Synthesis of Benzo[*g*]isochromenes through Photo-Dehydro-*Diels–Alder* Reaction

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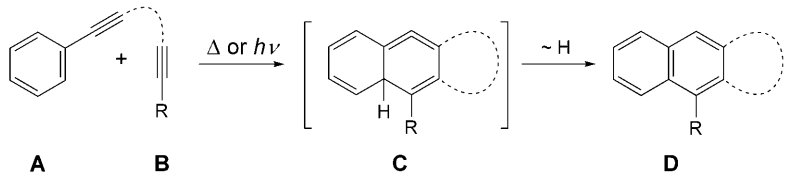
The Photo-Dehydro-*Diels–Alder* (PDDA) reaction is shown to be a versatile method for the preparation of highly functionalized naphthalenes. Thus, ketones **1** could be cyclized to the 1*H*-benzo[*g*]isochromen-4-(3*H*)-ones **11** and **12**, mostly in good yields. The influence of various substituents on the regioselectivity of the reaction was investigated, and the mechanism is discussed based on theoretical calculations.

1. Introduction. – The *Diels–Alder* reaction, *i.e.*, the [4+2] cycloaddition of a diene and an alkene (or alkyne), including hetero-analogues, belongs to the most-versatile methods for the preparation of carbo- and heterocyclic six-membered rings, and has been applied in a huge number of natural product syntheses [1]. When an enyne or an arylacetylene **A** instead of a diene reacts with an alkyne **B**, cyclic allenes **C** are formed, which are unstable in most cases and undergo hydrogen migration to afford an aromatic ring, *i.e.*, naphthalenes **D** (*Scheme 1*). This process is called Dehydro-*Diels–Alder* (DDA) reaction, and both thermal [2] and transition-metal-catalyzed processes [3] are well-known for a long time.

Scheme 1. *Dehydro*-Diels–Alder *Reaction*



In contrast to thermally initiated DDA processes, little is known about the photochemical variants of this reaction [4]. Very recently, we reported on the first systematic investigation of the Photo-Dehydro-*Diels–Alder* (PDDA) reaction and its application in the synthesis of highly functionalized naphthalenes [5]. Herein, we describe the preparation of 1*H*-benzo[*g*]isochromen-4-(3*H*)-ones through intramolecular PDDA reaction of different 4-aryl-1-[(3-arylprop-2-yn)oxy]but-3-yn-2-ones **1** (see *Scheme 2* below).

It should be noted that the 1*H*-benzo[*g*]isochromen-4-one[1]) scaffold is contained in some natural products exhibiting very interesting biological activities. The most-acquainted representative is surely hongconin, a constituent of the plant *Eleutherine americana* MERR. et HEYNE (Iridaceae), also known as '*Hong-Cong*' in Chinese [6a,b]. Hongconin, as well as other constituents with similar structures, have been shown to exhibit cardioprotective activities, and a series of total syntheses of hongconin have been reported [6c–h].

2. Results and Discussion. – 2.1. *Synthesis of Ketones.* To investigate the influence of structural variations on the photochemical behavior, we prepared a total of 18 compounds (**1a**–**r**), either differing in the Ar^1, Ar^2 substituents (**1a**–**n**) or the R substituent (**1o**–**r**), as shown in *Schemes 2* and *3* and *Table 1*. The synthesis of ketones **1a**–**n** commenced, in most cases, with ethyl glycolate (**2**). After alkylation of **2** with propargyl bromide, the resulting ether **3** was subjected to *Sonogashira* coupling [7] with different aryl iodides (Ar^1I). The thus obtained compounds **4** were converted [8] into the corresponding *Weinreb* amides **5** in two steps (with the exception of **5d**,**f**; see below). Treatment of compounds **5** with different lithium arylacetylenides then afforded the target ketones **1a**–**n** in yields of 44–92% (*Table 1*).

Table 1. *Substituents and Yields of Compounds* **1a**–**n**

Entry	Series	Ar^1	Ar^2	Yield [%]
1	**a**	C_6H_5	C_6H_5	79
2	**b**	4-Cl-C_6H_4	C_6H_5	62
3	**c**	4-Me-C_6H_4	C_6H_5	67
4	**d**	4-F-C_6H_4	C_6H_5	64
5	**e**	C_6H_5	4-Cl-C_6H_4	70
6	**f**	C_6H_5	4-F-C_6H_4	57
7	**g**	C_6H_5	4-Me-C_6H_4	66
8	**h**	C_6H_5	1-Naphthyl	67
9	**i**	1-Naphthyl	C_6H_5	78
10	**j**	C_6H_5	4-Me-SO_2-C_6H_4	61
11	**k**	C_6H_5	3,5-Me_2-C_6H_3	53
12	**l**	C_6H_5	4-CF_3-C_6H_4	92
13	**m**	Mesityl[a])	C_6H_5	37
14	**n**	C_6H_5	Mesityl	64

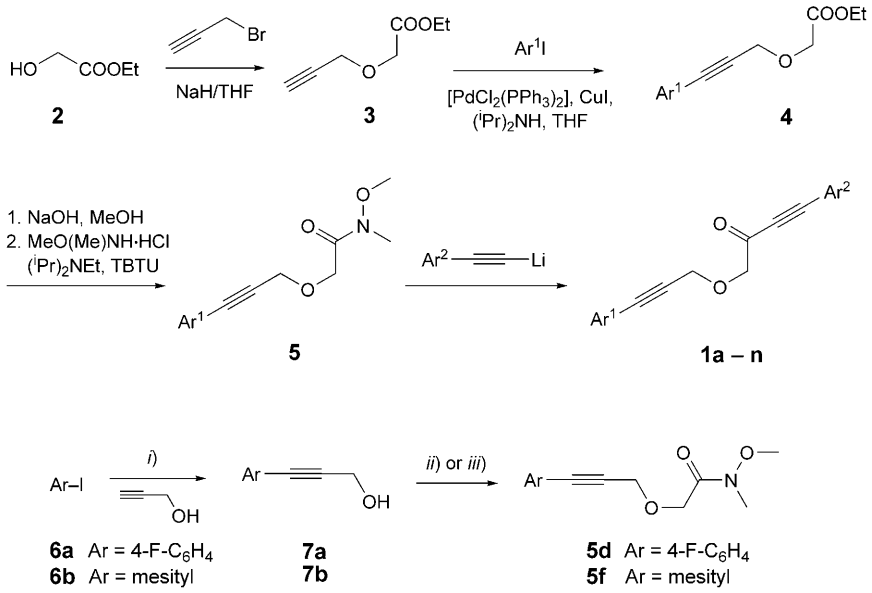
[a]) Mesityl = 2,4,6-trimethylphenyl.

Notably, the *Sonogashira* coupling of the 4-fluoro-substituted iodobenzene **6a** and the iodomesitylene **6b** with **3** failed. Therefore, compounds **5d** and **5f** were prepared by a slightly different route involving the propargyl alcohols **7a** and **7b**, respectively, as shown in *Scheme 2* and *Table 2*.

The preparation of the branched ketones **1o**–**r** required a different approach (*Scheme 3*). Starting with the aldehydes **8**, the propargyl alcohols **9** were prepared by

1) *Chemical Abstracts*' name: 1*H*-naphtho[2,3-*c*]pyran-4(3*H*)-one.

Scheme 2. *Synthesis of the Target Ketones* **1a**–**n**



i) $[PdCl_2(PPh_3)_2]$, CuI, $(i\text{-}Pr)_2NH$, THF. *ii*) For **5d**: 1. Ethyl bromoacetate, BuLi, THF; 2. KOH, MeOH; 3. MeO(Me)NH·HCl, $(i\text{-}Pr)_2NEt$, TBTU. *iii*) For **5f**: 1. Bromoacetic acid, BuLi, THF; 2. MeO(Me)NH·HCl, $(i\text{-}Pr)_2NEt$, TBTU (=2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate).

Table 2. *Yields of compounds* **4** *and* **5**

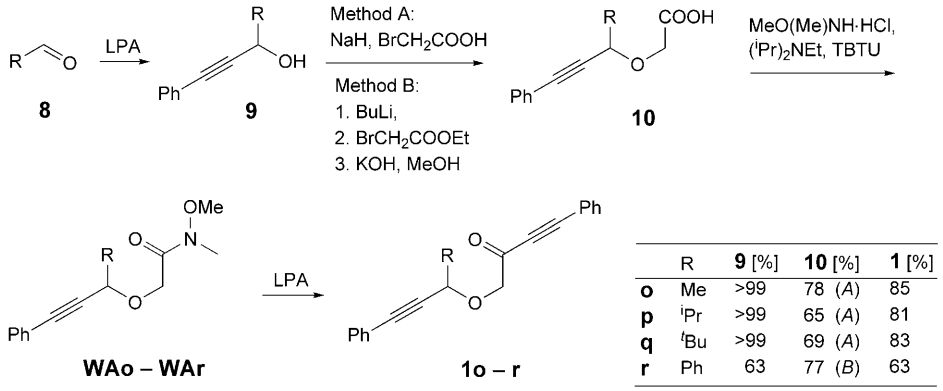
Entry	Series	Ar^1	Yield [%]	
			4	**5**
1	**a**	Ph	70	99
2	**b**	4-Cl-C_6H_4	68	99
3	**c**	4-Me-C_6H_4	67	87
4	**d**	4-F-C_6H_4	56[a])	93
5	**e**	1-Naphthyl	46	98
6	**f**	Mesityl[b])	–	25[c])

[a]) From **7a**. [b]) Mesityl=2,4,6-trimethylphenyl. [c]) Over two steps from **7b**.

treatment with lithium phenylacetylide (LPA). The conversion of **9** into the *O*-propargyl glycolic acids **10** was performed either by direct alkylation with bromoacetic acid (**1o**–**q**; *Method A*) or by alkylation with ethyl bromoacetate followed by saponification (**1r**; *Method B*). Finally, the target ketones **1o**–**r** were obtained in two steps *via* the corresponding *Weinreb* amides (**WA**).

2.2. *Photochemical Behavior of the Ketones* **1**. To find the optimal irradiation conditions, we explored at first the product distribution on irradiation of the parent compound **1a** in different solvents. The results are summarized in *Table 3*. As previously

Scheme 3. *Synthesis of the Target Ketones* **1o**–**r**



	R	**9** [%]	**10** [%]	**1** [%]
o	Me	>99	78 (*A*)	85
p	^{i}Pr	>99	65 (*A*)	81
q	^{t}Bu	>99	69 (*A*)	83
r	Ph	63	77 (*B*)	63

LPA = Lithium phenylacetylide

described [5], we assume that the photochemical ring-closure proceeds *via* the biradicals **BR(1)** as intermediates (*Scheme 4*). At this stage, two regioisomeric 1*H*-benzo[*g*]-isochromen-4-(3*H*)-ones, *i.e.*, compounds **11** and **12**, may be formed. The highest total yield (77%) of **11a** and **12a** was obtained when the reaction was run in *t*-BuOH as solvent (*Table 3*, *Entry 3*). However, the regioselectivity was low (**11a**/**12a** 1.3 : 1) and was not influenced by the solvent. Interestingly, degassing the solution with N_2 had, at best, a negative influence on the yields (*Entries 1* and *2*).

Table 3. *Yields and Product Distribution upon Irradiation of* **1a**. For details, see *Exper. Part.*

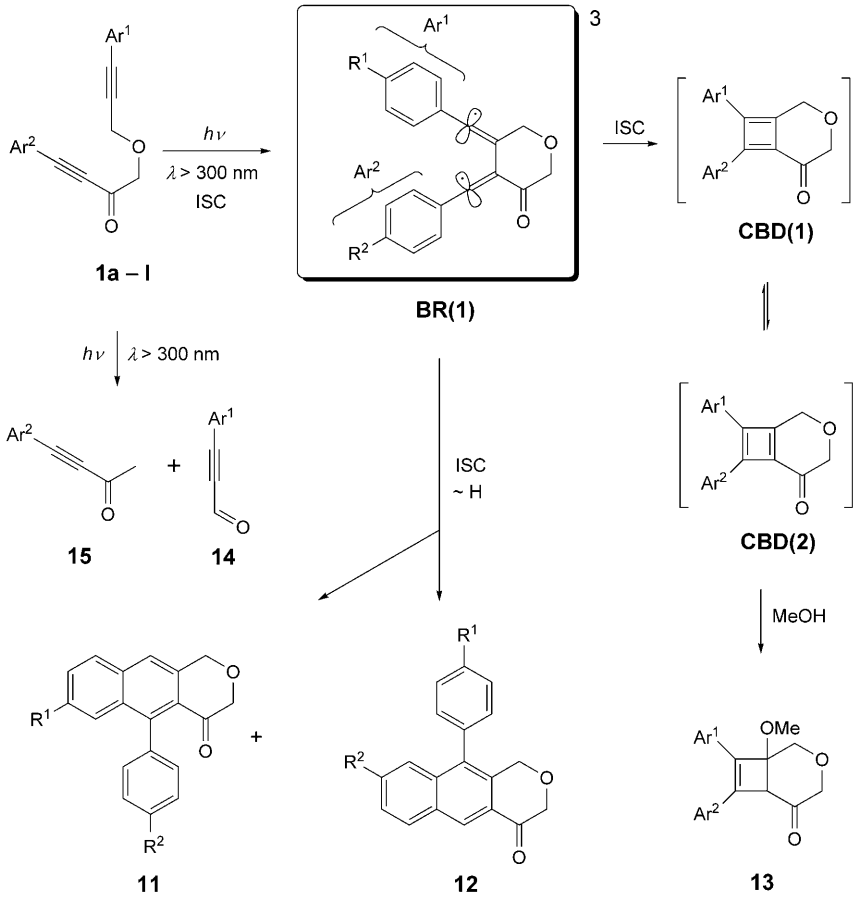
Entry	Solvent	**11a**+**12a** [%]	**11a**/**12a**	**13a** [%]	**14a**+**15a** [%]
1	MeOH[a])	44	1.3:1	20	12
2	MeOH[b])	41	1.3:1	18	9
3	*t*-BuOH	77	1.3:1	0	9
4	MeCN	29	1.3:1	0	11

[a]) Not degassed (aerobic). [b]) Degassed with N_2 (anaerobic).

Surprisingly, on irradiation of **1a** in MeOH, we obtained the 3-oxabicyclo[4.2.0]oct-7-en-5-one **13a** as a by-product. Presumably, this compound was formed by cyclization of the biradical **BR(1)** to the cyclobutadiene **CBD(1)**, competing with the PDDA reaction, and *Michael*-type addition of the solvent on the isomeric cyclobutadiene **CBD(2)**. The structure of **13a** was unambiguously established by X-ray crystal-structure analysis (*Fig. 1*).

It is known that the [2+2] cycloaddition of two acetylene moieties to an anti-aromatic cyclobutadiene ring may take place purely thermally from highly strained cyclic acetylenes [9], or between ethynylsulfones and ynamines [10], or mediated by Co complexes [11]. On the other hand, little is known about the photochemical realization of this reaction. In 1998, *Maier* and *Lautz* [12] reported the spectroscopic properties of

Scheme 4. *Photochemical Behavior of* **1a**–**l**



cyclobutadiene upon irradiation of the T-shaped acetylene dimer in a Xe matrix at 10 K.

The third kind of by-products, almost always formed in low yields, were the aldehydes **14** and the ynones **15** (*Scheme 4*). They presumably arose from a photochemically initiated intramolecular hydrogen migration, followed by a *Norrish* type-II cleavage [13] of the corresponding 1,4-biradical. At present, we cannot rule out that compounds **14** and **15** are formed by a photochemically initiated one-step *retro*-ene-like process [14], rather than in two steps *via* biradicals.

With the detailed irradiation results of compound **1a** at hand, we next investigated the congeners **1b**–**n**[2]). In almost all cases, we obtained the corresponding 1*H*-benzo[*g*]isochromen-4-(3*H*)-ones **11** and **12** in moderate-to-good yields, albeit often with low regioselectivity (*Table 4*). A considerable preference of **11** over **12** was achieved,

[2]) Even though *t*-BuOH was well-suited as solvent in the case of **12a**, the low solubility of some reactants **1** required the use of MeCN or MeOH.

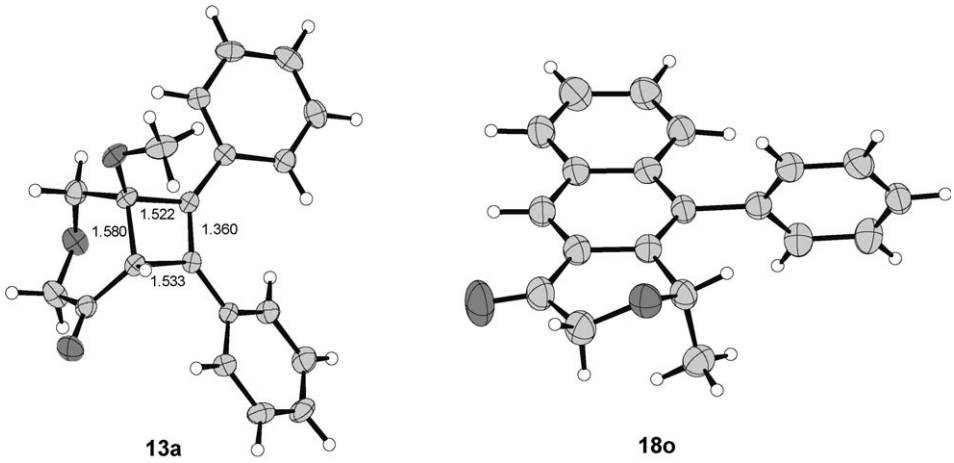


Fig. 1. *X-Ray crystal structures of* **13a** *and* **18o**. For details, see *Table 5*.

Table 4. *Yields and Product Distribution upon Irradiation of* **1b**–**n** *in Different Solvents.* For details, see *Exper. Part*.

