Asymmetric Brønsted Acid-catalyzed Intramolecular aza-Michael Reaction – Enantioselective Synthesis of Dihydroquinolinones

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Dedicated to Professor Heribert Offermanns on the occasion of his 75th birthday

The enantioselective synthesis of 2-aryl-substituted 2,3-dihydroquinolin-4-ones, a class of heterocyclic compounds with interesting biological activities, has been achieved through a Brønsted acid-catalyzed enantioselective intramolecular Michael addition. The products are available in moderate to high yields and with good enantioselectivities.

Key words: aza-Michael Addition, Brønsted Acid, *N*-Triflyl Phosphoramide, Dihydroquinolin-4-ones

Introduction

The asymmetric catalytic aza-Michael reaction offers a convenient route to a wide variety of enantioenriched amine derivatives and *N*-heterocyclic compounds [1 – 6]. In recent years efforts have been devoted in particular to the development of efficient organocatalytic approaches for both inter- and intramolecular versions of the aza-Michael reaction [3 – 6]. On the one hand progress was made with chiral primary and secondary amine catalysts. On the other hand, Brønsted acid-catalyzed aza-Michael reactions attracted further interest. Notably, different classes of *N*-heterocyclic compounds have been obtained in an enantioselective fashion by either amine- or Brønsted acid-catalyzed intramolecular aza-Michael reactions or domino sequences comprising an aza-Michael addition step [3 – 6]. For example You reported the application of Brønsted acid catalysis [7 – 14] in the synthesis of dihydroquinolinones [15], pyrrolidines and morpholines [16]. Enders described the synthesis of tetrahydroisoquinolines through a Brønsted acid-catalyzed reductive amination/aza-Michael domino reaction [17]. Our group and that of Gong reported independently the asymmetric synthesis of isoquinuclidines through a Brønsted acid-catalyzed Mannich/aza-Michael addition [18, 19].

Herein, we describe the application of Brønsted acid catalysis to the enantioselective synthesis of 2-aryl-substituted 2,3-dihydroquinolin-4-ones which represent a class of heterocyclic compounds with interesting biological activities [20, 21]. A similar approach was recently described by You [15]. Lu used a bifunctional thiourea catalyst for the asymmetric synthesis of this class of compounds [22]. In addition, racemic resolution [23] and metal-catalyzed processes [24, 25] have been applied to obtain chiral 2-aryl-substituted 2,3-dihydroquinolin-4-ones.

Results and Discussion

We started our investigation with a study of the intramolecular reaction of the *N*-methyl derivative **1a**. Various chiral BINOL-based *N*-triflyl phosphoramides **3a–i** [26 – 44] were evaluated in the intramolecular aza-Michael addition with **1a** as model substrate, and the results are summarized in Ta-

Table 1. Catalyst screening for the asymmetric intramolecular aza-Michael reaction.

Entry[a]	Catalyst **3**	Yield (%)[b]	Er[c]
1	**3a**	30	50 : 50
2	**3b**	82	55.5 : 44.5 (*R*)
3	**3c**	57	50 : 50
4	**3d**	–	–
5	**3e**	15	56.5 : 43.5 (*R*)
6	**3f**	3	n. d.
7	**3g**	8	57 : 43 (*R*)
8	**3h**	32	74 : 26 (*S*)
9	**3i**	43	56.5 : 43.5 (*S*)

[a] Reaction was performed with 0.05 mmol of the chalcone and 10 mol-% of catalyst in 0.25 mL of toluene at r. t. with stirring for 40 h; [b] yield after column chromatography; [c] Er = enantiomeric ratio; determined by chiral HPLC.

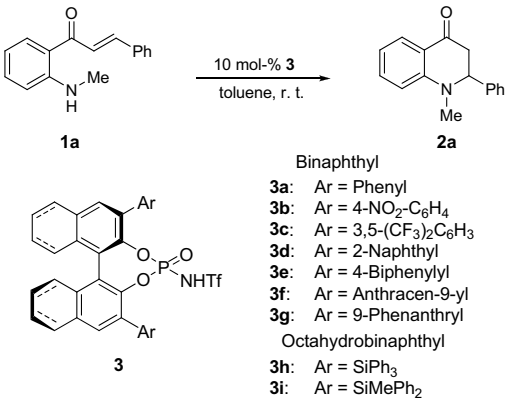
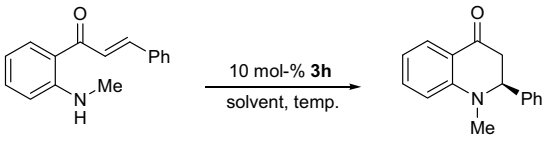


Table 2. Solvent and temperature evaluation in the asymmetric intramolecular aza-Michael reaction.



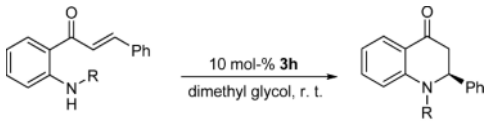
Entry[a]	Solvent	Temperature (°C)	Yield (%)[b]	Er[c]
1	CH_2Cl_2	r. t.	3	n. d.[d]
2	$CHCl_3$	r. t.	8	76.5 : 23.5
3	MeOH	r. t.	33	50 : 50
4	MeCN	r. t.	52	65.5 : 34.5
5	ethyl acetate	r. t.	29	75.5 : 24.5
6	THF	r. t.	23	76 : 24
7	Ph_2O	r. t.	4	n. d.
8	*n*-Bu_2O	r. t.	9	n. d.
9	Et_2O	r. t.	4	n. d.
10	ethyl diglycol	r. t.	59	71 : 29
11	dimethyl glycol	r. t.	51	76.5 : 23.5
12	dimethyl glycol	50	79	72.5 : 27.5
13	dimethyl glycol	10	10	78 : 22
14	dimethyl glycol	0	4	80.5 : 19.5
15[e]	dimethyl glycol	−25	–	–

[a] Reaction was performed with 0.05 mmol of the chalcone and 10 mol-% of catalyst **3h** in 0.25 mL solvent at the indicated temperature with stirring for 40 h; [b] yield after column chromatography; [c] Er = enantiomeric ratio; determined by chiral HPLC; [d] n. d. = not determined; [e] stirred for 4 days.

ble 1. Among the BINOL- and octahydro-BINOL-triflylphosphoramides tested, a promising level of enantioselectivity was observed with the octahydro-BINOL-triflylphosphoramide **3h** bearing triphenylsilyl residues at the 3,3'-positions (Table 1, entry 8). The absolute configuration of the product **2a** obtained with the silyl derivatives **3h** und **3i** is opposite to the one of the product obtained with catalysts **3b**, **3e** and **3g** (Table 1, entries 8 and 9 *vs.* entries 2, 5 and 7) [45].

