ene-1,4-diol (3.58 g, 40.7 mmol, 3.8 equiv).

R_f = 0.35 (CH_2Cl_2–MeOH, 17:1).

IR (film): 3381, 3007, 2934, 2861, 1854, 1653, 1451, 1370, 1303, 1234, 1160, 1093, 1008, 928, 849, 592 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.86–5.70 (m, 2 H), 4.13–4.00 (m, 3 H), 3.93–3.82 (m, 1 H), 3.40–3.20 (m, 3 H), 3.07–2.99 (m, 1 H), 2.02–1.89 (m, 2 H), 1.70–1.54 (m, 2 H), 1.28–0.99 (m, 4 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 132.4, 127.6, 82.8, 73.5, 68.6, 62.3, 32.1, 29.1, 24.0 (CH_2), 23.8.

MS (ESI, MeOH): *m*/*z* = 209 [M + Na^+].

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{10}H_{18}NaO_3$: 209.1148; found: 209.1146.

(*E*)-4-(2-Oxocyclohexyloxy)but-2-enal (23)

A soln of 2-[(*E*)-4-hydroxybut-2-enyloxy]cyclohexanol (0.80 g, 4.3 mmol, 1 equiv) in CH_2Cl_2 (3 mL) was added to a soln of DMP (4.58 g, 10.8 mmol, 2.5 equiv) in CH_2Cl_2 (35 mL) and the mixture was stirred at r.t. for 1 h. MTBE (50 mL) and sat. $NaHCO_3$ soln (40 mL) containing $Na_2S_2O_3$ (14.0 g) were added and the mixture was stirred until the white solid had completely dissolved. Further MTBE (50 mL) was added and the organic layer was washed with sat. $NaHCO_3$ soln (50 mL) and also with H_2O (50 mL) and then dried ($MgSO_4$). The solvent was removed and the residue purified by column chromatography (hexane–EtOAc, 2:1) to afford a colorless oil; yield: 0.48 g (61%).

R_f = 0.16 (hexane–EtOAc, 2:1).

IR (film): 3434, 2942, 2868, 1721, 1690, 1450, 1355, 1216, 1123, 969, 883, 838, 575 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.58 (d, *J* = 7.9 Hz, 1 H), 6.84 (dt, *J* = 15.8, 4.1 Hz, 1 H), 6.36 (ddt, *J* = 7.2, 15.8, 2.0 Hz, 1 H), 4.55 (ddd, *J* = 2.0, 3.9, 16.8 Hz, 1 H), 4.20 (ddd, *J* = 1.9, 4.2, 16.8 Hz, 1 H), 3.91–3.85 (m, 1 H), 2.54–2.47 (m, 1 H), 2.34–2.21 (m, 2 H), 2.04–1.89 (m, 2 H), 1.82–1.61 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 209.4, 193.2, 152.7, 131.7, 82.8, 68.5, 40.6, 34.4, 27.4, 23.2.

MS (EI): *m*/*z* (%) = 182 [M^+] (2), 164 (10), 136 (15), 135 (18), 114 (12), 107 (15), 98 (100), 97 (22), 86 (17), 83 (21), 79 (16), 70 (60), 69 (93), 68 (58), 67 (27), 57 (52), 55 (49).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{10}H_{14}O_3$: 182.0943; found: 182.0942.

(*E*)-3-[2-(3-Oxobutyl)phenyl]prop-2-enal (24)

A suspension of 4-(2-bromophenyl)butan-2-one (3.76 g, 16.6 mmol), 3,3-diethoxypropene (6.51 g, 50.0 mmol), $Pd(OAc)_2$ (224 mg, 1.0 mmol), KCl (1.24 g, 16.6 mmol), K_2CO_3 (3.44 g, 24.9 mmol), and tetrabutylammonium acetate (10.0 g, 33.2 mmol) in DMF (50 mL) was stirred at 100 °C for 15 h. The mixture was cooled to r.t., 2 M HCl (50 mL) and then MTBE (150 mL) were added and the resulting soln washed with H_2O (2 × 75 mL). The organic phase was dried (Na_2SO_4). After evaporation of the solvent the residue was purified by column chromatography (silica gel, hexane–EtOAc, 2:1); yield: 1.65 g (49%).

R_f = 0.34 (hexane–EtOAc, 2:1).

IR (film): 3411, 3333, 3063, 3027, 2821, 2743, 1715, 1677, 1622, 1600, 1483, 1364, 1294, 1162, 1128, 1094, 974, 757 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.75 (d, *J* = 7.9 Hz, 1 H), 7.83 (d, *J* = 15.8 Hz, 1 H), 7.62–7.59 (m, 1 H), 7.38–7.24 (m, 3 H), 6.68 (dd, *J* = 15.8, 7.9 Hz, 1 H), 3.08 (t, *J* = 7.5 Hz, 2 H), 2.76 (t, *J* = 7.5 Hz, 2 H), 2.16 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 206.9, 193.7, 149.5, 140.9, 132.4, 131.1, 130.2, 130.0, 127.1, 127.0, 44.7, 30.0, 26.6.

MS (EI): *m*/*z* (%) = 202 [M^+] (1), 184 (3), 169 (1), 159 (13), 144 (100), 141 (23), 131 (70), 129 (32), 128 (17), 117 (20), 116 (34), 115 (46), 103 (8), 91 (34), 89 (5), 77 (12), 65 (6), 43 (71).

HRMS (EI): *m*/*z* [M + H^+] calcd for $C_{13}H_{15}O_2$: 203.1072; found: 203.1071.

1-{2-[(*E*)-3-Hydroxyprop-1-enyl]phenylamino}propan-2-one

1-Chloropropan-2-one (463 mg, 5.0 mmol, 1.5 equiv) was added to a mixture of (*E*)-3-(2-aminophenyl)prop-2-en-1-ol (500 mg, 3.35 mmol, 1 equiv), $KHCO_3$ (335 mg, 3.35 mmol, 1 equiv), and KI (110 mg, 0.67 mmol, 0.2 equiv) in acetone (10 mL). The mixture was stirred at 50 °C for 24 h, then silica gel was added and the solvent removed on the rotary evaporator. The powder was purified by column chromatography (pentane–EtOAc, 1:1) to afford the product as a yellow solid; yield: 472 mg (69%).

R_f = 0.11 (pentane–EtOAc, 1:1).

IR (KBr): 3413, 1722, 1601, 1574, 1504, 1453, 1359, 1295, 1185, 1147, 1098, 1013, 958, 751, 608, 531, 498, 466 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.27–7.25 (m, 1 H), 7.20–7.14 (m, 1 H), 6.76–6.70 (m, 2 H), 6.48 (d, *J* = 8.1 Hz, 1 H), 6.25 (dt, *J* = 5.7, 15.7 Hz, 1 H), 4.78 (s, 1 H), 4.35 (d, *J* = 5.7 Hz, 2 H), 4.01 (s, 2 H), 2.26 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.1, 143.9, 131.3, 128.8, 127.8, 126.4, 123.4, 117.9, 110.9, 63.9, 54.3, 27.4.

MS (EI): *m*/*z* (%) = 205 [M^+] (21), 162 (55), 146 (14), 145 (11), 144 (100), 143 (29), 133 (10), 132 (92), 131 (20), 130 (90), 118 (22), 117 (40), 116 (16), 115 (31), 91 (20), 77 (16).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{12}H_{15}NO_2$: 205.1103; found: 205.1095.

(*E*)-3-[2-(2-Oxopropylamino)phenyl]prop-2-enal (25)

1-{2-[(*E*)-3-Hydroxyprop-1-enyl]phenylamino}propan-2-one (821 mg, 4.0 mmol, 1 equiv) was dissolved in EtOAc, (50 mL) and 2-iodylbenzoic acid (IBX; 3.36 g, 12.0 mmol, 3 equiv) was added. The resulting suspension was stirred at 50 °C for 5 h and was then filtered through Celite. The solvent was removed on a rotary evaporator and the residue purified by column chromatography (pentane–EtOAc, 1:1) to afford an orange solid; yield: 630 mg (78%). The product was stored under an argon atmosphere in the fridge.

R_f = 0.45 (pentane–EtOAc, 1:1).

IR (KBr): 3422, 1718, 1668, 1602, 1567, 1503, 1454, 1413, 1366, 1334, 1291, 1262, 1231, 1190, 1161, 1146, 1130, 1075, 962, 757 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 9.70 (d, *J* = 7.7 Hz, 1 H), 7.66 (d, *J* = 15.7 Hz, 1 H), 7.42 (d, *J* = 7.8 Hz, 1 H), 7.30 (m, 1 H), 6.78 (t, *J* = 7.5 Hz, 1 H), 6.66 (dd, *J* = 7.7, 15.7 Hz, 1 H), 6.55 (d, *J* = 8.2 Hz, 1 H), 5.07 (br s, 1 H), 4.06 (d, *J* = 4.1 Hz, 2 H), 2.30 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 203.0, 193.8, 147.7, 145.3, 132.6, 128.8, 128.8, 119.7, 118.1, 112.1, 53.8, 27.4.

MS (EI): *m*/*z* = 203 [M^+] (21), 160 (73), 132 (57), 131 (20), 130 (100), 118 (29), 117 (51), 115 (12), 103 (12), 77 (20).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{12}H_{13}NO_2$: 203.0947; found: 203.0938.

_N_-{2-[(_E_)-3-Oxoprop-1-enyl]phenyl}-_N_-(2-oxopropyl)acetamide (26)

A few drops of pyridine and AcCl (220 μL, 3.08 mmol, 1.25 equiv) were added to a soln of (*E*)-3-[2-(2-oxopropylamino)phenyl]prop-2-enal (500 mg, 2.46 mmol, 1 equiv) in toluene (10 mL). The mixture was stirred at 80 °C for 30 min, then H_2O (10 mL) was added. The organic layer was washed with H_2O (5 mL) and dried ($MgSO_4$) and the solvent was removed on the rotary evaporator. The residue was purified by column chromatography (hexane–EtOAc, 1:1) to afford a colorless resin; yield: 178 mg (30%).

R_f = 0.06 (hexane–EtOAc, 1:1).

IR (film): 3449, 2922, 1730, 1671, 1597, 1483, 1459, 1380, 1357, 1311, 1287, 1257, 1228, 1174, 1128, 1062, 1040, 980, 752, 600 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.73 (d, *J* = 7.7 Hz, 1 H), 7.85 (d, *J* = 16.1 Hz, 1 H), 7.73 (d, *J* = 7.4 Hz, 1 H), 7.40–7.51 (m, 3 H), 6.71 (dd, *J* = 7.7, 16.1 Hz, 1 H), 4.72 (d, *J* = 22.6 Hz, 1 H), 4.08 (d, *J* = 17.6 Hz, 1 H), 2.17 (s, 3 H), 1.82 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.5, 193.4, 170.7, 146.4, 142.5, 132.4, 132.0, 131.0, 129.1 (Ph-C), 128.4, 127.7, 59.1, 27.2, 21.9.

MS (EI): *m*/*z* (%) = 245 [M$^+$] (6), 203 (17), 202 (40), 186 (15), 160 (78), 132 (71), 131 (19), 130 (100), 103 (10), 77 (20).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{14}H_{15}NO_3$: 245.1052; found: 245.1054.

Lactone Products

***cis*-5-(4-Chlorophenyl)-4-phenyltetrahydrofuran-2-one (*cis*-1a)**

Colorless oil; yield: 121 mg (44%).

R_f = 0.07 (hexane–MTBE, 4:1).

t_R (50_20): 12.53 min.

IR (film): 3064, 3033, 2927, 1782, 1600, 1494, 1455, 1413, 1318, 1301, 1173, 1144, 1091, 1030, 1013, 980, 878, 818, 798, 734, 701, 515 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.07 (m, 5 H), 6.86–6.79 (m, 4 H), 5.79 (d, *J* = 6.8 Hz, 1 H), 4.08–4.00 (m, 1 H), 3.06 (dd, *J* = 17.6, 8.2 Hz, 1 H), 2.92 (dd, *J* = 17.4, 5.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.0, 136.1, 133.8, 133.4, 128.1, 127.8, 127.5, 127.3, 126.7, 83.6, 46.4, 34.7.

