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Titanium-Induced Syntheses of Furans, Benzofurans and Indoles

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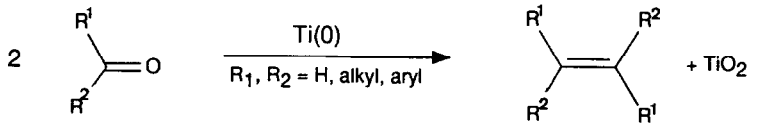
Abstract: *Highly reactive titanium on graphite as the reagent of choice promotes intramolecular McMurry type reactions of acyloxy- and acylamido carbonyl compounds affording furans, benzofurans and indoles in good to excellent yields. A variety of reducible groups in the substrates is tolerated (e.g. -F, -Cl, -Br, -I, -CF_3, -OMe, -CN, -thiophenyl, -COOR, -$CONR_2$) and strained products such as* ***11h*** *can be obtained, the X-ray analysis of which is reported. The experimental results indicate the possible formation of dianions from the aromatic aldehydes or ketones as reactive intermediates which attack the ester or amide functions in their proximity, rather than a radical path via ketyls.*

INTRODUCTION

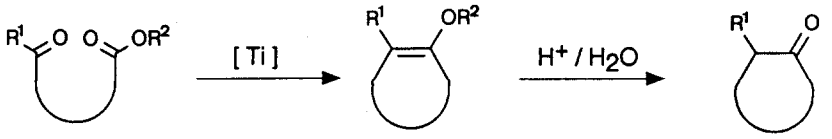
Among the variety of reactions induced by low-valent titanium,[1] the reductive coupling of carbonyl compounds to alkenes (Scheme 1), generally referred to as McMurry reaction,[2] has gained widespread acceptance and use due to its rather unique features. It does not only allow the formation of strained olefins, but also gives access to carbocyclic products of almost any ring size when applied to dialdehydes, ketoaldehydes or diketones, respectively.[2]



Scheme 1. Titanium-induced carbonyl coupling (McMurry reaction)

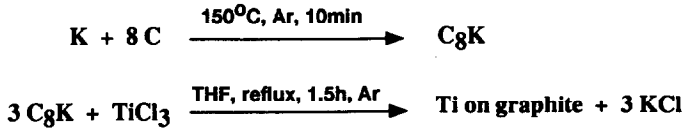
This remarkable scope results mainly from the template effect of the active titanium surface rendering the McMurry reaction superior to all classical methods of carbocycle formation. Moreover it has been successfully applied to most elegant natural product syntheses[2] and was recently extended to

oxoalkanoate cyclization, a procedure that affords cyclanones upon hydrolysis of the enol ethers initially formed (Scheme 2).[3] However, this intramolecular alkylidenation of alkanoates is reported to be more capricious than other McMurry type reactions necessitating a modified titanium reagent.[3a]



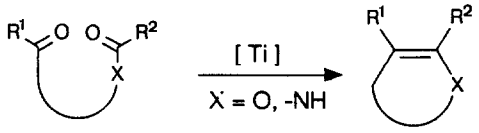
Scheme 2. McMurry type oxoalkanoate cyclization reactions

More appropriate procedures of metal activation might help to overcome such problems resulting from the inadequate quality of the metal employed. In this context, we have emphasized the advantages of metal-graphite reagents and have demonstrated their superiority over existing methods of metal activation in a variety of examples.[4]



Scheme 3. Preparation of metal-graphite compounds

Metal-graphite reagents are easily obtained by the reduction of the respective metal salt by potassium-graphite laminate (C_8K) in an etheral solvent (Scheme 3), and exhibit an unprecedented degree of metal dispersion and hence its reactivity. Since the particles are adsorped on the graphite surface[5] they additionally provide all preparative advantages of supported reagent systems such as *i.a.* easy work-up.[6] Thus, titanium on graphite *e.g.* turned out to efficiently promote all types of McMurry reactions including the cyclization of oxoalkanoates.[7] Furthermore, it was successfully used in organometallic chemistry[8] and in a slightly modified stoichiometry, it turned out to be best suited for annulation reactions as well as the coupling of highly oxygenated substrates, with which Rieke titanium failed to effect any cyclization.[9]

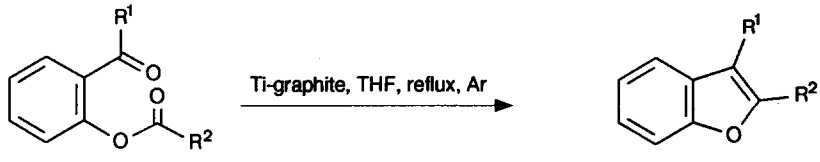


Scheme 4. McMurry type heterocycle syntheses

Based on the encouraging progress achieved by using this methodology, we envisaged the McMurry type ketoester cyclization described above to offer a new and simple entry to the formation of heterocycles (Scheme 4). Thus, the closely related acyloxycarbonyl compounds on treatment with titanium on graphite afforded products with the enol ether forming part of a heterocyclic ring system. This strategy was further extended to acylamido carbonyl compounds, although amides were hitherto considered to be inert towards low valent titanium.[2a] We now report in detail on scope and limitation of the furan and indole syntheses based on this new approach.[10]

RESULTS AND DISCUSSION

Cyclization of Acyloxycarbonyl Compounds.- Compounds **1a-f**, prepared by acylation of commercially available hydroxycarbonyl precursors, were treated with titanium on graphite (4 equivalents) in refluxing THF[7] under high dilution conditions. As shown in Table 1 substituted benzo[b]furans were obtained in good yield, except for substrates **1d** and **1e** which invariably afforded rather complex product mixtures even upon variation of the substrate/titanium ratio and of the addition time of the respective starting material to the titanium-graphite suspension. However, this failure is in accordance with a similar observation reported by Banerji et al. for compound **1d** using $TiCl_4$/Zn/dioxane as coupling agent.[11,12]



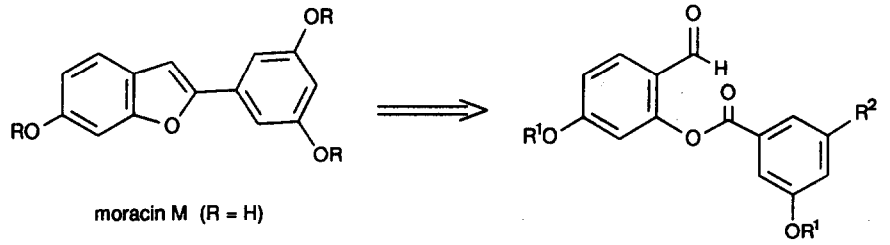
1 2

Table 1. Titanium on Graphite Induced Formation of Substituted Benzo[b]furans.

