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Persistent radical effect in the intramolecular addition of benzylic radicals onto ketenimines: selective cross-coupling of α-(indol-2-yl)-benzyl radicals with the 1-cyano-1-methylethyl radical

Mateo Alajarín,[a] Angel Vidal,*[a] María-Mar Ortín[a] and Delia Bautista[b]

[a] *Departamento de Química Orgánica, Facultad de Química, Universidad de Murcia, Campus de Espinardo, Espinardo 30100, Murcia, Spain. E-mail: alajarin@um.es,vidal@um.es; Fax: +34 968 364149; Tel: +34 968 367418*

[b] *Servicio Universitario de Instrumentación Científica, Universidad de Murcia, Campus de Espinardo, E-30100, Murcia, Spain. E-mail: dbc@um.es*

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The intramolecular addition of benzylic radicals, generated from benzyl phenyl selenides by the action of tris(trimethylsilyl)silane and AIBN or AIBMe, onto neighbouring ketenimine functions is studied. The persistent α-(indol-2-yl)benzyl radicals, resulting from such cyclization processes, undergo cross-coupling with the *tert*-alkyl radicals arising from the thermal decomposition of the AIBN or AIBMe initiators to give, respectively, 3-(1*H*-indol-2-yl)propiononitriles **10** or propanoates **14**. A rare spiropentacyclic compound **17** containing two indole fragments also resulted from one of these radical reactions. The crystal and molecular structures of **10d** and **17** have been solved by X-ray analysis.

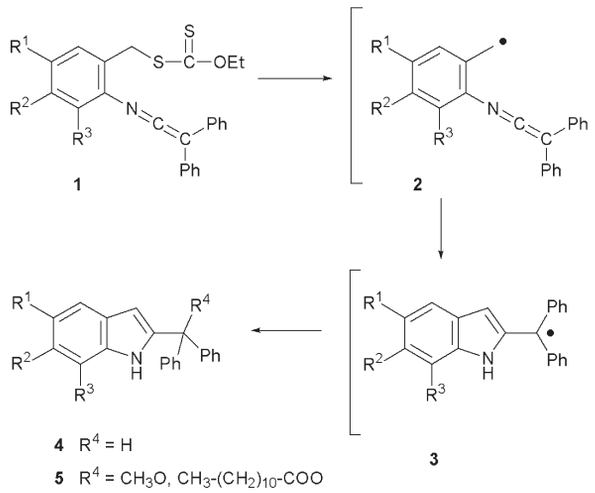
Introduction

In chemical systems involving both persistent[1] ($R^{\bullet}$) and transient ($A^{\bullet}$) radical intermediates, formed from the same or different precursors with equal or nearly equal rates, the cross-coupling product (R–A) is formed with high selectivity and usually becomes the main reaction product. These chemical systems are controlled by the so-called Persistent Radical Effect (PRE).[2] The formation of products such as R–H, derived from a disproportionation process, or ions (and products arising from them) generated by a redox process between ($R^{\bullet}$) and ($A^{\bullet}$) can be expected as well.

Most of the currently known examples of organic and metal–organic reactions in which the PRE operates were discovered accidentally. However, the selective formation of the cross-coupling product (R–A) in the radical reactions governed by the PRE has captured the attention of organic chemists. Thus, Studer has recently reported several clever organic syntheses based on this general principle.[3] The PRE has also found a number of applications in the field of stable free-radical polymerization.[4]

We have recently reported the unprecedented addition of benzylic radicals onto the central carbon atom of a ketenimine function,[5] a process that provided a novel radical-mediated synthesis of 2-alkylindoles (Scheme 1). Following xanthate based radical chemistry[6] we generated benzylic radicals **2**, which by cyclization followed by a prototropic imine–enamine equilibrium converted into the persistent tertiary triarylmethyl-type radicals **3**. These (indol-2-yl)(diphenyl)methyl radicals did not sustain the radical chain sequence. Instead, depending on the specific conditions used to generate the initial radicals **2**, they underwent reduction to indoles **4** or a redox process followed by other transformations of the resulting ions to give indoles **5**, bearing alkoxy or acyloxy substituents on the lateral chain at C2.

It is well known that a clean and efficient method for producing carbon centered radicals consists on the treatment of alkyl phenyl selenides with tris(trimethylsilyl)silane in the presence of 2,2′-azobisisobutyronitrile (AIBN) as radical initiator.[7]



Scheme 1 Intramolecular addition of benzylic radicals, generated from xanthates, onto ketenimines.

Herein we disclose the results obtained in the study of the intramolecular addition reaction of benzylic radicals onto *C*,*C*-disubstituted ketenimine functions (linked by means of its nitrogen atom to an *ortho*-position of the benzene ring), when the benzylic radicals are generated from benzyl phenyl selenides by treatment with tris(trimethylsilyl)silane in the presence of azoalkanes such as AIBN and AIBMe (dimethyl 2,2′-azobisisobutyrate). Under these reaction conditions the radical cyclizations turned out to be controlled by the Persistent Radical Effect, giving rise to 3-(1*H*-indol-2-yl)propiononitriles and propanoates, resulting from the selective cross-coupling of persistent α-(indol-2-yl)benzyl radicals with the 1-cyano-1-methylethyl and the 1-methoxycarbonyl-1-methylethyl radicals arising from AIBN and AIBMe, respectively.

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Results and discussion

Preparation of ketenimines

Ketenimines **9** were prepared from 2-azidobenzyl chlorides **6** in three steps (Scheme 2). Treatment of a solution of diphenyl diselenide in anhydrous ethanol with sodium borohydride provided sodium benzeneselenolate, which cleanly reacted with 2-azidobenzyl chlorides **6** leading to the formation of benzyl phenyl selenides **7**. Staudinger reaction[8] of azidoselenides **7** with triphenylphosphane, in diethyl ether solution at room temperature, yielded the triphenylphosphazenes **8**. Aza-Wittig reaction[9] of **8** with diphenyl ketene or methyl phenyl ketene, in dichloromethane solution at room temperature, gave *C*,*C*-diphenyl ketenimines **9a–d** or *C*-methyl-*C*-phenyl ketenimines **9e**,**f**, respectively (Table 1). Ketenimines **9** are stable compounds which were purified by column chromatography on silica gel,[10] and were fully characterized. Their IR spectra showed the characteristic absorption of the N=C=C grouping as a very strong band around 2000 cm^{-1}.

C,*C*-Diphenyl ketenimines

In our first experiments, the radical cyclization of the *C*,*C*-diphenyl ketenimines **9a–d** was carried out by a four-portion addition of a stoichiometric excess of tris(trimethylsilyl)silane (3 equiv) and a molar amount[11] of AIBN to a 0.01 M solution of the ketenimines in boiling benzene (Method A, see Experimental). Under these conditions ketenimines **9** were totally consumed and column chromatography of the final reaction mixtures allowed the isolation of the 3-(1*H*-indol-2-yl)propionitriles **10a–d** in moderate yields (Scheme 3) (Table 2). Two unidentified minor products (less than 10% each) were also present in the reaction crudes, as evidenced by GC.

Slight modifications of this experimental procedure for the conversions **9a–d** → **10a–d**, such as variations on the number of equivalents of tris(trimethylsilyl)silane and AIBN added to the reaction mixture in each portion (as in Method B, see below), led us to invariable results, and compounds **10a–d** were always the main reaction products, with no significant variations of the yields in which these compounds were obtained.

