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Coupling/cyclization of 1,6-enynes with aryl halides: an efficient and general route for the synthesis of functionalized hexahydroindole and hexahydrobenzofuran derivatives

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ABSTRACT

An efficient and general route for the synthesis of functionalized hexahydroindole and hexahydrobenzofuran derivatives has been developed via the palladium-catalyzed domino coupling/cyclization reaction of 1,6-enynes and aryl halides. The results indicated that the electronic properties of the aryl halides strongly affect the reaction yields.

1. Introduction

Indole and benzofuran rings are important components of many natural products and medicinally relevant compounds.[1] As such, they are also key intermediates in the process for the preparation of natural products and clinical medicines.[2] Because the availability of these building blocks can contribute to the production of more complex target molecules, many methods have been studied for the preparation of indole and benzofuran systems, ranging from classical techniques to recently discovered methods.[3–5] However, only a few examples of the synthesis of hexahydroindole and the hexahydrobenzofuran derivatives have been demonstrated. Yeh and Bäckvall reported the synthesis of hexahydroindole[6] and hexahydrobenzofuran[7] through intramolecular 1,4-nucleophilic additions of cyclic 1,3-dienes with amines or alcohols as nucleophiles. Bräse et al. synthesized hexahydroindole by an intramolecular Diels–Alder reaction.[8] Meanwhile, palladium-catalyzed cyclization reactions have been employed for the synthesis of different heterocycles.[9,10] This study aims to investigate the potential of palladium-catalyzed domino coupling/cyclization of enynes with aryl halides for the synthesis of substituted hexahydroindoles and hexahydrobenzofurans.

2. Results and discussion

Optimal parameters in the reaction of *N*-(3-phenylprop-2-ynyl)-*N*-(cyclohex-2-enyl)-4-methylbenzenesulfonamide (**4**) with methyl 4-bromobenzoate are listed in Table 1. The effect of temperature was initially surveyed in the presence of 2 mol % $Pd(OAc)_2$/4 mol % PPh_3 and 2 equiv of base $(n\text{-}Bu)_3N$ in DMF. No desired product was observed when the reaction was performed at 100 °C, and most of the staring material remained unchanged (Table 1, entry 1). Product **4b** was obtained in 66% yield when the reaction temperature was raised to 120 °C. However, no significant increase in the yield of product **4b** was observed when the reaction temperature was raised from 120 to 130 °C (Table 1, entries 2 and 3). Solvents frequently used in Heck reactions, such as CH_3CN, toluene, and DMF, were employed as the reaction media under the conditions indicated in Table 1. The best results were obtained in DMF (Table 1, entries 2, 4, and 5). Attempts to improve the yield of the domino coupling/cyclization reaction by utilizing other inorganic bases, such as K_2CO_3, $NaCO_3$, and $NaHCO_3$, were unsuccessful (Table 1, entries 8–10), and $(n\text{-}Bu)_3N$ was found to be more effective than those of inorganic bases. When the catalyst loading was less than 1.5 mol %, the product yield was lower (Table 1, entry 6). A high yield of 66% was

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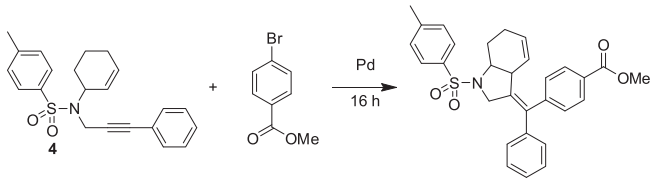
Table 1
Optimization of Cyclization Conditions[a]



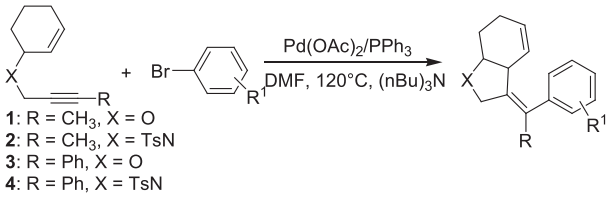
Entry[a]	[Pd]/PPh_3 (mol %)	Base (equiv)	Solvent	T (°C)[b]	Yield[c] (%)
1	$Pd(OAc)_2/PPh_3$ (2:4)	$(n\text{-}Bu)_3N$	DMF	100	Trace
2	$Pd(OAc)_2/PPh_3$ (2:4)	$(n\text{-}Bu)_3N$	DMF	120	66
3	$Pd(OAc)_2/PPh_3$ (2:4)	$(n\text{-}Bu)_3N$	DMF	130	65
4	$Pd(OAc)_2/PPh_3$ (2:4)	$(n\text{-}Bu)_3N$	CH_3CN	100	Trace
5	$Pd(OAc)_2/PPh_3$ (2:4)	$(n\text{-}Bu)_3N$	Toluene	120	29
6	$Pd(OAc)_2/PPh_3$ (1.5:3)	$(n\text{-}Bu)_3N$	DMF	120	51
7	$Pd(OAc)_2/PPh_3$ (3:6)	$(n\text{-}Bu)_3N$	DMF	120	66
8	$Pd(OAc)_2/PPh_3$ (2:4)	K_2CO_3	DMF	120	21
9	$Pd(OAc)_2/PPh_3$ (2:4)	Na_2CO_3	DMF	120	14
10	$Pd(OAc)_2/PPh_3$ (2:4)	$NaHCO_3$	DMF	120	16
11	$PdCl_2/PPh_3$ (2:4)	$(n\text{-}Bu)_3N$	DMF	120	Trace
12	$Pd(dba)_2$	$(n\text{-}Bu)_3N$	DMF	120	38
13	$Pd(PPh_3)_4$	$(n\text{-}Bu)_3N$	DMF	120	44

