Published on 26 November 2021. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 1/5/2022 8:57:23 AM.

NJC

ROYAL SOCIETY OF CHEMISTRY

PAPER

View Article Online
View Journal | View Issue

Check for updates

Cite this: *New J. Chem.*, 2022, **46**, 599

Enantioselective synthesis of 2,3-dihydrofurans using a bifunctional quinine/squaramide organocatalyst†

Zeynep Dilşad Susam, [a] Merve Bozdemir, [a] Gülsüm Gündoğdu [b] and Cihangir Tanyeli *[a]

Received 27th October 2021,
Accepted 26th November 2021

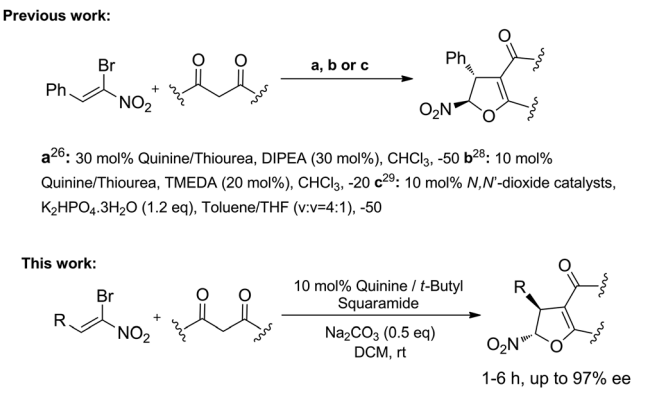
DOI: 10.1039/d1nj05121k

rsc.li/njc

Asymmetric organocatalytic domino type Michael-S_N2 reactions give access to enantiomerically enriched dihydrofuran derivatives that can be used as valuable chiral building blocks. A variety of α-bromonitroalkenes and 1,3-dicarbonyl compounds were allowed to react under optimized conditions, in the presence of a bifunctional quinine-derived sterically encumbered squaramide (H-bond donor) organocatalyst. The conditions developed in this article have great advantages over the methods known in the literature in terms of reaction duration (1–6 h *vs.* 24–96 h) and reaction temperature (room temperature *vs.* −20 °C to −50 °C) giving rise to quite diastereoselective products with good enantioselectivities up to 97% ee.

Introduction

Chiral dihydrofurans (DHFs) possessing easily transformable character to corresponding tetrahydrofurans[1,2] are widely found in many biologically active natural products[3,4] like phyllaemblic acid methyl ester[5–7] and nymphone.[8–10] Although there are a variety of synthetic methods[11–13] to obtain racemic dihydrofurans, enantiomerically enriched DHFs are of greater interest due to their significant biological activity. Many efforts have been devoted to obtaining enantiomerically enriched 2,3-DHFs with different methods such as ring enlargement,[14–18] cyclization,[19–22] kinetic resolution,[23] sulfoximine[24] and ylide annulation with sulfonium salts.[25] In the last decade, several research groups have reported organocatalytic asymmetric synthesis of 2,3-DHFs using various β-dicarbonyls coupled with α-bromonitroalkenes *via* domino Michael/S_N2 type reactions as given in Scheme 1.[26–29] In 2010, Fan *et al.* used 30 mol% of a thiourea/quinine bifunctional organocatalyst to synthesize chiral mono-, bi- and tricyclic 2,3-DHFs at −50 °C in chloroform with an additional base for trapping the HBr evolved in the medium, which inhibits the activity of the catalyst.[26] Although they reached 92% ee for the tricyclic products, other results were not as high as the tricyclic ones in terms of enantioselectivity; their monocyclic derivatives gave a maximum of 77% ee, which was obtained under harsh conditions. Simultaneously, Rueping *et al.* published the results for an epimer of the thiourea/quinine bifunctional organocatalyst used in the previous work.[27] They conducted similar reactions at −20 °C in chloroform to a maximum enantiomeric excess of 90%. They managed to raise the selectivity up to 99% ee as a result of an additional recrystallization step. A similar study was done by Feng and co-workers in the presence of an *S*-proline-derived *N*,*N*′-dioxide organocatalyst.[29] Despite obtaining the target products in up to 94% ee, the reactions required cryogenic temperatures and a stoichiometric amount of a basic additive. Since all of the aforementioned asymmetric reactions were carried out under cryogenic conditions with very long



Scheme 1 Overview of Michael/S_N2 type reactions.

[a] *Middle East Technical University, Department of Chemistry, 06800, Çankaya, Ankara, Turkey. E-mail: tanyeli@metu.edu.tr*
[b] *Turkish-German University, Faculty of Science, Department of Energy Science and Technology, 34820, Beykoz, Istanbul, Turkey*

† Electronic supplementary information (ESI) available. CCDC 1957076 and 1957077. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1nj05121k

Published on 26 November 2021. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 1/5/2022 8:57:23 AM.

reaction durations (24–96 h), developing more efficient alternative methods with appropriate organocatalysts is desirable.

Although there are some examples of organocatalytic studies on Michael/S_N2 type reactions, new catalyst systems are still in demand. In order to overcome the long reaction duration and to improve the stereoselectivity at ambient temperature, herein we describe sterically encumbered squaramide acidic motifs[30–37] as effective organocatalysts in Michael/S_N2 type reactions of β-dicarbonyl compounds and (*Z*)-α-bromonitroolefins.

Results and discussion

The starting materials were obtained by the bromination of nitroolefins.[38] In the literature both (*E*) and (*Z*)-α-bromonitroolefins were reported as bromination products without making any scientific structural elucidation.[26,27,29] However, Miller *et al.* reported that the (*E*)-isomer is converted to a (*Z*)-isomer in basic medium.[39] To prove and to be sure that the ultimate product of bromination is the (*Z*)-isomer, we analyzed the product by X-ray analysis (Fig. 1).

The optimization of the reaction conditions for (*Z*)-α-bromonitroolefin with acetylacetone was initiated with organocatalyst screening. Sterically encumbered squaramides anchored with 2-aminoDMAP[31] and quinine amine[30,32–37] units developed in our research group were used as bifunctional organocatalysts (Fig. 2) at room temperature.

In the first trials, 10 mol% of bifunctional organocatalysts **I–IV** were employed in the model reaction. Cs_2CO_3 was used as an additive to scavenge HBr evolved in the reaction medium. The best result was attained with organocatalyst **I**; only the *anti* diastereomer was obtained with 83% yield and 37% ee in a very short time (1 h) at ambient temperature (Table 1, entry 1). Further trials were done with different organic and inorganic bases as additives in the presence of organocatalyst **I** (entries 5–12). Among the bases screened, inorganic bases were found to work better than organic bases in terms of both yield and enantioselectivity. Na_2CO_3 gave the best result of 95% ee in an hour with full conversion (Table 1, entry 11).