Substrate	R^1	R^2	Time (h)[a]	Product	Yield(%)
1a	Ph	Ph	8	**2a**	88
1b	Ph	Me	8	**2b**	85
1c	Me	Ph	8	**2c**	80
1d	Me	Me	8	**2d**	---[b]
1e	H	Me	8	**2e**	---[b]
1f	H	Ph	8	**2f**	89

[a] time for addition of the substrate to the titanium-graphite suspension, [b] complex reaction mixture

This new benzofuran synthesis seemed to open a straightforward access to the phytoalexin moracin M, its trimethyl ether as well as other members of this group of biologically active 2-arylbenzofurans (Scheme 5).[13] Acylation of 2-hydroxy-4-methoxybenzaldehyde with commercially available 3,5-dimethoxybenzoylchloride under standard conditions gave compound **3a**. Unfortunately however, this acyloxyaldehyde as well as the closely related substrate **3b** decomposed on attempted cyclization. Plausible explanations for this failure are presently under investigation. Although methoxy substituents are known to be potential sites of reduction in titanium induced reactions,[14] they turned out to be compatible with our reagent in the indole series (*vide infra*).



Scheme 5. Retrosynthetic analysis for the attempted preparation of moracin M.

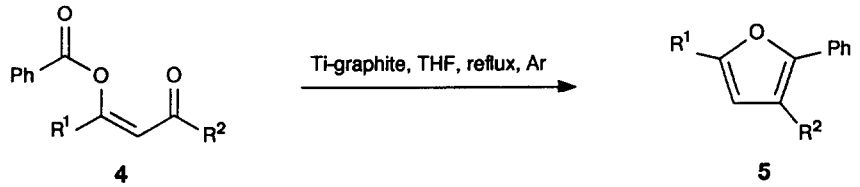


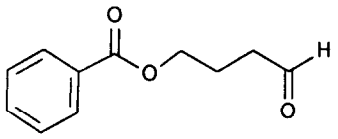
Table 2. Titanium-Graphite Induced Formation of Trisubstituted Furans.

Substrate	R^1	R^2	Time (h)[a]	Product	Yield(%)
4a	Ph	Ph	8	**5a**	92
4b	Me	Me	8	**5b**	58

[a] time for addition of the substrate to the titanium-graphite suspension

Substrates **4a-b**, readily obtained by benzoylation of the parent 1,3-dicarbonyl compounds, on treatment with titanium on graphite lead to the respective trisubstituted furans **5** in fair to good yields.[15] These two examples together with the results in Table 1 point at the fact, that the more aryl substituents in the starting material the better the results of the cyclization reaction. This trend might be one of the reasons

why acyloxycarbonyl compounds such as **6**, and **7a-c** did not afford relevant amounts of cyclized products, but were simply reduced to the corresponding alcohols or gave complex reaction mixtures. As outlined below in the mechanistic section the chain lenght between the ester and the carbonyl moiety additionally accounts for this limitation.



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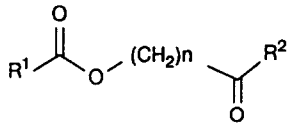
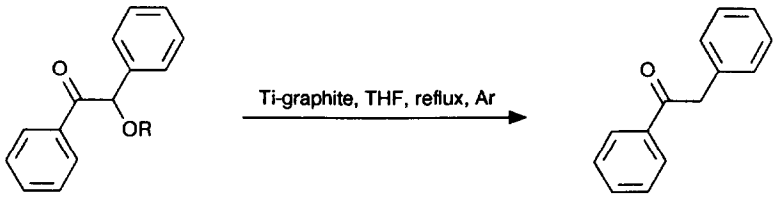


7a n = 4 $R^1 = R^2 = Ph$

7b n = 5 $R^1 = R^2 = Ph$

7c n = 3 $R^1 = Ph$ $R^2 = Me$

Although low valent titanium is well known to form cyclobutene derivatives from 1,4-dicarbonyl compounds,[7,16] substrates **8b** and **8c** did not afford oxetens. They were smoothly converted to deoxybenzoin **9** which was also obtained from benzoin (**8a**) upon treatment with titanium-graphite although in somewhat lower yield. Similar deoxygenations of acyloins have already been reported by McMurry et al.[17]



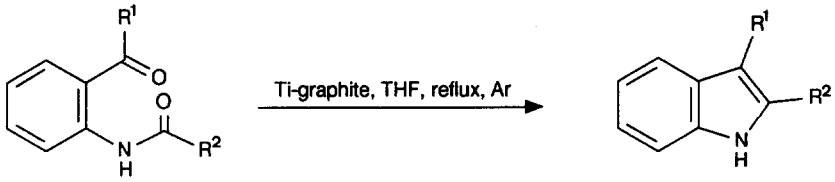
8 **9**

Table 3. Reduction of Benzoin Derivatives by Titanium on Graphite

Substrate	R	Time[a] (h)	Product	Yield (%)
8a	H	8	**9**	80
8b	Ac	8	**9**	92
8c	Bz	8	**9**	89

[a] time for addition of the product to the titanium-graphite suspension

Cyclization of Acylamido Carbonyl Compounds.- The remarkable tendency of acyloxycarbonyl compounds to form benzofurans on treatment with titanium(0) prompted us to extend these investigations to the closely related acylamido carbonyl compounds (**10**) which, in fact, turned out to afford substituted indoles (**11**) in excellent yields.[10] New synthetic approaches to this heterocyclic nucleus are of ongoing interest[18] due to its biological relevance and ubiquitous occurrence in nature.[19] Since the conventional syntheses are all hampered by several well-known shortcomings,[20] a detailed study of the scope of this new strategy to form the 2,3-carbon-carbon bond of indoles by an intramolecular McMurry type reaction was called for.



10 **11**

Table 4. Titanium-Graphite Induced Indole Synthesis

Substrate	R^1	R^2	Time (h)[a]	Product	Yield(%)
10a	Me	Ph	8+0	**11a**	75
10b	Me	Me	8+0	**11b**	70
10c	Ph	Ph	8+0	**11c**	90
10d	Ph	Me	8+0	**11d**	87
10e	Ph	H	8+0	**11e**	92
10f	Ph	$-(CH_2)_{14}CH_3$	3+0	**11f**	92
10g	H	Ph	0+2	**11g**	90
10h	Ph	t-Bu	0+3[b]	**11h**	84
10i	Me	H	0+3	**11i**	69
10j	Ph	R[c]	0+2	**11j**	79

[a] time for addition of the substrate + reflux period; [b] in DME; in THF (8h): 11h (56%); recov. 10h (40%) [c] R = thiophen-2-yl

The results of this investigation are summarized in Table 4 and deserve some comments. Thus, 2-acylamidocarbonyl compounds **10**, easily prepared by acylation of well accessible 2-aminoaryl aldehydes or -ketones, invariably undergo this reductive cyclization with titanium on graphite in THF[7] in good to excellent yields. Most gratifyingly, this reaction turned out to be even less sensitive than the

corresponding benzofuran synthesis as far as the substitution pattern of the substrates is concerned. All kinds of amides, including formamides as well as long chain-, aryl-, heteroaryl- and sterically crowded alkylamides cyclized smoothly and at comparable rates when exposed to an excess (4 equivalents) of the highly reactive titanium-graphite reagent. During the course of this investigation we got aware of the fact, that high dilution was neither necessary nor advantageous for this new indole synthesis. As shown in Tables 4 and 5, one can add the substrate at once with an overall concentration of about 0.05M without any noticeable effect on the yield. This molarity is not yet optimized and might further be increased if necessary. Moreover, this strategy is suitable for the formation of quite crowded systems, since compound **10h** was readily reduced to the hitherto unknown 2-*t*-butyl-3-phenylindole **11h** under standard conditions. In this case THF was replaced by the higher boiling DME as solvent in order to achieve complete conversion of the substrate. Despite the remarkable ease of formation, the X-ray structure of compound **11h** (Fig. 1) manifests the effect of strain in this molecule.[21]