[a] All reactions were carried out under argon for 16 h by using enyne (1.0 equiv), methyl 4-bromobenzoate (1.2 equiv), $Pd(OAc)_2$, PPh_3, base, and solvent (5 mL) under the indicated conditions.
[b] Oil bath temperature.
[c] Isolated yield.

obtained when 2 mol % $Pd(OAc)_2$ was applied (Table 1, entry 2), and no apparent improvement was observed on the yield when the Pd $(OAc)_2$ loading was more than 2 mol % (Table 1, entry 7). Other palladium catalysts, such as $Pd(dba)_2$, $Pd(PPh_3)_4$, and $PdCl_2$, exhibited lower catalytic activity than $Pd(OAc)_2$, based on the isolated yields of the product (Table 1, entries 11–13). Thus, the optimized reaction conditions included 2 mol % $Pd(OAc)_2$ as the catalyst, 4 mol % PPh_3 as the ligand, tributylamine as a base, DMF as the solvent, 16 h of reaction time, and a reaction temperature of 120 °C.

To establish the scope of this methodology, reactions of enyne substrates **1**, **2**, **3**, and **4** with a number of aryl halides were investigated (Table 2). Under the optimized reaction conditions, various substituted aryl bromides reacted with the substrates smoothly and produced the corresponding functionalized hexahydroindole and hexahydrobenzofuran derivatives. Yields of the hexahydroindole and hexahydrobenzofuran derivatives varied significantly with the substituents of the aryl halides. Reactions of enynes with aryl halides bearing electron-withdrawing groups produced better yields of products than those of reactions of enynes with aryl halides bearing electron-donating groups. For example, the reaction of *N*-(but-2-ynyl)-*N*-(cyclohex-2-enyl)-4-methylbenzenesulfonamide (**2**) with methyl 4-bromobenzoate resulted in 83% yield (Table 2, entry 12), whereas the reaction of 1-(3-(cyclohex-2-enyloxy)prop-1-ynyl) benzene (**3**) with 1-bromo-4-methoxybenzene gave the corresponding product in 40% yield (Table 2, entry 14), similar results were observed for *N*-(3-phenylprop-2-ynyl)-*N*-(cyclohex-2-enyl)-4-methylbenzenesulfonamide (**4**) with methyl 4-bromobenzoate and 1-bromo-4-methoxybenzene (Table 2, entries 19 and 20). Interestingly, the C–Br bond reacted selectively with the enyne when the aryl ring bears both bromo and chloro substituents (Table 2, entries 2, 3, 10, and 11). Differences in the enyne substrates have influence on the domino coupling/cyclization reaction. The outputs of reactions of substrates **3** or **4** with aryl halides were slightly lower than those of the reactions of **1** and **2** with the corresponding aryl halides. For example, the reaction of ethyl 4-bromobenzoate with enyne **1** gave the desired products in 74% yield (Table 2, entry 5), while the reaction of ethyl 4-bromobenzoate with enynes **3** gave the corresponding products in 61% yield (Table 2, entry 18), indicating the steric effects on the carbopalladation process. Noticeably, *N*-(but-2-ynyl)-*N*-(cyclopent-2-enyl)-4-methylbenzenesulfonamide and *N*-(but-2-ynyl)-*N*-(cyclohept-2-enyl)-4-methylbenzenesulfonamide had been tested and lead to complex products, probably the reason is the high torsional strain of the cycloalkenyl group (cyclopentenyl or cyclohepenyl).

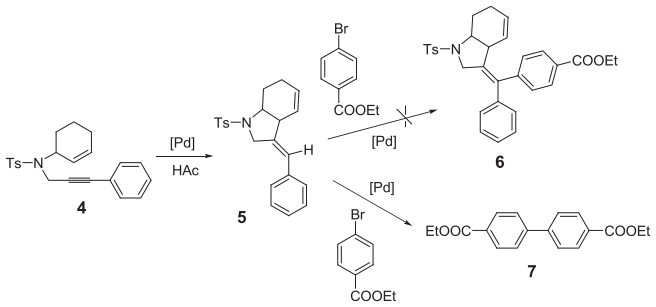
Table 2
Synthesis of hexahydroindole and hexahydrobenzofuran[a]



Entry	Enyne	R^1	Product	Yield[b] (%)
1	**1**	4-COMe	**1a**	73
2	**1**	3-Cl	**1b**	72
3	**1**	4-Cl	**1c**	76
4	**1**	4-CN	**1d**	81
5	**1**	4-CO_2Et	**1e**	74
6	**1**	4-CHO	**1f**	75
7	**2**	4-COMe	**2a**	78
8	**2**	4-CN	**2b**	85
9	**2**	H	**2c**	60
10	**2**	4-Cl	**2d**	83
11	**2**	3-Cl	**2e**	74
12	**2**	4-CO_2Me	**2f**	83
13	**2**	4-CO_2Et	**2g**	81
14	**2**	4-OMe	**2h**	40
15	**3**	4-Cl	**3a**	67
16	**3**	3-Cl	**3b**	57
17	**3**	4-SO_2Me	**3c**	70
18	**3**	4-CO_2Et	**3d**	61
19	**4**	4-OMe	**4a**	27
20	**4**	4-CO_2Me	**4b**	66
21	**4**	H	**4c**	40
22	**4**	4-COMe	**4d**	63

[a] Enyne (1.0 equiv), aryl bromide (1.2 equiv), $Pd(OAc)_2$ (2 mol %), PPh_3, $(n\text{-}Bu_3)N$ (2.0 equiv), and DMF (5 mL).
[b] Isolated yield.