In order to improve the enantioselectivity, various solvents and temperatures were tested. Chlorinated solvents and acyclic ethers were less suitable, affording only traces of the desired product **2a** (Table 2, entries 1 – 2 and 7 – 9). Ethyl acetate and THF proved to be better in terms of selectivity, and the product **2a** was obtained with 75.5 : 24.5 and 76 : 24 enantiomeric ratios, respectively (Table 2, entries 5 – 6).

Table 3. Evaluation of different *N*-protecting groups in the asymmetric intramolecular aza-Michael reaction.



1a, 4a–9a **2a, 10a–15a**

Entry[a]	Substrat	R	Product	Yield (%)[b]	Er[c]
1	**1a**	Me	**2a**	51	76 : 24
2	**4a**	Bn	**10a**	72	73.5 : 26.5
3	**5a**	Ph	**11a**	66	57.5 : 42.5
4	**6a**	*i*-Pr	**12a**	32	75 : 25
5	**7a**	Allyl	**13a**	46	75.5 : 24.5
6	**8a**	Ac	**14a**	–	–
7	**9a**	Ts	**15a**	–	–

[a] Reaction was performed with 0.05 mmol of the chalcone and 10 mol-% of catalyst **3h** in 0.25 mL of dimethyl glycol at r. t. with stirring for 40 h; [b] yield after column chromatography; [c] Er = enantiomeric ratio; determined by chiral HPLC.

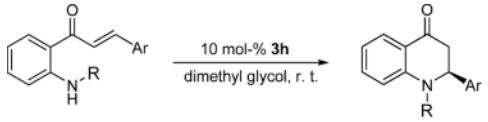
The best result with regard to both, yield and selectivity, was obtained in dimethyl glycol at room temperature (Table 2, entry 11). Higher temperature resulted in reduced selectivity and lower temperature had a detrimental influence on the yield. Therefore, the subsequent optimization and evaluation of the substrate scope was performed at room temperature in dimethyl glycol as solvent.

Substrates with different *N*-protecting groups were also tested. While *N*-Me and *N*-allyl groups provided comparable results in terms of yield and selectivity (Table 3, entries 1 and 5), the use of *N*-Bn resulted in the corresponding product with a slightly increased yield but decreased selectivity (Table 3, entry 2). The use of *N*-acyl and *N*-tosyl amine derivatives did not afford the desired products (Table 3, entries 6 and 7).

With the optimized conditions in hand, the scope of the reaction was investigated (Table 4). Chalcones **7** bearing aryl groups with electron donating groups (Me, MeO, PhO) afforded the corresponding products with good to excellent yields and selectivities. The selectivity was not visibly affected by the electronic nature of the substituents. However, the use of chalcones with sterically more demanding substituents resulted in lower yield.

The absolute configuration of product **10d** was determined as (*S*) by X-ray crystal structure analysis (Fig. 1).

Table 4. Substrate scope of the Brønsted acid-catalyzed aza-Michael addition reaction.



4, 7 **10, 13**

Entry[a]	**4, 7**	Ar	R	**10, 13**	Yield (%)[b]	Er[c]
1	**7a**	Ph	Allyl	**13a**	46	75.5 : 24.5
2	**7b**	2-Me-C_6H_4	Allyl	**13b**	45	76 : 24
3	**7c**	2-MeO-C_6H_4	Allyl	**13c**	63	76.5 : 23.5
4	**7d**	3-Me-C_6H_4	Allyl	**13d**	53	76 : 24
5	**7e**	3-PhO-C_6H_4	Allyl	**13e**	36	74.5 : 25.5
6	**7f**	4-MeO-C_6H_4	Allyl	**13f**	98	75 : 25
7	**7g**	4-F-C_6H_4	Allyl	**13g**	92	75.5 : 24.5
8	**7h**	3,4,5-$(MeO)_3$-C_6H_2	Allyl	**13h**	58	81.5 : 18.5
9	**7i**	1-naphthyl	Allyl	**13i**	74	74.5 : 25.5
10	**7j**	2-naphthyl	Allyl	**13j**	86	77 : 23
11	**7k**	furan	Allyl	**13k**	68	74.5 : 25.5
12	**4a**	Ph	Bn	**10a**	72	73.5 : 26.5
13	**4b**	2-MeO-C_6H_4	Bn	**10b**	71	76.5 : 23.5
14	**4c**	2-Br-C_6H_4	Bn	**10c**	29	81.5 : 18.5
15	**4d**	3-Br-C_6H_4	Bn	**10d**	58	76 : 24
16	**4e**	4-Br-C_6H_4	Bn	**10e**	57	74.5 : 25.5
17	**4f**	1-naphthyl	Bn	**10f**	41	78 : 22

[a] Reaction was performed with 0.05 mmol of the chalcone and 10 mol-% of catalyst **3h** in 0.25 mL of dimethyl glycol at r. t.; [b] yield after column chromatography; [c] Er = enantiomeric ratio; determined by chiral HPLC.