MS (EI): *m*/*z* (%) = 274 [M$^+$] (3), 272 (8), 178 (1), 165 (1), 139 (2), 132 (2), 115 (1), 104 (100), 78 (6), 51 (2).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{13}ClO_2$: 272.0604; found: 272.0605.

***trans*-5-(4-Chlorophenyl)-4-phenyltetrahydrofuran-2-one (*trans*-1a)**

Colorless oil; yield: 24 mg (9%).

R_f = 0.15 (hexane–MTBE, 4:1).

t_R (50_20): 12.79 min.

IR (film): 3064, 3032, 2925, 1787, 1601, 1493, 1455, 1413, 1268, 1195, 1144, 1091, 1002, 810, 760, 699, 511 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.28 (m, 5 H), 7.21–7.08 (m, 4 H), 5.38 (d, *J* = 8.8 Hz, 1 H), 3.58–3.48 (m, 1 H), 3.06 (dd, *J* = 17.6, 8.5 Hz, 1 H), 2.94 (dd, *J* = 17.4, 11.1 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.6, 137.2, 136.2, 134.4, 129.0, 128.7, 127.9, 127.2, 126.8, 86.5, 50.6, 36.9.

MS (EI): *m*/*z* (%) = 274 [M$^+$] (2), 272 (7), 139 (2), 132 (2), 131 (2), 115 (2), 111 (2), 104 (100), 78 (6), 77 (6), 51 (2).

HRMS (EI): *m*/*z* [M + Na$^+$] calcd for $C_{16}H_{13}ClNaO_2$: 295.0502; found: 295.0501.

***cis*-5-(4-Bromophenyl)-4-phenyltetrahydrofuran-2-one (*cis*-1b)**

Colorless oil; yield: 118 mg (37%).

R_f = 0.10 (hexane–EtOAc, 7:1).

t_R (50_20): 13.03 min.

IR (film): 3088, 3064, 3032, 2929, 1783, 1594, 1491, 1455, 1409, 1318, 1302, 1173, 1144, 1030, 1010, 980, 879, 795, 731, 701, 514 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.23 (m, 2 H), 7.19–7.13 (m, 3 H), 6.89–6.75 (m, 4 H), 5.79 (d, *J* = 6.8 Hz, 1 H), 4.10–4.02 (m, 1 H), 3.08 (dd, *J* = 17.4, 8.3 Hz, 1 H), 2.93 (dd, *J* = 17.4, 5.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.3, 136.4, 134.6, 131.0, 128.4, 127.8, 127.6, 127.3, 121.8, 83.9, 46.6, 35.0.

MS (EI): *m*/*z* (%) = 318 [M$^+$] (6), 316 (6), 185 (2), 165 (1), 132 (2), 104 (100), 78 (8), 77 (6), 51 (3).

HRMS (EI): *m*/*z* [M + Na$^+$] calcd for $C_{16}H_{13}BrNaO_2$: 338.9997; found: 338.9997.

***trans*-5-(4-Bromophenyl)-4-phenyltetrahydrofuran-2-one (*trans*-1b)**

Light yellow oil; yield: 37 mg (12%).

R_f = 0.22 (hexane–EtOAc, 7:1).

t_R (50_20): 13.35 min.

IR (film): 3063, 3031, 2924, 1786, 1594, 1491, 1455, 1416, 1268, 1194, 1142, 1071, 1035, 1004, 880, 808, 760, 699, 637, 504 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.43 (m, 2 H), 7.40–7.30 (m, 3 H), 7.20–7.14 (m, 2 H), 7.09–7.02 (m, 2 H), 5.37 (d, *J* = 8.6 Hz, 1 H), 3.57–3.46 (m, 1 H), 3.05 (dd, *J* = 17.7, 8.3 Hz, 1 H), 2.93 (dd, *J* = 17.6, 11.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.8, 137.3, 136.8, 131.8, 129.2, 128.1, 127.3, 127.2, 122.6, 86.6, 50.7, 37.1.

Methyl *cis*-4-(5-Oxo-3-phenyltetrahydrofuran-2-yl)benzoate (*cis*-1c)

Colorless solid; yield: 164 mg (56%).

R_f = 0.13 (hexane–MTBE, 3:1).

t_R (50_20): 13.34 min.

IR (KBr): 3033, 2954, 1779, 1708, 1437, 1280, 1176, 984, 698 cm^{-1}.

1H NMR (400 MHz, $CDCl_3$): δ = 7.77 (dt, *J* = 8.3, 1.8 Hz, 2 H), 7.09–7.05 (m, 3 H), 6.97 (m, 2 H), 6.82–6.77 (m, 2 H), 5.84 (d, *J* = 6.8 Hz, 1 H), 4.06 (m, 1 H), 3.84 (s, 3 H), 3.07 (dd, *J* = 17.4, 8.3 Hz, 1 H), 2.91 (dd, *J* = 17.4, 5.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.9, 166.2, 140.4, 136.1, 129.3, 128.9, 128.1, 127.5, 127.3, 125.3, 83.7, 51.7, 46.4, 34.8.

MS (EI): *m*/*z* (%) = 296 [M$^+$] (8), 265 (5), 191 (1), 178 (2), 165 (2), 133 (3), 115 (2), 104 (100), 78 (6).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{16}O_4$: 296.1049; found: 296.1048.

Methyl *trans*-4-(5-Oxo-3-phenyltetrahydrofuran-2-yl)benzoate (*trans*-1c)

Colorless solid; yield: 41 mg (14%).

R_f = 0.31 (hexane–MTBE, 3:1).

t_R (50_20): 13.67 min.

IR (KBr): 3030, 2961, 1786, 1717, 1435, 1277, 1106, 991, 775, 700 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.9 (dt, *J* = 8.3, 1.8, 2 H), 7.32–7.22 (m, 3 H), 7.16 (m, 2 H), 7.09 (m, 2 H), 5.38 (d, *J* = 8.6 Hz, 1 H), 3.83 (s, 3 H), 3.46 (m, 1 H), 2.99 (dd, *J* = 17.7, 8.6 Hz, 1 H), 2.86 (dd, *J* = 17.7, 10.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.8, 166.5, 142.7, 137.4, 130.4, 129.9, 129.2, 128.1, 127.4, 125.4, 86.7, 52.1, 50.8, 37.0.

MS (EI): *m*/*z* (%) = 296 [M$^+$] (9), 265 (2), 191 (1), 178 (1), 165 (2), 133 (3), 115 (2), 104 (100), 78 (7).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{18}H_{16}O_4$: 296.1049; found: 296.1048.

***cis*-4-Phenyl-5-[4-(trifluoromethyl)phenyl]tetrahydrofuran-2-one (*cis*-1d)**
Colorless solid; yield: 108 mg (35%).

R_f = 0.21 (hexane–MTBE, 3:1).

t_R (50_20): 11.34 min.

IR (KBr): 3091, 3065, 3034, 2931, 1775, 1759, 1623, 1429, 1422, 1330, 1187, 1163, 1121, 1069, 1029, 1018, 981, 859, 828, 739, 720, 700, 604, 516 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (d, *J* = 8.3 Hz, 2 H), 7.16–7.07 (m, 3 H), 7.06–7.00 (m, 2 H), 6.85–6.77 (m, 2 H), 5.86 (d, *J* = 6.8 Hz, 1 H), 4.13–4.05 (m, 1 H), 3.10 (dd, *J* = 17.7, 8.3 Hz, 1 H), 2.94 (dd, *J* = 17.4, 5.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.2, 139.7, 136.3, 130.1 (q, *J* = 33 Hz), 128.5, 127.8, 127.7, 126.0, 124.9 (q, *J* = 4 Hz), 123.8 (q, *J* = 269 Hz), 83.8, 46.7, 35.1.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –113.17.

MS (EI): *m*/*z* (%) = 306 [M$^+$] (4), 287 (3), 178 (1), 173 (1), 165 (1), 145 (2), 104 (100), 78 (7), 77 (5), 51 (2).

HRMS (EI): *m*/*z* [M + Na$^+$] calcd for $C_{17}H_{13}F_3NaO_2$: 329.0765; found: 329.0765.

***trans*-4-Phenyl-5-[4-(trifluoromethyl)phenyl]tetrahydrofuran-2-one (*trans*-1d)**
Colorless oil; yield: 27 mg (9%).

R_f = 0.38 (hexane–MTBE, 3:1).

t_R (50_20): 11.57 min.

IR (film): 3063, 3034, 2929, 1788, 1622, 1498, 1420, 1326, 1271, 1193, 1166, 1127, 1069, 1037, 1009, 851, 817, 761, 699, 611, 510 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.59 (d, *J* = 8.3 Hz, 2 H), 7.43–7.31 (m, 3 H), 7.31–7.27 (m, 2 H), 7.22–7.18 (m, 2 H), 5.48 (d, *J* = 8.6 Hz, 1 H), 3.58–3.48 (m, 1 H), 3.08 (dd, *J* = 17.7, 8.6 Hz, 1 H), 2.95 (dd, *J* = 17.7, 11.1 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.7, 141.8, 137.3, 130.9 (q, *J* = 33 Hz), 129.3, 128.2, 127.4, 125.7, 125.7 (q, *J* = 4 Hz), 123.9 (q, *J* = 272 Hz), 86.4, 50.8, 37.2.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –62.93.

MS (EI): *m*/*z* (%) = 306 [M$^+$] (5), 287 (4), 173 (2), 145 (3), 127 (2), 115 (2), 104 (100), 78 (7), 77 (5), 51 (2).

HRMS (EI): *m*/*z* [M + Na$^+$] calcd for $C_{17}H_{13}F_3NaO_2$: 329.0765; found: 329.0769.

***cis*-5-(3-Fluorophenyl)-4-phenyltetrahydrofuran-2-one (*cis*-1e)**
Colorless solid; yield: 119 mg (46%).

R_f = 0.22 (hexane–EtOAc, 6:1).

t_R (50_20): 11.53 min.

IR (KBr): 3079, 3031, 2962, 2927, 1775, 1765, 1756, 1591, 1489, 1455, 1382, 1304, 1273, 1179, 1148, 1139, 1082, 1027, 986, 969, 866, 791, 777, 729, 705, 693, 522 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.16–7.06 (m, 4 H), 6.87–6.79 (m, 3 H), 6.73–6.67 (m, 1 H), 6.65–6.59 (m, 1 H), 5.80 (d, *J* = 6.8 Hz, 1 H), 4.09–4.02 (m, 1 H), 3.07 (dd, *J* = 17.4, 8.3 Hz, 1 H), 2.93 (dd, *J* = 17.6, 5.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.3, 162.5 (d, *J* = 247 Hz), 138.2 (d, *J* = 8 Hz), 136.4, 129.5 (d, *J* = 8 Hz), 128.4, 127.8, 127.6, 121.3 (d, *J* = 3 Hz), 114.7 (d, *J* = 21 Hz), 112.9 (d, *J* = 23 Hz), 83.8 (d, *J* = 2 Hz), 46.8, 35.0.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –63.00.

MS (EI): *m*/*z* (%) = 256 [M$^+$] (8), 228 (3), 183 (1), 132 (1), 123 (1), 104 (1), 95 (2), 78 (7), 77 (5), 51 (2).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{13}FO_2$: 256.0900; found: 256.0901.

***trans*-5-(3-Fluorophenyl)-4-phenyltetrahydrofuran-2-one (*trans*-1e)**
Colorless oil; yield: 16 mg (6%).

R_f = 0.28 (hexane–EtOAc, 6:1).

t_R (50_20): 11.73 min.