The structural characterization of indoles **10a–d** relies on their analytical and spectroscopic data. In this respect, their IR spectra display two strong absorptions at 3358–3460 cm^{-1} and 2224–2229 cm^{-1} corresponding to the indolic N–H and nitrile C≡N vibrations, respectively. In the ^{1}H NMR spectra of these compounds the indolic NH proton resonates as a broad singlet at $\delta = 7.93$–8.01, and the indole H3 proton was observed at $\delta = 6.85$–6.91. Notoriously, the two methyl groups at C2 of the propiononitrile chain appeared as diastereotopic at very close chemical shifts $\delta = 1.47$–1.51 and $\delta = 1.50$–1.55. Their ^{13}C NMR spectra show the signals due to the quaternary carbon atoms of the propiononitrile chain C2 and C3 around $\delta = 38.5$ and $\delta = 60.0$, respectively. In these spectra the two methyl groups at C2 also appeared as diastereotopic $\delta = 26.1$–26.4 and $\delta = 27.5$–27.6, and the same occurs for the two phenyl groups at C3. The diastereotopicity observed at 25 °C (the NMR spectra were recorded at room temperature) for the methyl and phenyl groups placed on the propiononitrile chain of **10a–d** is presumably due to restricted rotation around the single bond C2–C3. In the ^{1}H NMR spectrum of the propiononitrile **10d**, its two CH_3–C2 methyl groups become equivalent at 40 °C.

An X-ray structure determination of compound **10d** ($R^1 = CH_3$, $R^2 = H$) was definitive for unequivocally establishing the structure of compounds **10a–d** (Fig. 1). The dihedral angles between the mean planes defined by the indole ring (the mean deviation from plane is 0.0192 Å) and the two phenyl rings at C3 are 89.4° (C21 to C26) and 80.2° (C31 to C36). The cyano group shows a slightly distorted linear structure [C(4)–C(7)–N(2) 174.2(2)°].

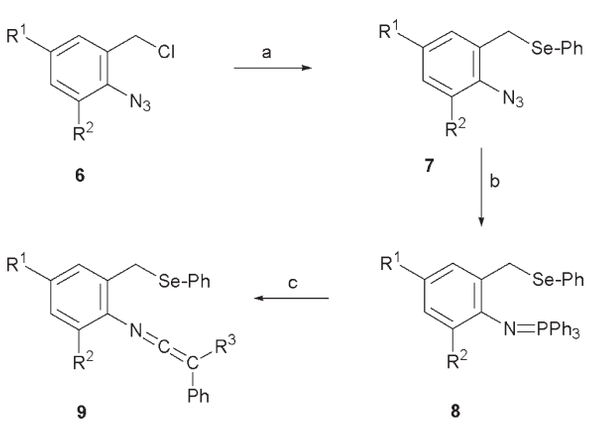
In the asymmetric unit, molecules of **10d** associate through intermolecular N–H···N hydrogen bonds [N1–N2 ($x - 1$, y, z) 3.067 Å], forming chains parallel to the x axis (Fig. 2).

A reasonable mechanistic explanation for the conversion **9** → **10** is the following: the *in situ* formed $[(CH_3)_3Si]_3Si^{\bullet}$ radical should add to the selenium atom of ketenimines **9** to give $PhSeSi[Si(CH_3)_3]_3$ and the expected benzylic radical **11**, which then may undergo a 5-*exo*-*dig* addition of the radical moiety onto the central carbon atom of the ketenimine function, followed by a prototropic imine–enamine equilibrium favouring the aromatic indole form **13**. This cyclization step is a favourable process due to the formation of a stabilized tertiary triarylmethyl-type radical. The (indol-2-yl)(diphenyl)methyl radical **13** would finally undergo radical–radical cross-coupling with the 1-cyano-1-methylethyl radical arising from AIBN to yield **10** (Scheme 4). The (indol-2-yl)methyl radicals **13**, in which the radical center is attached to the C2 carbon atom of an indole ring, are new examples of the scarce (heteroaryl)-methyl type radicals.[12]

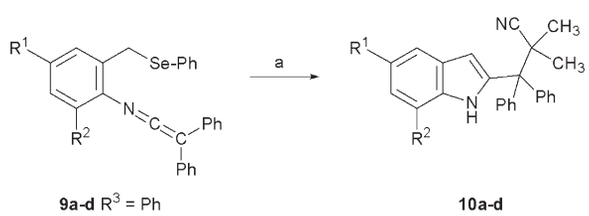
To further illustrate the synthetic potential of these PRE-controlled radical cyclizations we decided to test the reaction of ketenimines **9** with tris(trimethylsilyl)silane and some other azoalkane different from AIBN. With this aim, we selected dimethyl 2,2′-azobisisobutyrate (AIBMe) which has a half-life time ($t_{1/2}$) at 80 °C (boiling temperature of benzene) nearly equal to that of AIBN,[13] and accordingly the rate of formation of the 1-methoxycarbonyl-1-methylethyl radical resulting

Table 1 Ketenimines **9**

Compound	R^1	R^2	R^3	Yield (%)
9a	H	H	Ph	78
9b	H	CH_3	Ph	74
9c	Cl	H	Ph	59
9d	CH_3	H	Ph	90
9e	H	H	CH_3	58
9f	CH_3	H	CH_3	57



Scheme 2 *Reagents and conditions*: (a) PhSeSePh, $NaBH_4$, ethanol, 0 °C, then 2-azidobenzyl chloride **6**, rt, 3 h; (b) PPh_3, diethyl ether, rt, 6 h; (c) $PhR^3C{=}C{=}O$, dichloromethane, rt, 30 min.



Scheme 3 *Reagents and conditions*: (a) Tris(trimethylsilyl)silane (3 equiv), AIBN (1 equiv), benzene, reflux, 24 h (Method A).

Table 2 3-(1*H*-Indol-2-yl)propiononitriles **10** from ketenimines **9**

Compound	Method[a]	R^1	R^2	Yield (%)
10a	A	H	H	40
10b	A	H	CH_3	42
10c	A	Cl	H	45
10d	A	CH_3	H	54
10e	B	H	H	43
10f	B	CH_3	H	59

[a] See text and Experimental section.

from its thermal decomposition should be similar to the rate of formation of the 1-cyano-1-methylethyl radical coming from the decomposition of AIBN. Thus, gradual addition of tris(trimethylsilyl)silane (3 equiv) and AIBMe (1 equiv) to a 0.01 M solution of ketenimine **9b** in boiling benzene (Method A) afforded the methyl 3-(7-methyl-1*H*-indol-2-yl) propanoate **14** in 45% yield (Scheme 5). In this reaction, the reduced 2-diphenylmethyl-7-methylindole **15** was also isolated in 21% yield.[14]

C-Methyl-*C*-phenyl ketenimines

Next, we submitted *C*-methyl-*C*-phenyl ketenimines **9e**,**f** (see Scheme 1) to reaction with tris(trimethylsilyl)silane in the presence of AIBN. We wondered if the putative 1-(1*H*-indol-2-yl)-1-phenylethyl radicals **16**, of the heteroaryl phenyl methyl type, would be persistent enough to allow cross-coupling with the transient radical derived from AIBN.

The initial experiments of treating ketenimines **9e**,**f** with the system tris(trimethylsilyl)silane–AIBN were conducted by adding in three portions 1.5 equivalents of tris(trimethylsilyl)-silane and 1.2 equivalents of AIBN to a 0.01 M solution of the corresponding ketenimine in boiling benzene (Method B). Under these conditions the reaction products were the expected 3-(1*H*-indol-2-yl)-2,2,3-trimethyl-3-phenylpropiono-nitriles **10e**,**f** (Scheme 6), resulting from the cross-coupling of the intermediate, persistent radicals **16** and the 1-cyano-1-methylethyl radical.