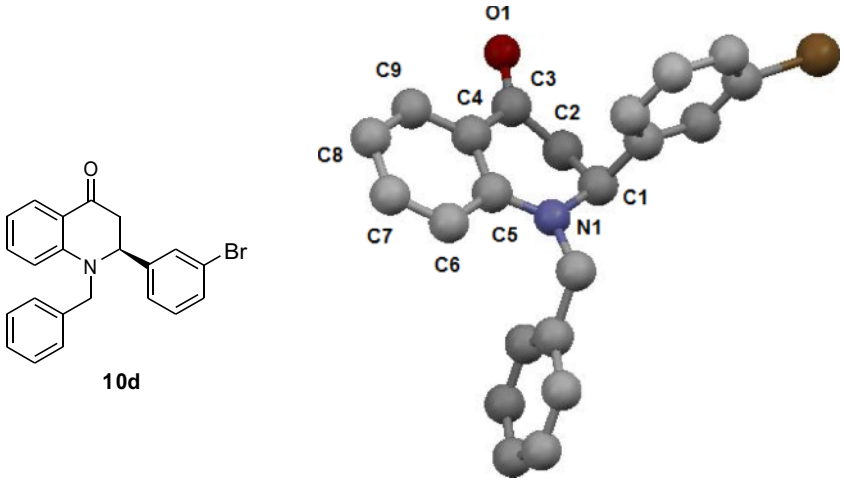


Fig. 1. Molecular structure of **10d** (left) in the crystal (hydrogen atoms have been omitted for clarity).

Conclusion

In conclusion we have developed a catalytic route to various *N*-allyl- and *N*-benzyl-protected 2-aryl-substituted dihydroquinolin-4-one derivatives. The products have become available in moderate to high yields and with good enantiomeric ratios. The results reported not only demonstrate that chiral Brønsted acids can be efficient catalysts for enantioselective intramolecular Michael additions, but also show the high potential of highly acidic *N*-triflyl phosphoramides in asymmetric catalysis.

Experimental Section

General

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Merck silica gel aluminum plates with F-254 indicator and visualized by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.040 – 0.063 mm). ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM 250 or a Bruker AV 300 spectrometer in $CDCl_3$. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated s (singlet), d (doublet), dd (doublet of doublets), t (triplet), m (multiplet); coupling constants (J) are in Hertz (Hz). Mass spectra (MS-EI, 70 eV) were conducted on a GC-MS Shimadzu QP2010 instrument (column: Equity® -5, length × I. D. 30 m × 0.25 mm, df 0.25 μm, lot # 28089-U, Supelco). IR spectra were recorded on a Jasco FT/IR-420 spectrometer and are reported as frequency of absorption (cm^{-1}). Optical rotations were measured on a Perkin Elmer 241 polarimeter. The enantiomeric excesses were determined by HPLC analysis using a chiral stationary phase column (column: Chiralcel OD-H or Chiralcel OJ-H or Chiralpak AD-H; eluent: hexane-2-propanol). Solvent mixtures are understood as volume/volume. The HPLC spectra of enantio-enriched compounds were calibrated with the corresponding racemic mixtures. Chemical yields refer to pure isolated substances. The yields and enantiomeric excesses are given in the corresponding tables.

General procedure for the enantioselective intramolecular 1,4-addition

0.05 mmol of the chalcone and 10 mol-% of octahydro-BINOL *N*-triflyl phosphoramide **3h** were dissolved in 0.25 mL of DME, and the reaction mixture was stirred at r. t. The product was directly charged on silica gel and purified by column chromatography using hexane-ethyl acetate mixtures as eluents to afford the desired product.

*1-Methyl-2-phenyl-2,3-dihydroquinolin-4(1H)-one (**2a**)*

Synthesized according to the general procedure: 6.1 mg, 51 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.78$ (dd, $J = 7.8$, 1.6 Hz, 1H), 7.41 – 7.34 (m, 1H), 7.25 – 7.16 (m, 3H), 7.10 – 7.06 (m, 2H), 6.71 – 6.64 (m, 2H), 4.59 (t, $J = 6.2$ Hz, 1H), 3.08 (dd, $J = 16.1$, 6.2 Hz, 1H), 2.88 – 2.79 (m, 4H). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 192.4$, 151.7, 139.9, 136.0, 128.9, 127.8, 127.6, 126.5, 119.7, 116.6, 112.9, 64.7, 45.4, 37.8. – IR (KBr): $\tilde{\nu} = 3061$, 3027, 2921, 1759, 1600, 1492, 1433, 807, 758, 718, 700. – MS-EI: m/z (%) = 237.0 (100) $[M]^+$, 222.9 (4), 160.0 (83), 146.0 (5), 77.0. – $[\alpha]_D^{25} = +141.8°$ ($c = 1.0$ in chloroform). – HPLC

conditions: AD-H column, *n*-hexane-2-propanol = 98 : 2, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 33.9 min; minor enantiomer: t_R = 31.6 min.

*1-Benzyl-2-phenyl-2,3-dihydroquinolin-4(1H)-one (**10a**)*

Synthesized according to the general procedure: 11.3 mg, 72 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.80 (dd, J = 7.7, 1.8 Hz, 1H), 7.31 – 7.04 (m, 11H), 6.69 – 6.62 (m, 2H), 4.77 (dd, J = 6.6, 4.6 Hz, 1H), 4.70 (d, J = 17.0 Hz, 1H), 4.17 (d, J = 17.0 Hz, 1H), 3.22 (dd, J = 15.9, 6.6 Hz, 1H), 2.90 (dd, J = 15.9, 4.6 Hz, 1H). –^{13}C NMR (63 MHz, $CDCl_3$): δ = 191.9, 150.7, 139.3, 137.3, 135.8, 128.8, 128.7, 127.7, 127.6, 127.2, 126.4, 126.2, 119.8, 116.5, 112.8, 62.4, 53.5, 44.8. – IR (KBr): $\tilde{\nu}$ = 3027, 2924, 2849, 1673, 1602, 1491, 1450, 805, 751, 698. – MS-EI: m/z (%) = 313.1 (44) [M]$^+$, 236.0 (12), 222.0 (17), 91.0 (100), 77.0 (15). – $[\alpha]_D^{25}$ = +43.3° (c = 1.0 in chloroform). – HPLC conditions: OD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 39.5 min; minor enantiomer: t_R = 25.7 min.