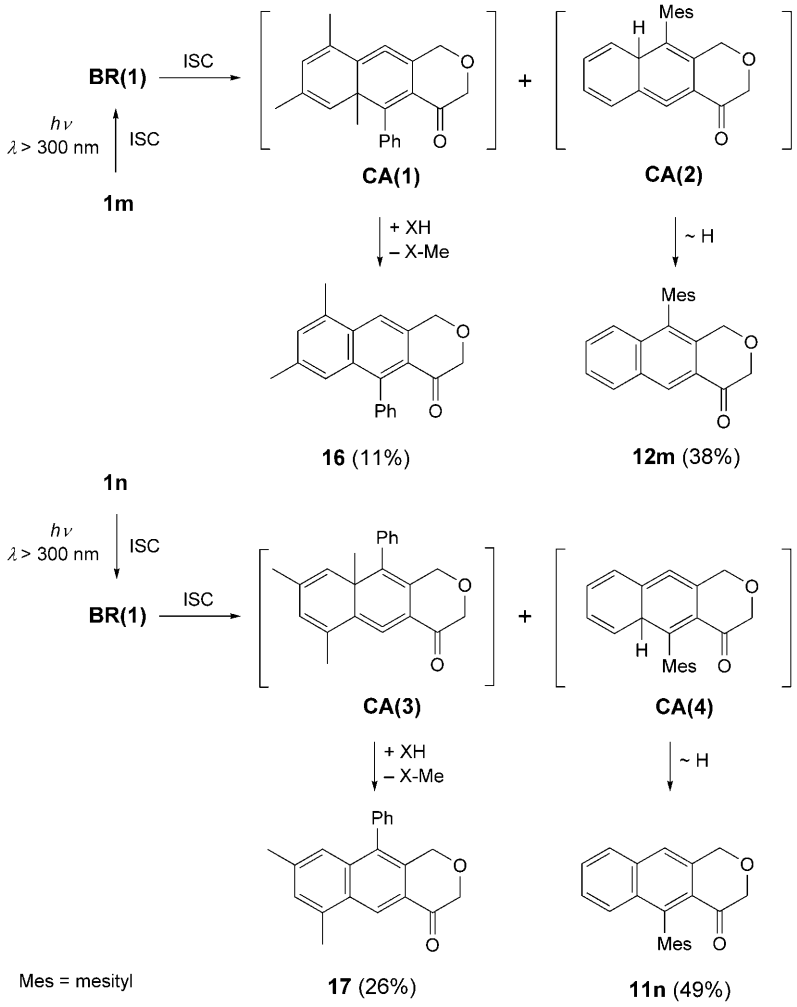
Substrate	Solvent	**11**+**12** [%]	**11**/**12**
1b	MeOH	52	1.2:1
1c	MeCN	65	1.6:1
1d	*t*-BuOH	45	1.6:1
1e	MeCN	42	1.7:1
1f	*t*-BuOH	73	1.1:1
1g	MeCN	76	1.2:1
1h	MeCN	0[a])	–
1i	MeCN	0[a])	–
1j	*t*-BuOH	46	6.6:1
1k	MeCN	54	1.2:1
1l	*t*-BuOH	34	2.4:1
1m[b])	*t*-BuOH	49	3.5:1
1n[c])	*t*-BuOH	75	1.9:1

[a]) Compounds **14** and **15** were formed exclusively. [b]) The data refer to **16**+**12m** (yield) and **16m**/**12** (ratio), resp. [c]) The data refer to **11n**+**17** (yield) and **11n**/**17** (ratio), resp. (see *Scheme 5*).

though, by introduction of a strongly electron-accepting methanesulfonyl (mesyl) group in 4-position of Ar^1 (*Table 4*; **1j**).

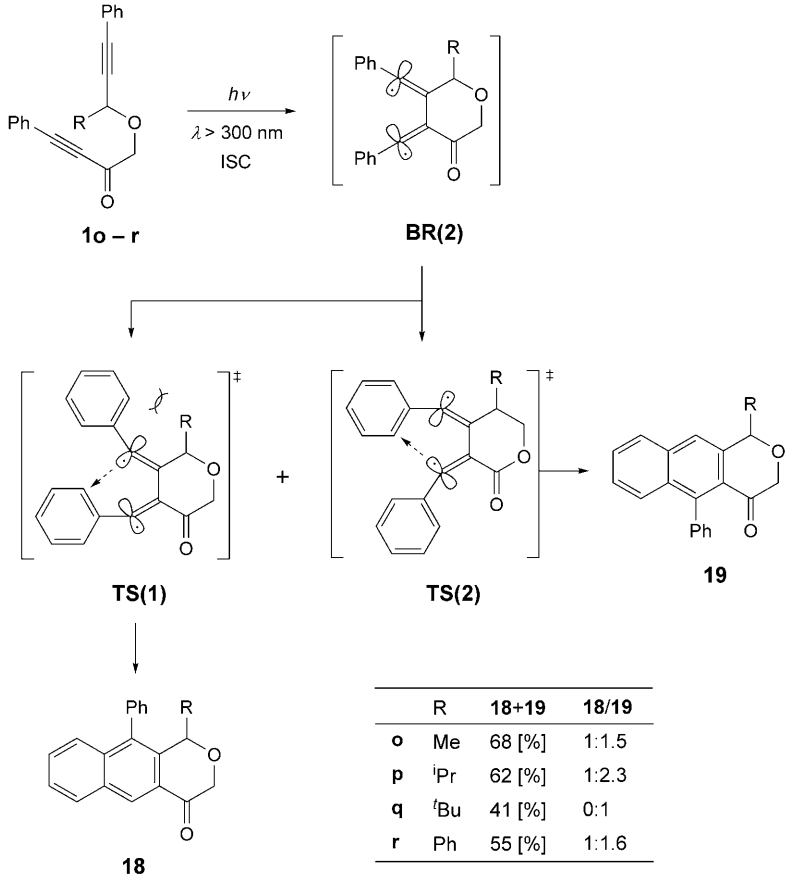
Compounds **1m,n**, bearing a mesityl group either as Ar^1 or as Ar^2, were investigated to find out whether Me groups in *ortho* position are able to suppress the attack of these positions and, consequently, the formation of the appropriate regioisomers. Although the naphthalenes **12m** (from **1m**) and **11n** (from **1n**) were formed as main products, we also isolated compounds **16** and **17**, originating from an attack of the mesityl group. In contrast to our previous observation [5], we found that the Me group in the attacked position does not undergo a 1,2-migration, but is obviously trapped by the solvent (XH) from cycloallenes **CA(1)** and **CA(3)**, respectively (*Scheme 5*).

Scheme 5. *Photochemical Behavior of* **1m** *and* **1n**



Compounds **1o**–**1r** are branched at the sp^3 C-atom of the propargyl moiety. Comparing the two transition states **TS(1)** and **TS(2)** formed from the biradical **BR(2)**, in the transition state **TS(1)** a steric hindrance between the upper phenyl group and the residue R may be expected, in contrast to **TS(2)** (*Scheme 6*). Consequently, we expected that products **19** are preferentially formed, depending on the size of the residue R. In fact, we observed that increasing steric demand of R increases the selectivity in favor of **19**. Whereas a Me group (**1l**) gave rise only to a slight excess of **19**, the ratio **18**/**19** increased to 1:2.3 in the case of an i-Pr group (**1p**), and the presence of a *t*-butyl group (**1q**) completely suppressed the formation of **18**, and only **19** was isolated (*Scheme 6*). Remarkably, a Ph group (**1r**) had only a marginal influence, suggesting

Scheme 6. *Photochemical Behavior of* **1o–r**



	R	18+19	18/19
o	Me	68 [%]	1:1.5
p	^{i}Pr	62 [%]	1:2.3
q	^{t}Bu	41 [%]	0:1
r	Ph	55 [%]	1:1.6

that π-stacking in **18** partly compensates the steric repulsion. An unambiguous structural assignment of **18o** was possible by X-ray crystal-structure analysis (*Fig. 1*).

2.3. *Mechanism of Photocyclization.* The mechanism of the PDDA reaction was previously discussed in detail [5]. Herein, only some special features of the new system will be elucidated[3]). For that, we have calculated the geometries and energies of the different species involved in the reaction of the parent compound **1a** by means of DFT methods (B3LYP/6-311++G**//B3LYP/6-31G*), and the results are summarized in *Scheme 7*.

After photochemical excitation of the ketones **1**, an intersystem crossing (ISC) takes place, as indicated by the observation that no reaction took place upon addition of a triplet quencher (isoprene). The efficient ISC can be rationalized by the conversion

[3]) More-detailed supporting information is available on request from the corresponding author (*P. W.*).

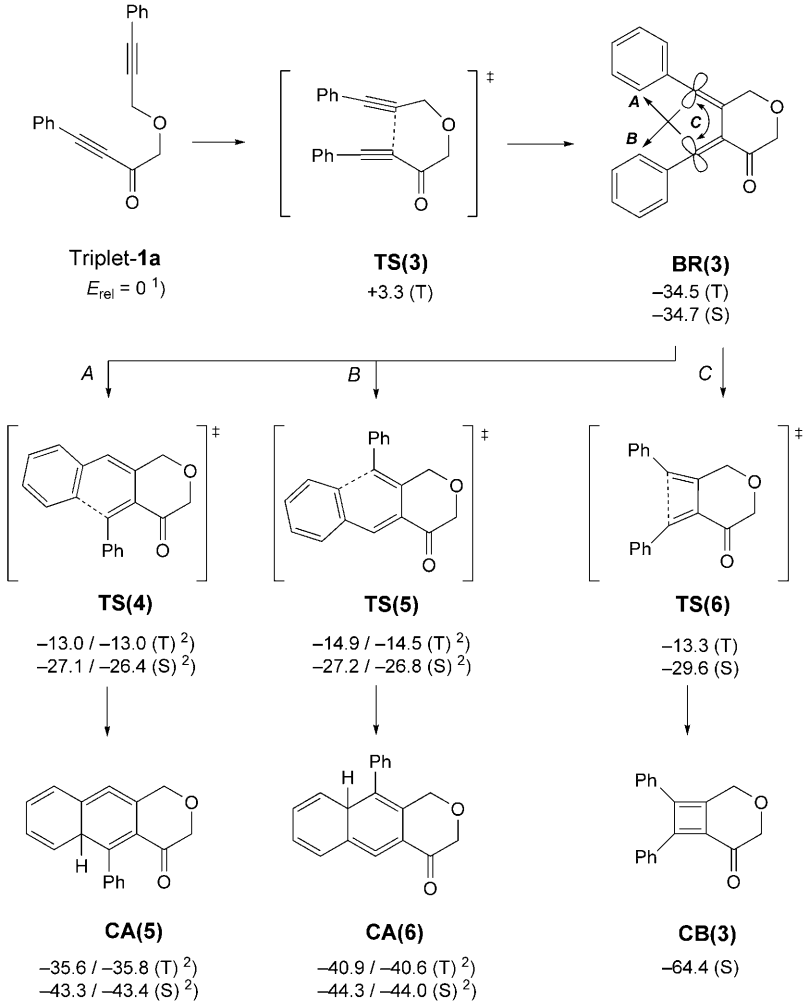
of the initially formed ^{1}(n-π^*) state into the ^{3}(π-π^*) state, which favors this process according to the *El-Sayed* rules [15].

The first C–C-bond formation between two acetylenic C-atoms proceeds *via* a very small activation barrier (3.3 kcal/mol), which is considerably smaller than in the previously investigated system [5]. Obviously, the longer chain between the acetylene units lowers this barrier owing to smaller ring strain in the transition state. The geometry of this transition state, **TS(3)**, is depicted in *Fig. 2*. The initial step, which is strongly exothermic ($\Delta E = -34.5$ kcal/mol), results in the formation of biradical **BR(3)** (*Scheme 7*). From this key intermediate, three processes may take place: the lower radical center attacks the upper phenyl ring (*A*); the upper radical center attacks the lower phenyl ring (*B*); or the radical centers recombine (*C*). Considering the energies of activation *via* the corresponding transition states **TS(4)**–**TS(6)** at the triplet (T) potential-energy surface (19.7–21.5 kcal/mol), it is expected that **BR(3)** is relatively long-lived and should be trapped by suitable reagents. For this purpose, we irradiated **1a** in the presence of various alkenes, but observed no influence upon the reaction course. Obviously, at the stage of **BR(3)** the system turns back to the singlet (S) state, which is very likely because both the singlet and triplet state of **BR(3)** are nearly degenerate ($\Delta E = 0.2$ kcal/mol). The singlet energies of activation *via* **TS(4)**–**TS(6)** (see *Fig. 2*) are much lower (5.1–8.0 kcal/mol), in accord with the failure of trapping **BR(3)**. The result that the energy of S-**TS(6)** is lower than that of S-**TS(4)** and S-**TS(5)** (suggesting that the cyclobutadienes should be the main products, with no PDDA reaction taking place) should not be overestimated because the calculated energies do not include the influence of the solvent.

The cycloallenes **CA(5)** and **CA(6)**, formed *via* **TS(4)** and **TS(5)**, are tautomers of the final PDDA products **11** and **12**, which could be formed from the cycloallenes by step-wise intramolecular hydrogen migration. Admittedly, our calculations indicate that this process would be characterized by a relatively high activation barrier (18–19 kcal/mol); therefore, we suppose that hydrogen migration is mediated by the solvent, as observed previously [5]. To corroborate this assumption, we irradiated **1a** in CH_3OD and found, indeed, deuterium incorporation. Finally, regarding the third reaction channel, *i.e.*, the formation of minor amounts of the cleavage products **14** and **15** (see *Scheme 4*), we could not yet obtain unequivocal information from calculations.

3. Conclusions. – We reported on the formation of a novel class of highly substituted arylnaphthalenes of the benzo[*g*]chromene type by the Photo-Dehydro-*Diels–Alder* (PDDA) reaction. We found that the regioselectivity of the final C–C bond-forming step at the stage of the initially formed biradicals **BR** can be improved both by strong electron withdrawing groups (**1j**) and by bulky substituents (**1q**) in the linker unit. In MeOH as solvent, we surprisingly obtained cyclobutenes **13** as by-products. The structure and energies of some relevant intermediates and transition states were calculated by means of DFT methods to obtain a detailed insight of the reaction mechanism. Obviously, the reaction starts from the triplet state giving buta-1,4-diene-1,4-diyl biradicals **BR(3)** (*Scheme 7*) as key intermediates. At this stage, the system turns back to the singlet state. Besides the expected PDDA reaction, an alternative reaction channel to

Scheme 7. *Transition States and Calculated Relative Energies of Intermediates*



1) Energies [kcal/mol] relative to triplet-**1a**.

2) Due to puckering of the pyrane ring, there are two conformers.

cyclobutadienes exists, which was unknown from previous systems [5]. Fortunately, this process can be suppressed by proper choice of the solvent.

We thank the *DFG* (We1850/5-1,3; *Heisenberg Fellowship* to *P. W.*) for financial support. *B. Ziemer* is acknowledged for solving the X-ray structures of **13a** and **18o**. We also thank the *Norddeutscher Verbund für Hoch- und Höchstleistungsrechnen* (*HLRN*) for generous allocation of computational capacity.

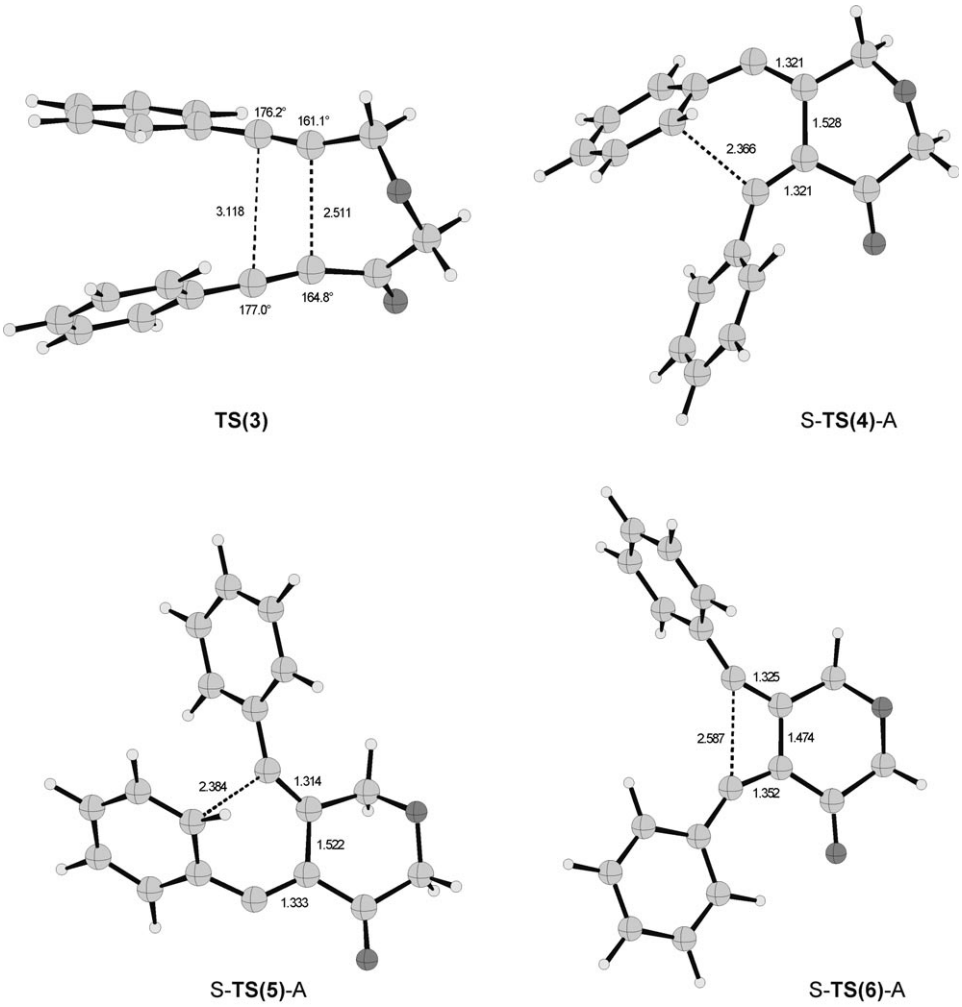


Fig. 2. *Calculated geometries of the transition states* **TS(3)**–**TS(6)**

Experimental Part

General. The following reagents were prepared according to literature procedures: *ethyl (prop-2-yn-1-yloxy)acetate* (**3**) [16], 1-chloro-4-ethynylbenzene [17], 1-ethynyl-4-methylbenzene [18], 1-ethynyl-4-fluorobenzene [17], 1-ethynylnaphthalene [19], 1-ethynyl-3,5-dimethylbenzene [20], 2-ethynyl-1,3,5-trimethylbenzene [21], 1-ethynyl-4-(trifluoromethyl)benzene [22], *4-phenylbut-3-yn-2-ol* (**9o**) [23], *4-methyl-1-phenylpent-1-yn-3-ol* (**9p**) [24], *4,4-dimethyl-1-phenylpent-1-yn-3-ol* (**9q**) [25], and *1,3-diphenylprop-2-yn-1-ol* (**9r**) [26]. THF was dried over Na metal in the presence of benzophenone as an indicator of dryness, and distilled under N_2 atmosphere at atmospheric pressure. CH_2Cl_2 was dried by heating to reflux over P_4O_{10}, and distilled at atmospheric pressure. All moisture-sensitive reagents were transferred *via* syringe under N_2 atmosphere. Moisture-sensitive reactions were carried out under N_2 atmosphere. Irradiations for photochemical reactions were performed with a 150-W high-pressure Hg-arc lamp (*Hanau*); anal. irradiations were performed with a 500-W high pressure Hg-arc lamp (*Osram HBO-500*) in a UV

cuvette (1×1 cm), using a *WG-295* (*Schott*) filter. Flash column chromatography (FC): silica gel (230–400 mesh; *Fluka*). Anal. TLC: silica-gel *60* F_{254} plates (*Merck*), detection under UV light. M.p.: *Büchi 530*; uncorrected. NMR Spectra: *Bruker DPX-300* apparatus; in $CDCl_3$ soln.; δ in ppm rel. to residual $CHCl_3$ (^{1}H: 7.26 ppm, ^{13}C: 77.0 ppm), *J* in Hz. IR: *Perkin-Elmer 881*; as KBr pastilles or (liquids and oils) on NaCl crystals as film; in cm^{-1}. EI-MS: *Hewlett-Packard 5995-A*, at 70 eV, 293–593 K; in *m*/*z* (rel.%). HR-EI-MS: *MSI Concept-1H*. Elemental analyses were carried out by the anal. laboratory of the institute of chemistry of the Humboldt-University Berlin.

