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Synthesis of spiro pyrrolidines via formal [3+2] cycloaddition of unusual enones and *cis*-3-benzoyl-1-cyclohexyl-2-phenylaziridine

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Abstract—The synthesis of a new class of spiro[tetrahydronaphthalen-one/butenolide]pyrrolidines has been accomplished by the 1,3-dipolar cycloaddition of azomethine ylide generated by thermal ring opening of *cis*-3-benzoyl-1-cyclohexyl-2-phenylaziridine with (*E*)-2-arylidene-1,2,3,4-tetrahydronaphthalen-1-ones and (*E*)-3-arylidene-5-phenyl-$\Delta^{4,5}$-butenolides. The structures of the products were confirmed by spectroscopic techniques as well as single crystal X-ray analysis of one of the products.

1. Introduction

1,3-Dipolar cycloaddition of azomethine ylides with olefins is a very useful reaction because it creates two carbon–carbon bonds in a single operation and results in the formation of a pyrrolidine ring in which high regio- and stereo-chemical control of the peripheral substituents can be achieved.[1] It has been applied in the synthesis of natural products.[2,3] Spiro compounds represent an important class of naturally occurring substances characterized by highly pronounced biological properties.[4–6] 1,2,3,4-Tetrahydronaphthalen-1-one derivatives also have been used for the synthesis of benzophenanthridine antitumor alkaloids[7] and ring B of tetracyclins.[8]

Butenolides form an important group of naturally occurring heterocycles, encompassing both fatty acid and terpenoidal biosynthetic origins.[9]

As a part of our ongoing research program[10] in the area of cycloadditions and construction of biologically active spiro compounds, we herein report the synthesis of spiro pyrrolidines by regioselective cycloadditions.

2. Results and discussion

The synthesis of a series of spiro[tetrahydronaphthalen-one/butenolide]pyrrolidines has been accomplished by the regioselective 1,3-dipolar cycloaddition of azomethine ylide generated by thermal ring opening of *cis*-3-benzoyl-1-cyclohexyl-2-phenylaziridine with (*E*)-2-arylidene-1,2,3,4-tetrahydronaphthalen-1-ones and (*E*)-3-arylidene-5-phenyl-$\Delta^{4,5}$-butenolides. Refluxing a solution of 2-arylidene-1,2,3,4-tetrahydronaphthalen-1-ones (**2a–g**) in dry xylene for 4–6 days with the aziridine (**1**) resulted in the formation of the spiro pyrrolidine derivatives (**3a–g**) (Scheme 1). The reaction gave a single product in all cases. Aziridine (**1**) undergoes thermal conrotatory ring opening to generate the azomethine ylide. This ylide reacts stereospecifically with arylidene-tetrahydronaphthalen-ones to give pyrrolidines (**3a–g**) through regioselective cycloaddition of azomethine ylide to the exocyclic double bond of the 2-arylidene-1,2,3,4-tetrahydronaphthalen-1-ones in all cases. No trace of the other regioisomer (**4a–g**) was detected.

The regio- and stereo-chemical outcome of the cycloaddition was determined by spectroscopic data. The IR spectrum of the product (**3a**) exhibited a peak at 1701 cm^{-1} due to the carbonyl group of tetrahydronaphthalen-1-one and a peak at 1676 cm^{-1} due to the carbonyl of the benzoyl group.

The ^1H NMR spectrum of (**3a**) exhibited peaks at δ 0.97–2.44 (m, 11H, cyclohexyl), 1.84–3.60 (m, 4H, 2×CH_2), 4.64 (d, J=11 Hz, 1H, H_c), 4.86 (d, J=11 Hz, 1H, H_b), 5.31 (s, 1H, H_a) and 6.96–7.98 (m, 19H, ArH). The signals in ^{13}C NMR spectrum of (**3a**) at δ 60.01 due to the spiro carbon, at δ 195.44 due to the benzoyl carbonyl and at δ 201.79 due to the carbonyl group add support for the proposed structures.