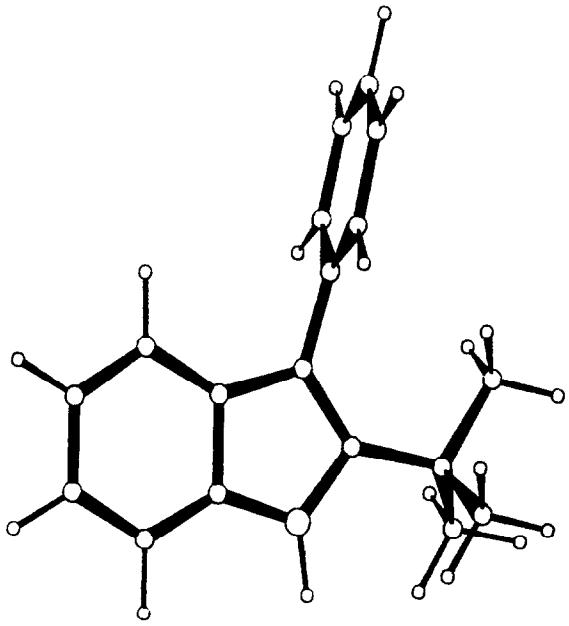
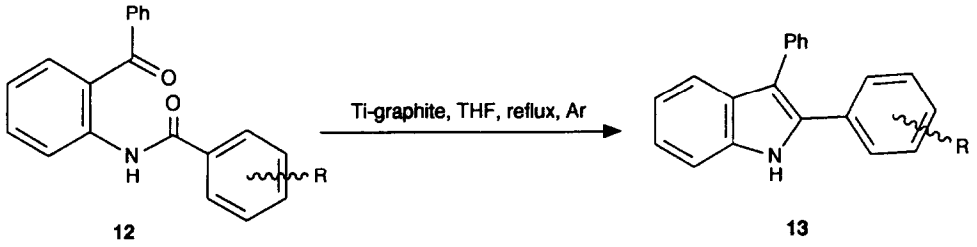


Fig. 1. X-ray structure of 2-t-butyl-3-phenylindole (**11h**)

Table 5 shows the results of a study of functional group compatibility since the high and yet insufficiently studied reduction potential of titanium(0)[1,2] towards other reducible sites in the substrate might limit this new heterocycle synthesis. 2-Aminobenzophenone as a model compound was treated with differently substituted benzoyl chlorides and the respective amides **12a-g** thus obtained were treated with an excess of titanium-graphite reagent under standard conditions. As shown in Table 5, the aryl iodide **12d** was the only substrate found to be further reduced on prolonged exposure, although the indole formation proceeded at a significantly higher rate than carbon-iodide bond cleavage.

In addition to the functional groups summarized in Table 5, thiophene was also tolerated during this reaction (*c.f.* conversion of **10j** to **11j**). Moreover, the trifunctional starting materials **14**, **16**, **18** and **20** shed further light onto the wide scope of this process. Thus, compound **14** was readily cyclized to indole **15** without participation of the vinylogeous position to any marked extend. Similarly, ketoester cyclization does not compete with indole formation when **16** was treated with titanium on graphite. Compounds **17a** and **17b** thus prepared could be separated by column chromatography. **17a**, on treatment with NaH in THF, was quantitatively transformed to **17b**. Such tricyclic systems were also obtained directly from the corresponding imide precursors, as examplified by the conversion of compound **18** to indole **19**. Beside their synthetic utility, these latter examples imply mechanistic information, which is discussed below. Carbamide **20** was the only substrate that failed to afford the anticipated indole derivative.

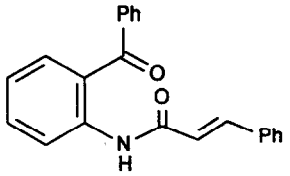


12 **13**

Table 5. Functional Group Compatibility with the Titanium-based Indole Formation

Substrate	R	Time (h)[a]	Product	Yield(%)
12a	3-F	8+0	**13a**	94
12b	4-Cl	8+0	**13b**	86
12c	3-Br	8+0	**13c**	81[b]
12d	4-I	0+1	**13d**	80[b,c]
12e	4-CF_3	8+0	**13e**	83
12f	3-OMe	3+0	**13f**	86
12g	4-CN	3+0	**13g**	76

[a] time for addition of the substrate + reflux period; [b] together with 2,3-diphenylindole (**11c**) (<10%); [c] complete conversion to 2,3-diphenylindole (**11c**) after 2h



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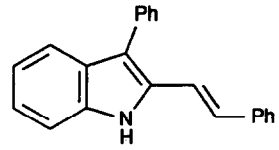

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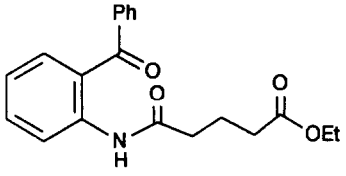

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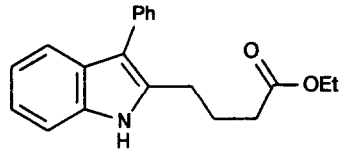
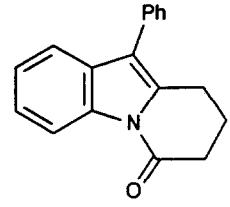
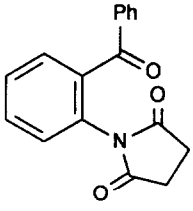


17a



17b



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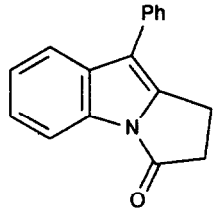

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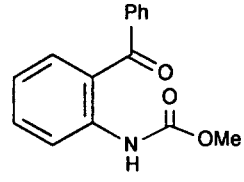

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Table 6. Indole Formation from Trifunctional Substrates with Titanium-Graphite in THF

Substrate	Time (h)[a]	Product (Yield)
14	8	**15** (68%)
16	8	**17a** (63%) **17b** (31%)
18	3	**19** (61%)
20	8	---[b]

