Supplementary Material (ESI) for Chemical Communications

Total Synthesis of (±)-Aspercyclide A and its C19 Methyl Ether

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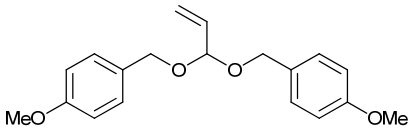
General directions

Solvents and reagents: Solvents were distilled as follows: THF and Et_2O over Na-benzophenone ketyl, toluene over Na, CH_2Cl_2 and DMF over CaH_2; HPLC grade EtOAc and petrol were used as commercially supplied. Reagents were used as commercially supplied unless otherwise stated and handled in accordance with COSHH regulations. **Chromatography:** Flash chromatography (FC) was carried out on Silica gel (BDH Silica gel for FC) according to the method described by Still.[1] Alumina was grade 1 basic supplied by BDH. TLC was performed on aluminium backed silica gel plates (Merck Silica gel 60 F_{254}) which were developed with UV fluorescence (254 nm and 365 nm) and $KMnO_4$(aq)/Δ. **FTIR spectra:** These were recorded on a Perkin-Elmer Paragon 1000 Fourier transform spectrometer. Only selected absorbances (ν_{max}) are reported. **^{1}H NMR spectra:** These were recorded at 400 MHz on a Bruker AM-400 instrument or at 500 MHz on a Bruker AM-500 instrument. Chemical shifts (δ_H) are given in parts per million (ppm) as referenced to the appropriate residual solvent peak. Coupling constants are reported to the nearest 0.1 Hz. Broad signals are assigned as br. **^{13}C NMR spectra:** These were recorded at 100 MHz on a Bruker AM-400 instrument or at 125 MHz on a Bruker AM-500 instrument. Chemical shifts (δ_C) are given in parts per million (ppm) as referenced to $CHCl_3$, and are assigned as s, d, t, and q, for C, CH, CH_2, and CH_3 respectively; The chemical shift of carbons on the fluorous-tag were recorded by applying fluorine-decoupling at δ -125.1 ppm during ^{13}C NMR acquisition. **Mass Spectra:** Low-resolution and high-resolution mass spectra (*m/z*) were recorded on a Micromass AutoSpec Premier [This instrument is a magnetic sector mass spectrometer and has EI, CI and LCIMS (FAB) ion sources] or Micromass LCT Premier [This instrument has an ESI ion source, coupled to a time-of-flight (ToF) analyser] spectrometers, with intensities quoted as percentages of the base peak, with molecular ions and major peaks being reported. Intensities are given as percentages of the base peak. values are valid to **±**5 ppm. **Melting points:** Analyses were carried out using a Khofler hot stage and are uncorrected.

Specific Procedures

3,3-Di-(4-methoxybenzyloxy)-prop-1-ene (**4b**)

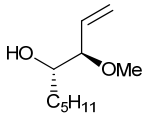


According to a procedure adapted from that described by Noyori,[2] to a -78 °C solution of CH_2Cl_2 (80 mL) was added sequentially: TMSOTf (220 μL, 1.22 mmol), *4-methoxybeznyl trimethylsilyl ether*[†] (33.00 g, 157 mmol) and acrolein (5.4 mL, 80.9 mmol). The resulting solution was stirred for 4 h at -78 C before addition of pyridine (2.80 mL). The solution was allowed to warm to r.t., poured into a saturated aqueous $NaHCO_3$ solution (100 mL) and extracted with Et_2O (3 × 100 mL). The organic fractions were combined, dried over Na_2SO_4/Na_2CO_3 (1:1)

[†] This compound was freshly prepared by dissolving 4-methoxybenzyl alcohol (1 eq) and *N*,*N*'-diisopropylethylamine (1.1 eq) in dry THF at 0 °C and slowly adding TMS-Cl (1.1 eq) under an atmosphere of nitrogen. The reaction mixture was allowed to warm to r.t. and stirring was continued for 2 h. Concentration under reduced pressure and purification by silica gel chromatography, EtOAc:petrol (1:9) afforded the silyl ether as a colourless oil, 82% yield.

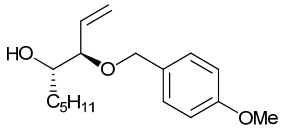
and concentrated under reduced pressure. The residue was purified by silica gel column chromatography, eluting with EtOAc:petrol (1:10) to give the PMB acetal as a colourless oil (22.86 g, 90%). IR (ν_{max}, cm^{-1}) 2835 (m), 1613 (m), 1515 (s), 1249 (s), 1034 (s), 820 (m); ^{1}H NMR (400 MHz, C_6H_6) δ_H 3.30 (s, 6H, 2 × OC*H*$_3$), 4.51 (d, 2H, 2 × C*H*H'Ar), 4.62 (d, 2H, 2 × CH*H'*Ar), 5.16-5.12 (m, 2H, C*H*OCH$_2$ and =C*H*H'), 5.47 (broad d, 1H, *J* = 17.4 and Hz, =CH*H'*), 5.96 (ddd, 1H, *J* = 17.4, 11.0 and 4.1 Hz, C*H*=CH$_2$), 6.80 (d, 4H, *J* = 8.7 Hz, Ar*H*), 7.26 (d, 4H, *J* = 8.7 Hz, Ar*H*); ^{13}C NMR (100 MHz, C_6H_6) δ_C 55.1 (2 × q), 67.3 (2 × t), 100.5 (d), 114.5 (4 × d), 118.7 (t), 129.9 (4 × d), 131.3 (2 × s), 136.4 (d), 160.1 (2 × s); MS (EI^+) *m/z* 314 ($[M]^+$, 20%), 258 (50), 228 (28), 197 (18), 121 ($[C_8H_9O]^+$, 100); HRMS (EI^+) Expected mass for $C_{19}H_{22}O_4$ $[M]^+$ 314.1518, found 314.1520 (Δ = 0.6 ppm).

(3*R,4*S**)-3-Methoxynon-1-en-4-ol** (**5a**)



According to a procedure adapted from that described by Boeckman,[3] an oven dried 250 mL round bottom flask was charged with anhydrous $CrCl_2$ (40 mg, 0.70 mmol), Mn(0) (930 mg, 16.97 mmol) and NaI (300 mg, 2.00 mmol) in a glove box. THF (50 mL) was added and the resulting mixture cooled to –30 ^{o}C for 20 min. Sequentially, *via* syringe, was added freshly distilled TMS-Cl (7.65 mL, 59.88 mmol), freshly distilled acrolein dimethyl acetal (2.72 mL, 22.95 mmol) and freshly distilled hexanal (1.20 mL, 9.98 mmol). The reaction mixture was stirred at –30 ^{o}C for 60 h and then quenched at this temperature with 1M HCl (50 mL) before allowing to warm to r.t. The reaction mixture was extracted with Et_2O (3 × 150 mL), with the organic layers combined, washed with saturated aqueous sodium bicarbonate solution (50 mL), dried (Na_2SO_4), filtered, concentrated *in vacuo*. The residue was purified by silica gel column chromatography, eluting with EtOAc:petrol (1:50→1:25→1:10) to give allyl ether **5a** as a colourless oil (962 mg, 56%). IR (ν_{max}, cm^{-1}) 3470 (-OH st, broad m), 2930 (s), 2860 (m), 1110 (s), 760 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.90 (t, 3H, *J* = 6.7 Hz, CH_3), 1.27-1.54 (m, 8H, 4 × CH_2), 2.07 (broad s, 1H, OH), 3.33 (s, 3H, OCH_3), 3.52 (dd, 1H, *J* = 8.0 and 4.1 Hz, C*H*-OMe), 3.74-3.70 (dt, 1H, *J* = 7.6 and 4.1, C*H*OH), 5.22 (broad dd, 1H, *J* = 17.4 and 1.4 Hz, 1 × =C*H*$_2$), 5.28 (dd, 1H, *J* = 10.4 and 1.4 Hz, 1 × =C*H*$_2$), 5.74-5.83 (ddd, 1H, *J* = 17.4, 10.4 and 8.0 Hz, C*H*=CH$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.0 (q), 22.6 (t), 25.4 (t), 31.8 (t), 32.1 (t), 56.4 (q), 73.0 (d), 86.0 (d), 120.0 (t), 134.2 (d); MS (CI^+) *m/z* 238 (100%), 203 (30), 190 ($[M + NH_4]^+$, 90), 155 (20), 132 (40), 114 (20); HRMS (CI^+) Expected mass for $C_{10}H_{24}NO_2$ $[M + NH_4]^+$ 190.1807, found 190.1809 (Δ = 1.1 ppm).

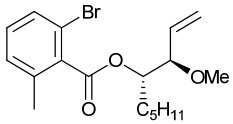
(3*R,4*S**)-3-(4-Methoxybenzyloxy)-non-1-en-4-ol** (**5b**)



According to a procedure adapted from that described by Boeckman,[2] an oven dried 250 mL round bottom flask was charged with anhydrous $CrCl_2$ (200 mg, 1.64 mmol), Mn(0) (3.08 g, 56 mmol) and NaI (1.34 g, 8.93 mmol) in a glove box. THF (100 mL) was added and the resulting mixture cooled to –30 ^{o}C for 20 min. Sequentially, *via* syringe, was added freshly distilled TMS-Cl (17.0 mL, 134.5 mmol), (16.12 g, 58.8 mmol) and freshly distilled hexanal (2.80 mL, 22.8 mmol). The reaction mixture was stirred at –30 ^{o}C for 60 h and then quenched

at this temperature with 1M HCl (100 mL) before allowing to warm to r.t. The reaction mixture was extracted with Et_2O (3 × 250 mL), with the organic layers combined, washed with saturated aqueous sodium bicarbonate solution (100 mL), dried (Na_2SO_4), filtered, concentrated *in vacuo*. The residue was purified by silica gel column chromatography, eluting with EtOAc:petrol (1:9→1:5) to give allyl ether **5b** as a colourless oil (4.02 g, 64%). IR (ν_{max}, cm^{-1}) 3448 (broad m), 2932 (m), 1613 (m) 1515 (s), 1249 (s), 1036 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.86 (t, 3H, *J* = 6.9 Hz, CH_2CH_3), 1.49-1.22 (m, 8H, 4 × CH_2), 2.13 (d, 1H, *J* = 3.6 Hz, OH), 3.72-3.59 (m, 2H, $CHOCH_2Ar$ and CHOH), 3.79 (s, 3H, OCH_3), 4.30 (d, 1H, *J* = 11.5 Hz, CHH'Ar), 4.55 (d, 1H, *J* = 11.5 Hz, CHH'Ar), 5.28 (dd, 1H, *J* = 17.2 and 1.8 Hz, =CHH'), 5.37 (dd, 1H, *J* = 10.3 and 1.8 Hz, 1 × $=CH_2$), 5.28 (dd, 1H, *J* = 10.4 and 1.4 Hz, 1 × $=CH_2$) and 5.74-5.83 (ddd, 1H, *J* = 17.2, 10.3 and 7.7 Hz, $CH=CH_2$), 6.86 (d, 2H, ArH), 7.23 (d, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.2 (q), 22.8 (t), 25.6 (t), 32.1 (t), 32.3 (t), 55.5 (q), 70.1 (t), 73.4 (d), 83.4 (d), 114.0 (2 × d), 120.2 (t), 129.6 (2 × d), 130.6 (s), 134.8 (d), 159.4 (s); MS (CI^+) *m/z* 296 ($[M + NH_4]^+$, 100%), 155 (16), 138 (49), 121 (94); HRMS (CI^+) Expected mass for $C_{17}H_{30}NO_3$ $[M + NH_4]^+$ 296.2226, found 296.2224 (Δ = 0.6 ppm).

2-Bromo-6-methylbenzoic acid (*S)-1-[(*R**)-1-methoxyallyl]hexyl ester** (**7a**)

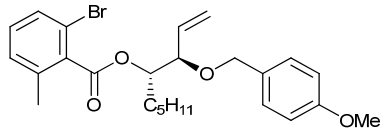


To a stirred solution of alcohol **5a** (100 mg, 0.55 mmol) in THF (3 mL) at -78 °C was added a solution of *n*-butyllithium in hexanes (1.4 M, 419 μL, 0.60 mmol). The resulting pale yellow solution was stirred continuously for 30 min before a solution of freshly prepared acid chloride **6**‡ (152 mg, 0.65 mmol) in THF (3 mL) at -78 °C was added *via* a dry-ice cooled cannula. After complete addition the reaction mixture was allowed to reach r.t. over 16 h. The reaction mixture was then diluted with Et_2O (10 mL), washed with saturated aqueous sodium hydrogen carbonate solution (2 × 10 mL) and brine (2 × 10 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo*. The resulting oil was purified by silica gel column chromatography, eluting with EtOAc:petrol (1:100→1:50→3:100→1:25→1:20→3:20→1:1) to give recovered alcohol **5a** (32 mg, 0.17 mmol, 32%; 98% based on recovered starting material) and ester **7a** as colourless plates (132 mg, 66%). m.p. 31.1-33.9 °C from Et_2O; IR (ν_{max}, cm^{-1}) 2930 (m), 1730 (C=O st, s), 1270 (s), 1100 (s) and 1070 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.88 (t, 3H, *J* = 7.2 Hz, CH_3), 1.24-1.45 (m, 4H, 2 × CH_2), 1.58-1.67 (m, 2H, CH_2), 1.73-1.83 (m, 2H, CH_2), 2.37 (s, 3H, $ArCH_3$), 3.33 (s, 3H, OCH_3), 3.85 (ddt, 1H, *J* = 8.2, 3.2 and 0.8 Hz, CH-OCH_3), 5.27 (dt, 1H, *J* = 8.2 and 3.7 Hz, CHOCOAr), 5.35 (ddd, 1H, *J* = 10.7, 1.2 and 0.8 Hz, 1 × $=CH_2$), 5.35 (ddd, 1H, *J* = 17.0, 1.2 and 1.2 Hz, 1 × = CH_2), 5.77 (ddd, 1H, *J* = 17.0, 10.7 and 7.6 Hz, $CH=CH_2$), 7.12 (d, 1H, *J* = 6.0 Hz, ArH), 7.13 (d, 1H, *J* = 3.1 Hz, ArH) and 7.38 (dd, 1H, *J* = 6.0 and 3.1 Hz, ArH); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.0 (q), 19.7 (q), 22.5 (t), 25.2 (t), 28.8 (t), 31.6 (t), 56.6 (q), 76.8 (d), 83.5 (d), 118.8 (s), 119.8 (t), 128.9 (d), 129.9 (d), 130.2 (d), 134.3 (d), 136.3 (s), 136.9 (s) and 167.8 (s); MS (CI) *m/z* 388 ($[^{81}BrM + NH_4]^+$, 90%), 386 ($[^{79}BrM + NH_4]^+$, 90), 371 ($[^{81}BrM + H]^+$, 50), 369 ($[^{79}BrM + H]^+$, 50), 355 (20), 339 ($[^{81}BrM – OMe]^+$, 20), 337 ($[^{79}BrM – OMe]^+$,

‡ This compound was prepared by treating the commercial carboxylic acid (1 eq) with oxalyl chloride (1.5 eq) in CH_2Cl_2. The solution was then cooled to 0 °C and catalytic DMF (1 drop) was added under an atmosphere of nitrogen. The reaction mixture was allowed to warm to r.t. and stirring was continued for 1 h at which time the reaction mixture was concentrated under reduced pressure to afford acid chloride **6** as a yellow oil which was used immediately.