The mass spectrum of (**3a**) showed peaks at m/z 539 (M^+, 3%), 105 (54%), and 434 (99%), which confirmed the formation of the cycloadduct. Similar results were obtained with other derivatives (**2b–g**). Finally the regiochemistry of

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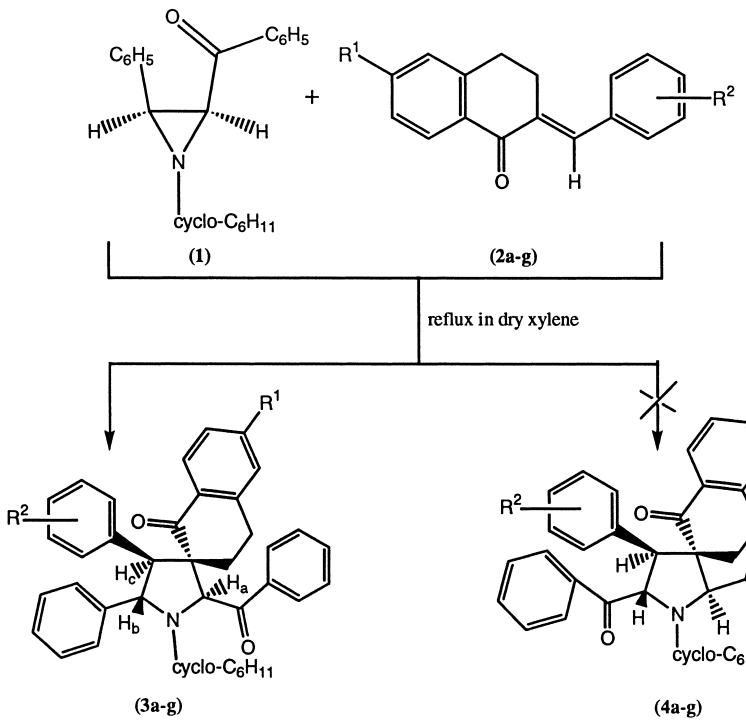


3a: R^1 = H, R^2 = H (59%) **3b**: R^1 = H, R^2 = *p*-CH_3 (40%) **3c**: R^1 = H, R^2 = *p*-OCH_3 (46%)
3d: R^1 = H, R^2 = *p*-Cl (45%) **3e**: R^1 = H, R^2 = *p*-NMe_2 (52%)
3f: R^1 = H, R^2 = *m*-NO_2 (62%) **3g**: R^1 = OCH_3, R^2 = *m*-NO_2 (49%)

Scheme 1.

the cycloaddition was confirmed by X-ray crystal analysis of (**3g**) (Fig. 1).

Similarly, refluxing a solution of aziridine (**1**) with (*E*)-3-arylidene-5-phenyl-$\Delta^{4,5}$-butenolides (**5a**–**d**) in toluene for 36–48 h resulted in the formation of spiro[butenolide-pyrrolidines] (**6a**–**d**) (Scheme 2). We could find no trace of the other regioisomer (**7a**–**d**) in all the cases that have been studied. The structure of each product (**6a**–**d**) was confirmed by spectroscopic data.