IR (film): 3065, 3033, 2926, 1787, 1616, 1593, 1490, 1454, 1419, 1270, 1195, 1146, 1035, 1003, 967, 907, 875, 789, 759, 699, 522 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.27 (m, 4 H), 7.24–7.18 (m, 2 H), 7.08–7.00 (m, 1 H), 6.98–6.92 (m, 2 H), 5.44 (d, *J* = 8.6 Hz, 1 H), 3.63–3.53 (m, 1 H), 3.09 (dd, *J* = 17.7, 8.6 Hz, 1 H), 2.94 (dd, *J* = 17.7, 10.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.8, 162.8 (d, *J* = 248 Hz), 140.4 (d, *J* = 7 Hz), 137.6, 130.3 (d, *J* = 8 Hz), 129.2, 128.1, 127.3, 121.1 (d, *J* = 3 Hz), 115.6 (d, *J* = 21 Hz), 112.6 (d, *J* = 22 Hz), 86.5 (d, *J* = 2 Hz), 50.6, 37.1.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –112.08.

MS (EI): *m*/*z* (%) = 256 [M$^+$] (10), 228 (3), 196 (1), 183 (2), 165 (1), 133 (2), 123 (2), 104 (100), 95 (3), 78 (7), 77 (6), 51 (2).

HRMS (EI): *m*/*z* [M + Na$^+$] calcd for $C_{16}H_{13}FNaO_2$: 279.0797; found: 279.0800.

***cis*-5-(3-Chlorophenyl)-4-phenyltetrahydrofuran-2-one (*cis*-1f)**
Colorless solid; yield: 135 mg (50%).

R_f = 0.09 (hexane–MTBE, 4:1).

t_R (50_20): 12.42 min.

IR (KBr): 3030, 1775, 1758, 1575, 1495, 1454, 1377, 1303, 1260, 1177, 1145, 1028, 982, 945, 882, 783, 741, 705, 685 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.17–7.08 (m, 4 H), 7.04 (t, *J* = 7.7 Hz, 1 H), 6.92–6.89 (m, 1 H), 6.86–6.80 (m, 2 H), 6.79–6.75 (m, 1 H), 5.78 (d, *J* = 7.1 Hz, 1 H), 4.09–4.02 (m, 1 H), 3.07 (dd, *J* = 17.4, 8.3 Hz, 1 H), 2.93 (dd, *J* = 17.6, 6.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.2, 137.7, 136.4, 134.1, 129.2, 128.5, 128.0, 127.9, 127.7, 125.9, 123.8, 83.8, 46.8, 35.0.

MS (EI): *m*/*z* (%) = 272 [M$^+$] (3), 244 (1), 178 (2), 165 (2), 139 (2), 132 (1), 131 (1), 115 (3), 104 (100), 91 (1), 89 (2), 77 (6), 63 (1).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{16}H_{13}ClO_2$: 272.0604; found: 272.0605.

***trans*-5-(3-Chlorophenyl)-4-phenyltetrahydrofuran-2-one (*trans*-1f)**
Colorless solid; yield: 31 mg (11%).

R_f = 0.17 (hexane–MTBE, 4:1).

t_R (50_20): 12.67 min.

IR (KBr): 3064, 3032, 2925, 1787, 1600, 1575, 1497, 1456, 1354, 1318, 1270, 1194, 1145, 1035, 1000, 891, 786, 760, 699, 643 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.15 (m, 8 H), 7.04–6.99 (m, 1 H), 5.38 (d, *J* = 8.6 Hz, 1 H), 3.60–3.50 (m, 1 H), 3.05 (dd, *J* = 17.4, 8.6 Hz, 1 H), 2.91 (dd, *J* = 17.6, 10.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.8, 139.9, 137.5, 134.7, 129.9, 129.2, 128.8, 128.1, 127.3, 125.7, 123.7, 86.4, 50.6, 37.0.

MS (EI): *m*/*z* (%) = 274 [M^+] (3), 272 (7), 144 (1), 165 (2), 139 (1), 132 (1), 115 (2), 104 (100), 78 (7), 51 (3).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{13}ClO_2$: 272.0604; found: 272.0608.

***cis*-5-(3-Bromophenyl)-4-phenyltetrahydrofuran-2-one (*cis*-1g)**
Purification by Kugelrohr distillation (5×10^{-4} mbar, 130–150 °C), followed by column chromatography (hexane–MTBE, 5:1); colorless solid; yield: 155 mg (49%).

R_f = 0.10 (hexane–MTBE, 5:1).

t_R (50_20): 12.89 min.

IR (KBr): 3064, 3030, 3007, 2927, 1773, 1756, 1598, 1570, 1495, 1476, 1454, 1434, 1416, 1320, 1303, 1261, 1177, 1145, 1073, 1028, 980, 937, 882, 781, 738, 702, 676, 508 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.23 (m, 1 H), 7.17–7.12 (m, 3 H), 7.07–7.04 (m, 1 H), 6.98 (t, *J* = 7.8 Hz, 1 H), 6.87–6.79 (m, 3 H), 5.77 (d, *J* = 6.8 Hz, 1 H), 4.08–4.01 (m, 1 H), 3.07 (dd, *J* = 17.6, 8.2 Hz, 1 H), 2.93 (dd, *J* = 17.6, 5.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.2, 137.9, 136.3, 130.9, 129.4, 128.9, 128.5, 127.9, 127.7, 124.3, 122.2, 83.7, 46.8, 34.9.

MS (EI): *m*/*z* (%) = 318 (7), 316 [M^+] (7), 185 (2), 183 (2), 165 (2), 115 (2), 104 (100), 78 (8), 76 (2), 51 (3).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{13}BrO_2$: 316.0099; found: 316.0099.

***trans*-5-(3-Bromophenyl)-4-phenyltetrahydrofuran-2-one (*trans*-1g)**
Colorless oil; yield: 53 mg (17%).

R_f = 0.18 (hexane–MTBE, 5:1).

t_R (50_20): 13.20 min.

IR (film): 3063, 3031, 2925, 1786, 1599, 1571, 1456, 1432, 1318, 1268, 1194, 1144, 1095, 1074, 1035, 998, 886, 784, 759, 733, 698, 678, 643 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.41–7.36 (m, 1 H), 7.34–7.20 (m, 4 H), 7.14–7.06 (m, 3 H), 7.01–6.95 (m, 1 H), 5.30 (d, *J* = 8.3 Hz, 1 H), 3.52–3.42 (m, 1 H), 2.99 (dd, *J* = 17.7, 8.6 Hz, 1 H), 2.84 (dd, *J* = 17.6, 10.7 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.8, 140.1, 137.5, 131.8, 130.2, 129.2, 128.5, 128.1, 127.3, 124.2, 122.8, 86.3, 50.6, 37.0.

MS (EI): *m*/*z* (%) = 318 (6), 316 [M^+] (6), 185 (2), 183 (2), 165 (2), 131 (2), 115 (3), 104 (100), 91 (2), 78 (8), 76 (2), 51 (3).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{16}H_{13}BrO_2$: 316.0099; found: 316.0100.

5-(2-Chlorophenyl)-4-phenyltetrahydrofuran-2-one (1h)
Diastereomeric mixture; yield: 87 mg (32%).

R_f = 0.11 (hexane–EtOAc, 6:1).

t_R (50_20): 12.13 (D1, *cis*); 12.51 min (D2, *trans*).

IR (film): 3064, 3032, 1786, 1597, 1575, 1497, 1478, 1455, 1445, 1266, 1194, 1174, 1145, 1034, 1001, 882, 759, 701, 621 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.52–6.87 (m, 9 H, D1 + D2), 6.14 (d, *J* = 6.1 Hz, 1 H, D2), 5.88 (d, *J* = 5.3 Hz, 1 H, D1), 4.33–4.26 (m, 1 H, D2), 3.73–3.74 (m, 1 H, D1), 3.27 (dd, *J* = 17.7, 8.6 Hz, 1 H, D2), 3.06 (dd, *J* = 17.7, 8.8 Hz, 1 H, D1), 2.96 (dd, *J* = 17.7, 2.3 Hz, 1 H, D2), 2.81 (dd, *J* = 17.9, 6.6 Hz, 1 H, D1).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 176.4 (D2), 176.1 (D1), 139.8, 137.7, 136.2, 133.7, 132.2, 130.8, 130.0, 129.7, 129.0, 128.8, 128.8, 128.2, 127.8, 127.4, 127.3, 127.2, 127.0, 126.9, 126.5, 126.4, 84.2 (D1), 82.3 (D2), 48.7 (D1), 44.3 (D2), 36.5 (D2), 35.8 (D1).

MS (EI): *m*/*z* (%) = 274 [M^+] (3), 272 (8), 165 (1), 139 (2), 132 (2), 131 (2), 104 (100), 78 (6), 77 (6), 51 (2).

HRMS (EI): *m*/*z* [M + Na^+] calcd for $C_{16}H_{13}ClNaO_2$: 295.0512; found: 295.0501.

***l*-4,5-Diphenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (*l*-7a)**
Purification by Kugelrohr distillation (3×10^{-2} mbar, 90–120 °C), followed by column chromatography (hexane–MTBE, 25:1), yellowish oil; yield: 164 mg (53%).

R_f = 0.42 (hexane–EtOAc, 14:1).

t_R (50_20): 10.42 min.

IR (film): 3065, 3036, 1806, 1500, 1174, 1055, 726, 703 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.21–7.06 (m, 8 H), 6.85–6.80 (m, 2 H), 4.27 (dd, *J* = 9.6, 5.3 Hz, 1 H), 3.31 (ddq, *J* = 18.4, 9.6, 1.3 Hz, 1 H), 2.76 (ddq, *J* = 18.2, 5.5, 1.4 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.8, 137.6, 131.3, 128.8, 128.5, 128.4, 127.8, 126.8, 126.8, 124.5 (q, *J* = 286 Hz), 88.5 (q, *J* = 29 Hz), 45.8, 36.8.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –77.5.

MS (EI): *m*/*z* (%) = 306 [M^+] (9), 278 (1), 191 (0.6), 178 (1), 165 (2), 115 (1), 104 (100), 77 (7).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{13}F_3O_2$: 306.0868; found: 306.0866.

***u*-4,5-Diphenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (*u*-7a)**
Colorless solid; yield: 95 mg (31%).

R_f = 0.35 (hexane–EtOAc, 14:1).

t_R (50_20): 11.11 min.

IR (KBr): 3069, 3038, 1792, 1500, 1307, 1176, 1136, 1029, 928, 761, 726, 699 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.56–7.49 (m, 2 H), 7.45–7.36, m, 6 H), 7.34–7.30 (m, 2 H), 3.99 (t, *J* = 9.3, 1 H), 3.14 (ddq, *J* = 27.5, 9.6, 1.2 Hz, 1 H), 2.91 (ddq, *J* = 27.0, 9.1, 1.2 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.2, 135.6, 133.9, 129.5, 129.3, 129.3, 128.8, 128.7, 125.5, 123.8 (q, *J* = 285 Hz), 87.5 (q, *J* = 29 Hz), 51.5, 35.2.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.6.

MS (EI): *m*/*z* (%) = 306 [M^+] (6), 278 (2), 209 (1), 178 (1), 165 (1), 131 (1), 115 (1), 104 (100), 77 (7).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{17}H_{13}F_3O_2$: 306.0868; found: 306.0867.

4-(4-Methoxyphenyl)-5-phenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (7b)
Diastereomeric mixture, colorless solid; yield: 310 mg (92%).

***l*-7b**
R_f = 0.19 (hexane–EtOAc, 14:1).

t_R (50_20): 11.61 min.

IR (film): 3065, 3037, 3005, 2959, 2842, 1806, 1613, 1586, 1516, 1451, 1417, 1297, 1257, 1174, 911, 833, 726, 703, 553, 523 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.25–7.01 (m, 5 H), 6.78–6.71 (m, 2 H), 6.67–6.60 (m, 2 H), 4.25 (dd, *J* = 9.5 Hz, 6.2 Hz, 1 H), 3.71 (s, 3 H), 3.32–3.22 (m, 1 H), 2.77–2.68 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.8, 159.1, 131.3, 129.6, 129.2, 128.8, 127.8, 126.9, 124.6 (q, *J* = 286 Hz), 113.8, 88.5 (q, *J* = 29 Hz), 55.2, 45.2, 36.6.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –76.9.