In order to make sure that the catalyst-additive system is the best one, a second organocatalyst screening was performed with Na_2CO_3 as the additive (entries 13–16). Although in all cases full conversion was achieved, the reaction time was slightly prolonged and none of them gave higher stereoselectivity, unfortunately (Scheme 2).

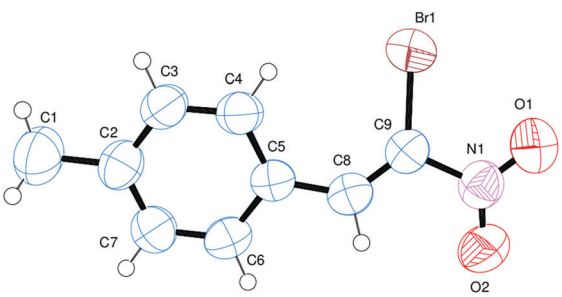


Fig. 1 X-Ray analysis of (*Z*)-1-(2-bromo-2-nitrovinyl)-4-methyl benzene **1f**.

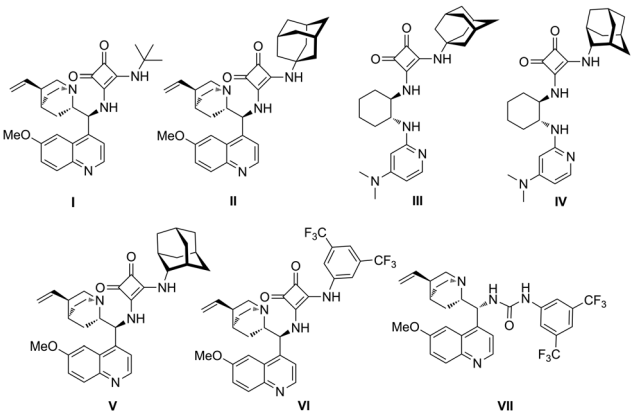
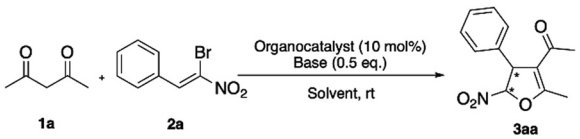


Fig. 2 Bifunctional organocatalysts I–VII.

Table 1 Optimization studies

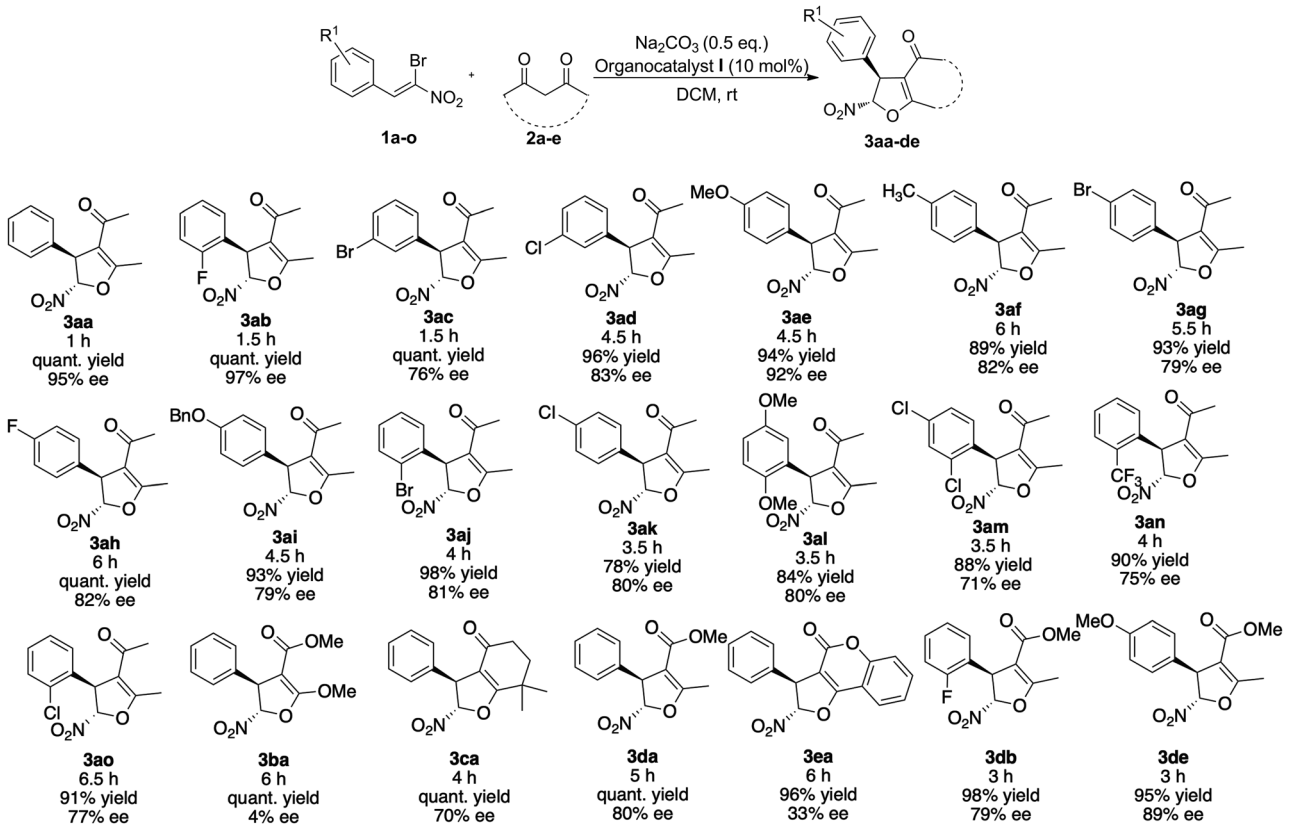


Entry[a]	Cat.	Base	Solvent	Time(h)	Yield[c](%)	ee[e](%)
1	I	Cs_2CO_3	DCM	1	83	37
2	II	Cs_2CO_3	DCM	1	32	13
3	III	Cs_2CO_3	DCM	1	50	14
4	IV	Cs_2CO_3	DCM	1	69	17
5	I	DBU	DCM	5	17	13
6[b]	I	DIPEA	DCM	5	78	39
7[b]	I	DMAP	DCM	5	35	9
8[b]	I	DABCO	DCM	5	70	30
9[b]	I	NaOAc	DCM	7	76	84
10[b]	I	$NaHCO_3$	DCM	7	81	85
11[d]	I	Na_2CO_3	DCM	1	>99	95
12	I	K_2CO_3	DCM	6	82	32
13[d]	V	Na_2CO_3	DCM	4	>99	81
14[d]	VI	Na_2CO_3	DCM	3	>99	84
15[d]	VII	Na_2CO_3	DCM	2.5	>99	73
16[d]	IV	Na_2CO_3	DCM	23	>99	5
17[d]	I	Na_2CO_3	$CHCl_3$	2	>99	79
18[d]	I	Na_2CO_3	CH_3CN	2	>99	14
19	I	Na_2CO_3	Hexane	5	97	42
20[d]	I	Na_2CO_3	THF	1	>99	17
21	I	Na_2CO_3	Xylene	7	98	46
22	I	Na_2CO_3	Toluene	2.5	97	23
23	I	Na_2CO_3	1,2-DCE	3	98	69
24	I	Na_2CO_3	$PhCF_3$	3	97	33
25[d,f]	I	Na_2CO_3	DCM	2	>99	73
26[d,g]	I	Na_2CO_3	DCM	5	>99	64
27[h]	I	Na_2CO_3	DCM	3	98	64
28[i]	I	Na_2CO_3	DCM	6	67	80
29[j]	I	Na_2CO_3	DCM	5	95	69
30[k]	I	Na_2CO_3	DCM	23	97	76