*1,2-Diphenyl-2,3-dihydroquinolin-4(1H)-one (**11a**)*

Synthesized according to the general procedure: 9.9 mg, 66 %, pale-yellow solid. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.89 (dd, J = 8.2, 1.7 Hz, 1H), 7.33 – 7.16 (m, 11H), 6.81 – 6.76 (m, 2H), 5.14 (t, J = 5.6 Hz, 1H), 3.36 (dd, J = 16.3, 5.6 Hz, 1H), 3.09 (dd, J = 16.3, 5.6 Hz, 1H). –^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.2, 150.2, 145.2, 140.0, 135.2, 129.6, 128.7, 127.6, 126.9, 125.9, 125.8, 120.7, 118.2, 116.3, 64.3, 44.9. – IR (KBr): $\tilde{\nu}$ = 3032, 2922, 2883, 2832, 1716, 1596, 1490, 777, 765, 748, 701. – MS-EI: m/z (%) = 299.0 (43) [M]$^+$, 222.0 (43), 77.0 (100). – $[\alpha]_D^{25}$ = –19.0° (c = 0.5 in chloroform). – HPLC conditions: OD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 18.1 min; minor enantiomer: t_R = 26.1 min.

*1-Isopropyl-2-phenyl-2,3-dihydroquinolin-4(1H)-one (**12a**)*

Synthesized according to the general procedure: 4.2 mg, 32 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.81 (dd, J = 7.8, 1.8 Hz, 1H), 7.47 – 7.40 (m, 1H), 7.21 – 7.10 (m, 5H), 6.95 (d, J = 8.7 Hz 1H), 6.69 – 6.62 (m, 1H), 4.70 (dd, J = 6.7, 2.2 Hz, 1H), 4.43 – 4.27 (m, 1H), 3.17 (dd, J = 15.9 Hz, 6.7 Hz, 1H), 2.84 (dd, J = 15.9, 2.2 Hz, 1H), 1.40 (d, J = 6.6 Hz, 3H), 1.08 (d, J = 6.7 Hz, 3H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.2, 150.4, 141.5, 135.9, 128.6, 128.1, 127.2, 126.2, 120.4, 115.6, 112.5, 54.0, 48.8, 44.6, 21.6, 19.7. – IR (KBr): $\tilde{\nu}$ = 3028, 2968, 2925, 1716, 1604, 1507, 1457, 1396, 1271, 1188, 752, 700. – MS-EI: m/z (%) = 265.1 (43) [M]$^+$, 222.0 (9), 188.1 (3), 146.1 (100), 77.0 (63). – $[\alpha]_D^{25}$ = +94.0° (c = 0.1 in chloroform). – HPLC conditions: OD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 13.9 min; minor enantiomer: t_R = 20.7 min.

*1-Allyl-2-phenyl-2,3-dihydroquinolin-4(1H)-one (**13a**)*

Synthesized according to the general procedure: 6.3 mg, 46 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.79 (dd, J = 7.8, 1.7 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.22 – 7.18 (m, 3H), 7.12 – 7.09 (m, 2H), 6.73 – 6.60 (m, 2H), 5.83 – 568 (m, 1H), 5,22 – 5.10 (m, 2H), 4.68 (t, J = 6.2 Hz, 1H), 4.11 – 4.01 (m, 1H), 3.63 – 3.53 (m, 1H), 3.07 (dd, J = 15.9, 6.2 Hz, 1H), 2.87 (dd, J = 15.9, 6.2 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.2, 150.9, 139.9, 135.8, 132.8, 128.9, 127.9, 127.7, 126.7, 119.9, 116.8, 116.6, 113.2, 62.4, 52.1, 45.2. – IR (KBr): $\tilde{\nu}$ = 3027, 2919, 1642, 1604, 1493, 752, 730, 698. – MS-EI: m/z (%) = 263.1 (22) [M]$^+$, 222.0 (4), 186.1 (14), 146.1 (4), 77 (100). – $[\alpha]_D^{25}$ = +139.0° (c = 0.2 in chloroform). – HPLC conditions: OD-H column, *n*-hexane-2-propanol = 95 : 5, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 16.9 min; minor enantiomer: t_R = 17.9 min.

*1-Allyl-2-o-tolyl-2,3-dihydroquinolin-4(1H)-one (**13b**)*

Synthesized according to the general procedure: 6.3 mg, 45 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.86 (dd, J = 7.8, 1.7 Hz, 1H), 7.46 – 7.39 (m, 1H), 7.17 – 7.06 (m, 4H), 6.82 – 6.71 (m, 2H), 5.89 – 5.76 (m, 1H), 5.25 – 5.18 (m, 2H), 4.98 (t, J = 6.5 Hz, 1H), 4.13 – 4.03 (m, 1H), 3.61 – 3.51 (m, 1H), 3.08 (dd, J = 15.9, 6.3 Hz, 1H), 2.86 (dd, J = 15.9, 6.6 Hz, 1H), 2.34 (s, 3H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.0, 164.3, 160.3, 150.6, 135.9, 132.7, 128.4, 128.3, 127.7, 119.9, 116.9, 116.7, 116.0, 115.9, 113.2, 61.7, 52.0, 45.3. – IR (KBr): $\tilde{\nu}$ = 3059, 2922, 1676, 1601, 1493, 1463, 1348, 1320, 1095, 924, 754. – MS–EI: m/z (%) = 277.0 (83) [M]$^+$, 235.9 (9), 186.2 (46), 146.0 (27), 91.0 (100). – $[\alpha]_D^{25}$ = +83.5° (c = 0.2 in chloroform). – HPLC conditions: AD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 9.6 min; minor enantiomer: t_R = 10.6 min.

