Tetrahedron 65 (2009) 1268–1275

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Microwave-assisted zinc chloride-catalyzed synthesis of substituted pyrroles from homopropargyl azides

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ARTICLE INFO

Article history:
Received 13 October 2008
Received in revised form 24 November 2008
Accepted 24 November 2008
Available online 3 December 2008

Keywords:
Pyrroles
Nitrogen heterocycles
Cyclization
5-*endo-dig* Cyclization
Zinc chloride
Homopropargyl azides
Alkynes

ABSTRACT

Ligand-free 5-*endo-dig* cyclization of 1,4- and 1,2,4-substituted but-3-yn-1-yl (homopropargyl) azides in the presence of zinc chloride (usually 20 mol %) in dichloroethane at elevated temperature provides 2,5-di- and 2,3,5-trisubstituted pyrroles in high to moderate yields (91–41%). Both conventional and microwave protocols furnished comparable results. A structure of 2-(4-fluorophenyl)-5-(4-methylphenyl)-1*H*-pyrrole was confirmed by X-ray crystallography.

1. Introduction

Formation of pyrrole containing compounds is of particular interest for the synthetic organic community since this ring system is often embedded in important natural products and medicinally active compounds.[1] Various reactions leading to pyrroles have been reported and numerous references can be found in review articles, handbooks, and encyclopedias.[2] The synthesis of a pyrrole ring, frequently *N*-substituted, has also been effectively established in the form of various metal-catalyzed cyclization reactions.[3,4] Azides, due to the relatively easy access, offer an interesting synthetic alternative in reactions leading to expulsion of dinitrogen, a benign and easy removable byproduct. Quite recently formation of pyrroles from homopropargyl (but-3-yn-1-yl) azides via gold/silver (2.5 mol % (dppm)Au_2Cl_2, 5 mol % $AgSbF_6$, CH_2Cl_2, 35 °C, 41–93%)[5] or platinum (5 mol % $PtCl_4$, 20 mol % 2,6-di-*tert*-butyl-4-methylpyridine, EtOH, 50 °C or reflux, 55–88%)[6] catalysis has been reported.

First-row transition metals such as zinc are potential homogeneous catalysts that can contribute to a more sustainable chemical enterprise, and are currently being pursued as a replacement to precious metals in chemical processes.[7] In our effort to find the effective application of zinc catalysts, we have recently reported cycloisomerizations of alk-3-yn-1-ones and 5-alkynyl-2′-deoxyuridines that lead to furans and furanopyrimidine nucleosides.[8,9] Here our efforts to provide an alternative to gold/silver and platinum used in the formation of substituted pyrroles from but-3-yn-1-yl azides are presented.

2. Results and discussion

The necessary starting materials, alkynols (**1**), were obtained via a ring opening process by treatment of oxiranes with lithium alkynides. Procedures involving $BF_3 \cdot Et_2O$ in THF (68–71%)[10] and non-catalyzed protocol in DMSO (73–85%)[11] were effective. Synthesis of homopropargyl azides was carried out according to the literature methods. Transformation of alkynols **1a–e** to mesylates followed up by in situ S_N2 reaction with sodium azide, or for **1f–h** a Mitsunobu protocol[12] employing diphenylphosphoryl azide (in the presence of diisopropyl azodicarboxylate and PPh_3), yielded homopropargyl azides **2** (74–93 or 62–77%, Scheme 1).[6] The substituents include alkyl (propyl, butyl), cycloalkyl (cyclopropyl, fused cyclohexyl), and aryl (phenyl, *p*-tolyl, and *p*-halophenyls) with detailed structures of **2a–h** illustrated in Table 1.

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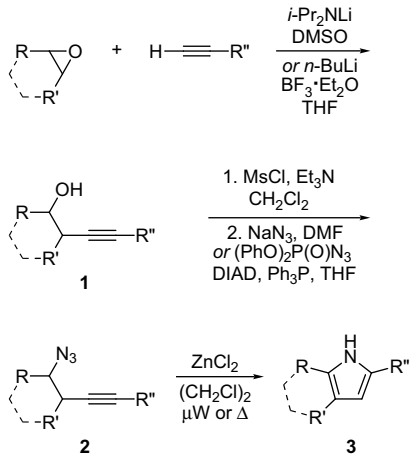
0040-4020/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2008.11.094



Scheme 1. Synthesis of pyrroles **3**. For full structures see Table 1.

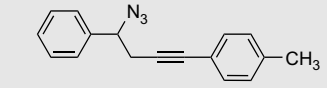
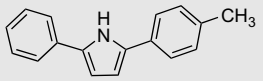
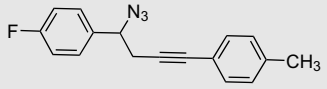
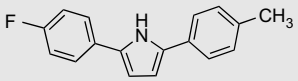
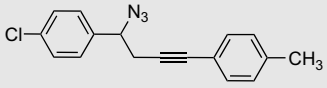
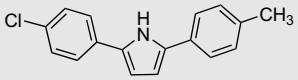
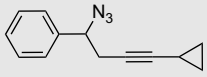
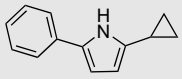
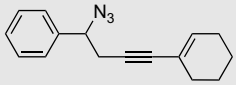
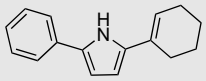
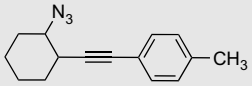
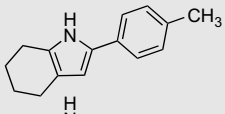
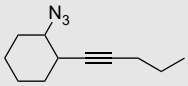
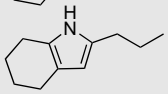
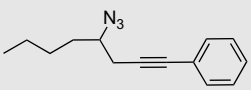
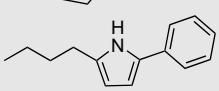
The general application of zinc halides toward pyrrole ring formation has experienced little attention in the literature.[4a,c,d,13] In particular, few cyclizations have been reported with the aid of $ZnCl_2$.[4a,c,d] In a search of non-precious metal catalyst, we turned our attention to 1.0 M $ZnCl_2$ etherate,[14] an inexpensive and easy to handle commercially available reagent. The catalytic properties of $ZnCl_2$/ether combinations have been previously investigated.[15] Already successfully used in our laboratory,[8] this reagent offers the benefit of reaction homogeneity that could be effectively applied to cyclization of **2a** (R=Ph, R′=H, R″=*p*-MeC_6H_4; Scheme 1) with an aid of conventional heating. This reaction routinely proceeded within 16 h in 1,2-dichloroethane at 75 °C with an optimized catalytic amount of $ZnCl_2$ established at 20 mol %. Pyrrole **3a** was isolated in 90% yield.

The use of microwave (μW)-assisted chemistry of azides already has precedence. Reports account usually for a dipolar cycloaddition reaction[16] or a simple preparation of organic azides.[17] Thus, in order to decrease the reaction time, the process was investigated further in a sealed vial in an environment of temperature- and pressure-controlled microwave reactor.