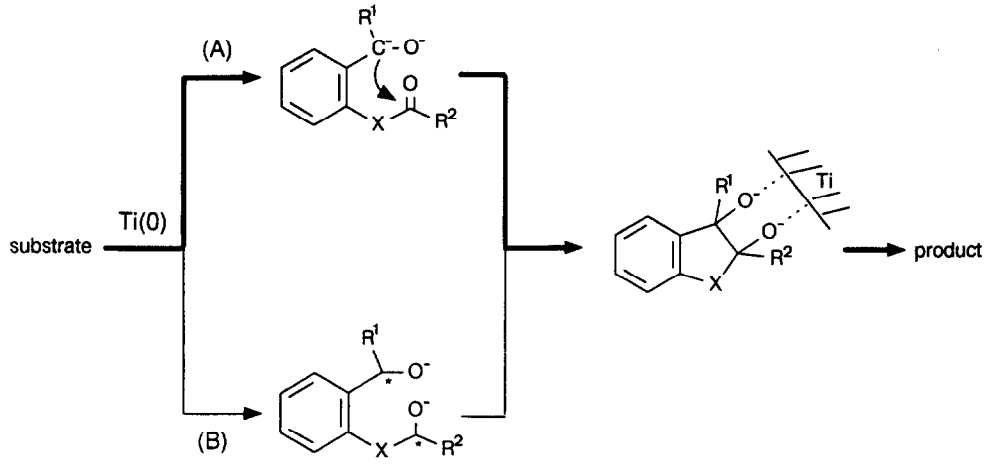
[a] time for addition of the substrate to the titanium-graphite reagent; [b] decomposition

Mechanistic Considerations.- Based on strong experimental support, the McMurry reaction is usually discussed in terms of single electron transfer from titanium to the carbonyl carbon atom, dimerization of the ketyls formed and subsequent deoxygenation of the pinacolates thus obtained due to the high oxygenophilicity of the low valent titanium.[2, 16a] It has been assumed, though not proved, that oxoester cyclization essentially follows an identical path,[3a] which therefore should also account for the reactions described above. Although we are aware of the fact that the mechanisms of heterogeneous reactions are particularly difficult to probe, some of the results outlined in the previous sections are in conflict with this conception.

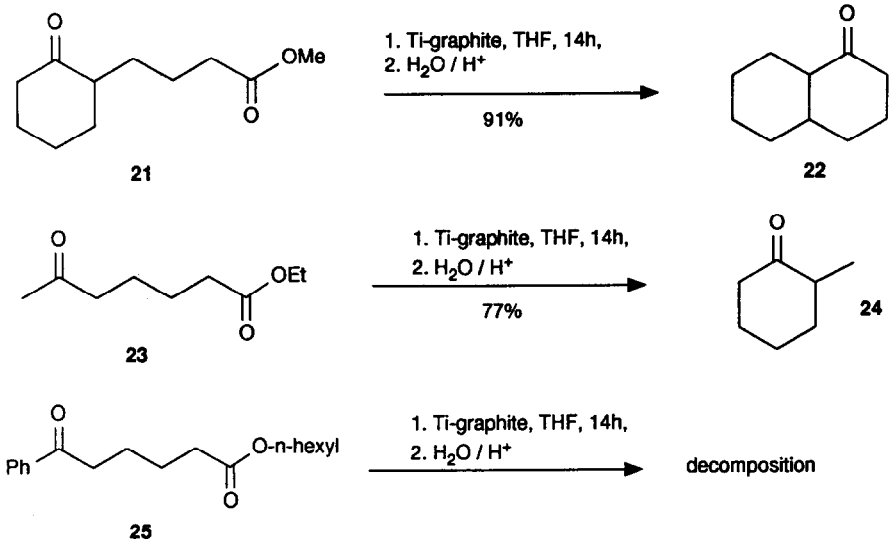
1. Low valent titanium, even in its most active form as titanium on graphite, does not form radical anions from esters to a significant extend. This follows clearly from the fact that titanium(0) does not effect acyloin condensations[16a] and that diesters such as 1,4-dibenzoyloxybutane were recovered unchanged even on prolonged heating.[22] Furthermore, 4-benzoyloxybutanal **6** was reduced at the aldehyde site only (60%) leaving the ester unaffected.

2. Although radical anions are more difficult to generate from an amide than from an ester, our titanium-based heterocycle syntheses proceeded equally well or even more readily with acylamido- than with acyloxy carbonyl compounds. Moreover, the trifunctional substrate **16** gave ketoamide coupling exlusively without ketoester cyclization interfering.

3. Amides without approximate carbonyl groups are inert towards titanium(0) as originally assumed for McMurry type reactions, since **17b** or **19** were unaffected by the excess of the reagent.



Scheme 6. Possible mechanisms: (A) dianion path (B) ketyl radical path



Scheme 7. Titanium-graphite induced reactions of oxoalkanoates

Stabilized radical anions derived *e.g.* from aromatic carbonyl compounds can easily be reduced further to the corresponding dianions due to their favourable electrochemical reduction potentials.[23] Such highly reactive dianions once formed readily attack adjacent ester or amide groups with comparable ease thus forming the C-C bond, followed by deoxygenation of the intermediate pinacolates *via* a titanium chelate. The kinetically favoured formation of a five-membered ring, the proximity of the reacting sites, the striking oxygenophilicity of the titanium metal as well as the aromaticity of the final products all contribute to make these heterocycle syntheses highly favourable. Furthermore, the exclusive 1,2-attack onto the unsaturated ketoamide **14** is more readily understood by the assumption of dianions rather than ketyl radicals. The fact that the indole formation proceeded even at rather high concentration of the substrate is an additional argument against ketyls, since they should dimerize under these conditions at least in part with formation of the respective intermolecular coupling products. Finally, it should be mentioned, that such a dianion pathway has already been cited by McMurry et al. in order to explain their results of a series of cross coupling experiments.[24]

The poor results obtained in attempted cyclization of acyloxycarbonyl compounds in the aliphatic series stem therefore mainly from the unfavourable reduction potentials of their dianion formation.[23] In addition, our experiments (Scheme 7) with different oxoalkanoates such as **21**, **23** and **25** by titanium on graphite affording the corresponding cyclanones show a strong influence of the chain length of the alcohol part of the ester on the outcome of these McMurry type oxoalkanoate cyclization reactions.[7,22] For this very reason the reaction of the acyloxycarbonyl compounds **6** and **7a-c** must be additionally disfavoured.

Further studies on these and related titanium based heterocycle syntheses are in progress.

