Enantioselective Nickel-Catalyzed Arylative Intramolecular 1,4-Allylations

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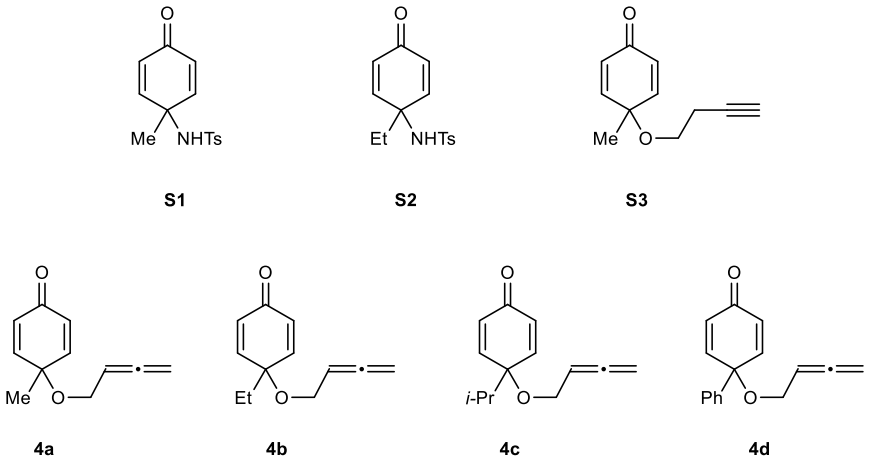
General Information

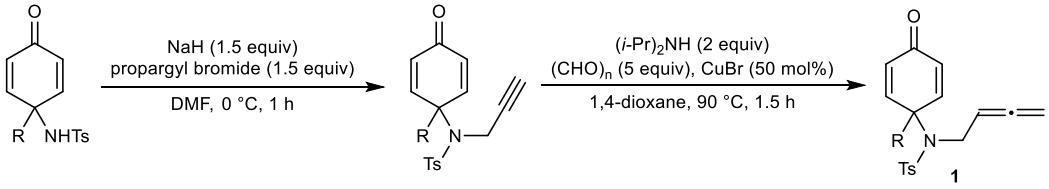
All air-sensitive reactions were carried out under a nitrogen atmosphere using oven-dried apparatus. Unless stated otherwise, all solvents used in reactions were anhydrous. THF, DMF and MeCN were dried and purified by passage through activated alumina columns using a solvent purification system. Anhydrous 1,4-dioxane was obtained from commercial sources. All commercially available reagents were used as received unless otherwise stated. Arylboronic acids were used as received unless the sample contained >10% boroxine as determined by ^{1}H NMR analysis. In this case, the boronic acid was stirred in a mixture of Et_2O and water for 30 minutes. The organic phase was separated, dried (Na_2SO_4), filtered, and concentrated under reduced pressure to give the corresponding boronic acid which was used without further purification. Petroleum ether refers to 40–60 °C petroleum ether. Flash column chromatography was carried out using silica gel (Fisher Scientific 60Å particle size 35–70 micron) or using a Interchim Puriflash 430 series purification system with IR-50SI 50μm pre-packed columns. Melting points were recorded on a Gallenkamp melting point apparatus and are uncorrected. The solvent of recrystallization is reported in parentheses. Infrared (IR) spectra were recorded on either a Shimadzu IRAffinity-1 or a Nicolet Avatar 360 FT instrument on the neat compound. ^{1}H and ^{13}C NMR spectra were referenced to external tetramethylsilane *via* the residual protonated solvent (^{1}H) or the solvent itself (^{13}C). All chemical shifts are reported in parts per million (ppm). For $CDCl_3$, the shifts are referenced to 7.27 ppm for ^{1}H NMR spectroscopy and 77.0 ppm for ^{13}C NMR spectroscopy. Coupling constants (*J*) are quoted to the nearest 0.1 Hz. Assignments were made using the DEPT sequence with secondary pulses at 90° and 135°. High-resolution mass spectra were recorded using electrospray ionization (ESI). X-ray diffraction data were collected at 120 K on either an Agilent SuperNova diffractometer using MoKα radiation at 0.71 Å or on an Agilent GV1000 using CuKα radiation, and refined in SHELXTL. Chiral HPLC analysis was performed on an Agilent 1290 series or Agilent 1260 series instrument using 4.6 × 250 mm columns. 2-[2-(Diphenylphosphino)ethyl]pyridine (**L1**, Sigma-Aldrich product 695599) was used as an achiral ligand to obtain authentic racemic compounds.

Preparation of Substrates

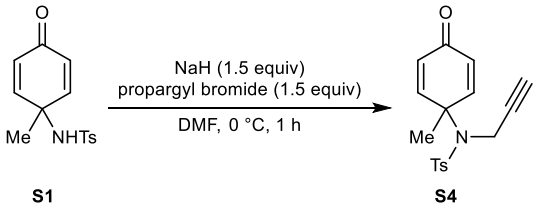


S1,[1] **S2**,[1] **S3**[2] were prepared according to previously reported procedures. Substrates **4a**–**4d** were prepared according to previously reported procedures.[3]

Preparation of Substrates 1a-1b



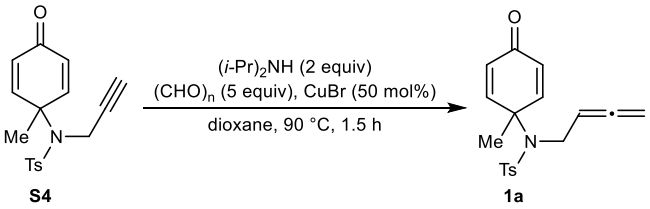
4-Methyl-*N*-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)-*N*-(prop-2-yn-1-yl)benzene-1-sulfonamide (S4)



To a solution of sulfonamide **S1**[1] (2.77 g, 10.0 mmol) in DMF (20 mL) at 0 °C under inert atmosphere was added NaH (60% dispersion in mineral oil, 0.60 g, 15 mmol) portionwise. Propargyl bromide (80% in toluene, 1.68 mL, 15.0 mmol) was added and the mixture was stirred for 1 h. The reaction was diluted with EtOAc (30 mL), washed with saturated aqueous NH_4Cl solution (25 mL) and brine/H_2O (1:1, 40 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The mixture was purified by column chromatography (40% EtOAc/petroleum ether) to give *alkyne* **S4** (2.70 g, 87%) as a white solid. R_f = 0.43 (40% EtOAc/petroleum ether); m.p. 123-124 °C (Et_2O); IR 3312, 3222, 3051, 2974, 2919, 2112 (C≡C), 1670 (C=O), 1629, 1314, 1148, 1088, 1030, 861, 815, 695, 547 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.81 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.30 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.03 (2H, d, *J* = 10.4 Hz, 2 ×

O=CCH=C**H**), 6.17 (2H, d, *J* = 10.0 Hz, 2 × O=CC**H**), 4.27 (2H, d, *J* = 2.4 Hz, CH_2), 2.44 (3H, s, ArC**H**$_3$), 2.36 (1H, t, *J* = 2.4 Hz, ≡C**H**), 1.61 (3H, s, NCC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.3 (C), 151.1 (2 × CH), 144.0 (C), 138.5 (C), 129.6 (2 × CH), 128.0 (2 × CH), 127.7 (2 × CH), 80.3 (C), 73.7 (CH), 60.1 (C), 36.3 (CH_2), 25.8 (CH_3), 21.6 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{17}H_{17}NNaO_3S]^+$ $[M + Na]^+$: 338.0821, found: 338.0824.

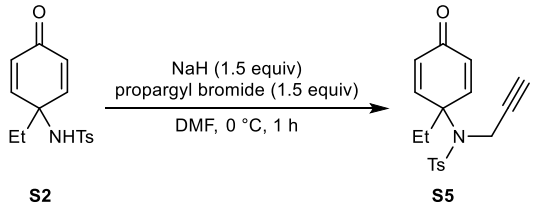
_N_-(Buta-2,3-dien-1-yl)-4-methyl-_N_-(1-methyl-4-oxocyclohexa-2,5-dien-1-yl)benzene-1-sulfonamide (1a)



S4 **1a**

To a solution of sulfonamide **S4** (2.90 g, 8.50 mmol) in 1,4-dioxane (45 mL) at room temperature under inert atmosphere was added paraformaldehyde (1.30 g, 42.5 mmol), CuBr (0.61 g, 4.3 mmol), and diisopropylamine (2.4 mL, 17 mmol). The reaction was heated at 90 °C for 1.5 h, cooled to room temperature, filtered through a pad of celite using EtOAc as eluent, and concentrated under reduced pressure. The mixture was purified by column chromatography (40% EtOAc/petroleum ether) to give *allene* **1a** (1.30 g, 45%) as a pale yellow solid. R_f = 0.63 (40% EtOAc/petroleum ether); m.p. 118-120 °C (Et_2O); IR 2979, 2924, 1956 (C=C=C), 1670 (C=O), 1629, 1445, 1309, 1183, 1146, 1085, 864, 812, 699, 648, 330, 529, 513 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.32 (2H, d, *J* = 8.4 Hz, Ar**H**), 6.94 (2H, d, *J* = 10.0 Hz, 2 × O=CCH=C**H**), 6.17 (2H, d, *J* = 10.0 Hz, 2 × O=CC**H**), 5.31 (1H, quin, *J* = 6.4 Hz, C**H**=C=CH_2), 4.76 (2H, dt, *J* = 6.8, 2.4 Hz, =C**H**$_2$), 4.01 (2H, dt, *J* = 6.8, 2.8 Hz, NC**H**$_2$), 2.44 (3H, s, ArC**H**$_3$), 1.57 (3H, s, NCC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 209.1 (C), 184.5 (C), 151.5 (2 × CH), 143.8 (C), 139.3 (C), 129.7 (2 × CH), 127.8 (2 × CH), 127.3 (2 × CH), 89.4 (CH), 76.7 (C), 60.0 (CH_2), 46.8 (CH_2), 26.0 (CH_3), 21.5 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{18}H_{19}NNaO_3S]^+$ $[M+Na]^+$: 352.0978, found: 352.0978.

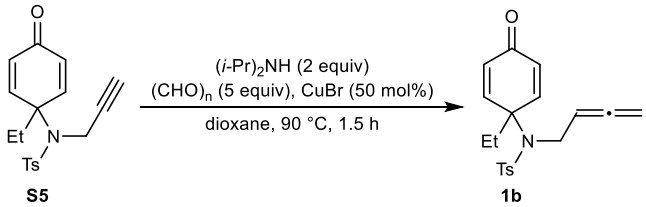
_N_-(1-Ethyl-4-oxocyclohexa-2,5-dien-1-yl)-4-methyl-_N_-(prop-2-yn-1-yl)benzene-1-sulfonamide (S5)



S2 **S5**

To a solution of sulfonamide **S2**[1] (1.06 g, 3.64 mmol) in DMF (7.5 mL) at 0 °C under inert atmosphere was added NaH (60% dispersion in mineral oil, 0.22 g, 5.46 mmol) was added portionwise. Propargyl bromide (80% in toluene, 0.60 mL, 5.5 mmol) was added and the mixture was stirred for 1 h. The mixture was diluted with EtOAc (15 mL), washed with saturated aqueous NH_4Cl solution (20 mL) and brine/H_2O (1:1, 20 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The mixture was purified by column chromatography (30% EtOAc/petroleum ether) to give *alkyne* **S5** (0.92 g, 77%) as a pale yellow solid. R_f = 0.37 (30% EtOAc/petroleum ether); m.p. 92-94 °C (Et_2O); IR 3273, 2970, 2939, 2882, 2118 (C≡C), 1665 (C=O), 1628, 1337, 1156, 1088, 904, 811, 649, 543 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.79 (2H, d, *J* = 8.2 Hz, Ar**H**), 7.29 (2H, d, *J* = 8.2 Hz, Ar**H**), 6.93 (2H, d, *J* = 10.2 Hz, 2 × O=CCH=C**H**), 6.24 (2H, d, *J* = 10.2 Hz, 2 × O=CC**H**), 4.32 (2H, d, *J* = 2.4 Hz, NC**H**$_2$), 2.44 (3H, s, ArC**H**$_3$), 2.36 (1H, t, *J* = 2.4 Hz, ≡C**H**), 2.05 (2H, q, *J* = 7.2 Hz, C**H**$_2$CH$_3$), 0.74 (3H, t, *J* = 7.2 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.9 (C), 149.1 (2 × CH), 144.0 (C), 138.5 (C), 129.8 (2 × CH), 129.5 (2 × CH), 127.8 (2 × CH), 80.4 (C), 73.7 (CH), 64.5 (C), 36.0 (CH_2), 29.4 (CH_2), 21.6 (CH_3), 8.4 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{18}H_{19}NNaO_3S]^+$ $[M+Na]^+$: 352.0978, found: 352.0976.

_N_-(Buta-2,3-dien-1-yl)-_N_-(1-ethyl-4-oxocyclohexa-2,5-dien-1-yl)-4-methylbenzene-1-sulfonamide (1b)



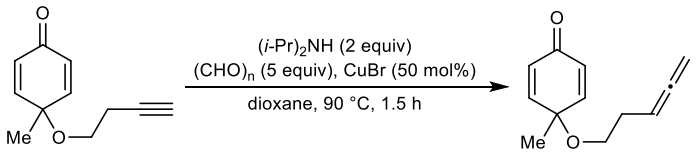
S5 **1b**

To a solution of alkyne **S5** (0.86 g, 2.63 mmol) in 1,4-dioxane (13 mL) at room temperature under inert atmosphere was added paraformaldehyde (0.40 g, 13.1 mmol), CuBr (188 mg, 1.30 mmol), and diisopropylamine (0.74 mL, 5.25 mmol). The reaction was heated at 90 °C for 1.5 h, cooled to room temperature, filtered through a pad of celite using EtOAc as eluent, and concentrated under reduced pressure. The mixture was purified by column chromatography (40% EtOAc/petroleum

ether) to give *allene* **1b** (0.30 g, 33%) as a yellow solid. R_f = 0.56 (40% EtOAc, 60% petroleum ether); m.p. 110-112 °C (Et_2O); IR 2968, 2934, 2925, 1952 (C=C=C), 1670 (C=O), 1632, 1437, 1305, 1144, 1091, 860, 814, 701, 647, 551, 517 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.28 (2H, d, *J* = 8.4 Hz, Ar**H**), 6.82 (2H, d, *J* = 10.4 Hz, 2 × O=CCH=C**H**), 6.24 (2H, d, *J* = 10.4 Hz, 2 × O=CC**H**), 5.31 (1H, quin, *J* = 6.8 Hz, C**H**=C=CH_2), 4.75 (2H, dt, *J* = 6.4, 2.8 Hz, =C$\mathbf{H}_2$), 4.03 (2H, dt, *J* = 6.8, 2.4 Hz, NC$\mathbf{H}_2$), 2.42 (3H, s, ArC$\mathbf{H}_3$), 2.01 (2H, q, *J* = 7.6 Hz, C$\mathbf{H}_2CH_3$), 0.70 (3H, t, *J* = 7.2 Hz, $CH_2C\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.8 (C), 185.0 (C), 149.2 (2 × CH), 143.7 (C), 139.2 (C), 129.62 (2 × CH), 129.56 (2 × CH), 127.2 (2 × CH), 89.5 (CH), 76.7 (C), 64.5 (CH_2), 46.6 (CH_2), 29.5 (CH_2), 21.5 (CH_3), 8.4 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{19}H_{21}NNaO_3S]^+$ $[M+Na]^+$: 366.1134, found: 366.1132.

Preparation of Substrate 5

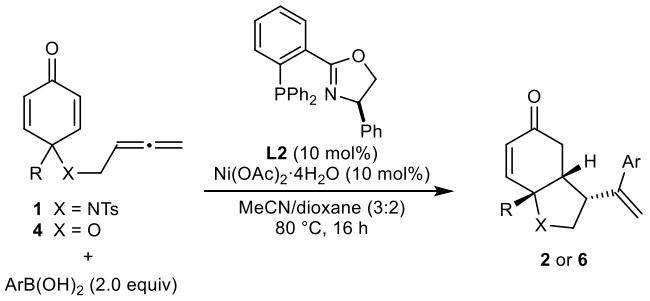
4-Methyl-4-(penta-3,4-dien-1-yloxy)cyclohexa-2,5-dien-1-one (5)



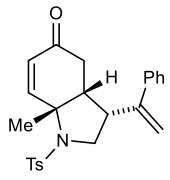
S3 **5**

To a solution of alkyne **S3**[2] (1.34 g, 7.60 mmol) in 1,4-dioxane (38 mL) at room temperature under inert atmosphere was added paraformaldehyde (1.14 g, 38.0 mmol), CuBr (546 mg, 3.80 mmol), and diisopropylamine (2.13 mL, 15.2 mmol). The reaction was heated at 90 °C for 1.5 h, cooled to room temperature, filtered through a pad of celite using EtOAc as eluent, and concentrated under reduced pressure. The mixture was purified by column chromatography (20% EtOAc/petroleum ether) to give *allene* **5** (252 mg, 17%) as a yellow oil. R_f = 0.57 (20% EtOAc/petroleum ether); IR 2981, 2928, 2967, 1956 (C=C=C), 1669 (C=O), 1631, 1515, 1438, 1382, 1178, 1084, 858, 727, 702, 541, 509, 461 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) 6.81-6.78 (2H, m, 2 × O=CCH=C**H**), 6.30-6.26 (2H, m, 2 × O=CC**H**), 5.09 (1H, quin, *J* = 6.8 Hz, C**H**=C=CH_2), 4.68 (2H, dt, *J* = 6.5, 3.1 Hz, =C$\mathbf{H}_2$), 3.37 (2H, t, *J* = 6.7 Hz, OC$\mathbf{H}_2$), 2.25-2.20 (2H, m, C$\mathbf{H}_2$CH=), 1.43 (3H, s, C$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 208.9 (C), 185.2 (C), 152.2 (2 × CH), 130.0 (2 × CH), 86.3 (CH), 75.1 (CH_2), 72.4 (C), 65.0 (CH_2), 29.3 (CH_2), 26.4 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{12}H_{14}NaO_2]^+$ $[M+Na]^+$: 213.0886, found: 213.0885.

Enantioselective Nickel-Catalyzed Arylative Intramolecular 1,4-Allylation: General Procedure



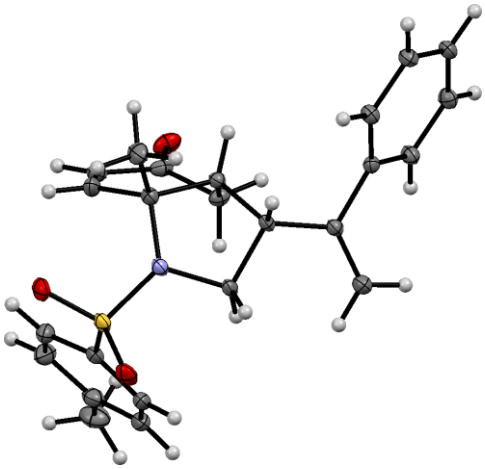
An oven-dried microwave vial fitted with a stirrer bar was charged with $Ni(OAc)_2 \cdot 4H_2O$ (7.5 mg, 0.03 mmol) and (*R*)-Ph-PHOX (**L2**, 12.2 mg, 0.03 mmol). The vial was capped with a crimp cap PTFE seal and purged with a stream of N_2. MeCN (0.9 mL) and 1,4-dioxane (0.6 mL) were added and the mixture was stirred at 80 °C for 15 min. In a separate vial, the allenyl cyclohexa-2,5-dienone **1** or **4** (0.30 mmol) and the arylboronic acid (0.60 mmol) were weighed out and the vial was purged with a stream of N_2. MeCN (0.45 mL) and 1,4-dioxane (0.3 mL) were added. The resulting solution was then transferred to the first microwave vial *via* syringe. The vial originally containing the substrate was rinsed with additional MeCN (0.45 mL) and 1,4-dioxane (0.3 mL), and the rinsing solution was transferred to the first microwave vial *via* syringe. The reaction was stirred at 80 °C for 18 h, cooled to room temperature, filtered through a plug of silica, and concentrated under reduced pressure. The residue was purified by flash column chromatography to give the title compound **2** or **6**.

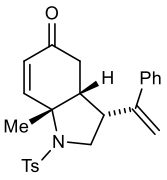


(3*R*,3a*R*,7a*R*)-7a-Methyl-1-(4-methylbenzenesulfonyl)-3-(1-phenylethenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indol-5-one (2a). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **1a** (98.8 mg, 0.30 mmol) and phenylboronic acid (73.1 mg, 0.60 mmol), and purified by column chromatography (20% EtOAc/petroleum ether) to give a colorless solid (93.7 mg, 77%). R_f = 0.36 (20% EtOAc/petroleum ether); m.p. 113-118 °C (Et_2O); $[\alpha]_D^{25}$ +88.9 (*c* 0.54, $CHCl_3$); IR 2929, 1679 (C=O), 1337, 1038, 1267, 1168, 1149, 1130, 1105, 1066, 898, 775, 581, 542 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.71 (2H, m, Ar**H**), 7.51-7.28 (7H, m, Ar**H**), 7.20 (1H, d, *J* = 10.3 Hz, O=CCH=C**H**), 5.89 (1H, dd, *J* = 10.3, 0.8 Hz, O=CC**H**=), 5.35 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 4.90 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 3.94-3.87 (2H, m, NC$\mathbf{H}_2$), 3.59-3.52 (1H, m, $NCH_2C\mathbf{H}$), 2.48-2.42 (1H, m, $O{=}CCH_2C\mathbf{H}$), 2.43 (3H, s, $ArC\mathbf{H}_3$), 1.91-1.81 (2H, m, O=CC$\mathbf{H}_2$), 1.74 (3H, s, $NCC\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0 (C), 149.0 (CH), 144.0 (C), 143.5 (C), 140.2 (C), 136.8 (C), 129.6 (2 × CH), 128.7 (2 × CH), 128.2 (CH), 128.1 (CH), 127.1 (2 × CH), 126.0

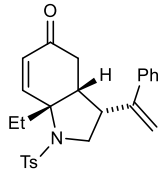
(2 × CH), 114.9 (CH_2), 63.7 (C), 49.5 (CH_2), 47.3 (CH), 41.7 (CH), 34.1 (CH_2), 28.7 (CH_3), 21.5 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{24}H_{25}NNaO_3S]^+$ $[M+Na]^+$: 430.1447, found: 430.1444. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (minor) = 16.2 min, t_r (major) = 18.4 min, 90% ee.

Slow diffusion of petroleum ether into a solution of **2a** in EtOAc gave crystals that were suitable for X-ray crystallography:



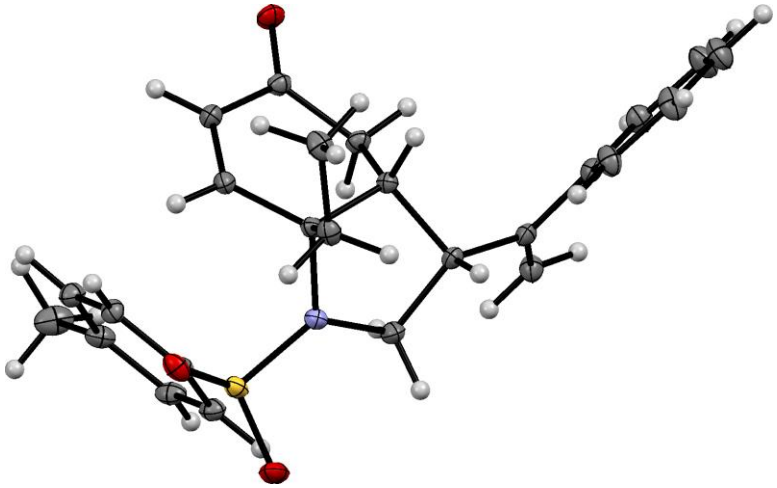


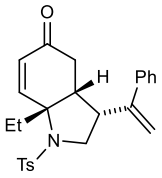
2a
CCDC 1584893
Flack parameter = 0.05(14)



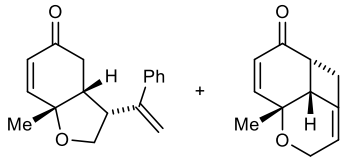
(3*R*,3a*R*,7a*R*)-7a-Ethyl-1-(4-methylbenzenesulfonyl)-3-(1-phenylethenyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indol-5-one (2b). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **1b** (102.9 mg, 0.30 mmol) and phenylboronic acid (73.1 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give a colorless solid (98.6 mg, 78%). R_f = 0.55 (30% EtOAc/petroleum ether); m.p. 173-175 °C (Et_2O); $[\alpha]_D^{25}$ +71.0 (*c* 0.62, $CHCl_3$); IR 2959, 2929, 2851, 1672 (C=O), 1496, 1385, 1342, 1165, 1105, 1064, 904, 773, 679, 589, 545 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.74-7.70 (2H, m, Ar**H**), 7.37-7.28 (7H, m, Ar**H**), 7.15 (1H, d, *J* = 10.4 Hz, O=CCH=C**H**), 5.99 (1H, dd, *J* = 10.4, 0.8 Hz, O=CC**H**=), 5.34 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 4.88 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 3.88-3.81 (2H, m, NC$\mathbf{H}_2$), 3.56-3.49 (1H, m, $NCH_2C\mathbf{H}$), 2.61 (1H, dt, *J* = 12.8, 5.6 Hz, $O{=}CCH_2C\mathbf{H}$), 2.42 (3H, s, Ar$C\mathbf{H}_3$), 2.39-2.29 (1H, m, O=CC$\mathbf{H}_2$), 2.07 (1H, dq, *J* = 14.0, 7.6 Hz, O=CC$\mathbf{H}_2$), 1.84 (1H, ddd, *J* = 16.4, 5.7, 1.0 Hz, C$\mathbf{H}_2CH_3$), 1.72 (1H, dd, *J* = 16.4, 12.8 Hz, C$\mathbf{H}_2CH_3$), 0.86 (3H, t, *J* = 7.6 Hz, $CH_2C\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1 (C), 148.3 (CH), 144.0 (C), 143.5 (C), 140.3 (C), 136.6 (C), 130.0 (CH), 129.6 (2 × CH), 128.8 (2 × CH), 128.2 (CH), 127.2 (2 × CH), 125.9 (2 × CH), 114.8 (CH_2), 67.9 (C), 49.2 (CH_2), 42.1 (CH), 41.5 (CH), 34.1 (CH_2), 33.2 (CH_2), 21.5 (CH_3), 9.9 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{25}H_{27}NNaO_3S]^+$ $[M+Na]^+$: 444.1604, found: 444.1589. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (minor) = 13.9 min, t_r (major) = 17.6 min, 92% ee.

Slow diffusion of petroleum ether into a solution of **2b** in EtOAc gave crystals that were suitable for X-ray crystallography:



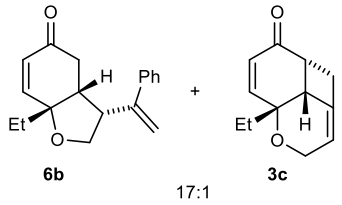


2b
CCDC 1584894
Flack parameter = 0.008(10)

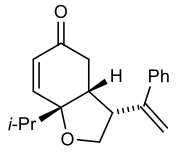


6a 11:1 **3b**

(3*R*,3a*R*,7a*R*)-7a-Methyl-3-(1-phenylethenyl)-2,3,3a,4,5,7a-hexahydro-1-benzofuran-5-one (6a). The General Procedure was followed using allenyl cyclohexa-2,5-dienone **4a** (52.8 mg, 0.30 mmol) and phenylboronic acid (73.1 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give an 11:1 inseparable mixture of *arylative cyclization product* **6a** and *cyclobutane* **3b** as a colorless oil (59.7 mg, 74%, adjusted yield of **6a**). R_f = 0.23 (20% EtOAc/petroleum ether); $[\alpha]_D^{25}$ –77.8 (*c* 0.72, $CHCl_3$); IR 2970, 2927, 1681 (C=O), 1495, 1371, 1049, 901, 779, 705, 531 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (5H, m, Ar**H**), 6.60 (1H, dd, *J* = 10.4 Hz, O=CCH=C**H**), 5.97 (1H, dd, *J* = 10.4 Hz, O=CC**H**=), 5.42 (1H, s, =C$\mathbf{H}_2$), 4.95 (1H, s, =C$\mathbf{H}_2$), 4.24 (1H, app t, *J* = 8.4 Hz, OC$\mathbf{H}_2$), 4.05 (1H, app t, *J* = 10.0 Hz, OC$\mathbf{H}_2$), 3.89 (1H, app q, *J* = 17.2, 8.5 Hz, $OCH_2C\mathbf{H}$), 2.61 (1H, q, *J* = 8.0 Hz, $O{=}CCH_2C\mathbf{H}$), 2.26 (1H, dd, *J* = 16.8, 8.4 Hz, O=CC$\mathbf{H}_2$), 2.08 (1H, dd, *J* = 16.8, 6.8 Hz, O=CC$\mathbf{H}_2$), 1.49 (3H, s, C$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5 (C), 150.1 (CH), 144.0 (C), 141.4 (C), 128.7 (CH), 128.6 (2 × CH), 127.9 (CH), 125.9 (2 × CH), 115.0 (CH_2), 78.6 (C), 69.5 (CH_2), 45.5 (CH), 44.0 (CH), 35.2 (CH_2), 27.3 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{17}H_{18}NaO_2]^+$ $[M+Na]^+$: 277.1199, found: 277.1193. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (major) = 7.2 min, t_r (minor) = 8.4 min, 91% ee.



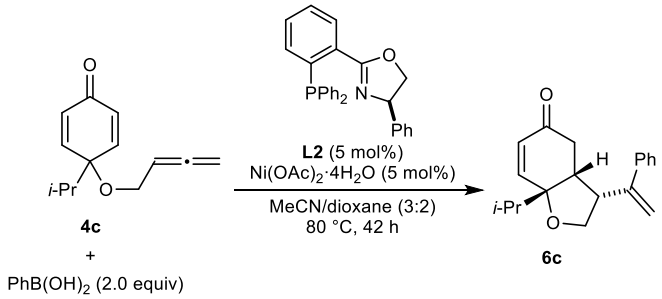
(3*R*,3a*R*,7a*R*)-7a-Ethyl-3-(1-phenylethenyl)-2,3,3a,4,5,7a-hexahydro-1-benzofuran-5-one (6b). The General Procedure was followed using allenyl cyclohexa-2,5-dienone **4b** (57.1 mg, 0.30 mmol) and phenylboronic acid (73.1 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give a 17:1 inseparable mixture of *arylative cyclization product* **6b** and *cyclobutane* **3c** as a colorless oil (65.2 mg, 78%, adjusted yield of **6b**). R_f = 0.29 (20% EtOAc/petroleum ether); $[\alpha]_D^{25}$ –68.8 (*c* 0.64, $CHCl_3$); IR 2965, 2932, 1682 (C=O), 1494, 1380, 1052, 906, 777, 703, 634 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (5H, m, Ar**H**), 6.58 (1H, dd, *J* = 10.4 Hz, O=CCH=C**H**), 6.06 (1H, dd, *J* = 10.4 Hz, O=CC**H**=), 5.43 (1H, s, =C$\mathbf{H}_2$), 4.94 (1H, s, =C$\mathbf{H}_2$), 4.20 (1H, app t, *J* = 7.2 Hz, OC$\mathbf{H}_2$), 4.00 (1H, app t, *J* = 10.0 Hz, OC$\mathbf{H}_2$), 3.80 (1H, app q, *J* = 8.5 Hz, $OCH_2C\mathbf{H}$), 2.67 (1H, app q, *J* = 7.8 Hz, $O{=}CCH_2C\mathbf{H}$), 2.27 (1H, dd, *J* = 16.8, 7.6 Hz, O=CC$\mathbf{H}_2$), 2.07 (1H, dd, *J* = 16.8, 6.8 Hz, O=CC$\mathbf{H}_2$), 1.88-1.71 (2H, m, C$\mathbf{H}_2CH_3$), 0.95 (3H, *J* = 7.6 Hz, $CH_2C\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7 (C), 149.2 (CH), 144.1 (C), 141.4 (C), 129.8 (CH), 128.6 (2 × CH), 127.9 (CH), 125.9 (2 × CH), 115.0 (CH_2), 81.6 (C), 69.1 (CH_2), 45.9 (CH), 41.1 (CH), 35.6 (CH_2), 33.1 (CH_2), 8.6 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{18}H_{21}O_2]^+$ $[M+H]^+$: 269.1536, found: 269.1527. Enantiomeric excess was determined by HPLC with a Chiralpak IA-3 column (98:2 *iso*-hexane:*i*-PrOH, 1 mL/min, 230 nm, 25 °C); t_r (major) = 21.6 min, t_r (minor) = 27.6 min, 92% ee.



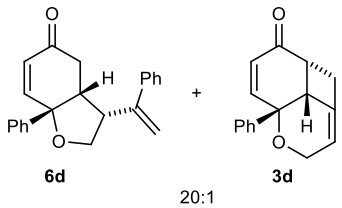
(3*R*,3a*R*,7a*R*)-3-(1-Phenylethenyl)-7a-(propan-2-yl)-2,3,3a,4,5,7a-hexahydro-1-benzofuran-5-one (6c). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **4c** (61.3 mg, 0.30 mmol) and phenylboronic acid (73.1 mg, 0.60 mmol), and purified by column chromatography (20% EtOAc/petroleum ether) to give a colorless oil (65.0 mg, 77%). R_f = 0.36 (20% EtOAc/petroleum ether); $[\alpha]_D^{25}$ –83.0 (*c* 0.53, $CHCl_3$); IR 2961, 2877, 1683 (C=O), 1495, 1385, 1256, 1041, 934, 906, 778, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.16 (5H, m, Ar**H**), 6.46 (1H, d, *J* = 10.2 Hz, O=CCH=C**H**), 6.02 (1H, d, *J* = 10.2 Hz, O=CC**H**=), 5.33 (1H, s, =C$\mathbf{H}_2$), 4.82 (1H, s, =C$\mathbf{H}_2$) 4.04 (1H, app t, *J* = 8.2 Hz, OC$\mathbf{H}_2$), 3.78 (1H, app t, *J* = 8.2 Hz, OC$\mathbf{H}_2$), 3.58 (1H, q, *J* = 8.8 Hz, $OCH_2C\mathbf{H}$), 2.62 (1H, q, *J* = 7.6 Hz, $O{=}CCH_2C\mathbf{H}$) 2.17 (1H, dd, *J* = 16.8, 6.1 Hz, O=CC$\mathbf{H}_2$), 2.01-1.88 (2H, m, O=CC$\mathbf{H}_2$ and C$\mathbf{H}(CH_3)_2$), 0.91 (3H, d, *J* = 6.8 Hz, C$\mathbf{H}_3$), 0.87 (3H, d, *J* = 6.8 Hz, C$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7 (C), 148.1 (CH), 144.1 (C), 141.4 (C), 130.7 (CH), 128.6 (2 × CH), 127.9 (CH), 125.8 (2 × CH), 115.0 (CH_2), 83.9 (C), 68.7 (CH_2), 46.7 (CH), 39.2 (CH), 36.6 (CH), 36.4 (CH_2), 17.35 (CH_3), 17.31 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{19}H_{23}O_2]^+$ $[M+H]^+$: 283.1693, found: 283.1689. Enantiomeric excess was determined by

HPLC with a Chiralpak AD-H column (98:2 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (major) = 9.4 min, t_r (minor) = 11.9 min, 94% ee.

Reaction Conducted on 2.00 mmol Scale:

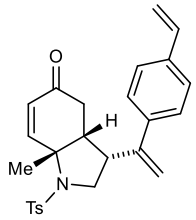


An oven-dried microwave vial fitted with a stirrer bar was charged with $Ni(OAc)_2{\cdot}4H_2O$ (24.8 mg, 0.10 mmol) and (*R*)-Ph-PHOX (**L2**, 40.7 mg, 0.10 mmol). The vial was capped with a crimp cap PTFE seal and purged with a stream of N_2. Deoxygenated MeCN (1.5 mL) and 1,4-dioxane (1.0 mL) were added and the mixture was stirred at 80 °C for 15 min. In a separate vial, the allenyl cyclohexa-2,5-dienone **4c** (408.6 mg, 2.00 mmol) and phenylboronic acid (487.2 mg, 4.00 mmol) were weighed out and the vial was purged with a stream of N_2. Deoxygenated MeCN (0.75 mL) and 1,4-dioxane (0.5 mL) were added. The resulting solution was then transferred to the first microwave vial *via* syringe. The vial originally containing the substrate was rinsed with additional deoxygenated MeCN (0.75 mL) and 1,4-dioxane (0.5 mL), and the rinsing solution was transferred to the first microwave vial *via* syringe. The reaction was stirred at 80 °C for 42 h, cooled to room temperature, filtered through a plug of silica, and concentrated under reduced pressure. The residue was purified by column chromatography to give the title compound **6c** as a colorless oil (355.0 mg, 63%). Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (98:2 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (major) = 9.4 min, t_r (minor) = 11.9 min, 94% ee.



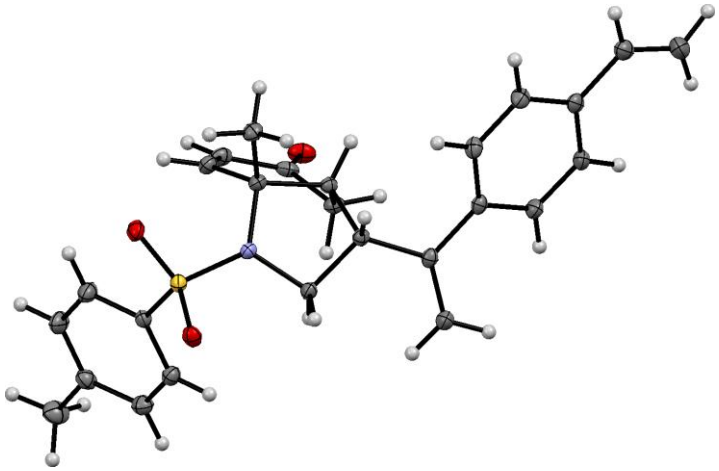
(3*R*,3a*R*,7a*R*)-7a-Phenyl-3-(1-phenylethenyl)-2,3,3a,4,5,7a-hexahydro-1-benzofuran-5-one (6d). The General Procedure was followed using allenyl cyclohexa-2,5-dienone **4d** (35.8 mg, 0.15 mmol) and phenylboronic acid (36.6 mg, 0.30 mmol), and purified by column chromatography (20% EtOAc/petroleum ether) to give a 20:1 inseparable mixture of *arylative cyclization product* **6d** and *cyclobutane* **3d** as colorless oil (39.4 mg, 80%, adjusted yield of **6d**). R_f = 0.36 (20% EtOAc/petroleum ether); $[\alpha]_D^{25}$ +39.3 (*c* 0.61, $CHCl_3$); IR 2925, 2886, 1682 (C=O), 1492, 1446, 1381, 1289, 1256, 1051, 928, 779, 762, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.21 (10H, m, Ar**H**), 6.58 (1H, dd, *J* = 10.2, 1.2 Hz,

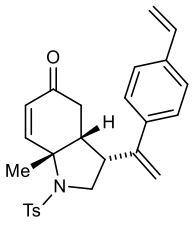
O=CCH=C**H**), 6.10 (1H, d, *J* = 10.2 Hz, O=CC**H**=), 5.42 (1H, s, C**H**$_2$), 4.99 (1H, s, C**H**$_2$), 4.47 (1H, app t, *J* = 8.6 Hz, OC**H**$_2$), 4.38 (1H, app t, *J* = 8.6 Hz, OC**H**$_2$), 3.74 (1H, q, *J* = 8.0 Hz, OCH$_2$C**H**), 2.92 (1H, dt, *J* = 9.8, 6.4 Hz, O=CCH$_2$C**H**), 2.39 (1H, dd, *J* = 16.2, 10.2 Hz, O=CC**H**$_2$), 2.16 (1H, dd, *J*= 16.2, 6.4 Hz, O=CC**H**$_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.9 (C), 147.9 (CH), 144.2 (C), 144.0 (C), 141.0 (C), 128.7 (CH), 128.6 (2 × CH), 128.5 (2 × CH), 127.9 (CH), 127.7 (CH), 125.8 (2 × CH), 125.0 (2 × CH), 115.0 (CH_2), 82.8 (C), 69.9 (CH_2), 46.4 (CH), 44.6 (CH), 35.2 (CH_2); HRMS (ESI) Exact mass calcd for $[C_{22}H_{20}NaO_2]^+$ $[M+Na]^+$: 339.1356, found: 339.1351. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (major) = 8.6 min, t_r (minor) = 9.3 min, 92% ee.



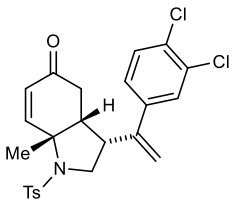
(3*R*,3a*R*,7a*R*)-3-[1-(4-Ethenylphenyl)ethenyl]-7a-methyl-1-(4-methylbenzenesulfonyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indol-5-one (2c). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **1a** (98.8 mg, 0.30 mmol) and 4-vinylphenylboronic acid (88.8 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give a colorless solid (82.2 mg, 63%). R_f = 0.44 (30% EtOAc/petroleum ether); m.p. 163-165 °C (Et_2O); $[\alpha]_D^{25}$ –81.4 (*c* 0.59, $CHCl_3$); IR 3008, 2972, 1679 (C=O), 1332, 1148, 1133, 1114, 1071, 1056, 989, 906, 849, 681, 583 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (2H, d, *J* = 8.2 Hz, Ar**H**), 7.38 (2H, d, *J* = 8.2 Hz, Ar**H**), 7.30-7.27 (4H, m, Ar**H**), 7.20 (1H, d, *J* = 10.0 Hz, O=CCH=C**H**), 6.70 (1H, dd, *J* = 17.6, 10.8 Hz, C**H**=CH$_2$), 5.89 (1H, d, *J* = 10.0 Hz, O=CC**H**=), 5.75 (1H, dd, *J* = 17.6, 0.6 Hz, CH=C**H**$_2$), 5.37 (1H, d, *J* = 1.4 Hz, C=C**H**$_2$), 5.27 (1H, dd, *J* = 10.8, 0.6 Hz, CH=C**H**$_2$), 4.89 (1H, d, *J* = 1.4 Hz, C=C**H**$_2$), 3.92-3.87 (2H, m, NC**H**$_2$), 3.58-3.52 (1H, m, NCH$_2$C**H**), 2.49-2.44 (1H, m, O=CCH$_2$C**H**), 2.43 (3H, s, ArC**H**$_3$), 1.89-1.80 (2H, m, O=CC**H**$_2$), 1.74 (3H, s, NCC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.0 (C), 149.0 (CH), 143.6 (2 × C), 139.6 (C), 137.6 (C), 136.8 (C), 136.0 (CH), 129.6 (2 × CH), 128.1 (CH), 127.1 (2 × CH), 126.5 (2 × CH), 126.2 (2 × CH), 114.7 (CH_2), 114.5 (CH_2), 63.7 (C), 49.5 (CH_2), 47.4 (CH), 41.6 (CH), 34.1 (CH_2), 28.7 (CH_3), 21.5 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{26}H_{27}NNaO_3S]^+$ $[M+Na]^+$: 456.1604, found: 456.1595. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 0.2 mL/min, 254 nm, 25 °C); t_r (major) = 90.9 min, t_r (minor) = 94.7 min, 99% ee.

Slow diffusion of petroleum ether into a solution of **2c** in EtOAc gave crystals that were suitable for X-ray crystallography:



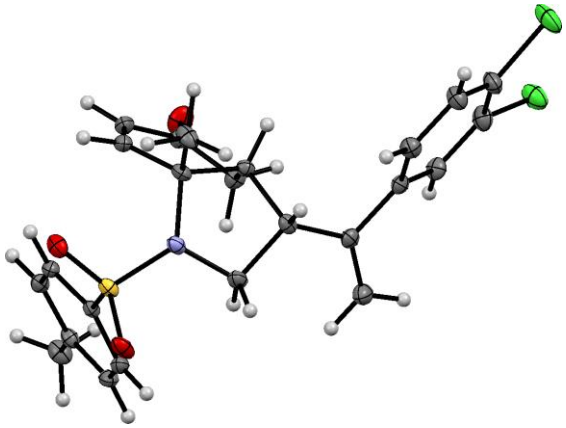


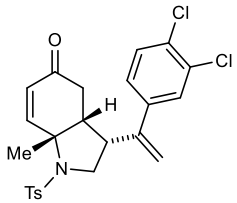
2c
CCDC 1584895
Flack parameter = 0.002(8)



(3*R*,3a*R*,7a*R*)-3-[1-(3,4-Dichlorophenyl)ethenyl]-7a-methyl-1-(4-methylbenzenesulfonyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indol-5-one (2d). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **1a** (98.8 mg, 0.30 mmol) and 3,4-dichlorophenylboronic acid (114.5 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give a colorless solid (73.2 mg, 51%). R_f = 0.46 (30% EtOAc/petroleum ether); m.p. 179-181 °C (Et_2O); $[\alpha]_D^{25}$ –61.5 (*c* 0.78, $CHCl_3$); IR 2957, 2852, 1679 (C=O), 1472, 1307, 1169, 1150, 1066, 893, 862, 663, 580 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.42 (1H, d, *J* = 8.4 Hz, Ar**H**), 7.39 (1H, d, *J* = 2.4 Hz, Ar**H**), 7.30 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.20 (1H, d, *J* = 10.2 Hz, O=CCH=C**H**), 7.14 (1H, dd, *J* = 8.0, 2.4 Hz, Ar**H**), 5.91 (1H, d, *J* = 10.2 Hz, O=CC**H**=), 5.38 (1H, d, *J* = 1.2 Hz, =C$\mathbf{H}_2$), 4.97 (1H, d, *J* = 2.0 Hz, =C$\mathbf{H}_2$), 3.87 (1H, dd, *J* = 8.9, 7.3 Hz, NC$\mathbf{H}_2$), 3.82-3.77 (1H, m, NC$\mathbf{H}_2$), 3.56-3.51 (1H, m, $NCH_2C\mathbf{H}$), 2.47-2.41 (4H, m, $O{=}CCH_2C\mathbf{H}$ and Ar$C\mathbf{H}_3$), 1.82 (2H, d, *J* = 9.3 Hz, O=CC$\mathbf{H}_2$), 1.74 (3H, s, NCC$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5 (C), 148.9 (CH), 143.7 (C), 142.0 (C), 140.3 (C), 136.7 (C), 133.1 (C), 132.4 (C), 130.7 (CH), 129.7 (2 × CH), 128.1 (CH), 127.9 (CH), 127.1 (2 × CH), 125.3 (CH), 116.6 (CH_2), 63.8 (C), 49.4 (CH_2), 47.3 (CH), 41.6 (CH), 34.2 (CH_2), 28.7 (CH_3), 21.5 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{24}H_{24}Cl_2NO_3S]^+$ $[M+H]^+$: 476.0848, found: 476.0842. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (minor) = 18.7 min, t_r (major) = 23.7 min, 87% ee.

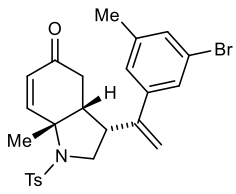
Slow diffusion of petroleum ether into a solution of **2d** in EtOAc gave crystals that were suitable for X-ray crystallography:



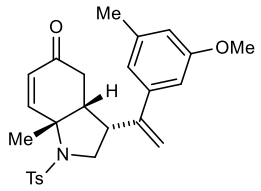


2d
CCDC 1584896
Flack parameter = –0.01(2)

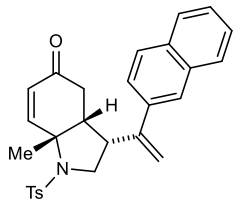
Note: The *meta*-chloro group is disordered over two possible positions. The occupancies of the two components were refined competitively, converging to a ratio of 0.95:0.05. This disorder is not shown above, for clarity.



(3*R*,3a*R*,7a*R*)-3-[1-(3-Bromo-5-methylphenyl)ethenyl]-7a-methyl-1-(4-methylbenzenesulfonyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indol-5-one (2e). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **1a** (98.8 mg, 0.30 mmol) and 3-bromo-5-methylphenylboronic acid (128.9 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give a colorless solid (84.0 mg, 56%). R_f = 0.49 (30% EtOAc/petroleum ether); m.p. 139-142 °C (Et_2O); $[\alpha]_D^{25}$ –70.6 (*c* 0.51, $CHCl_3$); IR 2963, 2923, 2863, 1682 (C=O), 1597, 1563, 1337, 1306, 1163, 1133, 1106, 1058, 985, 889, 852, 808, 682, 658, 581, 544 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.32-7.27 (3H, m, Ar**H**), 7.23 (1H, s, Ar**H**), 7.21 (1H, d, *J* = 10.3 Hz, O=CCH=C**H**), 7.02 (1H, s, Ar**H**), 5.91 (1H, d, *J* = 10.3 Hz, O=CC**H**=), 5.34 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 4.91 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 3.94-3.74 (2H, m, NC$\mathbf{H}_2$), 3.61-3.41 (1H, m, $NCH_2C\mathbf{H}$), 2.51-2.40 (4H, m, $O{=}CCH_2C\mathbf{H}$ and Ar$C\mathbf{H}_3$), 2.33 (3H, m, Ar$C\mathbf{H}_3$), 1.92-1.79 (2H, m, O=CC$\mathbf{H}_2$), 1.74 (3H, s, NCC$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.9 (C), 149.0 (CH), 143.6 (C), 142.9 (C), 142.2 (C), 140.5 (C), 136.7 (C), 131.9 (CH), 129.6 (2 × CH), 128.1 (C), 127.1 (2 × CH), 126.1 (CH), 125.6 (CH), 122.6 (C), 116.0 (CH_2), 63.7 (C), 49.4 (CH_2), 47.3 (CH), 41.6 (CH), 34.2 (CH_2), 28.6 (CH_3), 21.5 (CH_3), 21.2 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{25}H_{26}BrNNaO_3S]^+$ $[M+Na]^+$: 522.0709, found: 522.0713. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (minor) = 12.7 min, t_r (major) = 16.7 min, 88% ee.



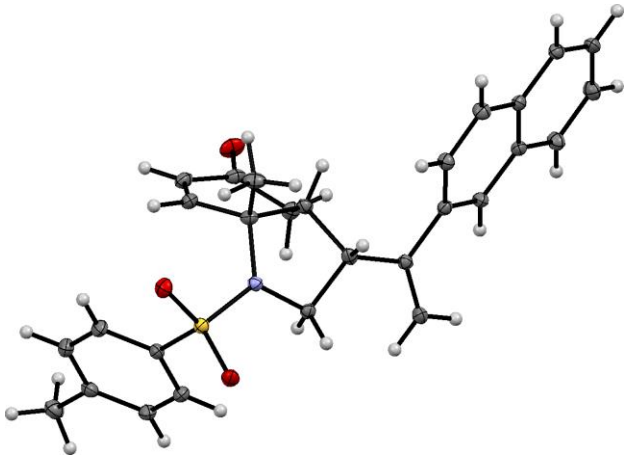
(3*R*,3a*R*,7a*R*)-3-[1-(3-Methoxy-5-methylphenyl)ethenyl]-7a-methyl-1-(4-methylbenzenesulfonyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indol-5-one (2f). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **1a** (98.8 mg, 0.30 mmol) and 3-methoxy-5-bromophenylboronic acid (99.6 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give a colorless solid (97.1 mg, 72%). R_f = 0.48 (30% EtOAc/petroleum ether); m.p. 55-60 °C (Et_2O); $[\alpha]_D^{25}$ –92.3 (*c* 0.39, $CHCl_3$); IR 2935, 2253, 1681 (C=O), 1589, 1333, 1292, 1150, 1111, 1059, 985, 907, 728, 662, 582 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.29 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.20 (1H, d, *J* = 10.4 Hz, O=CCH=C**H**), 6.70 (1H, s, Ar**H**), 6.65 (2H, dd, *J* = 10.0, 2.0 Hz, Ar**H**), 5.90 (1H, d, *J* = 10.4 Hz, O=CC**H**=), 5.34 (1H, d, *J* = 1.2 Hz, =C$\mathbf{H}_2$), 4.86 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 3.89-3.82 (2H, m, NC$\mathbf{H}_2$), 3.79 (3H, s, OC$\mathbf{H}_3$), 3.57-3.50 (1H, m, $NCH_2C\mathbf{H}$), 2.52-2.46 (1H, m, $O{=}CCH_2C\mathbf{H}$), 2.43 (3H, s, ArC$\mathbf{H}_3$), 2.33 (3H, s, ArC$\mathbf{H}_3$), 1.91 (1H, dd, *J* = 16.4, 5.6 Hz, O=CC$\mathbf{H}_2$), 1.81 (1H, dd, *J* = 16.4, 12.4 Hz, O=CC$\mathbf{H}_2$), 1.73 (3H, s, NCC$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2 (C), 159.7 (C), 149.0 (CH), 144.0 (C), 143.5 (C), 141.6 (C), 139.8 (C), 136.8 (C), 129.6 (2 × CH_2), 128.1 (CH), 127.1 (2 × CH_2), 119.4 (CH), 114.8 (CH_2), 113.8 (CH), 109.5 (CH), 63.7 (C), 55.2 (CH_3), 49.5 (CH_2), 47.4 (CH), 41.7 (CH), 34.2 (CH_2), 28.7 (CH_3), 21.7 (CH_3), 21.5 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{26}H_{29}NNaO_4S]^+$ $[M+Na]^+$: 474.1710, found: 474.1690. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 1.5 mL/min, 210 nm, 25 °C); t_r (minor) = 16.5 min, t_r (major) = 26.1 min, 90% ee.