General Procedure (*GP A*): Sonogashira *Coupling of* **3** *with Iodoarenes to Esters* **4**. The appropriate iodoarene (1 equiv.) and $[PdCl_2(PPh_3)_2]$ (5 mol-%) were suspended in anh. THF under N_2 atmosphere, and stirred for 5 min. CuI (10 mol-%), i-Pr_2NH (1.2 equiv.), and the appropriate ethyl 2-(prop-2-ynyloxy)-acetate **3** (1 equiv.) were added, and the course of the reaction was monitored by TLC. After completion of the reaction, the dark suspension was treated with 20% aq. tartaric acid soln., the aq. phase was separated and extracted with *t*-BuOMe (3×). The combined org. layers were washed with 20% aq. tartaric acid and H_2O, dried ($MgSO_4$), and concentrated under reduced pressure. Purification by FC (SiO_2; petroleum ether (PE)/AcOEt 100:4) afforded the corresponding pure products.

Ethyl [(3-Phenylprop-2-yn-1-yl)oxy]acetate (**4a**). From iodobenzene (2.15 g, 10.55 mmol) according to *GP A* in 30 min. Yield: 1.61 g (70%). Dark-yellow oil. IR (film): 1716, 1489, 1116, 1025, 758, 690. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.50–7.30 (*m*, 5 H); 4.55 (*s*, 2 H); 4.26 (*s*, 2 H); 4.24 (*q*, *J*=7.2, 2 H); 1.30 (*t*, *J*=7.2, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 169.6 (C_q); 131.4 (CH); 128.0 (CH); 122.0 (C_q); 86.9 (C_q); 83.6 (C_q); 63.9 (CH_2); 60.6 (CH_2); 58.7 (CH_2); 13.8 (Me). EI-MS: 218 (0.5, M^+), 173 (4), 145 (13), 131 (48), 115 (100), 101 (8).

Ethyl {[3-(4-Chlorophenyl)prop-2-yn-1-yl]oxy}acetate (**4b**). From 1-chloro-4-iodobenzene (1.68 g, 7.04 mmol) according to *GP A* in 60 min. Yield: 1.21 g (68%). Dark-yellow oil. IR (film): 1750, 1488, 1205, 1120, 829, 753. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.38 (*m*, 1 H); 7.37–7.36 (*m*, 1 H); 7.31–7.30 (*m*, 1 H); 7.29–7.28 (*m*, 1 H); 4.53 (*s*, 2 H); 4.26 (*q*, *J*=7.2, 2 H); 4.25 (*s*, 2 H); 1.30 (*t*, *J*=7.2, 3 H). ^{13}C-NMR (70 MHz, $CDCl_3$): 169.9 (C_q); 134.7 (C_q); 133.0 (CH); 128.7 (CH); 120.8 (C_q); 86.1 (C_q); 84.8 (C_q); 66.4 (CH_2); 61.1 (CH_2); 59.0 (CH_2); 14.2 (Me). EI-MS: 252 (0.5, M^+), 179 (16), 165 (72), 149 (100).

Ethyl {[3-(4-Methylphenyl)prop-2-yn-1-yl]oxy}acetate (**4c**). From 1-iodo-4-methylbenzene (1.53 g, 7.04 mmol) according to *GP A* in 60 min. Yield: 1.10 g (67%). Dark-yellow oil. IR (film): 1749, 1507, 1117, 1023, 816. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.35–7.32 (*m*, 2 H); 7.12 (*d*, *J*=7.9, 2 H); 4.53 (*s*, 2 H); 4.25 (*s*, 2 H); 4.24 (*q*, *J*=7.1, 2 H); 2.35 (*s*, 3 H); 1.30 (*t*, *J*=7.1, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 170.1 (C_q); 138.8 (C_q); 131.7 (CH); 129.0 (CH); 119.2 (C_q); 87.4 (C_q); 83.0 (C_q); 66.3 (CH_2); 61.0 (CH_2); 59.1 (CH_2); 21.5 (Me); 14.2 (Me).

Ethyl {[3-(4-Fluorophenyl)prop-2-yn-1-yl]oxy}acetate (**4d**). To a soln. of 1-fluoro-4-iodobenzene (**6a**; 3.00 g, 13.51 mmol) and propargyl alcohol (0.91 g, 16.22 mmol) in Et_3N (40 ml), $[PdCl_2(PPh_3)_2]$ (190 mg, 2 mol-%) was added. The mixture was stirred for 10 min, and CuI (26 mg, 1 mol%) was added. The resulting mixture was heated under N_2 atmosphere at 50°. After 3 h, the mixture was allowed to cool to r.t., and the ammonium salt was removed by filtration. The solvent was removed under reduced pressure, and the residue was purified by FC (SiO_2; PE/AcOEt 10:2) to afford pure *3-(4-fluorophenyl)prop-2-yn-1-ol* (**7a**) (2.03 g, quant.) as a yellow oil. Part of this material (1.50 g, 9.99 mmol) was dissolved in anh. THF (40 ml) at −78°. Then, BuLi (6.9 ml, 10.99 mmol; 1.6M soln. in hexane) was added, and the mixture was stirred for 45 min. Ethyl 2-bromoacetate (1.67 g, 9.99 mmol) in anh. THF (2 ml) was then added, and the resulting soln. was allowed to come to r.t., and stirred for a further 12 h. Quenching with sat. aq. NH_4Cl soln., aq. workup, and purification by FC (SiO_2; PE/AcOEt 10:1) afforded **4d** (1.33 g, 56%) as a yellow oil.

Data of **7a**. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.42–7.39 (*s*, 2 H); 7.02–6.97 (*s*, 2 H); 4.48 (*s*, 2 H); 2.02 (*s*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 162.5 (*d*, ^1J(F,C)=249.8; C_q); 133.6 (CH); 133.5 (CH); 118.6 (C_q); 115.7 (CH); 115.5 (CH); 86.9 (C_q); 84.6 (C_q); 51.5 (CH_2).

Data of **4d**. IR (film): 1749, 1599, 1218, 1120, 837. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.44–7.40 (*m*, 2 H); 7.03–6.87 (*m*, 2 H); 4.51 (*s*, 2 H); 4.23 (*s*, 2 H); 4.23 (*q*, *J*=7.2, 2 H); 1.29 (*t*, *J*=7.2, 3 H). ^{13}C-NMR (70 MHz, $CDCl_3$): 169.9 (C_q); 162.7 (*d*, ^1J(F,C)=250, C_q); 133.8 (CH); 133.7 (CH); 118.4 (C_q); 115.8 (CH); 115.7 (CH); 86.2 (C_q); 83.5 (CH); 66.4 (CH_2); 61.0 (CH_2); 59.0 (CH_2); 14.2 (Me). EI-MS: 236 (0.5, M^+), 163 (5), 133 (100). HR-EI-MS: 236.0813 (M^+, $C_{13}H_{13}FO_3^+$; calc. 236.0849).

Ethyl [(3-Naphthalen-1-ylprop-2-yn-1-yl)oxy]acetate (**4e**). From 1-iodonaphthalene (0.54 g, 2.11 mmol) according to *GP A* in 60 min. Yield: 0.26 g (46%). Dark-yellow oil. IR (film): 1748, 1395, 1019, 932, 800, 773. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.30 (*d*, *J* = 8.18, 1 H); 7.85 (*d*, *J* = 8.33, 2 H); 7.69 (*d*, ^3J = 7.13, 1 H); 7.60–7.50 (*m*, 2 H); 7.45–7.40 (*m*, 1 H); 4.71 (*s*, 2 H); 4.35 (*s*, 2 H); 4.26 (*q*, *J* = 7.15, 2 H); 1.30 (*t*, ^3J = 7.16, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 170.0 (C_q); 133.2 (C_q); 133.1 (C_q); 130.8 (CH); 129.1 (CH); 128.3 (CH); 126.9 (CH); 126.4 (CH); 126.0 (CH); 125.1 (CH); 119.9 (C_q); 88.6 (C_q); 85.4 (C_q); 66.4 (CH_2); 61.0 (CH_2); 59.2 (CH_2); 14.2 (Me). ESI-MS: 291 $[M+Na]^+$. HR-ESI-MS: 291.0992 ($C_{17}H_{16}O_3Na^+$, $[M+Na]^+$; calc. 291.0992).

Preparation of 3-(2,4,6-Trimethylphenyl)prop-2-yn-1-ol (**7b**) *by* Sonogashira *Coupling*. Iodomesitylene (**6b**; 2.00 g, 8.13 mmol), $[PdCl_2(PPh_3)_2]$ (0.57 g, 0.81 mmol), and Ph_3P (0.43 g, 1.63 mmol) were dissolved in Et_2NH under N_2 atmosphere and heated for 30 min at 45°. Then, CuI (0.30 g, 1.63 mmol) and popargylic alcohol (0.70 g, 12.19 mmol) were added, and the resulting suspension was stirred at 45°. The course of the reaction was monitored by TLC. After completion of the reaction, the suspension was diluted with *t*-BuOMe, washed with H_2O (3×) and brine (1×). The org. layer was dried ($MgSO_4$) and concentrated *in vacuo*. Purification by FC (SiO_2; PE/AcOEt 10 : 1) afforded the title product **7b**. Yield: 0.69 g (49%). Brownish solid. M.p. 53°. IR (KBr): 1475, 1349, 1016, 851, 726, 667. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.85 (*s*, 2 H); 4.57 (*s*, 2 H); 2.39 (*s*, 6 H); 2.28 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 140.3 (C_q); 137.9 (C_q); 127.6 (arom. CH); 119.2 (C_q); 94.7 (C_q); 83.4 (C_q); 51.9 (CH_2); 21.3 (Me); 21.0 (Me). EI-MS: 174 (97), 159 (100), 141 (32), 128 (41), 115 (38), 105 (11), 91 (21), 77 (16). HR-EI-MS: 174.1045 (M^+, $C_{12}H_{14}O^+$; calc. 174.1045).

General Procedure (*GP B*): *Conversion of Acetates* **4** *to the* Weinreb *Amides* **5**. The appropriate acetate **4** (1 equiv.) was dissolved in MeOH, and the corresponding portion of 1N KOH soln. (1 equiv.) in MeOH was added. The resulting soln. was stirred for 12 h, the solvent was removed under reduced pressure, and the residue was poured into a mixture of sat. $NaHCO_3$ soln. and *t*-BuOMe. The aq. phase was acidified with half-conc. HCl to pH 1, and then extracted with *t*-BuOMe (3×). The org. layer was dried ($MgSO_4$) and concentrated *in vacuo*. The resulting residue was dissolved in anh. CH_2Cl_2 under N_2 atmosphere, and TBTU (= 2-(1*H*-benzotriazol-1-yl)-1,1,3,3-tetramethyluronium tetrafluoroborate; 1 equiv.) was added. To this suspension, a soln. of MeO(Me)NH·HCl (1.3 equiv.) and i-Pr_2NEt (2.3 equiv.) in anh. CH_2Cl_2 was added dropwise. The resulting soln. was stirred for a further 12 h. Then *t*-BuOMe and aq. 20% tartaric acid soln. were added, the layers were separated, and the aq. phase was extracted with *t*-BuOMe (3×). The combined org. layers were washed with sat. $NaHCO_3$ soln. (1×) and H_2O, dried ($MgSO_4$), concentrated *in vacuo*, and purified by FC (SiO_2; CH_2Cl_2/MeOH 100:1) to afford the corresponding amide **5**.

N-*Methyl*-N-*methoxy-2-[(3-phenylprop-2-yn-1-yl)oxy]acetamide* (**5a**). From **4a** (1.42 g, 6.51 mmol) according to *GP B*. Yield: 1.50 g (99%). Yellow oil. IR (film): 1681, 1488, 1135, 758, 692. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.44–7.41 (*m*, 2 H); 7.31–7.24 (*m*, 3 H); 4.57 (*s*, 2 H); 4.44 (*s*, 2 H); 3.68 (*s*, 3 H); 3.18 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 131.7 (CH_2); 128.5 (CH_2); 128.3 (CH_2); 122.4 (C_q); 86.9 (C_q); 84.3 (C_q); 66.1 (CH_2); 61.4 (Me); 59.0 (Me). EI-MS: 234 (0.2, $[M+H]^+$), 202 (2), 173 (7), 115 (100). HR-EI-MS: 233.1051 (M^+, $C_{17}H_{14}O_3^+$; calc. 233.1052).

2-{[3-(4-Chlorophenyl)prop-2-yn-1-yl]oxy}-N-*methyl*-N-*methoxyacetamide* (**5b**). From acetate **4b** (1.20 g, 4.75 mmol) according to *GP B*. Yield: 1.26 g (99%). Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.35 (*m*, 2 H); 7.31–7.28 (*m*, 2 H); 4.56 (*s*, 2 H); 4.44 (*s*, 2 H); 3.71 (*s*, 3 H); 3.21 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 134.6 (C_q); 132.9 (CH); 128.6 (CH); 120.9 (C_q); 85.8 (C_q); 85.4 (C_q); 66.3 (CH_2); 66.2 (CH_2); 61.4 (CH_3); 59.0 (Me).

N-*Methyl*-N-*methoxy-2-{[3-(4-methylphenyl)prop-2-yn-1-yl]oxy}acetamide* (**5c**). From acetate **4c** (1.10 g, 4.84 mmol) according to *GP B*. Yield: 0.96 g (87%). Yellow oil. IR (KBr): 1688, 1509, 1428, 1133, 998, 818. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.33 (*d*, *J* = 8.1, 2 H); 7.11 (*d*, *J* = 7.9, 2 H); 4.56 (*s*, 2 H); 4.45 (*s*, 2 H); 3.70 (*s*, 3 H); 3.20 (*s*, 3 H); 2.34 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 138.7 (C_q); 131.6 (CH); 129.0 (CH); 119.4 (C_q); 87.1 (C_q); 83.6 (C_q); 66.8 (CH_2); 66.1 (CH_2); 61.4 (Me); 59.0 (Me); 38.7 (Me); 21.5 (Me). ESI-MS: 248 ($[M+H]^+$). HR-ESI-MS: 270.1100 ($[M+Na]^+$, $C_{14}H_{17}NaNO_3^+$; calc. 270.1101).

2-{[3-(4-Fluorophenyl)prop-2-yn-1-yl]oxy}-N-*methyl*-N-*methoxyacetamide* (**5d**). From acetate **4d** (1.26 g, 5.33 mmol) according to *GP B*. Yield: 1.25 g (93%). Yellow oil. IR (film): 1675, 1505, 1219,

838. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.44–7.40 (*m*, 2 H); 7.03–7.00 (*m*, 2 H); 4.54 (*s*, 2 H); 4.43 (*s*, 2 H); 3.70 (*s*, 3 H); 3.20 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 162.7 (*d*, ^1J(F,C) = 249.8, C_q); 133.7 (*d*, ^3J = 8.3, CH); 118.6 (C_q); 115.6 (*d*, ^2J = 22.8, CH); 115.5 (CH); 85.8 (C_q); 84.1 (C_q); 66.2 (CH_2); 61.4 (Me); 59.0 (CH_2); 38.6 (Me). ESI-MS: 252 ($[M+H]^+$). HR-ESI-MS: 252.1031 ($[M+H]^+$, $C_{13}H_{15}FNO_3^+$; calc. 252.1030).