EXPERIMENTAL

General. NMR spectra were recorded on a Bruker MSL 300 instrument at 300 MHz (^1H) and 75 MHz (^{13}C) in $CDCl_3$ (Aldrich) as solvent and TMS as internal standard. Chemical shifts (δ) are given in ppm, coupling constants (J) in Hertz. Multiplicity is assigned according to first order interpretation of the spectra. FT-IR (cm^{-1}) was performed on a Perkin Elmer 883 spectrometer. The melting points (Tottoli) are uncorrected. Column chromatography was invariably performed on Merck silica gel (230-240 mesh), TLC on precoated sheets (Merck 5554) using mixtures of toluene/ethyl acetate in various proportions as eluents. THF and DME were distilled over potassium/benzophenone, CH_2Cl_2 over CaH_2 prior to use. $TiCl_3$ was purchased from Aldrich, FRG, potassium from Riedel de Haen, Austria. In all experiments graphite KS 5-44 supplied by Lonza, Switzerland, was employed, although other graphite qualities turned out to be equally suitable for the preparation of metal-graphite reagents.[4,5]

Crystal structure analysis of compound 11h. Data collected at 295 K; space group **Pbca**, $Z = 8$ for $C_{18}H_{19}N$; a = 8.80 (2) Å, b = 12.32 (3) Å, c = 26.76 (7) Å, V = 2901 (2) Å^3, $d_{calc} = 1.14 g/cm^3$. Intensity data collected for one octant with $5.5° \leq 2\vartheta \leq 45°$, 2213 observed, 1957 unique and 749 significant ($F_{obs} > 4\sigma(F)$) structure factors. Structure refined with anisotropic atomic displacement parameters for all non-hydrogen atoms, H atoms at calculated positions, R = 0.1178 (unit weights) for 191 parameters and 749 observations. A difference electron density map showed features up to 0.3(1) e/Å^3 in the final Fourier synthesis. Atomic coordinates have been deposited at the Cambridge Crystallographic Data Center.

Starting Materials.

Preparation of the precursors for the McMurry type cyclization reactions. Representative procedure. To a stirred solution of 2-aminobenzophenone (3.94g, 20mmol) in CH_2Cl_2 (30ml) and pyridine (1.98g, 25mmol) was added pivaloyl chloride (2.89g, 24mmol). After being stirred for 3h at ambient temperature, HCl (0.1N, 20ml) was added, the aqueous layer extracted twice with CH_2Cl_2 (10ml), the combined organic layers washed with saturated $NaHCO_3$ (20ml) and water (10ml), dried over Na_2SO_4 and evaporated. The residue was purified by flash chromatography using toluene/ethyl acetate (15/1) as eluent, thus affording product **10h** as colourless crystals (5.23g, 93%).

Commercially available 2-aminobenzophenone, 2-aminoacetophenone, 2-aminobenzaldehyde, 2-hydroxybenzophenone, 2-hydroxyacetophenone, salicylaldehyde, 2-hydroxy-4-methoxybenzaldehyde, benzoin and 1,3-diphenyl-1,3-propanedione were acylated analogously. The data of the corresponding products are summarized in Table 7.

Preparation of ketoimide 18. Succinic anhydride (609mg, 6.08mmol) was added to a stirred solution of 2-aminobenzophenone (1.0g, 5.07mmol) in CH_2Cl_2 (30ml) and pyridine (1ml). After 4h at room temperature, TLC indicated complete conversion of the starting material. NaOH (1N, 20ml) was added, the aqueous phase separated, acidified (pH 3; H_2SO_4) and extracted with four portions of ethyl acetate (60ml). The combined organic layers were dried over Na_2SO_4, evaporated and the residue

dissolved in acetic anhydride (20ml) containing NaOAc (1.5g). After being refluxed for 3h, the mixture was diluted with CH_2Cl_2 (50ml), stirred with saturated $NaHCO_3$ (30ml) for 30min, the organic layer washed with water (10ml), dried over Na_2SO_4 and evaporated. The crude product was purified by column chromatography using toluene/ethyl acetate (2/1) as eluent affording the title compound as colourless crystals (800mg, 60%). **mp** 133-135°C. **^{1}H NMR**: 7.18-7.43 (m, 9H), 2.58(bs, 4H). **^{13}C NMR:** 195.05, 176.12, 137.34, 135.55, 133.01, 132.20, 131.13, 131.01, 129.84, 129.13, 128.84, 128.71, 128.41, 125.41.

Preparation of the formamides 10e and 10i. A mixture of acetic anhydride (2.21g, 21.6mmol) and formic acid (98%, 0.86ml) was heated under nitrogen at 60°C for 2h. After being cooled to room temperature, 2-aminobenzophenone (2.0g, 10.14mmol) was added in portions. After 30min the mixture was diluted with ether (30ml) and saturated $NaHCO_3$ (15ml) was slowly added with vigorous stirring. The aqueous layer was extracted twice with ether (20ml), the organic phase dried over Na_2SO_4, evaporated and the residue purified by column chromatography using toluene/ethyl acetate (15/1) as eluent. Thus, product **10e** was obtained as pale yellow oil (2.20g, 96%)(lit.[34m] oil). **^{1}H NMR**: 10.67(bs, 1H, -NH), 8.62(d, 1H, J=8.5), 8.42(s, 1H), 7.65(d, 2H, J=7.5), 7.39-7.57(m, 6H); **^{13}C NMR**: 199.19, 159.71, 139.22, 138.40, 134.08, 133.41, 132.59, 129.90, 128.35, 123.65, 122.70, 122.12.

Formamide **10i** (1.55g, 95%) was prepared analogeously from 2-aminoacetophenone (1.35g, 10mmol). **mp** 75-76 (lit.[34n] 79)°C **^{1}H NMR**: 11.55(bs, 1H, -NH), 8.67(d, 1H, J=8), 8.43(s, 1H), 7.85(d, 1H, J=8), 7.48(t, 1H, J=8), 7.10(t, 1H, J=8), 2.60(s, 3H); **^{13}C NMR**: 202.71, 159.91, 139.83, 135.05, 131.71, 123.08, 122.07, 121.53, 28.49.

McMurry Type Reactions

Preparation of titanium on graphite. A 200ml two-necked flask, equipped with a teflon coated magnetic stirring bar and a reflux condenser connected to an argon line was charged with graphite (3.0g, 250mmol) and heated to 150-160°C. Freshly cutted potassium (1.20g, 31mmol) was added in pieces with vigorous stirring at that temperature until the bronze-coloured potassium-graphite laminate (C_8K) was formed (5-10 min). After being cooled to room temperature it was suspended in anhydrous THF (40ml) and $TiCl_3$ (1.50g, 10.2mmol) was added to this mixture causing the solvent to boil. When the exothermic reaction had subsided, the slurry was heated for 1.5h to ensure complete reduction.

McMurry-type reactions of acyloxycarbonyl compounds. Representative procedure. A solution of substrate **1a** (1.51g, 5mmol) in anhydrous THF (60ml) was added dropwise over a period of 8 h to a freshly prepared refluxing suspension of titanium-graphite (*vide supra*) in THF (40ml) under argon. The mixture was allowed to cool to room temperature and filtered over a short plug of silica gel. The inorganic residue was washed with ethyl acetate (50ml) in several portions, the filtrate evaporated *in vacuo* and the crude product purified by column chromatography using toluene/ethyl acetate (25/1) as eluent, thus affording 2,3-diphenylbenzo[b]furan (**2a**) as colourless crystals (1.23g, 88%). All products listed in Tables 1, 2 and 3 were obtained according to this procedure.