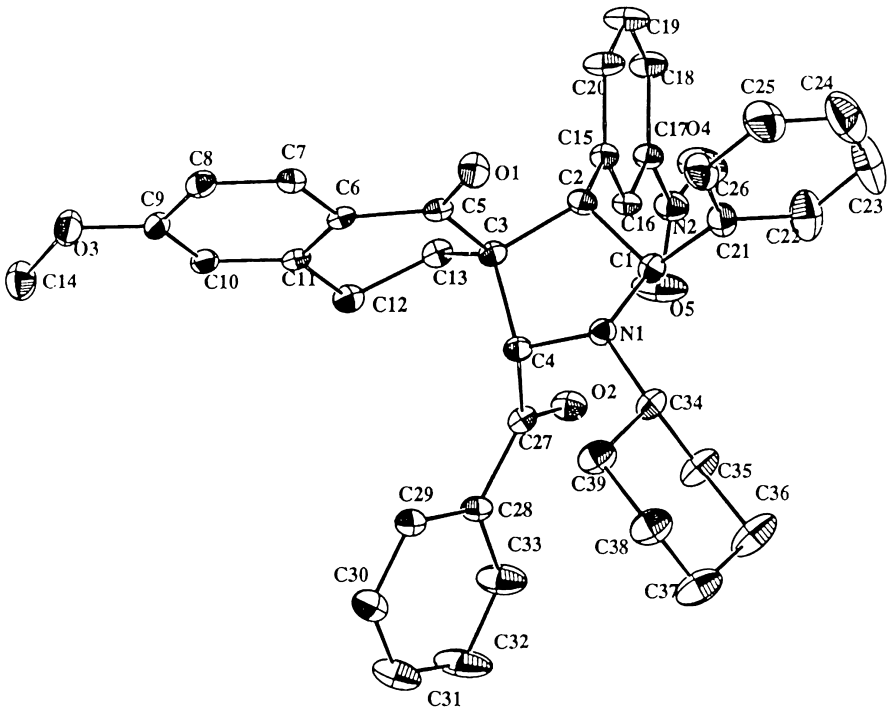
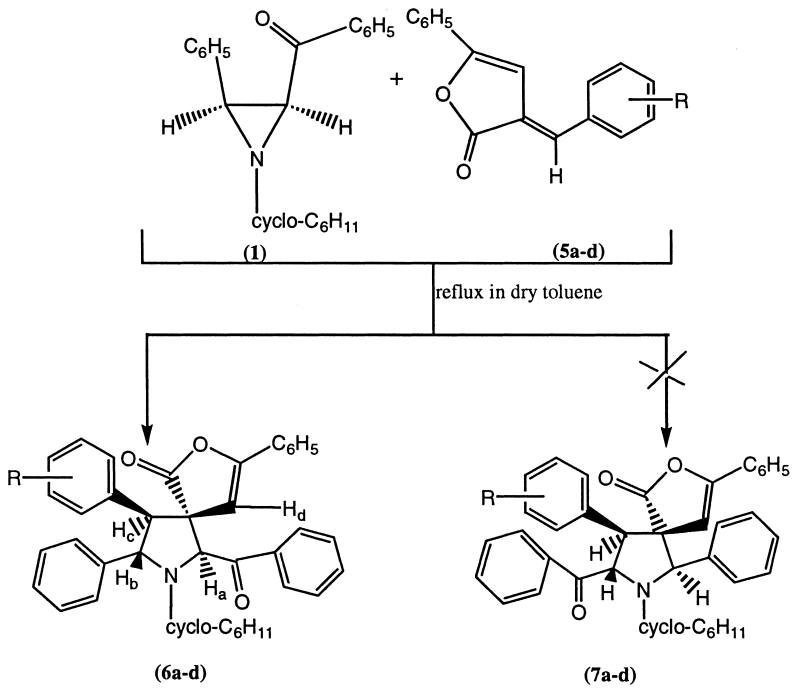


Figure 1. ORTEP diagram of **3g**.



Scheme 2. **6a**: R=H (61%), **6b**: R=4-Me (65%), **6c**: R=4-OMe (48%), **6d**: R=4-Cl (41).

The appearance of a singlet at δ 6.17 due to H_d proton in the ^{1}H NMR spectrum of the products confirmed that the cycloaddition had taken place at the exocyclic double bond and not at endocyclic double bond of the (*E*)-3-arylidene-5-phenyl-$\Delta^{4,5}$-butenolides (**5a–d**). The *trans* ylide generated form *cis*-aziridine (**1**) would react stereospecifically with (*E*)-3-arylidene-5-phenyl-$\Delta^{4,5}$-butenolides (**5a–d**) to give spiro pyrrolidines. Thus the stereochemistry the product was confirmed. The appearance of a singlet at δ 5.00 not as a doublet at δ 5.00 due to H_a proton in the ^{1}H NMR spectrum confirmed the formation of the regiomers (**6a–d**). Thus the regiochemistry was confirmed.

