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# Synthesis and characterization of biphenyl liquid crystal based on natural molecules and 2(5*H*)-furanone moiety

**Shi-He Luo · Qun-Fang Wang · Zhao-Yang Wang · Pai Peng**

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**Abstract** Using 4′-hexyloxybiphenyl-4-ol and *N*-(5-alkoxy-3-bromo-2(5*H*)-furanonyl) amino acids as reactants, a series of novel biphenyl liquid crystal compounds containing natural molecule moieties, such as menthol, borneol, and amino acids, were synthesized via esterification. The structures of all novel compounds were confirmed by FTIR, $^{1}$H NMR, $^{13}$C NMR, MS, and elemental analysis, and the liquid crystal properties of target compounds were characterized with DSC, XRD, and POM. The introduction of hexyloxy made the biphenyl esters have a potential to appear in mesomorphic phase and have a higher Tm, and bornyl moiety was more beneficial for the liquid crystal performance than a menthyl unit. Most compounds were mesomorphic phase liquid crystal molecules, and POM and XRD showed that they existed in smectic phase. These researches provide a theoretical basis for the synthesis of biphenyl ester liquid crystal materials via the utilization of 2(5*H*)-furanone derivates and natural molecules.

**Keywords** Biphenyl ester · 2(5*H*)-furanone · Liquid crystal · Synthesis · Amino acid · Menthol · Borneol

## Introduction

Biphenyls liquid crystals have been widely used in photoelectric display materials and other application areas for their many advantages, e.g., good physical and chemical stability, wide temperature range, appropriately low viscosity, fast response, and low

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driver voltage [1–6]. Especially, their alkoxy derivates could have a potential to afford a huge birefringence which will be beneficial to their optical performances [7]. Therefore, more and more researches have been focused on alkoxy biphenyls used in liquid crystalline areas [8–13].

On the other hand, chiral liquid crystal materials have many unique photoelectric performance, such as good optical properties, reflection choice for polarized light, circular dichroism, ferroelectricity, and piezoelectricity, which make them have vast potential application prospects in many fields, including non-linear optics, snap switch, microelectronics, etc. [14–17]. Thus, there are more and more reports on the introduction of different chiral moieties, such as menthyl [18–22], bornyl [23, 24], and amino acid units [25–27], into liquid crystal materials.

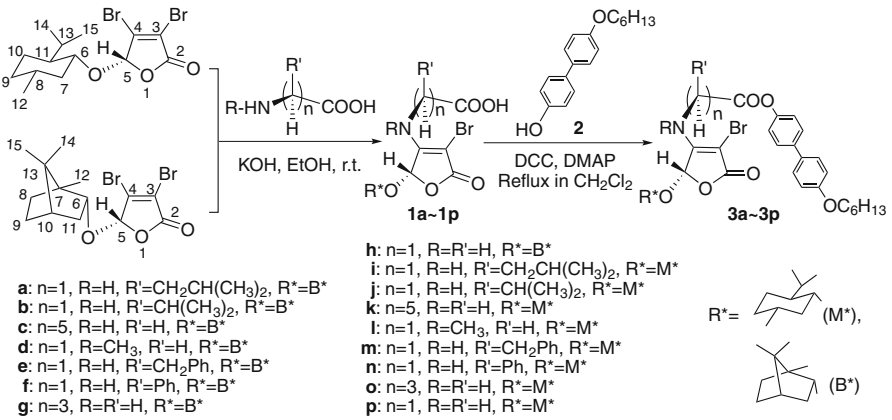
However, even introducing chiral menthyl [20, 22, 28, 29] or bornyl [24] into biphenyl liquid crystal materials became a new research direction, and there are few papers reporting the design and synthesis of biphenyl liquid crystals simultaneously containing chiral menthyl/bornyl and amino acid units, let alone alkoxy biphenyls. More importantly, it has been found that 2(5*H*)-furanone derivates could be used in liquid crystal research today [30, 31].

Therefore, on the basis of our previous work [31], in order to further expand the applications of 3,4-dihalo-2(5*H*)-furanone [31–34], a series of novel liquid crystal compounds **3** were here designed and synthesized via the esterification of 4′-hexyloxybiphenyl-4-ol **2** with *N*-[5-alkoxy-2(5*H*)-furanonyl] amino acids **1** (Scheme 1). The structures and liquid crystal properties of the target compounds **3a–3p** were systematically characterized by FTIR, $^{1}$H NMR, MS, DSC, XRD, and POM.

## Results and discussion

### Syntheses of target compounds by esterification

The traditional esterification process of phenols via the first acylation of carboxylic acids and then the dehydrohalogenation between acyl chloride and phenols produces




**Scheme 1** Synthetic route to target compounds 3a-3p

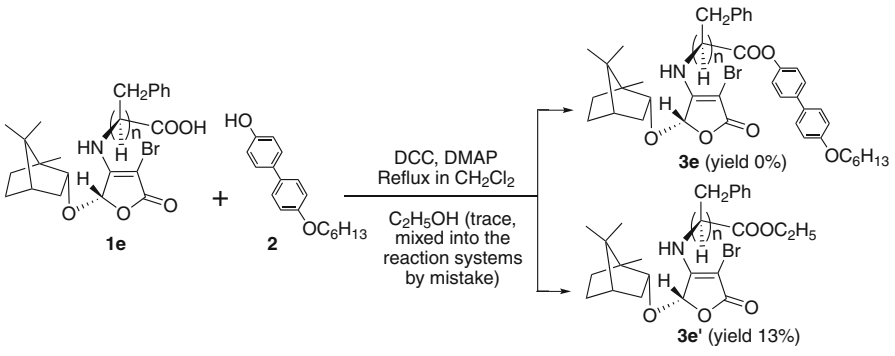
a large number of corrosive gases, such as sulfur dioxide and hydrogen chloride. Therefore, there are more and more reports on another relatively green esterification method via the dehydrating condensation between carboxylic acids and phenols [35]. In this work, we still chose the latter esterification method for the syntheses of the target compounds **3**.

However, this time, we used more available *N*,*N*′-dicyclohexylcarbodiimide (DCC) as dehydrating agent, though its by-product 1,3-dicyclohexylurea was sometimes difficult to remove clearly. Similarly, more common and cheaper *N*,*N*-dimethylaminopyridine (DMAP) was selected as catalyst. At the same time, the suitably higher reaction temperature than that reported before (room temperature) [31] was advantageous. And fortunately, the yields (29–55 %) of products **3** are also generally higher than before (16–25 %) [31], which may be linked to the existence of hexyloxy in biphenyl-4-ol because of its electron-donating effect for phenoxy anion in the reaction.

