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Synthesis of Benzo-fused Heterocycles by Intramolecular α-Arylation of Ketone Enolate Anions

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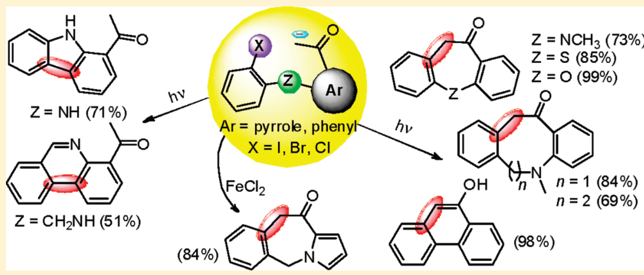
Supporting Information

ABSTRACT: A two-step synthesis of six-, seven-, eight-, and nine-member benzo-fused heterocycles in good to excellent yields is reported. The synthetic strategy involves the generation of a new intramolecular α-aryl ketone bond by the photostimulated $S_{RN}1$ reaction of ketone enolate anions linked to a pendant haloarene as the key step. On the other hand, an intramolecular $C_{Ar}-C_{Ar}$ coupling led to the formation of five- and six-member benzo-fused heterocycles (9*H*-carbazole and phenanthridine) when an aromatic amide anion is competitively formed.



■ INTRODUCTION

The α-arylated carbonyl compounds are versatile synthetic building blocks and the structural unit of a variety of bioactive natural products and therapeutic agents. In particular, dibenzo-[*b*,*f*]oxepinones (**1a**),[1] dibenzo[*b*,*f*]thiepinones (**1b**),[1a,b,f] dibenzo[*b*,*f*]azepinones (**1c**)[1b,f,2] and 5*H*-benzo[*e*]pyrrolo[1,2-*a*]azepinone (**2**)[3] are key elements for a number of biologically active molecules. For example, Bermoprofen (**3**)[4] is a nonsteroid antiinflammatory agent of clinical use and oxcarbazepine (**4**)[5] (Trileptal) is a widely prescribed drug for the treatment of epilepsy (Figure 1).

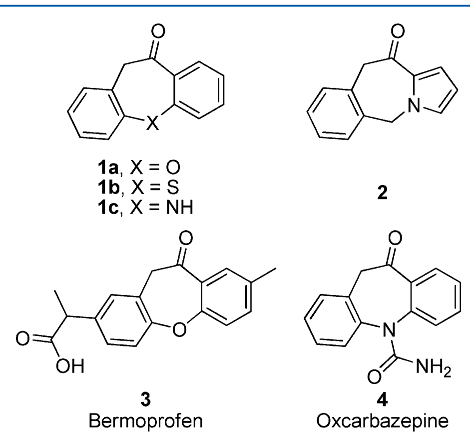


Figure 1. Examples of biologically active α-arylated carbonyl compounds.

Due to the importance of α-arylated carbonyl compounds, numerous methods are being implemented in their formation; the development of new methodologies for their synthesis is also a particularly active research area. The lack of general paths to form a bond between an arene and a carbon next to a carbonyl moiety (Cα) has encouraged the employ of heavy metal compounds, such as organolead,[6] organobismuth[7] and organocadmium[8] derivatives. However, their use is restricted since a stoichiometric amount is employed; they are also prepared through time-consuming procedures, often involving toxic and expensive materials. Furthermore, many of the procedures to form a new α-aryl ketone bond do not utilize a carbonyl compound but a less readily available derivative such as silyl enol ethers,[9] enol acetates[10] and α-halo ketones.[11]

Other methods also reported include the reaction of an enolate anion with a derivative of benzyne[12,13] and the nucleophilic aromatic substitution reaction of a stabilized enolate anion with aryl halides having electron-withdrawing groups.[14,15] However, these reactions have serious limitations due to the employ of drastic reaction conditions, limited substrate scope, moderated regioselectivity and rearrangement possibility.[16]

In the past decade particularly, the design, development and application of transition metal-catalyzed reactions for the formation of α-aryl carbonyl compounds has also been employed.[17] Some of these methods are attractive and successful.[18] However, in many cases, they still pose problems due to the use of hazardous reagents, additives, and expensive, sensitive reagents.

Photochemical reactions offer a mild and environmentally benign alternative access to α-arylated ketones in a simple way. Photoinduced S_N1 reaction has demonstrated to be useful in many cases; however, this reaction shows limited substrate scope.[19] A more straightforward method involves the aromatic unimolecular radical nucleophilic substitution or $S_{RN}1$ reac-

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tion,[20] in which an aryl halide reacts with an electron donor to produce finally an aryl radical that subsequently combines with a nucleophile. This reaction affords the possibility of achieving the nucleophilic substitution to electronically neutral aryl halides, as well as those bearing electron-donating or withdrawing substituents.

The scope of the $S_{RN}1$ reaction has increased considerably. It is nowadays a particularly valuable tool in synthetic chemistry. Several nucleophiles can be used to form new C−C or C−heteroatom bonds in good yields; it is also compatible with many substituents. When a substrate has both the leaving group and the nucleophilic center, the intramolecular radical-nucleophile coupling affords a variety of carbocyclic and heterocyclic systems fused to benzene.

The intramolecular $S_{RN}1$ has been successfully applied to the synthesis of natural products and to a variety of heterocyclic systems.[21] The first report on intramolecular $S_{RN}1$ reaction involves the synthesis of cephalotaxinone.[22] The key step of the synthetic strategy requires intramolecular nucleophilic aromatic substitution of an enolate anion onto an unactivated aromatic ring. The best yield of cephalotaxinone (94%) was obtained by irradiation of precursor in liquid ammonia with excess *t*-BuOK. A similar strategy is followed in the synthesis of the alkaloids: eupolauramine,[23] (±)-tortuosamine[24] and rugulovasine, an Ergot-type alkaloid.[25]

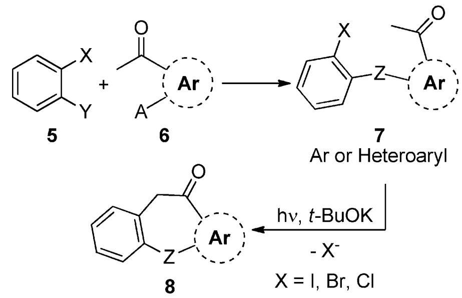
Other interesting heterocyclic compounds including substituted 9*H*-carbazoles,[26] phenanthridines and benzophenanthridines,[27] carbolines,[28] bractazonine alkaloid,[29] aporphine and homoaporphine alkaloids,[30] and azaheterocycles[31] were obtained in a similar approach exploiting the bidentate behavior of the anions of aromatic amides and alcohols.

Moreover, carbanions derived from amides,[32] 2-methylquinazolinones[33] and 2-alkyl-2-oxazolines[34] took part as nucleophiles in intramolecular coupling with aromatic and heteroaromatic radicals, giving five- and six-membered carbocyclic rings in moderate to high yields.

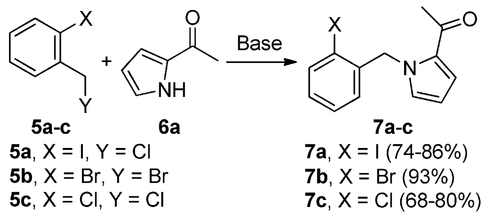
Cyclization of enolate anions with aromatic radicals by intramolecular $S_{RN}1$ reaction is expected to be extremely fast,[35] even in the formation of medium-size ring heterocycles. Semmelhack and co-workers reported that simple alkyl ketone enolate anions cyclize to give six-, seven-, eight-, and ten-membered carbocyclic rings.[36]

Our main goal was to develop an efficient application of the intramolecular $S_{RN}1$ reaction and to demonstrate the synthetic potential of this reaction in the synthesis of medium-size benzo-fused heterocycles. We studied a new synthetic strategy that involved, first, the construction of compounds like **7** having both the leaving group and the precursor of ketone carbanion tethered by a functional group Z as bridge formed by reaction of Y in **5** with A in **6**. In a second phase, the strategy includes the formation of new α-aryl ketone bond as a key step by an intramolecular $S_{RN}1$ reaction, giving the Z-heterocycles **8** (Scheme 1).

Scheme 1. Synthetic Strategy for the Synthesis of Benzo-fused Heterocycles



Scheme 2. Preparation of 1-(2-Halobenzyl)-2-acetylpyrrole 7a−c



RESULTS AND DISCUSSION

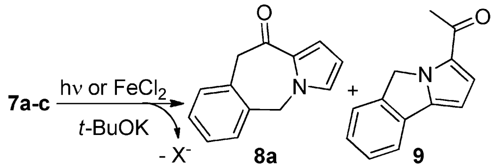
To establish the feasibility of our proposal, 1-(2-halobenzyl)-2-acetylpyrrole **7a−c** were chosen as substrate models for the study of the reaction mechanism. They were prepared from commercially available 2-halobenzyl chloride (**5a−c**) and 2-acetylpyrrole (**6a**) as shown in Scheme 2. Several variations of the approach depicted in Scheme 2 were tested.

When **7a−c** were treated with an excess of *t*-BuOK in liquid ammonia or DMSO, anions **7a−c**⁻ were formed. Under irradiation **7a−c**⁻ afforded 5*H*-benzo[e]pyrrolo[1,2-*a*]azepin-11(10*H*)-one **8a** in 38%, 31% and 45% yields respectively, together with a low amount of 3-acetyl-5*H*-pyrrolo[2,1-*a*]isoindole **9** (entries 1, 5 and 8, Table 1, eq 1). It was observed that similar substitution outcomes are obtained in both DMSO and liquid ammonia. Complete conversion of **7c** was accomplished by extending the reaction time and increasing the amount of base; however, the yields of **8a** did not improve (entries 9 and 10, Table 1).The reaction did not

Table 1. Photostimulated Reactions of 1-(2-Halobenzyl)-2-acetylpyrrole 7a−c Anions[a]

entry	substrate (%)[b]	solvent	time (h)	*t*-BuOK (equiv)	product (%)[c]	X⁻ %[d]
1	**7a**, X = I (---)	$NH_{3(liq.)}$	2	2	**8a** (38)[e], **9**[f]	[f]
2[g]	**7a** (90)	DMSO	2	2	**8a** (---)	<5
3[h]	**7a** (34)	DMSO	2	2	**8a** (3)	8
4[i]	**7a** (---)	DMSO	4.5	5	**8a** (84), **9** (11)	82
5	**7b**, X = Br (---)	DMSO	4	4	**8a** (31), **9**[f]	70
6[g]	**7b** (97)	DMSO	4	4	**8a** (---)	<5
7[j]	**7b** (37)	DMSO	4	4	**8a** (12)	8
8	**7c**, X = Cl (26)	$NH_{3(liq.)}$	2	4	**8a** (45), **9** (3)	78
9	**7c** (22)	$NH_{3(liq.)}$	2	6	**8a** (44), **9** (3)	76
10	**7c** (---)	$NH_{3(liq.)}$	6.5	5	**8a** (47), **9** (5)	76

[a]Reactions were performed in DMSO (4 mL) or in $NH_{3(l)}$ (150 mL), with substrates **7a−c** (0.25 mmol). Irradiation was conducted in a photochemical reactor equipped with two HPI-T 400 W lamps (cooled with air and water). [b]Substrate recovered. [c]Yields were determined by GC (internal standard method). [d]Halide anions were determined potentiometrically. [e]Isolated yield. [f]Not quantified. [g]Reactions were performed in the dark. [h]*p*-DNB (40 mol %) was added. [i]Reaction was performed with 0.5 equiv of $FeCl_2$ and 3 equiv of pinacolone in the dark. [j]*p*-DNB (30 mol %) was added.