MS (EI): *m*/*z* (%) = 336 [M^+] (24), 165 (1), 161 (1), 134 (100), 119 (11), 105 (2), 91 (8), 77 (4), 65 (3), 51 (1).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{18}H_{15}F_3O_3$: 336.0969; found: 336.0970.

***u*-7b**

R_f = 0.10 (hexane–EtOAc, 14:1).

t_R (50_20): 12.32 min.

IR (KBr): 3062, 3038, 3005, 2963, 2935, 2843, 1801, 1614, 1582, 1518, 1452, 1411, 1314, 1292, 1183, 1156, 1131, 1030, 922, 888, 798, 767, 725, 699, 530 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 7.49–7.42 (m, 2 H), 7.39–7.33 (m, 3 H), 7.21–7.24 (m, 2 H), 6.89–6.83 (m, 2 H), 3.88 (t, *J* = 9.6 Hz, 1 H), 3.77 (s, 3 H), 3.10–2.99 (m, 1 H), 2.87–2.77 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.3, 159.8, 135.6, 130.4, 129.4, 129.2, 128.7, 125.5, 123.9 (q, *J* = 286 Hz), 114.2, 87.4 (q, *J* = 29 Hz), 55.3, 50.9, 35.4.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.7.

MS (EI): *m*/*z* (%) = 336 [M^+] (14), 134 (100), 119 (9), 117 (7), 105 (2), 103 (1), 91 (7), 89 (1), 77 (4), 65 (3), 51 (2).

HRMS (ESI): *m*/*z* [M^+] calcd for $C_{18}H_{15}F_3O_3$: 336.0969; found: 336.0973.

4-[4-(Dimethylamino)phenyl]-5-phenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (7c)

Diastereomeric mixture, off-white solid which decomposes upon standing in air; yield: 259 mg (74%).

***l*-7c**

R_f = 0.45 (hexane–EtOAc, 6:1).

t_R (50_20): 12.47 min.

IR (KBr): 3090, 3030, 2986, 2894, 2811, 1796, 1616, 1526, 1450, 1353, 1269, 1199, 1182, 1166, 1058, 1021, 998, 937, 910, 889, 821, 812, 732, 700, 659, 522 cm^{-1}.

^1H NMR (400 MHz, CD_2Cl_2): δ = 7.19–7.08 (m, 3 H), 7.08–7.03 (m, 2 H), 6.62–6.56 (m, 2 H), 6.39–6.33 (m, 2 H), 4.13 (dd, *J* = 9.3 Hz, 6.6 Hz, 1 H), 3.12 (ddq, *J* = 18.2, 9.3, 1.3 Hz, 1 H), 2.75 (s, 6 H), 2.62 (ddq, *J* = 18.2, 6.7, 1.2 Hz, 1 H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 174.7, 150.8, 132.4, 130.0, 129.5, 128.5, 127.7, 125.5 (q, *J* = 285 Hz), 124.8, 112.6, 89.2 (q, *J* = 29 Hz), 46.0, 40.8, 37.2.

^{19}F NMR (282 MHz, CD_2Cl_2): δ = –77.3.

MS (EI): *m*/*z* (%) = 349 [M^+] (45), 174 (1), 147 (100), 131 (5), 117 (1), 105 (2), 91 (1), 77 (5), 51 (1).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{19}H_{18}F_3NNaO_2$: 372.1187; found: 372.1186.

***u*-7c**

R_f = 0.36 (hexane–EtOAc, 6:1).

t_R (50_20): 13.32 min.

IR (KBr): 2925, 2896, 2814, 1798, 1621, 1533, 1450, 1363, 1309, 1210, 1185, 1167, 1159, 1130, 1057, 1027, 921, 888, 788, 765, 725, 699, 653, 511 cm^{-1}.

^1H NMR (400 MHz, CD_2Cl_2): δ = 7.59–7.51 (m, 2 H), 7.49–7.42 (m, 3 H), 7.22–7.15 (m, 2 H), 6.78–6.70 (m, 2 H), 3.93 (t, *J* = 9.6 Hz, 1 H), 3.17–3.07 (m, 1 H), 2.98 (s, 6 H), 2.93–2.83 (m, 1 H).

^{13}C NMR (100 MHz, CD_2Cl_2): δ = 173.6, 150.8, 136.0, 130.1, 129.5, 128.8, 125.7, 124.3 (q, *J* = 286 Hz), 120.5, 112.2, 87.4 (q, *J* = 27 Hz), 51.0, 40.3, 35.4.

^{19}F NMR (282 MHz, CD_2Cl_2): δ = –71.9.

MS (EI): *m*/*z* (%) = 349 [M^+] (45), 174 (1), 147 (100), 131 (5), 118 (1), 105 (3), 91 (1), 77 (6), 51 (1).

HRMS (ESI): *m*/*z* [M + Na^+] calcd for $C_{19}H_{18}F_3NNaO_2$: 372.1187; found: 372.1186.

5-Acetyl-4,5-diphenyltetrahydrofuran-2-one (7d)

Diastereomeric mixture (D1 = *like*, D2 = *unlike*), colorless solid; yield: 77 mg (55%).

R_f = 0.05 (hexane–MTBE, 20:1).

t_R (70_20): 12.64 (D1), 13.19 min (D2).

IR (KBr): 3032, 2924, 2853, 1790, 1716, 1496, 1455, 1410, 1353, 1176, 1140, 1088, 1061, 1030, 992, 969, 754, 698 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.75–6.90 (m, 10 H, D1 and 10 H, D2), 4.61 (dd, *J* = 8.6, 4.5 Hz, 1 H, D1), 4.12 (d, *J* = 7.9 Hz, 1 H, D2), 3.02 (dd, *J* = 18.0, 8.9 Hz, 1 H, D1), 2.88–2.65 (m, 1 H, D1 and 2 H, D2), 2.21 (s, 3 H), 1.96 (s, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 204.8, 204.6, 175.5, 174.9, 138.8, 137.8, 137.7, 133.7, 129.0, 128.9, 128.8, 128.4, 128.2, 128.2, 128.0, 127.7, 127.2, 125.5, 125.2, 95.5, 95.4, 51.8 (D2), 46.3 (D1), 36.4, 36.3, 27.6, 25.4.

MS (EI) D1: *m*/*z* (%) = 237 (100), 219 (37), 178 (4), 168 (2), 167 (12), 165 (11), 152 (6), 131 (3), 115 (5), 106 (3), 105 (40), 91 (2), 89 (1), 77 (16), 63 (1), 51 (4).

MS (EI) D2: *m*/*z* (%) = 237 (100), 220 (6), 219 (37), 209 (2), 193 (5), 191 (10), 181 (1), 178 (4), 167 (12), 165 (11), 159 (1), 152 (6), 131 (3), 115 (5), 105 (40), 91 (2), 77 (16), 63 (1), 51 (4).

HRMS (ESI): : *m*/*z* [M + Na^+] calcd for $C_{18}H_{16}NaO_3$: 303.0992; found: 303.0990.

Methyl 5-Oxo-2,3-diphenyltetrahydrofuran-2-carboxylate (7e)

Diastereomeric mixture (D1 = *like*, D2 = *unlike*), colorless solid; yield: 115 mg (78%).

R_f = 0.25 (hexane–MTBE, 4:1).

t_R (70_20): 13.28 (D1), 13.77 min (D2).

IR (KBr): 3031, 1790, 1736, 1449, 1434, 1286, 1266, 1231, 1179, 1143, 1090, 1052, 1024, 1005, 954, 888, 751, 725, 697 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 7.72–7.65 (m, 2 H), 7.46–7.27 (m, 8 H), 7.19–7.06 (m, 8 H), 6.94–6.89 (m, 2 H), 4.52 (dd, *J* = 8.5, 4.3 Hz, 1 H, D1), 4.08 (dd, *J* = 8.3, 5.0 Hz, 1 H, D2), 3.81 (s, 3 H), 3.39 (s, 3 H), 3.11 (dd, *J* = 17.7, 8.5 Hz, 1 H, D1), 2.93–2.76 [m, 1 H (D1), 2 H (D2)].

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 174.5, 171.1, 168.5, 137.8, 137.7, 137.3, 134.2, 128.9, 128.8, 128.5, 128.3, 128.3, 128.3, 128.2, 127.9, 127.8, 127.5, 125.8, 125.6, 90.7, 90.6, 53.5, 52.5, 52.1, 49.0, 36.2, 35.9.

MS (EI) D1: *m*/*z* (%) = 296 [M^+] (1), 239 (2), 238 (18), 237 (100), 220 (3), 219 (18), 194 (1), 193 (3), 191 (6), 189 (2), 179 (2), 178 (4), 167 (6), 165 (8), 152 (5), 132 (1), 131 (3), 115 (4), 106 (3), 105 (30), 104 (79), 103 (10), 77 (18), 51 (4).

MS (EI) D2: *m/z* (%) = 296 [M$^+$] (1), 237 (51), 219 (8), 191 (3), 178 (3), 167 (3), 165 (5), 152 (3), 105 (24), 104 (100), 91 (2), 89 (1), 77 (15), 63 (1), 51 (3).

HRMS (ESI): *m/z* [M + Na$^+$] calcd for $C_{18}H_{16}NaO_4$: 319.0941; found: 319.0934.

Methyl 3-(4-Methoxyphenyl)-5-oxo-2-phenyltetrahydrofuran-2-carboxylate (7f)

Diastereomeric mixture (D1 = *like*, D2 = *unlike*), colorless solid; yield: 153 mg (94%).

R_f = 0.26 (hexane–EtOAc, 4:1).

t_R (70_20): 14.42 (D1), 15.10 min (D2).

IR (KBr): 2953, 2840, 1781, 1742, 1612, 1516, 1459, 1449, 1407, 1293, 1252, 1252, 1202, 1175, 1138, 1055, 1032, 962, 890, 828, 701 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.60 (m, 2 H), 7.46–7.34 (m, 3 H), 7.23–7.10 (m, 7 H), 6.92–6.78 (m, 4 H), 6.64–6.75 (m, 2 H), 4.46 (dd, *J* = 8.4, 4.8 Hz, 1 H, D1), 4.07–4.00 (m, 1 H, D2), 3.81 (s, 3 H), 3.79 (s, 3 H), 3.68 (s, 3 H), 3.42 (s, 3 H), 3.06 (dd, *J* = 17.8, 8.5 Hz, 1 H, D1), 2.93–2.68 (m, 3 H D1, D2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.7, 174.6, 171.1, 168.6, 159.4, 158.7, 137.7, 134.2, 129.4, 129.4, 129.1, 129.0, 128.8, 128.4, 128.1, 127.8, 125.8, 125.6, 114.1, 113.6, 90.6, 90.6, 55.2, 55.0, 53.4, 52.5, 51.4 (D2), 48.3 (D1), 36.2, 35.9.

MS (EI) D1: *m/z* (%) = 326 [M$^+$] (8), 294 (2), 267 (10), 249 (3), 225 (3), 197 (5), 178 (1), 165 (3), 153 (2), 152 (2), 135 (10), 134 (100), 119 (8), 115 (1), 105 (6), 91 (6), 89 (1), 78 (1), 77 (7), 65 (2).

MS (EI) D2: *m/z* (%) = 326 [M$^+$] (5), 267 (4), 225 (1), 197 (2), 165 (2), 153 (1), 135 (11), 134 (100), 119 (9), 105 (4), 91 (6), 89 (1), 77 (5), 65 (2), 51 (2).

HRMS (ESI): *m/z* [M + Na$^+$] calcd for $C_{19}H_{18}NaO_5$: 349.1046; found: 349.1040.

Methyl 3-[4-(Dimethylamino)phenyl]-5-oxo-2-phenyltetrahydrofuran-2-carboxylate (7g)

Diastereomeric mixture (D1 = *like*, D2 = *unlike*), off-white solid which decomposes upon standing; yield: 166 mg (98%).

R_f = 0.25 (hexane–EtOAc, 4:1).

t_R (70_20): 15.56 (D1), 16.67 min (D2).

