Supporting Information

Palladium-catalyzed annulation and intermolecular hydroamination

involving norbornene derivatives: synthesis of indanones and N-

alkylamines

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1) General Information

¹H and ¹³C NMR spectra were recorded on a Bruker ARX400 spectrometer (FT, 400 MHz for ¹H; 100 MHz for ¹³C) at room temperature, unless otherwise noted. Chemical shifts were reported in ppm on the scale relative to CDCl₃ (δ = 7.26 for ¹H-NMR, δ = 77.00 for ¹³C-NMR) or DMSO-*d*₆ (δ = 2.50 for ¹H-NMR, δ = 39.60 for ¹³C-NMR) as an internal reference. Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. HPLC/Q-TOF-MS analysis was performed with an Agilent 1290 LC systemcoupled with a 6530Q-TOF/MS accurate-mass spectrometer (Agilent Technologies, USA). The mass spectrometry was performed in the positive electrospray ionization (ESI+) mode. Reactions were monitored by thin-layer chromatography Column chromatography (petroleum ether/ethyl acetate) was performed on silica gel (200-300 mesh). Unless otherwise noted, all starting materials were commercially available and were used without further purification.

2) Typical Experimental Procedures

(a) Synthesis of (4a*R*,9a*S*)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3a)





The stirred mixture of benzamide (60.5 mg, 0.5 mmol, 1.0 equiv), Norbornene (94 mg, 1.0 mmol 2.0 equiv), Pd(PPh₃)₂Cl₂ (35.1 mg, 0.05 mmol, 10 mol%), PCy₃ (28 mg, 0.1 mmol, 20 mol%), Cu(OAc)₂ (279 mg, 1.5 mmol, 3.0 equiv), K₂CO₃ (138 mg, 1.0 mmol, 2.0 equiv), and DABCO (56 mg, 0.5 mmol, 1.0 equiv) in toluene (5 mL), place

in a preheated oil bath at 130 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate=20:1 unless otherwise noted) to provide the desired products 3a as a brownish red oil liquid.

Table S1. Screening of Optimal Reaction Conditions^a



Entry	variation from the standard conditions	Yield/% ^b
1	none	85 (60 ^c)
2	under O ₂ atmosphere	34
3	under N ₂ atmosphere	71
4	without Pd(PPh ₃) ₂ Cl ₂	0
5	Pd ₂ (dba) ₃ instead of Pd(PPh ₃) ₂ Cl ₂	trace
6	Pd(OAc) ₂ instead of Pd(PPh ₃) ₂ Cl ₂	45
7	PdCl ₂ instead of Pd(PPh ₃) ₂ Cl ₂	20
8	Pd(PPh ₃) ₄ instead of Pd(PPh ₃) ₂ Cl ₂	trace
9	PPh ₃ instead of PCy ₃	trace
10	'Bu ₃ P instead of PCy ₃	trace
11	X-Phos instead of PCy ₃	trace
12	CuCl ₂ instead of Cu(OAc) ₂	0
13	BQ instead of Cu(OAc) ₂	0
14	$K_2S_2O_8$ instead of Cu(OAc) ₂	0
15	K ₃ PO ₄ instead of K ₂ CO ₃	45
16	Cs ₂ CO ₃ instead of K ₂ CO ₃	trace
17	KOAc instead of K ₂ CO ₃	trace
18	^t BuOK instead of K ₂ CO ₃	67

19	K_2CO_3 (3 equiv)	75
20	K_2CO_3 (1 equiv)	70
21	MeCN instead of Toluene	32
22	Dioxane or DMF instead of Toluene	0
23	without DABCO	trace
24	at 140 °C	80
25	at 120 °C	62
26	reaction for 10 h	73
27	reaction for 14 h	79

^{*a*}Conditions: benzamide (0.5 mmol, 1.0 equiv), norbornene (1.0 mmol, 2 equiv), Pd(PPh₃)₂Cl₂ (10 mol%), PCy₃ (20 mol%), Cu(OAc)₂ (3 equiv), DABCO (1 equiv), K₂CO₃ (2 equiv), and toluene (5 mL) at 130 °C for 12 h under air atmosphere. ^{*b*}Isolated yield. ^{*c*}**1a** is used as the test substrate and worked on a larger 1 g scale. trace < 10.

We commenced our studies with a model reaction of benzamide (1a), and norbornene (NBE) as the substrates. After detailed screening of the reaction parameters, we found that the optimal conditions were the use of benzamide (0.5 mmol), norbornene (1.0 mmol), Pd(PPh₃)₂Cl₂ (10 mol%), PCy₃ (20 mol%), Cu(OAc)₂ (1.5 mmol, 3 equiv), K₂CO₃ (1.0 mmol, 2 equiv), DABCO (0.5 mmol, 1 equiv), and toluene (5 mL) at 130 °C under air atmosphere for 12 h, and the expected annulation target product 3a was acquired in a yield of 85%. Compared with air conditions, the yield of the reaction decreased when carried out in O₂ or N₂ atmosphere, and the target product 3a was obtained with 34% and 71% yields, respectively (Table 1, entries 2-3). In particular, the control experiment showed that palladium catalysts were decisive for this annulation reaction, due to the desired product was not observed when catalyst was lacked (Table 1, entry 4). Other available types of palladium species, for example Pd₂(dba)₃, Pd(OAc)₂, Pd(PPh₃)₄, and PdCl₂, showed lower catalytic efficiency (Table 1, entries 5-8). It was found that there almost no product was obtained when PPh₃, 'Bu₃P, and X-Phos instead of PCy₃ (Table 1, entries 9-11). Furthermore, when replacing oxidant Cu(OAc)₂ with

 $CuCl_2$, benzoquinone (BQ), and $K_2S_2O_8$, no target product was detected (Table 1, entries 12-14). Subsequently, during the routine screening of bases, it was discovered that K_2CO_3 played a crucial role in the silvlation reaction, due to other bases, such as K₃PO₄, Cs₂CO₃, KOAc, and 'BuOK, all were inferior to K₂CO₃ (Table 1, entries 15-18). We were pleased to find that increasing or decreasing the amount of K₂CO₃ will result in a slight decrease in yield (Table 1, entries 19-20). that Next, several solvents, including CH₃CN, DMF, and 1,4-dioxane, that frequently used in this transformation were checked. It could acquire acquire target product **3a** in 32% yield when using CH₃CN as reaction solvent (Table 1, entrie 21). Nevertheless, the expected product was unexpectedly not obtained when employing DMF, and 1,4-dioxane (Table 1, entrie 22). It seems that the absence of DABCO resulted in a lower efficiency of the reaction, the target product almost not could detect (Table 1, entry 23). We suppose this may be due to the fact that DABCO as an organic base, can promote the coordination between NBE and metal centers. Furthermore, it led to a lower or similar yield when the temperature was adjusted to a lower or higher value (Table 1, entries 24 and 25). Finally, the reaction was monitored by changing the reaction time to study the reaction condition. It led to 73% and 79% yield when the reaction time was adjusted to 10 h and 14 h (Table 1, entries 26-27). To our delight, **3a** can be acquired in 73% yield when **1a** is used as the test substrate and worked on a larger 1 g scale.

(b) Synthesis of N-((2S)-bicyclo[2.2.1]hept-5-en-2-yl)benzamide (4a)



The stirred mixture of benzamide (60.5 mg, 0.5 mmol, 1.0 equiv), norbornadiene (92 mg, 1.0 mmol 2.0 equiv), Pd(PPh₃)₂Cl₂ (35.1 mg, 0.05 mmol, 10 mol%), PCy₃ (28 mg, 0.1 mmol, 20 mol%), Cu(OAc)₂ (279 mg, 1.5 mmol, 3.0 equiv), K₃PO₄ (424 mg,

1.0 mmol, 4.0 equiv), and DABCO (56 mg, 0.5 mmol, 1.0 equiv) in toluene (5 mL), place in a preheated oil bath at 130 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate=5:1 unless otherwise noted) to provide the desired products **4a** as a pale yellow solid.

