Enantiospecific synthesis of [2.2]paracyclophane-4-thiol and derivatives

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Abstract
This paper describes a simple route to enantiomerically enriched [2.2]paracyclophane-4-thiol via the stereospecific introduction of a chiral sulfoxide to the [2.2]paracyclophane skeleton. The first synthesis of an enantiomerically enriched planar chiral benzothiazole is also reported.

Introduction
[2.2]Paracyclophane (1; R = H) is a fascinating compound comprising of two eclipsing benzene rings that are held in place by two ethyl bridges at the para positions (Figure 1). The close proximity of the arene moieties results in strong electronic and structural interactions between the two rings and between substituents appended to each layer [1,2]. The resulting unique properties have led to derivatives of [2.2]paracyclophane being employed in a wide range of disciplines including polymer, material and electronic chemistry [3-9]. Whilst enantiomerically pure derivatives have been utilised in chiral catalysis [10, 11] and as probes for biological recognition processes [12-14], the full potential of these systems has not been realised due to the difficulties encountered when trying to access enantiomerically pure [2.2]paracyclophane derivatives [15].

Chiral sulfur [2.2]paracyclophane derivatives are beginning to attract attention due to the great potential such compounds exhibit [16-18]. Non-cyclophane-based thiophenol derivatives
have been employed in the nucleophilic addition of thioacetals to suitable electrophiles \[19,20\], sigmatropic rearrangements \[21\] and as either thyl radical precursors \[22\] or as a source of hydrogen in radical chemistry \[23\]. With the appropriate sulfur derivative, stereoselective variants of all these transformations can be envisaged.

Currently, there are few examples of sulfur containing \[2.2\]paracyclopahne compounds; ary1 sulfonylation and the related sulfonylation facilitates the synthesis of sulfonic acids, sulfonamides and protected thiols \[24-26\] whilst directed metallation has allowed the formation of various sulfides \[27-30\]. Very few methodologies allow the synthesis of simple chiral monosubstituted thiols such as \[2.2\]paracyclopahne-4-thiol \(2\) (Figure 1); the first reported preparations of racemic \(2\) were the conversion of 4-hydroxy[2.2]paracyclopahne to the desired compound via a Newman-Kwart reaction or the direct reaction of 4-lithio[2.2]paracyclopahne with sulfur \[17\]. Use of enantiomerically pure 4-hydroxy[2.2]paracyclopahne or application of our own sulfoxide-metal exchange protocol \[31\] would permit enantiospecific variants of either route, but neither has been reported. An elegant entry to a variety of racemic alkyl sulfides and sulfoxides by an \(S_{n}Ar\) reaction mediated by a sulfonium salt has recently been divulged \[16\]. The only reported synthesis of enantiomerically pure \[2.2\]paracyclopahne-4-thiol entails the palladium-mediated addition of triisopropylsilane-thiol to a triflate formed from previously resolved \(\left(\text{R}^\text{p}\right)-4\)-hydroxy[2.2]paracyclopahne \[18\]. We are developing a ‘toolbox’ for the synthesis of enantiomerically enriched [2.2]paracyclopahne-4-thiol and related compounds.

### Results and Discussion

The synthesis of \((\text{S}_\text{p})-2\) is depicted in Scheme 1. Key to the success of this strategy was the resolution of the planar chirality of \[2.2\]paracylonaphane by incorporation of the \(\text{tert-buty}l\)-sulfinyl moiety to give the diastereoisomers \((\text{S}_\text{p},\text{R}_\text{S})-5\) and \((\text{R}_\text{p},\text{R}_\text{S})-5\). Standard iron-catalysed bromination of \(1\) gave \((\pm)-4\)-bromo[2.2]paracyclopahne \(3\) in good yield \[35,36\]. Halogen-lithium exchange and addition to Ellman’s \((\text{R})-\text{tert-buty}l\) tert-butanethiosulfinate \[37\] furnished a 1 : 1.4 mixture of \((\text{S}_\text{p},\text{R}_\text{S})-5\) and \((\text{R}_\text{p},\text{R}_\text{S})-5\) in a combined 72% yield \[33\]. The two diastereoisomers are readily separable by standard column chromatography, with the diastereoisomer \((\text{S}_\text{p},\text{R}_\text{S})-5\) being eluted first. As \((\text{R})-4\) was prepared with an ee of 80%, as judged by optical rotation, we assume that each diastereoisomer displays an ee of 80%. As the sulfinylation reaction proceeds with inversion at

![Scheme 1](image-url)
sulfur, the two diastereoisomers only differ by the chirality of the [2.2]paracyclophane therefore allowing the facile resolution of the planar chirality. The assignment of configuration is based on a combination of X-ray studies [33,38], formation of all stereoisomers and analogy to our previous tolylsulfinyl chemistry [31,39].

