Supporting Information

Mn-Catalyzed Radical Initiated Domino Transformations of Alkynylated Cyclohexadienones with $TMSN_3$ and O_2 to Bicyclic Azido Alcohols

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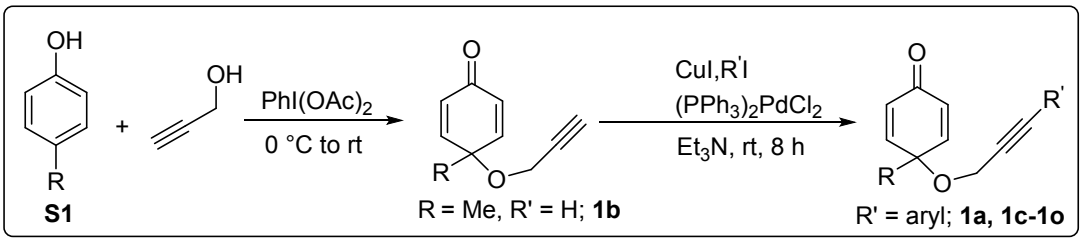
1. General information

All chemicals have been purchased from commercial sources and were used without further purification unless otherwise noted. All solvents are reagent grade or HPLC grade. Anhydrous acetonitrile (CH_3CN), dichloromethane (CH_2Cl_2) and *N,N*-dimethylformamide (DMF) were obtained from a dry solvent system. Dichloromethane was freshly distilled from CaH_2 and anhydrous tetrahydrofuran (THF) was freshly distilled from sodium-benzophenone. The synthetic transformations have been monitored by thin layer chromatography (TLC). TLC was performed on silica gel 60 F_{254} plates (glass plates). Concentration under reduced pressure was performed by rotary evaporation below 45 °C. Column chromatography was performed using silica gel (100-200 mesh) packed in glass columns. Yields refer to spectroscopically pure compounds after isolation. ^1H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ using 300, 400 or 500 MHz (^1H), 75, 100 or 125 MHz (^{13}C) and 377 MHz (^{19}F). Chemical shifts (δ-values) are reported in ppm, spectra were calibrated related to solvents' residual proton chemical shifts ($CDCl_3$, δ = 7.26) and solvents' residual carbon chemical shifts ($CDCl_3$, δ = 77.16 ppm), multiplicity is reported as follows: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved and coupling constant *J* in Hz. Melting points (mp) were determined in open capillaries and are uncorrected. Infrared spectra (IR) were recorded on a 0.1 mm KBr demountable cell. High-resolution mass spectra (HRMS) were obtained by electrospray ionization using a Q-TOF mass spectrometer in positive ion mode (M+H or M+Na) as indicated.

2. General procedure and data for bicyclic azido alcohols

General procedure for alkyl tethered cyclohexadienones (1a-1p):[1]



To a stirred solution of 4-substituted phenol (**S1**) (1.0 mmol) in 1 mL of propargyl alcohol was added phenyliodine (III) diacetate (1.5 mmol) in several portions at 0 °C. The resulting reaction mixture was stirred at room temperature for overnight. Then the reaction mixture was diluted with water (10 mL) and extracted with ethyl acetate (3 x 15 mL).The combined organic solvent was washed with brine (15 mL), dried (Na_2SO_4), filtered and concentrated under reduced pressure. The crude reaction mixture was purified by column chromatography (20% EtOAc in hexanes) to give *O*-tethered alkyne.

To the above *O*-tethered alkyne (10.0 mmol) in degassed Et_3N (1 M, 10 mL), was added $Pd(PPh_3)_2Cl_2$ (3 mol%), CuI (1.5 mol%) and aryl iodide (12 mmol). The mixture was stirred at room temperature for 8 h. The reaction was cooled to room temperature, water (50 mL) was added and the mixture was extracted with EtOAc (2 x 40 mL). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated *in vacuo*. The mixture was purified by column chromatography (EtOAc/hexane) to give aryl substituted alkynes **(1a, 1c-1o)** in good yields.

General procedure for bicyclic azido alcohols: To a solution of alkyne-tethered cyclohexadienone **1** (100-160 mg, 0.42 mmol) in acetonitrile (2 mL), were added $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol, 50 mol%) and $TMSN_3$ (0.28 mL, 2.1 mmol, 5 eq). Oxygen balloon was applied and the reaction mixture was stirred at room temperature for 6-24 h. After completion of reaction (monitored by TLC), the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using hexanes and ethyl acetate as eluents to afford the corresponding bicyclic azido alcohol **2**.

3-Azido-5-hydroxy-8a-methyl-4-phenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2a): By following the general procedure, the reaction was performed with **1a** (100 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 20 h. The residue was purified by flash column

chromatography on silica gel (10% EtOAc/hexanes) to afford **2a** (96 mg, 77%) as a pale orange solid. mp 117-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (m, 2H), 7.29 (m, 3H), 6.74 (d, *J* = 10.0 Hz, 1H), 6.15 (d, *J* = 10.0 Hz, 1H), 4.59 (d, *J* = 16.0 Hz, 1H), 4.48 (dd, *J* = 10.9, 2.5 Hz, 1H), 4.42 (dd, *J* = 16.0, 1.5 Hz, 1H), 3.10 (d, *J* = 2.6 Hz, 1H), 2.80 (dd, *J* = 10.9, 1.2 Hz, 1H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 150.3, 138.7, 128.6, 128.1, 127.8, 127.5, 126.5, 123.7, 75.8, 71.8, 61.1, 49.9, 22.8. IR (thin film): ν_{max}/cm^{-1} 3393, 2925, 2110, 1699, 1455, 1377, 1228, 1093, 758. HRMS (ESI): *m/z* calculated for $[M+Na]^+$ $C_{16}H_{15}N_3O_3Na$ 320.1011, found 320.1017.

3-Azido-5-hydroxy-8a-methyl-4-(*m*-tolyl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2c): By following the general procedure, the reaction was performed with **1c** (106 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 20 h. The residue was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford **2c** (98 mg, 75%) as a grey solid. mp 111-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22-7.15 (m, 4H), 6.74 (d, *J* = 10.0 Hz, 1H), 6.15 (d, *J* = 10.0 Hz, 1H), 4.58 (d, *J* = 16.0 Hz, 1H), 4.47 (dd, *J* = 10.9, 2.3 Hz, 1H), 4.41 (dd, *J* = 16.0, 1.4 Hz, 1H), 3.13 (d, *J* = 2.4 Hz, 1H), 2.78 (d, *J* = 11.5 Hz, 1H), 2.35 (s, 3H), 1.59 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.5, 150.3, 137.3, 135.8, 129.0, 128.3, 127.3, 126.5, 123.6, 75.9, 71.8, 61.1, 49.9, 22.8, 21.4. IR (thin film): ν_{max}/cm^{-1} 3374, 2941, 2108, 1697, 1455, 1379, 1295, 1105, 762. HRMS (ESI): *m/z* calculated for $[M+Na]^+$ $C_{17}H_{17}N_3O_3Na$ 334.1168, found 334.1171.

3-Azido-5-hydroxy-4-(4-methoxyphenyl)-8a-methyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2d): By following the general procedure, the reaction was performed with **1d** (112 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 18 h. The residue was purified by flash column chromatography on silica gel (15% EtOAc/hexanes) to afford **2d** (109 mg, 80%) as red semi solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.8 Hz, 2H), 6.90 (d, *J* = 8.8 Hz, 2H), 6.74 (d, *J* = 10.0 Hz, 1H), 6.15 (d, *J* = 10.0 Hz, 1H), 4.58 (d, *J* = 16.0 Hz, 1H), 4.47 (d, *J* = 10.9 Hz, 1H), 4.41 (dd, *J* = 16.0, 1.4 Hz, 1H), 3.81 (s, 3H), 3.13 (s, 1H), 2.77 (d, *J* = 11.7 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 150.4, 131.0, 129.7, 127.1, 126.5, 126.1, 123.3, 113.6, 75.9, 71.9, 61.1, 55.3, 49.89, 22.8. IR (thin film): ν_{max}/cm^{-1} 3382, 2988, 2111, 1696, 1426, 1339, 1290, 1133, 765. HRMS (ESI): *m/z* calculated for $[M+Na]^+$ $C_{17}H_{17}N_3O_4Na$ 350.1117, found 350.1123.

3-Azido-4-(4-chlorophenyl)-5-hydroxy-8a-methyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2e): By following the general procedure, the reaction was performed with **1e** (114.5 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 24 h. The residue was purified by flash column chromatography on silica gel (15% EtOAc/hexanes) to afford **2e** (49 mg, 35%) as a brown sticky solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, J = 8.6 Hz, 2H), 7.23 (d, J = 8.6 Hz, 2H), 6.74 (d, J = 10.0 Hz, 1H), 6.16 (d, J = 10.0 Hz, 1H), 4.59 (d, J = 16.1 Hz, 1H), 4.47 – 4.40 (m, 2H), 3.14 (s, 1H), 2.74 (d, J = 10.9 Hz, 1H), 1.58 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 150.2, 137.2, 129.9, 128.4, 128.3, 126.4, 122.5, 75.8, 71.8, 60.9, 49.8, 22.7. IR (thin film): ν_{max}/cm^{-1} 3390, 2999, 2110, 1692, 1438, 1300, 1275, 1112, 766.

3-Azido-5-hydroxy-8a-methyl-4-(4-nitrophenyl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2f): By following the general procedure, the reaction was performed with **1f** (119 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 24 h. The residue was purified by flash column chromatography on silica gel (15% EtOAc/hexanes) to afford **2f** (57.5 mg, 40%) as a brown sticky liquid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.21 (d, J = 8.8 Hz, 2H), 7.45 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 10.1 Hz, 1H), 6.18 (d, J = 10.1 Hz, 1H), 4.65 (d, J = 16.3 Hz, 1H), 4.51 – 4.41 (m, 2H), 3.13 (s, 1H), 2.79 (d, J = 10.9 Hz, 1H), 1.61 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 150.0, 146.7, 145.7, 130.0, 129.6, 126.5, 123.4, 121.5, 75.6, 71.8, 60.8, 49.5, 22.7. IR (thin film): ν_{max}/cm^{-1} 3368, 2932, 2110, 1728, 1611, 1515, 1348, 1248, 1067, 756.

4-(3-Azido-5-hydroxy-8a-methyl-6-oxo-4a,5,6,8a-tetrahydro-2*H*-chromen-4-yl)benzonitrile (2g): By following the general procedure, the reaction was performed with **1g** (110 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 24 h. The residue was purified by flash column chromatography on silica gel (15% EtOAc/hexanes) to afford **2g** (40.5 mg, 30%) as a pale yellow solid. mp 105-106 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 6.75 (d, J = 10.0 Hz, 1H), 6.17 (d, J = 10.0 Hz, 1H), 4.64 (d, J = 16.3 Hz, 1H), 4.44 (dd, J = 13.3, 6.6 Hz, 2H), 3.13 (s, 1H), 2.74 (d, J = 10.9 Hz, 1H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 150.0, 143.7, 131.9, 129.4, 126.5, 121.8, 119.0, 110.9, 75.6, 71.8, 60.8, 49.4, 22.8. IR (thin film): ν_{max}/cm^{-1} 2993, 1690, 1389, 1173, 1068, 771.

3-Azido-5-hydroxy-8a-methyl-4-(4-(trifluoromethyl)phenyl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2h): By following the general procedure, the reaction was performed with **1h** (129 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 24 h. The residue was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford **2h** (64.6 mg, 42%) as a pale brown solid. mp 95-96 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.1 Hz, 2H), 6.75 (d, J = 10.0 Hz, 1H), 6.17 (d, J = 10.0 Hz, 1H), 4.63 (d, J = 16.2 Hz, 1H), 4.50 – 4.42 (m, 2H), 3.13 (s, 1H), 2.78 (d, J = 11.8 Hz, 1H), 1.60 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 150.1, 142.5, 128.9 (q, J_{CF} = 30 Hz), 126.5, 125.1, 125.0 (q, J_{CF} = 270 Hz), 122.3, 75.7, 71.8, 60.9, 49.7, 22.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.5. IR (thin film): ν_{max}/cm^{-1} 3359, 3021, 2404, 2111, 1695, 1519, 1426, 1215, 744. HRMS (ESI): *m/z* calculated for $[M+Na]^+$ $C_{17}H_{14}F_3N_3O_3Na$ 388.0885, found 388.09.

3-Azido-5-hydroxy-8a-methyl-4-(naphthalen-1-yl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2i): By following the general procedure, the reaction was performed with **1i** (121 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 6 h. The residue was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford **2i** (99 mg, 68%) as a brown solid. mp 120-121 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (*dr* ratio 5:2 observed) δ 8.02 (d, J = 8.2 Hz, 1H), 7.85 (dd, J = 28.7, 8.0 Hz, 2H), 7.57 – 7.45 (m, 3H), 7.14 (d, J = 7.0 Hz, 1H), 6.77 (d, J = 10.1 Hz, 1H), 6.16 (d, J = 10.1 Hz, 1H), 4.61 (dd, J = 28.1, 12.8 Hz, 2H), 4.44 (d, J = 17.6 Hz, 1H), 2.97 (d, J = 10.3 Hz, 1H), 2.86 (d, J = 10.8 Hz, 1H), 1.71 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) (minor diastereomer in parathesis) δ 199.3, 150.1 (150.56), 137.4 (134.6), 133.3 (133.8), 131.3 (131.2), 130.1 (130.81), 128.6 (129.7), 128.12 (129.3), 126.6 (126.5), 126.4, 126.1 (126.2), 125.0 (125.6), 124.8 (125.2), 123.9 (123.8), 121.4, 75.3 (75.6), 71.8 (72.3), 61.1 (61.33), 52.0 (48.9), 22.9 (23.6). IR (thin film): ν_{max}/cm^{-1} 3490, 2926, 2108, 1695, 1447, 1380, 1295, 1091, 787. HRMS (ESI): *m/z* calculated for $[M+Na]^+$ $C_{20}H_{17}N_3O_3Na$ 370.1168, found 370.1168.