In order to better understand the mechanism for the domino reaction, enyne **4** was treated with palladium catalyst without aryl halide under the same conditions for the above reaction, the self-cyclization product **5** was isolated in a very low yield (<5%). However, changing the conditions by adding acetic acid to the reaction of **4** with palladium catalyst (without aryl halides), the yield of the self-cyclization product **5** can be increased to 50%. When the self-cyclization product **5** was treated with aryl halide, for example, ethyl 4-bromobenzoate, no coupling product **6** was observed, instead, an aryl coupling product **7** was isolated (Scheme 1). This



Scheme 1. Pathway of the cross cyclization reaction.

result suggested that coupling of the aryl group with triple bond will occur at first in our domino/cyclization reaction, not after the cyclization.

All new products were fully characterized by various spectroscopic techniques and high-resolution masss pectrometry. The molecular structure of **2e** (Fig. 1) was confirmed by single-crystal X-ray analysis.

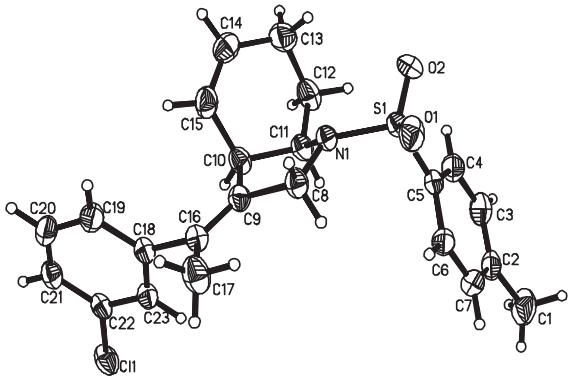
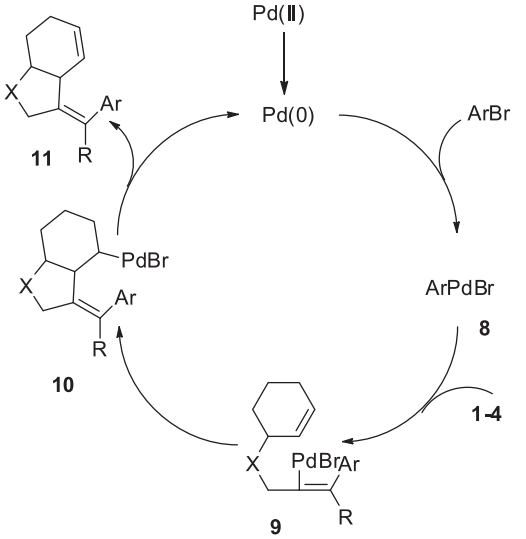


Fig. 1. Molecular structure of **2e**.

On the basis of the above results, a possible reaction mechanism is shown in Scheme 2. The oxidative addition of aryl halides to palladium(0) afforded arylpalladium species **8**. *syn* Carbopalladation of the arylpalladium species **8** with the carbon–carbon triple bond generated the alkenylpalladium intermediate **9**, which reacted with the carbon–carbon double bond through further carbopalladation reaction to afford **10**. Afterward, *syn* β-elimination of **10** produced HPdBr and the desired product **11**. A base assisted reduction regenerated the active palladium species, Pd(0).[2b,11]



Scheme 2. Proposed mechanism of the reaction.

3. Conclusions

An efficient and direct approach for constructing functionalized hexahydroindole and hexahydrobenzofuran derivatives from readily available 1,6-enynes and aryl halides was developed. Multiple new carbon–carbon bonds were formed in one step via palladium-catalyzed domino coupling/cyclization of 1,6-enynes and aryl halides. Results indicate that the electronic effects of the aryl halides and the steric effects of the substrates influenced the reaction yields. Further exploration of the reaction scope and other types of coupling/cyclizations of enynes is currently being done in our lab.

4. Experimental

4.1. General experiment

All the catalytic reactions were performed under an argon atmosphere using the oven-dried Schlenk flask. All solvents and materials were pre-dried, redistilled or recrystallized before use. The ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Column chromatography was performed on silica gel 300–400 mesh. Melting points were uncorrected. Infrared spectra were recorded on FT-IR spectrometer as KBr pellets or thin film from $CHCl_3$ on the NaCl window. All HRMS spectra were record using EI at 70 eV. X-ray crystallography diffraction data of **2e** were collected at room temperature with a Bruker SMART Apex CCD diffractometer with Mo-Kα radiation (λ=0.71073 Å) with a graphite monochromator using the ω-scan mode. Enynes, 3-(but-2-ynyloxy)cyclohex-1-ene (1),[12] *N*-(but-2-ynyl)-*N*-(cyclohex-2-enyl)-4-methylbenzenesulfon amide (2),[12] 1-(3-(cyclohex-2-enyloxy) prop-1-ynyl)benzene (3),[13] and *N*-(3-phenylprop-2-ynyl)-*N*-(cyclohex-2-enyl)-4-methylbenzenesulfon amide (4)[13] were prepared by published procedures.

4.2. Synthesis

A typical procedure for the coupling/cyclization of 1,6-enynes with aryl halides: enyne (1.0 equiv), aryl halides (1.2 equiv), Pd $(OAc)_2$ (2 mol%), and PPh_3 (4 mol%) were added to a degassed solution of $(n\text{-}Bu)_3$ (2 equiv) in DMF (5 mL), and the mixture was stirred at room temperature for half an hour and then heated at 120 °C for 16 h. The reaction mixture was then cooled, quenched with water, and extracted with ethylacetate (30 mL). The combined organic layers were washed with hydrochloric acid (5%), sodium carbonate (5%), and saturated sodium chloride solution, dried over $MgSO_4$, and concentrated. The residue was purified by flash column chromatography to give final product.