Of course, due to the lower activity of the phenolic hydroxyl group used here for esterification, some careful operations, especially the patient drying pretreatment to the reaction flask, were very necessary. These experiences came from the investigations on an unexpected by-product **3e**′ (Scheme 2). During the operation for the synthesis of target compound **3e**, trace alcohol was mixed into the reaction systems by mistake in the drying pretreatment. As a result, a product with obviously lower yield was obtained. And its following characterization data were also puzzling.

**3e**′: Yellowish solid, yield 13 % (calculated according to the reactant **1e**); m.p. 149.5–151.6 °C; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.84–0.88 (9H, *m*, $CH_3$-12, $CH_3$-14, $CH_3$-15), 1.23–1.33 (7H, *m*, $CH_2$-8, $CH_2$-9, $CH_3$-27), 1.60–1.65 (2H, *m*, $CH_2$-11), 2.10–2.25 (1H, *m*, $CH_2$-10), 3.05–3.35 (2H, *m*, $CH_2$-18), 3.50–3.89 (1H, *m*, CH-6), 3.97–4.69 (3H, *m*, CH-17, $CH_2$-26), 5.12–5.66 (2H, *m*, CH-5, NH), 7.10–7.19 (2H, *m*, ArH-20,24), 7.27–7.39 (3H, *m*, ArH-21,22,23); ESI–MS *m/z* (%): 508 ($[M + H]^+$, 14.0), 530 ($[M + Na]^+$, 30.0); Anal. Calcd for $C_{25}H_{32}BrNO_5$: C 59.29, H 6.37, N 2.77, found: C 59.15, H 6.27, N 2.58.

Surprisingly, there were no typical peaks from the biphenyl groups in the $^1$H NMR characterization. Especially, the results of MS were not the same as expected. In the end, combining the analysis on all operations, we confirmed that the




**Scheme 2** The production of unexpected compound 3e

compound was the by-product **3e′**. It was the result of the reaction of the trace alcohol with intermediate **1e**, because aliphatic alcohol preferentially reacted with the carboxyl group in *N*-[5-alkoxy-2(5*H*)-furanonyl] amino acid. In a word, target compounds **3** must be carefully synthesized with enough patience.

## Structure characterization of all new compounds

In the IR spectra, stretching absorption of the N–H groups was observed in the region 3,400–3,310 $cm^{-1}$ except for **3d** and **3l**. Stretching absorption bands of saturated C–H groups were observed in the region 2,960–2,950 $cm^{-1}$, while for unsaturated C–H groups, the region was 3,070–3,000 $cm^{-1}$. The strong C=O stretching band appeared at 1,785–1,705 $cm^{-1}$. The C=C stretching band in 2(5*H*)-furanone ring usually occurred in the 1,660–1,620 $cm^{-1}$ region, and the benzene ring skeletal stretching occurred at 1,600–1,450 $cm^{-1}$.

In $^{1}H$ NMR, there was a singlet at 5.25–5.96 ppm from the 5-H of 2(5*H*)-furanone. And there were a series of peaks at 6.90–7.60 ppm from the biphenyl groups. Due to the occurrence of unexpected product **3e′**, in order to further confirm the structure of new compounds, two compounds (**3c**, **3k**) were randomly chosen as representatives to be characterized with $^{13}C$ NMR. There were a series of peaks at 114.8–138.7 ppm from the biphenyl groups in their $^{13}C$ NMR spectra. Furthermore, there was a peak at 98.6–99.1 ppm from the 5-C of 2(5*H*)-furanone.

Therefore, combining with the results of mass spectroscopy and elemental analysis, these characterizations proved the structures of all newly synthesized compounds **3** were correct as expected.

## Liquid crystal characterization of target compounds

The liquid crystal properties of target compounds **3** were characterized with DSC, XRD, and POM. Using the DSC curve of compound **3c** as a representative, there are two endothermic peaks on the curve of heating (Fig. 1), which indicates a series of different phase transformations. Especially, it could be obviously seen that the melting point (the melting temperature, Tm) was 60.1 °C and the clear point (the isotropic temperature, Ti) was 147.6 °C. The transition temperatures and enthalpies of different compounds **3** are summarized in Table 1.

Compared with the previous similar reports on *N*-[5-menthoxy-2(5*H*)-furanonyl] amino acid biphenyl ester liquid crystal compounds [31], the introduction of hexyloxy made the biphenyl esters have a potential to appear in mesomorphic phase (e.g. **3i**, **3l**, **3o**) and have a higher Tm (e.g. **3j**, **3n**). At the same time, it could be found that the compounds containing bornyl usually had a higher Tm than those with a menthyl structure (e.g., **3a** vs. **3i**, **3f** vs. **3n**, **3g** vs. **3o**). This may be due to the obvious rigid polycyclic structure in the bornyl moiety.

However, the influences of amino acid units in the new target compounds were similar to our previous work [31]. For example, with the decrease of alkyl chain length in amino acid units, the new compounds (e.g., **3k** vs. **3o**) were more likely to appear as mesomorphic phase.