3-Azido-5-hydroxy-8a-methyl-4-(phenanthren-9-yl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2j): By following the general procedure, the reaction was performed with **1j** (142 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 12 h. The residue was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford **2j** (106 mg, 64%) as a pale

yellow solid. mp 128-129 °C. ^{1}H NMR (400 MHz, $CDCl_3$) (*dr* ratio 5:2 observed) δ 8.71 (dd, *J* = 23.6, 9.9 Hz, 2H), 8.09 (d, *J* = 7.6 Hz, 1H), 7.82 – 7.76 (m, 1H), 7.71 – 7.54 (m, 5H), 6.81 (d, *J* = 10.1 Hz, 1H), 6.18 (d, *J* = 10.1 Hz, 1H), 4.71 – 4.45 (m, 3H), 3.09 – 2.85 (m, 2H), 1.78 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) (minor diastereomer in parathesis) δ 199.3, 150.1 (150.57), 136.5, 131.3 (130.5),131.0, 130.2 (130.1), 130.0, 128.5 (129.2), 127.4, 126.9 (127.0), 126.8 (126.8), 126.5 (126.61), 126.4, 125.7, 124.7, 123.9, 123.1, 122.9, 121.2, 75.3 (75.67), 71.9 (72.34), 61.0 (61.5), 52.2 (48.5), 23.1 (23.7). IR (thin film): ν_{max}/cm^{-1} 3493, 2977, 2109, 1695, 1452, 1378, 1294, 1093, 761. HRMS (ESI): *m/z* calculated for $[M+Na]^+$ $C_{24}H_{19}N_3O_3Na$ 420.1324, found 420.1324.

3-Azido-8a-ethyl-5-hydroxy-4-phenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2l): By following the general procedure, the reaction was performed with **1l** (106 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 24 h. The residue was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford **2l** (91.5 mg 70%) as a greenish yellow solid. mp 90-91 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 77.39 – 7.35 (m, 2H), 7.29 (d, *J* = 7.7 Hz, 3H), 6.79 (d, *J* = 10.2 Hz, 1H), 6.23 (d, *J* = 10.2 Hz, 1H), 4.57 (d, *J* = 16.1 Hz, 1H), 4.52 (d, *J* = 10.9 Hz, 1H), 4.41 (dd, *J* = 16.1, 1.5 Hz, 1H), 3.14 (s, 1H), 2.90 (d, *J* = 10.9 Hz, 1H), 2.02 (m, 1H), 1.91 (m, 1H), 1.04 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.5, 148.9, 138.9, 128.6, 128.2, 127.8, 127.5, 123.7, 75.9, 74.6, 61.2, 47.4, 27.3, 8.2. IR (thin film): ν_{max}/cm^{-1} 3390, 2925, 2111, 1698, 1455, 1377, 1218, 1093, 756. HRMS (ESI): *m/z* calculated for $[M+Na]^+$ $C_{17}H_{17}N_3O_3Na$ 334.1168, found 334.1161.

3-Azido-5-hydroxy-8a-isopropyl-4-phenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2m): By following the general procedure, the reaction was performed with **1m** (112 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 10 h. The residue was purified by flash column chromatography on silica gel (6% EtOAc/hexanes) to afford **2m** (87.5 mg 64%) as a pale green solid. mp 72-73 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.32 – 7.27 (m, 3H), 6.86 (d, *J* = 10.3 Hz, 1H), 6.28 (d, *J* = 10.3 Hz, 1H), 4.63 – 4.51 (m, 2H), 4.37 (dd, *J* = 16.1, 1.4 Hz, 1H), 3.16 (d, *J* = 2.8 Hz, 1H), 3.07 (d, *J* = 11.8 Hz, 1H), 2.57 – 2.47 (m, 1H), 1.17 (d, *J* = 6.8 Hz, 3H), 0.96 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 145.9, 138.9, 128.9, 128.6, 128.2, 127.5, 123.5, 76.4, 61.3, 47.1, 28.9, 18.5, 15.8. IR (thin film): ν_{max}/cm^{-1} 3381, 2926, 2109, 1696, 1461, 1392, 1288, 1107, 765.

3-Azido-5-hydroxy-4,8a-diphenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2n): By following the general procedure, the reaction was performed with **1n** (126 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 24 h. The residue was purified by flash column chromatography on silica gel (10% EtOAc/hexanes) to afford **2n** (120.5 mg 80%) as a pale green sticky solid. ^{1}H NMR (400 MHz, $CDCl_3$) (*dr* 10:1.5 observed) δ 7.57 – 7.47 (m, 5H), 7.42 – 7.35 (m, 5H), 6.76 (d, *J* = 10.0 Hz, 1H), 6.10 (d, *J* = 10.0 Hz, 1H), 4.77 (d, *J* = 8.9 Hz, 1H), 4.58 (d, *J* = 15.9 Hz, 1H), 4.25 (d, *J* = 17.2 Hz, 1H), 3.65 (d, *J* = 10.7 Hz, 1H), 3.32 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 151.2, 139.8, 138.4, 129.6, 128.9, 128.7, 128.4, 128.2, 127.6, 127.2, 126.1, 125.3, 76.5, 76.3, 61.7, 46.9. IR (thin film): ν_{max}/cm^{-1} 3399, 2929, 2110, 1689, 1445, 1380, 1219, 1099, 759.

3-Azido-8a-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-5-hydroxy-4-phenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2o): By following the general procedure, the reaction was performed with **1o** (160.5 mg, 0.42 mmol) using $Mn(OAc)_3 2H_2O$ (56 mg, 0.21 mmol) and $TMSN_3$ (0.28 mL, 2.1 mmol) in acetonitrile (2 mL) at room temperature under oxygen atmosphere for 24 h. The residue was purified by flash column chromatography on silica gel (12% EtOAc/hexanes) to afford **2o** (139 mg 75%) as a white solid. mp 100-101 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 – 7.28 (m, 5H), 6.94 (d, *J* = 10.2 Hz, 1H), 6.19 (d, *J* = 10.2 Hz, 1H), 4.67 – 4.33 (m, 3H), 3.91 – 3.78 (m, 2H), 3.17 – 3.09 (m, 2H), 2.37 – 2.28 (m, 1H), 2.09 – 2.01 (m, 1H), 0.88 (s, 9H), 0.07 (d, *J* = 1.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 149.3, 138.8, 128.7, 128.1, 127.6, 127.5, 126.9, 123.8, 75.8, 73.8, 61.3, 58.8, 48.51, 37.4, 26.1, 18.5, -5.28, -5.33. IR (thin film): ν_{max}/cm^{-1} 3424, 2927, 1697, 1456, 1384, 1295, 1101, 766. HRMS (ESI): *m/z* calculated for $[M+Na]^+$ $C_{23}H_{31}N_3O_4NaSi$ 464.1982, found 464.1986.

3. Experimental procedure for compound 3

5-Hydroxy-8a-methyl-4-phenyl-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (3): To a solution of azido alcohol **2a** (100 mg, 0.336 mmol) in ^{t}BuOH:H_2O (3 mL, 1:1 ratio), were added phenylacetylene (34.5 mg, 0.336 mmol), $CuSO_4 5H_2O$ (0.8 mg, 0.0033 mmol) and Sodium ascorbate (6.7 mg, 0.0338 mmol). The reaction mixture was stirred at room temperature for 24 h. After completion of reaction (monitored by TLC), the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (1:1 EtOAc/hexanes) to afford **3** (113 mg, 84%) as a white solid. mp 210-212 °C. ^{1}H NMR

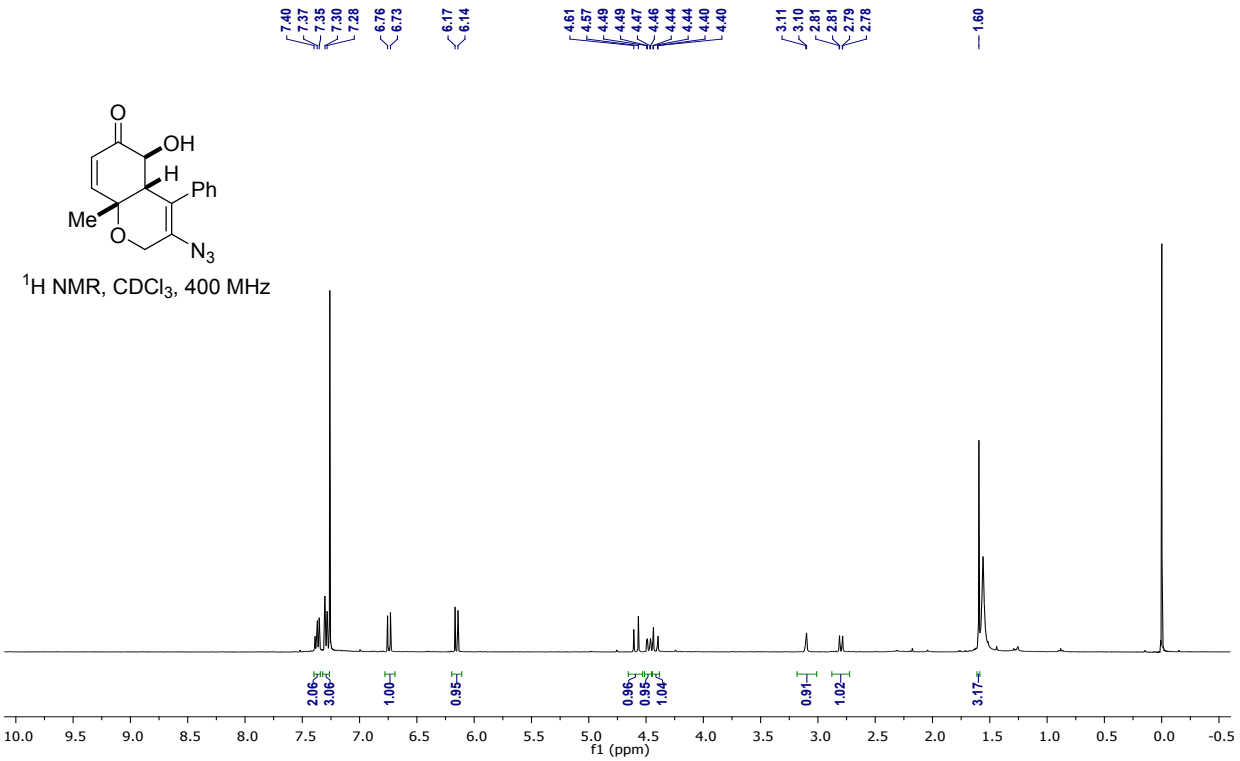
(500 MHz, $CDCl_3$) δ 7.78 – 7.72 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 2H), 7.50 – 7.45 (m, 4H), 7.44 (s, 1H), 7.34 – 7.30 (m, 2H), 7.00 (d, *J* = 10.0 Hz, 1H), 6.41 (d, *J* = 10.0 Hz, 1H), 5.47 (d, *J* = 17.4 Hz, 1H), 4.86 (d, *J* = 13.5 Hz, 1H), 4.74 (d, *J* = 17.4 Hz, 1H), 3.43 (s, 1H), 3.16 (d, *J* = 12.1 Hz, 1H), 1.88 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.2, 150.3, 147.0, 138.2, 132.0, 130.1, 129.9, 128.9, 128.5, 128.4, 127.9, 126.5, 125.9, 120.9, 75.4, 71.2, 63.3, 50.4, 22.8. IR (thin film): ν_{max}/cm^{-1} 3381, 2993, 1690, 1389, 1173, 1068, 771. HRMS (ESI): *m/z* calculated for $[M+H]^+$ $C_{24}H_{22}N_3O_3$ 400.1661, found 400.1665.

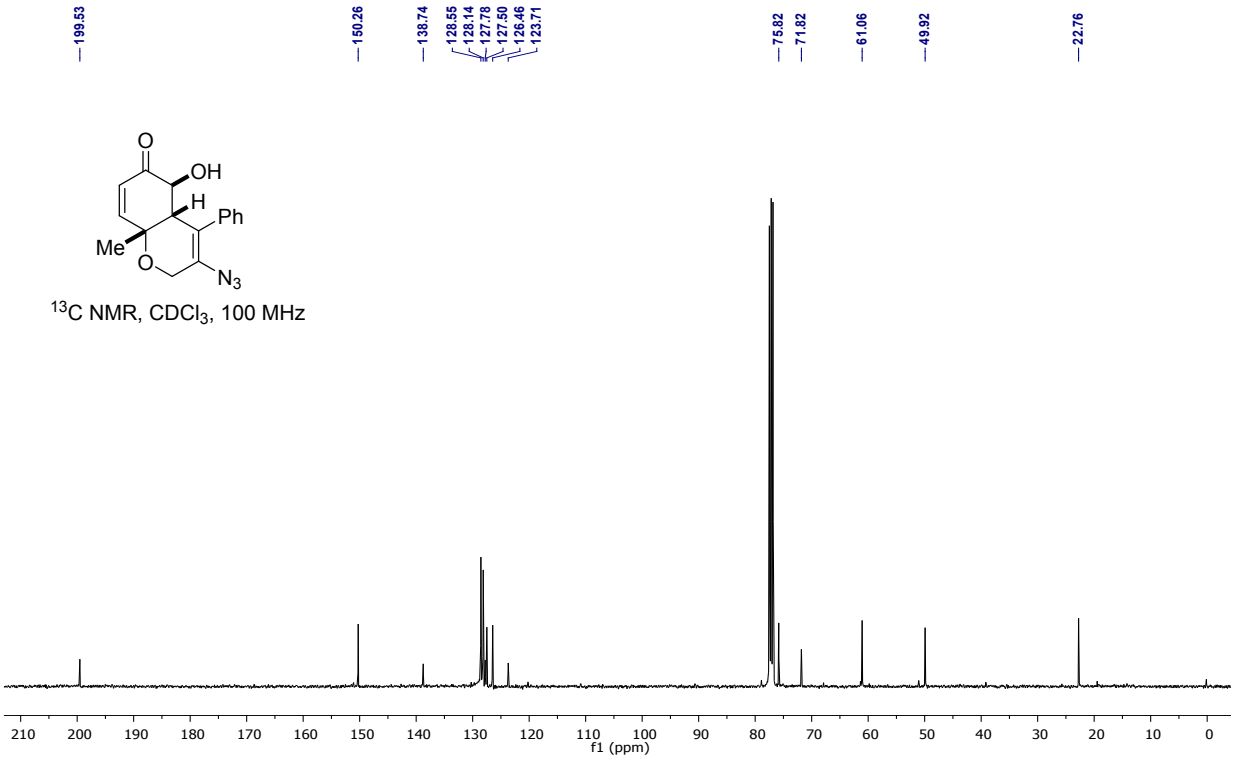
References

1. (a) J. K. Hexum, T. Tello-Aburto, N. B. Struntz, A. M. Harned and D. A. Harki, *ACS Med. Chem. Lett*. 2012, **3**, 459; (b) Y. Fukui, P. Liu, Q. Liu, Z.-T. He, N.-Y. Wu, P. Tian and G.-Q. Lin, *J. Am. Chem. Soc.*, 2014, **136**, 15607; (c) Z.-T. He, X.-Q. Tang, L.-B. Xie, M. Cheng, P. Tian and G.-Q. Lin, *Angew. Chem. Int. Ed*., 2015, **54**, 14815; (d) K. K. Gollapelli, S. Donikela, N. Manjula and R.Chegondi, *ACS Catal*., 2018, **8**, 1440.