*4.2.1. 1-(4-((1E)-1-(7,7a-Dihydrobenzofuran-3(2H,3aH,6H)-ylidene) ethyl) phenyl)ethanone (**1a**).* Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.94 (d, J=7.2 Hz, 2H), 7.35 (d, J=7.2 Hz, 2H), 5.61 (s, 1H), 5.04–5.01 (m, 1H), 4.56 (d, J=13.5 Hz, 1H), 4.41 (d, J=13.5 Hz, 1H), 4.22 (s, 1H), 3.27 (s, 1H), 2.61 (s, 3H), 2.13–1.91 (m, 6H), 1.60–1.56 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.7, 148.6, 139.8, 135.3, 128.5, 127.8, 127.3, 126.9, 124.8, 77.2, 69.6, 41.2, 26.5, 24.3, 21.1, 19.0; FT-IR (neat): ν_{max} 3024, 2922, 2852, 1681, 1602, 1267, 1083, 839 cm^{-1}; HRMS (EI) m/z: calcd for $C_{18}H_{20}O_2$: 268.1463; found: 268.1457.

*4.2.2. (3E)-3-(1-(3-Chlorophenyl)ethylidene)-2,3,3a,6,7,7a-hexahydrobenzo-furan (**1b**).* Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.28–7.24 (m, 3H), 7.15–7.12 (m, 1H), 5.63 (s, 1H), 5.09–5.05 (m, 1H), 4.60 (d, J=13.2 Hz, 1H), 4.41 (d, J=13.2 Hz, 1H), 4.22 (s, 1H), 3.26 (s, 1H), 2.15–1.89 (m, 6H), 1.63–1.59 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 145.4, 139.4, 134.1, 129.7, 127.7, 127.4, 126.8, 126.7, 125.9, 125.1, 77.2, 69.6, 41.3, 24.4, 21.3, 19.0; FT-IR (neat): ν_{max} 3024, 2924, 2850, 1593, 1562, 1440, 1082, 786 cm^{-1}; HRMS (EI) m/z: calcd for $C_{16}H_{17}ClO$: 260.0968; found: 260.0961.

*4.2.3. (3E)-3-(1-(4-Chlorophenyl)ethylidene)-2,3,3a,6,7,7a-hexahydrobenzo-furan (**1c**).* Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.32 (d, J=7.8 Hz, 2H), 7.19 (d, J=7.8 Hz, 2H), 5.62 (s, 1H), 5.06–5.05 (m, 1H), 4.55 (d, J=13.5 Hz, 1H), 4.41 (d, J=13.5 Hz, 1H), 4.21 (s, 1H), 3.24 (s, 1H), 2.14–1.86 (m, 6H), 1.62–1.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.0, 139.2, 132.3, 129.0, 128.7, 128.6, 126.8, 125.1, 77.2, 69.6, 41.3, 24.4, 21.4, 19.1; FT-IR (neat): ν_{max} 3026, 2922,

2850, 1593, 1489, 1440, 1082, 831 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{16}H_{17}ClO$: 260.0968; found: 260.0962.

*4.2.4. 4-((1E)-1-(7,7a-Dihydrobenzofuran-3(2H,3aH,6H)-ylidene) ethyl)benzo-nitrile (**1d**).* Viscous liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 7.65 (d, *J*=7.5 Hz, 2H), 7.37 (d, *J*=7.5 Hz, 2H), 5.64 (s, 1H), 5.00–4.97 (m, 1H), 4.57 (d, *J*=12.6 Hz, 1H), 4.42 (d, *J*=12.6 Hz, 1H), 4.23 (s, 1H), 3.23 (s, 1H), 2.14–1.84 (m, 6H), 1.62–1.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.4, 140.7, 132.3, 128.4, 127.3, 126.3, 124.5, 118.9, 110.4, 77.2, 69.7, 41.3, 24.3, 21.0, 19.2; FT-IR (neat): ν_{max} 3024, 2922, 2854, 2227, 1604, 1504, 1440, 1082, 842 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{17}H_{17}NO$: 251.1310; found: 251.1301.

*4.2.5. Ethyl 4-((1E)-1-(7,7a-Dihydrobenzofuran-3(2H,3aH,6H)-ylidene) ethyl) benzoate (**1e**).* Viscous liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 8.03 (d, *J*=6.9 Hz, 2H), 7.32 (d, *J*=7.2 Hz, 2H), 5.60 (s, 1H), 5.04–5.01 (m, 1H), 4.57 (d, *J*=12.9 Hz, 1H), 4.45–4.37 (m, 3H), 4.22 (s, 1H), 3.27 (s, 1H), 2.13–1.82 (m, 6H), 1.57 (m, 1H), 1.40 (t, *J*=6.0 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 148.4, 139.6, 130.2, 129.7, 128.7, 127.6, 126.9, 125.0, 77.3, 69.7, 60.9, 41.3, 24.4, 21.2, 19.1, 14.4; FT-IR (neat): ν_{max} 3026, 2922, 2850, 1716, 1276, 1105, 1082, 823 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{19}H_{22}O_3$: 298.1569; found: 298.1565.

*4.2.6. 4-((1E)-1-(7,7a-Dihydrobenzofuran-3(2H,3aH,6H)-ylidene) ethyl) benzaldehyde (**1f**).* Viscous liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 10.01 (s, 1H), 7.87 (d, *J*=6.3 Hz, 2H), 7.43 (d, *J*=6.9 Hz, 2H), 5.61 (s, 1H), 5.03–5.00 (m, 1H), 4.58 (d, *J*=13.2 Hz, 1H), 4.43 (d, *J*=13.2 Hz, 1H), 4.23 (s, 1H), 3.28 (s, 1H), 2.13–1.83 (m, 6H), 1.61–1.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 191.8, 150.1, 140.3, 134.8, 130.0, 128.3, 127.1, 126.9, 124.8, 77.2, 69.7, 41.3, 24.3, 21.1, 19.0; FT-IR (neat): ν_{max} 3026, 2920, 2850, 1698, 1602, 1504, 1440, 1082, 837 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{17}H_{18}O_2$: 254.1307; found: 254.1297.