Table S2. Screening of Optimal Reaction Conditions^a



Entry	variation from the standard conditions	Yield/% ^b
1	none	76 (62 ^c)
2	under O ₂ atmosphere	23
3	under N ₂ atmosphere	55
4	without Pd(PPh ₃) ₂ Cl ₂	0
5	Pd ₂ (dba) ₃ instead of Pd(PPh ₃) ₂ Cl ₂	26
6	Pd(OAc) ₂ instead of Pd(PPh ₃) ₂ Cl ₂	0
7	PdCl ₂ instead of Pd(PPh ₃) ₂ Cl ₂	60
8	Pd(PPh ₃) ₄ instead of Pd(PPh ₃) ₂ Cl ₂	trace
9	PPh ₃ instead of PCy ₃	35
10	'Bu ₃ P instead of PCy ₃	28
11	X-Phos instead of PCy ₃	22
12	CuCl ₂ instead of Cu(OAc) ₂	0
13	BQ instead of Cu(OAc) ₂	0
14	$K_2S_2O_8$ instead of Cu(OAc) ₂	0
15	K ₂ CO ₃ instead of K ₃ PO ₄	45
16	Cs ₂ CO ₃ instead of K ₃ PO ₄	trace
17	KOH instead of K ₃ PO ₄	51

18	⁴ BuOK instead of K ₃ PO ₄	trace
19	K ₃ PO ₄ (5 equiv)	73
20	K ₃ PO ₄ (3 equiv)	67
21	MeCN instead of Toluene	0
22	Dioxane or DMF instead of Toluene	0
23	without DABCO	40
24	at 140 °C	72
25	at 120 °C	60
26	reaction for 10 h	65
27	reaction for 14 h	68

^{*a*}Conditions: benzamide (0.5 mmol, 1.0 equiv), norbornadiene (1.0 mmol, 2 equiv), Pd(PPh₃)₂Cl₂ (10 mol%), PCy₃ (20 mol%), Cu(OAc)₂ (3 equiv), DABCO (1 equiv), K₃PO₄ (4 equiv), and toluene (5 mL) at 130 °C for 12 h under air atmosphere. ^{*b*}Isolated yield. ^{*c*}**1a** is used as the test substrate and worked on a larger 1 g scale. trace < 10.

We commenced our studies with a model reaction of benzamide (1a), and norbornadiene (NBD) as the substrates. After detailed screening of the reaction parameters, we found that the optimal conditions were the use of benzamide (0.5 mmol), norbornadiene (1.0 mmol), Pd(PPh₃)₂Cl₂ (10 mol%), PCy₃ (20 mol%), Cu(OAc)₂ (1.5 mmol, 3 equiv), K₃PO₄ (2.0 mmol, 4 equiv), DABCO (0.5 mmol, 1 equiv), and toluene (5 mL) at 130 °C under air atmosphere for 12 h, and the expected annulation target product **4a** was acquired in a yield of 76%. Compared with air conditions, the yield of the reaction decreased when carried out in O₂ or N₂ atmosphere, and the target product **4a** was obtained with 23% and 55% yields, respectively (Table 1, entries 2-3). In particular, the control experiment showed that palladium catalysts were decisive for this annulation reaction, due to the desired product was not observed when catalyst was lacked (Table 1, entry 4). Other available types of palladium species, for example Pd₂(dba)₃, Pd(OAc)₂, Pd(PPh₃)₄, and PdCl₂, showed lower catalytic efficiency (Table 1, entries 5-8). It was found that the target product was obtained in 35%, 28%, and 22% yields respectively, when PPh₃, ^{*t*}Bu₃P, and X-Phos instead of PCy₃ (Table 1, entries 9-11). Furthermore, when replacing oxidant $Cu(OAc)_2$ with $CuCl_2$, benzoquinone (BQ), and $K_2S_2O_8$, no target product was detected (Table 1, entries 12-14). Subsequently, during the routine screening of bases, it was discovered that K_3PO_4 , played a crucial role in the silvlation reaction, due to other bases, such as K₂CO₃, Cs₂CO₃, KOH, and 'BuOK, all were inferior to K_3PO_4 (Table 1, entries 15-18). We were pleased to find that increasing or decreasing the amount of K₃PO₄ will result in a slight decrease in yield (Table 1, entries 19-20). Next, several solvents, including CH₃CN, DMF, and 1,4-dioxane, that frequently used in this transformation were checked. Nevertheless, the expected product was unexpectedly not obtained when employing CH₃CN, DMF, and 1,4-dioxane (Table 1, entrie 21-22). It seems that the absence of DABCO resulted in a lower efficiency of the reaction, the target product was obtained in 40% yield (Table 1, entry 23). We suppose this may be due to the fact that DABCO as an organic base, can promote the coordination between NBE and metal centers. Furthermore, it led to a lower or similar yield when the temperature was adjusted to a lower or higher value (Table 1, entries 24 and 25). Finally, the reaction was monitored by changing the reaction time to study the reaction condition. It led to 65% and 68% yield when the reaction time was adjusted to 10 h and 14 h (Table 1, entries 26-27). To our delight, 4a can be acquired in 68% yield when 1a is used as the test substrate and worked on a larger 1 mmol scale.

3) The Kinetic Isotope Experiments

To gain additional insights into the mechanism for the reaction, kinetic isotopic effect (KIE) experiments were carried out, giving intermolecular competeitive experiment KIE and parallel experiment KIE values of 4.0 and 3.3, respectively. The result shows that the cleavage of C–H bond was a rate-determining step in this conversion. Moreover, when replacing norbornene with styrene or oxanorbornadiene (ONBD), no annulation product was detected. when NBD was used instead of NBE.

Herein, we detail our results.

Synthesis of (1a-D5)¹





To a strirred solution of benzoic acid-d₅ (0.61 g, 5 mmol, 1.0 equiv.), pyridine (0.25 ml, 3.1 mmol, 0.62 equiv.), and Boc₂O (1.40 g, 6.5 mmol, 1.3 equiv.) in 1, 4-dioxane (10 ml) at room temperature was added ammonium bicarbonate (0.50 g, 6.3 mmol, 1.26 equiv.). The reaction was stirred overnight at room temperature and then partitioned between EtOAc (50 ml) and H₂O (50 ml). The organic layer was separated, washed consecutively with water (50 ml) and 0.6 N aqueous HCl (50 ml), dried (NaSO₄), and filtered. The filtrate was concentrated under reduced pressure to provide **1a-D₅** as white solid in 83% yield (0.52 g).

Benzamide-D₅ (1a-D₅)¹

1H NMR (400 MHz, CDCl₃) δ 7.81 (s, 0.26H), 7.52 (s, 0.04H), 7.43 (s, 0.10H), 6.33 (s, 2H).



Intermolecular Competetion Experiment



To a 25 mL schlenk tube equipped with magnetic bar was added benzamide (1a, 30.3 mg, 0.25 mmol, 0.5 equiv), benzamide- D_5 (1a- D_5 , 31.5 mg, 0.25 mmol, 0.5 equiv), Norbornene (94 mg, 1 mmol, 2.0 equiv), Pd(PPh_3)₂Cl₂ (35.1 mg, 0.05 mmol, 10 mol %), Cu(OAc)₂ (279 mg, 1.5 mmol, 3.0 equiv), K₂CO₃ (138 mg, 1.0 mmol, 2.0 equiv), and DABCO (56 mg, 0.5 mmol, 1.0 equiv) in toluene (5 mL). The reaction mixture was placed in a pre-heated oil bath (130 °C) and stirred for 4 h. The reaction mixture was cooled to rt and filtered over celite. The solvent was then removed under reduced pressure and the residue was purified by column chromatography on silica gel with PE and EA (petroleum ether: ethyl acetate=100:1) as the eluent to afford product (28 mg).

¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 7.73 Hz, 0.8H), 7.60 (t, *J* = 7.32 Hz, 0.8H), 7.49 (d, *J* = 7.73 Hz, 0.8H), 7.34 (d, *J* = 7.32 Hz, 0.8H), 3.14 (d, *J* = 5.70 Hz, 1H), 2.59 (s, 1H), 2.49 (d, *J* = 6.10 Hz, 1H), 2.41 (s, 1H), 1.72-1.68 (m, 2H), 1.46-1.43 (m, 1H), 1.36-1.37 (m, 1H), 0.95-0.92 (m, 1H), 0.81-0.78 (m, 1H).





To a 25 mL schlenk tube equipped with magnetic bar was added benzamide (1a, 60.5 mg, 0.5 mmol, 1.0 equiv), Norbornene (94 mg, 1 mmol, 2.0 equiv), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol, 10 mol %), $Cu(OAc)_2$ (279 mg, 1.5 mmol, 3.0 equiv), K_2CO_3 (138 mg, 1.0 mmol, 2.0 equiv), and DABCO (56 mg, 0.5 mmol, 1.0 equiv) in toluene (5 mL). The reaction mixture was placed in a pre-heated oil bath (130 °C) and stirred for 6 h. The reaction mixture was cooled to rt and filtered over celite. The solvent was then removed under reduced pressure and the residue was purified by column

chromatography on silica gel with PE and EA (petroleum ether: ethyl acetate=100:1) as the eluent to afford product 3a in 40% yield as a colorless oil liquid (40 mg). $3a-D_4$ was obtained according to above procedure in 12% yield as a colorless oil liquid (12 mg).

Styrene Instead of Norbornene Experiment



Scheme 10

The stirred mixture of benzamide (60.5 mg, 0.5 mmol, 1.0 equiv), Styrene (104 mg, 1.0 mmol 2.0 equiv), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol, 10 mol %), $Cu(OAc)_2$ (279 mg, 1.5 mmol, 3.0 equiv), K_2CO_3 (138 mg, 1.0 mmol, 2.0 equiv), and DABCO (56 mg, 0.5 mmol, 1.0 equiv) in toluene (5 mL), place in a preheated oil bath at 130 °C for 12 h. It was found that the annulation product was not detected.

Oxanorbornadiene (ONBD) Instead of Norbornene Experiment





The stirred mixture of benzamide (60.5 mg, 0.5 mmol, 1.0 equiv), Oxanorbornadiene (ONBD) (210 mg, 1.0 mmol 2.0 equiv), $Pd(PPh_3)_2Cl_2$ (35.1 mg, 0.05 mmol, 10 mol%), $Cu(OAc)_2$ (279 mg, 1.5 mmol, 3.0 equiv), K_2CO_3 (138 mg, 1.0 mmol, 2.0 equiv), and DABCO (56 mg, 0.5 mmol, 1.0 equiv) in toluene (5 mL), place in a preheated oil bath at 130 °C for 12 h. It was found that the annulation product was not detected.

4) Larger-Scale Experiment



The stirred mixture of benzamide (1 g, 8.3 mmol, 1.0 equiv), Norbornene (1.56 g, 16.6 mmol, 2.0 equiv), $Pd(PPh_3)_2Cl_2$ (582.7 mg, 0.83 mmol, 10 mol %), $Cu(OAc)_2$ (4.5 g, 24.9 mmol, 3.0 equiv), K_2CO_3 (2.29 g, 16.6 mmol, 2.0 equiv), and DABCO (929.6 mg, 8.3 mmol, 1.0 equiv) in toluene (60 mL), place in a preheated oil bath at 130 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether: ethyl acetate=100:1) to provide the desired products **3a** as a brownish red oil liquid (986 mg, 60% yield).



Scheme 13

The stirred mixture of benzamide (1 g, 8.3 mmol, 1.0 equiv), Norbornadiene (1527.2 mg, 16.6 mmol, 2.0 equiv), $Pd(PPh_3)_2Cl_2$ (582.7 mg, 0.83 mmol, 10 mol %), $Cu(OAc)_2$ (4.5 g, 24.9 mmol, 3.0 equiv), K_3PO_4 (7.04 g, 33.2 mmol, 4.0 equiv), and DABCO (929.6 mg, 8.3 mmol, 1.0 equiv) in toluene (70 mL), place in a preheated oil bath at 130 °C for 12 h. After the completion of the reaction (monitored by TLC), the reaction mixture was filtered and the filtrate was evaporated under reduced pressure and the crude product was purified by column chromatography (petroleum ether:

ethyl acetate=10:1) to provide the desired products **4a** as a pale yellow solid (1235 mg, 62% yield).