IR (KBr): 2993, 2807, 1785, 1742, 1618, 1528, 1449, 1434, 1359, 1267, 1238, 1202, 1173, 1136, 1071, 1056, 1023, 950, 802, 755, 729, 697 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.70–7.61 (m, 2 H), 7.45–7.34 (m, 3 H), 7.20–7.08 (m, 7 H), 6.80–6.65 (m, 4 H), 6.48–6.40 (m, 2 H), 4.41 (dd, *J* = 8.3, 5.3 Hz, 1 H, D1), 3.98 (t, *J* = 7.3 Hz, D2, 1 H), 3.79 (s, 3 H), 3.46 (s, 3 H), 3.08–2.97 (m, 1 H, D1), 2.96 (s, 6 H), 2.88–2.67 (m, 3 H), 2.83 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.1, 175.0, 171.2, 168.8, 150.3, 149.7, 138.0, 134.4, 129.1, 128.7, 128.6, 128.3, 128.0, 127.8, 125.9, 125.8, 124.4, 124.2, 112.3, 112.1, 90.8, 90.7, 53.4, 52.5, 51.6, 48.4, 40.3, 40.3, 36.2, 35.9.

MS (EI) D1: *m/z* (%) = 340 [M$^+$] (7), 339 (35), 280 (2), 238 (5), 210 (3), 194 (1), 174 (2), 165 (2), 148 (11), 147 (100), 146 (26), 131 (4), 117 (1); 105 (3), 77 (5).

MS (EI) D2: *m/z* (%) = 340 [M$^+$] (7), 339 (32), 280 (2), 238 (4), 210 (2), 174 (2), 148 (11), 147 (100), 146 (29), 131 (5), 117 (1), 105 (3), 103 (2), 77 (5).

HRMS (ESI): *m/z* [M + Na$^+$] calcd for $C_{20}H_{21}NNaO_4$: 362.1363; found: 362.1356.

4-Methyl-5-phenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (12a)

Diastereomeric mixture (D1 = *like*, D2 = *unlike*), colorless oil; yield: 100 mg (82%).

R_f = 0.18 (hexane–MTBE, 9:1).

t_R (70_20): 8.98 (D1), 9.13 min (D2).

IR (film): 2983, 1806, 1495, 1452, 1426, 1389, 1361, 1281, 1171, 1104, 1014, 934, 916, 765, 718, 700 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.6–7.4 (m, 5 H, D1, 5 H, D2), 3.21–3.13 (m, 1 H, D1), 3.09–3.02 (m, 1 H, D1), 3.04–2.99 (m, 1 H, D2), 2.78–2.70 (m, 1 H, D2), 2.56–2.48 (m, 1 H, D2), 2.30–2.23 (m, 1 H, D1), 1.58–1.54 (m, 3 H, D2), 0.84 (d, *J* = 7.2 Hz, 3 H, D1).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.0 (D1), 173.3 (D2), 135.8, 129.5, 129.3, 128.7, 128.5, 126.1 (d, *J* = 1.4 Hz), 125.6, 125.3, 124.8 (q, *J* = 285 Hz), 88.1 (q, *J* = 29 Hz), 86.4 (q, *J* = 28 Hz), 39.8 (D2), 36.4 (D1), 36.1 (D2), 34.0 (D1), 18.0 (D1), 15.7 (D2).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.5 (D2), –76.7 (D1).

MS (EI) D1: *m/z* (%) = 244 [M$^+$] (9), 175 (100), 164 (2), 128 (2), 115 (4), 105 (61), 91 (4), 77 (15), 69 (3), 51 (4).

MS (EI) D2: *m/z* (%) = 244 [M$^+$] (11), 175 (100), 164 (2), 145 (1), 128 (2), 115 (6), 105 (60), 91 (4), 77 (16), 69 (3), 51 (5).

HRMS (ESI): *m/z* [M + Na$^+$] calcd for $C_{12}H_{11}F_3NaO_2$: 267.0603; found: 267.0603.

5-Phenyl-4-propyl-5-(trifluoromethyl)tetrahydrofuran-2-one (12b)

Diastereomeric mixture (D1 = *like*, D2 = *unlike*), colorless oil; yield: 123 mg (90%).

R_f = 0.3 (hexane–MTBE, 9:1).

t_R (70_20): 9.98 (D1), 10.33 min (D2).

IR (film): 2963, 2876, 1808, 1497, 1451, 1300, 1277, 1245, 1169, 1050, 1028, 947, 906, 765, 720, 701 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.6–7.4 (m, 5 H, D1, 5 H, D2), 3.03–2.89 (m, 2 H, D1), 2.90–2.82 (m, 1 H, D2), 2.82–2.74 (m, 1 H, D2), 2.59–2.51 (m, 1 H, D2), 2.39–2.31 (m, 1 H, D1), 2.18–2.09 (m, 1 H, D2), 1.81–1.70 (m, 1 H, D2), 1.55–1.44 (m, 1 H, D2), 1.38–1.37 (m, 1 H, D2), 1.37–1.13 (m, 4 H, D1), 1.02 (t, *J* = 7.4 Hz, 3 H, D2), 0.81 (t, *J* = 7.3 Hz, 3 H, D1).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.1, 173.4, 135.9, 131.7, 129.5, 129.2, 128.7, 128.5, 126.1 (d, *J* = 1.8 Hz), 125.6, 124.7 (q, *J* = 285 Hz), 124.3 (q, *J* = 276 Hz), 88.0, (q, *J* = 29 Hz), 86.4 (d, *J* = 28.4 Hz), 45.4 (D2), 39.2 (D1), 34.3, 33.5, 33.3, 32.5 (d, *J* = 1.8 Hz), 22.0, 20.2, 13.8 (D2), 13.6 (D1).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3 (D2), –76.5 (D1).

MS (EI) D1: *m/z* (%) = 272 [M$^+$] (2), 203 (100), 175 (7), 133 (2), 115 (5), 105 (44), 91 (4), 77 (11), 70 (10), 55 (7).

MS (EI) D2: *m/z* (%) = 272 [M$^+$] (9), 203 (100), 175 (20), 133 (2), 115 (5), 105 (47), 91 (3), 77 (14), 70 (29), 55 (12).

HRMS (ESI): *m/z* [M + Na$^+$] calcd for $C_{14}H_{15}NaF_3O_2$: 295.0916; found: 295.0914.

4-Isopropyl-5-phenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (12c)

Diastereomeric mixture (D1 = *unlike*, D2 = *like*), colorless solid; yield: 90 mg (66%).

R_f = 0.32 (hexane–MTBE, 9:1).

t_R (70_20): 9.84 (D1), 10.18 min (D2).

IR (KBr): 2962, 1805, 1495, 1472, 1451, 1426, 1395, 1376, 1269, 1168, 1124, 1092, 1015, 943, 917, 888, 767, 730, 709 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.59–7.39 (m, 5 H, D1, 5 H, D2), 3.01–2.89 (m, 2 H, D1), 2.80–2.73 (m, 1 H, D2), 2.66–2.52 (m, 2 H, D2), 2.56–2.49 (m, 1 H, D1), 2.40–2.33 (m, 1 H, D2), 2.00–1.90 (m, 1 H, D1), 1.01 (d, *J* = 6.6 Hz, 3 H, D2), 0.93 (d, *J* = 6.6 Hz, 3 H, D2), 0.89 (d, *J* = 6.9 Hz, 3 H, D1), 0.39 (d, *J* = 6.7 Hz, 3 H, D1).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.6, 173.9, 136.4, 131.3, 129.4, 129.2, 128.7, 128.3, 126.6, 126.0, 125.9, 123.6, 93.4 (d, *J* = 27.5 Hz), 88.2 (d, *J* = 29.3 Hz), 53.2, 43.4, 31.3, 29.3 (D1), 27.5, 27.2 (D1), 23.1 (D2), 21.4 (D1), 19.6 (D2), 14.6 (D1).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –70.8 (D2), –77.7 (D1).

MS (EI) D1: *m*/*z* (%) = 272 [M$^+$] (1), 203 (100), 175 (2.6), 161 (2), 160 (2), 133 (12), 115 (5), 105 (30), 91 (2), 77 (10), 70 (12), 69 (9), 55 (12).

MS (EI) D2: *m*/*z* (%) = 272 [M$^+$] (19), 203 (61), 175 (8), 160 (3), 133 (10), 115 (9), 105 (33), 77 (21), 70 (100), 69 (14), 55 (40).

HRMS (ESI): *m*/*z* [M + Na$^+$] calcd for $C_{14}H_{15}NaF_3O_2$: 295.0916; found: 295.0917.

***u*-12c** (single diastereomer obtained from crystallization (CH_2Cl_2–hexane).

R_f = 0.32 (hexane–MTBE, 9:1).

t_R (70_20): = 9.84 min.

IR (KBr): 2962, 2880, 1798, 1495, 1471, 1451, 1294, 1270, 1244, 1196, 1168, 1124, 1092, 1063, 1016, 943, 768, 730, 709 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58–7.38 (m, 5 H), 3.03–2.86 (m, 2 H), 2.60–2.46 (m, 1 H), 2.05–1.87 (m, 1 H), 0.89 (d, *J* = 6.80 Hz, 3 H), 0.39 (d, *J* = 6.61 Hz, 3 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.6, 131.3, 129.2, 128.3, 126.7–126.6 (m), 122.9, 88.2 (q, *J* = 28.7 Hz), 43.4, 29.3 (q, *J* = 2.5 Hz), 27.2, 21.4, 14.6.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –77.7.

MS (EI): *m*/*z* (%) = 272 [M$^+$] (1), 203 (100), 175 (2), 165 (1), 164 (1), 160 (2), 157 (2), 145 (1), 133 (11), 115 (4), 105 (29), 91 (2), 70 (12), 55 (11).

HRMS (ESI): *m*/*z* [M + Na$^+$] calcd for $C_{14}H_{15}F_3NaO_2$: 295.0916; found: 295.0915.

Methyl 3-Methyl-5-oxo-2-phenyltetrahydrofuran-2-carboxylate (12d)

Diastereomeric mixture (D1 = *like*, D2 = *unlike*), colorless solid and oil; yield: 101 mg (87%).

t_R (70_20): 10.99 (D1), 11.34 min (D2).

R_f = 0.1 (hexane–MTBE, 9:1).

IR (KBr): 2959, 1794, 1737, 1489, 1448, 1383, 1266, 1212, 1162, 1109, 1027, 996, 932, 804, 733, 700, 632 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61–7.30 (m, 5 H, D1, 5 H, D2), 3.764 (s, 3 H, D2), 3.757 (s, 3 H, D1), 3.34 (dq, *J* = 7.3, 3.1 Hz, 1 H, D1), 3.12–2.99 (m, 1 H, D2), 2.82 (dd, *J* = 17.4, 7.6 Hz, 1 H, D1), 2.64 (dd, *J* = 17.2, 7.9 Hz, 1 H, D2), 2.36 (dd, *J* = 17.3, 6.9 Hz, 1 H, D2), 2.29 (dd, *J* = 17.4, 3.0 Hz, 1 H, D1), 1.30 (d, *J* = 7.0 Hz, 3 H, D2), 0.76 (d, *J* = 7.2 Hz, 3 H, D1).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.6, 174.4, 171.3, 169.4, 137.7, 134.4, 128.8, 128.6, 128.5, 125.6, 125.3, 90.0, 89.6, 53.3 (D1), 52.8 (D2), 40.3, 37.9, 36.7, 36.1, 16.3 (D1), 16.3 (D2).

MS (EI) D1: *m*/*z* (%) = 234 [M$^+$] (1), 175 (100), 147 (1), 131 (1), 129 (5), 115 (4), 105 (74), 91 (4), 89 (1), 77 (18), 63 (1), 51 (4).

MS (EI) D2: *m*/*z* (%) = 234 [M$^+$] (1), 175 (100), 147 (1), 131 (2), 129 (6), 115 (4), 106 (6), 91 (5), 89 (1), 77 (18), 63 (1), 51 (4).

