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ORIGINAL PAPER

Diels–Alder reaction of fused pyran-2-ones with ethyl vinyl ether

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Abstract Ethyl vinyl ether was found to be an appropriate synthetic equivalent of acetylene for a set of Diels–Alder reactions with fused pyran-2-ones that yield fused carbocyclic systems. Transformations were conducted under microwave irradiation with DABCO (as a catalyst for the elimination of ethanol) and with *n*-butanol as the additive. A single-crystal X-ray diffraction structure is presented for *N*-(5,6,7,8-tetrahydro-6-methyl-8-oxonaphthalen-2-yl)benzamide.

Keywords Cycloadditions · X-ray structure determination · Microwave-assisted synthesis · Catalysis · Carbocycles · Synthetic equivalent

Introduction

2*H*-Pyran-2-ones and their fused derivatives are well known as appropriate dienes for a variety of Diels–Alder reactions [1–3]. Besides alkynes [4–11], alkenes [12–18] can also be used as dienophiles in Diels–Alder reactions: the CO_2-bridged cycloadduct (7-oxabicyclo[2.2.2]octene) that is formed in the first reaction step when the diene is the pyran-2-one scaffold is not usually stable under thermal reaction conditions, and eliminates CO_2 via a retro-Diels–Alder reaction, forming a new cyclohexadiene system that can either act as a new diene for a new Diels–Alder reaction or alternatively (when appropriate groups for elimination are present) aromatize into a benzene system.

Sometimes it is desirable to replace the CO_2 fragment of the 2*H*-pyran-2-one ring with a CH=CH fragment. This could be—at least theoretically—executed via the cycloaddition of acetylene, but such a pathway is of limited practical synthetic utility since acetylene is very unreactive in Diels–Alder reactions (besides being gaseous under normal conditions, thus further limiting its use) [19]. Therefore, we and other groups have been searching for synthetic equivalents of acetylene, and have identified ethyl vinyl ether, vinyl acetate, vinyl propionate, cyclohexyl vinyl ether, 1-vinyl-2-pyrrolidone, and *N*-vinylcaprolactam as possible candidates [20–32]. Even though some cyclohexadiene intermediates can be isolated and even characterized [32, 33], they are generally rather unstable [34]. However, it was shown that organic bases (such as DABCO) act as catalysts for the last reaction step in the aromatization of a cyclohexadiene intermediate (whereas they do not influence the preceding two steps: cycloaddition and elimination of CO_2) [31, 32].

The abovementioned dienophiles containing a vinyl moiety were indeed found to be appropriate for cycloadditions with substituted 3-acylamino-2*H*-pyran-2-ones, but so far there have been no studies utilizing fused pyran-2-ones. Our goal was therefore to investigate the possibilities offered by such fused compounds, as their cycloadducts would be similar to some biological frameworks, including a class of known agonists of 5-hydroxytryptamine receptors 1B (5-HT_{1B}).

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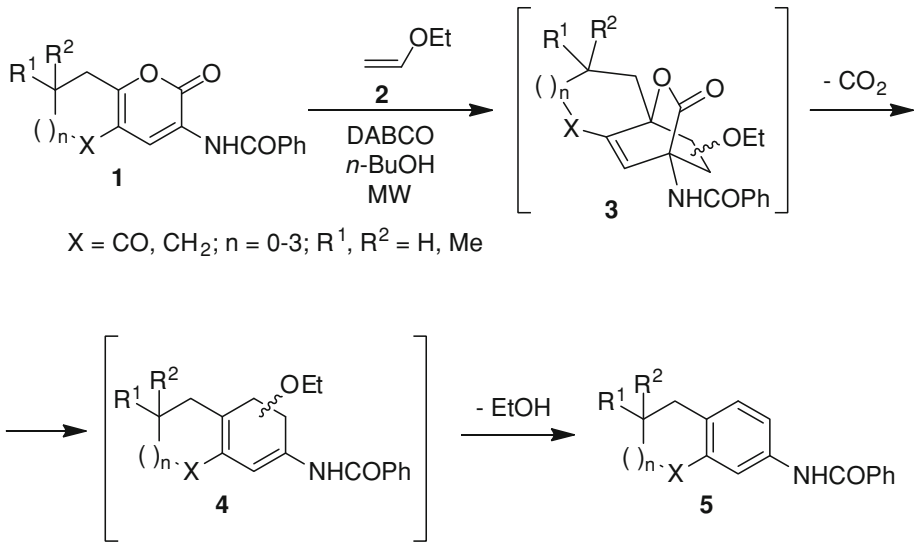
Scheme 1