5) Characterization Data



(4a*R*,9a*S*)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3a): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 85% (84 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.70 (d, *J* = 7.68 Hz, 1H), 7.60 (t, *J* = 7.68 Hz, 1H), 7.49 (d, *J* = 7.68 Hz, 1H), 7.35 (d, *J* = 7.41 Hz, 1H), 3.14 (d, *J* = 6.04 Hz, 1H), 2.59 (d, *J* = 2.47 Hz, 1H), 2.49 (d, *J* = 6.04 Hz, 1H), 2.40 (d, *J* = 2.74 Hz, 1H), 1.75-1.65 (m, 2H), 1.49-1.43 (m, 1H), 1.39-1.37 (m, 1H), 0.93 (d, *J* = 10.43 Hz, 1H), 0.79 (d, *J* = 10.43 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 208.9, 157.2, 139.0, 134.9, 127.4, 126.1, 123.1, 55.8, 48.0, 41.2, 40.3, 32.2, 28.8, 28.6. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-6-methoxy-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3b): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 72% (82 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.51 Hz, 1H), 6.90 (s, 1H), 6.87 (d, *J* = 8.51 Hz, 1H), 3.88 (s, 3H), 3.07 (d, *J* = 6.04 Hz, 1H), 2.57 (d, *J* = 1.92 Hz, 1H), 2.47 (d, *J* = 6.04 Hz, 1H), 2.39 (s, 1H), 1.71-1.62 (m, 2H), 1.42 (d, *J* = 9.88 Hz, 1H), 1.36 (d, *J* = 9.88 Hz, 1H), 0.94 (d, *J* = 10.70 Hz, 1H), 0.83 (d, *J* = 10.43 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.0, 165.5, 160.2, 132.4, 124.8, 115.3, 109.1, 56.2, 55.6, 48.0, 41.2, 40.1, 32.2, 28.8, 28.7. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-6-methyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3c): Purification by column chromatography on silica gel (petroleum ether) as a brownish red oil liquid, isolated yield 83% (88 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.60 (d, *J* = 7.73 Hz, 1H), 7.28 (s, 1H), 7.16 (d, *J* = 7.73 Hz, 1H), 3.08 (d, *J* = 5.76 Hz, 1H), 2.58 (s, 1H), 2.48 (d, *J* = 6.04 Hz, 1H), 2.44 (s, 3H), 2.39 (s, 1H), 1.69-1.63 (m, 2H), 1.45-1.42 (m, 1H), 1.38-1.36 (m, 1H), 0.93 (d, *J* = 10.70 Hz, 1H), 0.81 (d, *J* = 10.43 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 208.4, 157.8, 146.1, 136.8, 128.7, 126.5, 123.0, 56.0, 47.8, 41.2, 40.2, 32.2, 28.9, 28.7, 22.1. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-6-ethyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3d): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 85% (96 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 7.68 Hz, 1H), 7.30 (s, 1H), 7.18 (d, *J* = 7.68 Hz, 1H), 3.09 (d, *J* = 5.76 Hz, 1H), 2.73 (dd, *J* = 15.09 Hz, 7.68 Hz, 2H), 2.58 (d, *J* = 2.47 Hz, 1H), 2.47 (d, *J* = 6.04 Hz, 1H), 2.39 (d, *J* = 3.02 Hz, 1H), 1.70-1.62 (m, 2H), 1.44-1.42 (m, 1H), 1.38-1.35 (m, 1H), 1.28 (d, *J* = 7.68 Hz, 3H), 0.93 (d, *J* = 10.43 Hz, 1H), 0.81 (d, *J* = 10.43 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 208.4, 157.8, 152.3, 137.0, 127.6, 125.1, 123.1, 56.1, 47.9, 41.2, 40.2, 32.2, 29.3, 28.9, 28.7, 15.2. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-6-(tert-butyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3e): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 88% (112 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.23 Hz, 1H), 7.48 (s, 1H), 7.39 (d, *J* = 8.23 Hz, 1H), 3.10 (d, *J* = 6.04 Hz, 1H), 2.58 (d, *J* = 2.74 Hz, 1H), 2.58 (d, *J* = 2.47 Hz, 1H), 2.47 (d, *J* = 6.04 Hz, 1H), 2.41 (d, *J* = 3.02 Hz, 1H), 1.71-1.62 (m, 2H), 1.45-1.43 (m, 1H), 1.35 (s, 9H), 1.25 (s, 1H), 0.93 (d, *J* = 10.43 Hz, 1H), 0.83 (d, *J* = 10.43 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 208.5, 159.1, 157.6, 136.7, 125.2, 122.7, 122.5, 56.1, 48.1, 41.2, 40.2, 35.5, 32.2, 31.2, 28.9, 28.7. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-6-fluoro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3f): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 70% (76 mg). ¹H NMR (400 MHz, CDCl₃) δ 8.52 (s, 1H), 8.48-8.45 (m, 1H), 7.68 (d, *J* = 8.46 Hz, 1H), 3.26 (d, *J* = 5.96 Hz, 1H), 2.67 (d, *J* = 2.69 Hz, 1H), 2.64 (d, *J* = 6.15 Hz, 1H), 2.49 (s, 1H), 1.78-1.74 (m, 1H), 1.69-1.67 (m, 1H), 1.54-1.52 (m, 1H), 1.43-1.41 (m, 1H), 1.03 (d, *J* = 10.57 Hz, 1H), 0.78 (d, *J* = 10.69 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 206.6, 162.7, 147.8, 140.1, 129.2, 127.3, 118.5, 56.4, 48.2, 41.4, 40.8, 32.5, 28.9, 28.4. ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ -113.06. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-6-chloro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3g): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red solid, isolated yield 78% (90 mg), mp: 140-141 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.62 (d, *J* = 8.06 Hz, 1H), 7.48 (s, 1H), 7.32 (d, *J* = 8.06 Hz, 1H), 3.11 (d, *J* = 5.97 Hz, 1H), 2.59 (d, *J* = 2.99 Hz, 1H), 2.50 (d, *J* = 6.27 Hz, 1H), 2.40 (d, *J* = 2.99 Hz, 1H), 1.72-1.69 (m, 1H), 1.66-1.62 (m, 1H), 1.45-1.42 (m, 1H), 1.38-1.36 (m, 1H), 0.96 (d, *J* = 10.75 Hz, 1H), 0.79 (d, *J* = 10.75 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.3, 158.6, 141.4, 137.5, 128.2, 126.4, 124.3, 56.0, 47.7, 41.2, 40.4, 32.2, 28.8, 28.5. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-6-(trifluoromethyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9one (3h): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red solid, isolated yield 72% (96 mg), mp: 151-153 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, J = 8.05 Hz, 1H), 7.78 (s, 1H), 7.60 (d, J =7.95 Hz, 1H), 3.21 (d, J = 5.99 Hz, 1H), 2.63 (d, J = 2.79 Hz, 1H), 2.57 (d, J = 6.09Hz, 1H), 2.46 (d, J = 2.99 Hz, 1H), 1.76-1.71 (m, 1H), 1.68-1.65 (m, 1H), 1.49-1.46 (m, 1H), 1.42-1.39 (m, 1H), 0.99 (d, J = 10.63 Hz, 1H), 0.78 (d, J = 10.63 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 207.9, 157.2, 141.6, 136.2 (d, J = 31.90 Hz), 123.7 (q, J = 271.70 Hz), 124.5 (q, J = 3.50 Hz), 123.7, 123.4 (q, J = 3.90 Hz), 56.0, 48.0, 41.3, 40.7, 32.3, 28.8, 28.5. ¹⁹F {¹H} NMR (400 MHz, CDCl₃) δ -62.82. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-6-nitro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3i): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red solid, isolated yield 67% (81 mg), mp: 178-179 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.20 (dd, J = 6.95 Hz, 1.50 Hz, 1H), 7.89 (d, J = 8.86Hz, 1H), 7.83 (d, J = 8.27 Hz, 1H), 3.27 (d, J = 6.08 Hz, 1H), 2.66-2.62 (m, 2H), 2.50 (d, J = 3.65 Hz, 1H), 1.78-1.74 (m, 1H), 1.71-1.67 (m, 1H), 1.53-1.48 (m, 1H), 1.44-1.41 (m, 1H), 1.03 (d, J = 10.82 Hz, 1H), 0.77 (d, J = 10.70 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.1, 157.8, 152.1, 143.1, 133.4, 124.2 (q, J = 14.81 Hz), 122.3 (q, J = 128.01 Hz), 56.4, 48.0, 41.4, 40.9, 32.4, 28.7, 28.5. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-7-methoxy-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3j): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 73% (83 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.63 (d, *J* = 8.51 Hz, 1H), 6.90-6.87 (m, 2H), 3.88 (s, 3H), 3.07 (d, *J* = 6.04 Hz, 1H), 2.56 (d, *J* = 1.93 Hz, 1H), 2.47 (d, *J* = 6.04 Hz, 1H), 2.39 (s, 1H), 1.71-1.62 (m, 2H), 1.43-1.41 (m, 1H), 1.37-1.35 (m, 1H), 0.93 (d, *J* = 10.70 Hz, 1H), 0.83 (d, *J* = 10.43 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.0, 165.5, 160.2, 132.4, 124.8, 115.3, 109.1, 56.2, 55.6, 48.0, 41.2, 40.1, 32.2, 28.8, 28.7. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-7-methyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3k): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 68% (72 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.50 (s, 1H), 7.42 (d, *J* = 7.91 Hz, 1H), 7.37 (d, *J* = 7.54 Hz, 1H), 3.09 (d, *J* = 5.65 Hz, 1H), 2.58 (s, 1H), 2.48 (d, *J* = 6.03 Hz, 1H), 2.39 (s, 4H), 1.70-1.67 (m, 2H), 1.44-1.42 (m, 1H), 1.38-1.35 (m, 1H), 0.92 (d, *J* = 10.55 Hz, 1H), 0.79 (d, *J* = 10.55 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 209.0, 154.7, 139.2, 137.3, 136.2, 125.8, 123.1, 56.2, 47.7, 41.2, 40.3, 32.1, 28.8, 28.6, 21.1. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-7-chloro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (31): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 73% (85 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 1.89 Hz, 1H), 7.55 (dd, *J* = 8.14 Hz, 2.01 Hz, 1H), 7.43 (d, *J* = 8.03 Hz, 1H), 3.11 (d, *J* = 5.90 Hz, 1H), 2.59 (d, *J* = 3.31 Hz, 1H), 2.52 (d, *J* = 5.90 Hz, 1H), 2.39 (d, *J* = 2.42 Hz, 1H), 1.72-1.66 (m, 2H), 1.45-1.42 (m, 1H), 1.39-1.36 (m, 1H), 0.96 (d, *J* = 10.58 Hz, 1H), 0.78 (d, *J* = 10.58 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.5, 155.2, 140.5, 134.9, 133.8, 127.4, 123.0, 56.3, 47.6, 41.2, 40.5, 32.2, 28.8, 28.5. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-7-(trifluoromethyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9one (3m): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 70% (93 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.96 (s, 1H), 7.83 (d, J = 7.88 Hz, 1H), 7.63 (d, J = 8.06Hz, 1H), 3.21 (d, J = 5.96 Hz, 1H), 2.62 (d, J = 2.80 Hz, 1H), 2.56 (d, J = 6.13 Hz, 1H), 2.44 (d, J = 3.33 Hz, 1H), 1.74-1.71 (m, 1H), 1.69-1.65 (m, 1H), 1.49-1.46 (m, 1H), 1.41-1.38 (m, 1H), 0.98 (d, J = 10.51 Hz, 1H), 0.77 (d, J = 10.69 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 207.5, 160.2, 139.4, 131.3 (q, J = 3.40 Hz), 130.1 (q, J = 32.70 Hz), 126.9, 123.8 (q, J = 270.80 Hz), 120.4 (q, J = 3.90 Hz), 56.0, 48.1, 41.3, 40.6, 32.3, 28.8, 28.5. ¹⁹F {¹H} NMR (400 MHz, CDCl₃) δ -62.66. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-7-nitro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3n): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale yellow oil liquid, isolated yield 56% (68 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.70 (dd, *J* = 8.48 Hz, 5.48 Hz, 1H), 7.14 (dd, *J* = 8.48 Hz, 1.94 Hz, 1H), 7.43 (td, *J* = 8.66 Hz, 2.12 Hz, 1H), 3.12 (d, *J* = 6.01 Hz, 1H), 2.59 (d, *J* = 3.18 Hz, 1H), 2.52 (d, *J* = 6.18 Hz, 1H), 2.40 (d, *J* = 3.36 Hz, 1H), 1.73-1.70 (m, 1H), 1.66-1.63 (m, 1H), 1.45-1.43 (m, 1H), 1.39-1.36 (m, 1H), 0.97 (d, *J* = 10.60 Hz, 1H), 0.81 (d, *J* = 10.60 Hz, 1H). ¹³C {¹H} NMR (100 MHz, CDCl₃) δ 206.9, 167.4 (d, *J* = 261.62 Hz), 160.1 (d, *J* = 9.77 Hz), 135.5, 125.4 (d, *J* = 10.28 Hz), 115.7 (d, *J* = 24.16 Hz), 112.6 (d, *J* = 22.10 Hz), 56.1, 47.8 (d, *J* = 2.03 Hz), 41.2, 40.3, 32.2, 28.8, 28.6. The spectral data were in accordance with the literature.¹