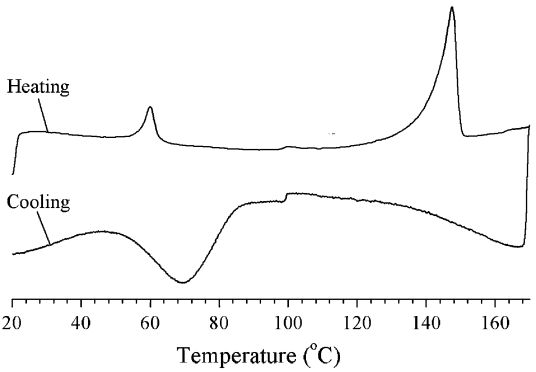



**Fig. 1** The DSC curve of target compound **3c**

**Table 1** The transition temperatures and enthalpies of target compounds **3**

| Compounds | The transition temperature T/ °C (enthalpies, ΔH/J $g^{-1}$) | |
|---|---|---|
| | Heating | Cooling |
| **3a** | Cr 77.7 (0.9) Sm 120.1 (2.4) I | I 104.5 (−1.6) Sm 66.3 (−1.1) Cr |
| **3b** | – | I 87.9 (−0.45) Cr |
| **3c** | Cr 60.1 (6.3) Sm 99.7 (0.5) Sm 147.6 (41.7) I | I 124.0 (−0.7) Sm 70.0 (−16.9) Cr |
| **3d** | Cr 109.3 (1.4) I | I 72.9 (−3.9) Cr |
| **3e** | Cr 58.6 (3.23) I | I 44.9 (−8.2) Cr |
| **3f** | Cr 112.1 (2.5) Sm 158.4 (1.4) I | I 151.8 (−0.7) Cr |
| **3g** | Cr 99.7 (0.9) Sm 144.0 (6.6) I | I 76.7 (−2.4) Cr |
| **3h** | Cr 68.3 (0.6) Sm 105.8 (0.2) I | I 104.9 (−0.2) Sm 54.3 (−1.2) Cr |
| **3i** | Cr 39.9 (3.9) Sm 60.0 (9.1) Sm 120.4 (−12.5) I | I 41.05 (−12.5) Cr |
| **3j** | Cr 76.0 (3.5) Sm 120.3 (0.7) I | I 48.5 (−0.68) Cr |
| **3k** | Cr 120.1 (1.7) I | I 112.7 (−0.7) Sm 48.7 (−0.5) Cr |
| **3l** | Cr 73.52 (1.2) Sm 97.58 (5.3) I | – |
| **3m** | Oil | Oil |
| **3n** | Cr 71.9 (1.4) Sm 120.5 (2.0) I | I 42.3 Cr |
| **3o** | Cr 57.2 (1.7) Sm 127.5 (7.0) I | I 107.0 (−14.9) Sm 45.6 (−3.5) Cr |
| **3p** | Oil | Oil |

Using **3c** as a representative of novel biphenyl ester liquid crystal compounds **3**, their liquid crystal properties were further confirmed with XRD. And the XRD spectrum of the compound **3c** under room temperature is shown in Fig. 2. Generally, for the liquid crystalline molecules displaying smectic, nematic, or cholesteric phase, there is a significant diffraction peak near 20°, but only the smectic phase liquid crystal molecule has another diffraction peak near 6°. Therefore, the XRD result shows that the compound **3c** may appear in smectic phase [36, 37].

In common, the liquid crystal compounds showing different transition temperatures and enthalpies in DSC curve could also be verified with variable temperature XRD. The XRD spectra of the compound **3c** under different temperatures are shown in Fig. 3. With the increase of the temperature, the diffraction peak near 20°

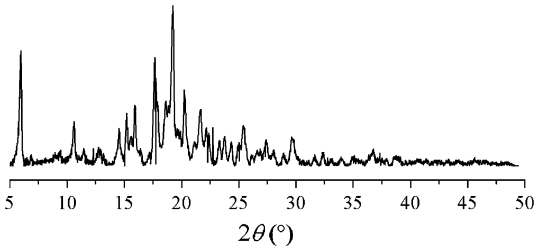



**Fig. 2** The XRD spectrum of 2(5*H*)-furanone compound **3c**

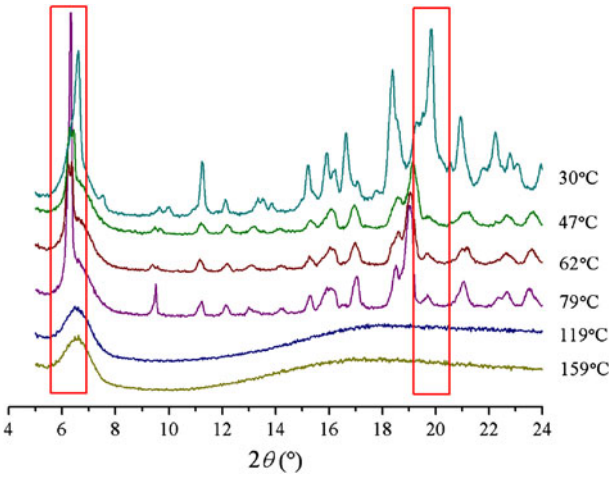



**Fig. 3** The XRD spectra of 2(5*H*)-furanone compound **3c** at different temperatures

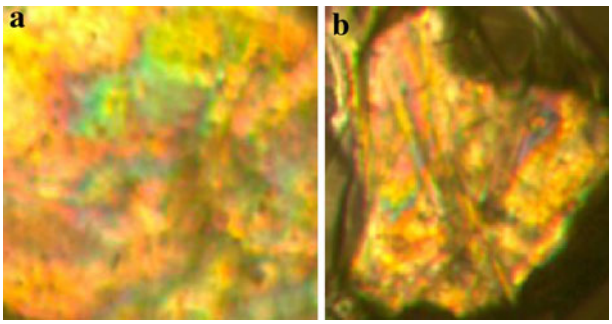



**Fig. 4** The optical texture of **3c** by POM (**a** the optical texture at 108 °C during heating; **b** the optical texture at 117 °C during cooling)

disappeared gradually, and no peak existed at the end. Similarly, at higher temperature, the diffraction peak near 6° gradually became a wide dispersion peak from a sharp peak. These indeed meant that the phase transition was altered from smectic phase to isotropic phase.

The textures of target compound **3c** observed with POM are shown in Fig. 4. There is a marble texture, which is one of the typical smectic phase textures [38].

A marble texture with fluidity and bright colors could be observed during heating (Fig. 4a) and cooling (Fig. 4b). The results are consistent with those tested by DSC and XRD.

## Conclusion

In summary, a series of *N*-[5-alkoxy-2(5*H*)-furanonyl] amino acid 4′-hexyloxybiphenyl esters have been synthesized as designed. The DSC, XRD, and POM results indicated that most of them were mesomorphic phase liquid crystal molecules. The new compounds with bornyl moiety were more likely to appear as mesomorphic phase than those with the menthyl unit. And the introduction of hexyloxy into the biphenyl esters to improve the liquid crystal performance was successful. These researches provide a basis for the further application of 2(5*H*)-furanone compounds in liquid crystal materials.

## Experimental

### General

Infrared spectra were recorded on a Bruker Vector 33 FT-IR instrument by the liquid film method in the absorption range 4,000–400 $cm^{-1}$. $^1H$ NMR spectra were obtained in $CDCl_3$ on a Varian DRX-400 MHz spectrometer and tetramethylsilane (TMS) was used as internal standard. Elemental analysis was performed with a Thermo Flashea TM 112 elemental analyzer. Mass spectra (MS) were recorded on a Thermo LCQ DECA XP MAX mass spectrometer.

Differential scanning calorimetry was performed with Perkin-Elmer DSC7 thermal analyzer at a heating rate of 10 °C $min^{-1}$ under a nitrogen atmosphere (flow velocity 20 mL $min^{-1}$). X-ray diffraction was recorded on a Bruker D8 ADVANCE X-ray diffractometer using CuK$\alpha$ radiation with a wavelength of $1.5418 \times 10^{-10}$ m, and scanning range $2\theta = 5$–50° at a scanning speed of 0.03° at 5 s per step. The optical textures were recorded on a Nikon ECLIPSE polarization optical microscope equipped with a heating and cooling stage.