N-*Methyl*-N-*methoxy-2-[(3-naphthalen-1-ylprop-2-yn-1-yl)oxy]acetamide* (**5e**). From acetate **4e** (243 mg, 0.906 mmol) according to *GP B*. Yield: 251 mg (98%). Brown oil. IR (film): 1715, 1459, 1199, 990, 801, 774. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.34–8.29 (*m*, 1 H); 7.85–7.81 (*m*, 2 H); 7.69–7.66 (*m*, 1 H); 7.58–7.38 (*m*, 3 H); 4.72 (*s*, 2 H); 4.54 (*s*, 2 H); 3.68 (*s*, 3 H); 3.20 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 133.3 (C_q); 133.0 (C_q); 130.7 (CH); 129.0 (CH); 128.3 (CH); 126.8 (CH); 126.4 (CH); 126.0 (CH); 125.1 (CH); 120.1 (C_q); 89.2 (C_q); 85.1 (C_q); 66.2 (CH_2); 61.4 (Me); 59.2 (CH_2); 38.6 (Me). ESI-MS: 284 ($[M+H]^+$). HR-ESI-MS: 306.1099 ($[M+Na]^+$, $C_{17}H_{17}NNaO_3^+$; calc. 306.1101).

N-*Methyl*-N-*methoxy-2-{[3-(2,4,6-trimethylphenyl)prop-2-yn-1-yl]oxy}acetamide* (**5f**). To a soln. of **7b** (500 mg, 2.87 mmol) in anh. THF at $-78°$ under N_2 atmosphere, BuLi (2.0 ml, 6.31 mmol; 1.6M soln. in hexane) was added, and the resulting soln. was stirred for 15 min. Then, the soln. was transferred *via* cannula to a soln. of 2-bromoacetic acid (399 mg, 2.87 mmol) and BuLi (2.0 ml, 6.31 mmol) in anh. THF at $-78°$ under N_2 atmosphere. The mixture was allowed to come to r.t., and stirred for 24 h. The reaction was quenched with sat. aq. $NaHCO_3$ soln., the layers were separated, and the aq. phase was extracted with *t*-BuOMe (3×). Then, the aq. layer was acidified with half-conc. HCl to pH 1, and extracted with *t*-BuOMe (3×). The combined org. layers were dried ($MgSO_4$) and concentrated *in vacuo* to afford crude *{[3-(2,4,6-trimethylphenyl)prop-2-yn-1-yl]oxy}acetic acid* (294 mg, 44%). Part of this intermediate (274 mg, 1.18 mmol) was dissolved in anh. CH_2Cl_2 under N_2 atmosphere, and TBTU (379 mg, 1.18 mmol) was added. To the resulting suspension, a soln. of MeO(Me)NH·HCl (150 mg, 1.53 mmol) and i-Pr_2NEt (350 mg, 2.71 mmol) in anh. CH_2Cl_2 was added dropwise. The resulting soln. was then stirred for a further 15 h. *t*-BuOMe and 20% aq. tartaric acid soln. were added, the layers were separated, and the aq. phase was extracted with *t*-BuOMe (3×). The combined org. phases were washed once each with sat. $NaHCO_3$ soln. and H_2O, dried ($MgSO_4$), concentrated under reduced pressure, and purified by FC (SiO_2; CH_2Cl_2/MeOH 100:1) to afford **5f**. Yield: 181 mg (56%).

Data of {[3-(2,4,6-Trimethylphenyl)prop-2-yn-1-yl]oxy}acetic Acid. IR (KBr): 1738, 1200, 1103, 910, 847, 676. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.86 (*s*, 2 H); 4.64 (*s*, 2 H); 4.35 (*s*, 2 H); 2.38 (*s*, 6 H); 2.28 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 147.9 (C_q); 140.4 (C_q); 138.2 (C_q); 127.6 (CH); 118.8 (C_q); 90.5 (C_q); 85.6 (C_q); 65.5 (CH_2); 59.4 (CH_2); 21.3 (Me); 20.9 (Me). EI-MS: 232 (49), 173 (62), 157 (100), 145 (31), 128 (43), 115 (46), 105 (12), 91 (12), 77 (15). HR-EI-MS: 232.1099 (M^+, $C_{14}H_{16}O_3^+$; calc. 232.1099).

Data of **5f**. IR (film): 1695, 1457, 1133, 1085, 998, 852. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.84 (*s*, 2 H); 4.64 (*s*, 2 H); 4.48 (*s*, 2 H); 3.68 (*s*, 3 H); 3.19 (*s*, 3 H); 2.37 (*s*, 6 H); 2.26 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 140.3 (C_q); 138.0 (C_q); 127.5 (CH); 119.2 (C_q); 91.6 (C_q); 84.8 (C_q); 65.9 (CH_2); 61.4 (Me); 61.2 (Me); 59.2 (CH_2); 21.3 (Me); 21.0 (Me). EI-MS: 275 ($[M+H]^+$). HR-ESI-MS: 276.1601 ($[M+H]^+$, $C_{16}H_{22}NO_3^+$; calc. 276.1600).

General Procedure (*GP C*) *for the Preparation of Acids* **10** *by Alkylation of Propargyl Alcohols* **9**. A solution of the appropriate alcohol **9** (1 equiv.) in anh. THF was dropped slowly under N_2 atmosphere to a suspension of NaH (60% in mineral oil; 2 equiv.) in THF, and the resulting suspension was stirred until the evolution of H_2 ceased. A soln. of 2-bromoacetic acid (1 equiv.) in anh. THF was added, and the resulting suspension was stirred until TLC indicated complete disappearance of the alcohol. Then, H_2O was added, and the mixture was concentrated under reduced pressure. The residue was taken up in H_2O and washed with Et_2O (3×). The aq. phase was acidified with half-conc. HCl to pH 1, and extracted with AcOEt (3×). The combined org. layers were dried (Na_2SO_4) and concentrated *in vacuo*.

[(1-Methyl-3-phenylprop-2-yn-1-yl)oxy]acetic Acid (**10o**). From **9o** (2.30 g, 15.73 mmol) according to *GP C*. Yield: 2.51 g (78%). Yellow oil. IR (film): 1734, 1728, 1727, 1117, 757. ^{1}H-NMR (300 MHz, $CDCl_3$): 11.20 (*s*, 1 H); 7.32–7.18 (*m*, 5 H); 4.50 (*q*, *J* = 6.4, 1 H); 4.44 (*d*, *J* = 17, 1 H); 4.26 (*d*, *J* = 17, 1 H); 1.47 (*d*, *J* = 6.4, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 175.7 (C_q); 131.5 (CH); 128.4 (CH); 128.1 (CH); 121.9 (C_q); 87.1 (C_q); 86.1 (C_q); 66.3 (CH); 64.8 (CH_2); 21.7 (Me). EI-MS: 203 (1.4, M^+), 162 (11), 145 (42), 128 (100), 77 (29). Anal. calc. for $C_{12}H_{12}O_3$: C 70.57, H 5.92; found: C 70.18, H 5.91.

{[1-(1-Methylethyl)-3-phenylprop-2-yn-1-yl]oxy}acetic Acid (**10p**). From **9p** (1.94 g, 11.13 mmol) according to *GP C*. Yield: 1.68 g (65%). Colorless solid. M.p. 58°. IR (KBr): 1745, 1734, 1727, 1247,

1126, 758. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.96 (*s*, 1 H); 7.34–7.20 (*m*, 5 H); 4.30 (*m*, 2 H); 4.20 (*d*, *J* = 6.0, 1 H); 2.00 (*sext.*, *J* = 6.8, 1 H); 0.99 (*m*, 6 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 175.8 (C_q); 131.6 (CH); 128.4 (CH); 128.2 (CH); 122.3 (C_q); 87.6 (C_q); 85.3 (C_q); 76.1 (CH); 65.1 (CH_2); 33.0 (CH); 18.5 (Me); 17.7 (Me). EI-MS: 231 (1.7, M^+), 189.1 (42), 173 (15), 131 (100), 77 (46). Anal. calc. for $C_{14}H_{16}O_3$: C 72.39, H 6.94; found: C 71.98, H 7.04.

{[1-(1,1-Dimethylethyl)-3-phenylprop-2-yn-1-yl]oxy}acetic Acid (**10q**). From **9q** (1,16 g, 6.16 mmol) according to *GP C*. Yield: 1.05 g (69%). Colorless solid. M.p. 75°. IR (KBr) 1738, 1734, 1122, 760. ^{1}H-NMR (300 MHz, $CDCl_3$): 10.45 (*s*, 1 H); 7.38–7.17 (*m*, 5 H); 4.29 (*m*, 2 H); 4.06 (*s*, 1 H); 1.02 (*s*, 9 H). ^{13}C-NMR (70 MHz, $CDCl_3$): 175.9 (C_q); 131.7 (CH); 128.5 (CH); 128.3 (CH); 122.4 (C_q); 87.7 (C_q); 85.5 (C_q); 79.5 (CH); 65.6 (CH_2); 35.8 (C_q); 25.7 (Me). EI-MS: 245 (0.25, M^+), 189 (59), 131 (100), 77 (26). Anal. calc. for $C_{15}H_{18}O_3$: C 73.15, H 7.37; found: C 73.67, H 6.91.

[(1,3-Diphenylprop-2-yn-1-yl)oxy]acetic Acid (**10r**). To a soln. of **9r** (5.00 g, 24.01 mmol) in anh. THF under N_2 atmosphere at −78° was added dropwise BuLi (16.5 ml, 26.41 mmol; 1.6M soln. in hexane), and the resulting green soln. was stirred for 10 min. Then, ethyl 2-bromoacetate (4.01 g, 24.01 mmol) was added, whereupon the color turned to yellow. The soln. was allowed to warm to r. t., stirred for a further 12 h, quenched with sat. aq. NH_4Cl soln.n and subjected to regular aq. workup to afford *ethyl [(1,3-diphenylprop-2-yn-1-yl)oxy]acetate* (4.50 g, 64%) as an orange oil. A portion of the latter (2.00 g, 6.80 mmol) in MeOH (6.8 ml) was treated dropwise with a 1M KOH soln. in MeOH. The resulting soln. was stirred for 16 h. The solvent was removed under reduced pressure, and the residue was taken up in sat. aq. $NaHCO_3$ soln., and extracted with *t*-BuOMe (2×). The aq. phase was acidified with half-conc. HCl to pH 1, and extracted with *t*-BuOMe. The combined org. layers were dried ($MgSO_4$) and concentrated *in vacuo* to afforded **10r** as a yellow solid (1.38 g, 77%).

Data of Ethyl [(1,3-diphenylprop-2-yn-1-yl)oxy]acetate. IR (film): 1726, 1287, 1210, 1176, 934, 708. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.68–7.65 (*m*, 2 H); 7.52–7.48 (*m*, 2 H); 7.44–7.33 (*m*, 6 H); 5.71 (*s*, 1 H); 4.42 (*d*, *J* = 16.4, 1 H); 4.24 (*q*, *J* = 7.2, 2 H); 4.23 (*d*, *J* = 16.4, 1 H); 1.30 (*t*, *J* = 7.2, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 170.2 (C_q); 137.6 (C_q); 131.8 (CH); 128.7 (CH); 128.6 (CH); 128.4 (CH); 128.3 (CH); 128.2 (CH); 127.8 (CH); 122.2 (CH); 88.6 (C_q); 85.5 (C_q); 72.0 (CH); 64.8 (CH_2); 61.0 (CH_2); 14.1 (Me). EI-MS: 294 (0.75, M^+), 191 (20), 163 (4), 122 (6), 105 (100), 77 (40). HR-EI-MS: 294.1256 (M^+, $C_{19}H_{18}O_3^+$; calc. 294.1256).

Data of **10r**. M.p. 32°. IR (KBr): 1730, 1450, 1244, 1112, 909, 755, 691. ^{1}H-NMR (300 MHz, $CDCl_3$): 9.76 (*s*, 1 H); 7.69–7.65 (*m*, 1 H); 7.53–7.34 (*m*, 9 H); 5.72 (*s*, 1 H); 4.48 (*d*, *J* = 17.0, 1 H); 4.32 (*d*, *J* = 17.0, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 175.5 (C_q); 137.2 (C_q); 133.8 (CH); 131.8 (CH); 130.1 (CH); 128.9 (CH); 128.8 (CH); 128.6 (CH); 128.5 (CH); 128.4 (CH); 128.3 (CH); 127.8 (CH); 121.9 (C_q); 89.0 (C_q); 85.0 (C_q); 72.2 (CH_2); 64.1 (CH_2). EI-MS: 266 (1.8, M^+), 207 (73), 191 (64), 122 (54), 105 (100), 77 (87). HR-EI-MS: 266.0941 (M^+, $C_{17}H_{14}O_3^+$; calc. 266.0943).

General Procedure (*GP D*) *for the Preparation of* Weinreb *Amides* (**WA**) *by Conversion of the Acids* **10**. To a soln. of **10** (1 equiv.) in anh. CH_2Cl_2 was added under N_2 atmosphere TBTU (1.05 equiv.), and the resulting suspension was stirred for 30 min. In a separate flask, i-Pr_2NEt (3.0 equiv.) and MeO-(Me)NH·HCl (1.0 equiv.) were dissolved in anh. CH_2Cl_2, and this soln. was transferred *via* cannula to the first flask. The resulting mixture was stirred for 2 h. Then, the mixture was quenched with 20% aq. tartaric acid soln., the layers were separated, and the aq. phase was extracted with Et_2O (2×). The combined org. layers were washed once each with H_2O and sat. $NaHCO_3$ soln. The org. layer was dried (Na_2SO_4) and concentrated under reduced pressure to afford the anal. pure **WA** compounds.

N-*Methyl*-N-*methoxy-2-[(1-methyl-3-phenylprop-2-yn-1-yl)oxy]acetamide* (**WAo**). From **10o** (2.05 g, 10.04 mmol) according to *GP D*. Yield: 2.11 g (85%). IR (KBr): 1688, 1684, 1677, 1091, 759. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.21 (*m*, 5 H); 4.57 (*q*, *J* = 6.4, 1 H); 4.41 (*s*, 2 H); 3.61 (*s*, 3 H); 3.11 (*s*, 3 H); 1.52 (*d*, *J* = 6.4, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 131.5 (CH); 128.3 (CH); 128.2 (CH); 122.4 (C_q); 88.2 (C_q); 85.2 (C_q); 65.9 (CH); 65.3 (CH_2); 61.3 (Me); 32.2 (Me); 21.9 (Me). EI-MS: 248 (0.14, $[M+1]^+$), 129 (100), 77 (17). Anal. calc. for $C_{14}H_{17}NO_3$: C 68.00, H 6.93, N 5.66; found: C 67.64, H 6.96, N 5.33.

N-*Methyl-2-{[1-(1-methylethyl)-3-phenylprop-2-yn-1-yl]oxy}*-N-*methoxyacetamide* (**WAp**). From **10p** (1.50 g, 6.46 mmol) according to *GP D*. Yield: 1.43 g (81%). IR (film): 1688, 1489, 1132, 1084. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.47–7.32 (*m*, 5 H); 4.53 (*s*, 2 H); 4.39 (*d*, *J* = 5.7, 1 H); 3.71 (*s*, 3 H); 3.21 (*s*,

3 H); 2.16 (*sext.*, $J=5.6$, 1 H); 1.13 (*m*, 6 H). ^{13}C-NMR (70 MHz, $CDCl_3$): 165.3 (C_q); 131.3 (CH); 128.0 (CH); 127.9 (CH); 122.3 (C_q); 86.6 (C_q); 86.1 (C_q); 75.2 (CH); 65.1 (CH_2); 61.0 (Me); 38.1 (CH); 32.8 (Me); 18.3 (Me); 17.4 (Me). EI-MS: 215 (14, $[M-MeO-MeN]^+$), 129 (41), 77 (23). Anal. calc. for $C_{16}H_{21}NO_3$: C 69.79, H 7.69, N 5.09; found: C 69.23, H 7.17, N 5.33.

2-{[1-(1,1-Dimethylethyl)-3-phenylprop-2-yn-1-yl]oxy}-N-*methyl*-N-*methoxyacetamide* (**WAq**). From **10q** (0.95 g, 3.86 mmol) according to *GP D*. Yield: 0.93 g (83%). IR (film): 1688, 1489, 1442, 1085, 758. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.39–7.19 (*m*, 5 H); 4.44 (*s*, 2 H); 4.16 (*s*, 1 H); 3.62 (*s*, 3 H); 3.12 (*s*, 3 H); 1.04 (*s*, 9 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 131.7 (CH); 128.3 (CH); 128.2 (CH); 122.8 (C_q); 86.9 (C_q); 86.7 (C_q); 78.8 (CH); 65.6 (CH_2); 61.4 (Me); 35.8 (C_q); 32.1 (Me); 25.9 (Me). EI-MS: 290 (0.1, $[M+1]^+$), 232 (9), 171 (11), 77 (20). Anal. calc. for $C_{17}H_{23}NO_3$: C 70.56, H 8.01, N 4.84; found: C 70.48, H 7.86, N 5.02.

2-[(1,3-Diphenylprop-2-yn-1-yl)oxy]-N-*methyl*-N-*methoxyacetamide* (**WAr**). From **10r** (0.47 g, 1.77 mmol) according to *GP D*. Yield: 0.44 g (80%). IR (film): 1695, 1079, 989, 758, 694. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.71–7.65 (*m*, 2 H); 7.51–7.48 (*m*, 2 H); 7.43–7.30 (*m*, 6 H); 5.76 (*s*, 1 H); 4.62 (*d*, $J=15.8$, 1 H); 4.43 (*d*, $J=15.8$, 1 H); 3.66 (*s*, 3 H); 3.20 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 137.9 (C_q); 131.8 (CH); 128.61 (CH); 128.60 (CH); 128.5 (CH); 128.3 (CH); 128.1 (CH); 128.0 (CH); 127.8 (CH); 122.4 (C_q); 88.2 (C_q); 86.1 (C_q); 71.8 (CH); 64.7 (CH_2); 61.4 (Me); 38.6 (Me). EI-MS: 278 (8, $[M-MeO]^+$), 249 (28, $[M-MeO-MeN]^+$), 221 (6), 191 (100). ESI-MS: 310 ($[M+H]^+$), 327 ($[M+NH_4]^+$), 332 ($[M+Na]^+$), 641 ($[2M+Na]^+$). HR-ESI-MS: 332.1268 ($[M+Na]^+$, $C_{19}H_{19}NNaO_3^+$; calc. 332.1262).