[a] Unless otherwise mentioned, all of the experiments were conducted with 0.10 mmol of **1a**, 0.18 mmol of **2a**, 0.05 mmol of base, 10 mol% organocatalyst and 0.20 mL of solvent with 0.5 M concentration at room temperature. [b] 0.10 mmol of base was used. [c] Isolated yields. [d] Conversions were determined by GC-MS analysis. [e] ee% values were determined by chiral HPLC analysis. [f] 5 mol% organocatalyst was used. [g] 2 mol% organocatalyst was used. [h] Concentration was 0.25 M. [i] Concentration was 0.1 M. [j] Reaction was performed at 0 °C. [k] Reaction was performed at −40 °C.

 This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2022

Published on 26 November 2021. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 1/5/2022 8:57:23 AM.



Scheme 2 Derivatization studies of different α-bromonitroolefins and β-dicarbonyl compounds.

After choosing the best working organocatalyst and additive, other parameters were investigated to determine optimal conditions for this reaction. Eight different solvents were screened; however, except for $CHCl_3$ (2 h, 79% ee, entry 17), a drastic decrease was observed in enantioselectivity and this is due to the fact that none of the solvents used dissolves the organocatalyst **I** as well as DCM (entries 18–24). Hence DCM was chosen as the best solvent. The other parameters, the effect of catalyst loading (entries 25 and 26), concentration of the reaction medium (entries 27 and 28) and temperature factors (entries 29 and 30), were also investigated to enrich the enantioselectivity. Unfortunately, none of the efforts gave better results. Thus, the optimized conditions for the asymmetric reaction of (*Z*)-α-bromonitroolefin with acetylacetone were decided as in entry 11 in Table 1.

In order to demonstrate the applicability of the optimized conditions, various α-bromonitroolefin derivatives were subjected to this reaction. All of the desired products were obtained with full conversion in a very short reaction duration (1–6 h) and good enantioselectivity of up to 97% ee (**3ab**). It is noteworthy that the reaction worked very well with unsubstituted, *o*-fluoro and *p*-methoxy substituted derivatives (**3aa**, **3ab**, and **3ae**) in 95%, 97% and 92% ee, respectively. It was observed that *para*-substituted derivatives gave rise to relatively long reaction durations. However, the direct effect of these groups on the enantioselectivity could not be observed. The other derivatives afforded quite similar results ranging between 76 and 83% ee. Besides, different α-bromonitroolefin derivatives, different β-dicarbonyl compounds were also tested (**3ba–3ea, 3db and 3de**). Among them, dimedone (**3ca**) and methyl acetoacetate (**3da**, **3db**, and **3de**) gave the best results varying between 70 and 89% ee.

The absolute configuration of **3aa** was determined as *S,S* by X-ray analysis (Fig. 3). The other derivatives (**3ab–3ao**, **3da**, **3ae**, **3db**, and **3de**) were assigned by analogy. A plausible transition state was suggested to explain the determined absolute

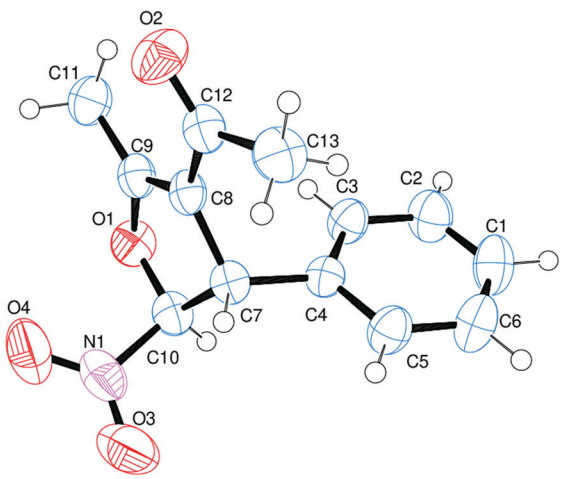


Fig. 3 X-Ray crystal structure of **3aa**.

Published on 26 November 2021. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 1/5/2022 8:57:23 AM.

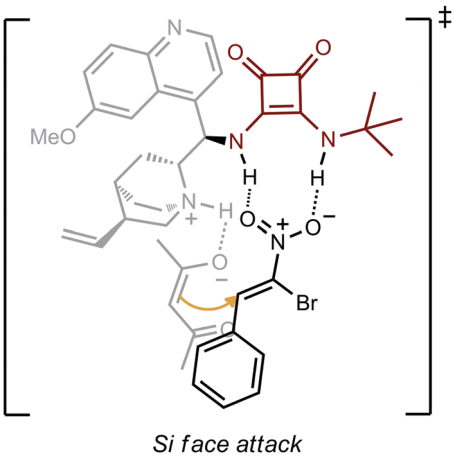


Fig. 4 Plausible transition state.

configuration. According to the proposed model, the nucleophile is activated by a quinuclidine moiety of the organocatalyst. Simultaneously, the electrophile is activated by double H-bonding with the squaramide hydrogens, allowing the nucleophile to attack from the *Si*-face (Fig. 4).

Conclusions

In this work, enantiomerically enriched 2,3-dihydrofurans were successfully synthesized in very short reaction durations in the presence of a *tert*-butyl squaramide quinine amine bifunctional organocatalyst. After the optimization studies, 14 different 2,3-DHF derivatives were synthesized with full conversion and very good enantioselectivities. The highest stereoselectivity of 97% ee was achieved with 10 mol% of the organocatalyst in 1.5 h. These enantioenriched adducts can easily be converted into 2,3-dihydrofuran-containing valuable precursors with additional steps.

