Neighboring effect of pyrazole rings: regio- and stereoselective Wagner–Meerwein rearrangement in electrophilic addition reactions of norbornadiene-fused pyrazoles

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The electrophilic addition reactions of norbornadiene-fused pyrazoles with bromine or *p*-nitrobenzenesulfenyl chloride provided the skeletally rearranged adducts regio- and stereoselectively probably *via* the neighboring group participation of a pyrazole ring accompanied by the formation of a bridged pyrazolium ion.

Introduction

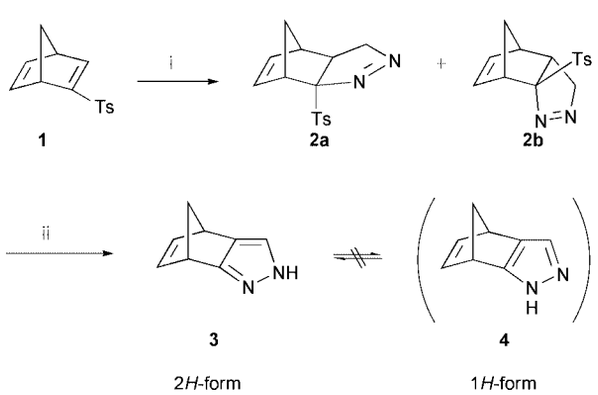
Neighboring group participation has been well recognized to control the rate and the stereoselectivity of organic reactions.[1,2] Recently, we found that the electrophilic addition reactions of norbornadiene-fused five-membered heteroaromatics such as furan, pyrrole, and thiophene underwent the stereoselective Wagner–Meerwein rearrangement, and the neighboring group participation of these rings was found to be more effective than that of a benzene ring.[3,4] We also reported that even electron-deficient six-membered heteroaromatics such as pyridazine and pyrazine have the ability to stabilize a remote cationic center to some extent.[5–7]

In this paper, we describe the synthesis of novel norbornadiene-fused pyrazoles and their electrophilic addition reactions with bromine and an arenesulfenyl chloride, where the neighboring pyrazole ring was demonstrated to influence not only the stereoselectivity but also the regioselectivity of the reaction.

Results and discussion

Syntheses of norbornadiene-fused pyrazoles

Synthesis of the norbornadiene-fused pyrazole **3** is illustrated in Scheme 1. The 1,3-dipolar cycloaddition reaction of 2-tosyl-



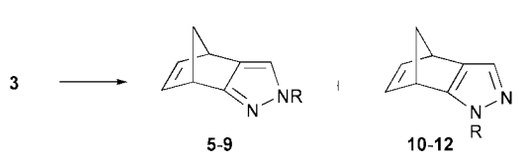
Scheme 1 *Reagents and conditions*: i, CH_2N_2, CH_2Cl_2, rt, 4 h, 97% (**2a** : **2b** = 5 : 1); ii, NaH, THF, rt, 24 h, 85%.

norbornadiene[8,9] **1** and diazomethane took place at the double bond which is electronically activated by the tosyl substituent to give a 5 : 1 mixture of *exo* and *endo* adducts **2a** and **2b**. The stereoselectivity is in contrast to that of the reaction of **1** with 2-diazopropane, which has been reported to give exclusively the corresponding *exo* adduct.[9]

The dehydrosulfonylation of the *exo* and *endo* mixture **2** with sodium hydride provided 4,7-dihydro-4,7-methano-2*H*-indazole (**3**) in good yield. The yield of the pyrazole **3** was unsatisfactory when BuLi (30%) or KOBu^t (6%) was used as a base.[10]

Tautomerism of pyrazoles has received much attention,[11,12] and tautomerism between the 2*H*-form **3** and the 1*H*-form **4** is possible for the norbornadiene-fused pyrazole. However, we could clearly determine the structure of **3** to be the 2*H*-tautomer by comparison of the ^{13}C chemical shift at the C-3 position with those of camphor-fused pyrazoles (*vide infra*).[13–16] The ^1H and ^{13}C NMR spectra of **3** at various temperatures from −100 °C to +150 °C exhibited no significant change in the spectrum such as broadening of peaks or change of chemical shifts. This indicates that no tautomerism is observed between **3** and **4** because the 2*H*-form is thermodynamically more stable than the 1*H*-form. The relative stability between the 2*H*-isomer **3** and the 1*H*-isomer **4** is in agreement with that of camphor-fused pyrazoles[13,14] and the carbocyclic congener, isodicyclopentadiene.[17]

The *N*-alkylation reaction of **3** with sodium hydride and methyl iodide gave the 2-methyl derivative **5** as the major product along with the 1-methyl derivative **10** (Scheme 2). In



Scheme 2

contrast, treatment of **3** with the Meerwein reagent provided the 1-ethyl derivative **11** predominantly, and a trace amount of the 2-ethyl isomer **6**. Phenyl isocyanate reacted with **3** to afford exclusively the 2-phenylcarbamoyl derivative **7**. Acylation reactions of **3** with sodium hydride and benzoyl chloride or *p*-nitrobenzoyl chloride gave 2-aroyl derivatives **8** and **9**, respectively. To our surprise, the *p*-nitrobenzoylation in the presence of triethylamine resulted in the formation of 1-*p*-nitrobenzoyl isomer **12** as a major product. The yields of the products as well as the ^{13}C NMR chemical shifts at the 3-position (δ_{C3}) of the fused pyrazoles and of **3** are listed in Table 1. The values of δ_{C3} clearly distinguish the 2*H*-isomer

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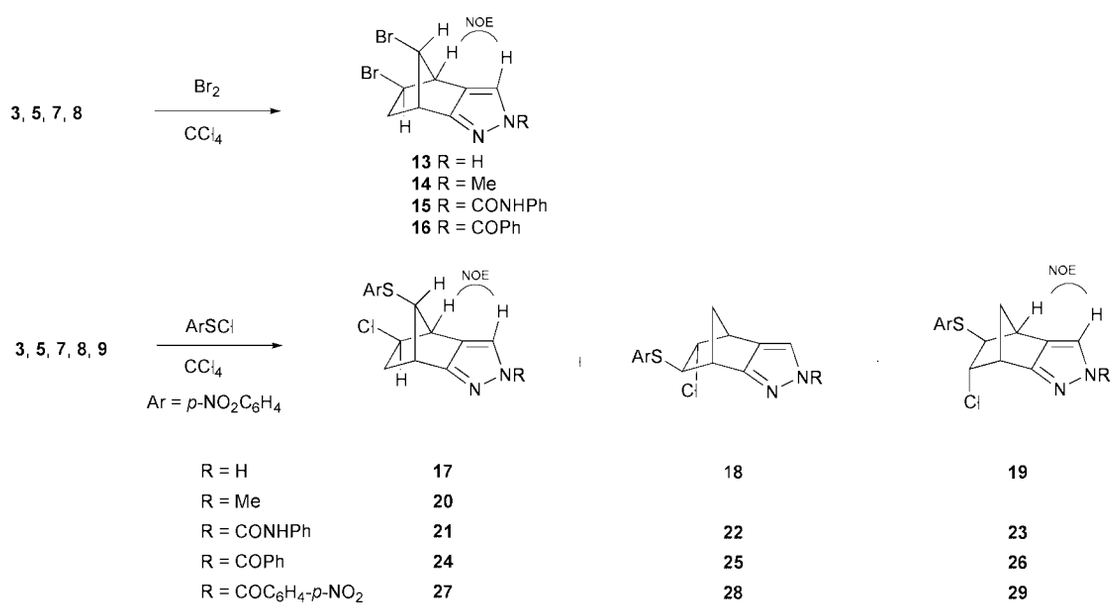
Table 1 Reagents, reaction conditions, and products of alkylation and acylation reactions of the norbornadiene-fused pyrazole **3**, and δ_{C3} values of fused pyrazoles

R	Reagents and conditions	Products (yield (%) and δ_{C3})
Me	MeI, NaH, THF, rt, 2 h	**5** (62, δ_{C3} 121.7) + **10** (34, δ_{C3} 130.7)
Et	Et_3OBF_4, CH_2Cl_2, rt, 12 h	**6** (1) + **11** (66, δ_{C3} 130.6)
PhNHCO	PhNCO, PhH, rt, 18 h	**7** (90, δ_{C3} 118.7)
PhCO	PhCOCl, NaH, THF, rt, 1 h	**8** (68, δ_{C3} 119.6)
p-$NO_2C_6H_4CO$	*p*-$NO_2C_6H_4COCl$, NaH, THF, rt, 1 h	**9** (60, δ_{C3} 119.2)
p-$NO_2C_6H_4CO$	*p*-$NO_2C_6H_4COCl$, Et_3N, CH_2Cl_2, rt, 1 h	**12** (41, δ_{C3} 137.6)
H		**3** (δ_{C3} 119.3)

Table 2 Electrophilic reactions of norbornadiene-fused pyrazoles

Pyrazole	R	Electrophile	Products (yield (%))
3	H	Br_2	**13** (32)
5	Me	Br_2	**14** (64)
7	CONHPh	Br_2	**15** (92)
8	COPh	Br_2	**16** (88)
3	H	ArSCl[a]	**17** (53) + **18** or **19** (5)
5	Me	ArSCl[a]	**20** (66)
7	CONHPh	ArSCl[a]	**21** (45) + **22**:**23** (1:1, 30)
8	COPh	ArSCl[a]	**24** (31) + **25** (15) + **26** (32)
9	COC_6H_4-*p*-NO_2	ArSCl[a]	**27** (3) + **28** (3) + **29** (57)
11	Et	Br_2	**30** (37)
12	COC_6H_4-*p*-NO_2	Br_2	**31** (81)
11	Et	ArSCl[a]	**32** (72)

[a] Ar = *p*-$NO_2C_6H_4$.