(1)

occur in the dark (entries 2 and 6, Table 1), and inhibition was observed when anions **7a–b**$^-$ were irradiated in the presence of *p*-dinitrobenzene (*p*-DNB), a strong electron-acceptor (entries 3 and 7, Table 1).

The modest yields of the desired product and low mass balance could be ascribed to the sensitiveness of the starting materials to irradiation.[37] This obstacle was overcome easily by using $FeCl_2$ salt as an alternative method to initiate $S_{RN}1$ reactions.[38]

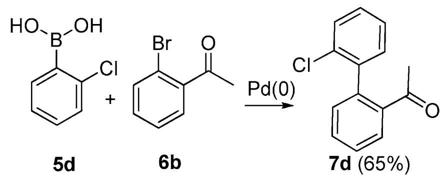
When **7a** was treated with 5 equiv of *t*-BuOK, 3 equiv of pinacolone (as electron-donor, entrainment reagent) and 0.5 equiv of $FeCl_2$ in DMSO, **8a** was obtained in 84% yield together with 11% of **9**, after 4.5 h of reaction (entry 4, Table 1).

The partial inhibition of the reaction in the presence of *p*-DNB and the lack of cyclization products in dark conditions provide evidence that the present cyclization could proceed via the $S_{RN}1$ mechanism. In addition, the fact that a similar ratio between **8a** and **9** is obtained from the reactions of **7a–c** (I, Br, Cl), under different conditions (entries 4, 8, 9, and 10, Table 1), indicates that all these reactions occur by the same mechanism.

In view of the results discussed above the mechanism sketched in Scheme 3 is proposed. The initiation step of the chain process is presumed to occur by iron or photoassisted intermolecular electron transfer (ET) to **7a–c**$^-$ yielding the radical dianion **10**.[39,40] Fragmentation of the C-X bond of **10** gives the distonic radical anion **11** and X^- ion. The intermediate radical anion **11**, via an intramolecular radical-carbanion coupling, yields the conjugated radical anion **12**. An ET from **12** to **7a–c**$^-$ affords the product **8a** and the radical dianion **10**, which propagates the reaction (Scheme 3). The intermediate distonic radical anion **11** can also couple with the pyrrole moiety to give the radical anion **13**, that by an ET and acid–base reaction gives the more stable tautomer **9** and radical dianion **10** (Scheme 3).[41]

To extend the studies of the intramolecular α-arylation reaction and to delineate the scope of the intramolecular $S_{RN}1$ reactions in the cyclization of enolate anions with aromatic radicals, new compounds like **7** were synthesized. Tables 2 and 3 display the results of the photostimulated intramolecular α-arylation reactions in liquid ammonia.

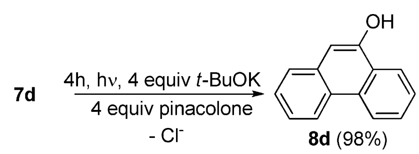
Cyclization precursor 2′-(2-chlorophenyl)acetophenone **7d** was prepared from (2-chlorophenyl)boronic acid (**5d**) and 2-bromoacetophenone (**6b**) via a Suzuki–Miyaura coupling with



(2)

biphenyl-2-yl-di-*t*-butylphosphine (JohnPhos) as ligand (eq 2).[42]

The best overall yield of the photostimulated cyclization of **7d** was obtained using excess of *t*-BuOK and pinacolone enolate ion as electron-donor. Under these reaction conditions, ketone **7d** affords excellent yield of the more stable tautomer phenanthren-9-ol (**8d**) (entry 1, Table 2, eq 3).



(3)

Having demonstrated the efficiency of the methodology for the preparation of six and seven-membered cycles, halophenyl ether and thioether ketones **7e–f** were prepared to study their potential use as substrates to afford oxygen and sulfur heterocycles. These similar substrates were synthesized from the commercially available 2-bromoacetophenone **6b** with 2-bromophenol[43] (**5e**) and 2-chlorobenzenethiol[44] (**5f**) respectively by CuI catalyzed reactions as shown in Scheme 4.

Scheme 3. Proposed Reaction Mechanism

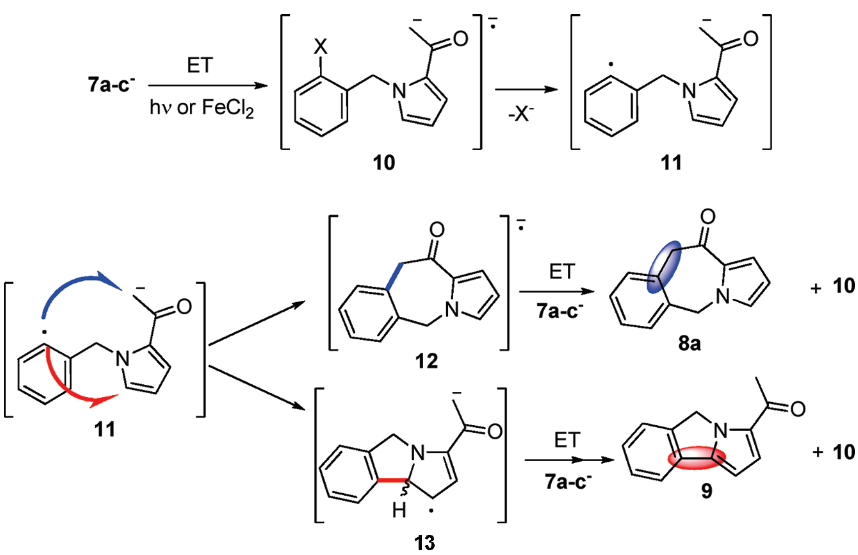
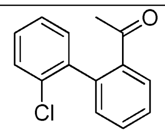
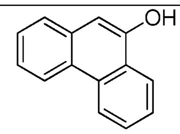
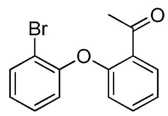
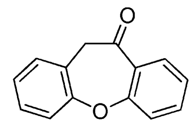
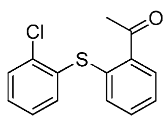
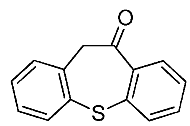
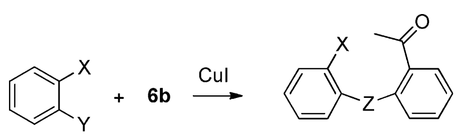


Table 2. Photostimulated Reactions of Ketone Enolate Anions 7d–f in Liquid Ammonia[a]

Entry	Substrate (%)[b]	*t*-BuOK (equiv)	Time (h)	Pinacolone (equiv)	Product (Yield %)[c]	X^- %[d]
1	 **7d** (---)	4	4	2	 **8d** (98)	[e]
2	 **7e** (61)	5.5	0.5	2	 **8e** (37)	[e]
3	**7e** (28)	5	1.3	2	**8e** (70)	[e]
4	**7e** (---)	4.8	2	2	**8e** (99)	92
5[f]	**7e** (100)	4.5	1.3	2	**8e** (---)	<8
6[g]	**7e** (33)	8	1.3	3.5	**8e** (48)	52
7	 **7f** (---)	5.2	4	2	 **8f** (85)	[e]
8[f]	**7f** (97)	8.7	4	3.7	**8f** (trace)	<8

[a]Reactions were performed in $NH_{3(l)}$ (250 mL), with substrates **7b–l** (0.15–0.25 mmol) and *t*-BuOK as base. Irradiation was conducted in a photochemical reactor equipped with two HPI-T 400 W lamps (cooled with air and water). [b]Substrate recovered. [c]Yields were determined by ^{1}H NMR (internal standard method). [d]Halide anions were determined potentiometrically. [e]Not determined. [f]Reactions were performed in the dark. [g]*p*-DNB (30 mol %) was added.

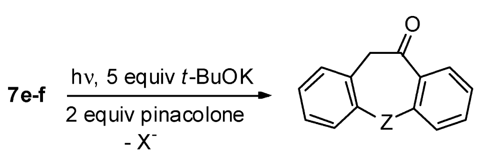
Scheme 4. Synthesis of Ketones 7e–f



5e-f **7e-f**

5e, X = Br, Y = OH **7e**, X = Br, Z = O (82%)
5f, X = Cl, Y = SH **7f**, X = Cl, Z = S (84%)

Having established suitable conditions for the cyclization reaction, the enolate anions of the 2′-(2-bromophenoxy)-acetophenone **7e** and 2′-((2-chlorophenyl)thio)acetophenone **7f** were irradiated with pinacolone enolate ion as entrainment reagent in liquid ammonia. These experiments afforded the ring closure products dibenzo[*b,f*]oxepin-10(11*H*)-one **8e** and dibenzo[*b,f*]thiepin-10(11*H*)-one **8f** in 99 and 85% yields, respectively (entries 4 and 7, Table 2, eq 4).



(4)

8e, X=O (99%)
8f, X=S (85%)

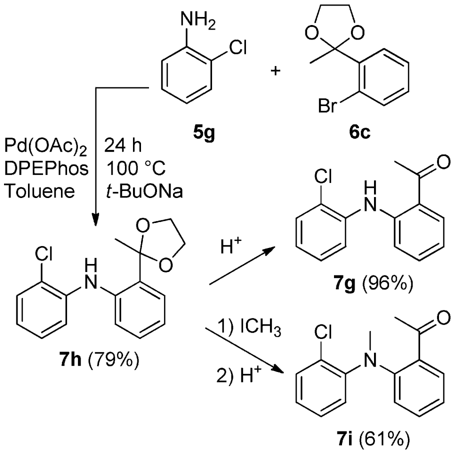
Shorter reaction time led to an incomplete conversion of **7e** (entries 2 and 3, Table 2). Cyclization of **7e–f** did not occur in the dark, and the starting material was completely recovered (entries 5 and 8, Table 2). Partial inhibition was observed when the photoassisted cyclization of **7e** was performed in presence of *p*-DNB (entry 6, Table 2). The fact that **7e–f** behaved like **7a–c** could indicate that all these reactions occur by the same mechanism.

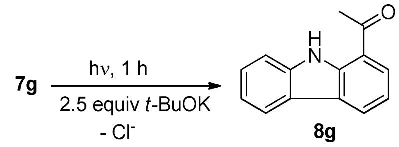
Attempts to synthesize the heterocycle **8e** from 2′-(2-chlorophenoxy)acetophenone **7e** by the benzyne mechanism were unsuccessful.[45] Recently, **8e** was synthesized in five steps from 2-phenoxybenzoic acid in 58% overall yields.[1e]

The analogous photocyclization reaction to afford a seven-member benzo-fused *N*-heterocycle was then examined. *N*-(2-(2-methyl-1,3-dioxolan-2-yl)phenyl)-2-chloro aniline (**7h**) was obtained from 2-chloroaniline (**5g**) and 2-(2-bromophenyl)-2-methyl-1,3-dioxolane (**6c**) by Pd(0) catalyzed reaction as shown in Scheme 5.[46] The hydrolysis of **7h** with dilute sulfuric acid gave the desired ketone *N*-(2-chlorophenyl)-2′-amino-acetophenone (**7g**). On the other hand, methylation of **7h** followed by hydrolysis with dilute sulfuric acid afford *N*-methyl-*N*-(2-chlorophenyl)-2′-aminoacetophenone (**7i**) (Scheme 5).