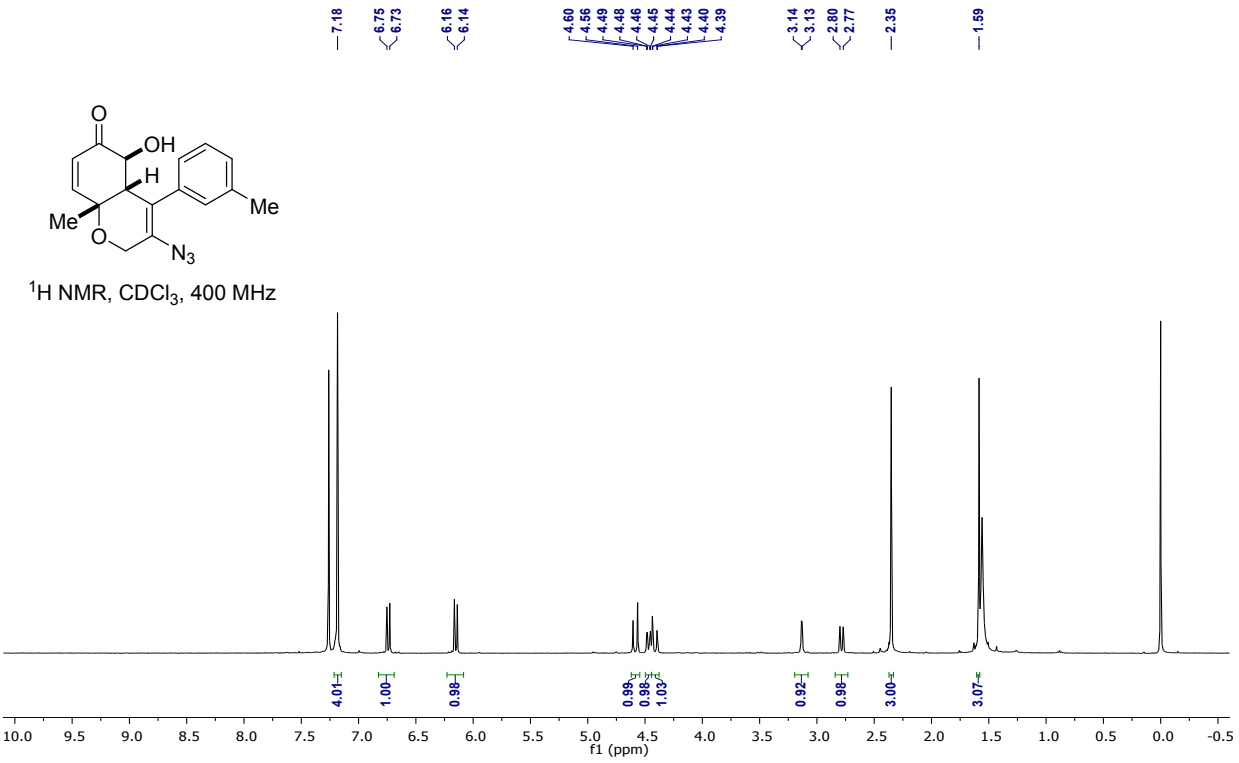
4. ^{1}H and ^{13}C NMR spectra of compounds

3-Azido-5-hydroxy-8a-methyl-4-phenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2a)

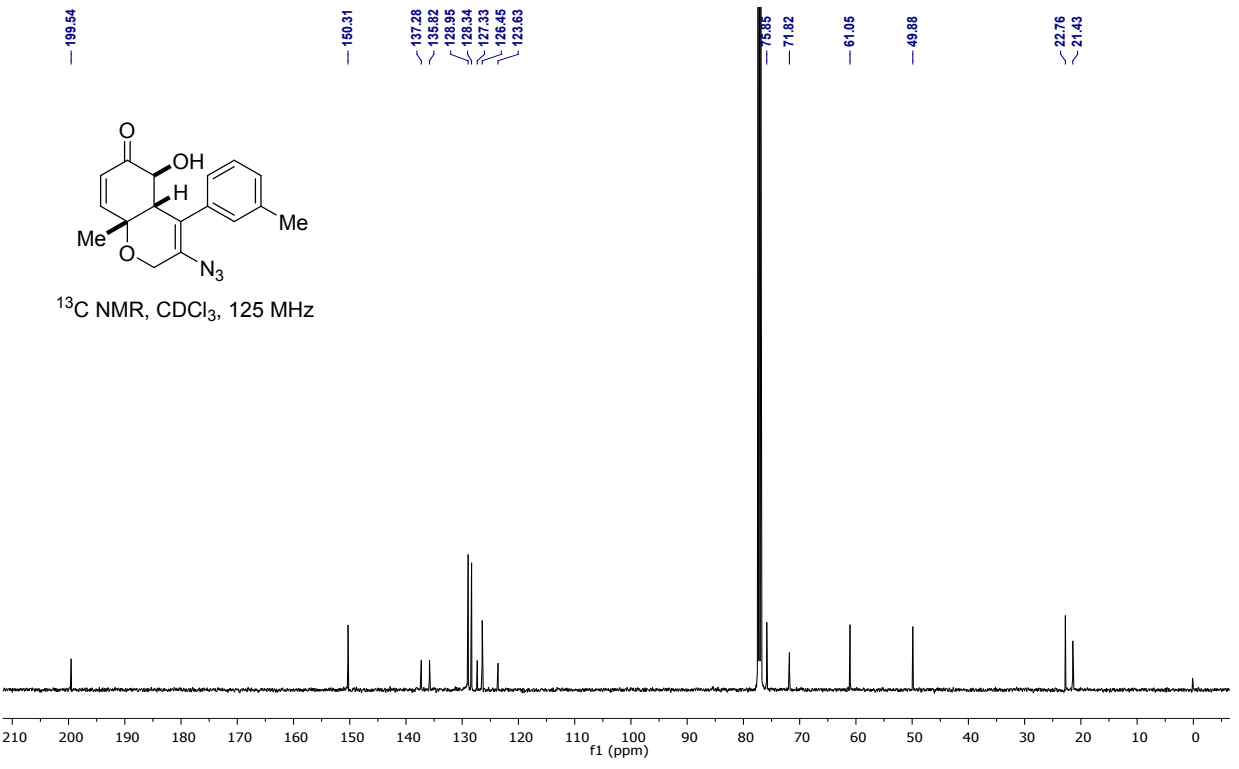




3-Azido-5-hydroxy-8a-methyl-4-(*m*-tolyl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2c)

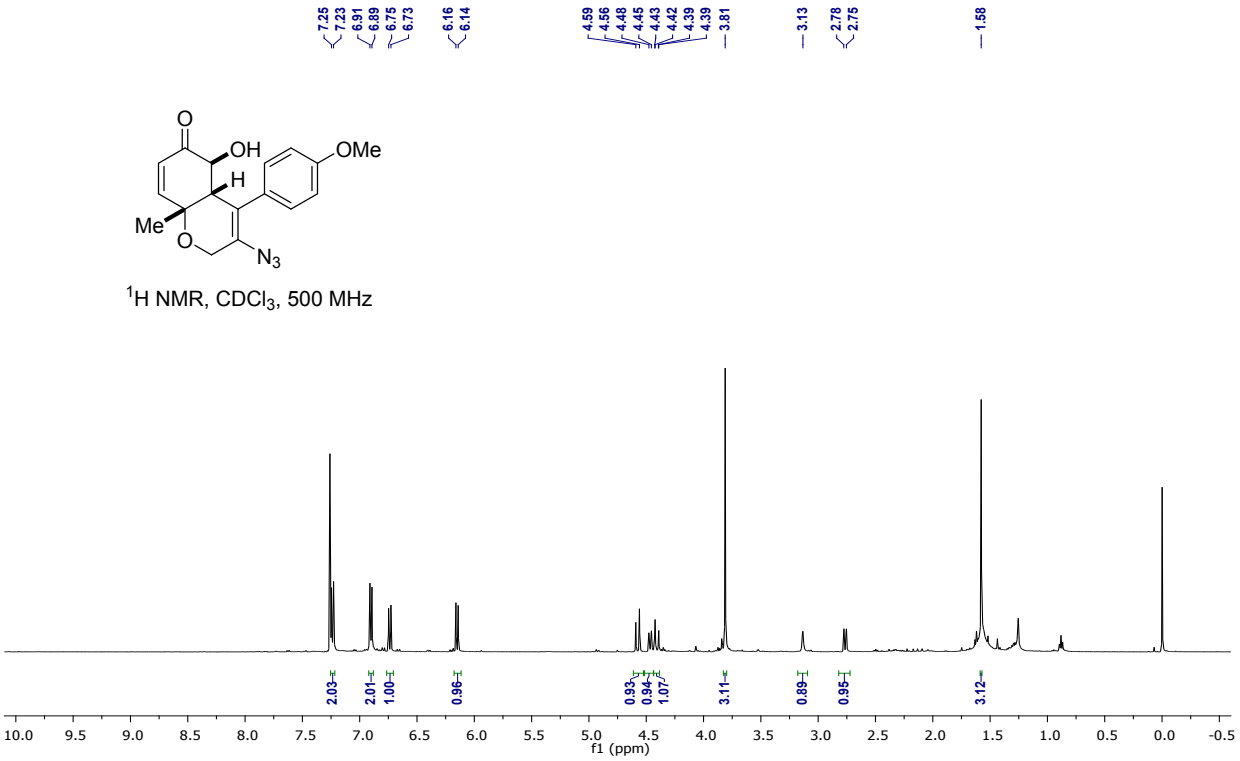


^{1}H NMR, $CDCl_3$, 400 MHz

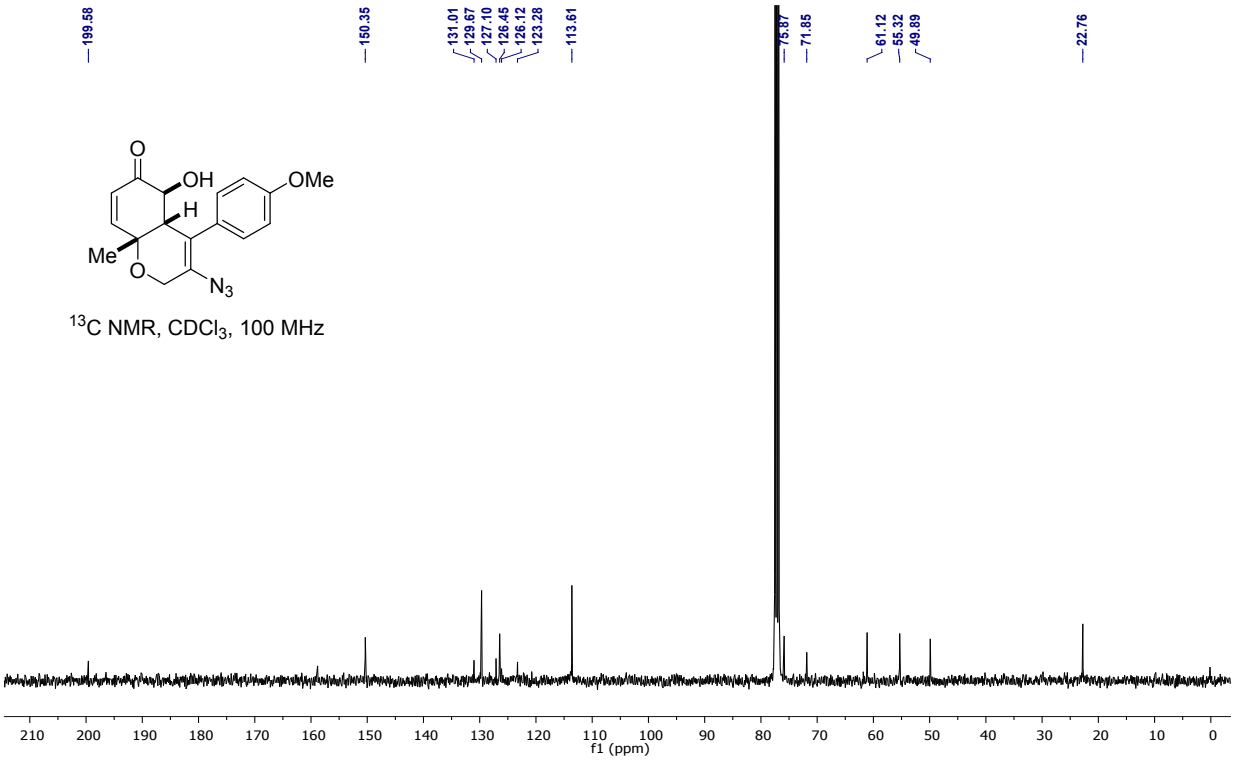


^{13}C NMR, $CDCl_3$, 125 MHz

3-Azido-5-hydroxy-4-(4-methoxyphenyl)-8a-methyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2d)