*1-Allyl-2-(2-methoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (**13c**)*

Synthesized according to the general procedure: 9.2 mg, 63 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.82 (dd, J = 7.8, 1.7 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.24 – 7.17 (m, 1H), 6.91 – 6.84 (m, 2H), 6.79 – 6.66 (m, 3H), 5.95 – 5.81 (m, 1H), 5.36 – 5.12 (m, 3H), 4.17 – 4.07 (m, 1H), 3.83 (s, 3H), 3.67 – 3.56 (m, 1H), 3.15 (dd, J = 15.9, 7.0 Hz, 1H), 2.99 (dd, J = 15.9, 3.6 Hz, 1H). –^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.9, 156.8, 150.9, 135.7, 133.1, 128.7, 127.6, 126.8, 120.4, 119.4, 116.1, 116.0, 112.3, 110.7, 56.6, 55.1, 52.5,

42.5. – IR (KBr): $\tilde{\nu}$ = 3059, 3002, 2924, 2853, 1716, 1667, 1598, 1558, 1487, 1177, 1044, 1024, 997, 980, 907, 806, 788, 719. – MS-EI: m/z (%) = 293.2 (89) $[M]^+$, 261.8 (9), 251.9 (10), 186.0 (43), 108.1 (27). – $[\alpha]_D^{25} = +83.8°$ (c = 1.0 in chloroform). – HPLC conditions: AD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 13.8 min; minor enantiomer: t_R = 11.9 min.

*1-Allyl-2-m-tolyl-2,3-dihydroquinolin-4(1H)-one (**13d**)*

Synthesized according to the general procedure: 7.3 mg, 53 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.86 (dd, J = 7.8, 1.7 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.20 – 6.95 (m, 4H), 6.80 – 6.70 (m, 2H), 5.92 – 5.72 (m, 1H), 5.28 – 5.17 (m, 2H), 4.71 (t, J = 6.4 Hz, 1H), 4.17 – 4.07 (m, 1H), 3.70 – 3.59 (m, 1H), 3.11 (dd, J = 15.9, 6.4 Hz, 1H), 2.93 (dd, J = 15.9, 6.4 Hz, 1H), 2.30 (s, 3H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.4, 150.9, 139.8, 138.6, 135.7, 132.9, 128.8, 128.7, 127.7, 127.5, 123.7, 119.9, 116.7, 116.5, 113.2, 62.4, 51.9, 45.3, 21.5. – IR (KBr): $\tilde{\nu}$ = 2957, 2926, 2857, 1725, 1677, 1605, 1487, 1466, 1348, 1320, 1177, 754, 704. – MS-EI: m/z (%) = 277.1 (72) $[M]^+$, 263.2 (4), 236.0 (14), 186.0, 146.1 (10), 91.1 (88). – $[\alpha]_D^{25} = +111.6°$ (c = 0.5 in chloroform). – HPLC conditions: OJ-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 18.7 min; minor enantiomer: t_R = 24.8 min.

*1-Allyl-2-(3-phenoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (**13e**)*

Synthesized according to the general procedure: 6.4 mg, 36 %, yellow oil. – ^{1}HNMR (250 MHz, $CDCl_3$): δ = 7.84 (dd, J = 7.8, 1.4 Hz, 1H), 7.42 – 7.27 (m, 3H), 7.21 (d, J = 7.8 Hz, 1H), 7.13 – 7.07 (m, 1H), 6.98 – 6.69 (m, 7H), 5.90 – 5.75 (m, 1H), 5.28 – 5.14 (m, 2H), 4.72 (t, J = 6.1 Hz, 1H), 4.18 – 4.08 (m, 1H), 3.70 – 3.60 (m, 1H), 3.13 (dd, J = 15.9, 6.1 Hz, 1H), 2.90 (dd, J = 15.9, 6.1 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.0, 157.9, 156.5, 150.7, 142.0, 135.8, 132.8, 130.3, 129.8, 127.7, 123.6, 121.2, 119.9, 119.2, 117.8, 116.8, 116.7, 116.7, 113.1, 62.2, 52.2, 45.1. – IR (KBr): $\tilde{\nu}$ = 3062, 2923, 1725, 1675, 1604, 1485, 988, 916, 754, 692. – MS-EI: m/z (%) = 355.2 (100) $[M]^+$, 314.4 (19), 186.0 (55), 168.1 (12), 145.7 (11), 76.8 (85). – $[\alpha]_D^{25} = +73.4°$ (c = 0.5 in chloroform). – HPLC conditions: AD-H column, *n*-hexane-2-propanol = 98 : 2, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 37.5 min; minor enantiomer: t_R = 35.5 min.

*1-Allyl-2-(4-methoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (**13f**)*

Synthesized according to the general procedure: 14.4 mg, 98 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.86 (dd, J = 7.8, 1.7 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.13 – 7.09 (m, 2H), 6.83 – 6.69 (m, 4H), 5.89 – 5.74 (m, 1H), 5.27 – 5.16 (m, 2H), 4.70 (t, J = 6.4 Hz, 1H), 4.15 – 4.05 (m, 1H), 3.77 (s, 3H), 3.70 – 3.60 (m, 1H), 3.09 (dd, J = 15.9, 5.9 Hz, 1H), 2.91 (dd, J = 15.9, 6.7 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.5, 159.2, 150.9., 135.7, 132.9, 131.8, 127.9, 127.7, 119.9, 116.7, 116.5, 114.3, 113.3, 61.9, 55.2, 51.8, 45.5. – IR (KBr): $\tilde{\nu}$ = 2929, 2834, 1675, 1604, 1510, 1490, 1107, 1031, 989, 924, 810, 799, 755, 703. – MS-EI: m/z (%) = 293.1 (39) $[M]^+$, 252.0 (7), 185.9 (31), 108.1 (27). – $[\alpha]_D^{25} = +122.6°$ (c = 1.0 in chloroform). – HPLC conditions: AD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 16.5 min; minor enantiomer: t_R = 17.8 min.