Scheme 3

from the 1*H*-isomer: the chemical shifts (δ_{C3}) at the 3-position of 2*H*-isomers are shifted upfield compared with those of 1*H*-isomers.

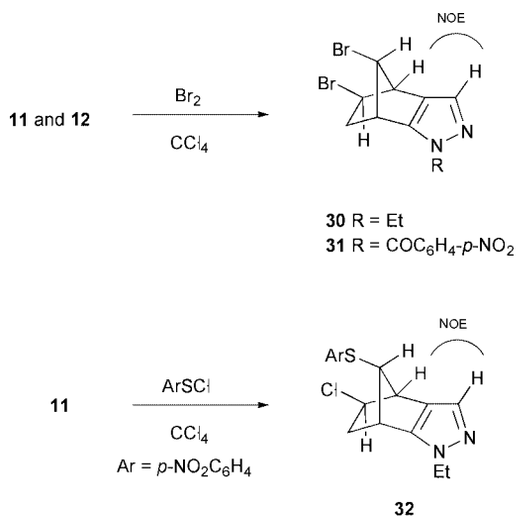
Electrophilic addition reactions of norbornadiene-fused pyrazoles

Treatment of the 2*H*-indazoles **3**, **5**, **7**, and **8** with bromine provided the skeletally rearranged adducts **13**, **14**, **15**, and **16**, respectively, in a regio- and stereoselective manner (Scheme 3, Table 2). Bromination of **9** seemed to give a similar rearranged adduct, but we could not purify the product due to contamination by some unknown products. The yields of **13** and **14** are moderate, but these are the only products we could isolate, and we could find no evidence for the formation of any other bromine adducts in spite of an extensive search. The stereochemistry of the two bromine atoms was deduced by the presence of a long-range spin coupling between 5- and 8-H due to the W-arrangement in the ^{1}H NMR spectra. The assignments of the spin coupling were confirmed by the homo decoupling experiments as well as by the H–H COSY spectra. The regiochemistry of the adducts was determined on the basis of the observation of the NOE between the protons at the 3- and 4-positions by NOE difference spectroscopy.

Treatment of the pyrazole **3** with *p*-nitrobenzenesulfenyl chloride resulted in the regio- and stereoselective formation of the rearranged adduct **17** along with the formation of a *trans* adduct, either **18** or **19**. Unfortunately the regiochemistry of the *trans* adduct is ambiguous. The reaction of the 2-methyl derivative **5** with the sulfenyl chloride gave only the rearranged adduct **20** in 66% yield. The reaction of the carbamoyl derivative **7** gave the rearranged adduct **21** along with the *trans* adducts **22** and **23**. Substitution of the benzoyl group was found

to decrease the yield of the rearranged adduct **24**, and the *trans* adducts **25** and **26** were formed in 15 and 32% yields, respectively. Furthermore, the *p*-nitrobenzoyl derivative **9** provided only a 3% yield of the rearranged adduct **27**, and the *trans* adduct **29** was produced as a major product whereas the yield of *trans* adduct **28** did not increase. The regiochemistry of the *trans* adducts **23**, **26**, and **29** as well as that of the rearranged adducts **17**, **20**, **21**, **24**, and **27** was determined on the basis of the observation of NOE between 3- and 4-H. The results of the chlorosulfenylation reactions indicated that the substitution of more electron-withdrawing groups on the nitrogen atom of the pyrazole ring would suppress the formation of skeletally rearranged adducts, in accordance with the increase in the yields of the *trans* adducts.

Similar to the reactions of 2*H*-indazoles, 1-ethyl- and 1-*p*-nitrobenzoyl derivatives **11** and **12** reacted with bromine to give only the rearranged adducts **30** and **31**, respectively (Scheme 4, Table 2). On treatment with *p*-nitrobenzenesulfenyl chloride, the 1-ethyl derivative **11** gave only the rearranged adduct **32**.



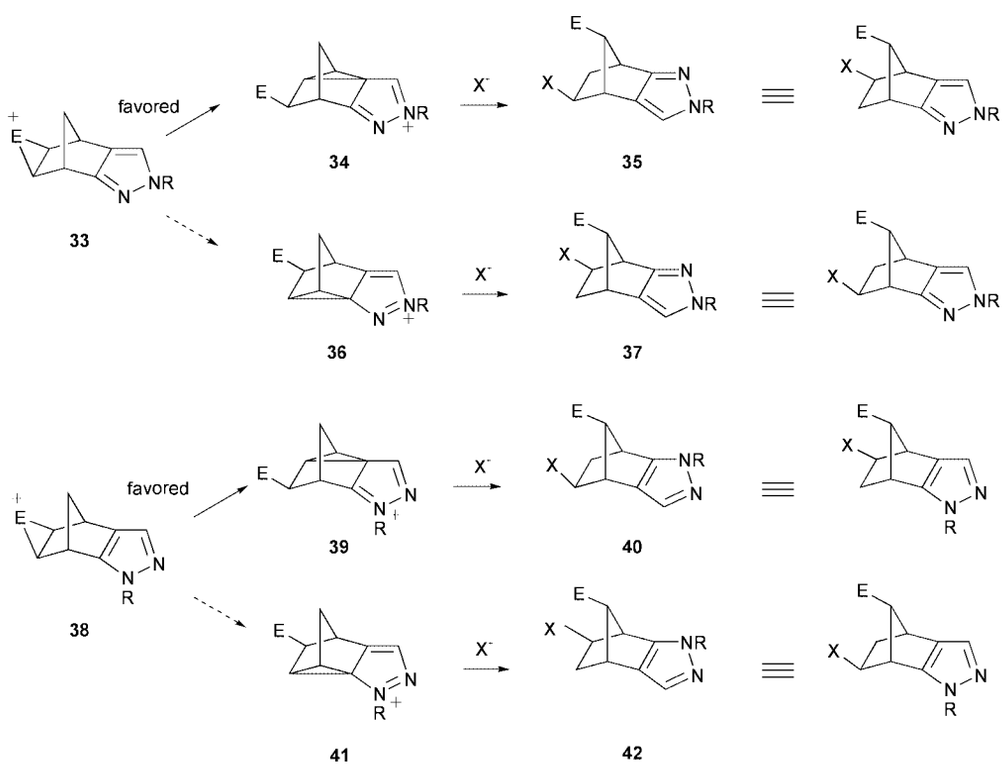
Scheme 4

Analysis of the mass spectrum suggested that a similar reaction with **12** also gave an adduct, but we could not determine the structure due to insolubility of the product in organic solvents.

A plausible mechanism for these reactions is shown in Scheme 5. The initially formed onium ion **33** (E = Br or SAr) undergoes regioselective cleavage of the C-5–E bond by the neighboring group participation of the pyrazole ring to afford the bridged 4*H*-pyrazolium ion **34**, which should lead to the rearranged product **35**. We did not observe the formation of the regioisomer **37** which is possibly formed *via* the bridged 3*H*-pyrazolium intermediate **36**. Similarly, the regioselective formation of **40** in the reactions of the 1*H*-pyrazoles is explained by the intermediacy of the bridged 4*H*-pyrazolium ion **39**. Both reactions with 2*H*- and 1*H*-pyrazoles were suggested to proceed by the intervention of bridged 4*H*-pyrazolium ions but not bridged 3*H*-pyrazolium ions.

Isolation of *trans* adducts in the reactions of 2*H*-pyrazoles with the sulfenyl chloride is probably due to the formation of a tight ion pair with a chloride ion for the episulfonium ion **33** (E = SAr).[18–23] The formation of the tight ion pair as well as the substitution of electron-withdrawing groups would retard the participation of the neighboring pyrazole ring, and the production of *trans* adducts would be allowed. However, we could not figure out the reason why one of two *trans* adducts was preferentially formed in the chlorosulfenylation reactions.

In order to obtain knowledge of bridged pyrazolium ions, we performed *ab initio* (6-31G*) calculations on the norbornenyl cations **43** and **44** (Fig. 1).[24] Calculations on both cations provided the optimized bridged structures **45** and **46**, respectively. No energy minimum was observed for the corresponding non-bridged structures **43** and **44**. The atomic distances between C-3a and C-4 of **45** (1.57 Å) and between C-6 and C-7a of **46** (1.59 Å) clearly indicate the presence of bonding interactions between these atoms when compared with those of **3**. The comparison of the total energies revealed that **45** is about 13 kcal mol^{-1} more stable than **46**. Similar results are obtained for the calculations on the 1*H*-pyrazole derivatives. Structure optimization of **47** and **48** provided the bridged structures **49** and **50**, respectively. The bridged 4*H*-pyrazolium ion **49** was found to be more stable than **50** by 16 kcal mol^{-1}. The relative