HRMS (ESI): *m*/*z* [M + Na$^+$] calcd for $C_{13}H_{14}NaO_4$: 257.0784; found: 257.0780.

Methyl 5-Oxo-2-phenyl-3-propyltetrahydrofuran-2-carboxylate (12e)

Diastereomeric mixture (D1 = *like*, D2 = *unlike*), colorless oil; yield: 93 mg (71%).

R_f = 0.25 (hexane–MTBE, 4:1).

t_R (70_20): 11.84 (D1), 12.18 min (D2).

IR (film): 3566, 2959, 2873, 2065, 1794, 1740, 1493, 1450, 1436, 1227, 1164, 1116, 1052, 1029, 906, 738, 701 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.60–7.23 (m, 5 H, D1 and 5 H, D2), 3.77 (s, 3 H, D1 and 3 H, D2), 3.20–3.13 (m, 1 H, D1), 2.94–2.85 (m, 1 H, D2), 2.72 (dd, *J* = 17.5, 7.7 Hz, 1 H, D1), 2.67 (dd, *J* = 17.1, 8.1 Hz, 1 H, D2), 2.46 (dd, *J* = 17.4, 8.5 Hz, 1 H, D2), 2.40 (dd, *J* = 17.4, 4.4 Hz, 1 H, D1), 1.92–1.82 (m, 1 H, D2), 1.52–1.10 (m, 4 H, D1 and 3 H, D2), 0.98 (t, *J* = 7.1 Hz, 3 H, D2), 0.79 (t, *J* = 7.0 Hz, 3 H, D1).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 174.8, 174.6, 171.3, 169.7, 137.9, 134.4, 128.8, 128.6, 128.5, 128.5, 125.7, 125.3, 90.1, 89.2, 53.3 (D1), 52.8 (D2), 45.5 (D2), 42.9 (D1), 34.0, 33.9, 32.9, 31.8, 21.2, 20.1, 13.9 (D2), 13.7 (D1).

MS (EI) D1: *m*/*z* (%) = 262 [M$^+$] (1), 205 (1), 204 (14), 203 (100), 175 (1), 160 (1), 157 (1), 133 (2), 131 (2), 129 (3), 128 (2), 117 (3), 115 (5), 106 (5), 105 (66), 103 (1), 91 (3), 77 (14), 51 (2).

MS (EI) D2: *m*/*z* (%) = 207 (2), 204 (16), 203 (100), 143 (2), 133 (3), 131 (3), 129 (3), 117 (5), 115 (6), 106 (5), 105 (70), 103 (3), 91 (3), 77 (16), 55 (3), 51 (3).

HRMS (ESI): *m*/*z* [M + Na$^+$] calcd for $C_{15}H_{18}NaO_4$: 285.1097; found: 285.1093.

Methyl 3-Isopropyl-5-oxo-2-phenyltetrahydrofuran-2-carboxylate (12f)

Diastereomeric mixture (D1 = *unlike*, D2 = *like*), colorless oil; yield: 94 mg (72%).

R_f = 0.24 (hexane–MTBE, 4:1).

t_R (70_20): 11.75 (D1), 12.07 min (D2).

IR (film): 2970, 2881, 1788, 1737, 1491, 1470, 1449, 1433, 1273, 1242, 1188, 1156, 1128, 1090, 1060, 1024, 980, 940, 743, 708 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.62–7.33 (m, 5 H, D1 and 5 H, D2), 3.79 (s, 3 H, D2), 3.74 (s, 3 H, D1), 3.23–3.19 (m, 1 H, D1), 2.96–2.91 (m, 1 H, D2), 2.65 (dd, *J* = 17.9, 8.4 Hz, 1 H, D1), 2.51 (dd, *J* = 17.8, 1.9 Hz, 1 H, D1), 2.47–2.40 (m, 2 H, D2), 2.29–2.21 (m, 1 H, D2), 1.85–1.75 (m, 1 H, D1), 0.97 (d, *J* = 6.7 Hz, 3 H, D2), 0.91 (d, *J* = 6.7 Hz, 3 H, D2), 0.87 (d, *J* = 6.9 Hz, 3 H, D1), 0.49 (d, *J* = 6.9 Hz, 3 H, D1).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.2, 174.9, 171.8, 169.5, 138.4, 134.0, 128.9, 128.5, 128.5, 128.3, 126.0, 125.7, 90.5, 89.6, 53.5, 52.8, 51.2, 47.5, 28.1, 26.5, 22.0, 21.5, 17.4, 15.4.

MS (EI) D1: *m*/*z* (%) = 262 [M$^+$] (1), 205 (2), 204 (14), 203 (100), 175 (2), 161 (3), 160 (2), 157 (3), 134 (2), 133 (19), 131 (3), 129 (1), 117 (1), 115 (5), 106 (4), 105 (46), 103 (1), 91 (2), 77 (13), 55 (4).

MS (EI) D2: *m*/*z* (%) = 205 (1), 204 (14), 203 (100), 175 (2), 161 (2), 160 (2), 157 (3), 134 (2), 133 (17), 131 (3), 129 (2), 115 (7), 106 (4), 105 (49), 91 (2), 77 (13), 69 (4), 55 (5), 51 (2).

HRMS (ESI): *m*/*z* [M + Na$^+$] calcd for $C_{15}H_{18}NaO_4$: 285.1097; found: 285.1092.

3-Ethyl-4-phenyl-4-(trifluoromethyl)oxetan-2-one (13a)

Diastereomeric mixture, colorless oil; yield: 84 mg (34%).

***l*-13a**

R_f = 0.08 (pentane–CH_2Cl_2, 15:1).

IR (film, mixture of diastereomers): 3069, 2978, 2942, 2884, 1851, 1502, 1452, 1327, 1306, 1268, 1176, 1129, 1079, 1041, 1027, 969, 941, 761, 726, 702 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.49 (m, 5 H), 4.00 (dd, *J* = 6.4, 10.2 Hz, 1 H), 1.49–1.63 (m, 1 H), 1.26–1.41 (m, 1 H), 0.99 (t, *J* = 7.4 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.5, 129.8, 129.3, 128.8, 126.4, 123.8 (q, *J* = 282.1 Hz), 78.9 (q, *J* = 32.81 Hz), 58.2, 19.8, 11.0.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –78.1.

MS (EI): *m*/*z* (%) = 244 [M^+] (12), 185 (30), 165 (14), 131 (24), 115 (14), 105 (42), 91 (14), 77 (30), 70 (100), 55 (53), 51 (11).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{12}H_{11}F_3O_2$: 244.0711; found: 244.0706.

***u*-13a**

R_f = 0.08 (pentane–CH_2Cl_2, 15:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.49 (m, 5 H), 3.85 (dd, *J* = 7.3, 9.3 Hz, 1 H), 2.04–2.26 (m, 2 H), 1.24 (t, *J* = 7.5 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.5, 133.3, 129.8, 128.7, 126.2, 123.5 (q, *J* = 282.7 Hz), 79.2 (q, J = 32.2 Hz), 63.4, 18.6, 12.3.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.9.

MS (EI): *m*/*z* (%) = 244 [M^+] (5), 200 (11), 185 (45), 165 (19), 164 (11), 131 (37), 116 (10), 115 (18), 105 (31), 103 (11), 91 (16), 77 (29), 70 (100), 55 (47), 51 (14).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{12}H_{11}F_3O_2$: 244.0711; found: 244.0709.

3-Butyl-4-phenyl-4-(trifluoromethyl)oxetan-2-one (13b)

Diastereomeric mixture, colorless oil; yield: 122 mg (45%).

***l*-13b**

R_f = 0.15 (pentane–CH_2Cl_2, 10:1).

IR (film, mixture of diastereomers): 2962, 2935, 2875, 1854, 1451, 1384, 1333, 1271, 1178, 1153, 1125, 1077, 1049, 970, 948, 806, 763, 719, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.49 (m, 5 H), 4.08–4.03 (m, 1 H), 1.18–1.50 (m, 6 H), 0.81 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6, 129.8, 129.3, 128.8, 126.4, 123.8 (q, *J* = 282.1 Hz), 79.0 (q, *J* = 32.6 Hz), 56.8, 28.5, 25.8, 22.2, 13.5.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –78.0.

MS (EI): *m*/*z* (%) = 272 [M^+] (6), 185 (10), 173 (10), 172 (100), 165 (19), 164 (14), 145 (11), 115 (20), 105 (47), 103 (19) 98 (62), 83 (11), 80 (22), 77 (30), 70 (21), 69 (29), 55 (42).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_{15}F_3O_2$: 272.1024; found: 272.1019.

***u*-13b**

Characterized from a mixture with the *like* isomer.

R_f = 0.15 (pentane–CH_2Cl_2, 10:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.47 (m, 5 H), 3.91 (dd, *J* = 6.9, 9.4 Hz, 1 H), 1.97–2.21 (m, 2 H), 1.17–1.73 (m, 4 H), 0.97 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.6, 133.3, 129.8, 128.7, 126.2, 119.0 (q, *J* = 282.6 Hz), 79.1 (q, *J* = 32.1 Hz), 61.9, 29.8, 24.7, 22.3, 13.6.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –74.0.

MS (EI): *m*/*z* (%) = 272 [M^+] (1), 173 (10), 172 (100), 165 (15), 164 (11), 115 (15), 105 (20), 103 (17), 98 (32), 80 (10), 77 (17), 69 (14), 55 (20).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_{15}F_3O_2$: 272.1024; found: 272.1020.

3-Isobutyl-4-phenyl-4-(trifluoromethyl)oxetan-2-one (13c)

Diastereomeric mixture, colorless oil; yield: 130 mg (48%).

***l*-13c**

R_f = 0.22 (pentane–CH_2Cl_2, 10:1).

IR (film, mixture of diastereomers): 2963, 2936, 2875, 1853, 1470, 1452, 1310, 1267, 1227, 1177, 1130, 1077, 1045, 1025, 980, 948, 762, 728, 715, 700 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.50 (m, 5 H), 4.13 (dd, *J* = 7.2, 9.6 Hz, 1 H), 1.72–1.86 (m, 1 H), 1.15–1.31 (m, 2 H), 0.89 (d, *J* = 6.6 Hz, 3 H), 0.87 (d, *J* = 6.6 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.7, 129.8, 129.3, 128.8, 126.4, 123.9 (q, *J* = 282.1 Hz), 79.0 (q, *J* = 32.6 Hz), 55.2, 34.7, 25.4, 22.6, 21.7.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –77.9.

MS (EI): *m*/*z* (%) = 272 [M^+] (9), 197 (12), 185 (11), 173 (12), 172 (84), 165 (31), 164 (16), 145 (11), 117 (12), 115 (34), 105 (67), 98 (100), 77 (41), 70 (25), 69 (59), 56 (14), 55 (92), 51 (14).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_{15}F_3O_2$: 272.1024; found: 272.1026.

***u*-13c**

R_f = 0.22 (pentane–CH_2Cl_2, 10:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.4–7.5 (m, 5 H), 3.99 (dd, *J* = 5.4, 9.7 Hz, 1 H), 1.99–2.11 (m, 1 H), 1.83–1.97 (m, 2 H), 1.04 (d, *J* = 6.4 Hz, 3 H), 1.01 (d, *J* = 6.28 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4, 133.4, 129.8, 128.7, 126.1, 123.5 (q, *J* = 282.9 Hz), 78.9 (q, *J* = 32.1 Hz), 60.0, 33.6, 26.4, 22.5, 22.1.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.9.

MS (EI): *m*/*z* (%) = 272 [M^+] (3), 173 (13), 172 (100), 165 (28), 164 (12), 117 (14), 115 (28), 105 (37), 103 (11), 98 (67), 77 (30), 70 (16), 69 (37), 56 (12), 55 (55).

HRMS (EI): *m*/*z* [M^+] calcd for $C_{14}H_{15}F_3O_2$: 272.1024; found: 272.1027.

3-Benzyl-4-phenyl-4-(trifluoromethyl)oxetan-2-one (13d)

Diastereomeric mixture (D1 = *like*, D2 = *unlike*), colorless oil; yield: 93 mg (30%).