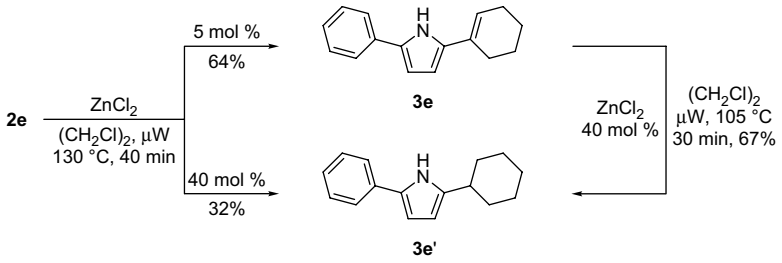
Thermal stability of a representative starting material was evaluated, to ensure safer operation at higher temperature. A DSC trace of azide **2a** was recorded. Gradual exothermal decomposition was observed with T_p=208 °C, T_e=156 °C, and T_i=135 °C.[18] Thus, it was established that practical operations can be carried out at temperatures at 135 °C.

The reactivity of several zinc containing compounds, mainly commercially available zinc(II) salts, were compared under microwave conditions.[19] In a glovebox, 0.1 M solutions of ZnI_2, $ZnBr_2$, or $ZnCl_2$ in ether were prepared and added in 20 mol % amounts to a solution of azide **2a** (0.2 mmol) in 1,2-dichloroethane (0.5 mL). After 40 min at 130 °C (ca. 2 bar) complete conversion to **3a** was observed with $ZnCl_2$ and $ZnBr_2$. The use of ZnI_2 led to full conversion of **2a**, however, multiple products except for pyrrole **3a** were observed in a post-reaction mixture. The quantitative formation of **3a** was also achieved with the μ^4-oxo-tetranuclear zinc cluster $Zn_4(OCOCF_3)_6O$.[20,21] This catalyst offers a homogeneous solution

Table 1
Preparation of pyrroles **3** via cyclization of **2** with the use of zinc chloride

Entry	Azide **2**		Pyrrole **3**		Yield [%][a]
1		**2a**		**3a**[23]	90, 90,[b] 90[c]
2		**2b**		**3b**	73
3		**2c**		**3c**	91
4		**2d**		**3d**	79
5		**2e**		**3e**	64[d]
6		**2f**		**3f**[24]	52,[e,f] 51[c,e]
7		**2g**		**3g**	41,[e,f] 61[c,e]
8		**2h**		**3h**	48,[e,f] 65[c,e]

[a] Reactions were carried out on a 1.0 mmol scale with 20 mol % of $ZnCl_2$ (1.0 M in ether) in 1,2-dichloromethane at 105 °C for 60 min in a microwave, unless referenced otherwise.
[b] Solid $ZnCl_2$.
[c] Reactions were carried out in 1,2-dichloroethane, 75 °C, for 16 h (conventional heating).
[d] $ZnCl_2$ (5 mol %; 1.0 M in ether).
[e] $ZnCl_2$ (40 mol %; 1.0 M in ether).
[f] Condition: 130 °C for 40 min.



Scheme 2. Reaction of azide **2e** with $ZnCl_2$.

without the addition of ether. However, this reagent was not pursued for preparative scale reactions leading to pyrroles **3** since it has not been commercially available.[22]

Solid anhydrous $ZnCl_2$ and $ZnBr_2$ subjected to microwave conditions at an elevated temperature also proved to be effective catalysts. ZnI_2 resulted in complete conversion of **2a** with substantial formation of side products. This observation is in contrast to the previously observed diminished reactivity of solid zinc halides as compared to etherates for cycloisomerization of butynones.[8a] Such an outcome can be interpreted as a solubility/homogenity issue, which plays an essential role for rt reactions, but is not a factor when an elevated temperature is involved. Even so, the ease in handling etherate solution of $ZnCl_2$ offered a convenient form of catalyst for preparative smaller scale reactions.

Results acquired using other Zn(II) compounds (acetate, triflate, and phthalocyanine) did not warrant further attention. Copper(I) chloride and iron(II) chloride were also ineffective. Although conversion of starting material **2a** indicated its reactivity with iron(III) chloride ($FeCl_3 \cdot 6H_2O$), a complicated post-reaction mixture was not a surprise. It is known that pyrroles are prone to polymerization with Lewis acids of this type.[1]

When in a small preparative scale 4-(*p*-tolyl)-1-phenylbutynyl azide (**2a**, 1.0 mmol) was treated with $ZnCl_2$ etherate or solid $ZnCl_2$ (20 mol %) in dichloroethane, complete conversion to **3a** was also noticed after 60 min (microwave, 105 °C) by ^{1}H NMR. Pyrrole **3a** was isolated, after workup by a silica gel short column chromatography, in both equal 90% yields (Table 1, entry 1).

Other alkynyl azides **2b–d**,**f–h** (0.1 mmol) with aryl–aryl or aryl–cycloalkyl (entries 2–4), fused cycloalkyl–aryl or cycloalkyl–alkyl (entries 6 and 7), and alkyl–aryl (entry 8) substituents were subjected to the reaction with $ZnCl_2$ etherate in a similar manner as **2a**. ^{1}H NMR and GC/MS examination of post-reaction mixtures indicated almost quantitative conversion to pyrrole **3** in the case of 1-aryl substituents. For 1-alkyl-substituted azides a catalyst load needed to be increased to 40 mol %. The workup of the reaction using a conventional silica gel short column chromatography allowed for the separation of the Zn(II) catalyst from the product to yield pyrroles **3b–d**,**f–h** with 41–91% yield (Table 1).

The reaction of **2e** (an azide bearing cyclohexenyl substituent) with $ZnCl_2$ etherate (20 mol %) gave two main products. GC/MS indicated two major *m*/*z* peaks: with 223 (M^+ of the expected pyrrole **3e**, 31%) and 225 (68%). Attempts to separate these two products with overlapping R_f values by column chromatography were unsuccessful. The formation of dihydropyrrole, which was observed in a thermal reaction of allenes with azides,[25] was briefly taken into consideration, however, after repeating the reaction with 40 mol % of $ZnCl_2$, the *m*/*z* 223 peak was absent and we were able to consistently isolate the *m*/*z* 225 product in 32% yield. The structure of an *m*/*z* 225 product was assigned based upon NMR as a pyrrole with reduced double bond of cyclohexene (**3e′**, Scheme 2). Examination of the starting materials **2e** and **1e** did not indicate the presence of a saturated cyclohexane ring. A reducing agent or a source of hydrogen is yet to be determined.[26] Interestingly, after diminishing the $ZnCl_2$ catalyst load to 5 mol % almost exclusive formation of pyrrole **3e** was observed that was isolated in 64% yield. Summary of ratios of **3e**/**3e′** in the post-reaction mixture as a function of catalyst concentration is presented in Table 2.

In addition, isolated **3e** was treated with 40 mol % of $ZnCl_2$ (105 °C, 30 min) to give conversion to **3e′**, as confirmed by GC/MS. Pyrrole **3e′** was isolate in 67% yield.