*4.2.7. 1-(4-((1E)-1-(1,2,7,7a-Tetrahydro-1-tosyl-3aH-indol-3(6H)-ylidene) ethyl)phenyl)ethanone (**2a**).* Colorless solid; mp 145–147 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.88 (d, *J*=7.8 Hz, 2H), 7.76 (d, *J*=7.8 Hz, 2H), 7.37 (d, *J*=7.8 Hz, 2H), 7.07 (d, *J*=7.8 Hz, 2H), 5.65 (s, 1H), 4.99–4.96 (m, 1H), 4.12 (d, *J*=15.0 Hz, 1H), 4.02 (d, *J*=15.0 Hz, 1H), 3.62 (s, 1H), 3.11 (s, 1H), 2.58 (s, 3H), 2.48 (s, 3H), 2.27–2.24 (m, 2H), 1.90–1.85 (m, 4H), 1.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 147.8, 143.6, 135.6, 134.1, 133.8, 129.7, 129.0, 128.5, 128.4, 127.8, 127.7, 124.8, 59.0, 51.4, 42.3, 26.6, 25.1, 21.6, 21.5, 20.1; FT-IR (KBr): ν_{max} 3022, 2854, 1681, 1604, 1336, 1155, 817, 704 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{25}H_{27}NO_3S$: 421.1712; found: 421.1710.

*4.2.8. 4-((1E)-1-(1,2,7,7a-Tetrahydro-1-tosyl-3aH-indol-3(6H)-ylidene)ethyl) benzo-nitrile (**2b**).* Colorless solid; mp 137–139 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, *J*=6.9 Hz, 2H), 7.58 (d, *J*=6.9 Hz, 2H), 7.37 (d, *J*=6.6 Hz, 2H), 7.10 (d, *J*=6.9 Hz, 2H), 5.67 (s, 1H), 4.94–4.91 (m, 1H), 4.12 (d, *J*=15.0 Hz, 1H), 4.01 (d, *J*=15.0 Hz, 1H), 3.61 (s, 1H), 3.07 (s, 1H), 2.47 (s, 3H), 2.26–2.24 (m, 2H), 1.92–1.85 (m, 4H), 1.62–1.59 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.5, 143.7, 135.0, 133.8, 132.3, 129.7, 128.7, 128.3, 127.8, 124.4, 118.7, 110.7, 58.9, 51.4, 42.3, 25.0, 21.6, 21.4, 20.1; FT-IR (KBr): ν_{max} 3024, 2854, 2229, 1604, 1336, 1155, 817, 704 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{24}H_{24}N_2O_2S$: 404.1558; found: 404.1553.

*4.2.9. (3E)-2,3,3a,6,7,7a-Hexahydro-3-(1-phenylethylidene)-1-tosyl-1H-indole (**2c**).* Colorless solid; mp 126–127 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J*=6.9 Hz, 2H), 7.37 (d, *J*=7.5 Hz, 2H), 7.28–7.21 (m, 3H), 6.96 (d, *J*=6.9 Hz, 2H), 5.66 (s, 1H), 5.06–5.03 (m, 1H), 4.12 (d, *J*=14.7 Hz, 1H), 4.03 (d, *J*=14.4 Hz, 1H), 3.62 (s, 1H), 3.13 (s, 1H), 2.48 (s, 3H), 2.28–2.25 (m, 2H), 1.91–1.84 (m, 4H), 1.63–1.59 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.5, 142.7, 134.0, 132.8, 130.0, 129.7, 128.3, 128.0, 127.8, 127.4, 126.8, 125.4, 59.0, 51.4, 42.3, 25.2, 21.8, 21.6, 20.1; FT-IR (KBr): ν_{max} 3024, 2910, 2870, 1597, 1490, 1440, 1346, 1163, 815, 769, 705 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{23}H_{25}NO_2S$: 379.1606; found: 379.1601.

*4.2.10. (3E)-3-(1-(4-Chlorophenyl)ethylidene)-2,3,3a,6,7,7a-hexahydro-1-tosyl-1H-indole (**2d**).* Colorless solid; mp 151–152 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, *J*=6.0 Hz, 2H), 7.37 (d, *J*=6.3 Hz, 2H), 7.25 (d, *J*=6.9 Hz, 2H), 6.90 (d, *J*=6.6 Hz, 2H), 5.67 (s, 1H), 5.01–4.99 (m, 1H), 4.10 (d, *J*=14.7 Hz, 1H), 4.00 (d, *J*=14.4 Hz, 1H), 3.61 (s, 1H), 3.09 (s, 1H), 2.47 (s, 3H), 2.25 (m, 2H), 1.92–1.82 (m, 4H), 1.60 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.6, 141.1, 134.0, 133.6, 132.6, 129.7, 128.8, 128.6, 128.4, 127.8, 125.0, 59.0, 51.4, 42.3, 25.1, 21.7, 21.6, 20.1; FT-IR (KBr): ν_{max} 3028, 2920, 2854, 1597, 1489, 1438, 1336, 1155, 815 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{23}H_{24}ClNO_2S$: 413.1216; found: 413.1209.