Results and discussion

Diels–Alder reactions between a set of fused pyran-2-ones **1** [35–37] and ethyl vinyl ether (**2**; see Scheme 1) were initially conducted in closed vessels (10 cm^3) under microwave irradiation [38–46] at 120 °C, with the addition of DABCO as the catalyst. We found that such conditions (analogous to those used previously) [31, 32] were not adequate to achieve quantitative conversion into the products **5**; indeed, the only way to achieve this was to apply higher reaction temperatures (140–180 °C). However, in order to reach temperatures above 120 °C while keeping the pressure below the upper limit [as the boiling point of the neat ethyl vinyl ether (**2**) is rather low (33 °C)], it was necessary to add some appropriate additives to decrease the vapor pressure, such as ionic liquids (e.g., [bmim]BF_4) or *n*-butanol (which, due to the easier isolation of the products, proved to be preferable) [47–50].

These final conditions (Table 1) were applied to synthesize a set of fused carbocyclic compounds consisting of tetrahydronaphthalene, dihydro-1*H*-indene, tetrahydro-5*H*-benzo[7]annulene, and hexahydrobenzo[8]annulene frameworks bearing a benzoylamino group. Starting from the fused pyran-2-ones **1** (1 mmol) and ethyl vinyl ether (**2**, 2 cm^3) with a catalytic amount of DABCO (15 mol%, 16.8 mg) and a small amount of *n*-butanol (320 mg), we obtained the products **5a**–**5g** with good yields (65–75%). The optimal temperatures varied between 140 and 180 °C, and the durations required were 135–210 min, but even these rather harsh conditions were insufficient in one case (**5d**) to achieve a quantitative conversion. The pure product **5d** could, however, be obtained with a suitable isolation procedure.

It is interesting to note that the C=O group has a strongly accelerating effect on the reaction when present at position

Table 1 Reaction conditions and yields for the microwave-assisted synthesis of **5** with ethyl vinyl ether (**2**) starting from **1**

Run	Starting **1**				Product	*T*/°C	*t*/min[a]	Yield/%[b]
		n	*X*	R^1, R^2				
1	**1a**	0	C=O	H, H	**5a**	140	135	75
2	**1b**	1	C=O	H, H	**5b**	140	135	70
3	**1c**	1	C=O	H, Me	**5c**	140	135	70
4	**1d**	1	C=O	Me, Me	**5d**	140	150	–[c]
5	**1d**	1	C=O	Me, Me	**5d**	170	180	62[d]
6	**1e**	0	CH_2	H, H	**5e**	150	210	73
7	**1f**	2	CH_2	H, H	**5f**	180	210	70
8	**1g**	3	CH_2	H, H	**5g**	180	180	65

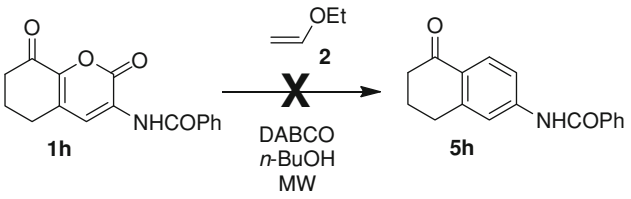
[a] Microwave irradiation in a closed vessel (10 cm^3) at 300 W

[b] Yield of isolated pure products (conversions >95%)

[c] Conversion 43%

[d] Conversion 75%

5 of the fused pyran-2-one system (compare, for example, **1b** with **1e**–**1g**), whereas the presence of C=O at position 8 on the fused pyran-2-one (i.e., **1h**) completely prevents cycloaddition; no cycloadduct was detected even under relatively severe conditions (135 min at 140 °C); see Scheme 2. Unfortunately, harsher conditions (180 min at 180 °C) were not appropriate, as they led to the decomposition of the reaction mixture. These results can be explained by increased delocalization of the diene system of the pyran-2-one ring caused by the additional carbonyl group at position 8 bonded to the other end of the diene fragment in **1h** (as opposed to the other cases **1a**–**1d**, where the second carbonyl group is bonded to the central part of the diene system, where it cannot cause such strong delocalization). Another effect of the carbonyl group at position 8 in **1h** might also be that it decreases the polarization of



Scheme 2

the diene system (both ends in **1h** bear carbonyl substituents), thus making the cycloaddition more like those with neutral electron demand (which are generally known to proceed poorly) [51].