Hence the increase in C=O absorption frequency in the IR spectrum of (**6b**) by 25 cm^{-1} from 1763 cm^{-1} in arylidene-butenolides to 1788 cm^{-1} in the product shows the loss of conjugation of the carbonyl group as the ylide had added across the exocyclic double bond. The ^{1}H NMR spectrum of the product (**6b**) exhibited peaks at δ 0.66–1.88 (m, 10H, cyclohexyl), 2.14 (s, 3H, *p*-Me), 2.48 (m, 1H, NCH), 3.88 (d, *J*=12 Hz, 1H, H*c*), 4.74 (d, *J*=12 Hz, 1H, H_b), 5.00 (s, 1H, H_a), 6.17 (s, 1H, H_d) and 6.97–7.88 (m, 19H, ArH). Further confirmation of the spiro heterocyclic structures was provided by ^{13}C NMR spectra. The ^{13}C NMR spectrum of product (**6b**) exhibited a peak at δ 20.91 due to the *p*-methyl substituent, a peak at δ 67.63 due to the spiro carbon, a peak at δ 161.99 due to the butenolide carbonyl carbon, a peak at δ 198.13 due to the benzoyl carbonyl carbon and the mass spectrum of (**6b**) exhibited a molecular ion peak at 567 (2%) and peaks at 105 (52%), 462 (100%), 380 (11%). These observed values confirmed the formation of the cyclo-adduct. Similar results were obtained with the other derivatives of arylidene-butenolides.

To the best of our knowledge, there have been no reports on the cycloaddition of azomethine ylide derived from aziridine (**1**) with the dipolarophiles 2-arylidene-1,2,3,4-tetrahydronaphthalen-1-ones (**2a–g**) and (*E*)-3-arylidene-5-phenyl-$\Delta^{4,5}$-butenolides (**5a–d**).

3. Conclusion

A new and efficient synthesis of spiro pyrrolidine ring systems from azomethine ylide generated from aziridine (**1**) with 2-arylidene-1,2,3,4-tetrahydro-naphthalen-1-ones and (*E*)-3-arylidene-5-phenyl-$\Delta^{4,5}$-butenolides has been described. The cycloaddition studied is of interest since it paves the way for the synthesis of a variety of biologically important spiro pyrrolidines derivatives using easily available starting materials.

4. Experimental

All melting points are uncorrected. IR spectra were recorded on a Perkin–Elmer instrument. Mass spectra were recorded on a JEOL DX 303 HF spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on JEOL spectrometer at 400 and 100 MHz and Bruker DPX 200 MHz, respectively, using $CDCl_3$ with TMS as internal standard. Elemental analyses were carried out on a CEST instrument. The starting materials (**1**),[11] (**2a–g**)[12] and (**5a–d**)[13] were prepared as per the literature procedures.

4.1. Crystallographic data for compound 3g[14]

Molecular formula: $C_{39}H_{38}N_2O_5$. Molecular weight 614, triclinic, PT, a=11.2284(1) Å, b=12.6346(2) Å, c=12.9056(3) Å, D_c=1.239 mg/m^3, V=1648.05(7) Å^3, α=102.453(2), β=96.412(2), γ=109.775(1). Mo Kα radiation, λ=0.71073 Å, absorption coefficient=0.082 mm^{-1}, F(000)=652. A crystal with dimensions of 0.40×0.20×0.14 mm^3 was used for X-ray data collection

at 293 K on a Siemens SMART CCD area detector using molybdenum radiation and a graphite mono chromator. θ Range for data collection was 2.73–28.36°. A total of 11676 reflections were measured. R indices on all data was $R1$=0.1913, $wR2$=0.2084. Goodness of fit on F^2 was 0.885.

4.2. General procedure

*The cycloaddition of 2-arylidene-1,2,3,4-tetrahydronaphthalen-1-ones (**2a–g**) with the ylide generated from aziridine (**1**).* A mixture of 2-arylidene-1,2,3,4-tetrahydronaphthalen-1-ones (**2a–g**) (0.5 mmol), aziridine (**1**) (0.5 mmol, 0.152 g) was refluxed in dry xylene (10 mL) for 4–6 days. After the completion of reaction as evidenced by the thin layer chromatography the solvent was removed on the rotary evaporator and the residue was chromatographed on silica gel (Acme 100–200 mesh, 50–60 g) using hexane–ethyl acetate mixture (19:1) (R_f 0.64) as eluent to give (**3a–g**). The products were recrystallized from ethanol.

*The cycloaddition of (E)-3-arylidene-5-phenyl-$\Delta^{4,5}$-butenolides (**5a–d**) with the ylide generated from aziridine (**1**).* A mixture of (*E*)-3-arylidene-5-phenyl-$\Delta^{4,5}$-butenolides (**5a–d**) and *cis*-3-benzoyl-1-cyclohexyl-2-phenylaziridine (**1**) was refluxed in toluene under nitrogen atmosphere for about 36–48 h until the disappearance of the starting materials as evidenced by the TLC. After the completion of reaction the solvent was removed on the rotary evaporator and the residue was chromatographed on silica gel using hexane–benzene mixture (3:2) (R_f 0.45) as eluent to give (**6a–d**). The products were recrystallized from ethanol.