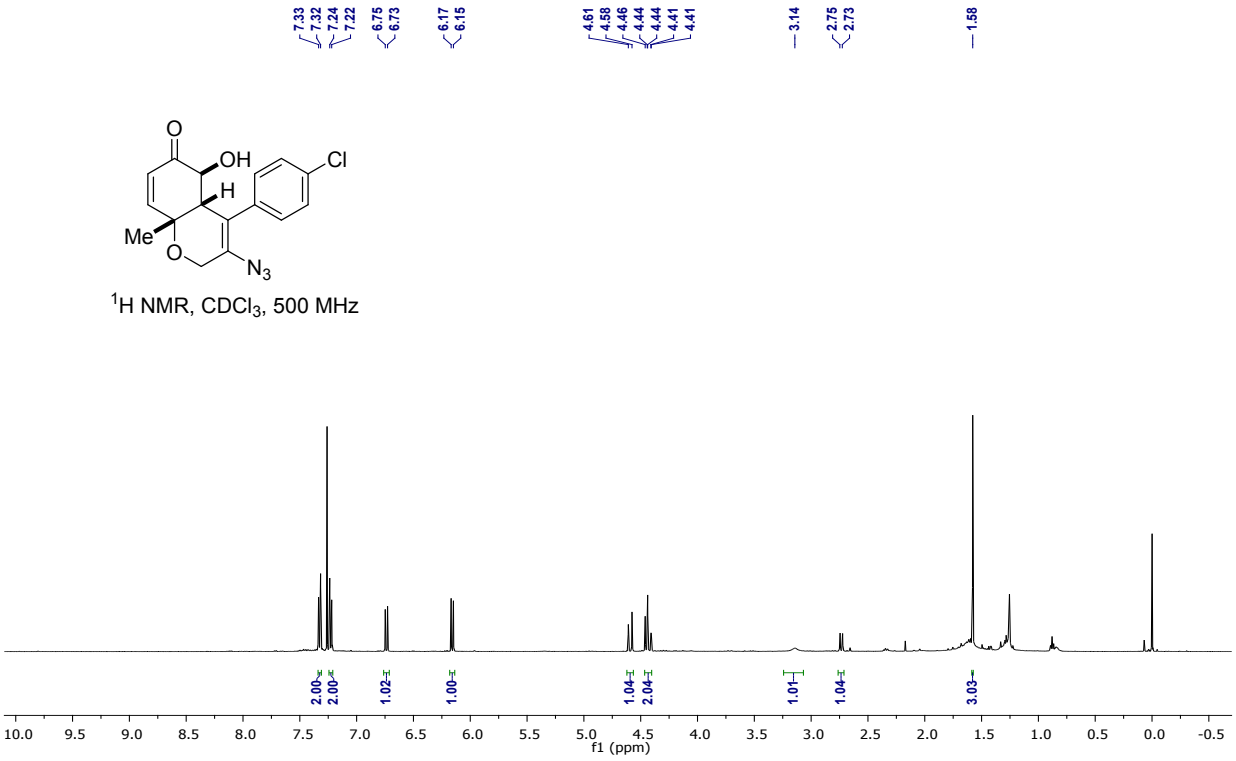


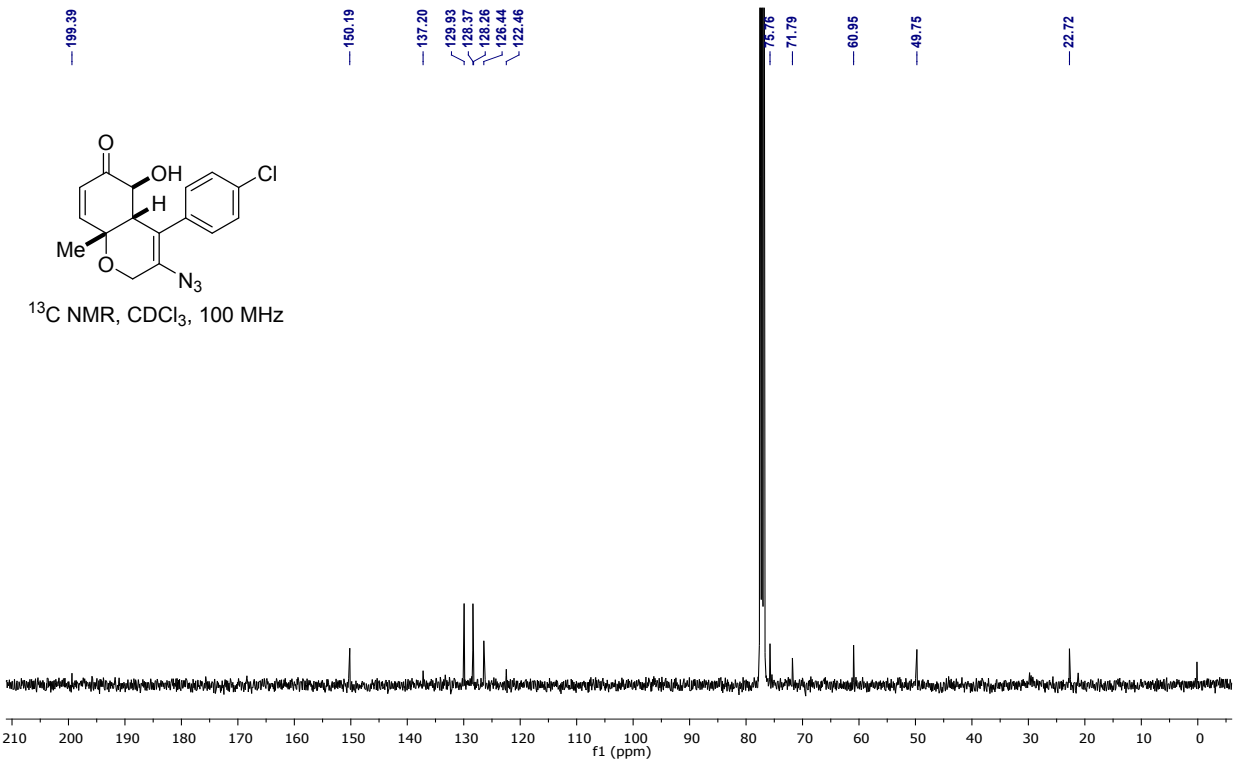
^{1}H NMR, $CDCl_3$, 500 MHz



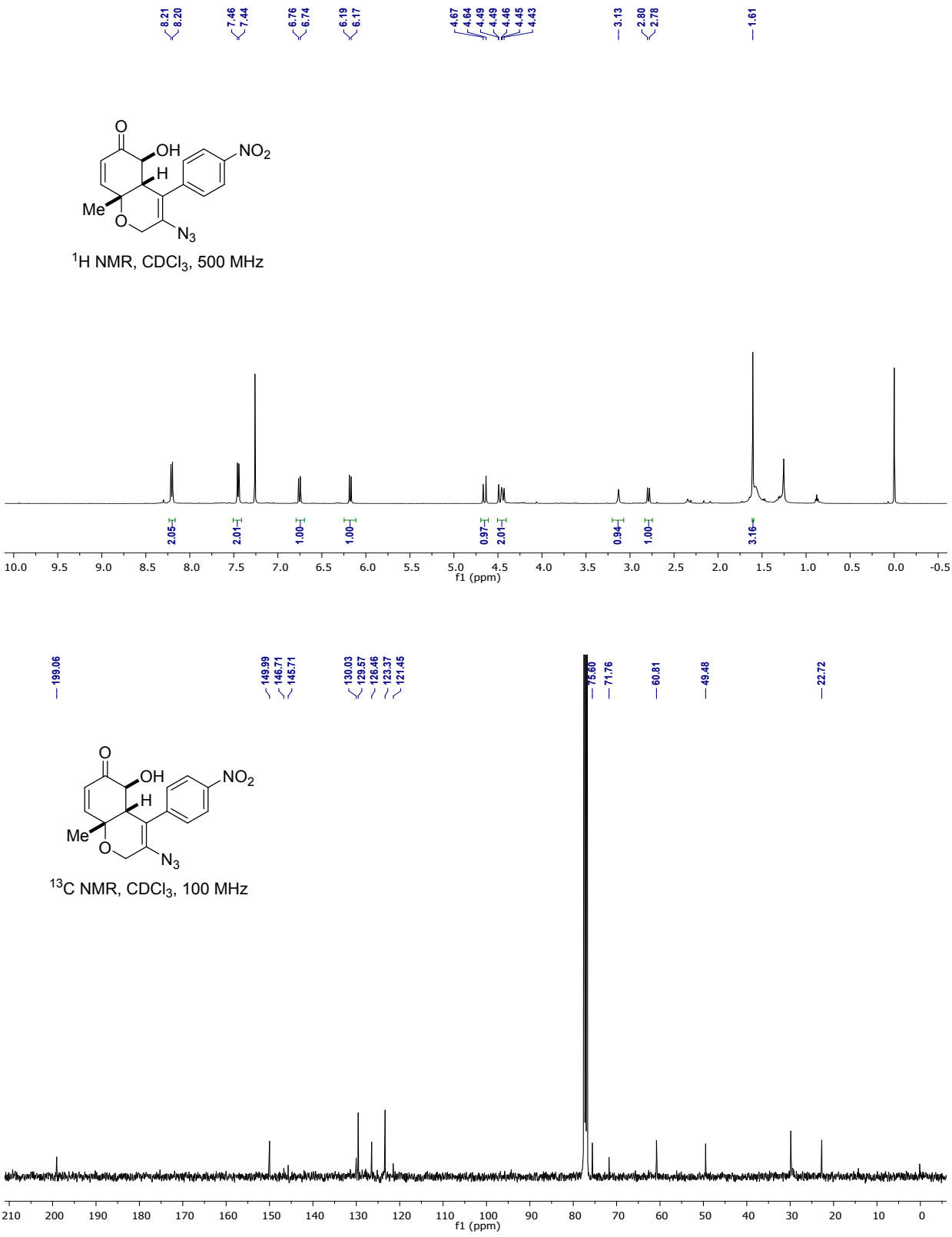
^{13}C NMR, $CDCl_3$, 100 MHz

3-Azido-4-(4-chlorophenyl)-5-hydroxy-8a-methyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2e)