Compounds **10e**,**f** were obtained in moderate yields after purification by column chromatography (Table 2), and characterized by their analytical and spectral data, which were essentially similar to those of the analogous **10a–d**.

The cyclization of ketenimine **9e** was also attempted under the experimental conditions of Method A. This variation led to an unexpected result, furnishing the expected propiono-nitrile **10e** (26% yield) but accompanied by the cyclopenta[*b*]-indole-1-spiro-2′-indoline **17** as the major reaction product (51%) (Scheme 7).

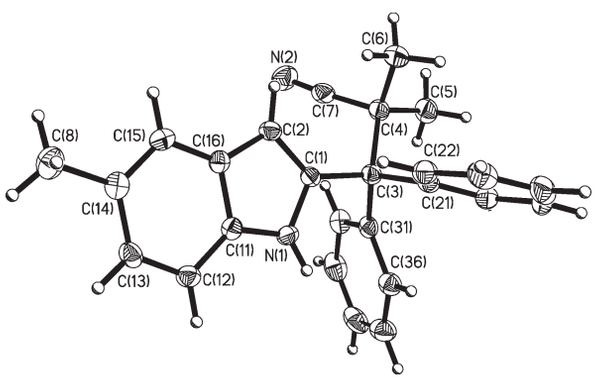


Fig. 1 Ellipsoid representation of compound **10d** with 50% probability ellipsoids and the crystallographic labelling scheme.

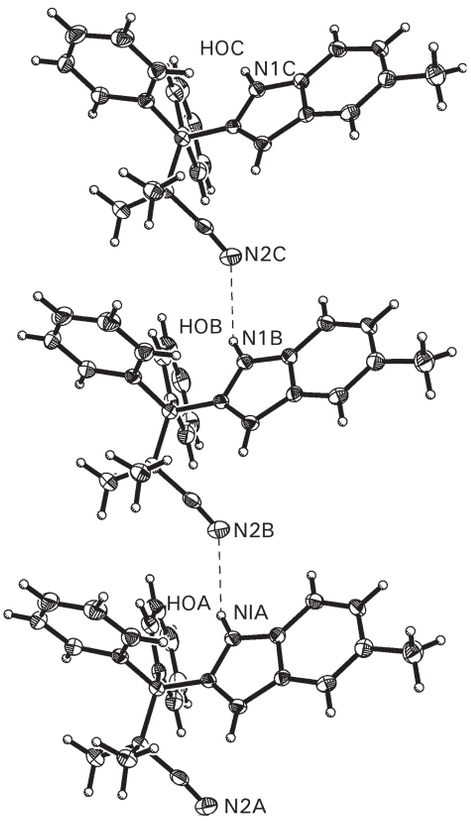
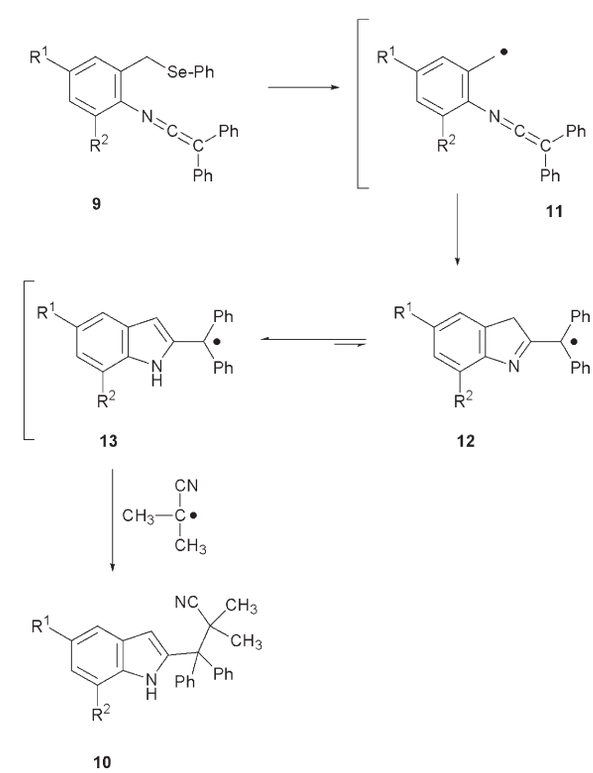
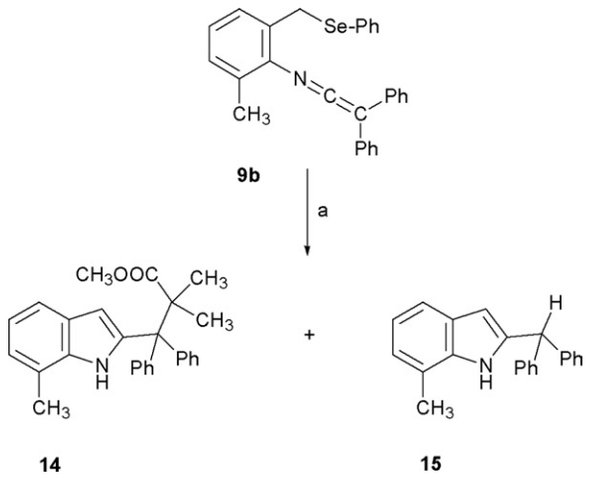


Fig. 2 View of the hydrogen bond interaction in the asymmetric unit of **10d**.

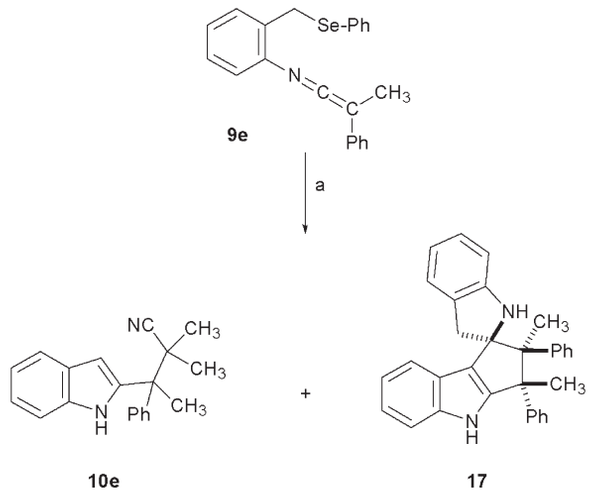
The structural assignment of compound **17** was not straightforward following its analytical and spectroscopic data and an X-ray structure determination was accomplished (Fig. 3). This analysis revealed the spirocyclic nature of compound **17**, a particular dimer of indolylmethyl radical **16e**. The diastereoisomer



Scheme 4 Proposed mechanism for the conversion **9** → **10**.



Scheme 5 *Reagents and conditions*: (a) Tris(trimethylsilyl)silane (3 equiv), AIBMe (1 equiv), benzene, reflux, 24 h (Method A).



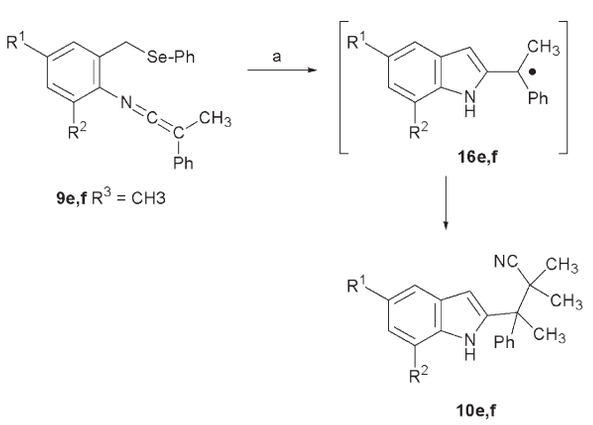
Scheme 7 *Reagents and conditions*: (a) Tris(trimethylsilyl)silane (3 equiv), AIBN (1 equiv), benzene, reflux, 24 h (Method A).

shown is the only one present in the crystals and should be also the only one detected by ^{1}H NMR analysis of the crude reaction mixture. In consequence, spirocycle **17** was formed in a highly diastereoselective manner, as only one out of four possible diastereoisomers is obtained.