Unlike the previously prepared 4-tolylsulfinyl[2.2]paracyclophane [31], direct sulfoxide-metal exchange was not possible with the tert-butyl derivative [38]; presumably, the tert-butyl group and the lower ring of the [2.2]paracyclophane moiety shield the sulfur from attack. As a result a stepwise procedure for the conversion of (S)<sub>p</sub><sub>R</sub><sub>S</sub>-5 to [2.2]paracyclophane-4-thiol (S)<sub>p</sub>-2 was investigated (Scheme 1). The first step, the reduction of (S)<sub>p</sub><sub>R</sub><sub>S</sub>-5 to sulfide (S)<sub>p</sub>-6, proved the most problematic; use of a large excess of trichlorosilane and triethylamine resulted in deoxygenation in moderate yield after recrystallisation [40]. By comparison, reduction of the less hindered aryl sulfoxide, (R)<sub>p</sub><sub>S</sub>-4-bromo-13-p-tolylsulfinyl[2.2]paracyclophane, occurs efficiently in 98% yield suggesting the tert-butyl group is the source of the problem [39]. Exchange of the tert-butyl group for an acetyl group was achieved by reaction of a mixture of (S)<sub>p</sub>-6 and acetyl chloride in toluene with boron tribromide [41]. The resulting thioacetic acid S-[2.2]paracyclophane ester (S)<sub>p</sub>-7 readily undergoes simple base-catalysed hydrolysis to give the desired (S)<sub>p</sub>-(+)-[2.2]paracyclophane-4-thiol (S)<sub>p</sub>-2.

There are two advantages to our methodology compared to the previously reported syntheses of [2.2]paracyclophane thioles; the first is that resolution of the planar chirality is complicit in the addition of the sulfur moiety and does not require resolution of any precursors. Secondly, the sulfinyl moiety permits further functionalisation of the [2.2]paracyclophane skeleton [33]. It is the latter reason that prompted the synthesis of the thiol via the tert-butyl derivative and not by direct sulfoxide-metal exchange; whilst this route would have delivered 2 more rapidly it would not have permitted elaboration of the [2.2]paracyclophane framework. The utility of the tert-butyl derivative is demonstrated in the synthesis of the planar chiral benzothiazazole (R)<sub>p</sub>-10 (Scheme 2).

Benzothiazoles are important heterocycles having found use as dyes, pharmaceuticals and ligands in catalysis [42]. Planar chiral heterocycles are still rare but show considerable potential as probes in stereocontrolled recognition processes in biological systems as highlighted by Gmeiner [12-14] and as ligands or catalysts [43-47]. We have previously prepared planar chiral benzimidazoles [32] and wanted to extend the range of heterocycles that could be accessed.

Diastereoisomer (R)<sub>p</sub><sub>R</sub><sub>S</sub>-5 was functionalised by sulfinyl-directed ortho lithiation with n-butyl lithium followed by reaction with tosyl azide. The resulting azo[2.2]paracyclophane was reduced in situ to give the amine (R)<sub>p</sub><sub>R</sub><sub>S</sub>-8 in good yield for the two steps (Scheme 2). Trichlorosilane-mediated deoxygenation proceeded uneventfully to furnished amino sulfide (R)<sub>p</sub>-9. Simultaneous sulfide deprotection and thiazole formation was achieved by treating (R)<sub>p</sub>-9 with concentrated hydrochloric acid, paraformaldehyde and pyridine [48]. Although the yield of (R)<sub>p</sub>-10 is not yet satisfactory, it shows the potential of our methodology for the formation of these valuable heterocycles.

In conclusion, we have developed a straightforward method for the synthesis of enantiomerically enriched [2.2]paracyclophane-4-thiol that does not rely on the resolution of precursors to the introduction of the sulfur moiety. Furthermore, we have shown that this methodology has the potential to produce a wide-range of thiol derivatives and this has permitted the first synthesis of a planar chiral benzothiazole, [2.2](4,7)benz[d]thiazoloparacyclophane. The use of these thiols in asymmetric synthesis is currently being investigated and will be reported in due course.