Scheme 5

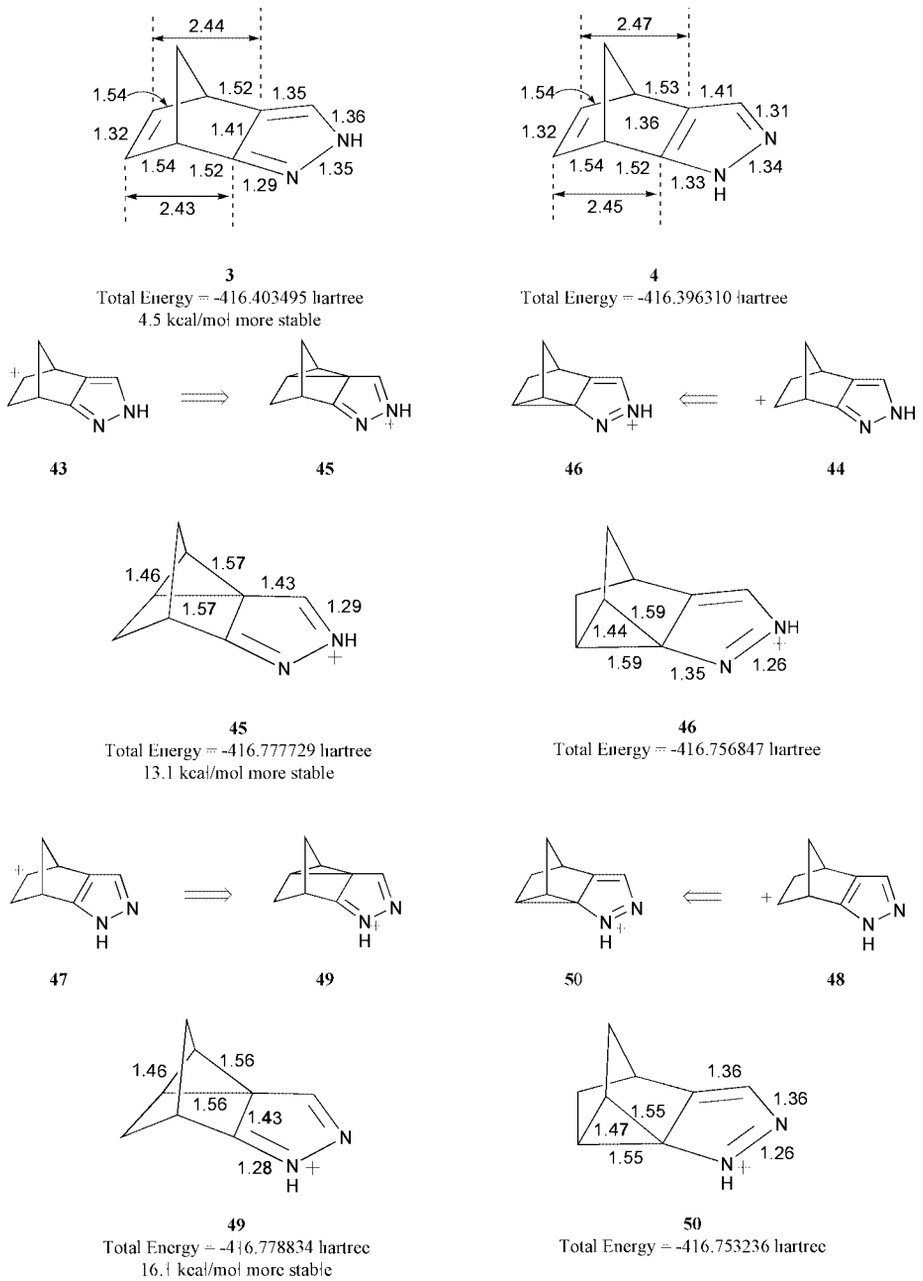


Fig. 1 Total energies and selected atomic distances (Å) of norbornadiene-fused pyrazoles and norbornenyl cations obtained by *ab initio* (6-31G*) calculations.

stabilities of bridged intermediates obtained by these calculations are in good agreement with the observed regioselectivity for the formation of rearranged adducts.

In conclusion, we have demonstrated that the electrophilic addition reactions of norbornadiene-fused pyrazoles undergo regio- and stereoselective Wagner–Meerwein rearrangement, which is attributable to the neighboring group participation of the pyrazole ring accompanied by the regioselective formation of the bridged 4*H*-pyrazolium ion intermediate.

Experimental

General

All the melting points were determined with a Yanagimoto hot-stage apparatus. IR spectra were obtained with a JEOL Diamond-20 spectrometer. NMR spectra were recorded with either a JEOL JNM-LA300 (^{1}H: 300 MHz; ^{13}C: 75 MHz) or JEOL JNM-LA400 (^{1}H: 400 MHz; ^{13}C: 100 MHz) spectrometer using TMS as internal standard. *J*-Values are given in Hz. Assignments of the ^{1}H and ^{13}C signals are based on DEPT, H–H COSY, and C–H COSY measurements. Mass spectra were measured with a Shimadzu GCMS-QP1000EX spectrometer operating in the electron impact mode (70 eV). High resolution mass spectra (HR-MS) were taken with a JEOL DX-300 spectrometer. Elemental analyses were performed with a Perkin-Elmer Model 240 apparatus. MPLC separations were carried out by a YAMAZEN YFLC-600-10V system with a YAMAZEN Ultra Pack™ Column (Si-40B, silica gel). Solvents were dried and purified by standard methods. Yields are based on isolated products with sufficient purity.

2-(*p*-Tolylsulfonyl)bicyclo[2.2.1]hepta-2,5-diene (1)

A solution of cyclopenta-1,3-diene (3.77 g, 57 mmol) and *p*-tolylsulfonylethyne (3.80 g, 21 mmol) in benzene (20 ml) was stirred at room temperature for 24 h under a nitrogen atmosphere. Solvent was removed and hexane was added to the residue. The resulting solid was collected by suction to give 2-tosylnorbornadiene[8,9] **1** (5.07 g, 98%) as a white solid (from hexane–ethyl acetate 2 : 1), mp 48–49 °C; ν_{max}(KBr)/cm^{-1} 3074, 3003, 2952, 1597, 1549, 1306, 1162, 1142; δ_H(400 MHz, $CDCl_3$)

2.08 (1H, d, *J* 6, 7-H_{syn}), 2.19 (1H, d, *J* 6, 7-H_{anti}), 2.43 (3H, s, Me), 3.69 (1H, br s, 1-H), 3.80 (1H, m, 4-H), 6.62 (2H, m, 5- and 6-H), 7.31 (2H, d, *J* 8), 7.47 (1H, d, *J* 4, 3-H), 7.70 (2H, d, *J* 8); δ_C(100 MHz, $CDCl_3$) 21.6 (Me), 50.8 (C-1), 51.5 (C-4), 74.0 (C-7), 127.9, 129.8, 136.1, 141.0 (C-5 or C-6), 142.5 (C-6 or C-5), 144.2, 152.9 (C-3), 157.7 (C-2); *m*/*z* 246 (M^+, 10%), 139 (C_7H_7SO, 20), 91 (tolyl, 100).

Cycloaddition reaction of the tosylnorbornadiene 1 with diazomethane

A solution of diazomethane prepared from *N*-nitroso-*N*-methylurea (1.03 g, 10 mmol) in diethyl ether (20 ml) was added at 0 °C to a solution of 2-tosylnorbornadiene **1** (492 mg, 2 mmol) in CH_2Cl_2 (25 ml). The mixture was stirred at room temperature for 1 h and a small amount of acetic acid was added to destroy the excess diazomethane. The mixture was concentrated under vacuum and hexane was added to the residue. The resulting solid was collected by suction to give a mixture of *exo* and *endo* adducts **2a** and **2b** (5:1) (558 mg, 97%) as a white powder (from cyclohexane), decomp. *ca.* 115 °C (Found: C, 62.2; H, 5.6; N, 9.9. $C_{15}H_{16}N_2O_2S$ requires C, 62.5; H, 5.6; N, 9.7%); ν_{max}(KBr)/cm^{-1} 2987, 1594, 1543, 1493, 1460, 1427, 1311, 1298, 1290, 1147; δ_H(400 MHz, $CDCl_3$) 0.74 (0.83H, d, *J* 10, **2a** 8-H_{syn}), 1.45 (0.83H, d, *J* 10, **2a** 8-H_{anti}), 1.65 (0.17H, d, *J* 9, **2b** 8-H_{syn}), 2.39 (0.17H, d, *J* 9, **2b** 8-H_{anti}), 2.48 (3H, s, Me), 2.64 (0.83H, dt, *J* 9 and 2, **2a** 3a-H), 2.78 (0.83H, br s, **2a** 4-H), 2.99 (0.17H, br s, **2b** 4-H), 3.13 (0.17H, dt, *J* 9 and 3, **2b** 3a-H), 3.23 (0.83H, br s, **2a** 7-H), 3.63 (0.17H, br s, **2b** 7-H), 3.99 (0.17H, dd, *J* 19 and 3, **2b** 3-H_{endo}), 4.15 (0.17H, dd, *J* 19 and 9, **2b** 3-H_{exo}), 4.36 (0.83H, dd, *J* 19 and 2, **2a** 3-H_{exo}), 4.49 (0.83H, dd, *J* 19 and 9, **2a** 3-H_{endo}), 5.83 (0.17H, m, **2b** 6-H), 6.08 (0.17H, m, **2b** 5-H), 6.35 (1.7H, m, **2a** 5- and 6-H), 7.39 (2H, d, *J* 8, tolyl), 7.84 (2H, d, *J* 8, tolyl); δ_C(100 MHz, $CDCl_3$) 21.5, 40.8, 41.3, 44.8, 45.0, 47.3, 48.4, 48.5, 48.9, 79.7, 80.7, 124.0, 124.9, 129.3, 129.5, 129.7, 133.1, 133.7, 134.3, 136.0, 136.4, 138.4, 145.0; *m*/*z* 260 ($M - N_2$, 1%), 195 ($M - N_2 - C_6H_5$, 9), 139 (Ts, 9), 105 ($M - N_2$ − Ts, 100).

4,7-Dihydro-4,7-methano-2*H*-indazole (3)

A mixture of the adducts **2a** and **2b** (864 mg, 3 mmol) and sodium hydride (60%, 264 mg, 6.6 mmol) in THF (14 ml) was stirred at room temperature for 24 h. Aqueous NH_4Cl (10 ml) was added and the product was extracted with CH_2Cl_2. The organic phase was dried over Na_2SO_4 and concentrated. Pentane was added to the residue and the resulting solid was recrystallized from hexane to give the pyrazole **3** (337 mg, 85%) as colorless needles, mp 101–102 °C (Found: C, 72.9; H, 6.2; N, 21.1. $C_8H_8N_2$ requires C, 72.7; H, 6.1; N, 21.2%); ν_{max}(KBr)/cm^{-1} 3172, 3116, 3056, 3039, 2977, 2940, 2892, 1583, 1440, 1400; δ_H(400 MHz, $CDCl_3$) 2.43 (1H, d, *J* 7, 8-H_{syn}), 2.56 (1H, d, *J* 7, 8-H_{anti}), 3.83 (1H, br s, 4-H or 7-H), 3.84 (1H, br s, 7-H or 4-H), 6.75 (1H, dd, *J* 5 and 3, 5-H or 6-H), 6.79 (1H, dd, *J* 5 and 3, 6-H or 5-H), 7.03 (1H, s, 3-H), 9.24 (1H, br, NH); δ_C(100 MHz, $CDCl_3$) 43.2 (C-4 or C-7), 44.5 (C-7 or C-4), 70.4 (C-8), 119.3 (C-3), 131.0 (C-3a), 142.0 (C-5 or C-6), 144.4 (C-6 or C-5), 171.3 (C-7a); *m*/*z* 132 (M^+, 59%), 131 (M − H, 100), 105 ($M - C_2H_3$, 37).