General Procedure (*GP E*) *for the Preparation of Compounds* **1** *from the* Weinreb *Amides* **5** *and* **WA**, *resp*. To a soln. of the appropriate arylacetylene (2.5 equiv.) in anh. THF was added BuLi (2.1 equiv, 1.6M soln. in hexane) at $-78°$ under N_2 atmosphere, and the mixture was stirred for 15 min. The resulting soln. was transferred *via* cannula to a soln. of the appropriate amide **5** (1 equiv.) in anh. THF under N_2 atmosphere at $-78°$, and the resulting soln. was stirred for 1 h at this temp. Then, the mixture was allowed to come to r.t., and stirred for a further 2 h. The soln. was poured into a vigorously stirred mixture of ice, 1M aq. KH_2PO_4 soln., and *t*-BuOMe. The layers were separated, and the aq. phase was extracted with *t*-BuOMe (3×). The combined org. phases were washed once each with 1M aq. KH_2PO_4 soln. and brine, and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford crude **1**, which was purified by FC (SiO_2; PE/AcOEt 20:1).

4-Phenyl-1-[(3-phenylprop-2-yn-1-yl)oxy]but-3-yn-2-one (**1a**). From **5a** (0.50 g, 2.14 mmol), ethynylbenzene (0.55 g, 5.36 mmol), and BuLi (4.50 mmol) according to *GP E*. Yield: 0.46 g (79%). IR (film): 1683, 1488, 1065, 903, 735. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.62–7.58 (*m*, 2 H); 7.50–7.29 (*m*, 8 H); 4.59 (*s*, 2 H); 4.50 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.4 (C_q); 133.2 (CH); 131.8 (CH); 131.1 (CH); 128.7 (CH); 128.3 (CH); 122.2 (C_q); 119.5 (C_q); 93.9 (C_q); 87.5 (C_q); 85.6 (C_q); 83.8 (C_q); 74.9 (CH_2); 59.3 (CH_2). EI-MS: 274 (3, M^+), 144 (100), 130 (35), 101 (25). HR-EI-MS: 274.0976 (M^+, $C_{19}H_{14}O_2^+$; calc. 274.0994).

1-{[3-(4-Chlorophenyl)prop-2-yn-1-yl]oxy}-4-phenylbut-3-yn-2-one (**1b**). From **5b** (0.30 g, 1.12 mmol), ethynylbenzene (0.29 g, 2.80 mmol), and BuLi (2.35 mmol) according to *GP E*. Yield: 0.21 g (62%). M.p. 66°. IR (KBr): 1676, 1488, 1069, 820, 755. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.54–7.51 (*m*, 2 H); 7.41–7.39 (*m*, 1 H); 7.35–7.30 (*m*, 4 H); 4.51 (*s*, 2 H); 4.42 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.3 (C_q); 134.8 (C_q); 133.2 (CH); 133.0 (CH); 131.1 (CH); 128.7 (CH); 120.7 (C_q); 119.4 (C_q); 94.0 (C_q); 68.4 (C_q); 85.6 (C_q); 84.8 (C_q); 75.0 (CH_2); 59.3 (CH_2). EI-MS: 308 (0.5, M^+), 231 (0.3), 215 (14), 165 (0.3), 144 (40), 129 (100). HR-EI-MS: 308.0605 (M^+, $C_{19}H_{13}ClO_2^+$; calc. 308.0604). Anal. calc. for $C_{19}H_{13}ClO_2$: C 73.91, H 4.24, Cl 11.48; found: C 73.73, H 4.23, Cl 11.10.

1-{[3-(4-Methylphenyl)prop-2-yn-1-yl]oxy}-4-phenylbut-3-yn-2-one (**1c**). From **5c** (0.50 g, 2.02 mmol), ethynylbenzene (0.52 g, 5.06 mmol), and BuLi (4.25 mmol) according to *GP E*. Yield: 0.39 g (67%). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.62–7.58 (*m*, 2 H); 7.48–7.45 (*m*, 1 H); 7.41–7.34 (*m*, 4 H); 7.14–7.11 (*m*, 2 H); 4.58 (*s*, 2 H); 4.50 (*s*, 2 H); 2.35 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.4 (C_q); 138.8 (C_q); 133.2 (CH); 131.6 (CH); 131.0 (CH); 129.0 (CH); 128.6 (CH); 119.4 (C_q); 119.1 (C_q); 93.9 (C_q); 87.6 (C_q); 85.6 (C_q); 83.0 (C_q); 74.8 (CH_2); 59.3 (CH_2); 21.4 (Me). ESI-MS: 311 ($[M+Na]^+$). HR-ESI-MS: 311.1043 ($[M+Na]^+$, $C_{20}H_{16}NaO_2^+$; calc. 311.1043).

1-[[3-(4-Fluorophenyl)prop-2-yn-1-yl]oxy}-4-phenylbut-3-yn-2-one (**1d**). From **5d** (0.80 g, 3.18 mmol), ethynylbenzene (0.81 g, 7.96 mmol), and BuLi (6.69 mmol) according to *GP E*. Yield: 0.59 g (64%). IR (film): 1684, 1504, 1220, 1064, 836, 758. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.61–7.58 (*m*, 2 H); 7.48–7.36 (*m*, 5 H); 7.04–6.98 (*m*, 2 H); 4.57 (*s*, 2 H); 4.49 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.3 (C_q); 162.7 (*d*, ^1J(F,C) = 250, C_q); 133.7 (*d*, *J* = 9, CH); 133.2 (CH); 131.1 (CH); 128.64 (CH); 128.63 (CH); 119.4 (C_q); 118.3 (C_q); 115.7 (*d*, *J* = 22, CH); 94.0 (C_q); 86.4 (C_q); 85.6 (C_q); 83.5 (C_q); 74.9 (CH_2); 59.2 (CH_2). ESI-MS: 293 ($[M+H]^+$). HR-ESI-MS: 293.0974 ($[M+H]^+$, $C_{19}H_{14}FO_2^+$; calc. 293.0972).

4-(4-Chlorophenyl)-1-[(3-phenylprop-2-yn-1-yl)oxy]but-3-yn-2-one (**1e**). From **5a** (0.50 g, 2.14 mmol), 1-chloro-4-ethynylbenzene (0.73 g, 5.36 mmol), and BuLi (4.50 mmol) according to *GP E*. Yield: 0.46 g (70%). IR (KBr): 1671, 1488, 1068, 832, 749, 687. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.47–7.44 (*m*, 2 H); 7.39–7.37 (*m*, 2 H); 7.31–7.24 (*m*, 5 H); 4.51 (*s*, 2 H); 4.41 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.3 (C_q); 137.5 (C_q); 134.4 (CH); 131.8 (CH); 129.1 (CH); 128.7 (CH); 128.3 (CH); 122.2 (C_q); 117.9 (C_q); 92.5 (C_q); 87.6 (C_q); 86.3 (C_q); 83.7 (C_q); 74.9 (CH_2); 59.3 (CH_2). ESI-MS: 309 ($[M+H]^+$), 331 ($[M+Na]^+$). HR-ESI-MS: 309.0680 ($[M+H]^+$, $C_{19}H_{14}ClO_2^+$; calc. 309.0682).

4-(4-Fluorophenyl)-1-[(3-phenylprop-2-yn-1-yl)oxy]but-3-yn-2-one (**1f**). From **5a** (0.50 g, 2.14 mmol), 1-ethynyl-4-fluorobenzene (0.64 g, 5.36 mmol), and BuLi (4.50 mmol) according to *GP E*. Yield: 0.36 g (57%). Yellow solid. M.p. 54°. IR (KBr): 1671, 1503, 1071, 840, 752, 688. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.63–7.58 (*m*, 2 H); 7.47–7.44 (*m*, 2 H); 7.34–7.31 (*m*, 3 H); 7.11–7.06 (*m*, 3 H); 4.59 (*s*, 2 H); 4.48 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.4 (C_q); 164.2 (*d*, ^1J(F,C) = 254, C_q); 135.6 (*d*, *J* = 9, CH); 131.8 (CH); 128.7 (CH); 128.3 (CH); 122.2 (C_q); 116.3 (*d*, *J* = 22, CH); 101.6 (C_q); 92.9 (C_q); 87.6 (C_q); 83.7 (C_q); 74.9 (CH_2); 59.3 (CH_2). EI-MS: 292 (3, M^+), 162 (71), 147 (100), 133 (7), 115 (85). HR-EI-MS: 292.0900 (M^+, $C_{19}H_{13}FO_2^+$; calc. 292.0900).

4-(4-Methylphenyl)-1-[(3-phenylprop-2-yn-1-yl)oxy]but-3-yn-2-one (**1g**). From **5a** (0.50 g, 2.14 mmol), 1-ethynyl-4-methylbenzene (0.62 g, 5.36 mmol), and BuLi (4.50 mmol) according to *GP E*. Yield 0.41 g (66%). Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.51–7.44 (*m*, 4 H); 7.34–7.31 (*m*, 3 H); 7.21–7.18 (*m*, 2 H); 4.59 (*s*, 2 H); 4.49 (*s*, 2 H); 2.39 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.4 (C_q); 141.9 (C_q); 133.3 (CH); 131.8 (CH); 129.5 (CH); 128.7 (CH); 128.3 (CH); 122.2 (C_q); 118.3 (C_q); 94.7 (C_q); 87.5 (C_q); 85.5 (C_q); 83.8 (C_q); 74.9 (CH_2); 59.3 (CH_2); 21.8 (Me). ESI-MS: 289 ($[M+H]^+$), 306 ($[M+NH_4]^+$), 311 ($[M+Na]^+$), 594 ($[2M+NH_4]^+$), 599 ($[2M+H]^+$). HR-ESI-MS: 289.1225 ($[M+H]^+$, $C_{20}H_{17}O_2^+$; calc. 289.1223).

4-Naphthalen-1-yl-1-[(3-phenylprop-2-yn-1-yl)oxy]but-3-yn-2-one (**1h**). From **5a** (0.50 g, 2.14 mmol), 1-ethynylnaphthalene (0.82 g, 5.36 mmol), and BuLi (4.50 mmol) according to *GP E*. Yield: 0.46 g (67%). Yellow oil. IR (film): 1682, 1072, 800, 759. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.38 (*d*, *J* = 8.6, 1 H); 7.98 (*d*, *J* = 8.3, 1 H); 7.90–7.87 (*m*, 2 H); 7.66–7.45 (*m*, 5 H); 7.33–7.31 (*m*, 3 H); 4.65 (*s*, 2 H); 4.58 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.6 (C_q); 133.6 (CH); 132.9 (C_q); 131.9 (CH); 131.8 (CH); 128.7 (CH); 128.5 (CH); 128.3 (CH); 127.8 (CH); 127.0 (CH); 125.7 (CH); 125.1 (CH); 122.2 (C_q); 117.0 (C_q); 92.6 (C_q); 90.4 (C_q); 87.6 (C_q); 83.8 (C_q); 75.0 (CH_2); 59.4 (CH_2). ESI-MS: 342 ($[M+NH_4]^+$), 347 ($[M+Na]^+$), 671 ($[2M+Na]^+$). HR-ESI-MS: 347.1043 ($[M+Na]^+$, $C_{23}H_{16}NaO_2^+$; calc. 347.1043).

1-[(3-Naphthalen-1-ylprop-2-yn-1-yl)oxy]-4-phenylbut-3-yn-2-one (**1i**). From **5e** (0.23 g, 0.81 mmol), ethynylbenzene (0.21 g, 2.03 mmol), and BuLi (1.71 mmol) according to *GP E*. Yield: 0.28 g (78%). Yellow oil. IR (film): 1682, 1072, 996, 775. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.33–8.30 (*m*, 1 H); 7.87–7.84 (*m*, 2 H); 7.72–7.69 (*m*, 1 H); 7.61–7.35 (*m*, 8 H); 4.76 (*s*, 2 H); 4.59 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.4 (C_q); 133.2 (CH); 133.1 (C_q); 131.1 (CH); 130.9 (CH); 129.2 (CH); 128.7 (CH); 128.3 (CH); 126.9 (CH); 126.5 (CH); 126.0 (CH); 125.1 (CH); 119.8 (C_q); 119.5 (C_q); 94.1 (C_q); 88.6 (C_q); 85.7 (C_q); 85.6 (C_q); 75.0 (CH_2); 59.5 (CH_2). ESI-MS: 342 ($[M+NH_4]^+$), 347 ($[M+Na]^+$), 671 ($[2M+Na]^+$). HR-ESI-MS: 347.1043 ($[M+Na]^+$, $C_{23}H_{16}NaO_2^+$; calc. 347.1043).

4-[4-(Methylsulfonyl)phenyl]-1-[(3-phenylprop-2-yn-1-yl)oxy]but-3-yn-2-one (**1j**). From **5a** (0.30 g, 1.29 mmol), 1-ethynyl-4-(methylsulfonyl)benzene (0.58 g, 3.12 mmol), and BuLi (2.70 mmol) according to *GP E*. Yield: 0.27 g (61%). Yellow solid. M.p. 85°. IR (KBr): 1684, 1308, 1149, 1055, 758, 654. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.98–7.95 (*m*, 2 H); 7.78–7.75 (*m*, 2 H); 7.46–7.43 (*m*, 2 H); 7.34–7.31 (*m*, 3 H); 4.59 (*s*, 2 H); 4.50 (*s*, 2 H); 3.07 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.1 (C_q); 142.2 (C_q);

133.9 (CH); 131.7 (CH); 128.8 (CH); 128.3 (CH); 127.6 (CH); 125.2 (C_q); 90.3 (C_q); 87.7 (C_q); 87.6 (C_q); 83.6 (C_q); 74.9 (CH_2); 59.4 (CH_2); 44.3 (Me). ESI-MS: 353 ($[M+H]^+$), 375 ($[M+Na]^+$), 727 ($[2M+Na]^+$). HR-ESI-MS: 353.0842 ($[M+H]^+$, $C_{20}H_{17}O_4S^+$; calc. 353.0842).

4-(3,5-Dimethylphenyl)-1-[(3-phenylprop-2-yn-1-yl)oxy]but-3-yn-2-one (**1k**). From **5a** (0.50 g, 2.14 mmol), 1-ethynyl-3,5-dimethylbenzene (0.70 g, 5.36 mmol), and BuLi (4.50 mmol) according to *GP E*. Yield: 0.34 g (53%). Yellow oil. IR (film): 1686, 1382, 1032, 853, 756, 689. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.48–7.44 (*m*, 2 H); 7.35–7.29 (*m*, 3 H); 7.22 (*s*, 2 H); 7.10 (*s*, 1 H); 4.59 (*s*, 2 H); 4.49 (*s*, 2 H); 2.30 (*s*, 6 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.4 (C_q); 138.4 (C_q); 133.1 (C_q); 131.8 (CH); 130.9 (CH); 128.7 (CH); 128.3 (CH); 122.2 (C_q); 119.0 (C_q); 94.8 (C_q); 87.5 (C_q); 85.2 (C_q); 83.8 (C_q); 74.9 (CH_2); 59.3 (CH_2); 21.0 (Me). EI-MS: 302 (2, M^+), 287 (3), 272 (18), 157 (100), 131 (38), 115 (70), 77 (76). HR-EI-MS: 302.1307 (M^+, $C_{21}H_{18}O_2^+$; calc. 302.1307).

1-[(3-Phenylprop-2-yn-1-yl)oxy]-4-[4-(trifluoromethyl)phenyl]but-3-yn-2-one (**1l**). From **5a** (0.39 g, 1.66 mmol), 1-ethynyl-4-(trifluoromethyl)benzene (0.71 g, 4.15 mmol), and BuLi (3.48 mmol) according to *GP E*. Yield: 0.52 g (92%). Yellow oil. IR (KBr): 1689, 1321, 1128, 1015, 843, 691. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.72–7.63 (*m*, 4 H); 7.47–7.43 (*m*, 2 H); 7.36–7.30 (*m*, 3 H); 4.59 (*s*, 2 H); 4.50 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.3 (C_q); 133.3 (CH); 131.8 (CH); 128.8 (CH); 125.6 (*q*, *J* = 4, CH); 125.3 (C_q); 122.1 (C_q); 87.7 (C_q); 86.8 (C_q); 83.8 (C_q); 74.9 (CH_2); 59.4 (CH_2). EI-MS: 342 (5, M^+), 197 (100), 169 (9), 115 (80). HR-EI-MS: 342.0868 (M^+, $C_{20}H_{13}F_3O_2^+$; calc. 342.0868).

4-Phenyl-1-{[3-(2,4,6-trimethylphenyl)prop-2-yn-1-yl]oxy}but-3-yn-2-one (**1m**). From **5f** (0.16 g, 0.59 mmol), ethynylbenzene (0.15 g, 1.48 mmol), and BuLi (1.24 mmol) according to *GP E*. Yield: 0.07 g (37%). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.61–7.57 (*m*, 2 H); 7.50–7.36 (*m*, 3 H); 6.86 (*s*, 2 H); 4.68 (*s*, 2 H); 4.53 (*s*, 2 H); 2.39 (*s*, 6 H); 2.27 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.5 (C_q); 140.4 (C_q); 138.2 (C_q); 133.2 (CH); 131.1 (CH); 128.7 (CH); 127.6 (CH); 119.5 (C_q); 119.0 (C_q); 93.9 (C_q); 91.0 (C_q); 85.6 (C_q); 85.4 (C_q); 74.6 (CH_2); 59.4 (CH_2); 21.3 (Me); 21.0 (Me). EI-MS: 316 (7, M^+), 301 (8), 286 (19), 173 (5), 157 (48), 144 (30), 129 (100). HR-EI-MS: 316.1463 (M^+, $C_{22}H_{20}O_2^+$; calc. 316.1463).