4.2.1. 2′-Benzoyl-1′-cyclohexyl-4′,5′-diphenyl-spiro[tetrahydronaphthalen-2,3′-pyrrolidine]-1-one (3a). Pale yellow solid, 0.16 g, 59%, mp 220–221°C; IR (KBr)$_\nu$C=O: 1701, 1676 cm^{-1}; ^{1}H NMR: δ 0.97–2.44 (m, 11H, cyclohexyl), 1.84–3.60 (m, 4H, 2×CH$_2$), 4.64 (d, J=11 Hz, H$_c$), 4.80 (d, J=11 Hz, H$_b$), 5.31 (s, 1H, H$_a$), 6.96–7.40 (m, 17H), 7.50 (d, J=7 Hz, 1H), 7.98 (d, J=7 Hz, 1H); ^{13}C NMR: δ 25.5, 25.6, 26.0, 26.1, 27.9, 33.7, 56.7, 60.0, 64.8, 65.4, 126.3, 126.7, 127.0, 127.5, 127.6, 127.8, 127.9, 128.3, 130.7, 132.4, 132.9, 135.5, 136.8, 141.7, 143.5, 195.4, 201.8; MS: m/z 539 (M$^+$, 3), 434 (99), 352 (100), 215 (20), 105 (54). Anal. calcd for $C_{38}H_{37}NO_2$; C, 84.57; H, 6.91; N, 2.60: found: C, 84.14; H, 6.86; N, 2.84.

4.2.2. 2′-Benzoyl-1′-cyclohexyl-5′-phenyl-4′-(4-methylphenyl) spiro[tetrahydronaphthalen-2,3′-pyrrolidine]-1-one (3b). Yellow solid, 0.11 g, 40%, mp 227–228°C; IR (KBr)$_\nu$C=O: 1700, 1678 cm^{-1}; ^{1}H NMR: δ 0.98–2.45 (m, 11H, cyclohexyl), 1.77–3.12 (m, 4H, 2×CH$_2$), 2.34 (s, 3H, *p*-CH$_3$), 4.82 (d, J=11 Hz, H$_c$), 5.12 (d, J=11 Hz, H$_b$), 5.37 (s, 1H, H$_a$), 6.92–7.70 (m, 16H), 7.89 (d, J=7 Hz, 1H), 8.20 (d, J=7 Hz, 1H); ^{13}C NMR: δ 21.0, 25.7, 25.9, 26.2, 26.4, 27.1, 33.6, 55.8, 58.9, 63.5, 71.2, 126.5, 127.5, 127.6, 127.9, 128.0, 128.5, 128.9, 129.7, 130.0, 132.0, 132.8, 132.9, 133.1, 134.6, 136.7, 142.8, 198.7, 205.2; MS: m/z 553 (M$^+$, 5), 448 (81), 145 (15), 128 (13), 105 (49). Anal. calcd for $C_{39}H_{39}NO_2$; C, 84.59; H, 7.10; N, 2.53: found: C, 84.65; H, 7.31; N, 2.15.

4.2.3. 2′-Benzoyl-1′-cyclohexyl-5′-phenyl-4′-(4-methoxyphenyl) spiro[tetrahydronaphthalen-2,3′-pyrrolidine]-1-one (3c). Yellow solid, 0.13 g, 46%, mp 248–249°C; IR (KBr)$_\nu$C=O: 1699, 1674 cm^{-1}; ^{1}H NMR: δ 0.80–2.50 (m, 11H, cyclohexyl), 1.75–3.45 (m, 4H, 2×CH$_2$), 3.60 (s, 3H, *p*-OCH$_3$), 4.52 (d, J=11 Hz, H$_c$), 4.72 (d, J=11 Hz, H$_b$), 5.24 (s, 1H, H$_a$), 7.20–7.49 (m, 16H), 7.95 (d, J=7 Hz, 1H), 8.06 (d, J=7 Hz, 1H); ^{13}C NMR: δ 25.3, 25.6, 25.8, 26.3, 27.7, 30.0, 32.7, 54.9, 57.3, 62.3, 70.2, 113.0, 126.6, 127.3, 127.6, 128.0, 128.2, 128.6, 128.9, 130.3, 131.5, 132.6, 133.2, 133.5, 144.0, 146.0, 157.6, 197.8, 203.5; MS: m/z 569 (M$^+$, 4), 464 (86), 232 (20), 202 (12), 179 (40), 105 (56). Anal. calcd for $C_{39}H_{39}NO_3$; C, 82.22; H, 6.90; N, 2.46: found: C, 82.45; H, 6.98; N, 2.41.