In order to simplify reaction workup, we used 20 mol % of $ZnCl_2$ and provided ample reaction time to ensure the absence of starting azide in the post-reaction mixture. This quantity of reagent furnished quantitative conversion of **2a** within 60 min at 105 °C in microwave conditions. Raising the temperature to 130 °C reduced a conversion time to 40 min, and sometimes a catalyst load to 10 mol % (5 mol % gave 96% of **3a** with 4% of **2a** remaining). Thus, the reaction can likely be carried out with a shorter time or lower catalyst load, but may require higher temperature for completion. However, larger $ZnCl_2$ amounts were needed for reaction of azides with alkyl groups. Thus, to improve the yield of alkyl-substituted pyrroles, we revisited conventional protocol that allowed the isolation of **3f–h** in slightly higher percentage (51–65%).

Pyrroles **3** were characterized by NMR, IR, mass spectra, and UV–vis spectroscopy. The characteristic NMR features for aryl and alkyl-substituted pyrroles **3a–h** include the ^{1}H H3/H4 signals

Table 2
Ratio of pyrroles **3e**/**3e′** as a function of mol % of $ZnCl_2$ catalyst[a]

$ZnCl_2$ (mol %)	Ratio of **3e**/**3e′**
40	<1: >99
20	32: 68
10	86: 14
5	>99: <1

[a] 1,2-Dichloroethane, μW, 130 °C, 40 min. Ratio determined by GC/MS from a post-reaction mixture.

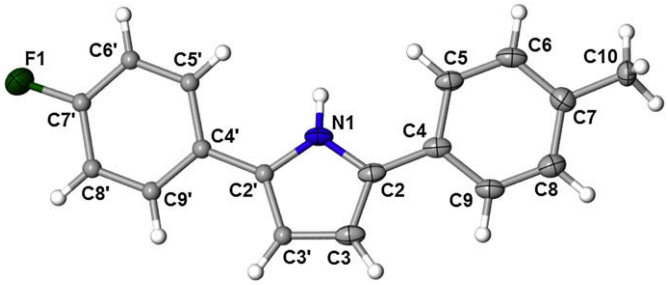


Figure 1. An ORTEP view of **3b** illustrating atom labeling scheme and thermal ellipsoids (50% probability level, asymmetric unit). Selected interatomic distances: N1–C2 1.3762(15); C2–C3 1.3827(19); C3–C3′ 1.410(3); C2–C4 1.4530(18). Key angles: C2–N1–C2′ 111.08(14); N1–C2–C3 106.32(12); C3–C2–C4 130.62(12); N1–C2–C4 123.01(11); C2–C3–C3′ 108.12(8).

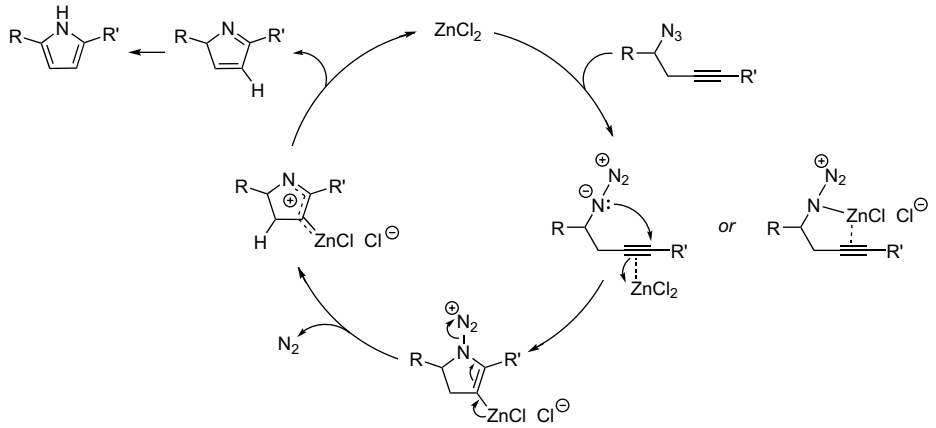


Figure 2. Mechanistic outline for cyclization of **2** into **3** with $ZnCl_2$.[5]

(6.68–5.67 ppm), and ^{13}C C3/C4 (H-substituted 108.2–104.2 and C-substituted 118.9–116.9 ppm). Mass spectra for **3a–h** exhibited intense molecular ions. Solid pyrroles **3** gave usually satisfactory elemental analyses.

The molecular structure of a representative pyrrole was confirmed by X-ray crystallography. Crystallization of compound **3b** from methylene chloride/hexanes gave single crystals suitable for X-ray analysis. Figure 1 illustrates the molecular structure of the expected 2,5-disubstituted pyrrole that crystallized in space group $Cmc2_1$ with atom N1 positioned on a mirror plane. The opposing aryl rings are related by mirror symmetry with the fluorine and methyl groups disordered with 50% site occupancies. The molecular structure of **3b** is nearly planar with phenyl ring planes parallel to each other and slightly twisted from pyrrole ring plane (dihedral angle N1–C2–C4–C5 13.46°).

The gold/silver-catalyzed formation of pyrroles from homopropargyl azides is believed to proceed via an intramolecular, stepwise mechanism (Fig. 2).[5] Since non-terminal alkynes were used in this work, the mechanistic pathway can be illustrated using the coordination of Zn to carbon–carbon triple bond. However, activation via coordination of Zn to nitrogen cannot be excluded. Required higher temperature as compared to Au/Ag or Pt, may indicate lower Zn ability to stabilize a cyclic cationic intermediate. With a lower catalyst load or temperature the presence of azides **2** in post-reaction mixtures was observed by ^1H NMR. Efforts to quantify a kinetic outcome were unsuccessful.

3. Conclusions

In summary, we have demonstrated that $ZnCl_2$ is an efficient, ligand-free, non-precious metal catalyst for cyclization of the homopropargyl azides. The catalyst proved to be more effective for aryl than for alkyl substituents. The relatively short reaction times via microwave-assisted protocol provide an alternative to currently available methods. Our approach allows for facile preparation of *N*-unprotected highly substituted pyrroles with aryl, (fused) cycloalkyl, and alkyl groups. This method allows for the introduction of substituents, such as cycloalkyls, that are not easily carried out by other methods.

4. Experimental section

4.1. General

Commercial chemicals were treated as follows: THF distilled from Na/benzophenone and 1,2-dichloroethane distilled from CaH_2. Acetylenes (GFS), oxiranes, and 1.0 M $ZnCl_2$ in ether (Aldrich), silica gel (Dynamic Absorbents, 40–63 μ), and other materials were used as received. NMR spectra were recorded on a Bruker Avance DPX-200 spectrometer (^1H of 200 MHz and ^{13}C of 50 MHz). Chemical shift values (δ) are given in parts per million. IR spectra were recorded on a Bio Rad FTS-175C spectrometer. Mass spectra were recorded on a GC/MS Hewlett Packard HP 6890GC instrument with 5973 mass selective detector. Microanalyses were conducted by Atlantic Microlab. Mps were recorded on a Büchi apparatus. The microwave reactions were carried out using capped vials in a CEM Discover or a Biotage Initiator reactors.