(4a*R*,9a*S*)-8-fluoro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3o): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 81% (87 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.58-7.53 (m, 1H), 7.25 (d, J = 3.10 Hz, 1H), 6.94 (t, J = 8.74 Hz, 1H), 3.14 (d, J = 6.06 Hz, 1H), 2.62 (d, J = 2.11 Hz, 1H), 2.50 (d, J = 6.06 Hz, 1H), 2.62 (d, J = 2.11 Hz, 1H), 2.50 (d, J = 6.06 Hz, 1H), 2.40 (d, J = 2.40 Hz, 1H), 1.65-1.62 (m, 2H), 1.44-1.41 (m, 1H), 1.37-1.35 (m, 1H), 0.97 (d, J = 10.87 Hz, 1H), 0.87 (d, J = 10.25 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 205.2, 159.7 (d, J = 25.14 Hz), 157.2, 136.8 (d, J = 8.21 Hz), 126.8, 121.9 (d, J = 4.33 Hz), 114.2 (d, J = 19.51 Hz), 56.2, 48.0, 41.5, 40.6, 32.2, 28.8, 28.5. ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ -113.36. The spectral data were in accordance with the literature.²



(4aR,9aS)-6,7-dimethyl-1,2,3,4,4a,9a-hexahydro-9H-1,4-methanofluoren-9-one

(3p): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 90% (102 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.46 (s, 1H), 7.25 (s, 1H), 3.05 (d, *J* = 6.04 Hz, 1H), 2.56 (s, 1H), 2.45 (d, *J* = 5.76 Hz, 1H), 2.36 (s, 1H), 2.34 (s, 3H), 2.28 (s, 3H), 1.69-1.66 (m, 1H), 1.62-1.59 (m, 1H), 1.43-1.40 (m, 1H), 1.36-1.34 (m, 1H), 0.91 (d, *J* = 10.43 Hz, 1H), 0.79 (d, *J* = 10.43 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 208.6, 155.4, 145.1, 137.2, 136.3, 126.8, 123.5, 56.1, 47.6, 41.1, 40.1, 32.1, 28.8, 28.6, 20.8, 19.7. HRMS (ESI) m/z calcd for C₁₆H₁₉O+ (M+H)⁺ 227.1430, found 227.1433.



(4aR,9aS)-6,7-dichloro-1,2,3,4,4a,9a-hexahydro-9H-1,4-methanofluoren-9-one

(3q): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 53% (71 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.76 (s, 1H), 7.61 (s, 1H), 3.11 (d, *J* = 6.14 Hz, 1H), 2.60 (d, *J* = 2.60 Hz, 1H), 2.53 (d, *J* = 5.90 Hz, 1H), 2.40 (d, *J* = 3.07 Hz, 1H), 1.64-1.63 (m, 2H), 1.45-1.42 (m, 1H), 1.39-1.36 (m, 1H), 0.99 (d, *J* = 10.62 Hz, 1H), 0.79 (d, *J* = 10.62 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 206.3, 155.9, 139.4, 138.6, 132.5, 128.1, 124.6, 56.2, 47.5, 41.2, 40.6, 32.3, 28.7, 28.5. HRMS (ESI) m/z calcd for C₁₄H₁₃Cl₂O+ (M+H)⁺ 267.0338, found 267.0341.



(4aR,9aS)-6-fluoro-5-(trimethylsilyl)-1,2,3,4,4a,9a-hexahydro-9H-1,4-

methanofluoren-9-one (3r): Purification by column chromatography on silica gel

(petroleum ether: ethyl acetate=100:1) as a brownish red oil liquid, isolated yield 65% (94 mg). ¹H NMR (400 MHz, CDCl₃) δ 7.71 (dd, J = 8.24 Hz, 5.81 Hz, 1H), 6.98 (t, J = 8.76 Hz, 1H), 3.23 (d, J = 6.02 Hz, 1H), 2.60 (s, 1H), 2.50 (d, J = 6.02 Hz, 1H), 2.29 (s, 1H), 1.50-1.45 (m, 2H), 1.39-1.37 (m, 1H), 1.31-1.29 (m, 1H), 0.94 (d, J =10.58 Hz, 1H), 0.81 (d, J = 10.56 Hz, 1H), 0.43 (s, 9H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 207.6, 172.4 (d, J = 252.19 Hz), 165.3 (d, J = 12.62 Hz), 135.0, 126.5 (d, J= 11.82 Hz), 123.7, 115.3 (d, J = 30.22 Hz), 55.9, 48.5, 41.8 (d, J = 246.93 Hz), 35.3, 31.9, 28.5 (d, J = 95.31 Hz), 28.2, 25.6 (d, J = 285.11 Hz). ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ -112.19. HRMS (ESI) m/z calcd for C₁₇H₂₂FOSi+ (M+H)⁺ 289.1418, found 289.1421.