Additionally, it seems that there is an inhibiting effect of the presence of the second methyl group at position 7 of the fused pyran-2-ones (compare **1d** with **1c** and **1b**). Even though both methyl groups are too far from the reacting diene system to exert any appreciable electronic effects, they do appear to cause certain steric interactions that might be responsible for the lower reactivity of **1d**.

In a separate experiment, **1b** and **2** were treated under conventional conditions in a closed vessel heated in an oil bath at 140 °C for 135 min (the temperature and the reaction time were the same as in run 2, Table 1). However, the ^{1}H NMR spectrum of the crude reaction mixture did not show any signals belonging to the product **5b**—starting materials **1b** and **2** remained unchanged.

Crystal structure of ***5c***

Crystals of **5c** suitable for X-ray structure determination were obtained by slow evaporation from chloroform at room temperature. Single-crystal X-ray analysis (Fig. 1) found substitution patterns that were in accordance with its NMR spectral data. In the crystal structure of **5c**, the mean plane through the amide group is inclined with respect to the C1–C4/C9–C10 ring (which is part of the tetralone moiety) by 12.89(10)°, and to the phenyl ring C13–C18 by 14.56(12)°, leading to near-planarity of the aromatic rings,

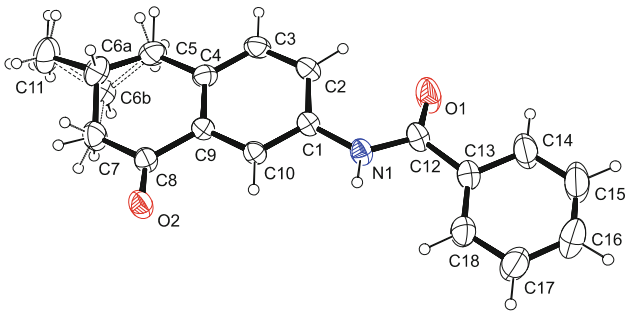


Fig. 1 The molecular structure of **5c**, showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 30% probability level. The disorder on C6 is indicated by *dashed lines*

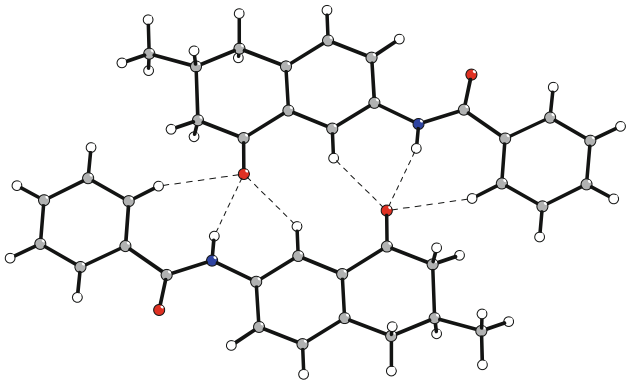


Fig. 2 Dimer formation in **5c**. *Dashed lines* indicate hydrogen bonds. Disorder on C6 is omitted for clarity

with a small twist angle between the C1–C4/C9–C10 ring and the phenyl ring C13–C18 of 1.82(11)°. Compound **5c** crystallizes as a centrosymmetric hydrogen-bonded dimer facilitated by N1–H1...O2 ($1-x$, $-y$, $-z$) interactions involving the amide and carbonyl groups of the tetralone moieties of adjacent molecules (Fig. 2). The dimers can be described by the graph-set motif $R_2^2(14)$ [52]. The dimeric structure is further stabilized by additional weak C–H...O2 hydrogen bonding (Table 2). Both molecules in the dimer are not in a plane; a separation of 0.720 Å was found between the mean planes through the C1–C4/C9–C10 rings of the adjacent molecules.