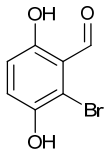
20), 308 (20), 291 (20), 276 (25), 202 (60), 199 ($[C_8H_7{}^{81}BrO]^+$, 20), 197 ($[C_8H_7{}^{79}BrO]^+$, 20) 155 ($[C_{10}H_{19}O]^+$, 100), 140 (30) and 52 (25); HRMS (CI) Expected mass for $C_{18}H_{26}O_3{}^{79}Br$ (M + H^+) 369.1059, found 369.1065 (Δ = 1.6 ppm). A single crystal X-ray structure determination was performed on this product (see Separate Supporting Information File).

2-Bromo-6-methylbenzoic acid (*S)-1-[(*R**)-1-(4-methoxybeznyloxy)-allyl]hexyl ester** (**7b**)



To a stirred solution of alcohol **5b** (60 mg, 0.22 mmol) in THF (2.5 mL) was added NaH (60% in oil, 26 mg, 0.65 mmol) at 0 °C under nitrogen. A solution of freshly prepared acid chloride **6**‡ (100 mg, 0.43 mmol) in THF (2.5 mL) was then added and the solution allowed to warm to r.t. before being heated to reflux for 4 h. The reaction was then cooled to r.t., diluted with Et_2O (15 mL) and cautiously quenched by the addition of water saturated Et_2O. The reaction mixture was washed with 0.1M HCl solution (10 mL) and brine (10 mL). The organic phase was separated, dried (Na_2SO_4) and concentrated under reduced pressure. The resulting oil was purified by silica gel column chromatography, eluting with EtOAc:petrol (1:9) to give **7b** as a colourless oil (87 mg, 85%). IR (ν_{max}, cm^{-1}) 2956 (s), 1731 (s), 1613 (m), 1513 (s), 1247 (s), 1068 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.86 (t, 3H, *J* = 7.0 Hz, CH_2CH_3), 1.53-1.20 (m, 6H, 3 × CH_2), 1.63 (m, 1H, C*H*H'C_4H_9), 1.76 (m, 1H, CH*H*'C_4H_9), 2.28 (s, 3H, ArCH_3), 3.78 (s, 3H, OCH_3), 4.02 (dd, 1H, *J* = 7.6 and 3.7 Hz, C*H*OCH_2Ar), 4.38 (d, 1H, *J* = 11.4 Hz, C*H*H'Ar), 4.53 (d, 1H, *J* = 11.4 Hz, CH*H*'Ar), 5.37-5.29 (m, 3H, =CH_2 and ArCO_2C*H*), 5.83 (ddd, 1H, *J* = 16.6, 11.0 and 7.6 Hz, C*H*=CH_2), 6.83 (d, 2H, *J* = 8.6 Hz, 2 × Ar*H*), 7.10 (m, 2H, 2 × Ar*H*) and 7.24 (d, 2H, *J* = 8.6 Hz, 2 × Ar*H*), 7.36 (m, 1H, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.2 (q), 20.0 (q), 22.7 (t), 25.3 (t), 29.6 (t), 31.9 (t), 55.5 (q), 70.3 (t), 77.1 (d), 81.0 (d), 113.9 (2 × d), 119.1 (s), 120.0 (t), 129.1 (d), 129.5 (2 × d), 130.1 (d), 130.4 (d), 130.6 (s), 134.9 (d), 136.6 (s), 137.2 (s), 159.4 (s), 167.9 (s); MS (ESI^+) *m/z* 515 ($[^{81}BrM + K]^+$, 32%), 513 ($[^{79}BrM + K]^+$, 32), 500 (26), 499 ($[^{81}BrM + Na]^+$, 100), 498 (28), 497 ($[^{79}BrM + Na]^+$, 100); HRMS (ESI^+) Expected mass for $C_{25}H_{31}{}^{79}BrO_4Na$ $[M + Na]^+$ 497.1303, found 497.1295 (Δ = 1.6 ppm).

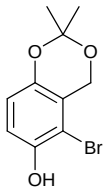
2-Bromo-3,6-dihydroxy-benzaldehyde[4]



According to the procedure described by Porco,[4] to a solution of commercial *gentisaldehyde* (5.00 g, 36.47 mmol) in $CHCl_3$ (150 mL) was added, dropwise, a solution of Br_2 (1.94 mL, 37.98 mmol) in $CHCl_3$ (30 mL) and the reaction was stirred at r.t. for 3 h. After this time, saturated aqueous sodium thiosulphate solution (100 mL) was added, and the resulting mixture stirred for 5 min after which time the red-brown colouration had changed to yellow. After extraction with CH_2Cl_2 (3 × 100 mL), the organic layers were combined, washed with brine (2 × 30 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give 2-bromo-3,6-dihydroxy-benzaldehyde as a yellow solid (7.68 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 5.39 (s, 1H, O*H*), 6.94 (d, 1H, *J* = 9.2 Hz, Ar*H*), 7.26 (d, 1H, *J* = 9.2 Hz, Ar*H*), 10.29 (s, 1H, C*H*O) and 11.66 (s, 1H, O*H*); MS (EI) *m/z* 218 ($[^{81}BrM]^+$, 100%),

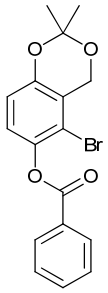
216 ([^{79}BrM]$^+$, 100), 200 ([^{81}BrM – OH]$^+$, 15), 198 ([^{79}BrM – OH]$^+$, 15), 172 ([$C_6H_3{}^{81}BrO]^+$, 15), 170 ([$C_6H_3{}^{79}BrO]^+$, 15), 118 (25), 108 ([$C_6H_4O_2]^+$, 30), 76 (60) and 43 (65).

5-Bromo-2,2-dimethyl-4*H*-benzo[1,3]dioxin-6-ol (**8**)



Using protocols adapted from Goddard[5] ($NaBH_4$) and Tietze[6] (DMP, CSA), to an ice-cooled stirred solution of *2-bromo-3,6-dihydroxy-benzaldehyde* (1.34 g, 6.17 mmol), in aqueous sodium hydroxide solution (1% w/v, 150 mL), was added, dropwise, a solution of $NaBH_4$ (300 mg, 7.93 mmol) in aqueous sodium hydroxide solution (10% w/v, 15 mL). After complete addition, stirring was continued for 6 h. After this time, the reaction mixture was diluted with Et_2O (200 mL), and the reaction was acidified with aqueous hydrochloric acid (1M). Following extraction with Et_2O (3 × 100 mL), the organic layers were combined, dried (Na_2SO_4), filtered and concentrated *in vacuo*. The resulting oil was immediately dissolved in 2,2-dimethoxypropane (3 mL), camphorsulphonic acid (20 mg) was added and the reaction mixture was stirred at r.t. for 16 h. After this time the reaction mixture was diluted with Et_2O (20 mL) and washed with saturated aqueous sodium hydrogen carbonate solution (10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated *in vacuo* and purified by silica gel column chromatography, eluting with EtOAc:petrol (1:10→3:20→1:5) to give acetonide **8** as a dark red oil (1.29 g, 81%). IR (ν_{max}, cm^{-1}) 3430 (O-H st, br m), 1480 (s), 1380 (m), 1260 (s) and 1200 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.55 (s, 6H, C(C*H*$_3$)$_2$), 4.75 (s, 2H, ArC*H*$_2$O), 5.18 (s, 1H, O*H*), 6.77 (d, 1H, *J* = 9.2 Hz, Ar*H*) and 6.92 (d, 1H, *J* = 9.2 Hz, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 24.4 (2q), 61.9 (t), 99.3 (s), 107.2 (s), 115.0 (d), 117.2 (d), 119.2 (s), 145.6 (s) and 146.1 (s); MS (EI) *m/z* 260 ([^{81}BrM + H]$^+$, 30%), 258 ([^{79}BrM + H]$^+$, 30), 202 ([^{81}BrMH – $OC_3H_6]^+$, 30), 100), 200 ([^{79}BrMH – $OC_3H_6]^+$, 100), 174 (30), 172 (30), 121 ([MH – $OC_3H_6Br]^+$, 30), 65 (25) and 59 ([$OC_3H_6]^+$, 35); HRMS (ES) Expected mass for $C_{10}H_{11}{}^{79}BrO_3$ (M^+) 257.9886, found 257.9892 (Δ = 2.3 ppm).

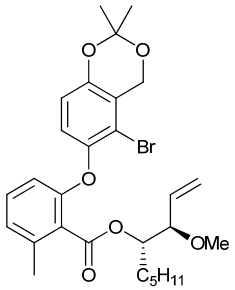
Benzoic acid 5-bromo-2,2-dimethyl-4*H*-benzo[1,3]dioxin-6-yl ester



To a stirred solution of phenol **8** (30 mg, 0.12 mmol) and 4-DMAP (1.2 mg, 0.01 mmol) in CH_2Cl_2 (2 mL) was added Et_3N (18 μL, 0.13 mmol) and benzoyl chloride (15 μL, 0.13 mmol) and stirred at r.t. for 16 h. After this time the reaction mixture was diluted with Et_2O (10 mL), and washed with saturated aqueous sodium hydrogen carbonate solution (10 mL) and brine (10 mL). The organic layer was dried (Na_2SO_4), filtered, concentrated *in vacuo* and purified by silica gel column chromatography, eluting with EtOAc:petrol

(1:100→1:50→3:100→1:25→1:20) to give benzoate **8a** as colourless blocks after recrystallisation from hot hexane (33 mg, 78%). m.p. 90.4-93.9 °C from hexane; IR (ν_{max}, cm^{-1}) 1740 (m), 1470 (w), 1230 (s), 1060 (m) and 875 (w); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 1.56 (s, 6H, C(C*H*$_3$)$_2$), 4.78 (s, 2H, ArC*H*$_2$O), 6.86 (d, 1H, *J* = 8.8 Hz, Ar*H*), 7.10 (d, 1H, *J* = 8.8 Hz, Ar*H*), 7.53 (dd, 2H, *J* = 8.0 and 6.7 Hz, 2 × Ar*H*), 7.66 (tt, 1H, *J* = 6.7 and 1.3 Hz, Ar*H*) and 8.23 (dd, 2H, *J* = 8.0 and 1.3 Hz, 2 × Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 24.5 (2q), 62.0 (t), 99.8 (s), 113.8 (s), 116.7 (d), 120.3 (s), 122.5 (s), 128.6 (2d), 129.0 (s), 130.4 (2d), 133.8 (d), 141.6 (s), 150.0 (s) and 164.7 (s); MS (EI) *m/z* 364 ([^{81}BrM]$^+$, 10%), 318 ([^{79}BrM]$^+$, 10%), 306 ([^{81}BrM – C_3H_6O]$^+$, 5), 260 ([^{79}BrM – C_3H_6O]$^+$, 5), 201 ([$C_7H_5{}^{81}BrO_2$]$^+$, 5), 199 ([$C_7H_5{}^{79}BrO_2$]$^+$, 5), 163 ([$C_{10}H_{11}O_2$]$^+$, 10), 105 ([C_7H_5O]$^+$, 100), 84 (15), 77 ([C_6H_5]$^+$, 30) and 49 (20); HRMS (EI) Expected mass for $C_{17}H_{15}{}^{79}BrO_4$ (M^+) 362.0154, found 362.0146 (Δ = 2.1 ppm). A single crystal X-ray structure determination was performed on this product (see Separate Supporting Information File).