1-[(3-Phenylprop-2-yn-1-yl)oxy]-4-(2,4,6-trimethylphenyl)but-3-yn-2-one (**1n**). From **5a** (0.50 g, 2.14 mmol), 2-ethynyl-1,3,5-trimethylbenzene (0.77 g, 5.36 mmol), and BuLi (4.50 mmol) according to *GP E*. Yield: 0.43 g (64%). IR (film): 1677, 1277, 1058, 853, 757. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.47–7.43 (*m*, 2 H); 7.35–7.29 (*m*, 3 H); 6.90 (*s*, 2 H); 4.59 (*s*, 2 H); 4.48 (*s*, 2 H); 2.46 (*s*, 6 H); 2.30 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.6 (C_q); 142.8 (C_q); 141.3 (C_q); 131.7 (CH); 128.6 (CH); 128.3 (CH); 128.0 (CH); 122.2 (C_q); 116.3 (C_q); 93.5 (C_q); 93.2 (C_q); 87.4 (C_q); 83.8 (C_q); 74.9 (CH_2); 59.3 (CH_2); 21.5 (Me); 20.8 (Me). ESI-MS: 317 ($[M+H]^+$), 334 ($[M+NH_4]^+$), 339 ($[M+Na]^+$), 655 ($[2M+Na]^+$). HR-ESI-MS: 317.1540 ($[M+H]^+$, $C_{22}H_{21}O_2^+$; calc. 317.1542).

1-[(1-Methyl-3-phenylprop-2-yn-1-yl)oxy]-4-phenylbut-3-yn-2-one (**1o**). From **WAo** (1.50 g, 6.06 mmol), ethynylbenzene (1.55 g, 15.16 mmol), and BuLi (12.73 mmol) according to *GP E*. Yield: 1.26 g (72%). Yellow oil. IR (film): 1671, 1659, 1061, 757. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.36–7.19 (*m*, 10 H); 4.56 (*q*, *J* = 6.8, 1 H); 4.43 (*m*, 2 H); 1.53 (*d*, *J* = 6.8, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.9 (C_q); 133.1 (CH); 131.2 (CH); 130.9 (CH); 128.6 (CH); 128.5 (CH); 128.2 (CH); 93.6 (C_q); 87.7 (C_q); 86.1 (C_q); 85.8 (C_q); 74.1 (CH_2); 66.4 (CH); 22.0 (Me). EI-MS: 287 (0.3, M^+), 273 (0.4), 144 (14), 129 (100), 77 (12). Anal. calc. for $C_{20}H_{16}O_2$: C 83.31, H 5.59; found: C 82.91, H 5.71.

1-{[1-(1-Methylethyl)-3-phenylprop-2-yn-1-yl]oxy}-4-phenylbut-3-yn-2-one (**1p**). From **WAp** (1.00 g, 3.63 mmol), ethynylbenzene (0.93 g, 9.08 mmol), and BuLi (7.63 mmol) according to *GP E*. Yield: 0.94 g (82%). Yellow oil. IR (film): 1685, 1670, 1065, 757. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.50–7.21 (*m*, 10 H); 4.42 (*m*, 2 H); 4.24 (*d*, *J* = 5.7, 1 H); 2.08 (*sext.*, *J* = 5.6, 1 H); 1.04 (*m*, 6 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 185.5 (C_q); 133.1 (CH); 131.7 (CH); 130.9 (CH); 128.6 (CH); 128.4 (CH); 128.2 (CH); 122.4 (C_q); 119.7 (C_q); 93.6 (C_q); 87.6 (C_q); 86.1 (C_q); 85.7 (C_q); 76.3 (CH); 74.4 (CH); 33.3 (CH); 18.6 (Me); 17.8 (Me). EI-MS: 316 (1, M^+), 215 (18), 129 (100), 77 (36). Anal. calc. for $C_{22}H_{20}O_2$: C 83.51, H 6.37; found C 82.94, H 6.79.

1-{[1-(1,1-Dimethylethyl)-3-phenylprop-2-yn-1-yl]oxy}-4-phenylbut-3-yn-2-one (**1q**). From **WAq** (0.90 g, 3.11 mmol), ethynylbenzene (0.79 g, 7.78 mmol), and BuLi (6.53 mmol) according to *GP E*. Yield: 0.84 g (82%). Yellow oil. IR (film): 1688, 1281, 758. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.46–7.15 (*m*, 10 H); 4.34 (*m*, 2 H); 4.03 (*s*, 1 H); 1.01 (*s*, 9 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 185.9 (C_q); 133.2

(CH); 132.1 (CH); 131.8 (CH); 128.8 (CH); 126.6 (CH); 128.4 (CH); 122.6 (C_q); 119.8 (C_q); 93.6 (C_q); 87.8 (C_q); 86.5 (C_q); 86.1 (C_q); 79.6 (CH); 74.8 (CH); 36.1 (C_q); 26.0 (Me). EI-MS: 144 (31), 129 (100), 77 (47). Anal. calc. for $C_{23}H_{22}O_2$: C 83.60, H 6.71; found: C 83.24, H 6.59.

1-[(1,3-Diphenylprop-2-yn-1-yl)oxy]-4-phenylbut-3-yn-2-one (**1r**). From **WAr** (0.44 g, 1.41 mmol), ethynylbenzene (0.36 g, 3.52 mmol), and BuLi (2.95 mmol) according to *GP E*. Yield: 0.15 g (30%). Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.58–7.29 (*m*, 15 H); 5.73 (*s*, 1 H); 4.63 (*d*, *J* = 17.8, 1 H); 4.46 (*d*, *J* = 17.8, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.9 (C_q); 137.6 (C_q); 133.2 (CH); 131.8 (CH); 131.0 (CH); 128.8 (CH); 128.6 (CH); 128.5 (CH); 128.3 (CH); 127.8 (CH); 122.1 (C_q); 119.6 (C_q); 94.0 (C_q); 88.9 (C_q); 86.0 (C_q); 85.6 (C_q); 73.3 (CH_2); 72.3 (CH). EI-MS: 350 (1, M^+), 207 (19), 129 (100), 77 (65). HR-EI-MS: 350.1307 (M^+, $C_{25}H_{18}O_2^+$; calc. 350.1307).

General Procedure (*GP F*) *for the Photolysis of Compounds* **1**. Irradiation of **1** was performed in MeOH, *t*-BuOH, MeCN, or *t*-BuOMe at concentrations of 10 mM using a high-pressure Hg-arc lamp (150 W). Light of wavelength below 300 nm was absorbed with a *Pyrex* glass jacket between the lamp and the reaction vessel. The reaction was monitored by TLC, and the product compositions were determined when the reactant had completely disappeared (after typically 1–5 h). The soln. was concentrated under reduced pressure, and purified by FC (SiO_2; PE/AcOEt 20:1) to afford the pure photoproducts. For the determination of the ratio of regioisomers, a 0.4 mM soln. of **1** in the appropriate solvent was irradiated for 1 h. The product mixture was concentrated under reduced pressure, and analyzed by ^{1}H-NMR (in $CDCl_3$). This was done by integration of the methylene signals of the two regioisomers in the crude reaction mixture.

Product Distribution upon Irradiation of Compounds **1** *under Different Reaction Conditions. Irradiation of* **1a** (see also *Table 3*). *1*) In aerobic MeOH with 250 mg (0.911 mmol) of **1a** for 3 h: **12a** (48 mg, 19%), **11a** (63 mg, 25%), and **13a** (56 mg, 20%), and an inseparable 1:1 mixture of **14a**/**15a** (30 mg, 12%). *2*) In anaerobic MeOH with 254 mg (0.926 mmol) of **1a** for 3 h: **12a** (54 mg, 21%), **11a** (50 mg, 20%), **13a** (54 mg, 18%), and **14a**/**15a** (24 mg, 9%). *3*) In *t*-BuOH with 456 mg (1.695 mmol) of **1a** for 3 h: **12a** (175 mg, 38%), **11a** (183 mg, 39%), and **14a**/**15a** (44 mg, 9%). The ratio of the PDDA reaction products was **12a**/**11a** 1:1.3. *4*) In MeCN with 146 mg (0.532 mmol) of **1a** for 3 h: **12a** (18 mg, 12%), **11a** (25 mg, 17%), and **14a**/**15a** (16 mg, 11%).

*Data of 10-Phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**12a**). M.p. 87°. IR (KBr): 1696, 1295, 1117, 745, 703. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.69 (*s*, 1 H); 8.05–8.01 (*m*, 1 H); 7.54–7.59 (*m*, 6 H); 7.29–7.25 (*m*, 2 H); 4.72 (*s*, 2 H); 4.43 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.9 (C_q); 136.7 (C_q); 135.9 (C_q); 135.1 (C_q); 133.7 (C_q); 131.9 (C_q); 130.3 (CH); 129.7 (CH); 129.1 (CH); 128.8 (CH); 128.6 (CH); 128.0 (CH); 127.97 (CH); 127.95 (CH); 127.2 (C_q); 126.4 (CH); 126.2 (CH); 73.7 (CH_2); 67.4 (CH_2). EI-MS: 274 (95, M^+), 244 (32), 202 (19), 197 (10), 77 (41). HR-EI-MS: 274.0994 (M^+, $C_{19}H_{14}O_2^+$; calc. 274.0994).

*Data of 5-Phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**11a**). M.p. 135°. IR (KBr): 1698, 1241, 1119, 755, 695. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.87 (*d*, *J* = 7.9, 1 H); 7.73 (*s*, 1 H); 7.62–7.49 (*m*, 5 H); 7.44–7.38 (*m*, 1 H); 7.26–7.23 (*m*, 2 H); 5.07 (*s*, 2 H); 4.35 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.6 (C_q); 143.2 (C_q); 138.9 (C_q); 136.4 (C_q); 135.1 (C_q); 132.1 (C_q); 128.8 (CH); 128.7 (CH); 128.1 (CH); 127.4 (CH); 127.2 (CH); 126.5 (CH); 124.9 (C_q); 123.3 (CH); 74.9 (CH_2); 69.3 (CH_2). EI-MS: 274 (60, M^+), 244 (100), 202 (12), 77 (34). HR-EI-MS: 274.0993 (M^+, $C_{19}H_{14}O_2^+$; calc. 274.0994).

Data of 1-Methoxy-7,8-diphenyl-3-oxabicyclo[4.2.0]oct-7-en-5-one (**13a**). M.p. 93°. IR (KBr) 1712, 1221, 1108, 761, 691. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.63–7.60 (*m*, 4 H); 7.42–7.33 (*m*, 6 H); 4.38–4.26 (*m*, 2 H); 4.35 (*d*, *J* = 12.1, 1 H); 4.30 (*d*, *J* = 18.8, 1 H); 4.06–3.99 (*m*, 3 H); 3.72 (*d*, *J* = 12.1, 1 H); 3.39 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 209.7 (C_q); 141.4 (C_q); 138.2 (C_q); 132.7 (C_q); 132.6 (C_q); 129.2 (CH); 128.80 (CH); 128.78 (CH); 128.6 (CH); 127.2 (CH); 126.5 (CH); 80.7 (C_q); 75.9 (CH_2); 69.6 (CH_2); 56.0 (CH); 51.3 (Me). EI-MS: 306 (82, M^+), 276 (42), 248 (40), 178 (100), 77 (30). HR-EI-MS: 306.1256 (M^+, $C_{20}H_{18}O_3^+$; calc. 306.1256).

Irradiation of **1b**. In MeOH with 97 mg (0.314 mmol) of **1b** for 3 h: **12b** (24 mg, 25%) and **11b** (26 mg, 27%); ratio **12b**/**11b** 1:1.2.

*Data of 10-(4-Chlorophenyl)-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**12b**). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.74 (*s*, 1 H); 8.11–8.08 (*m*, 1 H); 7.62–7.54 (*m*, 4 H); 7.51–7.35 (*m*, 2 H); 7.31–7.27 (*m*, 2 H); 4.76 (*s*, 2 H); 7.48 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.7 (C_q); 135.2 (C_q); 135.0 (C_q); 134.5

(C_q); 134.3 (C_q); 133.9 (C_q); 131.9 (C_q); 131.2 (CH); 130.4 (CH); 129.3 (CH); 129.2 (CH); 128.4 (CH); 126.6 (CH); 125.9 (CH); 73.8 (CH_2); 67.3 (CH_2). EI-MS: 308 (69, M^+), 278 (20), 250 (21), 215 (100), 197 (8). HR-EI-MS: 308.0604 (M^+, $C_{19}H_{13}ClO_2^+$; calc. 308.0604).

*Data of 7-Chloro-5-phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**11b**). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.81 (*d*, *J* = 8.7, 1 H); 7.71 (*s*, 1 H); 7.55–7.50 (*m*, 6 H); 7.22–7.18 (*m*, 2 H); 5.04 (*s*, 2 H); 4.32 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.4 (C_q); 142.4 (C_q); 138.1 (C_q); 136.8 (C_q); 133.6 (C_q); 133.3 (C_q); 132.7 (C_q); 129.8 (CH); 129.0 (CH); 128.8 (CH); 128.3 (CH); 127.6 (CH); 127.3 (CH); 123.3 (CH); 74.9 (CH_2); 69.2 (CH_2). EI-MS: 308 (70, M^+), 278 (90), 250 (8), 215 (100), 189 (7), 77 (20). HR-EI-MS: 308.0608 (M^+, $C_{19}H_{13}ClO_2^+$; calc. 308.0604).

Irradiation of **1c**. In MeOH with 100 mg (0.347 mmol) of **1c** for 3 h: **12c** (26 mg, 26%) and **11c** (39 mg, 39%); ratio **12c**/**11c** 1:1.6.

*Data of 10-(4-Methylphenyl)-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**12c**). M.p. 147°. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.61 (*s*, 1 H); 7.99–7.91 (*m*, 1 H); 7.46–7.43 (*m*, 1 H); 7.28–7.25 (*m*, 2 H); 7.10–7.07 (*m*, 2 H); 4.66 (*s*, 2 H); 4.35 (*s*, 2 H); 2.41 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.0 (C_q); 137.8 (C_q); 136.0 (C_q); 135.3 (C_q); 133.9 (C_q); 133.7 (C_q); 133.2 (CH); 131.9 (C_q); 131.7 (CH); 131.1 (C_q); 130.3 (CH); 129.7 (CH); 129.5 (CH); 129.1 (CH); 128.7 (CH); 127.3 (CH); 126.3 (CH); 73.8 (CH_2); 67.5 (CH_2); 21.3 (Me). EI-MS: 288 (40, M^+), 273 (3), 258 (5), 216 (9), 91 (29). HR-EI-MS: 288.1151 (M^+, $C_{20}H_{16}O_2^+$; calc. 288.1150).

*Data of 7-Methyl-5-phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**11c**). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.65–7.10 (*m*, 9 H); 4.96 (*s*, 2 H); 4.24 (*s*, 2 H); 2.30 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.7 (C_q); 142.5 (C_q); 139.1 (C_q); 136.4 (C_q); 135.5 (C_q); 133.5 (C_q); 132.9 (C_q); 131.2 (CH); 129.5 (CH); 128.9 (CH); 128.6 (CH); 128.1 (CH); 127.4 (CH); 127.2 (CH); 126.4 (CH); 123.0 (CH); 75.0 (CH_2); 69.4 (CH_2); 21.9 (Me). HR-EI-MS: 288.1151 (M^+, $C_{20}H_{16}O_2^+$; calc. 288.1150). EI-MS: 288 (90, M^+), 258 (100), 216 (20).

Irradiation of **1d**. In *t*-BuOH with 356 mg (1.218 mmol) of **1d** for 2 h: **12d** (51 mg, 14%) and **11d** (111 mg, 31%); ratio **12d**/**11d** 1:1.6.

*Data of 10-(4-Fluorophenyl)-1*H*-benzo[g]isochromen-4(3*H*)-one* (**12d**). Yellow oil. IR (film): 1725, 1508, 1242, 1119, 757. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.70 (*s*, 1 H); 8.06–8.03 (*m*, 1 H); 7.55–7.50 (*m*, 3 H); 7.37–7.36 (*m*, 2 H); 7.24–7.23 (*m*, 2 H); 4.71 (*s*, 2 H); 4.43 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.8 (C_q); 162.7 (*d*, ^1J(F,C) = 250, C_q); 134.0 (C_q); 131.9 (C_q); 131.5 (*d*, *J* = 8, CH); 130.4 (CH); 129.3 (CH); 128.3 (CH); 126.6 (CH); 126.0 (CH); 116.1 (CH); 73.7 (CH_2); 67.3 (CH_2). EI-MS: 292 (30, M^+), 262 (21), 220 (5), 197 (3). HR-EI-MS: 292.0901 (M^+, $C_{19}H_{13}FO_2^+$; calc. 292.0900).

*Data of 7-Fluoro-5-phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**11d**). Yellow solid. M.p. 131°. IR (KBr): 1695, 1597, 1195, 1130, 871, 694. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.86 (*dd*, *J* = 9.2, *J* = 5.7, 1 H); 7.73 (*s*, 1 H); 7.52–7.48 (*m*, 3 H); 7.42–7.34 (*m*, 1 H); 7.22–7.12 (*m*, 3 H); 5.04 (*s*, 2 H); 4.33 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.5 (C_q); 160.8 (*d*, ^1J(F,C) = 248, C_q); 138.4 (C_q); 135.8 (C_q); 132.1 (C_q); 129.9 (*d*, *J* = 9, CH); 128.7 (CH); 128.3 (CH); 127.5 (CH); 125.6 (C_q); 123.7 (CH); 119.4 (*d*, *J* = 25, CH); 112.0 (*d*, *J* = 22, CH); 74.9 (CH_2); 69.2 (CH_2). EI-MS: 292 (68, M^+), 262 (89), 234 (37). HR-EI-MS: 292.0899 (M^+, $C_{19}H_{13}FO_2^+$; calc. 292.0900).

Irradiation of **1e**. In MeCN with 100 mg (0.324 mmol) of **1e** for 1 h: **12e** (15 mg, 15%) and **11e** (27 mg, 27%); ratio **12e**/**11e** 1:1.7.