Table 7. Selected Analytical and Spectroscopic Data of the Substrates

Prod.	Yield (%)	mp (°C)	lit mp (°C)	^{13}C RCOR'	^{13}C -COXR	^{13}C other	^{1}H
1a	86	oil	oil[34a]	194.85	164.67		
1b	83	94-95	96.5[34b]	194.96	169.18	20.66[a]	
1c	89	84-86	88[34c]	197.51	165.22	29.77[b]	
1d	76	86-87	89[34d]	197.48	169.40	29.30[b], 21.09[a]	
1e	89	37-38	37[34e]	188.64	169.03	20.53[a]	10.02[c]
1f	89	oil	oil[34f]	188.46	165.04		10.22[c]
3a	80	94-95		187.16	165.42	56.05, 55.82	10.04[c]
3b	84	81-83		186.87	165.20	55.76, 55.37[e]	10.00[c]
4a	94	98-100	109[34g]	188.50	163.91	157.05, 110.20[f]	7.41[g]
4b	91	oil		197.05	163.67	162.77, 116.64[f]	6.08[g]
8b	84	79-80	84[34h]	193.94	170.45	20.74[a]	6.96[h]
8c	94	120-121	125[34h]	193.95	166.26		7.14[h]
10a	97	96-98	100[34i]	203.37	166.23	28.68[b]	12.71[i]
10b	89	76-77	77[34i]	202.49	169.04	28.26[b], 25.25[a]	11.54[i]
10c	94	89-91	91[34i]	200.36	165.88		12.01[i]
10d	78	83-84	88[34j]	199.42	168.93	25.07	10.75[i]
10f	91	45-46		199.55	172.23	[d]	10.89[i]
10g	73	71-73	74[34k]	195.93	166.20		12.08[i], 9.96[c]
10h	93	86-87		199.94	178.07	40.36, 27.71[j]	11.26[i]
10j	88	115-117		200.46	160.57	156.75	12.02[i]
12a	94	97-100		200.49	164.55		12.03[i]
12b	94	103-104		200.62	164.87		12.03[i]
12c	95	96-98		200.26	164.19		12.00[i]
12d	36	123-124		200.68	165.33		12.02[i]
12e	53	70-72	91[34l]	200.50	164.42		12.12[i]
12f	90	78-80		198.70	162.45	55.66[e]	11.98[i]
12g	88	174-176		200.52	163.74		12.13[i]
14	88	100-102		199.98	164.68		11.24[i], 6.65[m]
16	95	oil		199.52	172.81[n]	60.29, 14.22[k,l]	10.81[i]
20	87	72-74		199.37	154.44	52.45[e]	10.31[i]

[a] CH_3COX- [b] $RCOCH_3$ [c] -CHO [d] 38.52, 32.01, 29.75, 29.56, 29.42, 29.32, 25.55, 22.76, 14.17, [e] -OMe [f] olefinic carbons [g] olefinic proton [h] PhCH(OR)COPh [i] NH [j] $C(CH_3)_3$ [k] $-OCH_2CH_3$ [l] 37.12, 33.40, 20.60 ($-CH_2-$) [m] (d, 1H, J = 16) [n] and 171.21

2,3-Diphenylbenzofuran (2a): **mp** 119-122 (lit.[25] 121)^{0}C. **IR**: 3061, 2929, 1602, 1502, 1486, 1454, 1441, 1257, 1209, 1063, 962, 763, 746, 699. **^{1}H NMR**: 7.73-7.76 (m, 2H), 7.28-7.65 (m, 12H). **^{13}C NMR**: 154.29, 150.80, 133.14, 130.94, 130.52, 130.03, 129.19, 129.03, 128.64, 128.58, 127.87, 127.28, 124.92, 123.17, 120.27, 117.78, 111.34.

2-Methyl-3-phenylbenzofuran (2b): oil[26] **IR**: 3061, 2925, 2868, 1598, 1494, 1476, 1456, 1442, 1260, 1212, 1113, 1099, 1068, 1006, 766, 743, 693. **^{1} H NMR**: 7.85 (d, 2H), 7.52-7.60 (m, 4H), 7.28-7.42 (m, 3H), 2.52 (s, 3H). **^{13}C NMR**: 154.04, 150.95, 131.69, 131.43, 128.56, 126.97, 124.56, 122.59, 119.53, 111.52, 111.18, 9.72.

3-Methyl-2-phenylbenzofuran (2c): **mp** 34-36 (lit.[27] 34-34.5)^{0}C. **IR**: 3031, 2976, 2930, 1606, 1577, 1482, 1448, 1280, 1216, 1103, 1077, 927, 756, 739. **^{1}H NMR**: 7.99 (d, 2H), 7.63-7.70 (m, 4H), 7.39-7.53 (m, 3H), 2.61 (s, 3H); **^{13}C NMR**: 154.07, 150.90, 131.68, 131.42, 128.93, 128.41, 127.15, 124.53, 122.56, 111.13, 110.98, 9.59.

2-Phenylbenzofuran (2f): **mp** 120-121 (lit.[28] 120-121)^{0}C. **IR**: 3410, 3054, 2926, 2855, 1605, 1562, 1469, 1455, 1038, 1020, 919, 806, 763, 747. **^{1}H NMR**: 7.92 (d, 2H), 7.29-7.65 (m, 7H), 7.07 (s, 1H), **^{13}C NMR**: 156.18, 155.16, 130.8, 129.47, 128.98, 128.74, 125.18, 124.47, 123.14, 121.11, 111.38, 101.53.

2,3,5-Triphenylfuran (5a): **mp** 92-94 (lit.[29] 91-93)^{0}C. **^{1}H NMR**: 7.21-7.88 (m, 15H), 6.91 (s, 1H); **^{13}C NMR**: 152.83, 148.18, 134.60, 131.40, 130.82, 128.97, 128.78, 128.34, 128.07, 127.53, 126.40, 124.81, 124.09, 109.72.

3,5-Dimethyl-2-phenylfuran (5b): oil[30] **^{1}H NMR**: 7.63 (d, 2H), 7.42 (t, 2H), 7.26 (t, 1H), 5.97 (s, 1H), 2.35 (s ,3H), 2.27 (s, 3H); **^{13}C NMR**: 150.55, 131.74, 128.48, 126.66, 125.01, 117.36, 111.55, 13.67, 12.05.

Deoxybenzoin (9): **mp** 54-55 °C; identified by comparison with an authentic sample.

McMurry-type reactions of acylamidocarbonyl compounds. Representative procedure. A solution of compound **10g** (1.12g, 5mmol) in THF (10ml) was added at once to a freshly prepared boiling suspension of titanium-graphite under argon. Reflux was continued for 3h and the mixture filtered over silica after being cooled to room temperature. Washing of the inorganic solids with four portions of ethyl acetate (50ml) and evaporation of the solvent, followed by column chromatography with toluene as eluent afforded crystalline 2-phenylindole (**11g**) (870mg, 90%). **mp** 189-190 (lit.[18r] 186-187)°C. **IR**: 3448, 2930, 1540, 1481, 1457, 1446, 1401, 1352, 1339, 1300, 1230, 1075, 931, 906, 797, 762, 743, 689. **^{1}H NMR**: 8.32(bs, 1H, -NH), 7.69(d, 3H), 7.34-7.50(m, 4H), 7.15-7.27(m, 2H), 6.87(d, 1H, J=2); **^{13}C NMR**: 138.20, 137.08, 133.32, 129.54, 129.26, 127.96, 125.41, 122.60, 120.91, 120.52, 111.14, 100.25.