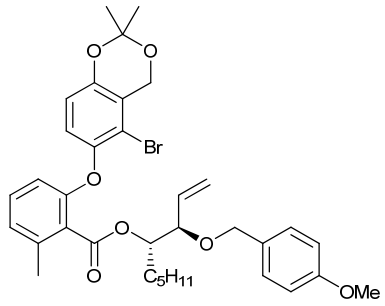
2-(5-Bromo-2,2-dimethyl-4*H*-benzo[1,3]dioxin-6-yloxy)-6-methyl-benzoic acid (*S)-1-[(*R**)-1-methoxy-allyl]-hexyl ester** (**9a**)



An oven-dried reaction vial was charged with a stirrer bar, phenol **8** (354 mg, 1.37 mmol), aryl bromide **7a** (254 mg, 0.69 mmol), CuO (20 mg, 0.14 mmol) and K_2CO_3 (286 mg, 2.06 mmol). The vial was equipped with a Suba-seal, then repeatedly evacuated and purged with nitrogen (× 5) before addition of in pyridine (7 mL). The Suba-seal was then replaced by a screw cap under a flow of nitrogen, and the reaction mixture was heated for 16 h at 120 °C. After this time the reaction mixture was allowed to cool to r.t., filtered through a pad of Celite®, washed with acetone (20 mL) and concentrated *in vacuo*. The residue was purified by silica gel column chromatography, eluting with EtOAc:petrol (1:100→1:50→3:100→1:25→1:20→3:50→7:100→2:25) to give biarylether **9a** as a pale yellow oil (258 mg, 70%). IR (ν_{max}, cm^{-1}) 2960 (w), 1730 (C=O st, m), 1460 (s), 1250 (s) and 1110 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.78 (t, 3H, *J* = 7.0 Hz, C*H*$_3$), 1.13-1.35 (m, 6H, 3 × C*H*$_2$), 1.54 (s, 6H, C(C*H*$_3$)$_2$), 1.57-1.67 (m, 2H, C*H*$_2$), 2.39 (s, 3H, ArC*H*$_3$), 3.28 (s, 3H, OC*H*$_3$), 3.76 (ddt, 1H, *J* = 7.6, 3.9 and 0.8 Hz, C*H*-OCH$_3$), 4.77 (s, 2H, ArC*H*$_2$O), 5.26 (dt, 1H, *J* = 9.2 and 3.9 Hz, C*H*OCOAr), 5.29 (ddd, 1H, *J* = 10.4, 1.6 and 0.8 Hz, 1 × =C*H*$_2$), 5.30 (ddd, 1H, *J* = 17.2, 1.6 and 0.8 Hz, 1 × =C*H*$_2$), 5.78 (ddd, 1H, *J* = 17.2, 10.4 and 7.6 Hz, C*H*=CH$_2$), 6.48 (d, 1H, *J* = 8.2 Hz, Ar*H*), 6.79 (d, 1H, *J* = 8.8 Hz, Ar*H*), 6.93 (app d, 2H, *J* = 8.8 Hz, 2 × Ar*H*) and 7.16 (t, 1H, *J* = 8.2 Hz, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.0 (q), 19.4 (q), 22.5 (t), 24.4 (q), 24.5 (q), 25.2 (t), 29.4 (t), 31.7 (t), 56.8 (q), 62.1 (t), 76.1 (d), 84.0 (d), 99.6 (s), 113.1 (d), 113.4 (s), 116.9 (d), 119.5 (t), 120.5 (s), 120.9 (d), 124.5 (s), 125.6 (d), 130.0 (d), 134.7 (d), 137.2 (s), 146.4 (s), 148.6 (s), 154.5 (s) and 167.4 (s); MS (CI) 566 ([^{81}BrM + NH_4]$^+$, 30%), 564 ([^{79}BrM + NH_4]$^+$, 30), 549 ([^{81}BrM + H]$^+$, 25), 547 ([^{79}BrM + H]$^+$, 25), 486 ([MNH_4 – Br]$^+$, 20), 467 ([MH – Br]$^+$, 30), 377 ([$C_{18}H_{16}{}^{81}BrO_4$]$^+$, 10), 375 ([$C_{18}H_{16}{}^{79}BrO_4$]$^+$, 10), 332 (10), 297 ([$C_{18}H_{16}O_4$]$^+$, 15), 274 (30), 228 ([$C_{14}H_{14}NO_2$]$^+$, 40), 220 (30), 218 (30), 190

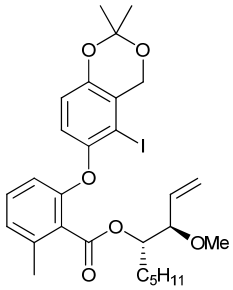
(10), 155 ($[C_{10}H_{19}O]^+$, 80), 140 (100) and 52 (75); HRMS (CI) Expected mass for $C_{28}H_{36}BrO_6$ ($[M + H]^+$) 547.1714, found 547.1695 (Δ = 3.5 ppm).

2-(5-Bromo-2,2-dimethyl-4*H*-benzo[1,3]dioxin-6-yloxy)-6-methyl-benzoic acid (*S)-1-[(*R**)-1-(4-methoxybenzyloxy)-allyl]-hexyl ester** (**9b**)



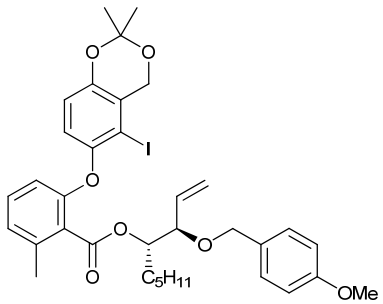
An oven-dried reaction vial was charged with a stirrer bar, phenol **8** (165 mg, 0.64 mmol), aryl bromide **7b** (150 mg, 0.315 mmol), K_2CO_3 (131 mg, 0.95 mmol) and dry pyridine (3 mL). The vial was equipped with a Suba-seal, then repeatedly evacuated and purged with nitrogen (× 3). Under a flow of nitrogen, CuO (5.0 mg, 63 μmol) was added and the Suba-seal was then replaced by a screw cap. The reaction mixture was then stirred at 120 °C for 16 h. After this time the reaction mixture was allowed to cool to r.t., filtered through a pad of Celite®, washed with ethyl acetate (20 mL) and concentrated *in vacuo*. The residue was passed through a short silica gel column, eluting with 100% CH_2Cl_2, then EtOAc:petrol (1:3). The product was further purified by silica gel column chromatography, eluting with EtOAc:petrol (1:19) to give recovered aryl bromide **7b** (40 mg, 27%) and biarylether **9b** as a pale yellow oil (112 mg, 54% isolated yield or 74% based on recovered starting material). IR (ν_{max}, cm^{-1}) 2955 (s), 1728 (s), 1612 (s), 1460 (s), 1250 (s), 1075 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.75 (t, 3H, *J* = 6.9 Hz, CH_2CH_3), 1.34-1.08 (m, 6H, 3 × CH_2), 1.40 (m, 1H, C*H*H'C_4H_9), 1.52 (s, 6H, $C(CH_3)_2$), 1.62 (m, 1H, CH*H*'C_4H_9), 2.32 (s, 3H, ArCH_3), 3.77 (s, 3H, OCH_3), 3.91 (dd, 1H, *J* = 7.3 and 4.4 Hz, C*H*OCH_2Ar), 4.34 (d, 1H, *J* = 11.5 Hz, C*H*H'Ar), 4.50 (d, 1H, *J* = 11.5 Hz, CH*H*'Ar), 5.34-5.25 (m, 3H, =CH_2 and ArCO_2C*H*), 5.83 (ddd, 1H, *J* = 17.6, 10.0 and 7.6 Hz, C*H*=CH_2), 6.44 (d, 1H, *J* = 8.3 Hz, Ar*H*), 6.73 (d, 1H, *J* = 8.9 Hz, Ar*H*), 6.80 (d, 2H, *J* = 8.5 Hz, 2 × Ar*H*), 6.90-6.84 (m, 2H, 2 × Ar*H*), 7.11 (apparent t, 1H, *J* = 8.0 Hz, Ar*H*), 7.20 (d, 2H, *J* = 8.5 Hz, 2 × Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.2 (q), 19.7 (q), 22.7 (t), 24.6 (q), 24.7 (q), 25.2 (t), 30.1 (t), 31.9 (t), 55.4 (q), 62.3 (t), 70.3 (t), 76.4 (d), 81.4 (d), 99.8 (s), 113.3 (s), 113.6 (d), 113.8 (2 × d), 117.1 (d), 119.7 (t), 120.7 (s), 121.1 (d), 124.7 (d), 125.7 (s), 129.4 (2 × d), 130.2 (d), 130.7 (s), 135.3 (d), 137.5 (s), 146.6 (s), 148.8 (s), 154.8 (s), 159.2 (s), 167.5 (s); MS (ESI^+) 694 (15%), 693 ($[^{81}BrM + K]^+$, 41%), 692 (15), 691 ($[^{79}BrM + K]^+$, 38), 678 (38), 677 ($[^{81}BrM + Na]^+$, 100), 676 (35), 675 ($[^{79}BrM + Na]^+$, 93); HRMS (ESI^+) Expected mass for $C_{35}H_{41}{}^{79}BrO_7Na$ $[M + Na]^+$ 675.1933, found 675.1936 (Δ = 0.4 ppm).

2-(5-Iodo-2,2-dimethyl-4*H*-benzo[1,3]dioxin-6-yloxy)-6-methyl-benzoic acid (*S)-1-[(*R**)-1-methoxy-allyl]-hexyl ester** (**10a**)



An oven-dried reaction vial was charged with a stirrer bar, aryl bromide **9a** (60 mg, 0.11 mmol), NaI (322 mg, 2.26 mmol) and CuI (21 mg, 0.11 mmol). The vial was equipped with a Suba-seal, and repeatedly evacuated and purged with nitrogen (× 5), before addition of *N*,*N*'-dimethylaminoethane (24 μL, 0.23 mmol) and degassed 1,4-dioxane (5 mL). The Suba-seal was replaced by a screw cap under a flow of nitrogen, and the reaction mixture was heated at 110 °C for 48 h. After this time the reaction mixture was allowed to cool to r.t., filtered through a pad of Celite®, washed with CH_2Cl_2 (10 mL) and concentrated *in vacuo*. The resulting oil was purified by PLC, eluting with EtOAc:petrol (1:20) to give aryl iodide **10a** as a pale yellow oil (63 mg, 94%). IR (ν_{max}, cm^{-1}) 2930 (w), 1730 (C=O st, m), 1460 (s), 1250 (s) and 1110 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.77 (t, 3H, *J* =7.0 Hz, C*H*$_3$), 1.12-1.21 (m, 6H, 3 × C*H*$_3$), 1.54 (s, 6H, C(C*H*$_3$)$_2$), 1.56-1.70 (m, 2H, C*H*$_2$), 2.40 (s, 3H, ArC*H*$_3$), 3.27 (s, 3H, OC*H*$_3$), 3.75 (ddt, 1H, *J* = 7.6, 3.9 and 0.8 Hz, C*H*-OCH$_3$), 4.66 (s, 2H, ArC*H*$_2$O), 5.26 (dt, 1H, *J* = 9.2 and 3.9 Hz, C*H*OCOAr), 5.29 (ddd, 1H, *J* = 10.6, 1.0 and 0.8 Hz, 1 × =C*H*$_2$), 5.29 (ddd, 1H, *J* = 16.9, 1.0 and 0.8 Hz, 1 × = C*H*$_2$), 5.76 (ddd, 1H, *J* = 16.9, 10.6 and 7.6 Hz, C*H*=CH$_2$), 6.47 (dd, 1H, *J* = 7.7 and 0.8 Hz, Ar*H*), 6.79 (d, 1H, *J* = 8.8 Hz, Ar*H*), 6.84 (d, 1H, *J* = 8.8 Hz, Ar*H*), 6.91 (dd, 1H, *J* = 7.7 and 0.8 Hz, Ar*H*) and 7.14 (t, 1H, *J* = 7.7 Hz, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.0 (q), 19.4 (q), 22.5 (t), 24.4 (q), 24.5 (q), 25.2 (t), 29.5 (t), 31.7 (t), 56.8 (q), 66.7 (t), 76.1 (d), 84.0 (d), 89.7 (s), 99.7 (s), 113.8 (d), 118.1 (d), 119.5 (t), 119.7 (d), 123.2 (s), 124.6 (d), 125.8 (s), 130.1 (d), 134.7 (d), 137.2 (s), 148.5 (s), 149.4 (s), 154.5 (s) and 167.3 (s); MS (ES) *m/z* 594 ([M]$^+$, 10%), 536 (15), 506 ([M – $C_4H_8O_2$]$^+$, 10), 409 ([M – I – C_3H_6O]$^+$, 15), 365 ([$C_{10}H_{15}IO_3$]$^+$, 15), 296 ([$C_{18}H_{16}O_4$]$^+$, 40), 238 ([$C_{15}H_{10}O$]$^+$, 100), 209 (20), 155 ([$C_{10}H_{19}O$]$^+$, 80), 84 (70), 71 ([C_4H_7O]$^+$, 45) and 49 (80); HRMS (ES) Expected mass for $C_{28}H_{35}IO_6$ (M$^+$) 594.1476, found 594.1478 (Δ = 0.3 ppm).