In the photoinitiated reaction of the anion **7g**$^-$ in liquid ammonia as solvent, 1-acetyl-9*H*-carbazole **8g** was formed in 71% yield; none of the expected seven-membered heterocycles could be detected (entry 1, Table 3, eq 5). Complete conversion of **7g** was accomplished by extending the reaction

Scheme 5. Preparation of the Ketones 7g−i



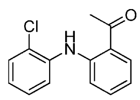
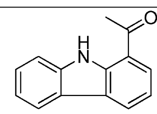
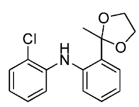
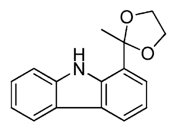
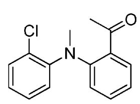
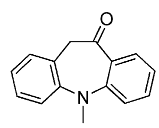
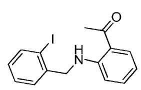
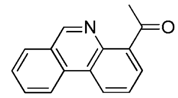
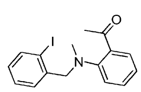
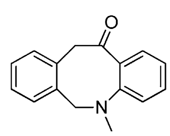
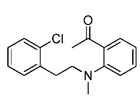
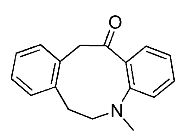


(5)

time, affording the ring closure product **8g** in 86% isolated yield (entry 2).

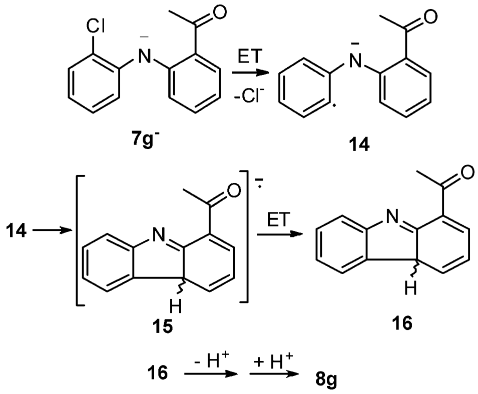
The regiochemistry in this reaction could be explained considering that the acidic hydrogen of the N−H group of the diarylamine should be more acidic that the hydrogen of the acetyl group in **7g**.[47] In this reaction, the distonic radical anion **14** (formed by ET to **7g**$^-$ and fragmentation of the C−Cl bond) via an intramolecular C_{Ar}−C_{Ar} coupling yields the conjugated radical anion **15**. An ET from **15** to **7g**$^-$ affords the intermediate **16**, which ultimately gives the tautomer more stable **8g** (Scheme 6).[26] A nonchain process initiated by an intra-

Table 3. Photostimulated Reactions of Ketone Enolate Anions 7g−l$^-$ in Liquid Ammonia[a]

Entry	Substrate (%)[b]	t-BuOK (equiv)	Time (h)	Pinacolone (equiv)	Product (Yield %)[c]	X$^-$ %[d]
1	 **7g** (21)	2.5	1	--	 **8g** (71)	64
2	**7g**	3	2.5	--	**8g** (86)[e]	86
3	 **7h** (---)	2.5	0.5	--	 **8h** (92)[e]	95
4	 **7i** (29)	7	3	3.6	 **8i** (41)	[f]
5	**7i** (---)	7	5	2.6	**8i** (73)	94
6	 **7j** (---)	3	2	--	 **8j** (51)[e]	86
7	 **7k** (---)	3	2	--	 **8k** (84)(78)[e]	[f]
8	 **7l** (35)	6	4	--	 **8l** (23)	57
9	**7l** (---)	7	5	2.5	**8l** (69)	90

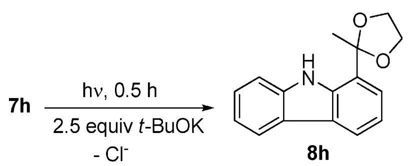
[a]Reactions were performed in $NH_{3(l)}$ (250 mL), with substrates **7b−l** (0.15−0.25 mmol) and t-BuOK as base. Irradiation was conducted in a photochemical reactor equipped with two HPI-T 400 W lamps (cooled with air and water). [b]Substrate recovered. [c]Yields were determined by ^{1}H NMR (internal standard method). [d]Halide anions were determined potentiometrically. [e]Isolated yield. [f]Not determined

Scheme 6. Possible Reaction Mechanism to Formation of Carbazole 8g



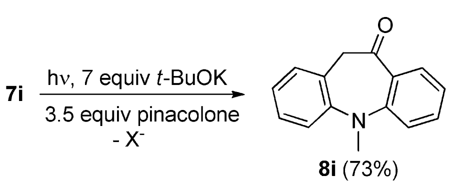
molecular ET of the amide anion to the haloarene is possible, and an intramolecular radical−radical coupling cannot be ruled out.

The protection of the carbonyl group in **7g** increased the rate of formation of the carbazole. When treated with 2.5 equiv of *t*-BuOK in liquid ammonia, diarylamine **7h** gave 1-(2-methyl-1,3-dioxolan-2-yl)-9*H*-carbazole **8h** in 92% yield after only 0.5 h of irradiation (entry 3, Table 3, eq 6).



(6)

As expected, the intramolecular radical-enolate anion coupling to afford seven-membered *N*-heterocycle by intramolecular α-arylation reaction occurred when the N−H group in **7g** was substituted. The acid−base reaction of **7i** with *t*-BuOK in excess in liquid ammonia gave ketone enolate anion **7i**⁻. When **7i**⁻ was irradiated in the presence of 3.6 equiv of pinacolone enolate anion, the expected 5-methyl-5*H*-dibenzo-[*b*,*f*]azepin-10(11*H*)-one **8i** was obtained in 41% yield (entry 4, Table 3). By increasing the reaction time, complete conversion was reached and the desired product **8i** was formed in 73% yield (entry 5, eq 7).



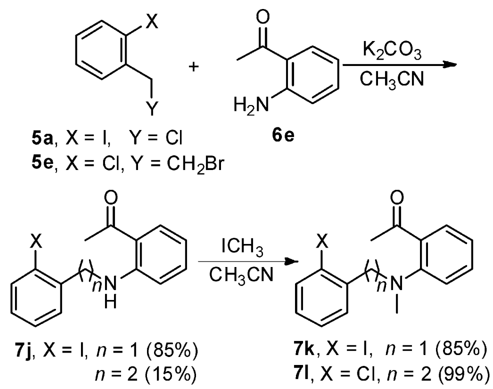
(7)

Of particular interest is the observation that by a simply modification of the starting material under similar condition, the regiospecificity of the reaction can be changed by the formation of valuable molecules such as the carbazoles[48] and dibenzo[*b*,*f*]azepinones.[1b,f,2]

Due to the efficiency of the methodology for the preparation of five-, six- and seven-membered benzo-fused carbo- and N-, O-, S-heterocycles, other substrates like **7** were prepared to establish their feasibility to form eight- and nine-membered benzo-fused N-heterocycles.

N-(2-Iodobenzyl)-2′-aminoacetophenone **7j** was prepared by benzylation of the commercially available 2′-aminoacetophenone **6e** with 2-iodobenzyl chloride **5a** in CH_3CN as solvent. The methylation of **7j** gave the ketone *N*-methyl-*N*-(2-iodobenzyl)-2′-aminoacetophenone **7k** as shown in Scheme 7.

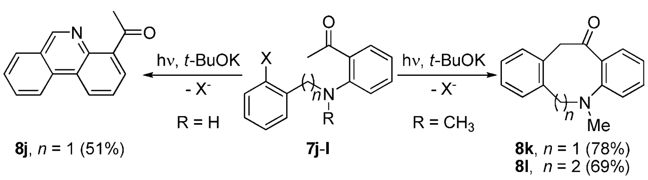
Scheme 7. Preparation of the Ketones 7j−l



Similarly, *N*-methyl-*N*-(2-chlorophenethyl)-2′-aminoacetophenone **7l** was obtained by alkylation of **6e** with 1-(2-bromoethyl)-2-chlorobenzene **5e** followed by methylation (Scheme 7).

In the photostimulated reaction of **7j** in liquid ammonia and in the presence of 3 equiv of *t*-BuOK, 4-acetylphenanthridine **8j** was achieved in 51% isolated yield and none of the desired eight-member heterocycle was detected (entry 6, Table 3, Scheme 8).

Scheme 8. Photostimulated Reactions of Ketone 7j−l



Interestingly, **7j** shows a similar behavior to **7g**, which only afford the product of the nucleophilic substitution via the bidentate anion of the aromatic amine.[27]

When the ketone **7k** was treated with 3 equiv of *t*-BuOK and irradiated for 2 h in liquid ammonia, the expected eight-member heterocycle 5-methyl-5,6-dihydrodibenzo[*b*,*f*]azocin-12(11*H*)-one **8k** was obtained in 78% isolated yield (entry 7, Table 3, Scheme 8). In addition, the cyclization of ketone **7l** was slower than of **7k** and only 23% of the desired nine-member ring was obtained after 4 h of irradiation (entry 8). Complete conversion was achieved when **7l** was irradiated for 5 h in the presence of 7 equiv of *t*-BuOK and 2.5 equiv of pinacolone enolate ion (entrainment reagent). Under this reaction condition, the nine-member ring 5-methyl-6,7-dihydro-5*H*-dibenzo[*b*,*f*]azonin-13(12*H*)-one **8l** was obtained in 69% yield (entry 9).

■ CONCLUSIONS

The present paper reports our studies on photostimulated intramolecular $S_{RN}1$ reactions using acetyl enolate anions as nucleophiles. The intramolecular radical-acetyl enolate anion coupling affords a new α-aryl ketone bond as the key step in the synthesis of six-, seven, eight and nine-member benzo-fused N-, O-, S-heterocycles.

9*H*-carbazole and phenanthridine were selectively formed via an intramolecular $C_{Ar}-C_{Ar}$ coupling when the Z-bridge group in the compounds like **7** has nitrogen capable of forming an aromatic amide anion.

Considering the good yields and the value of the molecules obtained, the slow cost, availability and/or simplicity of the starting material, and the short time and mild reaction conditions, this methodology could be a valuable alternative to access to cyclic α-arylated ketones in a simple approach.

■ EXPERIMENTAL SECTION

General Considerations. Gas chromatographic analyses were performed using a gas chromatograph with a flame ionization detector, and equipped with the following columns: 25 m x 0.20 mm x 0.25 μm column and 15 m × 0.25 mm × 0.25 μm column. ^{1}H NMR (400.16 MHz), ^{13}C NMR (100.63 MHz) spectra were obtained in acetone-d_6, DMSO-d_6 and $CDCl_3$ as solvents. Coupling constants are given in Hz and chemical shifts are reported in δ values in ppm. Data are reported as followed: chemical shift, multiplicity (s = singlet, s br = broad singlet, d = doublet, t = triplet, dd = double doublet, dt = double triplet, ddd = double double doublet, m = multiplet), coupling constants (Hz), and integration. Gas Chromatographic/Mass Spectrometer analyses were carried out on a GC/MS spectrometer equipped with a 30 m × 0.25 mm × 0.25 μm column. Irradiation was conducted in a reactor equipped with two 400-W lamps[49] (cooled with water). Potentiometric titration of halide ions where performed in a pHmeter using an Ag/Ag$^+$ electrode. Melting points were performed with an electrical instrument. The high resolution mass (HRMS) of pure products were recorded on equipment, operated with an ESI source operated in (positive/negative) mode, using nitrogen as nebulizing and drying gas and sodium formiate 10 mM as internal calibrate instrument.