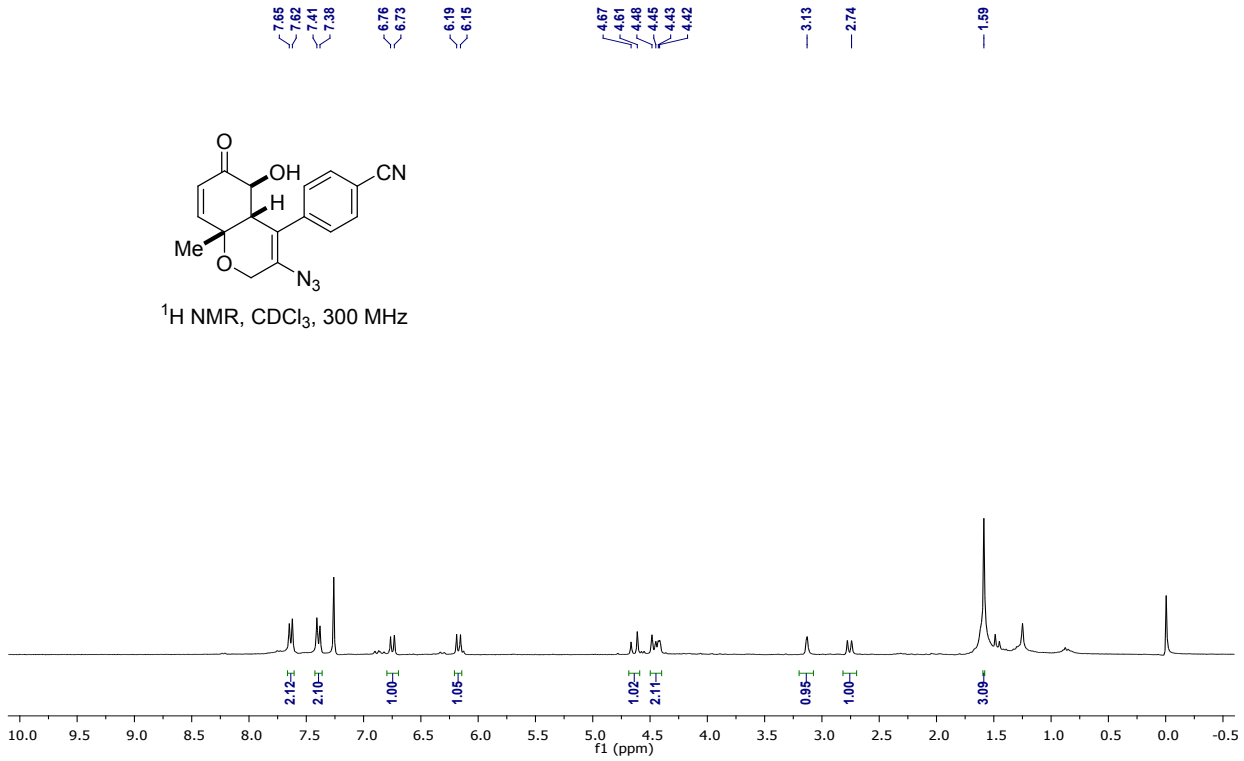


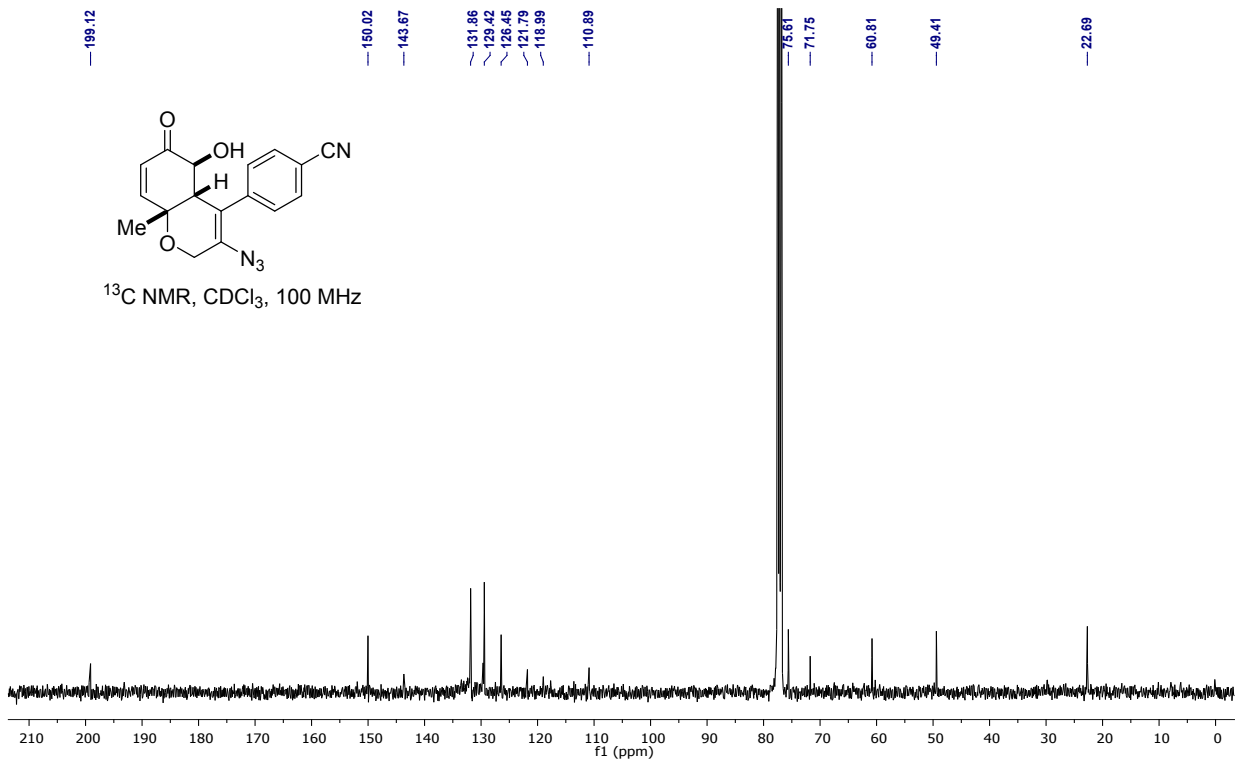


3-Azido-5-hydroxy-8a-methyl-4-(4-nitrophenyl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2f)

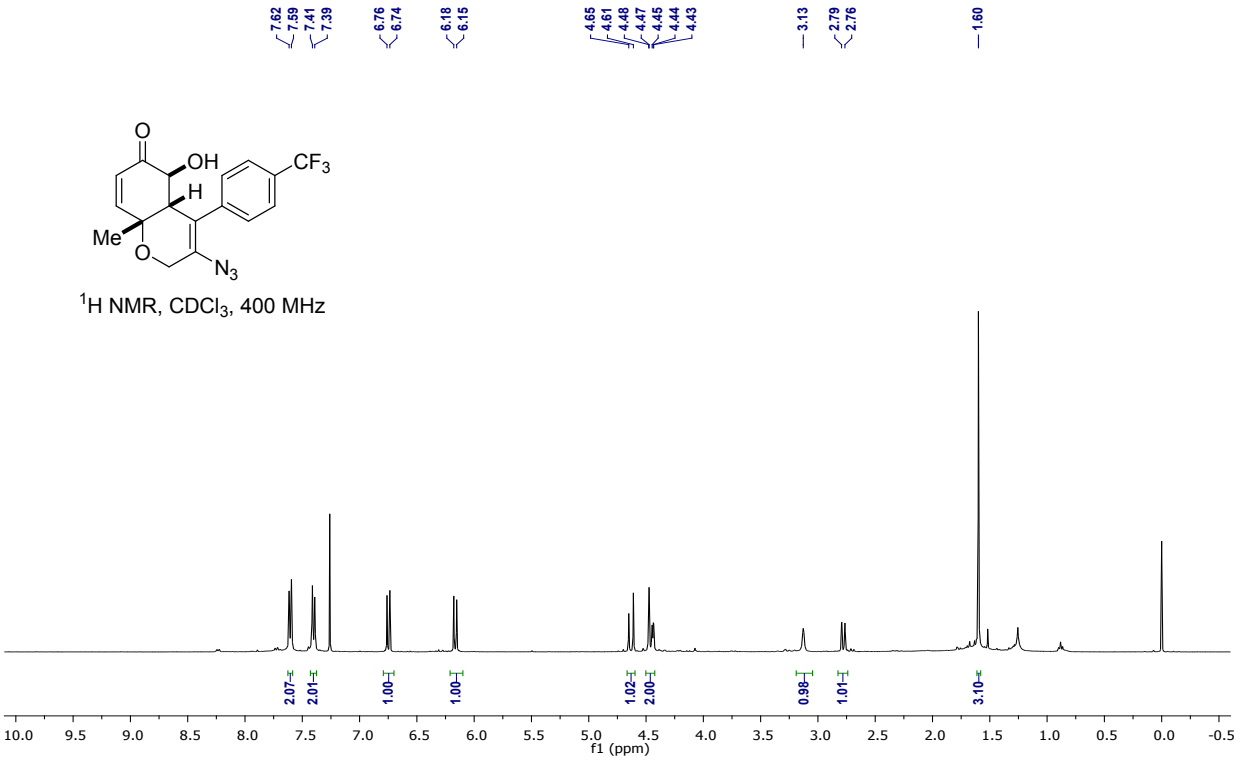


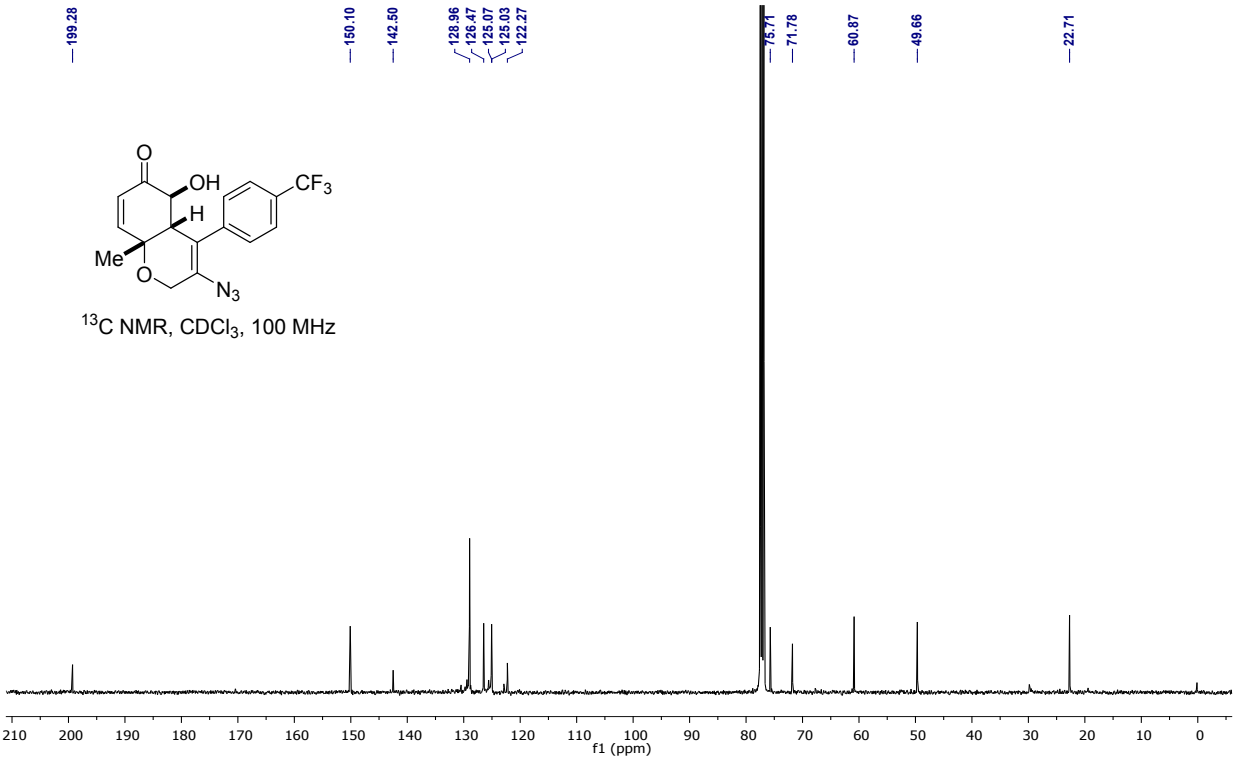
4-(3-Azido-5-hydroxy-8a-methyl-6-oxo-4a,5,6,8a-tetrahydro-2*H*-chromen-4-yl)benzonitrile (2g)



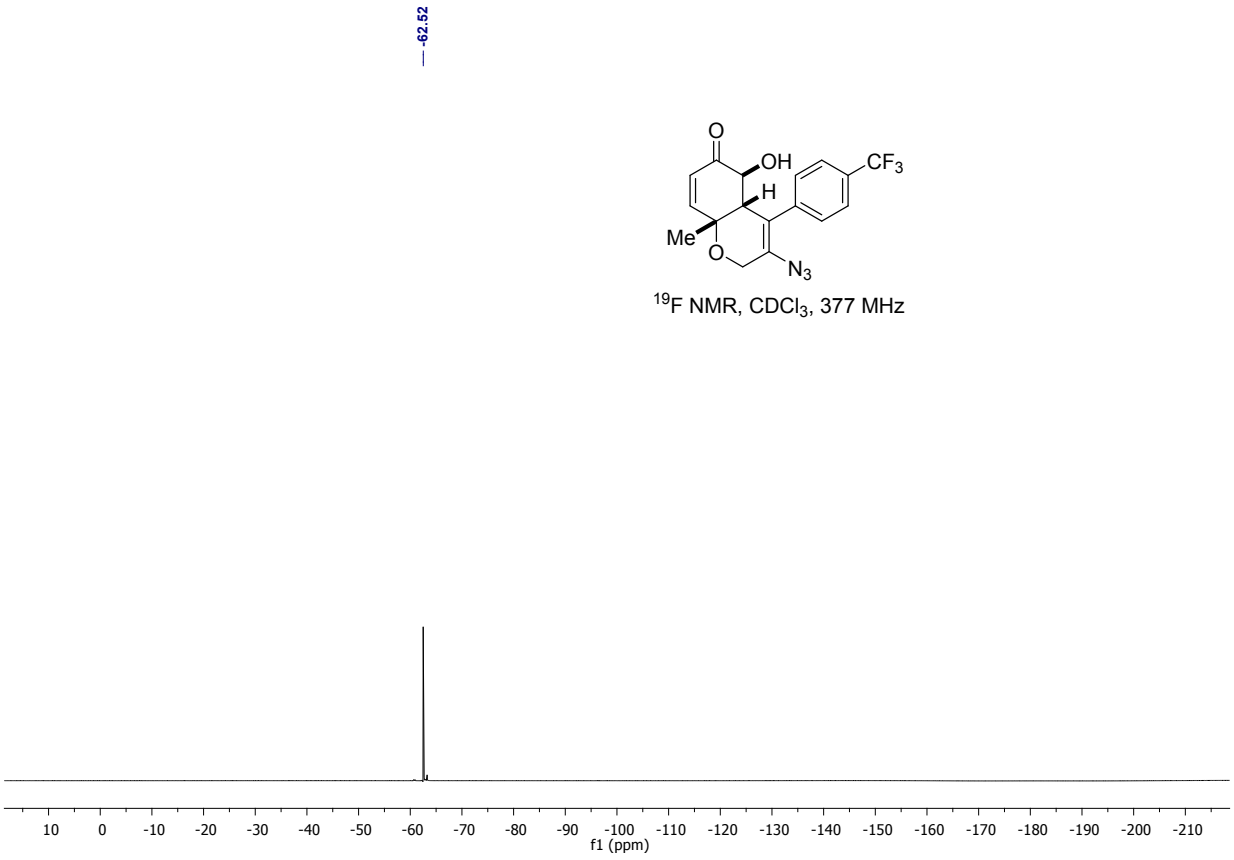


3-Azido-5-hydroxy-8a-methyl-4-(4-(trifluoromethyl)phenyl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2h)