Reaction of the pyrazole 3 with methyl iodide

A solution of the pyrazole **3** (132 mg, 1 mmol) in THF (5 ml) was added to a suspension of NaH (60%, 38 mg, 1.6 mmol) in THF (5 ml) at room temperature, and the mixture was stirred at room temperature for 20 min. Methyl iodide (257 mg, 1.8 mmol) was added to the mixture. The reaction mixture was then quenched with water and extracted with CH_2Cl_2 (3 × 10 ml). The combined organic phase was washed with water (10 ml) and dried over Na_2SO_4. After removal of the solvent, the residue was separated by MPLC (ethyl acetate) to give 4,7-dihydro-4,7-methano-2-methyl-2*H*-indazole (**5**) (90 mg, 62%) and 4,7-dihydro-4,7-methano-1-methyl-1*H*-indazole (**10**) (49 mg, 34%).

5: Colorless oil; ν_{max}(film)/cm^{-1} 3066, 2992, 2970, 1444, 1427, 1375, 1215; δ_H(300 MHz, $CDCl_3$) 2.40 (1H, br d, *J* 7, 8-H_{syn}), 2.53 (1H, dt, *J* 7 and 2, 8-H_{anti}), 3.73 (1H, s, Me), 3.79 (2H, m, 4-H and 7-H), 6.74 (1H, dd, *J* 5 and 2, 5-H or 6-H), 6.77 (1H, dd, *J* 5 and 2, 6-H or 5-H), 6.83 (1H, s, 3-H); δ_C(75 MHz, $CDCl_3$) 37.8 (Me), 43.4 (C-4 or C-7), 44.7 (C-7 or C-4), 70.5 (C-8), 121.7 (C-3), 131.3 (C-3a), 142.2 (C-5 or C-6), 144.4 (C-6 or C-5), 170.2 (C-7a); *m*/*z* 146 (M^+, 100%), 145 (M − H, 38). Picrate: yellow needles (from methanol), mp 156–157 °C (Found: C, 48.3; H, 3.7; N, 18.8. $C_{15}H_{13}N_5O_7$ requires C, 48.0; H, 3.5; N, 18.7%).

10: Colorless oil; ν_{max}(film)/cm^{-1} 3070, 2991, 2972, 1441, 1414, 1295, 1273; δ_H(300 MHz, $CDCl_3$) 2.51 (1H, br d, *J* 7, 8-H_{syn}), 2.58 (1H, dt, *J* 7 and 2, 8-H_{anti}), 3.74 (2H, m, 4-H and 7-H), 3.77 (3H, s, Me), 6.70 (1H, dd, *J* 5 and 2, 5-H or 6-H), 6.89 (1H, dd, *J* 5 and 2, 6-H or 5-H), 7.02 (1H, s, 3-H); δ_C(75 MHz, $CDCl_3$) 37.2 (Me), 44.5 (C-4 or C-7), 44.8 (C-7 or C-4), 73.6 (C-8), 130.7 (C-3), 135.4 (C-3a), 141.4 (C-5 or C-6), 146.8 (C-6 or C-5), 161.6 (C-7a); *m*/*z* 146 (M^+, 79%), 145 (M − H, 100), 131 (M − Me, 30). Picrate: yellow needles (from methanol), mp 145–146 °C (Found: C, 48.3; H, 3.4; N, 18.85. $C_{15}H_{13}N_5O_7$ requires C, 48.0; H, 3.5; N, 18.7%).

Reaction of the pyrazole 3 with the Meerwein reagent

A solution of the pyrazole **3** (264 mg, 2 mmol) and triethyloxonium tetrafluoroborate[25] (*ca.* 1 g) in CH_2Cl_2 (10 ml) was stirred at room temperature for 24 h. Aqueous $NaHCO_3$ (10 ml) was added to the reaction mixture and extracted with CH_2Cl_2 (3 × 10 ml). The combined organic phase was washed with water and brine over Na_2SO_4. After removal of the solvent, the residue was separated by TLC (silica gel, benzene–ethyl acetate 1:1) to give 1-ethyl-4,7-dihydro-4,7-methano-1*H*-indazole (**11**) (212 mg, 66%) as a colorless oil and 2-ethyl-4,7-dihydro-4,7-methano-2*H*-indazole (**6**) which was isolated as the picrate (11 mg, 1%).

Picrate of **6**: yellow needles (from methanol), mp 157–158 °C (Found: C, 49.3; H, 3.7; N, 18.2. $C_{16}H_{15}N_5O_7$ requires C, 49.4; H, 3.9; N, 18.0%); ν_{max}(KBr)/cm^{-1} 3099, 2985, 2946, 1610, 1433, 1414, 1369, 1319, 1273; δ_H(400 MHz, $CDCl_3$) 1.51 (3H, t, *J* 7, Me), 2.62 (1H, dm, *J* 8, 8-H_{syn}), 2.67 (1H, dm, *J* 8, 8-H_{anti}), 3.96 (1H, br s, 4-H or 7-H), 4.28 (1H, br s, 7-H or 4-H), 4.36 (2H, m, CH_2), 6.87 (1H, dm, *J* 5, 5-H or 6-H), 6.93 (1H, dd, *J* 5 and 3, 6-H or 5-H), 7.13 (1H, s, 3-H), 9.01 (2H, s).

11: colorless oil; ν_{max}(film)/cm^{-1} 3074, 2989, 2970, 1531, 1462, 1450, 1432, 1295; δ_H(400 MHz, $CDCl_3$) 1.43 (3H, t, *J* 7, Me), 2.55 (1H, d, *J* 7, 8-H_{syn}), 2.61 (1H, d, *J* 7, 8-H_{anti}), 3.78 (1H, br s, 4-H or 7-H), 3.81 (1H, br s, 7-H or 4-H), 4.10 (2H, q, *J* 7, CH_2), 6.73 (1H, dd, *J* 5 and 3, 5-H or 6-H), 6.92 (1H, dd, *J* 5 and 3, 6-H or 5-H), 7.06 (1H, s, 3-H); δ_C(100 MHz, $CDCl_3$) 15.8 (Me), 44.6 (C-4 or C-7), 44.9 (C-7 or C-4), 45.7 (CH_2), 73.3 (C-8), 130.6 (C-3), 135.4 (C-3a), 141.3 (C-5 or C-6), 147.0 (C-6 or C-5), 160.7 (C-7a); *m*/*z* 160 (M^+, 80%), 145 (M − Me, 100), 131 (M − Et, 92). Picrate: yellow prisms (from methanol), mp 141–142 °C (Found: C, 49.5; H, 3.7; N, 17.9. $C_{16}H_{15}N_5O_7$ requires C, 49.4; H, 3.9; N, 18.0%).

4,7-Dihydro-4,7-methano-2-(phenylcarbamoyl)-2*H*-indazole (7)

A solution of the pyrazole **3** (40 mg, 0.3 mmol) and phenyl isocyanate (40 mg, 0.34 mmol) in benzene (10 ml) was stirred at room temperature for 24 h. The mixture was concentrated and the resulting solid was collected by suction to give the carbamoylpyrazole **7** (68 mg, 90%) as colorless needles (from hexane–ethyl acetate 1:1), mp 169–170 °C (Found: C, 71.6; H, 5.2; N, 16.7. $C_{15}H_{13}N_3O$ requires C, 71.7; H, 5.2; N, 16.7%); ν_{max}(KBr)/cm^{-1} 3284, 3135, 3018, 2973, 2933, 1702, 1691, 1678, 1652, 1593, 1562, 1546, 1529, 1517, 1502, 1444, 1382, 1348,

1317, 1299, 1240, 1228; δ_H(400 MHz, $CDCl_3$) 2.44 (1H, br d, *J* 8, 8-H_{syn}), 2.60 (1H, dt, *J* 8 and 2, 8-H_{anti}), 3.81 (1H, br d, *J* 2, 4-H or 7-H), 3.86 (1H, br d, *J* 2, 7-H or 4-H), 6.70 (1H, dd, *J* 5 and 3, 5-H or 6-H), 6.79 (1H, dd, *J* 5 and 3, 6-H or 5-H), 7.12 (1H, tt, *J* 8 and 1), 7.35 (2H, tt, *J* 8 and 1), 7.56 (2H, dt, *J* 8 and 1), 7.72 (1H, s, 3-H), 8.79 (1H, br s, NH); δ_C(100 MHz, $CDCl_3$) 42.9 (C-4 or C-7), 44.2 (C-7 or C-4), 68.0 (C-8), 118.7 (C-3), 119.5, 124.1, 129.1, 134.3 (C-3a), 137.3, 140.7 (C-5 or C-6), 144.1 (C-6 or C-5), 148.2 (CO), 173.5 (C-7a); *m*/*z* 251 (M^+, 19%), 132 (M − PhNCO, 100).