(3*R*,3a*R*,7a*R*)-7a-Methyl-1-(4-methylbenzenesulfonyl)-3-[1-(naphthalen-2-yl)ethenyl]-2,3,3a,4,5,7a-hexahydro-1*H*-indol-5-one (2g). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **1a** (98.8 mg, 0.30 mmol) and 2-naphthylboronic acid (103.2 mg, 0.60 mmol), and purified by column chromatography (20% EtOAc/petroleum ether) to give a colorless solid (109.7 mg, 80%). R_f = 0.51 (30% EtOAc/petroleum ether); m.p. 174-177 °C (Et_2O); $[\alpha]_D^{25}$ –65.8 (*c* 0.79, $CHCl_3$); IR 2921, 1678 (C=O), 1391, 1151, 1057, 864, 788, 707, 676, 647, 623, 585, 550 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84-7.80 (3H, m, Ar**H**), 7.76-7.73 (3H, m, Ar**H**), 7.51-7.43 (3H, m, Ar**H**), 7.32-7.30 (2H, m, Ar**H**), 7.20 (1H, d, *J* = 10.4 Hz, O=CCH=C**H**), 5.88 (1H, dd, *J* = 10.4, 0.8 Hz, O=CC**H**=), 5.49 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 5.00 (1H, d, *J* = 2.0 Hz, =C$\mathbf{H}_2$), 4.08-4.02 (1H, m, NC$\mathbf{H}_2$), 3.95 (1H, dd, *J* = 9.2, 7.2 Hz, NC$\mathbf{H}_2$), 3.61 (1H, dd, *J* = 10.8, 9.2 Hz, $NCH_2C\mathbf{H}$), 2.53-2.46 (1H, m, $O{=}CCH_2C\mathbf{H}$), 2.44 (3H, m, ArC$\mathbf{H}_3$), 1.96-1.83 (2H, m, O=CC$\mathbf{H}_2$), 1.77 (3H, s, NCHC$\mathbf{H}_3$); ^{13}C NMR (101 MHz,

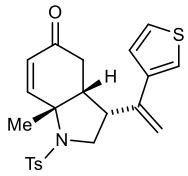
$CDCl_3$) δ 197.9 (C), 149.0 (CH), 144.0 (C), 143.6 (C), 137.6 (C), 136.8 (C), 133.2 (C), 133.0 (C), 129.6 (2 × CH), 128.5 (CH), 128.1 (2 × CH), 127.6 (CH), 127.1 (2 × CH), 126.5 (CH), 126.3 (CH), 124.9 (CH), 124.2 (CH), 115.4 (CH_2), 63.8 (C), 49.5 (CH_2), 47.4 (CH), 41.8 (CH), 34.2 (CH_2), 28.7 (CH_3), 21.5 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{28}H_{28}NO_3S]^+$ $[M+H]^+$: 458.1784, found: 458.1773. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (95:5 *iso*-hexane:EtOH, 1.0 mL/min, 254 nm, 25 °C); t_r (major) = 46.5 min, t_r (minor) = 54.1 min, 87% ee.

Slow diffusion of petroleum ether into a solution of **2g** in EtOAc gave crystals that were suitable for X-ray crystallography:



2g
CCDC 1584897
Flack parameter = –0.064(15)

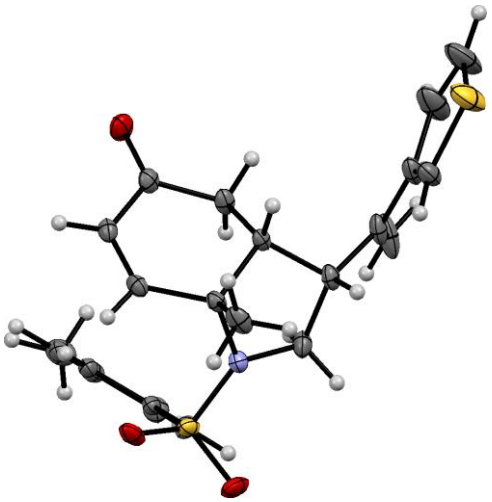
Note: The alkene-naphthyl group is disordered over two positions. The occupancies of the two components was refined competitively, converging to a ratio of 0.84:0.16. This disorder is not shown above, for clarity.

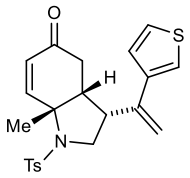


(3*R*,3a*R*,7a*R*)-7a-Methyl-1-(4-methylbenzenesulfonyl)-3-[1-(thiophen-3-yl)ethenyl]-2,3,3a,4,5,7a-hexahydro-1*H*-indol-5-one (2h). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **1a** (98.8 mg, 0.30 mmol) and 3-thienylboronic acid (76.8 mg, 0.60 mmol), and purified by column chromatography (20% EtOAc/petroleum ether) to give a yellow solid (86.8 mg, 70%). R_f = 0.50 (30% EtOAc/petroleum ether); m.p. 118-121 °C (Et_2O); $[\alpha]_D^{25}$ –67.7 (*c* 0.65, $CHCl_3$); IR 2969, 2927, 1678 (C=O), 1337, 1150, 1131, 1111, 1068, 794, 670, 582, 547 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.73 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.31-7.29 (3H, m, Ar**H**), 7.22 (1H, d, *J* = 10.3 Hz, O=CCH=C**H**), 7.18 (1H, dd, *J* = 2.9, 1.4 Hz, Ar**H**), 7.13 (1H, dd, *J* = 5.1, 1.4 Hz, Ar**H**), 5.92 (1H, dd, *J* = 10.3, 0.8 Hz, O=CC**H**=), 5.45 (1H, d, *J* = 0.8 Hz, =C**H**$_2$), 4.87 (1H, s, =C**H**$_2$), 3.85-3.77 (2H, m, NC**H**$_2$), 3.60-3.55 (1H, m, NCH$_2$C**H**), 2.64-2.58 (1H, m, O=CCH$_2$C**H**), 2.42 (3H, s, ArC**H**$_3$), 1.90 (1H, dd, *J* = 16.6, 6.0 Hz, O=CC**H**$_2$), 1.82 (1H, dd, *J* = 16.6, 12.3 Hz, O=CC**H**$_2$), 1.76 (3H, s, NCC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1 (C),

148.9 (CH), 143.6 (C), 141.4 (C), 138.2 (C), 136.8 (C), 129.6 (2 × CH), 128.1 (CH), 127.1 (2 × CH), 126.3 (CH), 125.6 (CH), 120.6 (CH), 113.3 (CH_2), 63.8 (C), 49.2 (CH_2), 47.7 (CH), 42.0 (CH), 34.3 (CH_2), 28.7 (CH_3), 21.5 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{22}H_{23}NNaO_3S_2]^+$ $[M+Na]^+$: 436.1012, found: 436.0987. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (minor) = 23.8 min, t_r (major) = 25.6 min, 92% ee.

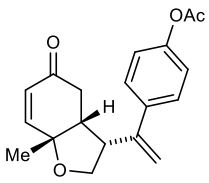
Slow diffusion of petroleum ether into a solution of **2h** in EtOAc gave crystals that were suitable for X-ray crystallography:





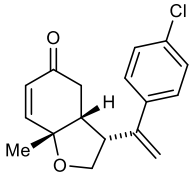
2h
CCDC 1584898
Flack parameter = –0.020(11)

Note: The thiophene ring of the molecule starting from S31 is disordered over two orientations, resulting in split positions for the sulfur and one of the carbon atoms of this ring. The occupancies of the disordered atoms were refined competitively, converging to a ratio of 0.63:0.37. This disorder is not shown above, for clarity.

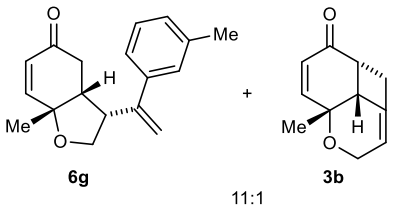


(3*R*,3a*R*,7a*R*)-4-[1-(7a-Methyl-5-oxo-2,3,3a,4,5,7a-hexahydro-1-benzofuran-3-yl)ethenyl]phenyl acetate (6e). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **4a** (52.8 mg, 0.30 mmol) and 4-acetoxyphenylboronic acid (108.0 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give a colorless solid (64.1 mg, 68%). R_f = 0.25 (30% EtOAc/petroleum ether); m.p. 88-93 °C (Et_2O); $[\alpha]_D^{25}$ –87.2 (*c* 0.78, $CHCl_3$); IR 2969, 2928, 2881, 1747 (C=O), 1681 (C=O), 1506, 1370, 1196, 1170, 1014, 911, 855, 790, 655 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.41-7.38 (2H, m, Ar**H**), 7.10-7.07 (2H, m, Ar**H**), 6.61 (1H, d, *J* = 10.2 Hz, O=CCH=C**H**), 5.97 (1H, d, *J* = 10.2 Hz, O=CC**H**=), 5.41 (1H, d, *J* = 0.8 Hz, =C$\mathbf{H}_2$), 4.97 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 4.24 (1H, dd, *J* = 8.8, 7.6 Hz, OC$\mathbf{H}_2$), 4.03 (1H, dd, *J* = 10.4, 9.2 Hz, OC$\mathbf{H}_2$), 3.83 (1H, dd, *J* = 17.6, 8.8 Hz, $OCH_2C\mathbf{H}$), 2.63 (1H, td, *J* = 8.4, 6.8 Hz,

O=CCH$_2$C**H**), 2.32 (3H, s, O=CC**H**$_3$), 2.27 (1H, dd, *J* = 16.9, 7.9 Hz, O=CC**H**$_2$), 2.10 (1H, d, *J* = 16.9, 6.8 Hz, O=CC**H**$_2$), 1.50 (3H, s, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4 (C), 169.3 (C), 150.4 (CH), 150.2 (C), 143.2 (C), 139.2 (C), 128.9 (CH), 127.0 (2 x CH), 121.7 (2 x CH), 115.5 (CH_2), 78.8 (C), 69.6 (CH_2), 45.7 (CH), 44.1 (CH), 35.4 (CH_2), 27.2 (CH_3), 21.1 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{19}H_{20}NaO_4]^+$ $[M+Na]^+$: 335.1254, found: 335.1253. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH), 1 mL/min, 254 nm, 25 °C); t_r (major) = 13.9 min, t_r (minor) = 24.1 min, 92% ee.

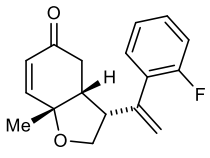


(3*R*,3a*R*,7a*R*)-3-[1-(4-Chlorophenyl)ethenyl]-7a-methyl-2,3,3a,4,5,7a-hexahydro-1-benzofuran-5-one (6f). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **4a** (52.8 mg, 0.30 mmol) and 4-chlorophenylboronic acid (93.8 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give a colorless oil (47.4 mg, 55%). R_f = 0.39 (30% EtOAc/petroleum ether); $[\alpha]_D^{25}$ −73.5 (*c* 0.49, $CHCl_3$); IR 3054, 2978, 1683 (C=O), 1492, 1264, 1120, 1012, 838, 785, 732, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (4H, s, Ar**H**), 6.60 (1H, d, *J* = 10.0 Hz, O=CCH=C**H**), 5.98 (1H, d, *J* = 10.4 Hz, O=CC**H**=), 5.41 (1H, d, *J* = 1.2 Hz, =C**H**$_2$), 4.98 (1H, d, *J* = 1.6 Hz, =C**H**$_2$), 4.23 (1H, dd, *J* = 8.8, 7.2 Hz, OC**H**$_2$), 4.03 (1H, app t, *J* = 10.4, 8.8 Hz, OC**H**$_2$), 3.81 (1H, q, *J* = 8.4 Hz, OCH$_2$C**H**), 2.60 (1H, td, *J* = 8.0, 6.8 Hz, O=CCH$_2$C**H**), 2.23 (1H, dd, *J* = 16.8, 8.0 Hz, O=CC**H**$_2$), 2.08 (1H, dd, *J* = 16.8, 6.8 Hz, O=CC**H**$_2$), 1.49 (3H, s, OCC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2 (C), 150.1 (CH), 143.0 (C), 139.9 (C), 133.8 (C), 128.85 (CH), 128.77 (2 × CH), 127.3 (2 × CH), 115.6 (CH_2), 78.7 (C), 69.5 (CH_2), 45.5 (CH), 44.1 (CH), 35.3 (CH_2), 27.1 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{17}H_{17}ClNaO_2]^+$ $[M+Na]^+$: 311.0809, found: 311.0798. Enantiomeric excess was determined by HPLC with a Chiralpak IA-3 column (98:2 *iso*-hexane:*i*-PrOH, 1.5 mL/min, 230 nm, 25 °C); t_r (major) = 20.2 min, t_r (minor) = 33.0 min, 90% ee.

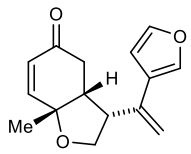


(3*R*,3a*R*,7a*R*)-7a-Methyl-3-[1-(3-methylphenyl)ethenyl]-2,3,3a,4,5,7a-hexahydro-1-benzofuran-5-one (6g). The General Procedure was followed using allenyl cyclohexa-2,5-dienone **4a** (52.8 mg, 0.30 mmol) and 3-methylphenylboronic acid (71.5 mg, 0.60 mmol), and purified by column chromatography (30% EtOAc/petroleum ether) to give a 10:1 inseparable mixture of *arylative cyclization product* **6g** and *cyclobutane* **3b** as colorless oil (56.1 mg, 66%, adjusted yield of **6g**). R_f = 0.39 (30% EtOAc/petroleum ether); $[\alpha]_D^{25}$ −88.2 (*c* 0.68, $CHCl_3$); IR 3053, 2971, 1681 (C=O), 1413, 1266,

1119, 1036, 901, 872, 791, 732, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.27-7.22 (1H, m, Ar**H**), 7.19-7.17 (2H, m, Ar**H**), 7.14-7.11 (1H, m, Ar**H**), 6.61 (1H, d, *J* = 10 Hz, O=CCH=C**H**), 5.98 (1H, d, *J* = 10 Hz, O=CC**H**=), 5.40 (1H, s, =C$\mathbf{H}_2$), 4.93 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 4.24 (1H, dd, *J* = 8.8, 7.2 Hz, OC$\mathbf{H}_2$), 4.05 (1H, dd, *J* = 10.4, 8.4 Hz, OC$\mathbf{H}_2$), 3.89 (1H, dd, *J* = 17.2, 8.8 Hz, $OCH_2C\mathbf{H}$), 2.62 (1H, td, *J* = 8.8, 6.8 Hz, $O{=}CCH_2C\mathbf{H}$), 2.38 (3H, s, ArC$\mathbf{H}_3$), 2.28 (1H, dd, *J* = 16.8, 8.4 Hz, O=CC$\mathbf{H}_2$), 2.10 (1H, dd, *J* = 16.8, 6.8 Hz, O=CC$\mathbf{H}_2$), 1.50 (3H, s, OCC$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7 (C), 150.1 (CH), 144.2 (C), 141.5 (C), 138.2 (C), 128.8 (CH), 128.7 (CH), 128.5 (CH), 126.7 (CH), 123.0 (CH), 114.8 (CH_2), 78.7 (C), 69.6 (CH_2), 45.7 (CH), 44.0 (CH), 35.3 (CH_2), 27.4 (CH_3), 21.5 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{18}H_{21}O_2]^+$ $[M+H]^+$: 269.1536, found: 269.1540. Enantiomeric excess was determined by HPLC with a Chiralpak IC-3 column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (major) = 14.7 min, t_r (minor) = 18.1 min, 93% ee.

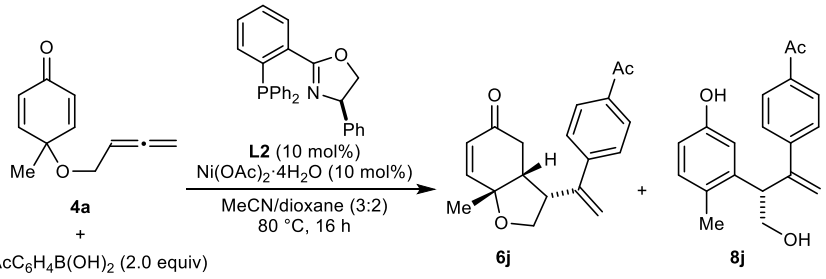


(3*R*,3a*R*,7a*R*)-3-[1-(2-Fluorophenyl)ethenyl]-7a-methyl-2,3,3a,4,5,7a-hexahydro-1-benzofuran-5-one (6h). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **4a** (52.8 mg, 0.30 mmol) and 2-fluorophenylboronic acid (83.9 mg, 0.60 mmol), and purified by column chromatography (20% EtOAc/petroleum ether) to give a colorless oil (47.4 mg, 58%). R_f = 0.34 (20% EtOAc/petroleum ether); $[\alpha]_D^{25}$ –84.6 (*c* 0.52, $CHCl_3$); IR 2971, 2929, 1682 (C=O), 1630, 1486, 1448, 1371, 1268, 1209, 1153, 1118, 1088, 1033, 906, 751 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.32-7.26 (2H, m, Ar**H**), 7.16-7.12 (1H, m, Ar**H**), 7.09-7.03 (1H, m, Ar**H**), 6.62 (1H, d, *J* = 10.2 Hz, O=CCH=C**H**), 5.98 (1H, d, *J* = 10.2 Hz, O=CC**H**=), 5.37 (1H, d, *J* = 1.2 Hz, =C$\mathbf{H}_2$), 5.11 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 4.27 (1H, dd, *J* = 8.4, 6.8 Hz, OC$\mathbf{H}_2$), 4.03 (1H, ddd, *J* = 10.4, 8.4, 1.2 Hz, OC$\mathbf{H}_2$), 3.98-3.91 (1H, m, $OCH_2C\mathbf{H}$), 2.56 (1H, dt, *J* = 8.4, 6.8 Hz, $O{=}CCH_2C\mathbf{H}$), 2.37 (1H, dd, *J* = 16.8, 8.8 Hz, O=CC$\mathbf{H}_2$), 2.18 (1H, dd, *J* = 16.8, 6.8 Hz, O=CC$\mathbf{H}_2$), 1.46 (3H, s, C$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.8 (C), 159.6 (C, d, J^1 = 252.5 Hz), 150.2 (CH), 140.9 (C), 129.9 (CH, d, J^3 = 4 Hz), 129.7 (C, d, J^3 = 13.1 Hz), 129.4 (CH, d, J^3 = 8.1 Hz), 128.6 (CH), 124.5 (CH, d, J^4 = 4.0 Hz), 118.5 (CH_2, d, J^4 = 1.0 Hz), 116.0 (CH, d, J^2 = 23.2 Hz), 78.6 (C), 69.9 (CH_2), 46.2 (CH, d, J^4 = 2.0 Hz), 44.2 (CH), 35.4 (CH_2), 27.5 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{17}H_{17}FNaO_2]^+$ $[M+Na]^+$: 295.1105, found: 295.1109. Enantiomeric excess was determined by HPLC with a Chiralpak IC-3 column (90:10 *iso*-hexane:*i*-PrOH), 1 mL/min, 254 nm, 25 °C); t_r (major) = 12.9 min, t_r (minor) = 24.2 min, 89% ee.



(3*R*,3a*R*,7a*R*)-3-[1-(Furan-3-yl)ethenyl]-7a-methyl-2,3,3a,4,5,7a-hexahydro-1-benzofuran-5-one benzoate (6i). The title compound was prepared according to the General Procedure using allenyl cyclohexa-2,5-dienone **4a** (52.8 mg, 0.30 mmol) and 3-furylboronic acid (67.1 mg, 0.60 mmol), and purified by column chromatography (40% EtOAc/petroleum ether) to give a colorless oil (50.8 mg, 69%). R_f = 0.37 (40% EtOAc/petroleum ether); $[\alpha]_D^{25}$ −44.4 (*c* 1.08, $CHCl_3$); IR 3055, 2975, 1682 (C=O), 1418, 1375, 1265, 1028, 732, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (1H, s, Ar**H**), 7.39-7.38 (1H, m, Ar**H**), 6.59 (1H, d, *J* = 10.2 Hz, O=CCH=C**H**), 6.52-6.51 (1H, m, Ar**H**), 5.98 (1H, d, *J* = 10.2 Hz, O=CC**H**=), 5.40 (1H, s, =C**H**$_2$), 4.89 (1H, d, *J* = 1.2 Hz, =C**H**$_2$), 4.15 (1H, dd, *J* = 9.2, 7.6 Hz, OC**H**$_2$), 4.02-3.98 (1H, m, OC**H**$_2$), 3.55 (1H, dd, *J* = 17.6, 8.8 Hz, OCH_2C**H**), 2.73 (1H, dt, *J* = 9.2, 6.8 Hz, O=CCH_2C**H**), 2.32 (1H, dd, *J* = 17.2, 6.8 Hz, O=CC**H**$_2$), 2.18 (1H, dd, *J* = 16.8, 6.8 Hz, O=CC**H**$_2$), 1.51 (3H, s, C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.2 (C), 150.2 (CH), 143.7 (CH), 138.5 (CH), 134.9 (C), 129.2 (CH), 127.6 (C), 112.4 (CH_2), 108.0 (CH), 78.8 (C), 68.9 (CH_2), 45.4 (CH), 44.5 (CH), 35.2 (CH_2), 26.8 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{15}H_{17}O_3]^+$ $[M+H]^+$: 245.1172, found: 245.1172. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (major) = 8.3 min, t_r (minor) = 15.6 min, 93% ee.

(3*R*,3a*R*,7a*R*)-3-[1-(4-Acetylphenyl)ethenyl]-7a-methyl-2,3,3a,4,5,7a-hexahydro-1-benzofuran-5-one (6j) and methyl 4-[(*S*)-4-hydroxy-3-(5-hydroxy-2-methylphenyl)but-1-en-2-yl]benzoate (8j)



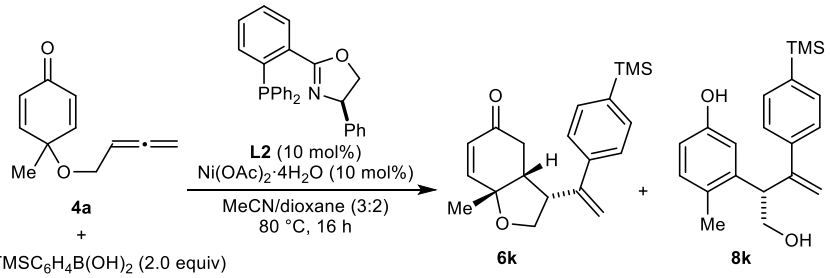
The General Procedure was followed using allenyl cyclohexa-2,5-dienone **4a** (52.8 mg, 0.30 mmol) and 4-acetylphenylboronic acid (96.4 mg, 0.60 mmol). Purification by column chromatography (40% EtOAc/petroleum ether) gave **6j** as a colorless oil (45.0 mg, 51%) followed by **8j** as a colorless oil (14.6 mg, 16%).

Data for **6j**; R_f = 0.17 (40% EtOAc/petroleum ether); $[\alpha]_D^{25}$ −87.0 (*c* 0.69, $CHCl_3$); IR 3055, 2974, 1681 (C=O), 1626, 1604, 1358, 1265, 1046, 1013, 848, 787, 732, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.97-7.94 (2H, m, Ar**H**), 7.49-7.46 (2H, m, Ar**H**), 6.61 (1H, d, *J* = 10.2 Hz,

O=CCH=C**H**), 5.98 (1H, d, *J* = 10.2 Hz, O=CC**H**=), 5.52 (1H, d, *J* = 0.7 Hz, =C$\mathbf{H}_2$), 5.07 (1H, d, *J* = 1.5 Hz, =C$\mathbf{H}_2$), 4.25 (1H, dd, *J* = 8.7, 7.3 Hz, OC$\mathbf{H}_2$), 4.09-3.99 (1H, m, OC$\mathbf{H}_2$), 3.88 (1H, dd, *J* = 17.3, 8.7 Hz, OCH$_2$C**H**), 2.71-2.55 (1H, m, O=CCH$_2$C**H**), 2.61 (3H, s, O=CC$\mathbf{H}_3$), 2.22 (1H, dd, *J* = 16.9, 7.7 Hz, O=CC$\mathbf{H}_2$), 2.07 (1H, dd, *J* = 16.9, 6.8 Hz, O=CC$\mathbf{H}_2$), 1.50 (3H, s, OCC$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1 (C), 197.4 (C), 150.2 (CH), 146.1 (C), 143.4 (C), 136.5 (C), 128.9 (CH), 128.7 (2 × CH), 126.2 (2 × CH), 117.0 (CH_2), 78.8 (C), 69.5 (CH_2), 45.4 (CH), 44.2 (CH), 35.4 (CH_2), 27.1 (CH_3), 26.6 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{19}H_{20}NaO_3]^+$ $[M+Na]^+$: 319.1305, found: 319.1306. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH), 1 mL/min, 254 nm, 25 °C); t_r (major) = 12.9 min, t_r (minor) = 24.1 min, 89% ee.

*Data for **8j***: R_f = 0.12 (40% EtOAc/petroleum ether); $[\alpha]_D^{25}$ +11.1 (*c* 0.36, $CHCl_3$); IR 3339 (OH), 3054, 2926, 1674 (C=O), 1603, 1265, 1057, 1013, 846, 733, 703 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (2H, d, *J* = 8.6 Hz, Ar**H**), 7.38 (2H, d, *J* = 8.6 Hz, Ar**H**), 7.03 (1H, d, *J* = 8.2 Hz, Ar**H**), 6.80 (1H, d, *J* = 2.7 Hz, Ar**H**), 6.63 (1H, dd, *J* = 8.2, 2.7 Hz, Ar**H**), 5.61 (1H, s, =C$\mathbf{H}_2$), 5.35 (1H, s, ArO**H**), 5.27 (1H, s, =C$\mathbf{H}_2$), 4.30 (1H, t, *J* = 6.5 Hz, ArC**H**), 4.02-3.96 (1H, m, C$\mathbf{H}_2$OH), 3.95-3.86 (1H, m, C$\mathbf{H}_2$OH), 2.57 (3H, s, ArC$\mathbf{H}_3$), 2.29 (3H, s, ArC$\mathbf{H}_3$), 1.79 (1H, br t, *J* = 5.8 Hz, CH$_2$O**H**); ^{13}C NMR (101 MHz, ($CDCl_3$) δ 197.9 (C), 154.2 (C), 147.3 (C), 146.6 (C), 138.9 (C), 136.1 (C), 131.8 (CH), 128.5 (2 × CH and C), 126.5 (2 × CH), 116.2 (CH_2), 114.1 (CH), 113.9 (CH), 64.5 (CH_2), 48.0 (CH), 26.6 (CH_3), 18.8 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{19}H_{21}O_3]^+$ $[M+H]^+$: 297.1485, found: 297.1484. Enantiomeric excess was determined by HPLC with a Chiralpak IC-3 column (90:10 *iso*-hexane:*i*-PrOH), 1.5 mL/min, 254 nm, 25 °C); t_r (minor) = 44.7 min, t_r (major) = 50.0 min, 92% ee.

(3*R*,3a*R*,7a*R*)-7a-Methyl-3-(1-[4-(trimethylsilyl)phenyl]ethenyl)-2,3,3a,4,5,7a-hexahydro-1-benzofuran-5-one (6k) and 3-[(*S*)-1-hydroxy-3-[4-(trimethylsilyl)phenyl]but-3-en-2-yl]-4-methylphenol (8k)



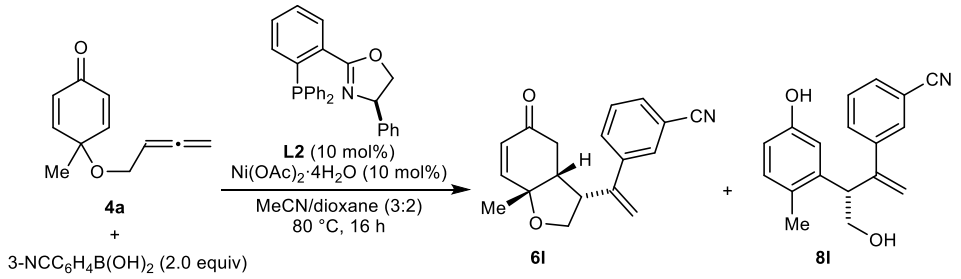
The General Procedure was followed using allenyl cyclohexa-2,5-dienone **4a** (52.8 mg, 0.30 mmol) and 4-(trimethylsilyl)phenylboronic acid (116.5 mg, 0.60 mmol). Purification by column

chromatography (30% EtOAc/petroleum ether) gave **6k** as a colorless solid (33.8 mg, 35%) followed by **8k** as a white amorphous solid (14.1 mg, 14%).

Data for **6k**: R_f = 0.44 (30% EtOAc/petroleum ether); m.p. 90-93 °C (Et_2O); $[\alpha]_D^{25}$ −63.2 (*c* 0.76, $CHCl_3$); IR 2955, 1683 (C=O), 1387, 1248, 1154, 1117, 1035, 828, 733, 701, 664 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (2H, d, *J* = 8.2 Hz, Ar**H**), 7.37 (2H, d, *J* = 8.2 Hz, Ar**H**), 6.61 (1H, d, *J* = 10.2 Hz, O=CCH=C**H**), 5.58 (1H, d, *J* = 10.2 Hz, O=CC**H**=), 5.44 (1H, d, *J* = 0.5 Hz, =C$\mathbf{H}_2$), 4.95 (1H, d, *J* = 1.5 Hz, =C$\mathbf{H}_2$), 4.25 (1H, dd, *J* = 8.8, 7.3 Hz, OC$\mathbf{H}_2$), 4.06 (1H, dd, *J* = 10.3, 8.8 Hz, OC$\mathbf{H}_2$), 3.91 (1H, dd, *J* = 17.4, 8.4 Hz, $OCH_2C\mathbf{H}$), 2.63 (1H, td, *J* = 8.4, 6.8 Hz, $O{=}CCH_2C\mathbf{H}$), 2.27 (1H, dd, *J* = 16.8, 8.4 Hz, O=CC$\mathbf{H}_2$), 2.08 (1H, dd, *J* = 16.8, 6.8 Hz, O=CC$\mathbf{H}_2$), 1.50 (3H, s, C$\mathbf{H}_3$), 0.28 (9H, s, Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7 (C), 150.1 (CH), 144.1 (C), 141.7 (C), 140.3 (C), 133.7 (2 × CH), 128.8 (CH), 125.3 (2 × CH), 115.0 (CH_2), 78.7 (C), 69.6 (CH_2), 45.5 (CH), 44.0 (CH), 35.3 (CH_2), 27.4 (CH_3), −1.2 (3 × CH_3); HRMS (ESI) Exact mass calcd for $[C_{20}H_{27}O_2Si]^+$ $[M+H]^+$: 327.1775, found: 327.1756. Enantiomeric excess was determined by HPLC with a Chiralpak AS-H column (90:10 *iso*-hexane:*i*-PrOH, 1.0 mL/min, 254 nm, 25 °C); t_r (major) = 7.2 min, t_r (minor) = 11.7 min, 93% ee.

Data for **8k**: R_f = 0.32 (40% EtOAc/petroleum ether); $[\alpha]_D^{25}$ −28.6 (*c* 0.14, $CHCl_3$); IR 3382 (OH), 2957, 2926, 1723, 1462, 1381, 1264, 1248, 1124, 1075, 840, 829, 735, 703 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 7.45 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.34 (2H, d, *J* = 8.3 Hz, Ar**H**), 7.05 (1H, d, *J* = 8.0 Hz, Ar**H**), 6.87 (1H, d, *J* = 3.0 Hz, Ar**H**), 6.63 (1H, dd, *J* = 8.0, 2.5 Hz, Ar**H**), 5.59 (1H, s, =C$\mathbf{H}_2$), 5.13 (1H, s, =C$\mathbf{H}_2$), 4.97 (1H, br s, O**H**), 4.32 (1H, t, *J* = 6.5 Hz, ArC**H**), 3.98 (1H, dd, *J* = 11.5, 6.5 Hz, C$\mathbf{H}_2$OH), 3.89 (1H, dd, *J* = 11.5, 6.5 Hz, C$\mathbf{H}_2$OH), 2.31 (3H, s, ArC$\mathbf{H_3}$), 0.25 (9H, s, Si(C$\mathbf{H}_3$)$_3$); ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.0 (C), 147.8 (C), 141.9 (C), 139.9 (C), 139.5 (C), 133.4 (2 × CH), 131.7 (CH), 128.7 (C), 125.5 (2 × CH), 114.8 (CH_2), 114.1 (CH), 113.6 (CH), 64.4 (CH_2), 48.2 (CH), 18.2 (CH_3), −1.2 (3 × CH_3); HRMS (ESI) Exact mass calcd for $[C_{20}H_{26}NaO_2Si]^+$ $[M+Na]^+$: 349.1594, found: 349.1599. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH), 1 mL/min, 280 nm, 25 °C); t_r (major) = 8.8 min, t_r (minor) = 13.5 min, 94% ee.

(3*R*,3a*R*,7a*R*)-3-[1-(7a-Methyl-5-oxo-2,3,3a,4,5,7a-hexahydro-1-benzofuran-3-yl)ethenyl]benzonitrile (6l) and 3-[(*S*)-4-hydroxy-3-(5-hydroxy-2-methylphenyl)but-1-en-2-yl]benzonitrile (8l)



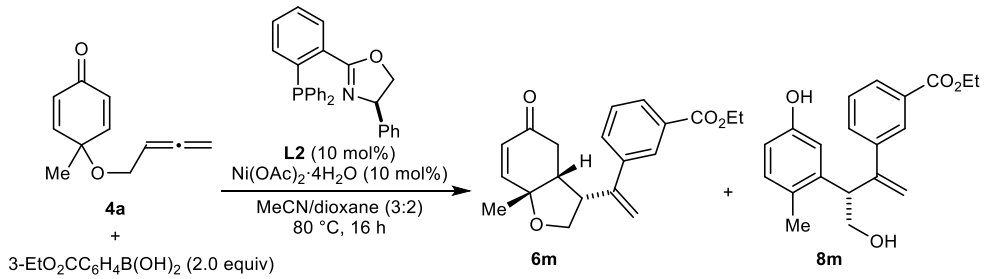
The General Procedure was followed using allenyl cyclohexa-2,5-dienone **4a** (105.6 mg, 0.60 mmol) and 3-cyanophenylboronic acid (176.3 mg, 1.20 mmol). Purification by column chromatography (40% EtOAc/petroleum ether) gave **6l** as a colorless oil (46.9 mg, 28%) followed by **8l** as a white amorphous solid (99.3 mg, 59%).

Data for **6l**: R_f = 0.23 (40% EtOAc/petroleum ether); $[\alpha]_D^{25}$ −80.0 (*c* 0.35, $CHCl_3$); IR 3058, 2972, 2230 (C≡N), 1681 (C=O), 1482, 1373, 1266, 1119, 1036, 904, 805, 732, 703, 671 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66-7.59 (3H, m, Ar**H**), 7.49 (1H, t, *J* = 8.0 Hz, Ar**H**), 6.61 (1H, d, *J* = 10.0 Hz, O=CCH=C**H**), 6.00 (1H, d, *J* = 10.0 Hz, O=CC**H**=), 5.49 (1H, s, =C**H**$_2$), 5.10 (1H, d, *J* = 1.6 Hz, =C**H**$_2$), 4.25 (1H, dd, *J* = 8.8, 7.2 Hz, OC**H**$_2$), 4.02 (1H, t, *J* = 9.6 Hz, OC**H**$_2$), 3.80 (1H, q, *J* = 8.8 Hz, OCH_2C**H**), 2.63 (1H, dt, *J* = 8.4, 7.2 Hz, O=CCH_2C**H**), 2.21 (1H, dd, *J* = 16.8, 7.6 Hz, O=CC**H**$_2$), 2.09 (1H, dd, *J* = 16.8, 6.8 Hz, O=CC**H**$_2$), 1.51 (3H, s, OCC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8 (C), 150.2 (CH), 142.7 (C), 142.4 (C), 131.4 (CH), 130.5 (CH), 129.6 (CH), 129.3 (CH), 128.9 (CH), 118.5 (C), 117.5 (CH_2), 112.9 (C), 78.9 (C), 69.5 (CH_2), 45.4 (CH), 44.2 (CH), 35.5 (CH_2), 27.0 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{18}H_{17}NNaO_2]^+$ $[M+Na]^+$: 302.1151, found: 302.1149. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (90:10 *iso*-hexane:*i*-PrOH), 1 mL/min, 254 nm, 25 °C); t_r (major) = 16.9 min, t_r (minor) = 28.0 min, 89% ee.

Data for **8l**: R_f = 0.16 (40% EtOAc/petroleum ether); $[\alpha]_D^{25}$ −4.7 (*c* 0.86, $CHCl_3$); IR 3436 (OH), 2926, 2230, 1667, 1620, 1587, 1501, 1292, 1265, 1056, 1015, 907, 808, 735, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (1H, td, *J* = 1.8, 0.5 Hz, Ar**H**), 7.51 (1H, d, *J* = 1.7 Hz, Ar**H**), 7.49 (1H, d, *J* = 1.7 Hz, Ar**H**), 7.37-7.34 (1H, m, Ar**H**), 7.01 (1H, dd, *J* = 8.2, 0.8 Hz, Ar**H**), 6.76 (1H, d, *J* = 2.7 Hz, Ar**H**), 6.62 (1H, dd, *J* = 8.2, 2.7 Hz, Ar**H**), 5.51 (1H, s, =C**H**$_2$), 5.25 (1H, d, *J* = 0.9 Hz, =C**H**$_2$), 4.21 (1H, td, *J* = 6.6, 1.2 Hz, ArC**H**), 3.98-3.86 (2H, m, C**H**$_2$OH), 2.26 (3H, s, ArC**H**$_3$), the two O**H** protons were not observed clearly); ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3 (C), 146.3 (C), 143.1 (C), 138.4 (C), 131.9 (CH), 131.0 (CH), 130.8 (CH), 130.1 (CH), 129.2 (CH), 128.4 (C),

118.7 (C), 116.5 (CH_2), 114.04 (CH), 114.02 (CH), 112.3 (C), 64.3 (CH_2), 48.0 (CH), 18.7 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{18}H_{17}NNaO_2]^+$ $[M+Na]^+$: 302.1151, found: 302.1146. Enantiomeric excess was determined by HPLC with a Chiralpak IC-3 column (90:10 *iso*-hexane:*i*-PrOH), 1.5 mL/min, 254 nm, 25 °C); t_r (minor) = 34.0 min, t_r (major) = 41.5 min, 91% ee.

(3*R*,3a*R*,7a*R*)-3-[1-(7a-Methyl-5-oxo-2,3,3a,4,5,7a-hexahydro-1-benzofuran-3-yl)ethenyl]benzoate (6m) and ethyl 3-[(*S*)-4-hydroxy-3-(5-hydroxy-2-methylphenyl)but-1-en-2-yl]benzoate (8m)

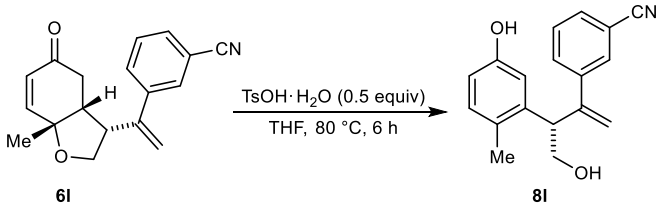


The General Procedure was followed using allenyl cyclohexa-2,5-dienone **4a** (52.8 mg, 0.30 mmol) and 3-ethoxycarbonylphenylboronic acid (116.4 mg, 0.60 mmol). Purification by column chromatography (30% EtOAc/petroleum ether) gave **6m** as pale yellow oil (62.7 mg, 64%) followed by **8m** as a white amorphous (21.2 mg, 22%).

Data for **6m**: R_f = 0.23 (30% EtOAc/petroleum ether); $[\alpha]_D^{25}$ −58.7 (*c* 0.75, $CHCl_3$); IR 3055, 2980, 1715 (C=O), 1684 (C=O), 1289, 1265, 1024, 906, 875, 732, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 (1H, t, *J* = 1.9 Hz, Ar**H**), 7.99 (1H, dt, *J* = 7.7, 1.4 Hz, Ar**H**), 7.59 (1H, ddd, *J* = 7.8, 2.0, 1.2 Hz, Ar**H**), 7.44 (1H, td, *J* = 8.0, 0.4 Hz, Ar**H**), 6.61 (1H, d, *J* = 10.0 Hz, O=CCH=C**H**), 5.98 (1H, d, *J* = 10.4 Hz, O=CC**H**=), 5.50 (1H, d, *J* = 1.2 Hz, =C$\mathbf{H}_2$), 5.03 (1H, d, *J* = 1.6 Hz, =C$\mathbf{H}_2$), 4.40 (2H, q, *J* = 7.2 Hz, C$\mathbf{H}_2$CH$_3$), 4.26 (1H, dd, *J* = 8.8, 7.2 Hz, OC$\mathbf{H}_2$), 4.05 (1H, dd, *J* = 10.4, 8.8 Hz, OC$\mathbf{H}_2$), 3.91 (1H, dd, *J* = 17.2, 8.8 Hz, OCH$_2$C**H**), 2.63 (1H, td, *J* = 8.4, 6.8 Hz, O=CCH$_2$C**H**), 2.24 (1H, dd, *J* = 16.8, 8.0 Hz, O=CC$\mathbf{H}_2$), 2.07 (1H, dd, *J* = 16.8, 6.8 Hz, O=CC$\mathbf{H}_2$), 1.50 (3H, s, OCC$\mathbf{H}_3$), 1.42 (3H, t, *J* = 7.2 Hz, CH$_2$C$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.3 (C), 166.3 (C), 150.2 (CH), 143.3 (C), 141.6 (C), 130.9 (C), 130.4 (CH), 129.0 (CH), 128.8 (CH), 128.8 (CH), 126.8 (CH), 116.1 (CH_2), 78.8 (C), 69.6 (CH_2), 61.1 (CH_2), 45.5 (CH), 44.0 (CH), 35.4 (CH_2), 27.3 (CH_3), 14.3 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{20}H_{22}NaO_4]^+$ $[M+Na]^+$: 349.1410, found: 349.1409. Enantiomeric excess was determined by HPLC with a Chiralpak IA-3 column (98:2 *iso*-hexane:*i*-PrOH, 0.5 mL/min, 230 nm, 25 °C); t_r (major) = 103.5 min, t_r (minor) = 121.8 min, 91% ee.

Data for **8m**: R_f = 0.21 (40% EtOAc/petroleum ether); $[\alpha]_D^{25}$ +36.4 (*c* 0.33, $CHCl_3$); IR 3369 (OH), 2925, 2855, 1715 (C=O), 1462, 1368, 1290, 1264, 1020, 907, 735, 703 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (1H, t, *J* = 2.0 Hz, Ar**H**), 7.91 (1H, dt, *J* = 7.6, 1.2 Hz, Ar**H**), 7.50 (1H, ddd, *J* = 6.8, 2.0, 0.8 Hz, Ar**H**), 7.34 (1H, t, *J* = 7.6 Hz, Ar**H**), 7.03 (1H, d, *J* = 8.0 Hz, Ar**H**), 6.81 (1H, d, *J* = 2.8 Hz, Ar**H**), 6.62 (1H, dd, *J* = 8.4, 2.8 Hz, Ar**H**), 5.60 (1H, s, =C**H**$_2$), 5.23 (1H, s, =C**H**$_2$), 4.39-4.30 (3H, m, C**H**$_2$CH$_3$ AND CH$_2$O**H)**, 4.00 (1H, dd, *J* = 11.2, 6.8 Hz, C**H**$_2$OH), 3.90 (1H, dd, *J* = 11.6, 6.4 Hz, C**H**$_2$OH), 2.32 (3H, s, ArC**H**$_3$), 1.72 (1H, br s, O**H**), 1.39 (3H, t, *J* = 6.8 Hz, CH$_2$C**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.6 (C), 154.1 (C), 147.2 (C), 141.9 (C), 139.1 (C), 131.8 (CH), 130.6 (CH), 130.5 (C), 128.7 (CH), 128.6 (C), 128.4 (CH), 127.5 (CH), 115.2 (CH_2), 114.1 (CH), 113.8 (CH), 64.6 (CH_2), 61.1 (CH_2), 48.1 (CH), 18.8 (CH_3), 14.3 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{20}H_{23}O_4]^+$ $[M+H]^+$: 327.1591, found: 327.1598. Enantiomeric excess was determined by HPLC with OD-H (90:10 *iso*-hexane:*i*-PrOH), 1 mL/min, 280 nm, 25 °C); t_r (major) = 18.2 min, t_r (minor) = 37.0 min, 91% ee.

Acid-Catalyzed of Hexahydrobenzofuran-5-one 6l into Phenol 8l

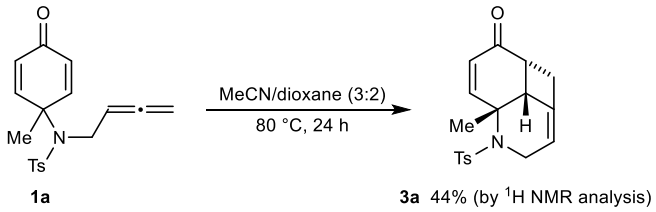


6l **8l**

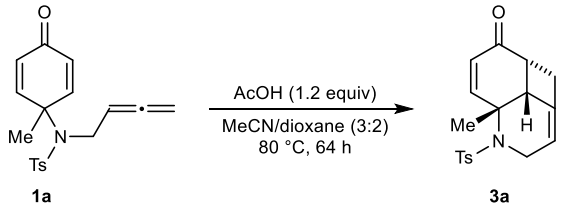
An oven-dried microwave vial fitted with a stirrer bar was charged with 6,5-bicycle **6l** (14.0 mg, 0.05 mmol) and *p*-toluenesulfonic acid monohydrate (4.8 mg, 0.025 mmol), then capped with a crimp cap PTFE seal and purged with a stream of N_2. THF (0.5 mL) was added and the mixture was stirred at 80 °C for 6 h. The reaction was cooled to room temperature, filtered through a plug of silica and concentrated under reduced pressure. The residue was purified by column chromatography to give phenol **8l** as a colorless oil (9.1 mg, 65%).

Independent Formation of the [2+2] Cycloaddition Products

(±)-(3a1*R*,4a*R*,7a*R*)-7a-Methyl-1-tosyl-1,2,3a1,4,4a,7a-hexahydro-5*H*-cyclobuta[de]quinolin-5-one (3a)



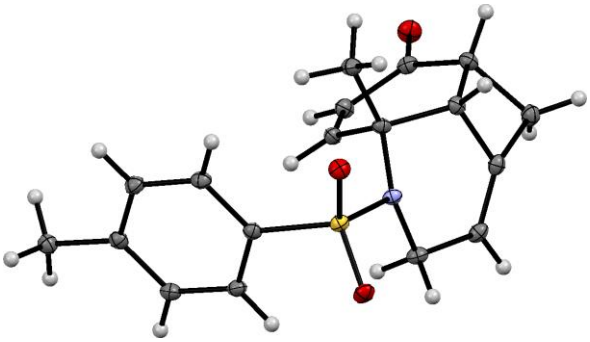
An oven-dried microwave vial fitted with a stirrer bar was charged with allenyl cyclohexa-2,5-dienone **1a** (98.8 mg, 0.30 mmol) and the vial was capped and purged with a stream of N_2. MeCN (1.8 mL) and 1,4-dioxane (1.2 mL) were added. The reaction was stirred at 80 °C for 24 h, cooled to room temperature, filtered through a plug of silica using EtOAc as eluent, and concentrated under reduced pressure. ^{1}H NMR analysis of the residue using an internal standard showed **3a** was formed in 44% yield. Full experimental characterization of **3a** was performed on material obtained by the procedure described below:



An oven-dried microwave vial fitted with a stirrer bar was charged with allenyl cyclohexa-2,5-dienone **1a** (98.8 mg, 0.30 mmol) and the vial was capped and purged with a stream of N_2. MeCN (1.8 mL) and 1,4-dioxane (1.2 mL) were added followed by AcOH (28 μL). The reaction was stirred at 80 °C for 64 h, cooled to room temperature, filtered through a plug of silica using EtOAc as eluent, and concentrated under reduced pressure. The residue was purified by column chromatography (30% EtAc/petroleum ether) to give the *cyclobutane* **3a** as a colorless solid (43.4 mg, 44%). R_f = 0.30 (30% EtOAc/petroleum ether); m.p. 110-112 °C (Et_2O); IR 2919, 2850, 1664 (C=O), 1595, 1450, 1339, 1167, 1154, 1143, 928, 850, 813, 749, 720, 675, 617, 544 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (2H, m, Ar**H**), 7.33-7.30 (2H, m, Ar**H**), 6.57 (1H, dd, *J* = 10.8, 2.0 Hz, O=CCH=C**H**), 5.93 (1H, d, *J* = 10.4 Hz, O=CC**H**=), 5.36 (1H, quin d, *J* = 2.4, 0.8 Hz, NCH_2C**H**=), 4.74-4.68 (1H, m, NC**H**$_2$), 3.75-3.69 (1H, m, NC**H**$_2$), 3.27-3.21 (2H, m, CHC**H**$_2$C=CH), 3.05-3.01 (1H, m, O=CC**H**CH_2), 2.64-2.59 (1H, m, O=CCHC**H**), 2.45 (3H, s, ArC**H**$_3$), 1.55 (3H, s, NCC**H**$_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.1 (C), 151.4 (CH), 143.5 (C), 139.8 (C), 135.1 (C), 129.7 (2 × CH), 129.3 (CH), 126.9 (2 × CH), 112.0 (CH), 55.8 (C), 48.7 (CH),

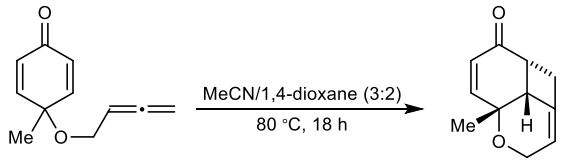
46.5 (CH_2), 40.4 (CH), 38.7 (CH_2), 25.9 (CH_3), 21.6 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{18}H_{20}NO_3S]^+$ $[M+H]^+$: 330.1158, found: 330.1160.

Slow diffusion of petroleum ether into a solution of **3a** in EtOAc gave crystals that were suitable for X-ray crystallography:



3a
CCDC 1584899

(±)-(3a1*R*,4a*R*,7a*R*)-7a-Methyl-3a1,4,4a,7a-tetrahydrocyclobuta[de]chromen-5(2*H*)-one (3b)

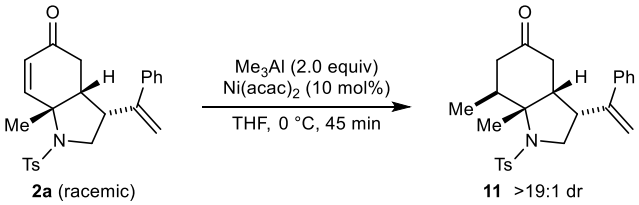


4a **3b**

An oven-dried microwave vial fitted with a stirrer bar was charged with allenyl cyclohexa-2,5-dienone **4a** (17.6 mg, 0.10 mmol), then capped with a crimp cap PTFE seal and purged with a stream of N_2. MeCN (0.6 mL) and 1,4-dioxane (0.4 mL) were added and the mixture was stirred at 80 °C for 18 h. The reaction was cooled to room temperature, filtered through a plug of silica using EtOAc as eluent, and concentrated under reduced pressure. The residue was purified by column chromatography to give the *cyclobutane* **3b** as a colorless oil (4 mg, 25%). R_f = 0.21 (20% EtOAc/petroleum ether); IR 2962, 2926, 1714, 1669 (C=O), 1258, 1081, 1015, 863, 791, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.62 (1H, dd, *J* = 10.6, 1.8 Hz, O=CCH=C**H**), 6.05 (1H, dd, *J* = 10.6, 0.6 Hz, O=CC**H**=), 5.38-5.35 (1H, m, OCH_2C**H**=), 4.37-4.32 (1H, m, O**C**$\mathbf{H}_2$), 4.19-4.14 (1H, m, O**C**$\mathbf{H}_2$), 3.45-3.36 (1H, m, O=CCHC$\mathbf{H}_2$), 3.34-3.31 (1H, m, O=CCHC**H**), 3.15-3.10 (1H, m, O=CC**H**), 2.72-2.67 (1H, m, O=CCHC$\mathbf{H}_2$), 1.36 (3H, s, C$\mathbf{H}_3$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2 (C), 152.0 (CH), 134.7 (C), 130.9 (CH), 113.3 (CH), 67.6 (C), 63.8 (CH_2), 46.7 (CH), 40.8 (CH), 39.8 (CH_2), 27.2 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{11}H_{12}NaO_2]^+$ $[M+Na]^+$: 199.0730, found: 199.0730.

Further Transformations

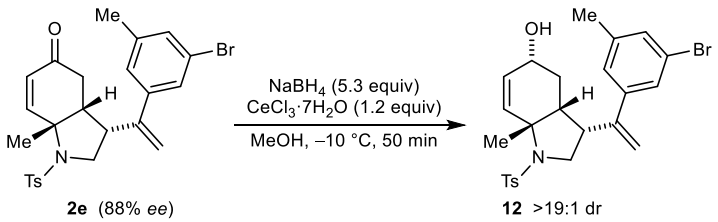
(±)-(3*R*,3a*R*,7*S*,7a*R*)-7,7a-Dimethyl-3-(1-phenylethenyl)-1-(4-methylbenzenesulfonyl)-octahydro-5*H*-indol-5-one (11)



2a (racemic) **11** >19:1 dr

An oven-dried microwave vial fitted with a stirrer bar was charged with *rac*-**2a** (40.7 mg, 0.10 mmol) and $Ni(acac)_2$ (2.6 mg, 0.01 mmol). The vial was capped with a crimp cap PTTE seal and purged with a stream of nitrogen. THF (1 mL) was added and the mixture was stirred at 0 °C for 20 min. A solution of Me_3Al (2.0 M in hexane, 0.1 mL, 0.2 mmol) was then added and the reaction was stirred at 0 °C for 45 min. The reaction was diluted with EtOAc (5 mL) and washed with saturated aqueous Rochelle salt solution (1 mL). The organic layer was dried (Na_2SO_4) and concentrated under reduced pressure. The mixture was purified by column chromatography (30% EtOAc/pentane) to give the *title compound* **11** (32.2 mg, 76%) as a colorless solid. R_f = 0.53 (30% EtOAc/pentane); m.p. 160-163 °C (Et_2O); IR 2957, 2925, 1709 (C=O), 1323, 1158, 1097, 907, 778, 728, 676, 584, 547 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.82 (2H, d, *J* = 8.0 Hz, Ar**H**), 7.36-7.29 (5H, m, Ar**H**), 7.26-7.24 (2H, m, Ar**H**), 5.34 (1H, d, *J* = 1.6 Hz, =C**H**$_2$), 4.94 (1H, d, *J* = 1.9 Hz, =C**H**$_2$), 3.88 (1H, dd, *J* = 8.8, 6.4 Hz, NC**H**$_2$), 3.69-3.65 (1H, m, O=CCH$_2$C**H**CH), 3.64-3.59 (1H, m, NC**H**$_2$), 3.28-3.21 (1H, m, CH$_3$C**H**), 2.82 (1H, dd, *J* = 14.8, 4.8 Hz, CH$_3$CHC**H**$_2$), 2.46 (3H, s, ArC**H**$_3$), 2.30-2.25 (1H, m, NCH$_2$C**H**), 2.03-1.96 (2H, m, O=CC**H**$_2$CHCH and CH$_3$CHC**H**$_2$), 1.84 (1H, ddd, *J* = 16.4, 7.8, 1.9 Hz, O=CC**H**$_2$CHCH), 1.52 (3H, s, NCC**H**$_3$), 0.96 (3H, d, *J* = 7.6 Hz, C**H**$_3$CH); ^{13}C NMR (101 MHz, $CDCl_3$) δ 211.0 (C), 144.7 (C), 143.5 (C), 140.5 (C), 137.7 (C), 129.7 (2 x CH), 128.7 (2 x CH), 128.1 (CH), 127.4 (2 x CH), 126.0 (2 x CH), 115.1 (CH_2), 71.4 (C), 49.3 (CH_2), 46.3 (CH), 44.1 (CH_2), 42.3 (CH), 38.0 (CH), 37.2 (CH_2), 24.8 (CH_3), 21.5 (CH_3), 17.5 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{25}H_{30}NO_3S]^+$ $[M+H]^+$: 424.1941, found: 424.1951.