To the best of our knowledge, the preparation of the cyclopenta[*b*]indole-1-spiro-2′-indoline skeleton has been previously reported only once in the chemical literature.[15]

Apart from stereochemical considerations, the proposed mechanism for explaining the conversion **9e** → **17** is depicted in Scheme 8. The formation of the spiro compound **17** would start with the coupling of radicals **16e** and **19** to give the dimeric species **20**, an indole and an indoline ring linked by a two carbon chain *via* their respective C2 carbon atoms. The nucleophilic attack of the indole moiety through its C3 carbon atom on the C2 iminic carbon of the indoline fragment would provide the spiranic intermediate **21**, which finally should convert into the reaction product **17** by an imine–enamine prototropic equilibrium.

The formation of **17** when ketenimine **9e** is submitted to the reaction conditions of Method A, but not under the conditions of Method B, should be related to the differences between both methods concerning the rate of addition of AIBN to the reaction medium. Whereas in Method A only 0.3 equivalents of AIBN were added after 6 h, in Method B this amount raised to 0.8 equivalents for the same reaction time, thus increasing the concentration of 1-cyano-1-methylethyl radical and, consequently, the probability of cross-coupling between **16e** and that radical.



Scheme 6 *Reagents and conditions*: (a) Tris(trimethylsilyl)silane (1.5 equiv), AIBN (1.2 equiv), benzene, reflux, 24 h (Method B).

Conclusion

In summary, we have shown in this report how ketenimines undergo intramolecular addition of free carbon-centered radicals to afford new examples of persistent tertiary radicals bearing an heteroaromatic ring (indole) at the carbon-center radical: (indol-2-yl)(diphenyl)methyl and 1-(indol-2-yl)-1-phenylethyl radicals. These radicals undergo selective cross-coupling with 1-cyano-1-methylethyl and 1-methoxycarbonyl-1-methylethyl radicals, present in the reaction medium, to give respectively 3-(1*H*-indol-2-yl)propiononitriles and 3-(1*H*-indol-2-yl)propanoates. The Persistent Radical Effect controls these radical processes.

Experimental

All melting points were determined on a Kofler hot-plate melting point apparatus and are uncorrected. IR spectra were obtained on a Nicolet Impact 400 spectrophotometer. NMR spectra were recorded on a Bruker Avance 300 (300 MHz and 75 MHz for ^{1}H and ^{13}C, respectively) or a Bruker Avance 400 (400 MHz and 100 MHz for ^{1}H and ^{13}C, respectively) in $CDCl_3$ as solvent, and the chemical shifts are expressed in

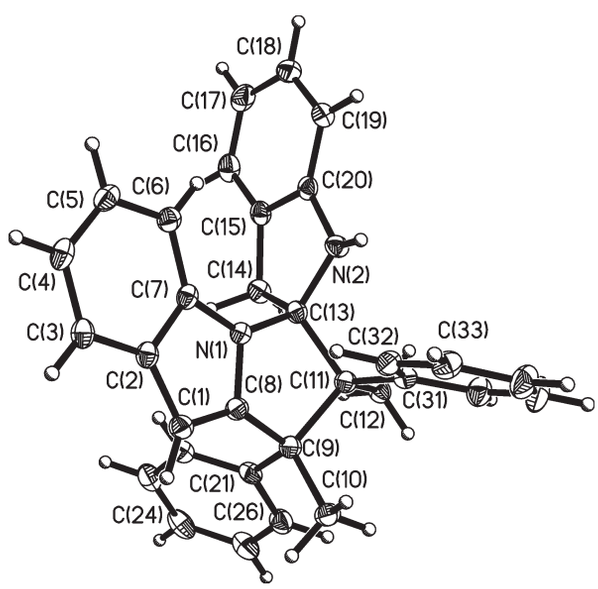
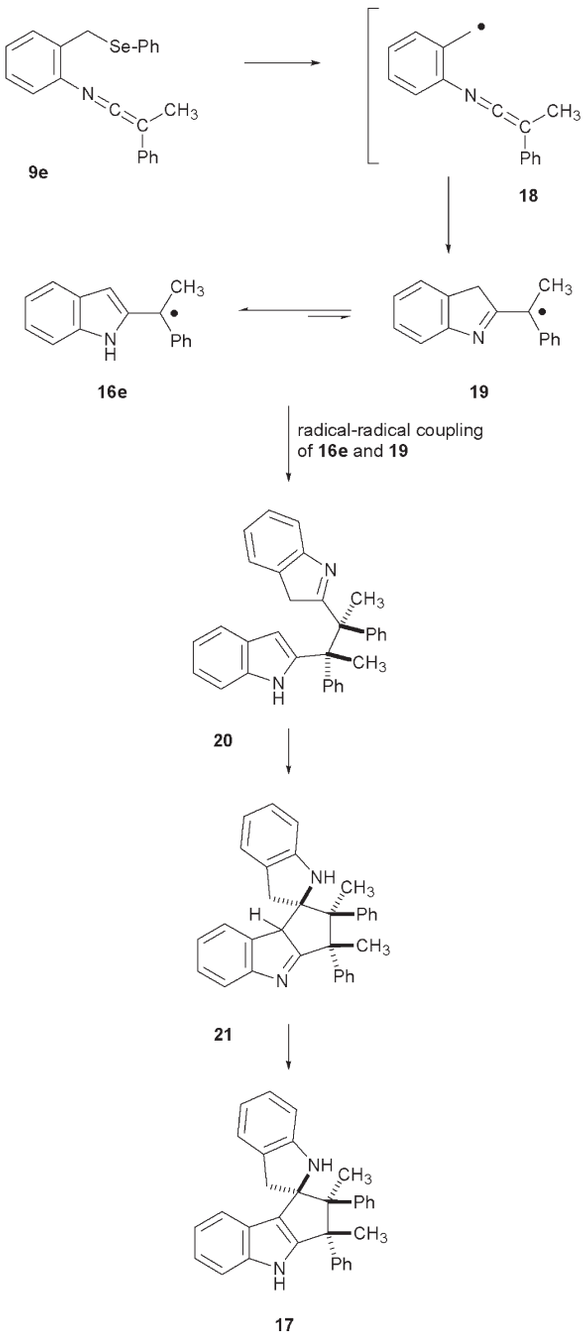


Fig. 3 Ellipsoid representation of compound **17** with 50% probability ellipsoids and the crystallographic labelling scheme.



Scheme 8 Proposed mechanism for the conversion **9e** → **17**.

ppm relative to Me_4Si at $\delta = 0.00$ for ^1H and to $CDCl_3$ at $\delta = 77.1$ for ^{13}C. J values are given in Hz. Mass spectra were recorded on a Hewlett-Packard 5993C spectrometer or on a VG-Autospec spectrometer. Microanalyses were performed on a Carlo Erba EA-1108 instrument.

X-Ray structure determination

The crystal and molecular structures of compounds **10d** and **17** have been determined by X-ray diffraction studies. Crystals were mounted on glass fibres and transferred to the cold gas stream of the diffractometer (**10d** Siemens P4 and **17** Bruker Smart APEX). Data were recorded with Mo-Kα radiation ($\lambda = 0.71073$Å) in ω-scan mode. Structures were solved by the direct method and refined anisotropically on F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany). The hydrogens and N were located in the Fourier difference maps and refined freely. Methyl groups were refined using rigid groups and other hydrogens were refined using a riding method.