2-Benzoyl-4,7-dihydro-4,7-methano-2*H*-indazole (8)

A solution of the pyrazole **3** (132 mg, 1 mmol) in THF was added to a suspension of NaH (60%, 60 mg, 1.5 mmol) in THF (2 ml), and the mixture was stirred at room temperature for 30 min. Benzoyl chloride (169 mg, 1.2 mmol) was added to the mixture and stirring was continued for 1 h. The reaction mixture was quenched with water (10 ml) and extracted with CH_2Cl_2 (3 × 10 ml). The combined organic phase was washed with water and brine, and dried over Na_2SO_4. After removal of solvent, the residue was separated by TLC (silica gel, benzene) to give the benzoylpyrazole **8** (160 mg, 68%), colorless prisms (from hexane), mp 78–79.5 °C (Found: C, 76.0; H, 5.1; N, 11.9. $C_{15}H_{12}N_2O$ requires C, 76.25; H, 5.1; N, 11.9%); ν_{max}(KBr)/cm^{-1} 3126, 3087, 3059, 2991, 2968, 2931, 1678 (CO), 1639, 1450, 1377, 1344, 1298; δ_H(400 MHz, $CDCl_3$) 2.42 (1H, br d, *J* 8, 8-H_{syn}), 2.58 (1H, dt, *J* 8 and 2, 8-H_{anti}), 3.82 (1H, m, 4-H or 7-H), 3.87 (1H, m, 7-H or 4-H), 6.67 (1H, dd, *J* 5 and 3, 5-H or 6-H), 6.75 (1H, dd, *J* 5 and 3, 6-H or 5-H), 7.47 (2H, tt, *J* 8 and 2), 7.55 (1H, tt, *J* 8 and 2), 7.83 (1H, s, 3-H), 8.01 (2H, dt, *J* 8 and 2); δ_C(100 MHz, $CDCl_3$) 42.6 (C-4 of C-7), 44.1 (C-7 or C-4), 66.5 (C-8), 119.6 (C-3), 127.9, 130.8, 132.1, 132.8 (C-3a), 134.5, 140.6 (C-5 or C-6), 143.3 (C-6 or C-5), 167.1 (CO), 175.5 (C-7a); *m*/*z* 236 (M^+, 5%), 131 (M − PhCO, 15), 105 (PhCO, 100).

4,7-Dihydro-4,7-methano-2-(*p*-nitrobenzoyl)-2*H*-indazole (9)

By a similar procedure to that described above, the reaction of pyrazole **3** (132 mg, 1 mmol) and *p*-nitrobenzoyl chloride (220 mg, 1.2 mmol) provided the 2-(*p*-nitrobenzoyl)pyrazole **9** (186 mg, 66%), colorless plates (from ethanol), mp 161–162 °C (Found: C, 64.0; H, 3.85; N, 15.0. $C_{15}H_{11}N_3O_3$ requires C, 64.05; H, 3.9; N, 14.9%); ν_{max}(KBr)/cm^{-1} 3118, 3080, 3054, 2978, 2943, 1671 (CO), 1604, 1525, 1518, 1450, 1409, 1378, 1336, 1301; δ_H(300 MHz, $CDCl_3$) 2.43 (1H, br d, *J* 8, 8-H_{syn}), 2.61 (1H, br d, *J* 8, 8-H_{anti}), 3.82 (1H, br s, 7-H), 3.90 (1H, br s, 4-H), 6.68 (1H, dd, *J* 5 and 3, 6-H), 6.77 (1H, dd, *J* 5 and 3, 5-H), 7.84 (1H, s, C-3), 8.18 (2H, dd, *J* 7 and 2), 8.31 (2H, dd, *J* 7 and 2); NOE observed between 3-H and 4-H; δ_C(75 MHz, $CDCl_3$) 42.5 (C-4), 44.0 (C-7), 66.2 (C-8), 119.2 (C-3), 122.9, 131.7, 135.3 (C-3a), 138.5, 140.4 (C-5), 143.2 (C-6), 149.4, 165.0 (CO), 176.2 (C-7a); *m*/*z* 281 (M^+, 25%), 150 ($NO_2C_6H_4CO$, 100).

4,7-Dihydro-4,7-methano-1-(*p*-nitrobenzoyl)-1*H*-indazole (12)

A solution of *p*-nitrobenzoyl chloride (191 mg, 1 mmol) in CH_2Cl_2 (5 ml) was added to a solution of the pyrazole **3** (132 mg, 1 mmol) and triethylamine (111 mg, 1.2 mmol) in CH_2Cl_2 (10 ml) during 30 min at room temperature. The mixture was stirred at room temperature for 1 h and water (10 ml) was added. The organic layer was separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 10 ml). The combined organic phase was washed with water and brine, and dried over Na_2SO_4. After removal of the solvent, the resulting solid was recrystallized from ethyl acetate to give 1-(*p*-nitrobenzoyl)pyrazole **12** (114 mg, 41%) as yellow needles, mp 136–137 °C (Found: C, 64.0; H, 3.9; N, 15.2. $C_{15}H_{11}N_3O_3$ requires C, 64.05; H, 3.9; N, 14.9%); ν_{max}(KBr)/cm^{-1} 3110, 3079, 3052, 2977, 2940, 1691 (CO), 1602, 1523, 1459, 1408, 1390, 1348, 1311; δ_H(300 MHz, $CDCl_3$) 2.74 (2H, m, 8-H_{syn} and 8-H_{anti}), 3.89 (1H, br s, 4-H), 4.44 (1H, br s, 7-H), 6.95 (1H, dd, *J* 5 and 2, 5-H or 6-H), 7.01 (1H, dd, *J* 5 and 2, 5-H), 7.44 (1H, s, C-3), 8.28 (2H, dm, *J* 9), 8.33 (2H, dm, *J* 9); δ_C(75 MHz, $CDCl_3$) 44.6 (C-4), 48.0 (C-7), 75.4 (C-8), 123.0, 132.4, 137.5, 137.6 (C-3), 142.7 (C-5 or C-6), 142.8 (C-3a), 146.1 (C-6 or C-5), 150.0, 164.8 (CO), 166.8 (C-7a); *m*/*z* 281 (M^+, 18%), 150 ($NO_2C_6H_4CO$, 100).

General procedure for the bromination reaction of the norbornadiene-fused pyrazoles

A solution of bromine (80 mg, 0.5 mmol) in carbon tetrachloride (2 ml) was added to a solution of a norbornadiene-fused pyrazole (0.5 mmol) in carbon tetrachloride (3 ml) and the mixture was stirred at room temperature for 3 h. Dichloromethane was added and the organic phase was washed with aqueous sodium thiosulfate and aqueous sodium hydrogen carbonate, and dried over Na_2SO_4. After removal of the solvent, the resulting solid was collected by suction. Yields of the products are listed in Table 2.

For the isolations of **13** and **30**, the residues were separated by chromatography (silica gel, benzene–ethyl acetate 1 : 1) and TLC (silica gel, benzene), respectively.

5-*exo*,8-*anti*-Dibromo-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazole (13). White powder (from cyclohexane); mp 130–131 °C (Found: C, 32.65; H, 2.8; N, 9.85. $C_8H_8Br_2N_2$ requires C, 32.9; H, 2.8; N, 9.6%); ν_{max}(KBr)/cm^{-1} 3182, 3012, 2987, 2951, 1577, 1452, 1439, 1412; δ_H(400 MHz, $CDCl_3$) 2.29 (1H, dd, *J* 13 and 8, 6-H_{endo}), 2.89 (1H, dt, *J* 13 and 4, 6-H_{exo}), 3.65 (1H, d, *J* 4, 7-H), 3.74 (1H, ddd, *J* 8, 4, and 1, 5-H), 3.83 (1H, br s, 4-H), 4.17 (1H, br s, 8-H_{syn}), 7.28 (1H, s, 3-H), 10.15 (1H, br, NH); δ_C(100 MHz, $CDCl_3$) 36.8 (C-6), 45.4 (C-5), 46.6 (C-7), 51.3 (C-4), 55.7 (C-8), 120.6 (C-3), 122.6 (C-3a), 158.1 (C-7a); *m*/*z* 294/292/290 (M^+, 3/5/3%), 132 (**3**, 50), 105 (**3** − C_2H_3, 100).

5-*exo*,8-*anti*-Dibromo-4,5,6,7-tetrahydro-4,7-methano-2-methyl-2*H*-indazole (14). Colorless prisms (from ethyl acetate); mp 184–185 °C (Found: C, 35.5; H, 3.15; N, 9.3. $C_9H_{10}Br_2N_2$ requires C, 35.3; H, 3.3; N, 9.15%); ν_{max}(KBr)/cm^{-1} 3013, 2996, 2973, 2946, 1439, 1389, 1278, 1259, 1247; δ_H(300 MHz, $CDCl_3$) 2.26 (1H, dd, *J* 13 and 8, 6-H_{endo}), 2.85 (1H, dt, *J* 13 and 4, 6-H_{exo}), 3.58 (1H, d, *J* 4, 7-H), 3.73 (1H, ddd, *J* 8, 4, and 1, 5-H), 3.76 (1H, s, 4-H), 3.83 (3H, s, Me), 4.15 (1H, d, *J* 1, 8-H_{syn}), 7.05 (1H, s, 3-H); NOE observed between 3-H and 4-H; δ_C(75 MHz, $CDCl_3$) 36.9 (C-6), 38.7 (Me), 45.7 (C-5), 46.8 (C-7), 51.5 (C-4), 55.7 (C-8), 122.2 (C-3), 122.9 (C-3a), 158.2 (C-7a); *m*/*z* 308/306/304 (M^+, 5/9/5%), 225 (M − Br, 79), 132 (M − Me − Br_2, 19).