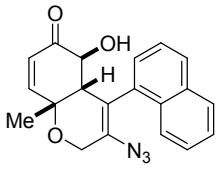


^{19}F NMR spectrum of compound 2h

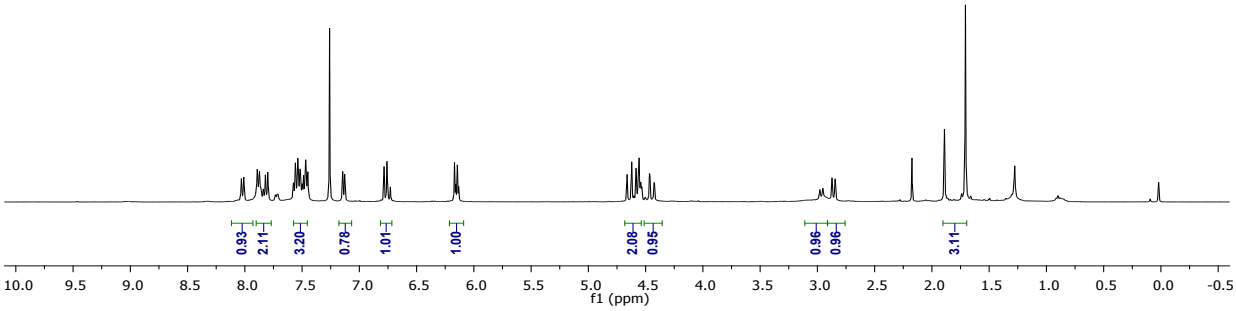


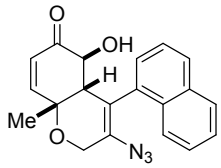
^{19}F NMR, $CDCl_3$, 377 MHz

3-Azido-5-hydroxy-8a-methyl-4-(naphthalen-1-yl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2i)

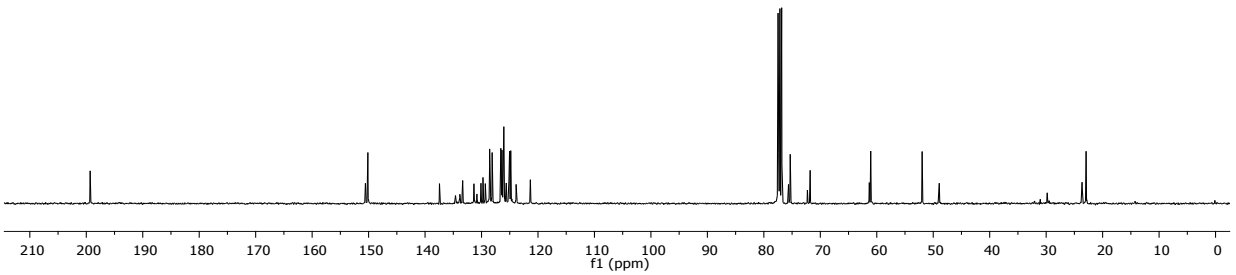


^{1}H NMR, $CDCl_3$, 400 MHz

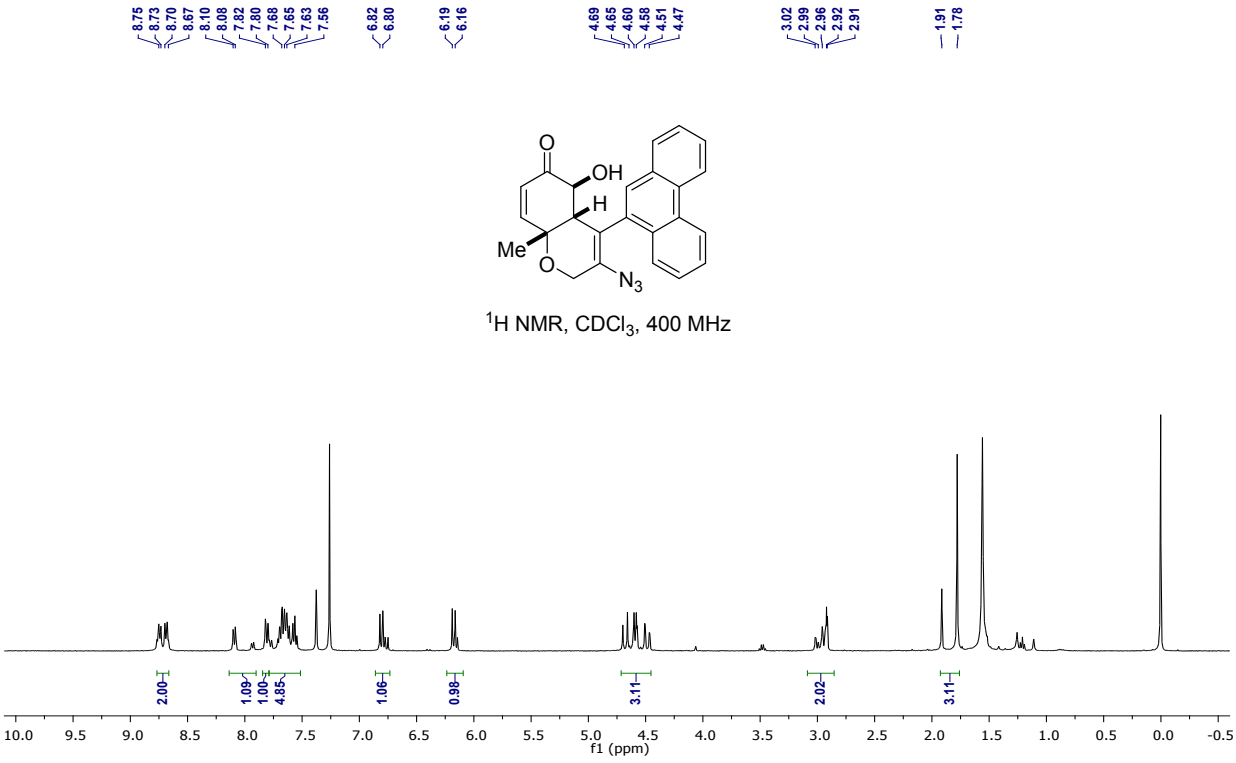




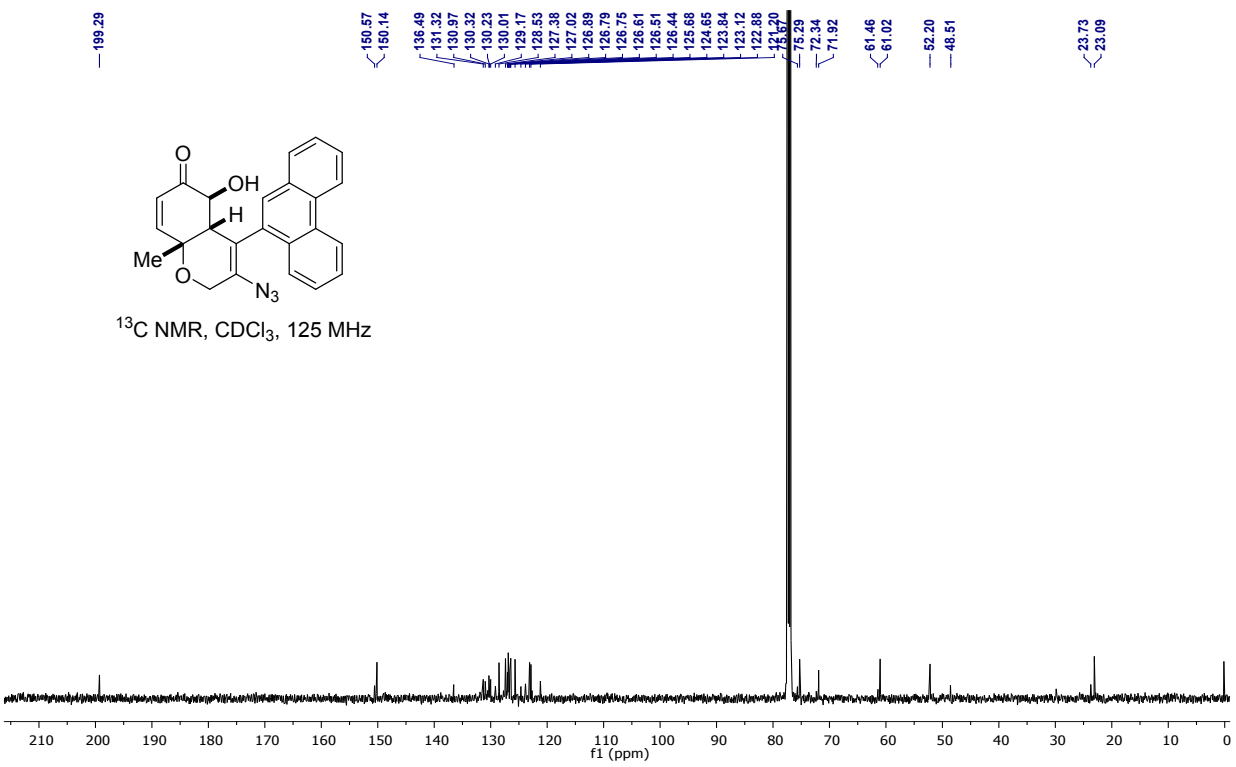
^{13}C NMR, $CDCl_3$, 100 MHz



3-Azido-5-hydroxy-8a-methyl-4-(phenanthren-9-yl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2j)

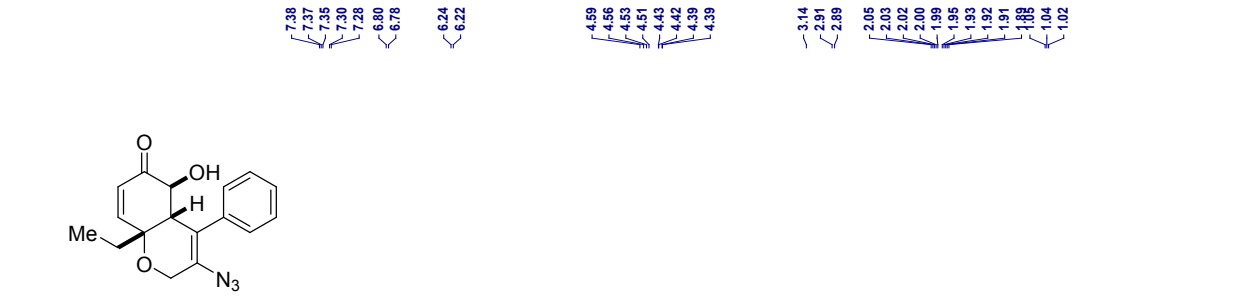


^{1}H NMR, $CDCl_3$, 400 MHz

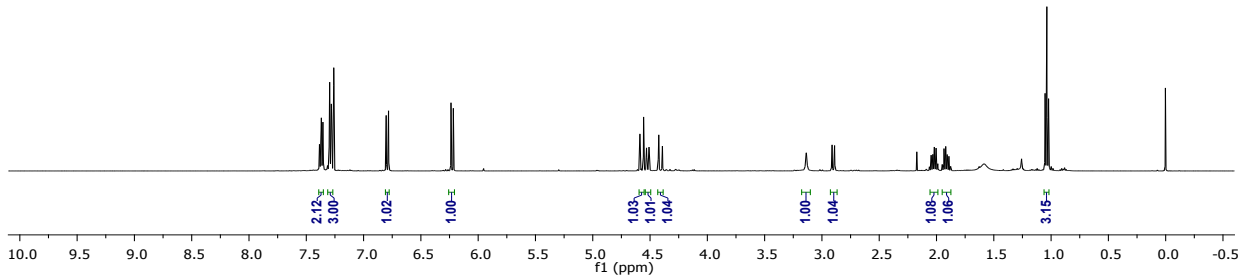


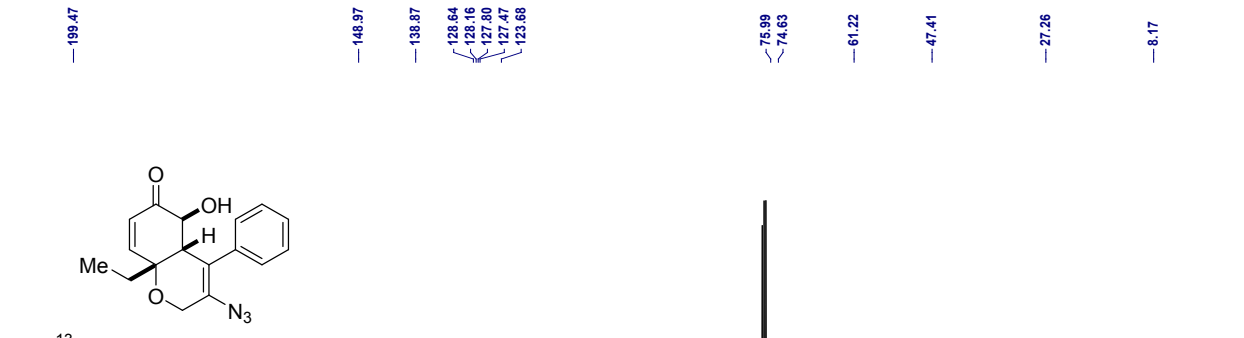
^{13}C NMR, $CDCl_3$, 125 MHz

3-Azido-8a-ethyl-5-hydroxy-4-phenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2l)