Materials

2-Azidobenzyl chloride **6a**,[16] 2-azido-3-methylbenzyl chloride **6b**,[17] 2-azido-5-chlorobenzyl chloride **6c**,[17] 2-azido-5-methylbenzyl chloride **6d**,[18] methyl phenyl ketene,[19] diphenyl ketene[20] and dimethyl 2,2′-azobisisobutyrate (AIBMe)[21] were prepared by literature procedures.

Preparation of 2-azidobenzyl phenyl selenides 7

An orange solution of diphenyl diselenide (1.56 g, 5 mmol) in anhydrous ethanol (30 ml) was stirred at 0 °C under an atmosphere of nitrogen. Powdered sodium borohydride (0.47 g, 12.5 mmol) was added in five portions of 0.094 g each. The solution became colourless when all sodium borohydride was added. A solution of the corresponding 2-azidobenzyl chloride **6** (10 mmol) in anhydrous ethanol (15 ml) was then added dropwise over 15 min. The mixture was stirred at room temperature for 3 h, cooled and quenched by addition of 10% hydrochloric acid (50 ml). The resulting solution was extracted with hexanes (3×50 ml), and the combined extracts were washed with 10% hydrochloric acid (50 ml), saturated sodium hydrogen carbonate (50 ml) and water (50 ml), and dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by short column chromatography (silica gel, using hexanes as eluent).

2-Azidobenzyl phenyl selenide (7a). (2.42 g, 84%); yellow oil (Found: C, 54.3; H, 3.6; N, 14.3. $C_{13}H_{11}N_3Se$ requires C, 54.2; H, 3.85; N, 14.6%); ν_{max}(neat)/cm^{-1} 2124, 1577, 1493, 1450, 1437, 1295, 1023, 756 and 693; δ_H 4.03 (2 H, s), 6.93 (1 H, td, $J = 7.0$ and 1.2), 7.03 (1 H, dd, $J = 7.7$ and 1.8), 7.07 (1 H, dd, $J = 7.7$ and 1.2), 7.19–7.25 (4 H, m), 7.43–7.47 (2 H, m); δ_C 27.4, 118.3, 124.6, 127.6, 128.4, 128.9, 130.1 (s), 130.4 (s), 130.7, 134.3, 138.0 (s).

2-Azido-3-methylbenzyl phenyl selenide (7b). (2.54 g, 84%); yellow oil (Found: C, 55.3; H, 4.6; N, 14.1. $C_{14}H_{13}N_3Se$ requires C, 55.6; H, 4.3; N, 13.9%); ν_{max}(neat)/cm^{-1} 2103, 1475, 1462, 1437, 1301, 1023, 781, 738 and 692; δ_H 2.40 (3 H, s), 4.11 (2 H, s), 6.88 (1 H, dd, $J = 7.7$ and 1.8), 6.93 (1 H, t, $J = 7.7$), 7.00 (1 H, dd, $J = 7.7$ and 1.8), 7.18–7.28 (3 H, m), 7.44–7.51 (2 H, m); δ_C 18.1, 28.7, 125.7, 127.6, 128.4, 129.0, 130.1 (s), 130.4, 132.8 (s), 133.0 (s), 134.2, 136.5 (s).

2-Azido-5-chlorobenzyl phenyl selenide (7c). (2.84 g, 88%); yellow oil (Found: C, 48.1; H, 3.3; N, 13.3. $C_{13}H_{10}ClN_3Se$ requires C, 48.4; H, 3.1; N, 13.0%); ν_{max}(neat)/cm^{-1} 2122, 2083, 1486, 1477, 1300, 1111, 1022, 810, 737 and 690; δ_H 3.93 (2 H, s), 6.91 (1 H, d, $J = 3.0$), 6.97 (1 H, d, $J = 8.0$), 7.17 (1 H, dd, $J = 8.0$ and 3.0), 7.22–7.28 (3 H, m), 7.41–7.46 (2 H, m); δ_C 26.9, 119.4, 128.0, 128.2, 129.0, 129.4 (s), 129.6 (s), 130.5, 132.1 (s), 134.7, 136.5 (s).

2-Azido-5-methylbenzyl phenyl selenide (7d). (2.66 g, 88%); yellow oil (Found: C, 55.3; H, 4.1; N, 13.7. $C_{14}H_{13}N_3Se$ requires C, 55.6; H, 4.3; N, 13.9%); ν_{max}(neat)/cm^{-1} 2126, 2086, 1495, 1475, 1300, 1241, 1161, 1024, 738 and 694; δ_H 2.20 (3 H, s), 4.00 (2 H, s), 6.80–6.81 (1 H, m), 6.96 (1 H, d, $J = 8.0$), 7.03 (1 H, dd, $J = 8.0$ and 1.5), 7.20–7.27 (3 H, m), 7.42–7.48 (2 H, m); δ_C 20.7, 27.4, 118.2, 127.6, 128.9, 129.0, 129.8 (s), 130.2 (s), 131.4, 134.3, 135.1 (s).

Preparation of 2-(triphenylphosphoranylideneamino)benzyl phenyl selenides 8

To a solution of the corresponding 2-azidobenzyl phenyl selenide **7** (5 mmol) in anhydrous diethyl ether (15 ml) triphenylphosphane (1.31 g, 5 mmol) was added. The reaction mixture was stirred at room temperature under nitrogen for 6 h. Then, the precipitated compounds **8** were isolated by filtration.

These compounds were used in the following step without further purification. For analytical samples, compounds **8** were recrystallized from diethyl ether.

2-(Triphenylphosphoranylideneamino)benzyl phenyl selenide (8a). (2.43 g, 93%); mp 140–142 °C; colourless prisms (Found: C, 71.2; H, 4.8; N, 2.6. $C_{31}H_{26}NPSe$ requires C, 71.3; H, 5.0; N, 2.7%); ν_{max}(Nujol)/cm^{-1} 1588, 1577, 1436, 1331, 1310, 1109, 1051, 1021, 757, 735, 718 and 691; δ_H 4.49 (2 H, s), 6.42 (1 H, d, J = 8.0), 6.54 (1 H, td, J = 7.6 and 1.0), 6.76 (1 H, td, J = 7.6 and 1.8), 7.09–7.21 (4 H, m), 7.36–7.56 (11 H, m), 7.73–7.84 (6 H, m); δ_C 31.3, 117.0, 121.0 (d, J = 10.1), 126.2, 127.4, 128.6 (d, J = 12.8), 128.7, 129.4 (d, J = 2.1), 131.2 (d, J = 99.5), 131.6 (d, J = 2.8), 132.5 (s), 132.6, 132.7 (d, J = 9.9), 132.9 (s), 133.5 (s); δ_P (162.3 MHz; $CDCl_3$; H_3PO_4) 2.5; m/z (EI) 523 (M^+, 7%), 366 (100).