Experimental section

Nuclear magnetic spectra for ^{1}H and ^{13}C were recorded in $CDCl_3$ solvent on a Bruker Spectrospin Avance DPX-400 spectrometer. Signals expressed in the NMR spectra were designated as s (singlet), d (doublet), dd (doublet of doublet) t (triplet) or m (multiplet), and the coupling constants (J) are given in Hertz (Hz). The mass spectra were taken on a Thermo Scientific DSQ II Single Quadropole GC/MS. HRMS data were recorded on an Agilent 6224 TOF LC/MS at UNAM, Bilkent University. HPLC chromatograms were obtained using Thermo-Finnigan and Agilent Technologies 1260 Infinity II instruments, using Daicel Chiralpak ODH, ASH, OJH and IA chiral columns with different *n*-hexane and 2-propanol solvent systems. The values of optical rotations of our chiral products were measured with the help of a Rudolph Scientific Autopol III polarimeter and reported as $[\alpha]_D^T$ (c is in gram per 100 mL solvent). Melting points were measured by using a Thomas Hoover capillary melting point apparatus. IR data were recorded on a Thermo Nicolet IS10 ATR/FT-IR spectrophotometer (the band position is in cm^{-1}). Progress of all reactions was monitored by using TLC (precoated silica gel plates of Merck Silica Gel 60 F_{254}) and UV-light. Flash column chromatography was done using Merck Silica Gel 60, particle size: 0.063–0.200 nm. Naming of products was done using ChemBioDraw Ultra 16.0.

General procedure for asymmetric domino Michael-S_N2 addition reactions: 1,3-dicarbonyl compound 2 addition to α-bromonitroolefin 1

Synthesis of racemic products. In DCM (0.2 mL), Na_2CO_3 (0.05 mmol) and an α-bromonitroalkene derivative (0.10 mmol) were dissolved. Then, a 1,3-dicarbonyl compound derivative (0.18 mmol) was added to this mixture and stirred at room temperature. The reactions were monitored by GC-MS. After completion of the reaction, the reaction mixtures were directly loaded into a flash column chromatography unit, and eluted with ethyl acetate:*n*-hexane to obtain pure products.

Synthesis of chiral products. In DCM (0.2 mL), *t*-butyl/quinine (0.01 mmol), Na_2CO_3 (0.05 mmol) and an α-bromonitroalkene derivative (0.10 mmol) were dissolved. Then, a 1,3-dicarbonyl compound derivative (0.18 mmol) was added to this mixture and stirred at room temperature. The reactions were monitored by GC-MS. After completion of the reaction, the reaction mixtures were directly loaded into a flash column chromatography unit, and eluted with ethyl acetate:*n*-hexane to obtain pure products.

1-((4*S*,5*S*)-2-Methyl-5-nitro-4-phenyl-4,5-dihydrofuran-3-yl)ethan-1-one (3aa). 3aa was obtained starting from (*Z*)-(2-bromo-2-nitrovinyl) benzene and acetyl acetone with 95% ee and full conversion in 1 h as a white solid. Mp = 95 °C. $[\alpha]_D^{25} = -182.49°$ (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.25 (m, 3H), 7.19–7.14 (m, 2H), 5.67 (d, J = 1.8 Hz, 1H), 4.58 (d, J = 2.7 Hz, 1H), 2.48 (d, J = 1.4 Hz, 3H), 1.97 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.1, 165.9, 136.4, 128.5, 127.7, 126.1, 114.6, 108.4, 55.3, 28.8, 13.5. HPLC: Chiralpak ODH, 95 : 5 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{minor} = 10.9 min, t_{major} = 13.0 min. IR(neat): 2919, 1678, 1608, 1561, 1420, 1365, 1216, 1186 cm^{-1}.

1-((4*R*,5*S*)-4-(2-Fluorophenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3ab). 3ab was obtained starting from (*Z*)-1-(2-bromo-2-nitrovinyl)-2-fluorobenzene and acetyl acetone with 97% ee and full conversion in 1.5 h as a white solid. Mp = 76 °C. $[\alpha]_D^{25} = -268.65°$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.20 (m, 1H), 7.14–6.82 (m, 3H), 5.73 (s, 1H), 4.91 (s, 1H), 2.47 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.2, 164.8, 128.1, 128.1–128.0 (d, J = 8.3 Hz), 126.1, 126.1, 122.5–122.5 (d, J = 3.7 Hz), 122.5, 114.0–113.9 (d, J = 21.4 Hz), 113.7, 112.3, 106.3, 47.0, 27.1, 12.1. HPLC: Chiralpak ODH, 98 : 2 (*n*-hexane/*i*-PrOH), flow rate 0.5 mL min^{-1}, 254 nm, temp = 25 °C, t_{minor} = 26.9 min, t_{major} = 28.4 min. IR(neat): 2920, 1733, 1631, 1572, 1489, 1375, 1204, 1170 cm^{-1}. HRMS: Exact mass calculated for $[C_{13}H_{12}FNO_4 + H]^+$: 266.0829; found as 266.0823.

1-((4*S*,5*S*)-4-(3-Bromophenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3ac). 3ac was obtained starting from (*Z*)-1-bromo-3-(2-bromo-2-nitrovinyl) benzene and acetyl acetone with 76% ee and full conversion in 1.5 h as a yellowish viscous compound. $[\alpha]_D^{25} = -147.12°$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ

 This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2022

Published on 26 November 2021. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 1/5/2022 8:57:23 AM.

7.45–7.39 (m, 1H), 7.31–7.26 (m, 1H), 7.22–7.16 (m, 1H), 7.12 (d, J = 7.7 Hz, 1H), 5.65 (d, J = 1.7 Hz, 1H), 4.56 (s, 1H), 2.49 (d, J = 1.3 Hz, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 190.5, 165.2, 137.8, 129.9, 129.0, 128.1, 124.0, 121.6, 113.7, 107.0, 53.9, 27.7, 12.6. HPLC: Chiralpak ASH, 98 : 2 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{minor} = 19.6 min, t_{major} = 27.4 min. IR(neat): 3005, 1685, 1640, 1619, 1564, 1364, 1210, 1181 cm^{-1}. HRMS: Exact mass calculated for $[M + H]^+$: 326.0029; found as 326.0023.

1-((4*S*,5*S*)-4-(3-Chlorophenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3ad). 3ad was obtained starting from (*Z*)-1-(2-bromo-2-nitrovinyl)-3-chlorobenzene and acetyl acetone with 83% ee and 96% isolated yield in 4.5 h as a white solid. Mp = 79 °C. $[\alpha]_D^{25}$ = −137.48° (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (dd, J = 3.6, 1.5 Hz, 2H), 7.13 (s, 1H), 7.11–7.05 (m, 1H), 5.65 (d, J = 1.7 Hz, 1H), 4.57 (d, J = 1.1 Hz, 1H), 2.49 (d, J = 1.3 Hz, 3H), 2.03 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.5, 167.1, 139.5, 135.5, 130.8, 129.0, 127.2, 125.5, 115.7, 108.9, 55.9, 29.7, 14.6. HPLC: Chiralpak ODH, 98 : 2 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{minor} = 18.4 min, t_{major} = 19.7 min. IR(neat): 2920, 1734, 1682, 1613, 1561, 1363, 1215, 1182 cm^{-1}.