Materials. Iodomethane, 2-iodobenzyl chloride, 2-bromobenzyl chloride, 2-chlorobenzyl chloride, 1-(2-bromoethyl)-2-chlorobenzene, 2-acetylpyrrole, (2-chlorophenyl)boronic acid, 2-bromoacetophenone, 2-bromophenol, 2-chlorobenzenethiol, 2-chloroaniline, 2′-aminoacetophenone, N^1,N^2-dimethylethan-1,2-diamine, tetrabutylammonium bromide (TBAB), 2-naphthoic acid, *t*-BuOK, NaOH, Cs_2CO_3, NaH, y CuI were commercially available and used as received from the supplier. DMSO was stored under molecular sieves (4 Å). Tetrahydrofuran (THF) and toluene was distilled from Na−benzophenone and stored under N_2 atmosphere. All solvents were analytical grade and used as received from the supplier. Silica gel (0.063−0.200 mm) was used in column chromatography, and 1, 2 and 4 mm silica gel (60 PF254) plates were employed in radial thin-layer chromatography purification.

Experimental Procedures and Characterization Data for the Starting Materials. The starting materials were synthesized by utilizing standard synthetic organic methods according to literature procedures: compounds 1-(2-halobenzyl)-2-acetylpyrrole **7a**−**c**,[50] 2′-(2-chlorophenyl)acetophenone (**7d**),[42] 2′-(2-bromophenoxy)-acetophenone (**7e**),[43] 2′-((2-chlorophenyl)thio)acetophenone (**7f**).[44]

Synthesis of 1-(2-Halobenzyl)-2-acetylpyrrole (7a−c). *Method A.* From the anion of the 2-acetylpyrrole **6a**$^-$ in organic solvent. A flame-dried Schlenk tube under nitrogen atmosphere was charged with sodium hydride in mineral oil (60%, 0.088 g, 2.2 mmol), 2-acetylpyrrole (0.20 g, 1.84 mmol) and 5 mL of DMSO. The mixture was stirred at room temperature for 75 min and then a solution of 2-iodobenzyl chloride (0.53 g, 2.12 mmol) in dry diethyl ether was added. The reaction was stirred for 22 h and then diluted with water and CH_2Cl_2. The aqueous phase was extracted with CH_2Cl_2 (4 × 20 mL). The resulting solution was dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was purified by column chromatography on silica gel affording 1-(2-iodobenzyl)-2-acetylpyrrole **7a** in 74% yield (0.442 g, 1.36 mmol).

Method B. Typical phase Transfer Catalysis. A round-bottomed flask was charged with 2-acetylpyrrole (0.221 g, 2.03 mmol, 1.27 equiv), TBAB (0.0645 g, 0.2 mmol, 10 mol %), a 50% aqueous solution of NaOH (1 mL) and 2.5 mL of CH_2Cl_2. The mixture was stirred at rt and 2-iodobenzyl chloride (0.3961 g, 1.57 mmol) was added in portions. The reaction was carried out at this temperature until the electrophile had been consumed as judged by GC analysis (3 h approximately). Each individual reaction was not optimized in terms of temperature, quantity of catalyst or reaction time. The mixture was diluted with water and CH_2Cl_2. The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic phase was dried ($MgSO_4$), filtered, and the solvent removed *in vacuo* to provide the crude product as a light-colored solid. **7a** was purified by column chromatography on silica gel eluting with a petroleum ether/diethyl ether gradient (90:10→70:30) and 79% (0.4047 g, 1.24 mmol) was isolated as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.5 Hz, 1H), 7.05 (m, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.84 (m, 1H), 6.46 (d, *J* = 7.6 Hz, 1H), 6.23 (m, 1H), 5.56 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3 (C), 140.7 (C), 139.3 (CH), 130.4 (CH), 130.3 (CH), 128.9 (CH), 128.5 (CH), 127.1 (CH), 120.2 (CH), 108.8 (C), 97.4 (C), 57.7 (CH2), 27.2 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 6.94/7.84, 6.94/7.20, 6.84/7.05, 6.46/7.20, 6.23/7.05, 6.23/6.84. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C δ 7.84/139.3, 7.20/128.5, 7.05/120.2, 6.94/128.9, 6.84/130.3, 6.46/127.1, 6.23/108.8, 5.56/57.7, 2.42/27.2. GC-MS (*m*/*z*): 326 (M$^+$ + 1, 1); 325 (M$^+$, 77); 217 (38); 199 (15); 198 (M$^+$ − 127, 100); 183 (18); 182 (6); 156 (27); 155 (12); 154 (19); 128 (5); 127 (9); 91 (7); 90 (34); 89 (22); 77 (9); 63 (8); 51 (5). mp 100.3−101.5 °C. HRMS: calcd for $C_{13}H_{13}NOI$ 326.0036; found [MH]$^+$ 326.0047.

*1-(2-Bromobenzyl)-2-acetylpyrrole (**7b**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.8 Hz, 1H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.04 (m, 1H), 6.87 (m, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.22 (m, 1H), 5.64 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.4 (C), 137.9 (C), 132.7 (CH), 130.5 (CH), 128.8 (CH), 127.8 (CH), 127.7 (CH), 122.4 (C), 120.4 (CH), 108.9 (CH), 52.9 (CH2), 27.3 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/ δ_H 7.10/7.55, 6.87/7.04, 6.53/7.16, 6.22/7.04, 6.22/6.87. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/ δ_C 7.55/132.7, 7.16/127.7, 7.10/128.8, 7.04/120.4, 6.87/130.5, 6.53/127.7, 6.22/108.9, 5.65/52.9, 2.42/27.3. GC-MS (*m*/*z*): 279 (M$^+$ + 1, 3); 278 (M$^+$, 1); 277 (4); 264 (4); 199 (12); 198 (M$^+$ − 79, 100); 183 (14); 171 (30); 169 (46); 156 (23); 155 (12); 154 (13); 127 (8); 91 (5); 90 (26); 89 (20); 77 (6); 63 (9); 51 (5). mp 80−81 °C. (lit.[3b,c] 80−81 °C).

*1-(2-Chlorobenzyl)-2-acetylpyrrole (**7c**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12 (t, *J* = 7.4 Hz, 1H), 7.04 (m, 1H), 6.89 (m, 1H), 6.61 (d, *J* = 7.5 Hz, 1H), 6.22 (m, 1H), 5.68 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.3 (C), 136.2 (C), 132.5 (C), 130.6 (CH), 130.5 (C), 129.3 (CH), 128.5 (CH), 127.7 (CH), 127.1 (CH), 120.3 (CH), 108.7 (CH), 50.3 (CH2), 27.2 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.18/7.37, 7.12/7.18, 6.89/7.04, 6.61/7.12, 6.2/7.04, 6.22/6.89. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 7.37/129.3, 7.18/128.5, 7.12/127.1, 7.04/120.3, 6.89/130.6, 6.61/127.7, 6.22/108.7, 5.68/50.3, 2.43/27.2. GC-MS (*m*/*z*): 235 (M$^+$ + 2,4); 233 (M$^+$, 13); 220 (4); 218 (11); 199 (13); 198 (M$^+$ − 35, 83); 190 (14); 183 (9); 156 (14); 154 (7); 127 (37); 126 (8); 125 (100); 99 (8); 90 (7); 89 (23); 63 (8); 51 (5). Mp 69−70 °C. HRMS: calcd for $C_{13}H_{13}ClNO$ 234.0680; found [MH]$^+$ 234.0687.

*2′-(2-Chlorophenyl)acetophenone (**7d**).* (2-Chlorophenyl)-boronic acid (0.128 g, 0.82 mmol, 1.5 equiv), 2-bromoacetophenone (0.995 g, 0.54 mmol), $Pd(OAc)_2$ (0.0026 g, 2.0 mol %), KF (0.087 g, 1.5 mmol, 3 equiv), and [1,1′-biphenyl]-2-yl-di-*tert*-butylphosphine (0.0068 g, 4 mol %) were sequentially added to an flame-dried Schlenk tube. The mixture was suspended in THF (1.5 mL) and stirred for 2 h at rt. The mixture was directly purified by column chromatography on silica gel with a petroleum ether/diethyl ether gradient (100:0 → 90:10) to provide 2′-(2-chlorophenyl)acetophenone in 65% yield (0.0817 g, 0.35 mmol) as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.53 (td, *J* = 7.5, 1.4 Hz, 1H), 7.49−7.41 (m, 2H), 7.34−7.29 (m, 2H), 7.28 (m, 1H), 7.26−7.21 (m, 1H), 2.21 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.4 (C), 140.0 (C), 139.4 (C), 138.2 (C), 132.5 (C), 131.1 (CH), 131.0 (CH), 130.9 (CH), 129.4 (CH), 129.0 (CH), 128.2 (CH), 128.0 (CH), 126.8

(CH), 29.0 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.45/7.73, 7.45/7.53, 7.31/7.45, 7.28/7.53, 7.24/7.31, 7.23/7.45. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/ δ_C 7.75/128.2, 7.53/131.0, 7.45/128.0, 7.45/129.4, 7.31/129.0, 7.31/126.8, 7.28/131.1, 7.24/130.9, 2.20/29.0. GC-MS (m/z): 215 (M^+ − 15, 2), 197 (1), 196 (13), 195 (M^+ − 35, 100), 152 (27), 151 (9), 149 (6), 76 (12). HRMS: calcd for $C_{14}H_{12}ClO$ 231.0571; found $[MH]^+$ 231.0592.

*Synthesis of 2′-(2-bromophenoxy)acetophenone (**7e**).* A flame-dried Schlenk tube was charged with molecular sieves 4 Å (0,562 g), Cs_2CO_3 (4 mmol), CuI (0.1 mmol) and 2-naphthoic acid (4 mmol), evacuated and filled with nitrogen. Toluene (1.5 mL), 2-bromophenol (4 mmol), 2-bromoacetophenone (2 mmol) and ethyl acetate (0.1 mmol) where added via syringe. The reaction tube was purged with nitrogen, and the mixture was heated with stirring to 100 °C for 29 h. Upon cooling at room temperature, dichloromethane was added and the solvent was removed by filtration. The organic phase was concentrated, and 2-bromophenol was distilled under reduced pressure using a Kügelrohr apparatus. The 2′-(2-bromophenoxy)-acetophenone **7e** was purified by column chromatography on silica gel with a petroleum ether/diethyl ether gradient (100:0 → 90:10) as colorless oil in 82% yield (0.465 g, 1.7 mmol). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 7.8, 1.8 Hz, 1H), 7.67 (dd, J = 8.0, 1.6 Hz, 1H), 7.41 (ddd, J = 8.3, 7.3, 1.8 Hz, 1H), 7.31 (ddd, J = 8.1, 7.5, 1.6 Hz, 1H), 7.17 (td, J = 7.8, 1.0 Hz, 1H), 7.10−7.06 (m, 1H), 6.98 (dd, J = 8.1, 1.5 Hz, 1H), 6.74 (dd, J = 8.3, 0.9 Hz, 1H), 2.72 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8 (C), 155.9 (C), 152.6 (C), 134.1 (CH), 133.6 (CH), 130.7 (CH), 129.7 (C), 128.9 (CH), 125.7 (CH), 123.4 (CH), 120.7 (CH), 117.5 (CH), 115.0 (C), 31.8 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.41/7.87, 7.31/7.67, 7.17/7.86, 7.17/7.41, 7.08/7.67, 7.08/7.31, 6.98/7.31, 6.74/7.42. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 7.85/130.7, 7.67/134.1, 7.40/133.6, 7.30/128.9, 7.16/123.4, 7.07/125.7, 6.96/120.7, 6.74/117.5, 2.72/31.8. GC-MS (m/z): 292 (M^+ + 2, 1); 290 (M^+ − 1, 1); 277 (12); 275 (12); 212 (23); 211 (M^+ − 79, 100); 197 (10); 196 (73); 168 (34); 139 (34); 121 (7); 119 (30); 118 (15); 106 (10); 92 (7); 91 (20); 77 (6); 76 (13); 75 (10); 65 (6); 64 (8); 63 (12); 51 (6); 50 (11).