*4.2.11. (3E)-3-(1-(3-Chlorophenyl)ethylidene)-2,3,3a,6,7,7a-hexahydro-1-tosyl-1H-indole (**2e**).* Colorless solid; mp 123–124 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, *J*=7.8 Hz, 2H), 7.38 (d, *J*=7.2 Hz, 2H), 7.20 (s, 2H), 6.86 (s, 1H), 5.68 (s, 1H), 5.01–4.98 (m, 1H), 4.10 (d, *J*=15.0 Hz, 1H), 4.03 (d, *J*=15.0 Hz, 1H), 3.64 (s, 1H), 3.07 (s, 1H), 2.49 (s, 3H), 2.25–2.23 (m, 2H), 1.93–1.82 (m, 4H), 1.61 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.5, 143.7, 134.1, 134.0, 129.7, 128.7, 128.3, 127.8, 127.5, 126.9, 125.6, 125.0, 58.9, 51.2, 42.1, 25.2, 21.7, 21.6, 20.2; FT-IR (KBr): ν_{max} 3026, 2908, 2841, 1593, 1492, 1444, 1340, 1161, 815 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{23}H_{24}ClNO_2S$: 413.1216; found: 413.1210.

*4.2.12. Methyl 4-((1E)-1-(1,2,7,7a-tetrahydro-1-tosyl-3aH-indol-3(6H)-ylidene) ethyl)benzoate (**2f**).* Colorless solid; mp 110–112 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.95 (d, *J*=8.1 Hz, 2H), 7.76 (d, *J*=7.2 Hz, 2H), 7.37 (d, *J*=7.2 Hz, 2H), 7.04 (d, *J*=7.8 Hz, 2H), 5.64 (s, 1H), 4.98–4.94 (m, 1H), 4.12 (d, *J*=15.0 Hz, 1H), 4.03 (d, *J*=15.0 Hz, 1H), 3.62 (s, 1H), 3.09 (s, 1H), 2.48 (s, 3H), 2.26–2.22 (m, 2H), 1.91–1.85 (m, 4H), 1.64–1.55 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.8, 147.5, 143.6, 134.1, 133.9, 129.7, 129.1, 128.6, 128.3, 127.8, 127.5, 124.9, 58.9, 52.1, 51.4, 42.2, 25.1, 21.6, 21.5, 20.1; FT-IR (KBr): ν_{max} 3026, 2916, 2860, 1720, 1606, 1492, 1435, 1346, 1282, 1159, 813 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{25}H_{27}NO_4S$: 437.1661; found: 437.1656.

*4.2.13. Ethyl 4-((1E)-1-(1,2,7,7a-tetrahydro-1-tosyl-3aH-indol-3 (6H)-ylidene)ethyl)benzoate (**2g**).* Colorless solid; mp 127–128 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.96 (d, *J*=7.8 Hz, 2H), 7.76 (d, *J*=7.8 Hz, 2H), 7.37 (d, *J*=7.8 Hz, 2H), 7.04 (d, *J*=7.5 Hz, 2H), 5.65 (s, 1H), 4.98–4.95 (m, 1H), 4.34 (q, *J*=7.2 Hz, 2H), 4.12 (d, *J*=14.4 Hz, 1H), 4.03 (d, *J*=14.7 Hz, 1H), 3.62 (s, 1H), 3.09 (s, 1H), 2.48 (s, 3H), 2.26–2.23 (m, 2H), 1.91–1.85 (m, 4H), 1.60–1.55 (m, 1H), 1.39 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 147.4, 143.6, 134.0, 129.7, 129.6, 129.1, 128.9, 128.2, 127.8, 127.5, 124.9, 61.0, 59.0, 51.4, 42.3, 25.1, 21.6, 21.5, 20.1, 14.3; FT-IR (KBr): ν_{max} 3026, 2860, 1714, 1606, 1492, 1336, 1267, 1155, 812 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{26}H_{29}NO_4S$: 451.1817; found: 451.1816.

*4.2.14. (3E)-2,3,3a,6,7,7a-Hexahydro-3-(1-(4-methoxyphenyl) ethylidene)-1-tosyl-1H-indole (**2h**).* Colorless solid; mp 156–158 °C; ^1H NMR (300 MHz, $CDCl_3$): δ 7.76 (d, *J*=8.1 Hz, 2H), 7.36 (d, *J*=7.5 Hz, 2H), 6.90 (d, *J*=7.8 Hz, 2H), 6.81 (d, *J*=8.1 Hz, 2H), 5.65 (s, 1H), 5.08–5.05 (m, 1H), 4.10 (d, *J*=14.4 Hz, 1H), 4.02 (d, *J*=15.0 Hz, 1H), 3.79 (s, 3H), 3.61 (s, 1H), 3.14 (s, 1H), 2.47 (s, 3H), 2.27–2.25 (m, 2H), 1.92–1.82 (m, 4H), 1.60 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.3, 143.5, 135.1, 134.1, 132.5, 129.6, 129.5, 128.4, 127.9, 127.8, 125.5, 113.7, 59.0, 55.2, 51.4, 42.3, 25.2, 21.9, 21.6, 20.1; FT-IR (KBr): ν_{max} 3022, 2906, 2845, 1608, 1510, 1456, 1338, 1242, 1159, 813 cm^{-1}; HRMS (EI) *m/z*: calcd for $C_{24}H_{27}NO_3S$: 409.1712; found: 409.1708.