**Experimental**

NMR spectra were recorded on a Bruker 400 MHz, Bruker 300 MHz, Varian 500 MHz or Varian 400 MHz using residual isotopic solvent as internal reference. Infrared spectra were recorded on a Perkin-Elmer 1600 Fourier Transform spectrometer. Mass spectra and exact mass data were recorded by Dr. Ali Abdul-Sada at the University of Sussex or by the EPSRC national mass spectrometry service, Swansea. Melting points were recorded on a Gallenkamp melting point apparatus and are
uncorrected. Optical rotation was recorded on a Perkin Elmer
241 polarimeter using a sodium lamp emitting at 589 nm. All
samples were measured in chloroform (c = 1) in a 10 cm cell
and an average taken of 10 readings; average temperature was
27 °C. Glassware was oven dried and reactions were performed
under an inert atmosphere of nitrogen or argon where applicable.
Chromatography refers to flash column chromatography
on Merck Kieselgel 60 (230–400 mesh) or Fischer Daviso 60
silica gel unless otherwise stated. TLC refers to analytical thin-
layer chromatography performed using pre-coated glass-backed
plates (Merck Kieselgel 60 F254) and visualised with ultraviolet
light, iodine, acidic ammonium molybdate (IV), acidic ethan-
olic vanillin, aqueous potassium manganate(VII), ninhydrin or
acidic anisaldehyde as appropriate. Petrol refers to redistilled
petroleum ether (60–80 °C), and ether to diethyl ether. Ether
and THF were distilled from sodium-benzophenone ketyl,
toluene from 4Å molecular sieves or calcium chloride. Dioxane
was stored over sodium wire and DMF was stored over 4Å
molecular sieves.

(±)-4-Bromo[2.2]paracyclophane (3)
All stages of this reaction were performed in the dark by
covering the flasks with aluminium foil. Bromine (7.8 mL, 0.15
mol, 1.05 equiv) was dissolved in DCM (1.5 L). 10% of the
solution (150 mL) was transferred to a flask containing iron
filings (2.4 g, 0.04 mol, 0.3 equiv) and stirred at rt for 1.5 h. A
solution of [2.2]paracyclophane (30.0 g, 0.14 mol, 1.0 equiv) in
butylsulfinyl[2.2]paracyclophane ([R]-4-Bromo[2.2]paracyclophane ([Rp,Rs])

To a solution of (±)-4-Bromo[2.2]paracyclophane (5.50 g, 19.16
mmol, 1.0 equiv) in THF (180 mL) at ~78 °C was added n-BuLi (2.5 M in hexanes; 8.5 mL, 21.08 mmol, 1.1 equiv) dropwise over 15 min. After 45 min, (R)-tert-butyl tert-butane-
thiosulfinate (R)-4 (80% ee, 5.57 g, 28.74 mmol, 1.5 equiv) was
added as a solid and the reaction stirred at rt overnight. The
solvent was removed and the resulting residue purified by chro-
matography (Et2O/n-heptane gradient) to yield (Rp,Rs)-5 (1.79
g, 30%) and (S,Rs)-5 (2.51 g, 42%).

(Rp,Rs)-(±)-4-tert-Butylsulfinyl[2.2]paracyclophane
[(R,Rs)-5]
mp 124–126 °C; [α]D –39.6 (c 1, CHCl3) (assumed 80% ee see
text); v_max (film) 2962, 2926, 1585, 1456, 1473, 1500, 1170,
1054, 1024, 908 and 847 cm–1; δ_H (500 MHz, CDCl3) 7.02
(1H, s, H-5, 6.83 (1H, d, J = 7.5 Hz, H-13, 6.62 (1H, d, J = 7.5
Hz, H-7), 6.54 (1H, d, J = 8.0 Hz, H-12), 6.52 (2H, s, H-15,
H-16), 6.48 (1H, d, J = 8.0 Hz, H-8), 3.54 (1H, d, J = 13.5,
12.3, 2.5 Hz, H-2 endo), 3.27 (1H, d, J = 13.0, 9.1, 5.5 Hz,
H-1 endo), 3.16–3.06 (5H, m, H-1 endo, 2 × H-9 & 2 × H-10),
2.89 (1H, d, J = 10.0, 8.9, 5.5 Hz, H-2 exo), 1.05 (9H, s,
t-Bu); δ_C (125 MHz, CDCl3) 140.7 (C), 139.5 (C), 139.0 (C),
138.9 (C), 138.9 (C), 136.0 (CH), 134.6 (CH), 131.3 (CH),
132.7 (CH), 132.6 (CH), 132.3 (CH), 130.3 (CH), 56.6 (C),
35.2 (CH2), 35.1 (CH2), 34.7 (CH2), 33.6 (CH2), 22.7 (CH3);
m/z (EI+) 256 [M−Bu]+, 240, 152, 135, 123, 104, 91, 78
(Found: [M]+, 312.1539. C20H22OS requires [M]+, 312.1542).