All reagents and solvents were commercially available and used as received. Using furfural, natural L-menthol, L-borneol, and amino acids as starting materials, the intermediate *N*-[5-alkoxy-2(5*H*)-furanonyl] amino acids **1a**–**1p** were prepared according to the literature [31, 34, 39–41]. 4′-Hexyloxybiphenyl-4-ol **2** was also self-made and according to the literature [42, 43], and its structure characterization data were consistent with the reported [11, 42, 43].

### Typical procedure for synthesis of target compounds **3a**–**3p**

A flame-dried 50-mL round-bottomed flask was charged with **1** (0.2 mmol), and DCC (0.2 mmol) in dried $CH_2Cl_2$ (20 mL), the mixture was stirred for 0.5 h under reflux, then, **2** (0.2 mmol) in dried $CH_2Cl_2$ (5 mL) was dropwise added into the

mixture in half an hour. After that, DMAP (0.24 mmol) was added. The reaction was stirred for 72 h under reflux. Then, the resulting mixture was extracted with water (20 mL × 2). The organic layers were dried with magnesium sulfate, and concentrated under vacuum to give a crude product, which was purified by column chromatography on silica gel with gradient eluent of mixtures of petroleum ether and ethyl acetate to afford the samples **3a**–**3p** for analysis.

*4′-Hexyloxybiphenyl-4-yl 2-((S)-4-bromo-5-oxo-2-((1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy)-2,5-dihydrofuran-3-ylamino)-4-methylpentanoate (**3a**)*

Yellowish viscous solid, yield 44 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.86–1.09 (18H, *m*, $CH_3$-12, $CH_3$-14, $CH_3$-15, $CH_3$-20, $CH_3$-21, $CH_3$-40), 1.22–1.31 (6H, *m*, $CH_2$-8, $CH_2$-9, $CH_2$-38), 1.33–1.40 (5H, *m*, CH-19, $CH_2$-37, $CH_2$-39), 1.67–1.88 (6H, *m*, $CH_2$-11, $CH_2$-18, $CH_2$-36), 2.22–2.33 (1H, *m*, CH-10), 3.97–4.02 (3H, *m*, CH-6, $CH_2$-35), 4.90 (1H, *s*, NH-16), 5.35 (1H, *t*, $J = 3.6$ Hz, CH-17), 5.75 (1H, *s*, CH-5), 6.97 (2H, *d*, $J = 9.2$ Hz, ArH-31,33), 7.15 (2H, *d*, $J = 8.2$ Hz, ArH-24,26), 7.43 (2H, *d*, $J = 9.2$ Hz, ArH-30,32), 7.57 (2H, *d*, $J = 8.4$ Hz, ArH-25,27); IR (Film) *v*: 3,352, 3,071, 3,036, 2,955, 2,924, 2,855, 1751, 1643, 1609, 1462, 1250, 1130, 957, 818, 567; ESI-MS *m/z* (%): 720 ($[M + Na]^+$, 100.0); Anal. Calcd for $C_{38}H_{50}BrNO_6$: C 65.51, H 7.23, N 2.01, found: C 65.29, H 7.02, N 1.89.

*4′-Hexyloxybiphenyl-4-yl 2-((S)-4-bromo-5-oxo-2-((1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy)-2,5-dihydrofuran-3-ylamino)-3-methylbutanoate (**3b**)*

Yellowish viscous solid, yield 55 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.81–1.00 (18H, *m*, $CH_3$-12, $CH_3$-14, $CH_3$-15, $CH_3$-19, $CH_3$-20, $CH_3$-39), 1.23–1.29 (6H, *m*, $CH_2$-8, $CH_2$-9, $CH_2$-37), 1.32–1.37 (4H, *m*, $CH_2$-36, $CH_2$-38), 1.65–1.72 (2H, *m*, $CH_2$-11), 1.76–1.84 (2H, *m*, $CH_2$-35), 1.87–1.94 (1H, *m*, CH-18), 2.25–2.31 (1H, *m*, CH-10), 3.99 (2H, *t*, $J = 6.4$ Hz, $CH_2$-34), 4.01–4.07 (1H, *m*, CH-6), 4.93 (1H, *b*, NH-16), 5.37 (1H, *d*, $J = 10.0$ Hz, CH-17), 5.74 (1H, *s*, CH-5), 6.96 (2H, *d*, $J = 8.4$ Hz, ArH-30,32), 7.15 (2H, *d*, $J = 8.4$ Hz, ArH-23,25), 7.48 (2H, d, $J = 8.8$ Hz, ArH-29,31), 7.57 (2H, *d*, $J = 8.8$ Hz, ArH-24,26); IR (Film) *v*: 3,379, 3,067, 3,036, 2,955, 2,874, 1,763, 1,651, 1,609, 1,497, 1,470, 1,246, 1,130, 956, 829, 633; ESI-MS *m/z* (%): 701 ($[M + NH_4]^+$, 4.8); Anal. Calcd for $C_{37}H_{48}BrNO_6$: C 65.10, H 7.09, N 2.05, Found: C 64.90, H 7.00; N 2.12.

*4′-Hexyloxybiphenyl-4-yl 6-((S)-4-bromo-5-oxo-2-((1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy)-2,5-dihydrofuran-3-ylamino)hexanoate (**3c**)*

Yellowish solid, yield 47 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.85 (6H, *s*, $CH_3$-14, $CH_3$-15), 0.89–0.93 (6H, *m*, $CH_3$-12, $CH_3$-40), 1.25–1.38 (8H, *m*, $CH_2$-8, $CH_2$-9, $CH_2$-19, $CH_2$-38), 1.43–1.56 (4H, *m*, $CH_2$-39, $CH_2$-37), 1.64–1.74 (6H, *m*, $CH_2$-11, $CH_2$-18, $CH_2$-20), 1.78–1.84 (2H, *m*, $CH_2$-36), 2.22–2.31 (1H, *m*, CH-10),