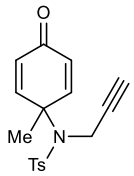
(3*R*,3a*R*,7a*R*)-3-[1-(3-Bromo-5-methylphenyl)ethenyl]-7a-methyl-1-(4-methylbenzenesulfonyl)-2,3,3a,4,5,7a-hexahydro-1*H*-indol-5-ol (12)



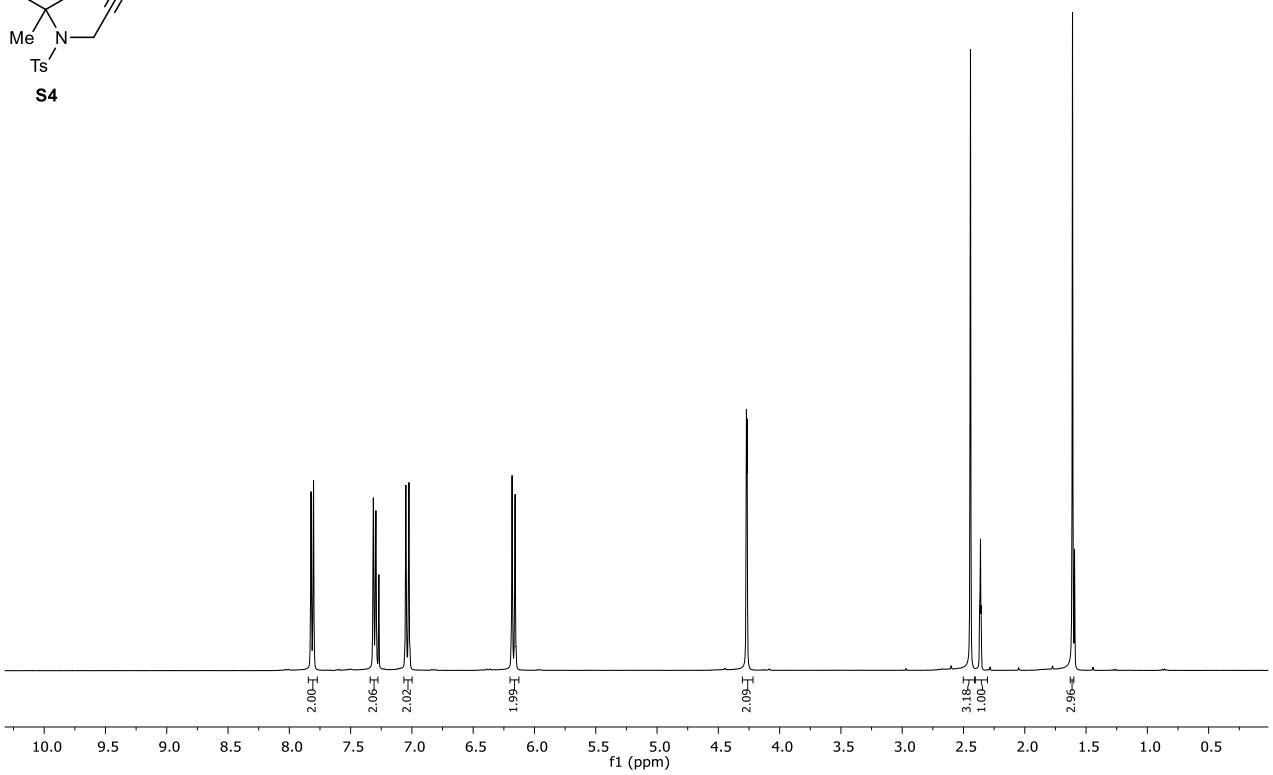
2e (88% *ee*) **12** >19:1 dr

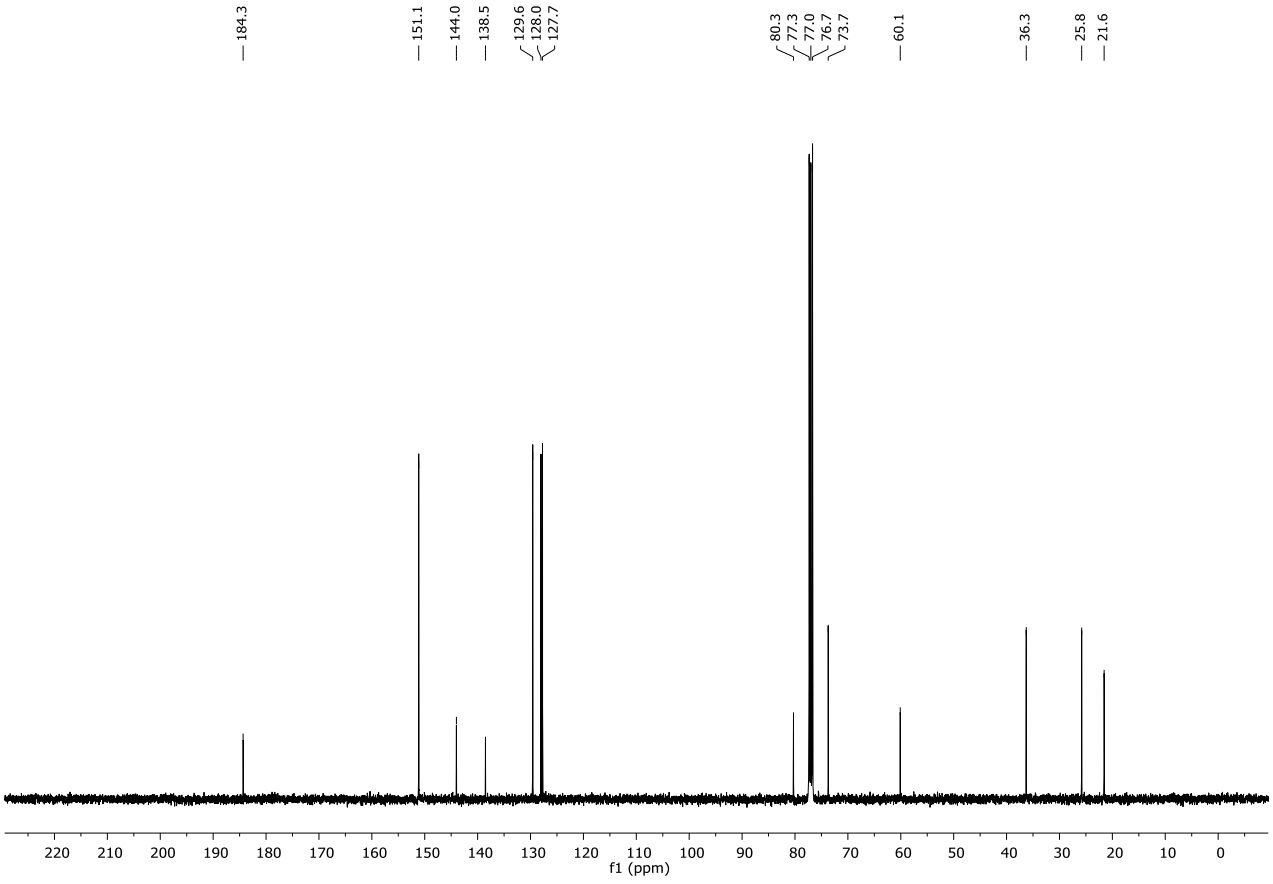
To a solution of ketone **2e** (49.9 mg, 0.10 mmol) in undried MeOH (1 mL) at –10 °C was added $CeCl_3 \cdot 7H_2O$ (44.7 mg, 0.12 mmol), followed by $NaBH_4$ (20.1 mg, 0.53 mmol) portionwise. The reaction was stirred at –10 °C for 50 min, quenched carefully with 1 M aqueous HCl solution (0.5 mL), diluted with H_2O (5 mL), and extracted with EtOAc (3 x 5 mL). The combined organic layers were dried (Na_2SO_4), filtered, and concentrated under reduced pressure. The mixture was purified by column chromatography (30% EtOAc/petroleum ether) to give the *allylic alcohol* **12** (49.8 mg, 99%) as a white solid. R_f = 0.26 (30% EtOAc/petroleum ether); m.p. 74-77 ^oC (Et_2O); $[\alpha]_D^{25}$ –30.8 (*c* 0.52, $CHCl_3$); IR 3490 (OH), 2924, 1596, 1561, 1443, 1326, 1145, 1111, 1090, 962, 853, 759, 707, 678, 582, 546 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.76 (2H, d, *J* = 8.4 Hz, Ar**H**), 7.32-7.25 (5H, m, Ar**H**), 7.06-7.05 (1H, m, Ar**H**), 6.24 (1H, dd, *J* = 10.2, 2.0 Hz, HOCHCH=C**H**), 5.69 (1H, dt, *J* = 10.2, 1.5 Hz, HOCHC**H**=), 5.32 (1H, d, *J* = 1.5 Hz, =C$\mathbf{H}_2$), 4.90 (1H, d, *J* = 1.8 Hz, =C$\mathbf{H}_2$), 3.95-3.92 (1H, m, HOC**H**), 3.81-3.77 (1H, m, NC$\mathbf{H}_2$), 3.75-3.68 (1H, m, $NCH_2C\mathbf{H}$), 3.41 (1H, dd, *J* = 10.8, 8.4 Hz, NC$\mathbf{H}_2$), 2.43 (3H, s, ArC$\mathbf{H}_3$), 2.34 (3H, s, ArC$\mathbf{H}_3$), 1.98-1.92 (1H, m, $HOCHCH_2C\mathbf{H}$), 1.61 (3H, s, NCC$\mathbf{H}_3$), 1.46-1.40 (1H, m, HOCHC$\mathbf{H}_2$), 1.12 (1H, d, *J* = 7.2 Hz, O**H**), 0.71 (1H, ddd, *J* = 13.6, 12.4, 10.4 Hz, HOCHC$\mathbf{H}_2$); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.5 (C), 143.0 (C), 142.7 (C), 140.3 (C), 137.2 (C), 132.8 (CH), 131.6 (CH), 130.5 (CH), 129.3 (2 x CH), 127.4 (2 x CH), 126.2 (CH), 125.6 (CH), 122.5 (C), 115.4 (CH_2), 66.7 (CH), 65.0 (C), 48.8 (CH_2), 45.9 (CH), 41.2 (CH), 29.7 (CH_2), 29.6 (CH_3), 21.5 (CH_3), 21.2 (CH_3); HRMS (ESI) Exact mass calcd for $[C_{25}H_{29}BrNO_3S]^+$ $[M+H]^+$: 502.1046, found: 502.1028.

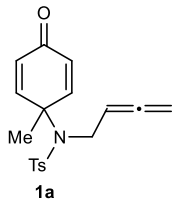
NMR Spectra



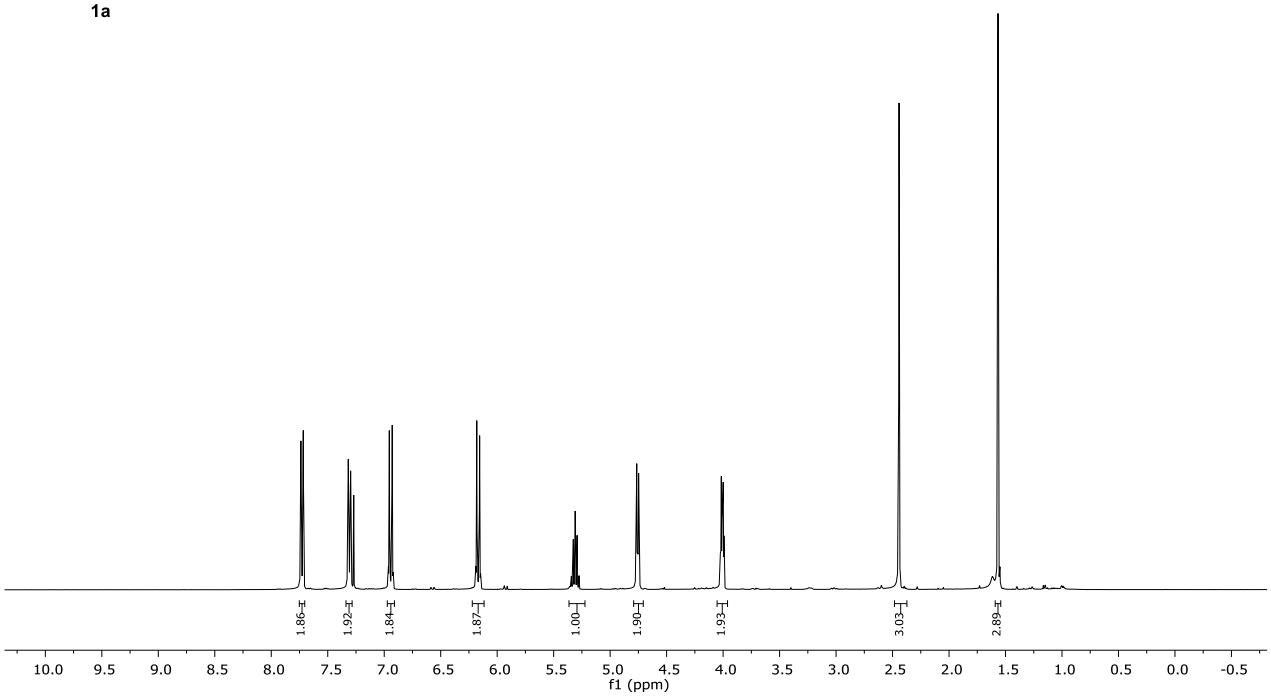
S4

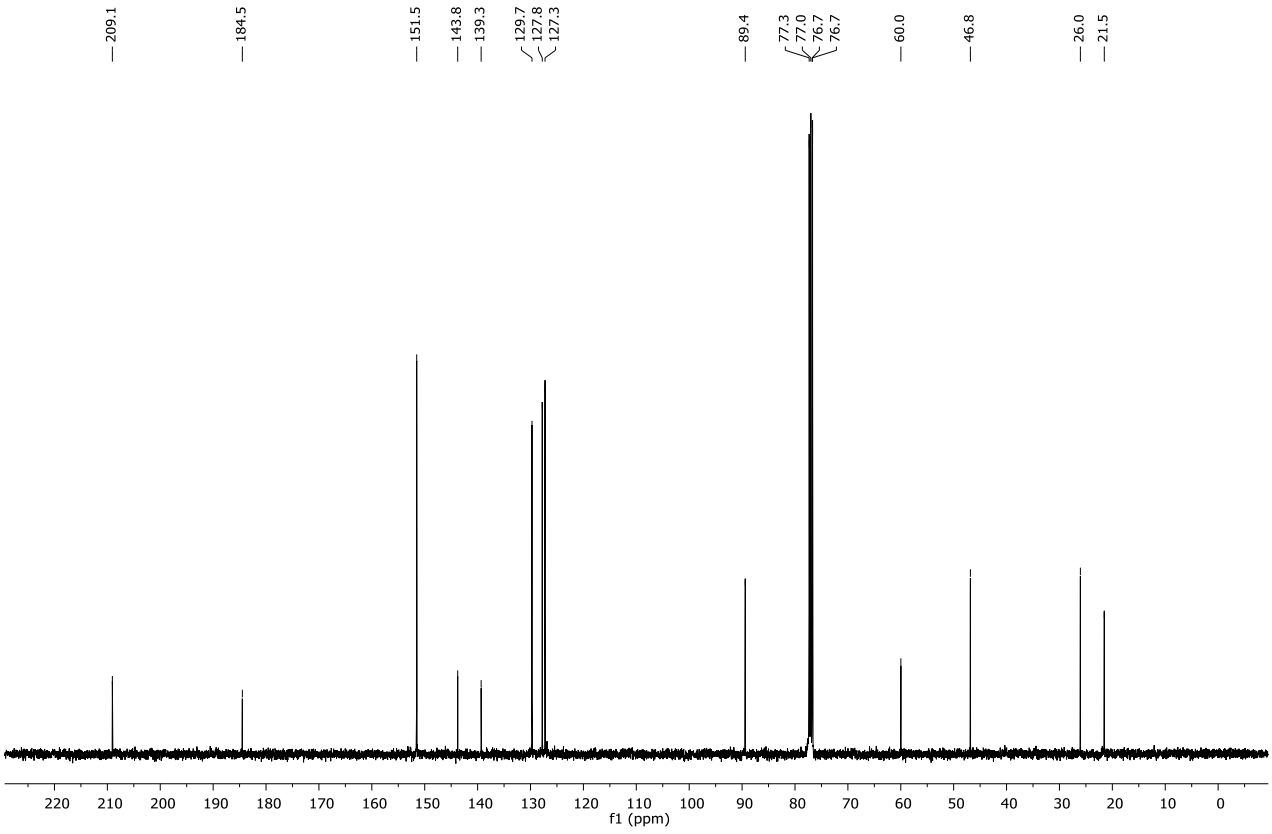


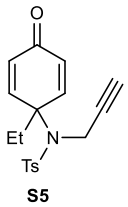



O
Me
N
Ts

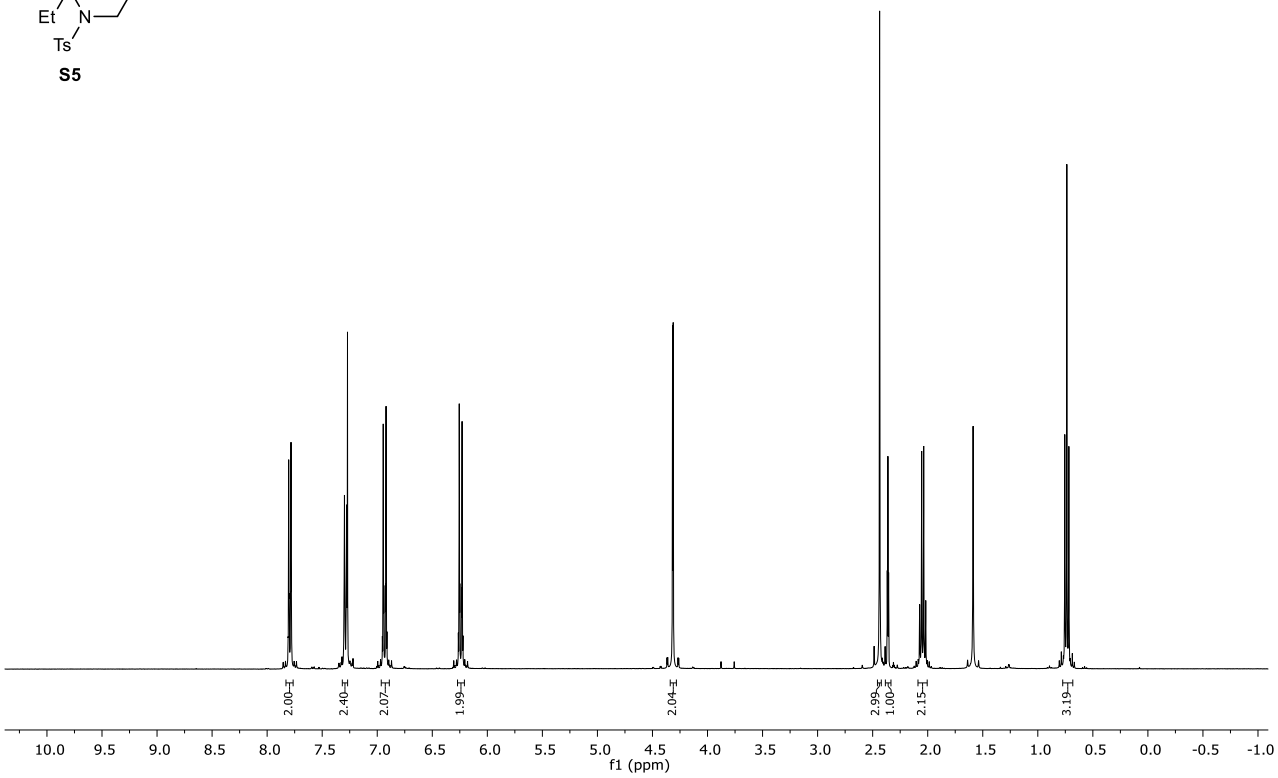
1a


1.86
1.92
1.84
1.87
1.00
1.90
1.93
3.03
2.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


209.1
184.5
151.5
143.8
139.3
129.7
127.8
127.3
89.4
77.3
77.0
76.7
76.7
60.0
46.8
26.0
21.5
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Et
N
Ts

S5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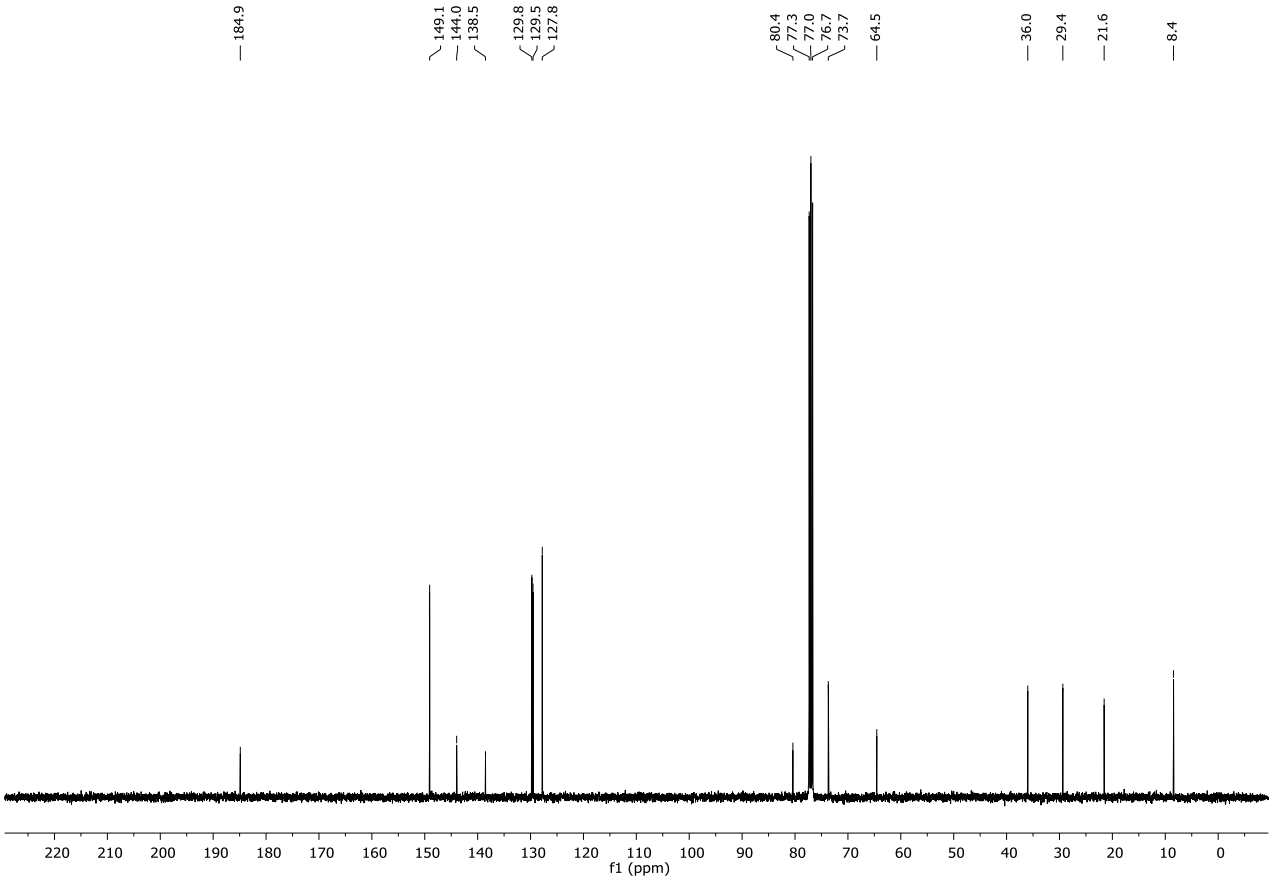
2.40
2.07
1.99
2.04
2.99
1.00
2.15
3.19
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)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149.1
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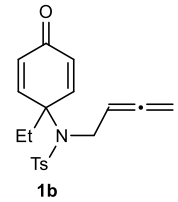
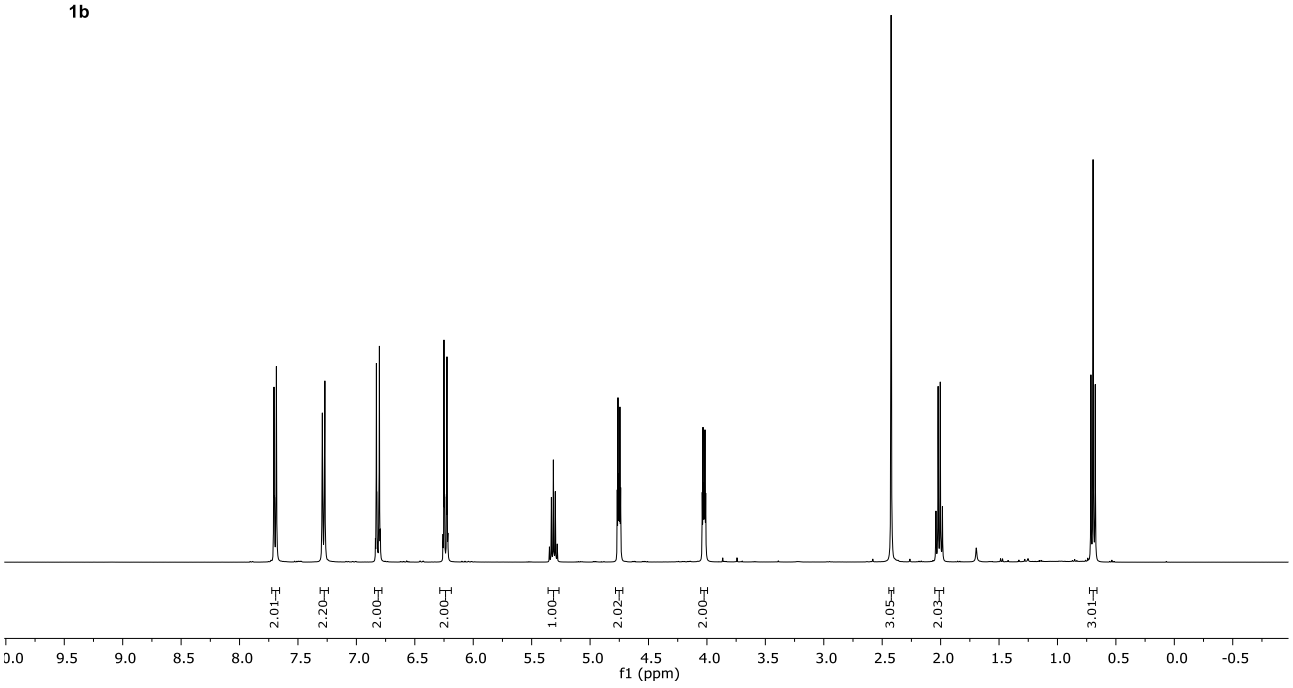
138.5
129.8
129.5
127.8
80.4
77.3
77.0
76.7
73.7
64.5
36.0
29.4
21.6
8.4
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
Et
N
Ts

1b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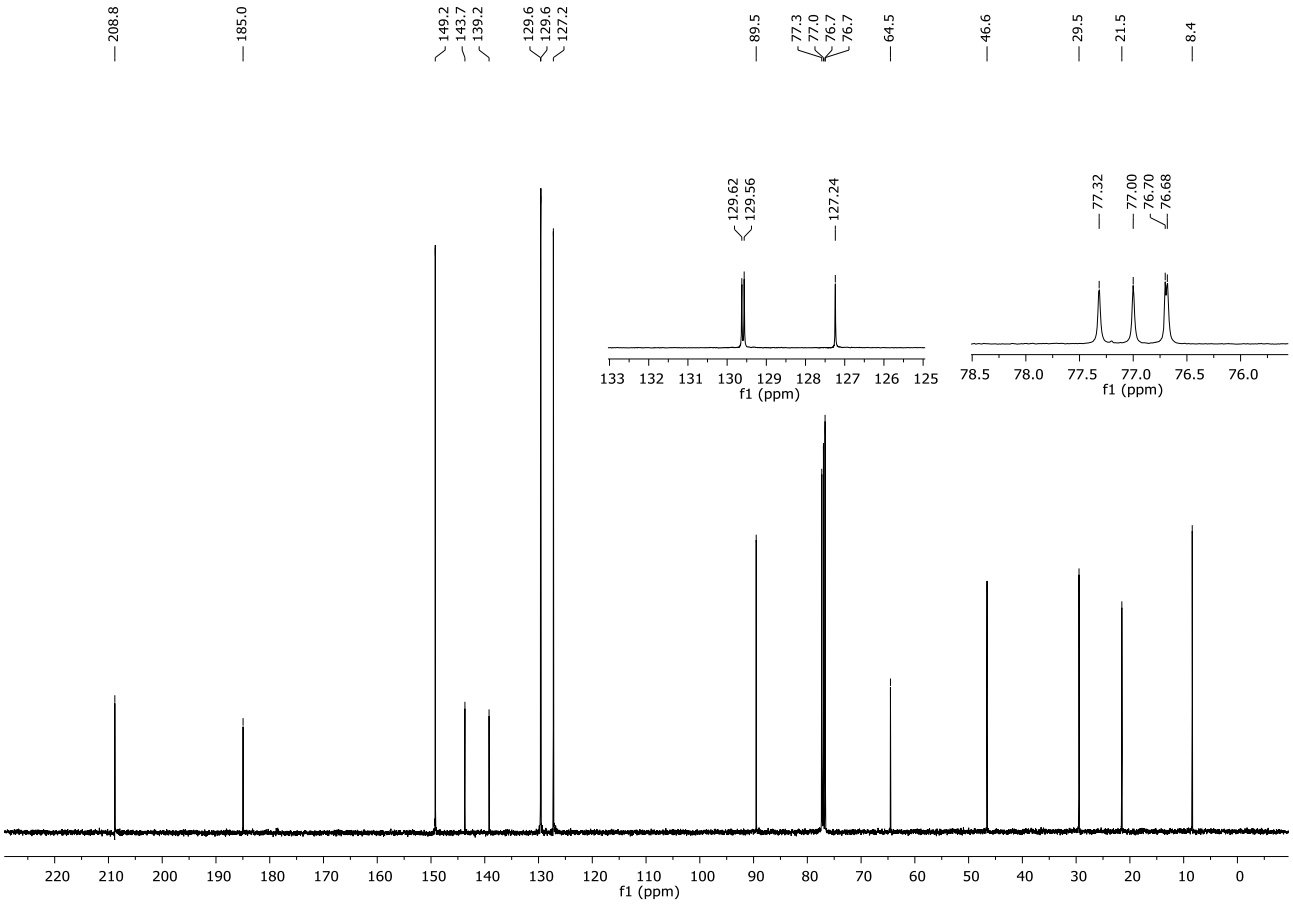
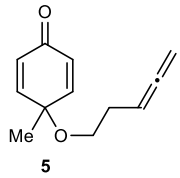
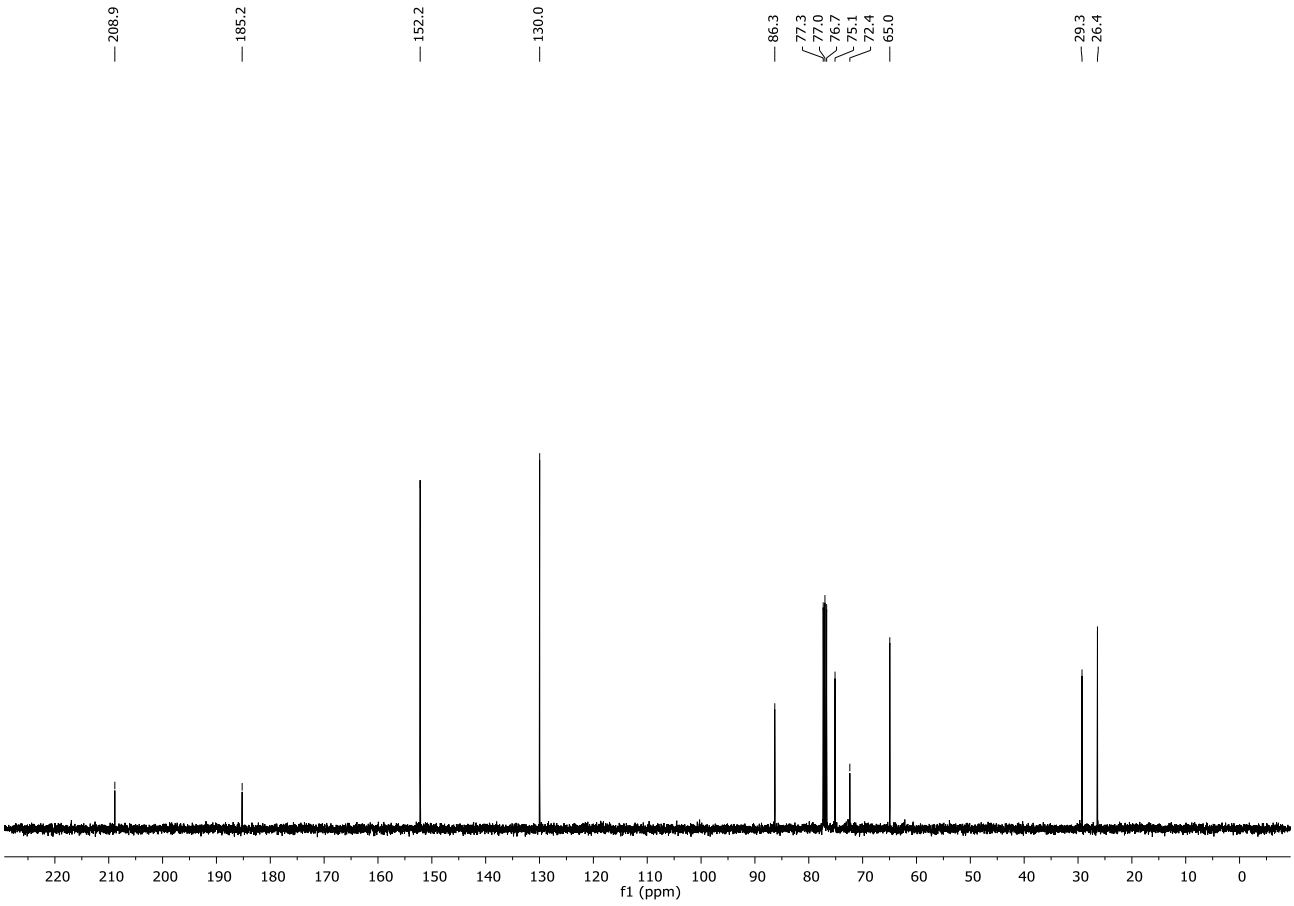
2.20
2.00
2.00
1.00
2.02
2.00
3.05
2.03
3.01
f1 (ppm)


208.8
185.0
149.2
143.7
139.2
129.6
129.6
127.2
89.5
77.3
77.0
76.7
76.7
64.5
46.6
29.5
21.5
8.4
129.62
129.56
127.24
77.32
77.00
76.70
76.68
f1 (ppm)


O
Me
O

5

2.01
2.01
1.00
2.05
2.09
2.10
3.03
f1 (ppm)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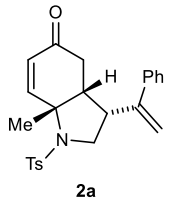
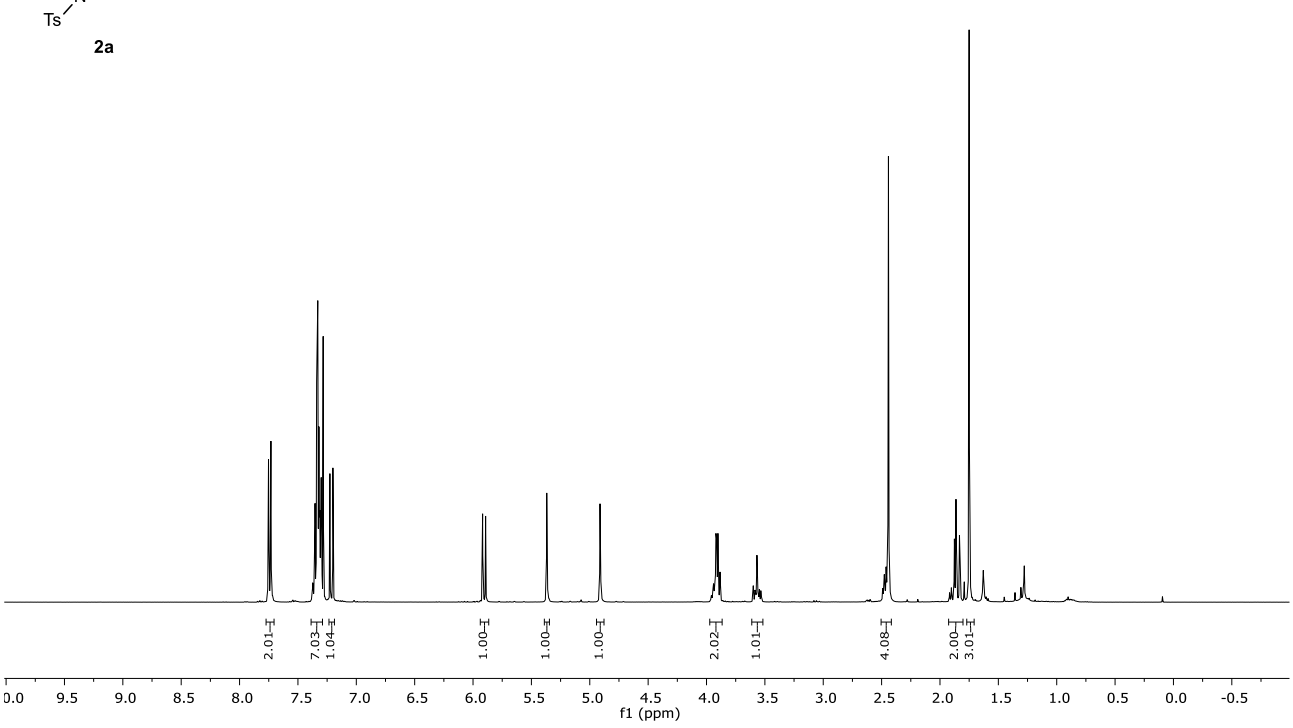
185.2
152.2
130.0
86.3
77.3
77.0
76.7
75.1
72.4
65.0
29.3
26.4
f1 (ppm)


O
H
Ph
Me
N
Ts

2a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1.04
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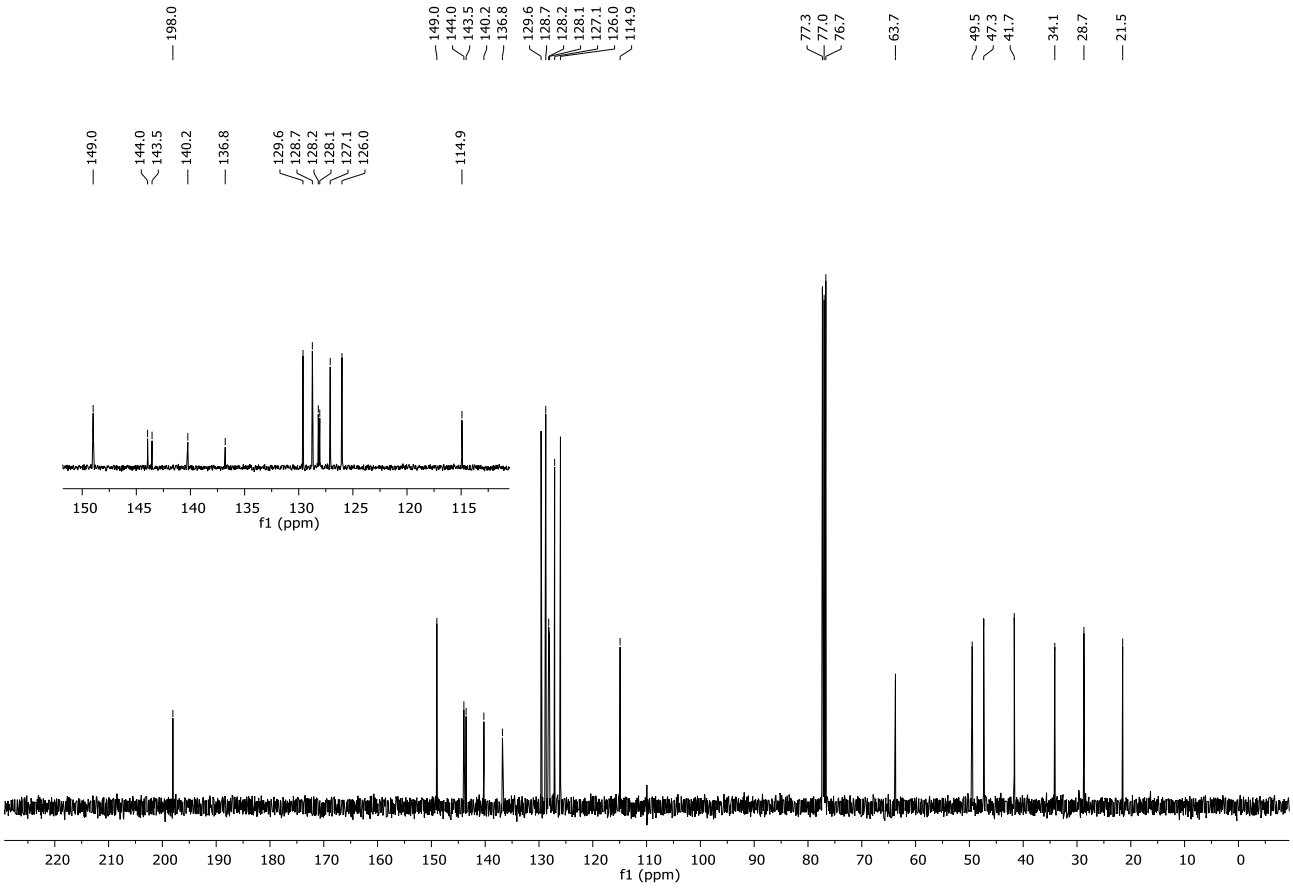
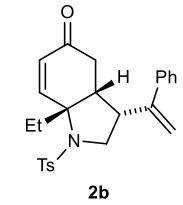
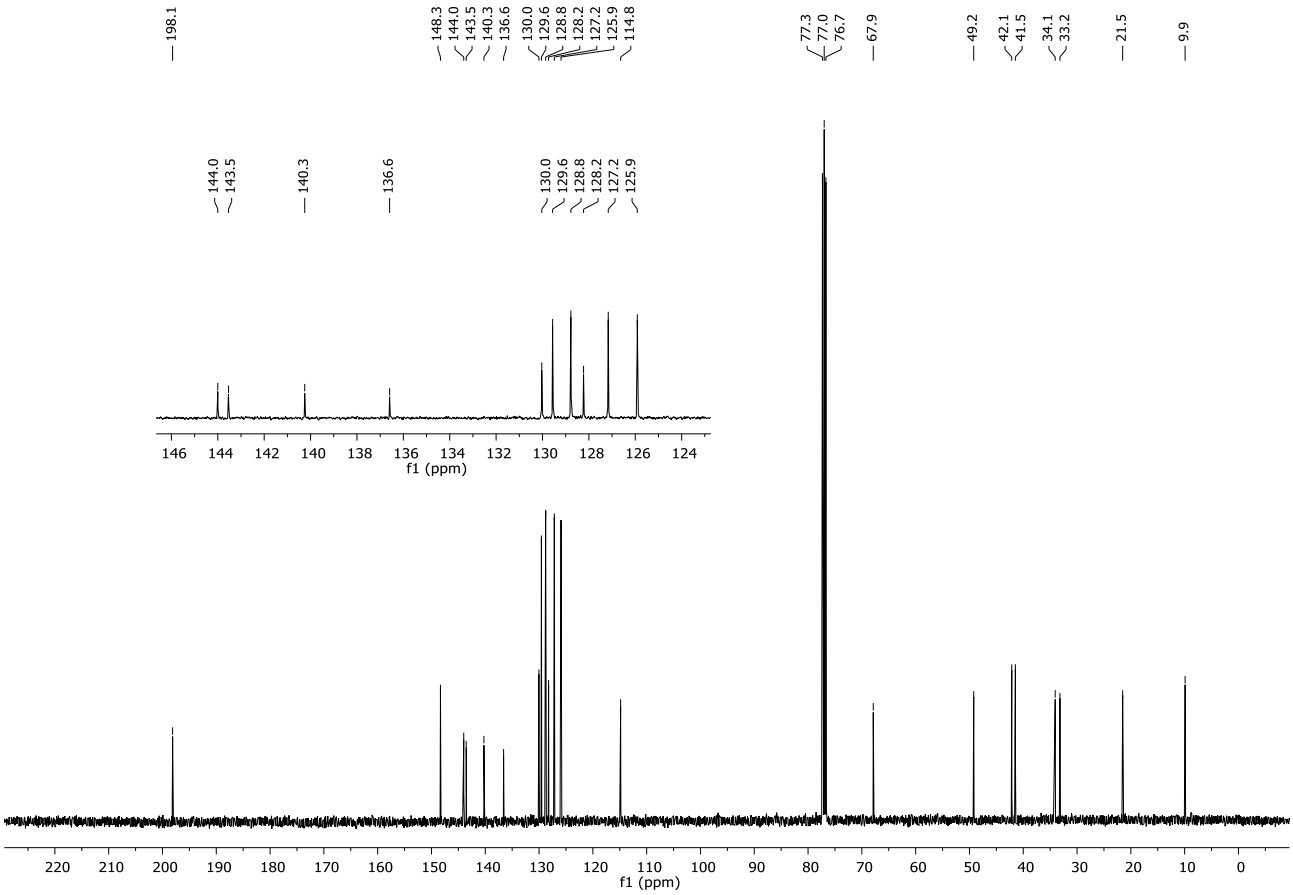
1.00
1.00
2.02
1.01
4.08
2.00
3.01
f1 (ppm)

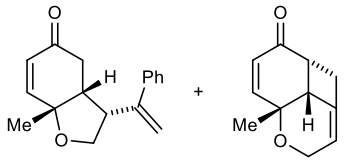

198.0
149.0
144.0
143.5
140.2
136.8
129.6
128.7
128.2
128.1
127.1
126.0
114.9
77.3
77.0
76.7
63.7
49.5
47.3
41.7
34.1
28.7
21.5
f1 (ppm)


O
H
Ph
Et
N
Ts

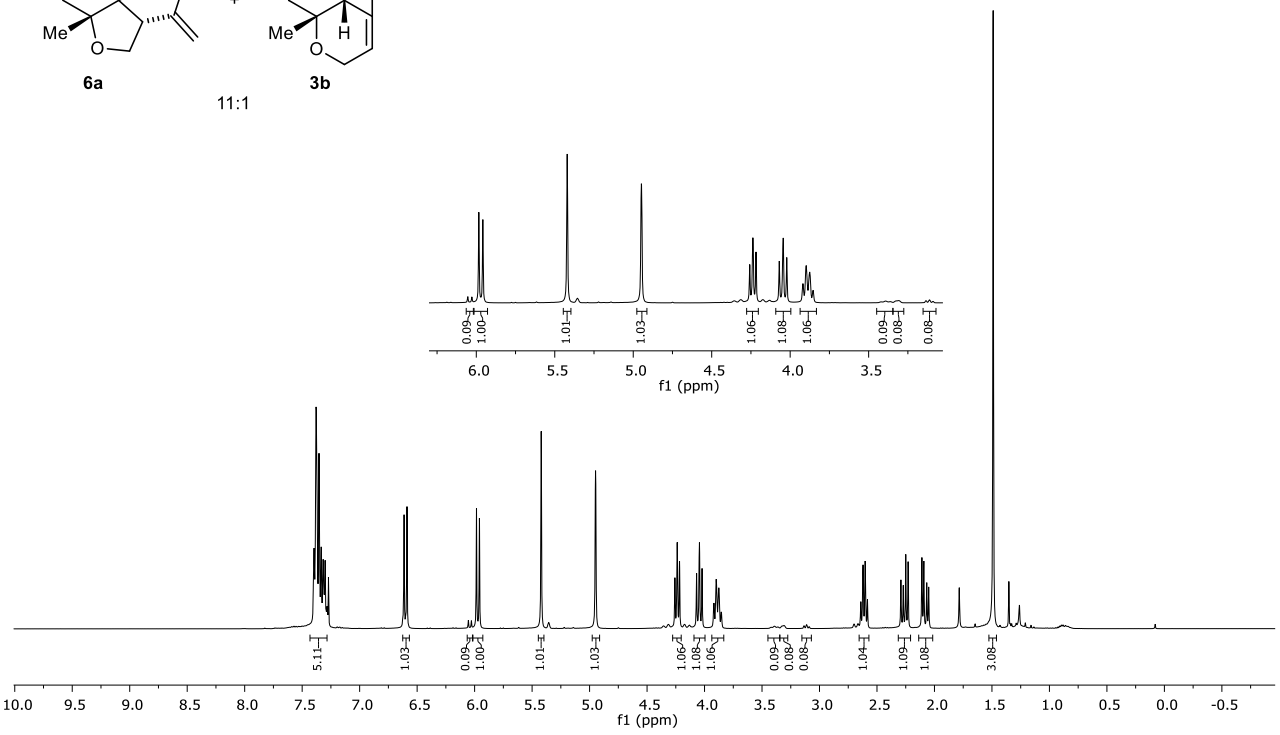
2b

2.01
7.02
1.02
1.00
1.02
1.00
2.02
1.03
1.06
3.06
1.05
1.10
1.03
1.06
3.09
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


198.1
148.3
144.0
143.5
140.3
136.6
130.0
129.6
128.8
128.2
127.2
125.9
114.8
77.3
77.0
76.7
67.9
49.2
42.1
41.5
34.1
33.2
21.5
9.9
144.0
143.5
140.3
136.6
130.0
129.6
128.8
128.2
127.2
125.9
146 144 142 140 138 136 134 132 130 128 126 124
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
H
Ph
Me
O
6a
+
O
Me
H
O
3b