(Sp,Rs)-(±)-4-tert-Butylsulfinyl[2.2]paracyclophane
[(Sp,Rs)-5]
mp 122–124 °C; [α]D +151.4 (c 1, CHCl3) (assumed 80% ee see
text); v_max (film) 2970, 2927, 2852, 1587, 1474, 1459,
1432, 1410, 1175, 1039, 847 and 805 cm–1; δ_H (500 MHz,
CDCl3) 6.93 (1H, d, J = 10.0 Hz, H-13, 6.58 (1H, d, J = 10.0
Hz, H-12), 6.54–6.47 (5H, m, H-5, H-7, H-8, H-15, H-16), 4.35
(1H, t, J = 14.5 Hz, H-2 endo), 3.37 (1H, d, J = 12.5, 13.0,
7.0 Hz, H-1 endo), 3.22–2.98 (5H, m, H-1 exo, 2 × H-9 and 2 ×
H-10), 2.82–2.77 (1H, m, H-2 exo), 1.05 (9H, s, t-Bu); δ_C (125
MHz, CDCl3) 142.2 (C), 140.7 (C), 139.3 (C), 139.0 (C), 137.7
(CH3), 135.7 (CH), 134.2 (CH), 133.3 (CH), 133.0 (CH), 132.7
(CH), 132.6 (CH), 132.5 (CH), 56.6 (C), 36.1 (CH2), 35.2
(CH2), 35.0 (CH2), 34.2 (CH2), 23.1 (CH3); m/z (EI+) 256 [M−t-Bu]+,
240, 152, 135, 123, 104, 91, 78 (Found: [M]+, 312.1545. C20H22OS requires [M]+, 312.1542).

(Sp,Sp)-(±)-4-tert-Butylsulfinyl[2.2]paracyclophane
[(Sp,Sp)-6]
Triethylamine (11.92 mL, 85.58 mmol, 10 equiv) was added to a
solution of trichlorosilane (17.9 mL, 128.36 mmol, 15 equiv)
and (Sp,Rs)-(±)-4-tert-butylsulfinyl[2.2]paracyclophane (2.67 g,
8.56 mmol, 1.0 equiv) in toluene (41 mL). The reaction was
heated to reflux for 18 hours. After cooling to 0 °C a solution of
aqueous NaOH (3.0 M; 200 mL) was added carefully. The

aqueous phase was extracted with Et₂O (3 × 100 mL) and the combined organic phases dried (MgSO₄). After removal of the solvent, the residue was purified by chromatography (5% Et₂O/hexane) followed by trituration of the yellow semi-solid with petrol gave (S₉)-6 as a white solid (1.0 g, 41.0%); mp = 53 °C; [α]D = +89.5 (c 1, CHCl₃) as a white solid (0.51 g, 1.80 mmol, 1.0 equiv); mp = 144−146 °C; [α]D = +164.0 (c 1, CHCl₃) (assumed 80% ee see text); νmax(film) 3011, 2929, 2848, 2558, 1587, 1548, 1499, 1480, 1449, 1432, 1411, 1060, 938, 897, 849, 804 and 791 cm⁻¹; δH (500 MHz, CDCl₃) 7.21 (1H, d, J = 7.5 Hz, H-13), 6.57 (1H, d, J = 7.5 Hz, H-8), 6.47 (1H, d, J = 7.5 Hz, H-7), 6.43 (1H, d, J = 7.5 Hz, H-12), 6.40 (2H, t, J = 7.5 Hz, H-15, H-16), 6.22 (1H, s, H-5), 3.41 (1H, t, J = 12.0 Hz, H-2 endo), 3.26 (1H, ddd, J = 13.0, 6.0, 3.9 Hz, H-1 endo), 3.13 (1H, s, S-H), 3.11–3.01 (4H, m, 2 × H-9, 2 × H-10), 2.83 (1H, ddd, J = 12.0, 5.5, 3.7 Hz, H-1 exo), 1.17 (9H, s, -t-Bu); δC (125 MHz, CDCl₃) 145.7 (C), 144.4 (C), 139.9 (C), 139.4 (C), 139.1 (C), 134.2 (CH), 133.5 (CH), 133.0 (CH), 132.9 (CH), 132.8 (CH), 132.5 (CH), 131.0 (CH), 46.3 (C), 35.4 (CH₂), 34.8 (CH₂), 34.7 (CH₂), 30.9 (CH₃); m/z (El+) 296 [M⁺], 240 [M − t-Bu]⁺, 207 [M − S-Bu]⁺, 136, 104, 91, 78 (Found: [M⁺], 296.1591. C₁₂H₂₂S₄O requires [M⁺], 296.1593).