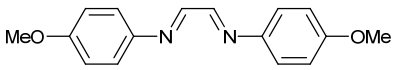
2-(5-Iodo-2,2-dimethyl-4*H*-benzo[1,3]dioxin-6-yloxy)-6-methyl-benzoic acid (*S)-1-[(*R**)-1-(4-methoxybenzyloxy)-allyl]-hexyl ester (10b)**



An oven-dried reaction vial was charged with a stirrer bar, aryl bromide **9b** (55 mg, 84 μmol), NaI (250 mg, 1.67 mmol), CuI (16 mg, 84 μmol) and 1,4-dioxane (5 mL). The vial was equipped with a Suba-seal, and repeatedly evacuated then purged with nitrogen (× 3). Under a flow of nitrogen, *N*,*N*'-dimethylaminoethane (18 μL, 169 μmol) was added and the Suba-seal was replaced by a screw cap. The reaction mixture was then stirred at 120 °C for 48 h. After this time the reaction mixture was allowed to cool to r.t., filtered through a pad of Celite®,

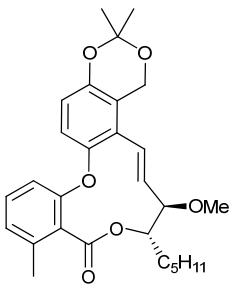
washed with CH_2Cl_2 (20 mL) and concentrated *in vacuo*. The resulting oil was purified by silica gel column chromatography, eluting with EtOAc:petrol (1:1) to give aryl iodide **10b** as a pale yellow oil (52 mg, 88%). IR (ν_{max}, cm^{-1}) 2954 (w), 1728 (m), 1513 (m), 1456 (s), 1252 (s), 1075 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.75 (t, 3H, *J* = 6.9 Hz, CH_2CH_3), 1.33-1.06 (m, 6H, 3 × CH_2), 1.39 (m, 1H, C*H*H'C_4H_9), 1.52 (s, 6H, $C(CH_3)_2$), 1.62 (m, 1H, CH*H*'C_4H_9), 2.32 (s, 3H, ArCH_3), 3.77 (s, 3H, OCH_3), 3.91 (dd, 1H, *J* = 7.5 and 4.3 Hz, C*H*OCH_2Ar), 4.33 (d, 1H, *J* = 11.5 Hz, C*H*H'Ar), 4.49 (d, 1H, *J* = 11.5 Hz, CH*H*'Ar), 5.33-5.24 (m, 3H, =CH_2 and ArCO_2C*H*), 5.83 (ddd, 1H, *J* = 17.6, 10.0 and 7.6 Hz, C*H*=CH_2), 6.44 (d, 1H, *J* = 8.3 Hz, Ar*H*), 6.75 (d, 1H, *J* = 8.8 Hz, Ar*H*), 6.83-6.77 (m, 3H, 3 × Ar*H*), 6.88 (d, 1H, *J* = 7.4 Hz, Ar*H*), 7.11 (apparent t, 1H, *J* = 7.9 Hz, Ar*H*), 7.19 (d, 2H, *J* = 8.5 Hz, 2 × Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.2 (q), 19.7 (q), 22.7 (t), 24.6 (q), 24.7 (q), 25.3 (t), 30.1 (t), 32.0 (t), 55.5 (q), 66.9 (t), 70.3 (t), 76.4 (d), 81.4 (d), 89.9 (s), 99.9 (s), 113.8 (2 × d), 113.9 (d), 118.2 (d), 119.7 (t), 120.0 (d), 123.4 (s), 124.8 (d), 125.9 (s), 129.4 (2 × d), 130.2 (d), 130.7 (s), 135.3 (d), 137.6 (s), 148.7 (s), 149.6 (s), 154.8 (s), 159.2 (s), 167.5 (s); MS (ESI^+) 740 (18%), 739 ($[M + K]^+$, 47), 724 (35), 723 ($[M + Na]^+$, 100); HRMS (ESI^+) Expected mass for $C_{35}H_{42}IO_7$ $[M + H]^+$ 701.1975, found 701.1989 (Δ = 2.0 ppm).

***N*,*N*'-Bis(4-methoxyphenyl)diazabutadiene** (**11**)

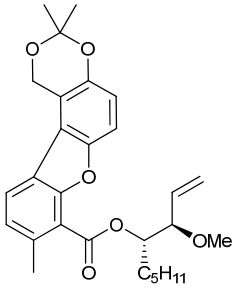


According to a procedure adapted from that described by Nolan,[7] 4-methoxyaniline (4.26 g, 34.60 mmol) was added to a stirring solution of glyoxal (40% aqueous solution, 17.30 mmol). After 5 min, precipitation occurred and the solution became highly viscous; the reaction was left for 16 h. After this time the resulting solid was filtered off and washed sequentially with water and methanol to give a yellow solid which was recrystallised from CH_2Cl_2 to give *N*,*N*'-bis(4-methoxybenzene)-diazabutadiene (**11**) as yellow needles (3.39 g, 73%). m.p. 122.9-124.6 °C from CH_2Cl_2; IR (ν_{max}, cm^{-1}) 2840 (w), 1460 (w), 1110 (m), 1030 (m) and 820 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 3.85 (s, 6H, 2 × OCH_3), 6.96 (d, 4H, *J* = 9.2 Hz, 4 × Ar*H*), 7.34 (d, 4H, *J* = 9.2 Hz, 4 × Ar*H*) and 8.42 (s, 2H, 2 × C*H*=N); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 55.5 (2q), 114.5 (4d), 123.1 (4d), 143.0 (2s), 157.6 (2d) and 159.8 (2s); MS (ES) *m/z* 269 ($[M + H]^+$, 100%) and 124 (10); HRMS (EI) Expected mass for $C_{16}H_{17}N_2O_2$ ($[M + H]^+$) 269.1290, found 269.1284 (Δ = 2.2 ppm).

(14*R,15*S**,*E*)-14-Methoxy-1,11,11-trimethyl-15-pentyl-14,15-dihydro-5*H*-benzo[*b*]10,12-dioxo[1,2-*j*][1,5]dioxacycloundecin-17(9*H*)-one** (**12a**) and **3,3,9-trimethyl-1*H*-2,4,7-trioxa-benzo[*c*]fluorene-8-carboxylic acid (*S**)-1-[(*R**)-1-methoxy-allyl]-hexyl ester** (**13a**)



12a



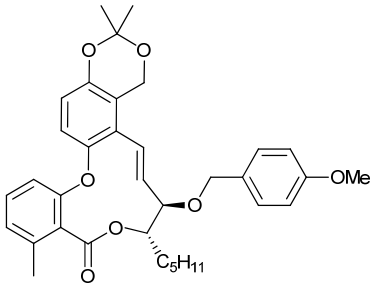
13a

An oven-dried reaction vial was charged with a stirrer bar, aryl iodide **10a** (63 mg, 0.07 mmol), $Pd(acac)_2$ (13 mg, 0.05 mmol), Cs_2CO_3 (76 mg, 0.23 mmol), *N,N'*-di(4-methoxybenzene)-diazabutadiene (**11**, 22.5 mg, 0.08 mmol) and AgI (50 mg, 0.21 mmol). The vial was equipped with a Suba-seal, and repeatedly evacuated and purged with nitrogen (× 5), before addition of degassed 1,4-dioxane (2 mL). The Suba-seal was replaced by a screw cap under a flow of nitrogen, and the reaction mixture was heated for 36 h at 120°C. After this time the reaction mixture was allowed to cool to r.t., filtered through a pad of Celite®, washed with acetone (10 mL) and concentrated *in vacuo*. The residue was purified by PLC, eluting with CH_2Cl_2:petrol:toluene (50:49:1) to give:

Macrocycle **12a** as off-white needles (25.7 mg, 52%). m.p. 119.9-125.6 °C from Et_2O (decomposed); IR (ν_{max}, cm^{-1}) 2930 (w), 1740 (m, C=O st), 1460 (s), 1250 (s), 1240 (s) and 1100 (m); ^1H NMR (400 MHz, $CDCl_3$) δ_H 0.91 (t, 3H, *J* = 7.0 Hz, C*H*$_3$), 1.31-1.40 (m, 4H, 2 × C*H*$_2$), 1.53 (s, 3H, 1 × C(C*H*$_3$)$_2$), 1.54 (s, 3H, 1 × C(C*H*$_3$)$_2$), 1.58-1.70 (m, 2H, C*H*$_2$), 1.98-2.07 (m, 2H, C*H*$_2$), 2.35 (s, 3H, ArC*H*$_3$), 3.32 (s, 3H, OC*H*$_3$), 3.58 (t, 1H, *J* = 9.3 Hz, C*H*-OCH$_3$), 4.63 (d, 1H, *J* = 15.6 Hz, 1 × ArC*H*$_2$O), 4.73 (d, 1H, *J* = 15.6 Hz, 1 × ArC*H*$_2$O), 5.25 (dt, 1H, *J* = 9.3 and 2.4 Hz, C*H*OCOAr), 5.89 (dd, 1H, *J* = 16.0 and 9.3 Hz, C*H*=CHAr), 6.04 (d, 1H, *J* = 16.0 Hz, CH=C*H*Ar), 6.79 (d, 1H, *J* = 8.0 Hz, Ar*H*), 6.79 (d, 1H, *J* = 8.8 Hz, Ar*H*), 6.84 (d, 1H, *J* = 8.0 Hz, Ar*H*), 7.11 (t, 1H, *J* = 8.0 Hz, Ar*H*) and 7.23 (d, 1H, *J* = 8.8 Hz, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.0 (q), 19.3 (q), 22.5 (t), 24.6 (q), 24.7 (q), 25.3 (t), 31.6 (t), 32.0 (t), 56.8 (q), 59.8 (t), 75.7 (d), 86.0 (d), 99.2 (s), 113.1 (d), 116.1 (d), 118.9 (s), 123.9 (d), 124.2 (d), 125.9 (d), 126.7 (s), 128.4 (s), 129.6 (d), 135.3 (s), 137.6 (d), 146.1 (s), 148.1 (s), 154.6 (s) and 167.8 (s); MS (CI) *m/z* 484 ($[M + NH_4]^+$, 60%), 467 ($[M + H]^+$, 10), 426 ($[M - C_3H_6O]^+$, 5), 355 ($[M - C_3H_6O - C_4H_6O + NH_4]^+$, 100), 338 ($[MH - C_3H_6O - C_4H_6O]^+$, 40), 327 (15), 97 (15) and 52 (85); HRMS (CI) Expected mass for $C_{28}H_{38}NO_6$ ($M + NH_4^+$) 484.2714, found 484.2699 (Δ = 3.1 ppm).

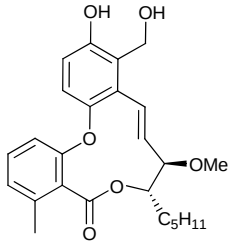
Dibenzofuran **13a** as a colourless oil (1.4 mg, 4%). IR (ν_{max}, cm^{-1}) 2930 (w), 2360 (s), 2340 (s) 1720 (m) and 1280 (s); ^1H NMR (400 MHz, $CDCl_3$) δ_H 0.93 (t, 3H, *J* = 7.0 Hz, C*H*$_3$), 1.33-1.42 (m, 6H, 3 × C*H*$_2$), 1.64 (s, 6H, C(C*H*$_3$)$_2$), 1.73-1.83 (m, 2H, C*H*$_2$), 2.65 (s, 3H, ArC*H*$_3$), 3.41 (s, 3H, OC*H*$_3$), 3.87 (ddt, 1H, *J* = 7.7, 4.4 and 0.8 Hz, C*H*-OCH$_3$), 5.32 (s, 2H, ArC*H*$_2$O), 5.39 (ddd, 1H, *J* = 16.8, 1.6 and 0.8 Hz, 1 × =C*H*$_2$), 5.39 (ddd, 1H, *J* = 10.6, 1.6 and 0.8 Hz, 1 × =C*H*$_2$), 5.42 (dt, 1H, *J* = 8.4 and 4.4 Hz, C*H*OCOAr), 5.91 (ddd, 1H, *J* = 16.8, 10.6 and 7.7 Hz, C*H*=CH$_2$), 6.97 (d, 1H, *J* = 8.8 Hz, Ar*H*), 7.22 (d, 1H, *J* = 8.0 Hz, Ar*H*), 7.38 (d, 1H, *J* = 8.8 Hz, Ar*H*) and 7.66 (d, 1H, *J* = 8.0 Hz, Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.0 (q), 20.7 (q), 22.6 (t), 24.6 (t), 25.2 (2q), 29.7 (t), 31.7 (t), 56.9 (q), 59.9 (t), 76.2 (d), 84.3 (d), 99.4 (s), 110.0 (s), 111.0 (d), 113.4 (s), 116.6 (d), 117.5 (s), 119.7 (d), 122.7 (t), 123.5 (d), 125.4 (s), 134.8 (d), 136.9 (s), 146.7 (s), 151.0 (s), 154.9 (s) and 165.8 (s); MS (ES) *m/z* 484 ($[M + NH_4]^+$, 100%), 467 ($[M + H]^+$, 70), 426 ($[M + NH_4 - C_3H_6O]^+$, 20), 339 ($[MH - C_3H_6O - C_4H_6O]^+$, 20), 297 ($[M - [C_{10}H_{19}O]^+$, 50), 279 ($[C_{18}H_{15}O_3]^+$, 60), 266 (15), 249 (20), 226 (55), 208 (55) and 155 ($[C_{10}H_{19}O]^+$, 35); HRMS (ES) Expected mass for $C_{28}H_{35}O_6$ (]M + H]$^+$) 467.2449, found 467.2434 (Δ = 3.2 ppm).

(14*R,15*S**,*E*)-14-(4-Methoxybenzyloxy)-1,11,11-trimethyl-15-pentyl-14,15-dihydro-5*H*-benzo[*b*]10,12-dioxo[1,2-*j*][1,5]dioxacycloundecin-17(9*H*)-one** (**12b**)



A degassed solution of 1,4-dioxane (3 mL) was added aryl iodide **9b** (40 mg, 61.2 μmol), $Pd(acac)_2$ (2 mg, 6.6 μmol), Cs_2CO_3 (40 mg, 123 μmol) and **11** (2 mg, 13.8 μmol). The reaction mixture was stirred at 120°C for 24 h. After this time the reaction mixture was allowed to cool to r.t., filtered through a pad of Celite®, washed with ethyl acetate (20 mL) and concentrated *in vacuo*. The residue was passed through a short silica gel column, eluting with EtOAc:petrol (1:3) and further purified by plate-TLC, eluting with CH_2Cl_2:petrol:toluene (50:49:1) to give **12b** as a colourless oil (12 mg, 34%). The analogous reaction was also performed on aryl iodide **10b** to afford **12b** in 47% yield. IR (ν_{max}, cm^{-1}) 2928 (m), 1738 (m), 1513 (m), 1460 (s), 1251 (s), 1081 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.89 (t, 3H, *J* = 6.9 Hz, CH_2CH_3), 1.50-1.25 (m, 6H, 3 × CH_2), 1.58 (m, 1H, C*H*H'C_4H_9), 1.52 (s, 3H, CCH_3), 1.53 (s, 3H, CC*H'*$_3$), 2.02 (m, 1H, CH*H'*C_4H_9), 2.31 (s, 3H, ArCH_3), 3.74 (apparent t, 1H, *J* = 8.7 Hz, C*H*OCH_2Ar), 3.79 (s, 3H, OCH_3), 4.32 (d, 1H, *J* = 11.6 Hz, C*H*H'Ar), 4.57 (d, 1H, *J* = 11.6 Hz, CH*H'*Ar), 4.62 (d, 1H, *J* = 15.4 Hz, C*H*H'Ar), 4.70 (d, 1H, *J* = 15.4 Hz, CH*H'*Ar), 5.30 (m, 1H, ArCO_2CH), 6.00-5.88 (m, 2H, C*H*=C*H*), 6.75 (d, 1H, *J* = 8.3 Hz, Ar*H*), 6.78 (d, 1H, *J* = 8.8 Hz, Ar*H*), 6.80 (d, 1H, *J* = 7.7 Hz, Ar*H*), 6.86 (d, 2H, *J* = 8.6 Hz, 2 × Ar*H*), 7.07 (apparent t, 1H, *J* = 8.0 Hz, Ar*H*), 7.21 (m, 3H, 3 × Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.2 (q), 19.5 (q), 22.8 (t), 24.9 (q), 24.9 (q), 25.4 (t), 31.9 (t), 32.1 (t), 55.5 (q), 60.1 (t), 70.7 (t), 76.0 (d), 82.8 (d), 99.5 (s), 113.3 (d), 114.1 (2 × d), 116.4 (d), 119.1 (d), 124.1 (d), 124.4 (d), 126.1 (s), 126.9 (s) 128.6 (s), 129.7 (2 × d), 129.8 (d), 130.1 (s), 135.4 (s), 138.0 (d), 146.3 (s), 148.2 (s), 154.8 (s), 159.5 (s), 168.0 (s); MS (CI^+) 592 (15%), 591 (41), 590 ($[M + NH_4]^+$, 92), 532 (21), 515 (27), 297 (13), 138 (18), 121 (100); HRMS (CI^+) Expected mass for $C_{35}H_{44}NO_7$ $[M + NH_4]^+$ 590.3118, found 590.3114 (Δ = 0.7 ppm).