1-((4*S*,5*S*)-4-(4-Methoxyphenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3ae). 3ae was obtained starting from (*Z*)-1-(2-bromo-2-nitrovinyl)-4-methoxybenzene and acetyl acetone with 92% ee and 94% isolated yield in 4.5 h as a dark yellowish viscous compound. $[\alpha]_D^{25}$ = −178.60° (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.14–7.01 (m, 2H), 6.92–6.77 (m, 2H), 5.63 (d, J = 1.7 Hz, 1H), 4.53 (s, 1H), 3.74 (s, 3H), 2.46 (d, J = 1.4 Hz, 3H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.2, 165.7, 158.8, 128.4, 127.3, 114.7, 113.9, 108.7, 54.7, 54.3, 28.7, 13.4. HPLC: Chiralpak ASH, 95 : 5 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{minor} = 13.6 min, t_{major} = 19.1 min. IR(neat): 2933, 1686, 1620, 1562, 1510,1366, 1255, 1179 cm^{-1}.

1-((4*S*,5*S*)-2-Methyl-5-nitro-4-(*p*-tolyl)-4,5-dihydrofuran-3-yl)ethan-1-one (3af). 3af was obtained starting from (*Z*)-1-(2-bromo-2-nitrovinyl)-4-methylbenzene and acetyl acetone with 82% ee and 89% isolated yield in 6 h as a white solid. Mp = 95 °C. $[\alpha]_D^{25}$ = −140.50° (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.16–7.09 (m, 2H), 7.07–7.03 (m, 2H), 5.65 (d, J = 1.8 Hz, 1H), 4.54 (s, 1H), 2.47 (d, J = 1.4 Hz, 3H), 2.29 (s, 3H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 193.3, 166.9, 138.6, 134.5, 130.2, 128.8, 127.0, 115.6, 109.7, 55.9, 29.9, 21.1, 14.5. HPLC: Chiralpak ODH, 98 : 2 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{minor} = 12.7 min, t_{major} = 13.7 min. IR(neat): 2918, 1734, 1680, 1613, 1565, 1369, 1215, 1185 cm^{-1}.

1-((4*S*,5*S*)-4-(4-Bromophenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3ag). 3ag was obtained starting from (*Z*)-1-bromo-4-(2-bromo-2-nitrovinyl) benzene and acetyl acetone with 79% ee and 93% isolated yield in 5.5 h as a dark yellow solid. Mp = 131 °C. $[\alpha]_D^{25}$ = −100.58° (*c* = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66–7.60 (m, 2H), 7.48–7.44 (m, 2H), 5.63 (d, J = 1.8 Hz, 1H), 4.55 (d, J = 5.7 Hz, 1H), 2.48 (d, J = 1.4 Hz, 3H), 2.01 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 191.6, 166.0, 135.5, 131.7, 129.9, 127.8, 107.9, 67.1, 54.8, 13.1. HPLC: Chiralpak ASH, 95 : 5 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{minor} = 14.7 min, t_{major} = 18.5 min. IR(neat): 2992, 1734, 1677, 1609, 1562, 1362, 1210, 1180 cm^{-1}. HRMS: Exact mass calculated for $[M + H]^+$: 326.0029; found as 326.0023.

1-((4*S*,5*S*)-4-(4-Fluorophenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3ah). 3ah was obtained starting from (*Z*)-1-(2-bromo-2-nitrovinyl)-4-fluorobenzeneand acetyl acetone with 82% ee and full conversion in 6 h as a yellow solid. Mp = 66 °C. $[\alpha]_D^{25}$ = −145.08° (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18–7.11 (m, 2H), 7.07–6.97 (m, 2H), 5.64 (d, J = 1.8 Hz, 1H), 4.58 (s, 1H), 2.48 (d, J = 1.4 Hz, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.8, 166.9, 163.9, 133.3–133.3 (d, J = 3.2 Hz), 133.3, 128.9, 128.9, 116.6, 116.4, 115.9, 109.2, 55.6, 29.7, 14.6. HPLC: Chiralpak ASH, 95 : 5 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{minor} = 17.3 min, t_{major} = 20.9 min. IR(neat): 2821, 1685, 1617, 1569, 1509, 1363, 1217, 1188 cm^{-1}. HRMS: Exact mass calculated for $[M + H]^+$: 266.0829; found as 266.0823.

1-((4*S*,5*S*)-4-(4-(Benzyloxy)phenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3ai). 3ai was obtained starting from (*Z*)-1-(benzyloxy)-4-(2-bromo-2-nitrovinyl) benzene and acetyl acetone with 79% ee and 93% isolated yield in 4.5 h as a light yellow solid. Mp = 137 °C. $[\alpha]_D^{25}$ = −88.0° (*c* = 0.25, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.24 (m, 6H), 7.07 (d, J = 8.7 Hz, 2H), 6.92 (t, J = 5.6 Hz, 2H), 5.63 (d, J = 1.7 Hz, 1H), 4.99 (s, 2H), 4.53 (s, 1H), 2.46 (d, J = 1.2 Hz, 3H), 1.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.3, 165.7, 158.0, 135.6, 128.6, 127.6, 127.3, 127.1, 126.4, 114.8, 114.6, 108.6, 69.1, 54.7, 28.8 13.5. HPLC: Chiralpak ASH, 90 : 10 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{minor} = 19.9 min, t_{major} = 25.5 min. IR(neat): 2919, 1680, 1610, 1564, 1511, 1369, 1215, 1182 cm^{-1}.

1-((4*R*,5*S*)-4-(2-Bromophenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3aj). 3aj was obtained starting from (*Z*)-1-bromo-2-(2-bromo-2-nitrovinyl)benzene and acetyl acetone with 79% ee and 98% isolated yield in 4.5 h as a colorless oil.$[\alpha]_D^{23}$ = −77.08° (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.9, 1.3 Hz, 1H), 7.36 (td, J = 7.6, 1.3 Hz, 1H), 7.25 (td, J = 7.7, 1.7 Hz, 1H), 7.07–6.99 (m, 1H), 5.75 (d, J = 1.8 Hz, 1H), 5.28 (s, 1H), 2.58 (s, 3H), 2.04 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 192.9, 167.7, 136.0, 133.8, 130.2, 128.4, 128.1, 124.2, 115.1, 108.9, 54.5, 29.6, 14.4. HPLC: Chiralpak ODH, 80 : 20 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 230 nm, temp = 25 °C, t_{minor} = 6.9 min, t_{major} = 7.4 min. IR(neat): 2923, 1687, 1643, 1621, 1569, 1366, 1210, 1184 cm^{-1}. HRMS: Exact mass calculated for $[M + H]^+$: 326.0028; found as 326.0077.