*2′-((2-Chlorophenyl)thio)acetophenone (**7f**).* A flame-dried Schlenk tube was charged with 2-bromoacetophenone (1 mmol), 2-chlorobenzenethiol (0.5 mmol), CuI (0.05 mmol), N[1],N[2]-dimethylethan-1,2-diamine (4.0 mmol) and water (6.5 mL) under nitrogen at room temperature. The reaction mixture was heated to 120 °C for 36 h, allowed to cool to room temperature and the resulting mixture was extracted with CH_2Cl_2 (4 × 5 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The 2-bromoacetophenone was distilled under reduced pressure using a Kügelrohr apparatus. The colored residue was purified by silica gel column chromatography with a petroleum ether/diethyl ether gradient (90:10 → 50:50) to afford the 2′-((2-chlorophenyl) thio)acetophenone **7f** in 84% yield (0.110 g, 0.42 mmol) as white crystal. Mp 87−88.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (dd, J = 7.7, 1.6 Hz, 1H), 7.57 (dd, J = 7.6, 1.8 Hz, 1H), 7.52 (dd, J = 7.9, 1.4 Hz, 1H), 7.36 (td, J = 7.7, 1.8 Hz, 1H), 7.31−7.27 (m, 2H), 7.22 (td, J = 7.5, 1.2 Hz, 1H), 6.80 (dd, J = 8.0, 1.2 Hz, 1H), 2.67 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2 (C), 139.5 (C), 138.9 (C), 136.8 (CH), 134.9 (C), 132.5 (C), 132.2 (CH), 130.8 (CH), 130.4 (CH), 130.38 (CH), 128.0 (CH), 127.8 (CH), 124.9 (CH), 28.1 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.36/7.52, 7.29/7.58, 7.29/7.36, 7.22/7.85, 7.22/7.29, 6.80/7.29. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/ δ_C 7.84/130.8, 7.57/136.8, 7.52/130.5, 7.36/130.38, 7.29/132.2, 7.29/127.8, 7.22/124.9, 6.80/128.0, 2.67/28.1. GC-MS (m/z): 265 (5); 264 (39); 263 (15); 262 (M^+, 100); 249 (35); 248 (13); 247 (90); 227 (14); 213 (9); 212 (66); 185 (12); 184 (65); 183 (17); 152 (19); 151 (37); 139 (37); 138 (6); 137 (38); 135 (10); 134 (7); 113 (4); 108 (14); 91 (16); 82 (6); 77 (5); 76 (6); 75 (10); 74 (6); 69 (14); 63 (9); 51 (7); 50 (8); 45 (6). HRMS (IE) calcd for $C_{14}H_{12}OSCl$ 263.0292; found $[MH]^+$ 263.0298.

*N-(2-(2-Methyl-1,3-dioxolan-2-yl)phenyl)-2-chloro aniline (**7h**).* A flame-dried Schlenk tube was charged with 2-chloroaniline (0.29 g, 2.27 mmol), *t*-BuONa (0.265 g, 2.75 mmol), $Pd(OAc)_2$ (0.010 g, 2 mmol %) and DPEphos (0.04 g, 0.075 mmol), evacuated and filled with nitrogen. The 2-(2-bromophenyl)-2-methyl-1,3-dioxolane (obtained from the 2-bromoacetophenone)[51] (0.47 g, 1.94 mmol) was added to the flash, followed by toluene (4 mL). The reaction was heated with stirring to 110 °C for 24 h. The mixture was then cooled to room temperature and partitioned between water and CH_2Cl_2. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The crude product was purified by radial thin-layer chromatography eluting with petroleum/CH_2Cl_2 (90/10) to afford the 2-chloro-N-(2-(2-methyl-1,3-dioxolan-2-yl)phenyl)aniline in 79% (0.458 g, 1.58 mmol) as a white solid, m.p 79.7−80.7. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (s br, 1H), 7.52 (dd, J = 7.7, 1.6 Hz, 1H), 7.38−7.32 (m, 3H), 7.24−7.19 (m, 1H), 7.14−7.10 (m, 1H), 6.94 (td, J = 7.6, 1.1 Hz, 1H), 6.81 (td, J = 7.9, 1.5 Hz, 1H), 4.15−4.06 (m, 2H), 3.93−3.84 (m, 2H), 1.68 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.0 (C), 139.8 (C), 131.0 (C), 129.9 (CH), 128.7 (CH), 127.2 (CH), 126.7 (CH), 122.8 (C), 121.0 (CH), 120.6 (CH), 118.4 (CH), 116.6 (CH), 109.3 (C), 64.3(2 CH2), 25.1 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.21/7.35, 7.12/7.35, 6.94/7.52, 6.94/7.21, 6.81/7.35, 6.81/7.12, 3.88/4.10. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/ δ_C 7.52/126.7, 7.35/129.9, 7.35/118.4, 7.35/116.6, 7.21/128.7, 7.12/127.2, 6.95/121.0, 6.81/120.6, 4.10/64.3, 3.88/64.3, 1.68/25.1. ^{1}H−^{13}C HMBC NMR ($CDCl_3$) δ_H/δ_C 7.52/139.8, 7.52/128.7, 7.52/109.3, 7.35/140.0, 7.35/131.0, 7.35/127.2, 7.35/122.8, 7.35/120.6, 7.21/139.8, 7.21/126.7, 7.12/140.0, 7.12/131.0, 7.12/116.6, 6.94/131.0, 6.94/118.4, 6.81/122.8, 6.81/116.6, 4.10/109.3, 3.88/109.3, 1.68/131.0, 1.68/109.3. GC-MS (m/z): 292 (M^+ + 1, 4), 291 (M^+ + 1, 35), 290 (M^+, 12), 289 (100), 276 (21), 274 (73), 254 (27), 246 (16), 245 (11), 244 (37), 232 (14), 230 (40), 210 (62), 196 (10), 195 (46), 194 (12), 193 (12), 192 (16), 182 (12), 181 (11), 180 (31), 168 (12), 167 (46), 166 (22), 164 (23), 139 (11), 120 (56), 116 (13), 115 (27), 87 (16), 83 (31), 77 (10), 75 (12). HRMS (IE) calcd for $C_{16}H_{17}ClNO_2$ 290.0942; found $[MH]^+$ 290.0956.

*N-Methyl-N-(2-chlorophenyl)-2′-aminoacetophenone (**7i**).* A mixture of *N*-(2-(2-methyl-1,3-dioxolan-2-yl)phenyl)-2-chloro aniline **7h** (0.226 g, 0.78 mmol), *t*-BuOK (0.134 g, 1.19 mmol), and iodomethane (0.227 g, 1.6 mmol) in DMSO (5 mL) was stirred at 50 °C for 3 h. The mixture was diluted with water and extracted with CH_2Cl_2 (2 × 15 mL) and ethyl acetate (2 × 15 mL). The organic extracts were dried and concentrated. The residue was dissolved in dioxane (1 mL) in a round-bottomed flask fitted with a reflux condenser. Water (5 mL), followed by H_2SO_4 concentrated (4 drops) was added and the reaction was heated with stirring to 90 °C for 4 h. The solution was basified with Na_2CO_3 and extracted. The crude product was purified by radial thin layer chromatography with a petroleum ether/methylene chloride gradient (90:10 → 70:30) in 61% yield as a colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38−7.34 (m, 3H), 7.19 (td, J = 7.7, 1.5 Hz, 1H), 7.06−6.98 (m, 4H), 3.25 (s, 3H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2 (C), 148.1 (C), 147.0 (C), 134.3 (C), 131.6 (CH), 131.2 (CH), 129.2 (C), 129.0 (CH), 127.8 (CH), 125.0 (CH), 124.9 (CH), 122.2 (CH), 120.4 (CH), 42.0 (CH2), 29.1 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.19/7.36, 7.02/7.36, 7.02/7.19. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/ δ_C 7.36/131.2, 7.36/129.0, 7.36/124.9, 7.19/127.8, 7.02/131.6, 7.02/125.0, 7.02/122.2, 7.02/120.4, 3.25/42.0, 2.42/29.1. ^{1}H−^{13}C HMBC NMR ($CDCl_3$) δ_H/δ_C 7.36/203.2, 7.36/147.0, 7.36/131.6, 7.36/127.8, 7.19/147.0, 7.19/131.2, 7.02/134.3, 7.02/129.2, 7.02/124.9, 7.02/122.2, 7.02/120.4, 3.25/147.0, 2.42/203.2. GC-MS (m/z): 262 (M^+ + 2, 4), 261 (M^+ + 1, 26), 259 (M^+ − 1, 72), 246 (28), 245 (12), 244 (M^+ − 15, 100), 242 (55), 209 (22), 194 (11), 181 (38), 180 (58), 166 (15), 152 (14), 140 (15), 139 (10), 138 (13), 105 (13), 77 (28), 75 (15), 51 (11).

*N-(2-Chlorophenyl)-2′-aminoacetophenone (**7g**).* In a round-bottomed flask was dissolved *N*-(2-(2-methyl-1,3-dioxolan-2-yl)-phenyl)-2-chloro aniline **7h** (0.11 g, 0.38 mmol) in dioxane (1 mL). Water (5 mL), followed by H_2SO_4 concentrated (2 drops) was added and the reaction was heated with stirring to 90 °C for 4 h. The mixture was then cooled to room temperature, basified with Na_2CO_3 and extracted with CH_2Cl_2 and ethyl acetate. The *N*-(2-chlorophenyl)-2′-aminoacetophenone **7g** was purified by radial thin layer chromatography eluting with petroleum/diethyl ether (90/10) in 96% yield as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.62 (s br, 1H), 7.84 (dd, J = 8.0, 1.4 Hz, 1H), 7.49 (dd, J = 8.1, 1.3 Hz, 1H), 7.44 (dd, J = 8.0, 1.4 Hz, 1H), 7.36−7.32 (m, 1H), 7.25−7.20 (m, 2H), 7.01 (td, J = 7.8, 1.5 Hz, 1H), 6.82−6.78 (m, 1H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.2 (C), 146.4 (C), 137.7 (CH), 134.4 (CH), 132.4 (CH), 130.3 (CH), 127.3 (C), 127.1 (CH), 124.1 (CH), 122.6 (CH), 120.2 (C), 117.5 (CH), 114.6 (CH), 28.1 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.34/7.85, 7.22/7.49, 7.22/7.34, 7.01/7.44, 7.01/7.22, 6.80/7.84, 6.80/7.34. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 7.84/132.4, 7.49/122.6, 7.44/130.3, 7.34/134.4, 7.22/127.1, 7.22/114.6, 7.01/124.1, 6.80/117.5, 2.66/28.1. GC-MS (m/z): 248 (M^+ + 2, 5), 247 (M^+ + 1, 35), 246 (M^+, 15), 245 (M^+ − 1, 100), 232 (12), 230 (35), 210 (67), 196 (11), 195 (81), 182 (9), 180 (12), 168 (13), 167 (40), 166 (22), 140 (10), 139 (14), 120 (56), 83 (19). HRMS calcd for $C_{14}H_{12}ClNaNO$ 268.0500; found $[MH]^+$ 268.0515.