Supramolecular aggregation is stabilized by π–π interactions between two parallel C1–C4/C9–C10 rings (centroid $Cg1$), with a $Cg1...Cg1$ ($1-x$, $1-y$, $-z$) centroid-to-centroid distance of 4.0797(10) Å, a perpendicular distance from the centroid $Cg1$ to the plane of the other ring of 3.5646(7) Å, and a slippage between the centroids of 1.984 Å. These interactions are consistent with well-defined π–π stacking interactions [53–55], and can be regarded as medium to strong, since strong interactions exhibit rather short centroid–centroid contacts ($Cg\cdots Cg$ < 3.8 Å), small slip angles (<25°), and small vertical displacements (<1.5 Å), which translate into a sizeable overlap of the aromatic planes. In comparison, medium to weak interactions exhibit rather long centroid–centroid distances (>4.0 Å), together with large slip angles (>30°) and large vertical displacements (>2.0 Å) [56–59]. Supramolecular aggregation is further controlled by weak C3–H3...$Cg1$ ($\frac{1}{2}-x$, $-\frac{1}{2}+y$, $-z$) hydrogen bonding between two adjacent tetralone moieties (Fig. 3; Table 2).

Conclusions

We have shown that ethyl vinyl ether can be applied as a useful synthetic equivalent of acetylene in Diels–Alder reactions with a variety of dienes within fused pyran-2-one

Table 2 Hydrogen bonds for **5c**

D–H...A	*d*(D–H)/Å	*d*(H...A)/Å	*d*(D...A)/Å	<(DHA)/°	Symmetry transformation for acceptors
N1–H1...O2	0.86	2.25	3.0765(19)	162.1	$1 - x, -y, -z$
C10–H10...O2	0.93	2.54	3.332(2)	143.2	$1 - x, -y, -z$
C18–H18...O2	0.93	2.56	3.420(2)	153.8	$1 - x, -y, -z$
C3–H3...*Cg*1	0.93	2.80	3.535(2)	137.0	$½ - x, -½ + y, -z$

*Cg*1 is a C1–C4/C9–C10 ring centroid

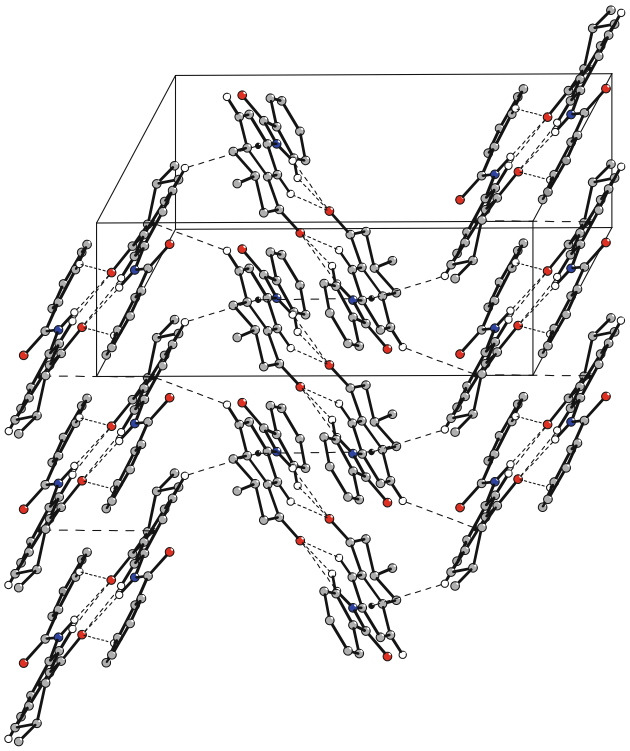


Fig. 3 Packing diagram for **5c**. *Dashed lines* indicate π–π interactions and hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown and disorder on C6 are omitted

systems. The reactions were executed under microwave irradiation with the addition of *n*-butanol (to allow the system to be heated up to the necessary temperatures) and DABCO (as the catalyst for the elimination of ethanol). Additionally, a single-crystal X-ray structure of one of the products was determined.