11:1


0.09
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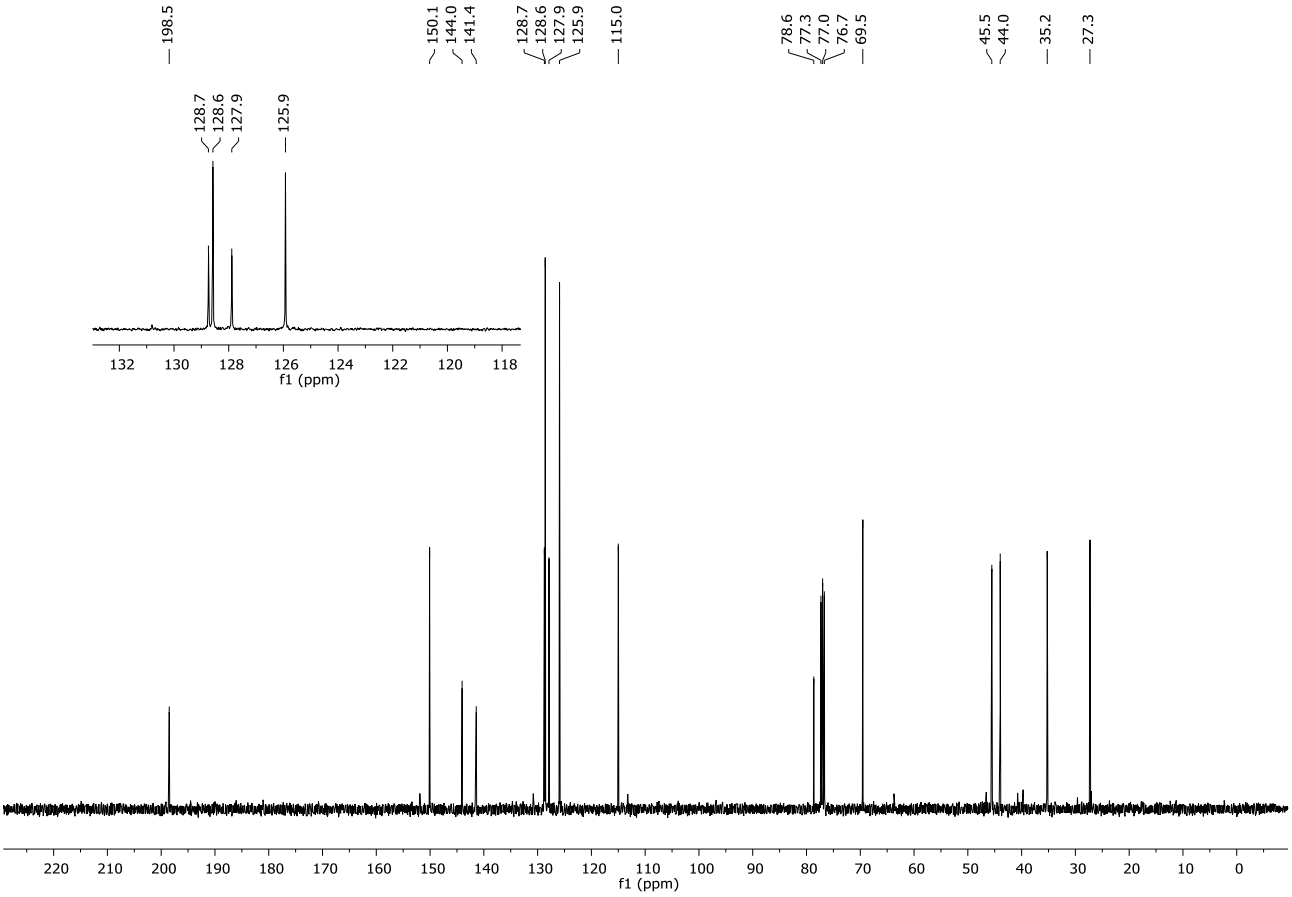
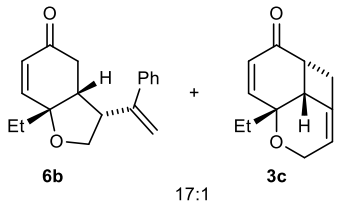
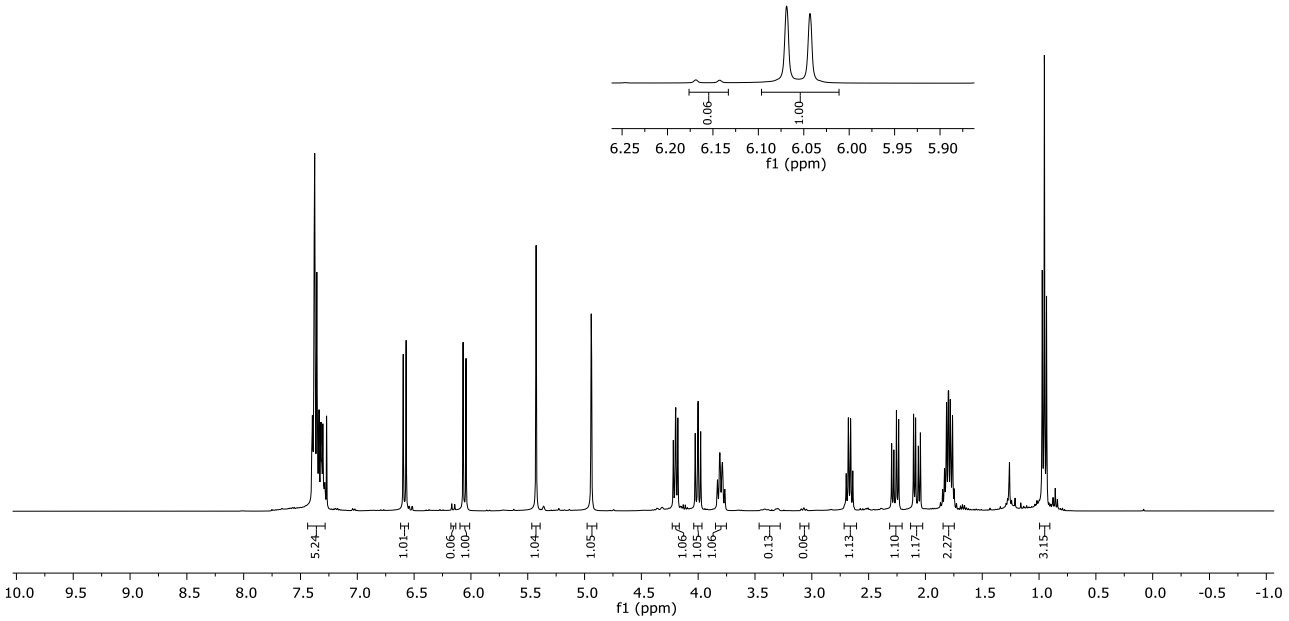
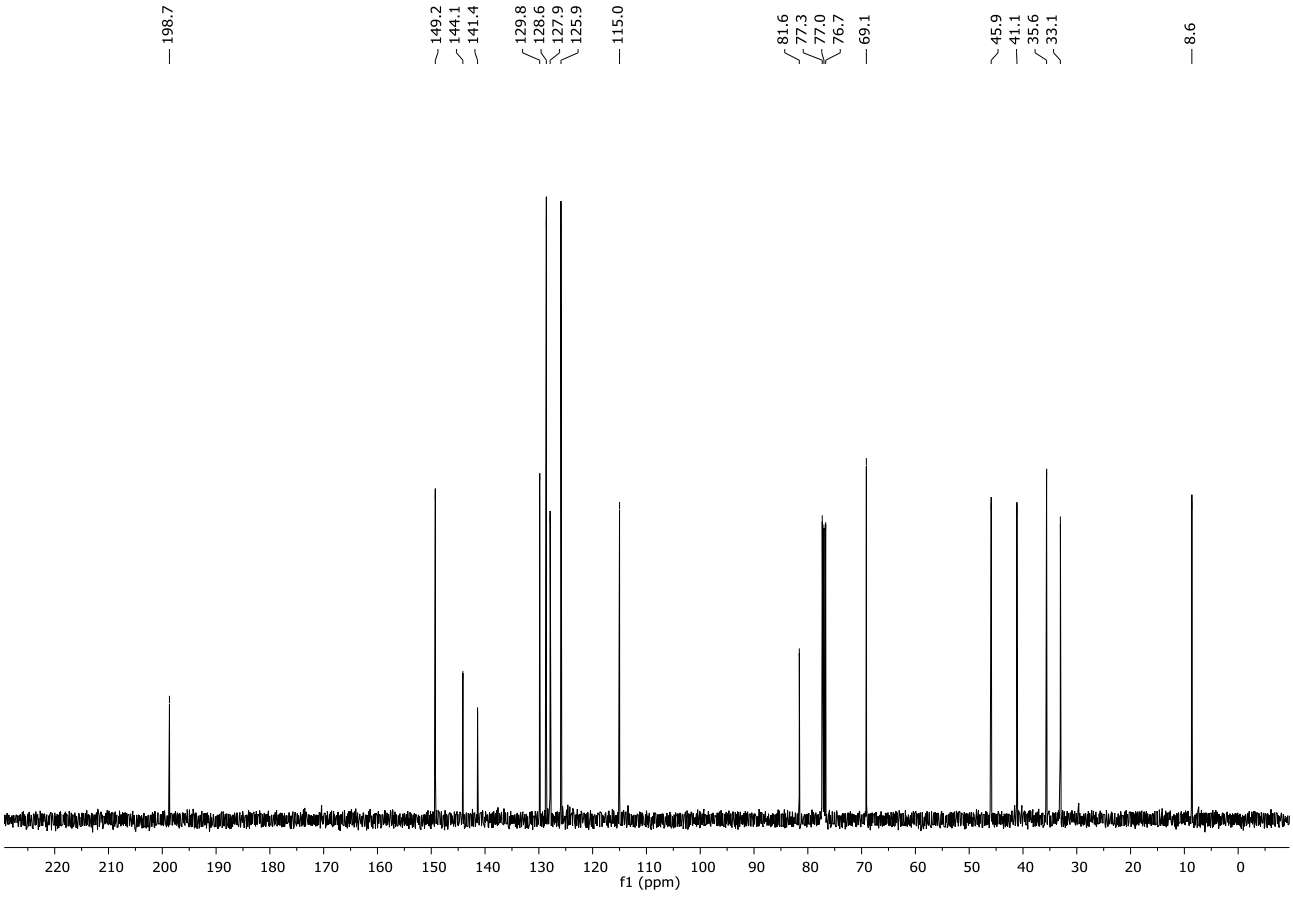
1.03
1.06
1.08
1.06
0.09
0.08
0.08
6.0
5.5
5.0
4.5
4.0
3.5
f1 (ppm)
5.11
1.03
0.09
1.00
1.01
1.03
1.06
1.08
1.06
0.09
0.08
0.08
1.04
1.09
1.08
3.08
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

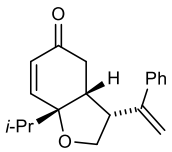

198.5
150.1
144.0
141.4
128.7
128.6
127.9
125.9
115.0
78.6
77.3
77.0
76.7
69.5
45.5
44.0
35.2
27.3
128.7
128.6
127.9
125.9
132
130
128
126
124
122
120
118
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
H
Ph
Et
O
+
O
Et
H
O

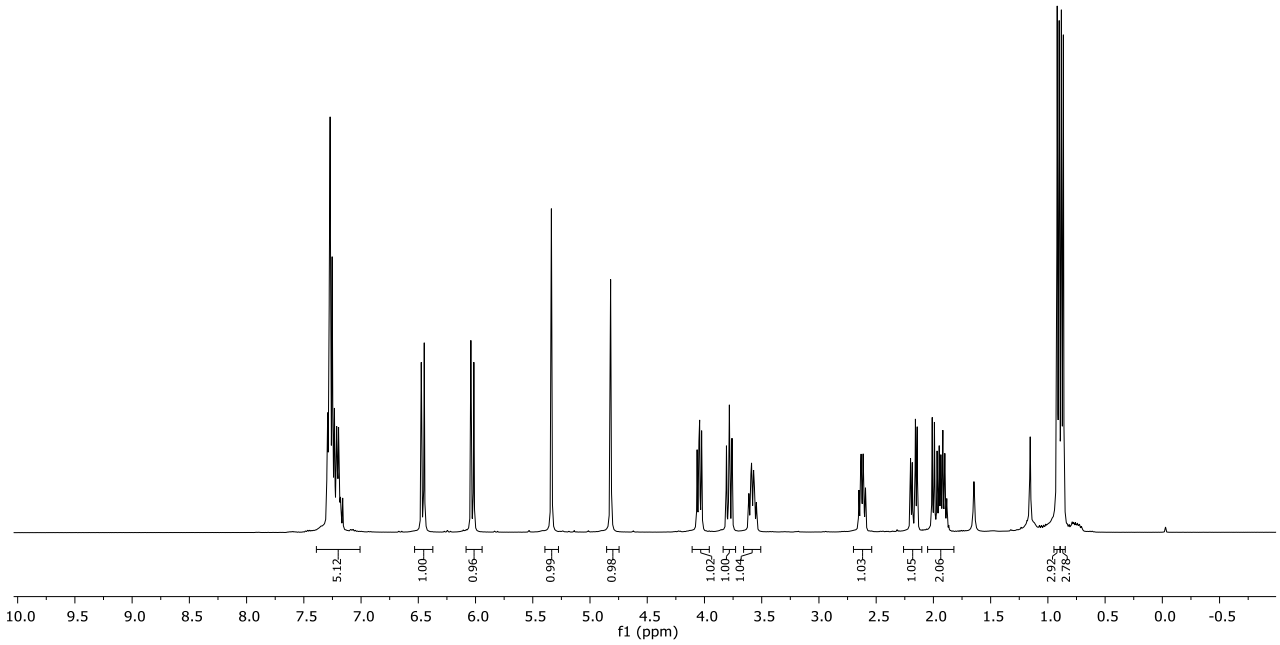
6b 17:1 **3c**

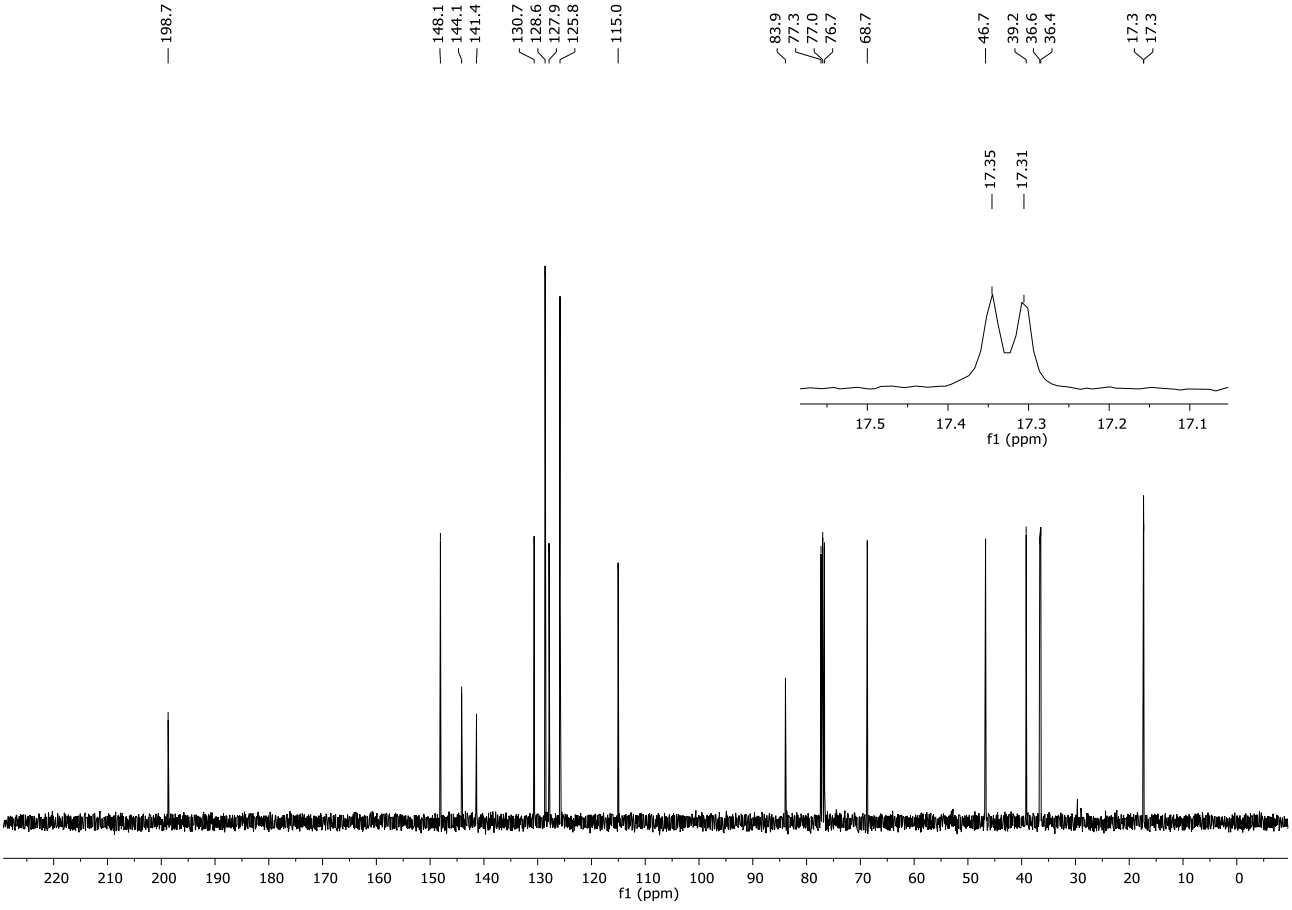

0.06
1.00
6.25 6.20 6.15 6.10 6.05 6.00 5.95 5.90
f1 (ppm)
5.24
1.01
0.06
1.00
1.04
1.05
1.06
1.05
1.06
0.13
0.06
1.13
1.10
1.17
2.27
3.15
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

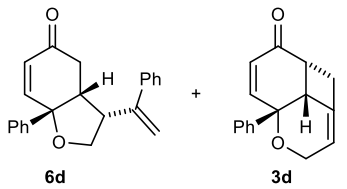

198.7
149.2
144.1
141.4
129.8
128.6
127.9
125.9
115.0
81.6
77.3
77.0
76.7
69.1
45.9
41.1
35.6
33.1
8.6
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
H
Ph
i-Pr
O

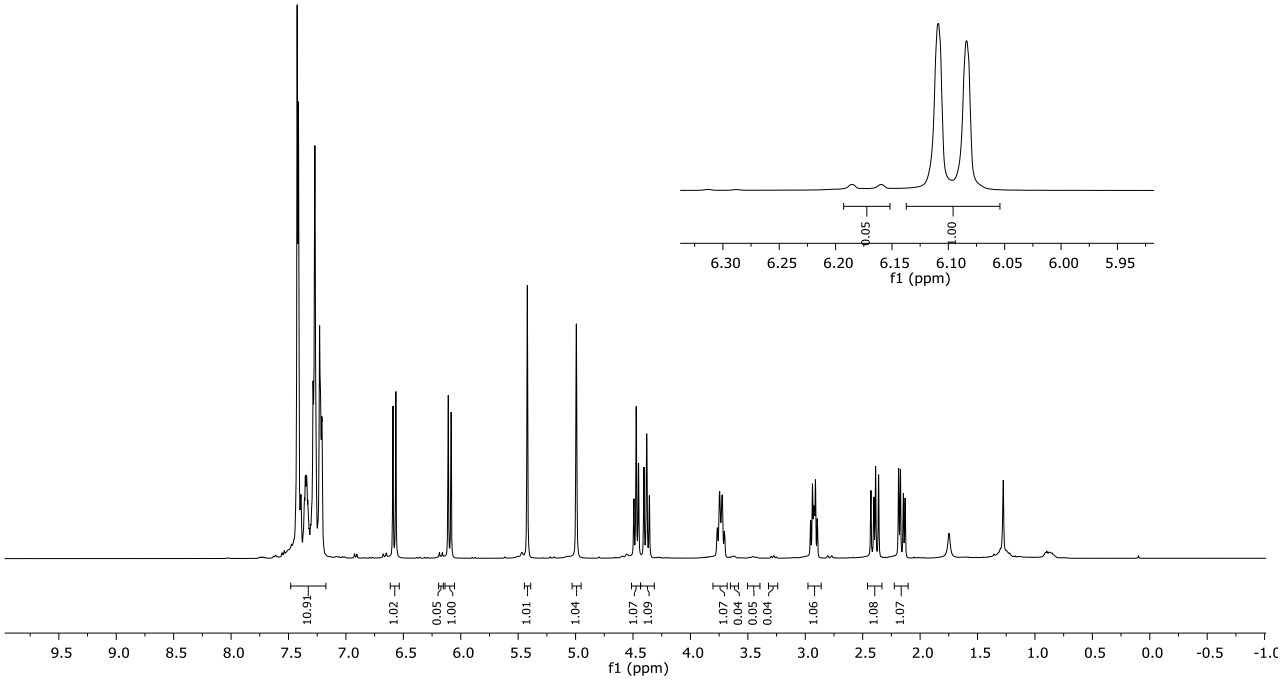
6c


5.12
1.00
0.96
0.99
0.98
1.02
1.00
1.04
1.03
1.05
2.06
2.92
2.78
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


198.7
148.1
144.1
141.4
130.7
128.6
127.9
125.8
115.0
83.9
77.3
77.0
76.7
68.7
46.7
39.2
36.6
36.4
17.3
17.3
17.35
17.31
17.5 17.4 17.3 17.2 17.1
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
H
Ph
Ph
O
+
O
Ph
H
O

6d 20:1 **3d**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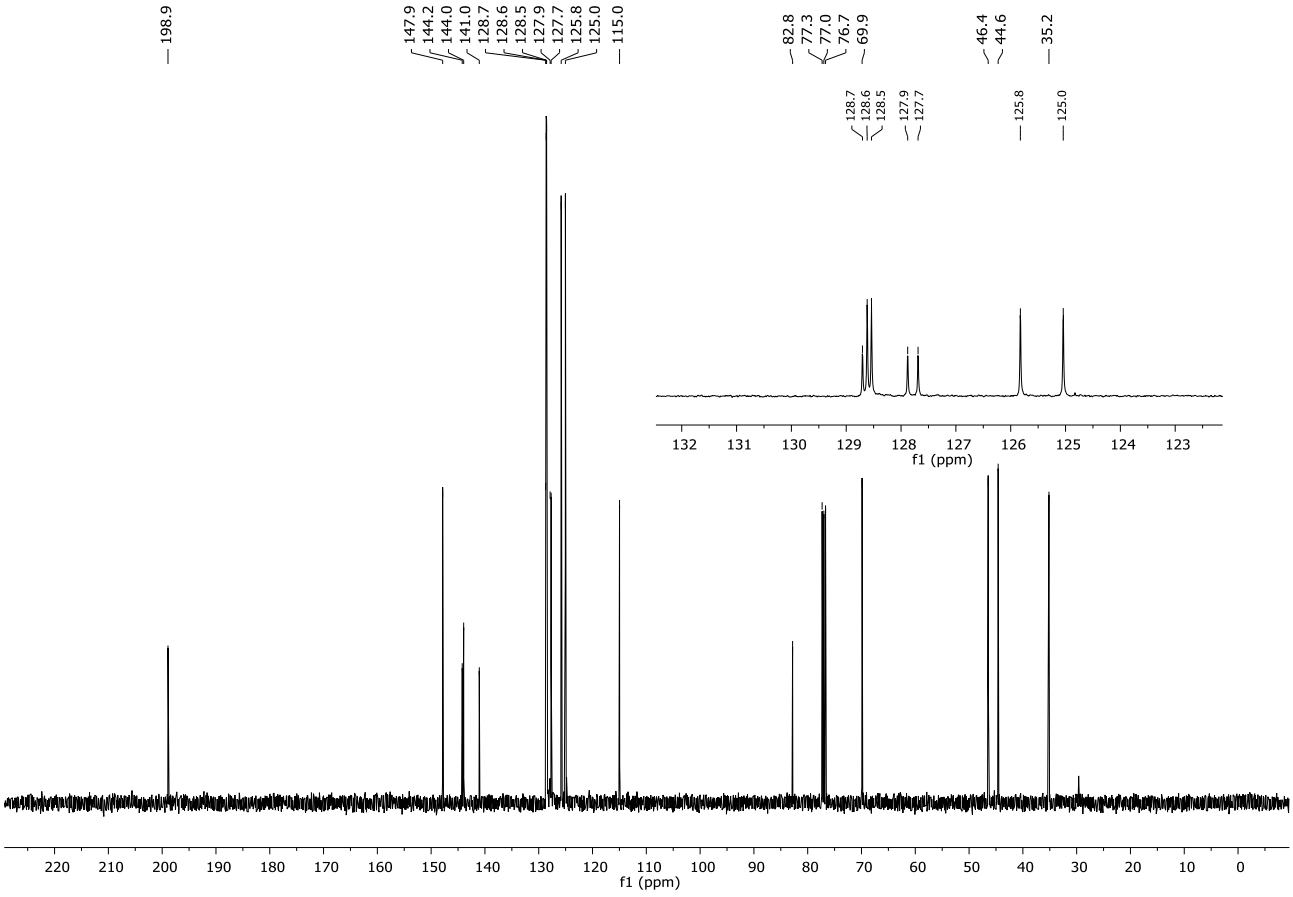
1.00
1.01
1.04
1.07
1.09
1.07
0.04
0.05
0.04
1.06
1.08
1.07
f1 (ppm)
0.05
1.00
f1 (ppm)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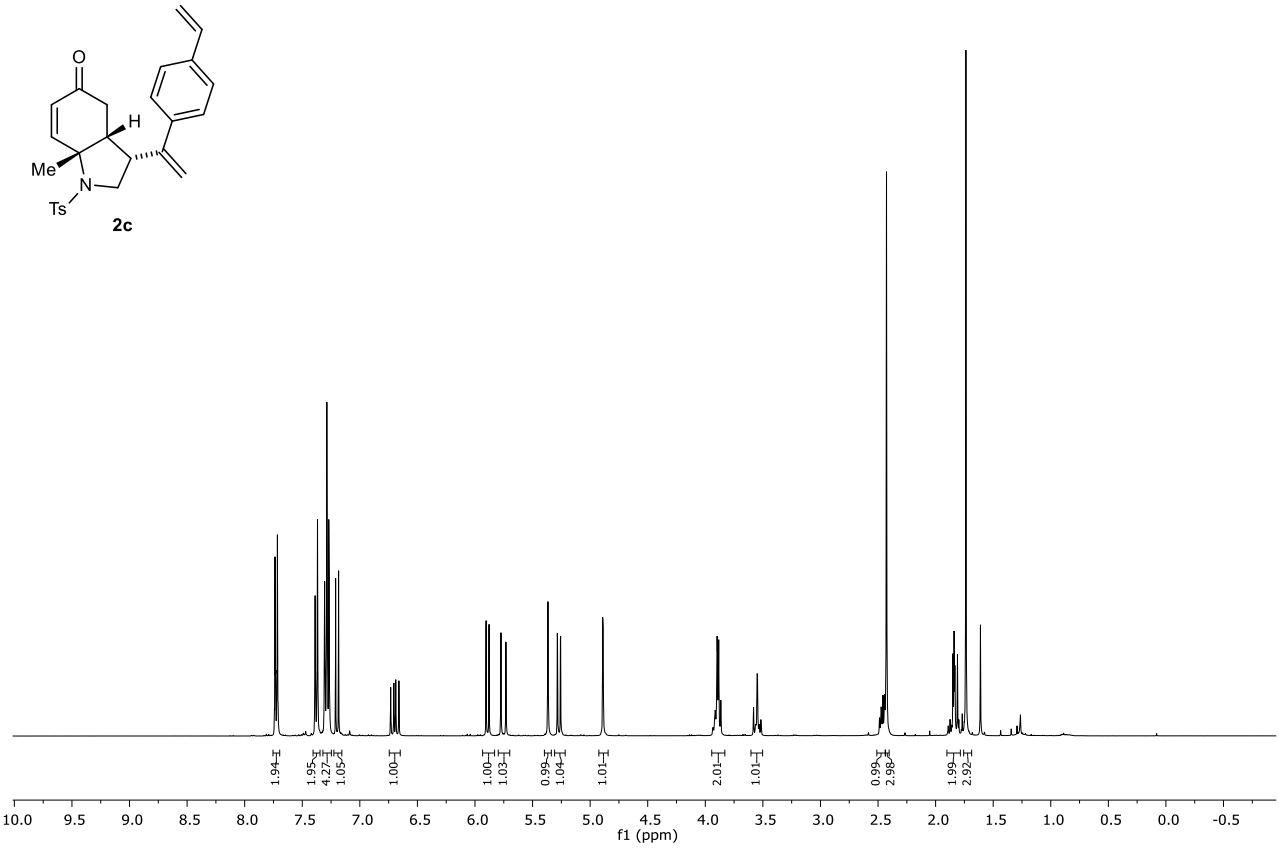
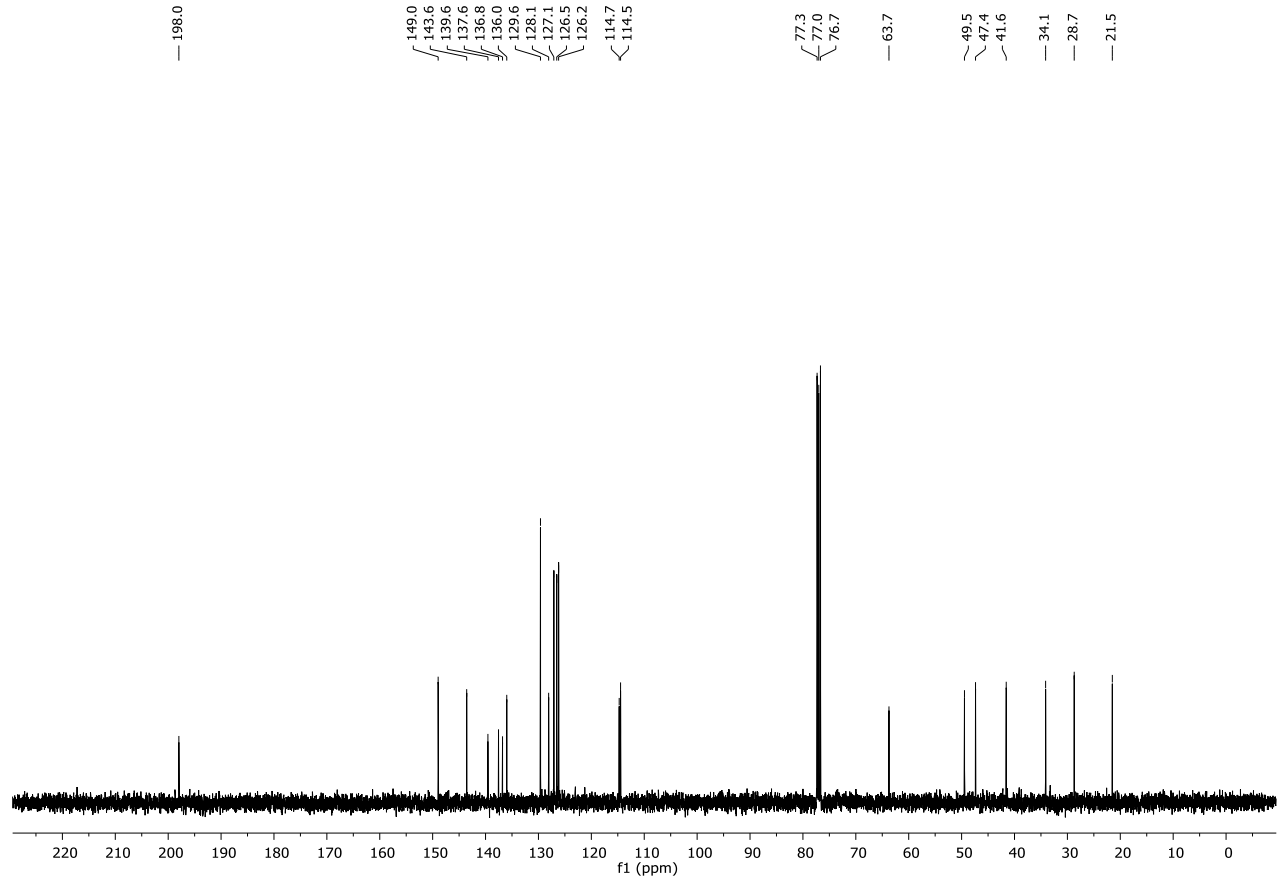
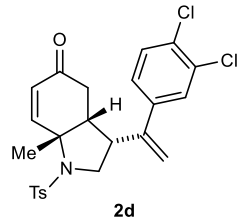
144.0
141.0
128.7
128.6
128.5
127.9
127.7
125.8
125.0
115.0
82.8
77.3
77.0
76.7
69.9
46.4
44.6
35.2
128.7
128.6
128.5
127.9
127.7
125.8
125.0
f1 (ppm)
f1 (ppm)

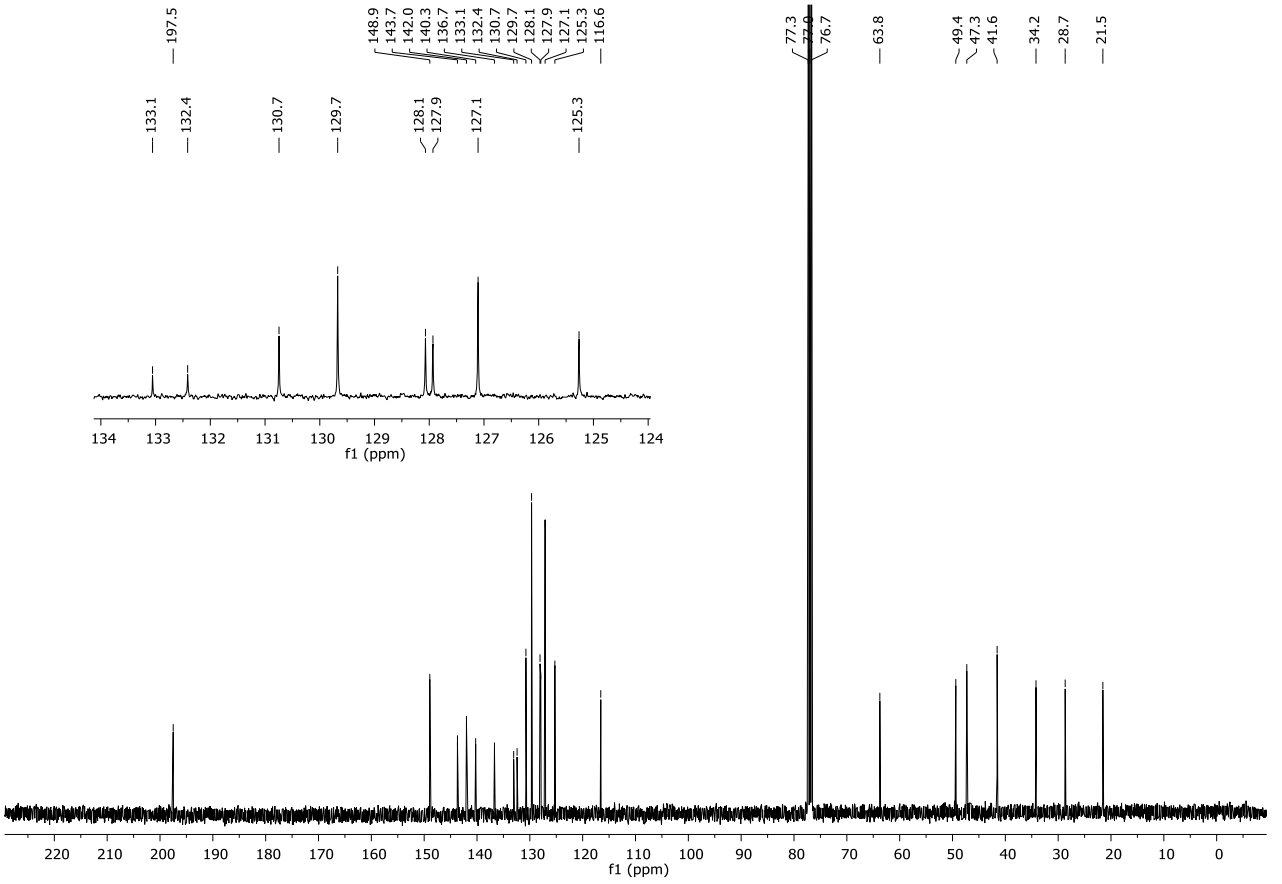

O
H
Me
N
Ts
2c
1.94
1.95
4.27
1.05
1.00
1.00
1.03
0.99
1.04
1.01
2.01
1.01
0.99
2.98
1.99
2.92
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

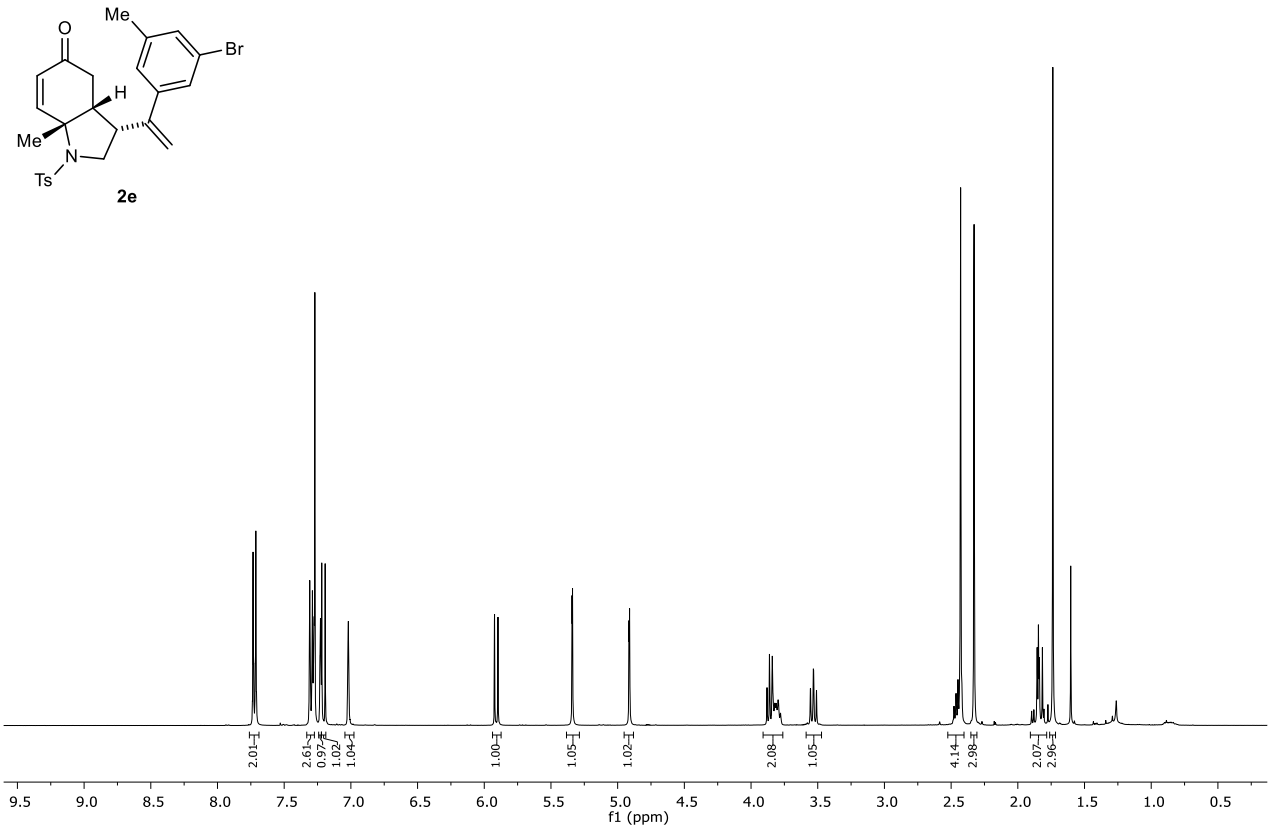

198.0
149.0
143.6
139.6
137.6
136.8
136.0
129.6
128.1
127.1
126.5
126.2
114.7
114.5
77.3
77.0
76.7
63.7
49.5
47.4
41.6
34.1
28.7
21.5
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

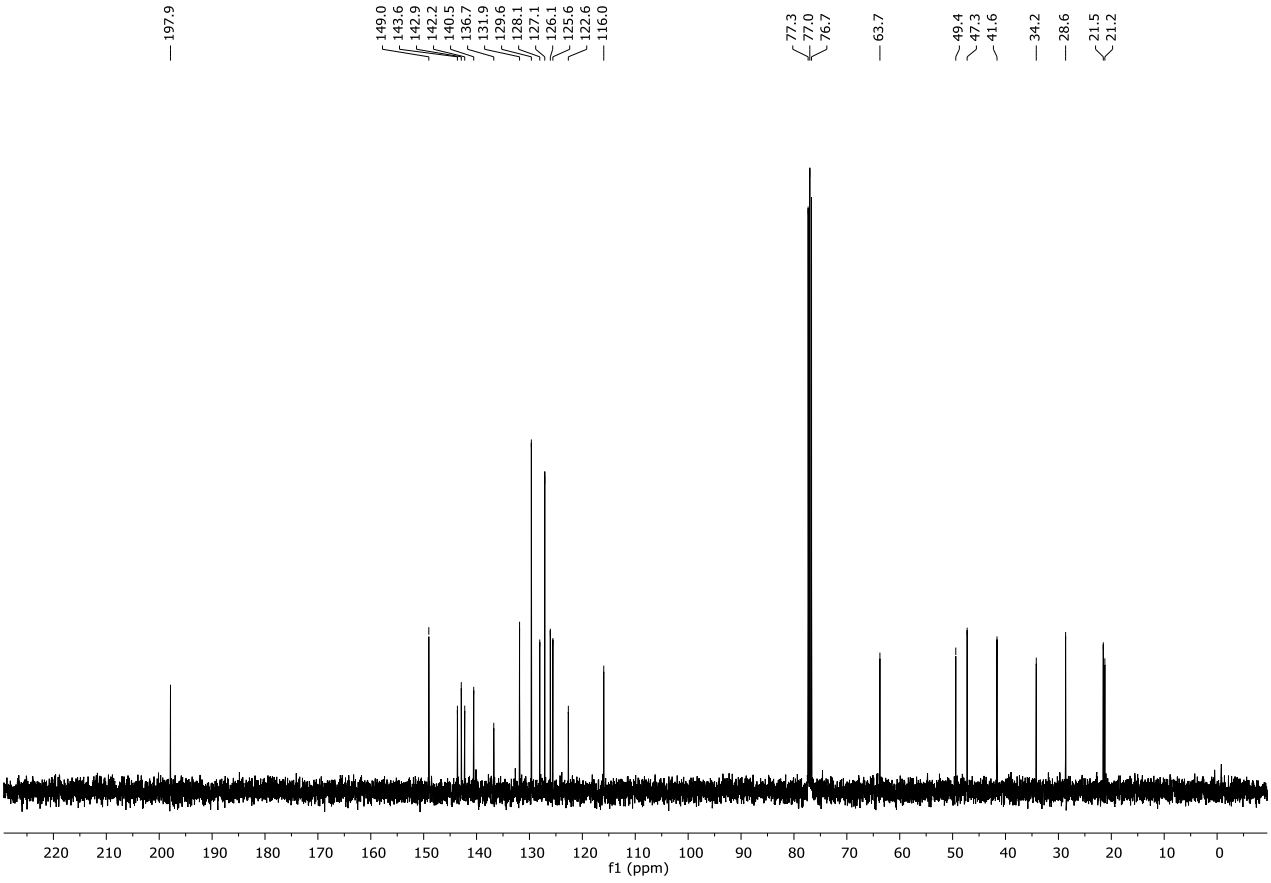

O
Cl
Cl
H
Me
N
Ts

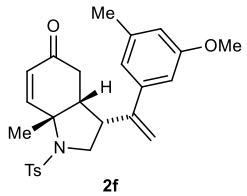
2d

2.00
1.00
1.00
2.00
1.03
1.01
1.00
1.01
1.00
1.03
1.05
1.01
4.01
2.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


197.5
148.9
143.7
142.0
140.3
136.7
133.1
132.4
130.7
129.7
128.1
127.9
127.1
125.3
116.6
77.3
77.0
76.7
63.8
49.4
47.3
41.6
34.2
28.7
21.5
133.1
132.4
130.7
129.7
128.1
127.9
127.1
125.3
134 133 132 131 130 129 128 127 126 125 124
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

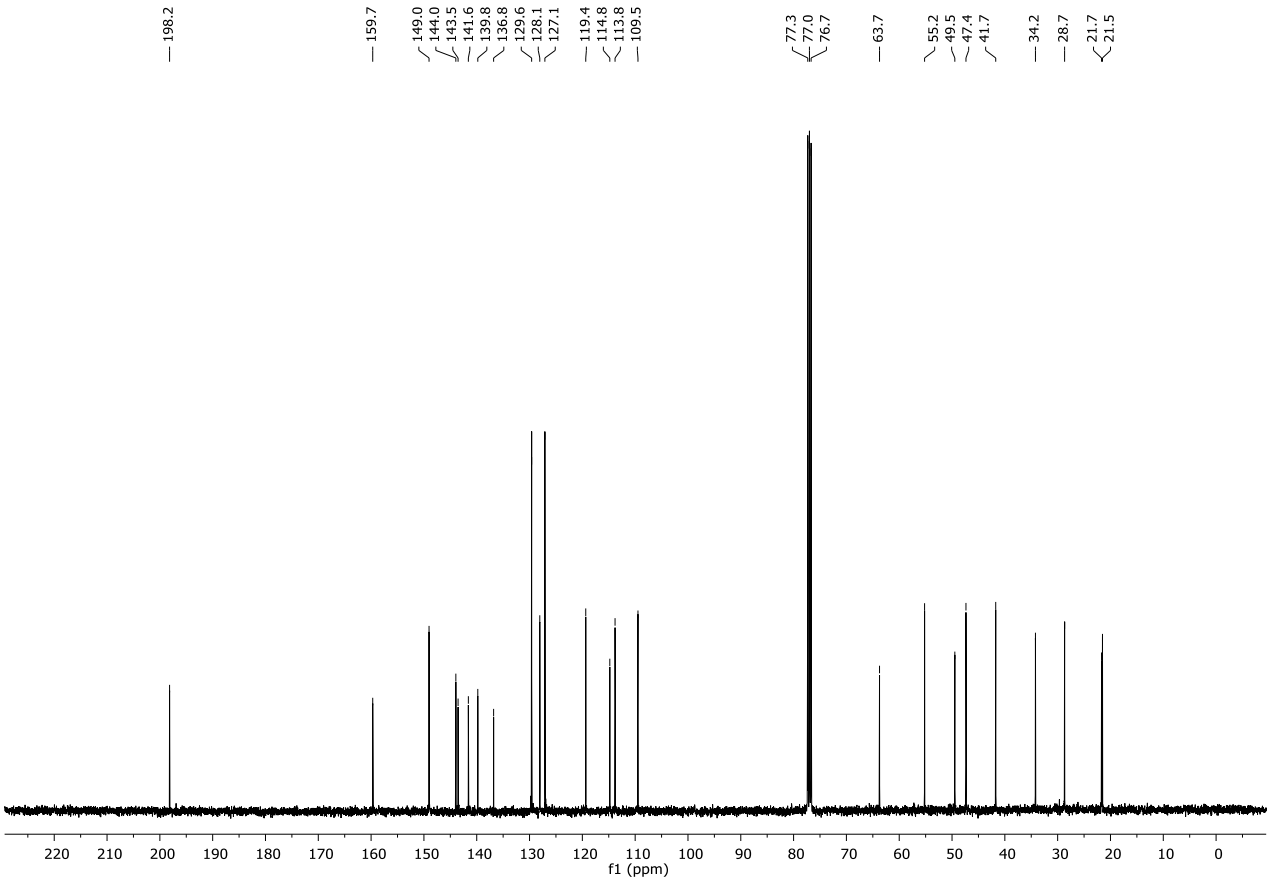

Me
Br
O
H
Me
N
Ts
2e
2.01
2.61
0.97
1.02
1.04
1.00
1.05
1.02
2.08
1.05
4.14
2.98
2.07
2.96
f1 (ppm)

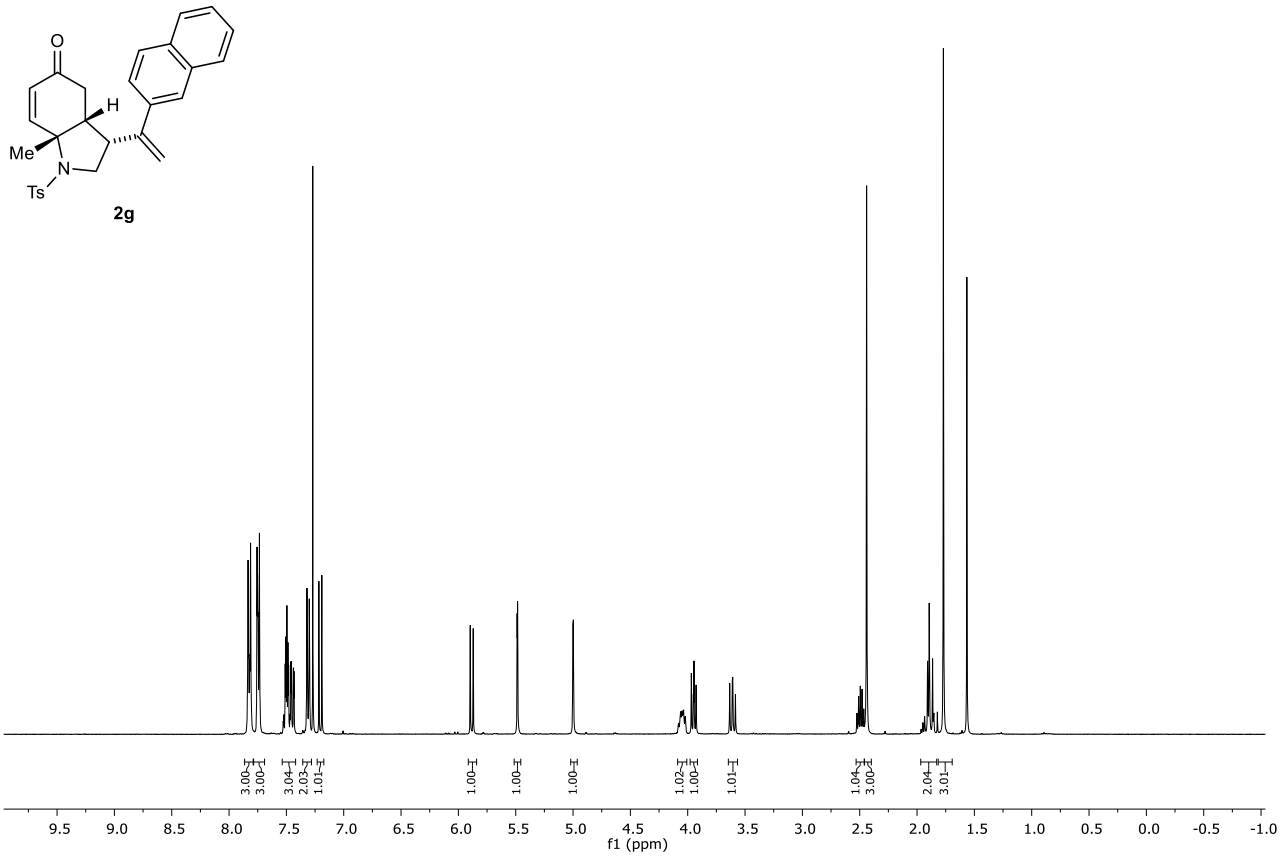

197.9
149.0
143.6
142.9
142.2
140.5
136.7
131.9
129.6
128.1
127.1
126.1
125.6
122.6
116.0
77.3
77.0
76.7
63.7
49.4
47.3
41.6
34.2
28.6
21.5
21.2
f1 (ppm)

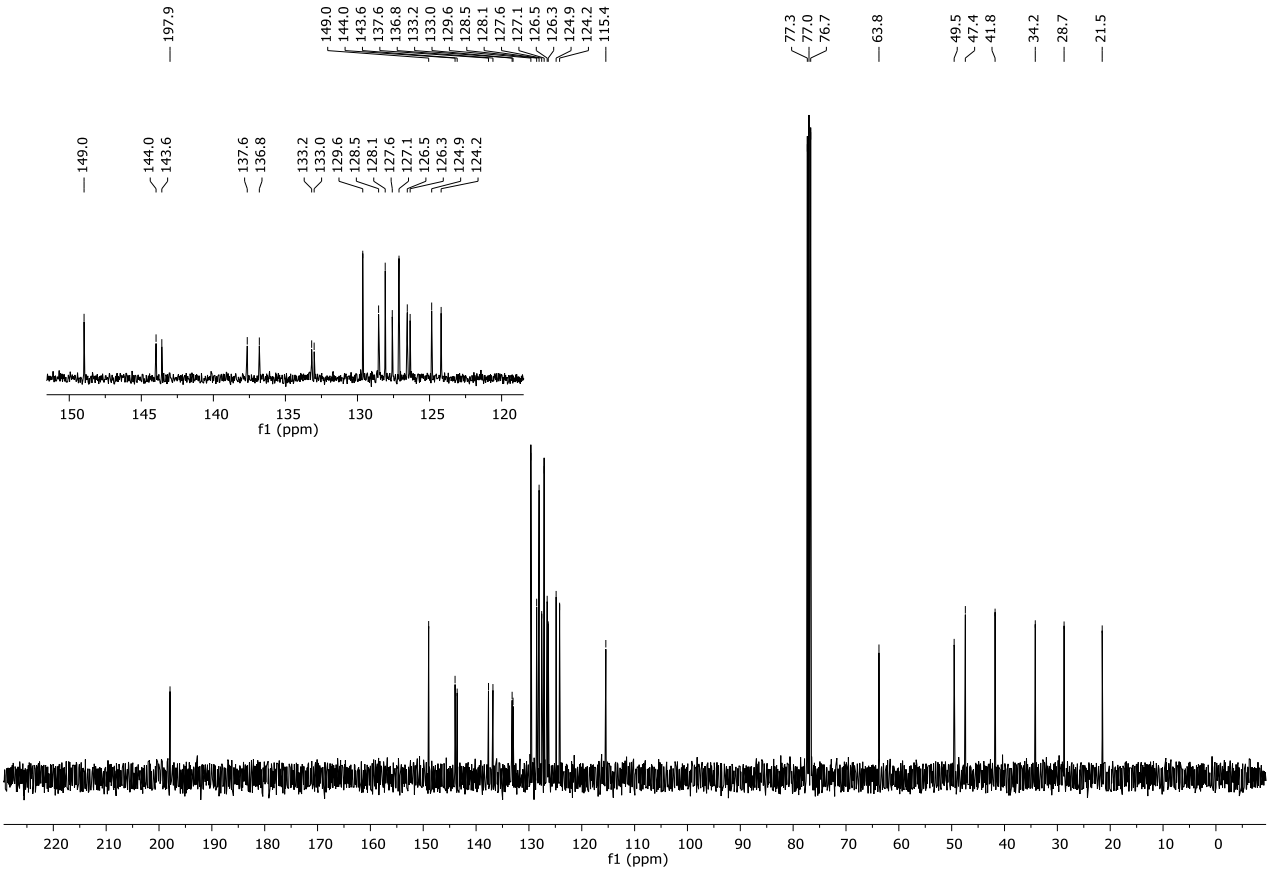

Me
OMe
O
H
Me
N
Ts

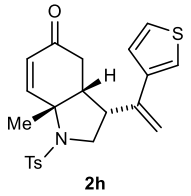
2f

2.02
2.04
1.02
1.01
2.00
1.02
1.00
1.00
2.05
3.05
1.01
1.13
3.03
3.01
1.09
1.11
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


198.2
159.7
149.0
144.0
143.5
141.6
139.8
136.8
129.6
128.1
127.1
119.4
114.8
113.8
109.5
77.3
77.0
76.7
63.7
55.2
49.5
47.4
41.7
34.2
28.7
21.7
21.5
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

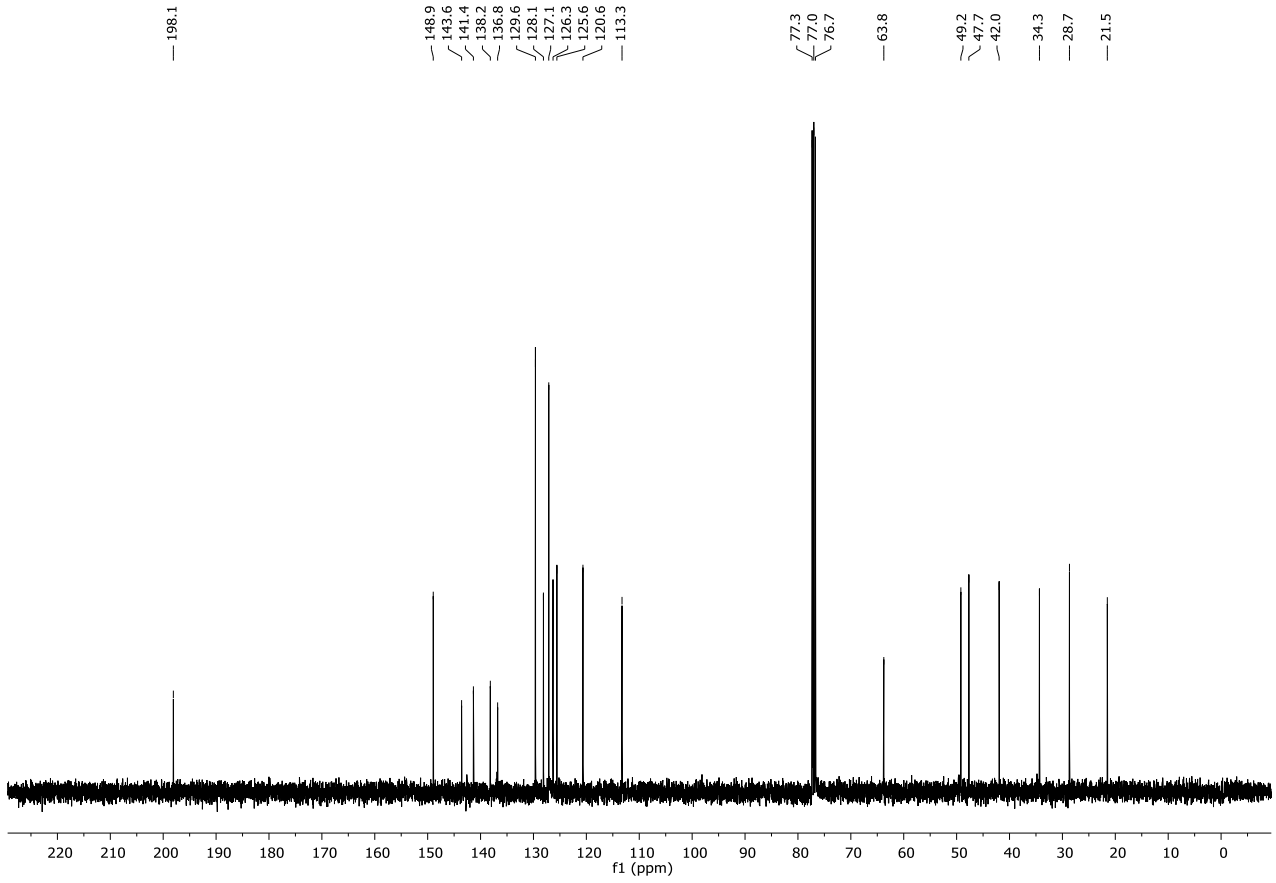

O
H
Me
N
Ts
2g
3.00
3.00
3.04
2.03
1.01
1.00
1.00
1.00
1.02
1.00
1.01
1.04
3.00
2.04
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