R_f = 0.08 (pentane–CH_2Cl_2, 10:1).

IR (film): 3066, 3034, 2930, 1854, 1499, 1452, 1329, 1268, 1177, 1146, 1109, 1080, 1047, 1024, 991, 954, 938, 750, 726, 699 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 7.51–7.21 (m, 10 H, D2 and 8 H, D1), 7.07–7.03 (m, 2 H, D1), 4.45 (t, *J* = 8.2 Hz, 1 H, D1), 4.23 (t, *J* = 7.7 Hz, 1 H, D2), 3.5 (dd, *J* = 8.2, 14.8 Hz, 1 H, D2), 3.31 (dd, *J* = 7.4, 14.7 Hz, 1 H, D2), 2.72 (d, *J* = 8.2 Hz, 2 H, D1).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.9, 136.5, 135.4, 132.8, 130.0, 129.8, 129.0, 129.0, 128.8, 128.8, 128.7, 128.6, 128.5, 127.4, 127.2, 126.6, 126.2, 123.8 (q, *J* = 282.36 Hz, D1), 123.5 (q, *J* = 282.8 Hz, D2), 79.5 (q, *J* = 32.3 Hz, D2), 79.3 (q, *J* = 32. 7 Hz, D1), 63.0 (D2), 57.4 (D1), 31.7 (D1), 31.0 (D2).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –77.7 (D1), –73.7 (D2).

MS (EI) D1: *m/z* (%) = 306 [M$^+$] (52), 307 (10), 193 (14), 178 (10), 132 (34), 131 (100), 115 (25), 105 (27), 104 (33), 103 (14), 91 (15), 78 (10), 77 (24).

MS (EI) D2: *m/z* (%) = 306 [M$^+$] (79), 307 (14), 262 (32), 261 (14), 193 (49), 191 (11), 184 (34), 178 (30), 165 (15), 133 (13), 132 (83), 131 (100), 115 (74), 105 (41), 104 (57), 103 (21), 91 (33), 78 (19), 77 (37), 51 (15).

HRMS (EI): *m/z* [M$^+$] calcd for $C_{17}H_{13}F_3O_2$: 306.0868; found: 306.0869.

Methyl 3-Isobutyl-4-oxo-2-phenyloxetane-2-carboxylate (13e)
Diastereomeric mixture (D1 = *like*, D2 = *unlike*), colorless oil; yield: 57 mg (22%).

R_f = 0.26 (pentane–CH_2Cl_2, 2:1).

IR (film): 2958, 1872, 2043, 1840, 1743, 1450, 1389, 1370, 1255, 1192, 1158, 1131, 1058, 934, 815, 757, 736, 699, 506, 420 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.50–7.39 (m, 5 H, D1 and 5 H, D2), 4.26 (t, *J* = 8.2 Hz, 1 H, D2), 3.94 (t, *J* = 8.2 Hz, 1 H, D1), 3.84 (s, 3 H, D2), 3.82 (s, 3 H, D1), 2.04–1.90 (m, 1 H, D1), 1.77–1.65 (m, 2 H, D1 and 1 H, D2), 1.17 (t, *J* = 8.2 Hz, 2 H, D2), 1.02–0.97 (m, 6 H, D1), 0.87–0.81 (m, 6 H, D2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.9, 169.5, 168.8, 168.4, 136.5, 132.6, 129.2, 129.0, 128.7, 128.6, 125.7, 125.6, 81.1, 80.9, 60.9 (D1), 57.8 (D2), 53.4, 53.1, 35.3, 34.5 (D2), 25.7 (D1), 25.5, 22.5, 22.5, 22.2, 22.0.

MS (ESI, MeOH): *m/z* = 285 [M + Na$^+$].

HRMS (ESI): *m/z* [M + Na$^+$] calcd for $C_{15}H_{18}NaO_4$: 285.1097; found: 285.1099.

3-Methyl-4,5-diphenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (20a)
Diastereomeric mixture [D1 = diastereomer **I**, D2 = diastereomer **II** (see Figure 6)], colorless solid and oil; yield: 132 mg (83%).

R_f = 0.38–0.34 (hexane–MTBE, 9:1).

t_R (70_20): 11.62 (D1), 12.05 min (D2).

IR (KBr): 3036, 2937, 1803, 1707, 1501, 1455, 1272, 1172, 1137, 1070, 1031, 948, 784, 764, 725, 704 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.06 (m, 10 H, D2 and 6 H, D1), 6.85 (d, *J* = 7.7 Hz, 2 H, D1), 6.70 (d, *J* = 7.4 Hz, 2 H, D1), 3.78 (d, *J* = 12.7 Hz, 1 H, D1), 3.44–3.28 (m, 2 H, D2), 2.89–2.74 (m, 1 H, D1), 1.16 (d, *J* = 7.0 Hz, 3 H, D1), 1.13–1.08 (m, 3 H, D2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.7, 175.5, 135.7, 133.2, 132.3, 130.6, 129.7, 129.7, 129.3, 129.3, 128.9, 128.9, 128.6, 128.5, 128.3, 127.9, 126.7 (q, *J* = 2 Hz), 125.4 (q, *J* = 2 Hz), 124.2 (q, 280 Hz), 85.8 (q, *J* = 30 Hz), 85.1 (q *J* = 30 Hz), 60.2 (D2), 54.3 (D1), 40.4 (D2), 39.3 (D1), 14.1 (D2), 13.0 (D1).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.1, –75.6.

MS (EI) D1: *m/z* (%) = 320 [M$^+$] (2), 189 (1), 178 (2), 165 (2), 118 (100), 115 (8), 105 (6), 91 (7), 77 (7), 65 (1), 51 (2).

MS (EI) D2: *m/z* (%) = 320 [M$^+$] (1), 189 (1), 178 (2), 118 (100), 115 (7), 105 (5), 91 (7), 89 (2), 77 (7), 65 (1), 51 (2).

HRMS (ESI): *m/z* [M + Na$^+$] calcd for $C_{18}H_{15}F_3NaO_2$: 343.0915; found: 343.0950.

4-(4-Chlorophenyl)-3-methyl-5-phenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (20b)
Diastereomeric mixture [D1 = diastereomer **I**, D2 = diastereomer **II** (see Figure 6)]; yellowish oil; yield: 126 mg (71%).

R_f = 0.24 (hexane–EtOAc, 9:1).

t_R (70_20): 12.46 (D1), 12.93 min (D2).

IR (film): 3033, 2981, 2937, 1804, 1496, 1451, 1271, 1173, 1138, 1094, 1031, 958, 832, 761, 711, 700 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.38 (m, 4 H, D1), 7.37–7.32 (m, 1 H, D1), 7.29–7.21 (m, 6 H, D2), 7.21–7.16 (m, 3 H, D2), 6.95 (d, *J* = 7.8 Hz, 2 H, D1), 6.69 (d, 7.8 Hz, 2 H, D1), 3.81 (d, *J* = 12.5 Hz, 1 H, D1), 3.45–3.32 (m, 2 H, D2), 2.86–2.77 (m, 1 H, D1), 1.23 (d, *J* = 7.0 Hz, 3 H, D1), 1.18 (d, *J* = 6.6 Hz, 3 H, D2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.2, 175.1, 135.5, 135.0, 134.6, 131.8, 130.0, 130.9, 130.3, 129.5, 129.4, 129.2, 128.7, 128.6, 128.2, 126.7, 125.3, 123.0, 123.0, 85.6 (q, *J* = 30.2 Hz), 84.9 (q, *J* = 28 Hz), 59.6, 53.7, 40.4, 39.4, 14.1, 12.9.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –71.0, –75.6.

MS (EI) D1: *m/z* (%) = 354 [M$^+$] (3), 165 (2), 154 (32), 152 (100), 127 (2), 125 (3), 118 (3), 117 (32), 115 (15), 105 (6), 101 (2), 91 (3), 89 (2), 77 (6), 75 (2).

MS (EI) D2: *m/z* (%) = 354 [M$^+$] (3), 282 (1), 179 (2), 154 (33), 152 (100), 127 (2), 125 (2), 117 (31), 115 (15), 105 (6), 91 (4), 77 (6), 75 (2).

HRMS (ESI): *m/z* [M + Na$^+$] calcd for $C_{18}H_{14}ClF_3NaO_2$: 377.0527; found: 377.0528.

3-Methyl-5-phenyl-4-styryl-5-(trifluoromethyl)tetrahydrofuran-2-one (20c)
Diastereomeric mixture [D1 = diastereomer **I**, D2 = diastereomer **II** (see Figure 6)], colorless solid and oil; yield: 142 mg (82%).

R_f = 0.3 (hexane–MTBE, 9:1).

t_R (70_20): 13.02 (D1), 13.32 min (D2).

IR (KBr): 3063, 3030, 2980, 2938, 1803, 1496, 1450, 1315, 1284, 1258, 1227, 1171, 1134, 1069, 1024, 969, 948, 754, 732, 701 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71–7.65 (m, 4 H), 7.55–7.27 (m, 16 H), 6.70 (d, *J* = 15.6 Hz, 1 H, D2), 6.66 (d, *J* = 15.9 Hz, 1 H, D1), 6.47–6.38 (m, 1 H, D2), 5.54 (dd, *J* = 15.7, 9.5 Hz, D1), 3.34 (dd, *J* = 11.9, 9.6 Hz, D1), 3.17 (t, *J* = 11.0 Hz, 1 H, D2), 2.99–2.89 (m, 1 H, D2), 2.51–2.42 (m, 1 H, D1), 1.30 (m, 3 H, D1), 1.28 (d, *J* = 7.2 Hz, 3 H, D2).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 175.6 (D2), 175.4 (D1), 136.2 (D2), 136.0 (D2), 135.9 (D1), 135.8 (D2), 135.4 (D1), 130.8 (D1), 129.6 (D1), 129.4 (D2), 128.8 (D2), 128.8 (D1), 128.6 (D2), 128.4 (D1), 126.7 (D2), 126.5 (D1), 125.8 (D2), 124.1 (q, *J* = 286 Hz, D2), 124.1 (D1), 123.0 (D1), 87.7, 83.9 (q, *J* = 28 Hz, D2), 57.9 (D2), 52.2 (D1), 40.3 (D2), 39.1 (D1), 13.7 (D2), 12.6 (D1).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.8 (D2), –76.5 (D1).

MS (EI) D1: *m/z* (%) = 346 [M$^+$] (9), 202 (2), 144 (100), 129 (77), 115 (10), 105 (6), 103 (2), 91 (6), 89 (2), 77 (8), 65 (2).

MS (EI) D2: *m/z* (%) = 346 [M$^+$] (11), 202 (2), 144 (100), 129 (75), 115 (9), 105 (7), 102 (2), 89 (2), 77 (8), 65 (2).

HRMS (ESI): *m/z* [M + Na$^+$] calcd for $C_{20}H_{17}F_3NaO_2$: 369.1073; found: 369.1075.

20c-II
Single diastereomer isolated by crystallization (CH_2Cl_2–hexane).

R_f = 0.3 (hexane–MTBE, 9:1).

t_R (70_20): 13.32 min.

IR (KBr): 3063, 3042, 2979, 2938, 1803, 1495, 1450, 1315, 1259, 1228, 1171, 1133, 1069, 1021, 967, 754, 732, 701 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.72–7.62 (m, 2 H), 7.55–7.31 (m, 8 H), 6.69 (d, *J* = 15.7 Hz, 1 H), 6.48–6.34 (m, 1 H), 3.22–3.10 (m, 1 H), 3.00–2.85 (m, 1 H), 1.27 (d, *J* = 6.99 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.6, 136.2, 136.0, 135.8, 129.4, 128.8, 128.6, 126.7, 125.8, 124.1 (q, *J* = 288 Hz), 123.2, 83.9 (q, *J* = 28 Hz), 57.9, 40.3, 13.7.

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.8.

MS (EI), *m*/*z* (%) = 346 [M$^+$] (6), 215 (1), 202 (2), 144 (100), 129 (75), 115 (9), 105 (7), 102 (2), 89 (2), 77 (8), 65 (2).