4.2. General procedure for the synthesis of but-3-yn-1-ols 1a–e (DMSO)[11]

A round-bottom flask, equipped with a magnetic stirring bar and fitted with a nitrogen inlet adapter and rubber septum, was charged with THF (25 mL) and alkyne **1** (19 mmol) via syringes. The reaction vessel was placed in a dry ice/acetone bath. After 10 min, a solution of LDA (2 M in THF/heptane/ethylbenzene, 10 mL, 20 mmol) was added via syringe within 5 min with stirring. The reaction mixture was stirred for 10 min after which time the bath was removed and the flask was allowed to warm to rt. DMSO (100 mL) was added via syringe over 5 min, followed by a solution of oxirane **2** (15 mmol) in THF (5 mL) via syringe over 1 min. After 3 h, the reaction mixture was poured into water (ca. 50 mL) and extracted with ether (4×50 mL). The combined organic phases were washed with saturated aq NaCl (2×150 mL) and dried over $MgSO_4$. After filtration, the solvent was removed by rotary evaporation. Silica gel column chromatography (hexanes/ethyl acetate 20:1→5:1) gave **1a** (2.790 g, 79%), **1b** (3.174 g, 83%), **1c** (2.975 g, 73%), **1d** (2.117 g, 76%), and **1e** (2.882 g, 85%).

*4.2.1. 4-(4-Methylphenyl)-1-phenylbut-3-yn-1-ol (**1a**)*

Light-yellow solid, mp 59–61 °C. IR (cm^{-1}, KBr) 3269 br m, 1509 s, 1053 s, 817 s, 749 s, 699 s, 545 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 6.8×10^{-5} M) 245 (18 000), 255 (17 000). NMR: ^1H ($CDCl_3$) 7.56–7.23 (m, 7H), 7.11 (d, 2H, J=8.0 Hz), 4.96 (t, 1H, J=6.4 Hz), 2.85 (d, 2H, J=6.4 Hz), 2.44 (s, 1H, exchangeable), 2.35 (s, 3H); (DMSO-d_6) 7.47–7.24 (m, 5H), 7.21 (d, 2H, J=8.2 Hz), 7.13 (d, 2H, J=8.2 Hz), 5.60 (d, 1H, J=4.4 Hz), 4.84–4.73 (m, 1H), 2,74 (d, 1H, J=6.3 Hz), 2,73 (d, 1H, J=6.3 Hz), 2.28 (s, 3H); ^{13}C ($CDCl_3$) 142.8, 138.2, 131.7, 129.1, 128.6, 128.0, 125.9, 120.2, 85.2, 83.4, 72.7, 30.8, 21.6. MS *m*/*z* 130 (100%), 115 (21%), 107 (49%), 79 (40%), 77 (25%); no other peaks of >20%. Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.19; H, 6.99.

*4.2.2. 1-(4-Fluorophenyl)-4-(4-methylphenyl)but-3-yn-1-ol (**1b**)*

Light-yellow solid, mp 70–72 °C. IR (cm^{-1}, KBr) 3390 br, 1602 s, 1505 s, 1221 s, 1158 s, 1064 s, 1013 s, 818 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 5.9×10^{-5} M) 244 (23 000), 255 (21 000). NMR ($CDCl_3$): ^1H 7.41 (dd, 2H, J=8.6, 5.4[27] Hz), 7.28 (d, 2H, J=8.2 Hz), 7.10 (d, 2H, J=8.2 Hz), 7.06 (dd/apparent t, 2H, J=8.6, 8.6[27] Hz), 4.93 (td, 1H, J=6.2, 3.4 Hz), 2.82 (d, 2H, J=6.2 Hz), 2.48 (d, 1H, J=3.4 Hz), 2.34 (s, 3H); ^{13}C 162.5 (d, J=245.8 Hz), 138.6, 138.3, 131.7, 129.2, 127.6 (d, J=8.1 Hz), 120.1, 115.4 (d, J=21.4 Hz), 84.9, 83.7, 72.1, 30.9, 21.6. MS m/z 130 (100%), 125 (71%), 115 (23%), 97 (35%); no other peaks of >20%. Anal. Calcd for $C_{17}H_{15}FO$: C, 80.29; H, 5.95. Found: C, 80.36; H, 5.93.

*4.2.3. 1-(4-Chlorophenyl)-4-(4-methylphenyl)but-3-yn-1-ol (**1c**)*

Light-yellow solid, mp 113–114 °C. IR (cm^{-1}, KBr) 3420 br m, 2918 m, 1510 s, 1091 s, 1011 s, 818 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 4.8×10^{-5} M) 223 (21 000), 243 (34 000), 254 (30 000). NMR ($CDCl_3$): ^1H 7.45 (AB, 2H, J=7.6 Hz), 7.31 (AB, 2H, J=7.6 Hz), 7.29 (d, 2H, J=7.8 Hz), 7.11 (d, 2H, J=7.8 Hz), 4.94 (t, 1H, J=6.4 Hz), 2.83 (d, 2H, J=6.4 Hz), 2.35 (s, 3H); ^{13}C 141.3, 138.2, 133.5, 131.6, 129.1, 128.5, 127.3, 120.0, 84.8, 83.6, 72.0, 30.6, 21.5. MS m/z 172 (72%), 157 (100%), 143 (21%), 141 (79%), 77 (36%); no other peaks of >20%. Anal. Calcd for $C_{17}H_{15}ClO$: C, 75.47; H, 5.58. Found: C, 75.30; H, 5.67.

*4.2.4. 4-Cyclopropyl-1-phenylbut-3-yn-1-ol (**1d**)*

Column chromatography eluent CH_2Cl_2/MeOH (100:0→96:4). Colorless oil. IR (cm^{-1}, neat) 3407 br s, 3010 s, 2906 s, 1737 m, 1454 s, 1049 s, 756 s, 700 s. NMR ($CDCl_3$): ^1H 7.49–7.18 (m, 5H), 4.73 (dt, 1H, J=6.3, 3.4 Hz), 2.63 (d, 1H, J=3.4 Hz), 2.55–2.49 (m, 2H), 1.30–1.10 (m, 1H), 0.76–0.52 (m, 4H); ^{13}C 142.9, 128.3, 127.7, 125.8, 86.4, 72.6, 71.5, 30.1, 8.1, −0.4. MS m/z 107 (80%), 79 (100%), 77 (49%); no other peaks of >20%. Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.39; H, 7.69.

*4.2.5. 4-Cyclohex-1-en-1-yl-1-phenylbut-3-yn-1-ol (**1e**)*

Light-yellow oil. IR (cm^{-1}, KBr) 3391 br s, 3062 m, 3028 s, 2925 s, 2858 s, 2835 s, 1494 s, 1452 s, 1435 s, 1047 s, 755 s, 700 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 1.1×10^{-4} M) 229 (13 000). NMR ($CDCl_3$): ^1H 7.45–7.27 (m, 5H), 6.06 (t, 1H, J=1.9 Hz), 4.86 (td, 1H, J=6.3, 3.4 Hz), 2.74 (d, 2H, J=6.3 Hz), 2.44 (d, 1H, J=3.4 Hz), 2.15–2.02 (m, 4H), 1.70–1.51 (m, 4H); ^{13}C 142.9, 134.5, 128.5, 127.9, 125.9, 120.6, 85.3, 83.0, 72.7, 30.8, 29.5, 25.7, 22.4, 21.6. MS m/z 120 (100%), 107 (74%), 105 (33%), 91 (24%), 79 (55%), 77 (32%); no other peaks of >20%. Anal. Calcd for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 84.05; H, 8.09.