3-Methyl-2-phenylindole (11a): **mp** 90-92 (lit.[18f] 91-93) ^{0}C. **IR**: 3416, 3043, 2941, 2917, 1607, 1480, 1461, 1448, 1375, 1287, 1089, 740. **^{1}H NMR**: 8.06 (bs, 1H, -NH), 7.18-7.61 (m, 9H), 2.52 (s, 3H); **^{13}C NMR**: 136.17, 134.31, 131.62, 130.00, 128.80, 128.02, 127.77, 122.56, 119.77, 119.23, 110.94, 108.97, 9.89.

2,3-Dimethylindole (11b): **mp** 100-104 (lit.[18f] 104-106) ^{0}C. **IR**: 3400, 3056, 2977, 2931, 2863, 1613, 1591, 1483, 1462, 1384, 1333, 1299, 1111, 1008, 739. **^{1}H NMR**: 7.56-7.60 (m, 2H), 7.17-7.30 (m, 3H), 2.38 (s, 3H), 2.32 (s, 3H); **^{13}C NMR**: 135.50, 130.91, 130.07, 121.10, 119.26, 118.16, 110.30, 107.29, 11.60, 8.62.

2,3-Diphenylindole (11c): **mp** 122-124 (lit.[31] 124-125) ^{0}C **IR**: 3413, 3059, 2977, 2873, 1602, 1504, 1483, 1455, 1439, 1329, 1251, 1100, 1071, 764, 745, 700. **^{1}H NMR**: 8.18 (s, 1H, -NH), 7.93 (d, 1H), 7.38-7.66 (m, 13H); **^{13}C NMR**: 136.08, 135.30, 134.30, 132.81, 130.36, 128.8, 128.75, 128.41, 127.86, 126.44, 122.88, 120.64, 119.88, 111.20.

2-Methyl-3-phenylindole (11d): **mp** 58-61 (lit.[31] 59-60) ^{0}C **IR**: 3400, 3058, 2978, 2870, 1620, 1602, 1560, 1496, 1459, 1440, 1331, 1306, 1255, 1103, 1075, 1019, 770, 149, 704. **^{1}H NMR**: 7.82 (d, 1H), 7.79 (s, 1H, -NH), 7.56-7.67 (m, 4H), 7.23-7.46 (m, 4H), 2.51 (s, 3H); **^{13}C NMR**: 135.70; 135.50; 131.67; 129.65, 128.71, 128.12, 126.02, 121.72, 120.20, 119.00, 114.71, 110.59, 12.57.

3-Phenylindole (11e): **mp** 84-86 (lit.[32] 85) °C. **IR**: 3419, 3076, 3035, 2928, 1647, 1618, 1599, 1541, 1487, 1457, 1417, 1238, 1117, 1104, 768, 740, 694. **^{1}H NMR**: 8.08 (d, 1H, J=7, -NH), 7.78(dd, 2H, J=8, 1.2), 7.56(t, 2H, J=7.5), 7.27-7.45(m, 6H); **^{13}C NMR**: 136.92, 135.82, 129.00, 127.71, 126.21, 125.98, 122.62, 122.04, 120.55, 120.04, 118.49, 111.66.

3-Phenyl-2-pentadecylindole (11f): oil. **IR**: 3412, 3061, 2925, 2855, 1603, 1495, 1459, 1432, 770, 742, 701. **^{1}H NMR**: 7.97(bs, 1H, -NH), 7.71(d, 1H, J=8), 7.15-7.58(m, 8H), 2.89(t, 2H), 1.15-1.80(m, 26H), 0.96(t, 3H). **^{13}C NMR**: 136.31, 135.79, 135.50, 129.90, 128.68, 128.29, 126.12, 121.76, 120.13, 119.16, 110.59, 32.18, 30.13, 29.92, 29.78, 29.62, 26.61, 22.93, 14.35.

2-t-Butyl-3-phenylindole (11h): **mp** 126-127 °C. **IR**: 3434, 3059, 2963, 2929, 2869, 1605, 1539, 1491, 1476, 1456, 1324, 1251, 1010, 746, 702. **^{1}H NMR**: 8.04(bs, 1H, -NH), 7.01-7.41(m, 9H), 1.33(s, 9H). **^{13}C NMR**: 142.68, 137.28, 133.85, 131.87, 131.00, 128.07, 126.80, 121.77, 119.84, 119.26, 110.27, 33.54, 31.34.

3-Methylindole (11i): **mp** 94-96 (lit.[33] 95-96)°C. **IR**: 3440, 3046, 2930, 1603, 1488, 1450, 1432, 786, 745, 696. **^{1}H NMR**: 7.85(bs, 1H, -NH), 7.65(d, 1H, J=8), 7.15-7.39(m, 3H), 6.99(d, 1H, J=1.5), 2.39(s, 3H); **^{13}C NMR**: 137.51, 128.60, 122.14, 121.82, 119.39, 119.10, 112.01, 111.18, 9.85.

3-Phenyl-2-(thiophen-2'-yl)indole (11j): **mp** 113-114 °C. **IR**: 3413, 3060, 3029, 2927, 1600, 1522, 1512, 1486, 1456, 1442, 1414, 1329, 1250, 1026, 850, 744, 699. **^{1}H NMR**: 8.19bs, 1H, -NH), 7.70(d, 1H, J=8), 7.26-7.65(m, 9H), 7.15(d, 1H, J=4); 7.06(t, 1H, J=4); **^{13}C NMR**: 135.98, 134.72, 130.74, 129.28, 128.77, 128.49, 127.64, 127.06, 125.54, 123.24, 120.78, 119.88, 110.98.

2-(3'-fluorophenyl)-3-phenylindole (13a): **mp** 121-123 °C. **IR**: 3406, 2900-3060, 1612, 1583, 1554, 1502, 1475, 1453, 1332, 1245, 1184, 909, 880, 772, 746, 702, 682. **^{1}H NMR**: 8.17(bs, 1H, -NH), 7.79(d, 1H, J=8), 7.17-7.55(m, 11H), 7.06(t, 1H, J=8); **^{13}C NMR**: 163.08(J=245), 136.25, 135.14, 135.04, 132.86, 130.48, 128.89, 128.41, 126.83, 126.50, 124.03, 123.37, 122.95, 120.88, 120.13, 116.25, 115.25, 114.96, 114.86, 114.58, 111.25. **^{19}F NMR**: -95.33. **MS** (m/e): 287 (M^+), 272, 257, 239, 207, 183, 165, 142, 133.

2-(4'-chlorophenyl)-3-phenylindole (13b): oil. **IR**: 3410, 3058, 1601, 1528, 1502, 1480, 1454, 1429, 1329, 1312, 1295, 1265, 1252, 1097, 1013, 832, 773, 741, 701. **^{1}H NMR**: 8.12(bs, 1H, -NH), 7.79(d, 1H, J=8), 7.26-7.54(m, 12H); **^{13}C NMR**: 136.21, 134.97, 133.75, 133.09, 131.32, 130.32, 129.55, 129.26, 129.06, 128.87, 128.45, 126.69, 125.53, 123.18, 120.81, 119.97, 115.79, 111.20. **MS** (m/e): 305, 303 (M^+), 267, 239, 207, 165, 134, 120.