N-(2-Iodobenzyl)-2′-aminoacetophenone (7j). A mixture of 2′-aminoacetophenone (0.350 g, 2.59 mmol), K_2CO_3 (0.519 g, 3.76 mmol), and 2-iodobenzyl chloride (0.323 g, 1.28 mmol) in acetonitrile (5 mL) was stirred at 85 °C in a sealed tube for 72 h. The mixture was diluted with water and was extracted with CH_2Cl_2 (3 × 15 mL) and diethyl ether (2 × 10 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the solvent removed *in vacuo*. The residue was purified by column chromatography (silica gel, petroleum ether/diethyl ether (90:10)) to give *N*-(2-iodobenzyl)-2′-aminoacetophenone **7j** (0.3828 g, 1.09 mmol, 85%). The solid was recrystallized in petroleum ether as white needles crystals, m.p.: 128.3−129.3 °C (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s br, 1H), 7.85 (d, J = 7.8 Hz, 1H), 7.78 (dd, J = 8.1, 1.4 Hz, 1H), 7.31−7.24 (m, 3H), 6.98−6.93 (m, 1H), 6.64−6.60 (m, 1H), 6.52 (d, J = 8.5 Hz, 1H), 4.42 (d, J = 6.0 Hz, 2H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.1 (C), 150.6 (C), 140.1 (C), 139.4 (CH), 135.1 (CH), 132.7 (CH), 128.9 (CH), 128.4(CH), 128.0 (CH), 118.0 (C), 114.7 (CH), 112.2 (CH), 98.2 (C), 51.9 (CH2), 28.0 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 6.95/7.85, 6.95/7.23, 6.63/7.78, 6.63/7.27, 6.52/7.27. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 7.85/139.4, 7.78/132.7, 7.27/135.1, 7.27/128.4, 7.27/128.0, 6.95/128.9, 6.63/114.7, 6.52/112.2, 4.42/51.9, 2.62/28.0. ^{1}H−^{13}C HMBC NMR ($CDCl_3$) δ_H/δ_C 7.85/140.1, 7.85/128.4, 7.85/98.2, 7.78/201.1, 7.78/150.6, 7.78/135.1, 7.27/150.5, 7.27/140.1, 7.27/132.5, 7.27/128.9, 7.27/98.2, 6.95/128.0, 6.63/118.0, 6.63/112.2, 6.52/118.0, 6.52/114.7, 4.42/150.6, 4.42/140.1, 4.42/128.0, 4.42/98.2, 2.62/201.1, 2.62/132.7, 2.62/118.0. GC-MS (m/z): 353 (M^+ + 2, 2), 352 (M^+ + 1, 14), 351 (M^+, 100), 232 (59), 224 (40), 222 (19), 217 (58), 209 (47), 206 (13), 204 (15), 182 (28), 181 (12), 180 (54), 152 (21), 148 (20), 146 (12), 134 (46), 132 (11), 130 (20), 120 (12), 106 (13), 105 (47), 104 (11), 103 (12), 92 (11) 91 (37), 90 (94), 89 (49), 78 (18) 77 (51), 76 (18), 65 (18), 64 (13), 63 (25), 51 (25), 50 (12). HRMS (IE) calcd for $C_{15}H_{15}INO$ 352.0193; found $[MH]^+$ 352.0211.

N-Methyl-N-(2-iodobenzyl)-2′-aminoacetophenone (7k). A mixture of 1-(2-((2-iodobenzyl)amino)phenyl)ethanone (0.139 g, 0.396 mmol), K_2CO_3 (0.121 g, 0.87 mmol), and iodomethane (0.336 g, 2.37 mmol) in acetonitrile (5 mL) was stirred at 80 °C in a sealed tube for 72 h. The mixture was diluted with water and was extracted with CH_2Cl_2 (4 × 20 mL). The organic extracts were dried and concentrated. The residue was purified by radial thin-layer chromatography eluting with petroleum ether/diethyl ether (90/10) to give *N*-methyl-*N*-(2-iodobenzyl)-2′-aminoacetophenone **7k** (0.133 g, 92%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89−7.82 (m, 1H), 7.46 (dd, J = 7.6, 1.5 Hz, 1H), 7.37−7.31 (m, 1H), 7.28−7.25 (m, 2H), 7.02−6.53 (m, 3H), 4.31 (s, 2H), 2.77 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.2 (C), 150.8 (C), 139.6 (CH), 139.3 (C), 132.6 (C), 131.8 (CH), 129.5 (CH), 129.2 (CH), 129.0 (CH), 128.2 (CH), 120.6 (CH), 118.6 (CH), 99.4 (C), 64.2 (CH3), 42.7 (CH3), 29.5 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 6.77/7.85, 6.77/7.46, 6.77/7.34, 6.77/7.26. ^{1}H−^{1}C HSQC NMR ($CDCl_3$) δ_H/δ_C 7.84/139.6, 7.46/129.5, 7.34/131.8, 7.26/129.2, 7.26/128.2, 6.77/129.0, 6.77/120.6, 6.77/118.6, 4.31/64.2, 2.77/42.7, 2.63/29.5. GC-MS (m/z): 366 (M^+ + 1, 10), 365 (M^+, 65), 351 (6), 350 (47), 348 (16), 246 (22), 238 (16), 223 (30), 217 (53), 204 (10), 194 (49), 180 (13), 162 (15), 152 (12), 148 (100), 146 (17), 132 (15), 130 (47), 120 (26), 118 (24) 111 (11), 106 (15), 105 (19), 104 (19), 103 (12), 91 (61), 90 (80), 89 (42), 78 (18), 77 (53), 76 (13,) 65 (19), 64 (11), 63 (21), 51 (22). HRMS (IE) calcd for $C_{16}H_{16}INaNO$ 388.0169; found $[MH]^+$ 388.0196.

N-Methyl-N-(2-chlorophenethyl)-2′-aminoacetophenone (7l). A mixture of 2′-aminoacetophenone (0.28 g, 2.09 mmol), K_2CO_3 (0.41 g, 2.96 mmol), and 1-(2-bromoethyl)-2-chlorobenzene (0.686 g, 3.12 mmol) in acetonitrile (5 mL) was stirred at 85 °C in a sealed tube for 72 h. The mixture was diluted with water and was extracted with CH_2Cl_2 (3 × 15 mL) and diethyl ether (2 × 10 mL). The combined organic phase was dried (Na_2SO_4), filtered, and the solvent removed *in vacuo*. The 1-(2-bromoethyl)-2-chlorobenzene was distilled under reduced pressure using a Kügelrohr apparatus. The residue was dissolved in acetonitrilo (5 mL), and K_2CO_3 (0.55 g, 4 mmol), and iodomethane (0.568 g, 4 mmol) were added. The mixture was stirred at 85 °C in a sealed tube for 72 h. The solution was extracted with CH_2Cl_2 (2 × 15 mL) and ethyl acetate (2 × 15 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated under reduced pressure. The residue was purified by radial thin-layer chromatography eluting with petroleum ether affording the *N*-methyl-*N*-(2-chlorophenethyl)-2′-aminoacetophenone **7l** (0.072 g, 0.25 mmol, 12%) as colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42−7.35 (m, 2H), 7.33−7.30 (m, 1H), 7.16−7.09 (m, 4H), 6.98 (td, J = 7.5, 0.9 Hz, 1H), 3.31−3.27 (m, 2H), 2.97−2.93 (m, 2H), 2.88 (s, 3H), 2.52 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.1 (C), 150.8 (C), 137.0 (C), 134.3 (C), 134.0 (C), 131.6 (CH), 130.9 (CH), 129.5 (CH), 129.3 (CH), 127.8 (CH), 126.9 (CH), 121.3 (CH), 119.0 (CH), 56.4 (CH2), 41.9 (CH3), 31.0 (CH2), 29.0 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.12/7.38, 7.12/7.31, 6.98/7.38, 2.95/3.29. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 7.38/129.3, 7.38/131.5, 7.31/129.5, 7.12/130.9, 7.12/127.8, 7.12/126.9, 7.12/119.0, 6.98/121.3, 3.29/56.4, 3.29/31.0, 2.95/56.4, 2.95/31.0, 2.88/41.9, 2.50/29.0. GC-MS (m/z): 164 (1), 163 (18), 162 (100), 144 (5), 134 (6), 120 (31), 119 (6), 118 (6), 91 (10), 77 (13). HRMS (IE) calcd for $C_{17}H_{18}ClNaNO$ 310.0969; found $[MNa]^+$ 310.0978.

Representative Procedure for Photostimulated Reactions. Preparation of 5*H*-benzo[*e*]pyrrolo[1,2-*a*]azepin-11(10*H*)-one **8a**.

The following procedure is representative of all of these reactions. Liquid ammonia (150 mL), previously dried over Na metal, was distilled into a 250 mL three-necked round-bottomed flask equipped with a coldfinger condenser and a magnetic stirrer under a nitrogen atmosphere. The base *t*-BuOK (2.0 equiv, 0.056 g, 0.50 mmol) was added to the liquid ammonia, then the substrate 1-(2-iodobenzyl)-2-acetylpyrrole **7a** (1.0 equiv, 0.081 g, 0.25 mmol) was added to the solution dissolved in 1 mL of dried ethyl ether when the reaction flask was already being irradiated. The irradiation was conducted in a reactor equipped with two HPI-T 400 W lamps (cooled with air and water). The irradiation was continued for 2 h. The reaction was quenched with ammonium nitrate and the ammonia was allowed to evaporate. Water was added to the residue and the mixture was extracted with CH_2Cl_2 (3 × 30 mL). The organic extract was dried over anhydrous $MgSO_4$ then filtered and the solvent was removed to leave the crude product. 5*H*-Benzo[*e*]pyrrolo[1,2-*a*]azepin-11(10*H*)-one **8a** was separated and isolated by radial thin-layer chromatography on silica gel. In other similar experiments, the products were quantified by CG or NMR by using the internal standard method. The yield of halide ions in the aqueous solution was determined potentiometrically.

Photostimulated Reaction of 1-(2-Iodobenzyl)-2-acetylpyrrole (7a) in DMSO. The reaction was carried out in a two-necked 20 mL round-bottomed flask, equipped with a nitrogen inlet and magnetic stirrer at room temperature. DMSO (5 mL) was dried and deoxygenated, then *t*-BuOK (2.0 equiv, 0.056 g, 0.5 mmol) and substrate **7a** (1.0 equiv, 0.080 g, 0.25 mmol) were added and the reaction mixture was irradiated for 2 h. The reaction was quenched with water and ammonium nitrate in excess. The residue was extracted with CH_2Cl_2 (4 × 20 mL) and the organic extract was washed with water, dried with anhydrous $MgSO_4$ and filtered. The solvent was removed to leave the crude product. The product **8a** was separated and isolated by radial thin-layer chromatography on silica gel eluting with petroleum ether/diethyl ether (90:10) and was isolated as a white solid in 38% yield (0.019 g, 0.10 mmol).

Reaction of 1-(2-Iodobenzyl)-2-acetylpyrrole Enolate Ion (7a) Induced by $FeCl_2$ in DMSO. The reaction was carried out in an oven-dried Schlenk tube covered of the light at rt. DMSO (5 mL) was dried and deoxygenated, *t*-BuOK (0.087 g, 0.75 mmol, 5.0 equiv), pinacolone (0.045 g, 0.45 mmol, 3.0 equiv) and $FeCl_2$ (0.094 g, 0.75 mmol, 0.50 equiv) were added. After 10 min substrate **7a** (0.048 g, 0.15 mmol, 1.0 equiv) was added and the reaction mixture was stirred for 4.5 h. Water and ammonium nitrate were added to the residue and the mixture was extracted with CH_2Cl_2 (4 × 15 mL). The organic extract was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed to leave the crude products.