3-Methyl-2-(triphenylphosphoranylideneamino)benzyl phenyl selenide (8b). (2.01 g, 75%); mp 114–115 °C; colourless prisms (Found: C, 71.3; H, 5.2; N, 2.6. $C_{32}H_{28}NPSe$ requires C, 71.6; H, 5.3; N, 2.6%); ν_{max}(Nujol)/cm^{-1} 1588, 1576, 1434, 1186, 1111, 753, 743, 713 and 695; δ_H 1.86 (3 H, s), 4.04 (2 H, s), 6.56 (1 H, td, J = 7.3 and 2.1), 6.84–6.88 (2 H, m), 7.13–7.17 (3 H, m), 7.27–7.38 (8 H, m), 7.43–7.46 (3 H, m), 7.59–7.66 (6 H, m); δ_C 21.4, 31.4, 118.6 (d, J = 3.2), 126.2, 127.7 (d, J = 1.9), 128.4 (d, J = 12.1), 128.7, 129.3 (d, J = 2.8), 131.3 (d, J = 2.9), 132.4 (d, J = 9.6), 132.5, 132.6 (s), 132.7 (s), 132.9 (d, J = 101.5), 133.1 (d, J = 5.2), 147.0 (d, J = 1.4); δ_P (162.3 MHz; $CDCl_3$; H_3PO_4) 4.6; m/z (EI) 537 (M^+, 5%), 380 (100).

5-Chloro-2-(triphenylphosphoranylideneamino)benzyl phenyl selenide (8c). (2.53 g, 91%); mp 159–160 °C; colourless prisms (Found: C, 66.7; H, 4.8; N, 2.3. $C_{31}H_{25}ClNPSe$ requires C, 66.85; H, 4.5; N, 2.5%); ν_{max}(Nujol)/cm^{-1} 1582, 1436, 1333, 1141, 1111, 1019, 884, 757, 736, 721 and 692; δ_H 4.39 (2 H, s), 6.29 (1 H, d, J = 8.5), 6.69 (1 H, dd, J = 8.5 and 2.5), 7.02 (1 H, t, J = 2.1), 7.19–7.20 (3 H, m), 7.40–7.45 (6 H, m), 7.50–7.53 (5 H, m), 7.73–7.78 (6 H, m); δ_C 30.8, 121.4 (s), 121.6 (d, J = 10.0), 126.6, 127.0, 128.7 (d, J = 12.1), 128.9, 129.0, 130.9 (d, J = 100.0 Hz), 131.8 (d, J = 2.7), 132.7 (d, J = 9.7), 132.8 (s), 133.0, 134.5 (d, J = 22.3), 148.3 (s); δ_P (162.3 MHz; $CDCl_3$; H_3PO_4) 3.6; m/z (EI) 402 (48%), 400 (100), 183 (28).

5-Methyl-2-(triphenylphosphoranylideneamino)benzyl phenyl selenide (8d). (2.60 g, 97%); mp 142–144 °C; colourless prisms (Found: C, 71.7; H, 5.1; N, 2.5. $C_{32}H_{28}NPSe$ requires C, 71.6; H, 5.3; N, 2.6%); ν_{max}(Nujol)/cm^{-1} 1606, 1576, 1438, 1328, 1110, 811, 757, 735, 720 and 695; δ_H 2.13 (3 H, s), 4.48 (2 H, s), 6.33 (1 H, dd, J = 8.0 and 1.0), 6.57 (1 H, dd, J = 8.0 and 1.8), 6.95 (1 H, t, J = 2.2), 7.16–7.21 (3 H, m), 7.32–7.56 (11 H, m), 7.73–7.83 (6 H, m); δ_C 20.5, 31.1, 120.6 (d, J = 9.8), 125.9, 126.0 (s), 127.9, 128.5 (d, J = 12.0), 128.6, 130.1 (d, J = 1.9), 131.3 (d, J = 99.5), 131.5 (d, J = 2.8), 132.0 (s), 132.4, 132.6 (d, J = 9.7), 133.6 (s), 146.7 (s); δ_P (162.3 MHz; $CDCl_3$; H_3PO_4) 2.0; m/z (EI) 537 (M^+, 5%), 380 (100).

Preparation of ketenimines 9

To a solution of the corresponding 2-(triphenylphosphoranylideneamino)benzyl phenyl selenide **8** (1.5 mmol) in anhydrous dichloromethane (20 ml) a solution of methyl phenyl ketene or diphenyl ketene (1.5 mmol) in the same solvent (5 ml) was added. After stirring at room temperature for 30 min the solvent was removed under reduced pressure and the resulting material was chromatographed on a silica gel column, using hexanes–diethyl ether (9 : 1) as eluent.

Ketenimine 9a. (0.51 g, 78%); yellow oil (Found: C, 73.8; H, 4.5; N, 3.1. $C_{27}H_{21}NSe$ requires C, 74.0; H, 4.8; N, 3.2%); ν_{max}(neat)/cm^{-1} 2001, 1600, 1579, 1490, 1486, 1172, 1077, 1023, 761, 738 and 693; δ_H 4.32 (2 H, s), 7.10–7.12 (3 H, m), 7.16–7.25 (5 H, m), 7.32–7.39 (9 H, m), 7.44–7.47 (2 H, m); δ_C 27.9, 77.3 (s), 123.1, 126.5, 127.4, 127.6, 127.9, 128.3, 128.9, 130.3 (s), 130.6, 134.0, 134.7 (s), 138.7 (s), 189.9 (s).

Ketenimine 9b. (0.50 g, 74%); yellow oil (Found: C, 74.5; H, 4.9; N, 3.1. $C_{28}H_{23}NSe$ requires C, 74.3; H, 5.1; N, 3.1%); ν_{max}(neat)/cm^{-1} 2017, 1593, 1495, 1172, 1075, 1023, 999, 760, 737, 694 and 645; δ_H 2.27 (3 H, s), 4.13 (2 H, s), 6.89 (1 H, dd, J = 7.4 and 1.3), 6.96 (1 H, t, J = 7.4), 7.06 (1 H, dd, J = 7.4 and 1.3), 7.14–7.22 (5 H, m) 7.28–7.42 (10 H, m); δ_C 19.1, 28.9, 73.1 (s), 126.1, 126.2, 127.3, 128.0, 128.2, 128.8, 128.9, 130.0, 130.6 (s), 132.1 (s), 132.5 (s), 134.0, 134.7 (s), 137.5 (s), 185.9 (s).

Ketenimine 9c. (0.42 g, 59%); yellow oil (Found: C, 68.8; H, 4.5; N, 3.1. $C_{27}H_{20}ClNSe$ requires C, 68.6; H, 4.3; N, 3.0%); ν_{max}(neat)/cm^{-1} 1995, 1596, 1578, 1495, 1476, 1173, 1137, 1103, 1075, 1023, 896 and 819; δ_H 4.21 (2 H, s), 7.03 (1 H, d, J = 2.3), 7.14 (1 H, dd, J = 8.4 and 2.3), 7.17–7.25 (6 H, m), 7.31–7.35 (8 H, m), 7.42–7.45 (2 H, m); δ_C 27.5, 78.2 (s), 124.2, 126.7, 127.8, 128.0, 128.2, 128.9, 129.0, 129.7 (s), 130.4, 133.0 (s), 133.7 (s), 134.4, 136.6 (s), 137.2 (s), 191.0 (s).

Ketenimine 9d. (0.61 g, 90%); yellow oil (Found: C, 74.6; H, 5.2; N, 3.0. $C_{28}H_{23}NSe$ requires C, 74.3; H, 5.1; N, 3.1%); ν_{max}(neat)/cm^{-1} 1999, 1596, 1580, 1488, 1454, 1436, 1264, 1141, 1075, 820, 737, 693, 643 and 610; δ_H 2.23 (3 H, s), 4.27 (2 H, s), 6.92 (1 H, d, J = 2.0), 6.98 (1 H, dd, J = 8.0 and 2.0), 7.15–7.24 (6 H, m), 7.28–7.37 (8 H, m), 7.43–7.47 (2 H, m); δ_C 21.1, 27.9, 77.6 (s), 123.0, 126.4, 127.3, 127.8, 128.9, 129.0, 130.4 (s), 131.2, 134.0, 134.2 (s), 134.5 (s), 135.7 (s), 137.7 (s), 189.3 (s).