Experimental

Melting points were determined on a micro hot stage apparatus. ^{1}H NMR spectra were recorded at 29 °C with a Bruker (Rheinstetten, Germany) Avance DPX 300 spectrometer at 300 MHz or Bruker Avance III spectrometer at 500 MHz, using TMS as an internal standard. ^{13}C NMR spectra were recorded on the Bruker Avance DPX 300 at 75.5 MHz at 29 °C, and were referenced against the central line of the solvent signal ($CDCl_3$ triplet at 77.0 ppm or DMSO-d_6 septet at 39.5 ppm). The coupling constants (*J*) are given in hertz. IR spectra were obtained with a Bio-Rad (Hercules, CA, USA) FTS 3000MX spectrometer as KBr pellets for all compounds. MS spectra were recorded with a VG Analytical (Wythenshawe, UK) AutoSpec Q and Waters-Micromass (Milford, MA, USA) Q-TOF Premier spectrometers. Elemental analyses (C, H, N) were conducted using a PerkinElmer (Waltham, MA, USA) 2400 series II CHNS/O analyzer, and the results obtained experimentally were found to be in good agreement (±0.3%) with the calculated values. The starting compounds **1** were prepared according to published procedures [35–37]. All other reagents and solvents were used as received from commercial suppliers.

Microwave reactions were conducted in air using a focused microwave unit (Discover by CEM Corporation, Matthews, NC, USA). This machine consists of a continuous, focused microwave power delivery system with an operator-selectable power output from 0 to 300 W. Reactions were performed in darkness in glass vessels (capacity 10 cm^3) sealed with a septum. The pressure was controlled by a load cell connected to the vessel via the septum. The temperature of the contents of the vessel was monitored using a calibrated infrared temperature controller mounted under the reaction vessel and by measuring the temperature of the outer surface of the reaction vessel. The mixtures were stirred with a Teflon-coated magnetic stirring bar in the vessel. Temperature, pressure, and power profiles were recorded using commercially available software provided by the manufacturer of the microwave unit.

X-ray structure determination

Single-crystal X-ray diffraction data were collected at room temperature with a Bruker Nonius Kappa CCD diffractometer using graphite monochromated Mo–Kα radiation ($\lambda = 0.71073$ Å). The data were processed using DENZO [60]. The structure was solved using direct methods implemented in SHELXS-97 [61], and refined by

Table 3 Crystallographic data for **5c**

Formula	$C_{18}H_{17}NO_2$
M_r	279.33
T/K	293(2)
Crystal system	Monoclinic
Space group	$P\ 2_1/a$
a/Å	15.6343(5)
b/Å	5.8573(2)
c/Å	16.1854(4)
β/°	100.684(3)
Volume/Å^3	1,456.48(8)
Z	4
D_{calc}/Mg/m^3	1.274
μ/mm^{-1}	0.083
F(000)	592
Crystal size/mm^3	0.50 × 0.35 × 0.20
Reflections collected	5,198
Unique reflections/R_{int}	3,309(0.0229)
Parameters	201
R, wR_2 [$I > 2\sigma(I)$][a]	0.0614, 0.1577
R, wR_2 (all data)[b]	0.0898, 0.1786
GOF, S[c]	1.042

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$

[b] $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$

[c] $S = \{\sum[(F_o^2 - F_c^2)^2]/(n/p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined

a full-matrix least-squares procedure based on F^2 with SHELXL-97 [62]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were readily located in difference Fourier maps and were placed at calculated positions and treated using the appropriate riding models. In the crystal structure of **5c**, atom C6 is disordered over two positions in the ratio 0.81:0.19. The crystallographic data are listed in Table 3. CCDC-851204 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

*General procedure for the synthesis of **5a–5g***

A mixture of the starting fused pyran-2-one **1** (1 mmol), 2 cm^3 ethyl vinyl ether (**2**), 16.8 mg DABCO (15 mol%), and 300 mg *n*-butanol in a sealed vial (10 cm^3) was irradiated in the focused microwave equipment for the time specified (Table 1). The final temperature was set to 140 °C (for **5a–5c**), 150 °C (for **5e**), 170 °C (for **5d**), or 180 °C (for **5f**, **5g**), the power was set to 300 W, and the ramp time to 5 min. Thereafter, the reaction mixture was cooled, volatile components were removed in vacuo, the remaining solid was treated with *i*-Pr_2O and cooled. The precipitated products **5a–5c**, **5e**, **5f** were filtered off and washed with *i*-Pr_2O. In the case of **5d**, the crude solid remaining after the evaporation of volatile components was separated by column chromatography on silica gel with a mixed mobile phase of petrol ether:ethyl acetate = 7:1 which changed gradually to 3:1.