2.61 (2H, *t*, $J = 7.2$ Hz, $CH_2$-21), 3.44–3.55 (2H, *m*, $CH_2$-17), 3.94–4.01 (3H, *m*, CH-6, $CH_2$-35), 4.92 (1H, *s*, NH-16), 5.73 (2H, *s*, CH-5), 6.96 (2H, *d*, $J = 8.8$ Hz, ArH-31,33), 7.11 (2H, *d*, $J = 8.4$ Hz, ArH-24,26), 7.48 (2H, *d*, $J = 8.8$ Hz, ArH-30,32), 7.54 (2H, *d*, $J = 8.8$ Hz, ArH-25,27); $^{13}$C NMR (100 MHz, $CDCl_3$-TMS) $\delta$: 14.0 (C-12), 14.1 (C-40), 18.6 (C-14), 19.6 (C-15), 22.6 (C-39), 24.4 (C-20), 25.7 (C-37), 25.9 (C-19), 26.6 (C-9), 28.0 (C-8), 29.7 (C-36), 30.4 (C-18), 31.6 (C-38), 34.0 (C-21), 37.1 (C-11), 43.9 (C-17), 44.9 (C-10), 47.6 (C-7), 49.5 (C-13), 68.1 (C-35), 77.3 (C-6), 87.6 (C-3), 99.1 (C-5), 114.8 (C-31, C-33), 121.7 (C-24, C-26), 127.7 (C-25, C-27), 128.1 (C-30, C-32), 132.6 (C-29), 138.7 (C-28), 149.4 (C-23), 154.9 (C-34), 158.8 (C-4), 167.5 (C-2), 172.0 (C-22); IR (Film) *v*: 3,348, 3,040, 2,928, 2,866, 1,759, 1,632, 1,524, 1,497, 1,462, 1,207, 1,138, 937, 825, 613; ESI-MS *m/z* (%): 698 ($[M + H]^+$, 21.0), 720 ($[M + Na]^+$, 16.0); Anal. Calcd for $C_{38}H_{50}BrNO_6$: C 65.51, H 7.23, N 2.01, found: C 65.32, H 7.02, N 1.89.

*4′-Hexyloxybiphenyl-4-yl 2-(((S)-4-bromo-5-oxo-2-((1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy)-2,5-dihydrofuran-3-yl)-N-methylamino)acetate (**3d**)*

Yellowish solid, yield 31 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.85–0.92 (12H, *m*, $CH_3$-14, $CH_3$-15, $CH_3$-12, $CH_3$-37), 1.24–1.31 (6H, *m*, $CH_2$-8, $CH_2$-9, $CH_2$-35), 1.33–1.37 (4H, *m*, $CH_2$-34, $CH_2$-36), 1.67–1.86 (4H, *m*, $CH_2$-11, $CH_2$-33), 2.21–2.31 (1H, *m*, CH-10), 3.29 (3H, *s*, $CH_3$-17), 3.94–3.97 (1H, *m*, CH-6), 3.99 (2H, *t*, $J = 6.4$ Hz, $CH_2$-32), 4.48–4.85 (2H, *dd*, $J_1 = 11.2$ Hz, $J_2 = 18.4$ Hz, $CH_2$-18), 5.82 (1H, *s*, CH-5), 6.96 (2H, *d*, $J = 7.6$ Hz, ArH-29,30), 7.18 (2H, *d*, $J = 8.4$ Hz, ArH-21,22), 7.48 (2H, *d*, $J = 8.4$ Hz, ArH-27,28), 7.56 (2H, *d*, $J = 8.8$ Hz, ArH-23,24); IR (Film) *v*: 3,318, 3,036, 2,928, 2,865, 1,751, 1,624, 1,574, 1,524, 1,493, 1,199, 1,169, 961, 826, 637; ESI-MS *m/z* (%): 694 ($[M + K]^+$, 100.0); Anal. Calcd for $C_{35}H_{44}BrNO_6$: C 64.22, H 6.77, N 2.14, found: C 64.02, H 6.57, N 2.04.

*4′-Hexyloxybiphenyl-4-yl 2-((S)-4-bromo-5-oxo-2-((1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy)-2,5-dihydrofuran-3-ylamino)-3-phenylpropanoate (**3e**)*

Yellowish viscous solid, yield 38 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.73–0.93 (12H, *m*, $CH_3$-12, $CH_3$-14, $CH_3$-15, $CH_3$-43), 1.27–1.31 (6H, *m*, $CH_2$-8, $CH_2$-9, $CH_2$-42), 1.33–1.35 (2H, *m*, $CH_2$-41), 1.42–1.48 (2H, *m*, $CH_2$-40), 1.65–1.71 (2H, *m*, $CH_2$-11), 1.76–1.84 (2H, *m*, $CH_2$-39), 2.22–2.33 (1H, *m*, CH-10), 3.11–3.31 (2H, *dd*, $J_1 = 14.4$ Hz, $J_2 = 14.4$ Hz, $CH_2$-18), 3.99 (2H, *t*, $J = 6.4$ Hz, $CH_2$-38), 4.09–4.15 (2H, *m*, CH-6, CH-17), 5.08 (1H, *s*, NH-16), 5.53 (1H, *s*, CH-5), 6.96 (2H, *d*, $J = 8.4$ Hz, ArH-35,36), 7.15 (2H, *d*, $J = 8.4$ Hz, ArH-27,28), 7.18–7.26 (4H, *m*, ArH-20,21,23,24), 7.30–7.39 (1H, *m*, ArH-22), 7.48 (2H, *d*, $J = 8.4$ Hz, ArH-33,34), 7.56 (2H, *d*, $J = 8.4$ Hz, ArH-29,30); IR (Film) *v*: 3,364, 3,036, 2,924, 2,865, 1,751, 1,636, 1,609, 1,497, 1,450, 1,204, 1,165, 972, 802, 630; ESI-MS *m/z* (%): 751 ($[M + NH_4]^+$, 8.3); Anal. Calcd for $C_{41}H_{48}BrNO_6$: C 67.39, H 6.62, N 1.92, found: C 67.23, H 6.52, N 1.77.

*4′-Hexyloxybiphenyl-4-yl 2-((S)-4-bromo-5-oxo-2-((1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy)-2,5-dihydrofuran-3-ylamino)-2-phenylacetate (**3f**)*

Yellowish viscous solid, yield 31 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.82–0.93 (12H, *m*, $CH_3$-12, $CH_3$-14, $CH_3$-15, $CH_3$-42), 1.24–1.28 (6H, *m*, $CH_2$-8, $CH_2$-9, $CH_2$-41), 1.32–1.35 (2H, *m*, $CH_2$-40), 1.42–1.49 (2H, *m*, $CH_2$-39), 1.64–1.67 (2H, *m*, $CH_2$-11), 1.75–1.83 (2H, *m*, $CH_2$-38), 2.19–2.28 (1H, *m*, CH-10), 3.96–4.02 (3H, *m*, CH-6, $CH_2$-37), 5.19–5.21 (1H, *m*, CH-17), 6.16–6.25 (1H, *m*, CH-5, NH-16), 6.93 (2H, *d*, $J = 8.4$ Hz, ArH-34,35), 7.17 (2H, *d*, $J = 8.4$ Hz, ArH-26,27), 7.31 (2H, *d*, $J = 8.4$ Hz, ArH-32,33), 7.36–7.42 (5H, *m*, ArH-19,20, 21,22,23), 7.50 (2H, *d*, $J = 8.8$ Hz, ArH-28,29); IR (Film) *v*: 3,391, 3,063, 3,036, 2,928, 2,855, 1,755, 1,674, 1,609, 1,524, 1,450, 1,207, 1,165, 972, 829, 644; ESI-MS *m/z* (%): 718 ($[M + H]^+$, 9.4); Anal. Calcd for $C_{40}H_{46}BrNO_6$: C 67.03, H 6.47, N 1.95, found: C 67.00, H 6.27, N 1.83.