(4aR,11aS)-1,2,3,4,4a,11a-hexahydro-11H-1,4-methanobenzo[b]fluoren-11-one

(3s): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=100:1) as a pale yellow solid, isolated yield 76% (94 mg), mp: 198-199 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.27 (s, 1H), 7.97 (d, J = 8.29 Hz, 1H), 7.92 (s, 1H), 7.88 (d, J = 8.29 Hz, 1H), 7.58 (t, J = 7.09 Hz, 1H), 7.49 (d, J = 7.62 Hz, 1H), 3.33 (d, J = 6.55 Hz, 1H), 2.68 (d, J = 2.67 Hz, 1H), 2.61 (d, J = 6.55 Hz, 1H), 2.53 (d, J =3.08 Hz, 1H), 1.71-1.66 (m, 2H), 1.55-1.50 (m, 1H), 1.44-1.39 (m, 1H), 0.97 (d, J = 10.43 Hz, 1H), 0.83 (d, J = 10.43 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 209.5, 150.7, 137.5, 136.5, 132.3, 130.4, 128.5, 127.9, 126.1, 124.5, 123.7, 56.5, 47.7, 42.6, 41.0, 32.8, 28.8, 28.8. The spectral data were in accordance with the literature.¹



N-((2S)-bicyclo[2.2.1]hept-5-en-2-yl)benzamide (4a): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a pale yellow solid, isolated yield 76% (81 mg), mp: 144-145 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.74 (d, J = 7.29 Hz, 1H), 7.47 (t, J = 7.29 Hz, 1H), 7.49 (d, J = 7.68 Hz, 1H), 7.39 (t, J = 7.79 Hz, 2H), 6.32 (s, 1H), 6.18-6.16 (m, 1H), 6.12-6.10 (m, 1H), 3.96-3.93 (m, 1H), 2.90 (s, 2H), 1.83-1.77 (m, 1H), 1.58 (d, J = 8.79 Hz, 1H), 1.47 (d, J = 8.79 Hz, 1H), 1.36-1.32 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.3, 138.7, 134.8, 134.7, 131.2, 128.4, 126.8, 50.4, 47.9, 46.0, 41.0, 35.3. HRMS (ESI) m/z calcd for C₁₄H₁₆NO+ (M+H)⁺ 214.1226, found 214.1229.



MeO

N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-4-methoxybenzamide (4b): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a brownish red oil liquid, isolated yield 81% (98 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.71 (d, J = 8.29 Hz, 2H), 6.89 (d, J = 7.70 Hz, 2H), 6.17 (s, 2H), 6.12 (s, 1H), 3.93 (s, 1H), 3.83 (s, 3H), 2.89 (s, 2H), 1.80 (t, J = 9.64 Hz, 1H), 1.58 (d, J = 8.15 Hz, 1H), 1.46 (d, J = 8.15 Hz, 1H), 1.31 (d, J = 11.86 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.8, 162.0, 138.6, 134.7, 128.6, 127.1, 113.6, 55.3, 50.4, 47.9, 46.0, 41.0, 35.4. HRMS (ESI) m/z calcd for C₁₅H₁₈NO₂+ (M+H)⁺ 244.1332, found 244.1335.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-4-methylbenzamide (4c): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a pale yellow oil liquid, isolated yield 72% (82 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.64 (d, J = 7.69 Hz, 2H), 7.21 (d, J = 7.69 Hz, 2H), 6.19-6.17 (s, 2H), 6.13 (s, 1H), 3.95 (s, 1H), 2.90 (s, 1H), 2.38 (s, 3H), 2.33 (s, 1H), 1.84-1.78 (m, 2H), 1.59 (d, J = 8.79 Hz, 1H), 1.47 (d, J = 8.79 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.2, 141.6, 138.7, 134.7, 132.0, 129.1, 126.8, 50.4, 47.9, 46.1, 41.0, 35.4, 21.4. HRMS (ESI) m/z calcd for C₁₅H₁₈NO+ (M+H)⁺ 228.1383, found 228.1386.



N-((2S)-bicyclo[2.2.1]hept-5-en-2-yl)-4-fluorobenzamide (4d): Purification by

column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a brownish red oil liquid, isolated yield 92% (106 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.75 (t, J = 6.64 Hz, 2H), 7.05 (d, J = 8.39 Hz, 2H), 6.35 (s, 1H), 6.16 (s, 1H), 6.10 (s, 1H), 3.90 (s, 1H), 2.88 (s, 2H), 1.78 (t, J = 10.83 Hz, 1H), 1.57 (d, J = 8.74 Hz, 1H), 1.46 (d, J = 8.74 Hz, 1H), 1.33 (d, J = 11.88 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.3, 164.5 (d, J = 252.57 Hz), 138.7, 134.6, 131.0 (d, J = 2.98 Hz), 129.1 (d, J = 8.86 Hz), 115.4 (d, J = 21.73 Hz), 50.6, 47.9, 46.0, 41.0, 35.2. ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ -114.07. HRMS (ESI) m/z calcd for C₁₄H₁₅FNO+ (M+H)⁺ 232.1132, found 232.1135.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-4-chlorobenzamide (4e): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a brownish red oil liquid, isolated yield 85% (105 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.68 (d, *J* = 8.04 Hz, 2H), 7.36 (d, *J* = 8.04 Hz, 2H), 6.26 (d, *J* = 4.89 Hz, 1H), 6.18-6.17 (m, 1H), 6.12-6.11 (m, 1H), 3.93-3.90 (m, 1H), 2.89 (s, 2H), 1.83-1.78 (m, 1H), 1.59 (d, *J* = 8.74 Hz, 1H), 1.46 (d, *J* = 9.09 Hz, 1H), 1.34-1.30 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.3, 138.8, 137.5, 134.6, 133.2, 128.7, 128.3, 50.6, 47.9, 46.1, 41.0, 35.3. HRMS (ESI) m/z calcd for C₁₄H₁₅ClNO+ (M+H)⁺ 248.0837, found 248.0840.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3-methoxybenzamide (4f): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a brownish red oil liquid, isolated yield 73% (89 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.28 (s, 1H), 7.23 (d, *J* = 7.69 Hz, 1H), 7.19 (d, *J* = 7.34 Hz, 1H), 6.94 (d, *J* = 7.69 Hz, 1H), 6.18 (d, *J* = 4.54 Hz, 1H), 6.11 (s, 1H), 6.06 (s, 1H), 3.88 (s, 1H), 3.77 (s, 3H), 2.84 (s, 2H), 1.77-1.72 (m, 1H), 1.53 (d, *J* = 8.74 Hz, 1H), 1.40 (d, *J* = 8.74 Hz, 1H),

1.26 (d, J = 12.23 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.1, 159.7, 138.7, 136.4, 134.7, 129.4, 118.5, 117.4, 112.3, 55.4, 50.5, 47.9, 46.0, 41.0, 35.3. HRMS (ESI) m/z calcd for C₁₅H₁₈NO₂+ (M+H)⁺ 244.1332, found 244.1335.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3-methylbenzamide (4g): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a pale yellow oil liquid, isolated yield 77% (87 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.56 (s, 1H), 7.53-7.51 (m, 1H), 7.28 (d, *J* = 4.80 Hz, 2H), 6.24 (d, *J* = 4.80 Hz, 1H), 6.19-6.16 (m, 1H), 6.13-6.11 (m, 1H), 3.96-3.93 (m, 1H), 2.90 (s, 2H), 2.37 (s, 3H), 1.83-1.78 (m, 1H), 1.59 (d, *J* = 8.80 Hz, 1H), 1.47 (d, *J* = 8.80 Hz, 1H), 1.35-1.30 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.5, 138.7, 138.3, 134.8, 134.7, 132.0, 128.3, 127.5, 123.7, 50.4, 47.9, 46.0, 41.0, 35.3, 21.3. HRMS (ESI) m/z calcd for C₁₅H₁₈NO+ (M+H)⁺ 228.1383, found 228.1386.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3-chlorobenzamide (4h): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a brownish red oil liquid, isolated yield 83% (103 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.71 (s, 1H), 7.61 (d, *J* = 7.69 Hz, 1H), 7.43 (d, *J* = 8.04 Hz, 1H), 7.32 (t, *J* = 7.69 Hz, 1H), 6.35 (d, *J* = 5.24 Hz, 1H), 6.17 (s, 1H), 6.11-6.10 (m, 1H), 3.92-3.89 (m, 1H), 2.89 (s, 2H), 1.81-1.76 (m, 1H), 1.59 (d, *J* = 8.74 Hz, 1H), 1.47 (d, *J* = 8.74 Hz, 1H), 1.35-1.32 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 166.0, 138.8, 136.6, 134.6, 134.6, 131.2, 129.8, 127.2, 125.0, 50.7, 47.9, 46.0, 41.0, 35.2. HRMS (ESI) m/z calcd for C₁₄H₁₅ClNO+ (M+H)⁺ 248.0837, found 248.0840.