*1-Allyl-2-(4-fluorophenyl)-2,3-dihydroquinolin-4(1H)-one (**13g**)*

Synthesized according to the general procedure: 12.9 mg, 92 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.86 (dd, J = 7.8, 1.7 Hz, 1H), 7.45 – 7.38 (m, 1H), 7.18 – 7.11 (m, 2H), 7.02 – 6.94 (m, 2H), 6.80 – 6.71 (m, 2H), 5.90 – 5.75 (m, 1H), 5.28 – 5.18 (m, 2H), 4.74 (t, J = 6.1 Hz, 1H), 4.17 – 4.07 (m, 1H), 3.68 – 3.58 (m, 1H), 3.13 (dd, J = 15.9, 6.1 Hz, 1H), 2.89 (dd, J = 15.9, 6.1 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.0, 164.3, 160.3, 150.6, 135.9, 132.7, 128.4, 128.3, 127.7, 119.9, 116.9, 116.7, 116.0, 115.9, 113.2, 61.7, 52.0, 45.3. – IR (KBr): $\tilde{\nu}$ = 2958, 2928, 2857, 1725, 1676, 1603, 1508, 990, 924, 839, 799, 754, 705. – MS-EI: m/z (%) = 281.0 (33) $[M]^+$, 239.9 (11), 186.1 (20), 145.0 (4), 96.0 (93). – $[\alpha]_D^{25} = +130.3°$ (c = 1.0 in chloroform). – HPLC conditions: AD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 12.3 min; minor enantiomer: t_R = 14.8 min.

*1-Allyl-2-(3,4,5-trimethoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (**13h**)*

Synthesized according to the general procedure: 10.2 mg, 58 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.88 (dd, J = 7.8, 1.7 Hz, 1H), 7.45 – 7.38 (m, 1H), 6.85 – 6.69 (m, 2H), 6.41 (s, 2H), 5.92 – 5.77 (m, 1H), 5.30 – 5.19 (m, 2H), 4.66 (dd, J = 7.3, 5.8 Hz, 1H), 4.15 – 4.06 (m, 1H), 3.81 (s, 3H), 3.74 (s, 6H), 3.72 – 3.61 (m, 1H), 3.09 (dd, J = 15.9, 5.8 Hz, 1H), 2.93 (dd, J = 15.9, 7.3 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.3, 153.5, 151.0, 137.5, 135.8, 135.5, 133.0, 127.7, 120.0, 116.8, 116.7, 113.4, 103.7, 63.0, 60.8, 56.0, 52.1, 45.6. – IR (KBr): $\tilde{\nu}$ = 2926, 2852, 1725, 1675, 1601, 1489, 1008, 921, 799, 755, 687. – MS-EI: m/z (%) = 353.1 (88) $[M]^+$, 321.9 (4), 312.3 (8), 280.7 (3), 250.2 (4), 186.1 (63), 167.1, 146.1 (12). – $[\alpha]_D^{25} = +93.4°$ (c = 0.5 in chloroform). – HPLC conditions: AD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 33.3 min; minor enantiomer: t_R = 51.9 min.

*1-Allyl-2-(naphthalen-1-yl)-2,3-dihydroquinolin-4(1H)-one (**13i**)*

Synthesized according to the general procedure: 13.4 mg, 86 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 8.04 – 8.00 (m, 1H), 7.92 – 7.85 (m, 2H), 7.77 (d, J = 8.0 Hz, 1H), 7.58 – 7.43 (m, 3H), 7.34 – 7.22 (m, 2H), 6.85 (d, J = 8.5 Hz, 1H), 6.80 – 6.73 (m, 1H), 5.96 – 5.81 (m, 1H), 5.57 (t, J = 6.2 Hz, 1H), 5.32 – 5.19 (m, 2H), 4.25 – 4.15 (m, 1H), 3.68 – 3.58 (m, 1H), 3.31 (dd, J = 15.8, 6.8 Hz, 1H), 3.17 (dd, J = 15.9, 5.3 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.0, 151.2, 135.9, 134.4, 134.0, 132.7, 130.4, 129.4, 128.6, 127.9, 126.4, 125.7, 125.3, 124.1, 122.4, 119.4, 116.7, 116.5, 112.8, 59.0, 52.2, 43.6. – IR (KBr): $\tilde{\nu}$ = 3060, 2922, 1675, 1638, 1599, 159, 1496, 993, 957, 916, 868, 799, 783, 761. – MS-EI: m/z (%) = 312.9 (56) $[M]^+$, 272.1 (10), 186.1 (37), 145.2 (6), 127.0 (92). – $[\alpha]_D^{25}$ = +24.0° (c = 1.0 in chloroform). – HPLC conditions: OD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 32.2 min; minor enantiomer: t_R = 38.6 min.

*1-Allyl-2-(naphthalen-2-yl)-2,3-dihydroquinolin-4(1H)-one (**13j**)*

Synthesized according to the general procedure: 11.6 mg, 74 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.89 (dd, J = 7.8, 1.6 Hz, 1H), 7.84 – 7.70 (m, 3H), 7.60 (d, J = 0.9 Hz, 1H), 7.50 – 7.35 (m, 4H), 6.86 – 6.74 (m, 2H), 5.91 – 5.76 (m, 1H), 5.29 – 5.18 (m, 2H), 4.92 (t, J = 6.5 Hz, 1H), 4.24 – 4.13 (m, 1H), 3.75 – 3.64 (m, 1H), 3.17 (dd, J = 15.9, 6.0 Hz, 1H), 3.05 (dd, J = 15.9, 7.0 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.2, 151.0, 137.3, 135.8, 133.3, 133.0, 132.8, 129.0, 127.9, 127.8, 127.7, 126.4, 126.2, 125.9, 124.4, 120.0, 116.9, 116.7, 113.4, 62.7, 51.9, 45.2. – IR (KBr): $\tilde{\nu}$=3057, 2925, 1719, 1671, 1600, 1561, 1490, 987, 919, 859, 821, 799, 750. – MS-EI: m/z (%) = 313.0 (63) $[M]^+$, 272.2 (14), 186.0 (43), 127.0 (89). – $[\alpha]_D^{25}$ = +121.3° (c = 1.0 in chloroform). – HPLC conditions: AD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 16.9 min; minor enantiomer: t_R = 19.0 min.