1-((4*S*,5*S*)-4-(4-Chlorophenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3ak). 3ak was obtained starting from (*Z*)-1-(2-bromo-2-nitrovinyl)-4-chlorobenzene and acetyl acetone with 81% ee and 78% isolated yield in 4 h as a colorless oil.$[\alpha]_D^{33}$ = −128.18° (*c* = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H), 5.63 (d, J = 1.8 Hz, 1H), 4.57 (d, J = 1.7 Hz, 1H), 2.47 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.6, 167.0, 136.0, 134.7, 129.7, 128.5, 115.8, 109.1, 55.7, 29.7, 14.6. HPLC: Chiralpak ASH, 90 : 10 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 230 nm, temp = 25 °C, t_{minor} = 8.6 min, t_{major} = 10.5 min. IR(neat): 2923, 1686, 1641, 1619, 1566, 1365, 1211, 1178 cm^{-1}. HRMS: Exact mass calculated for $[M + H]^+$: 282.0533; found as 282.0262.

Published on 26 November 2021. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 1/5/2022 8:57:23 AM.

1-((4*S*,5*S*)-4-(2,5-Dimethoxyphenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3al). 3al was obtained starting from (*Z*)-2-(2-bromo-2-nitrovinyl)-1,4-dimethoxybenzene and acetyl acetone with 80% ee and 78% isolated yield in 3.5 h as a white solid. Mp = 73 °C.$[\alpha]_D^{32} = -196.60°$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (d, J = 8.9 Hz, 1H), 6.76 (dd, J = 8.9, 3.0 Hz, 1H), 6.47 (d, J = 2.9 Hz, 1H), 5.66 (d, J = 2.0 Hz, 1H), 4.98 (t, J = 1.7 Hz, 1H), 3.80 (s, 3H), 3.67 (s, 3H), 2.44 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 193.5, 167.4, 153.9, 151.1, 126.6, 114.6, 114.4, 113.3, 112.1, 109.8, 56.1, 55.7, 49.6, 29.5, 14.5. HPLC: Chiralpak ODH, 95 : 5 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 230 nm, temp = 25 °C, t_{minor} = 12.3 min, t_{major} = 13.7 min. IR(neat): 2924, 1685, 1642, 1618, 1566, 1500, 1464, 1366, 1210, 1090 cm^{-1}. HRMS: Exact mass calculated for $[M + H]^+$: 308.1134; found as 308.0783.

1-((4*R*,5*S*)-4-(2,4-Dichlorophenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3am). 3am was obtained starting from (*Z*)-1-(2-bromo-2-nitrovinyl)-2,4-dichlorobenzene and acetyl acetone with 71% ee and 88% isolated yield in 3.5 h as a white solid. Mp = 174 °C (decomp). $[\alpha]_D^{33} = -115.58°$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.45 (d, J = 2.2 Hz, 1H), 7.19 (dd, J = 8.4, 2.2 Hz, 1H), 6.89 (d, J = 8.4 Hz, 1H), 5.63 (d, J = 1.8 Hz, 1H), 5.17–5.06 (m, 1H), 2.48 (s, 3H), 2.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.4, 167.8, 135.4, 134.7, 133.2, 130.4, 129.1, 128.1, 115.0, 108.5, 52.0, 29.5, 14.6. HPLC: Chiralpak ODH, 95 : 5 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 230 nm, temp = 25 °C, t_{minor} = 9.6 min, t_{major} = 11.0 min. IR(neat): 2926, 1687, 1643, 1570, 1471, 1366, 1210, 1183, 1091 cm^{-1}. HRMS: Exact mass calculated for $[M]^+$: 315.0065; found as 314.9922.

1-((4*S*,5*S*)-2-Methyl-5-nitro-4-(2-(trifluoromethyl)phenyl)-4,5-dihydrofuran-3-yl)ethan-1-one (3an). 3an was obtained starting from(*Z*)-1-(2-bromo-2-nitrovinyl)-2-(trifluoromethyl)benzene and acetyl acetone with 75% ee and 90% isolated yield in 4 h as a colorless oil. $[\alpha]_D^{24} = -193.0°$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 7.8 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.7 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 5.64 (d, J = 1.7 Hz, 1H), 5.09 (s, 1H), 2.51 (s, 3H), 1.91 (s, 3H). ^{13}C NMR (101 MHz, chloroform-*d*) δ 192.8, 168.0, 135.2, 133.1, 129.0, 128.6, 128.2, 127.0 (q, J = 5.7 Hz), 125.3, 115.5, 109.4, 50.8, 29.7, 14.4 (Other CF_3 coupling could not be identified). HPLC: Chiralpak IA, 98 : 2 (*n*-hexane/*i*-PrOH), flow rate 0.7 mL min^{-1}, 230 nm, temp = 25 °C, t_{minor} = 10.5 min, t_{major} = 11.4 min. IR(neat): 2960, 2923, 1687, 1644, 1571, 1336, 1205, 1160 cm^{-1}. HRMS: Exact mass calculated for $[M]^+$: 315.0718; found as 315.0623.

1-((4R,5S)-4-(2-Chlorophenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-yl)ethan-1-one (3ao). 3ao was obtained starting from (*Z*)-1-(2-bromo-2-nitrovinyl)-2-chlorobenzene and acetyl acetone with 77% ee and 91% isolated yield in 6.5 h as a white solid. Mp = 74–78 °C. $[\alpha]_D^{32} = -89.96°$ (c = 0.5, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46–7.40 (m, 1H), 7.28–7.20 (m, 2H), 7.00–6.94 (m, 1H), 5.67 (d, J = 1.8 Hz, 1H), 5.23–5.07 (m, 1H), 2.49 (s, 3H), 1.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 168.0, 135.2, 133.1, 129.0, 128.2, 127.0, 127.0, 115.5, 109.4, 50.8, 29.7, 14.4. HPLC: Chiralpak ODH, 90 : 10 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 230 nm, temp = 25 °C, t_{minor} = 7.9 min, t_{major} = 8.3 min. IR(neat): 2924, 2156, 1687, 1643, 1620, 1568, 1436, 1367, 1210, 1089 cm^{-1}. HRMS: Exact mass calculated for $[M + H]^+$: 282.0533; found as 282.0274.