5H-Benzo[e]pyrrolo[1,2-a]azepin-11(10H)-one (8a). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34−7.28 (m, 3H), 7.27−7.22 (m, 1H), 7.10 (dd, *J* = 4.1, 1.8 Hz, 1H), 6.94 (t, *J* = 2.1 Hz, 1H), 6.15 (dd, *J* = 4.1, 2.5 Hz, 1H), 5.24 (s, 2H), 4.07 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3 (C), 135.0 (C), 134.1 (C), 132.3 (C), 129.7 (CH), 129.2 (CH), 128.1 (CH), 127.7 (CH), 127.4 (CH), 118.4 (CH), 109.0 (CH), 53.6 (CH2), 49.0 (CH2). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.24/7.31, 6.94/7.10, 6.15/7.10, 6.15/6.94. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 7.31/129.7, 7.31/129.2, 7.31/128.1, 7.24/127.4, 7.10/118.4, 6.94/127.7, 6.15/109.0, 5.24/53.6, 4.07/49.0. ^{1}H−^{13}C HMBC NMR δ_H/δ_C 7.31/134.1, 7.31/129.2, 7.31/128.1, 7.31/127.4, 7.24/135.0, 7.24/129.7, 7.10/132.3, 7.10/127.7, 7.10/109.0, 6.94/132.3, 6.94/118.4, 6.94/109.0, 6.15/132.3, 6.15/127.7, 6.15/118.4, 5.24/135.0, 5.24/132.3, 5.24/128.1, 4.07/184.3, 4.07/134.1, 4.07/129.7. GC-MS (*m*/*z*): 199 (M^+ + 2, 1), 198 (M^+ + 1, 14), 197 (M^+, 99), 169 (33), 168 (86), 167 (13), 142 (10), 116 (20), 104 (100), 103 (32), 83 (25), 78 (45), 77 (22), 51 (10).

3-Acetyl-5H-pyrrolo[2,1-a]isoindole (9). The product was separated by radial thin-layer chromatography on silica gel eluting with petroleum ether/diethyl ether (90:10) as a colorless solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64−7.62 (m, 1H), 7.51−7.49 (m, 1H), 7.42−7.38 (m, 1H), 7.34−7.30 (m, 1H), 7.08 (d, *J* = 4.1 Hz, 1H), 6.41 (d, *J* = 4.1 Hz, 1H), 5.22 (s, 2H), 2.48 (s, 3H). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.40/7.63, 7.32/7.50, 6.41/7.08. ^{1}H−^{13}C HSQC RMN (Cl_3CD): δ_H/δ_C 7.63/120.1, 7.50/123.3, 7.40/128.0, 7.32/127.0, 7.08/121.5, 6.41/99.9, 5.22/53.9, 2.48/25.7. GC-MS (*m*/*z*): 199 (M^+ + 2, 1), 198 (M^+ + 1, 14), 197 (M^+, 100), 183 (11), 182 (M^+ − 15, 94), 155 (11), 154 (84), 153 (14), 128 (10), 127 (40), 126 (15), 77 (13).

Phenanthren-9-ol (8d). Compound **8d** was obtained according to the general procedure. The phenanthren-9-ol was purified by radial thin-layer chromatography eluting with a petroleum ether/diethyl ether gradient (80:20→50:50) and was isolated as a light-colored solid (CAS 484−17−3). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71−8.62 (m, 1H), 8.63−8.55 (m, 1H), 8.32−8.30 (m, 1H), 7.73−7.67 (m, 2H), 7.64 (ddd, *J* = 8.0, 7.0, 1.3 Hz, 1H), 7.57−7.45 (m, 2H), 7.01 (s, 1H), 5.43 (s, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.5 (C), 132.7 (C), 131.5 (C), 127.2 (CH), 126.9 (CH), 126.7 (CH), 126.4 (CH), 125.5 (C), 124.3 (CH), 122.7 (CH), 122.6 (CH), 122.3 (CH), 106.1 (CH). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.70/8.67, 7.64/8.31, 7.51/7.70, 7.51/8.59. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 8.67/122.7, 8.59/122.6, 8.31/122.3, 7.70/127.2, 7.70/126.7, 7.64/126.4, 7.51/126.9, 7.51/124.3, 7.01/106.1. ^{1}H−^{13}C HMBC NMR ($CDCl_3$) δ_H/δ_C 8.67/126.4, 8.60/132.7, 8.60/126.9, 8.31/149.5, 8.31/131.5, 8.31/127.2, 7.70/131.5, 7.70/126.7, 7.70/124.3, 7.70/122.3, 7.70/106.1, 7.64/122.7, 7.64/125.5, 7.51/132.7, 7.51/126.7, 7.51/122.6, 7.01/149.5, 7.01/126.7. GC-MS (*m*/*z*): 195 (M^+ + 1, 8), 194 (M^+, 71), 166 (49), 165 (100), 164 (13), 163 (28), 139 (10), 83 (28), 82 (33), 63 (12).

Dibenzo[b,f]oxepin-10(11H)-one (8e).[1b,e,f,2a] The oxepinone **8e** was purified by column chromatography on silica gel eluting with petroleum ether/diethyl ether (90:10) as a white solid: mp 51−53 °C (lit.[1e] 48−50 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.54 (ddd, *J* = 8.3, 7.2, 1.8 Hz, 1H), 7.38 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.32−7.23 (m, 3H), 7.21−7.17 (m, 2H), 4.10 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4 (C), 160.2 (C), 156.9 (C), 134.9 (CH), 130.5 (CH), 129.7 (CH), 128.5 (CH), 126.4 (C), 126.3 (CH), 126.2 (C), 123.8 (CH), 121.5 (CH), 120.4 (CH), 48.2 (CH2). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.54/8.06, 7.27/7.54, 7.19/8.06, 7.19/7.53, 7.19/7.30. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 8.06/130.5, 7.54/134.9, 7.38/121.5, 7.27/129.7, 7.27/128.5, 7.27/120.4, 7.19/126.3, 7.19/123.8, 4.10/48.2. ^{1}H−^{13}C HMBC NMR ($CDCl_3$) δ_H/δ_C 8.06/190.4, 8.06/160.2, 8.06/134.9, 7.54/160.2, 7.54/130.5, 7.38/160.2, 7.38/123.8, 7.27/156.9, 7.27/128.5, 7.27/126.2, 7.19/126.4, 7.19/121.5, 7.19/120.4, 4.10/190.4, 4.10/156.9, 4.10/129.7, 4.10/126.2. GC-MS (*m*/*z*): 211 (M^+ + 1, 14); 210 (M^+, 100); 209 (27); 182 (20); 181 (94); 165 (7); 154 (5); 153 (17); 152 (25); 151 (6); 91 (10); 89 (8); 77 (6); 76 (26); 64 (8); 63 (12); 51 (8); 50 (8).

Dibenzo[b,f]thiepin-10(11H)-one (8f).[1a,b,f] Compound **8f** was obtained according to the general procedure. The benzothiepinone was purified by radial thin-layer chromatography eluting with petroleum ether/diethyl ether (90:10) and 0.041 g (70%, 0.18 mmol) was isolated as a yellow pale solid: mp 73.5−75.0 °C (lit.[1a] 72−73 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.64 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.60 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.46−7.40 (m, 2H), 7.36 (td, *J* = 7.5, 1.2 Hz, 1H), 7.33−7.29 (m, 1H), 7.20 (td, *J* = 7.6, 1.4 Hz, 1H), 4.37 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.4 (C), 140.2 (C), 137.6 (C), 136.1 (C), 134.5 (C), 132.5 (CH), 131.5 (CH), 131.2 (CH), 130.9 (CH), 129.9 (CH), 129.4 (CH), 127.2 (CH), 126.8 (CH), 51.0 (CH2). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.43/7.64, 7.36/7.43, 7.31/8.20, 7.20/7.64, 7.20/7.36. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 8.20/131.5, 7.64/131.2, 7.60/130.8, 7.43/132.5, 7.43/129.4, 7.36/129.9, 7.31/126.8, 7.20/127.2, 4.37/51.0. GC-MS (*m*/*z*): 228 (M^+ + 2, 5); 227 (M^+ + 1, 17); 226 (M^+, 100); 225 (28); 198 (9); 197 (49); 195 (6); 194 (13); 193 (7); 166 (7); 165 (53); 164 (6); 153 (6); 152 (13); 121 (6); 99 (5); 98 (10); 82 (8); 77 (6); 76 (7); 69 (7); 63 (9). HRMS (IE) calcd for $C_{14}H_{11}OS$ 227.0525; found $[MH]^+$ 227.0527.

1-Acetyl-9H-carbazole (8g).[52] The carbazole **8g** was purified by radial thin-layer chromatography eluting with petroleum ether/diethyl ether (90/10) and 0.024 g (86%, 0.12 mmol) was isolated as a yellow pale solid: mp 136−137 °C ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.57 (s br, 1H), 8.27 (d, *J* = 7.6 Hz, 1H), 8.08 (d, *J* = 7.8 Hz, 1H), 7.94 (dd, *J* = 7.7, 0.8 Hz, 1H), 7.53−7.52 (m, 1H), 7.48−7.44 (m, 1H), 7.29−7.23 (m, 2H), 2.74 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.3 (C), 140.0 (C), 139.0 (C), 127.9 (CH), 126.5 (CH), 126.1 (CH), 124.9 (C), 122.0 (C), 120.3 (CH), 120.1 (CH), 119.3 (C), 118.2 (CH), 111.3 (CH), 26.7 (CH_3). ^{1}H−^{1}H COSY NMR (400 MHz, $CDCl_3$) δ_H/δ_H 7.46/8.08, 7.46/7.52, 7.26/8.27, 7.26/8.08, 7.26/7.94, 7.26/7.46. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 8.27/126.1, 8.08/120.3, 7.94/127.9, 7.52/111.3, 7.46/126.6, 7.27/120.1, 7.24/118.2, 2.76/26.7. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 8.27/139.0, 8.27/127.9, 8.27/122.0, 8.08/140.0, 8.08/126.1, 7.94/200.3, 7.94/139.0, 7.94/126.1, 7.52, 7.52, 7.46/139.0, 7.46/126.1, 7.26/127.9, 7.26/124.9, 7.26/122.0, 7.26/119.3, 7.26/111.3, 2.74/200.3, 2.74/127.9, 2.74/119.3. GC-MS (*m*/*z*): 211 (M^+ + 2, 1), 210 (M^+ + 1, 16), 209 (M^+, 100), 195 (13), 194 (97), 166 (58), 140 (13), 139 (34), 83 (12), 69 (11).

1-(2-Methyl-1,3-dioxolan-2-yl)-9H-carbazole (8h). The product was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/diethyl ether (90:10). White solid was isolated in 93% yield (0.035 g, 0.14 mmol), mp 223−225 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.79 (s, 1H), 8.07 (t, *J* = 8.2 Hz, 2H), 7.65 (d, *J* = 8.1 Hz, 1H), 7.45−7.35 (m, 2H), 7.14 (t, *J* = 7.6 Hz, 2H), 4.13−4.04 (m, 2H), 3.78−3.70 (m, 2H), 1.76 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 140.0 (C), 135.7 (C), 125.5 (C), 125.4 (CH), 123.4 (C), 122.1 (CH), 121.9, 119.9 (CH), 119.8 (CH), 118.5 (CH), 118.2 (CH), 111.7 (CH), 108.2 (C), 64.1 (CH2), 26.1 (CH3). ^{1}H−^{1}H COSY NMR (DMSO-d_6) δ_H/δ_H 7.38/8.07, 7.38/7.65, 7.14/8.07, 7.14/7.38, 3.74/4.08. ^{1}H−^{13}C HSQC NMR (DMSO-d_6) δ_H/δ_C 8.07/119.9, 8.07/119.8, 7.64/111.7, 7.38/125.4, 7.38/122.1, 7.14/118.5, 7.14/118.2, 4.08/64.1, 3.74/64.1, 1.76/26.1. ^{1}H−^{13}C HMBC NMR (DMSO-d_6) δ_H/δ_C 8.07/140.0, 8.07/135.7, 8.07/125.5, 8.07/122.1, 7.64/121.9, 7.64/118.5, 7.38/140.0, 7.38/135.7, 7.38/119.9, 7.38/108.2, 7.14/125.4, 7.14/123.4, 7.14/122.1, 7.14/111.7, 4.08/108.2, 4.08/64.1, 3.74/108.2, 3.74/64.1, 1.76/125.4, 1.76/108.2. GC-MS (*m*/*z*): 254 (M^+ + 1, 8), 253 (M^+, 47), 238 (M^+ − 15, 100), 209 (21), 194

(72), 166 (29), 139 (15), 97 (14), 83 (14). HRMS calcd for $C_{16}H_{16}NO_2$ 254.1176; found $[MH]^+$ 254.1200.