*4′-Hexyloxybiphenyl-4-yl 4-((S)-4-bromo-5-oxo-2-((1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy)-2,5-dihydrofuran-3-ylamino)butanoate (**3g**)*

Yellowish solid, yield 31 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.84 (6H, *s*, $CH_3$-14, $CH_3$-15), 0.88–0.93 (6H, *m*, $CH_3$-12, $CH_3$-38), 1.24–1.28 (6H, *m*, $CH_2$-8, $CH_2$-9, $CH_2$-36), 1.32–1.36 (2H, *m*, $CH_2$-37), 1.41–1.49 (2H, *m*, $CH_2$-35), 1.61–1.64 (2H, *m*, $CH_2$-11), 1.76–1.84 (2H, *m*, $CH_2$-34), 2.06–2.14 (2H, *m*, $CH_2$-18), 2.23–2.30 (1H, *m*, CH-10), 2.69–2.77 (2H, *m*, $CH_2$-19), 3.58–3.68 (2H, *m*, $CH_2$-17), 3.96–4.03 (3H, *m*, CH-6, $CH_2$-33), 5.13 (1H, *s*, NH-16), 5.75 (1H, *s*, CH-5), 6.96 (2H, *d*, $J = 8.8$ Hz, ArH-29,31), 7.12 (2H, *d*, $J = 8.4$ Hz, ArH-22,24), 7.47 (2H, *d*, $J = 8.4$ Hz, ArH-28,30), 7.54 (2H, *d*, $J = 8.4$ Hz, ArH-23,25); IR (Film) *v*: 3,318, 3,036, 2,928, 2,865, 1,751, 1,639, 1,558, 1,528, 1,497, 1,204, 1,134, 949, 829, 579; ESI-MS *m/z* (%): 692 ($[M + Na]^+$, 25.0); Anal. Calcd for $C_{35}H_{44}BrNO_6$: C 64.66, H 6.93, N 2.09, found: C 64.56, H 6.87, N 2.00.

*4′-Hexyloxybiphenyl-4-yl 2-((S)-4-bromo-5-oxo-2-((1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yloxy)-2,5-dihydrofuran-3-ylamino)acetate (**3h**)*

Yellowish liquid, yield 36 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.83–1.11 (12H, *m*, $CH_3$-12, $CH_3$-14, $CH_3$-15, $CH_3$-36), 1.25–1.34 (8H, *m*, $CH_2$-8, $CH_2$-9, $CH_2$-34, $CH_2$-35), 1.57–1.64 (4H, *m*, $CH_2$-11, $CH_2$-33), 1.73–1.87 (2H, *m*, $CH_2$-32), 2.22–2.36 (1H, *m*, CH-10), 3.65–4.24 (5H, *m*, CH-6, $CH_2$-17, $CH_2$-31), 5.35 (1H, *s*, NH), 5.58 (1H, *s*, CH-5), 6.87–7.16 (4H, *m*, ArH-20,21,28,29), 7.30–7.61 (4H, *m*, ArH-22,23,26,27); IR (Film) *v*: 3,360, 3,036, 2,924, 2,851, 1,736, 1,655, 1,609, 1,493, 1,466, 1,261, 1,166, 1,018, 803, 664; ESI-MS *m/z* (%): 642 ($[M + H]^+$, 6.4); Anal. Calcd for $C_{34}H_{42}BrNO_6$: C 63.75, H 6.61, N 2.19, found: C 63.55, H 6.41, N 2.28.

*4′-Hexyloxybiphenyl-4-yl 2-((S)-4-bromo-2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-5-oxo-2,5-dihydrofuran-3-ylamino)-4-methylpentanoate (**3i**)*

White viscous solid, yield 32 %, $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.82–1.00 (12H, *m*, $CH_3$-12, $CH_3$-14, $CH_3$-15, $CH_3$-40), 1.25–1.29 (13H, *m*, CH-8, $CH_2$-9, CH-11, CH-13, $CH_3$-20, $CH_3$-21, $CH_2$-38), 1.33–1.38 (4H, *m*, $CH_2$-37, $CH_2$-39), 1.57–1.59 (5H, *m*, $CH_2$-10, $CH_2$-18, CH-19), 1.76–1.84 (2H, *m*, $CH_2$-36), 2.01–2.25 (2H, *m*, $CH_2$-7), 3.96–4.10 (3H, *m*, CH-6, $CH_2$-35), 4.89 (1H, *b*, NH), 5.25–5.44 (2H, *m*, CH-5, CH-17), 6.88 (2H, *d*, $J = 8.0$ Hz, ArH-31,33), 6.94 (2H, *d*, $J = 8.4$ Hz, ArH-24,26), 7.41–7.46 (4H, *m*, ArH-30,32,25,27); IR (Film) *v*: 3,391, 3,005, 2,920, 2,851, 1,732, 1,643, 1,500, 1,466, 1,250, 1,184, 968, 818, 644; ESI-MS *m/z* (%): 722 ($[M + Na]^+$, 17.0); Anal. Calcd for $C_{38}H_{52}BrNO_6$: C 65.32, H 7.50, N 2.00, found: C 65.22, H 7.43, N 2.02.

*4′-Hexyloxybiphenyl-4-yl 2-((S)-4-bromo-2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-5-oxo-2,5-dihydrofuran-3-ylamino)-3-methylbutanoate (**3j**)*

White viscous solid, yield 32 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.60 (3H, *d*, $J = 6.8$ Hz, $CH_3$-12), 0.77–0.98 (16H, *m*, CH-13, $CH_3$-14, $CH_3$-15, $CH_3$-19, $CH_3$-20, $CH_3$-39), 1.05–1.15 (2H, *m*, $CH_2$-9), 1.25–1.36 (8H, *m*, CH-8, CH-11, $CH_2$-36, $CH_2$-37, $CH_2$-38), 1.59–1.62 (2H, *m*, $CH_2$-10), 1.78–1.85 (3H, *m*, CH-18, $CH_2$-35), 2.02–2.23 (2H, *m*, $CH_2$-7), 3.45–3.51 (1H, *m*, CH-6), 3.90–4.10 (3H, *m*, CH-17, $CH_2$-34), 5.35 (1H, *b*, NH), 5.92 (1H, *s*, CH-5), 6.98 (2H, *d*, $J = 8.4$ Hz, ArH-30,32), 7.18 (2H, *d*, $J = 8.4$ Hz, ArH-23,25), 7.50 (2H, *d*, $J = 8.0$ Hz, ArH-29,31), 7.57 (2H, *d*, $J = 8.4$ Hz, ArH-24,26); IR (Film) *v*: 3,364, 3,040, 2,924, 2,855, 1,782, 1,659, 1,609, 1,466, 1,246, 1,180, 949, 822, 606; ESI-MS *m/z* (%): 686 ($[M + H]^+$, 15.0); Anal. Calcd for $C_{38}H_{50}BrNO_6$: C 64.90, H 7.36, N 2.05, found: C 64.75, H 7.26, N 2.10.