2-(3'-bromophenyl)-3-phenylindole (13c): **mp** 120-122 °C. **IR**: 3414, 2900-3060, 1595, 1548, 1454, 1331, 1313, 1250, 1069, 786, 772, 745. **^{1}H NMR**: 8.12(bs, 1H, -NH), 7.78(d, 1H, J=8), 7.67(d, 1H, J=2), 7.16-7.53(m, 11H). **^{13}C NMR**: 136.28, 135.01, 134.79, 132.49, 130.87, 130.74, 130.35, 130.30, 129.29, 128.87, 128.48, 127.19, 126.80, 125.54, 123.37, 122.88, 120.88, 120.13, 116.31, 111.24. **MS** (m/e): 349, 347 (M^+), 267, 239, 207, 165, 134, 120.

2-(4'-iodophenyl)-3-phenylindole (13d): **mp** 107-108 °C. **IR**: 3411, 3058, 1602, 1499, 1477, 1454, 1443, 1428, 1005, 824, 772, 745, 701. **^{1}H NMR**: 8.21(bs, 1H, -NH), 7.65-7.70(m, 3H), 7.16-7.46(m, 10H). **^{13}C NMR**: 138.12, 136.34, 135.01, 132.52, 130.39, 129.99, 128.91, 126.80, 123.37, 120.91, 120.10, 111.18, 93.51. **MS**: 395 (M^+), 267, 239, 207, 134.

2-(4'-trifluoromethylphenyl)-3-phenylindole (13e): **mp** 121-124 °C. **IR**: 3413, 3062, 2927, 1617, 1604, 1515, 1487, 1455, 1445, 1431, 1405, 1325, 1169, 1125, 1094, 1064, 1017, 844, 749, 701. **^{1}H NMR**: 8.16(bs, 1H, -NH), 7.80(d, 1H, J=8), 7.20-7.65(m, 12H); **^{13}C NMR**: 136.46, 134.79, 132.52, 130.42, 129.81, 129.64, 129.32, 129.02, 128.77, 128.38, 128.29, 126.99, 126.44, 126.18, 125.80, 125.58, 123.69, 122.79, 121.04, 120.65, 120.28, 119.84, 116.96, 111.36. **^{19}F NMR**: -62.56. **MS** (m/e): 337 (M^+), 267, 165, 134.

2-(3'-methoxyphenyl)-3-phenylindole (13f): **mp** 46-50 °C. **IR**: 3413, 2830-3065, 1602, 1552, 1502, 1477, 1458, 1435, 1262, 1218, 1047, 909, 771, 732. **^{1}H NMR**: 8.30(bs, 1H, -NH), 7.91(d, 1H, J=8), 7.67(dd, 2H, J=8, 1.5), 7.58(t, 2H, J=8), 7.36-7.50(m, 5H), 7.13-7.18(m, 2H), 7.03(dd, 1H, J=8, 1). **^{13}C**

NMR: 159.71, 136.04, 135.33, 134.05, 130.42, 129.84, 129.22, 128.99, 128.68, 128.41, 126.47, 122.91, 120.59, 120.52, 119.84, 115.44, 113.89, 113.73, 111.17, 55.17.

2-(4'-cyanophenyl)-3-phenylindole (13g): **mp** 168-170 °C. **IR**: 3399, 3062, 2926, 2855, 2227, 1606, 1510, 1451, 1444, 1330, 1250, 908, 841, 773, 746, 732, 701. **^{1}H NMR**: 8.43(bs, 1H, -NH), 7.68(d, 2H, J=8), 7.18-7.59(m, 12H). **^{13}C NMR**: 137.47, 136.72, 134.53, 132.62, 131.88, 130.36, 129.09, 128.51, 127.22, 124.06, 121.13, 120.39, 119.03, 117.86, 111.43, 110.87.

2-(2'-phenylethen-1'-yl)-3-phenylindole (15): **mp** 102-104 °C. **IR**: 3427, 2850-3060, 1599, 1496, 1487, 1444, 1321, 1018, 954, 773, 752, 695. **^{1}H NMR**: 8.31(bs, 1H, -NH), 7.78(d, 1H, J=8), 7.17-7.62(m, 13H), 6.93(d, 1H, J=17); **^{13}C NMR**: 137.24, 136.75, 134.82, 132.78, 130.39, 128.99, 128.87, 128.50, 127.93, 127.60, 126.77, 126.61, 123.82, 120.68, 119.97, 119.10, 118.26, 110.91,

Ethyl (3'-phenyl-indol-2'-yl)butanoate (17a): **mp** 90-92 °C. **IR**: 3402, 3060, 3026, 2983, 2940, 1719, 1620, 1603, 1496, 1459, 1374, 1333, 1304, 1257, 1188, 1145, 1017, 909, 742, 702. **^{1}H NMR**: 8.60(bs, 1H, -NH), 7.82(d, 1H, J=8), 7.25-7.66(m, 8H), 4.25(q, 2H, J=7), 3.00(t, 2H, J=7), 2.44(t, 2H, J=7), 2.12(quint., 2H, J=7), 1.36(t, 3H, J=7). **^{13}C NMR**: 173.74, 135.57, 135.50, 134.92, 129.78, 128.65, 128.03, 126.12, 121.79, 120.00, 119.07, 115.03, 110.75, 60.64, 33.60, 25.56, 25.23, 14.29.

10-Phenyl-tetrahydropyridino[1,2-a]indol-4-one (17b): **mp** 155-157 °C. **IR** (nujol): 1712, 1614, 1457, 1376, 1363 **^{1}H NMR**: 8.62(d, 1H, J=8), 7.64(d, 1H, J=7.5), 7.33-7.54(m, 7H), 3.05(t, 2H, J=6), 2.84(t, 2H, J=6), 2.07(quint., 2H, J=6). **^{13}C NMR**: 169.60, 134.94, 134.24, 133.40, 129.61, 129.45, 128.80, 127.22, 124.66, 124.24, 118.88, 118.61, 116.67, 34.70, 22.96, 21.47.

9-Phenyl-1,2-dihydropyrrolo[1,2-a]indol-3-one (19): **mp** 175-177 °C. **IR** (nujol): 1738, 1611, 1459, 1376, 1354. **^{1}H NMR** (DMSO-d_6): 8.07(dd, 1H, J=5.5, 1.5), 7.86(dd, 1H, J=4.5, 2.5), 7.71(d, 2H, J=7.5), 7.58(t, 2H, J=7.5), 7.39(m, 3H), 3.38(t, 2H), 3.18(t, 2H, J=5); **^{13}C NMR**: 172.35, 141.91, 133.44, 133.18, 130.23, 129.24, 127.61, 126.77, 124.39, 123.59, 119.71, 113.23, 34.52, 20.09.

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