N-(2,3-Dihydro-3-oxo-1H-inden-5-yl)benzamide (**5a**, $C_{16}H_{13}NO_2$)

Yield 188 mg (75%), recrystallization from ethanol. M.p. 205–208 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.73 (m, 2H, 1-CH_2), 3.14 (m, 2H, 2-CH_2), 7.50 (m, 3H, 7-H and 2H of Ph), 7.59 (m, 1H, Ph), 7.81 (d, J = 1.8 Hz, 1H, 4-H), 7.91 (m, 2H, Ph), 8.08 (br s, 1H, NH), 8.18 (dd, J_1 = 8.5 Hz, J_2 = 1.8 Hz, 1H, 6-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 24.9, 36.3, 113.7, 127.0, 127.1, 127.6, 128.4, 131.7, 134.6, 137.0, 138.4, 150.3, 165.6, 206.1 ppm; IR (KBr): $\bar{\nu}$ = 1,699, 1,677, 1,653, 1,639, 1,620, 1,599, 1,576, 1,542, 1,532, 1,492 cm^{-1}; MS (ES+, TOF): m/z = 252 (MH^+); HRMS calcd for $C_{16}H_{14}NO_2$ (MH^+) 252.1019, found 252.1042.

N-(5,6,7,8-Tetrahydro-8-oxonaphthalen-2-yl)benzamide (**5b**, $C_{17}H_{15}NO_2$)

Yield 186 mg (70%), recrystallization from ethanol. M.p. 137–140 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.14 (m, 2H, 6-CH_2), 2.64 (m, 2H), 2.96 (m, 2H, 5-CH_2 and 7-CH_2), 7.30 (d, J = 8.1 Hz, 1H, 4-H), 7.53 (m, 3H, Ph), 7.91 (m, 2H, Ph), 7.96 (d, J = 2.4 Hz, 1H, 1-H), 8.24 (br s, 1H, NH), 8.28 (dd, J_1 = 8.1 Hz, J_2 = 2.4 Hz, 1H, 3-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 23.2, 28.9, 38.8, 118.3, 126.2, 127.4, 128.4, 129.4, 131.6, 132.5, 134.7, 137.4, 140.3, 166.1, 198.9 ppm; IR (KBr): $\bar{\nu}$ = 1,662, 1,603, 1,585, 1,532, 1,497, 1,352 cm^{-1}; MS (ES+, TOF): m/z = 266 (MH^+); HRMS calcd for $C_{17}H_{16}NO_2$ (MH^+) 266.1181, found 266.1187.

N-(5,6,7,8-Tetrahydro-6-methyl-8-oxonaphthalen-2-yl)-benzamide (**5c**, $C_{18}H_{17}NO_2$)

Yield 195 mg (70%), recrystallization from petrol ether. M.p. 189–191 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.15 (d, J = 6.1 Hz, 3H, Me), 2.33 (m, 2H, CH_2), 2.69 (m, 2H, CH_2), 2.99 (m, 1H, 6-H), 7.30 (d, J = 8.4 Hz, 1H, 4-H), 7.54 (m, 3H, Ph), 7.89 (m, 3H, 1-H and Ph), 8.03 (br s, 1H, NH), 8.25 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H, 3-H) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 21.3, 30.5, 37.4, 46.9, 188.0, 126.2, 127.3, 128.6, 129.7, 131.8, 132.4, 134.8, 137.2, 139.8, 166.0, 198.7 ppm; IR (KBr): $\bar{\nu}$ = 3,348, 1,660, 1,605, 1,586, 1,532, 1,497, 1,452 cm^{-1}; MS (ES+, TOF): m/z = 280 (MH^+), 302 (MNa^+).

N-(5,6,7,8-Tetrahydro-6,6-dimethyl-8-oxonaphthalen-2-yl)benzamide (**5d**, $C_{19}H_{19}NO_2$)

Yield after column chromatography (R_f = 0.31; PE:AcOEt = 3:1): 182 mg (62%), recrystallization from

ethanol. M.p. 242–244 °C; ^{1}H NMR (300 MHz, DMSO-d_6): $\delta = 1.02$ (s, 6H, 2 × Me), 2.50 (s, 2H, CH_2), 2.84 (s, 2H, CH_2), 7.33 (d, $J = 8.4$ Hz, 1H, 4-H), 7.57 (m, 3H, Ph), 7.98 (m, 3H, 3-H and Ph), 8.29 (d, $J = 2.1$ Hz, 1H, 1-H), 10.4 (br s, 1H, NH) ppm; ^{13}C NMR (75.5 MHz, DMSO-d_6): $\delta = 27.7$, 33.5, 42.0, 51.7, 117.3, 125.8, 127.6, 128.3, 129.7, 131.4, 131.6, 134.6, 137.6, 137.9, 165.5, 197.5 ppm; IR (KBr): $\bar{\nu} = 3{,}331$, 1,664, 1,603, 1,531, 1,495, 1,306 cm^{-1}; MS (ES+, TOF): $m/z = 294$ (MH^+); HRMS calcd for $C_{19}H_{20}NO_2$ (MH^+) 294.1494, found 294.1498.