(Sp)-(+)-Thioacetic acid S-[2.2]paracyclophan-4-yl ester ([S₉]-7)

Boron tribromide (0.36 mL, 3.77 mmol, 1.1 equiv) was added to a solution of (Sp)-(+)-2-butylsulfinyl[2.2]paracyclophane (Sp)-6 (1.0 g, 3.43 mmol, 1.0 equiv) and acetyl chloride (1.7 mL, 24.01 mmol, 7.0 equiv) in toluene (34.3 mL) at rt. The reaction was stirred for 1 hour then poured into a solution of ice cold saturated aqueous Na₂CO₃ (200 mL). Aqueous phase was extracted with Et₂O (3 × 50 mL). The combined organic phase was washed with aqueous Na₂S₂O₃ (10% w/v) (3 × 50 mL), dried (MgSO₄) and concentrated. Purification by chromatography (10% Et₂O/hexane) afforded (Sp)-7 as a white solid (0.53 g, 55%); mp = 134−136 °C; [α]D = +84.3 (c 1, CHCl₃) (assumed 80% ee see text); νmax(film) 2920, 2850, 1649, 1498, 1476, 1447, 1432, 1408, 1113, 954, 906, 850 and 792 cm⁻¹; δH (500 MHz, CDCl₃) 6.68 (1H, s, H-5, H-13), 6.64 (1H, d, J = 10.0 Hz, H-12), 6.54 (2H, dd, J = 8.0, 3.5 Hz, H-7, H-8), 6.50 (2H, s, H-15, H-16), 6.45 (1H, d, J = 8.0 Hz, 12-H), 3.84 (1H, t, J = 11.0 Hz, H-2 endo), 3.20−3.14 (1H, m, H-1 endo), 3.12–2.97 (5H, m, H-1 exo, 2 × H-9, 2 × H-10), 2.83 (1H, ddd, J = 12.0, 5.5, 3.7 Hz, H-1 exo), 1.17 (9H, s, t-Bu); δC (125 MHz, CDCl₃) 145.7 (C), 144.4 (C), 139.9 (C), 139.4 (C), 139.1 (C), 134.2 (CH), 133.5 (CH), 133.0 (CH), 132.9 (CH), 132.8 (CH), 132.5 (CH), 131.0 (CH), 46.3 (C), 35.4 (CH₂), 34.8 (CH₂), 34.7 (CH₂), 30.9 (CH₃); m/z (El+) 240 [M⁺], 240 [M − t-Bu]⁺, 207 [M − S-Bu]⁺, 136, 104, 91, 78 (Found: [M⁺], 240.0696. C₁₂H₁₈O₅S requires [M⁺], 240.0697).

(Rp,R₉)-(−)-4-tert-Butylsulfinyl-5-amino[2.2]-paracyclophane ([Rp,R₉]-8)