Methyl(4*S*,5*S*)-2-methoxy-5-nitro-4-phenyl-4,5-dihydrofuran-3-carboxylate (3ba). 3ba was obtained starting from (*Z*)-(2-bromo-2-nitrovinyl) benzene and dimethyl malonate with 4% ee with full conversion in 6 h as a yellowish viscous compound. $[\alpha]_D^{25} = -50.34°$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (d, J = 8.6 Hz, 2H), 7.23–7.13 (m, 3H), 5.34 (d, J = 5.9 Hz, 1H), 4.13 (d, J = 5.9 Hz, 1H), 3.78 (s, 3H), 3.47 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 162.8, 162.5, 129.1, 127.9, 127.8, 127.6, 127.2, 65.2, 52.9, 52.4, 45.0, 36.7. HPLC: Chiralpak OJH, 95 : 5 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{major} = 27.3 min, t_{minor} = 40.7 min. IR(neat): 2957, 1737, 1555, 1501, 1436, 1366, 1288, 1118 cm^{-1}.

(2*S*,3*S*)-7,7-Dimethyl-2-nitro-3-phenyl-3,5,6,7-tetrahydrobenzofuran-4(2H)-one (3ca)[40]. 3ca was obtained starting from (*Z*)-(2-bromo-2-nitrovinyl) benzene and dimedone with 70% ee with full conversion in 4 h as a white solid. Mp = 139 °C. $[\alpha]_D^{25} = -108.37°$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34–7.20 (m, 3H), 7.17–7.08 (m, 2H), 5.89 (d, J = 2.0 Hz, 1H), 4.54 (s, 1H), 2.67–2.47 (m, 2H), 2.24 (d, J = 2.8 Hz, 2H), 1.13 (d, J = 2.5 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 192.0, 174.0, 135.9, 128.3, 127.4, 125.9, 114.0, 110.3, 52.1, 50.2, 36.2, 33.6, 27.7, 27.5. HPLC: Chiralpak IA, 90 : 10 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{major} = 12.5 min, t_{minor} = 19.7 min. IR(neat): 2934, 1666, 1651, 1563, 1392, 1369, 1256, 1188 cm^{-1}.

Methyl(4*S*,5*S*)-2-methyl-5-nitro-4-phenyl-4,5-dihydrofuran-3-carboxylate (3da). 3da was obtained starting from (*Z*)-(2-bromo-2-nitrovinyl) benzene and methyl acetoacetate with 80% ee with full conversion in 5 h as a white solid. Mp = 75 °C. $[\alpha]_D^{25} = -169.84°$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36–7.28 (m, 2H), 7.27–7.22 (m, 1H), 7.22–7.09 (m, 2H), 5.70 (d, J = 1.7 Hz, 1H), 4.53 (s, 1H), 3.56 (d, J = 19.8 Hz, 3H), 2.44 (d, J = 1.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.5, 163.9, 137.8, 129.2, 128.4, 127.0, 109.6, 107.4, 55.7, 51.5, 13.8. HPLC: Chiralpak ASH, 98 : 2 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{minor} = 10.7 min, t_{major} = 12.8 min. IR(neat): 2956, 1707, 1671, 1604, 1562, 1431, 1319, 1226, 1184 cm^{-1}.

(2*S*,3*S*)-2-Nitro-3-phenyl-2,3-dihydro-4H-furo[3,2-c]chromen-4-one (3ea). 3ea was obtained starting from (*Z*)-(2-bromo-2-nitrovinyl) benzene and 4-hydroxycoumarin with 33% ee with 96% isolated yield in 6 h as a white solid. Mp = 147 °C. $[\alpha]_D^{25} = -25.43°$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 9.2 Hz, 1H), 7.62 (d, J = 8.8 Hz, 1H), 7.45–7.28 (m, 5H), 7.20 (dd, J = 5.6, 4.3 Hz, 1H), 6.19 (d, J = 2.1 Hz, 1H), 4.89 (d, J = 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 164.6, 157.0, 154.6, 134.5, 132.8, 128.6, 128.0, 126.1, 123.7, 122.1, 116.3, 110.4, 110.1, 103.9, 52.7. HPLC: Chiralpak IA, 95 : 5 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 254 nm, temp = 25 °C, t_{major} = 45.7 min, t_{minor} = 49.6 min. IR(neat): 3030, 1717, 1657, 1608, 1569, 1497, 1453, 1408 cm^{-1}.

Methyl(4*R*,5*S*)-4-(2-fluorophenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-carboxylate (3db). 3db was obtained starting from (*Z*)-1-(2-bromo-2-nitrovinyl)-2-fluorobenzene and methyl acetoacetate with 79% ee with 98% isolated yield in 3 h as a colorless oil.

 This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2022

Published on 26 November 2021. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 1/5/2022 8:57:23 AM.

$[\alpha]_D^{23} = -108.04^\circ$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29–7.21 (m, 1H), 7.05 (dddd, J = 9.3, 7.2, 4.4, 2.6 Hz, 3H), 5.77 (d, J = 2.0 Hz, 1H), 4.83 (s, 1H), 3.55 (s, 3H), 2.44 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 163.6, 160.3 (d, J = 248.4 Hz), 130.0 (d, J = 8.3 Hz), 128.5 (d, J = 3.4 Hz), 124.5 (d, J = 3.6 Hz), 116.0 (d, J = 21.5 Hz), 108.8, 105.9, 51.4, 49.2, 49.2, 13.7. HPLC: Chiralpak ASH, 90 : 10 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 230 nm, temp = 25 °C, t_{minor} = 5.4 min, t_{major} = 6.4 min. IR(neat): 3320, 2953, 2194, 2157, 2042, 2003, 1710, 1667, 1569, 1492, 1439, 1362, 1322, 1226, 1205, 1104, 1063 cm^{-1}. HRMS: Exact mass calculated for $[M]^+$: 281.0700; found as 281.2479.

Methyl(4S,5S)-4-(4-methoxyphenyl)-2-methyl-5-nitro-4,5-dihydrofuran-3-carboxylate (3de). **3de** was obtained starting from (*Z*)-1-(2-bromo-2-nitrovinyl)-4-methoxybenzene and methyl acetoacetate with 89% ee with 95% isolated yield in 3 h as a yellow oil. $[\alpha]_D^{23} = -116.40^\circ$ (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, chloroform-*d*) δ 7.16 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 8.7 Hz, 2H), 5.76 (d, J = 1.8 Hz, 1H), 4.67–4.41 (m, 1H), 3.83 (s, 3H), 3.64 (s, 3H), 2.53 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.1, 163.8, 159.5, 129.7, 128.0, 114.4, 109.7, 107.5, 55.2, 55.0, 51.3, 13.7, 0.9. HPLC: Chiralpak ASH, 90 : 10 (*n*-hexane/*i*-PrOH), flow rate 1.0 mL min^{-1}, 230 nm, temp = 25 °C, t_{minor} = 6.6 min, t_{major} = 7.9 min. IR(neat): 2952, 2839, 2176, 1708, 1666, 1610, 1569, 1512, 1438, 1359, 1255, 1182, 1062, 1032 cm^{-1}. HRMS: Exact mass calculated for $[M]^+$: 293.0899; found as 293.1771.