4.3. General procedure for the synthesis of but-3-yn-1-ols 1f–h ($BF_3\cdot Et_2O$, THF)[10]

A round-bottomed flask, equipped with a magnetic stir bar and fitted with a rubber septum, was flame-dried and purged with dry nitrogen. The flask was charged with freshly distilled THF (80 mL) via syringe. Then alkyne **1** (60 mmol) was added to the reaction vessel at −78 °C (dry ice/acetone bath) via syringe followed by *n*-butyllithium (1.6 M, 38.0 mL, 60.8 mmol) via syringe. After 10 min, $BF_3\cdot Et_2O$ (98%; 8.0 mL, 39 mmol) was added and the reaction mixture was stirred for another 10 min. Finally, oxirane **2** (40 mmol) was added to the reaction mixture via syringe and stirring was continued for an additional 30 min at −78 °C. The reaction was quenched by the slow addition of saturated aq NH_4Cl (50 mL). The water phase was extracted with ethyl acetate (3×50 mL). Combined organic phases were dried over anhydrous $MgSO_4$. Solvent was removed by rotary evaporation and the residue was purified by silica gel column chromatography (hexanes/ethyl acetate 10:1) to give **1f** (6.124 g, 71%), **1g** (4.552 g, 68%), and **1h** (5.660 g, 70%).

*4.3.1. trans-2-[(4-Methylphenyl)ethynyl]cyclohexanol (**1f**)*

Light-yellow solid, mp 58–60 °C. IR (cm^{-1}, KBr) 3381 br m, 2941 s, 2859 s, 1510 s, 1445 s, 1302 m, 1068 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 5.1×10^{-5} M) 245 (26 000), 256 (24 000). NMR ($CDCl_3$): ^1H 7.30 (d, 2H, J=8.0 Hz), 7.08 (d, 2H, J=8.0 Hz), 3.53 (td, 1H, J=9.4, 4.1 Hz), 2.55–2.28 (m, 2H), 2.32 (s, 3H), 2.15–1.91 (m, 2H), 1.85–1.09 (m, 6H); ^{13}C 138.0, 131.6, 129.0, 120.3, 90.1, 82.8, 73.6, 39.6, 33.2, 31.2, 25.0, 24.3, 21.5. MS m/z 214 (100%), 199 (38%), 171 (33%), 157 (23%), 155 (31%), 143 (43%), 131 (27%), 129 (82%), 128 (43%), 118 (21%), 115 (40%), 105 (32%); no other peaks of >20%. Anal. Calcd for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.88; H, 8.67.

*4.3.2. trans-2-(Pent-1-ynyl)cyclohexanol (**1g**)*

Colorless oil. IR (cm^{-1}, neat) 3416 br s, 2925 s, 2863 s, 1449 s, 1266 m, 1065 s, 734 s. NMR ($CDCl_3$): ^1H 3.45–3.29 (m, 1H), 2.34 (d, 1H, J=2.0 Hz), 2.20–2.06 (m, 2H), 2.05–1.85 (m, 2H), 1.81–1.07 (m, 9H), 0.96 (t, 3H, J=7.4 Hz); ^{13}C 82.6, 81.4, 73.9, 39.1, 33.0, 31.5, 25.0, 24.3, 22.5, 20.8, 13.5. MS m/z 137 (100%), 123 (37%), 105 (26%), 95 (50%), 93 (31%), 91 (49%), 81 (53%), 79 (60%), 77 (30%), 67 (55%), 55 (28%); no other peaks of >20%. Anal. Calcd for $C_{11}H_{18}O$: C, 79.46; H, 10.91. Found: C, 79.17; H, 11.13.

*4.3.3. 1-Phenyloct-1-yn-4-ol (**1h**)*

Colorless oil. IR (cm^{-1}, neat) 3368 br, 2924 s, 1597 m, 1483 s, 1026 m, 761 s, 695 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 7.4×10^{-5} M) 241 (24 000), 252 (22 000). NMR ($CDCl_3$): ^1H 7.47–7.37 (m, 2H), 7.36–7.26 (m, 3H), 3.85 (m/ABX, 1H), 2.67 (ABX, 1H, J=16.7, 4.6 Hz), 2.57 (ABX, 1H, J=16.7, 6.8 Hz), 1.98 (s, 1H), 1.74–1.56 (m, 2H), 1.54–1.20 (m, 4H), 0.95 (t, 3H, J=6.9 Hz); ^{13}C 131.8, 128.4, 128.0, 123.5, 86.4, 83.2, 70.4, 36.2, 28.6, 27.9, 22.8, 14.2. MS m/z 116 (100%), 69 (26%); no other peaks of >20%. Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.67; H, 9.00.

4.4. General procedure for the synthesis of but-3-yn-1-yl azides 2a–e (NaN_3)[6]

Caution. A series of letters discuss explosion of sodium azide in a reaction mixture containing dichloromethane.[28] We recommend not to scale up this reaction and suitable safety measures, including mandatory use of a protective shield. Violent decomposition may be a special concern for low molecular weight azides.[29] A round-bottom flask was charged with but-3-yn-1-ol **1** (3 mmol), dichloromethane (30 mL), triethylamine (1.7 mL), and methanesulfonyl chloride (0.35 mL, 4.52 mmol). The solution was stirred at rt for 45 min. Water was added and the aqueous phase was extracted with ethyl acetate. The combined organic extract was washed with saturated aq NaCl solution, dried over anhydrous $MgSO_4$, and concentrated to afford the crude mesylate, which was used to the next reaction without further purification. NaN_3 (0.470 g, 7.23 mmol) was added to a solution of the crude mesylate in DMF (30 mL) and stirred at rt overnight. Water (50 mL) was added and the aqueous phase was extracted with ethyl acetate (4×25 mL). The combined organic extracts were washed with saturated aq NaCl solution (2×100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. Silica gel column chromatography (hexanes/chloroform 50:1→10:1) gave **2a** (0.689 g, 88%), **2b** (0.761 g, 91%), **2c** (0.825 g, 93%), **2d** (0.472 g, 74%), and **2e** (0.650 g, 86%).

*4.4.1. 4-(4-Methylphenyl)-1-phenylbut-3-yn-1-yl azide (**2a**)*

Light-yellow oil. IR (cm^{-1}, neat) 3325 br w, 3030 s, 2918 s, 2488 w, 2103 s, 1510 s, 1454 s, 1250 s, 817 s, 757 s, 700 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 1.1×10^{-4} M) 245 (28 000), 255 (21 000). NMR ($CDCl_3$): ^1H 7.50–7.39 (m, 5H), 7.35 (d, 2H, J=8.0 Hz), 7.14 (d, 2H, J=8.0 Hz), 4.79 (t, 1H, J=6.8 Hz), 2.96 (ABX, 1H, J=16.9, 7.6 Hz), 2.91 (ABX, 1H, J=16.9, 6.2 Hz), 2.38 (s, 3H); ^{13}C 138.7, 138.1, 131.5, 129.1,

128.8, 128.6, 126.9, 120.2, 84.8, 83.4, 64.8, 28.2, 21.5. Anal. Calcd for $C_{17}H_{15}N_3$: C, 78.13; H, 5.79. Found: C, 78.48; H, 5.72.