*4′-Hexyloxybiphenyl-4-yl 6-((S)-4-bromo-2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-5-oxo-2,5-dihydrofuran-3-ylamino)hexanoate (**3k**)*

Yellowish solid, yield 30 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.79 (3H, *d*, $J = 7.2$ Hz, $CH_3$-12), 0.83–0.93 (10H, *m*, CH-13, $CH_3$-14, $CH_3$-15, $CH_3$-39), 0.95–1.04 (2H, *m*, $CH_2$-9), 1.32–1.51 (10H, *m*, CH-8, CH-11, $CH_2$-18, $CH_2$-36, $CH_2$-37, $CH_2$-38), 1.62–1.69 (6H, *m*, $CH_2$-10, $CH_2$-17, $CH_2$-19), 1.76–1.90 (2H, *m*, $CH_2$-35), 2.10–2.25 (2H, *m*, $CH_2$-7), 2.60 (2H, *t*, $J = 7.2$ Hz, $CH_2$-20), 3.43–3.57 (3H, *m*, CH-6, $CH_2$-16), 3.97 (2H, *t*, $J = 6.8$ Hz, $CH_2$-34), 4.77 (1H, *s*, NH), 5.71 (1H, *s*, CH-5), 6.94 (2H, *d*, $J = 8.8$ Hz, ArH-30,32), 7.09 (2H, *d*, $J = 8.8$ Hz, ArH-23,25), 7.46 (2H, *d*, $J = 8.8$ Hz, ArH-29,31), 7.52 (2H, *d*, $J = 8.4$ Hz, ArH-24,26); $^{13}$C NMR (100 MHz, $CDCl_3$-TMS) $\delta$: 14.0 (C-39), 15.9 (C-12), 21.0 (C-10), 22.1 (C-14), 22.6 (C-15), 22.8 (C-38), 24.3 (C-19), 24.9 (C-36), 25.7 (C-11), 25.8 (C-18), 29.2 (C-35), 30.3 (C-17), 31.5 (C-13), 31.6 (C-37), 33.9 (C-20), 34.0 (C-9), 42.4 (C-7), 43.6 (C-16), 48.1 (C-8), 68.1 (C-34), 77.2 (C-6), 81.9 (C-3), 98.6 (C-5), 114.8 (C-30, C-32), 121.6 (C-23, C-25), 127.6 (C-24, C-26), 128.0 (C-29, C-31), 132.5 (C-28), 138.7 (C-27), 149.4 (C-22), 156.8 (C-33), 158.8 (C-4), 167.7 (C-2), 171.9

(C-21); IR (Film) *v*: 3,321, 3,032, 2,924, 2,855, 1,732, 1,651, 1,574, 1,497, 1,462, 1,204, 1,126, 937, 826, 640; ESI-MS *m/z* (%): 722 ($[M + Na]^+$, 12.0); Anal. Calcd for $C_{38}H_{52}BrNO_6$: C 65.32, H 7.50, N 2.00, found: C 65.12, H 7.33, N 2.08.

*4′-Hexyloxybiphenyl-4-yl 2-(((S)-4-bromo-2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-5-oxo-2,5-dihydrofuran-3-yl)-N-methylamino)acetate (**3l**)*

White viscous solid, yield 31 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.79 (3H, *d*, $J = 6.8$ Hz, $CH_3$-12), 0.86–0.96 (10H, *m*, CH-13, $CH_3$-14, $CH_3$-15, $CH_3$-37), 0.98–1.14 (2H, *m*, $CH_2$-9), 1.31–1.40 (6H, *m*, CH-8, CH-11, $CH_2$-35, $CH_2$-36), 1.43–1.50 (2H, *m*, $CH_2$-34), 1.64–1.70 (2H, *m*, $CH_2$-10), 1.76–1.84 (2H, *m*, $CH_2$-33), 2.19–2.27 (2H, *m*, $CH_2$-7), 3.26 (3H, *s*, $CH_3$-17), 3.58–3.66 (1H, *ddd*, $J = 4.4$ Hz, $J = 4.0$ Hz, $J = 4.4$ Hz, CH-6), 3.99 (2H, *t*, $J = 6.4$ Hz, $CH_2$-32), 4.39–4.45 (2H, *dd*, $J_1 = 16.0$ Hz, $J_2 = 18.4$ Hz, $CH_2$-18), 5.90 (1H, *s*, CH-5), 6.97 (2H, *d*, $J = 8.8$ Hz, ArH-29,30), 7.17 (2H, *d*, $J = 8.4$ Hz, ArH-21,22), 7.48 (2H, *d*, $J = 8.8$ Hz, ArH-27,28), 7.56 (2H, *d*, $J = 8.8$ Hz, ArH-23,24); IR (Film) *v*: 3,345, 3,040, 2,928, 2,866, 1,757, 1,632, 1,524, 1,497, 1,466, 1,246, 1,109, 957, 826, 640; ESI-MS *m/z* (%): 680 ($[M + Na]^+$, 19.0); Anal. Calcd for $C_{35}H_{46}BrNO_6$: C 64.02, H 7.06, N 2.17, found: C 64.00, H 7.20, N 2.11.