*Data of 8-Chloro-10-phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**12e**). Yellow oil. M.p. 180°. IR (film): 1695, 1486, 1293, 1118, 964, 707. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.58 (*s*, 1 H); 7.98 (*d*, *J* = 8.7, 1 H); 7.56–7.46 (*m*, 5 H); 7.27–7.24 (*m*, 2 H); 4.70 (*s*, 2 H); 4.42 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.5 (C_q); 136.0 (C_q); 135.8 (C_q); 135.5 (C_q); 135.3 (C_q); 135.0 (C_q); 131.8 (CH); 130.2 (C_q); 129.7 (CH); 129.0 (CH); 128.4 (CH); 127.7 (CH); 127.6 (CH); 127.5 (C_q); 125.2 (CH); 73.7 (CH_2); 67.4 (CH_2). ESI-MS: 309 ($[M+H]^+$), 331 ($[M+Na]^+$), 639 ($[2M+Na]^+$). HR-ESI-MS: 309.0860 ($[M+H]^+$, $C_{19}H_{14}ClO_2^+$; calc. 309.0682).

*Data of 5-(4-Chlorophenyl)-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**11e**). Yellow solid. M.p. 95–99°. IR (KBr): 1693, 1384, 1239, 1121, 1088, 860, 759. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.57 (*d*, *J* = 7.9, 1 H); 7.73 (*s*, 1 H); 7.63–7.58 (*m*, 1 H); 7.52–7.39 (*m*, 4 H); 7.18 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.7 (C_q); 141.8 (C_q); 137.3 (C_q); 136.4 (C_q); 135.2 (C_q); 133.3 (C_q); 132.6 (C_q); 130.3 (CH); 129.0 (CH); 128.43

(CH); 128.36 (CH); 127.6 (CH); 126.7 (CH); 125.0 (C_q); 123.7 (CH); 74.9 (CH_2); 69.3 (CH_2). ESI-MS: 309 ($[M+H]^+$), 331 ($[M+Na]^+$), 639 ($[2M+Na]^+$). HR-ESI-MS: 309.0861 ($[M+H]^+$, $C_{19}H_{14}ClO_2^+$; calc. 309.0682).

Irradiation of **1f**. In *t*-BuOH with 334 mg (1.143 mmol) of **1f** for 1.5 h: **12f** (116 mg, 35%) and **11f** (126 mg, 38%); ratio **12f**/**11f** 1:1.1.

*Data of 8-Fluoro-10-phenyl-1*H*-benzo[g]isochromen-4(3*H*)-one* (**12f**). Yellow oil. IR (film): 1692, 1507, 1241, 1119, 961, 758. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.68 (*s*, 1 H); 8.04 (*dd*, $^3J=8.75$, $^4J=5.74$, 1 H); 7.58–7.50 (*m*, 3 H); 7.34–7.24 (*m*, 3 H); 7.11–7.07 (*m*, 1 H); 4.71 (*s*, 2 H); 4.42 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.6 (C_q); 136.3 (C_q); 134.8 (C_q); 133.2 (*d*, $^3J=9.3$, CH); 129.6 (CH); 129.0 (CH); 128.4 (CH); 127.8 (CH); 126.9 (C_q); 117.2 (*d*, $^2J=25.3$, CH); 110.0 (*d*, $^2J=20.3$, CH); 73.7 (CH_2); 67.4 (CH_2). EI-MS: 292 (82, M^+), 262 (9), 234 (100), 215 (7). HR-EI-MS: 292.0901 (M^+, $C_{19}H_{13}FO_2^+$; calc. 292.0900).

*Data of 5-(4-Fluorophenyl)-1*H*-benzo[g]isochromen-4(3*H*)-one* (**11f**). Yellow solid. M.p. 170°. IR (KBr): 1694, 1507, 1118, 959, 757. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.85 (*d*, $J=7.5$, 1 H); 7.73 (*s*, 1 H); 7.63–7.57 (*m*, 1 H); 7.53–7.50 (*m*, 1 H); 7.44–7.39 (*m*, 1 H); 7.20–7.18 (*m*, 4 H); 5.06 (*s*, 2 H); 4.33 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.8 (C_q); 162.2 (*d*, ^1J(F,C)=246, C_q); 136.4 (C_q); 135.2 (C_q); 134.6 (C_q); 132.9 (C_q); 131.8 (CH); 130.5 (*d*, $J=8$, CH); 128.9 (CH); 128.4 (CH); 127.5 (CH); 126.7 (CH); 125.1 (C_q); 123.6 (CH); 75.0 (CH_2); 69.3 (CH_2). EI-MS: 292 (70, M^+), 262 (100), 234 (32). HR-EI-MS: 292.0900 (M^+, $C_{19}H_{13}FO_2^+$; calc. 292.0900).

Irradiation of **1g**. In MeCN with 155 mg (0.538 mmol) of **1g** for 1.5 h: **12g** (46 mg, 30%) and **11g** (72 mg, 46%); ratio **12g**/**11g** 1:1.2.

*Data of 8-Methyl-10-phenyl-1*H*-benzo[g]isochromen-4(3*H*)-one* (**12g**). IR (film): 1695, 1295, 1118, 798, 700. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.64 (*s*, 1 H); 7.93 (*d*, $J=7.9$, 1 H); 7.57–7.44 (*m*, 3 H); 7.37–7.17 (*m*, 4 H); 4.68 (*s*, 2 H); 4.41 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.9 (C_q); 139.6 (C_q); 136.9 (C_q); 135.3 (C_q); 135.1 (C_q); 133.9 (C_q); 130.2 (C_q); 130.1 (CH); 129.8 (CH); 129.0 (CH); 128.8 (CH); 128.6 (CH); 128.0 (CH); 127.7 (CH); 126.5 (C_q); 125.2 (CH); 116.3 (C_q); 73.7 (CH_2); 67.4 (CH_2); 22.2 (Me). ESI-MS: 289 ($[M+H]^+$), 311 ($[M+Na]^+$), 599 ($[2M+Na]^+$). HR-ESI-MS: 289.1225 ($[M+H]^+$, $C_{20}H_{17}O_2^+$; calc. 289.1229).

*Data of 5-(4-Methylphenyl)-1*H*-benzo[g]isochromen-4(3*H*)-one* (**11g**). IR (film): 1696, 1211, 1118, 754. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.87–7.83 (*m*, 1 H); 7.70 (*s*, 1 H); 7.59 (*d*, $J=7.9$, 2 H); 7.42–7.31 (*m*, 3 H); 7.12 (*d*, $J=7.9$, 2 H); 5.03 (*s*, 2 H); 4.31 (*s*, 2 H); 2.47 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.7 (C_q); 143.4 (C_q); 136.8 (C_q); 136.4 (C_q); 135.8 (C_q); 135.1 (C_q); 132.9 (C_q); 131.9 (CH); 130.8 (CH); 128.8 (CH); 128.7 (CH); 127.3 (CH); 126.4 (CH); 125.0 (C_q); 123.1 (CH); 74.9 (CH_2); 69.3 (CH_2); 21.4 (Me). ESI-MS: 289 ($[M+H]^+$), 311 ($[M+Na]^+$), 599 ($[2M+Na]^+$). HR-ESI-MS: 289.1226 ($[M+H]^+$, $C_{20}H_{17}O_2^+$; calc. 289.1229).

Irradiation of **1h**. In MeCN with 179 mg (0.552 mmol) of **1h** for 2 h: inseparable 1:1 mixture of **15a**/**14h** (96 mg, 54%). ^{1}H-NMR (300 MHz, $CDCl_3$): 9.57 (*s*, 1 H, **14h**); 8.33 (*d*, $^3J=7.91$, 1 H, **14h**); 8.00 (*d*, $J=7.3$, 1 H, **14h**); 7.92–7.88 (*m*, 2 H, **14h**); 7.68–7.35 (*m*, 8 H, **14h**/**15a**); 2.44 (*s*, 3 H, **15a**). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.6 (C_q, **15a**); 176.6 (CHO, **14h**); 133.7 (CH, **14h**); 133.03 (CH, **14h**); 133.00 (CH, **15a**); 132.1 (CH, **14h**); 130.7 (CH, **15a**); 128.6 (CH, **15a**); 127.9 (CH, **14h**); 127.0 (CH, **14h**); 125.6 (CH, **14h**); 125.2 (CH, **14h**); 119.9 (C_q, **15a**); 116.9 (C_q, **14h**); 93.4 (C_q, **14h**); 93.1 (C_q, **14h**); 90.3 (C_q, **15a**); 88.2 (C_q, **15a**); 32.7 (Me, **15a**).

Irradiation of **1i**. In MeCN with 228 mg (0.703 mmol) of **1i** for 2 h: **15i** (67 mg, 49%) and **14a** (53 mg, 58%).

Data of 3-Phenylprop-2-ynal (**14a**). ^{1}H-NMR (300 MHz, $CDCl_3$) 9.43 (*s*, 1 H); 7.63–7.59 (*m*, 2 H); 7.52–7.47 (*m*, 1 H); 7.43–7.38 (*m*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 176.8 (CHO); 133.3 (CH); 131.3 (CH); 128.7 (CH); 119.4 (C_q); 95.1 (C_q); 88.4 (C_q).

Data of 4-(Naphthalen-1-yl)but-3-yn-2-one (**15i**). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.31 (*d*, $J=8.3$, 1 H); 7.97 (*d*, $J=8.3$, 1 H); 7.91–7.83 (*m*, 2 H); 7.67–7.45 (*m*, 3 H); 2.57 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.5 (C_q); 133.2 (CH); 131.5 (CH); 128.5 (CH); 127.7 (CH); 126.9 (CH); 125.7 (CH); 125.2 (CH); 117.4 (C_q); 92.9 (C_q); 88.7 (C_q); 32.9 (CH_3).

Irradiation of **1j**. In *t*-BuOH with 216 mg (0.613 mmol) of **1j** in 3 h: inseparable 1:1.8 mixture of **12j**/**15j** (8 and 15%, resp.) together with **11j** (82 mg, 38%); ratio **12j**/**11j** 1:6.6.

Data of **12j/15j**. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.74 (*s*, 1 H, **12j**); 8.23 (*d*, *J* = 8.7, 1 H, 12j); 8.18–1.87 (*m*, 1 H, **12j**); 7.99–7.94 (*m*, 3 H, **15j**); 7.77–7.73 (*m*, 3 H, **12j/15j**); 7.57–7.55 (*m*, 3 H, **12j**); 7.28–7.25 (*m*, 2 H, **12j**); 4.74 (*s*, 2 H, **12j**); 4.46 (*s*, 2 H, **12j**); 3.07 (*s*, 3 H, **15j**); 3.04 (*s*, 3 H, **12j**); 2.48 (*s*, 3 H, **15j**). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.3 (C_q, **12j**); 184.0 (C_q, **15j**); 141.9 (C_q); 140.3 (C_q); 138.0 (C_q); 136.0 (C_q); 135.2 (C_q); 134.0 (C_q); 133.8 (C_q); 133.5 (CH, **15j**); 132.1 (CH); 129.6 (CH); 129.3 (CH); 128.9 (CH); 127.6 (CH, **15j**); 127.5 (CH); 127.0 (CH); 125.7 (C_q); 122.8 (CH); 90.2 (C_q, **15j**); 86.7 (C_q, **15j**); 73.7 (CH_2, **12j**); 67.3 (CH_2, **12j**); 44.3 (Me, **15j**); 44.2 (Me, **12j**); 32.7 (Me, **15j**).

*Data of 5-[4-(Methylsulfonyl)phenyl]-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**11j**). IR (KBr): 1694, 1298, 1152, 959, 771. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.10–8.06 (*m*, 2 H); 7.89 (*d*, ^3J = 8.12, 1 H); 7.79 (*s*, 1 H); 7.68–7.58 (*m*, 1 H); 7.46–7.40 (*m*, 2 H); 7.35–7.32 (*m*, 2 H); 5.08 (*s*, 2 H); 4.34 (*s*, 2 H); 3.19 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.7 (C_q); 145.5 (C_q); 140.7 (C_q); 139.3 (C_q); 136.4 (C_q); 135.2 (C_q); 129.9 (CH); 129.2 (CH); 127.9 (CH); 127.7 (CH); 127.2 (CH); 127.1 (CH); 124.7 (C_q); 124.2 (CH); 74.8 (CH_2); 69.2 (CH_2); 44.6 (Me). ESI-MS: 353 ($[M+H]^+$), 370 ($[M+NH_4]^+$), 375 ($[M+Na]^+$), 705 ($[2M+H]^+$), 722 ($[2M+NH_4]^+$), 727 ($[2M+Na]^+$). HR-ESI-MS: 353.0842 ($[M+H]^+$, $C_{20}H_{17}O_4S^+$; calc. 353.0842).

Irradiation of **1k**. In MeCN with 125 mg (0.413 mmol) of **1k** for 2 h: **12k** (34 mg, 27%) and **11k** (34 mg, 27%); ratio **12k/11k** 1:1.2.

*Data of 7,9-Dimethyl-10-phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**12k**). Yellow oil. IR (KBr): 1696, 1443, 1280, 1119, 744, 704. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.49 (*s*, 1 H); 7.59 (*s*, 1 H); 7.37–7.35 (*m*, 3 H); 7.18–7.15 (*m*, 2 H); 7.09 (*s*, 1 H); 4.46 (*s*, 2 H); 4.28 (*s*, 2 H); 2.37 (*s*, 3 H); 1.81 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.9 (C_q); 140.6 (C_q); 135.7 (C_q); 135.6 (CH); 135.4 (C_q); 134.5 (C_q); 133.6 (C_q); 132.0 (CH); 129.7 (CH); 128.6 (CH); 128.5 (CH); 128.3 (CH); 127.8 (CH); 126.5 (C_q); 73.4 (CH_2); 67.6 (CH_2); 24.5 (Me); 21.0 (Me). EI-MS: 302 (50, M^+), 272 (100), 230 (11), 167 (26). HR-EI-MS: 302.1307 (M^+, $C_{21}H_{18}O_2^+$; calc. 302.1307).

*Data of 5-(3,5-Dimethylphenyl)-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**11k**). Yellow solid. M.p. 163°. IR (KBr): 1696, 1595, 1238, 1116, 856, 754. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.86–7.83 (*m*, 1 H); 7.69 (*s*, 1 H); 7.60–7.56 (*m*, 2 H); 7.42–7.39 (*m*, 1 H); 7.10 (*s*, 1 H); 6.84 (*s*, 2 H); 5.05 (*s*, 2 H); 4.34 (*s*, 2 H); 2.39 (*s*, 6 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.6 (C_q); 143.7 (C_q); 138.7 (C_q); 137.4 (C_q); 136.3 (C_q); 135.1 (C_q); 132.9 (C_q); 128.9 (CH); 128.7 (CH); 128.4 (CH); 127.3 (CH); 126.6 (CH); 126.3 (CH); 124.8 (C_q); 123.0 (CH); 75.0 (CH_2); 69.4 (CH_2); 21.4 (Me). EI-MS: 302 (100, M^+), 272 (12), 244 (48), 230 (20), 105 (15). HR-EI-MS: 302.1307 (M^+, $C_{21}H_{18}O_2^+$; calc. 302.1307).

Irradiation of **1l**. In *t*-BuOH with 151 mg (0.441 mmol) of **1l** for 2 h: **12l** (10 mg, 7%), **11l** (41 mg, 27%), and **15l** (15 mg, 16%); ratio **12l/11l** 1:2.4.

*Data of 10-Phenyl-8-(trifluoromethyl)-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**12l**). IR (KBr): 1696, 1292, 1121, 1068, 797, 674. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.73 (*s*, 1 H); 8.16 (*d*, *J* = 8.5, 1 H); 7.80 (*s*, 1 H); 7.71–7.66 (*m*, 1 H); 7.59–7.53 (*m*, 3 H); 7.29–7.26 (*s*, 2 H); 4.73 (*s*, 2 H); 4.45 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.5 (C_q); 137.3 (C_q); 135.6 (C_q); 135.3 (C_q); 134.0 (C_q); 133.0 (C_q); 133.1 (C_q); 131.4 (CH); 129.6 (CH); 129.1 (CH); 128.4 (CH); 127.5 (CH); 123.9 (*q*, *J* = 4.6, CH); 122.1 (*q*, *J* = 2.7, CH); 73.7 (CH_2); 67.3 (CH_2). EI-MS: 342 (69, M^+), 312 (12), 284 (89), 197 (12). HR-EI-MS: 342.0868 (M^+, $C_{20}H_{13}F_3O_2^+$; calc. 342.0868).

*Data of 5-[4-(Trifluoromethyl)phenyl]-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**11l**). IR (KBr): 1694, 1324, 1118, 1066, 757. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.88 (*d*, *J* = 8.3, 1 H); 7.78–7.75 (*m*, 3 H); 7.66–7.33 (*m*, 5 H); 5.07 (*s*, 2 H); 4.34 (*s*, 2 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.6 (C_q); 136.4 (C_q); 135.2 (C_q); 132.1 (C_q); 132.0 (CH); 131.8 (CH); 129.3 (CH); 129.1 (CH); 128.2 (CH); 127.7 (CH); 126.9 (CH); 125.1 (*q*, *J* = 3.6, CH); 124.8 (C_q); 74.8 (CH_2); 69.2 (CH_2). EI-MS: 342 (18, M^+), 312 (22), 284 (5), 197 (15). HR-EI-MS: 342.0868 (M^+, $C_{20}H_{13}F_3O_2^+$; calc. 342.0868).

Data of 4-[4-(Trifluoromethyl)phenyl]but-3-yn-2-one (**15l**). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.72–7.65 (*m*, 4 H); 2.47 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 184.2 (C_q); 133.1 (CH); 127.9 (CH); 125.6 (*q*, *J* = 4, CH); 125.6 (*d*, *J* = 37, C_q); 123.7 (C_q); 89.3 (C_q); 87.7 (C_q); 32.7 (Me).