To a solution of (Rp,R₉)-(−)-4-tert-butylsulfinyl[2.2]paracyclophane ([Rp,R₉]-S) (5.8 g, 18.6 mmol, 1.0 equiv) in THF (350 mL) at 0 °C was added n-BuLi (2.5 M in hexanes; 16.5 mL, 41.25 mmol, 2.2 equiv) dropwise over 30 min to give an orange solution. After 1 h atosyl azide (9.20 g, 46.70 mmol, 2.5 equiv) was added and the reaction warmed to rt over 18 h. NaBH₄ (6.45 g, 171 mmol, 9 equiv) and tetra-n-butyl ammonium iodide (6.31 g, 17.1 mmol, 0.9 equiv) were added and the reaction stirred for a further 24 h at rt whereupon a further portion of NaBH₄ (2.80 g, 74.0 mmol, 4.0 equiv) was added. After further stirring at rt for 5 days the reaction was poured into saturated aqueous Na₂CO₃ (250 mL) causing effervescence. The aqueous phase was extracted with Et₂O (500 mL + 200 mL) and the combined organic extracts dried (MgSO₄) and the solvent removed. The residue was purified by chromatography (neutralized silica gel 40% Et₂O/n-heptane) to yield 8 as a pale yellow solid powder, which was recrystallised from CHCl₃/heptane (4.00 g, 66%); mp = 130−132 °C; [α]D = −118.0 (c 1, CHCl₃) (assumed 80% ee see text); νmax(film) 3430, 3055, 2987, 1637, 1421, 1265, 896, 739 and 705 cm⁻¹; δH (500 MHz, CDCl₃) 7.15 (1H, d, J = 8.0 Hz, H-13), 6.89 (1H, d, J = 7.5 Hz, H-16), 6.63 (1H, d, J = 8.0 Hz, H-15), 6.42 (1H, d, J = 8.0 Hz, H-7), 6.35 (1H, d, J = 7.5 Hz, H-12), 6.01 (1H, d, J = 7.5 Hz, H-8), 5.62 (2H, s, broad, NH₂), 3.46 (1H, t, J = 12.0 Hz, H-2 endo), 3.23–3.18 (1H, m, H-1 endo), 3.12–3.01 (4H, m, H-1 exo, H-9 endo, 2 × H-10), 2.71–2.62 (2H, m, H-2 exo, H-9 exo), 1.19 (9H, s, t-Bu); δC (125 MHz, CDCl₃) 150.6 (C), 141.6 (C), 138.5
(C), 138.1 (C), 133.1 (C), 132.1 (C), 131.9 (CH), 129.7 (CH), 127.1 (CH), 126.5 (CH), 123.0 (CH), 114.7 (CH), 60.19 (C), 34.1 (CH$_2$), 33.9 (CH$_3$), 32.8 (CH$_2$), 30.8 (CH$_2$), 23.6 (CH$_3$); m/z (ESI$^+$) 350.1547 [M+Na]$^+$ (Found: [M+Na]$^+$, 350.1549. C$_{29}$H$_{52}$OSNa requires [M+Na]$^+$, 350.1546).

(R$_p$)-(-)-4-tert-Butylsulfanyl-5-amino[2.2]paracyclophane [(R$_p$)-9]

Triethylamine (1.47 mL, 10.53 mmol, 10 equiv) followed by trichlorosilane (2.60 mL, 25.76 mmol, 150 equiv) were added carefully to a solution of (R$_p$)-4-(-)-t-tert-butylsulfanyl-5-amino[2.2]paracyclophane [(R$_p$)-8] (0.50 g, 1.61 mmol, 1.0 equiv) in toluene (8 mL) at 0 °C and the reaction heated to reflux for 16 h. The reaction was cooled to 0 °C and aqueous NaOH (3H, 100 mL) was added. The aqueous phase was extracted with Et$_2$O (3 × 50 mL), dried (MgSO$_4$) and concentrated to give a pale yellow solid. Purification by chromatography (neutralized silica, 20% Et$_2$O/hexane) gave (R$_p$)-9 as a pale yellow solid (0.19 g, 40%); mp = 72–74 °C; [α]$^p$ = −192.3 (c 0.5, CH$_2$Cl$_2$) (Found: [M]+, 255 [M+H]$^+$, 311 [M]$^-$Bu); δ$_C$ (125 MHz, CDCl$_3$), 1.21 (9H, s, tertButyl); δ$_H$, 3.06–2.99 (5H, m, H-1, H-9, 2 × H-10); δ$_H$, 3.27–3.21 (1H, m, H-1 endo), 3.17–3.11 (1H, m, H-9 endo), 3.06–2.99 (5H, m, H-1 exo, H-2 exo, H-9 exo, 2 × H-10); δ$_C$ (125 MHz, CDCl$_3$), 154.4 (CH), 151.8 (C), 139.2 (C), 137.2 (C), 134.8 (C), 134.4 (C), 128.2 (C), 132.3 (CH), 131.7 (CH), 130.5 (CH), 126.2 (CH), 124.9 (CH), 35.0 (CH$_2$), 34.5 (CH$_2$), 33.5 (CH$_2$), 32.4 (CH$_2$); m/z (EI$^+$) 265 [M]$^+$, 161, 104, 78 (Found: [M]$^+$, 265.0921. C$_{17}$H$_{13}$NS requires [M]$^+$, 265.0920).

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