N-((2S)-bicyclo[2.2.1]hept-5-en-2-yl)-2-fluorobenzamide (4i): Purification by

column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a brownish red oil liquid, isolated yield 93% (107 mg). ¹H NMR (400 MHz, CDCl₃): δ 8.03 (td, J = 7.90 Hz, 1.63 Hz, 1H), 7.43-7.38 (m, 1H), 7.21 (t, J = 7.63 Hz, 1H), 7.08-7.03 (m, 1H), 6.80 (s, 1H), 6.17-6.14 (m, 1H), 6.10-6.08 (m, 1H), 3.96-3.92 (m, 1H), 2.89 (s, 2H), 1.81-1.76 (m, 1H), 1.57 (d, J = 8.99 Hz, 1H), 1.45 (d, J = 8.85 Hz, 1H), 1.31 (dt, J = 12.40 Hz, 3.41 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 162.7 (d, J = 3.24 Hz), 160.4 (d, J = 246.67 Hz), 138.7, 134.5, 132.9 (d, J = 8.86 Hz), 131.8 (d, J = 2.12 Hz), 124.6 (d, J = 3.26 Hz), 121.2 (d, J = 11.53 Hz), 115.8 (d, J = 24.76 Hz), 50.3, 47.8, 46.0, 40.9, 35.3. ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ -113.31. HRMS (ESI) m/z calcd for C₁₄H₁₅FNO+ (M+H)⁺ 232.1132, found 232.1135.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3,4-dimethylbenzamide (4j): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a brownish red oil liquid, isolated yield 87% (105 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.52 (s, 1H), 7.45 (d, *J* = 7.67 Hz, 1H), 7.12 (d, *J* = 7.84 Hz, 1H), 6.31 (d, *J* = 6.13 Hz, 1H), 6.17-6.15 (m, 1H), 6.11-6.09 (m, 1H), 3.94-3.91 (m, 1H), 2.88 (s, 2H), 2.26 (s, 6H), 1.80-1.75 (m, 1H), 1.57 (d, *J* = 9.37 Hz, 1H), 1.48 (d, *J* = 8.69 Hz, 1H), 1.35-1.31 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.4, 140.1, 138.6, 136.7, 134.7, 132.3, 129.5, 128.1, 124.1, 50.3, 47.9, 46.0, 40.9, 35.1, 19.7, 19.6. HRMS (ESI) m/z calcd for C₁₆H₂₀NO+ (M+H)⁺ 242.1539, found 242.1542.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3,5-dimethoxybenzamide (4k): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a brownish red oil liquid, isolated yield 80% (109 mg). ¹H NMR (400 MHz, CDCl₃): δ 6.85 (d, *J* = 1.87 Hz, 2H), 6.52 (s, 1H), 6.35 (d, *J* = 6.47 Hz, 1H), 6.16-6.14 (m, 1H), 6.09-6.07 (m, 1H), 3.90-3.87 (m, 1H), 3.77 (s, 6H), 2.86 (s, 2H), 1.79-1.73 (m, 1H),

1.55 (d, J = 8.86 Hz, 1H), 1.44 (d, J = 8.86 Hz, 1H), 1.34-1.29 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.1, 160.7, 138.6, 137.0, 134.6, 104.8, 103.1, 55.4, 50.5, 47.8, 46.0, 40.9, 35.1. HRMS (ESI) m/z calcd for C₁₆H₂₀NO₃+ (M+H)⁺ 274.1438, found 274.1441.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3,5-difluorobenzamide (4l): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a brownish red oil liquid, isolated yield 76% (95 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.31-7.28 (m, 2H), 6.96-6.91 (m, 1H), 6.35 (d, *J* = 5.28 Hz, 1H), 6.22-6.20 (m, 1H), 6.13-6.11 (m, 1H), 3.94-3.91 (m, 1H), 2.92 (s, 2H), 1.85-1.79 (m, 1H), 1.62 (d, *J* = 8.86 Hz, 1H), 1.49 (d, *J* = 8.86 Hz, 1H), 1.38-1.34 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 164.9, 162.9 (dd, *J* = 250.34 Hz, 12.38 Hz), 138.9, 138.2 (t, *J* = 8.25 Hz), 134.5, 110.1 (dd, *J* = 18.57 Hz, 7.57 Hz), 106.6 (t, *J* = 25.45 Hz), 50.8, 47.8, 46.0, 41.0, 35.2. ¹⁹F{¹H} NMR (400 MHz, CDCl₃) δ -102.78. HRMS (ESI) m/z calcd for C₁₄H₁₄F₂NO+ (M+H)⁺ 250.1038, found 250.1041.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-2-naphthamide (4m): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a pale yellow soild, isolated yield 63% (83 mg), mp: 189-191 °C. ¹H NMR (400 MHz, CDCl₃): δ 8.25 (s, 1H), 7.91-7.80 (m, 4H), 7.57-7.50 (m, 2H), 6.38 (d, *J* = 5.36 Hz, 1H), 6.21-6.20 (m, 1H), 6.16-6.15 (m, 1H), 4.03-4.02 (m, 1H), 2.95 (d, *J* = 13.22 Hz, 2H), 1.86 (t, *J* = 10.00 Hz, 1H), 1.63 (d, *J* = 8.58 Hz, 1H), 1.53 (d, *J* = 8.58 Hz, 1H), 1.41-1.37 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 167.4, 138.7, 134.7, 134.6, 132.6, 132.1, 128.8, 128.4, 127.7, 127.5, 127.1, 126.7, 123.6, 50.6, 48.0, 46.1, 41.0, 35.4. HRMS (ESI) m/z calcd for C₁₈H₁₈NO+ (M+H)⁺ 264.1383, found 264.1386.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)thiophene-2-carboxamide (4n): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a brownish red oil liquid, isolated yield 56% (61 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.49 (d, *J* = 3.57 Hz, 1H), 7.45 (d, *J* = 5.00 Hz, 1H), 7.06 (t, *J* = 3.93 Hz, 1H), 6.19-6.17 (m, 1H), 6.12-6.10 (m, 1H), 6.07 (s, 1H), 3.94-3.91 (m, 1H), 2.91 (s, 2H), 1.84-1.78 (m, 1H), 1.60 (d, *J* = 8.58 Hz, 1H), 1.46 (d, *J* = 8.93 Hz, 1H), 1.34-1.31 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 161.6, 139.2, 138.8, 134.6, 129.6, 127.8, 127.5, 50.5, 47.9, 46.1, 41.0, 35.4. HRMS (ESI) m/z calcd for C₁₂H₁₄NOS+ (M+H)⁺ 220.0791, found 220.0794.