4.2.4. 2′-Benzoyl-1′-cyclohexyl-5′-phenyl-4′-(4-chlorophenyl) spiro[tetrahydronaphthalen-2,3′-pyrrolidine]-1-one (3d). Yellow needle, 0.13 g, 45%, mp 230–231°C; IR (KBr)$_\nu$C=O: 1698, 1676 cm^{-1}; ^{1}H NMR: δ 0.92–2.50 (m, 11H, cyclohexyl), 1.75–3.26 (m, 4H, 2×CH$_2$), 4.45 (d, J=11 Hz, H$_c$), 4.70 (d, J=11 Hz, H$_b$), 5.12 (s, 1H, H$_a$), 6.90–7.51 (m, 16H), 7.60 (d, J=7 Hz, 1H), 8.01 (d, J=7 Hz, 1H); ^{13}C NMR: δ 25.6, 25.9, 26.2, 26.4, 27.1, 33.6, 55.2, 58.5, 63.3, 70.3, 126.5, 127.6, 127.8, 128.0, 128.1, 128.5, 128.9, 129.4, 130.1, 131.9, 132.8, 132.9, 134.6, 136.8, 141.8, 199.7, 204.2; MS: m/z 573 (M$^+$, 4), 575 (M^{2+}, 3), 468 (63), 324 (16), 228 (16), 105 (20). Anal. calcd for $C_{38}H_{36}NClO_2$; C, 79.49; H, 6.32; N, 2.44: found: C, 79.59; H, 6.19; N, 2.49.

4.2.5. 2′-Benzoyl-1′-cyclohexyl-5′-phenyl-4′-(4-dimethylaminophenyl) spiro[tetrahydronaphthalen-2,3′-pyrrolidine]-1-one (3e). Pale yellow solid, 0.15 g, 52%, mp 223–224°C; IR (KBr)$_\nu$C=O: 1697, 1674 cm^{-1}; ^{1}H NMR: δ 0.89–2.44 (m, 11H, cyclohexyl), 1.90–3.60 (m, 4H, 2×CH$_2$), 2.91 (s, 6H, *p*-NMe$_2$), 4.61 (d, J=11 Hz, H$_c$), 4.80 (d, J=11 Hz, H$_b$), 5.41 (s, 1H, H$_a$), 6.60–7.39 (m, 16H), 7.73 (d, J=7 Hz, 1H), 7.93 (d, J=7 Hz, 1H); ^{13}C NMR: δ 25.6, 25.7, 26.1, 26.6, 27.9, 33.7, 40.7, 56.1, 60.1, 65.0, 65.4, 126.2, 126.8, 127.5, 127.7, 127.9, 128.0, 128.4, 131.3, 132.8, 136.9, 141.8, 143.8, 196.2, 204.3; MS: m/z 582 (M$^+$, 2), 477 (90), 353 (34), 167 (13), 105 (21). Anal. calcd for $C_{40}H_{42}N_2O_2$; C, 82.44; H, 7.26; N, 4.81: found: C, 82.67; H, 7.13; N, 4.64.