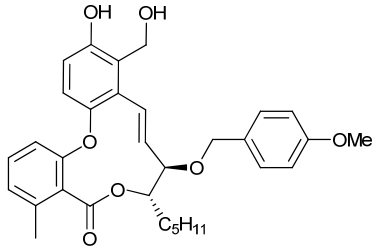
(±)-Aspercyclide B C19 methyl ether (**14a**)



A solution of acetonide **12a** (14 mg, 0.030 mmol) in THF:1M HCl (1:1 *v/v*, 4 mL) was heated at 80 °C for 3 h. After this time the solution was allowed to cool to r.t. before being extracted with Et_2O (3 × 5 mL). The organic extracts were combined, washed with brine (10 mL), dried (Na_2SO_4), filtered and concentrated *in vacuo* to give methyl ether **14a** as a colourless oil (12 mg, 94%). IR (ν_{max}, cm^{-1}) 3310 (br w, OH st), 2920 (m), 1740 (m, C=O st), 1450 (s), 1250 (s) and 1100 (s); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.91 (t, 3H, *J* = 7.0 Hz, CH_3), 1.31-1.54 (m, 4H, 2 × CH_2), 1.59-1.69 (m, 2H, CH_2), 1.99-2.07 (m, 2H, CH_2), 2.34 (s, 3H, ArCH_3), 3.58 (app t, 1H, *J* = 9.4 Hz,

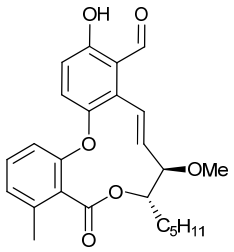
C*H*-OCH_3), 3.70 (s, 3H, OCH_3), 4.87 (s, 2H, $ArCH_2OH$), 5.21 (dt, 1H, *J* = 9.4 and 2.4 Hz, C*H*OCOAr), 5.77 (dd, 1H, *J* = 16.2 and 9.4 Hz, C*H*=CHAr), 6.18 (d, 1H, *J* = 16.2 Hz, CH=C*H*Ar), 6.75 (d, 1H, *J* = 8.0 Hz, Ar*H*), 6.83 (d, 1H, *J* = 8.0 Hz, Ar*H*), 6.84 (d, 1H, *J* = 8.8 Hz, Ar*H*), 7.10 (t, 1H, *J* = 8.0 Hz, Ar*H*), 7.21 (d, 1H, *J* = 8.8 Hz, Ar*H*) and 7.77 (br s, 1H, O*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.0 (q), 19.3 (q), 22.5 (t), 25.3 (t), 29.7 (t), 32.0 (t), 56.9 (q), 61.6 (t), 75.7 (d), 86.0 (d), 112.7 (d), 115.8 (d), 123.5 (s), 123.8 (d), 124.9 (d), 126.5 (s), 127.4 (d), 129.6 (d), 130.6 (s), 135.2 (s), 137.4 (d), 145.5 (s), 153.5 (s), 154.4 (s) and 167.9 (s); MS (ES) *m/z* 875 ($[M_2 + Na]^+$, 40%), 749 (20), 677 ($[M + C_{14}H_{13}O_3 + Na]^+$, 20), 655 ($[M + C_{14}H_{13}O_3]^+$, 30), 576 (20), 511 (25), 497 (30), 490 ($[C_{16}H_{21}O_2]_2^+$, 60), 449 ($[M + Na]^+$, 75), 409 (20), 395 ($[M - OMe]^+$, 20), 315 ($[C_{17}H_{24}NaO_4]^+$, 40), 245 ($[C_{16}H_{21}O_2]^+$, 100), 229 ($[C_{14}H_{13}O_3]^+$, 40), 204 (40) and 157 ($[C_8H_6NaO_2]^+$, 35); HRMS (ES) Expected mass for $C_{25}H_{30}O_6Na$ ($M + Na^+$) 449.1952, found 449.1940 (Δ = 2.7 ppm).

(±)-Aspercyclide B C19 4-methoxybenzyl ether (**14b**)



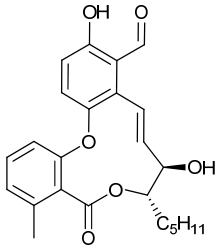
To a solution of acetonide **12b** (26 mg, 45 μmol) in THF:MeOH (1:3 *v/v*, 6 mL) was added *p*-toluenesulfonic acid monohydrate (2.6 mg, 13.6 μmol). The resulting mixture was stirred at 40 °C for 2 h and then allowed to cool to r.t. The mixture was diluted with ethyl acetate (20 mL), washed with water (20 mL) and then brine (20 mL). The organic phase was then separated, dried (N_a2SO_4) and concentrated under reduced pressure. The residue was purified by plate-TLC, eluting with CH_2Cl_2:petrol:toluene (50:49:1) to give **14b** as a colourless resin (20 mg, 82%). IR (ν_{max}, cm^{-1}) 3392 (broad w), 2929 (m), 1737 (m), 1514 (m), 1456 (m), 1252 (s), 1077 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.89 (t, 3H, *J* = 6.9 Hz, CH_2CH_3), 1.50-1.23 (m, 6H, 3 × CH_2), 1.57 (m, 1H, C*H*H'C_4H_9), 2.02 (m, 1H, CH*H*'C_4H_9), 2.30 (s, 3H, $ArCH_3$), 3.75 (apparent t, 1H, *J* = 9.3 Hz, C*H*OCH_2Ar), 3.78 (s, 3H, OCH_3), 4.35 (d, 1H, *J* = 11.5 Hz, C*H*H'Ar), 4.54 (d, 1H, *J* = 11.5 Hz, CH*H*'Ar), 4.84-4.75 (m, 2H, CH_2OH), 5.25 (apparent t, 1H, *J* = 9.2 Hz $ArCO_2CH$), 5.79 (dd, 1H, *J* = 16.0 and 9.4 Hz, C*H*=CHAr), 6.07 (d, 1H, *J* = 16.0 Hz, CH=C*H*Ar), 6.71 (d, 1H, *J* = 8.3 Hz, Ar*H*), 6.84-6.77 (m, 2H, 2 × Ar*H*), 6.86 (d, 2H, *J* = 8.5 Hz, 2 × Ar*H*), 7.06 (apparent t, 1H, *J* = 8.0 Hz, Ar*H*), 7.18 (d, 1H, *J* = 8.7 Hz, Ar*H*), 7.21 (d, 2H, *J* = 8.5 Hz, 2 × Ar*H*); ^{13}C NMR (100 MHz, $CDCl_3$) δ_C 14.2 (q), 19.4 (q), 22.7 (t), 25.3 (q), 31.9 (t), 32.1 (t), 55.5 (q), 61.8 (t), 71.1 (t), 75.9 (d), 83.1 (d), 112.9 (d), 114.1 (2 × d), 116.0 (d), 123.7 (s), 124.0 (d), 125.4 (d), 126.7 (s), 127.3 (s) 129.7 (d), 129.8 (2 × d), 130.2 (d), 130.7 (s), 135.4 (s), 137.7 (d), 145.8 (s), 153.7 (s), 154.6 (s), 159.5 (s), 168.1 (s); MS (ESI^+) 556 (36%), 555 ($[M + Na]^+$, 97), 551 (35), 550 ($[M + NH_4]^+$, 100), 515 ($[M - H_2O]^+$, 32); HRMS (ESI^+) Expected mass for $C_{32}H_{36}O_7Na$ $[M + Na]^+$ 555.2359, found 555.2364 (Δ = 0.9 ppm).

(±)-Aspercyclide A C19 methyl ether (**15a**)



To a solution of aspercyclide B C19 methyl ether **14a** (12 mg, 0.028 mmol) in CH_2Cl_2 (1 mL) was added activated MnO_2 (12.3 mg, 0.14 mmol). The resulting suspension was heated at 40 °C for 4 h. After this time the suspension was allowed to cool to r.t. before being filtered through a pad of Celite® and concentrated *in vacuo*. The resulting off-white solid was recrystallized from CH_2Cl_2 to give aspercyclide A C19 methyl ether as colourless elongated plates (5.0 mg, 42%). m.p. 118.4-121.5 °C from CH_2Cl_2; IR (ν_{max}, cm^{-1}) 2920 (w), 1740 (C=O st, m), 1650 (m), 1460 (m), 1250 (s), 1240 (s), 1100 (m) and 730 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.92 (t, 3H, J = 7.0 Hz, C*H*$_3$), 1.32-1.41 (m, 4H, 2 × C*H*$_2$), 1.49-1.55 (m, 2H, C*H*$_2$), 1.62-1.71 (m, 1H, 1 × C*H*$_2$), 2.02-2.10 (m, 1H, 1 × C*H*$_2$), 2.36 (s, 3H, ArC*H*$_3$), 3.35 (s, 3H, OC*H*$_3$), 3.66 (app t, 1H, *J* = 9.4 Hz, C*H*-OCH$_3$), 5.25 (dt, 1H, *J* = 9.4 and 2.7 Hz, C*H*OCOAr), 5.98 (dd, 1H, *J* = 16.0 and 9.4 Hz, C*H*=CHAr), 6.51 (d, 1H, *J* = 16.0 Hz, CH=C*H*Ar), 6.70 (d, 1H, *J* = 7.9 Hz, Ar*H*), 6.89 (d, 1H, *J* = 7.9 Hz, Ar*H*), 6.98 (d, 1H, *J* = 8.8 Hz, Ar*H*), 7.14 (t, 1H, *J* = 7.9 Hz, Ar*H*), 7.58 (d, 1H, *J* = 8.8 Hz, Ar*H*), 10.16 (s, 1H, ArC*H*O) and 11.54 (br s, 1H, O*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 14.0 (q), 19.3 (q), 22.5 (t), 25.2 (t), 31.6 (t), 32.0 (t), 57.2 (q), 75.7 (d), 85.8 (d), 112.7 (d), 117.5 (d), 118.5 (s), 124.3 (d), 124.8 (d), 126.6 (s), 129.7 (d), 133.8 (d), 135.4 (s), 135.6 (s), 140.1 (d), 145.0 (s), 154.0 (s), 159.7 (s), 167.5 (s) and 195.4 (d); MS (EI) *m/z* 424 ([M]$^+$, 10), 337 (10), 324 (40), 292 ([$C_{17}H_{24}O_4$]$^+$, 80), 281 (20), 277 (20), 264 (40), 255 ([$C_{15}H_{11}O_4$]$^+$, 20), 235 (20), 135 (20), 83 (25), 72 ([C_4H_8O]$^+$, 75), 69 (35), 59 (100) and 55 (60); HRMS (EI) Expected mass for $C_{25}H_{28}O_6$ (M^+) 424.1885, found 424.1886 (Δ = 0.2 ppm). A single crystal X-ray structure determination was performed on this product (see Separate Supporting Information File).