*1-Allyl-2-(furan-2-yl)-2,3-dihydroquinolin-4(1H)-one (**13k**)*

Synthesized according to the general procedure: 8.6 mg, 68 %, yellow oil. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.90 – 7.86 (m, 1H), 7.40 – 7.30 (m, 2H), 6.75 – 6.68 (m, 2H), 6.23 (dd, J = 3.3, 1.8 Hz, 1H), 6.09 – 6.08 (m, 1H), 5.96 – 5.81 (m, 1H), 5.35 – 5.20 (m, 2H), 4.79 (dd, J = 5.9, 4.3 Hz, 1H), 4.23 – 4.13 (m, 1H), 3.93 – 3.83 (m, 1H), 3.13 (dd, J = 16.2, 5.9 Hz, 1H), 3.01 (dd, J = 16.2, 4.3 Hz, 1H). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.3, 152.5, 149.5, 142.4, 135.6, 133.2, 127.7, 119.6, 116.9, 116.8, 113.4, 110.1, 108.0, 56.1, 52.7, 41.9. – IR (KBr): $\tilde{\nu}$ = 2924, 1670, 1604, 1489, 1032, 911, 756. – MS-EI: m/z (%) = 252.9 (52) $[M]^+$, 212.1 (5), 186.3 (7), 146.3 (6), 67.1 (7). – $[\alpha]_D^{25}$ = +4.6° (c = 0.5 in chloroform). – HPLC conditions: OD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 15.6 min; minor enantiomer: t_R = 17.7 min.

*1-Benzyl-2-(methoxyphenyl)-2,3-dihydroquinolin-4(1H)-one (**10b**)*

Synthesized according to the general procedure: 12.1 mg, 71 %, yellow solid. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.85 (dd, J = 7.8, 1.6 Hz, 1H, Ar), 7.37 – 7.18 (m, 7H, Ar), 6.94 – 6.65 (m, 5H, Ar), 5.24 (dd, J = 7.2, 2.8 Hz, 1H, CH), 4.74 (d, J = 17.0 Hz, 1H, NCH_2), 4.22 (d, J = 17.0 Hz, 1H, NCH_2), 3.80 (s, 3H, OCH_3), 3.28 (dd, J = 16.0, 7.2 Hz, 1H, CH_2), 3.05 (dd, J = 16.0, 2.8 Hz, 1H, CH_2). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 192.8, 156.9, 151.0, 137.7, 135.9, 128.8, 127.7, 127.3, 126.6, 126.5, 126.2, 120.4, 119.5, 116.3, 112.3, 110.7, 104.9, 57.3, 55.1, 54.0, 42.4. – IR (KBr): $\tilde{\nu}$ = 3058, 3032, 2999, 2962, 2935, 2836, 1943, 1672, 1602, 1585, 1558, 1495, 1469, 1461, 1449, 1414, 1396, 1345, 1321, 1287, 1264, 1244, 1222, 1205, 1174, 1120, 1097, 1052, 1024, 1006, 970, 952, 931, 864, 808, 795, 754, 732, 719, 694, 598, 576, 553, 527, 506, 477, 458, 403. – MS-EI (70 eV): m/z (%) = 343.2 (5) $[M]^+$, 252.0 (3), 236.0 (4), 107.1 (2), 91.0 (100). – $[\alpha]_D^{25}$ = +1.7° (c = 1.0 in chloroform). – HPLC conditions: OD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 15.6 min; minor enantiomer: t_R = 20.0 min.

*1-Benzyl-2-(2-bromophenyl)-2,3-dihydroquinolin-4(1H)-one (**10c**)*

Synthesized according to the general procedure: 11.5 mg, 29 %, yellow solid. – ^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.87 (dd, J = 7.8, 1.6 Hz, 1H, Ar), 7.59 – 7.52 (m, 1H, Ar), 7.41 – 7.30 (m, 6H, Ar), 7.15 – 7.07 (m, 3H, Ar), 6.79 – 6.69 (m, 2H, Ar), 5.24 (dd, J = 7.4, 3.0 Hz, 1H, CH), 4.73 (d, J = 17.0 Hz, 1H, NCH_2), 4.17 (d, J = 17.0 Hz, 1H, NCH_2), 3.33 (dd, J = 16.0, 7.4 Hz, 1H, CH2), 3.07 (dd, J = 16.0, 3.0 Hz, 1H, CH_2). – ^{13}C NMR (63 MHz, $CDCl_3$): δ = 191.7, 150.8, 137.9, 137.0, 136.1, 133.8, 129.4, 128.9, 127.9, 127.7, 127.5, 127.4, 126.3, 122.8, 119.7, 116.8, 112.5, 61.7, 54.0, 42.3. – IR (KBr): $\tilde{\nu}$ = 3075, 3020, 2962, 2921, 1739, 1669, 1602, 1559, 1493, 1471, 1449, 1422,1410, 1396, 1351, 1324, 1222, 1173, 1114, 1055, 1006, 966, 935, 885, 807, 764, 728, 691, 671. – MS-ESI (+): m/z = 392.1 (Br^{79}), 394.1 (Br^{81}). – $[\alpha]_D^{25}$ = +9.1° (c = 1.0 in chloroform). – HPLC conditions: AS-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: t_R = 30.8 min; minor enantiomer: t_R = 57.9 min.

*1-Benzyl-2-(3-bromophenyl)-2,3-dihydroquinolin-4(1H)-one (**10d**)*

Synthesized according to the general procedure: 22.8 mg, 58 %, yellow solid. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.87$ (dd, $J = 7.8$, 1.6 Hz, 1H, Ar), 7.41 – 7.27 (m, 8H, Ar), 7.16 – 7.04 (m, 2H, Ar), 6.79 – 6.72 (m, 2H, Ar), 4.84 – 4.77 (m, 2H, CH, NCH_2), 4.22 (d, $J = 17.0$ Hz, 1H, NCH_2), 3.28 (dd, $J = 16.0$, 6.6 Hz, 1H, CH_2), 2.93 (dd, $J = 16.0$, 4.4 Hz, 1H, CH_2). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 191.5$, 150.5, 142.0, 137.1, 136.2, 131.1, 130.6, 129.9, 128.9, 127.8, 127.5, 126.4, 125.1, 123.0, 119.9, 117.0, 112.9, 62.0, 53.7, 44.7. – IR (KBr): $\tilde{\nu} = 3063$, 3030, 2924, 2854, 1722, 1673, 1599, 1560, 1485, 1452, 1391, 1347, 1294, 1217, 1172, 1072, 1027, 1008, 963, 946, 887, 834, 791, 754, 696. – MS-ESI (+): $m/z = 392.1$ (Br^{79}), 394,1 (Br^{81}). – $[\alpha]_D^{25} = +30.3°$ ($c = 1.0$ in chloroform). – HPLC conditions: AS-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: $t_R = 37.8$ min; minor enantiomer: $t_R = 54.8$ min.