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)furan-2-carboxamide (40): Purification by column chromatography on silica gel (petroleum ether: ethyl acetate=10:1) as a pale yellow oil liquid, isolated yield 70% (71 mg). ¹H NMR (400 MHz, CDCl₃): δ 7.37 (s, 1H), 7.05 (d, *J* = 3.22 Hz, 1H), 6.46 (s, 1H), 6.44 (s, 1H), 6.14-6.12 (m, 1H), 6.07-6.05 (m, 1H), 3.90-3.87 (m, 1H), 2.85 (s, 2H), 1.77-1.72 (m, 1H), 1.55 (d, *J* = 8.58 Hz, 1H), 1.46 (d, *J* = 8.93 Hz, 1H), 1.33-1.28 (m, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 158.0, 148.0, 143.5, 138.7, 134.5, 113.9, 111.9, 49.5, 47.9, 45.9, 40.9, 35.0. HRMS (ESI) m/z calcd for C₁₂H₁₄NO₂+ (M+H)⁺ 204.1019, found 204.1022.

6) References

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Alkenes: Cleavage of C-H and C-N Bonds. Org. Lett., 2019, 21, 1774–1778.

7) Scanned ¹H NMR and ¹³C NMR Spectra of All Compounds.

(4a*R*,9a*S*)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3a): ¹H NMR (400 MHz, CDCl₃)



¹H NMR (400 MHz, CDCl₃)





(4a*R*,9a*S*)-6-methyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3c): ¹H NMR (400 MHz, CDCl₃)





(4a*R*,9a*S*)-6-ethyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3d): ¹H NMR (400 MHz, CDCl₃)





(4a*R*,9a*S*)-6-(tert-butyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3e): ¹H NMR (400 MHz, CDCl₃)







¹⁹F{¹H} NMR (400 MHz, CDCl₃)



(4a*R*,9a*S*)-6-chloro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3g): ¹H NMR (400 MHz, CDCl₃)



¹³C{¹H} NMR (100 MHz, CDCl₃)



(4a*R*,9a*S*)-6-(trifluoromethyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9one (3h): ¹H NMR (400 MHz, CDCl₃)



¹³C{¹H} NMR (100 MHz, CDCl₃)



(4a*R*,9a*S*)-6-nitro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3i): ¹H NMR (400 MHz, CDCl₃)



(4a*R*,9a*S*)-7-methoxy-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3j): ¹H NMR (400 MHz, CDCl₃)



(4a*R*,9a*S*)-7-methyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3k): ¹H NMR (400 MHz, CDCl₃)



(4a*R*,9a*S*)-7-chloro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3l): ¹H NMR (400 MHz, CDCl₃)



(4a*R*,9a*S*)-7-(trifluoromethyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3m):







(4a*R*,9a*S*)-7-nitro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3n): ¹H NMR (400 MHz, CDCl₃)



¹³C{¹H} NMR (100 MHz, CDCl₃)



(4a*R*,9a*S*)-8-fluoro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3o): ¹H NMR (400 MHz, CDCl₃)



¹³C{¹H} NMR (100 MHz, CDCl₃)







(4a*R*,9a*S*)-6,7-dimethyl-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3p): ¹H NMR (400 MHz, CDCl₃)



(4a*R*,9a*S*)-6,7-dichloro-1,2,3,4,4a,9a-hexahydro-9*H*-1,4-methanofluoren-9-one (3q): ¹H NMR (400 MHz, CDCl₃)







(4a*R*,9a*S*)-6-fluoro-5-(trimethylsilyl)-1,2,3,4,4a,9a-hexahydro-9*H*-1,4methanofluoren-9-one (3r): ¹H NMR (400 MHz, CDCl₃)





(4a*R*,11a*S*)-1,2,3,4,4a,11a-hexahydro-11*H*-1,4-methanobenzo[b]fluoren-11-one (3s): ¹H NMR (400 MHz, CDCl₃)



¹³C{¹H} NMR (100 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)benzamide (4a): ¹H NMR (400 MHz, CDCl₃)





N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-4-methoxybenzamide (4b): ¹H NMR (400 MHz, CDCl₃)



¹³C{¹H} NMR (100 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-4-methylbenzamide (4c): ¹H NMR (400 MHz, CDCl₃)





N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-4-fluorobenzamide (4d): ¹H NMR (400 MHz, CDCl₃)





N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-4-chlorobenzamide (4e): ¹H NMR (400 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3-methoxybenzamide (4f): ¹H NMR (400 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3-methylbenzamide (4g): ¹H NMR (400 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3-chlorobenzamide (4h): ¹H NMR (400 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-2-fluorobenzamide (4i): ¹H NMR (400 MHz, CDCl₃)





N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3,4-dimethylbenzamide (4j): ¹H NMR (400 MHz, CDCl₃)



¹³C{¹H} NMR (100 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3,5-dimethoxybenzamide (4k): ¹H NMR (400 MHz, CDCl₃)



¹³C{¹H} NMR (100 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-3,5-difluorobenzamide (4l): ¹H NMR (400 MHz, CDCl₃)



¹³C{¹H} NMR (100 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)-2-naphthamide (4m): ¹H NMR (400 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)thiophene-2-carboxamide (4n): ¹H NMR (400 MHz, CDCl₃)



N-((2*S*)-bicyclo[2.2.1]hept-5-en-2-yl)furan-2-carboxamide (40): ¹H NMR (400 MHz, CDCl₃)





8) The X-ray Single-Crystal Diffraction Analysis of 3s

To grow the crystals used to collect the X-ray data for **3s**, the following method was used: the sample was dissolved with 2 mL petroleum ether and 2 mL DCM in a small vial, which was kept aside at room temperature to obtain crystals.

A suitable crystal was selected a ROD, Synergy Custom system, HyPix diffractometer. The crystal was kept at 297.00(2) K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. The data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2382994).



Figure S1. The X-ray Diffraction Configuration of **3s** (The thermal ellipsoid was drawn at the 50% probability level).

Datablock 202408294_auto



Crystallographic data for compounds 3s:

```
Alert level G
PLAT199_ALERT_1_G Reported _cell_measurement_temperature ..... (K)
                                                                        293 Check
PLAT200_ALERT_1_G Reported __diffrn_ambient_temperature ..... (K)
                                                                        293 Check
                                             (Centro SpGr)
PLAT793_ALERT_4_G Model has Chirality at C12
                                                                         R Verify
PLAT793_ALERT_4_G Model has Chirality at C13
                                                                          S Verify
                                                   (Centro SpGr)
                                                                         R Verify
                                                  (Centro SpGr)
(Centro SpGr)
PLAT793_ALERT_4_G Model has Chirality at C14
PLAT793_ALERT_4_G Model has Chirality at C16
                                                                          S Verify
PLAT909_ALERT_3_G Percentage of I>2sig(I) Data at Theta(Max) Still
                                                                        66% Note
PLAT941_ALERT_3_G Average HKL Measurement Multiplicity .....
                                                                        2.1 Low
PLAT969_ALERT_5_G The 'Henn et al.' R-Factor-gap value .....
                                                                       3.416 Note
             Predicted wR2: Based on SigI**2 3.85 or SHELX Weight 12.30
PLAT978_ALERT_2_G Number C-C Bonds with Positive Residual Density.
                                                                          4 Info
   0 ALERT level A = Most likely a serious problem - resolve or explain
   0 ALERT level B = A potentially serious problem, consider carefully
  0 ALERT level C = Check. Ensure it is not caused by an omission or oversight
  10 ALERT level G = General information/check it is not something unexpected
   2 ALERT type 1 CIF construction/syntax error, inconsistent or missing data
   1 ALERT type 2 Indicator that the structure model may be wrong or deficient
   2 ALERT type 3 Indicator that the structure quality may be low
   4 ALERT type 4 Improvement, methodology, query or suggestion
  1 ALERT type 5 Informative message, check
```