4.2.6. 2′-Benzoyl-1′-cyclohexyl-5′-phenyl-4′-(3-nitrophenyl) spiro[tetrahydronaphthalen-2,3′-pyrrolidine]-1-one (3f). Yellow solid, 0.18 g, 62%, mp 210–211°C; IR (KBr)$_\nu$C=O: 1692, 1674 cm^{-1}; ^{1}H NMR: δ 0.70–2.30 (m, 11H, cyclohexyl), 1.79–3.80 (m, 4H, 2×CH$_2$), 4.51 (d, J=11 Hz, H$_c$), 4.91 (d, J=11 Hz, H$_b$), 5.32 (s, 1H, H$_a$), 6.90–7.41 (m, 16H), 7.80 (d, J=7 Hz, 1H), 8.29 (d, J=7 Hz, 1H); ^{13}C NMR: δ 25.3, 25.5, 25.9, 26.2, 28.2, 29.8, 32.7, 57.3, 62.1, 70.3, 120.3, 124.9, 127.1, 128.3, 128.5, 128.6, 128.7, 128.8, 132.0, 132.3, 133.5, 134.0, 136.6, 138.2, 143.3, 147.4, 152.1, 198.2, 200.2; MS: m/z 584 (M$^+$, 2), 479 (26), 202 (12), 127 (12), 105 (44). Anal. calcd for $C_{38}H_{36}N_2O_4$; C, 78.06; H, 6.21; N, 4.79: found: C, 78.18; H, 6.18; N, 4.98.

4.2.7. 2′-Benzoyl-1′-cyclohexyl-5′-phenyl-4′-(3-nitrophenyl) spiro[6-methoxytetrahydronaphthalen-2,3′-pyrrolidine]-1-one (3g). Yellow crystal, 0.15 g, 49%, mp 212–213°C; IR (KBr)$_\nu$C=O: 1700, 1676 cm^{-1}; ^{1}H NMR: δ

0.78–2.51 (m, 11H, cyclohexyl), 1.69–3.80 (m, 4H, 2×CH_2), 3.80 (s, 3H, OMe), 4.64 (d, J=11 Hz, H_c), 5.19 (d, J=11 Hz, H_b), 5.30 (s, 1H, H_a), 6.42–8.10 (m, 15H), 8.21 (d, J=7 Hz, 1H), 8.45 (d, J=7 Hz, 1H); ^{13}C NMR: δ 25.7, 25.9, 26.2, 26.7, 29.0, 29.7, 30.4, 32.1, 55.5, 55.7, 57.8, 63.4, 70.8, 112.2, 113.7, 121.8, 127.4, 127.6, 128.3, 128.5, 128.8, 129.1, 131.2, 133.6, 141.8, 144.6, 153.9, 196.8, 204.4; MS: *m/z* 614 (M^+, 1), 509 (100), 352 (43), 232 (11%), 178 (23), 105 (37). Anal. calcd for $C_{39}H_{38}N_2O_5$; C, 76.12; H, 6.23; N, 4.56: found: C, 76.20; H, 6.45; N, 4.78.

4.2.8. 2′-Benzoyl-1′-cyclohexyl-4′,5,5′-triphenyl-spiro-[butenolide-3,3′-pyrrolidine] (6a). Yellow solid, 0.17 g, 61%, mp 198–200°C; IR (KBr)$_\nu$C═O: 1689, 1788 cm^{-1}; ^{1}H NMR: δ 0.98–1.82 (m, 10H, cyclohexyl, CH_2), 2.60 (m, 1H, NCH, cyclohexyl), 3.96 (d, J=9 Hz, H_c), 4.79 (d, J=9 Hz, H_b), 5.00 (s, H_a), 6.16 (s, H_d), 7.10–7.53 (m, 14H), 7.92–8.04 (m, 6H); ^{13}C NMR: δ 25.4, 26.0, 33.4, 57.0, 61.5, 63.2, 65.0, 67.0, 67.5, 103.6, 118.5, 125.0, 126.9, 127.4, 127.7, 127.9, 128.1, 128.2, 128.4, 128.5, 128.7, 128.7, 128.9, 129.1, 129.9, 130.2, 133.5, 137.1, 142.1, 164.9, 198.3; MS: *m/z* 553 (M^+, 6), 448 (60), 304 (13), 158 (16), 105 (43). Anal. calcd for $C_{38}H_{35}NO_3$; C, 82.46; H, 6.33; N, 2.53: found: C, 82.72; H, 6.48; N, 2.15.