*4.4.2. 1-(4-Fluorophenyl)-4-(4-methylphenyl)but-3-yn-1-yl azide (**2b**)*

Light-yellow oil. IR (cm^{-1}, neat) 3323 w, 3034 m, 2923 m, 2481 w, 2102 s, 1604 s, 1506 s, 1229 s, 1157 s, 833 s, 816 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 5.4×10^{-5} M) 245 (29 000), 256 (27 000). NMR ($CDCl_3$): ^1H 7.38 (dd, 2H, J=8.6, 5.4[27] Hz), 7.26 (d, 2H, J=8.2 Hz), 7.10 (d, 2H, J=8.2 Hz), 7.10 (dd/apparent t, 2H, J=8.6, 8.6[27] Hz), 4.74 (t, 1H, J=6.8 Hz), 2.90 (ABX, 1H, J=16.9, 7.1 Hz), 2.83 (ABX, 1H, J=16.9, 6.5 Hz), 2.34 (s, 3H); ^{13}C 162.8 (d, J=247.3 Hz), 138.3, 134.5, 131.6, 129.2, 128.7 (d, J=8.2 Hz), 120.1, 115.8 (d, J=21.6 Hz), 84.4, 83.7, 64.1, 28.3, 21.6. Anal. Calcd for $C_{17}H_{14}FN_3$: C, 73.10; H, 5.05. Found: C, 73.40; H, 5.11.

*4.4.3. 1-(4-Chlorophenyl)-4-(4-methylphenyl)but-3-yn-1-yl azide (**2c**)*

White solid, mp 40–41 °C. IR (cm^{-1}, KBr) 2116 m, 1510 s, 1492 s, 1270 s, 1091 s, 814 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 4.4×10^{-5} M) 228 (18 000), 245 (26 000), 256 (24 000). NMR ($CDCl_3$): ^1H 7.38 (AB, 2H, J=8.7 Hz), 7.34 (AB, 2H, J=8.7 Hz), 7.26 (d, 2H, J=8.0 Hz), 7.10 (d, 2H, J=8.0 Hz), 4.73 (t, 1H, J=6.8 Hz), 2.89 (ABX, 1H, J=16.8, 7.1 Hz), 2.83 (ABX, 1H, J=16.8, 6.5 Hz), 2.34 (s, 3H); ^{13}C 138.4, 137.2, 134.5, 131.6, 129.2, 129.1, 128.4, 120.0, 84.2, 83.7, 64.1, 28.2, 21.6. Anal. Calcd for $C_{17}H_{14}ClN_3$: C, 69.03; H, 4.77. Found: C, 69.13; H, 4.59.

*4.4.4. 4-Cyclopropyl-1-phenylbut-3-yn-1-yl azide (**2d**)*

Light-yellow oil. IR (cm^{-1}, neat) 2973 s, 2864 s, 2100 s, 1382 s, 1153 s, 113 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 8.5×10^{-5} M) 216 (28 000). NMR ($CDCl_3$): ^1H 7.48–7.25 (m, 5H), 4.62 (t, 1H, J=6.9 Hz), 2.65 (dABX, 1H, J=16.8, 7.9, 1.9 Hz), 2.60 (dABX, 1H, J=16.8, 5.8, 1.9 Hz), 1.31–1.12 (m, 1H), 0.81–0.57 (m, 4H); ^{13}C 138.8, 128.7, 128.5, 126.8, 86.4, 71.0, 65.0, 27.6, 8.0, −0.4. Anal. Calcd for $C_{13}H_{13}N_3$: C, 73.91; H, 6.20. Found: C, 73.11; H, 6.20.

*4.4.5. 4-Cyclohex-1-en-1-yl-1-phenylbut-3-yn-1-yl azide (**2e**)*

Light-yellow oil that partly crystallizes over days in a freezer, mp 37–39 °C. IR (cm^{-1}, KBr) 3327 br w, 3030 m, 2930 s, 2859 s, 2670 w, 2487 w, 2100 s, 1250 s, 758 s, 700 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 1.3×10^{-4} M) 227 (12 000). NMR ($CDCl_3$): ^1H 7.43–7.29 (m, 5H), 6.03 (t, 1H, J=1.8 Hz), 4.66 (t, 1H, J=6.9 Hz), 2.80 (ABX, 1H, J=16.9, 7.9 Hz), 2.75 (ABX, 1H, J=16.9, 6.0 Hz), 2.11–2.01 (m, 4H), 1.67–1.50 (m, 4H); ^{13}C 138.8, 134.6, 128.8, 128.6, 126.9, 120.6, 85.1, 82.6, 65.0, 29.3, 28.2, 25.7, 22.4, 21.6. Anal. Calcd for $C_{16}H_{17}N_3$: C, 76.46; H, 6.82. Found: C, 76.37; H, 6.92.

4.5. General procedure for the synthesis of but-3-yn-1-yl azides 2f–h [DIAD, $(PhO)_2P(O)N_3$][6]

Diisopropyl azodicarboxylate (1.2 mL, 3.1 mmol) was slowly added to a solution of Ph_3P (1.5 g, 5.7 mmol) in THF (25 mL) at 0 °C and the reaction mixture was stirred for 20 min. The solution of but-3-yn-1-ol **1** (4 mmol) in THF (15 mL), cooled to 0 °C, was added slowly, followed by diphenylphosphoryl azide (1.4 mL, 6.5 mmol), via syringe. Then stirring was continued for 3 h. The reaction mixture was poured into water (ca. 20 mL) and extracted with ethyl acetate (4×20 mL). The combined organic phases were washed with saturated aq NaCl (2×50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation. Silica gel column chromatography (hexanes/chloroform 50:1 → 10:1) gave **2f** (0.738 g, 77%), **2g** (0.498 g, 65%), and **2h** (0.526 g, 62%).

*4.5.1. cis-2-[(4-Methylphenyl)ethynyl]cyclohexyl azide (**2f**)*

Light-yellow oil. IR (cm^{-1}, neat) 3320 br w, 2942 s, 2863 s, 2511 w, 2097 s, 1509 s, 1449 s, 1261 s, 1104 m, 817 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 8.8×10^{-5} M) 244 (17 000), 255 (15 000). NMR ($CDCl_3$): ^1H 7.35 (d, 2H, J=8.1 Hz), 7.10 (d, 2H, J=8.1 Hz), 3.50 (dt, 1H, J=8.8, 3.5 Hz), 3.08 (td, 1H, J=5.6, 3.5 Hz), 2.34 (s, 3H), 2.05–1.29 (m, 8H); ^{13}C 138.0, 131.6, 129.1, 120.5, 88.4, 84.2, 61.2, 34.8, 29.8, 28.0, 23.3, 22.2, 21.6. Anal. Calcd for $C_{15}H_{17}N_3$: C, 75.28; H, 7.16. Found: C, 75.20; H, 7.24.