Ketenimine 9e. (0.33 g, 58%); yellow oil (Found: C, 70.5; H, 5.2; N, 3.8. $C_{22}H_{19}NSe$ requires C, 70.2; H, 5.1; N, 3.7%); ν_{max}(neat)/cm^{-1} 2004, 1600, 1580, 1486, 1437, 1373, 1190, 1065, 1021, 757, 737 and 692; δ_H 2.12 (3 H, s), 4.33 (2 H, s), 7.07–7.35 (12 H, m), 7.47–4.51 (2 H, m); δ_C 12.3, 28.1, 67.1 (s), 122.9, 124.5, 125.2, 127.2, 127.4, 128.2, 128.7, 129.0, 130.5, 134.0, 134.2 (s), 135.6 (s), 139.7 (s), 193.8 (s).

Ketenimine 9f. (0.33 g, 57%); yellow oil (Found: C, 70.7; H, 5.1; N, 3.3. $C_{23}H_{21}NSe$ requires C, 70.8; H, 5.4; N, 3.6%); ν_{max}(neat)/cm^{-1} 2000, 1599, 1579, 1492, 1446, 1380, 1242, 1067, 1026, 827, 758, 735 and 691; δ_H 2.10 (3 H, s), 2.23 (3 H, s), 4.30 (2 H, s), 6.91–7.00 (2 H, m), 7.07–7.14 (2 H, m), 7.21–7.34 (7 H, m), 7.47–7.51 (2 H, m); δ_C 12.3, 21.0, 28.0, 67.0 (s), 122.7, 124.4, 125.0, 127.3, 128.7, 128.8, 128.9, 130.6 (s), 131.1, 134.0, 135.8 (s), 136.9 (s), 137.2 (s), 193.1 (s).

Reaction of ketenimines 9 with tris(trimethylsilyl)silane and AIBN or AIBMe: preparation of 3-(1*H*-indol-2-yl)propiononitriles 10 and methyl 3-(1*H*-indol-2-yl)propanoate 14

Method A. A solution of the corresponding ketenimine **9** (0.75 mmol) in anhydrous benzene (75 ml) was heated under nitrogen at reflux temperature and tris(trimethylsilyl)silane (0.28 g, 1.125 mmol) and AIBN (0.025 g, 0.15 mmol) were added. Further additions of tris(trimethylsilyl)silane and AIBN were made as follows: 1) after 3 h since the first addition, AIBN (0.012 g, 0.075 mmol), 2) after 6 h since the first addition, tris(trimethylsilyl)silane (0.093 g, 0.375 mmol) and AIBN (0.025 g, 0.15 mmol) and 3) after 9 h since the first addition, tris(trimethylsilyl)silane (0.19 g, 0.75 mmol) and AIBN (0.061 g, 0.375 mmol). After 15 h since the last addition the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column, using hexanes–diethyl ether (9 : 1) as eluent.

Method B. A solution of the corresponding ketenimine **9** (0.75 mmol) in anhydrous benzene (75 ml) was heated under nitrogen at reflux temperature and tris(trimethylsilyl)silane (0.23 g, 0.94 mmol) and AIBN (0.050 g, 0.3 mmol) were added. Further additions of tris(trimethylsilyl)silane and AIBN were made as follows: 1) after 3 h since the first addition, tris(trimethylsilyl)silane (0.047 g, 0.19 mmol) and AIBN (0.050 g, 0.3 mmol) and 2) after 6 h since the first addition, AIBN (0.050 g, 0.3 mmol). After 15 h since the last addition the solvent was removed under reduced pressure and the crude residue was chromatographed on a silica gel column, using hexanes–diethyl ether (9 : 1) as eluent.

3-(1*H*-Indol-2-yl)-2,2-dimethyl-3,3-diphenylpropiononitrile (10a). Method A (0.11 g, 40%); mp 227–229 °C (from dichloromethane); colourless prisms (Found: C, 85.9; H, 6.1; N, 7.8. $C_{25}H_{22}N_2$ requires C, 85.7; H, 6.3; N, 8.0%); ν_{max}(Nujol)/cm^{-1} 3376, 2224, 1600, 1298, 1161, 795, 751, 743 and 705; δ_H 1.48 (3 H, s), 1.52 (3 H, s), 6.91 (1 H, s), 7.01–7.16 (4 H, m), 7.21 (1 H, d, J = 7.8), 7.30–7.34 (5 H, m), 7.60–7.65 (4 H, m), 7.97 (1 H, br s); δ_C 26.3, 27.6, 38.5 (s), 59.9 (s), 105.0, 111.0, 120.0, 120.7, 122.4, 127.3 (s), 127.5, 127.6, 128.0, 128.5, 129.6, 131.2, 136.2 (s), 139.8 (s), 140.7 (s), 142.7 (s); m/z (EI) 350 (M$^+$, 63%), 278 (100).

3-(7-Methyl-1*H*-indol-2-yl)-2,2-dimethyl-3,3-diphenylpropiononitrile (10b). Method A (0.11 g, 42%); mp 197–198 °C (from chloroform–*n*-hexane); colourless prisms (Found: C, 85.9; H, 6.3; N, 7.7. $C_{26}H_{24}N_2$ requires C, 85.7; H, 6.6; N, 7.7%); ν_{max}(Nujol)/cm^{-1} 3452, 2229, 1598, 1441, 1289, 1161, 813, 745 and 703; δ_H 1.47 (3 H, s), 1.51 (3 H, s), 2.30 (3 H, s), 6.89–7.06 (3 H, m), 7.19–7.34 (8 H, m), 7.46 (1 H, d, J = 7.6), 7.63–7.67 (2 H, m), 7.98 (1 H, br s); δ_C 16.4, 26.1, 27.5, 38.4 (s), 59.9 (s), 105.5, 118.3, 120.1 (s), 120.3, 122.9, 126.7 (s), 127.5, 127.7 (s), 127.9, 128.4, 128.5, 129.6, 131.3, 135.9 (s), 139.9 (s), 140.4 (s), 142.7 (s); m/z (EI) 364 (M$^+$, 5%), 296 (100).

3-(5-Chloro-1*H*-indol-2-yl)-2,2-dimethyl-3,3-diphenylpropiononitrile (10c). Method A (0.13 g, 45%); mp 198–200 °C (from chloroform–*n*-hexane); colourless prisms (Found: C, 78.3; H, 5.3; N, 7.2. $C_{25}H_{21}ClN_2$ requires C, 78.0; H, 5.5; N, 7.3%); ν_{max}(Nujol)/cm^{-1} 3358, 2227, 1601, 1577, 1391, 1160, 1062, 877, 797, 736 and 698; δ_H 1.47 (3 H, s), 1.50 (3 H, s), 6.85 (1 H, s), 7.09–7.13 (3 H, m), 7.30–7.35 (6 H, m), 7.56–7.63 (4 H, m), 8.01 (1 H, br s); δ_C 26.3, 27.6, 38.5 (s), 60.0 (s), 104.7, 112.0, 120.1, 122.7, 125.7 (s), 127.4 (s), 127.7, 128.1, 128.4 (s), 128.6, 129.6, 131.1, 134.5 (s), 139.6 (s), 142.3 (s), 142.5 (s); m/z (EI) 386 (M$^+$ + 2, 10%), 384 (M$^+$, 27), 318 (45), 316 (100).