5-*exo*,8-*anti*-Dibromo-4,5,6,7-tetrahydro-4,7-methano-2-(phenylcarbamoyl)-2*H*-indazole (15). White powder (from ethanol); mp 160–161 °C (Found: C, 43.7; H, 3.05; N, 10.3. $C_{15}H_{13}Br_2N_3O$ requires C, 43.8; H, 3.2; N, 10.2%); ν_{max}(KBr)/cm^{-1} 3344, 3030, 2991, 2951, 1724, 1712, 1594, 1529, 1446, 1349, 1315, 1230; δ_H(300 MHz, $CDCl_3$) 2.36 (1H, dd, *J* 13 and 8, 6-H_{endo}), 2.95 (1H, dt, *J* 13 and 4, 6-H_{exo}), 3.61 (1H, d, *J* 4, 7-H), 3.81 (1H, ddd, *J* 8, 4, and 1, 5-H), 3.85 (1H, s, 4-H), 4.21 (1H, br s, 8-H_{syn}), 7.16 (1H, t, *J* 7), 7.38 (2H, t, *J* 7), 7.56 (2H, d, *J* 7), 8.00 (1H, s, 3-H), 8.85 (1H, br, NH); NOE observed between 3-H and 4-H; δ_C(75 MHz, $CDCl_3$) 36.7 (C-6), 44.1 (C-5), 46.5 (C-7), 51.0 (C-4), 54.8 (C-8), 119.6, 120.4 (C-3), 124.7, 126.0 (C-3a), 129.3, 136.5, 147.0 (CO), 161.4 (C-7a); *m*/*z* 413/411/409 (M^+, 3/5/3%), 294/292/290 (M − PhNCO, 9/19/9), 213/211 (M − PhNCO − Br, 57/58), 132 (M − PhNCO − Br_2, 24), 119 (PhNCO, 100).

2-Benzoyl-5-*exo*,8-*anti*-dibromo-4,5,6,7-tetrahydro-4,7-methano-2*H*-indazole (16). Colorless prisms (from diethyl ether); mp 149–150 °C (Found: C, 45.6; H, 2.8; N, 7.1. $C_{15}H_{12}Br_2N_2O$ requires C, 45.5; H, 3.05; N, 7.0%); ν_{max}(KBr)/cm^{-1} 3050, 3000, 2950, 1687, 1491, 1348, 1244; δ_H(300 MHz,

$CDCl_3$) 2.39 (1H, dd, *J* 14 and 8, 6-H_{endo}), 2.95 (1H, dt, *J* 14 and 4, 6-H_{exo}), 3.63 (1H, d, *J* 4, 7-H), 3.86 (1H, ddd, *J* 8, 4, and 1, 5-H), 3.87 (1H, s, 4-H), 4.22 (1H, br s, 8-H_{syn}), 7.45 (2H, t, *J* 7.5), 7.61 (1H, t, *J* 7.5), 8.03 (2H, d, *J* 7.5), 8.12 (1H, s, 3-H); NOE observed between 3-H and 4-H; δ_C(75 MHz, $CDCl_3$) 36.7 (C-6), 43.8 (C-5), 46.5 (C-7), 50.8 (C-4), 54.4 (C-8), 121.7 (C-3), 126.2 (C-3a), 128.1, 131.1, 131.5, 133.0, 163.5 (C-7a), 166.6 (CO); *m*/*z* 398/396/394 (M^+, 2/4/2%), 315 (M − Br, 24), 290 (M − PhCO, 5), 235 (M − Br_2, 5), 132 (M − PhCO − Br_2, 6), 105 (PhCO, 100).

5-*exo*,8-*anti*-Dibromo-1-ethyl-4,5,6,7-tetrahydro-4,7-methano-1*H*-indazole (30). White powder (from hexane); mp 60–61 °C (Found: C, 37.6; H, 3.8; N, 8.9. $C_{10}H_{12}Br_2N_2$ requires C, 37.5; H, 3.8; N, 8.75%); ν_{max}(KBr)/cm^{-1} 2999, 2978, 2949, 1531, 1442, 1433, 1387, 1253; δ_H(400 MHz, $CDCl_3$) 1.44 (3H, t, *J* 7, Me), 2.14 (1H, ddd, *J* 13, 8, and 1, 6-H_{endo}), 2.85 (1H, dt, *J* 13 and 4, 6-H_{exo}), 3.67 (2H, m, 5-H and 7-H), 3.77 (1H, br s, 4-H), 4.12 (2H, q, *J* 7, CH_2), 4.19 (1H, br s, 8-H_{syn}), 7.21 (1H, s, 3-H); NOE observed between 3-H and 4-H; δ_C(100 MHz, $CDCl_3$) 15.5 (Me), 36.1 (C-6), 45.0 (C-7), 45.9 (CH_2), 46.6 (C-5), 51.8 (C-4), 55.4 (C-8), 124.2 (C-3a), 130.4 (C-3), 146.7 (C-7a); *m*/*z* 322/320/318 (M^+, 3/5/3%), 239 (M − Br, 39), 160 (M − Br_2, 13), 133 (M − C_2H_3 − Br_2, 100).

5-*exo*,8-*anti*-Dibromo-4,5,6,7-tetrahydro-4,7-methano-1-(*p*-nitrobenzoyl)-1*H*-indazole (31). Colorless prisms (from carbon tetrachloride–chloroform 3:1); mp 203–204 °C (Found: C, 41.1; H, 2.5; N, 9.3. $C_{15}H_{11}Br_2N_3O_3$ requires C, 40.85; H, 2.5; N, 9.5%); ν_{max}(KBr)/cm^{-1} 3070, 3026, 1699, 1603, 1518, 1469, 1392, 1319, 1253; δ_H(400 MHz, $CDCl_3$) 2.31 (1H, dd, *J* 14 and 8, 6-H_{endo}), 2.96 (1H, dt, *J* 14 and 4, 6-H_{exo}), 3.68 (1H, ddd, *J* 8, 4, and 1, 5-H), 3.84 (1H, s, 4-H), 4.24 (1H, t, *J* 3, 7-H), 4.32 (1H, br s, 8-H_{syn}), 7.57 (1H, s, 3-H), 8.31 (2H, dt, *J* 9 and 2), 8.35 (2H, dt, *J* 9 and 2); NOE observed between 3-H and 4-H; δ_C(100 MHz, $CDCl_3$) 34.9 (C-6), 43.4 (C-5), 49.1 (C-7), 51.4 (C-4), 55.7 (C-8), 123.2, 129.9 (C-3a), 132.7, 136.3, 136.6 (C-3), 150.3, 151.9, 164.3 (CO); *m*/*z* 443/441/439 (M^+, 2/4/2%), 360 (M − Br, 24), 281 (M − Br_2, 2), 150 ($NO_2C_6H_4CO$, 100).

General procedure for the reaction of the norbornadiene-fused pyrazoles with *p*-nitrobenzenesulfenyl chloride

A solution of a norbornadiene-fused pyrazole (0.5 mmol) and *p*-nitrobenzenesulfenyl chloride (114 mg, 0.6 mol) in CCl_4 (10 ml) was stirred at room temperature for 24 h. After removal of the solvent, the residue was separated by TLC (silica gel, benzene–ethyl acetate 1:1) for **3** and **11**, TLC (silica gel, hexane–ethyl acetate 3:1) for **5**, and MPLC (benzene) for **7**, **8**, and **9**, respectively. Products and yields are listed in Table 2.

5-*exo*-Chloro-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(*p*-nitrophenylsulfenyl)-2*H*-indazole (17). Colorless needles (from ethyl acetate); mp 223–224 °C (Found: C, 52.4; H, 3.8; N, 13.0. $C_{14}H_{12}ClN_3O_2S$ requires C, 52.3; H, 3.8; N, 13.1%); ν_{max}(KBr)/cm^{-1} 3268, 3101, 3053, 2985, 1593, 1575, 1509, 1409, 1400; δ_H(400 MHz, acetone-d_6) 2.26 (1H, ddd, *J* 13, 8, and 1, 6-H_{endo}), 2.63 (1H, dt, *J* 13 and 4, 6-H_{exo}), 3.70 (1H, d, *J* 4, 7-H), 3.76 (1H, s, 4-H), 3.92 (1H, ddd, *J* 8, 4, and 1, 5-H), 4.01 (1H, br s, 8-H_{syn}), 7.51 (1H, s, 3-H), 7.64 (2H, dd, *J* 9 and 2), 8.20 (2H, dd, *J* 9 and 2), 11.61 (1H, br, NH); NOE observed between 3-H and 4-H; δ_C(100 MHz, DMSO-d_6) 37.5 (C-6), 43.8 (C-7), 50.4 (C-4), 59.1 (C-5), 61.9 (C-8), 120.8 (C-3), 121.9 (C-3a), 124.0, 126.9, 144.7, 147.0, 159.6 (C-7a); *m*/*z* 323/321 (M^+, 1/3%), 286 (M − Cl, 1), 167 (M − ArS, 9), 132 (M − ArSCl, 10), 131 (M − ArSCl − H, 56), 119 ($C_7H_7N_2$, 100).

5-*endo*-Chloro-4,5,6,7-tetrahydro-4,7-methano-6-*exo*-(*p*-nitrophenylsulfenyl)-2*H*-indazole (18) or 6-*endo*-chloro-4,5,6,7-tetrahydro-4,7-methano-5-*exo*-(*p*-nitrophenylsulfenyl)-2*H*-indazole (19). White powder; mp 70–72 °C (HR-MS found: 321.0343. $C_{14}H_{12}ClN_3O_2S$ requires 321.0346); ν_{max}(KBr)/cm^{-1} 3371, 3187, 3062, 2920, 1594, 1577, 1512, 1479, 1444, 1334; δ_H(400 MHz, $CDCl_3$) 2.33 (1H, dm, *J* 10, 8-H_{syn}), 2.40 (1H, dt, *J* 10 and 2, 8-H_{anti}), 3.24 (1H, t, *J* 4, **18** 4-H or **19** 7-H), 3.47 (1H, br s, **18** 7-H or **19** 4-H), 3.68 (1H, d, *J* 4, **18** 6-H or **19** 5-H), 4.38 (1H, t, *J* 4, **18** 5-H or **19** 6-H), 7.43 (1H, s, 3-H), 7.45 (2H, dd, *J* 7 and 2), 8.16 (2H, dd, *J* 7 and 2); *m*/*z* 323/321 (M^+, 6/15%), 286 (M − Cl, 14), 167 (M − ArS, 49), 132 (M − ArSCl, 18), 131 (M − ArSCl − H, 100), 119 ($C_7H_7N_2$, 9).