(±)-Aspercyclide A (**1**)



To a solution of diol **14b** (10 mg, 19 μmol) in CH_2Cl_2 (5 mL) was added activated MnO_2 (16 mg, 184 mmol) and the resulting suspension stirred at r.t. for 30 mins. After this time the reaction mixture was filtered through a pad of Celite® and $BF_3{\cdot}Et_2O$ (10 μL, 81 μmol) was added to the filtrate and the mixture stirred for a further 5 mins. The solution was then diluted with Et_2O (20 mL), washed with distilled water (20 mL), separated, dried (Na_2SO_4) and concentrated *in vacuo*. The residue was purified by silica gel chromatography, eluting with EtOAc:petrol (1:4) to afford aspercyclide A **1** as a white solid (5.5 mg, 72%). m.p. 195-197 °C; IR (ν_{max}, cm^{-1}) 3442 (w), 2926 (w), 1721 (m), 1652 (m), 1454 (s), 1252 (s), 1236 (s), 1074 (m), 966 (m) and 733 (m); ^{1}H NMR (400 MHz, $CDCl_3$) δ_H 0.91 (t, 3H, *J* = 7.0 Hz, CH_2CH_3), 1.60-1.30 (m, 6H, 3 × C*H*$_2$), 1.68 (m, 1H, CHC*H*H'), 1.93 (br s, 1H, O*H*), 2.08 (m, 1H, CHCH*H'*), 2.35 (s, 3H, ArC*H*$_3$), 4.15 (apparent td, 1H, *J* = 9.1 and 3.2 Hz,

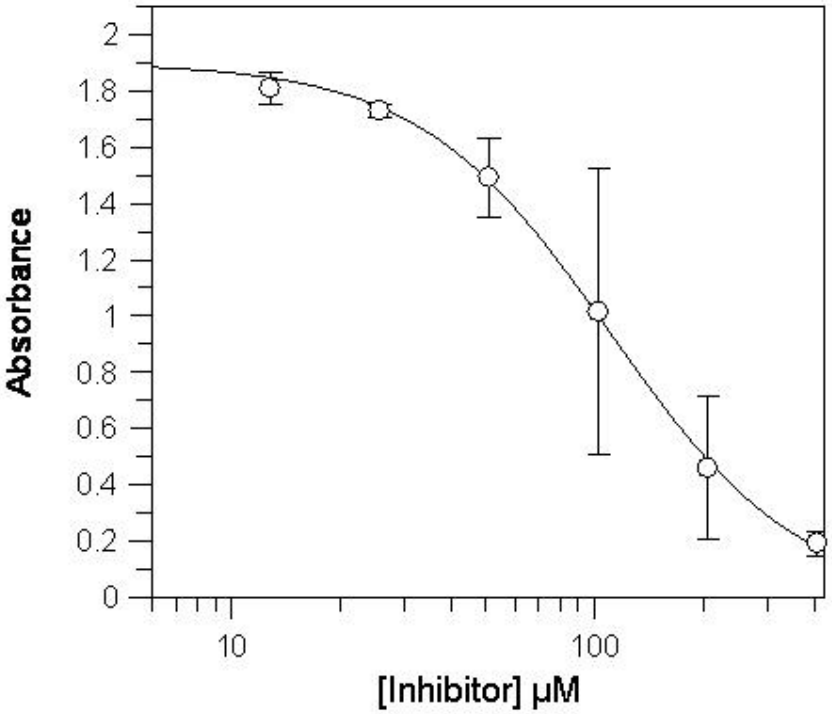
C*H*OH), 5.20 (dt, 1H, *J* = 9.4 and 2.4 Hz, $ArCO_2CH$), 6.04 (dd, 1H, *J* = 16.0 and 9.1 Hz, C*H*=CHAr), 6.46 (d, 1H, *J* = 16.0 Hz, CH=C*H*Ar), 6.68 (d, 1H, *J* = 8.3 Hz, Ar*H*), 6.87 (d, 1H, *J* = 7.7 Hz, Ar*H*), 6.95 (d, 1H, *J* = 8.9 Hz, Ar*H*), 7.12 (apparent t, 1H, *J* = 8.0 Hz, Ar*H*), 7.55 (d, 1H, *J* = 9.0 Hz, Ar*H*), 10.11 (s, 1H, ArC*H*O) and 11.55 (s, 1H, O*H*); ^{13}C NMR (126 MHz, $CDCl_3$) δ_C 14.2 (q), 19.5 (q), 22.7 (t), 25.4 (t), 31.8 (t), 31.9 (t), 113.1 (d), 117.8 (d), 118.8 (s), 123.4 (d), 124.6 (d), 126.8 (s), 130.0 (d), 133.8 (d), 135.5 (s), 135.8 (s), 141.0 (d), 145.3 (s), 154.3 (s), 159.9 (s), 167.9 (s) and 195.7 (d), (two additional carbons signals obscured by $CDCl_3$); MS (EI^+) *m/z* 410 ($[M]^+$, 15%), 310 (34), 297 (15), 282 (31), 281 (100), 264 (51), 135 (18); HRMS (EI^+) Expected mass for $C_{24}H_{26}O_6$ (M^+) 410.1729, found 410.1724 (Δ = 1.3 ppm).

IgE Receptor Binding Enzyme-linked Immunosorbent Assay (ELISA)

Compounds **1** and **15a** were evaluated in a receptor binding ELISA assay using IgE-Fc (Ceε □ 2-4) protein,[8] a chimeric construct of the α-subunit of FcεRI fused to the Fc region of IgG [referred to below as AG (alpha-gamma) receptor protein],[9] Biotinylated anti-IgE (Vector Laboratories), Streptavidin-Horse Radish Peroxidase conjugate (Biosource International, Inc.) and *o*-phenylenediamine dihydrochloride (OPD, Sigma-Aldrich) in P96 Maxisorp NUNC Immunoplates (Nalge Europe Ltd.). The protocol was as follows: The plates were coated with AG receptor protein (100 μL, 2 μgmL^{-1}) in aqueous carbonate buffer (0.045 M $NaHCO_3$ + 0.018 M Na_2CO_3, pH 9.8) for 14 h at 4 °C. The plates were then washed with PBS-Tween 20 (3 × 300 μL, 0.1% v/v, 2-3 min) to remove residual AG receptor protein and unbound sites were then blocked by incubation with a solution of Bovine Serum Albumin (BSA) in PBS (300 μL, 2% v/v) for 14 h at 4 °C. The plates were washed with PBS-Tween 20 (3 × 300 μL, 0.1% v/v, 2-3 min) and pre-mixed solutions of the IgE-Fc protein (15 $ngmL^{-1}$ in 100 μL PBS) and the antagonist (*i.e.* compound **1** or **15a**, initially 0.5 mM in DMSO, with subsequent dilutions) were added, the wells thoroughly stirred, and the plates incubated for 1 h at 37 °C. The final concentration of DMSO in all the wells was 5% v/v. The plates were then washed with PBS-Tween 20 (3 × 300 μL, 0.1% v/v, with the first wash taking ~30 min *cf.* 2-3 min in normal washes to ensure removal of DMSO). Bound IgE-Fc was detected by incubation with biotinylated anti-IgE (1/5000 dilution in 1% v/v BSA in PBS) for 1 h at 37 °C followed by washing with PBS-Tween 20 (3 × 300 μL, 0.1% v/v, 2-3 min) and then further incubation with streptavidin-HRP (1/5000 dilution in 1% v/v BSA in PBS) and washing with PBS alone (3 × 300 μL, 0.1% v/v, 2-3 min). A solution of OPD (50 L, 0.2 $mgmL^{-1}$ in peroxide buffer) was added to the plates and after 5 min at 37 °C in the dark the enzyme reaction was halted by addition of an aqueous solution of HCl (50 μL, 3 M). Absorbance detection of the plates was then performed at 492 nm using an ELISA plate reader (Titertek Multiskan). Rose Bengal (Sigma-Aldrich) was used as a control antagonist.

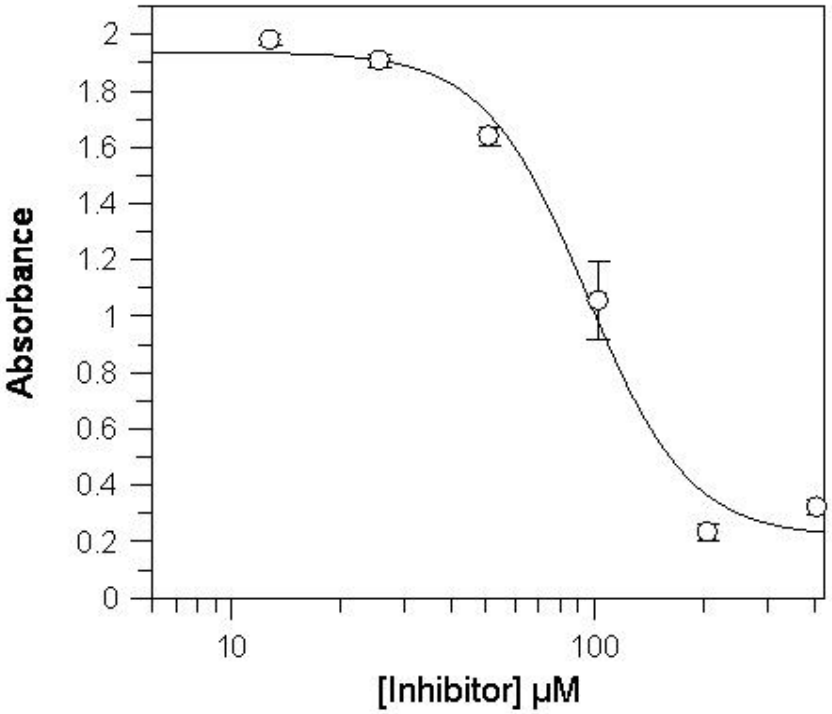
Data were fitted using the standard IC_{50} equation in the GraFit program.[10]

Aspercyclide A, **1**



Parameter	Value	Std. Error
Y Range	1.9164	0.1123
IC 50	109.7756	9.1641
Slope factor	1.6571	0.1768
Background	-0.0163	0.0962

Methyl ether, **15a**



Parameter	Value	Std. Error
Y Range	1.7230	0.1537
IC 50	94.9041	9.9277
Slope factor	3.0822	0.8781
Background	0.2154	0.1212

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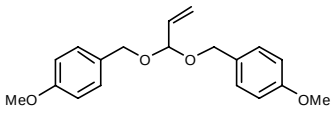
10. R. J. Leatherbarrow, *GraFit version 5*, 2001, Horley, UK: Erithacus SoftwareLtd.

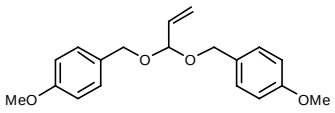
NMR Data for all New Compounds

^{1}H NMR (400 MHz, C_6D_6)



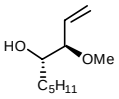
3,3-Di-(4-methoxybenzyloxy)-prop-1-ene

^{13}C NMR (100 MHz, C_6D_6)



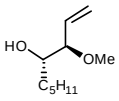
3,3-Di-(4-methoxybenzyloxy)-prop-1-ene

^{1}H NMR (400 MHz, $CDCl_3$)



5a

^{13}C NMR (100 MHz, $CDCl_3$)



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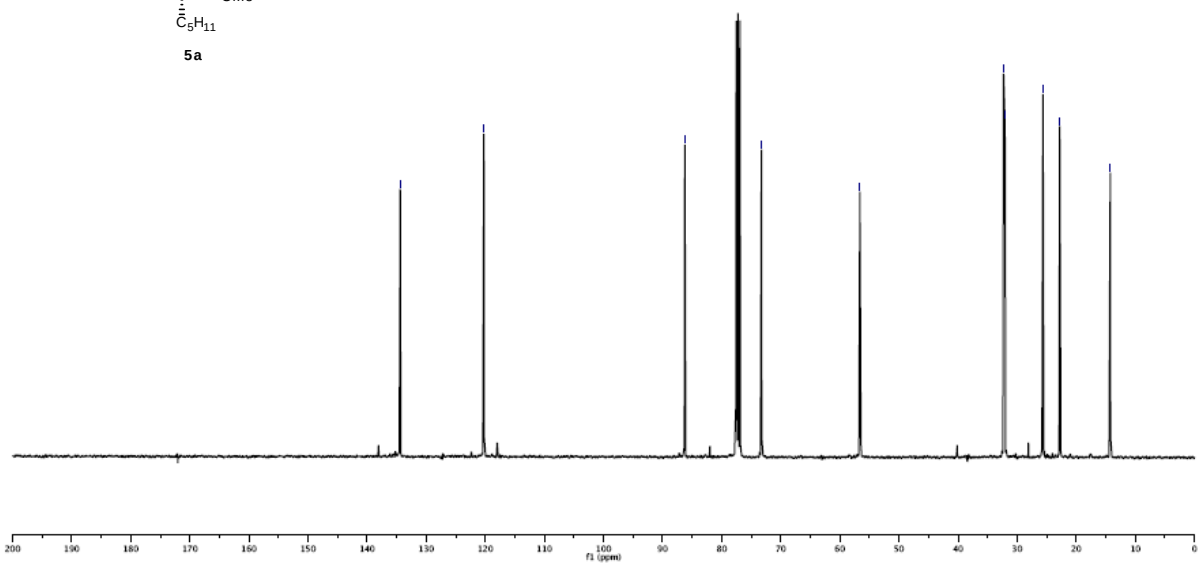

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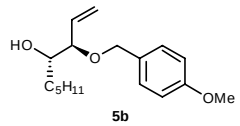
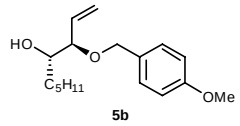


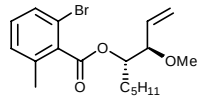
5b

^{13}C NMR (100 MHz, $CDCl_3$)



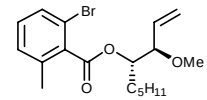
5b

^{1}H NMR (400 MHz, $CDCl_3$)



7a

^{13}C NMR (100 MHz, $CDCl_3$)



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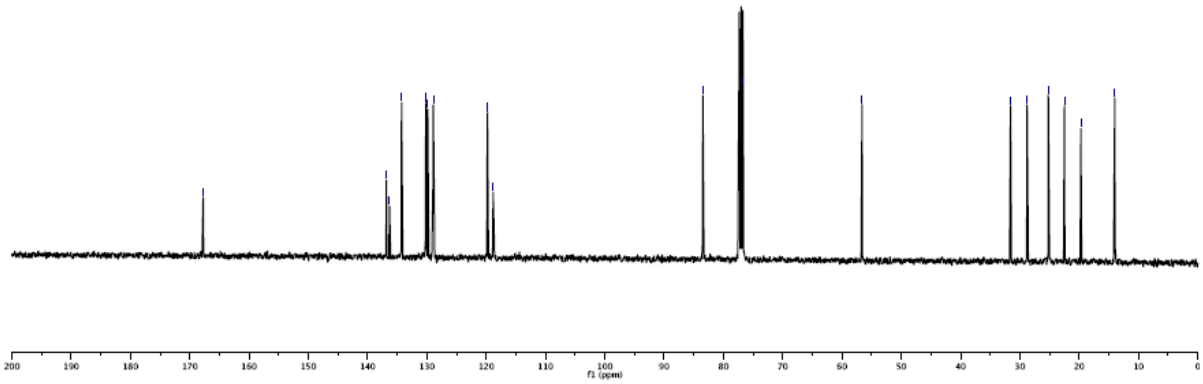