*4.2.15. (3E)-3-((4-Chlorophenyl)(phenyl)methylene)-2,3,3a,6,7,7a-hexahydrobenzofuran (**3a**).* Viscous liquid; ^1H NMR (300 MHz, $CDCl_3$): δ 7.34–7.08 (m, 9H), 5.73 (s, 1H), 5.21–5.18 (m, 1H), 4.72 (d, *J*=13.5 Hz, 1H), 4.26–4.24 (m, 2H), 3.48 (s, 1H), 2.18 (m, 1H),

2.04–1.88 (m, 2H), 1.62 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 142.2, 141.1, 140.5, 133.0, 130.5, 128.7, 128.4, 128.3, 128.0, 127.8, 127.1, 124.4, 76.2, 69.5, 42.4, 24.5, 19.3; FT-IR (neat): ν_{max} 3022, 2924, 2852, 1600, 1504, 1440, 1074, 827, 702 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{21}H_{19}ClO$: 322.1124; found: 322.1116.

*4.2.16. (3E)-3-((3-Chlorophenyl)(phenyl)methylene)-2,3,3a,6,7,7a-hexahydrobenzofuran (**3b**).* Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.31–7.05 (m, 9H), 5.74 (s, 1H), 5.22–5.19 (m, 1H), 4.72 (d, *J*=13.5 Hz, 1H), 4.30–4.24 (m, 2H), 3.48 (s, 1H), 2.19–2.15 (m, 1H), 2.06–1.88 (m, 2H), 1.65–1.60 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.7, 142.4, 140.9, 134.3, 132.9, 129.8, 129.1, 128.4, 128.3, 127.8, 127.4, 127.1, 127.0, 124.4, 76.2, 69.5, 42.4, 24.5, 19.2; FT-IR (neat): ν_{max} 3022, 2924, 2850, 1602, 1504, 1440, 1074, 827 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{21}H_{19}ClO$: 322.1124; found: 322.1121.

*4.2.17. (3E)-2,3,3a,6,7,7a-Hexahydro-3-((4-(methylsulfonyl) phenyl) (phenyl) methylene)benzofuran (**3c**).* Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.93 (d, *J*=7.5 Hz, 2H), 7.49 (d, *J*=8.1 Hz, 2H), 7.32–7.27 (m, 3H), 7.09 (d, *J*=6.9 Hz, 2H), 5.74 (s, 1H), 5.14–5.11 (m, 1H), 4.73 (d, *J*=14.1 Hz, 1H), 4.32–4.25 (m, 2H), 3.46 (s, 1H), 3.09 (s, 3H), 2.18–2.14 (m, 1H), 2.05–1.88 (m, 2H), 1.65–1.62 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 147.7, 143.5, 140.4, 138.9, 132.5, 130.1, 128.5, 128.4, 128.3, 127.7, 127.4, 123.9, 76.3, 69.6, 44.5, 42.3, 24.4, 19.2; FT-IR (neat): ν_{max} 3024, 2920, 2850, 1602, 1444, 1320, 1138, 1072, 702 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{22}H_{22}O_3S$: 366.1290; found: 366.1286.

*4.2.18. Ethyl 4-((1E)-(7,7a-dihydrobenzofuran-3(2H,3aH,6H)-ylidene) (phenyl) methyl)benzoate (**3d**).* Viscous liquid; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.04 (d, *J*=8.1 Hz, 2H), 7.37–7.23 (m, 5H), 7.10 (d, *J*=6.9 Hz, 2H), 5.71 (s, 1H), 5.18–5.14 (m, 1H), 4.74 (d, *J*=14.1 Hz, 1H), 4.39 (q, *J*=7.2 Hz, 1H), 4.30–4.26 (m, 2H), 3.49 (s, 1H), 2.18 (m, 1H), 2.05–1.87 (m, 2H), 1.65–1.61 (m, 1H), 1.40 (t, *J*=7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 145.6, 142.4, 140.7, 133.5, 129.8, 129.1, 128.9, 128.5, 128.3, 127.8, 127.2, 124.3, 76.3, 69.5, 60.9, 42.4, 24.5, 19.2, 14.4; FT-IR (neat): ν_{max} 3024, 2920, 2850, 1716, 1606, 1444, 1276, 1103, 1072, 702 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{24}H_{24}O_3$: 360.1725; found: 360.1724.

*4.2.19. (3E)-2,3,3a,6,7,7a-Hexahydro-3-((4-methoxyphenyl) (phenyl) methylene)-1-tosyl-1H-indole (**4a**).* Colorless solid; mp 136–138 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.55 (d, *J*=7.5 Hz, 2H), 7.27 (s, 5H), 6.89 (d, *J*=6.3 Hz, 2H), 6.77 (d, *J*=7.8 Hz, 2H), 6.68 (d, *J*=8.4 Hz, 2H), 5.77 (s, 1H), 5.15–5.12 (m, 1H), 4.22 (d, *J*=15.3 Hz, 1H), 4.00 (d, *J*=15.3 Hz, 1H), 3.84 (s, 1H), 3.78 (s, 3H), 3.32 (s, 1H), 2.46 (s, 3H), 2.23–2.17 (m, 2H), 1.97–1.92 (m, 1H), 1.69–1.58 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 158.5, 143.3, 141.4, 135.7, 135.6, 134.6, 133.3, 129.9, 129.6, 128.6, 128.1, 127.7, 127.3, 125.1, 113.7, 58.2, 55.2, 51.6, 42.5, 26.0, 21.5, 20.3; FT-IR (KBr): ν_{max} 3014, 2864, 1647, 1336, 1244, 1153, 821, 765, 704 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{29}H_{29}NO_3S$: 471.1868; found: 471.1867.