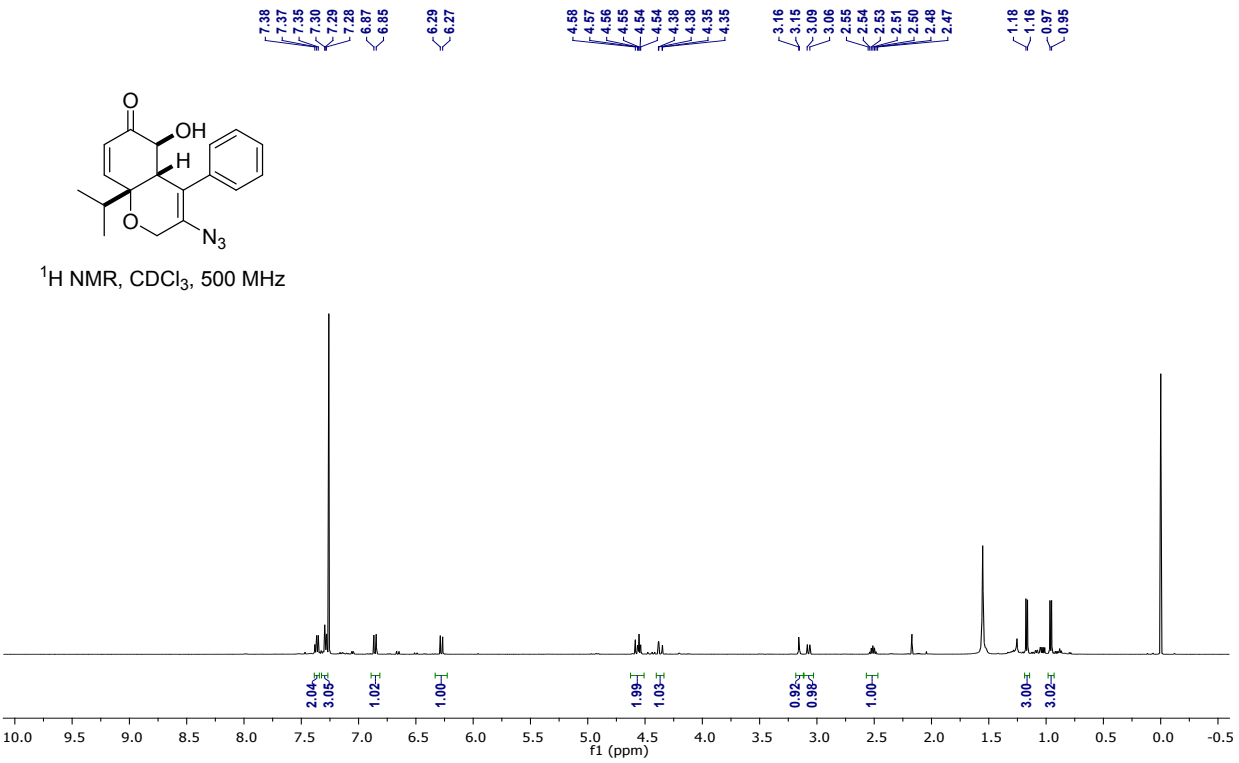
^{1}H NMR, $CDCl_3$, 500 MHz

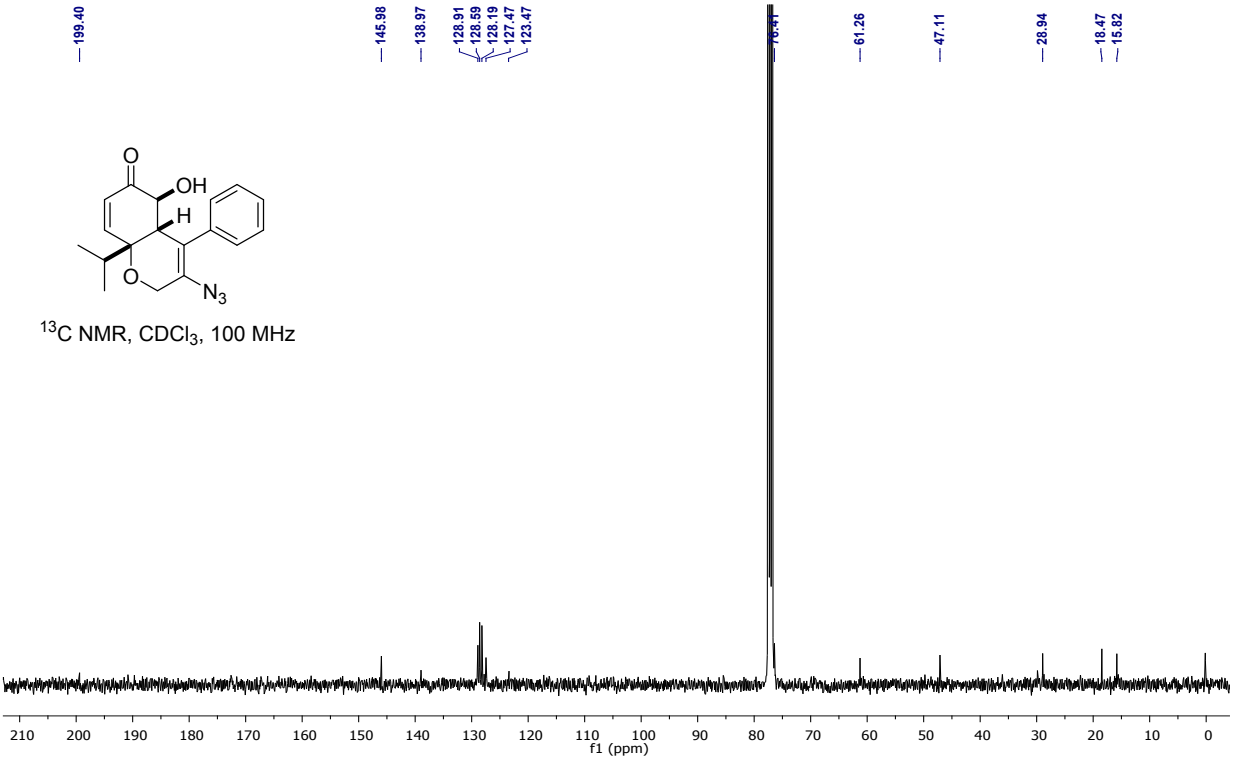




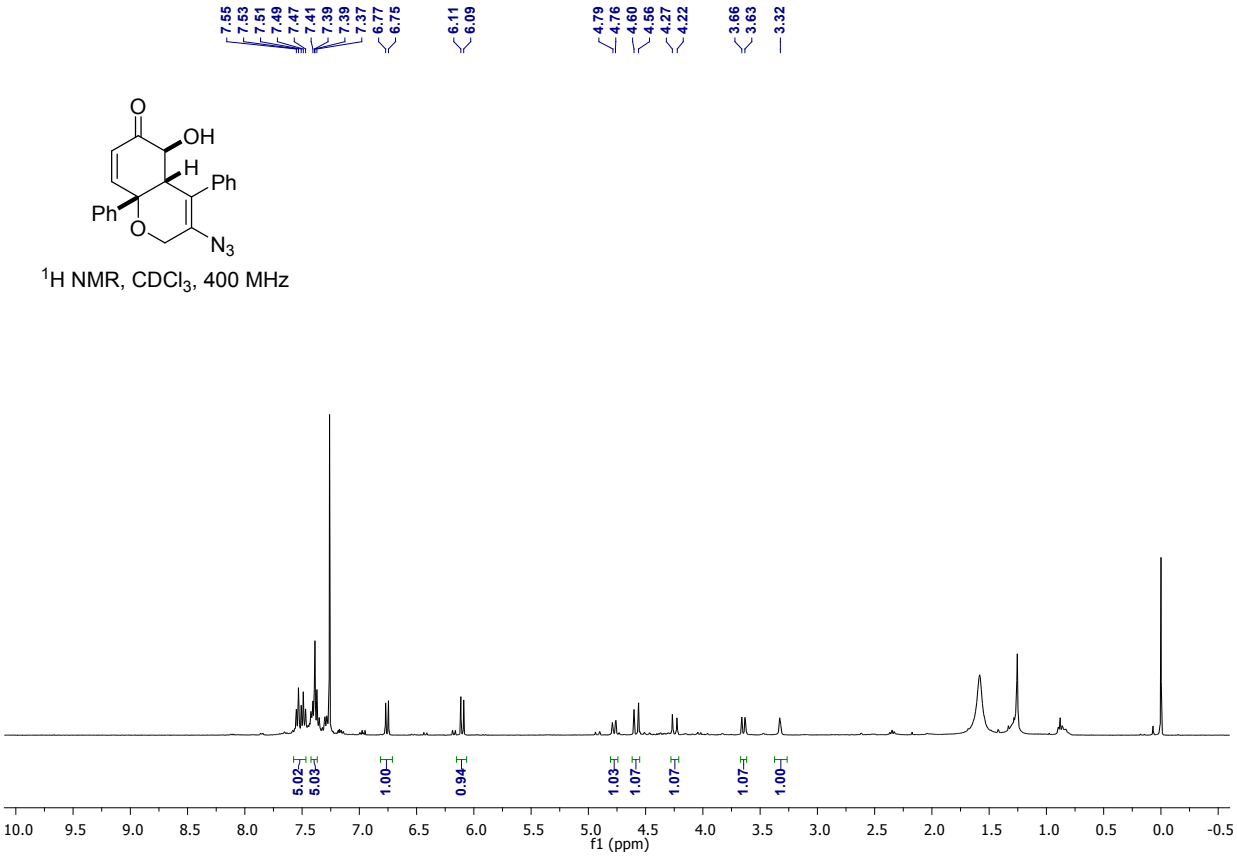
^{13}C NMR, $CDCl_3$, 100 MHz

3-Azido-5-hydroxy-8a-isopropyl-4-phenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2m)

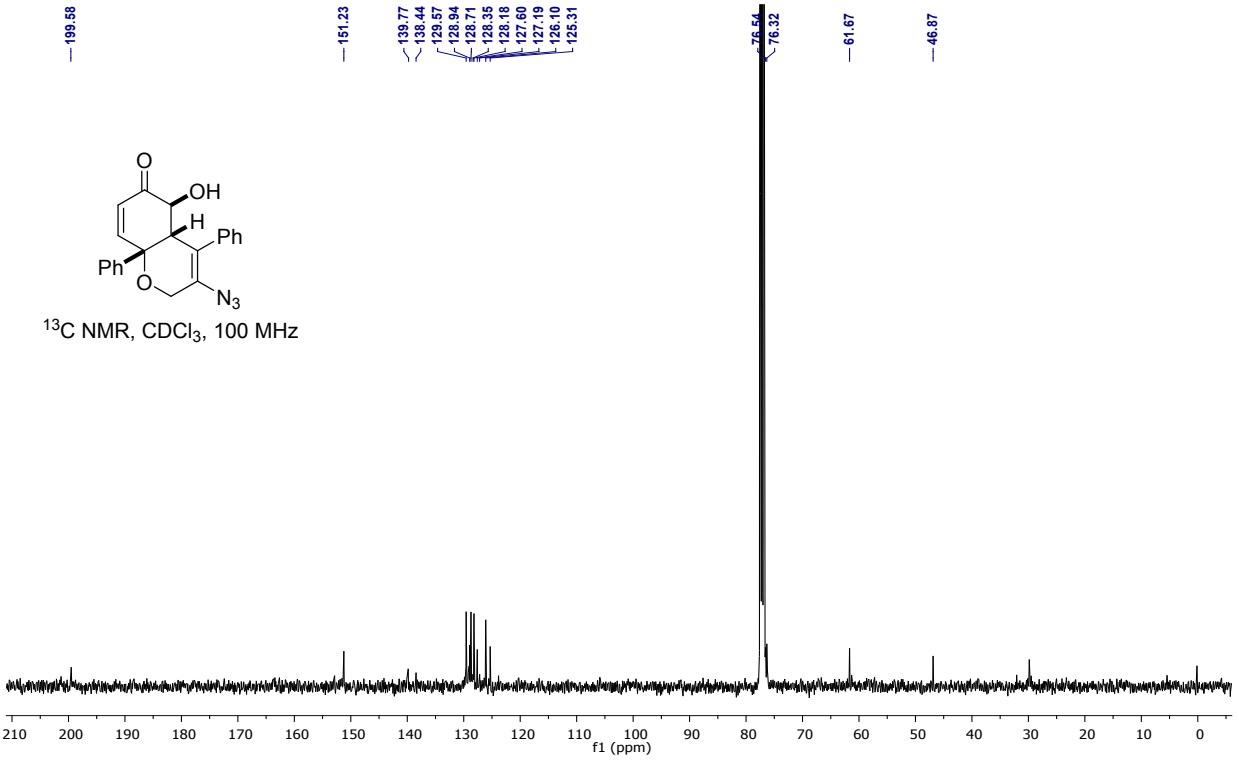




3-Azido-5-hydroxy-4,8a-diphenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2n)