5-*exo*-Chloro-4,5,6,7-tetrahydro-4,7-methano-2-methyl-8-*anti*-(*p*-nitrophenylsulfenyl)-2*H*-indazole (20). White powder (from ethanol); mp 179–180 °C (Found: C, 53.9; H, 4.25; N, 12.6. $C_{15}H_{14}ClN_3O_2S$ requires C, 53.65; H, 4.2; N, 12.5%); ν_{max}(KBr)/cm^{-1} 3100, 3022, 2989, 1593, 1579, 1512, 1503, 1477, 1439, 1417, 1389; δ_H(300 MHz, $CDCl_3$) 2.28 (1H, ddd, *J* 13, 8, and 1, 6-H_{endo}), 2.68 (1H, dt, *J* 13 and 4, 6-H_{exo}), 3.63 (1H, d, *J* 4, 7-H), 3.71 (1H, s, 4-H), 3.85 (3H, s, Me), 3.82–3.87 (2H, m, 5-H and 8-H_{syn}), 7.07 (1H, s, 3-H), 7.41 (2H, dt, *J* 9 and 2), 8.23 (2H, dt, *J* 8 and 2); NOE observed between 3-H and 4-H; δ_C(75 MHz, $CDCl_3$) 37.7 (C-6), 38.7 (Me), 44.8 (C-7), 51.4 (C-4), 58.5 (C-5), 63.0 (C-8), 122.5 (C-3), 123.6 (C-3a), 124.1, 127.0, 145.5, 147.1, 160.7 (C-7a); *m*/*z* 337/335 (M^+, 1/3%), 300 (M − Cl, 2), 181 (M − ArS, 11), 146 (M − ArSCl, 10), 145 (M − ArSCl − H, 56), 133 ($C_8H_8N_2$, 100), 119 ($C_7H_7N_2$, 14).

5-*exo*-Chloro-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(*p*-nitrophenylsulfenyl)-2-(*N*-phenylcarbamoyl)-2*H*-indazole (21). White powder (from ethanol); mp 191–192 °C (Found: C, 57.4; H, 3.8; N, 12.8. $C_{21}H_{17}ClN_4O_3S$ requires C, 57.2; H, 3.9; N, 12.7%); ν_{max}(KBr)/cm^{-1} 3365, 3095, 3032, 3001, 2951, 1730, 1595, 1579, 1529, 1510, 1446, 1352, 1340; δ_H(400 MHz, $CDCl_3$) 2.39 (1H, ddd, *J* 13, 8, and 1, 6-H_{endo}), 2.81 (1H, dt, *J* 13 and 4, 6-H_{exo}), 3.66 (1H, d, *J* 4, 7-H), 3.81 (1H, s, 4-H), 3.92 (1H, br s, 8-H_{syn}), 3.95 (1H, ddd, *J* 8, 4, and 1, 5-H), 7.17 (1H, br t, *J* 7), 7.39 (2H, br t, *J* 7), 7.44 (2H, br d, *J* 7), 7.57 (2H, br d, *J* 7), 8.02 (1H, s, 3-H), 8.16 (2H, d, *J* 7), 8.86 (1H, br, NH); NOE observed between 3-H and 4-H; δ_C(100 MHz, $CDCl_3$), 37.3 (C-6), 44.6 (C-7), 50.9 (C-4), 57.4 (C-5), 62.8 (C-8), 119.6, 120.6 (C-3), 124.3, 124.8, 126.5 (C-3a), 127.5, 129.3, 136.6, 145.8, 146.2, 147.1 (*CO*NHPh), 163.7 (C-7a); *m*/*z* 323/321 (M − PhNCO, 1/3%), 286 (M − ArS, 3), 167 (M − PhNCO − ArS, 10), 119 ($C_7H_7N_2$, 100).

A 1:1 mixture of 5-*endo*-chloro-4,5,6,7-tetrahydro-4,7-methano-6-*exo*-(*p*-nitrophenylsulfenyl)-2-(phenylcarbamoyl)-2*H*-indazole (22) and 6-*endo*-chloro-4,5,6,7-tetrahydro-4,7-methano-5-*exo*-(*p*-nitrophenylsulfenyl)-2-(phenylcarbamoyl)-2*H*-indazole (23). White powder (from hexane–ethyl acetate 95:5); mp 149–153 °C (Found: C, 57.45; H, 3.65; N, 12.8. $C_{21}H_{17}ClN_4O_3S$ requires C, 57.2; H, 3.9; N, 12.7%); ν_{max}(KBr)/cm^{-1} 3363, 3346, 3160, 3097, 3059, 2993, 2981, 1732, 1597, 1535, 1518, 1446, 1356, 1338, 1196; δ_H(400 MHz, $CDCl_3$) 2.35 (1H, d, *J* 8, **22** 8-H_{syn} and **23** 8-H_{syn}), 2.48 (0.5H, d, *J* 8, **22** 8-H_{anti}), 2.48 (0.5H, d, *J* 8, **23** 8-H_{anti}), 3.34 (0.5H, t, *J* 4, **22** 4-H), 3.37 (0.5H, t, *J* 4, **23** 7-H), 3.42 (0.5H, s, **22** 7-H), 3.44 (0.5H, s, **23** 4-H), 3.72 (1H, br d, *J* 4, **22** 6-H and **23** 5-H), 4.39 (0.5H, t, *J* 4, **22** 5-H), 4.45 (0.5H, t, *J* 4, **23** 6-H), 7.17 (1H, br t, *J* 7), 7.38 (2H, br t, *J* 7), 7.48 (2H, d, *J* 7), 7.61 (2H, br d, *J* 7), 8.05 (0.5H, s, **23** 3-H), 8.14 (0.5H, s, **22** 3-H), 8.22 (2H, d, *J* 7), 8.97 (1H, br, NH); recrystallization of the 1:1 mixture of **22** and **23** from hexane–ethyl acetate (3:1) provided a 1:5 mixture (mp 138–140 °C) of **22** and **23**, thus the assignments are based on the spectrum of the enriched sample and NOE observed between 3-H and 4-H in **23**; δ_C(400 MHz, $CDCl_3$) 43.8, 44.9, 46.0, 47.0 (CH_2), 48.0 (CH_2), 48.5, 56.1, 57.1, 63.3, 63.9, 119.6, 119.7, 120.1, 123.6, 124.3, 124.5, 124.6, 126.0, 127.9, 128.1, 128.2, 129.2, 129.3, 136.7, 144.8, 144.9, 147.3, 164.3, 164.4 (5C missing in the sp^2 region); *m*/*z* 323/321 (M − PhNCO, 6/17%), 286 (M − ArS, 2), 167 (M − PhNCO − ArS, 34), 119 ($C_7H_7N_2$, 100).

2-Benzoyl-5-*exo*-chloro-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(*p*-nitrophenylsulfenyl)-2*H*-indazole (24). White powder (from ethanol); mp 172–173 °C (Found: C, 59.5; H, 3.6; N, 9.7. $C_{21}H_{16}ClN_3O_3S$ requires C, 59.2; H, 3.8; N, 9.9%); ν_{max}(KBr)/cm^{-1} 3149, 3029, 3004, 2979, 1685, 1595, 1577, 1504, 1479, 1334; δ_H(300 MHz, $CDCl_3$) 2.42 (1H, ddd, *J* 14, 8, and 1, 6-H$_{endo}$), 2.81 (1H, dt, *J* 14 and 4, 6-H$_{exo}$), 3.68 (1H, d, *J* 4, 7-H), 3.83 (1H, s, 4-H), 3.92 (1H, br s, 8-H$_{syn}$), 4.00 (1H, ddd, *J* 8, 4, and 1, 5-H), 7.43 (1H, dm, *J* 9), 7.51 (2H, dm, *J* 7), 7.63 (2H, tt, *J* 7 and 2), 8.05 (2H, br d, *J* 7), 8.14 (1H, s, 3-H), 8.15 (2H, d, *J* 9); NOE observed between 3-H and 4-H; δ_C(75 MHz, $CDCl_3$) 37.3 (C-6), 44.7 (C-7), 50.7 (C-4), 57.3 (C-5), 62.3 (C-8), 121.9 (C-3), 124.2, 126.7 (C-3a), 127.4, 128.2, 131.1, 131.6, 133.0, 145.7, 146.1, 165.8, 166.7; *m*/*z* 427/425 (M$^+$, 1/3%), 390 (M − Cl, 1), 236 (M − ArSCl, 2), 105 (PhCO, 100).

2-Benzoyl-5-*endo*-chloro-4,5,6,7-tetrahydro-4,7-methano-6-*exo*-(*p*-nitrophenylsulfenyl)-2*H*-indazole (25). White powder (from methanol); mp 119–120 °C (Found: C, 59.4; H, 3.7; N, 9.9. $C_{21}H_{16}ClN_3O_3S$ requires C, 59.2; H, 3.8; N, 9.9%); ν_{max}(KBr)/cm^{-1} 3137, 3016, 2983, 1674, 1595, 1576, 1511, 1481, 1392, 1340; δ_H(400 MHz, $CDCl_3$) 2.36 (1H, d, *J* 10, 8-H$_{syn}$), 2.49 (1H, d, *J* 10, 8-H$_{anti}$), 3.38 (1H, br d, *J* 4, 4-H), 3.45 (1H, br s, 7-H), 3.73 (1H, br d, *J* 4, 6-H), 4.44 (1H, t, *J* 4, 5-H), 7.45 (1H, br t, *J* 9), 7.51 (2H, br t, *J* 8), 7.61 (2H, br t, *J* 8), 8.01 (2H, br d, *J* 8), 8.16 (1H, s, 3-H), 8.23 (2H, dt, *J* 9 and 2); δ_C(100 MHz, $CDCl_3$) 45.0, 45.9, 47.6 (C-8), 56.2, 64.2, 124.3, 125.0, 126.4, 128.2, 128.3, 131.1, 132.0, 132.9, 144.4, 166.7, 166.8; *m*/*z* 427/425 (M$^+$, 2/6%), 390 (M − Cl, 3), 236 (M − ArSCl, 10), 105 (PhCO, 100).