*4.5.2. cis-2-Pent-1-yn-1-ylcyclohexyl azide (**2g**)*

Colorless oil. IR (cm^{-1}, neat) 3320 w, 2937 s, 2859 s, 2510 w, 2097 s, 1444 s, 1261 s, 1000 m. NMR ($CDCl_3$): ^1H 3.39 (dt, 1H, J=8.8, 3.6 Hz), 2.89–2.76 (m, 1H), 2.17 (td, 2H, J=7.0, 2.0 Hz), 1.98–1.20 (m, 10H), 0.98 (t, 3H, J=7.3 Hz); ^{13}C 84.1, 79.4, 61.4, 34.0, 30.1, 27.9, 23.4, 22.4, 22.1, 20.9, 13.6. Anal. calcd for $C_{11}H_{17}N_3$: C, 69.07; H, 8.96. Found: C, 69.34; H, 9.19.

*4.5.3. 1-(3-Phenylprop-2-yn-1-yl)pentyl azide (**2h**)*

Light-yellow oil. IR (cm^{-1}, neat) 3340 w, 2963 s, 2934 s, 2862 s, 2502 w, 2099 s, 1596 m, 1486 s, 1338 s, 1258 s, 1071 m, 750 s, 690 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 7.0×10^{-5} M) 241 (19 000), 252 (18 000). NMR ($CDCl_3$): ^1H 7.48–7.38 (m, 2H), 7.37–7.27 (m, 3H), 3.66–3.46 (m, 1H), 2.70 (d, 2H, J=6.0 Hz), 1.85–1.27 (m, 6H), 0.97 (t, 3H, J=7.0 Hz); ^{13}C 131.7, 128.4, 128.1, 123.5, 85.6, 83.1, 61.4, 33.5, 28.3, 26.0, 22.6, 14.1. Anal. Calcd for $C_{14}H_{17}N_3$: C, 73.98; H, 7.54. Found: C, 74.03; H, 7.65.

4.6. General procedure for the synthesis of pyrroles 3a–h (microwave)

A 5 mL microwave reactor vial, equipped with a magnetic stirring bar and fitted with a rubber septum, was charged with azide **2** (1.00 mmol) and 1,2-dichloroethane (2 mL). Zinc chloride (1.0 M in ether; for **2a**–**d** 0.20 mL, 0.20 mmol, for **2e** 0.05 mL, 0.05 mmol, for **2e**,**f**–**h** 0.40 mL, 0.40 mmol) was added dropwise with a syringe and the vial was capped. The reaction was carried out with the following microwave reactor parameters: temperature 105 °C, run time 60 min (130 °C, 40 min for **2e**,**f**–**h**), power high (pressure ca. 2 bar). Silica gel column chromatography (10×2 cm; hexanes/ethyl acetate 100:0 → 20:1) gave **3a** (0.210 g, 90%), **3b** (0.183 g, 73%), **3c** (0.244 g, 91%), **3d** (0.140 g, 76%), **3e** (0.142 g, 64%), **3e′** (0.073 g, 32%), **3f** (0.110 g, 52%), **3g** (0.067 g, 41%), and **3h** (0.095 g, 48%).

4.7. General procedure for the synthesis of pyrroles 3a,f–h (conventional)

A Schlenk flask, equipped with a magnetic stirring bar and fitted with a rubber septum, was charged with azide **2** (1.00 mmol) and 1,2-dichloroethane (2 mL). Zinc chloride (1.0 M in ether; for **2a** 0.20 mL, 0.20 mmol and for **2f**–**h** 0.40 mL, 0.40 mmol) was added dropwise with a syringe. The solution was stirred at 75 °C (oil bath) for 16 h. After cooling, silica gel column chromatography (10×2 cm, hexanes/ethyl acetate 100:0 → 20:1) gave **3a** (0.210 g, 90%), **3f** (0.108 g, 51%), **3g** (0.100 g, 61%), and **3h** (0.130 g, 65%).

*4.7.1. 2-(4-Methylphenyl)-5-phenyl-1H-pyrrole (**3a**)*

White solid. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 5.6×10^{-5} M) 230 (12 000), 326 (28 000). ^{13}C NMR ($CDCl_3$) 136.3, 133.4, 132.8, 132.7, 129.7, 129.0, 126.4, 123.9, 123.2, 107.9, 107.5, 21.3. ^1H NMR, IR, and MS data and mp matched with those reported earlier.[23]

*4.7.2. 2-(4-Fluorophenyl)-5-(4-methylphenyl)-1H-pyrrole (**3b**)*

White solid, mp 183–185 °C. IR (cm^{-1}, KBr) 3460 br m, 1502 m, 1276 m, 1234 m, 1052 m, 833 s, 775 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 3.2×10^{-5} M) 230 (15 000), 325 (42 000). NMR ($CDCl_3$): ^1H 8.45 (s, 1H), 7.48 (dd, 2H, J=8.8, 5.2[27] Hz), 7.42 (d, 2H, J=8.0 Hz), 7.21 (d, 2H, J=8.0 Hz), 7.09 (dd/apparent t, 2H, J=8.8, 8.8[27] Hz), 6.55–6.48 (m, 2H), 2.37 (s, 3H); ^{13}C 161.7 (d, J=246.1 Hz), 136.4, 133.5, 132.0, 129.8,

129.1, 125.6, 125.4, 123.9, 116.0 (d, J=21.7 Hz), 107.8, 107.5, 21.3. MS m/z 251 (M^+, 100%); no other peaks of >20%. Anal. Calcd for $C_{17}H_{14}FN$: C, 81.25; H, 5.62. Found: C, 81.15; H, 5.64.

*4.7.3. 2-(4-Chlorophenyl)-5-(4-methylphenyl)-1H-pyrrole (**3c**)*

White solid, mp 229–230 °C. IR (cm^{-1}, KBr) 3464 br m, 1487 m, 1278 m, 1100 m, 1048 m, 822 s, 774 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 6.7×10^{-5} M) 233 (11 000), 337 (36 000). NMR (DMSO-d_6): ^{1}H 11.26 (s, 1H), 7.79 (d, 2H, J=8.6 Hz), 7.67 (d, 2H, J=8.0 Hz), 7.42 (d, 2H, J=8.6 Hz), 7.19 (d, 2H, J=8.0 Hz), 6.61 (apparent t, 1H, J=2.5 Hz), 6.55 (apparent t, 1H, J=2.5 Hz), 2.31 (s, 3H); ^{13}C 135.1, 133.7, 131.5, 131.3, 129.8, 129.7, 129.2, 128.5, 125.4, 124.0, 108.2, 107.3, 20.7. MS m/z 269 (51%), 267 (M^+, 100%); no other peaks of >20%. Anal. Calcd for $C_{17}H_{14}ClN$: C, 76.26; H, 5.27. Found: C, 76.20; H, 5.21.