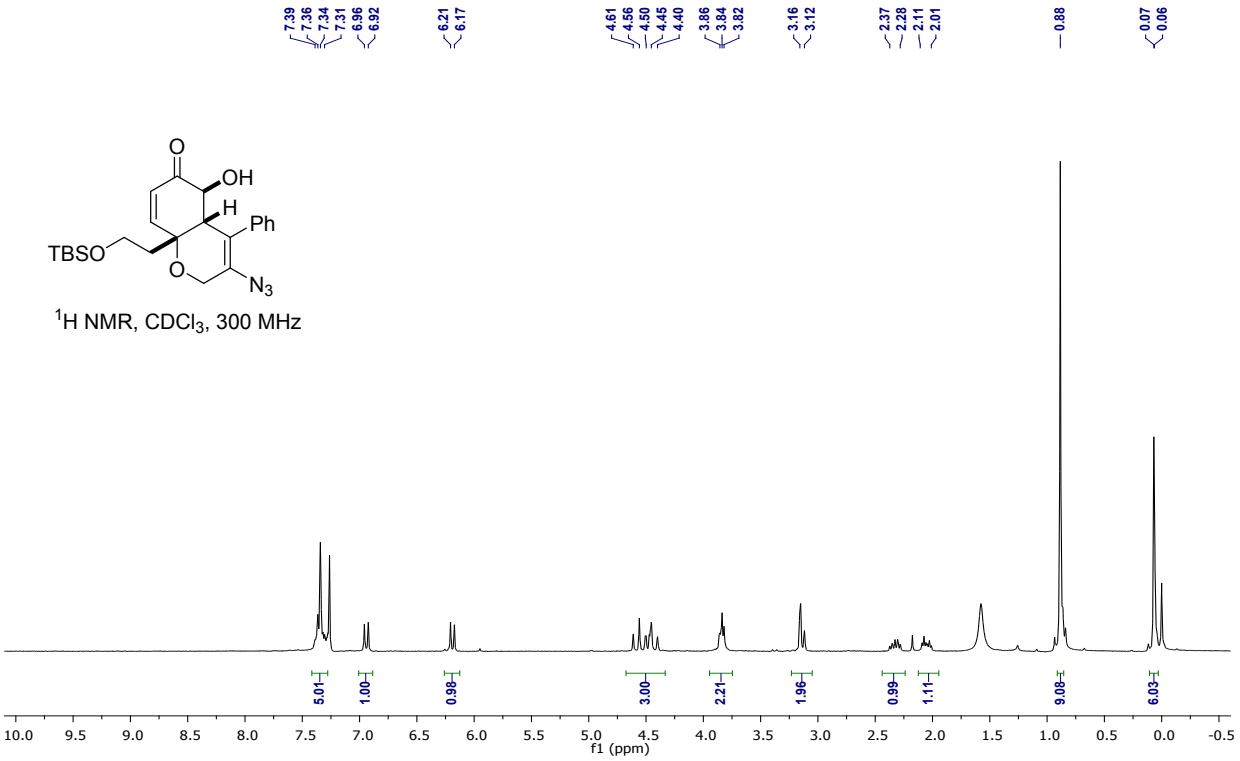


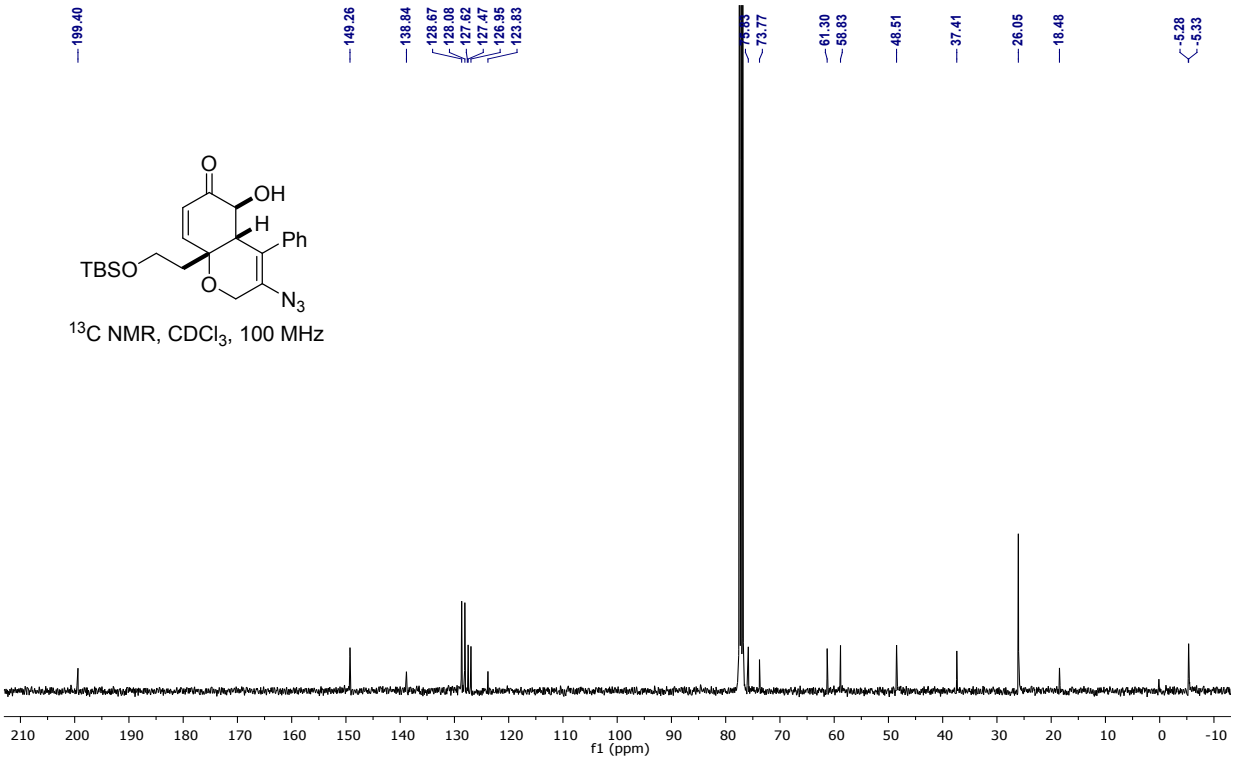
^{1}H NMR, $CDCl_3$, 400 MHz



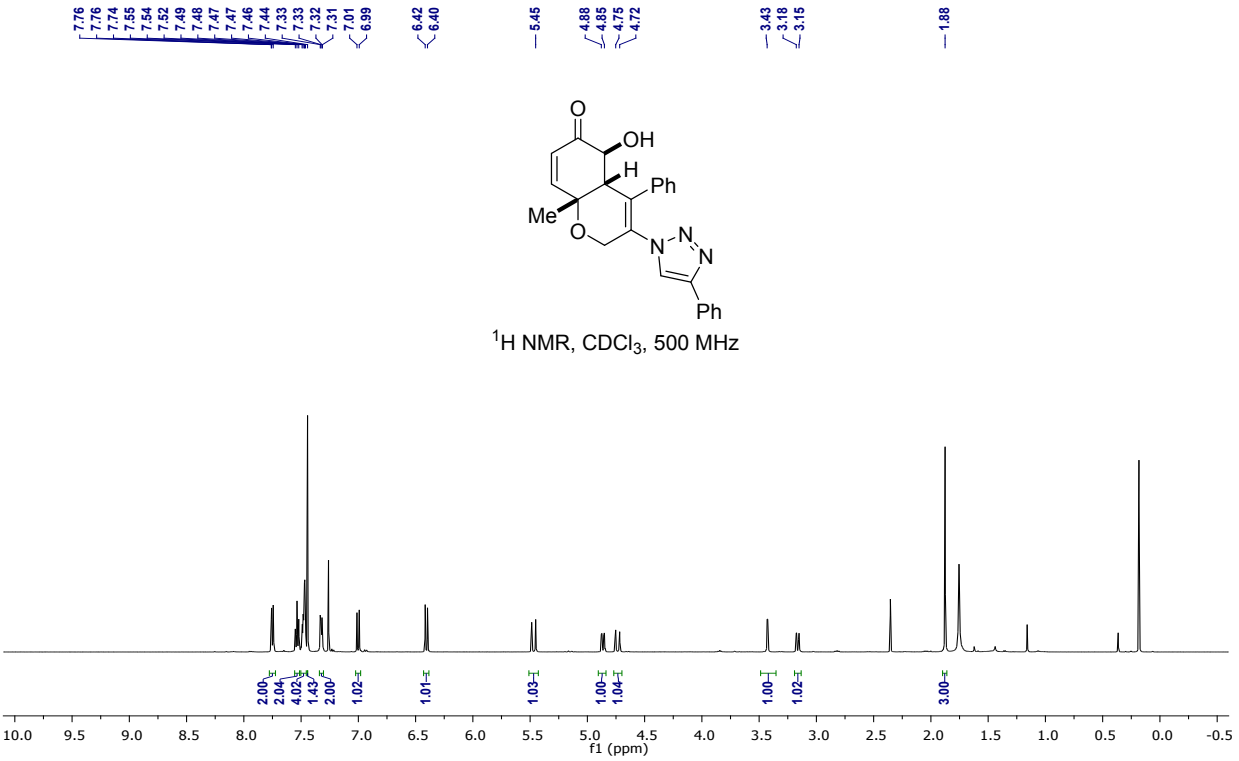
^{13}C NMR, $CDCl_3$, 100 MHz

3-Azido-8a-(2-((*tert*-butyldimethylsilyl)oxy)ethyl)-5-hydroxy-4-phenyl-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (2o)

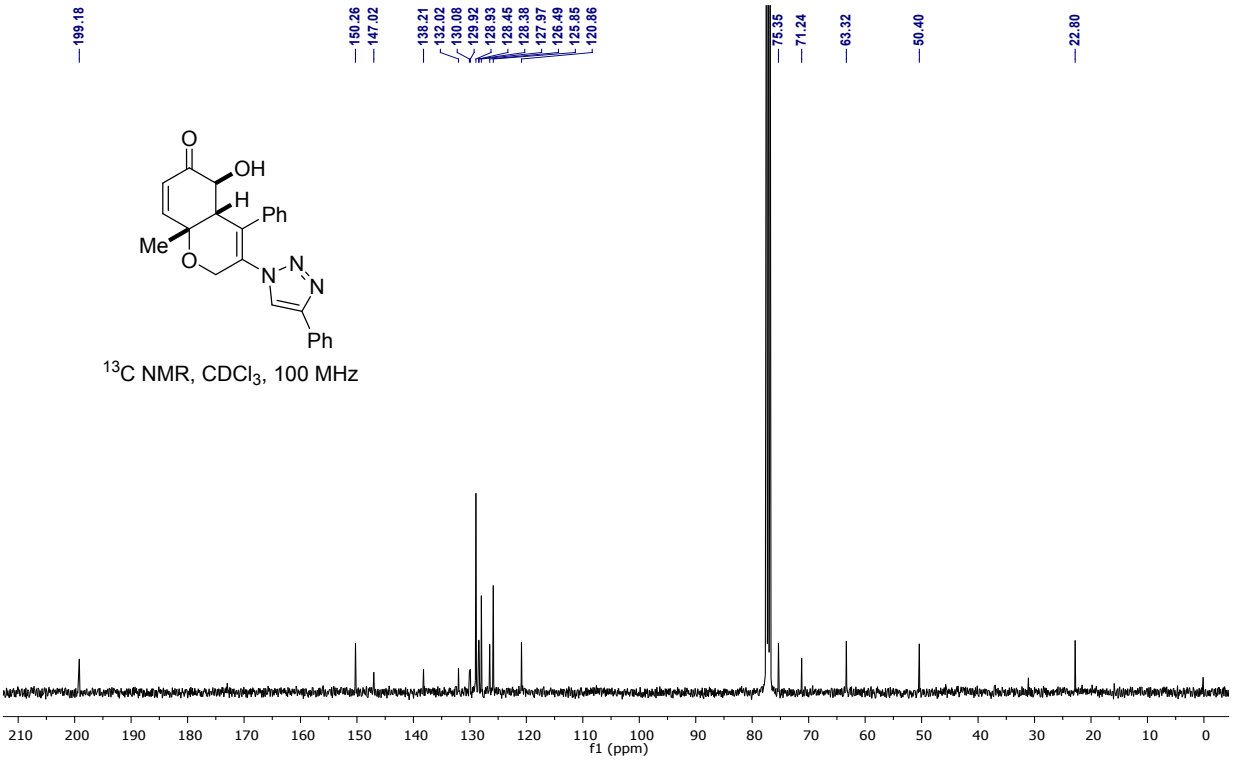




5-Hydroxy-8a-methyl-4-phenyl-3-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-4a,8a-dihydro-2*H*-chromen-6(5*H*)-one (3)

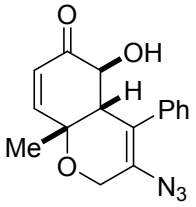


^{1}H NMR, $CDCl_3$, 500 MHz



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

5. X-ray crystallographic data of compound 2a



Structure of compound 2a

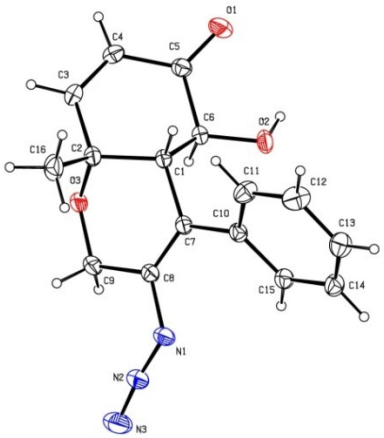


Figure S1. A view of **2a**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii.

Crystallization of 2a: To a mixture of compound **2a** (10 mg) and methanol (2 mL) in a culture vial. The vial was covered with perforated aluminium foil and left aside for 2 days for crystal growth. After slow evaporation of the solvent, pale orange crystals were obtained.

X-ray data for the compound **2a** was collected at room temperature on a Bruker D8 QUEST instrument with an IμS Mo microsource (λ = 0.7107 A) and a PHOTON-100 detector. The raw data frames were reduced and corrected for absorption effects using the Bruker Apex 3 software suite programs[1]. The structure was solved using intrinsic phasing method[2] and further refined with the SHELXL[2] program and expanded using Fourier techniques. Anisotropic displacement parameters were included for all non-hydrogen atoms. O bound H atom was located in difference Fourier maps and their positions were refined. All H atoms were positioned geometrically and

treated as riding on their parent C atoms [C-H = 0.93-0.97 Å, and Uiso(H) = 1.5Ueq(C) for methyl H or 1.2Ueq(C) for other H atoms].

Crystal structure determination of 2a

Crystal Data for $C_{16}H_{15}N_3O_3$ (M =297.31 g/mol): monoclinic, space group P21/c (no. 14), a = 7.053(5) Å, b = 18.102(12) Å, c = 11.924(7) Å, β = 106.894(10)°, V = 1456.6(16) Å3, Z = 4, T = 294.15 K, μ(MoKα) = 0.096 mm-1, Dcalc = 1.356 g/cm3, 13457 reflections measured (4.5° ≤ 2Θ ≤ 61.282°), 4364 unique (Rint = 0.0442, Rsigma = 0.0580) which were used in all calculations. The final R1 was 0.0627 (I > 2σ(I)) and wR2 was 0.2169 (all data). **CCDC 1975072** contains supplementary Crystallographic data for the structure. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0) 1223 336 033; email: deposit@ccdc.cam.ac.uk].

1. Bruker (2016). APEX3, SAINT and SADABS. Bruker AXS, Inc., Madison, Wisconsin, USA.
2. Sheldrick G. M. (2015) Acta Crystallogr C71: 3-8.