4.2.9. 2′-Benzoyl-1′-cyclohexyl-5,5′-diphenyl-4′-(4-methylphenyl)-spiro[butenolide-3,3′-pyrrolidine] (6b). Yellow solid, 0.18 g, 65%, mp 206–208°C; IR (KBr)$_\nu$-C═O: 1689, 1788 cm^{-1}; ^{1}H NMR: δ 0.66–1.88 (m, 10H, cyclohexyl, CH_2), 2.14 (s, 3H, *p*-Me), 2.48 (m, 1H, NCH, cyclohexyl), 3.88 (d, J=12 Hz, H_c), 4.74 (d, J=12 Hz, H_b), 5.00 (s, H_a), 6.17 (s, H_d), 6.97–7.49 (m, 13H), 7.67–7.88 (m, 6H); ^{13}C NMR: δ 20.9, 25.3, 25.9, 33.4, 57.0, 61.5, 63.2, 65.0, 67.0, 67.0, 67.6, 103.6, 119.5, 125.0, 127.4, 127.9, 128.1, 128.2, 128.4, 128.5, 128.6, 128.7, 128.9, 129.1, 129.9, 130.2, 133.2, 137.1, 142.1, 162.0, 198.1; MS: *m/z* 567 (M^+, 2), 462 (100), 380 (11), 247 (9), 105 (52). Anal. calcd for $C_{39}H_{37}NO_3$; C, 82.54; H, 6.53; N, 2.47: found: C, 82.42; H, 6.15; N, 2.69.

4.2.10. 2′-Benzoyl-1′-cyclohexyl-5,5′-diphenyl-4′-(4-methoxyphenyl)-spiro[butenolide- 3,3′-pyrrolidine] (6c). Yellow solid, 0.14 g, 48%, mp 203–204°C; IR (KBr)$_\nu$C═O: 1697, 1787 cm^{-1}; ^{1}H NMR: δ 0.88–1.88 (m, 10H, cyclohexyl, CH_2), 2.16 (m, 1H, NCH, cyclohexyl), 3.64 (s, 3H, *p*-OMe), 3.88 (d, J=11 Hz, H_c), 4.79 (d, J=11 Hz, H_b), 5.01 (s, H_a), 6.17 (s, H_d), 6.67–7.50 (m, 13H), 7.72–8.10 (m, 6H); ^{13}C NMR: δ 25.3, 25.9, 33.4, 46.5, 57.0, 61.5, 63.2, 65.0, 67.0, 67.7, 102.7, 118.5, 125.0, 126.9, 127.4, 127.7, 127.9, 128.1, 128.2, 128.4, 128.5, 128.7, 128.8, 128.9, 129.1, 129.9, 130.2, 132.2, 138.1, 142.1, 162.0, 198.2; MS: *m/z* 583 (M^+, 3), 478 (49), 247 (13), 194 (11), 105 (47). Anal. calcd for $C_{39}H_{37}NO_4$; C, 80.27; H, 6.35; N, 2.40: found: C, 80.39; H, 6.54; N, 2.02.

4.2.11. 2′-Benzoyl-1′-cyclohexyl-5,5′-diphenyl-4′-(4-chlorophenyl)-spiro[butenolide- 3,3′-pyrrolidine] (6d). Pale yellow solid, 0.12 g, 41%, mp 214–215°C; IR (KBr)$_\nu$-C═O: 1695 1786 cm^{-1}; ^{1}H NMR: δ 0.88–1.88 (m, 10H, cyclohexyl, CH_2), 2.57 (m, 1H, NCH, cyclohexyl), 3.90 (d, J=11 Hz, H_c), 4.71 (d, J=11 Hz, H_b), 5.02 (s, H_a), 6.14 (s, H_d), 7.04–7.50 (m, 13H), 7.75–7.94 (m, 6H); ^{13}C NMR: δ 25.3, 25.8, 32.4, 51.5, 60.4, 63.2, 64.1, 66.2, 68.8, 102.9, 118.5, 123.9, 125.9, 126.4, 127.7, 127.9, 128.2, 128.3, 128.4, 128.7, 128.9, 129.1, 129.8, 130.3, 132.7, 138.1, 142.1, 162.3, 198.4; MS: *m/z* 587 (M^+, 2), 589 (M^{2+}, 3), 482 (31), 434 (9), 275 (15), 105 (56). Anal. calcd for $C_{38}H_{34}NClO_3$; C, 77.68; H, 5.79; N, 2.38: found: C, 77.43; H, 5.91; N, 2.51.

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