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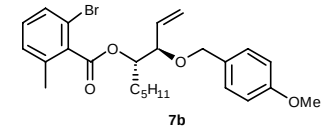

7b

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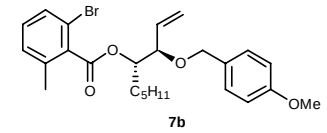

7b

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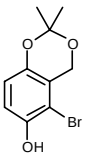

8

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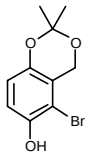

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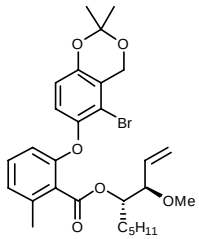

9a

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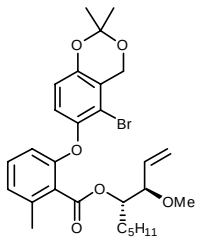

9a

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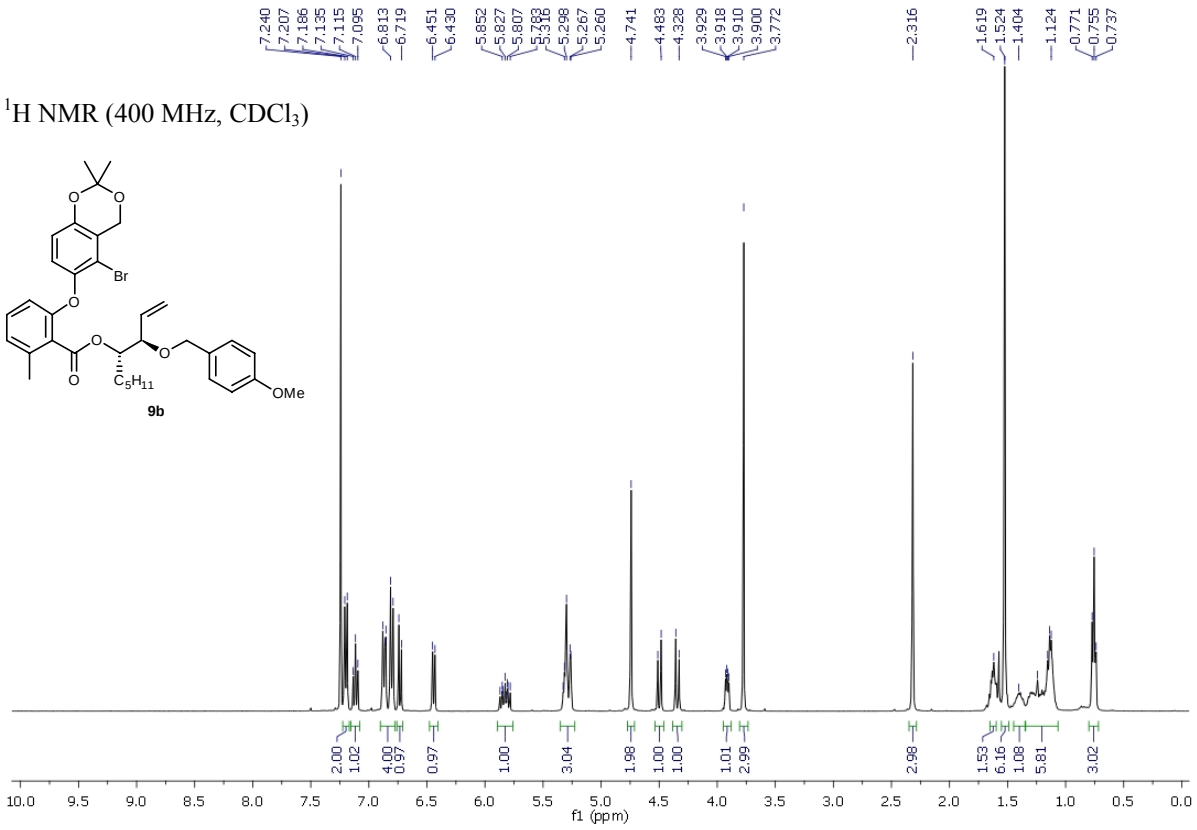

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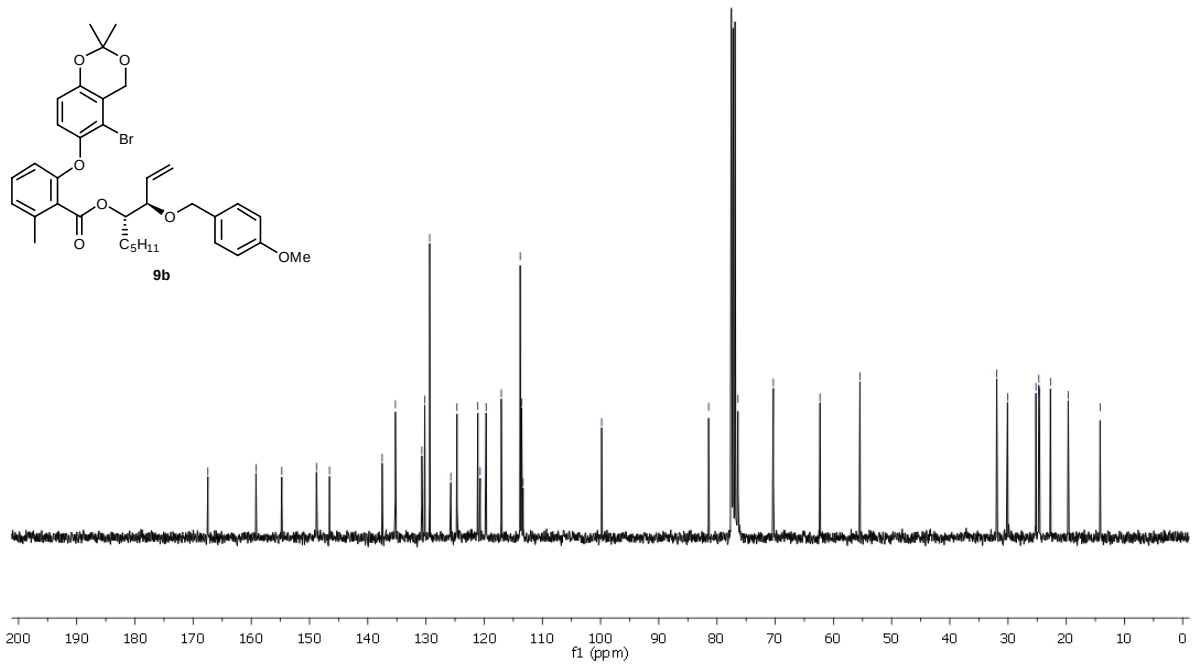

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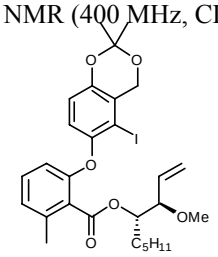

10a

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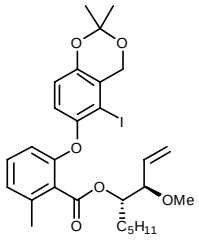

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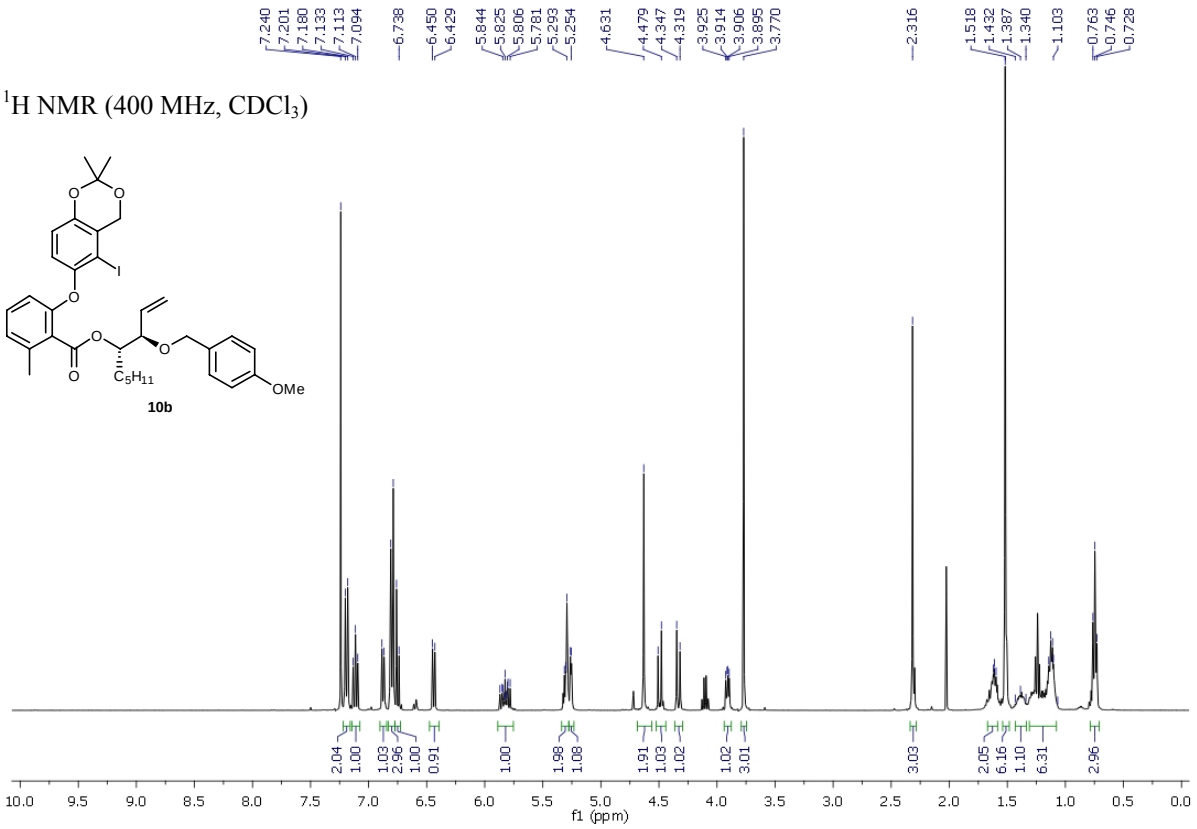

10b

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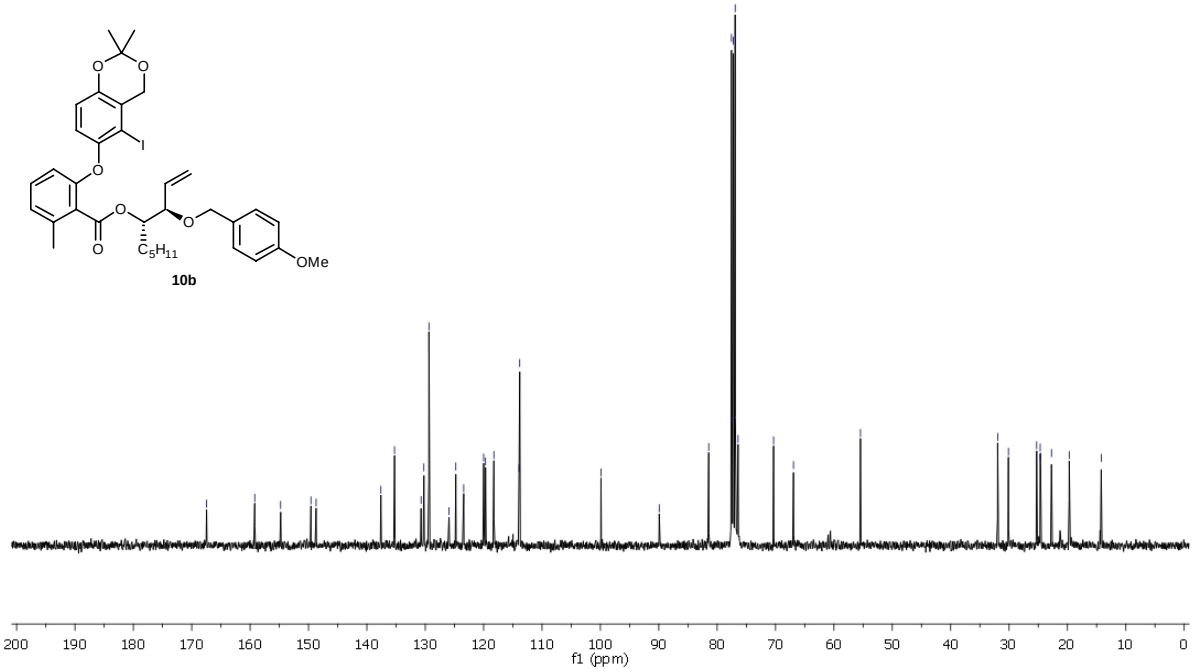

10b

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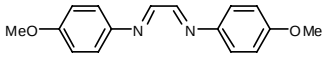
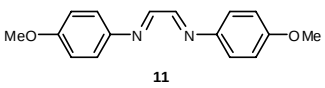


11

^{13}C NMR (100 MHz, $CDCl_3$)



11

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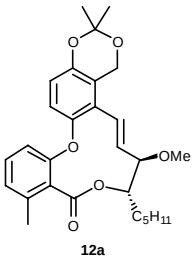
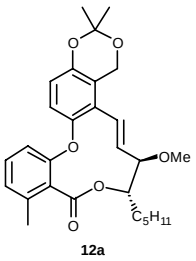


12a

^{13}C NMR (100 MHz, $CDCl_3$)