*4.7.4. 2-Cyclopropyl-5-phenyl-1H-pyrrole (**3d**)*

White solid, mp 49–50 °C. IR (cm^{-1}, KBr) 3438 br m, 1605 m, 1518 m, 1044 m, 756 s, 691 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 6.5×10^{-5} M) 222 (9000), 303 (25 000). NMR ($CDCl_3$): ^{1}H 8.22 (s, 1H), 7.51–7.12 (m, 5H), 6.40 (apparent t, 1H, J=3.0 Hz), 5.92 (apparent t, 1H, J=3.0 Hz), 1.87 (tt, 1H, J=8.3, 5.1 Hz), 0.95–0.79 (m, 2H), 0.78–0.64 (m, 2H); ^{13}C 135.9, 133.0, 130.8, 128.9, 125.8, 123.5, 106.1, 105.9, 8.4, 6.8. MS m/z 183 (M^+, 100%), 156 (57%); no other peaks of >20%. Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15. Found: C, 85.13; H, 7.15.

*4.7.5. 2-Cyclohex-1-en-1-yl-5-phenyl-1H-pyrrole (**3e**)*

Light-yellow solid, mp 86–87 °C. IR (cm^{-1}, KBr) 3429 m, 2929 m, 1602 s, 1506 m, 1450 m, 1250 m, 1050 m, 775 s, 758 s, 692 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 3.8×10^{-5} M) 229 (14 000), 324 (26 000). NMR ($CDCl_3$): ^{1}H 8.42 (br s, 1H), 7.58–7.19 (m, 5H), 6.54 (apparent t, 1H, J=3.0 Hz), 6.28 (apparent t, 1H, J=3.0 Hz), 6.07–5.96 (m, 1H), 2.58–2.40 (m, 2H), 2.38–2.20 (m, 2H), 1.95–1.62 (m, 4H); ^{13}C 135.0, 132.8, 131.8, 129.0, 126.1, 123.8, 119.2, 107.0, 106.5, 26.2, 25.5, 22.7, 22.5.[30] MS m/z 223 (M^+, 72%), 195 (48%); no other peaks of >20%.

*4.7.6. 2-Cyclohexyl-5-phenyl-1H-pyrrole (**3e′**)*

Light-yellow solid, mp 68 °C. IR (cm^{-1}, KBr) 3434 m, 2927 s, 2853 s, 1607 m, 1510 s, 1449 m, 1046 m, 779 s, 756 s, 694 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 6.0×10^{-5} M) 302 (21 000). NMR ($CDCl_3$): ^{1}H 8.17 (s, 1H), 7.52–7.13 (m, 5H), 6.45 (apparent t, 1H, J=2.9 Hz), 6.01 (apparent t, 1H, J=2.9 Hz), 2.72–2.50 (m, 1H), 2.18–1.21 (m, 10H); ^{13}C 139.7, 133.2, 130.3, 128.9, 125.7, 123.5, 105.9, 105.1, 37.1, 33.4, 26.4, 26.2. MS m/z 225 (96%), 182 (100%), 169 (27%), 156 (33%); no other peaks of >20%.

*4.7.7. 2-(4-Methylphenyl)-4,5,6,7-tetrahydro-1H-indole (**3f**)*

White solid. IR (cm^{-1}, KBr) 3442 s, 2929 s, 2850 s, 1537 s, 1367 m, 823 m, 797 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 5.7×10^{-5} M) 308 (21 000). ^{13}C NMR ($CDCl_3$) 135.3, 130.6, 129.6, 128.2, 123.6, 118.9, 104.7, 23.9, 23.6, 23.0, 21.6, 21.2. MS m/z 211 (M^+, 73%), 183 (100%); no other peaks of >20%. ^{1}H NMR data and mp matched with those reported earlier.[24]

*4.7.8. 2-Propyl-4,5,6,7-tetrahydro-1H-indole (**3g**)*

This compound was isolated using alumina oxide column chromatography (hexanes/ethyl acetate 100:0→100:1). Light-yellow oil. IR (cm^{-1}, KBr) 3374 br s, 2929 s, 2845 s, 1604 m, 1444 m, 779 s. NMR ($CDCl_3$): ^{1}H 7.40 (s, 1H), 5.67 (d, 1H, J=2.4 Hz), 2.60–2.44 (m, 6H), 1.90–1.50 (m, 6H), 1.05 (t, 3H, J=1.5 Hz); ^{13}C 131.1, 125.3, 116.9, 104.2, 30.2, 24.1, 23.7, 23.2, 23.1, 22.9, 14.3. MS m/z 163 (46%), 134 (100%); no other peaks of >20%.

*4.7.9. 2-Butyl-5-phenyl-1H-pyrrole (**3h**)*

White solid, mp 37–39 °C. IR (cm^{-1}, KBr) 3403 br m, 2953 m, 2929 m, 1607 m, 1513 s, 1042 s, 753 s, 690 s. UV–vis (ε, $M^{-1}\,cm^{-1}$; ether; 8.0×10^{-5} M) 228 (7000), 236 (5000), 302 (20 000). NMR ($CDCl_3$): ^{1}H 8.13 (s, 1H), 7.57–7.12 (m, 5H), 6.45 (apparent t, 1H, J=2.8 Hz), 6.00 (apparent t, 1H, J=2.8 Hz), 2.68 (t, 2H, J=7.6 Hz), 1.68 (quintet, 2H, J=7.6 Hz), 1.44 (sextet, 2H, J=7.6 Hz), 0.98 (t, 3H, J=7.2 Hz); ^{13}C 134.4, 133.2, 130.6, 128.9, 125.8, 123.5, 107.1, 106.2, 31.9, 27.8, 22.6, 14.0. MS m/z 199 (M^+, 72%), 156 (100%); no other peaks of >20%. Anal. Calcd for $C_{14}H_{17}N$: C, 84.37; H, 8.60. Found: C, 84.08; H, 8.63.

4.8. Crystallography

Crystals of **3b** (transparent plate, colorless) were grown from the dichloromethane/hexanes mixture by slow evaporation. A crystallographical table is provided in Supplementary data. Crystallographic data for the structure of **3b** were deposited with Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-699779. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

Acknowledgement is made to the donors of the Petroleum Research Fund (ACS-PRF#46094) administered by the American Chemical Society, Oakland University and its Research Excellence Program in Biotechnology for support of this research. A.S. is grateful for Provost's Graduate Student Research Award. We are thankful to Dr. Krystyna Brzezinska (University of California Santa Barbara) for DSC measurements, Prof. Takashi Ohshima, Prof. Kazushi Mashima, and Dr. Takanori Iwasaki (Osaka University) for the generous supply of $Zn_4(OCOCF_3)_6O$, Prof. Harriet Lindsay (Eastern Michigan University) for helpful discussions, and CEM for Discover microwave loan.

Supplementary data

^{1}H and ^{13}C NMR spectra for alcohols **1**, azides **2**, and pyrroles **3**, and an X-ray table. This material is available via the Internet at www.sciencedirect.com. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2008.11.094.

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