3-(5-Methyl-1*H*-indol-2-yl)-2,2-dimethyl-3,3-diphenylpropiononitrile (10d). Method A (0.15 g, 54%); mp 181–183 °C (dichloromethane–diethyl ether); colourless prisms (Found: C, 85.9; H, 6.4; N, 7.5. $C_{26}H_{24}N_2$ requires C, 85.7; H, 6.6; N, 7.7%); ν_{max}(Nujol)/cm^{-1} 3460, 2229, 1601, 1585, 1496, 1448, 1315, 1266, 1165, 806, 742 and 710; δ_H 1.51 (3 H, s), 1.55 (3 H, s), 2.47 (3 H, s), 6.85 (1 H, s), 7.00 (1 H, d, J = 8.2), 7.13 (1 H, d, J = 8.2), 7.19–7.20 (1 H, m), 7.29–7.34 (6 H, m), 7.43 (1 H, s), 7.66–7.68 (3 H, m), 7.93 (1 H, br s); δ_C 21.5, 26.4, 27.6, 38.6 (s), 60.0 (s), 104.7, 110.7, 120.3, 124.0, 127.5, 127.6, 127.9, 128.5, 129.3 (s), 129.7, 131.2, 134.6 (s), 140.0 (s), 140.8 (s), 142.8 (s); m/z (EI) 364 (M$^+$, 5%), 296 (100).

Crystal data: $C_{26}H_{24}N_2$, M = 364.47, monoclinic, a = 7.6460(10), b = 21.303(2), c = 12.5050(10) Å, U = 1968.6(4) Å^3, T = 173(2) K, space group $P2(1)/n$, Z = 4, absorption coefficient = 0.071 mm^{-1}, 3892 reflections measured, 3457 unique (R_{int} = 0.0219) which were used in all calculations. The final $wR(F^2)$ was 0.0882 (all data).†

3-(1*H*-Indol-2-yl)-2,2,3-trimethyl-3-phenylpropiononitrile (10e). Method B (0.093 g, 43%); mp 133–135 °C (from diethyl ether); colourless prisms (Found: C, 83.6; H, 6.9; N, 9.4. $C_{20}H_{20}N_2$ requires C, 83.3; H, 7.0; N, 9.7%); ν_{max}(Nujol)/cm^{-1} 3348, 2239, 1446, 1400, 1350, 1294, 1101, 1031, 804, 740 and 705; δ_H 1.46 (3 H, s), 1.48 (3 H, s), 1.91 (3 H, s), 6.80 (1 H, d, J = 2.0), 7.00–7.15 (2 H, m), 7.17–7.25 (1 H, m), 7.27–7.41 (5 H, m), 7.56–7.68 (1 H, m), 7.81 (1 H, br s); δ_C 23.4, 24.7, 24.8, 38.9 (s), 49.4 (s), 102.9, 110.7, 120.0, 120.5, 121.5 (s), 122.1, 125.8 (s), 127.6, 128.2, 129.0, 135.8 (s), 141.5 (s); m/z (EI) 288 (M$^+$, 12%), 220 (100).

3-(5-Methyl-1*H*-indol-2-yl)-2,2,3-trimethyl-3-phenylpropiononitrile (10f). Method B (0.13 g, 59%); mp 150–152 °C (from diethyl ether); colourless prisms (Found: C, 83.6; H, 7.0; N, 9.2. $C_{21}H_{22}N_2$ requires C, 83.4; H, 7.3; N, 9.3%); ν_{max}(Nujol)/cm^{-1} 3393, 2240, 1586, 1460, 1411, 1315, 1295, 1176, 1031, 807, 734 and 704; δ_H 1.45 (3 H, s), 1.48 (3 H, s), 1.91 (3 H, s), 2.44 (3 H, s), 6.71 (1 H, d, J = 1.8), 6.98 (1 H, dd, J = 8.1 and 1.3), 7.13 (1 H, d, J = 8.1 Hz), 7.24–7.40 (6 H, m), 7.71 (1 H, br s); δ_C 21.5, 23.5, 24.7, 24.8, 38.9 (s), 49.5 (s), 102.6, 110.4, 120.2, 123.7, 125.8 (s), 127.6, 127.9 (s), 128.2, 129.0, 129.3 (s), 134.1 (s), 141.6 (s); m/z (EI) 302 (M$^+$, 29%), 234 (100).

Methyl 3-(7-methyl-1*H*-indol-2-yl)-2,2-dimethyl-3,3-diphenylpropanoate (14). Method A (0.13 g, 45%); mp 187–189 °C (from chloroform–*n*-hexane); colourless prisms (Found: C, 81.4; H, 6.6; N, 3.6. $C_{27}H_{27}NO_2$ requires C, 81.6; H, 6.85; N, 3.5%); ν_{max}(Nujol)/cm^{-1} 3299, 1697, 1500, 1355, 1268, 1221, 1135, 807, 751 and 709; δ_H 1.30 (3 H, s), 1.56 (3 H, s), 2.50 (3 H, s), 3.66 (3 H, s), 6.15 (1 H, d, J = 2.1), 6.96–7.01 (4 H, m), 7.15–7.27 (8 H, m), 7.36–7.39 (1 H, m), 11.17 (1 H, s); δ_C 16.8, 27.1, 28.0, 52.8, 53.0 (s), 61.2 (s), 108.2, 117.9, 119.4, 120.5 (s), 122.0, 126.4 (s), 126.9, 127.1, 127.3, 128.1, 128.7, 130.2, 136.1 (s), 142.2 (s), 144.4 (s), 145.4 (s), 180.9 (s); m/z (EI) 397 (M$^+$, 6%), 296 (100).

Cyclopenta[*b*]indole-1-spiro-2′-indoline 17. Method A (0.084 g, 51%); mp 264–265 °C (chloroform–*n*-hexane); colourless prisms (Found: C, 87.4; H, 6.3; N, 6.2. $C_{32}H_{28}N_2$ requires C, 87.2; H, 6.4; N, 6.4%); ν_{max}(Nujol)/cm^{-1} 3422, 1610, 1599, 1332, 1305, 1193, 1163, 1032, 967, 853, 777, 751 and 702; δ_H 1.34 (3 H, s), 1.39 (3 H, s), 3.22 (1 H, d, J = 17.5), 3.31 (1 H, d, J = 17.5), 4.20 (1 H, s), 6.27 (1 H, s), 6.39 (1 H, d, J = 7.7), 6.66 (1 H, t, J = 7.4), 6.91 (1 H, d, J = 7.4) 6.97–7.06 (3 H, m), 7.12–7.16 (2 H, m), 7.24–7.26 (9 H, m),

† CCDC reference numbers 223156 and 223157. See http://www.rsc.org/suppdata/nj/b3/b312930f/ for crystallographic data in .cif or other electronic format.

7.67–7.79 (1 H, m); δ_C 19.3, 24.8, 41.0, 51.9 (s), 65.4 (s), 90.0 (s), 94.4, 107.6, 111.8, 118.6, 120.0, 121.0, 121.1, 123.9, 126.3 (s), 126.9, 127.4, 127.6, 127.7, 128.0, 128.6, 128.7, 130.5 (s), 133.4 (s), 142.3 (s), 146.2 (s), 147.9 (s), 148.9 (s); m/z (EI) 440 (M^+, 7%), 220 (100).

Crystal data: $C_{32}H_{28}N_2$, $M = 440.56$, triclinic, $a = 10.1741(8)$, $b = 10.6139(9)$, $c = 11.3542(9)$ Å, $U = 1137.81(16)$ Å^3, $T = 100(2)$ K, space group $P\bar{1}$, $Z = 2$, absorption coefficient = 0.075 mm^{-1}, 12 460 reflections measured, 4621 unique ($R_{int} = 0.0337$) which were used in all calculations. The final $wR(F^2)$ was 0.1065 (all data).†

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