N-(2,3-Dihydro-1H-inden-5-yl)benzamide (**5e**, $C_{16}H_{15}NO$)

Yield 173 mg (73%), recrystallization from ethanol. M.p. 113–116 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 2.09$ (deg tt, $J = 7.4$ Hz, 2H, 2-CH_2), 2.89 (t, $J = 7.4$ Hz, 2H), 2.93 (t, $J = 7.4$ Hz, 2H, 1-CH_2 and 3-CH_2), 7.20 (d, $J = 8.0$ Hz, 1H, 7-H), 7.29 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.3$ Hz, 1H, 6-H), 7.48–7.56 (m, 3H, Ph), 7.61 (br s, 1H, 4-H), 7.77 (br s, 1H, NH), 7.86 (m, 2H, Ph) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 25.6$, 32.4, 33.0, 116.8, 118.5, 124.5, 127.0, 128.7, 131.6, 135.2, 136.0, 140.6, 145.2, 165.7 ppm; IR (KBr): $\bar{\nu} = 1{,}643$, 1,599, 1,578, 1,540, 1,492 cm^{-1}; MS (ES+, TOF): $m/z = 238$ (MH^+); HRMS calcd for $C_{16}H_{16}NO$ (MH^+) 238.1226, found 238.1229.

N-(6,7,8,9-Tetrahydro-5H-benzo[7]annulen-2-yl)-benzamide (**5f**, $C_{18}H_{19}NO$)

Yield 186 mg (70%), recrystallization from ethanol. M.p. 165–168 °C; ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 1.64$ (m, 4H, 2 × CH_2), 1.83 (m, 2H, CH_2), 2.77 (m, 4H, 2 × CH_2), 7.08 (d, $J = 8.0$ Hz, 1H, 4-H), 7.35 (dd, $J_1 = 8.0$ Hz, $J_2 = 2.0$ Hz, 1H, 3-H), 7.39 (d, $J = 2.0$ Hz, 1H, 1-H), 7.50 (m, 3H, Ph), 7.80 (br s, 1H, NH), 7.85 (m, 2H, Ph) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 28.2$, 28.4, 32.6, 36.1, 36.7, 117.7, 121.0, 127.0, 128.6, 129.4, 131.5, 135.1, 135.7, 139.9, 144.2, 165.6 ppm; IR (KBr):$\bar{\nu} = 3{,}260$, 2,916, 2,847, 1,645, 1,601, 1,600, 1,594, 1,579, 1,531, 1,501 cm^{-1}; MS (ES+, TOF): $m/z = 266$ (MH^+).

N-(5,6,7,8,9,10-Hexahydrobenzo[8]annulen-2-yl)-benzamide (**5g**, $C_{19}H_{21}NO$)

Yield 181 mg (65%), recrystallization from ethanol. M.p. 134–137 °C; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.35$ (m, 4H, 2 × CH_2), 1.65 (m, 4H, 2 × CH_2), 2.71 (m, 4H, 2 × CH_2), 7.05 (d, $J = 7.8$ Hz, 1H, 4-H), 7.45 (m, 5H, 1-H, 3-H, Ph), 7.84 (m, 2H, Ph), 7.99 (s, 1H, NH) ppm; ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 25.8$, 25.9, 31.8, 32.1, 32.2, 32.3, 118.2, 120.7, 127.0, 128.6, 129.5, 131.5, 135.1, 136.0, 137.7, 142.0, 165.6 ppm; IR (KBr): $\bar{\nu} = 3{,}287$, 2,916, 2,845, 1,651, 1,615, 1,603, 1,592, 1,580, 1,537, 1,499 cm^{-1}; MS (ES+, TOF): $m/z = 280$ (MH^+).

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