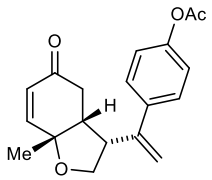

197.9
149.0
144.0
143.6
137.6
136.8
133.2
133.0
129.6
128.5
128.1
127.6
127.1
126.5
126.3
124.9
124.2
115.4
77.3
77.0
76.7
63.8
49.5
47.4
41.8
34.2
28.7
21.5
150 145 140 135 130 125 120
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
S
H
Me
N
Ts

2h

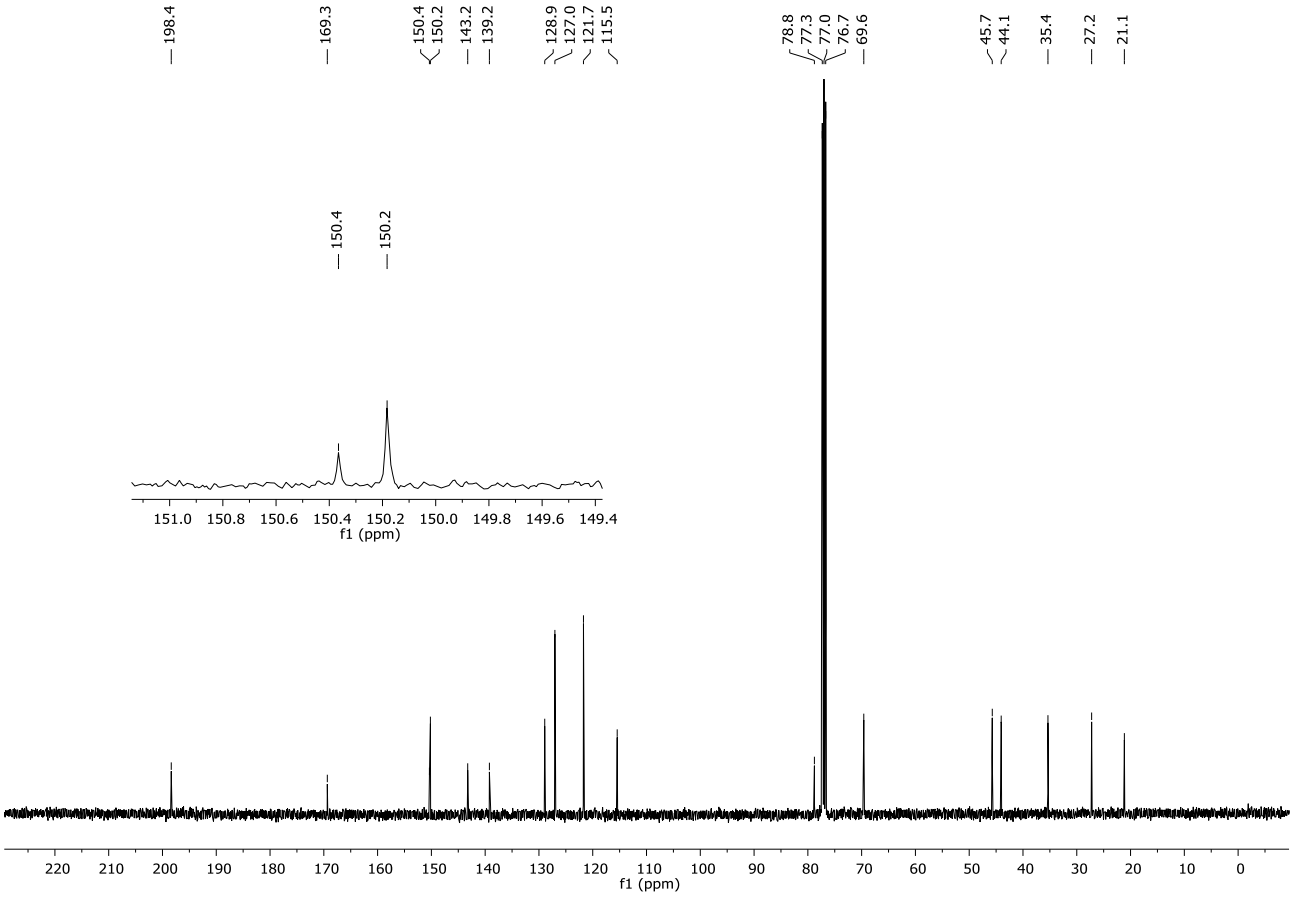
1.95
2.84
1.00
0.99
0.96
0.98
1.00
1.02
2.03
1.04
1.08
3.10
1.01
1.05
2.87
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

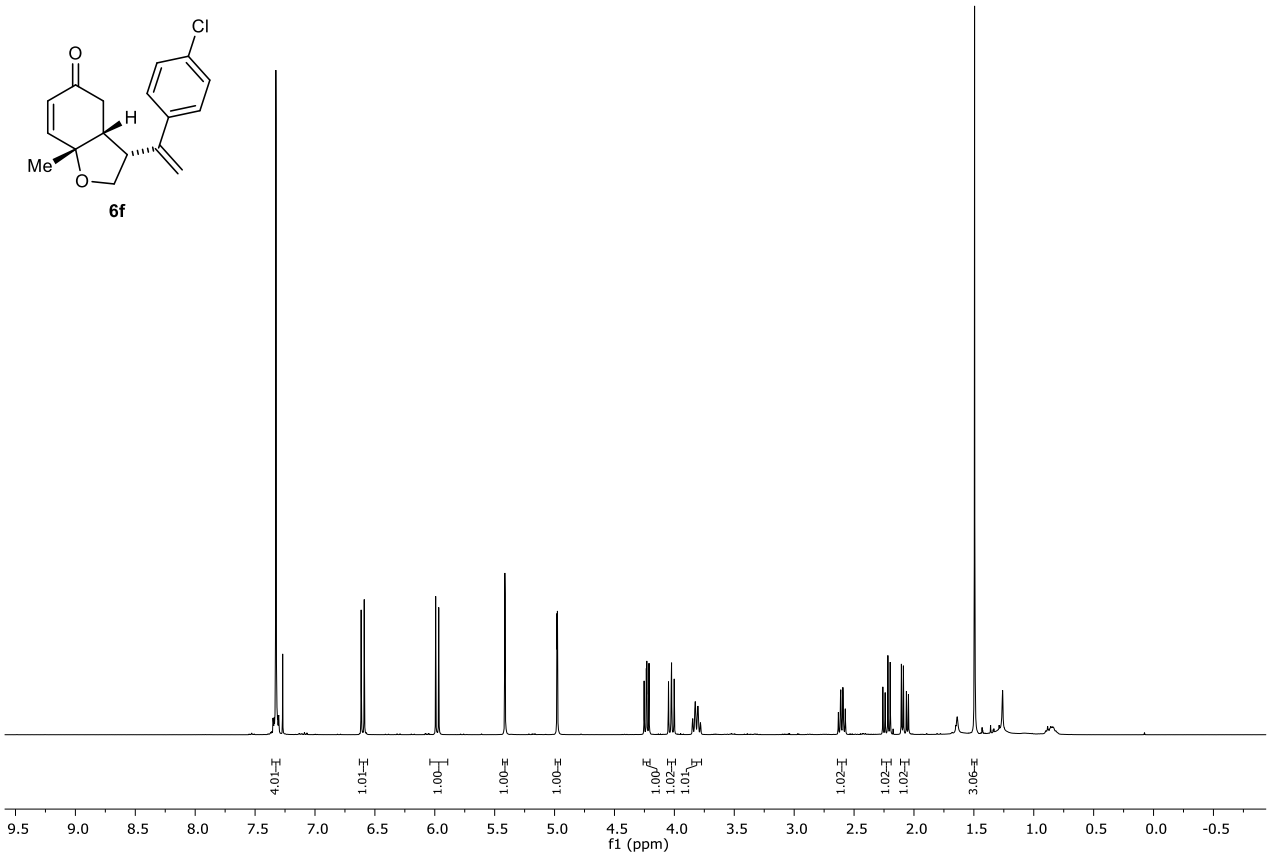

198.1
148.9
143.6
141.4
138.2
136.8
129.6
128.1
127.1
126.3
125.6
120.6
113.3
77.3
77.0
76.7
63.8
49.2
47.7
42.0
34.3
28.7
21.5
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

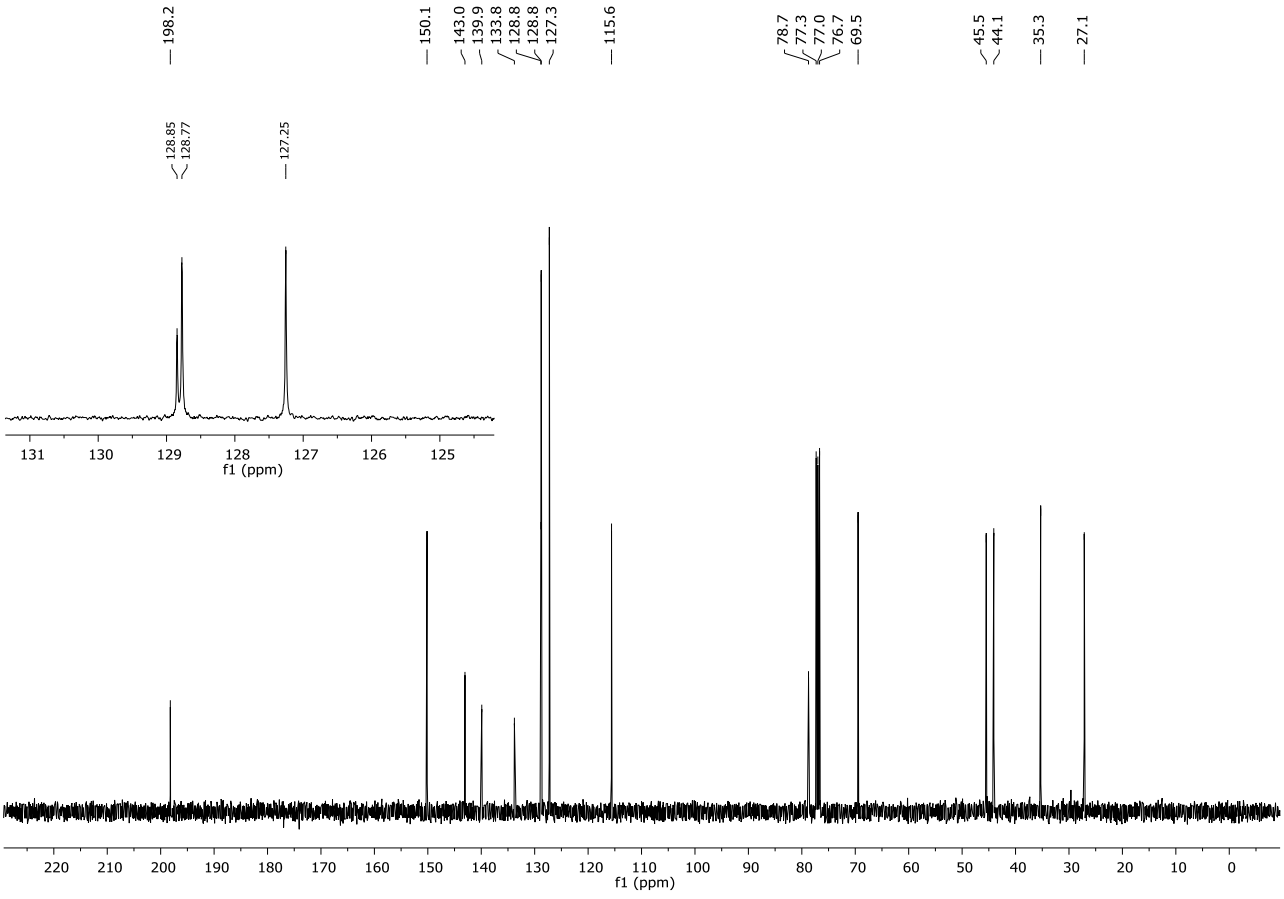

OAc
O
H
Me
O

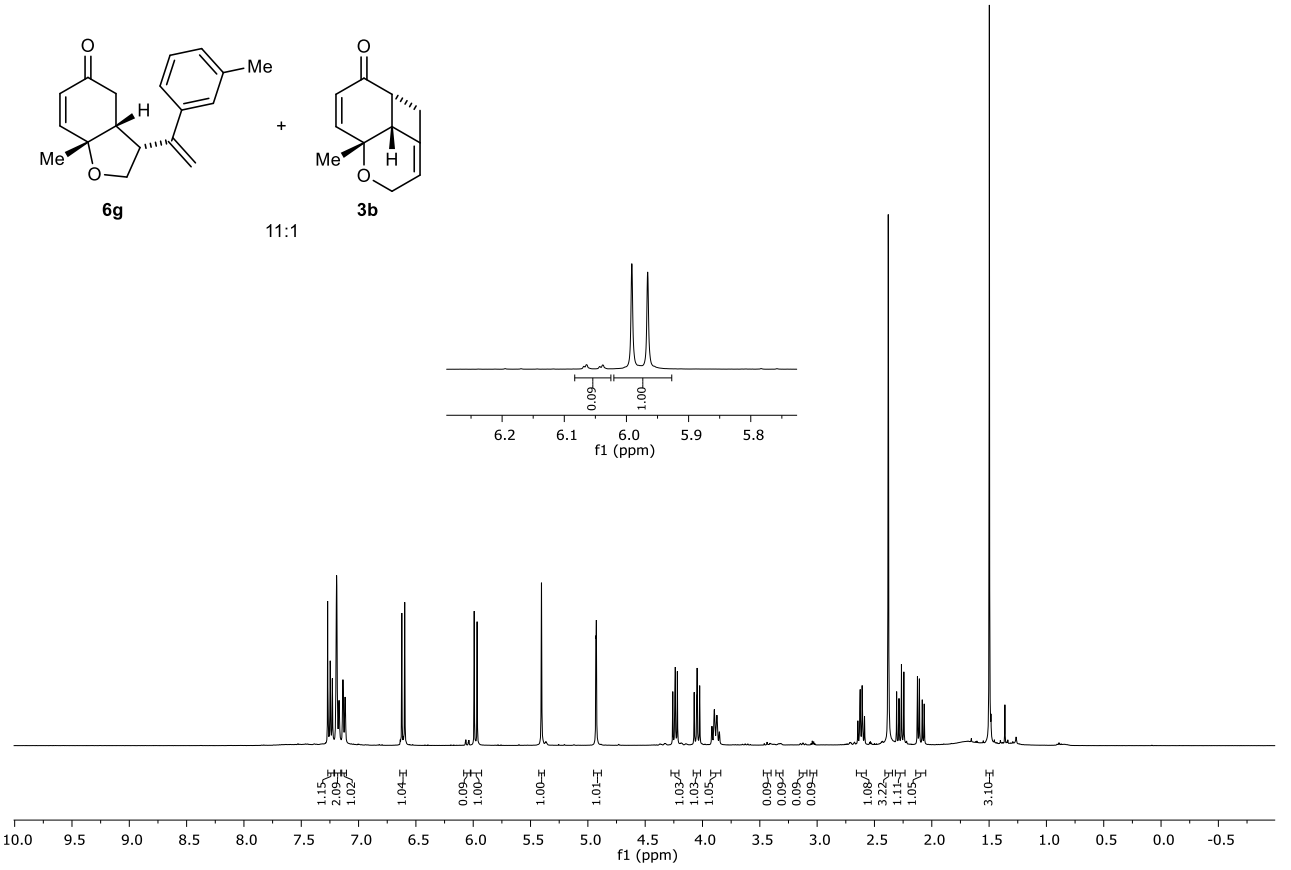
6e

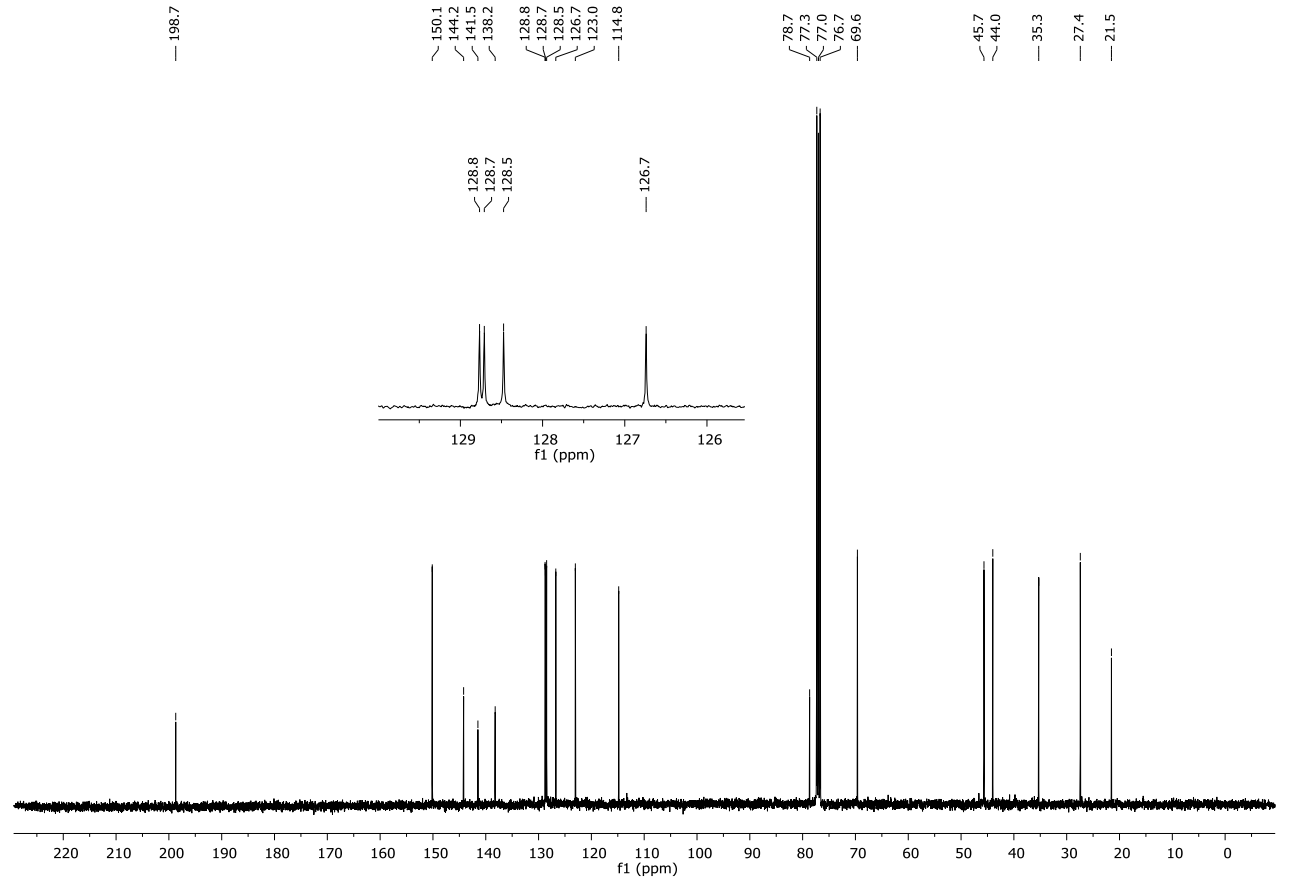
2.01
2.00
1.01
1.00
1.01
1.01
1.04
1.05
1.06
1.05
3.00
1.08
1.04
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

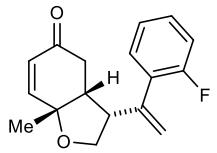

198.4
169.3
150.4
150.2
143.2
139.2
128.9
127.0
121.7
115.5
78.8
77.3
77.0
76.7
69.6
45.7
44.1
35.4
27.2
21.1
150.4
150.2
151.0 150.8 150.6 150.4 150.2 150.0 149.8 149.6 149.4
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Cl
O
H
Me
O
6f
4.01
1.01
1.00
1.00
1.00
1.00
1.02
1.01
1.02
1.02
1.02
3.06
f1 (ppm)


198.2
150.1
143.0
139.9
133.8
128.8
128.8
127.3
115.6
78.7
77.3
77.0
76.7
69.5
45.5
44.1
35.3
27.1
128.85
128.77
127.25
f1 (ppm)
f1 (ppm)

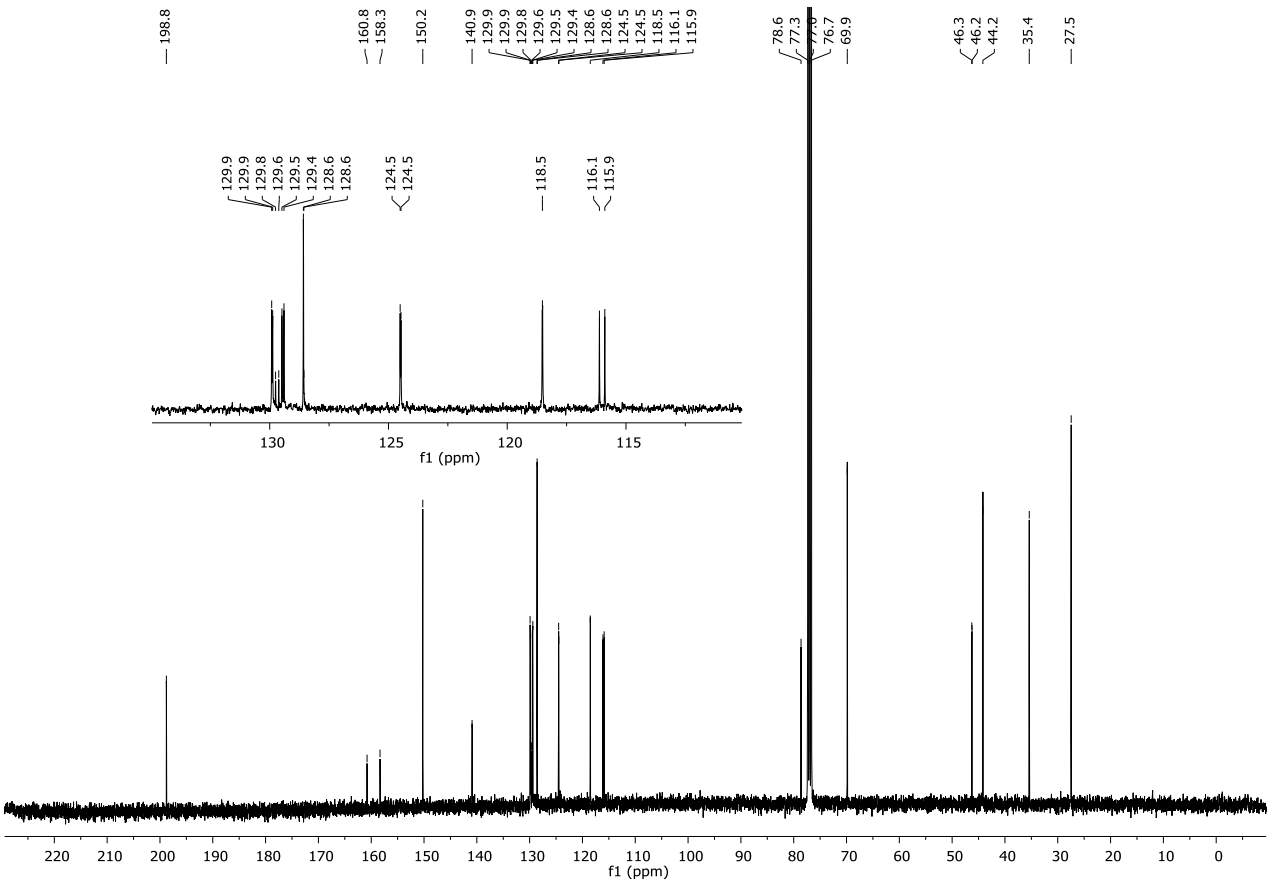

O
Me
H
Me
O
6g
+
O
Me
H
O
3b
11:1
0.09
1.00
6.2
6.1
6.0
5.9
5.8
f1 (ppm)
1.15
2.09
1.02
1.04
0.09
1.00
1.00
1.01
1.03
1.03
1.05
0.09
0.09
0.09
0.09
1.08
3.22
1.11
1.05
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

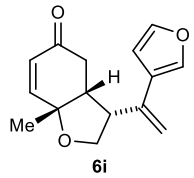

198.7
150.1
144.2
141.5
138.2
128.8
128.7
128.5
126.7
123.0
114.8
78.7
77.3
77.0
76.7
69.6
45.7
44.0
35.3
27.4
21.5
128.8
128.7
128.5
126.7
129
128
127
126
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
H
F
Me
O

6h

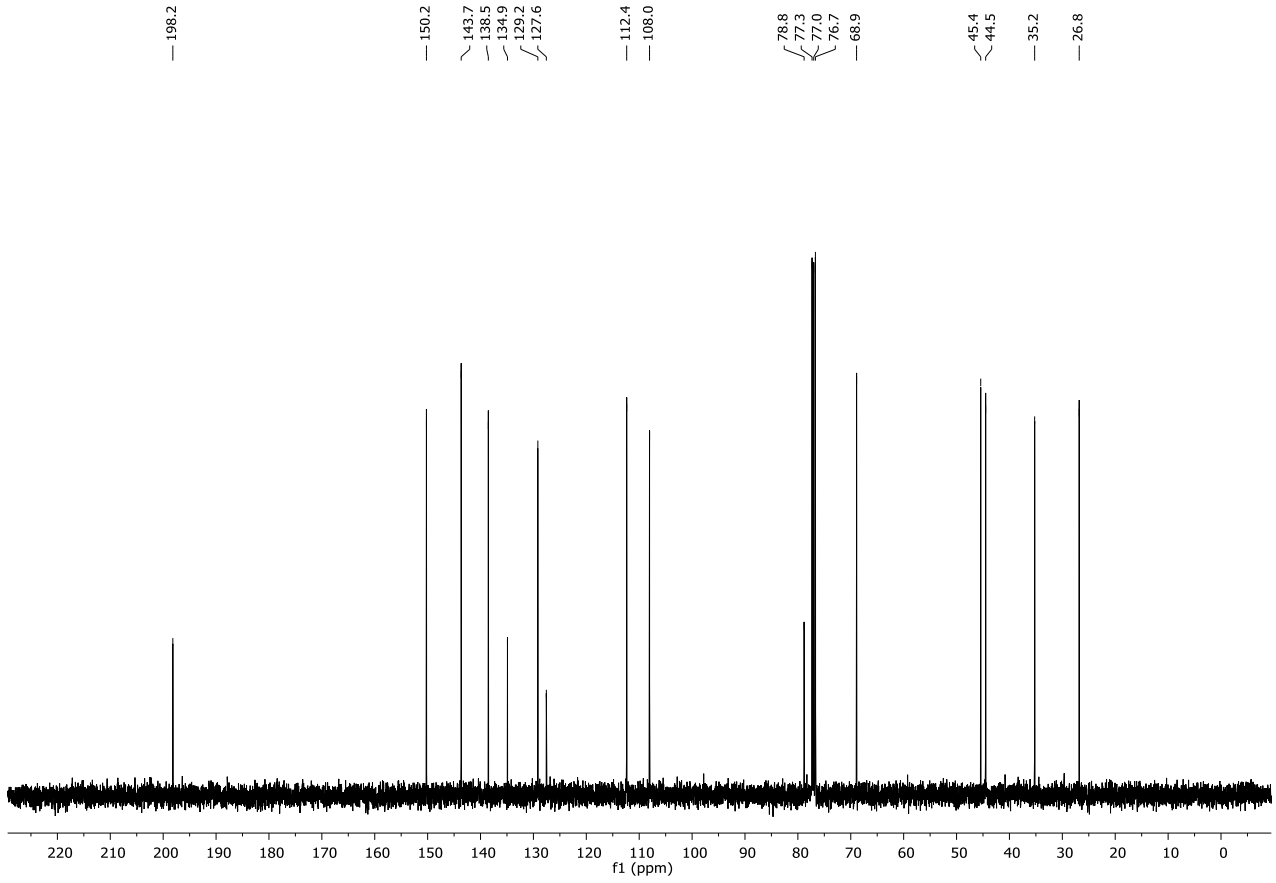
2.77
1.03
1.07
1.01
1.00
1.00
1.00
1.01
1.04
1.06
1.09
1.06
1.06
3.11
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

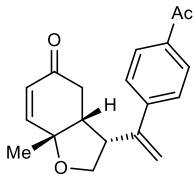

198.8
160.8
158.3
150.2
140.9
129.9
129.9
129.8
129.6
129.5
129.4
128.6
128.6
124.5
124.5
118.5
116.1
115.9
78.6
77.3
76.7
69.9
46.3
46.2
44.2
35.4
27.5
130 125 120 115
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
O
H
Me
O

6i

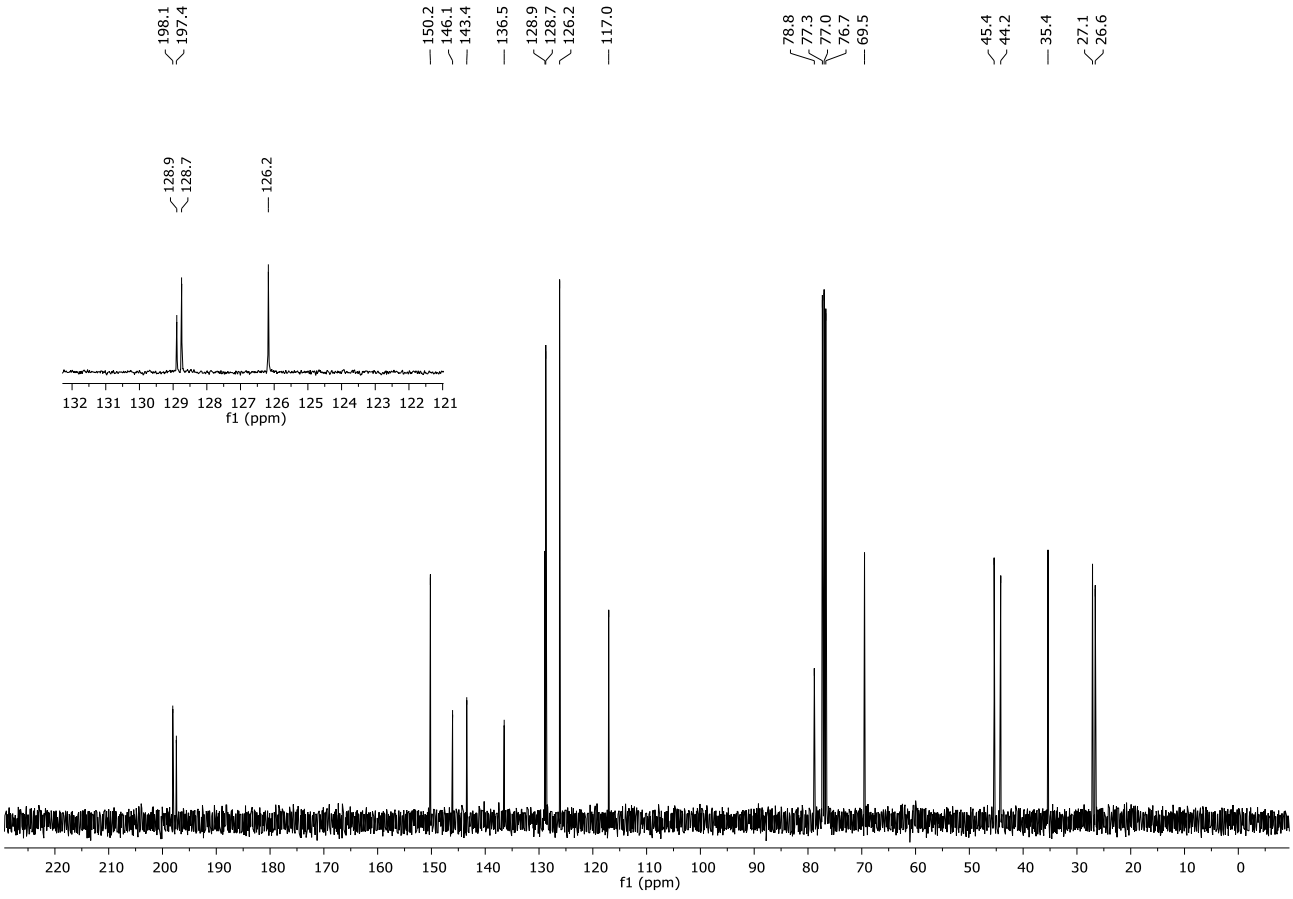
1.00
0.96
1.00
0.96
1.01
1.03
1.04
1.07
1.05
1.06
1.09
1.08
1.07
3.13
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

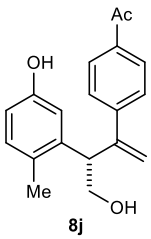

198.2
150.2
143.7
138.5
134.9
129.2
127.6
112.4
108.0
78.8
77.3
77.0
76.7
68.9
45.4
44.5
35.2
26.8
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
O
H
Me
O

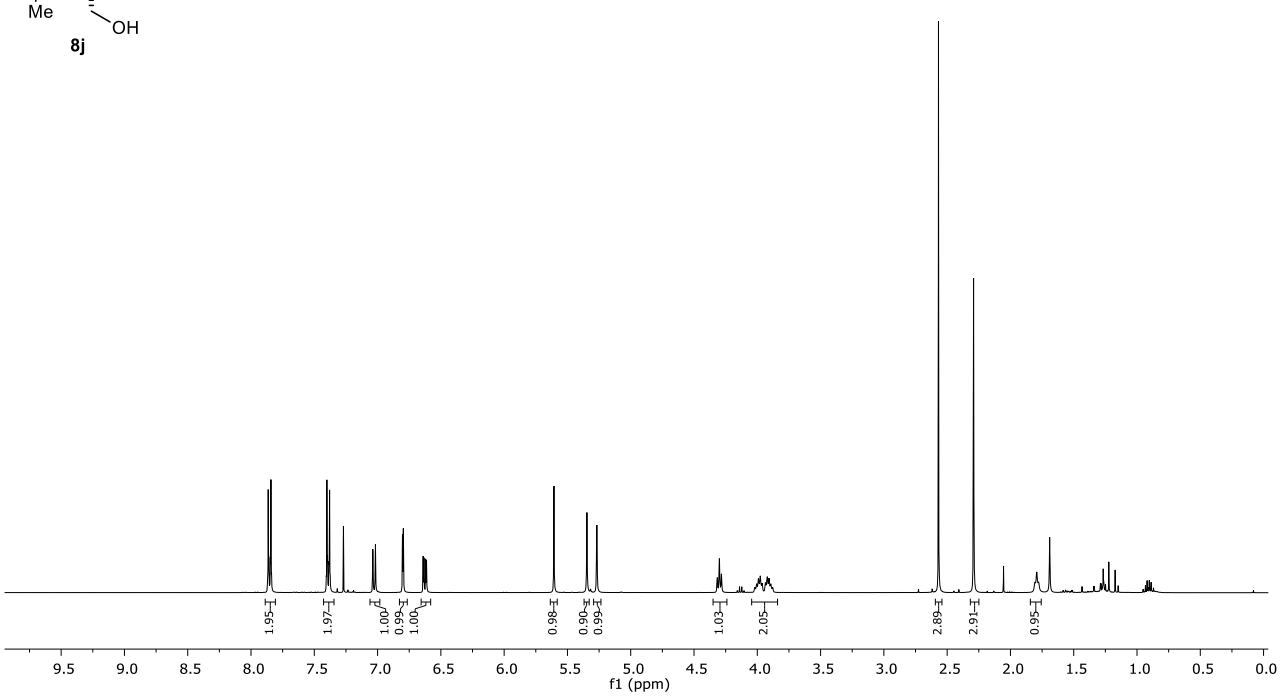
6j

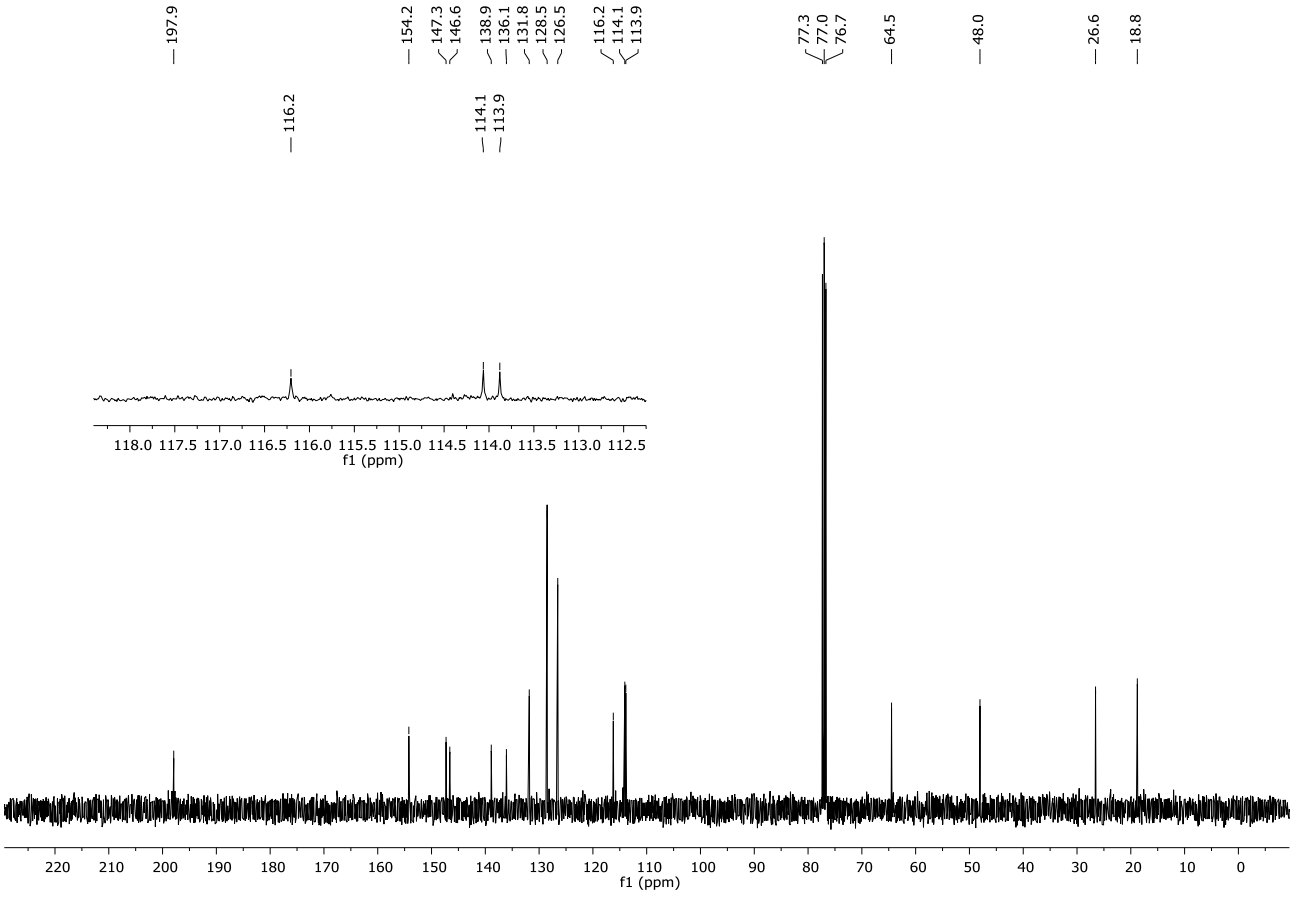
2.00
2.02
1.01
1.00
1.01
1.03
1.01
1.04
1.02
4.09
1.03
1.07
3.03
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

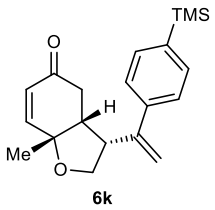

198.1
197.4
150.2
146.1
143.4
136.5
128.9
128.7
126.2
117.0
78.8
77.3
77.0
76.7
69.5
45.4
44.2
35.4
27.1
26.6
128.9
128.7
126.2
132 131 130 129 128 127 126 125 124 123 122 121
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Ac
OH
Me
OH

8j

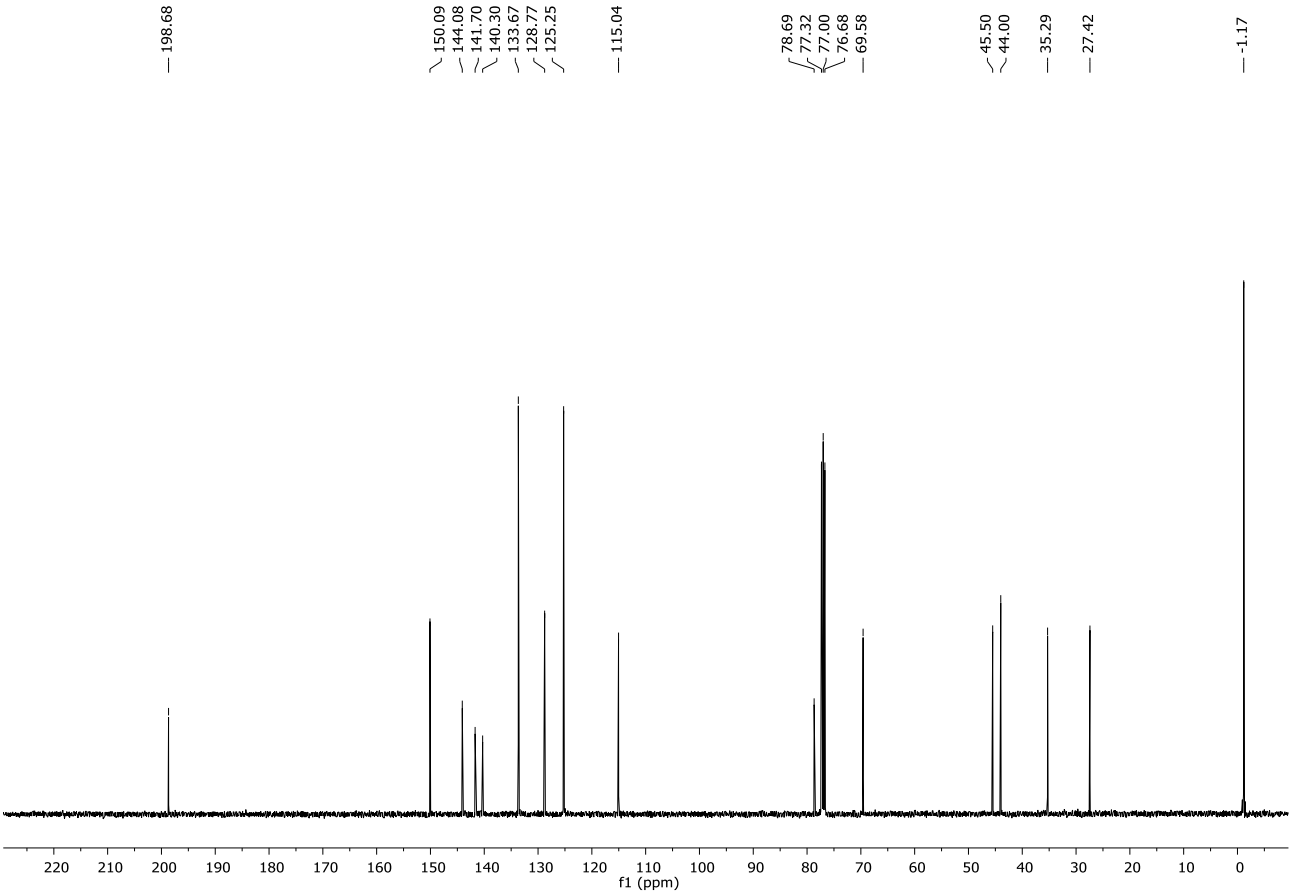

1.95
1.97
1.00
0.99
1.00
0.98
0.90
0.99
1.03
2.05
2.89
2.91
0.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

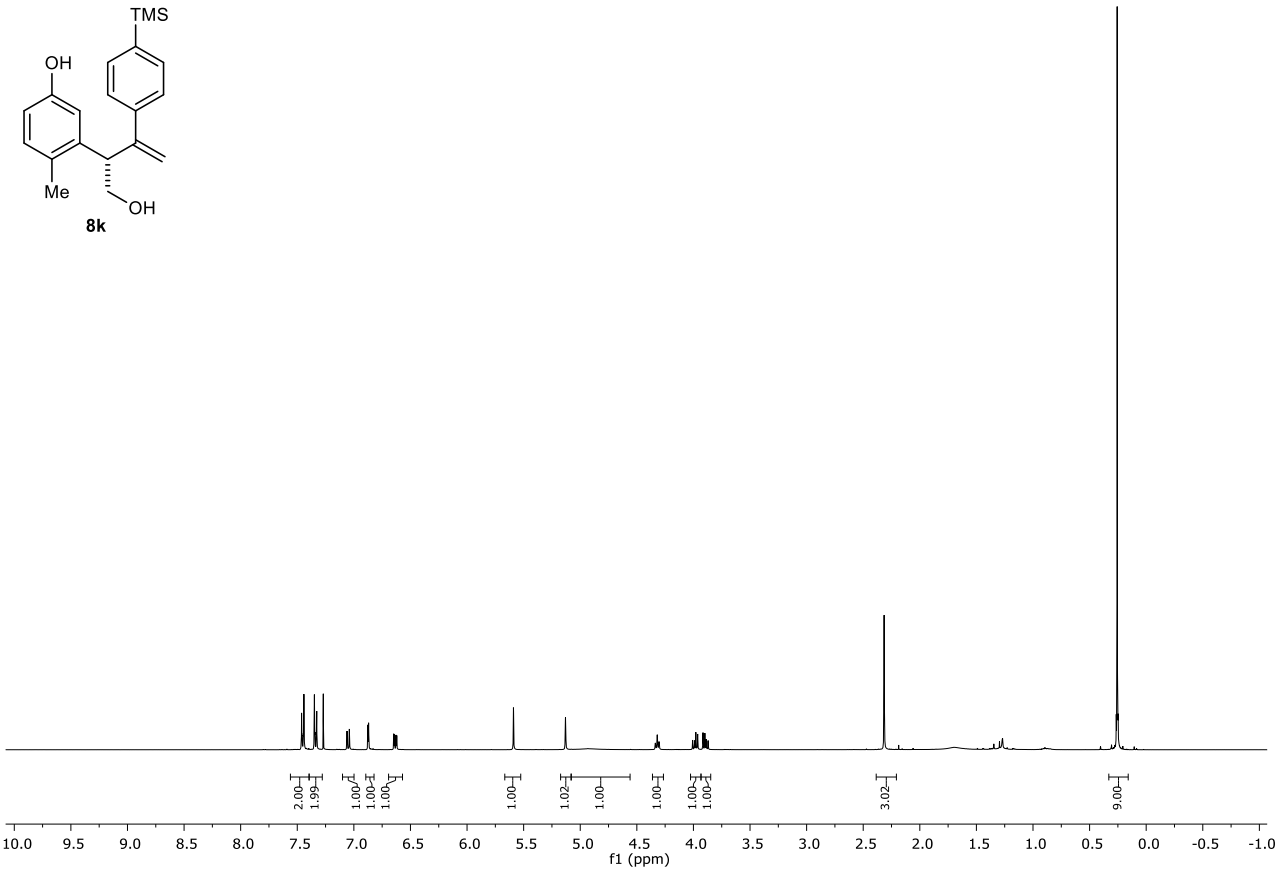

197.9
154.2
147.3
146.6
138.9
136.1
131.8
128.5
126.5
116.2
114.1
113.9
77.3
77.0
76.7
64.5
48.0
26.6
18.8
116.2
114.1
113.9
118.0 117.5 117.0 116.5 116.0 115.5 115.0 114.5 114.0 113.5 113.0 112.5
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

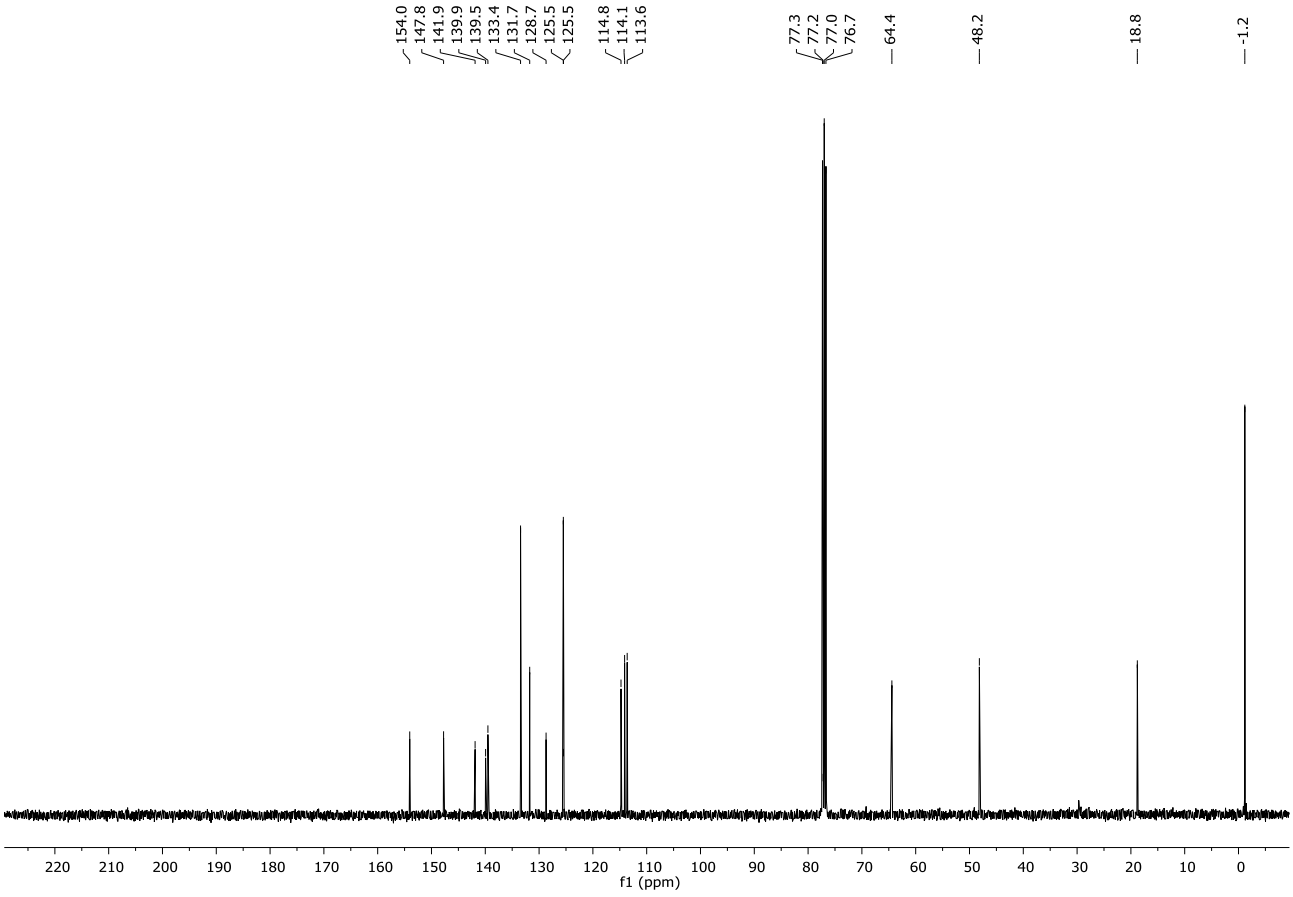

TMS
O
H
Me
O

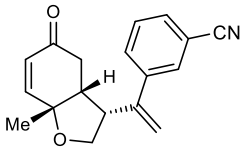
6k

1.97
2.00
1.00
1.01
1.00
1.00
1.00
1.00
1.00
1.00
1.01
1.13
3.02
9.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

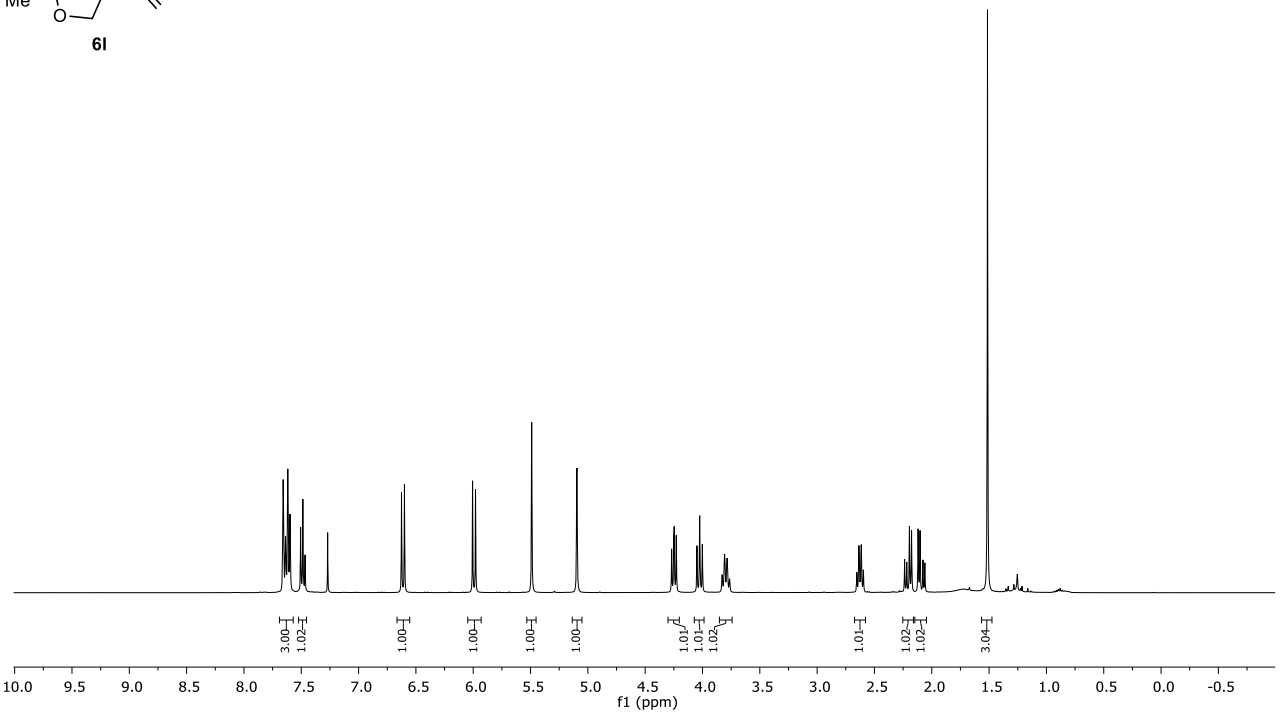

198.68
150.09
144.08
141.70
140.30
133.67
128.77
125.25
115.04
78.69
77.32
77.00
76.68
69.58
45.50
44.00
35.29
27.42
-1.17
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