*5-Methyl-5H-dibenzo[b,f]azepin-10(11H)-one (**8i**).*[1b,f,2] Compound **8i** was obtained according to the general procedure. The azepinone was purified by radial thin-layer chromatography on silica gel eluting with petroleum ether/diethyl ether (90:10) as light yellow crystals, mp 106.5−107.5 °C (lit.[1b] 102−103 °C). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (dd, J = 7.9, 1.8 Hz, 1H), 7.51 (ddd, J = 8.7, 7.1, 1.8 Hz, 1H), 7.32−7.30 (m, 1H), 7.25−7.14 (m, 4H), 7.00−6.96 (m, 1H), 3.91 (s, 2H), 3.60 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 149.6 (C), 148.1 (C), 133.9 (CH), 131.2 (CH), 129.2 (C), 128.6 (CH), 127.2 (CH), 125.6 (CH), 125.4 (C), 120.4 (CH), 119.7 (CH), 116.5 (CH), 49.1 (CH2), 40.3 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.19/7.51, 6.98/8.16, 6.98/7.51. ^{1}H−^{13}C HSQC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 8.15/131.2, 7.51/133.9, 7.31/128.6, 7.19/127.2, 7.19/125.6, 7.19/120.4, 7.19/116.5, 6.98/119.7, 3.91/49.1, 3.60/40.3. ^{1}H−^{13}C HMBC NMR (400 MHz, $CDCl_3$) δ_H/δ_C 8.16/190.3, 8.16/149.6, 8.16/133.9, 7.51/149.6, 7.51/131.2, 7.19/190.3, 7.19/148.1, 7.19/128.6, 7.19/125.4, 7.19/119.7, 7.19/119.7, 6.98/125.4, 6.98/116.5, 3.91/190.3, 3.91/, 3.91/148.1, 3.91/129.2, 3.91/125.4, 3.60/149.6, 3.60/148.1, 3.60/116.5. GC-MS (m/z): 225 (M^+ + 2, 1), 224 (M^+ + 1, 14), 223 (M^+, 100), 222 (9), 208 (31), 195 (11), 194 (53), 180 (22), 179 (13), 152 (14), 77 (10).

*4-Acetylphenanthridine (**8j**).* Compound **8j** was obtained according to the general procedure. The phenanthridine was purified by radial thin-layer chromatography eluting with a petroleum ether/ethyl acetate gradient (95:5→80:20) and was isolated as a light-colored solid, mp 93.7−95.5 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.69 (dd, J = 8.2, 1.1 Hz, 1H), 8.62 (d, J = 8.3 Hz, 1H), 8.08 (d, J = 7.9 Hz, 1H), 7.92−7.86 (m, 2H), 7.78−7.74 (m, 1H), 7.73−7.69 (m, 1H), 2.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 204.9 (C), 153.4 (CH), 141.7 (C), 140.9 (C), 132.2 (C), 131.3 (CH), 128.8 (CH), 127.9 (CH), 127.6 (CH), 126.6 (CH), 126.1 (C), 125.0 (CH), 124.2 (C), 122.0 (CH), 32.9 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 8.61/9.32, 7.89/8.62, 7.76/8.08, 7.76/7.89, 7.71/8.69, 7.71/7.89. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 9.32/153.4, 8.69/125.0, 8.62/122.0, 8.09/128.8, 7.89/131.3, 7.89/127.6, 7.76/127.9, 7.71/126.6, 2.95/32.9. ^{1}H−^{13}C HMBC NMR ($CDCl_3$) δ_H/δ_C 9.32/141.7, 9.32/132.2, 9.32/128.8, 9.32/126.1, 8.69/141.7, 8.69/132.2, 8.69/127.6, 8.62/127.9, 8.62/126.1, 8.62/124.2, 8.08/153.4, 8.08/131.3, 7.89/204.9, 7.89/141.7, 7.89/132.27,.89/128.8, 7.89/125.0, 7.76/126.1, 7.76/122.0, 7.71/140.9, 7.71/122.0, 2.95/204.9. GC-MS (m/z): 223 (M^+ + 2, 16), 222 (M^+ + 1, 14), 221 (M^+,100), 220 (18), 207 (23), 206 (7), 204 (75), 194 (20), 193 (16), 180 (10), 179 (39), 178 (79), 177 (24), 152 (25), 151 (53), 150 (28), 103 (12), 89 (14), 76 (19), 75 (16). HRMS calcd for $C_{15}H_{12}NO$ 222.0913; found $[MH]^+$ 222.0921.

*5-Methyl-5,6-dihydrodibenzo[b,f]azocin-12(11H)-one (**8k**).* Compound **8k** was purified by radial thin-layer chromatography eluting with a petroleum ether/diethyl ether gradient (90/10: 70/30) and 0.034 g (78%, 0.14 mmol) was isolated as a yellow pale solid, mp 108−109 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 7.6, 1.3 Hz, 1H), 7.44−7.40 (m, 1H), 7.30−7.21 (m, 4H), 7.12−7.10 (m, 1H), 7.04 (d, J = 8.2 Hz, 1H), 6.93−6.89 (m, 1H), 4.20 (s, 2H), 4.07 (s, 2H), 3.00 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7 (C), 152.8 (C), 135.6 (C), 135.1 (C), 132.5 (CH), 131.0 (C), 130.7 (CH), 129.3 (CH), 128.6 (CH), 128.2 (CH), 127.0 (CH), 118.8 (CH), 115.0 (CH), 64.4 (CH2), 48.1 (CH2), 37.8 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.10/7.24, 7.04/7.42, 6.90/7.61, 6.90/7.42, 3.00/4.20. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 7.61/129.3, 7.42/132.5, 7.24/130.7, 7.24/128.6, 7.24/127.0, 7.10/128.6, 7.04/115.0, 6.90/118.8, 4.20/64.4, 4.07/48.1, 3.00/37.8. ^{1}H−^{13}C HMBC NMR ($CDCl_3$) δ_H/δ_C 7.61/201.7, 7.61/152.8, 7.61/132.5, 7.42/152.8, 7.42/129.3, 7.24/135.1, 7.24/130.7, 7.24/128.6, 7.24/127.0, 7.10/135.6, 7.10/130.7, 7.10/127.0, 7.04/131.0, 7.04/118.8, 6.90/131.0, 6.90/115.0, 4.20/152.8, 4.20/135.6, 4.20/135.1, 4.20/128.6, 4.20/37.8, 4.07/201.7, 4.07/135.6, 4.07/130.7, 3.00/152.8, 3.00/64.4. GC-MS (m/z): 239 (M^+ + 2, 1), 238 (M^+ + 1, 17), 237 (M^+, 94), 236 (52), 218 (11), 209 (20), 208 (79), 195 (44), 194 (75), 193 (40), 181 (10), 180 (10), 179 (36), 178 (30), 166 (12), 165 (27), 132 (26), 105 (32), 104 (100), 103 (21), 91 (18), 89 (13), 78 (45), 77 (53), 76 (12), 63 (16), 51 (24). HRMS calcd for $C_{16}H_{15}NNaO$ 260.1051; found $[MNa]^+$ 260.1074.

*5-Methyl-6,7-dihydro-5H-dibenzo[b,f]azonin-13(12H)-one (**8l**).* Compound **8l** was obtained according to the general procedure and was purified by radial thin-layer chromatography eluting with petroleum ether/dichloromethane (50/50) and was isolated as a white solid, mp 121.5−123.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, J = 7.7, 1.7 Hz, 1H), 7.46 (dd, J = 7.4, 0.8 Hz, 1H), 7.38 (ddd, J = 8.8, 7.2, 1.8 Hz, 1H), 7.27 (dt, J = 7.4, 1.9 Hz, 1H), 7.17 (td, J = 7.4, 1.3 Hz, 1H), 7.09 (d, J = 6.9 Hz, 1H), 6.99 (d, J = 8.2 Hz, 1H), 6.92−6.88 (m, 1H), 4.24 (s, 2H), 3.25−3.22 (s, 2H), 3.17−3.12 (m, 2H), 2.95 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 201.7 (C), 151.9 (C), 140.0 (C), 134.5 (C), 132.8 (CH), 132.6 (CH), 131.1 (CH), 129.6 (CH), 128.8 (C), 126.8 (CH), 126.6 (CH), 119.4 (CH), 115.7 (CH), 60.1 (CH2), 44.2 (CH2), 37.9 (CH2), 36.0 (CH3). ^{1}H−^{1}H COSY NMR ($CDCl_3$) δ_H/δ_H 7.38/7.62, 7.27/7.46, 7.17/7.46, 7.17/7.27, 7.08/7.17, 6.99/7.38, 6.90/7.60, 6.90/7.38, 6.90/7.08, 3.14/3.23. ^{1}H−^{13}C HSQC NMR ($CDCl_3$) δ_H/δ_C 7.60/131.1, 7.46/132.8, 7.38/132.6, 7.27/126.8, 7.17/126.6, 7.08/129.6, 6.99/115.7, 6.90/119.4, 4.24/44.2, 3.23/60.1, 3.23/37.9, 3.14/60.1, 3.14/37.9, 2.95/36.0. ^{1}H−^{13}C HMBC NMR ($CDCl_3$) δ_H/δ_C 7.60/201.7, 7.60/151.9, 7.60/132.6, 7.46/140.0, 7.46/126.6, 7.46/44.2, 7.38/151.9, 7.38/131.1, 7.27/134.5, 7.27/129.6, 7.17/140.0, 7.08/134.5, 7.08/37.9, 6.99/128.8, 6.99/119.4, 6.90/128.8, 6.90/115.7, 4.24/201.7, 4.24/139.4, 4.24/134.5, 4.24/132.8, 3.23/37.9, 3.14/140.0, 3.14/134.5, 3.14/129.6, 3.14/60.1, 2.95/151.9, 2.95/115.7, 2.95/60.1. GC-MS (m/z): 253 (M^+ + 2, 1), 252 (M^+ + 1, 17), 251 (M^+, 100), 236 (12), 234 (13), 233 (11), 232 (13), 222 (12), 208 (14), 160 (14), 147 (51), 146 (44), 132 (12), 118 (11), 117 (14), 115 (15), 107 (10), 106 (13), 105 (27), 104 (39), 91 (47), 78 (16), 77 (27). HRMS calcd for $C_{17}H_{17}NNaO$ 274.1208; found $[MNa]^+$ 274.1225.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR, ^{13}C NMR and 2D NMR experiment. This material is available free of charge via the Internet at http://pubs.acs.org.

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