*4.2.20. Methyl 4-((1E)-(1,2,7,7a-tetrahydro-1-tosyl-3aH-indol-3(6H)-ylidene) (phenyl)methyl)benzoate (**4b**).* Colorless solid; mp 128–130 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, *J*=7.2 Hz, 2H), 7.56 (d, *J*=7.5 Hz, 2H), 7.29–7.26 (m, 5H), 6.89–6.83 (m, 4H), 5.79–5.76 (m, 1H), 5.06–5.02 (m, 1H), 4.25 (d, *J*=15.6 Hz, 1H), 4.03 (d, *J*=15.3 Hz, 1H), 3.90 (s, 3H), 3.86 (s, 1H), 3.24 (s, 1H), 2.47 (s, 3H), 2.30–2.16 (m, 2H), 1.97–1.92 (m, 1H), 1.69–1.66 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ166.7, 145.6, 143.4, 140.2, 137.1, 135.1, 134.5, 129.7, 129.1, 128.9, 128.8, 128.7, 128.5, 128.3, 127.7, 124.6, 58.1, 52.1, 51.5, 42.5, 25.9, 21.5, 20.2; FT-IR (KBr): ν_{max} 3026, 2866, 1720, 1346, 1278, 1161, 1101, 815, 761, 705 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{30}H_{29}NO_4S$: 499.1817; found: 499.1816.

*4.2.21. 2,3,3a,6,7,7a-Hexahydro-3-(diphenylmethylene)-1-tosyl-1H-indole (**4c**).* Colorless solid; mp 133–135 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, *J*=7.8 Hz, 2H), 7.26–7.22 (m, 8H), 6.89 (d, *J*=7.2 Hz, 2H), 6.75 (d, *J*=6.9 Hz, 2H), 5.76 (s, 1H), 5.11–5.08 (m, 1H), 4.23 (d, *J*=15.6 Hz, 1H), 4.02 (d, *J*=15.6 Hz, 1H), 3.83 (s, 1H), 3.28 (s, 1H), 2.45 (s, 3H), 2.27–2.16 (m, 2H), 1.97–1.90 (m, 1H), 1.67–1.60 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.3, 140.9, 140.8, 136.0, 135.9, 134.6, 129.6, 128.8, 128.6, 128.3, 128.1, 127.6, 127.3, 126.9, 125.0, 58.1, 51.5, 42.5, 25.9, 21.5, 20.1; FT-IR (KBr): ν_{max} 3024, 2866, 1692, 1346, 1161, 816, 754, 702 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{28}H_{27}NO_2S$: 441.1762; found: 441.1765.

*4.2.22. 1-(4-((1E)-(1,2,7,7a-Tetrahydro-1-tosyl-3aH-indol-3(6H)-ylidene) (phenyl)methyl)phenyl)ethanone (**4d**).* Colorless solid; mp 161–163 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.83 (d, *J*=7.2 Hz, 2H), 7.54 (d, *J*=7.5 Hz, 2H), 7.28–7.25 (m, 5H), 6.87–6.85 (m, 4H), 5.76 (s, 1H), 5.05–5.02 (m, 1H), 4.23 (d, *J*=15.6 Hz, 1H), 4.02 (d, *J*=15.6 Hz, 1H), 3.84 (s, 1H), 3.24 (s, 1H), 2.56 (s, 3H), 2.46 (s, 3H), 2.24–2.15 (m, 2H), 1.97–1.90 (m, 1H), 1.63 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 197.6, 145.8, 143.4, 140.2, 137.1, 135.7, 135.0, 134.5, 129.6, 129.2, 129.1, 128.9, 128.6, 128.5, 128.1, 127.6, 124.5, 58.1, 51.5, 42.5, 26.5, 25.8, 21.5, 20.1; FT-IR (KBr): ν_{max} 3026, 2866, 1682, 1346, 1161, 815, 761, 705 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{30}H_{29}NO_3S$: 483.1868; found: 483.1876.

*4.2.23. (3Z)-3-Benzylidene-2,3,3a,6,7,7a-hexahydro-1-tosyl-1H-indole (**5**).* Colorless solid; mp 131–132 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.75 (d, *J*=7.8 Hz, 2H), 7.37–7.22 (m, 5H), 7.14 (d, *J*=7.2 Hz, 2H), 6.22 (s, 1H), 5.88 (d, *J*=9.3 Hz, 1H), 5.74 (d, *J*=9.6 Hz, 1H), 4.32 (d, *J*=15.3 Hz, 1H), 4.22 (d, *J*=14.7 Hz, 1H), 3.89 (s, 1H), 2.97 (s, 1H), 2.42 (s, 3H), 2.21–2.16 (m, 2H), 1.94–1.89 (m, 1H), 1.69–1.57 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 143.4, 139.9, 136.5, 135.4, 129.8, 129.2, 128.5, 128.2, 127.3, 127.1, 124.1, 123.9, 57.6, 49.9, 44.2, 26.1, 23.4, 21.5; FT-IR (KBr): ν_{max} 3030, 2862, 1492, 1336, 1166, 821, 763, 700 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{22}H_{23}NO_2S$: 365.1449; found: 365.1445.

*4.2.24. Diethyl biphenyl-4,4′-dicarboxylate(**7**).* Colorless solid; mp 113–114 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.13 (d, *J*=8.4 Hz, 4H), 7.68 (d, *J*=8.1 Hz, 4H), 4.41 (q, *J*=7.1 Hz, 4H), 1.42 (t, *J*=7.1 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.3, 144.3, 130.2, 130.0, 127.2, 61.1, 14.4; FT-IR (KBr): ν_{max} 2993, 1705, 1607, 1556, 1278, 1180, 1113, 1024, 877 cm^{-1}; HRMS (EI) *m*/*z*: calcd for $C_{18}H_{18}O_4$: 298.1205; found: 298.1202.

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Supplementary data

CCDC-775882 (**2e**) contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif. Copies of ^{1}H NMR, ^{13}C NMR spectra of all compounds are provided. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2010.09.029. These data include MOL files and InChIKeys of the most important compounds described in this article.

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