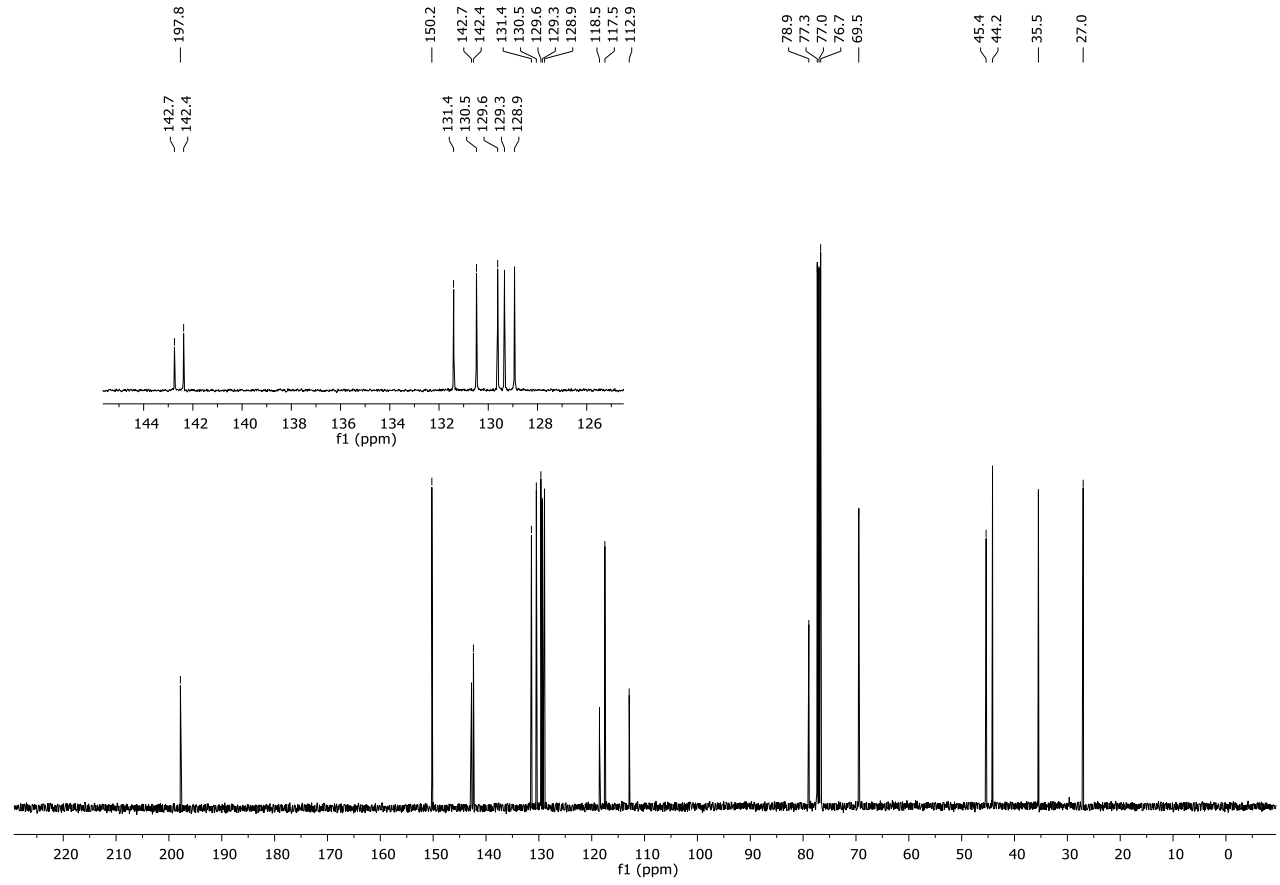

TMS
OH
Me
OH
8k
2.00
1.99
1.00
1.00
1.00
1.00
1.02
1.00
1.00
1.00
1.00
3.02
9.00
f1 (ppm)

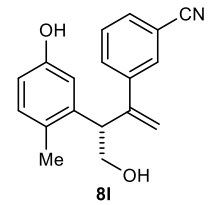

154.0
147.8
141.9
139.9
139.5
133.4
131.7
128.7
125.5
125.5
114.8
114.1
113.6
77.3
77.2
77.0
76.7
64.4
48.2
18.8
-1.2
f1 (ppm)


O
CN
H
Me
O

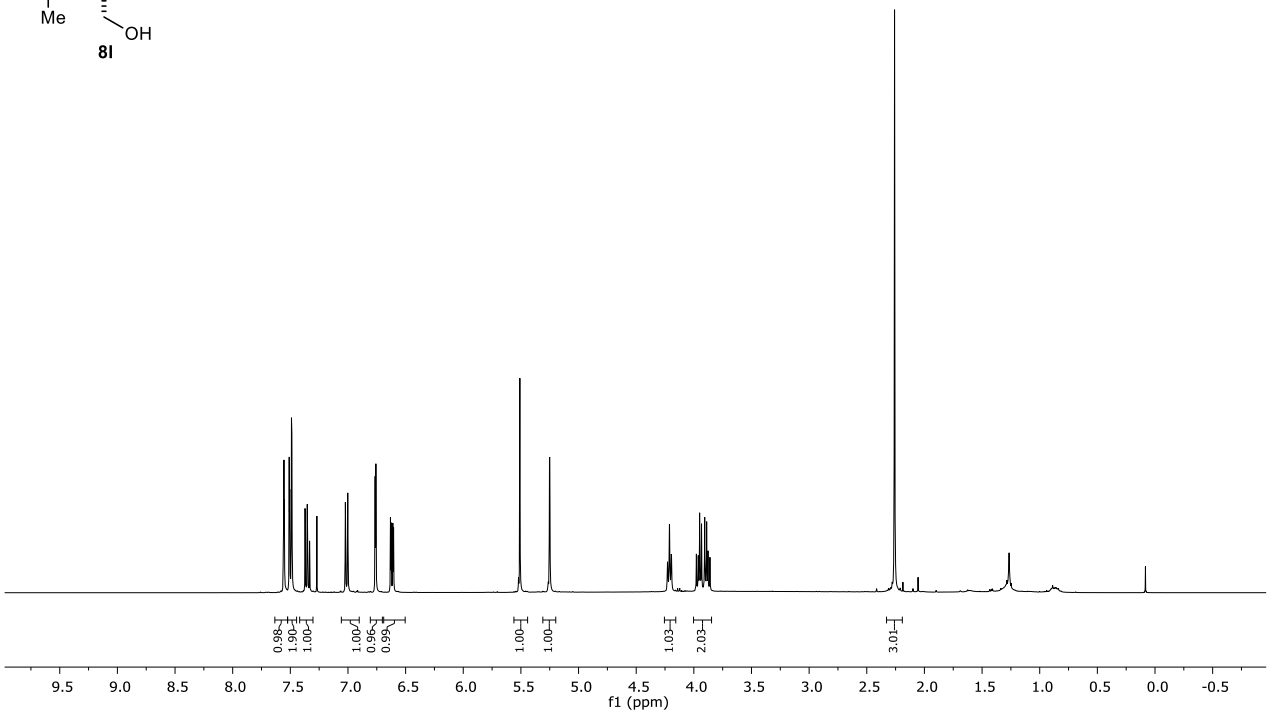
6l

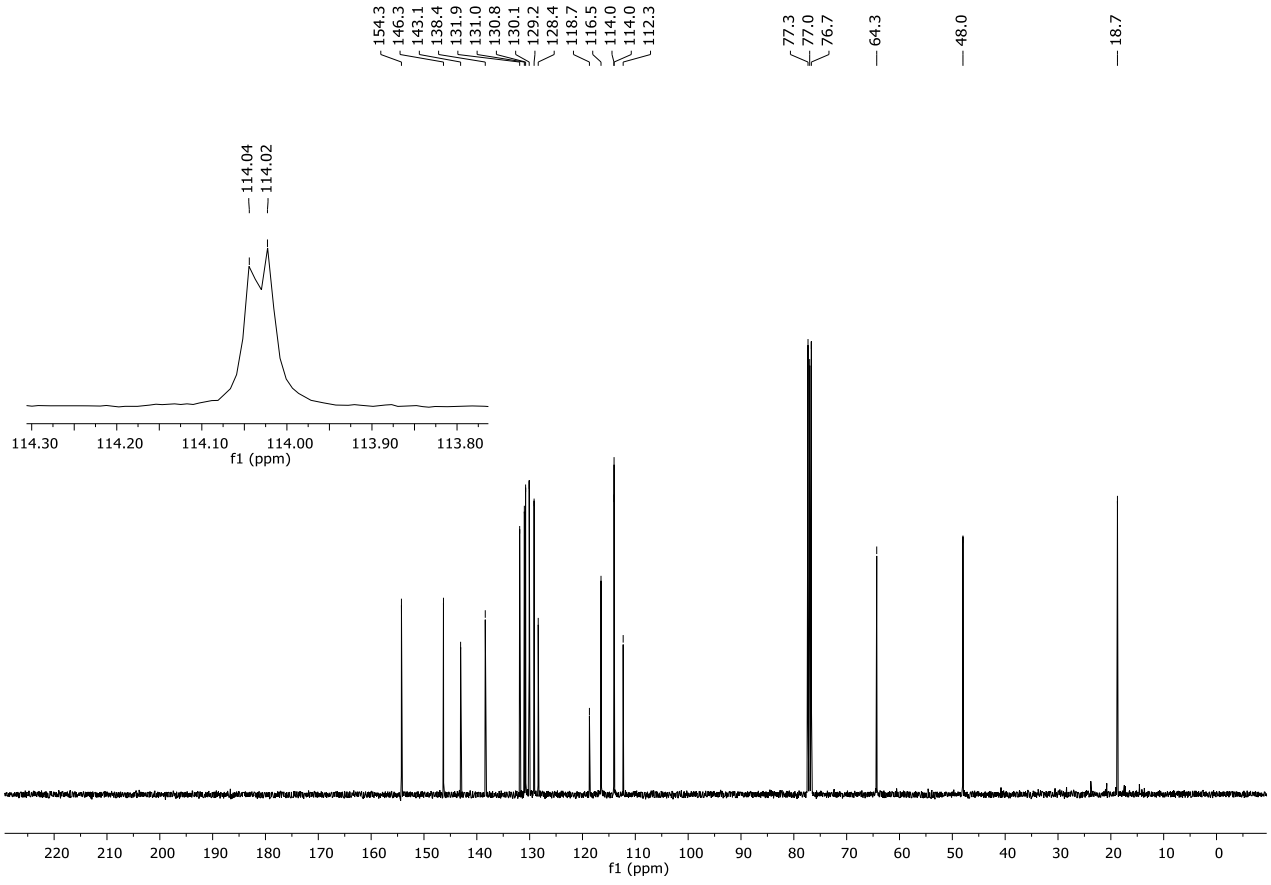

3.00
1.02
1.00
1.00
1.00
1.00
1.01
1.01
1.02
1.01
1.02
1.02
3.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

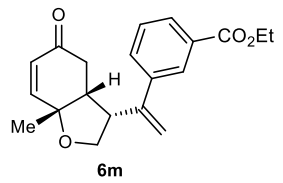

197.8
150.2
142.7
142.4
131.4
130.5
129.6
129.3
128.9
118.5
117.5
112.9
78.9
77.3
77.0
76.7
69.5
45.4
44.2
35.5
27.0
144 142 140 138 136 134 132 130 128 126
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
CN
Me
OH

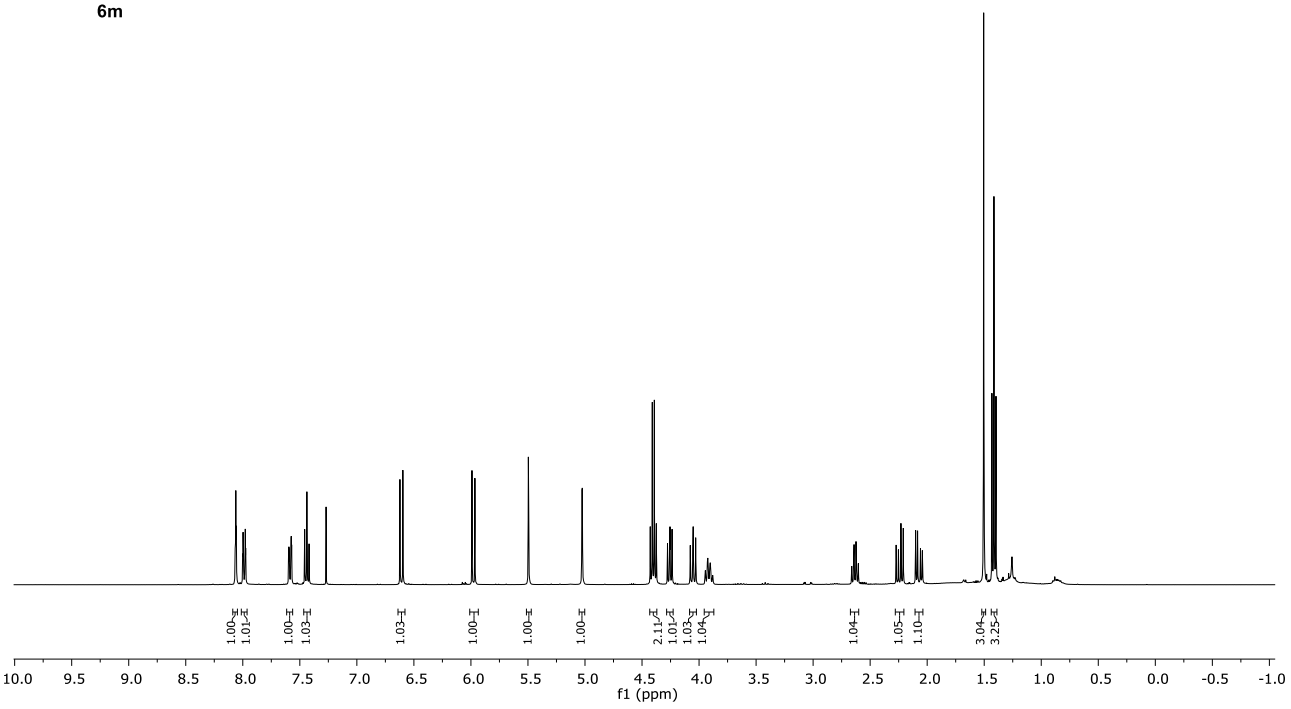
8l

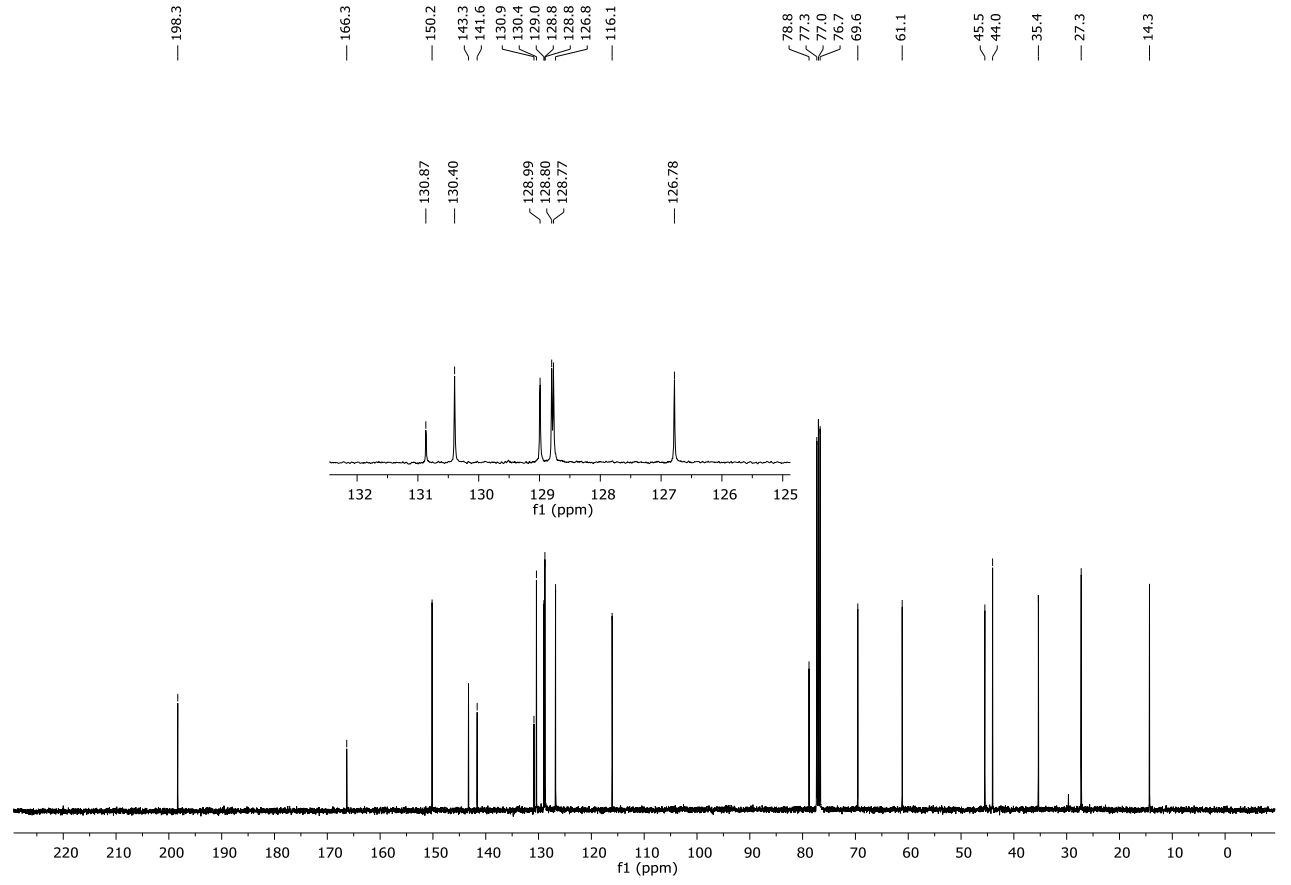

0.98
1.90
1.00
1.00
0.96
0.99
1.00
1.00
1.03
2.03
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

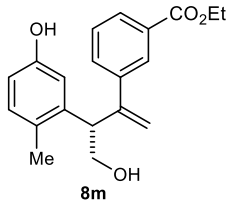

154.3
146.3
143.1
138.4
131.9
131.0
130.8
130.1
129.2
128.4
118.7
116.5
114.0
114.0
112.3
77.3
77.0
76.7
64.3
48.0
18.7
114.04
114.02
114.30 114.20 114.10 114.00 113.90 113.80
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
CO2Et
H
Me
O

6m

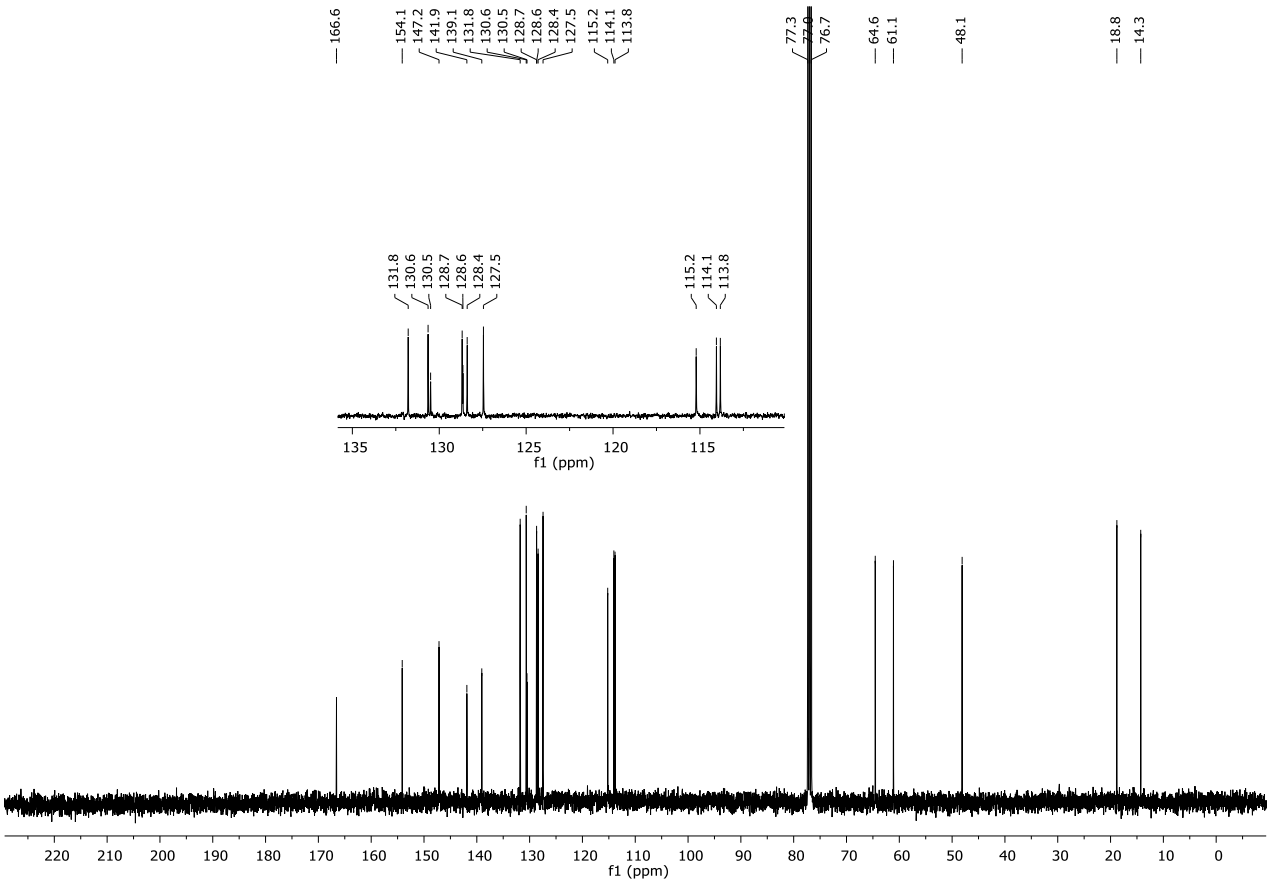

1.00
1.01
1.00
1.03
1.03
1.00
1.00
1.00
2.11
1.01
1.03
1.04
1.04
1.05
1.10
3.04
3.25
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

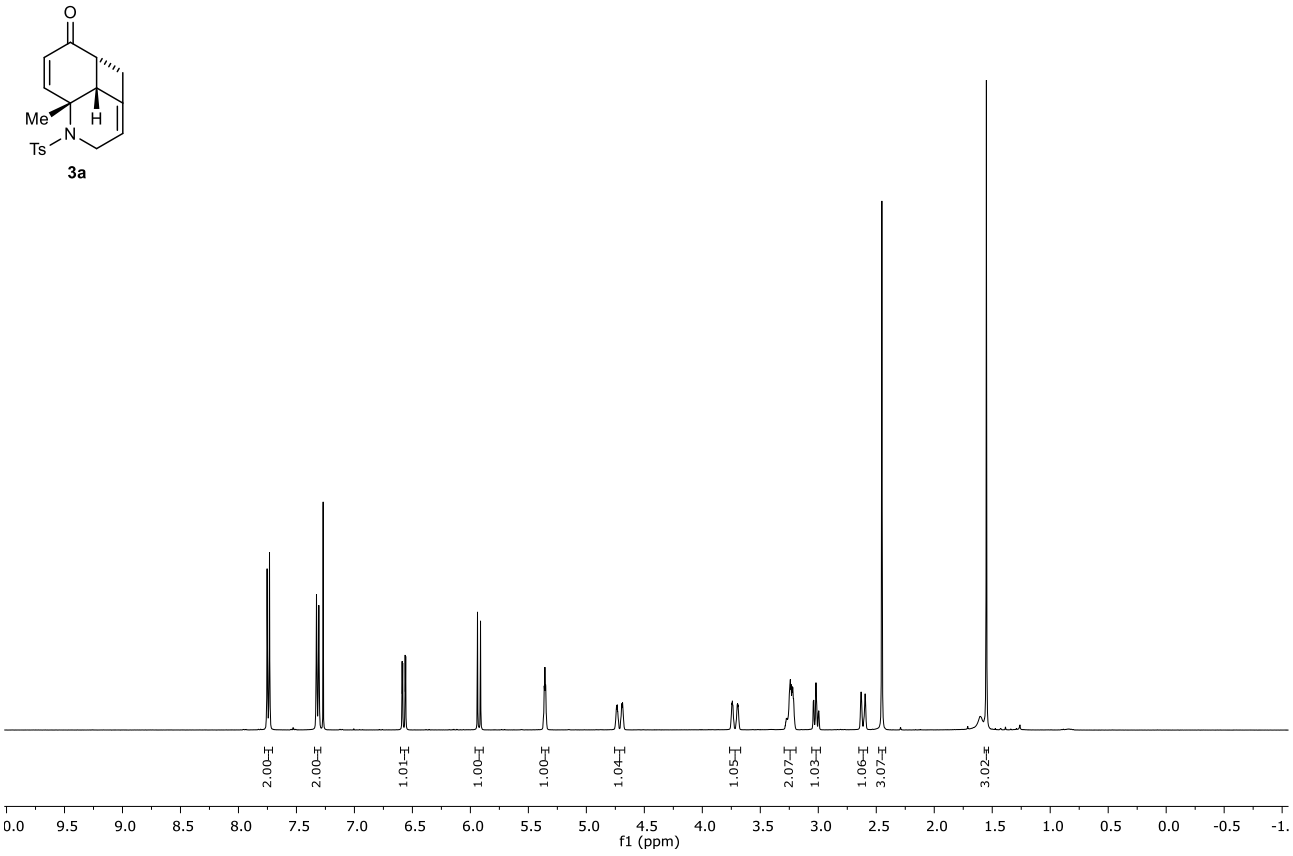

198.3
166.3
150.2
143.3
141.6
130.9
130.4
129.0
128.8
128.8
126.8
116.1
78.8
77.3
77.0
76.7
69.6
61.1
45.5
44.0
35.4
27.3
14.3
130.87
130.40
128.99
128.80
128.77
126.78
132 131 130 129 128 127 126 125
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

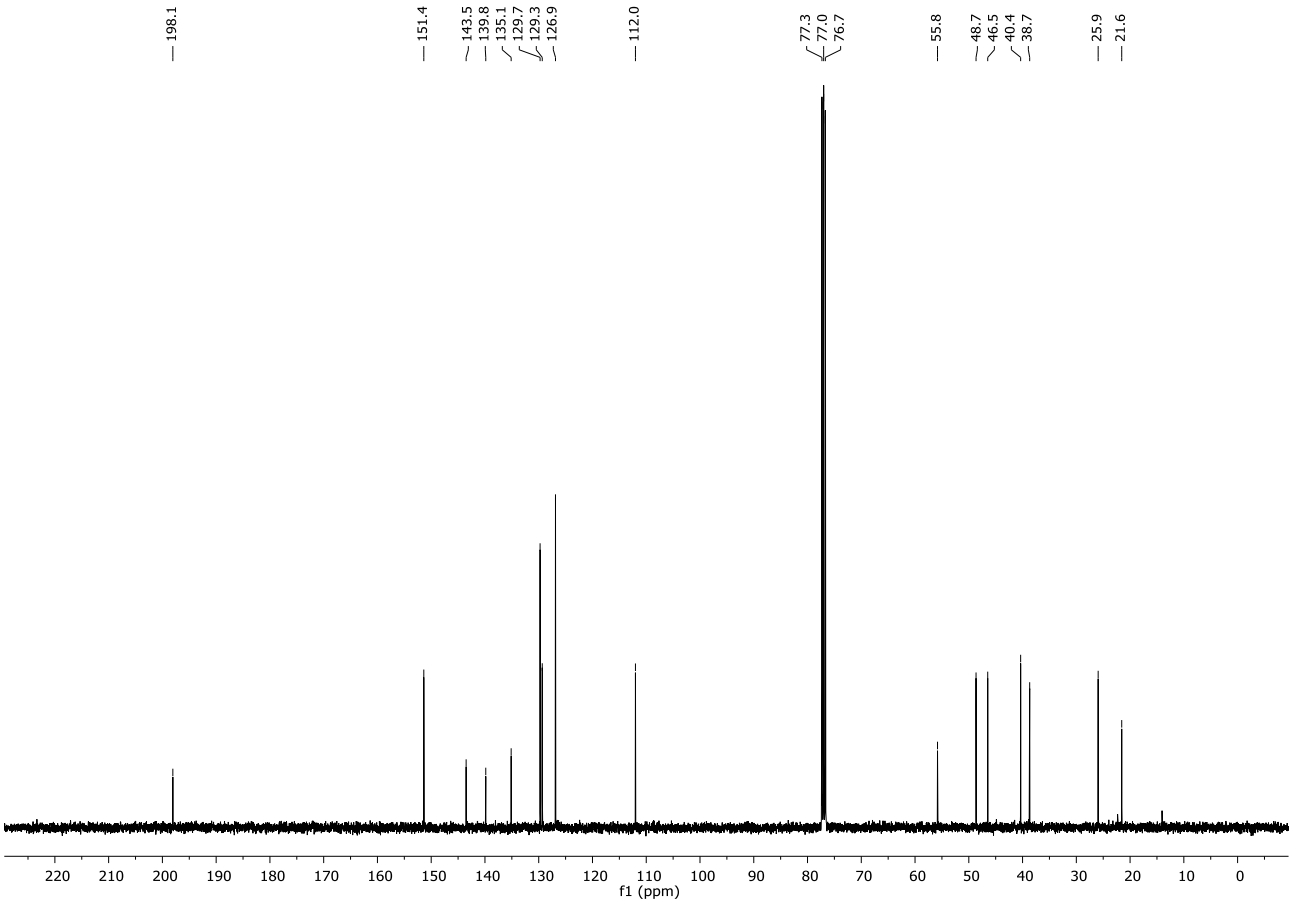

OH
CO2Et
Me
OH

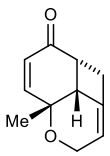
8m

1.00
1.00
1.00
1.01
1.00
1.00
1.00
1.00
1.01
3.04
1.00
1.00
3.00
1.10
3.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


166.6
154.1
147.2
141.9
139.1
131.8
130.6
130.5
128.7
128.6
128.4
127.5
115.2
114.1
113.8
77.3
77.0
76.7
64.6
61.1
48.1
18.8
14.3
131.8
130.6
130.5
128.7
128.6
128.4
127.5
115.2
114.1
113.8
135 130 125 120 115
f1 (ppm)
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

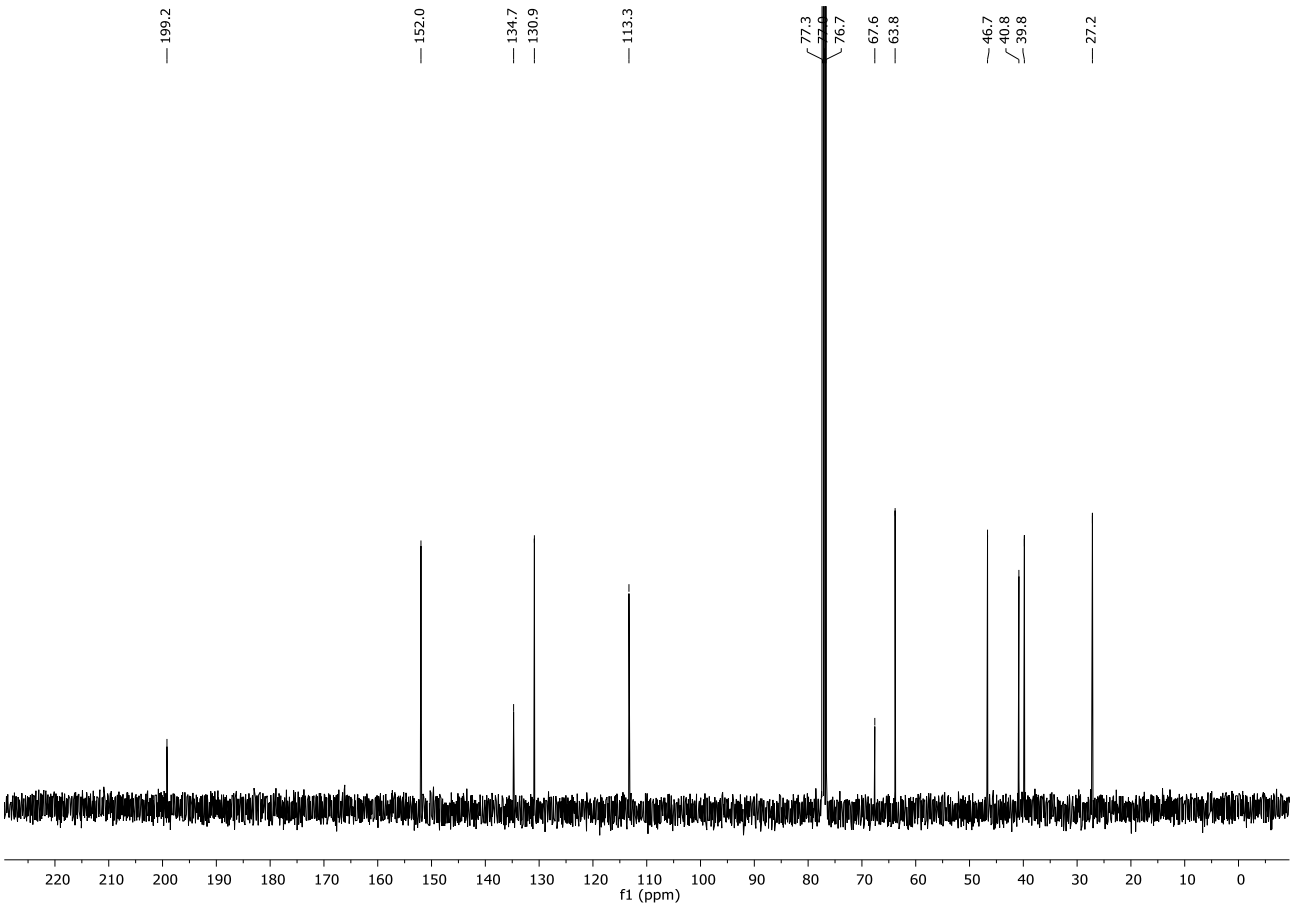

O
Me
H
N
Ts
3a
2.00
2.00
1.01
1.00
1.00
1.04
1.05
2.07
1.03
1.06
3.07
3.02
f1 (ppm)

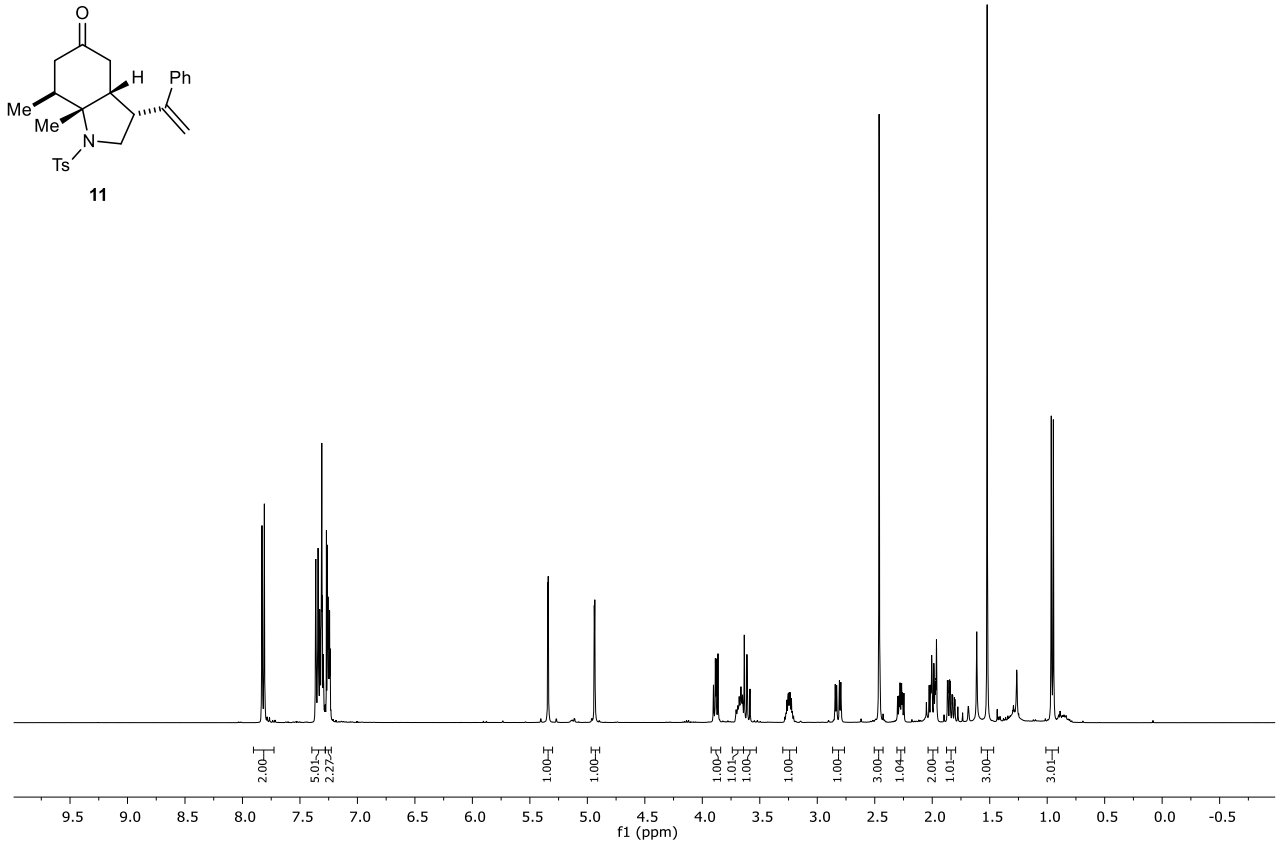

198.1
151.4
143.5
139.8
135.1
129.7
129.3
126.9
112.0
77.3
77.0
76.7
55.8
48.7
46.5
40.4
38.7
25.9
21.6
f1 (ppm)

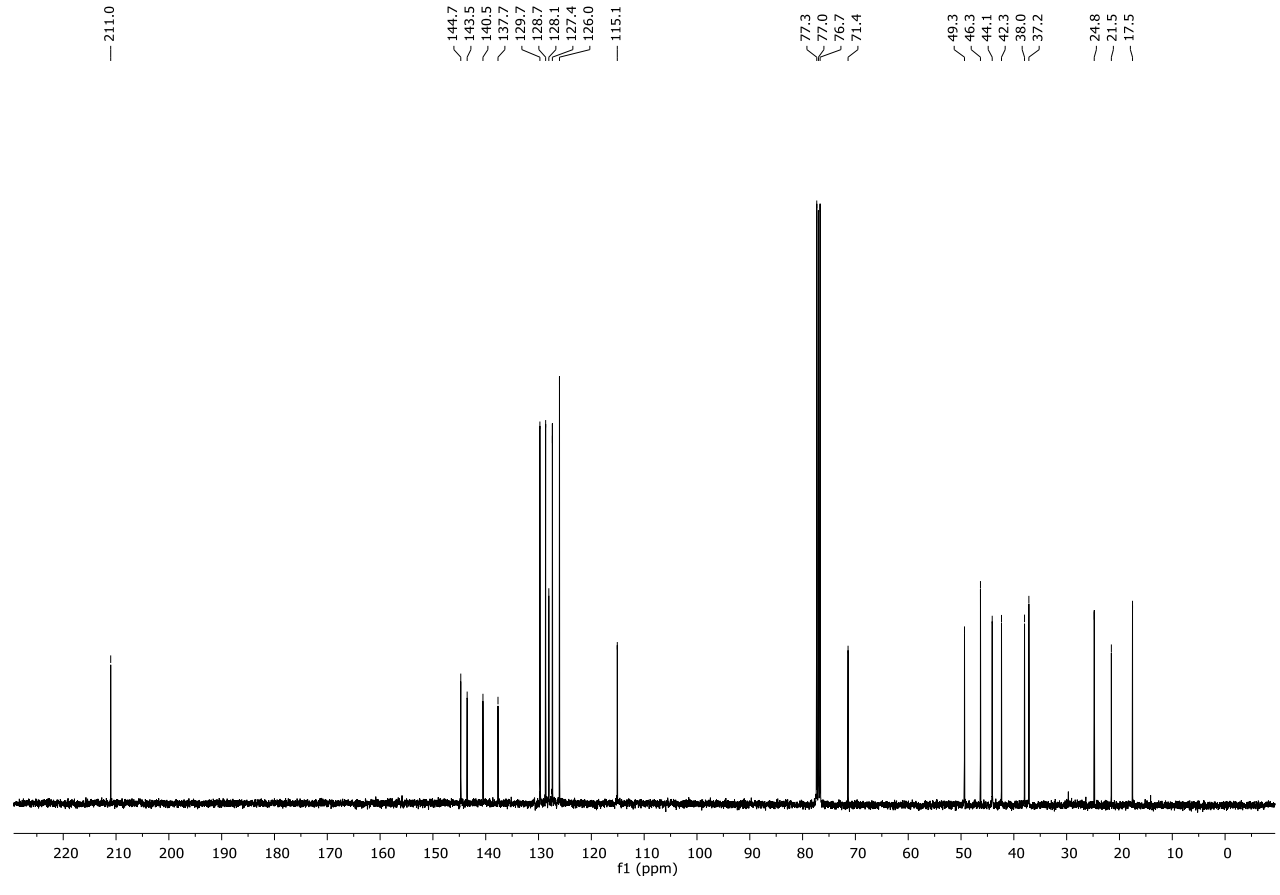

O
Me
H
O

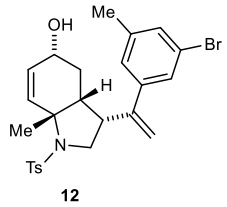
3b

1.00
1.00
1.00
1.05
1.09
1.03
1.01
1.02
1.03
3.11
f1 (ppm)


199.2
152.0
134.7
130.9
113.3
77.3
77.0
76.7
67.6
63.8
46.7
40.8
39.8
27.2
f1 (ppm)


O
H
Ph
Me
Me
N
Ts
11
2.00
5.01
2.27
1.00
1.00
1.00
1.01
1.00
1.00
1.00
3.00
1.04
2.00
1.01
3.00
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

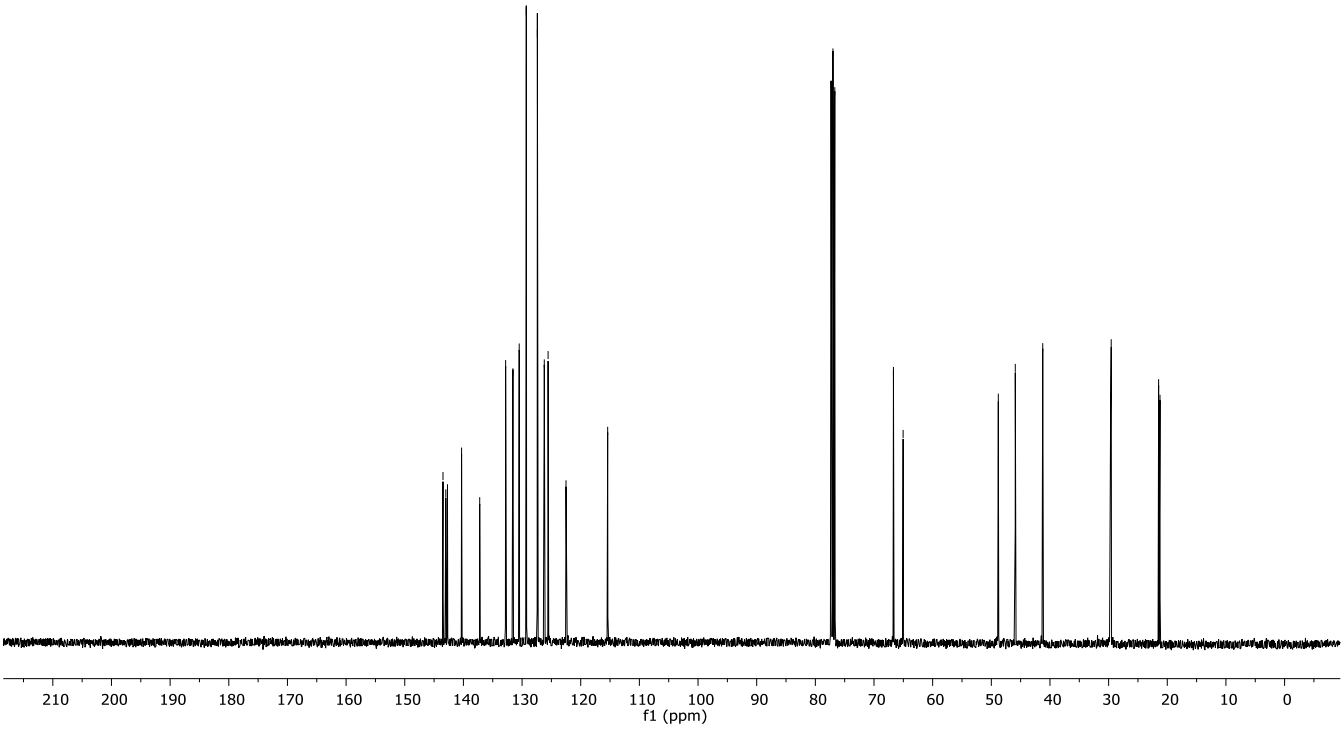

211.0
144.7
143.5
140.5
137.7
129.7
128.7
128.1
127.4
126.0
115.1
77.3
77.0
76.7
71.4
49.3
46.3
44.1
42.3
38.0
37.2
24.8
21.5
17.5
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OH
Me
Br
H
Me
N
Ts

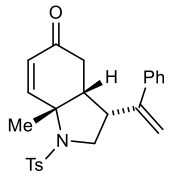
12

2.00
5.28
1.00
1.00
1.01
1.00
1.00
1.03
1.01
1.03
1.00
3.01
3.01
1.00
3.00
1.08
1.01
1.03
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

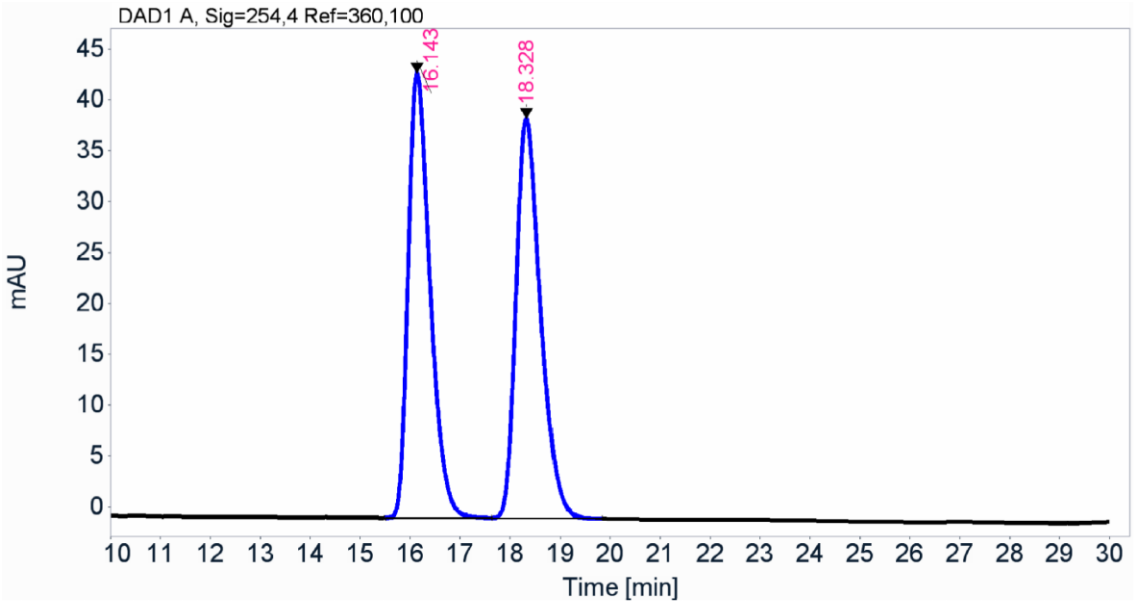

143.5
143.0
142.7
140.3
137.2
132.8
131.6
130.5
129.3
127.4
126.2
125.6
122.5
115.4
77.3
77.0
76.7
66.7
65.0
48.8
45.9
41.2
29.7
29.6
21.5
21.2


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

HPLC traces

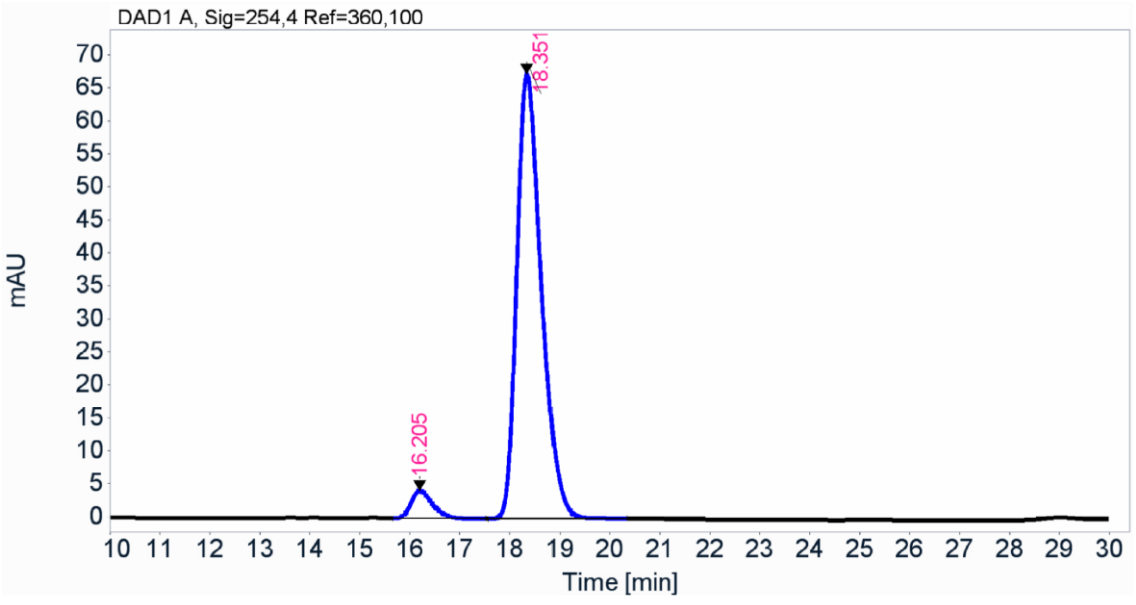


2a



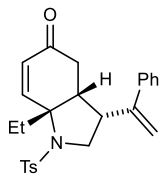
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
16.143	BB	0.4632	1329.800	43.6837	49.86
18.328	BB	0.5168	1337.030	39.3084	50.14

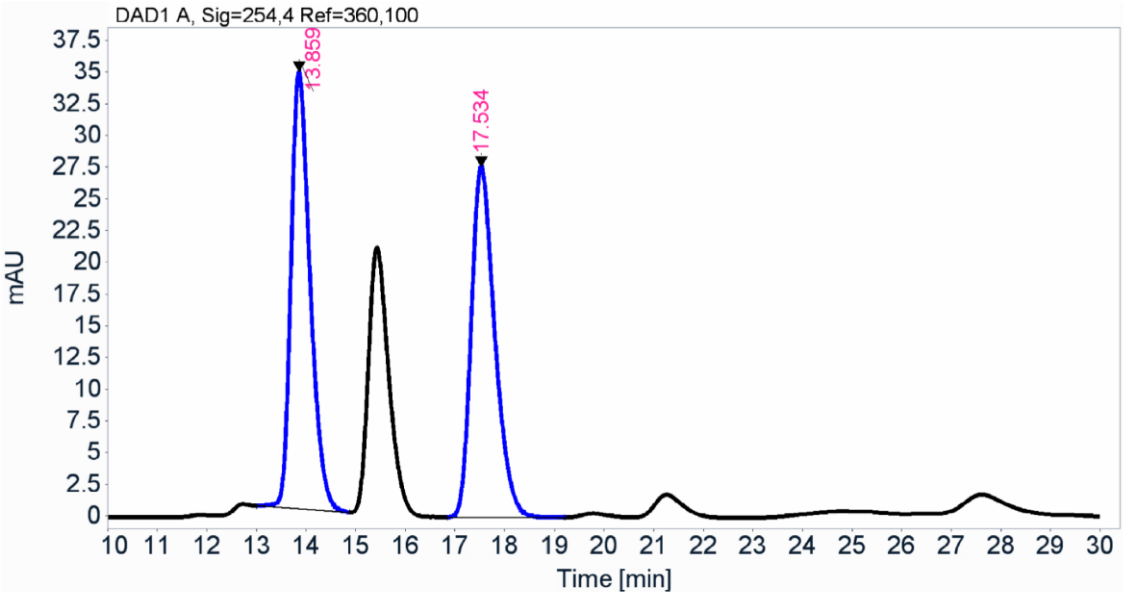


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
16.205	BB	0.4408	125.263	4.1901	5.18
18.351	BB	0.5152	2293.277	67.3543	94.82