2-Benzoyl-6-*endo*-chloro-4,5,6,7-tetrahydro-4,7-methano-5-*exo*-(*p*-nitrophenylsulfenyl)-2*H*-indazole (26). Colorless prisms (from chloroform–carbon tetrachloride 1:2); mp 198–199 °C (Found: C, 59.5; H, 3.7; N, 10.0. $C_{21}H_{16}ClN_3O_3S$ requires C, 59.2; H, 3.8; N, 9.9%); ν_{max}(KBr)/cm^{-1} 3134, 3008, 2962, 1680, 1593, 1581, 1511, 1477, 1392, 1355, 1336, 1320, 1309, 1294, 1247, 1238; δ_H(400 MHz, $CDCl_3$) 2.35 (1H, d, *J* 11, 8-H$_{syn}$), 2.49 (1H, d, *J* 11, 8-H$_{anti}$), 3.42 (1H, br d, *J* 4, 7-H), 3.46 (1H, br s, 4-H), 3.75 (1H, br d, *J* 4, 5-H), 4.41 (1H, t, *J* 4, 6-H), 7.48 (1H, br t, *J* 9), 7.51 (2H, br t, *J* 8), 7.61 (2H, br t, *J* 8), 8.10 (2H, br d, *J* 8), 8.15 (1H, s, 3-H), 8.19 (2H, dt, *J* 9 and 2); NOE observed between 3-H and 4-H; δ_C(100 MHz, $CDCl_3$) 43.5 (C-4), 46.8 (C-5), 47.8 (C-8), 57.0 (C-7), 63.2 (C-6), 121.3 (C-3), 124.2, 128.0, 128.1, 128.4 (C-3a), 131.4, 131.9, 132.8, 144.7, 145.9, 164.8, 166.8; *m*/*z* 427/425 (M$^+$, 2/6%), 390 (M − Cl, 3), 236 (M − ArSCl, 30), 105 (PhCO, 100).

5-*exo*-Chloro-4,5,6,7-tetrahydro-4,7-methano-2-(*p*-nitrobenzoyl)-8-*anti*-(*p*-nitrophenylsulfenyl)-2*H*-indazole (27). Yellow prisms (from chloroform–methanol 2:1); mp 261–262 °C (Found: C, 53.4; H, 3.2; N, 11.9. $C_{21}H_{15}ClN_4O_5S$ requires C, 53.6; H, 3.2; N, 11.9%); ν_{max}(KBr)/cm^{-1} 3141, 3027, 3004, 2983, 1710, 1597, 1577, 1508, 1479, 1340; δ_H(300 MHz, $CDCl_3$) 2.42 (1H, ddd, *J* 13, 8, and 1, 6-H$_{endo}$), 2.81 (1H, dt, *J* 13 and 4, 6-H$_{exo}$), 3.67 (1H, d, *J* 4, 7-H), 3.85 (1H, s, 4-H), 3.92 (1H, br s, 8-H$_{syn}$), 4.00 (1H, ddd, *J* 8, 4, and 1, 5-H), 7.44 (2H, dt, *J* 9 and 2), 8.16 (2H, dt, *J* 9 and 2), 8.16 (1H, s, 3-H), 8.23 (2H, dt, *J* 9 and 2), 8.35 (2H, dt, *J* 9 and 2); NOE observed between 3-H and 4-H; δ_C(75 MHz, $CDCl_3$) 35.8 (C-6), 44.7 (C-7), 50.7 (C-4), 57.0 (C-5), 62.4 (C-8), 121.8 (C-3), 123.2, 124.3, 127.6, 127.7, 132.2, 137.2, 145.8, 166.7 (CO), 3C missing; *m*/*z* 316 (M − ArS, 1%), 281 (M − ArSCl, 2), 150 (ArCO, 100).

5-*endo*-Chloro-4,5,6,7-tetrahydro-4,7-methano-2-(*p*-nitrobenzoyl)-6-*exo*-(*p*-nitrophenylsulfenyl)-2*H*-indazole (28). Yellow powder (from chloroform–methanol 2:1); mp 112–113 °C (Found: C, 53.8, H, 3.3; N, 11.6. $C_{21}H_{15}ClN_4O_5S$ requires C, 53.6; H, 3.2; N, 11.9%); ν_{max}(KBr)/cm^{-1} 3106, 3075, 3008, 2987, 1697, 1593, 1527, 1514, 1479, 1356, 1340; δ_H(400 MHz, $CDCl_3$) 2.37 (1H, dm, *J* 11, 8-H$_{syn}$), 2.53 (1H, d, *J* 11, 8-H$_{anti}$), 3.38 (1H, t, *J* 4, 4-H), 3.45 (1H, br s, 7-H), 3.77 (1H, d, *J* 4, 6-H), 4.44 (1H, t, *J* 4, 5-H), 7.47 (2H, d, *J* 9), 8.17 (2H, d, *J* 9), 8.25 (2H, d, *J* 9), 8.26 (1H, s, 3-H), 8.36 (2H, d, *J* 9); δ_C(100 MHz, $CDCl_3$) 44.9 (C-4), 45.9 (C-5), 47.5 (C-8), 56.1 (C-7), 64.0 (C-6), 123.2 (C-3), 124.3, 124.7, 127.4, 128.3 (C-3a), 132.2, 137.6, 144.2, 146.1, 149.9, 164.9, 167.6; *m*/*z* 472/470 (M$^+$, 2/6%), 435 (M − Cl, 7), 316 (M − ArS, 12), 281 (M − ArSCl, 7), 150 (ArCO, 100).

6-*endo*-Chloro-4,5,6,7-tetrahydro-4,7-methano-2-(*p*-nitrobenzoyl)-5-*exo*-(*p*-nitrophenylsulfenyl)-2*H*-indazole (29). Yellow prisms (from chloroform); mp 211–212 °C (Found: C, 53.5; H, 3.0; N, 11.8. $C_{21}H_{15}ClN_4O_5S$ requires C, 53.6; H, 3.2; N, 11.9%); ν_{max}(KBr)/cm^{-1} 3101, 3070, 3033, 2987, 1685, 1596, 1527, 1512, 1479, 1336, 1319, 1295, 1276; δ_H(400 MHz, $CDCl_3$) 2.36 (1H, dm, *J* 11, 8-H$_{syn}$), 2.53 (1H, d, *J* 11, 8-H$_{anti}$), 3.41 (1H, t, *J* 4, 4-H), 3.48 (1H, br s, 7-H), 3.75 (1H, d, *J* 4, 6-H), 4.44 (1H, t, *J* 4, 5-H), 7.49 (2H, dt, *J* 9 and 2), 8.17 (1H, s, 3-H), 8.20 (2H, dt, *J* 9 and 2), 8.26 (2H, dt, *J* 9 and 2), 8.35 (2H, dt, *J* 9 and 2); δ_C(100 MHz, $CDCl_3$) 43.5 (C-4), 46.8 (C-5), 47.7 (C-8), 57.0 (C-7), 63.0 (C-6), 121.3 (C-3), 123.1, 124.3, 128.2, 129.3 (C-3a), 132.4, 137.5, 144.4, 146.0, 149.9, 165.0, 165.8; *m*/*z* 472/470 (M$^+$, 5/14%), 435 (M − Cl, 23), 316 (M − ArS, 16), 281 (M − ArSCl, 16), 150 (ArCO, 100).

5-*exo*-Chloro-1-ethyl-4,5,6,7-tetrahydro-4,7-methano-8-*anti*-(*p*-nitrophenylsulfenyl)-1*H*-indazole (32). Colorless prisms (from ethyl acetate); mp 158–159 °C (Found: 54.8; H, 4.5; N, 12.2. $C_{16}H_{16}ClN_3O_2S$ requires C, 54.9; H, 4.6; N, 12.0%); ν_{max}(KBr)/cm^{-1} 2997, 1579, 1508, 1504, 1477, 1334; δ_H(400 MHz, $CDCl_3$) 1.46 (3H, t, *J* 7, Me), 2.14 (1H, ddd, *J* 13, 8, and 1, 6-H$_{endo}$), 2.66 (1H, dt, *J* 13 and 4, 6-H$_{exo}$), 3.65 (1H, d, *J* 4, 7-H), 3.71 (1H, s, 4-H), 3.78 (1H, dd, *J* 8 and 4, 5-H), 3.95 (1H, br s, 8-H$_{syn}$), 4.15 (2H, q, *J* 7, CH_2), 7.22 (1H, s, 3-H), 7.43 (2H, d, *J* 9), 8.15 (2H, d, *J* 9); NOE observed between 3-H and 4-H; δ_C(100 MHz, $CDCl_3$) 15.6 (Me), 36.9 (C-6), 44.6 (C-7), 45.9 (CH_2), 51.7 (C-4), 57.9 (C-5), 63.8 (C-8), 124.2, 125.3 (C-3a), 127.6, 130.7 (C-3), 145.7, 146.6, 149.3; *m*/*z* 351/349 (M$^+$, 1/3%), 314 (M − Cl, 1), 195 (M − ArS, 29), 147 (M − ArSCl − CH, 100).

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