Author contributions

Authors Zeynep Dilşad Susam and Merve Bozdemir worked equally for the preparation of this manuscript and experiments under the supervision of Prof. Cihangir Tanyeli. Author Gülsüm Gündoğdu worked on the X-ray crystal analyses of the given products.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

We are thankful for the financial support from the Middle East Technical University – Scientific Research Projects Coordination and Scientific and Technological Research Council of Turkey, TÜBİTAK (Project No: 113Z156 & 217Z035). We also thank Ferdi KARADAŞ for X-ray analysis and Deniz TÖZENDEMİR for her contributions.

Notes and references

1 B. H. Lipshutz, *Chem. Rev.*, 1986, **86**, 795–819.
2 M. M. Faul and B. E. Huff, *Chem. Rev.*, 2000, **100**, 2407–2473.
3 B. M. Fraga, *Natural Sesquiterpenoids*, The Royal Society Of Chemistry, 1992.
4 A. T. Merritt and S. V. Ley, *Nat. Prod. Rep.*, 1992, **9**, 243–287.
5 T. C. Casey, J. Carlisle, P. Tisselli, L. Male, N. Spencer and R. S. Grainger, *J. Org. Chem.*, 2010, **75**, 7461–7464.
6 Q. Liu, Y.-F. Wang, R.-J. Chen, M.-Y. Zhang, Y.-F. Wang, C.-R. Yang and Y.-J. Zhang, *J. Nat. Prod.*, 2009, **72**, 969–972.
7 Y.-J. Zhang, T. Tanaka, Y. Iwamoto, C.-R. Yang and I. Kouno, *Tetrahedron Lett.*, 2000, **41**, 1781–1784.
8 I.-S. Chen, J.-J. Chen, C.-Y. Duh and I.-L. Tsai, *Phytochemistry*, 1997, **45**, 991–996.
9 G. Maiti, S. Adhikari and S. C. Roy, *Tetrahedron Lett.*, 1994, **35**, 6731–6732.
10 S. I. Yoshida, T. Ogiku, H. Ohmizu and T. Iwasaki, *J. Org. Chem.*, 1997, **62**, 1310–1316.
11 M. Bottex, M. Cavicchioli, B. Hartmann, N. Monteiro and G. Balme, *J. Org. Chem.*, 2001, **66**, 175–179.
12 S. Ma and W. Gao, *Synlett*, 2002, 65–68.
13 V. Calò, F. Scordari, A. Nacci, E. Schingaro, L. D'Accolti and A. Monopoli, *J. Org. Chem.*, 2003, **68**, 4406–4409.
14 M. E. Alonso and A. Morales, *J. Org. Chem.*, 1980, **45**, 4532–4533.
15 R. K. Bowman and J. S. Johnson, *Org. Lett.*, 2006, **8**, 573–576.
16 K. Saigo, H. Kurihara, H. Miura, A. Hongu, N. Kubota, H. Nohira and M. Hasegawa, *Synth. Commun.*, 1984, **14**, 787–796.
17 W. Xia, C. Yang, B. O. Patrick, J. R. Scheffer and C. Scott, *J. Am. Chem. Soc.*, 2005, **127**, 2725–2730.
18 V. K. Yadav and R. Balamurugan, *Org. Lett.*, 2001, **3**, 2717–2719.
19 S. Arai, K. Nakayama, Y. Suzuki, K. Hatano and T. Shioiri, *Tetrahedron Lett.*, 1998, **39**, 9739–9742.
20 S. Son and G. C. Fu, *J. Am. Chem. Soc.*, 2007, **129**, 1046–1047.
21 J.-L. Zhou, L.-J. Wang, H. Xu, X.-L. Sun and Y. Tang, *ACS Catal.*, 2013, **3**, 685–688.
22 F.-L. Zhu, Y.-H. Wang, D.-Y. Zhang, J. Xu and X.-P. Hu, *Angew. Chem.*, 2014, **126**, 10387–10391.
23 F. Ozawa, A. Kubo, Y. Matsumoto, T. Hayashi, E. Nishioka, K. Yanagi and K. Moriguchi, *Organometallics*, 1993, **12**, 4188–4196.
24 H. J. Gais, L. R. Reddy, G. S. Babu and G. Raabe, *J. Am. Chem. Soc.*, 2004, **126**, 4859–4864.
25 J.-C. Zheng, C.-Y. Zhu, X.-L. Sun, Y. Tang and L.-X. Dai, *J. Org. Chem.*, 2008, **73**, 6909–6912.
26 L.-P. Fan, P. Li, X.-S. Li, D.-C. Xu, M.-M. Ge, W.-D. Zhu and J.-W. Xie, *J. Org. Chem.*, 2010, **75**, 8716–8719.
27 M. Rueping, A. Parra, U. Uria, F. Besselièvre and E. Merino, *Org. Lett.*, 2010, **12**, 5680–5683.
28 M. Rueping and M.-Y. Lin, *Chem. – Eur. J.*, 2010, **16**, 4169–4172.
29 J. Feng, L. Lin, K. Yu, X. Liu and X. Feng, *Adv. Synth. Catal.*, 2015, **357**, 1305–1310.
30 F. Manoni and S. J. Connon, *Angew. Chem., Int. Ed.*, 2014, **53**, 2628–2632.
31 M. Işık, M. Y. Unver and C. Tanyeli, *J. Org. Chem.*, 2015, **80**, 828–835.
32 E. Kanberoğlu and C. Tanyeli, *Asian J. Org. Chem.*, 2016, **5**, 114–119.
33 D. Susam and C. Tanyeli, *New J. Chem.*, 2017, **41**, 3555–3561.

Published on 26 November 2021. Downloaded by Middle East Technical University (Orta Dogu Teknik U) on 1/5/2022 8:57:23 AM.

34 S. Karahan and C. Tanyeli, *New J. Chem.*, 2017, **41**, 9192–9202.
35 D. Hasılcıoğulları and C. Tanyeli, *Tetrahedron Lett.*, 2018, **59**, 1414–1416.
36 S. Karahan and C. Tanyeli, *Org. Biomol. Chem.*, 2020, **18**, 479–487.
37 D. Tözendemir and C. Tanyeli, *Beilstein J. Org. Chem.*, 2021, **17**, 494–503.
38 J. G. Greger, S. J. P. Yoon-Miller, N. R. Bechtold, S. A. Flewelling, J. P. MacDonald, C. R. Downey, E. A. Cohen and E. T. Pelkey, *J. Org. Chem.*, 2011, **76**, 8203–8214.
39 D. B. Miller, P. W. Flanagan and H. Shechter, *J. Org. Chem.*, 1976, **41**, 2112–2120.
40 X. Zhang, K. Feng, A. Xia, Y. Zheng, C. Li, X. Du and D. Xu, *Eur. J. Org. Chem.*, 2018, 2918–2925.

 This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2022