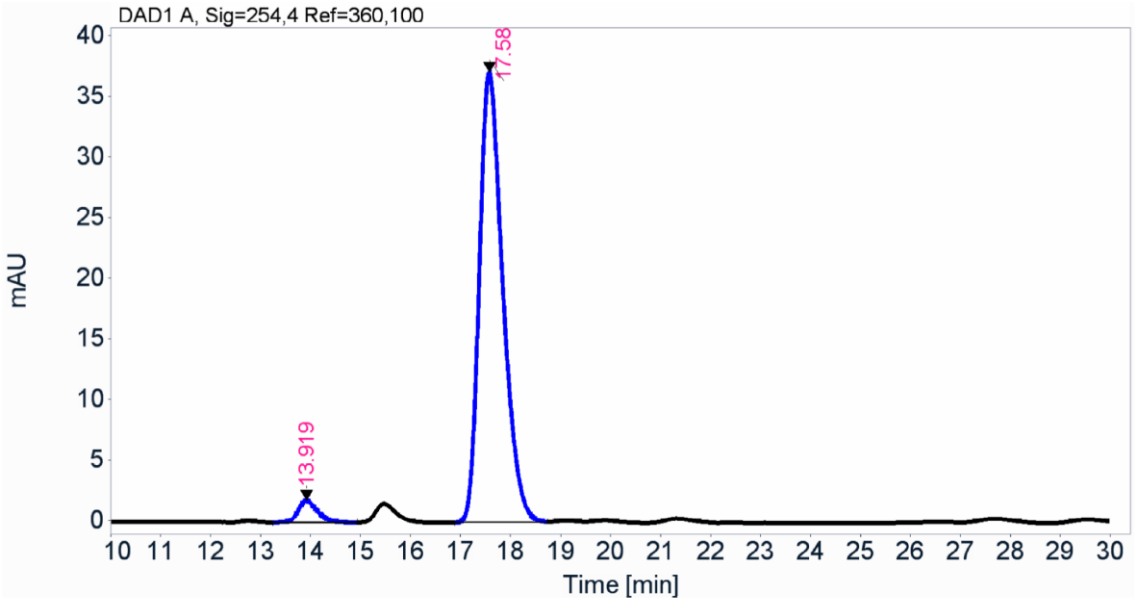


2b



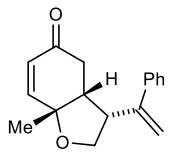
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
13.859	BB	0.4074	925.419	34.4523	50.36
17.534	BB	0.5010	912.019	27.6391	49.64

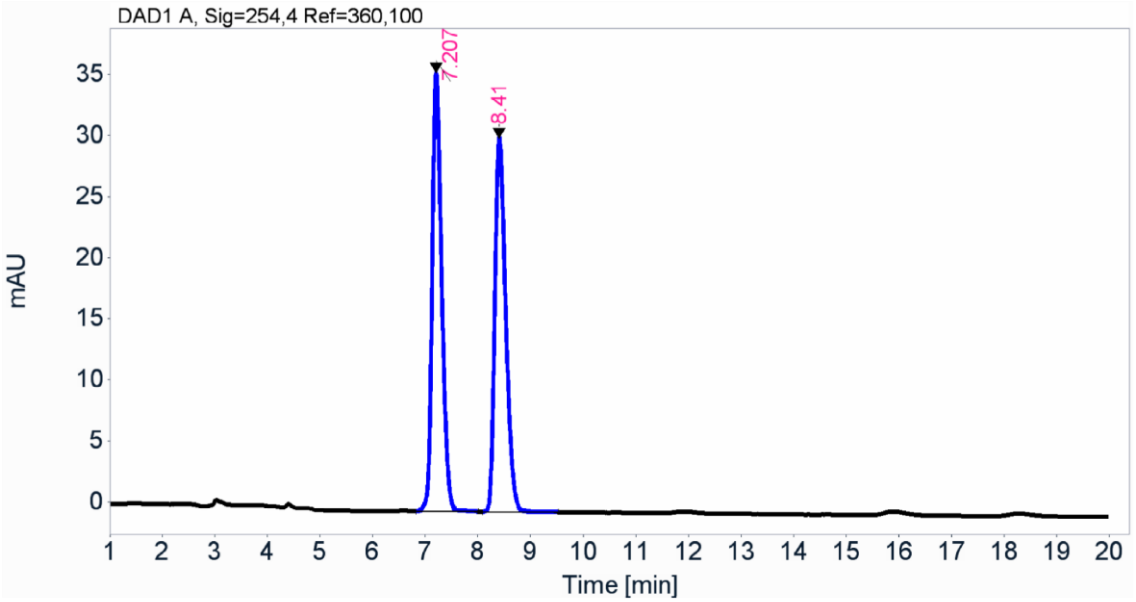


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
13.919	BB	0.3938	48.109	1.8000	3.83
17.580	BB	0.4958	1207.651	37.0929	96.17

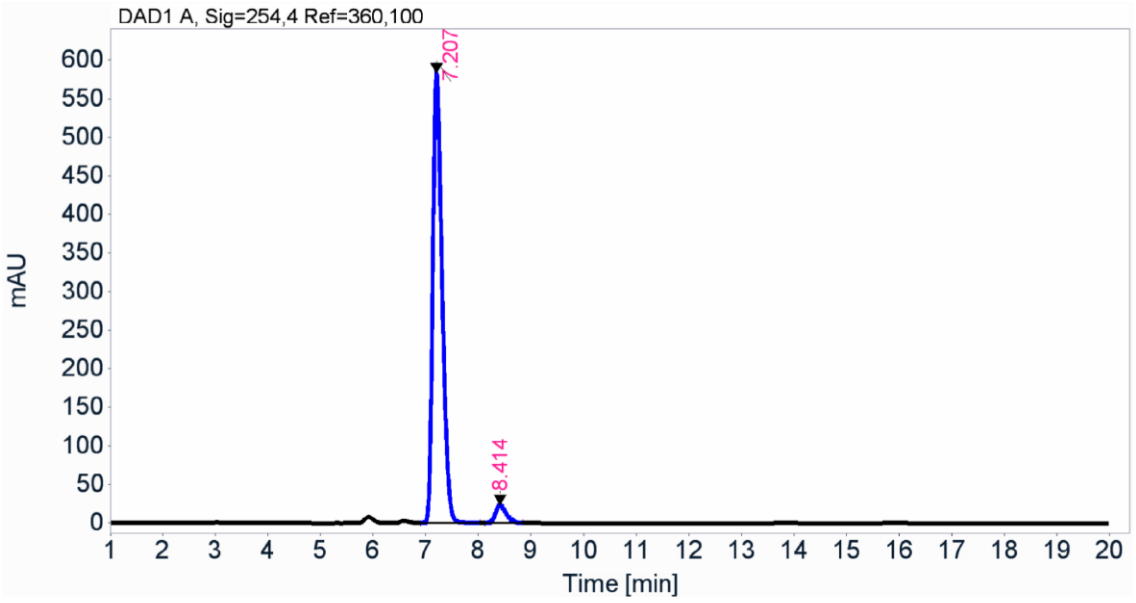


6a



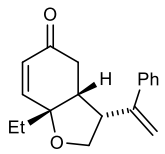
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
7.207	BB	0.1900	448.799	35.8714	50.56
8.410	BB	0.2196	438.822	30.5503	49.44

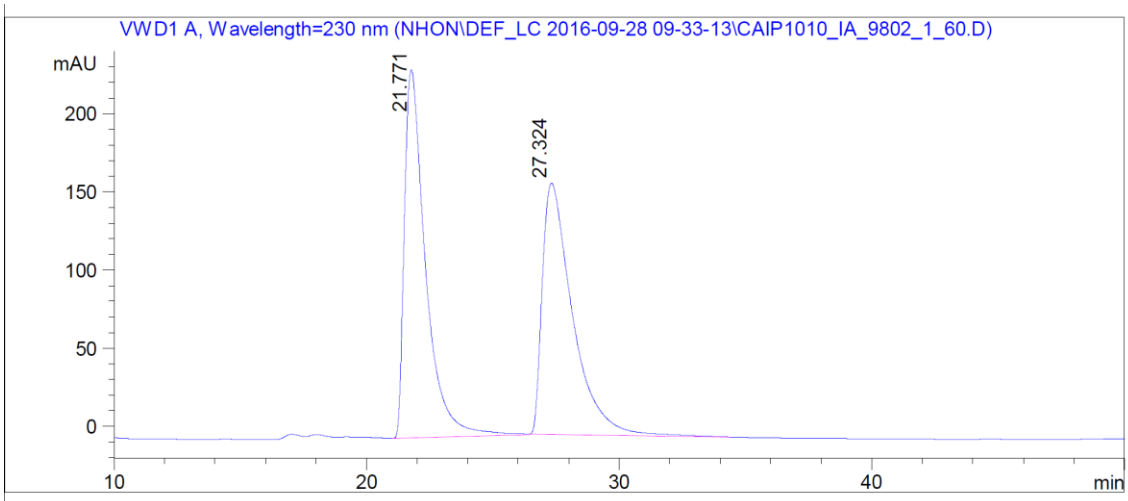


Signal: DAD1 A, Sig=254,4 Ref=360,100

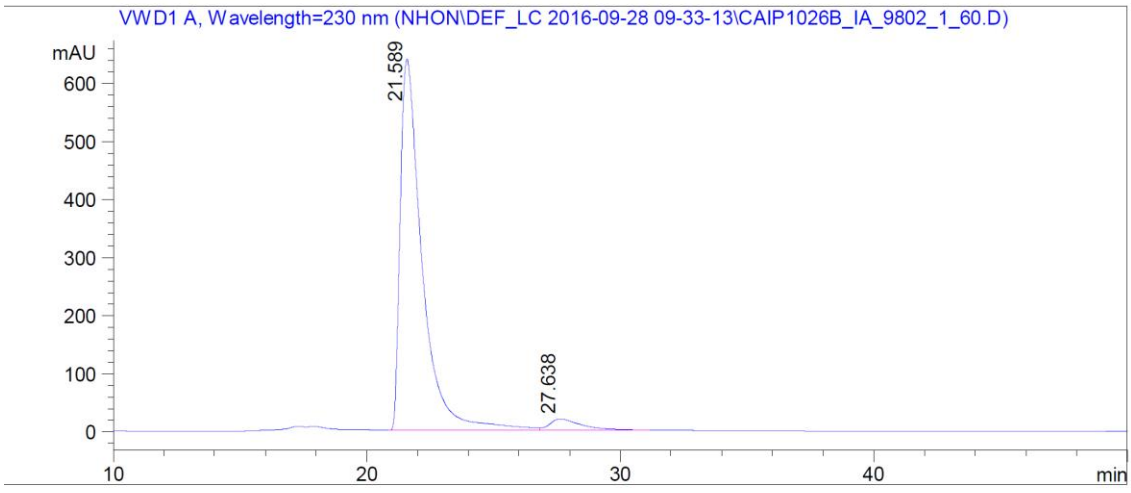
RT [min]	Type	Width [min]	Area	Height	Area%
7.207	BB	0.1906	7222.781	582.6636	95.74
8.414	BB	0.2150	321.366	22.7287	4.26



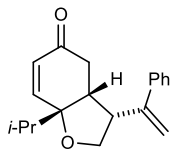
6b



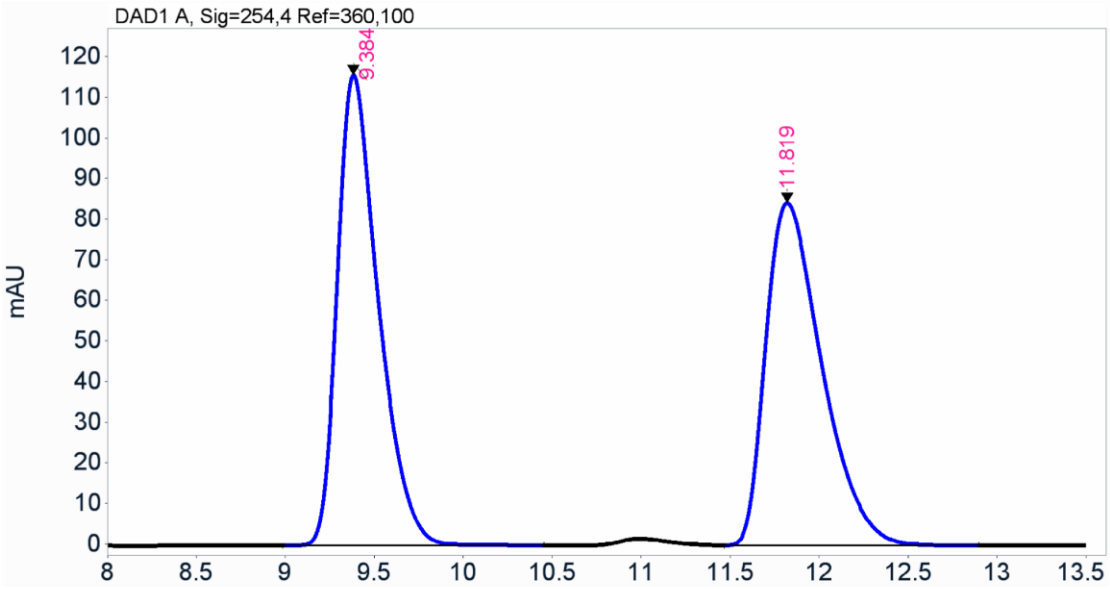
Meas. R	Area %	Width	Symmetr.
21.771	50.457	0.971	0.453
27.324	49.543	1.397	0.414



Meas. R	Area %	Width	Symmetr.
21.589	95.794	0.881	0.397
27.638	4.206	1.253	0.474



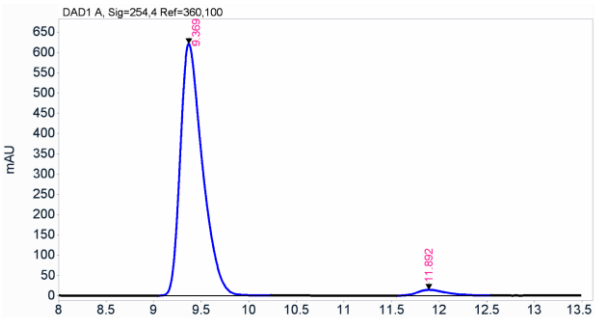
6c



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
9.384	BB	0.2384	1850.935	115.8368	50.08
11.819	BB	0.3374	1845.265	84.2799	49.92

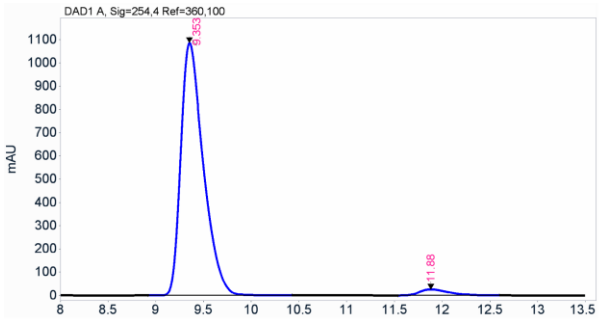
Reaction on a 0.30 mmol scale:



Signal: DAD1 A, Sig=254,4 Ref=360,100

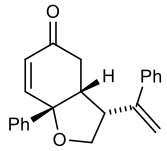
RT [min]	Type	Width [min]	Area	Height	Area%
9.369	MM	0.2697	10055.219	621.4306	96.97
11.892	MM	0.3594	314.253	14.5739	3.03

Reaction on a 2.00 mmol scale:

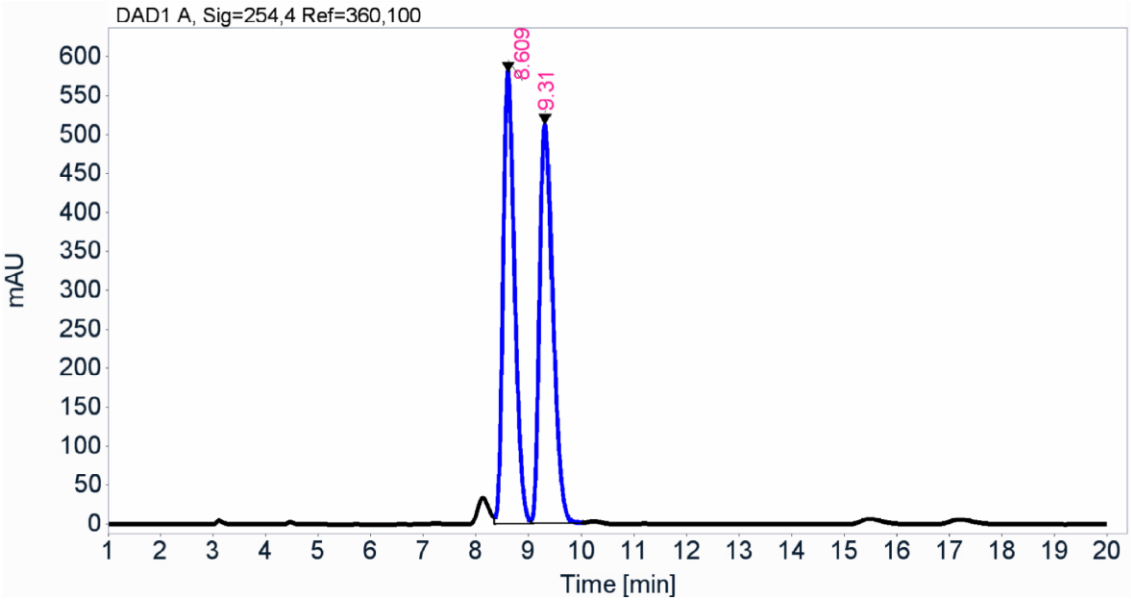


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
9.353	MM	0.2717	17708.504	1086.1705	96.95
11.880	MM	0.3542	556.521	26.1863	3.05

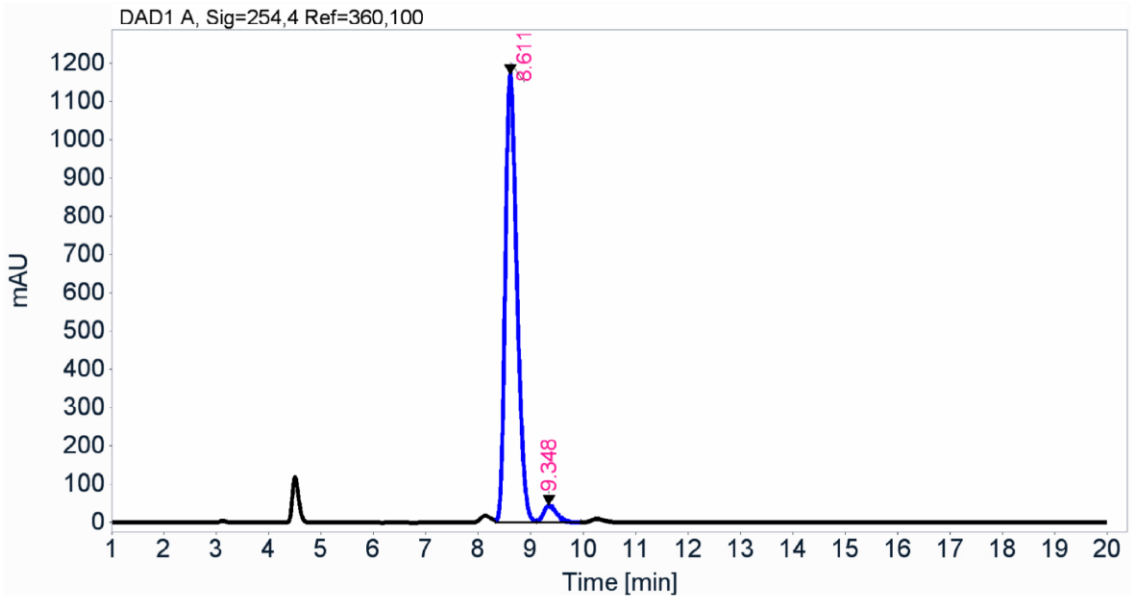


6d



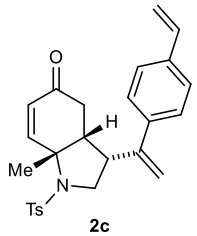
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.609	VV	0.2338	8829.673	579.4590	50.06
9.310	VB	0.2687	8809.753	512.1179	49.94

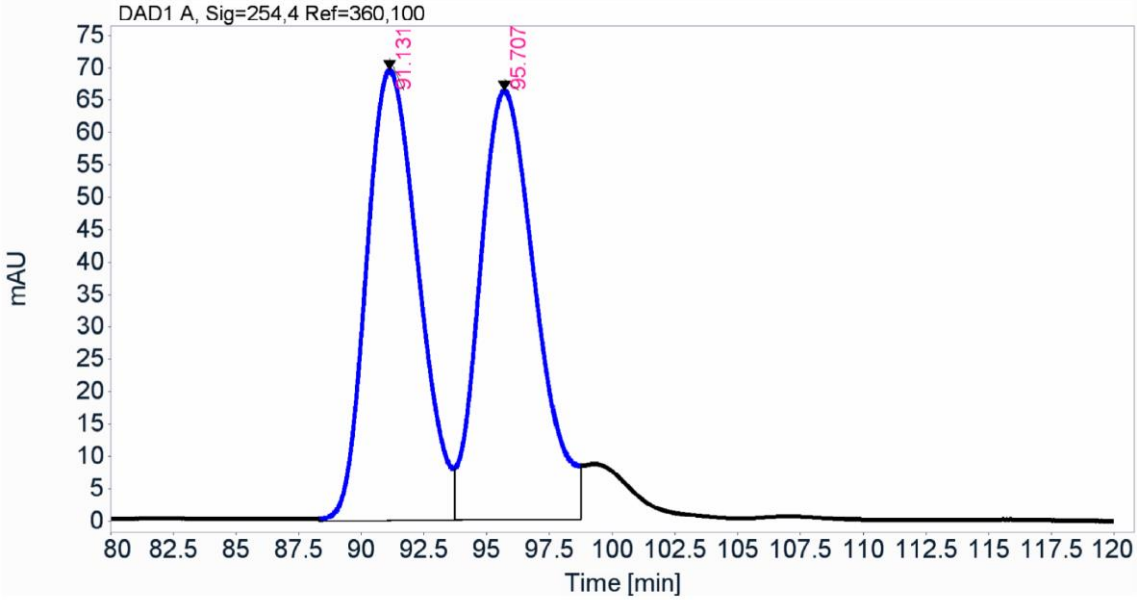


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.611	VV	0.2356	18029.584	1171.0482	96.03
9.348	VB	0.2597	744.774	43.9597	3.97

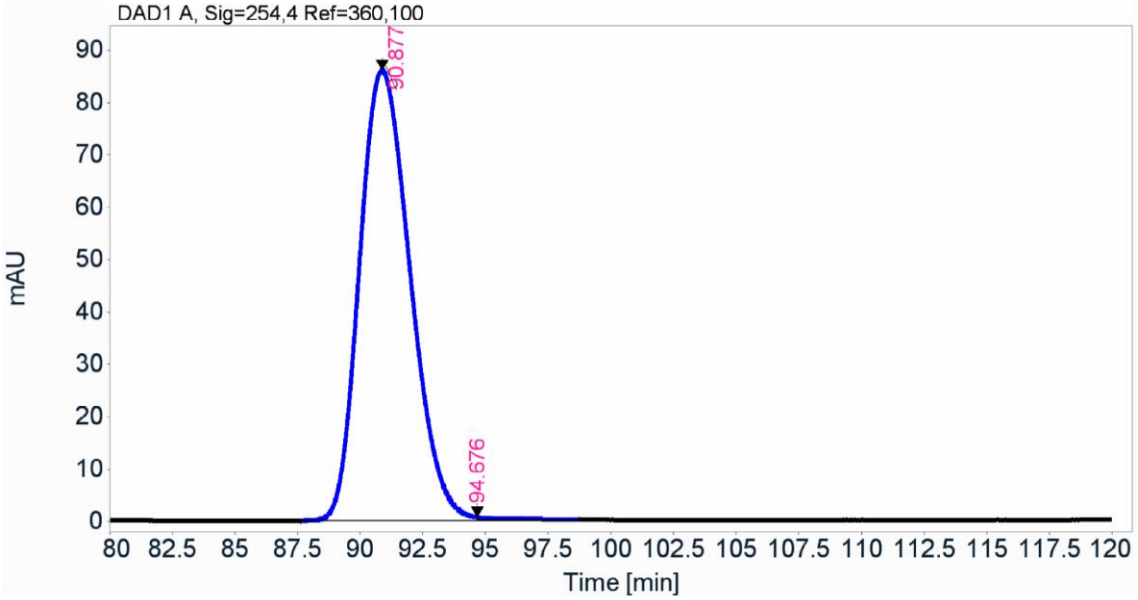


2c



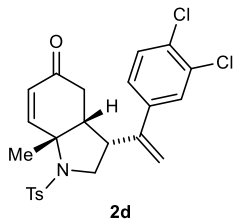
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
91.131	MF	2.3938	9979.544	69.4808	49.30
95.707	FM	2.5824	10263.090	66.2375	50.70

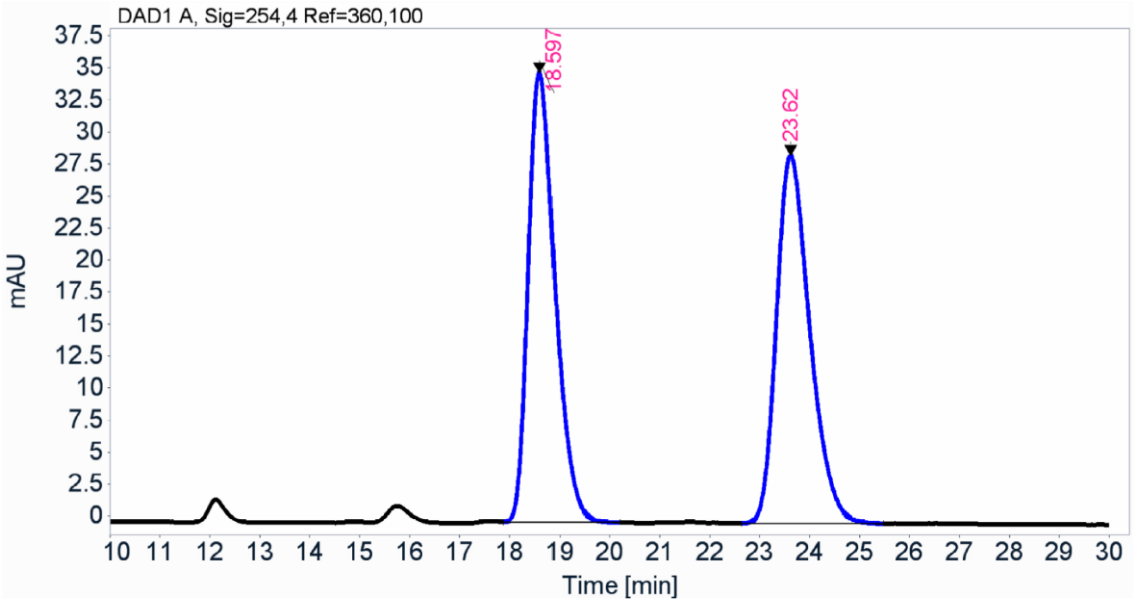


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
90.877	MF	2.3392	12070.413	85.9994	99.43
94.676	FM	1.8634	68.674	0.6142	0.57

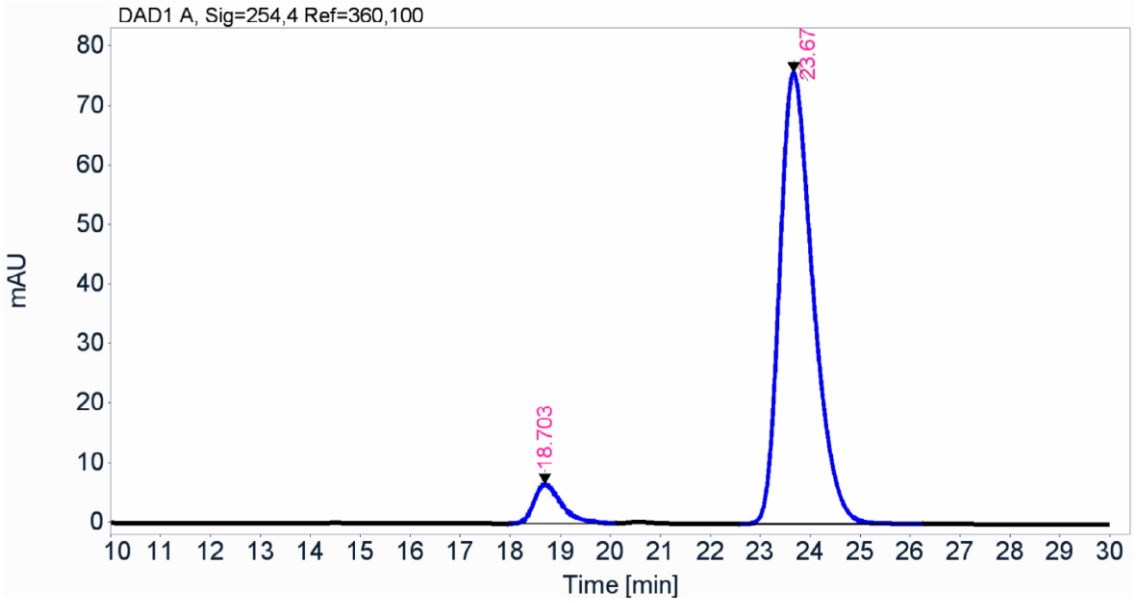


2d



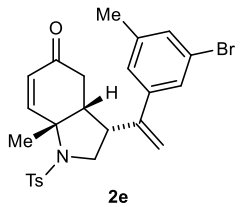
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
18.597	BB	0.5641	1298.673	35.0610	49.32
23.620	BB	0.7020	1334.641	28.7261	50.68

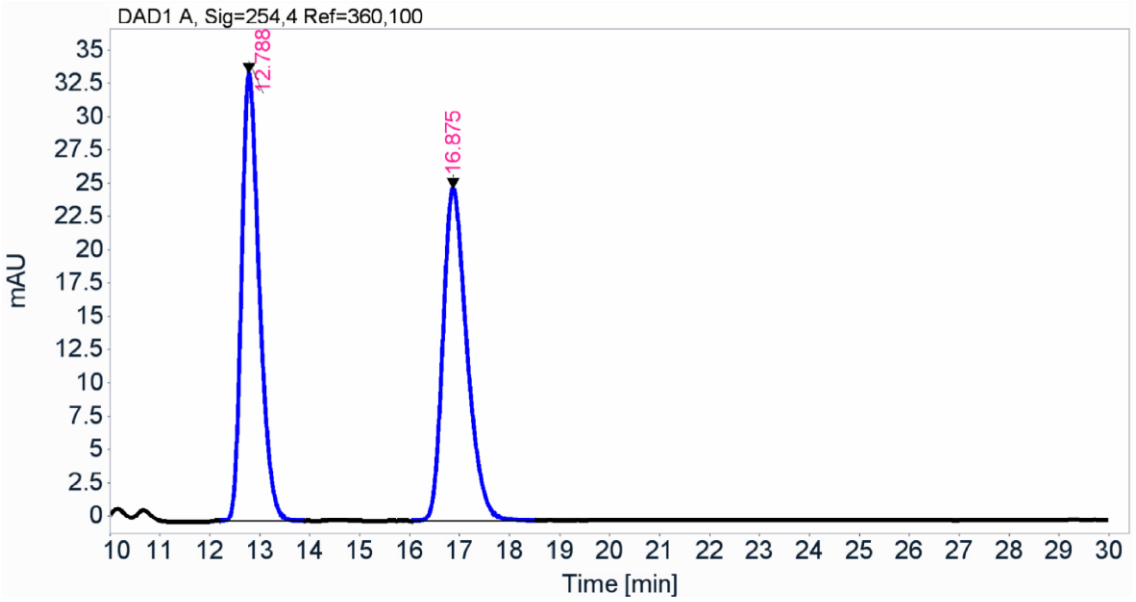


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
18.703	BB	0.5730	248.955	6.5864	6.64
23.670	BB	0.7049	3502.795	75.8360	93.36

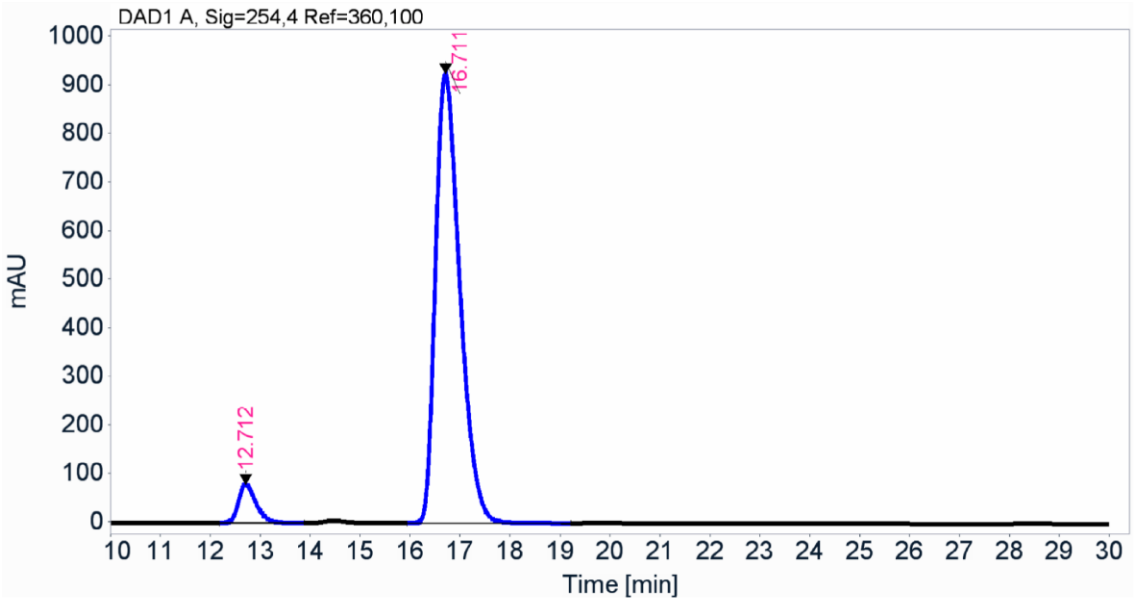


2e



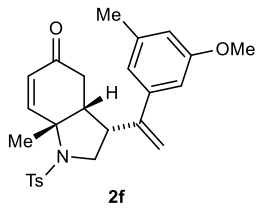
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
12.788	BB	0.3754	827.380	33.5895	49.85
16.875	BB	0.5069	832.462	24.9759	50.15

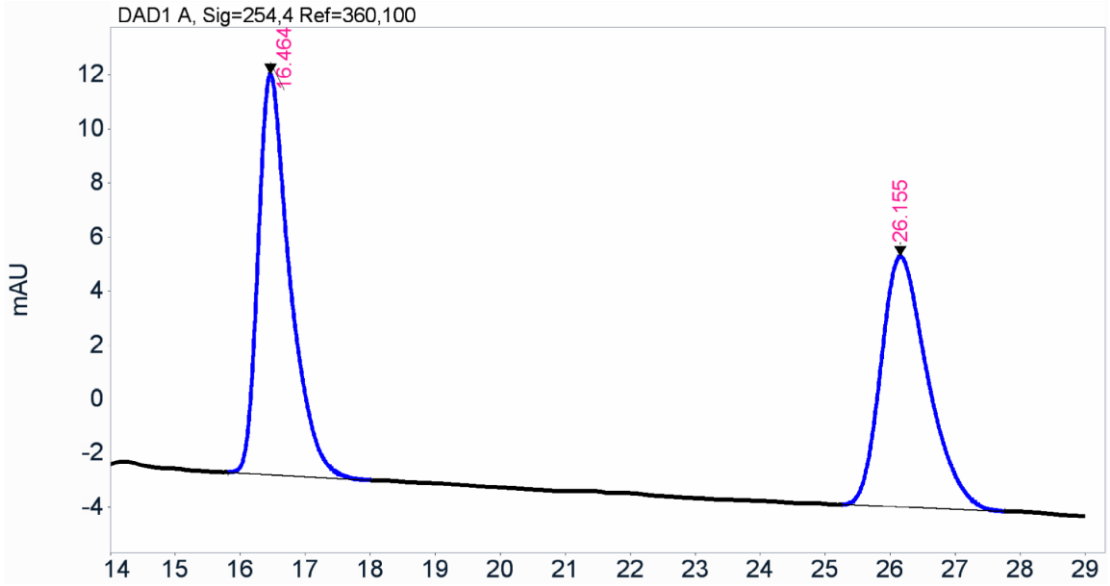


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
12.712	BB	0.3700	1934.287	79.4538	5.81
16.711	BB	0.5236	31374.342	925.3215	94.19

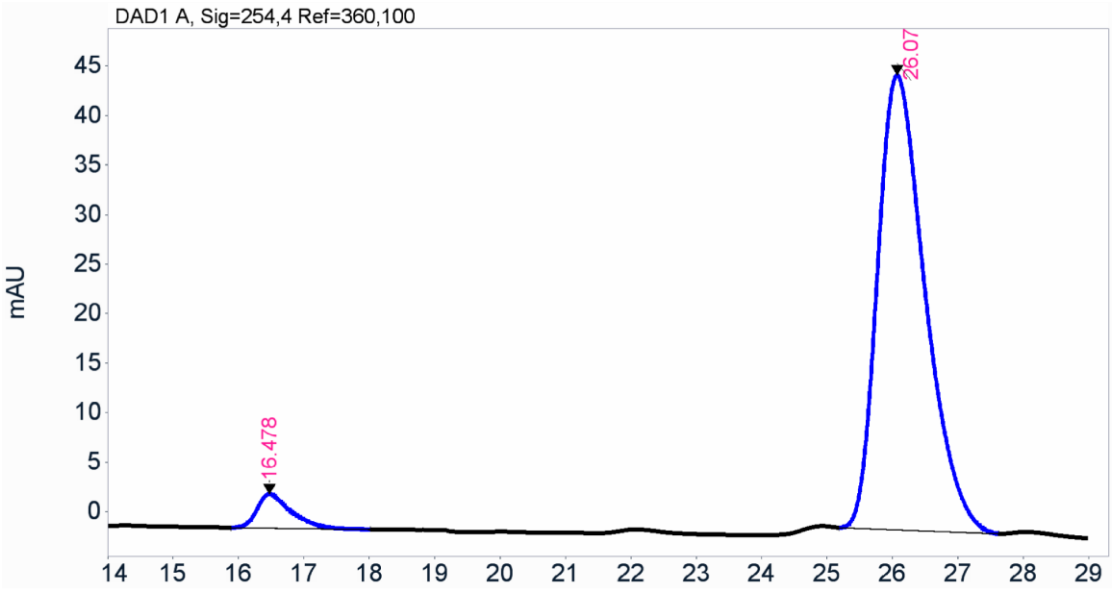


2f



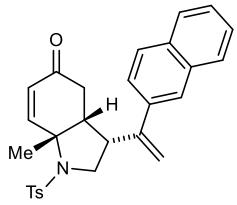
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
16.464	BB	0.5045	501.405	14.8294	51.91
26.155	BB	0.7526	464.575	9.2714	48.09

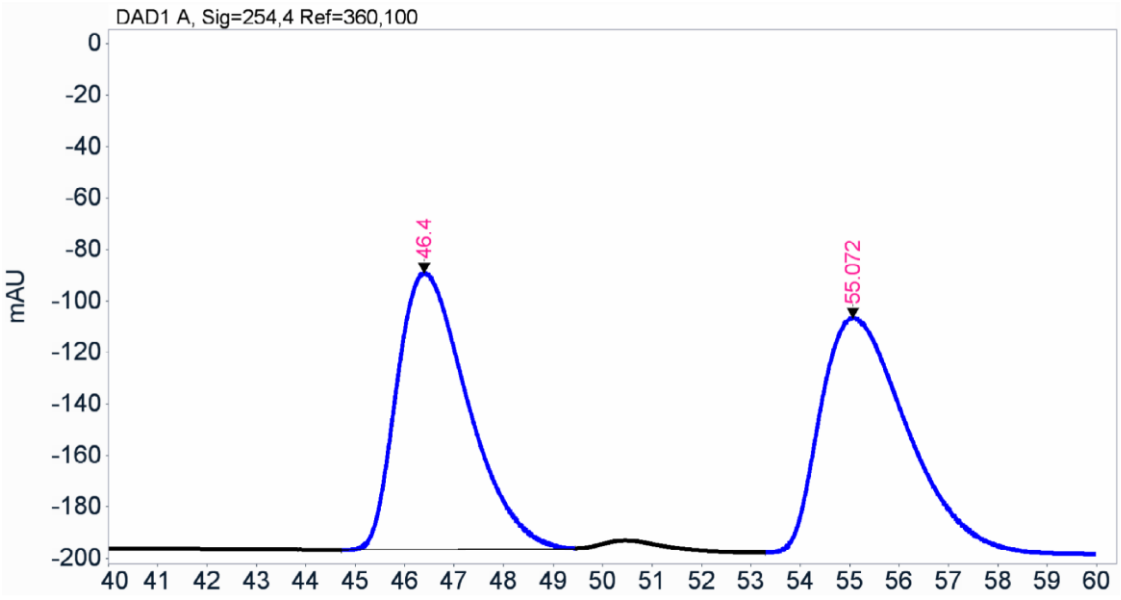


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
16.478	BB	0.5150	124.318	3.4615	5.10
26.070	BB	0.7683	2313.137	45.8760	94.90

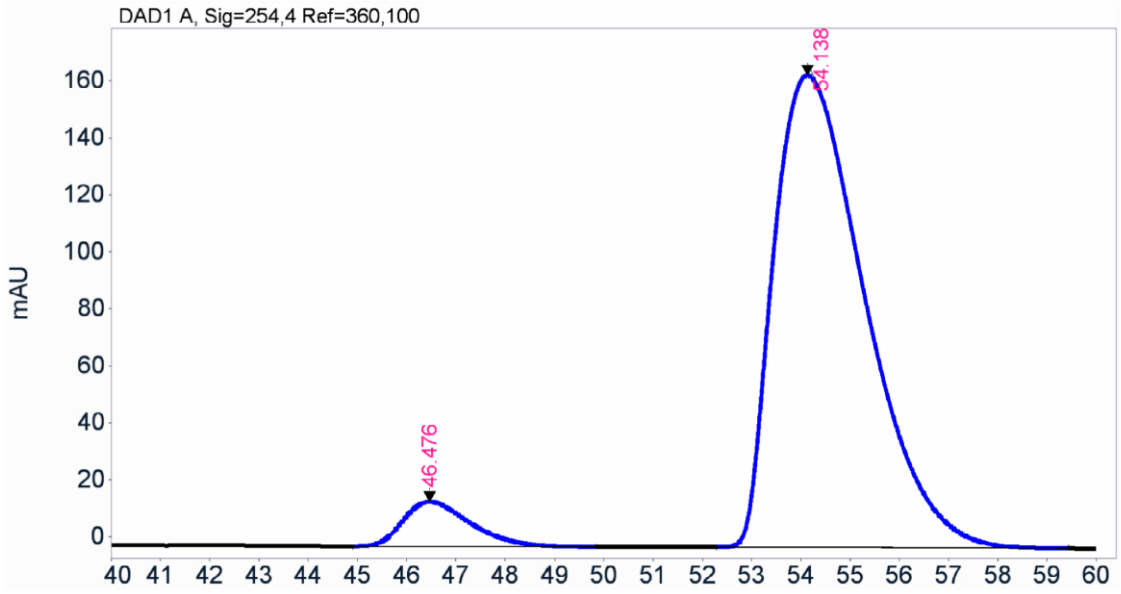


2g



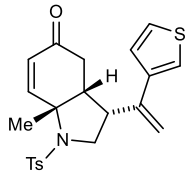
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
46.400	BB	1.5231	10677.564	107.2881	48.94
55.072	BBA	1.8578	11137.969	91.2624	51.06

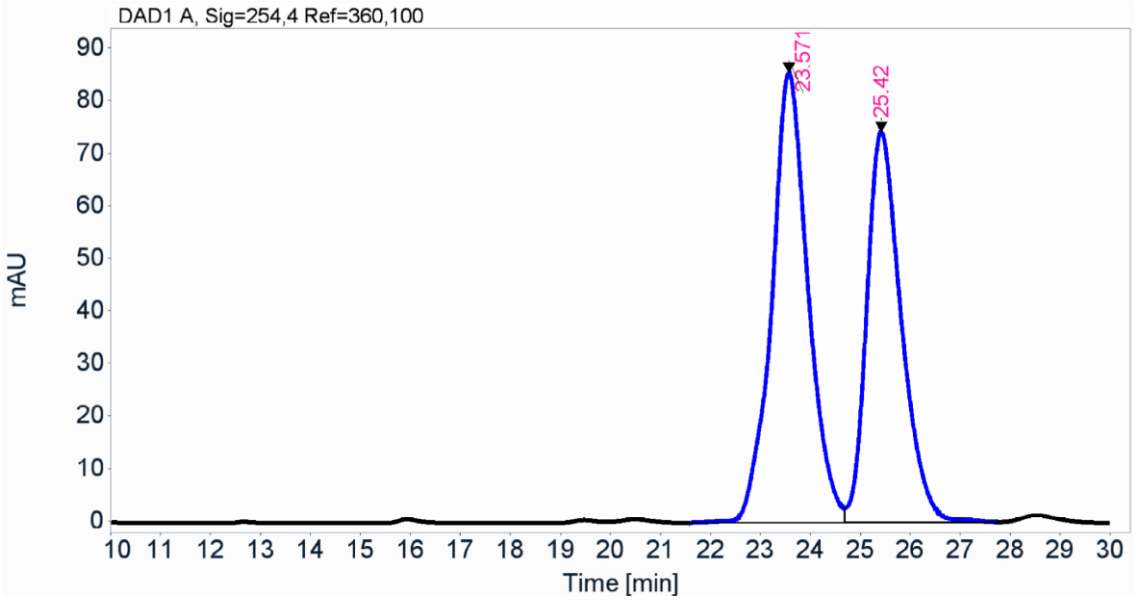


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
46.476	BB	1.2102	1483.849	15.7345	6.54
54.138	BB	1.9615	21218.686	165.7479	93.46

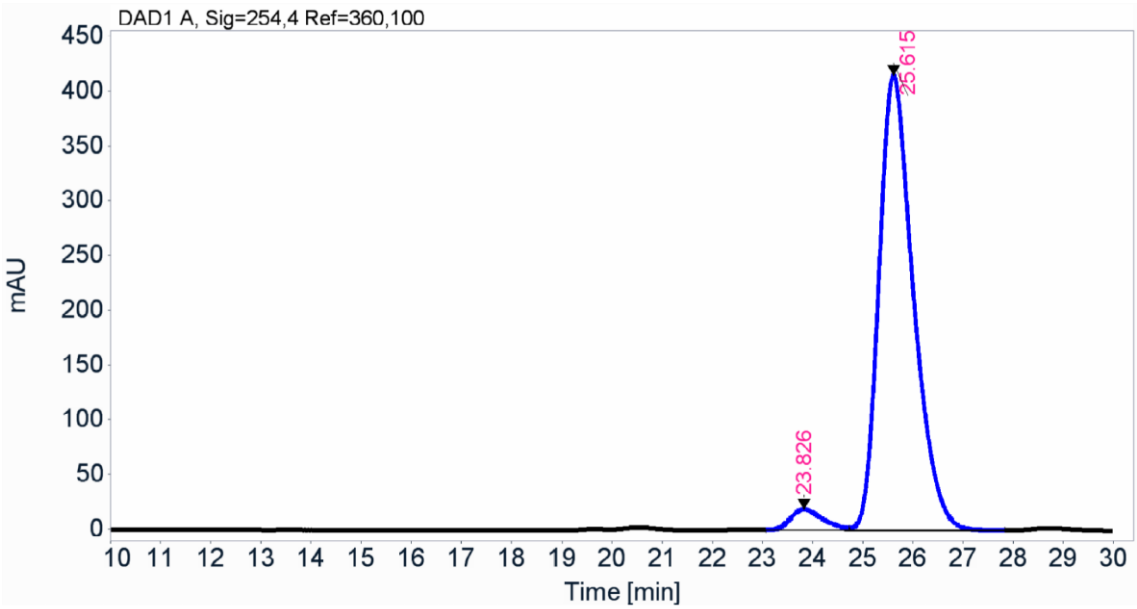


2h



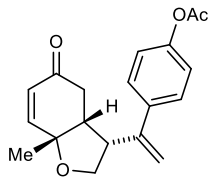
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
23.571	BV	0.7398	4310.020	85.5448	54.72
25.420	VB	0.7240	3565.765	74.2846	45.28

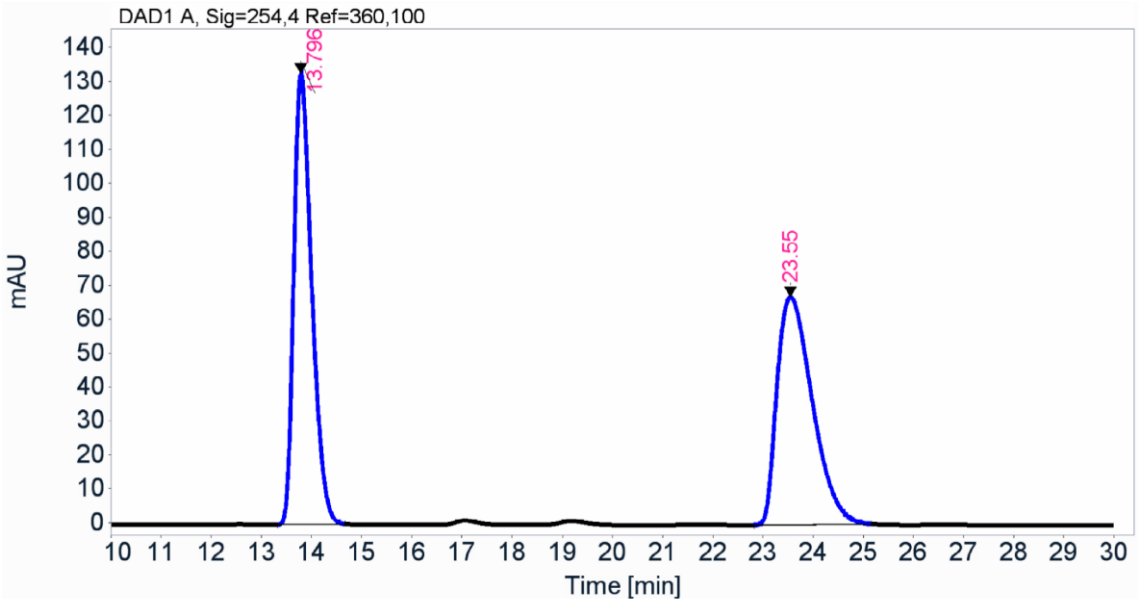


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
23.826	BV	0.6816	852.135	19.0592	4.12
25.615	VB	0.7212	19806.674	414.7364	95.88

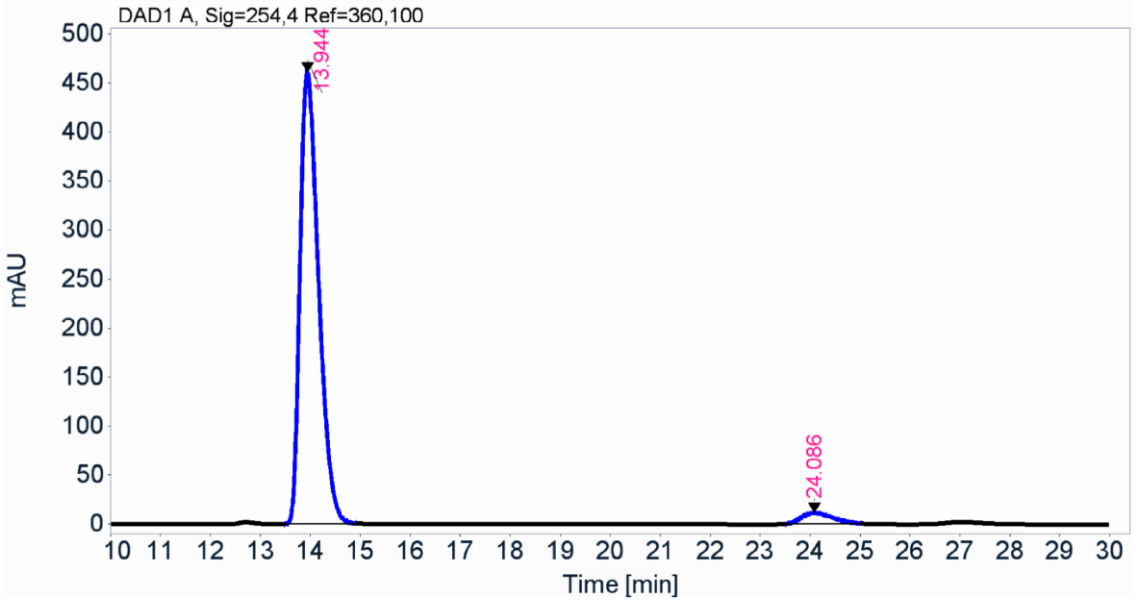


6e



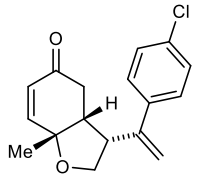
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
13.796	MM	0.4140	3297.411	132.7430	50.05
23.550	MM	0.8172	3290.920	67.1215	49.95