Irradiation of **1m**. In *t*-BuOH with 66 mg (0.209 mmol) of **1m** for 1.5 h: **12m** (25 mg, 38%) and **16** (7 mg, 11%).

*Data of 10-(2,4,6-Trimethylphenyl)-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**12m**). ^{1}H-NMR (300 MHz, $CDCl_3$): 8.69 (*s*, 1 H); 8.06–8.03 (*m*, 1 H); 7.73–7.70 (*m*, 1 H); 7.56–7.45 (*m*, 2 H); 7.28 (*d*, *J* = 8.3, 1 H);

4.55 (*s*, 2 H); 4.43 (*s*, 2 H); 2.40 (*s*, 3 H); 1.81 (*s*, 6 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.1 (C_q); 137.7 (C_q); 136.3 (C_q); 134.6 (C_q); 134.5 (C_q); 133.7 (C_q); 132.4 (C_q); 132.1 (C_q); 130.6 (CH); 129.4 (CH); 128.7 (CH); 127.7 (CH); 126.6 (CH); 125.2 (CH); 73.8 (CH_2); 67.0 (CH_2); 21.1 (Me); 19.9 (Me). EI-MS: 316 (35, M^+), 301 (6), 271 (10), 258 (5). HR-EI-MS: 316.1464 (M^+, $C_{22}H_{20}O_2^+$; calc. 316.1463).

*Data of 7,9-Dimethyl-5-phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**16**). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.82 (*s*, 1 H); 7.50–7.47 (*m*, 2 H); 7.28 (*s*, 1 H); 7.21–7.18 (*m*, 2 H); 7.13 (*s*, 2 H); 5.07 (*s*, 2 H); 4.31 (*s*, 2 H); 2.70 (*s*, 3 H); 2.31 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.8 (C_q); 139.4 (C_q); 135.9 (C_q); 135.3 (C_q); 133.6 (C_q); 132.8 (CH); 132.0 (CH); 128.9 (CH); 129.8 (C_q); 128.0 (CH); 127.1 (CH); 125.7 (CH); 119.5 (CH); 74.9 (CH_2); 69.7 (CH_2); 23.8 (Me); 20.8 (Me); 17.5 (Me). EI-MS: 302 (29, M^+), 287 (17), 272 (18), 230 (16), 167 (13), 77 (33).

Irradiation of **1n**. In *t*-BuOH with 122 mg (0.384 mmol) of **1n** for 1.5 h: **11n** (60 mg, 49%) and **17** (32 mg, 26%).

*Data of 5-(2,4,6-Trimethylphenyl)-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**11n**). Red-yellow solid. IR (KBr): 1695, 1288, 1118, 715. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.77 (*s*, 1 H); 7.55–7.48 (*m*, 3 H); 7.27–7.21 (*m*, 2 H); 7.07 (*s*, 1 H); 6.86 (*s*, 1 H); 4.61 (*s*, 2 H); 4.35 (*s*, 2 H); 2.71 (*s*, 3 H); 2.28 (*s*, 3 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.1 (C_q); 141.0 (C_q); 139.2 (C_q); 137 (C_q); 136.9 (C_q); 135.9 (C_q); 133.7 (C_q); 129.8 (CH); 129.7 (CH); 128.6 (CH); 127.9 (CH); 127.6 (CH); 126.1 (C_q); 124.1 (CH); 123.5 (CH); 73.7 (CH_2); 67.4 (CH_2); 22.2 (Me); 19.6 (Me). EI-MS: 302 (100, M^+), 272 (7), 244 (53), 230 (8). HR-EI-MS: 302.1306 (M^+, $C_{21}H_{18}O_2^+$; calc. 302.1307).

*Data of 6,8-Dimethyl-10-phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**17**). Yellow oil. IR (KBr): 1687, 1382, 1238, 1118, 855, 751. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.87 (*d*, ^3J=8.29, 1 H); 7.71 (*s*, 1 H); 7.62–7.57 (*m*, 1 H); 7.43–7.34 (*m*, 2 H); 7.00 (*s*, 2 H); 5.07 (*s*, 2 H); 4.33 (*s*, 2 H); 2.40 (*s*, 3 H); 1.72 (*s*, 6 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.4 (C_q); 142.6 (C_q); 136.7 (C_q); 136.6 (C_q); 135.5 (C_q); 135.1 (C_q); 131.9 (C_q); 129.0 (CH); 128.1 (CH); 127.7 (CH); 127.5 (CH); 126.8 (CH); 125.0 (C_q); 123.0 (CH); 74.7 (CH_2); 69.5 (CH_2); 21.3 (Me); 20.0 (Me). EI-MS: 316 (82, M^+), 302 (3), 286 (100), 271 (30), 244 (9). HR-EI-MS: 316.1464 (M^+, $C_{22}H_{20}O_2^+$; calc. 316.1463).

Irradiation of **1o**. In MeOH with 350 mg (1.214 mmol) of **1o** for 2 h: inseparable mixture of **18o**/**19o** (238 mg, 68%) in the ratio 1:1.5. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.59 (*s*, 1 H, **19o**); 7.95 (*d*, *J*=9.0, 1 H, **18o**); 7.94–7.16 (*m*, 18 H, **18o**/**19o**); 5.10 (*q*, *J*=6.4, 1 H, **18o**); 5.01 (*q*, *J*=6.8, 1 H, **19o**); 4.48 (*m*, 2 H, **19o**); 4.45 (*m*, 2 H, **18o**); 1.91 (*d*, *J*=6.4, 3 H, **19o**); 1.32 (*d*, *J*=6.8, 3 H, **18o**). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.6 (C_q, **18o**); 195.1 (C_q, **19o**); 142.8; 140.7; 138.3; 137.0; 135.5; 135.4; 135.1; 132.4 (C_q, **18o**/**19o**); 131.7; 130.6; 129.5; 129.2; 129.1; 128.5; 128.4; 128.1; 127.9; 127.7; 127.6; 127.0; 126.4; 126.2; 122.8 (CH, **18o**/**19o**); 73.3 (CH_2, **19o**); 72.9 (CH, **19o**); 69.6 (CH, **18o**); 66.7 (CH_2, **18o**); 19.8 (Me, **19o**); 19.3 (Me, **18o**).

Irradiation of **1p**. In MeOH with 267 mg (0.844 mmol) of **1p** for 2 h: inseparable mixture of **18p**/**19p** (166 mg, 62%) in the ratio 1:2.3. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.49 (*s*, 1 H, **18p**); 7.88–7.03 (*m*, 19 H, **18p**/**19p**); 4.56 (*m*, 2 H, **19p**); 4.51 (*m*, 1 H, **19p**); 4.30 (*m*, 2 H, **18p**); 4.15 (*m*, 1 H, **18p**); 1.86 (*m*, 1 H, **18p**); 1.01 (*m*, 6 H, **19p**); 0.84 (*d*, *J*=6.8, 3 H, **18p**); 0.45 (*d*, *J*=6.8, 3 H, **18p**). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 196.6 (C_q, **18p**); 195.4 (C_q, **19p**); 142.8; 138.9; 137.1; 134.8; 132.4 (C_q, **18p**/**19p**); 131.9; 130.1; 128.9; 128.4; 127.9; 127.6 (CH, **18p**/**19p**); 81.8 (CH, **18p**); 77.9 (CH, **19p**); 71.5 (CH_2, **18p**); 67.6 (CH_2, **19p**); 32.3 (CH, **18p**); 30.4 (CH, **19p**); 19.7 (Me, **18p**); 19.2 (Me, **19p**); 17.4 (Me, **18p**).

Irradiation of **1q**. In MeOH with 150 mg (0.454 mmol) of **1q** for 2 h: **19q** (62 mg, 41%).

*Data of 1-(1,1-Dimethylethyl)-5-phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**19q**). IR (film): 1696, 1213, 1120, 749, 696. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.50–7.00 (*m*, 10 H); 4.66 (*s*, 1 H); 4.37 (*m*, 2 H); 1.03 (*s*, 9 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.8 (C_q); 142.0 (C_q); 138.9 (C_q); 136.6 (C_q); 134.6 (C_q); 132.6 (C_q); 130.1 (CH); 128.3 (CH); 127.8 (CH); 127.2 (CH); 126.7 (CH); 125.8 (CH); 83.9 (CH); 71.6 (CH_2); 37.4 (C_q); 27.8 (Me). EI-MS: 330 (4, M^+), 273 (86), 202 (100), 77 (42). Anal. calc. for $C_{23}H_{22}O_2$: C 83.60, H 6.71; found: C 82.98, H 6.61.

Irradiation of **1r**. In *t*-BuOH with 120 mg (0.342 mmol) of **1r** for 2 h: **18r** (25 mg, 21%) and **19r** (41 mg, 34%); ratio **18r**/**19r** 1:1.6.

*Data of 1,10-Diphenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**18r**). M.p. 182°. IR (film): 1691, 1586, 1293, 1101, 960, 754, 700. ^{1}H-NMR (300 MHz, $CDCl_3$): 8.77 (*s*, 1 H); 8.12–8.07 (*m*, 1 H); 7.74–7.41 (*m*, 1 H); 7.60–7.47 (*m*, 4 H); 7.42–7.33 (*m*, 2 H); 7.28–7.20 (*m*, 2 H); 7.15–10 (*m*, 1 H); 7.01–6.98

(*m*, 2 H); 6.69 (*d*, *J* = 7.5, 1 H); 5.93 (*s*, 1 H); 4.26 (*d*, *J* = 18.1, 1 H); 4.15 (*d*, *J* = 18.1, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 195.7 (C_q); 137.8 (C_q); 137.0 (C_q); 136.5 (C_q); 135.5 (C_q); 134.4 (C_q); 132.2 (C_q); 130.3 (CH); 130.2 (CH); 129.9 (C_q); 129.5 (CH); 129.3 (CH); 129.2 (CH); 128.5 (CH); 128.4 (CH); 128.3 (CH); 128.09 (CH); 128.07 (CH); 127.8 (CH); 127.6 (C_q); 126.72 (CH); 126.65 (CH); 75.6 (CH); 67.3 (CH_2). EI-MS: 350 (3, M^+), 320 (7), 202 (18), 149 (100), 77 (49). HR-EI-MS: 350.1304 (M^+, $C_{25}H_{18}O_2^+$; calc. 350.1307).

*Data of 1,5-Diphenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**19r**). IR (film): 1728, 1377, 1119, 844, 699. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.75–7.71 (*m*, 2 H); 7.57–7.36 (*m*, 11 H); 7.29–7.26 (*m*, 2 H); 6.03 (*s*, 1 H); 4.38 (*s*, 1 H); 4.37 (*s*, 1 H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 194.9 (C_q); 143.1 (C_q); 139.03 (C_q); 139.00 (C_q); 138.90 (C_q); 134.9 (C_q); 132.7 (C_q); 130.9 (CH); 129.0 (CH); 128.8 (CH); 128.7 (CH); 128.63 (CH); 128.57 (CH); 128.2 (CH); 128.0 (CH); 127.8 (CH); 127.2 (CH); 126.7 (CH); 125.6 (CH); 125.3 (C_q); 80.9 (CH); 72.5 (CH_2). EI-MS: 350 (28, M^+), 320 (79), 202 (3), 149 (100), 77 (10). HR-EI-MS: 350.1307 (M^+, $C_{25}H_{18}O_2^+$; calc. 350.1307).

X-Ray Crystallography. The crystallographic data of *1-methoxy-7,8-diphenyl-3-oxabicyclo[4.2.0]oct-7-en-5-one* (**13a**) and of *1-methyl-10-phenyl-1*H*-benzo[*g*]isochromen-4(3*H*)-one* (**18o**) are collected in *Table 5*. Details of the structure investigations are available on request from the *Cambridge Crystallographic Data Centre*, on quoting the depository numbers CCDC-299200 (**13a**) and CCDC-299199 (**18o**). The data of an analog of **13a** bearing a 4-chlorphenyl group instead of a phenyl group in 8-position have also been deposited (CCDC-299201).

Table 5. *Crystallographic Data of* **13a** *and* **18o**

	13a	**18o**
Empirical formula	$C_{20}H_{18}O_3$	$C_{20}H_{16}O_2$
Formula weight	306.34	288.33
Temperature [K]	180(2)	180(2)
Wavelength [Å]	0.71073	0.71073
Crystal system, space group	Monoclinic, *C* 2/*c*	Triclinic, *P* -1
Unit cell dimensions: *a* [Å]	20.800(6)	6.203(2)
b [Å]	6.8731(14)	10.741(4)
c [Å]	23.935(7)	11.452(4)
α [°]	90	83.23(4)
β [°]	111.88(3)	77.90(4)
γ [°]	90	80.48(4)
Volume [Å^3]	3175.1(14)	733.0(5)
Z, calc. density [Mg/m^3]	8, 1.282	2, 1.306
Absorption coefficient [mm^{-1}]	0.085	0.083
F(000)	1296	304
Crystal size [mm]	0.76 × 0.76 × 0.40	0.58 × 0.50 × 0.36
θ-Range for data collection	2.22 to 25.25°	2.54 to 25.25°
Limiting indices	$-24 \le h \le 24$; $-8 \le k \le 8$; $-28 \le l \le 28$	$-7 \le h \le 7$; $-12 \le k \le 12$; $-13 \le l \le 13$
Refl. collected/unique	10237/2872 (R(int) = 0.1098)	4932/2481 (R(int) = 0.0498)
Completeness to θ (= 25.25°)	99.7%	93.4%
Max. and min. transmission	0.9667 and 0.9380	0.9707 and 0.9533
Refinement	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data; restraints; parameters	2872; 0; 281	2481; 0; 222
Goodness-of-fit on F^2	1.058	0.949
Final R indices ($I > 2\sigma(I)$)	$R1 = 0.0523$, $wR2 = 0.1275$	$R1 = 0.0612$, $wR2 = 0.1478$
R Indices (all data)	$R1 = 0.0610$, $wR2 = 0.1326$	$R1 = 0.1007$, $wR2 = 0.1696$
Extinction coefficient	0.0061(13)	0.084(17)
Largest diff. peak and hole	0.398 and −0.335 e A^{-3}	0.203 and −0.209 e A^{-3}

Quantum-Chemical Calculations. Geometry optimizations were performed with the Gaussian-03 program package [27] using the B3LYP hybrid functional [28] and the 6-31G* basis set. At the same level of theory, frequency calculations were carried out to characterize each structure as minimum (triplet-**1a**, **BR(3)**, **CA(5)**, **CA(6)**) or transition state (**TS(3)**–**TS(6)**), resp., and to obtain the zero-point vibrational energies. Afterwards, single-point calculations were performed with the same DFT functional using the extended basis set 6-311++G** to obtain improved energies. The energies of all calculated species are summarized in *Table 6*.

Table 6. *Results of Quantum-Chemical Calculations.* 'S' and 'T' refer to singlet and triplet states, resp., and 'A' and 'B' denote different conformers.

Compound	S/I[a])	E_1[b])	E_2[c])	ZPE[d])	E_3[e])	E_{rel}[f])	E_a[g])
1a	3/0	−882.6588433	−882.8940822	169.43389	−553855.4	±0	
TS(3)	3/1	−882.6514335	−882.8877381	168.71386	−553852.2	+3.3	3.3
T-**BR(3)**	3/0	−882.7193023	−882.9506586	170.42390	−553889.9	−34.5	
S-**BR(3)**	1/0	−882.7196085	−882.9507643	170.30794	−553890.1	−34.7	
T-**TS(4)**-A	3/1	−882.6886345	−882.9171218	170.89353	−553868.4	−13.0	21.5
T-**TS(4)**-B	3/1	−882.6887996	−882.9171075	170.95596	−553868.4	−13.0	21.5
S-**TS(4)**-A	1/1	−882.7089089	−882.9396493	170.97892	−553882.5	−27.1	7.6
S-**TS(4)**-B	1/1	−882.7084357	−882.9387624	171.12683	−553881.8	−26.4	8.3
T-**TS(5)**-A	3/1	−882.6919149	−882.9204862	171.14256	−553870.3	−14.9	19.6
T-**TS(5)**-B	3/1	−882.6910808	−882.9196566	170.98826	−553869.9	−14.5	20.0
S-**TS(5)**-A	1/1	−882.7099952	−882.9402898	171.25701	−553882.6	−27.2	7.5
S-**TS(5)**-B	1/1	−882.709098	−882.9394051	171.10479	−553882.2	−26.8	7.9
T-**TS(6)**	3/1	−882.6869116	−882.9157172	169.67684	−553868.8	−13.3	21.2
S-**TS(6)**	1/1	−882.7168799	−882.9453217	171.00078	−553886.0	−30.6	4.1
T-**CA(5)**-A	3/0	−882.7265088	−882.9542775	171.65612	−553891.0	−35.6	
T-**CA(5)**-B	3/0	−882.7267044	−882.9545939	171.65519	−553891.2	−35.8	
S-**CA(5)**-A	1/0	−882.7388198	−882.968590	172.91494	−553898.7	−43.3	
S-**CA(5)**-B	1/0	−882.7369100	−882.9668307	171.66791	−553898.8	−43.4	
T-**CA(6)**-A	3/0	−882.7360407	−882.9637126	172.28960	−553896.3	−40.9	
T-**CA(6)**-B	3/0	−882.7349839	−882.9629742	172.09589	−553896.0	−40.6	
S-**CA(6)**-A	1/0	−882.740898	−882.9695724	172.54964	−553899.7	−44.3	
S-**CA(6)**-B	1/0	−882.7401708	−882.9688943	172.36466	−553899.4	−44.0	
CB(3)	1/0	−882.7756857	−883.0005656	171.87959	−553919.8	−64.4	

[a]) Ratio of spin multiplicity (S) to number of imaginary frequencies (I). [b]) Energy at the B3LYP/6-31G* level (in a.u.). [c]) Energy at the B3LYP/6-311++G** energy level (in a.u.). [d]) Zero-point energy (in kcal/mol). [e]) $E_3 = E_2 + ZPE$ (in kcal/mol). [f]) Relative energy compared to **1a**. [g]) Activation energy.

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