*1-Benzyl-2-(4-bromophenyl)-2,3-dihydroquinolin-4(1H)-one (**10e**)*

Synthesized according to the general procedure: 22.5 mg, 57 %, yellow solid. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.87$ (dd, $J = 7.8$, 1.6 Hz, 1H, Ar), 7.41 – 7.27 (m, 8H, Ar), 7.01 (d, $J = 8.4$ Hz, 2H, Ar), 7.15 – 7.07 (m, 3H, Ar), 6.78 – 6.71 (m, 2H, Ar), 4.82 – 4.75 (m, 2H, CH, NCH_2), 4.21 (d, $J = 17.0$ Hz, 1H, NCH_2), 3.28 (dd, $J = 16.0$, 6.6 Hz, 1H, CH_2), 2.91 (dd, $J = 16.0$, 4.5 Hz, 1H, CH_2). – ^{13}C NMR (63 MHz, $CDCl_3$): $\delta = 191.5$, 150.6, 138.6, 137.2, 136.1, 132.1, 128.9, 128.3, 127.8, 127.5, 126.4, 121.8, 119.9, 116.9, 112.9, 61.9, 53.6, 44.8. – IR (KBr): $\tilde{\nu} = 3064$, 3014, 2921, 2852, 1724, 1675, 1604, 1565, 1491, 1466, 1347, 1293, 1271, 1173, 1126, 1024, 803, 754, 698, 666. – MS-ESI (+): $m/z = 391.7$ (Br^{79}), 394,1 (Br^{81}). – $[\alpha]_D^{25} = +15.3°$ ($c = 1.0$ in chloroform). – HPLC conditions: AS-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: $t_R = 46.1$ min; minor enantiomer: $t_R = 54.9$ min.

*1-Benzyl-2-(naphthalen-1-yl)-2,3-dihydroquinolin-4(1H)-one (**10f**)*

Synthesized according to the general procedure: 7.4 mg, 41 %, yellow solid. – ^{1}H NMR (250 MHz, $CDCl_3$): $\delta = 7.91 – 7.86$ (m, 3H, Ar), 7.69 (dd, $J = 7.7$, 1.8 Hz, 1H, Ar), 7.55 – 7.21 (m, 10H, Ar), 6.80 – 6.74 (m, 2H, Ar), 5.60 (dd, $J = 7.2$, 3.3 Hz, 1H, CH), 4.76 (d, $J = 17.0$ Hz, 1H, NCH_2), 4.15 (d, $J = 17.0$ Hz, 1H, NCH_2), 3.39 (dd, $J = 15.7$, 7.2 Hz, 1H, CH_2), 3.10 (dd, $J = 15.7$, 3.3 Hz, 1H, CH_2). – ^{13}C NMR (63 MHz, $CDCl_3$):128.9, 127.9, 127.4, 126.5, 126.3, 125.7, 125.3, 123.6, 122.2, 119.4, 116.6, 112.5, 59.1, 53.8, 43.4. – IR (KBr): $\tilde{\nu} = 3054$, 3016, 2864, 1671, 1625, 1601, 1560, 1491, 1469, 1448, 1404, 1348, 1321, 1291, 1259, 1223, 1193, 1172, 1116, 1054, 1025, 1008, 943, 907, 862, 811, 798, 767, 727, 693, 638, 583, 562, 546, 534, 517, 501, 484, 471, 458, 420. – MS-EI (70 eV): m/z (%) = 363.2 (4) $[M]^+$, 272.1 (2), 127.0 (4), 91.0 (100). – $[\alpha]_D^{25} = +49.3°$ ($c = 0.5$ in chloroform). – HPLC conditions: OD-H column, *n*-hexane-2-propanol = 90 : 10, flow rate = 0.6 mL min^{-1}, major enantiomer: $t_R = 40.2$ min; minor enantiomer: $t_R = 72.0$ min.

Table 5. Crystal structure data and numbers pertinent to data collection and structure refinement for **10d**.

	10d
Formula	$C_{22}H_{18}BrNO$
M_r	392.28
Crystal size, mm^3	0.37 × 0.31 × 0.29
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a, Å	9.0521(4)
b, Å	13.4433(4)
c, Å	15.0807(5)
V, Å^3	1835.17(12)
Z	4
D_{calcd}, g cm^{-3}	1.42
μ(MoK_α), cm^{-1}	2.2
F(000), e	800
hkl range	±12, −18→16, ± 20
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.6757
Refl. measured / unique / R_{int}	64986 / 4729 / 0.0722
Param. refined	226
$R(F)$ / $wR(F^2)$[a] (all refls.)	0.0471 / 0.1012
x (Flack)	0.023(9)
GoF (F^2)[b]	1.124
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.59/−0.914

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (AP)^2 + BP]^{-1}$, where $P = (\mathrm{Max}(F_o^2, 0) + 2F_c^2)/3$; [b] $\mathrm{GoF} = [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Crystal structure determination

Crystallographic data were collected with a Stoe IPDS II two-circle-diffractometer with monochromatic MoK_α radiation ($\lambda = 0.71073$ Å). The structure was solved by Direct Methods using SHELXS-97 and refined against F^2 on all data by full-matrix least-squares methods using SHELXL-97 [46, 47]. Details regarding the crystal structure determination are summarized in Table 5.

CCDC 897124 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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