*4′-Hexyloxybiphenyl-4-yl 2-((S)-4-bromo-2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-5-oxo-2,5-dihydrofuran-3-ylamino)-3-phenylpropanoate (**3m**)*

Yellowish liquid, yield 29 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.85 (3H, *d*, $J = 7.2$ Hz, $CH_3$-12), 0.91–0.98 (10H, *m*, CH-13, $CH_3$-14, $CH_3$-15, $CH_3$-43), 1.00–1.09 (2H, *m*, $CH_2$-9), 1.32–1.40 (6H, *m*, CH-8, CH-11, $CH_2$-41, $CH_2$-42), 1.43–1.49 (2H, *m*, $CH_2$-40), 1.67–1.75 (2H, *m*, $CH_2$-10), 1.77–1.84 (2H, *m*, $CH_2$-39), 2.00–2.11 (2H, *m*, $CH_2$-7), 3.52–3.68 (1H, *ddd*, $J_1 = 3.6$ Hz, $J_2 = 4.0$ Hz, $J_3 = 4.4$ Hz, CH-6), 3.93–4.01 (2H, *m*, $CH_2$-18), 4.31 (2H, *t*, $J = 6.4$ Hz, $CH_2$-38), 5.34–5.97 (3H, *m*, CH-5, NH, CH-17), 6.88 (2H, *d*, $J = 8.0$ Hz, ArH-33,34), 6.94 (2H, *d*, $J = 8.0$ Hz, ArH-27,28), 7.37–7.46 (5H, *m*, ArH-20,21,22,23,24), 7.52–7.56 (2H, *m*, ArH-33,34), 7.71–7.75 (2H, *m*, ArH-29,30); IR (Film) *v*: 3,372, 3,067, 3,032, 2,932, 2,870, 1,728, 1,651, 1,501, 1,454, 1,277, 1,173, 953, 822, 567; ESI-MS *m/z* (%): 734 ($[M + H]^+$, 10.0); Anal. Calcd for $C_{41}H_{50}BrNO_6$: C 67.20, H 6.88, N 1.91, found: C 67.01, H 6.78, N 1.82.

*4′-Hexyloxybiphenyl-4-yl 2-((S)-4-bromo-2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-5-oxo-2,5-dihydrofuran-3-ylamino)-2-phenylacetate (**3n**)*

Yellowish solid, yield 34 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.79–0.97 (15H, *m*, $CH_2$-9, $CH_3$-12, CH-13, $CH_3$-14, $CH_3$-15, $CH_3$-42), 1.25–1.36 (8H, *m*, CH-8, CH-11, $CH_2$-39, $CH_2$-40, $CH_2$-41), 1.67–1.74 (2H, *m*, $CH_2$-10), 1.76–1.84 (2H, *m*, $CH_2$-38), 2.17–2.33 (2H, *m*, $CH_2$-7), 3.52–3.62 (1H, *m*, CH-6), 4.31 (2H, *t*, $J = 6.4$ Hz, $CH_2$-37), 5.57–5.90 (3H, *m*, CH-5, NH, CH-17), 6.88 (2H, *d*, $J = 8.0$ Hz, ArH-30,32), 6.94 (2H, *d*, $J = 8.4$ Hz, ArH-26,27), 7.39–7.46 (5H, *m*,

ArH-19, 20,21,22,23), 7.53–7.56 (2H, *m*, ArH-29,31), 7.70–7.75 (2H, *m*, ArH-28,29); IR (Film) *v*: 3,372, 3,067, 3,032, 2,932, 2,870, 1,728, 1,651, 1,501, 1,454, 1,277, 1,173, 953, 822, 567; ESI-MS *m/z* (%): 720 ($[M + H]^+$, 5.0); Anal. Calcd for $C_{40}H_{48}BrNO_6$: C 66.85, H 6.73, N 1.95, found: C 66.78, H 6.59, N 1.79.

*4′-Hexyloxybiphenyl-4-yl 4-((S)-4-bromo-2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-5-oxo-2,5-dihydrofuran-3-ylamino)butanoate (**3o**)*

Yellowish viscous solid, yield 30 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.77–1.16 (15H, *m*, $CH_2$-9, $CH_3$-12, CH-13, $CH_3$-14, $CH_3$-15, $CH_3$-38), 1.28–1.34 (4H, *m*, $CH_2$-36, $CH_2$-37), 1.39–1.43 (2H, *m*, CH-8, CH-11), 1.57–1.60 (2H, *m*, $CH_2$-35), 1.73–1.82 (4H, *m*, $CH_2$-10, $CH_2$-34), 1.92–2.07 (4H, *m*, $CH_2$-7, $CH_2$-18), 2.20–2.86 (2H, *m*, $CH_2$-19), 3.47–3.64 (2H, *m*, $CH_2$-17), 3.97–4.09 (3H, *m*, CH-6, $CH_2$-33), 4.68–5.35 (2H, *m*, CH-5, NH), 6.95 (2H, *d*, $J = 7.6$ Hz, ArH-29,31), 7.17 (2H, *d*, $J = 7.6$ Hz, ArH-22,24), 7.48 (2H, *d*, $J = 8.4$ Hz, ArH-28,30), 7.51 (2H, *d*, $J = 8.4$ Hz, ArH-23,25); IR (Film) *v*: 3,333, 3,005, 2,924, 2,851, 1,705, 1,609, 1,535, 1,497, 1,450, 1,231, 1,173, 964, 822, 644; ESI-MS *m/z* (%): 694 ($[M + Na]^+$, 7.3); Anal. Calcd for $C_{36}H_{48}BrNO_6$: C 64.47, H 7.21, N 2.09, found: C 64.35, H 7.15, N 2.00.

*4′-Hexyloxybiphenyl-4-yl 2-((S)-4-bromo-2-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyloxy)-5-oxo-2,5-dihydrofuran-3-ylamino)acetate (**3p**)*

Yellowish viscous solid, yield 32 %; $^1$H NMR (400 MHz, $CDCl_3$-TMS) $\delta$: 0.85 (3H, *d*, $J = 6.8$ Hz, $CH_3$-12), 0.91–0.97 (10H, *m*, CH-13, $CH_3$-14, $CH_3$-15, $CH_3$-36), 1.01–1.10 (2H, *m*, $CH_2$-9), 1.28–1.34 (8H, *m*, CH-8, CH-11, $CH_2$-33, $CH_2$-34, $CH_2$-35), 1.61–1.68 (2H, *m*, $CH_2$-10), 1.78–1.82 (2H, *m*, $CH_2$-32), 2.14–2.27 (2H, *m*, $CH_2$-7), 3.54–3.61 (1H, *ddd*, $J_1 = 4.0$ Hz, $J_2 = 4.0$ Hz, $J_3 = 4.4$ Hz, CH-6), 4.26–4.36 (4H, *m*, $CH_2$-17, $CH_2$-31), 5.33 (1H, *s*, NH), 5.73 (1H, *s*, CH-5), 6.87–7.15 (4H, *m*, ArH-20,21,28,29), 7.35–7.55 (4H, *m*, ArH-22,23,26,27); IR (Film) *v*: 3,368, 3,032, 2,928, 2,855, 1,748, 1,655, 1,524, 1,458, 1,204, 1,126, 941, 822, 598; ESI-MS *m/z* (%): 666 ($[M + Na]^+$, 20.0); Anal. Calcd for $C_{34}H_{44}BrNO_6$: C 63.55, H 6.90, N 2.18, found: C 63.39, H 6.78, N 2.06.

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