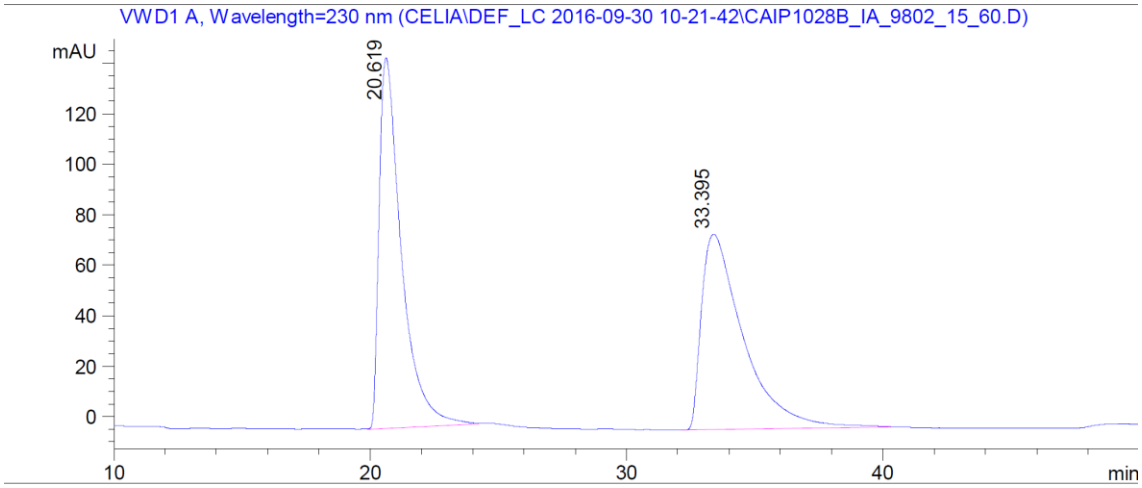


Signal: DAD1 A, Sig=254,4 Ref=360,100

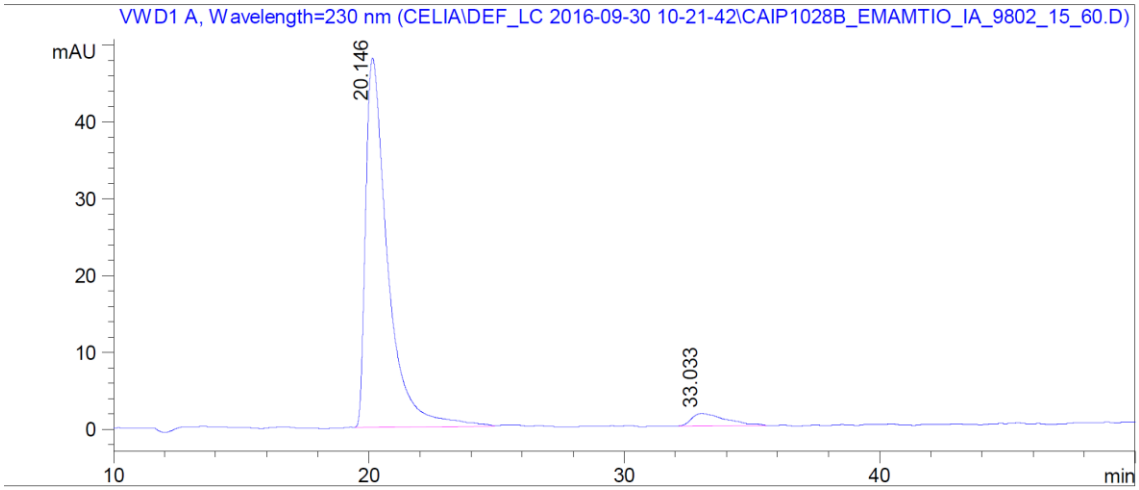
RT [min]	Type	Width [min]	Area	Height	Area%
13.944	MM	0.4315	11924.091	460.5724	96.05
24.086	MM	0.7277	490.200	11.2274	3.95



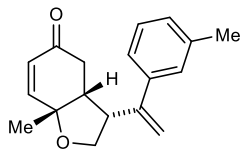
6f



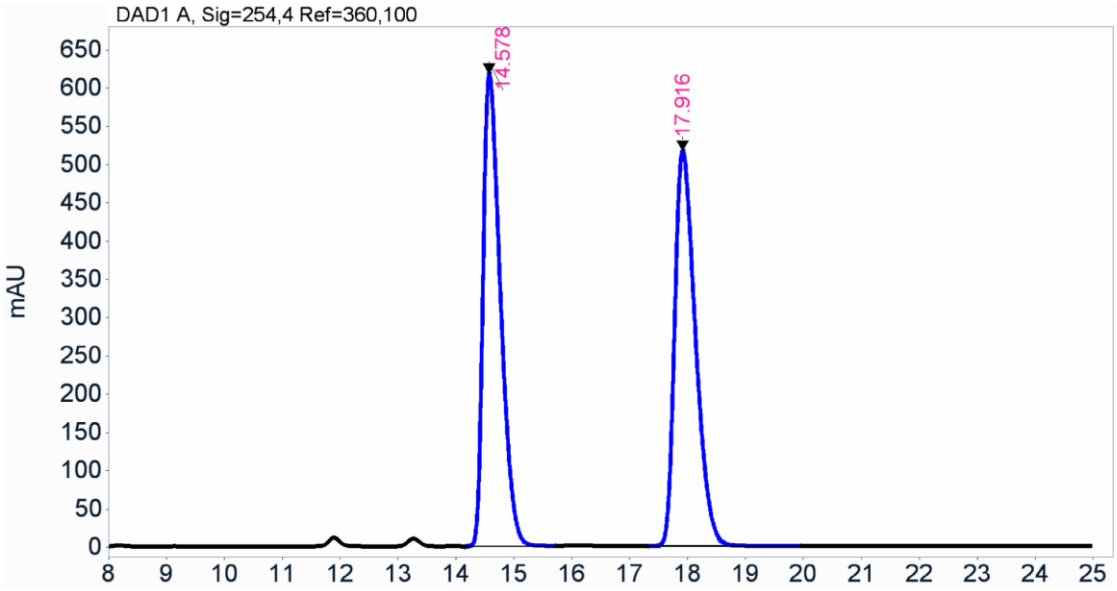
Meas. R	Area %	Width	Symmetr.
20.619	50.066	1.003	0.413
33.395	49.934	1.897	0.380



Meas. R	Area %	Width	Symmetr.
20.146	94.973	0.997	0.437
33.033	5.027	1.577	0.399

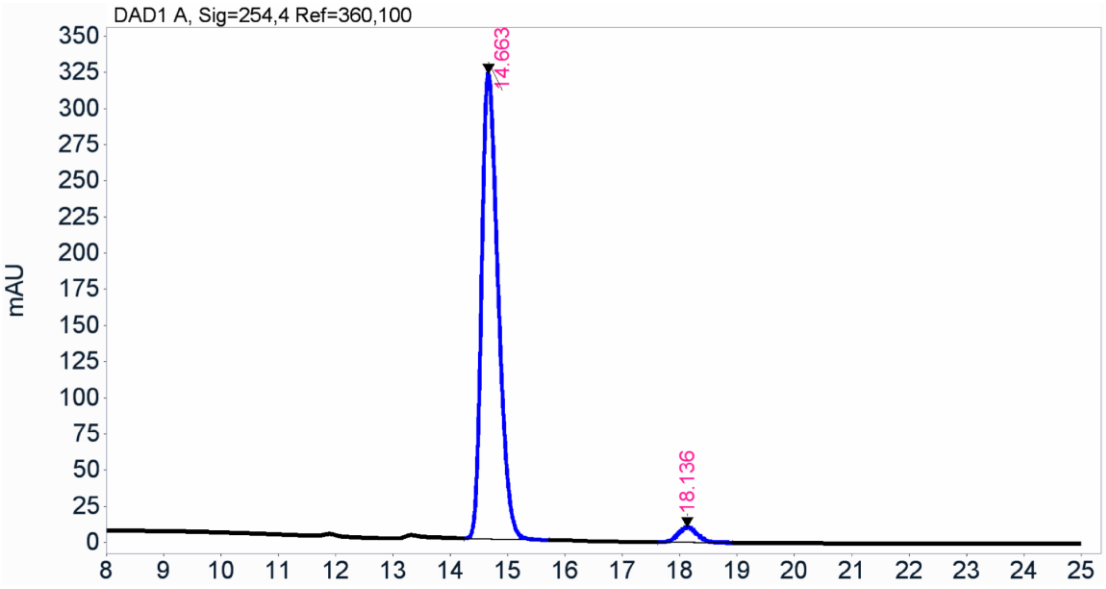


6g



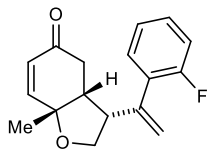
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
14.578	BB	0.3182	12826.607	617.9027	49.89
17.916	BB	0.3847	12882.472	516.9658	50.11

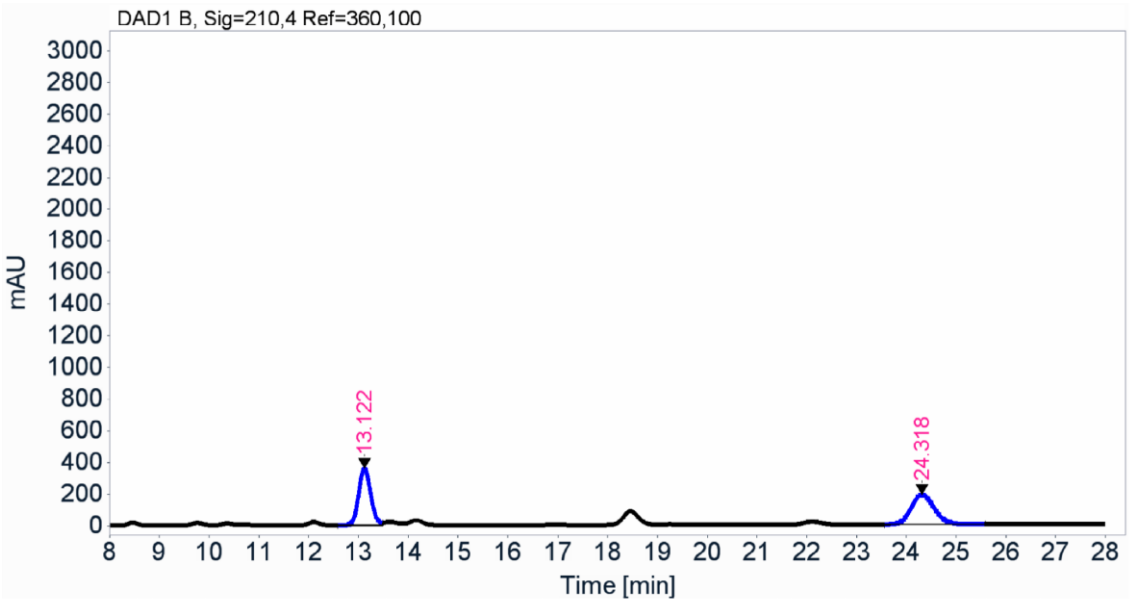


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
14.663	BB	0.3088	6413.282	321.3834	96.33
18.136	BB	0.3662	244.094	10.3874	3.67

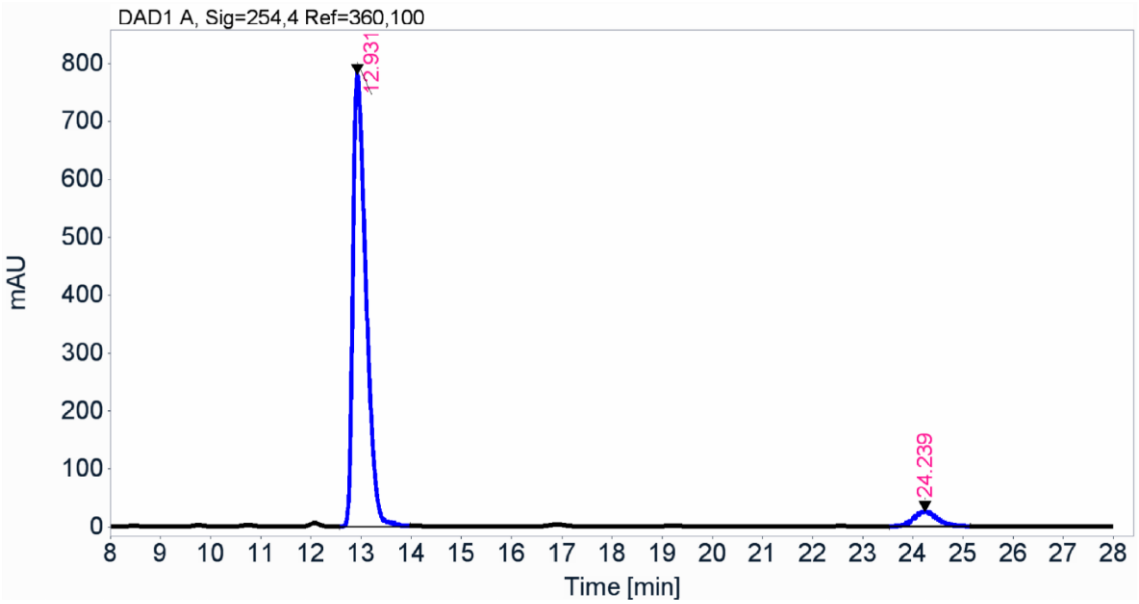


6h



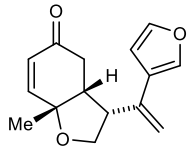
Signal: DAD1 B, Sig=210,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
13.122	BV	0.2637	6078.377	358.7408	50.04
24.318	BB	0.5050	6068.752	187.7845	49.96

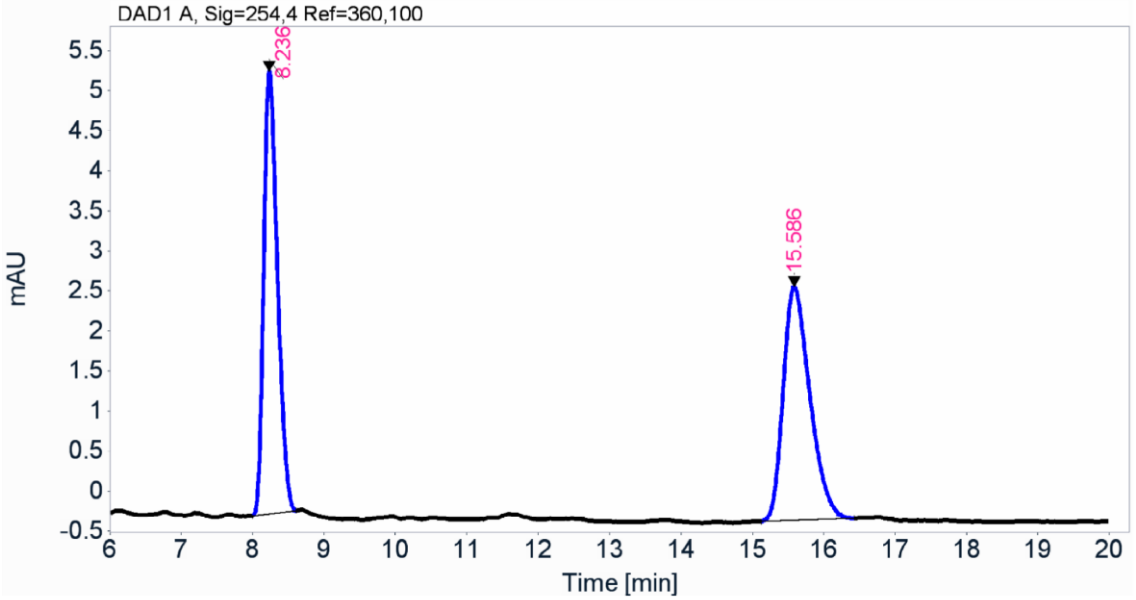


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
12.931	MM	0.3026	14165.936	780.1082	94.53
24.239	MM	0.5399	819.972	25.3114	5.47

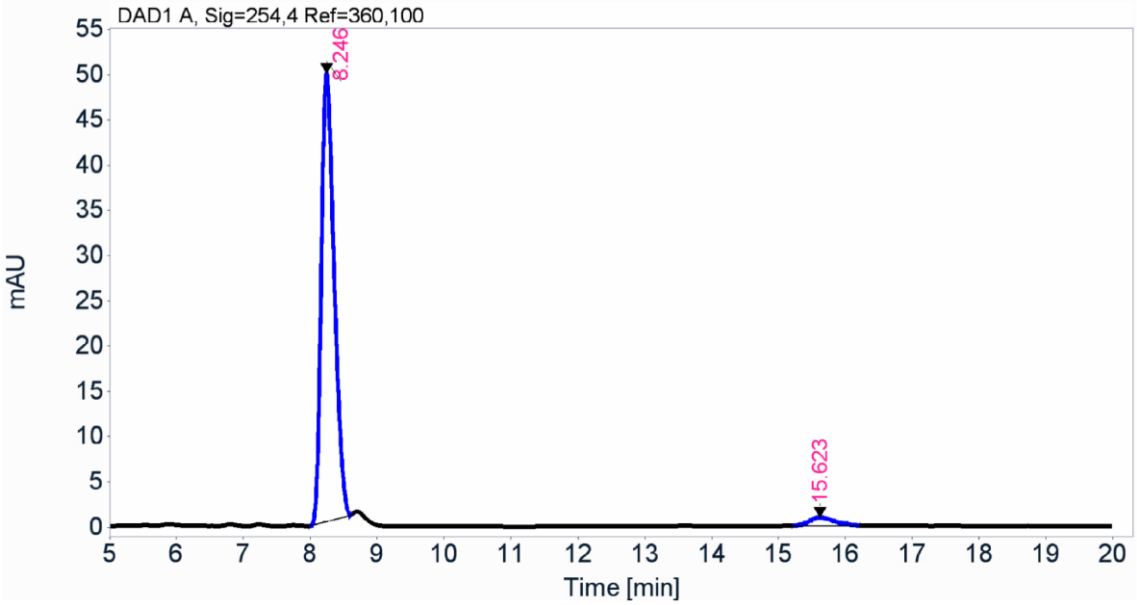


6i



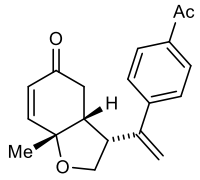
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.236	BB	0.2037	73.752	5.5267	49.36
15.586	BB	0.3894	75.651	2.9088	50.64

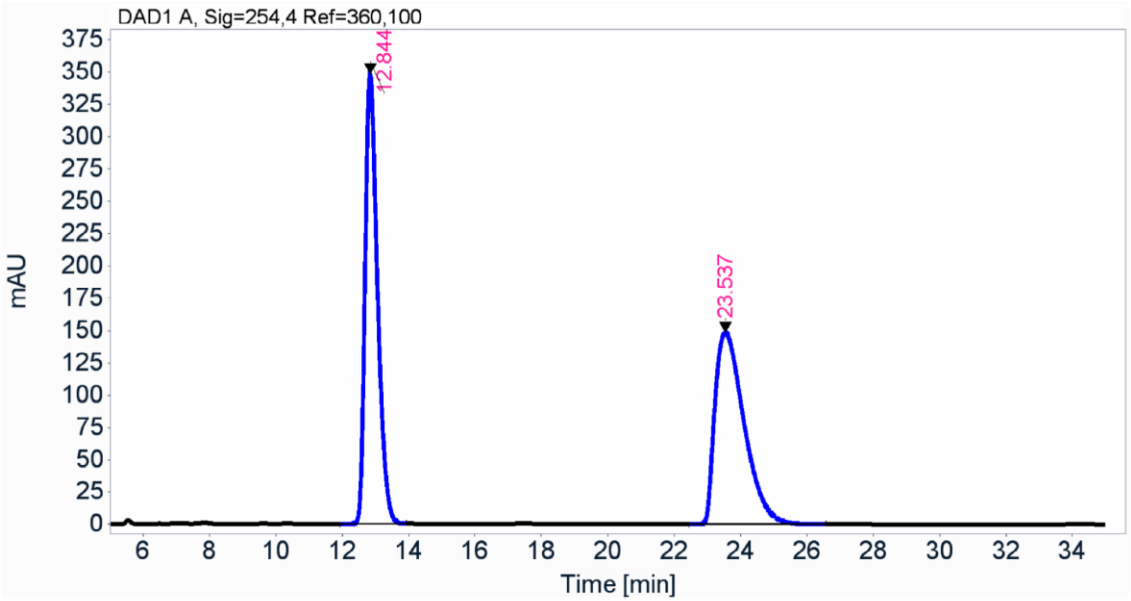


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.246	MM	0.2228	662.477	49.5642	96.26
15.623	MM	0.4498	25.769	0.9548	3.74

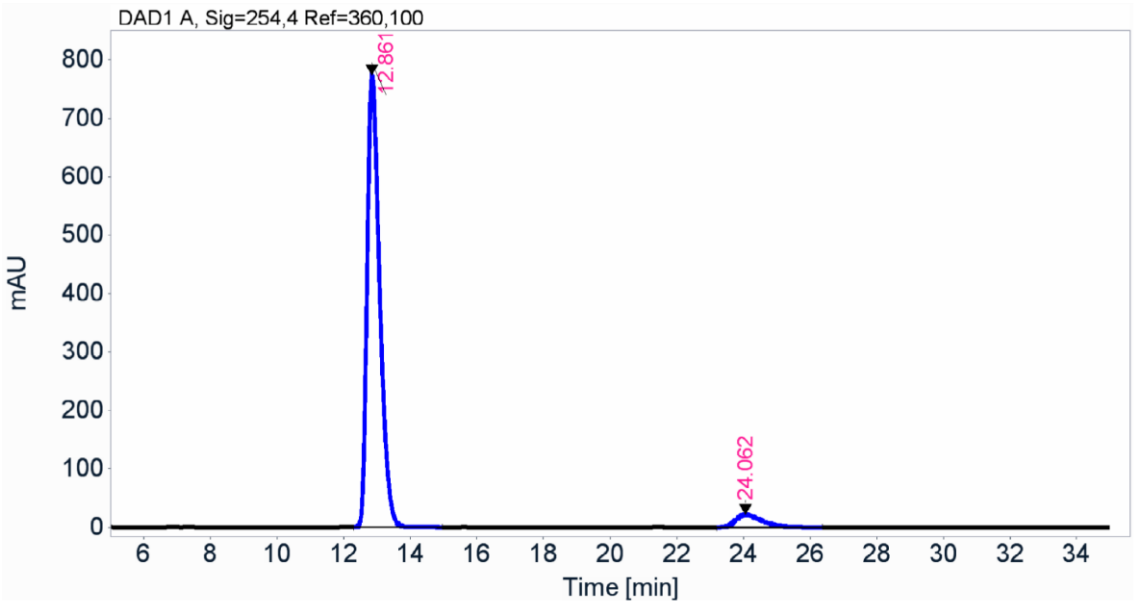


6j



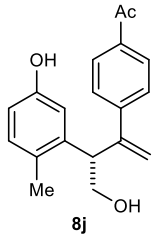
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
12.844	BB	0.3925	9030.498	348.3251	49.94
23.537	BB	0.9593	9053.084	148.4891	50.06

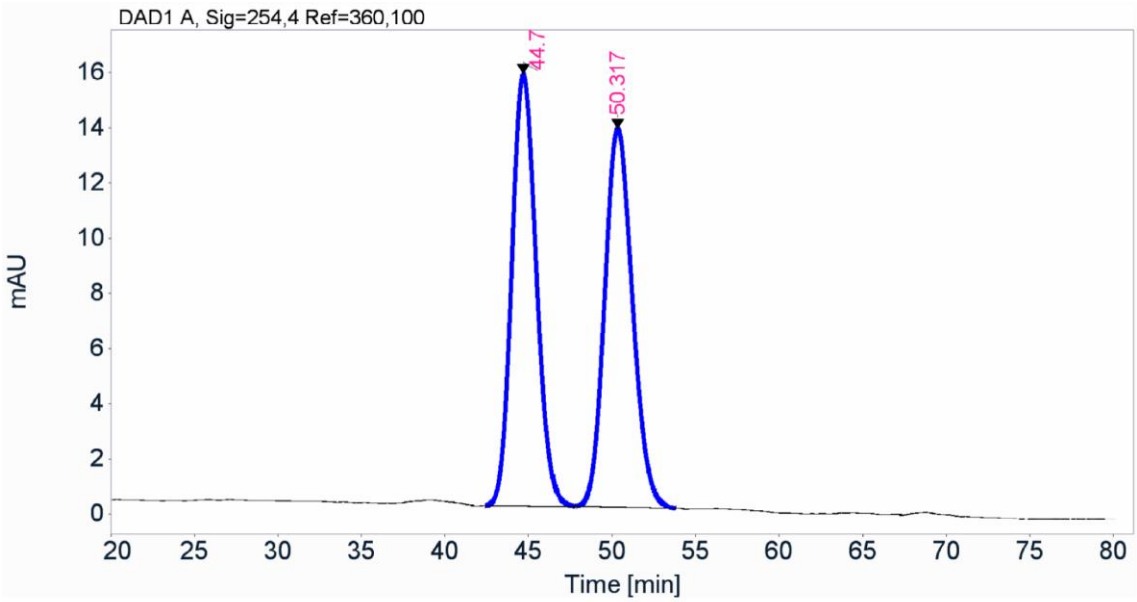


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
12.861	BB	0.3997	20269.092	773.5542	94.62
24.062	BB	0.8234	1151.484	21.2768	5.38

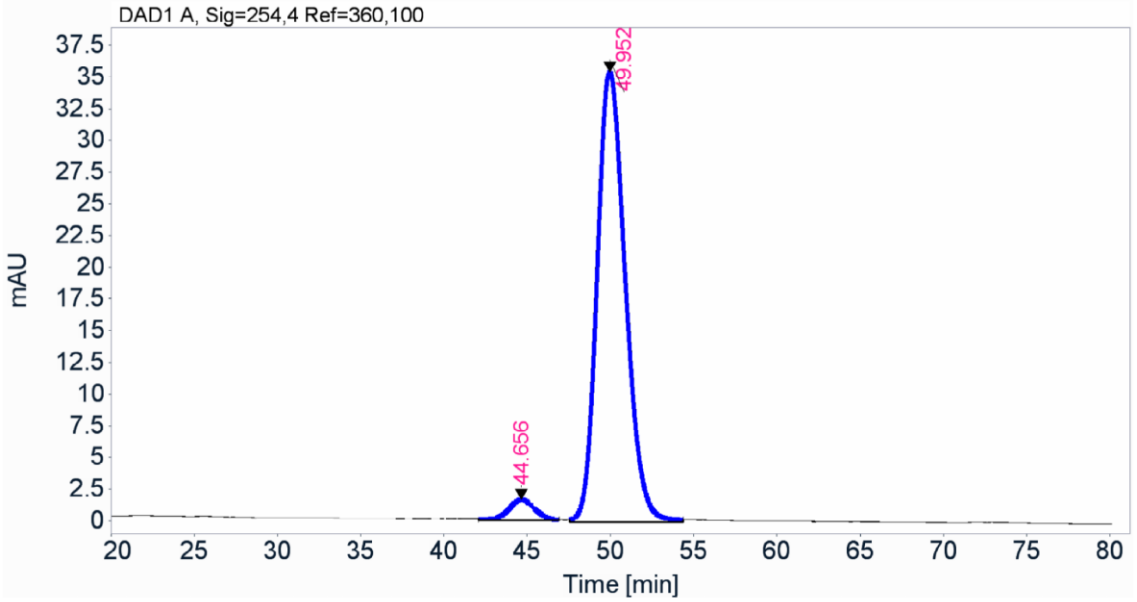


8j



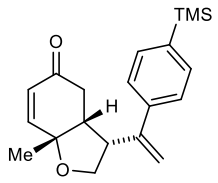
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
44.700	BB	1.4141	1592.557	15.6380	50.05
50.317	BB	1.6216	1589.620	13.7008	49.95

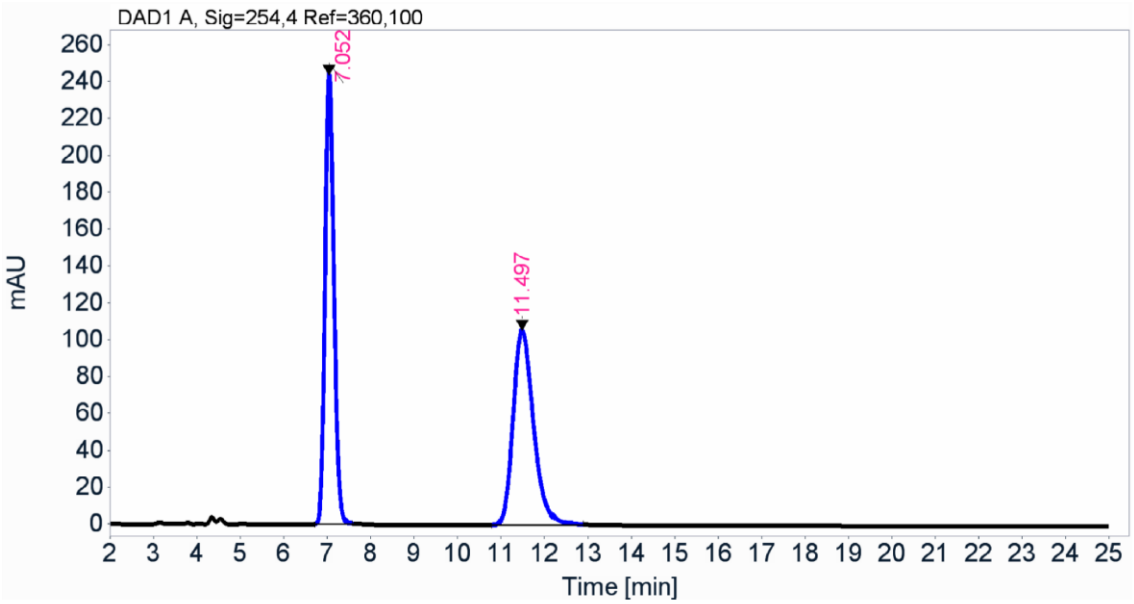


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
44.656	MM	1.8209	178.184	1.6309	4.08
49.952	MM	1.9676	4186.523	35.4628	95.92

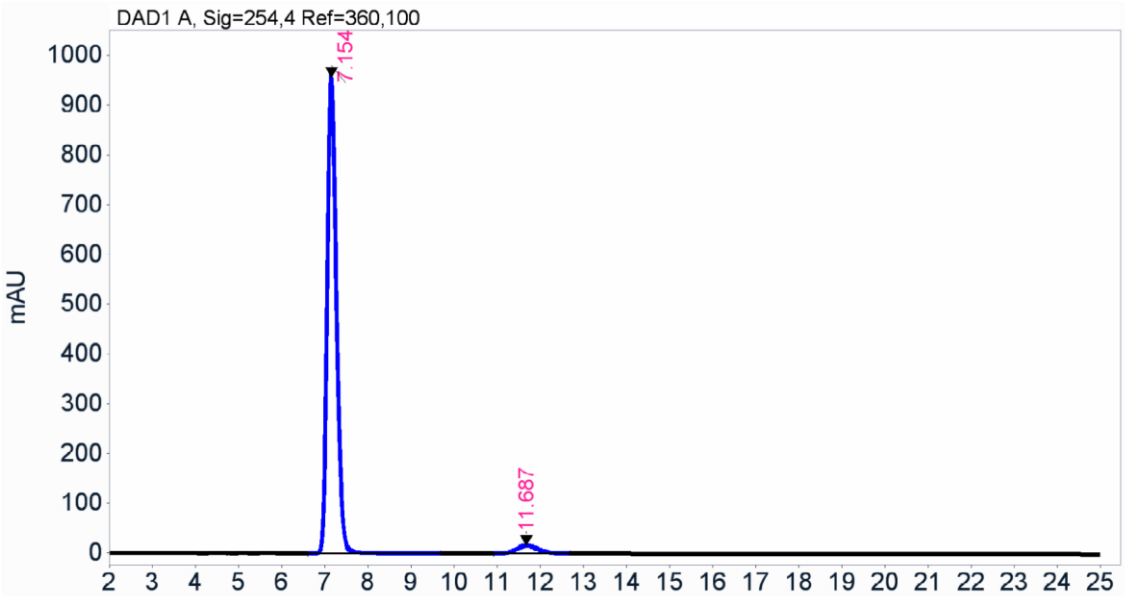


6k



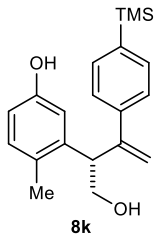
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
7.052	MM	0.2385	3489.686	243.8624	50.22
11.497	MM	0.5461	3459.281	105.5840	49.78

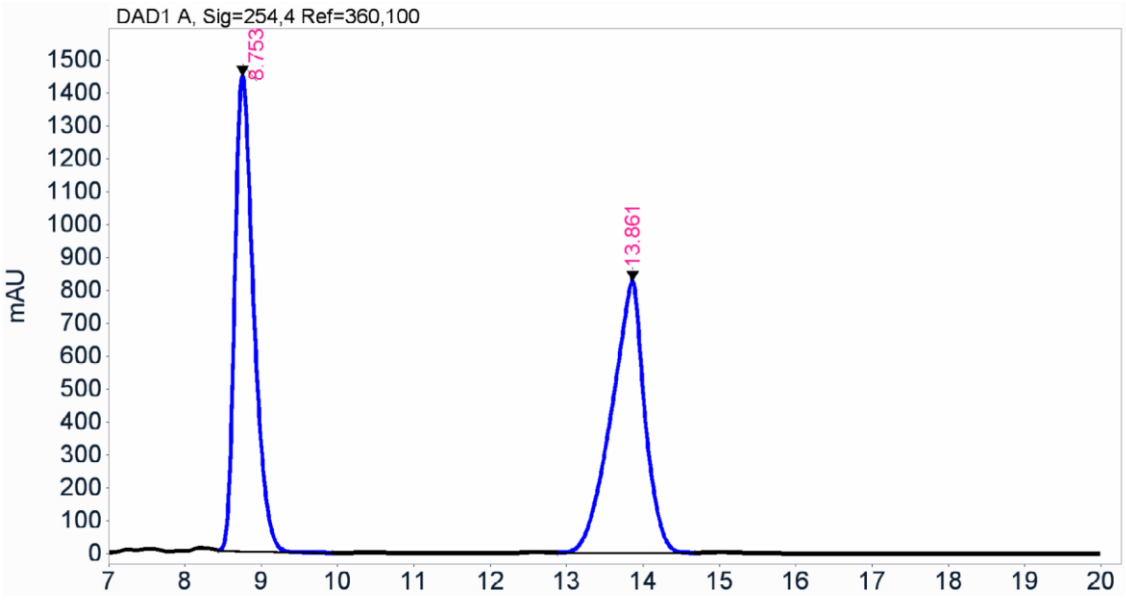


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
7.154	BB	0.2327	14323.915	956.4127	96.28
11.687	MM	0.5599	553.358	16.4722	3.72

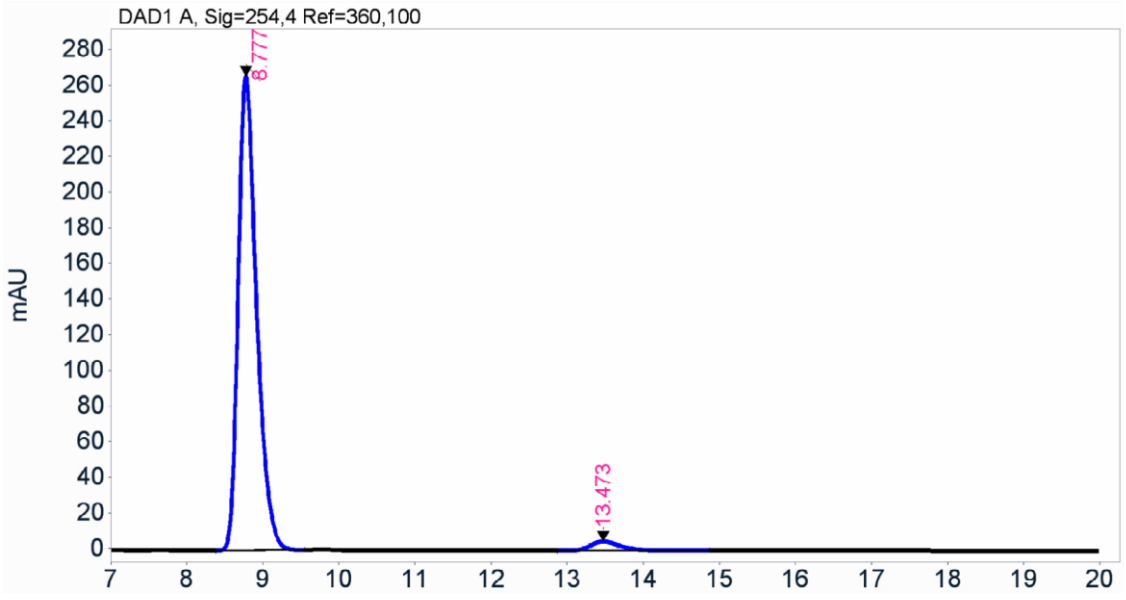


8k



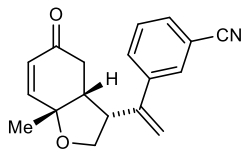
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.753	VB	0.2629	24891.861	1445.1952	49.83
13.861	VB	0.4259	25061.650	826.1180	50.17

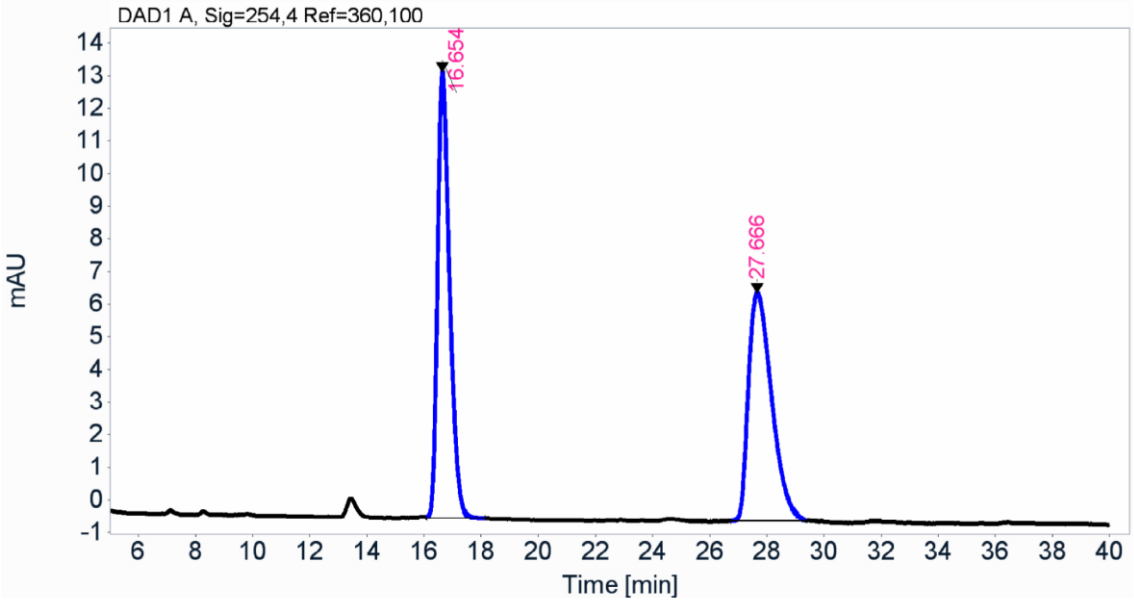


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
8.777	BB	0.2516	4457.850	265.8970	96.85
13.473	BB	0.4097	145.216	5.3319	3.15

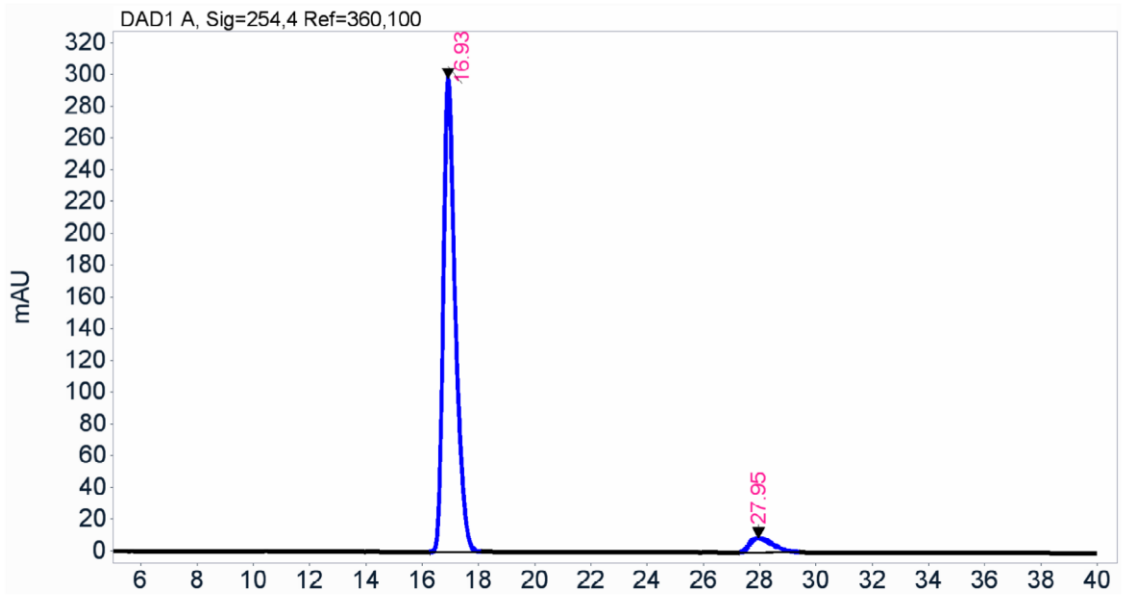


6l



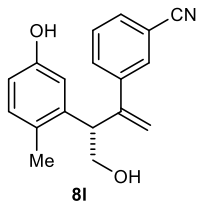
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
16.654	BB	0.4411	400.841	13.6306	50.41
27.666	BB	0.8404	394.338	6.9663	49.59

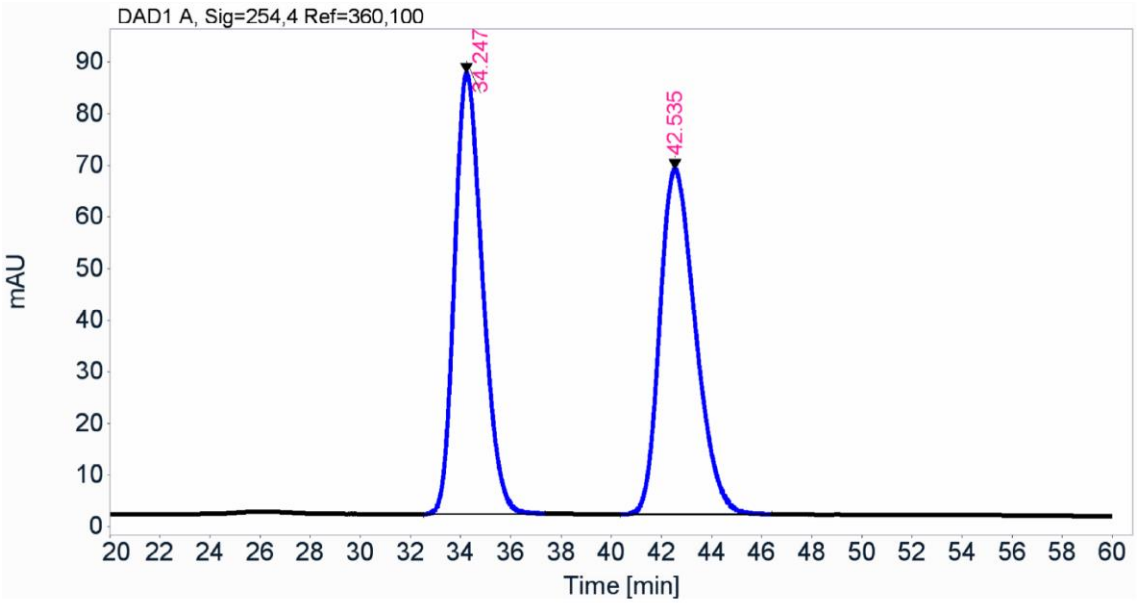


Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
16.930	MM	0.4961	8875.673	298.1926	94.45
27.950	MM	0.9534	521.583	9.1178	5.55

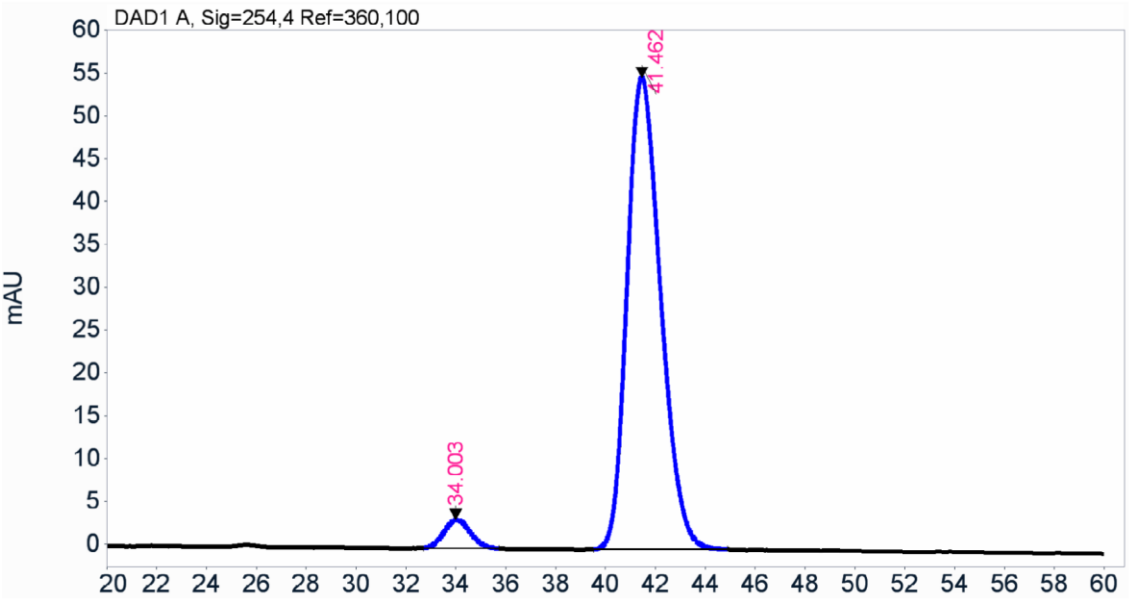


8l



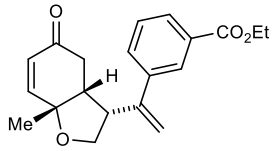
Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
34.247	BB	1.1861	6593.869	85.2783	49.96
42.535	BB	1.4885	6604.920	66.7457	50.04

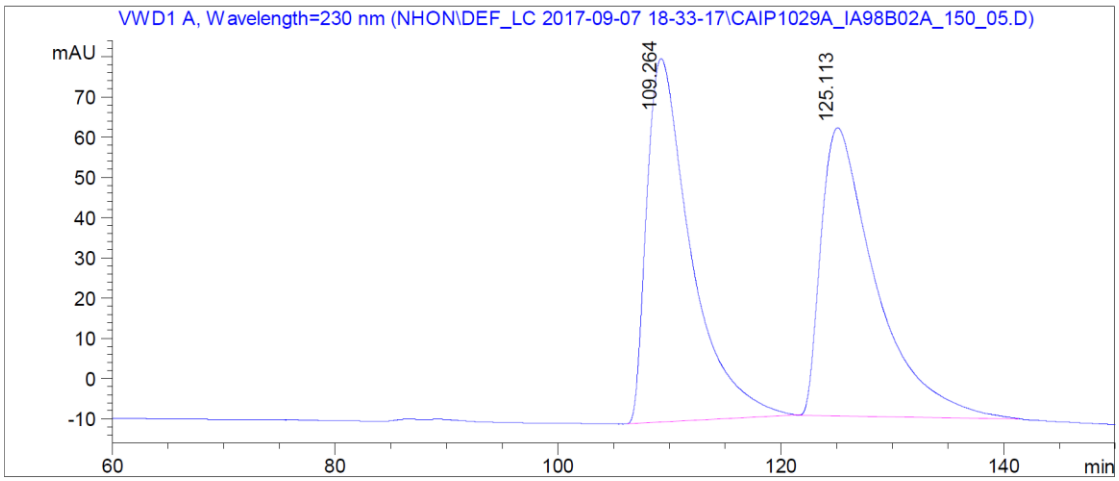


Signal: DAD1 A, Sig=254,4 Ref=360,100

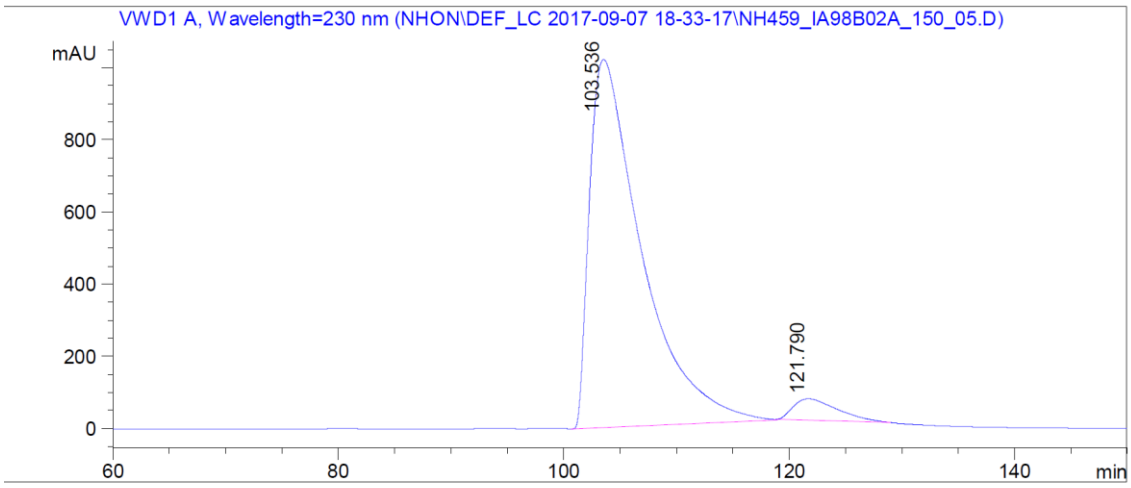
RT [min]	Type	Width [min]	Area	Height	Area%
34.003	BB	0.8898	241.182	3.3032	4.47
41.462	BB	1.3871	5151.126	55.0788	95.53



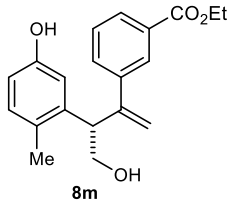
6m



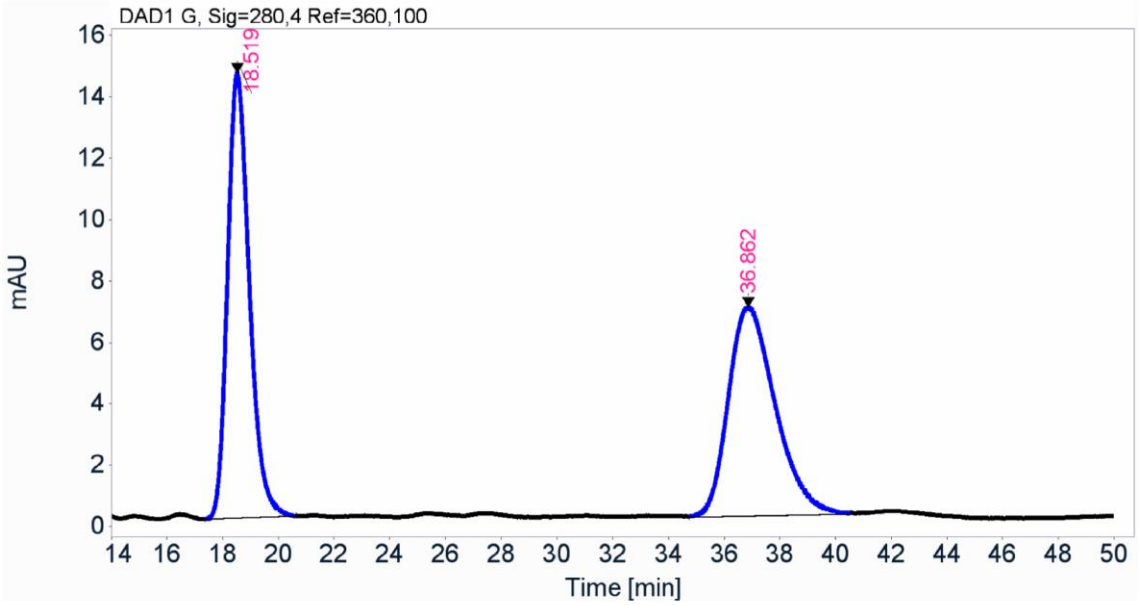
Meas. R	Area %	Width	Symmetr.
109.264	50.456	4.581	0.476
125.113	49.544	5.679	0.428



Meas. R	Area %	Width	Symmetr.
103.536	95.277	5.353	0.347
121.790	4.723	4.575	0.510

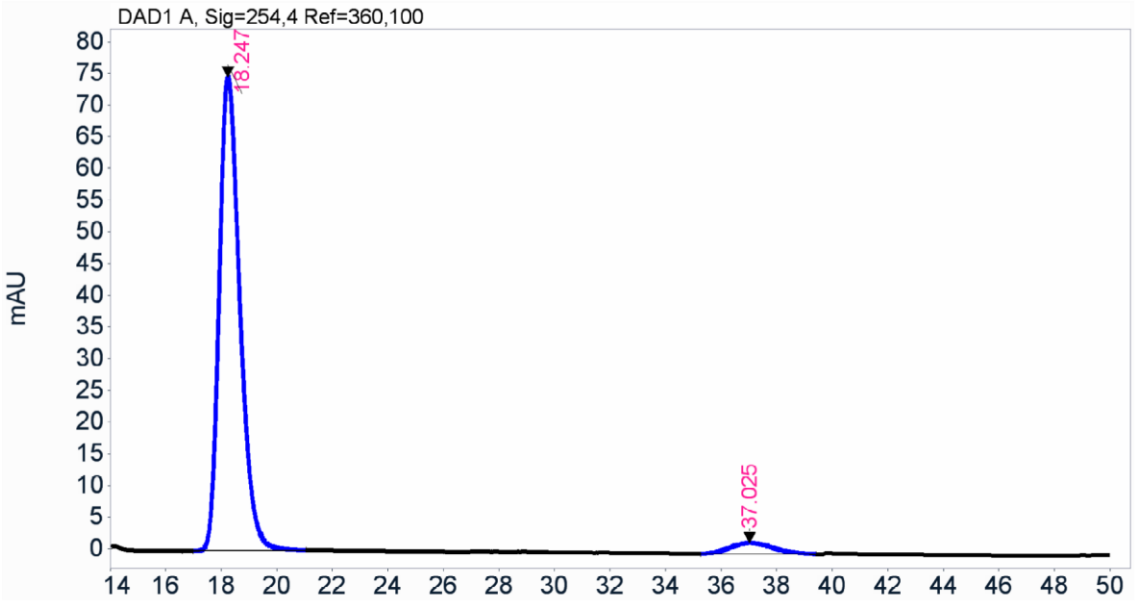


8m



Signal: DAD1 G, Sig=280,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
18.519	BB	0.8353	787.944	14.4693	49.64
36.862	MM	1.9649	799.514	6.7815	50.36



Signal: DAD1 A, Sig=254,4 Ref=360,100

RT [min]	Type	Width [min]	Area	Height	Area%
18.247	BB	0.7974	3852.034	74.7266	95.38
37.025	MM	1.7731	186.770	1.7556	4.62

References

1. Tello-Aburto, R.; Kalstabakken, K. A.; Harned, A. M. *Org. Biomol. Chem.* **2013**, *11*, 5596.
2. Keilitz, J.; Newman, S. G.; Lautens, M. *Org. Lett.* **2013**, *15*, 1148.
3. He, Z.-T.; Tang, X.-Q.; Xie, L.-B.; Cheng, M.; Tian, P.; Lin, G.-Q. *Angew. Chem., Int. Ed.* **2015**, *54*, 14815.