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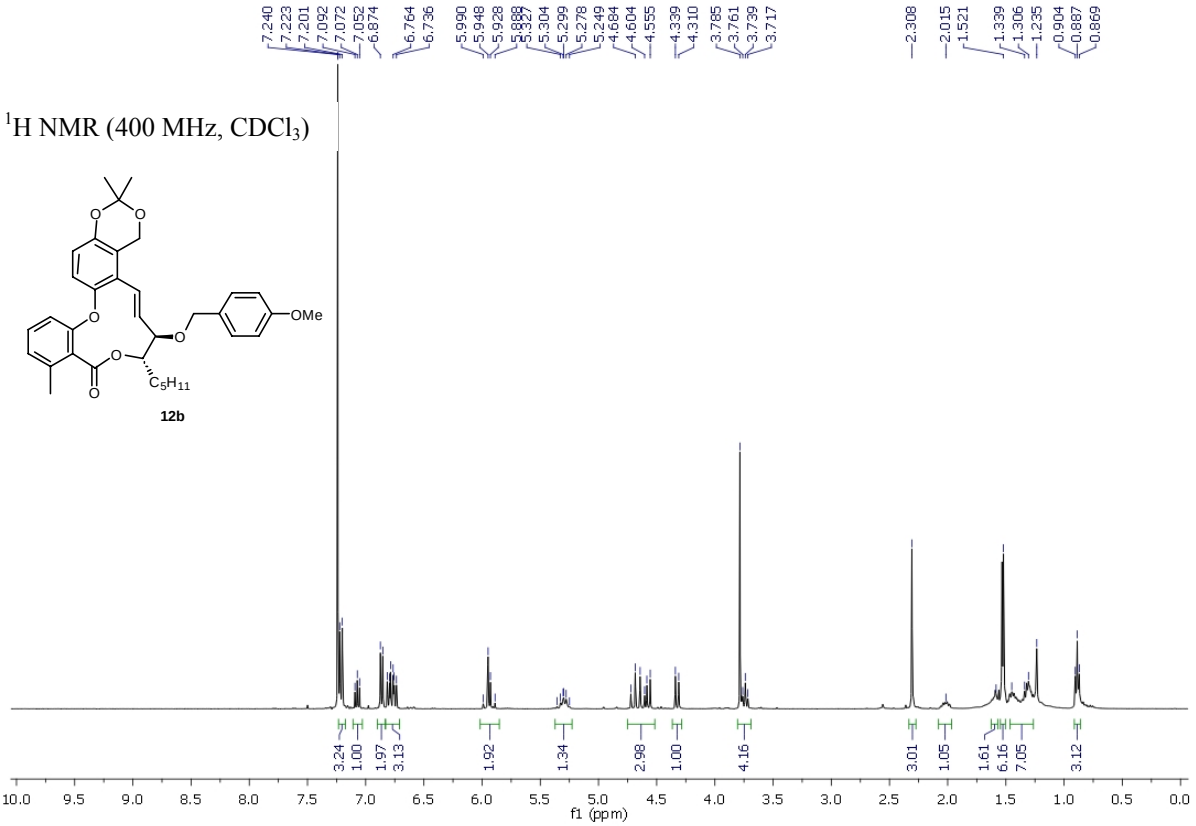

12b

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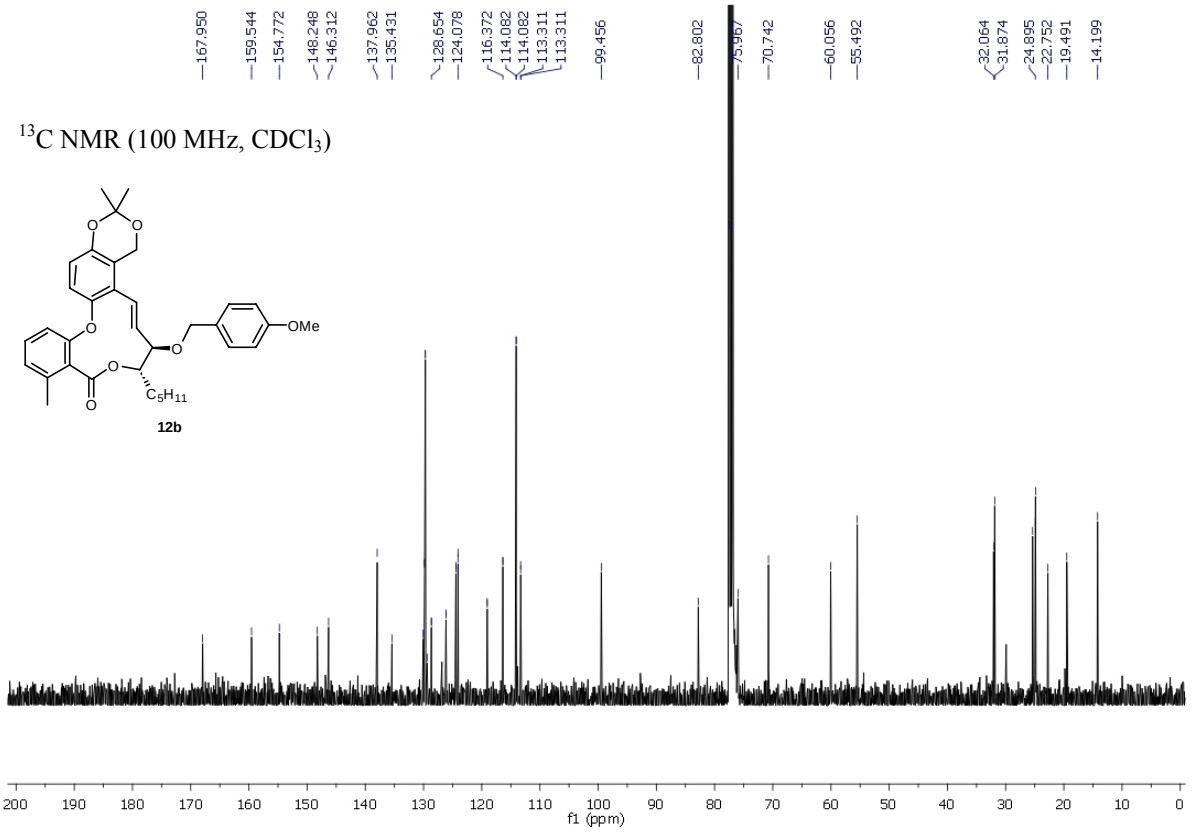

12b

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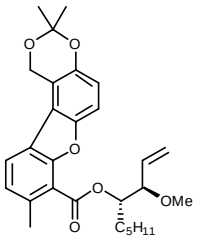

13a

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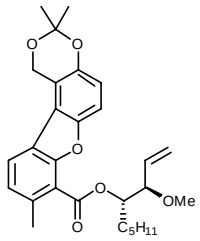

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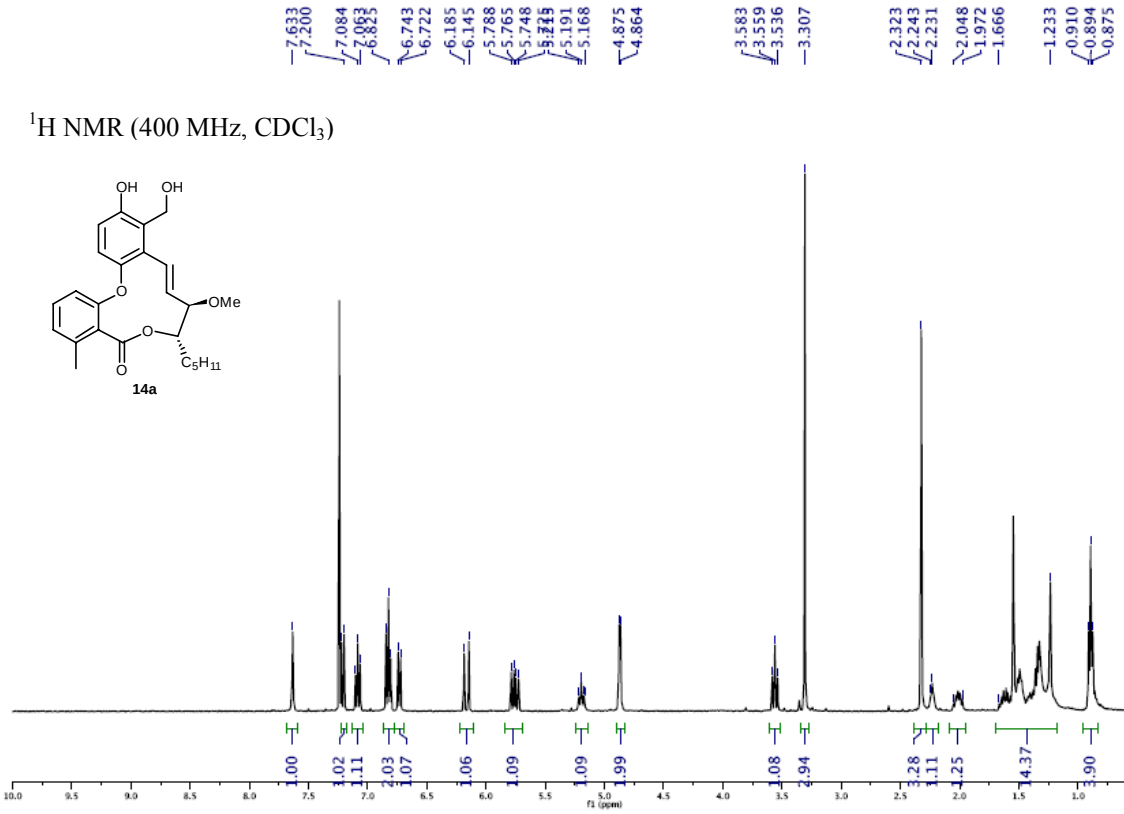

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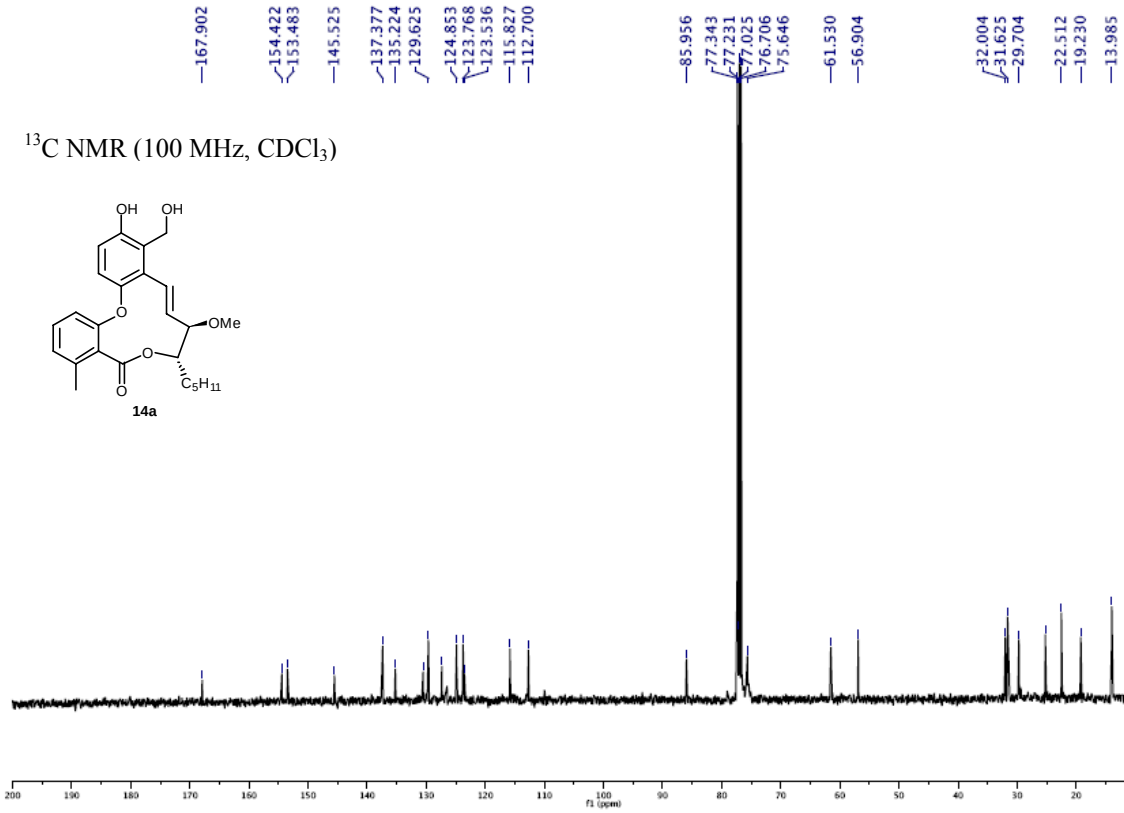
14a



^{13}C NMR (100 MHz, $CDCl_3$)

14a

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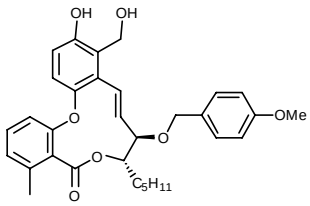

14b

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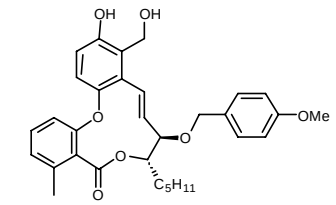

14b

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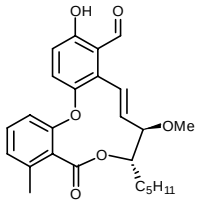

15a

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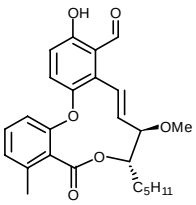

15a

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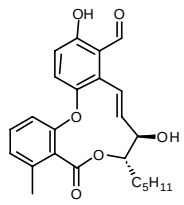
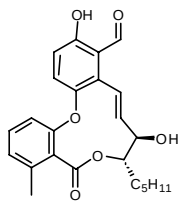


1

^{13}C NMR (125 MHz, $CDCl_3$)



1

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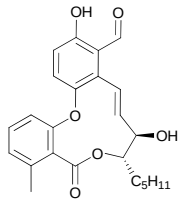
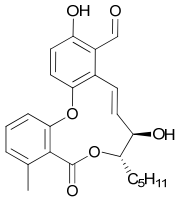


1

(Authentic Sample - Merck)

^{13}C NMR (125 MHz, $CDCl_3$)



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(Authentic Sample - Merck)