HRMS (ESI): *m*/*z* [M + Na$^+$] calcd for $C_{20}H_{17}F_3NaO_2$: 369.1073; found: 369.1070.

3-(2-Chlorobenzyl)-5-phenyl-5-(trifluoromethyl)tetrahydrofuran-2-one (21)

Diastereomeric mixture, yellowish oil; yield: 81 mg (46%).

R_f = 0.13 (hexane–MTBE, 40:1).

t_R (70_20): 13.07 (D1), 13.17 min (D2).

IR (film): 3065, 2931, 1799, 1573, 1475, 1449, 1304, 1268, 1095, 1032, 976, 910, 679, 651, 599, 548 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.21 (m, 12 H), 7.22–7.02 (m, 6 H), 3.48–3.24 (m, 3 H), 3.05–2.79 (m, 3 H), 2.73–2.45 (m, 3 H), 2.36–2.22 (m, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.6, 175.0, 135.4, 135.4, 135.3, 134.0, 134.0, 131.1, 130.9, 129.9, 129.8, 129.7, 129.5, 128.7, 128.6, 127.2, 127.2, 126.3, 126.1, 125.5, 122.3, 121.7, 83.1 (q, *J* = 30.6 Hz), 83.1 (q, *J* = 32.0 Hz), 39.4, 38.8, 35.7, 34.8, 34.7, 33.5.

^{19}F NMR (282 MHz, $CDCl_3$): δ = – 79.5 (D1), –79.6 (D2).

MS (EI) D1: *m*/*z* (%) = 321 (2), 319 (100), 299 (15), 285 (8), 202 (2), 182 (5), 172 (18), 159 (3), 147 (69), 127 (17), 125 (43), 115 (16), 105 (65), 91 (8), 89 (10), 77 (23), 63 (3), 51 (5).

MS (EI) D2: *m*/*z* (%) = 319 (100), 299 (15), 285 (4), 202 (2), 182 (6), 172 (21), 159 (3), 147 (79), 125 (47), 105 (50), 77 (21), 63 (4), 51 (5).

HRMS (ESI): *m*/*z* [M + Na$^+$] calcd for $C_{18}H_{14}ClF_3NaO_2$: 377.0527; found: 377.0533.

(3a*R,6a*S**)-6a-Phenyltetrahydrofuro[3,4-*b*]furan-2(3*H*)-one (27)**

A soln of IMes·HCl (23.3 mg, 0.0684 mmol, 0.2 equiv) and KO*t*-Bu (6.73 mg, 0.060 mmol, 0.175 equiv) in freshly distilled THF (14 mL) was stirred at r.t. for 30 min. (*E*)-4-(2-Oxo-2-phenylethoxy)but-2-enal (**22**, 69.8 mg, 0.342 mmol, 1 equiv) was added and the mixture was stirred at 60 °C for 16 h. Silica gel was added and the solvent removed on the rotary evaporator. The residue was purified by column chromatography (hexane–EtOAc, 2:1) to afford **27** as colorless oil; yield: 25 mg (36%).

R_f = 0.18 (hexane–EtOAc, 2:1).

IR (film): 3523, 3061, 2978, 2928, 2863, 1776, 1498, 1449, 1417, 1274, 1233, 1203, 1176, 1104, 1060, 1033, 951, 925, 760, 701 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.32 (m, 5 H), 4.30 (d, *J* = 10.7 Hz, 1 H), 4.22 (dd, *J* = 7.0, 9.5 Hz, 1 H), 3.95 (dd, *J* = 3.3, 9.6 Hz, 1 H), 3.87 (d, *J* = 10.7 Hz, 1 H), 3.17–3.10 (m, 1 H), 2.95–2.86 (m, 1 H), 2.56 (dd, *J* = 2.4, 18.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.3, 138.9, 128.8, 128.3, 124.6, 95.5, 80.4, 76.1, 47.6, 34.7.

MS (EI): *m*/*z* (%) = 204 [M$^+$] (36), 146 (31), 105 (100), 77 (29).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{12}H_{12}O_3$: 204.0787; found: 204.0787.

(3a*R,5a*S**,9a*R**)-Hexahydro-7*H*-furo[3,2-*c*]benzofuran-2(3*H*)-one (28)**

A soln of IMes·HCl (37.5 mg, 0.11 mmol, 0.2 equiv) and KO*t*-Bu (10.8 mg, 0.096 mmol, 0.175 equiv) in freshly distilled THF (20 mL) was stirred for 30 min at r.t. (*E*)-4-(2-Oxocyclohexyloxy)but-2-enal (**23**, 100 mg, 0.55 mmol, 1 equiv) was added and the mixture was stirred at 60 °C for 5 h. Silica gel was added and the solvent removed on the rotary evaporator. The residue was purified by column chromatography (hexane–EtOAc, 1:3.5) to afford **28** as a light yellow oil; yield: 41 mg (41%).

R_f = 0.34 (hexane–EtOAc, 1:3.5).

IR (film): 3509, 2939, 2864, 1774, 1452, 1423, 1320, 1290, 1261, 1227, 1209, 1154, 1080, 1051, 1023, 983, 960, 949, 933, 885 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.25 (t, *J* = 9.4 Hz, 1 H), 3.98 (dd, *J* = 6.3, 9.0 Hz, 1 H), 3.65 (dd, *J* = 4.5, 9.7 Hz, 1 H), 2.88–2.73 (m, 2 H), 2.47 (d, *J* = 16.1 Hz, 1 H), 1.98–1.62 (m, 5 H), 1.52–1.23 (m, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.4, 93.7, 80.7, 72.6, 41.2, 35.2, 31.4, 26.8, 21.9, 21.1.

MS (EI): *m*/*z* (%) = 182 [M$^+$] (37), 141 (88), 125 (11), 124 (35), 123 (100), 114 (12), 113 (59), 111 (69), 110 (41), 109 (18), 105 (13), 104 (10), 98 (31), 97 (52), 96 (24), 95 (40), 94 (20), 85 (33), 84 (15), 83 (27), 82 (19), 81 (22), 80 (16), 79 (28), 77 (11), 70 (20), 69 (78), 68 (69), 67 (74), 57 (25), 55 (92), 54 (12), 53 (14).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{10}H_{14}O_3$: 182.0943; found: 182.0941.

(3a*R,9a*R**)-3a-Methyl-3a,4,5,9b-tetrahydronaphtho[2,1-*b*]furan-2(1*H*)-one (29)**

A soln of IMes·HCl (10.2 mg, 0.030 mmol, 0.15 equiv) and KO*t*-Bu (3.14 mg, 0.028 mmol, 0.14 equiv) in freshly distilled THF (4 mL) was stirred for 30 min at r.t. (*E*)-3-[2-(3-Oxobutyl)phenyl]prop-2-enal (**24**, 40.5 mg, 0.20 mmol, 1 equiv) was added and the mixture was stirred at 60 °C for 16 h. Silica gel was added and the solvent removed on the rotary evaporator. The residue was purified by column chromatography (hexane–EtOAc, 4.5:1) to afford **29** as a white solid; yield: 22 mg (55%).

R_f = 0.52 (hexane–EtOAc, 2:1).

IR (film): 3013, 2949, 1767, 1489, 1452, 1425, 1384, 1348, 1319, 1287, 1222, 1189, 1115, 1074, 1045, 972, 931, 889, 770, 741 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24–7.13 (m, 3 H), 6.98–6.95 (m, 1 H), 3.49 (dd, *J* = 7.7, 13.3 Hz, 1 H), 3.25–3.15 (m, 1 H), 3.04–2.92 (m, 1 H), 2.88–2.70 (m, 2 H), 2.28–2.15 (m, 2 H), 1.01 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 175.9, 135.5, 135.2, 128.5, 127.1, 126.1, 124.6, 85.3, 47.4, 33.6, 30.8, 26.4, 18.9.

MS (EI): *m*/*z* (%) = 202 [M$^+$] (26), 174 (38), 159 (25), 156 (46), 143 (16), 142 (19), 141 (14), 132 (14), 131 (100), 130 (22), 129 (32), 128 (30), 117 (25), 116 (23), 115 (46), 91 (21).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{13}H_{14}O_2$: 202.0994; found: 202.0991.

(3a*R,9a*S**)-3a-Methyl-3a,4,5,9b-tetrahydrofuro[2,3-*c*]quinolin-2(1*H*)-one (30)**

DBU (4.5 μL, 0.030 mmol, 0.1 equiv) was added to a soln of (*E*)-3-[2-(2-oxopropylamino)phenyl]prop-2-enal (**25**, 61.0 mg, 0.30 mmol, 1 equiv) and IMes·HCl (12.6 mg, 0.0370 mmol, 0.125 equiv) in THF (6 mL). The mixture was stirred at 60 °C for 16 h and the solvent was removed on the rotary evaporator. The residue was purified by column chromatography (pentane–MTBE, 1:1) to afford **30** as an orange oil; yield: 14 mg (23%).

R_f = 0.53 (pentane–MTBE, 1:1).

IR (KBr): 3410, 2978, 2929, 2871, 1786, 1612, 1497, 1383, 1312, 1287, 1250, 1209, 1186, 1134, 1122, 1078, 1049, 974, 890, 751 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.07 (t, *J* = 7.7 Hz, 1 H), 6.85 (d, *J* = 7.4 Hz, 1 H), 6.66 (t, *J* = 7.4 Hz, 1 H), 6.51 (d, *J* = 8.0 Hz, 1 H),

3.99 (br s, 1 H), 3.67 (d, *J* = 9.9 Hz, 1 H), 3.44–3.52 (m, 2 H), 2.70–2.85 (m, 2 H), 1.15 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.8, 143.1, 128.3, 125.0, 119.1, 117.0, 112.6, 80.3, 53.1, 45.6, 30.1, 18.2.

MS (EI): *m*/*z* (%) = 203 [M$^+$] (100), 204 (15), 161 (11), 160 (83), 158 (23), 144 (17), 143 (11), 133 (11), 132 (94), 118 (21), 117 (35), 115 (12), 77 (16).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{12}H_{13}NO_2$: 203.0946; found: 203.0943.

(3a*R,9b*R**)-5-Acetyl-3a-methyl-3a,4,5,9b-tetrahydrofuro[2,3-*c*]quinolin-2(1*H*)-one (31)**

DBU (4.3 μL, 0.030 mmol, 0.1 equiv) was added to a soln of *N*-{2-[(*E*)-3-oxoprop-1-enyl]phenyl}-*N*-(2-oxopropyl)acetamide (**26**, 69.9 mg, 0.285 mmol, 1 equiv) and IMes·HCl (12.3 mg, 0.0360 mmol, 0.125 equiv) in freshly distilled THF (15 mL). The mixture was stirred at 60 °C for 16 h, silica gel was added and the solvent removed on the rotary evaporator. The residue was purified by column chromatography (hexane–EtOAc, 1:1) to afford **31** as a white solid; yield: 18 mg (26%).

R_f = 0.22 (hexane–EtOAc, 1:2).

IR (film): 1781, 1649, 1606, 1489, 1462, 1377, 1341, 1322, 1296, 1272, 1211, 1185, 1166, 1130, 1087, 1052, 980, 938, 889, 770 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37–7.10 (m, 4 H), 4.26 (br s, 1 H), 3.63 (br d, 1 H), 3.38 (t, *J* = 10.4 Hz, 1 H), 2.83 (d, *J* = 10.6 Hz, 2 H), 2.27 (s, 3 H), 0.78 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 174.5, 170.6, 137.9, 129.9, 127.8, 126.0, 125.1, 124.0, 84.7, 55.3, 44.7, 29.0, 23.1, 20.4.

MS (EI): *m*/*z* (%) = 245 [M$^+$] (56), 204 (13), 203 (100), 161 (10), 160 (80), 158 (21), 144 (24), 132 (77), 130 (31), 118 (15), 117 (22), 115 (10), 77 (16).

HRMS (EI): *m*/*z* [M$^+$] calcd for $C_{14}H_{15}NO_3$: 245.1052; found: 245.1050.

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